JOC Article

Synthesis and Structure of Trigonal and Tetragonal Connectors for a "Tinkertoy" Construction Set

Peter F. H. Schwab, Bruce C. Noll, and Josef Michl*

Department of Chemistry and Biochemistry, University of Colorado, Boulder, Colorado 80309-0215

michl@eefus.colorado.edu

Received February 15, 2002

We describe a convergent synthesis of eight 1,3,5- and 1,2,4,5-substituted benzene derivatives with long rigid arms containing 4-pyridyl, 2,2′-bipyridyl, and 2,2′-bipyrimidyl termini, meant to be used as trigonal or tetragonal connectors for the construction of large molecular structures. The synthesis involved copper-free Pd-mediated coupling of terminal acetylenes to aryl halides. First, one of the termini of 1,3-diethynylbicyclo[1.1.1]pentane was coupled with a brominated aza heterocycle, and second, 3 equiv of the resulting extended arm were coupled with 1,3,5-triiodobenzene or 4 with 1,2,4,5-tetraiodobenzene. An improved large-scale synthesis for 1,3-diethynylbicyclo[1.1.1]pentane is described. The structures of two of the arms were determined by single-crystal X-ray analysis. Several long molecular rods with 4-pyridyl termini were obtained as byproducts, and a single-crystal X-ray structure is reported for the shortest of these.

Introduction

The construction of large molecular structures and connectors from smaller molecular building blocks comprising rods and connectors has been likened[1−3] to playing with the "Tinkertoy"[4] molecular construction set. The field has seen increasing attention recently, and impressive progress has been reported.[5−13] Many types of molecular rods[14] and trigonal,[15−20] tetragonal,[18,21−26] and hexagonal[19] connectors have been synthesized for the purpose. For one of these construction projects, we required especially large trigonal and tetragonal connectors carrying metal-ligating termini. We describe the synthesis and structure of several of these compounds presently.

Results and Discussion

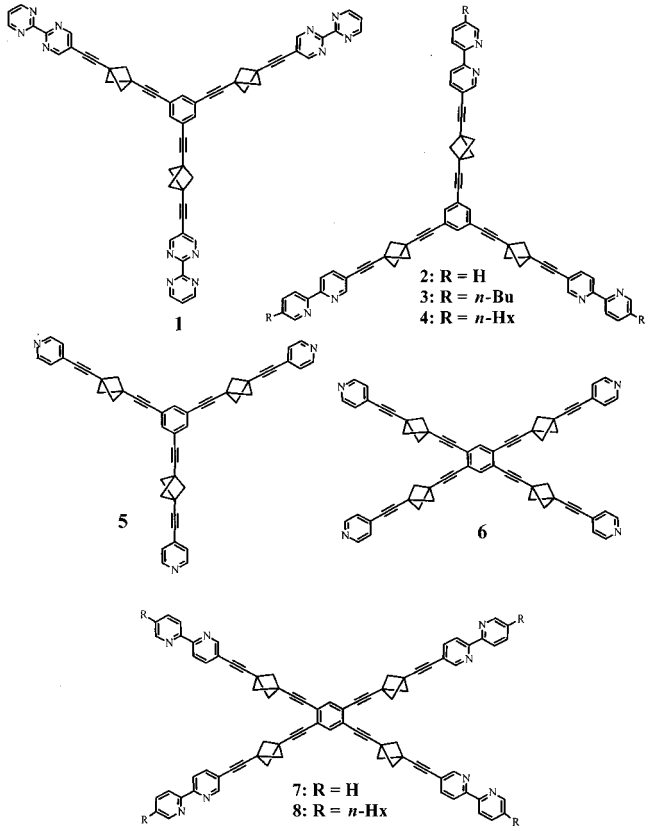
A convergent approach was chosen in which the complete long arms were synthesized separately and then coupled to a 1,3,5-trihalobenzene to obtain the trigonal connectors or to a 1,2,4,5-tetrahalobenzene to obtain the tetragonal ones. This synthetic pathway involved only one step in which three or four bonds had to be formed and permitted the use of the same arms for both types of connectors. Given an initially desired connector size, molecular modeling suggested the heterocycles **1**−**8** as synthetic targets (Chart 1).

Synthesis of the Arms. Having identified 1,3-diethynylbicyclo[1.1.1]pentane (**9**) as one of our main

(1) Kaszynski, P.; Michl, J. *J. Am. Chem. Soc.* **1988**, *110*, 5225.
(2) Michl, J.; Kaszynski, P.; Friedli, A. C.; Murthy, G. S.; Yang, H.-C.; Robinson, R. E.; McMurdie, N. D.; Kim, T. In *Strain and Its Implications in Organic Chemistry*; de Meijere, A., Blechert, S., Eds.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1989; NATO ASI Series, Vol. 273, p 463.
(3) Kaszynski, P.; Friedli, A. C.; Michl, J. *J. Am. Chem. Soc.* **1992**, *114*, 601.
(4) Tinkertoy is a trademark of Playskool, Inc., Pawtucket, RI 02862 and designates a children's toy construction set consisting of straight wooden sticks and other simple elements insertable into spool-like connectors.
(5) Lehn, J.-M.; Ball, P. *New Chem.* **2000**, 300.
(6) Leininger, S.; Olenyuk, B.; Stang, P. J. *Chem. Rev.* **2000**, *100*, 853.
(7) Fujita, M. *Chem. Soc. Rev.* **1998**, *27*, 417.
(8) Caulder, D. L.; Raymond, K. N. *Acc. Chem. Res.* **1999**, *32*, 975.
(9) Balzani, V.; Gomez-Lopez, M.; Stoddart, J. F. *Acc. Chem. Res.* **1998**, *31*, 405.
(10) Haley, M. M.; Brad Wan, W. In *Advances in Strained and Interesting Organic Molecules*; Halton, B., Ed.; JAI Press: New York, 2000; Vol. 8; pp 1−41.
(11) Bunz, U. H. F.; Rubin, Y.; Tobe, Y. *Chem. Soc. Rev.* **1999**, *28*, 107.
(12) Siemsen, P.; Gubler, U.; Bosshard, C.; Gunter, P.; Diederich, F. *Chem. Eur. J.* **2001**, *7*, 1333.
(13) Cotton, F. A.; Lin, C.; Murillo, C. A. *Acc. Chem. Res.* **2001**, *34*, 759.
(14) Schwab, P. F. H.; Levin, M. D.; Michl, J. *Chem. Rev.* **1999**, *99*, 1863.
(15) Schöberl, U.; Magnera, T. F.; Harrison, R. M.; Fleischer, F.; Pflug, J. L.; Schwab, P. F. H.; Meng, X.; Lipiak, D.; Noll, B. C.; Allured, V. S.; Rudalevige, T.; Lee, S.; Michl, J. *J. Am. Chem. Soc.* **1997**, *119*, 3907.
(16) Sonoda, M.; Inaba, A.; Itahashi, K.; Tobe, Y. *Org. Lett.* **2001**, *3*, 2419.
(17) Constable, E. C.; Cargill Thompson, A. M. W. *J. Chem. Soc., Chem. Commun.* **1992**, 617.
(18) Amoroso, A. J.; Cargill Thompson, A. M. W.; Maher, J. P.; McCleverty, J. A.; Ward, M. D. *Inorg. Chem.* **1995**, *34*, 4828.
(19) Rucareanu, S.; Mongin, O.; Schuwey, A.; Hoyler, N.; Gossauer, A.; Amrein, W.; Hediger, H.-U. *J. Org. Chem.* **2001**, *66*, 4973.
(20) (a) Li, J.; Ambroise, A.; Yang, S. I.; Diers, J. R.; Seth, J.; Wack, C. R.; Bocian, D. F.; Holten, D.; Lindsey, J. S. *J. Am. Chem. Soc.* **1999**, *121*, 8927. (b) Yu, L.; Lindsey, J. S. *J. Org. Chem.* **2001**, *66*, 7402.
(21) Harrison, R. M.; Brotin, T.; Noll, B. C.; Michl, J. *Organometallics* **1997**, *16*, 3401.
(22) Magnera, T. F.; Peslherbe, L. M.; Körblová, E.; Michl, J. *J. Organomet. Chem.* **1997**, *548*, 83.
(23) Iengo, E.; Minatel, R.; Milani, B.; Marzilli, L. G.; Alessio, E. *Eur. J. Inorg. Chem.* **2001**, 609.
(24) Shinmori, H.; Kajiwara, T.; Osuka, A. *Tetrahedron Lett.* **2001**, *42*, 3617.
(25) Taylor, D. M.; Fukushima, H.; Morgan, H. *Supramol. Sci.* **1995**, *2*, 75.
(26) Burrell, A. K.; Officer, D. L.; Plieger, P. G.; Reid, D. C. W. *Chem. Rev.* **2001**, *101*, 2751.

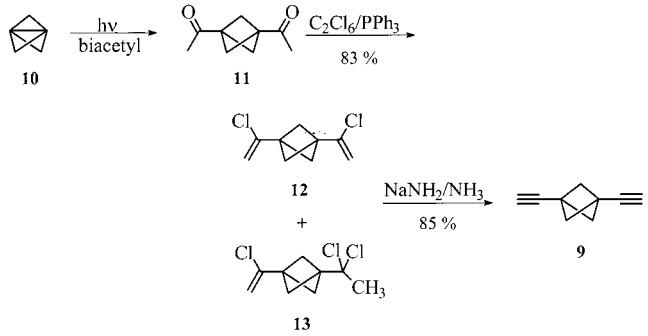
10.1021/jo020111b CCC: $22.00
Published on Web 07/09/2002

CHART 1



building blocks, we needed the compound in large quantities. Because of the explosive nature of **9**,[27] success depended on the development of a reliable high-yield procedure that could be repeated easily and often to avoid storing large amounts of **9**. The starting material for **9** is [1.1.1]propellane[3,28−32] (**10**), produced from 1,1-dibromo-2,2-bis(chloromethyl)cyclopropane[33] in a recently described procedure[34] that affords an essentially quantitative yield. This product is converted to 1,3-diacetylbicyclo[1.1.1]pentane (**11**) by photoaddition of biacetyl.[35,36] Reaction of **11** with hexachloroethane and triphenylphosphine followed by elimination yields **9**, as shown in Scheme 1. While the preparation of **11** proceeds well on large scale, the published procedure[37] for its conversion to **12** did not scale up well in our hands. The reaction was slow and yielded product mixtures. We found that

SCHEME 1



the use of molten triphenylphosphine as a solvent dramatically reduced reaction times in the first reaction step but still yielded an 8:1 mixture of a low-boiling (75 °C/0.5 Torr) desired major product, 1,3-di(1-chlorovinyl)-bicyclo[1.1.1]pentane (**12**), with a high-boiling minor impurity (120 °C). Since a stoichiometric amount of tetrachloroethylene was formed, it appeared likely that the second product was an adduct **13** of HCl to one of the double bonds in **12**, and this was supported by its ^{1}H NMR spectrum. Indeed, both materials yielded the same elimination product **9**, and a separation is not necessary. In the elimination step, we used sodium amide as reported by Szeimies[37,38] (Scheme 1). It is very important to add **12** free of solvent and of any tetrachloroethylene contamination, since in the presence of an organic solvent, the monoethynyl derivative appears to partition into the organic layer, avoiding the second elimination step. Moreover, higher boiling solvents are difficult to separate from the volatile **9**. We stored **9** in diethyl ether solution. When needed, the ether was evaporated off through a tube cooled with dry ice into which **9** sublimed at 50 °C and 1 Torr (overheating should be avoided due the possible explosiveness of the product or of impurities containing terminal acetylenes). After weighing, **9** was washed directly into the reaction flask with a solvent of choice. The modified procedure allows the synthesis of **9** on a gram scale within a few days.

The next step was the attachment of an aromatic heterocycle to one of the acetylene termini of **9**. Differential protection of one of the termini appeared laborious, and we have therefore taken advantage of the large scale availability of this material and of the ease of its separation by sublimation. We ran the coupling reactions with the requisite heterocycles using a 6-fold excess of **9** and were able to recover 90−95% of the unused reactant. Much larger excess of **9** was avoided since ethyne homocoupling then began to interfere. Although the reactions are thus statistical in nature, the singly substituted products were obtained in good yields.

Aryl-acetylene coupling reactions are well precedented.[39−46] They are usually performed in a tertiary or

(27) (a) Detz, C. M.; Sargent, H. B. In *Acetylene—Physical and Chemical Properties and Explosive Behavior*; Grayson, M., Eckroth, D., Eds.; Kirk-Othmer: New York, 1978; p 192. (b) A sample of **9** exploded in our laboratory during sublimation, probably as a result of overheating.

(28) Wiberg, K. B.; Walker, F. H. *J. Am. Chem. Soc.* **1982**, *104*, 5239.

(29) Semmler, K.; Szeimies, G.; Belzner, J. *J. Am. Chem. Soc.* **1985**, *107*, 6410.

(30) (a) Belzner, J.; Gareiss, B.; Polborn, K.; Schmid, W.; Semmler, K.; Szeimies, G. *Chem. Ber.* **1989**, *122*, 1509. (b) Belzner, J.; Bunz, U.; Semmler, K.; Szeimies, G.; Opitz, K.; Schlüter, A. D. *Chem. Ber.* **1989**, *122*, 397. (c) Alber, F.; Szeimies, G. *Chem. Ber.* **1992**, *125*, 757.

(31) Levin, M. D.; Kaszynski, P.; Michl, J. *Chem. Rev.* **2000**, *100*, 169.

(32) Lynch, K. M.; Dailey, W. P. *Org. Synth.* **1997**, *75*, 98.

(33) Lynch, K. M.; Dailey, W. P. *Org. Synth.* **1997**, *75*, 89.

(34) Shtarev, A. B.; Pinkhassik, E.; Levin, M. D.; Stibor, I.; Michl, J. *J. Am. Chem. Soc.* **2001**, *123*, 3484.

(35) Kaszynski, P.; Michl, J. *J. Org. Chem.* **1988**, *53*, 4593.

(36) Levin, M. D.; Kaszynski, P.; Michl, J. *Org. Synth.* **2000**, *77*, 249.

(37) Bunz, U.; Szeimies, G. *Tetrahedron Lett.* **1990**, *31*, 651.

(38) Bunz, U.; Szeimies, G. *Tetrahedron Lett.* **1989**, *30*, 2087.

(39) Stephens, R. D.; Castro, C. E. *J. Org. Chem.* **1963**, *28*, 3313.

(40) Cassar, L. *J. Organomet. Chem.* **1975**, *93*, 253.

(41) Stille, J. K.; Simpson, J. H. *J. Am. Chem. Soc.* **1987**, *109*, 2138.

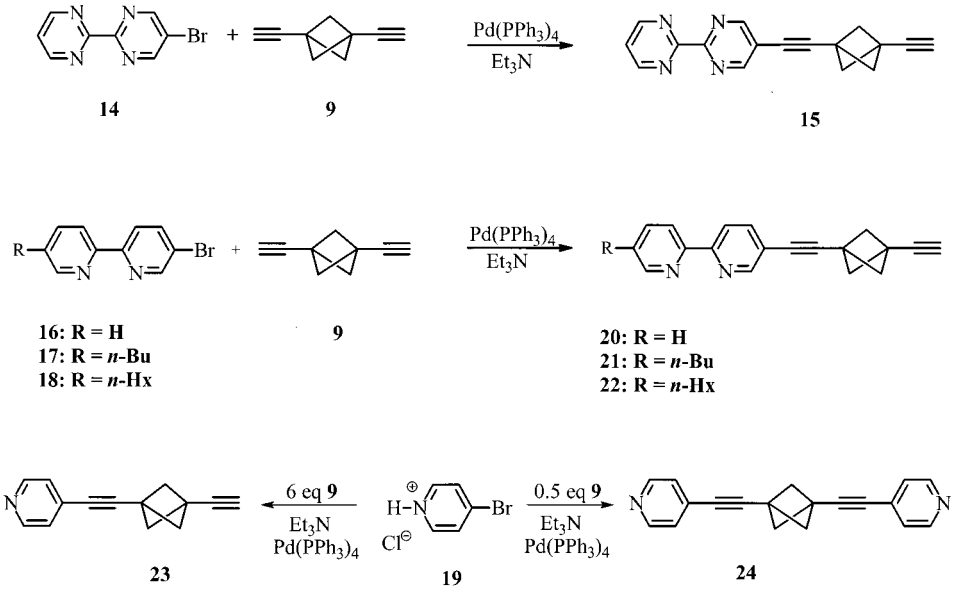
(42) Dang, H. P.; Linstrumelle, G. *Tetrahedron Lett.* **1978**, 191.

(43) Negishi, E.; Takahashi, T.; Baba, S.; Van Horn, D. E.; Okukado, N. *J. Am. Chem. Soc.* **1987**, *109*, 2393.

(44) Hatanaka, Y.; Hiyama, T. *J. Org. Chem.* **1988**, *53*, 918.

(45) Alami, M.; Ferri, F.; Linstrumelle, G. *Tetrahedron Lett.* **1993**, *34*, 6403.

SCHEME 2



secondary amine as the solvent, with a Pd catalyst and a Cu (I) salt as cocatalyst.[46−48] Under these conditions, we experienced very low yields and complicated product mixtures in initial reactions with 5-bromo-2,2′-bipyrimidine (**14**) to form 1-(2,2′-bipyrimidin-5-yl)ethynyl-3-ethynylbicyclo[1.1.1]pentane (**15**). We attributed these problems to the ability of Cu salts to interact with the bipyridyl and bipyrimidyl units. Copper-free conditions were reported by Alami et al.[45] and developed independently by Ziessel's group[49] for similar heteroaryl compounds and by Lindsey's group for porphyrins.[50,51] The elimination of the Cu cocatalyst improved the purity of our products dramatically, but the reaction time increased to up to 1 week in the case of bipyrimidine substitution. The complete elimination of oxygen from the triethylamine solution proved to be crucial. Its presence apparently disrupts the catalytic cycle by oxidizing Pd(0) to Pd(II), which then brings about an oxidative coupling of two terminal acetylenes. The best catalyst was $Pd(PPh_3)_4$, mainly because it does not require a reduction step for activation. With Pd(II) catalysts, we always detected byproducts containing butadiynes even after complete degassing of the solutions.

This coupling procedure worked well with 5-bromo-2,2′-bipyrimidine (**14**), 5-bromo-2,2′-bipyridine (**16**), 5-bromo-5′-*n*-butyl-2,2-bipyridine (**17**), 5-bromo-5′-*n*-hexylbipyridine (**18**), and 4-bromopyridinium hydrochloride (**19**) (Scheme 2) to produce 1-(2,2′-bipyrimidin-5-yl)ethynyl-3-ethynylbicyclo[1.1.1]pentane (**15**), 1-(2,2′-bipyridin-5-yl)ethynyl-3-ethynylbicyclo[1.1.1]pentane (**20**), 1-(5′-*n*-butyl-2,2′-bipyridin-5-yl)ethynyl-3-ethynylbicyclo[1.1.1]-pentane (**21**), 1-(5′-*n*-hexyl-2,2′-bipyridin-5-yl)ethynyl-3-ethynylbicyclo[1.1.1]pentane (**22**), and 1-(4-pyridyl)ethynyl-3-ethynylbicyclo[1.1.1]pentane (**23**). The last reaction was repeated on a small scale with a 2:1 ratio of **19** to **9** in order to obtain the disubstituted 1,3-di(4-pyridyl)-ethynylbicyclo[1.1.1]pentane (**24**) (Scheme 2), which was also observed as a minor byproduct in the previous reaction.

Attachment of Three Arms to a Benzene Ring. Attempts to use the same reaction conditions for the coupling of the remaining terminal acetylene unit of the resulting rod **15** to 1,3,5-triiodobenzene[15] in triethylamine were initially unsuccessful. The intermediates and products were insoluble, and the reaction did not go to completion. The use of piperidine solved the problem. When the temperature was kept under 55 °C to avoid reductive removal of the C−I bonds and the degradation of the arms, 1,3,5-tris((3-(2,2′-bipyrimidin-5-yl)ethynyl)-bicyclo[1.1.1]pent-1-ylethynyl)benzene (**1**) was formed in about 70% yield (Scheme 3). It is best to use **15** in a 5% excess in order to compensate for a small loss of material due to oxidative ethyne homocoupling. The stepwise progress of the reaction was followed by ^{1}H NMR. The trigonal connector **1** is chemically and thermally stable but suffers from very low solubility in hexanes, benzene, toluene, ethers, alcohols, ethyl acetate, and acetonitrile; it only dissolves well in chloroform and methylene chloride and moderately well in DMF. The coupling of **20**−**23** (Scheme 3) to 1,3,5-triiodobenzene proceeded similarly.

The connectors **2** and **5** have high thermal stability, but their solubility in most organic solvents, such as THF or diethyl ether, is very limited. Again, chloroform, methylene chloride, and to a lesser degree, DMF, are suitable solvents. Both derivatives can be dissolved in 2 M hydrochloric acid and reextracted from the aqueous layer after basification. The separation of the trialkylated

(46) (a) Sonogashira, K.; Tohda, Y.; Hagihara, N. *Tetrahedron Lett.* **1975**, 4467. (b) Sonogashira, K. In *Metal-Catalyzed Cross-Coupling Reactions*; Diederich, F., Stang, P. J., Eds.; Wiley-VCH: New York, 1998; pp 203−229.

(47) (a) Nicolaou, K. C.; Zipkin, R. E.; Dolle, R. E.; Harris, B. D. *J. Am. Chem. Soc.* **1984**, *106*, 3548. (b) Just, G.; O'Connor, B. *Tetrahedron Lett.* **1988**, *29*, 753. (c) Chemin, D.; Linstrumelle, G. *Tetrahedron* **1992**, *48*, 1943.

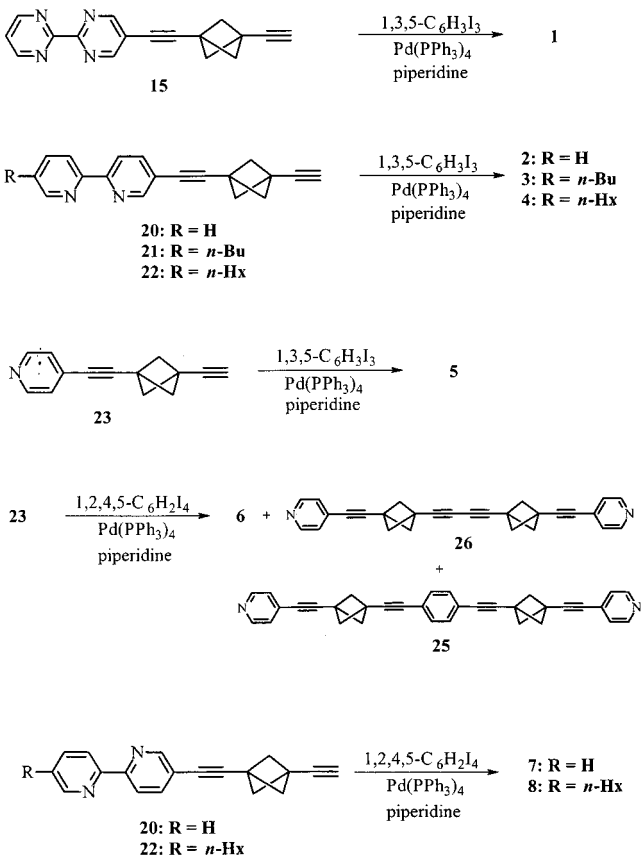
(48) Shvartsberg, M. S.; Moroz, A. A.; Kozhevnikova, A. N. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1978**, *4*, 875.

(49) Grosshenny, V.; Romero, F. M.; Ziessel, R. *J. Org. Chem.* **1997**, *62*, 1491.

(50) Wagner, R. W.; Johnson, T. E.; Li, F.; Lindsey, J. S. *J. Org. Chem.* **1995**, *60*, 5266.

(51) Ravikanth, M.; Strachan, J.-P.; Li, F.; Lindsey, J. S. *Tetrahedron* **1998**, *54*, 7721.

SCHEME 3



compounds **3** and **4** from byproducts was more challenging and was finally accomplished by HPLC. These connectors also possess high thermal stability and their solubility in organic solvents is generally improved, but only **4** dissolves reasonably well in THF.

Attachment of Four Arms to a Benzene Ring. We initially attempted the coupling reactions using 1,2,4,5-tetrabromobenzene, following the synthesis of 1,2,4,5-tetra(4-pyridylethynyl)benzene accomplished by Amoroso et al.[18] We hoped that the use of the aryl bromide would eliminate the reduction processes that we had observed with the aryl iodide in our syntheses of the 1,3,5-trisubstituted templates. The loss of a halogen by reduction was expected to be far more detrimental in the 1,2,4,5 substitution pattern since there were three times as many possible side products. However, under the drastic conditions used by Amoroso et al.,[18] both **20** and **23** decomposed in separate synthesis attempts before more than one arm was attached to the benzene ring. At lower temperatures, there was no reaction between the aryl bromide and the acetylenes. After these unsuccessful attempts, we repeated the reactions with 1,2,4,5-tetraiodobenzene.

The reaction of **23** with 1,2,4,5-tetraiodobenzene in piperidine under copper-free Pd(0) catalysis to produce 1,2,4,5-tetra((3-(4-pyridyl)ethynyl)bicyclo[1.1.1]pent-1-ylethynyl)benzene (**6**) (Scheme 3) was significantly slower than the analogous reaction with 1,3,5-triiodobenzene. Because of the five possible intermediates on the way to the tetrasubstituted product, the probability of side reactions and the possible number of unwanted byproducts were much larger. The reaction proceeded in a stepwise fashion, and the anticipated intermediates gave rise to very complicated ^{1}H NMR patterns that ultimately coalesced into a single aryl proton peak. The reaction took up to 10 days to run to completion, and the addition of catalyst in regular intervals was necessary. The regulation of the temperature between 45 and 50 °C was extremely critical since below that temperature range, no reaction took place, while above it, the reduction of the aryl iodide became a major side reaction. Also, it appeared that the reaction worked better at higher concentrations. The isolated yields were lower compared to the corresponding trisubstituted analogues. In the reaction with **23**, the major byproduct was the 1,4-disubstituted benzene derivative (**25**) (Scheme 3), an indication that the addition of an acetylene unit directly adjacent to an already attached one might be more difficult, possibly as a result of steric demands. This result could also explain the very slow reaction rates. The three-armed derivative was clearly detected by ^{1}H NMR spectroscopy but was not characterized further. Because of the extended reaction time, the oxidative homocoupling of **23** could never be completely suppressed, and we were able to isolate and characterize bis((3-(4-pyridyl)ethynyl)-bicyclo[1.1.1]pent-1-yl)butadiyne (**26**) from the reaction mixtures (Scheme 3). The tetragonal connector **6** was purified by HPLC and was the only connector we were able to crystallize. However, the needles were too small for X-ray analysis.

The coupling reactions between **20** or **22** and 1,2,4,5-tetraiodobenzene to form 1,2,4,5-tetra((3-(2,2′-bipyridin-5-yl)ethynyl)bicyclo[1.1.1]pent-1-ylethynyl)benzene (**7**) or 1,2,4,5-tetra((3-(5′-*n*-hexyl-2,2′-bipyridin-5-yl)ethynyl)-bicyclo[1.1.1]pent-1-ylethynyl)benzene (**8**), respectively, were even slower than the corresponding reaction with **23**, taking almost 14 days to go to completion (Scheme 3). A higher concentration of reactants again improved the yield and decreased the formation of the 1,4-disubstituted byproducts. The product mixtures were separated by HPLC. Unfortunately, the solubility of **7** is very low in most organic solvents, except in chloroform and methylene chloride, severely limiting its utility. Compound **8** proved to be more soluble than the other templates with four substituents, e.g., in toluene and THF, but could not be dissolved in diethyl ether.

X-ray Structure Analysis. Although we were unable to grow suitable single crystals of the connectors themselves, we succeeded in obtaining X-ray structure analyses for the essential constituents **20** and **23** and for the linear rod **24**.

1-(2,2′-Bipyridin-5-ylethynyl)-3-ethynylbicyclo-[1.1.1]pentane (20). This crystallized in the space group *Pnma*. In the crystal, the molecule is curved along the backbone as a result of a bend at the junction of the essentially linear 1,3-diethynylbicyclo[1.1.1]pentane and bipyridine units. The pyridine rings are coplanar, with disorder at the nitrogen sites because the long axis of the molecule lies on a crystallographic mirror plane. The bridgehead-to-bridgehead distance in the bicyclo[1.1.1]-pentane unit is 1.88 Å. The distance from the center of the C−C bond between the two pyridine rings, representing the position of the binding site, to the terminal carbon atom is 12.05 Å.

The molecules pack in alternating stacks (Figure 1), one propagating in the direction of the *c* axis, the other

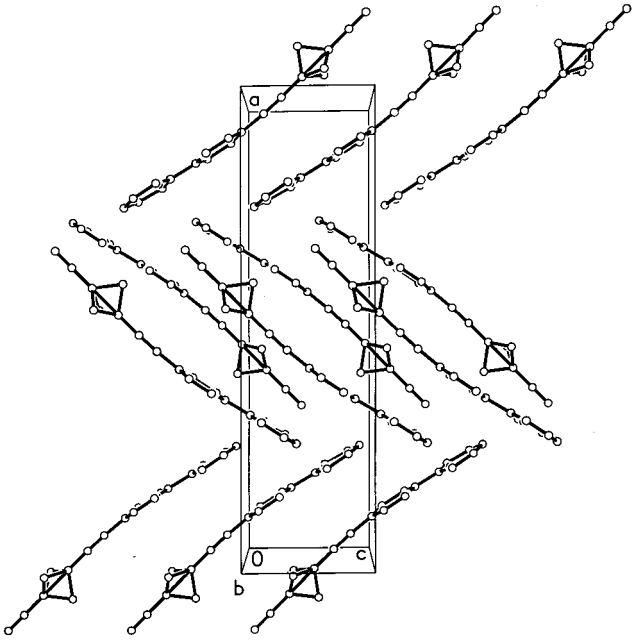


FIGURE 1. Crystal packing of **20**. View down unit cell *b* axis.

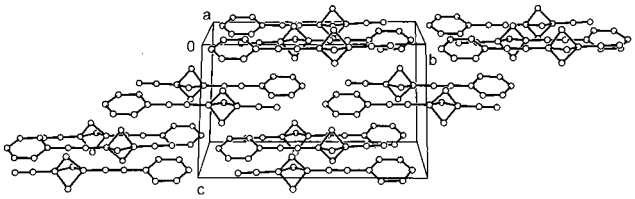


FIGURE 2. Crystal packing of **23**. View down unit cell *a* axis.

in the direction of the vector bisecting the angle α between the *b* and *c* axes. Successive layers of the stacks are arched in opposite directions, creating oval tunnels in which the molecules are aligned with a 2.66 Å contact between a hydrogen on the bicyclo[1.1.1.]pentane bridge and a bipyridyl nitrogen. There is a 2.79 Å close contact between a hydrogen on a pyridine ring of one stack and a nitrogen of a pyridine ring of a stack of the other orientation. The acetylenic hydrogen appears to form a 2.50 Å long hydrogen bond to the center of the outer aromatic ring of a neighbor molecule, slightly bent at 160.8°.

1-(4-Pyridylethynyl)-3-ethynylbicyclo[1.1.1]pentane (23). This crystallized in a monoclinic crystal system. The backbone of the molecule is essentially linear, with a length of 11.38 Å from the nitrogen atom to the terminal carbon atom. The distance between the bridgehead carbon atoms of the bicyclo[1.1.1]pentane unit is 1.88 Å. In the crystal, the molecules form linear chains with alternating orientation propagating in the direction of the *b* axis (Figure 2). The structure is similar to that of 4-ethynylpyridine[52] and contains even shorter N···H−C hydrogen bonds, with a N−H distance of only 2.29 Å and a N−H−C angle of 173.3 °.

1,3-Bis(4-pyridylethynyl)bicyclo[1.1.1]pentane (24). This crystallized in the space group $P2_1/c$. The nitrogen-to-nitrogen separation along the linear backbone of the molecule is 15.63 Å, and the bridgehead-to-bridgehead C−C distance is 1.87 Å. In the crystal, the molecules pack in a herringbone pattern (Figure 3). There is a 2.90 Å close contact between a pyridyl nitrogen and a bridge hydrogen on the bicyclo[1.1.1]pentane unit generated by inversion.

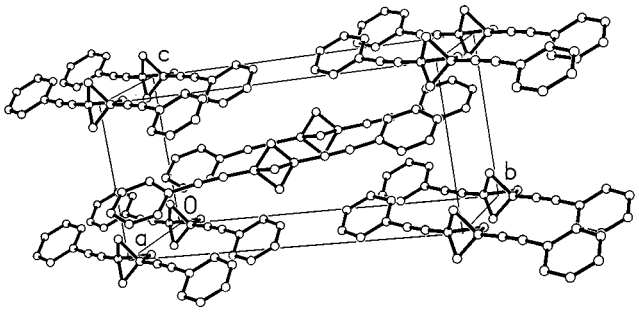


FIGURE 3. Crystal packing of **24**. View down unit cell *b* axis.

TABLE 1. Selected Distances in Molecular Rods 20, 23, and 24 (Å, from X-ray data)

	bridgehead[a]	backbone[b]	metal site[c]
20	1.88	15.55	12.05[d]
23	1.88	11.38	13.98[d]
24	1.87	15.63	20.83[e]

[a] Distance between bridgehead carbon atoms in the bicyclopentane unit. [b] Distance between the two terminal carbon or nitrogen atoms measured along the backbone of the molecule. [c] Assumed metal ion to nitrogen atom distance: 2.6 Å. [d] Distance from the terminal alkyne carbon to the metal site. [e] Distance between metal sites.

Table 1 compares some important distances in the molecules.

Connector Size. The results permit a fairly accurate extrapolation to estimate connector size. The expected radius of the pyridine- and bipyridine-containing connectors is about 14.3 and 18.5 Å, respectively. However, because of the location of the binding sites, the effective separation of a metal site from the center of the molecule is larger in the pyridine-terminated than in the bipyridine-terminated structure and is 16.9 and 15.0 Å, respectively.

The result is important for the estimation of distances in potential molecular structures built with the connectors. For example, the bipyridyl and bipyrimidine units complex well to mercury atoms[15] and we are hoping to exploit such complexation in molecular construction.

The X-ray structures of the compounds also provide additional data concerning the use of bicyclo[1.1.1]-pentane modules in molecular rods. The presently observed distances between bridgehead carbon atoms (1.87−1.88 Å) are somewhat longer than the average for all such distances in the Cambridge database (1.81 Å).[14] Of course, this carbon−carbon bond distance is long when compared to the "parent module", [1.1.1]propellane, where it is only 1.587 Å.[53]

Conclusions

A series of tri- and tetrasubstituted benzene derivatives **1**−**8** with extended rigid arms carrying mono- or

(52) Ohkita, M.; Suzuki, T.; Nakatani, K.; Tsuji, T. *Chem. Commun.* **2001**, 1454.

(53) Seiler, P.; Belzner, J.; Bunz, U.; Szeimies, G. *Helv. Chim. Acta* **1988**, *71*, 2100.

bidentate binding sites at the termini were synthesized as connectors for a molecular construction kit. The compounds are thermally stable but do not crystallize well, and the compounds without alkyl groups suffer from low solubility in most common organic solvents other than chloroform and methylene chloride. Introduction of alkyl groups into these star-shaped molecules improved the solubility in toluene and THF, but not in diethyl ether.

As a part of the synthesis, an efficient large-scale preparation of 1,3-diethynylbicyclo[1.1.1]pentane (**9**) was developed by modifying a previously reported[37,38] small-scale procedure.

An improved procedure for the coupling of terminal acetylenes to heteroaryl halides was utilized based on copper-free Pd catalysis, after we found that the standard Hagihara−Sonogashira[46] conditions are not applicable to bipyrimidine and bipyridine derivatives, probably because of interference by copper complexation. Similar results were reported a few years ago by Ziessel's group.[49]

Experimental Section

General Considerations. All reactions were carried out under argon atmosphere with dry solvent, freshly distilled under anhydrous conditions, unless otherwise noted. Standard Schlenk and vacuum line techniques were employed for all manipulations of air- or moisture-sensitive compounds. Yields refer to isolated chromatographically and spectroscopically homogeneous materials, unless otherwise stated.

1,3-Diacetylbicyclo[1.1.1]pentane (**11**),[34] 1,3,5-triiodobenzene,[15] 5-bromo-2,2′-bipyrimidine (**14**),[54] 5-bromo-2,2′-bipyridine (**16**),[54] 5-bromo-5′-*n*-butyl-2,2-bipyridine (**17**),[54] and 5-bromo-5′-*n*-hexylbipyridine (**18**)[54] were prepared as described elsewhere.

4-Bromopyridinium hydrochloride was purchased and sublimed prior to use. 1,2,4,5-Tetraiodobenzene, triphenylphosphine, hexachloroethane, $NaNH_2$, and $Pd(PPh_3)_4$ were purchased and used without further purification.

Triethylamine and piperidine were distilled from CaH_2 under argon immediately prior to use.

Physical Measurements. Melting points were determined with a standard apparatus and are uncorrected. ^1H NMR and ^{13}C NMR spectra were acquired at room temperature with a 500 MHz spectrometer and referenced to residual ^1H and to ^{13}C present in deuterated solvents. GC−MS spectra were measured on an instrument with a fused silica capillary column (cross-linked 5% phenyl methyl silicone). EI^+MS spectra were measured with a hybrid tandem mass spectrometer. Elemental analyses were performed by Desert Analytics, Tucson, AZ and Galbraith Laboratories, Knoxville, TN.

HPLC separations were performed at 25 °C with an instrument connected to a dual wavelength absorbance detector or a photodiode array detector and an evaporative light scattering detector.

X-ray Structure Determination. Crystals were examined under light hydrocarbon oil. The specimen crystal was affixed with a small amount of silicone vacuum grease to a thin glass fiber atop a tapered copper mounting pin and transferred to the goniometer of a diffractometer equipped with an LT-2a low-temperature apparatus operating at 153 or 143 K. Further details are provided in Supporting Information.

1,3-Di(1-chlorovinyl)bicyclo[1.1.1]pentane (12).[37] A mixture of **11** (1.82 g, 0.012 mol), hexachloroethane (5.66 g, 0.024 mol), and triphenylphosphine (6.27 g, 0.025 mol) was slowly heated to 100 °C under stirring. After 1 h, the reaction flask was attached to a Kugelrohr apparatus, and the reaction mixture was distilled under vacuum (0.5 Torr) with one receiving flask kept at room temperature, the second one cooled to 0 °C with ice, and a third one cooled to −78 °C with dry ice. The temperature in the oven was slowly raised to 120 °C, and the distillation was continued until only solids remained in the distillation flask. After cooling to room temperature, the first receiving flask was moved into the Kugelrohr oven. The distillation was resumed and the oven temperature slowly raised back to 120 °C. In the ice-cooled flask, 1.89 g (83%) of **12** was collected in a 20:1 mixture with **13**. The second flask contained mostly tetrachloroethylene but should always be checked for product. ^1H NMR ($CDCl_3$, 300 MHz) δ 2.04 (s, 6 H), 5.15 (d, 2 H, J = 1.5 Hz), 5.20 (d, 2 H, J = 1.5 Hz).[37] For **13**: ^1H NMR ($CDCl_3$, 300 MHz) δ 1.99 (s, 6 H), 2.06 (s, 3 H), 5.17 (d, 1 H, J = 1.5 Hz), 5.23 (d, 1 H, J = 1.5 Hz).

1,3-Diethynyl[1.1.1]bicyclopentane (9).[37] ***Warning: This compound has exploded upon heating.***[27] Anhydrous NH_3 (40 mL) was condensed into a flask containing $NaNH_2$ (3.8 g, 0.097 mol) under stirring at −78 °C, and **12** (3.22 g, 0.017 mol) was added dropwise from a syringe. The reaction mixture was stirred for 30 min at −60 °C, slowly warmed to −30 °C over the course of 2 h, and refluxed for 3 h. Then, dry diethyl ether (20 mL) was added dropwise, and the NH_3 was allowed to evaporate slowly through a bubbler filled with mineral oil. More diethyl ether (100 mL) was added, and the slurry was stirred for 30 min at room temperature. From an addition funnel, aqueous HCl (2 M) was added slowly under continued stirring until the excess $NaNH_2$ was consumed, and the aqueous layer was acidified. The two layers were separated, and the aqueous layer was extracted with diethyl ether (3 × 15 mL). The organic layers were combined, washed with saturated aqueous Na_2CO_3 (2 × 15 mL), and dried over Na_2SO_4. The solution was gently concentrated at atmospheric pressure and 45 °C. With a minimum amount of diethyl ether left, the flask was connected to a sublimation tube cooled with dry ice, and the product was sublimed under vacuum (0.5 Torr) after the remaining diethyl ether had evaporated into a liquid nitrogen trap. The product **9** was weighed in the tube and subsequently rinsed with dry diethyl ether into a round-bottom flask for storage: 1.64 g, (85%), mp 65 °C (lit.[37] 65−67 °C). ^1H NMR ($CDCl_3$, 300 MHz) δ 2.05 (s, 2 H), 2.31 (s, 6 H).[37]

1-(2,2′-Bipyrimidin-5-yl)ethynyl-3-ethynylbicyclo[1.1.1]-pentane (15). A flask was charged with **14** (1.0 g, 4.22 mmol), evacuated, and put under argon. Freshly sublimed **9** (4.3 g, 37.1 mmol) was washed into the flask with dry triethylamine (30 mL). The solution was degassed by three freeze−pump−thaw cycles, and $Pd(PPh_3)_4$ (243 mg, 0.21 mmol) was added from a tip tube. The yellow reaction mixture was stirred and refluxed for 10 days. A white solid precipitated. The triethylamine was evaporated directly from the reaction mixture into a liquid nitrogen cooled trap. Excess **9** was sublimed from the crude product. The remaining solid was dissolved in benzene and washed with 2 M NaOH (15 mL). The aqueous layer was extracted with benzene (2 × 15 mL), and the organic phases were combined. After drying over Na_2SO_4 and evaporation of the solvents under reduced pressure the product was chromatographed by PTLC (alumina, chloroform) to yield **15** as a white powder. After recrystallization from benzene small colorless plates of **15** were obtained: 0.827 g (72%); mp 178 °C (dec); ^1H NMR ($CDCl_3$, 500 MHz) δ 2.09 (s, 1 H), 2.43 (s, 6 H), 7.39 (t, J = 4.9 Hz, 1 H), 8.95 (s, 2 H), 8.98 (d, J = 4.9 Hz, 2 H); ^{13}C {^1H} NMR ($CDCl_3$, 124 MHz) δ 30.33, 58.75, 68.57, 73.67, 82.00, 97.02, 119.72, 121.53, 158.11, 159.65, 159.95, 161.88; IR (KBr) 407, 732, 531, 561, 640, 652, 746, 768, 814, 843, 942, 1128, 1259, 1370, 1384, 1410, 1450, 1519, 1557, 2224, 2874, 2913, 2965, 2994, 3299 cm^{-1}; MS (EI^+) m/z 272 (M, 20), 271 (M − H, 40), 247 (M − C_2H, 10), 193 (8), 166 (20), 139 (70), 111 (30), 97 (35), 69 (70), 57 (95), 42 (100); MS (ESI^+) m/z (rel int) 295 ($[M + Na]^+$, 100), 273 ($[M + H]^+$, 98); HRMS calcd 271.0984 ($[M - H]^+$), found 271.0976. Anal. Calcd for $C_{17}H_{12}N_4$: C, 74.98; H, 4.44. Found: C, 75.26; H, 4.67.

(54) Schwab, P. F. H.; Fleischer, F.; Michl, J. *J. Org. Chem.* **2002**, 67, 443.

1-(2,2′-Bipyridin-5-yl)ethynyl-3-ethynylbicyclo[1.1.1]-pentane (20). A flask was charged with **16** (603 mg, 2.56 mmol), evacuated, and put under argon. Freshly sublimed **9** (1.87 g, 16.2 mmol) was rinsed into the flask under argon with dry triethylamine (30 mL). The solution was degassed by three freeze−pump−thaw cycles, $Pd(PPh_3)_4$ (50 mg, 0.0512 mmol) was added from a tip tube, and the mixture was stirred at 70 °C for 12 h. After cooling to room temperature, the triethylamine was evaporated under reduced pressure, and the excess **9** was sublimed from the crude reaction mixture (50 °C, 0.5 Torr). The crude yellow product was then washed with diethyl ether (150 mL) and filtered. After evaporation of the solvent, **20** was isolated as a white solid by chromatography on alumina/hexanes−ethyl acetate 20:1 and recrystallized from diethyl ether as colorless plates (0.525 g, 76%). An analytically pure sample was obtained by sublimation (120 °C, 0.5 Torr): mp 184 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.09 (s, 1 H), 2.42 (s, 6 H), 7.28 (dd, J = 6.8 Hz, J = 4.9 Hz, 1 H), 7.78 (td, J = 8.1 Hz, J = 1.8 Hz, 1 H), 7.79 (dd, J = 8.4 Hz, J = 1.8 Hz, 1 H), 8.32 (d, J = 8.4 Hz, 1 H), 8.33 (d, J = 8.1 Hz, 1 H), 8.66 (br s, 2 H); ^{13}C {^{1}H} NMR ($CDCl_3$, 124 MHz) δ 30.09, 30.51, 58.74, 68.35, 77.16, 82.31, 92.22, 119.93, 120.24, 121.33, 123.90, 136.92, 139.60, 149.21, 151.77, 154.71, 155.42; IR (KBr) 423, 442, 502, 551, 592, 639, 759, 802, 823, 920, 994, 1064, 1097, 1218, 1257, 1348, 1384, 1405, 1447, 1489, 1526, 1538, 1596, 2101, 2229, 2608, 2876, 2915, 2965, 2993, 3039, 3167 cm^{-1}; MS (EI) *m*/*z* (rel int) 270 (M, 45), 269 ([M − H]$^+$, 100), 246 ([M − C_2H]$^+$, 15), 205 (15), 192 (10), 180 ([M − bcp − CCH]$^+$, 10), 168 (7), 152 (5), 128 (3), 78 (20), 57 (22), 41 (25); MS (ESI$^+$) *m*/*z* 293 ([M + Na]$^+$, 100), 271 ([M + H]$^+$, 100); HRMS calcd 270.1157, found 270.1147. Anal. Calcd for $C_{19}H_{14}N_2$: C, 84.42; H, 5.22; N, 10.36. Found: C, 84.76; H, 5.51; N, 10.34.

1-(5′-*n*-Butyl-2,2′-bipyridin-5-yl)ethynyl-3-ethynylbicyclo[1.1.1]pentane (21). A solution of **17** (600 mg, 2.06 mmol) in dry triethylamine (10 mL) under argon was transferred to a two-neck flask. Freshly sublimed **9** (3.52 g, 0.030 mol) was washed into the flask with dry triethylamine (25 mL), and the solution was degassed by three freeze−pump−thaw cycles. Then, $Pd(PPh_3)_4$ (60 mg, 2.5 mol %) was added from a tip tube. The reaction mixture was stirred at 70 °C for 12 h. The triethylamine was evaporated under reduced pressure directly from the reaction flask, and excess **9** was sublimed out. The crude product mixture was washed thoroughly with diethyl ether, and the solid residue was filtered off. The filtrate was concentrated under reduced pressure, and the resulting crude solid was chromatographed (alumina, hexanes−ethyl acetate, 10:1) to obtain **21** as a white powder: 556 mg (82%); mp 151 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.92 (t, J = 7.3 Hz, 3 H), 1.34 (m, 2 H), 1.60 (m, 2 H), 2.09 (s, 1 H), 2.45 (s, 6 H), 2.65 (t, J = 7.7 Hz, 2 H), 7.60 (dd, J = 8.1 Hz, J = 2.1 Hz, 1 H), 7.77 (dd, J = 8.3 Hz, J = 2.2 Hz, 1 H), 8.25 (d, J = 8.1 Hz, 1 H), 8.25 (d, J = 7.7 Hz, 1 H), 8.45 (d, J = 2.1 Hz, 1 H), 8.65 (d, J = 1.4 Hz, 1 H); ^{13}C {^{1}H} NMR ($CDCl_3$, 124 MHz) δ 13.82, 22.16, 30.05, 30.50, 32.53, 33.14, 58.71, 68.32, 77.20, 82.30, 92.00, 119.47, 119.93, 120.95, 136.80, 138.55, 139.55, 149.36, 151.73, 153.05, 154.87; IR (KBr) 413, 457, 654, 686, 743, 791, 839, 1024, 1049, 1243, 1384, 1464, 1538, 1587, 2857, 2877, 2915, 2959, 2993, 3280 cm^{-1}; MS (EI$^+$) *m*/*z* (relative intensity) 326 ([M]$^+$, 75), 325 ([M − H]$^+$, 95), 283 ([M − C_3H_7]$^+$, 100), 268 (5), 254 (12), 217 (13), 204 (6), 190 (11), 177 (5), 165 (5), 141 (7), 115 (4), 77 (4); HRMS calcd 326.1783, found 326.1778. Anal. Calcd for $C_{23}H_{22}N_2$: C, 84.63; H, 6.79; N, 8.58. Found: C, 84.34; H, 7.08; N, 8.43.

1-(5′-*n*-Hexyl-2,2′-bipyridin-5-yl)ethynyl-3-ethynylbicyclo[1.1.1]pentane (22). A solution of **18** (520 mg, 1.63 mmol) in dry triethylamine (10 mL) under argon was transferred into a 50 mL two-neck flask via cannula. Freshly sublimed **9** (1.12 g, 9.81 mmol) was rinsed into the flask with dry triethylamine (15 mL), and the solution was degassed by three freeze−pump−thaw cycles. Then, $Pd(PPh_3)_4$ (47 mg, 2.5 mol %) was added from a tip tube. The reaction mixture was heated to 70 °C for 15 h. The solvent was evaporated, and excess **9** was sublimed out under reduced pressure. The crude product was dissolved in chloroform and washed with NaOH/EDTA (0.1 M in water, 2 × 20 mL). The organic layer was dried over Na_2SO_4, and the solvents were evaporated under reduced pressure. The crude product was chromatographed by PTLC (alumina/hexanes−ethyl acetate, 15:1), and **22** was obtained as a white powder: 438 mg (76%); mp 146 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.85 (t, J = 7.3 Hz, 3 H), 1.30 (m, 6 H), 1.59 (m, 2 H), 2.09 (s, 1 H), 2.41 (s, 6 H), 2.62 (t, J = 7.7 Hz, 2 H), 7.58 (dd, J = 8.1 Hz, J = 1.8 Hz, 1 H), 7.75 (dd, J = 8.3 Hz, J = 2.0 Hz, 1 H), 8.26 (d, J = 8.4 Hz, 1 H), 8.29 (d, J = 8.4 Hz, 1 H), 8.47 (d, J = 1.6 Hz, 1 H), 8.66 (d, J = 1.6 Hz, 1 H); ^{13}C {^{1}H} NMR ($CDCl_3$, 124 MHz) δ 14.03, 22.52, 28.75, 30.05, 30.51, 30.98, 31.57, 32.84, 58.71, 68.33, 77.20, 82.31, 91.98, 119.45, 119.90, 120.92, 136.76, 138.56, 139.54, 149.41, 151.74, 153.07, 154.94; IR (KBr) 403, 534, 640, 653, 743, 835, 928, 1024, 1050, 1130, 1224, 1255, 1272, 1384, 1465, 1537, 1589, 2854, 2876, 2926, 2959, 2992, 3291 cm^{-1}; MS (EI$^+$) *m*/*z* (rel int) 354 ([M]$^+$, 100), 353 ([M − H]$^+$, 80), 297 ([M − C_4H_9]$^+$, 9), 283 ([M − C_5H_{11}]$^+$, 95), 268 (5), 254 (12), 241 (5), 217 (13), 204 (6), 190 (11), 178 (5), 163 (5), 149 (7), 115 (4), 83 (4), 69 (15), 55 (14); HRMS calcd 354.2096, found 354.2089. Anal. Calcd for $C_{25}H_{26}N_2$: C, 84.71; H, 7.39; N, 7.90. Found: C, 84.64; H, 7.34; N, 7.87.

1-(4-Pyridyl)ethynyl-3-ethynylbicyclo[1.1.1]pentane (23). Freshly sublimed **19** (560 mg, 2.87 mmol) was charged into a two-neck flask, evacuated, and placed under argon. Freshly sublimed **9** (1.73 g, 14.9 mmol) was rinsed into the flask with dry piperidine (30 mL), and the solution was degassed by three freeze−pump−thaw cycles. Then, $Pd(PPh_3)_4$ (162 mg, 5 mol %) was added from a tip tube. The reaction mixture was heated to 70 °C for 15 h. The solvent was evaporated, and excess **9** was sublimed out under reduced pressure. The crude product was rinsed thoroughly with diethyl ether (150 mL) and filtered. The filtrate was washed with NaOH/EDTA (0.1 M in water, 2 × 20 mL). The organic layer was dried over Na_2SO_4, and the solvents were evaporated under vacuum. The crude product was chromatographed by PTLC (alumina/hexanes−ethyl acetate 5:1), and **23** was obtained as a white powder, which crystallized from diethyl ether as colorless prisms (403 mg, 73%). For an analytically pure sample the compound was sublimed: mp 152 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.09 (s, 1 H), 2.40 (s, 6 H), 7.21 (dd, J = 4.3 Hz, J = 1.4 Hz, 2 H), 8.52 (dd, J = 4.3 Hz, J = 1.4 Hz, 2 H); ^{13}C {^{1}H} NMR ($CDCl_3$, 124 MHz) δ 30.44, 30.56, 58.93, 68.69, 77.39, 82.41, 93.11, 126.04, 131.41, 149.92; IR (KBr) 422, 442, 502, 531, 550, 592, 741, 802, 823, 920, 994, 1065, 1218, 1257, 1348, 1384, 1405, 1446, 1489, 1538, 1596, 1935, 2101, 2229, 2877, 2914, 2966, 2994, 3039, 3167 cm^{-1}; MS (EI$^+$) *m*/*z* (rel int) 193 ([M]$^+$, 23), 192 ([M − H]$^+$, 100), 178 (6), 168 ([M − C_2H]$^+$, 5), 165 (50), 152 (5), 128 (11), 114 ([C_2-bcp-C_2]$^+$, 25), 100 ([M − bcp − C_2H]$^+$, 14), 89 (10), 75 (25), 63 (22), 51 (34), 39 (10); MS (ESI$^+$) *m*/*z* 194 ([M + H]$^+$, 100); HRMS calcd 192.0813 ([M − H]$^+$), found 192.0804. Anal. Calcd for $C_{14}H_{11}N$: C, 87.01; H, 5.74; N, 7.25. Found: C, 86.81; H, 5.54; N, 7.51.

1,3-Bis(4-pyridyl)ethynylbicyclo[1.1.1]pentane (24). Freshly sublimed **19** (55 mg, 0.286 mmol) was charged into a two-neck flask, evacuated, and placed under argon. Freshly sublimed **9** (16 mg, 0.137 mmol) was rinsed into the flask with dry piperidine (10 mL), and the solution was degassed by three freeze−pump−thaw cycles. Then, $Pd(PPh_3)_4$ (2 mg, 5 mol %) was added from a tip tube. The reaction mixture was heated to 70 °C for 15 h. After evaporation of the solvent, the crude product was rinsed thoroughly with diethyl ether (150 mL) and filtered. The filtrate was washed with NaOH/EDTA (0.1 M in water, 2 × 20 mL). The organic layer was dried over Na_2SO_4, and the solvents were evaporated under reduced pressure. The crude product was chromatographed by PTLC (alumina/hexanes−ethyl acetate 5:1) and **24** was obtained as a white powder, which crystallized from diethyl ether as small colorless prisms: 23 mg (60%); mp 167 °C; ^{1}H NMR ($CDCl_3$,

300 MHz) δ 2.49 (s, 6 H), 7.23 (dd, J = 4.3 Hz, J = 1.4 Hz, 4 H), 8.52 (dd, J = 4.3 Hz, J = 1.4 Hz, 4 H); ^{13}C {^{1}H} NMR ($CHCl_3$, 124 MHz) δ 31.01, 59.15, 78.17, 92.96, 126.02, 131.32, 149.98; IR (KBr) 403, 549, 596, 792, 823, 988, 1076, 1220, 1306, 1384, 1410, 1493, 1536, 1594, 2235, 2875, 2912, 2989, 3075 cm^{-1}; MS (EI$^+$) *m*/*z* (rel int) 270 ([M]$^+$, 20), 269 ([M − H]$^+$, 40), 242 (7), 213 (5), 192 ([M − pyr]$^+$,5) 174 (100), 165 (5), 149 (5), 128 (11), 114 ([C_2-bcp-C_2]$^+$, 3), 101 ([pyr − C_2H]$^+$, 3), 91 ([HC_2-bcp]$^+$, 93), 77 (20), 63 (13), 51 (20), 41 (10); HRMS calcd 270.1157, found 270.1146. Anal. Calcd for $C_{19}H_{14}N_2$: C, 84.42; H, 5.22. Found: C, 84.64; H, 5.62.

1,3,5-Tris((3-(2,2′-bipyrimidin-5-yl)ethynyl)bicyclo[1.1.1]-pent-1-ylethynyl)benzene (1). A flask charged with **15** (120 mg, 0.441 mmol) and 1,3,5-triiodobenzene (67 mg, 0.147 mmol) was evacuated and filled with argon. Freshly distilled dry piperidine (25 mL) was added through a cannula, and the solution was degassed by three freeze−pump−thaw cycles. Then, $Pd(PPh_3)_4$ (130 mg, 0.0147) was added from a tip tube, and the yellow solution was heated to 55 °C for 18 h. The reaction mixture was poured into 2 M NaOH (5 mL). The organic layer was separated, and the aqueous layer was extracted with toluene (2 × 10 mL). After drying over Na_2SO_4 and evaporation of the solvents, the crude product was chromatographed by PTLC (alumina, chloroform) to yield **1** as a white powder: 94 mg (72%); mp 195 °C (dec); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.43 (s, 6 H), 7.36 (s, 1 H), 7.42 (t, J = 4.9 Hz, 1 H), 8.98 (s, 2 H), 9.01 (d, J = 4.9 Hz, 2 H); ^{13}C {^{1}H} NMR ($CDCl_3$, 124 MHz) δ 30.47, 30.92, 58.86, 73.75, 78.74, 88.80, 97.07, 119.68, 121.48, 123.26, 134.33, 158.01, 159.53, 159.85, 161.69; IR (KBr) 407, 531, 631, 660, 683, 747, 770, 837, 877, 940, 1163, 1247, 1285, 1384, 1411, 1450, 1524, 1563, 1773, 2222, 2877, 2915, 2968, 2988, 3035 cm^{-1}; MS (FAB$^+$/NOBA) *m*/*z* 889 ([M + H]$^+$); MS (ESI$^+$) *m*/*z* (rel int) 911 ([M + Na]$^+$, 100), 889 ([M + H]$^+$, 40); HRMS calcd 889.3264 ([M + H]$^+$), found 889.3291. Anal. Calcd for $C_{57}H_{36}N_{12}$: C, 77.01; H, 4.08; N, 18.91. Found: C, 76.72; H, 3.99; N 18.98.

1,3,5-Tris((3-(2,2′-bipyridin-5-yl)ethynyl)bicyclo[1.1.1]-pent-1-ylethynyl)benzene (2). A flask charged with **20** (120 mg, 0.446 mmol) and 1,3,5-triiodobenzene (64 mg, 0.146 mmol) was evacuated and filled with argon. Dry piperidine (15 mL) was added through a cannula, and argon was bubbled through the solution for 10 min before it was degassed by three freeze−pump−thaw cycles. Then, $Pd(PPh_3)_4$ (16 mg, 0.013 mmol, 2.5 mol %) was added from a tip tube, and the reaction mixture was heated to 55 °C for 24 h under stirring. After cooling to room temperature, aqueous NaOH (4 M, 2.5 mL) was added, and the mixture was stirred for 15 min. The solvents were evaporated under reduced pressure, and the crude product was dissolved in chloroform. The organic layer was washed with aqueous EDTA solution (1 M, 3 × 5 mL) and dried over Na_2SO_4. After evaporation of the solvent, the crude product was purified by PTLC (alumina/hexanes−ethyl acetate 2:1) to yield pure **2** as a white solid: 81 mg (61%); mp 195 °C (dec); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.46 (s, 18 H), 7.27 (dd, J = 6.8 Hz, J = 4.9 Hz, 3 H), 7.37 (s, 3 H), 7.78 (td, J = 8.1 Hz, J = 1.8 Hz, 3 H), 7.79 (dd, J = 8.4 Hz, J = 1.8 Hz, 3 H), 8.32 (d, J = 8.4 Hz, 3 H), 8.32 (d, J = 8.1 Hz, 3 H), 8.64 (d, J = 3.2 Hz, 3 H), 8.66 (s, 3 H); ^{13}C {^{1}H} NMR ($CDCl_3$, 124 MHz) δ 31.04, 31.07, 59.24, 77.61, 78.98, 89.41, 92.63, 120.20, 120.53, 121.59, 123.69, 124.18, 134.65, 137.23, 139.90, 149.52, 152.07, 155.00, 155.69; IR (KBr) 532, 584, 614, 651, 680, 731, 745, 795, 855, 876, 928, 992, 1020, 1037, 1061, 1090, 1120, 1145, 1241, 1282, 1368, 1384, 1416, 1432, 1456, 1489, 1543, 1571, 1586, 1731, 2216, 2876, 2914, 2988, 3048 cm^{-1}; MS (FAB$^+$/NOBA) *m*/*z* (rel int) 883 ([M + H]$^+$, 15), 820 (5), 679 (5), 575 (5), 501 (7), 423 (5) 371 (10), 307 (41), 219 (5), 154 (bipy, 100); MS (ESI$^+$) *m*/*z* (rel int) 884 ([M + 2H]$^+$, 70), 883 ([M + H]$^+$, 68); HRMS calcd 883.3549 ([M + H]$^+$), found 883.3569. Anal. Calcd for $C_{63}H_{42}N_6$: C, 85.69; H, 4.79; N, 9.52. Found: C, 85.44; H, 4.97; N, 9.22.

1,3,5-Tris((3-(5′-*n*-butyl-2,2′-bipyridin-5-yl)ethynyl)bicyclo[1.1.1]pent-1-ylethynyl)benzene (3). A flask was charged with **21** (270 mg, 0.831 mmol) and 1,3,5-triiodobenzene (121 mg, 0.27 mmol), evacuated, and filled with argon. Dry piperidine (20 mL) was added from a syringe, and the solution was degassed by three freeze−pump−thaw cycles. Then, $Pd(PPh_3)_4$ (15 mg, 5 mol %) was added from a tip tube. The reaction mixture was stirred at 60 °C for 15 h, 2 M NaOH (10 mL) saturated with EDTA was added, the two layers were separated after mixing for 10 min, and the aqueous layer was extracted with toluene (3 × 15 mL). The organic layers were combined, and the solvents were evaporated under reduced pressure. Then, the crude residue was dissolved in chloroform and dried over Na_2SO_4. After evaporation of the solvent, the solid residue was placed into a frit and washed with diethyl ether. The remaining solid was dissolved in chloroform and chromatographed by PTLC (alumina/hexanes−ethyl acetate, 10:1) to obtain **3** as a white powder (152 mg, 53%). An analytically pure sample was isolated by HPLC (C_{16}, chloroform/acetonitrile): mp 172 °C (dec); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.90 (t, J = 7.3 Hz, 9 H), 1.34 (m, 6 H), 1.60 (m, 6 H), 2.45 (s, 18 H), 2.62 (t, J = 7.7 Hz, 6 H), 7.36 (s, 3 H), 7.57 (dd, J = 8.4 Hz, J = 2.1 Hz, 3 H), 7.77 (dd, J = 7.3 Hz, J = 2.1 Hz, 3 H), 8.25 (d, J = 8.4 Hz, 3 H), 8.27 (d, J = 8.4 Hz, 3 H), 8.45 (d, J = 1.6 Hz, 3 H), 8.65 (d, J = 1.6 Hz, 3 H); ^{13}C {^{1}H} NMR ($CDCl_3$, 124 MHz) δ 13.80, 22.14, 30.74, 32.53, 33.10, 58.91, 77.40, 78.66, 89.11, 92.08, 119.44, 119.88, 120.88, 123.38, 134.32, 136.71, 138.48, 139.49, 149.36, 151.71, 153.04, 154.88; IR (KBr) 584, 642, 652, 682, 743, 806, 841, 877, 931, 1025, 1053, 1211, 1261, 1283, 1384, 1416, 1465, 1538, 1585, 2219, 2856, 2874, 2924, 2958 cm^{-1}; MS (ESI$^+$) *m*/*z* (rel int) 1074 ([M + Na]$^+$, 5), 1051 ([M + H]$^+$, 100) 526 ([M + 2H]$^{2+}$, 30). Anal. Calcd for $C_{75}H_{66}N_6$: C, 85.68; H, 6.33; N, 7.99. Found: C, 85.78; H, 6.42; N, 8.03.

1,3,5-Tris((3-(5′-*n*-hexyl-2,2′-bipyridin-5-yl)ethynyl)-bicyclo[1.1.1]pent-1-ylethynyl)benzene (4). In a two-neck flask, **22** (124 mg, 0.350 mmol) and 1,3,5-triiodobenzene (54 mg, 0.119 mmol) were combined, evacuated, and put under argon. Freshly distilled dry piperidine (20 mL) was added from a syringe, and the mixture was stirred at room temperature until the solid was dissolved. Then, the solution was degassed by three freeze−pump−thaw cycles. After warming to room temperature, $Pd(PPh_3)_4$ (10 mg, 2.5 mol %) was added from a tip tube, and the reaction mixture was stirred at 55 °C for 24 h. Aqueous NaOH (4 M, 2.5 mL) was added, and the solution was stirred for 15 min before the solvents were evaporated under reduced pressure. The crude solid was dissolved in chloroform and washed with aqueous EDTA solution (1 M, 3 × 5 mL). After drying over Na_2SO_4, the organic solvent was evaporated under reduced pressure, and the crude product was purified by PTLC (alumina, hexane/ethyl acetate, 5:1) to yield **4** as a white solid: 95 mg (71%); mp 169 °C (dec); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.86 (t, J = 7.3 Hz, 9 H), 1.31 (m, 18 H), 1.60 (m, 6 H), 2.46 (s, 18 H), 2.63 (t, J = 7.7 Hz, 6 H), 7.36 (s, 3 H), 7.59 (dd, J = 8.1 Hz, J = 1.8 Hz, 3 H), 7.77 (dd, J = 8.3 Hz, J = 2.0 Hz, 3 H), 8.27 (d, J = 8.4 Hz, 3 H), 8.29 (d, J = 8.4 Hz, 3 H), 8.47 (d, J = 1.6 Hz, 3 H), 8.66 (d, J = 1.6 Hz, 3 H); ^{13}C {^{1}H} NMR ($CDCl_3$, 124 MHz) δ 14.05, 22.55, 28.77, 30.79, 31.01, 31.59, 32.86, 58.96, 77.43, 78.70, 89.15, 92.13, 119.51, 119.94, 120.94, 123.41, 134.36, 136.77, 138.59, 139.55, 149.41, 151.75, 153.10, 154.94; IR (KBr) 652, 682, 742, 835, 878, 1024, 1053, 1208, 1283, 1384, 1417, 1464, 1538, 1585, 2854, 2924, 2955 cm^{-1}; MS (ESI$^+$) *m*/*z* (rel int) 1158 ([M + Na]$^+$, 5), 1136 ([M + H]$^+$, 100), 568 ([M + 2H]$^{2+}$, 50). Anal. Calcd. for $C_{81}H_{78}N_6$: C, 85.68; H, 6.93; N, 7.40. Found: C, 85.57; H, 7.18; N, 7.27.

1,3,5-Tris((3-(4-pyridyl)ethynyl)bicyclo[1.1.1]pent-1-yl-ethynyl)benzene (5). In a two-neck flask, **23** (200 mg, 1.037 mmol) and 1,3,5-triiodobenzene (150 mg, 0.33 mmol) were combined, evacuated, and placed under argon. Freshly distilled dry piperidine (20 mL) was added from a syringe, and the mixture was stirred at room temperature until the solid was dissolved. Then, the solution was degassed by three freeze−pump−thaw cycles. After warming to room temperature, Pd-

(PPh_3)$_4$ (20 mg, 5 mol %) was added from a tip tube, and the reaction mixture was stirred at 55 °C for 18 h. Aqueous NaOH (4 M, 2.5 mL) was added, and the solution was stirred for 15 min before the solvents were evaporated under reduced pressure. The crude solid was dissolved in chloroform and washed with aqueous EDTA solution (1 M, 3 × 5 mL). Then, the organic layer was extracted with HCl (2 M, 5 × 5 mL). The aqueous layer was basified with NaOH (2 M, 30 mL) and extracted with chloroform (4 × 10 mL). After drying over Na_2SO_4, the organic solvent was evaporated under reduced pressure, and the crude product was purified by PTLC (alumina/hexane−ethyl acetate, 5:1) to yield **5** as a white solid: 116 mg (54%); mp 178 °C (dec); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.44 (s, 18 H), 7.22 (dd, J = 4.3 Hz, J = 1.4 Hz, 6 H), 7.35 (s, 3 H), 8.52 (dd, J = 4.3 Hz, J = 1.4 Hz, 6 H); ^{13}C {^{1}H} NMR ($CDCl_3$, 124 MHz) δ 30.55, 30.87, 58.88, 77.77, 78.72, 88.99, 99.92, 123.37, 125.76, 131.14, 134.37, 149.67; IR (KBr) 549, 571, 596, 682, 800, 819, 877, 989, 1081, 1216, 1281, 1384, 1405, 1489, 1539, 1593, 2227, 2877, 2914, 2968, 2987 cm^{-1}; MS (EI$^+$) m/z (rel int) 651 ([M]$^+$, 6), 650 ([M − H]$^+$, 4), 537 (100), 459 (35), 443 (17), 412 (14), 378 (5), 315 (15), 287 (8), 264 (5), 228 (7), 167 (5), 142 (9), 128 (27), 84 (11), 55 (23); HRMS calcd 651.2674, found 651.2681. Anal. Calcd for $C_{48}H_{33}N_3$: C, 88.45; H, 5.10; N, 6.45. Found: C, 88.43; H, 4.90; N, 6.58.

1,2,4,5-Tetra((3-(4-pyridyl)ethynyl)bicyclo[1.1.1]pent-1-ylethynyl)benzene (6). A 25 mL two-neck flask was charged with **23** (113 mg, 0.585 mmol) and 1,2,4,5-tetraiodobenzene (81 mg, 0.139 mmol), evacuated, and filled with argon. Dry piperidine (15 mL) was added from a syringe, and the solution was degassed by three freeze−pump−thaw cycles. Then, Pd(PPh_3)$_4$ (17 mg, 2.5 mol %) was added from a tip tube, and the reaction mixture was stirred for 4 days at 55 °C. More Pd(PPh_3)$_4$ (17 mg, 2.5 mol %) was added from a tip tube, and the reaction was continued for 4 more days. Then, NaOH/EDTA (0.1 M in water, 5 mL) was added, and the mixture was stirred for 10 min. The phases were separated, and the aqueous layer was extracted with toluene (3 × 5 mL). The organic layers were combined, and the solvents were evaporated under reduced pressure. The crude product was dissolved in chloroform and dried over Na_2SO_4 before the solvent was evaporated under vacuum. The solid was chromatographed by PTLC (alumina, chloroform), and **6** was obtained as small needles after crystallization from chloroform: 55 mg (47%); mp 199 °C (dec); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.48 (s, 24 H), 7.23 (dd, J = 4.5 Hz, J = 1.5 Hz, 8 H), 7.40 (s, 2 H), 8.52 (dd, J = 4.5 Hz, J = 1.5 Hz, 8 H); ^{13}C {^{1}H} NMR ($CDCl_3$, 124 MHz) δ 30.71, 31.11, 59.02, 77.95, 77.98, 92.75, 93.77, 125.10, 125.74, 131.06, 134.85, 149.71; IR (KBr) 548, 584, 652, 694, 731, 747, 818, 856, 899, 992, 1021, 1038, 1091, 1120, 1216, 1241, 1260, 1287, 1369, 1384, 1405, 1447, 1487, 1532, 1571, 1592, 1629, 2227, 2605, 2852, 2877, 2915, 2968, 3048 cm^{-1}; MS (FAB$^+$/NOBA) m/z 843 ([M + H]$^+$); MS (ESI$^+$) m/z (rel int) 843 ([M + H]$^+$, 100). Anal. Calcd for $C_{62}H_{42}N_4$: C, 88.33; H, 5.02; N, 6.65. Found: C, 88.43; H, 4.90; N, 6.58.

Two byproducts were isolated by HPLC (chloroform/acetonitrile/Et_3N) and characterized: (a) **1,4-Di((3-(4-pyridyl)-ethynyl)bicyclo[1.1.1]pent-1-ylethynyl)benzene (25)**: 15 mg (23%); mp 172 °C (dec); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.46 (s, 12 H), 7.23 (dd, J = 4.9 Hz, J = 1.4 Hz, 4 H), 7.31 (s, 4 H), 8.52 (dd, J = 4.9 Hz, J = 1.4 Hz, 4 H); ^{13}C {^{1}H} NMR ($CHCl_3$, 124 MHz) δ 30.56, 31.04, 58.94, 77.77, 79.96, 89.74, 93.04, 122.57, 125.78, 131.19, 131.62, 149.67; IR (KBr) 403, 549, 596, 792, 823, 988, 1076, 1220, 1306, 1384, 1410, 1493, 1536, 1594, 2235, 2875, 2912, 2989, 3075 cm^{-1}; MS (EI$^+$) m/z (rel int) 460 ([M]$^+$, 22), 459 ([M − H]$^+$, 45), 458 ([M − 2H]$^+$, 2), 405 (35), 343 (30), 314 (20), 265 (100), 235 (35), 183 (12), 97 (22), 75 (30), 63 (25), 57 (35); HRMS calcd 460.1939 [M]$^+$, found 460.1922. Anal. Calcd for $C_{34}H_{24}N_2$: C, 88.68; H, 5.25; N, 6.07. Found: C, 88.98; H, 5.49; N, 5.84. (b) **Bis((3-(4-pyridyl)-ethynyl)bicyclo[1.1.1]pent-1-yl)butadiyne (26)**: 12 mg (5%); mp 160 °C (dec); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.40 (s, 12 H), 7.22 (dd, J = 4.3 Hz, J = 1.4 Hz, 4 H), 8.51 (dd, J = 4.3 Hz, J = 1.4 Hz, 4 H); ^{13}C {^{1}H} NMR ($CHCl_3$, 124 MHz) δ 30.52, 30.65, 52.25, 59.02, 64.86, 77.76, 92.65, 125.78, 131.11, 149.68; IR (KBr) 403, 539, 596, 782, 823, 978, 1066, 1220, 1306, 1374, 1412, 1496, 1516, 1592, 2236, 2865, 2909, 2981, 3078 cm^{-1}. MS (EI$^+$) m/z (rel int) 384 ([M]$^+$, 30), 383 ([M − H]$^+$, 100), 382 ([M − 2H]$^+$, 55), 381 ([M − 3H]$^+$, 85), 383 ([M − 4H]$^+$, 20), 367 (80), 354 (30), 340 (30), 328 (13), 306 ([M − pyr]$^+$, 45), 290 (35), 254 (20), 240 (40), 228([M − 2pyr]$^+$, 213 (35), 189 (15), 163 (11), 128 (17), 114 ([C_2-bcp-C_2]$^+$, 12), 101 ([pyr-C_2H]$^+$, 15), 89 (15), 75 (30), 63 (25), 51 (25); HRMS calcd 383.1548 [M −H]$^+$, found 383.1563. Anal. Calcd for $C_{28}H_{20}N_2$: C, 87.47; H, 5.24; N, 7.29. Found: C, 87.51; H, 5.62; N, 7.65.

1,2,4,5-Tetra((3-(2,2′-bipyridin-5-yl)ethynyl)bicyclo-[1.1.1]pent-1-ylethynyl)benzene (7). A 25 mL two-neck flask was charged with **20** (309 mg, 1.14 mmol) and 1,2,4,5-tetraiodobenzene (158 mg, 0.272 mmol), evacuated, and filled with argon. Dry piperidine (10 mL) was added from a syringe, and the solution was degassed by three freeze−pump−thaw cycles. Then, Pd(PPh_3)$_4$ (33 mg, 2.5 mol %) was added from a tip tube, and the reaction mixture was stirred for 6 days at 50 °C. Additional Pd(PPh_3)$_4$ (18 mg, 1.25 mol %) was added from a tip tube, and the reaction was continued for 5 more days. Then, NaOH (4 M in water, 5 mL) was added, and the mixture was stirred for 10 min. The solvents were removed under reduced pressure, and chloroform was added. The organic layer was washed with EDTA (1 M, 3 × 10 mL), dried over Na_2SO_4, and evaporated under reduced pressure. The crude product mixture was separated by HPLC (C_{18}, acetonitrile/chloroform−2.5% Et_3N), and **7** was obtained as an off-white solid: 174 mg (56%); mp 212 °C (dec); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.51 (s, 12 H), 7.29 (dd, J = 6.8 Hz, J = 4.9 Hz, 2 H), 7.41 (s, 1 H), 7.78 (td, J = 8.1 Hz, J = 1.8 Hz, 2 H), 7.79 (dd, J = 8.4 Hz, J = 1.8 Hz, 2 H), 8.32 (d, J = 8.4 Hz, 2 H), 8.32 (d, J = 8.1 Hz, 2 H), 8.64 (d, J = 3.2 Hz, 2 H), 8.66 (s, 2 H); ^{13}C {^{1}H} NMR ($CDCl_3$, 124 MHz) δ 31.20, 31.32, 59.38, 77.78, 78.23, 92.49, 94.19, 120.13, 120.54, 121.61, 124.19, 125.41, 135.11, 137.22, 139.89, 149.52, 152.08, 155.05, 155.70; IR (KBr) 534, 614, 652, 694, 731, 747, 796, 856, 899, 992, 1021, 1038, 1091, 1120, 1225, 1241, 1260, 1288, 1369, 1384, 1433, 1457, 1486, 1543, 1571, 1586, 2225, 2876, 2913, 2987, 3048 cm^{-1}; MS (FAB$^+$/3-NOBA) m/z 1151 ([M + H]$^+$); MS (ESI$^-$) m/z 1151 ([M + H]$^+$). Anal. Calcd for $C_{82}H_{54}N_8$: C, 85.54; H, 4.73. Found: C, 85.88; H, 4.92.

1,2,4,5-Tetra((3-(5′-*n*-hexyl-2,2′-bipyridin-5-yl)ethynyl)-bicyclo[1.1.1]pent-1-ylethynyl)benzene (8). A 25 mL two-neck flask was charged with **22** (183 mg, 0.518 mmol) and 1,2,4,5-tetraiodobenzene (68 mg, 0.116 mmol), evacuated, and filled with argon. Dry piperidine (10 mL) was added from a syringe, and the solution was degassed by three freeze−pump−thaw cycles. Then, Pd(PPh_3)$_4$ (15 mg, 2.5 mol %) was added from a tip tube, and the reaction mixture was stirred for 6 days at 50 °C. Additional Pd(PPh_3)$_4$ (18 mg, 1.25 mol %) was added from a tip tube, and the reaction was continued for 5 more days. Then, NaOH (4 M in water, 5 mL) was added, and the mixture was stirred for 10 min. The solvents were removed under reduced pressure, and the crude solid was dissolved in chloroform. The organic layer was washed with EDTA (1 M, 3 × 10 mL), dried over Na_2SO_4, and evaporated under reduced pressure. The crude product mixture was separated by PTLC (alumina/hexanes−chloroform 1:1), and **8** was isolated in a mixture with triphenylphosphine oxide. The solid was dissolved in chloroform, and acetonitrile was added until a white precipitate became visible. After centrifugation (3200 rpm), the liquid was carefully separated. The white solid was characterized as **8**: 53 mg, (30%); mp 165 °C (dec); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.86 (t, J = 7.3 Hz, 12 H), 1.29 (m, 24 H), 1.62 (m, 8 H), 2.51 (s, 24 H), 2.64 (t, J = 7.7 Hz, 8 H), 7.41 (s, 2 H), 7.59 (dd, J = 8.1 Hz, J = 1.8 Hz, 4 H), 7.78 (dd, J = 8.3 Hz, J = 2.0 Hz, 4 H), 8.28 (d, J = 8.4 Hz, 4 H), 8.29 (d, J = 8.4 Hz, 4 H), 8.46 (d, J = 1.6 Hz, 4 H), 8.65 (d, J = 1.6 Hz, 4 H); ^{13}C {^{1}H} NMR ($CDCl_3$, 124 MHz) δ 14.05, 22.54, 28.76,

29.67, 31.01, 31.58, 32.85, 59.08, 77.57, 77.93, 91.99, 93.92, 119.42, 119.93, 120.92, 125.12, 132.93, 136.78, 138.58, 139.56, 149.42, 151.75, 153.08, 154.98; IR (KBr) 652, 682, 742, 835, 878, 1024, 1053, 1208, 1283, 1384, 1417, 1464, 1538, 1585, 2854, 2924, 2955 cm^{-1}; MS (ESI^+) *m/z* (rel int) 1509 ($[M + Na]^+$, 100), 1487 ($[M + H]^+$, 90). Anal.Calcd for $C_{106}H_{102}N_8$: C, 85.56; H, 6.91; N, 7.53. Found: C, 85.12; H, 7.06; N, 7.25.

Acknowledgment. This paper is dedicated to Prof. Waldemar Adam on the occasion of his 65th birthday. The work was supported by USARO Grants DAAG55-98-1-0310 and DAAD-19-01-1-0521. P. F. H. S. is thankful to the CU Graduate School and the Institute of International Exchange/Germanistic Society of America for fellowships.

Supporting Information Available: ORTEP representations of the single X-ray structures of compounds **20**, **23**, **24**; table summarizing the crystallographic parameters of compounds **20**, **23**, **24**; tables with detailed information on the reported X-ray structures of compounds **20**, **23**, **24**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO020111B