A Facile Route to Bridgehead Disubstituted Bicyclo[1.1.1]pentanes Involving Palladium-Catalyzed Cross-Coupling Reactions

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3-Alkylbicyclo[1.1.1]pent-1-yl Grignard reagents have been coupled with bromoarenes in the presence of catalytic amounts (0.8–2.0 mol.%) of $PdCl_2$(dppf) in diethyl ether containing 1,4-dioxane as a co-solvent at room temperature. The yields of the coupling step range from 73% to 98%. By using di- or tribromoarenes, coupling products of types **10** and **11** have been obtained. The X-ray structures of four model compounds (**4a**, **4d**, **4j**, **4n**) have been determined, each of which shows a short, nonbonded C1–C3 distance in the bicyclo[1.1.1]pentyl subunit of about 1.89 Å.

Introduction

Ever since the facile access to [1.1.1]propellane (**1**) from the tetrahalide **2** became available,[1][2] the once tedious synthesis of the parent bicyclo[1.1.1]pentane (**3**)[3] and its derivatives[4] has been greatly simplified. 1,3-Disubstituted bicyclo[1.1.1]pentanes have been obtained by radical chain addition of numerous reagents to [1.1.1]propellane[5][6][7][8][9] and further chemical modification of the substituents has led to a substantial increase in the number of known compounds of this type. The remarkably short C1−C3 distance of 1.86 Å in **3** and its derivatives is unprecedented for two carbon atoms that are not directly bonded.[10] Early theoretical investigations of **3**[11] predicted "through bond" and "through space" interaction between the bridgehead carbons. Photoelectron spectroscopy of halogen- and alkynyl-substituted bicyclo[1.1.1]pentanes has shown the ability of these hydrocarbons to mediate electronic interactions.[12] These results make the bicyclo[1.1.1]pentane system an interesting entity for the study of electron-transfer and energy-transfer processes. To this end, a flexible synthetic procedure for a wide range of 1,3-disubstituted bicyclo[1.1.1]pentanes would be desirable, which, in spite of the aforementioned synthetic successes, has hitherto not been available. We now report on an efficient synthesis of 1-aryl-3-alkyl- and 1,3-diaryl-substituted bicyclo[1.1.1]pentanes **4**, a key step of which is palladium-catalyzed coupling of a Grignard intermediate with an aryl bromide.[13]

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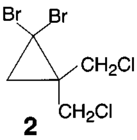

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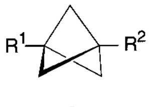

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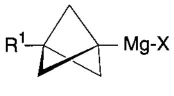
Results and Discussion

Some time ago it was observed that **1** could add Grignard reagents across the central C1−C3 bond.[14] A further study revealed that this reaction most probably proceeds by a radical chain mechanism and requires careful choice of solvent and reaction conditions.[15] In this investigation, *tert*-butylmagnesium chloride, cyclohexylmagnesium chloride, isopropylmagnesium chloride and phenylmagnesium bromide have been used as the Grignard reagents. These were allowed to react with [1.1.1]propellane in diethyl ether or, in the case of the latter reagent, in diethoxymethane for 2−6 days at room temperature under nitrogen. The intermediate Grignard reagent **5** (**a**: R^1 = *tert*-butyl; **b**: R^1 = cyclohexyl; **c**: R^1 = isopropyl; **d**: R^1 = phenyl) was then mixed with the appropriate aryl bromide **6** and the catalyst and the reactions were allowed to proceed for 48 h at ambient temperature in diethyl ether and dioxane. Preceding investigations had shown that Ni(II) catalysts, which had proven successful in the Kumada coupling,[16] did not lead to the desired products in our case. Bis(acetonitrile)palladium dichloride [$Pd(CH_3CN)_2Cl_2$] and a 1:2 mixture of bis(dibenzylideneacetone)palladium(0) and tris(*o*-tolyl)phosphane [P(*o*-Tol)$_3$] were effective catalysts, but could not compete with [1,1′-bis(diphenylphosphanyl)ferrocene]palladium(II) dichloride [$PdCl_2$(dppf), **7**], which gave the best results when added at a concentration of 1.3−3.0 mol.% with respect to the bromides **6**. No biphenyls were found as side products.



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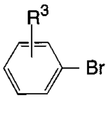

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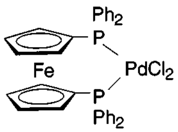

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Our results are presented in Table 1. The yields quoted are based on the aryl bromide used; it was assumed that the formation of propellane **1** from precursor **2** proceeded with 70% yield,[1][2] and that the addition of the Grignard

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reagent to **1** was effected quantitatively. Yields of **4** based on tetrahalide **2** are given in parentheses.

Table 1. Yields of **4** from reactions of **5** with aryl bromides **6** catalyzed by **7**

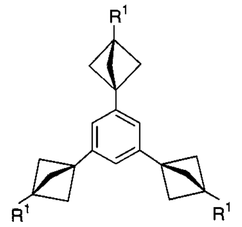
Entry	**5**, R^1 =	Ar-Br **6**; Ar =	**4**	% Yield [a]	**7** (mol.%) [b]
1	*t*Bu	Ph	**a**	88 (37)	1.3
2	*t*Bu	2-Naphthyl	**b**	93 (42)	1.3
3	*t*Bu	4-Ph-C_6H_4	**c**	96 (43)	1.3
4	*t*Bu	4-Cl-C_6H_4	**d**	90 (40)	1.3
5	*t*Bu	4-CF_3-C_6H_4	**e**	98 (44)	2.4
6	*t*Bu	3-CH_3O-C_6H_4	**f**	87 (34)	1.4
7	*t*Bu	4-CH_3O-C_6H_4	**g**	97 (37)	2.8
8	Cy	4-Cl-C_6H_4	**h**	89 (38)	2.8
9	Cy	4-Me_3Si-C_6H_4	**i**	96 (40)	2.6
10	*i*Pr	4-Me_3Si-C_6H_4	**j**	91 (36)	3.0
11	*t*Bu	3-Furanyl	**k**	56 [c] (23)	1.3
12	*t*Bu	2-Pyridyl	**l**	48 [c] (21)	1.3
13	Ph	Ph	**m**	82 (49)	2.0
14	Ph	4-Cl-C_6H_4	**n**	87 (39)	2.4
15	Ph	4-CF_3-C_6H_4	**o**	73 (39)	2.2

[a] Isolated yields based on ArBr **6**; values in parentheses based on **2**. − [b] Based on **6**. − [c] 100% conversion of ArBr.

Table 1 shows that the coupling reaction is successful irrespective of the electronic nature of the substituent on the bromoaromatic compound. Thus, 1-bromo-4-(trifluoromethyl)benzene gives essentially the same result as 1-bromo-4-methoxybenzene (entries 5 and 7). This is also true for 3-bromofuran as compared with 2-bromopyridine (entries 11 and 12). The isolated yields of **4k** and **4l** were low, because these products partially decomposed during the workup procedure. Not unexpetedly, entries 4, 8 and 14 show that the halide selectivity of this reaction is remarkably high: the bromide reacts exclusively in each case. In addition, it is not surprising that the coupling reaction tolerates the presence of a trimethylsilyl group (entries 9 and 10). To accomplish the reaction within 48 h, in most cases 2.0 mol.% of catalyst **7** was sufficient; only in a few cases was a somewhat higher concentration of **7** necessary, but in no case was more than 3.0 mol.% required.

A particularly interesting aspect of this investigation was the use of di- and tribromobenzenes in attempts to find reaction conditions for successful di- and tri-coupling in good yields. When **5a** was reacted with 1,3,5-tribromobenzene in a molar ratio of 3.5:1 in the presence of 4.6 mol.% of **7** (with respect to 1,3,5-tribromobenzene), a 1:1 mixture of **8a** (37%) and **9a** (42%) was obtained. However, with a 5:1 ratio of **5a** to 1,3,5-tribromobenzene, only **8a** was isolated in 98% yield. Under the same conditions, **5b** was converted into **8b** in 95% yield. 1,4-Dibromobenzene gave a 90% yield of **10a** upon reaction with **5a**, while an analogous reaction with **5c** led to **10c** in 93% yield. Using 1,3-dibromo-5-(trimethylsilyl)benzene, the yields of the reactions with **5a** and **5b** affording **11a** and **11b** were 76% and 89%, respectively. The catalyst was used at a level of 2.8−10 mol.% with respect to **6**.

The isolated yield of **12a**, prepared from 2,6-dibromopyridine and **5a**, was only 20%, despite the fact that the dibromide had been fully consumed within 24 h.



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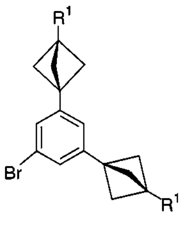

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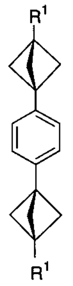

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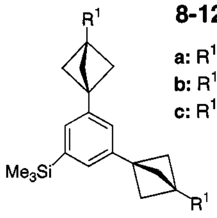

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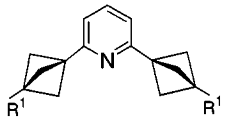
8-12:
a: R^1= *t*-Bu
b: R^1= Cyclohexyl
c: R^1 = *i*-Propyl



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It is interesting to note that the coupling reactions of **5** with bromobenzenes are highly sensitive to steric congestion. Attempts to use 1,2-dibromobenzene or 1,2,5,6-tetrabromobenzene as coupling components did not lead to any products.

X-ray Structures of Selected Model Compounds 4

The structures of compounds **4a**, **4d**, **4j**, and **4n** were determined by X-ray diffraction analysis. Figure 1 shows the crystal structure of compound **4a**.

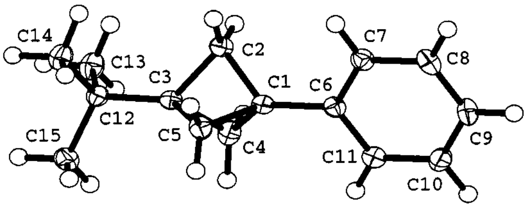

Figure 1. ORTEP plot of compound **4a**; 50% probability ellipsoids; selected bond lengths [Å] and angles [°]: C1−C3 1.8914(16), C1−C2 1.5459(17), C3−C12 1.5175(15), C1−C6 1.4925(15); C1−C2−C3 75.21(8), C5−C1−C2 86.81(9), C5−C1−C4 87.22(9), C12−C3−C2 127.19(11), C5−C1−C6−C7 89.75(15), C2−C1−C6−C7 28.44(16)

The bridgehead-to-bridgehead distance C1−C3 in **4a** amounts to 1.8914(16) Å, which is typical for bicyclo[1.1.1]pentanes substituted with electron-donating groups.[18] The C1−C3 distances in **4d** [1.8966(20) Å], **4j** [1.8822(26) Å] and **4n** [1.8923(23) Å] differ only marginally. In **4a**, **4d**, and **4j**, the torsional angles C2−C1−C6−C7 are 28.44(16)°, 29.56(22)° and 29.49(29)°, respectively, which reflect a minimization of the steric interaction of the methylene bridges of the bicyclo[1.1.1]pentyl cages with the *ortho* protons of the aromatic rings.

Figure 2 shows the crystal structure of compound **4n** (hydrogens omitted for clarity), which elucidates the matter of the orientation of the two aryl substituents at C1 and C3 of the bicyclo[1.1.1]pentyl subunit. The observed torsional angle C7−C6−C12−C17 is about 1°, showing that the in-plane conformation is favored.

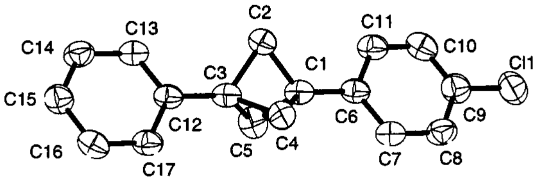

Figure 2. ORTEP plot of compound **4n**; 50% probability ellipsoids; selected bond lengths [Å] and angles [°]: C1−C3 1.892(7), C1−C2 1.552(7), C1−C6 1.486(5); C1−C2−C3 73.7(4), C7−C6−C12−C17 1.05(7)

Conclusion

In this report, we have surveyed the possibilities for cross-coupling bicyclo[1.1.1]pentylmagnesium halides with a variety of aryl bromides. The presented results show that palladium catalysis offers a viable means of synthesizing 1,3-disubstituted bicyclo[1.1.1]pentanes in high overall yields. This methodology will allow the synthesis of a wide range of new, hitherto inaccessible compounds.

Experimental Section

I. General Methods: ^{1}H-, ^{13}C-, and ^{19}F-NMR spectra were measured on a Bruker DPX300 spectrometer. − IR spectra were recorded on a Perkin−Elmer 881 spectrometer. − MS spectra were measured on an MSI Concept 1H apparatus. − Melting points were determined on a Büchi 530 apparatus and are uncorrected. − Elemental analyses were carried out by the Analytical Laboratory of the Institute of Chemistry at the Humboldt University.

1,1-Dibromo-2,2-bis(chloromethyl)cyclopropane (**2**),[1][2] [1.1.1]-propellane (**1**),[1][2] and dichloro[1,1′-bis(diphenylphosphanyl)ferrocene]palladium(II) [PdCl$_2$(dppf), **7**][17] were prepared by literature methods. 3-Chloro-2-(chloromethyl)prop-1-ene and *tert*-butylmagnesium chloride (2.0 M in diethyl ether) were purchased from Aldrich, isopropylmagnesium chloride and cyclohexylmagnesium chloride from Fluka, and an 8% solution of methyllithium (MeLi) in diethoxymethane from Chemetall. All reactions were carried out under nitrogen atmosphere.

II. Starting Materials

1-Bromo-4-(trimethylsilyl)benzene: *n*-Butyllithium (BuLi) (15.6 mL of a 1.60 M solution in hexane, 25.0 mmol) was added to a solution of 1,4-dibromobenzene (5.90 g, 25.0 mmol) in diethyl ether at −78°C. After 1 h at 0°C, a solution of chlorotrimethylsilane (2.99 g, 27.5 mmol) in diethyl ether (10 mL) was added dropwise. The resulting mixture was stirred for 1 h at room temperature, and then water was added, the organic layer was separated in a separatory funnel, and the aqueous layer was extracted with *n*-pentane (2×50 mL). The combined organic layers were washed twice with water, dried (MgSO$_4$), and the solvent was removed in vacuo, affording 1-bromo-4-(trimethylsilyl)benzene (5.60 g, 98%), which was used without further purification.

1,3-Dibromo-5-(trimethylsilyl)benzene: BuLi (15.6 mL of a 1.60 M solution in hexane, 25.0 mmol) was added to a solution of 1,3,5-tribromobenzene (7.87 g, 25.0 mmol) in diethyl ether at −78°C. After 1 h at 0°C, a solution of chlorotrimethylsilane (2.99 g, 27.5 mmol) in diethyl ether (10 mL) was added dropwise and the mixture was stirred for 1 h at room temperature. Water was then added, the organic layer was separated, and the aqueous layer was extracted with *n*-pentane (2×50 mL). The combined organic layers were washed twice with water, dried (MgSO$_4$), and the solvent was removed in vacuo, affording 1,3-dibromo-5-(trimethylsilyl)benzene (6.70 g, 87%) as a slightly yellow solid of m.p. 39°C, which was used without further purification.

III. General Procedure for the Palladium-Catalyzed Coupling Reactions

(a) Preparation of Grignard Reagents 5a−c: To a solution of [1.1.1]propellane **1** in diethyl ether, obtained from **2** by treatment with 2.00 equiv. of MeLi according to ref.[1] (in an assumed yield of 70% based on **2**), 1.00 equivalent (based on **1**) of the appropriate Grignard reagent (**a**: *tert*-butylmagnesium chloride; **b**: cyclohexylmagnesium chloride; **c**: 2-propylmagnesium chloride) was added at 0°C. The resulting mixture was stirred for 48 h at room temperature. After this time, propellane **1** had been completely consumed and the Grignard reagents **5a**−**c** had been formed quantitatively.

(b) Preparation of Grignard Reagent 5d: To a solution of [1.1.1]propellane **1** in diethoxymethane, obtained from **2** by treatment with 2.00 equiv. of MeLi according to ref.[1] (in an assumed yield of 70% based on **2**), 1.00 equivalent of phenylmagnesium bromide was added at 0°C. To remove impurities from the Grignard reagent prior to use, the ether solvent was removed in vacuo under nitrogen, the remaining waxy solid was washed three times with *n*-pentane, the pentane was removed using a syringe, and the solid was finally redissolved in diethoxymethane. After the addition of phenylmagnesium bromide to the solution of **1**, the mixture was stirred for 6 d at room temperature. After this time, propellane **1** had been completely consumed and the Grignard reagent **5d** had been formed quantitatively.

(c) Coupling Reactions: A solution of **5a**, **b**, **c** or **d** was added to a mixture of PdCl$_2$(dppf) and the aryl bromide in 1,4-dioxane (25 mL). The solution turned from red to yellow and was stirred for 48 h at room temperature. For workup, aqueous NH$_4$Cl was added, the organic layer was separated, and the aqueous layer was extracted with *n*-pentane (2×50 mL). The combined organic layers were washed twice with water, dried with MgSO$_4$, and the solvent was removed in vacuo. The crude coupling product **4** was purified by flash chromatography on silica gel, eluting with *n*-pentane. The yields are based on the aryl bromide used.

1. Single Coupling Reactions

(3-*tert*-Butylbicyclo[1.1.1]pent-1-yl)benzene (4a): Tetrahalide **2** (5.00 g, 16.8 mmol) was converted into **1**, which was allowed to react with *tert*-butylmagnesium chloride (10.8 mmol) according to the general procedure. Reaction of the solution of **5a** with bromobenzene (1.10 g, 7.01 mmol) and PdCl$_2$(dppf) (66 mg, 0.090 mmol) in 1,4-dioxane (25 mL) afforded, after standard workup and purification, **4a** (1.23 g, 88% based on bromobenzene) as colorless needles (from acetone), m.p. 60°C. − ^{1}H NMR (300 MHz, CDCl$_3$): δ = 0.89 (s, 9 H), 1.82 (s, 6 H), 7.25 (m, 5 H). − ^{13}C NMR (75 MHz, CDCl$_3$): δ = 25.1 (q, 4 C), 29.4 (s), 38.9 (s), 46.9 (s), 48.5 (t, 3 C), 126.0 (d), 126.1 (d, 2 C), 128.1 (d, 2 C), 141.9 (s). − IR (KBr): $\tilde{\nu}$ = 2959 cm^{-1}, 2952, 2900, 2864, 1443, 1359, 1199, 746. − MS (EI): *m/z* (%): 200 [M$^+$] (13), 142 (82), 123 (42), 57 (54). − C$_{15}$H$_{20}$ (200.3): calcd. C 89.94, H 10.06; found C 89.90, H 10.18.

2-(3-*tert*-Butylbicyclo[1.1.1]pent-1-yl)naphthalene (4b): Tetrahalide **2** (6.00 g, 20.2 mmol) was converted into **1**, which was allowed to react with *tert*-butylmagnesium chloride (13.0 mmol) according to the general procedure. Reaction of the solution of **5a** with 2-bromonaphthalene (1.86 g, 8.98 mmol) and PdCl$_2$(dppf) (88 mg, 0.12 mmol) in 1,4-dioxane (25 mL) afforded, after standard workup and purification, **4b** (2.10 g, 93%) as a colorless solid of m.p. 101 °C. − ^{1}H NMR (300 MHz, CDCl$_3$): δ = 0.93 (s, 9 H), 1.91 (s, 6 H), 7.40 (m, 3 H), 7.62 (s, 1 H), 7.85 (m, 3 H). − ^{13}C NMR (75 MHz, CDCl$_3$): δ = 26.0 (q, 3 C), 29.5 (s), 39.1 (s), 47.1 (s), 48.6 (t, 3 C), 124.3 (d), 124.7 (d), 125.2 (d), 126.0 (d), 127.6 (d), 127.7 (d), 132.1 (s), 133.3 (s), 139.3 (s). − IR (KBr): $\tilde{\nu}$ = 2929 cm^{-1}, 2900, 2862, 1459, 1360, 1200, 824, 796, 739. − MS (EI): *m/z* (%): 250 [M$^+$] (2), 193 (100), 178 (46), 165 (27), 152 (36), 55 (44), 41 (58). − C$_{19}$H$_{22}$ (250.4): calcd. C 91.14, H 8.86; found C 91.16, H 8.84.

4-(3-*tert*-Butylbicyclo[1.1.1]pent-1-yl)biphenyl (4c): Tetrahalide **2** (6.00 g, 20.2 mmol) was converted into **1**, which was allowed to react with *tert*-butylmagnesium chloride (13.0 mmol) according to the general procedure. Reaction of the solution of **5a** with 4-bromobiphenyl (2.10 g, 9.01 mmol) and PdCl$_2$(dppf) (88 mg, 0.12 mmol) in 1,4-dioxane (25 mL) afforded, after standard workup and purification, **4c** (2.40 g, 96%) as a colorless solid of m.p. 310 °C. − ^{1}H NMR (300 MHz, CDCl$_3$): δ = 0.91 (s, 9 H), 1.86 (s, 6 H), 7.31−7.51 (m, 9 H). − ^{13}C NMR (75 MHz, CDCl$_3$): δ = 26.0 (q, 3 C), 29.5 (s), 38.7 (s), 48.0 (s), 48.6 (t, 3 C), 126.5 (d), 126.9 (d), 128.7 (d), 139.2 (s), 141.0 (s). − IR (KBr): $\tilde{\nu}$ = 2930 cm^{-1}, 2929, 2902, 1584, 1563, 1470, 1443, 1359, 1222, 1142, 764. − MS (EI): *m/z* (%): 219 (100), 204 (20), 191 (19), 179 (14), 57 (14), 55 (21), 41 (24). − C$_{21}$H$_{24}$ (276.4): calcd. C 91.25, H 8.75; found C 90.91, H 8.93.

1-(3-*tert*-Butylbicyclo[1.1.1]pent-1-yl)-4-chlorobenzene (4d): Tetrahalide **2** (6.00 g, 20.2 mmol) was converted into **1**, which was allowed to react with *tert*-butylmagnesium chloride (13.0 mmol) according to the general procedure. Reaction of the solution of **5a** with 1-bromo-4-chlorobenzene (1.72 g, 8.98 mmol) and PdCl$_2$(dppf) (88 mg, 0.12 mmol) in 1,4-dioxane (25 mL) afforded, after standard workup and purification, **4d** (1.90 g, 90%) as colorless needles (from acetone) of m.p. 78 °C. − ^{1}H NMR (300 MHz, CDCl$_3$): δ = 0.89 (s, 9 H), 1.81 (s, 6 H), 7.12 (d, 2 H), 7.24 (d, 2 H). − ^{13}C NMR (75 MHz, CDCl$_3$): δ = 26.0 (q, 3 C), 29.4 (s), 38.5 (s), 46.9 (s), 48.6 (t, 3 C), 127.5 (d, 2 C), 128.2 (d, 2 C), 134.3 (s), 140.4 (s). − IR (KBr): $\tilde{\nu}$ = 2949 cm^{-1}, 2938, 2902, 2868, 1510, 1472, 1360, 1202, 1089, 789. − MS (EI): *m/z* (%): 199 (1), 177 (100), 142 (47), 83 (25), 57 (22), 41 (32). − C$_{15}$H$_{19}$Cl (234.8): calcd. C 76.74, H 8.16, Cl 15.10; found C 76.64, H 8.24, Cl 15.07.

1-(3-*tert*-Butylbicyclo[1.1.1]pent-1-yl)-4-(trifluoromethyl)benzene (4e): Tetrahalide **2** (5.00 g, 16.8 mmol) was converted into **1**, which was allowed to react with *tert*-butylmagnesium chloride (10.8 mmol) according to the general procedure. Reaction of the solution of **5a** with 1-bromo-4-(trifluoromethyl)benzene (1.69 g, 7.50 mmol) and PdCl$_2$(dppf) (132 mg, 0.18 mmol) in 1,4-dioxane (25 mL) afforded, after standard workup and purification, **4e** (1.98 g, 98%) as colorless needles (from acetone) of m.p. 95 °C. − ^{1}H NMR (300 MHz, CDCl$_3$): δ = 0.91 (s, 9 H), 1.86 (s, 6 H), 7.30 (d, 2 H), 7.53 (d, 2 H). − ^{13}C NMR (75 MHz, CDCl$_3$): δ = 25.9 (q, 3 C), 29.4 (s), 38.7 (s), 47.1 (s), 48.6 (t, 3 C), 125.1 (d, 2 C), 125.5 (q), 126.4 (d, 2 C), 129.8 (s), 145.8 (s). − IR (KBr): $\tilde{\nu}$ = 2970 cm^{-1}, 2959, 2937, 2906, 2868, 1615, 1475, 1406, 1363, 1202, 1065, 858 cm^{-1}. − MS (EI): *m/z* (%): 211 (37), 109 (24), 83 (35), 71 (23), 69 (28), 57 (100), 55 (49), 43 (45), 41 (49). − C$_{16}$H$_{19}$F$_3$ (268.3): calcd. C 71.62, H 7.14; found C 71.67, H 7.36.

1-(3-*tert*-Butylbicyclo[1.1.1]pent-1-yl)-3-methoxybenzene (4f): Tetrahalide **2** (7.50 g, 25.3 mmol) was converted into **1**, which was allowed to react with *tert*-butylmagnesium chloride (15.0 mmol) according to the general procedure. Reaction of the solution of **5a** with 3-bromo-1-methoxybenzene (1.87 g, 10.0 mmol) and PdCl$_2$(dppf) (103 mg, 0.14 mmol) in 1,4-dioxane (25 mL) afforded, after standard workup and purification, **4f** (2.00 g, 87%) as a colorless solid of m.p. 35 °C. − ^{1}H NMR (300 MHz, CDCl$_3$): δ = 0.90 (s, 9 H), 1.81 (s, 6 H), 3.78 (s, 3 H), 6.73 (m, 1 H), 6.80 (m, 1 H), 7.21 (t, 2 H). − ^{13}C NMR (75 MHz, CDCl$_3$): δ = 26.0 (q, 3 C), 29.4 (s), 38.9 (s), 46.8 (s), 48.5 (t, 3 C), 55.2 (q), 111.6 (d), 111.8 (d), 118.5 (d), 129.1 (d), 143.6 (s), 159.5 (s). − IR (KBr): $\tilde{\nu}$ = 2970 cm^{-1}, 2960, 2905, 2868, 1610, 1580, 1430, 1313, 1200, 1178, 1049, 777. − MS (EI): *m/z* (%): 230 (1), 215 (1), 173 (100), 158 (35), 91 (30), 77 (24), 55 (53), 29 (39). − C$_{16}$H$_{22}$O (230.4): calcd. C 83.43, H 9.63; found C 83.19, H 9.58.

1-(3-*tert*-Butylbicyclo[1.1.1]pent-1-yl)-4-methoxybenzene (4g): Tetrahalide **2** (5.00 g, 16.8 mmol) was converted into **1**, which was allowed to react with *tert*-butylmagnesium chloride (10.8 mmol) according to the general procedure. Reaction of the solution of **5a** with 4-bromo-1-methoxybenzene (1.22 g, 6.52 mmol) and PdCl$_2$(dppf) (136 mg, 0.19 mmol) in 1,4-dioxane (25 mL) afforded, after standard workup and purification, **4g** (1.45 g, 97%) as a colorless solid of m.p. 83 °C. − ^{1}H NMR (300 MHz, CDCl$_3$): δ = 0.89 (s, 9 H), 1.79 (s, 6 H), 3.79 (s, 3 H), 6.81 (d, 2 H), 7.13 (d, 2 H). − ^{13}C NMR (75 MHz, CDCl$_3$): δ = 26.0 (q, 3 C), 29.4 (s), 38.4 (s), 46.7 (s), 48.6 (t, 3 C), 55.3 (q), 113.5 (d, 2 C), 124.7 (d, 2 C), 134.3 (s), 158.1 (s). − IR (KBr): $\tilde{\nu}$ = 2901 cm^{-1}, 2863, 2836, 1610, 1516, 1497, 1360, 1294, 1188, 1131, 1034, 839. − MS (EI): *m/z* (%): 214 (5), 199 (60), 57 (71), 41 (100), 15 (67). − C$_{16}$H$_{22}$O (230.4): calcd. C 83.43, H 9.63; found C 83.56, H 9.58.

4-Chloro-1-(3-cyclohexylbicyclo[1.1.1]pent-1-yl)benzene (4h): The general procedure was followed. Starting from tetrahalide **2** (4.50 g, 15.2 mmol), propellane **1** was converted into Grignard reagent **5b** by reaction with cyclohexylmagnesium chloride (9.00 mmol). The coupling reaction of **5b** with 1-bromo-4-chlorobenzene (1.24 g, 6.48 mmol) and PdCl$_2$(dppf) (132 mg, 0.18 mmol) in 1,4-dioxane (25 mL) afforded **4h** (1.51 g, 89%) as a white solid of m.p. 70 °C. − ^{1}H NMR (300 MHz, CDCl$_3$): δ = 0.90−1.80 (m, 11 H), 1.80 (s, 6 H), 7.14 (d, 2 H), 7.22 (d, 2 H). − ^{13}C NMR (75 MHz, CDCl$_3$): δ = 26.1 (t), 26.3 (t, 2 C), 29.3 (t, 2 C), 37.9 (d), 40.2 (s), 42.6 (s), 49.9 (t, 3 C), 127.5 (d, 2 C), 128.1 (d, 2 C), 131.9 (s), 140.4 (s). − IR (KBr): $\tilde{\nu}$ = 2963 cm^{-1}, 2915, 2907, 2866, 2850, 1486, 1445, 1271, 1259, 1160, 1089, 1013, 834. − MS (EI): *m/z* (%): 177 (36), 142 (29), 141 (43), 139 (69), 67 (50), 55 (53), 41 (100), 39 (60), 29 (40), 27 (48). − C$_{17}$H$_{21}$Cl (260.8): calcd. C 78.29, H 8.12, Cl 13.59; found C 78.23, H 8.31, Cl 14.04.

1-(3-Cyclohexylbicyclo[1.1.1]pent-1-yl)-4-(trimethylsilyl)benzene (4i): The general procedure was followed. Starting from tetrahalide **2** (5.00 g, 16.8 mmol), propellane **1** was converted into Grignard reagent **5b** by reaction with cyclohexylmagnesium chloride (10.8 mmol). The coupling reaction of **5b** with 1-bromo-4-(trimethylsilyl)benzene (1.60 g, 6.98 mmol) and PdCl$_2$(dppf) (132 mg, 0.18 mmol) in 1,4-dioxane (25 mL) afforded **4i** (2.01 g, 96%) as a white solid of m.p. 62 °C. − ^{1}H NMR (300 MHz, CDCl$_3$): δ = 0.25 (s, 9 H) 0.75−1.70 (m, 11 H), 1.82 (s, 6 H), 7.21 (d, 2 H), 7.45 (d, 2 H). − ^{13}C NMR (75 MHz, CDCl$_3$): δ = −1.1 (q, 3 C), 26.1 (t), 26.3 (t, 2 C), 29.3 (t, 2 C), 38.0 (d), 40.6 (s), 42.9 (t, 3 C), 125.5 (d, 2 C), 133.1 (d, 2 C), 137.8 (s), 142.4 (s). − IR (KBr): $\tilde{\nu}$ = 2955 cm^{-1}, 2920, 2901, 2862, 2850, 1444, 1271, 1258, 1246, 1108, 850, 828. − MS (EI): *m/z* (%): 298 [M$^+$] (1), 224 (18), 215 (23), 177 (26), 175 (19), 149 (15), 73 (100). − C$_{20}$H$_{30}$Si (298.544): calcd. C 80.46, H 10.13; found C 80.09, H 10.13.

1-(3-Isopropylbicyclo[1.1.1]pent-1-yl)-4-(trimethylsilyl)benzene (4j): The general procedure was followed. Starting from tetrahalide **2** (4.50 g, 15.2 mmol), propellane **1** was converted into Grignard reagent **5c** by reaction with isopropylmagnesium chloride (9.00 mmol). The coupling reaction of **5c** with 1-bromo-4-(trimethylsilyl)benzene (1.39 g, 6.06 mmol) and $PdCl_2$(dppf) (132 mg, 0.18 mmol) in 1,4-dioxane (25 mL) afforded **4j** (1.42 g, 91%) as white needles (from acetone) of m.p. 35°C. − ^1H NMR (300 MHz, $CDCl_3$): $\delta = 0.25$ (s, 9 H), 0.88 (d, 6 H), 1.73 (m, 1 H), 1.82 (s, 6 H), 7.24 (d, 2 H), 7.48 (d, 2 H). − ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = -1.1$ (q, 3 C), 18.9 (q, 2 C), 28.4 (d), 43.6 (s), 46.3 (s), 49.6 (t, 3 C), 125.5 (d, 2 C), 133.2 (d, 2 C), 137.9 (s), 142.4 (s). − IR (KBr): $\tilde{\nu} = 2981$ cm^{-1}, 2959, 2907, 2866, 1463, 1362, 1246, 1173, 1102, 858, 829. − MS (EI): *m/z* (%): 175 (14), 73 (100), 59 (14), 45 (12), 43 (16), 41 (18). − $C_{17}H_{26}Si$ (258.5): calcd C 79.00, H 10.14; found C 78.97, H 10.16.

3-(3-*tert*-Butylbicyclo[1.1.1]pent-1-yl)furan (4k): The general procedure was followed. Starting from tetrahalide **2** (5.00 g, 16.8 mmol), propellane **1** was converted into Grignard reagent **5a** by reaction with *tert*-butylmagnesium chloride (10.8 mmol). The coupling reaction of **5a** with 3-bromofuran (1.03 g, 7.01 mmol) and $PdCl_2$(dppf) (66 mg, 0.090 mmol) in 1,4-dioxane (25 mL) afforded **4k** (750 mg, 56%) as a colorless solid of m.p. 29°C. − ^1H NMR (300 MHz, $CDCl_3$): $\delta = 0.87$ (s, 9 H), 1.76 (s, 6 H), 6.27 (s, 1 H), 7.20 (s, 1 H), 7.32 (s, 1 H). − ^{13}C NMR (75 MHz, $CDCl_3$): $\delta =$ 25.9 (q, 3 C), 29.5 (s), 31.6 (s), 45.1 (s), 49.0 (t, 3 C), 109.7 (d), 126.1 (d), 138.8 (d), 142.8 (s). − IR (KBr): $\tilde{\nu} = 2959$ cm^{-1}, 2958, 2906, 1476, 1461, 1361, 1205, 1162, 1028, 869, 774. − MS (EI): *m/z* (%): 190 [M$^+$] (2), 133 (88), 119 (29), 105 (30), 91 (52), 83 (35), 79 (39), 57 (53), 55 (100), 41 (68). − $C_{13}H_{18}O$ (190.285): calcd. C 82.06, H 9.54; found C 82.18, H 9.37.

2-(3-*tert*-Butylbicyclo[1.1.1]pent-1-yl)pyridine (4l): The general procedure was followed. Starting from tetrahalide **2** (6.00 g, 20.2 mmol), propellane **1** was converted into Grignard reagent **5a** by reaction with *tert*-butylmagnesium chloride (13.0 mmol). The coupling reaction of **5a** with 2-bromopyridine (1.42 g, 8.99 mmol) and $PdCl_2$(dppf) (88 mg, 0.12 mmol) in 1,4-dioxane (25 mL) afforded **4l** (870 mg, 48%) as a colorless solid of m.p. 42°C. − ^1H NMR (300 MHz, $CDCl_3$): $\delta = 0.91$ (s, 9 H), 1.93 (s, 6 H), 7.20 (m, 2 H), 7.60 (m, 1 H), 8.54 (m, 1 H). − ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 25.9$ (q, 3 C), 29.4 (s), 39.8 (s), 47.2 (s), 48.2 (t, 3 C), 120.6 (d), 121.3 (d, 2 C), 136.1 (d, 2 C), 149.2 (d), 160.5 (s). − IR (KBr): $\tilde{\nu} =$ 2959 cm^{-1}, 2902, 2864, 1360, 1224, 1200, 833, 786, 760. − MS (EI): *m/z* (%): 186 (31), 144 (100), 117 (19), 78 (21). − $C_{14}H_{19}N$ (201.3): calcd. C 83.53, H 9.51, N 6.96; found C 83.41, H 9.48, N 6.85.

1,3-Diphenylbicyclo[1.1.1]pentane (4m): The general procedure was followed. Starting from tetrahalide **2** (5.00 g, 16.8 mmol), propellane **1** was converted into Grignard reagent **5d** by reaction with phenylmagnesium bromide (10.8 mmol). The coupling reaction of **5d** with bromobenzene (1.57 g, 10.0 mmol) and $PdCl_2$(dppf) (147 mg, 0.201 mmol) in 1,4-dioxane (25 mL) afforded **4m** (1.80 g, 82%) as a colorless solid of m.p. 72°C. − ^1H NMR (300 MHz, $CDCl_3$): $\delta = 2.32$ (s, 6 H), 7.30 (m, 10 H). − ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 40.8$ (s, 2 C), 54.0 (t, 3 C), 126.1 (d, 2 C), 126.6 (d, 4 C), 128.2 (d, 4 C), 140.9 (s, 2 C). − IR (KBr): $\tilde{\nu} = 3055$ cm^{-1}, 3025, 2966, 2939, 2905, 2865, 1600, 1493, 1304, 1184, 1025, 765. − MS (EI): *m/z* (%): 220 [M$^+$] (45), 219 (100), 205 (17), 143 (30), 115 (31), 103 (49), 91 (42), 77 (53), 51 (19). − $C_{17}H_{16}$ (220.3): calcd. C 92.68, H 7.32; found C 92.58, H 7.57.

4-Chloro-1-(3-phenylbicyclo[1.1.1]pent-1-yl)benzene (4n): The general procedure was followed. Starting from tetrahalide **2** (5.00 g, 16.8 mmol), propellane **1** was converted into Grignard reagent **5d** by reaction with phenylmagnesium bromide (10.8 mmol). The coupling reaction of **5d** with 1-bromo-4-chlorobenzene (1.43 g, 7.47 mmol) and $PdCl_2$(dppf) (132 mg, 0.180 mmol) in 1,4-dioxane (25 mL) afforded **4n** (1.65 g, 87%) as a white solid of m.p. 142°C. − ^1H NMR (300 MHz, $CDCl_3$): $\delta = 2.31$ (s, 6 H), 7.30 (m, 9 H). − ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 40.3$ (s), 40.8 (s), 54.0 (t, 3 C), 126.1 (d), 126.6 (d, 2 C), 127.6 (d, 2 C), 128.2 (d, 2 C), 128.3 (d, 2 C), 132.3 (s), 139.4 (s), 140.6 (s). − IR (KBr): $\tilde{\nu} = 2964$ cm^{-1}, 2939, 2905, 2866, 1488, 1396, 1301, 1182, 1091, 835. − MS (EI): *m/z* (%): 254 [M$^+$] (6), 219 (96), 115 (98), 103 (63), 101 (54), 91 (100), 77 (97), 75 (52), 51 (87), 39 (52). − $C_{17}H_{15}Cl$ (254.8): calcd. C 80.15, H 5.93, Cl 13.92; found C 79.93, H 6.29, Cl 13.91.

1-(3-Phenylbicyclo[1.1.1]pent-1-yl)-4-(trifluoromethyl)benzene (4o): The general procedure was followed. Starting from tetrahalide **2** (5.00 g, 16.8 mmol), propellane **1** was converted into Grignard reagent **5d** by reaction with phenylmagnesium bromide (10.8 mmol). The coupling reaction of **5d** with 1-bromo-4-(trifluoromethyl)benzene (2.03 g, 9.02 mmol) and $PdCl_2$(dppf) (147 mg, 0.201 mmol) in 1,4-dioxane (25 mL) afforded **4o** (1.89 g, 73%) as a white solid of m.p. 115°C. − ^1H NMR (300 MHz, $CDCl_3$): $\delta = 2.35$ (s, 6 H), 7.30 (m, 8 H), 7.56 (d, 2 H). − ^{13}C NMR (75 MHz, $CDCl_3$): $\delta =$ 40.5 (s), 41.0 (s), 54.0 (t, 3 C), 125.5 (q), 125.13 (d), 126.1 (d), 126.6 (d, 2 C), 128.3 (d, 4 C), 128.3 (d, 2 C), 140.4 (s), 144.8 (s). − IR (KBr): $\tilde{\nu} = 2979$ cm^{-1}, 2911, 2874, 1407, 1324, 1300, 1188, 1070, 851. − MS (EI): *m/z* (%): 288 [M$^+$] (10), 219 (25), 151 (35), 128 (41), 115 (69), 91 (78), 77 (100), 51 (64), 39 (44). − $C_{18}H_{15}F_3$ (288.3): calcd. C 74.99, H 5.24; found C 74.71, H 5.63.

2. Multiple Coupling Reactions

2,6-Bis(3-*tert*-butylbicyclo[1.1.1]pent-1-yl)pyridine (12a): According to the general procedure, tetrahalide **2** (5.00 g, 16.8 mmol) was converted into **1**, which was allowed to react with *tert*-butylmagnesium chloride (10.8 mmol). Reaction of the solution of **5a** with 1,6-dibromopyridine (1.13 g, 5.07 mmol) and $PdCl_2$(dppf) (132 mg, 0.18 mmol) in 1,4-dioxane (25 mL) afforded, after standard workup and purification, **12a** (330 mg, 20%) as a white solid of m.p. 165°C. − ^1H NMR (300 MHz, $CDCl_3$): $\delta = 0.90$ (s, 18 H), 1.89 (s, 12 H), 6.98 (d, 2 H), 7.48 (t, 1 H). − ^{13}C NMR (75 MHz, $CDCl_3$): $\delta =$ 26.0 (q, 6 C), 29.4 (s, 2 C), 40.0 (s, 2 C), 47.1 (s, 2 C), 48.3 (t, 6 C), 117.9 (d), 135.7 (d, 2 C), 159.9 (s, 2 C). − IR (KBr): $\tilde{\nu} = 2952$ cm^{-1}, 2928, 2905, 2865, 1585, 1569, 1458, 1359, 1200, 830. − MS (EI): *m/z* (%): 323 [M$^+$] (2), 308 (20), 252 (21), 210 (29), 182 (20), 168 (37), 91 (20), 57 (61), 55 (60), 41 (100). − $C_{23}H_{33}N$ (323.5): calcd. C 85.39, H 10.28, N 4.33; found C 85.10, H 9.94, N 4.33.

1,4-Bis(3-*tert*-butylbicyclo[1.1.1]pent-1-yl)benzene (10a): According to the general procedure, tetrahalide **2** (6.00 g, 20.2 mmol) was converted into **1**, which was allowed to react with *tert*-butylmagnesium chloride (13.0 mmol). Reaction of the solution of **5a** with 1,4-dibromobenzene (944 mg, 4.00 mmol) and $PdCl_2$(dppf) (176 mg, 0.24 mmol) in 1,4-dioxane (25 mL) afforded, after standard workup and purification, **10a** (1.16 g, 90%) as a white solid of m.p. 280°C. − ^1H NMR (300 MHz, $CDCl_3$): $\delta = 0.89$ (s, 18 H), 1.80 (s, 12 H), 7.16 (s, 4 H). − ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 26.0$ (q, 6 C), 29.4 (s, 2 C), 38.7 (s, 2 C), 46.9 (s, 2 C), 48.5 (t, 6 C), 128.8 (d, 4 C), 139.7 (s, 2 C). − IR (KBr): $\tilde{\nu} = 2959$ cm^{-1}, 2947, 2903, 2865, 1359, 1211, 1201, 790, 775. − MS (EI): *m/z* (%): 322 [M$^+$] (1), 265 (25), 208 (18), 83 (33), 67 (24), 57 (73), 41 (100). − $C_{24}H_{34}$ (322.5): calcd. C 89.37, H 10.63; found C 89.59, H 11.01.

1,4-Bis(3-isopropylbicyclo[1.1.1]pent-1-yl)benzene (10c): According to the general procedure, tetrahalide **2** (5.00 g, 16.8 mmol) was converted into **1**, which was allowed to react with 2-propylmagnesium chloride (10.8 mmol). Reaction of the solution of **5c** with 1,4-dibromobenzene (710 mg, 3.01 mmol) and $PdCl_2$(dppf) (132 mg, 0.18 mmol) in 1,4-dioxane (25 mL) afforded, after standard workup and purification, **10c** (821 mg, 93%) as a white solid of m.p. 183°C.

Table 2. Crystal data for compounds **4a**, **4d**, **4j** and **4n**

	4a	**4d**	**4j**	**4n**
Empirical formula	$C_{15}H_{20}$	$C_{15}H_{19}Cl$	$C_{17}H_{26}Si$	$C_{17}H_{15}Cl$
M_r	200.21	234.75	258.47	254.74
a [Å]	5.9395(8)	6.0011(14)	23.098(4)	5.878(2)
b [Å]	7.4457(14)	12.642(3)	6.0914(6)	7.502(2)
c [Å]	27.610(4)	18.851(4)	23.883(4)	15.342(4)
α [°]	90	109.14(3)	90	90
β [°]	90	97.76(3)	103.358(19)	96.61(3)
γ [°]	90	93.17(3)	90	90
Z	4	4	8	2
D [Mg/m^3]	1.090	1.171	1.050	1.259
crystal system	orthorhombic	triclinic	monoclinic	monoclinic
space group	$P2_12_12_1$	P-1	$I\ 2/a$	$P\ 2_1/c$
crystal size [mm]	0.72 × 0.36 × 0.20	1.00 × 0.28 × 0.08	0.80 × 0.44 × 0.08	0.80 × 0.48× 0.12
θ range [°]	2.83–25.24	2.32–25.25	2.21–25.24	3.49–25.50
measured reflns.	7192	8874	9238	3074
independent reflns.	2198	4521	2953	1165
μ [mm^{-1}]	0.061	0.259	0.128	0.263
max./min. transmission	0.9880/0.9577	0.9796/0.7816	0.9899/0.9048	0.979/0.854
parameters	216	441	168	101
F(000)	440	504	1136	268
GoF	1.034	1.020	1.044	1.128
max. Δρ [eÅ^{-3}]	0.150	0.388	0.406	0.501
$R1$[a]	0.0287	0.0336	0.0456	0.0863
$wR2$[b]	0.0760	0.0882	0.1268	

[a] $R1 = \Sigma||F_o| - |F_c|/\Sigma|F_o|$ for all reflections with $I > 2\sigma(I)$. – [b] $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_c^2)^2]\}^{0.5}$ for all reflections; $w^{-1} = \sigma^2(F^2) + (aP)^2 + bP$, where $P = (2F_c^2 + F_o^2)/3$ and a and b are constants set by the program.

– ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.88 (d, 12 H), 1.75 (m, 2 H), 1.80 (s, 12 H), 7.16 (s, 4 H). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.8 (q, 4 C), 28.4 (d, 2 C), 40.2 (s, 2 C), 43.5 (s, 2 C), 49.6 (t, 6 C), 125.8 (d, 4 C), 139.7 (s, 2 C). – IR (KBr): ṽ = 2960 cm^{-1}, 2959, 2926, 2901, 2863, 1461, 1360, 1268, 1175, 842. – MS (EI): *m/z* (%): 251 (28), 183 (26), 115 (34), 109 (25), 83 (44), 69 (41), 67 (46), 55 (27), 43 (38), 41 (100). – $C_{22}H_{30}$ (294.5): calcd. C 89.73, H 10.27; found C 89.35, H 10.19.

1,3-Bis(3-*tert*-butylbicyclo[1.1.1]pent-1-yl)-5-(trimethylsilyl)benzene (11a): According to the general procedure, tetrahalide **2** (7.50 g, 25.3 mmol) was converted into **1**, which was allowed to react with *tert*-butylmagnesium chloride (18.0 mmol). Reaction of the solution of **5a** with 1,3-dibromo-5-(trimethylsilyl)benzene (1.54 g, 5.00 mmol) and $PdCl_2$(dppf) (103 mg, 0.14 mmol) in 1,4-dioxane (25 mL) afforded, after standard workup and purification, **11a** (1.52 g, 77%) as a white solid of m.p. 128°C. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.26 (s, 9 H), 0.89 (s, 18 H), 1.83 (s, 12 H), 7.08 (s, 1 H), 7.21 (s, 2 H). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = −1.1 (q, 3 C), 26.0 (q, 6 C), 29.5 (s, 2 C), 35.7 (s, 2 C), 41.2 (s, 2 C), 48.5 (t, 6 C), 128.7 (d, 3 C), 133.5 (s), 140.7 (s, 2 C). – IR (KBr): ṽ = 2954 cm^{-1}, 2903, 2866, 1473, 1359, 1280, 1243, 1200, 1147, 974, 855, 752. – MS (EI): *m/z* (%): 337 (23), 97 (7), 83 (19), 73 (100), 57 (17), 55 (13), 41 (15). – $C_{27}H_{42}Si$ (394.7): calcd. C 82.16, H 10.73; found C 81.97, H 10.60.

1,3-Bis(3-cyclohexylbicyclo[1.1.1]pent-1-yl)-5-(trimethylsilyl)benzene (11b): According to the general procedure, tetrahalide **2** (7.50 g, 25.3 mmol) was converted into **1**, which was allowed to react with cyclohexylmagnesium chloride (18.0 mmol). Reaction of the solution of **5b** with 1,3-dibromo-5-(trimethylsilyl)benzene (1.23 g, 3.99 mmol) and $PdCl_2$(dppf) (220 mg, 0.30 mmol) in 1,4-dioxane (25 mL) afforded, after standard workup and purification, **11b** (1.60 g, 90%) as a white solid of m.p. 112°C. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.25 (s, 9 H), 0.70–1.80 (m, 22 H), 1.82 (s, 12 H), 7.05 (s, 1 H), 7.21 (s, 2 H). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = −1.1 (q, 3 C), 26.1 (t, 2 C), 26.4 (t, 4 C), 29.4 (t, 4 C), 38.0 (d, 2 C), 40.7 (s, 2 C), 42.6 (s, 2 C), 49.9 (t, 6 C), 128.7 (d), 124.3 (d, 2 C), 139.9 (s), 140.8 (s, 2 C). – IR (KBr): ṽ = 2957 cm^{-1}, 2921, 2903, 2860, 1444, 1257, 1244, 873, 856, 756. – MS (EI): *m/z* (%): 122 (5), 109 (31), 93 (21), 82 (27), 81 (34), 79 (32), 67 (100), 55 (50), 41 (60). – $C_{31}H_{46}Si$ (446.8): calcd. C 83.34, H 10.38; found C 83.31, H 10.38.

1,3,5-Tris(3-*tert*-butylbicyclo[1.1.1]pent-1-yl)benzene (8a): According to the general procedure, tetrahalide **2** (7.50 g, 25.3 mmol) was converted into **1**, which was allowed to react with *tert*-butylmagnesium chloride (18.0 mmol). Reaction of the solution of **5a** with 1,3,5-tribromobenzene (1.02 g, 3.24 mmol) and $PdCl_2$(dppf) (205 mg, 0.28 mmol) in 1,4-dioxane (25 mL) afforded, after standard workup and purification, **8a** (1.41 g, 98%) as a white solid of m.p. 309°C. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.89 (s, 27 H), 1.82 (s, 18 H), 6.91 (s, 3 H). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = 26.0 (q, 9 C), 29.4 (s, 3 C), 38.9 (s, 3 C), 46.9 (s, 3 C), 48.8 (t, 9 C), 121.6 (d, 3 C), 141.6 (s, 3 C). – IR (KBr): ṽ = 2904 cm^{-1}, 2865, 1599, 1473, 1460, 1360, 1224, 879. – MS (EI): *m/z* (%): 387 (32), 123 (32), 97 (61), 82 (2), 57 (83), 55 (59), 41 (53). – $C_{33}H_{48}$ (444.7): calcd. C 89.12, H 10.88; found C 88.75, H 10.63.

1,3,5-Tris(3-*tert*-butylbicyclo[1.1.1]pent-1-yl)benzene (8a) and 5-Bromo-1,3-bis(3-*tert*-butylbicyclo[1.1.1]pent-1-yl)benzene (9a): According to the general procedure, tetrahalide **2** (10.0 g, 33.7 mmol) was converted into **1**, which was allowed to react with *tert*-butylmagnesium chloride (23.0 mmol). Reaction of the solution of **5a** with 1,3,5-tribromobenzene (1.90 g, 6.04 mmol) and $PdCl_2$(dppf) (205 mg, 0.28 mmol) in 1,4-dioxane (25 mL) afforded, after standard workup and purification, **8a** (990 mg, 37%) as a white solid of m.p. 309°C and **9a** (1.02 g, 42%) as colorless needles (from acetone) of m.p. 98°C. – **9a**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.89 (s, 18 H), 1.81 (s, 12 H), 7.26 (s, 2 H), 7.48 (s, 1 H). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = 25.9 (q, 6 C), 29.4 (s, 2 C), 38.3 (s, 2 C), 48.6 (s, 2 C), 48.7 (t, 6 C), 122.2 (d, 2 C), 128.2 (d), 131.7 (s), 145.8 (s). – IR (KBr): ṽ = 2904 cm^{-1}, 2865, 1599, 1460, 1444, 1360, 1281, 1198, 879. – MS (EI): *m/z* (%): 343 (10), 315 (18), 301 (80), 222 (35), 141 (42), 115 (39), 83 (100), 57 (95). − $C_{24}H_{33}Br$ (401.4): calcd. C 71.81, H 8.29, Br 19.90; found C 71.49, H 8.23, Br 19.88.

1,3,5-Tris(3-cyclohexylbicyclo[1.1.1]pent-1-yl)benzene (8b): According to the general procedure, tetrahalide **2** (7.50 g, 25.3 mmol) was converted into **1**, which was allowed to react with cyclohexylmagnesium chloride (18.0 mmol). Reaction of the solution of **5b** with 1,3,5-tribromobenzene (950 mg, 3.02 mmol) and $PdCl_2$(dppf) (220 mg, 0.30 mmol) in 1,4-dioxane (25 mL) afforded, after standard workup and purification, **8b** (1.50 g, 95%) as a white solid of m.p. 245 °C. − ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.80-1.80$ (m, 33 H), 1.80 (s, 18 H), 6.89 (s, 3 H). − ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 26.1$ (t, 3 C), 26.3 (t, 6 C), 29.6 (t, 6 C), 35.4 (s, 3 C), 38.0 (d, 3 C), 42.6 (s, 3 C), 49.9 (t, 9 C), 121.6 (d, 3 C), 141.5 (s, 3 C). − IR (KBr): $\tilde{\nu} = 2959$ cm^{-1}, 2921, 2863, 2850, 1598, 1446, 1257, 703. − MS (EI): *m/z* (%): 522 [M$^+$] (1), 149 (32), 133 (11), 109 (100), 67 (90), 55 (76), 41 (50). − $C_{39}H_{54}$ (522.9): calcd. C 89.59, H 10.41; found C 89.51, H 10.23.

X-ray Crystallographic Studies: Crystal data are given in Table 2. Crystals of **4a**, **4d**, and **4j** suitable for X-ray diffraction analysis were prepared by crystallization from acetone at −20 °C, while crystals of **4n** were obtained from dichloromethane at −20 °C. The X-ray structures of **4a**, **4d**, **4j**, and **4n** were determined on a STOE Imaging Plate Diffraction System. Measurements were carried out at 180 K using graphite-monochromated Mo-K_α radiation ($\lambda = 0.71073$ Å). Unit cell parameters were determined from least-squares analyses of 1454 reflections ($5.70° < 2\theta < 52.2°$) (**4a**), 5000 reflections ($4.60° < 2\theta < 52.2°$) (**4d**), 2115 reflections ($5.00 < 2\theta < 50.2°$) (**4j**), and 1095 reflections ($5.40 < 2\theta < 50.2°$) (**4n**). Intensities were measured by φ-oscillation scans. The structures were solved by direct methods and refined anisotropically on F^2 (SHELX-97).[19] Hydrogen atoms were included isotropically in the full-matrix least-squares refinement (**4a**, **4d**, and **4j**) or constrained as a riding model (**4n**).[20]

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[20] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-116255 (for **4d**), CCDC-116256 (for **4j**), CCDC-116257 (for **4a**), and CCDC-116258 (for **4n**). Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [Fax: (internat.) +44(0)1223 336033; E-mail: deposit@ccdc.cam.ac.uk].

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