Nickel- and Palladium-Catalyzed Cross-Coupling Reactions at the Bridgehead of Bicyclo[1.1.1]pentane Derivatives – A Convenient Access to Liquid Crystalline Compounds Containing Bicyclo[1.1.1]pentane Moieties

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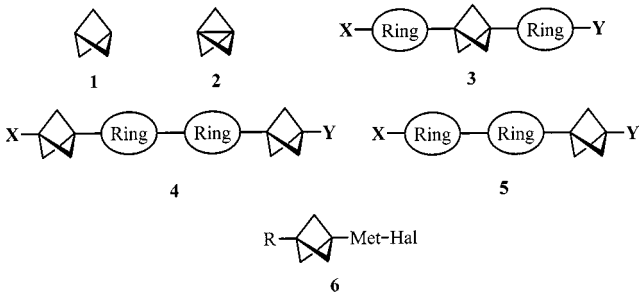
Dedicated to Professor Günther Wulff on the occasion of his 65th birthday

Keywords: Bicyclo[1.1.1]pentane / Haloarenes, cross-coupling of / [1.1.1]Propellane / Palladium / Catalysis / Small-ring systems

Radical addition reactions of organyl iodides **7a–s** onto [1.1.1]propellane (**2**) followed by halogen–lithium exchange and transmetallation with zinc chloride, as well as additions of Grignard reagents to **2**, have furnished a variety of 3-substituted bicyclo[1.1.1]pentyl-1-magnesium (**14**) and -zinc (**19**) derivatives. The latter have been coupled with various alkenyl, aryl, and biaryl halides and triflates under $NiCl_2$dppe, $Pd(PPh_3)_4$, or $PdCl_2$(dppf) catalysis to give a number of 1,3-disubstituted bicyclo[1.1.1]pentyl derivatives **17**, **20**, and **23**, several of which exhibit liquid crystalline properties, in moderate to very good yields. The coupling products **20ca**, **23ab**, **23ae**, **23ff**, and **23fg** have been further transformed to yield bicyclo[1.1.1]pentyl derivatives **32**, **24ab**, **24ae**, **27ff**, and **27fg**, respectively, bearing alkynyl, cyano, and/or alkenyl groups.

Introduction

The design and preparation of rigid rod-like molecules has long been of interest to physical-organic chemists.[1] Among such structures, 1,3-disubstituted derivatives of bicyclo[1.1.1]pentane (**1**) have, for several reasons, attracted particular attention during the past decade. In spite of the considerable strain energy of the bicyclo[1.1.1]pentane unit,[2,3] such derivatives are remarkably thermally stable, persisting up to 300 °C, and are resistant to oxygen and many mild reagents.[4] They are also transparent to visible and UV light and, being intrinsically linear, are capable of stabilizing mesophases.[4b] Since the preparation of the first bicyclo[1.1.1]pentane derivatives in 1966,[5] a wide range of such systems has now become readily accessible, the key development being the discovery of an efficient two-step preparation[6] of the ideal precursor, [1.1.1]propellane (**2**),[7] from commercially available starting materials (for recent improvements in the preparation of **2**, see also ref.[8]). The chemistry of [1.1.1]propellanes and bicyclo[1.1.1]pentanes derived therefrom has been studied quite extensively since 1989,[9] and the results have been reviewed several times.[3,4a,8a,10–12] However, to date most attention has been paid to compounds containing two or more bicyclo[1.1.1]-pentane units (the so-called [*n*]staffanes, for a review see ref.[3]) and to functionalized derivatives of **1** and their chemical transformations.[8a,9] In the present contribution, we describe our results concerning the preparation of quasi-linear molecules of types **3**–**5** using a metal-catalyzed cross-coupling reaction as a key synthetic step.



Results and Discussion

1. Preparation of Starting Materials

The key intermediates used in the cross-coupling reactions with haloarenes were 1-bicyclo[1.1.1]pentylzinc or -magnesium reagents of type **6**. The simplest access to metal derivatives **6**, in which R is an aryl, alkyl, or functionalized alkyl substituent, is offered by halogen–metal exchange reactions of the corresponding bridgehead iodinated bicyclo-[1.1.1]pentyl derivatives **8**. The latter are easily accessible through the radical addition of alkyl iodides across the central σ-bond in [1.1.1]propellane (**2**) under photochemical conditions[4a,13] (Scheme 1, conditions B) or under methyllithium catalysis.[12,14] It was found[15] that by using a stoichiometric quantity of MeLi (Scheme 1, conditions A), better and more reproducible yields of compounds **8** (Table 1) were obtained. For example, compounds **8a** and **8c** had previously been prepared by photochemical means in 65%[13b] and 34% yield,[4a] respectively, whereas under MeLi mediation, the additions gave significantly higher yields (83% and 97%). Nevertheless, in the cases of **8f** and **8j**, better results were achieved under photochemical conditions be-

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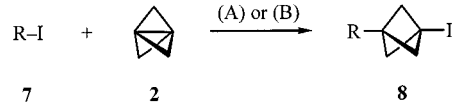
cause of competing side reactions (β-elimination) in the presence of MeLi. Products **8k** and **8l** could not be obtained by additions of vinyl and allyl iodides; under the action of MeLi, only the methyl derivative was formed, which was isolated in yields of 55% and 60%, respectively. Under irradiation, the main components of the reaction mixtures were oligobicyclo[1.1.1]pentyl diiodides (diiodostaffanes[3]) and rearranged products, although the photochemically induced addition of allyl iodide to **2** has been reported.[13] The vinyl derivative **8k** was indeed formed in ca. 20% yield (as estimated by NMR), but could not be isolated from the complex reaction mixture. With 4-substituted 1-iodocyclohexanes **7o–q**, 2:1 mixtures of *cis*- and *trans*-1,4-disubstituted cyclohexane derivatives **8o–q** were obtained, irrespective of the configuration of the starting iodide. Compounds **8** were found to be rather unstable, both thermally and towards silica gel, which prevented their further purification in most cases. Nevertheless, the purity of the crude products, ≥ 95% under MeLi mediation, is normally adequate for any subsequent transformations and, moreover, compounds **8** may be stored at –78 °C for several months.



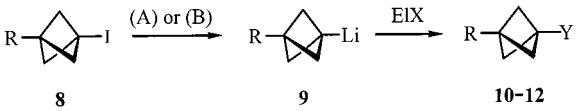
Scheme 1. For details see Table 1

Table 1. Addition of alkyl and aryl iodides **7** to [1.1.1]propellane (**2**)

Entry	R-I	Conditions[a]	Product	Yield (%)
a	Me-I	A	**8a**	83
b	*n*Pr-I	A	**8b**	94
c	*n*Bu-I	A	**8c**	97
d	nC_7H_{15}-I	A	**8d**	81
e	nC_8H_{17}-I	A	**8e**	98
f	I-$(CH_2)_2$OTHP	B	**8f**	92
g	I-$(CH_2)_3$OTHP	A	**8g**	98
h	I-$(CH_2)_4$OTHP	A	**8h**	96
i	I-$(CH_2)_8$OTHP	A	**8i**	97
j	$CH_3CH_2C{\equiv}CCH_2CH_2$-I	A	**8j**	25
j	$CH_3CH_2C{\equiv}CCH_2CH_2$-I	B	**8j**	67
k	CH_2=CH-I	A, B	**8k**	–[b]
l	CH_2=$CHCH_2$-I	A, B	**8l**	–[c]
m	*trans*-CH_3CH=$CH(CH_2)_2$I	A	**8m**	100
n		A	**8n**	84
o	*cis*-Ph 	A	**8o**	95[d]
p	*cis*-F 	A	**8p**	92[d]
q	*trans*-*n*Pr 	A	**8q**	88[d]
r	Ph	B	**8r**	21
s	*p*-Me-C_6H_4-I	B	**8s**	10

[a] A: MeLi, Et_2O, 20 °C, 24 h; B: hν, 0 °C, 1–4 h. – [b] No product **8k** isolated, only **8a** was isolated in 55% yield. – [c] No product **8l** formed, only **8a** was isolated in 60% yield. – [d] A 2:1 mixture of *cis* and *trans* isomers was obtained.

The corresponding lithium derivatives were obtained from the iodides **8** by treatment with either lithium 4,4′-di-*tert*-butylbiphenylide (LiDBB[16a]) or *tert*-butyllithium at –78 °C,[8a,9a,9d,16b,16c] and trapped with a variety of electrophiles. Comparison of the two series of experiments (Scheme 2, Table 2) showed that better yields were frequently obtained following lithiation with *tert*-butyllithium. Thus, the acids **10c–e,h,i,o** were obtained in yields of 44–60%, while **10b** was produced almost quantitatively. Satisfactory results were also achieved with most of the other electrophiles investigated (Table 2). As in the published procedure,[9] the addition of lithium derivatives **9** to nitriles furnished a good yield of ketone **12b** only in the case of *p*-fluorobenzonitrile. Generally better results were achieved using acid chlorides as electrophiles (Table 2). Chlorozinc reagents may be prepared almost quantitatively from **9** by transmetallation with anhydrous $ZnCl_2$ (see below).



Scheme 2. For details see Table 2

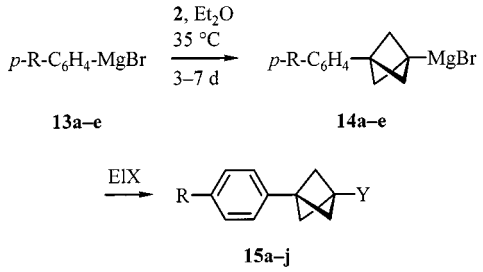
Table 2. Functionalization of 3-substituted bicyclo[1.1.1]pent-1-yl iodides **8** by lithiation/electrophilic substitution

Starting Material	R	Method of Lithiation[a]	ElX	Product	Y	Yield (%)
8b	*n*Pr	B	CO_2	**10b**	COOH	97
8c	*n*Bu	A	CO_2	**10c**	COOH	60
8d	nC_7H_{15}	A	CO_2	**10d**	COOH	54
8e	nC_8H_{17}	A	CO_2	**10e**	COOH	45
8h	$(CH_2)_4$OTHP	A	CO_2	**10h**	COOH	56
8i	$(CH_2)_8$OTHP	A	CO_2	**10i**	COOH	53
8o	Ph *cis/trans* = 2:1	A	CO_2	**10o**	COOH	44
8b	*n*Pr	B	Me_2C=O	**11b**	Me_2C-OH	52
8c	*n*Bu	B	Ph  =O	**11ca**	PhOH	70
8c	*n*Bu	B	Me_3SiCl	**11cb**	Me_3Si	78
8i	$(CH_2)_8$OTHP	B	MeOH	**11i**	H	93
8b	*n*Pr	B	*p*-F-C_6H_4-CN	**12b**	*p*-F-C_6H_4-CO	78
8c	*n*Bu	B	nC_3H_7CN	**12c**	nC_3H_7CO	17
8e	nC_8H_{17}	B	C_2H_5COCl	**12e**	C_2H_5CO	75
8h	$(CH_2)_4$OTHP	B	nC_3H_7COCl	**12h**	nC_3H_7CO	79
8o	Ph *cis/trans* = 2:1	B	C_2H_5COCl	**12o**	C_2H_5CO	74

[a] A: LiDBB, THF, –78 °C, 1 h. – B: *t*BuLi, Et_2O, –78 °C, 1 h.

Bicyclo[1.1.1]pentyl iodides **8**, in which R is an aryl or substituted aryl group, cannot be prepared as easily as iodides **8a–j,m–q**, because the addition of aryl iodides to the central bond in **2** proceeds only under photochemical conditions and gives the adducts in moderate yields only.[4,8a] In the majority of publications, 3-phenylbicyclo[1.1.1]pentyl iodide (**8r**) has been used without purification,[4a] which is unacceptable for transition metal catalyzed coupling reactions. The alternative route to **8r** reported by Della et al.[8a] is a tedious six-step preparation starting from **2**. Upon purification by chromatography on silica gel, the phenyl and *p*-tolyl derivatives, **8r** and **8s**, respectively, could be isolated in pure form, albeit only in yields of 21% and 10% due to significant decomposition. Moreover, the yield decreased considerably upon increasing the scale of the preparation. As an alternative access to 3-aryl-substituted bridgehead metal derivatives of type **6**, the known addition of Grignard reagents to [1.1.1]propellanes[12a,17] was examined, in spite

of the long reaction times and moderate yields reported for this process. The bridgehead bicyclo[1.1.1]pentylmagnesium bromide derivatives thus formed were trapped with various electrophiles (Scheme 3 and Table 3).



Scheme 3. For details see Table 3

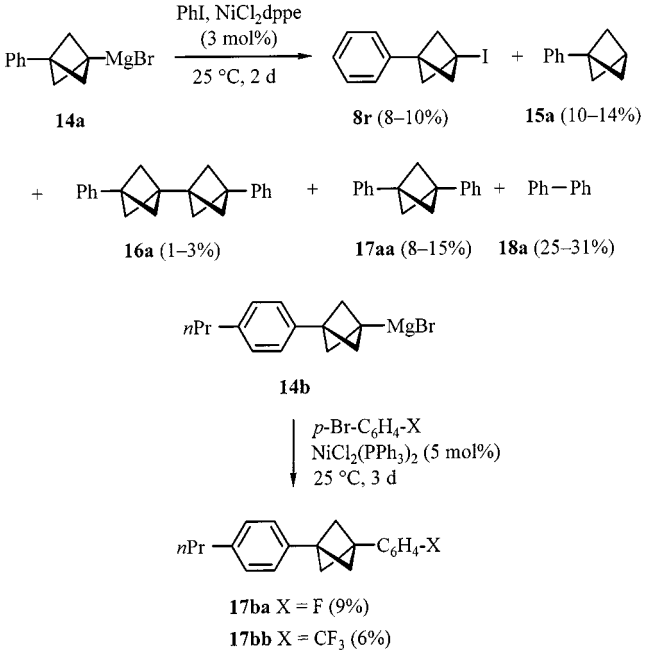
Table 3. Formation of 3-arylbicyclo[1.1.1]pent-1-ylmagnesium bromides **14** and their reactions with electrophiles

Starting Material	R	Time [d]	Reaction with Electrophile EIX	Product	Y	Yield (%)
13a	H	3	H_2O	**15a**	H	80
13b	*n*Pr	6	H_2O	**15ba**	H	99
13c	*n*Bu	6	H_2O	**15ca**	H	65
13d	F	5	H_2O	**15da**	H	60
13e	*p*-Et-C_6H_4-	7	H_2O	**15e**	H	13
13d	F	5	CH_2=CH-CH_2Br	**15db**	CH_2=CH-CH_2	35
13b	*n*Pr	6	*p*-F-C_6H_4-CN	**15bb**	*p*-F-C_6H_4-CO	31
13b	*n*Pr	6	*p*-Cl-C_6H_4-CN	**15bc**	*p*-Cl-C_6H_4-CO	49
13c	*n*Bu	6	Br_2	**15cb**	Br	36
13b	*n*Pr	6	NCS	**15bd**,	Cl	24
				15ba	H	24

The results of these test runs showed that this procedure could only favorably be used for the addition of unsubstituted phenyl- and *p*-(*n*-propyl)phenylmagnesium bromide, mainly because of difficulties encountered in purifying any of the other final coupling products (see below). Compounds **15ca** and **15da** were not isolated following these test runs; the relative yields of the overall reactions (Grignard additions and subsequent trapping) were determined by GC and NMR analyses. Attempted additions of vinyl- and allylmagnesium bromides to **2** were unsuccessful. This may be attributed to the limited solubilities of the Normant reagent and **13e** in diethyl ether (Table 3).

2. Metal-Catalyzed Cross-Coupling of Bicyclo[1.1.1]pentylmetal Derivatives 6 with Aryl Halides

The first catalysts to be tested in the cross-coupling of bridgehead magnesium derivatives of type **14** were the phosphanenickel(II) complexes reported by Kumada et al.[18] However, neither with $NiCl_2(PPh_3)_2$ nor $NiCl_2$dppe were good yields of the diarylbicyclo[1.1.1]pentanes **17** obtained in attempted cross-coupling reactions of **14** with aryl iodides. Thus, coupling of the phenyl derivative **14a** with phenyl iodide in the presence of 3 mol-% $NiCl_2$dppe led only to a complex mixture (Scheme 4), which apparently contained products derived from all conceivable cross-coupling reactions of the starting materials, including reactions of some residual phenylmagnesium bromide used in the preparation of **14a**, as well as halogen–metal exchange products. Compounds **8r**, **15a**, and **18a** were identified by means of GC and NMR analyses of the reaction mixture. It is noteworthy that the spectroscopic data of 3,3′-diphenyl[2]staffane (**16a**) isolated from this reaction mixture were in complete agreement with those reported by Michl et al.,[4a,19] but not with those erroneously attributed to this compound in an earlier study;[20] it was later established that the latter product was in fact 1-phenylbicyclo[1.1.1]pentane (**15a**).[4a] Coupling of **14b** with *p*-substituted bromobenzenes under $NiCl_2(PPh_3)_2$ catalysis provided the desired products **17ba** and **17bb** in even lower yields (Scheme 4).

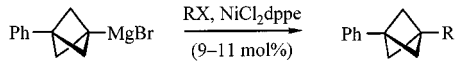


Scheme 4

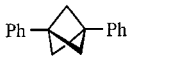
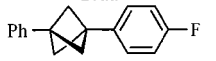
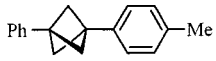
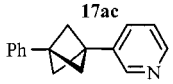
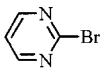
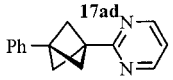
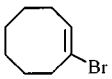
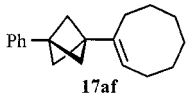
Apparently, the rate of cross-coupling under these conditions was prohibitively slow. Improvements could be achieved by (i) employing an excess of the organometallic intermediate **14**, (ii) by a better choice of the metal in the intermediate of type **6**, and (iii) by a better choice of catalyst. Utilization of four equivalents of **14a** in the presence of 10 mol-% of catalyst improved the yields of the cross-coupling products to a certain extent (Table 4), but, taking into consideration the difficulties associated with producing **14**, the overall approach remained less than satisfactory. The best yield (41%) was obtained for the cross-coupling product of 3-iodopyridine, **17ad**. The coupling product of 1-bromocyclooctene, **17af**, could not be obtained in sufficiently pure form under these experimental conditions.

Attempted coupling of **14a** with iodobenzene in the presence of 5 mol-% $Pd(PPh_3)_4$ led to essentially the same results as those presented in Scheme 4; the yield of **17aa** was only 8%. No significant improvement was observed when **14a** was coupled after transmetallation with $ZnCl_2$.[21] Chlorozinc derivatives of type **19** (Scheme 5), easily prepared from the corresponding bridgehead lithium derivat-

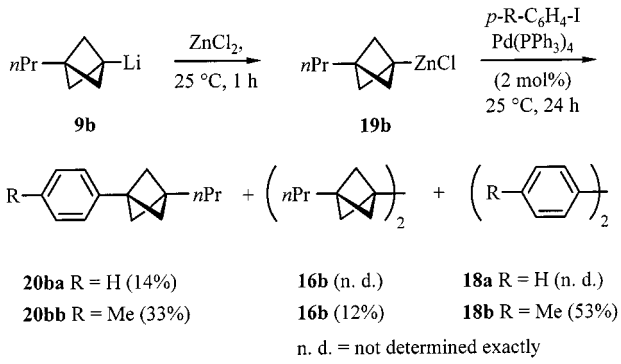
Table 4. $NiCl_2$dppe-catalyzed cross-coupling of aryl and alkenyl halides with 4 equivalents of 3-phenylbicyclo[1.1.1]pent-1-ylmagnesium bromide **14a** at 25 °C



14a **17**

RX	t [h]	Product	Yield (%)
PhI	36	 **17aa**	23
p-Br-C_6H_4-F	48	 **17ab**	38
p-I-C_6H_4-Me	36	 **17ac**	21
	16	 **17ad**	41
	48	 **17ae**	35
	72	 **17af**	11

ives **9** by transmetallation with $ZnCl_2$·THF[21] in diethyl ether/pentane mixtures, also gave discouraging results in their cross-coupling reactions with aryl iodides under $Pd(PPh_3)_4$ catalysis in that the rate of homocoupling still exceeded that of the cross-coupling reaction.

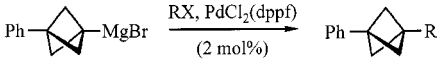


Scheme 5

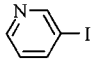
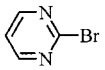
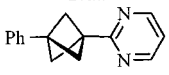
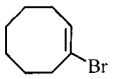
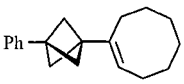
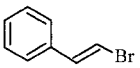
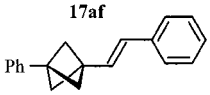
Even using a two-fold excess of **9b**, the three coupling products **20bb**, **16b**, and **18b** were obtained in yields of just 33%, 12%, and 53%, respectively (Scheme 5).

Since dichloro[1,1′-bis(diphenylphosphanyl)ferrocene]-palladium(II) [$PdCl_2$(dppf)] was found to be by far the most active and selective catalyst for the coupling of *n*-, *sec*-, and *tert*-alkylzinc and -magnesium halides with aromatic halides,[22] and in view of the fact that this catalyst has also been successfully employed in the preparation of various liquid crystalline materials,[23] it was tested in the cross-coupling reactions of bicyclo[1.1.1]pentylmagnesium and -zinc halide derivatives, **14** and **19**, respectively (Table 5).

Table 5. $PdCl_2$(dppf)-catalyzed cross-coupling of aryl and alkenyl halides with 3-phenylbicyclo[1.1.1]pent-1-ylmagnesium bromide **14a** at 25 °C



14a **17**

RX	t [h]	Product	Yield (%)
	48	 **17aa**	trace
	24	 **17ae**	61
	24	 **17af**	50
	24	 **17ag**	76

In the presence of 2 mol-% $PdCl_2$(dppf), couplings of 3-phenylbicyclo[1.1.1]pent-1-ylmagnesium bromide (**14a**) with essentially the same series of aryl and alkenyl halides as used in the $NiCl_2$dppe-catalyzed reactions (Table 4) gave compounds **17ae** and **17af** in much better yields. However, the cross-coupling product of 3-iodopyridine (**17ad**), which was obtained in the highest yield under $NiCl_2$dppe catalysis, was not formed at all in this case. Instead, a trace of 1,3-diphenylbicyclo[1.1.1]pentane (**17aa**) was detected, which must have resulted from a coupling reaction with bromobenzene or phenylmagnesium bromide, probably still present in the reaction mixture after the preparation of **14a**. Thus, for the coupling of heterocycles,[24] $NiCl_2$dppe may complement $PdCl_2$(dppf) as a catalyst (for methods of C–C bond formation in different heterocycles through Ni- and Pd-catalyzed cross-coupling, see ref.[24]).

To test the viability of chlorozinc derivatives **19** in cross-coupling reactions, one and two equivalents of **19b** were treated with one equivalent of 4-iodotoluene in the presence of 5 mol-% $PdCl_2$(dppf). After 1 h at room temperature, the coupling product **20bb** had been formed in 82–86% yield (GC) along with 9–13% of the homocoupling product 4,4′-dimethylbiphenyl (**18b**). Neither longer reaction times, the use of an excess of the chlorozinc reagent, nor its portionwise addition, had any significant influence on the results (Scheme 6).

Under optimized conditions, various *p*-substituted bromobenzenes, as well as iodobenzene and 2-bromopyrimidine, were coupled with various 3-substituted bicyclo[1.1.1]-pentylzinc chlorides **19**. With the exception of the product derived from *p*-dibromobenzene (**20ca**) the yields were reasonably good throughout (Table 6). However, the *p*-bromophenyl derivative **20ca** may easily be obtained in almost

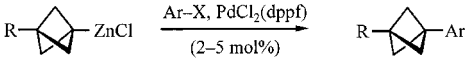
19b

p-Me-C_6H_4-I
$PdCl_2$(dppf) (5 mol%)
25 °C, THF

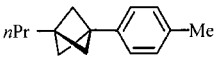
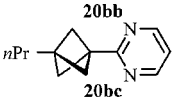
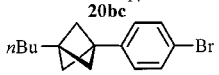
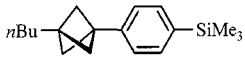
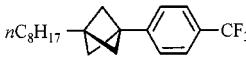
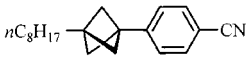
		20bb +	**18b** +	p-Me-C_6H_4-I
	[h]	%	%	%
1 equiv. **19b**	1	82	9	9
	21	86	13	1
2 equiv. **19b**	1	86	12	2
	21	86	12	2

Scheme 6

Table 6. $PdCl_2$(dppf)-catalyzed cross-coupling of various aryl halides with 3-substituted bicyclo[1.1.1]pent-1-ylzinc chlorides **19** in THF at 25 °C

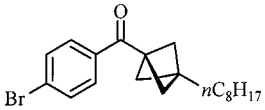


19 **20**

Ar-X	**19**/R equiv.	t [h]	Product	Yield (%)
PhI	**b**/nPr 1	2	 **20ba**	79
p-Me-C_6H_4-I	**b**/nPr 2	2	 **20bb**	84
	**b**/nPr 2	2	 **20bc**	75
p-Br-C_6H_4-Br	**c**/nBu 1.05	24	 **20ca**	13
p-Me_3Si-C_6H_4-Br	**c**/nBu 2	24	 **20cb**	72
p-F-C_6H_4-Br	**e**/$n$$C_8H_{17}$ 1.05	20	 **20ea**	43
p-CF_3-C_6H_4-Br	**e**/$n$$C_8H_{17}$ 1.05	20	 **20eb**	68
p-NC-C_6H_4-Br	**e**/$n$$C_8H_{17}$ 1.5	20	 **20ec**	75

quantitative yield by bromination of the p-(trimethylsilyl)-phenyl derivative **20cb** in methanol[25] (see Experimental Section). The trimethylsilyl derivative **20cb** was obtained in good yield only when two equivalents of the chlorozinc reagent **19c** were employed. All the products **20** were accompanied by the aryl halide homocoupling products, i.e. the correspondingly disubstituted biaryls, in yields of 10–13%.

Only **20ca** was formed alongside a 58% isolated yield of 4,4′-dibromobiphenyl. Amazingly, in many cases the starting aryl halide and the coupling product had identical R_f values upon TLC analysis, which presented additional difficulties in the purification of the final products. This was not too serious for small scale preparations (1 mmol), but on a 15–20-mmol scale the product had to be distilled or recrystallized following column chromatography (see Experimental Section). The fact that the p-cyanophenyl derivative **20ec** was isolated in 75% yield demonstrates the tolerance of chlorozinc reagents towards a cyano group under the coupling conditions. The addition product of **19e**, i.e. the ketone **21**. was isolated in iust 2.5% yield.



21

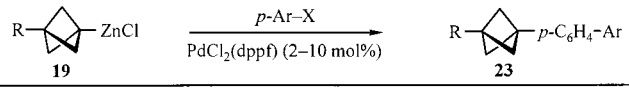
As in the attempted coupling of the bridgehead Grignard reagent **14a**, treatment of 3-phenylbicyclo[1.1.1]pent-1-ylzinc chloride (**19r**) with 2- or 5-iodopyrimidine led exclusively to the metal–halogen-exchanged product 3-phenyl-1-iodobicyclopentane (**8r**).

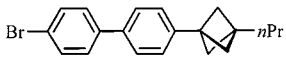
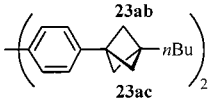
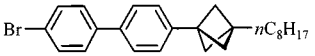
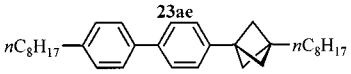
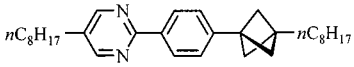
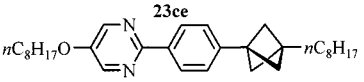
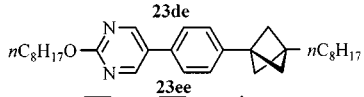
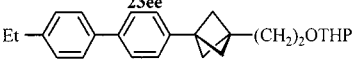
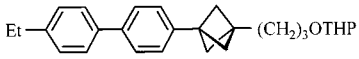
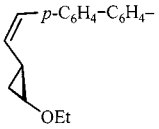
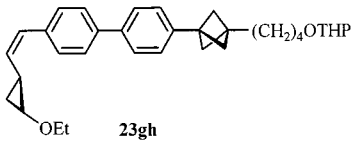
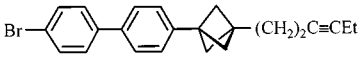
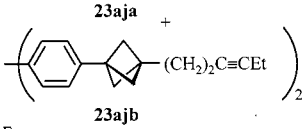
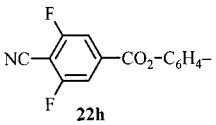
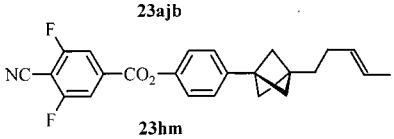
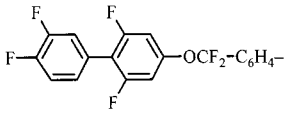
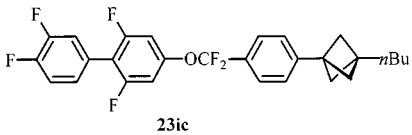
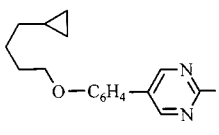
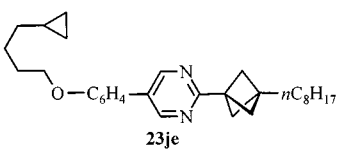
$PdCl_2$(dppf)-catalyzed coupling of 3-substituted bicyclo[1.1.1]pentylzinc chlorides **19** was also tested in the preparation of biaryl derivatives such as phenylpyrimidines and biphenyls containing bicyclo[1.1.1]pentyl moieties. Besides biaryl bromides, triflates of hydroxybiaryls[26] can also be employed in such reactions (Table 7).[27] With appropriate variation of the solvent and proportions of reagents, diarylbicyclo[1.1.1]pentyl derivatives containing one or two bicyclo[1.1.1]pentane units were obtained in moderate to good yields (examples **23ac**,**be**,**de**,**ee**). Actually, the crude yields were even better, as losses were incurred during work-up. For unknown reasons, the (tetrahydropyranyloxyethyl)-substituted bicyclo[1.1.1]pentylzinc chloride **19f** gave the correspondingly substituted (p-ethylbiphenyl) derivative **23ff** in particularly low yield (10%). As in the case of the monoaryl derivatives, the starting materials and coupling products tended to be inseparable by column chromatography on silica gel, although the final products could be purified by recrystallization from methanol, albeit with slightly decreased yields. The mono- and bis-coupling products of 4,4′-dibromobiphenyl (**22a**), i.e. **23aja** and **23ajb**, could be separated by column chromatography using benzene as a co-eluent.

3. Chemical Transformations of the Coupling Products

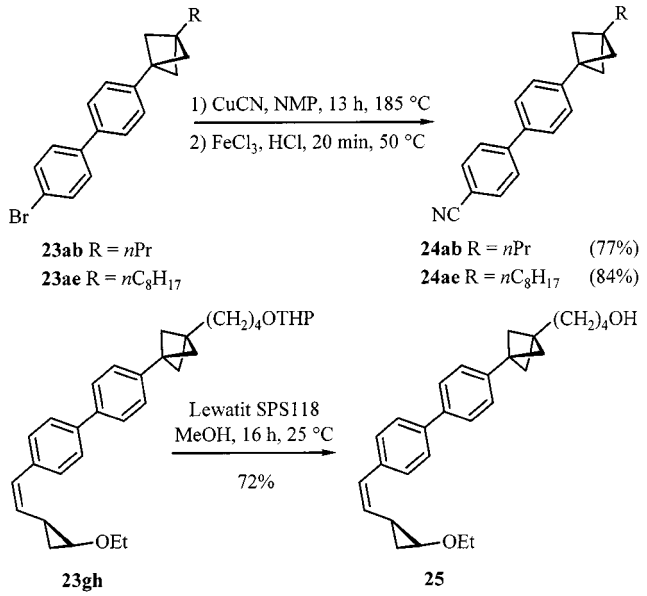
In order to introduce certain functional groups, e.g. a cyano group,[28] with a view to improving particular liquid crystalline features of the molecules, a series of subsequent manipulations had to be performed with the coupling products, as the correspondingly substituted products were not directly accessible by such coupling reactions. Although it should be possible to couple 4-bromo-4′-cyanobiphenyl (see, e.g., the successful coupling of p-bromobenzonitrile, Table 6), the desired p-cyanobiphenyl-substituted end products **24ab**,**ae** can also readily be prepared from **23ab**,**ae**, the products of monocoupling of 4,4′-dibromobiphenyl (Scheme 7).

Table 7. $PdCl_2$(dppf)-catalyzed cross-coupling of biaryl halides and triflates *p*-Ar–X (**22**) with 0.5–4 equiv. of 3-substituted bicyclo[1.1.1]-pent-1-ylzinc chlorides **19** in Et_2O or THF at 25 °C



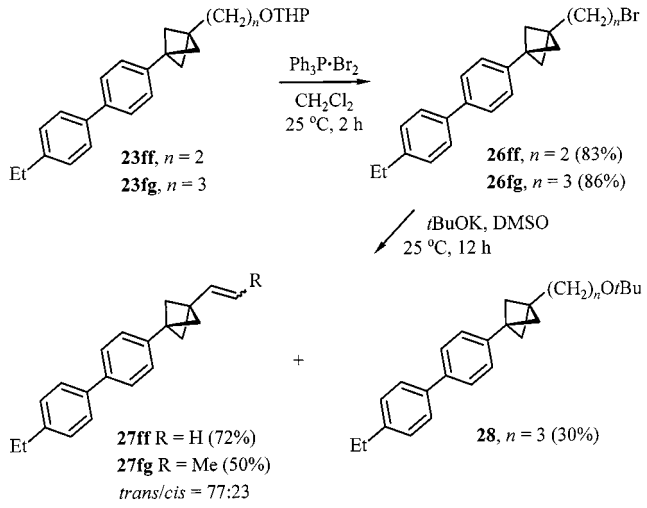
p-Ar	X	**19**/R Equiv.	t [h] Solvent	Product	Yield (%)
p-Br-C_6H_4-C_6H_4- **22a**	Br	**b**/*n*Pr 0.5	24 Et_2O	 **23ab**	43
p-Br-C_6H_4-C_6H_4- **22a**	Br	**c**/*n*Bu 3	24 THF	 **23ac**	87
p-Br-C_6H_4-C_6H_4- **22a**	Br	**e**/*n*C_8H_{17} 0.5	24 Et_2O	 **23ae**	62
nC_8H_{17}-C_6H_4- **22b**	Br	**e**/*n*C_8H_{17} 2	24 Et_2O	 **23be**	80
nC_8H_{17}-pyrimidine-C_6H_4- **22c**	OTf	**e**/*n*C_8H_{17} 3	16[a] THF	 **23ce**	63
n$C_8H_{17}O$-pyrimidine-C_6H_4- **22d**	OTf	**e**/*n*C_8H_{17} 1.6	20 THF	 **23de**	70
n$C_8H_{17}O$-pyrimidine-C_6H_4- **22e**	OTf	**e**/*n*C_8H_{17} 4	16[a] THF	 **23ee**	79
p-Et-C_6H_4-C_6H_4- **22f**	Br	**f**/$(CH_2)_2$OTHP 2	48 THF	 **23ff**	10
p-Et-C_6H_4-C_6H_4- **22f**	Br	**g**/$(CH_2)_3$OTHP 4	48 THF	 **23fg**	61
 **22g**	Br	**h**/$(CH_2)_4$OTHP 4	25 THF	 **23gh**	48
p-Br-C_6H_4-C_6H_4- **22a**	Br	**j**/EtC≡C$(CH_2)_2$ 3	72 THF	 **23aja** +  **23ajb**	39 50
 **22h**	Br	**m**/*trans*-CH_3CH=$CH(CH_2)_2$ 1.6	48 THF	 **23hm**	39
 **22i**	Br	**c**/*n*Bu 2.7	48 THF	 **23ic**	85
 **22j**	Br	**e**/*n*C_8H_{17} 4	24 THF	 **23je**	84

[a] This reaction was performed at 65 °C.



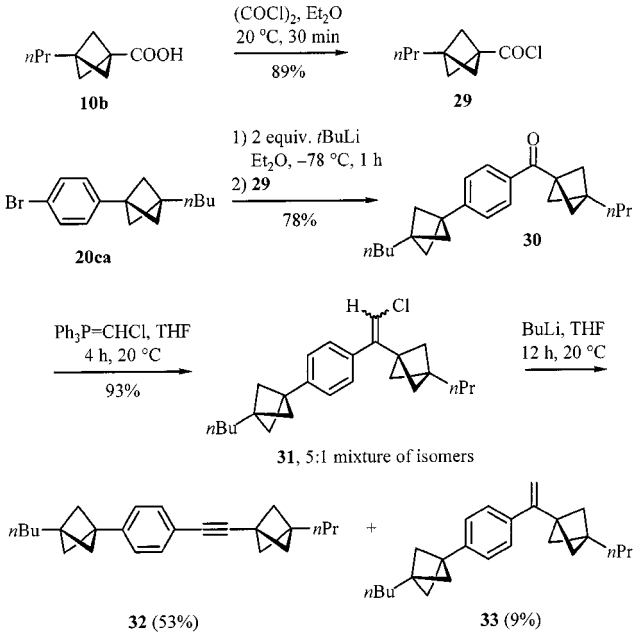
Scheme 7

Since all attempts to prepare 3-vinyl- and 3-allylbicyclo[1.1.1]pentyl iodides **8k**,**l** have hitherto proved unsuccessful (Table 1), the preparation of compounds of type **23** containing a double bond in the end group was attempted by transformation of the tetrahydropyranyl-protected hydroxyalkyl derivatives **23ff**,**fg**,**gh**. The latter can be smoothly deprotected to give hydroxyalkyl derivatives such as **25**, or directly transformed by treatment with triphenylphosphane/bromine to give bromides **26ff**,**fg**. Dehydrobromination of **26ff** with *t*BuOK/DMSO proceeded normally, although the solubility of **26ff** in DMSO was extremely low (Scheme 8). In the case of **26fg**, however, a mixture of the *tert*-butoxide substitution product **28** and the allyl rearrangement product **27fg** was obtained (Scheme 8).



Scheme 8

Particular difficulties were encountered when attempts were made to construct molecules with ethynyl groups directly bound to bicyclo[1.1.1]pentyl moieties. A previously pursued strategy involved the low-yielding photochemical addition of 1,1,1-trichloroethane to propellane **2**[29] and subsequent twofold dehydrochlorination. Attempts to perform a direct coupling of the bicyclo[1.1.1]pentylzinc chloride derivative **19c** with 1-iodo-2-(trimethylsilyl)ethyne[30] under $PdCl_2$(dppf) catalysis failed completely: the metal–halogen exchange product **8c** was formed exclusively and could be isolated in almost quantitative yield. Therefore, a new approach based on the well-known rearrangement of vinyl carbenoids (the so-called Fritsch–Buttenberg–Wichell rearrangement[31]) was elaborated. In view of the facile preparation of bicyclo[1.1.1]pentyl ketones from bridgehead bicyclo[1.1.1]pentyllithium derivatives and acid chlorides (see Table 2), the *n*-propylbicyclo[1.1.1]pentylcarboxylic acid **10b** was converted into the acid chloride **29**,[8a] and this in turn was reacted with the (*p*-lithiophenyl)bicyclo[1.1.1]pentyl derivative obtained from **20ca** and *t*BuLi to give the ketone **30** in 78% yield (Scheme 9).



Scheme 9

Wittig olefination with chloromethylenetriphenylphosphorane, followed by treatment of the chloroalkene **31** with BuLi, provided the desired internal acetylene **32** in 53% yield, along with the 1,1-disubstituted ethylene **33** resulting from metal–halogen exchange on **31** and subsequent hydrolysis.

To summarize the results presented herein, $PdCl_2$(dppf)-catalyzed coupling of 3-substituted bridgehead bicyclo[1.1.1]pentylzinc chlorides constitutes the most powerful tool for the construction of rod-like molecules containing bicyclo[1.1.1]pentyl fragments. Several of these new bicyclo[1.1.1]pentyl derivatives do indeed exhibit quite interesting liquid crystalline properties, which have been reported separately.[32]

Experimental Section

General: ^{1}H and ^{13}C NMR: Spectra were recorded at 200 or 250 MHz (^{1}H), and at 62.9 MHz [^{13}C and additional DEPT (Dis-

tortionless Enhancement by Polarization Transfer)] with Varian XL 200 and Bruker AM 250 instruments in $CDCl_3$ solution; $CHCl_3$/$CDCl_3$ as internal reference; δ in ppm, *J* in Hz. – IR: Perkin–Elmer 298. – FT-IR: Bruker IFS 66; samples in KBr pellets or as films between NaCl plates. – MS (EI): Finnigan MAT 95 spectrometer (70 eV). – M.p.: Büchi 510 capillary melting point apparatus; uncorrected values. – GC analyses: Siemens Sichromat 1–4, 25-m capillary column CP-SIL-5-CB. – GC separations: Intersmat 130 instrument, 20% SE-30 on Chromaton W-AW-DMCS, 1500 × 8.2 mm column. – TLC: Macherey–Nagel precoated sheets, 0.25 mm Sil G/UV_{254}. – Column chromatography: Merck silica gel, grade 60, 230–400 mesh. – Starting materials: Anhydrous diethyl ether and THF were obtained by distillation from sodium benzophenone ketyl, pyridine from CaH_2, and dichloromethane from P_4O_{10}. Compounds **2**,[6,8a,10] **7f**,[33] **7g**,[34] **7i**,[35] 4-bromobutyl- and propylbenzenes,[36] 4-bromo-4′-ethylbiphenyl (**22f**),[37] (4-bromophenyl)trimethylsilane,[38] **22g**,[39] lithium 4,4′-di-*tert*-butylbiphenylide,[16a] and $PdCl_2$(dppf)[22] were prepared according to published procedures. Vinyl iodide was obtained in 50% yield by treating vinylmagnesium bromide with I_2 in THF solution. Iodides **7j**,[40] **7h**, and **7m**[41] were prepared from the corresponding alcohols[42] in 88%, 80%, and 67% yield, respectively, using the I_2/Ph_3P/ImH reagent;[43] compounds **7o**,**p** were obtained using the reagent $[(PhO)_3PMe]I$.[44] – **7j:** ^{1}H NMR: δ = 1.14 (t, *J* = 7.5 Hz, 3 H, CH_3), 2.18 (qt, *J* = 7.5, 2.2 Hz, 2 H, CH_2), 2.76 (qt, *J* = 7.1, 2.2 Hz, 2 H, CH_2), 3.24 (t, *J* = 7.1 Hz, 2 H, CH_2I). – ^{13}C NMR: δ = 14.0 (CH_3), 2.6, 12.4, 24.1 (CH_2), 78.1, 83.8 (C). – **22f:** ^{1}H NMR: δ = 1.26 (t, *J* = 7.5 Hz, 3 H, CH_3), 2.69 (q, *J* = 7.5 Hz, 2 H, CH_2), 7.25 (d, *J* = 8.6 Hz, 2 H, C_6H_4), 7.35–7.55 (m, 6 H, C_6H_4). – ^{13}C NMR: δ = 15.6 (CH_3), 28.5 (CH_2), 126.8, 128.4, 128.5, 131.8 (2 CH), 121.2, 137.3, 140.0, 142.8 (C). All other chemicals were used as received from commercial suppliers (Merck, Acros, BASF, Bayer, Hoechst, Degussa AG, or Hüls AG). All reactions were performed under argon. Organic extracts were dried with $MgSO_4$.

General Procedure (GP 1) for the Preparation of 8a–e,g–i,m–q: To a solution of the appropriate iodoalkane **7** (28 mmol) and [1.1.1]propellane (**2**) (30 mmol) in anhydrous Et_2O (100 mL), a 1.56 M solution of MeLi in Et_2O (18 mL, 28 mmol) was added dropwise at –40 °C. The reaction mixture was allowed to warm to room temp., stirred for 24 h, and then cooled to –40 °C once more, whereupon MeOH (20 mL) was added. The resulting solution was poured into an ice-cold mixture of H_2O (50 mL) and pentane (50 mL). After separation of the layers, the organic phase was washed with H_2O (2 × 50 mL), dried, and concentrated under reduced pressure at 0 °C. The residue was used for the next step without purification.

1-Iodo-3-methylbicyclo[1.1.1]pentane (8a): From MeI (2.56 g, 1.12 mL, 18 mmol), compound **8a**[13b] (3.11 g, 83%) was obtained according to GP 1. – ^{1}H NMR: δ = 1.22 (s, 3 H, CH_3), 2.21 (s, 6 H, 3 CH_2). – ^{13}C NMR: δ = 18.3 (CH_3), 62.1 (3 CH_2), 7.0, 44.6 (C).

1-Iodo-3-propylbicyclo[1.1.1]pentane (8b): From PrI (6.80 g, 3.92 mL, 40 mmol), compound **8b** (8.88 g, 94%) was obtained according to GP 1. – IR: $\tilde{\nu}$ = 2980 cm^{-1}, 2960, 2910, 2870, 1446, 1171, 985, 836. – ^{1}H NMR: δ = 0.88 (t, *J* = 7.4 Hz, 3 H, CH_3), 1.18–1.34 (m, 2 H, CH_2), 1.48 (t, *J* = 7.8 Hz, 2 H, CH_2), 2.19 (s, 6 H, 3 CH_2). – ^{13}C NMR: δ = 14.0 (CH_3), 60.7 (3 CH_2), 20.0, 34.2 (CH_2), 7.9, 48.5 (C).

1-Butyl-3-iodobicyclo[1.1.1]pentane (8c): From BuI (14.72 g, 9.10 mL, 80 mmol), compound **8c**[4a] (19.41 g, 97%) was obtained according to GP 1.

1-Heptyl-3-iodobicyclo[1.1.1]pentane (8d): From 1-iodoheptane (4.30 g, 3.12 mL, 19 mmol), compound **8d** (4.48 g, 81%) was obtained according to GP 1. – IR: $\tilde{\nu}$ = 2926 cm^{-1}, 1466, 1378, 1261, 1174, 1130, 1022, 984, 839, 722, 669. – ^{1}H NMR: δ = 0.88 (t, *J* = 6.6 Hz, 3 H, CH_3), 1.23 (m, 10 H, 5 CH_2), 1.48 (t, *J* = 6.4 Hz, 2 H, CH_2), 2.19 (s, 6 H, 3 CH_2). – ^{13}C NMR: δ = 14.1 (CH_3), 60.6 (3 CH_2), 22.6, 26.8, 29.2, 29.4, 31.8, 32.1 (CH_2), 8.2, 48.6 (C).

1-Iodo-3-octylbicyclo[1.1.1]pentane (8e): From 1-iodooctane (4.08 g, 3.07 mL, 17 mmol), compound **8e** (5.10 g, 98%) was obtained according to GP 1. – IR: $\tilde{\nu}$ = 2990 cm^{-1}, 2960, 2925, 2875, 2855, 1450, 1175, 840. – ^{1}H NMR: δ = 0.89 (t, *J* = 6.6 Hz, 3 H, CH_3), 1.27 (m, 12 H, 6 CH_2), 1.42–1.55 (m, 2 H, CH_2), 2.18 (s, 6 H, 3 CH_2). – ^{13}C NMR: δ = 14.1 (CH_3), 60.5 (3 CH_2), 22.6, 26.8, 29.4, 29.5, 29.6, 31.8, 32.1 (CH_2), 8.1, 48.5 (C).

1-Iodo-3-[3-(tetrahydropyran-2-yloxy)propyl]bicyclo[1.1.1]pentane (8g): From **7g** (20.0 g, 74 mmol), compound **8g** (24.4 g, 98%) was obtained according to GP 1. – ^{1}H NMR: δ = 1.45–1.90 (m, 10 H, 5 CH_2), 2.17 (s, 6 H, 3 CH_2), 3.25–3.35 (m, 1 H, OCH_2), 3.35–3.50 (m, 1 H, OCH_2), 3.60–3.70 (m, 1 H, OCH_2), 3.70–3.85 (m, 1 H, OCH_2), 4.54 (t, *J* = 3.2 Hz, 1 H, OCH). – ^{13}C NMR: δ = 60.3 (3 CH_2), 19.5, 25.3, 26.9, 28.7, 30.5, 62.2, 66.9 (CH_2), 98.6 (CH), 7.6, 48.1 (C).

1-Iodo-3-[4-(tetrahydropyran-2-yloxy)butyl]bicyclo[1.1.1]pentane (8h): From **7h** (5.1 g, 18 mmol), compound **8h** (6.1 g, 96%) was obtained according to GP 1. – IR: $\tilde{\nu}$ = 2938 cm^{-1}, 1453, 1353, 1329, 1261, 1200, 1175, 1128, 1078, 1035, 988, 906, 869, 837. – ^{1}H NMR: δ = 1.22–1.90 (m, 12 H, 6 CH_2), 2.18 (s, 6 H, 3 CH_2), 3.36 (dt, *J* = 9.5, 6.6 Hz, 1 H, OCH_2), 3.42–3.56 (m, 1 H, OCH_2), 3.71 (dt, *J* = 9.5, 6.9 Hz, 1 H, OCH_2), 3.85 (ddd, *J* = 11.4, 7.5, 3.5 Hz, 1 H, OCH_2), 4.57 (t, *J* = 3.2 Hz, 1 H, OCH). – ^{13}C NMR: δ = 60.4 (3 CH_2), 19.6, 23.5, 25.4, 29.5, 30.6, 31.8, 62.3, 67.2 (CH_2), 98.8 (CH), 7.8, 48.3 (C).

1-Iodo-3-[8-(tetrahydropyran-2-yloxy)octyl]bicyclo[1.1.1]pentane (8i): From **7i** (4.70 g, 13.8 mmol), compound **8i** (5.44 g, 97%) was obtained according to GP 1. – ^{1}H NMR: δ = 1.22–1.38 (m, 10 H, 5 CH_2), 1.39–1.92 (m, 10 H, 5 CH_2), 2.18 (s, 6 H, 3 CH_2), 3.36 (dt, *J* = 9.5, 6.6 Hz, 1 H, OCH_2), 3.43–3.53 (m, 1 H, OCH_2), 3.71 (dt, *J* = 9.5, 6.9 Hz, 1 H, OCH_2), 3.85 (ddd, *J* = 11.4, 7.5, 3.5 Hz, 1 H, OCH_2), 4.55 (t, *J* = 3.2 Hz, 1 H, OCH). – ^{13}C NMR: δ = 60.5 (3 CH_2), 19.6, 25.4, 26.1, 27.0, 29.3, 29.4, 29.6, 30.7, 32.0, 62.3, 67.5 (CH_2), 98.7 (CH), 8.1, 48.5 (C).

1-Iodo-3-[(*E*)-pent-3-enyl]bicyclo[1.1.1]pentane (8m): From (*E*)-5-iodopent-2-ene (9.729 g, 49.63 mmol), compound **8m** (13.0 g, 100%) was obtained according to GP 1. – ^{1}H NMR: δ = 1.58 (t, *J* = 8.0 Hz, 2 H, CH_2), 1.61 (d, *J* = 5.6 Hz, 3 H, CH_3), 1.85–2.05 (m, 2 H, CH_2), 2.20 (s, 6 H, 3 CH_2), 5.25–5.51 (m, 2 H, CH=CH). – ^{13}C NMR: δ = 17.9 (CH_3), 60.5 (3 CH_2), 29.8, 31.8 (CH_2), 125.3, 130.4 (CH), 8.0, 48.3 (C).

1-Cyclohexyl-3-iodobicyclo[1.1.1]pentane (8n): From iodocyclohexane (1.09 g, 0.67 mL, 5.2 mmol), compound **8n** (1.21 g, 84%) was obtained according to GP 1. – ^{1}H NMR: δ = 0.68–0.97 (m, 2 H, CH_2), 1.00–1.82 (m, 9 H), 2.17 (s, 6 H, 3 CH_2). – ^{13}C NMR: δ = 58.6 (3 CH_2), 25.9, 29.6 (2 CH_2), 25.8 (CH_2), 39.3 (CH), 8.9, 52.4 (C).

1-Iodo-3-(4-phenylcyclohexyl)bicyclo[1.1.1]pentane (8o): From *cis*-4-phenylcyclohexyl iodide **7o** (4.49 g, 15.7 mmol), compound **8o** (5.26 g, 95%) was obtained according to GP 1 as a 2:1 mixture of *cis* and *trans* isomers. An analytical sample of *trans*-**8o** was obtained after repeated (4 times) recrystallization from pentane; m.p.

105 °C (dec.). – IR: $\tilde{\nu}$ = 3080 cm^{-1}, 3055, 3020, 2985, 2960, 2910, 2870, 2850, 1600, 1592, 1546, 1173, 968, 852, 835, 800, 756, 700. – ^1H NMR: δ = 1.07 (dq, *J* = 12.8, 3.2 Hz, 2 H, CH_2), 1.43 (dq, *J* = 12.8, 3.2 Hz, 2 H, CH_2), 1.52 (tt, *J* = 12.4, 3.4 Hz, 1 H, CH), 1.75 (dm, *J* = 13.2, Hz, 2 H, CH_2), 1.91 (dm, *J* = 13.2 Hz, 2 H, CH_2), 2.19 (s, 6 H, 3 CH_2), 2.41 (tt, *J* = 12.2, 3.2 Hz, 1 H, CH), 7.12–7.33 (m, 5 H, Ph). – ^{13}C NMR: δ = 58.6 (3 CH_2), 29.8, 33.5 (2 CH_2), 125.9, 126.7 (2 CH), 38.8, 43.8, 128.3 (CH), 8.6, 52.1, 147.1 (C). – $C_{17}H_{21}I$ (352.3): calcd. C 57.96, H 6.01, I 36.03; found C 57.81, H 6.06, I 36.03. – After evaporation of the solvent from the mother liquor, another recrystallization from pentane gave an analytical sample of *cis*-**8o**; m.p. 49 °C (dec.). – IR: $\tilde{\nu}$ = 3075 cm^{-1}, 3060, 3020, 2985, 2960, 2870, 2845, 1595, 1490, 1442, 1358, 1162, 858, 839, 825, 818, 746, 700. – ^1H NMR: δ = 1.07 (dq, *J* = 12.8, 3.2 Hz, 2 H, CH_2), 1.43 (dq, *J* = 12.8, 3.2 Hz, 2 H, CH_2), 1.52 (tt, *J* = 12.4, 3.4 Hz, 1 H, CH), 1.75 (dm, *J* = 13.2 Hz, 2 H, CH_2), 1.91 (dm, *J* = 13.2 Hz, 2 H, CH_2), 2.19 (s, 6 H, 3 CH_2), 2.41 (tt, *J* = 12.2, 3.2 Hz, 1 H, CH), 7.12–7.33 (m, 5 H, Ph). – ^{13}C NMR: δ = 58.6 (3 CH_2), 29.8, 33.5 (2 CH_2), 125.9, 126.7 (2 CH), 38.8, 43.8, 128.3 (CH), 8.6, 52.1, 147.1 (C).

1-[4-(4-Fluorophenyl)cyclohexyl]-3-iodobicyclo[1.1.1]pentane (8p): From *cis*-**7p** (155 mg, 0.51 mmol), compound **8p** (174 mg, 92%) was obtained according to GP 1 as a 2:1 mixture of *cis* and *trans* isomers. – ^1H NMR: δ = 0.95–1.96 (m, 9 H), 2.18 (s, 6 H, 3 CH_2, *trans*), 2.28 (s, 6 H, 3 CH_2, *cis*), 2.39 (m, 1 H, CH, *trans*), 2.60 (m, 1 H, CH, *cis*), 6.90–7.02 (m, 2 H, C_6H_4), 7.05–7.20 (m, 2 H, C_6H_4).

1-Iodo-3-[4-(4-propylphenyl)cyclohexyl]bicyclo[1.1.1]pentane (8q): From *trans*-**7q** (17 mg, 0.05 mmol), compound **8q** (18 mg, 88%) was obtained according to GP 1 as a 2:1 mixture of *cis* and *trans* isomers. – ^1H NMR: δ = 0.92 (t, *J* = 7.2 Hz, 3 H, CH_3), 1.01–2.00 (m, 11 H), 2.20 (s, 6 H, 3 CH_2, *trans*), 2.31 (s, 6 H, 3 CH_2, *cis*), 2.35–2.50 (m, 1 H, CH), 2.54 (t, *J* = 7.0 Hz, 2 H, CH_2), 7.05–7.12 (m, 4 H, C_6H_4).

General Procedure (GP 2) for the Preparation of 8f,j,r,s: A solution of the appropriate iodoalkane **7f**,**j**,**r**,**s** (29 mmol) and [1.1.1]propellane (**2**) (30 mmol) in anhydrous Et_2O (100 mL) was irradiated in a Pyrex vessel at 0 °C for 1 h (**7f**,**j**) or 4 h (**7r**,**s**) with light from a 500-W medium-pressure Hanovia mercury lamp. The volatiles were then evaporated, and the residue was either used without further purification (**8f**), recrystallized from pentane at –30 °C (**8j**), or chromatographed (**8r**,**s**) (25 g of silica gel, column 16 × 2 cm, pentane).

1-Iodo-3-[2-(tetrahydropyran-2-yloxy)ethyl]bicyclo[1.1.1]pentane (8f): From **7f** (25.61 g, 0.1 mol), compound **8f** (29.67 g, 92%) was obtained according to GP 2. – ^1H NMR: δ = 1.40–1.85 (m, 6 H, 3 CH_2), 1.75 (t, *J* = 6.9 Hz, 2 H, CH_2), 2.22 (s, 6 H, 3 CH_2), 3.20–3.40 (m, 1 H, OCH_2), 3.40–3.60 (m, 1 H, OCH_2), 3.60–3.70 (m, 1 H, OCH_2), 3.71–3.92 (m, 1 H, OCH_2), 4.49 (t, *J* = 3.2 Hz, 1 H, OCH). – ^{13}C NMR: δ = 60.8 (3 CH_2), 19.3, 25.3, 30.5, 31.7, 62.1, 65.0 (CH_2), 98.7 (CH), 7.4, 46.3 (C).

1-(Hex-3-ynyl)-3-iodobicyclo[1.1.1]pentane (8j): From **7j** (17.7 g, 85 mmol), compound **8j** was obtained according to GP 2 [crude: 15.6 g, 67%; pure **8j** can be isolated, albeit in moderate yield, from the residual starting iodide (which is more active in a coupling reaction) by low-temperature recrystallization from pentane; recrystallized pure material: 9.53 g, 41%]; m.p. 32–34 °C. – ^1H NMR: δ = 1.08 (t, *J* = 7.5 Hz, 3 H, CH_3), 1.67 (t, *J* = 6.9 Hz, 2 H, CH_2), 2.05–2.18 (m, 4 H, 2 CH_2), 2.23 (s, 6 H, 3 CH_2). – ^{13}C NMR: δ = 14.1 (CH_3), 60.5 (3 CH_2), 12.3, 16.3, 31.2 (CH_2), 7.4, 47.8, 78.4, 82.2 (C).

1-Iodo-3-phenylbicyclo[1.1.1]pentane (8r): From iodobenzene (**7r**) (645 mg, 354 μL, 3.16 mmol), compound **8r**[4a] (179 mg, 21%) was obtained according to GP 2.

1-Iodo-3-(*p*-tolyl)bicyclo[1.1.1]pentane (8s): From 4-iodotoluene (**7s**) (678 mg, 3.11 mmol), compound **8s**[45] (89 mg, 10%) was obtained according to GP 2.

General Procedure (GP 3) for the Lithiation of 3-Substituted 1-Iodobicyclo[1.1.1]pentanes 8: To a 0.3 M solution of LiDBB in THF (50 mL, 15 mmol), a solution of **8** (6 mmol) in THF (10 mL) was added dropwise at –78 °C. After stirring the deep-blue reaction mixture for 1 h at this temp., a 10-fold excess of powdered dry ice was added in a single portion. The mixture was allowed to warm to room temp. and then extracted with 5% $NaHCO_3$ solution (2 × 50 mL). The combined aqueous phases were acidified to pH = 2–3 with conc. HCl at 0 °C, saturated with NaCl, and extracted with Et_2O (4 × 50 mL). The combined organic phases were dried and, after evaporation of the solvent under reduced pressure, purified as specified below.

General Procedure (GP 4) for the Lithiation of 3-Substituted 1-Iodobicyclo[1.1.1]pentanes 8: To a solution of **8** (30 mmol) in Et_2O (100 mL), a 1.5 M solution of *t*BuLi in *n*-pentane (40 mL, 60 mmol) was added over a period of 40 min at −78 °C. After stirring the reaction mixture for 1 h at this temp., the appropriate electrophile was added and the mixture was worked-up under the conditions specified below.

3-Propylbicyclo[1.1.1]pentane-1-carboxylic Acid (10b): From **8b** (17.71 g, 75 mmol), compound **10b** (11.22 g, 97%) was obtained according to GP 4, in almost pure form following work-up as in GP 3. An analytical sample was recrystallized from hexane; m.p. 71–72 °C. – ^1H NMR: δ = 0.89 (t, *J* = 6.7 Hz, 3 H, CH_3), 1.15–1.35 (m, 2 H, CH_2), 1.40 (t, *J* = 7.0 Hz, 2 H, CH_2), 1.90 (s, 6 H, 3 CH_2), 9.65 (s, 1 H, OH). – ^{13}C NMR: δ = 14.2 (CH_3), 51.5 (3 CH_2), 19.5, 33.4 (CH_2), 37.5, 40.2, 176.5 (C). – $C_9H_{14}O_2$ (154.2): calcd. C 70.10, H 9.15; found C 70.04, H 9.07

3-Butylbicyclo[1.1.1]pentane-1-carboxylic Acid (10c): From **8c** (1.06 g, 4.24 mmol), compound **10c**[4a] (430 mg, 60%) was obtained according to GP 3 and subsequent column chromatography (5 g of silica gel, column 12 × 1 cm, hexane/Et_2O, 4:1).

3-Heptylbicyclo[1.1.1]pentane-1-carboxylic Acid (10d): From **8d** (4.27 g, 14.6 mmol), compound **10d** (1.66 g, 54%) was obtained according to GP 3 and subsequent column chromatography (100 g of silica gel, column 20 × 4 cm, hexane/Et_2O, 9:1, gradient Et_2O), R_f = 0.60 (Et_2O); m.p. 42 °C. – IR: $\tilde{\nu}$ = 2957 cm^{-1}, 2913, 2853, 2589, 1704, 1517, 1469, 1425, 1339, 1317, 1287, 1214, 960, 751, 723. – ^1H NMR: δ = 0.89 (t, *J* = 6.6 Hz, 3 H, CH_3), 1.22 (m, 10 H, 5 CH_2), 1.43 (t, *J* = 6.4 Hz, 2 H, CH_2), 1.92 (s, 6 H, 3 CH_2), 10.50 (s, 1 H, OH). – ^{13}C NMR: δ = 14.1 (CH_3), 51.5 (3 CH_2), 22.7, 26.3, 29.6, 29.7, 31.2, 31.8 (CH_2), 37.6, 40.3, 176.7 (C). – $C_{13}H_{22}O_2$ (210.3): calcd. C 74.24, H 10.55; found C 74.16, H 10.70.

3-Octylbicyclo[1.1.1]pentane-1-carboxylic Acid (10e): From **8e** (1.24 g, 4.05 mmol), compound **10e** (410 mg, 45%) was obtained according to GP 3 and subsequent column chromatography (5 g of silica gel, column 12 × 1 cm, hexane/Et_2O, 4:1); m.p. 33–36 °C. – ^1H NMR: δ = 0.88 (t, *J* = 6.6 Hz, 3 H, CH_3), 1.29 (m, 12 H, 6 CH_2), 1.40–1.52 (m, 2 H, CH_2), 1.91 (s, 6 H, 3 CH_2), 10.20 (s, 1 H, OH). – ^{13}C NMR: δ = 14.1 (CH_3), 51.6 (3 CH_2), 22.7, 26.3, 29.3, 29.6, 29.7, 31.2, 31.9 (CH_2), 37.6, 40.4, 176.6 (C). – $C_{14}H_{24}O_2$ (224.3): calcd. C 74.95, H 10.78; found C 74.64, H 10.81.

3-[4-(Tetrahydropyran-2-yloxy)butyl]bicyclo[1.1.1]pentane-1-carboxylic Acid (10h): From **8h** (9.50 g, 27.1 mmol), compound **10h** (4.10 g, 56%) was obtained according to GP 3 in almost pure form as an oil. – ^{1}H NMR: δ = 0.95–1.80 (m, 12 H, 6 CH_2), 1.92 (s, 6 H, 3 CH_2), 3.40–4.35 (m, 4 H, OCH_2), 4.55 (t, *J* = 3.2 Hz, 1 H, OCH).

3-[8-(Tetrahydropyran-2-yloxy)octyl]bicyclo[1.1.1]pentane-1-carboxylic Acid (10i): From **8i** (5.0 g, 12.3 mmol), compound **10i** (2.12 g, 53%) was obtained as an oil according to GP 3 and subsequent filtration with Et_2O through a 1 cm pad of silica gel. – IR: ṽ = 3100 cm^{-1}, 2980, 2930, 2890, 2860, 1719, 1220, 1208, 1192, 1140, 1125, 1040, 1027. – ^{1}H NMR: δ = 1.10–1.32 (m, 10 H, 5 CH_2), 1.35–1.82 (m, 10 H, 5 CH_2), 1.84 (s, 6 H, 3 CH_2), 3.38 (dt, *J* = 9.5, 6.9 Hz, 1 H, OCH_2), 3.45–3.56 (m, 1 H, OCH_2), 3.73 (dt, *J* = 9.5, 6.9 Hz, 1 H, OCH_2), 3.87 (ddd, *J* = 11.4, 7.5, 3.7 Hz, 1 H, OCH_2), 4.55 (t, *J* = 3.2 Hz, 1 H, OCH), 10.68 (s, 1 H, OH). – ^{13}C NMR: δ = 51.4 (3 CH_2), 19.4, 25.4, 26.1, 26.2, 29.3, 29.4, 29.5, 29.6, 29.6, 31.1, 62.1, 67.6 (CH_2), 98.6 (CH), 37.5, 40.2, 175.8 (C). – MS (EI): *m*/*z* (%) = 324 (1) [M$^+$], 323 (4) [M$^+$ – H], 85 (100). – $C_{19}H_{32}O_4$ (324.5): calcd. C 70.33, H 9.94; found C 70.45, H 9.83.

3-(4-Phenylcyclohexyl)bicyclo[1.1.1]pentane-1-carboxylic Acid (10o): From **8o** (5.20 g, 14.76 mmol, 2:1 mixture of *cis* and *trans* isomers), compound **10o** (1.77 g, 44%) was obtained according to GP 3 as an oil. – ^{1}H NMR: δ = 0.80–1.95 (m, 9 H), 1.91 (s, 6 H, 3 CH_2, *trans*), 2.03 (s, 6 H, 3 CH_2, *cis*), 2.44 (m, 1 H, CH, *trans*), 2.56–2.75 (m, 1 H, CH, *cis*), 7.15–7.35 (m, 5 H, Ph), 10.09 (s, 1 H, OH).

2-(3-Propylbicyclo[1.1.1]pent-1-yl)propan-2-ol (11b): To the lithium derivative **9b**, prepared from **8b** (5.10 g, 21.6 mmol) according to GP 4, anhydrous acetone (2.50 g, 3.20 mL, 43 mmol) in Et_2O (10 mL) was added dropwise at –78 °C. The mixture was allowed to warm to room temp. and then washed with brine (2 × 30 mL). The organic phase was dried, the solvent was evaporated, and the residue was separated by preparative GC at 130 °C to give **11b** (1.91 g, 52%); m.p. 34 °C. – IR: ṽ = 3420 cm^{-1}, 2970, 2920, 2870, 1450, 1372, 1266, 1185, 951. – ^{1}H NMR: δ = 0.90 (t, *J* = 7.2 Hz, 3 H, CH_3), 1.14 (s, 6 H, 2 CH_3), 1.23 (s, 1 H, OH), 1.19–1.41 (m, 4 H, 2 CH_2), 1.50 (s, 6 H, 3 CH_2). – ^{13}C NMR: δ = 25.7 (2 CH_3), 14.3 (CH_3), 47.1 (3 CH_2), 19.8, 34.1 (CH_2), 37.2, 46.4, 69.1 (C). – MS (EI): *m*/*z* (%) = 167 (0.1) [M$^+$ – H], 153 (6) [M$^+$ – CH_3], 150 (5) [M$^+$ – H_2O], 135 (51), 121 (100), 107 (70), 59 (84), 49 (99). – $C_{11}H_{20}O$ (168.27): calcd. C 78.51, H 11.98; found C 78.53, H 11.92.

***trans*-1-(3-Butylbicyclo[1.1.1]pent-1-yl)-4-phenylcyclohexanol (11ca):** To the lithium derivative **9c**, prepared from **8c** (2.50 g, 10 mmol) according to GP 4, 4-phenylcyclohexanone (1.74 g, 10 mmol) in Et_2O (20 mL) was added over a period of 15 min at –78 °C. After work-up as described above for **11b**, column chromatography of the residue (150 g of silica gel, column 15 × 5 cm, hexane/Et_2O, 1:1) furnished **11ca** (2.10 g, 70%), R_f = 0.40; m.p. 95 °C (pentane). – IR: ṽ = 3450 cm^{-1}, 3080, 3060, 3025, 2960, 2920, 2870, 1602, 1445, 1276, 1254, 1150, 1138, 988, 960, 760, 700. – ^{1}H NMR: δ = 0.89 (t, *J* = 7.0 Hz, 3 H, CH_3), 0.99 (s, 1 H, OH), 1.16–1.38 (m, 4 H, 2 CH_2), 1.51 (s, 6 H, 3 CH_2), 1.40–1.94 (m, 10 H, 5 CH_2), 2.43 (tt, *J* = 12.3, 3.6 Hz, 1 H, CH), 7.14–7.33 (m, 5 H, Ph). – ^{13}C NMR: δ = 14.1 (CH_3), 46.6 (3 CH_2), 31.6, 33.4 (2 CH_2), 22.9, 28.8, 29.0 (CH_2), 125.9, 126.9 (2 CH), 44.0, 128.3 (CH), 37.4, 46.4, 68.4, 147.4 (C). – MS (EI): *m*/*z* (%): 298 (0.7) [M$^+$], 280 (13) [M$^+$ – H_2O], 149 (59), 91 (100), 55 (51). – $C_{21}H_{30}O$ (298.5): calcd. C 84.51, H 10.13; found C 84.34, H 10.14.

1-Butyl-3-(trimethylsilyl)bicyclo[1.1.1]pentane (11cb): The lithium derivative **9c**, prepared from **8c** (250 mg, 1 mmol) according to GP 4, was quenched with TMSCl (326 mg, 381 μL, 3 mmol) and the reaction mixture was worked-up as described above for **11b**. After evaporation of the solvent, the residue was purified by bulb-to-bulb distillation under reduced pressure to give **11cd** (153 mg, 78%). – IR: ṽ = 2965 cm^{-1}, 2940, 2910, 2875, 1475, 1256, 910, 845. – ^{1}H NMR: δ = 0.08 (s, 9 H, 3 CH_3), 0.87 (t, *J* = 7.0 Hz, 3 H, CH_3), 1.10–1.36 (m, 6 H, 3 CH_2), 1.52 (s, 6 H, 3 CH_2). – ^{13}C NMR: δ = –3.4 (3 CH_3), 14.1 (CH_3), 50.2 (3 CH_2), 22.9, 28.4, 33.6 (CH_2), 29.4, 46.3 (C).

1-[8-(Tetrahydropyran-2-yloxy)octyl]bicyclo[1.1.1]pentane (11i): The lithium derivative **9i**, prepared from **8i** (1.220 g, 3 mmol) according to GP 4, was quenched with MeOH (2 mL). After work-up as described above for **11b** followed by column chromatography of the residue (30 g of silica gel, column 15 × 3 cm, hexane/Et_2O, 9:1), **11i** (784 mg, 93%) was obtained as an oil, R_f = 0.25. – ^{1}H NMR: δ = 1.10–1.39 (m, 10 H, 5 CH_2), 1.43–1.90 (m, 10 H, 5 CH_2), 1.58 (s, 6 H, 3 CH_2), 2.40 (s, 1 H, CH), 3.36 (dt, *J* = 9.5, 6.6 Hz, 1 H, OCH_2), 3.42–3.52 (m, 1 H, OCH_2), 3.70 (dt, *J* = 9.5, 6.9 Hz, 1 H, OCH_2), 3.84 (ddd, *J* = 11.4, 7.5, 3.7 Hz, 1 H, OCH_2), 4.55 (t, *J* = 3.2 Hz, 1 H, OCH). – ^{13}C NMR: δ = 50.3 (3 CH_2), 19.6, 25.5, 26.2, 26.5, 29.4, 29.5, 29.7, 30.7, 32.5, 52.3, 62.2, 67.6 (CH_2), 27.3, 98.7 (CH), 45.8 (C). – $C_{18}H_{32}O_2$ (280.4): calcd. C 77.09, H 11.50; found C 76.93, H 11.45.

1-(4-Fluorobenzoyl)-3-propylbicyclo[1.1.1]pentane (12b): To the lithium derivative **9b**, prepared from **8b** (427 mg, 1.8 mmol) according to GP 4, a solution of 4-fluorobenzonitrile (247 mg, 2.0 mmol) in anhydrous Et_2O (5 mL) was added dropwise at –78 °C. After stirring the reaction mixture for 1 h at room temp., 5% aq. HCl (2 mL) was added and stirring was continued for a further 1 h at this temp. The organic phase was subsequently washed with 5% $NaHCO_3$ solution and brine (10 mL each), dried, and concentrated. Column chromatography of the residue (50 g of silica gel, column 15 × 3 cm, hexane/Et_2O, 9:1) furnished **12b** (327 mg, 78%) as an oil, R_f = 0.35. – IR: ṽ = 3075 cm^{-1}, 2970, 2920, 2880, 1669, 1602, 1508, 1359, 1241, 1230, 1207, 1158, 935, 855, 620. – ^{1}H NMR: δ = 0.91 (t, *J* = 7.2 Hz, 3 H, CH_3), 1.21–1.40 (m, 2 H, CH_2), 1.40–1.53 (m, 2 H, CH_2), 2.09 (s, 6 H, 3 CH_2), 7.06 (tt, *J* = 8.6, 2.4 Hz, 2 H, C_6H_4), 8.03 (m, 2 H, C_6H_4). – ^{13}C NMR: δ = 14.2 (CH_3), 53.4 (3 CH_2), 19.5, 33.5 (CH_2), 115.4 (d, *J* = 21.7 Hz), 131.5 (d, *J* = 9.3 Hz) (2 CH), 40.8, 44.0, 133.0, 165.4 (d, *J* = 254.3 Hz), 196.19 (C).

1-(3-Octylbicyclo[1.1.1]pent-1-yl)propan-1-one (12e): To the lithium derivative **9e**, prepared from **8e** (1.07 g, 3.49 mmol) according to GP 4, a solution of propionyl chloride (1.02 g, 956 μL, 11 mmol) in Et_2O (5 mL) was added dropwise at –78 °C. The mixture was allowed to warm to room temp. and then the reaction was quenched with MeOH (5 mL). The resulting mixture was washed with 5% $NaHCO_3$ solution and brine (15 mL each), dried, and concentrated. Column chromatography of the residue (40 g of silica gel, column 15 × 3 cm, hexane/Et_2O, 9:1) furnished **12e** (620 mg, 75%) as an oil, R_f = 0.38. – ^{1}H NMR: δ = 0.89 (t, *J* = 6.8 Hz, 3 H, CH_3), 1.02 (t, *J* = 7.7 Hz, 3 H, CH_3), 1.28 (m, 12 H, 6 CH_2), 1.44 (t, *J* = 6.8 Hz, 2 H, CH_2), 1.85 (s, 6 H, 3 CH_2), 2.43 (q, *J* = 7.7 Hz, 2 H, CH_2).

1-{3-[4-(Tetrahydropyran-2-yloxy)butyl]bicyclo[1.1.1]pent-1-yl}butan-1-one (12h): Compound **12h** was prepared from **8h** (350 mg, 1 mmol) and butyryl chloride (217 mg, 208 μL, 2 mmol) as described in the preceding preparation. Column chromatography (20 g of silica gel, column 15 × 2 cm, hexane/Et_2O, 4:1) furnished **12h** (233 mg, 79%) as an oil, R_f = 0.30. – ^{1}H NMR: δ = 0.90 (t, *J* = 7.2 Hz, 3 H, CH_3), 1.22–1.95 (m, 14 H, 7 CH_2), 1.85 (s, 6 H, 3 CH_2), 2.39 (t, *J* = 7.1 Hz, 2 H, CH_2), 3.37 (dt, *J* = 9.5, 6.9 Hz,

1 H, OCH_2), 3.44–3.55 (m, 1 H, OCH_2), 3.73 (dt, J = 9.5, 6.9 Hz, 1 H, OCH_2), 3.87 (ddd, J = 11.4, 7.5, 3.8 Hz, 1 H, OCH_2), 4.58 (t, J = 3.2 Hz, 1 H, OCH).

1-[3-(4-Phenylcyclohex-1-yl)bicyclo[1.1.1]pent-1-yl]propan-1-one (12o): Compound **12o** was prepared from **8o** (700 mg, 2 mmol, 2:1 mixture of *cis* and *trans* isomers) and propionyl chloride (370 mg, 348 μL, 4 mmol) as described for **12e**. Column chromatography (20 g of silica gel, column 15 × 3 cm, hexane/Et_2O, 9:1) furnished **12o** (416 mg, 74%) as an oil, R_f = 0.32. – ^{1}H NMR: δ = 0.91 (t, J = 7.4 Hz, 3 H, CH_3), 1.02–1.84 (m, 9 H), 1.85 (s, 6 H, 3 CH_2, *trans*), 1.97 (s, 6 H, 3 CH_2, *cis*), 2.38–2.48 (m, 1 H, CH, *trans*), 2.44 (t, J = 7.3 Hz, 2 H, CH_2), 2.53–2.72 (m, 1 H, CH, *cis*), 7.15–7.35 (m, 5 H, Ph).

General Procedure (GP 5) for the Preparation of 3-Arylbicyclo[1.1.1]pent-1-ylmagnesium Bromides 14a–e: A solution of the appropriate arylmagnesium bromide **13** [prepared from the corresponding aryl bromide (16 mmol) and magnesium turnings (401 mg, 16.5 mmol) in anhydrous Et_2O (**13a–d**) or THF (**13e**) (20 mL)] was added to a 0.3 M solution of **2** in Et_2O (60 mL, 18 mmol). The resulting mixture was stirred under reflux for several days (see Table 3) with GC monitoring. The solution was then carefully concentrated under reduced pressure and, unless otherwise specified, the residue was taken up in anhydrous Et_2O (15 mL).

1-Phenylbicyclo[1.1.1]pentane (15a): A solution of **14a** [prepared from bromobenzene (1.88 g, 1.26 mL, 12 mmol), Mg turnings (300 mg, 12.3 mmol), and **2** (13.5 mmol, 40 mL of a 0.3 M solution) according to GP 5] was carefully treated with H_2O (10 mL) at 0 °C. The organic phase was then washed with further H_2O (2 × 10 mL), dried, and concentrated. **15a**[46] (1.37 g, 80%) was obtained after preparative GC separation of the residue.

1-(4-Propylphenyl)bicyclo[1.1.1]pentane (15ba): This compound was obtained in analogy to the previous preparation, starting from **14b** [prepared from 4-bromopropylbenzene (1.20 g, 6 mmol) and **2** (6.75 mmol, 22.5 mL of a 0.3 M solution) according to GP 5]. Column chromatography (50 g of silica gel, column 15 × 3 cm, PE) gave **15ba** (1.11 g, 99%) as an oil, R_f = 0.50. – ^{1}H NMR: δ = 0.93 (t, J = 7.4 Hz, 3 H, CH_3), 1.62 (sext., J = 7.4 Hz, 2 H, CH_2), 2.06 (s, 6 H, 3 CH_2), 2.52 (s, 1 H, CH), 2.55 (t, J = 7.4 Hz, 2 H, CH_2), 7.11 (m, 4 H, C_6H_4). – ^{13}C NMR: δ = 13.9 (CH_3), 52.2 (3 CH_2), 24.7, 37.8 (CH_2), 125.8, 128.2 (2 CH), 26.6 (CH), 47.0, 139.0, 140.7 (C).

1-(4-Fluorobenzoyl)-3-(4-propylphenyl)bicyclo[1.1.1]pentane (15bb): To a solution of **14b** [prepared from 4-bromopropylbenzene (757 mg, 3.8 mmol) and **2** (4.28 mmol, 14.25 mL of a 0.3 M solution) according to GP 5], a solution of 4-fluorobenzonitrile (484 mg, 4 mmol) in Et_2O (5 mL) was added dropwise at 0 °C. After stirring the reaction mixture for 48 h under reflux, 5% aq. HCl (2 mL) was added and stirring was continued for a further 10 h at room temp. The organic phase was washed with 5% aq. $NaHCO_3$ solution and brine (10 mL each), dried, and concentrated. After column chromatography (30 g of silica gel, column 25 × 2 cm, hexane/Et_2O, 9:1), **15bb** (362 mg, 31%) was obtained, R_f = 0.35; m.p. 99 °C. – IR: $\tilde{\nu}$ = 3070 cm^{-1}, 3050, 3030, 2970, 2960, 2935, 2915, 2875, 1658, 1593, 1503, 1410, 1358, 1306, 1298, 1239, 1226, 1211, 1154, 880, 858, 818, 790, 618. – ^{1}H NMR: δ = 0.94 (t, J = 7.4 Hz, 3 H, CH_3), 1.64 (sext., J = 7.4 Hz, 2 H, CH_2), 2.53 (s, 6 H, 3 CH_2), 2.58 (t, J = 7.2 Hz, 2 H, CH_2), 7.08–7.25 (m, 6 H, C_6H_4), 8.03–8.14 (m, 2 H, C_6H_4). – ^{13}C NMR: δ = 13.7 (CH_3), 55.1 (3 CH_2), 24.5, 37.7 (CH_2), 115.5 (d, J = 22.0 Hz), 125.9, 128.4, 131.5 (d, J = 9.0 Hz) (2 CH), 42.2, 43.1, 133.0, 136.9, 141.4, 165.5 (d, J = 255.0 Hz), 196.0 (C). – MS (EI): m/z (%) = 308 (23) [M^+], 265 (24) [$M^+ - C_3H_7$], 185 (25), 143 (37), 123 (100), 95 (22). – $C_{21}H_{21}FO$ (308.4): calcd. C 81.79, H 6.86; found C 81.69, H 6.73.

1-(4-Chlorobenzoyl)-3-(4-propylphenyl)bicyclo[1.1.1]pentane (15bc): From 4-chlorobenzonitrile (550 mg, 4 mmol) and **14b** [prepared from the same quantities of its precursors as in the preceding preparation], **15bc** (602 mg, 49%) was obtained following the same procedure as above, R_f = 0.38; m.p. 98 °C. – IR: $\tilde{\nu}$ = 3095 cm^{-1}, 3080, 3035, 2980, 2960, 2920, 2880, 1666, 1588, 1404, 1362, 1303, 1295, 1212, 1092, 880, 861, 791. – ^{1}H NMR: δ = 0.93 (t, J = 7.4 Hz, 3 H, CH_3), 1.63 (sext., J = 7.4 Hz, 2 H, CH_2), 2.52 (s, 6 H, 3 CH_2), 2.56 (t, J = 7.2 Hz, 2 H, CH_2), 7.13 (d, J = 8.2 Hz, 2 H, C_6H_4), 7.17 (d, J = 8.2 Hz, 2 H, C_6H_4), 7.39 (dd, J = 8.6, 2.0 Hz, 2 H, C_6H_4), 7.97 (dd, J = 8.6, 2.0 Hz, 2 H, C_6H_4). – ^{13}C NMR: δ = 16.7 (CH_3), 55.0 (3 CH_2), 24.4, 37.6 (CH_2), 125.8, 128.3, 128.7, 130.2 (2 CH), 42.2, 43.0, 134.9, 136.8, 139.1, 141.3, 196.2 (C). – MS (EI): m/z (%) = 326/324 (9:24) [M^+], 295 (15), 281 (22), 185 (37), 113 (58), 109 (100). – $C_{21}H_{21}ClO$ (324.8): calcd. C 77.64, H 6.52; found C 77.52, H 6.63.

1-Chloro-3-(4-propylphenyl)bicyclo[1.1.1]pentane (15bd): To a suspension of *N*-chlorosuccinimide (950 mg, 7.1 mmol) in anhydrous THF (5 mL), a solution of **14b** [prepared from 4-bromopropylbenzene (1.195 g, 6 mmol) according to GP 5] in anhydrous THF (5 mL) was added dropwise. After stirring for 15 h at room temp. and then for 7 h under reflux, the reaction mixture was diluted with pentane (30 mL) and washed with 5% aq. HCl, 5% NaOH solution, and water (20 mL each), dried, and concentrated. Column chromatography of the residue (50 g of silica gel, column 15 × 3 cm, PE) gave **15ba** (277 mg, 24%), R_f = 0.50, and **15bd** (320 mg, 24%), R_f = 0.34; m.p. 42 °C. – ^{1}H NMR: δ = 0.93 (t, J = 7.3 Hz, 3 H, CH_3), 1.62 (sext., J = 7.3 Hz, 2 H, CH_2), 2.41 (s, 6 H, 3 CH_2), 2.55 (t, J = 7.4 Hz, 2 H, CH_2), 7.07–7.14 (m, 4 H, C_6H_4). – ^{13}C NMR: δ = 13.8 (CH_3), 58.9 (3 CH_2), 24.6, 37.7 (CH_2), 126.2, 128.5 (2 CH), 39.8, 48.9, 134.7, 141.5 (C). – MS (EI): m/z (%) = 222/220 (1:3) [M^+], 185 (100) [$M^+ - Cl$], 179/177 (17:54) [$M^+ - C_3H_7$], 144 (56).

1-Bromo-3-(4-butylphenyl)bicyclo[1.1.1]pentane (15cb): To a solution of **14c** [prepared from 4-bromobutylbenzene (3.197 g, 2.65 mL, 15 mmol) and **2** (16.9 mmol, 56.3 mL of a 0.3 M solution) according to GP 5], a solution of Br_2 (2.397 g, 0.77 mL, 15 mmol) in anhydrous THF (10 mL) was added dropwise at 0 °C. After stirring the reaction mixture for 1 h at room temp., it was treated with satd. NH_4Cl solution (10 mL). The layers were separated and the organic phase was washed with 0.1 M $Na_2S_2O_3$ solution and water (20 mL each), dried, and concentrated. Column chromatography (150 g of silica gel, column 15 × 5 cm, PE) furnished **15cb** (1.54 g, 36%) as an oil, R_f = 0.26. – ^{1}H NMR: δ = 0.91 (t, J = 7.5 Hz, 3 H, CH_3), 1.33 (sext., J = 7.8 Hz, 2 H, CH_2), 1.57 (quint, J = 7.8 Hz, 2 H, CH_2), 2.50 (s, 6 H, 3 CH_2), 2.58 (t, J = 7.7 Hz, 2 H, CH_2), 7.08 (d, J = 8.0 Hz, 2 H, C_6H_4), 7.12 (d, J = 8.0 Hz, 2 H, C_6H_4). – ^{13}C NMR: δ = 13.9 (CH_3), 60.1 (3 CH_2), 22.3, 33.6, 35.2 (CH_2), 126.0, 128.4 (2 CH), 36.8, 43.4, 134.9, 141.7 (C).

1-Allyl-3-(4-fluorophenyl)bicyclo[1.1.1]pentane (15db): At 0 °C, a solution of **14d** [prepared from 4-bromofluorobenzene (1.23 g, 0.77 mL, 7 mmol) according to GP 5] in Et_2O (10 mL) was added dropwise to a solution of allyl bromide (1.21 g, 865 μL, 10 mmol) in anhydrous Et_2O (10 mL). After stirring under reflux for 6 h, the mixture was treated with H_2O (5 mL). The layers were separated and the organic phase was washed with 5% aq. HCl, 5% $NaHCO_3$ solution, and H_2O (10 mL each), dried, and concentrated. Separation by preparative GC gave **15db** (495 mg, 35%) as an oil. – IR: $\tilde{\nu}$ = 3075 cm^{-1}, 3045, 2965, 2905, 2870, 2830, 1643, 1606, 1520,

1504, 1410, 1296, 1267, 1220, 1153, 992, 916, 840, 812. – ^{1}H NMR: δ = 1.87 (s, 6 H, 3 CH_2), 2.29 (d, J = 7.2 Hz, 2 H, CH_2), 5.02 (d, J = 10.4 Hz, 1 H, =CH_2), 5.03 (d, J = 16.8 Hz, 1 H, =CH_2), 5.77 (ddt, J = 16.8, 10.4, 7.2 Hz, 1 H, =CH), 6.95 (tt, J = 8.8, 2.2 Hz, 2 H, C_6H_4), 7.14 (ddt, J = 8.8, 5.6, 2.2 Hz, 2 H, C_6H_4). – ^{13}C NMR: δ = 52.2 (3 CH_2), 36.6, 115.9 (CH_2), 114.8 (d, J = 21.0 Hz), 127.5 (d, J = 8.0 Hz) (2 CH), 135.4 (CH), 37.8, 41.8, 137.3 (d, J = 3.0 Hz), 161.7 (d, J = 244.0 Hz) (C). – $C_{14}H_{15}F$ (202.26): calcd. C 83.13, H 7.48; found C 83.22, H 7.45.

1-(4′-Ethylbiphenyl-4-yl)bicyclo[1.1.1]pentane (15e): Work-up of the reaction mixture from the attempted preparation of **14e** starting from 4-bromo-4′-ethylbiphenyl (**22f**) (262 mg, 1 mmol) and **2** (1.13 mmol, 3.8 mL of a 0.3 M solution) as described above for **15a** and subsequent column chromatography (20 g of silica gel, column 15 × 2 cm, hexane) gave **15e** (32 mg, 13%) as an oil, R_f = 0.45. – ^{1}H NMR: δ = 1.31 (t, J = 7.3 Hz, 3 H, CH_3), 2.11 (s, 6 H, 3 CH_2), 2.45 (s, 1 H, CH), 2.71 (t, J = 7.3 Hz, 2 H, CH_2), 7.20–7.35 (m, 4 H, C_6H_4), 7.35–7.65 (m, 4 H, C_6H_4).

General Procedure (GP 6) for the Preparation of 3-Alkylbicyclo-[1.1.1]pent-1-ylzinc Chlorides 19: To a solution of the appropriate lithium derivative **9**, prepared from **8** according to GP 4, a 2.0 M solution of $ZnCl_2$ in anhydrous THF (1.2 mL, 2.4 mmol, prepared from $ZnCl_2 \cdot THF$[21]) was added dropwise at –78 °C. The reaction mixture was then allowed to warm to room temp. and stirred for 1 h. After careful evaporation of the solvent, the residue was taken up in anhydrous THF (5 mL) unless specified otherwise.

General Procedure (GP 7) for Cross-Coupling under Transition Metal Catalysis: A solution of the appropriate bicyclo[1.1.1]pentylmagnesium or -zinc halide (**14** or **19**, respectively; 0.5–4 mmol, prepared according to GP 5 or GP 6) in Et_2O (THF) was cannulated in one portion into a mixture of the aryl (alkenyl) halide or triflate (1 mmol) and the catalyst (2–10 mol-%) in anhydrous Et_2O or THF (5 mL) at ambient temp. A deep-green (sometimes deep-red) colour appeared immediately. After stirring for 10–60 min, the colour changed to yellow or brown. The mixture was stirred for a further 2–72 h at this temp. (see Table 4–7), then treated with H_2O (1 mL), and filtered through Celite (unless specified otherwise). After evaporation of the solvent, the residue was separated by column chromatography. In the preparations of **23ac**,**ff**,**fg**,**aja**,**ajb**, the solvent (THF) was carefully evaporated under reduced pressure and replaced by hexane (10 mL) prior to treatment with water.

1,3-Diphenylbicyclo[1.1.1]pentane (17aa): To a solution of **14a** [prepared from PhBr (628 mg, 421 μL, 4 mmol) according to GP 5], a 2.0 M solution of $ZnCl_2$ in THF (3 mL, 6 mmol) was added at 0 °C. After stirring for 1 h at room temp., the suspension was added to a mixture of PhBr (628 mg, 421 μL, 4 mmol) and $Pd(PPh_3)_4$ (92 mg, 0.08 mmol) in THF (5 mL) and the resulting mixture was stirred for a further 24 h. Standard work-up followed by column chromatography (40 g of silica gel, column 14 × 3 cm, hexane, R_f = 0.25) gave 211 mg of a mixture containing **17aa** (70%; 15% yield) and 3,3′-diphenyl(bis-1,1′-bicyclo[1.1.1]pentyl) (**16a**) (30%; 13% yield). A sample of pure **16a**[4a] was obtained by twofold recrystallization from MeOH. Evaporation of the solvent from the mother liquor followed by twofold recrystallization of the residue from pentane gave a sample of pure **17aa**; m.p. 100 °C. – IR: ṽ = 3080 cm^{-1}, 3060, 3030, 2970, 2910, 2870, 1605, 1496, 1448, 1308, 1189, 1030, 758, 702. – ^{1}H NMR: δ = 2.32 (s, 6 H, 3 CH_2), 7.19–7.39 (m, 10 H, 2 Ph). – ^{13}C NMR: δ = 54.0 (3 CH_2), 126.1, 126.5 (4 CH), 128.2 (2 CH), 40.8, 140.9 (2 C). – MS (EI): m/z (%) = 220 (43) [M^+], 219 (100) [M^+ – H], 205 (16) [M^+ – H – CH_2], 143 (21) [M^+ – C_6H_5], 129 (18), 103 (30), 77 (26) [$C_6H_5^+$]. – $C_{17}H_{16}$ (220.3): calcd. C 92.68, H 7.32; found C 92.76, H 7.34.

1-(4-Fluorophenyl)-3-phenylbicyclo[1.1.1]pentane (17ab): From **14a** [prepared from PhBr (628 mg, 421 μL, 4 mmol) according to GP 5], 4-bromofluorobenzene (175 mg, 110 μL, 1 mmol), and $NiCl_2$dppe (59 mg, 0.11 mmol) in Et_2O, **17ab** (90 mg, 38%) was obtained according to GP 7 and subsequent column chromatography (25 g of silica gel, column 16 × 2 cm, PE), R_f = 0.25; m.p. 120 °C. – IR: ṽ = 3040 cm^{-1}, 2970, 2915, 2875, 1602, 1505, 1450, 1310, 1220, 1192, 1161, 845, 800, 751, 706. – ^{1}H NMR: δ = 2.31 (s, 6 H, 3 CH_2), 7.00 (tt, J = 8.8, 2.0 Hz, 2 H, C_6H_4), 7.13–7.36 (m, 7 H, Ar). – ^{13}C NMR: δ = 54.1 (3 CH_2), 114.9 (d, J = 21.4 Hz), 126.1, 126.5, 127.0 (d, J = 7.9 Hz) (2 CH), 128.2 (CH), 40.3, 40.7, 136.8, 140.7, 161.7 (d, J = 244.6 Hz) (C). – MS (EI): m/z (%) = 238 (90) [M^+], 237 (50) [M^+ – H], 223 (67) [M^+ – H – CH_2], 209 (36), 203 (31), 196 (100), 172 (33), 170 (49). – $C_{17}H_{25}F$ (238.3): calcd. C 85.68, H 6.35; found C 85.83, H 6.39.

1-Phenyl-3-(*p*-tolyl)bicyclo[1.1.1]pentane (17ac): From **14a** [prepared from PhBr (628 mg, 421 μL, 4 mmol) according to GP 5], 4-iodotoluene (218 mg, 1 mmol), and $NiCl_2$dppe (47 mg, 0.09 mmol) in Et_2O, **17ac** (50 mg, 21%) was obtained according to GP 7 and subsequent column chromatography (50 g of silica gel, column 15 × 3 cm, PE) as an oil, R_f = 0.27. – ^{1}H NMR: δ = 2.31 (s, 6 H, 3 CH_2), 2.35 (s, 3 H, CH_3), 7.10–7.37 (m, 9 H, Ar). – ^{13}C NMR: δ = 21.1 (CH_3), 54.0 (3 CH_2), 126.0, 126.1, 126.4, 128.2 (2 CH), 128.9 (CH), 40.6, 40.8, 136.1, 138.0, 141.0 (C).

1-Phenyl-3-(3-pyridyl)bicyclo[1.1.1]pentane (17ad): From **14a** [prepared from PhBr (628 mg, 421 μL, 4 mmol) according to GP 5], 3-iodopyridine (210 mg, 1.02 mmol), and $NiCl_2$dppe (60 mg, 0.11 mmol) in Et_2O, **17ad** (93 mg, 41%) was obtained according to GP 7 and subsequent column chromatography (20 g of silica gel, column 15 × 2 cm, PE), R_f = 0.22. – ^{1}H NMR: δ = 2.39 (s, 6 H, 3 CH_2), 7.19–7.39 (m, 6 H, Ar), 7.58 (dt, J = 7.7, 1.8 Hz, 1 H, Ar), 8.49 (m, 1 H, Ar), 8.56 (m, 1 H, Ar). – ^{13}C NMR: δ = 54.0 (3 CH_2), 123.0, 126.1, 126.7, 128.2, 133.7, 147.9, 148.1 (CH), 39.0, 41.5, 136.0, 140.4 (C). – MS (EI): m/z (%) = 221 (7) [M^+], 220 (18) [M^+ – H], 206 (13) [M^+ – H – CH_2], 103 (28), 91 (25) [$C_7H_7^+$], 77 (100) [$C_6H_5^+$].

2-(3-Phenylbicyclo[1.1.1]pent-1-yl)pyrimidine (17ae): From **14a** [prepared from PhBr (628 mg, 421 μL, 4 mmol) according to GP 5 and taken up in THF (4 mL)], 2-bromopyrimidine (318 mg, 2 mmol), and $PdCl_2$(dppf) (29 mg, 0.04 mmol) in THF (5 mL), **17ae** (271 mg, 61%) was obtained according to GP 7 and subsequent column chromatography (20 g of silica gel, column 15 × 2 cm, PE/Et_2O, 4:1), R_f = 0.18; m.p. 111 °C. – ^{1}H NMR: δ = 2.50 (s, 6 H, 3 CH_2), 7.18 (t, J = 5.0 Hz, 1 H, Ar), 7.21–7.39 (m, 5 H, Ar), 8.73 (d, J = 5.0 Hz, 2 H, Ar). – ^{13}C NMR: δ = 53.9 (3 CH_2), 120.0, 126.2, 126.7, 128.5, 157.1 (CH), 41.3, 42.0, 140.5, 168.1 (C). – MS (EI): m/z (%) = 222 (28) [M^+], 221 (100) [M^+ – H], 207 (42) [M^+ – H – CH_2], 145 (19), 131 (18), 77 (19) [$C_6H_5^+$]. – $C_{15}H_{14}N_2$ (222.28): calcd. C 81.05, H 6.35, N 12.60; found C 80.96, H 6.45, N 12.58.

1-(Cycloocten-1-yl)-3-phenylbicyclo[1.1.1]pentane (17af): From **14a** [prepared from PhBr (330 mg, 221 μL, 2.1 mmol) according to GP 5 and taken up in THF (4 mL)], 1-bromocyclooctene (378 mg, 2 mmol), and $PdCl_2$(dppf) (20 mg, 0.027 mmol) in THF, **17af** (256 mg, 50%) was obtained according to GP 7 and subsequent column chromatography (20 g of silica gel, column 15 × 2 cm, PE) as an oil, R_f = 0.42. – ^{1}H NMR: δ = 1.39–1.59 (m, 8 H, 4 CH_2), 2.03 (s, 6 H, 3 CH_2), 2.06–2.25 (m, 4 H, 2 CH_2), 5.45 (t, J = 6.1 Hz, 1 H, =CH), 7.10–7.32 (m, 5 H, Ph). – ^{13}C NMR: δ = 52.7 (3 CH_2), 26.0, 26.1, 26.2, 26.6, 29.3, 29.8 (CH_2), 124.2, 126.2, 126.2, 128.1 (CH), 40.6, 42.7, 139.6, 141.5 (C).

(*E*)-β-(3-Phenylbicyclo[1.1.1]pent-1-yl)styrene (17ag): From **14a** [prepared from PhBr (330 mg, 221 μL, 2.1 mmol) according to GP

5 and taken up in THF (4 mL)], (*E*)-2-bromostyrene (366 mg, 2 mmol), and $PdCl_2$(dppf) (29 mg, 0.04 mmol) in THF, **17ag** (376 mg, 76%) was obtained according to GP 7 and subsequent column chromatography (20 g of silica gel, column 15 × 2 cm, PE), R_f = 0.32; m.p. 65 °C. – ^{1}H NMR: δ = 2.13 (s, 6 H, 3 CH_2), 6.38 (m, 2 H, CH=CH), 7.10–7.39 (m, 10 H, 2 Ph). – ^{13}C NMR: δ = 53.7 (3 CH_2), 126.0, 126.1, 126.4, 127.2, 128.1, 128.5, 129.0, 130.5 (CH), 39.8, 41.8, 137.1, 141.0 (C). – MS (EI): *m*/*z* (%) = 246 (6) [M^+], 245 (29) [M^+ – H], 215 (20), 153 (39), 141 (71), 128 (100). – $C_{19}H_{18}$ (246.3): calcd. C 92.64, H 7.36; found C 92.52, H 7.50.

1-(4-Fluorophenyl)-3-(4-propylphenyl)bicyclo[1.1.1]pentane (17ba): From **14b** [prepared from 4-bromopropylbenzene (1.20 g, 6 mmol) according to GP 5], 4-bromofluorobenzene (1.05 g, 659 µL, 6 mmol), and $NiCl_2(PPh_3)_2$ (196 mg, 0.3 mmol) in Et_2O, **17ba** (157 mg, 9%) was obtained according to GP 7 and subsequent column chromatography (60 g of silica gel, column 20 × 3 cm, PE) followed by recrystallization from MeOH, R_f = 0.21; m.p. 66 °C. – IR: $\tilde{\nu}$ = 3055 cm^{-1}, 3030, 2970, 2910, 2875, 1603, 1516, 1307, 1221, 1161, 848, 811. – ^{1}H NMR: δ = 0.95 (t, *J* = 7.4 Hz, 3 H, CH_3), 1.64 (sext., *J* = 7.4 Hz, 2 H, CH_2), 2.29 (s, 6 H, 3 CH_2), 2.59 (t, *J* = 7.4 Hz, 2 H, CH_2), 7.00 (t, *J* = 8.8 Hz, 2 H, C_6H_4), 7.10–7.26 (m, 6 H, C_6H_4). – ^{13}C NMR: δ = 13.8 (CH_3), 54.2 (3 CH_2), 24.6, 37.8 (CH_2), 115.0 (d, *J* = 21.3 Hz), 126.0, 127.7 (d, *J* = 8.2 Hz), 128.3 (2 CH), 40.3, 40.6, 137.0 (d, *J* = 3.0 Hz), 138.1, 141.0, 161.8 (d, *J* = 244.1 Hz) (C). – MS (EI): *m*/*z* (%) = 280 (17) [M^+], 279 (35) [M^+ – H], 238 (30), 237 (100) [M^+ – C_3H_7], 109 (54), 91 (36) [$C_7H_7^+$]. – $C_{20}H_{21}F$ (280.4): calcd. C 85.67, H 7.55; found C 85.79, H 7.47.

1-(4-Propylphenyl)-3-[4-(trifluoromethyl)phenyl]bicyclo[1.1.1]-pentane (17bb): From **14b** [prepared from 4-bromopropylbenzene (1.20 g, 6 mmol) according to GP 5], 4-bromobenzotrifluoride (1.35 g, 840 µL, 6 mmol), and $NiCl_2(PPh_3)_2$ (227 mg, 0.35 mmol) in Et_2O, **17bb** (122 mg, 6%) was obtained according to GP 7 and subsequent column chromatography (100 g of silica gel, column 20 × 4 cm, PE) followed by recrystallization from MeOH, R_f = 0.31; m.p. 95 °C. – ^{1}H NMR: δ = 0.96 (t, *J* = 7.4 Hz, 3 H, CH_3), 1.65 (sext., *J* = 7.5 Hz, 2 H, CH_2), 2.32 (s, 6 H, 3 CH_2), 2.60 (t, *J* = 7.6 Hz, 2 H, CH_2), 7.13 (d, *J* = 8.2 Hz, 2 H, C_6H_4), 7.21 (d, *J* = 8.2 Hz, 2 H, C_6H_4), 7.28 (d, *J* = 8.4 Hz, 2 H, C_6H_4), 7.57 (d, *J* = 8.4 Hz, 2 H, C_6H_4). – ^{13}C NMR: δ = 13.9 (CH_3), 54.2 (3 CH_2), 24.7, 37.8 (CH_2), 125.1 (q, *J* = 3.8 Hz), 126.0, 126.5, 128.4 (2 CH), 40.5, 40.8, 124.3 (q, *J* = 271.7 Hz), 128.7 (q, *J* = 32.5 Hz), 137.7, 141.2, 145.0 (q, *J* = 1.1 Hz) (C). – MS (EI): *m*/*z* (%) = 330 (12) [M^+], 329 (13) [M^+ – H], 288 (19), 287 (100) [M^+ – C_3H_7], 159 (16), 115 (18), 91 (16) [$C_7H_7^+$]. – $C_{21}H_{21}F_3$ (330.4): calcd. C 76.34, H 6.41; found C 76.43, H 6.47.

1-Phenyl-3-propylbicyclo[1.1.1]pentane (20ba): From **19b** (1 mmol), prepared according to GP 6, PhI (204 mg, 112 µL, 1 mmol), and $PdCl_2$(dppf) (37 mg, 0.05 mmol) in THF, **20ba** (147 mg, 79%) was obtained according to GP 7 and subsequent column chromatography (20 g of silica gel, column 15 × 2 cm, pentane) as an oil, R_f = 0.52. – IR: $\tilde{\nu}$ = 3075 cm^{-1}, 3040, 2970, 2920, 2885, 2880, 1620, 1453, 1386, 1304, 1272, 1168, 754, 705. – ^{1}H NMR: δ = 0.94 (t, *J* = 7.1 Hz, 3 H, CH_3), 1.25–1.42 (m, 2 H, CH_2), 1.44–1.54 (m, 2 H, CH_2), 1.89 (s, 6 H, 3 CH_2), 7.12–7.32 (m, 5 H, Ph). – ^{13}C NMR: δ = 14.4 (CH_3), 52.2 (3 CH_2), 19.9, 34.0 (CH_2), 126.0, 126.1 (2 CH), 128.0 (CH), 38.9, 41.5, 141.7 (C). – MS (EI): *m*/*z* (%) = 186 (2) [M^+], 143 (29) [M^+ – C_3H_7], 98 (45), 91 (36), 41 (100).

1-Propyl-3-(*p*-tolyl)bicyclo[1.1.1]pentane (20bb): From **19b** (1 mmol), prepared according to GP 6, 4-iodotoluene (109 mg, 0.5 mmol), and $PdCl_2$(dppf) (8 mg, 0.011 mmol) in THF, **20bb** (84 mg, 84%) was obtained according to GP 7 and subsequent column chromatography (20 g of silica gel, column 14 × 2 cm, pentane) as an oil, R_f = 0.53. – ^{1}H NMR: δ = 0.91 (t, *J* = 7.0 Hz, 3 H, CH_3), 1.22–1.42 (m, 2 H, CH_2), 1.44–1.53 (m, 2 H, CH_2), 1.84 (s, 6 H, 3 CH_2), 2.30 (s, 3 H, CH_3), 7.07 (s, 4 H, C_6H_4). – ^{13}C NMR: δ = 14.4, 21.1 (CH_3), 52.2 (3 CH_2), 19.9, 34.0 (CH_2), 125.9, 128.7 (2 CH), 38.9, 41.3, 135.6, 138.7 (C). – MS (EI): *m*/*z* (%) = 200 (1) [M^+], 185 (10) [M^+ – CH_3], 171 (10) [M^+ – C_2H_5], 157 (100). In an analogous coupling, from **19b** (3 mmol), 4-iodotoluene (438 mg, 2 mmol), and $Pd(PPh_3)_4$ (47 mg, 0.04 mmol) in THF, **20bb** (111 mg, 28%) and 3,3′-dipropyl(bis-1,1′-bicyclo[1.1.1]pentyl) (**16b**) (39 mg, 12%) were obtained according to GP 7 and subsequent column chromatography (25 g of silica gel, column 18 × 2 cm, pentane), R_f = 0.78. – ^{1}H NMR: δ = 0.88 (t, *J* = 7.2 Hz, 6 H, 2 CH_3), 1.18–1.43 (m, 8 H, 4 CH_2), 1.37 (s, 12 H, 6 CH_2). – ^{13}C NMR: δ = 14.4 (2 CH_3), 49.0 (6 CH_2), 19.9, 34.4 (2 CH_2), 39.1, 41.0 (2 C). – MS (EI): *m*/*z* (%) = 217 (0.2) [M^+ – H], 203 (0.6) [M^+ – CH_3], 189 (2) [M^+ – C_2H_5], 175 (18) [M^+ – C_3H_7], 133 (28), 119 (53), 105 (61), 91 (100).

2-(3-Propylbicyclo[1.1.1]pent-1-yl)pyrimidine (20bc): From **19b** (2 mmol), prepared according to GP 6, 2-bromopyrimidine (159 mg, 1 mmol), and $PdCl_2$(dppf) (26 mg, 0.035 mmol) in THF, **20bc** (142 mg, 75%) was obtained according to GP 7 and subsequent column chromatography (30 g of silica gel, column 25 × 2 cm, Et_2O) as an oil, R_f = 0.29. – ^{1}H NMR: δ = 0.90 (t, *J* = 7.2 Hz, 3 H, CH_3), 1.28–1.45 (m, 2 H, CH_2), 1.49–1.58 (m, 2 H, CH_2), 2.05 (s, 6 H, 3 CH_2), 7.15 (t, *J* = 4.9 Hz, 1 H, Ar), 8.69 (d, *J* = 4.9 Hz, 2 H, Ar). – ^{13}C NMR: δ = 14.1 (CH_3), 51.9 (3 CH_2), 19.6, 33.5 (CH_2), 156.8 (2 CH), 118.5 (CH), 39.4, 42.6, 168.1 (C).

1-Butyl-3-[4-(trimethylsilyl)phenyl]bicyclo[1.1.1]pentane (20cb): A reaction mixture obtained from **19c** (44 mmol), prepared according to GP 6, (4-bromophenyl)trimethylsilane (5.04 g, 22 mmol), and $PdCl_2$(dppf) (805 mg, 1.1 mmol) according to GP 7 was poured into ice-cold satd. NH_4Cl solution (100 mL) and diluted with hexane (200 mL). The layers were separated and the organic phase was washed with 10% NH_4Cl solution, H_2O, and brine (50 mL each), dried, and concentrated. Column chromatography of the residue (180 g of silica gel, column 20 × 7 cm, hexane) gave a fraction with R_f = 0.59, which was distilled under reduced pressure to yield **20cb** (4.31 g, 72%), b.p. 102–103 °C (0.1 Torr). – ^{1}H NMR: δ = 0.30 (s, 9 H, 3 CH_3), 0.95 (t, *J* = 7.0 Hz, 3 H, CH_3), 1.25–1.50 (m, 4 H, 2 CH_2), 1.57 (t, *J* = 7.0 Hz, 2 H, CH_2), 1.95 (s, 6 H, 3 CH_2), 7.28 (d, *J* = 7.4 Hz, 2 H, C_6H_4), 7.54 (d, *J* = 7.4 Hz, 2 H, C_6H_4). – ^{13}C NMR: δ = –1.1 (3 CH_3), 14.2 (CH_3), 52.1 (3 CH_2), 22.9, 28.9, 31.2 (CH_2), 125.5, 133.2 (2 CH), 39.1, 40.9, 137.8, 142.3 (C). – $C_{18}H_{28}Si$ (271.49): calcd. C 79.34, H 10.36; found C 79.50, H 10.90. – 4,4′-Bis(trimethylsilyl)biphenyl[47] (395 mg, 12%, R_f = 0.42) was also isolated from the reaction mixture by column chromatography.

1-(4-Bromophenyl)-3-butylbicyclo[1.1.1]pentane (20ca): (a) Work-up of a reaction mixture obtained from **19c** (23 mmol), prepared according to GP 6, 1,4-dibromobenzene (5.19 g, 22 mmol), and $PdCl_2$(dppf) (805 mg, 1.1 mmol) in THF according to GP 7 as in the preceding coupling and subsequent column chromatography (200 g of silica gel, column 20 × 7 cm, hexane) gave **20ca** (829 mg, 13.5%, R_f = 0.53) and 4,4′-dibromobiphenyl (1.99 g, 58%, R_f = 0.40). (b) To an emulsion of **20cb** (17.08 g, 62.7 mmol) in anhydrous MeOH (660 mL), a solution of Br_2 (15.20 g, 4.90 mL, 95.1 mmol) in MeOH (50 mL) was added over a period of 24 h at room temp. After stirring for a further 12 h, the mixture was poured into ice-cold H_2O (1 L) and extracted with pentane (3 × 200 mL). The combined organic phases were washed with H_2O, 5% $NaHCO_3$ solution, and further H_2O (200 mL each). After evaporation of the

solvent, column chromatography of the residue (200 g of silica gel, column 20 × 7 cm, hexane) furnished **20ca** (16.87 g, 96%) as an oil, R_f = 0.53. – ^{1}H NMR: δ = 0.95 (t, J = 7.0 Hz, 3 H, CH_3), 1.25–1.45 (m, 4 H, 2 CH_2), 1.52 (t, J = 7.0 Hz, 2 H, CH_2), 1.91 (s, 6 H, 3 CH_2), 7.10 (d, J = 7.6 Hz, 2 H, C_6H_4), 7.43 (d, J = 7.6 Hz, 2 H, C_6H_4). – ^{13}C NMR: δ = 14.1 (CH_3), 52.1 (3 CH_2), 22.9, 28.8, 31.3 (CH_2), 127.8, 131.0 (2 CH), 39.0, 41.0, 120.0, 140.6 (C). – $C_{15}H_{19}Br$ (279.2): calcd. C 64.52, H 6.86; found C 64.40, H 6.90.

1-(4-Fluorophenyl)-3-octylbicyclo[1.1.1]pentane (20ea): From **19e** (2.1 mmol), prepared according to GP 6, 4-bromofluorobenzene (350 mg, 220 μL, 2 mmol), and $PdCl_2$(dppf) (29 mg, 0.040 mmol) in THF, **20ea** (237 mg, 43%) was obtained according to GP 7 and subsequent column chromatography (50 g of silica gel, column 15 × 3 cm, PE) as an oil, R_f = 0.50. – IR: ṽ = 3050 cm^{-1}, 2960, 2930, 2860, 1608, 1523, 1510, 1460, 1276, 1232, 1225, 1158, 842, 816. – ^{1}H NMR: δ = 0.89 (t, J = 6.6 Hz, 3 H, CH_3), 1.18–1.42 (m, 12 H, 6 CH_2), 1.48–1.56 (m, 2 H, CH_2), 1.86 (s, 6 H, 3 CH_2), 6.96 (tt, J = 8.8, 2.2 Hz, 2 H, C_6H_4), 7.14 (ddt, J = 8.8, 5.6, 2.2 Hz, 2 H, C_6H_4). – ^{13}C NMR: δ = 14.1 (CH_3), 52.2 (3 CH_2), 22.7, 26.7, 29.4, 29.7, 29.9, 31.6, 32.0 (CH_2), 114.7 (d, J = 21.1 Hz), 127.5 (d, J = 4.0 Hz) (2 CH), 38.9, 41.0, 137.5, 161.6 (d, J = 244.1 Hz) (C). – MS (EI): m/z (%) = 274 (3) [M$^+$], 174 (25), 162 (47), 161 (100), 123 (82), 109 (40), 55 (14). – $C_{19}H_{27}F$ (274.4): calcd. C 83.16, H 9.92; found C 83.10, H 10.18

1-Octyl-3-[4-(trifluoromethyl)phenyl]bicyclo[1.1.1]pentane (20eb): From **19e** (2.1 mmol), prepared according to GP 6, 4-bromobenzotrifluoride (450 mg, 280 μL, 2 mmol), and $PdCl_2$(dppf) (29 mg, 0.040 mmol) in THF, **20eb** (444 mg, 68%) was obtained according to GP 7 and subsequent column chromatography (50 g of silica gel, column 15 × 3 cm, PE) as an oil, R_f = 0.59. – IR: ṽ = 3050 cm^{-1}, 2960, 2930, 2860, 1622, 1460, 1412, 1328, 1174, 1130, 1070, 1022, 850, 690. – ^{1}H NMR: δ = 0.86 (t, J = 6.6 Hz, 3 H, CH_3), 1.18–1.40 (m, 12 H, 6 CH_2), 1.48–1.56 (m, 2 H, CH_2), 1.90 (s, 6 H, 3 CH_2), 7.30 (d, J = 8.4 Hz, 2 H, C_6H_4), 7.53 (d, J = 8.4 Hz, 2 H, C_6H_4). – ^{13}C NMR: δ = 14.1 (CH_3), 52.9 (3 CH_2), 22.7, 26.7, 29.4, 29.7, 29.9, 31.6, 32.0 (CH_2), 125.0 (q, J = 4.0 Hz), 126.4 (2 CH), 39.3, 41.3, 124.4 (q, J = 271.9 Hz), 128.5 (q, J = 32.1 Hz), 145.6 (q, J = 1.3 Hz) (C). – MS (EI): m/z (%) = 324 (4) [M$^+$], 305 (28) [M$^+$ – F], 211 (100). – $C_{20}H_{27}F_3$ (324.4): calcd. C 74.04, H 8.39; found C 73.76, H 8.66.

4-(3-Octylbicyclo[1.1.1]pent-1-yl)benzonitrile (20ec): From **19e** (3 mmol), prepared according to GP 6, 4-bromobenzonitrile (364 mg, 2 mmol), and $PdCl_2$(dppf) (26 mg, 0.036 mmol) in THF, **20ec** (420 mg, 75%) and 4-bromophenyl 3-octylbicyclo[1.1.1]pent-1-yl ketone (**21**) (17 mg, 2.5%) were obtained according to GP 7 and subsequent column chromatography (50 g of silica gel, column 15 × 3 cm, PE/Et_2O, 9:1).

20ec: Oil, R_f = 0.23. – IR: ṽ = 2965 cm^{-1}, 2930, 2875, 2860, 2235, 1670, 1613, 1461, 1276, 1163, 852, 730. – ^{1}H NMR: δ = 0.89 (t, J = 6.6 Hz, 3 H, CH_3), 1.18–1.40 (m, 12 H, 6 CH_2), 1.46–1.56 (m, 2 H, CH_2), 1.90 (s, 6 H, 3 CH_2), 7.28 (d, J = 8.0 Hz, 2 H, C_6H_4), 7.56 (d, J = 8.0 Hz, 2 H, C_6H_4). – ^{13}C NMR: δ = 14.1 (CH_3), 52.2 (3 CH_2), 22.6, 26.5, 29.3, 29.6, 29.8. 31.4, 31.9 (CH_2), 126.8, 131.9 (2 CH), 39.3, 41.4, 109.8, 119.1, 146.9 (C). – MS (EI): m/z (%) = 281 (1) [M$^+$], 182 (16), 168 (100), 154 (13), 116 (13). – $C_{20}H_{27}N$ (281.4): calcd. C 85.35, H 9.67, N 4.98; found C 85.02, H 9.75, N 4.90.

21: R_f = 0.28. – ^{1}H NMR: δ = 0.89 (t, J = 6.6 Hz, 3 H, CH_3), 1.24 (m, 12 H, 6 CH_2), 1.43–1.55 (m, 2 H, CH_2), 2.12 (s, 6 H, 3 CH_2), 7.55 (d, J = 8.0 Hz, 2 H, C_6H_4), 7.86 (d, J = 8.0 Hz, 2 H, C_6H_4). – ^{13}C NMR: δ = 14.1 (CH_3), 53.4 (3 CH_2), 22.7, 26.3, 29.3, 29.6, 29.8, 31.4, 31.8 (CH_2), 130.4, 131.7 (2 CH), 41.0, 44.1, 127.8, 135.4, 197.0 (C).

1-(4′-Bromobiphenyl-4-yl)-3-propylbicyclo[1.1.1]pentane (23ab): From **19b** (5 mmol), prepared according to GP 6, 4,4′-dibromobiphenyl (**22a**) (3.12 g, 10 mmol), and $PdCl_2$(dppf) (73 mg, 0.1 mmol), **23ab** (730 mg, 43%) was obtained according to GP 7 with work-up as described above for compound **20cb** and subsequent column chromatography (50 g of silica gel, column 15 × 3 cm, PE/Et_2O, 9:1), R_f = 0.35; m.p. 156 °C. – IR: ṽ = 3040 cm^{-1}, 2960, 2930, 2910, 2875, 2840, 1482, 1390, 1268, 1081, 1006, 811. – ^{1}H NMR: δ = 0.94 (t, J = 7.0 Hz, 3 H, CH_3), 1.28–1.44 (m, 2 H, CH_2), 1.50 (t, J = 6.0 Hz, 2 H, CH_2), 1.92 (s, 6 H, 3 CH_2), 7.27 (d, J = 8.0 Hz, 2 H, C_6H_4), 7.45–7.60 (m, 6 H, C_6H_4). – ^{13}C NMR: δ = 14.4 (CH_3), 52.3 (3 CH_2), 19.9, 33.9 (CH_2), 126.6, 126.7, 128.6, 131.8 (2 CH), 39.1, 41.3, 121.3, 137.8, 140.0, 141.2 (C). – MS (EI): m/z (%) = 342/340 (8:6) [M$^+$], 299 (9) [M$^+$ – C_3H_7], 91 (29), 73 (100). – $C_{20}H_{21}Br$ (341.3): calcd. C 70.39, H 6.20, Br 23.41; found C 70.47, H 6.20, Br 23.40.

4,4′-Bis(3-butylbicyclo[1.1.1]pent-1-yl)biphenyl (23ac): From **19c** (30 mmol), prepared according to GP 6, 4,4′-dibromobiphenyl (**22a**) (3.12 g, 10 mmol), and $PdCl_2$(dppf) (73 mg, 0.1 mmol) in THF, **23ac** (3.47 g, 87%) was obtained according to GP 7 under conditions as those in the preceding preparation and subsequent column chromatography (100 g of silica gel, column 20 × 5 cm, hexane), followed by recrystallization from MeOH (500 mL); R_f = 0.35; m.p. 134–135 °C. – ^{1}H NMR: δ = 0.91 (t, J = 6.8 Hz, 6 H, 2 CH_3), 1.24–1.43 (m, 8 H, 4 CH_2), 1.48–1.57 (m, 4 H, 2 CH_2), 1.90 (s, 12 H, 6 CH_2), 7.24 (d, J = 8.2 Hz, 4 H, C_6H_4), 7.48 (d, J = 8.2 Hz, 4 H, C_6H_4). – ^{13}C NMR: δ = 14.1 (2 CH_3), 52.2 (6 CH_2), 22.9, 28.9, 31.4 (2 CH_2), 126.5, 126.8 (4 CH), 39.1, 41.3, 139.1, 140.6 (2 C). – MS (EI): m/z (%) = 398 (8) [M$^+$], 383 (2) [M$^+$ – CH_3], 355 (9) [M$^+$ – C_3H_7], 341 (100) [M$^+$ – C_4H_9]. – $C_{30}H_{38}$ (398.6): calcd. C 90.39, H 9.61; found C 90.32, H 9.52.

1-(4′-Bromobiphenyl-4-yl)-3-octylbicyclo[1.1.1]pentane (23ae): From **19e** (4.7 mmol), prepared according to GP 6, 4,4′-dibromobiphenyl (**22a**) (3.12 g, 10 mmol), and $PdCl_2$(dppf) (63 mg, 0.086 mmol) in Et_2O, **23ae** (1.19 g, 62%) was obtained according to GP 7 and subsequent column chromatography (100 g of silica gel, column 20 × 5 cm, hexane), followed by recrystallization from MeOH (500 mL), R_f = 0.35; m.p. 98–103 °C. – IR: ṽ = 3040 cm^{-1}, 2960, 2870, 2855, 1482, 1386, 1262, 1080, 1004, 821. – ^{1}H NMR: δ = 0.90 (t, J = 6.6 Hz, 3 H, CH_3), 1.30 (m, 12 H, 6 CH_2), 1.44–1.56 (m, 2 H, CH_2), 1.90 (s, 6 H, 3 CH_2), 7.27 (d, J = 8.0 Hz, 2 H, C_6H_4), 7.35–7.55 (m, 6 H, C_6H_4). – ^{13}C NMR: δ = 14.1 (CH_3), 52.2 (3 CH_2), 22.7, 26.7, 29.3, 29.7, 29.9, 31.7, 31.9 (CH_2), 126.6, 126.7, 128.6, 131.8 (2 CH), 39.1, 41.3, 121.3, 137.9, 140.1, 141.3 (C). – $C_{25}H_{31}Br$ (411.4): calcd. C 72.98, H 7.60, Br 19.42; found C 72.99, H 7.59, Br 19.15.

1-(4′-Bromobiphenyl-4-yl)-3-(hex-3-ynyl)bicyclo[1.1.1]pentane (23aja) and 4,4′-Bis[3-(hex-3-ynyl)bicyclo[1.1.1]pent-1-yl]biphenyl (23ajb): From **19j** (41.7 mmol), prepared according to GP 6, **22a** (4.338 g, 13.9 mmol), and $PdCl_2$(dppf) (400 mg, 0.547 mmol) in THF, **23aja** (2.081 g, 39%) and **23ajb** (3.121 g, 50%) were obtained according to GP 7 and subsequent column chromatography (200 g of silica gel, column 20 × 7 cm, hexane/benzene, 4:1).

23aja: R_f = 0.38; m.p. 115–117 °C (MeOH). – ^{1}H NMR: δ = 1.12 (t, J = 7.4 Hz, 3 H, CH_3), 1.75 (t, J = 7.1 Hz, 2 H, CH_2), 1.96 (s, 6 H, 3 CH_2), 2.15–2.20 (m, 4 H, 2 H_2), 7.28 (d, J = 9.4 Hz, 2 H, C_6H_4), 7.40–7.60 (m, 6 H, C_6H_4). – $C_{23}H_{23}Br$ (379.3): calcd. C 72.82, H 6.11; found C 72.61, H 6.25.

23ajb: R_f = 0.28; m.p. 136–139 °C (MeOH). – ^{1}H NMR: δ = 1.04 (t, J = 7.4 Hz, 6 H, 2 CH_3), 1.69 (t, J = 7.0 Hz, 4 H, 2 CH_2), 1.88 (s, 12 H, 6 CH_2), 2.00–2.15 (m, 8 H, 4 CH_2), 7.20 (d, J = 8.2 Hz, 4 H, C_6H_4), 7.41 (d, J = 8.2 Hz, 4 H, C_6H_4). – ^{13}C NMR: δ = 14.3 (2 CH_3), 52.2 (6 CH_2), 12.4, 16.2, 31.1 (2 CH_2), 126.4, 126.8 (4 CH), 38.6, 41.4, 79.4, 81.6, 139.1, 140.2 (2 C). – $C_{34}H_{38}$ (446.7): calcd. C 91.42, H 8.58; found C 91.30, H 8.65.

1-Octyl-3-(4′-octylbiphenyl-4-yl)bicyclo[1.1.1]pentane (23be): From **19e** (2 mmol), prepared according to GP 6, 4-bromo-4′-octylbiphenyl (**22b**) (345 mg, 1 mmol), and $PdCl_2$(dppf) (65 mg, 0.089 mmol) in Et_2O, **23be** (357 mg, 80%) was obtained according to GP 7 and subsequent column chromatography (50 g of silica gel, column 15 × 3 cm, PE), R_f = 0.34; m.p. 89 °C (MeOH). – IR: ṽ = 3030 cm^{-1}, 2960, 2925, 2855, 1595, 1460, 1271, 1162, 1009, 822. – ^{1}H NMR: δ = 0.83–0.98 (m, 6 H, 2 CH_3), 1.19–1.42 (m, 24 H, 12 CH_2), 1.44–1.56 (m, 2 H, CH_2), 1.90 (s, 6 H, 3 CH_2), 2.63 (t, J = 7.7 Hz, 2 H, CH_2), 7.22 (t, J = 8.0 Hz, 4 H, C_6H_4), 7.49 (t, J = 8.0 Hz, 4 H, C_6H_4). – ^{13}C NMR: δ = 14.1 (2 CH_3), 52.2 (3 CH_2), 29.3 (2 CH_2), 22.7, 26.7, 29.4, 29.4, 29.5, 29.7, 29.8, 29.9, 31.5, 31.7, 31.9, 35.6 (CH_2), 126.4, 126.7, 126.9, 128.8 (2 CH), 39.1, 41.4, 138.5, 139.1, 140.4, 141.9 (C). – MS (EI): m/z (%) = 444 (0.2) [M$^+$], 378 (19), 279 (21), 180 (13), 86 (54), 57 (53), 41 (100). – $C_{33}H_{48}$ (444.7): calcd. C 89.12, H 10.88; found C 89.19, H 10.84.

5-Octyl-2-[4-(3-octylbicyclo[1.1.1]pent-1-yl)phenyl]pyrimidine (23ce): From **19e** (1.5 mmol), prepared according to GP 6, 4-(5-octylpyrimidine-2-yl)phenyl trifluoromethanesulfonate (**22c**) (208 mg, 0.5 mmol), and $PdCl_2$(dppf) (24 mg, 0.033 mmol) in THF, **23ce** (140 mg, 63%) was obtained according to GP 7 and subsequent column chromatography (25 g of silica gel, column 20 × 2 cm, PE/Et_2O, 19:1), R_f = 0.21; m.p. 34 °C. – ^{1}H NMR: δ = 0.80–0.96 (m, 6 H, 2 CH_3), 1.33 (m, 22 H, 11 CH_2), 1.48–1.56 (m, 2 H, CH_2), 1.56–1.72 (m, 2 H, CH_2), 1.90 (s, 6 H, 3 CH_2), 2.61 (t, J = 7.6 Hz, 2 H, CH_2), 7.32 (d, J = 8.2 Hz, 2 H, C_6H_4), 8.34 (d, J = 8.2 Hz, 2 H, C_6H_4), 8.58 (s, 2 H, Ar). – ^{13}C NMR: δ = 14.0 (2 CH_3), 52.2 (3 CH_2), 22.6, 22.7, 26.6, 29.0, 29.2, 29.3, 29.4, 29.6, 29.8, 30.1, 30.7, 31.7, 31.8, 31.9 (CH_2), 126.2, 127.6, 156.9 (2 CH), 39.1, 41.5, 132.6, 135.5, 144.0, 162.5 (C). – MS (EI): m/z (%) = 447 (34) [M$^+$ + H], 446 (11) [M$^+$], 432 (16) [M$^+$ – CH_2], 381 (38), 334 (100), 295 (33), 282 (29). – $C_{31}H_{46}N_2$ (446.7): calcd. C 83.35, H 10.38, N 6.27; found C 83.28, H 10.37, N 6.24.

2-[4-(3-Octylbicyclo[1.1.1]pent-1-yl)phenyl]-5-octyloxypyrimidine (23de): From **19e** (1.5 mmol), prepared according to GP 6, 4-(5-octyloxypyrimidine-2-yl)phenyl trifluoromethanesulfonate (**22d**) (400 mg, 0.92 mmol), and $PdCl_2$(dppf) (36 mg, 0.049 mmol) in THF, **23de** (300 mg, 70%) was obtained according to GP 7 and subsequent column chromatography (50 g of silica gel, column 15 × 3 cm, PE/Et_2O, 9:1), R_f = 0.26; m.p. 45 °C. – IR: ṽ = 3050 cm^{-1}, 2960, 2930, 2860, 1613, 1577, 1548, 1442, 1285, 857, 788. – ^{1}H NMR: δ = 0.89 (t, J = 6.6 Hz, 6 H, 2 CH_3), 1.29 (m, 22 H, 11 CH_2), 1.48–1.58 (m, 2 H, CH_2), 1.83 (quint, J = 6.5 Hz, 2 H, CH_2), 1.91 (s, 6 H, 3 CH_2), 4.08 (t, J = 6.5 Hz, 2 H, OCH_2), 7.31 (d, J = 8.5 Hz, 2 H, C_6H_4), 8.26 (d, J = 8.5 Hz, 2 H, C_6H_4), 8.44 (s, 2 H, Ar). – ^{13}C NMR: δ = 14.0, 14.1 (CH_3), 52.2 (3 CH_2), 22.6, 22.7, 25.8, 26.6, 29.0, 29.1, 29.2, 29.3, 29.6, 29.8, 31.7, 31.7, 31.9, 68.7 (CH_2), 126.2, 127.2, 143.6 (2 CH), 39.1, 41.5, 135.4, 143.2, 151.3, 157.5 (C). – MS (EI): m/z (%) = 462 (30) [M$^+$], 447 (12) [M$^+$ – CH_3], 430 (18), 396 (23), 386 (20), 349 (100) [M$^+$ – C_8H_{17}], 311 (20), 256 (16), 237 (17), 186 (15), 57 (72). – $C_{31}H_{46}N_2O$ (462.6): calcd. C 80.46, H 10.02, N 6.06; found C 80.60, H 10.13, N 6.11.

5-[4-(3-Octylbicyclo[1.1.1]pent-1-yl)phenyl]-2-octyloxypyrimidine (23ee): From **19e** (4 mmol), prepared according to GP 6, 4-(2-octyloxypyrimidine-5-yl)phenyl trifluoromethanesulfonate (**22e**) (432 mg, 1 mmol), and $PdCl_2$(dppf) (43 mg, 0.059 mmol) in THF, **23ee** (365 mg, 79%) was obtained according to GP 7 and subsequent column chromatography (50 g of silica gel, column 15 × 3 cm, PE/Et_2O, 9:1), R_f = 0.17; m.p. 85 °C. – IR: ṽ = 3060 cm^{-1}, 2925, 2906, 2855, 1600, 1542, 1455, 1343, 1025, 840, 805. – ^{1}H NMR: δ = 0.83–0.98 (m, 6 H, 2 CH_3), 1.29 (m, 22 H, 11 CH_2), 1.42–1.58 (m, 2 H, CH_2), 1.84 (quint, J = 7.4 Hz, 2 H, CH_2), 1.91 (s, 6 H, 3 CH_2), 4.39 (t, J = 6.7 Hz, 2 H, OCH_2), 7.32 (d, J = 8.1 Hz, 2 H, C_6H_4), 7.44 (d, J = 8.1 Hz, 2 H, C_6H_4), 8.68 (s, 2 H, Ar). – ^{13}C NMR: δ = 14.1 (2 CH_3), 52.5 (3 CH_2), 22.7, 22.7, 26.0, 26.7, 28.9, 29.2, 29.3, 29.4, 29.7, 29.9, 31.2, 31.8, 31.9, 67.9 (CH_2), 126.9, 127.0, 147.1 (2 CH), 39.2, 41.3, 128.1, 132.4, 141.8, 164.7 (C). – MS (EI): m/z (%) = 462 (25) [M$^+$], 349 (100) [M$^+$ – C_8H_{17}], 311 (30), 237 (39), 207 (11), 199 (12), 180 (17), 167 (12), 149 (33), 111 (13), 91 (18), 57 (44). – $C_{31}H_{46}N_2O$ (462.60): calcd. C 80.46, H 10.02, N 6.06; found C 80.49, H 10.03, N 6.14.

1-(4′-Ethylbiphenyl-4-yl)-3-[2-(tetrahydropyran-2-yloxy)ethyl]-bicyclo[1.1.1]pentane (23ff): From **19f** (89 mmol), prepared according to GP 6, **22f** (11.38 g, 43.6 mmol), and $PdCl_2$(dppf) (1.30 g, 1.78 mmol) in THF, **23ff** (1.605 g, 10%) and 3,3′-bis[2-(tetrahydropyran-2-yloxy)ethyl]-1,1′-bis(bicyclo[1.1.1]pentyl) (1.107 g, 6.4%) were obtained according to GP 7 and subsequent column chromatography (200 g of alumina deactivated with 5% H_2O, column 30 × 5 cm, hexane/EtOAc, 40:1).

23ff: R_f = 0.33; m.p. 30–32 °C. – ^{1}H NMR: δ = 1.28 (t, J = 7.4 Hz, 3 H, CH_3), 1.48–1.75 (m, 6 H, 3 CH_2), 1.75–1.95 (m, 2 H, CH_2), 2.05 (s, 6 H, 3 CH_2), 2.75 (q, J = 7.4 Hz, 2 H, CH_2), 3.45–3.65 (m, 2 H, OCH_2), 3.80–4.05 (m, 2 H, OCH_2), 4.68 (t, J = 3.2 Hz, 1 H, OCH), 7.22–7.37 (m, 4 H, C_6H_4), 7.50–7.65 (m, 4 H, C_6H_4). – ^{13}C NMR: δ = 15.6 (CH_3), 52.8 (3 CH_2), 19.6, 25.5, 28.5, 30.8, 31.6, 62.3, 65.8 (CH_2), 126.4, 126.7, 127.0, 128.2 (2 CH), 98.9 (CH), 36.9, 41.8, 138.5, 139.2, 140.1, 143.1 (C).

3,3′-Bis[2-(tetrahydropyran-2-yloxy)ethyl]-1,1′-bis(bicyclo[1.1.1]-pentyl): Oil, R_f = 0.50. – ^{1}H NMR: δ = 1.48 (s, 12 H, 6 CH_2), 1.40–1.65 (m, 12 H, 6 CH_2), 1.69 (t, J = 7.0 Hz, 4 H, 2 CH_2), 3.30 (dt, J = 9.5, 7.0 Hz, 2 H, OCH_2), 3.35–3.50 (m, 2 H, OCH_2), 3.65 (dt, J = 9.5, 6.9 Hz, 2 H, OCH_2), 3.85 (ddd, J = 11.4, 7.5, 3.7 Hz, 2 H, OCH_2), 4.50 (t, J = 3.2 Hz, 2 H, OCH). – ^{13}C NMR: δ = 49.4 (6 CH_2), 19.5, 25.4, 30.1, 31.7, 62.1, 66.1 (2 CH_2), 98.7 (2 CH), 36.3, 39.4 (2 C).

1-(4′-Ethylbiphenyl-4-yl)-3-[3-(tetrahydropyran-2-yloxy)propyl]-bicyclo[1.1.1]pentane (23fg): From **19g** (115 mmol), prepared according to GP 6, **22f** (7.48 g, 28.6 mmol), and $PdCl_2$(dppf) (1.40 g, 1.91 mmol) in THF, **23fg** (6.82 g, 61%) was obtained according to GP 7 and subsequent column chromatography (250 g of alumina deactivated with 5% H_2O, column 30 × 5 cm, hexane/EtOAc, 15:1) as an oil, R_f = 0.31. – ^{1}H NMR: δ = 1.20 (t, J = 6.9 Hz, 3 H, CH_3), 1.38–1.65 (m, 8 H, 4 CH_2), 1.68–1.90 (m, 2 H, CH_2), 1.88 (s, 6 H, 3 CH_2), 2.61 (q, J = 6.9 Hz, 2 H, CH_2), 3.28–3.41 (m, 1 H, OCH_2), 3.41–3.55 (m, 1 H, OCH_2), 3.58–3.71 (m, 1 H, OCH_2), 3.75–3.91 (m, 1 H, OCH_2), 4.53 (t, J = 3.2 Hz, 1 H, OCH), 7.11–7.25 (m, 4 H, C_6H_4), 7.39–7.49 (m, 4 H, C_6H_4). – $C_{27}H_{34}O_2$ (390.6): calcd. C 83.03, H 8.78; found C 82.71, H 8.99.

1-{4′-[2-(*Z*)-(*trans*-2-Ethyloxycyclopropyl)vinyl]biphenyl-4-yl}-3-{[4-(tetrahydropyran-2-yloxy]butyl}bicyclo[1.1.1]pentane (23gh): From **19h** (2 mmol), prepared according to GP 6, **22g** (170 mg, 0.5 mmol), and $PdCl_2$(dppf) (24 mg, 0.033 mmol) in THF, **23gh** (115 mg, 48%) was obtained according to GP 7 and subsequent column chromatography (20 g of silica gel, column 15 × 2 cm, PE/Et_2O, 4:1) as an oil, R_f = 0.25. – ^{1}H NMR: δ = 0.73 (q, J =

6.4 Hz, 1 H, Cpr), 1.12–1.22 (m, 1 H, Cpr), 1.19 (t, J = 7.0 Hz, 3 H, CH_3), 1.30–1.92 (m, 12 H, 6 CH_2), 1.92 (s, 6 H, 3 CH_2), 2.11 (m, 1 H, Cpr), 3.31 (ddd, J = 6.4, 3.7, 2.6 Hz, 1 H, Cpr), 3.42 (dt, J = 9.5, 6.6 Hz, 1 H, OCH_2), 3.46–3.56 (m, 1 H, OCH_2), 3.60 (q, J = 7.0 Hz, 2 H, OCH_2), 3.76 (dt, J = 9.5, 6.6 Hz, 1 H, OCH_2), 3.88 (m, 1 H, OCH_2), 4.59 (t, J = 3.2 Hz, 1 H, OCH), 5.05 (dd, J = 11.5, 10.0 Hz, 1 H, =CH), 6.38 (d, J = 11.5 Hz, 1 H, =CH), 7.26–7.32 (m, 2 H, C_6H_4), 7.45–7.58 (m, 6 H, C_6H_4). – ^{13}C NMR: δ = 15.1 (CH_3), 52.2 (3 CH_2), 15.9, 19.7, 23.4, 25.5, 29.9, 30.8, 31.5, 63.4, 66.1, 67.6 (CH_2), 20.0, 61.4, 98.9, 126.5, 126.7, 126.8, 127.8, 129.1, 132.7 (CH), 39.0, 41.4, 136.4, 138.8, 139.3, 140.6 (C).

{3-[(*E*)-Pent-3-enyl]bicyclo[1.1.1]pent-1-yl}phenyl 4-Cyano-3,5-difluorobenzoate (23hm): From **19m** (23.65 mmol), prepared according to GP 6, 4-bromophenyl 4-cyano-3,5-difluorobenzoate (**22h**) (5.0 g, 14.79 mmol), and $PdCl_2$(dppf) (542 mg, 0.74 mmol) in THF, **23hm** (2.272 g, 39%) was obtained according to GP 7 and subsequent column chromatography (250 g of silica gel, column 30 × 5 cm, hexane/Et_2O, 10:1), R_f = 0.42; m.p. 75–77 °C (MeOH/H_2O, 95:5). – ^{1}H NMR: δ = 1.55–1.70 (m, 5 H, CH_2 + CH_3), 1.98 (s, 6 H, 3 CH_2), 1.95–2.05 (m, 2 H, CH_2), 4.88–5.02 (m, 2 H, CH=CH), 7.05 (d, J = 8.3 Hz, 2 H, C_6H_4), 7.35 (d, J = 8.3 Hz, 2 H, C_6H_4), 8.05 (d, J = 7.5 Hz, 2 H, $C_6H_2F_2$). – ^{13}C NMR: δ = 18.0 (CH_3), 52.3 (3 CH_2), 29.7, 31.3 (CH_2), 107.0 (dd, J = 23.0, 4.0 Hz), 126.6, 130.3 (2 CH), 124.8, 131.1 (CH), 163.5 (dd, J = 261.5, 6.9 Hz) (2 C), 39.2, 41.6, 108.8, 125.4, 148.8, 156.1 (t, J = 21.0 Hz), 163.4, 165.6 (t, J = 6.3 Hz) (C).

4-[4-(3-Butylbicyclo[1.1.1]pent-1-yl)-α,α-difluorobenzyloxy]-2,3′,4′,6-tetrafluorobiphenyl (23ic): From **19c** (42.69 mmol), prepared according to GP 6, (4-bromophenyl)difluoromethyl 3,5,3′,4′-tetrafluorobiphenyl-1-yl ether (**22i**) (7.00 g, 15.65 mmol), and $PdCl_2$(dppf) (572 mg, 0.782 mmol) in THF, **23ic** (6.508 g, 85%) was obtained according to GP 7 and subsequent column chromatography (250 g of silica gel, column 30 × 5 cm, hexane), R_f = 0.38; m.p. 89–91 °C (MeOH/H_2O, 90:1). – ^{1}H NMR: δ = 0.95 (t, J = 5.5 Hz, 3 H, CH_3), 1.22–1.45 (m, 4 H, 2 CH_2), 1.55 (t, J = 8.0 Hz, 2 H, CH_2), 1.95 (s, 6 H, 3 CH_2), 6.95 (d, J = 9.2 Hz, 2 H, $C_6H_2F_2$), 7.15–7.30 (m, 3 H, $C_6H_3F_2$), 7.35 (d, J = 8.3 Hz, 2 H, C_6H_4), 7.65 (d, J = 8.3 Hz, 2 H, C_6H_4). – ^{13}C NMR: δ = 14.1 (CH_3), 52.2 (3 CH_2), 22.9, 28.8, 31.3 (CH_2), 105.3 (d, J = 29.3 Hz), 122.5, 125.3 (t, J = 3.8 Hz) (2 CH), 117.3 (dd, J = 16.2, 4.7 Hz), 119.5 (dd, J = 14.2, 5.0 Hz), 126.7 (t, J = 5.2 Hz) (CH), 159.8 (dd, J = 249.0, 9.1 Hz) (2 C), 39.2, 41.2, 119.3 (t, J = 354.8 Hz), 122.5, 125.9 (t, J = 21.9 Hz), 125.0 (t, J = 5.4 Hz), 130.5 (t, J = 30.8 Hz), 149.9 (dd, J = 248.6, 14.6 Hz), 150.4 (dd, J = 252.2, 14.8 Hz), 150.8 (t, J = 14.8 Hz) (C).

5-[4-(4-Cyclopropylbutyloxy)phenyl]-2-(3-octylbicyclo[1.1.1]pent-1-yl)pyrimidine (23je): From **19e** (6 mmol), prepared according to GP 6, 5-[4-(4-cyclopropylbutyloxy)phenyl]-2-bromopyrimidine (**22j**) (520 mg, 1.5 mmol), and $PdCl_2$(dppf) (53 mg, 0.072 mmol) in THF, **23je** (566 mg, 84%) was obtained according to GP 7 and subsequent column chromatography (50 g of silica gel, column 15 × 3 cm, PE/Et_2O, 19:1), R_f = 0.17; m.p. 57 °C. – IR: $\tilde{\nu}$ = 3080 cm^{-1}, 3005, 2960, 2855, 2625, 1610, 1586, 1432, 1258, 1172, 850, 800. – ^{1}H NMR: δ = 0.03 (m, 2 H, Cpr), 0.41 (m, 2 H, Cpr), 0.61–0.78 (m, 1 H, Cpr), 0.89 (t, J = 6.5 Hz, 3 H, CH_3), 1.22–1.37 (m, 14 H, 7 CH_2), 1.47–1.65 (m, 4 H, 2 CH_2), 1.85 (quint, J = 7.1 Hz, 2 H, CH_2), 1.96 (s, 6 H, 3 CH_2), 4.03 (t, J = 6.5 Hz, 2 H, OCH_2), 6.97 (d, J = 9.0 Hz, 2 H, C_6H_4), 8.34 (d, J = 9.0 Hz, 2 H, C_6H_4), 8.53 (s, 2 H, Ar). – ^{13}C NMR: δ = 14.1 (CH_3), 52.1 (3 CH_2), 4.4 (2 CH_2), 22.6, 26.0, 26.5, 29.0, 29.2, 29.6, 29.7, 31.5, 31.8, 34.4, 68.0 (CH_2), 114.3, 129.4, 155.0 (2 CH), 10.7 (CH), 34.4, 37.4, 130.1, 130.6, 161.1, 162.4 (C). – MS (FAB): m/z (%) = 447 (100) [M^+ + H], 446 (11) [M^+], 338 (52), 334 (41), 55 (57). – $C_{30}H_{42}N_2O$ (446.7): calcd. C 80.67, H 9.48, N 6.27; found C 80.75, H 9.48, N 6.33.

General Procedure (GP 8) for the Preparation of Triflates 22c–e: To a solution of the appropriate phenol[27] (1.5 mmol) in anhydrous pyridine (5 mL), trifluoromethanesulfonic anhydride (460 mg, 274 μL, 1.63 mmol) was added at 0 °C. After stirring for 24 h at room temp., the mixture was poured into ice-cold water (20 mL) and extracted with Et_2O (3 × 15 mL). The combined extracts were dried, the solvent was evaporated, and the residue was purified by column chromatography (25 g of silica gel, column 15 × 2 cm, CH_2Cl_2).

4-(5-Octylpyrimidine-2-yl)phenyl Trifluoromethanesulfonate (22c): Compound **22c** (593 mg, 95%) was obtained from 2-(4-hydroxyphenyl)-5-octylpyrimidine (427 mg, 1.5 mmol) according to GP 8, R_f = 0.50. – ^{1}H NMR: δ = 0.89 (t, J = 6.5 Hz, 3 H, CH_3), 1.20–1.45 (m, 10 H, 5 CH_2), 1.59–1.73 (m, 2 H, CH_2), 2.64 (t, J = 7.7 Hz, 2 H, CH_2), 7.38 (d, J = 9.0 Hz, 2 H, C_6H_4), 8.52 (d, J = 9.0 Hz, 2 H, C_6H_4), 8.63 (s, 2 H, Ar). – ^{13}C NMR: δ = 13.9 (CH_3), 22.5, 29.0, 29.1, 29.2, 30.0, 30.6, 31.7 (CH_2), 121.2, 129.8, 150.9 (2 CH), 118.7 (q, J = 320.9 Hz), 133.6, 137.9, 150.9, 160.7 (C).

4-(5-Octyloxypyrimidine-2-yl)phenyl Trifluoromethanesulfonate (22d): Compound **22d** (496 mg, 77%) was obtained from 2-(4-hydroxyphenyl)-5-octyloxypyrimidine (451 mg, 1.5 mmol) according to GP 8, R_f = 0.61. – ^{1}H NMR: δ = 0.89 (t, J = 6.7 Hz, 3 H, CH_3), 1.22–1.25 (m, 10 H, 5 CH_2), 1.84 (quint, J = 76.9 Hz, 2 H, CH_2), 4.11 (t, J = 6.5 Hz, 2 H, OCH_2), 7.36 (dt, J = 8.9, 2.4 Hz, 2 H, C_6H_4), 8.44 (dt, J = 8.9, 2.4 Hz, 2 H, C_6H_4), 8.45 (s, 2 H, Ar). – ^{13}C NMR: δ = 13.5 (CH_3), 22.6, 25.8, 29.0, 29.1, 29.2, 31.7, 68.9 (CH_2), 121.2, 129.3, 143.7 (2 CH), 118.7 (q, J = 320.0 Hz), 137.7, 150.5, 151.9, 155.6 (C).

4-(2-Octyloxypyrimidine-5-yl)phenyl Trifluoromethanesulfonate (22e): Compound **22e** (561 mg, 86%) was obtained from 5-(4-hydroxyphenyl)-2-octyloxypyrimidine (451 mg, 1.5 mmol) according to GP 8, R_f = 0.39. – ^{1}H NMR: δ = 0.89 (t, J = 6.6 Hz, 3 H, CH_3), 1.22–1.55 (m, 10 H, 5 CH_2), 1.87 (quint, J = 7.1 Hz, 2 H, CH_2), 4.41 (t, J = 7.7 Hz, 2 H, OCH_2), 7.40 (dt, J = 8.8, 2.5 Hz, 2 H, C_6H_4), 7.59 (dt, J = 8.8, 2.5 Hz, 2 H, C_6H_4), 8.69 (s, 2 H, Ar). – ^{13}C NMR: δ = 13.8 (CH_3), 22.4, 25.8, 28.7, 29.0, 29.1, 31.6, 68.0 (CH_2), 121.1, 128.1, 157.1 (2 CH), 118.6 (q, J = 320.8 Hz), 126.1, 134.95, 149.3, 165.1 (C).

General Procedure (GP 9) for the Preparation of Cyanides from 23ab,ae: A mixture of **23ab** or **23ae** (0.75 mmol) and CuCN (170 mg, 1.9 mmol) in anhydrous *N*-methyl-2-pyrrolidone (2 mL) was stirred at 185 °C for 13 h. After cooling to room temp., the mixture was treated with a solution of $FeCl_3$ (120 mg, 0.74 mmol) in 1% aq. HCl (5 mL), stirred for 20 min at 50 °C, and extracted with Et_2O (3 × 20 mL). The combined extracts were dried, the solvent was evaporated, and the residue was purified by column chromatography (25 g of silica gel, column 18 × 2 cm, PE/Et_2O, 9:1).

4′-(3-Propylbicyclo[1.1.1]pent-1-yl)biphenyl-4-carbonitrile (24ab): From **23ab** (295 mg, 0.864 mmol), **24ab** (191 mg, 77%) was obtained according to GP 9, R_f = 0.20; m.p. 108 °C. – ^{1}H NMR: δ = 0.95 (t, J = 7.2 Hz, 3 H, CH_3), 1.28–1.44 (m, 2 H, CH_2), 1.46–1.53 (m, 2 H, CH_2), 1.93 (s, 6 H, 3CH_2), 7.32 (dt, J = 8.3, 1.9 Hz, 2 H, C_6H_4), 7.52 (dt, J = 8.3, 1.9 Hz, 2 H, C_6H_4), 7.67 (m, 4 H, C_6H_4). – ^{13}C NMR: δ = 14.4 (CH_3), 52.3 (3 CH_2), 19.9, 33.9 (CH_2), 126.9, 127.0, 127.6, 132.6 (2 CH), 39.2, 41.3, 110.6, 119.0, 137.0, 142.4, 145.6 (C). – MS (EI): m/z (%) = 287 (4) [M^+], 244 (100) [M^+ – C_3H_7], 230 (11), 203 (13). – $C_{21}H_{21}N$ (287.4): calcd. C 87.76, H 7.37, N 4.87; found C 87.84, H 7.57, N 4.92.

4′-(3-Octylbicyclo[1.1.1]pent-1-yl)biphenyl-4-carbonitrile (24ae): From **23ae** (309 mg, 0.75 mmol), **24ae** (225 mg, 84%) was obtained according to GP 9, R_f = 0.23; m.p. 80 °C. – IR: $\tilde{\nu}$ = 3040 cm^{-1}, 2960, 2945, 2920, 2910, 2865, 2850, 2840, 2225, 1605, 1492, 1470, 1274, 1160, 1006, 837, 823, 801, 733, 729. – ^{1}H NMR: δ = 0.89 (t, J = 6.6 Hz, 3 H, CH_3), 1.29 (m, 12 H, 6 CH_2), 1.44–1.58 (m, 2 H, CH_2), 1.90 (s, 6 H, 3 CH_2), 7.32 (d, J = 8.2 Hz, 2 H, C_6H_4), 7.51 (d, J = 8.2 Hz, 2 H, C_6H_4), 7.64 (d, J = 8.5 Hz, 2 H, C_6H_4), 7.70 (d, J = 8.5 Hz, 2 H, C_6H_4). – ^{13}C NMR: δ = 14.0 (CH_3), 52.1 (3 CH_2), 22.6, 26.6, 29.2, 29.6, 29.8, 31.5, 31.8 (CH_2), 126.7, 126.8, 127.3, 132.4 (2 CH), 39.1, 41.1, 110.5, 118.8, 136.8, 142.2, 145.3 (C). – MS (EI): m/z (%) = 357 (7) [M^+], 258 (13), 244 (100) [M^+ – C_8H_{17}], 219 (10), 206 (33). – $C_{26}H_{31}N$ (357.52): calcd. C 87.34, H 8.74, N 3.92; found C 87.27, H 8.71, N 4.08.

4-(3-{4′-[2-(*trans*-2-Ethyloxycyclopropyl)vinyl]biphenyl-4-yl}-bicyclo[1.1.1]pent-1-yl)butan-1-ol (25): A solution of **23gh** (115 mg, 0.24 mmol) in MeOH (5 mL) was stirred with the strongly acidic ion-exchange resin Lewatit SPS 118 (50 mg) for 16 h at room temp., filtered through Celite, and the filtrate was concentrated. Column chromatography of the residue (20 g of silica gel, column 15 × 2 cm, PE/Et_2O, 4:1) furnished **25** (69 mg, 72%) as an oil, R_f = 0.25. – ^{1}H NMR: δ = 0.73 (q, J = 6.1 Hz, 1 H, Cpr), 1.12–1.26 (m, 2 H, Cpr, OH), 1.20 (t, J = 7.0 Hz, 3 H, CH_3), 1.33–1.48 (m, 2 H, CH_2), 1.52–1.68 (m, 4 H, 2 CH_2), 1.92 (s, 6 H, 3 CH_2), 2.12 (m, 1 H, Cpr), 3.32 (ddd, J = 6.4, 3.7, 2.6 Hz, 1 H, Cpr), 3.58 (q, J = 7.0 Hz, 2 H, CH_2), 3.68 (q, J = 5.4 Hz, 2 H, CH_2), 5.06 (dd, J = 11.5, 10.0 Hz, 1 H, =CH), 6.37 (d, J = 11.5 Hz, 1 H, =CH), 7.26–7.32 (m, 2 H, C_6H_4), 7.46–7.58 (m, 6 H, C_6H_4). – ^{13}C NMR: δ = 15.1 (CH_3), 52.1 (3 CH_2), 15.9, 22.9, 31.5, 32.9, 62.4, 66.1 (CH_2), 19.6, 61.3, 126.4, 126.6, 126.7, 127.8, 129.0, 132.7 (CH), 38.9, 41.3, 136.4, 138.7, 139.2, 140.5 (C).

General Procedure (GP 10) for the Conversion of 23ff,fg to the Corresponding Bromides: To a stirred solution of triphenylphosphane (1.05 g, 4 mmol) in CH_2Cl_2 (15 mL), a solution of Br_2 (671 mg, 216 μL, 4.2 mmol) in CH_2Cl_2 (5 mL) was added at –10 °C. To this mixture, a solution of **23ff** or **23fg** (4 mmol) in CH_2Cl_2 (5 mL) was added over a period of 15 min at 0 °C. After stirring for 2 h at room temp., the mixture was diluted with CH_2Cl_2 (30 mL), washed with brine (20 mL), dried, and the solvent was evaporated. The residue was purified by column chromatography (50 g of silica gel, column 15 × 3 cm, hexane/EtOAc, 20:1).

1-(2-Bromoethyl)-3-(4′-ethylbiphenyl-4-yl)bicyclo[1.1.1]pentane (26ff): From **23ff** (1.60 g, 4.25 mmol), **26ff** (1.25 g, 83%) was obtained according to GP 10 as an oil, R_f = 0.52. – ^{1}H NMR: δ = 1.27 (t, J = 7.6 Hz, 3 H, CH_3), 2.01 (s, 6 H, 3 CH_2), 2.16 (t, J = 7.3 Hz, 2 H, CH_2), 2.69 (q, J = 7.6 Hz, 2 H, CH_2), 3.41 (t, J = 7.3 Hz, 2 H, $BrCH_2$), 7.26 (dd, J = 6.8, 1.6 Hz, 4 H, C_6H_4), 7.51 (dd, J = 8.2, 5.5 Hz, 4 H, C_6H_4). – ^{13}C NMR: δ = 15.6 (CH_3), 52.5 (3 CH_2), 28.5, 30.2, 35.0 (CH_2), 126.4, 126.8, 127.0, 128.2 (2 CH), 38.0, 41.9, 138.4, 139.4, 139.6, 143.2 (C). – $C_{21}H_{23}Br$ (355.3): calcd. C 70.99, H 6.52; found C 70.58, H 6.55.

1-(3-Bromopropyl)-3-(4′-ethylbiphenyl-4-yl)bicyclo[1.1.1]pentane (26fg): From **23fg** (11.05 g, 28.29 mmol), **26fg** (8.96 g, 86%) was obtained according to GP 10 as an oil, R_f = 0.50. – ^{1}H NMR: δ = 1.20 (t, J = 7.6 Hz, 3 H, CH_3), 1.58–1.70 (m, 2 H, CH_2), 1.75–1.95 (m, 2 H, CH_2), 1.87 (s, 6 H, 3 CH_2), 2.59 (q, J = 7.6 Hz, 2 H, CH_2), 3.38 (t, J = 6.8 Hz, 2 H, $BrCH_2$), 7.20 (dd, J = 8.1, 1.7 Hz, 4 H, C_6H_4), 7.44 (dd, J = 8.3, 1.8 Hz, 4 H, C_6H_4). – $C_{22}H_{25}Br$ (369.3): calcd. C 71.54, H 6.82; found C 71.31, H 6.76.

General Procedure (GP 11) for the Dehydrobromination of 26ff,fg: To a solution of sublimed *t*BuOK (1.23 g, 11 mmol) in anhydrous DMSO (100 mL), compound **26ff** or **26fg** (10 mmol) was added portionwise over a period of 40 min such that the temperature was maintained at 25 °C. After stirring for 12 h at room temp., the mixture was poured into ice-cold water (200 mL) and extracted with Et_2O (3 × 50 mL). The combined extracts were washed with H_2O (3 × 50 mL), dried, and the solvent was evaporated. The residue was purified by column chromatography (70 g of silica gel, column 15 × 3 cm, hexane/EtOAc, 30:1).

1-(4′-Ethylbiphenyl-4-yl)-3-vinylbicyclo[1.1.1]pentane (27ff): From **26ff** (1.066 g, 3 mmol), **27ff** (594 mg, 72%) was obtained according to GP 11, R_f = 0.70; m.p. 83–86 °C (MeOH). – ^{1}H NMR: δ = 1.33 (t, J = 7.6 Hz, 3 H, CH_3), 2.16 (s, 6 H, 3 CH_2), 2.70 (q, J = 7.6 Hz, 2 H, CH_2), 5.07 (dd, J = 10.4, 2.1 Hz, 1 H, =CH_2), 5.10 (dd, J = 17.2, 2.1 Hz, 1 H, =CH_2), 6.02–6.09 (m, 1 H, =CH), 7.35 (t, J = 8.4 Hz, 4 H, C_6H_4), 7.57 (dd, J = 8.2, 6.2 Hz, 4 H, C_6H_4). – ^{13}C NMR: δ = 15.6 (CH_3), 53.4 (3 CH_2), 28.5, 115.0 (CH_2), 126.5, 126.8, 127.0, 128.2 (2 CH), 137.6 (CH), 40.2, 41.3, 138.4, 139.4, 139.9, 143.2 (C).

1-(4′-Ethylbiphenyl-4-yl)-3-(prop-1-enyl)bicyclo[1.1.1]pentane (27fg) and 1-(3-*tert*-Butyloxypropyl)-3-(4′-ethylbiphenyl-4-yl)bicyclo-[1.1.1]pentane (28): From **26fg** (8.50 g, 23 mmol), **27fg** (3.32 g, 50%, E/Z = 77:23) and **28** (2.51 g, 30%) were obtained according to GP 11.

27fg: R_f = 0.63; m.p. 89–92 °C (MeOH). – ^{1}H NMR: δ = 1.27 (t, J = 7.6 Hz, 3 H, CH_3), 1.71 (dd, J = 6.0, 1.0 Hz, 3 H, CH_3, E), 1.76 (d, J = 5.3 Hz, 3 H, CH_3, Z), 2.07 (s, 6 H, 3 CH_2), 2.70 (q, J = 7.6 Hz, 2 H, CH_2), 5.52 (dq, J = 16.5, 6.0 Hz, 1 H, =CH, E), 5.67 (dd, J = 16.5, 1.0 Hz, 1 H, =CH, E), 7.20–7.30 (m, 4 H, C_6H_4), 7.45–7.55 (m, 4 H, C_6H_4). – $C_{22}H_{24}$ (288.4): calcd. C 91.61, H 8.39; found C 91.55, H 8.28.

28: R_f = 0.35; m.p. 85–86 °C (MeOH). – ^{1}H NMR: δ = 1.21 (s, 9 H, 3 CH_3), 1.27 (t, J = 7.6 Hz, 3 H, CH_3), 1.57 (m, 4 H, 2 CH_2), 1.92 (s, 6 H, 3 CH_2), 2.69 (q, J = 7.6 Hz, 2 H, CH_2), 3.36 (m, 2 H, OCH_2), 7.27 (dd, J = 7.8, 3.4 Hz, 4 H, C_6H_4), 7.50 (dd, J = 7.9, 3.6 Hz, 4 H, C_6H_4). – $C_{26}H_{34}O$ (362.4): calcd. C 86.13, H 9.45; found C 86.01, H 9.39.

3-Propylbicyclo[1.1.1]pentane-1-carbonyl Chloride (29): To a solution of **10b** (5.40 g, 35.0 mmol) in anhydrous Et_2O, oxalyl chloride (8.87 g, 6.0 mL, 69.9 mmol) was added dropwise at 20 °C followed by two drops of DMF. After stirring the solution for 30 min at this temp., the solvent was evaporated under reduced pressure and the residue was purified by bulb-to-bulb distillation at 45 °C (0.1 Torr) to give **29** (5.37 g, 89%) in almost pure form. – ^{1}H NMR: δ = 0.90 (t, J = 7.5 Hz, 3 H, CH_3), 1.20–1.35 (m, 2 H, CH_2), 1.48 (t, J = 7.4 Hz, 2 H, CH_2), 2.0 (s, 6 H, 3 CH_2). – ^{13}C NMR: δ = 14.1 (CH_3), 52.6 (3 CH_2), 19.5, 32.9 (CH_2), 40.0, 45.4, 171.0 (C).

1-Propyl-3-[4-(3-butylbicyclo[1.1.1]pent-1-yl)benzoyl]bicyclo[1.1.1]-pentane (30): To a solution of **20ca** (2.625 g, 9.40 mmol) in anhydrous Et_2O (100 mL), a 1.7 M solution of *t*BuLi in pentane (11.1 mL, 18.9 mmol) was added dropwise at –78 °C. After stirring for 1 h at this temp., **29** (2.12 g, 12.28 mmol) was added in a single portion and the reaction mixture was allowed to warm to room temp. It was stirred for a further 30 min at this temp. and then poured into cold 5% $NaHCO_3$ solution (50 mL). The layers were separated and the organic layer was washed with 5% $NaHCO_3$ solution and brine (20 mL each), dried, and concentrated. Column chromatography of the residue (100 g of silica gel, column 20 × 4 cm, hexane/Et_2O, 10:1) gave **30** (2.47 g, 78%) as an oil, R_f = 0.48. – ^{1}H NMR: δ = 0.85–1.00 (m, 6 H, 2 CH_3), 1.25–1.40 (m, 6 H, 3 CH_2), 1.40–1.55 (m, 4 H, 2 CH_2), 1.93 (s, 6 H, 3 CH_2), 2.15 (s, 6 H, 3 CH_2), 7.25

(d, J = 7.2 Hz, 2 H, C_6H_4), 7.95 (d, J = 7.2 Hz, 2 H, C_6H_4). – ^{13}C NMR: δ = 14.1, 14.3 (CH_3), 52.1, 53.3 (3 CH_2), 19.6, 22.8, 28.7, 31.2, 33.6 (CH_2), 126.0, 128.8 (2 CH), 39.2, 40.7, 41.4, 44.1, 134.6, 146.6, 197.4 (C). – $C_{24}H_{32}O$ (336.5): calcd. C 85.66, H 9.59; found C 85.92, H 9.43.

β-Chloro-4-(3-butylbicyclo[1.1.1]pent-1-yl)-α-(3-propylbicyclo[1.1.1]-pent-1-yl)styrene (31): To a suspension of chloromethyltriphenylphosphonium chloride (4.51 g, 13 mmol) in anhydrous THF (50 mL), a 2.33 M solution of BuLi in hexane (5.6 mL, 13 mmol) was added over a period of 20 min at –78 °C. After stirring for 30 min at this temp., a solution of **30** (1.88 g, 5.59 mmol) in Et_2O (20 mL) was added over 30 min and the resulting mixture was stirred for a further 30 min at –78 °C. It was then allowed to warm to room temp. and stirred for a further 4 h. Thereafter, H_2O (5 mL) was added and the resulting mixture was poured into an ice-cold Et_2O/H_2O mixture (100 mL + 100 mL). After separation of the layers, the organic layer was washed with H_2O and brine (50 mL each), dried, and the solvent was evaporated. The residue was then thoroughly extracted with hexane (100 mL) for 2 h. The resulting hexane solution was filtered, concentrated, and rapidly filtered through 60 g of silica gel (column 20 × 4 cm, hexane/Et_2O, 10:1) to give **31** (1.92 g, 93%, 5:1 mixture of isomers) as an oil, R_f = 0.68. – ^1H NMR (major isomer): δ = 0.88–1.05 (m, 6 H, 2 CH_3), 1.25–1.65 (m, 10 H, 5 CH_2), 1.95 (s, 6 H, 3 CH_2), 2.05 (s, 6 H, 3 CH_2), 6.03 (m, 1 H, =CH), 7.09 (d, J = 7.0 Hz, 2 H, C_6H_4), 7.15 (d, J = 7.0 Hz, 2 H, C_6H_4). – ^{13}C NMR: δ = 14.2, 14.4 (CH_3), 52.1, 53.3 (3 CH_2), 19.8, 22.9, 28.9, 31.4, 33.6 (CH_2), 125.7, 128.0 (2 CH), 116.4 (CH), 39.0, 40.5, 41.3, 42.0, 137.6, 140.8, 141.7 (C).

1-[4-(3-Butylbicyclo[1.1.1]pent-1-yl)phenyl]-2-(3-propylbicyclo[1.1.1]pent-1-yl)acetylene (32) and 4-(3-Butylbicyclo[1.1.1]-pent-1-yl)-α-(3-propylbicyclo[1.1.1]-pent-1-yl)styrene (33): A solution of chloroethylene **31** (1.85 g, 5 mmol) in anhydrous THF (50 mL) was treated with a 2.33 M solution of BuLi in hexane (2.36 mL, 5.5 mmol) and the mixture was stirred at room temp. for 12 h. It was then poured into ice-cold H_2O (30 mL) and the layers were separated. The organic layer was washed with H_2O and brine (10 mL each), dried, and the solvent was evaporated. The residue was separated by column chromatography (60 g of silica gel, column 20 × 3 cm, hexane) to give **32** (886 mg 53%) and **33** (159 mg, 9%).

32: R_f = 0.42; m.p. 93–95 °C. – ^1H NMR: δ = 0.90 (t, J = 7.1 Hz, 3 H, CH_3), 0.91 (t, J = 6.8 Hz, 3 H, CH_3), 1.20–1.60 (m, 10 H, 5 CH_2), 1.88 (s, 6 H, 3 CH_2), 2.00 (s, 6 H, 3 CH_2), 7.10 (d, J = 6.6 Hz, 2 H, C_6H_4), 7.32 (d, J = 6.6 Hz, 2 H, C_6H_4). – ^{13}C NMR: δ = 14.1, 14.3 (CH_3), 52.1, 54.8 (3 CH_2), 19.8, 22.9, 28.8, 31.3, 33.6 (CH_2), 125.9, 131.4 (2 CH), 38.5, 39.0, 41.4, 42.4, 79.5, 88.9, 121.0, 141.4 (C). – $C_{25}H_{32}$ (332.5): calcd. C 90.30, H 9.70; found C 90.21, H 9.63.

33: R_f = 0.55; oil. – ^1H NMR: δ = 0.85–1.10 (m, 6 H, 2 CH_3), 1.25–1.65 (m, 10 H, 5 CH_2), 1.89 (s, 6 H, 3 CH_2), 1.95 (s, 6 H, 3 CH_2), 5.08 (m, 1 H, =CH_2), 5.15 (m, 1 H, =CH_2), 7.20 (d, J = 7.0 Hz, 2 H, C_6H_4), 7.35 (d, J = 7.0 Hz, 2 H, C_6H_4). – ^{13}C NMR: δ = 14.2, 14.4 (CH_3), 52.1, 52.2 (3 CH_2), 19.9, 23.0, 28.9, 31.5, 34.0, 112.7 (CH_2), 125.7, 126.8 (2 CH), 39.0, 39.4, 41.4, 42.8, 138.8, 140.5, 148.7 (C).

Acknowledgments

This work was supported by the Deutsche Forschungsgemeinschaft (Project Me 405/15-3), the Fonds der Chemischen Industrie, and, by generous gifts of chemicals, the companies BASF AG, Bayer AG, Chemetall GmbH, Degussa, Hoechst, and Hüls AG. We are grateful to Dr. Burkhard Knieriem for his careful proofreading of the manuscript.

[1] [1a] J. Michl, in: *Applications of Organometallic Chemistry in the Preparation and Processing of Advanced Materials* (Eds.: J. E. Harrod, R. M. Laine), Kluwer, Dordrecht, The Netherlands, **1995**, p. 243 ff. – [1b] R. M. Harrison, T. F. Magnera, J. Vacek, J. Michl, in: *Modular Chemistry* (Ed.: J. Michl), Kluwer, Dordrecht, The Netherlands, **1997**, p. 1 ff. – [1c] J. Michl, P. Kaszynski, A. C. Friedli, G. S. Murthy, H.-C. Yang, R. E. Robinson, N. D. McMurdie, T. Kim, in: *Strain and Its Implications in Organic Chemistry* (Eds.: A. de Meijere, S. Blechert), NATO ASI Ser. C, Kluwer Academic Publishers, Dordrecht, The Netherlands, **1989**, vol. 273, p. 463–482.

[2] K. B. Wiberg, *Angew. Chem.* **1986**, *98*, 312–322; *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 312–322.

[3] [3a] P. Kaszynski, J. Michl, in: *Advances in Strain in Organic Chemistry* (Ed.: B. Halton), JAI Press Ltd., Greenwich, **1995**, vol. 4, pp. 283–311, and references cited therein. – [3b] M. D. Levin, P. Kaszynski, J. Michl, *Chem. Rev.* **2000**, *100*, 169–234.

[4] [4a] P. Kaszynski, A. C. Friedli, J. Michl, *J. Am. Chem. Soc.* **1992**, *114*, 601–620, and references cited therein. – [4b] P. Kaszynski, A. C. Friedli, N. D. McMurdie, J. Michl, *Mol. Cryst., Liq. Cryst*. **1990**, *191*, 193–197.

[5] K. B. Wiberg, D. S. Connor, *J. Am. Chem. Soc.* **1966**, *88*, 4437–4442.

[6] [6a] K. Semmler, G. Szeimies, J. Belzner, *J. Am. Chem. Soc.* **1985**, *107*, 6410–6411. – [6b] J. Belzner, U. Bunz, K. Semmler, G. Szeimies, K. Opitz, A.-D. Schlüter, *Chem. Ber.* **1989**, *122*, 397–398. – [6c] F. Alber, G. Szeimies, *Chem. Ber.* **1992**, *125*, 757–758.

[7] K. B. Wiberg, F. H. Walker, *J. Am. Chem. Soc.* **1982**, *104*, 5239–5240.

[8] [8a] E. W. Della, D. K. Taylor, *J. Org. Chem*. **1994**, *59*, 2986–2996, and references cited therein. – [8b] K. M. Lynch, W. P. Daily, *J. Org. Chem*. **1995**, *60*, 4666–4668.

[9] For several recent communications, see: [9a] C. Mazal, A. J. Paraskos, J. Michl, *J. Org. Chem*. **1998**, *63*, 2116–2119. – [9b] S. Mazieres, M. K. Raymond, G. Raabe, A. Prodi, J. Michl, *J. Am. Chem. Soc*. **1997**, *119*, 6682–6683. – [9c] K. P. Dockery, W. G. Bentrude, *J. Am. Chem. Soc*. **1997**, *119*, 1388–1399. – [9d] W. Adcock, G. T. Binmore, A. R. Krstic, J. C. Walton, J. Wilkie, *J. Am. Chem. Soc*. **1995**, *117*, 2758–2766. – [9e] E. W. Della, I. J. Lochert, *Org. Prep. Proc. Int*. **1996**, *28*, 411–442. – [9f] J. T. Banks, K. U. Ingold, E. W. Delly, J. C. Walton, *Tetrahedron Lett*. **1996**, *37*, 8059–8060. – [9g] R. Pellicciary, M. Raimondo, M. Marinozzi, B. Natalini, G. Constyntino, C. Tompsen, *J. Med. Chem*. **1996**, *39*, 2874–2876. – [9h] J. D. D. Rehm, B. Ziemer, G. Szeimies, *Eur. J. Org. Chem*. **1999**, 2079–2085.

[10] K. B. Wiberg, S. T. Waddell, *J. Am. Chem. Soc.* **1990**, *112*, 2194–2216, and references cited therein.

[11] K. B. Wiberg, *Acc. Chem. Res.* **1984**, *17*, 379–386. K. B. Wiberg, *Chem. Rev.* **1989**, *89*, 975–983.

[12] [12a] G. Szeimies in: *Advances in Strain in Organic Chemistry* (Ed.: B. Halton), JAI Press Ltd., Greenwich, **1992**, vol. 2, pp. 1–51, and references cited therein. – [12b] P. Kaszynski, J. Michl, in: *The Chemistry of the Cyclopropyl Group* (Ed.: Z. Rappoport), Wiley, New York, **1995**, vol. 2, p. 773 ff.

[13] [13a] J. Michl, P. Kaszynski, N. D. McMurdie, *J. Org. Chem*. **1991**, *56*, 307–316. – [13b] N. S. Zefirov, L. S. Surmina, N. K. Sadovaya, A. V. Blokhin, M. A. Tyurekhodzhaeva, Yu. N. Bubnov, L. I. Lavrinovich, A. V. Ignatenko, Yu. K. Grishin, O. A. Zelenkina, N. G. Kolotyrkina, S. V. Kudrevich, A. S. Koz′min, *Zh. Org. Khim*. **1990**, *26*, 2317–2333; *J. Org. Chem. USSR (Engl. Transl.)* **1990**, *26*, 2002–2014.

[14] J. Belzner, Dissertation, Universität München, **1988**.

[15] M. Messner, Dissertation, Universität Hamburg, **1992**.

[16] [16a] P. K. Freeman, L. L. Hutchinson, *J. Org. Chem*. **1983**, *48*, 4705–4708, and references cited therein. – [16b] E. W. Della, H. Gangodawila, P. E. Pigou, *J. Org. Chem*. **1988**, *53*, 592–596. – [16c] Direct radical substitution of an iodine atom with formation of a C–C bond was observed when MeLi or *n*BuLi were used for the lithiation of bicyclo[1.1.1]pentyl iodides of type **8**: J. L. Adcock, A. A. Gakh, *J. Org. Chem*. **1992**, *57*, 6206–6210.

[17] G. Szeimies in: *Strain and Its Implications in Organic Chemistry*

(Eds.: A. de Meijere, S. Blechert), NATO ASI Ser. C, Kluwer Academic Publishers, Dordrecht, The Netherlands, **1989**, vol. 273, p. 361–381.

[18] K. Tamao, K. Sumitani, Y. Kiso, M. Zembayashi, A. Fujioka, S. I. Kodama, I. Nakajima, A. Minato, M. Kumada, *Bull. Chem. Soc. Jpn.* **1976**, *49*, 1958–1969.

[19] The staffane **16a** has recently been prepared by practically the same catalytic procedure in 20–40% yield. A much better result (66%) was obtained by oxidative coupling of the bridgehead cuprates.[9a]

[20] T. B. Patrick, K. K. Johri, D. H. White, W. S. Bertrand, R. Mokhtar, M. R. Kilbourn, M. J. Welch, *Can. J. Chem*. **1986**, *64*, 138–141.

[21] Commercial $ZnCl_2$ was twice melted in vacuo (0.1 Torr), recrystallized from anhydrous THF, and dried for 4 h at 20 °C/ 0.1 Torr. NMR analysis of a precisely weighed sample (D_2O, DMSO as internal reference) indicated the product to have the composition $ZnCl_2 \cdot THF$. This complex is much more soluble in THF than pure $ZnCl_2$ and was used in all transmetallations for further coupling experiments.

[22] T. Hayashi, M. Konishi, Y. Kobori, M. Kumada, T. Higuchi, K. Hirotsu, *J. Am. Chem. Soc.* **1984**, *106*, 158–163, and references cited therein.

[23] [23a] M. A. Tius, X. Gu, J. W. Truesdell, S. Savariar, P. P. Crooker, *Synthesis* **1988**, 36–40. – [23b] M. Hird, G. W. Gray, K. J. Toyne, *Mol. Cryst., Liq. Cryst*. **1991**, *206*, 187–204.

[24] [24a] V. N. Kalinin, *Synthesis* **1992**, 413–432, and references cited therein. – [24b] E. Negishi, F. T. Luo, R. Frisbee, H. Matsuhita, *Heterocycles* **1982**, *18*, 117–122. – [24c] T. Sakamoto, S. Nishimura, Y. Kondo, H. Yamanaka, *Synthesis* **1988**, 485–486.

[25] K. A. Walker, L. J. Markoski, J. S. Moore, *Synthesis* **1992**, 1265–1268.

[26] [26a] Q. Y. Chen, Y. B. He, *Tetrahedron Lett.* **1987**, *28*, 2387–2388. – [26b] V. Snieckus, J. M. Fu, *Tetrahedron Lett*. **1990**, *31*, 1665–1668. – [26c] J. M. Saa, G. Martorell, A. Garsia-Raso, *Tetrahedron Lett*. **1990**, *31*, 2357–2360.

[27] The appropriately substituted arylpyrimidines, phenols, and oligofluorinated compounds were kindly supplied by Hoechst AG and the Chisso Petrochemical Corporation, respectively. We are indebted to Dr. R. Wingen and Dr. R. Tarao for this support.

[28] [28a] R. Eidenschink, D. Erdmann, J. Krause, L. Pohl, *Angew. Chem*. **1977**, *89*, 103; *Angew. Chem. Int. Ed. Engl*. **1977**, *16*, 100. – [28b] G. W. Gray, S. M. Kelly, *J. Chem. Soc., Perkin Trans. 2* **1981**, 26–31.

[29] U. Bunz, G. Szeimies, *Tetrahedron Lett*. **1989**, *30*, 2087–2088.

[30] M. I. Al-Hassan, *J. Organomet. Chem*. **1989**, *372*, 183–186.

[31] See, e.g., an application of this method for the first preparation of dicyclopropylacetylene: G. Köbrich, D. Merkel, *Angew. Chem*. **1970**, *82*, 257–258; *Angew. Chem. Int. Ed. Engl*. **1970**, *9*, 243–244.

[32] The incorporation of a bicyclo[1.1.1]pentyl unit into a molecule leads to an increase of the liquid crystal transition temperatures and to lowering of the clearing points. For selected results, see: [32a] A. de Meijere, M. Messner, V. Vill, *Mol. Cryst., Liq. Cryst*. **1994**, *257*, 161–167. – [32b] A. de Meijere, M. Messner, S. I. Kozhushkov, D. Demus, K. Kobayashi, K. Miyazawa, S. Matsui, H. Hiroyuki (Chisso Petrochemical), Jpn. Pat. Appl. 97/ 44,615, 13.02.1997; PCT Int. Appl. WO 98 35,924, 20.08.1998; *Chem. Abstr*. **1998**, *129*, 223643t.

[33] L. Paquette, A. M. Doherty, C. M. Rayner, *J. Am. Chem. Soc.* **1992**, *114*, 3910–3926.

[34] S. Hartmann, D. N. Minnikin, H.-J. Röming, M. S. Baird, C. Ratledge, P. R. Wheeler, *Chem. Phys. Lipids* **1994**, *71*, 99–108.

[35] K. Mori, *Tetrahedron* **1974**, *30*, 3817–3820.

[36] G. W. Gray, M. Hird, B. Lacey, K. J. Toyne, *J. Chem. Soc., Perkin Trans. 2* **1989**, 2041–2053.

[37] G. W. Gray, A. Mosley, *J. Chem. Soc., Perkin Trans. 2* **1976**, 97–102.

[38] P. A. A. Klusener, J. C. Hanekamp, L. Brandsma, P. v. R. Schleyer, *J. Org. Chem.* **1990**, *55*, 1311–1321.

[39] G. McGaffin, A. de Meijere, *Synthesis* **1994**, 583–591.

[40] [40a] Y. Tamary, H. Ochiai, F. Sanda, Z. Yoshida, *Tetrahedron Lett*. **1985**, *26*, 5529–5532. – [40b] T. A. Shustrova, E. M. Auvinen, E. V. Vasil′eva, I. A. Favorskaya, *Zh. Org. Khim*. **1981**, *17*, 329–332; *J. Org. Chem. USSR (Engl. Transl.)* **1981**, *17*, 277–279.

[41] N. Morisaki, H. Funabashi, J. Furukawa, R. Shimazawa, A. Kanematsu, *Chem. Pharm. Bull*. **1992**, *40*, 2945–2953.

[42] [42a] M. F. Ausell, J. C. Emmett, R. V. Coombs, *J. Chem. Soc. C* **1968**, 217–225. – [42b] M. V. Bhatt, S. U. Kulharni, *Synthesis* **1983**, 269–275. – [42c] A. Claesson, *Acta Chem. Scand., Ser. B* **1974**, *28*, 993–997. – [42d] K. Fujita, E. Moret, M. Schlosser, *Chem. Lett*. **1982**, 1819–1822.

[43] E. J. Corey, S. G. Pyne, W. Su, *Tetrahedron Lett*. **1983**, *24*, 4883–4886.

[44] H. N. Rydon, *Org. Synth*. **1971**, *51*, 44–47.

[45] K. B. Wiberg, N. McMurdie, *J. Am. Chem. Soc*. **1994**, *116*, 11990–11998.

[46] [46a] E. W. Della, P. E. Pigou, C. H. Schiesser, D. K. Taylor, *J. Org. Chem.* **1991**, *56*, 4659–4664. – [46b] T. B. Patrick, S. Khazaeli, S. Nadji, K. Hering-Smith, D. Reif, *J. Org. Chem.* **1993**, *58*, 705–708.

[47] M. D. Kurtis, A. L. Allred, *J. Am. Chem. Soc*. **1965**, *87*, 2254–2563.

Received October 8, 1999
[O99560]