Novel Liquid Crystalline Compounds Containing Bicyclo[3.1.0]hexane Core Units[‡]

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Dedicated to Professor Reinhard W. Hoffmann on the occasion of his 70th birthday

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Additions of ethyl or *tert*-butyl diazoacetates to 4-substituted cyclopentenes **6** and **17** under dirhodium tetraacetate/tetraoctanoate catalysis led to mixtures of *tert*-butyl *endo*,*exo*- and *exo*,*exo*-3-carboxyl(aryl)bicyclo[3.1.0]hexane-6-carboxylates **7** and **18** in yields of 54–90% from which *exo*,*exo*-diastereomers were isolated in yields of 39–63%. Diester *exo*,*exo*-**7** was saponified and converted into diaryl diesters *exo*,*exo*-**9a**,**b** in overall yields of 42 and 46%, respectively. The esters *exo*,*exo*-**18** were reduced to the corresponding hydroxymethyl derivatives, these were transformed to the iodomethyl compounds which in turn were coupled with various alkylmagnesium halides, via Li_2CuCl_4 catalysis, to give 3-aryl-6-alkylbicyclo[3.1.0]hexyl derivatives *exo*,*exo*-**21** in overall yields of 72–83%. Fluorinated 3-(2-arylethyl)-6-pentylbicyclo[3.1.0]hexane *exo*,*exo*-**32** could be prepared in five steps from 4-ethoxy-2,3-difluorobenzaldehyde **26a** adopting essentially the same synthetic strategy, but in an overall yield of only 8%, and 6-(4-cyanophenyl)-3-pentylbicyclo[3.1.0]hexane *exo*,*exo*-**38b** was obtained by $Pd(OAc)_2$ catalyzed cyclopropanation of 4-pentylcyclopentene **34b** with (4-cyanophenyl)diazomethane **36b** in 29% yield. A comparison of the liquid crystalline properties of these newly prepared compounds containing a bicyclo[3.1.0]hexane core with those of the known analogous compounds with a cyclohexane fragment shows that as a rule, a bicyclo[3.1.0]hexane moiety decreases the transition temperature, while the dielectric ($\Delta\varepsilon$) and optical (Δn) anisotropies are comparable. However, the bicyclo[3.1.0]hexane unit has a poorer mesogenic potential.

Introduction

Starting from the first observations of the phenomenon of liquid crystallinity by Reinitzer in 1888[1a] and by Lehmann in 1889,[1b] the design and preparation of molecules possessing liquid crystalline properties has been of interest to physical-organic chemists for a long time, and it is difficult to name any another branch of synthetic organic chemistry which continues to develop so impetuously.[2] Among the liquid crystalline compounds, cyclopropane derivatives, especially 1,2-disubstituted cyclopropanes, provide more rigid conformations than those with similar alkyl groups that are widely used as fragments in liquid crystalline compounds. The first example of such a compound with a cyclopropane ring appeared as early as 1971[3] and, according to the database LiqCryst4.4,[4] more than 85,000 such compounds have been synthesized to date. However, no liquid crystalline compound of type **1** with a 3,6-disubstituted bicyclo[3.1.0]hexane moiety is listed among them.

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According to MOPAC/AM1 calculations, such compounds have molecular shapes similar to analogues with a 1,4-disubstituted cyclohexane moiety and, because of the

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former being slimmer, they might have superior mesogenic properties.[5] These predictions prompted us to embark on a program to prepare such compounds and test their properties.

Results and Discussion

Preparation

No general synthetic approach to 3,6-disubstituted bicyclo[3.1.0]hexanes **1** has been reported, except for several low-yielding non-selective reactions.[6] The first liquid crystalline compound with such a skeleton was an aza analogue, a Schiff's base of 3-substituted (3-azabicyclo[3.1.0]hexyl)-amine **5**, which was prepared in 2000[7] by applying the Kulinkovich-de Meijere[8,9] reductive aminocyclopropanation to *N*-arylpyrroline **4**, which was obtained from (*Z*)-1,4-bis-(methanesulfonyloxy)but-2-ene (**2**)[10] and aniline, as a key step (Scheme 1). Indeed, this compound did demonstrate better liquid crystalline properties than its analogues with a 1,4-disubstituted cyclohexane instead of the 3-azabicyclo[3.1.0]hexane moiety.[7] However, due to the fact that compounds of the type **5** are not chemically inert and are poorly soluble in standard liquid crystalline base mixtures, they cannot be practically applied. Therefore, synthetic approaches to analogous compounds with an all-carbon framework were developed.

The first model compound with a bicyclo[3.1.0]hexane skeleton was prepared by utilizing a dirhodium tetraacetate-catalyzed cyclopropanation[11] with ethyl diazoacetate to the known *tert*-butyl cyclopent-3-ene-1-carboxylate (**6**)[12] as a key step. After chromatographic separation, the main diastereomer *exo*,*exo*-**7**, isolated in 64% yield, was saponified and converted into diaryl diesters *exo*,*exo*-**9a** and *exo*,*exo*-**9b** in yields of 42 and 46%, respectively, applying established procedures (Scheme 1). An X-ray crystal structure analysis of the diester **9a** confirmed the *exo*,*exo*-orientation of the substituents on the bicyclo[3.1.0]hexane skeleton (Figure 1). Both diesters **9a** and **9b** exhibit liquid crystalline properties (see below), yet they could not be considered for practical applications due to the lack of chemical inertness of the two ester groups.

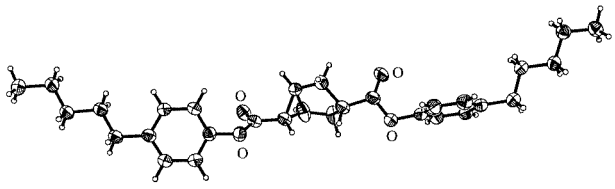
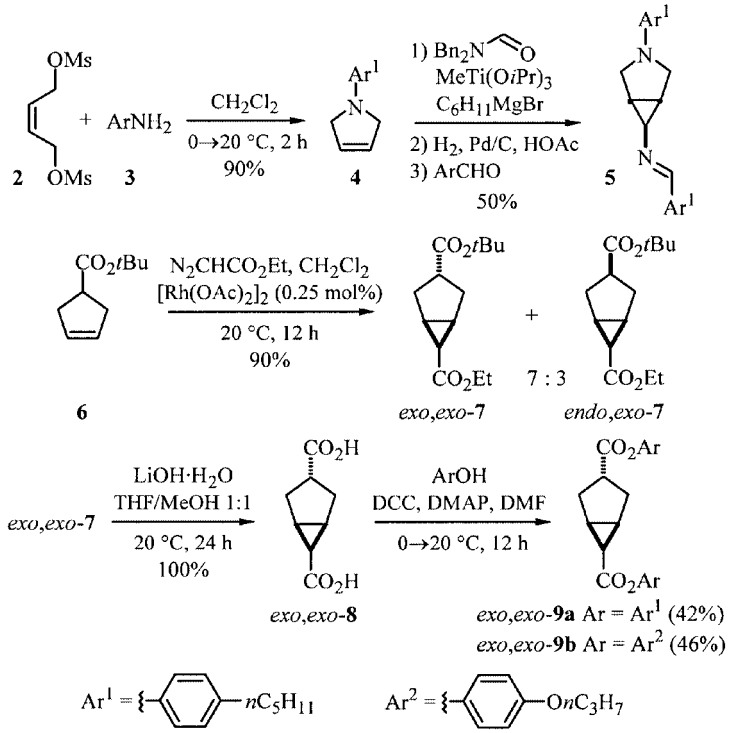
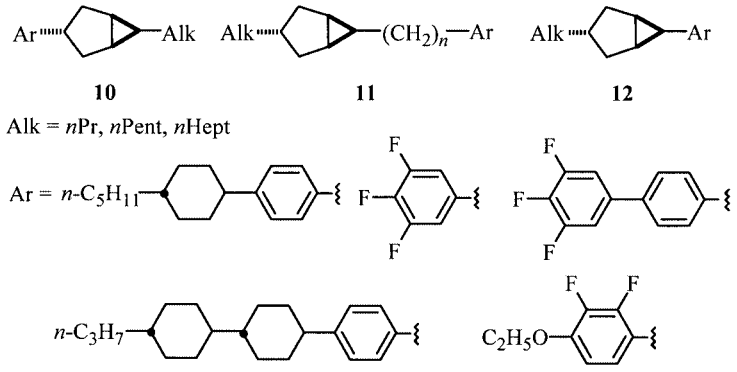


Figure 1. Structure of bis(*p*-pentylphenyl) *exo*,*exo*-bicyclo[3.1.0]-hexane-3,6-dicarboxylate (*exo*,*exo*-**9a**) in the crystal[13]

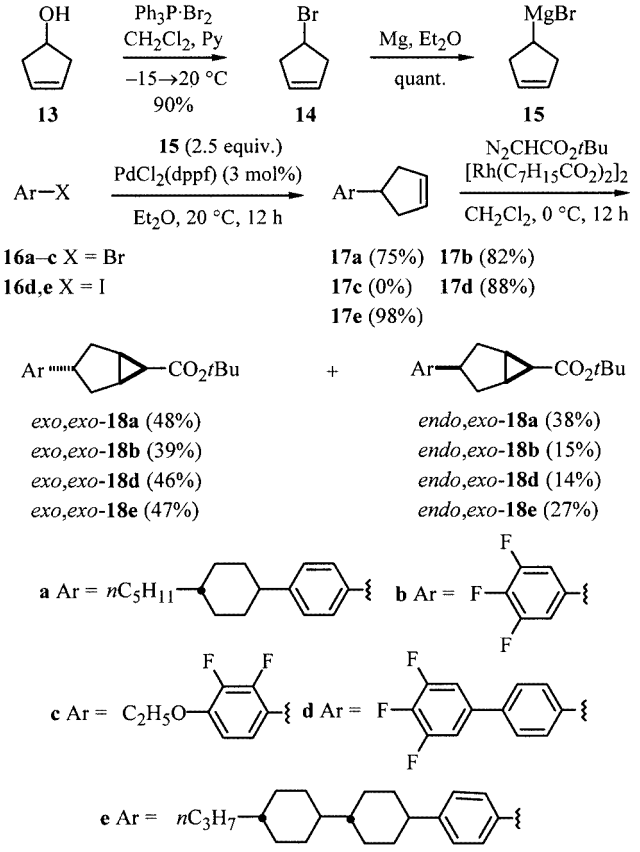
However, the observed stereoselectivity of the rhodium catalyzed cyclopropanation of 4-substituted cyclopentenes with an alkyl diazoacetate demonstrated that this reaction could also be applied to the synthesis of more elaborate *exo*,*exo*-3,6-disubstituted bicyclo[3.1.0]hexane derivatives of types **10**−**12** containing typical moieties commonly applied for liquid crystalline compounds.[14]



Scheme 1. Syntheses of 3-aryl-6-*exo*-(arylmethyleneamino)-3-azabicyclo[3.1.0]hexane **5** and diaryl bicyclo[3.1.0]hexane-3,6-dicarboxylates **9a**,**b**



The first synthetic challenge en route to compounds of type **10**, i.e. the synthesis of appropriate 4-arylcyclopentenes **17**, was overcome by a palladium-catalyzed [$PdCl_2$(dppf)][15] cross-coupling reaction[16] of appropriately substituted aryl halides **16** with the Grignard reagent prepared from cyclopenten-4-yl bromide (**14**)[17] (Scheme 2). The bromide **14** was prepared by conversion of cyclopent-3-en-1-ol (**13**)[18] with $Ph_3P{\cdot}Br_2$ in 90% yield.



Scheme 2. Preparation of 4-arylcyclopentenes **17** and their dirhodium tetraoctanoate catalyzed cyclopropanation with *tert*-butyl diazoacetate

Using such cross coupling, the 4-arylcyclopentenes **17a**−**e** were obtained in yields of 75−98%, except for **17c** because the treatment of **15** with the aryl bromide **16c** gave only the homocoupling product from **16c**, presumably via an arylmagnesium bromide initially formed by a Grignard exchange reaction.

Dirhodium tetraoctanoate catalyzed cyclopropanation of these 4-arylcyclopentenes **17** with *tert*-butyl diazoacetate[19] led, in spite of the bulky substituent on the diazoacetate and the bulky catalyst, only to a moderate excess of the desired *exo*,*exo*-diastereomers *exo*,*exo*-**18**, which were isolated in yields of 39−48% after crude chromatographic separation followed by recrystallization from methanol (Scheme 2).

The configurational assignments rest on the ^{1}H NMR spectra and on X-ray structural analyses of the esters *endo*,*exo*-**18a** and *exo*,*exo*-**18b** (Figure 2).

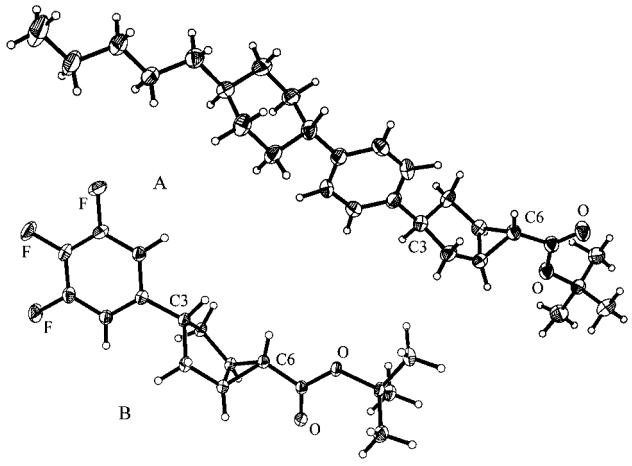
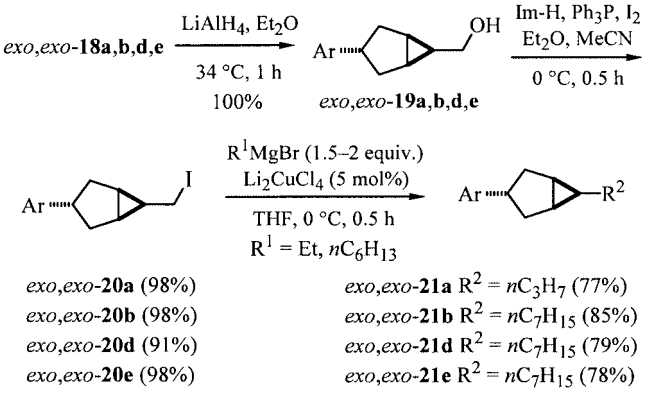


Figure 2. Structures of *tert*-butyl esters *endo*,*exo*-**18a** (A) and *exo*,*exo*-**18b** (B) in the crystal[13]

A comparison of these two structures reveals an interesting feature in that the main difference between these two molecules in the solid phase is the conformation of the five-membered ring. Apparently, the bulky aryl substituents strive for a quasi-equatorial position on the cyclopentane ring in both the *endo*,*exo*-**18a** and the *exo*,*exo*-**18b**. As a result, the bicyclo[3.1.0]hexane moiety in *endo*,*exo*-**18a** adopts a chair-like conformation, while in *exo*,*exo*-**18b** it prefers the boat-like shape that prevails in unsubstituted bicyclo[3.1.0]hexane according to both experimental[20] and computational results.[21] Therefore, the configuration at carbon atom C3 may be of secondary importance for the

achievement of a rod-like shape of the molecule in contrast to the configuration at C6.

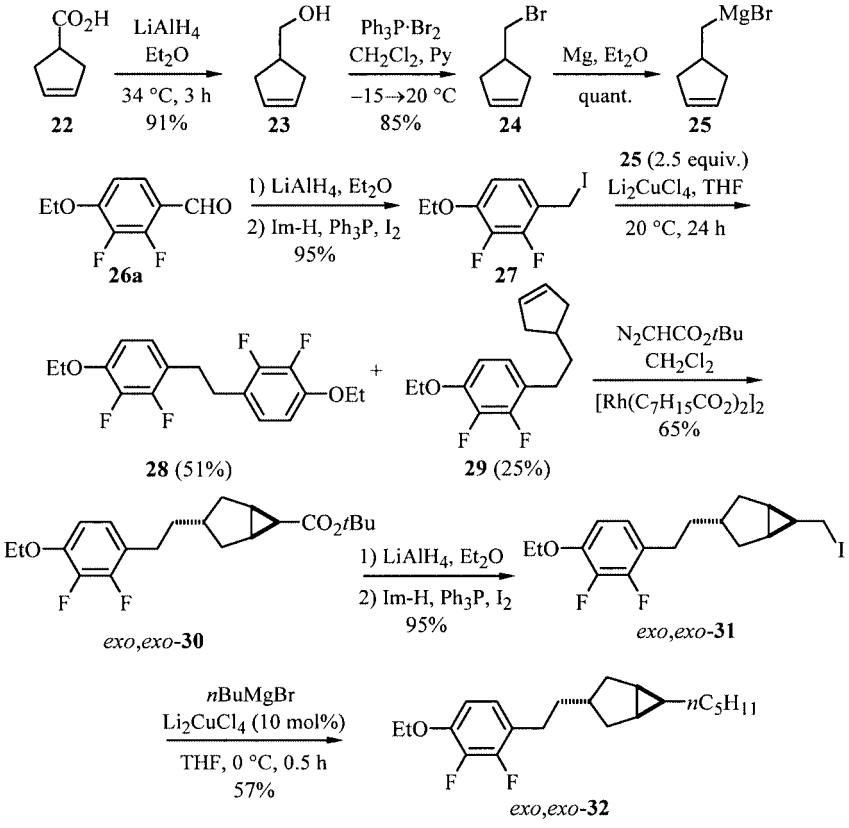
The transformation of the *tert*-butoxycarbonyl group in **18** into an alkyl moiety was achieved in three steps by reduction to the hydroxymethyl derivatives **19**, their subsequent conversion into the iodomethyl derivatives **20** and finally Li_2CuCl_4 catalyzed cross-coupling with various alkylmagnesium bromides[22a] according to the protocol of Nicolaou et al.[22b] (Scheme 3). Thus, the 6-alkyl-3-arylbicyclo[3.1.0]hexane derivatives **21a**, **21b**, **21d**, and **21e** were prepared from the corresponding esters in overall yields of 75, 83, 72 and 76%, respectively.



Scheme 3. Preparation of 6-alkyl-3-arylbicyclo[3.1.0]hexane derivatives **21** as potentially liquid crystalline compounds of the type **10**

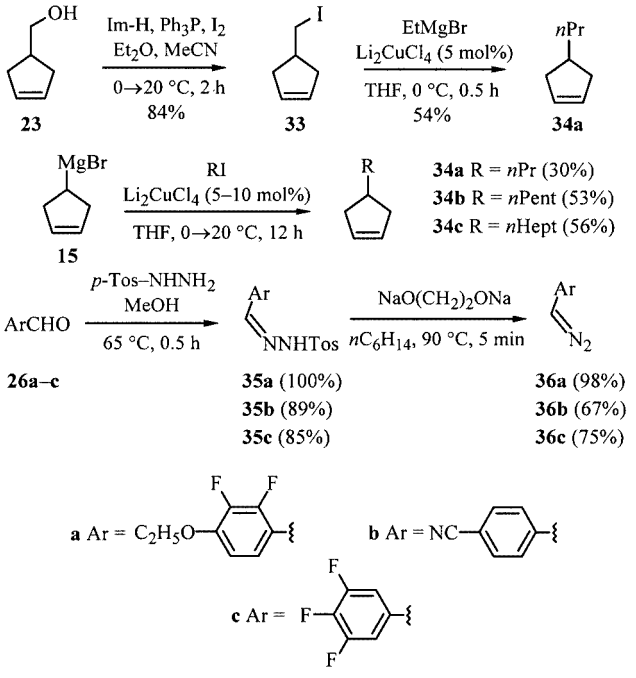
This synthetic protocol did not work quite as well for the preparation of *exo*,*exo*-3-[2-(4-ethoxy-2,3-difluorophenyl)-ethyl]-6-pentylbicyclo[3.1.0]hexane (*exo*,*exo*-**32**) because the Li_2CuCl_4 catalyzed cross coupling of 1-ethoxy-2,3-difluoro-4-(iodomethyl)benzene (**27**) (prepared in two steps from the corresponding aldehyde **26a** in 95% overall yield) with cyclopent-4-ylmagnesium bromide (**25**) [prepared in three steps from the commercially available cyclopent-3-enecarboxylic acid (**22**) in 77% overall yield] furnished the target product **29** in 25% yield only (Scheme 4) along with the homocoupling product **28** (51% yield). The former was converted into *exo*,*exo*-**32** according to the synthetic sequence described above i.e. dirhodium tetraoctanoate catalyzed cyclopropanation with *tert*-butyl diazoacetate to give *exo*,*exo*-**30**, its reduction to the hydroxymethyl compound, conversion into the iodomethyl derivative *exo*,*exo*-**31** and eventually Li_2CuCl_4 catalyzed cross coupling with *n*-butylmagnesium bromide with an overall yield of 35% (Scheme 4).

The most convenient approach to 3-alkyl-6-arylbicyclo[3.1.0]hexanes of type **12** would be by direct cyclopropanation of appropriately 4-substituted cyclopentenes **34** with aryldiazomethanes **36**. In spite of an inexhaustible number of cyclopropanations with diazomethane itself, especially via $Pd(OAc)_2$ catalysis,[23] there are only 75 examples of corresponding cyclopropanations with aryldiazomethanes. Most of these reactions have been performed under photolytic conditions[24] or by catalysis with ZnX_2,[25]

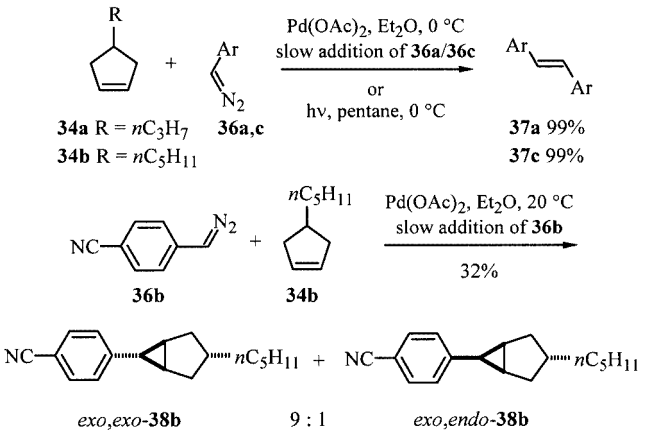


Scheme 4. Preparation of the 3-(2-arylethyl)-6-pentylbicyclo[3.1.0]hexane derivative *exo*,*exo*-**32** as a potentially liquid crystalline compound of type **11**

CuBr[26] or $[Rh(OAc)_2]_2$ in pentamethylene sulfide[27] furnishing the corresponding aryl-substituted cyclopropanes in moderate to good[27] yields. In view of the intended approach to potentially liquid crystalline compounds of type **12**, the corresponding 4-alkylcyclopentenes **34a**–**c** were prepared by cross-coupling reactions of alkyl iodides with cyclopentenylmagnesium bromide **15** or of 4-(iodomethyl)-cyclopentene (**33**) with ethylmagnesium bromide (Scheme 5) catalyzed by Li_2CuCl_4. The yields in both approaches were only moderate (30–56%). The necessary aryldiazomethanes **36a**–**c** were obtained from the corresponding tosylhydrazones **35** using an established procedure.[28]



Scheme 5. Synthesis of the main building blocks for the potentially liquid crystalline compounds of type **12**



Scheme 6. Preparation of *exo*,*exo*- and *exo*,*endo*-6-(4-cyanophenyl)-3-pentyl-bicyclo[3.1.0]hexane (*exo*,*exo*-**38b** and *exo*,*endo*-**38b**) as potentially liquid crystalline compounds of the type **12**

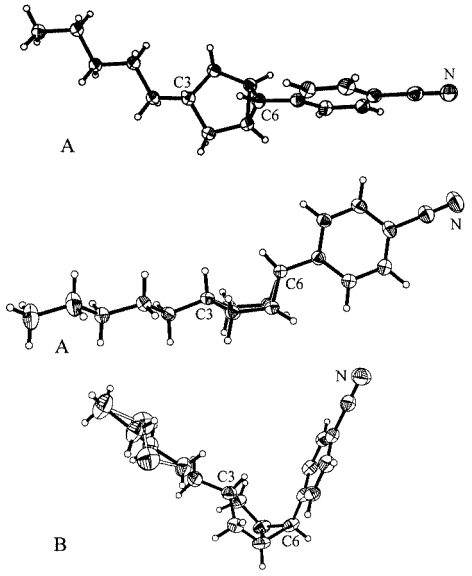


Figure 3. Structure of compounds *exo*,*exo*-**38b** (A) and *exo*,*endo*-**38b** (B) in the crystal.[13]

Unfortunately, irradiation of aryldiazomethanes **36a**,**c** in pentane solutions of the cyclopentenes **34a**,**b** as well as slow additions of **36a**,**c** to ethereal solutions of **34a**,**b** in the presence of palladium(II) acetate gave *trans*-stilbenes **37a**,**c** as the sole products in almost quantitative yield (Scheme 6).

However, upon slow addition of aryldiazomethane **36b** to an ethereal solution of 4-pentylcyclopentene (**34b**) in the presence of palladium(II) acetate (7 mol %) the target molecule **38b** was obtained, albeit in 32% yield only, as a 9:1 mixture of *exo*,*exo*-**38b** and *exo*,*endo*-**38b** which was separated by HPLC. Contrary to the cyclopropanation products obtained with *tert*-butyl diazoacetate (Scheme 2), these two diastereomers of **38b** differ with respect to the orientation of the substituent on the three-membered ring, while the *n*-pentyl group is *exo* on the five-membered ring in both molecules. The configurations at carbon atoms C3 and C6 in these compounds were established beyond all reasonable doubt by X-ray crystal structure analyses (Figure 3).

As in the potentially liquid crystalline compounds *endo*,*exo*-**18a** and *exo*,*exo*-**18b** (see Figure 2), the substituent on the cyclopentane ring (this time *n*-pentyl) adopts a quasi-equatorial position in both *exo*,*exo*-**38b** and *exo*,*endo*-**38b**, while the bicyclo[3.1.0]hexane unit adopts a boat-like conformation. However, the orientation of the *p*-cyanophenyl substituent on the three-membered ring determines the overall shape of the molecule. Whereas *exo*,*exo*-**38b** is more rod-like, its diastereomer *exo*,*endo*-**38b** is more horseshoe-shaped. Surprisingly, a search for substituted bicyclo[3.1.0]-hexanes in the Cambridge Crystallographic Database[29] displayed only 14 such molecules, and only one of them[30] was a 3,6-disubstituted specimen. The analyses of the previously reported molecular structures as well as of the ones described here reveal some interesting features. First of all, the conformational flexibility of the bicyclo[3.1.0]hexane skeleton is noteworthy. Depending on the position and nature of the substituents, the skeleton can adopt the whole

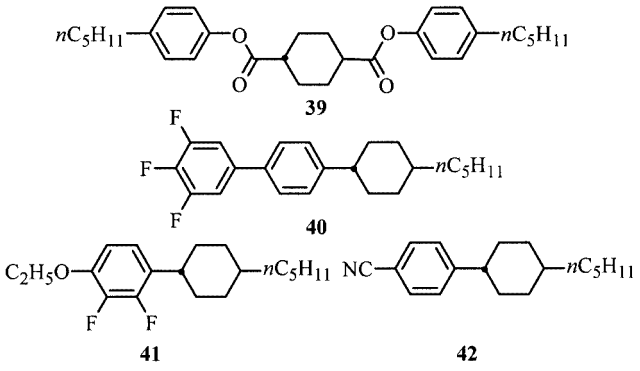
range of conformations from "chair-like" as in *endo*,*exo*-**18a** to "boat-like" as in the unsubstituted bicyclo[3.1.0]hexanes[20,21] and in the other derivatives reported here. The dihedral angles between planes C1−C2−C4−C5 and C2−C3−C4 vary from −35.0 to 39.9°, while that for the unsubstituted bicyclo[3.1.0]hexane was previously found to be 25.2 ± 2.8°.[20b] Interestingly, in all the newly prepared substituted compounds, substituents on C3 occupy a quasi-equatorial position on the cyclopentane ring and the configuration at C3 is therefore not crucial for the molecule to achieve a rod-like shape (cf. *endo*,*exo*-**18a** and *exo*,*exo*-**18b**, Figure 2). However, the change of the substituent orientation on C6 from *exo* to *endo* as in *exo*,*endo*-**38b** is accompanied by a change in the overall molecular shape from rod-like to horseshoe-like. The orientation of planar (aryl or carboxyl) substituents on C6 is normal for alkyl- and carboxyl-substituted cyclopropanes,[31] and is either perpendicular as in *exo*,*endo*-**38b** or bisected as in *exo*,*exo*-**38b** and carboxyl-substituted compounds.

In order to quantify the energetic effect of a 3-aryl substituent on the molecular shape in bicyclo[3.1.0]hexanes **9a**, *endo*,*exo*-**18a**, *exo*,*exo*-**18b**, *exo*,*endo*-**38b**, and *exo*,*exo*-**38b**, the heats of formation of unsubstituted bicyclo[3.1.0]hexane, *endo*-3-phenylbicyclo[3.1.0]hexane, and *exo*-3-phenylbicyclo[3.1.0]hexane were calculated using the DFT method (B3LYP)[32] with the 6−31G** basis set. As found by various computations before,[21,33] bicyclo[3.1.0]hexane prefers a boat-like over a chair-like conformation with $\Delta\Delta H$ = 3.1−3.3 kcal·mol^{-1}, which is consistent with experimental results.[20] For *endo*-3-phenylbicyclo[3.1.0]hexane (as a model for compound *endo*,*exo*-**18a**), the chair-like conformation with a quasi-equatorial orientation of the phenyl group was found to be lower in energy than the boat-like conformation with a quasi-axial orientation of the phenyl group but by $\Delta\Delta H$ = 0.9 kcal·mol^{-1} only (Table 1). This conformation was indeed observed for compound *endo*,*exo*-**18a** in the crystal. Accordingly, the conformational energy of a 3-phenyl substituent on bicyclo[3.1.0]hexane should be at least 3.1 + 0.9 = 4.0 kcal·mol^{-1}: The eclipsing torsional strain caused by the phenyl group in the boat conformation overrides that in the chair conformation. Contrary to this, in *exo*-3-phenylbicyclo[3.1.0]hexane (as a model for compounds **9a**, *exo*,*exo*-**18b**, *exo*,*endo*-**38b** and *exo*,*exo*-**38b**) the molecule adopts a boat-like conformation with a quasi-equatorial orientation of the phenyl substituent and $\Delta\Delta H$ = 4.2 kcal·mol^{-1}. This must be attributable to the concerted action of two energetic factors namely the general preference (by ca. 0.5−1.0 kcal·mol^{-1})[34] of alkyl substituents on a cyclopentane ring to adopt a quasi-equatorial orientation and the energetic advantage of a boat-like conformation in the bicyclo[3.1.0]hexane fragment (by ca. 3.1−3.3 kcal·mol^{-1}). As a result, bicyclo[3.1.0]hexanes **9a**, *exo*,*exo*-**18b**, *exo*,*endo*-**38b** and *exo*,*exo*-**38b** adopt boat-like conformations with quasi-equatorial orientations of the substituents at the 3-positions

The packing of the studied molecules in the crystals differs greatly from one to the other, but in all cases the most important short intermolecular interactions are of the type C−H···O=C/N≡C, where the CH groups are either part of an aromatic or a cyclopropyl ring. Interestingly, both types of interaction exist simultaneously in all of the studied structures, which probably indicates similar strengths for these attractive interactions.[35] The molecules, linked by these contacts, form herringbone-arranged ribbons in the crystals of **9a**, centrosymmetric dimers in **18a** as well as in **18b** and layers in the crystals of both isomers of **38b**.

Liquid Crystalline Physical Properties of the New Compounds

Phase transition temperatures, the dielectric anisotropies ($\Delta\varepsilon$), birefringences (Δn), and bulk viscosities (η) of the newly prepared bicyclo[3.1.0]hexanes *exo*,*exo*-**9a**, *exo*,*exo*-**21a**,**b**,**d**,**e**, *exo*,*exo*-**32**, and *exo*,*exo*-**38b** (see Table 2) need to be compared with data from the isomorphous liquid crystalline compounds **39**−**42** containing a 1,4-disubstituted cyclohexane moiety.[36,37]



The comparison (Table 2) reveals that a bicyclo[3.1.0]hexane moiety, as a rule, decreases the clearing temperature (except for entry 7). The dielectric ($\Delta\varepsilon$) and optical (Δn) anisotropies are comparable. However, the bicyclo[3.1.0]-hexane moiety may induce a greater anisotropy of the pola-

Table 1. Total energies and heats of formation of bicyclo[3.1.0]hexane and its 3-phenyl derivatives calculated at the B3LYP/6−31G** level of theory[32]

Compound	Total Energy (Hartree)		$\Delta H_f°$ (kcal·mol^{-1})	
	boat	chair	boat	chair
Bicyclo[3.1.0]hexane	−234.498557	−234.493756	11.0	14.1
exo-3-Phenylbicyclo[3.1.0]hexane	−465.474238	−465.467703	44.3	48.5
endo-3-Phenylbicyclo[3.1.0]hexane	−465.468105	−465.469625	48.1	47.2

Table 2. Physical properties of the newly synthesized substances compared with those of the structurally analogous liquid crystalline compounds **39**−**42**

Entry	Compound	Phase-transition temperatures [°C]	Δε	Δ*n*	η [mPaS]
1	*exo*,*exo*-**9a**	C 60.48 (N, 86.43) I	0.5[a]	0.070[a]	–
2	**39**	C 95.1 SA 131.1 (N, 155.3) I	−1.1[a]	0.117[a]	–
3	*exo*,*exo*-**21a**	C 18.5 SmB 107.9 I	0.3 [b]	0.070[b]	23.3[b]
4	*exo*,*exo*-**21b**	C 12.8 I	1.4 [b]	−0.090[b]	16.5[b]
5	*exo*,*exo*-**21d**	C 30.1 I	10.1 [b]	0.090[b]	52.0[b]
6	*exo*,*exo*-**21e**	C 36.9 SmX 246.7 I	−0.6 [a]	0.117[a]	61.3[a]
7	**40**	C 30.4 (N, 58.0) I	10.3 [b]	0.124[b]	44.3[b]
8	*exo*,*exo*-**32**	C < room temp. I	−3.46 [b]	0.020[b]	–
9	**41**	C 44.7 (N, 48.8) I	−4.76 [b]	0.074[b]	29.8[b]
10	*exo*,*exo*-**38b**	C 34.4 (N, 44.2) I	14.0 [b]	0.124[b]	–
11	**42**	C 31 (N, 55) I	11.0 [b]	0.118[b]	20.9[b]

[a] Extrapolated; 5% in the base nematic mixture Merck ZLI-1132®. [b] Extrapolated; 15% in the base nematic mixture Merck ZLI-1132®.

rizability, which tends to increase the Δε value according to the equation of Maier and Meier[38] (entries 1,8,10). In general, the bicyclo[3.1.0]hexane derivatives have a poorer mesogenic potential than the isomorphous cyclohexane derivatives.

Experimental Section

General: NMR Spectra were recorded on a Bruker AM 250 instrument (250 MHz for ^{1}H and 62.9 MHz for ^{13}C NMR). Multiplicities were determined by DEPT (Distortionless Enhancement by Polarization Transfer) measurements. Chemical shifts refer to δ_{TMS} = 0.00 via the chemical shifts of residual $CHCl_3$ signals. IR: Bruker IFS 66 (FT-IR) spectrophotometer, measured as KBr pellets or oils between KBr plates. MS (EI, 70 eV): Finnigan MAT 95 spectrometer. Melting points: Büchi 510 capillary melting point apparatus, uncorrected values. TLC: Macherey−Nagel precoated sheets, 0.25 mm Sil G/UV$_{254}$. Column chromatography: Merck silica gel, grade 60, 230−400 mesh. Transition temperatures: measured with a polarizing microscope Nikon XTP-11 in conjunction with a Mettler hot stage FP 82 and a control unit FP 80. The physical properties of the synthesized liquid crystalline compounds were determined using the following instruments and under the following conditions: Dielectric anisotropies (Δε) were measured at 25 °C with a Hewlett−Packard 4284A LCR meter; birefringences (Δ*n*) were measured at 25 °C with an Atago 4T & 2T Abbé refractometer; viscosities (μ) were determined at 20 °C with a Lauda Viscoboy viscometer. Starting materials: *tert*-butyl cyclopent-3-ene-1-carboxylate (**6**),[12] $PdCl_2$(dppf),[17] cyclopent-3-en-1-ol (**13**),[18] *tert*-butyl diazoacetate,[19] (cyclopenten-4-yl)methanol (**23**),[39] and (4-cyanophenyl)diazomethane (**36b**)[28] were prepared according to previously published procedures. All operations in anhydrous solvents were performed under an argon atmosphere in flame-dried glassware. Diethyl ether and THF were dried by distillation from sodium benzophenone ketyl, pyridine and DMF from calcium hydride, CH_2Cl_2 and MeCN from P_2O_5. The appropriately substituted aryl halides, phenols and oligofluorinated compounds were kindly supplied by the Chisso Petrochemical Corporation. All other chemicals were used as commercially available. Organic extracts were dried over $MgSO_4$.

3-*tert*-Butyl 6-Ethyl *exo*,*exo*-Bicyclo[3.1.0]hexane-3,6-dicarboxylate (*exo*,*exo*-7): To a stirred solution of *tert*-butyl cyclopent-3-ene-1-carboxylate (**6**) (2.64 g, 15.7 mmol) and $Rh_2(OAc)_4$ (0.0176 g, 0.04 mmol, 0.25 mol %) in anhydrous dichloromethane (15 mL) was added ethyl diazoacetate (1.79 g, 15.7 mmol) at ambient temp. over a period of 12 h. The mixture was filtered through a pad of alumina and concentrated under reduced pressure. The residue was essentially a 7:3 mixture of two diastereomers (according to its ^{1}H NMR spectrum). The main component was isolated by column chromatography (170 g of silica gel, column 27 × 4 cm, hexane/Et_2O, 9:1) to give *exo*,*exo*-**7** (2.52 g, 63%) as a colorless oil, R_f = 0.30. ^{1}H NMR: δ = 1.20 (s, 9 H, 3 CH_3), 1.40 (t, *J* = 7.0 Hz, 3 H, CH_3), 1.45 (m, 1 H, CH), 1.80 (d, *J* = 4.0 Hz, 2 H, 2 CH), 2.20 (d, *J* = 4.0 Hz, 4 H, 2 CH_2), 2.83 (quin, *J* = 4.0 Hz, 1 H, CH), 4.15 (q, *J* = 7.0 Hz, 2 H, OCH_2) ppm. ^{13}C NMR: δ = 14.3 (CH_3) 23.6 (CH), 25.7 (3 CH_3), 27.0 (2 CH), 29.7 (2 CH_2), 44.1 (CH), 60.1 (CH_2), 79.9 (C), 171.7 (C), 175.3 (C) ppm. $C_{14}H_{22}O_4$ (254.32): calcd. C 66.11, H 8.72; found C 65.85, H 8.70.

***exo*,*exo*-Bicyclo[3.1.0]hexane-3,6-dicarboxylic Acid (*exo*,*exo*-8):** To a solution of diester *exo*,*exo*-**7** (1.50 g, 5.90 mmol) in a 1:1 mixture of MeOH and THF (25 mL) was added a solution of LiOH·H_2O (1.47 g, 35 mmol) in H_2O (6 mL), and the resultant solution was stirred at ambient temp. for 24 h. The reaction mixture was acidified to pH ≈ 3 with an aq. 1 M solution of H_3PO_4 and extracted with Et_2O (4 × 150 mL). The combined organic extracts were dried and concentrated under reduced pressure to give crude *exo*,*exo*-**8** (1.00 g, 100%) as a colorless solid which was used without purification and characterization.

Bis(4-pentylphenyl) *exo*,*exo*-Bicyclo[3.1.0]hexane-3,6-dicarboxylate (*exo*,*exo*-9a): To a stirred solution of diacid *exo*,*exo*-**8** (368 mg, 2.16 mmol), 4-pentylphenol (710 mg, 4.33 mmol) and DMAP (43 mg, 0.35 mmol, 8 mol %) in anhydrous DMF (2 mL) at 0 °C was added DCC (1.037 g, 5.03 mmol), and the mixture was stirred at ambient temp. for an additional 12 h. The mixture was taken up in THF (50 mL), preadsorbed on silica gel (5 g) by evaporating of all the volatiles, and purified by column chromatography (80 g of silica gel, column 25 × 3 cm, hexane/Et_2O, 3:1) to give *exo*,*exo*-**9a** (421 mg, 42%) as a colorless solid, m.p. 60−61 °C, R_f = 0.28. ^{1}H NMR: δ = 0.90 (t, *J* = 6.5 Hz, 6 H, 2 CH_3), 1.29−1.35 (m, 8 H, 4 CH_2), 1.45 (m, 1 H, CH), 1.55−1.67 (m, 4 H, 2 CH_2), 1.69−1.72 (m, 2 H, 2 CH), 2.25−2.45 (m, 4 H, 2 CH), 2.60 (t, *J* = 8.0 Hz, 4 H, CH_2), 2.68−2.79 (m, 1 H, CH), 6.95−7.05 (m, 4 H, Ar-H), 7.14−7.23 (m, 4 H, Ar-H) ppm. ^{13}C NMR: δ = 14.0 (2 CH_3), 22.2 (CH), 22.5 (2 CH_2), 28.5 (2 CH), 31.1 (2 CH_2), 31.4 (2 CH_2), 31.5 (2 CH_2), 35.5 (2 CH_2), 39.5 (CH), 120.98 (2 CH), 121.15 (2 CH), 129.22 (2 CH), 129.27 (2 CH), 140.38 (C), 140.55 (C), 148.49 (C), 148.54 (C), 172.0 (C), 173.3 (C) ppm. MS (EI): *m*/*z* (%) = 462 (22)

[M+], 299 (100) [M+ − $C_{11}H_{15}O$], 164 (25), 107 (40). $C_{30}H_{38}O_4$ (462.63): calcd. C 77.89, H 8.28; found C 78.15, H 7.92.

Bis(4-propoxyphenyl) *exo*,*exo*-Bicyclo[3.1.0]hexane-3,6-dicarboxylate (*exo*,*exo*-9b): Under the conditions of the previous experiment, from diacid *exo*,*exo*-**8** (300 mg, 1.76 mmol), 4-propoxyphenol (536 mg, 3.53 mmol), DCC (846 mg, 4.10 mmol), and DMAP (43 mg, 0.35 mmol, 9.9 mol %) in anhydrous DMF (2 mL), diester *exo*,*exo*-**9b** (356 mg, 46%) was obtained after column chromatography (80 g of silica gel, column 25 × 3 cm, hexane/Et_2O, 3:1) as an oil, R_f = 0.25. IR (KBr): $\tilde{\nu}$ = 3110 cm^{-1}, 3067, 3046, 2968, 2940, 2880, 1743, 1592, 1505, 1310, 1243, 1192, 1144, 1016, 866, 770. ^1H NMR: δ = 1.02 (t, *J* = 7.5 Hz, 3 H, CH_3), 1.03 (t, *J* = 7.5 Hz, 3 H, CH_3), 1.69 (t, *J* = 3.0 Hz, 1 H, CH), 1.72−1.86 (m, 6 H, 2 CH_2 + 2 CH), 2.16 (m, 2 H, CH_2), 2.22−2.49 (m, 2 H, CH_2), 2.62−2.78 (quin, *J* = 6.5 Hz, 1 H, CH), 3.82−3.93 (m, 4 H, 2 OCH_2), 6.68−7.05 (m, 8 H, Ar-H) ppm. ^{13}C NMR: δ = 10.4 (2 CH_3), 22.1 (CH), 22.5 (2 CH_2), 28.5 (2 C), 31.4 (2 CH_2), 39.4 (CH), 69.8 (CH_2), 70.2 (CH_2), 115.0 (2 CH), 115.5 (2 CH), 115.9 (2 CH), 122.0 (CH), 122.2 (CH), 143.8 (C), 143.9 (C), 153.2 (C), 156.8 (C), 172.3 (C), 173.6 (C) ppm. $C_{26}H_{30}O_6$ (438.5): calcd. C 71.21, H 6.90; found C 71.07, H 6.89.

Preparation of Bromides 14 and 24, General Procedure 1 (GP1): To a solution of triphenylphosphane (55.08 g, 210 mmol) in anhydrous dichloromethane (250 mL) was added bromine (33.56 g, 10.82 mL, 210 mmol) at −30 to −15 °C over a period of 0.5 h under an argon atmosphere. After an additional 15 min of stirring, a mixture of the respective alcohol (200 mmol) and anhydrous pyridine (200 mmol) was added dropwise at −15 °C over a period of 1 h, and the mixture was stirred at 20 °C for an additional 12 h. After this, volatile materials were "bulb-to-bulb" distilled, at first under a water-aspirator vacuum and 30 °C oil bath temperature, and then under further reduced pressure (0.1 Torr) with a 100 °C oil bath, to a second flask which was cooled with acetone/dry ice. The distillation was continued until the temperature in the first flask reached 80 °C. The receiver flask was allowed to warm to 20 °C, and the solvent was removed by distillation at atmospheric pressure using a 30 cm Vigreux column. The residue was distilled under reduced pressure.

4-Bromocyclopentene (14): From cyclopent-3-en-1-ol (**13**) (16.82 g, 200 mmol), triphenylphosphane (55.08 g, 210 mmol), bromine (33.56 g, 10.82 mL, 210 mmol) and pyridine (15.82 g, 16.2 mL, 200 mmol), bromide **14** (26.44 g, 90%) was obtained according to GP1 as a colorless liquid, b.p. 61 °C (92 mbar). The ^1H and ^{13}C NMR spectra of **14** were identical to those previously reported.[40]

4-(Bromomethyl)cyclopentene (24): From (cyclopenten-4-yl)methanol (**23**) (41.61 g, 424 mmol), triphenylphosphane (116.77 g, 445 mmol), bromine (71.15 g, 22.9 mL, 445 mmol) and pyridine (33.54 g, 34.3 mL, 424 mmol), bromide **24** (58.1 g, 85%) was obtained according to GP1 as a colorless liquid, b.p. 83 °C (92 mbar). The ^1H and ^{13}C NMR spectra of **24** were identical to those previously reported.[41]

General Procedure 2 (GP2) for the $PdCl_2$(dppf)-Catalyzed Cross Coupling: A solution of (cyclopenten-4-yl)magnesium bromide (**15**) freshly prepared from 4-bromocyclopentene (**14**) (45 mmol) and magnesium (50 mmol) in anhydrous Et_2O (30 mL) was added via a cannula in one portion to a mixture of the aryl halide **16** (18 mmol) and the catalyst (3 mol %) in anhydrous Et_2O (100 mL) at ambient temp. Upon coupling of the aryl bromides, the initial orange color rapidly changed to yellow after 10 min of stirring, then to green or brown. In the case of iodides, the reactions were slightly exothermic, and the initial deep green color changed to light green or yellow, then to green or brown. The mixture was stirred for an additional 12 h at this temp., then poured into ice-cold saturated aq. NH_4Cl solution (100 mL) and diluted with Et_2O (100 mL). The organic phase was washed with 10% aq. NH_4Cl solution, H_2O and brine (50 mL each), dried and concentrated under reduced pressure. The residue was purified by column chromatography.

1-(Cyclopenten-4-yl)-4-[(*trans*-4-pentyl)cyclohexyl]benzene (17a): From 4-[(*trans*-4-pentyl)cyclohexyl]phenyl bromide (**16a**) (5.73 g, 18.53 mmol), bromide **14** (6.81 g, 46.3 mmol), and $PdCl_2$(dppf) (0.407 g, 0.56 mmol), compound **17a** (4.10 g, 75%) was obtained according to GP2 after column chromatography (300 g of silica gel, column 40 × 4.5 cm, hexane) as a colorless oil with m.p. ca. 10−12 °C, R_f = 0.53. ^1H NMR: δ = 0.98 (t, *J* = 6.0 Hz, 3 H, CH_3), 1.14 (t, *J* = 12.0 Hz, 2 H, CH_2 *c*Hex), 1.20−1.37 (m, 9 H), 1.54 (td, *J* = 2.8, 12.0, 2 H, CH_2 *c*Hex), 1.95 (m, 4 H, 2 CH_2 *c*Hex), 2.40−2.50 (m, 1 H, CH *c*Hex), 2.51 (ddd, *J* = 2.0, 8.8, 14.5 Hz, 2 H, CH_2 *c*Pent), 2.87 (dd, *J* = 8.8, 14.5 Hz, 2 H, CH_2 *c*Pent), 3.51 (p, *J* = 8.8 Hz, 1 H, CH *c*Pent), 5.85 (br. s, 2 H, 2 =CH), 7.15 (d, *J* = 8.3 Hz, 2 H, Ar-H), 7.26 (d, *J* = 8.3 Hz, 2 H, Ar-H) ppm. ^{13}C NMR: δ = 14.1 (CH_3), 22.7 (CH_2), 26.7 (CH_2), 32.2 (CH_2), 33.6 (2 CH_2), 34.4 (2 CH_2), 37.3 (CH), 37.4, (CH_2), 42.9 (CH), 44.2 (CH), 44.3 (2 CH_2), 126.7 (2 CH), 126.8 (2 CH), 129.9 (2 CH), 144.6 (C), 145.3 (C) ppm. Bis(cyclopenten-4-yl) (0.683 g, R_f = 0.58, oil) and 1,1′-bis{4-[(trans-4-pentyl)cyclohexyl]phenyl} (0.101 g, R_f = 0.47, solid) were also isolated as by-products.

4-(3,4,5-Trifluorophenyl)cyclopentene (17b): From 1-bromo-3,4,5-trifluorobenzene (**16b**) (4.22 g, 20 mmol), bromide **14** (7.35 g, 50 mmol), and $PdCl_2$(dppf) (0.439 g, 0.60 mmol), **17b** (3.27 g, 82%) was obtained according to GP2 after column chromatography (300 g of silica gel, column 40 × 4.5 cm, hexane) as a colorless oil, R_f = 0.52. ^1H NMR: δ = 2.37 (ddd, *J* = 2.0, 9.0, 14.5 Hz, 2 H, CH_2), 2.82 (dd, *J* = 6.7, 14.5 Hz, 2 H, CH_2), 3.39 (tt, *J* = 6.7, 9.0 Hz, 1 H, CH), 5.76 (br. s, 2 H, 2 CH), 6.84 (ddd, *J* = 4.5, 11.0, 13.5 Hz, 2 H, Ar-H) ppm. ^{13}C NMR: δ = 41.1 (2 CH_2), 43.1 (CH), 110.6 (ddd, *J* = 6.4, 13.5, 20.3 Hz, 2 CH), 129.5 (2 CH), 151.0 (ddd, *J* = 4.2, 9.9, 248.6 Hz, 2 C), 137.9 (dt, *J* = 15.4, 247.8 Hz, C), 143.9 (dt, *J* = 4.5, 9.1 Hz, C) ppm. Bis(cyclopenten-4-yl) (145 mg, R_f = 0.58, oil) and 1,1′-bis(3,4,5-trifluorophenyl) (202 mg, R_f = 0.35, solid) were also isolated as by-products.

4-[4-(3,4,5-Trifluorophenyl)phenyl]cyclopentene (17d): From 1-iodo-4-(3,4,5-trifluorophenyl)benzene (**16d**) (5.74 g, 17.17 mmol), bromide **14** (6.31 g, 42.9 mmol), and $PdCl_2$(dppf) (0.377 g, 0.52 mmol), **17d** (4.17 g, 88%) was obtained according to GP2 after column chromatography (250 g of silica gel, column 25 × 6 cm, hexane) as an oil with m.p. ca. 10 °C, R_f = 0.40. ^1H NMR: δ = 2.50 (dd, *J* = 7.0, 14.5 Hz, 2 H, CH_2), 2.90 (dd, *J* = 9.0, 14.5 Hz, 2 H, CH_2), 3.54 (tt, *J* = 7.0, 9.0 Hz, 1 H, CH), 5.84 (br. s, 2 H, 2 =CH), 7.19 (ddd, *J* = 4.5, 6.5, 9.0 Hz, 2 H, Ar-H), 7.36 (d, *J* = 8.3 Hz, 2 H, Ar-H), 7.44 (d, *J* = 8.3 Hz, 2 H, Ar-H) ppm. ^{13}C NMR: δ = 41.3 (2 CH_2), 42.7 (CH), 110.7 (ddd, *J* = 7.1, 14.15, 21.2 Hz, 2 CH), 126.7 (2 CH), 126.8 (2 CH), 129.8 (2 CH), 135.7 (C), 137.1 (dt, *J* = 4.8, 7.9 Hz, C), 139.0 (dt, *J* = 15.5, 251.2 Hz, C), 148.0 (C), 151.5 (ddd, *J* = 4.3, 10.0, 249.1 Hz, 2 C) ppm.

1-(Cyclopenten-4-yl)-4-{*trans*-4-[(*trans*-4-propyl)cyclohexyl]-cyclohexyl}benzene (17e): From 4-[(*trans*-4-pentyl)cyclohexyl]-phenyl iodide (**16e**) (5.50 g, 13.4 mmol), bromide **14** (4.40 g, 29.9 mmol), and $PdCl_2$(dppf) (0.263 g, 0.36 mmol), **17e** (4.61 g, 98%) was obtained according to GP2 after column chromatography (250 g of silica gel, column 25 × 6 cm, hexane) as a colorless solid, m.p. 186−187 °C (MeOH), R_f = 0.46. IR (KBr): $\tilde{\nu}$ = 2957 cm^{-1},

2850, 1623, 1514, 1445, 1255, 1147, 978, 892, 820, 755, 697. ^{1}H NMR: δ = 0.97 (t, *J* = 7.0 Hz, 3 H, CH_3), 1.05−1.15 (m, 2 H, CH_2 *c*Hex), 1.20−1.30 (m, 6 H), 1.33−1.54 (m, 6 H), 1.85−2.03 (m, 9 H), 2.40−2.50 (m, 1 H, CH *c*Hex), 2.53 (dd, *J* = 7.9, 14.0 Hz, 2 H, CH_2 *c*Pent), 2.88 (dd, *J* = 7.9, 14.0 Hz, 2 H, CH_2 *c*Pent), 3.52 (p, *J* = 7.9 Hz, 1 H, CH *c*Pent), 5.85 (br. s, 2 H, 2 =CH), 7.21 (d, *J* = 8.3 Hz, 2 H, Ar-H), 7.26 (d, *J* = 8.3 Hz, 2 H, Ar-H) ppm. ^{13}C NMR: δ = 14.5 (CH_3), 20.1 (CH_2), 30.1 (2 CH_2), 30.4 (2 CH_2), 33.6 (2 CH_2), 34.7 (2 CH_2), 37.6 (CH), 39.9 (CH_2), 41.3 (2 CH_2), 42.9 (CH), 43.0 (CH), 43.4 (CH), 44.2 (CH), 126.8 (2 CH), 126.9 (2 CH), 129.9 (2 CH), 144.7 (C), 145.4 (C) ppm. $C_{26}H_{38}$ (350.56): calcd. C 89.07, H 10.93; found C 89.02, H 10.80.

General Procedure 3 (GP3) for the $[Rh(C_7H_{15}COO)_2]_2$ Catalyzed Cyclopropanation of Cyclopentenes 17 with *tert*-Butyl Diazoacetate: To a stirred solution of the respective cyclopentene **17** (25 mmol) and dirhodium tetraoctanoate (0.5 mol %) in anhydrous dichloromethane (100 mL) was added *tert*-butyl diazoacetate (37.5 mmol) at 0 to +5 °C over a period of 12 h. After evaporation of the solvent under reduced pressure, the residue was separated by column chromatography. Since the compounds **18d**,**e** are not soluble enough in the eluting solvent mixture, they were pre-absorbed on silica gel (20 g) from dichloromethane before chromatography.

***tert*-Butyl 3-{[4-(*trans*-4-pentyl)cyclohexyl]phenyl}bicyclo[3.1.0]-hexane-6-carboxylates (*exo*,*exo*-18a and *endo*,*exo*-18a):** Column chromatography (350 g of silica gel, column 45 × 4.5 cm, hexane/Et_2O, 15:1) of the reaction mixture prepared from the cyclopentene **17a** (4.10 g, 13.8 mmol), N_2CHCO_2tBu (2.95 g, 2.87 mL, 20.75 mmol) and $[Rh(C_7H_{15}COO)_2]_2$ (0.054 g, 0.07 mmol) according to GP3 yielded the two cycloadducts *exo*,*exo*-**18a** (2.73 g, 48%) and *endo*,*exo*-**18a** (2.17 g, 38%) with R_f = 0.45 and 0.43, respectively.

***exo*,*exo*-18a:** Colorless crystals, m.p. 113−115 °C (MeOH). ^{1}H NMR: δ = 0.92 (t, *J* = 6.8 Hz, 3 H, CH_3), 1.08 (t, *J* = 12.0 Hz, 2 H, CH_2 *c*Hex), 1.10−1.31 (m, 10 H), 1.48 (s, 9 H, 3 CH_3), 1.62 (br. s, 1 H, CH *c*Pr), 1.95−2.05 (m, 9 H), 2.25 (dd, *J* = 7.3, 12.5 Hz, 2 H, CH_2 *c*Pent), 2.45 (tt, *J* = 2.6, 12.3 Hz, 1 H, CH_2 *c*Hex), 2.70 (tt, *J* = 6.7, 8.9 Hz, 1 H, CH *c*Pent), 7.13 (br. s, 4 H, Ar-H) ppm. ^{13}C NMR: δ = 14.1 (CH_3), 22.7 (CH_2), 23.0 (CH), 26.6 (CH_2), 27.8 (2 CH), 28.1 (3 CH_3), 32.2 (CH_2), 33.6 (2 CH_2), 34.3 (2 CH_2), 35.7 (2 CH_2), 37.2 (CH), 37.4 (CH_2), 39.6 (CH), 44.1 (CH), 79.9 (C), 126.7 (2 CH), 127.0 (2 CH), 141.1 (C), 145.7 (C), 173.1 (C) ppm.

***endo*,*exo*-18a:** Colorless crystals, m.p. 68−70 °C (MeOH). ^{1}H NMR: δ = 0.88 (t, *J* = 6.8 Hz, 3 H, CH_3), 1.05 (t, *J* = 12.0 Hz, 2 H, CH_2 *c*Hex), 1.10−1.31 (m, 9 H), 1.42 (t, *J* = 6.5 Hz, 2 H), 1.49 (s, 9 H, 3 CH_3), 1.60 (br. s, 1 H, CH *c*Pr), 1.75 (dd, *J* = 2.0, 5.6 Hz, 2 H), 1.85 (dm, = 9.5 Hz, 4 H), 1.95 (tt, *J* = 2.4, 7.2 Hz, 2 H), 2.38 (dd, *J* = 8.0, 13.2 Hz, 2 H, CH_2 *c*Pent), 2.40−2.55 (m, 1 H.), 2.89 (tt, *J* = 6.5, 8.0 Hz, 1 H, CH *c*Pent), 7.11 (br. s, 4 H, Ar-H) ppm. ^{13}C NMR: δ = 14.1 (CH_3), 22.6 (CH_2), 23.5 (CH), 26.6 (CH_2), 27.9 (3 CH_3), 28.1 (2 CH), 32.1 (CH_2), 33.6 (2 CH_2), 34.3 (2 CH_2), 35.0 (2 CH_2), 37.3 (CH), 37.4 (CH_2), 41.8 (CH), 44.1 (CH), 80.2 (C), 126.7 (2 CH), 127.0 (2 CH), 143.0 (C), 145.4 (C), 170.7 (C). The structure of this compound was confirmed by a single crystal X-ray diffraction study.

***tert*-Butyl *exo*,*exo*-3-(3,4,5-trifluorophenyl)bicyclo[3.1.0]hexane-6-carboxylate (*exo*,*exo*-18b):** Column chromatography (350 g of silica gel, column 45 × 4.5 cm, hexane/Et_2O, 20:1) of the reaction mixture obtained from the cyclopentene **17b** (4.99 g, 25.2 mmol), N_2CHCO_2tBu (5.37 g, 5.24 mL, 37.8 mmol) and $[Rh(C_7H_{15}COO)_2]_2$ (0.098 g, 0.13 mmol) according to GP3 gave 4.87 g (62%) of a non-separable mixture of two isomeric cycloadducts *exo*,*exo*-**18b** and *endo*,*exo*-**18b** in a ratio of ca. 3:1 with R_f = 0.31. The major component was formed in 47% yield as determined by ^{1}H NMR spectroscopy. After crystallization from methanol, *exo*,*exo*-**18b** was obtained in pure form as colorless crystals (2.46 g, 31%), m.p. 88 °C. After evaporation of the mother liquor, the remaining oil (2.22 g) which consisted of these two diastereomers in a ratio of 1:2 was crystallized from MeOH again at −20 °C. This procedure yielded an additional 0.610 g of *exo*,*exo*-**18b**; total yield 39%. IR (KBr): $\tilde{\nu}$ = 3051 cm^{-1}, 2957, 2923, 2861, 1709, 1622, 1533, 1404, 1368, 1321, 1151, 1036, 832, 692. ^{1}H NMR: δ = 1.44 (s, 9 H, 3 CH_3), 1.54 (t, *J* = 2.3 Hz, 1 H, CH *c*Pr), 1.80 (dd, *J* = 3.0, 12.3 Hz, 2 H, CH_2), 1.90 (m, 2 H, 2 CH cycloprop.), 2.23 (dd, *J* = 7.3, 12.3 Hz, 2 H, CH_2), 2.63 (tt, *J* = 7.3, 10.4 Hz, 1 H, CH), 6.76 (dd, *J* = 6.5, 9.0 Hz, 2 H, Ar-H) ppm. ^{13}C NMR: δ = 23.0 (CH), 27.3 (2 CH), 28.1 (3 CH_3), 35.5 (2 CH_2), 39.5 (CH), 80.27 (C), 111.0 (ddd, *J* = 6.8, 13.6, 20.4 Hz, 2 CH), 138.1 (dt, *J* = 15.4, 264.2 Hz, C), 140.3 (dt, *J* = 4.6, 6.7 Hz, C), 151.1 (ddd, *J* = 4.5, 9.6, 250.0 Hz, 2 C), 172.7 (C) ppm. $C_{17}H_{19}F_3O_2$ (312.32): calcd. C 65.37, H 6.13; found C 65.22, H 6.09. The configuration of this compound has been determined by an X-ray crystal structure analysis.

***tert*-Butyl *exo*,*exo*-3-[4-(3,4,5-Trifluorophenyl)phenyl]bicyclo[3.1.0]-pentane-6-carboxylate (*exo*,*exo*-18d):** Column chromatography (450 g of silica gel, column 40 × 5.6 cm, hexane/Et_2O, 10:1) of the reaction mixture obtained from the cyclopentene **17d** (4.07 g, 14.8 mmol), N_2CHCO_2tBu (3.51 g, 3.42 mL, 24.69 mmol) and $[Rh(C_7H_{15}COO)_2]_2$ (0.064 g, 0.082 mmol) according to GP3 gave a non-separable mixture of the two isomers *exo*,*exo*-**18d** and *endo*,*exo*-**18d** with R_f = 0.30 which was recrystallized from MeOH/$CHCl_3$ (15:1) to give 2.07 g (36%) of *exo*,*exo*-**18d** as colorless crystals, m.p. 150−151 °C. After evaporation of the mother liquor, the residue was recrystallized again to give an additional 0.606 g of *exo*,*exo*-**18d**; total yield 46%. ^{1}H NMR: δ = 1.47 (s, 9 H, 3 CH_3), 1.62 (t, *J* = 2.2 Hz, 1 H, CH *c*Pr), 1.85−2.08 (m, 4 H, 2 CH *c*Pr + CH_2), 2.28 (dd, *J* = 7.3, 12.5 Hz, 2 H, CH_2), 2.75 (tt, *J* = 7.3, 10.3 Hz, 1 H, CH), 7.17 (dd, *J* = 6.5, 9.0 Hz, 2 H, Ar-H), 7.27 (d, *J* = 8.3 Hz, 2 H, Ar-H), 7.41 (d, *J* = 8.3 Hz, 2 H, Ar-H) ppm. ^{13}C NMR: δ = 23.1 (CH), 27.7 (2 CH), 28.2 (3 CH_3), 35.7 (2 CH_2), 39.7 (CH), 80.3 (C), 111.7 (ddd, *J* = 7.1, 14.3, 21.3 Hz, 2 CH), 126.8 (2 CH), 127.9 (2 CH), 136.1 (C), 137.1 (dt, *J* = 4.6, 6.7 Hz, C), 139.1 (dt, *J* = 23.8, 251.5 Hz, C), 144.3 (C), 151.3 (ddd, *J* = 4.5, 10.3, 259.1 Hz, 2 C), 173.0 (C) ppm. $C_{23}H_{23}F_3O_2$ (388.41): calcd. C 71.12, H 5.97; found C 70.88, H 6.03.

***tert*-Butyl *exo*,*exo*-3-{[*trans*-4-(*trans*-4-propylcyclohexyl)cyclohexyl]-phenyl}bicyclo[3.1.0]hexane-6-carboxylate (*exo*,*exo*-18e):** Column chromatography (350 g of silica gel, column 45 × 4.5 cm, hexane/Et_2O, 15:1) of the reaction mixture obtained from the cyclopentene **17e** (4.31 g, 12.3 mmol), N_2CHCO_2tBu (2.62 g, 2.55 mL, 18.44 mmol) and $[Rh(C_7H_{15}COO)_2]_2$ (0.049 g, 0.06 mmol) according to GP3 gave some recovered starting material **17e** (0.889 g, 21%, R_f = 0.73) and the crudely separated cycloadducts *endo*,*exo*-**18e** (1.52 g, 27%) and *exo*,*exo*-**18e** with R_f = 0.39 and 0.44, respectively. After recrystallization from MeOH/$CHCl_3$ (10:1), 2.68 g (47%) of pure *exo*,*exo*-**18e** was obtained as colorless crystals, m.p. 281−283 °C (dec.). IR (KBr): $\tilde{\nu}$ = 3048 cm^{-1}, 3007, 2927, 2846, 1709, 1450, 1410, 1157, 1062, 840, 557. ^{1}H NMR: δ = 0.88 (t, *J* = 7.1 Hz, 3 H, CH_3), 0.97−1.18 (m, 8 H), 1.27−1.42 (m, 2 H), 1.45 (s, 9 H, 3 CH_3), 1.63 (br. s, 1 H, CH *c*Pr), 1.73−1.97 (m, 16 H), 2.23 (dd, *J* = 7.0, 12.3 Hz, 2 H, CH_2 *c*Pent), 2.41 (tt, *J* = 2.6, 12.0 Hz, 2 H, CH_2 *c*Hex), 2.67 (tt, *J* = 7.0, 9.4 Hz, 1 H, CH *c*Pent), 7.11 (br. s, 4 H, Ar-H) ppm. ^{13}C NMR: δ = 10.3 (2 CH_2), 14.4

(CH_3), 20.0 (CH_2), 23.0 (CH), 27.8 (2 CH), 28.2 (3 CH_3), 30.1 (2 CH_2), 33.6 (2 CH_2), 34.6 (2 CH_2), 35.8 (2 CH_2), 37.6 (CH), 39.6 (CH), 39.8 (CH_2), 42.9 (CH), 43.4 (CH), 44.2 (CH), 80.0 (C), 126.7 (2 CH), 127.1 (2 CH), 141.1 (C), 145.8 (C), 173.3 (C) ppm. $C_{32}H_{48}O_2$ (464.7): calcd. C 82.70, H 10.41; found C 82.53, H 10.19.

***tert*-Butyl *exo*,*exo*-3-[2-(4-Ethoxy-2,3-difluorophenyl)ethyl]bicyclo-[3.1.0]hexane-6-carboxylate (*exo*,*exo*-30):** Column chromatography (100 g of silica gel, column 30 × 3 cm, hexane/Et_2O, 10:1) of the reaction mixture obtained from the cyclopentene **29** (0.692 g, 2.74 mmol), N_2CHCO_2tBu (0.974 g, 0.95 mL, 6.85 mmol) and $[Rh(C_7H_{15}COO)_2]_2$ (0.0107 g, 0.014 mmol) according to GP3 gave *exo*,*exo*-**30** (0.654 g, 65%) as a colorless oil, R_f = 0.23. ^{1}H NMR: δ = 1.41 (t, *J* = 7.0 Hz, 3 H, CH_3), 1.47 (s, 9 H, 3 CH_3), 1.50 (t, *J* = 2.5 Hz, 1 H, CH *c*Pr), 1.55−1.70 (m, 2 H, CH_2), 1.85 (dd, *J* = 2.5, 12.3 Hz, 2 H, CH_2), 1.90 (m, 2 H, 2 CH *c*Pr), 2.23 (dd, *J* = 7.3, 12.3 Hz, 2 H, CH_2), 2.42−2.51 (m, 3 H, CH_2, CH), 4.05 (q, *J* = 7.0 Hz, 2 H, OCH_2), 6.59 (dd, *J* = 7.0, 7.6 Hz, 1 H, Ar-H), 6.72 (dd, *J* = 7.6, 8.5 Hz, 1 H, Ar-H) ppm. ^{13}C NMR: δ = 14.7 (CH_3), 23.3 (CH), 27.6 (CH_2), 27.9 (2 CH), 28.0 (3 CH_3), 34.1 (2 CH_2), 35.0 (CH_2), 40.7 (CH), 65.3 (CH_2), 79.8 (C), 109.2 (CH), 123.0 (dd, *J* = 4.5, 10.6 Hz, CH), 123.4 (d, *J* = 5.1 Hz, C), 140.1 (dd, *J* = 12.8, 251.0 Hz, C), 142.7 (dd, *J* = 3.5, 9.2 Hz, C), 151.1 (dd, *J* = 10.8, 250.0 Hz, C), 173.1 (C) ppm. $C_{21}H_{28}F_2O_3$ (366.4): calcd. C 68.82, H 7.70; found C 68.60, H 7.85.

General Procedure 4 (GP4) for the Reduction of *tert*-Butyl Esters 18: To a stirred solution of the respective *tert*-butyl ester **18** (10 mmol) in anhydrous diethyl ether (80 mL) was added $LiAlH_4$ (6.4 mL of a 1.17 M solution in Et_2O, 7.5 mmol) at ambient temperature over a period of 20 min. After this, the reaction mixture was stirred at 34 °C for 1 h, cooled to 10 °C, quenched with a saturated aq. solution of Na_2SO_4 (1 mL), dried and concentrated under reduced pressure. The resultant alcohols **19** were used without further purification.

***exo*,*exo*{3-[4-(*trans*-4-Pentylcyclohexyl)phenyl]bicyclo[3.1.0]hex-6-yl}methanol (*exo*,*exo*-19a):** From the ester **18a** (2.17 g, 5.29 mmol), the alcohol *exo*,*exo*-**19a** (1.80 g, 100%) was obtained according to GP4 as a colorless solid, m.p. 141 °C (hexane). IR (KBr): $\tilde{\nu}$ = 3325 cm^{-1}, 3017, 2957, 2931, 2851, 1514, 1465, 1443, 1415, 1368, 1289, 1264, 1237, 1208, 1117, 1062, 1022, 997, 943, 895, 827, 768, 725, 663, 556. ^{1}H NMR: δ = 0.91 (t, *J* = 6.9 Hz, 3 H, CH_3), 1.04 (dq, *J* = 3.0, 12.3 Hz, 2 H), 1.17−1.34 (m, 8 H), 1.40 (pd, = 3.0, 13.5 Hz, 4 H), 1.73 (dd, *J* = 7.8, 13.5 Hz, 1 H), 1.83−1.91 (m, 7 H), 2.19 (dd, *J* = 7.5, 12.5 Hz, 2 H, CH_2), 2.43 (tq, *J* = 3.3, 12.5 Hz, 2 H), 2.72 (tt, *J* = 7.4, 10.1 Hz, 1 H, CH), 3.46 (d, *J* = 7.0 Hz, 2 H, CH_2O), 7.13 (br. s, 4 H, Ar-H) ppm. ^{13}C NMR: δ = 14.1 (CH_3), 22.3 (2 CH), 22.4 (CH), 22.7 (CH_2), 26.7 (CH_2), 32.2 (CH_2), 33.6 (2 CH_2), 34.4 (2 CH_2), 35.8 (2 CH_2), 37.3 (CH), 37.4 (CH_2), 40.3 (CH), 44.1 (CH), 66.0 (CH_2), 126.7 (2 CH), 127.1 (2 CH), 141.7 (C), 145.6 (C) ppm. $C_{24}H_{36}O$ (340.53): calcd. C 84.64, H 10.66; found C 84.90, H 10.55.

***exo*,*exo*{3-(3,4,5-Trifluorophenyl)bicyclo[3.1.0]hex-6-yl}methanol (*exo*,*exo*-19b):** From the ester **18b** (2.42 g, 7.75 mmol), the alcohol *exo*,*exo*-**19b** (1.87 g, 100%) was obtained according to GP4 as a colorless solid, m.p. 40 °C. ^{1}H NMR: δ = 1.09 (tt, *J* = 3.3, 7.0 Hz, 1 H, CH *c*Pr), 1.21−1.31 (m, 2 H, 2 CH *c*Pr), 1.73 (ddd, *J* = 3.8, 11.0, 12.5 Hz, 2 H, CH_2), 2.14 (dd, *J* = 7.5, 12.5 Hz, 2 H, CH_2), 2.44 (s, 1 H, OH), 2.63 (tt, *J* = 7.5, 11.0 Hz, 1 H, CH), 3.40 (d, *J* = 7.0 Hz, 2 H, CH_2O), 6.73 (dd, *J* = 6.8, 9.0 Hz, 2 H, Ar-H) ppm. ^{13}C NMR: δ = 21.9 (2 CH), 22.1 (CH), 35.4 (2 CH_2), 40.0 (CH), 65.3 (CH_2), 110.9 (ddd, *J* = 6.7, 13.8, 20.4 Hz, 2 CH), 137.7 (dt, *J* = 15.4, 250.0 Hz, C), 140.3 (dt, *J* = 6.9, 11.3 Hz, C), 150.8 (ddd, *J* = 4.1, 9.8, 248.7 Hz, 2 C) ppm.

***exo*,*exo*{3-[4-(3,4,5-Trifluorophenyl)phenyl]bicyclo[3.1.0]hex-6-yl}methanol (*exo*,*exo*-19d):** From the ester **18d** (2.45 g, 6.31 mmol), the alcohol *exo*,*exo*-**19d** (2.00 g, 100%) was obtained according to GP4 as a colorless solid, m.p. 78−80 °C (hexane). IR (KBr): $\tilde{\nu}$ = 3300 cm^{-1}, 3087, 3025, 2995, 2945, 2930, 2859, 1615, 1539, 1510, 1443, 1403, 1363, 1250, 1120, 1048, 946, 866, 828, 767, 702, 539. ^{1}H NMR: δ = 1.22 (tt, *J* = 3.3, 7.0 Hz, 1 H, CH *c*Pr), 1.35 (m, 2 H, 2 CH *c*Pr), 1.89 (ddd, *J* = 2.8, 11.0, 12.8 Hz, 2 H, CH_2), 2.06 (s, 1 H, OH), 2.22 (dd, *J* = 7.5, 12.8 Hz, 2 H, CH_2), 2.79 (tt, *J* = 7.5, 11.0 Hz, 1 H, CH), 3.48 (d, *J* = 7.0 Hz, 2 H, CH_2O), 7.14 (dd, *J* = 6.5, 8.8 Hz, 2 H, Ar-H), 7.27 (d, *J* = 8.3 Hz, 2 H, Ar-H), 7.40 (d, *J* = 8.3 Hz, 2 H, Ar-H) ppm. ^{13}C NMR: δ = 22.2 (2 CH), 22.3 (CH), 35.7 (2 CH_2), 40.3 (CH), 65.7 (CH_2), 110.6 (ddd, *J* = 7.1, 14.1, 21.3 Hz, 2 CH), 126.6 (2 CH), 127.9 (2 CH), 135.8 (C), 137.1 (dt, *J* = 4.6, 7.8 Hz, C), 138.9 (dt, *J* = 15.4, 251.4 Hz, C), 144.9 (C), 151.3 (ddd, *J* = 4.4, 10.1, 249.2 Hz, 2 C) ppm. $C_{19}H_{17}F_3O$ (318.33): calcd. C 71.68, H 5.38; found C 71.51, H 5.11.

***exo*,*exo*-(3-{[*trans*-4-(*trans*-4-Propylcyclohexyl)cyclohexyl]phenyl}-bicyclo[3.1.0]hex-6-yl)methanol (*exo*,*exo*-19e):** From the ester **18e** (2.68 g, 5.76 mmol), the alcohol *exo*,*exo*-**19e** (2.26 g, 100%) was obtained according to GP4 as a colorless solid, m.p. 259−260 °C (dec.) (hexane). IR (KBr): $\tilde{\nu}$ = 3325 cm^{-1}, 3018, 2958, 2847, 1515, 1445, 1119, 1062, 1020, 943, 895, 824, 559. ^{1}H NMR: δ = 0.78 (m, 1 H, CH *c*Pr), 0.89 (t, *J* = 7.1 Hz, 3 H, CH_3), 1.03−1.61 (m, 8 H), 1.30−1.57 (m, 6 H), 1.73 (dd, *J* = 7.8, 13.5 Hz, 1 H), 1.68 (s, 1 H, OH), 1.73−1.95 (m, 11 H), 2.19 (dd, *J* = 7.5, 12.5 Hz, 2 H, CH_2), 2.42 (tq, *J* = 3.3, 11.9 Hz, 2 H), 2.72 (tt, *J* = 7.5, 11.3 Hz, 1 H, CH), 3.46 (d, *J* = 7.3 Hz, 2 H, CH_2O), 7.13 (br. s, 4 H, Ar-H) ppm. ^{13}C NMR: δ = 14.4 (CH_3), 20.0 (CH_2), 22.2 (2 CH), 22.3 (CH), 30.0 (2 CH_2), 30.3 (2 CH_2), 33.6 (2 CH_2), 34.6 (2 CH_2), 35.8 (2 CH_2), 37.6 (CH), 39.8 (CH_2), 40.3 (CH), 42.8 (CH), 43.4 (CH), 44.1 (CH), 66.0 (CH_2), 126.7 (2 CH), 127.1 (2 CH), 141.7 (C), 145.6 (C) ppm. $C_{28}H_{42}O$ (394.62): calcd. C 85.22, H 10.73; found C 85.04, H 10.48.

General Procedure 5 (GP5) for the Conversion of the Alcohols 19, 23 to Iodides 20, 33: To a stirred solution of the respective alcohol **19**, **23** (4 mmol), imidazole (5.5 mmol), and Ph_3P (5.2 mmol) in a mixture of anhydrous MeCN (30 mL) and anhydrous Et_2O (50 mL; since the solubility of the alcohols **19a**,**e** in this mixture was not sufficient, anhydrous THF (20 mL) was also added in these two cases) was added iodine (6.0 mmol) in one portion at −10 °C under argon in the dark. After stirring at 0 °C for an additional 30 min, the reaction mixture was diluted with Et_2O (100 mL) and washed successively with saturated aq. $Na_2S_2O_3$ solution (50 mL) and brine (100 mL), then dried and concentrated under reduced pressure in the dark. The residue was taken up with CH_2Cl_2 (minimal quantity, 5−35 mL) and purified by column chromatography.

***exo*,*exo*-6-Iodomethyl-3-[4-(*trans*-4-pentylcyclohexyl)phenyl]-bicyclo[3.1.0]hexane (*exo*,*exo*-20a):** Column chromatography (50 g of silica gel, column 20 × 3 cm, hexane/Et_2O, 5:1) of the reaction mixture obtained from the alcohol *exo*,*exo*-**19a** (1.76 g, 5.17 mmol), Im-H (482 mg, 7.08 mmol), Ph_3P (1.76 g, 6.71 mmol), and I_2 (1.97 g, 7.75 mmol) according to GP5 gave the iodide *exo*,*exo*-**20a** (2.28 g, 98%) as a colorless solid, m.p. 96−97 °C (hexane-MeOH), R_f = 0.54. ^{1}H NMR: δ = 0.9 (t, *J* = 6.6 Hz, 3 H, CH_3), 1.05 (t, *J* = 11.3 Hz, 2 H), 1.18−1.45 (m, 15 H), 1.71−1.81 (m, 1 H, CH), 1.85 (dd, *J* = 8.0, 8.5 Hz, 4 H, 2 CH_2), 2.17 (dd, *J* = 7.5, 12.5 Hz, 2 H, CH_2), 2.42 (tt, *J* = 3.1, 10.5 Hz, 1 H, CH), 2.70 (tt, *J* = 7.5, 11.2 Hz, 1 H, CH), 3.14 (d, *J* = 7.5 Hz, 2 H, CH_2I), 7.09 (d, *J* = 7.5 Hz, 2 H, Ar-H), 7.13 (d, *J* = 7.5 Hz, 2 H, Ar-H) ppm. ^{13}C NMR: δ = 12.4 (CH_2), 14.1 (CH_3), 22.7 (CH_2), 24.5 (CH), 26.6 (CH_2), 30.6 (2 CH), 32.2 (CH_2), 33.6 (2 CH_2), 34.4 (2 CH_2), 36.2

(2 CH_2), 37.3 (CH), 37.4 (CH_2), 40.2 (CH), 44.1 (CH), 126.7 (2 CH), 127.1 (2 CH), 141.4 (C), 145.7 (C) ppm. MS (EI): *m*/*z* (%) = 450 (8) [M^+], 323 (100) [$M^+ - I$]. HRMS (EI): calcd. for $C_{24}H_{35}I$ [M^+] 450.1783, found 450.1783.

***exo*,*exo*-6-Iodomethyl-3-(3,4,5-trifluorophenyl)bicyclo[3.1.0]hexane (*exo*,*exo*-20b):** Column chromatography (80 g of silica gel, column 30 × 3 cm, hexane/Et_2O, 5:1) of the reaction mixture obtained from the alcohol *exo*,*exo*-**19b** (1.88 g, 7.76 mmol), Im-H (0.723 g, 10.62 mmol), Ph_3P (2.64 g, 10.08 mmol), and I_2 (2.95 g, 11.61 mmol) according to GP5 gave the iodide *exo*,*exo*-**20b** (2.66 g, 98%) as a colorless oil, R_f = 0.60. ^1H NMR: δ = 1.32 (tt, *J* = 3.0, 7.5 Hz, 1 H, CH *c*Pr), 1.33−1.36 (m, 2 H, 2 CH *c*Pr), 1.72 (ddd, *J* = 3.0, 11.0, 12.8 Hz, 2 H, CH_2), 2.17 (dd, *J* = 7.5, 12.8 Hz, 2 H, CH_2), 2.65 (tt, *J* = 7.5, 11.0 Hz, 1 H, CH), 3.11 (d, *J* = 7.5 Hz, 2 H, CH_2I), 6.77 (ddd, *J* = 3.2, 4.0, 8.8 Hz, 2 H, Ar-H) ppm. ^{13}C NMR: δ = 11.5 (CH_2), 24.4 (CH), 30.1 (2 CH), 35.8 (2 CH_2), 39.9 (CH), 111.0 (ddd, *J* = 6.6, 13.7, 20.4 Hz, 2 CH), 137.9 (dt, *J* = 15.4, 249.1 Hz, C), 140.4 (dt, *J* = 4.5, 11.3 Hz, C), 150.9 (ddd, *J* = 4.3, 9.9, 249.0 Hz, 2 C) ppm. MS (EI): *m*/*z* (%) = 352 (10) [M^+], 225 (100) [$M^+ - I$]. HRMS (EI): calcd. for $C_{13}H_{12}F_3I$ [M^+] 351.9936, found 351.9936. $C_{13}H_{12}F_3I$ (352.13): calcd. C 44.34, H 3.44, I 36.04; found C 44.36, H 3.50, I 35.80.

***exo*,*exo*-6-Iodomethyl-3-[4-(3,4,5-trifluorophenyl)phenyl]bicyclo-[3.1.0]hexane (*exo*,*exo*-20d):** Column chromatography (100 g of silica gel, column 35 × 3 cm, hexane/Et_2O, 10:1) of the reaction mixture obtained from the alcohol *exo*,*exo*-**19d** (2.00 g, 6.29 mmol), Im-H (0.508 g, 7.46 mmol), Ph_3P (1.86 g, 7.09 mmol), and I_2 (2.19 g, 8.62 mmol) according to GP5 gave the iodide *exo*,*exo*-**20d** (2.44 g, 91%) as a colorless oil, R_f = 0.55, which solidified upon standing at 0 °C overnight, m.p. 60−61 °C. ^1H NMR: δ = 1.29 (tt, *J* = 3.0, 7.5 Hz, 1 H, CH *c*Pr), 1.35−1.47 (m, 2 H, 2 CH *c*Pr), 1.86 (ddd, *J* = 3.0, 10.8, 12.8 Hz, 2 H, CH_2), 2.24 (dd, *J* = 7.5, 12.8 Hz, 2 H, CH_2), 2.79 (tt, *J* = 7.5, 10.8 Hz, 1 H, CH), 3.17 (d, *J* = 7.5 Hz, 2 H, CH_2I), 7.17 (ddd, *J* = 0.5, 7.2, 8.8 Hz, 2 H, Ar-H), 7.28 (d, *J* = 8.3 Hz, 2 H, Ar-H), 7.37 (d, *J* = 8.3 Hz, 2 H, Ar-H) ppm. ^{13}C NMR: δ = 12.1 (CH_2), 24.4 (CH), 30.5 (2 CH), 36.1 (2 CH_2), 40.1 (CH), 111.7 (dd, *J* = 18.3, 32.0 Hz, 2 CH), 126.6 (2 CH), 127.9 (2 CH), 135.9 (C), 136.9 (dt, *J* = 4.5, 15.0 Hz, C), 139.0 (dt, *J* = 15.4, 251.9 Hz, C), 144.6 (C), 151.2 (ddd, *J* = 4.3, 10.1, 249.3 Hz, 2 C) ppm. $C_{19}H_{16}F_3I$ (428.22): calcd. C 53.29, H 3.77, I 29.63; found C 52.69, H 3.80, I% 29.50.

***exo*,*exo*-6-Iodomethyl-3-{[*trans*-4-(*trans*-4-propylcyclohexyl)cyclo-hexyl]phenyl}-bicyclo[3.1.0]hexane (*exo*,*exo*-20e):** Column chromatography (100 g of silica gel, column 35 × 3 cm, hexane/Et_2O, 10:1) of the reaction mixture obtained from the alcohol *exo*,*exo*-**19e** (1.87 g, 4.74 mmol), Im-H (0.442 g, 6.49 mmol), Ph_3P (1.61 g, 6.14 mmol), and I_2 (1.80 g, 7.10 mmol) according to GP5 gave the iodide *exo*,*exo*-**20e** (2.36 g, 99%) as a colorless solid, m.p. 197 °C (dec.) (hexane), R_f = 0.64. IR (KBr): $\tilde{\nu}$ = 3020 cm^{-1}, 2925, 2846, 1512, 1446, 1223, 1167, 976, 842, 820, 560. ^1H NMR: δ = 0.81 (m, 1 H, CH *c*Pr), 0.85 (t, *J* = 7.1 Hz, 3 H, CH_3), 1.05−1.80 (m, 2 H), 1.22−1.31 (m, 6 H), 1.34−1.46 (m, 6 H), 1.67−1.93 (m, 13 H), 2.18 (dd, *J* = 7.4, 12.5 Hz, 2 H, CH_2), 2.42 (tt, *J* = 3.0, 11.8 Hz, 1 H, CH), 2.70 (tt, *J* = 7.4, 11.3 Hz, 1 H, CH), 3.15 (d, *J* = 7.8 Hz, 2 H, CH_2I), 7.12 (s, 4 H, Ar-H) ppm. ^{13}C NMR: δ = 12.5 (CH_2), 14.4 (CH_3), 20.0 (CH_2), 24.4 (CH), 30.1 (2 CH_2), 30.3 (2 CH_2), 30.6 (2 CH), 33.6 (2 CH_2), 34.6 (2 CH_2), 36.2 (2 CH_2), 37.6 (CH), 39.8 (CH_2), 40.1 (CH), 42.9 (CH), 43.4 (CH), 44.1 (CH), 126.7 (2 CH), 127.1 (2 CH), 141.4 (C), 145.6 (C) ppm. $C_{28}H_{41}I$ (504.51): calcd. C 66.65, H 8.19, I 25.15; found C 66.39, H 8.08, I 25.05.

1-Ethoxy-2,3-difluoro-4-(iodomethyl)benzene (27): 4-Ethoxy-2,3-difluorobenzaldehyde (**26a**) (2.00 g, 10.74 mmol) was reduced with $LiAlH_4$ (4.60 mL of a 1.17 M solution in Et_2O, 5.38 mmol) according to GP4 to give 2.02 g (100%) of crude (4-ethoxy-2,3-difluorophenyl)methanol. The latter was treated with Im-H (1.04 g, 15.27 mmol), Ph_3P (3.792 g, 14.46 mmol), and I_2 (4.22 g, 16.7 mmol) according to GP5. The residue was vigorously stirred with Et_2O (150 mL), filtered through a 3 cm pad of silica gel and concentrated under reduced pressure to give the iodide **27** (3.04 g, 95%) as a colorless solid which contained some Ph_3PO impurity, m.p. 89−92 °C, R_f (hexane/Et_2O, 10:1) = 0.43. The iodide **27** was used without further purification. ^1H NMR: δ = 1.45 (t, *J* = 7.0 Hz, 3 H, CH_3), 4.10 (q, *J* = 7.0 Hz, 2 H, OCH_2), 4.41 (s, 2 H, CH_2I), 6.65 (ddd, *J* = 1.8, 7.3, 8.5 Hz, 1 H, Ar-H), 7.02 (ddd, *J* = 2.2, 8.5, 9.0 Hz, 1 H, Ar-H) ppm. ^{13}C NMR: δ = 14.7 (CH_3), 65.2 (CH_2), 109.4 (CH), 123.4 (d, *J* = 5.0 Hz, C), 124.0 (d, *J* = 8.3 Hz, CH), 140.8 (dd, *J* = 14.1, 246.3 Hz, C), 146.8 (dd, *J* = 3.0, 9.4 Hz, C), 149.7 (dd, *J* = 10.5, 247.1 Hz, C) ppm.

***exo*,*exo*-6-Iodomethyl-3-[2-(4-ethoxy-2,3-difluorophenyl)ethyl]-bicyclo[3.1.0]hexane (*exo*,*exo*-31):** The ester *exo*,*exo*-**30** (653 mg, 1.78 mmol) was treated with $LiAlH_4$ (1.14 mL of a 1.17 M solution in Et_2O, 1.34 mmol) according to GP4 to give 527 mg (100%) of crude ***exo*,*exo*{3-[2-(4-ethoxy-2,3-difluorophenyl)ethyl]bicyclo-[3.1.0]hex-6-yl}methanol** as a colorless oil. ^1H NMR: δ = 1.05−1.35 (m, 3 H, CH *c*Pr), 1.39 (t, *J* = 7.0 Hz, 3 H, CH_3), 1.55−1.70 (m, 4 H, 2 CH_2), 1.89 (dd, *J* = 3.5, 12.0 Hz, 2 H, CH_2), 2.09−2.15 (m, 1 H, CH), 2.30 (s, 1 H, OH), 2.46 (dd, *J* = 6.3, 14.0 Hz, 2 H, CH_2), 3.31 (d, *J* = 7.5 Hz, 2 H, OCH_2), 4.02 (q, *J* = 7.0 Hz, 2 H, OCH_2), 6.58 (dd, *J* = 7.0, 8.6 Hz, 1 H, Ar-H), 6.72 (dd, *J* = 8.6, 10.5 Hz, 1 H, Ar-H) ppm. ^{13}C NMR: δ = 14.6 (CH_3), 22.1 (2 CH), 24.9 (CH), 27.5 (CH_2), 34.1 (2 CH_2), 35.2 (CH_2), 43.1 (CH), 65.1 (CH_2), 65.3 (CH_2), 109.1 (d, *J* = 3.2 Hz, CH), 123.0 (dd, *J* = 5.3, 9.6 Hz, CH), 123.5 (d, *J* = 5.4 Hz, C), 141.3 (dd, *J* = 14.8, 246.6 Hz, C), 146.1 (dd, *J* = 2.8, 8.1 Hz, C), 149.5 (dd, *J* = 10.4, 245.1 Hz, C) ppm. This was treated with Im-H (166 mg, 2.44 mmol), Ph_3P (607 mg g, 2.31 mmol), and I_2 (680 mg, 2.68 mmol) according to GP5 to give the iodide *exo*,*exo*-**31** (687 mg, 95%) as a colorless oil after column chromatography (70 g of silica gel, column 25 × 3 cm, hexane/Et_2O, 10:1), R_f = 0.40. ^1H NMR: δ = 1.10−1.35 (m, 3 H, CH *c*Pr), 1.40 (t, *J* = 7.0 Hz, 3 H, CH_3), 1.57−1.78 (m, 4 H, 2 CH_2), 1.90 (dd, *J* = 2.8, 12.5 Hz, 2 H, CH_2), 2.11−2.17 (m, 1 H, CH), 2.41 (dd, *J* = 5.8, 13.5 Hz, 2 H, CH_2), 3.15 (d, *J* = 7.8 Hz, 2 H, CH_2I), 4.05 (q, *J* = 7.0 Hz, 2 H, OCH_2), 6.60 (dd, *J* = 7.0, 8.5 Hz, 1 H, Ar-H), 6.72 (dd, *J* = 8.5, 9.4 Hz, 1 H, Ar-H) ppm. ^{13}C NMR: δ = 12.2 (CH_2), 14.3 (CH_3), 22.3 (2 CH), 24.7 (CH), 27.6 (CH_2), 34.3 (2 CH_2), 35.1 (CH_2), 43.3 (CH), 65.2 (CH_2), 109.5 (d, *J* = 3.0 Hz, CH), 123.5 (dd, *J* = 5.7, 10.1 Hz, CH), 123.8 (d, *J* = 5.3 Hz, C), 141.8 (dd, *J* = 14.0, 245.4 Hz, C), 146.6 (dd, *J* = 3.2, 9.2 Hz, C), 150.1 (dd, *J* = 10.8, 246.3 Hz, C) ppm. $C_{17}H_{21}IF_2O$ (406.24): calcd. C 50.26, H 5.21; found C 49.95, H 5.15.

4-(Iodomethyl)cyclopentene (33): The alcohol **23** (15.05 g, 153.3 mmol) was treated with Im-H (14.30 g, 210 mmol), Ph_3P (50.58 g, 192.8 mmol), and I_2 (58.36 g, 230 mmol) according to GP5, but the iodine was added in small portions at 0 °C over a period of 1 h. "Bulb-to-bulb" distillation of the residue at 100 °C/0.1 Torr gave the iodide **33** (26.8 g, 84%) as a colorless oil. The ^1H and ^{13}C NMR spectra of **33** were identical to those reported previously.[42]

General Procedure 6 (GP6) for the Li_2CuCl_4 Catalyzed Cross Coupling of the Iodides with Alkylmagnesium Bromides: A solution of the respective alkylmagnesium bromide (1.5−2 equiv.) in Et_2O was added in one portion to a solution of the respective iodide (5 mmol) in anhydrous THF (50 mL) at −5 °C. The mixture was stirred for 5 min before a solution of Li_2CuCl_4 (5−10 mol %), freshly pre-

pared from anhydrous LiCl (0.5−1.0 mmol) and anhydrous $CuCl_2$ (0.25−0.5 mmol) in THF (3 mL), was added in one portion. After completion of the vigorous exothermic reaction, the mixture was stirred for an additional 0.5 h at 0 °C and then poured into a mixture of ice-cold saturated aq. NH_4Cl solution (50 mL) and diethyl ether (100 mL). The organic phase was washed with saturated aq. NH_4Cl solution and brine (50 mL each), dried and concentrated at reduced or ambient pressure. The residue was purified by column chromatography or distilled under ambient or reduced pressure.

***exo*,*exo*-3-[4-(*trans*-4-pentylcyclohexyl)phenyl]-6-propylbicyclo-[3.1.0]hexane (*exo*,*exo*-21a):** Column chromatography (300 g of silica gel, column 50 × 4.5 cm, hexane) of the reaction mixture obtained from the iodide *exo*,*exo*-**20a** (2.28 g, 5.06 mmol), EtMgBr (7.56 mmol, 2.32 mL of a 3.26 M solution), LiCl (0.021 g, 0.5 mmol) and $CuCl_2$ (0.034 g, 0.25 mmol) according to GP6 gave the hydrocarbon *exo*,*exo*-**21a** (1.36 g, 77%) as a colorless solid, m.p. 100−101 °C (MeOH), R_f = 0.55. IR (KBr): $\tilde{\nu}$ = 2957 cm^{-1}, 2850, 1514, 1465, 1444, 1378, 1297, 1263, 1212, 1182, 1144, 1112, 1050, 1018, 973, 896, 825, 730, 585. ^1H NMR: δ = 0.72 (tt, *J* = 3.6, 6.8 Hz, 1 H, CH *c*Pr), 0.89 (t, *J* = 7.0 Hz, 3 H, CH_3), 0.92 (t, *J* = 7.5 Hz, 3 H, CH_3), 1.05−1.50 (m, 16 H), 1.71−1.81 (m, 1 H, CH), 1.84 (dd, *J* = 8.0, 8.8 Hz, 8 H, 4 CH_2), 2.11 (dd, *J* = 7.3, 12.3 Hz, 2 H, CH_2), 2.42 (tt, *J* = 3.1, 12.0 Hz, 1 H, CH), 2.67 (tt, *J* = 7.5, 11.0 Hz, 1 H, CH), 7.09 (d, *J* = 7.6 Hz, 2 H, Ar-H), 7.13 (d, *J* = 7.6 Hz, 2 H, Ar-H) ppm. ^{13}C NMR: δ = 14.07 (CH_3), 14.12 (CH_3), 19.7 (CH), 22.69 (CH_2), 22.71 (CH_2), 24.2 (2 CH), 26.6 (CH_2), 32.2 (CH_2), 33.6 (2 CH_2), 34.4 (2 CH_2), 35.1 (CH_2), 36.4 (2 CH_2), 37.3 (CH), 37.7 (CH_2), 40.6 (CH), 44.1 (CH), 126.6 (2 CH), 127.1 (2 CH), 142.4 (C), 145.4 (C) ppm. $C_{26}H_{40}$ (352.58): calcd. C 88.56, H 11.44; found C 88.85, H 11.25.

***exo*,*exo*-6-Heptyl-3-(3,4,5-trifluorophenyl)bicyclo[3.1.0]hexane (*exo*,*exo*-21b):** Column chromatography (100 g of silica gel, column 35 × 3 cm, hexane) of the reaction mixture obtained from the iodide *exo*,*exo*-**20b** (2.55 g, 7.24 mmol), $C_6H_{13}MgBr$ (10.86 mmol, 16.21 mL of a 0.67 M solution), LiCl (0.030 g) and $CuCl_2$ (0.049 g) according to GP6 gave the hydrocarbon *exo*,*exo*-**21b** (1.91 g, 85%) as a colorless oil, m.p. ca. 10−12 °C, R_f = 0.60. ^1H NMR: δ = 0.67 (tt, *J* = 3.3, 6.7 Hz, 1 H, CH *c*Pr), 0.89 (t, *J* = 6.5 Hz, 3 H, CH_3), 1.10 (t, *J* = 6.3 Hz, 2 H), 1.17 (t, *J* = 6.8 Hz, 2 H), 1.21−1.41 (m, 10 H), 1.73 (ddd, *J* = 3.3, 11.0, 12.1 Hz, 2 H, CH_2), 2.13 (dd, *J* = 7.5, 12.1 Hz, 2 H, CH_2), 2.64 (tt, *J* = 7.5, 11.0 Hz, 1 H, CH), 6.80 (ddd, *J* = 3.3, 7.3, 13.7 Hz, 2 H, Ar-H) ppm. ^{13}C NMR: δ = 14.1 (CH_3), 20.0 (CH), 22.7 (CH_2), 29.4 (CH_2), 29.5 (CH_2), 29.6 (CH_2), 31.9 (CH_2), 32.8 (CH_2), 32.9 (2 CH), 36.0 (2 CH_2), 40.5 (CH), 111.0 (ddd, *J* = 6.3, 13.8, 20.2 Hz, 2 CH), 137.8 (dt, *J* = 15.3, 248.7 Hz, C), 141.5 (dt, *J* = 4.5, 11.1 Hz, C), 150.9 (ddd, *J* = 4.3, 14.3, 252.9 Hz, 2 C) ppm. $C_{19}H_{25}F_3$ (310.39): calcd. C 73.52, H 8.12; found C 73.25, H 8.08.

***exo*,*exo*-6-Heptyl-3-[4-(3,4,5-trifluorophenyl)phenyl]bicyclo-[3.1.0]hexane (*exo*,*exo*-21d):** Column chromatography (120 g of silica gel, column 40 × 3 cm, hexane) of the reaction mixture obtained from the iodide *exo*,*exo*-**20d** (2.34 g, 5.47 mmol), $C_6H_{13}MgBr$ (10.94 mmol, 16.33 mL of a 0.67 M solution), LiCl (0.030 g) and $CuCl_2$ (0.049 g) according to GP6 gave the hydrocarbon *exo*,*exo*-**21d** (1.67 g, 79%) as a colorless oil which solidified at 0 °C, m.p. 34 °C (MeOH), R_f = 0.51. IR (KBr): $\tilde{\nu}$ = 2923 cm^{-1}, 1613, 1536, 1509, 1364, 1250 (CF), 1029, 826, 764, 561, 534. ^1H NMR: δ = 0.77 (tt, *J* = 3.5, 6.8 Hz, 1 H, CH *c*Pr), 0.93 (t, *J* = 6.8 Hz, 3 H, CH_3), 1.15 (m, 2 H), 1.22 (t, *J* = 6.8 Hz, 2 H), 1.25−1.45 (m, 10 H), 1.87 (ddd, *J* = 3.3, 11.0, 12.3 Hz, 2 H, CH_2), 2.20 (dd, *J* = 7.5, 12.3 Hz, 2 H, CH_2), 2.78 (tt, *J* = 7.5, 11.0 Hz, 1 H, CH), 7.17 (dd, *J* = 6.5, 8.8 Hz, 2 H, Ar-H), 7.29 (d, *J* = 8.3 Hz, 2 H, Ar-H), 7.41 (d, *J* = 8.3 Hz, 2 H, Ar-H) ppm. ^{13}C NMR: δ = 14.1 (CH_3), 20.0 (CH), 22.7 (CH_2), 24.2 (2 CH), 29.4 (CH_2), 29.5 (CH_2), 29.6 (CH_2), 31.9 (CH_2), 32.9 (CH_2), 36.3 (2 CH_2), 40.7 (CH), 110.7 (ddd, *J* = 7.0, 13.9, 21.2 Hz, 2 CH), 126.6 (2 CH), 128.0 (2 CH), 135.7 (C), 137.2 (dt, *J* = 4.7, 12.5 Hz, C), 139.1 (dt, *J* = 14.9, 241.5 Hz, C), 145.6 (C), 151.4 (ddd, *J* = 4.4, 10.1, 249.3 Hz, 2 C) ppm. $C_{25}H_{29}F_3$ (386.48): calcd. C 77.69, H 7.56; found C 77.37, H 7.60.

***exo*,*exo*-6-Heptyl-3-{[*trans*-4-(*trans*-4-propylcyclohexyl)cyclohexyl]-phenyl}bicyclo[3.1.0]hexane (*exo*,*exo*-21e):** Column chromatography (300 g of silica gel, column 50 × 4.5 cm, hexane) of the reaction mixture obtained from the iodide *exo*,*exo*-**20e** (2.31 g, 4.581 mmol), $C_6H_{13}MgBr$ (9.16 mmol, 13.67 mL of a 0.67 M solution), LiCl (0.030 g) and $CuCl_2$ (0.049 mg) according to GP6 gave the hydrocarbon *exo*,*exo*-**21e** (1.65 g, 78%) as a colorless solid, m.p. 237−239 °C (MeOH/$CHCl_3$, 10:1), R_f = 0.57. IR (KBr): $\tilde{\nu}$ = 3019 cm^{-1}, 2957, 2850, 1513, 1466, 1441, 1050, 997, 892, 818, 722, 549. ^1H NMR: δ = 0.71 (tt, *J* = 2.9, 6.5 Hz, 1 H, CH *c*Pr), 0.87 (t, *J* = 7.3 Hz, 3 H, CH_3), 0.89 (t, *J* = 6.7 Hz, 3 H, CH_3), 0.98−1.12 (m, 12 H), 1.12−1.52 (m, 13 H), 1.61 (br. s, 2 H), 1.67−2.00 (m, 12 H), 2.11 (dd, *J* = 7.3, 12.5 Hz, 2 H, CH_2), 2.40 (tt, *J* = 3.3, 11.8 Hz, 1 H, CH), 2.68 (tt, *J* = 7.3, 11.0 Hz, 1 H, CH), 7.11 (br. s, 4 H, Ar-H) ppm. ^{13}C NMR: δ = 14.1 (CH_3), 14.4 (CH_3), 19.9 (CH), 20.0 (CH_2), 22.7 (CH_2), 24.2 (2 CH), 29.4 (CH_2), 29.5 (CH_2), 29.6 (CH_2), 30.1 (2 CH_2), 30.4 (2 CH_2), 31.9 (CH_2), 32.9 (CH_2), 33.6 (2 CH_2), 34.6 (2 CH_2), 36.4 (2 CH_2), 37.6 (CH), 39.8 (CH_2), 40.6 (CH), 42.9 (CH), 43.4 (CH), 44.2 (CH), 126.6 (2 CH), 127.1 (2 CH), 142.4 (C), 145.4 (C) ppm. $C_{34}H_{54}$ (462.77): calcd. C 88.24, H 11.76; found C 88.09, H 11.64.

1-[2-(Cyclopentene-4-yl)ethyl]-4-ethoxy-2,3-difluorobenzene (29): The reaction mixture obtained from iodide **27** (3.58 g, 12.0 mmol), (cyclopentene-4-yl)methylmagnesium bromide [freshly prepared from 4-(bromomethyl)cyclopentene (**24**) (2.901 g, 18 mmol) and Mg (0.433 g, 18 mmol)], LiCl (0.101 g) and $CuCl_2$ (0.161 g) according to GP6 was concentrated under reduced pressure, and the residue was recrystallized from hexane/benzene, 2:1 to give **1,2-bis(4-ethoxy-2,3-difluorophenyl)ethane** (**28**) (1.05 g, 51%) as a colorless solid. ^1H NMR: δ = 1.43 (t, *J* = 7.0 Hz, 6 H, 2 CH_3), 2.86 (s, 4 H, 2 CH_2), 4.08 (q, *J* = 7.0 Hz, 4 H, 2 OCH_2), 6.63 (dt, *J* = 1.5, 7.3 Hz, 1 H, Ar-H), 6.68 (dt, *J* = 2.0, 8.0 Hz, 1 H, Ar-H), 7.46 (ddd, *J* = 2.3, 7.3, 12.5 Hz, 1 H, Ar-H), 7.67 (ddd, *J* = 1.5, 8.0, 12.0 Hz, 1 H, Ar-H) ppm. ^{13}C NMR: δ = 14.7 (2 CH_3), 29.2 (2 CH_2), 65.3 (2 CH_2), 109.1 (2 CH), 121.6 (d, *J* = 13.6 Hz, 2 C), 123.5 (dd, *J* = 5.7, 10.3 Hz, 2 CH), 141.5 (dd, *J* = 15.3, 248.6 Hz, 2 C), 146.8 (dd, *J* = 3.5, 8.1 Hz, 2 C), 148.1 (dd, *J* = 9.9, 243.8 Hz, 2 C) ppm. The mother liquor was concentrated under reduced pressure and purified by column chromatography (100 g of silica gel, column 30 × 3 cm, hexane/benzene, 2:1) to give compound **29** (0.758 g, 25%) as a colorless oil, R_f = 0.50. ^1H NMR: δ = 1.44 (t, *J* = 7.0 Hz, 3 H, CH_3), 1.68 (q, *J* = 7.6 Hz, 2 H, CH_2), 2.02 (dd, *J* = 7.0, 14.0 Hz, 2 H, CH_2), 2.23 (sept, *J* = 7.0 Hz, 1 H, CH), 2.51 (dd, *J* = 9.0, 14.0 Hz, 2 H, CH_2), 2.61 (t, *J* = 7.0 Hz, 2 H, CH_2), 4.09 (q, *J* = 7.0 Hz, 2 H, OCH_2), 5.67 (s, 2 H, 2 =CH), 6.64 (dt, *J* = 2.0, 8.0 Hz, 1 H, Ar-H), 6.81 (dt, *J* = 2.0, 8.0 Hz, 1 H, Ar-H) ppm. ^{13}C NMR: δ = 14.8 (CH_3), 27.2 (CH_2), 37.0 (CH), 37.1 (CH_2), 38.8 (2 CH_2), 65.3 (CH_2), 109.3 (d, *J* = 2.7 Hz, CH), 123.2 (dd, *J* = 4.5, 10.4 Hz, CH), 123.4 (d, *J* = 4.3 Hz, C), 129.8 (2 CH), 141.5 (dd, *J* = 14.7, 246.5 Hz, C), 146.2 (dd, *J* = 2.8, 11.1 Hz, C), 149.8 (dd, *J* = 10.6, 245.1 Hz, C) ppm. $C_{15}H_{18}F_2O$ (252.3): calcd. C 71.40, H 7.19; found C 71.11, H 6.95.

***exo*,*exo*-3-[2-(4-Ethoxy-2,3-difluoro-phenyl)ethyl]-6-pentylbicyclo-[3.1.0]hexane (*exo*,*exo*-32):** Column chromatography (80 g of silica

gel, column 25 × 3 cm, hexane) of the reaction mixture obtained from the iodide *exo*,*exo*-**31** (686 mg, 1.69 mmol), C_4H_9MgBr (3.39 mmol, 3.9 mL of a 0.87 M solution), LiCl (14.3 mg) and $CuCl_2$ (22.7 mg) according to GP6 gave the product *exo*,*exo*-**32** (325 mg, 57%) as a colorless oil, R_f = 0.25. ^{1}H NMR: δ = 0.92 (t, J = 6.8 Hz, 3 H, CH_3), 0.99−1.55 (m, 15 H), 1.44 (t, J = 7.0 Hz, 3 H, CH_3), 1.91 (dd, J = 5.8, 11.8 Hz, 2 H, CH_2), 2.15−2.21 (m, 1 H, CH), 2.52 (dd, J = 6.0, 14.0 Hz, 2 H, CH_2), 4.07 (q, J = 7.0 Hz, 2 H, OCH_2), 6.63 (ddd, J = 1.8, 7.25, 8.1 Hz, 1 H, Ar-H), 6.78 (t, J = 8.1 Hz, 1 H, Ar-H) ppm. ^{13}C NMR: δ = 14.1 (CH_3), 14.7 (CH_3), 20.4 (CH), 22.7 (CH_2), 24.2 (2 CH), 27.8 (CH_2), 29.3 (CH_2), 31.8 (CH_2), 32.9 (CH_2), 34.7 (2 CH_2), 36.4 (CH_2), 44.2 (CH), 65.3 (CH_2), 109.2 (d, J = 3.0 Hz, CH), 123.1 (dd, J = 5.8, 10.5 Hz, CH), 123.4 (d, J = 5.1 Hz, C), 141.5 (dd, J = 15.0, 246.8 Hz, C), 146.3 (dd, J = 2.9, 8.2 Hz, C), 149.7 (dd, J = 10.2, 244.9 Hz, C) ppm. $C_{21}H_{30}F_2O$ (336.45): calcd. C 74.96, H 8.98; found C 74.71, H 8.95.

4-Propylcyclopentene (34a): A) The reaction mixture obtained from iodide **33** (23.735 g, 114.1 mmol), ethylmagnesium bromide (228 mmol, 65 mL of a 3.51 M solution in Et_2O), LiCl (0.483 g) and $CuCl_2$ (0.766 g) according to GP6 was concentrated under ambient pressure using a 30 cm rectification column, and the residue was distilled under ambient pressure to give **34a** (6.803 g, 54%) as a colorless liquid, b.p. 119−122 °C (ref.[43] 115 °C). ^{1}H NMR: δ = 0.83 (t, J = 6.6 Hz, 3 H, CH_3), 1.15−1.43 (m, 4 H, 2 CH_2), 1.94 (dd, J = 6.6, 13.9 Hz, 2 H, CH_2), 2.00−2.23 (m, 1 H, CH), 2.45 (dd, J = 8.6, 13.9 Hz, 2 H, CH_2), 5.59 (br. s, 2 H, 2 =CH) ppm. ^{13}C NMR: δ = 14.3 (CH_3), 21.5 (CH_2), 37.4 (CH), 38.8 (CH_2), 38.9 (2 CH_2), 130.0 (2 CH) ppm.

B) Under the same conditions as above, the cyclopentene **34a** (2.0 g, 30%) was obtained from *n*-propyl iodide (10.2 g, 6.92 mL, 60 mmol), (cyclopentene-4-yl)magnesium bromide [freshly prepared from 4-bromocyclopentene (**14**) (11.03 g, 75 mmol) and Mg (1.80 g, 75 mmol)], LiCl (0.509 g) and $CuCl_2$ (0.807 g).

4-Pentylcyclopentene (34b): Column chromatography (350 g of silica gel, column 50 × 4.5 cm, hexane) of the reaction mixture obtained from *n*-pentyl iodide (9.90 g, 6.53 mL, 50 mmol), (cyclopentene-4-yl)magnesium bromide [freshly prepared from 4-bromocyclopentene (**14**) (8.82 g, 60 mmol) and Mg (1.45 g, 60 mmol)], LiCl (0.212 g) and $CuCl_2$ (0.360 g) according to GP6 gave the cyclopentene derivative **34b** (3.667 g, 53%) as a colorless oil, R_f = 0.65. ^{1}H NMR: δ = 0.86 (t, J = 6.1 Hz, 3 H, CH_3), 1.18−1.53 (m, 8 H, 4 CH_2), 1.94 (dd, J = 7.4, 14.1 Hz, 2 H, CH_2), 2.21 (sept, J = 7.4 Hz, 1 H, CH), 2.45 (dd, J = 8.0, 14.1 Hz, 2 H, CH_2), 5.66 (br. s, 2 H, 2 =CH) ppm. ^{13}C NMR: δ = 14.1 (CH_3), 22.7 (CH_2), 28.1 (CH_2), 32.1 (CH_2), 36.5 (CH_2), 37.7 (CH), 39.0 (2 CH_2), 130.0 (2 CH) ppm. $C_{10}H_{18}$ (138.24): calcd. C 86.88, H 13.12; found C 86.54, H 13.11.

4-Heptylcyclopentene (34c): Column chromatography (350 g of silica gel, column 50 × 4.5 cm, hexane) of the reaction mixture obtained from *n*-heptyl iodide (11.31 g, 8.2 mL, 50 mmol), (cyclopentene-4-yl)magnesium bromide [freshly prepared from 4-bromocyclopentene (**14**) (8.82 g, 60 mmol) and Mg (1.45 g, 60 mmol)], LiCl (0.212 g) and $CuCl_2$ (0.360 g) according to GP6 gave the cyclopentene derivative **34c** (4.66 g, 56%) as a colorless oil, R_f = 0.62. ^{1}H NMR: δ = 0.88 (t, J = 6.6 Hz, 3 H, CH_3), 1.16−1.36 (m, 12 H, 6 CH_2), 1.90 (dd, J = 7.4, 13.0 Hz, 2 H, CH_2), 2.20 (sept, J = 7.4 Hz, 1 H, CH), 2.45 (dd, J = 7.4, 13.0 Hz, 2 H, CH_2), 5.66 (br. s, 2 H, 2 =CH) ppm. ^{13}C NMR: δ = 14.1 (CH_3), 22.7 (CH_2), 28.4 (CH_2), 29.4 (CH_2), 29.8 (CH_2), 31.9 (CH_2), 36.6 (CH_2), 37.7 (CH), 39.0 (2 CH_2), 130.0 (2 CH) ppm. $C_{12}H_{22}$ (166.3): calcd. C 86.66, H 13.34; found C 86.44, H 13.11.

General Procedure 7 (GP7) for the Preparation of Tosylhydrazones 35: To a solution of tosylhydrazine (5.05 mmol) in methanol (10 mL) was added a solution of the respective arene carbaldehyde (5 mmol) in MeOH (5 mL) in one portion at 65 °C. The reaction mixture was stirred for an additional 30 min at this temp. and cooled to 0 °C. The precipitate was filtered, washed with cold MeOH (5 mL) and dried at ambient temp. under reduced pressure (10^{-2} Torr) for 24 h.

Tosylhydrazone of 4-Ethoxy-2,3-difluorobenzaldehyde (35a): From 4-ethoxy-2,3-difluorobenzaldehyde (**26a**) (1.00 g, 5.37 mmol) and tosylhydrazine (1.05 g, 5.64 mmol), tosylhydrazone **35a** (1.90 g, 98%) was obtained as a colorless powder according to GP7, m.p. 149−151 °C (decomp.). IR (KBr): $\tilde{\nu}$ = 3185 cm^{-1}, 2982, 2930, 1623, 1518, 1458, 1334, 1167, 1083. ^{1}H NMR ([D$_6$]DMSO): δ = 1.33 (t, J = 7.0 Hz, 3 H, CH_3), 2.35 (s, 3 H, CH_3), 4.14 (q, J = 7.0 Hz, 2 H, OCH_2), 7.02 (t, J = 8.2 Hz, 1 H, Ar-H), 7.38 (d, J = 8.7 Hz, 2 H, Ar-H), 7.41 (t, J = 8.2 Hz, 1 H, Ar-H), 7.74 (d, J = 8.7 Hz, 2 H, Ar-H), 7.97 (s, 1 H, =CH), 11.89 (s, 1 H, NH) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 14.3 (CH_3), 20.9 (CH_3), 65.1 (CH_2), 110.3 (d, J = 2.5 Hz, CH), 114.9 (d, J = 8.1 Hz, C), 120.7 (t, J = 4.1 Hz, CH), 127.0 (2 CH), 129.6 (2 CH), 136.0 (C), 139.1 (CH), 140.0 (dd, J = 13.5, 244.9 Hz, C), 143.4 (C), 149.0 (dd, J = 11.4, 251.2 Hz, C), 149.1 (dd, J = 3.3, 7.7 Hz, C) ppm.

Tosylhydrazone of 4-Cyanobenzaldehyde (35b): From 4-cyanobenzaldehyde (**26a**) (10.0 g, 76.3 mmol) and tosylhydrazine (12.3 g, 66.1 mmol), tosylhydrazone **35b** (17.7 g, 89%) was obtained as a colorless powder according to GP7, m.p. 154−156 °C (ref. 44, 155−156 °C). The ^{1}H and ^{13}C NMR spectra of **35b** were identical to those reported earlier.[44]

(4-Ethoxy-2,3-difluorophenyl)diazomethane (36a): This compound was prepared as a yellow oil in 98% yield on a 5 mmol scale according to the procedure of Creary.[26] IR (film): $\tilde{\nu}$ = 2988 cm^{-1}, 2066, 1617, 1511, 1304, 1082. ^{1}H NMR: δ = 1.40 (t, J = 6.0 Hz, 3 H, CH_3), 4.13 (q, J = 6.0 Hz, 2 H, CH_2), 5.00 (s, 1 H, HC=N), 6.55 (t, J = 8.5 Hz, 1 H, Ar-H), 7.70 (t, J = 8.5 Hz, 1 H, Ar-H) ppm. ^{13}C NMR: δ = 14.4 (CH_3), 63.3 (CH), 65.7 (CH_2), 110.8 (CH), 115.5 (CH), 121.6 (d, J = 13.5 Hz, C), 142.4 (dd, J = 21.0, 265.0 Hz, C), 145.6 (dd, J = 22.0, 247.0 Hz, C), 146.8 (dd, J = 3.2, 8.5 Hz, C) ppm.

***exo*,*exo*-6-(4-Cyanophenyl)-3-pentylbicyclo[3.1.0]hexane (*exo*,*exo*-38b):** To a stirred solution of **34b** (0.966 g, 6.99 mmol) and palladium acetate (0.110 g, 0.49 mmol, 7 mol %) in diethyl ether (15 mL) was added dropwise a solution of 4-cyanophenyldiazomethane (**36b**)[26] (1.10 g, 7.68 mmol) in Et_2O over a period of 12 h at ambient temp. The reaction mixture was filtered through a pad of silica gel, concentrated under reduced pressure and separated by HPLC (eluting with MeOH/H_2O 85:15) to give *exo*,*exo*-**38b** (0.513 g, 29%) and *exo*,*endo*-**38b** (0.053 g, 3%) as colorless solids.

***exo*,*exo*-38b:** M.p. 34−35 °C. ^{1}H NMR (C_6D_6): δ = 0.88 (t, J = 6.5 Hz, 3 H, CH_3), 1.50 (m, 14 H), 2.08 (dd, J = 12.0, 3.0 Hz, 2 H, 2 CH), 7.04 (d, J = 8.5 Hz, 2 H, Ar-H), 7.48 (d, J = 8.5 Hz, 2 H, Ar-H) ppm. ^{13}C NMR (C_6D_6): δ = 14.0 (CH_3), 22.5 (2 CH), 22.6 (CH), 24.2 (CH_2), 28.2 (CH_2), 31.8 (CH_2), 32.8 (2 CH_2), 36.2 (CH), 36.5 (CH_2), 109.4 (C), 118.5 (C), 130.2 (2 CH), 132.0 (2 CH), 144.9 (C) ppm. MS (EI): *m*/*z* (%) = 253 (100) [M^+], 182 (95) [$M^+ - C_5H_{11}$], 168 (16), 154 (40), 142 (65), 137 (35), 127 (15), 116 (50).

***exo*,*endo*-38b:** M.p. 45−47 °C. ^{1}H NMR (C_6D_6): δ = 0.79 (t, J = 7.5 Hz, 3 H, CH_3), 0.93−1.03 (m, 8 H), 1.08 (p, J = 6.0 Hz, 1 H, CH), 1.11−1.21 (m, 4 H, 2 CH_2), 1.59 (t, 1 H, CH), 1.65 (dd, J = 6.0, 12.0 Hz, 2 H, 2 CH), 6.80 (d, J = 8.5 Hz, 2 H, Ar-H), 7.01 (d,

Table 3. Crystallographic data and parameters for the refinements of compounds **9a**, *endo*,*exo*-**18a**, *exo*,*exo*-**18b**, *exo*,*exo*-**38b**, and *exo*,*endo*-**38b**.

Compound	*exo*,*exo*-**9a**	*endo*,*exo*-**18a**	*exo*,*exo*-**18b**	*exo*,*exo*-**38b**	*exo*,*endo*-**38b**
Empirical formula	$C_{30}H_{38}O_4$	$C_{28}H_{42}O_2$	$C_{17}H_{19}F_3O_2$	$C_{18}H_{23}N$	$C_{18}H_{23}N$
Molecular mass	462.63	410.62	312.32	253.37	253.37
Temperature, K	133(2)	120(2)	120.0(2)	120(2)	220.0(2)
Wavelength, Å	0.71073				
Crystal system	monoclinic	monoclinic	triclinic	triclinic	triclinic
Space group	$C2/c$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
Unit cell dimensions (Å,°)					
a	28.793(1)	20.075(1)	5.7364(3)	9.7909(4)	6.0817(5)
b	5.9710(5)	9.9072(6)	11.0353(6)	11.8250(5)	8.5321(7)
c	32.423(3)	12.7752(7)	12.8208(7)	14.2577(6)	15.048(3)
α	90	90	76.584(2)	104.734(1)	81.97(3)
β	111.767(7)	101.10(2)	87.759(2)	103.126(1)	85.25(3)
γ	90	90	87.674(2)	97.423(1)	87.91(3)
Volume ($Å^3$)	5176.8(5)	2493.3(3)	788.43(7)	1523.8(1)	770.29(18)
Z	8	4	2	4	2
Density (calculated, $Mg.m^{-3}$)	1.269	1.094	1.316	1.104	1.092
μ, mm^{-1}	0.087	0.066	0.108	0.063	0.063
$F(000)$	2128	904	328	552	276
Crystal size, mm^3	–	0.28 × 0.20 × 0.03	0.36 × 0.21 × 0.16	0.40 × 0.24 × 0.10	0.40 × 0.25 × 0.20
θ_{max} (°) for data collection	24.06	27.50	30.17	30.00	30.55
Reflections collected	28013	22856	8036	13531	6797
Independent reflections [R_{int}]	4058 [0.0696]	4802 [0.1501]	4178 [0.0295]	8684 [0.0309]	4553 [0.0303]
Refinement method	Full-matrix least-squares on F^2				
Data/restraints/parameters	4058/0/309	4802/0/419	4178/0/275	8684/0/527	4553/0/272
Goof on F^2	1.053	0.894	1.039	0.935	0.948
R_1, wR_2 indices [$I > 2\sigma(I)$]	0.0506, 0.1342	0.0796, 0.1829	0.0434, 0.1096	0.0489, 0.1171	0.0487, 0.1249
R_1, wR_2 indices (all data)	0.0690, 0.1421	0.1563, 0.2124	0.0573, 0.1191	0.0783, 0.1300	0.0893, 0.1401
Largest diff. peak and hole, e·$Å^{-3}$	0.587 and −0.373	0.369 and −0.242	0.347 and −0.207	0.313 and −0.190	0.236 and −0.149

^3J = 8.5 Hz, 2 H, Ar-H) ppm. ^{13}C NMR (C_6D_6): δ = 14.2 (CH_3), 22.8 (2 CH), 24.3 (CH), 24.4 (CH_2), 28.6 (CH_2), 32.2 (CH_2), 32.9 (2 CH_2), 36.5 (CH), 36.9 (CH_2), 110.4 (C), 119.0 (C), 130.1 (2 CH), 132.1 (2 CH), 144.1 (C) ppm.

Crystal Structure Determinations: Suitable crystals of the compounds for X-ray crystal structure determinations were grown by slow evaporation of an Et_2O/hexane solution (**9a**, *exo*,*exo*-**38b** and *exo*,*endo*-**38b**) or a MeOH/Et_2O solution (*endo*,*exo*-**18a** and *exo*,*exo*-**18b**). Crystallographic data and parameters of the refinements are listed in Table 3. The single-crystal X-ray data for all compounds were collected at low temperature using graphite monochromated Mo-K_α radiation on a STOE AED2 (**9a**), Bruker SMART CCD 1 K (*exo*,*exo*-**18b**) or SMART CCD 6000 (*endo*,*exo*-**18a,** *exo*,*exo*-**38b** and *exo*,*endo*-**38b**) diffractometer. Upon slow cooling, the crystals of the *exo*,*endo*-**38b** cracked at about 200 K, which indicates a possible phase transition, and the data for this compound were therefore collected at 220 K. The structures were solved by direct methods and refined with anisotropic a. d. p. for all non-hydrogen atoms using the Bruker SHELXTL program suite. The crystals of *endo*,*exo*-**18a** were non-merohedral twins and the final refinement was performed without overlapping reflections.

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