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Synthesis of [1.1.1]Propellanes by Cyclization of 3-Alkylidenecyclobutylidenes

Monika Kenndoff [1]

München, Institut für Organische Chemie der Universität

Andrea Singer and Günter Szeimies

Berlin, Institut für Chemie der Humboldt-Universität

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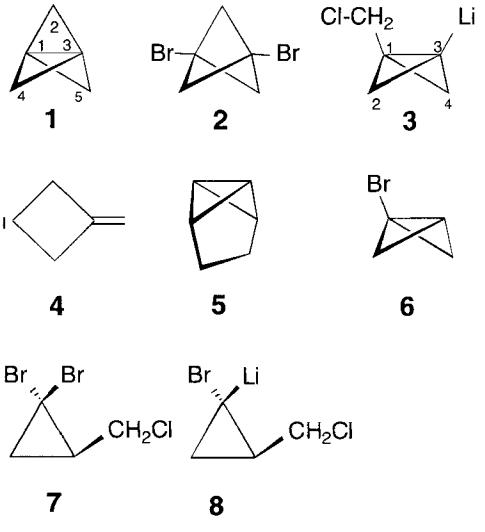
Abstract. Starting from tricyclo[3.1.0.0^{2,6}]hexane **5** and 1-bromobicyclo[1.1.0]butane **6**, a series of [1.1.1]propellanes **15** and **21** has been synthesized which carry alkyl, aryl, alkenyl, and alkynyl groups. Propellane formation proceeded *via* 1-bromo-1-chloro-3-alkylidenecyclobutanes of type **13** and **19**, which on treatment with methyllithium gave rise to the generation of carbenes **14** and **20** as short-lived intermediates. For these carbenes, the most efficient path of stabilization is obviously the intramolecular cycloaddition. *Ab initio* MO calculations at the Becke3LYP/6-31G* and MP2/6-31G* level of theory indicated that 3-alkylidenecyclobutylidenes **4** and **37a–d** are not local energy minima but collapse to the corresponding [1.1.1]propellanes. On this basis, propellane formation should follow a carbenoid reaction path.

Although the first synthesis of the parent [1.1.1]propellane **1** was achieved by reduction of 1,3-dibromobicyclo[1.1.1]pentane **2** [2], this method is of minor importance for the preparation of **1** and its derivatives, because **2** is not easily accessible.1,3 Bridging of bicyclo[1.1.0]butanes of type **3** has proved to be the most effective route to [1.1.1]propellanes [3]. The third method, cyclization of carbenes **4**, detected in 1987 [4], has attracted only little attention, although its usefulness has been demonstrated by us in two additional reports [5, 6]. In this paper we show that carbene cyclization leads to [1.1.1]propellanes with a considerable variety of substituents. The experiments were carried out with tricyclo[3.1.0.0^{2,6}]hexane **5** [7] and 1-bromobicyclo [1.1.0]-butane **6** [8] as starting materials.

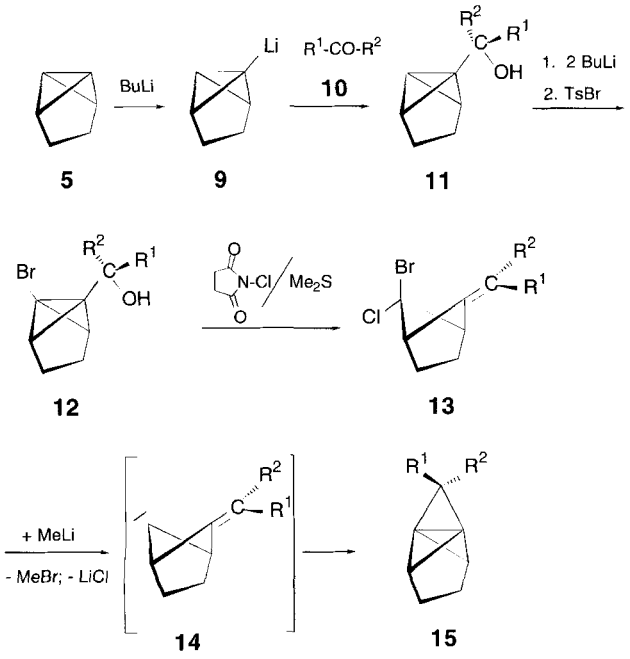


1 **2** **3** **4** **5** **6** **7** **8**

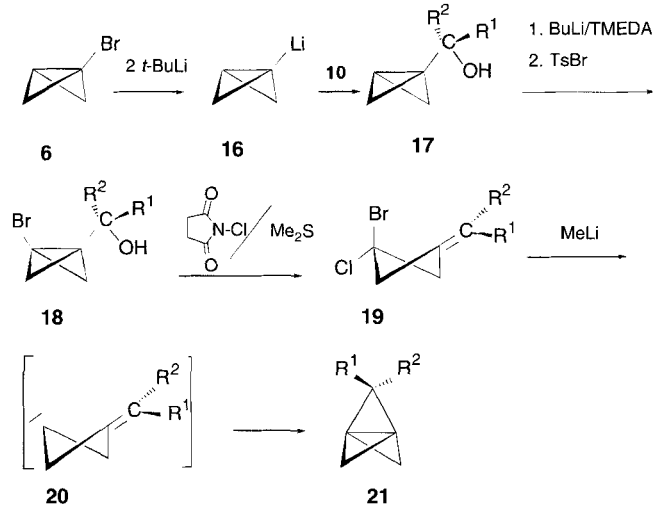
A. The Synthetic Procedure

The synthetic procedure followed in this report is outlined in Schemes 1 and 2. Whereas tricyclo[3.1.0.0^{2,6}]-hexane **5** has become easily available by the work of Christl [7], the findings of Nilsen and Skattebøl [18a] on the formation of 1-bromobicyclo[1.1.0]butane **6** have not been used much. Starting from allyl chloride, **6** could be isolated in 40–55% yield *via* 1,1-dibromo-2-chloromethylcyclopropane **7** and its conversion to **8** with methyllithium (MeLi) in ether at –40 °C [8b].

Starting from **6**, the procedure for the synthesis of the corresponding propellane is outlined in Scheme 2.



Scheme 1



Scheme 2

1 Carbinols 11 and 17

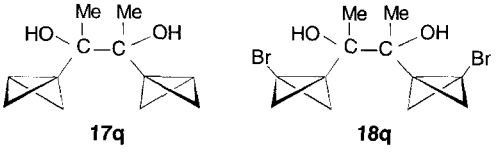
1-*Tricyclo*[3.1.0.0^{2,6}]hexyl*lithium* **9** was obtained by metalation of **5** with *n*-butyllithium (BuLi) in ether at room temperature. 1-Bicyclo[1.1.0]butyllithium **16** was generated by lithium bromine exchange of **6** with 2.0 equiv. of *tert*-butyllithium (*t*-BuLi) in ether/pentane at –78 °C. For the synthesis of **11**, ketones or aldehydes **10** were added to a solution of **9** cooled in an ice bath, whereas the addition of bicyclobutyllithium **16** to the carbonyl compounds **10** was carried out at –78 °C. Results are shown in Table 1, in which also the substituents R^1 and R^2 of **10** are specified.

Table 1 Substituents R^1 and R^2 and Yields of **11** and **17**

10:	R^1	R^2	**11** (% Yield)	**17** (% Yield)
a	Ph	H	–	70
b	4-$MeOC_6H_4$	H	–	73
c	Ph	Me	29	79
d	Ph	*t*-Bu	58	–
e [a])	C_6H_4-	C_6H_4	62	72
f	Me	Me	35	–
g	*i*-Pr	*i*-Pr	67	71
h	*t*-Bu	*t*-Bu	56	–
i [b])	C_2H_4-	C_2H_4	51	72
j [c])	C_2H_4-	CH_2	55	–
k [d])	CMe_2CMe_2-	CH_2	–	97
l [e])	H_2C=CH	H	–	71
m [f])	MeCH=CH	H	–	73
n [g])	Me_2C=CH	Me	–	87
o [h])	CH=CH-CH_2-	CH_2CH_2	–	78
p	Me_3C-C≡C	H	–	73

[a]) 9-Fluorenone. [b]) Cyclopentanone. [c]) Cyclobutanone. [d]) 2,2,3,3-Tetramethylcyclobutanone. [e]) Acrolein. [f]) (*E*)-Crotonaldehyd. [g]) Mesityl oxide. [h]) Cyclohex-2-enone.

In addition to aldehydes and ketones of Table 1, biacetyl was also treated with bicyclobutyllithium **16** giving rise to a 62:38 mixture of diastereomers of type **17q** in a total yield of 46%. Configurational assignment of **17q** could not be carried out.



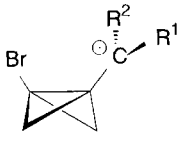
2 Bromination of the Second Bicyclobutane Bridgehead Position

Substitution of hydrogen against bromine at C-6 of **11** and C-3 of **17** to afford **12** and **18** was achieved by metalation, for **11** with 2.2 equiv. of BuLi and occasionally of MeLi in ether, for **17** with BuLi/TMEDA, followed by reaction with tosyl bromide [9]. As observed earlier [6], BuLi tends to lithiate the ortho position of aromatic rings fixed to the carbon atom which also carries the OH group. MeLi was found to be incapable of this unwanted side reaction. Specific difficulties were encountered with the bromination of **17e**, which was carried out several times. In all cases a mixture of **17e** and **18e** was isolated which could not be separated. Attempted separation by distillation under high vacuum led to polymerization of the material. Neither the carbinols **11** and **17** nor their brominated counterparts **12** and **18** could

be purified by chromatographic methods without massive destruction of the bicyclo[1.1.0]butane framework. If purification could not be achieved satisfactorily, the raw material was used for the next step. The yields of bromocarbinols **12** ranged from 37% to 88%, those of **18** from 30% to 79%. It should be noted that **18q** is doubly brominated as shown in the formula.

3 Conversion of Bromoalcohols 12 and 18 to Dihalides 13 and 19

The substitution of the hydroxyl group against chloride of bicyclo[1.1.0]butylcarbinols of type **12** and **18**, which, in addition, carry the hydroxyl group in benzylic, allylic or tertiary alkyl positions, cannot be effected without complete bicyclobutylcarbinyl/3-methylencyclobutyl rearrangement [10]. Based on our prior experience [6], the method of Corey, Kim and Takeda [11], using dimethyl sulfide/*N*-chlorosuccinimide (NCS) as reagent, was suited best for the conversion of **12** → **13** and of **18** → **19**. In most cases, the yields were only moderate; in addition, the isolation and purification of the dihalides were difficult because of their facile decomposition. However, characterization by NMR spectroscopy was possible in all cases. The necessary precondition for the synthesis of dihalides **13** and **19** is the formation of the carbenium ion **22** or **23**, which is produced by elimination of dimethyl sulfoxide from the precursors **24** and **25**. The formation of these intermediates demands steric accessibility of the reagent to the hydroxyl group of **12** and **18**. In cases of severe steric crowding, this accessibility was not always fulfilled, making attempts of converting the bromoalcohols to the dihalides **13** and **19** unsuccessful, as observed with **12d** and **12h**. Unsatisfactory results were obtained with **12g**, **12i** and **12j**. The yields of the corresponding dihalides **13** were less than 10% and the products strongly contaminated by impurities which could not be removed. Alternative methods for the conversion of the carbinols into the chlo-rides, like thionyl chloride in pyridine or triphenyl phosphine/carbon tetrachloride, gave even poorer yields. Therefore, the synthesis of the corresponding propellanes could not be pursued. **13c**, **13e**, and **13f** were isolated in yields of 62, 66 and 35%, whereas the yields of dihalides **19** were in the range of 13 to 56%. The attempted conversion of **18l** to **19l** was not succesful.



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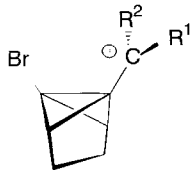

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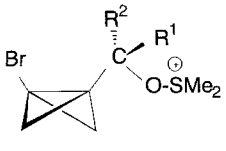

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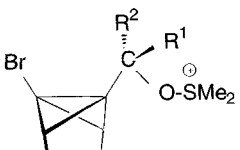

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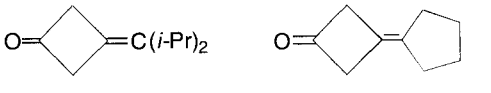
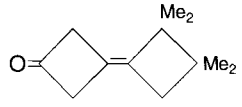
The reaction of **18g, i, k**, and **p** with Me_2S/NCS lead to the ketones **26a–d** as additional products in yields of 19, 15, 15, and 7.5%. An excess of NCS and addition of lithium chloride to the reaction mixture suppressed the formation of the ketones nearly completely. The formation of the ketones is probably based on competitive capture of carbenium ion **27** by succinimide anion leading to **28**, which is easily hydrolyzed to **26** on aqueous workup.

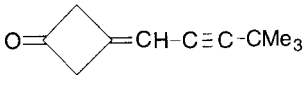


26a

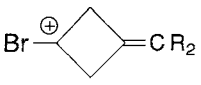
26b



26c



26d



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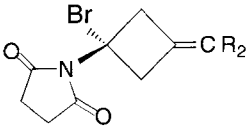

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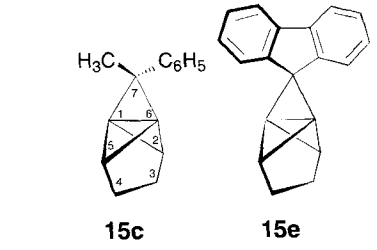
4 Synthesis of [1.1.1]Propellanes 15 and 21

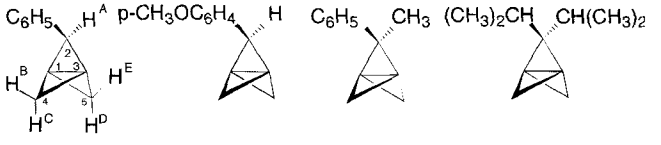
The synthesis of propellanes **15** and **21** was achieved by reaction of dihalides **13** and **19** with one equivalent of MeLi in ether at about –25 °C. After aqueous workup under nitrogen, volatile propellanes were flash-distilled with the solvent into a dry-ice cooled trap and isolated by fractional distillation. Less volatile propellanes were obtained after removal of the solvent by fractional distillation of the organic portion. Propellane **15e** was a solid. The structures of the propellanes were established by their NMR spectra; the ^{13}C chemical shifts of the three C_1-bridges appear at rather low field and are very specific for the [1.1.1]propellane framework [3, 12]. Due to their quick reaction with oxygen, combustion analyses were not carried out. The yields of **15c, e** and **f** were 63%, 87% and 30%. Results for propellanes **21** are given in Table 2.

Table 2 Yields and Selected ^{13}C Chemical Shifts (in C_6D_6) of **21**

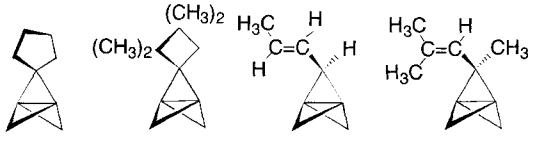
21	% Yield	δC-1, C-3	δC-2	δC-4, C-5
a	56	6.55	93.65	69.78; 74.06
b	45	6.78	93.24	69.68; 74.02
c	33	11.53	103.51	69.41; 71.04
g	64	13.80	116.39	67.27; 71.10
i	60	13.76	103.44	69.52
k	30	10.80	104.88	66.56; 69.39
m	82	6.49	91.03	69.19; 72.41
n	59	12.40	95.64	68.91; 69.27
o	20	12.10	98.27	67.46; 67.92
p	41	8.51	75.20	69.59; 74.23



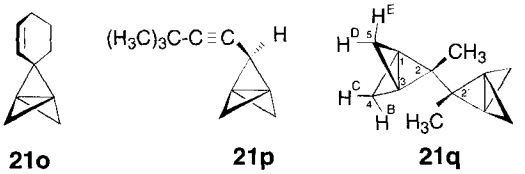
15c **15e** **15f**



21a **21b** **21c** **21g**



21i **21k** **21m** **21n**



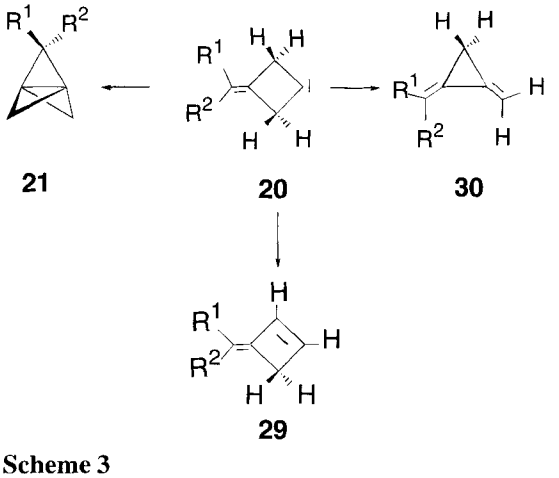
21o **21p** **21q**

Whereas most of the propellanes could be stored under nitrogen at −25 °C in the refrigerator for several months, spiropropellane **21k** showed a high propensity for polymerization. A solution of **21k** in C_6D_6 in NMR concentration was completely polymerized after 4.5 h at room temperature. Easy polymerization was also observed with bispropellane **21q**, which was isolated in 37% yield after generation from tetrahalide **19q** with 2 equiv. of MeLi in ether. The ^{13}C NMR chemical shifts of **21q** were in accordance with the data given in Table 2.

5 Considering the Propellane Formation

The obvious mechanistic interpretation of the formation of propellanes **21** from the dihalides **19** leads to the assumption of the intermediacy of carbene **20** in its singlet electronic state. The fastest reaction of **20** then is the intramolecular addition of the carbenic carbon to the CC double bond, forming propellane **21**. However, there are at least two different modes of stabilization for carbene **20**, which have to be considered seriously: hydrogen migration leading to methylenecyclobutene **29**, and ring contraction under formation of bismethylenecyclopropane **30** (see Scheme 3). Hydrogen migration to give rise to cyclobutene **32** is a well documented property of cyclobutylidene **31** [13], and it is not easy to see why the allylic hydrogens in carbene **20** should not migrate. This mode of stabilization should play only a minor role for carbene **14** because of the high strain energy of the *trans*-cyclopentene analog bridgehead olefin **33** [14].

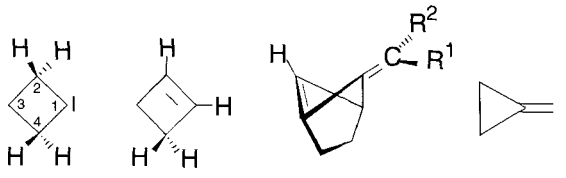
Ring contraction of **31** to afford methylencyclopropane **34** is also a known process [13]. Brinker has reported the results of the Bamford–Stevens reaction of **35**, which *inter alia* led to diene **36** as a major product [15]. It is not clear, if this result provides evidence for the **20** → **30** rearrangement, or if an alternate mechanism is operative.



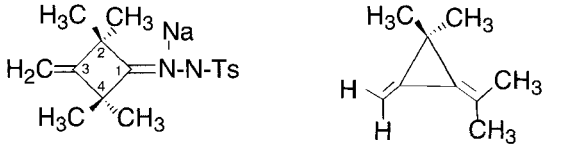
21 **20** **30** **29**

Scheme 3

If the formation of propellanes **21** takes place *via* free carbenes **20**, then the activation energy for cyclization must be lower than the ones for ring contraction and for hydrogen migration. To obtain insight into the energetics of the carbene cyclization affording propellanes **21**, *ab initio* MO calculations using the GAUSSIAN 94 program package [16] have been carried out for **4**, and for the structurally realated carbenes **37a–d** in their singlet electronic states, for the parent propellane **1** and the propellanes **38a–d**. The calculations were performed at the B3LYP/6-31G* [17] and the MP2/6-31G* [17]

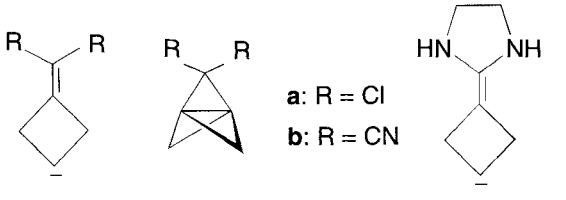


31 **32** **33** **34**

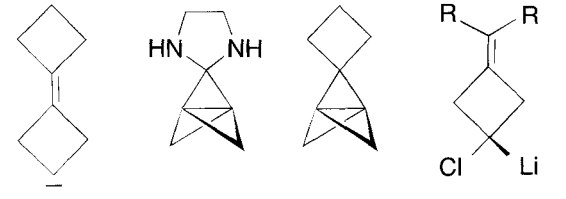


35 **36**

level of theory. **4** was also treated by the QCISD/6-31G* [17] formalism. Density-functional theory (DFT) [18] has shown to be a reliable method to calculate the energy difference of singlet and triplet carbenes [19]. The Becke3LYP functional [17] (B3LYP) has been applied to different problems in organic chemistry and has consistently given good results [20].



37 **38** **37c**



37d **38c** **38d** **39**

The outcome of our calculations on carbene **4** and on carbenes **37a–d** gave a uniform picture: in all cases the singlet carbene was not a local energy minimum. When symmetry restrictions were removed, the planar carbene structure collapsed to the corresponding propellane (**4** and **38a–d**) without an energy barrier in between. The QCISD/6-31G* calculation of **4** (C_s symmetry, plane perpendicular to the four-membered ring) led to a stationary point of the carbene, which, however, was not a local energy minimum. Vibrational analysis afforded a negative frequency of –133.5 cm^{-1}, which could be related to a cyclobutane bending motion towards the formation of the propellane.

The conclusion to be drawn from these results then is the assumption that propellane formation by reaction of dihalides of type **13** and **19** with organolithium bases proceeds, in conventional terminology, via a carbenoid mechanism: elimination of LiCl from **39** and cyclization to the corresponding propellane should take place in a concerted fashion.

We thank the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for financial support and Mr. Oliver Jarosch for his advice concerning the use of Gaussian 94.

Experimental

For analytical instruments and general procedures, see ref. [21]. For detailed spectroscopic data of all new coumpounds, see [1].

Starting Materials: The following compounds were synthesized according to published procedures: 4-tolylsulfonyl bromide (TsBr) [22], cyclobutanone (**10j**) [23], 2,2,3,3-tetramethylcyclobutanone (**10k**) [24], 4,4-dimethyl-2-pentynal (**10p**) [25] tricyclo[3.1.0.$0^{2,6}$]hexane (**5**) [7], 1-bromobicyclo[1.1.0]butane (**6**) [6].

n-Butyllithium (BuLi) was purchased from Chemetall AG, Frankfurt/Main, Germany, as a 1.6 M solution in *n*-hexane, *tert*-butyllithium (*t*-BuLi) from Aldrich as 1.7 M solution in pentane. Methyllithium (MeLi) was prepared from lithium and bromomethane in ether. The concentration of RLi of these solutions was determined by double titration according to Gilman [26]. *N*-Chlorosuccinimide (NCS) and dimethyl sulfide (Me_2S) were commercial products.

1-Tricyclo[3.1.0.$0^{2,6}$]hexyl Carbinols (11)

1-Tricyclo[3.1.0.$0^{2,6}$]hexyllithium (**9**): From a solution of 1.2 equiv. of BuLi in hexane (1.60 M) the solvent was removed by distillation under nitrogen and the residue dissolved in about the same volume of ether. To this solution tricyclo-[3.1.0.$0^{2,6}$]hexane **5** (1.0 equiv.) was added dropwise and the reaction mixture was stirred under nitrogen at room temperature for 17 h. The colorless suspension of **9** was used for further reaction.

1-Phenyl-1(-1-tricyclo[3.1.0.$0^{2,6}$]hexyl)ethanol (**11c**)

To a suspension of **9** (25.0 mmol) in ether under nitrogen, cooled in an ice bath, was added dropwise under stirring a solution of acetophenone (**10c**) (3.00 g, 25.0 mmol) in ether (10 ml). After stirring for 4 h at room temperature, the yellow reaction mixture was hydrolyzed with 2N NaOH, the organic material extracted with ether ad the ether phase dried over $MgSO_4$. Distillative workup after removal of the solvent afforded **11c** (1.43 g, 29%) as a colorless oil of *b.p.* 70 °C (bath)/10^{-4} Torr. – ^{1}H NMR ($CDCl_3$, 60 MHz): δ 1.34 (broad s, 4 H, 3'-, 4'-H_2), 1.52 (s, 3 H, Me), 1.85 (s, 1 H, OH), 1.95 (broad s, 1 H, 6'-H), 2.15 (s, 2 H, 2'-, 5'-H), 7.20–7.50 (m, 5 H, aromatic H). – ^{13}C NMR ($CDCl_3$, 20 MHz): δ 7.33 (d), 25.99 (m), 26.14 (s), 29.53 (q), 35.45, 36,86 (2 d), 72.85 (s), 125.03, 125.64, 127.85 (3 d), 147.66 (s).

2,2-Dimethyl-1-phenyl-1-(1-tricyclo[3.1.0.0^{2,6}]hexyl)-1-propanol (**11d**)

To a suspension of **9** (37.4 mmol) in ether under nitrogen, cooled in an ice bath, was added dropwise under stirring a solution of *tert*-butyl phenyl ketone (**10d**) (6.07 g, 37.4 mmol) in ether (20 ml). After stirring for 6 h at room temperature and after standard workup (see above) distillation of the organic material afforded **11d** (5.23 g, 58%) as a colorless oil of *b.p.* 89–92 °C/0.01 Torr. – ^{1}H NMR ($CDCl_3$, 60 MHz): δ 0.92 (s, 9 H, Me), 1.30–1.48 (m, 5 H, 3'-, 4'-H_2, OH), 1.83 (broad s, 1 H, 6'-H), 2.08, 2.33 (2 d, J = 4.5 Hz, 2 H, 2'-, 5'-H), 7.10–7.48 (m, 5 H, aromatic H). – ^{13}C NMR ($CDCl_3$, 20 MHz): δ 7.48 (d), 23.84 (s), 25.73 (m), 26.26 (q), 37.20, 37.86 (2d), 39.56 (s), 79.51 (s), 126.27, 126.70, 127.43 (3 d), 144.57 (s). – MS (70 eV), *m/z* (%): 186 (13), 105 (100).
$C_{17}H_{22}O$ (242.4): calcd. C 84.25, H 9.15; found C 84.72, H 9.34.

9-(1-Tricyclo[3.1.0.0^{2,6}]hexyl)-9-fluorenol (**11e**)

To a suspension of **9** (65.0 mmol) in ether under nitrogen, cooled in an ice bath, was added dropwise under stirring a solution of fluorenone (**10e**) (11.70 g, 64.9 mmol) in ether (120 ml). The reaction mixture was stirred for 5 h at room temperature. Standard workup followed by distillation of the organic material afforded **11e** as a viscous oil of *b.p.* 165 °C (bath)/10^{-4} Torr, which after crystallization from pentane, led to **11e** (10.50 g, 62%) as colorless crystals of *m.p.* 103–107 °C. – ^{1}H NMR ($CDCl_3$, 60 MHz): δ 1.30 (broad s, 4 H, 3'-, 4'-H_2), 1.85 (broad s, 1 H, 6'-H), 2.12 (m, 2 H, 2'-, 5'-H), 2.17 (s, 1 H, OH), 6.98–7.57 (m, 8 H, aromatic H). – ^{13}C NMR ($CDCl_3$, 20 MHz): δ 6.72 (d), 22.29 (s), 26.08 (m), 36.32 (d), 79.27 (s), 119.85, 123.73, 127.70, 128.64 (4 d), 138.96, 147.42 (2 s).

2-(1-Tricyclo[3.1.0.0^{2,6}]hexyl)propan-2-ol (**11f**)

Following the general procedure, a suspension of **9** (62.4 mmol) in ether and acetone (**10f**) (3.63 g, 62.5 mmol) reacted for 5 h at room temperature. Standard workup followed by distillation of the organic material afforded **11f** (3.02 g, 35%) as a pale yellow liquid of *b.p.* 84–87 °C/12 Torr. – ^{1}H NMR ($CDCl_3$, 60 MHz): δ 1.33 (broad s, 10 H, CMe_2, 3'-,4'-H_2), 1.45 s, 1 H, OH), 1.78 (broad s, 1 H, 6'-H), 2.18 (m, 2 H, 2'H, 5'-H). – ^{13}C NMR ($CDCl_3$, 20 MHz): δ 7.84 (d), 25.81 (s), 26.14 (m), 29.23 (q), 35.19 (d), 68.60 (s).

2,4-Dimethyl-3-(1-tricyclo[3.1.0.0^{2,6}]hexyl)pentan-3-ol (**11g**)

Following the general procedure, a suspension of **9** (75.0 mmol) in ether and diisopropyl ketone (**10g**) (8.56 g, 75.0 mmol) reacted for 4.5 h at room temperature. Standard workup followed by distillation of the organic material afforded **11g** (9.73 g, 67%) as a colorless liquid of *b.p.* 115–118 °C/15 Torr. – ^{1}H NMR ($CDCl_3$, 60 MHz): δ 0.80, 0.90 (2 d, J = 6.4 Hz, 12 H, Me), 1.30 (broad s, 5 H, 3'-, 4'-H_2, OH), 1.83–2.15 (m, 5 H, 2-, 4-, 2'-, 5'-, 6'-H). – ^{13}C NMR ($CDCl_3$, 20 MHz): δ = 6.69 (d), 16.99, 17.57 (2 q), 20.32 (s), 26.02 (m), 33.77 (d), 34.53 (d), 76.17 (s). – MS (70 eV), *m/z* (%): 194 (0.8) [M$^+$], 43 (100).
$C_{13}H_{22}O$ (194.3): calcd. C 80.36, H 11.41; found C 80.13, H 11.17. $C_{13}H_{22}O$ calcd. 194.167; found 194.168 (HRMS).

2,2,4,4-Tetramethyl-3-(1-tricyclo[3.1.0.0^{2,6}]hexyl)pentan-3-ol (**11h**)

Following the general procedure, a suspension of **9** (75.0 mmol) in ether and di-*tert*-butyl ketone (**10h**) (1.71 g, 12.0 mmol) reacted for 9 h at room temperature. Standard workup followed by distillation of the organic material afforded **11h** (1.50 g, 56%) as a colorless oil of *b.p.* 58–59 °C (bath)/0.01 Torr. – ^{1}H NMR ($CDCl_3$, 60 MHz): δ 1.08 (s, 18 H, Me), 1.25 (s, 1 H, OH), 1.38 (s, 4 H, 3'-, 4'-H_2), 2.05 (broad s, 1 H, 6'-H), 2.10 (m, 2 H, 2'-, 5'-H). – ^{13}C NMR ($CDCl_3$, 20 MHz): δ 9.45 (d), 22.44 (s), 25.59 (m), 29.29 (q), 36.23 (d), 42.34 (s), 79.69 (s).

1-(1-Tricyclo[3.1.0.0^{2,6}]hexyl)cyclopentan-1-ol (**11i**)

As described for **11c**., a suspension of **9** (98.0 mmol) in ether and cyclopentanone (**10i**) (8.27 g, 98.3 mmol) in 50 ml of ether reacted for 4.5 h at room temperature. Standard workup followed by distillation of the organic material gave rise to **11i** (8.20 g, 51%) as a colorless oil of *b.p.* 69–71 °C/0.01 Torr. – ^{1}H NMR ($CDCl_3$, 60 MHz): δ 1.29 (broad s, 4 H, 3'-, 4'-H_2), 1.40–1.91 (m, 10 H, 2-, 3-, 4-, 5-H_2, 6'-H, OH), 2.12 (broad s, 2 H, 2'-, 5'-H). – ^{13}C NMR ($CDCl_3$, 20 MHz): δ 7.72 (d), 23.84 (m), 26.23 (m), 35.68 (d), 39.68 (m), 79.66 (s). – MS (70 eV), *m/z* (%): 164 (8) [M$^+$], 79 (100).
$C_{11}H_{16}O$ (164.3): calcd. C 80.44, H 9.82; found C 79.41, H 9.47. $C_{11}H_{16}O$ calcd. 164.120; found 164.121 (HRMS).

1-(1-Tricyclo[3.1.0.0^{2,6}]hexyl)cyclobutan-1-ol (**11j**)

As described for **11c**, a suspension of **9** (14.0 mmol) in ether and cyclobutanone (**10j**) (0.94 g, 13.4 mmol) in 10 ml of ether reacted for 4 h at room temperature. Standard workup followed by distillation of the organic material gave rise to **11j** (900 mg, 45%) as a colorless oil of *b.p.* 47–52 °C (bath)/0.01 Torr. In two further experiments the yield of **11j** was 51% and 55%. – ^{1}H NMR ($CDCl_3$, 60 MHz): δ 1.35 (broad s, 4 H, 3'-, 4'-H_2), 1.40–1.75 (m, 2 H, 3-H_2), 1.85 (m, 1 H, 6'-H), 1.80–2.15 (m, 4 H, 2-, 4-H_2), 2.00 (s, 1 H, OH), 2.20 (m, 2 H, 2'-, 5'-H). – ^{13}C NMR ($CDCl_3$, 20 MHz): δ 7.39 (d), 12.63 (m), 22.84 (s), 26.32 (m), 35.20 (d), 35.20 (m), 72.81 (s). – MS (70 eV), *m/z* (%): 150 (3) [M$^+$], 79 (100).
$C_{10}H_{14}O$ (150.2): calcd. C 79.96, H 9.39; found C 79.96, H 9.41. $C_{10}H_{14}O$ calcd. 150.104; found 150.104 (HRMS).

1-Bicyclo[1.1.0]butyl Carbinols 17 (General Procedure)

To a solution of *t*-BuLi in pentane (2.0 equiv.), cooled in a dry-ice bath and protected by a nitrogen atmosphere, a solution of 1-bromobicyclo[1.1.0]butane (**6**) in ether (1.0 equiv., concentration 0.5 mol/l) was added dropwise under stirring. The reaction mixture was kept for 1 h at –78 °C, followed by addition of the carbonyl compound **10** (1.0 equiv.), dissolved in ether, again under stirring at –78 °C. After 1 h the cooling bath was removed and stirring continued for 3 h at room temperature. The mixture was cooled in an ice bath and hydrolyzed by addition of 2N NaOH. The layers were separated, the aqueous part extracted twice with ether, the combined organic layers dried over $MgSO_4$ and filtered. The solvent was removed *in vacuo* and the carbinol **17** distilled.

(1-Bicyclo[1.1.0]butyl)phenylmethanol (**17a**)

According to the general procedure, *t*-BuLi (69.5 mmol) and

6 (4.30 g, 32.3 mmol) were allowed to react to 1-bicyclo[1.1.0]-butyllithium (**16**), to which benzaldehyde (**10a**) (3.44 g, 32.4 mmol) was added. Standard workup afforded **17a** (3.63 g, 70%) as a colorless liquid of *b.p.* 69–72 °C/0.01 Torr. – ^{1}H NMR ($CDCl_3$, 60 MHz): δ 0.63, 0.75 (2 broad s, 2 H, *endo*-2'-, *endo*-4'-H), 1.25–1.42 (m, 2 H, *exo*-2'-, *exo*-4'-H), 1.57–1.75 (m, 1 H, 3'-H), 2.31 (d, J = 3 Hz, 1 H, OH), 4.75 (d, J = 3 Hz, 1 H, C<u>H</u>OH), 7.22 (broad s, 5 H, aromatic H).

(1-Bicyclo[1.1.0]butyl)-(4-methoxyphenyl)methanol (**17b**)

According to the general procedure, *t*-BuLi (96.0 mmol) and **6** (6.40 g, 48.1 mmol) were allowed to react to **16**, to which 4-methoxybenzaldehyde (**10b**) (6.50 g, 47.7 mmol) was added. Standard workup afforded **17b** (6.63 g, 73%) as a colorless liquid of *b.p.* 103–104 °C/0.001 Torr. – ^{1}H NMR ($CDCl_3$, 60 MHz): δ 0.52-0.80 (m, 2 H, *endo*-2'-, *endo*-4'-H), 1.05–1.46 (m, 2 H, *exo*-2'-, *exo*-4'-H), 1.55–1.76 (m, 1 H, 3'-H), 2.42 (d, J = 3.5 Hz, 1 H, OH), 3.70 (s, 1 H, Me), 6.57–7.30 (m, 4 H, aromatic H). – ^{13}C NMR ($CDCl_3$, 20 MHz): δ 0.34 (d), 14.76 (s), 31.44, 32.05 (2 t), 54.80 (q), 72.55 (s), 113.19, 127.13 (2 d), 134.73, 158.45 (2 s). – MS (70 eV), *m/z* (%): 190 (84) [M$^+$], 133 (100).
$C_{12}H_{14}O_2$ (190.2): calcd. C 75.76, H 7.42; found C 75.50, H 7.45. $C_{12}H_{14}O_2$ calcd. 190.099; found 190.098 (HRMS).

1-(1-Bicyclo[1.1.0]butyl)-1-phenylethanol (**17c**)

According to the general procedure, *t*-BuLi (63.2 mmol) and **6** (4.00 g, 30.1 mmol) were allowed to react to **16**, to which acetophenone (**10c**) (3.60 g, 30.0 mmol) was added. Standard workup afforded **17c** (4.15 g, 79%) as a colorless liquid of *b.p.* 56–59 °C/0.001 Torr. – ^{1}H NMR ($CDCl_3$, 60 MHz): δ 0.52–0.66 (m, 2 H, *endo*-2'-, *endo*-4'-H), 0.80–1.00 (m, 1 H, 3'-H), 1.40–1.67 (m, 2 H, *exo*-2'-, *exo*-4'-H), 1.52 (s, 3 H, Me), 2.05 (s, 1 H, OH), 7.12–7.57 (m, 5 H, aromatic H). – ^{13}C NMR ($CDCl_3$, 20 MHz): δ 1.97 (d), 19.18 (s), 28.38 (q), 30.14, 31.17 (2 t), 72.70 (s), 125.10, 126.70, 127.82 (3 d), 147.03 (s). – MS (70 eV), *m/z* (%): 174 (16) [M$^+$], 43(100).
$C_{12}H_{14}O$ (174.2): calcd. C 82.72, H 8.10; found C 82.09, H 8.22. $C_{12}H_{14}O$ calcd. 174.104; found 174.103 (HRMS).

9-(1-Bicyclo[1.1.0]butyl)-9-fluorenol (**17e**)

According to the general procedure, *t*-BuLi (107 mmol) and **6** (7.08 g, 53.2 mmol) were allowed to react to **16**, to which fluorenone (**10e**) (9.60 g, 53.3 mmol) was added. Standard workup afforded **17e** (8.95 g, 72%) as a pale yellow, viscous liquid of *b.p.* 110–120 (bath) °C/0.001 Torr. – ^{1}H NMR ($CDCl_3$, 60 MHz): δ 0.57 (s, 2 H, *endo*-2'-, *endo*-4'-H), 1.60 (broad s, 3 H, *exo*-2'-, 3'-, *exo*-4'-H), 2.20 (s, 1 H, OH), 7.10–7.70 (m, 8 H, aromatic H). – ^{13}C NMR ($CDCl_3$, 20 MHz): δ 0.61 (d), 15.27 (s), 30.66 (t), 79.76 (s), 119.89, 123.86, 127.52, 128.67 (4 d), 138.88, 147.78 (2 s).

1-(1-Bicyclo[1.1.0]butyl)-2,4-dimethyl-3-pentanol (**17g**)

According to the general procedure, *t*-BuLi (233.3 mmol) and **6** (14.8 g, 111 mmol) were allowed to react to **16**, to which diisopropyl ketone (**10g**) (12.6 g, 110 mmol) was added. Standard workup afforded **17g** (13.1 g, 71%) as a colorless liquid of *b.p.* 34–40 °C/0.01 Torr. – ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.40 (s, 2 H, *endo*-2'-, *endo*-4'-H), 0.86 (d, J = 6.9 Hz, 6 H, CH<u>Me</u>$_2$), 0.97 (d, J = 7.3 Hz, 6 H, CH<u>Me</u>$_2$), 1.03 (s, 1 H, OH), 1.54 (d, J = 2.4 Hz, 2 H, *exo*-2'-, *exo*-4'-H), 1.59 (t, J = 2.4 Hz, 1 H, 3'-H), 2.07 (sept, J = 6.9 Hz, 2 H, C<u>H</u>Me$_2$). – ^{13}C NMR ($CDCl_3$, 100 MHz): δ 0.61 (d), 13.74 (s), 17.14, 17.31 (2 q), 29.41 (t), 34.01 (d), 74.96 (s). – MS (70 eV), *m/z* (%): 168 (2) [M$^+$], 71 (100).
$C_{11}H_{20}O$ calcd. 168.1514; found 168.1772 (HRMS).

1-(1-Bicyclo[1.1.0]butyl)-1-cyclopentanol (**17i**)

According to the general procedure, *t*-BuLi (135.3 mmol) and **6** (8.60 g, 64.7 mmol) were allowed to react to **16**, to which cyclopentanone (**10i**) (5.38 g, 64.0 mmol) was added. Standard workup afforded **17i** (6.36 g, 72%) as a colorless liquid of *b.p.* 83–86 °C/12 Torr. – ^{1}H NMR ($CDCl_3$, 60 MHz): δ 0.57 (s, 2 H, *endo*-2'-, *endo*-4'-H), 0.77–1.05 (m, 1 H, 3'-H), 1.34–1.92 (m, 11 H, *exo*-2'-, *exo*-4'-H, OH, $[CH_2]_4$). – ^{13}C NMR ($CDCl_3$, 20 MHz): δ 1.94 (d), 16.23 (s), 23.69 (m), 30.71 (m), 38.62 (m), 80.45 (s). – MS (70 eV), *m/z* (%): 138 (5) [M$^+$], 57 (100).
$C_9H_{14}O$ (138.2): calcd. C 78.21, H 10.21; found C 78.71, H 10.22. $C_9H_{14}O$ calcd. 138.103; found 138.096 (HRMS).

1-(1-Bicyclo[1.1.0]butyl)-2,2,3,3-tetramethyl-1-cyclobutanol (**17k**)

According to the general procedure, *t*-BuLi (66.3 mmol) and **6** (4.20 g, 31.6 mmol) were allowed to react to **16**, to which 2,2,3,3-tetramethylcyclobutanone (**10k**) (3.60 g, 28.5 mmol) was added. Standard workup afforded **17k** (4.97 g, 97%) as a colorless viscous liquid of *b.p.* 43–45 °C/0.01 Torr.
– ^{1}H NMR ($CDCl_3$, 60 MHz): δ 0.49, 0.75 (2 broad s, 2 H, *endo*-2'-, *endo*-4'-H), 1.01, 1.05, 1.10. 1.16 (4 s, 12 H, Me), 1.27 (s, 1 H, OH), 1.37–2.11 (m, 5 H, *exo*-2'-, *exo*-4'-H, 3'-H, 4-H$_2$). – ^{13}C NMR ($CDCl_3$, 20 MHz): δ 0.21 (d), 14.54 (s), 18.96, 22.20, 24.62, 25,71 (4 q), 28.32, 34.10 (2 t), 33.71 (s), 42.98 (t), 46.31 (s), 74.57 (s). – MS (70 eV), *m/z* (%): 180 (4) [M$^+$], 95 (100).
$C_{12}H_{20}O$ calcd. 180.151; found 180.148 (HRMS).

1-(1-Bicyclo[1.1.0]butyl)prop-2-en-1-ol (**17l**)

According to the general procedure, *t*-BuLi (221 mmol) and **6** (14.3 g, 107.5 mmol) were allowed to react to **16**, to which acroleine (**10l**) (6.00 g, 107.0 mmol) was added. Standard workup afforded **17l** (8.16 g, 71%) as a colorless liquid of *b.p.* 65–67 °C/12 Torr. – ^{1}H NMR ($CDCl_3$, 60 MHz): δ 0.57–0.80 (m, 2 H, *endo*-2'-, *endo*-4'-H), 1.26–1.40 (m, 1 H, 3'-H), 1.48–1.73 (m, 2 H, *exo*-2'-, *exo*-4'-H), 2.06–2.30 (d, J = 4.4 Hz, 1 H, OH), 4.31–4.56 (m, 1 H, C<u>H</u>OH), 4.93–5.38 (m, 2 H, CH=C<u>H</u>$_2$), 5.53–6.08 (m, 1 H, C<u>H</u>=CH$_2$). – ^{13}C NMR ($CDCl_3$, 20 MHz): δ 0.19 (d), 13.03 (s), 30.90, 32.20 (2 t), 71.61 (d), 114.77 (t), 138.27 (d). – MS (70 eV), *m/z* (%): 110 (5) [M$^+$], 57 (100).
$C_7H_{10}O$ (110.2): calcd. C 76.33, H 9.15; found C 76.82, H 9.31.

E-1-(1-Bicyclo[1.1.0]butyl)but-2-en-1-ol (**17m**)

According to the general procedure, *t*-BuLi (115 mmol) and **6** (7.00 g, 52.6 mmol) were allowed to react **16**, to which crotonaldehyde (**10m**) (3.70 g, 52.8 mmol) was added. Standard workup afforded **17m** (4.80 g, 73%) as a colorless liquid of *b.p.* 70–76 °C (bath)/12 Torr. – ^{1}H NMR ($CDCl_3$, 60 MHz): δ 0.60–0.77 (m, 2 H, *endo*-2'-, *endo*-4'-H), 1.29 (broad s, 1 H, 3'-H), 1.47–1.81 (m, 5 H, *exo*-2'-, *exo*-4'-H, Me), 2.10 (s, 1 H, OH), 4.27–4.50 (m, 1 H, C*H*OH), 5.25–

5.92 (m, 2 H, C*H*=C*H*). – ^{13}C NMR ($CDCl_3$, 20 MHz): δ 0.04 (d), 13.30 (s), 17.18 (q), 30.99, 31.93 (2 t), 71.61 (d), 126.40 (d), 131.55 (d). – MS (70 eV), *m/z* (%): 124 (8) [M^+], 57 (100).
$C_8H_{12}O$ calcd. 124.089; found 124.088 (HRMS).

2-(1-Bicyclo[1.1.0]butyl)-4-methylpent-3-en-2-ol (**17n**)

According to the general procedure, *t*-BuLi (131.1 mmol) and **6** (8.30 g, 62.4 mmol) were allowed to react to **16**, to which mesityl oxide (**10n**) (5.91 g, 60.2 mmol) was added. Standard workup afforded **17n** (7.97 g, 87%) as a colorless viscous liquid of *b.p.* 38–45 °C (bath)/0.01 Torr. – ^{1}H NMR ($CDCl_3$, 60 MHz): δ 0.59 (broad s, 2 H, *endo*-2'-, *endo*-4'-H), 0.80–1.06 (m, 1 H, 3'-H), 1.34 (s, 3 H, Me), 1.42–1.67 (m, 3 H, *exo*-2'-, *exo*-4'-H, OH), 1.72, 1.86 (2 broad s, 6 H, Me), 5.15–5.32 (m, 1 H, C<u>H</u>OH). – ^{13}C NMR ($CDCl_3$, 20 MHz): δ 2.03 (d), 18.06 (s), 18.78 (q), 26.78, 28.02 (2 q), 30.08, 30.81 (2 t), 70.88 (s), 129.64 (d), 133.91 (s). – MS (70 eV), *m/z* (%): 152 (9) [M^+], 91 (100).
$C_{10}H_{16}O$ (152.2): calcd. C 78.90, H 10.59; found C 78.15, H 10.31. $C_{10}H_{16}O$ calcd. 152.120; found 152.115 (HRMS).

1-(1-Bicyclo[1.1.0]butyl)-cyclohex-2-en-1-ol (**17o**)

According to the general procedure, *t*-BuLi (85.0 mmol) and **6** (5.50 g, 41.4 mmol) were allowed to react to **16**, to which cyclohex-2-en-1-one (**10o**) (3.80 g, 39.5 mmol) was added. Standard workup afforded **17o** (4.60 g, 78%) as a colorless viscous liquid of *b.p.* 55–58 °C (bath)/0.001 Torr. – ^{1}H NMR ($CDCl_3$, 60 MHz): δ 0.46–0.65 (m, 2 H, *endo*-2'-, *endo*-4'-H), 0.80–1.02 (m, 1 H, 3'-H), 1.42–2.16 (m, 9 H, *exo*-2'-, *exo*-4'-H, OH, C<u>H</u>$_2$-C<u>H</u>$_2$-C<u>H</u>$_2$), 5.37–5.94 (m, 2 H, CH=CH). – ^{13}C NMR ($CDCl_3$, 20 MHz): δ 0.28 (d), 17.00 (s), 18.88 (t), 24.78 (t), 29.08, 30.23 (2 t), 35.84 (t), 67.67 (s), 129.03 (d), 130.43 (d). – MS (70 eV), *m/z* (%): 150 (13) [M^+], 91 (100).
$C_{10}H_{14}O$ (150.2): calcd. C 79.96, H 9.39; found C 79.55, H 9.33.

1-(1-Bicyclo[1.1.0]butyl)-4,4-dimethyl-2-pentyn-1-ol (**17p**)

According to the general procedure, *t*-BuLi (101.0 mmol) and **6** (6.40 g, 48.1 mmol) were allowed to react to **16**, to which 4,4-dimethyl-2-pentynal (**10p**) (5.28 g, 47.9 mmol) was added. Standard workup afforded **17p** (5.75 g, 73%) as a colorless liquid of *b.p.* 50–54 °C (bath)/0.01 Torr. – ^{1}H NMR ($CDCl_3$, 60 MHz): δ 0.61, 0.90 (2 broad s, 2 H, *endo*-2'-, *endo*-4'-H), 1.20 (s, 9 H, Me), 1.16–2.09 (m, 4 H, *exo*-2'-, *exo*-4'-H, OH, 3'-H). – ^{13}C NMR ($CDCl_3$, 20 MHz): δ 1.61 (d), 13.51 (s), 27.27 (s), 30.99 (q), 31.41, 34.63 (2 t), 63.01 (d), 77.12 (s), 93.96 (s). – MS (70 eV), *m/z* (%): 164 (22) [M^+], 57 (100).
$C_{11}H_{16}O$ (138.2): calcd. C 80.44, H 9.82; found C 79.91, H 9.97.

2,3-Bis(1-bicyclo[1.1.0]butyl)butan-2,3-diol (**17q**)

According to the general procedure, *t*-BuLi (267.7 mmol) and **6** (16.95 g, 127.5 mmol) were allowed to react **16**, to which biacetyl (**10q**) (5.50 g, 63.7 mmol) was added. Standard workup afforded a 62:38 diastereomeric mixture **17q** (5.70 g, 46%) as a colorless viscous liquid of *b.p.* 70–76 °C (bath)/0.001 Torr, which was not separated. The components could be characrterized by ^{13}C NMR spectroscopy.
Major component: ^{13}C NMR ($CDCl_3$, 20 MHz): δ –0.86 (d), 14.61 (s), 21.08 (q), 30.71, 32.41 (2 t), 76.12 (s).
Minor component: ^{13}C NMR ($CDCl_3$, 20 MHz): δ –0.66 (d), 15.00 (s), 19.67 (q), 30.42, 32.43 (2 t), 76.28 (s).
MS (70 eV), *m/z* (%): 97 (33) [M^+/2], 43 (100).
$C_{12}H_{18}O_2$ (194.3): calcd. C 74.19, H 9.34; found C 74.33, H 9.79.

6-Bromo-1-tricyclo[3.1.0.0^{2,6}]hexyl Carbinols (12) (General Procedure)

Carbinol **11** (1.00 equiv.) in ether (concentration 0.5 mol/l) was added dropwise under magnetical stirring to BuLi (in some cases MeLi) (2.2 equiv.) in ether (concentration 1.5 mol/l), which was kept under nitrogen atmosphere and cooled in an icebath. Stirring was continued for 16 h at room temperature. The reaction mixture was again cooled in an ice bath, charged with 4-tolylsulfonyl bromide (TsBr) (1.0 equiv.) in small portions, stirred for 4 h at room temperature, and then hydrolyzed under icebath cooling with 2N NaOH. The layers were separated, the aqueous part extracted three times with ether and the combined ether layers dried with $MgSO_4$. After filtration and removal of the solvent under reduced pressure the oily residue was purified by distillation.

1-(6-Bromotricyclo[3.1.0.0^{2,6}]hex-1-yl)-1-phenylethanol (**12c**)

BuLi (11.4 mmol), **11c** (1.00 g, 4.99 mmol) and TsBr (1.20 g, 5.10 mmol) were allowed to react according to the general procedure. Standard workup afforded **12c** (810 mg, 58%) as a pale yellow oil, *b.p.* 140–150 °C (bath)/12 Torr. – ^{1}H NMR ($CDCl_3$, 60 MHz): δ 1.35–1.67 (m, 4 H, 3'-, 4'-H$_2$), 1.67 (broad s, 3 H, Me), 2.08 (s, 1H, OH), 2.42 (broad s, 2 H, 2'-, 5'-H), 7.13–7.50 (m, 5 H, aromatic H). – ^{13}C NMR ($CDCl_3$, 20 MHz): δ 25.56 (s), 26.08 (m), 29.08 (q), 30.05 (s), 41.89, 43.68 (2 d), 73.15 (s), 124.79, 126.97, 128.03 (3 d), 146.75 (s).

1-(6-Bromotricyclo[3.1.0.0^{2,6}]hex-1-yl)-2,2-dimethyl-1-phenyl-1-propanol (**12d**)

BuLi (19.0 mmol), **11d** (2.00 g, 8.25 mmol) and TsBr (1.94 g, 8.25 mmol) were allowed to react according to the general procedure. Standard workup afforded **12c** (1.00 g, 38%) as a colorless oil, *b.p.* 95–103 °C (bath)/0.001 Torr. – ^{1}H NMR ($CDCl_3$, 60 MHz): δ 0.95 (s, 9 H, Me), 1.40–1.72 (m, 4 H, 3'-, 4'-H$_2$), 2.04 (s, 1 H, OH), 2.37, 2.67 (2 d, J = 5.4 Hz, 2 H, 2'-, 5'-H), 7.04–7.50 (m, 5 H, aromatic H). – ^{13}C NMR ($CDCl_3$, 20 MHz): δ 25.53, 25.71 (2 m), 26.17 (q), 39.41 (s), 44.22, 44.77 (2 d), 80.87 (s), 126.58, 126.82, 127.21 (3 t), 143.45 (s). – MS (70 eV), *m/z* (%): 265 (47), 263 (55), 163 (100).
$C_{13}H_{12}{}^{79}BrO$ calcd. 263.007; found 263.007 (HRMS for $M^+ - C_4H_9$).

9-(6-Bromotricyclo[3.1.0.0^{2,6}]hex-1-yl)-9-fluorenol (**12e**)

MeLi (42.0 mmol), **11e** (5.20 g, 20.0 mmol) and TsBr (4.75 g, 20.2 mmol) were allowed to react according to the general procedure. Standard workup afforded **12e** (5.39 g, 79%) as a colorless waxy solid, which was characterized by the NMR spectra and used for further experiments without purification. – ^{1}H NMR ($CDCl_3$, 60 MHz): δ 1.20–1.57 (m, 4 H, 3'-, 4'-H$_2$), 2.25 (s, 1 H, OH), 2.40 (s, 2 H, 2'-, 5'-H), 7.15–7.70 (m, 8 H, aromatic H). – ^{13}C NMR ($CDCl_3$, 20 MHz): δ 24.90,(2s),

25.84 (m), 39.41 (s), 28.08 (s), 42.86 (d), 79.05 (s), 120.03, 124.27, 128.00, 129.06 (4 d), 138.96, 147.42 (2 s).

2-(6-Bromotricyclo[3.1.0.0^{2,6}]hex-1-yl)propan -2-ol (**12f**)

BuLi (33.4 mmol), **11f** (2.00 g, 14.5 mmol) and TsBr (3.45 g, 14.7 mmol) were allowed to react according to the general procedure. Standard workup afforded **12f** (1.86 g, 59%) as a colorless oil, *b.p.* 52–55 °C (bath)/10^{-4} Torr. – ^{1}H NMR ($CDCl_3$, 60 MHz): δ 1.30–1.60 (m, 4 H, 3'-, 4'-H_2), 1.35 (s, 6 H, Me), 2.05 (s, 1 H, OH), 2.40 (m, 2 H, 2'-, 5'-H). – ^{13}C NMR ($CDCl_3$, 20 MHz): δ 25.59 (s), 26.11 (m), 28.62 (q), 29.44 (s), 41.98 (d), 68.73 (s).

3-(6-Bromotricyclo[3.1.0.0^{2,6}]hex-1-yl)-2,4-dimethyl-pentan-3-ol (**12g**)

BuLi (43.8 mmol), **11g** (3.70 g, 19.0 mmol) and TsBr (4.48 g, 19.1 mmol) were allowed to react according to the general procedure. Standard workup afforded **12g** (4.58 g, 88%) as a colorless oil, *b.p.* 77–79 °C (bath)/0.01 Torr. – ^{1}H NMR ($CDCl_3$, 60 MHz): δ 0.87, 0.97 (2 d, J = 6.4 Hz, each 6 H, CHMe$_2$), 1.15–1.74 (m, 5 H, 3'-, 4'-H_2, OH), 2.05 (sept, J = 6.4 Hz, 2 H, CHMe$_2$), 2.30, (s, 2 H, 2'-, 5'-H). – ^{13}C NMR ($CDCl_3$, 20 MHz): δ 16.99, 17.90 (2 q), 25.62 (m), 27.68 (s), 33.77 (d), 41.77 (d), 77.60 (s). – MS (70 eV), *m/z* (%): 231 (17), 229 (19), 43 (100).
$C_{13}H_{21}BrO$ (273.2): calcd. C 57.15, H 7.75; found C 58.62, H 7.88; $C_{10}H_{14}{}^{79}BrO$ calcd. 229.022; found 229.019 (HRMS for $M^+ - C_3H_7$).

3-(6-Bromotricyclo[3.1.0.0^{2,6}]hex-1-yl)-2,2,4,4-tetramethyl-pentan-3-ol (**12h**)

BuLi (10.4 mmol), **11h** (1.00 g, 4.50 mmol) and TsBr (1.10 g, 4.68 mmol) were allowed to react according to the general procedure. Standard workup afforded **12h** (500 mg, 37%) as a yellow oil, *b.p.* 98–105 °C (bath)/0.1 Torr. – ^{1}H NMR ($CDCl_3$, 60 MHz): δ 1.10 (broad s, 19 H, 6 Me, OH), 1.40–1.65 (m, 4 H, 3'-, 4'-H_2), 2.35 (s, 2'-, 5'-H). – ^{13}C NMR ($CDCl_3$, 20 MHz): δ 25.44 (m), 28.62 (s), 29.47 (q), 30.95 (s), 41.89 (s), 43.10 (d), 81.36 (s).

1-(6-Bromotricyclo[3.1.0.0^{2,6}]hex-1-yl)cyclopentan-1-ol (**12i**)

BuLi (109.9 mmol), **11i** (8.20 g, 49.9 mmol) and TsBr (11.75 g, 50.0 mmol) were allowed to react according to the general procedure. Standard workup afforded **12i** (7.23 g, 60%) as a colorless oil, *b.p.* 60–63 °C (bath)/0.01 Torr. – ^{1}H NMR ($CDCl_3$, 60 MHz): δ 1.10–1.99 (m, 13 H, $(CH_2)_4$ of cyclopentane, 3'-, 4'-H_2, OH), 2.41 (s, 2 H, 2'-, 5'-H). – ^{13}C NMR ($CDCl_3$, 20 MHz): δ 23.56 (m), 25.66, 27.84 (2 s), 26.20 (m), 39.28 (m), 42.62 (d), 79.20 (s). – MS (70 eV), *m/z* (%): 244 (3), 242 (4) [M$^+$], 85 (100).

1-(6-Bromotricyclo[3.1.0.0^{2,6}]hex-1-yl)cyclobutan-1-ol (**12j**)

BuLi (68.0 mmol), **11j** (4.70 g, 30.0 mmol) and TsBr (7.05 g, 30.0 mmol) were allowed to react according to the general procedure. Standard workup afforded **12j** (4.30 g, 63%) as a colorless oil, *b.p.* 110–120 °C (bath)/12 Torr. – ^{1}H NMR ($CDCl_3$, 60 MHz): δ 1.22–1.67 (m, 4 H, 3'-, 4'-H_2), 1.67–1.97 (m, 2 H, 3-H_2), 1.97–2.35 (m, 5 H, 2-, 4-H_2, OH), 2.42 (s, 2 H, 2'-, 5'-H). – ^{13}C NMR ($CDCl_3$, 20 MHz): δ = 12.27 (m), 25.47, 27.65 (2 s), 26.20 (m), 35.59 (m), 41.98 (d), 79.60 (s). – MS (70 eV), *m/z* (%): 230 (0.06), 228 (0.07) [M$^+$], 77 (100).

2. 3-Bromo-1-bicyclo[1.1.0]butyl Carbinols (18) (General Procedure)

Carbinol **17** (1.00 equiv.) in ether (concentration 0.7 mol/l) was added dropwise under magnetical stirring to a mixture of BuLi (in some cases MeLi) (2.2 equiv.) and tetramethyl ethylenediamine (TMEDA) (2.2 equiv.) in ether (concentration 1.5 mol/l), which was kept under nitrogen atmosphere and cooled in an icebath. Stirring was continued for 16 h at room temperature. The reaction mixture was again cooled in an icebath, charged with 4-tolylsulfonyl bromide (TsBr) (1.0 equiv.) in small portions, stirred for 4 h at room temperature, and then hydrolyzed under icebath cooling with 2N NaOH. The layers were separated, the aqueous part extracted three times with ether and the combined ether layers dried with $MgSO_4$. After filtration and removal of the solvent under reduced pressure the oily residue was purified by distillation.

(3-Bromobicyclo[1.1.0]but-1-yl)phenylmethanol (**18a**)

BuLi (51.2 mmol), TMEDA (5.95 g, 51.2 mmol), **17a** (3.91 g, 24.4 mmol) and TsBr (5.64 g, 24.0 mmol) were allowed to react according to the general procedure. Standard workup afforded **18a** (3.40 g, 59%) as a colorless oil, *b.p.* 81–86 °C (bath)/0.001 Torr. The bromocarbinol **18a** decomposed in part when stored at room temperature. It was immediately used for further reaction after distillation and characterized only by its ^{1}H-NMR spectrum. – ^{1}H NMR ($CDCl_3$, 60 MHz): δ 1.30 (s, 2 H, *endo*-2'-, *endo*-4'-H), 1.77, 2.11 (2 d, ^4J = 6.0 Hz, 2 H, *exo*-2'-, *exo*-4'-H), 2.60 (s, 1 H, OH), 4.95 (s, 1 H, CHOH), 6.90–7.46 (m, 5 H, aromatic H).

(3-Bromobicyclo[1.1.0]but-1-yl)-4-methoxyphenylmethanol (**18b**)

BuLi (51.9 mmol), TMEDA (6.03 g, 51.9 mmol), **17b** (4.50 g, 23.7 mmol) and TsBr (5.56 g, 23.6 mmol) were allowed to react according to the general procedure. Standard workup afforded **18b** (2.69 g, 42%) as a yellow viscous oil, *b.p.* 130–145 °C (bath)/0.001 Torr. At a bath temperature of 145 °C, partial decomposition of **18b** was observed. – ^{1}H NMR ($CDCl_3$, 60 MHz): δ 1.30 (broad s, 2 H, *endo*-2'-, *endo*-4'-H), 1.81, 2.05 (2 d, J = 5.6 Hz, 2 H, *exo*-2'-, *exo*-4'-H), 2.27 (broad s, 1 H, OH), 3.72 (s, 3 H, Me), 4.82 (broad s, 1 H, CHOH), 6.65–7.40 (m, 4 H aromatic H). – ^{13}C NMR ($CDCl_3$, 20 MHz): δ 19.63 (s), 37.93, 39.17 (2 s), 54.95 (q), 71.58 (d), 113.53, 127.79 (2 d), 134.03, 158.96 (2 s). – MS (70 eV), *m/z* (%): 270 (0.1), 268 (0.2) [M$^+$], 133 (100).

(3-Bromobicyclo[1.1.0]but-1-yl)-1-phenylethan-1-ol (**18c**)

BuLi (49.9 mmol), TMEDA (5.80 g, 49.9 mmol), **17c** (3.86 g, 22.2 mmol) and TsBr (5.10 g, 21.7 mmol) were allowed to react according to the general procedure. Standard workup afforded **18c** (2.80 g, 51%) as a pale yellow oil, *b.p.* 76–78 °C (bath)/0.001 Torr. At a bath temperature of 100 °C, compound **16c** decomposed quickly. – ^{1}H NMR ($CDCl_3$, 60 MHz): δ 1.10, 1.25 (2 broad s, each 1H, *endo*-2'-, *endo*-4'-H), 1.65, (s, 3 H, Me), 1.95–2.05 (m, 2 H, *exo*-2'-, *exo*-4'-H), 2.26 (broad s, 1 H, OH), 6.97–7.77 (m, 5 H, aromatic H). – ^{13}C NMR ($CDCl_3$, 20 MHz): δ 21.81, 23.41 (2 s), 27.89 (q), 36.49, 38.53 (2 t), 73.09 (s), 125.03, 127.09, 128.03 (3 d), 146.48 (s). – MS (70 eV), *m/z* (%): 252 (0.1) [M$^+$], 43 (100).

9-(3-Bromobicyclo[1.1.0]but-1-yl)fluoren-9-ol (**18e**)

BuLi (18.2 mmol), TMEDA (2.11 g, 18.2 mmol), **17e** (1.99 g, 8.49 mmol) and TsBr (2.00 g, 8.51 mmol) were allowed to react according to the general procedure. Standard workup afforded a crystalline solid (1.30 g), which according to its ^{1}H NMR spectrum was a 90:10 mixture of **18e** and **17e**, giving rise to a 45% yield of **18e**. Attempted separation of the components by distillation led to complete decomposition of the material. Attempted separation by column chromatography was not successful. **18e** could be characterized by its ^{1}H NMR spectrum. The material was used for further experiments without purification. – ^{1}H NMR ($CDCl_3$, 60 MHz): δ 1.02 (s, 2 H, *endo*-2'-, *endo*-4'-H), 1.96 (s, 2 H, *exo*-2'-, *exo*-4'-H), 2.46 (broad s, 1 H, OH), 6.97–7.75 (m, 8 H, aromatic H).

3-(3-Bromobicyclo[1.1.0]but-1-yl)-2,4-dimethylpentan-3-ol (**18g**)

BuLi (94.8 mmol), TMEDA (11.01 g, 94.7 mmol), **17g** (7.25 g, 43.1 mmol) and TsBr (10.13 g, 43.1 mmol) were allowed to react according to the general procedure. Standard workup afforded **18g** (6.50 g, 61%) as a colorless oil of *b.p.* 47–52 °C (bath)/0.01 Torr. – ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.94 (s, 2 H, *endo*-2'-, *endo*-4'-H), 0.96, 1.00 (2 d, J = 6.8 Hz, 12 H, Me) 1.32 (broad s, 1 H, OH), 1.94 (s, 2 H, *exo*-2'-, *exo*-4'-H), 2.12 (sept, J = 6.8 Hz, 2 H, C*H*Me$_2$). – ^{13}C NMR ($CDCl_3$, 100 MHz): δ 17.28, 17.89 (2 q), 23.07, 24.55 (2 s), 34.20 (d), 36.81 (t), 76.57 (s). – MS (70 eV), *m/z* (%): 270 (0.1), 233 (6), 231 (6) [M$^+$– Me], 43 (100).
$C_{10}H_{16}{}^{79}BrO$ calcd. 231.0385; found 231.0391 (HRMS for M$^+$ – Me).

1-(3-Bromobicyclo[1.1.0]but-1-yl)cyclopentan-1-ol (**18i**)

BuLi (95.0 mmol), TMEDA (11.15 g, 96.0 mmol), **17i** (6.00 g, 43.4 mmol) and TsBr (10.14 g, 43.1 mmol) were allowed to react according to the general procedure. Standard workup afforded **18i** (4.92 g, 53%) as a colorless oil of *b.p.* 59–61 °C/0.01 Torr. – ^{1}H NMR ($CDCl_3$, 60 MHz): δ 1.16 (s, 2 H, *endo*-2'-, *endo*-4'-H), 1.59–1.92 (m, 9 H, $[CH_2]_4$, OH), 2.00 (s, 2 H, *exo*-2'-, *exo*-4'-H). – ^{13}C NMR ($CDCl_3$, 20 MHz): δ 20.87, 21.35 (2 s), 23.38, 37.59, 38.20 (3 t), 80.14 (s). – MS (70 eV), *m/z* (%): 137 (46) [M$^+$ – Br], 91 (100).

1-(3-Bromobicyclo[1.1.0]but-1-yl)-2,2,3,3-tetramethylcyclobutan-1-ol (**18k**)

BuLi (79.3 mmol), TMEDA (9.22 g, 79.3 mmol), **17k** (6.50 g, 36.1 mmol) and TsBr (8.46 g, 36.0 mmol) were allowed to react according to the general procedure. Standard workup afforded **18k** (5.55 g, 59%) as a colorless oil of *b.p.* 48–53 °C (bath)/0.001 Torr. – ^{1}H NMR ($CDCl_3$, 60 MHz): δ 0.94. 1.05 (2 s, each 6 H, Me), 1.17 (s, 2 H, *endo*-2'-, *endo*-4'-H), 1.31, 1.65 (2 broad s, each 1 H, cyclobutane H), 1.80 (s, 1 H, OH), 2.09 (s, 2 H, *exo*-2'-, *exo*-4'-H). – ^{13}C NMR ($CDCl_3$, 20 MHz): δ 18.32 (q), 19.44, 20.47 (2 s), 22.60, 24.72, 25.96 (3 q), 34.95 (s), 36.23, 41.43, 42.80 (3 t), 46.95 (s), 75.81 (s). – MS (70 eV), *m/z* (%): 260 (7), 258 (7) [M$^+$], 95 (100).
$C_{12}H_{19}{}^{79}BrO$ calcd. 258.062; found 258.073 (HRMS).

1-(3-Bromobicyclo[1.1.0]but-1-yl)-2-propen-1-ol (**18l**)

BuLi (76.3 mmol), TMEDA (8.54 g, 73.5 mmol), **17l** (3.99 g, 36.2 mmol) and TsBr (8.53 g, 36.3 mmol) were allowed to react according to the general procedure. Standard workup afforded **18l** (5.44 g, 79%) as a pale yellow oil of *b.p.* 36–40 °C (bath)/0.01 Torr. – ^{1}H NMR ($CDCl_3$, 60 MHz): δ 1.13–1.40 (m, 2 H, *endo*-2'-, *endo*-4'-H), 1.88–2.13 (m, 3 H, *exo*-2'-, *exo*-4'-H, OH), 4.54 (d, J = 5.5 Hz, 1 H, C<u>H</u>OH), 5.05–5.45 (m, 2 H, CH=C<u>H</u>$_2$), 5.67–6.12 (m, 1 H, C<u>H</u>=CH$_2$). – ^{13}C NMR ($CDCl_3$, 20 MHz): δ 18.26, 19.29 (2 s), 38.38, 38.80 (2 t), 70.81 (d), 116.01 (t), 137.51 (d). – MS (70 eV), *m/z* (%): 190 (0.4), 188 (0.2) [M$^+$], 57 (100).

E-1-(3-Bromobicyclo[1.1.0]but-1-yl)but-2-en-1-ol (**18m**)

BuLi (101 mmol), TMEDA (11.7 g, 101 mmol), **17m** (6.11 g, 49.2 mmol) and TsBr (11.56 g, 49.2 mmol) were allowed to react according to the general procedure. Standard workup afforded **18m** (4.22 g, 42%) as a colorless liquid of *b.p.* 58–63 °C (bath)/0.01 Torr. – ^{1}H NMR ($CDCl_3$, 60 MHz): δ 1.25 (broad s, 2 H, *endo*-2'-, *endo*-4'-H), 1.74 (d, J = 5 Hz, 3 H, Me), 1.92–2.05 (m, 3 H, *exo*-2'-, *exo*-4'-H, OH), 4.48 (d, J = 6 Hz, 1 H, C<u>H</u>OH), 5.35–6.02 (m, 2 H, C<u>H</u>=C*H*). – ^{13}C NMR ($CDCl_3$, 20 MHz): δ 17.60 (q), 18.60, 19.54 (2 s), 38.47, 38.80 (2 t), 70.57 (d), 127.76 (d), 130.91 (d).

2-(3-Bromobicyclo[1.1.0]but-1-yl)-4-methylpent-3-en-2-ol (**18n**)

BuLi (115 mmol), TMEDA (13.4 g, 115 mmol), **17n** (7.97 g, 52.4 mmol) and TsBr (12.32 g, 52.4 mmol) were allowed to react according to the general procedure. Standard workup afforded **18n** (9.00 g, 74%) as a colorless liquid of *b.p.* 50–58 °C (bath)/0.01 Torr. – ^{1}H NMR ($CDCl_3$, 60 MHz): δ 1.10–1.21 (m, 2 H, *endo*-2'-, *endo*-4'-H), 1.30 (s, 3 H, Me), 1.75 (broad s, 4 H, Me, OH), 1.85 (broad s, 3 H, Me), 2.00–2.09 (m, 2 H, *exo*-2'-, *exo*-4'-H), 5.17–5.32 (m, 1 H, C<u>H</u>=CMe$_2$). – ^{13}C NMR ($CDCl_3$, 20 MHz): δ 19.14 (q), 21.60, 23.11 (2 s), 27.14, 27.56 (2 q), 36.95, 38.13 (2 t), 128.82 (d), 134.88 (s). – MS (70 eV), *m/z* (%): 214 (13), 212 (12) [M$^+$–H_2O], 91 (100).

1-(3-Bromobicyclo[1.1.0]but-1-yl)-2-cyclohexen-1-ol (**18o**)

BuLi (52.1 mmol), TMEDA (5.94 g, 51.2 mmol), **17o** (3.66 g, 24.4 mmol) and TsBr (5.64 g, 24.0 mmol) were allowed to react according to the general procedure. Standard workup afforded **18o** (3.59 g, 65%) as a colorless liquid of *b.p.* 64–65 °C (bath)/0.001 Torr, the color of which turned from colorless to yellow and to brown after 3 h at room temperature. – ^{1}H NMR ($CDCl_3$, 60 MHz): δ 1.02–1.19 (m, 2 H, *endo*-2'-, *endo*-4'-H), 1.52–2.05 (m, 9 H, $(CH_2)_3$, OH, *exo*-2'-, *exo*-4'-H), 5.45–6.01 (m, 2 H, CH=CH). – ^{13}C NMR ($CDCl_3$, 20 MHz): δ 18.81 (t), 20.66, 22.44 (2 s), 25.03 (t), 35.98, 36.38, 37.65 (3 t), 68.54 (s), 129.06, 130.54 (2 d). – MS (70 eV), *m/z* (%): 230 (1), 228 (1) [M$^+$], 91 (100).

1-(3-Bromobicyclo[1.1.0]but-1-yl)-4,4-dimethylpent-2-yn-1-ol (**18p**)

BuLi (94.0 mmol), TMEDA (10.9 g, 93.8 mmol), **17p** (7.35 g, 44.8 mmol) and TsBr (10.52 g, 44.7 mmol) were allowed to react according to the general procedure. Standard workup afforded **18p** (3.30 g, 30%) as a pale yellow, viscous oil of *b.p.* 64–70°C (bath)/0.001 Torr. The forerun, *b.p.* 55–60 °C (bath)/0.001 Torr (1.95 g, 27%), consisted of nearly pure **17p**. – ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.24 (s, 9 H, Me), 1.30, 1.42 (2 broad s, each 1 H, *endo*-2'-, *endo*-4'-H), 2.10, 2.26 (2 d, J = 6.2 Hz, 2 H, *exo*-2'-, *exo*-4'-H), 2.38 (broad s, 1 H,

OH), 4.86 (s, 1 H, C*H*OH). – ^{13}C NMR ($CDCl_3$, 100 MHz): δ 18.18, 18.51 (2 s), 27.39 (s), 30.83 (q), 38.16, 40.61 (2 t), 62.16 (d), 75.78 (s), 96.08 (s). – MS (70 eV), *m/z* (%): 229 (21), 227 (22) [M^+–CH_3], 41 (100).
$C_{10}H_{12}{}^{79}BrO$ calcd. 227.007; found 227.005 (HRMS for M^+ –CH_3).

2,3-Bis(3-bromobicyclo[1.1.0]but-1-yl)butan-2,3-diol (**18q**)
BuLi (91.8 mmol), TMEDA (10.7 g, 91.8 mmol), **17q** (4.15 g, 21.4 mmol) and TsBr (10.0 g, 42.7 mmol) were allowed to react according to the general procedure. Standard workup afforded **18q** (3.15 g, 42%) as a pale yellow, viscous oil of *b.p.* 110–125°C (bath)/0.001 Torr. Above 125 °C, **18q** decomposed to a black tar. According to NMR analysis, **18q** consisted of a 62:38 mixture of diastereomers.
Major Isomer: ^{1}H NMR ($CDCl_3$, 60 MHz): δ 1.11, 1.16 (2 d, J = 2 Hz, each 2 H, *endo*-2'-, *endo*-4'-H), 1.40 (s, 6 H, Me), 1.97, 2.19 (2 d, J = 6.4 Hz, each 2 H, *exo*-2'-, *exo*-4'-H), 2.33 (broad s, 2 H, OH). – ^{13}C NMR ($CDCl_3$, 20 MHz): δ 19.32, 20.19 (2 s), 20.00 (q), 37.32, 39.37 (2 t), 76.88 (s).
Minor Isomer: ^{1}H NMR ($CDCl_3$, 60 MHz): δ 1.02, 1.14 (2 d, J = 2 Hz, each 2 H, *endo*-2'-, *endo*-4'-H), 1.38 (s, 6 H, Me), 1.96, 2.11 (2 d, J = 6.5 Hz, each 2 H, *exo*-2'-, *exo*-4'-H), 2.33 (broad s, 2 H, OH). – ^{13}C NMR ($CDCl_3$, 20 MHz): δ 19.15 (q), 19.72, 20.24 (2 s), 37.20, 39.48 (2 t), 76.86 (s).
$C_{12}H_{16}Br_2O_2$ (352.1): calcd. C 40.94, H 4.58; found C 42.37, H 4.89; $C_6H_8{}^{79}BrO$ calcd. 174.976; found 174.987 (HRMS for M^+/2).

Exo-5-bromo-endo-5-chloro-6-alkylidenebicyclo[2.1.1]-hexanes (13) (General procedure)

N-Chlorosuccinimide (NCS) (1.00 equiv.) and dimethyl sulfide (DMS) (1.00 equiv.) were mixed at 0 °C in dichloromethane (concentration approximately 0.4 mol/l). The milky suspension was cooled to –25 °C and a solution of **12** (0.85 equiv.) in dichloromethane (concentration 0.4–0.6 mol/l) was added dropwise under stirring. The bath temperature was raised to 25 °C and stirring continued for 3 to 5 h. The clear dichloromethane solution was extracted three times with 1N NaOH and four times with a saturated aqueous NaCl solution, dried over $MgSO_4$, filtered, and the solvent removed *in vacuo*. Purification of the residual **13** was carried out by distillation under reduced pressure; in a few cases, **13** was a solid and could be purified by crystallization.

Exo-5-bromo-endo-5-chloro-6-(1-phenylethylidene)bicyclo-[2.1.1]hexane (**13c**)

NCS (2.75 g, 20.6 mmol), DMS (1.28 g, 20.6 mmol) and **12c** (4.79 g, 17.2 mmol) were allowed to react according to the general procedure and afforded **13c** (3.16 g, 62%) as a colorless viscous oil of *b.p.* 100–110 °C (bath)/0.001 Torr. – ^{1}H NMR ($CDCl_3$, 60 MHz): δ 1.62-2.22 (m, 4 H, 2-, 3-H_2), 1.95 (s, 3 H, Me), 3.40 (s, 2 H, 1-, 4-H), 7.20 (s, 5 H, aromatic H). – ^{13}C NMR ($CDCl_3$, 20 MHz): δ 18.26 (q), 23.69, 23.84 (m), 60.61, 60.91 (2 d), 72.60 (s), 122.25 (s), 126.61, 128.09 (2 d), 137.72, 140.63 (2 s). – MS (70 eV), *m/z* (%): 296 (0.5) [M^+], 166 (100).

Exo-5-bromo-endo-5-chloro-6-(9-fluorenylidene)bicyclo-[2.1.1]hexane (**13e**)

NCS (5.95 g, 44.5 mmol), DMS (2.79 g, 44.9 mmol) and **12e** (12.6 g, 37.1 mmol) were allowed to react according to the general procedure and afforded **13e** (8.76 g, 66%, from ethanol) as colorless crystals of *m.p.* 181–182 °C. – ^{1}H NMR ($CDCl_3$, 60 MHz): δ 1.78–2.35 (m, 4 H, 2-, 3-H_2), 4.10 (s, 2 H, 1-, 4-H), 7.30–7.70 (m, 8 H, aromatic H). – ^{13}C NMR ($CDCl_3$, 20 MHz): δ 24.11 (m), 62.24 (d), 70.48 (s), 119.85, 122.52, 127.03, 127.73 (4 d), 124.21, 137.84, 139.69, 143.27 (4 s). – MS (70 eV), *m/z* (%): 360, 358, 356 (4) [M^+], 241 (100).
$C_{19}H_{14}BrCl$ (357.7): calcd. C 63.80, H 3.95; found C 62.98, H 3.89.

Exo-5-bromo-endo-5-chloro-6-isopropylidenebicyclo-[2.1.1]hexane (**13f**)

NCS (5.86 g, 43.9 mmol), DMS (2.73 g, 43.9 mmol) and **12f** (7.95 g, 36.6 mmol) were allowed to react according to the general procedure and afforded crude **13f** that decomposed on attempted distillation. In a second identical experiment purification of **13f** was carried out by low temperature crystallization from dichloromethane at –60 °C, which gave rise to **13f** (3.00 g, 35%) as colorless needles of *m.p.* 39–41 °C. – ^{1}H NMR ($CDCl_3$, 60 MHz): δ 1.58 (s, 6 H, Me), 1.78–2.03 (m, 4 H, 2-, 3-H_2), 3.28 (s, 2 H, 1-, 4-H). – ^{13}C NMR ($CDCl_3$, 20 MHz): δ 19.54 (q), 23.62 (m), 59.64 (d), 73.51 (s), 117.82, 133.88 (2 s). – MS (70 eV), *m/z* (%): 238 (3), 336 (10), 234 (7) [M^+], 119 (100).

Attempted synthesis of **13d**, **g**, **h**, **i**, and **j**

According to the general procedure, **12d**, **12g**, **12h**, **12i**, and **12j** were added to a mixture of NCS and DMS. Whereas **12d** and **12h** were re-isolated unchanged, **12g**, **12i** and **12j** did react to complex product mixtures, which only contained traces of the expected dihalides **13**, which could not be separated from the by-products. Treatment of the above bromoalkohols with thionyl chloride/pyridine or triphenyl phoshine/carbon tetrachloride was also not successful.

1-Bromo-1-chloro-3-alkylidenecyclobutanes 19 (General procedure)

To the suspension of NCS (approximately 1.50 equiv.) and DMS (approximately 1.50 equiv.) in dichloromethane, prepared as described for **13**, 1.00 equiv. of **18** were added and the mixture treated as above. The standard workup afforded a crude product, which was analyzed by NMR spectroscopy and purified by distillation or column chromatography. If the propensity to form ketones of type **26** was high, an excess of NCS, DMS with respect to **18** was used and triethylamine was added.

1-Bromo-1-chloro-3-benzylidenecyclobutane (**19a**)

NCS (419 mg, 3.14 mmol), DMS (195 mg, 3.14 mmol), triethylamine (63 mg, 0.62 mmol), and **18a** (500 mg, 2.09 mmol) were allowed to react according to the general procedure. Standard workup afforded **19a** (300 mg, 56%) as a pale yellow oil of *b.p.* 84–88 °C (bath)/0.001 Torr. – ^{1}H NMR ($CDCl_3$, 60 MHz): δ 3.67–4.12 (m, 4 H, 2-, 4-H_2), 6.12–6.35 (m, 1 H, C=C*H*), 6.80–7.36 (m, 5 H, aromatic H). – ^{13}C NMR ($CDCl_3$, 20 MHz): δ 58.79, 59.12 (2 t), 66.24 (s), 124.91, 126.76, 127.18, 128.42 (4 d), 136.21, 137.27 (2 s). – MS (70 eV), *m/z* (%): 260 (1.5), 258 (6.1), 256 (4.4) [M^+], 115 (100).
$C_{11}H_{10}{}^{79}Br{}^{35}Cl$ calcd. 257.963; found 257.967 (HRMS).

1-Bromo-1-chloro-3-(4-methoxybenzylidene)cyclobutane (**19b**)

NCS (4.65 g, 34.8 mmol), DMS (2.10 g, 34.8 mmol), triethylamine (500 mg, 4.94 mmol), and **18b** (6.70 g, 24.9 mmol) were allowed to react according to the general procedure. Standard workup afforded a brown oil, from which all volatile by-products were removed *in vacuo* at 0.001 Torr and 130 °C (bath). The black residue was extracted four times with 250 ml of pentane, the solvent removed from the combined pentane extracts *in vacuo* and the remaining oil purified by column chromatography over silica and hexane/dichloromethane (1:1) as eluent. The third fraction contained **19b** (3.08 g, 43%) as a yellow oil. – ^{1}H NMR ($CDCl_3$, 60 MHz): δ 3.71–4.06 (m, 4 H, 2-, 4-H_2), 3.81 (s, 3 H, Me), 6.02–6.22 (m, 1 H, C=C<u>H</u>), 6.66–7.29 (m, 4 H, aromatic H). – ^{13}C NMR ($CDCl_3$, 20 MHz): δ 25.16 (q), 58.82, 59.24 (2 t), 66.48 (s), 114.04 (d), 124.43 (d), 126.97, 129.24 (2 s), 128.45 (d), 158.62 (s). – MS (70 eV), *m/z* (%): 290 (3), 289 (24), 288 (16), 287 (100), 286 (15), 285 (75) (peaks for M^+ and M^+–H).

$C_{12}H_{11}{}^{79}Br^{35}Cl$ calcd. 284.968; found 284.973 (HRMS).

1-Bromo-1-chloro-3-(1-phenylethylidene)cyclobutane (**19c**)

NCS (1.16 g, 8.69 mmol), DMS (540 mg, 8.69 mmol) and **18c** (2.10 g, 8.30 mmol) were allowed to react according to the general procedure. Standard workup afforded a pale yellow oil of *b.p.* 90–94 °C (bath)/0.001 Torr, which according to the NMR spectra contained 20% of an impurity. Further purification was effected by column chromatography over silica with hexane/dichloromethane 1:1 as eluent. The second fraction gave rise to **19c** (1.16 g, 51%) as a pale yellow oil. – ^{1}H NMR ($CDCl_3$, 60 MHz): δ 1.84–2.00 (m, 3 H, Me), 3.80–3.98 (m, 4 H, 2-, 4-H_2), 7.07–7.40 (m, 5 H, aromatic H). – ^{13}C NMR ($CDCl_3$, 20 MHz): δ 17.63 (q), 57.97, 58.70 (2 t), 66.09 (s), 123.94 (s), 126.43, 126.85, 128.21 (3 d), 130.76, 139.81 (2 s). – MS (70 eV), *m/z* (%): 274 (1.1), 272 (6.2), 270 (5.0) [M^+], 129 (100).

$C_{12}H_{12}BrCl$ (271.6): calcd. C 53.07, H 4.45; found C 53.61, H 4.66; $C_{12}H_{12}{}^{79}Br^{35}Cl$ calcd. 269.981; found 269.983 (HRMS).

1-Bromo-1-chloro-3-(9-fluorenyliden)cyclobutane (**19e**)

NCS (530 mg, 3.97 mmol), DMS (250 mg, 4.02 mmol) and **18e** (1.00 g, 3.19 mmol; **18e** contained 10% of **17e**) were allowed to react according to the general procedure. Standard workup afforded after removal of all volatile by-products a crystalline solid, which was purified from ethanol to give **19e** (300 mg, 28%) as pale yellow plates, *m.p.* 190–195 °C. – ^{1}H NMR ($CDCl_3$, 60 MHz): δ 4.45 (s, 4 H, 2-, 4-H_2), 7.04–7.76 (m, 8 H, aromatic H). – ^{13}C NMR ($CDCl_3$, 100 MHz): δ 59.97 (t), 66.06 (s), 119.94, 123.00, 127.15, 127.82 (4 d), 130.48, 131.97, 137.57, 139.81 (4 s). – MS (70 eV), *m/z* (%): 334 (3), 332 (14), 330 (11) [M^+], 115 (100).

$C_{17}H_{12}BrCl$ (331.6): calcd. C 61.57, H 3.65; found C 60.67, H 3.62.

1-Bromo-1-chloro-3-(2,4-dimethyl-3-pentylidene)cyclobutane (**19g**)

NCS (4.05 g, 30.3 mmol), DMS (1.89 g, 30.4 mmol), triethylamine (310 mg, 3.06 mmol) and **18g** (1.53 g, 6.19 mmol) were allowed to react according to the general procedure. Standard workup afforded a viscous oil, which was purified by preparative layer chromatography on silica with dichloromethane/hexane 1:1 as solvent, leading to **19g** (500 mg, 30%), and to 3-(2,4-dimethyl-3-pentylidene)cyclobutanone (**26a**) (200 mg, 19%).

In a second experiment, NCS (31.3g, 234 mmol), DMS (14.6 g, 235 mmol), triethylamine (2.38 g, 23.5 mmol), LiCl (2.00 g, 47.2 mmol) reacted according to the general procedure with **18g** (5.80 g, 23.5 mmol). After standard workup the oily residue was purified by column chromatography (silica, dichloromethane/hexane 1:1 as eluent) giving rise to **26a** (156 mg, 4%), and to **19g** (3.30 g (53%) as a colorless viscous oil.

19g: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.99, 1.00 (2 d, J = 6.8 Hz, each 6 H, Me), 2.32 (sept, J = 6.8 Hz, 2 H, C<u>H</u>Me_2), 3.80 (s, 4 H, 2-, 4-H_2). – ^{13}C NMR ($CDCl_3$, 100 MHz): δ 21.19, 21.24 (2q), 29.52 (d), 57.81 (t), 67.44 (s), 118.44 (s), 146.66 (s). – MS (70 eV), *m/z* (%): 268 (5), 266 (21), 264 (15) [M^+], 107 (100).

$C_{11}H_{18}{}^{79}Br^{35}Cl$ calcd. 264.0280; found 264.0280 (HRMS).

26a: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.04 (d, J = 4.9 Hz, 12 H, Me), 2.45 (sept, J = 4.9 Hz, 2 H, C<u>H</u>Me_2), 3.61 (s, 4 H, 2-, 4-H_2). – ^{13}C NMR ($CDCl_3$, 100 MHz): δ 21.16 (q), 30.53 (d), 53.28 (t), 115.00 (s), 145.93 (s), 207.80 (s). – MS (70 eV), *m/z* (%): 166 (18) [M^+], 95 (100).

$C_{11}H_{18}O$ calcd. 166.1358; found 166.1319 (HRMS).

1-Bromo-1-chloro-3-(cyclopentylidene)cyclobutane (**19i**)

NCS (3.20 g, 24.0 mmol), DMS (1.48 g, 24.0 mmol), triethylamine (0.300 g, 2.96 mmol) and **18i** (4.10 g, 18.9 mmol) were allowed to react according to the general procedure. Standard workup afforded a pale yellow oil of *b.p.* 52–57 °C (bath)/0.01 Torr, which according to the NMR spectra contained besides **19i** also the ketone **26b**. Further purification of the distillate was effected by column chromatography over silica with hexane/dichloromethane 1:1 as eluent. The first fraction gave rise to **17i** (1.91 g, 43%) as a slightly yellow oil. The second fraction contained **26b** (380 mg, 15%) as a colorless liquid.

19i: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.65–1.69 (m, 4 H, 3'-, 4'-H_2), 2.06–2.08 (m, 4 H, 2'-, 5'-H_2), 3.61–3.69 (m, 4 H, 2-, 4-H_2). – ^{13}C NMR ($CDCl_3$, 100 MHz): δ 26.59 (t), 29.92 (t), 57.58 (t), 67.33 (s), 115.58 (s), 138.67 (s). – MS (70 eV), *m/z* (%): 238 (2), 236 (11), 234 (8) [M^+], 91 (100).

26b: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.70–1.73 (m, 4 H, 3'-, 4'-H_2), 2.17–2.24 (m, 4 H, 2'-, 5'-H_2), 3.47–3.49 (m, 4 H, 2-, 4-H_2). – ^{13}C NMR ($CDCl_3$, 100 MHz): δ 26.97 (t), 31.12 (t), 53.11 (t), 112.89 (s), 137.77 (s), 206.72 (s). – MS (70 eV), *m/z* (%): 136 (18) [M^+], 93 (100).

1-Bromo-1-chloro-3-(2,2,3,3-tetramethylcyclobutyl-1-idene)cyclobutane (**19k**)

NCS (5.14 g, 38.5 mmol), DMS (2.39 g, 38.5 mmol), triethylamine (0.860 g, 8.50 mmol) and **18k** (5.55 g, 21.4 mmol) were allowed to react according to the general procedure. Standard workup afforded a pale yellow oil, which was distilled at 0.01 Torr. The main fraction (1.30 g) was collected at 57–60 °C (bath) and consisted according to the NMR spectra of pure **19k**. The forerun was a mixture of **19k** and 3-(2,2,3,3-tetramethylcyclobutyl-1-idene)cyclobutanone (**26c**) which was separated by column chromatography with dichloromethane/hexane 1:1 as eluent. The total amount of **19k** was 2.26 g (38%), that of **26c** 0.580 g (15%, colorless liquid).

19k: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.01, 1.02, 1.02, 1.04 (4 s, 12 H, Me), 2.16–2.18 (m, 2 H, 4'-H_2), 3.60–3.74 (m, 4 H, 2-, 4-H_2). – ^{13}C NMR ($CDCl_3$, 100 MHz): δ 22.25, 22.42, 24.19, 24.25 (4 q), 36.83 (s), 40.06 (t), 47.05 (s), 56.69, 57.06 (2 t), 67.84 (s), 115.27 (s), 141.79 (s). – MS (70 eV), *m/z* (%): 278 (1), 276 (0.7) [M$^+$], 105 (100).
$C_{12}H_{18}BrCl$ (331.6): calcd. C 51.91, H 6.53; found C 53.20, H 6.65; $C_{11}H_{18}{}^{81}Br^{35}Cl$ calcd. 263.002; found 263.000 (HRMS for M$^+$-Me).
26c: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.02, 1.03, 1.04, 1.07 (4 s, 12 H, Me), 2.27–2.29 (m, 2 H, 4'-H_2), 3.49–3.56 (m, 4 H, 2-, 4-H_2). – ^{13}C NMR ($CDCl_3$, 100 MHz): δ 22.24, 24.35 (2 q), 36.84 (s), 40.85 (t), 46.86 (s), 52.06, 53.42 (2 t), 111.95 (s), 141.06 (s), 207.20 (s).

1-Bromo-1-chloro-3-(E-2-buten-1-ylidene)cyclobutane (**19m**)

NCS (9.80 g, 73.4 mmol), DMS (4.56 g, 73.4 mmol), triethylamine (1.70 g, 16.8 mmol) and **18m** (8.30 g, 40.9 mmol) were allowed to react according to the general procedure. Standard workup followed by distillation afforded **19m** (3.72 g, 41%) as a colorless liquid of *b.p.* 37–41 °C (bath)/0.01 Torr. – ^{1}H NMR ($CDCl_3$, 60 MHz): δ 1.75 (d, J = 7 Hz, 3 H, Me), 3.75 (broad s, 4 H, 2-, 4-H_2), 5.39–5.97 (m, 3 H, vinylic H). – ^{13}C NMR ($CDCl_3$, 20 MHz): δ 18.17 (q), 56.97, 58.12 (2 t), 66.12 (s), 124.82, 126.85, 128.85 (3 d), 127.36 (s). – MS (70 eV), *m/z* (%): 224 (6), 222 (25), 220 (18) [M$^+$], 79 (100).
$C_8H_{10}{}^{79}Br^{35}Cl$ calcd. 219.965; found 219.968 (HRMS).

1-Bromo-1-chloro-3-(4-methylpent-3-enyl-2-en-1-ylidene)-cyclobutane (**19n**)

NCS (13.87 g, 103.6 mmol), DMS (6.45 g, 103.6 mmol), triethylamine (1.008 g, 9.96 mmol) and **18n** (8.00 g, 34.6 mmol) were allowed to react according to the general procedure. Standard workup followed by distillation afforded **19n** (4.10 g, 47%) as a colorless liquid of *b.p.* 57–68 °C (bath)/0.01 Torr. – ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.64, 1.66, 1.75 (3 s, 9 H, Me), 3.59–3.77 (m, 4 H, 2-, 4-H_2), 5.50 (s, 1 H, vinylic H). – ^{13}C NMR ($CDCl_3$, 100 MHz): δ 17.98, 19.77, 26.31 (3 q), 57.30, 58.14 (2 t), 66.53 (s), 122.78 (s), 123.59 (d), 129.84, 134.01 (2 s). – MS (70 eV), *m/z* (%): 252 (6), 250 (26), 248 (19) [M$^+$], 93 (100).
$C_{10}H_{14}BrCl$ (249.6): calcd. C 48.13, H 5.65; found C 48.21, H 5.71; $C_{10}H_{14}{}^{79}Br^{35}Cl$ calcd. 247.997; found 248.004 (HRMS).

1-Bromo-1-chloro-3-(cyclohex-2-en-1-ylidene)cyclobutane (**19o**)

NCS (2.94 g, 22.0 mmol), DMS (1.37 g, 22.0 mmol), triethylamine (0.550 g, 5.44 mmol) and **18o** (2.50 g, 10.9 mmol) were allowed to react according to the general procedure. Standard workup followed by column chromatography with dichloromethane/hexane 1:1 afforded **19o** (0.970 g, 36%) as a colorless viscous oil which decomposed on attempted distillation. – ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.63–1.75 (m, 2 H, 5'-H_2), 2.08–2.16 (m, 4 H, 4'-, 6'-H_2), 3.69–3.85 (m, 4 H, 2-, 4-H_2), 5.77–5.97 (m, 2 H, vinylic H). – ^{13}C NMR ($CDCl_3$, 100 MHz): δ 22.02, 25.18, 25.62 (3 t), 56.55, 56.79 (2 t), 66.43 (s), 120.48 (s), 124.03, 128.96 (2 d), 130.02 (s). – MS (70 eV), *m/z* (%): 250 (7), 248 (30), 246 (23) [M$^+$], 91 (100).
$C_{10}H_{12}{}^{79}Br^{35}Cl$ calcd. 245.981; found 245.985 (HRMS).

1-Bromo-1-chloro-3-(4,4-dimethylpent-2-yn-1-ylidene)-cyclobutane (**19p**)

NCS (10.98 g, 82.2 mmol), DMS (5.11 g, 82.2 mmol), triethylamine (0.830 g, 8.20 mmol), lithium chloride (2.50 g, 59.0 mmol) and **18p** (2.00 g, 8.23 mmol) were allowed to react according to the general procedure. Standard workup and distillation of the oily residue at 60–70 °C (bath)/0.001 Torr led to a mixture of **19p** and **26d** which were separated by column chromatography with dichloromethane/hexane 1:1 affording **19p** (0.500g, 23%) as a colorless viscous oil and **26d** (100 mg, 7.5%) as colorless liquid.
19p: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.23 (s, 9 H, Me), 3.08–3.87 (m, 4 H, 2-, 4-H_2), 5.46 (qui, J = 2.5 Hz, 1 H, vinylic H). – ^{13}C NMR ($CDCl_3$, 100 MHz): δ 28.10 (s), 31.05 (q), 58.02, 58.23 (2 t), 65.09 (s), 74.33 (s), 103.52 (s), 106.33 (d), 140.56 (s). – MS (70 eV), *m/z* (%): 264 (3), 262 (15), 260 (11) [M$^+$], 130 (100).
$C_{11}H_{14}{}^{81}Br^{35}Cl$ calcd. 261.994; found 261.993 (HRMS).
26d: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.25 (s, 9 H, Me), 3.68–3.72 (m, 4 H, 2-, 4-H_2), 5.71–5.73 (m, 1 H, vinylic H). – ^{13}C NMR ($CDCl_3$, 100 MHz): δ 28.11 (s), 31.08 (q), 54.26, 54.56 (2 t), 75.70 (s), 103.60 (s), 105.56 (d), 137.67 (s), 210.40 (s).

*Bis-2,3-(3-bromo-3-chlorocyclobutylidene)butane (**19q**)*

NCS (14.59 g, 109 mmol), DMS (6.78 g, 109 mmol), triethylamine (1.06 g, 10.4 mmol), lithium chloride (4.80 g, 114 mmol) and **18q** (6.40 g, 18.1 mmol) were allowed to react according to the general procedure. Standard workup and purification of the oily residue by column chromatography with dichloromethane/hexane 1:8 afforded **19q** (0.900g, 13%) as a colorless viscous oil, which decomposed on attempted distillation. – ^{1}H NMR ($CDCl_3$, 60 MHz): δ 1.60–1.65 (m, 6 H, Me), 3.54–3.80 (m, 8 H, 2'-, 4'-H_2). – ^{13}C NMR ($CDCl_3$, 20 MHz): δ 16.45 (q), 57.17, 58.24 (2 t), 66.03 (s), 122.90 (s), 131.22 (s). – MS (70 eV), *m/z* (%): 392 (8), 390 (27), 388 (33), 386 (12) [M$^+$], 157 (100).
$C_{12}H_{14}{}^{79}Br_2{}^{35}Cl_2$ calcd. 385.8839; found 385.8976 (HRMS).

Attempted synthesis of 1-bromo-1-chloro-3-(2-propen-1-ylidene)cyclobutane (**19l**)

NCS (1.35 g, 10.1 mmol), DMS (0.630 g, 10.1 mmol), triethylamine (0.20 g, 1.98 mmol) and **18l** (1.27 g, 6.72 mmol) were allowed to react according to the general procedure. Standard workup led to an oily residue, which according to its NMR spectra did not contain the expected dihalide **19l**.

[1.1.1]Propellanes 15, 21 (General Procedure)

A solution of MeLi in ether (the concentration was determined prior to use and was approximately 1.5 mol/l; 1.3 equiv. of MeLi were used), kept under nitrogen, was cooled to –25 °C. To this solution was added dropwise under stirring a solution of dihalide **13** or **19** in ether (1.00 equiv., concentration approximately 0.3 to 0.4 mol/l). Stirring was continued for 1 h at –25 °C (bath), the mixture allowed to warm to room temperature and kept at this temperature under stirring for 3 to 18 h. After cooling in an icebath, 2N NaOH was added under stirring and the aqueous layer removed by pipette or syringe under nitrogen. The ether layer was dried over $MgSO_4$ and filtration was carried out under nitrogen. The solvent was removed under reduced pressure at room temperature and the

residual oil purified by short-path distillation. Care was taken that the propellane did not come into contact with oxygen, which caused partial or complete polymerization.

7-Methyl-7-phenyltetracyclo[4.1.0.0^{1,5}.0^{2,6}]heptane (**15c**)

MeLi (8.70 mmol) and **13c** (2.00 g, 6.72 mmol) were allowed to react according to the general procedure. Standard workup after 18 h afforded **15c** (770 mg, 63%) as a colorless, viscous oil of *b.p.* 25 °C (bath)/0.001 Torr. – ^{1}H NMR (C_6D_6, 60 MHz): δ 1.35 (s, 3 H, Me), 1.42–1.71 (m, 4 H, 3-, 4-H_2), 2.82 (d, J = 4.4 Hz, 1 H, 2-H *syn* to Phe), 3.35 (d, J = 4.4 Hz, 1 H, 5-H *syn* to Me), 6.90–7.37 (m, 5 H, aromatic H); the assignment of 2-H and 5-H could be reversed. – ^{13}C NMR (C_6D_6, 20 MHz): δ 21.05 (q), 22.50 (s), 24.32, 24.59 (2 m), 80.08, 81.05 (2 d), 101.35 (s), 127.12, 128.33, 129.09 (3 d), 142.66 (s).
$C_{14}H_{14}$ (182.3): calcd. C 92.26, H 7.74; found C 90.22, H 7.64.

Tetracyclo[4.1.0.0^{1,5}.0^{2,6}]heptane-7-spiro-(9'-fluorene) (**15e**)

MeLi (6.70 mmol) and **13e** (2.00 g, 5.59 mmol) were allowed to react according to the general procedure. Standard workup after 3 h afforded **15e** (1.18 g, 87%) as pale yellow crystals (from ether) of *m.p.* 84–85 °C. – ^{1}H NMR (C_6D_6, 60 MHz): δ 1.55 (s, 4 H, 3-, 4-H_2), 4.34 (s, 2 H, 2-, 5-H), 6.74–7.45 (m, 8 H, aromatic H). – ^{13}C NMR (C_6D_6, 20 MHz): δ 23.61 (m), 27.73 (s), 80.72 (d), 101.37 (s), 120.01, 125.11, 127.08, 128.01 (4 d), 141.18, 141.84 (s).
$C_{19}H_{14}$ (242.3): calcd. C 94.18, H 5.82; found C 94.13, H 5.91.

7,7-Dimethyltetracyclo[4.1.0.0^{1,5}.0^{2,6}]heptane (**15f**)

MeLi (16.8 mmol) and **13f** (3.30 g, 14.0 mmol) were allowed to react according to the general procedure. Standard workup after 18 h followed by distillation of the volatile material at 25 °C (bath)/0.001 Torr into a dry-ice cooled trap and removal of the ether in vacuo afforded **15f** (500 mg, 30%) as a waxy colorless mass of unpleasant odor. Solutions of **15f** in C_6D_6 for NMR spectroscopy turned cloudy after 30 min at room temperature. – ^{1}H NMR (C_6D_6, 60 MHz): δ 1.15 (s, 6 H, Me), 1.60 (s, 4 H, 3-, 4-H_2), 3.28 (s, 2 H, 2-, 5-H). – ^{13}C NMR (C_6D_6, 20 MHz): δ 19.63 (q), 23.14 (s), 24.47 (m), 78.81 (d), 91.11 (s).

2-Phenyltricyclo[1.1.1.0^{1,3}]pentane (**21a**)

MeLi (7.50 mmol) and **19a** (1.50 g, 5.82 mmol) were allowed to react according to the general procedure. Standard workup after 4 h followed by distillation of the volatile material afforded **21a** (460 mg, 56%) as a colorless viscous liquid of *b.p.* 30–40 °C (bath)/0.001 Torr. – ^{1}H NMR (C_6D_6, 400 MHz): δ 1.71 (d, $^2J(H^DH^E)$ = 1.8 Hz, 1 H, H^D), 1.80 (dd, $^2J(H^EH^D)$ = 1.8 Hz, $^4J(H^EH^B)$ = 6.9 Hz, 1 H, H^E), 2.00 (dd, $^2J(H^CH^B)$ = 2.3 Hz, $^4J(H^CH^A)$ = 5.0 Hz, 1 H, H^C), 2.42 (dd, $^2J(H^BH^C)$ = 2.3 Hz, $^4J(H^BH^E)$ = 6.9 Hz, 1 H, H^B), 3.75 (d, $^4J(H^AH^C)$ = 5.0 Hz, 1 H, H^A), 7.02–7.26 (m, 5 H, aromatic H). – ^{13}C NMR (C_6D_6, 100 MHz): δ 6.55 (s), 69.78, 74.06 (2 t), 93.65 (d), 127.56, 128.32, 130.35 (3 d), 134.57(s).

2-(4-Methoxyphenyl)tricyclo[1.1.1.0^{1,3}]pentane (**21b**)

MeLi (4.00 mmol) and **19b** (1.00 g, 3.48 mmol) were allowed to react according to the general procedure. Standard workup after 3 h followed by distillation of the volatile material afforded **21b** (270 mg, 45%) as a colorless viscous liquid of *b.p.* 70–80 °C (bath)/0.01 Torr. – ^{1}H NMR (C_6D_6, 400 MHz): δ 1.74 (d, $^2J(H^DH^E)$ = 1.6 Hz, 1 H, H^D), 1.83 (dd, $^2J(H^EH^D)$ = 1.6 Hz, $^4J(H^EH^B)$ = 7.0 Hz, 1 H, H^E), 2.05 (dd, $^2J(H^CH^B)$ = 2.2 Hz, $^4J(H^CH^A)$ = 4.9 Hz, 1 H, H^C), 2.49 (dd, $^2J(H^BH^C)$ = 2.2 Hz, $^4J(H^BH^E)$ = 7.0 Hz, 1 H, H^B), 3.74 (d, $^4J(H^AH^C)$ = 4.9 Hz, 1 H, H^A), 6.67–7.17 (AA'BB' system, 4 H, aromatic H). – ^{13}C NMR (C_6D_6, 100 MHz): δ 6.78 (s), 54.75 (q), 69.68, 74.02 (2 t), 93.24 (d), 113.88 (d), 126.64 (s), 131.40 (d), 159.42 (s).

2-Methyl-2-phenyltricyclo[1.1.1.0^{1,3}]pentane (**21c**)

MeLi (9.00 mmol) and **19c** (2.00 g, 7.36 mmol) were allowed to react according to the general procedure. Standard workup after 3 h followed by distillation of the volatile material afforded **21c** (380 mg, 33%) as a colorless viscous liquid of *b.p.* 65–75 °C (bath)/0.01 Torr. – ^{1}H NMR (C_6D_6, 400 MHz): δ 1.27 (s, 3 H, Me), 1.61 (d, $^2J(H^DH^E)$ = 1.8 Hz, 1 H, H^D), 1.83 (d, $^2J(H^CH^B)$ = 2.7 Hz, 1 H, H^C), 2.07 (dd, $^2J(H^EH^D)$ = 1.8 Hz, $^4J(H^EH^B)$ = 7.7 Hz, 1 H, H^E), 2.62 (dd, $^2J(H^BH^C)$ = 2.7 Hz, $^4J(H^BH^E)$ = 7.7 Hz, 1 H, H^B), 7.01–7.28 (m, 5 H, aromatic H). – ^{13}C NMR (C_6D_6, 100 MHz): δ 11.53 (s), 19.50 (q), 69.41, 71.04 (2 t), 103.51 (s), 127.94, 128.53, 129.39 (3 d), 142.10(s).

2,2-Diisopropyltricyclo[1.1.1.0^{1,3}]pentane (**21g**)

MeLi (4.50 mmol) and **19g** (1.00 g, 3.76 mmol) were allowed to react according to the general procedure. Standard workup after 4 h followed by distillation of the volatile material afforded **21g** (360 mg, 64%) as a colorless viscous liquid of *b.p.* 20–25 °C (bath)/0.01 Torr. At 25 °C in C_6D_6, the ^{1}H NMR spectrum of **21g** showed dynamical phenomena due to hindered rotation of the isopropyl groups. At –60 °C, the NMR spectra of **21g** were similar to those of unsymmetrically 2,2-disubstituted [1.1.1]propellanes. – ^{1}H NMR (C_6D_6, 400 MHz, 25 °C): δ 0.80–1.10 (broad s, 12 H, Me), 1.60 (broad s, 2 H, H^C, H^D), 1.80 (broad s, 2 H, $HCMe_2$), 2.35 (broad s, 2 H, H^B, H^E). – ^{1}H NMR (THF-d_8, 400 MHz, –60 °C): δ 0.90 (d, ^3J = 6.8 Hz, 6 H, Me), 1.01 (d, ^3J = 7.3 Hz, 6 H, Me), 1.66 (d, $^2J(H^CH^B)$ = 2.9 Hz, 1 H, H^C), 1.78 (d, $^2J(H^DH^E)$ = 1.8 Hz, 1 H, H^D), 1.84 (sept, ^3J = 6.8 Hz, 1 H, $HCMe_2$), 2.18 (sept, ^3J = 7.3 Hz, 1 H, $HCMe_2$), 2.34 (dd, $^2J(H^EH^D)$ = 1.8 Hz, $^4J(H^EH^B)$ = 8.0 Hz, 1 H, H^E), 2.65 (dd, $^2J(H^BH^C)$ = 2.9 Hz, $^4J(H^BH^E)$ = 8.0 Hz, 1H, H^B). – ^{13}C NMR (THF-d_8, 100 MHz, –60 °C): δ = 13.80 (s), 20.56, 24.27 (2 q), 25.85, 28.92 (2 d), 67.27, 71.10 (2 t), 116.39 (s).

Tricyclo[1.1.1.0^{1,3}]pentane-2-spiro-1'-cyclopentane (**21i**)

MeLi (6.80 mmol) and **19i** (1.24 g, 5.26 mmol) were allowed to react according to the general procedure. Standard workup after 3 h followed by distillation of the volatile material afforded **21i** (380 mg, 60%) as a colorless viscous liquid of *b.p.* 20–25 °C (bath)/0.001 Torr. – ^{1}H NMR (C_6D_6, 400 MHz): δ 1.42–1.46 (m, 4 H, 3'-, 4'-H_2), 1.53–1.57 (m, 2'-, 5'-H_2), 1.70 (s, 2 H, H^C, H^D), 2.26 (s, 2 H, H^B, H^E). – ^{13}C NMR (C_6D_6, 100 MHz): δ 13.76 (s), 26.55 (t), 28.42 (t), 69.52 (t), 103.44 (s).

Tricyclo[1.1.1.0^{1,3}]pentane-2-spiro-1'-(2',2',3',3'-tetramethylcyclobutane) (**21k**)

MeLi (8.50 mmol) and **19k** (2.00 g, 7.20 mmol) were allowed to react according to the general procedure. Standard workup

after 3 h followed by distillation of the volatile material afforded **21k** (350 mg, 30%) as a colorless liquid of *b.p.* 20–25 °C (bath)/0.001 Torr. **21k** polymerized slowly, even when kept under nitrogen at −25 °C. – ^{1}H NMR (C_6D_6, 400 MHz): δ 0.94, 0.96 (2 s, 12 H, Me), 1.61 (d, $^2J(H^DH^E)$=1.6 Hz, 1H, H^D), 1.66 (s, 2 H, 4'-H_2), 1.77 (d, $^2J(H^CH^B)$=1.8 Hz, 1H, H^C), 1.91 (dd, $^2J(H^EH^D)$=1.6 Hz, $^4J(H^EH^B)$=7.14 Hz, 1H, H^E), 2.13 (dd, $^2J(H^BH^D)$=1.8 Hz, $^4J(H^BH^E)$=7.14 Hz, 1H, H^B). – ^{13}C NMR (C_6D_6, 100 MHz): δ 10.80 (s), 24.21, 24.27 (2 q), 34.98 (s), 37.01 (t), 42.59 (s), 66.56, 69.39 (2 t), 104.88 (s).

2-(E-1-Propenyl)tricyclo[1.1.1.0^{1,3}]pentane (**21m**)

MeLi (8.75 mmol) and **19m** (1.50 g, 6.77 mmol) were allowed to react according to the general procedure. Standard workup after 5 h followed by distillation of the volatile material afforded **21m** (590 mg, 82%) as a colorless liquid of *b.p.* 50–60 °C (bath)/12 Torr. – ^{1}H NMR (C_6D_6, 400 MHz): δ 1.47 (ddd, ^3J(3'-H, 2'-H) = 6.9 Hz, ^4J(3'-H, 1'-H) = 1.7 Hz, ^5J(3'-H, H^A)=0.9 Hz, 3 H, Me), 1.56 (d, $^2J(H^DH^E)$=1.4 Hz, 1H, H^D), 1.65 (dd, $^2J(H^EH^D)$=1.4 Hz, $^4J(H^EH^B)$=7.1 Hz, 1H, H^E), 1.96 (dd, $^2J(H^CH^B)$=2.0 Hz, $^4J(H^CH^A)$=4.6 Hz, 1H, H^C), 2.65 (dd, $^2J(H^BH^C)$=2.0 Hz, $^4J(H^EH^B)$=7.1 Hz, 1H, H^B), 3.04 (dd, $^3J(H^A$, 1-H')=7.4 Hz, $^4J(H^AH^C)$= 4.6 Hz, 1H, H^A), 5.19 (ddq, ^3J(1'-H, 2'-H)=15.2 Hz, ^3J(1'-H, H^A)=7.4 Hz, ^4J(1'-H, 3'-H)=1.7 Hz, 1 H, 1'-H), 5.45 (dqd, ^3J(2'-H, 1'-H)=15.2 Hz, ^3J(2'-H, 3'-H)=6.9 Hz, ^4J(2'-H, H^A)=1.7 Hz, 1 H, 2'-H). – ^{13}C NMR (C_6D_6, 100 MHz): δ 6.49 (s), 17.82 (q), 69.19, 72.41 (2 t), 91.03 (d), 123.75 (d), 130.58 (d).

2-Methyl-2-(2-methyl-1-propenyl)tricyclo[1.1.1.0^{1,3}] pentane (**21n**)

MeLi (10.4 mmol) and **19n** (2.00 g, 8.01 mmol) were allowed to react according to the general procedure. Standard workup after 3 h followed by distillation of the volatile material afforded **21n** (630 mg, 59%) as a colorless liquid of *b.p.* 30–35 °C (bath)/0.01 Torr. – ^{1}H NMR (C_6D_6, 400 MHz): δ 1.12 (s, 3 H, Me), 1.52 (broad s, 3 H, Me), 1.59 (broad s, 1 H, H^D), 1.77 (broad s, 4 H, Me, H^C), 2.48 (d, $^4J(H^BH^E)$=7.7 Hz, 1 H, H^E), 2.52 (dd, $^2J(H^CH^B)$=1.4 Hz, $^4J(H^EH^B)$=7.7 Hz, 1 H, H^B), 5.28 (broad s, 1 H, 1'-H). – ^{13}C NMR (C_6D_6, 100 MHz): δ 12.40 (s), 16.20, 19.18, 25.34 (3 q), 68.91, 69.27 (2 t), 95.64 (s), 124.29 (d), 135.12 (d).

Tricyclo[1.1.1.0^{1,3}]pentane-2-spiro-1'-(2'-cyclohexene) (**21o**)

MeLi (2.50 mmol) and **19o** (500 mg, 2.02 mmol) were allowed to react according to the general procedure. Standard workup after 4 h followed by distillation of the volatile material afforded **21o** (53 mg, 20%) as a colorless liquid of *b.p.* 20–25 °C (bath)/0.01 Torr. – ^{1}H NMR (C_6D_6, 400 MHz): δ 1.52–1.57 (m, 4 H, 5'-, 6'-H_2), 1.59 (d, $^2J(H^DH^E)$=2.4 Hz, 1 H, H^D), 1.64 (d, $^2J(H^CH^B)$=2.3 Hz, 1 H, H^C), 1.76–1.81 (m, 2 H, 4'-H_2), 2.55 (dd, $^2J(H^EH^D)$=2.4 Hz), $^4J(H^EH^B)$=7.7 Hz, 1 H, H^E), 2.59 (dd, $^2J(H^BH^C)$=2.3 Hz, $^4J(H^BH^E)$=7.7 Hz, 1 H, H^B), 5.53 (td, ^3J(2'-H, 3'-H)=10.5 Hz, ^4J(2'-H, 4'-H)=2.1 Hz, 1 H, 2'-H), 5.65 (td, ^3J(3'-H, 2'-H)=10.5 Hz, ^4J(3'-H, 4'-H)=3.6 Hz, 1H, 3'-H). – ^{13}C NMR (C_6D_6, 100 MHz): δ 12.10 (s), 23.13, 25.47, 31.73 (3 t), 67.46, 67.92 (2 t), 98.27 (s), 124.41 (d), 131.62 (d).

2-(4,4-Dimethylbut-1-ynyl)tricyclo[1.1.1.0^{1,3}]pentane (**21p**)

MeLi (3.70 mmol) and **19p** (800 mg, 3.06 mmol) were allowed to react according to the general procedure. Standard workup after 3 h followed by distillation of the volatile material afforded **21p** (110 mg, 25%) as a colorless, viscous liquid of *b.p.* 30–35 °C (bath)/0.01 Torr. In an second experiment, 1.30 g (4.97 mmol) of **19p** led to 300 mg (41%) of **21p**. – ^{1}H NMR (C_6D_6, 400 MHz): δ 1.09 (s, 9 H, Me), 1.48 (d, $^2J(H^DH^E)$= 2.1 Hz, 1 H, H^D), 1.59 (dd, $^2J(H^EH^D)$=2.1 Hz, $^4J(H^EH^B)$=7.1 Hz, 1 H, H^E), 2.02 (dd, $^2J(H^CH^B)$=1.7 Hz, $^4J(H^CH^A)$=5.4 Hz, 1 H, H^C), 2.80 (d, $^4J(H^AH^C)$=5.4 Hz, 1 H, H^A), 3.16 (dd, $^2J(H^BH^C)$=1.7 Hz, $^4J(H^BH^E)$=7.1 Hz, 1 H, H^B). – ^{13}C NMR (C_6D_6, 100 MHz): δ 8.51 (s), 27.50 (s), 30.89 (q), 69.59, 74.23 (2 t), 73.34 (s), 75.20 (d), 92.12 (s).

2,2'-Dimethyl-2,2'-bis-(tricyclo[1.1.1.0^{1,3}]pentane) (**21q**)

MeLi (4.90 mmol) and **19q** (800 mg, 2.06 mmol) were allowed to react according to the general procedure. Standard workup after 3 h followed by distillation of the volatile material afforded **21p** (120 mg, 37%) as a colorless, viscous liquid of *b.p.* 45–53 °C (bath)/0.001 Torr. – ^{1}H NMR (C_6D_6, 400 MHz): δ 1.14 (s, 6 H, Me), 1.54 (ddd, $^2J(H^DH^E)$=2.5 Hz, $^4J(H^DH^B)$ =0.7 Hz, $^4J(H^DH^C)$=0.4 Hz, 1 H, H^D), 1.67 (ddd, $^2J(H^CH^B)$= 1.9 Hz, $^4J(H^CH^E)$=0.8 Hz, $^4J(H^CH^D)$=0.4 Hz, 1 H, H^C), 2.29 (ddd, $^2J(H^EH^D)$=2.5 Hz, $^4J(H^EH^B)$=7.7 Hz, $^4J(H^EH^C)$=0.8 Hz, 1H, H^E), 3.35 (ddd, $^2J(H^BH^C)$=1.9 Hz, $^4J(H^BH^E)$=7.7 Hz, $^4J(H^BH^D)$=0.7 Hz, 1 H, H^B). – ^{13}C NMR (C_6D_6, 100 MHz): δ 16.13 (s), 17.33 (q), 67.91, 70.03 (2 t), 99.29 (s).

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Address for correspondence:
Prof. Dr. Günter Szeimies
Humboldt-Universität zu Berlin
Institut für Chemie
Hessische Straße 1–2
D-10115 Berlin