Iron-Catalyzed Coupling of Tricyclo[4.1.0.0^{2,7}]hept-1-ylmagnesium Bromide and Related Grignard Reagents with Propargylic and Allylic Halides☆

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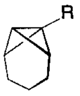
Several uncatalyzed and transition metal-catalyzed cross coupling reactions of the Grignard compounds **1c** or **2c** with propargylic or allylic halides were investigated. Fe(acac)$_3$ was the most effective catalyst for the preparation of allyl- and propargylbicyclo[1.1.0]butanes **7** and **5**. In the latter case, the formation of the isomeric allenylbicyclo[1.1.0]butanes **6** was also observed. Stereoelectronic factors of substituents like a trimethylsilyl group as a directing group could be utilized for the formation of either **5** or **6**. A number of bicyclo[1.1.0]butanes **15**–**21** with two substituents in the bridgehead positions were accessible by that route as well. In the case of the bis-allenyl compound **24c**, an ene-type reaction leading to the first known derivative of a [4.1.1]propella-2,4-diene **25** was observed. Base-catalyzed isomerizations of the propargylbicyclo[1.1.0]butanes **5** opened a new route to alkynylbicyclo[1.1.0]butanes **30**–**32**.

We have recently shown that cross coupling of tricyclo[4.1.0.0^{2,7}]hept-1-yl Grignard reagent **1c** with aryl, heteroaryl, and vinyl halides can be effected by Ni(0) catalysis[1]. 1-Haloalkynes could also be connected to the bridgehead position of bicyclo[1.1.0]butanes, thus opening access to 1-alkynyl- and 1,3-dialkynylbicyclo[1.1.0]butanes[1]. The coupling products have, at least in part, proved to be valuable intermediates for further syntheses[2,3]. In continuation of this investigation we report here on our efforts to couple propargylic and allylic halides with tricyclo[4.1.0.0^{2,7}]hept-1-ylmagnesium bromide (**1c**) and related compounds. The products of these reactions could be potential precursors for a transition metal-catalyzed cycloisomerization affording [*n*.1.1]propellanes.



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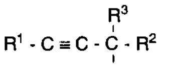
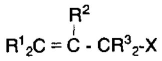
1, 2	a	b	c	d
R	H	Li	MgBr	Br



$R^1-C\equiv C-\underset{X}{\overset{R^3}{C}}-R^2$

3

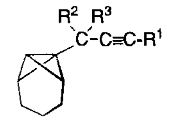


$R^1{}_2C=\overset{R^2}{C}-CR^3{}_2-X$

4

3	a	b	c	d	e	f	g	h	i	j	k	l
R^1	H	H	H	H	H	H	H	SiMe$_3$	SiMe$_3$	SiMe$_3$	SiMe$_3$	CH$_2$Cl
R^2	H	H	H	Me	Me	(CH$_2$)$_5$	Et	H	H	Me	Me	H
R^3	H	H	H	H	Me		Me	H	H	H	Me	H
X	Cl	Br	OTs	Cl	Cl	Cl	Cl	Br	Cl	Cl	Cl	Cl

4	a	b	c	d	e
R^1	H	H	H	Me	Me
R^2	H	H	Me	H	H
R^3	H	H	H	H	Me
X	Cl	Br	Cl	Cl	Cl



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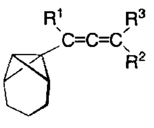

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(R^1, R^2, R^3 as in **3**)

1. The Catalyst

Does the reaction of the anyway activated propargylic and allylic halides (**3** and **4**) to afford the tricycloheptanes **5**/**6** and **7** really need a catalyst? To answer this question, tricyclo[4.1.0.0^{2,7}]hept-1-yllithium (**1b**) was treated with the corresponding halides without a catalyst. Whereas the reaction of **1b** and also the Grignard reagent **1c** with allyl chloride (**4a**) afforded only traces of 1-allyltricyclo[4.1.0.0^{2,7}]heptane (**7a**), the use of allyl bromide (**4b**) gave rise to an 18% yield of **7a**. Treatment of propargyl chloride and bromide (**3a** and **b**) with **1b** led to a 7 and 11% yield, resp., of 1-propargyltricyclo[4.1.0.0^{2,7}]heptane (**5a**). Neither the reaction of propargyl chloride nor of tosylate **3c** with **1c** gave the expected **5a** in yields higher than in trace amounts. Moreover, 3-bromo-1-(trimethylsilyl)-1-propyne (**3h**) did not couple effectively with **1b**. Besides some bromotricyclo[4.1.0.0^{2,7}]heptane (**1d**), an 12% yield of 1,6-bis(trimethylsilyl)-1,5-hexadiyne (**8**) was isolated. These results indicate that cross coupling of **1b** and **c** with allyl and propargyl halides without a proper catalyst is an insufficient process.

It is well-known that cross coupling reactions of organometallic reagents with organyl halides are catalyzed by a wide variety of transition metal compounds[4]. The efficacy of several catalysts in the coupling reaction of **1c** with propargyl chloride is given in Table 1. Besides the alkyne **5a**, in all cases 1-(1,2-propadienyl)tricyclo[4.1.0.0^{2,7}]heptane (**6a**) was also formed as observed frequently in uncatalyzed S_N2' displacement reactions of propargyl chlorides[5].

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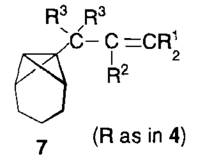


(R as in 4)

7

$Me_3Si-C\equiv C-CH_2-CH_2-C\equiv C-SiMe_3$

8

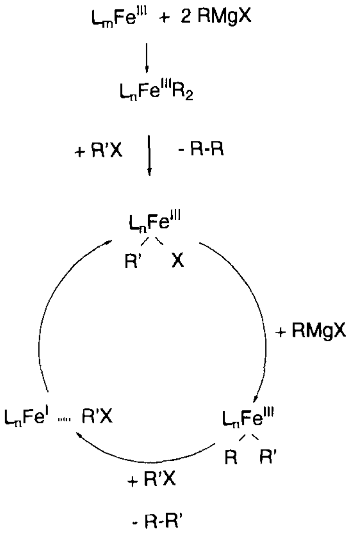
Table 1. Yields of **5a** and **6a** on variation of the catalyst (0.5–1.0%) in the reaction of **1c** with propargyl chloride

Catalyst	yield of **5a+6a** (%)	Ratio of **5a**:**6a**
$FeCl_3$	18	1.0:1.0
$Fe(dbm)_3$[a]	18	1.0:0.7
$Fe(acac)_3$[b]	47	1.0:0.8
CuCl	26	1.0:1.7
$Cu(acac)_2$	30	1.0:2.3
$Ni(acac)_2$	7	1.0:15
$NidppeCl_2$[c]	0	--- ---
$CoCl_2$	16	1.0:7.8
$Co(PPh_3)_2Cl_2$	0	--- ---

[a] dbm = dibenzoylmethanato. – [b] acac = acetylacetonato. – [c] dppe = 1,2-bis(diphenylphosphanyl)ethane.

Table 1 shows that the highest yields of cross coupling products **5a** and **6a** were obtained by using tris(acetylacetonato)iron $\{Fe(acac)_3\}$ as a catalyst. The capability of iron enolate complexes of diketones to catalyze cross coupling of organometallic compounds with halides has been thoroughly studied by Kochi and his group[6]. Although the mechanism of this reaction is not known with certainty, our results are well in accord with the catalytic cycle proposed by Kochi[6], as depicted in Scheme 1.

Scheme 1

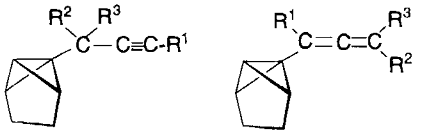


The core of this mechanism is the reductive elimination of the two organic ligands R and R' to afford the product R–R'. This step is possibly induced by π complexation of the Fe(III) catalyst with the unsaturated halide, which subsequently adds oxidatively to the Fe(I) center. The question of propargylic versus allenylic structure of the coupling of propargyl halides would depend on the structure of the iron complex (η^1-propargylic, η^1-allenylic, or η^3), on the rate of its reductive elimination, and on the energy barriers separating the three possible structures as discussed by Keinan and Bosch for cross coupling reactions of propargylic acetates unter Pd(0) catalysis conditions[7].

Control experiments showed that neither iron- nor nickel-catalyzed cross coupling of **1c** with allenylic chlorides (instead of the isomeric propargylic chlorides) was an effective process. Onyl traces of the desired products were observable.

2. Propargyl- and Allenylbicyclo[1.1.0]butanes

Besides propargyl chloride (**3a**), 3-chloro-1-butyne (**3d**), 3-chloro-3-methyl-1-butyne (**3e**), 1-chloro-1-ethynylcyclohexane (**3f**), 3-chloro-3-methyl-1-pentyne (**3g**), 3-bromo- and 3-chloro-1-(trimethylsilyl)-1-propyne (**3h** and **3i**), 3-chloro-1-(trimethylsilyl)-1-butyne (**3j**), and 3-chloro-3-methyl-1-(trimethylsilyl)-1-butyne (**3k**) were treated with **1c** and, in part, with **2c** in the presence of approximately 0.5% of $Fe(acac)_3$. The yields of coupling products **5**/**6** and **9**/**10** (Table 2) show a remarkable specificity: coupling with secondary and tertiary propargyl halides with terminal hydrogen at the alkyne end leads to allenes **6** and **10** only. If the terminal alkyne carbon carries a trimethylsilyl group, no allene formation is observed. Steric hindrance at the reactive site and terminal silylation as given in **3k** lowers the yield of the propargylic coupling product **5k** to 3%. In this case, alkanediyne **11** is isolated in 24% yield as the main product, indicating that besides the Kochi coupling process at least one more complicated still unknown coupling mechanism is operative (see below).



(R1, R2, R3 as in 3)

9 **10**

$Me_3Si-C\equiv C-CMe_2-CMe_2-C\equiv C-SiMe_3$

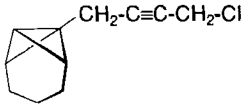
11

The reaction of 1,4-dichloro-2-butyne (**3l**) with **1c** in 1:1 molar ratio afforded at 26% yield of alkyne **12**, whereas the reaction of a 1:2 molar ratio of the reagents led to **13** in 13% yield.

The $Fe(acac)_3$-catalyzed reaction of allyl chloride (**4a**) with **1b** as well as with **1c** afforded **7a** in 56 and 51% yield, resp., whereas the reaction of **4c** with **1c** afforded **7c** in only 12% yield. Two methyl groups at C-1 (**4d**) or at C-1 and C-3 (**4e**) did not lead to cross coupling products; in the latter case, a 16% yield of known diene **14**[8] was isolated.

Table 2. Products and yields of the reaction of **1c** and **2c** with propargylic halides or tosylates catalyzed by Fe(acac)$_3$

R-MgBr	Halide	%Yield	Alkyne	Allene	
1c	**3c**	47	**5a**	**6a**	(1:3)
1c	**3d**	27	--	**6d**	
1c	**3e**	37	--	**6e**	
1c	**3f**	36	--	**6f**	
1c	**3g**	39	--	**6g**	
1c	**3h**	17	**5h**	--	
1c	**3i**	41	**5h**	--	
1c	**3j**	48	**5j**	--	
1c	**3k**	3	**5k**	--	
2c	**3a**	50	**9a**	**10a**	(3:2)
2c	**3c**	47	**9a**	**10a**	(1:4)
2c	**3e**	36	--	**10e**	
2c	**3h**	20	**9h**	--	
2c	**3i**	7	**9h**	--	



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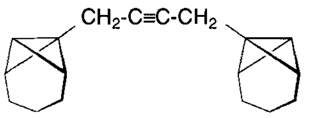
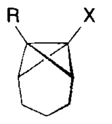


13

Me$_2$C=CH-CMe$_2$-CMe$_2$-CH=CMe$_2$

14



	15	16	17	18	19	20	21
R	Me	SiMe$_3$	HC=CMe$_2$	MeC=CH$_2$	C≡C-SiMe$_3$	C≡C-CMe$_3$	C≡C-H

15-20	a	b	c	d	e
X	H	Li	MgBr	HC=C=CMe$_2$	CH$_2$-C≡C-SiMe$_3$

15-20	f	g	h
X	CH$_2$-C≡CH	HC=C=CH$_2$	CH$_2$-CH=CH$_2$

Table 3. Results of "secondary coupling" of **15c**–**20c** with propargylic halides and allyl chloride

R-Mg	Halide	Product	*(% Yield)*
15c	**3e**	**15d**	*(14)*
15c	**3i**	**15e**	*(37)*
16c	**3e**	**16d**	*(40)*
16c	**3i**	**16e**	*(32)*
17c	**3e**	**17d**	*(54)*
17c	**3i**	**17e**	*(53)*
17c	**3a**	**17f** + **17g**	*(30, ratio 2:3)*
18c	**3i**	**18e**	*(68)*
18c	**3a**	**18f** + **18g**	*(69, ratio 1:1.8)*
19c	**3e**	**19d**	*(50)*
19c	**3i**	**19e**	*(49)*
20c	**3e**	**20d**	*(61)*
15c	**4a**	**15h**	*(20)*
16c	**4a**	**16h**	*(22)*
17c	**4a**	**17h**	*(31)*
19c	**4a**	**19h**	*(43)*

3. Coupling of Propargylic Halides to Bridgehead-Substituted Tricyclo[4.1.0.0^{2,7}]heptanes

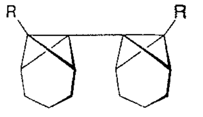
The sensitivity of the Fe(acac)$_3$-catalyzed cross coupling process to steric hindrance left the question open if substituents in one bicyclo[1.1.0]butane bridgehead position allowed a secondary coupling at the other bridgehead. To obtain an insight into this problem, the tricyclo[4.1.0.0^{2,7}]heptanes **15a** – **20a** were converted via the lithiated intermediates **15b** – **20b** into the Grignard reagents **15c** – **20c**, and these were subjected to the reaction with propargylic halides **3a**, **e**, **i**, and allyl chloride (**4a**) under Fe(acac)$_3$ catalysis conditions. Results are given in Table 3 which show that the "secondary coupling" is not less effective than the first one.

In two reactions further products were isolated which could shed some light on the mechanism of the coupling process. The reaction of **16c** with **3i** led to a 10% yield of **22**, whereas the reaction of **19c** with **4a** afforded a 4% yield of **23**. A possible route to these compounds might proceed by oxidative addition of the halide R'X to Fe(I)L$_n$ affording R'Fe(III)XL$_n$, conversion of 2 molecules of this intermediate to R$'_2$Fe(III)L$_n$ and X$_2$Fe(III)L$_n$, reaction with the Grignard reagent RMgBr giving rise to R$_2$Fe(III)L$_n$, followed by reductive elimination of R–R. This side reaction seems to become important if the intended cross coupling process giving R–R' is slow.

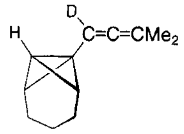
The bridgehead hydrogen atom of 1-(3,3-dimethylallenyl)tricyclo[4.1.0.0^{2,7}]heptane (**6e**) is obviously less acidic than the allenic one: reaction of **6e** with BuLi followed by workup with D$_2$O led to a 66% recovery of **6e-D**, which according to MS analysis contained only traces of **6e-D$_2$**. Attempts at metalating 1-allyltricyclo[4.1.0.0^{2,7}]heptane (**7a**) and 1-propargyltricyclo[4.1.0.0^{2,7}]heptane (**5a**) selectively in the bicyclobutane bridgehead position also failed. Therefore, a "secondary coupling" of 1-allenyl, 1-allyl-, and 1-propargyl-bicyclo[1.1.0]butanes is not possible.

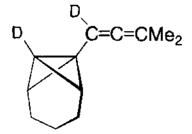
4. Formation of a [4.1.1]Propella-2,4-diene

Tricyclo[3.1.0.0^{2,6}]hexane (**2a**) is one of the few bicyclo[1.1.0]butane derivatives that can be metalated in both bridgehead positions under controlled reaction conditions[9]. After transmetalation of **24a** with $MgBr_2$ to give the Grignard reagent **24b** the question was, if **24b** could be coupled with **3e** to afford the "secondary" coupling product **24c**. When the reaction was carried out under the usual conditions with $Fe(acac)_3$ as a catalyst, a crystalline compound $C_{16}H_{20}$ was isolated in 15% yield. However, the NMR spectra of the material showed that its structure was not the expected bis-allene **24c**, but the propelladiene **25**.



	22	23
R	$SiMe_3$	$C{\equiv}C\text{-}SiMe_3$


6e-D


6e-D₂

In a formal sense, **25** is the product of an intramolecular thermal ene reaction of the two allenic units in **24c** as depicted in **26**. However, the reaction conditions, under which **25** is formed, are very mild (0–25°C) leading us to assume that the cyclization of **24c** to **25** might also be catalyzed by iron compounds present in the reaction mixture. Indeed, transition metal-catalyzed[10] ene reactions have been observed earlier, while Lewis acid catalysis of allenes leads to [2+2] cycloadducts[11]. The structure of **25** is established on the basis of its NMR spectra, including COSY, NOESY, HETCOR, and COLOCS and of an X-ray analysis[12].

It should be noticed that propellane **25** contains a frozen norcaradiene substructure[13]; in addition, the question of homoaromaticity in this compound seems particularly interesting[14,15].

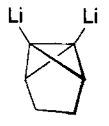
The reaction of **24b** with *tert*-propargylic chlorides affording propellanes of type **25** could not be generalized. The reaction of **24b** with **3f** afforded bis-allene **27** in 9% yield as the sole product.

5. Desilylation and Isomerization of Some Coupling Products

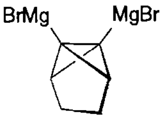
Desilylation of the coupling products carrying a trimethylsilyl group at the alkyne carbon atom could be easily effected by reaction with sodium or potassium hydroxide in methanol[16]. Results are compiled in Table 4. Tetra-*n*-butylammonium fluoride was ineffective as a desilylating reagent for **5h**. Probably traces of acidic or electrophilic side products present in the commercially available material destroyed the bicyclo[1.1.0]butane framework.

In cases where a subsequent alkylation of the terminal alkyne position was intended, desilylation with methyllithium[17] was the proper procedure followed by alkylation of the corresponding lithium alkynide in a one-pot reaction. In this way, disilane **28a** was converted into **28b** in 77% yield and **29a** into **29b** in 65% yield. As the cross coupling reactions of 1-alkynylsilanes afforded only 1-propargylbicyclo[1.1.0]butanes, desilylation of the coupling products constitutes an effective route to 1-propargylbicyclo[1.1.0]butanes free of isomers. This circumvents the separation of propargylic and allenylic bicyclo[1.1.0]butanes. In the case of the mixture of **5a** and **6a**, the separation was achieved by reaction with methylmagnesium bromide, which metalated only **5a**, removal of the allene **6a** in vacuo and aqueous workup of the residue. The mixture of **9a** and **10a** was separated by the analogous sequence.

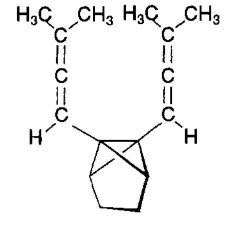
In the propargylic and allenylic bicyclo[1.1.0]butanes **5a** and **6a** the triple bond is shifted on treatment with a catalytic amount of potassium *tert*-butoxide in dimethyl sulfoxide to give alkyne **30** in high yield. Similar treatment of **9a** and **10a** provided **31**. The mixture of **17f** and **17g** was converted to **32** in the same way.



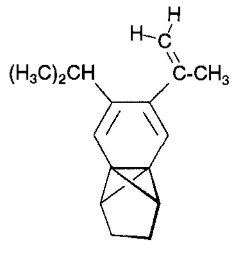
24a



24b



24c



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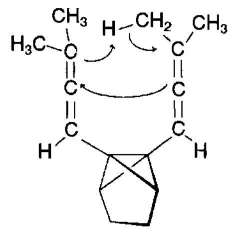

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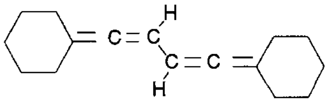

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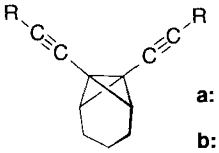

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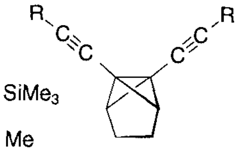
a: R = SiMe₃

b: R = Me



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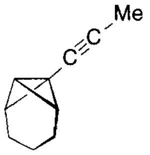

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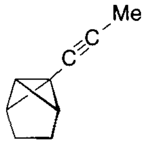

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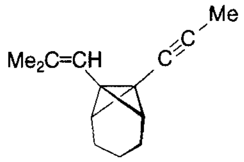

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Table 4. Desilylation of Coupling Products

Silane	Reagent	Product	*(% Yield)*
5h	NaOH/MeOH	**5a**	*(92)*
5h	Bu_4NF/THF	**5a**	*(0)*
5j	NaOH/MeOH	**5d**	*(81)*
15e	NaOH/MeOH	**15f**	*(80)*
15e	KOH/MeOH	**15f**	*(70)*
16e	NaOH/MeOH	**16f**	*(79)*
17e	NaOH/MeOH	**17f**	*(57)*
18e	NaOH/MeOH	**18f**	*(53)*
19e	NaOH/MeOH	**21f**	*(78)*
19h	NaOH/MeOH	**21h**	*(47)*

6. Conclusion

Among the methods investigated in this paper, the $Fe(acac)_3$-catalyzed cross coupling turned out to be the most efficient synthesis of allyl-, propargyl- and allenyl-substituted bicyclo[1.1.0]butanes. The yields were relatively low, but this drawback was compensated by the high purity of the products. Due to the very mild reaction conditions applied, a rearrangement of the bicyclo[1.1.0]butyl subunits in the starting compounds or the products, as described frequently for reactions involving transition metals and bicyclo[1.1.0]butanes, was never observed. Only if the cross coupling was slow, homo coupling became a serious side reaction.

In the coupling reactions of propargylic substrates, stereoelectronic factors could nicely be exploited for the preparation of either pure propargylic or pure allenylic products. One of the best examples is the formation of **6d** or its isomer **5d** (after desilylation). Interestingly, this selectivity is contradictory to results obtained in the copper-mediated C−C coupling of related propargylic compounds. The latter reactions always proceeded in a S_N2' manner, even if the incoming nucleophile had to be attached in α-position to a trimethylsilyl group[18] or in a neopentylic position[19].

The formation of the [4.1.1]propelladiene **25** finally confirmed the concept of utilizing the cross coupling products for the synthesis of [*n*.1.1]propellanes.

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Experimental

^1H NMR: Bruker WP 80 CW (at 80 MHz) or Varian VXR 400S (at 400 MHz). – ^{13}C NMR: Bruker WP 80 FT (20 MHz) or Varian VXR 400S (100 MHz). In all cases, tetramethylsilane was used as an internal reference. – IR: Bruker IR-IFS 45. – MS: Finnigan MAT 90 (besides M^+ a maximum of 9 peaks of highest intensity are listed here. For the full set of data see ref.[20]). – Most of the new compounds were sensitive to air and had to be handled under nitrogen.

I. *Starting Materials*

Tricyclo[4.1.0.0^{2,7}]heptane (**1a**)[21], 1-methyltricyclo[4.1.0.0^{2,7}]heptane (**15a**)[22], 1-(trimethylsilyl)tricyclo[4.1.0.0^{2,7}]heptane (**16a**)[23], 1-(2-methyl-1-propenyl)tricyclo[4.1.0.0^{2,7}]heptane (**17a**)[1], 1-isopropenyltricyclo[4.1.0.0^{2,7}]heptane (**18a**)[1], 1-[(trimethylsilyl)ethynyl]tricyclo[4.1.0.0^{2,7}]heptane (**19a**)[1], 1-(3,3-dimethyl-1-butynyl)tricyclo[4.1.0.0^{2,7}]heptane (**20a**)[20], 1,7-bis[(trimethylsilyl)ethynyl]tricyclo[4.1.0.0^{2,7}]heptane (**28a**)[1], and tricyclo[3.1.0.0^{2,6}]hexane (**2a**)[24] were synthesized according to published procedures. The Grignard reagents **1c**, **2c**, **15c**, **16c**, **17c**, **18c**, **19c**, and **20c** were prepared by lithiation of the corresponding bicyclo[1.1.0]butanes with *n*-butyllithium (BuLi) followed by transmetalation with anhydrous magnesium bromide as described earlier for **1c**[1]. The di-Grignard compound **24b** was prepared from the dilithio compound **24a**[9] and two equivalents of anhydrous magnesium bromide. The propargylic and allylic halides were either commercially available or prepared as described in the literature: propargyl tosylate (**3c**)[25a], 3-chloro-1-butyne (**3d**)[26], 3-chloro-3-methyl-1-butyne (**3e**)[25b], 1-chloro-1-ethynylcyclohexane (**3f**)[25c], 3-chloro-3-methyl-1-pentyne (**3g**)[27], 3-bromo-1-(trimethylsilyl)-1-propyne (**3h**)[25d], 3-chloro-1-(trimethylsilyl)-1-propyne (**3i**)[25e], 3-chloro-1-(trimethylsilyl)-1-butyne (**3j**)[25f], 3-chloro-3-methyl-1-(trimethylsilyl)-1-butyne (**3k**)[28], 1,4-dichloro-2-butyne (**3l**)[25g], 1-chloro-3-methyl-2-butene (**4d**)[29], 4-chloro-2,4-dimethyl-2-pentene (**4e**)[30]. Some of the transition metal catalysts were not commercially available: tris(-dibenzoylmethanato)iron $\{Fe(dbm)_3\}$[31], [1,2-bis(diphenylphosphanyl)ethane]nickel dichloride $\{NidppeCl_2\}$[32] and bis(triphenylphosphane)cobalt dichloride $\{Co(PPh_3)_2Cl_2\}$[33]. Titriplex solution was prepared according to the ref.[1].

II. *General Procedures*

1. *Transition Metal-Catalyzed Coupling:* To the catalyst in ether (20.0 ml for 16.0 mmol of substrate) the organic halide (or tosylate) was added, and the mixture was cooled to 0°C. Then the Grignard or organolithium compound was slowly added with stirring at 0°C. Stirring was continued for 3 h at 0°C. Workup was performed according to II.2. or II.3.

2. *Workup of Reactions with Grignard Reagents:* 1,4-Dioxane (3 equiv. relative to Mg) was added to the reaction mixture at 0°C. The resulting suspension was filtered and the colorless precipitate thoroughly rinsed with ether. The filtrate was hydrolyzed with 2 N aqueous ammonia (50.0 ml for 16.0 mmol of substrate). After separation, the aqueous layer was extracted twice with a small amount of ether. The combined organic layers were extracted three times with the titriplex solution (25.0 ml for 16.0 mmol of substrate) and finally washed with two portions of water. After drying with magnesium sulfate and filtration the solvent was removed at 0°C (bath)/12 Torr. The isolation of the product(s) from the crude material is described in the individual experiments.

3. *Workup of Reactions with Organolithium Reagents:* The reaction mixture was hydrolyzed with 2 N aqueous ammonia (50.0 ml for 16.0 mmol of substrate). After separation, the aqueous layer was extracted twice with a small amount of ether. The combined organic layers were extracted three times with the titriplex solution (25.0 ml for 16.0 mmol of substrate) and finally washed twice with water. After drying with magnesium sulfate and filtration the solvent was removed at 0°C (bath)/12 Torr. The isolation of the product(s) from the crude material is described in the individual experiments.

4. *Normal Hydrolytic Workup:* The reaction mixture was hydrolyzed with water (50.0 ml for 16.0 mmol of substrate). After separation the aqueous layer was extracted twice with a small amount of ether. The combined organic layers were dried with mag-

nesium sulfate. After filtration the solvent was removed at 0°C (bath)/12 Torr. The isolation of the product(s) from the crude material is described in the individual experiments.

5. *Desilylation:* To the silyl compound in methanol (MeOH) aqueous sodium hydroxide was added dropwise with stirring at 30°C. Stirring was continued for 30 min at that temp. Workup according to II.4.

6. *Isomerization:* To potassium *tert*-butoxide (KO*t*Bu) in dimethyl sulfoxide (DMSO) the mixture of alkyne and allene was added dropwise with stirring at 20°C. Stirring was continued for 30 min at that temp. Workup according to II.4.

III. *Uncatalyzed Reactions*

1. **1b** *and Allyl Bromide* (**4b**): **1b** was prepared from BuLi (20.0 ml, 32.0 mmol) and **1a** (3.01 g, 32.0 mmol). **4b** (3.87 g, 32.0 mmol) was added slowly with stirring at 0°C. Stirring was continued at room temp. for 1 h. The resulting clear solution was hydrolyzed with 20 ml of 2 N aqueous ammonia at 0°C. Workup was continued similarly as described in II.4. The subsequent distillation at 49–55°C/15 Torr provided **7a** (780 mg, 18%) as a colorless liquid. – IR (film): $\tilde{\nu}$ = 3079 cm^{-1} (=C–H), 2982, 2928, 2856, 1695, 1641, 1488, 1472, 1441, 1415, 1151, 1061, 1044, 994, 912, 807, 774, 717, 690. – UV (cyclohexane): λ_{max} (qualitative) = fast decrease above 200 nm. – ^1H NMR ($CDCl_3$, 80 MHz): δ = 1.20 (m, 1H, 7-H), 1.33 (m, 6H, 3-H_2, 4-H_2, 5-H_2), 2.23 (m, 2H, 2-H, 6-H), 2.55 (d, 2H, 1'-H_2), 4.93, 5.09, 5.73 (m, 3H, olefin H). – ^{13}C NMR ($CDCl_3$, 20 MHz): δ = 7.97 (d, C-7), 18.29 (s, C-1), 20.66 (t, C-3, C-5), 21.11 (t, C-4), 33.98 (t, C-1'), 41.68 (d, C-2, C-6), 115.34 (t, C-3'), 136.57 (d, C-2'). – MS (70 eV), *m/z* (%): 134 (7) [M^+], 119 (23), 105 (21), 93 (67), 92 (21), 91 (100), 79 (35), 77 (61). – $C_{10}H_{14}$ (134.2): calcd. C 89.49, H 10.51; found C 89.11, H 10.89. – $C_{10}H_{14}$: calcd. 134.109, found 134.112 (MS).

2. **1b** *and Propargyl Chloride* (**3a**): **1b** was prepared from BuLi (20.0 ml, 32.0 mmol) and **1a** (3.01 g, 32.0 mmol). The addition of **3a** (2.38 g, 32.0 mmol) and the workup were carried out according to the procedure described in III.1. At 21°C (bath)/0.01 Torr the volatile material was condensed to a trap cooled to −78°C. The ^1H-NMR spectrum showed 1-propargyltricyclo[4.1.0.$0^{2,7}$]heptane (**5a**) and unidentified impurities. 310 mg (7%) of that material was obtained. The synthesis of pure **5a** and the spectroscopical data are listed in III.3.

3. **1b** *and Propargyl Bromide* (**3b**): **1b** was prepared from BuLi (20.0 ml, 32.0 mmol) and **1a** (3.01 g, 32.0 mmol). The addition of **3b** (3.81 g, 32.0 mmol) and the workup were performed similarly as described in III.1. Distillation of the crude material at 60–65°C/13 Torr provided 465 mg (11%) of **5a** as a colorless liquid. – IR (film): $\tilde{\nu}$ = 3312 cm^{-1} (≡C–H), 2929, 2857, 2120 (C≡C), 1492, 1457, 1442, 1335, 1302, 1257, 1147, 1115, 1050, 1000, 900, 889, 822, 772, 678, 625. – UV (cyclohexane): λ_{max} (qualitative) = fast decrease above 200 nm, 235 nm (sh). – ^1H NMR ($CDCl_3$, 80 MHz): δ = 1.33 (m, 7H, 3-H_2, 4-H_2, 5-H_2, 7-H), 1.98 (t, 1H, 3'-H), 2.43 (m, 2H, 2-H, 6-H), 2.81 (d, 2H, 1'-H_2). – ^{13}C NMR ($CDCl_3$, 20 MHz): δ = 8.75 (d, C-7), 16.36 (s, C-1), 19.48 (t, C-1'), 20.32 (t, C-3, C-5), 21.02 (t, C-4), 41.92 (d, C-2, C-6), 69.18 (d, C-3'), 81.11 (s, C-2'). – MS (70 eV), *m/z* (%): 132 (10) [M^+], 117 (36), 115 (48), 104 (20), 93 (82), 91 (100), 79 (32), 78 (29), 77 (69), 65 (28). – $C_{10}H_{12}$ (132.2): calcd. C 90.85, H 9.15; found C 90.71, H 9.21. – $C_{10}H_{12}$: calcd. 132.094, found 132.093 (MS).

4. **1b** *and* **3h**: **1b** was prepared from 10.0 ml of BuLi (16.0 mmol) and **1a** (1.51 g, 16.0 mmol). The addition of **3h** (3.06 g, 16.0 mmol) and the workup were carried out as in III.1. The distillation of the crude product at 15 Torr provided at 94°C 415 mg of a mixture of 1-bromotricyclo[4.1.0.$0^{2,7}$]heptane (**1d**)[34] contaminated with a small amount of 1,6-bis(trimethylsilyl)-1,5-hexadiyne (**8**). At 110°C 321 mg consisting mainly of **8**[35] and only traces of **1d** was obtained. 220 mg (12%) of pure **8** could be separated by low-temp. crystallization.

IV. *Coupling of* **1c** *and* **3a** *in the Presence of Different Catalysts*

In these experiments mixtures of **5a** and 1-allenyltricyclo[4.1.0.$0^{2,7}$]heptane (**6a**) were obtained. The ratio of **5a** to **6a** was determined by integration of the ^1H-NMR signals for 3'-H_2 of **6a** and 1'-H_2 of **5a**. Separation and characterization of **6a** are described in XII.3.

1. *Iron(III) Chloride:* BuLi (50.0 ml, 80.0 mmol), **1a** (7.53 g, 80.0 mmol), $MgBr_2$ (14.7 g, 80.0 mmol), $FeCl_3$ (64.9 mg, 400 μmol), **3a** (5.96 g, 80.0 mmol), and 1,4-dioxane (20.5 ml, 240 mmol) were treated according to II.1. Distillation at 21°C (bath)/0.02 Torr provided 1.93 g (18%) of **5a** and **6a** in a ratio of 1:1.

2. *Fe(dbm)$_3$:* BuLi (100 ml, 160 mmol), **1a** (15.1 g, 160 mmol), $MgBr_2$ (29.5 g, 160 mmol), $Fe(dbm)_3$ (580 mg, 800 μmol), **3a** (11.9 g, 160 mmol), and 1,4-dioxane (40.8 ml, 480 mmol) were treated according to II.1. Distillation at 21°C (bath)/0.04 Torr provided 3.90 g (18%) of **5a** and **6a** in a ratio of 1:0.7.

3. *Fe(acac)$_3$:* BuLi (100 ml, 160 mmol), **1a** (15.1 g, 160 mmol), $MgBr_2$ (29.5 g, 160 mmol), $Fe(acac)_3$ (283 mg, 800 μmol), **3a** (11.9 g, 160 mmol), and 1,4-dioxane (40.8 ml, 480 mmol) were allowed to react according to II.1. Distillation at 21°C (bath)/0.04 Torr provided 8.67 g (41%) of **5a** and **6a** in a ratio of 1:0.8. A repetition of this experiment on a 80.0-mmol scale of substrate gave the same ratio of products but in 47% yield.

4. *Copper(I) Bromide:* BuLi (20.0 ml, 32.0 mmol), **1a** (3.01 g, 32.0 mmol), $MgBr_2$ (5.89 g, 32.0 mmol), CuBr (46.0 mg, 321 μmol), **3a** (2.38 g, 32.0 mmol), and 1,4-dioxane (8.18 ml, 96.0 mmol) were treated according to II.1. Distillation at 20°C (bath)/0.01 Torr provided 1.11 g (26%) of **5a** and **6a** in a ratio of 1:1.7.

5. *Copper(II) Acetylacetonate [Cu(acac)$_2$]:* BuLi (20.0 ml, 32.0 mmol), **1a** (3.01 g, 32.0 mmol), $MgBr_2$ (5.89 g, 32.0 mmol), $Cu(acac)_2$ (83.8 mg, 320 μmol), **3a** (2.38 g, 32.0 mmol), and 1,4-dioxane (8.18 ml, 96.0 mmol) were treated according to II.1. Distillation at 22°C (bath)/0.01 Torr provided 1.25 g (30%) of **5a** and **6a** in a ratio of 1:2.3.

6. *Nickel(II) Acetylacetonate [Ni(acac)$_2$]:* BuLi (20.0 ml, 32.0 mmol), **1a** (3.01 g, 32.0 mmol), $MgBr_2$ (5.89 g, 32.0 mmol), $Ni(acac)_2$ (82.2 mg, 320 μmol), **3a** (2.38 g, 32.0 mmol), and 1,4-dioxane (8.18 ml, 96.0 mmol) were treated according to II.1. Distillation at 22°C (bath)/0.01 Torr provided 292 mg (7%) of **5a** and **6a** in a ratio of 1:15.

7. *Cobalt(II) Chloride:* BuLi (20.0 ml, 32.0 mmol), **1a** (3.01 g, 32.0 mmol), $MgBr_2$ (5.89 g, 32.0 mmol), $CoCl_2$ (41.5 mg, 320 μmol), **3a** (2.38 g, 32.0 mmol), and 1,4-dioxane (8.18 ml, 96.0 mmol) were treated according to II.1. Distillation at 22°C (bath)/0.01 Torr provided 695 mg (16%) of **5a** and **6a** in a ratio of 1:7.8.

V. *Fe(acac)$_3$-Catalyzed Reactions of* **1c** *and* **2c** *with Propargylic Halides or Tosylates*

1. *Mixture of* **5a** *and* **6a** *from* **1c** *and* **3c**: BuLi (10.0 ml, 16.0 mmol), **1a** (1.51 g, 16.0 mmol), $MgBr_2$ (2.95 g, 16.0 mmol), $Fe(acac)_3$ (28.3 mg, 80.0 μmol), **3c** (3.36 g, 16.0 mmol), and 1,4-dioxane (4.09 ml, 48.0 mmol) were treated according to II.1. Distillation of the crude material at 20°C (bath)/0.01 Torr provided 997 mg (47%) of **5a** and **6a** in a ratio of 1:3.

2. *1-(1,2-Butadienyl)tricyclo[4.1.0.$0^{2,7}$]heptane* (**6d**): BuLi (20.0 ml, 32.0 mmol), **1a** (3.01 g, 32.0 mmol), $MgBr_2$ (5.89 g, 32.0 mmol),

Fe(acac)$_3$ (56.5 mg, 160 µmol), **3d** (2.83 g, 32.0 mmol), and 1,4-dioxane (8.18 ml, 96.0 mmol) were treated according to II.1. Distillation of the crude material at 27°C (bath)/0.02 Torr provided 1.26 g (27%) of **6d** as a colorless liquid. – IR (film): $\tilde{\nu}$ = 2983 cm^{-1}, 2929, 2857, 1494, 1442, 1370, 1286, 1149, 1063, 1040, 1020, 995, 947, 889, 864, 807, 759, 694, 636. – UV (cyclohexane): λ_{max} (lg ε) = 222 nm (3.811). – ^{1}H NMR (CDCl$_3$, 400 MHz): δ = 1.00–1.50 (m, 7H, 3-H$_2$, 4-H$_2$, 5-H$_2$, 7-H), 1.62 (dd, 3H, 4'-H$_3$), 2.50 (m, 2H, 2-H, 6-H), 5.00–5.50 (m, 2H, 1'-H, 3'-H). – ^{13}C NMR (CDCl$_3$, 100 MHz): δ = 14.91 (q, C-4'), 15.99 (d, C-7), 18.60 (s, C-1), 20.55, 20.58 (t, C-3 and C-5 in unknown sequence), 20.95 (t, C-4), 43.30, 43.40 (d, C-2 and C-6 in unknown sequence), 87.64, 91.86 (d, C-1' and C-3' in unknown sequence), 205.24 (s, C-2'). – MS (70 eV), *m/z* (%): 146 (24) [M$^+$], 131 (74), 117 (66), 116 (34), 115 (48), 105 (26), 91 (100), 79 (23), 77 (42). – C$_{11}$H$_{14}$ (146.2): calcd. C 90.35, H 9.65; found C 90.79, H 9.45. – C$_{11}$H$_{14}$: calcd. 146.109, found 146.104 (MS).

3. *1-(3-Methyl-1,2-butadienyl)tricyclo[4.1.0.0^{2,7}]heptane* (**6e**): BuLi (20.0 ml, 32.0 mmol), **1a** (3.01 g, 32.0 mmol), MgBr$_2$ (5.89 g, 32.0 mmol), Fe(acac)$_3$ (56.5 mg, 160 µmol), **3e** (3.28 g, 32.0 mmol), and 1,4-dioxane (8.18 ml, 96.0 mmol) were treated according to II.1. Distillation of the crude material at 27°C (bath)/0.02 Torr provided 1.90 g (37%) of **6e** as a colorless liquid. **6e** could be handled in air for short periods of time. – IR (film): $\tilde{\nu}$ = 2983 cm^{-1}, 2931, 2857, 1496, 1446, 1362, 1236, 1215, 1187, 1041, 1006, 875, 822, 814, 766, 741, 704, 694, 562. – UV (cyclohexane): λ_{max} (lg ε) = 213 nm (4.080). – ^{1}H NMR (CDCl$_3$, 400 MHz): δ = 1.20–1.40 (m, 7H, 3-H$_2$, 4-H$_2$, 5-H$_2$, 7-H), 1.69 (d, 6H, Me), 2.50 (m, 2H, 2-H, 6-H), 5.26 (sept, 1H, 1'-H). – ^{13}C NMR (CDCl$_3$, 100 MHz): δ = 15.77 (d, C-7), 19.10 (s, C-1), 20.63 (t, C-3, C-5), 20.99 (q, Me), 21.01 (t, C-4), 43.31 (d, C-2, C-6), 90.28 (d, C-1'), 96.82 (s, C-3'), 202.15 (s, C-2'). – MS (70 eV), *m/z* (%): 160 (35) [M$^+$], 145 (94), 130 (31), 129 (32), 117 (97), 115 (61), 105 (37), 91 (100), 77 (41), 67 (31). – C$_{12}$H$_{16}$ (160.3): calcd. C 89.94, H 10.06; found C 89.74, H 10.20. – C$_{12}$H$_{16}$: calcd. 160.125, found 160.123 (MS).

4. *1-(2-Cyclohexylidenethenyl)tricyclo[4.1.0.0^{2,7}]heptane* (**6f**): BuLi (20.0 ml, 32.0 mmol), **1a** (3.01 g, 32.0 mmol), MgBr$_2$ (5.89 g, 32.0 mmol), Fe(acac)$_3$ (56.5 mg, 160 µmol), **3f** (4.56 g, 16.0 mmol), and 1,4-dioxane (8.18 ml, 96.0 mmol) were treated according to II.1. Distillation of the crude material at 60°C (bath)/0.001 Torr provided 2.30 g (36%) of **6f** as a colorless, viscous liquid. – IR (film): $\tilde{\nu}$ = 2984 cm^{-1}, 2927, 2854, 1495, 1446, 1264, 1255, 1063, 1043, 1021, 994, 971, 875, 820, 812, 757, 695. – UV (cyclohexane): λ_{max} (lg ε) = 215 nm (4.033 sh). – ^{1}H NMR (CDCl$_3$, 400 MHz): δ = 1.20–1.40 (m, 7H, 3-H$_2$, 4-H$_2$, 5-H$_2$, 7-H), 1.45–1.70 (m, 6H, 5'-H$_2$, 6'-H$_2$, 7'-H$_2$), 2.05–2.20 (m, 4H, 4'-H$_2$, 8'-H$_2$), 2.50–2.58 (m, 2H, 2-H, 6-H), 5.29 (t, 1H, 1'-H). – ^{13}C NMR (CDCl$_3$, 100 MHz): δ = 15.82 (d, C-7), 19.34 (s, C-1), 20.60 (t, C-3, C-5), 20.97 (t, C-4), 26.27 (t, C-6'), 27.72 (t, C-5', C-7'), 32.14 (t, C-4', C-8'), 43.28 (d, C-2, C-6), 89.87 (d, C-1'), 104.60 (s, C-3'), 198.55 (s, C-2'). – MS (70 eV), *m/z* (%): 200 (56) [M$^+$], 143 (54), 131 (44), 129 (83), 128 (48), 117 (63), 115 (50), 91 (100), 79 (73), 77 (47). – C$_{15}$H$_{20}$ (200.3): calcd. C 89.94, H 10.06; found C 89.52, H 10.13. – C$_{15}$H$_{20}$: calcd. 200.156, found 200.153 (MS).

5. *1-(3-Methyl-1,2-pentadienyl)tricyclo[4.1.0.0^{2,7}]heptane* (**6g**): BuLi (30.0 ml, 48.0 mmol), **1a** (4.52 g, 48.0 mmol), MgBr$_2$ (8.84 g, 48.0 mmol), Fe(acac)$_3$ (84.8 mg, 240 µmol), **3g** (5.60 g, 48.0 mmol), and 1,4-dioxane (12.3 ml, 144 mmol) were treated according to II.1. Distillation of the crude material at 40°C (bath)/0.001 Torr provided 3.29 g (39%) of **6g** as a colorless liquid. – IR (film): $\tilde{\nu}$ = 2965 cm^{-1}, 2931, 2856, 1496, 1458, 1446, 1367, 1332, 1325, 1146, 995, 950, 874, 822, 813, 771, 759, 704, 693. – UV (cyclohexane): λ_{max} (lg ε) = 214 nm (4.144). – ^{1}H NMR (CDCl$_3$, 400 MHz): δ = 0.97 (t, 3H, 5'-H$_3$), 1.28–1.38 (m, 7H, 3-H$_2$, 4-H$_2$, 5-H$_2$, 7-H), 1.70 (dt, 3H, Me), 1.94 (dq, 2H, 4'-H$_2$), 2.52 (m, 2H, 2-H, 6-H), 5.38 (tq with similar coupling constant, thus sext, 1H, 1'-H). – ^{13}C NMR (CDCl$_3$, 100 MHz): δ = 12.38 (q, C-5'), 15.91 (d, C-7), 19.16 (s, C-1), 19.51 (q, Me), 20.64, 20.66 (t, C-3, C-5 in unknown sequence), 21.05 (t, C-4), 27.38 (t, C-4'), 43.09, 43.37 (d, C-2, C-6 in unknown sequence), 92.22 (d, C-1'), 103.26 (s, C-3'), 201.26 (s, C-2'). – MS (70 eV), *m/z* (%): 174 (60) [M$^+$], 159 (82), 145 (76), 131 (68), 129 (50), 117 (85), 115 (53), 105 (67), 91 (100). – C$_{13}$H$_{18}$ (174.3): calcd. C 89.59, H 10.41; found C 89.55, H 10.39. – C$_{13}$H$_{18}$: calcd. 174.141, found 174.135 (MS).

6. *1-[3-(Trimethylsilyl)-2-propynyl]tricyclo[4.1.0.0^{2,7}]heptane* (**5h**): BuLi (20.0 ml, 32.0 mmol), **1a** (3.01 g, 32.0 mmol), MgBr$_2$ (5.89 g, 32.0 mmol), Fe(acac)$_3$ (56.5 mg, 160 µmol), **3h** (6.12 g, 32.0 mmol), and 1,4-dioxane (8.18 ml, 96.0 mmol) were treated according to II.1. The fraction taken at 20°C (bath)/0.01 Torr already contained some **5h**. At 20°C (bath)/0.001 Torr 1.08 g (17%) of **5h** was obtained as a colorless liquid. – IR (film): $\tilde{\nu}$ = 2989 cm^{-1}, 2959, 2931, 2899, 2856, 2178 (C≡C), 1442, 1298, 1250, 1147, 1049, 1023, 998, 978, 894, 842, 771, 760, 698, 643. – UV (cyclohexane): λ_{max} (lg ε) = 238 nm (3.671), 247 (3.663). – ^{1}H NMR (CDCl$_3$, 80 MHz): δ = 0.16 (s, 9H, SiMe$_3$), 1.33 (m, 7H, 3-H$_2$, 4-H$_2$, 5-H$_2$, 7-H), 2.44 (m, 2H, 2-H, 6-H), 2.88 (s, 2H, 1'-H$_2$). – ^{13}C NMR (CDCl$_3$, 20 MHz): δ = 0.13 (q, SiMe$_3$), 8.61 (d, C-7), 16.30 (s, C-1), 20.33 (t, C-3, C-5), 20.66, 21.03 (t, C-4, C-1' in unknown sequence), 41.87 (d, C-2, C-6), 85.57, 103.47 (s, C-2', C-3' in unknown sequence). – MS (70 eV), *m/z* (%): 204 (5) [M$^+$], 189 (22), 135 (11), 130 (24), 129 (16), 93 (31), 91 (22), 83 (14), 77 (12), 73 (100). – C$_{13}$H$_{20}$Si (204.4): calcd. C 76.40, H 9.86; found C 75.94, H 9.69. – C$_{13}$H$_{20}$Si: calcd. 204.133, found 204.132 (MS).

7. **5h**: BuLi (20.0 ml, 32.0 mmol), **1a** (3.01 g, 32.0 mmol), MgBr$_2$ (5.89 g, 32.0 mmol), Fe(acac)$_3$ (56.5 mg, 160 µmol), **3i** (4.69 g, 32.0 mmol), and 1,4-dioxane (8.18 ml, 96.0 mmol) were treated according to II.1. Distillation of the crude material at 34°C (bath)/0.01 Torr provided 2.70 g (41%) of **5h** as a colorless liquid.

8. *1-[1-Methyl-3-(trimethylsilyl)-2-propynyl]tricyclo[4.1.0.0^{2,7}]heptane* (**5j**): BuLi (20.0 ml, 32.0 mmol), **1a** (3.01 g, 32.0 mmol), MgBr$_2$ (5.89 g, 32.0 mmol), Fe(acac)$_3$ (56.5 mg, 160 µmol), **3j** (5.14 g, 32.0 mmol), and 1,4-dioxane (8.18 ml, 96.0 mmol) were treated according to II.1. Distillation of the crude material at 40–45°C (bath)/0.001 Torr provided 3.32 g (48%) of **5j** as a colorless liquid. – IR (film): $\tilde{\nu}$ = 2961 cm^{-1}, 2931, 2856, 2170 (C≡C), 1447, 1369, 1304, 1250, 1108, 1061, 1015, 943, 914, 902, 866, 841, 814, 760, 698, 645. – UV (cyclohexane): λ_{max} (lg ε) = 237 nm (3.286), 245 (3.325). – ^{1}H NMR (CDCl$_3$, 400 MHz): δ = 0.10 (s, 9H, SiMe$_3$), 1.24 (d, 3H, Me), 1.27 (m, 7H, 3-H$_2$, 4-H$_2$, 5-H$_2$, 7-H), 2.44, 2.38 (m, each 1H, 2-H, 6-H in unknown sequence), 2.98 (q, 1H, 1'-H). – ^{13}C NMR (CDCl$_3$, 100 MHz): δ = 0.23 (q, SiMe$_3$), 8.99 (d, C-7), 20.57 (q, Me), 20.57, 20.62, 21.18 (t, C-3, C-4, C-5 in unknown sequence), 21.96 (s, C-1), 26.76 (d, C-1'), 39.51, 41.70 (d, C-2, C-6 in unknown sequence), 84.70, 108.61 (s, C-2', C-3' in unknown sequence). – MS (70 eV), *m/z* (%): 218 (6%) [M$^+$], 203 (14), 145 (11), 144 (13), 129 (14), 97 (21), 93 (13), 91 (11), 83 (11), 73 (100). – C$_{14}$H$_{22}$Si (218.4): calcd. C 76.99, H 10.15; found C 76.64, H 10.28. – C$_{14}$H$_{22}$Si: calcd. 218.149, found 218.146 (MS).

9. *1-[1,1-Dimethyl-3-(trimethylsilyl)-2-propynyl]tricyclo[4.1.0.0^{2,7}]heptane* (**5k**) *and 3,3,4,4-Tetramethyl-1,6-bis(trimethylsilyl)-1,5-hexadiyne* (**11**): BuLi (10.0 ml, 16.0 mmol), **1a** (1.51 g, 16.0 mmol), MgBr$_2$ (2.95 g, 16.0 mmol), Fe(acac)$_3$ (28.3 mg, 80.0 µmol), **3k** (2.80 g, 16.0 mmol), and 1,4-dioxane (4.09 ml, 48.0 mmol) were treated according to II.1. After removal of the solvent a mixture of

a solid and a liquid was obtained. Again, distillation at 40°C (bath)/0.001 Torr furnished a mixture. By crystallization, 535 mg (24%) of colorless crystals of **11** was obtained. From the remaining liquid 110 mg (3%) of **5k** could be isolated at 23°C (bath)/0.03 Torr as a colorless liquid (still contaminated with a small amount of **11**). – **5k**: IR (film): $\tilde{\nu}$ = 2998 cm^{-1}, 2971, 2928, 2856, 2157, 1457, 1358, 1250, 1215, 1149, 1138, 1072, 1049, 959, 888, 861, 841, 759, 697. – ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.10 (s, 9H, $SiMe_3$), 1.27 (s, 6H, Me_2), 1.27–1.29 (m, 6H, 3-H_2, 4-H_2, 5-H_2), 1.33 (t, 1H, 7-H), 2.46 (m, 2H, 2-H, 6-H). – ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 0.32 (q, $SiMe_3$), 9.54 (d, C-7), 20.69 (t, C-3, C-5), 21.17 (t, C-4), 25.66 (s, C-1), 28.67 (q, Me_2), 31.34 (s, C-1′), 39.16 (d, C-2, C-6), 83.36, 112.44 (s, C-2′, C-3′ in unknown sequence). – MS (70 eV), *m/z* (%): 217 (10) [M^+], 159 (18), 158 (18), 143 (25), 97 (51), 91 (9), 73 (100). – $C_{15}H_{24}Si$: calcd. 217.141, found 217.140 (MS). – **11**: m.p. 122–123°C. – IR (KBr): $\tilde{\nu}$ = 2981 cm^{-1}, 2958, 2899, 2158 (C≡C), 1457, 1377, 1366, 1250, 1197, 1140, 957, 860, 841, 824, 759, 697, 642, 487. – UV (cyclohexane): λ_{max} (qualitative) = fast decrease above 200 nm. – ^{1}H NMR ($CDCl_3$, 80 MHz): δ = 0.18 (s, 18H, $SiMe_3$), 1.33 (s, 12H, CMe_2). – ^{13}C NMR ($CDCl_3$, 20 MHz): δ = 0.31 (q, $SiMe_3$), 25.78 (q, $C\mathit{Me}_2$), 38.87 (s, C-3, C-4), 85.27, 112.44 (s, C-1, C-6, and C-2, C-5 in unknown sequence). – MS (70 eV), *m/z* (%): 278 (8) [M^+], 263 (3), 175 (5), 155 (8), 141 (10), 140 (64), 139 (31), 125 (11), 124 (15), 123 (21), 109 (11), 99 (4), 98 (11), 97 (100), 83 (7), 74 (3), 73 (39), 69 (4). – $C_{16}H_{30}Si_2$ (278.6): calcd. C 68.98, H 10.85; found C 69.19, H 10.70. – $C_{16}H_{30}Si_2$: calcd. 278.188, found 278.182 (MS).

10. *Mixture of 1-Propargyltricyclo[3.1.0.0^{2,6}]hexane* (**9a**) *and 1-(1,2-Propadienyl)tricyclo[3.1.0.0^{2,6}]hexane* (**10a**) *from* **3a**: BuLi (20.0 ml, 32.0 mmol), **2a** (2.56 g, 32.0 mmol), $MgBr_2$ (5.89 g, 32.0 mmol), $Fe(acac)_3$ (56.5 mg, 160 μmol), **3a** (2.38 g, 32.0 mmol), and 1,4-dioxane (8.18 ml, 96.0 mmol) were treated according to II.1. Distillation of the crude material at 20°C (bath)/0.15 Torr afforded 1.88 g (50%) of a mixture of **9a** and **10a** in a ratio of 3:2. The separation of this mixture and the characterization of **9a** and **10a** are described in XII.4.

11. *Mixture of* **9a** *and* **10a** *from* **3c**: BuLi (20.0 ml, 32.0 mmol), **2a** (2.56 g, 32.0 mmol), $MgBr_2$ (5.89 g, 32.0 mmol), $Fe(acac)_3$ (56.5 mg, 160 μmol), **3c** (6.73 g, 32.0 mmol), and 1,4-dioxane (8.18 ml, 96.0 mmol) were treated according to II.1. Distillation of the crude material at 0°C (bath)/0.01 Torr provided 1.76 g (47%) of a mixture of **9a** and **10a** in a ratio of 1:4.

12. *1-(3-Methyl-1,2-butadienyl)tricyclo[3.1.0.0^{2,6}]hexane* (**10e**): BuLi (10.0 ml, 16.0 mmol), **2a** (1.28 g, 16.0 mmol), $MgBr_2$ (2.95 g, 16.0 mmol), $Fe(acac)_3$ (28.3 mg, 80.0 μmol), **3e** (1.64 g, 16 mmol), and 1,4-dioxane (4.09 ml, 48.0 mmol) were treated according to II.1. Distillation of the crude material at 26°C (bath)/0.01 Torr provided 834 mg (36%) of **10e** as a colorless liquid. Compound **10e** was stable upon exposure to air for a short period. – IR (film): $\tilde{\nu}$ = 3038 cm^{-1} (=C–H), 2981, 2948, 2912, 2870, 1490, 1454, 1444, 1362, 1233, 1203, 1186, 1072, 1012, 974, 857, 816, 779, 744, 562. – UV (cyclohexane): λ_{max} (lg ε) = 204 nm (3.489). – ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.23–1.41 (m, 5H, 3-H_2, 4-H_2, 6-H), 1.68–1.69 (d, 6H, Me), 2.19 (m, 2H, 2-H, 5-H), 5.33 (sept, 1H, 1′-H). – ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 12.00 (d, C-6), 15.64 (s, C-1), 20.83 (q, Me), 25.88 (t, C-3, C-4), 37.89 (d, C-2, C-5), 85.72 (d, C-1′), 96.43 (s, C-3′), 202.41 (s, C-2′). – MS (70 eV), *m/z* (%): 146 (14) [M^+], 131 (100), 129 (30), 128 (22), 117 (21), 116 (45), 115 (46), 91 (91), 79 (29), 77 (31). – $C_{11}H_{14}$ (146.2): calcd. C 90.35, H 9.65; found C 90.36, H 9.52. – $C_{11}H_{14}$: calcd. 146.109, found 146.104 (MS).

13. *1-[3-(Trimethylsilyl)-2-propynyl]tricyclo[3.1.0.0^{2,6}]hexane* (**9h**): BuLi (10.0 ml, 16.0 mmol), **2a** (1.28 g, 16.0 mmol), $MgBr_2$ (2.95 g, 16.0 mmol), $Fe(acac)_3$ (28.3 mg, 80.0 μmol), **3h** (2.75 g, 16.0 mmol), and 1,4-dioxane (4.09 ml, 48.0 mmol) were treated according to II.1. Distillation of the crude material at 22°C (bath)/0.001 Torr provided a liquid-solid mixture. By separation of the solid 834 mg of a mixture of **9h** and **8** (molecular ratio 3:1, i.e. 20 and 13% yield, resp.). – **9h**: IR (film): $\tilde{\nu}$ = 2954 cm^{-1}, 2912, 2871, 2178 (C≡C), 1422, 1408, 1312, 1250, 1108, 1023, 975, 941, 909, 841, 813, 760, 693, 645. – UV (cyclohexane): λ_{max} (lg ε) = 220 nm (3.002), 252 (2.591). – ^{1}H NMR ($CDCl_3$, 80 MHz): δ = 0.15 (s, 9H, $SiMe_3$), 1.31 (m, 4H, 3-H_2, 4-H_2), 1.73 (m, 1H, 6-H), 2.10 (m, 2H, 2-H, 5-H), 2.90 (s, 2H, 1′-H_2). – ^{13}C NMR ($CDCl_3$, 20 MHz): δ = 0.16 (s, $SiMe_3$), 6.49 (d, C-6), 14.67 (s, C-1), 26.21 (t, C-3, C-4), 36.72 (d, C-2, C-5), 84.75, 104.44 (s, C-2′ and C-3′ in unknown sequence). – MS (70 eV), *m/z* (%): 190 (5) [M^+], 175 (30), 116 (18), 97 (20), 83 (15), 79 (35), 73 (100), 69 (16). – $C_{12}H_{18}Si$: calcd. 190.118, found 190.116 (MS).

14. **9h** *from* **2c** *and* **3i**: BuLi (34.3 ml, 54.8 mmol), **2a** (4.39 g, 54.8 mmol), $MgBr_2$ (10.1 g, 54.8 mmol), $Fe(acac)_3$ (96.8 mg, 274 μmol), **3i** (8.04 g, 54.8 mmol), and 1,4-dioxane (14.0 ml, 164 mmol) were treated according to II.1. Distillation of the crude material at 30°C (bath)/0.001 Torr yielded 696 mg (7%) of **9h**.

15. *1-(4-Chloro-2-butynyl)tricyclo[4.1.0.0^{2,7}]heptane* (**12**): BuLi (20.0 ml, 32.0 mmol), **1a** (3.01 g, 32.0 mmol), $MgBr_2$ (5.89 g, 32.0 mmol), $Fe(acac)_3$ (56.5 mg, 160 μmol), **3l** (3.94 g, 32.0 mmol), and 1,4-dioxane (8.18 ml, 96.0 mmol) were treated according to II.1. Distillation of the crude material at 50–70°C (bath)/0.001 Torr provided 1.50 g (26%) of **12** as a colorless liquid. – IR (film): $\tilde{\nu}$ = 2989 cm^{-1}, 2928, 2856, 2232 (C≡C), 1441, 1335, 1306, 1263, 1145, 1049, 896, 821, 771, 752, 695, 677, 646. – UV (cyclohexane): λ_{max} (lg ε) = 200 nm (3.375 sh), 240 (2.786 sh). – ^{1}H NMR ($CDCl_3$, 80 MHz): δ = 1.30 (m, 7H, 3-H_2, 4-H_2, 5-H_2, 7-H), 2.39 (m, 2H, 2-H, 6-H), 2.86 (t, 2H, 1′-H_2), 4.10 (t, 2H, 4′-H_2). – ^{13}C NMR ($CDCl_3$, 20 MHz): δ = 8.84 (d, C-7), 16.39 (s, C-1), 19.84 (t, C-1′), 20.32 (t, C-3, C-5), 21.08 (t, C-4), 30.96 (t, C-4′), 41.98 (d, C-2, C-6), 76.21, 84.14 (s, C-2′ and C-3′ in unknown sequence). – MS (70 eV), *m/z* (%): 180 (8) [M^+], 145 (28), 131 (26), 129 (42), 128 (35), 117 (47), 115 (46), 93 (100), 91 (91), 77 (61). – $C_{11}H_{13}Cl$ (180.7): calcd. C 73.13, H 7.25; found C 73.34, H 7.45. – $C_{11}H_{13}Cl$: calcd. 180.070, found 180.069 (MS).

16. *1,4-Bis(tricyclo[4.1.0.0^{2,7}]hept-1-yl)-2-butyne* (**13**): BuLi (40.0 ml, 64.0 mmol), **1a** (6.03 g, 64.0 mmol), $MgBr_2$ (11.78 g, 64.0 mmol), $Fe(acac)_3$ (113 mg, 320 μmol), **3l** (3.94 g, 32.0 mmol), and 1,4-dioxane (16.4 ml, 192 mmol) were treated according to II.1. Distillation of the crude material at 90°C (bath)/0.001 Torr provided 960 mg (13%) of **13** as a viscous oil. Only traces of the mono-coupled product **12** were detected. – **13**: IR (film): $\tilde{\nu}$ = 2987 cm^{-1}, 2928, 2855, 1491, 1457, 1444, 1335, 1315, 1145, 1049, 896, 854, 821, 771, 677, 661, 644. – UV (cyclohexane): λ_{max} (lg ε) = fast decrease above 200 nm, 250 (3.459 sh). – ^{1}H NMR ($CDCl_3$, 80 MHz): δ = 1.29 (m, 14H, 3′-H_2, 4′-H_2, 5′-H_2, 7′-H, 3″-H_2, 4″-H_2, 5″-H_2, 7″-H), 2.38 (m, 4H, 2′-H, 6′-H, 2″-H, 6″-H), 2.76 (s, 4H, 1-H_2, 4-H_2). – ^{13}C NMR ($CDCl_3$, 20 MHz): δ = 8.54 (d, C-7′, C-7″), 17.02 (s, C-1′, C-1″), 19.63 (t, C-1, C-4), 20.38 (t, C-3′, C-5′, C-3″, C-5″), 21.05 (t, C-4′, C-4″), 41.83 (d, C-2′, C-6′, C-2″, C-6″), 77.75 (s, C-2, C-3). – MS (70 eV), *m/z* (%): 238 (10) [M^+], 157 (33), 129 (55), 128 (41), 117 (35), 115 (45), 93 (42), 91 (100), 79 (33), 77 (51). – $C_{18}H_{22}$ (238.4): calcd. C 90.70, H 9.30; found C 91.22, H 8.96. – $C_{18}H_{22}$: calcd. 238.172, found 238.170 (MS).

VI. *Reaction of* **1b** *or* **1c** *with Allylic Chlorides*

1. **7a** *from* **1b**: BuLi (10.0 ml, 16.0 mmol), **1a** (1.51 g, 16.0 mmol), $Fe(acac)_3$ (28.3 mg, 80.0 μmol), and **4a** (1.22 g, 16.0 mmol) were

treated according to II.1. Distillation of the crude material at 20°C (bath)/0.01 Torr provided 1.20 g (56%) of **7a**.

2. **7a** *from* **1c**: BuLi (50.0 ml, 80.0 mmol), **1a** (7.53 g, 80.0 mmol), $MgBr_2$ (14.7 g, 80.0 mmol), Fe(acac)$_3$ (100 mg, 283 µmol), **4a** (6.12 g, 80.0 mmol), and 1,4-dioxane (20.5 ml, 240 mmol) were treated according to II.1. Distillation of the crude material at 21°C (bath)/0.01 Torr provided 5.48 g (51%) of **7a**.

3. *1-(2-Methyl-2-propenyl)tricyclo[4.1.0.0^{2,7}]heptane* (**7c**): BuLi (30.0 ml, 48.0 mmol), **1a** (4.52 g, 48.0 mmol), $MgBr_2$ (8.84 g, 48.0 mmol), Fe(acac)$_3$ (84.8 mg, 240 µmol), **4c** (4.35 g, 48.0 mmol), and 1,4-dioxane (12.3 ml, 144 mmol) were treated according to II.1. Distillation of the crude material at 24°C (bath)/0.03 Torr provided 873 mg (12%) of **7c** as a colorless liquid. – IR (film): $\tilde{\nu}$ = 3075 cm^{-1} (=C–H), 2983, 2927, 2855, 1651 (C=C), 1442, 1415, 1372, 1228, 1149, 1047, 1015, 999, 955, 887, 801, 771, 738, 721. – UV (cyclohexane): λ_{max} = fast decrease above 200 nm. – ^1H NMR ($CDCl_3$, 80 MHz): δ = 1.18 (m, 1H, 7-H), 1.30 (m, 6H, 3-H_2, 4-H_2, 5-H_2), 1.79 (s, 3H, Me), 2.23 (m, 2H, 2-H, 6-H), 2.45 (s, 2H, 1'-H_2), 4.72, 4.80 (m, each 1H, 3'-H_2). – ^{13}C NMR ($CDCl_3$, 20 MHz): δ = 8.88 (d, C-7), 18.39 (s, C-1), 20.63 (t, C-3, C-5), 20.99 (t, C-4), 22.69 (q, Me), 39.68 (t, C-1'), 42.25 (d, C-2, C-6), 110.40 (t, C-3'), 145.75 (s, C-2'). – MS (70 eV), *m/z* (%): 148 (8) [M^+], 133 (52), 119 (24), 106 (14), 105 (58), 93 (32), 92 (17), 91 (100), 79 (37), 77 (45). – $C_{11}H_{16}$ (148.2): calcd. C 89.12, H 10.88; found C 89.12, H 11.23. – $C_{11}H_{16}$: calcd. 148.125, found 148.123 (MS).

4. **1c** *and* **4e**: BuLi (20.0 ml, 32.0 mmol), **1a** (3.01 g, 32.0 mmol), $MgBr_2$ (5.89 g, 32.0 mmol), Fe(acac)$_3$ (56.5 mg, 160 µmol), **4e** (4.24 g, 32.0 mmol), and 1,4-dioxane (8.18 ml, 96.0 mmol) were treated according to II.1. Distillation of the crude material at 22°C (bath)/0.001 Torr provided 492 mg (16%) of *2,4,4,5,5,7-hexamethyl-2,6-octadiene* (**14**)[8].

VII. *Coupling of Propargylic Halides and Bridgehead-Substituted Tricyclo[4.1.0.0^{2,7}]heptanes*

1. *1-Methyl-7-(3-methyl-1,2-butadienyl)tricyclo[4.1.0.0^{2,7}]heptane* (**15d**): BuLi (20.0 ml, 32.0 mmol), **15a** (3.46 g, 32.0 mmol), $MgBr_2$ (5.89 g, 32.0 mmol), Fe(acac)$_3$ (56.5 mg, 160 µmol), **3e** (3.28 g, 32.0 mmol), and 1,4-dioxane (8.18 ml, 96.0 mmol) were treated according to II.1. Distillation of the crude material at 20°C (bath)/0.01 Torr provided 783 mg (14%) of **15d** as a colorless liquid. – IR (film): $\tilde{\nu}$ = 2978 cm^{-1}, 2934, 2854, 1526, 1446, 1377, 1362, 1255, 1231, 1215, 1186, 1118, 1008, 982, 973, 804, 755, 642, 575, 559. – UV (cyclohexane): λ_{max} (lg ε) = 217 nm (4.040 sh). – ^1H NMR ($CDCl_3$, 80 MHz): δ = 1.29 (s, 3H, 1-Me), 1.34 (m, 6H, 3-H_2, 4-H_2, 5-H_2), 1.70 (d, J = 5 Hz, 6H, CMe_2), 2.19 (m, 2H, 2-H, 6-H), 4.98 (sept, 1H, 1'-H). – ^{13}C NMR ($CDCl_3$, 20 MHz): δ = 12.6 (q, 1-Me), 20.72 (s, C-1 or C-7), 20.96 (t, C-3, C-5), 21.11 (t, C-4), 21.51 (q, CMe_2), 22.29 (s, C-1 or C-7), 45.65 (d, C-2, C-6), 87.84 (d, C-1'), 96.50 (s, C-3'), 203.09 (s, C-2'). – MS (70 eV), *m/z* (%): 174 (38) [M^+], 159 (100), 132 (94), 130 (34), 117 (49), 115 (33), 105 (48), 91 (82), 77 (32), 67 (31). – $C_{13}H_{18}$ (174.3): calcd. C 89.59, H 10.41; found C 89.37, H 10.49. – $C_{13}H_{18}$: calcd. 174.141, found 174.136 (MS).

2. *1-Methyl-7-[3-(trimethylsilyl)-2-propynyl]tricyclo[4.1.0.0^{2,7}]heptane* (**15e**): BuLi (30.0 ml, 48.0 mmol), **15a** (5.19 g, 48.0 mmol), $MgBr_2$ (8.84 g, 48.0 mmol), Fe(acac)$_3$ (84.8 mg, 240 µmol), **3i** (7.04 g, 48.0 mmol), and 1,4-dioxane (12.3 ml, 144 mmol) were treated according to II.1. Distillation of the crude material at 20–40°C (bath)/0.001 Torr provided 3.90 g (37%) of **15e** as a colorless liquid. – IR (film): $\tilde{\nu}$ = 2958 cm^{-1}, 2926, 2897, 2855, 2177 (C≡C), 1457, 1442, 1424, 1312, 1250, 1021, 992, 983, 843, 760, 698, 668, 641. – UV (cyclohexane): λ_{max} (lg ε) = 247 nm (3.274), 256 (3.094 sh), 279 (2.685). – ^1H NMR ($CDCl_3$, 80 MHz): δ = 0.14 (s, 9H, $SiMe_3$), 1.28 (m, 6H, 3-H_2, 4-H_2, 5-H_2), 1.40 (s, 3H, Me), 2.08 (m, 2H, 2-H, 6-H), 2.73 (s, 2H, 1'-H_2). – ^{13}C NMR ($CDCl_3$, 20 MHz): δ = 0.01 (q, $SiMe_3$), 10.97 (q, Me), 15.42, 15.76 (s, C-1, C-7 in unknown sequence), 18.09 (t, C-1'), 20.27 (t, C-3, C-5), 21.12 (t, C-4), 42.02 (d, C-2, C-6), 85.69, 103.99 (s, C-2', C-3' in unknown sequence). – MS (70 eV), *m/z* (%): 218 (8) [M^+], 203 (18), 145 (13), 144 (15), 129 (18), 107 (23), 105 (11), 91 (17), 79 (15), 73 (100). – $C_{14}H_{22}Si$ (218.4): calcd. C 76.99, H 10.15; found C 76.87, H 10.06. – $C_{14}H_{22}Si$: calcd. 218.149, found 218.149 (MS).

3. *1-(3-Methyl-1,2-butadienyl)-7-(trimethylsilyl)tricyclo[4.1.0.0^{2,7}]heptane* (**16d**) *and 7,7'-Bis(trimethylsilyl)-1,1'-bi(tricyclo[4.1.0.0^{2,7}]heptane)* (**22**): BuLi (15.6 ml, 25.0 mmol), **16a** (4.16 g, 25.0 mmol), $MgBr_2$ (4.60 g, 24.0 mmol), Fe(acac)$_3$ (44.1 mg, 125 µmol), **3e** (2.56 g, 25.0 mmol), and 1,4-dioxane (6.39 ml, 75.0 mmol) were treated according to II.1. Distillation of the crude material at 40°C (bath)/0.001 Torr provided 2.34 g (40%) of **16d** as a colorless liquid. At 70°C (bath)/0.001 Torr 536 (13%) colorless crystals of **22**[36] were obtained. – **16d**: IR (film): $\tilde{\nu}$ = 2979 cm^{-1}, 2955, 2933, 2855, 1457, 1444, 1362, 1247, 1233, 1187, 1008, 955, 862, 837, 807, 756, 746, 562. – UV (cyclohexane): λ_{max} (lg ε) = 216 nm (4.415). – ^1H NMR ($CDCl_3$, 80 MHz): δ = 0.05 (s, 9H, $SiMe_3$), 1.38 (m, 6H, 3-H_2, 4-H_2, 5-H_2), 1.71 (d, 6H, CMe_2), 2.30 (m, 2H, 2-H, 6-H), 5.23 (sept, 1H, 1'-H). – ^{13}C NMR ($CDCl_3$, 20 MHz): δ = –1.39 (s, $SiMe_3$), 13.27 (s, C-1 or C-7), 20.75 (q, CMe_2), 21.00 (t, C-3, C-5), 21.09 (t, C-4), 27.36 (s, C-1 or C-7), 43.08 (d, C-2, C-6), 89.63 (d, C-1'), 96.63 (s, C-3'), 202.18 (s, C-2'). – MS (70 eV), *m/z* (%): 232 (33) [M^+], 217 (9), 159 (18), 158 (18), 149 (14), 143 (24), 129 (8), 128 (9), 73 (100). – $C_{15}H_{24}Si$ (232.4): calcd. C 77.51, H 10.41; found C 77.90, H 10.51. – $C_{15}H_{24}Si$: calcd. 232.165, found 232.162 (MS).

4. *1-(Trimethylsilyl)-7-[3-(trimethylsilyl)-2-propynyl]tricyclo[4.1.0.0^{2,7}]heptane* (**16e**): BuLi (20.0 ml, 32.0 mmol), **16a** (5.32 g, 32.0 mmol), $MgBr_2$ (5.89 g, 32.0 mmol), Fe(acac)$_3$ (56.5 mg, 160 µmol), **3i** (4.69 g, 32.0 mmol), and 1,4-dioxane (8.18 ml, 96.0 mmol) were treated according to II.1. Distillation of the crude material at 60–80°C (bath)/0.001 Torr provided 2.82 g (32%) of **16e** as a colorless liquid. At 120°C (bath)/0.001 Torr 543 mg (10%) **22** was obtained as colorless crystals. – **16e**: IR (film): $\tilde{\nu}$ = 2957 cm^{-1}, 2928, 2854, 2178 (C≡C), 1507, 1441, 1423, 1308, 1248, 1174, 1024, 956, 933, 840, 759, 698, 682, 643. – UV (cyclohexane): λ_{max} (lg ε) = fast decrease above 200 nm, 240 (2.252 sh). – ^1H NMR ($CDCl_3$, 80 MHz): δ = –0.08, 0.14 (s, each 9H, $SiMe_3$ in unknown sequence), 1.32 (m, 6H, 3-H_2, 4-H_2, 5-H_2), 2.14 (m, 2H, 2-H, 6-H), 2.87 (s, 2H, 1'-H_2). – ^{13}C NMR ($CDCl_3$, 20 MHz): δ = –0.69, 0.13 (q, $SiMe_3$ in unknown sequence), 6.58 (s, C-1), 20.36 (t, C-1'), 20.63 (t, C-3, C-5), 21.12 (t, C-4), 26.72 (s, C-7), 41.05 (d, C-2, C-6), 86.00, 104.26 (s, C-2', C-3' in unknown sequence). – MS (70 eV), *m/z* (%): 276 (5) [M^+], 261 (30), 188 (22), 187 (28), 173 (14), 155 (10), 149 (11), 145 (9), 106 (11), 73 (100). – $C_{16}H_{28}Si_2$ (276.6): calcd. C 69.48, H 10.20; found C 70.11, H 9.86. – $C_{16}H_{28}Si_2$: calcd. 276.173, found 276.172 (MS).

5. *1-(3-Methyl-1,2-butadienyl)-7-(2-methyl-1-propenyl)tricyclo[4.1.0.0^{2,7}]heptane* (**17d**): BuLi (20.0 ml, 32.0 mmol), **17a** (4.74 g, 32.0 mmol), $MgBr_2$ (5.89 g, 32.0 mmol), Fe(acac)$_3$ (56.5 mg, 160 µmol), **3e** (3.28 g, 32.0 mmol), and 1,4-dioxane (8.18 ml, 96.0 mmol) were treated according to II.1. Distillation of the crude material at 50°C (bath)/0.001 Torr provided 3.67 g (54%) of **17d** as a colorless liquid. – IR (film): $\tilde{\nu}$ = 2980 cm^{-1}, 2927, 2855, 1653, 1521, 1506, 1457, 1447, 1375, 1361, 1216, 1050, 1009, 982, 803, 587, 560. – UV (cyclohexane): λ_{max} (lg ε) = 241 nm (4.095). – ^1H NMR ($CDCl_3$, 400 MHz): δ = 1.43 (m, 6H, 3-H_2, 4-H_2, 5-H_2),

1.70 (d, 6H, =C=CMe$_2$), 1.75, 1.80 (s, each 3H, =CMe$_2$ in unknown sequence), 2.50 (m, 2H, 2-H, 6-H), 5.00 (m, 1H, 1″-H), 5.02 (sept, 1H, 1′-H). – ^{13}C NMR (CDCl$_3$, 100 MHz): δ = 19.43 (q, =C*Me*Me), 21.04 (t, C-3, C-5), 21.17 (t, C-4), 21.31 (q, =C=C*Me*$_2$), 25.61 (q, =CMe*Me*), 26.27, 27.97 (s, C-1 and C-7 in unknown sequence), 47.05 (d, C-2, C-6), 87.85 (d, C-1′), 96.85 (s, C-3′), 120.73 (d, C-1″), 135.23 (s, C-2″), 203.17 (s, C-2′). – MS (70 eV), *m/z* (%): 214 (34) [M$^+$], 199 (55), 171 (100), 157 (39), 156 (38), 143 (81), 142 (41), 129 (75), 128 (52), 91 (47). – C$_{16}$H$_{22}$ (214.4): calcd. C 89.65, H 10.35; found C 89.45, H 10.23. – C$_{16}$H$_{22}$: calcd. 214.172, found 214.169 (MS).

6. *1-(2-Methyl-1-propenyl)-7-[3-(trimethylsilyl)-2-propynyl]tricyclo[4.1.0.0^{2,7}]heptane* (**17e**): BuLi (10.0 ml, 16.0 mmol), **17a** (2.37 g, 16.0 mmol), MgBr$_2$ (2.95 g, 16.0 mmol), Fe(acac)$_3$ (28.3 mg, 80.0 μmol), **3i** (2.35 g, 16.0 mmol), and 1,4-dioxane (4.09 ml, 48.0 mmol) were treated according to II.1. Distillation of the crude material at 60°C (bath)/0.001 Torr provided 2.21 g (53%) of **17e** as a colorless liquid. – IR (film): ṽ = 2962 cm^{-1}, 2924, 2855, 2178 (C≡C), 1446, 1422, 1375, 1333, 1320, 1250, 1100, 1051, 1024, 984, 842, 760, 698, 644. – UV (cyclohexane): λ$_{max}$ (lg ε) = 241 nm (3.951). – ^{1}H NMR (CDCl$_3$, 80 MHz): δ = 0.14 (s, 9H, SiMe$_3$), 1.36 (m, 6H, 3-H$_2$, 4-H$_2$, 5-H$_2$), 1.72, 1.76 (s, each 3H, Me), 2.37 (m, 2H, 2-H, 6-H), 2.69 (s, 2H, 1″-H$_2$), 5.18 (m, 1H, 1′-H). – ^{13}C NMR (CDCl$_3$, 100 MHz): δ = –0.02 (q, SiMe$_3$), 18.76 (t, C-1″), 19.06 (q, C*Me*Me), 20.48 (t, C-3, C-5), 20.57 (s, C-1 or C-7), 21.07 (t, C-4), 21.88 (s, C-1 or C-7), 25.55 (q, CMe*Me*), 44.36 (d, C-2, C-6), 85.91, 103.59 (s, C-2″ and C-3″ in unknown sequence), 119.54 (d, C-1′), 134.91 (s, C-2′). – MS (70 eV), *m/z* (%): 258 (5) [M$^+$], 207 (13), 185 (26), 184 (13), 169 (15), 131 (14), 105 (22), 93 (13), 91 (23), 73 (100). – C$_{17}$H$_{26}$Si (258.5): calcd. C 78.99, H 10.14; found C 78.93, H 10.02. – C$_{17}$H$_{26}$Si: calcd. 258.180, found 258.178 (MS).

7. *Mixture of 1-(2-Methyl-1-propenyl)-7-propargyltricyclo[4.1.0.0^{2,7}]heptane* (**17f**) *and 1-(2-Methyl-1-propenyl)-7-(1,2-propadienyl)tricyclo[4.1.0.0^{2,7}]heptane* (**17g**): BuLi (12.5 ml, 20.0 mmol), **17a** (2.96 g, 20.0 mmol), MgBr$_2$ (3.68 g, 20.0 mmol), Fe(acac)$_3$ (35.3 mg, 100.0 μmol), **3a** (1.49 g, 20.0 mmol), and 1,4-dioxane (5.11 ml, 60.0 mmol) were treated according to II.1. Distillation of the crude material at 60°C (bath)/0.001 Torr provided 1.12 g (30%) of a mixture of **17f** and **17g** in a ratio of 2:3. Since pure **17f** was prepared by a different method (see X.5.), assignment of the NMR signals of **17g** was possible. – **17g**: ^{1}H NMR (CDCl$_3$, 400 MHz): δ = 1.31–1.54 (m, 6H, 3-H$_2$, 4-H$_2$, 5-H$_2$), 1.75, 1.80 (m, each 3H, Me), 2.40 (m, 2H, 2-H, 6-H), 4.87 (d, 2H, 3″-H$_2$), 5.23 (m, 1H, 1′-H), 5.20 (t, 1H, 1″-H). – ^{13}C NMR (CDCl$_3$, 100 MHz): δ = 19.39 (q, C*Me*Me), 20.89 (t, C-3, C-5), 21.08 (t, C-4), 24.98 (s, C-1 or C-7), 25.60 (q, CMe*Me*), 28.15 (s; C-1 or C-7), 46.82 (d, C-2, C-6), 76.92 (t, C-3″), 89.53 (d, C-1″), 120.12 (d, C-1′), 136.00 (s, C-2′), 210.25 (s, C-2″).

8. *1-Isopropenyl-7-[3-(trimethylsilyl)-2-propynyl]tricyclo[4.1.0.0^{2,7}]heptane* (**18e**): BuLi (20.0 ml, 32.0 mmol), **18a** (4.30 g, 32.0 mmol), MgBr$_2$ (5.89 g, 32.0 mmol), Fe(acac)$_3$ (56.5 mg, 160 μmol), **3i** (4.69 g, 32.0 mmol), and 1,4-dioxane (8.18 ml, 96.0 mmol) were treated according to II.1. Distillation of the crude material at 80°C (bath)/0.001 Torr provided 5.31 g (68%) of **18e** as a colorless liquid. – IR (film): ṽ = 2960 cm^{-1}, 2934, 2856, 2178 (C≡C), 1626, 1442, 1420, 1375, 1322, 1308, 1250, 1025, 977, 843, 760, 698, 643. – UV (cyclohexane): λ$_{max}$ (lg ε) = 230 nm (4.013). – ^{1}H NMR (CDCl$_3$, 80 MHz): δ = 1.35 (m, 6H, 3-H$_2$, 4-H$_2$, 5-H$_2$), 1.75 (s, 3H, Me), 2.58 (m, 2H, 2-H, 6-H), 2.71 (s, 2H, 1″-H$_2$), 4.65 (m, 2H, =CH$_2$). – ^{13}C NMR (CDCl$_3$, 100 MHz): δ = –0.09 (q, SiMe$_3$), 18.36 (t, C-1″), 20.46 (t, C-3, C-5), 20.85 (t, C-4), 20.91 (q, Me), 25.77, 26.59 (s, C-1 and C-7 in unknown sequence), 41.01 (d, C-2, C-6), 85.95, 103.23 (s, C-2″, C-3″), 108.98 (t, =CH$_2$), 141.28 (s, *C*=CH$_2$). – MS (70 eV), *m/z* (%): 244 (7) [M$^+$], 229 (10), 171 (11), 170 (10), 169 (7), 155 (13), 129 (7), 91 (8), 74 (7), 73 (100). – C$_{16}$H$_{24}$Si (244.5): calcd. C 78.61, H 9.90; found C 78.21, H 9.90. – C$_{16}$H$_{24}$Si: calcd. 244.165, found 244.166 (MS).

9. *Mixture of 1-Isopropenyl-7-(propargyl)tricyclo[4.1.0.0^{2,7}]heptane* (**18f**) *and 1-Isopropenyl-7-(1,2-propadienyl)tricyclo[4.1.0.0^{2,7}]heptane* (**18g**): BuLi (20.0 ml, 32.0 mmol), **18a** (4.30 g, 32.0 mmol), MgBr$_2$ (5.89 g, 32.0 mmol), Fe(acac)$_3$ (56.5 mg, 160 μmol), **3a** (2.38 g, 32.0 mmol), and 1,4-dioxane (8.18 ml, 96.0 mmol) were treated according to II.1. Distillation of the crude material at 23°C (bath)/0.001 Torr provided 3.80 g (69%) of a mixture of **18f** and **18g** in a ratio of 1:1.8. Since pure **18f** was prepared by another method (see X.6), assignment of the NMR signals of **18g** was possible. – **18g**: ^{1}H NMR (CDCl$_3$, 400 MHz): δ = 1.29–1.48 (m, 6H, 3-H$_2$, 4-H$_2$, 5-H$_2$), 1.62 (m, 3H, Me), 2.77 (m, 2H, 2-H, 6-H), 4.77 (m, 2H, =CH$_2$), 4.87 (d, 2H, 3″-H$_2$), 5.23 (t, 1H, 1″-H). – ^{13}C NMR (CDCl$_3$, 100 MHz): δ = 20.14 (q, Me), 20.85 (t, C-4), 20.96 (t, C-3, C-5), 27.48, 33.64 (s, C-1 and C-7 in unknown sequence), 43.61 (d, C-2, C-6), 77.11 (t, C-3″), 88.70 (d, C-1″), 109.07 (t, =CH$_2$), 141.45 (s, *C*=CH$_2$), 210.46 (s, C-2″).

10. *1-(3-Methyl-1,2-butadienyl)-7-[(trimethylsilyl)ethynyl]tricyclo[4.1.0.0^{2,7}]heptane* (**19d**): BuLi (10.0 ml, 16.0 mmol), **19a** (3.05 g, 16.0 mmol), MgBr$_2$ (2.95 g, 16.0 mmol), Fe(acac)$_3$ (28.3 mg, 80.0 μmol), **3e** (1.64 g, 16.0 mmol), and 1,4-dioxane (4.09 ml, 48.0 mmol) were treated according to II.1. Distillation of the crude material at 80–90°C (bath)/0.001 Torr provided 2.07 g (50%) of **19d** as a colorless, viscous oil. – IR (film): ṽ = 2981 cm^{-1}, 2935, 2858, 2146 (C≡C), 1442, 1434, 1362, 1249, 1012, 995, 877, 842, 759, 686, 640, 619, 565, 466, 451. – UV (cyclohexane): λ$_{max}$ (lg ε) = 224 nm (3.963 sh), 253 (4.062). – ^{1}H NMR (CDCl$_3$, 80 MHz): δ = 0.11 (s, 9H, SiMe$_3$), 1.39 (m, 6H, 3-H$_2$, 4-H$_2$, 5-H$_2$), 1.71 (d, 6H, Me), 2.72 (m, 2H, 2-H, 6-H), 5.07 (sept, 1H, 1′-H). – ^{13}C NMR (CDCl$_3$, 20 MHz): δ = 0.46 (s, SiMe$_3$), 16.97 (s, C-1 or C-7), 20.33 (t, C-3, C-5), 20.42 (t, C-4), 21.18 (q, Me), 32.32 (s, C-1 or C-7), 49.65 (d, C-2, C-6), 84.00 (s, C-1″ or C-2″), 86.39 (d, C-1′), 97.63 (s, C-3′), 105.11 (s, C-1″ or C-2″), 203.79 (s, C-2′). – MS (70 eV), *m/z* (%): 256 (20) [M$^+$], 183 (51), 182 (35), 181 (25), 168 (22), 167 (59), 165 (23), 155 (18), 153 (18), 73 (100). – C$_{17}$H$_{24}$Si (256.5): calcd. C 79.62, H 9.43; found C 79.31, H 9.25. – C$_{17}$H$_{24}$Si: calcd. 256.165, found 256.164 (MS).

11. *1-[(Trimethylsilyl)ethynyl]-7-[3-(trimethylsilyl)-2-propynyl]tricyclo[4.1.0.0^{2,7}]heptane* (**19e**): BuLi (10.0 ml, 16.0 mmol), **19a** (3.05 g, 16.0 mmol), MgBr$_2$ (2.95 g, 16.0 mmol), Fe(acac)$_3$ (28.3 mg, 80.0 μmol), **3i** (2.35 g, 16.0 mmol), and 1,4-dioxane (4.09 ml, 48.0 mmol) were treated according to II.1. Distillation of the crude material at 100°C (bath)/0.001 Torr furnished 2.36 g (49%) of **19e** as low-melting, colorless crystals. m.p. 20–30°C. – IR (film): ṽ = 2959 cm^{-1}, 2858, 2179 (C≡C), 2151 (C≡C), 1576, 1559, 1423, 1249, 1082, 1026, 857, 842, 759, 697, 668, 500. – UV (cyclohexane): λ$_{max}$ (lg ε) = 236 nm (3.973 sh). – ^{1}H NMR (CDCl$_3$, 400 MHz): δ = 0.11, 0.12 (s, each 9H, SiMe$_3$), 1.20–1.36 (m, 4H, 3-H$_2$, 5-H$_2$), 1.42–1.50 (m, 2H, 4-H$_2$), 2.65 (m, 2H, 2-H, 6-H), 2.80 (s, 2H, 1″-H$_2$). – ^{13}C NMR (CDCl$_3$, 100 MHz): δ = 0.08, 0.39 (s, SiMe$_3$), 9.87 (s, C-1), 19.37 (t, C-1″), 20.00 (t, C-3, C-5), 20.45 (t, C-4), 28.27 (s, C-7), 48.21 (d, C-2, C-6), 84.06, 86.63, 102.48, 104.46 (s, C-1′, C-2′, C-2″, C-3″ in unknown sequence). – MS (70 eV), *m/z* (%): 300 (7) [M$^+$], 227 (9), 213 (9), 212 (36), 211 (24), 197 (18), 183 (9), 97 (8), 74 (8), 73 (100). – C$_{18}$H$_{28}$Si$_2$ (300.6): calcd. C 71.92, H 9.39; found C 71.81, H 8.94. – C$_{18}$H$_{28}$Si$_2$: calcd. 300.173, found 300.167 (MS).

12. *1-(3,3-Dimethyl-1-butynyl)-7-(3-methyl-1,2-butadienyl)tricyclo[4.1.0.$0^{2,7}$]heptane* (**20d**): BuLi (7.56 ml, 12.1 mmol), **20a** (2.11 g, 12.1 mmol), $MgBr_2$ (2.23 g, 12.1 mmol), $Fe(acac)_3$ (21.4 mg, 60.5 µmol), **3e** (1.24 g, 12.1 mmol), and 1,4-dioxane (3.09 ml, 36.3 mmol) were treated according to II.1. Distillation of the crude material at 60–70°C (bath)/0.001 Torr furnished 1.78 g (61%) of **20d** as a colorless solid. m.p. 38.5–39.5°C. – IR (KBr): $\tilde{\nu}$ = 2969 cm^{-1}, 2869, 2209 (C≡C), 1753, 1702, 1698, 1651, 1632, 1477, 1458, 1364, 1263, 1204, 1143, 1074, 1012, 530. – UV (cyclohexane): λ_{max} (lg ε) = 225 nm (4.023), 240 (3.993 sh). – ^1H NMR ($CDCl_3$, 400 MHz): δ = 1.20 (s, 9H, CMe_3), 1.25–1.40 (m, 4H, 3-H_2, 5-H_2), 1.45–1.55 (m, 2H, 4-H_2), 1.74 (d, 6H, CMe_2), 2.65 (m, 2H, 2-H, 6-H), 5.12 (sept, $^5J_{1'',Me}$ = 2.8 Hz, 1H, 1″-H). – ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 16.65 (s, C-7), 20.41 (t, C-3, C-5), 20.57 (t, C-4), 21.32 (q, CMe_2), 27.74 (s, C-1), 29.43 (s, C-3′), 31.69 (q, CMe_3), 49.18 (d, C-2, C-6), 76.41 (s, C-1′ or C-2′), 87.08 (d, C-1″), 88.65 (s, C-1′ or C-2′), 97.51 (s, C-3″), 208.65 (s, C-2″). – MS (70 eV), *m/z* (%): 240 (40) [M^+], 195 (65), 183 (94), 169 (63), 167 (81), 165 (100), 155 (59), 153 (87), 141 (82), 128 (63). – $C_{18}H_{24}$ (240.4): calcd. C 89.94, H 10.06; found C 89.92, H 10.23. – $C_{18}H_{24}$: calcd. 240.188, found 240.187 (MS).

13. *1-Allyl-7-methyltricyclo[4.1.0.$0^{2,7}$]heptane* (**15h**): BuLi (20.0 ml, 32.0 mmol), **15a** (3.46 g, 32.0 mmol), $MgBr_2$ (5.89 g, 32.0 mmol), $Fe(acac)_3$ (56.5 mg, 160 µmol), **4a** (2.45 g, 32.0 mmol), and 1,4-dioxane (8.18 ml, 96.0 mmol), were treated according to II.1. Distillation of the crude material at 22°C (bath)/0.02 Torr provided 968 mg (20%) of **15h** as a colorless liquid. – IR (film): $\tilde{\nu}$ = 3079 cm^{-1} (=C–H), 3005, 2977, 2925, 2854, 1641 (C=C), 1460, 1441, 1415, 1378, 1279, 1093, 993, 981, 933, 910, 662, 646, 576, 556. – UV (cyclohexane): λ_{max} = fast decrease above 200 nm. – ^1H NMR ($CDCl_3$, 80 MHz): δ = 1.29 (m, 6H, 3-H_2, 4-H_2, 5-H_2), 1.36 (s, 3H, Me), 1.90 (m, 2H, 2-H, 6-H), 2.38 (d, 2H, 1′-H_2), 4.48–5.28 (m, 2H, 3′-H_2), 5.60–6.14 (m, 1H, 2′-H). – ^{13}C NMR ($CDCl_3$, 20 MHz): δ = 11.84 (q, Me), 15.33, 17.87 (s, C-1, C-7 in unknown sequence), 20.69 (t, C-3, C-5), 21.29 (t, C-4), 31.86 (t, C-1′), 42.95 (d, C-2, C-6), 114.86 (t, C-3′), 137.48 (d, C-2′). – MS (70 eV), *m/z* (%): 148 (24) [M^+], 133 (29), 119 (21), 107 (67), 105 (70), 92 (20), 91 (100), 79 (68), 77 (29). – $C_{11}H_{16}$ (148.2): calcd. C 89.12, H 10.88; found C 89.04, H 10.90. – $C_{11}H_{16}$: calcd. 148.125, found 148.122 (MS).

14. *1-Allyl-7-(trimethylsilyl)tricyclo[4.1.0.$0^{2,7}$]heptane* (**16h**): BuLi (15.6 ml, 25.0 mmol), **16a** (4.16 g, 25.0 mmol), $MgBr_2$ (4.60 g, 25.0 mmol), $Fe(acac)_3$ (44.1 mg, 125 µmol), **4a** (1.91 g, 25.0 mmol), and 1,4-dioxane (6.39 ml, 75.0 mmol) were treated according to II.1. Distillation of the crude material at 20°C (bath)/0.001 Torr provided 1.11 g (22%) of **16h** as a colorless liquid. – IR (film): $\tilde{\nu}$ = 3079 cm^{-1} (=C–H), 2954, 2926, 2854, 1640 (C=C), 1501, 1443, 1260, 1247, 1181, 992, 965, 911, 865, 837, 797, 756, 744, 690, 626. – UV (cyclohexane): λ_{max} = fast decrease above 200 nm. – ^1H NMR ($CDCl_3$, 80 MHz): δ = 0.04 (s, 9H, $SiMe_3$), 1.31 (m, 6H, 3-H_2, 4-H_2, 5-H_2), 1.99 (m, 2H, 2-H, 6-H), 2.54 (d, 2H, 1′-H_2), 4.79–5.26 (m, 2H, vinyl-H), 5.61–6.13 (m, 1H, vinyl-H). – ^{13}C NMR ($CDCl_3$, 20 MHz): δ = –0.87 (q, $SiMe_3$), 6.22 (s, C-1 or C-7), 21.09 (t, C-3, C-5), 21.18 (t, C-4), 27.87 (s, C-1 or C-7), 34.17 (t, C-1′), 41.87 (d, C-2, C-6), 115.10 (t, C-3′), 137.40 (d, C-2′). – MS (70 eV), *m/z* (%): 206 (3) [M^+], 132 (16), 131 (8), 123 (7), 117 (9), 104 (5), 91 (14), 74 (8), 73 (100). – $C_{13}H_{22}Si$ (206.4): calcd. C 75.65, H 10.74; found C 76.02, H 10.66. – $C_{13}H_{22}Si$: calcd. 206.1491, found 206.1484 (MS).

15. *1-Allyl-7-(2-methyl-1-propenyl)tricyclo[4.1.0.$0^{2,7}$]heptane* (**17h**): BuLi (21.3 ml, 34.1 mmol), **17a** (5.06 g, 34.1 mmol), $MgBr_2$ (6.28 g, 34.1 mmol), $Fe(acac)_3$ (60.2 mg, 171 µmol, **4a** (2.61 g, 34.1 mmol), and 1,4-dioxane (8.72 ml, 102 mmol) were treated according to II.1. Distillation of the crude material at 74°C (bath)/0.001 Torr provided 1.99 g (31%) of **17h** as a colorless liquid. – IR (film): $\tilde{\nu}$ = 3077 cm^{-1} (=C–H), 2979, 2965, 2924, 2854, 1666 (C=C), 1641, 1442, 1415, 1375, 1099, 1051, 993, 910, 839, 714. – UV (cyclohexane): λ_{max} (lg ε) = 233 nm (3.942). – ^1H NMR ($CDCl_3$, 80 MHz): δ = 1.38 (m, 6H, 3-H_2, 4-H_2, 5-H_2), 1.74, 1.79 (s, 3H, Me_2), 2.23 (m, 2H, 2-H, 6-H), 2.36, 2.43 (m, 2H, 1′-H_2), 4.84–5.26 (m, 3H, vinyl-H), 5.58–6.13 (m, 1H, vinyl-H). – ^{13}C NMR ($CDCl_3$, 20 MHz): δ = 19.20 (q, C*Me*Me), 20.84 (s, C-1 or C-7), 21.02 (t, C-3, C-5), 21.35 (t, C-4), 24.35 (s, C-1 or C-7), 25.66 (q, CMe*Me*), 32.69 (t, C-1′), 45.25 (d, C-2, C-6), 115.19 (t, C-3′), 120.64 (d, C-1″), 134.27 (s, C-2″), 136.88 (d, C-2′). – MS (70 eV), *m/z* (%): 188 (13) [M^+], 173 (47), 145 (100), 131 (51), 119 (34), 117 (73), 105 (98), 91 (94), 79 (33), 77 (35). – $C_{14}H_{20}$ (188.3): calcd. C 89.29, H 10.71; found C 89.25, H 10.64. – $C_{14}H_{20}$: calcd. 188.156, found 188.153 (MS).

16. *1-Allyl-7-[(trimethylsilyl)ethynyl]tricyclo[4.1.0.$0^{2,7}$]heptane* (**19h**) *and 7,7′-Bis[(trimethylsilyl)ethynyl]-1,1′-bi(tricyclo[4.1.0.$0^{2,7}$]heptane)* (**23**): BuLi (10.0 ml, 16.0 mmol), **19a** (3.05 g, 16.0 mmol), $MgBr_2$ (2.95 g, 16.0 mmol), $Fe(acac)_3$ (28.3 mg, 80.0 µmol), **4a** (1.22 g, 16.0 mmol), and 1,4-dioxane (4.09 ml, 48.0 mmol) were treated according to II.1. Distillation of the crude material at 68°C (bath)/0.001 Torr provided 1.57 g (43%) of **19h** as a colorless liquid. The residue contained some crystalline material which could be purified by recrystallization from ether at –78°C. 117 mg (4%) of **23** was obtained as colorless crystals. – **19h**: IR (film): $\tilde{\nu}$ = 2957 cm^{-1}, 2934, 2858, 2148 (C≡C), 1641, 1443, 1416, 1249, 1082, 996, 916, 873, 854, 842, 759, 697, 625. – UV (cyclohexane): λ_{max} (lg ε) = 229 nm (2.903). – ^1H NMR ($CDCl_3$, 400 MHz): δ = 0.13 (s, 9H, $SiMe_3$), 1.23–1.35 (m, 4H, 3-H_2, 5-H_2), 1.45–1.53 (m, 2H, 4-H_2), 2.55 (m, 2H, 2-H, 6-H), 2.59 (d, 2H, 1′-H_2), 5.04–5.08, 5.15–5.19, 5.87–5.97 (m, each 1H, vinyl-H). – ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 0.38 (q, $SiMe_3$), 9.41 (s, C-7), 20.22 (t, C-3, C-5), 20.46 (t, C-4), 30.20 (s, C-1), 32.79 (t, C-1′), 48.63 (d, C-2, C-6), 83.80, 105.73 (s, C-1″, C-2″ in unknown sequence), 116.33 (t, C-3′), 135.40 (d, C-2′). – MS (70 eV), *m/z* (%): 230 (16) [M^+], 215 (16), 159 (14), 157 (16), 156 (21), 155 (19), 141 (14), 131 (19), 129 (14), 128 (14), 73 (100). – $C_{15}H_{22}Si$ (230.4): calcd. C 78.19, H 9.62; found C 78.04, H 9.58. – $C_{15}H_{22}Si$: calcd. 230.149; found 230.149 (MS). – **23**: m.p. 132–135°C (dec.). – IR (KBr): $\tilde{\nu}$ = 2933 cm^{-1}, 2857, 2146 (C≡C), 1636, 1440, 1249, 1153, 1092, 1042, 1020, 931, 844, 788, 759, 710, 668, 579. – UV (cyclohexane): λ_{max} (lg ε) = 252 nm (4.065). – ^1H NMR ($CDCl_3$, 400 MHz): δ = 0.13 (s, 18H, $SiMe_3$), 1.18–1.36 (m, 8H, 3-H_2, 5-H_2, 3′-H_2, 5′-H_2), 1.45–1.57 (m, 4H, 4-H_2, 4′-H_2), 2.91 (m, 4H, 2-H, 6-H, 2′-H, 6′-H). – ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 0.34 (q, $SiMe_3$), 11.83 (s, C-1, C-1′), 20.66 (t, C-4, C-4′), 20.67 (t, C-3, C-5, C-3′, C-5′), 32.21 (s, C-7, C-7′), 48.15 (d, C-2, C-6, C-2′, C-6′), 83.43, 105.67 (s, alkynyl-C in unknown sequence). – MS (70 eV), *m/z* (%): 378 (13) [M^+], 306 (9), 305 (27), 289 (12), 275 (11), 247 (9), 245 (9), 231 (12), 73 (100). – $C_{24}H_{34}Si_2$: calcd. 378.220, found 378.224 (MS).

VIII. *Metalation Experiments with Allenyltricyclo[4.1.0.$0^{2,7}$]heptanes*

1-(1-Deuterio-3-methyl-1,2-butadienyl)tricyclo[4.1.0.$0^{2,7}$]heptane (**6d-D**): From a mixture of 3.12 ml (4.99 mmol) of BuLi and hexane the solvent was removed in vacuo, and the residue was diluted with 5 ml of ether at 0°C. Then **6d** (799 mg, 4.99 mmol) was added. After 2 d at room temp. the solution was cooled to 0°C and deuterium oxide (D_2O) (2.00 ml, 111 mmol) was added. Workup was carried out according to II.4. Distillation of the crude material at 20°C (bath)/0.001 Torr furnished 532 mg (66%) of **6d-**

D as a colorless liquid. There was no evidence for undeuterated material in the ^{1}H-NMR spectrum. – IR (film): $\tilde{\nu}$ = 2983 cm^{-1}, 2930, 2856, 1492, 1442, 1375, 1362, 1187, 1098, 1045, 1024, 942, 805, 757, 735, 708, 695, 660, 549. – ^{1}H NMR (CDCl$_3$, 400 MHz): δ = 1.35 (m, 7H, 3-H$_2$, 4-H$_2$, 5-H$_2$, 7-H), 1.69 (s, 6H, Me$_2$), 2.52 (m, 2H, 2-H, 6-H). – ^{13}C NMR (CDCl$_3$, 100 MHz): δ = 15.75 (d, C-7), 20.61 (t, C-3, C-5), 21.00 (q and t overlapping, Me$_2$ and C-4), 43.30 (d, C-2, C-6), 90.02 (t, C-1′), 96.95 (s, C-3′), 202.11 (s, C-2′). – MS (70 eV), *m/z* (%): 162 (41), 161 (50) [M$^+$], 147 (81), 146 (100), 131 (51), 119 (56), 118 (97), 117 (53), 116 (51), 92 (93). – $C_{12}H_{15}D$: calcd. 161.131, found 161.129 (MS).

IX. Couplings of **24b**

1. *8-Isopropenyl-9-isopropyltetracyclo[4.4.0.0^{1,5}.0^{2,6}]deca-7,9-diene* (**25**): BuLi (20.0 ml, 32.0 mmol), **2a** (1.28 g, 16.0 mmol), MgBr$_2$ (5.89 g, 32.0 mmol), Fe(acac)$_3$ (56.5 mg, 160 μmol), **3e** (3.28 g, 32.0 mmol), and 1,4-dioxane (8.18 ml, 96.0 mmol) were treated according to II.1. Distillation of the crude material at 50°C (bath)/0.001 Torr provided 963 mg of a solid/liquid mixture. The solid was removed and recrystallized from ether at −18°C. 470 mg (14%) of **25** was obtained as colorless crystals. The material can be sublimated at 40°C (bath)/0.001 Torr. Two repetitions of this experiment with 32 mmol each of **2a** provided 15% of **25** in each case. The exact assignment of all NMR signals was possible by COSY, NOESY, HETCOR, und COLOCS spectra. m.p. 51–53°C. – IR (KBr): $\tilde{\nu}$ = 3023 cm^{-1} (=C–H), 2958, 2868, 1639, 1461, 1443, 1382, 1370, 1288, 1085, 988, 923, 896, 837, 825, 745, 600, 493. – UV (cyclohexane): λ_{max} (lg ε) = 228 nm (3.673), 296 (3.037). – ^{1}H NMR (CDCl$_3$, 400 MHz): δ = 0.99 (d, *J* = 6.8 Hz, 6H, CH*Me*$_2$), 1.41 (s, 4H, 3-H$_2$, 4-H$_2$), 1.77 (s, 2H, 2-H, 5-H), 1.81 (s, 3H, Me), 2.39 (sept, 1H, 1″-H), 4.72, 4.91 (m, each 1H, =CH$_2$), 5.68 (d, *J* = 2.2 Hz, 1H, 7-H), 5.79 (m, 1H, 10-H). – ^{13}C NMR (CDCl$_3$, 100 MHz): δ = 11.66, 12.59 (s, C-1 and C-6 in unknown sequence), 23.27 (q, CH*Me*$_2$), 24.38 (q, Me), 26.06 (t, C-3, C-4), 28.83 (d, C-1″), 32.10 (d, C-2, C-5), 113.72 (t, =CH$_2$), 115.55 (d, C-10), 119.81 (d, C-7), 145.63 (s, *C*=CH$_2$), 145.97 (s, C-8), 146.26 (s, C-9). – MS (70 eV), *m/z* (%): 212 (24) [M$^+$], 197 (100), 182 (60), 169 (61), 167 (68), 165 (47), 155 (37), 153 (34), 141 (66), 129 (40). – $C_{16}H_{20}$ (212.3): calcd. C 90.51, H 9.49; found C 90.18, H 9.25. – $C_{16}H_{20}$. calcd. 212.1565, found 212.1538 (MS).

2. *1,4-Dicyclohexyliden-1,3-butadiene* (**27**): BuLi (40.0 ml, 64.0 mmol), **2a** (2.56 g, 32.0 mmol), MgBr$_2$ (11.9 g, 64.0 mmol), Fe(acac)$_3$ (113 mg, 320 μmol), **3f** (9.13 g, 64.0 mmol), and 1,4-dioxane (16.4 ml, 192 mmol) were treated according to II.1. Distillation of the crude material at 120°C (bath)/0.001 Torr provided 1.43 g of a crystalline material. After recrystallization from ether at −18°C 633 mg (9%) of **27** was obtained as colorless crystals. Compound **27** could be sublimated at 60–80°C (bath)/0.001 Torr, m.p. 107–110°C. – IR (KBr): $\tilde{\nu}$ = 3030 cm^{-1} (=C–H), 2989, 2925, 2854, 1963 (C=C=C), 1447, 1337, 1313, 1238, 1218, 984, 972, 921, 849, 821, 597, 589, 437. – UV (cyclohexane): λ_{max} (lg ε) = 212 nm (4.235), 284 (3.064), 299 (2.909). – ^{1}H NMR (CDCl$_3$, 400 MHz): δ = 1.48–1.61 (m, 12H, 3′-H$_2$, 4′-H$_2$, 5′-H$_2$, 3″-H$_2$, 4″-H$_2$, 5″-H$_2$), 2.08–2.16 (m, 8H, 2′-H$_2$, 6′-H$_2$, 2″-H$_2$, 6″-H$_2$), 5.45 (m, 2H, 2-H, 3-H). – ^{13}C NMR (CDCl$_3$, 100 MHz): δ = 26.12 (t, C-4′, C-4″), 27.42 (t, C-3′, C-5′, C-3″, C-5″), 31.60 (t, C-2′, C-6′, C-2″, C-6″), 88.92 (d, C-2, C-3), 104.13 (s, C-1′, C-1″), 200.18 (s, C-1, C-4). – MS (70 eV), *m/z* (%): 214 (100) [M$^+$], 171 (23), 145 (23), 143 (18), 131 (25), 129 (34), 128 (17), 117 (23), 116 (17), 91 (27). – $C_{16}H_{22}$ (214.3): calcd. C 89.65, H 10.35; found C 89.32, H 10.29. – $C_{16}H_{22}$: calcd. 214.172, found 214.173 (MS).

X. *Desilylations*

1. **5a**: **5h** (201 mg, 983 μmol), MeOH (6.00 ml), and NaOH (2 N, 2.00 ml) were treated according to II.5. Distillation of the crude material at 22°C (bath)/0.01 Torr provided 120 mg (92%) of **5a**.

2. *1-(1-Methyl-2-propynyl)tricyclo[4.1.0.0^{2,7}]heptane* (**5d**): **5j** (702 mg, 3.21 mmol), MeOH (13.0 ml), and NaOH (2 N, 4 ml) were treated according to II.5. Distillation of the crude material at 20°C (bath)/0.04 Torr provided 379 mg (81%) of **5d** as a colorless liquid. – IR (film): $\tilde{\nu}$ = 3311 cm^{-1} (≡C–H), 2976, 2931, 2857, 1450, 1371, 1334, 1306, 1249, 1149, 1103, 1074, 1062, 1006, 881, 841, 804, 761, 672, 633. – UV (cyclohexane): λ_{max} (lg ε) = 232 nm (3.220). – ^{1}H NMR (CDCl$_3$, 400 MHz): δ = 1.23–1.32 (m, 7H, 3-H$_2$, 4-H$_2$, 5-H$_2$, 7-H), 1.27 (d, *J* = 7.1 Hz, 3H, Me), 2.03 (d, *J* = 2.3 Hz, 1H, 3′-H), 2.39–2.41, 2.45–2.46 (m, each 1H, 2-H and 6-H in unknown sequence), 2.98 (qd, 1H, 1′-H). – ^{13}C NMR (CDCl$_3$, 100 MHz): δ = 8.91 (d, C-7), 20.41 (q, Me), 20.43, 20.48 (t, C-3 and C-5 in unknown sequence), 21.10 (t, C-4), 21.86 (s, C-1), 25.62 (d, C-1′), 39.60, 41.37 (d, C-2 and C-6 in unknown sequence), 68.67 (d, C-3′), 86.11 (s, C-2′). – MS (70 eV), *m/z* (%): 146 (14) [M$^+$], 131 (63), 117 (43), 116 (29), 115 (34), 105 (26), 93 (64), 91 (100), 79 (26), 77 (58). – $C_{11}H_{14}$ (146.2): calcd. C 90.35, H 9.65; found C 88.69, H 9.49. – $C_{11}H_{14}$: calcd. 146.109, found 146.110 (MS).

3. *1-Methyl-7-(2-propynyl)tricyclo[4.1.0.0^{2,7}]heptane* (**15f**): **15e** (665 mg, 3.04 mmol), MeOH (15.0 ml), and NaOH (2 N, 5.00 ml) were treated according to II.5. Distillation of the crude material at 21°C (bath)/0.01 Torr provided 358 mg (80%) of **15f** as colorless liquid. In a second experiment **15e** (792 mg, 3.63 mmol) was added to a mixture of potassium hydroxide (218 mg) in methanol (1.5 ml) and heated to 60°C for 30 min. Distillation of the crude material at 21°C (bath)/0.01 Torr provided 370 mg (70%) of **15f** as a colorless oil. – IR (film): $\tilde{\nu}$ = 3312 cm^{-1} (≡C–H), 2925, 2855, 2121 (C≡C), 1460, 1442, 1428, 1379, 1313, 1302, 1277, 1249, 995, 986, 933, 840, 729, 631, 572, 552. – UV (cyclohexane): λ_{max} = fast decrease above 200 nm. – ^{1}H NMR (CDCl$_3$, 400 MHz): δ = 1.21–1.33 (m, 6H, 3-H$_2$, 4-H$_2$, 5-H$_2$), 1.40 (s, 3H, Me), 1.96 (t, *J* = 2.6 Hz, 1H, 3′-H), 2.08 (m, 2H, 2-H, 6-H), 2.68 (d, 2H, 1′-H$_2$). – ^{13}C NMR (CDCl$_3$, 100 MHz): δ = 11.05 (q, Me), 15.43, 15.72 (s, C-1, C-7 in unknown sequence), 16.77 (t, C-1′), 20.21 (t, C-3, C-5), 21.08 (t, C-4), 42.23 (d, C-2, C-6), 69.20 (d, C-3′), 81.65 (s, C-2′). – MS (70 eV), *m/z* (%): 146 (28) [M$^+$], 131 (56), 117 (45), 116 (29), 115 (39), 107 (79), 105 (29), 91 (100), 79 (50), 77 (32). – $C_{11}H_{14}$ (146.2): calcd. C 90.35, H 9.65; found C 90.32, H 10.06. – $C_{11}H_{14}$: calcd. 146.109, found 146.111 (MS).

4. *1-(2-Propynyl)-7-(trimethylsilyl)tricyclo[4.1.0.0^{2,7}]heptane* (**16f**): **16e** (1.45 g, 5.24 mmol), MeOH (26.0 ml), and NaOH (2 N, 8.00 ml) were treated according to II.5. Distillation of the crude material at 23°C (bath)/0.02 Torr provided 841 mg (79%) of **16f** as a colorless liquid. – IR (film): $\tilde{\nu}$ = 3314 cm^{-1} (≡C–H), 2954, 2928, 2897, 2854, 2125 (C≡C), 1507, 1441, 1427, 1261, 1247, 1175, 969, 925, 865, 837, 758, 748, 682, 668, 628. – UV (cyclohexane): λ_{max} (lg ε) = 253 nm (2.398). – ^{1}H NMR (CDCl$_3$, 80 MHz): δ = 0.10 (s, 9H, SiMe$_3$), 1.34 (m, 6H, 3-H$_2$, 4-H$_2$, 5-H$_2$), 1.99 (t, 1H, 3′-H), 2.17 (m, 2H, 2-H, 6-H), 2.80 (d, 2H, 1′-H$_2$). – ^{13}C NMR (CDCl$_3$, 20 MHz): δ = −0.81 (q, SiMe$_3$), 6.70 (s, C-7), 19.09 (t, C-1′), 20.57 (t, C-3, C-5), 21.09 (t, C-4), 26.54 (s, C-1), 41.23 (d, C-2, C-6), 69.52 (d, C-3′), 81.85 (s, C-2′). – MS (70 eV), *m/z* (%): 204 (2) [M$^+$], 189 (19), 161 (8), 130 (13), 129 (24), 121 (8), 91 (9), 83 (14), 74 (8), 73 (100). – $C_{13}H_{20}Si$ (204.4): calcd. C 76.40, H 9.86; found C 76.82, H 9.66. – $C_{13}H_{20}Si$: calcd. 204.133, found 204.131 (MS).

5. **17f**: **17e** (767 mg, 2.97 mmol), MeOH (26.0 ml), and NaOH (2 N, 14.0 ml) were treated according to II.5. Distillation of the crude material at 50°C (bath)/0.001 Torr provided 316 mg (57%) of **17f** as a colorless liquid. – IR (film): $\tilde{\nu}$ = 3312 cm^{-1} (≡C–H), 2965, 2925, 2854, 2125 (C≡C), 1444, 1426, 1375, 1334, 1313, 1254, 1100, 1052, 1018, 995, 839, 668, 636, 444. – UV (cyclohexane): λ_{max} (lg ε) = 223 nm (4.033). – ^{1}H NMR (CDCl$_3$, 400 MHz): δ = 1.32–1.45 (m, 6H, 3-H$_2$, 4-H$_2$, 5-H$_2$), 1.75, 1.80 (s, each 3H, Me in unknown sequence), 1.99 (t, *J* = 2.7 Hz, 1H, 3″-H), 2.40 (m, 2H, 2-H, 6-H), 2.67 (d, 2H, 1″-H$_2$), 5.20 (m, 1H, 1′-H). – ^{13}C NMR (CDCl$_3$, 100 MHz): δ = 17.52 (t, C-1″), 19.22 (q, C*Me*Me), 20.50 (t, C-3, C-5), 20.79 (s, C-1 or C-7), 21.11 (t, C-4), 22.01 (s, C-1 or C-7), 25.61 (q, CMe*Me*), 44.66 (d, C-2, C-6), 69.36 (d, C-3″), 81.46 (s, C-2″), 119.33 (d, C-1′), 135.76 (s, C-2′). – MS (70 eV), *m/z* (%): 186 (10) [M$^+$], 171 (69), 143 (100), 129 (94), 128 (89), 117 (40), 115 (72), 105 (71), 91 (80), 77 (39). – $C_{14}H_{18}$ (186.3): calcd. C 90.26, H 9.74; found C 90.07, H 9.75. – $C_{14}H_{18}$: calcd. 186.141, found 186.142 (MS).

6. **18f**: **18e** (3.31 g, 13.5 mol), MeOH (115 ml), and NaOH (2 N, 61.7 ml) were treated according to II.5. Distillation of the crude material at 23°C (bath)/0.001 Torr provided 1.23 g (53%) of **18f** as a colorless liquid. – IR (film): $\tilde{\nu}$ = 3311 cm^{-1} (≡C–H), 3084 (=C–H), 2971, 2932, 2856, 2125 (C≡C), 1626, 1527, 1440, 1425, 1376, 1322, 1260, 1168, 994, 985, 906, 866, 636. – UV (cyclohexane): λ_{max} (lg ε) = 229 nm (2.959). – ^{1}H NMR (CDCl$_3$, 80 MHz): δ = 1.36 (m, 6H, 3-H$_2$, 4-H$_2$, 5-H$_2$), 1.71 (s, 3H, Me), 1.96 (t, 1H, 3″-H), 2.61 (m, 2H, 2-H, 6-H), 2.64 (d, 2-H, 1″-H$_2$), 4.66 (m, 2-H, =CH$_2$). – ^{13}C NMR (CDCl$_3$, 100 MHz): δ = 17.20 (t, C-1″), 20.52 (t, C-3, C-5), 20.92 (t, C-4), 21.02 (q, Me), 25.84, 26.79 (s, C-1 and C-7 in unknown sequence), 41.45 (d, C-2, C-6), 69.46 (d, C-3″), 81.14 (s, C-2″), 109.01 (t, =CH$_2$), 141.45 (s, *C*=CH$_2$). – MS (70 eV), *m/z*: 172 (8) [M$^+$], 157 (55), 143 (39), 142 (72), 141 (33), 129 (100), 128 (61), 115 (50), 91 (46), 77 (25). – $C_{13}H_{16}$ (172.3): calcd. C 90.64, H 9.36; found C 90.54, H 9.29. – $C_{13}H_{16}$: calcd. 172.125, found 172.125 (MS).

7. *1-Ethynyl-7-(2-propynyl)tricyclo[4.1.0.0^{2,7}]heptane* (**21f**): **19e** (812 mg, 2.70 mmol), MeOH (12.0 ml), and NaOH (2 N, 4.00 ml) were treated according to II.5. Distillation of the crude material at 20°C (bath)/0.02 Torr provided 329 mg (78%) of **21f** as a colorless liquid. – IR (film): $\tilde{\nu}$ = 3294 cm^{-1} (≡C–H), 2998, 2934, 2858, 2105 (C≡C), 1507, 1442, 1423, 1343, 1333, 1306, 1268, 1248, 989, 935, 865, 642, 582, 481. – UV (cyclohexane): λ_{max} (lg ε) = 213 nm (3.784). – ^{1}H NMR (CDCl$_3$, 400 MHz): δ = 1.22–1.39 (m, 4H, 3-H$_2$, 5-H$_2$), 1.44–1.52 (m, 2H, 4-H$_2$), 2.05 (t, *J* = 2.8 Hz, 1H, 3″-H), 2.07 (s, 1H, 2′-H), 2.68 (m, 2H, 2-H, 6-H), 2.81 (d, 2H, 1″-H$_2$). – ^{13}C NMR (CDCl$_3$, 100 MHz): δ = 17.97 (t, C-1″), 19.80 (t, C-3, C-5), 20.40 (t, C-4), 26.95 (s, C-1 or C-7, the other signal being hidden), 47.71 (d, C-2, C-6), 67.83, 70.22 (d, C-3″ and C-2′ in unknown sequence), 79.92, 82.17 (s, C-1′ and C-2″ in unknown sequence). – MS (70 eV), *m/z* (%): 156 (10) [M$^+$], 155 (56), 153 (29), 141 (86), 129 (31), 128 (78), 127 (31), 117 (23), 115 (100), 63 (23). – $C_{12}H_{12}$ (156.2): calcd. C 92.26, H 7.74; found C 91.55, H 7.68. – $C_{12}H_{11}$ [M – 1]: calcd. 155.086, found 155.086 (MS).

8. *1-Allyl-7-ethynyltricyclo[4.1.0.0^{2,7}]heptane* (**21h**): **19h** (1.013 g, 4.38 mmol), MeOH (22.1 ml), and NaOH (2 N, 6.80 ml) were treated according to II.5. Distillation of the crude material at 22°C (bath)/0.001 Torr provided 325 mg (47%) of **21h** as a colorless liquid. – IR (film): $\tilde{\nu}$ = 3309 cm^{-1} (≡C–H), 3080 (=C–H), 2981, 2933, 2858, 2104 (C≡C), 1641, 1442, 1437, 1248, 982, 915, 840, 667, 637, 584, 563. – UV (cyclohexane): λ_{max} (lg ε) = 211 nm (3.825). – ^{1}H NMR (CDCl$_3$, 400 MHz): δ = 1.22–1.39 (m, 4H, 3-H$_2$, 5-H$_2$), 1.44–1.53 (m, 2H, 4-H$_2$), 2.07 (s, 1H, 2″-H), 2.54 (m, 2H, 2-H, 6-H), 2.60 (d, 2H, 1′-H$_2$), 5.04–5.08, 5.15–5.20 (m, each 1H, 3′-H$_2$), 5.88–5.98 (m, 1H, 2′-H). – ^{13}C NMR (CDCl$_3$, 100 MHz): δ = 20.09 (t, C-3, C-5), 20.18 (s, C-7), 20.46 (t, C-4), 29.18 (s, C-1), 32.70 (t, C-1′), 48.07 (d, C-2, C-6), 67.49 (d, C-2″), 83.43 (s, C-1″), 116.29 (t, C-3′), 135.39 (d, C-2′). – MS (70 eV), *m/z* (%): 158 (5) [M$^+$], 143 (52), 130 (45), 129 (90), 128 (92), 117 (31), 116 (26), 115 (100), 91 (53), 77 (31). – $C_{12}H_{14}$: calcd. 158.109, found 158.101 (MS).

XII. *Methylations, Isomerizations, and Separations*

1. *1,7-Di-1-propynyltricyclo[4.1.0.0^{2,7}]heptane* (**28b**): To **28a** (4.56 g, 15.9 mmol) in THF (25 ml) a solution of MeLi in ether (1.5 M, 30 ml, 45.0 mmol) was added at 0°C. After 30 min at 0°C and 8 h at room temp. a colorless precipitate had formed. Then methyl iodide (6.23 ml, 100 mmol) was added at 0°C. After 16 h at room temp. the reaction mixture was worked up according to II.3. Distillation of the crude material at 48°C (bath)/0.001 Torr provided 2.09 g (77%) of **28b** as a colorless liquid. – IR (film): $\tilde{\nu}$ = 3002 cm^{-1}, 2915, 2856, 2237 (C≡C), 1508, 1442, 1377, 1343, 1329, 1111, 1101, 1032, 905, 894, 851, 788, 656, 473. – UV (cyclohexane): λ_{max} (lg ε) = 233 nm (3.883). – ^{1}H NMR (CDCl$_3$, 80 MHz): δ = 1.25–1.51 (m, 6H, 3-H$_2$, 4-H$_2$, 5-H$_2$), 1.93 (s, 6H, Me), 2.76 (m, 2H, 2-H, 6-H). – ^{13}C NMR (CDCl$_3$, 20 MHz): δ = 3.31 (q, Me), 17.91 (s, C-1, C-7), 18.94 (t, C-3, C-5), 19.39 (t, C-4), 50.43 (d, C-2, C-6), 74.64, 77.00 (s, C-1′, C-1″ and C-2′, C-2″ in unknown sequence). – MS (70 eV), *m/z* (%): 170 (98) [M$^+$], 155 (96), 154 (56), 153 (100), 152 (37), 141 (46), 129 (49), 128 (71), 127 (30), 115 (84). – $C_{13}H_{14}$ (170.3): calcd. C 91.71, H 8.29; found C 91.44, H 8.21. – $C_{13}H_{14}$: calcd. 170.109, found 170.111 (MS).

2. *1,6-Di-1-propynyltricyclo[3.1.0.0^{2,6}]hexane* (**29b**)

a) *1-[(Trimethylsilyl)ethynyl]tricyclo[3.1.0.0^{2,6}]hexane:* BuLi (10.0 ml, 16.0 mmol), **2a** (1.28 g, 16.0 mmol), MgBr$_2$ (2.95 g, 16.0 mmol), NiCl$_2$dppe (84 mg, 160 μmol), chloro(trimethylsilyl)ethyne[25h] (2.12 g, 16.0 mmol), and 1,4-dioxane (4.09 ml, 48.0 mmol) were treated according to ref.[1] (workup after 24 h). Distillation of the crude material at 26°C (bath)/0.001 Torr provided 593 mg (21%) of the product as a colorless liquid. A repetition of this experiment with 64.0 mmol of **2a** and a reaction time of 72 h raised the yield to 46%. – IR (film): $\tilde{\nu}$ = 3051 cm^{-1}, 2957, 2911, 2873, 2158 (C≡C), 1467, 1408, 1288, 1250, 1111, 1020, 991, 909, 862, 842, 813, 759, 719, 698, 638. – UV (cyclohexane): λ_{max} (lg ε) = 201 nm (3.877), 212 (3.748), 220 (3.734), 278 (2.410). – ^{1}H NMR (CDCl$_3$, 400 MHz): δ = 0.17 (s, 9H, SiMe$_3$), 1.24–1.47 (m, 4H, 3-H$_2$, 4-H$_2$), 2.27 (m, 1H, 6-H), 2.47 (m, 2H, 2-H, 5-H). – ^{13}C NMR (CDCl$_3$, 100 MHz): δ = 0.22 (q, SiMe$_3$), 4.37 (s, C-1, this carbon has a significant prolonged relaxation time), 15.73 (d, C-6), 25.22 (t, C-3, C-4), 41.86 (d, C-2, C-5), 86.03, 103.54 (s, C-1′ and C-2′ in unknown sequence). – MS (70 eV), *m/z* (%): 176 (16) [M$^+$], 162 (16), 161 (100), 159 (7), 145 (9), 135 (19), 133 (9), 83 (13), 73 (11). – $C_{11}H_{16}Si$ (176.3): calcd. C 74.93, H 9.15; found C 75.82, H 8.85. – $C_{11}H_{16}Si$: calcd. 176.102, found 176.103 (MS).

b) *1,6-Bis[(trimethylsilyl)ethynyl]tricyclo[3.1.0.0^{2,6}]hexane* (**29a**): BuLi (20.0 ml, 32.0 mmol), product from a) (5.18 g, 29.4 mmol), MgBr$_2$ (5.89 g, 32.0 mmol), NiCl$_2$dppe (169 mg, 320 μmol), chloro(trimethylsilyl)ethyne (4.25 g, 32.0 mmol), and 1,4-dioxane (8.18 ml, 48.0 mmol) were treated as described in XII.2.c. Distillation of the crude material at 74°C (bath)/0.001 Torr provided 879 mg (11%) of **29a** as a colorless liquid. The preceding fraction consisted of 649 mg (13%) of starting compound. – **29a**: IR (film): $\tilde{\nu}$ = 3048 cm^{-1}, 2956, 2897, 2884, 2162 (C≡C), 1407, 1296, 1285, 1252, 974, 914, 908, 857, 840, 758, 717, 697, 640. – UV (cyclohexane): λ_{max} (lg ε) = 243 nm (3.684), 2.93 (2.564). – ^{1}H NMR (CDCl$_3$, 400 MHz): δ = 0.18 (s, 18H, SiMe$_3$), 1.44 (s, 4H, 3-H$_2$, 4-H$_2$), 2.76 (s, 2H, 2-H, 5-H). – ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 0.24 (q, $SiMe_3$), 16.93 (s, C-1, C-6), 25.01 (t, C-3, C-4), 48.75 (d, C-2, C-5), 88.90, 99.32 (s, C-1′, C-1″ and C-2′, C-2″ in unknown sequence). – MS (70 eV), *m/z* (%): 272 (53) [M^+], 258 (13), 257 (51), 197 (7), 184 (11), 183 (21), 169 (25), 159 (7), 74 (8), 73 (100). – $C_{16}H_{24}Si_2$ (272.5): calcd. C 70.51, H 8.88; found C 70.75, H 8.47. – $C_{16}H_{24}Si_2$: calcd. 272.142, found 272.144 (MS).

c) **29b**: **29a** (564 mg, 2.07 mmol) in 25 ml of THF, MeLi (10 ml of a 1.5 M solution in ether, 15.0 mmol), and MeI (2.07 ml, 33.3 mmol) were treated similarly as described in XII.1. Distillation of the crude material at 20°C (bath)/0.001 Torr provided 210 mg (65%) of **29b** as a colorless liquid. – IR (film): ṽ = 3048 cm^{-1}, 2950, 2915, 2871, 2246 (C≡C), 1490, 1467, 1445, 1377, 1331, 1249, 1035, 1018, 912, 893, 827, 467, 450. – UV (cyclohexane). λ_{max} (lg ε) = 233 nm (3.714), 277 (2.569). – ^{1}H NMR ($CDCl_3$, 80 MHz): δ = 1.41 (s, 4H, 3-H_2, 4-H_2), 1.80 (s, 6H, Me), 2.55 (s, 2H, 2-H, 5-H). – ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 4.37 (q, Me), 14.91 (s, C-1, C-6), 25.22 (t, C-3, C-4), 46.56 (d, C-2, C-5), 72.37, 79.93 (s, C-1′, C-1″ and C-2′, C-2″ in unknown sequence). – MS (70 eV), *m/z* (%): 156 (100) [M^+], 155 (43), 154 (21), 153 (47), 152 (24), 141 (73), 129 (25), 128 (45), 127 (24), 115 (79). – $C_{12}H_{12}$: calcd. 156.094, found 156.095 (MS).

3. *Separation of* **5a** *and* **6a**: A solution of ethylmagnesium bromide was prepared from magnesium wires (972 mg, 40.0 mmol) and ethyl bromide (1.50 ml, 20.1 mmol) in 20 ml of ether. 1.94 g (14.7 mmol) of a mixture of **5a** and **6a** (1:0.8 ratio) was added at 30°C. After 3 h at that temp. all volatile materials were removed up to a temp. of 120°C (bath)/0.001 Torr. The ether was removed from the distillate at 0°C (bath)/15 Torr. At 22°C (bath)/0.01 Torr 400 mg (46%) of **6a** was isolated as a colorless liquid. The residue of the first distillation was crushed, digested with 20 ml of ether and subsequently worked up according to II.3. Distillation of the crude material at 22°C (bath)/0.01 Torr provided 990 mg (92%) of **5a** as a colorless liquid. – **6a**: IR (film): ṽ = 2985 cm^{-1}, 2929, 2857, 1949 (C=C=C), 1494, 1444, 1320, 1150, 1061, 1038, 994, 944, 873, 852, 809, 759, 701. – UV (cyclohexane): λ_{max} (lg ε) = 221 nm (3.904). – ^{1}H NMR ($CDCl_3$, 80 MHz): δ = 1.36 (m, 7H, 3-H_2, 4-H_2, 5-H_2, 7-H), 2.55 (m, 2H, 2-H, 6-H), 4.81 (d, 2H, 3′-H_2), 5.43 (t, 1H, 1′-H). – ^{13}C NMR ($CDCl_3$, 20 MHz): δ = 15.99 (d, C-7), 17.75 (s, C-1), 20.51 (t, C-3, C-5), 20.93 (t, C-4), 43.28 (d, C-2, C-6), 76.84 (t, C-3′), 91.68 (d, C-1′), 209.45 (s, C-2′). – MS (70 eV), *m/z* (%): 132 (24) [M^+], 131 (31), 117 (91), 116 (25), 115 (57), 104 (29), 91 (100), 78 (29), 77 (41), 65 (23). – $C_{10}H_{12}$ (132.2): calcd. C 90.85, H 9.15; found C 90.99, H 9.21. – $C_{10}H_{12}$: calcd. 132.094, found 132.093 (MS).

4. *Separation of* **9a** *and* **10a**: Magnesium turnings (2.00 g, 82.3 mmol), ethyl bromide (2.00 ml, 26.8 mmol), 25.0 ml of ether, and the mixture of **9a** and **10a** (1:4) (1.76 g, 14.9 mmol) were treated similarly as described in XII.3. From the crude material that was obtained from the destillate at 0°C (bath)/0.01 Torr 1.05 g (75%) of **10a** could be isolated as a colorless liquid. From the crude material that was obtained from the residue at 0°C (bath)/0.01 Torr 236 mg (67%) of **9a** was isolated as a colorless liquid. – **9a**: IR (film): ṽ = 3308 cm^{-1} (≡C–H), 3038, 2949, 2911, 2871, 2125 (C≡C), 1427, 1322, 1308, 1275, 1108, 985, 882, 853, 833, 813, 771, 730, 693, 636. – UV (cyclohexane): λ_{max} (lg ε) = 217 nm (3.075). – ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.18–1.42 (m, 4H, 3-H_2, 4-H_2, AA′BB′ system), 1.71 (m, 1H, 6-H), 1.96 (t, *J* = 2.8 Hz, 1H, 3′-H), 2.10 (m, 2H, 2-H, 5-H), 2.87 (d, 2H, 1′-H_2). – ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 6.47 (d, C-6), 14.53 (s, C-1), 15.26 (t, C-1′), 26.17 (t, C-3, C-4), 36.72 (d, C-2, C-5), 68.35 (d, C-3′), 82.00 (s, C-2′). – MS (70 eV), *m/z* (%): 118 (10) [M^+], 117 (59), 116 (13), 115 (57), 103 (18), 91 (41), 79 (100), 78 (25), 77 (43). – C_9H_{10} (118.2): calcd. C 91.47, H 8.53; found C 90.66, H 8.42. – C_9H_9 [M – 1]: calcd. 117.070, found 117.067 (MS). – **10a**: IR (film): ṽ = 3040 cm^{-1}, 2949, 2912, 2871, 1953 (C=C=C), 1488, 1468, 1447, 1328, 1295, 1275, 1071, 975, 948, 909, 851, 805, 775, 715. – UV (cyclohexane): λ_{max} (lg ε) = 202 nm (4.078). – ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.34 (m, 4H, 3-H_2, 4-H_2, AA′BB′ system), 1.83 (m, 1H, 6-H), 2.22 (m, 2H, 2-H, 5-H), 4.80 (d, *J* = 6.6 Hz, 2H, 3′-H_2), 5.50 (t, 1H, 1′-H). – ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 12.10 (d, C-6), 14.52 (s, C-1), 25.82 (t, C-3, C-4), 37.89 (d, C-2, C-5), 76.32 (t, C-3′), 87.44 (d, C-1′), 209.60 (s, C-2′). – MS (70 eV), *m/z* (%): 118 (16) [M^+], 117 (100), 116 (16), 115 (65), 103 (17), 91 (55), 79 (29), 78 (17), 77 (26), 65 (13). – C_9H_{10} (118.2): calcd. C 91.47, H 8.53; found C 91.53, H 8.50. – C_9H_9 [M – 1]: calcd. 117.070, found 117.067 (MS).

5. *1-(1-Propynyl)tricyclo[4.1.0.0^{2,7}]heptane* (**30**): A mixture of **5a** and **6a** (4.25 g, 32.1 mmol), KO*t*Bu (425 mg, 3.79 mmol) and DMSO (80.0 ml) was treated according to II.6. Distillation of the crude material at 20°C (bath)/0.01 Torr provided 3.38 g (80%) of **30** as a colorless liquid. – IR (film): ṽ = 2999 cm^{-1}, 2929, 2856, 2235 (C≡C), 1670, 1475, 1458, 1443, 1377, 1330, 1256, 1151, 1106, 1048, 1008, 859, 853, 798, 744. – UV (cyclohexane): λ_{max} (lg ε) = 211 nm (3.682). – ^{1}H NMR ($CDCl_3$, 80 MHz): δ = 1.35 (m, 6H, 3-H_2, 4-H_2, 5-H_2), 1.86 (s, 3H, Me), 1.91 (t, 1H, 7-H), 2.65 (m, 2H, 2-H, 6-H). – ^{13}C NMR ($CDCl_3$, 20 MHz): δ = 3.91 (q, Me), 7.27 (s, C-1), 18.02 (d, C-7), 20.11 (t, C-3, C-5), 20.75 (t, C-4), 45.77 (d, C-2, C-6), 74.84, 78.54 (s, C-1′, C-2′). – MS (70 eV), *m/z* (%): 132 (60) [M^+], 131 (19), 117 (100), 116 (35), 115 (93), 104 (18), 103 (17), 91 (72), 78 (18), 77 (29). – $C_{10}H_{12}$ (132.2): calcd. C 90.85, H 9.15; found C 90.77, H 9.30. – $C_{10}H_{12}$: calcd. 132.094, found 132.096 (MS).

6. *1-(1-Propynyl)tricyclo[3.1.0.0^{2,6}]hexane* (**31**): A mixture of **9a** and **10a** (1.88 g, 15.9 mmol), KO*t*Bu (190 mg, 1.69 mmol), and DMSO (40.0 ml) was treated according to II.6. Distillation of the crude material at 20°C (bath)/0.2 Torr provided 1.41 g (75%) of **31** as a colorless liquid. – IR (film): ṽ = 3047 cm^{-1}, 2949, 2914, 2872, 2238 (C≡C), 1670, 1467, 1447, 1377, 1289, 1270, 1215, 1114, 1037, 952, 909, 859, 835, 771. – UV (cyclohexane): λ_{max} (lg ε) = 203 nm (3.743), 260 (2.520), 270 (2.418). – ^{1}H NMR ($CDCl_3$, 80 MHz): δ = 1.34 (m, *J* = 5 Hz, 4H, 3-H_2, 4-H_2), 1.86 (s, 3H, Me), 2.14 (m, 1H, 6-H), 2.34 (m, 2H, 2-H, 5-H). – ^{13}C NMR ($CDCl_3$, 20 MHz): δ = 4.06 (q, Me), 4.33 (s, C-1), 13.36 (d, C-6), 25.38 (quint, C-3, C-4), 40.59 (d, C-2, C-5), 75.33, 77.03 (s, C-1′ and C-2′ in unknown sequence). – MS (70 eV), *m/z* (%): 118 (65) [M^+], 117 (100), 116 (23), 115 (100), 103 (36), 91 (68), 89 (12), 78 (22), 77 (29), 63 (18). – C_9H_{10} (118.2): calcd. C 91.47, H 8.53; found C 91.18, H 8.49. – C_9H_{10}: calcd. 118.078, found 118.077 (MS).

7. *1-(2-Methyl-1-propenyl)-7-(1-propynyl)tricyclo[4.1.0.0^{2,7}]-heptane* (**32**): A mixture of **17d** and **17e** (1.12 g, 6.01 mmol), KO*t*Bu (100 mg, 891 μmol), and DMSO (10.0 ml) was treated according to II.6. Distillation of the crude material at 50°C (bath)/0.001 Torr provided 783 mg (70%) of **32** as a colorless liquid. – IR (film): ṽ = 2927 cm^{-1}, 2885, 2232 (C≡C), 1668, 1513, 1444, 1375, 1343, 1335, 1108, 1052, 1020, 989, 934, 908, 891, 836, 793, 645. – UV (cyclohexane): λ_{max} (lg ε) = 234 nm (3.597). – ^{1}H NMR ($CDCl_3$, 80 MHz): δ = 1.44 (m, 6H, 3-H_2, 4-H_2, 5-H_2), 1.81 (br. s, 6H, =C*Me*Me, ≡CMe), 1.88 (s, 3H, =CMe*Me*), 2.61 (m, 2H, 2-H, 6-H), 5.20 (m, 1H, 1′-H). – ^{13}C NMR ($CDCl_3$, 20 MHz): δ = 4.12 (q, ≡CMe), 14.93 (s, C-7), 19.54 (q, =C*Me*Me), 20.45 (t, C-3, C-5), 20.81 (t, C-4), 25.59 (q, =CMe*Me*), 29.59 (s, C-1), 49.64 (d, C-2, C-6), 76.06, 76.96 (s, C-1″ and C-2″ in unknown sequence), 119.85 (d, C-1′), 137.27 (s, C-2′). – MS (70 eV), *m/z* (%): 186 (43)

[M$^+$], 171 (85), 156 (49), 143 (100), 142 (37), 141 (46), 129 (66), 128 (81), 115 (57), 91 (58). – $C_{14}H_{18}$: calcd. 186.141, found 186.147 (MS).

☆ Dedicated to Prof. Dr. *Helmut Quast* on the occasion of his 60th birthday.

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