Tetrahedron 64 (2008) 10188–10194

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Novel Mg-organic reagents in organic synthesis. Cp_2TiCl_2 catalyzed intermolecular cyclomagnesiation of cyclic and acyclic 1,2-dienes using Grignard reagents

Vladimir A. D'yakonov *, Aleksey A. Makarov, Askhat G. Ibragimov, Leonard M. Khalilov, Usein M. Dzhemilev

Institute of Petrochemistry and Catalysis, Russian Academy of Sciences, 450075 Ufa, 141 Prospekt Oktyabrya, Russian Federation

ARTICLE INFO

Article history:
Received 22 May 2008
Received in revised form 26 July 2008
Accepted 14 August 2008
Available online 16 August 2008

Keywords:
Metallacycles
Cyclomagnesiation
Allenes
Homogeneous catalysis
Titanium
Dzhemilev reaction

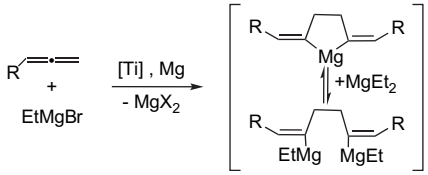
ABSTRACT

High-yield (>80%) catalytic intermolecular cyclomagnesiation of cyclic and acyclic allenes with the aid of Grignard reagents has been realized in the presence of Cp_2TiCl_2. The synthesized unsaturated bi- and tricyclic organomagnesium compounds (OMC) have been successfully converted in situ into thiophenes, unsaturated ketones, cyclic and acyclic hydrocarbons with high regio- and stereoselectivity.

1. Introduction

Discovered by Barbier and Grignard, reaction between organic halogenides and metallic magnesium is one of the most popular and widely used procedures to synthesize organomagnesium compounds (OMC) of various structures. The recorded amount of publications is devoted to the synthesis and application of OMC obtained by this classic method.[1] The reaction has a number of limitations, which are connected with the usage of hydrocarbon halides of certain structures, capable of reacting with magnesium. Apart from the hydrocarbon halide, the presence of functional groups influences the selectivity of OMC formation. Introduction of metal complex catalysis allows the scope of Grignard reagents applicability to be expanded and to elaborate promising procedures for practical utilization based on hydro-, carbo-, and cyclomagnesiation reactions of unsaturated compounds.[2] Among these, the catalytic cyclomagnesiation reaction of unsaturated compounds (Dzhemilev reaction), in our opinion, is worthy to consider as an effective procedure to obtain cyclic OMC with high regio- and stereoselectivity[2a,3] giving rise in situ to hard-to-reach carbocyclic and heterocyclic compounds as well as bifunctional ones.[4] Substrates such as α-olefins,[2g,3b,3e] terminal allenes,[2c,5] acetylenes,[6] norbornenes,[3c] and α,ω-dienes[2f,3f] have been used as examples to study this reaction.

Earlier[2c] we gave details concerning facile preparation of 2,5-dialkylidenemagnesacyclopentanes (and/or 1,4-dimagnesium compounds) with quantitative yields via the interaction between terminal allenes and Grignard reagents in the presence of chemically activated magnesium and catalytic Cp_2TiCl_2 (Scheme 1).



Scheme 1. Cyclomagnesiation of terminal 1,2-dienes.

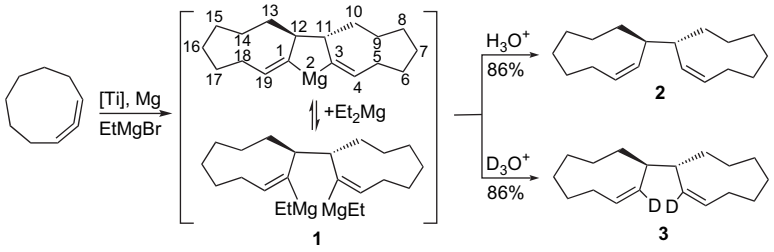
Herein we report on the results of our further investigations in the field of cyclic 1,2-dienes' cyclomagnesiation in the presence of Grignard reagents and Cp_2TiCl_2 as a catalyst.

2. Results and discussion

We established that cyclic 1,2-dienes undergo the catalytic cyclomagnesiation reaction. Thus, cyclonona-1,2-diene was found

* Corresponding author. Tel./fax: +7 347 2312750.
E-mail addresses: ink@anrb.ru, dyakonovva@rambler.ru (V.A. D'yakonov).

0040-4020/$ – see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2008.08.041



Scheme 2. Intermolecular cyclomagnesiation of cyclonona-1,2-diene.

to enter readily into the reaction with EtMgBr in the presence of metallic Mg (acceptor of halogenide ions) and Cp_2TiCl_2 catalyst at ambient temperature (5 mol %, Et_2O, 4 h) to produce 2-magnesatricyclo[10.7.0^{1,12}.0^{3,11}]nonadeca-3(4),19-diene (and/or 1,4-dimagnesium compound) **1**. Acid hydrolysis and deuterolysis of OMC **1** led to (2*Z*,2′*Z*)-1,1′-bi(cyclonon-2-ene) **2** and (2*Z*,2′*Z*)-2,2′-dideutero-1,1′-bi(cyclonon-2-ene) **3** in yields >85% (Scheme 2).

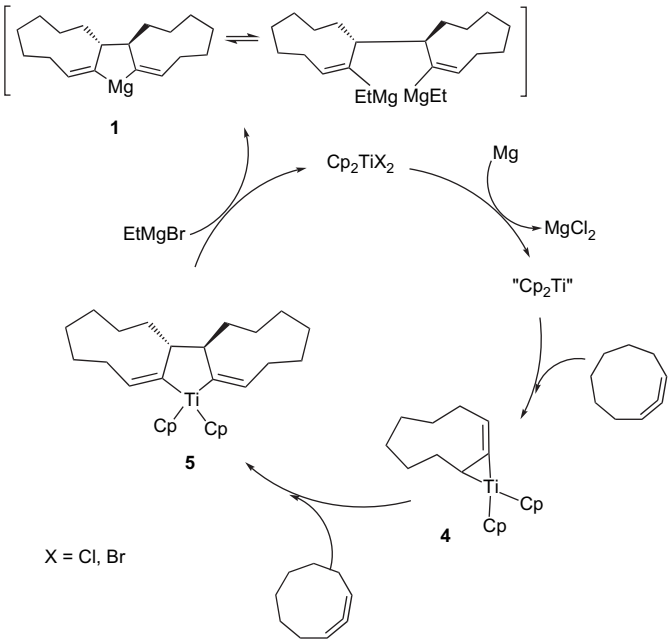
In the ^{13}C NMR spectrum of hydrocarbon **2** one could observe nine signals of non-equivalent carbon atoms. Two downfield signals (δ 129.0 and 134.2 ppm) were assigned to the internal bond located at the allylic position toward tertiary C1 or C1′ atom (δ 42.2 ppm) in the cyclononene fragment. The spectrum also contains six peaks at δ 25–32 ppm attributed to the methylene carbon atoms of a cyclic moiety. Mass spectrum of **2** exhibits the signal of molecular ion M^+ 246. On the base of the spectroscopic data obtained compound **2** was identified as (2*Z*,2′*Z*)-1,1′-bi(cyclonon-2-ene).

In the ^{13}C NMR spectrum of hydrocarbon **3**, which was a result of OMC **1** deuterolysis, one could observe the triplet splitting of equivalent C2(C2′) atoms at 133.8 ppm on D atom (J_{CD}=22.3 Hz). Deuterium isotope effect on α-atoms was −0.43 ppm. In the ^{1}H NMR spectrum there is no signal at 5.2 ppm of protons attached to C2(C2′) atoms. In the MS spectrum of compound **3** the intensive peak for the molecular ion M^+ 248 was found, thus proving the structure of (2*Z*,2′*Z*)-2,2′-dideutero-1,1′-bi(cyclonon-2-ene). Two symmetrical deuterium atoms in the molecule of **3** at C2 and C2′ gave evidence about the formation of magnesacyclopentane **1** (and/or 1,4-dimagnesium compound).

Cyclomagnesiation of cyclonona-1,2-diene was practically completed within 3–4 h in diethyl ether. The yield of OMC **1** was not more than 5–8% in THF. The reaction does not proceed without Mg at all. The decrease in the catalyst amounts from 5 to 2 mol % and increase in the reaction duration to 20 h caused a decrease in the yield of the products to 64%. The use of MeMgBr, EtMgCl, EtMgI, *i*-PrMgBr, *n*-BuMgBr, or *i*-BuMgBr instead of EtMgBr did not substantially influence the yield of the cyclomagnesiation products.

The findings obtained and the data reported allow us to propose the mechanistic scheme of OMC **1** formation, which includes the reduction of Cp_2TiCl_2 to 'Cp_2Ti' in the presence of chemically activated magnesium with consecutive coordination of an allene molecule to a central atom of the catalyst to afford titanacyclopropane intermediate **4**. The formation of the latter was circumstantially proven by the presence of cyclononene and 2,3-dideuterocyclononene identified by means of mass spectrometry in the hydrolysis and deuterolysis products, respectively. The subsequent insertion of the second nonadiene molecule into the active Ti–C bond led to titanacyclopentane intermediate **5**, the transmetallation of which with a Grignard reagent at the final reaction gave OMC **1** (Scheme 3).

Apparently, the high regioselectivity of the reaction is the result of electron density excess on the sp-hybridized carbon atom of cyclonona-1,2-diene and π–d interaction between the electrons of the allene double bond and the vacant Ti atom d-orbital. This can promote a certain spatial orientation of the cyclonona-1,2-diene molecule relative to the central atom of the catalyst to give titanacyclopentane **5** intermediate with double bond located at the vinyl position toward the titanium atom of cyclononene moiety.

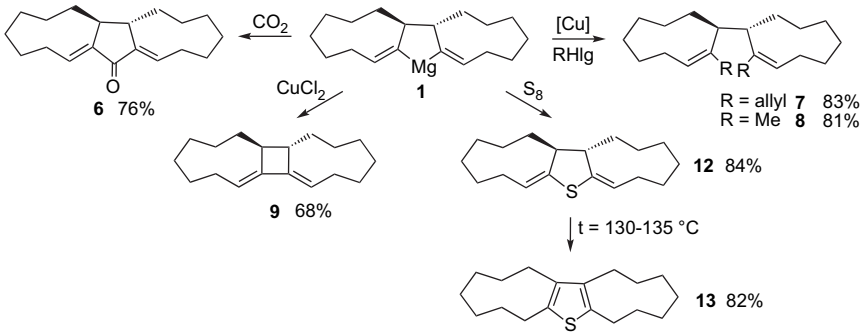


Scheme 3. The mechanistic scheme proposed for the cyclomagnesiation reaction.

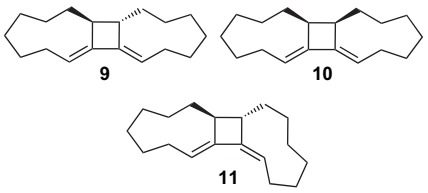
For the more conclusive evidence of the OMC **1** structure and also to elaborate novel 'one-pot' methods to synthesize hard-to-reach carbo- and heterocyclic compounds, we performed a series of transformations for OMC **1** with allyl chloride, methyl iodide, copper(II) chloride, carbon(IV) oxide, and element sulfur (Scheme 4).

By moderate bobbling of the dried carbon(IV) oxide through the reaction mixture containing OMC **1** the unsaturated tricyclic ketone **6** has been obtained in 76% yield. The cross-coupling reaction of prepared in situ magnesacyclopentane (and/or 1,4-dimagnesium compound) **1** with organic halides (Me iodide, allyl chloride) in the presence of catalytic CuCl (10 mol %) gave rise to 2,2′-dimethyl-1,1′-bi(cyclonon-2-en-1-yl) **7** and 2,2′-diallyl-1,1′-bi(cyclonon-2-en-1-yl) **8** in yields of 81 and 83%, respectively.

Analogous to that already reported on the transformations of substituted aluminacyclopentanes to appropriate cyclobutanes in the presence of $CuCl_2$, we have succeeded in synthesizing (10*R*,11*S*)-tricyclo[9.7.0^{1,11}.0^{2,10}]octadeca-2(3),18-diene **9** in 68% yield via intramolecular carbocyclization of OMC **1**. In accordance with the reported data,[7,8] both thermal and catalytic (2π+2π)-cyclodimerization of cyclonona-1,2-diene resulted in the formation of complex mixture containing three stereoisomers **9**–**11** (Scheme 5), in which the maximum content of diastereoisomer **9** was not more than 63% (Table 1).



Scheme 4. Some transformations of OMC **1**.



Scheme 5.

Table 1
Comparative diastereomerical product yields in cyclonona-1,2-diene cyclodimerization

Method	'Diastereomerical purity' (%)		
	9	**10**	**11**
Thermal[9]	63	31	6
Catalytic[10]	57	22	8
Proposed	100	0	0

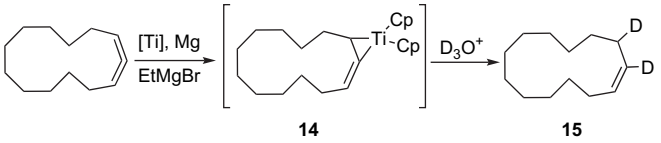
As is evident, the method, which we propose, can be used to synthesize 'diastereomerically pure' (10*R*,11*S*)-tricyclo-[9.7.0^{1,11}.0^{2,10}]octadeca-2(3),18-diene **9**. The structure of **9** was proven by spectroscopic methods and also by comparison of physico-chemical constants of compound **9** obtained according to the procedure described.[7a] The (*R*,*S*)-configurations of C11 and C12 atoms in hydrocarbon **9** enables us to unambiguously define the configuration of chiral centers at C11 and C12 atoms of OMC **1** and also define its structure as (11*R*,12*S*)-2-magnesa-tricyclo[10.7.0^{1,12}.0^{3,11}]nonadeca-3(4),19-diene.

The interaction between OMC **1** and element sufur S_8 was shown to afford thiophane **12** in 84% yield. The latter, as it has become clear, isomerizes quantitatively to give thiophene **13** while heating to 130–140 °C.

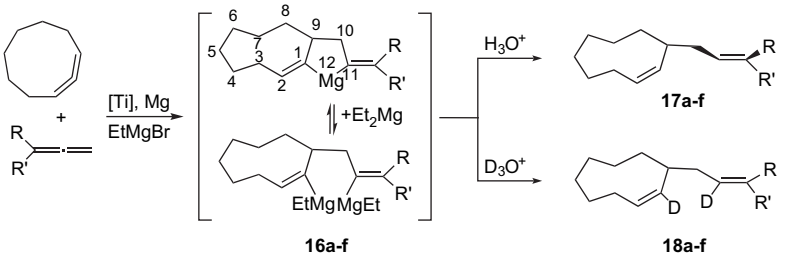
We regret to say that all attempts to involve cyclotrideca-1,2-diene into intermolecular cyclomagnesiation reaction under reaction conditions elaborated for cyclonona-1,2-diene failed. Allene conversion did not exceed 25%. The CS/MS analysis of product contents after quenching the reaction mixture with 10% DCl in D_2O showed under chosen conditions the presence of dideuterocyclotridecene **15** together with monodeuterocyclotridecene—the minor mixture component (3–5%). Apparently, the cyclomagnesiation reaction stops because of steric influence at the stage of titanacyclopropane intermediate **14** or it is a result of greater ring strain in 1,2-cyclononadiene and a greater thermodynamic driving force for the formation of its complex with Ti(II) that results in greater reactivity in our reaction (Scheme 6).

Further, after obtaining successful results on intermolecular cyclomagnesiation of cyclic 1,2-dienes, we attempted to involve cyclic and acyclic 1,2-dienes into combined cyclomagnesiation with the aid of Grignard reagents and Cp_2TiCl_2 catalyst. The realization of this reaction, as we supposed, would allow us to elaborate the method for obtaining bicyclic alkylidenmagnesacyclopentanes (and/or 1,4-dimagnesium compounds) not described previously.

At the first stage, we investigated combined cyclomagnesiation of cyclonona-1,2-diene and hepta-1,2-diene with an excess amount of EtMgBr in the presence of chemically activated Mg and Cp_2TiCl_2 catalyst at the cyclonona-1,2-diene/hepta-1,2-diene/EtMgBr/Mg/Cp_2TiCl_2 molar ratio of 10:10:40:24:1 under chosen conditions (Et_2O, 4 h, rt). As a result, 11-pentalidene-12-magnesabicyclo[7.3.0^{1,9}]dodec-1(2)-ene (and/or 1,4-dimagnesium compound) **16a** has been obtained in 88% yield. As the minor component of the resultant mixture the products of cyclonona-1,2-diene and hepta-1,2-diene homocyclomagnesiation, the total content of which does not exceed 5–8%, was found also to produce in a 1:1 ratio (Scheme 7).

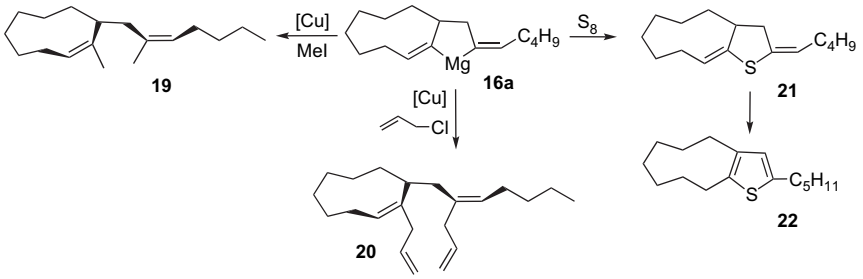


Scheme 6. Cyclomagnesiation of cyclotrideca-1,2-diene.



[Ti] = Cp_2TiCl_2; **a**: R = *n*-C_4H_9, R' = H; **b**: R = *n*-C_6H_{13}, R' = H; **c**: R = Ph, R' = H; **d**: R = Bn, R' = H; **e**: R = *n*-C_5H_{11}, R' = CH_3; **f**: R = Ph, R' = CH_3.

Scheme 7. Combined cyclomagnesiation of cyclonona-1,2-diene and terminal 1,2-dienes.



Scheme 8. Transformations of OMC **16a**.

The structure of OMC obtained has been proven by analysis of the ^{1}H and ^{13}C NMR spectra of hydrolysis **17** and deuterolysis **18** products.

The compounds **17a–f** and **18a–f** were analyzed by one-dimensional (NMR ^{1}H, ^{13}C, Dept 135°) and two-dimensional experiments (HH COSY, HSQC, HMBC). Based on experiments carried out, the complete reference of signals in the ^{1}H and ^{13}C NMR spectra has been made, which allows unambiguous exterminating of the position and types of bondings in cyclic and acyclic fragments. Thus, the allyl position of alkenyl substituents in compounds **16a**,**b** is confirmed by the presence of cross-peaks between the proton at C1 (δ 5.52 ppm) and the C3 atoms in HMBC spectra. Besides, *Z*-configuration of double bonds at C1 and C11 atoms is unambiguously determined by the magnitude of vicinal spin–spin interaction constant (SSIC) as ^3J (H(C1), H(C2))=10 Hz and ^3J (H(C11), H(C12))=11 Hz.[9]

The position of the deuterium atom at C2 and C11 atoms in the partially deuterized compounds **17a**,**b** is determined by the absence of the appropriate proton signals at δ 5.15 and 5.34 ppm, and also by triplet signals due to carbon C2 and C11 splitting ($^1J_{CD}$=23 Hz), which ^{13}C NMR spectra exhibit.

Together with hepta-1,2-diene, phenyl-, benzyl-, and hexylallene have been involved in combined intermolecular cyclomagnesiation reaction with cyclonona-1,2-diene. These reactions were established to proceed with retention of appropriateness described above.

High regio- and stereospecificity of the reaction was observed also in the case, when in the combined cyclomagnesiation with cyclonona-1,2-diene 3,3-disubstituted allenes were implicated. Based on the example of the reaction of cyclonona-1,2-diene with 3-methyl-3-phenyl- and 3-methyl-3-amylallene, it was shown that double bond in the side chain moiety has also *Z*-configuration. This fact was concluded by the proton transfer from C11 (δ 5.48 ppm) onto the cis methyl substituent at C12 (δ 2.03 ppm) atom from NOESY spectrum for compounds **17e**,**f**. In partially deuterized analogs **18e**,**f** there are no signals at δ 5.5 and 5.1 ppm characteristic of the proton at C11 and of the C2 proton attached to the double bond in cyclononane fragment.

By the analogy with tricyclic OMC **1** we have synthesized new bicyclic alkylidenmagnesacyclopentanes (and/or dimagnesium compounds) and examined its reactivity in cross-coupling reactions with different organic halogenides and S_8. The aforesaid reactions were shown to afford bifunctional and also carbo- and heterocyclic compounds **19–21** involving two active Mg–C bonds (Scheme 8).

The cross-coupling reaction of OMC **16a** and MeI was shown to proceed with retention of the *Z*-configuration of double bonds in the molecule of **19**. Thus, in the ^{13}C NMR spectrum of **19** one could observe the bands belonging to two trisubstituted bonds located in the cyclic fragment and in the side chain as well. The position of the double bond at the C2 atom is confirmed by the correlation peak between protons of methyl groups at 1.57 ppm and methine carbon at 37.1 ppm in two-dimensional HMBC spectrum for compound **19**. The *Z*-configuration of the double bond between C1 and C2 in the cyclic fragment was concluded from the presence of cross-peaks between the methyl group protons at C2 (δ 1.57 ppm) and H(C1) at 5.41 ppm from the two-dimensional NOESY spectrum. The position of the double bond in the side chain was confirmed by cross-peaks between protons of the allylic methylene group at C10 (δ 36.2 ppm) and the methyl group protons at 1.69 ppm from the HMBC experiment. The presence of cross-peaks between the cis-located proton at C12 (δ 5.16 ppm) and the methyl group protons at C11 (δ 1.69 ppm) in the NOESY spectrum is the direct proof, indicating *Z*-configuration of the double bond.

3. Conclusions

Therefore, we have performed for the first time intermolecular cyclomagnesiation of cyclonona-1,2-diene and terminal allenes with the aid of Grignard reagents in the presence of Cp_2TiCl_2 as catalyst. As a result, the unsaturated bi- and tricyclic OMCs (and/or 1,4-dimagnesium compounds) have been synthesized, which, as was shown in a number of examples, can be successfully used to obtain carbocyclic, heterocyclic, and bifunctional compounds of the assigned structures.

4. Experimental section

4.1. General

All solvents were dried (hexane over $LiAlH_4$, Et_2O and THF over Na) and freshly distilled before use. All reactions were carried out under a dry argon atmosphere. The reaction products were analyzed using chromatography on a 'Chrom-5' instrument (1200×3 mm column packed with 5% of SE-30 and 15% PEG-6000 on Chromaton N-AW, carrier gas: He). The IR spectra were recorded on Specord 75-IR. Mass spectral measurements were performed on a Finnigan-4021 spectrometer at 70 eV and working temperature 200 °C. Elemental analysis of samples was determined on Carlo Erba, model 1106. The ^{1}H and ^{13}C NMR spectra were recorded as $CDCl_3$ solutions on spectrometer 'Bruker Avance-400' (100 MHz for ^{13}C and 400 MHz for ^{1}H). The chemical shifts are reported as δ values in parts per million relative to internal standard Me_4Si. ^{13}C NMR spectra were edited by *J*-modulation (JMOD) on CH constants. Individuality and purity of the synthesized compounds were controlled with the use of TLC on Silufol UV-254 plates, I_2 was used as a developer.

4.2. (2*Z*,2′*Z*)-1,1′-Bi(cyclonon-2-ene) (2)

A 50 mL glass reactor was charged with chemically activated (with EtBr or I_2) Mg (12 mmol), EtMgBr (2 M solution in diethyl ether, 22 mmol), Cp_2TiCl_2 (0.5 mmol), and cyclonona-1,2-diene (10 mmol) under a dried argon atmosphere at 0 °C. The resulting

solution was allowed to warm to rt and stirred for 4 h. The reaction mixture (crude **1**) was quenched with an 8–10% aqueous solution of HCl (or DCl, 10–12% solution in D_2O). The organic layer was diluted with hexane, separated, and dried over $MgSO_4$. Evaporation and vacuum distillation gave **2** (2.1 g, 86%) as a colorless liquid, bp 138–140 °C (1 Torr). ^{1}H NMR (400 MHz, $CDCl_3$): δ=5.48 (m, 2H), 5.20 (m, 2H), 2.36 (m, 2H), 2.19 (m, 2H), 1.99 (m, 2H), 1.18–1.61 (m, 20H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ=134.2, 128.9, 42.2, 31.9, 26.7, 26.4, 26.0, 25.9, 25.2 ppm. IR (film): 1620, 1450, 1370, 710 cm^{-1}. MS (70 eV, EI): *m*/*z* 246 $[M]^+$ (5), 218 (2), 189 (2), 175 (3), 149 (7), 135 (5), 123 (16), 91 (19), 81 (100), 79 (36), 67 (59), 55 (25), 41 (32). $C_{18}H_{30}$ (246.4): calcd C 87.73, H 12.27; found C 87.65, H 12.24.

4.3. (2*Z*,2′*Z*)-2,2′-Dideutero-1,1′-bi(cyclonon-2-ene) (3)

Yield: 2.1 g, 86%, as a colorless liquid, bp 138–140 °C (1 Torr). ^{1}H NMR (400 MHz, $CDCl_3$): δ=5.51 (t, *J*=7.6 Hz, 2H), 2.37 (m, 2H), 2.19 (m, 2H), 2.0 (m, 2H), 1.21–1.62 (m, 20H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ=133.8 (t, J_{CD}=22.3 Hz), 128.8, 42.1, 31.9, 26.6, 26.4, 26.0, 25.9, 25.2 ppm. IR (film): 2160 (ν_{C-D}) cm^{-1}. MS (70 eV, EI): *m*/*z* 248 $[M]^+$ (6), 207 (4), 191 (3), 177 (4), 151 (6), 136 (9), 124 (61), 93 (18), 82 (100), 81 (87), 68 (55), 67 (60), 56 (25), 55 (43), 42 (34), 41 (54). $C_{18}H_{28}D_2$ (248.4): calcd C 87.02, H 11.36, D 1.62; found C 86.84, H+D 12.92.

4.4. (11*R*,12*S*)-2-Oxotricyclo[10.7.0^{1,12}.0^{3,11}]nonadeca-3(4),19-diene (6)

Through crude **1** the dried CO_2 (two-fold excess toward EtMgBr) was bubbled. The reaction mixture was allowed to warm to 20 °C and stirred for 1 h. The reaction mixture was quenched with an 8–10% (aq) solution of HCl. The layers were separated and the aqueous phase was extracted with Et_2O or hexane. The organic layer was diluted with hexane, separated, and dried over $MgSO_4$. The product **6** was isolated by column chromatography on silica gel (40–100 mesh grade) with hexane/ethylacetate (50:1) as eluent. Yield: 2.0 g, 76%, as a colorless liquid, R_f=0.43. ^{1}H NMR (400 MHz, $CDCl_3$): δ=6.54 (t, *J*=6.2 Hz, 2H), 2.5 (m, 1H), 2.0–2.17 (m, 6H), 1.45 (m, 5H), 1.24–1.63 (m, 9H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ=194.9, 143.0, 137.6, 47.4, 34.9, 27.9, 26.6, 26.0, 25.4, 24.3 ppm. IR (film): 1600, 1460, 1380 cm^{-1}. MS *m*/*z*: 272 (M^+). $C_{19}H_{28}O$ (272.4): calcd C 83.77, H 10.36, O 5.87; found C 83.71, H 10.37, O 5.89.

4.5. 2,2′-Diallyl-1,1′-bi(cyclonon-2-en-1-yl) (7)

To crude **1** at −20 °C, CuCl (1 mmol) and allyl chloride (30 mmol) were added dropwise. The reaction mixture was allowed to warm to 20 °C and stirred for 6 h. The reaction mixture was quenched with an 8–10% (aq) solution of HCl. The layers were separated and the aqueous phase was extracted with Et_2O or hexane. The organic layer was diluted with hexane, separated, and dried over $MgSO_4$. Evaporation and vacuum distillation gave **7** (yield 2.7 g, 83%) as a colorless oil, bp 154–155 °C (0.1 Torr). ^{1}H NMR (400 MHz, $CDCl_3$): δ=5.79 (m, 2H), 5.28 (t, *J*=8.0 Hz, 2H), 4.99 (d, *J*=8.8 Hz, 4H), 2.74 (m, 2H), 2.59 (d, *J*=8.0 Hz, 4H), 2.06 (m, 2H), 2.17 (m, 2H), 1.42–1.69 (m, 20H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ=140.9, 137.9, 125.4, 115.4, 42.2, 35.0, 30.7, 27.0, 26.9, 26.7, 26.6, 24.2 ppm. IR (film): 1610, 1450, 1410, 1360, 690 cm^{-1}. MS *m*/*z*: 326 (M^+). $C_{24}H_{38}$ (326.5): calcd C 88.27, H 11.73; found C 88.03, H 11.71.

4.6. 2,2′-Dimethyl-1,1′-bi(cyclonon-2-en-1-yl) (8)

Yield: 2.2 g, 81%, as a colorless liquid, bp 154–156 °C (1 Torr). ^{1}H NMR (400 MHz, $CDCl_3$): δ=5.42 (t, *J*=8 Hz, 2H), 2.95 (m, 2H), 2.01–2.10 (m, 4H), 1.59 (s, 6H), 1.21–1.62 (m, 20H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ=137.9, 126.3, 39.7, 31.8, 27.7, 27.3, 27.2, 26.9, 23.5, 18.3 ppm. IR (film): 1650, 1450, 1370 cm^{-1}. MS *m*/*z*: 274 (M^+). $C_{20}H_{34}$ (274.5): calcd C 87.51, H 12.49; found C 87.43, H 12.47.

4.7. (10*R*,11*S*)-Tricyclo[9.7.0^{1,11}.0^{2,10}]octadeca-2(3),18-diene (9)

To crude **1** at 0 °C, dried $CuCl_2$ (15 mmol) was added. The reaction mixture was allowed to warm to 20 °C and stirred for 1 h. The reaction mixture was quenched with an 8–10% (aq) solution of HCl. The layers were separated and the aqueous phase was extracted with Et_2O or hexane. The organic layer was diluted with hexane, separated, and dried over $MgSO_4$. Evaporation and vacuum distillation gave **9** (1.7 g, 68% yield) as colorless needles, mp 81–83 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ=5.54 (t, *J*=8 Hz, 2H), 2.17 (m, 4H), 2.20 (m, 2H), 1.87 (m, 4H), 1.46–1.54 (m, 12H), 1.27 (m, 4H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ=145.4, 116.1, 49.7, 31.4, 30.2, 28.9, 28.2, 26.9, 20.8 ppm. MS (70 eV, EI): *m*/*z* 244 $[M]^+$ (23), 215 (7), 201 (11), 187 (17), 173 (17), 161 (16), 148 (24), 133 (28), 119 (25), 105 (37), 91 (100), 79 (74), 67 (50), 55 (43), 41 (64). $C_{18}H_{28}$ (244.4): calcd C 88.45, H 11.55; found C 88.31, H 11.52.

4.8. (7*E*,8a*E*)-1,2,3,4,5,6,10,11,12,13,14,15,15a,15b-Tetradecahydrodicyclonona[*b*,*d*]thiophene (12)

To crude **1** at 0 °C, S_8 (15 mmol) was added. The reaction mixture was allowed to warm to 20 °C and stirred for 8 h. The reaction mixture was quenched with an 8–10% (aq) solution of HCl. The layers were separated and the aqueous phase was extracted with Et_2O or hexane. The organic layer was diluted with hexane, separated, and dried over $MgSO_4$. The product was isolated by column chromatography on silica gel (40–100 mesh grade) with hexane as eluent. Yield 2.3 g, 84%, as a light yellow oil, R_f=0.45. ^{1}H NMR (400 MHz, $CDCl_3$): δ=5.41 (dd, *J*=10.0, 7.2 Hz, 2H), 2.71 (m, 2H), 2.20 (m, 4H), 1.61 (m, 4H), 1.28–1.51 (m, 16H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ=142.5, 120.1, 51.9, 32.9, 28.1, 26.6, 25.8, 25.2, 24.5 ppm. MS *m*/*z*: 276 (M^+). $C_{18}H_{28}S$ (276.4): calcd C 78.19, H 10.21, S 11.60; found C 78.03, H 10.16, S 11.56.

4.9. 1,2,3,4,5,6,7,8,9,10,11,12,13,14,15-Tetradecahydrodicyclonona[*b*,*d*]thiophene (13)

Yield: 2.3 g, 98%, as a yellow oil, bp 180–182 °C (1 Torr). ^{1}H NMR (400 MHz, $CDCl_3$): δ=2.83 (t, *J*=6.4 Hz, 4H), 2.59 (t, *J*=6.0 Hz, 4H), 1.68 (m, 4H), 1.62 (m, 4H), 1.48 (m, 4H), 1.41 (m, 8H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ=137.5, 135.6, 29.4, 27.4, 27.3, 26.6, 26.1, 24.8, 24.2 ppm. MS *m*/*z*: 276 (M^+). $C_{18}H_{28}S$ (276.4): calcd C 78.19, H 10.21, S 11.60; found C 78.06, H 10.18, S 11.55.

4.10. Interaction between cyclonona-1,2-diene and terminal allenes in the presence of EtMgHlg (Hlg=Cl, Br) and Cp_2TiCl_2 catalyst

A glass reactor under atmosphere of dry argon at ~0 °C was charged under stirring with chemically activated Mg (24 mmol), Cp_2TiCl_2 (1.0 mmol), cyclonona-1,2-diene (10 mmol), terminal allene (10 mmol), and EtMgHlg (Hlg=Cl, Br) (40 mmol, 2 M solution in Et_2O). The temperature was raised to ambient (20–22 °C), and the mixture was stirred for 4 h. The reaction mixture (crude **16a**–**f**) was quenched with an 8–10% (aq) solution of HCl (or DCl, 10–12% solution in D_2O). The organic layer was diluted with hexane, separated, and dried over $MgSO_4$. Evaporation and vacuum distillation furnished the target products **17a**–**f** or **18a**–**f**.

*4.10.1. (Z)-3-((Z)-Hept-2-enyl)cyclonon-1-ene (**17a**)*

Yield: 3.8 g, 88%, as a colorless liquid, bp 102–103 °C (1 Torr). ^{1}H NMR (400 MHz, $CDCl_3$): δ=5.52 (d, *J*=10.0 Hz, t, *J*=8.0 Hz, 1H), 5.36

(d, J=10.8 Hz, t, J=7.0 Hz, 1H), 5.34 (d, J=10.8 Hz, t, J=6.2 Hz, 1H), 5.15 (d, J=9.0 Hz, t, J=10.1 Hz, 1H), 2.5 (m, 1H), 2.0–2.17 (m, 6H), 1.45 (m, 5H), 1.24–1.63 (m, 9H), 091 (t, J=7.0 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ=135.4, 130.8, 129.6, 128.5, 37.5, 35.0, 33.7, 32.1, 27.3, 27.0, 26.7, 26.3, 26.2, 24.8, 22.6, 14.2 ppm. IR (film): 1620, 1440, 1370, 700 cm^{-1}. MS m/z: 220 (M^+). $C_{16}H_{28}$ (220.4): calcd C 87.19, H 12.81; found C 86.99, H 12.79.

*4.10.2. (Z)-2-Deutero-3-((Z)-2-deuterohept-2-enyl)cyclonon-1-ene (**18a**)*

Yield: 3.8 g, 88%, as a colorless liquid, bp 102–103 °C (1 Torr). ^{1}H NMR (400 MHz, $CDCl_3$): δ=5.52 (t, J=8.0 Hz, 1H), 5.36 (t, J=8.0 Hz, 1H), 2.49 (m, 1H), 2.05–2.18 (m, 6H), 1.20–1.54 (m, 12H), 1.63 (m, 2H), 0.89 (t, J=7.0 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ=135.0 (t, J_{CD}=23.0 Hz), 130.7, 129.5, 128.1 (t, J_{CD}=23.0 Hz), 37.4, 34.9, 33.7, 32.1, 27.3, 27.0, 26.7, 26.3, 26.2, 24.8, 22.6, 14.1 ppm. IR (film): 2160 (ν_{C-D}) cm^{-1}. MS m/z: 222 (M^+). $C_{16}H_{26}D_2$ (222.4): calcd C 86.41, H 11.78, D 1.81; found C 86.37, H+D 13.57.

*4.10.3. (Z)-3-((Z)-Non-2-enyl)cyclonon-1-ene (**17b**)*

Yield: 4.2 g, 84%, as a colorless liquid, bp 131–133 °C (1 Torr). ^{1}H NMR (400 MHz, $CDCl_3$): δ=5.54 (d, J=10.0 Hz, t, J=8.0 Hz, 1H), 5.37 (d, J=10.8 Hz, t, J=7.0 Hz, 1H), 5.33 (d, J=10.8 Hz, t, J=6.2 Hz, 1H), 5.15 (d, J=9.0 Hz, t, J=10.1 Hz, 1H), 2.5 (m, 1H), 2.0–2.18 (m, 6H), 1.45 (m, 5H), 1.22–1.64 (m, 13H), 091 (t, J=7.0 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ=135.4, 130.9, 129.6, 128.4, 37.5, 35.1, 33.7, 32.1, 29.0, 29.1, 27.3, 27.0, 26.7, 26.2, 26.1, 24.8, 22.5, 14.1 ppm. IR (film): 1610, 1450, 1365, 710 cm^{-1}. MS m/z: 248 (M^+). $C_{18}H_{32}$ (248.4): calcd C 87.02, H 12.98; found C 86.86, H 12.97.

*4.10.4. (Z)-2-Deutero-3-((Z)-2-deuteronon-2-enyl)cyclonon-1-ene (**18b**)*

Yield: 4.2 g, 84%, as a colorless liquid, bp 131–133 °C (1 Torr). ^{1}H NMR (400 MHz, $CDCl_3$): δ=5.54 (t, J=8.0 Hz, 1H), 5.35 (t, J=8.0 Hz, 1H), 2.49 (m, 1H), 2.04–2.18 (m, 6H), 1.64 (m, 2H), 1.21–1.56 (m, 16H), 0.91 (t, J=7.0 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ=135.1 (t, J_{CD}=23.0 Hz), 130.8, 129.5, 128.2 (t, J_{CD}=23.5 Hz), 37.4, 35.0, 33.8, 32.1, 29.1, 29.2, 27.3, 27.1, 26.7, 26.5, 26.2, 24.7, 22.6, 14.0 ppm. IR (film): 2160 (ν_{C-D}) cm^{-1}. MS m/z: 250 (M^+). $C_{16}H_{26}D_2$ (250.4): calcd C 86.32, H 12.07, D 1.61; found C 86.28, H+D 13.67.

*4.10.5. (Z)-3-((Z)-Phenylprop-2-enyl)cyclonon-1-ene (**17c**)*

Yield: 3.8 g, 79%, as a colorless oil, bp 144–146 °C (1 Torr). ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.01–7.35 (m, 5H, Ph), 6.51 (d, J=8 Hz, 1H), 5.48 (m, 1H), 5.20 (m, 1H), 5.11 (m, 1H), 2.53 (m, 1H), 1.94–2.17 (m, 6H), 1.42–1.71 (m, 8H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ=136.6, 135.1, 133.8, 129.6, 128.05, 128.0, 126.4, 126.3, 37.5, 36.6, 33.5, 26.9, 26.5, 26.3, 26.1, 25.7 ppm. IR (film): 3050, 1620, 1460, 1370, 720 cm^{-1}. MS m/z: 240 (M^+). $C_{18}H_{24}$ (240.4): calcd C 89.94, H 10.06; found C 89.81, H 10.05.

*4.10.6. (Z)-2-Deutero-3-((Z)-2-deutero-3-phenylprop-2-enyl)cyclonon-1-ene (**18c**)*

Yield: 3.8 g, 79%, as a colorless oil, bp 144–146 °C (1 Torr). ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.01–7.35 (m, 5H, Ph), 6.43 (s, 1H), 5.55 (t, J=8.0 Hz, 1H), 2.54 (m, 1H), 1.95–2.15 (m, 6H), 1.42–1.72 (m, 8H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ=136.3 (t, J_{CD}=23.0 Hz), 135.1, 133.6 (t, J_{CD}=23.0 Hz), 129.6, 128.05, 128.0, 126.3, 126.2, 37.5, 36.5, 33.5, 26.9, 26.4, 26.3, 26.1, 25.8 ppm. IR (film): 2160 (ν_{C-D}) cm^{-1}. MS m/z: 242 (M^+). $C_{18}H_{22}D_2$ (242.4): calcd C 89.19, H 9.15, D 1.66; found C 89.03, H+D 10.80.

*4.10.7. (Z)-3-((Z)-4-Phenylbut-2-enyl)cyclonon-1-ene (**17d**)*

Yield: 4.1 g, 81%, as a colorless oil, bp 146–148 °C (1 Torr). ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.23 (m, 5H, Ph), 5.55 (m, 2H), 5.22 (m, 2H), 3.43 (d, J=7.0 Hz, 2H), 2.61 (m, 1H), 2.40 (m, 1H), 2.15 (m, 4H), 2.09 (m, 1H), 1.29–1.68 (m, 8H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ=141.3, 135.8, 129.8, 129.6, 128.8, 128.7, 128.5, 125.9, 42.1, 37.3, 34.9, 31.8, 26.9, 26.6, 26.2, 26.1, 25.7 ppm. IR (film): 3040, 1620, 1440, 1370, 720 cm^{-1}. MS m/z: 254 (M^+). $C_{19}H_{26}$ (254.4): calcd C 89.70, H 10.30; found C 89.59, H 10.28.

*4.10.8. (Z)-2-Deutero-3-((Z)-2-deuterio-4-phenylbut-2-enyl)cyclonon-1-ene (**18d**)*

Yield: 4.1 g, 81%, as a colorless oil, bp 146–148 °C (1 Torr). ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.22 (m, 5H, Ph), 5.54 (t, J=8.0 Hz, 1H), 5.24 (t, J=8.0 Hz, 1H), 3.41 (d, J=7.0 Hz, 2H), 2.62 (m, 1H), 2.40 (m, 1H), 2.15 (m, 4H), 2.08 (m, 1H), 1.28–1.67 (m, 8H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ=141.2, 135.6 (t, J_{CD}=23.5 Hz), 129.8, 129.7, 128.8, 128.7, 128.2 (t, J_{CD}=23.0 Hz), 125.9, 42.2, 37.3, 34.9, 31.9, 26.9, 26.7, 26.2, 26.1, 25.4 ppm. IR (film): 2160 (ν_{C-D}) cm^{-1}. MS m/z: 256 (M^+). $C_{19}H_{24}D_2$ (256.4): calcd C 89.00, H 9.43, D 1.57; found C 88.91, H+D 10.98.

*4.10.9. (Z)-3-((Z)-3-Methyloct-2-enyl)cyclonon-1-ene (**17e**)*

Yield: 4.0 g, 83%, as a colorless liquid, bp 126–128 °C (1 Torr). ^{1}H NMR (400 MHz, $CDCl_3$): δ=5.55 (m, 1H), 5.16 (m, 1H), 5.12 (t, J=7.0 Hz, 1H), 2.49 (m, 1H), 1.98–2.18 (m, 6H), 1.68 (s, 3H), 1.15–1.72 (m, 16H), 0.91 (t, J=7.0 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ=136.1, 135.4, 129.2, 123.5, 37.5, 35.4, 33.5, 31.9, 31.8, 27.7, 26.8, 26.5, 26.1, 26.0, 24.6, 23.5, 22.7, 14.1 ppm. IR (film): 1610, 1450, 1380, 700 cm^{-1}. MS m/z: 248 (M^+). $C_{19}H_{26}$ (248.4): calcd C 87.02, H 12.98; found C 86.88, H 12.96.

*4.10.10. (Z)-2-Deutero-3-((Z)-2-deutero-3-methyloct-2-enyl)cyclonon-1-ene (**18e**)*

Yield: 4.0 g, 83%, as a colorless liquid, bp 126–128 °C (1 Torr). ^{1}H NMR (400 MHz, $CDCl_3$): δ=5.54 (t, J=8 Hz, 1H), 2.49 (m, 1H), 1.97–2.23 (m, 6H), 1.68 (s, 3H), 1.13–1.71 (m, 16H), 0.91 (t, J=7.0 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ=136.0, 135.0 (t, J_{CD}=23.0 Hz), 129.1, 123.4 (t, J_{CD}=23.0 Hz), 37.4, 35.2, 33.5, 31.9, 31.8, 27.6, 26.7 26.4, 26.1, 26.0, 24.6, 23.4, 22.6, 14.1 ppm. IR (film): 2160 (ν_{C-D}) cm^{-1}. MS m/z: 250 (M^+). $C_{18}H_{30}D_2$ (250.4): calcd C 86.32, H 12.07, D 1.61; found C 86.24, H+D 13.64.

*4.10.11. (Z)-3-((Z)-Phenylbut-2-enyl)cyclonon-1-ene (**17f**)*

Yield: 3.8 g, 76%, as a colorless liquid, bp 151–152 °C (1 Torr). ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.02–7.36 (m, 5H, Ph), 5.56 (m, 1H), 5.48 (t, J=6.8 Hz, 1H), 5.11 (m, 1H), 2.53 (m, 1H), 2.03 (s, 3H, CH_3), 1.95–2.15 (m, 6H), 1.67 (m, 2H), 1.42–1.60 (m, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ=142.4, 136.6, 135.1, 129.6, 128.05, 128.0, 126.4, 126.3, 37.6, 36.6, 33.5, 26.8, 26.5, 26.2, 26.1, 25.6, 24.5 ppm. IR (film): 3050, 1620, 1440, 1360, 690 cm^{-1}. MS (70 eV, EI): m/z 254 $[M]^+$ (11), 131 (100), 115 (10), 91 (21), 81 (21), 67 (14), 55 (10), 41 (20). $C_{19}H_{26}$ (254.4): calcd C 89.70, H 10.30; found C 89.63, H 10.29.

*4.10.12. (Z)-2-Deutero-3-((Z)-2-deutero-3-phenylbut-2-enyl)cyclonon-1-ene (**18f**)*

Yield: 3.8 g, 76%, as a colorless liquid, bp 151–152 °C (1 Torr). ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.11–7.36 (m, 5H, Ph), 5.56 (t, J=8.0 Hz, 1H), 2.52 (m, 1H), 2.05 (s, 3H, CH_3), 1.95–2.25 (m, 6H), 1.67 (m, 2H), 1.41–1.58 (m, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ=142.4, 136.5, 134.9 (t, J_{CD}=23.0 Hz), 129.3, 128.05, 128.0, 126.1 (t, J_{CD}=22.5 Hz), 126.3, 37.4, 36.5, 33.5, 26.8, 26.5, 26.1, 26.0, 25.5, 24.5 ppm. IR (film): 2160 (ν_{C-D}) cm^{-1}. MS (70 eV, EI): m/z 256 $[M]^+$ (7), 132 (100), 116 (9), 92 (12), 82 (12), 68 (8), 67 (9), 55 (5), 41 (8). $C_{19}H_{24}D_2$ (256.4): calcd C 89.00, H 9.43, D 1.57; found C 88.94, H+D 10.99.

4.11. 1-Methyl-9-[(2*Z*)-2-methylhept-2-en-1-yl]-cyclononene (19)

To crude **16a** at −20 °C, CuCl (1 mmol) and iodomethane (allylchloride) (30 mmol) were added dropwise. The reaction

mixture was allowed to warm to 20 °C and stirred for 6 h. The reaction mixture was quenched with an 8–10% (aq) solution of HCl. The layers were separated and the aqueous phase was extracted with Et_2O or hexane. The organic layer was diluted with hexane, separated, and dried over $MgSO_4$. Evaporation and vacuum distillation furnished **19** (4.1 g, 83% yield) as a colorless oil, bp 124–126 °C (1 Torr). ^{1}H NMR (400 MHz, $CDCl_3$): δ=5.41 (t, J=8 Hz, 1H), 5.16 (t, J=7 Hz, 1H), 2.97 (m, 1H), 2.07 (m, 2H), 1.95–2.05 (m, 4H), 1.69 (s, 3H), 1.57 (s, 3H), 1.29–1.68 (m, 14H), 0.89 (t, J=7.0 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ=137.9, 134.1, 126.6, 126.2, 37.1, 36.2, 32.3, 31.9, 28.1, 27.7, 27.3, 27.2, 27.0, 23.7, 23.5, 22.5, 18.1, 14.0 ppm. IR (film): 1600, 1440, 1370, 710 cm^{-1}. MS m/z: 248 (M^+). $C_{18}H_{32}$ (248.4): calcd C 87.02, H 12.98; found C 86.92, H 12.96.

4.12. 1-Allyl-9-[(2*E*)-2-allylhept-2-en-1-yl]cyclononene (20)

Yield: 5.2 g, 86% as a colorless oil, bp 165–166 °C (1 Torr). ^{1}H NMR (400 MHz, $CDCl_3$): δ=5.75–5.88 (m, 2H), 5.38 (t, J=8.4 Hz, 1H), 5.19 (t, J=8.0 Hz, 1H), 5.01–5.07 (m, 4H), 2.94 (m, 1H), 2.74 (d, J=6.8 Hz, 2H), 2.65 (d, J=7.2 Hz, 2H), 2.12 (d, J=7.6 Hz, 2H), 2.06 (m, 4H), 1.05–1.74 (m, 14H), 0.91 (t, J=7.0 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ=140.5, 137.7, 137.6, 136.2, 127.3, 126.7, 115.7, 115.5, 41.7, 37.6, 36.2, 34.2, 32.2, 31.8, 27.9, 27.8, 27.4, 27.1, 27.0, 23.8, 22.5, 14.0 ppm. IR (film): 1620, 1450, 1420, 1360, 690 cm^{-1}. MS m/z: 300 (M^+). $C_{22}H_{36}$ (300.5): calcd C 87.93, H 12.07; found C 87.85, H 12.05.

4.13. 2-Pentyl-5,6,7,8,9,10-hexahydro-4*H*-cyclonona[*b*]thiophene (22)

Yield: 4.2 g, 84%, as a light yellow oil, bp 141–143 °C (1 Torr). ^{1}H NMR (400 MHz, $CDCl_3$): δ=6.41 (s, 1H), 2.80 (t, J=6.0 Hz, 2H), 2.71 (t, J=7.6 Hz, 2H), 2.62 (t, J=6.0 Hz, 2H), 1.65 (m, 6H), 1.34–1.46 (m, 10H), 0.92 (t, J=6.0 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ=141.6, 137.9, 136.2, 126.3, 31.4, 31.3, 30.1, 29.2, 28.3, 27.8, 27.4, 26.5, 25.1, 24.4, 22.4, 14.0 ppm. MS m/z: 250 (M^+). $C_{18}H_{28}S$ (250.4): calcd C 76.74, H 10.46, S 12.80; found C 76.67, H 10.43, S 12.78.

Acknowledgements

The work was financially supported by the Russian Foundation for Basic Research (Grant No. 08-03-00789), by Grants of the RF President (MC-1039.2007.3 and Sci.Sh.-2349.2008.3), and by Russian Science Support Foundation.

References and notes

1. (a) Grignard, V. *Compt. Rend* **1900**, *130*, 1322–1389; (b) Kharash, M. S.; Reinmuth, O. *Grignard Reactions of Nonmetallic Substances*; Prentice Hall: New York, NY, 1954; (c) Ioffe, S. T.; Nesmeyanov, A. N. *Handbook of Magnesium-Organic Compounds*; Pergamon: London, 1957; (d) Ioffe, S. T.; Nesmeyanov, A. N. *The Organic Compounds of Magnesium, Beryllium, Calcium, Strontium and Barium*. Methods of Elemento-Organic Chemistry; North-Holland: Amsterdam, 1967; Vol. 2; (e) Coates, G. E.; Wade, K. *Organometallic Compounds*; Methuen: London, 1967; (f) Nützel, K. *Metalloorganische Verbindungen Be, Mg, Ca, Sr, Ba, Zn, Cd*. Houben-Weyl, Methoden der Organischen chemie; Thieme: Stuttgart, 1973; Bd. 13/2a, pp S.47–S.68; (g) *Comprehensive Organometallic Chemistry. The Synthesis, Reactions and Structures of Organometallic Compounds*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, New York, NY, Toronto, Sydney, Paris, Frankfurt, 1982; Vol. 1; (h) *Dictionary of Organometallic Compounds*; Chapman and Hall: London, New York, NY, Toronto, 1984.
2. (a) Dzhemilev, U. M.; Ibragimov, A. G. *Russ. Chem. Rev.* **2005**, *74*, 807–823; (b) Dzhemilev, U. M.; Ibragimov, A. G. Hydrometallation of Unsaturated Compounds. In *Modern Reduction Methods*; Andersson, P., Munslow, I., Eds.; Wiley-VCH GmbH KGaA: Weinheim, 2008; pp 437–479; (c) Dzhemilev, U. M.; D'yakonov, V. A.; Khafizova, L. O.; Ibragimov, A. G. *Tetrahedron* **2004**, *60*, 1287–1291; (d) Hoveyda, A. H.; Xu, Z. M. *J. Am. Chem. Soc.* **1991**, *113*, 5079–5080; (e) Takahashi, T.; Seki, T.; Nitto, Y.; Saburi, M.; Rousset, C. J.; Negishi, E. *J. Am. Chem. Soc.* **1991**, *113*, 6266–6268; (f) Knight, K. S.; Waymouth, R. M. *J. Am. Chem. Soc.* **1991**, *113*, 6268–6270; (g) Lewis, D. P.; Muller, P. M.; Whitby, R. J.; Jones, R. V. H. *Tetrahedron Lett.* **1991**, *32*, 6797–6800; (h) Rousset, C. J.; Negishi, E.; Suzuki, N.; Takahashi, T. *Tetrahedron Lett.* **1992**, *33*, 1965–1968; (i) Houri, A. F.; Didiuk, M. T.; Xu, Z. M.; Horan, N. R.; Hoveyda, A. H. *J. Am. Chem. Soc.* **1993**, *115*, 6614–6624; (k) Hoveyda, A. H.; Morken, J. P. *J. Org. Chem.* **1993**, *58*, 4237–4244.
3. Dzhemilev, U. M.; Sultanov, R. M.; Gaimaldinov, R. G.; Tolstikov, G. A. *Bull. Acad. Sci. USSR, Div. Chem. Sci.* **1991**, *40*, 1229–1234; (b) Dzhemilev, U. M.; Sultanov, R. M.; Gaimaldinov, R. G.; Muslukhov, R. R.; Lomakina, S. I.; Tolstikov, G. A. *Bull. Acad. Sci. USSR, Div. Chem. Sci.* **1992**, *41*, 770–788; (c) Dzhemilev, U. M.; Sultanov, R. M.; Gaimaldinov, R. G. *Russ. Chem. Bull., Int. Ed.* **1993**, *42*, 149–153; (d) Knight, K. S.; Wang, D.; Waymouth, R. M.; Ziller, J. *J. Am. Chem. Soc.* **1994**, *116*, 1845–1854; (e) Dzhemilev, U. M.; Sultanov, R. M.; Gaimaldinov, R. G. *J. Organomet. Chem.* **1995**, *491*, 1–10; (f) Lewis, D. P.; Whitby, R. J. *Tetrahedron* **1995**, *51*, 4541–4550; (g) Negishi, E.; Rousset, C. I.; Choveiry, D.; Maye, I. P.; Suzuki, N.; Takahashi, T. *Inorg. Chim. Acta* **1998**, *280*, 8–20.
4. (a) Richter, W. J.; Neugebauer, B. *Synthesis* **1985**, 1059–1060; (b) Richter, W.J. *Chem. Ber.* **1983**, *116*, 3293–3300; (c) Richter, W. J. *Angew. Chem.* **1982**, *94*, 932–934; (d) Herberich, G. E.; Eigendorf, U.; Ganter, C. *J. Organomet. Chem.* **1991**, *402*, C17–19; (e) Baker, R.; Cookson, R. C.; Saunders, A. D. *J. Chem. Soc., Perkin Trans. 1* **1976**, 1815–1818; (f) Rieke, R. D.; Sell, M. S.; Xiong, H. *J. Am. Chem. Soc.* **1995**, *117*, 5429–5437; (g) Xiong, H.; Rieke, R. D. *J. Am. Chem. Soc.* **1992**, *114*, 4415–4417; (h) Rieke, R. D.; Sell, M. S.; Xiong, H. *J. Org. Chem.* **1995**, *60*, 5143–5149; (i) Xiong, H.; Rieke, R. D. *J. Org. Chem.* **1992**, *57*, 7007–7008; (k) Rieke, R. D.; Xiong, H. *J. Org. Chem.* **1992**, *57*, 6560–6565; (l) Xiong, H.; Rieke, R. D. *Tetrahedron Lett.* **1991**, *32*, 5269–5272; (m) Xiong, H.; Rieke, R. D. *J. Org. Chem.* **1989**, *54*, 3247–3249.
5. Dzhemilev, U. M.; Ibragimov, A. G.; D'yakonov, V. A.; Pudas, M.; Bergmann, U.; Khafizova, L. O.; Tyumkina, T. V. *Russ. J. Org. Chem.* **2007**, *43*, 681–684.
6. Dzhemilev, U. M.; Ibragimov, A. G.; D'yakonov, V. A.; Zinnurova, R. A. *Russ. J. Org. Chem.* **2007**, *43*, 176–180.
7. (a) Skattebol, L.; Solomon, S. *J. Am. Chem. Soc.* **1965**, *87*, 4506–4507; (b) Moore, W. R.; Bach, R. D.; Ozretich, T. M. *J. Am. Chem. Soc.* **1969**, *91*, 5918–5919.
8. Binger, P.; Schuchardt, U. *Chem. Ber.* **1980**, *113*, 1063–1071.
9. Gordon, A. J.; Ford, R. A. *The Chemist's Companion*; John Wiley and Sons: New York, NY, London, Sydney, Toronto, 1972, pp 300–302.