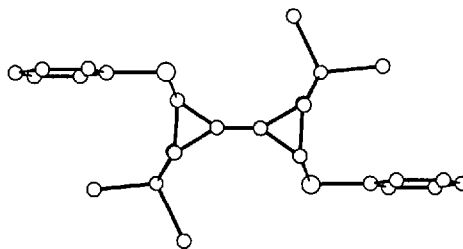


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Shaochun You [1], Matthias Gubler [2], and Markus Neuenchwander*

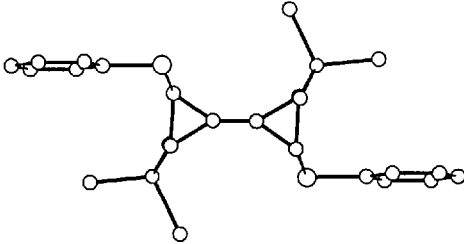
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Based on previous work of *Doering* [4], we showed a few years ago that oxidative treatment of dilithio-bi(cyclopentadienyl)diide (**1**) with CuCl₂ gives unstable pentafulvalene (**2**) in a high yield [5], and we applied the same sequence to the synthesis of so far unknown fulvalenes [6]. Subsequently, in a synthetic attempt towards cyclopenta[*a*]pentalenes [7] *Hafner* and *Thiele* investigated the Cu^{II}-induced reaction of disodium-di(cyclopentadienyl)methane-diide (**3**; R=H) and convincingly demonstrated that intramolecular oxidative coupling **3** \rightarrow **4** is an important pathway [8]. Even more interesting is the fact that **4** (R=H) as well as **4** (R = *t*-Bu) rearrange stereoselectively to cyclopenta[*a*]pentalenes on heating in pentane.

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**Short Communication; Coupling Reactions, part 8. For part 7 see [3]. The authors thank the Swiss National Science Foundation (project No. 20-26167-89) for financial support.

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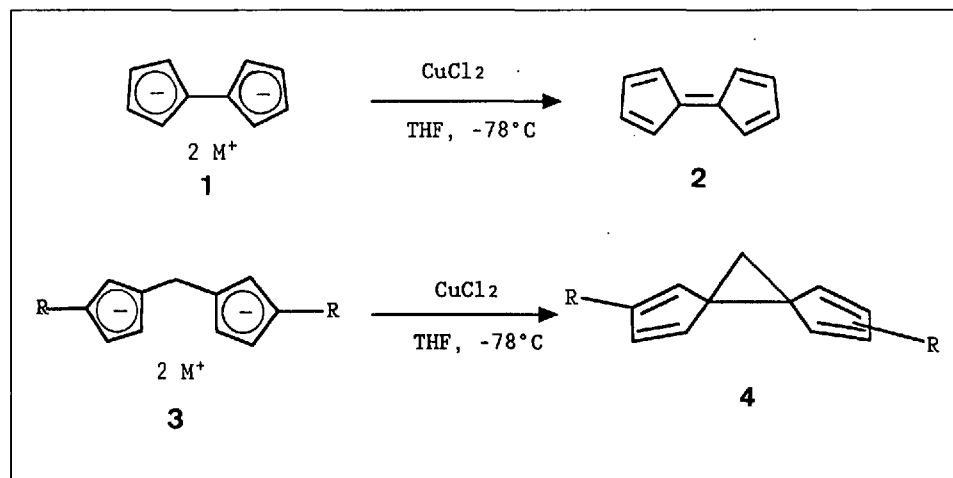
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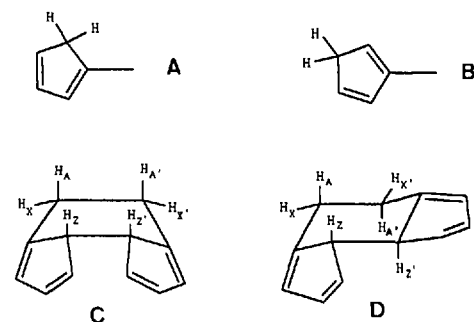
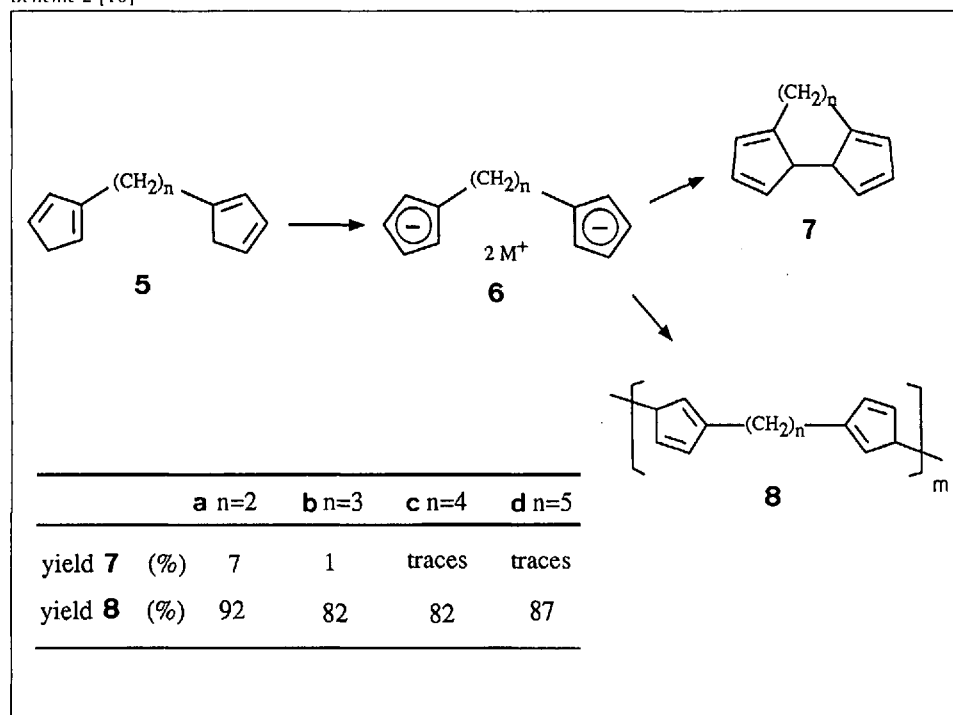
Scheme 1



troscopical investigations show that, as expected, tautomeric cyclopentadienes **A** and **B** are dominating, so that in each case **5** three tautomers (with combinations **AA**, **AB**, and **BB**) may be formed. This is supported by the number of lines of the proton noise-decoupled ¹³C-NMR spectra. It is easily seen that, with increasing length of the alkyl chain, both rings are completely decoupled from each other so that for the ring C-atoms (with exception of the quaternary ones), there is only one set of lines of type **A** as well as of type **B**.

The result of CuCl₂-induced coupling of di(cyclopentadienides) **6** is surprising in so far that the yields of intramolecular coupling products are very small even in the case of **7a** (*n* = 2) and in dilute solutions, and they rapidly decay to zero with increasing *n*.

Scheme 2 [10]



Regioselectivity and stereoselectivity of intramolecular coupling **6** → **7** have been investigated in the case **6a** → **7a** (*n*=2), where all the spectra clearly show that only one diastereoisomer with the molecular formula C₁₂H₁₂ has been formed, being consistent with structure **7a**: first of all the M⁺ as well as the intensity of the isotope peaks are consistent with the molecular formula C₁₂H₁₂. It is interesting to see that the basic MS fragmentation is the formation of two units of C₆H₆ (which is very reasonable for structure **7a**). In the UV spectrum, the long-wavelength absorption at 249 nm fits to the presence of cyclopentadiene rings. In the ¹³C-NMR spectrum, the lines of one quaternary (150.1 ppm), three tertiary vinylic C-atoms (135.4; 132.3; 123.7 ppm) and one tertiary alkyl-C-atom (56.3 ppm) are in agreement with two symmetrically placed cyclopentadiene rings, while the original CH₂CH₂ bridge generates one signal at 27.1 ppm. The conclusion from the spectroscopically confirmed structure **7a** (*n* = 2) is that

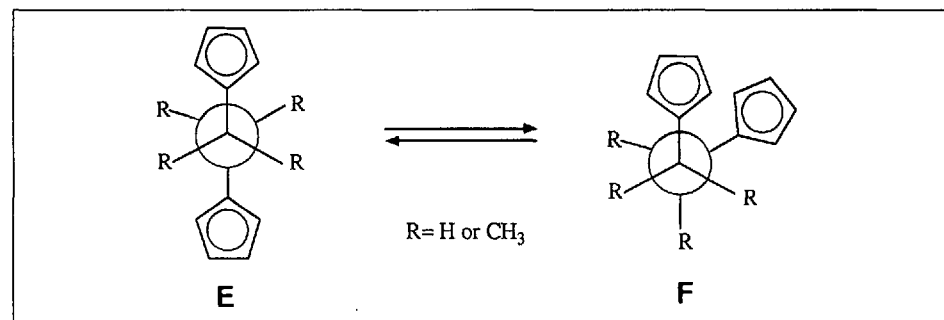
Obviously in both cases **1** and **3**, intramolecular oxidative coupling is significant, although the preparative yields are considerably decreasing from 73% (**2** [5]) to 24% (**4** [8]). If one assumes that α,ω -di(cyclopentadienyl) diradicals are formed by oxidative treatment of dianions of type **1** and **3** [9] then the chances for an intramolecular bond formation are ideal for **1**, and they are expected to dramatically decrease with increasing length of the alkyl chain between the rings. On the other hand, the chances of polymer formation by intermolecular coupling should increase in the same series; these polymers with cyclopentadiene units in the chain should be very reactive.

Besides the questions concerning the competition between intramolecular/intermolecular coupling, regioselectivity as well as stereoselectivity of coupling reactions are of interest as well. In this context, we investigated the Cu^{II}-induced coupling of a series of α,ω -di(cyclopentadienyl)alkyl-diides with varying length of the alkyl chain.

2. Oxidative Coupling of Homologous α,ω -Di(cyclopentadienyl)alkyl-diides **6 (*n* = 2–5)**

α,ω -Di(cyclopentadienyl)alkanes **5a–d** (*n* = 2–5) are quite easily available by reaction of an excess of sodium cyclopentadienide with the corresponding α,ω -dibromoalkanes at –30° [11]; they easily undergo *Diels-Alder* polycycloadditions [12]. Spec-

Scheme 3



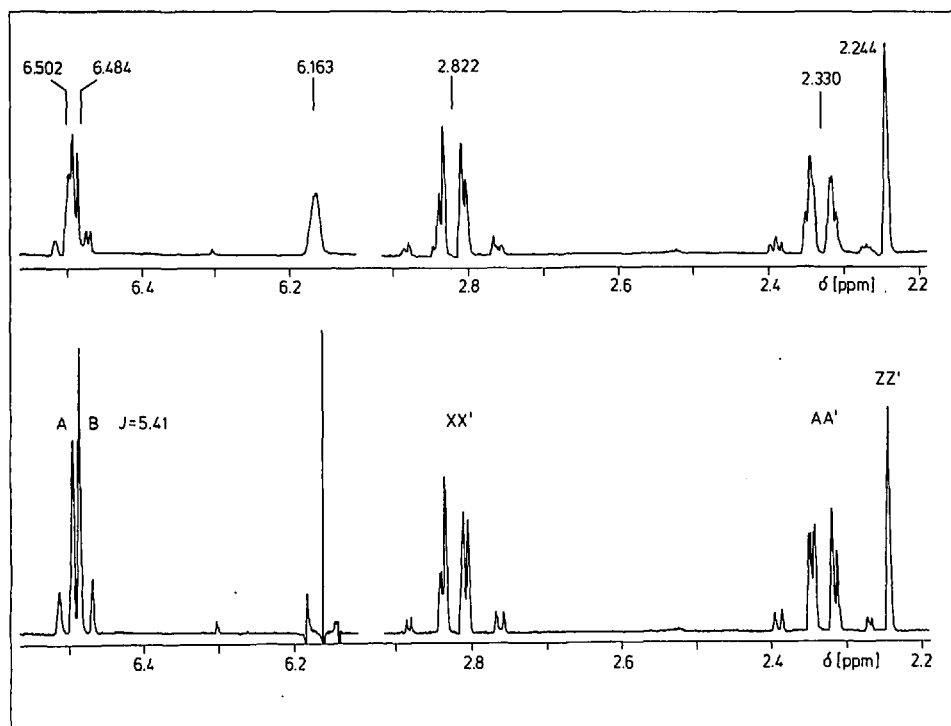


Fig. 1. ^1H -NMR Spectrum (300 MHz, CDCl_3) of **7a** ($n = 2$) with expansions of the vinylic and the alkyl range (above), and irradiation at 6.16 ppm (below)

Table. ^{13}C -NMR Results (δ in ppm) of α,ω -Di(cyclopentadienyl)alkanes **5** and Polymers **8**

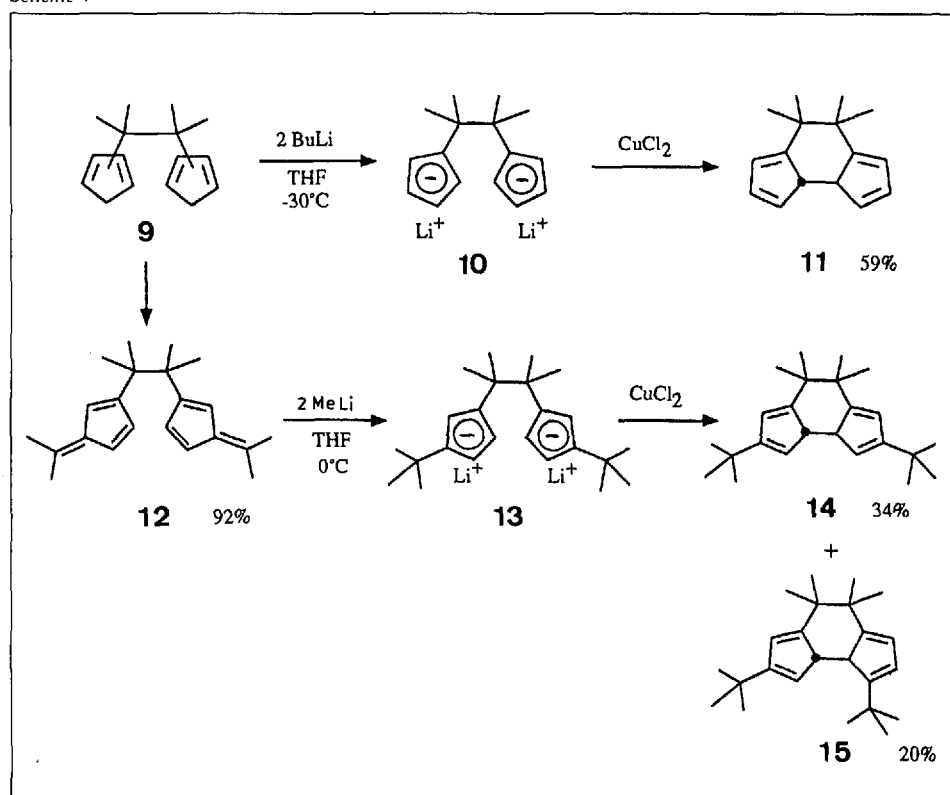
No.					$-(\text{CH}_2)_n-$
5a^{a)}	146.8–149.4	126.0–134.7	41.3–43.4	–	29.3–30.9
5b^{a)}	146.9–149.8	125.9–134.8	41.2–43.3	–	27.9–30.5
5c^{a)}	147.2–150.0	125.8–134.8	41.2–43.5	–	28.6–32.4
5d^{a)}	147.4–150.2	125.8–135.0	41.3–43.6	–	28.7–31.2
8a–8^{b)}	145 ^{c)}	128–130 ^{c)}	41–42 ^{c)}	54–64 ^{c)}	30–31 ^{c)}

^{a)} 100 MHz, CDCl_3 , ^{b)} Solid-state NMR (Bruker AMX) under MAS conditions. ^{c)} Center of the broad peak.

the coupling mode is not a 1,1'-coupling, but a 2,2'-coupling of the di(cyclopentadienyl) diide **6a**. The central problem in order to determine the steric course of the coupling step is to distinguish between achiral **7aC** (having a mirror plane) and C_2 -symmetric **7aD**.

Expansions of the high-resolution ^1H -NMR spectrum of **7a** are shown in Fig. 1. The most interesting features are the complex pattern of the H-atoms of the CH_2CH_2 bridge as well as of the vinylic H-atoms of the cyclopentadiene rings [13]. Decoupling of H-C(5)/H-C(10) at 6.160 ppm gives an AB-type spectrum of the remaining vinylic protons of the cyclopentadiene rings with a typical $J_{AB} = 5.41$ Hz (Fig. 1). Furthermore, the AA'XX'-type spectrum centered at 2.822 and 2.330 ppm, although still slightly disturbed by further small long-range couplings, allows an approximate analysis. The system is characterized by a geminal 2J -coupling ($J_{AX} = -12.5$ Hz), a large 3J -coupling ($J_{AA'} = 13.75$ Hz), and two small to medium 3J -couplings ($J_{XX'} = 2.15$ Hz and $J_{AX} = 5.45$ Hz). These couplings convincingly prove the C_2 -symmetrical cyclohexane chair arrangement of **7aD**.

Scheme 4



Similarly to other polymers with cyclopentadiene units [14], powdered polymers **8** are very easily cross-linked by traces of oxygen so that an investigation of polymer solutions was impossible [15]. Therefore, solid-state NMR experiments have been performed [16]. Despite relatively broad lines, the ^{13}C -NMR results of the polymers **8** are completely compatible with the proposed structure, and chemical shifts of the observed signals are very similar to those of the corresponding monomeric α,ω -di(cyclopentadienyl)alkanes (Table).

3. Oxidative Coupling of 2,3-Dimethyl-2,3-di(cyclopentadienyl)butane-diides **10** and **13**

The most important conclusion from Chapt. 2 is that oxidative couplings of α,ω -di(cyclopentadienyl)alkane diides **6** predominantly proceed by an intermolecular mode (even in dilute solutions) to give reactive polymers **8** in high yields. This is especially surprising for deprotonated α,ω -di(cyclopentadienyl)alkanes **6** where we expected a much higher extent of the intramolecular coupling **6a** \rightarrow **7a** ($n = 2$). A reasonable tentative explanation is that, even in the case of **6a** ($n = 2$), the reactive species (possibly the diradical) is reacting from the conformation with two *trans*-diaxial cyclopentadiene rings, while the transition metal obviously does not seem to enhance intramolecular coupling.

In this case, it would be interesting to replace the H-atoms of the CH_2CH_2 bridge of **6a** by larger substituents in order to increase the importance of the *gauche*-conformation **F** in the equilibrium **E** \rightarrow **F** [17]

which is supposed to be the favourable conformation in view of an intramolecular coupling of type **6a** → **7a**. Due to the fact that a formal replacement of the H-atoms of the CH₂CH₂ bridge of **5a** (*n* = 2) by Me groups is relatively easy, we decided to investigate the Cu^{II} induced oxidative coupling of dianions **10** and **13** in more detail (Scheme 4).

2,3-Dimethyl-2,3-di(cyclopentadienyl)butane (**9**) is quite easily available by reductive coupling of two molecules of 6,6-dimethylpentafulvene in the presence of Na [18]. Recently, we used this coupling in another context for the Thiele-synthesis of 2,3-dimethyl-2,3-di[2-(6,6-dimethyl)pentafulvenyl]butane (**12**), which is isolated in a high yield of 90–95% [19]. Deprotonation **9** → **10** is realized by addition of 2 mol-equiv. of BuLi to the THF solution of **9** at –30°. If the solution of the dianion **10** is slowly added to a slurry of abs. CuCl₂ in THF, then 7,7,8,8-tetramethyltricyclo[7.3.0.0^{2,6}]dodeca-3,5,9,11-tetraene (**11**) is formed in a 59% yield [20]. Similarly, dianion **13** may be elegantly prepared by nucleophilic attack of MeLi at the exocyclic C-atoms of the fulvene units of difulvene **12**, a reaction which is well known for simple pentafulvenes [21]. Adding the solution of the resulting dianion **13** to a slurry of abs. CuCl₂ in abs. THF gives a mixture of 4,11- (**14**) and 3,11-di(*tert*-butyl) derivatives **15** with 34 and 20% yields [20]. Out of this mixture, C₂-symmetrical compound **14** has been isolated.

The structure of the isolated tricyclic compounds **11** and **14** follows from the spectroscopic data which show close similarities to those of **7a** (*n* = 2). In both cases, the basic MS peak corresponds to M⁺/2, and in the UV, the cyclopentadiene rings absorb at 248 nm. In the ¹³C-NMR spectrum, the chemical shifts of **14** and **11** show the expected trends compared with **7a**. In the ¹H-NMR spectrum of **11**, the chemical shifts as well as the splitting pattern of the protons support the proposed structure (besides the configuration): Irradiation of H–C(1)/H–

C(2) at 2.4 ppm makes the clean ABX system of the vinylic protons visible and allows an unambiguous assignment of these protons.

There are more problems in distinguishing the boat arrangement **C** from the C₂-symmetrical chair arrangement **D** (see formula) although the chemical shifts of the Me groups seem to be quite typical for axial (0.90 ppm) and equatorial (1.24 ppm) Me groups of cyclohexanes of type **D**. Unfortunately, extensive NOE experiments [22] proved to be not very conclusive, so that the boat conformation may not be completely ruled out. The C₂-symmetrical chair arrangement may be unambiguously proved by adding chiral shift reagents resulting in a splitting of most of the NMR signals of Fig. 2 [23].

These results convincingly show that the intramolecular coupling mode **6a** → **7a** may be considerably enhanced by replacing the H-atoms of the CH₂CH₂ bridge of dianion **6a** (*n* = 2) by Me groups (see **10** → **11**) possibly by favouring *gauche*-conformations **F** which should be ideal for the envisaged intramolecular process. All the intramolecular couplings **6a** → **7a**, **10** → **11**, and **13** → **14** are regioselective and involve a 2,2'-coupling of the cyclopentadiene units. Within the limits of high-field NMR identification, these couplings proceed stereoselectively to give the C₂-symmetrical compounds **7a** (*n* = 2), **11**, and **14** in which the cyclohexane ring is arranged in a fixed chair conformation.

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- [9] It is interesting to note that a marked colour change is observed during the reaction **1** → **2**: the starting brownish colour of the slurry of anh. CuCl₂ in THF turns to an intense green during reaction at –78°. The final colour of the mixture is deep red, corresponding to **2**, while colourless CuCl has been precipitated.
- [10] Preparative yields. Yields of polymers **8** after purification by precipitation in MeOH, filtration under Ar, rinsing with MeOH, and drying at 10^{–2} Torr/RT, for 3–5 h.
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- [16] We are grateful to Bruker-Spectrospin AG, Fällanden, Switzerland for solid-state NMR experiments under 'magic angle spinning' (MAS) conditions.
- [17] According to MMII force-field calculations (QCPE 395, version 1980), the energy differences between **E** and **F** are 1.1 kcal/mol in favour of **E** for protons (R = H) and only 0.4 kcal/mol in favour of **E** for Me groups (R = Me). This clearly shows that in the conformational equilibrium **E** → **F**, **F** is more important for R = Me than for R = H.
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- [23] Adding of 2 mol-equiv. of Eu(hfc)₃ and 2 mol-equiv. of Ag(fod) to 1 mol-equiv. of **11** in CDCl₃ results in a doubling of the ¹H-NMR signals at 6.1, 2.4 and 0.9 ppm.

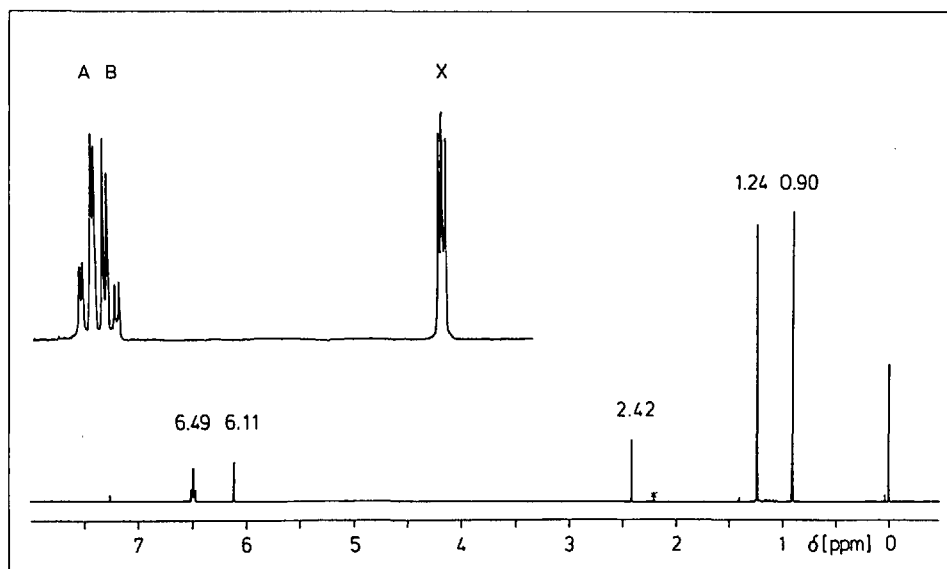


Fig. 2. ¹H-NMR Spectrum (300 MHz, CDCl₃) of **11** with expansions of the vinylic range after decoupling at 2.4 ppm (above)