# Hydroboration Polymerization. 2.[1] Synthesis of Organoboron Polymers by the Reaction between Diyne and Thexylborane

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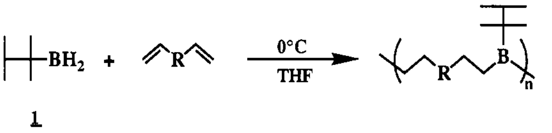
ABSTRACT: Synthesis of organoboron polymers by polyaddition between thexylborane (1) and diynes (2) is described. When a terminal diyne such as 1,7-octadiyne (**2a**) was used as a monomer, a moderate amount of cross-linking reaction occurred due to the dihydroboration of vinylborane units in the main chain of the polymer. Even when an organoboron polymer was prepared from a stoichiometric amount of 1 and **2a**, the obtained polymer showed in $^1$H NMR only 60% of vinyl protons on the basis of an assumption of linear structure. That is, the resulting polymer had 20% branched structure. As the result of the cross-linking reaction, gelation was observed when an excess amount of 1 was used. The gel obtained with the excess of 1, however, dissolved again by the treatment with methanol. On the other hand, when an internal diyne such as 3,9-dodecadiyne (**2b**) was used as a monomer, no gelation was observed even in the presence of an excess amount of 1. Little contribution of branched structure was detected by the spectroscopic analyses of the polymer prepared from an equimolar amount of 1 and **2b**.

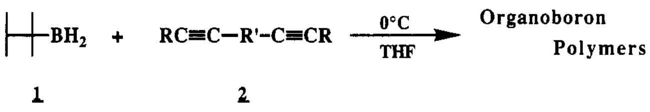
## Introduction

Organoborons are useful precursors for the preparation of a wide variety of functional compounds in organic synthesis.[2] From this point of view, synthesis of polymeric organoboron compounds should be an attractive target for the preparation of new materials and reactive intermediates producing functional polymers. However, there have been very few examples of the preparation of organoboron polymers. Chung prepared the polymers having organoboron branches by ring-opening metathesis polymerization[3] or Ziegler-Natta polymerization.[4] These organoboron-branched polymers were used for the preparation of alcohol-functionalized polymers. Recently, we reported the synthesis of organoboron polymers consisting of C-B bonds in the main chain by a polyaddition reaction between diene and thexylborane (1) (i.e., "Hydroboration polymerization", Scheme I).[5] Since polymers prepared by hydroboration polymerization can be regarded as a polymer homologue of trialkylborane, these polymers are expected to show reactivities similar to those of conventional organoboron compounds. In fact, these polymers were successfully converted into polymers having functional groups. For example, the reaction of organoboron polymers with carbon monoxide[6] or with KCN in the presence of acylating reagent[7] gave the corresponding poly(alcohol)s or poly(ketone)s, respectively. The reaction with dichloromethyl methyl ether in the presence of base followed by oxidative treatment also produced poly(alcohol)s.[8] If diyne compounds are used in the present hydroboration polymerization, the structure of the resulting polymers should be quite different from those from dienes, because the reactivity toward hydroboration itself is different. As a result, the properties for materials and the reactivities of the polymers might be expected to be different. Here we describe a hydroboration polymerization between diyne compounds (2) and thexylborane (1).

**Scheme I**



**Scheme II**



| | R | R' |
|---|---|---|
| **2a**; | H, | $-(CH_2)_4-$ |
| **2b**; | Et, | $-(CH_2)_4-$ |
| **2c**; | Et, | $-(CH_2)_3-$ |
| **2d**; | Et, | $-(CH_2)_5-$ |
| **2e**; | Me, | $-(CH_2)_4-$ |

## Results and Discussion

According to a previous report,[9] acetylenes are reactive toward hydroboration reaction as well as olefins. The reactivity of a terminal acetylene group toward hydroboration is quite different from that of an internal acetylene group. That is, the terminal acetylenes preferentially give dihydroboration products via a further hydroboration of the initially formed vinylborane species, when the borane components are not sterically hindered. If a borane is bulky like disiamylborane,[10] however, the monohydroboration products are predominantly produced. On the other hand, the internal acetylenes give monohydroboration products regardless of the bulkiness of borane reacted. In this paper, both terminal and internal diynes were examined respectively for the hydroboration polymerization with bifunctional thexylborane (1) (Scheme II).

**Hydroboration Polymerization between 1 and a Terminal Diyne.** As a preliminary experiment, 1,7-octadiyne (**2a**) was used as the terminal diyne component, and the hydroboration polymerization with various amounts of 1 was examined. Reaction was carried out by adding 1 to a THF solution of **2a** at 0 °C using a microfeeder.[11] Results of GPC measurements (dried THF as an eluent with constant nitrogen bubbling[5]) are summarized in Figure 1 and Table I. Some peaks were observed in lower molecular weight region, which might be due to cyclic oligomers. However, the major products in this hydroboration polymerization were polymeric materials from these results. When the feed ratio of 1 to **2a** approached

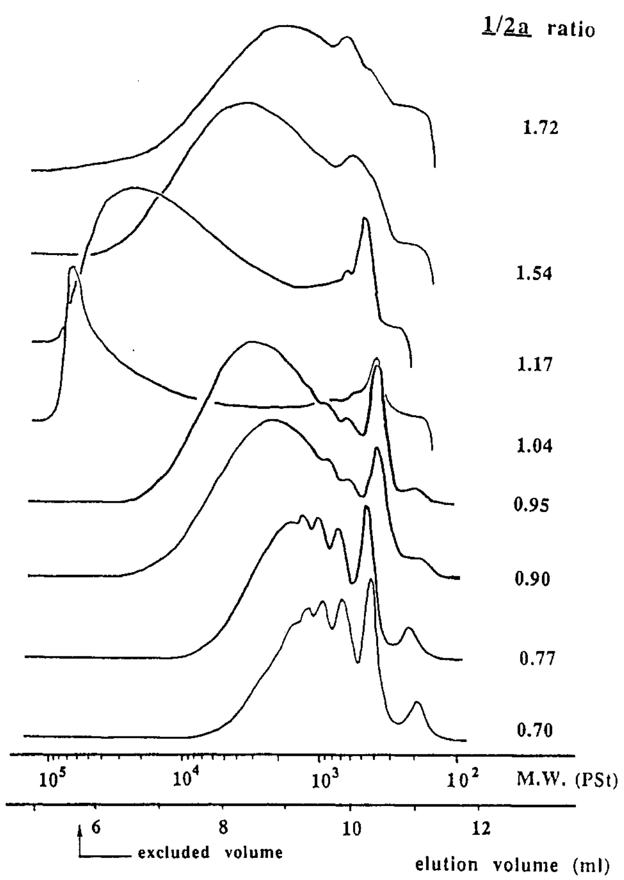


**Figure 1.** Dependence of molecular weight of **3a** on the feed ratio of the monomer (**1**/**2a**).

**Table I**
**Dependence of Molecular Weight on the Feed Ratio of 1 to 2a**[a]

| run | **2a**, g (mmol) | **1**, g (mmol) | **1**/**2a** | $\bar{M}_n$[b] | $\bar{M}_w$[b] |
|---|---|---|---|---|---|
| 1 | 0.089 (0.84) | 0.057 (0.59) | 0.70 | 750 | 1140 |
| 2 | 0.092 (0.87) | 0.065 (0.66) | 0.77 | 930 | 1540 |
| 3 | 0.057 (0.54) | 0.047 (0.48) | 0.90 | 1120 | 2610 |
| 4 | 0.080 (0.75) | 0.070 (0.71) | 0.95 | 1210 | 2960 |
| 5 | 0.081 (0.77) | 0.079 (0.80) | 1.04 | *c*, *d* | *c*, *d* |
| 6 | 0.090 (0.85) | 0.098 (1.00) | 1.17 | 2330[c] | 13900[c] |
| 7 | 0.066 (0.62) | 0.094 (0.95) | 1.54 | 1460[c] | 4240[c] |
| 8 | 0.061 (0.58) | 0.097 (0.99) | 1.72 | 1230[c] | 2680[c] |

[a] Reactions were carried out by adding **1** to a 1.0 M THF solution of **2a** using a microfeeder (45 μmol/min). [b] GPC (dried THF), polystyrene standard. [c] These systems initially formed the corresponding gels, which dissolved by the treatment with MeOH. [d] The molecular weight was higher than excluded volume ($>6 \times 10^4$).

unity, the molecular weight of the obtained polymer was increased as is usual for step-polymerization. Beyond unity, however, gelation was observed at every feed ratio.

Interestingly, all the gels became soluble after treatment with alcohols such as methanol or ethanol. Thus, GPC measurements were performed after alcoholysis. Generally, alkylborane or alkenylborane is known to be stable toward alcoholic protons under mild conditions.[12] However, a carbon atom having two C–B bonds (i.e., *gem*-diboramethylenes) was reported to be cleaved quite easily under protic conditions.[13] This means that the gel should be cleaved at *gem*-diboramethylene units in the main chain of the polymer (Scheme III). The decrease of molecular weight by using an excess of **1** might also be explained in a similar way. That is, excess of **1** should result in an increase of the proportion of *gem*-diboramethylene units as well as that of 1,2-diboraethylene units in the main chain of the polymer. The former units are readily broken by treatment with alcohol to form the soluble polymer. This alcoholysis may cause the chain scission of polymers. Accordingly, the increase of this structure in the main chain resulted in the decrease of molecular weight of the polymer after alcoholysis.

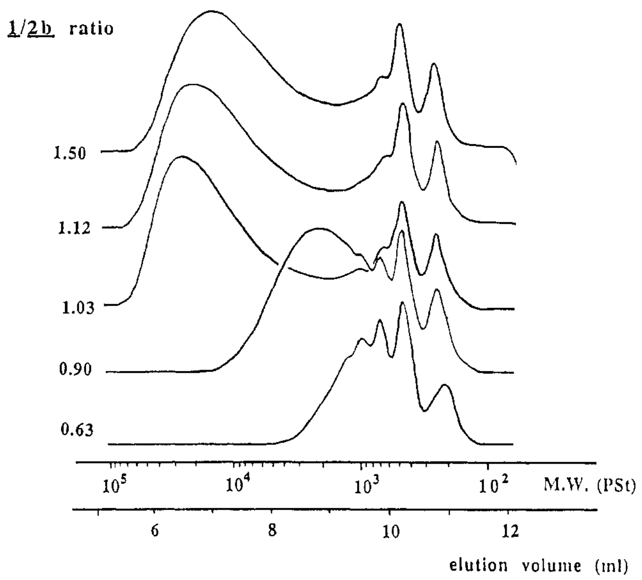
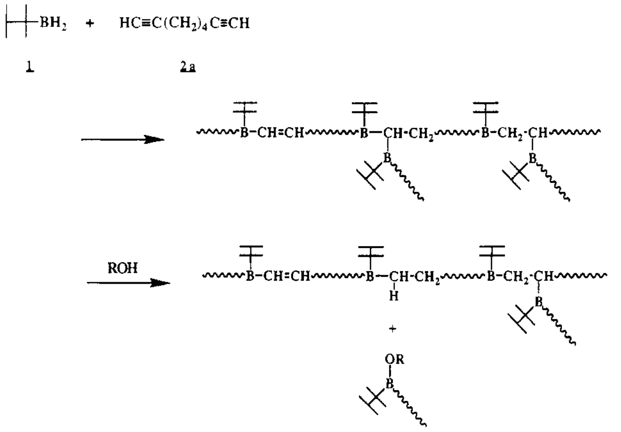


**Figure 2.** Dependence of molecular weight of **3b** on the feed ratio of the monomer (**1**/**2b**).

**Scheme III**



In the $^1$H NMR spectrum of the polymer obtained with an equivalent amount of **1**, only 60% of the vinyl protons were observed based on the assumption of a linear structure (i.e., monohydroboration product). From this result, it may be concluded that the polymerization using terminal diyne monomer resulted in the formation of a highly branched structure in the polymer chain due to the double hydroboration reaction. This branched structure might cause the broadening the molecular weight distribution of the obtained organoboron polymers.

**Hydroboration Polymerization between 1 and an Internal Diyne.** Similar to the case of **2a** and **1**, polymerizations were carried out at several feed ratios of **1** and 3,9-dodecadiyne (**2b**). As shown in Figure 2 and Table II, the polymer peaks in GPC shifted to a higher molecular weight region when the feed ratio of **1** to **2b** was increased. Beyond unity, however, the molecular weight of the resulting polymer (**3b**) did not increase, in sharp contrast to a terminal diyne. This dependence on feed ratio was quite similar to the hydroboration polymerization of dienes.[5] If monomers were added in the opposite way, i.e., **2b** was added to a THF solution of **1**, the resulting polymer showed a lower molecular weight ($M_n$ = 460, $M_w$

**Table II**
**Dependence of Molecular Weight on the Feed Ratio of 1 to 2b**[a]

| run | **2b**, g (mmol) | **1**, g (mmol) | **1**/**2b** | $\bar{M}_n$[b] | $\bar{M}_w$[b] |
|---|---|---|---|---|---|
| 1 | 0.094 (0.58) | 0.036 (0.37) | 0.63 | 560 | 860 |
| 2 | 0.121 (0.74) | 0.065 (0.67) | 0.90 | 790 | 1980 |
| 3 | 0.053 (0.32) | 0.033 (0.33) | 1.03 | 1410 | 13900 |
| 4 | 0.099 (0.61) | 0.067 (0.69) | 1.12 | 1190 | 11800 |
| 5 | 0.090 (0.56) | 0.082 (0.84) | 1.50 | 1130 | 8920 |

[a] Reactions were carried out by adding **1** to a 1.0 M THF solution of **2b** using a microfeeder (45 μmol/min). [b] GPC (dried THF), polystyrene standard.

**Table III**
**Hydroboration Polymerization of Various Internal Diynes**[a]

| run | diyne 2 | 1/2 | $\bar{M}_n$[b] | $\bar{M}_w$[b] |
|---|---|---|---|---|
| 1 | $EtC{\equiv}C(CH_2)_3C{\equiv}CEt$ (**2c**) | 1.07 | 570 | 5300 |
| 2 | $EtC{\equiv}C(CH_2)_4C{\equiv}CEt$ (**2b**) | 1.03 | 1410 | 13900 |
| 3 | $EtC{\equiv}C(CH_2)_5C{\equiv}CEt$ (**2d**) | 1.12 | 2080 | 17900 |
| 4 | $MeC{\equiv}C(CH_2)_4C{\equiv}CMe$ (**2e**) | 1.06 | 1030 | 10640 |

[a] Reactions were carried out by adding **1** to a 1.0 M THF solution of **2** using a microfeeder (45 μmol/min). [b] GPC (dried THF), polystyrene standard.

= 2 940). The decrease of molecular weight at feed ratios beyond unity and in the case of inverse monomer addition may be explained by the presence of excess of **1**, which can be replaced by organoboron units in polymer chains by the so-called disproportionation.

In the $^1H$ NMR spectrum of polymer **3b** obtained with an equimolar amount of **1**, more than 90% of vinyl protons were observed based on the assumption of **3b** having a linear structure. These results are taken to indicate that the vinylborane moiety almost remained unreacted in this polymerization. The resulting C=C bonds of vinylboranes have three substituents and are hardly subjected to further hydroboration due to steric hindrance. In other words, the hydroboration polymerization of internal diynes with **1** takes place in a way similar to that of dienes. On the other hand, only 60% of the vinyl groups remained in the case of terminal diyne as described before.

As mentioned above, due to the poor reactivity toward hydroboration of an alkenylborane unit from internal diyne, gelation can be avoided. Other internal diynes were also examined for hydroboration polymerization by using a small excess of **1**. The results are summarized in Table III. 3,8-Undecadiyne (**2c**), 3,10-tridecadiyne (**2d**), and 2,8-decadiyne (**2e**) as well as 3,9-dodecadiyne (**2b**) produced the corresponding organoboron polymers. In the case of **2c**, the molecular weight was relatively lower than other cases. Although detailed structures of the polymers were not clarified, the contribution of cyclic oligomers may not be small in the products.

**Stability of Organoboron Polymer 3b.** The thermal stability of **3b** was examined by TGA under nitrogen and under air (Figure 3). Under nitrogen, the weight loss started at 100 °C and was completed at 500 °C. Under air, a larger residue remained after pyrolysis in comparison with that under nitrogen. Organoboron polymer **3b** was rather unstable in air (vide infra). Thus, oxidation (i.e., decomposition of the polymer) should competitively take place during TGA under air although the structures of oxidized products were not clear at the present time.

Air stability of **3b** was monitored by checking the change of molecular weights in GPC after air was bubbled through the THF solution of **3b** (Figure 4). Throughout the air bubbling, the molecular weight of **3b** decreased to several hundreds. As the decomposition of the polymer proceeded, UV absorbance of the polymer was decreased in GPC measurement. Vinylboranes are known to have strong UV absorptions.[14] Thus, the decrease of UV absorbance can be attributed to the decomposition of this structure in the polymer chains. From the IR spectrum of the sample after 1 h, a strong carbonyl peak at 1710 $cm^{-1}$ was observed and is attributed to the oxidation of vinylborane moieties to form the corresponding ketones.

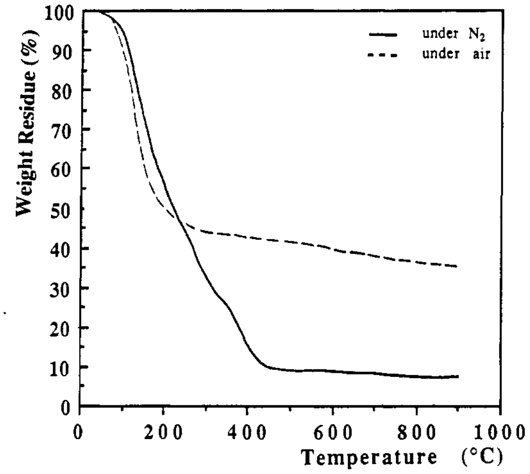


**Figure 3.** Results of TGA measurement of **3b** under nitrogen and under air.

In conclusion, diynes can be used as unsaturated monomers in hydroboration polymerization. Terminal diyne and internal diyne showed different polymerization behavior due to the steric effect on the second (further) hydroboration reaction. In the previous paper,[6-8] we demonstrated the usefulness of organoboron polymers prepared by hydroboration polymerization from dienes[5] as a novel type of reactive polymer. The organoboron polymers prepared from diynes, especially from internal diynes, consist mainly of divinylborane units. Thus, different reactivity and stability originating from this structure can be expected in comparison with the organoboron polymers prepared from dienes. The reactions of these poly(divinylborane)s will be discussed in the near future.

## Experimental Section

**Materials and Instruments.** Compound **1** was prepared by the reaction of borane–dimethyl sulfide and 2,3-dimethyl-2-butene as reported earlier[15] and was purified by distillation.[5] Tetrahydrofuran was dried over lithium aluminum hydride and distilled before use. **2a**–**2e** were purchased from Wako Pure Chemicals Inc. or Nacalai Tesque Inc. and purified by distillation.

$^1H$ NMR spectra were recorded in $CDCl_3$ on a Hitachi R-600 instrument (tetramethylsilane as an internal standard). IR spectra were obtained on a Perkin-Elmer 1600 spectrometer. Gel permeation chromatographic analysis was carried out on a Tosoh HLC-8020 (TSK gel G3000) by using dried THF as an eluent with constant nitrogen bubbling after calibration with standard polystyrene samples. Thermogravimetric analysis (TGA) was done on a Shimadzu DT-30 instrument (15 °C/min) under air or nitrogen.

**Hydroboration Polymerization between 1 and 1,7-Octadiyne (2a).** A general procedure for the polymerization between **1** and **2a** is described as follows: **1** was added by using a microfeeder (45 μmol/min) at 0 °C under nitrogen to a 1.0 M THF solution of **2a**. The reaction mixture was stirred for 1 h at that temperature under nitrogen. GPC measurement was performed after the treatment with alcohol as described in Results and Discussion. When excess **1** was used for this polymerization, gelation was observed. The obtained gel was dissolved by treatment with ethanol (0.1 mL), and the resulting solution was

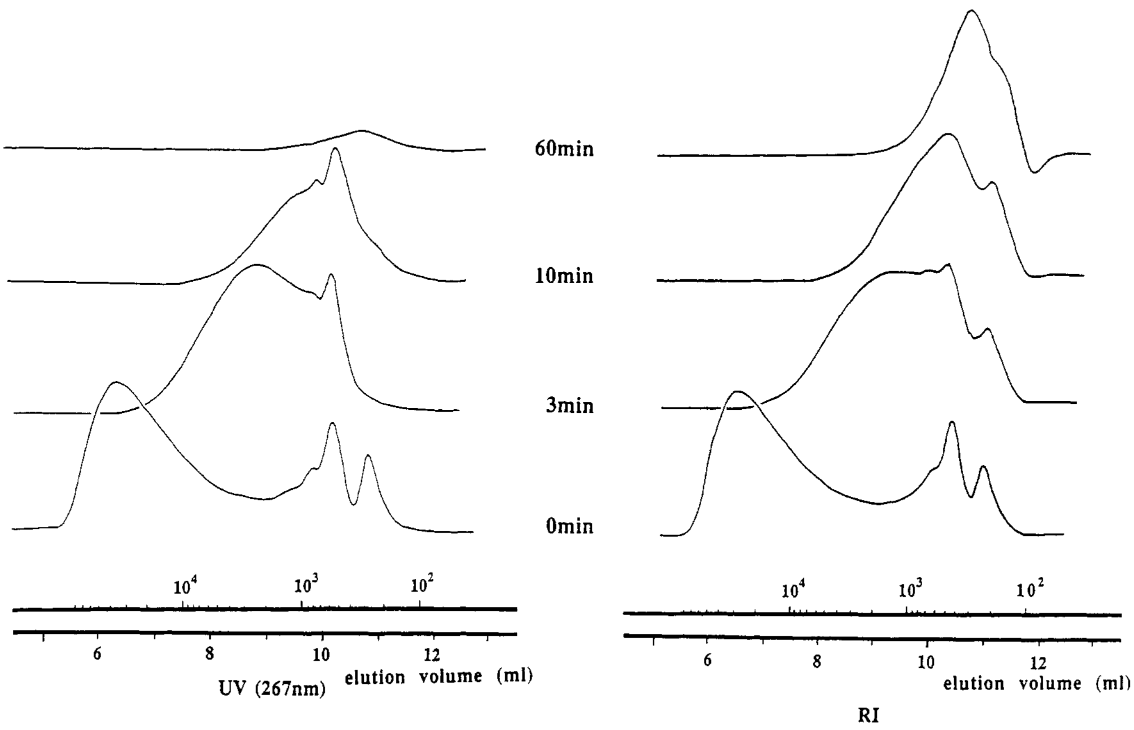


**Figure 4.** GPC traces of air decomposition of **3b**.

subjected to GPC measurement. The ratios of **1** to **2a** are listed in Table I. **3a** after methanolysis (Table I, run 5): $^1$H NMR ($\delta$, ppm) 0.53–2.56 ($CH_3$), 1.10–2.56 ($CH_2$, CH), 6.32 (C=CH); IR ($CHCl_3$) 2952, 2866, 1610, 1462, 1433, 1372, 1289, 1150, 999, 913 cm$^{-1}$.

**Hydroboration Polymerization between 1 and Internal Diyne (2b). Stoichiometric Study.** A general procedure for the polymerization between **1** and **2b** is described as follows: **1** was added by using a microfeeder (45 μmol/min) at 0 °C under nitrogen to a 1.0 M THF solution of **2b**. The reaction mixture was stirred for 1 h at that temperature. GPC measurement was performed as described in Results and Discussion. The ratios of **1** to **2b** are listed in Table II. **3b** (Table II, run 4): $^1$H NMR ($\delta$, ppm) 0.49–1.17 ($CH_3$), 1.17–2.52 ($CH_2$, CH), 5.14–5.98 (C=CH); IR ($CHCl_3$) 2959, 2869, 1567, 1462, 1373, 1211, 1049, 850 cm$^{-1}$.

**Organoboron Polymers (3c–3e).** **3c**–**3e** were obtained in quantitative yields by using a procedure similar to that described for **3b**. **3c** from **1** (0.109 g, 1.11 mmol) and **2c** (0.154 g, 1.04 mmol): $^1$H NMR ($\delta$, ppm) 0.47–1.19 ($CH_3$), 1.19–2.64 ($CH_2$, CH), 5.32–6.14 (C=CH); IR ($CHCl_3$) 2959, 2869, 1598, 1462, 1373, 1262, 1063 cm$^{-1}$. **3d** from **1** (0.044 g, 0.45 mmol) and **2d** (0.072 g, 0.41 mmol): $^1$H NMR ($\delta$, ppm) 0.45–1.07 ($CH_3$), 1.07–2.52 ($CH_2$, CH), 5.28–5.74 (C=CH); IR ($CHCl_3$) 2960, 2870, 1603, 1462, 1372, 1062, 904 cm$^{-1}$. **3e** from **1** (0.091 g, 0.93 mmol) and **2e** (0.119 g, 0.88 mmol): $^1$H NMR ($\delta$, ppm) 0.57–1.06 ($CCH_3$), 1.08–2.54 ($CH_2$, CH, =$CCH_3$), 5.30–5.87 (C=CH); IR ($CHCl_3$) 2957, 1606, 1463, 1374, 1238, 978, 909 cm$^{-1}$.

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