Specific ^{13}C Isotope Enrichment of Isoprene

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A synthetic scheme has been developed to prepare isoprene specifically ^{13}C-labelled at all different positions and in any combination of positions, from methyl methacrylate and methyl iodide. According to this scheme (4-^{13}C)isoprene was prepared with high label incorporation (99%).

Introduction

Isoprene (2-methyl-1,3-butadiene) is the building block of the terpenes. It is also the monomer component in natural rubber (1,4-*cis* polyisoprene) and in gutta percha (1,4-*trans* polyisoprene). Nowadays isoprene, mainly obtained from industrial cracking processes, is also widely used in other polymer applications such as latex paints.

Polymer materials can be studied using site-directed isotopically labelled materials in combination with isotope-sensitive spectroscopic techniques such as solid-state NMR spectroscopy.[1] This is a very powerful method for studying polymer systems at the atomic level without perturbation.

A threefold strategy is followed in order to achieve this objective. First, highly enriched, site-directed, isotopically labelled monomers are prepared by conventional organic synthesis. Secondly, isotopically labelled polymers and copolymers are prepared from these monomers. These polymers can be processed further when necessary, e.g. by blending. Third, these isotopically labelled polymer systems are studied with solid-state ^{13}C NMR techniques and other isotope-sensitive techniques in order to obtain structural and dynamic information at the atomic level. This information will be correlated with the bulk properties of the materials.

We recently used this approach in the studies of polymer materials.[2−6] In our group a number of important labelled monomers have already been prepared with 99% ^{13}C enrichment, namely acrylonitrile,[3] styrene,[3] ethyl acrylate,[7] maleic anhydride,[2,3] and methyl methacrylate.[8] Our purpose of preparing ^{13}C-labelled isoprene is to use it in anionic block copolymer synthesis. We have prepared block copolymers from isoprene and methyl methacrylate.[9] For these kind of anionic syntheses a very high purity of the monomer is required. The block copolymer will be synthesized in isotopically labelled form, and will be used to prepare blends of poly(methyl methacrylate) and polyisoprene. Using solid-state NMR techniques,[6,10] the interface of these blends can be studied specifically due to the amplification of its carbon signals. ^{13}C-labelled monomers are also used to study polymerization mechanisms.[11−14]

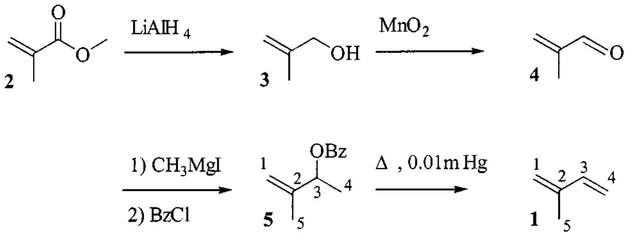
The synthesis of ^{13}C-labelled isoprene is described here. The synthetic scheme is based on the recently developed scheme to synthesize ^{13}C-labelled methyl methacrylate.[8] The synthesis of isoprene from methyl methacrylate allows the isoprene molecule to be labelled with ^{13}C at any desired carbon position or in any combination of carbon positions. According to this scheme (4-^{13}C)isoprene was prepared in a 99% isotopically enriched form.

Results

Synthetic Scheme

For the preparation of isoprene we started from methyl methacrylate. We have described the preparation of methyl methacrylate ^{13}C-enriched at any of its four carbon positions and in any combination of positions, in a yield of 30% from acetic acid.[8] The fifth carbon atom in isoprene originates from methyl iodide, which is also available with a ^{13}C isotope.

(4-^{13}C)Isoprene was synthesized with 99% ^{13}C enrichment, according to Scheme 1. All reaction steps were optimized using unlabelled compounds.



Scheme 1. Synthetic scheme for the preparation of isoprene (**1**) from methyl methacrylate; (4-^{13}C)isoprene (**1a**) was prepared using this scheme

Scheme 1 shows the conversion of methyl methacrylate (**2**) into isoprene (**1**). Methyl methacrylate is reduced by means of $LiAlH_4$ giving methallyl alcohol (**3**) in 83% yield. This alcohol is oxidized with MnO_2 to give methacrolein (**4**) in 75% yield. The last carbon atom of isoprene (C-4) is introduced in the next step using methylmagnesium iodide, prepared from methyl iodide and magnesium. Methacrolein (**4**) is added to this Grignard reagent to give the magnesium alkoxide, which is subsequently reacted with benzoyl chlor-

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ide to form the benzoate ester **5** in 60% yield. Elimination of benzoic acid using flash vacuum thermolysis[15−18] (750°C, 0.01 Torr) yielded the final product isoprene (**1**) in 96%.

(4-^{13}C)Isoprene was prepared according to the same scheme, from methacrolein (**4**) and (^{13}C)methyl iodide in 49% yield.

The overall yield of isoprene from methyl methacrylate is 36%. This scheme allows for the specific ^{13}C labelling of isoprene at any desired position or in any combination of positions.

Characterization

Mass Spectrometry

Mass spectrometry is a very valuable technique to determine the incorporation of isotopes and the molecule composition. The electron-impact mass spectrum of isoprene (**1**) has its molecular ion peak at 68 mass units. The molecular ion peak of the ^{13}C-enriched isoprene (**1a**) is shifted one mass unit to 69 mass units, because of the substitution of one ^{12}C for a ^{13}C. Double focussing mass spectrometry yielded a mass of 68.0612 for isoprene (**1**) and a mass of 69.0682 for the labelled compound **1a**. These values are in good agreement with the calculated values (C_5H_8 = 68.0626; $^{13}C^{12}C_4H_8$ = 69.0660).

From the peak intensities at m/z = 65 up to m/z = 70 of both the labelled and unlabelled compound, the isotope incorporation was calculated using the computer program "Label" from the Technical University of Denmark, Lyngby. For (4-^{13}C)isoprene (**1a**) >98% isotope incorporation was found, in agreement with the 99% enrichment of the starting material, methyl iodide. During the synthesis no isotope dilution took place.

^{1}H NMR Spectroscopy

^{1}H NMR spectroscopy was used to determine the purity of the product and the correct position of the ^{13}C isotope. The proton NMR spectra were assigned with the help of the simulation program PERCH from the University of Kuopio. Table 1 shows the ^{1}H NMR data of (4-^{13}C)isoprene (**1a**). For isoprene (**1**), the spectrum is the same with the exception of the CH coupling of the 4-H protons. The data are in complete agreement with literature values.[19] The $^{1}J_{C,H}$ coupling constants of (4-^{13}C)isoprene were also determined ($^{1}J_{C\text{-}4,4\text{-}H\mathit{trans}}$ = 159.0 Hz, $^{1}J_{C\text{-}4,4\text{-}H\mathit{cis}}$ = 154.9 Hz). The $^{2}J_{C,H}$ (literature value 0.2 Hz)[19] was not visible. From the ^{1}H NMR spectrum of **1a** it is unambiguously clear that the ^{13}C isotope is located at the C-4 position. The intensity of the signals of the 4-H protons show that a high incorporation of ^{13}C is achieved; it is estimated at 99%, within experimental error.

^{13}C NMR Spectroscopy

The ^{1}H noise-decoupled ^{13}C NMR spectra give direct information about the location of the ^{13}C label. The spectrum of (4-^{13}C)isoprene (**1a**) shows a very intense signal at δ = 113.6. From the ^{1}H NMR spectrum we already concluded that the ^{13}C label is located at the C-4 position, thus the chemical shift for this position is δ = 113.6. In the literature[19−21] we found contradicting values for the chemical shift of carbon atom 4, namely δ = 113.6[19,20] or 116.7.[21] Therefore, additional APT measurements were performed, which made it unambiguously clear once more that the chemical shift for C-4 is at δ = 113.6, and that for C-1 at δ = 116.7. The other resonances occur at δ = 17.7 (C-5), 139.6 (C-3) and 142.2 (C-2), see Table 2. From the natural abundance signals in **1a** the following ^{13}C,^{13}C coupling constant could be determined: $^{1}J_{C\text{-}3,C\text{-}4}$ = 68.7 Hz.

Table 1. ^{1}H NMR characteristics of (4-^{13}C)isoprene (**1a**)

δ (ppm)	H	Multiplicity	J (Hz)		Intensity
1.75	5-H	dd	$^{4}J_{1\text{-}H\mathit{cis}}$ $^{4}J_{1\text{-}H\mathit{trans}}$	1.42 0.77	3
4.91	1-H$_{cis}$	ddddq	$^{2}J_{1\text{-}H\mathit{trans}}$ $^{4}J_{5\text{-}H}$ $^{4}J_{3\text{-}H}$ $^{5}J_{4\text{-}H\mathit{cis}}$ $^{5}J_{4\text{-}H\mathit{trans}}$	2.28 1.42 −0.57 0.60 0.82	1
4.92	1-H$_{trans}$	ddddq	$^{2}J_{1\text{-}H\mathit{cis}}$ $^{4}J_{5\text{-}H}$ $^{4}J_{3\text{-}H}$ $^{5}J_{4\text{-}H\mathit{cis}}$ $^{5}J_{4\text{-}H\mathit{trans}}$	2.28 0.77 −0.57 0.60 1.28	1
4.98	4-H$_{trans}$	ddddd	$^{1}J_{C\text{-}4,H}$ $^{2}J_{4\text{-}H\mathit{cis}}$ $^{3}J_{3\text{-}H}$ $^{5}J_{1\text{-}H\mathit{cis}}$ $^{5}J_{1\text{-}H\mathit{trans}}$	159.0 1.19 10.65 0.82 1.28	1
5.10	4-H$_{cis}$	ddddd	$^{1}J_{C\text{-}4,H}$ $^{2}J_{4\text{-}H\mathit{trans}}$ $^{3}J_{3\text{-}H}$ $^{5}J_{1\text{-}H\mathit{cis}}$ $^{5}J_{1\text{-}H\mathit{trans}}$	154.9 1.19 17.45 0.60 0.60	1
6.39	3-H	dddd	$^{3}J_{4\text{-}H\mathit{cis}}$ $^{3}J_{4\text{-}H\mathit{trans}}$ $^{4}J_{1\text{-}H\mathit{cis}}$ $^{4}J_{1\text{-}H\mathit{trans}}$	17.45 10.65 −0.57 −0.57	1

Table 2. ^{13}C NMR characteristics (^{1}H decoupled) of (4-^{13}C)isoprene (**1a**)

δ (ppm)	C	Multiplicity	J (Hz)
17.7	C-5	s	–
113.6	C-4	s	–
116.7	C-1	s	–
139.6	C-3	d	$^{1}J_{C,C}$ = 68.7
142.2	C-2	s	–

Discussion

(4-^{13}C)Isoprene (**1a**) was synthesized in good yield and high purity, with high isotope incorporation (99%) and without isotope scrambling, in a scheme that allows for the isotope incorporation at any position and in any combination of positions. The starting materials used are methyl methacrylate[8] and methyl iodide. The synthesis of isoprene labelled with ^{13}C at the C-1 and C-2 positions, respectively, has been described before.[13,14] (1-^{13}C)Isoprene was prepared from (^{13}C)formaldehyde and propanal in a Mannich reaction giving methacrolein, which was converted into isoprene by a Wittig reaction.[13] (2-^{13}C)Isoprene was prepared from (2-^{13}C)acetone in a Grignard reaction with vinylmagnesium bromide, followed by dehydration.[14] These routes, however, cannot be used to label all other positions or combinations of positions in the isoprene molecule.

For a discussion of the synthesis of methyl methacrylate, we refer to our scheme in the literature.[8] Methyl methacrylate (**2**) was reduced with $LiAlH_4$ and subsequently oxidized with MnO_2. Direct reduction of **2** to give methacrolein (**4**) is possible with diisobutylaluminium hydride (Dibal-H), but the yield of the two separate reactions together was higher, and the cost of Dibal-H is also higher. Methacrolein (**4**) was reacted with 1.15 equiv. of MeMgI. The slight excess of MeI is used because this is the last carbon atom to be incorporated into isoprene. In this way the synthetic scheme is optimized with regard to all carbon positions. At first, the alkoxide was quenched with water to give the alcohol 2-methyl-1-buten-3-ol, which was esterified in a subsequent step with benzoyl chloride and pyridine. This yielded 56% of the ester **5**. Direct esterification of the magnesium alkoxide with benzoyl chloride gave a slightly higher yield of **5**, namely 60% (52% based on methyl iodide). Purification of this ester was very important, because any trace of impurities could otherwise show up in the final product. For this reason the heavier benzoyl moiety was chosen over an acetyl group. Elimination of benzoic acid to give isoprene (**1**) was carried out in a flash vacuum thermolysis apparatus.[16,22] The temperature in the apparatus was 750 °C, and the pressure was maintained at 0.01 Torr. The benzoic acid sublimed onto the glass as white crystals immediately after coming out of the hot part of the apparatus.[17,18,23] The volatile product **1** was collected in a cold trap cooled with liquid nitrogen, in 96% yield.

For anionic polymerization purposes, commercially available isoprene is dried over CaH_2 for 1−2 days at 4 °C, and then dried over *n*BuLi for 15 min. at 0 °C prior to use. The unlabelled isoprene prepared here was dried in the same manner, and was shown to be of the very high purity required for living anionic polymerization. It was polymerized to give polyisoprene and the diblock copolymer poly(isoprene-*b*-methyl methacrylate).[9] Thus, from isoprene prepared according to Scheme 1, polymers and copolymers of different molecular weights, containing ^{13}C isotopes at predetermined positions, can be made successfully. The synthesis of tailor-made poly(isoprene-*b*-methyl methacrylate) diblock copolymers is described by Zune et al.[9] Blends of polyisoprene, poly(methyl methacrylate) and the diblock copolymer in an isotopically labelled form, will be prepared and studied using solid-state NMR techniques.

This route shows how to prepare isoprene with high purity in an overall yield of 36% from methyl methacrylate. The scheme also enables us to prepare the versatile synthons and monomers methallyl alcohol (**3**) and methacrolein (**4**) labelled at any carbon position or in any combination of positions.

Conclusion

A synthetic scheme was developed to prepare isoprene labelled with 99% ^{13}C at any carbon position or in any combination of positions. Isoprene (**1**) and (4-^{13}C)isoprene (**1a**) were prepared from methyl methacrylate using this scheme. We have prepared various other monomers in ^{13}C-labelled form, like acrylates,[7] acrylonitrile,[3] maleic anhydride,[2,3] styrene[3] and methyl methacrylate.[8] With the addition of isoprene, methacrolein and methallyl alcohol, we are able to prepare even more polymers and copolymers. In this way we can obtain structural and functional information about these systems at the atomic level. Methallyl alcohol (**3**), methacrolein (**4**) and isoprene (**1**) are important monomers, as well as important and useful synthons in organic synthesis. Isoprene is a very useful synthon in Diels−Alder reactions. The use of these isotopically labelled compounds in organic synthesis will provide access to many more labelled compounds.

Experimental Section

General Remarks: ^{1}H NMR spectra were recorded with a Jeol FX-200, a Bruker DPX-300 spectrometer, or a Bruker DMX-600 using tetramethylsilane (TMS; $\delta = 0$) as internal standard. ^{1}H-noise-decoupled ^{13}C NMR spectra were recorded with a Jeol FX-200 at 50.1 MHz, a Bruker DPX-300 at 75.5 MHz or with a Bruker DMX-600 at 150.9 MHz, with $CDCl_3$ ($\delta = 77$) as internal standard. Mass spectra were recorded with a Finnigan MAT 900 mass spectrometer, coupled with a Varian GC, and with a Finnigan ITD 700 equipped with a Packard 438A GC. The mass spectra were collected in EI mode at 70 eV. Flash vacuum thermolysis[16]−[22] was performed using a commercial Thermolyne 21100 tube furnace containing an unpacked quartz tube (length 40 cm, diameter 2.5 cm). Dry diethyl ether was obtained by distilling from P_2O_5. Petroleum ether 40−60 (PE) was distilled from CaH_2. Methyl iodide (99% ^{13}C) was purchased from Cambridge Isotope Laboratories, Inc. All other reagents were purchased from Aldrich Chemical Co. or Acros Chimica.

Methallyl Alcohol (3): To a suspension of $LiAlH_4$ (1.50 g, 40 mmol) in 50 mL of dry diethyl ether under a nitrogen atmosphere and cooled to −30°C was slowly added a solution of methyl methacrylate (**2**) (4.27 mL, 4.0 g, 40 mmol) in 10 mL of dry diethyl ether. After stirring for 4 h at −30°C, water (3 mL) was slowly added until no more gas evolved. After 30 min the mixture had reached room temperature, and 50 mL diethyl ether and 50 mL of water were added for extraction. The water layer was washed three times with 100 mL of diethyl ether. The collected diethyl ether layers were dried with 50 mL of brine and $MgSO_4$. The product was obtained by distilling off the solvent through a vigreux column. The yield was 2.38 g (33 mmol, 83%) of **3**. − ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 1.74$ (m, only one coupling could be determined: $^{4}J_{H,H} = 1.4$ Hz, 3 H, 4-H), 2.63 [s (broad), 1 H, OH], 4.01 (m, 2 H, 2-H), 4.85 (m, only one coupling could be determined: $^{4}J_{H,H} = 1.4$ Hz, 1 H, 3-H_{trans}), 4.97 (m, 1 H, 3-H_{cis}). − ^{13}C NMR (50.1 MHz, $CDCl_3$): $\delta = 19.1$ (C-4), 66.5 (C-1), 109.6 (C-3), 144.8 (C-2).

Methacrolein (4): To a solution of methallyl alcohol (**3**) (2.38 g, 33 mmol) in diethyl ether was added MnO_2 (10 equiv., 28.7 g, 0.33 mol). After stirring overnight the solids were filtered through a thin layer of HyfloTM, and rinsed with a small quantity of diethyl ether. The methacrolein solution in diethyl ether was dried with $MgSO_4$ for 2 h. Evaporation of the solvent yielded 1.75 g (25 mmol, 76%) of methacrolein (**4**). − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.86 (dd, $^{4}J_{\text{H,H}}$ = 1.0, 1.5 Hz, 3 H, 4-H), 6.00 (dq, $^{2}J_{\text{H,H}}$ = 1.0 Hz, $^{4}J_{\text{H,H}}$ = 1.0 Hz, 1 H, 3-H_{cis}), 6.30 (dq, $^{4}J_{\text{H,H}}$ = 1.5 Hz, $^{2}J_{\text{H,H}}$ = 1.0 Hz, 1 H, 3-H_{trans}), 9.56 (s, 1 H, 1-H). − ^{13}C NMR (50.1 MHz, $CDCl_3$): δ_C = 13.8 (C-4), 134.2 (C-3), 145.9 (C-2), 194.5 (C-1).

3-Benzoyloxy-2-methyl-1-butene (5): Mg turnings (0.70 g, 29 mmol, 1.15 equiv.) were flame-dried under a nitrogen atmosphere while stirring vigorously. To the Mg, 10 mL of dry diethyl ether was added and, subsequently, MeI (1.80 mL 4.09 g, 29 mmol, 1.15 equiv.) in 10 mL of dry diethyl ether was added slowly. When no more Mg was visible methacrolein (**4**) (2.07 mL, 1.75 g, 25 mmol) in 10 mL of dry diethyl ether was added dropwise and the mixture was stirred for 2 h. Benzoyl chloride (3.0 mL, 3.62 g, 25.8 mmol) in 10 mL of dry diethyl ether was added slowly to the mixture and stirred for 3 h. Workup was accomplished by adding water and extracting three times with diethyl ether, washing the collected ether layers with a dilute $NaHCO_3$ solution, water, brine and finally drying with $MgSO_4$. The product was concentrated in vacuo. Purification was accomplished by column chromatography (PE/diethyl ether 95:5 and 97:3) and vacuum distillation (53 °C at 0.1 Torr). This yielded 60% (2.84 g, 15 mmol) of the benzoate ester **5** (yield based on MeI is 52%). − B.p. 53 °C (0.1 Torr) (ref.[24] 124−126 °C at 13 Torr). − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.45 (d, $^{3}J_{\text{H,H}}$ = 7.0 Hz, 3 H, 4-H), 1.82 [dd (shown as triplet), $^{4}J_{\text{H,H}}$ = 1.1 Hz, $^{4}J_{\text{H,H}}$ = 1.1 Hz, 3 H, 5-H], 4.90 (dq, $^{4}J_{\text{H,H}}$ = 1.1 Hz, $^{2}J_{\text{H,H}}$ = 1.6 Hz, 1 H, 1-H_{trans}), 5.06 (dq, $^{4}J_{\text{H,H}}$ = 1.1 Hz, $^{2}J_{\text{H,H}}$ = 1.6 Hz, 1 H, 1-H_{cis}), 5.54 (q, $^{3}J_{\text{H,H}}$ = 7.0 Hz, 1 H, 3-H), 7.38−8.08 (m, 5 H, Ph). − ^{13}C NMR (50.1 MHz, $CDCl_3$): δ = 18.3 (C-5), 19.2 (C-4), 73.9 (C-3), 111.6 (C-1), 128.2 (*m*-Ph), 129.5 (*o*-Ph), 130.6 (*i*-Ph), 132.7 (*p*-Ph), 144.5 (C-2), 165.7 (CO). − MS (70 eV): *m*/*z* (%) = 51 (16), 52 (8), 68 (58) [$CH_2CH(CH_3)C(CH_2)^+$], 77 (31) [$C_6H_5^+$], 85 (2) [$CH_2C(CH_3)CH(CH_3)O^+$], 105 (100) [$C_6H_5CO^+$], 123 (8), 190 (6) [M^+].

(4-^{13}C)5 (5a): Preparation proceeded as for **5**, using methacrolein (**4**) (20 mmol, 1.4 g), Mg (0.49 g, 20 mmol), (^{13}C)methyl iodide (3.30 g, 1.45 mL, 23 mmol, 1.15 equiv.), and benzoyl chloride (2.90 g, 2.4 mL, 20.6 mmol). This yielded 2.30 g of **5a** [12.0 mmol, 52% relative to (^{13}C)methyl iodide]. − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.45 (dd, $^{1}J_{\text{C,H}}$ = 127.8 Hz, $^{3}J_{\text{H,H}}$ = 7.0 Hz, 3 H, 4-H), 1.83 [dd (shown as triplet), $^{4}J_{\text{H,H}}$ = 1.1 Hz, 1.1 Hz, 3 H, 5-H], 4.91 (dq, $^{2}J_{\text{H,H}}$ = 1.6 Hz, $^{4}J_{\text{H,H}}$ = 1.1 Hz, 1 H, 1-H_{trans}), 5.06 (dq, $^{2}J_{\text{H,H}}$ = 1.6 Hz, $^{4}J_{\text{H,H}}$ = 1.1 Hz, 1 H, 1-H_{cis}), 5.54 (dq, $^{2}J_{\text{C,H}}$ = 2.4 Hz, $^{3}J_{\text{H,H}}$ = 7.0 Hz, 1 H, 3-H), 7.38−8.08 (m, 5 H, Ph). − ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 18.4 (s, C-5), 19.2 [s, C-4 (label peak)], 74.0 (d, $^{1}J_{\text{C,C}}$ = 39.0 Hz, C-3), 111.7 (s, C-1), 128.3 (s, *m*-Ph), 129.6 (s, *o*-Ph), 130.6 (s, *i*-Ph), 132.8 (s, *p*-Ph), 144.6 (s, C-2), 165.8 (s, CO). − MS (70 eV): *m*/*z* (%) = 51 (17), 53 (9), 69 (19) [$CH_2CH(CH_3)C(^{13}CH_2)^+$], 77 (14) [$C_6H_5^+$], 86 (2) [$CH_2C(CH_3)CH(^{13}CH_3)O^+$], 105 (100) [$C_6H_5CO^+$], 123 (14), 191 (12) [$M^+$].

Isoprene (1): Benzoate ester **5** (2.84 g, 15 mmol) was placed into a flash vacuum thermolysis apparatus.[16]−[22] The ester was heated to 40 °C, the Pyrex tube was heated to 750 °C, and the pressure was maintained at 0.01 Torr. After the thermolysis the benzoic acid sublimed onto the glass, while the isoprene was collected in a cold trap cooled with liquid N_2. The isoprene was further distilled under a static vacuum to give 0.98 g (14.4 mmol, 96%) isoprene (**1**). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.77 (dd, $^{4}J_{1\text{-H}cis,5\text{-H}}$ = 1.42 Hz, $^{4}J_{1\text{-H}trans,5\text{-H}}$ = 0.77 Hz, 3 H, H-5), 4.91 (ddddq, $^{2}J_{1\text{-H}trans,1\text{-H}cis}$ = 2.28 Hz, $^{4}J_{5\text{-H},1\text{-H}cis}$ = 1.42 Hz, $^{4}J_{3\text{-H},1\text{-H}cis}$ = −0.57 Hz, $^{5}J_{4\text{-H}trans,1\text{-H}cis}$ = 0.82 Hz, $^{5}J_{4\text{-H}cis,1\text{-H}cis}$ = 0.60 Hz, 1 H, 1-H_{cis}), 4.92 (ddddq, $^{2}J_{1\text{-H}cis,1\text{-H}trans}$ = 2.28 Hz, $^{4}J_{5\text{-H},1\text{-H}trans}$ = 0.77 Hz, $^{4}J_{3\text{-H},1\text{-H}trans}$ = −0.57 Hz, $^{5}J_{4\text{-H}cis,1\text{-H}trans}$ = 0.60 Hz, $^{5}J_{4\text{-H}trans,1\text{-H}trans}$ = 1.28 Hz, 1 H, 1-H_{trans}), 4.98 (dddd, $^{2}J_{4\text{-H}cis,4\text{-H}trans}$ = 1.19 Hz, $^{3}J_{3\text{-H},4\text{-H}trans}$ = 10.65 Hz, $^{5}J_{1\text{-H}cis,4\text{-H}trans}$ = 0.82 Hz, $^{5}J_{1\text{-H}trans,4\text{-H}trans}$ = 1.28 Hz, 1 H, 4-H_{trans}), 5.12 (dddd, $^{2}J_{4\text{-H}trans,4\text{-H}cis}$ = 1.19 Hz, $^{3}J_{3\text{-H},4\text{-H}cis}$ = 17.45 Hz, $^{5}J_{1\text{-H}cis,4\text{-H}cis}$ = 0.60 Hz, $^{5}J_{1\text{-H}trans,4\text{-H}cis}$ = 0.60 Hz, 1 H, 4-H_{cis}), 6.43 (dddd, $^{3}J_{4\text{-H}trans,3\text{-H}}$ = 10.65 Hz, $^{3}J_{4\text{-H}cis,3\text{-H}}$ = 17.45 Hz, $^{4}J_{1\text{-H}cis,3\text{-H}}$ = −0.57 Hz, $^{4}J_{1\text{-H}trans,3\text{-H}}$ = −0.57 Hz, 1 H, 3-H). − ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 17.7 (C-5), 113.6 (C-4), 116.7 (C-1), 139.6 (C-3), 142.3 (C-2). − MS (70 eV): *m*/*z* (%) = 52 (6), 53 (41) [$CH_2CHCCH_2^+$], 54 (20) [$CH_2CHCCH_3^+$], 65 (13), 66 (7), 67 (100) [M^+-1], 68 (56) [M^+], 69 (11) [M^++1]. − HRMS (C_5H_8): calcd. 68.0626; found 68.0612.

(4-^{13}C)1 (1a): Preparation was performed as for **1,** using benzoate ester **5a** (2.30 g, 12.0 mmol). Yield: 0.78 g, 11.3 mmol, 94%. − ^{1}H NMR (600 MHz, $CDCl_3$): see Table 1. − ^{13}C NMR (150.9 MHz, $CDCl_3$): see Table 2. − MS (70 eV): *m*/*z* (%) = 53 (31), 54 (46) [$^{13}CH_2CHCCH_2^+$], 55 (35) [$^{13}CH_2CHCCH_3^+$], 66 (22), 67 (10), 68 (100) [M^+-1], 69 (46) [M^+], 70 (11) [M^++1]. − HRMS ($^{13}C_1{}^{12}C_4H_8$): calcd. 69.0660; found 69.0682. − ^{13}C incorporation: >98%.

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