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Communications to the Editor

A Practical Palladium-Catalyzed Telomerization for the Synthesis of Functionalized Alcohols

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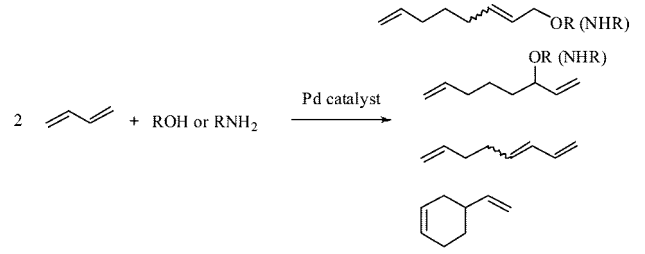
Abstract:

The synthesis of octadienyl-substituted alcohols via palladium-catalyzed telomerization is described. 2-*N*-Methylaminoethanol, ethylene glycol, and 1,2-propylenediol react smoothly with 1,3-butadiene to give valuable intermediates for speciality polymers in high selectivity and quantitative yield on multi-100 g-scale.

Introduction

The palladium-catalyzed telomerization of 1,3-dienes with nucleophiles to give functionalized octa-2,7-dienes constitutes an environmentally benign methodology, that proceeds in 100% atom efficient manner.[1,2] Due to their ready availability and low price,[3] 1,3-butadiene and alcohols or amines are attractive starting materials for this reaction (Scheme 1). In general, telomerizations lead to a mixture of *cis*/*trans* isomers where the linear products are formed preferentially. As previous studies have shown, major byproducts include 3-substituted octa-1,7-diene (**2**) (branched product), 1,3,7-octatriene (**3**) (formed by the linear dimerization of butadiene), and 4-vinylcyclohexene (**4**) (formed by the Diels−Alder reaction of two molecules of butadiene).

Scheme 1. **Telomerization of 1,3-butadiene with alcohols or amines**



Previously, telomerization products have been shown to be useful as intermediates in the total synthesis of several natural products,[4] as well as in industry, as precursors for plasticizer alcohols (octanols),[5] solvents, corrosion inhibitors, nonvolatile herbicides, and monomers for polymers.[6] Hence, this methodology has been the subject of intensive research in both academic and industrial laboratories.[7] Elegant mechanistic studies of the telomerization of methanol and 1,3-butadiene in the presence of palladium-phosphine catalysts have been performed by Jolly and co-workers.[8] Later on, we also investigated this reaction, which led to an extended mechanistic proposal.[9] As shown in Scheme 2, it is proposed that in the presence of palladium(0) species **5**, two molecules of 1,3-butadiene couple to form the PPh_3-Pd-(η^1,η^3-octadiendiyl) complex **6**. Protonation of **6** by methanol at the C6 atom of the C_8 chain leads to the PPh_3-Pd-(η^2,η^3-C_8H_{13}) species **7**.

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‡ Evonik Röhm GmbH.

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(3) The current industrial price for 1,3-butadiene is in the range of 1.0−1.2 Euro/kg.

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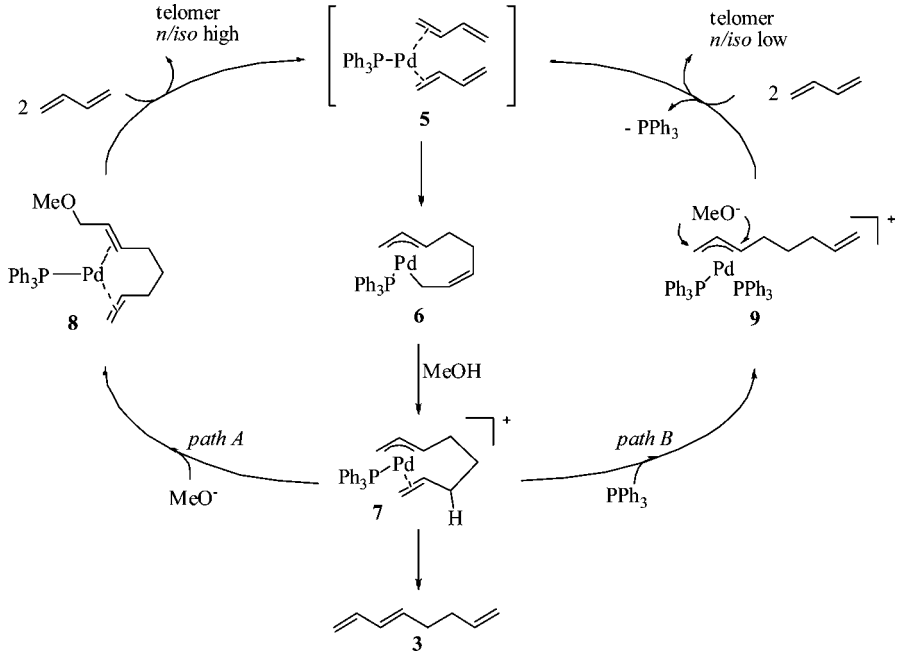
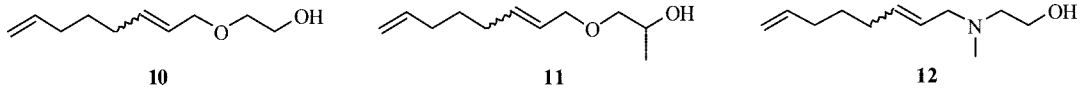
Scheme 2. **Proposed reaction mechanism**



Scheme 3. **Functionalized alcohols via telomerizations**



Around the year 2000 we started a program to develop more efficient catalysts for telomerizations, especially with methanol as nucleophile.[10] Inspired by the proposed mechanism we assumed that palladium complexes with one more strongly bound ligand should lead to improved catalysts. Indeed, among the different studied catalytic systems, palladium-monocarbene complexes turned out to be superior when compared to palladium-phosphine complexes.[11]

Here, we present the convenient synthesis of functionalized alcohols **10**−**12** with octadienyl chains on multi-100 g-scale (Scheme 3). The resulting products are interesting monomers for novel polyesters, polyolefins, and films. In this respect it is noteworthy that there exists an increasing interest in catalytic telomerizations of functionalized nucleophiles.[12] Obviously, di- and multisubstituted substrates offer follow-up reactions after telomer formation. In this respect, diols have become particularly attractive starting materials. However, the control of regio- and chemoselectivity is challenging in these reactions.

For example, the telomerization of 1,3-butadiene with ethylene glycol gave, in addition to the cyclic and linear dimers of 1,3-butadiene, the bis-octadienylethers as byproducts. Already in 1980 Dzhemilev et al. demonstrated that all of these side products are formed in the presence of a $Pd(acac)_2$-

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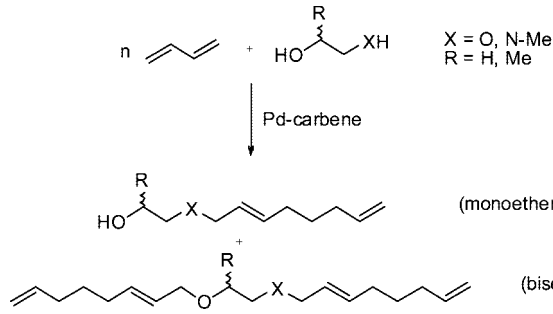
Table 1. **Variation of Reaction Conditions**[a]



					yield/%		
entry	substrate	[Pd]/mol %	*T*/°C	*t*/h	monoether	bisether	chemoselectivity/%
1	ethylene glycol	0.001	60	24	4	0	−
2	ethylene glycol	0.001	80	24	55	33	62
3	ethylene glycol	0.001	100	24	61	28	68
4[b]	1,2-propanediol	0.001	80	16	67	19	75
5[c]	2-*N*-methylaminoethanol	0.005	80	24	95	<1	99
6[c]	2-*N*-methylaminoethanol	0.005	90	24	99	<1	99
7[c]	2-*N*-methylaminoethanol	0.005	100	24	98	<1	99

[a] General conditions: 160 mL autoclave, 1,3-dimesitylimidazol-2-ylidenepalladiumtetramethyldivinyldisiloxane, ligand = 1,3-dimesitylimidazolium chloride, Pd/ligand = 1/10, 5 mL of 0.5 mol % $C_2H_4(ONa)_2/C_2H_6O_2$ (1,2-ed), 15 mL of THF, butadiene/substrate = 2:1, 30 bar nitrogen pressure. [b] 100 mL autoclave, 10 mL of 0.5 mol % $C_3H_6(ONa)_2/C_3H_8O_2$, 15 mL of THF. [c] 160 mL autoclave, $Pd(acac)_2$, ligand = 1,3-dimesitylimidiazolium chloride, Pd/ligand = 1:10, 15 g of butadiene, 10 mL of MeOH, 10 mL of internal standard. Yields calculated with respect to butadiene, chemoselectivity (monoether) = yield of monoether/[yield of (monoether + bisether + octatriene + 4-vinylcyclohexene)].

PPh_3-$Al(C_2H_5)_3$ catalyst system.[13] Due to the addition of $Al(C_2H_5)_3$ the workup and isolation of the desired product was also complicated. In 2003, Behr et al. described the palladium-catalyzed telomerization of 1,3-butadiene with glycols in aqueous biphasic and single-phase systems.[14] Despite high catalyst activity (turnover numbers up to 4300), significant amounts of the bis-octadienyl telomer are formed with a mono/bis ratio of ca. 1:1. The authors concluded that good chemoselectivity and high catalyst activity cannot be achieved under single-phase conditions. However, we recently showed that the telomerization of various diols with 1,3-butadiene proceeds in the presence of low levels (2−10 ppm Pd) of *in situ* generated palladium-carbene catalysts with good chemoselectivity.

In order to prepare octadienyl-substituted alcohols and amines we chose 2-*N*-methylaminoethanol, ethylene glycol, and 1,2-propanediol as nucleophiles. Initially, the reaction of 1,3-butadiene with 2-*N*-methylaminoethanol was studied in more detail.[15] At the starting point, the influence of different parameters (temperature, pressure, substrate ratio, solvent) on yield and selectivity of the resulting products was investigated. Applying the molecularly defined 1,3-dimesitylimidazol-2-ylidenepalladiumtetramethyldivinyldisiloxane[16] as catalyst reduced the amount of side products like 1,3,7-octatriene, vinylcyclohexene, and branched products. Also, catalysts generated *in situ*, formed from palladium acetylacetonate and 1,3-dimesitylimidazolium chloride, proved to be active. In Table 1 selected variations of the reaction conditions like temperature and catalyst concentration are shown for the telomerization of 2-*N*-methylaminoethanol and ethylene glycol. Figure 1 displays the conversion-time curve of the resulting products and the selectivity with respect to the temperature.

While tetrahydrofuran and toluene are not suitable solvents for the telomerization of 2-*N*-methylaminoethanol, in the presence of methanol, which is a competing nucleophile, the reaction proceeded selectively to give the *N*- and not the *O*-telomer. The catalytic reaction does not occur to a considerable extent below temperatures of 80 °C. In comparison, the

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(16) This catalyst is commercially available from Umicore.

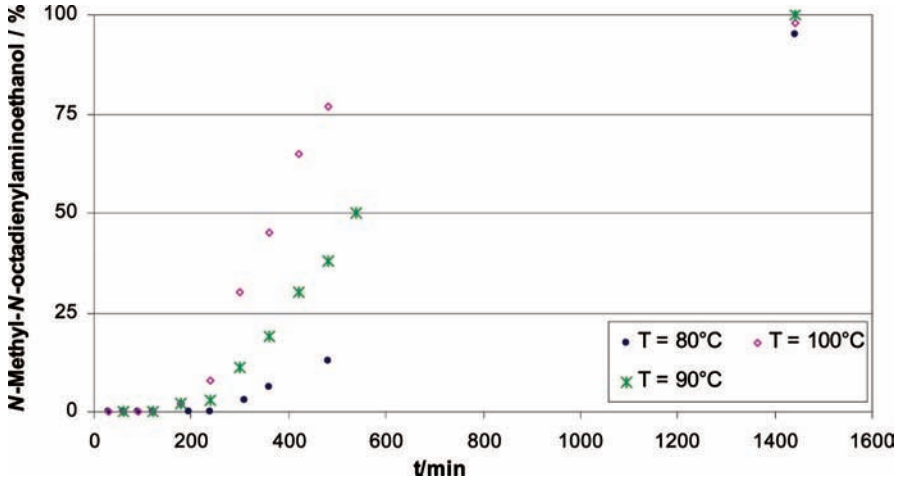
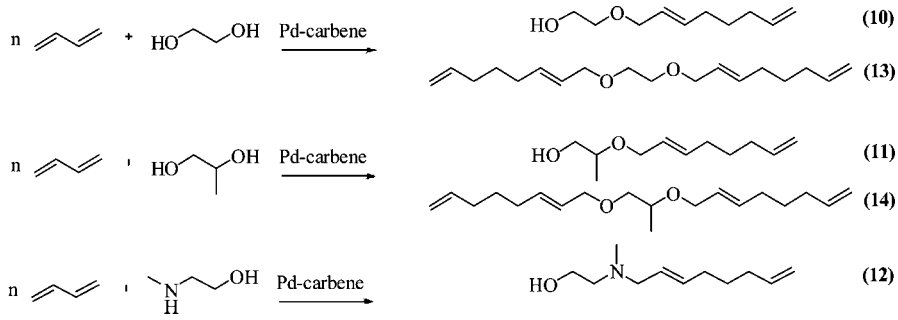


Figure 1. **Temperature dependence of Pd-catalyzed telomerization of 2-*N*-methylaminoethanol.**

Scheme 4. **Synthesis of main- and side products of the performed telomerization reaction**



telomerization of methanol is known to take place already at 50 °C. Apparently, the chelating effect of the *N*-methylaminoethanol deactivates the active palladium species to some extent. Above 80 °C, high activity is observed at low catalyst loadings (0.005 mol % Pd), and the desired monotelomer is obtained in ≥95% yield. Notably, the bis-octadienyl derivative is observed in <1%! The reaction proceeded well on 10 g scale and could be scaled up to 400 g scale (2 L autoclave) without any problem.

Next, telomerizations of ethylene glycol and 1,2-propenediol were run under similar conditions, albeit with only 0.001 mol % Pd (Scheme 4). In contrast to 2-*N*-methylaminoethanol, the chemoselectivity towards the desired monotelomer is lower. Hence, **10** and **11** are obtained in 50−60% yield after distillation. In addition, the corresponding bis-octadienylether, **13** and **14**, are obtained in 10−30% yield. Again these reactions were performed without any difficulties on 200 g scale.

In summary, we have shown that the telomerization of 2-*N*-methylaminoethanol, ethylene glycol, and 1,2-propenediol with 1,3-butadiene proceeds in the presence of low levels (10−50 ppm Pd) of palladium-carbene catalysts. On multi-100 g-scale excellent conversion and chemoselectivity towards the mono-octadienyl derivatives are observed for the reactions of 2-*N*-methylaminoethanol and 1,2-propenediol. Somewhat lower chemoselectivity is obtained with ethylene glycol. In general, this protocol allows for the efficient preparation of unsaturated alcohols, which are useful monomers for novel polyesters, polyolefins, and other applications. Currently, further up-scaling on kilogram scale is under way.

Experimental Section

All manipulations were performed under argon atmosphere using standard Schlenk techniques. Chemicals were purchased from Aldrich, Fluka, and Acros. Ethylene glycol and 1,3-propanediol were distilled prior to use. All products were characterized by ^{1}H NMR, ^{13}C NMR, MS, HRMS and elemental analysis (EA). ^{1}H- and ^{13}C NMR spectra were recorded on a Bruker AV 300 spectrometer. The ^{1}H NMR chemical shifts and the ^{13}C NMR chemical shifts were reported relative to the center of solvent resonance ($CDCl_3$: 7.27 (^{1}H), 77.23 (^{13}C)). EI mass spectra were recorded on a MAT 95XP spectrometer (Thermo ELECTRON CORPORATION). GC was performed on a Hewlett-Packard HP 6890 chromatograph with a 30 m HP5 column.

Telomerization of 1,3-Butadiene with 2-*N*-Methylaminoethanol. Palladium acetylacetonate (70.4 mg, 2.3×10^{-4} mol) and 1,3-dimesitylimidazoliumchloride (394 mg, 1.16×10^{-3} mol) were added in a dried and secured vessel under argon. Afterwards 100 mL of methanol and 187 mL of 2-*N*-methylaminoethanol (2.3 mol) were added. The mixture was transferred under argon into a secured 2 L stainless steel Parr autoclave. The autoclave was cooled with dry ice, and 250 g (4.6 mol) of 1,3-butadiene was condensed into it. By addition of nitrogen pressure the total pressure was increased to 20 bar. The vessel was heated to the desired reaction temperature which is up to 90 °C. After 10 h the autoclave was cooled to room temperature and the main product was isolated from the reaction mixture via distillation. Isolated yield of **12** = 90% (380 g).

***N*-Methyl-*N*-(octa-2,7-dienyl)aminoethanol (12):** ^{1}H NMR ($CDCl_3$, 500.13 MHz): δ = 5.76 (ddt, 1H, J = 17.0 Hz, J = 10.2 Hz, J = 6.8 Hz), 5.56−5.50 (m, 1H), 5.45−5.40 (m, 1H, J = 15.5 Hz), 4.98−4.89 (m, 2H), 3.55 (t, 2H, J = 5.5 Hz), 3.08 (br, 1H, O*H*), 2.96 (d, 2H, J = 6.6 Hz), 2.48 (t, 2H, J = 5.5 Hz), 2.18 (s, 3H), 2.01 (m, 4H), 1.43 (quint, 2H, J = 7.5 Hz). ^{13}C NMR ($CDCl_3$, 125.8 MHz): δ = 138.5, 134.0, 126.8, 114.5, 59.9, 58.4, 58.0, 41.4, 33.1, 31.7, 28.4. MS (EI, 70 eV): m/z = 183 $[M]^+$ (1.16), 152 (100), 109 (9.23), 81 (10.46), 67 (79.82), 55 (23.74). HRMS: calcd 183.16177 ($C_{11}H_{21}ON$), found 183.161673. EA: calcd C 72.08, H 11.55, N 7.64; found C 72.20, H 11.50, N 7.46.

Telomerization of 1,3-Butadiene with Ethylene Glycol. 1,3-Dimesitylimidazol-2-ylidenepalladiumtetramethyldivinyldisiloxane (32.9 mg; 5.5×10^{-5} mol) and 1,3-dimesitylimidazoliumchloride (189 mg, 5.5×10^{-4} mol) were added in a dried and secured vessel under argon. Afterwards 100 mL of tetrahydrofuran and 172 mL of ethylene glycol (3.1 mol) containing 0.5 mol % sodium-1,2-bisethanolate were added. The mixture was transferred under argon into a secured 2 L stainless steel Parr autoclave. The autoclave was cooled with dry ice, and 300 g (5.5 mol) of 1,3-butadiene was condensed into it. By addition of nitrogen pressure the total pressure was increased to 20 bar. The vessel was heated to the desired reaction temperature which is up to 80 °C. After 10 h the autoclave was cooled to room temperature, and the main products were isolated from the reaction mixture via distillation. Isolated yield of **10** = 50% (234 g), isolated yield of the corresponding bisether **13** = 20% (76 g).

Octa-2,7-dienyl-2-hydroxyethylether (10): ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 5.77 (ddt, 1H, J = 17.1 Hz, J = 10.3 Hz, J = 6.8 Hz), 5.74−5.49 (m, 2H), 4.98 (ddt, 1H, J = 17.1 Hz, J = 2.1 Hz, J = 1.5 Hz), 4.93 (ddt, 1H, J = 10.2 Hz, J = 2.1 Hz, J = 1.3 Hz), 3.95 (dq, 2H, J = 6.2 Hz, J = 0.9 Hz), 3.60 (m, 4H), 2.59 (bs, 1H, O*H*), 2.08−1.99 (m, 4H), 1.46 (quint, 2H, J = 7.5 Hz). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 138.4, 134.7, 126.2, 114.5, 71.8, 70.9, 61.7, 33.1, 31.6, 28.1. MS (EI, 70 eV): m/z (relative intensity) = 169 $[M^+]$ (15.59), 125 (17.45), 109 (19.31), 67 (100), 57 (46.21), 41 (30.06). HRMS: calcd for 169.12231 ($C_{10}H_{17}O_2$), found: 169.122390. EA: calcd for C 70.55, H 10.66; found: C 70.57, H 10.42.

Ethyl-1,2-di(octa-2,7-dienyl)ether (13): ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 5.78 (ddt, 2H, J = 16.8 Hz, J = 10.2 Hz, J = 6.6 Hz), 5.73−5.51 (m, 4H), 4.99 (ddt, 2H, J = 17.1 Hz, J = 2.1 Hz, J = 1.5 Hz), 4.94 (ddt, 2H, J = 10.2 Hz, J = 2.1 Hz, J = 1.3 Hz), 3.96 (dq, 4H, J = 6.0 Hz, J = 0.9 Hz), 3.56 (s, 4H), 2.09−2.01 (m, 8H), 1.47 (quint, 4H, J = 7.5 Hz). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 138.5, 138.5, 134.3, 134.3, 126.5, 126.5, 114.5, 114.5, 72.0, 72.0, 69.1, 69.1, 33.1, 33.1, 31.6, 31.6, 28.2, 28.2. GC−MS: m/z (relative intensity) = 169 (28.44), 125 (24.82), 107 (15.54), 81 (28.29), 67 (100), 55 (44.24), 41 (28.37). EA: calcd for C 77.65, H 10.86; found: C 77.59, H 10.75.

Octa-2,7-dienyl-2-hydroxypropylether (11): ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 5.78 (ddt, 1H, J = 16.9 Hz, J = 10.0 Hz, J = 6.6 Hz), 5.68 (dtt, 1H, J = 15.4 Hz, J = 6.6 Hz, J = 1.2 Hz), 5.54 (dtt, 1H, J = 15.4 Hz, J = 6.1 Hz, J = 1.2 Hz), 4.99 (ddt, 1H, J = 17.1 Hz, J = 2.0 Hz, J = 1.7 Hz), 4.94 (ddt, 1H, J = 10.3 Hz, J = 2.1 Hz, J = 1.2 Hz), 3.97−3.92 (m, 3H), 3.39 (dd, 1H, J = 9.3 Hz, J = 3.2 Hz), 3.19 (dd, 1H, J = 9.5 Hz, J = 8.1 Hz), 2.52 (d, 1H, J = 2.2 Hz, O*H*), 2.08−2.02 (m, 4H), 1.47 (quint, 2H, J = 7.5 Hz), 1.13 (d, 3H, J = 6.4 Hz, C*H*$_3$).^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 138.5, 134.6, 126.3, 114.6, 75.4, 71.9, 66.4, 33.1, 31.6, 28.2, 18.6 (CH_3). GC−MS: m/z (relative intensity) = 184 $[M^+]$ (<1), 125 (3.9), 109 (37.34), 81 (29.40), 67 (100), 59 (40.59), 45 (44.27). HRMS: calcd for 207.13555 ($C_{11}H_{20}O_2Na$), found 207.13561. EA: calcd for C 71.70, H 10.94, O 17.36; found C 71.61, H 11.02.

Propyl-1,2-di(octa-2,7-dienyl)ether (14): ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 5.80 (ddt, 2H, J = 16.7 Hz, J = 10.2 Hz, J = 6.6 Hz), 5.72−5.52 (m, 4H), 5.03−4.97 (m, 2H), 4.97−4.92 (m, 2H), 4.02−3.99 (m, 2H), 3.99−3.91 (m, 2H), 3.65 (q, 1H, J = 5.9 Hz), 3.44 (dd, 1H, J = 10.0 Hz, J = 5.9 Hz), 3.33 (dd, 1H, J = 10.0 Hz, J = 4.9 Hz), 2.09−2.03 (m, 8H), 1.52−1.44 (m, 4H), 1.15 (d, 3H, J = 6.4 Hz, C*H*$_3$).^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 138.6, 138.6, 134.1, 133.7, 127.1, 126.7, 114.5, 114.5, 73.8, 73.5, 72.0, 69.8, 33.2, 33.2, 31.6, 31.6, 28.3, 28.2, 17.4 (CH_3). GC−MS: m/z (relative intensity) = 292 $[M^+]$ (<1), 183 (9.38), 125 (24.45), 109 (44.29), 67 (100), 55 (29.15), 41 (19.17). HRMS: calcd for 292.23968 ($C_{19}H_{32}O_2$), found 292.240343. EA: calcd for C 78.03, H 11.03, O 10.94; found C 78.20, H 11.32.

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