

Stereoselective Synthesis of Trisubstituted Olefins through 2,5-Dialkylidenemagnesacyclopentanes

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Abstract—An efficient one-pot procedure for the synthesis of trisubstituted olefins with *Z*-configured double bonds has been developed on the basis of cross coupling of 2,5-dialkylidenemagnesacyclopentanes (generated in situ) with alkyl, allyl, and aryl halides in the presence of transition metal (Cu, Zr, Fe, Co, Ni, Pd) salts and complexes.

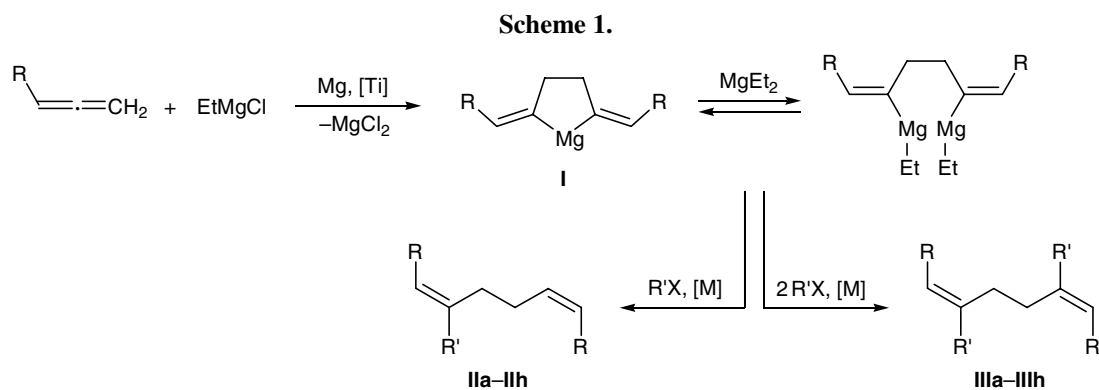
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Hydromagnesation of disubstituted acetylenes with isobutylmagnesium bromide [1, 2] or diisobutylmagnesium [3], catalyzed by Cp_2TiCl_2 , provides an efficient method for the preparation of (*E*)-alkenyl-containing organomagnesium reagents. Cross coupling of the latter with organic halogen derivatives opens the way to stereoselective design of trisubstituted olefins that can be used for the preparation of a number of practically important compounds, including those possessing biological activity [4–9]. Available information on the synthesis of (*E*)-alkenyl organomagnesiums from 1,2-dienes is strongly limited [10].

We recently [11] synthesized 2,5-dialkylidenemagnesacyclopentanes by catalytic cyclomagnesation of 1,2-dienes with EtMgCl . The products contain highly reactive vinylic Mg–C bonds and (*Z*)-alkenyl

fragments and are therefore exceptionally promising from the viewpoint of selective synthesis of trisubstituted (1*Z*,5*Z*)-diolefins. The goal of the present study was to extend the scope of application of non-Grignard organomagnesium reagents in cross coupling reactions, as well as to develop an efficient one-pot procedure for the synthesis of trisubstituted (*Z*)-olefins via cross coupling of 2,5-dialkylidenemagnesacyclopentanes with organic halogen derivatives.

The reaction of 2,5-dihexylidenemagnesacyclopentane (**Ia**) with MeI in the presence of $\text{CuCl}\cdot 2\text{Ph}_3\text{P}$ as catalyst was used as model system to determine optimal conditions for the process; at a **Ia**-to- MeI ratio of 1:2.5 and catalyst concentration of 10 mol % (tetrahydrofuran, $\sim 20^\circ\text{C}$), the yield of diolefin **IIIa** was $\sim 85\%$ ($[\text{M}]^+$ 250). The ^{13}C NMR spectrum of **IIIa**



R = C_5H_{11} , X = I, R' = Me (**a**), Et (**b**), Ph (**e**); X = Cl, R' = $\text{CH}_2=\text{CHCH}_2$ (**c**), $\text{CH}_2=\text{C}(\text{Me})\text{CH}_2$ (**d**); R = C_7H_{15} , R' = Me, X = I (**f**); R' = $\text{CH}_2=\text{CHCH}_2$, X = Cl (**g**); R = PhCH_2 , R' = $\text{CH}_2=\text{CHCH}_2$, X = Cl (**h**); [Ti] = Cp_2TiCl_2 ; [M] = Cu, Pd, Ni, Co.

contained upfield signals from C^5/C^{12} at δ_C 28.07 ppm and C^8/C^9 at δ_C 29.86 ppm, which are typical of carbon atoms in the allylic position with respect to *cis*-configured double bonds in an alkadiene fragment. The double-bonded C^6/C^{11} and C^7/C^{10} atoms resonated at δ_C 126.56 and 137.44 ppm, respectively. These data allowed us to assigned the structure of (6*Z*,10*Z*)-7,10-dimethylhexadeca-6,10-diene to hydrocarbon **IIIa**.

We also tested various transition metal salts and complexes (Cu, Zr, Fe, Co, Ni, Pd) as catalysts in the cross coupling of magnesacyclopentane **Ia** with MeI. As a result, the following activity series was obtained: CuCl + 2 Ph₃P (85%) > CuCl (84%) > Pd(acac)₂ + 2 Ph₃P (83%) > Cu(acac)₂ + 2 Ph₃P (82%) > CuI (81%) > PdCl₂ + 2 Ph₃P (72%) > Ni(acac)₂ + 2 Ph₃P (69%) > Pd(Ph₃P)₄ (68%) > Fe(acac)₃ + 2 Ph₃P (57%) > Pd(Ph₃P)₂Cl₂ (55%) > Pd(dba)₂ + 2 Ph₃P (54%) > NiCl₂ + 2 Ph₃P (32%) > CoCl₂ + 2 Ph₃P (28%). It is seen that Cu, Pd, and Ni compounds ensure the highest yields of target cross-coupling product **IIIa**.

The reaction of 2,5-dihexylidenemagnesacyclopentane (**Ia**) with an equimolar amount of methyl iodide gave ~64% of (6*Z*,10*Z*)-7-methylhexadeca-6,10-diene (**IIa**) having di- and trisubstituted double bonds with *cis* configuration. This follows from the presence of upfield signals in the ¹³C NMR spectrum at δ_C 28.05 and 29.18 ppm for C^5 and C^8 and at δ_C 26.97 and 27.42 ppm for C^9 and C^{12} , respectively. Apart from compound **IIa**, ~10% of (6*Z*,10*Z*)-7,10-dimethylhexadeca-6,10-diene (**IIIa**) was formed via cross coupling of magnesacyclopentadiene **Ia** with two molecules of methyl iodide.

Under the optimal conditions (10 mol % of CuCl + 2 Ph₃P, THF, 20°C, 8 h) we performed reactions of 2,5-dialkylidenemagnesacyclopentanes **Ib–Ih** with ethyl and phenyl iodides and allyl and 2-methylprop-2-en-1-yl chlorides and obtained the corresponding products **IIb–IIh** or **IIIb–IIIh** in 75–85% yield (Scheme 1). The ratio of compounds **II** and **III** depended on the ratio of initial 2,5-dialkylidenemagnesacyclopentanes **I** and organic halogen derivatives.

Our results demonstrate that transition-metal catalyzed cross coupling of 2,5-dialkylidenemagnesacyclopentanes with halogen derivatives provides an efficient method for the stereoselective synthesis of di- and trisubstituted diolefins in high yields.

EXPERIMENTAL

The hydrolysis products were analyzed by GLC on a Chrom-5 chromatograph (carrier gas helium; 1200×3-mm column packed with 5% of SE-30 or 15% of

PEG-6000 on Chromaton N-AW). The IR spectra were recorded on a Specord 75IR spectrometer from thin films (neat). The ¹H and ¹³C NMR spectra were measured from solutions in CDCl₃ on Jeol FX-90Q (89.55 MHz for ¹H and 22.5 MHz for ¹³C) and Bruker AM-300 spectrometers (300 MHz for ¹H and 75.46 MHz for ¹³C). The mass spectra (electron impact, 70 eV) were obtained on an MKh-1306 instrument (ion source temperature 200°C). All experiments were carried out under dry argon. Solutions of ethylmagnesium bromide in THF were prepared by the procedure described in [12]; THF was heated under reflux over metallic sodium and then distilled under argon prior to use. Commercial Cp₂TiCl₂ was used. Initial 1,2-dienes were synthesized according to [13]. Reactions with organometallic compounds were carried out in a stream of dry argon. The yields were determined by GLC analysis of the hydrolysis products.

Reaction of 2,5-dialkylidenemagnesacyclopentanes with organic halides (general procedure). A glass reactor was charged under dry argon at 0°C with 12 mmol of a freshly prepared solution of EtMgCl in THF, 6 mmol of magnesium powder, 10 mmol of the corresponding 1,2-diene, and 0.5 mmol of Cp₂TiCl₂. The mixture was allowed to warm up to room temperature, stirred for 8 h on a magnetic stirrer, and cooled to –20°C, 1 mmol of CuCl–2 Ph₃P was added, 5 or 12.5 mmol of the corresponding halogen derivative was added dropwise, and the mixture was allowed to warm up to room temperature and stirred for 6 h. The mixture was then treated with 5% hydrochloric acid and extracted with diethyl ether, the extract was dried over MgSO₄, the solvent was removed, and compounds **IIa–IIh** and **IIIa–IIIh** were isolated by vacuum distillation.

(6*Z*,10*Z*)-7-Methylhexadeca-6,10-diene (IIa). bp 110–111°C (1 mm). IR spectrum, ν , cm⁻¹: 3050, 2910, 2810, 1640, 1490, 1460, 1000, 920, 890, 710, 700. ¹H NMR spectrum, δ , ppm: 0.65–0.89 m (6H, CH₃), 1.11–1.35 m (12H, CH₂), 1.61 s (3H, CH₃), 1.81–2.21 m (8H, CH₂C=C), 4.86–4.97 m (1H, HC=C), 5.0–5.36 m (2H, HC=C). ¹³C NMR spectrum, δ_C , ppm: 14.05 (C¹), 14.16 (C¹⁶), 22.51 (C²), 22.61 (C¹⁵), 22.63 (CH₃), 26.97 (C⁹), 27.42 (C¹²), 28.05 (C⁵), 29.18 (C⁸), 29.27 (C⁴), 29.89 (C¹³), 31.45 (C³), 31.56 (C¹⁴), 126.56 (C⁶), 128.97 (C¹⁰), 130.75 (C¹¹), 136.46 (C⁷). Found, %: C 85.01; H 13.15. $[M]^+$ 236. C₁₇H₃₂. Calculated, %: C 86.36; H 13.64.

(6*Z*,10*Z*)-7,10-Dimethylhexadeca-6,10-diene (IIIa). bp 121–122°C (1 mm). IR spectrum, ν , cm⁻¹:

3030, 2900, 2800, 1650, 1490, 1450, 1000, 910, 890, 720, 700. ^1H NMR spectrum, δ , ppm: 0.62–0.87 t (6H, CH_3 , $J = 6.0$ Hz), 1.10–1.36 m (12H, CH_2), 1.72 s (6H, CH_3), 1.80–2.22 m (8H, $\text{CH}_2\text{C}=\text{C}$), 4.88–4.95 m (2H, $\text{CH}=\text{C}$). ^{13}C NMR spectrum, δ_{C} , ppm: 13.96 (C^1 , C^{16}), 22.52 (C^2 , C^{15}), 22.63 (CH_3), 28.07 (C^5 , C^{12}), 29.75 (C^4 , C^{13}), 29.86 (C^8 , C^9), 31.60 (C^3 , C^{14}), 126.56 (C^6 , C^{11}), 137.44 (C^7 , C^{10}). Found, %: C 84.89; H 12.95. $[M]^+$ 250. $\text{C}_{18}\text{H}_{34}$. Calculated, %: C 86.32; H 13.68.

(6Z,10Z)-7-Ethylhexadeca-6,10-diene (IIb). bp 120–122°C (1 mm). IR spectrum, ν , cm^{-1} : 3030, 2900, 2800, 1650, 1495, 1460, 1000, 910, 895, 720, 695. ^1H NMR spectrum, δ , ppm: 0.65–1.05 m (9H, CH_3), 1.13–1.39 m (12H, CH_2), 1.81–2.21 m (10H, $\text{CH}_2\text{C}=\text{C}$), 4.84–4.95 m (1H, $\text{HC}=\text{C}$), 5.05–5.34 m (2H, $\text{HC}=\text{C}$). ^{13}C NMR spectrum, δ_{C} , ppm: 14.05 (C^1), 13.02 (CH_3), 14.12 (C^{16}), 22.53 (C^2), 22.60 (C^{15}), 25.81 (C^9), 26.48 (CH_2), 27.85 (C^{12}), 28.11 (C^5), 29.19 (C^8), 29.31 (C^4), 29.79 (C^{13}), 31.42 (C^3), 31.54 (C^{14}), 126.51 (C^6), 128.87 (C^{10}), 130.74 (C^{11}), 137.46 (C^7). Found, %: C 85.75; H 12.99. $[M]^+$ 250. $\text{C}_{18}\text{H}_{34}$. Calculated, %: C 86.32; H 13.68.

(6Z,10Z)-7,10-Diethylhexadeca-6,10-diene (IIIb). bp 140–142°C (1 mm). IR spectrum, ν , cm^{-1} : 3050, 2900, 2810, 1650, 1480, 1450, 1000, 920, 890, 725, 700. ^1H NMR spectrum, δ , ppm: 0.62–0.99 m (12H, CH_3), 1.12–1.38 m (12H, CH_2), 1.81–2.25 m (12H, $\text{CH}_2\text{C}=\text{C}$), 4.80–4.91 m (2H, $\text{CH}=\text{C}$). ^{13}C NMR spectrum, δ_{C} , ppm: 12.58 (CH_3), 14.02 (C^1 , C^{16}), 22.55 (C^2 , C^{15}), 26.52 (CH_2), 28.17 (C^5 , C^{12}), 29.74 (C^4 , C^{13}), 29.89 (C^8 , C^9), 31.63 (C^3 , C^{14}), 126.46 (C^6 , C^{11}), 138.64 (C^7 , C^{10}). Found, %: C 84.75; H 13.06. $[M]^+$ 278. $\text{C}_{20}\text{H}_{38}$. Calculated, %: C 86.25; H 13.75.

(6E,10Z)-7-Allylhexadeca-6,10-diene (IIc). bp 133–134°C (1 mm). IR spectrum, ν , cm^{-1} : 3030, 2900, 2870, 1640, 1490, 1460, 1380, 1000, 920, 890, 720. ^1H NMR spectrum, δ , ppm: 0.72–0.91 m (6H, CH_3), 1.21–1.45 m (12H, CH_2), 1.89–2.21 m (8H, $\text{CH}_2\text{C}=\text{C}$), 2.52–2.74 d (2H, $\text{C}=\text{CCH}_2\text{C}=\text{C}$), 4.83–4.90 m (2H, $\text{H}_2\text{C}=\text{C}$), 5.0–5.14 t (1H, $\text{HC}=\text{C}$, $J = 6.0$ Hz), 5.26–5.38 m (2H, $\text{HC}=\text{CH}$), 5.58–5.86 m (1H, $\text{H}_2\text{C}=\text{CH}$). ^{13}C NMR spectrum, δ_{C} , ppm: 14.05 (C^1), 14.09 (C^{16}), 22.54 (C^2), 22.62 (C^{15}), 25.99 (C^9), 27.84 (C^{12}), 28.15 (C^5), 29.28 (C^8), 29.37 (C^4), 29.98 (C^{13}), 31.46 (C^3), 31.46 (C^{14}), 41.86 (CH_2), 115.49 ($=\text{CH}_2$), 126.61 (C^6), 129.34 (C^{10}), 130.75 (C^{11}), 137.26 (C^7), 137.50 ($\text{CH}=\text{C}$). Found, %: C 86.12; H 12.55. $[M]^+$ 262. $\text{C}_{19}\text{H}_{34}$. Calculated, %: C 86.94; H 13.06.

(6E,10E)-7,10-Diallylhexadeca-6,10-diene (IIIc). bp 164–166°C (1 mm). IR spectrum, ν , cm^{-1} : 3030,

2950, 2860, 1650, 1490, 1450, 1390, 1000, 910, 890, 720. ^1H NMR spectrum, δ , ppm: 0.75–0.92 t (6H, CH_3 , $J = 6.0$ Hz), 1.21–1.42 m (12H, CH_2), 1.91–2.25 m (8H, $\text{CH}_2\text{C}=\text{C}$), 2.55–2.75 d (4H, $\text{C}=\text{CCH}_2\text{C}=\text{C}$), 4.85–4.96 m (4H, $\text{H}_2\text{C}=\text{C}$), 5.0–5.15 t (2H, $\text{CH}_2\text{CH}=\text{C}$, $J = 6.0$ Hz), 5.55–5.85 m (2H, $\text{H}_2\text{C}=\text{CH}$). ^{13}C NMR spectrum, δ_{C} , ppm: 13.92 (C^1 , C^{16}), 22.54 (C^2 , C^{15}), 29.0 (C^4 , C^{13}), 29.20 (C^5 , C^{12}), 29.72 (C^8 , C^9), 29.75 (C^4 , C^{13}), 31.64 (C^3 , C^{14}), 41.84 (CH_2), 115.52 ($=\text{CH}_2$), 126.56 (C^6 , C^{11}), 136.44 (C^7 , C^{10}), 137.50 ($\text{CH}=\text{C}$). Found, %: C 86.25; H 11.81. $[M]^+$ 302. $\text{C}_{22}\text{H}_{38}$. Calculated, %: C 87.34; H 12.66.

(6E,10Z)-7-(2-Methylprop-2-en-1-yl)hexadeca-6,10-diene (IIId). bp 144–145°C (1 mm). IR spectrum, ν , cm^{-1} : 3030, 2900, 2860, 1640, 1480, 1460, 1390, 1000, 910, 890, 720. ^1H NMR spectrum, δ , ppm: 0.79–0.91 m (6H, CH_3), 1.21–1.45 m (12H, CH_2), 1.63 s (3H, CH_3), 1.95–2.21 m (8H, $\text{CH}_2\text{C}=\text{C}$), 2.69–2.74 d (2H, $\text{C}=\text{CCH}_2\text{C}=\text{C}$), 4.8 s (2H, $\text{H}_2\text{C}=\text{C}$), 5.0–5.14 t (1H, $\text{CH}_2\text{CH}=\text{C}$, $J = 6.0$ Hz), 5.22–5.38 m (2H, $\text{CH}=\text{CH}$). ^{13}C NMR spectrum, δ_{C} , ppm: 14.03 (C^1), 14.09 (C^{16}), 20.21 (CH_3), 22.52 (C^2), 22.59 (C^{15}), 25.94 (C^9), 27.79 (C^{12}), 28.25 (C^5), 29.29 (C^8), 29.47 (C^4), 29.88 (C^{13}), 31.36 (C^3), 31.41 (C^{14}), 46.49 (CH_2), 111.82 ($=\text{CH}_2$), 126.69 (C^6), 129.24 (C^{10}), 130.66 (C^{11}), 137.21 (C^7), 144.41 ($\text{CH}_3\text{C}=\text{C}$). Found, %: C 85.14; H 12.75. $[M]^+$ 276. $\text{C}_{20}\text{H}_{36}$. Calculated, %: C 86.88; H 13.12.

(6E,10E)-7,10-Bis(2-methylprop-2-en-1-yl)hexadeca-6,10-diene (IIIId). bp 187–188°C (1 mm). IR spectrum, ν , cm^{-1} : 3030, 2950, 2860, 1650, 1480, 1450, 1390, 1000, 920, 890, 720. ^1H NMR spectrum, δ , ppm: 0.81–0.92 t (6H, CH_3 , $J = 6.0$ Hz), 1.21–1.35 m (12H, CH_2), 1.65 s (6H, CH_3), 2.05–2.20 m (8H, $\text{CH}_2\text{C}=\text{C}$), 2.75–2.85 m (4H, $\text{C}=\text{CCH}_2\text{C}=\text{C}$), 4.85 s (4H, $\text{H}_2\text{C}=\text{C}$), 5.25–5.45 m (2H, $\text{C}=\text{CH}$). ^{13}C NMR spectrum, δ_{C} , ppm: 14.06 (C^1 , C^{16}), 20.24 (CH_3), 22.62 (C^2 , C^{15}), 27.96 (C^5 , C^{12}), 28.45 (C^8 , C^9), 29.78 (C^4 , C^{13}), 31.67 (C^3 , C^{14}), 46.52 (CH_2), 111.84 ($=\text{CH}_2$), 127.70 (C^6 , C^{11}), 136.88 (C^7 , C^{10}), 144.53 ($\text{CH}_3\text{C}=\text{C}$). Found, %: C 86.46; H 12.11. $[M]^+$ 302. $\text{C}_{24}\text{H}_{42}$. Calculated, %: C 87.19; H 12.81.

(6E,10Z)-7-Phenylhexadeca-6,10-diene (IIe). bp 172–174°C (1 mm). IR spectrum, ν , cm^{-1} : 3050, 2950, 2860, 1640, 1490, 1450, 1390, 1000, 920, 890, 710. ^1H NMR spectrum, δ , ppm: 0.76–0.94 m (6H, CH_3), 1.23–1.94 m (12H, CH_2), 1.95–2.22 m (8H, $\text{CH}_2\text{C}=\text{C}$), 5.0–5.37 m (2H, $\text{CH}=\text{CH}$), 5.55–5.85 m (1H, $\text{C}=\text{CH}$), 7.0–7.5 m (5H, Ph). ^{13}C NMR spectrum, δ_{C} , ppm: 14.03 (CH_3), 14.12 (C^{10}), 22.58 (CH_2), 22.61 (C^9), 27.61 (C^3), 27.82 (C^6), 29.54 (CH_2), 30.35 (C^7),

30.63 (CH₂), 31.51 (C⁸), 31.58 (CH₂), 32.12 (C²), 125.23 (C_{arom}), 126.35 (CH=), 126.64 (C_{arom}), 128.09 (C⁴), 128.16 (C¹), 128.37 (C_{arom}), 130.62 (C⁵), 145.34 (C_{arom}). Found, %: C 87.67; H 10.93. [M]⁺ 298. C₂₂H₃₄. Calculated, %: C 88.52; H 11.48.

(6E,10Z)-7,10-Diphenylhexadeca-6,10-diene (IIIe). bp 248–249°C (1 mm). IR spectrum, ν, cm⁻¹: 3030, 2950, 2860, 1650, 1490, 1450, 1390, 1000, 910, 890, 720. ¹H NMR spectrum, δ, ppm: 0.63–0.88 t (6H, CH₃, J = 6.0 Hz), 1.12–1.36 m (12H, CH₂), 1.80–2.24 m (8H, CH₂C=C), 4.86–4.95 m (2H, CH=C), 7.0–7.55 m (10H, Ph). ¹³C NMR spectrum, δ_C, ppm: 13.98 (C¹, C¹⁶), 22.58 (C², C¹⁵), 29.56 (C⁴, C¹³), 30.25 (C⁵, C¹²), 30.46 (C⁸, C⁹), 31.60 (C³, C¹⁴), 125.15 (C_{arom}), 126.58 (C⁶, C¹¹), 126.62 (C_{arom}), 127.42 (C⁷, C¹⁰), 128.47 (C_{arom}), 142.54 (C_{arom}). Found, %: C 88.36; H 9.86. [M]⁺ 374. C₂₈H₃₈. Calculated, %: C 89.78; H 10.22.

(8Z,12Z)-9-Methylicosa-8,12-diene (IIIf). bp 155–157°C (1 mm). IR spectrum, ν, cm⁻¹: 3030, 2920, 2800, 1650, 1480, 1460, 1000, 910, 890, 720, 700. ¹H NMR spectrum, δ, ppm: 0.65–0.89 m (6H, CH₃), 1.13–1.35 m (20H, CH₂), 1.62 s (3H, CH₃), 1.81–2.25 m (8H, CH₂C=C), 4.87–4.94 m (1H, HC=C), 5.1–5.46 m (2H, HC=C). ¹³C NMR spectrum, δ_C, ppm: 14.05 (C¹, C²⁰); 22.71 (C², C¹⁹); 22.65 (CH₃); 26.97 (C¹¹); 27.67 (C⁷); 27.82 (C¹⁴); 28.05 (C¹⁰); 29.33, 29.42, 29.81, 29.97 (C⁵, C⁶, C¹⁶, C¹⁷); 30.21 (C¹⁵); 30.34 (C³, C¹⁸); 31.46 (C⁴); 125.86 (C⁸); 129.87 (C¹³); 130.24 (C¹²); 138.15 (C⁹). Found, %: C 85.73; H 13.06. [M]⁺ 292. C₂₁H₄₀. Calculated, %: C 86.22; H 13.78.

(8Z,12Z)-9,12-Dimethylicosa-8,12-diene (IIIIf). bp 166–168°C (1 mm). IR spectrum, ν, cm⁻¹: 3050, 2910, 2820, 1650, 1480, 1450, 1050, 920, 890, 710, 700. ¹H NMR spectrum, δ, ppm: 0.65–0.89 t (6H, CH₃, J = 6.0 Hz), 1.15–1.35 m (20H, CH₂), 1.65 s (6H, CH₃), 1.85–2.23 m (8H, CH₂C=C), 4.89–4.97 m (2H, CH=C). ¹³C NMR spectrum, δ_C, ppm: 14.05 (C¹, C²⁰), 22.57 (C², C¹⁹), 22.64 (CH₃), 28.07 (C⁶, C¹⁵), 29.64 and 29.75 (C⁴, C⁵, C¹⁶, C¹⁷), 29.89 (C¹⁰, C¹¹), 30.09 (C⁷, C¹⁴), 31.62 (C³, C¹⁸), 126.66 (C⁸, C¹³), 137.45 (C⁹, C¹²). Found, %: C 85.92; H 13.05. [M]⁺ 306. C₂₂H₄₂. Calculated, %: C 86.19; H 13.81.

(8E,12Z)-9-Allylicosa-8,12-diene (IIIf). bp 176–177°C (1 mm). IR spectrum, ν, cm⁻¹: 3030, 2950, 2870, 1640, 1490, 1460, 1380, 1000, 910, 890, 720. ¹H NMR spectrum, δ, ppm: 0.75–0.92 m (6H, CH₃), 1.21–1.42 m (20H, CH₂), 1.89–2.21 m (8H, CH₂C=C), 2.55–2.74 d (2H, C=CCH₂C=C), 4.81–4.90 m (2H,

H₂C=C), 5.0–5.14 t (1H, HC=C, J = 6.0 Hz), 5.25–5.36 m (2H, HC=CH), 5.58–5.84 m (1H, H₂C=CH). ¹³C NMR spectrum, δ_C, ppm: 14.06 (C¹, C²⁰); 22.52 (C², C¹⁹); 26.27 (C¹¹); 27.85 (C¹⁴); 28.13 (C⁶); 29.21 (C⁷); 29.27 (C¹⁰); 29.37, 29.46, 29.56, 29.98 (C⁴, C⁵, C¹⁶, C¹⁷); 30.14 (C¹⁵); 31.42 (C³, C¹⁸); 41.74 (CH₂); 115.36 (=CH₂); 126.72 (C⁸); 129.41 (C¹²); 130.65 (C¹³); 137.16 (C⁹); 137.52 (CH=). Found, %: C 86.15; H 12.78. [M]⁺ 262. C₂₃H₄₂. Calculated, %: C 86.71; H 13.29.

(8E,12E)-9,12-Diallylicosa-8,12-diene (IIIg). bp 207–208°C (1 mm). IR spectrum, ν, cm⁻¹: 3030, 2960, 2860, 1650, 1490, 1450, 1390, 1050, 920, 890, 720. ¹H NMR spectrum, δ, ppm: 0.74–0.91 m (6H, CH₃), 1.22–1.44 m (20H, CH₂), 1.90–2.23 m (8H, CH₂C=C), 2.56–2.75 d (4H, C=CCH₂C=C), 4.84–4.96 m (4H, H₂C=C), 5.05–5.15 t (2H, HC=C, J = 6.0 Hz), 5.56–5.84 m (2H, H₂C=CH). ¹³C NMR spectrum, δ_C, ppm: 14.01 (C¹, C²⁰), 22.56 (C², C¹⁹), 28.16 (C⁶, C¹⁵), 29.06 and 29.26 (C⁴, C⁵, C¹⁶, C¹⁷), 29.28 (C⁷, C¹⁴), 29.78 (C¹⁰, C¹¹), 31.67 (C³, C¹⁸), 41.91 (CH₂), 115.48 (=CH₂), 126.58 (C⁸, C¹³), 136.34 (C⁹, C¹²), 137.56 (CH=). Found, %: C 86.52; H 12.31. [M]⁺ 358. C₂₆H₄₆. Calculated, %: C 87.07; H 12.93.

(2E,6Z)-3-Allyl-1,8-diphenylocta-2,6-diene (IIIh). bp 200–202°C (1 mm). IR spectrum, ν, cm⁻¹: 3030, 2920, 2800, 1650, 1490, 1460, 1000, 920, 890, 720, 700. ¹H NMR spectrum, δ, ppm: 1.90–2.25 m (4H, CH₂C=C), 2.55–2.76 d (2H, C=CCH₂C=C), 3.35–3.48 m (4H, CH₂Ph), 4.85–4.96 m (2H, H₂C=C), 5.0–5.15 m (3H, HC=CH, CH=C), 5.55–5.86 m (1H, H₂C=CH), 7.11–7.36 m (10H, Ph). ¹³C NMR spectrum, δ_C, ppm: 29.69 (C⁴, C⁵), 33.48 (C⁸), 33.89 (C¹), 41.59 (CH₂), 115.82 (=CH₂), 125.41 (C_{arom}), 127.50 (C²), 127.74 (C⁷), 128.14 (C_{arom}), 129.08 (C_{arom}), 130.71 (C⁶), 136.69 (=CH), 138.20 (C³), 141.17 (C_{arom}). Found, %: C 90.98; H 8.05. [M]⁺ 302. C₂₃H₂₆. Calculated, %: C 91.34; H 8.66.

(2E,6E)-3,6-Diallyl-1,8-diphenylocta-2,6-diene (IIIh). bp 180–181°C (1 mm). IR spectrum, ν, cm⁻¹: 3030, 2900, 2800, 1650, 1490, 1450, 1000, 910, 890, 720, 700. ¹H NMR spectrum, δ, ppm: 1.91–2.25 m (4H, CH₂CH=C), 2.55–2.75 d (4H, C=CHCH₂C=C), 3.32–3.41 d (4H, CH₂Ph), 4.85–4.96 m (4H, H₂C=C), 5.0–5.15 t (2H, HC=C, J = 6.0 Hz), 5.55–5.85 m (2H, H₂C=CH), 7.15–7.35 m (10H, Ph). ¹³C NMR spectrum, δ_C, ppm: 28.81 (C⁴, C⁵), 33.9 (C¹, CH₂Ph), 41.61 (C⁷, CH₂), 115.98 (C⁹, =CH₂), 125.68 (C_{arom}), 127.56 (C², =CH), 128.19 (C_{arom}), 129.11 (C_{arom}), 136.8 (C⁸, =CH), 138.35 (C³, C⁶), 141.18 (C_{arom}). Found, %:

C 91.01; H 8.12. $[M]^+$ 342. $C_{26}H_{30}$. Calculated, %: C 91.17; H 8.83.

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