

Supporting Information

Efficient Preparation of Terminal Conjugated Dienes by Coupling of Dienol Phosphates with Grignard Reagents under Iron Catalysis

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Table of contents

Instrumentation and Chemicals

Experimental Procedures

Characterization Data

¹H. ¹³C NMR Spectra

Instrumentation and Chemicals

^1H and ^{13}C NMR spectra were recorded on a JEOL ECX-400 spectrometer. Chemical shifts are given in ppm from TMS as an internal reference.

Mass spectra were recorded on a Hewlett-Packard HP 5973 mass spectrometer via a GC/MS coupling with a Hewlett-Packard HP 6890 chromatograph equipped with a capillary column HP-5MS (50m \times 0.25mm \times 0.25 μm). Ionisation was performed by electronic impact (EI, 70eV). Mass spectra are reported as m/z (% of relative intensity).

THF (H_2O < 5 ppm) was purchased from SdS-Carlo Erba and stored under a nitrogen atmosphere. Ether, DME and NMP were purchased from SdS-Carlo Erba. Zinc chloride, iron (III) acetylacetonate, potassium *tert*-butylate, diphenylchlorophosphate, diethylchlorophosphate, acetic anhydride, triethylamine and pyridine were purchased from Acros. Ether and DME were distilled from sodium-benzophenone under a nitrogen atmosphere. NMP, pyridine and triethylamine were distilled under a nitrogen atmosphere.

All reactions were carried out under a nitrogen atmosphere under mechanical stirring.

All starting materials were purchased from Acros or Aldrich and were used without further purification.

Alkyl, aryl and alkenyl Grignard reagents (Table 1 and 2) were prepared in THF from the commercially available aryl bromides or chlorides, by using the standard method, and titrated according to the procedure published by Watson.¹

Yields refer to isolated compounds. The purity was $\geq 98\%$ as determined by GC analysis. All compounds gave satisfactory elemental analysis. The analytical data for the known compounds found to match with the literature data.

Experimental Procedures

Fe-catalyzed coupling reaction between dienol phosphates and Grignard reagents. General procedure.

An oven-dried and nitrogen flushed 250 mL four-necked flask, equipped with a mechanical stirrer and a thermometer, was charged with a solution of $\text{Fe}(\text{acac})_3$ (1 mol%, 0.25 mmol) in THF (50 mL). The dienol phosphate (25 mmol) was added at once under stirring, then, the Grignard reagent (30 mmol) was added dropwise for 20 min. After 15 min, the reaction mixture was quenched with a 1 M aqueous HCl solution (50 mL). The aqueous phase was extracted with cyclohexane (3 \times 30 mL), dried with MgSO_4 and concentrated under reduced pressure. The product was purified by distillation or by column chromatography.

Preparation of (*E*)-dodeca-9,11-dienyl acetate; the pheromone of *Diparopsis castanea*

1/ Synthesis of (*E*)-buta-1,3-dienyl diethyl phosphate (5)

An oven-dried and nitrogen flushed 100 mL four-necked flask, equipped with a mechanical stirrer and a thermometer, was charged with potassium *tert*-butylate (3.37 g, 30 mmol) and THF (40 mL). At -78°C , crotonaldehyde (25 mmol) was added dropwise under stirring. After 1 h, diethylchlorophosphate (27.5 mmol) was added dropwise, then, the reaction was allowed to warm to room temperature. Stirring was continued for 2 h, then, the reaction mixture was quenched with a 1 M aqueous HCl solution (50 mL). The aqueous phase was extracted with

ethyl acetate (3×30 mL) and the combined organic layers were washed with brine (50 mL), dried with MgSO_4 and concentrated *in vacuo*. The product was purified by distillation under reduced pressure (Bp= 78°C/0.3 torr). 4.457 g (86% yield) of a yellow oil were obtained.

2/ Preparation of $\text{BrMgO}(\text{CH}_2)_8\text{MgBr}$

8-bromooctan-1-ol then the Grignard reagent $\text{BrMgO}(\text{CH}_2)_8\text{MgBr}$ are prepared according to the procedures reported in the literature.²

3/ Synthesis of dodeca-9,11-dien-1-ol (15)

Dodeca-9,11-dien-1-ol was obtained by coupling $\text{BrMgO}(\text{CH}_2)_8\text{MgBr}$ with (*E*)-buta-1,3-dienyl diethyl phosphate in the presence of $\text{Fe}(\text{acac})_3$ according to the procedure described above. The final product was purified by distillation under reduced pressure (Bp= 44°C/0.3 torr). 5.617 g (77% yield) of a colorless oil were obtained.

4/ Preparation of (*E*)-Dodeca-9,11-dienyl acetate (16)

An oven-dried and nitrogen flushed 5 mL necked flask, equipped with a magnetical stirrer, was charged with 182 mg of 1,3-dodecadien-12-ol (1 mmol), 0.2 mL of pyridine and 0.19 mL of acetic anhydride. After 1 h at room temperature, the reaction mixture was quenched with a 1 M aqueous HCl solution (2 mL). The aqueous phase was extracted with diethyl ether (3×10 mL), dried with MgSO_4 and concentrated *in vacuo*. The product was purified by chromatography on a silicagel column (cyclohexane-EtOAc 80:20). 214 mg (95% yield) of a colorless oil were obtained.

Characterization Data

¹H. ¹³C NMR Spectra

(*E*)-Buta-1,3-dienyl diethyl phosphate (5).

IR (neat, cm^{-1}): 2989, 1656, 1280, 1132, 1035. RMN ¹H (400MHz, CDCl_3) δ (ppm): 6.72 (dd, $J = 12.5\text{Hz}$ and $J_{\text{P-H}} = 6.4\text{Hz}$, 1H), 6.22 (ddd, $J = 16.9\text{Hz}$, 10.3Hz and 11.0Hz, 1H), 6.05 (dd, $J = 12.5\text{Hz}$ and 11.0Hz, 1H), 5.19 (d, $J = 16.9\text{Hz}$, 1H), 5.07 (d, $J = 10.3\text{Hz}$, 1H), 4.18 (dq, $J = 7.3\text{Hz}$ and $J_{\text{P-H}} = 7.1\text{Hz}$, 1H), 1.36 (t, $J = 7.3\text{Hz}$, 6H). RMN ¹³C (100.5MHz, CDCl_3) δ (ppm): 139.6, 130.9, 118.0, 116.9, 64.4, 15.9. SM (EI, 70eV) m/z : 206 (M^+ , 100%), 178 (16%), 155 (63%), 127 (66%), 99 (65%), 81 (53%), 68 (29%), 52 (17%). Anal. calcd. for $\text{C}_8\text{H}_{15}\text{O}_4\text{P}$: C, 46.60; H, 7.33. Found: C, 46.87; H, 7.58. HRMS calcd. for $\text{C}_8\text{H}_{15}\text{O}_4\text{P}$: 206.0708. Found: 206.0748.

Dodeca-1,3-diene (6)³ was purified by distillation under reduced pressure (Bp= 39°C/0.5 torr). 3.835 g (92% yield) of a colorless oil were obtained (*E/Z*= 98:2).

IR (neat, cm^{-1}): 2932, 1653, 1603, 1002, 896. RMN ¹H (400MHz, CDCl_3) δ (ppm): 6.30 (ddd, $J = 16.9\text{Hz}$, 10.5Hz and 10.1Hz, 1H), 6.03 (dd, $J = 15.4\text{Hz}$ and 10.5Hz, 1H), 5.69 (dt, $J = 15.4\text{Hz}$ and 6.9Hz, 1H), 5.08 (d, $J = 16.9\text{Hz}$, 1H), 4.95 (d, $J = 10.1\text{Hz}$, 1H), 2.06 (dt, $J = 7.3\text{Hz}$ and 6.9Hz, 2H), 1.30 (pentet, $J = 7.3\text{Hz}$, 2H), 1.26 (m, 10H), 0.88 (t, $J = 7.3\text{Hz}$, 3H). RMN ¹³C (100.5MHz, CDCl_3) δ (ppm): 137.4, 135.7, 130.8, 114.6, 32.6, 31.9, 29.5, 29.3, 29.2, 29.2, 22.7, 14.1. SM (EI, 70eV) m/z : 166 (M^+ , 50%), 138 (6%), 124 (4%), 109 (16%), 95 (35%), 81 (68%), 67 (98%), 54 (100%). Anal. calcd. for $\text{C}_{12}\text{H}_{22}$: C, 86.67; H, 13.33. Found: C, 86.79; H, 13.08. HRMS calcd. for $\text{C}_{12}\text{H}_{22}$: 166.1722. Found: 166.1743.

2-Methyldodeca-1,3-diene (7)⁵ was purified by distillation under reduced pressure (Bp= 44°C/0.3 torr). 3.826 g (85% yield) of a colorless oil were obtained (*E/Z*= 90:10).

IR (neat, cm⁻¹): 2935, 1648. RMN ¹H (400MHz, CDCl₃) δ (ppm): 6.12 (*E*, d, *J*= 15.6Hz, 0.9H), 5.81 (*Z*, d, *J*= 11.5Hz, 0.1H), 5.65 (*E*, dt, *J*= 15.6Hz and 6.9Hz, 0.9H), 5.40 (*Z*, dt, *J*= 11.5Hz and 6.9Hz, 0.1H), 4.93 (*Z*, s, 0.2H), 4.85 (*E*, s, 1.8H), 2.25 (*Z*, dt, *J*= 7.3Hz and 6.9Hz, 0.2H), 2.09 (*E*, dt, *J*= 7.3Hz and 6.9Hz, 1.8H), 1.87 (*Z*, s, 0.3H), 1.82 (*E*, s, 2.7H), 1.38 (pentet, *J*= 7.3Hz, 2H), 1.26 (m, 10H), 0.87 (t, *J*= 7.3Hz, 3H). RMN ¹³C (100.5MHz, CDCl₃) δ (ppm): 142.2 (*E*), 141.9 (*Z*), 132.6 (*E*), 132.1 (*Z*), 131.1 (*E*), 130.5 (*Z*), 115.0 (*Z*), 114.1 (*E*), 32.8 (*E*), 31.9, 30.2 (*Z*), 29.5, 29.4, 29.3, 24.2, 28.7, 23.3 (*Z*), 22.7, 18.7 (*E*), 14.1. SM (EI, 70eV) *m/z*: 180 (*M*⁺, 33%), 137 (3%), 124 (8%), 109 (14%), 95 (67%), 81 (71%), 68 (100%), 55 (21%). Anal. calcd. for C₁₃H₂₄: C, 86.59; H, 13.41. Found: C, 86.25; H, 13.11. HRMS calcd. for C₁₃H₂₄: 180.1878. Found: 180.1844.

Tetradeca-1,3,5-triene (8) was purified by distillation under reduced pressure (Bp= 61°C/0.5 torr). 4.233 g (88% yield) of a colorless oil were obtained (*E,E/E,Z*= 99:1).

IR (neat, cm⁻¹): 2932, 1627, 1004. RMN ¹H (400MHz, CDCl₃) δ (ppm): 6.34 (ddd, *J*= 16.9Hz, 10.1Hz and 10.1Hz, 1H), 6.16 (m, 2H), 6.05 (dd, *J*= 14.8Hz and 10.1Hz, 1H), 5.73 (dt, *J*= 14.8Hz and 7.3Hz, 1H), 5.17 (d, *J*= 16.9Hz, 1H), 5.04 (d, *J*= 10.1Hz, 1H), 2.08 (dt, *J*= 7.3Hz and 7.3Hz, 2H), 1.37 (pentet, *J*= 7.3Hz, 2H), 1.26 (m, 10H), 0.87 (t, *J*= 6.9Hz, 3H). RMN ¹³C (100.5MHz, CDCl₃) δ (ppm): 137.2, 136.2, 133.6, 130.9, 130.0, 116.2, 32.8, 31.9, 29.5, 29.4, 29.3, 29.2, 22.7, 14.1. SM (EI, 70eV) *m/z*: 192 (*M*⁺, 43%), 135 (2%), 121 (3%), 107 (6%), 91 (43%), 79 (100%), 67 (14%), 55 (6%). Anal. calcd. for C₁₄H₂₄: C, 87.42; H, 12.58. Found: C, 87.13; H, 12.32. HRMS calcd. for C₁₄H₂₄: 192.1878. Found: 192.1912.

Trideca-2,4-diene (9)⁶ was purified by distillation under reduced pressure (Bp= 41°C/0.2 torr). 3.244 g (90% yield) of a colorless oil were obtained (*Z,E/E,E*= 93:7).

IR (neat, cm⁻¹): 2937, 1673. RMN ¹H (400MHz, CDCl₃) δ (ppm): 6.32 (*Z,E*, dd, *J*= 15.1Hz and 11.0Hz, 0.93H), 6.02 (*E,E*, m, 0.07H), 5.79 (*Z,E*, ddd, *J*= 11.0Hz, 11.0Hz and 1.8Hz, 0.93H), 5.66 (*Z,E*, dt, *J*= 15.1Hz and 7.3Hz, 0.93H), 5.56 (*E,E*, m 0.07H), 5.36 (*Z,E*, dq, *J*= 11.0Hz and 6.9Hz, 0.93H), 2.10 (*Z,E*, dt, *J*= 7.3Hz and 7.3Hz, 1.86H), 2.04 (*E,E*, dt, *J*= 7.3Hz and 7.3Hz, 0.14H), 1.74 (dd, *J*= 6.9Hz and 1.8Hz, 3H), 1.37 (pentet, *J*= 7.3Hz, 2H), 1.27 (m, 10H), 0.86 (t, *J*= 7.3Hz, 3H). RMN ¹³C (100.5MHz, CDCl₃) δ (ppm): 134.7 (*Z,E*), 132.1 (*E,E*), 131.7 (*E,E*), 130.1 (*E,E*), 129.5 (*Z,E*), 126.7 (*E,E*), 125.2 (*Z,E*), 123.8 (*Z,E*), 32.9, 32.6 (*E,E*), 31.9, 29.5, 29.4, 29.3, 29.2, 22.7, 18.0 (*E,E*), 14.1, 13.3 (*Z,E*). SM (EI, 70eV) *m/z*: 180 (*M*⁺, 29%), 123 (2%), 109 (5%), 95 (16%), 81 (62%), 68 (100%), 55 (12%). Anal. calcd. for C₁₃H₂₄: C, 86.59; H, 13.41. Found: C, 86.32; H, 13.25. HRMS calcd. for C₁₃H₂₄: 180.1878. Found: 180.1851.

2-Methyltrideca-2,4-diene (10)⁶ was purified by distillation under reduced pressure (Bp= 56°C/0.3 torr). 4.517 g (93% yield) of a colorless oil were obtained (*E/Z*= 99:1).

IR (neat, cm⁻¹): 2932, 1680. RMN ¹H (400MHz, CDCl₃) δ (ppm): 6.21 (dd, *J*= 15.1Hz and 11.0Hz, 1H), 5.78 (d, *J*= 11.0Hz, 1H), 5.55 (dt, *J*= 15.1Hz and 6.9Hz, 1H), 2.07 (dt, *J*= 6.9Hz and 6.9Hz, 2H), 1.75 (s, 3H), 1.73 (s, 3H), 1.36 (pentet, *J*= 6.9Hz, 2H), 1.26 (m, 10H), 0.86 (t, *J*= 6.9Hz, 3H). RMN ¹³C (100.5MHz, CDCl₃) δ (ppm): 132.7, 132.2, 126.6, 125.1, 32.9, 31.9, 29.7, 29.5, 29.3, 29.2, 25.9, 22.7, 18.2, 14.1. SM (EI, 70eV) *m/z*: 194 (*M*⁺, 29%), 138 (3%), 123 (3%), 109 (10%), 95 (100%), 82 (74%), 67 (40%), 55 (16%). Anal. calcd. for C₁₄H₂₆: C, 86.52; H, 13.48. Found: C, 86.29; H, 13.17. HRMS calcd. for C₁₄H₂₆: 194.2035. Found: 194.2084.

3-Methyltrideca-4,6-diene (11) was purified by chromatography on a silicagel column (cyclohexane). 3.817 g (78% yield) of a colorless oil were obtained (*E,Z/E,E*= 60:40).

IR (neat, cm^{-1}): 2932, 1698, 1460, 1378, 985. RMN ^1H (400MHz, CDCl_3) δ (ppm): 6.25 (*E,Z*, dd, J = 15.1Hz and 11.0Hz, 0.6H), 6.03-5.93 (m, 0.8H), 5.94 (*E,Z*, dd, J = 11.0Hz and 11.0Hz, 0.6H), 5.58 (*E,E*, dt, J = 14.7Hz and 7.3Hz, 0.4H), 5.53 (*E,Z*, dd, J = 15.1Hz and 7.8Hz, 0.6H), 5.44 (*E,E*, dd, J = 15.1Hz and 7.8Hz, 0.4H), 5.31 (*E,Z*, dt, J = 11.0Hz and 7.3Hz, 0.6H), 2.16 (*E,E*, dt, J = 7.3Hz and 7.3Hz, 1.2H), 2.10-2.01 (*E,Z*, m, 1.8H), 1.39-1.22 (m, 10H), 0.99 (*E,Z*, d, J = 6.9Hz, 1.8H), 0.97 (*E,E*, d, J = 6.9Hz, 1.2H), 0.89-0.83 (m, 6H). RMN ^{13}C (100.5MHz, CDCl_3) δ (ppm): 140.3 (*E,Z*), 138.1 (*E,E*), 132.5 (*E,E*), 130.4 (*E,E*), 130.2 (*E,Z*), 128.7 (*E,Z*), 128.6 (*E,E*), 123.9 (*E,Z*), 38.6 (*E,Z*), 38.3 (*E,E*), 32.6 (*E,E*), 31.7, 29.7, 29.6, 28.9, 27.7 (*E,Z*), 22.6, 20.1, 14.1, 11.8. SM (EI, 70eV) m/z : 194 (M^+ , 28%), 165 (7%), 137 (3%), 124 (7%), 109 (31%), 95 (50%), 81 (100%), 67 (38%), 55 (18%). Anal. calcd. for $\text{C}_{14}\text{H}_{26}$: C, 86.52; H, 13.48. Found: C, 86.44; H, 13.26. HRMS calcd. for $\text{C}_{14}\text{H}_{26}$: 194.2035. Found: 194.2049.

3-Methyleneundec-1-ene (12)⁷ was purified by distillation under reduced pressure (Bp= 70°C/0.4 torr). 2.446 g (61% yield) of a yellow oil were obtained.

IR (neat, cm^{-1}): 2957, 1595, 991, 893. RMN ^1H (400MHz, CDCl_3) δ (ppm): 6.36 (dd, J = 17.4Hz and 10.4Hz, 1H); 5.23 (dd, J = 17.4Hz and 1.8Hz, 1H); 5.05 (dd, J = 10.4Hz and 1.8Hz, 1H); 4.99 (s, 1H), 4.98 (s, 1H); 2.20 (t, J = 7.6Hz, 2H); 1.47 (pentet, J = 7.6Hz, 2H); 1.27 (m, 10H); 0.88 (t, J = 7.3Hz, 3H). RMN ^{13}C (100.5MHz, CDCl_3) δ (ppm): 146.7, 139.0, 115.4, 113.0, 31.9, 31.4, 29.6, 29.5, 29.3, 28.2, 22.7, 14.1. SM (IE, 70eV) m/z : 166 (M^+ , 1%), 138 (2%), 110 (8%), 95 (24%), 81 (22%), 68 (100%), 55 (13%). Anal. calcd. for $\text{C}_{12}\text{H}_{22}$: C, 86.67; H, 13.33. Found: C, 86.45; H, 13.01. HRMS calcd. for $\text{C}_{12}\text{H}_{22}$: 166.1722. Found: 166.1726.

2-Butylcyclohexa-1,3-diene (13)⁸ was purified by chromatography on a silicagel column (cyclohexane). 2.660 g (78% yield) of a yellow oil were obtained.

IR (neat, cm^{-1}): 3954, 1715, 1674, 988. RMN ^1H (400MHz, CDCl_3) δ (ppm): 5.87 (m, 1H), 5.64 (m, 2H), 2.17 (m, 2H), 2.07 (m, 4H), 1.42 (pentet, J = 7.3Hz, 2H), 1.32 (sextet, J = 7.3Hz, 2H), 0.90 (t, J = 7.3Hz, 3H). RMN ^{13}C (100.5MHz, CDCl_3) δ (ppm): 140.2, 124.8, 123.4, 118.3, 37.1, 29.7, 26.5, 22.4, 14.0. SM (EI, 70eV) m/z : 136 (M^+ , 58%), 107 (9%), 93 (55%), 79 (100%), 65 (7%), 51 (4%). Anal. calcd. for $\text{C}_{10}\text{H}_{16}$: C, 88.16; H, 11.84. Found: C, 87.83; H, 11.61. HRMS calcd. for $\text{C}_{10}\text{H}_{16}$: 136.1252. Found: 136.1271.

1-(Buta-1,3-dienyl)-4-fluorobenzene (14)⁴ was purified by chromatography on Florisil (petroleum ether). 1.089 g (49% yield) of a colorless oil were obtained (*E/Z*= 80:20).

IR (neat, cm^{-1}): 3032, 1650, 1603, 1489, 1456, 998, 896. RMN ^1H (400MHz, CDCl_3) δ (ppm): 7.42-7.25 (m, *Harom*, 2H), 7.08-6.94 (m, *Harom*, 2H), 6.81 (*Z*, ddd, J = 16.9Hz, 10.5Hz and 10.1Hz, 0.2H), 6.69 (*E*, dd, J = 15.6Hz and 10.5Hz, 0.8H), 6.51 (*E*, d, J = 15.6Hz, 0.8H), 6.48 (*E*, ddd, J = 16.9Hz, 10.5Hz and 10.1Hz, 0.8H), 6.40 (*Z*, d, J = 11.4Hz, 0.2H), 6.24 (*Z*, dd, J = 11.4Hz and 10.5Hz, 0.2H), 5.37 (*Z*, d, J = 16.9Hz, 0.2H), 5.32 (*E*, d, J = 16.9Hz, 0.8H), 5.22 (*Z*, d, J = 10.1Hz, 0.2H), 5.17 (*E*, d, J = 10.1Hz, 0.8H). RMN ^{13}C (100.5MHz, CDCl_3) δ (ppm): 162.3 (d), 137.0 (*E*), 133.2 (*E*), 132.8 (*Z*), 131.5 (*E*), 129.4 (*E*), 129.2 (*Z*), 127.9 (*E*), 127.8 (*E*), 127.4 (*Z*), 127.3 (*Z*), 119.9 (*Z*), 117.7 (*E*), 115.6 (*E*), 115.4 (*E*), 115.2 (*Z*), 115.0 (*Z*). SM (EI, 70eV) m/z : 148 (M^+ , 100%), 133 (58%), 127 (36%), 120 (11%), 115 (13%), 75 (9%). Anal. calcd. for $\text{C}_{10}\text{H}_9\text{F}$: C, 81.06; H, 6.12. Found: C, 81.31; H, 6.28. HRMS calcd. for $\text{C}_{10}\text{H}_9\text{F}$: 148.0688. Found: 148.0683.

(E)-Dodeca-9,11-dien-1-ol (15)⁹ (*E/Z* = 96:4).

IR (neat, cm⁻¹): 3357, 2930, 1693, 1056, 970. RMN ¹H (400MHz, CDCl₃) δ (ppm): 6.63 (Z, ddd, *J* = 16.9Hz, 10.5Hz and 10.1Hz, 0.04H), 6.30 (*E*, ddd, *J* = 16.9Hz, 10.5Hz and 10.1Hz, 0.96H), 6.03 (*E*, dd, *J* = 15.1Hz and 10.5Hz, 0.96H), 5.99 (Z, m, 0.04H), 5.70 (*E*, dt, *J* = 15.1Hz and 6.9Hz, 0.96H), 5.46 (Z, m, 0.04H), 5.16 (Z, d, *J* = 16.9Hz, 0.04H), 5.08 (*E*, d, *J* = 16.9Hz, 0.96H), 5.06 (Z, d, *J* = 10.1Hz, 0.04H), 4.92 (*E*, d, *J* = 10.1Hz, 0.96H), 3.61 (t, *J* = 7.1Hz, 2H), 2.15 (Z, dt, *J* = 7.3Hz and 6.9Hz, 0.08H), 2.06 (*E*, dt, *J* = 7.3Hz and 6.9Hz, 1.92H), 1.54 (pentet, *J* = 7.1Hz, 2H), 1.47 (m, 1H), 1.33 (pentet, *J* = 7.3Hz, 2H), 1.29 (m, 8H). RMN ¹³C (100.5MHz, CDCl₃) δ (ppm): 137.3 (*E*), 135.5 (*E*), 132.9 (Z), 132.1 (Z), 130.8 (*E*), 129.0 (Z), 116.8 (Z), 114.6 (*E*), 63.0, 32.7, 32.5, 29.4, 29.3, 29.2, 29.1, 27.8 (Z), 26.8 (Z), 25.8 (Z), 25.7 (*E*). SM (EI, 70eV) *m/z*: 182 (M⁺, 5%), 164 (5%), 135 (8%), 121 (13%), 107 (11%), 95 (26%), 81 (59%), 67 (100%), 54 (64%). Anal. calcd. for C₁₂H₂₂O₂: C, 79.06; H, 12.16. Found: C, 78.93; H, 12.05. HRMS calcd. for C₁₂H₂₂O₂: 182.1671. Found: 182.1709.

(E)-Dodeca-9,11-dienyl acetate (16)¹⁰ (*E/Z* = 96:4).

IR (neat, cm⁻¹): 2929, 1735, 1697, 1038, 971. RMN ¹H (400MHz, CDCl₃) δ (ppm): 6.64 (Z, ddd, *J* = 16.9Hz, 10.5Hz and 10.1Hz, 0.04H), 6.30 (*E*, ddd, *J* = 16.9Hz, 10.5Hz and 10.1Hz, 0.96H), 6.03 (*E*, dd, *J* = 15.1Hz and 10.5Hz, 0.96H), 6.00 (Z, m, 0.04H), 5.70 (*E*, dt, *J* = 15.1Hz and 6.9Hz, 0.96H), 5.44 (Z, m, 0.04H), 5.16 (Z, d, *J* = 16.9Hz, 0.04H), 5.08 (*E*, d, *J* = 16.9Hz, 0.96H), 5.06 (Z, d, *J* = 10.1Hz, 0.04H), 4.92 (*E*, d, *J* = 10.1Hz, 0.96H), 4.05 (t, *J* = 6.9Hz, 2H), 2.07 (dt, *J* = 7.3Hz and 6.9Hz, 2H), 2.05 (s, 3H), 1.62 (pentet, *J* = 6.9Hz, 2H), 1.37 (pentet, *J* = 7.3Hz, 2H), 1.29 (m, 8H). RMN ¹³C (100.5MHz, CDCl₃) δ (ppm): 171.3, 137.3 (*E*), 135.6 (*E*), 132.9 (Z), 132.2 (Z), 130.8 (*E*), 129.1 (Z), 116.8 (Z), 114.6 (*E*), 64.5, 32.6, 29.4, 29.3, 29.1, 29.1, 28.4, 27.9 (Z), 26.0, 21.3. SM (EI, 70eV) *m/z*: 224 (M⁺, 3%), 164 (23%), 135 (20%), 121 (28%), 107 (18%), 95 (33%), 81 (79%), 67 (100%), 54 (54%). Anal. calcd. for C₁₄H₂₄O₂: C, 74.95; H, 10.78. Found: C, 74.67; H, 10.54. HRMS calcd. for C₁₄H₂₄O₂: 224.1776. Found: 224.1796.

Notes and References

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