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Ti-catalyzed reactions of 4,4′-bis(trimethylsilyl)bicyclohexyl-2,2′-diene with various electrophiles

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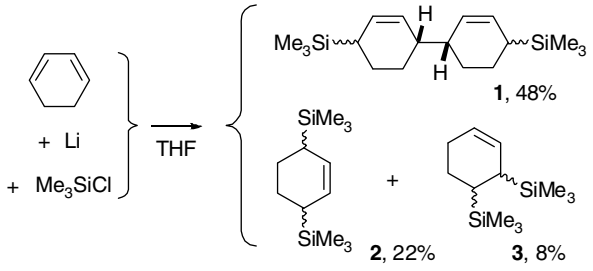
ABSTRACT

Reductive disilylation (Li + Me_3SiCl – THF) of 1,3-cyclohexadiene led to 4,4′-bis(trimethylsilyl)bicyclohexyl-2,2′-diene (**1**). In the presence of $TiCl_4$ in dichloromethane, **1** reacted with some acyl chlorides, anhydrides, and aldehydes to give tricyclo[7.4.0.0^{3,8}]trideca-4,12-diene-2-yl derivatives.

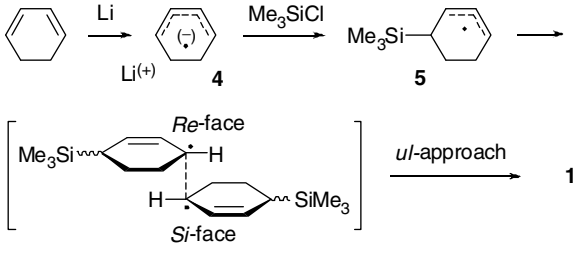
The bis-silylation of dienic or trienic hydrocarbons is a particularly interesting transformation, which allows the simultaneous creation of two new Si–C bonds. This reaction constitutes a convenient route to obtain bis(silyl) unsaturated compounds that can represent useful intermediates or can be used as building blocks in organic synthesis. A very simple procedure is the reductive disilylation of 1,3-dienes by lithium and chlorotrimethylsilane giving rise to a mixture of 1,4-bis(trimethylsilyl)-2-butene derivatives and 1,8-bis(trimethylsilyl)-2,6-octadiene derivatives.[1]

In previous work,[2] we have obtained stereoselectively unsaturated disilanes with 1,3,5-cycloheptatriene. We have now applied these results to the reaction of 1,3-cyclohexadiene. In presence of lithium and chlorotrimethylsilane in THF, cyclohexadiene led to a mixture of 4,4′-bis(trimethylsilyl)bicyclohexyl-2,2′-diene (**1**), 1,4-bis(trimethylsilyl)cyclohex-2-ene (**2**), and 3,4-bis(trimethylsilyl)-cyclohex-1-ene (**3**).[3] After the separation by distillation **1** appeared as a mixture of isomers (Scheme 1).[4]

To explain the formation of **1**–**3**, we can expect a sequence of reactions involving the initial formation of the anion radical **4** which is trapped by trimethylchlorosilane to give allylic radical **5** (further reduction of **5** into allylic anion and its trapping by trimethylchlorosilane led to **2** and **3**). The stereoselectivity of the dimerization of **5** comes from a transition state corresponding to an unlike relative approach[5] with an *anti* geometry indifferent to the uncontrolled centers bearing trimethylsilyl groups. Transition state with a possibility of large molecular orbitals overlap did not occur (Scheme 2).



Scheme 1. Synthesis of 4,4′-bis(trimethylsilyl)bicyclohexyl-2,2′-diene (**1**).



Scheme 2. Formation of the allylic radical **5** and its dimerization into **1**.

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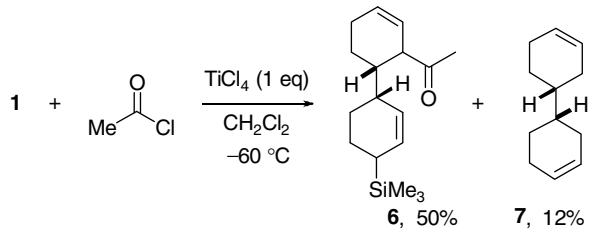


Scheme 3. Reaction of **1** with the acetyl chloride.

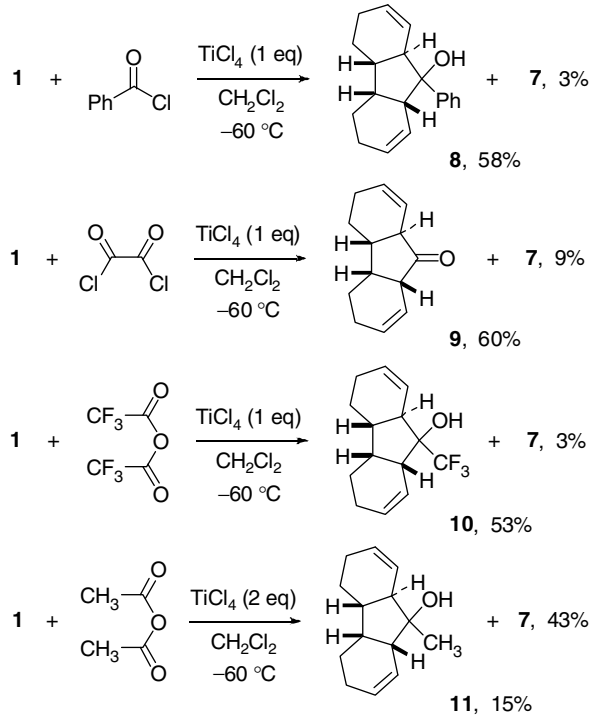
In the aim to reveal the reactivity of **1** toward electrophilic reagents, this disilyldiene has been added in the presence of $TiCl_4$ to various compounds. For example, acetyl chloride gave rise to silylated monoketone **6** and the bicyclohexyl-3,3′-diene **7** (Scheme 3).[6]

In contrast, addition to benzoyl chloride, oxalyl chloride, trifluoroacetic anhydride, and acetic anhydride occurred with cyclization giving rise to the tricyclo[7.4.0.0^{3,8}]trideca-4,12-diene-2-yl skeleton in fair yields except for the last which required 2 equiv $TiCl_4$. In each case only one stereoisomer has been obtained (Scheme 4).[7]

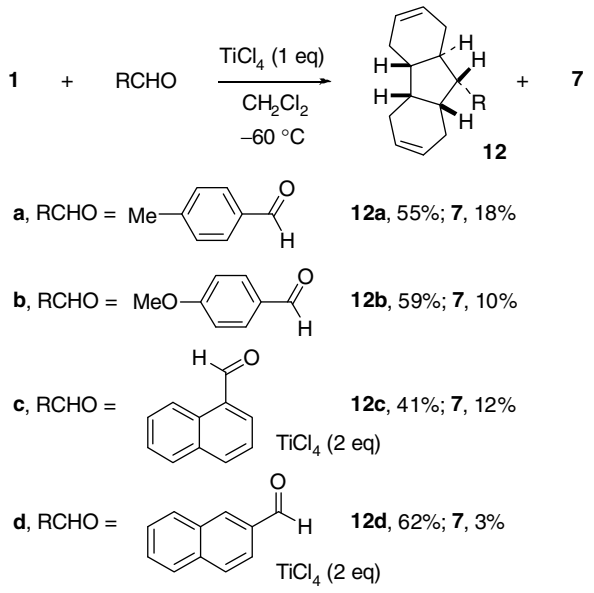
In a similar manner, some aromatic aldehydes underwent a double alkylation leading, again, to the tricyclo[7.4.0.0^{3,8}]trideca-4,12-diene-2-yl skeleton in fair yields (Scheme 5).[8]

With *o*-bromobenzaldehyde, the carbonyl group was too hindered and also electron-poor to favor the double alkylation, and the desilylated alcohol **13** (two isomers) was the only product with **7** (Scheme 6).[9]

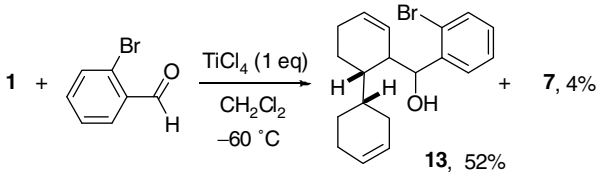
Pleasingly, **12d** was crystallized and X-ray crystallographic analysis clearly showed that the five stereogenic centers of the cyclopentane ring were controlled (Fig. 1). For **1**, as the chirality around the C(1)–C(1)′ bond cannot be modified in the course of the reaction, we conclude that its structure is (R^*,S^*). Consequently, as **1** is a mixture of three isomers (1.5:1:1), the two stereogenic centers bearing the trimethylsilyl groups were uncontrolled (Scheme 2).



Scheme 4. Reaction of **1** with acyl chlorides and anhydrides.



Scheme 5. Reaction of **1** with aromatic aldehydes.



Scheme 6. Reaction of **1** with *o*-bromobenzaldehyde.

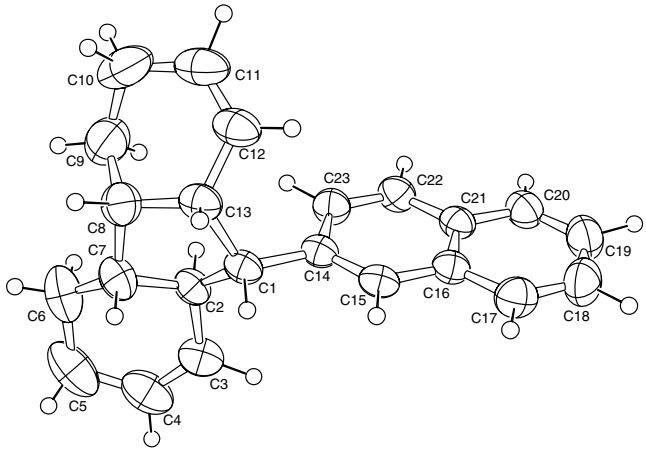
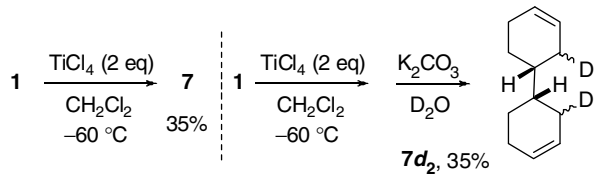


Figure 1. ORTEP drawing for **12d**. Non-hydrogen atoms are drawn with 50% probability thermal ellipsoids.[10]

All the electrophilic substitution reactions afforded bicyclohexyl-3,3′-diene **7** among other products.[11] Consequently, **1** was treated with $TiCl_4$ at low temperature for 72 h. After usual work-up, **7** was isolated in 35% yield (Scheme 7). Moreover, when the reactive mixture was poured into cold anhydrous K_2CO_3 solution in deuterium oxide, we have isolated the isotopomere **7*d*$_2$**. The NMR data showed that two methylene groups were deuterated.[12] As allylsilane moiety is stable in aqueous basic medium, the observed protolysis can involve a metathesis (transmetalation reaction) of the allylsilane unit to an allyltrichlorotitane which is easily protolysed in basic medium (titanium presents a strong oxophilic character).[13]



Scheme 7. Titanium-mediated protolysis of **1**.

In conclusion, we have described a direct way to the synthesis of tricyclic compounds from 1,3-cyclohexadiene. Previous results in this area used elaborate precursors.[14] Moreover, a good control of the stereochemistry is observed and these results may be applied to the synthesis of more complex products.

Acknowledgments

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References and notes

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2. Aouf, C.; El Abed, D.; Giorgi, M.; Santelli, M. *Tetrahedron Lett.* **2007**, *48*, 4969–4972.
3. For a previous synthesis of products **2** and **3**, see: (a) Dunoguès, J.; Calas, R.; Dedier, J.; Pisciotti, F.; Lapouyade, P. *J. Organomet. Chem.* **1970**, *25*, 51–55; (b) Eaborn, C.; Jackson, R. A.; Pearce, R. *J. Chem. Soc., Perkin Trans. 1* **1974**, 2055–2061.
4. 4,4′-Bis(trimethylsilyl)bicyclohexyl-2,2′-diene (**1**), colorless oil, bp 135–145 °C (0.2 mm Hg), ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.03–0.01 (m, 18H), 1.43–1.30 (m, 8H), 1.80–1.55 (m, 2H), 2.07–2.06 (m, 2H), 5.68–5.50 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$), major isomer, δ = −3.3 (q), 23.8 (t), 26.4 (d), 26.8 (t), 40.3 (d), 128.1 (d), 128.4 (d), other isomers, δ = −1.9 (q), 22.8 (t), 23.8 (t), 26.5 (d), 26.6 (t), 27.1 (d), 38.2 (d), 39.8 (d), 128.8 (d), 129.1 (d), 129.2 (d), 129.4 (d), 129.5 (d); MS: *m*/*z* (%) = 306 (M^+, 4), 153 (25), 79 (28), 73 (100), 45 (20).
Compound **2**, colorless oil, bp 50 °C (0.2 mm Hg), ^{1}H NMR (300 MHz, $CDCl_3$) δ −0.027, −0.016 (s, 18H), 1.82–1.30 (m, 6H), 5.60 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$), major isomer, δ = −2.5 (q), 23.5 (t), 26.6 (d), 126.0 (d); minor isomer, δ = −3.2 (q), 24.6 (t), 26.1 (d), 126.5 (d); MS: *m*/*z* (%) = 226 (M^+, 80), 211 (50), 152 (40), 78 (41), 73 (100), 45 (30). **3**, ^{13}C NMR (75 MHz, $CDCl_3$) δ = −2.1 (q), 20.7 (d), 22.1 (t), 23.8 (t), 26.9 (d), 124.3 (d), 128.2 (d).
5. Seebach, D.; Prelog, V. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 654–660.
6. A 50 mL two-necked flask equipped with a thermometer, a stopcock to a rubber balloon filled with argon and a magnetic stirring bar was charged with anhydrous CH_2Cl_2 (25 mL). The solution was cooled to −60 °C and $TiCl_4$ was introduced (0.5 mL, 4.4 mmol). Then a solution of acetyl chloride (0.3 mL, 4.4 mmol) in CH_2Cl_2 (2 mL) was slowly added. The solution was cooled to −90 °C and **1** (2 g, 6.5 mmol) in CH_2Cl_2 (5 mL) was added. After 2 h of stirring, the solution was allowed to warm to −60 °C for 20 h. The reaction mixture was poured onto ice and NH_4Cl. After the common work-up procedure, the crude product was flash chromatographed on silica gel eluting with petroleum ether/ether (90:10) to give **6** (607 mg, 2.2 mmol). Compound **6**, colorless oil, ^{1}H NMR (300 MHz, $CDCl_3$) δ −0.07 (s, 9H), 1.22 (br s, 2H), 1.38 (m, 3H), 160–1.55 (m, 2H), 2.02–1.99 (m, 5H), 2.14 (s, 3H), 5.62 (br s, 2H), 5.81 (br s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ −3.4 (q), 23.5 (t), 23.8 (t), 25.3 (d), 26.2 (t), 26.3 (d), 28.5 (t), 39.8 (d), 40.0 (d), 49.0 (q), 124.3 (d), 124.7 (d), 126.7 (d), 134.0 (d), 209.3 (s).
All new compounds gave correct elemental analysis.
7. 2-Phenyltricyclo[7.4.0.0^{3,8}]trideca-4,12-diene-2-ol (**8**), yellow oil, ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.59–1.51 (m, 3H), 1.80–1.70 (m, 2H), 2.09–1.99 (m, 4H), 2.20 (br s, 1H), 2.49 (d, m, *J* = 9.4 Hz, 1H), 3.05 (d, sext, *J* = 9.6, 2.1 Hz, 1H), 5.57–5.47 (m, 2H), 5.68 (1/2 AB, q, *J* = 9.8, 3.2 Hz, 1H), 6.19 (dddd, *J* = 9.7, 5.01, 3.94, 1.75 Hz, 1H), 7.25 (d, *J* = 7.2 Hz, 1H), 7.35 (dd, *J* = 8.1, 7.2 Hz, 2H), 7.51 (dd, *J* = 8.1, 1.0 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.2 (t), 25.5 (t), 26.9 (t), 27.1 (t), 39.9 (d), 44.1 (d), 52.2 (d), 54.8 (d), 81.0 (s), 124.4 (d), 125.2 (d), 125.5 (d, 2C), 126.6 (d), 128.2 (d, 2C), 130.2 (d), 134.3 (d), 145.5 (s).
Tricyclo[7.4.0.0^{3,8}]trideca-4,12-dien-2-one (**9**), colorless oil, ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.23 (br s, 2H), 1.60–1.55 (m, 5H), 2.01–1.96 (m, 5H), 5.64 (br s, 2H), 5.90–5.82 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.8 (t), 25.9 (t), 26.2 (t), 29.0 (t), 38.1 (d), 38.4 (d), 39.8 (d), 46.5 (d), 124.3 (d), 126.8 (d), 127.2 (d), 138.9 (d), 211.8 (s); MS: *m*/*z* (%) = 188 (M^+, 25), 170 (33), 79 (100), 51 (20).
2-Trifluoromethyltricyclo[7.4.0.0^{3,8}]trideca-4,12-dien-2-ol (**10**), colorless oil, ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.08 (d, *J* = 5.1 Hz, 1H), 1.12 (dd, *J* = 12.2, 5.1 Hz, 1H), 1.60–1.54 (m, 2H), 1.89–1.83 (m, 2H), 2.21–2.15 (m, 4H), 2.61 (d, *J* = 9.7 Hz, 1H), 2.72 (br s, 1H), 5.83 (br s, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.9 (t), 23.6 (t), 24.0 (t), 26.8 (t), 39.0 (d), 41.6 (d), 44.6 (d), 50.7 (d), 82.1 (d, $^2J^{(CF)}$ = 26.4 Hz), 123.7 (d), 124.0 (d), 124.3 (q, $^1J^{(CF)}$ = 311.9 Hz), 129.2 (d), 133.2 (d).
2-Methyltricyclo[7.4.0.0^{3,8}]trideca-4,12-dien-2-ol (**11**), colorless oil, ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.90 (dt, *J* = 6.9, 3.4 Hz, 1H), 1.16 (s, 3H), 1.26–1.18 (m, 2H), 1.65–1.48 (m, 4H), 2.20–2.02 (m, 3H), 2.38–2.29 (m, 2H), 5.61 (1/2 AB, q, *J* = 10.2, 3.3 Hz, 1H), 5.71 (1/2 AB, t, *J* = 10.0, 3.1 Hz, 1H), 5.85 (1/2 AB, q, *J* = 9.9, 2.0 Hz, 1H), 5.98 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.2 (q), 24.1 (t), 26.8 (t), 29.5 (t), 32.0 (t), 38.8 (d), 42.1 (d), 50.1 (d), 51.4 (d), 78.7 (s), 125.2 (d), 127.3 (d), 127.9 (d), 130.9 (d).
8. 2-*p*-Tolyltricyclo[7.4.0.0^{3,8}]trideca-4,12-diene (**12a**), colorless oil, ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.89 (t, *J* = 5.0 Hz, 1H), 1.27 (s, 3H), 1.73–1.44 (m, 5H), 2.04–2.01 (m, 3H), 2.20–2.18 (m, 2H), 2.33 (d, *J* = 3.0 Hz, 2H), 5.59 (br s, 2H), 5.69–5.66 (m, 2H), 7.03 (d, *J* = 7.9 Hz, 2H), 7.10, (d, *J* = 7.9 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$), δ = 21.2 (q), 22.8 (t), 23.8 (t), 24.0 (t), 27.2 (t), 39.7 (d), 41.8 (d), 45.3 (d), 45.7 (d), 53.0 (d), 127.2 (d), 127.5 (d), 127.8 (d), 128.7 (d, 2C), 129.2 (d), 129.5 (d, 2C), 135.3 (s), 138.4 (s).
2-*p*-Anisyltricyclo[7.4.0.0^{3,8}]trideca-4,12-diene (**12b**), colorless oil, ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.22 (t, *J* = 7.2 Hz, 2H), 1.43–1.40 (m, 2H), 1.63–1.56 (m, 2H), 2.02–1.86 (m, 5 H), 2.18–2.16 (m, 2H), 3.78 (s, 3H), 5.57 (br s, 2H), 5.67 (br s, 2H), 6.80 (d, *J* = 8.1 Hz, 1H), 6.86 (d, *J* = 8.8 Hz, 1H), 7.04 (d, *J* = 8.3 Hz, 1H), 7.16 (d, *J* = 8.5 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$), δ = 21.4 (t), 22.6 (t), 23.7 (t), 26.6 (t), 39.7 (d), 40.7 (d), 45.1 (d), 46.8 (d), 50.5 (d), 55.4 (q), 113.4 (d, 2C), 113.9 (d, 2C), 128.7 (d, 2C), 130.4 (d, 2C), 136.1 (s), 158.1 (s).
2-(1-Naphthyl)tricyclo[7.4.0.0^{3,8}]trideca-4,12-diene (**12c**), colorless oil, two isomers (2.3:1), ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.28–1.23 (m, 1H), 1.78–1.72 (m, 3H), 2.5–2.0 (m, 5H), 2.99–2.91 (m, 2H), 3.40–3.35 (m, 1H), 3.74 (t, *J* = 11.7 Hz, 1H), 5.85–5.50 (m, 4H), 7.34 (d, *J* = 7.2 Hz, 1H), 7.55–7.45 (m, 2H), 7.74 (d, *J* = 8.1 Hz, 1H), 7.90 (dd, *J* = 4.0, 2.3 Hz, 1H), 8.14 (d, *J* = 8.0 Hz, 1H), 8.25 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$), δ = 22.9 (t), 23.7 (t), 24.1 (t), 27.3 (t), 39.5 (d), 41.3 (d), 41.5 (d), 45.7 (d), 48.6 (d), 124.0 (d), 124.3 (d), 125.4 (d), 125.6 (d), 126.0 (d), 126.5 (d), 128.2 (d, 2C), 128.4 (d), 128.9 (d), 129.3 (d), 133.5 (s), 133.9 (s), 137.4 (s).
2-(2-Naphthyl)tricyclo[7.4.0.0^{3,8}]trideca-4,12-diene (**12d**), white crystals, mp 148 °C, ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.22 (t, *J* = 7.0 Hz, 1H), 1.30 (qd, *J* = 12.0, 4.6 Hz, 1H), 1.80–1.60 (m, 3H), 1.96–1.85 (m, 2H), 2.25–2.18 (m, 2H), 2.32 (sext. *J* = 6.1 Hz, 1H), 2.64 (br. t, *J* = 8.0 Hz, 1H), 3.08 (m, 2H), 4.98 (d, *J* = 10.2 Hz, 1H), 5.59 (br s, 1H), 5.69–5.65 (m, 2H), 7.30 (dd, *J* = 7.0, 1.5 Hz, 2H), 7.44–7.41 (m, 2H), 7.59 (s, 1H), 7.86–7.74 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$),δ = 22.6 (t), 23.8 (t), 24.1 (t), 27.4 (t), 39.8 (d), 42.0 (d), 45.2 (d), 45.9 (d), 53.7 (d), 125.2 (d), 125.8 (d), 127.3 (d), 127.6 (d, 2C), 127.8 (d, 2C), 128.4 (d), 129.3 (d), 129.4 (d, 2C), 132.3 (s), 133.6 (s), 139.3 (s).
9. Compound **13**. Colorless oil, two isomers (4:1), ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.79–1.68 (m, 6H), 2.07–2.01 (m, 7H), 2.66 (br s, 1H), 5.18 (br s, 1H), 5.42 (t, *J* = 11.0 Hz, 1H), 5.68 (m, 2H), 5.99 (dm, *J* = 8.0 Hz, 1H), 7.10 (t, *J* = 7.5 Hz, 1H), 7.32 (t, *J* = 7.5 Hz, 1H), 7.49 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$), major isomer δ = 22.3 (t), 24.3 (t), 26.3 (t), 27.7 (t), 30.7 (t), 33.9 (d), 40.8 (d), 42.6 (d), 74.0 (d), 121.9 (s), 124.1 (d), 127.13 (d), 127.2 (d), 127.5 (d), 128.4 (d), 128.6 (d), 132.7 (d), 133.0 (d), 142.5 (s); minor isomer δ = 21.9 (t), 24.1 (t), 25.5 (t), 28.3 (t), 34.0 (d), 40.8 (d), 42.5 (d), 73.0 (d), 121.6 (s), 124.2 (d), 126.9 (d), 127.17 (d), 127.3 (d), 128.5 (d), 128.7 (d), 132.9 (d), 133.1 (d), 142.7 (s).
10. **12d**. Crystal data and structure refinement. CCDC-680455 contains the supplementary crystallographic data. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44-1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk]. Formula: $C_{23}H_{24}$; M_w: 300.42; crystal color: colorless; crystal size/mm^3: 0.4 × 0.2 × 0.15; crystal system: monoclinic; space group: $P2_1/c$; *a*/Å: 12.3730(3); *b*/Å: 6.1630(1); *c*/Å: 23.8020(7); β/°: 110.9350(9); *V*/Å^3: 1695.20(7); *Z*: 4; D_c/g cm^{-3}: 1.094; μ(Mo Kα)/cm^{-1}: 1.178; No. of unique data: 3188; No. parameters refined: 208; No. refl. in refinement: (3188; $F^2 > 4\sigma F^2$: 2451); *R*: 0.0676 [$F^2 > 4\sigma F^2$]; *wR*: 0.1833 [$F^2 > 4\sigma F^2$] ($w = 1/[\sigma^2(F_o^2) + (0.1036P)^2 + 0.5747P]$) where $P = (F_o^2 + 2F_c^2)/3$; goodness of fit: 1.133; residual fourier/e Å^{-3}: −0.272; 0.271.
11. Compound **7**, colorless oil, ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.25–1.18 (m, 2H), 1.41–1.26 (m, 2H), 1.81–1.75 (m, 4H), 2.06–1.82 (m, 6H), 5.65 (br s, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 25.9 (t), 26.2 (t), 29.4 (t), 38.8 (d), 127.0 (d), 127.17 (d); MS: *m*/*z* (%) = 162 (M^+, 39), 134 (50), 119 (26), 105 (15), 91 (38), 79 (100), 67 (25), 53 (20).
12. Compound **7d$_2$**, colorless oil, ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.06–1.80 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 29.4 (m) with reduced intensity; ^{2}H NMR δ 1.86 ($W_{1/2}$ = 6.08 Hz; decoupled, $W_{1/2}$ = 3.56 Hz); MS: *m*/*z* (%) = 164 (M^+, 30), 134 (40), 121 (18), 106 (9), 92 (26), 80 (100), 67 (17), 54 (18); HRMS calcd for $C_{12}H_{16}D_2$, 164.1534; found, 164.1545.
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14. The tricyclo[7.4.0.0^{3,8}]tridecane constitutes the skeleton of gibberellanes, see: (a) Ho, T.-L. *Carbocycle Construction in Terpene Synthesis*; VCH Publisher: Weinheim, 1988; (b) Pinto, A. C.; Epifanio, R. de A.; Camargo, W. *Tetrahedron* **1993**, *49*, 5039–5046; For examples of synthesis, see: (a) Jamart-Grégoire, B.; Brosse, N.; Ianelli, S.; Nardelli, M.; Caubère, P. *J. Org. Chem.* **1993**, *58*, 4572–4578; (b) Denmark, S. E.; Wallace, M. A.; Walker, C. B., Jr. *J. Org. Chem.* **1990**, *55*, 5543–5545.