A New Selective Allyl Transfer Reagent: Facile Entry to β-Hydroxy Enol Silyl Ethers Bearing Two Contiguous Stereogenic Centers

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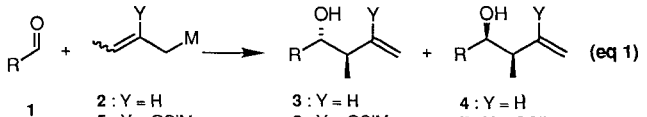
η^3-Allyltitanium(III) complexes functionalized on the C-2 with a silyloxy group can be prepared by the reaction of titanocene dichloride with isopropylmagnesium chloride in the presence of the corresponding 2-silyloxybutadienes. These complexes undergo a highly regio- and diastereoselective addition with aldehydes to produce, depending on the treatment applied, *anti* diastereomeric β-hydroxy silyl enol ethers or β-hydroxy ketones. Two defined contiguous stereocenters make the enol silyl ethers containing them versatile synthons for further stereocontrolled transformations. The reaction constitutes a new method for directing electrophiles to the α-position of the α,β-enone system.

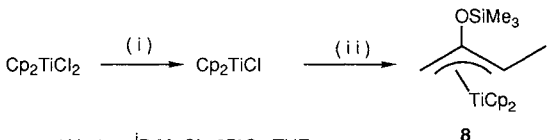
The reaction of allylic organometallic reagents **2** with aldehydes **1** according to equation 1 constitutes a useful procedure for controlling the stereochemistry in acyclic systems.[1]



The diastereoselective[2] and more recently enantioselective[3] routes to *anti*- or *syn*-β-methylhomoallyl alcohols, **3** or **4** respectively, have been developed in relation to the synthesis of polypropionate derived natural products.[4] The relevance of this addition reaction obviously lies in the potential of further transformations of the carbon–carbon double bond in the resulting products **3** and **4**. In particular, the homoallylic alcohols may be converted into aldols, which render the allylmetal addition to aldehydes synthetically analogous to the aldol addition of metal enolates.

In conjunction with our program directed toward the application of organometallic compounds in organic synthesis, we were interested in extending the scope of the allylic organometallic method. With this in mind, we have undertaken to refunctionalize the C-2 alkene atom of the adducts by introducing the trimethylsilyloxy substituent (Y = $OSiMe_3$ in **6** or **7**, eq 1). The approach appeared to be particularly attractive for two reasons. First, $OSiMe_3$ substituent could be removed easily by simple acid treatment of the reaction mixture to give the aldol product directly. Second, the enol silyl ether function could be conserved to use it in subsequent transformations. Indeed, the unusual versatility of silyl enol ethers has led to various uses in organic synthesis.[5] The presence of two directly adjacent stereogenic centers in **6** or **7** shows promise for their synthetic utility in the stereocontrolled construction of open chain systems.

Unlike the allylmetal reagents containing α-heteroatom substituents, the β-substituted crotylmetal reagent **5** is difficult to obtain directly. We therefore focused our attention on η^3-allylmetal species, synthetically equivalent to the η^1-complex **5**, which react regioselectively on the more substituted γ-carbon atom. Such regiocontrol can be achieved with (η^3-allyl)titanocenes,[6] which also have another striking feature: they generally add to aldehydes and ketones with good *anti* stereoselectivity.[7] The η^3-allyltitanocenes may be obtained by reaction of titanocene dichloride either with an allyl Grignard reagent or with an alkyl Grignard reagent and a diene.[8] Here the latter method was employed, since it offers the opportunity to introduce the trimethylsilyloxy group selectively into the allyl moiety. The synthetic route to the allyltitanium reagent **8** is outlined in Scheme 1.

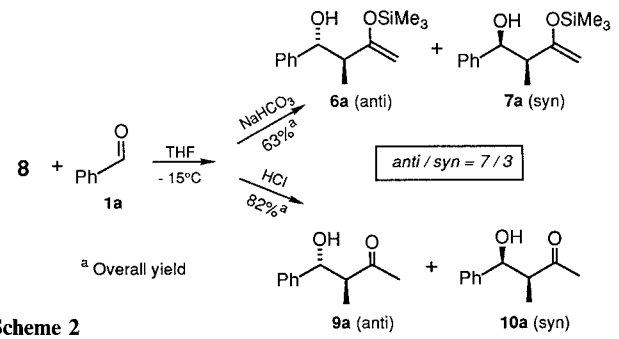


Scheme 1

The operational conditions were chosen to take into account the relative instability of **8** at higher temperatures. Thus, the reaction was performed in two separate reduction steps: Cp_2TiCl formed at first at room temperature was allowed to react within ten minutes with a second equivalent of isopropylmagnesium chloride in the presence of 2-(trimethylsilyloxy)buta-1,3-diene at −15 °C. Complex **8** thus formed in situ was used directly in the addition reactions.

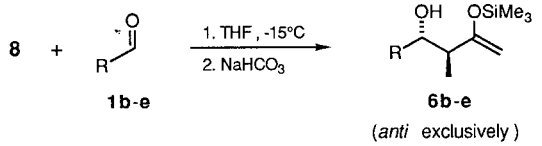
When benzaldehyde was added to a dark violet tetrahydrofuran solution of **8** at −15 °C, a reaction occurred rapidly and the color of the solution changed to yellow-brown. After basic ($NaHCO_3$ aq) or alternatively acidic (1 M HCl) treatment, β-hydroxy enol silyl ether (**6a** and **7a**) or β-hydroxy ketone (**9a** and **10a**), respectively, were obtained as a mixture of two diastereomers, *anti*/*syn* = 7:3[9] (Scheme 2). It is noteworthy that we have observed the identical moderate stereoselectivity in the analogous reaction starting from isoprene (Y = Me instead of $OSiMe_3$).

Having demonstrated the feasibility of the preparation of the functionalized complex **8** and its successful addition to benzaldehyde, our attention was directed towards the use of aliphatic aldehydes as substrates. The reactions employing aldehydes **1b–e** (Scheme 3) were performed in the same manner and conditions as above. *We noticed*



Scheme 2

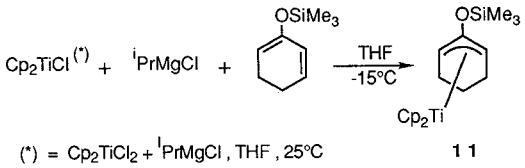
that, with all the aliphatic aldehydes examined, the addition of allyltitanium reagent ***8*** *occurred in the highly stereoselective way* (*anti*/*syn* = ~ 100:0).[10] The unique diastereomers have been assigned as *anti*, based on the coupling constants between CH(OH) and $CH(CH_3)$ (compounds **6d** and **6e**), which are closely similar to those observed for the silyloxy-free homoallylic alcohols **3** (equation 1).[11] The high *anti* stereoselectivity appears to be independent of the nature of the aldehyde alkyl chain. Neither increasing the chain length (**1c** vs **1b**) nor increasing the steric hindrance at the α-carbon atom (**1e** vs **1d** and **1b**) affects the stereochemical course of the reaction. The remarkable level of *anti* selection observed in this silyloxy modified allyltitanation reaction is of manifest synthetic interest. The latter lies particularly in the structural variety of the specific constructions of the adjacent sequences of stereocenters, which can now be developed via the highly versatile enol silyl ether function.[5]



R = alkyl, **b**: Et (68%); **c**: n-pentyl (57%); **d**: ^{i}Pr (60%); **e**: ^{t}Bu (65%)

Scheme 3

To examine the structural scope of this reaction we next tried to apply it to a simple cyclic system. The allyltitanium reagent **11** was prepared in situ starting from 2-(trimethylsilyloxy)cyclohexa-1,3-diene (Scheme 4) similarly to reagent **8**. Complex **11** reacted with benzaldehyde **(1a)** or aliphatic aldehydes **1b–e** in tetrahydrofuran solution at −10°C to afford cyclic β-hydroxy enol silyl ethers **12a–e** in good yields and generally in high diastereoselectivity (Scheme 5). The *anti* stereochemistry was assigned to the major diastereomers from the vicinal coupling constants of compounds **12a**, **12d** and **12e**, consistent with the analogous literature data.[12] Similar to the acyclic series, the degree of diastereoselectivity is also almost independent of the aldehyde aliphatic chain. The only marked difference between the cyclic and the acyclic series (reagents **11** and **8**, respectively) is in the reactions employing benzaldehyde. In the first, the *anti*/*syn* ratio from benzaldehyde **(1a)** equal to ~ 100:0 accords with the high level of diastereoselectivity observed for aliphatic aldehydes **1b–e**, whereas in the second the moderate *anti*/*syn* ratio (7:3) from **1a** contrasts significantly with the generally excellent stereoselectivity for **1b–e.**

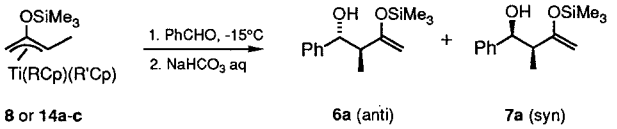


Scheme 4

entry	R	Product	anti/syn ratio (yield %)
1	Ph	**12a**	≅ 100/0 (71)
2	Et	**12b**	9/1 (68)
3	n-C_5H_{11}	**12c**	95/5 (58)
4	Me_2CH	**12d**	≅ 100/0 (65)
5	Me_3C	**12e**	≅ 100/0 (70)

Scheme 5

The outstanding stereochemical feature of the addition of the reagent **8** to **1a**, prompted us to examine the effect of modifying the structure of **8** on the stereoselectivity of this reaction. With this aim in mind we prepared three precursor titanocene dichlorides **13a–c**,[11] in which alkyl substituents were introduced into the cyclopentadienyl ring(s), namely $(MeCp)_2TiCl_2$ **(13a)** Cp(*t*-BuCp)$TiCl_2$ **(13b)** and $(t\text{-BuCp})_2TiCl_2$ **(13c)**. Thereafter, the allyltitanium reagents **14a–c**, derived from **13a–c**, reacted with **1a** (Scheme 6). As can be seen in Scheme 6, the introduction of the methyl substituent on each of the two cyclopentadiene rings has no effect on the diastereomeric ratio of the resulting enol silyl ethers **6a** (*anti*)/**7a** (*syn*) (entries 1 and 2, Scheme 6). However, further increasing the steric hindrance at the metal center led to a progressive loss of *anti* stereoselectivity (entries 3 and 4, Scheme 6).



1) R = R' = H : **6a/7a** = 7/3 (63%)[a]; 2) R = R' = Me : **6a/7a** = 7/3 (59%)[a];
3) R = H, R' = ^{t}Bu : **6a/7a** = 57/43 (62%)[a]; 4) R = R' = ^{t}Bu : **6a/7a** = 51/49 (68%)[a].

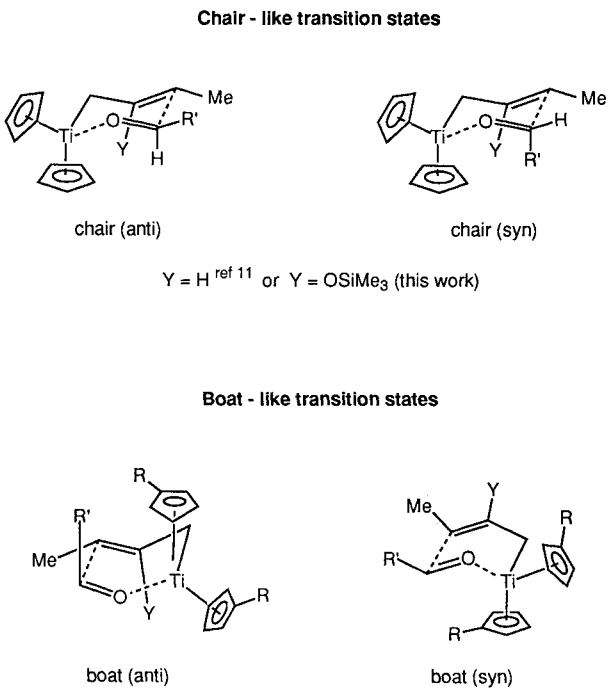
[a] Overall yield

Scheme 6

The stereochemical trend that we observed for the addition of reagents **8** and **14a–c** to **1a** is quite the opposite from that exhibited for the analogous non-substituted

(Y = H) crotyltitanocene species.[11] In the latter case, increases in steric hindrance (R) in η^3-crotyltitanocene reagents [$(RCp)_2Ti$ (η^3-C_4H_7), R = H, Me, *i*-Pr] leads to significant improvements in the *anti* diastereoselection of their addition to aldehydes. This trend has been explained by the authors on the basis of a six-membered chair-like transition state, which would be destabilized for the formation of *syn*-isomer by a pseudo-1,3-diaxial interaction between the aldehyde group and the cyclopentadienyl substituent R (Figure).

With a view to overcome the contradiction encountered between our results and the model advaned,[11] we presume that the addition of acyclic reagents **8** and **14** to aldehydes proceeds via transition states with a boat-like structure[13] (Figure). Such a preference for the boat over the chair transition state might be due to the presence of the substituent Y ($OSiMe_3$ or Me, see above) in the allyl moiety.



Figure

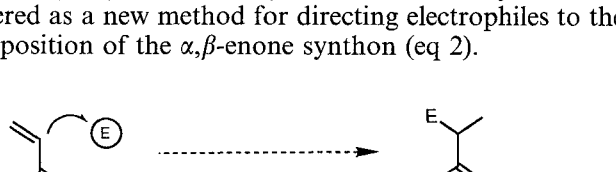
Thus, a pseudo-1,3-diaxial interaction between Y and the RCp ring is expected to destabilize both chair conformations. On the contrary, no such disfavoring effect exists for any of the boat conformations presented in the Figure.

The decrease in *anti* selectivity over the addition of **8** to an aromatic aldehyde **1a** can be explained by a mechanism involving a boat-like transition state. Thus, destabilizing π-π interactions are expected to exist between the Ph and the Cp rings in the transition state boat (*anti*). Consequently, the transition state boat (*syn*) starts to compete with the favored *anti* conformation. Further decrease of the *anti* stereoselection with increasing steric hindrance (R) on the cyclopentadiene ring acounts as well for the model assuming a "boat" transition state.

Unlike for the acyclic allyl reagent **8**, no exception to the high stereoselection was observed when benzaldehyde was added to the cyclic reagent **11** (Scheme 5). Indeed, a "boat" transition state seems to be difficult to achieve here for steric reasons, and the competing chair transition state would operate to result in the overall high *anti* stereoselectivity.

In conclusion, we have demonstrated the feasibility of preparing an η^3-allyltitanium reagent functionalized on the C-2 atom by a silyloxy group. The reagent adds to aldehydes in a highly regio- and stereocontrolled fashion to afford, depending on the treatment applied, *anti* diastereomeric β-hydroxy silyl enol ethers or β-hydroxy ketones. The excellent stereoselectivity of this reaction can be favorably compared with that of the structurally related Mukaiyama aldolisation, which does not exhibit exceptional simple stereoselection.[14] Two contiguous methyl- and hydroxy-bearing stereocenters make the enol silyl ethers possessing them versatile building blocks for a stereocontrolled chain extension, and especially for the specific construction of the polyketide fragments.[4]

The silyloxy modified allylation reaction may be considered as a new method for directing electrophiles to the α-position of the α,β-enone synthon (eq 2).



(eq 2)

This interesting regiochemical feature distinguishes it from the Mukaiyama-type additions of electrophiles with 2-silyloxybutadienes (vinyl-substituted silyl enol ethers), always occurring at the 1-position.[15]

Organometallic reactions were conducted under an Ar atmosphere using vacuum line techniques. The solvents used were distilled under Ar from sodium–benzophenone ketyl. Aldehydes **1a–e**, Cp_2TiCl_2 and *i*-PrMgCl (2 M solution in THF) were purchased from Aldrich Chemical Co. Substituted titanocene dichlorides **13a–c**,[11] 2-(trimethylsilyloxy)buta-[16a] and -cyclohexa-1,3-diene[16b] were prepared according to the published procedures. Aldehydes and silyloxydienes were distilled under Ar prior to use. ^1H and ^{13}C NMR spectra were recorded at 400 and 100.53 MHz, respectively. Mass spectra were obtained by EI (70 eV) or positive ion FAB MS technique employing thioglycerol as the matrix solvent. Gas chromatography GC was carried out on 30 m × 0.25 mm copper column packed with methyl silicone with a flow rate of 1.6 mL/min. Column flash chromatography was performed on silica gel 60 (Merck) by using hexane/Et_2O 5:1 to 6:1 as eluents. Satisfactory microanalyses obtained for all new compounds: C ± 0.38, H ± 0.39.

Allyltitanium Reagents (8 or 11) and Their Reaction with Aldehydes; General Procedure:

i-PrMgCl (2 mL, 2 M solution in THF) was added dropwise by syringe at r.t. to a stirred suspension of Cp_2TiCl_2 (1.00 g, 4.03 mmol) in THF (25 mL). After stirring for 15 min the resulting green solution of Cp_2TiCl was cooled to −15 °C. A solution of *i*-PrMgCl in THF (2 mL, 4 mmol) and silyloxydiene (6 mmol, ca.

1 mL) were added slowly and simultaneously by syringes to give a violet reaction mixture. After stirring for 5 min the aldehyde (4.5 mmol) was added neat by syringe at −15° to −10°C. After an additional 10 min period acidic or basic workup was performed alternatively to afford the corresponding β-hydroxy ketone or β-hydroxy enol silyl ether, respectively.

Acidic Workup:

The reaction mixture was quenched with 2 M HCl (4 mL) and with stirring air was passed through the solution for 5 min. The solution was diluted with Et_2O/hexane (4:1, 120 mL) and the precipitate of Cp_2TiCl_2 was recovered by filtration (0.7 g, 70%). The organic layer was washed with small portions of H_2O, dried ($MgSO_4$) and concentrated in vacuo. The second small portion of Cp_2TiCl_2 was separated by filtration through a thin layer of Celite. The filtrate was concentrated in vacuo to provide the crude β-hydroxy ketone that was further purified by flash chromatography. Starting from benzaldehyde a mixture of diastereomers **9a** and **10a** (**9a**/**10a** = 7:3) was obtained (yield 82%).

IR (neat): ν = 3484, 1703 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 0.88 (d, J = 7.2 Hz, 0.7 × 3 H), 1.06 (d, J = 7.2 Hz, 0.3 × 3 H), 2.10 (s, 0.3 × 3 H), 2.19 (s, 0.7 × 3 H), 2.75–2.98 (m, 1 H), 3.10 (br s, 1 H, D_2O exchangeable), 4.70 (d, J = 9.0 Hz, 0.7 H), 5.04 (d, J = 4.3 Hz, 0.3 H), 7.20–7.81 (m, 5 H).

MS: m/z = 178 (M^+, 2), 160 (28), 145 (10), 117 (20), 107 (95), 79 (55), 77 (35), 72 (100).

Basic Workup:

The reaction mixture (−10°C) was poured into a separatory funnel containing cold Et_2O (120 mL), and treated with ice-cold sat. aq $NaHCO_3$ (30 mL). The Et_2O layer was separated and the aqueous layer was extracted with cold Et_2O. The combined organics were washed with H_2O, dried ($MgSO_4$) and concentrated in vacuo. The residue was treated with Et_2O/hexane = 1:1 (30 mL) and the small portion of titanium derivatives eliminated by filtration through a frit. The major portion of Cp_2TiCl_2 can be recovered by acidifying the aqueous layer. After concentration of the organic filtrate in vacuo, the crude β-hydroxy enol silyl ether was purified by flash chromatography on a short silica gel column eluting with hexane/Et_2O (5 to 6:1). The yields and spectral data of silyl enol ethers are as follows:

6a + 7a (*anti*/*syn* = 7:3, 63%):

^1H NMR (C_6D_6): δ = 0.10 (s, 0.3 × 9 H), 0.14 (s, 0.7 × 9 H), 0.92 (d, J = 6.8 Hz, 0.7 × 3 H), 1.07 (d, J = 6.9 Hz, 0.3 × 3 H), 2.26 (d, J = 3.3 Hz, 0.3 H, D_2O exchangeable), 2.35–2.50 (m, 1 H + 0.7 H, partly D_2O exchangeable), 4.02 (br s, 0.3 × 2 H), 4.10 (br s, 0.7 × 2 H), 4.61 (dd, J = 6.8, 3.3 Hz, 0.7 H), 4.98 (m, 0.3 H), 7.08–7.40 (m, 5 H).

^{13}C NMR ($CDCl_3$): δ = 0.2, 11.7, 15.3, 47.4, 48.5, 75.3, 76.4, 90.2, 91.4, 126.1, 126.8, 127.0, 127.6, 128.0, 128.2, 128.5, 129.1, 129.8, 134.5, 142.7, 142.8, 160.1, 161.2.

MS: m/z = 235 (M^+ − Me, 10), 179 (100), 144 (6), 129 (27), 117 (20), 105 (15), 91 (18), 77 (20).

6b (68%):

IR (neat): ν = 3476, 2963, 1626, 1460, 1254, 1121, 1085, 1008, 972 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 0.18 (s, 9 H), 0.91 (t, J = 7.4 Hz, 3 H), 1.01 (d, J = 7.0 Hz, 3 H), 1.20–1.45 (m, 2 H), 2.12 (pseudoquintet, 1 H), 2.29 (d, J = 4.1 Hz, 1 H, D_2O exchangeable), 3.34 (m, 1 H), 4.05 (br s, 2 H).

^{13}C NMR ($CDCl_3$): δ = 0.1, 10.1, 15.2, 27.5, 45.4, 74.9, 90.7, 160.6.

MS: m/z = 202 (M^+, 5), 144 (77), 129 (51), 113 (16), 91 (43).

6c (57%):

^1H NMR (C_6D_6): δ = 0.11 (s, 9 H), 0.90 (t, J = 6.8 Hz, 3 H), 1.10 (d, J = 6.6 Hz, 3 H), 1.16–1.70 (m, 8 H), 2.05 (br s, 2 H), 2.10–2.13 (m, 1 H), 3.60 (m, 1 H), 4.06 (br s, 2 H).

^{13}C NMR ($CDCl_3$): δ = 0.0, 14.0, 15.2, 22.6, 31.8, 34.6, 45.0, 45.8, 73.6, 90.6, 160.6.

6d (60%):

^1H NMR ($CDCl_3$): δ = 0.20 (s, 9 H), 0.89 (d, J = 6.6 Hz, 3 H), 0.92 (d, J = 6.6 Hz, 3 H), 1.03 (d, J = 6.8 Hz, 3 H), 1.68 (m, 1 H), 2.20 (d, J = 6.1 Hz, 1 H, D_2O exchangeable), 2.12–2.33 (m, 1 H), 3.11 (pseudoquartet, 7.2 Hz, 1 H), 4.07 (m, 2 H).

^{13}C NMR ($CDCl_3$): δ = 0.1, 15.8, 16.5, 20.2, 30.9, 43.2, 78.4, 90.7, 160.5.

MS: m/z = 201 (M^+ − Me, 5), 144 (90), 129 (55), 91 (35).

6e (65%):

^1H NMR ($CDCl_3$): δ = 0.21 (s, 9 H), 0.92 (s, 9 H), 1.18 (d, J = 7.1 Hz, 3 H), 2.44 (dq, J = 3.1, 7.0 Hz, 1 H), 3.04 (dd, J = 3.1, 7.4 Hz, 1 H), 3.10 (d, J = 7.4 Hz, 1 H), 3.95 (m, 1 H), 4.05 (m, 1 H).

^{13}C NMR ($CDCl_3$): δ = 0.5, 20.2, 26.8, 40.9, 43.8, 83.7, 90.9, 162.6.

MS: m/z = 215 (M^+ − Me, 10), 173 (25), 144 (30), 129 (30), 91 (25).

12a (71%):

^1H NMR (C_6D_6): δ = 0.24 (s, 9 H), 1.22–1.35 (m, 2 H), 1.48–1.64 (m, 2 H), 1.92–2.00 (m, 2 H), 2.43–2.51 (m, 1 H), 5.04–5.08 (m, 1 H), 5.20 (d, J = 3.2 Hz, 1 H).

^{13}C NMR ($CDCl_3$): δ = 0.8, 22.0, 23.5, 24.8, 47.2, 73.5, 108.5, 126.5, 128.5, 129.5, 130.2, 134.7, 150.3.

MS: m/z = 276 (M^+, 4), 259 (10), 170 (100), 155 (20), 107 (40).

12b (*anti*/*syn* = 9:1) (68%):

^1H NMR (C_6D_6): δ = 0.11 (s, 0.1 × 9 H), 0.13 (s, 0.9 × 9 H), 1.04 (t, J = 7.4 Hz, 0.9 × 3 H), 1.13 (t, J = 7.4 Hz, 0.1 × 3 H), 1.27–1.60 (m, 6 H), 1.76 (d, J = 5.0 Hz, 0.9 H), 1.85–2.00 (m, 2 H), 2.24–2.31 (m, 1 H), 3.76–3.81 (m, 0.1 H), 3.90–3.97 (m, 0.9 H), 4.89 (ddd, J = 6.8, 6.9, 1.3 Hz, 0.1 H), 4.99 (m, 0.9 H).

^{13}C NMR ($CDCl_3$): δ = 0.2, 1.0, 9.6, 11.0, 21.0, 21.7, 23.4, 23.9, 26.1, 26.9, 43.9, 44.1, 73.2, 76.1, 105.4, 106.9, 150.7, 152.5.

MS: m/z = 228 (M^+, 25), 213 (6), 199 (7), 181 (10), 170 (100), 81 (20).

12c (*anti*/*syn* = 95:5) (58%):

^1H NMR (C_6D_6): δ = 0.16 (s, 0.95 × 9 H), 0.18 (s, 0.05 × 9 H), 0.95 (t, J = 6.6 Hz, 3 H), 1.20–1.75 (m, 12 H), 1.90–2.00 (m, 3 H), 2.16–2.26 (m, 1 H), 3.60–3.72 (m, 0.05 H), 3.74–3.86 (m, 0.95 H), 4.87 (ddd, J = 4.2, 4.2, 1.6 Hz, 0.05 H), 4.95 (ddd, J = 6.7, 6.9, 1.4 Hz, 0.95 H).

^{13}C NMR ($CDCl_3$): δ = 0.2, 0.7, 13.9, 21.1, 21.7, 22.6, 23.6, 23.9, 25.2, 26.2, 30.6, 32.0, 33.3, 34.5, 44.5, 71.7, 75.0, 105.4, 106.8, 150.7.

MS: m/z = 270 (M^+, 30), 255 (10), 253 (18), 199 (14), 181 (13), 170 (100).

12d (65%):

^1H NMR (C_6D_6): δ = 0.10 (s, 9 H), 0.76 (d, J = 6.6 Hz, 3 H), 0.95 (d, J = 6.6 Hz, 3 H), 1.40–1.75 (m, 5 H), 1.85–2.00 (m, 2 H), 2.13–2.30 (m, 1 H), 3.48 (d, J = 3.4 Hz, 1 H), 4.95 (m, 1 H).

^{13}C NMR ($CDCl_3$): δ = 0.2, 19.1, 19.8, 21.6, 22.1, 23.9, 30.1, 42.2, 75.8, 107.5, 150.5.

MS: m/z = 242 (M^+, 30), 227 (6), 211 (18), 199 (16), 181 (20), 170 (100), 81 (30).

12e (70%):

^1H NMR (C_6D_6): δ = 0.16 (s, 9 H), 1.02 (s, 9 H), 1.25–1.74 (m, 4 H), 1.82–2.00 (m, 2 H), 2.41 (m, 1 H), 3.95 (d, J = 2.7 Hz, 1 H), 5.06 (m, 1 H).

^{13}C NMR ($CDCl_3$): δ = 0.3, 22.1, 23.6, 23.8, 27.3, 35.2, 41.7, 76.6, 107.6, 150.9.

MS: m/z = 256 (M^+, 7), 211 (3), 199 (10), 181 (10), 170 (100), 159 (23), 81 (13).

(1) For reviews, see:
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