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Synthesis of [$^3H_2$]-(11*S*,17*R*)-11,17-Dimethylhentriacontane: a Useful Tool for the Study of the Internalisation of Communication Pheromones of Ant *Camponotus vagus*

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Abstract—The convergent synthesis in high enantiomeric and diastereoisomeric purity of [$^3H_2$]-(11*S*,17*R*)-11,17-dimethylhentriacontane, a communication pheromone of ant *Camponotus vagus* is described. The stereogenic centres were introduced from commercially available (*S*)-citronellol and (*R*)-citronellal and the tritiation step was conducted in the last step of the synthesis with tritium gas over the Wilkinson catalyst. © 2000 Elsevier Science Ltd. All rights reserved.

Chiral methyl branched subunits are found in several classes of naturally occurring compounds and are particularly present in insect pheromones. During the last 15 years, several total syntheses[1] have been performed starting from natural products (citronellic acid, tartaric acid,…), or using selective alkylation reactions of chiral iron complexes[2] or enzymatic resolutions.[3,4] A few years ago, Clément et al. identified, from the ant *Camponotus vagus's* communication pheromones, numerous long chain alkanes bearing one, two or three methyl groups.[5,6] Among them, 11,17-dimethylhentriacontane **1** seems to be one of the most important compounds with respect to the activity of the ant.[7] In order to determine the influence of dimethylhentriacontane and the absolute stereochemistry of the active pheromone, we synthesised the four possible stereoisomers of 11,17-dimethylhentriacontane.[8] The processes of the biosynthesis of such long chain alkanes are essentially achieved, into microsomes of enocytal cells, through elongation, reduction and decarboxylation process from acetate, isoleucine, propionate, valine, and equally C16 and C18 fatty acids precursors.[9] Nevertheless, the mechanism of the reception of these alkanes is still unclear and could occur through an active internalisation process involving a protein. Thus, to better understand how hydrocarbons are incorporated and metabolised into the organism, we projected the use of tritiated molecules and notably a tritiated analogue of 11,17-dimethylhentriacontane. To facilitate analyses, radioactive labels have to be amalgamated and our choice was to localise the tritium atoms between the two methyl groups.

Our retrosynthetic strategy shown in Scheme 1 is based on a convergent synthesis coupling two building blocks both prepared from citronellol. This latter was chosen since both pure enantiomers are available.[10] A combination of different transformations (ozonolysis, alkylation reactions, Wittig cross coupling, etc.) on each end of citronellol, had given a rapid synthesis of all stereoisomers of 11,17-dimethylhentriacontane. In order to introduce tritium atoms in the last step of the synthesis and starting from the (*S*)-citronellol and (*S*)-citronellal, we focussed our attention on the synthesis of the (*R*,*S*)-dimethylhentriacont-13-ene precursor of the (*R*,*S*)-isomer [$^3H_2$]-**1**.

Synthesis of fragment **A** (Scheme 2) started from (*S*)-citronellol which was converted by ozonolysis to a 1/1 mixture of aldehyde **2** and its hemiacetal form **3** in 98% yield.[11] The Wittig olefination of the mixture **2**+**3** with *n*-heptylidenetriphenylphosphorane gave the (*Z*)-ethylenic alcohol **4** as the major isomer in 75% yield.[12] Reduction of the double bond under H_2 atmospheric pressure over the Wilkinson catalyst provided 3-methyltridecan-1-ol 5 in 89% yield without racemisation of the stereocentre.[13] The bromination under the well described conditions (tetrabromomethane/triphenylphosphine)[14] of the alcohol **5** afforded the bromide **6** which was then converted into triphenylphosphonium salt **7** (74% yield from **4**).

Aldehyde **8** was obtained in 90% yield from (*S*)-citronellal in three steps: addition of dodecylmagnesium bromide, conversion of alcohol function as tosylate and ozonolysis of the trisubstituted double bond (Scheme 3). We have

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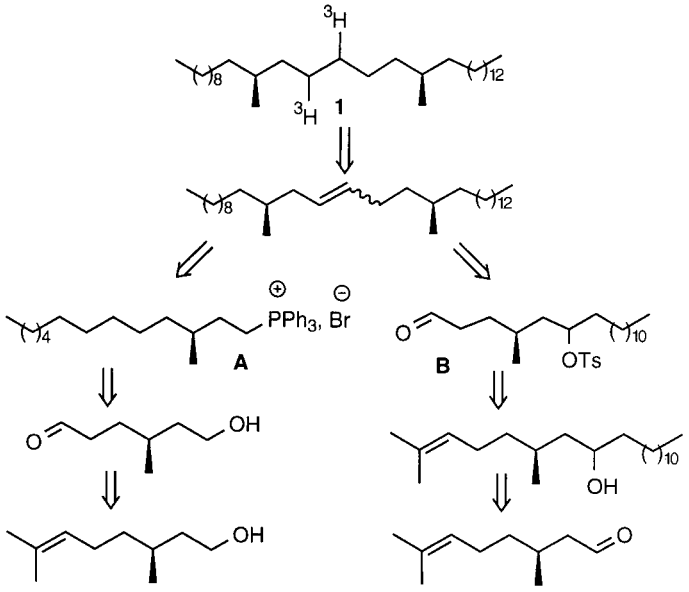
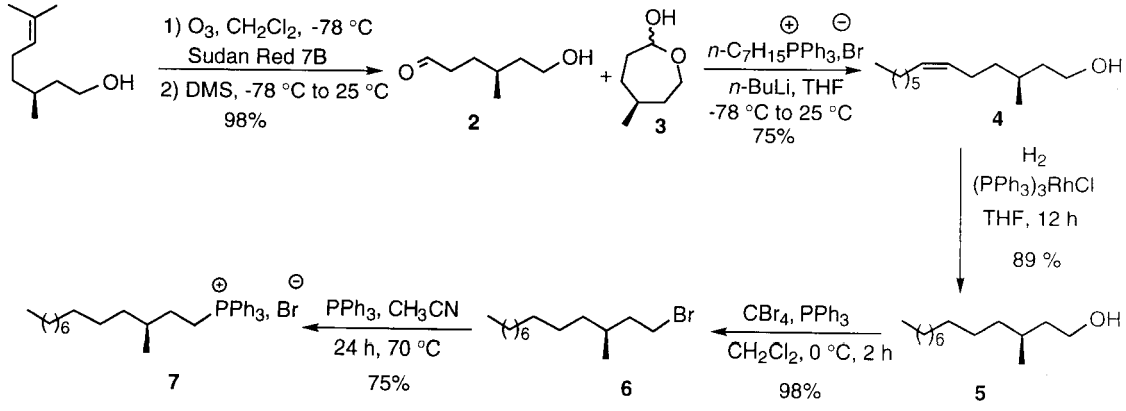


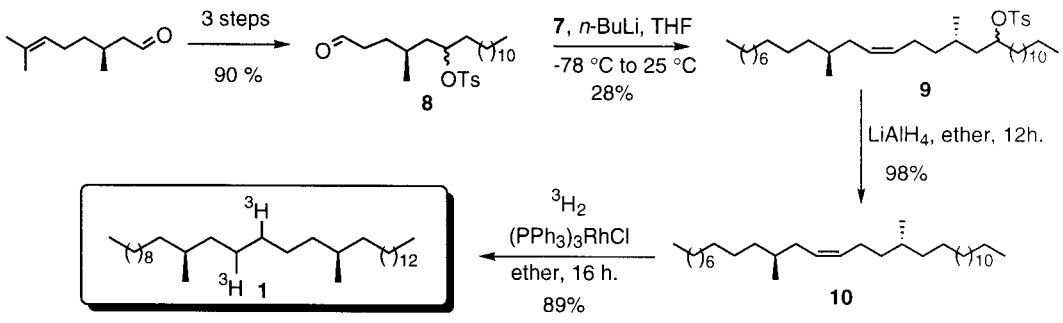
Scheme 1. Retrosynthetic pathway.



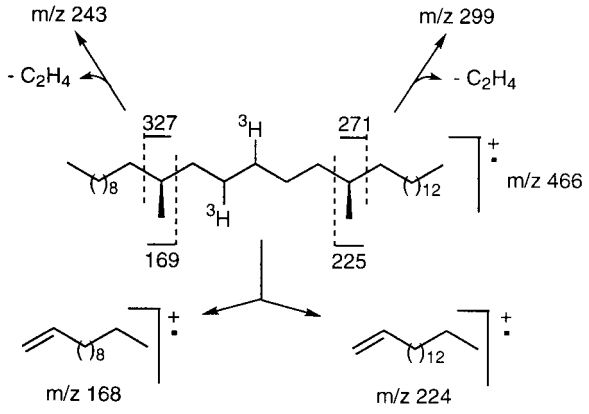
Scheme 2. Synthesis of fragment A.

chosen to remove the tosylate function after elaboration of the hydrocarbon skeleton in order to permit easy separation of **9** from the small amount of symmetric olefin (11,16-dimethylhexacos-13-ene) formed by oxidation of the phosphorane derived from **7**.[15]

A Wittig olefination between the phosphorane generated from **7** and the aldehyde **8** led in 28% yield to the required carbon skeleton. It should be noticed that the low yield of the reaction could be attributed to the long chain borne by the aldehyde. Many attempts to improve the yield of this cross coupling reaction did not lead to better results.[16] The (11*S*,17*R*)-11,17-dimethylhentriacont-13-ene **10** was then obtained in a pure form in 78% yield by reduction of the tosylate function with lithium aluminium hydride.[17] Finally, olefin **10** under tritium atmosphere in the presence of Wilkinson catalyst furnished 13,14-ditritio-11,17-dimethylhentriacontane.[18] The overall yield was 12% from (*S*)-citronellol (8 steps) or 22% from (*S*)-citronellal (6 steps).



Scheme 3. Synthesis of [$^3H_2$]-(11*S*,17*R*)-11,17-dimethylhentriacontane.



Scheme 4. [$^3H_2$]-Dimethylhentriacontane: fragmentation under 70 eV.

To confirm the position of tritium atoms, an analysis by mass spectroscopy was carried out. Mass spectra analysis of **1** clearly shows that the isotopic enrichment achieved is close to the theory (52 Ci/mmol compared to a maximum expected of 58 Ci/mmol) (Scheme 4). The molecular peak is not observed but there is a peak at m/z=453, corresponding to a loss of a methyl group. Moreover, in this series the major fragmentation occurs generally in α-position of the methyl group. Mass spectra of **1**, in the field m/z=168–170 (west part) and m/z=224–228 (east part of **1**), shows the absence of tritium atoms, indicating that the reduction of the double bond was indeed highly selective and gave no scrambling at all along the chain, as has been shown using heterogeneous conditions (palladium on support) for the reduction of such double bonds.[19]

In conclusion, this total and stereocontrolled synthesis of [$^3H_2$]-(*S*,*R*)-dimethylhentriacontane **1** shows the versatile and powerful worth of (*S*)-citronellol as chiral building block. Each end may be used separately to introduce any lengh of carbon chain with or without a second stereocentre. Biological tests are currently underway to investigate the mechanism of internalisation of this pheromone type.

Experimental

All reactions were carried out under an argon atmosphere. Tetrahydrofuran and diethyl ether were dried and freshly distilled from sodium/benzophenone. Dichloromethane was dried by distillation over calcium hydride. Flash chromatography was carried out with Merck silica gel (silica gel, 230–400 mesh). ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AC 200 or a Bruker AMX 400 (nuclear magnetic resonance) spectrometer. Chemical shifts are given in ppm referring to Me_4Si used as internal standard for ^{1}H and ^{13}C NMR spectra (solvent=$CDCl_3$). Coupling constants are given in Hertz. The mass spectra were obtained on a Hewlett Packard apparatus (engine 5989A) in the GC/MS mode. IR spectra were recorded on a IR-FT Perkin–Elmer 1600 apparatus and principal patterns are given in cm^{-1}.

(*S*)-4-Methyl-6-hydroxyhexanal (2). (*S*)-Citronellol (780 mg, 5 mmol) and Sudan Red 7B (0.3 mg) in dichloromethane (50 mL) at −80°C were submitted to a stream of ozone until the red colour disappeared. The yellow solution was immediately purged of ozone by a stream of argon, followed by the addition of dimethyl sulfide (1 mL, 15 mmol). The solution was allowed to warm to room temperature, concentrated and purified by flash chromatography on silica gel which gave a mixture (1/1) of **2** and its hemiacetal form **3** (648 mg, 98% yield). R_f=0.26 (diethyl ether/petroleum ether: 1/1). IR (film): 3390, 2812, 2750, 1719, 1650, 1457, 1375, 1063, 919, 731. ^{1}H NMR δ: 0.89 (3H, d, J=6.2 Hz); 1.35–1.74 (5H, m); 2.43 (1H, dddd, J=1.7, 6.7, 8.4, 17.3 Hz); 2.47 (1H, dddd, J=1.7, 6.3, 8.5, 17.3 Hz); 3.62–3.73 (2H, m); 9.76 (1H, t, J=1.7 Hz). ^{13}C NMR δ: 19.3; 28.7; 29.2; 31.6; 41.6; 60.6; 203.1; hemiacetal 3:^{1}H NMR δ: 0.91 (3H, d, J=6.2 Hz); 1.30–1.74 (7H, m); 3.53 (1H, dt, J=3.4, 12.8 Hz); 3.90 (1H, bt, J=12.8 Hz); 5.14 (1H, dd, J=5.3, 9.2 Hz). ^{13}C NMR δ: 23.1; 30.9; 34.0; 36.4; 39.4; 60.2; 96.4.

Heptyltriphenylphosphonium bromide. To a solution of 1-bromoheptane (17.90 g, 100 mmol) in acetonitrile (100 mL) was added triphenylphosphine (28.82 g, 110 mmol). After refluxing for 24 h, the mixture was concentrated, the crude product was dissolved into dichloromethane (10 mL) then added dropwise to 3 L of diethyl ether. After stirring for 1 h, the precipitate was filtered and dried under vacuum affording pure white solid (43.60 g, 99% yield). R_f=0.36 (5% methanol/dichloromethane). Mp: 165°C. IR (CCl_4): 3054, 2984, 2305, 1424, 1265, 896. ^{1}H NMR δ: 0.78 (3H, t, J=6.6 Hz); 1.17–1.21 (8H, m); 1.58–1.60 (2H, m); 3.74–3.81 (2H, m); 7.61–7.87 (15H, m). ^{13}C NMR δ:13.9; 22.4 (d, J_{CP}=4.8 Hz); 22.6 (d, J_{CP}=50.2 Hz); 28.7; 30.1; 30.4; 31.2; 118.0 (3C, d, J_{CP}=85 Hz); 130.5 (6C, d, J_{CP}=11.5 Hz); 133.5 (6C, d, J_{CP}=9.5 Hz); 135.1 (3C, d, J_{CP}=3.5 Hz).

(*S*,*Z*)-3-Methyltridec-6-en-1-ol (4). To a suspension of heptyltriphenylphosphonium bromide (6.53 g, 14.8 mmol) (previously dried by three azeotropic distillations with benzene) in tetrahydrofuran (37 mL) was added, at −40°C, *n*-butyllithium (8.8 mL, 14.1 mmol, 1.6 M in hexane). The purple solution of ylide was slowly warmed to room temperature and stirred for 2 h. After cooling to −80°C, mixture of **2** and **3** (490 mg, 3.7 mmol) (previously dried by three azeotropic distillations with benzene) was added. The reaction mixture was then allowed to warm to room temperature, quenched by a saturated solution of ammonium chloride (10 mL), water (10 mL), petroleum ether (10 mL) and extracted with diethyl ether (3×10 mL). The combined organic layers were washed with brine (3×10 mL) and dried over magnesium sulfate. After concentration, the crude product was purified by flash chromatography to give **4** (587 mg, 75% yield) (*Z*/*E*=9/1). R_f=0.39 (diethyl ether/petroleum ether: 1/1). IR (film): 3353, 2924, 2801, 1653, 1460, 1377, 1060, 967. ^{1}H NMR δ: 0.82–0.89 (6H, m); 1.20–1.40 (11H, m); 1.40–1.61 (2H, m); 1.95–2.02 (4H, m); 3.60–3.70 (2H, m); 5.28–5.34 (2H, m). (*Z*)-isomer: ^{13}C NMR δ: 14.1; 19.5; 22.7; 24.7; 27.3; 29.0; 29.2; 29.7; 31.8; 37.2; 39.8; 60.9; 129.7; 130.0; meaningful signals for (*E*)-isomer: 130.2; 130.4. Anal. Calcd for $C_{14}H_{28}O$: C, 79.2; H, 13.3. Found: C, 79.13; H, 13.22.

(*S*)-3-Methyltridecan-1-ol (5). To 820 mg (3.9 mmol) of (*S*)-3-methyltridec-6-en-1-ol **4** in tetrahydrofuran (20 mL)

was added Wilkinson catalyst (100 mg, 13% w/w) and submitted to hydrogen atmosphere. After 3 h, Wilkinson catalyst (100 mg, 13% w/w) was again added. The reaction mixture was stirred at room temperature for 18 h under hydrogen atmosphere. After concentration, the crude product was purified by flash chromatography on silica gel to give **5** (740 mg, 89% yield). R_f=0.40 (diethyl ether/pentane: 1/1). IR (film): 3353, 2923, 2855, 1465, 1095, 1049, 956, 845. ^{1}H NMR δ: 0.76–1.05 (6H, m); 1.00–1.40 (19H, bs); 1.42–1.68 (2H, m); 3.50 (2H, td, J=4.0; 5.3 Hz). ^{13}C NMR δ14.1; 19.7; 22.7; 27.0; 29.2; 29.3; 29.4 (3C); 30.2; 32.1; 37.3; 39.4; 61.2. Anal. Calcd for $C_{14}H_{30}O$: C, 78.4; H, 14.1. Found: C, 78.29; H, 14.02.

(*S*)-1-Bromo-3-methyltridecane (6). To a mixture of **5** (740 mg, 3.5 mmol) and carbon tetrabromide (1.7 g, 5.2 mmol) in anhydrous dichloromethane (18 mL) was added, at 0°C, triphenylphosphine (1.36 g, 5.2 mmol). The reaction mixture was slowly allowed to warm to room temperature. The reaction was monitored by TLC. After 3 h, the reaction mixture was concentrated and purified by flash chromatography on silica gel to give **6** (886 mg, 92% yield). R_f=0.73 (diethyl ether/petroleum ether: 1/1). IR (film): 2985, 2873, 1456, 1260, 1215, 721. ^{1}H NMR δ: 0.84–0.87 (6H, m); 1.10–1.36 (19H, bs); 1.58–1.70 (2H, m); 3.31–3.47 (2H, m). ^{13}C NMR δ: 14.4; 19.0; 22.8; 27.1; 29.3; 29.5 (3C); 29.7; 31.4; 32.0; 33.5; 36.9; 41.1. Anal. Calcd for $C_{14}H_{29}Br$: C, 60.6; H, 10.5. Found: C, 60.35; H, 10.34.

(*S*)-3-Methyltridecyltriphenylphosphonium bromide (7). To a solution of **6** (871 mg, 3.2 mmol) in acetonitrile (31 mL) was added triphenylphosphine (1 g, 3.7 mmol). After refluxing for 48 h, the reaction mixture was concentrated and the crude material was chromatographed on silica gel giving **7** (1.5 g, 91% yield). R_f=0.26 (5% methanol/dichloromethane). IR (film): 3053, 2923, 2854, 1483, 1437, 1271, 1190, 1114, 996. ^{1}H NMR δ: 0.73–0.90 (3H, m); 0.90–1.06 (19H, bs); 1.13–1.40 (11H, m); 1.50–1.71 (2H,m); 3.70–3.86 (2H, m); 7.63–7.93 (15H, m); ^{13}C NMR δ: 13.9; 19.3; 20.5 (1C, d, J_{CP}=50.0 Hz); 22.7; 24.5; 27.4–28.8 (4C); 29.6 (1C, d, J_{CP}=5.5 Hz); 31.7 (2C); 33.0 (1C, d, J_{CP}=15.0 Hz); 35.9; 118.5 (3C, d, J_{CP}=85.0 Hz); 130.9 (6C, d, J_{CP}=12.5 Hz); 133.5 (6C, d, J_{CP}=10.2 Hz); 135.3 (3C, d, J_{CP}=3.3 Hz).

(*S*)-4-Methyl-6-(*p*-toluenesulfonyloxy)octadecanal (8). Compound **8** was prepared in three steps from (*S*)-citronellal according to Ref. 8. IR (film): 2925, 2855, 1724, 1461, 1359, 1177, 1097, 897, 737. ^{1}H NMR δ: 0.70–1.00 (6H, m); 1.00–1.70 (27H, m); 2. 22–2.44 (2H, m); 2.42 (3H, s);4.52–4.70 (1H, m); 7.28–7.32 (2H, d, J=8.2 Hz); 7.74–7.78 (2H, d, J=8.1 Hz); 9.70 (1H, t, J=1.6 Hz). ^{13}C NMR δ: 14.2; 19.6; 21.6; 22.7; 24.6; 28.3; 28.7; 29.4 (3C); 29.5; 29.7 (3C); 32.0; 35.0; 41.4; 41.6; 82.6; 127.8 (2C); 129.7 (2C); 134.7; 144.5; 202.2; meaningful signals for the other diastereoisomer: 19.0; 24.5; 28.6; 34.4;41.3; 41.5; 82.4; 202.3.

(11*S*,17*S*)-11,17-Dimethyl-19-(*p*-toluenesulfonyloxy)-hentriacont-13-ene (9). To a suspension of **7** (500 mg, 0.9 mmol) (previously dried by three azeotropic distillations with benzene) in tetrahydrofuran (12 mL) was added, at −60°C, *n*-butyllithium (0.62 mL, 1 mmol, 1.6 M in hexane). The orange solution of ylide was slowly warmed to room temperature and stirred for 2 h. After cooling to −80°C, the aldehyde **8** (717 mg, 1.6 mmol) (previously dried by three azeotropic distillations with benzene) was added. The reaction mixture was then allowed to warm to room temperature, quenched by saturated solution of ammonium chloride (15 mL), water (10 mL), petroleum ether (10 mL) and extracted with diethyl ether (3×10 mL). The combined organic layers were washed with brine (3×10 mL) and dried over magnesium sulfate. After concentration, the crude product was purified by flash chromatography to give **9** (132 mg, 21% yield) as a 1/1 mixture of diastereoisomers. R_f=0.55 (diethyl ether/petroleum ether: 1/4). IR (film): 2922, 2852, 1599, 1495, 1462, 1366, 1305, 1187, 1176, 1119, 1097, 1020, 967, 894, 814, 723, 688, 665. ^{1}H NMR δ: 0.68–0.98 (12H, m); 1.00–1.43 (40H, m); 1.43–1.74 (4H, m); 1.74–2.14 (4H, m); 2.41 (3H, s); 4.52–4.75 (1H, m); 5.22–5.39 (2H, m); 7.59 (2H, d, J=7.9 Hz); 7.77 (2H, d, J=8.1 Hz). ^{13}C NMR δ: 14.2 (2C), 19.6; 19.3; 21.7; 22.8; 22.7; 24.7; 25.0 (2C); 28.7; 29.4–29.8 (10C); 32.1; 31.9; 33.1; 34.4; 34.6; 36.8; 36.9; 41.8; 82.9; 127.8 (2C); 129.6; 129.8; 135.0; 144.2; meaningful signals for the other diastereoisomer: 29.1; 35.1; 37.3; 83.0; 129.7; 130.3; 135.1; 144.3.

(11*S*,17*R*)-11,17-Dimethylhentriacont-13-ene (10). To a suspension of lithium aluminium hydride (10 mg, 0.2 mmol) in anhydrous diethyl ether (10 mL), **9** (132 mg, 0.2 mmol) was added. After stirring for 10 h at room temperature, the reaction was monitored by TLC. The reaction was quenched by 3 mL of ethanol, filtered on celite 545 and alkene **10** (55 mg, 93% yield) was obtained after concentration. R_f=0.77 (diethyl ether/petroleum ether: 1/10). IR (film): 3026, 2952, 2860, 1475, 1326. ^{1}H NMR δ: 0.60–0.91 (12H, m); 0.91–1.54 (48H, m); 1.65–2.11 (4H, m); 5.14–5.48 (2H, m). ^{13}C NMR δ: 14.2 (2C); 19.6; 19.7; 22.7; 22.8; 25.0; 27.2; 27.3; 29.1–30.3 (14C); 31.9; 32.0; 33.1; 32.5; 34.5; 36.8; 37.1 (2C); 129.8; 131.0. Anal. Calcd for $C_{33}H_{66}$: C, 85.6; H, 14.4;. Found: C, 85.84; H, 14.22.

(11*S*,17*R*)-11,17-Dimethyl-13,14-ditritiohentriacontane (1). To a solution of the alkene **10** (25 mg, 0.054 mmol) in diethyl ether (5 mL), was added the Wilkinson catalyst (30 mg). The flask was connected to a Toppler ramp tritium mannifold in a glove compartment then frozen with liquid nitrogen and degassed under vacuum during a minute approximately. The mixture was then placed under a tritium atmosphere and slowly warmed to room temperature with a control of the absorption of tritium. The tritium uptaken was monitored and a constant pressure of 1 atm tritium was maintained within the reaction vessel. After 16 h at this temperature, the reaction was stopped by filtration on Millex filter. The flask and the filter were washed and rinsed with dichloromethane (2×20 mL), then the organic layers are concentrated, the crude mixture was then diluted with 50 mL of MeOH and the labile tritium is removed. The crude mixture obtained is filtered on silica gel (eluent: pentane) then purified by HPLC using a C18 Nucleosil column eluting with a mixture of acetone/methanol/H_2O (95/2.5/2.5). radiochemical yield >95%. Specific activity=52 Ci/mmole as determined by MS. ^{1}H NMR δ: 0.79–0.88 (12H,

bt); 1.23 (54H, bs). MS (70 eV): *m/z*=453(9); 439(6); 425(3); 327(25); 299(5); 271(23); 243(6); 225(17); 224(29); 169(17); 168(37); 113(20); 99(31); 85(68); 71(85); 57(100).

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