Supporting Information

General. All ^{1}H NMR spectra taken at 400MHz and ^{13}C NMR spectra taken at 100MHz using Bruker ARX 400 are reported in ppm (δ).

Solvents. Anhydrous diethyl ether (Et_2O) was freshly distilled from sodium-benzophenone before use. Anhydrous dichloromethane (CH_2Cl_2) was distilled from CaH_2.

Materials. Unlabelled materials were purchased from Aldrich Inc., Acros Chemicals or other commercial suppliers, and purified before use. $^{13}CBr_4$ was purchased from Eurisotop (France) and used without any purification. Zinc bromide was flame-dried under nitrogen atmosphere and dissolved after cooling in dry ether to obtain a 1M solution

General procedure for ^{13}C-labelled dibromo compounds:

To a solution of PPh_3 (794 mg, 3 mmol) in dry CH_2Cl_2 (5 mL) was added $^{13}CBr_4$ (435 mg, 1.31 mmol) in one portion at 0°C. After stirring for 10 min, the resulting orange solution was cooled to -40°C, and the aldehyde (1.34 mmol) in CH_2Cl_2 (2 mL) was added. The temperature was allowed to raise gradually to 0°C, and the solution stirred 2h at 0°C. After dilution with Et_2O (10mL) and celite-filtration, evaporation of the solvents gave the crude dibromo compound which was purified by flash-chromatography.

1-^{13}C-1,1-dibromo-3-*tert*-butoxy oct-1-ene **6**: From 2-*tert*-butoxy heptanal (250 mg). Yield: 78%. ^{1}H NMR (400MHz, CDCl3): δ 0.89 (t, 3H, *J*=6.8Hz), 1.19 (s, 9H), 1.25-1.55 (m, 8H), 4.04-4.11 (m, 1H), 6.42 (dd, 1H, *J*=7.8Hz, 0.7Hz); ^{13}C NMR (100MHz, CDCl3): δ 14.2, 22.6, 24.9, 28.5, 31.7, 35.7, 72.9, 74.2, 86.8 (d, *J*=82.6Hz), 143.5 (d, *J*=82.6Hz).

1-^{13}C-1,1-dibromo dec-1-ene: From nonanal (450 mg). Yield: 95%. ^{1}H NMR (400MHz, CDCl3): δ 0.91 (t, 3H, *J*=7.1Hz), 1.29-1.30 (m, 10H), 1.44 (t, 2H, *J*=7.0Hz), 2.11 (m, 2H), 6.41 (dt, 1H, *J*=7.2Hz, 1.2Hz); ^{13}C NMR (50MHz, CDCl3): δ 14.3, 22.8, 27.9, 29.2, 29.4, 29.5, 32.0, 33.2, 88.6 (s; d, *J*=83.0Hz), 138.9 (d, *J*=83.0Hz).

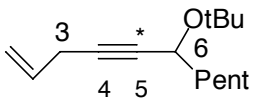
1-^{13}C-1,1-dibromo-2-cyclohexyl ethylene : From cyclohexylcarboxaldehyde (mg). Yield: %. ^{1}H NMR (400MHz, CDCl3): δ 1.07-1.74 (m, 10H), 2.23 (m, 1H), 6.25 (dd, 1H, *J*=8.9Hz, 1.1Hz) ; ^{13}C NMR (50MHz, CDCl3): δ 25.60, 25.91, 31.4, 42.6, 87.2, 143.8 (d, *J*=76.0Hz). .

General procedure for the Fritsch-Buttenberg-Wiechell rearrangement:

To a solution of ^{13}C-labelled dibromoalkene (1 mmol) in Et_2O (5 mL) was added *n*-BuLi (1.6 M in hexane, 1.4 mL, 2.2 mmol) dropwise at -55°C. The reaction mixture was warmed to room temp. in 30 min, and cooled again to -10°C. Allylmagnesium bromide (1.43 M in Et_2O, 1.40 mL, 2.0 mmol) or crotylmagnesium bromide (1.52 M in Et_2O, 1.30 mL, 2.0 mmol) and $ZnBr_2$ (1.0 M in Et_2O, 3 mL, 3 mmol) were added consecutively. The resulting yellow solution was stirred between 2.5 h and 5h at 0°C, and cooled again to -20°C. After addition of $PhSO_2Cl$ (O.3 mL, 2.2 mmol), the reaction mixture was stirred 30 min at -20°C, then allowed to warm to room temp. After completion of the reaction, the mixture was hydrolyzed by a satd soln of NH_4Cl (ca 10 mL), followed by a few drops of ethanolamine. After the usual work-up, the crude products were purified by a silica-gel column chromatography to give the ^{13}C-labelled alkyne.

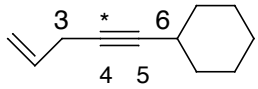
6-*tert*-Butoxy undec-1-en-4-yne **10**:

The labelled position was ascertained by C(5) - H(6) long range COSY coupling, and C(6) appears as a doublet with $J_{C(5)-C(6)}$ = 76.5 Hz.



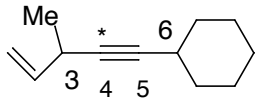
From compound **6** (283 mg). Yield: 74%. ^{1}H NMR (400MHz, $CDCl_3$): δ 0.88 (t, 3H, *J*=7.0Hz), 1.24 (s, 9H), 1.27-1.34 (m, 4H), 1.36-1.50 (m, 2H), 1.58-1.65 (m, 2H), 2.84-2.98 (m, 2H), 4.00-4.13 (m, 1H), 5.07 (dt, 1H, *J*=10Hz, 1.7Hz), 5.30 (dt, 1H, *J*=17Hz, 1.7Hz), 5.79 (m, 1H); ^{13}C NMR (100MHz, $CDCl_3$): δ 13.9, 22.5, 23.1 (d, *J*=10.1Hz), 25.2, 28.2, 31.5, 37.8, 62.0 (d, *J*=76.5Hz, C(6)), 74.2, 80.3(d, *J*=173.0 Hz, C(4)), 85.1 (s, d, *J*=76.5 Hz; d, *J*=173.0Hz, C(5)), 115.7, 132.7.

5-Cyclohexyl pent-1-en-4-yne **14**:
The labelled position was ascertained by C(4) - H(3) and C(5) - H(6) long range COSY couplings.



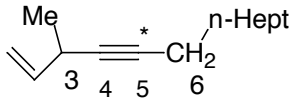
From 1-^{13}C-1,1-dibromo-2-cyclohexyl ethylene (269 mg). Yield: 47 % (based on GC analysis). ^{1}H NMR (400MHz, $CDCl_3$): δ 1.20-1.90 (m, 10H), 2.40 (m, 1H), 2.97 (m, 2H), 5.11 (dt, 1H, *J*=10.0Hz, 1.6Hz), 5.34 (dt, 1H, *J*=19.6Hz, 1.6Hz), 5.85 (m, 1H); ^{13}C NMR (100MHz, $CDCl_3$): δ 25.4, 26.3, 30.0, 33.5, 76.6 (C(4)), 87.7 (C(5)), 116.5, 137.8.

5-Cyclohexyl-3-methyl pent-1-en-4-yne **16**:
The labelled position was ascertained by C(4) - H(3) and C(5) - H(6) long range COSY couplings.



From 1-^{13}C-1,1-dibromo-2-cyclohexyl ethylene (269 mg). Yield: 67 % (based on GC analysis). ^{1}H NMR (400MHz, $CDCl_3$): δ 1.20-1.90 (m, 13H), 2.41 (m, 1H), 3.15 (m, 1H), 5.02 (dt, 1H, *J*=8.3Hz, 1.6Hz), 5.29 (dt, 1H, *J*=16.8Hz, 1.6Hz), 5.82 (m, 1H); ^{13}C NMR (100MHz, $CDCl_3$): δ 20.9, 24.7, 26.1, 30.2, 33.7, 81.7 (C(4)), 87.1 (C(5)), 114.2, 141.3.

3-Methyl tridec-1-en-4-yne **18**:
$^{3}J_{C-H}$ coupling is observed by non decoupled ^{13}C measurements: under irradiation of the methyl on C(3), the C(4) multiplet is simplified, and not C(5). By irradiation of C(6), the C(5) multiplet is simplified in the same way.



From 1-^{13}C-1,1-dibromo dec-1-ene (300 mg). Yield: 55 %. ^{1}H NMR (400MHz, $CDCl_3$): δ 0.88 (t, 3H, *J*=7.2Hz), 1.23 (d, 3H, *J*=7.5Hz), 1.27-1.40 (m, 10H), 1.50 (m, 2H), 2.19 (m, 2H), 3.12 (m, 1H), 5.01 (dt, 1H, *J*=10Hz, 1.7Hz), 5.26 (dt, 1H, *J*=17Hz, 1.7Hz), 5.82 (m, 1H); ^{13}C NMR (100MHz, $CDCl_3$): δ 14.7, 19.1, 22.0, 23.0, 29.2, 29.5, 29.6, 30.1, 32.2, 82.1 (s; d, *J*=65.0Hz; d, *J*=139.5, C(4)), 82.9 (s; d, *J*=67.0; d, *J*=141.5, C(5)), 113.8, 140.5.