Spiroacetal biosynthesis in fruit flies is complex: Distinguishable origins of the same major spiroacetal released by different *Bactrocera spp.*

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Supporting Information: Selected GC/MS incorporation studies, mass spectral data of spiroacetals and synthesis of selected labelled precursors.

General Procedures

^{1}H NMR spectra were recorded at 400 or 500 MHz with the residual $CHCl_3$ in the $CDCl_3$ solvent (δ 7.24 ppm) or the signal of benzene in the C_6D_6 solvent (δ 7.15 ppm) as internal standards. ^{13}C NMR spectra were recorded at 100 or 125 MHz with either the central peak of the $CDCl_3$ triplet (δ 77.00 ppm) or the multiplet of benzene (δ 128.0 ppm) as internal standards. *J* values are reported in Hz. The GCMS data were recorded on a gas chromatograph – mass spectrometer at 70 eV, fitted with a 30 m × 0.25 mm BP5 column. The standard program was set as 2 minutes at 100 ^{o}C, followed by a temperature increase of 16 ^{o}C/min, and left for 10 min at 250 ^{o}C. Flash chromatography was carried out using Merck kieselgel 60 (230 – 400 mesh) or Scharlau silica gel (200 – 400 mesh). Moisture or air sensitive experiments were conducted in oven or flame-dried glasswares under an atmosphere of nitrogen. Anhydrous solvents used in moisture sensitive reactions were dried accordingly before used. THF and diethyl ether were distilled off sodium wire; DCM was distilled off CaH_2, under a nitrogen atmosphere.

Feeding protocols

B. tryoni and *B. cucumis* were laboratory reared on a standard artificial diet of sugar, protein hydrolysate and water for 10-14 days post emergence. Potential precursors were administered as a homogenous 2-3% w/w mixture on sucrose to female *B. tryoni or male B. cucumis*. in 250 mL conical flasks fitted with new septa (see figure 1). SPME samples were taken at 12 hours, then after three days or fly death and then glands were excised and were crushed into pentane and analysed by GC/MS. Dioxygen [$^{18}O_2$] of > 99% atom % [^{18}O] was obtained from Isotech., Miamisburg, Ohio. SPME analyses were conducted with a Carboxen PDMS fibre (Supelco).

Incorporation Level Categories

Incorporation of the lowest level reveals the indicative deuterated patterns in fragments found by very careful searching on the very left or first scan of the peak in question. A molecular ion with deuterium may or may not be seen. “Some” incorporation implies, a small amount of readily seen *bona-fide* incorporation including the presence of the deuterated molecular ion (eg. M^+ = 184 to 188). The “good” descriptor is assigned

to an incorporation where significant incorporation can be seen. Usually but not always the deuterated form is a shoulder on the side of peak of the unlabelled spiroacetal. “Highest levels of incorporation” are used to describe those precursors which are incorporated and at a massive level, usually greater than 50% of the endogenous material 12 hours after administration. “No incorporation or not discernable” is assigned to a feeding result when no evidence of deuterium incorporation can be seen by GC/MS. There is a possibility the compound has been incorporated, but at a level not detectable.

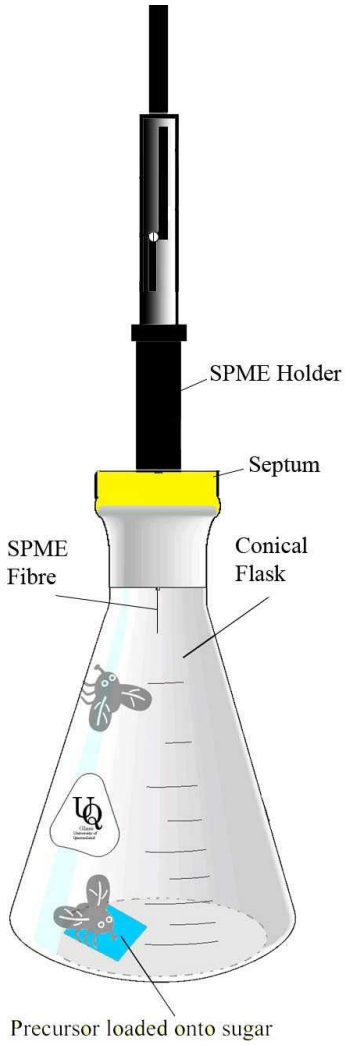


Figure 1. Fruit-fly chamber used for administration of potential [^{2}H]-labelled precursors. (250 mL conical flask (with SPME holder))

Selected GC/MS Incorporation Studies

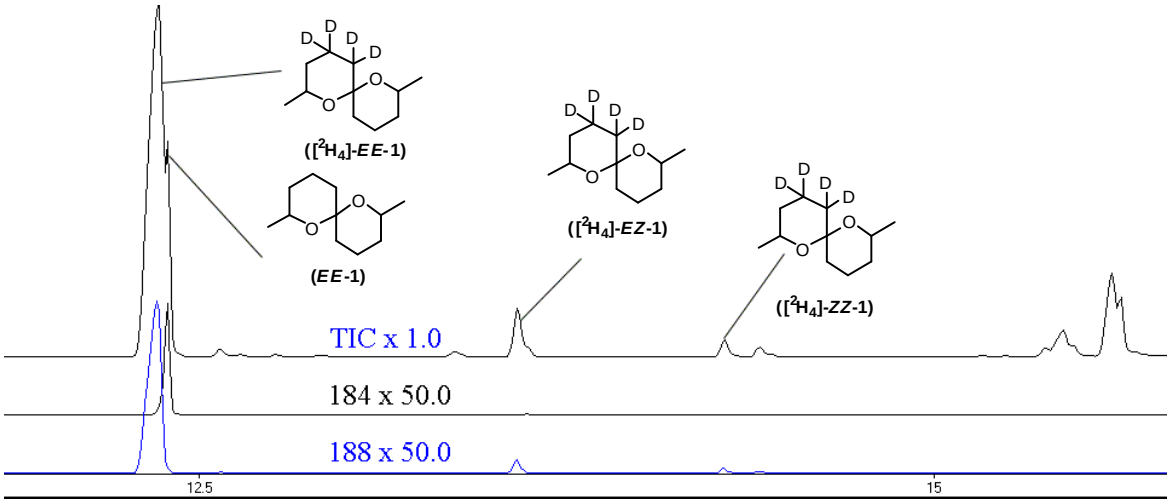


Figure 2. Gas chromatogram with single ion monitoring of glandular extract (pentane) of *B. cucumis* after feeding on [4,4,5,5-$^2H_4$]-2,6-dioxoundecane ([$^2H_4$]-3) for 3 days.

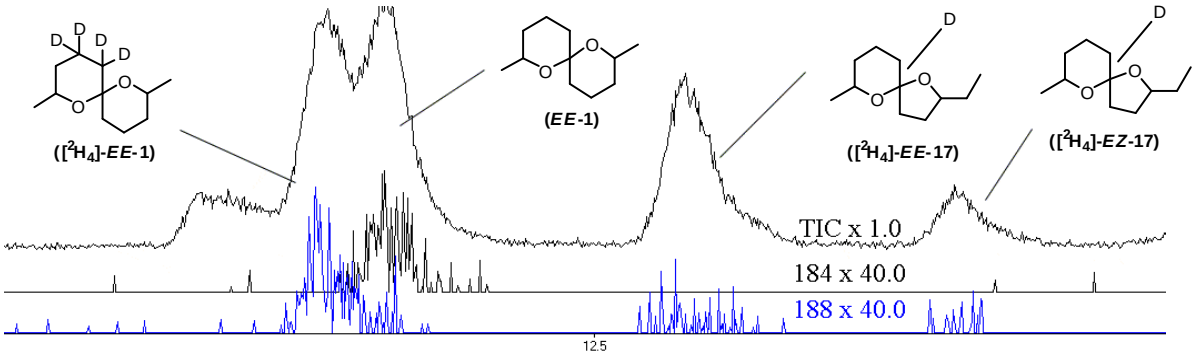


Figure 3. Gas chromatogram with single ion monitoring of SPME extract of *B. tryoni* after feeding on [4,4,5,5-$^2H_4$]-6-undecanone ([$^2H_4$]-11) for 3 days.

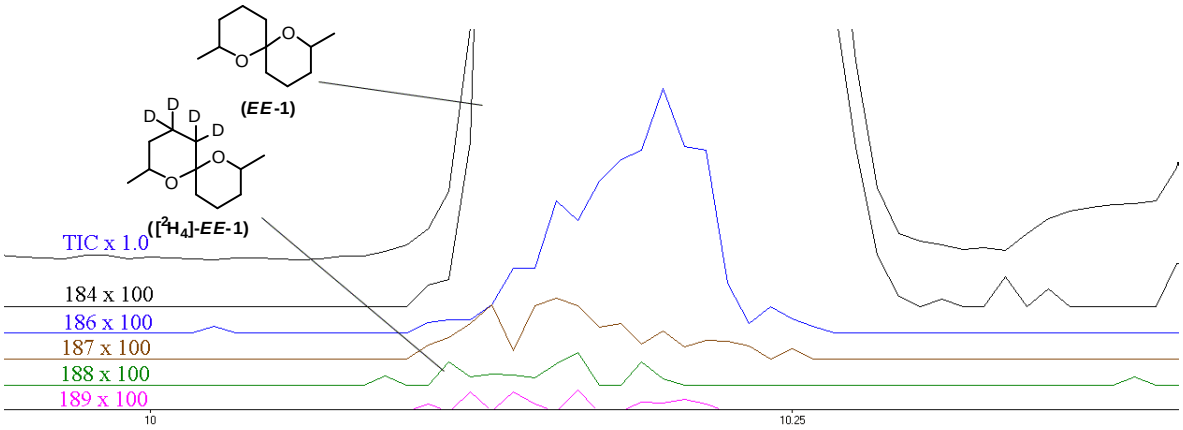
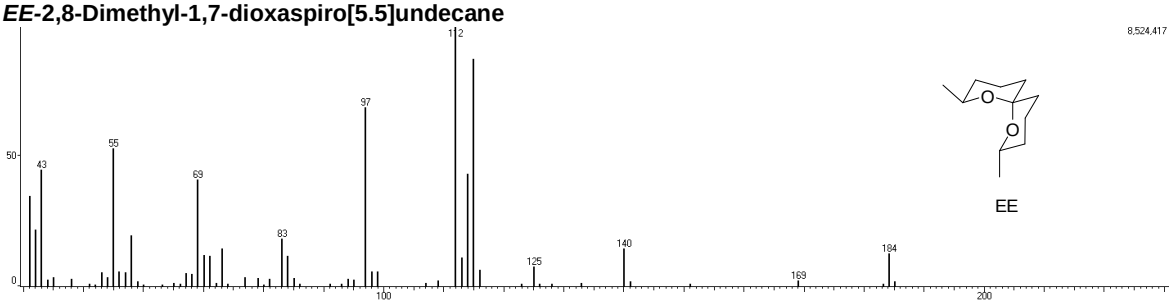


Figure 4. Gas chromatogram zoom with single ion monitoring of SPME extract of *B. cucumis* derived *EE*-2,8-dimethyl-1,7-dioxaspiro[5.5]undecane [$^2H_4$]-1 after feeding on [5,5,6,6-$^2H_4$]-7-oxododecanal ([$^2H_4$]-14, (palladium labelled) for 36 hours.

The mass spectral data of ^{2}H and ^{18}O labelled and unlabelled spiroacetals.

***EE*-2,8-Dimethyl-1,7-dioxaspiro[5.5]undecane**



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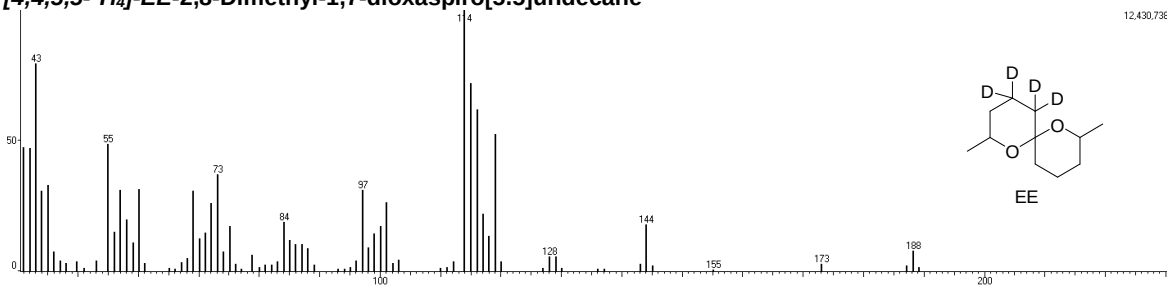
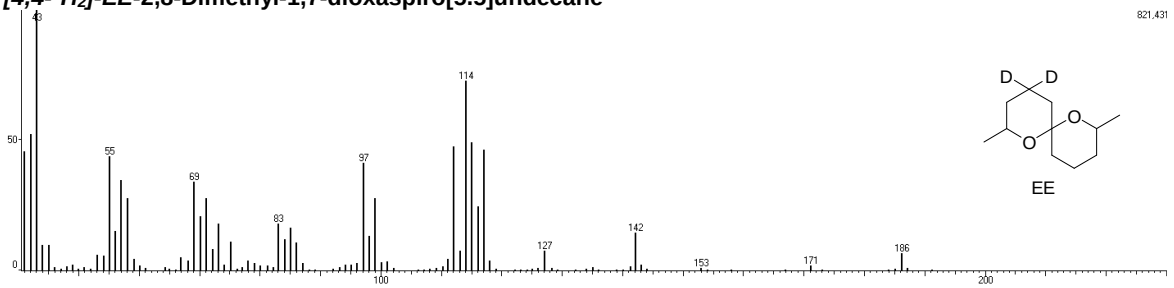
***[4,4,5,5-$^{2}H_4$]-EE*-2,8-Dimethyl-1,7-dioxaspiro[5.5]undecane**



70 (12.4), 71 (14.4), 72 (25.9), 73 (36.6), 84 (18.5), 85 (11.7), 86 (10.1), 87 (10.0), 97 (30.8), 99 (14.4), 100 (16.9), 101 (26.2), 114 (100), 115 (71.5), 116 (61.4), 117 (21.9), 118 (13.2), 119 (52.0), 127 (1.1), 128 (5.5), 144 (17.5), 155 (0.6), 173 (2.7), 188 (7.8).

***[4,4-$^{2}H_2$]-EE*-2,8-Dimethyl-1,7-dioxaspiro[5.5]undecane**



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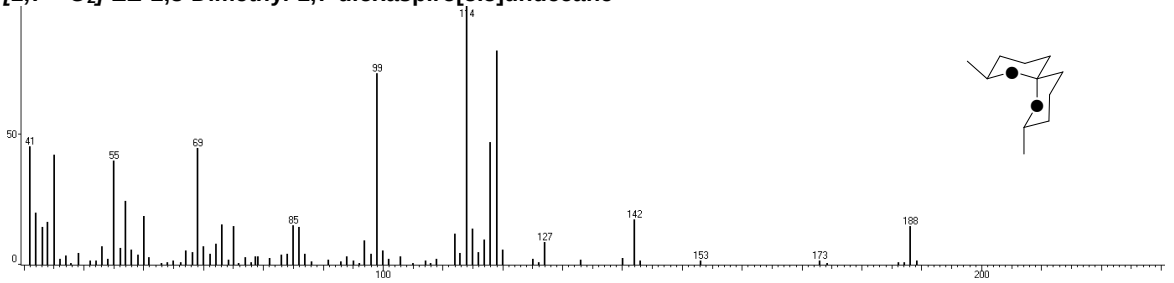
***[1,7-$^{18}O_2$]-EE*-2,8-Dimethyl-1,7-dioxaspiro[5.5]undecane**



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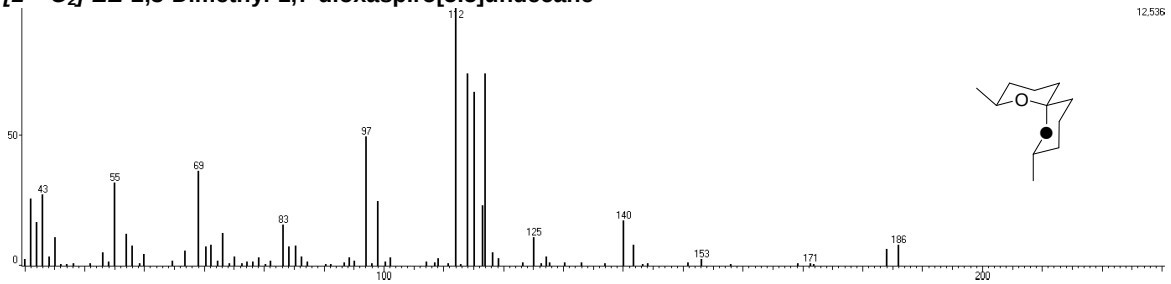
***[1-$^{18}O_2$]-EE*-2,8-Dimethyl-1,7-dioxaspiro[5.5]undecane**



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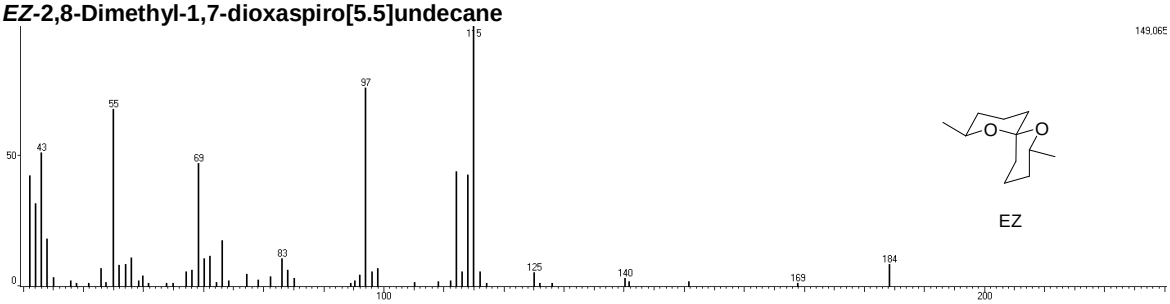
***EZ*-2,8-Dimethyl-1,7-dioxaspiro[5.5]undecane**



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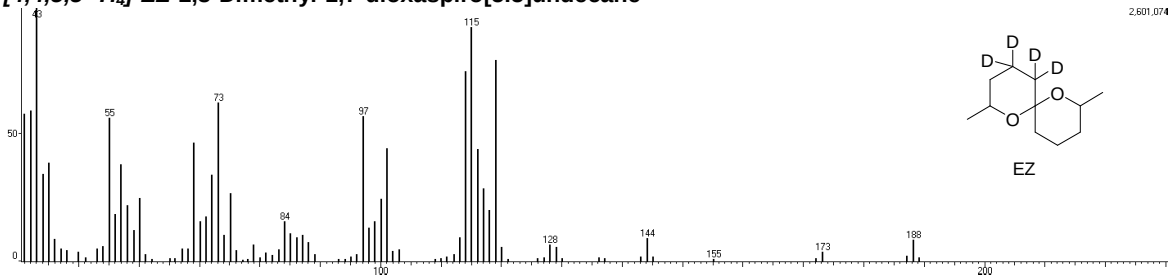
***[4,4,5,5-$^2H_4$]-EZ*-2,8-Dimethyl-1,7-dioxaspiro[5.5]undecane**



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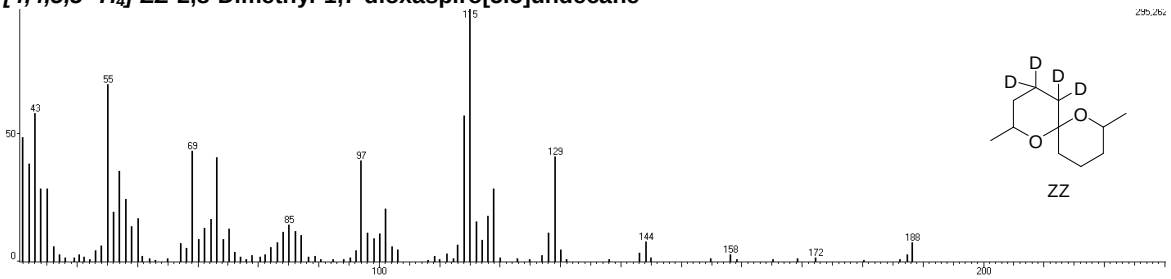
***[4,4,5,5-$^2H_4$]-ZZ*-2,8-Dimethyl-1,7-dioxaspiro[5.5]undecane**



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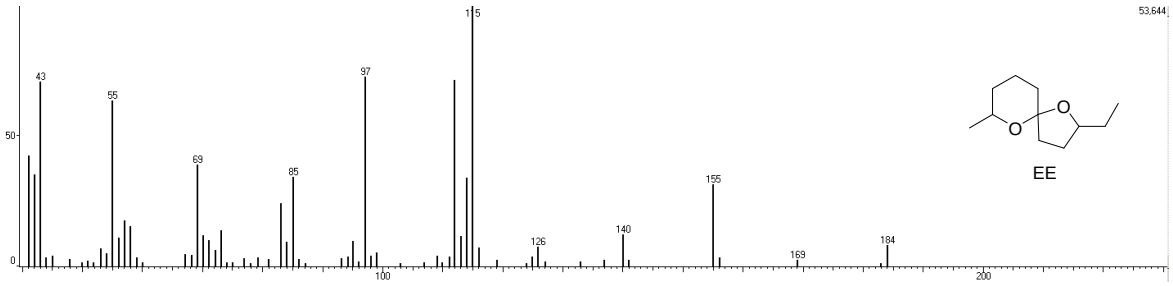
***EE*-2-Ethyl-7-methyl-1,6-dioxaspiro[4.5]undecane**



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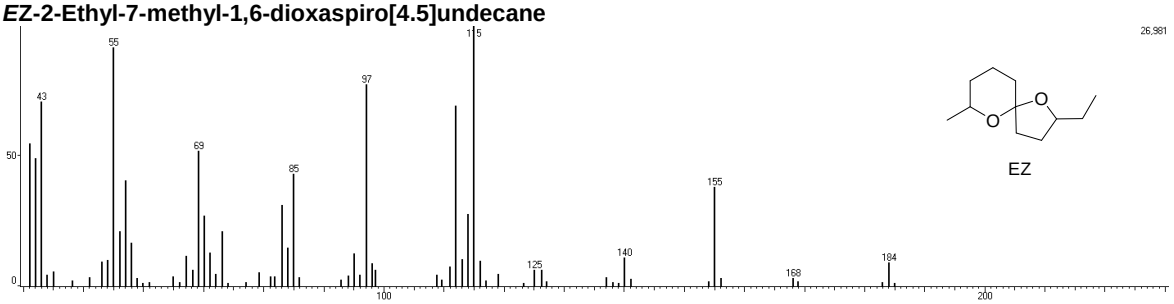
***EZ*-2-Ethyl-7-methyl-1,6-dioxaspiro[4.5]undecane**



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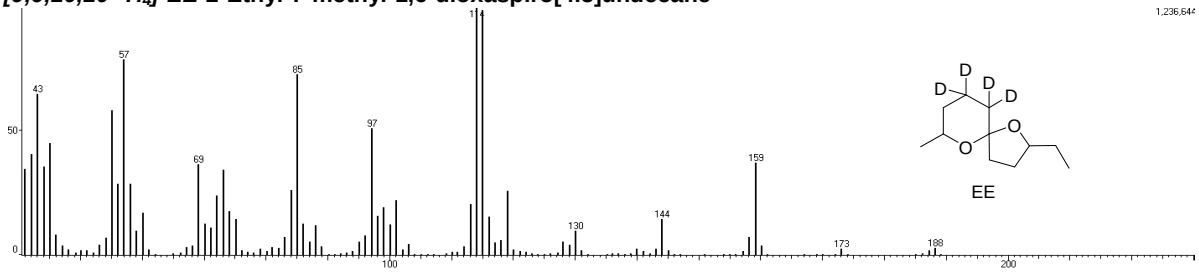
***[9,9,10,10-$^{2}H_4$]-EE*-2-Ethyl-7-methyl-1,6-dioxaspiro[4.5]undecane**



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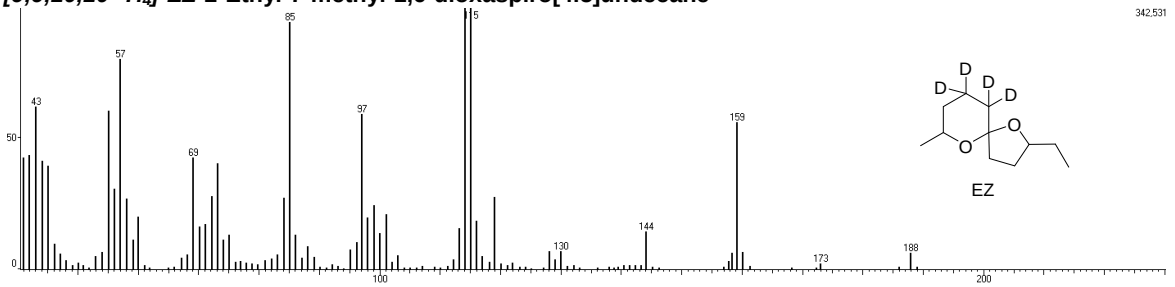
***[9,9,10,10-$^{2}H_4$]-EZ*-2-Ethyl-7-methyl-1,6-dioxaspiro[4.5]undecane**



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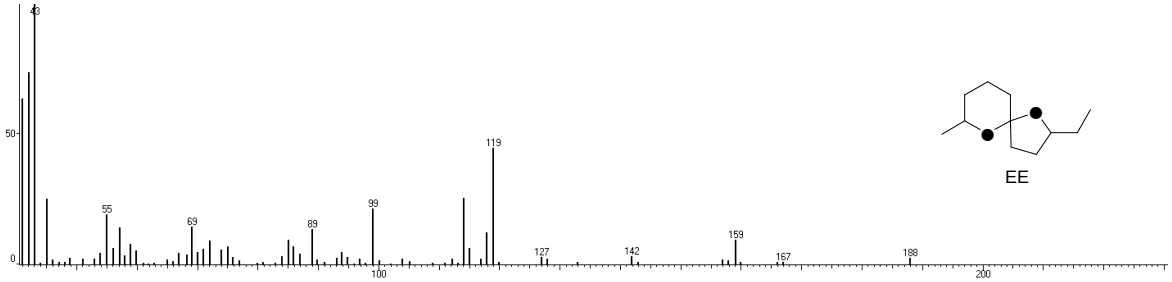
***[1,6-$^{18}O_2$]-EE*-2-Ethyl-7-methyl-1,6-dioxaspiro[4.5]undecane**



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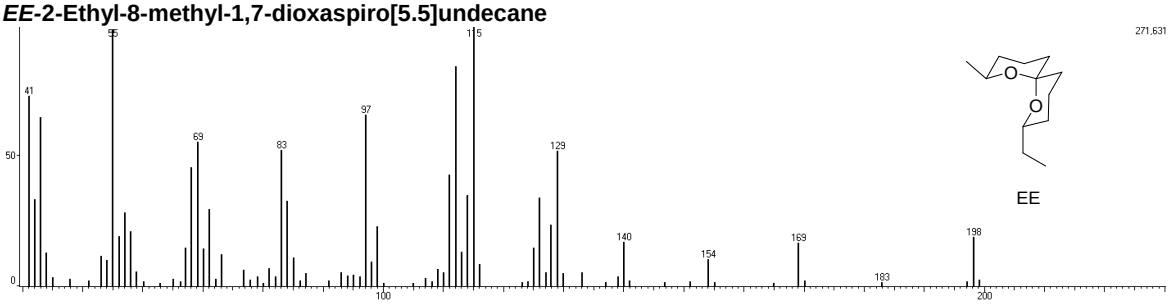
***EE*-2-Ethyl-8-methyl-1,7-dioxaspiro[5.5]undecane**



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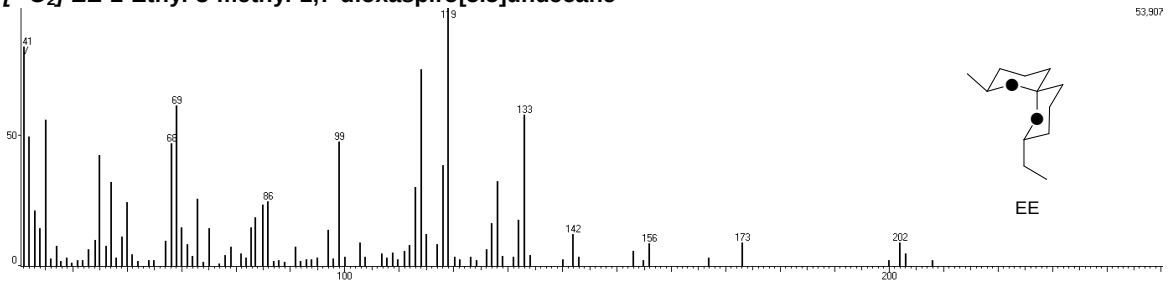
***[$^{18}O_2$]-EE*-2-Ethyl-8-methyl-1,7-dioxaspiro[5.5]undecane**



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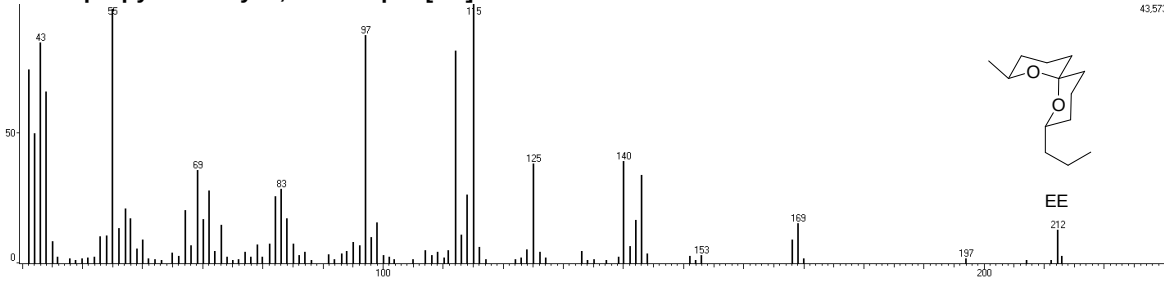
***EE*-2-*n*-propyl-8-methyl-1,7-dioxaspiro[5.5]undecane**



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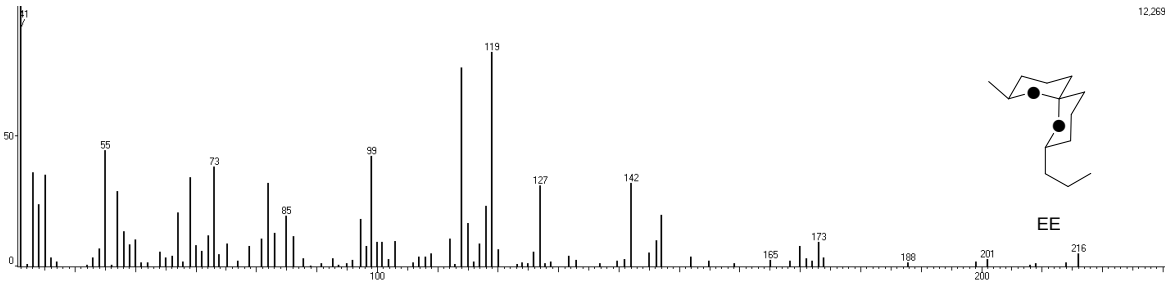
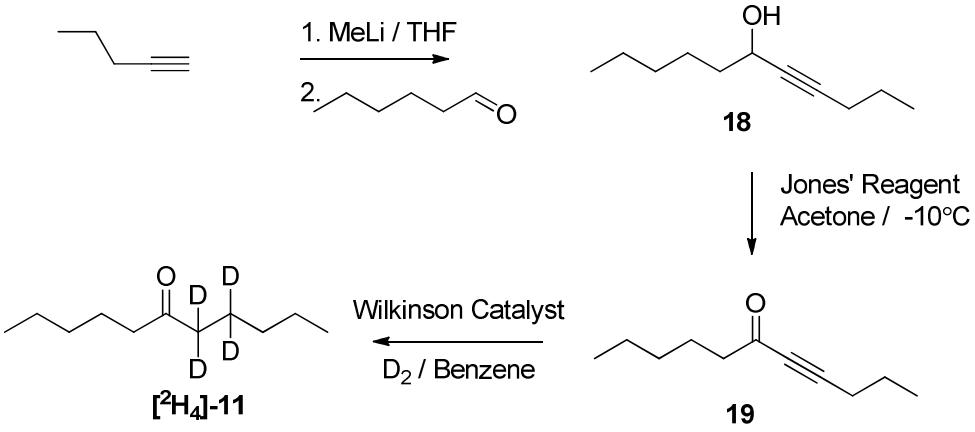
[1,7-$^{18}O_2$]-EE-2-n-Propyl-8-methyl-1,7-dioxaspiro[5.5]undecane

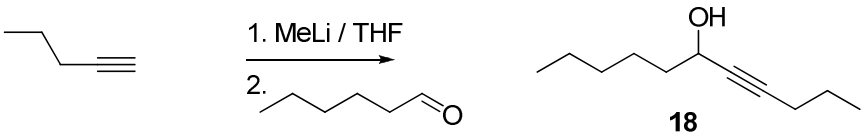


41 (100), 43 (31.3), 45 (40.7), 55 (48.0), 57 (28.9), 58 (15.2), 67 (21.4), 69 (37.0), 73 (39.5), 82 (37.3), 97 (21.0), 99 (48.7), 103 (11.0), 112 (12.4), 114 (87.5), 115 (20.1), 117 (11.4), 118 (22.7), 119 (89.4), 127 (35.1), 142 (36.7), 147 (22.3), 170 (8.7), 173 (11.2), 199 (2.1), 201 (3.1), 214 (1.6), 216 (6.2).

Synthesis of [4,4,5,5-$^2H_4$]-6-Undecanone ([$^2H_4$]-11)



6-Hydroxyundec-4-yne (18)



To a solution of 1-pentyne (3.5 g, 51.5 mmol), in THF (40 mL) at -10ºC, was added methyl lithium (33.8 mL, 54 mmol, 1.6 M in ether) dropwise. The deprotonation was allowed to stir for 20 min, then hexanal (5.15 g, 51.5 mmol), was added in a solution of THF (15 mL) dropwise. The reaction was allowed to stir for 1.5 hours then poured on to ice and extracted into hexane (3 x 30 mL). The combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated *in vacuo.* The residue was purified by flash chromatography (EtOAc:Hexane, 1:10) to give **18** as a sweet smelling oil (7.96 g, 92%).

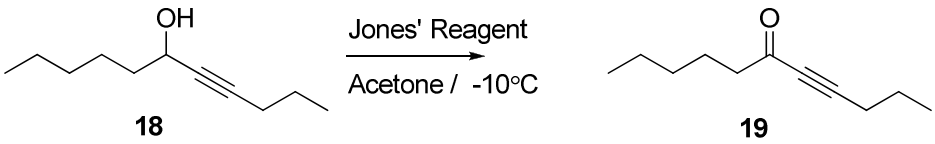
^{1}H NMR (500 MHz, $CDCl_3$) δ 0.88 (t, 3H, *J* = 7.1 Hz), 0.96 (t, 3H, *J* = 7.4 Hz), 1.26- 1.35 (m, 4H), 1.39-1.45 (m, 2H), 1.50 (sextet, 2H, *J* = 7.3 Hz), 1.60-1.70 (m, 2H), 2.17 (td, 2H, *J* = 7.1, 2.0 Hz), 4.33 (tt, 1H, *J* = 6.6, 2.0 Hz).

^{13}C NMR (125 MHz, $CDCl_3$) δ 13.4, 14.0, 20.6, 22.1, 22.6, 24.9, 31.5, 38.2, 62.7, 81.5, 85.2.

GC/MS EI m/z (%) 168 ($M^{+\cdot}$, 0.1), 153 (0.3), 125 (12.7), 112 (3.6), 97 (100), 79 (8.5), 55 (30.0), 41 (43.0).

HRMS Calculated for $C_{11}H_{20}O$: 168.1514 Found: 168.1509

6-Oxoundec-4-yne (19)



18 **19**

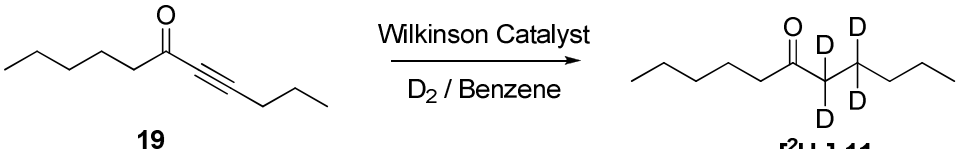
To a solution of alcohol **18** (285 mg, 1.70 mmol) in acetone (10 mL) at -10 ºC was added sufficient Jones' reagent (~ 1 mL) dropwise that left a persistant yellow tint after 30 min. The reaction was checked by TLC then extracted into hexane (3 x 25 mL), dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (EtOAc:Hexane, 1:20) to give the title product **19** (260 mg, 93%) as a colourless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 0.88 (t, 3H, *J* = 6.5 Hz), 1.00 (t, 3H, *J* = 7.5 Hz), 1.23-1.35 (m, 2H), 1.58 (sextet, 2H, *J* = 7.3 Hz), 1.64 (quintet, 2H, *J* = 7.5 Hz), 2.34 (t, 2H, *J* = 7.0 Hz), 2.52 (t, 2H, *J* = 7.5 Hz).

^{13}C NMR (125 MHz, $CDCl_3$) δ 13.5, 13.9, 20.9, 21.3, 22.4, 23.9, 31.1, 45.5, 81.0, 94.1, 188.7.

GC/MS EI m/z (%) 167 ($M^{+\cdot}$+1, 0.1), 152 (0.2), 137 (5.0), 110 (43.0), 95 (100), 82 (13.8), 67 (21.6), 53 (32.1), 41 (37.1).

[4,4,5,5-^{2}H$_4$]-6-Undecanone ([^{2}H$_4$]-11)



19 **[^{2}H$_4$]-11**

To a degassed solution of propargylic ketone **19** (110 mg, 0.66 mmol) in benzene (10 mL) was added Wilkinson catalyst (31 mg, 0.033 mmol, 5 mol%). The system was purged with nitrogen and evacuated (this was repeated three times) then charged with deuterium (balloon). After several minutes the solution underwent a colour change from

cherry-red to ginger-ale and was left stirring for 36 hours. The reaction was checked by GC/MS, purged with nitrogen then hexane (30 mL) added to precipitate the Wilkinson catalyst. The mixture was filtered through Celite^{TM}, concentrated *in vacuo* and purified by flash chromatography (EtOAc:Hexane, 1:20) to give [$^{2}H_4$]-**11** as a colourless oil (103 mg, 90%).

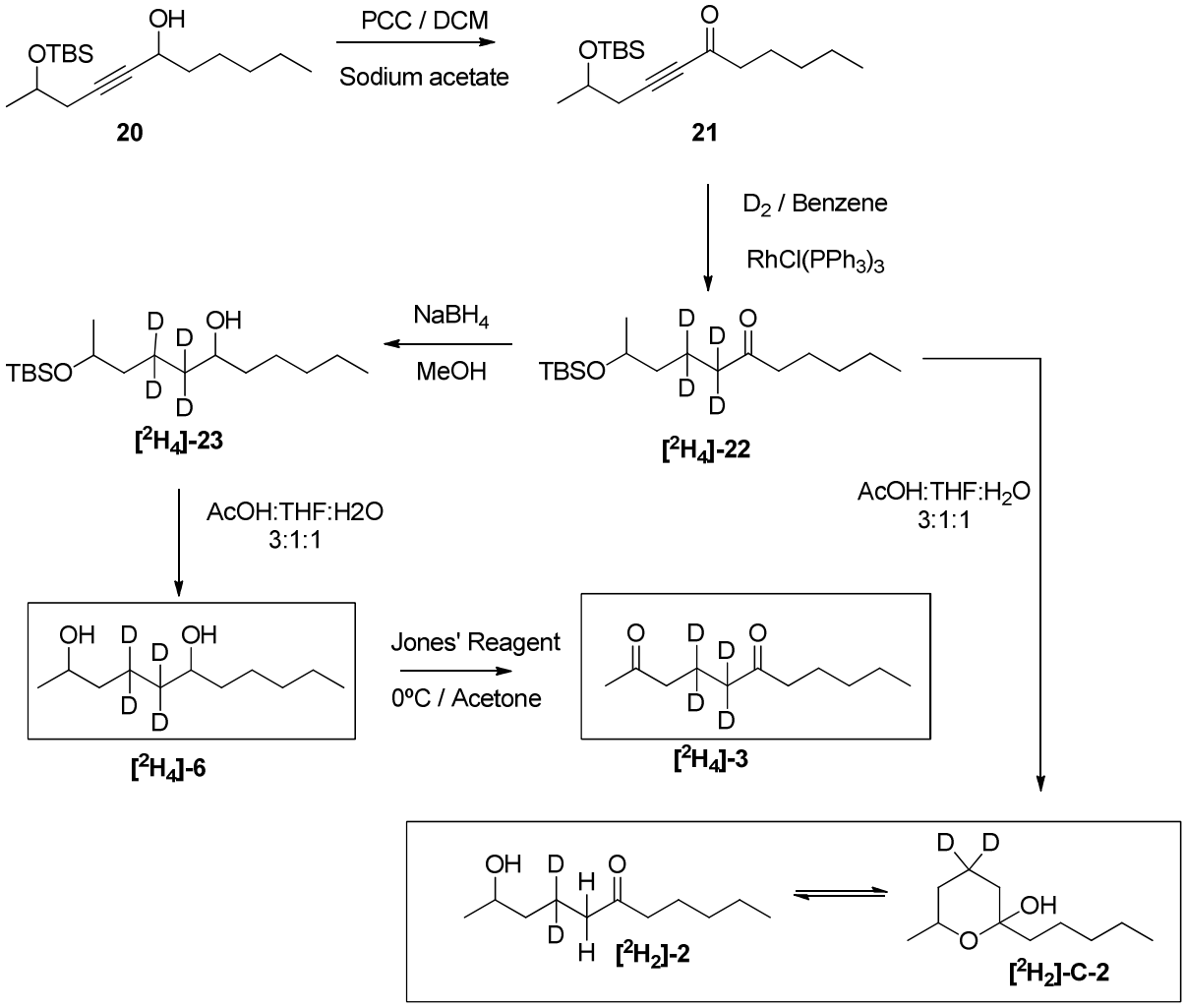
Data for [$^{2}H_4$]-11 labelled with Wilkinson / D_2

^{1}H NMR (500 MHz, $CDCl_3$) δ 0.865 (t, 3H, *J* = 7.2 Hz), 0.866 (t, 3H, *J* = 7.2 Hz), 1.20-1.33 (m, 8H), 1.47 (quintet, 2H, *J* = 7.4 Hz), 2.36 (t, 2H, *J* = 7.2 Hz).
^{13}C NMR (125 MHz, $CDCl_3$) δ 13.9 (2C), 22.4, 22.5, 22.7 (quintet, $^{1}J_{C\text{-}D}$ = 19.4 Hz), 23.5, 31.2, 31.4, 41.9 (quintet, $^{1}J_{C\text{-}D}$ = 19.1 Hz), 42.8, 212.0.
GC/MS EI m/z (%) 174 ($M^{+\cdot}$, 1.0), 156 (0.1), 145 (0.3), 131 (1.4), 116 (0.7), 103 (9.5), 99 (8.7), 87 (3.0), 75 (13.9), 74 (12.7), 73 (15.7), 60 (67.5), 43 (100).

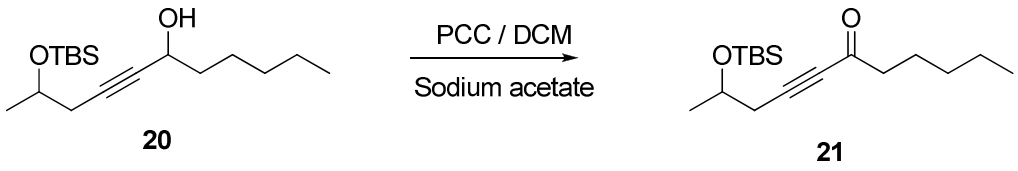
Data for unlabelled 6-undecanone (11)

^{1}H NMR (500 MHz, $CDCl_3$) δ 0.86 (t, 6H, *J* = 7.0 Hz), 1.21-1.31 (m, 8H), 1.57 (app. quintet, 4H, *J* = 7.7 Hz), 2.36 (t, 4H, *J* = 7.4 Hz).
^{13}C NMR (125 MHz, $CDCl_3$) δ 13.9 (2C), 22.5 (2C), 23.6 (2C), 31.4 (2C), 42.8 (2C), 211.8.
GC/MS EI m/z (%) 170 ($M^{+\cdot}$, 0.6), 141 (0.3), 127 (1.3), 114 (0.9), 99 (12.0), 71 (23.4), 58 (36.2), 43 (100), 41 (26.3).

Synthesis of [$^2H_2$]-2, [$^2H_4$]-3 and [$^2H_4$]-6



2-(tert-Butyldimethylsilyloxy)undec-4-yn-6-one (21)

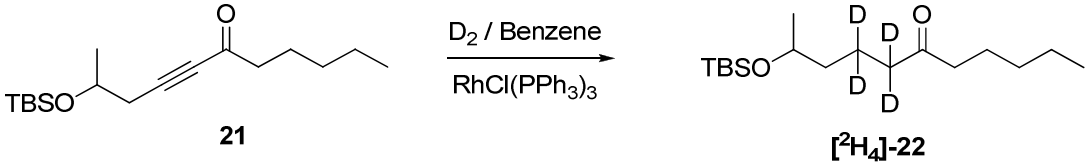


To a mixture of alcohol **20**[1] (2.57 g , 8.63 mmol), sodium acetate (1.1 g ,12.9 mmol) and DCM (350 mL) was added PCC (2.79 g, 12.9 mmol) portionwise over 10 min with vigorous stirring. The reaction was left under a nitrogen atmosphere and monitored by TLC. After 3 hours, hexane (100 mL) was added and the suspension filtered through a

bed of celite/silica. The filtrate was concentrated *in vacuo* and purified by flash chromatography (EtOAc:Hexane, 1:30) to give **21** as a pale yellow oil (2.3 g, 91%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 0.076 (s, 3H), 0.083 (s, 3H), 0.89 (s, 12H), 1.25 (d, 3H, *J* = 6.1 Hz) 1.26-1.38 (m, 4H), 1.67 (quintet, 2H, *J* = 7.4 Hz) 2.43 (dd, 1H, *J* = 17.0, 6.5 Hz), 2.51 (dd, 1H, *J* = 16.9, 5.7 Hz), 2.52 (t, 2H, *J* = 7.4 Hz), 4.02 (sextet, 1H, *J* = 6.1 Hz).
^{13}C NMR (125 MHz, $CDCl_3$) δ -4.8, -4.6, 13.8, 18.0, 22.3, 23.5, 23.8, 25.8 (3C), 29.8, 31.1, 45.4, 66.9, 82.1, 91.2, 188.2.
GC/MS EI m/z (%) 296 ($M^{+\cdot}$, 0.1), 281 (0.8), 252 (0.2), 239 (7.9), 225 (0.5), 195 (55.8), 183 (3.0), 169 (29.1), 159 (40.8), 139 (11.1), 103 (16.8), 75 (98.5), 73 (100).
HRMS Calculated for $C_{17}H_{32}O_2Si$: 296.2172 Found: 296.2167

[4,4,5,5-$^{2}H_4$]-2-(*tert*-Butyldimethylsilyloxy)undecan-6-one [$^{2}H_4$]-22



21 **[$^{2}H_4$]-22**

To a degassed solution of propargylic ketone **21** (1.65 g, 5.55 mmol) in benzene (40 mL) was added Wilkinson catalyst (255 mg, 0.275 mmol, 5 mol%). The system was purged with nitrogen and evacuated, (this was repeated three times) then charged with deuterium (balloon). After several minutes the solution underwent a colour change from cherry-red to ginger-ale and was left stirring for 36 hours. The reaction was checked by GC/MS, purged with nitrogen then hexane (100 mL) added to precipitate the Wilkinson catalyst. The mixture was then filtered through Celite^{TM}, concentrated *in vacuo* and purified by flash chromatography (EtOAc:Hexane, 1:20) to give **[$^{2}H_4$]-22** as a colourless oil (1.62 g, 97%).

Data for labelled 2-(tert-Butyldimethylsilyloxy)undecan-6-one ([$^{2}H_4$]-22)

^{1}H NMR (500 MHz, $CDCl_3$) δ 0.011 (s, 6H), 0.82-0.88 (m, 12H), 1.08 (d, 3H, *J* = 6.1 Hz), 1.20-1.39 (m, 6H), 1.53 (quintet, 2H, *J* = 7.6 Hz), 2.34 (t, 2H, *J* = 7.6 Hz), 3.76 (sextet, 1H, *J* = 6.1 Hz).

^{13}C NMR (125 MHz, $CDCl_3$) δ -4.8, -4.4, 13.9, 18.1, 19.3 (quintet, $CH_2\underline{C}D_2$, $^1J_{C\text{-}D}$ = 19.6 Hz), 22.4, 23.5, 23.7, 25.9 (3C), 31.4, 38.9, 41.9 (quintet, $\underline{C}D_2CO$, $^1J_{C\text{-}D}$ = 18.8 Hz), 42.7, 68.3, 211.5.

GC/MS EI m/z (%) 304 ($M^{+\cdot}$, 0.1), 289 (1.5), 247 (44.0), 205 (20.0), 173 (5.4), 159 (8.4), 147 (86.8), 119 (9.3), 99 (14.8), 75 (100), 73 (64.5), 43 (43.1).

***Data for unlabelled* 2-(*tert*-Butyldimethylsilyloxy)undecan-6-one (22)**

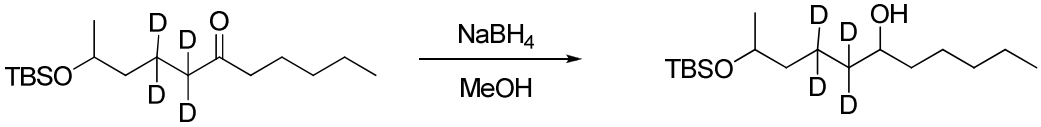
^{1}H NMR (500 MHz, $CDCl_3$) δ 0.016 (br s, 6H), 0.85 (s, 9H), 0.86 (t, 3H, *J* = 7.0 Hz), 1.09 (d, 3H, *J* = 6.1 Hz), 1.18-1.42 (m, 6H), 1.47-1.67 (m, 4H), 2.35 (t, 2H, *J* = 7.5 Hz), 2.36 (t, 2H, *J* = 7.3 Hz), 3.75 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ -4.7, -4.4, 13.9, 18.1, 20.2, 22.4, 23.5, 23.7, 25.9 (3C), 31.4, 39.1, 42.7, 42.8, 68.4, 211.5.

GC/MS EI m/z (%) 300 ($M^{+\cdot}$, 0.05), 285 (1.2), 267 (0.02), 257 (0.01), 243 (36.2), 225 (2.1), 201 (21.4), 187 (1.7), 169 (2.6), 159 (9.4), 145 (59.5), 129 (4.9), 119 (7.1), 95 (17.4), 75 (100), 73 (38.0), 55 (26.5), 43 (32.0).

HRMS Calculated $C_{17}H_{36}NaO_2Si$ (M+Na): 323.2382 Found: 323.2381

[4,4,5,5-^{2}H$_4$]-2-(tert-butyldimethylsilyloxy)undecan-6-ol ([^{2}H$_4$]-23)



[^{2}H$_4$]-22 **[^{2}H$_4$]-23**

Data for* ([^{2}H$_4$]-23) *labelled with D_2 / Wilkinson

^{1}H NMR (500 MHz, $CDCl_3$) δ 0.026 (s, 6H), 0.87 (br m, 12H), 1.10 (d, 3H, *J* = 6.0 Hz), 1.20-1.45 (m, 10H), 3.54-3.58 (br m, 1H), 3.75 (br app. sextet, 1H, *J* = 6.2 Hz).

^{13}C NMR (125 MHz, $CDCl_3$) Mixture of diastereomers δ -4.68 & -4.67, -4.4, 14.0, 18.2, 20.8 (quintet, $^1J_{C\text{-}D}$ = 19.0 Hz) & 20.9 (quintet, $^1J_{C\text{-}D}$ = 19.1 Hz), 22.6, 23.7 & 23.8, 25.29 & 25.30, 25.9 (3C), 31.9, 36.5 (quintet, $^1J_{C\text{-}D}$ = 19.1 Hz) & 36.6 (quintet, $^1J_{C\text{-}D}$ = 18.9 Hz), 37.4, 39.4 & 39.5, 68.5 & 68.6, 71.77 & 71.80.

GC/MS EI m/z (%) 249 ($M^{+\cdot}$-57, 1.6), 231 (0.7), 217 (0.3), 205 (0.4), 191 (0.3), 173 (0.7), 159 (7.7), 147 (2.1), 133 (0.9), 119 (16.0), 99 (17.1), 85 (18.6), 75 (100), 73 (45.5), 57 (49.6), 43 (56.0), 41 (36.9).

See also ref 1 for **23** unlabelled and labelled with Pd/D_2

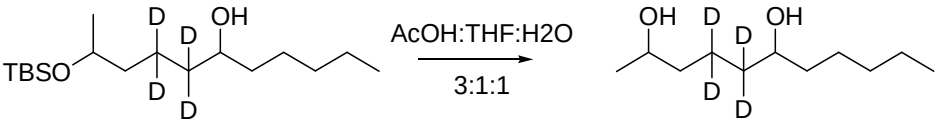
Data for unlabelled* 2-(tert-butyldimethylsilyloxy)undecan-6-ol**, ***23

^{1}H NMR (400 MHz, $CDCl_3$) Mixture of diastereomers δ 0.026 (s, 6H), 0.86 (9H), 0.87 (t, *J* = 6.9 Hz, 3H), 1.10 (d, *J* = 6.1 Hz, 3H), 1.24-1.50 (m, 14H), 3.54-3.60 (m, 1H), 3.73-3.80 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) -4.7, -4.4, 14.0, 18.2, 21.7 & 21.9, 22.6, 23.75 & 23.80, 25.29 & 25.31, 25.9 (3C), 31.90 & 31.91, 37.4, 37.45 & 37.55, 39.6 & 39.7, 68.5 & 68.6, 71.9 & 72.0.

Anal. Calc. For $C_{17}H_{38}O_2Si$: C, 67.48; H, 12.66%, Found: C, 67.50; H, 12.52.

[4,4,5,5-$^2H_4$]-2,6-Undecanediol ([$^2H_4$]-6)



Protected alcohol **[$^2H_4$]-24** (550 mg, 1.80 mmol) was dissolved in a solution of AcOH:THF:H_2O (6:2:2 mL) and heated at 50ºC for 12 hours. The solution was concentrated *in vacuo* and purified by flash chromatography (EtOAc:Hexane, 1:1) which afforded **[$^2H_4$]-6** (302 mg, 87%) as a colourless paste

.

Data for* [$^2H_4$]-6 *labelled with D_2 / Wilkinson

^{1}H NMR (500 MHz, $CDCl_3$) Mixture of diastereomers δ 0.86 (t, 3H, *J* = 7.0 Hz), 1.16 (d, 3H, *J* = 6.2 Hz), 1.20-1.33 (m, 5H), 1.35-1.49 (m, 5H), 1.85 (br s, 2OH), 3.55-3.57 (br m, 1H), 3.77 (qt, 0.5H, *J* = 6.2, 1.3 Hz), 3.78 (sextet, 0.5H, *J* = 6.2 Hz).

^{13}C NMR (125 MHz, $CDCl_3$) Mixture of diastereomers δ 13.9, 20.6 (quintet, CD_2, *J* = 18.1 Hz) & 20.7 (quintet, CD_2, *J* = 18.4 Hz), 22.5, 23.3 & 23.4, 25.3, 31.8, 35.8 (quintet, $0.5CD_2$, *J* = 17.9 Hz) & 36.1 (quintet, CD_2, *J* = 18.5 Hz), 37.3 & 37.4, 38.5 & 38.7, 67.3 & 67.6, 71.2 & 71.4.

GC/MS EI m/z (%) 174 ($M^{+\cdot}$-18, 0.1), 159 (0.6), 145 (1.4), 130 (1.0), 121 (1.4), 103 (15.8), 85 (31.8), 74 (12.8), 57 (40.8), 55 (43.4), 45 (70.6), 43 (100), 41 (47.1).

GC/MS EI as di-TMS ether m/z(%) 336 ($M^{+\cdot}$, 0.01), 321 (0.6), 265 (21.1), 173 (58.5), 147 (15.1), 132 (32.3), 117 (40.2), 103 (21.9), 73 (100).

See also ref 1 for **6** unlabelled and labelled with Pd/D_2

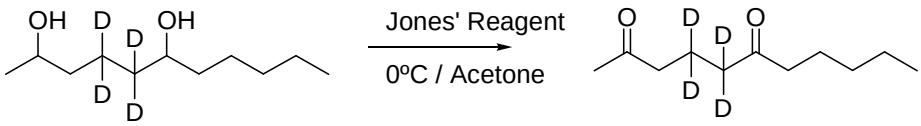
***Data for unlabelled* 2,6-undecanediol (6)**

^{1}H NMR (400 MHz, $CDCl_3$) δ 0.85 (t, 3H, *J* = 7.2 Hz), 1.14 (d, 3H, *J* = 6.4 Hz), 1.20-1.32 (m, 5H,), 1.33-1.48 (m, 9H), 2.24 (br s, 2OH), 3.50-3.58 (br m, 1H), 3.71-3.80 (br m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) Mixture of diastereomers δ 14.0, 21.6 & 21.8, 22.6, 23.4 & 23.5, 25.4, 31.9, 37.0 & 37.2, 37.4 & 37.6, 39.0 & 39.1, 67.7 & 67.9, 71.6 & 71.7.

GC/MS EI m/z (%) 171 ($M^{+\cdot}$-17, 0.1), 170 (0.2), 155 (0.4), 145 (1.0), 127 (1.0), 117 (1.6), 99 (21.0), 83 (16.6), 81 (46.4), 70 (17.5), 57 (37.0), 55 (82.4), 45 (46.0), 43 (100), 41 (61.9).

[4,4,5,5-$^2H_4$]-2,6-Undecanedione ([$^2H_4$]-3)



To a solution of diol **[$^2H_4$]-6** (50 mg, 0.71 mmol) in acetone at -10 ºC was added sufficient Jones' reagent (~ 0.5 mL) dropwise that left a persistant yellow tint after 30 min. The reaction was checked by TLC then extracted into hexane (3 x 30 mL), the

organic layers were combined, washed with brine then dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (EtOAc:Hexane, 1:5) to give **[$^2H_4$]-3** as a viscous colourless oil (103 mg, 81%).

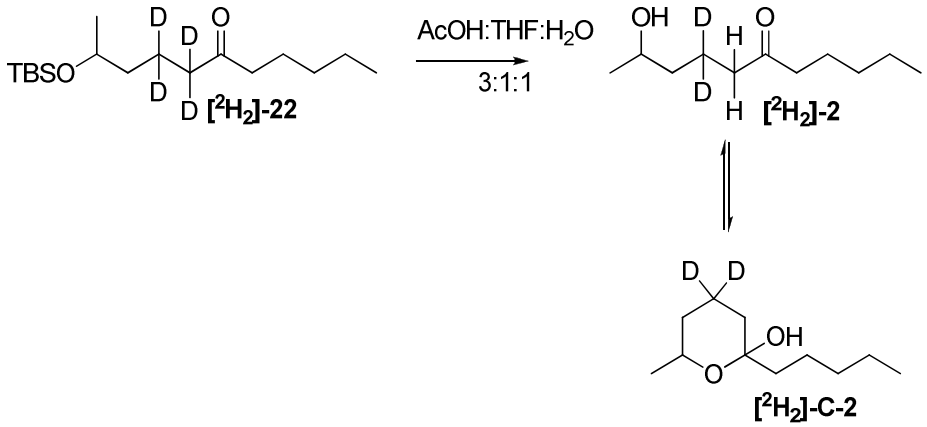
Data for* [$^2H_4$]-3 *labelled with D_2 / Wilkinson

^{1}H NMR (500 MHz, $CDCl_3$) δ 0.86 (t, 3H, *J* = 6.9 Hz), 1.21-1.30 (m, 4H), 1.55 (quintet, 2H, *J* = 7.7 Hz), 2.10 (s, 3H), 2.34 (t, 2H, *J* = 7.6 Hz), 2.41 (s, 2H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 14.0, 17.1 (quintet, $\underline{C}D_2$, $^1J_{C\text{-}D}$ = 19.9 Hz), 22.5, 23.6, 29.9, 31.5, 40.6 (quintet, $\underline{C}D_2CO$, $^1J_{C\text{-}D}$ = 19.1), 42.5, 42.9, 208.4, 211.0 ($CD_2\underline{C}O$).
GC/MS EI m/z (%) 188 ($M^{+\cdot}$, 0.1), 153 (0.2), 145 (1.9), 132 (15.4), 117 (7.2), 99 (13.9), 89 (27.0), 73 (18.5), 71 (20.1), 58 (17.4), 43 (100).

Data for unlabelled 2,6-Dioxoundecane (3)

^{1}H NMR (400 MHz, $CDCl_3$) δ 0.83 (t, 3H, *J* = 6.8 Hz), 1.18-1.28 (br m, 6H), 1.49 (quintet, 2H, *J* = 7.4 Hz), 1.77 (quintet, 2H, *J* = 7.1 Hz), 2.07 (s, 3H), 2.32 (t, 2H, *J* = 7.4 Hz), 2.38 (t, 3H, *J* = 7.0 Hz), 2.41 (t, 2H, *J* = 7.1 Hz).
^{13}C NMR (100 MHz, $CDCl_3$) δ 13.8, 17.7, 22.4, 23.5, 29.8, 31.3, 41.4, 42.5, 42.7, 208.5, 210.9.
GC/MS EI m/z (%) 184 ($M^{+\cdot}$, 0.1), 169 (0.05), 156 (0.3), 141 (4.5), 128 (38.7), 113 (16.7), 99 (37.4), 95 (24.0), 85 (63.7), 71 (77.4), 58 (32.9), 55 (59.9), 43 (100).

[4,4-$^2H_2$]-2-Hydroxy-6-oxoundecane ([4,4-$^2H_2$]-2) and [$^2H_2$]-6-Methyl-2-pentyl-tetrahydro-2H-pyran-2-ol ([4,4-$^2H_2$]-C-2)

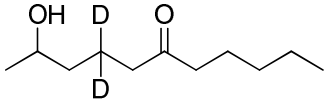


TBS-ketone **[$^2H_4$]-22** (285 mg, 0.937 mmol) (from reduction with Wilkinson catalyst) was dissolved in a solution of AcOH:THF:H_2O (3:1:1 mL) and heated at 50ºC for 6 hours. The solution was concentrated *in vacuo* and then purified by flash chromatography (EtOAc:Hexane, 1:5) to give an equilibrium of **[$^2H_2$]-2** and **[$^2H_2$]-C-2**

The interconverting forms (cyclic tetrahydropyranol and straight chain hydroxyketone) resulted in complex NMR spectra and even the non-deuterated interconverting forms could only be partially distinguished from each other.

Data for [$^2H_2$]-2 (labelled with D_2 / Wilkinson)

Straight chain form: [4,4-$^2H_2$]-2-hydroxy-6-oxoundecane ([$^2H_2$]-2)



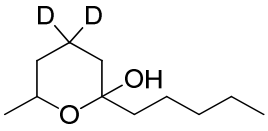
[$^2H_2$]-2

^{1}H NMR (500 MHz, $CDCl_3$) δ 0.87 (br t, 3H, *J* = 7.2 Hz), 1.16 (d, 3H, *J* = 6.2 Hz), 1.31-1.58 (m, 8H), 2.37 (t, 2H, *J* = 7.5 Hz), 2.40 (br s, 2H), 3.74 (sextet, 1H, *J* = 6.5 Hz), 3.85-4.00 (m, cyclic form CH)

^{13}C NMR (125 MHz, $CDCl_3$) δ 13.9, 19.0 (quintet, $^1J_{C\text{-}D}$ = 19.6 Hz), 22.4, 23.4, 23.5, 31.4, 38.5, 42.3, 42.8, 67.5, 211.6.

GC/MS EI (TMS protected derivative) m/z(%) 260 ($M^{+\cdot}$, 0.1), 245 (12.3), 227 (0.6), 216 (1.9), 203 (8.1), 173 (6.8), 147 (20.6), 130 (18.7), 117 (84.8), 99 (23.7), 75 (61.2), 73 (100), 43 (47.1).

Data for cyclic tetrahydropyranol form ([$^2H_2$]-C-2)

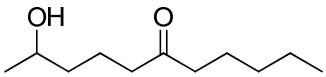


[$^2H_2$]-C-2

^{1}H NMR spectra complex with overlapping signals

^{13}C NMR (CD_2 not seen or obscured by straight chain form), (125 MHz, $CDCl_3$) δ 14.0, 22.0, 22.6, 22.8, 32.1, 32.1, 32.7, 43.6, 66.0, 97.0.

Data for unlabelled straight chain form 2-Hydroxy-6-oxoundecane (2)



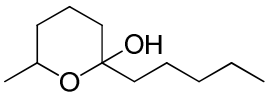
2

^{1}H NMR (500 MHz, C_6D_6) δ 0.94 (t, 3H, *J* = 7.3 Hz), 1.14-1.15 (d, 3H, *J* = 6.2 Hz), 1.2-1.8 (overlapping multiplets, 10H), 2.08 (t, 2H, *J* = 7.5 Hz), 2.10 (t, 2H, *J* = 7.2 Hz), 3.65 (dqd, 1H, *J* = 7.7, 6.2, 4.7 Hz).

^{13}C NMR (125 MHz, $CDCl_3$) δ 14.0, 20.1, 22.7, 23.67, 23.69, 31.6, 38.9, 42.3, 42.5, 67.2, 209.4.

GC/MS EI (broad peak) m/z(%) 168 ($M^{+\cdot}$-18, 9.2), 153 (0.1), 139 (0.1), 125 (17.6), 112 (43.7), 99 (16.9), 97 (29.1), 83 (22.8), 71 (32.2), 70 (20.4), 69 (32.4), 58 (27.1), 55 (96.4), 43 (100).

Data for unlabelled cyclic form 6-Methyl-2-pentyl-tetrahydro-2H-pyran-2-ol (C-2)

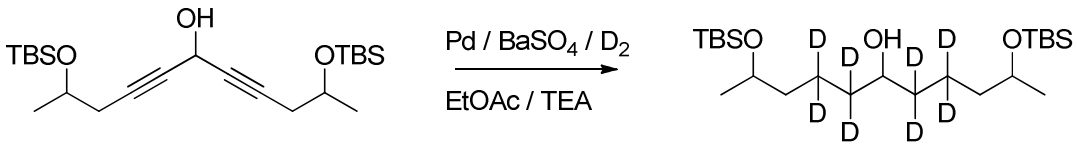


C-2

^{1}H NMR (500 MHz, C_6D_6) δ 0.97 (t, 3H, *J* = 7.0 Hz), 1.14-1.75 (overlapping multiplet, 15H), 1.23 (d, 3H, *J* = 6.27 Hz), 4.11 (dtd, 1H, *J* = 17.6, 6.3, 2.3 Hz).

^{13}C NMR (125 MHz, C_6D_6) δ 14.2, 19.5, 22.3, 23.0, 23.2, 32.5, 32.8, 33.3, 43.9, 65.9, 96.7.

[4,4,5,5,7,7,8,8-$^2H_8$]-2,10-Bis-(*tert*-butyl-dimethyl-silanyloxy)-undecan-6-ol ([$^2H_8$]-25)



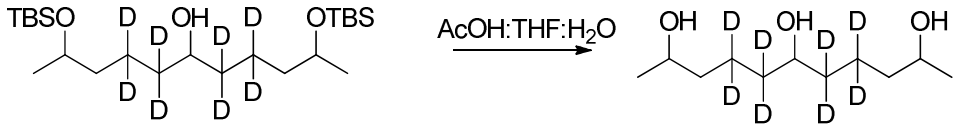
24 **[$^2H_8$]-25**

Dipropargylic alcohol[2] **24** was deuterated and purified in a fashion analogous to that used for [^{2}**H$_4$**] **-11** (except Pd / $BaSO_4$ 5% in EtOAc with 1% triethylamine was used) affording **([^{2}H$_8$]-25)** (0.52 g, 72%) as a colourless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 0.012 (s, 6H), 0.85 (s, 18H), 1.08-1.09 (d, 6H, *J* = 6.1 Hz), 1.28-1.47 (m, 4H), 3.54 (br s, 1H), 3.75 (m, 2H).
^{13}C NMR (100 MHz, $CDCl_3$) δ -4.70 & -4.68, -4.40 (2C), 18.1, 20.4-21.9 (br m, 2C), 23.7, 23.8, 25.9 (6C), 36.0-37.7 (m, 2C), 39.4-39.7 (m, 2C), 68.4-68.5 (m, 2C), 71.5 (br).

See also ref 2 for spectral data of unlabelled **11**.

[4,4,5,5,7,7,8,8-$^2H_8$]-2,6,10-Undecanetriol ([$^2H_8$]-5)

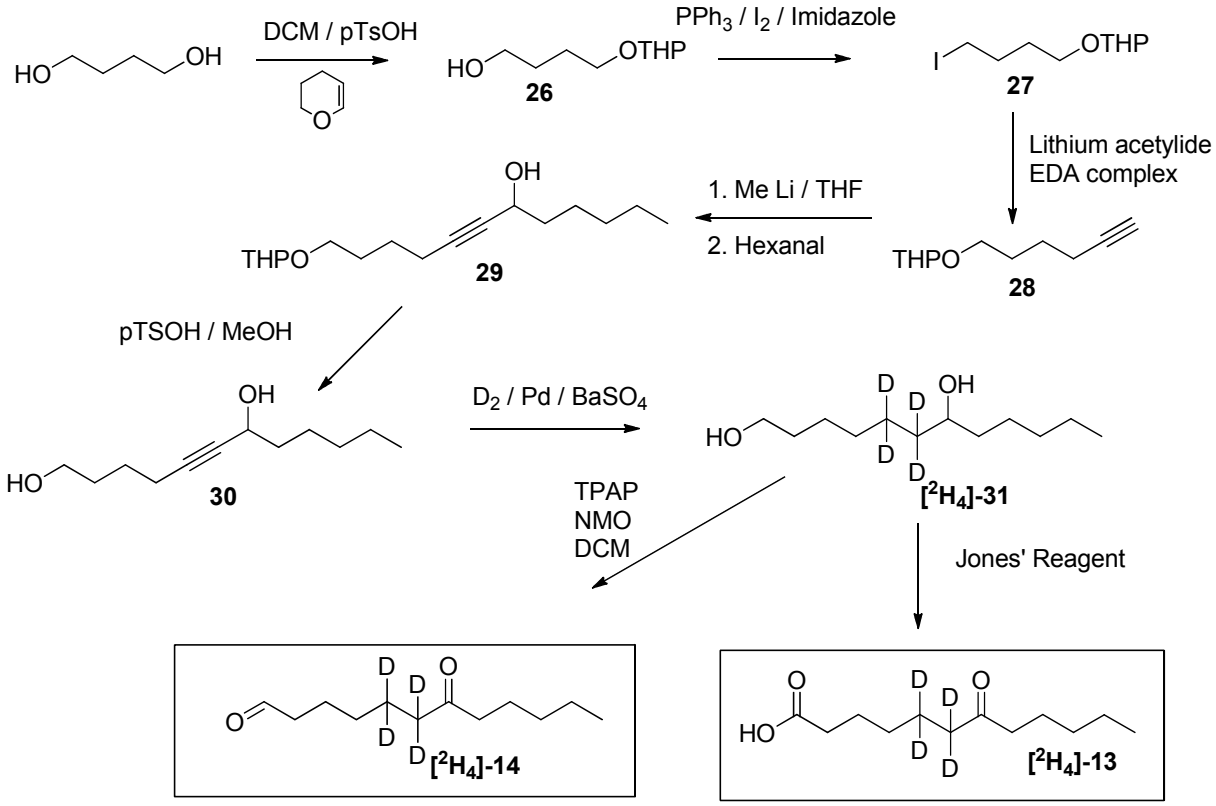


[$^2H_8$]-25 **[$^2H_8$]-5**

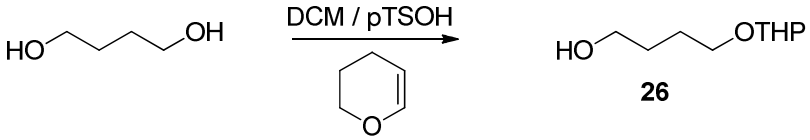
Di-protected triol **([^{2}H$_8$]-25)** was desilylated and purified using a method identical to that used for [$^2H_4$]-**6** to give [4,4,5,5,7,7,8,8-$^2H_8$]-triol **([^{2}H$_8$]-5)** (234 mg, 61%) as a colourless oil.
^{1}H NMR (400 MHz, $CDCl_3$) δ 1.15 (d, 6H, *J* = 6.2 Hz), 1.34-1.47 (m, 4H), 2.33 (br s, 3OH), 3.56 (br m, 1H), 3.74-3.81 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 20.0-20.7 (br m, 2C), 23.5, 23.6, 35.3-37.2 (br m, 2C), 38.6-38.9 (m, 2C), 67.6, 67.9, 70.7-71.8 (br m).

Synthesis of $[^2H_4]$-13 and $[^2H_4]$-14



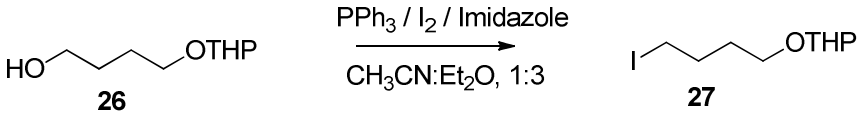
4-(Tetrahydro-2H-pyran-2-yloxy)butan-1-ol 26



pTsOH (1.6 g, 8.5 mmol, 5 mol%) was added portion-wise over 5 minutes to a solution of 1,4-butanediol (15g, 0.17 mol), dihydropyran (14.3 g, 0.17 mol) in DCM (400 mL) at 0ºC and left stirring for 5 hours. The solution was washed with aqueous $NaHCO_3$ (3 x 50 mL, sat.) followed by brine (50 mL) then dried over Na_2SO_4 and concentrated *in vacuo*. The crude oil was then purified by flash chromatography eluting with 1:20 then 1:5 (EtOAc:Hexane) which gave **26** as a colourless oil (11.3 g, 38%).

GC/MS EI m/z (%) 173 ($M^{+\cdot}$-1, 0.1), 128 (0.1), 116 (0.3), 101 (11.6), 85 (51.9), 73 (64.8), 55 (95.3), 43 (77.2), 41 (100).

2-(4-Iodobutoxy)-tetrahydro-2H-pyran 27



To an ice cold solution of triphenylphosphine (21.1 g, 80.5 mmol), imidazole (7.8 g, 115 mmol) and alcohol **26** (10 g, 57.5 mmol) in dry CH_3CN:Et_2O (300 mL, 1:3) was added iodine (20.4 g, 80.5 mmol) over 10 minutes. The reaction was allowed to warm to room temperature and followed by TLC. After 3 hours the reaction was recooled to 0ºC and methanol (5 mL) was added to quench excess triphenylphosphonium iodide. The mixture was concentrated *in vacuo*, triturated with cold hexane (3 x 50 mL) reconcentrated, then purified by washing through a silica pad with hexane which provided **27** as colourless oil (13.2 g, 81%) after solvent removal.

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.45-1.59 (m, 4H), 1.63-1.72 (m, 3H), 1.73-1.83 (m, 1H), 1.87-1.95 (m, 2H), 3.20 (t, 2H, *J* = 7.0 Hz), 3.38 (dt, 1H, *J* = 9.8, 6.2 Hz), 3.44-3.50 (m, 1H), 3.72 (dt, 1H, *J* = 9.8, 6.4 Hz), 3.82 (ddd, 1H, *J* = 11.3, 7.7, 3.6 Hz), 4.53 (dd, 1H, *J* = 4.2, 2.7 Hz).

^{13}C NMR (100 MHz, $CDCl_3$) δ 6.8, 19.6, 25.4, 30.5, 30.6, 30.7, 62.3, 66.2, 98.8.

GC/MS EI m/z (%) 284 ($M^{+\cdot}$, 0.23), 283 (2.1), 226 (0.3), 183 (87.2), 155 (6.8), 85 (100), 55 (87.6), 41 (62.3).

2-(Hex-5-ynyloxy)-tetrahydro-2H-pyran 28

To a solution of lithium acetylide complex (2.2 g, 21.5 mmol) in freshly distilled DMSO (10 mL) at 5ºC was added a solution iodide **27** (5.1 g, 18.0 mmol) in DMSO (5 mL) dropwise. The reaction was monitored by TLC and after 2 hours the reaction was

poured onto ice cold NH_4Cl. The slurry was extracted with hexane (3 x 30 mL) then washed with copper sulfate (5%, 20 mL) and brine (20 mL). The organic layers were combined dried over Na_2SO_4 and solvent removal *in vacuo* provided an oil which was purified by flash chromatography (hexane) to give alkyne **28** (2.52 g, 77 %) as a colourless oil.

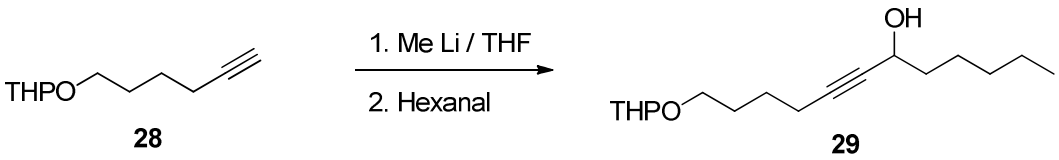
^{1}H NMR (200 MHz, $CDCl_3$) δ 1.40-1.70 (m, 10H), 1.88 (t, 1H, *J* = 2.5 Hz), 2.15 (dt, 2H, *J* = 6.9, 2.5 Hz), 3.33-3.83 (m, 4H), 4.50 (t, 1H, *J* = 3.3 Hz).

^{13}C NMR (50 MHz, $CDCl_3$) δ 18.1, 19.4, 25.2, 25.3, 28.6, 30.6, 62.0, 66.7, 68.3, 84.1, 98.6.

GC/MS EI m/z (%) 181 ($M^{+\cdot}$-1, 0.3), 153 (0.3), 125 (2.0), 111 (4.0), 101 (17.3), 85 (100), 79 (36.8), 67 (28.1), 56 (38.1), 41 (95.9).

Anal. Calculated for $C_{11}H_{18}O_2$: C 72.49, H 9.95. Found: C 72.27, H 10.16.

12-(Tetrahydro-2H-pyran-2-yloxy)dodec-7-yn-6-ol 29



28 **29**

To a solution of THP protected alkyne **28** (1.05 g, 5.77 mmol) in dry THF (20 mL) at -20ºC (CO_2 / EtOH / ice) was added methyl lithium (4.80 mL, 5.77 mmol, 1.2 M) dropwise. The deprotonation was left stirring at -20 ºC for 30 minutes then hexanal (577 mg, 5.77 mmol) in THF (5 mL) was added dropwise. The reaction was allowed to stir at room temperature for 1 hour then poured onto ice cold NH_4Cl (20 mL, sat.), extracted into ether (2 x 40 mL) and then the organic phases were combined and washed with brine (15 mL) and dried over $MgSO_4$. After solvent removal *in vacuo* the residue was purified by flash chromatography on silica gel (EtOAc:Hexane 1:10) affording **29** as colourless oil (1.43 g, 88%).

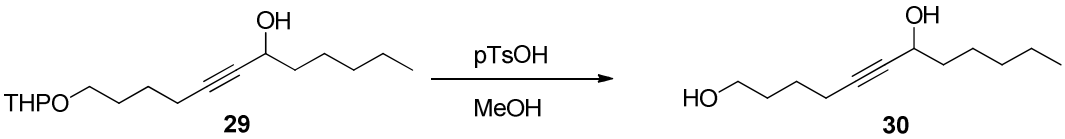
^{1}H NMR (400 MHz, $CDCl_3$) δ 0.87 (t, 3H, *J* = 7.0 Hz), 1.22-1.83 (m,16H), 2.23 (dt, 2H, *J* = 1.9, 7.0 Hz), 3.39 (dt, 1H, *J* = 6.7, 9.2 Hz), 3.48 (m, 1H), 3.73 (dtd, 1H, *J* = 9.7, 6.4, 1.3 Hz), 3.83 (m, 1H), 4.31(tt, 1H, *J* = 2.0, 6.5 Hz), 4.56 (dd, 1H, = 2.7, 4.3 Hz).

^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0, 18.6, 19.6, 22.6, 24.9, 25.4, 25.5, 28.9, 30.7, 31.5, 38.2, 62.3, 62.8, 70.0, 81.7, 85.1, 98.8.

GC/MS EI m/z (%) 264 ($M^{+\cdot}$-18, 0.1), 235 (0.1), 211 (1.3), 193 (1.0), 181 (1.8), 127 (3.3), 111 (4.4), 101 (7.0), 85 (100), 79 (16.7), 55 (39.7), 43 (85.8), 41 (96.5).

Anal. Calculated for $C_{17}H_{30}O_3$: C 72.30, H 10.71. Found: C 72.22, H 11.01.

1,7-Dihydroxydodec-5-yne (30)



29 **30**

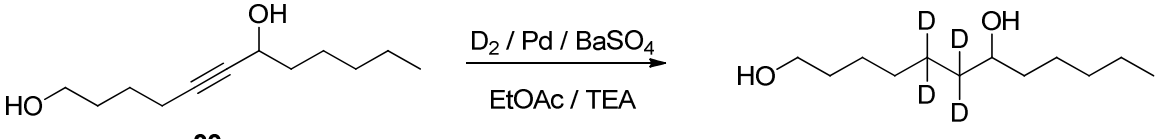
To a solution of protected alcohol **29** (850 mg, 3.01 mmol) in MeOH (30 mL) at 0ºC was added pTsOH (15 mg, 0.08 mmol) and left stirring. After 4 hours TLC revealed the absence of starting material and then aqueous $NaHCO_3$ (sat. 10 mL) was added and methanol was removed *in vacuo*. The aqueous mixture was then extracted with EtOAc (3 x 35 mL), washed with brine (20 mL) and the subsequent organic phases were combined and dried over Na_2SO_4 and concentrated *in vacuo*. The residue was purified on silica gel (EtOAc:Hexane, 1:1) which gave diol **30** as a viscous oil (560 mg, 94%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 0.86 (t, 3H, *J* = 7.0 Hz), 1.22-1.41 (m, 6H), 1.52-1.70(m, 6H), 1.82 (br s, OH), 2.09 (br s, OH), 2.23 (td, 2H, *J* = 7.0, 2.1 Hz), 3.64 (t, 2H, *J* = 6.2 Hz), 4.31 (br tt, H, *J* = 6.5, 1.8 Hz).

^{13}C NMR (100 MHz, $CDCl_3$) δ 13.9, 18.4, 22.5, 24.9 (br, 2C), 31.4, 31.7, 38.1, 62.3, 62.6, 81.8, 84.9.

GC/MS EI m/z (%) 197 ($M^{+\cdot}$-1, 0.02), 180 (0.3), 151 (0.7), 124 (16.0), 109 (9.0), 83 (13.6), 81 (70.1), 79 (57.1), 55 (44.5), 53 (33.2), 43 (70.6), 41 (100).

[5,5,6,6-^{2}H$_4$]-1,7-Dihydroxydodecane ([^{2}H$_4$]-31)



30 **[^{2}H$_4$]-31**

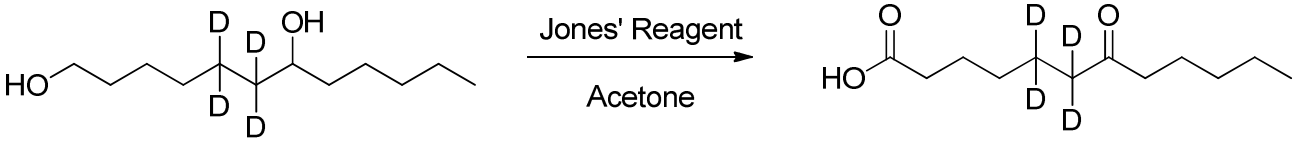
Alkyne **30** (130 mg, 0.66 mmol) was dissolved in a solution of EtOAc (20 mL) and TEA (0.5 mL) then Pd / $BaSO_4$ (5 mg) was added. The flask was twice evacuated and purged with nitrogen then re-evacuated and filled with D_2 by balloon. After 45 min of vigorous stirring the heterogeneous mixture turned from brown to black at which time GC/MS analysis revealed the absence of starting material. The flask was evacuated and purged with nitrogen, then the suspension was filtered through celite, concentrated *in vacuo* and purified as for **30** to give the title product **[$^2H_4$]-31** (111 mg, 82 %) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 0.85 (t, 3H, *J* = 6.9 Hz), 1.23-1.38 (m, 12H), 1.52 (quintet, 2H, *J* = 7.3 Hz), 1.88 (br s, 2OH), 3.48-3.54 (br m, 1H), 3.57 (t, 2H, *J* = 6.5 Hz).

^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0, 22.6, 25.3, 25.4-25.7 (m, CD_2), 29.1-29.4 (m), 31.9, 32.6, 36.6-37.3 (m, CD_2), 37.4, 62.8, 71.7 & 71.8 & 71.9 ($\underline{C}$-CH_2, $\underline{C}$-CDH, $\underline{C}$-CD_2).

GC/MS EI (%) 189 ($M^{+\cdot}$-17, 0.3), 135 (3.5), 116 (3.2), 98 (28.3), 83 (33.3), 71 (24.0), 57 (48.6), 55 (80.6), 43 (100), 41 (77.7).

[5,5,6,6-$^2H_4$]-7-Oxododecanoic acid ([$^2H_4$]-13)



[$^2H_4$]-31 **[$^2H_4$]-13**

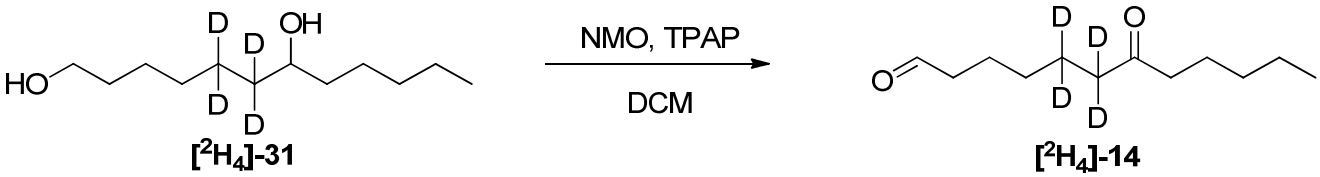
To a solution of alcohol **[$^2H_4$]-31** (400 mg, 2.0 mmol) in acetone (10 mL) at -10 ºC was added sufficient Jones' reagent (~ 3 mL) dropwise that left a persistant yellow tint after 30 min. The reaction was checked by TLC then extracted into hexane (3 x 10 mL), dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (EtOAc:Hexane, 1:1) which afforded the title product **([$^2H_4$]-13)** as a white solid (301 mg, 71%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 0.87 (t, 3H, *J* = 7.2 Hz), 1.22-1.32 (m, 6H), 1.54 (quintet, 2H, *J* = 7.5 Hz), 1.60 (quintet, 2H, *J* = 7.5 Hz), 2.33 (t, 2H, *J* = 7.5 Hz), 2.36 (t, 2H, *J* = 7.4 Hz).

^{13}C NMR (100 MHz, $CDCl_3$) δ 13.9, 22.4-22.7 (br CD_2), 22.4, 23.5, 24.4, 29.7, 31.4, 33.7, 41.7-42.5 (br m, CD_2), 42.8, 179.1, 211.5.

GC/MS EI as the methyl ester (%) 201 ($M^{+\cdot}$-31, 0.4), 182 (0.6), 175 (1.5), 156 (1.3), 143 (1.5), 131 (1.4), 128 (3.7), 116 (6.2), 99 (8.1), 71 (16.4), 59 (18.2), 55 (17.9), 43 (100).

[5,5,6,6-^{2}H$_4$]-7-Oxododecanal ([^{2}H$_4$]-14)



[^{2}H$_4$]-31 **[^{2}H$_4$]-14**

To a solution of **[^{2}H$_4$]-31** (121 mg, 0.59 mmol) in DCM (10 mL) with sieves under nitrogen, was added NMO (274 mg, 2.35 mmol) and TPAP (10 mg). The mixture was stirred for 5 hours then filtered through silica gel with DCM, concentrated *in vacuo* and then purified further by flash chromatography (EtOAc:Hexane, 1:10) to give **[^{2}H$_4$]-14** as a colourless paste (104 mg, 88%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 0.86 (t, 3H, *J* = 7.3 Hz) 1.19-1.30 (m, 6H), 1.53 (quintet, 2H, *J* = 7.4 Hz), 1.60 (quintet, 2H, *J* = 7.6 Hz), 2.35 (t, 2H, *J* = 7.4 Hz), 2.41 (td, 2H, *J* = 7.3, 1.5 Hz), 9.73 (br t, 1H, *J* = 1.6 Hz).

^{13}C NMR (125 MHz, $CDCl_3$) δ 14.2, 21.9-22.0 (br m), 22.7, 23.75 23.76, 28.7-28.8 (br m), 31.7, 41.5-42.7 (br m), 43.0, 43.9, 202.8, 211.7.

GC/MS EI (%) 202 ($M^{+\cdot}$,0.1), 185 (0.1), 174 (0.1), 159 (0.9), 146 (1.0), 130 (0.9), 116 (1.3), 99 (8.0), 84 (8.8), 71 (12.0), 60 (19.9), 43 (100).

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[1] Brett D. Schwartz, Christopher J. Moore, Fredrik Rahm, Patricia Y. Hayes, William Kitching and James J. De Voss *J. Am. Chem. Soc.*, **2008**, *130* (44), 14853–14860.

[2] Brett D. Schwartz, Patricia Y. Hayes, William Kitching, and James J. De Voss *J. Org. Chem.*, **2005**, *70* (8), 3054–3065.