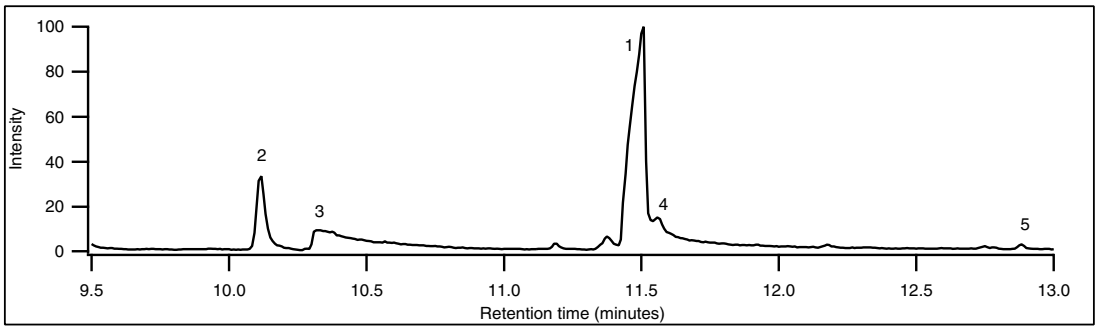
Supplementary Information

SPME-GCMS Conditions.

SPME-GCMS analyses (75 μm carboxen^{TM}-PDMS fibre) were performed on a Shimadzu GC-17A, with a Shimadzu GCMS-QP5050 detector, using a DB5 column. Temperature program: 40^{o}C for 4 minutes; 10^{o}C min^{-1} until 270^{o}C, hold 25 minutes. Representative GC trace. (Relative intensity of amides to spiroacetals changed with sampling conditions).



Retention times and identities (Fig. 1 in manuscript):

(E,E)-2,8-dimethyl-1,7-dioxaspiro[5.5]undecane **(2)**: 10.1 minutes

N-(3-methylbutyl)acetamide **(3)**: 10.3 minutes

N-(3-methylbutyl)propanamide **(1)**: 11.5 minutes

(E,E)-2-ethyl-8-methyl-1,7-dioxaspiro[5.5]undecane **(4)**: 11.6 minutes

(E,E)-2-propyl-8-methyl-1,7-dioxaspiro[5.5]undecane **(5)**: 12.9 minutes

Enantioselective GC Conditions.

Chiral GCMS analyses were performed on a Shimadzu GC-17A, with a Shimadzu GCMS-QP5050 detector, using a 50 m β-cyclodextrin column (0.25 mm internal diameter) at a column pressure of 234.6 kPa and total flow of 51.8 ml min^{-1}. Temperature program: 40^{o}C for 2 minutes; 20^{o}C min^{-1} until 120^{o}C; 1^{o}C min^{-1} until 180^{o}C.

Table 1 Spiroacetal identities of female *B. tryoni* abdomens. See Fig. 2 in manuscript

Peak	Compound	RT (m)	%
A	2,7-dimethyl-1,6-dioxaspiro[4.5]decane (Isomer 1)	10.76	2
B	2-methyl-1,6-dioxaspiro[4.5]decane (Isomer 1)	11.04	<1
C	2,7-dimethyl-1,6-dioxaspiro[4.5]decane (Isomer 2)	11.19	<1
D	2-methyl-1,6-dioxaspiro[4.5]decane (Isomer 2)	11.51	<1
E	(2R,6S,8R)-*(E,E)*-2,8-dimethyl-1,7-dioxaspiro[5.5]undecane	12.27	<1
F	(2S,6R,8S)-*(E,E)*-2,8-dimethyl-1,7-dioxaspiro[5.5]undecane	12.46	83
G	*(E,E)*-2-ethyl-7-methyl-1,6-dioxaspiro[4.5]undecane	12.91	<1
H	2,7-dimethyl-1,6-dioxaspiro[4.5]decane (Isomer 3)	13.18	<1
I	Nonanal	13.29	~1
J	*(E,Z)*-2-ethyl-7-methyl-1,6-dioxaspiro[4.5]undecane	13.51	<1
K	(2S,6R,8S)-*(E,E)*-2-ethyl-8-methyl-1,7-dioxaspiro[5.5]undecane	15.41	5
L	(2S,6S,8R)-*(E,Z)*-2,8-dimethyl-1,7-dioxaspiro[5.5]undecane	15.86	~1
M	(2R,6R,8S)-*(E,Z)*-2,8-dimethyl-1,7-dioxaspiro[5.5]undecane	16.23	~1
N	Decanal	17.35	<1
O	*(E,E)*-2-ethyl-2,8-dimethyl-1,7-dioxaspiro[5.5]undecane	18.85	<1
P	(2S,6R,8S)-*(E,E)*-2-propyl-8-methyl-1,7-dioxaspiro[5.5]undecane	19.22	<1

Synthesis and Characterisation of **15** and **16**

3-methyloct-7-en-3-ol (10). A solution of pent-4-enylmagnesium bromide was prepared from 5-bromopent-1-ene (1.5 ml, 12.68 mmol) and magnesium (0.76 g, 31.70 mmol) in anhydrous Et_2O (15 ml) under nitrogen in the usual manner, and cooled to 0^oC. 2-Butanone (1.38 ml, 15.41 mmol) was added and the reaction stirred for 15 minutes before being carefully quenched with saturated NH_4Cl solution (25 ml) and diluted with Et_2O (15 ml). The layers were separated and the aqueous phase extracted with Et_2O (2 x 15 ml). The combined organic extracts were washed with H_2O (25 ml) and brine (25 ml), dried over $MgSO_4$ and concentrated *in vacuo*. Purification by flash chromatography (20% Et_2O in petroleum spirit) afforded alcohol **10** (1.16 g, 64%) as a colourless oil. Anal. Found: C, 75.6; H, 12.9. Calc. for $C_9H_{18}O$: C, 76.0; H, 12.8%; δ_H(500 MHz; $CDCl_3$) 0.87 (3H, t, *J* 7.5), 1.12 (3H, s), 1.37-1.44 (4H, m), 1.46 (2H, q, *J* 7.5), 2.00-2.06 (2H, m), 4.93 (1H, ddt, *J* 10.2, 2.1, 1.2), 4.99 (1H, ddt, *J* 17.2, 2.1, 1.6), 5.79 (1H, ddt, *J* 17.1, 10.2, 6.7); δ_C(125 MHz; $CDCl_3$) 8.2,

23.2, 26.4, 34.2 (2C), 40.7, 72.8, 114.5, 138.8; *m/z* (EI) 127 (M^+-15, 0.5%), 113 (3), 73 (52), 57 (19), 55 (29), 43 (100).

5-(*tert*-butyldimethylsilyloxy)-5-methylheptanal (11). 18-crown-6 (80 mg, 0.30 mmol) was added to a suspension of potassium hydride (2.0 g, 50.06 mmol, 35% dispersion in mineral oil, washed with hexane) in dry THF (10 ml) under nitrogen and cooled to 0°C. 3-methyloct-7-en-3-ol **(9)** (0.83 g, 5.84 mmol) in THF (15 ml) was then added from a PE-dropping funnel, followed 5 minutes later by TBDMS-Cl (1.62 g, 10.75 mmol). The reaction was allowed to warm to room temperature and stirred for 10 minutes. The reaction was re-cooled to 0°C, diluted with Et_2O (25 ml) and cautiously quenched with H_2O (15 ml). The two phases were separated, the organic layer washed with H_2O (15 ml) and brine (15 ml), dried over $MgSO_4$ and concentrated *in vacuo*. The crude product was columned in hexane to afford *tert*-butyldimethyl(3-methyl-oct-7-en-3-yloxy)silane (1.49 g) as a colourless oil, which was dissolved in CH_2Cl_2 (75 ml) and cooled to –78°C. Ozone was bubbled through the solution for 10 minutes (50ml/min) until a blue colour persisted. The solution was then purged with oxygen for 5 minutes and nitrogen for 10 minutes, whilst being warmed to room temperature. PPh_3 (1.21 g, 4.61 mmol) was added to the colourless solution and stirred until TLC indicated decomposition of the ozonide. The solvent was removed *in vacuo* and the crude aldehyde purified by flash chromatography (1:20 EtOAc:hexane) to give aldehyde **11** (1.06 g, 70% over two steps). δ_H(400 MHz; $CDCl_3$) 0.04 (6H, s), 0.82 (3H, t, *J* 7.5), 0.83 (9H, s), 1.14 (3H, s), 1.35-1.44 (2H, m), 1.46 (2H, q, *J* 7.5), 1.64 (2H, m), 2.38 (2H, td, *J* 7.3, 1.9), 9.74 (1H, t, *J* 1.9); δ_C(100 MHz; $CDCl_3$) –1.98, -1.95, 8.6, 16.8, 18.3, 25.9 (3C), 27.0, 34.7, 41.1, 44.4, 75.7, 202.7; *m/z* (EI) 243 (M^+-15, 0.5%), 229 (5), 187 (13), 131 (25), 109 (37), 83 (46), 75 (100), 73 (73), 55 (63), 41 (29); HRMS: Calc. for $C_{14}H_{30}O_2SiNa$: 281.1913. Found: 281.1909.

2,10-bis(*tert*-butyldimethylsilyloxy)-10-methyldodec-4-yn-6-ol (13). *Tert*-butyldimethyl(pent-4-yn-2-yloxy)silane **(12)** (0.83 g, 4.16 mmol) was stirred in dry THF (20 ml) at –10°C under nitrogen and BuLi (2.49 ml, 1.5M solution in hexanes, 3.74 mmol) was added slowly by syringe. The solution was stirred for 10 minutes, then cooled to –78°C and 5-(*tert*-butyldimethylsilyloxy)-5-methylheptanal **(11)** (0.86

g, 3.33 mmol) in THF (3 ml) added. The reaction was allowed to warm to room temperature and stirred for 10 minutes, before being quenched with saturated NH_4Cl solution (25 ml). The two layers were separated and the aqueous phase extracted with Et_2O (2 x 15 ml). The combined organic extracts were washed with H_2O (20 ml), dried over $MgSO_4$ and concentrated *in vacuo*. Purification by flash chromatography (1:10 EtOAc:hexane) afforded a diastereomeric mixture of propargylic alcohol **13** (1.16 g, 76%) as a colourless oil. Anal. Found: C, 65.5; H, 11.5. Calc. for $C_{25}H_{52}O_3Si_2$: C, 65.7; H, 11.5%; δ_H(400 MHz; $CDCl_3$) 0.039 (6H, s), 0.045 (3H, s), 0.053 (3H,s), 0.82 (3H, t, *J* 7.5), 0.84 (9H, s), 0.87 (9H, s), 1.13 (3H, s), 1.19 (3H, d, *J* 6.1), 1.38-1.44 (4H, m), 1.44 (2H, q, *J* 7.5), 1.59-1.67 (2H, m), 2.23 (1H, ddd, *J* 16.4, 7.3, 2.0), 2.35 (1H, ddd, *J* 16.4, 5.5, 1.8), 3.90 (1H, sextet, *J* 6.2), 4.33 (1H, m); δ_C(100 MHz; $CDCl_3$) –4.75, -4.66, –1.97, -1.94, 8.56 and 8.58, 18.1, 18.3, 19.8, 23.3, 25.8 (3C), 25.9 (3C), 27.07 and 27.11, 29.6, 34.61 and 34.68, 38.7, 41.4, 62.8, 67.7, 75.8, 82.7, 82.8; *m/z* (EI) 427 (M^+-29, 0.01%), 187 (14), 159 (45), 119 (46), 75 (100), 73 (82), 55 (18), 41 (17).

2,10-bis(*tert*-butyldimethylsilyloxy)-10-methyldodec-4-yn-6-one (14). PDC (1.63 g, 4.33 mmol) was added portionwise to a stirred solution of 2,10-bis(*tert*-butyldimethylsilyloxy)-10-methyldodec-4-yn-6-ol **(13)** (0.95 g, 2.08 mmol) in CH_2Cl_2 (35 ml) and was left to stir overnight. Celite was added to the reaction, which was subsequently filtered through a celite plug and the filtrate concentrated *in vacuo*. Purification of the crude product by flash chromatography (1:10 EtOAc:hexane) gave propargylic ketone **14** (0.87 g, 92%) as a colourless oil. Anal. Found: C, 66.0; H, 10.9. Calc. for $C_{25}H_{50}O_3Si_2$: C, 66.0; H, 11.1%; δ_H(500 MHz; $CDCl_3$) 0.035 (6H, s), 0.049 (3H, s), 0.058 (3H,s), 0.82 (3H, t, *J* 7.5), 0.83 (9H, s), 0.86 (9H, s), 1.13 (3H, s), 1.22 (3H, d, *J* 6.0), 1.34-1.42 (2H, m), 1.44 (2H, q, *J* 7.5), 1.66 (2H, m), 2.40 (1H, dd, *J* 16.7, 6.6), 2.48 (1H, dd, *J* 16.7, 6.0), 2.482 (2H, t, *J* 7.4), 3.99 (1H, sextet, *J* 6.1); δ_C(125 MHz; $CDCl_3$) –4.83, -4.67, –1.97, -1.95, 8.6, 18.0, 18.3, 18.9, 23.5, 25.7 (3C), 25.9 (3C), 27.0, 29.8, 34.6, 40.9, 46.0, 66.9, 75.7, 82.1, 91.2, 188.1; *m/z* (EI) 439 (M^+-15, 0.1%), 425 (0.4), 397 (2), 195 (33), 187 (14), 159 (35), 75 (83), 73 (100), 55 (24), 41 (21).

2,10-bis(*tert*-butyldimethylsilyloxy)-10-methyldodecan-6-one. Hydrogen gas was purged through a flask containing 2,10-bis(*tert*-butyldimethylsilyloxy)-10-methyldodec-4-yn-6-one **(14)** (0.50 g, 1.10 mmol) in THF (8 ml) and palladium on carbon (50 mg, 10wt % Pd). The reaction was left to stir under a hydrogen atmosphere for 40 minutes before celite was added and the mixture filtered through a celite plug. The filtrate was concentrated *in vacuo* and the crude product purified by flash chromatography (1:20 EtOAc:hexane) to give 2,10-bis(*tert*-butyldimethylsilyloxy)-10-methyldodecan-6-one (0.45 g, 89%) as a colourless oil. Anal. Found: C, 65.4; H, 11.9. Calc. for $C_{25}H_{54}O_3Si_2$: C, 65.4; H, 11.9%; δ_H(400 MHz; $CDCl_3$) 0.021 (3H, s), 0.023 (3H, s), 0.03 (6H,s), 0.81 (3H, t, *J* 7.5), 0.83 (9H, s), 0.86 (9H, s), 1.09 (3H, d, *J* 6.0), 1.13 (3H, s), 1.22-1.67 (8H, m), 1.42 (2H, q, *J* 7.5), 2.34 (2H, t, *J* 7.6), 2.36 (2H, t, *J* 7.6), 3.76 (1H, sextet, *J* 6.0); δ_C(100 MHz; $CDCl_3$) –4.73, -4.40, –1.96, -1.93, 8.6, 18.1, 18.3, 18.6, 20.1, 23.7, 25.89 (3C), 25.91 (3C), 27.1, 34.6, 39.1, 41.3, 42.7, 43.3, 68.3, 75.8, 211.2; *m/z* (EI) 457 (M^+-1, 0.01%), 429 (0.2), 401 (2), 199 (55), 187 (16), 157 (21), 145 (21), 75 (100), 73 (61), 55 (41).

2-ethyl-2,8-dimethyl-1,7-dioxaspiro[5.5]undecane (15 and **16).** A solution of 2,10-bis(*tert*-butyldimethylsilyloxy)-10-methyldodecan-6-one (0.20 g, 0.44 mmol) in 75% aqueous AcOH (4 ml) was heated at 60^{o}C for 20 hours, cooled to room temperature and extracted with pentane (3 x 15 ml). The combined organic extracts were stirred with cold saturated $NaHCO_3$ solution (20 ml) for 10 minutes and the layers separated. The organic phase was dried over $MgSO_4$ and cautiously concentrated *in vacuo*. The crude product was purified by Prep GC (Shimadzu GC-9A, OV3 column, isothermal temperature of 150^{o}C) to give an isomeric mixture of 2-ethyl-2,8-dimethyl-1,7-dioxaspiro[5.5]undecane (14 mg, 16%, ~50% **16**:~50% **15**). (On occasion the crude product was also purified by flash chromatography (5% Et_2O in pentane) to give a fraction of 2-ethyl-2,8-dimethyl-1,7-dioxaspiro[5.5]undecane enriched in **15**. (~30% **16**:~70% **15**)). HRMS: Calc. for $C_{13}H_{24}O_2Na$: 235.1674. Found: 235.1675.

Axial ethyl/equatorial methyl isomer (16). δ_H(750 MHz; C_6D_6) 0.80 (3H, t, *J* 7.6), 1.132 (3H, d, *J* 6.3), 1.08-1.19 (2H, m), 1.18 (3H, s), 1.27-1.36 (3H, m), 1.37-1.55 (2H, m), 1.63-1.72 (3H, m), 1.73-1.80 (1H, m), 1.96-2.09 (2H, m), 2.28 (1H, dq, *J* 15.3, 7.6), 4.02 (1H, dqd, *J* 11.3, 6.3, 2.2); δ_C(188 MHz; C_6D_6) 10.10, 15.78, 19.75, 22.07, 28.76, 30.47, 33.43, 33.64, 37.10, 38.09, 65.95, 75.48, 96.49; *m/z* (EI) 212

(M^+, 1.37%), 197 (1), 183 (24), 168 (1), 143 (12), 142 (8), 140 (3), 125 (40), 115 (14), 112 (21), 97 (16), 83 (24), 55 (86), 43 (100).

Axial methyl/equatorial ethyl isomer (15). δ_H(750 MHz; C_6D_6) 0.97 (3H, t, *J* 7.5), 1.08-1.15 (1H, m), 1.128 (3H, d, *J* 6.3), 1.23-1.36 (5H, m), 1.35 (3H, s), 1.37-1.55 (4H, m), 1.58-1.62 (1H, m), 1.73-1.80 (1H, m), 1.96-2.09 (1H, m), 2.11-2.18 (1H, m), 3.93 (1H, dqd, *J* 11.3, 6.3, 2.2); δ_C(188 MHz; C_6D_6) 7.97, 15.98, 19.72, 21.99, 22.88, 33.43, 35.25, 37.03, 37.74, 38.34, 65.96, 73.67, 96.14; *m/z* (EI) 212 (M^+, 1.92%), 197 (3), 183 (13), 168 (1), 143 (15), 142 (11), 140 (8), 125 (37), 115 (21), 112 (33), 97 (19), 83 (29), 55 (93), 43 (100).