Supporting Information for:

Synthesis of *rac*-Lindenene *via* a thermally induced cyclopropanation reaction

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General experimental techniques

^{1}H NMR spectra were recorded on Brüker DPX200 (200MHz), Brüker DPX400 (400MHz), Brüker AV400 and Brüker AVB500 (500MHz) spectrometers at ambient temperatures. Chemical shifts (δ_H) are quoted in parts per million (ppm) and are referenced to the residual solvent peak. Signal splittings are recorded as singlet (s), doublet (d), doublet of doublets (dd), doublet of doublet of doublets (ddd) triplet (t), quartet (q), broad (br), apparent doublet (app d), doublet of multiplets (dm), apparent doublet of triplets (app dt) and multiplet (m). Coupling constants, *J*, are measured to the nearest 0.5 Hz and are presented as observed. Proton spectra assignments are supported by ^{1}H-^{1}H COSY where necessary. ^{13}C NMR spectra were recorded on Brüker AV400 (100.6 MHz) and Brüker AV500 (125.8MHz) spectrometers at ambient temperatures. Chemical shifts (δ_H) are reported in parts per million (ppm) and are referenced to the residual solvent peak. Carbon spectra assignments are supported by DEPT analysis and HSQC spectra where necessary. Mass spectra were recorded using Fisons Platform spectrometer (ES mode) and Micromass GCT (CI or ES mode). Only molecular ions (M^+), and fragments from molecular ions and other major peaks are reported. Some spectra were recorded by Mr. R. G. Proctor, Dr. N. Oldham and Dr. J. Kirkpatrick on a Micromass Autospec spectrometer (EI or CI mode) and are accurate to ±5 ppm. Infrared spectra were recorded on a Perkin Elmer 1000 Paragon Fourier Transform spectrometer as a thin film between NaCl plates, and where necessary as KBr disks. Absorption maxima (ν_{max}) are reported in wavenumbers (cm^{-1}) and the relative intensities of the signals are indicated as strong (s), medium (m) or weak (w), as appropriate. Melting points were carried out on a Reicher-Koffler block apparatus and are uncorrected. Thin layer chromatography (TLC) was performed using Merck aluminium foil backed plates pre-coated with silica gel 60 F_{254} (1.05554). Visualisation was effected by quenching of UV fluorescence (λ_{max}= 254nm), or by staining with basic potassium permanganate solution, followed by heating. Retention factors (R_f) are reported to ± 0.05. Column chromatography was performed using ICN silica 32-63, 60Å or Fluorosil® where required.

All reactions involving water-sensitive compounds were carried out in oven-dried Schlenk glassware under argon atmosphere unless stated otherwise. Argon gas was dried by passage through phosphorus pentoxide and self-indicating silica gel. Triethylamine (NEt_3), diisopropylamine (HN^iPr_2) dichloromethane (DCM) and methanol (MeOH), were distilled from calcium hydride under argon or reduced pressure and stored over 4Å molecular sieves under argon until used. Toluene was dried over 4Å molecular sieves under argon. P.E. refers to the fraction of light petroleum ether boiling between 30 and 40^{o}C. Solvents were evaporated on a Büchi R110 Rotovaporator. All other reagents were purified in accordance with the instructions in D. Perrin and W. Armarego, "Purification of Laboratory Chemicals", Pergamon Press, 3rd Ed., 1988 or used as obtained from commercial sources. All chemicals were handled in accordance with the safety instructions identified in "Good Laboratory Practice" September 2004.

The synthesis of THP-protected hydroxyacetone **18**[1] has been reported previously by this group and was prepared according to the procedure of Hagiwara and Uda.[2] 1-(*tert*-Butyl)-5-(methylsulfonyl)-1H-tetrazole was prepared according to the procedures of Aissa.[10]

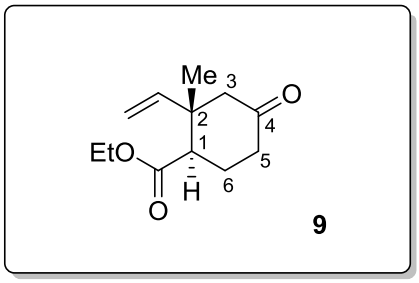
Single crystal X-ray diffraction reports

Single crystal X-ray diffraction data were obtained for compounds **14** and **15**. In each case, a typical crystal was mounted using the oil drop technique, in perfluoropolyether oil at 150(2) K using a Cryostream N_2 open-flow cooling device.[3] Diffraction data were collected using graphite monochromated Mo-Kα radiation (λ = 0.71073 Å) on a Nonius Kappa CCD diffractometer. For all data collections, series of ω-scans were performed in such a way as to collect a complete data set to a maximum resolution of 0.77 Å. Data reduction including unit cell refinement and inter-frame scaling was carried out using DENZO-SMN/SCALEPACK.[4] Intensity data were processed and corrected for absorption effects by the multi-scan method, based on repeat measurements of identical and Laue equivalent reflections. Structure solution was carried out with direct methods using the programs SIR92[5] within the CRYSTALS software suite.[6] In general, coordinates and anisotropic displacement parameters of all non-hydrogen atoms were refined freely except where disorder necessitated the use of "same distance restraints" together with thermal similarity and vibrational restraints to maintain sensible geometry/displacement parameters. Hydrogen atoms were generally visible in the difference map and refined with soft restraints prior to inclusion in the final refinement using a riding model.[7] Crystallographic data (excluding structure factors) for both of the structures have been deposited with the Cambridge Crystallographic Data Centre (CCDC 953764 (**14**) and 953765 (**15**)). Copies of the data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif. A table summarising the X-ray crystallographic data follows (Table SI1).

Table SI 1 X-ray crystallographic information for compounds **14** and **15**.

Crystal identification	**14**	**15**
CCDC no.	953764	953765
Chemical Formula	$C_{13}H_{18}O_3$	$C_{13}H_{18}O_3$
Formula weight, *M*	222.28	222.28
Temperature, *K* /°	150	150
λ /Å	0.71073	0.71073
Crystal system	Triclinic	Monoclinic
Space group	*P* -1	$P\ 2_1/n$
a /Å	6.8219(2)	11.5140(2)
b /Å	9.1724(4)	7.34560(10)
c /Å	9.3248(4)	14.5121(3)
α /°	88.1107(17)	90
β /°	79.4709(16)	113.2854(8)
γ /°	80.956(2)	90
V /Å³	566.52(4)	1127.42(3)
Z	2	4
D_c /g cm^{-3}	1.30	1.31
Absorption coefficient, μ /mm^{-1}	0.091	0.092
F(000)	240	480
Size /mm	0.15 × 0.15 × 0.20	0.20 × 0.20 × 0.50
Crystal description	Colourless block	Colourless block
θ range collected /°	$5.0 \le \theta \le 27.5$	$5.0 \le \theta \le 27.5$
Index ranges, *hkl*	$-8 \le h \le 8$,	$-14 \le h \le 14$,
Refl. Measured	8424	16706
Refl. Unique	2444	2561
R_{int}	0.036	0.016
Reflections obs., *n* ($I > n\sigma(I)$)	2444	1963
Transmission coefficients (min.,	0.98, 0.98	0.68, 0.98
Param. Refined	173	145
R or *R*1 (obs. refl.)	$R = 0.075$	$R = 0.036$
wR or *R*2 (all data)	$wR = 0.118$	$wR = 0.087$
Goodness of fit (GOF)	1.00	0.99
Residual electron (min., max.) /eÅ³	–0.32, 0.32	–0.19, 0.27

(±)-Ethyl (1R,2S)-2-methyl-4-oxo-2-vinylcyclohexane-1-carboxylate (9)

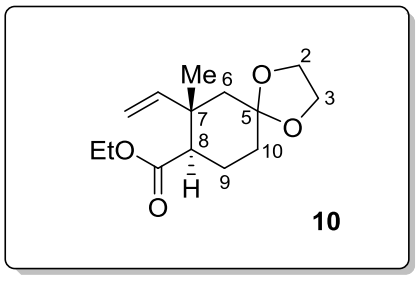


9

Prepared by a modification of the procedure of Bohlmann *et al.*[8] To a stirred solution vinyl magnesium bromide (110mL, 1.0M in THF, 109.8mmol) in anhydrous THF (100mL) under Argon atmosphere was added a solution of CuBr-SMe_2 (5.9g, 28.1mmol) in SMe_2 (65mL) at -78°C. After stirred at this temperature for 0.5h, a solution of Hagemann's ester (10.0g, 54.9mmol) in anhydrous THF (20mL) was added by slowly rinsing down the flask (to prevent any unwanted 1,2-addition). The mixture was allowed to stir at -78°C for 6 h, under Ar atmosphere and then warmed to 0°C and quenched with saturated aqueous NH_4Cl (100mL). The aqueous layer was extracted with Et_2O (3×50mL) then the combined organic extracts were washed with H_2O (50mL) and dried over anhydrous $MgSO_4$. After filtration the solvent was removed *in vacuo* to afford the crude product as a brown coloured oil, which was purified by flash chromatography using 5:1 hexanes/Et_2O to furnish the title compound **9** as a pale orange coloured oil (10.16g, 88%).

R_f 0.55 (1:1 hexanes/Et_2O); ν_{max} (film)/cm^{-1} 3087w, 2966s, 1727s, 1639w, 1377s, 1155s, 1033s; δ_H (400MHz, $CDCl_3$) 1.10 (3H, s, 2-C$\underline{H}_3$), 1.28 (3H, t, *J*=7.2 Hz, $CO_2CH_2C\underline{H}_3$), 2.10 (2H, m, 6-C$\underline{H}_2$), 2.28 (1H, m, 1×4-C$\underline{H}_2$), 2.42 (1H, d, *J*=14.5 Hz, 1×6-C$\underline{H}_2$), 2.58 (1H, d, *J*=14.5 Hz, 1×6-C$\underline{H}_2$), 2.60 (1H, m, 1×5-C$\underline{H}_2$), 2.67 (1H, t, *J*=6.0 Hz, 1-C$\underline{H}$), 4.15 (2H, dq, *J*=7.0 Hz, 1.4 Hz, $CO_2C\underline{H}_2CH_3$), 5.03 (1H, d, *J*=17.5 Hz, $=CH_{cis}C\underline{H}_{trans}$), 5.06 (1H, d, *J*=10.5 Hz, $=C\underline{H}_{cis}CH_{trans}$), 5.77 (1H, dd, *J*=17.5, 10.5 Hz, C$\underline{H}$=CH_2); δ_C (100.6MHz, $CDCl_3$) 14.3 ($CO_2CH_2\underline{C}H_3$), 22.3 (2-$\underline{C}H_3$), 24.7 ($\underline{C}$-6), 38.2 ($\underline{C}$-5), 42.9 ($\underline{C}$-2), 48.6 ($\underline{C}$-1), 50.2 ($\underline{C}$-3), 60.4 ($CO_2\underline{C}H_3CH_3$), 113.6 (=$\underline{C}H_2$), 144.7 (H$\underline{C}$=CH_2), 173.4 (R$\underline{C}O_2$R), 209.9 ($\underline{C}$-4); HRMS: Found 228.1601; $C_{12}H_{22}NO_3$ ($M+NH_4^+$) requires 228.1600.

(±)-Ethyl (7S,8R)-7-methyl-7-vinyl-1,4-dioxaspiro[4.5]decane-8-carboxylate (10)



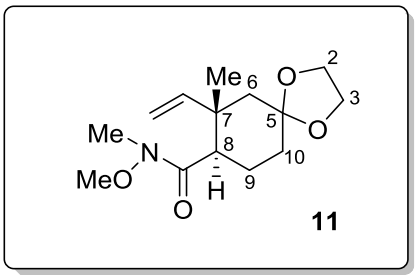
10

To a solution of ketone **9** (2.0g, 9.51mmol) in benzene (50mL) was added ethylene glycol (0.71g,11.41mmol) and *p*-toluenesulphonic acid (0.01g) and the resultant mixture was heated at reflux under Dean-Stark conditions for 24h. After cooling to RT and quenching with dilute aqueous $NaHCO_3$ (100mL), the layers were separated and the organic phase was washed with first 0.1M aqueous $NaHCO_3$ (50mL) then H_2O (50mL). The organic extract was then dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo* to afford a pale orange coloured oil. Flash chromatography of this crude product using an elution gradient of 10:1 hexanes/Et_2O to 5:1 hexanes/Et_2O afford the

title product **10** as a pale yellow coloured oil (2.33g, 96%). Spectra of the title compound **10** were in agreement with those reported previously by Kametani *et al*.[9]

R_f 0.45 (hexanes:Et_2O, 3:1); ν_{max}(film)/cm^{-1}; 2941s, 1730s, 1638w, 1446w, 1373s, 1177s, 1094s, 949w, 917w; δ_H(400MHz, $CDCl_3$) 1.19 (3H, s, 7-C$\underline{H}_3$), 1.22 (3H, t, *J*=7.0Hz, $RCO_2CH_2C\underline{H}_3$), 1.44-2.07 (6H, m, 6-C$\underline{H}_2$, 9-C$\underline{H}_2$, 10-C$\underline{H}_2$), 2.35 (1H, dd, *J*=3.5 Hz, 11.5 Hz, 8-C$\underline{H}$), 3.93 (4H, m, 2-C$\underline{H}_2$, 2×C$\underline{H}_2$), 4.09 (2H, dq, *J*=2.0 Hz, 7.0 Hz, $RCO_2C\underline{H}_2CH_3$), 4.96 (1H, d, *J*=10.5 Hz, =C$\underline{H}_{cis}CH_{trans}$), 4.99 (1H, d, *J*=17.5 Hz, =$CH_{cis}C\underline{H}_{trans}$), 5.89 (1H, dd, *J*=10.5 Hz, 17.5 Hz, C$\underline{H}$=CH_2), δ_c(100.6MHz, $CDCl_3$) 14.3 ($CO_2CH_2\underline{C}H_3$), 18.8 (7-$\underline{C}H_3$), 22.8 (C-9), 33.7 (C-10), 40.2 (C-7), 45.5 (C-6), 50.5 (C-8), 60.0 ($RCO_2\underline{C}H_2CH_3$), 63.7 and 64.6 (C-2, C-3), 108.1 (C-5), 110.9 (=$\underline{C}H_2$), 147.8 (H$\underline{C}$=CH_2), 173.8 (R$\underline{C}O_2$Et); HRMS: Found 255.1594, $C_{14}H_{23}O_4$ (MH^+) requires 255.1596.

(±)-(7R,8S)-N-methoxy-N,7-dimethyl-7-vinyl-1,4-dioxaspiro[4.5]decane-8-carboxamide (11)

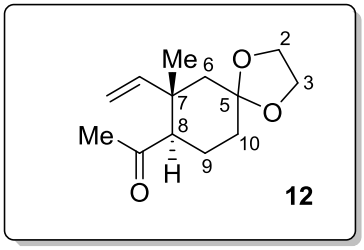


11

To a slurry of ester **10** (500mg, 1.97mmol) and Me(MeO)NH·HCl (301mg, 3.05mmol) in anhydrous THF (5mL) at -20°C under nitrogen was added ^{i}PrMgCl (2.96mL, 2.0M in THF) over 15 min maintaining the temperature below -5°C, during which time the solution developed a bright red colour. The mixture was aged for 20 min at -10°C then quenched with saturated aqueous NH_4Cl (10mL). The product was extracted with Et_2O (2 × 20mL), and the combined organic extracts washed with H_2O (20mL), brine (20mL), dried over anhydrous $MgSO_4$ and concentrated *in vacuo* to yield **11** as a colourless oil (533mg, 100%) which was used without further purification in the next step;

R_f 0.20 (PE:Et_2O, 1:1); ν_{max}(film)/cm^{-1} 3083w, 2937s, 1659s, 1417s, 1379s, 1122s, 1091s; δ_H(400MHz, $CDCl_3$) 1.25 (3H, s, 7-C$\underline{H}_3$), 1.57 (1H, m, 1 × 10-C$\underline{H}_2$), 1.61 (1H, d, *J*=13.0Hz, 1 × 6-C$\underline{H}_2$), 1.72 (2H, m, 1 × 6-C$\underline{H}_2$, 1 × 9-C$\underline{H}_2$), 1.90 (1H, m, 1 × 10-C$\underline{H}_2$), 2.07 (1H, m, 1 × 9-C$\underline{H}_2$), 2.87 (1H, app d, *J*=9Hz, 8-C$\underline{H}$), 3.15 (3H, s, RCON(OMe)C$\underline{H}_3$), 3.67 (3H, s, RCON(Me)OC$\underline{H}_3$), 3.87-4.02 (4H, m, 2-C$\underline{H}_2$, 3-C$\underline{H}_2$), 4.93 (1H, d, *J*=10.5Hz, RCH=C$\underline{H}_{cis}H_{trans}$), 4.97 (1H, d, *J*=17.5Hz, RCH=$CH_{cis}\underline{H}_{trans}$), 5.88 (1H, dd, *J*=10.5Hz, 17.5Hz, RC$\underline{H}$=CH_2); δ_c(100.6MHz, $CDCl_3$) 19.7 (7-$\underline{C}H_3$), 23.4 (9-C), 32.0 (RCON(OMe)$\underline{C}H_3$), 34.0 (10-C), 40.6 (7-C), 44.4 (8-C), 45.4 (6-C), 61.3 (RCON(Me)O$\underline{C}H_3$), 63.7 and 64.5 (2-C, 3-C), 108.4 (5-C), 110.8 (RCH=$\underline{C}H_2$), 147.7 (R$\underline{C}$H=CH_2), 210.1 (R$\underline{C}$ONMe(OMe)); HRMS: found 270.1701, (MH^+) requires 270.1705.

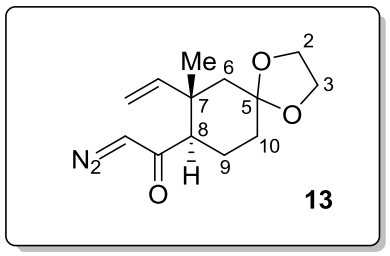
(±)-(7S,8S)-7-methyl-8-acetyl-7-vinyl-1,4-dioxaspiro[4.5]decane (12)



To a stirred solution of Weinreb amide **11** (7.00g) in anhydrous THF (90mL) at -78°C under nitrogen was added MeLi (32.64mL, 1.6M in pentanes) drop-wise. After stirring the mixture for 45 minutes at -78°C the reaction was quenched with saturated NH_4Cl (50mL) and warmed to RT where the organic layer was extracted with Et_2O (100mL), washed with water (50mL), brine (50mL), dried over anhydrous $MgSO_4$ and concentrated *in vacuo* to yield methyl ketone **12** as a colourless oil (5.83g, 100%). Further purification was not necessary though flash chromatography (PE:Et_2O, 4:1) afforded **12** in 98% from the crude product.

R_f 0.40 (PE:Et_2O, 1:1); ν_{max}(film)/cm^{-1} 3039s, 2913s, 1717s, 1644w, 1298s, 1093s; δ_H(400MHz, $CDCl_3$) 1.13 (3H, s, 7-C$\underline{H}_3$), 1.47-1.58 (2H, m, 1 × 6-C$\underline{H}_2$, 1 × 10-C$\underline{H}_2$), 1.63-1.69 (2H, m, 1 × 6-C$\underline{H}_2$, 1 × 9-C$\underline{H}_2$), 1.80-1.86 (1H, m, 1 × 10-C$\underline{H}_2$), 1.95-2.06 (1H, m, 1 × 9-C$\underline{H}_2$), 2.11 (3H, s, RCOC$\underline{H}_3$), 2.51 (1H, dd, *J*=3.5Hz, 12.0Hz, 8-C$\underline{H}$), 3.87-3.97 (4H, m, 2-C$\underline{H}_2$, 3-C$\underline{H}_2$), 5.00 (1H, d, *J*=17.5Hz, RCH=C$H_{cis}\underline{H}_{trans}$), 5.02 (1H, d, *J*=11.0Hz, RCH=C$\underline{H}_{cis}H_{trans}$), 5.90 (1H, dd, *J*=11.0Hz, 17.5Hz, RC$\underline{H}$=CH_2); δ_c(100.6MHz, $CDCl_3$) 18.0 (7-C$\underline{H}_3$), 22.3 (9-C), 32.4 (RCOC$\underline{H}_3$), 33.9 (10-C), 40.7 (7-C), 46.0 (6-C), 57.5 (8-C), 63.7 and 64.6 (2-C, 3-C), 108.0 (5-C), 111.7 (RCH=C$\underline{H}_2$), 148.1 (RC$\underline{H}$=CH_2), 210.9 (RCOMe); HRMS: found 245.1491, (MH^+) requires 245.1491.

(±)-(7S,8S)-8-(1-diazoethan-2-one)-7-methyl-7-vinyl-1,4-dioxaspiro[4.5]decane (13)

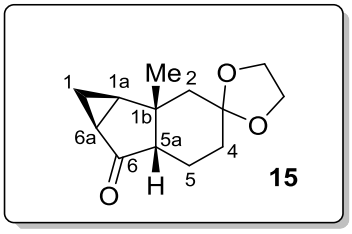


To a two-necked flask under nitrogen equipped with a magnetic stirrer and with a pressure-equalising dropping funnel attached was added LHMDS (29mL, 1M) and anhydrous THF (100mL). The resulting solution was cooled to -78°C before a solution of methyl ketone **12** (5.80g, 25.9mmol) in anhydrous THF (20mL) was added drop-wise over 20 min. The dropping funnel was washed with anhydrous THF (2 × 10mL) and the reaction mixture was stirred at -78°C for 10 min, whereupon 2,2,2-trifluoroethyl trifluoroacetate (3.83mL, 28.6mmol) was added rapidly in one portion. The reaction was left to stir at -78°C for a further 10 min, after which the mixture was poured into a separating funnel containing Et_2O (100mL) and 5% HCl (100mL). The phases were separated and the aqueous layer extracted with Et_2O (100mL). The combined organic layers were washed with brine (100mL), dried over anhydrous $MgSO_4$ and concentrated *in vacuo*. The residue was immediately dissolved in MeCN (80mL) to which H_2O (0.47mL, 25.9mmol), Et_3N (2.87mL, 38.9mmol) and TsN_3 (7.66g, 38.9mmol) were added sequentially, each over 30 seconds. The resulting yellow solution was allowed to stir at RT for 12 h before being poured into a separatory funnel containing Et_2O (100mL)

and 5% NaOH (100mL). The organic layer was separated and washed successively with 5% NaOH (3 × 50mL), H_2O (3 × 50mL) and brine (3 × 50mL), then dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo* to yield a crude yellow oil. Flash chromatography (PE:Et_2O, 3:1) furnished diazoketone **13** as a bright yellow coloured oil (5.90g, 89%).

R_f 0.30 (PE:Et_2O, 1:1); ν_{max}(film)/cm^{-1} 3085m, 2939s, 2880s, 2101s, 1637s, 1374s, 1331s, 1124s, 1091s, 1057s; δ_H(400MHz, $CDCl_3$) 1.19 (3H, s, 7-CH_3), 1.52 and 1.86 (2 × 1H, m, 10-CH_2), 1.64 (2H, m, 6-CH_2), 1.70 and 1.89 (2 × 1H, m, 9-CH_2), 2.23 (1H, m, 8-CH), 3.94 (4H, m, 2-CH_2, 3-CH_2), 5.00 (1H, d, *J*=10.5Hz, RCH=C$H_{cis}H_{trans}$), 5.02 (1H, d, *J*=17.5Hz, RCH=C$H_{cis}H_{trans}$), 5.20 (1H, br s, RCOCHN_2), 5.91 (1H, dd, *J*=10.5Hz, 17.5Hz, RCH=CH_2); δ_c(100.6MHz, $CDCl_3$) 18.7 (7-CH_3), 22.7 (9-C), 34.0 (10-C), 50.0 (7-C), 45.7 (6-C), 53.8 (8-C), 55.8 (RCOCHN_2), 63.7 and 64.4 (2-C, 3-C), 108.1 (5-C), 111.8 (RCH=CH_2), 147.8 (RCH=CH_2), 195.9 (RCOCHN_2).

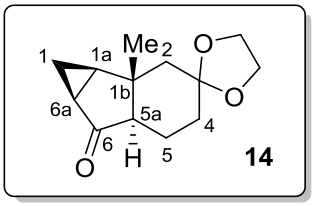
(±)-(1aR,1bS,5aS,6aS)-1b-methylhexahydro-1H-spiro[cyclopropa[a]indene-3,2'-[1,3]dioxolan]-6(2H)-one (15)



To a suspension of Cu(acac)$_2$ (73mg, 5mol%) in benzene (50mL) under nitrogen at 50°C was added diazoketone **13** in benzene (10mL) *via* a syringe pump over 10 min. The suspension was left to stir until TLC indicated the reaction had gone to completion, after which the benzene was removed *in vacuo*. Flash chromatography (PE:Et_2O, 5:1) of the crude product delivered cyclopropanoid **15** as colourless crystals (782mg, 64%).

m.p. 79-81°C; R_f 0.35 (PE:Et_2O, 1:1); ν_{max}(KBr disc)/cm^{-1} 2946s, 1713s, 1210s, 1084s, 1030s; δ_H(400MHz, $CDCl_3$) 1.11-1.18 (2H, m, 1-CH_2), 1.25-1.40 (1H, m, 1 × 4-CH_2), 1.32 (3H, s, 1b-CH_3), 1.51-1.59 (2H, m, 1 × 4-CH_2, 1 × 2-CH_2), 1.66-1.70 (1H, m, 1 × 5-CH_2), 1.74-1.76 (1H, m, 1 × 2-CH_2), 1.81-1.87 (3H, m, 1a-CH, 6a-CH, 5a-CH), 2.00-2.11 (1H, m, 1 × 5-CH_2), 3.85-4.00 (4H, m, 2×OCH_2); δ_c(100.6MHz, $CDCl_3$) 14.2 (1-C), 17.2 (5-C), 23.8 (1b-CH_3), 26.8 (6a-C), 30.9 (4-C), 34.0 (1a-C), 39.3 (1b-C), 44.3 (5a-C), 44.7 (2-C), 63.7 64.5 (O**C**H_2), 108.3 (3-C), 213.4 (6-C); HRMS: found 223.1333, (MH^+) requires 223.1334.

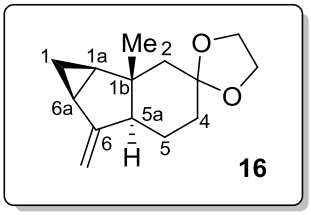
(±)-(1aR,1bS,5aR,6aS)-1b-methylhexahydro-1H-spiro[cyclopropa[a]indene-3,2'-[1,3]dioxolan]-6(2H)-one (14)



Diazoketone **13** (500mg) was dissolved in DCM (50mL) and the solution heated to reflux for 96h. The reaction was monitored by analysing aliquots of the solution by ^{1}H NMR. Once the reaction was found to be complete, the solvent was removed under vacuum, furnishing the title compound **14** as a colourless oil (440mg, 99%).

R_f 0.3 (P.E. 30-40:Et_2O; 1:1); ν_{max}(KBr disc)/cm^{-1} 2931s, 1716s, 1308s, 1008s, 932s; δ_H(400MHz, $CDCl_3$) 0.89 (3H, s, 1b-C$\underline{H}_3$), 1.06 (1H, ddd, *J* = 6.0Hz, 7.5Hz, 10.5Hz, 1×1-C$\underline{H}$), 1.20-1.24 (1H, m, 1×1-C$\underline{H}$), 1.35 (1H, dq, *J* = 4.0Hz, 13.0Hz, 1×5-C$\underline{H}$), 1.52 (1H, dt, *J* = 5.5Hz, 13.0Hz, 1×4-C$\underline{H}$), 1.71-1.79 (2H, m, 1a-C$\underline{H}$, 1×4-C$\underline{H}$), 1.87-1.94 (2H, m, 1×5-C$\underline{H}$, 6a-C$\underline{H}$), 1.95 (1H, d, *J* = 13.0Hz, 1×2-C$\underline{H}$), 2.08 (1H, d, *J* = 13.0Hz, 1×2-C$\underline{H}$), 2.42 (1H, dd, *J* = 2.0Hz, 12.0Hz, 5a-C$\underline{H}$), 3.87-3.90 and 3.95-4.03 (4H, m, 2×OC$\underline{H}_2$); δ_C(100.6MHz, $CDCl_3$) 14.6 (1-C$\underline{C}$), 16.9 (5-C$\underline{C}$), 19.4 (6a-C$\underline{C}$), 26.5 (1a-C), 28.8 (1b-C$\underline{H}_3$), 34.8 (1b-C$\underline{C}$), 35.8 (4-C$\underline{C}$), 48.5 (2-C$\underline{C}$), 63.6 and 64.7 (2 × O$\underline{C}H_2$), 68.2 (5a-C$\underline{C}$), 109.9 (3-C$\underline{C}$), 216.3 (6-C$\underline{C}$); *m/z* (ES)$^+$ 223 [(M+H)$^+$, 100%], 201 [34], 178 [23], 95 [10]; HRMS (CI)$^+$ found 223.1335 (MH$^+$), $C_{13}H_{19}O_3$ requires 223.1334.

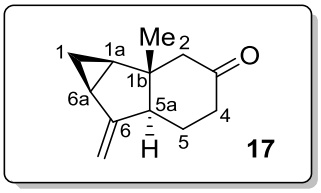
(±)-(1aR,1bS,5aS,6aS)-1b-methyl-6-methyleneoctahydro-1H-spiro[cyclopropa[a]indene-3,2'-[1,3]dioxolane] (16)



NaHMDS (0.91mL, 2.0M in THF, 1.81mmol) was added to a solution of ketone **14** (309mg, 1.39mmol) and 1-(*tert*-butyl)-5-(methylsulfonyl)-1H-tetrazole[10] (290mg, 1.67mmol) in anhydrous THF (18mL) at -78°C, and the mixture was stirred for 16h, maintaining -78°C with slow warming to RT. The reaction was subsequently quenched with saturated aqueous NH_4Cl (50mL) and extracted with Et_2O (2 × 50mL). The combined organic layers were washed with water (50mL) and brine (50mL), dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. Purification of the crude residue by column chromatography (P.E. 30-40:benzene (10:1) generated compound **16** as a colourless oil (223mg, 72%).

R_f 0.3 (P.E. 30-40:Et_2O, 8:1); ν_{max}(film)/cm^{-1} 2960s, 2874m, 1729s, 1463m, 1274s, 1123s, 1073s, 743m; δ_H(400MHz, $CDCl_3$) 0.71 (3H, s, 1b-C$\underline{H}_3$), 0.74-0.80 (1H, m, 1×1-C$\underline{H}$), 0.86-0.90 (1H, m, 1×1-C$\underline{H}$), 1.23-1.34 (2H, m, 1×1a-C$\underline{H}$, 1×5-C$\underline{H}$), 1.51-1.62 (2H, m, 1×5-C$\underline{H}$, 1×4-C$\underline{H}$), 1.83 (1H, d, *J* = 13.0Hz, 1×2-C$\underline{H}$), 1.86-1.91 (2H, m, 1×6a-C$\underline{H}$, 1×5-C$\underline{H}$), 2.03 (1H, dd, *J* = 2.0Hz, 13.0Hz, 1×2-C$\underline{H}$), 2.43 (1H, dd, *J* = 2.5Hz, 12.0Hz, 1×5a-C$\underline{H}$), 3.86-3.89 and 3.95-4.03 (4H, 2 × m, 2×OC$\underline{H}_2$), 4.64 (1H, s, 1×=C$\underline{H}_2$), 4.92 (1H, s, 1×=C$\underline{H}_2$); δ_C(100.6MHz, $CDCl_3$) 16.5 (1-C$\underline{C}$), 17.1 (1b-C$\underline{H}_3$), 19.0 (5-C$\underline{C}$), 22.8 (6a-C$\underline{C}$), 28.8 (1a-C$\underline{C}$), 35.7 (4-C$\underline{C}$), 38.0 (1b-C$\underline{C}$), 47.6 (2-C$\underline{C}$), 63.4 (O$\underline{C}H_2$), 64.2 (5a-C$\underline{C}$), 64.5 (O$\underline{C}H_2$), 104.7 (=$\underline{C}H_2$), 110.3 (3-C$\underline{C}$), 152.4 (6-C$\underline{C}$); HRMS (GCMS) found 221.1547 (M+H)$^+$, $C_{14}H_{21}O_2$ requires 221.1542.

(±)-(1aR,1bS,5aS,6aS)-1b-methyl-6-methyleneoctahydrocyclopropa[a]inden-3(1H)-one (17)

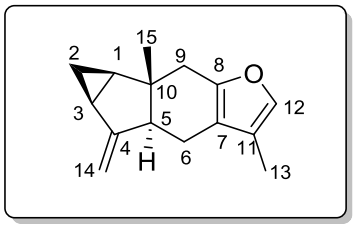


17

To a suspension of $PdCl_2(MeCN)_2$ (11mg, 5mol%) in acetone (20mL) was added a solution of ketal **16** (161mg, 0.73mmol) in acetone (5mL) and the mixture was stirred at RT for 6h. Evaporation to dryness *in vacuo* followed by flash chromatography of the residue using PE:Et_2O (10:1) afforded ketone **17** as a volatile, colourless oil (62mg, 64%);

R_f 0.2 (PE:Et_2O, 10:1); ν_{max}(film)/cm^{-1} 2942s, 1730s, 1654m, 1292m, 959s; δ_H(400MHz, $CDCl_3$) 0.56 (3H, s, 1b-C$\underline{H}_3$), 0.78-0.81 (1H, m, 1×1-C$\underline{H}$), 0.84-0.89 (1H, m, 1×1-C$\underline{H}$), 1.39-1.50 (2H, m, 1a-C$\underline{H}$, 1×5-C$\underline{H}$), 1.82-1.88 (1H, m, 1×5-C$\underline{H}$), 2.02 (1H, br t, *J* = 9.5Hz, 6a-C$\underline{H}$), 2.24 (1H, ddd, *J* = 8.0Hz, 11.5Hz, 16.5Hz, 1×4-C$\underline{H}$), 2.46 (1H, dd, *J* = 5.5Hz, 16.5Hz, 1×4-C$\underline{H}$), 2.54 (1H, d, *J* = 14.5Hz, 1×2-C$\underline{H}$), 2.61 (1H, d, *J* = 14.5Hz, 1×2-CH), 2.88 (1H, dd, *J* = 2.5Hz, 12.5Hz, 5a-C$\underline{H}$), 4.71 (1H, s, 1×=C$\underline{H}_2$), 5.00 (1H, s, 1×=C$\underline{H}_2$); δ_C(100.6MHz, $CDCl_3$) 16.7 (1-$\underline{C}$), 19.0 (1b-$\underline{C}H_3$), 20.1 (5-C), 23.2 (6a-$\underline{C}$), 27.4 (1a-$\underline{C}$), 39.7 (4-$\underline{C}$), 40.0 (1b-$\underline{C}$), 55.5 (2-$\underline{C}$), 61.8 (5a-$\underline{C}$), 106.0 (=$\underline{C}H_2$), 151.4 (6-$\underline{C}$), 211.7 (3-$\underline{C}$); HRMS (GCMS) found 177.1280 $(M+H)^+$, $C_{12}H_{17}O$ requires 177.1279.

(±)-Lindenene (1)

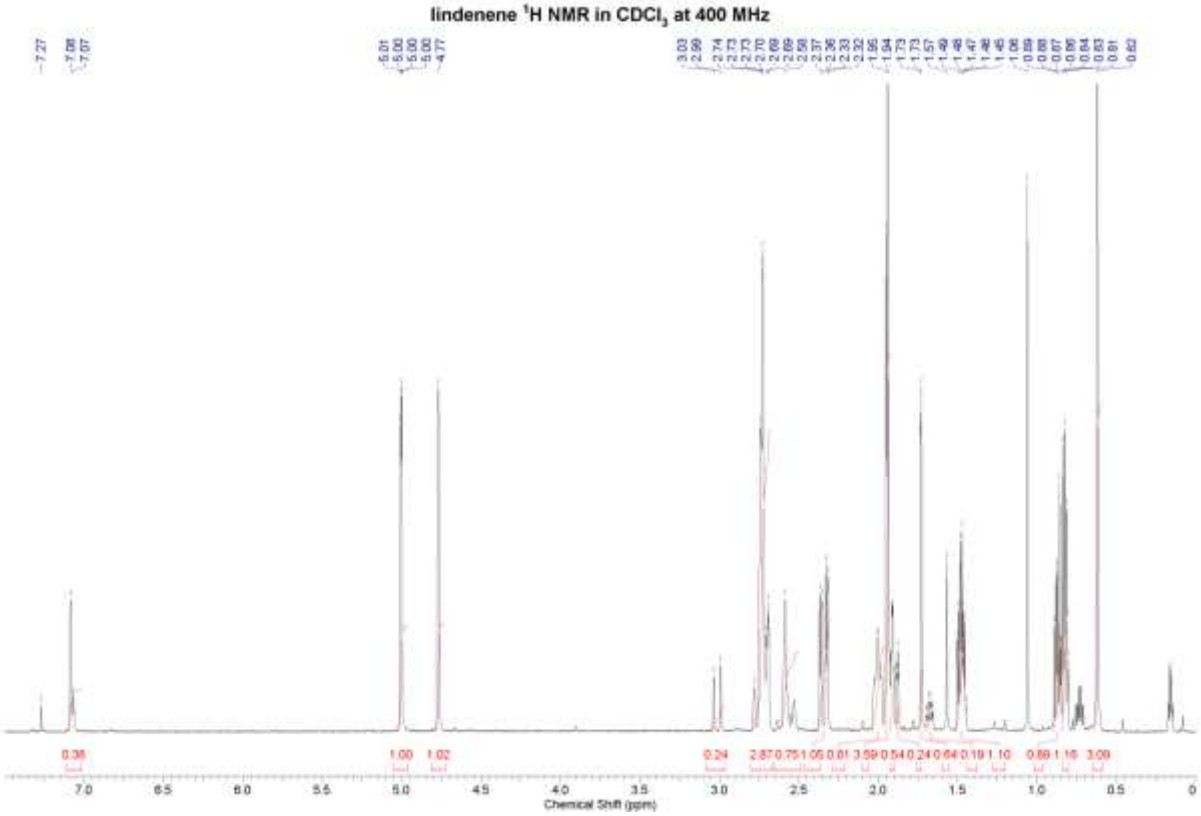


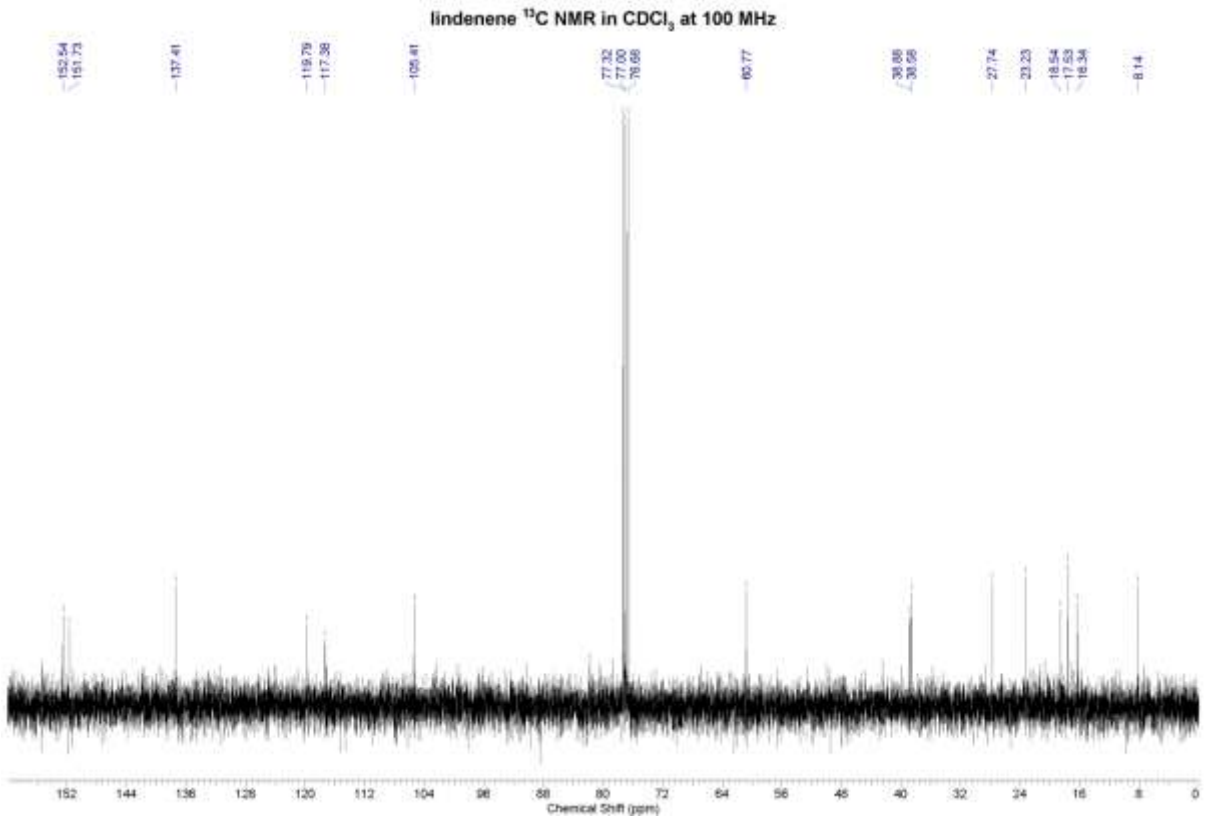
Ketone **17** (350mg, 1.55mmol) in anhydrous THF (5mL) was added drop-wise to a solution of LDA at -78°C prepared from diisopropylamine (161mg, 1.6mmol) and ^{n}BuLi (1.00mL, 1.6M, 1.6mmol) in THF (10mL) at -78°C. After stirring for 10 min, $ZnCl_2$ (1mL, 0.5M in THF, 0.5mmol) was added drop-wise followed immediately by THP-protected hydroxyacetone **18**[1, 2] (0.47g, 3mmol) in one portion and the reaction was warmed to 0°C. The mixture was stirred at that temperature for 4h and then quenched with sat. NH_4Cl (10mL) and allowed to warm to RT. The aqueous layer was extracted with Et_2O (50mL) and the organic phase washed with H_2O (30mL) and brine (30mL), dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude oil was immediately dissolved in THF (20mL) and H_2O (10mL), to which *p*-toluenesulphonic acid monohydrate 10mg) was added. The mixture was heated to 50°C and left to stir for 24h. Evaporation of the THF was achieved under reduced pressure and the resulting solution was neutralised with saturated aqueous $NaHCO_3$ (20mL) then extracted with Et_2O (50mL). The organic layer was washed with H_2O (50mL) and brine (50mL) and left to dry over anhydrous $MgSO_4$. Filtration and removal of the solvent *in vacuo* furnished a crude yellow oil which was purified by column chromatography (P.E. 30-40:benzene, 10:1) to yield lindenene (**1**) as a colourless oil (164mg, 47%).

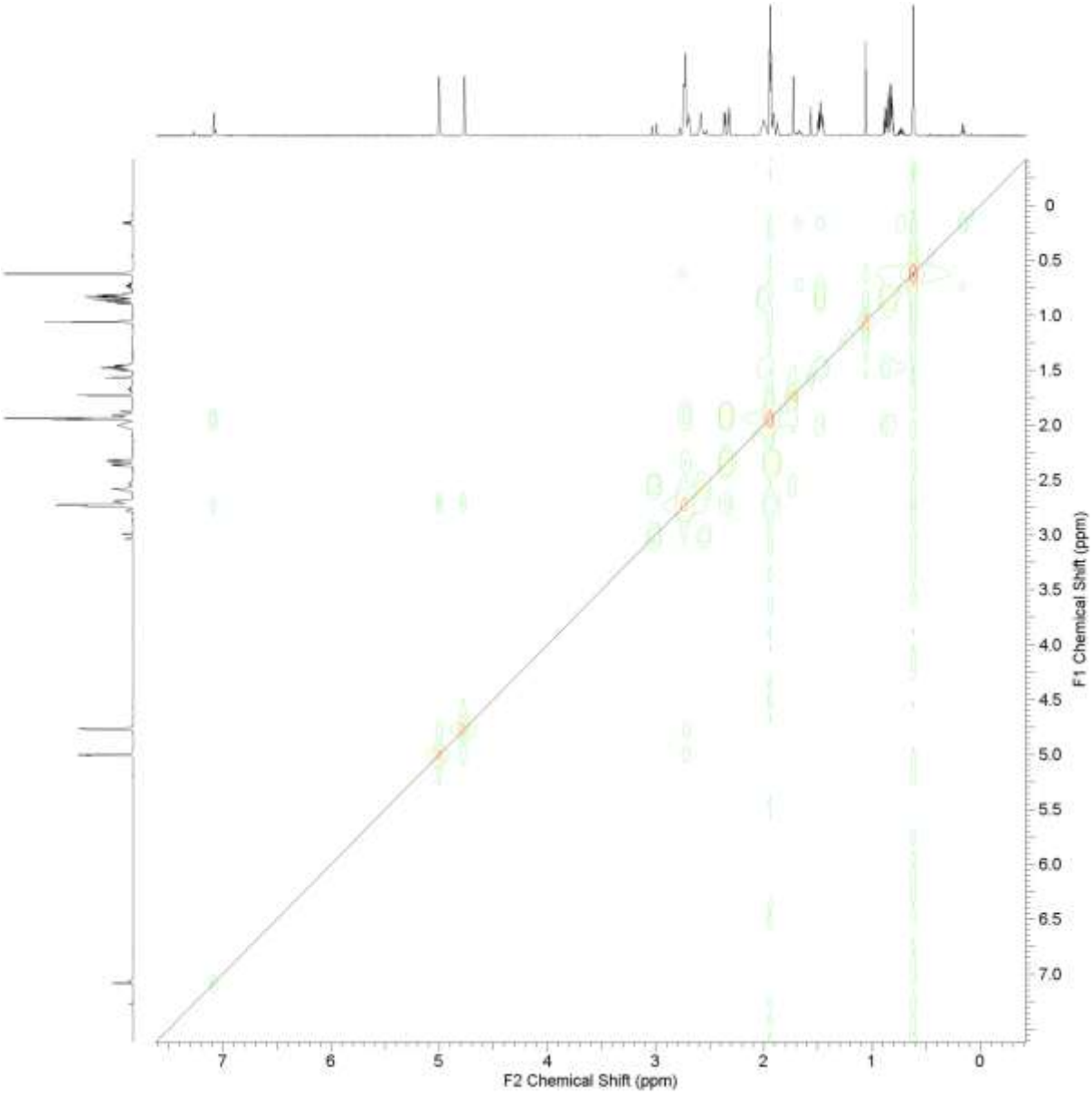
R_f 0.5 (P.E. 30-40); ν_{max}(film)/cm^{-1} 3070s, 1660m, 1625m, 1560s, 880s; δ_H(400MHz, $CDCl_3$) 0.63 (3H, s, 15-CH_3), 0.81-0.85 (1H, m, 2-CH), 0.86-0.90 (1H, m, 2-CH), 1.49 (1H, app dt, *J* = 3.5Hz,

7.5Hz, 1-CH), 1.90 (1H, dm, J = 15.0Hz, 6-CH), 1.95 (3H, s, 13-CH_3), 2.01 (1H, br t, J = 9.0Hz, 3-CH), 2.35 (1H, dd, J = 4.5Hz, 15.5Hz, 6-CH), 2.69-2.79 (3H, m, 9-CH_2, 5-CH), 4.78 (1H, s, 14-CH_b), 5.01 (1H, s, 14-CH_a), 7.09 (1H, br s, 12-CH); δ_c(100.6MHz, $CDCl_3$) 8.1 (13-C), 16.3 (2-CH), 17.5 (15-C), 18.5 (6-C), 23.2 (3-C), 27.7 (1-C), 38.6 (9-C), 38.9 (10-C), 60.8 (5-C), 105.4 (14-C), 117.4 (7-C), 119.8 (11-C), 137.4 (12-C), 151.7 (8-C), 152.5 (4-C); m/z $(EI)^+$ 232 $[(M+NH_4)^+$, 100%], 215 $[(M+H)^+$, 23], 196 [12], 155 [30], 123 [10], 96 [6]; HRMS $(CI)^+$ found 215.1439 $(M+H)^+$, $C_{15}H_{19}O$ requires 215.1436.

^1H and ^{13}C NMR data for (±)-Lindenene (**1**) in $CDCl_3$.







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