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Anisole: a further step to sustainable hydroformylation

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Supplementary Information

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1. Hydroformylation in ethanol solutions

Table S1. Hydroformylation of olefins in ethanol solutions[a]

Run	Substrate	Time (h)	*C* (%)	TOF[b] (h^{-1})	Selectivity (%) aldehydes[c]	Selectivity (%) acetals
1	1-Hexene (**1a**)	1.5	>99	990	95	5
		3	>99		84	16
2[d]	1-Hexene (**1a**)	1	>99	2200	87	13
3	1-Octene (**2a**)	2.0	>99	880	97	3
4	Styrene (**3a**)	1.5	98	990	100	-
5	Estragole (**4a**)	2.0	>99	740	95	5
6	Limonene (**5a**)	24	84	67	80	19
7	Carveol (**6a**)	24	75	80	99	traces
8	Perillyl alcohol (**7a**)	24	80	86	99	traces
9[e]	Myrtenol (**9a**)	24	50	9	50	49
10[f]	Nopol (**10a**)	48	47	4	35	65

[a] Conditions: substrate - 0.40 M (8 mmol), $[Rh(COD)(OMe)]_2$ - 0.25 mM (5 µmol), ligand - Ph_3P (P/Rh = 10), gas phase - 40 atm (CO/H_2 = 1/1), 80 ºC, ethanol - 20 mL. Conversion (*C*) and selectivity were calculated based on the substrate reacted using an internal standard (*p*-xylene). [b] TOF - turnover frequency (mol of the substrate converted per mol of Rh per hour) were calculated based on the slope of the nearly linear section of the kinetic curve for substrates **1a** – **4a** and at low conversions (≤ ca. 30-40%) for substrates **5a** – **10a** .[c] In the case of substrates **9a** and **10a**, hemiacetals **9c** and **10c** derived from aldehydes **9b** and **10b** are also included. [d] 100 ^{o}C. [e] Substrate - 0.20 M (4 mmol), ligand - 2,4-di-^{t}buPhO)$_3$P(P/Rh = 10), 100 ^{o}C. [f] Substrate - 0.20 M (4 mmol), ligand – (2,4-di-^{t}buPhO)$_3$P (P/Rh = 30), 120 ^{o}C.

2. Toluene *versus* anisole as solvents for hydroformylation

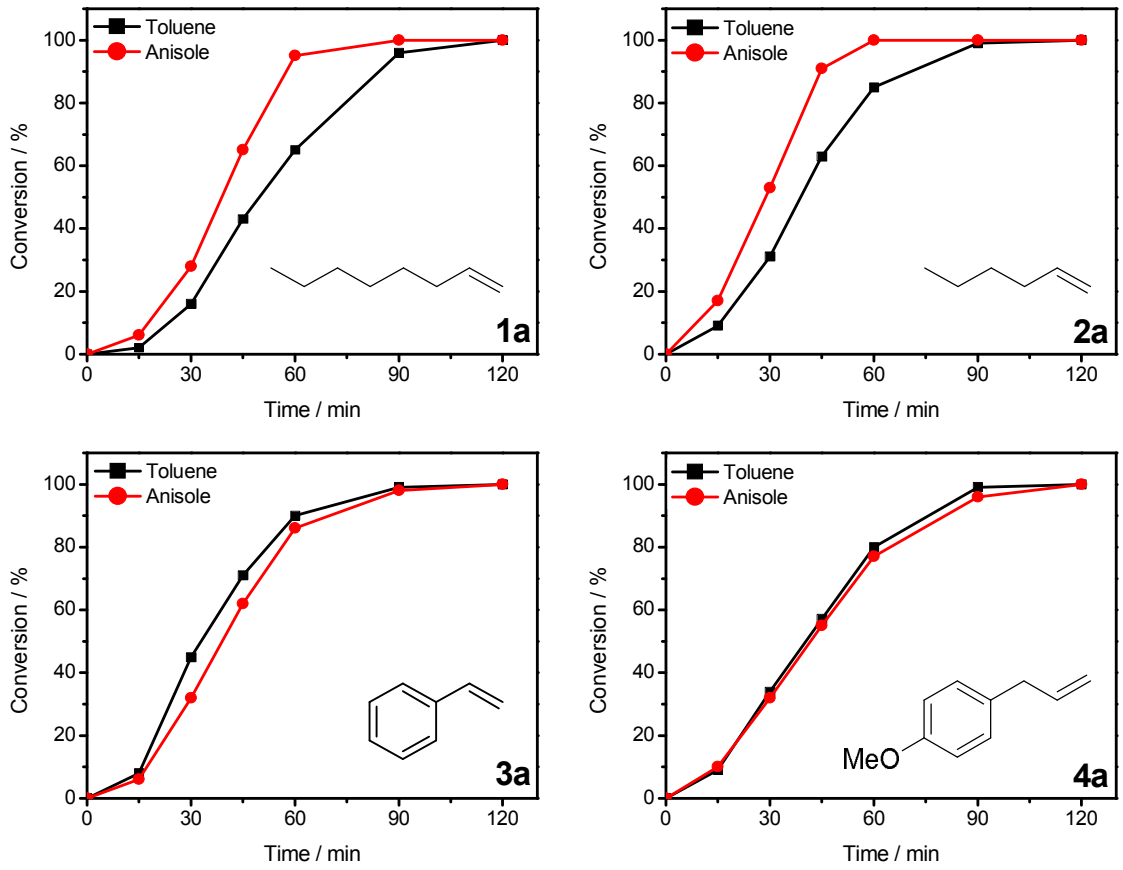


Figure S1 Hydroformylation of 1-octene (**1a**), 1-hexene (**2a**), styrene (**3a**), and estragole (**4a**) in toluene and anisole solutions. Conditions: substrate - 0.40 M (8 mmol), $[Rh(COD)(OMe)]_2$ - 0.25 mM (5 µmol), ligand - Ph_3P (P/Rh = 10), gas phase - 40 atm (CO/H_2 = 1/1), 80 ºC, solvent - 20 mL.

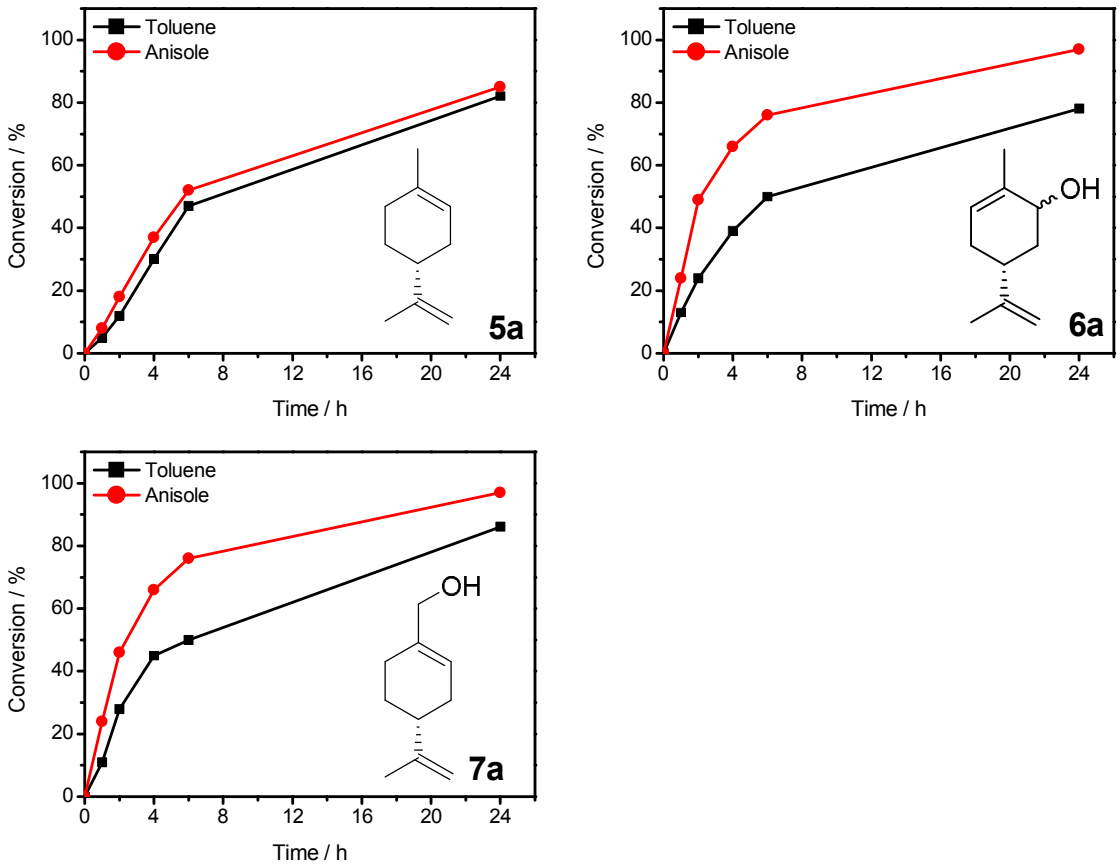
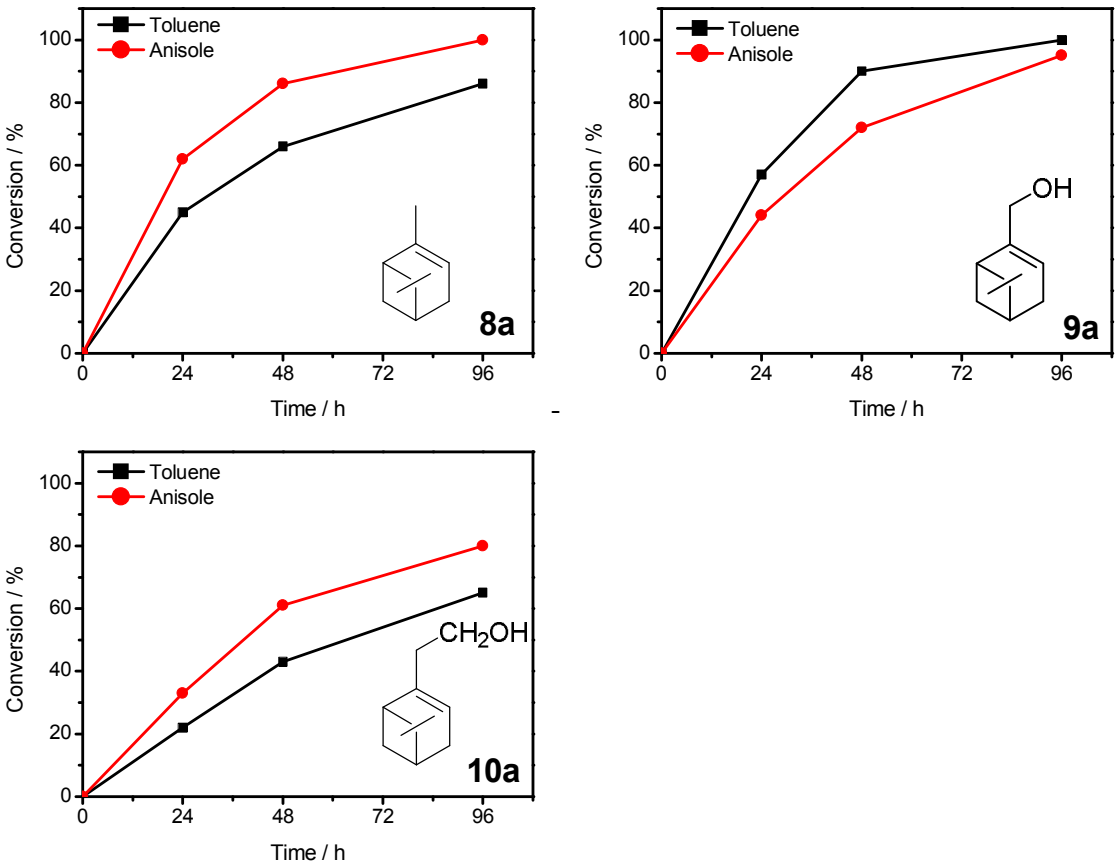


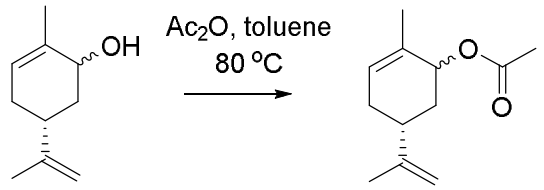
Figure S2 Hydroformylation of limonene (**5a**), carveol (**6a**), and perillyl alcohol (**7a**) in toluene and anisole solutions. Conditions: substrate - 0.40 M (8 mmol), $[Rh(COD)(OMe)]_2$ - 0.25 mM (5 µmol), ligand - Ph_3P (P/Rh = 10), gas phase - 40 atm (CO/H_2 = 1/1), 80 ºC, solvent - 20 mL.



Scheme S3 Hydroformylation of α-pinene (**8a**), myrtenol (**9a**), and nopol (**10a**) [b] in toluene and anisole solutions. Conditions: substrate - 0.40 M (8 mmol), $[Rh(COD)(OMe)]_2$ - 0.25 mM (5 µmol), ligand – (2,4-di- ^{t}buPhO)$_3$P (P/Rh = 10), gas phase - 80 atm (CO/H_2 = 1/1), 100 ºC, solvent - 20 mL. [b] P/Rh = 30, 120 ^{o}C.

3. Hydroformylation of carvyl acetate (11a)

3.1 Synthesis of carvyl acetate (**11a**)



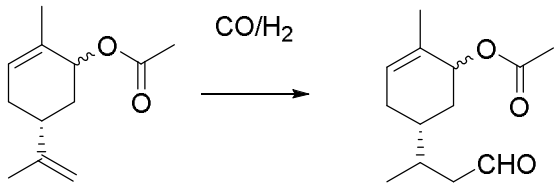
6a
Carveol

11a

A solution of carveol (0.2 mol), acetic anhydride (1 mol, 5 eq.) in toluene (60 mL) was transferred to a 100 mL homemade stainless steel pressure reactor with magnetic stirring. The solution was heated to 80 ^{o}C and stirrer. After 36 h, the reaction solution was analyzed by gas chromatography showing a quantitative yield of carvyl acetate. The reaction mixture was washed with saturated aqueous solution of $NaHCO_3$ (4x) and with brine. The organic phase was dried with anhydrous $MgSO_4$, filtered, and concentrated in vacuum. The crude was distilled in a Kugelrohr distillation apparatus at 70 ^{o}C and 10^{-1} mbar. The isolated compound **11a** was identified by GC-MS and by GC co-injection using an authentic sample (Sigma-Aldrich).

3.2 Hydrofomylation of carvyl acetate (**11a**)

Table S2. Hydroformylation of carvyl acetate (**11a**)[a]



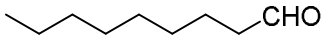
11a
Carvyl acetate

11b

Run	Substrate	Solvent	Time (h)	*C* (%)	TOF[b] (h^{-1})	Selectivity for aldehydes (%) linear	branched
1	Carvyl acetate (11a)	toluene	24	84	75	100 (11b)	
2	Carvyl acetate (11a)	anisole	24	89	70	100 (11b)	

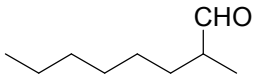
[a] Conditions: substrate - 0.40 M (8 mmol), $[Rh(COD)(OMe)]_2$ - 0.25 mM (5 µmol), ligand - Ph_3P (P/Rh = 10), gas phase – 40 atm (CO/H_2 = 1/1), 80 ºC, solvent - 20 mL. Conversion (*C*) and selectivity were calculated based on the substrate reacted using an internal standard (*p*-xylene). [b] TOF – initial turnover frequency (mol of the substrate converted per mol of Rh per hour) measured at low conversions (≤ ca. 30-40%).

4. Product characterization data



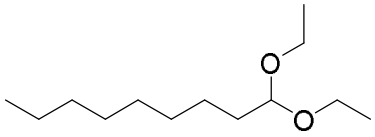
1b

Nonanal (1b): (linear, longer GC retention time): MS (70 eV, EI): m/z (%)141 (1) [M^+-H], 124 (1), 114 (5), 99 (6), 98 (29), 96 (20), 95 (21), 85 (3), 83 (10), 82 (23), 81 (26), 71 (18), 70 (48), 69 (39), 68 (32), 67 (28), 57 (100), 56 (60), 55 (47), 54 (12), 45 (15), 44 (53).



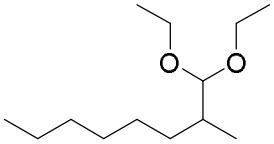
1c

2-methyloctanal (1c): (branched, shorter GC retention time): MS (70 eV, EI): m/z (%)100 (3), 95 (2), 92 (1), 91 (2), 85 (2), 84 (3), 71 (20), 69 (4), 68 (2), 67 (4), 59 (4), 58 (100), 57 (32), 56 (4), 55 (10).



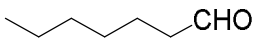
1d

1,1-diethoxynonane (1d): (linear, longer GC retention time): MS (70 eV, EI): m/z (%) 215 (0.2) [M^+-H], 187 (0.1) [M^+-C_2H_5], 171 (17) [M^+-C_2H_5O], 125 (1), 104 (5), 103 (100) [M^+-$C_5H_{11}O_2$], 85 (12), 83 (16), 75 (44), 72 (4), 69 (35), 67 (3), 57 (21), 55 (10), 48 (33), 44 (3).



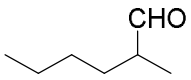
1e

1,1-diethoxy-2-methyloctane (1e): (branched, shorter GC retention time): MS (70 eV, EI): m/z (%) 171 (10) [M^+-C_2H_5O], 143 (1), 125 (2), 104 (6), 103 (100) [M^+-$C_5H_{11}O_2$], 99 (10), 86 (3), 83 (8), 75 (49), 71 (15), 69 (20), 57 (10), 55 (7), 47 (33).



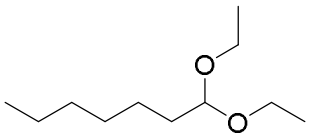
2b

Heptanal (2b): (linear, longer GC retention time): MS (70 eV, EI): m/z (%) 114 (0.4) [M^+], 86 (18), 81 (30), 68 (19), 69 (6), 71 (32), 70 (100), 68 (19), 57 (56), 55 (64), 45 (20), 44 (95).



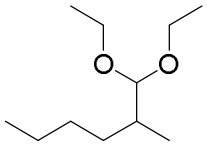
2c

2-methylhexanal (2c): (branched, shorter GC retention time): MS (70 eV, EI): m/z (%) 114 (0.3) [M^+], 85 (5) [M^+-CHO], 72 (5), 58 (100), 57 (29), 55 (8).



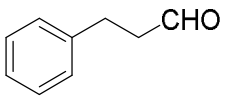
2d

1,1-diethoxyheptane (2d): (linear, longer GC retention time): MS (70 eV, EI): m/z (%) 187 (0.4) [M^+-H], 143 (32) [M^+-C_2H_5O), 103 (100) [M^+-$C_5H_{11}O_2$], 97 (39), 85 (11), 75 (55), 69 (10), 57 (20), 55 (38), 47 (42).



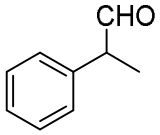
2e

1,1-diethoxy-2-methylhexane (2e): (branched, shorter GC retention time): MS (70 eV, EI): m/z (%) 143 (17) [M^+-C_2H_5O), 103 (100) [M^+-$C_5H_{11}O_2$], 97 (22), 75 (66), 71 (12), 56 (12), 55 (23), 47 (50).



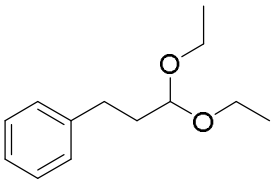
3b

3-phenylpropanal (3b): (linear, longer GC retention time): MS (70 eV, EI): m/z (%) 134 (49) [M^+], 133 (10), 115 (8), 116 (6), 117 (2), 105 (31) [M^+-CHO], 103 (15), 92 (89), 91 (100), 79 (24), 78 (44), 77 (31), 65 (21), 51 (18).



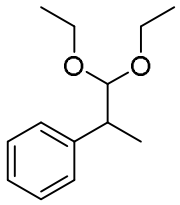
3c

2-phenylpropanal (3c): (branched, shorter GC retention time):MS (70 eV, EI): m/z (%) 134 (9) [M^+], 106 (12), 105 (100) [M^+-CHO], 103 (14), 91 (8), 79 (24), 77 (19), 63 (3), 51 (9).



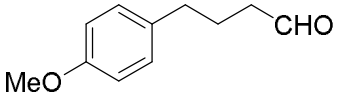
3d

(3,3-diethoxypropyl)benzene (3d): (branched, longer GC retention time): MS (70 eV, EI): m/z (%) 207 (17) [M^+-H], 163 (13) [M^+-C_2H_5O], 162 (24), 133 (18), 118 (16), 117 (49), 105, (31), 103 (87) [M^+-$C_5H_{11}O_2$], 91 (20), 91 (100), 44 (29), 45 (12), 47 (56), 65 (15), 75 (63), 77 (17), 78 (12), 79 (12).



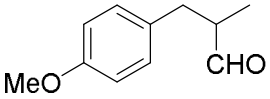
3e

(1,1-diethoxypropan-2-yl)benzene (3e): (branched, shorter GC retention time): MS (70 eV, EI): m/z (%)207 (6) [M^+-H], 163 (7) [M^+-C_2H_5O], 135 (20), 105 (37), 103 (100) [M^+-$C_5H_{11}O_2$], 91 (13), 79 (13), 77 (17), 75 (77), 47 (72).



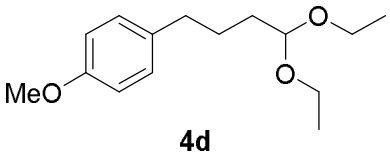
4b

4-(4-methoxyphenyl)butanal (4b): (linear, longer GC retention time): MS (70 eV, EI): m/z (%) 178 (12) [M^+], 135 (11) [M^+-CH_2CHO], 134 (100), 122 (8), 121 (81), 119 (9), 91 (12), 78 (8), 77 (12), 65 (4), 51 (3).



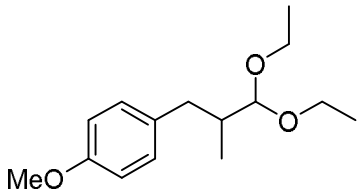
4c

3-(4-methoxyphenyl)-2-methylpropanal (4c): (branched, shorter GC retention time): MS (70 eV, EI): m/z (%) 178 (13) [M^+], 149, 134, 122 (9), 121 (100) [M^+-C_3H_5O], 91 (8), 78 (6), 77 (9), 65 (3), 51 (2).



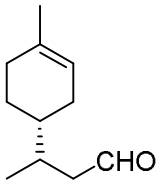
4d

1-(4,4-diethoxybutyl)-4-methoxybenzene (4d): (linear, longer GC retention time): MS (70 eV, EI): m/z (%) 207 (1) [M^+-C_2H_5O], 206 (4), 161 (27), 134 (100), 121 (47), 103 (8) [M^+-$C_5H_{11}O_2$], 91 (7), 85 (10), 75 (10), 57 (12), 47 (10).



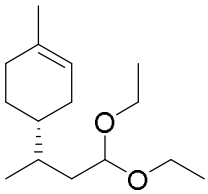
4e

1-(3,3-diethoxy-2-methylpropyl)-4-methoxybenzene (4e): (branched, shorter GC retention time): MS (70 eV, EI): m/z (%) 207 (6) [M^+-C_2H_5O], 206 (26), 191 (15), 177 (13), 161 (11), 121 (100), 103 (44) [M^+-$C_5H_{11}O_2$], 91 (12), 77 (11), 75 (49), 47 (35).



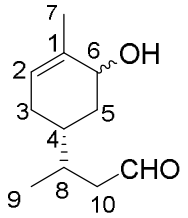
5b

(R)-3-((R)-4-methylcyclohex-3-en-1-yl)butanal (5b): MS (70 eV, EI): m/z (%) 166 (5) [M^+], 148 (29), 133 (33), 123 (7), 122 (12), 121 (24), 107 (30), 106 (38), 105 (17), 95 (58), 94 (20), 93 (100), 92 (47), 91 (31), 81 (23), 79 (35), 77 (19), 71 (17), 69 (14), 68 (40), 67 (73), 55 (26), 53 (15).



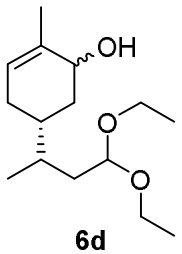
5d

(R)-4-((R)-4,4-diethoxybutan-2-yl)-1-methylcyclohex-1-ene(5d): MS (70 eV, EI): m/z (%) 194 (13)[M^+-C_2H_5OH], 149 (43), 148 (38), 133 (100), 121 (23), 119 (17), 107 (28), 106 (33), 105 (21), 103 (64) [M^+-$C_5H_{11}O_2$], 99 (65), 94 (20), 93 (71), 92 (24), 91 (23), 81 (28), 79 (25), 75 (63), 71 (59), 67 (23), 55 (19), 47 (54).



6b

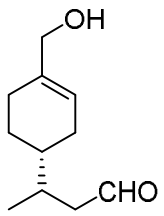
(3R)-3-((1R)-5-hydroxy-4-methylcyclohex-3-en-1-yl)butanal (6b): (novel compound; isolated as a mixture of four stereoisomers), the first pair of isomers (not separable by GC; shorter GC retention time): MS (70 eV, EI): m/z 182 (0.2) [M^+], 167 (0.8) [M^+-CH_3], 165 (0.4) [M^+-OH], 153 (0.2) [M^+-CHO], 137 (11), 121 (12), 120 (11), 111 (11), 110 (11), 109 (100), 108 (25), 107 (10), 95 (15), 93 (25), 91 (21), 84 (16), 81 (17), 79 (18), 77 (15), 69 (22), 55 (26); the second pair of isomers (not separable by GC; longer GC retention time): MS (70 eV, EI): m/z 167 (2) [M^+-CH_3], 165 (0.5) [M^+-OH], 153 (0.4) [M^+-CHO], 138 (14), 137 (23), 131 (30), 123 (10), 122 (8), 121 (18), 120 (57), 119 (41), 111 (22), 109 (100), 108 (16), 107 (16), 105 (38), 97 (12), 95 (29), 94 (20), 93 (75), 91 (45), 84 (31), 83 (26), 81 (28), 72 (16), 69 (49), 67 (26), 57 (17), 55 (54), 53 (15). ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, Me_4Si): δ=0.87, 0.88 and 0.89 (d, ^2J≈7 Hz, 3H; C^9H_3), 1.10–1.40 (m, 1H; C^5*H*H), 1.40–1.60 (m, 2H; C^3*H*H, C^4*H*), 1.68 and 1.70 (s, 3H; C^7H_3), 1.90–2.05 (m, 3H; C^3H*H*, C^5H*H*, C^8*H*), 2.10–2.25 (m, 1H; C^{10}*H*H), 2.30–2.50 (m, 1H; C^{10}H*H*), 3.92 and 4.08 (br.s, 1H; C^6*H*), 5.37 and 5.47 (br.s, 1H; C^2*H*), 9.68 ppm (br. d, ^3J≈2 Hz, 1H; C*H*O); ^{13}C NMR (100 MHz, $CDCl_3$, 25°C, TMS): δ=16.64, 16.81, 17.02 and 17.24 (C^9); 18.98 and 21.02 (C^7); 28.33, 28.37, 29.51 and 29.59 (C^3); 32.01, 32.12, 32.22 and 32.25 (C^8); 32.71, 32.87, 38.21 and 38.42 (C^4); 34.80, 35.87, 36.28 and 37.32 (C^5); 48.32, 48.47, 48.49 and 48.82 (C^{10}); 68.42, 68.47, 70.92 and 70.96 (C^6); 123.56, 123.60 and 125.17 (C^2); 134.78, 134.81 and 136.93 (C^1); 203.08, 203.11, 203.25 and 203.30 ppm (*C*HO).



6d

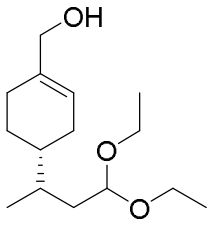
(5R)-5-((R)-4,4-diethoxybutan-2-yl)-2-methylcyclohex-2-en-1-ol (6d): minor isomer (*trans*, shorter GC retention time): MS (70 eV, EI): m/z (%) 211 (1) [M^+-C_2H_5O], 165 (23), 164 (27),

149 (16), 147 (16), 131 (48), 123 (12), 121 (32), 119 (18), 109 (100), 108 (30), 105 (37), 103 (99) [M^+-$C_5H_{11}O_2$], 99 (60), 95 (22), 93 (28), 91 (22), 81 (29), 77 (14), 75 (79), 71 (61), 56 (17), 55 (26), 47 (55); major isomer (*cis*, longer GC retention time): MS (70 eV, EI): m/z (%) 211 (1)[M^+-C_2H_5O], 165 (12), 164 (14), 149 (17), 147 (24), 146 (19), 131 (74), 120 (66), 119 (47), 109 (34), 107 (18), 105 (72), 103 (91)[M^+-$C_5H_{11}O_2$], 100 (19), 99 (100), 93 (56), 91 (33), 81 (28), 79 (22), 77 (18), 75 (83), 72 (24), 71 (86), 69 (16), 57 (16), 55 (32), 47 (60).



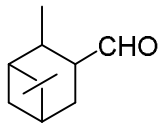
7b

(R)-3-((R)-4-(hydroxymethyl)cyclohex-3-en-1-yl)butanal (7b): MS (70 eV, EI): m/z (%) 164 (1) [M^+-H_2O],121 (13), 120 (100), 109 (10), 107 (21), 105 (17), 95 (6), 94 (8), 93 (31), 92 (11), 91 (29), 83 (6), 81 (15), 79 (38), 77 (16), 71 (8), 69 (9), 67 (17), 57 (7), 55 (21), 53 (6).



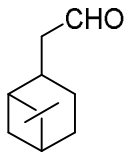
7d

((R)-4-((R)-4,4-diethoxybutan-2-yl)cyclohex-1-en-1-yl)metanol (**7d)**: MS (70 eV, EI): m/z (%) 210 (1) [M^+-C_2H_5OH], 165 (14), 147 (22), 135 (17), 131 (24), 120 (21), 118 (24), 109 (17), 107 (37), 105 (41), 103 (100) [M^+-$C_5H_{11}O_2$], 99 (92), 95 (13), 93 (30), 91 (45), 81 (24), 79 (47), 77 (17), 75 (86), 71 (82), 59 (16), 57 (14), 55 (26), 47 (63), 45 (12).



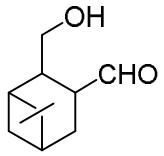
8b

2,6,6-trimethylbicyclo[3.1.1]heptane-3-carbaldehyde (8b): (linear, longer GC retention time): MS (70 eV, EI): m/z (%) 166 (0.3) [M^+], 151 (5), 137 (16), 123 (16), 111 (84), 93 (96), 83 (94), 67 (64), 55 (100), 41 (78).



8d

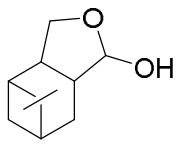
2-(6,6-dimethylbicyclo[3.1.1]heptan-2-yl)acetaldehyde (8d): major isomer **8d** (*trans*, shorter GC retention time): MS (70 eV, EI): m/z (%) 166 (1.1) [M^+], 151 (17) [M^+-CH_3], 133 (22), 123 (44), 122 (75), 111 (19), 110 (15), 109 (23), 107 (57), 105 (26), 95 (30), 93 (36), 91 (25), 83 (36), 82 (46), 81 (61), 80 (24), 79 (100), 78 (23), 77 (19), 69 (62), 68 (19), 67 (67), 66 (17), 56 (19), 55 (89); minor isomer **8d** (*cis*, longer GC retention time): MS (70 eV, EI): m/z (%) 166 (0.5) [M^+], 151 (11) [M^+-CH_3], 133 (16), 123 (34), 122 (57), 109 (18), 107 (49), 105 (22), 95 (28), 93 (30), 91 (24), 83 (29), 82 (45), 81 (56), 80 (23), 79 (100), 78 (21), 77 (20), 69 (64), 68 (20), 67 (68), 66 (17), 56 (17), 55 (90).



9b

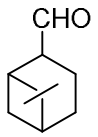
2-(hydroxymethyl)-6,6-dimethylbicyclo[3.1.1]heptane-3-carbaldehyde (9b): major isomer **9b** (*trans*, shorter GC retention time): MS (70 eV, EI): m/z (%) 164 (18) [M^+-H_2O], 149 (24), 135 (21), 133 (18), 121 (35), 119 (37), 112 (29), 111 (75), 109 (24), 108 (24), 107 (41), 105 (34), 97 (22), 95 (61), 94 (20), 93 (85), 91 (84), 83 (27), 82 (20), 81 (56), 80 (22), 79 (100), 77

(53), 69 (68), 68 (41), 67 (63), 65 (18), 57 (16), 55 (48); minor isomer **9b** (*cis*, longer GC retention time): MS (70 eV, EI): m/z (%) 167 (7) [M^+-CH_3], 164 (3) [M^+-H_2O], 149 (17), 135 (28), 133 (15), 123 (24), 121 (37), 109 (20), 108 (15), 107 (60), 105 (27), 95 (45), 94 (18), 93 (100), 92 (20), 91 (75), 83 (43), 82 (51), 81 (59), 80 (20), 79 (96), 77 (49), 70 (27), 69 (96), 67 (70), 65 (16), 57 (21), 55 (65).



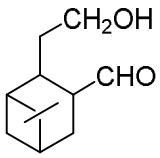
9c

5,5-dimethyloctahydro-4,6-methanoisobenzofuran-1-ol (9c): MS (70 eV, EI): m/z (%) 182 (0.2) [M^+], 164 (43) [M^+-H_2O], 149 (38), 125 (41), 121 (44), 119 (19), 111 (41), 109 (19), 108 (23), 107 (33), 105 (20), 97 (18), 96 (15), 95 (78), 94 (20), 93 (92), 91 (67), 83(25), 82 (36), 81 (56), 80 (30), 79 (100), 77 (41), 69 (53), 68 (19), 67 (58), 55 (36).



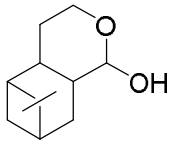
9d

6,6-dimethylbicyclo[3.1.1]heptane-2-carbaldehyde (9d): major isomer **9d** (longer GC retention time): MS (70 eV, EI): m/z (%) 152 (0.5) [M^+], 137 (17) [M^+-CH_3], 123 (45), 109 (29), 83 (49), 82 (86), 81 (68), 79 (43), 70 (33), 69 (82), 68 (19), 67 (100), 55 (37); minor isomer **9d** (shorter GC retention time): MS (70 eV, EI): m/z (%) 152 (0.5) [M^+], 137 (17) [M^+-CH_3], 123 (45), 109 (29), 83 (49), 82 (68), 81 (68), 79 (43), 70 (33), 69 (82), 68 (19), 67 (100), 55 (37).



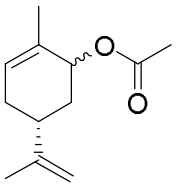
10b

2-(2-hydroxyethyl)-6,6-dimethylbicyclo[3.1.1]heptane-3-carbaldehyde (10b): major isomer **10b** (*trans*, shorter GC retention time): MS (70 eV, EI): m/z (%) 181 (2) [M^+-CH_3], 178 (3) [M^+-H_2O], 163 (24) [M^+-CH_3-H_2O], 151 (29), 147 (20), 135 (30), 121 (24), 112 (21), 111 (100), 109 (27), 107 (47), 105 (43), 95 (77), 94 (22), 93 (57), 91 (46), 83 (36), 81 (49), 79 (86), 77 (29), 69 (88), 67 (64), 55 (71); minor isomer **10b** (*cis*, longer GC retention time): MS (70 eV, EI): m/z (%) 181 (9) [M^+-CH_3], 178 (0.4) [M^+-H_2O], 163 (6) [M^+-CH_3-H_2O], 123 (31), 121 (30), 111 (43), 109 (44), 108 (19), 107 (48), 105 (29), 98 (23), 95 (53), 93 (74), 91 (41), 83 (46), 82 (28), 81 (62), 79 (67), 77 (28), 69 (100), 67 (71), 57 (20), 55 (87).



10c

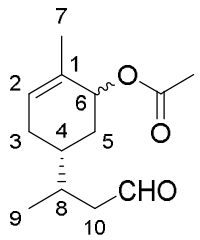
6,6-dimethyloctahydro-1H-5,7-methanoisochromen-1-ol (10c): major isomer **10c** (shorter GC retention time): MS (70 eV, EI): m/z (%) 181 (2) [M^+-CH_3], 178 (2) [M^+-H_2O], 165 (25), 147 (20), 123 (61), 122 (53), 121 (29), 109 (21), 107 (42), 105 (17), 95 (43), 93 (34), 91 (20), 83 (22), 82 (35), 81 (99), 79 (72), 78 (20), 77 (16), 69 (100), 67 (97), 55 (51); minor isomer **10c** (longer GC retention time): MS (70 eV, EI): m/z (%) 165 (20), 147 (14), 123 (52), 122 (43), 121 (23), 109 (20), 107 (36), 105 (15), 95 (41), 93 (31), 91 (21), 83 (20), 82 (33), 81 (92), 79 (63), 78 (15), 77 (16), 69 (100), 67 (86), 55 (50).



11a
Carvyl acetate

(5R)-2-methyl-5-(prop-1-en-2-yl)cyclohex-2-en-1-yl acetate(11a): (isolated as a mixture of two stereoisomers), the first isomer (shorter GC retention time): MS (70 eV, EI): m/z 194 (1), 152 (67), 134 (32), 119 (100), 109 (99), 108 (19), 107 (18), 105 (35), 93 (38), 92 (38), 91 (84),

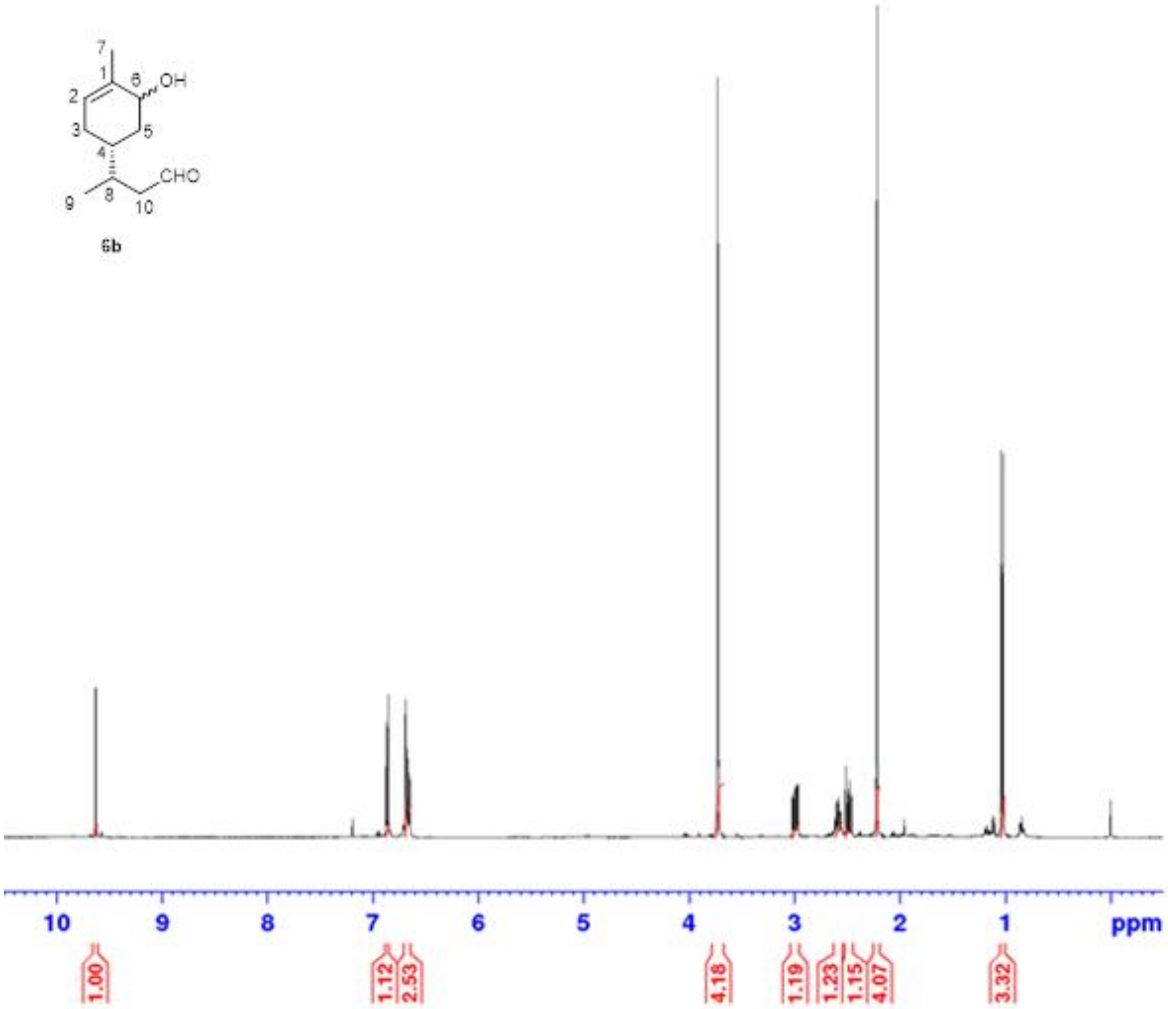
84 (82), 79 (30), 77 (31), 55 (22); the second isomer (longer GC retention time): MS (70 eV, EI): m/z 152 (46), 134 (42), 119 (90), 109 (79), 108 (17), 105 (35), 93 (32), 92 (36), 91 (79), 84 (100), 79 (29), 77 (28), 55 (22).



11b

(5R)-2-methyl-5-((R)-4-oxobutan-2-yl)cyclohex-2-en-1-yl acetate (11b): (novel compound; isolated as a mixture of four stereoisomers) the first pair of isomers (not separable by GC; shorter GC retention time): MS (70 eV, EI): m/z 182 (40), 164 (28), 149 (8), 138 (7), 131 (25), 121 (24), 120 (41), 119 (36), 110 (11), 109 (100), 108 (46), 105 (57), 95 (11), 94 (17), 93 (71), 92 (17), 91 (48), 84 (13), 81 (12), 79 (30) 77 (30), 72 (8); the second pair of isomers (not separable by GC; longer GC retention time): MS (70 eV, EI): m/z 182 (29), 164 (12), 131 (29), 121 (20), 120 (49), 119 (42), 110 (11), 109 (100), 108 (45), 105 (57), 95 (11), 94 (18), 93 (73), 92 (17), 91 (49), 84 (14), 81 (12), 79 (33), 77 (30), 72 (11), 69 (11), 67 (9), 57 (11), 55 (18). ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, Me_4Si): δ=0.83, 0.85 and 0.86 (d, ^{2}J≈7 Hz, 3H; $C^{9}H_3$), 1.10–1.40 (m, 1H; $C^{5}HH$), 1.50–2.00 (m, 5H; $C^{3}H_2$, $C^{4}H$, $C^{5}HH$, $C^{8}H$), 1.53 and 1.58 (s, 3H; $C^{7}H_3$), 1.97 (s, 3H, $OCOCH_3$), 2.10–2.25 (m, 1H; $C^{10}HH$), 2.35–2.45 (m, 1H; $C^{10}HH$), 5.12 and 5.29 (br.s, 1H; $C^{6}H$), 5.48 and 5.61 (br.s, 1H; $C^{2}H$), 9.66 ppm (br. s, 1H; C*H*O); ^{13}C NMR (100 MHz, $CDCl_3$, 25°C, TMS): δ=16.02, 16.40 and 16.53 (C^{9}); 18.33 and 20.18 (C^{7}); 20.62, 20.78 and 20.79 ($OCOCH_3$); 27.39, 27.52, 28.64 and 28.76 (C^{3}); 31.03, 31.15, 31.28 and 31.44 (C^{8}); 31.22, 31.64, 32.29 and 32.63 (C^{5}); 32.82, 32.99, 37.17 and 37.42 (C^{4}); 47.66, 47.76, 47.84 and 48.08 (C^{10}); 70.06, 70.11, 72.56 and 72.60 (C^{6}); 125.13, 125.17 and 127.28 (C^{2}); 130.77, 130.80 and 132.79 (C^{1}); 170.23 and 170.25 ($OCOCH_3$); 201.71, 201.75, 201.80 and 201.84 ppm (*C*HO).

5. NMR data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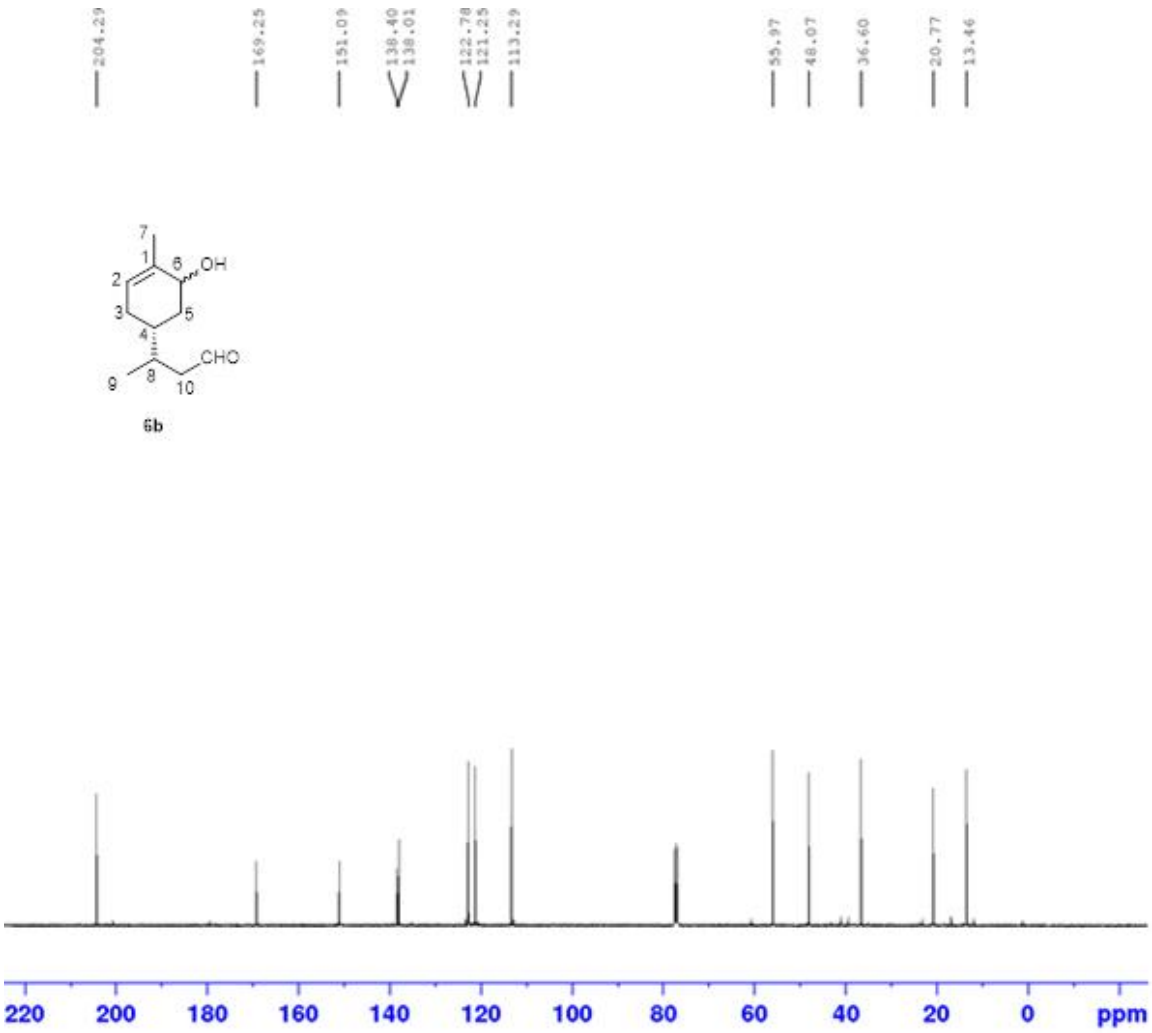
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140
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100
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ppm

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2
6
O
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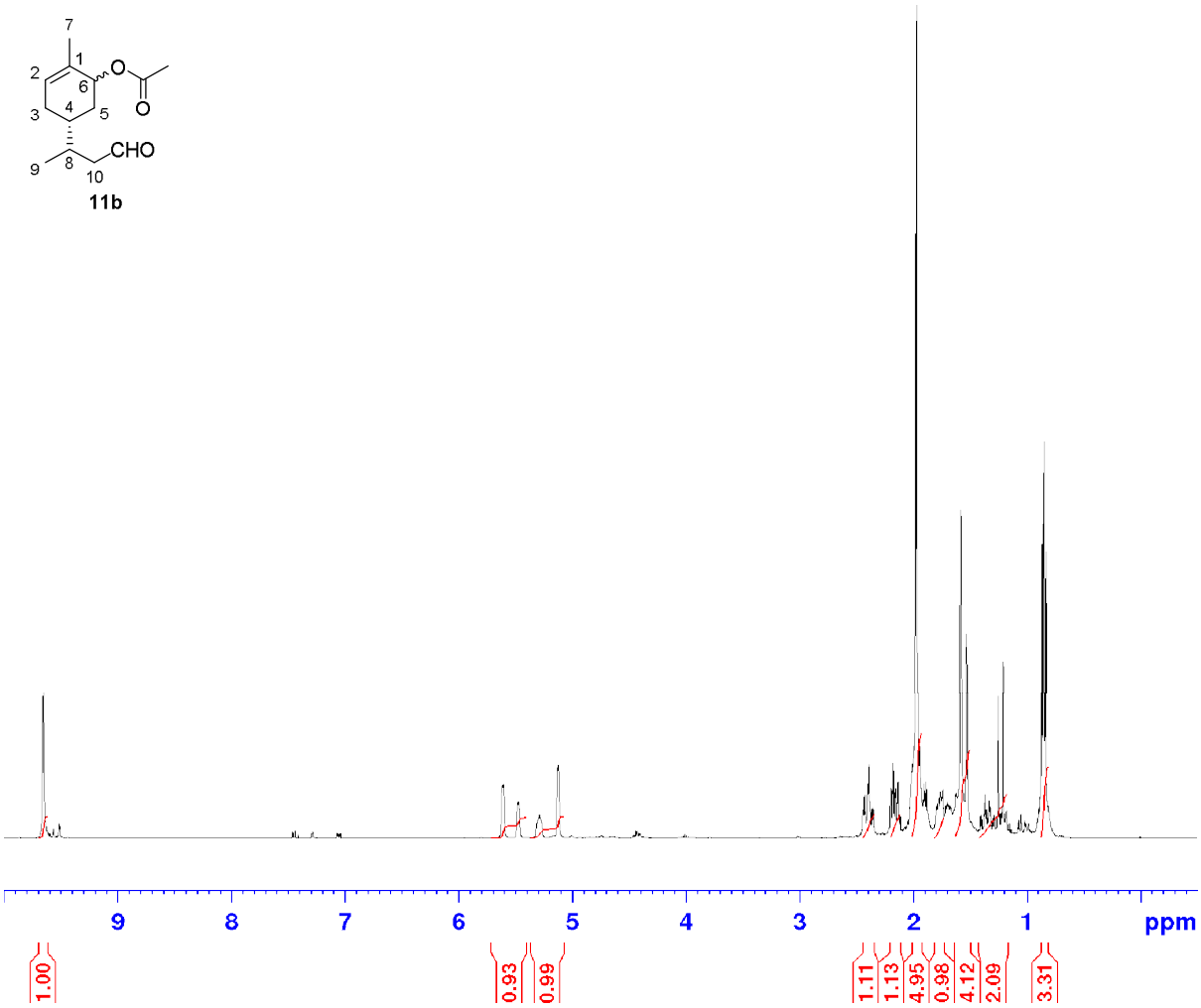
4
5
O
CHO
9
8
10

11b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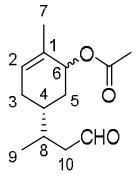
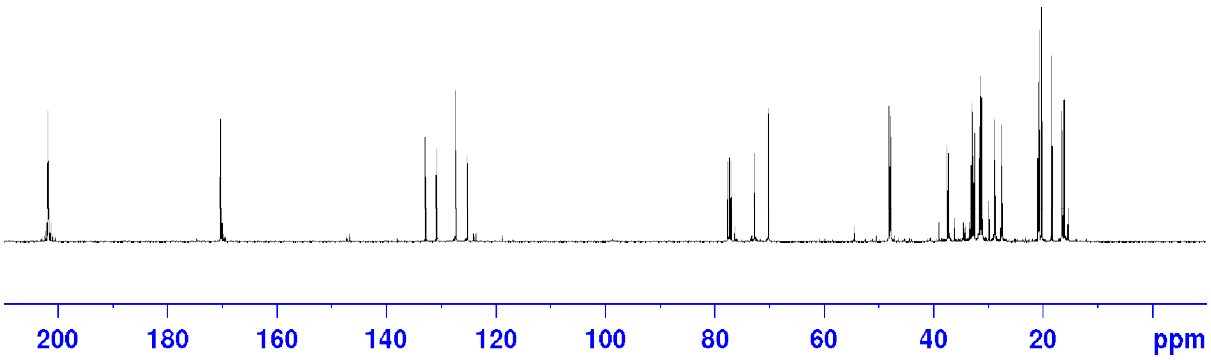
11b