Anisole: a further step to sustainable hydroformylation

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Supplementary Information

1. Hydroformylation in ethanol solutions ......................................................................................... 2
2. Toluene versus anisole as solvents for hydroformylation ............................................................... 3
3. Hydroformylation of carvyl acetate (11a) .................................................................................... 6
4. Product characterization data ........................................................................................................... 8
5. NMR data ....................................................................................................................................... 19
1. Hydroformylation in ethanol solutions

Table S1. Hydroformylation of olefins in ethanol solutions

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

$^a$ Conditions: substrate - 0.40 M (8 mmol), [Rh(COD)(OMe)]$_2$ - 0.25 mM (5 µmol), ligand - Ph$_3$P (P/Rh = 10), gas phase - 40 atm (CO/H$_2$ = 1/1), 80 °C, 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 °C. $^e$ Substrate - 0.20 M (4 mmol), ligand - 2,4-di-°BuPhO)$_3$P (P/Rh = 10), 100 °C. $^f$ Substrate - 0.20 M (4 mmol), ligand – (2,4-di-°BuPhO)$_3$P (P/Rh = 30), 120 °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 - Ph₃P (P/Rh = 10), gas phase - 40 atm (CO/H₂ = 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 - Ph₃P (P/Rh = 10), gas phase - 40 atm (CO/H₂ = 1/1), 80 °C, 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-^\textsuperscript{t}BuPhO)\(_3\)P (P/Rh = 10), gas phase - 80 atm (CO/H\(_2\) = 1/1), 100 °C, solvent - 20 mL.\(^b\) P/Rh = 30, 120 °C.
3. Hydroformylation of carvyl acetate (11a)

3.1 Synthesis of carvyl acetate (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 °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 NaHCO₃ (4x) and with brine. The organic phase was dried with anhydrous MgSO₄, filtered, and concentrated in vacuum. The crude was distilled in a Kugelrohr distillation apparatus at 70 °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 Hydroformylation of carvyl acetate (11a)

Table S2. Hydroformylation of carvyl acetate (11a)\(^a\)

<table>
<thead>
<tr>
<th>Run</th>
<th>Substrate</th>
<th>Solvent</th>
<th>Time (h)</th>
<th>(C) (%)</th>
<th>TOF(^b) (h(^{-1}))</th>
<th>Selectivity for aldehydes (%) linear branched</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Carvyl acetate (11a)</td>
<td>toluene</td>
<td>24</td>
<td>84</td>
<td>75</td>
<td>100 (11b)</td>
</tr>
<tr>
<td>2</td>
<td>Carvyl acetate (11a)</td>
<td>anisole</td>
<td>24</td>
<td>89</td>
<td>70</td>
<td>100 (11b)</td>
</tr>
</tbody>
</table>

\(^a\) Conditions: substrate - 0.40 M (8 mmol), [Rh(COD)(OMe)]\(_2\) - 0.25 mM (5 \(\mu\)mol), ligand - Ph\(_3\)P (P/Rh = 10), gas phase – 40 atm (CO/H\(_2\) = 1/1), 80 \(^\circ\)C, 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 (\(\leq\) ca. 30-40%).
4. Product characterization data

**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).

**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).

**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$_2$H$_5$], 171 (17) [M$^+$-C$_2$H$_5$O], 125 (1), 104 (5), 103 (100) [M$^+$-C$_5$H$_{11}$O$_2$], 85 (12), 83 (16), 75 (44), 72 (4), 69 (35), 67 (3), 57 (21), 55 (10), 48 (33), 44 (3).
**1,1-diethoxy-2-methyloctane (1e):** (branched, shorter GC retention time): MS (70 eV, EI): m/z (%) 171 (10) [M⁺-C₅H₅O], 143 (1), 125 (2), 104 (6), 103 (100) [M⁺-C₅H₁₁O₂], 99 (10), 86 (3), 83 (8), 75 (49), 71 (15), 69 (20), 57 (10), 55 (7), 47 (33).

![2b](image)

**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](image)

**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](image)

**1,1-diethoxyheptane (2d):** (linear, longer GC retention time): MS (70 eV, EI): m/z (%) 187 (0.4) [M⁺-H], 143 (32) [M⁺-C₅H₅O], 103 (100) [M⁺-C₅H₁₁O₂], 97 (39), 85 (11), 75 (55), 69 (10), 57 (20), 55 (38), 47 (42).

![2e](image)
1,1-diethoxy-2-methylhexane (2e): (branched, shorter GC retention time): MS (70 eV, EI): m/z (%) 143 (17) [M+–C$_2$H$_5$O], 103 (100) [M+–C$_5$H$_{11}$O$_2$], 97 (22), 75 (66), 71 (12), 56 (12), 55 (23), 47 (50).

![3b](image)

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](image)

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](image)

(3,3-diethoxypropyl)benzene (3d): (branched, longer GC retention time): MS (70 eV, EI): m/z (%) 207 (17) [M$^+$–H], 163 (13) [M$^+$–C$_2$H$_5$O], 162 (24), 133 (18), 118 (16), 117 (49), 105 (31), 103 (87) [M$^+$–C$_5$H$_{11}$O$_2$], 91 (20), 91 (100), 44 (29), 45 (12), 47 (56), 65 (15), 75 (63), 77 (17), 78 (12), 79 (12).
(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+-C₂H₅O], 135 (20), 105 (37), 103 (100) [M+-C₅H₁₁O₂], 91 (13), 79 (13), 77 (17), 75 (77), 47 (72).

4-(4-methoxyphenyl)butanal (4b): (linear, longer GC retention time): MS (70 eV, EI): m/z (%) 178 (12) [M⁺], 135 (11) [M⁺-CH₂CHO], 134 (100), 122 (8), 121 (81), 119 (9), 91 (12), 78 (8), 77 (12), 65 (4), 51 (3).

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⁺-C₃H₅O], 91 (8), 78 (6), 77 (9), 65 (3), 51 (2).

1-(4,4-diethoxybutyl)-4-methoxybenzene (4d): (linear, longer GC retention time): MS (70 eV, EI): m/z (%) 207 (1) [M⁺-C₂H₅O], 206 (4), 161 (27), 134 (100), 121 (47), 103 (8) [M⁺-C₅H₁₁O₂], 91 (7), 85 (10), 75 (10), 57 (12), 47 (10).
1-(3,3-diethoxy-2-methylpropyl)-4-methoxybenzene (4e): (branched, shorter GC retention time): MS (70 eV, El): m/z (%) 207 (6) [M$^+\cdot$C$_2$H$_5$O], 206 (26), 191 (15), 177 (13), 161 (11), 121 (100), 103 (44) [M$^+\cdot$C$_5$H$_{11}$O$_2$], 91 (12), 77 (11), 75 (49), 47 (35).

(R)-3-((R)-4-methylcyclohex-3-en-1-yl)butanal (5b): MS (70 eV, El): 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).

(R)-4-((R)-4,4-diethoxybutan-2-yl)-1-methylcyclohex-1-ene (5d): MS (70 eV, El): m/z (%) 194 (13)[M$^+\cdot$C$_2$H$_5$OH], 149 (43), 148 (38), 133 (100), 121 (23), 119 (17), 107 (28), 106 (33), 105 (21), 103 (64) [M$^+\cdot$C$_5$H$_{11}$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).
(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, El): m/z 182 (0.2) [M+], 167 (0.8) [M+CH3], 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, El): m/z 167 (2) [M+], 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). 1H NMR (400 MHz, CDCl3, 25°C, Me4Si): δ=0.87, 0.88 and 0.89 (d, 2J≈7 Hz, 3H; C9H3), 1.10–1.40 (m, 1H; C5H), 1.68 and 1.70 (s, 3H; C7H3), 1.90–2.05 (m, 3H; C3HH, C5HH, C6H), 2.10–2.25 (m, 1H; C10HH), 2.30–2.50 (m, 1H; C10HH), 3.92 and 4.08 (br.s, 1H; C6H), 5.37 and 5.47 (br.s, 1H; C2H), 9.68 ppm (br. d, 3J=2 Hz, 1H; CHO); 13C NMR (100 MHz, CDCl3, 25°C, TMS): δ=16.64, 16.81, 17.02 and 17.24 (C9); 18.98 and 21.02 (C7); 28.33, 28.37, 29.51 and 29.59 (C3); 32.01, 32.12, 32.22 and 32.25 (C5); 32.71, 32.87, 38.21 and 38.42 (C4); 34.80, 35.87, 36.28 and 37.32 (C5); 48.32, 48.47, 48.49 and 48.82 (C10); 68.42, 68.47, 70.92 and 70.96 (C6); 123.56, 123.60 and 125.17 (C2); 134.78, 134.81 and 136.93 (C1); 203.08, 203.11, 203.25 and 203.30 ppm (CHO).

(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, El): m/z (%) 211 (1) [M+-C2H5O], 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+ - C₅H₁₁O₂], 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 [M+ - C₂H₅O], 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+ - C₅H₁₁O₂], 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).

(R)-3-((R)-4-(hydroxymethyl)cyclohex-3-en-1-yl)butanal (7b): MS (70 eV, EI): m/z (%) 164 [M+ - H₂O], 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).

((R)-4-((R)-4,4-diethoxybutan-2-yl)cyclohex-1-en-1-yl)metanol (7d): MS (70 eV, EI): m/z (%) 210 (1) [M+ - C₂H₅OH], 165 (14), 147 (22), 135 (17), 131 (24), 120 (21), 118 (24), 109 (17), 107 (37), 105 (41), 103 (100) [M+ - C₅H₁₁O₂], 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).
2,6,6-trimethylbicyclo[3.1.1]heptane-3-carbaldehyde (8b): (linear, longer GC retention time): MS (70 eV, El): m/z (%) 166 (0.3) \([M^+]\), 151 (5), 137 (16), 123 (16), 111 (84), 93 (96), 83 (94), 67 (64), 55 (100), 41 (78).

2-(6,6-dimethylbicyclo[3.1.1]heptan-2-yl)acetaldehyde (8d): major isomer 8d (trans, shorter GC retention time): MS (70 eV, El): 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, El): 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).

2-(hydroxymethyl)-6,6-dimethylbicyclo[3.1.1]heptane-3-carbaldehyde (9b): major isomer 9b (trans, shorter GC retention time): MS (70 eV, El): 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⁺-CH₃], 164 (3) [M⁺-H₂O], 149 (17), 135 (28), 133 (15), 123 (24), 121 (37), 109 (20), 108 (15), 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).

5,5-dimethyloctahydro-4,6-methanoisobenzofuran-1-ol (9c): MS (70 eV, EI): m/z (%) 182 (0.2) [M⁺], 164 (43) [M⁺-H₂O], 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).

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⁺-CH₃], 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⁺-CH₃], 123 (45), 109 (29), 83 (49), 82 (68), 81 (68), 79 (43), 70 (33), 69 (82), 68 (19), 67 (100), 55 (37).
2-(2-hydroxyethyl)-6,6-dimethylbicyclo[3.1.1]heptane-3-carbaldehyde (10b): major isomer 10b (trans, shorter GC retention time): MS (70 eV, El): m/z (%) 181 (2) [M⁺-CH₃], 178 (3) [M⁺-H₂O], 163 (24) [M⁺-CH₃-H₂O], 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, El): m/z (%) 181 (9) [M⁺-CH₃], 178 (0.4) [M⁺-H₂O], 163 (6) [M⁺-CH₃-H₂O], 123 (31), 121 (30), 117 (28), 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).

6,6-dimethyloctahydro-1H-5,7-methanoisochromen-1-ol (10c): major isomer 10c (shorter GC retention time): MS (70 eV, El): m/z (%) 181 (2) [M⁺-CH₃], 178 (2) [M⁺-H₂O], 165 (25), 147 (20), 123 (61), 122 (53), 121 (29), 109 (21), 107 (42), 105 (17), 95 (43), 93 (34), 91 (20), 83 (22), 81 (99), 79 (72), 78 (20), 77 (16), 69 (100), 67 (97), 55 (51); minor isomer 10c (longer GC retention time): MS (70 eV, El): 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).

(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, El): 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).

(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$_4$Si): $\delta$=0.83, 0.85 and 0.86 (d, J=7 Hz, 3H; C$_9$H$_3$), 1.10–1.40 (m, 1H; C$_6$H), 1.50–2.00 (m, 5H; C$_3$H$_2$, C$_4$H, C$_5$H, C$_6$H, 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), 4.12 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; CHO); $^{13}$C NMR (100 MHz, CDCl$_3$, 25°C, TMS): $\delta$=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$_5$); 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 (CHO).
5. NMR data