

Electronic Supplementary Information

Sustainable route from the renewable myrcene to methyl ethers via direct hydroalkoxylation

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1 General Remarks

All preparations and manipulations were performed under a dry, oxygen-free argon atmosphere using standard Schlenk techniques. Myrcene is commercially available from Acros Organics (Geel, Belgium) with a purity of 90%. All non-aqueous solvents used in this publication were purchased dry from Acros Organics (Geel, Belgium). All were 99% pure or better. Other chemicals were purchased from commercial suppliers and were of the highest purity available. They were used as received without further purification. Argon gas (99.998%) was purchased from Air Liquide Deutschland GmbH (Düsseldorf, Germany). ¹H and ¹³C spectra were recorded on a Bruker model DPX500 spectrometer at room temperature. ¹H and ¹³C NMR chemical shifts were reported on the δ -scale (ppm) relative to Me₄Si as an external standard. Carbon atoms were assigned by 2D experiments. Routine gas chromatographic analyses were done on an HP 6890 instrument (Hewlett–Packard GmbH, Waldbronn, Germany) equipped with an FI-detector and an HP5 capillary column (30 m, diameter 0.25 mm, film thickness 0.25 mm) connected with an autosampler. GC-MS analyses were carried out on a Hewlett–Packard 5973 (70 eV).

2 General Procedure for Hydroalkoxylation Experiments

All optimisation experiments were conducted in a homemade multiplex reactor,¹ while experiments to monitor catalyst performance were conducted in a 300 ml laboratory autoclave from Parr Instrument Company (Moline, Illinois, USA). In a typical experiment, AlCl₃ (1.0 g, 7.5 mmol) was dissolved in acetone (26.0 g, 30 ml). The

mixture was treated with ultrasound for 2 min. Methanol (48.1 g, 1.5 mol) and myrcene (20.4 g, 150.0 mmol) were added and the solution was again subjected to ultrasound for 3 min. The reaction mixture was transferred into the evacuated reactor and the stirrer speed was set to 800 rpm. Subsequently, the reactor was pressurised with 0.5 MPa argon to keep the methanol in solution and heated to 80 °C. After 4 h, the reaction was stopped by reducing the stirring velocity and rapid cooling to room temperature using an ice bath. A sample was taken and analysed by gas chromatography with di-*n*-butyl ether as an internal standard and isopropanol as an additional solvent.

3 Synthesis and Characterisation of the Pure Methyl Ethers

The pure methyl ethers **1–3** were prepared via etherification of commercially available corresponding alcohols. In a typical experiment, a round-bottomed flask equipped with a reflux condenser and a dropping funnel was charged with potassium hydride (30% in mineral oil, 88.0 mg, 2.2 mmol) in the presence of argon. Mineral oil was removed by extracting it three times with pentane. A solution of the corresponding alcohol (308.0 mg, 2.0 mmol) in 5 ml of THF was added during 15 min while cooling with an ice bath. The reaction medium was allowed to warm up to room temperature and was stirred for 2 h. Afterwards, methyl iodide (312.0 mg, 2.2 mmol) was dissolved in 3 ml of THF and added dropwise to the reaction mixture during 10 min. After stirring for 3 h at room temperature, the solution was carefully hydrolysed with 20 ml of water and the aqueous phase was extracted three times with 20 ml of dichloromethane. The combined organic phases were dried over MgSO₄ and the solvent was removed under reduced pressure. The crude product mixture was purified via column chromatography (silica gel, ethyl acetate/cyclohexane 10:1) to give the pure methyl ether.

3.1 3-Methoxy-3,7-dimethylocta-1,6-diene (linalyl methyl ether, **1**)

Yield: 297.0 mg (85%), $R_f = 0.5$, ¹H NMR (500.13 MHz, CDCl₃, 25 °C, TMS): $\delta = 1.23$ ppm (s, 3H; -CH₃), 1.54 (m, 2H; =CHCH₂CH₂-), 1.60 (s, 3H; =C(CH₃)₂), 1.67 (s, 3H; =C(CH₃)₂), 1.98 (dt, ³J(H,H) = 8.4 Hz, 2H; =CHCH₂CH₂-), 3.15 (s, 3H; -O-CH₃), 5.10-5.18 (m, 3H; =CHCH₂CH₂-, -CH=CH₂), 5.76 (dd, ³J(H,H) = 6.8 Hz, 1H; -CH=CH₂). ¹³C{¹H} (125.77 MHz, CDCl₃, 25 °C; TMS): $\delta = 17.4$ ppm (s, 1C; =C(CH₃)₂), 21.4 (s, 1C; =CHCH₂CH₂-), 22.2 (s, 1C; =C(CH₃)₂), 25.5 (s, 1C; -CH₃), 39.2 (s, 1C;

=CHCH₂CH₂-), 49.8 (s, 1C; -O-CH₃), 76.6 (s, 1C; -C(CH₃)(O)-), 114.4 (s, 1C; -CH=CH₂), 124.3 (s, 1C; =CHCH₂CH₂-), 131.1 (s, 1C; =C(CH₃)₂), 142.7 (s, 1C; -CH=CH₂). MS (m/z): 168 (M⁺, 2%), 153 (2), 136 (17), 121 (20), 111 (12), 97 (25), 93 (18), 85 (33), 81 (25), 80 (20), 73 (100).

3.2 (Z)-1-Methoxy-3,7-dimethylocta-2,6-diene (neryl methyl ether, 2)

Yield: 325.0 mg (93%), R_f = 0.5, ¹H NMR (500.13 MHz, CDCl₃, 25 °C, TMS): δ = 1.61 ppm (s, 3H; =C(CH₃)₂), 1.68 (s, 3H; -CH₃), 1.75 (s, 3H; =C(CH₃)₂), 2.08 (m, 4H; =CHCH₂CH₂-), 3.31 (s, 3H; -O-CH₃), 3.90 (d, ³J(H,H) = 6.8 Hz, 2H; -CH₂-O-CH₃), 5.10 (t, ³J(H,H) = 6.8 Hz, 1H; =CHCH₂CH₂-), 5.34 (t, ³J(H,H) = 6.8 Hz, 1H; =CH-CH₂-O-CH₃). ¹³C{¹H} (125.77 MHz, CDCl₃, 25 °C; TMS): δ = 17.5 ppm (s, 1C; =C(CH₃)₂), 23.4 (s, 1C; -CH₃), 25.6 (s, 1C; =C(CH₃)₂), 26.7 (s, 1C; =CHCH₂CH₂-), 32.2 (s, 1C; =CHCH₂CH₂-), 57.6 (s, 1C; -O-CH₃), 64.3 (s, 1C; -CH₂-O-CH₃), 121.8 (s, 1C; =CH-CH₂-O-CH₃), 123.8 (s, 1C; =CHCH₂CH₂-), 131.7 (s, 1C; =C(CH₃)₂), 140.3 (s, 1C; -C(CH₃)=). MS (m/z): 168 (M⁺, 2%), 153 (2), 136 (2), 121 (2), 97 (9), 85 (98), 81 (14), 73 (100).

3.3 (E)-1-Methoxy-3,7-dimethylocta-2,6-diene (geranyl methyl ether, 3)

Yield: 332.0 mg (98%), R_f = 0.5, ¹H NMR (500.13 MHz, CDCl₃, 25 °C, TMS): δ = 1.60 ppm (s, 3H; =C(CH₃)₂), 1.67 (s, 6H; =C(CH₃)₂, -CH₃), 2.07 (m, 4H; =CHCH₂CH₂-), 3.32 (s, 3H; -O-CH₃), 3.93 (d, ³J(H,H) = 6.8 Hz, 2H; -CH₂-O-CH₃), 5.10 (t, ³J(H,H) = 6.8 Hz, 1H; =CHCH₂CH₂-), 5.34 (t, ³J(H,H) = 6.8 Hz, 1H; =CH-CH₂-O-CH₃). ¹³C{¹H} (125.77 MHz, CDCl₃, 25 °C; TMS): δ = 16.3 ppm (s, 1C; -CH₃), 17.6 (s, 1C; =C(CH₃)₂), 25.6 (s, 1C; =C(CH₃)₂), 26.4 (s, 1C; =CHCH₂CH₂-), 39.6 (s, 1C; =CHCH₂CH₂-), 57.6 (s, 1C; -O-CH₃), 68.9 (s, 1C; -CH₂-O-CH₃), 120.7 (s, 1C; =CH-CH₂-O-CH₃), 123.9 (s, 1C; =CHCH₂CH₂-), 131.5 (s, 1C; =C(CH₃)₂), 140.2 (s, 1C; -C(CH₃)=). MS (m/z): 168 (M⁺, 2%), 153 (2), 136 (12), 121 (13), 97 (19), 85 (30), 81 (21), 73 (100).

4 References

1 A. Behr, G. Henze, L. Johnen and S. Reyer, *J. Mol. Catal. A: Chem.*, 2008, **287**, 95.