Synthesis of Tsetse Fly Attractants from a Cashew Nut Shell Extract by Isomerising Metathesis

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Supporting Information

Experimental procedures and data

General Methods. All reactions were performed in oven-dried glassware containing a teflon-coated stirring bar. Solvents were purified, dried by standard procedures, and degassed by three freeze-pump-thaw cycles prior to use. All reactions were monitored by GC using *n*-hexadecane or *n*-decane as an internal standard. Response factors of the products with regard to *n*-(hexa-)decane were obtained experimentally by analysing known quantities of the substances. GC analyses were carried out using a HP6890 with HP-5 capillary column (Phenyl Methyl Siloxane 30 m x 320 x 0.25, 100/2.3-30-300/3) and a time program beginning with 2 min at 60 °C, followed by a 30 °C/min ramp to 300 °C, then 3 min at this temperature. Column chromatography was performed using a Combi Flash Companion-Chromatography-System (Isco-Systems) and Redi*Sep* packed columns (12 g). NMR spectra were obtained on Bruker AMX 400 systems using $CDCl_3$ as solvent, with proton and carbon resonances at 400 MHz and 101 MHz, respectively. Mass spectrometric data were acquired on a GC-MS Saturn 2100 T (Varian). Infrared spectra were recorded on a Perkin Elmer Spectrum 100 FT-IR Spectrometer with ATR sample assembly. Bands are given in cm^{-1} with intensities (vs very strong, s strong, m medium, w weak). The high resolution mass spectrum was measured on a Waters GTC Premier. Commercial substrates were used as received unless otherwise stated. Purification *via* preparative HPLC was carried out using a Dionex UltiMate 3000; column, Supelco Analytical, Ascentis C18, 250 × 21.2 mm, 5 µm particle size; flow, 12 mL/min; eluent, aqueous: water, organic: acetonitrile; For compounds **2** and **7** the following gradient was used: 0–2 min, 50% organic; 2–35 min, linear increase of organic to 100 %; 35–37 min, 100 % organic; 37–39 min, linear decrease to 50 % organic; 39–42 min, 50 % organic. Headspace GC analyses were carried out using a Perkin Elmer AutoSystem XL with Supelco packed column (80/100 Poropak, 6 FT x 1/8 In. S.S.).

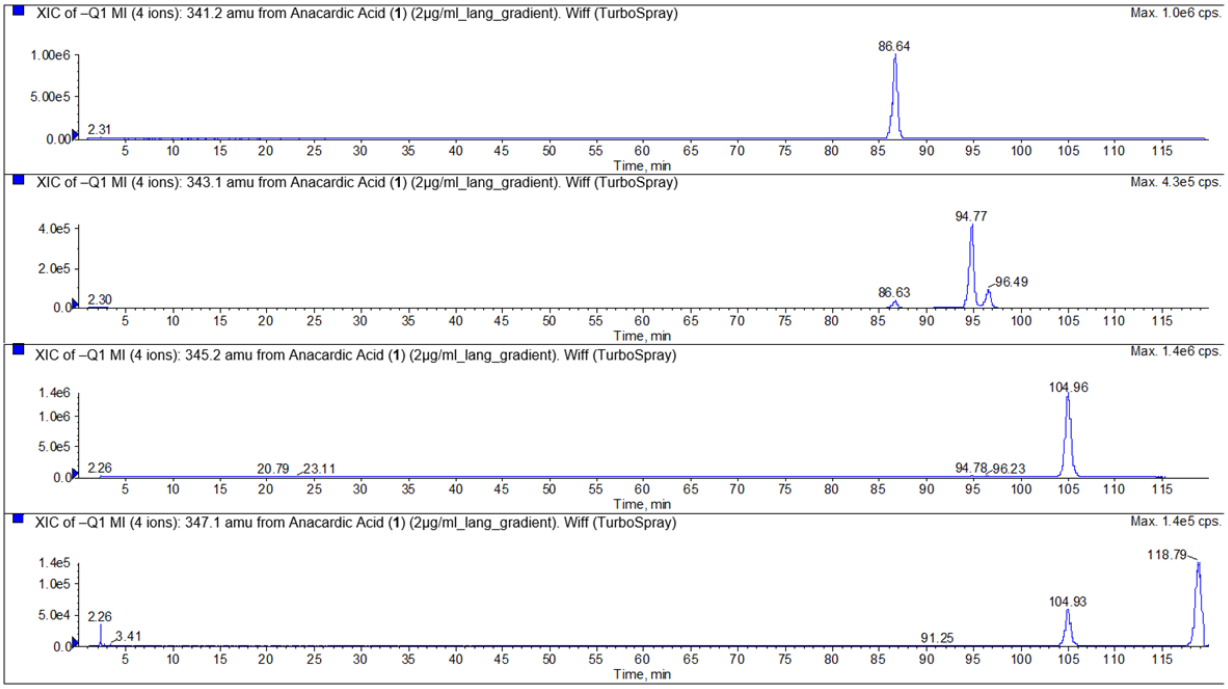
But-2-ene was obtained from Apollo Scientific Ltd as a mixture of *E/Z*-isomers (purity: 99% by GC, ratio of *E*/*Z*-isomers: 68% / 31%) and ethene from Air Liquide GmbH (purity: 99.9%).

Separation of anacardic acid from Cashew nut shell liquid (CNSL)

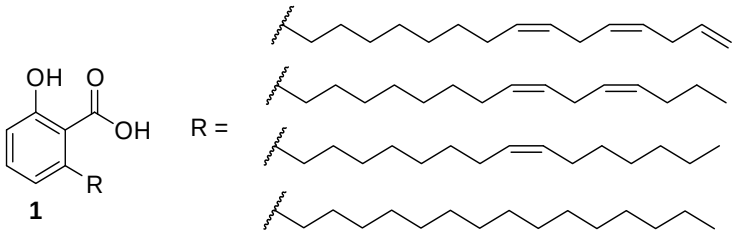
Cashew nut shells (400 g), collected from Naliendele in Mtwara, Tanzania, were comminuted into ~1 mm small particles which were than treated by Soxhlet extraction with Et_2O (500 mL) at 35 °C for 6 h. Removal of the solvent *in vacuo* resulted in a highly viscous brown oil (90.0 g, 23 wt-%).

The crude CNSL was used without further purification. CNSL (40.0 g) was dissolved in 5% aqueous methanol (240 mL), and calcium hydroxide (20.0 g, 259 mmol) was added in portions under stirring. After complete addition of calcium hydroxide, the temperature of the reaction mixture was raised to 50 °C and stirring was continued for 2.5 h. The precipitated calcium anacardate was filtered, washed with methanol (200 mL), and the solvent was removed under reduced pressure. Calcium anacardate was suspended in distilled water (200 mL), HCl (30 mL, 12 M) was added, and the mixture stirred for 1 h. EtOAc (200 mL) was added to the suspension to yield a brown organic layer in a two phase mixture. After separation, the aqueous layer was extracted with EtOAc (2 × 100 mL), and the combined organic phases were washed with distilled water (100 mL). The organic layer was further dried over $MgSO_4$ and concentrated under reduced pressure to yield a viscous dark brown oil (23.1 g, 58 wt-%). The solvent extracted anacardic acids consist of a mixture with a varying degree of saturation in the fifteen-carbon olefinic side chain, namely the saturated compound as well as the mono-, di-, and triene, which were analysed by HPLC-MS (Figure 1).

Figure 1. HPLC-MS measurement of the crude anacardic acid (**1**).



Characterisation data of anacardic acids (1)



1a, triene (M = 341.2)

1b, diene (M = 343.1)

1c, monoene (M = 345.2)

1d, saturated (M = 347.1)

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 10.97 (br. s., 1 H), 7.38 (t, J = 7.9 Hz, 1 H), 6.89 (d, J = 7.7 Hz, 1 H), 6.79 (d, J = 7.5 Hz, 1 H), 5.77 - 5.88 (m, 0.2 H), 5.31 - 5.45 (m, 3.2 H), 4.97 - 5.08 (m, 0.4 H), 2.98 - 3.01 (m, 2 H), 2.77 - 2.85 (m, 1.6 H), 2.43 (t, J = 7.5 Hz, 0.1 H), 2.00 - 2.07 (m, 3.6 H), 1.58 - 1.73 (m, 2.2 H), 1.27 - 1.43 (m, 13.6 H), 0.87 - 1.00 (m, 2.5 H) ppm; ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 176.2, 163.6, 147.8, 136.8, 135.5, 130.4, 130.1, 129.9, 129.9, 129.8, 129.3, 128.1, 128.0, 127.6, 126.8, 122.8, 115.9, 114.7, 110.3, 36.5, 32.0, 31.8, 31.5, 29.7, 29.7, 29.6, 29.6, 29.4, 29.3, 29.2, 29.0, 27.2, 27.2, 25.6, 25.5, 22.8, 22.6, 14.1, 13.8 ppm; IR (neat): $\tilde{\nu}$ = 3008 (w), 2923 (s), 2853 (m), 2593 (vw), 2537 (vw), 1644 (s), 1607 (s), 1576 (w), 1446 (s), 1300 (m), 1244 (s), 1207 (s), 1166 (m), 1125 (w), 991 (w), 909 (m), 822 (m), 784 (m), 706(s) cm^{-1}; HRMS-EI (TOF) calcd. $C_{16}H_{22}O_3$: 342.2195; found: 342.2223. The analytical data matched those reported in the literature for anacardic acid (R. Paramashivappa, P. P.

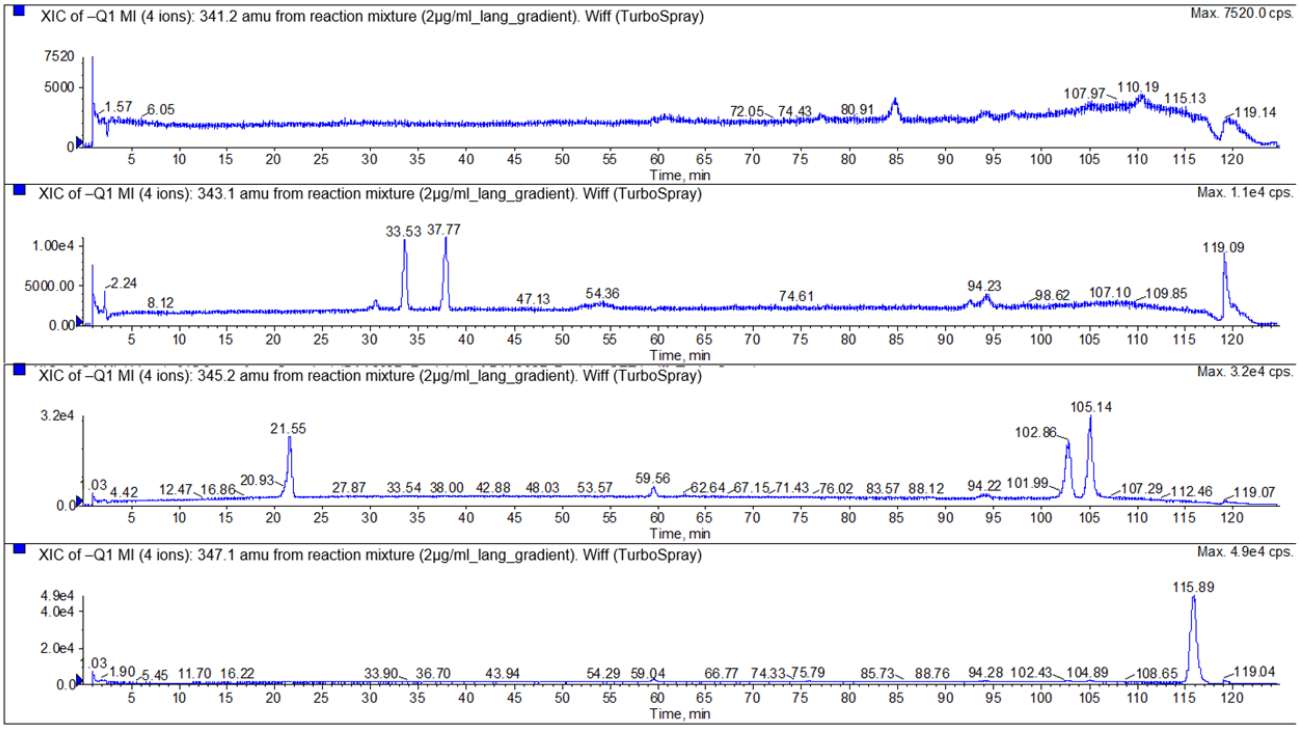
Kumar, P. J. Vithayathil, and A. S. Rao, *Journal of Agricultural and Food Chemistry*, **2001**, *49*, 2548–2551).

General procedure for the selective ethenolysis of anacardic acids (1)

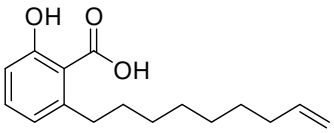
An oven-dried 10 mL headspace vial with a Teflon coated stirring bar was charged with catalyst, closed with a septum cap and purged with ethene three times. The solvent was degassed by three freeze-pump-thaw cycles and further ethene sparging (10 min). Under ethene atmosphere, dichloromethane (1 mL) and anacardic acid (**1**) (85.6 mg, 0.25 mmol) were added *via* syringe. The vial was placed in an autoclave and the system was purged with ethene three times. The resulting mixture was stirred at 25 °C under 10 bar ethene pressure overnight. After cooling to 0 °C, the pressure was slowly released and *n*-hexadecane (50 µL) was added as internal standard. The reaction mixture was diluted with EtOAc (3 mL). A sample (0.25 mL) was taken, diluted with EtOAc (3 mL) and washed with water (3 mL). The organic layer was dried over $MgSO_4$ and filtered through a pipette. The yield of the corresponding 3-(non-8-enyl)phenol (**5**, obtained by decarboxylation during GC measurement) was determined by GC analysis of the reaction mixture.

Following the general reaction procedure for the selective ethenolysis, anacardic acids (**1**) were converted to the 2-hydroxy-6-(non-8-enyl)benzoic acid (**4**) in the presence of Hoveyda-Grubbs I catalyst **Ru-3** (1.50 mg, 2.00 µmol). The reaction mixture was analysed by HPLC-MS which showed that only the saturated acid remained unreacted in the reaction mixture, when started from the anacardic acids compound mixture (Figure 2).

Figure 2. HPLC-MS measurements of the reaction mixture after selective ethenolysis of (**1**).



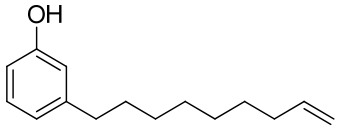
Synthesis of 2-hydroxy-6-(non-8-enyl)benzoic acid (4)



Following the general procedure for the selective ethenolysis of anacardic acids (**1**) 2-hydroxy-6-(non-8-enyl)benzoic acid (**4**) was obtained as a white powder after purification by HPLC. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.38 (t, 1 H), 6.89 (d, J = 8.3 Hz, 1 H), 6.79 (d, J = 7.4 Hz, 1 H), 5.82 (ddt, J = 17.1, 10.3, 6.7 Hz, 1 H), 5.03 - 4.93 (m, 2 H), 3.00 (t, J = 8.3 Hz, 2 H), 2.08 – 2.03 (m, 2 H), 1.64 – 1.58 (m, 2 H), 1.41 – 1.34 (m, 8 H) ppm; ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 176.34, 163.54, 147.80, 139.16, 135.44, 122.80, 115.86, 114.12, 110.43, 36.42, 33.77, 31.94, 29.71, 29.29, 29.06, 28.88 ppm; IR (neat): $\tilde{\nu}$ = 3080 (w), 2981 (w), 2920 (m), 2850 (m), 2712 (w), 2595 (w), 2545 (w), 1649 (s), 1603 (s), 1596 (w), 1487 (w), 1444 (vs), 1308 (m), 1243 (vs), 1222 (s), 1204 (s), 1168 (m), 1128 (w), 1110 (w), 1067 (w), 994 (w), 916 (m), 896 (m), 828 (m), 811 (m), 787 (w), 732 (vs), 707 (vs) cm^{-1}; CHN elemental analysis calcd. C: 73.25, H: 8.43; found C: 73.06, H: 8.37; HRMS-EI (TOF) calcd. $C_{16}H_{22}O_3$: 262.1569; found: 262.1578; melting point: 86.7 °C.

Preparative scale synthesis of 3-(non-8-enyl)phenol (5) *via* selective ethenolysis of anacardic acids (1)

In a glovebox, a PTFA-lined steel autoclave with stirring bar was charged with metathesis catalyst **Ru-3** (21.6 mg, 36.0 μmol). Under nitrogen atmosphere, DCM (30 mL, degassed by three freeze-pump-thaw cycles and 10 min ethene sparging) and anacardic acids (**1**) (2.50 g, 7.30 mmol) were added *via* syringe. The vessel was placed in an autoclave, the system was evacuated (10 mbar) and purged with ethene three times. The resulting mixture was stirred at 25 °C under ethene pressure (10 bar) for 16 h. The solvent was removed *in vacuo*. Purification of the crude product mixture *via* Kugelrohr distillation (120°C, 10^{-2} mbar) yielded 3-(non-8-enyl)phenol (**5)** as light yellow oil (1.41 g, 6.46 mmol, 89%).



^{1}H-NMR (200 MHz, $CDCl_3$) δ = 7.10 - 7.22 (m, 1 H), 6.78 (d, J = 7.6 Hz, 1 H), 6.56 - 6.71 (m, 2 H), 5.84 (ddt, J = 17.0, 10.2, 6.7, 6.7 Hz, 1 H), 4.90 - 5.13 (m, 2 H), 4.84 (d, J = 0.5 Hz, 1 H), 2.47 - 2.65 (m, 2 H), 1.96 - 2.20 (m, 2 H), 1.50 - 1.72 (m, 2 H), 1.19 - 1.45 (m, 8 H) ppm; ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 154.7, 144,3, 138.6, 128.7, 120.3, 114.6, 113.5, 111.8, 35.1, 33.1, 30.6, 28.7, 28.6, 28.4, 28.3 ppm; IR (neat): $\tilde{\nu}$ = 3328 (m), 3076 (w), 2925 (s), 2854 (m), 1640 (w), 1610 (m), 1588 (s), 1487 (m), 1455 (s), 1350 (w), 1262 (m), 1234 (m), 1153 (m), 998 (w), 908 (s), 874 (w), 778 (s), 749 (m), 723 (w), 693 (vs) cm^{-1}; MS (Ion trap, EI): m/z (%) = 218 [M^+] (22), 135 (18), 121 (33), 120 (21), 107 (100), 79 (15), 77 (27); HRMS-EI (TOF) calcd. $C_{15}H_{22}O$: 218.3360; found 218,1664; CHN: $C_{15}H_{22}O$ calcd: C: 82.52, H:10.16; measured: C: 82.15, H: 9.97. The analytical data matched those reported in the literature for 3-(non-8-enyl)phenol (J. A. Mmongoyo, Q. A. Mgani, S. J. M. Mdachi, P. J. Pogorzelec, and D. J. Cole-Hamilton, *European Journal of Lipid Science and Technology*, **2012**, *114*, 1183–1192).

General procedure for the isomerising ethenolysis of 3-(non-8-enyl)phenol (5)

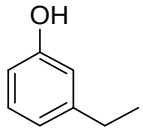
In a glove box, 35 mL Fisher Porter vessel with stirring bar was charged with di-μ–bromobis(tri-*tert*-butylphosphine)palladium(I) **Pd-1** (5.00 mg, 6.00 μmol) and ruthenium-based metathesis catalysts **Ru-4/-5** or **-8**. Subsequently, THF and 3-(non-8-enyl)phenol (**5**) (125 mg (92%-wt), 0.50 mmol) were added, the tube was closed and removed from the glove box. The tube was pressurised with ethene and the mixture was allowed to stir at the given temperature for the given time. After cooling to -78 °C, the pressure was slowly released and *n*-decane (50.0 μL) was added as internal standard. The reaction

mixture was diluted with EtOAc (3 mL). A sample (0.5 mL) was taken, extracted with EtOAc (3 mL) and washed with water (3 mL). The organic layer was dried over $MgSO_4$ and filtered through a pipette. The yield was determined by GC analysis of the reaction mixture.

Synthesis of a mixture of 3-ethylphenol (2) and 3-propylphenol (3)

Following the general procedure for the isomerising ethenolysis of 3-(non-8-enyl)phenol (**5**) (250 mg (92%-wt), 1 mmol) using **Ru-8** (13.2 mg, 20.0 μmol), **Pd-1** (10.0 mg, 13.0 μmol), and THF (4 mL) the reaction mixture was stirred under an ethene pressure (5.0 bar) for 16 hours at 50 °C. After cooling to -78 °C, the pressure was slowly released, and a subsequent hydrogenation was performed by addition of methanol (4.0 mL) and activated charcoal (20.0 mg). The resulting mixture was stirred under hydrogen pressure (5.0 bar) for 3 h at 50 °C. The mixture was filtered through celite (0.3 cm^3) and the solvent was removed by distillation (vigreux), the residue was filtered through a silica plug (5 cm^3). The crude reaction mixture was analysed by NMR to give a mixture of 3-ethyl- (**2**) and 3-propylphenol (**3**) (1:1.4, 103 mg, 0.85 mmol, 85 %).

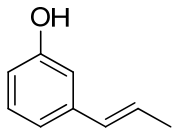
Synthesis of 3-ethylphenol (2)



Following the general procedure for the isomerising ethenolysis of 3-(non-8-enyl)phenol (**5**) (250 mg (92%-wt), 1 mmol) using **Ru-8** (13.2 mg, 20.0 μmol), **Pd-1** (10.0 mg, 13.0 μmol), and THF (4 mL) the reaction mixture was stirred under an ethene pressure (4.0 bar) for 16 hours at 50 °C. After cooling to -78 °C, the pressure was slowly released. The resulting reaction mixture was filtered through a silica plug (5 cm^3) (pentane: diethylether, 1:1) and the solvent removed under reduced pressure. Subsequently, the mixture of, 127 mg, 1.00 mmol) was reacted in an ethenolysis reaction using **Ru-8** (13.2 mg, 20.0 mmol) in THF (4 mL) under an ethene pressure (4.0 bar) for 16 hours at 50 °C. After cooling to -78 °C, the pressure was slowly released. Hydrogenation was performed by addition of methanol (5.0 mL) and activated charcoal (100 mg). The resulting mixture was stirred under hydrogen pressure (5.0 bar) for 3 h at 50 °C. The mixture was filtered through celite (0.3 cm^3), the solvent removed by distillation (vigreux) and the residue filtered through a silica plug (5 cm^3). The crude reaction mixture

was analysed by NMR to give 3-ethylphenol (**2**) (101 mg, 0.84 mmol, 84 %) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.16 (t, *J* = 7.8 Hz, 1 H), 6.79 (dd, *J* = 7.5, 0.8 Hz, 1 H), 6.63 - 6.72 (m, 2 H), 4.82 (s, 1 H), 2.62 (q, *J* = 7.5 Hz, 2 H), 1.23 (t, *J* = 7.5 Hz, 3 H) ppm; ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 155.5, 146.2, 129.5, 120.4, 114.7, 112.5, 28.7, 15.4 ppm; IR (neat): $\tilde{\nu}$ = 2966 (w), 2931 (w), 2873 (w), 1739 (w), 1588 (s), 1492 (w), 1456 (s), 1366 (w), 1253 (m), 1229 (m), 1153 (s), 1052 (w), 984 (w), 905 (s), 862 (w), 778 (m), 725 (m), 691 (vs); MS (Ion trap, EI): m/z (%) = 121.8 (58), 107.8 (7), 106.9 (100), 91.0 (9), 78.9 (14), 76.9 (35), 50.9 (8); HRMS-EI (TOF) calcd. $C_8H_{10}O$: 122.0723; found: 122.0723. The analytical data matched those reported in the literature for 3-ethylphenol [CAS: 620-17-7] (R. Shen, T. Chen, Y. Zhao, R. Qiu, Y. Zhou, S. Yin, X. Wang, M. Goto, and L.-B. Han, J. Am. Chem. Soc., **2011** , 133, 17037–17044).

Synthesis of 3-(prop-1-enyl)phenol (7)

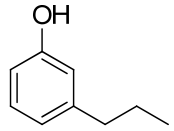


Compound **5** was prepared following the standard procedure for the isomerising ethenolysis. To the solution of the catalysts in THF (4 mL) **5** (250 mg (92%-wt), 1.00 mmol) was added and the reaction mixture was stirred for 16 h under ethene pressure (2 bar). After cooling to -78 °C, the pressure was slowly released under inert conditions. The tube was warmed to 0 °C and 2-butene (2.80 g, 50.0 mmol) was condensed in. The mixture was allowed to stir overnight at 50 °C. The mixture was again cooled to 0 °C and the pressure was released. The solvent was removed *in vacuo*, and the crude product was purified by flash column chromatography (SiO_2, diethylether – pentane 0-30%), yielding **7** as a colorless oil (123 mg, 0.92 mmol, 92%). Further purification was carried out using preparative HPLC. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.17 (t, *J* = 7.8 Hz, 1 H), 6.92 (d, *J* = 7.7 Hz, 1 H), 6.80 - 6.84 (m, 1 H), 6.68 (dd, *J* = 8.0, 2.5 Hz, 1 H), 6.32 - 6.39 (m, 1 H), 6.18 - 6.28 (m, 1 H), 4.79 (s, 1 H), 1.88 (dd, *J* = 6.5, 1.4 Hz, 3 H) ppm; ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 155.6, 139.7, 130.6, 129.7, 126.3, 118.7, 113.7, 112.4, 18.4 ppm; IR (neat): $\tilde{\nu}$ = 3323 (m), 3025 (w), 2970 (w), 2934 (w), 2913 (w), 2877 (w), 2852 (w), 1739 (m), 1655 (w), 1581 (s), 1491 (m), 1443 (s), 1365 (m), 1293 (m), 1230 (s), 1154 (vs), 1078 (w), 959 (s), 907 (m), 864 (m), 766 (vs), 684 (vs); MS (Ion trap, EI): m/z (%) = 134.0 (100), 133.0 (83), 105.0 (52), 91.0 (43), 79.0 (30), 77.0 (47), 51.0 (25); HRMS-EI (TOF) calcd. $C_9H_{10}O$: 134.0732; found: 134.0733. The analytical data matched those reported in the literature for 3-(prop-1-enyl)phenol [CAS: 79755-53-6] (H. O. House, W. A. Kleschick, and E. J. Zaiko, *J. Org. Chem*., **1978**, *43*, 3653–3661).

Isomerising butenolysis of 3-(non-8-enyl)phenol (5)

In a glove box an oven-dried 35 mL glass pressure tube with stirring bar was charged with **Pd-1** (5.00 mg, 6.00 μmol) and ruthenium-based metathesis catalysts **Ru-8** (6.50 mg, 10.0 μmol). Subsequently THF (2 mL) and 3-(non-8-enyl)phenol (**5**) (125 mg (92%-wt), 0.50 mmol) were added, the tube was closed and removed from the glove box. The tube was cooled to 0 °C and 2-butene (1.40 g, 25 mmol) was condensed in. The mixture was allowed to stir overnight at 50 °C. Subsequently, the reaction mixture was cooled to 0 °C and the pressure was slowly released. The resulting mixture was analysed by GC with *n*-decane (50.0 μL) as internal standard. The GC sample was prepared as aforementioned. The reaction mixture contained ethenyl- (6 %), propenyl- (64 %), butenyl- (16 %), pentenylphenol (11 %), and traces of higher homologues.

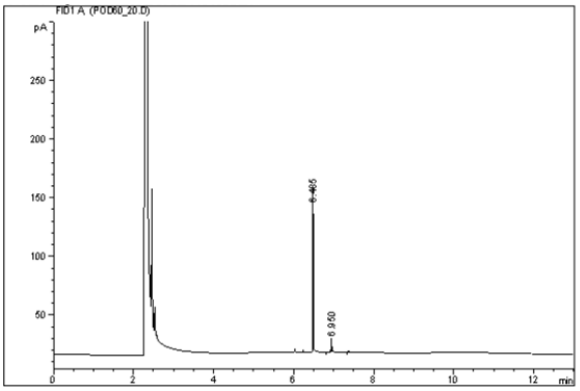
Preparative scale one-pot synthesis of 3-propylphenol (3)



In a glove box an oven-dried 70 mL glass pressure tube with stirring bar was charged with **Pd-1** (40.4 mg, 52.0 μmol), [1,3-Bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene]dichloro[[2-(1-methyl-2-oxopropoxy)phenyl]methene] ruthenium(II) **Ru-8** (52.5 mg, 0.08 mmol), THF (16 mL) and 3-(non-8-enyl)phenol (**5**) (950 mg, 4.00 mmol). The closed tube was removed from the glove box and pressurized with ethene (7.5 bar). The mixture was stirred at 50 °C for 16 hours. After cooling to -78 °C, the pressure was slowly released under inert conditions. The tube was warmed to 0 °C and 2-butene (11.2 g, 200 mmol) was condensed in. The mixture was allowed to stir overnight at 50 °C. Subsequently, the reaction mixture was cooled to 0 °C and the pressure was slowly released. Hydrogenation was performed by addition of methanol (25 mL) and activated charcoal (300 mg). The resulting mixture was stirred under hydrogen pressure (5.0 bar) for 3 h at 50 °C. The mixture was filtered through celite (1 cm³) and the solvent was removed by distillation (vigreux), the residue dissolved in Et_2O, filtered through a silica plug (5 cm³) to yield the desired product (**3**) as a bright yellow oil (425 mg, 3.12 mmol. 78 %) after removal of the solvent. Further purification was carried out using preparative HPLC. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.13 - 7.20 (m, 8 H), 6.76 - 6.81 (m, 8 H), 6.65 - 6.71 (m, 17 H), 5.06 (br. s., 6 H), 2.52 - 2.59 (m, 17 H), 1.59 - 1.70 (m,

18 H), 0.96 (t, J = 7.3 Hz, 26 H) ppm; ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 155.3, 144.7, 129.3, 121.0, 115.3, 112.5, 37.9, 24.3, 13.8 ppm; IR (NaCl): $\tilde{\nu}$ = 3317 (m), 3039 (w), 2959 (m), 2930 (m), 2871 (w), 1712 (w), 1588 (s), 1489 (w), 1453 (s), 1378 (w), 1340 (w), 1250 (s), 1152 (s), 1097 (w), 1066 (w), 1000 (w), 940 (m), 873 (m), 774 (vs), 748 (m), 718.4 (w), 692 (vs) cm^{-1}; MS (Ion trap, EI): m/z (%) =135.9 (52), 120.9 (16), 108.0 (47), 107.0 (100), 79.0 (19), 77.0 (47), 51.0 (11); HRMS-EI (TOF) calcd. $C_9H_{12}O$: 136.0888; found: 136.0880. The analytical data matched those reported in the literature for 3-propylphenol [CAS: 621-27-2] (I. Ujva´ry, I; Mikite G. *Organic Process Research & Development* **2003**, *7*, 585–587).

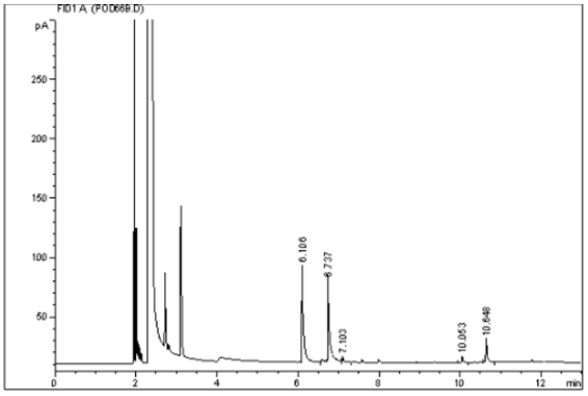
GC of the crude product mixture



GC- and Headspace GC-analysis

Figure 3 shows the GC spectrum of the reaction mixture after isomerising ethenolysis of 3-(non-8-enyl)phenol (**5**). The smaller peak at t_R = 10.648 corresponds to the unreacted, saturated cardanol, whereas t_R = 6.373 and t_R = 6.106 correspond to 3-(prop-1-enyl)phenol and 3-hydroxystyrene, respectively.

Figure 3: GC-FID chromatogram of reaction mixture after isomerising ethenolysis of 3-(non-8-enyl)phenol (**5**).



The gas as well as the liquid phase were further analysed on a GC using a packed column. The measurement was performed under isothermal conditions (150 °C) with a carrier gas (Helium) flow of 30 mL/min. The expected gaseous components (ethene, propene, and butene) were measured as references. The samples were injected manually, injecting either 1 µL of a liquid or 5 µL of a gaseous sample.

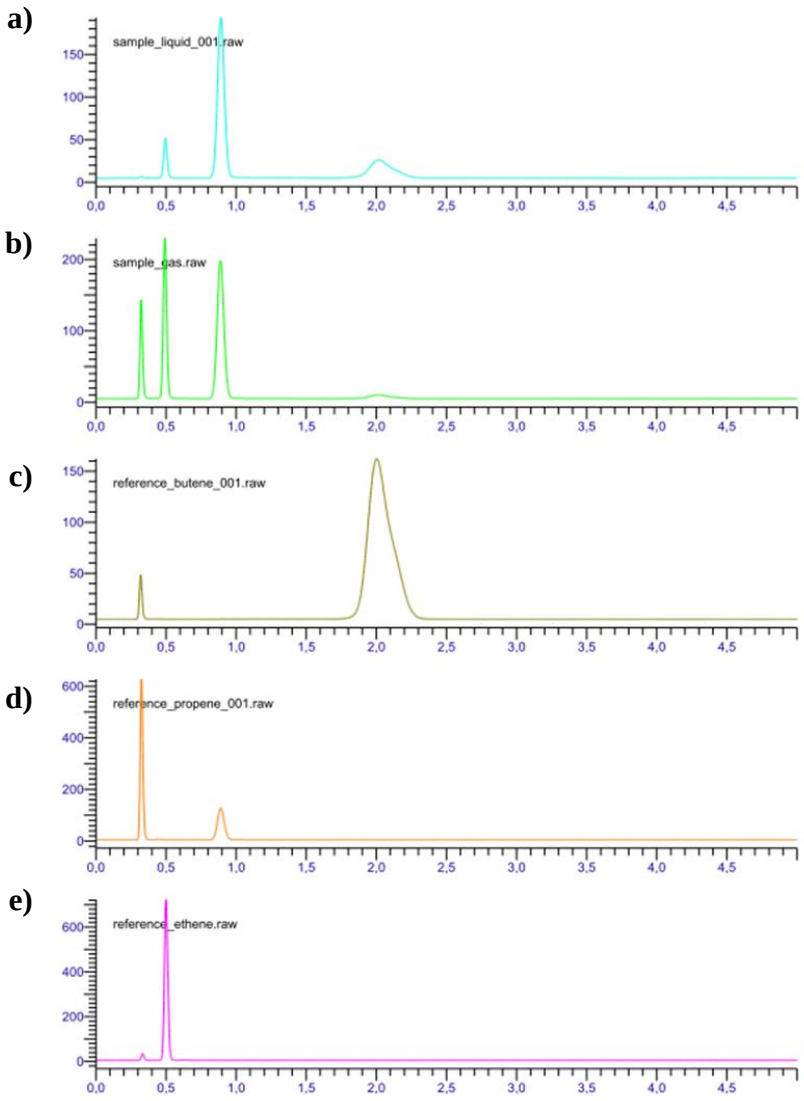


Figure 1: Headspace-GC-TCD chromatograms showing analysed reaction mixture (gas and liquid) and corresponding reference substances (ethene, propene and butene).

Area-Data for gases after isomerising metathesis of 5

Table S-1: Report Table sample_gas

Compound	Retention time / min	Area / µV·s	Corrected Area / %
air	0.324	188465.71	--
ethene	0.493	394505.58	14064.37
propene	0.888	66462.39	15794.73
butene	2.014	58377.17	1040.41

Table S-2: Report Table sample_liquid

Compound	Retention time / min	Area / µV·s	Corrected Area / %
air	0.326	2531.62	--
ethene	0.495	84312.63	3005.80
propene	0.891	653939.90	15540.40
butene	2.017	250367.63	4462.09

Percentage of each gas in the liquid phase was calculated as follows: $\frac{area(liquid)}{area(liquid)+ area(gas)}$

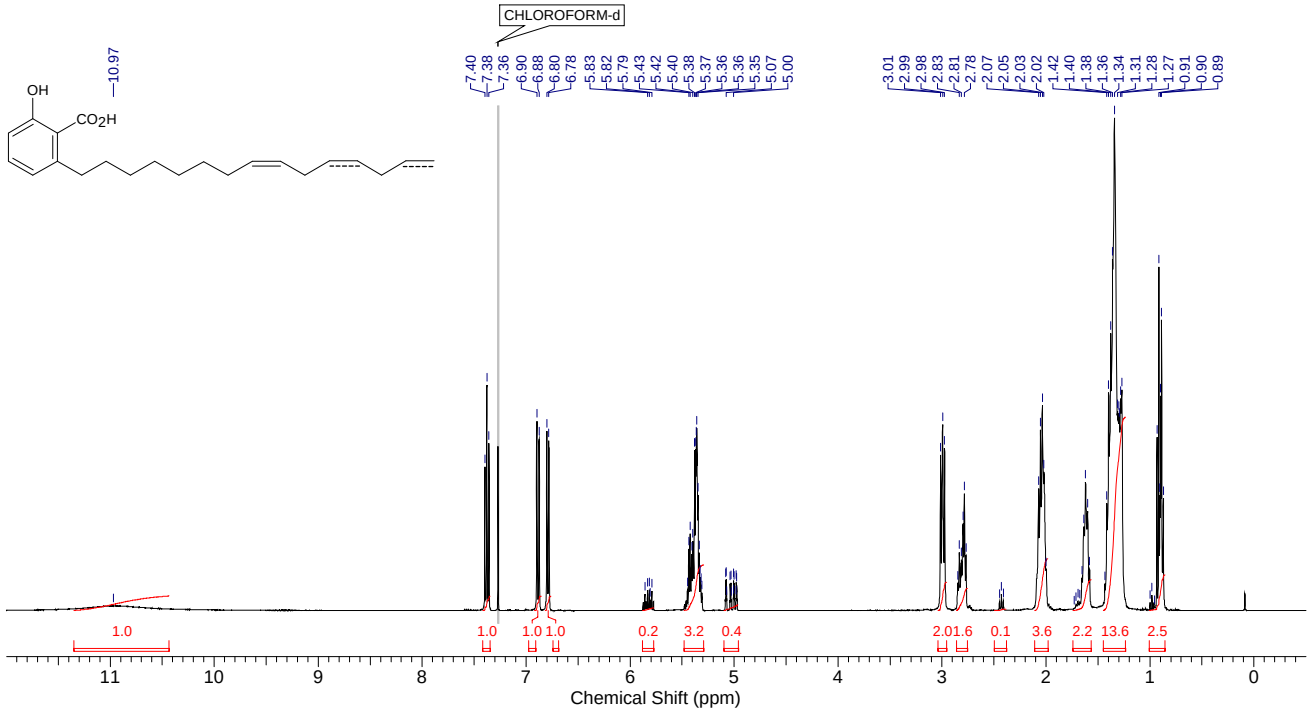
This normalised ratio of the gases in liquid equals their relative solubility:

Ethene / propene / butene = 1 / 2.8 / 4.6

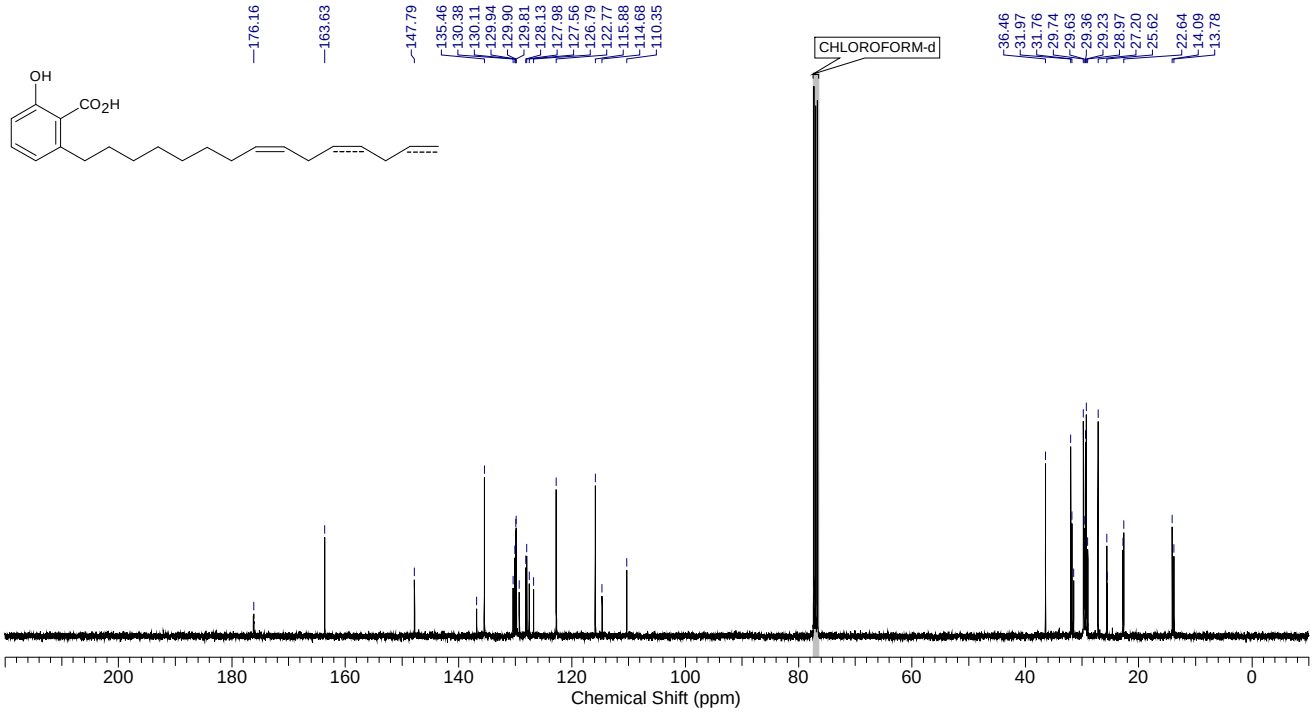
Spectra

Anacardic Acids (1)

^{1}H-NMR (400 MHz, $CDCl_3$)

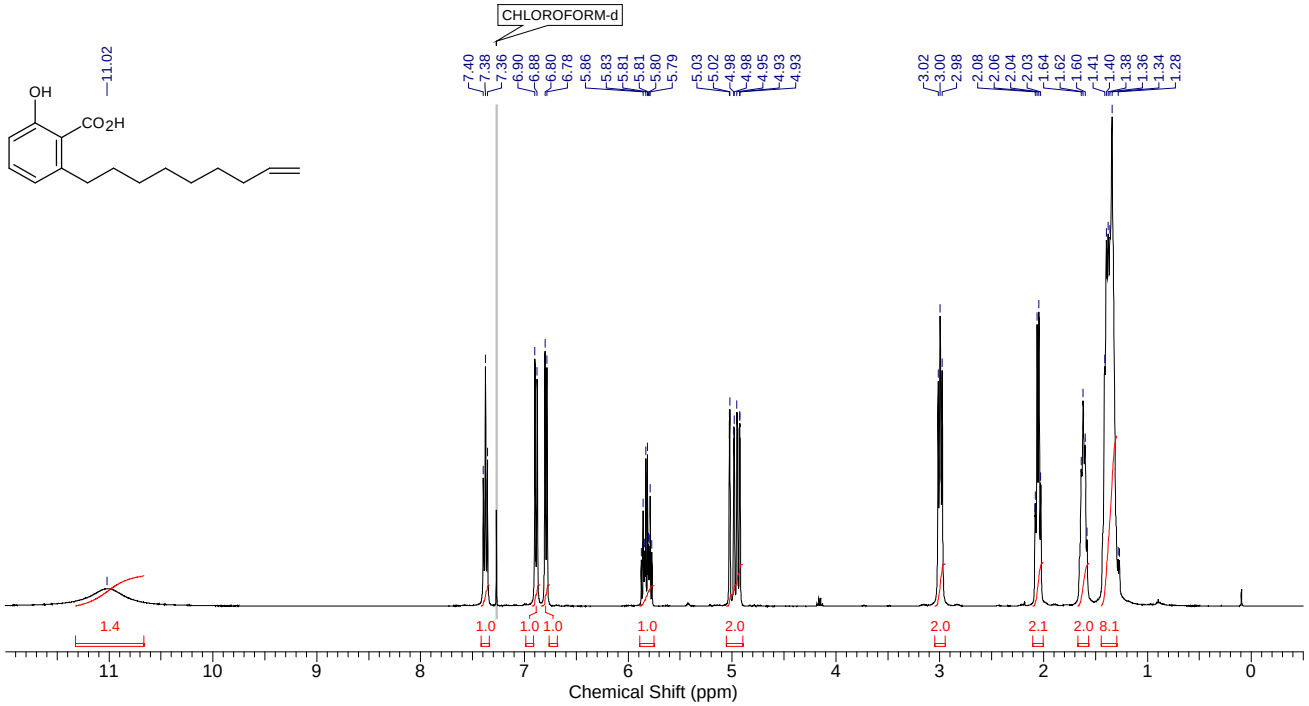


^{13}C-NMR (101 MHz, $CDCl_3$)

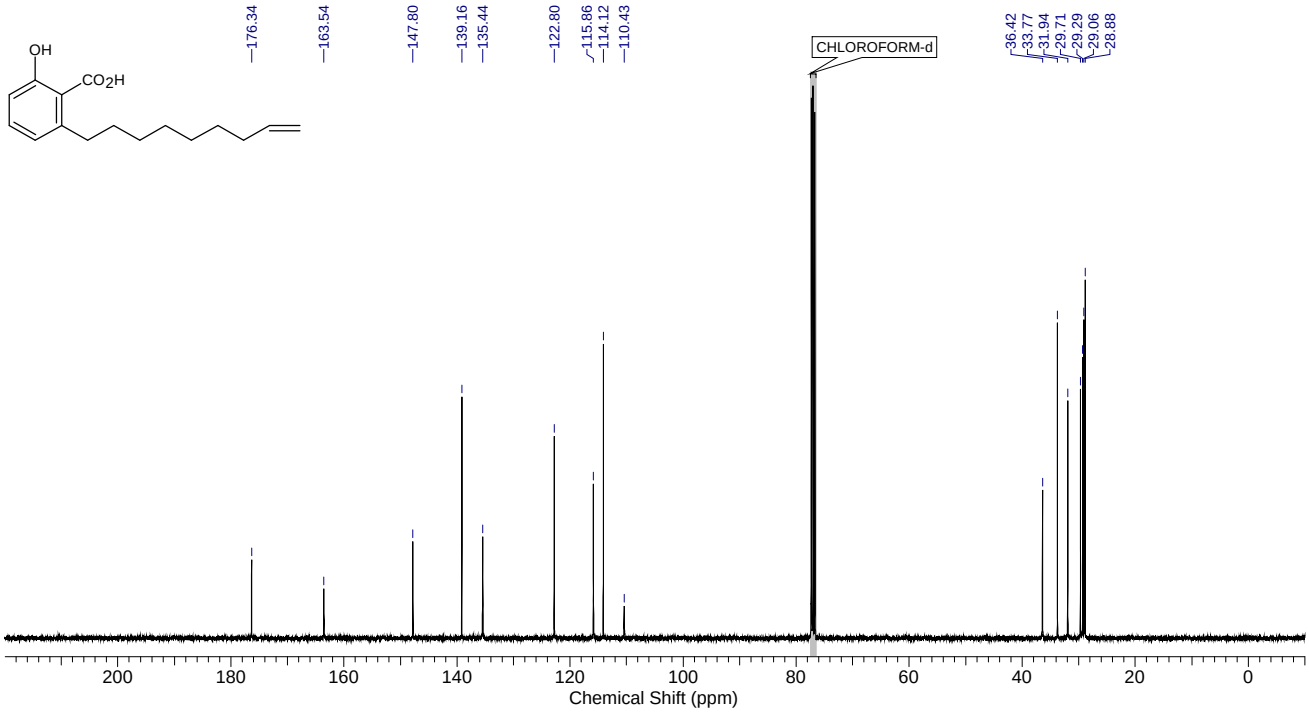

176.16
163.63
147.79
135.46
130.38
130.11
129.94
129.90
129.81
128.13
127.98
127.56
126.79
122.77
115.88
114.68
110.35
CHLOROFORM-d
36.46
31.97
31.76
29.74
29.63
29.36
29.23
28.97
27.20
25.62
22.64
14.09
13.78
OH
CO2H
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

2-hydroxy-6-(non-8-enyl)benzoic acid (4)

^{1}H-NMR (400 MHz, $CDCl_3$)

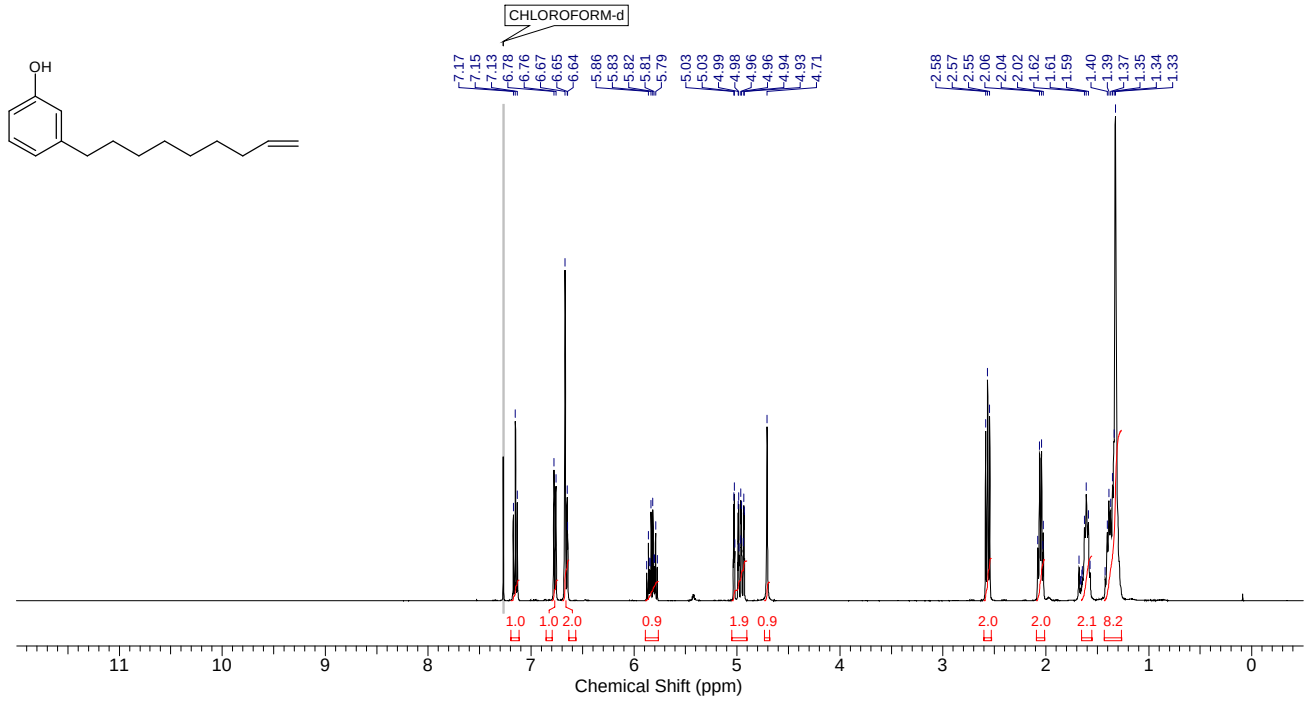


^{13}C-NMR (101 MHz, $CDCl_3$)

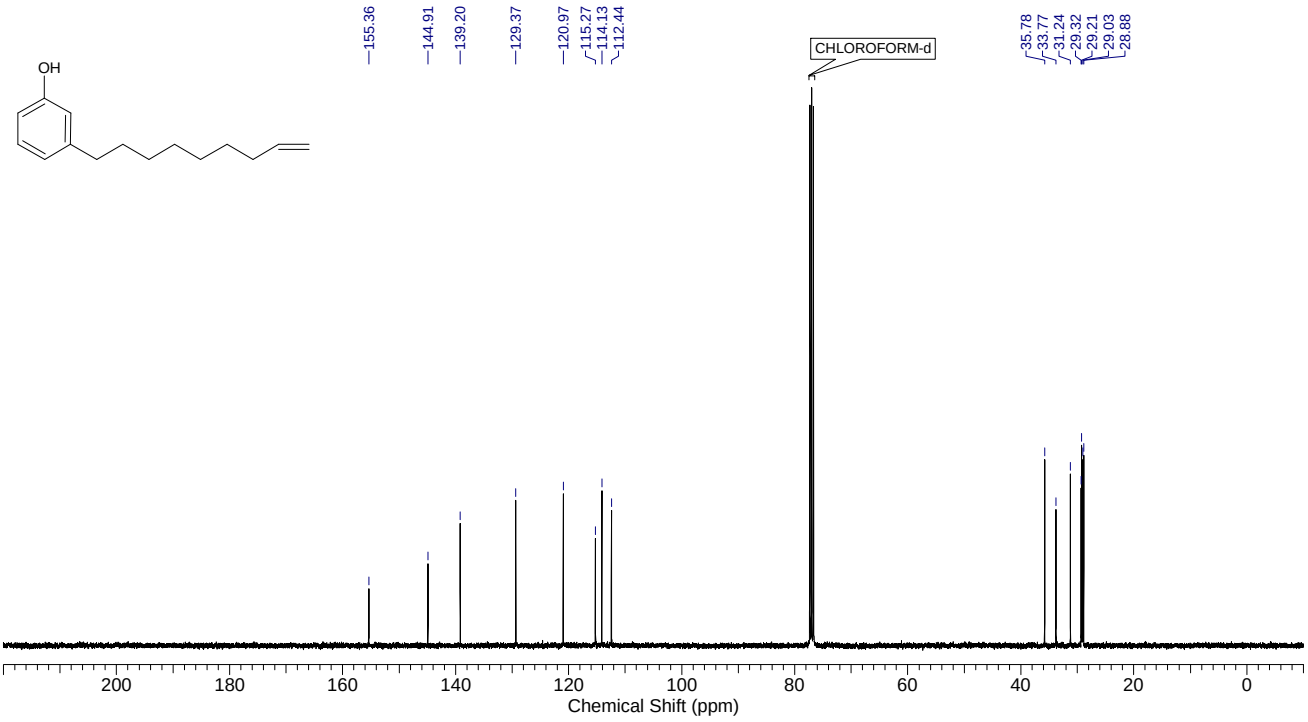


3-(non-8-enyl)phenol (5)

^{1}H-NMR (400 MHz, $CDCl_3$)

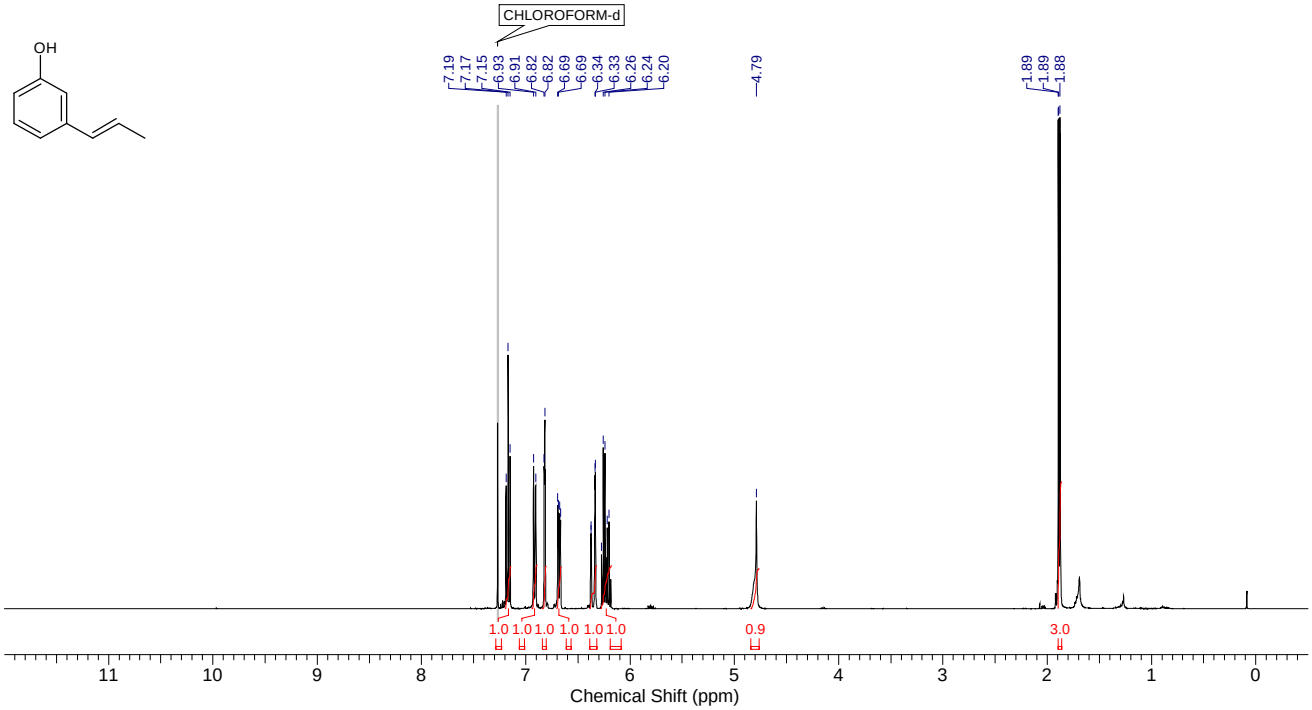


^{13}C-NMR (101 MHz, $CDCl_3$)

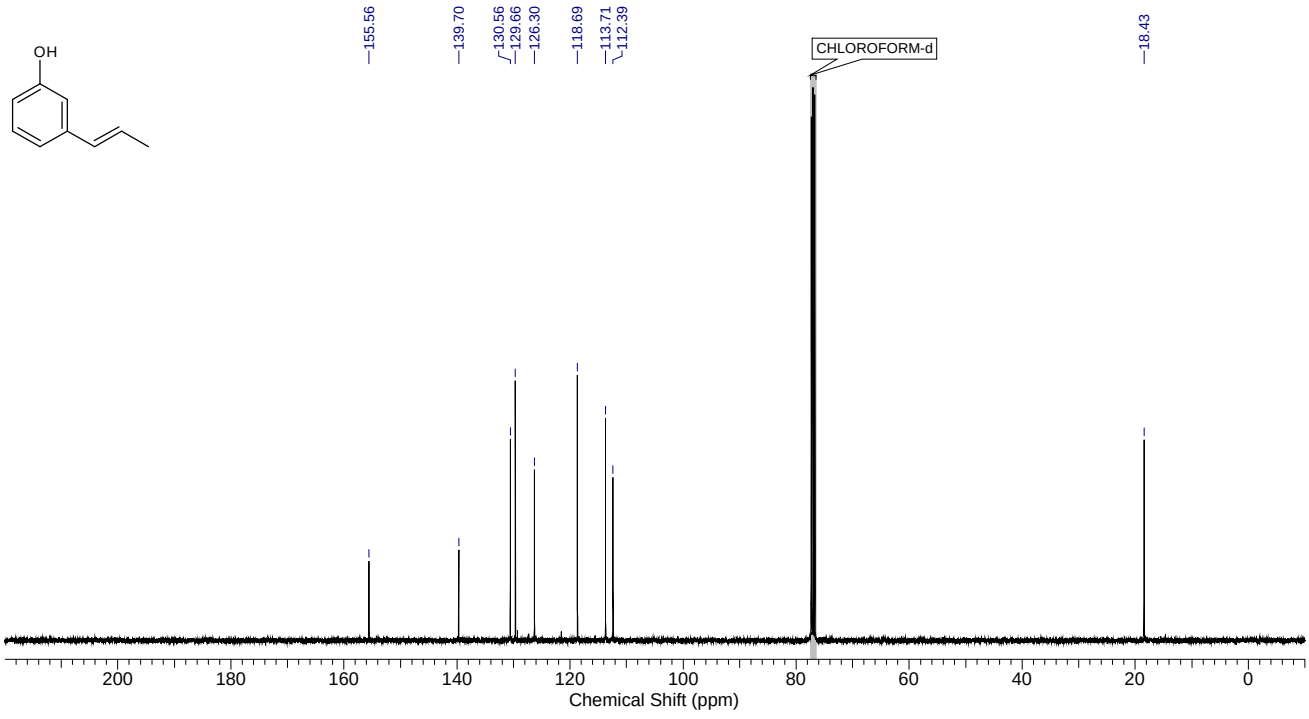


3-(prop-1-enyl)phenol (7)

^{1}H-NMR (400 MHz, $CDCl_3$)

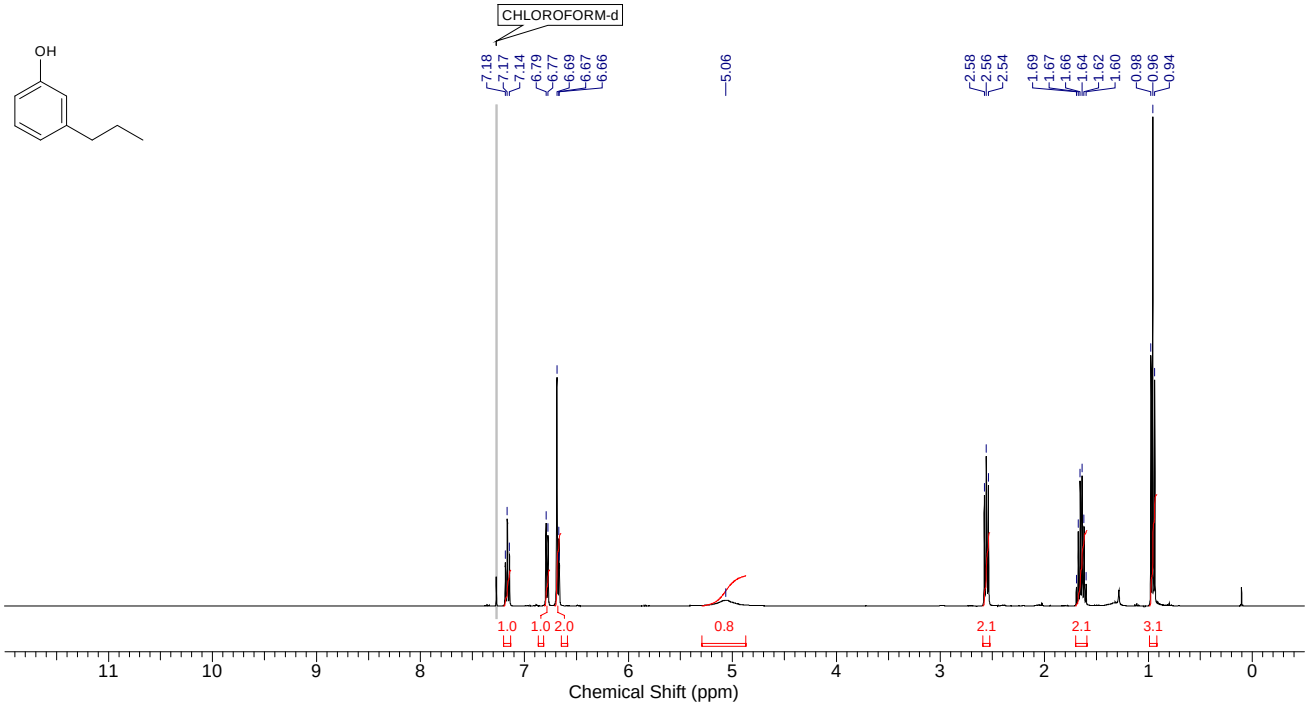


^{13}C-NMR (101 MHz, $CDCl_3$)

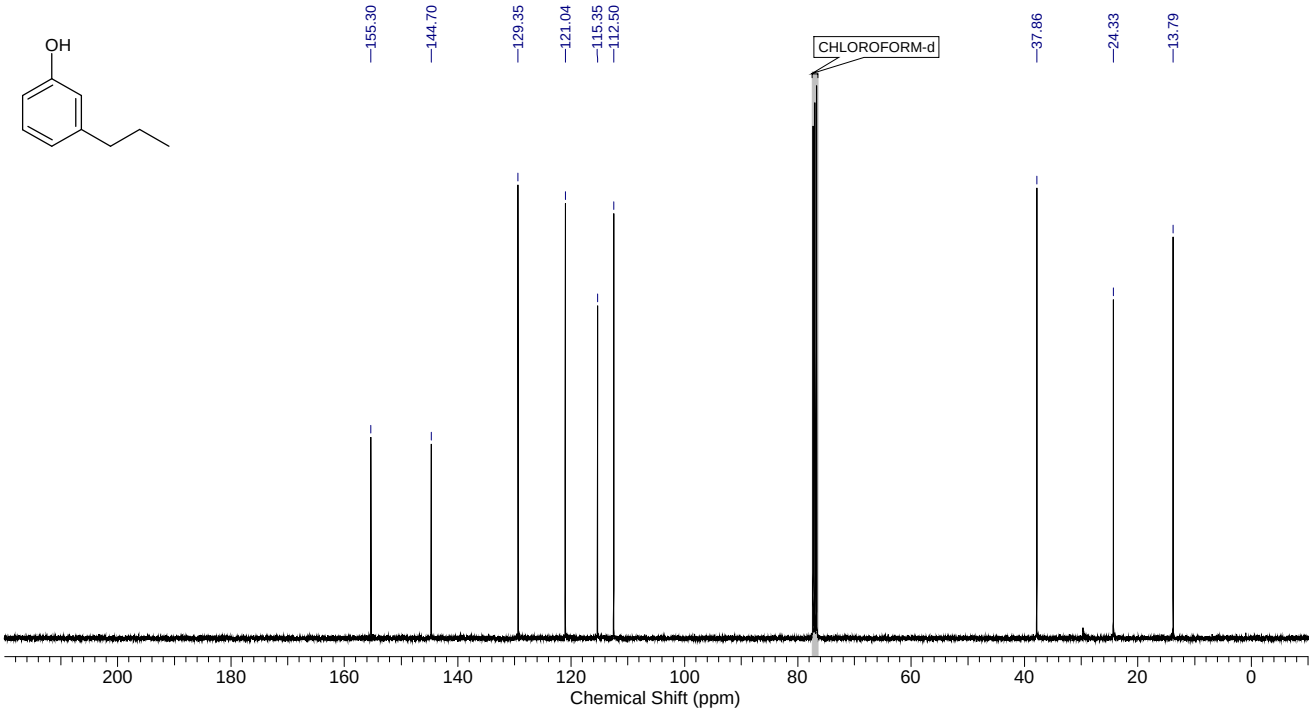


3-propylphenol (3)

^{1}H-NMR (400 MHz, $CDCl_3$)

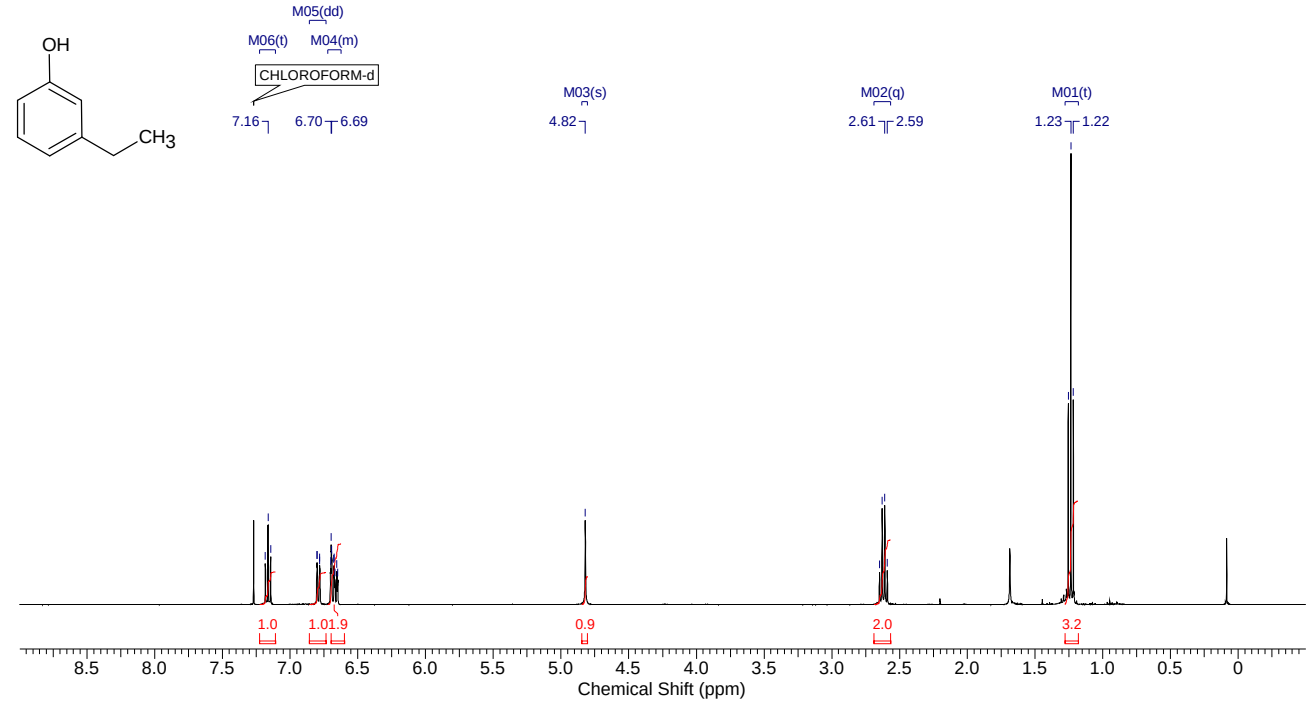


^{13}C-NMR (101 MHz, $CDCl_3$)



3-ethylphenol (2)

^{1}H-NMR (400 MHz, $CDCl_3$)



^{13}C-NMR (101 MHz, $CDCl_3$)