Supporting Information

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Methyl Perillate as a Highly Functionalized Natural Starting Material for Terephthalic Acid

Esmer Jongedijk,[b] Frits van der Klis,[c] Rozemarijn de Zwart,[c] Daan S. van Es,[c] and Jules Beekwilder*[a]

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Supporting Information

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Supplemental Materials and Methods
Figure S1 GC-MS chromatogram of *Salvia dorisiana* essential oil and a mix of standards. Essential oil concentration was 53.2 µg/mL in pentane, with 4.66 µg/mL cis-nerolidol (internal standard). Shown is total ion count (TIC), 100% = 5.13E6. Standard mix consisted of limonene (1) 8.36 µg/mL, perillyl aldehyde (2) 5.36 µg/mL, perillyl alcohol (3) 5.27 µg/mL, methyl perillate (4) 6.68 µg/mL, perilla acetate (5) 4.62 µg/mL and cis-nerolidol (6) 4.66 µg/mL in pentane, shown is TIC, 100% = 2.20E7. Identity of compounds a-f and x was determined by library hit: α-myrcene (a), some monoterpenes (b), myrtenyl acetate (c), a monoterpeno acetate (d), caryophyllene (e), some sesquiterpenes (f), and in the standard mix there was a small contamination of cuminyl acetate (x).
Figure S2 Oxidation of perillyl aldehyde with a silver oxide catalyst yielded near pure PA a. $^1$H-NMR spectrum of product in CDCl$_3$, PA peak numbers are indicated, b. $^{13}$C-NMR spectrum in CDCl$_3$, peak numbers indicated, c. GC-MS chromatogram (product in CHCl$_3$ methylated with TMSH), peak of methylperillate is visible at RT 15.75, d. Mass spectrum of the methylperillate peak at RT 15.75.
Fig. S3 GC-MS chromatograms of the methylation reaction of perillic acid (PA) to methylperillate (MPA) at different time-points, reaction samples diluted in chloroform and dried over MgSO4. The reaction yielded 8-methoxy-methyl perillate (MMPA) as a by-product. The longer the reaction time, the more MMPA was formed. At RT 17.75 a peak of another minor by-product is visible, the amount of this by-product increased with time as well. A short reaction time of 21 h ensured complete conversion of PA to MPA and small amount of the by-products, which could be readily separated by column-chromatography.
Fig. S4 Methylation of perillic acid with p-TSA yielded a mixture of methylperillate (MPA) and methoxymethylperillate (MMPA). The mixture could be readily separated with column chromatography or Kugelrohr distillation. a. GC-MS chromatograms of the reaction product mixture, MPA and MMPA products after separation and an MPA reference standard, b-d. characterization of MPA after separation, b. $^1$H-NMR in CDCl$_3$ of MPA, c. $^{13}$C-NMR (100.62 MHz, CDCl$_3$) of MPA, d. FT-IR of MPA, e-j. characterization of MMPA after separation, e. MS spectrum of methoxy methyl perillate (GC peak at RT 18.85), f. $^1$H-NMR (CDCl$_3$) of MMPA, g. $^{13}$C-NMR (100.62 MHz, CDCl$_3$) of MMPA, h. FT-IR of MMPA, i. DEPT135 spectrum of MMPA, j. 2D-HSQC (CDCl$_3$) spectrum of MMPA.
Fig. S4 b.

Fig. S4 c.
| Number | cm⁻¹ | Number | cm⁻¹ | Number | cm⁻¹ |
|--------|------|--------|------|--------|------|
| Peak1  | 708  | Peak7  | 1045 | Peak13 | 1380 |
| Peak2  | 742  | Peak8  | 1083 | Peak14 | 1435 |
| Peak3  | 803  | Peak9  | 1146 | Peak15 | 1649 |
| Peak4  | 887  | Peak10 | 1201 | Peak16 | 1712 |
| Peak5  | 922  | Peak11 | 1248 | Peak17 | 2937 |
| Peak6  | 975  | Peak12 | 1309 | Peak18 | 3082 |

Fig. S4 d.
Fig. S4 h.

Fig. S4 i.
Fig. S5 Dehydrogenation reaction of limonene to p-cymene at different reaction times, presence of limonene, p-cymene, dehydrogenation intermediates and acetone aldol-addition products was analyzed. a. GC-MS of dehydrogenation product at different reaction times, b. 1H-NMR of time 1h, c. 13C-NMR of 1h, d. 1H-NMR 3.5h, e. 13C-NMR 3.5h, f. 1H-NMR 20.25h, g. 13C-NMR 20.25h
Fig. S5 b

Fig. S5 c
Reaction time 3.5h

1, 2, 4 + 5 = 4H

Non-characterized dehydrogenation intermediates

7 = 3H

9 + 10 = 6H

Diacetone alcohol

8 = 1H

Reaction time 3.5h

3 + 7

4 + 6

5

2

10

9

7
Fig. S5 f

Fig. S5 g
Fig. S6. Methyl cumate, the product of dehydrogenation from MP. Byproducts related to acetone are detected, and some other byproducts are visible, b. $^1$H-NMR (400.17 MHz, CDCl3), methyl cumate peaks are indicated, and that of the acetone related by-products diacetone alcohol and mesityl oxide, c.$^{13}$C-NMR (100.62 MHz, CDCl3)
Fig. S7 GC-MS chromatograms of dehydrogenation reaction on mixed *Salvia* monoterpenes. The reaction yielded a mix of all the dehydrogenated forms, together with the starting materials, diacetone alcohol and some non-identified compounds.
Fig. S7 Oxidation of methyl cuminic acid (MCA) with nitric acid yields terephthalic acid (TA) in one step a. $^1$H-NMR of produced TA in DMSO, b. $^{13}$C-NMR of produced TA in DMSO, c. DEPT135 of produced TA (DMSO-D6) d. FT-IR of produced TA and TA reference compound, e. LC-MS and LC-MS/MS chromatograms of produced TA and TA reference compound, f. quantification of TA in product 69.7%, g. MS and MS/MS spectra of TA, h. MS and MS/MS spectra of byproduct. i. GC-MS chromatogram of silylated product.
Fig. S7c.

Fig. S7d.

Blue line: terephthalic acid reference compound
Green line: produced terephthalic acid by oxidation from cumic acid
Fig. S7c.

Calculation amount of TA formed:

\[
\frac{13303778}{4.5} = 2956395.1 \text{ (surface per concentration)}
\]

\[
\frac{17729538}{2956395.1} = 5.997 \text{ mg/mL} \text{ TA in oxidation product, so 69.7% TA in product}
\]

Fig. S7c.
**MS peak 1**

RT: 10.13 AV: 1 NL: 8.81E5
T: FTMS – c ESI Full ms [95.00-1300.00]

![Graph of MS peak 1](image)

Fig. S7g.

**MS/MS peak 1**

RT: 10.20 AV: 1 NL: 2.27E6
T: FTMS – c ESI d Full ms2 165.02@cid35.00 [50.00-180.00]

![Graph of MS/MS peak 1](image)

**MS peak 2**

RT: 25.87 AV: 1 NL: 3.79E5
T: FTMS – c ESI Full ms [95.00-1300.00]

![Graph of MS peak 2](image)

Fig. S7h.

**MS/MS peak 2**

RT: 25.93 AV: 1 NL: 6.01E5
T: FTMS – c ESI d Full ms2 239.63@cid35.00 [55.00-250.00]

![Graph of MS/MS peak 2](image)
Supplemental Scheme S1: Reaction scheme from MPA to MCA
Table S1 Quantification of perillic acid related monoterpenes in *Salvia dorisiana* hydrodistilled essential oil

| Compound            | g per kg essential oil |
|---------------------|------------------------|
| (-)-Limonene        | 83 (±22)               |
| Perillyl aldehyde   | 3.7 (±1.0)             |
| Perillyl alcohol    | 11.9 (±4.8)            |
| Methyl perillate    | 204 (±83)              |
| Perilla acetate     | 4.2 (±0.6)             |

Quantification was done by linear fit to authentic reference compound standard curve. ± standard deviation, n=5. Oil yield was 1.26 g oil / 100 g DW biomass (± 0.94 g, n=7).
| Compound[a] | Functional groups | Reactions needed | Natural source | Fermentative production |
|-------------|-------------------|-----------------|----------------|-------------------------|
| sugars      | oxygenated ring   | solubilization, hydrodeoxygenation, oxidation (100-600 °C, 0.1-83 bar) | biomass (sugars) | n.a.                    |
| lignin and lignocellulose | aromatic ring | Grinding, drying, cooling, solubilizing, pyrolysis, separation, oxidation (50-1000 °C) | biomass (lignin) | n.a.                    |
| isobutanol (via pX) | oxygenated carbohydrate | dehydration, dimerization, dehydrocyclization, oxidation (175–225 °C, 15–30 bar) (existing infrastructure Amoco) | biomass (sugars) | Yes[1] |
| fructose (via DMF, pX) | oxygenated ring | dehydration, hydrodeoxygenation, Diels-Alder, dehydration, oxidation (100-300 °C, 10-100 bar) | biomass (sugars) | n.a.                    |
| muconic acid | oxygenated carbohydrate | microbial synthesis, isomerization, Diels-Alder, catalytic dehydrogenation (150 °C) | biomass (sugars) | Yes[2] |
| FDCA        | 2 acid groups     | dehydration, oxidation, Diels-Alder, dehydration (100-200 °C, 5-20 bar) | biomass (sugars) | Yes[3] |
| limonene, pinene | oxygenated ring, functionalized p-position | dehydrogenation, oxidation | essential oil (Citrus) | Yes[4] |
| malic acid  | oxygenated carbohydrate | dimerization/condensation, esterification, Diels–Alder/retro-Diels–Alder/elimination | biomass (sugars) | Yes[6] |
| methyl perlic acid | oxygenated ring, acid group, functionalized p-position | dehydrogenation, oxidation | essential oil (Perilla, Salvia) | Yes[6] |

[a] Overview existing TA processes from Collias et al.[7]

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3: F. Koopman, N. Wierckx, J. H. de Winde, H. J. Ruijssenaars, Bioresour Technol 2010, 101, 6291-6296.
4: E. Jongedijk, K. Cankar, M. Buchhaupt, J. Schrader, H. Bouwmeester, J. Beekwilder, Appl Microbiol Biot 2016, 100, 2927-2938; E. Jongedijk, K. Cankar, J. Ranzijn, S. van der Krol, H. Bouwmeester, J. Beekwilder, Yeast 2015, 32, 159-171.
5: E. Jongedijk, K. Cankar, M. Buchhaupt, J. Schrader, H. Bouwmeester, J. Beekwilder, Appl Microbiol Biot 2016, 100, 2927-2938; A. E. Mars, J. P. Gorissen, I. van den Beld, G. Eggink, Appl Microbiol Biot 2001, 56, 101-107.
Table S3 Different oxidations of (-)-perillaldehyde to PA, or directly to MPA, that were tested. These included Pinnick oxidations (method of oxidation numbers 2 and 3) and oxidations catalyzed by gold/titanium oxide (number 4) and silver oxide (number 1). Highest efficiency was achieved using oxidation with silver oxide. Literature references, reaction details and the obtained result of all oxidation methods are indicated in the table.
Table S4 Reaction conditions tested for dehydrogenation reactions of limonene to p-cymene

| Catalyst     | Temperature | Yield of p-cymene (mol%) |
|--------------|-------------|--------------------------|
| 5% Pd/C      | 100 °C      | 0                        |
| 5% Pd/C      | 150 °C      | 80                       |
| 5% Pd/Al₂O₃ | 150 °C      | 56                       |
| 5% Pd/Al₂O₃ | 125 °C      | 69                       |
| 5% Pd/Al₂O₃ | 100 °C      | 75                       |
| 5% Pd/Al₂O₃ | 75 °C       | 0                        |
| 5% Pd/Al₂O₃ | 50 °C       | 0                        |

Reaction time was 17-21 hours.
Limonene : acetone : Pd molar equivalents were 1 : 19 : 0.007.
Catalysts were dry and reduced. Reactions were performed under nitrogen.
Table S5 Selectivity of dehydrogenation limonene to p-cymene at different reaction times

| Catalyst      | Temperature | Time  | Yield of p-cymene (mole%) | Ratio p-cymene : diacetone alcohol : mesityl oxide |
|---------------|-------------|-------|---------------------------|-----------------------------------------------|
| 5% Pd/Al₂O₃  | 125 °C      | 1 h   | 82**                      | 1 : 0.14 : 0.00                             |
| 5% Pd/Al₂O₃  | 125 °C      | 3.5 h | 82                        | 1 : 0.13 : 0.00                             |
| 5% Pd/Al₂O₃  | 125 °C      | 20 h  | 80                        | 1 : 0.15 : 0.18                             |
| 5% Pd/Al₂O₃  | 125 °C      | 27 h  | 77                        | 1 : 0.19 : 0.21                             |

**optimal conditions, optimized for limonene.
2. Materials and Methods

2.1 Chemicals

\((R)-(+)\text{-limonene (97\%, Sigma Aldrich), perillyl alcohol (96\%, Sigma Aldrich), (S)-(\text{-})-perillaldehyde (Sigma Aldrich), (S)-(\text{-})-perillyl acetate (Wako), (S)-(\text{-})-perillic acid (95\%, Sigma Aldrich), cis-nerolidol (98\%, Fluka), pentane (≥99.0\%, CHROMASOLV® for HPLC, Sigma Aldrich), cumin acid (4-isopropylbenzoid acid, ≥98\%, Sigma Aldrich), magnesium sulphate (dried, 1-2 mol hydration water, Alfa Aesar), ethyl acetate (pure, Acros Organics), hydrochloric acid (37\%, reag. Ph. Eur., VWR), p-toluenesulfonic acid monohydrate (p-TSA, 98.5\%, ACS reagent, Sigma Aldrich), methanol (for analysis, Merck), petroleum ether (PE, ACS reagent, boiling range 40-60°C, Acros Organics), trimethyl sulfonium hydroxide solution (TMSH, ~0.25 M in methanol, Sigma Aldrich), sicapent (Merck), silica gel 60 (0.040-0.063 mm, 230-400 mesh, Alfa Aesar), acetone (≥99.8\%, Actu-All Chemicals), palladium 5\% on alumina powder (reduced, Escalet 1241, Strem Chemicals), palladium 5\% on activated carbon (reduced, dry powder, Strem Chemicals), platinum on carbon (extent of labelling 10wt% loading, matrix activated carbon support, Aldrich), ruthenium 5\% on carbon (Strem Chemicals), chloroform (HPLC grade, stabilized with ethanol, min. 99.9\%, Actu-All Chemicals), sodium chloride (VWR Chemicals), celite 545 (Sigma Aldrich), nitric acid (65\%, G.R. for analysis, Merck), sodium nitrite (puriss, p.a. ACS >99.0\%, Fluka), silylation reagent (BSTFA + TMCS, 99:1, Supelco), DMSO-D\textsubscript{6} (99.5\% D, containing 0.03 \% v/v trimethylsilane (TMS), Aldrich)\)

2.2 Plant growth, multiplication and measurements

\textit{Salvia dorisiana} plants were obtained from a local nursery. Standard growth conditions were 12 h day / 12 h night, 20°C / 18°C in the greenhouse.

2.3 Leaf extraction
Fresh leaves ≤ 3 cm were snap frozen in liquid nitrogen and ground with pestle and mortar. 139.8 mg of powder was extracted with 6 mL pentane containing 4.66 μg/mL cis-nerolidol as internal standard for analysis by GC-MS.

2.4 Essential oil distillation

Hydrodistillation was performed on lab-scale according to Stahl (Stahl, 1962). Hundred grams of fresh *Salvia dorisiana* leaves ≤ 3 cm were cut. The leaves were cooked in 1 L demi water in a 2 L round bottom flask for 1 h without organic solvent, and afterwards the pure essential oil layer was removed from the 4°C cooling bulb with a long Pasteur pipette. The essential oil was dried over a MgSO₄ column, and the oil yield in w/w% of fresh weight (FW) of the leaves determined, average yield from one distillation 0.13 g (0.13 w/w%).

Steam distillation was performed for larger-scale oil harvesting, in a home-made kettle and cooling system [http://indekoperenketel.nl/]. Tap water (30 L) was heated to 100°C and the steam lead through 16.34 kg of *Salvia dorisiana* prunings during 1 h. Steam with extracted volatiles was then cooled-down gradually to 10-15°C. The water layer of the condensate was continuously removed by a separation funnel during distillation. The water layer was extracted one time with diethyl ether, and this was combined with the oil layer. The solvent was evaporated and the essential oil was dried over MgSO₄, yield 10.7 g (0.065 w/w%).

2.5 Quantification of monoterpenes

The oil was diluted to 53.2 μg/mL in pentane for analysis by GC-MS. A standard series of limonene, methylperillate, perillyl alcohol, perillyl aldehyde and perillyl acetate was prepared ranging from 0.1- 50 μg/mL in pentane. Oil and leaf compounds were quantified using a linear and 2nd order polynomial fitted equation from the standard series.

2.6 GC-MS analysis
GC-MS analysis of essential oil was performed on a 7890A gas chromatograph (Agilent) equipped with a mass selective detector (Model 5975C, Agilent) with settings as reported previously (Jongedijk et al., 2015).

GC-MS analysis of synthesis products was performed on an Interscience TraceGC Ultra GC with AS3000 II autosampler, connected to an Interscience TraceDSQ II XL quadrupole mass selective detector with settings as reported previously (van der Klis et al., 2012; van der Klis et al., 2017).

2.7 LC-MS analysis

LC-MS was performed on an Accela HPLC tower connected to a LTQ/Orbitrap hybrid mass spectrometer (Thermo Fisher Scientific), conditions and settings as described previously (van der Hooft et al., 2012).

2.8 NMR analysis

NMR spectra were recorded on a Bruker Avance III spectrometer operating at 400.17 MHz ($^{1}\text{H}$) and 100.62 MHz ($^{13}\text{C}$). Proton NMR chemical shifts are quoted in parts per million (ppm) referenced to the appropriate solvent peak. Carbon NMR was fully decoupled by broadband decoupling.

2.9 FT-IR

Fourier transform infrared (FT-IR) spectra were obtained on a Varian Scimitar 1000 FT-IR spectrometer equipped with a Pike MIRacle ATR Diamond/ZnSe single reflection plate and a DTSG-detector. The measurement resolution was set at 4 cm$^{-1}$, and the spectra were collected in the range 4000-650 cm$^{-1}$ with 64 co-added scans.

2.10 Synthesis of methylperillate
Perillyl aldehyde (50 g) was oxidized to perillic acid using silver oxide, prepared in-situ from silver nitrate and sodium hydroxide as described previously (Wang et al., 1993). After oxidation, the combined filtrate and washings were acidified with dilute hydrochloric acid until pH ~ 1.5 and filtered. Pure perillic acid was obtained, 33.65 g (yield 61%). The product was characterized by $^1$H-NMR and $^{13}$C-NMR. The product was characterized by GC-MS after derivatisation with TMSH. $^1$H-NMR (400.17 MHz, CDCl$_3$): δ 1.41 (2H, m, $J$=4.0Hz, H-5,), 1.68 (3H, s, H-10), 1.82 and 1.84 (2H, d, $J$=8.0Hz, H-6), 2.08 (2H, m, $J$=8.0Hz, H-3), 2.28-2.42 (1H, m, $J$=16.0Hz, H-4), 4.56 and 4.70 (2H, s, H-9), 7.07 (1H, s, H-2), 11.05 (1H, s, H-11); $^{13}$C-NMR (100.62 MHz, CDCl$_3$): δ 20.69 (C-10), 24.15 (C-6), 26.95 (C-5), 31.26 (C-3), 39.94 (C-4), 109.28 (C-9), 129.48 (C-1), 141.87 (C-2), 148.61 (C-8), 172.82 (C-7).

Perillic acid was esterified with excess methanol, using tolenesulfonic acid as catalyst (Dayal et al., 1981). Perillic acid (3.00 mmol, 0.50 g) was dissolved in methanol (0.32 mol, 13 mL) and $p$-toluenesulfonic acid (0.15 mmol, 0.029 g), stirred (350 rpm) and heated to reflux (65 °C) for 22 h under N$_2$. The solution was cooled to room temperature and diluted with 12 mL chloroform, washed twice with saturated sodium bicarbonate (15 mL) and once with brine (15 mL). The organic layer (bottom) was diluted with chloroform to 20 mL, dried with magnesium sulphate and filtered. The solvent was removed using a rotary evaporator at 40 °C. The slightly-yellow oil was identified by GC-MS. A by-product was detected, that was identified as 8-methoxy-methylperillate by NMR and GC-MS. The product mixture was separated on column (2.3 cm diameter, 10 g silica, eluent PE:EtOAc 90:10). Fractions were evaporated and analysed with $^1$H-NMR, $^{13}$C-NMR and GC-MS. Methylperillate yield: 0.259 g (47 mole%). The procedure was scaled up at least 10 times with similar results. $^1$H-NMR (400.17 MHz, CDCl$_3$): δ 1.43-1.48 (1H, m, $J$=4.0Hz, H-5), 1.75 (3H, s, H-10), 1.82-1.84 (2H, m, $J$=4.0Hz, H-5), 2.08 (2H, m, $J$=4.0Hz, H-6), 2.13-2.18 (2H, m, $J$=8.0Hz, H-3), 2.25-2.40 (1H, m, $J$=4.0Hz, H-4), 3.72 (3H, s, H-11), 4.66 and 4.70 (2H, s, H-9), 6.93 (1H, m, $J$=4.0Hz,
During methylation 8-methoxy-methylperillate (MMPA) was formed as a by-product. Longer reaction times yielded more MMPA (Fig. 1, Fig. A3). A reaction time of 21h ensured complete conversion of perillic acid to MPA with minimal MMPA formation. MMPA and other minor by-products could readily be separated from MPA by column chromatography or Kugelrohr distillation (Fig. A4). According to our knowledge the compound MMPA has not been reported before, characterization data of MPA and MMPA are added in Fig. A4.

2.11 Dehydrogenation to methyl cumate

Dehydrogenation conditions were initially optimized for limonene (Table 2). Methylperillate was dehydrogenated to methyl cumate using a supported palladium catalyst (Grau et al., 1999). Purified methylperillate (96% pure), 2.66 mmol, 0.479 g, 0.5 mL, was dissolved in acetone (0.300 mol, 22 mL) in a stirred (830 rpm) 75 mL reactor (MRS5000, Parr instrument company, Illinois, USA) with 5% Pd/Al2O3 catalyst (0.2038 g, ~0.096 mmol Pd), flushed 3 times with N2 and then heated to 125 °C for 1 h under N2. Subsequently, the reactor was let to cool down to room temperature. Then the solution was filtered over a Celite pad and washed with acetone. The solvent was removed using a rotary evaporator at 40 °C. The product was analysed with 1H-NMR, 13C-NMR and GC-MS. Some minor by-products related to acetone were observed, among these were diacetone alcohol, that can be formed by aldol addition of two molecules of acetone, and mesityl oxide, the dehydration product of diacetone alcohol. Yield: 0.721 g, 45% pure (total yield methylcumate from methylperillate 69 mole%). 1H-NMR (400.17 MHz, CDCl3) δ 1.25 (6H, s, H-9 and H-10), 2.92-2.98 (1H, m, J=8.0Hz, H-8), 3.89 (3H, 2, H-11), 7.27-7.29 (2H, m, J= 8.0Hz, H-3 and H-5), 7.94-7.96 (2H, m, J=8.0Hz, H-2 and H-6); 13C-NMR (100.62 MHz, CDCl3) δ 23.63-23.64 (C-9 and C-10), 30.83 (C-8), 34.19 (C-7), 51.85(C-
NMR characterization matches that reported in literature (Zhu et al., 2013).

2.12 Oxidation of cumic acid to terephthalic acid

A 50 mL round bottom flask was equipped with a magnetic stirring bar and a Liebig condenser. The round bottom flask was placed on a stirring plate with an aluminium heating mantle. The flask was charged with water (20 mL), followed by 65% nitric acid (14.4 g) and sodium nitrite (10 mg) to initiate the reaction. The mixture was stirred and gently heated to ~40 °C until the mixture became yellow. Next, cumic acid (5.0 g) was added to the stirred nitric acid solution, to give a white suspension. The suspension was heated to reflux, and became clear after ~30 min at reflux. After 24 h reflux, the reaction mixture had turned into a white suspension again. The mixture was allowed to cool down to room temperature, and the white solid was collected from the suspension by filtration (type 3 glass filter). The filter cake was washed with demineralized water, and dried under vacuum to constant weight (40 °C, ~50 mbar, in the presence of Sicapent). The product was obtained as a white powder. Yield: 4.5 g (89 mole%). The product was analysed with GC-MS after silylation, and with ¹H-NMR and ¹³C-NMR. ¹H-NMR (400.17 MHz, DMSO-D₆) δ 13.32 (2H, s, H-7 and H-8), 8.03 (4H, s, H-2, H-3, H-5 and H-6); ¹³C-NMR (100.62 MHz, DMSO-D₆) δ 129.43 (C-2, C-3, C-5, C-6), 134.44 (C-1, C-4), 166.64 (C-7, C-8).