Divergent Pathways to Furosesquiterpenes. First Total Syntheses of (+)-Zedoarol and (Rac)-Gweicurculactone.

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Supporting Information
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I. General Information

All reactions were carried out under an argon atmosphere with dry solvents under anhydrous conditions. Dry diethyl ether (Et₂O), and tetrahydrofuran (THF), were obtained by refluxing the solvents with sodium and benzophenone for several hours whereas methylene chloride (CH₂Cl₂) was dried by distillation from CaH₂. The solvents were kept under argon using molecular sieves 4Å in their bottles. Reagents were purchased at the highest commercial quality and used without further purification.

Reactions were monitored by thin-layer chromatography (TLC) carried out on S-2 0.25 mm E. Merck silica gel plates (60F-254) using UV light as visualizing agent and ethanolic p-anisaldehyde as developing agent. E. Merck silica gel (60, particle size 0.040–0.063 mm) was used for flash column chromatography. Silica gel was neutralized with 1% Et₃N and used in all indicative cases where compounds are sensitive to acidic conditions. Preparative thin-layer chromatography separations were carried out on 0.25 or 0.50 mm E. Merck silica gel plates (60F-254).

NMR spectra were recorded on Brüker 300 AM and Agilent 500 spectrometer and calibrated using TMS as an internal reference. The following abbreviations are used to designate multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad, brd = broad doublet, brt = broad triplet, pst = pseudo triplet. High-resolution mass spectra (HRMS) were recorded on an Agilent ESI-TOF (time of flight) mass spectrometer at a 4000 V emitter voltage. Optical rotations were recorded on a Perkin-Elmer Model 343 polarimeter at 589 nm, and are reported in units of 10⁻¹(deg cm² g⁻¹).
II. Experimental procedures and physical properties of compounds

(R,S)-furanogermenteone (2)

In a well-dried schlenk tube a solution of compound 1 (235 mg, 1.00 mmol) in dry THF (7 ml) was introduced and deoxygenated in high vacuum with the aid of liquid nitrogen. Then oil free KH (40 mg, 1.00 mmol) was added at once and the mixture was immediately capped and heated for 10 min at 65 °C. The mixture was cooled down at room temperature and quenched by the addition of 5 ml of saturated aqueous ammonium chloride. The aqueous layer was extracted with Et₂O (3 X 10 ml) and the combined organic extracts were dried over anhydrous sodium sulfate, filtered and concentrated in vacuo. Purification by neutralized silica gel flash column chromatography (petroleum/ Et₂O = 100:1) gave 2 (193 mg, 82%) as a white solid. Compound 2 lacks of optical activity. Rf = 0.30 (petroleum/ Et₂O = 3:1). ¹H NMR (300 MHz, CDCl₃): δ = 7.09 (brs, 1H), 5.14 (brt, 1H), 3.44 (d, J = 15Hz, 1H), 3.41 – 3.30 (m, 1H), 3.21 (brd, J = 15Hz, 2H), 2.60 – 2.46 (m, 1H), 2.31 – 2.06 (m, 2H), 2.02 – 1.88 (m, 1H), 1.88 (s, 3H), 1.82 – 1.76 (m, 1H), 1.69 (brs, 3H), 1.08 (d, J = 6Hz, 3H); ¹³C NMR (75 MHz, CDCl₃): δ = 213.3, 148.8, 136.5, 131.8, 131.7, 121.9, 113.7, 47.3, 38.4, 36.4, 36.3, 29.6, 18.3, 17.3, 8.12.

Compound 3

In a well-dried schlenk tube, a solution of compound 1 (235 mg, 1.00 mmol) in dry THF (7 ml) was introduced and deoxygenated in high vacuum with the aid of liquid nitrogen. In the resulting solution a 1M solution of KHMDS in toluene (1ml, 1.00 mmol) was introduced and the schlenk was capped and heated to 90 °C for 10 min. The mixture was cooled down at room temperature and quenched by the addition of 5 ml of saturated aqueous ammonium chloride. The aqueous layer was extracted with Et₂O (3 X 10 ml) and the combined organic extracts were dried over anhydrous sodium sulfate, filtered and concentrated in vacuo.
Purification by neutralized silica gel flash column chromatography (petroleum/\(\text{Et}_2\text{O} = 100:1\)) provided compound 3 as a yellow oil (139 mg, 65%). \(R_f = 0.73\) (petroleum/\(\text{Et}_2\text{O} = 3:1\)). Compound 3 was obtained as racemic mixture. \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta = 7.18\) (brs, 1H), 6.36 (brs, 1H), 3.09 [d, (a,b system), \(J = 15.8\)Hz, 1H], 2.79 – 2.76 (m, 1H), 2.57 – 2.51 (m, 1H), 2.48 – 2.41 (m, 1H), 2.15 – 2.11 (m, 1H), 2.01 (brs, 3H), 1.97 (d, \(J = 1.2\)Hz, 3H), 1.47 – 1.40 (m, 1H), 1.12 (d, \(J = 7\)Hz, 3H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta = 150.4, 140.5, 139.3, 135.0, 133.3, 119.4, 117.3, 116.0, 44.5, 33.4, 31.2, 23.2, 21.4, 19.6, 7.9\); HRMS: calcd for \(\text{C}_{15}\text{H}_{19}\text{O}^+\) [M + H\(^+\)]: 215.1436, found 215.1439.

![Gweicurculactone (4)](image)

**Racemic (R,S)-Gweicurculactone (4)**

A solution of compound 3 (30 mg, 0.14 mmol) in DCM was stirred at room temperature for 1 day before evaporated to dryness and purified by neutralized silica gel flash column chromatography (petroleum/\(\text{Et}_2\text{O} = 30:1\)). Racemic compound 4 (11 mg, 35%) was obtained as a reddish solid which was found to be identical to the natural substance\(^2\) except from its optical rotation. \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta = 6.86\) (s, 1H), 6.70 (s, 1H), 3.10 – 3.00 (m, 1H), 2.84 – 2.74 (m, 1H), 2.71 – 2.61 (m, 1H), 2.21 (s, 3H), 2.14 – 2.05 (m, 1H), 1.95 (s, 3H), 1.51 (m, 1H), 1.28 (d, \(J = 4.8\) Hz, 3H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta = 170.7, 156.7, 154.9, 146.3, 144.3, 136.6, 118.0, 116.4, 103.7, 44.0, 33.8, 32.1, 24.8, 20.2, 7.8\); HRMS: calcd for \(\text{C}_{13}\text{H}_{17}\text{O}_2^+\) [M + H\(^+\)]: 229.1228, found 229.1223.

![5-Hydroxy-furanogermanone (7)](image)

**R(S)-5-Hydroxy-furanogermanone (7)**

In a well-dried schlenk tube, a solution of compound 1\(^1\) (50 mg, 0.22 mmol) in dry THF (7 ml) was introduced and it was saturated with dry oxygen gas (passed through anhydrous CaCl\(_2\)). In the resulting solution, oil free KH (9 mg, 0.22 mmol) was added at once and the mixture was immediately capped and heated for 10 min at 65 °C. The mixture was cooled down at
room temperature and quenched by the addition of 5 ml of saturated aqueous ammonium chloride. The aqueous layer was extracted with Et₂O (3 X 10 ml) and the combined organic extracts were dried over anhydrous sodium sulfate, filtered and concentrated in vacuo. Purification by neutralized silica gel flash column chromatography (petroleum/ Et₂O = 50:1) gave 7 (24 mg, 45%) as a colourless oil. Compound 7 was obtained as racemic mixture. Rₗ = 0.13 (petroleum/ Et₂O = 3:1). ¹H NMR (300 MHz, CDCl₃): δ = 7.13 (brs, 1H), 5.27 (brt, 1H), 4.23 – 3.96 (m, 1H), 3.92 – 3.69 (m, 1H), 3.47 – 3.04 (m, 3H), 2.43 – 2.02 (m, 4H), 1.91 (s, 3H), 1.40 (brs, 3H); ¹³C NMR (75 MHz, CDCl₃): δ = 211.5, 148.8, 136.8, 132.5, 130.5, 122.4, 113.6, 78.6, 39.0, 31.1, 28.0, 27.1, 22.5, 17.1, 8.0; HRMS: calcd for C₁₅H₂₁O₃⁺ [M + H⁺]: 249.1490, found 249.1487.

**Compound 10 and mixture of compounds 11**

To a stirred solution of compound 9 (100 mg, 0.52 mmol) in dry THF (2 ml) was added a solution of 1M LiHMDS in THF (0.48 ml, 0.48 mmol) under argon atmosphere at -78 °C. After 30 min, R(-)-10-camphorosulphonyl oxaziridine (108 mg, 0.48 mmol) dissolved in dry THF (0.5 ml) was added at the same temperature and the resulting solution was stirred for 45 min at the same temperature. Then the reaction mixture was quenched by the addition of 1.5 ml saturated aqueous sodium thiosulphate and the aqueous layer was extracted with Et₂O (3 X 8 ml). The combined organic extracts are dried over anhydrous sodium sulfate, filtered and concentrated in vacuo. Purification by silica gel flash column chromatography (petroleum/ Et₂O = 50:1) provided compound 10 (54 mg, 52%) as a pale yellow oil. The compound was readily transformed to its regioisomeric compounds 11 over 2h at rt or within few minutes when dissolved in CDCl₃. Rᵣ = 0.48 (petroleum/ Et₂O = 3:1). ¹H NMR (500 MHz, CDCl₃): δ = 7.11 (s, 1H), 5.96 (dd, J = 17.4Hz, 10.7Hz, 1H), 5.21 (d, J = 10.7Hz, 1H), 5.18 (d, J = 17.4Hz, 1H), 3.37 (s, 1H), 3.05 [d, (a,b system), J = 1.4Hz, 1H], 2.85 [d, (a,b system), J = 1.4Hz, 1H], 2.08 (s, 3H), 1.36 (s, 3H). Its stereochemistry was elucidated by NOESY NMR spectroscopy of its acetyl derivative 21. Acetyl derivative also fails to give a stable compound and also readily transforms to a mixture of acetylated compounds. For acetyl derivative 20: Compound 10 (20 mg, 0.10 mmol) was dissolved in DCM (1 ml) and treated with Ac₂O (46 μL, 0.50 mmol) at rt for 6h. The resulting mixture was quenched with water and extracted with Et₂O (3 X 8 ml).
The combined organic extracts are dried over anhydrous sodium sulfate, filtered and concentrated in vacuo. Purification by silica gel flash column chromatography (petroleum/ Et₂O = 50:1) provided 20 (21 mg, 85%) as a pale yellow oil. Rₜ = 0.62 (petroleum/ Et₂O = 3:1)

¹H NMR (500 MHz, CDCl₃): δ = 7.12 (s, 1H), 6.30 (d, J = 5 Hz, 1H), 5.92 (dd, J = 20 Hz, 10 Hz, 1H), 5.21 (d, J = 10Hz, 1H), 5.17 (d, J =20Hz, 1H), 3.03 [d, (a,b system), J = 20Hz, 1H], 2.85 [d, (a,b system), J = 20Hz, 1H], 2.19 (s, 3H), 1.92 (s, 3H), 1.32 (s, 3H); HRMS: calcd for C₁₄H₂₁O₆⁺ [M + H⁺]: 249.1127, found 249.1119.

For compounds 11 (mixture of isomers almost 1:1 ratio): ¹H NMR (500 MHz, CDCl₃): δ = 7.14 (s, 1H), 7.11 (s, 1H), 6.13 (dd, J = 20Hz, J =15Hz, 1H), 5.80 (dd, J = 20Hz, J = 10Hz, 1H), 5.22 (m, 1H), 5.03 (d, J = 11Hz , 1H), 4.98 (d, J = 18Hz, 1H), 4.17 (brs, 1H), 3.8 (brs, 1H), 3.06 [d, (a,b system), J = 17Hz, 1H], 2.78 [d, (a,b system), J = 17Hz, 1H], 3.03 [d, (a,b system), J = 17Hz, 1H], 2.91 [d, (a,b system), J = 17Hz, 1H], 2.2 (s, 3H), 2.18 (s, 3H), 1.43 (s, 1H), 1.03 (s, 1H); ¹³C NMR (75 MHz, CDCl₃): δ = 193.9, 193.9, 165.7, 165.5, 143.8, 140.3, 140.1, 138.0, 119.0, 118.9, 118.3, 117.5, 115.4, 113.5, 80.2, 78.7, 46.8, 46.5, 35.2, 35.0, 25.6, 16.3, 8.7, 8.6.

7-hydroxy-furanogermenone (13) and compounds 14

To a stirred solution of furanogermenone (2) (48 mg, 0.21 mmol) in dry THF (2 ml) was added a 1.6M solution of nBuLi in pentane (0.15 ml, 0.25 mmol) under argon atmosphere at -78 °C. After 40 min, the solution was warmed to rt for 15 min before R(-)-10-camphorosulphonyl oxaziridine (56 mg, 0.25 mmol) dissolved in dry THF (0.5 ml) introduced to the reaction mixture at -78 °C. The reaction was stirred for 45 min at the same temperature. Then, the reaction mixture was quenched by the addition of 1.5 ml saturated aqueous sodium dicarbonate and the aqueous layer was extracted with Et₂O (3 X 7 ml). The combined organic extracts were dried over anhydrous sodium sulfate, filtered and concentrated in vacuo. Purification by silica gel flash column chromatography (petroleum/ Et₂O = 100:1) provided compound 13 (21 mg, 40%) as a colourless oil, along with compound 14 (4 mg, 8%) as a colourless oil and starting material 2 (20 mg, 42%). For compound 13: Rₜ = 0.18 (petroleum/ Et₂O = 3:1). [α]²⁵D = + 4.5 (c 1.1, CHCl₃). ¹H NMR (300 MHz, CDCl₃): δ = 7.08 (brs, 1H), 4.96 (brs, 2H), 3.91 (brs, 1H), 3.36 (d, J = 16Hz, 1H), 3.09 (d, J = 16Hz, 1H), 2.63 – 2.46 (m, 1H), 2.36 – 2.10 (m, 2H), 2.07 (s, 3H), 1.72 – 1.56 (m, 2H), 1.26 (s, 3H), 1.06 (d, J = 7 Hz, 3H).
Derivatization of compound 13 using (S)-camphanic acid: Compound 13 (4 mg, 0.016 mmol) was dissolved in THF (0.5 ml) before (S)-camphanic acid (3.2 mg, 0.016 mmol) and EDC (3 mg, 0.016) introduced in the reaction mixture at rt. The reaction mixture was left for stirring at the same temperature for 12 h before quenched with saturated NaHCO₃ (3 ml) and extracted with Et₂O (3 x 5 ml). The combined organic extracts were dried with anhydrous sodium sulfate, filtered and evaporated in vacuo. Estimation of the enantiomeric excess of compound 13 was judged by the crude NMR of the reaction mixture.

**Compound 15**

To a stirred suspension of PDC (18 mg, 0.048 mmol) and silica gel (10 mg) in dry CH₂Cl₂ (1 ml) was added dropwise at room temperature a solution of the alcohol 13 (10 mg, 0.04 mmol) in dry CH₂Cl₂ (1 ml). The reaction mixture was vigorously stirred under argon atmosphere for 4h. The resulting dark brown slurry was filtered through a short column of celite, eluted with Et₂O and chromatographed on neutralized silica gel column (petroleum/ Et₂O = 100:1) to give 15 (9 mg, 90%) as a colourless oil. The compound is readily transforms to a mixture of zedoarol (18) and several other unidentified compounds. Rₚ = 0.63 (petroleum/Et₂O = 3:1).

¹H NMR (300 MHz, CDCl₃): δ = 7.10 (brs, 1H), 5.29 – 5.16 (m, 1H), 3.54 [d, (a,b system), J = 16.5Hz, 1H], 3.31 [d, (a,b system), J = 16.5Hz, 1H], 3.00 – 2.83(m, 1H), 2.32 –1.94 (m, 4H), 2.04 (s, 7H), 1.57 (s, 3H), 1.27 (s, 3H).
Zedoarol (17)

To a stirred suspension of PDC (55 mg, 0.15 mmol) and silica gel (30 mg) in dry CH₂Cl₂ (1 ml) was added dropwise at room temperature a solution of the alcohols 14 (30 mg, 0.12 mmol) in dry CH₂Cl₂ (1 ml). The reaction mixture was vigorously stirred under argon atmosphere for 24 h. The resulting dark brown slurry was filtered through a short column of celite, eluted with Et₂O and chromatographed on neutralized silica gel column (petroleum/ Et₂O = 50:1) to give zedoarol 17 (23 mg, 77%) as a colourless oil.

Alternatively:

A stirred solution of compound 15 (10 mg, 0.04 mmol) in toluene (1 ml) was heated for 4 h at 140°C. Then, the mixture was concentrated in vacuo. Purification by neutralized silica gel flash column chromatography (petroleum/ Et₂O = 50:1) provided zedoarol 17 (8 mg, 80%) as a colourless oil.

R_f = 0.44 (petroleum/ Et₂O = 3:1). [a]_D = + 10.2 (c 1.0, CHCl₃) (literature³ [a]_D = + 11.6 (c 1.0)). ^1H NMR (300 MHz, CDCl₃): δ = 7.05 (brs, 1H), 5.30 (brs, 1H), 5.14 (brs, 1H), 3.83 (d, J = 18 Hz, 1H), 3.65 (d, J = 18 Hz, 1H), 2.97 (t, J = 9.5 Hz, 1H), 2.58 – 2.48 (m, 1H), 2.13 (brs, 3H), 2.06 (m, 1H), 1.92 (m, 1H), 1.90 (m, 1H), 1.46 (m, 1H), 1.14 (d, J = 6.7 Hz, 3H); ^13C NMR (75 MHz, CDCl₃) δ = 196.9, 158.3, 140.6, 134.0, 122.4, 119.7, 115.1, 84.1, 50.9, 40.5, 38.9, 29.9, 27.2, 14.3, 9.5. HRMS: calcd for C_{15}H_{19}O₃$^+$ [M + H$^+$]: 247.1334, found 247.1329.

Compound 16

A stirred solution of 13 (20 mg, 0.08 mmol) in toluene (1.5 ml) was heated for 4 h at 140°C. Then, the mixture was concentrated in vacuo. Purification by neutralized silica gel flash column chromatography (petroleum/ Et₂O = 50:1) provided zedoarol 17 (2 mg, 10%) as a colourless oil, 16 (13 mg, 65%) as a colourless oil. R_f = 0.30 (petroleum/ Et₂O = 3:1). [a]_D = + 3.1 (c 0.8, CHCl₃). ^1H NMR (300 MHz, CDCl₃): δ = 7.03 (brs, 1H), 5.21 (brs, 1H), 5.03 (brs, 1H), 5.03 (brs, 1H),
4.52 (d, J = 8.6Hz, 1H), 3.76 [d, (a,b system), J = 17.7Hz, 1H], 3.52 [d, (a,b system), J = 17.7Hz, 1H], 2.67 (t, J = 8.7Hz, 1H), 3.42 (d, J = 8.8Hz, 1H), 2.26 (q, J = 7.3Hz, 1H), 2.07 (brs, 3H), 1.95 – 1.85 (m, 1H), 1.86 – 1.76 (m, 1H), 1.15 (d, J = 6.9Hz, 3H); 

$^{13}$C NMR (75 MHz, CDCl$_3$) = 3147.3, 143.2, 137.4, 122.6, 119.5, 113.1, 80.4, 74.2, 45.9, 37.4, 31.7, 27.9, 15.5, 9.5.

HRMS: calcd for C$_{15}$H$_{21}$O$_3$ $^+$ [M + H$^+$]: 249.1490, found 249.1482.

Compound 19

A solution of zedoarol (17) (30 mg, 0.12 mmol) in MeOH (2.5 ml) was treated with KOH (130 mg, 2.4 mmol) at rt. The reaction was stirred at the same temperature for 30 min before quenched with saturated aqueous NH$_4$Cl solution and extracted with Et$_2$O (3 x 7 ml). The combined organic extracts were dried with anhydrous sodium sulfate, filtered and evaporated in vacuo. The crude mixture was purified by neutralized silica gel flash column chromatography to provide compound 19 (27 mg, 99%) as a colourless oil. $^1$H NMR (500 MHz, CDCl$_3$) δ = 7.34 (s, 1H), 7.24 (s, 1H), 3.66 (m, 1H), 3.15 (m, 1H), 2.98 (m, 1H), 2.45 (s, 3H), 2.32 (s, 3H), 1.52 (m, 1H), 1.53 (m, 1H), 1.23 (d, J = 5 Hz, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) = 179.5, 157.2, 155.3, 147.5, 141.6, 135.4, 125.5, 123.1, 122.6, 42.6, 36.8, 29.5, 24.8, 18.4, 10.6. HRMS: calcd for C$_{15}$H$_{21}$O$_3$ $^+$ [M + H$^+$]: 249.1225, found 249.1228.

Compound 20

A solution of compound 13 (10 mg, 0.04 mmol) in DCM (1 ml) was treated with p-toluenesulfonic acid monohydrate (8 mg, 0.04 mmol) at 0 °C. The reaction was stirred at the same temperature for 1.5 h before quenched with NaHCO$_3$ and extracted with ether (3 x 10 ml). The combined organic extracts were dried with anhydrous sodium sulfate, filtered and evaporated in vacuo. The crude mixture was purified by neutralized silica gel flash column chromatography to provide compound 20 (8 mg, 75%) as a colourless oil. [a]$^D$ = -4.6 (c 0.2, CHCl$_3$) $^1$H NMR (500 MHz, CDCl$_3$) δ = 7.11 (s, 1H), 4.50 (d, J = 12 Hz, 1H), 3.17 (s, 1H), 3.08 (d,
$J = 15 \text{ Hz, 1H}$, 2.75 (d, $J = 15 \text{ Hz, 1H}$), 2.58 (d, $J = 9 \text{ Hz, 1H}$), 2.08 (s, 3H), 1.89-1.80 (m, 4H), 1.62 (m, 1H), 1.33 (s, 1H), 1.15 (d, $J = 6 \text{ Hz, 3H}$); $^{13}$C NMR (125 MHz, CDCl$_3$)= 148.4, 137.7, 120.9, 120.8, 91.2, 80.8, 71.4, 46.6, 43.0, 41.6, 35.7, 24.9, 21.8, 12.7, 8.2. HRMS: calcd for C$_{15}$H$_{23}$O$_4^+ [M + H^+]$: 267.1596, found 267.1601.

### NMR Comparison of synthetic and natural Zedoarol$^3$

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NMR Comparison of synthetic and natural Gweicurculactone

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<tr>
<td>12</td>
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<td>13</td>
<td>2.21 (s, 3H)</td>
<td>2.21 (s, 3H)</td>
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<td>14</td>
<td>1.28 (d, $J$ = 4.8 Hz, 3H)</td>
<td>1.27 (d, 4.5 Hz, 3H)</td>
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<td>15</td>
<td>1.95 (s, 3H)</td>
<td>1.95 (s, 3H)</td>
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</table>

References

NMR Spectra of compounds
Compound 3, 125 MHz, CDCl3
Compound 3, 500 MHz, CDCl3
Compound 3, 500 MHz, CDCl3
gweicurulactone (4). 500MHz, CDCl3
gweicurculactone (4). 125MHz, CDCl3
Compound 10, 500 MHz, CDCl3
Compound 10, 500 MHz, CDCl₃
Compound 20, 500 MHz, CDCl3

NOESY correlations
Compound 11, 125 MHz, CDCl3
Compound 7, 75 MHz, CDCl3
Compound 13, 75 MHz, CDCl3
Compound 13, 500 MHz, CDCl3

NOESY correlations
Camphanic acid derivatization of compound 13
500 MHz CDCl₃
Zedoarol (17), 500 MHz, CDCl3
Zedoarol (17), 125 MHz, CDCl3
Zedoarol (17), 500 MHz, CDCl3
Compound 16, 500 MHz, CDCl3
Compound 16, 125 MHz, CDCl3
Compound 16, 500 MHz, CDCl3

NOESY correlations

NOESY_01
EA1307-4TH_SPOT_NOESY

S 44
Compound 19, 500 MHz, CDCl3
Compound 19, 500 MHz, CDCl3

[Image of a molecule structure and a COSY spectrum diagram]
Compound 19, 125 MHz, CDCl3
Compound 20, 500 MHz