Supplementary Material for Chemical Communications

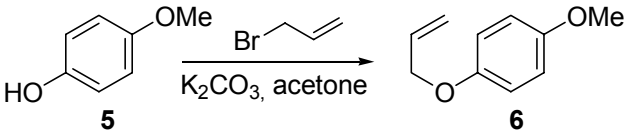
A concise and diastereoselective total synthesis of *cis* and *trans*-pterocarpans

Electronic Supplementary Information
Experimental

General

Infrared spectra were recorded in liquid film between NaCl plates on a FT-IR Mattson Genesis II. NMR spectra were determined on a Bruker Avance DPX 300 and Bruker Avance-500. ^{1}H NMR and ^{13} C NMR spectra were recorded in deuterated solvent and are reported to trimethylsilane. Carbon substitution degrees were established by DEPT multipulse sequence, and ^{13} C NMR peak assignments were made with the aid of 2D NMR (HMBC, HMQC, COSY and NOESY). LRMS were determined on a Hewlett–Packard 5988A instrument. HRMS were registered on an Autospec-Q VG Analytical (FISONS) mass spectrometer. RX data were determined on a Bruker SMART APEX CCD instrument. All solvents were purified and dried following standard procedures[1].

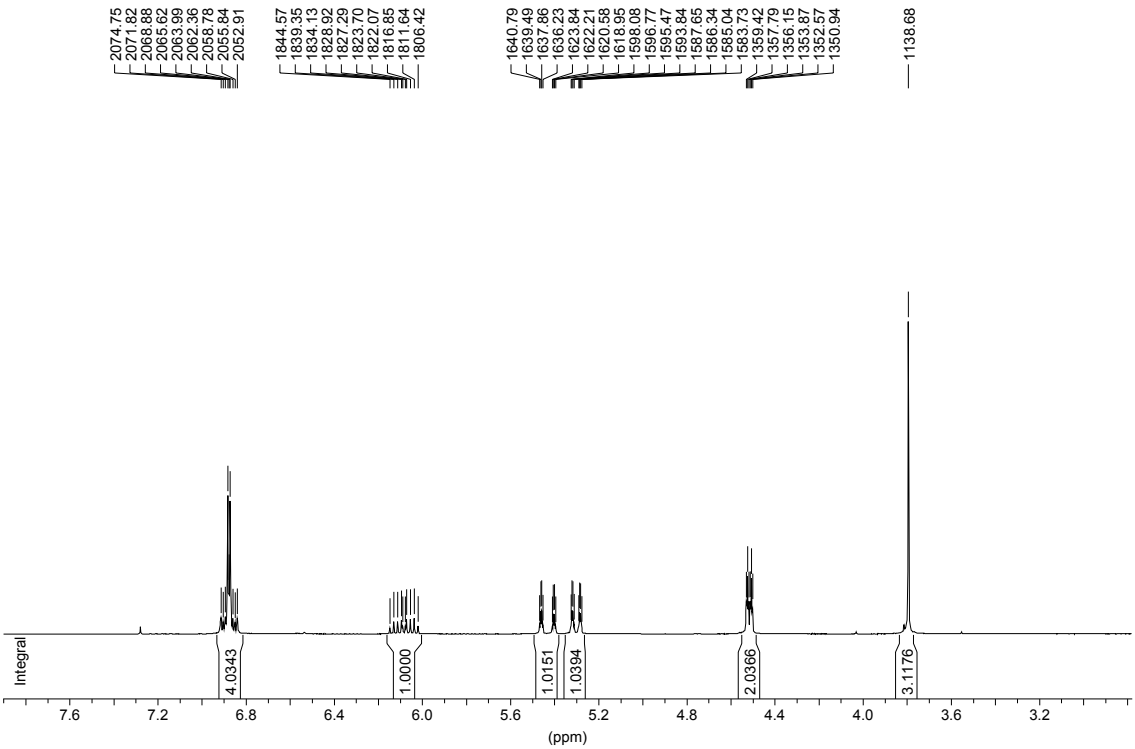
Allyl *p*-methoxyphenyl ether (6)

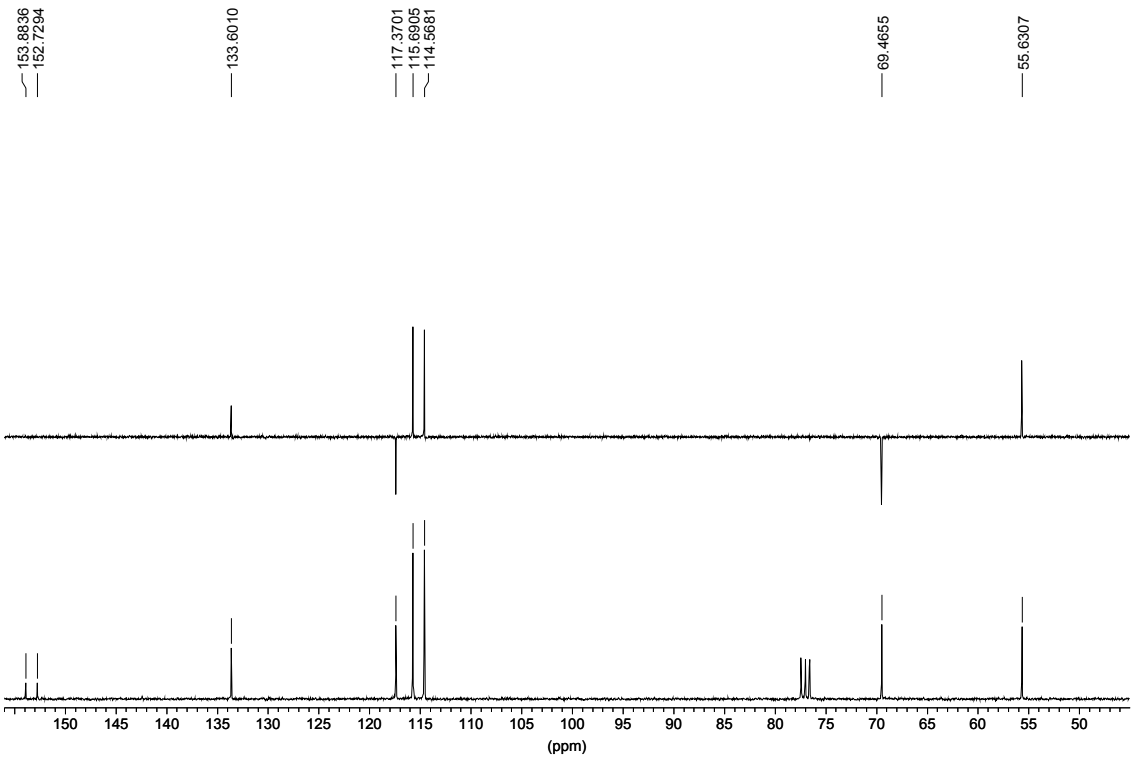


5 **6**

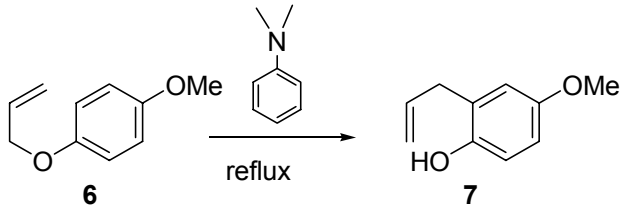
To a stirred solution of **5** (5 g, 40.27 mmol) in acetone (30 mL), K_2CO_3 (5.56 g, 40.27 mmol) and allyl bromide (5.45 mL, 48.32 mmol) were added. The resulting solution was heated to reflux for 4 hours. The mixture was then diluted with CH_2Cl_2 (100 mL) and washed with NaOH 2M. The organic layer was dried over anhyd. Na_2SO_4, and the solvent was removed. The residue was submitted to flash chromatography (hexane/Et_2O 85:15), affording **6** (6.31 g, 38.47 mmol, 95%), as colourless oil: IR (film) ν_{max} 3074, 2999, 2942, 2839,1593, 1509, 1457, 1227, 1034, 827 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.87 (4H, m, H-2, 3, 5, 6), 6.09 (1H, ddt, *J*= 17.3, *J*= 10.4, *J*= 5.2 Hz, H-2'), 5.43 (1H, dq, *J*= 17.3, *J*= 1.6 Hz, H-3'*t*), 5.30 (1H, dq, *J*= 10.4, *J*= 1.6 Hz, H-3'*c*), 4.51 (2H, dt, *J*= 5.2, *J*= 1.6 Hz, H- 1'), 3.79 (3H, s, OCH_3); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 153.88 (C, C-4*), 152.72 (C, C-1*), 133.60 (CH, C-2'), 117.37 (CH_2, C-3'), 115.69 (CH, C-3, C-5), 114.56 (CH, C-2, C-6), 69.46 (CH_2, C-1'), 55.63 (OCH_3). * may be interchanged; HREIMS (*m/z*) calcd. for $C_{10}H_{12}O_2$ 164.0837 $[M]^+$, found 164.0836.

[1] Casey, M.; Leonard, J.; Lygo, B.; Procter, G. "Advanced Practical Organic Chemistry" Chapman and Hall, New York, 1990.



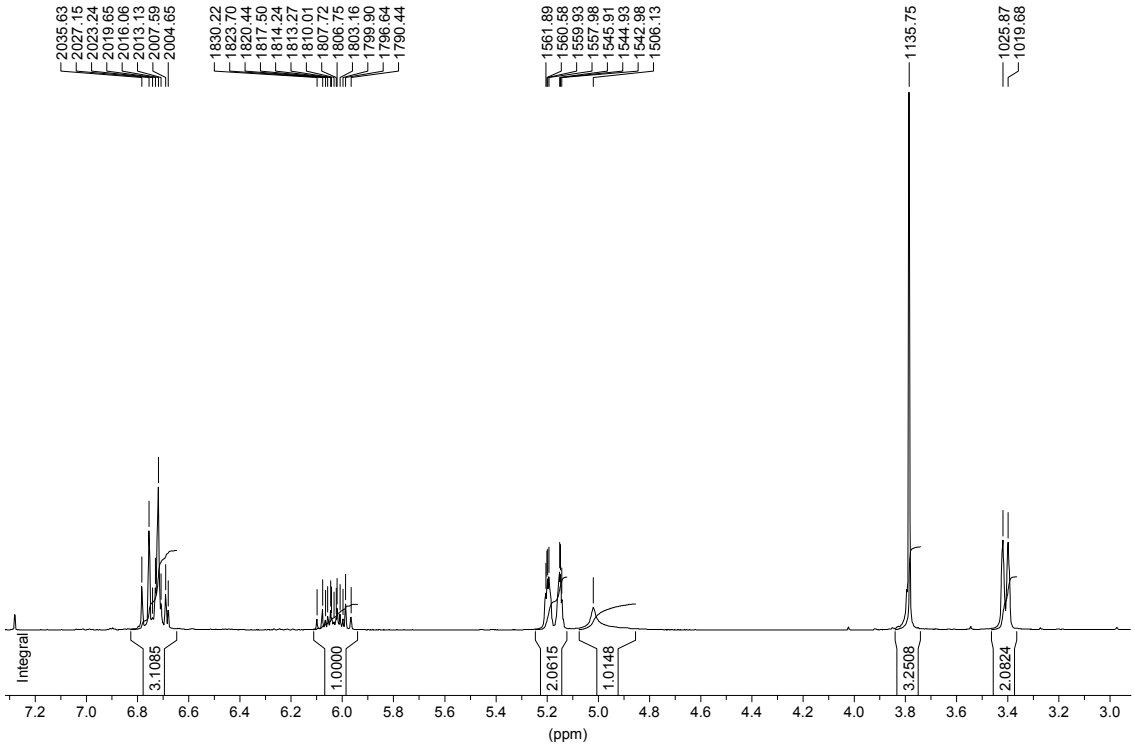


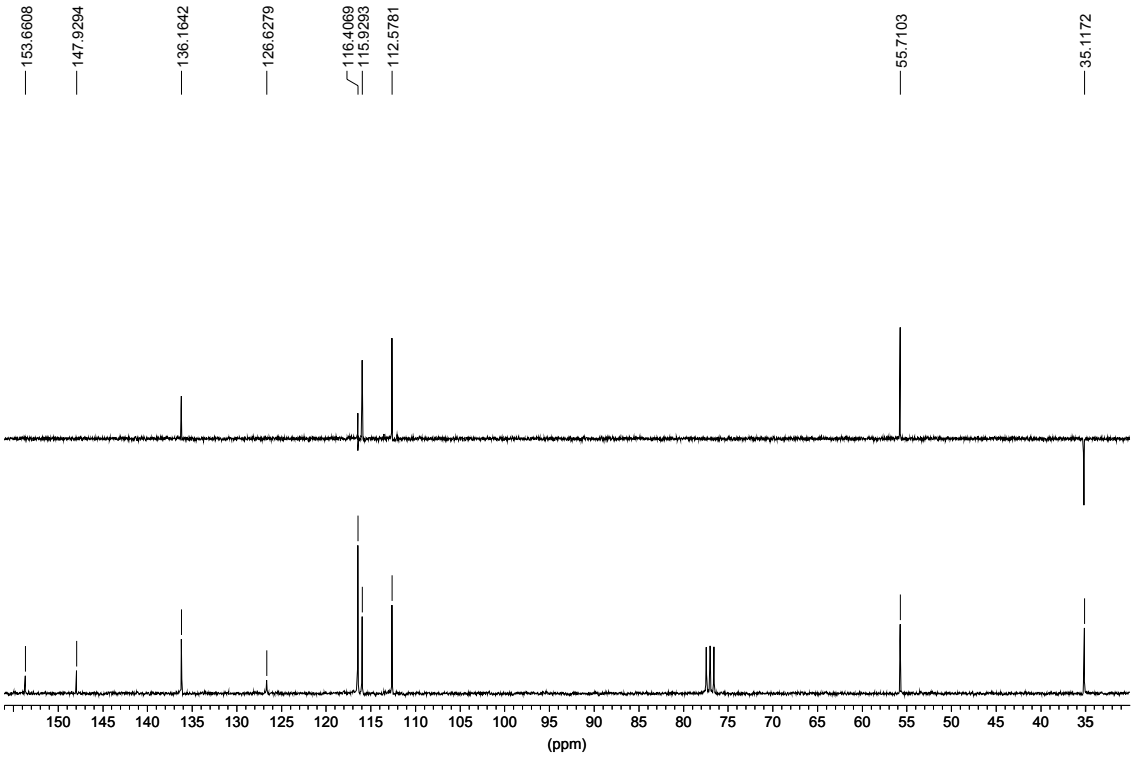
2-Allyl-4-methoxy-phenol (7)



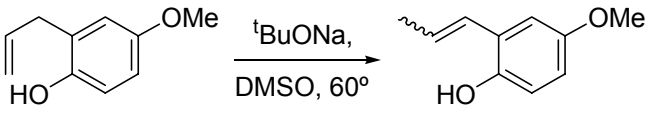
6 **7**

Compound **6** (6.31 g, 38.47 mmol) was dissolved under N_2 atmosphere in 10 mL (79.38 mmol) of *N,N*-dimethylaniline. The solution was heated to reflux for 10h. The mixture was diluted with CH_2Cl_2 (100 mL), and washed with HCl 5% (3 x 50 mL). The dried (Na_2SO_4) extract was concentrated *in vacuo* and purified by chromatography over silica gel, eluting with hexane/ Et_2O 9:1, to give **7** (5.86 g, 35.78 mmol, 93%) as colourless oil: IR (film) ν_{max}, 3414, 3074, 2944, 2836, 1615, 1504, 1437, 1207, 808 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 6.68-6.79 (3H, m, H-3, 5, 6), 6.03 (1H, ddt, *J*= 17.8, *J*= 9.8, *J*= 6.3 Hz, H-2'), 5.17 (2H, m, H-3'), 5.01 (1H, bs, OH), 3.79 (3H, s, OCH_3) 3.41 (2H, dt, *J*= 6.3, *J*= 1.6 Hz, H-1'); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 153.66 (C, C-4), 147.92 (C, C-1), 136.16 (CH, C-2'), 126.62 (C, C-2), 116.41 (CH_2, C-3'), 116.41 (CH, C-6*), 115.92 (CH, C-3*), , 112.57 (CH, C-5), 55.71 (OCH_3), 35.11 (CH_2, C-1'). * may be interchanged; HREIMS (*m/z*) calcd. for $C_{10}H_{12}O_2$ 164.0837 $[M]^+$, found 164.0835.



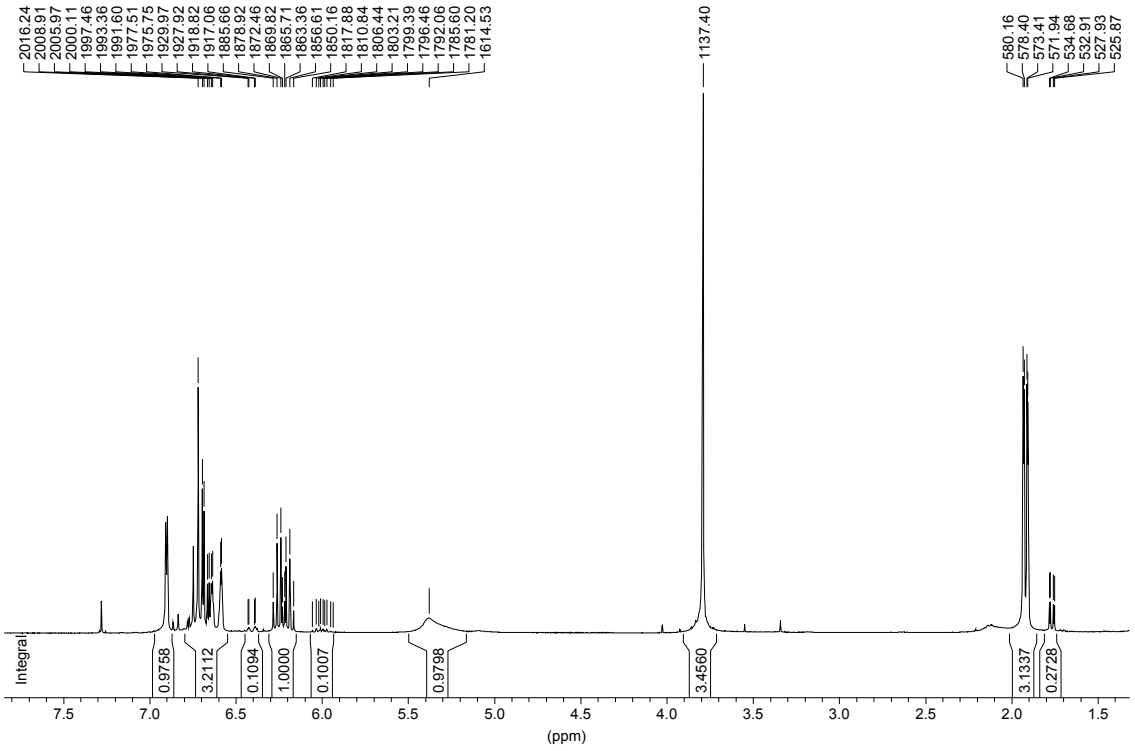


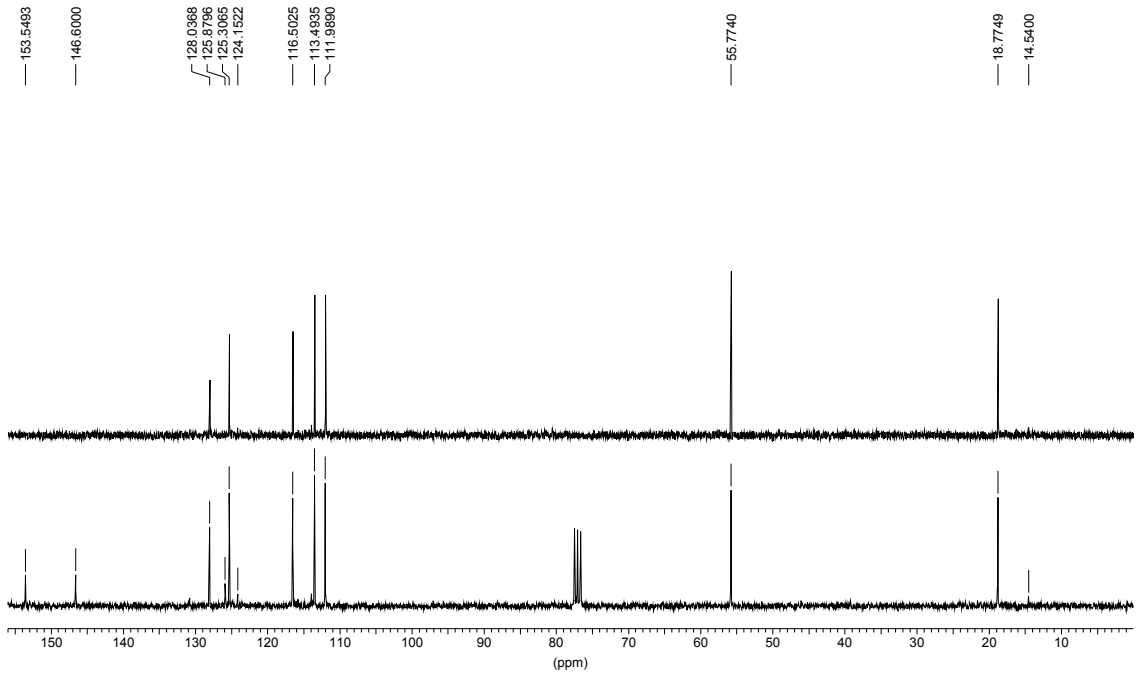
4-Methoxy-2-(1-propenyl)phenol (15)



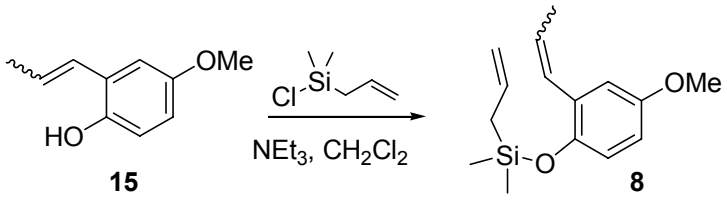
7 **15**

Compound **7** (5.86 g, 35.78 mmol) was dissolved in 125 mL of DMSO, under N_2 atmosphere, and sodium *tert*-butoxide (13.7 g, 143 mmol) was added. The mixture was stirred at 60ºC for 12 h, then was cooled to 0ºC and quenched by addition of HCl 5% (100 mL). The aqueous layer was extracted with CH_2Cl_2 (3 x 100 mL). After washing with brine, the dried (Na_2SO_4) extract was concentrated *in vacuo* and purified by chromatography over silica gel, eluting with hexane/ Et_2O 9:1, to give product **15** (4.86 g, 29.6 mmol, 83%) as a colourless oil and a mixture of *cis* /*trans* isomers (1:12): IR (film) ν_{max}, 3472, 2947, 2838, 1605, 1499, 1435, 1354, 1276, 1204, 810 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz), *(signals of trans isomer)* δ 6.62 (1H, dq, *J*= 15.8 Hz, *J*= 1.8 Hz, H-1'), 6.22 (1H, dq, *J*= 15.8, J= 6.7 Hz, H-2'), 1.92 (3H, dd, *J*= 6.7, *J*= 1.8 Hz, H-3'), *(signals of cis isomer)* δ 6.41 (1H, dq, *J*= 11.5, *J*=1.9 Hz, H-1'), 6.00 (1H, dq, *J*= 11.5, *J*= 6.4 Hz, H-2'), 1.77 (3H, dd, *J*= 6.4, *J*=1.9 Hz, H-3'), *(signals of both)* δ 6.91 (1H, d, *J*= 2.9 Hz, H-3), 6.74 (1H, d, *J*= 8.8 Hz, H-6), 6.68 (1H, dd, *J*= 8.8, *J*= 2.9 Hz, H-5), 5.38 (1H, bs, OH), 3.79 (3H, s, OCH_3); ^{13}C NMR ($CDCl_3$, 75 MHz) *(signals of trans isomer)*, δ 128.03 (CH, C-1'), 125.31 (CH, C-2'), 18.77 (CH_3, C-3'). *(signals of cis isomer)* δ130.80 (CH, C-1'), 124.15 (CH, C-2'), 14.54 (CH_3, C-3'). *(signals of both)* δ 153.54 (C, C-4), 146.60 (C, C-1), 125.88 (C, C-2), 116.50 (CH, C-6), 113.49 (CH, C-5), 111.98 (CH, C-3), 55.77 (OCH_3); HREIMS (*m/z*) calcd. for $C_{10}H_{12}O_2$ 164.0837 $[M]^+$, found 164.0834.



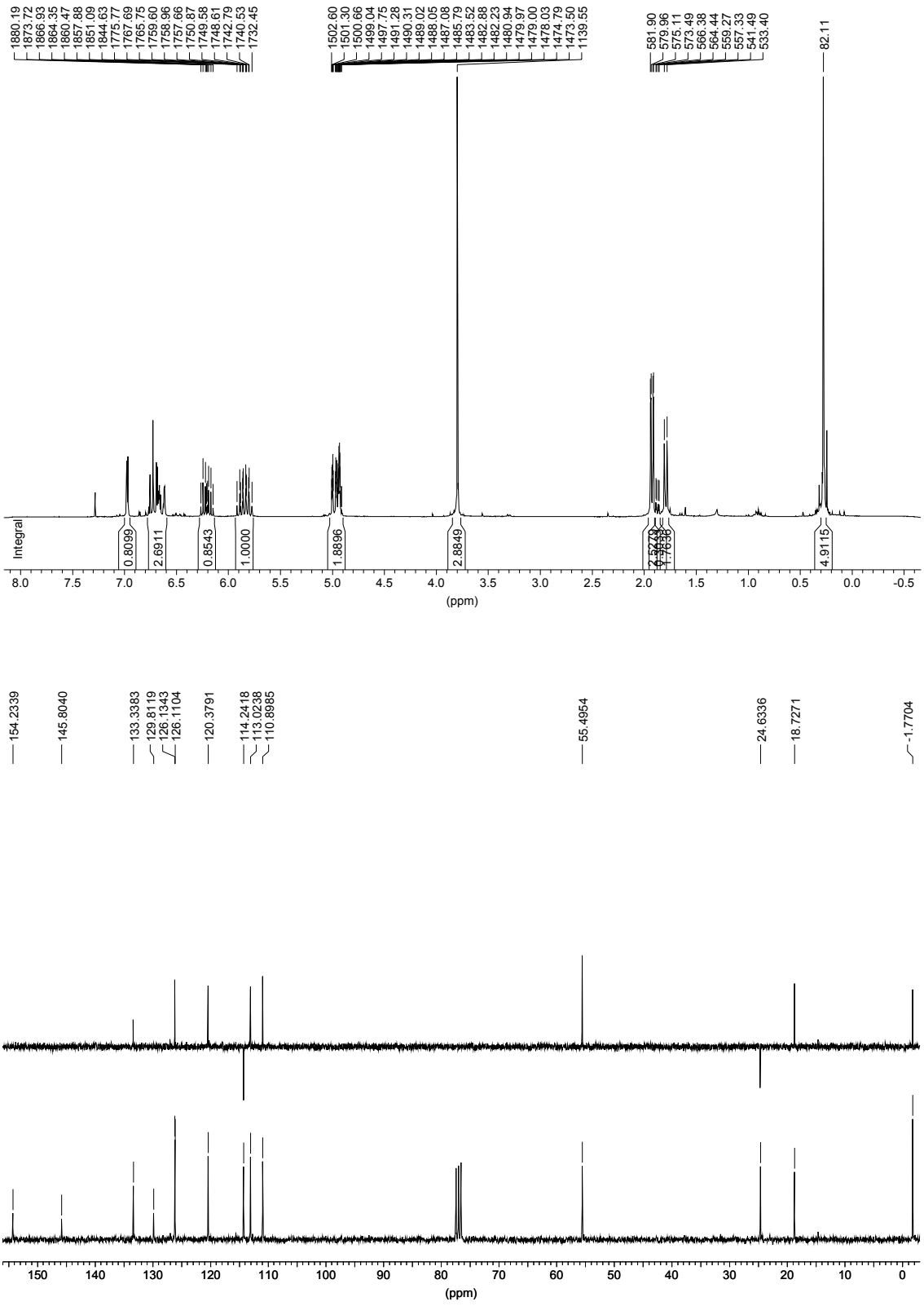


Allyl-(4-methoxy-2-propenyl-phenoxy)-dimethylsilane (8)

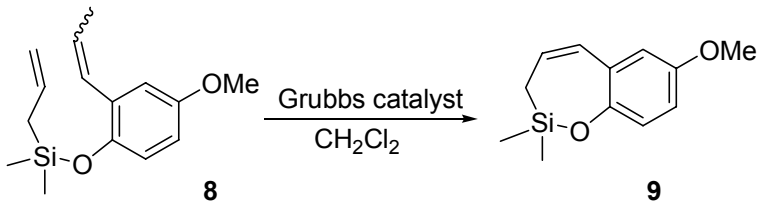


15 **8**

Compound **15** (4.86 g, 29.6 mmol) was dissolved in anhydrous CH_2Cl_2 (200 mL) at 0ºC under N_2 atmosphere. NEt_3 anhydrous (4.9 mL, 35.52 mmol) and allylchlorodimethylsilane (4.75 mL, 32.56 mmol) were added. The reaction mixture was stirred at 0ºC for 4h, and then, a saturated solution of $NaHCO_3/H_2O$ was added The whole mixture was extracted with CH_2Cl_2 (3 x 75 mL). The organic layer was dried over anhyd. Na_2SO_4, and concentrated *in vacuo*. Flash chromatography (hexane: Et_2O, 98:2) of the residue gave **8** (10.7 g, 41 mmol, 87%) (*cis*:*trans* 1:8) as a colourless oil: IR (film) ν_{max}, 2956, 1626, 1489, 1429, 1262, 1215, 904, 827 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz), *(signals of trans isomer)* δ 6.64 (1H, dq, *J*= 15.8, *J*= 1.9 Hz, H-1'), 6.20 (1H, dq, *J*= 15.8, *J*= 6.5 Hz, H-2'), 1.91 (3H, dd, *J*=6.5, *J*=1.9 Hz, H-3'), *(signals of cis isomer)* δ 1.87 (3H, dd, *J*=7.1, *J*=1.9 Hz, H-3'), *(signals of both)* δ 6.96 (1H, d, *J*= 2.9 Hz, H-3), 6.74 (1H, d, *J*= 8.7 Hz, H-6), 6.67 (1H, dd, *J*= 8.7, *J*=2.9 Hz, H-5), 5.84 (1H, ddt, *J*= 16.8, *J*= 10.0, *J*=8.1 Hz, H-2''), 4.97 (2H, m, H-3''), 3.79 (3H, s, OCH_3), 1.79 (2H, d, *J*= 8.1 Hz, H-1''), 0.26 (6H, s, $SiMe_2$); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 154.23 (C, C-4), 145.80 (C, C-1), 133.34 (CH, C-2''), 129,81 (C, C-2), 126.15, 126.13 (CH, C-1', C-2'), 120.37 (CH, C-6), 114.24 (CH_2, C-3''), 113.02 (CH, C-5), 110.89 (CH, C-3), 55.49 (OCH_3), 24.63 (CH_2, C-1''), 18.74 (CH_3, C-3'), -1.75 ($SiMe_2$). HREIMS (*m/z*) calcd. for $C_{15}H_{22}O_2Si$ 262.1389 $[M]^+$, found 262. 1385.



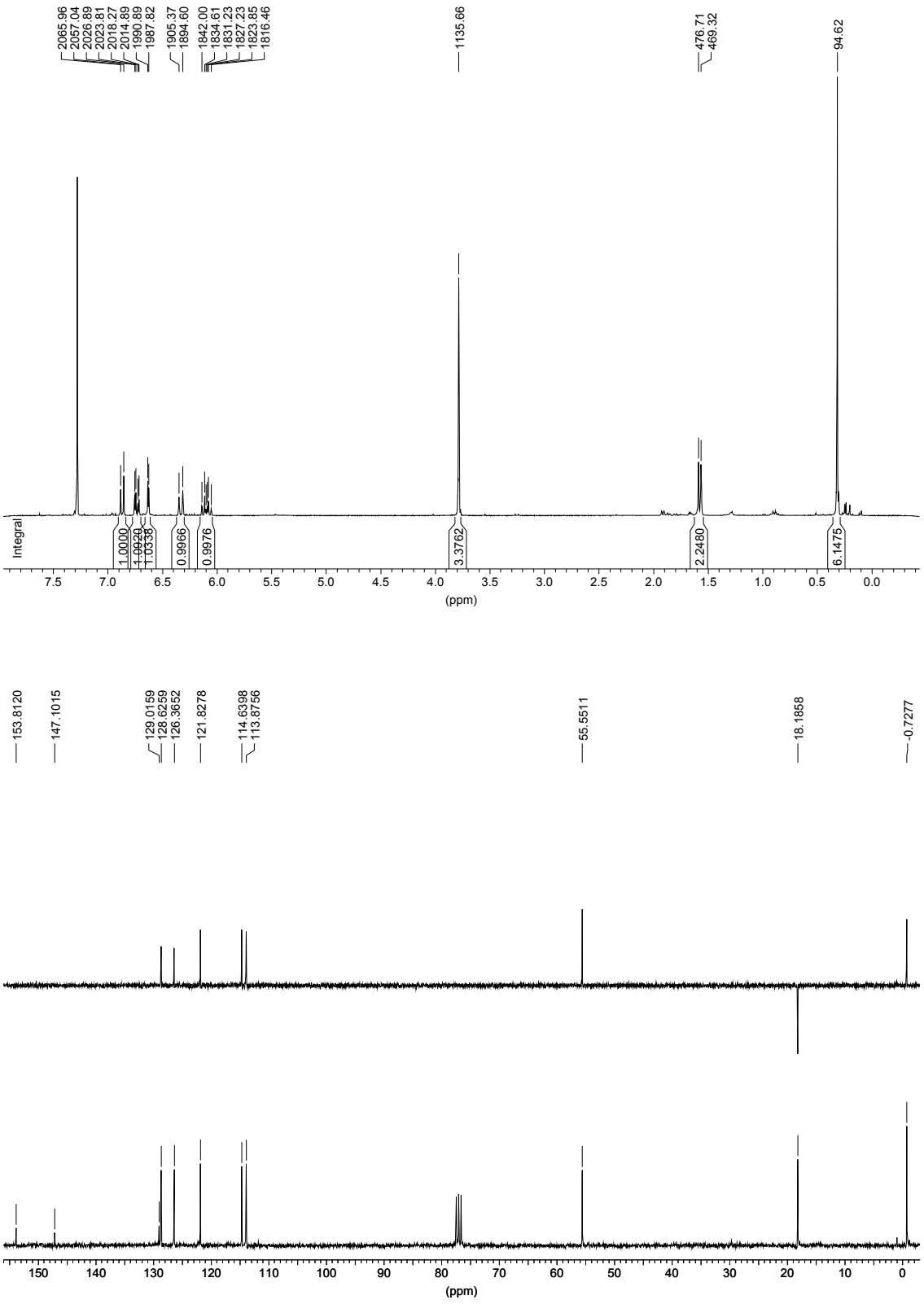
2,2-Dimethyl-7-methoxy-2,3-dihydrobenzo[*f*][1,2]oxasilepin (9)



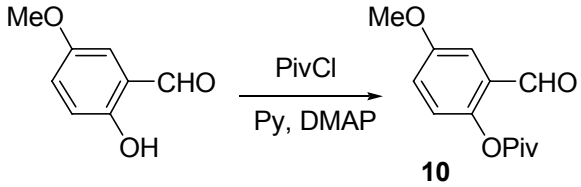
8 **9**

A) Benzyliden-bis-(tricyclohexylphosphine)dichlororuthenium (391 mg, 0.47 mmol) was added to a 0.01 M stirred solution of **8** (826 mg, 3.16 mmol) in degasified anhyd. CH_2Cl_2. The mixture was stirred under reflux for 17 h, and then $Pb(AcO)_4$ (0.59 mmol) was added, and the slurry stirred at room temperature for 18 h. After that, the mixture was filtered through silica and washed with CH_2Cl_2. The solvent was removed *in vacuo*. Flash chromatography (hexane: Et_2O, 98:2) of the residue gave **9** (445 mg, 2.02 mmol, 76%) as a colourless oil IR (film) ν_{max} 3013, 2950, 2839, 1609, 1490, 1418, 1259, 1220, 1144, 1042, 935, 890, 842, 811 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 6.87 (1H, d, *J*= 8.9 Hz, H-9), 6.73 (1H, dd, *J*= 8.9, *J*= 3.1 Hz, H-8), 6.63 (1H, d, *J*= 3.1 Hz, H-6), 6.33 (1H, d, *J*= 10.8 Hz, H-5), 6.09 (1H, dt, *J*= 10.8, *J*= 7.4 Hz, H-4), 3.78 (3H, s, OCH_3), 1.57 (2H, d, *J*= 7.4 Hz, H-3), 0.31 (6H, $SiMe_2$); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 153.81 (C, C-7), 147.10 (C, C-9a), 129.01 (C, C-5a), 128.62 (CH, C-4), 126.36 (CH, C-5), 121.83 (CH, C-9), 114.64 (CH, C-6), 113.87 (CH, C-8), 55.55 (OCH_3), 18.18 (CH_2, C-3), -0.73 ($SiMe_2$). HREIMS (m/z) calcd. for $C_{12}H_{16}O_2Si$ 220.0919 $[M]^+$, found 220.0919.

B) [1,3-Bis-(2,4,6-trimethylphenyl)-2-imidazolidinylidene)dichloro(phenylmethylene)-(tricyclohexylphosphine)ruthenium] (24 mg, 0.028 mmol) was added to a stirred solution 0.02 M of **8** (1.50 g, 5.72 mmol) in anhyd., under N_2 atmosphere. The mixture was stirred under reflux for 30 min, and then, the solvent was removed *in vacuo*. Flash chromatography (hexane: Et_2O, 98:2) of the residue gave **9** (1.13 g, 5.15 mmol, 90%)



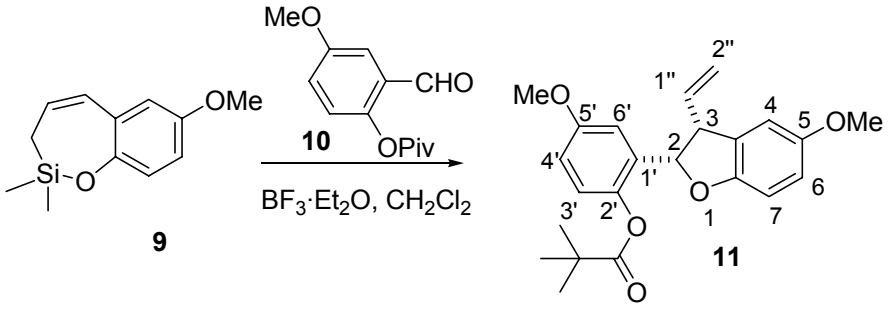
5-Methoxy-2-pivaloyloxybenzaldehyde (10).



10

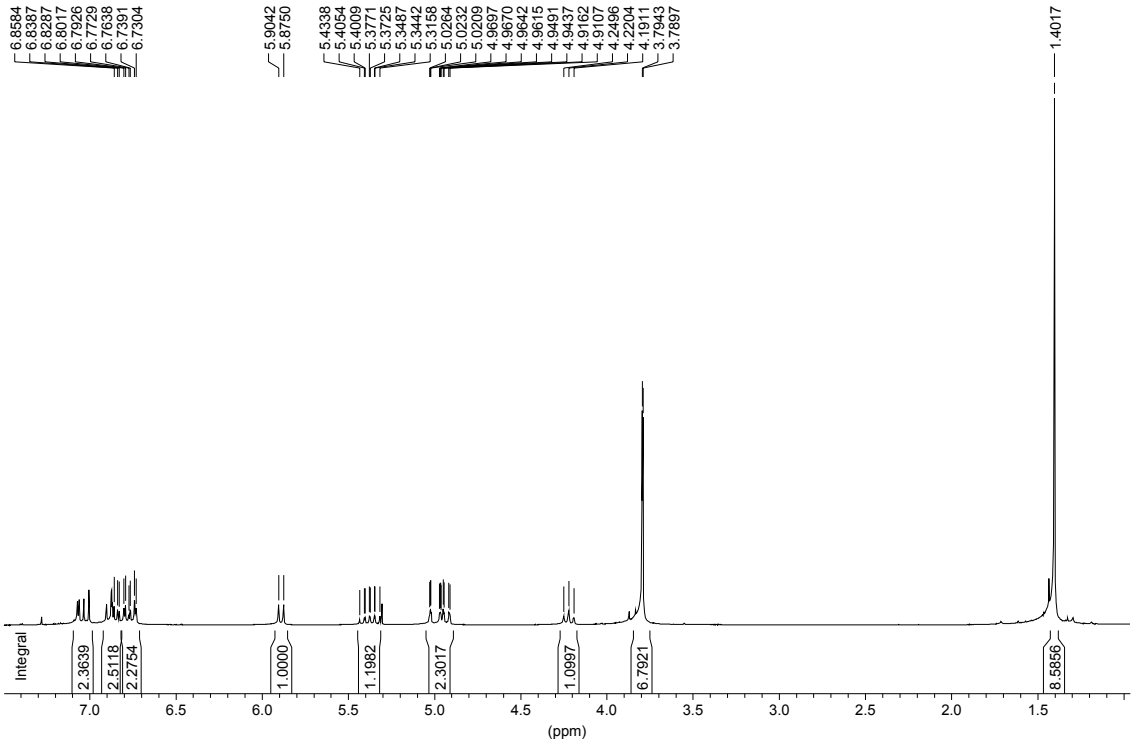
To a solution of 2-hydroxy-5-methoxybenzaldehyde (1 g, 6.57 mmnol) in anhydrous CH_2Cl_2 (75 mL) under N_2 atmosphere, DMAP (80 mg, 0.66 mmol), anhyd. pyridine (1.6 mL, 19.71 mmol) and pivaloyl chloride (2.3 mL, 18.4 mmol) were added. The mixture was heated to reflux for 6 h, then quenched with HCl 5% (50 mL), and extracted with CH_2Cl_2 (3 x 50 mL). The organic layer was dried over anhyd. Na_2SO_4, and the solvent was removed. Flash chromatography of the residue (hexane:Et_2O 9:1) afforded **10** (1.32 g, 5.6 mmol, 85%), as a colourless oil: ^{1}H NMR ($CDCl_3$, 300 MHz): δ(ppm) 10.10 (1H, s, CHO),7.37 (1H, d, *J*=3.0 Hz, H-3), 7.17 (1H, dd, *J*=8.9, *J*=3.0 Hz, H-4), 7.05 (1H, d, *J*=8.9 Hz, H-6), 3.85 (3H, s, OCH_3), 1.41 (9H, s, $OCOC(CH_3)_3$; ^{13}C RMN: δ(ppm) 185.68 (CH), 175.25 (C), 157.21 (C), 140.66 (C), 130.53 (C), 123.64 (CH), 115.71 (CH), 111.97 (CH), 55.57 (CH_3), 38.52 (C), 27.06 (C).

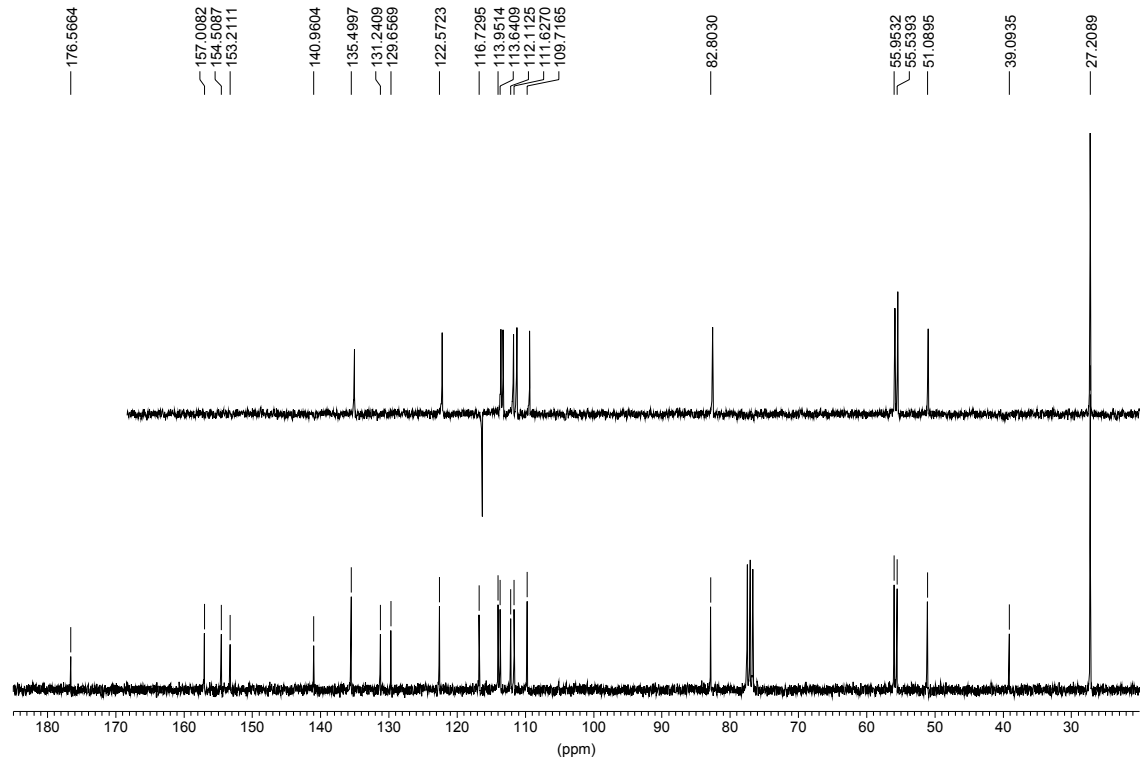
(2*S,3*R**)-5-Methoxy-2-(5-methoxy-2-pivaloyloxyphenyl)-3-vinyl-2,3-dihydro-benzofuran (11)**.



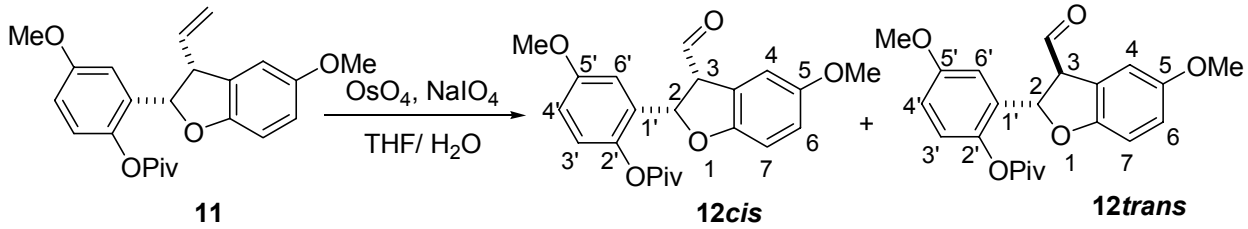
9 **11**

To a stirred solution of **9** (243 mg, 1.1 mmol) in CH_2Cl_2 (3 mL) under N_2 atmosphere at –45 ºC, $BF_3.Et_2O$ (0.28 mL, 2.2 mmol) was added. After 5 min, a solution of **10** (285 mg, 1.21 mmnol) in CH_2Cl_2 (2.5 mL) was added dropwise. The reaction mixture was stirred at –45 ºC for 2 h and was allowed to warm to room temperature; afterwards was heated to reflux for 17 h, then diluted with CH_2Cl_2 and washed with brine. The dried (Na_2SO_4) extract was concentrated *in vacuo* and purified by chromatography over silica gel, eluting with hexane/ Et_2O 95:5, to give compound **11** (262 mg, 0.68 mmol, 62%), as a colourless oil: IR (film) ν_{max} 3078, 2972, 2936, 2910, 2834, 1750, 1607, 1487, 1429, 1364, 1273 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) 7.06 (1H, d, *J*= 3.0 Hz, H-6'), 7.02 (1H, d, *J*= 8.9 Hz, H-3'), 6.87 (1H, d, *J*= 8.6 Hz, H-7), 6.85 (1H, dd, *J*= 8.9, *J*= 3.0 Hz, H-4'), 6.78 (1H, dd, *J*= 8.6, *J*= 2.6 Hz, H-6), 6.73 (1H, d, *J*= 2.6 Hz, H-4), 5.89 (1H, d, *J*= 8.8 Hz, H-2), 5.37 (1H, ddd, *J*= 17.7, *J*= 9.2, *J*= 7.8 Hz, H-1''), 5.00 (1H, bd, *J*= 17.7 Hz, H-2''a), 4.93 (1H, dd, *J*= 9.2, *J*= 1.7 Hz, H-2''b), 4.22 (1H, dd, *J*= 8.8, *J*= 7.8 Hz, H-3), 3.79 (6H, s, OCH_3), 1.40 (9H, s, $OCOC(CH_3)_3$); gNOESY-2D, NOEs observed: 5.89 (4.22), 4.22 (5.89, 5.37, 5.00); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 176.56 (C, O<u>C</u>OC$(CH_3)_3$), 157.00 (C, C-5'), 154.51 (C, C-5), 153.21 (C, C-7a), 140.96 (C, C-2'), 135.50 (CH, C-1''), 131.24 (C, C-1'), 129.65 (C, C-3a), 122.57 (CH, C-3'), 116.73 (CH_2, C-2''), 113.95 (CH, C-6), 113.64 (CH, C-4'), 112.11 (CH, C-6'), 111.63 (CH, C-4), 109.72 (CH, C-7), 82.80 (CH, C-2), 55.95 (CH_3, OCH_3), 55.54 (CH_3, OCH_3), 51.09 (CH, C-3), 39.09 (C, OCO<u>C</u>$(CH_3)_3$), 27.20 (CH_3, OCOC(<u>C</u>$H_3)_3$); HRFABMS (*m/z*) calcd. for $C_{23}H_{26}O_5Na$ 405.1678 $[M+Na]^+$, found 405.1676.





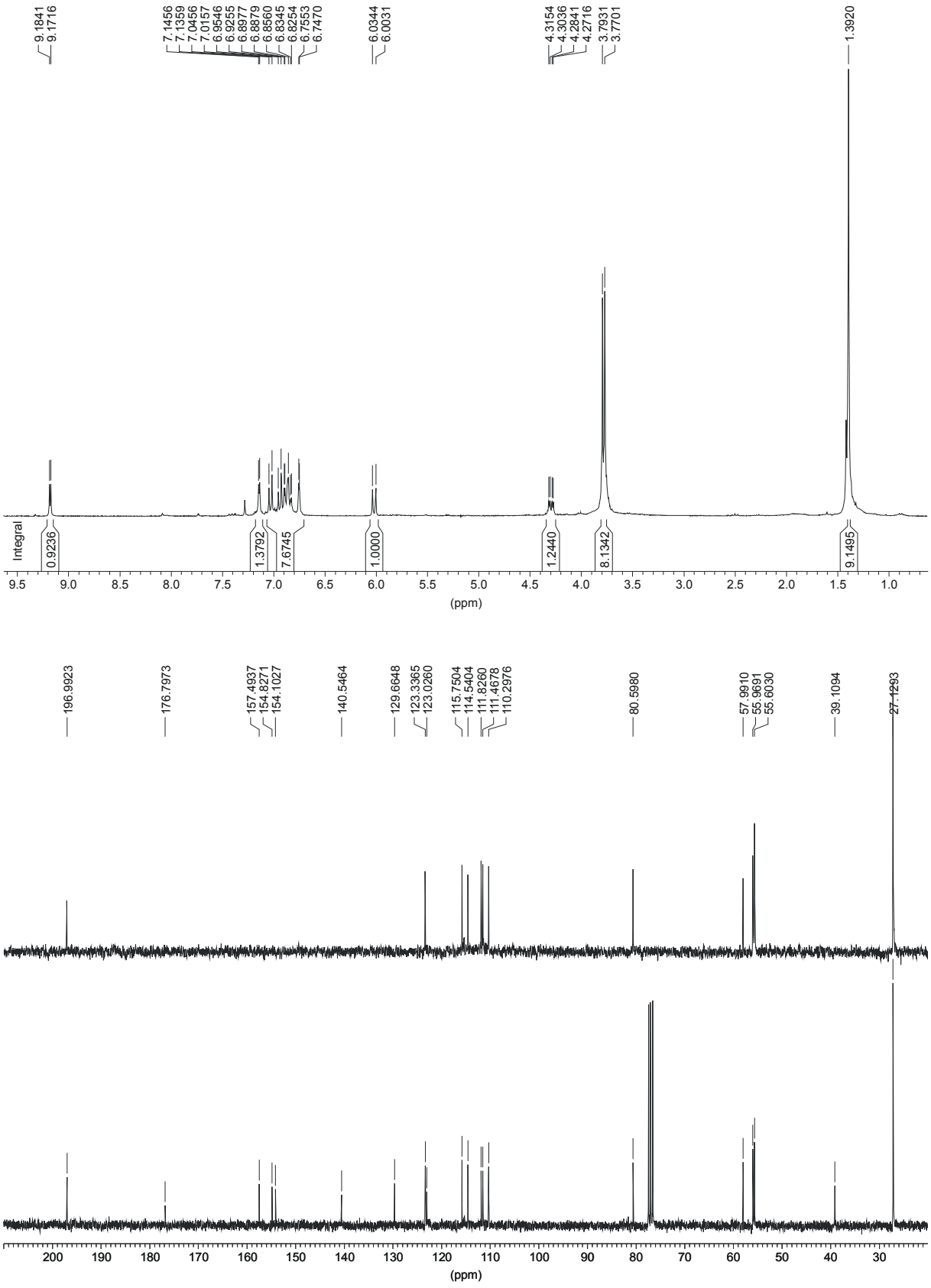
5-Methoxy-2-(5-methoxy-2-pivaloyloxyphenyl)-3-formyl-2,3-dihydrobenzofuran (12).



11 **12*cis*** **12*trans***

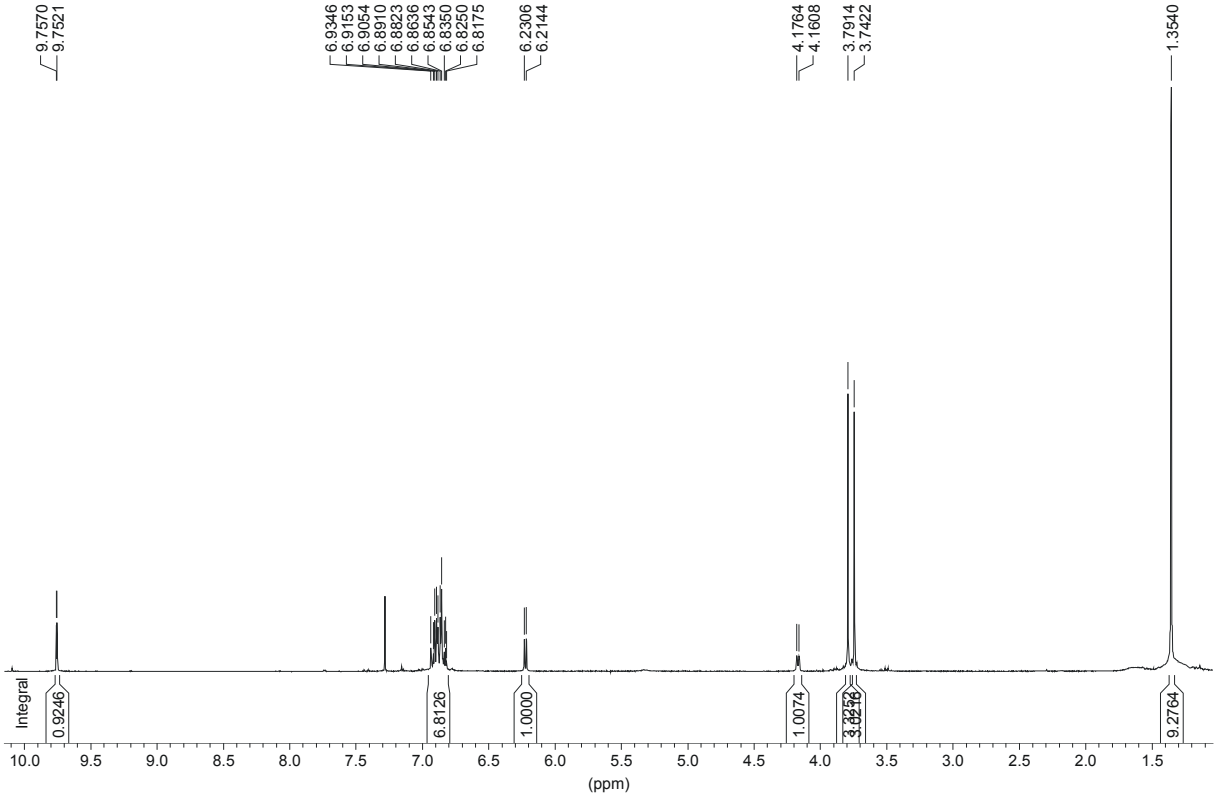
Compound **11** (187 mg, 0.49 mmol) was dissolved in THF/H_2O 3:2 (4mL) and cooled at 0ºC. The flask was protected from the light. OsO_4 (196 μL, 0.012 mmol, 2.5% in isopropanol) and $NaIO_4$ (419 mg, 1.96 mmol) were added. The mixture was stirred at 0ºC for 5 h, then water was added and was extracted with Et_2O. The dried (Na_2SO_4) extract was concentrated *in vacuo* and purified by chromatography over silica gel, eluting with hexane/ Et_2O 85:15, to give compound **12*cis*** (124 mg, 0.32 mmol, 65%) and **12*trans*** (20 mg, 0.05 mmol, 11%) as colourless oils:

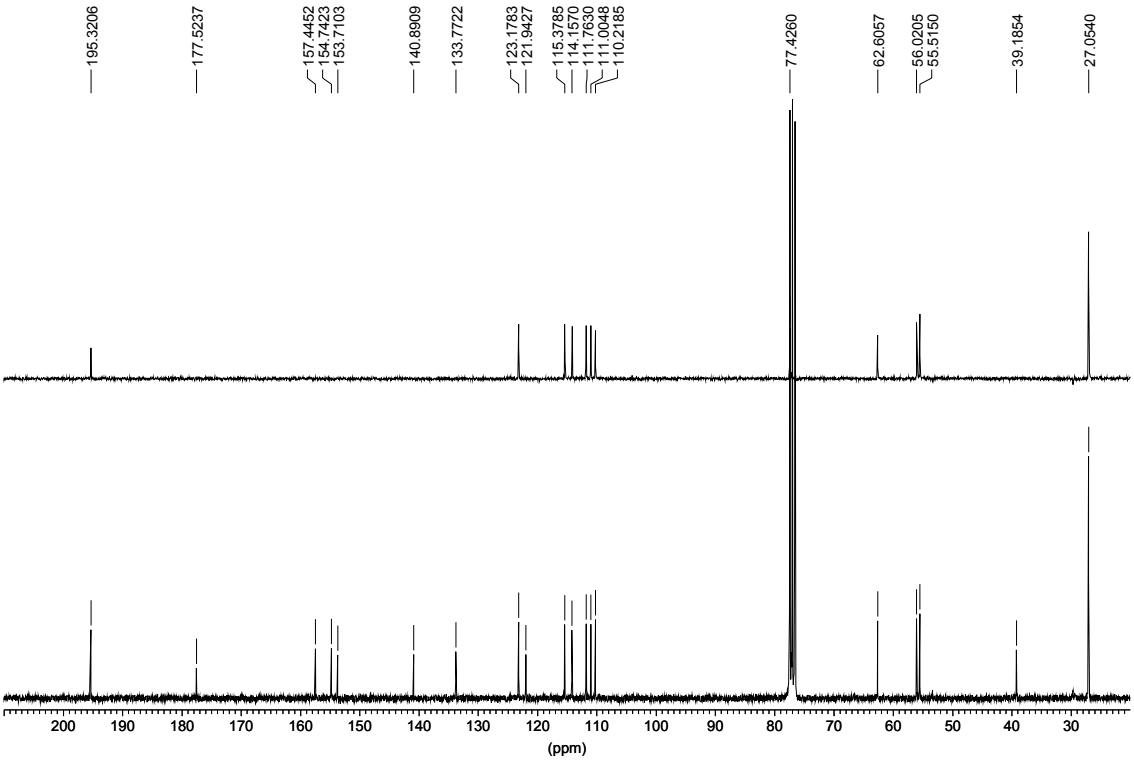
Compound **12*cis***: IR (film) ν_{max} 2967, 2937, 2835, 1749, 1672, 1489, 1432, 1274, 1198, 1108, 1031, 805 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 9.18 (1H, d, *J*= 3.7 Hz, CHO), 7.14 (1H, d, *J*= 2.9 Hz, H-6'), 7.03 (1H, d, *J*= 8.9 Hz, H-3'), 6.94 (1H, d, *J*= 8.9 Hz, H-7), 6.87 (1H, dd, *J*= 8.9, *J*= 2.9 Hz, H-4'), 6.84 (1H, dd, *J*= 8.7, *J*= 2.5 Hz, H-6), 6.75 (1H, d, *J*= 2.5 Hz, H-4), 6.02 (1H, d, *J*= 9.4 Hz, H-2), 4.29 (1H, dd, *J*= 9.4, *J*= 3.7 Hz, H-3), 3.79 (3H, s, OCH_3), 3.77 (3H, s, OCH_3'), 1.39 (9H, s, $OCOC(CH_3)_3$). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 196.99 (CH, CHO), 176.80 (C, O<u>C</u>OC$(CH_3)_3$), 157.49 (C, C-5'), 154.83 (C, C-5), 154.10 (C, C-7a), 140.55 (C, C-2'), 129.66 (C, C-1'), 123.34 (CH, C-3'), 123.03 (C, C-3a), 115.75 (CH, C-6), 114.54 (CH, C-4'), 111.83 (CH, C-6'), 111.47 (CH, C-4), 110.30 (CH, C-7), 80.60 (CH, C-2), 57.99 (CH, C-3), 55.97 (CH_3, OCH_3), 55.60 (CH_3, OCH_3), 39.11 (C, OCO<u>C</u>$(CH_3)_3$), 27.13 (CH_3, OCOC(<u>C</u>$H_3)_3$); HRFABMS (*m/z*) calcd. for $C_{22}H_{24}O_6Na$ 407.1470 $[M+Na]^+$, found 407.1477.



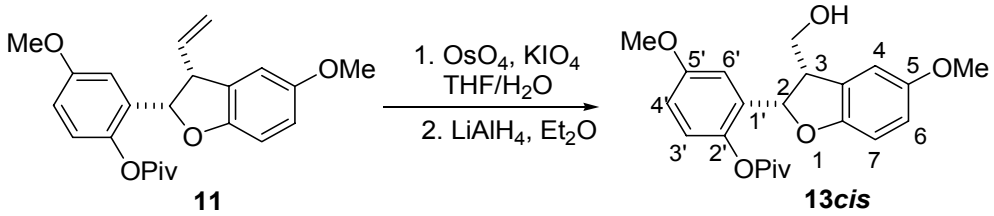
Compound **12*trans***: IR (film) ν_{max} 2964, 2935, 2835, 1747, 1608, 1488, 1430, 1274, 1206, 1115, 1033, 803 cm^{-1} , ^1H NMR ($CDCl_3$, 300 MHz) δ 9.76 (1H, d, *J*= 1.5 Hz, CHO), 6.93-

6.82 (6H, m, H-4, H-6, H-7, H-3', H-4', H-6'), 6.22 (1H, d, *J*= 4.8 Hz, H-2), 4.17 (1H, d, *J*= 4.8 Hz, H-3), 3.79 (3H, s, OCH_3), 3.74 (3H, s, OCH_3'), 1.35 (9H, s, $OCOC(CH_3)_3$); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 195.32 (CH, CHO), 177.52 (C, $O\underline{CO}C(CH_3)_3$), 157.44 (C, C-5'), 154.74 (C, C-5), 153.71 (C, C-7a), 140.89 (C, C-2'), 133.77 (C, C-1'), 123.18 (CH, C-3'), 121.94 (C, C-3a), 115.38 (CH, C-6), 114.16 (CH, C-4'), 111.76 (CH, C-6'), 111.00 (CH, C-4), 110.22 (CH, C-7), 76.96 (CH, C-2), 62.61 (CH, C-3), 56.02 (CH_3, OCH_3), 55.51 (CH_3, OCH_3), 39.18 (C, $OCO\underline{C}(CH_3)_3$), 27.05 (CH_3, $OCOC(\underline{C}H_3)_3$); HRFABMS (*m/z*) calcd. for $C_{22}H_{24}O_6Na$ 407.1470 $[M+Na]^+$, found 407.1472.



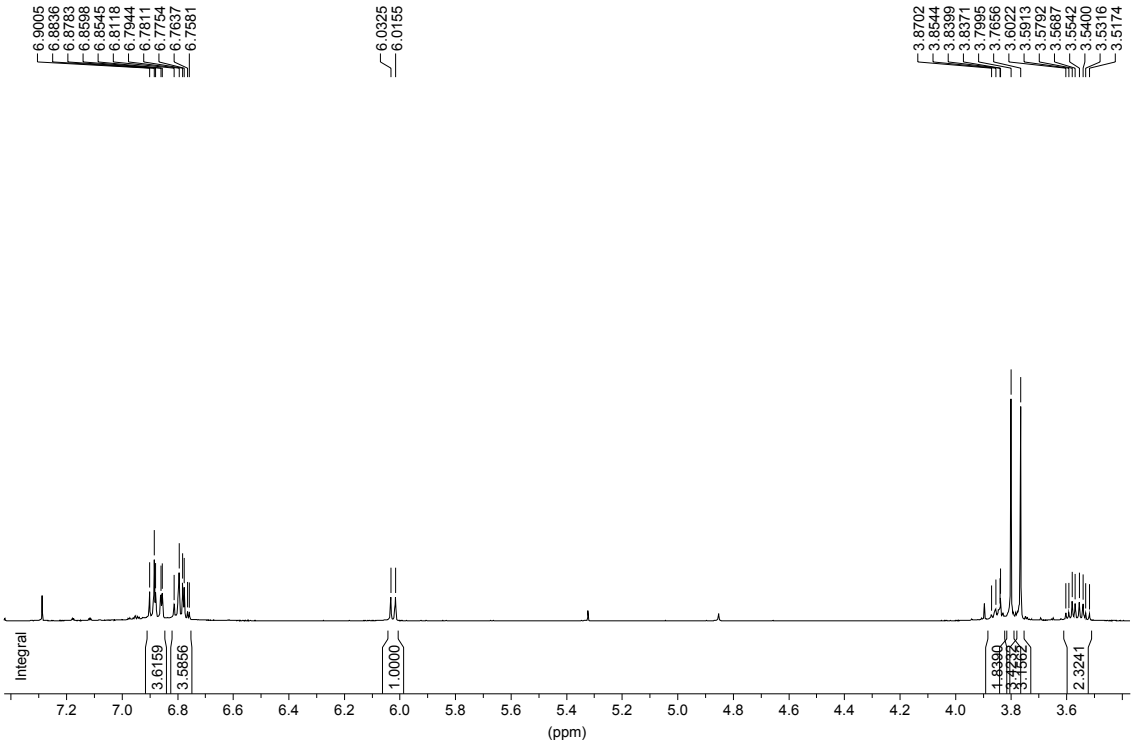


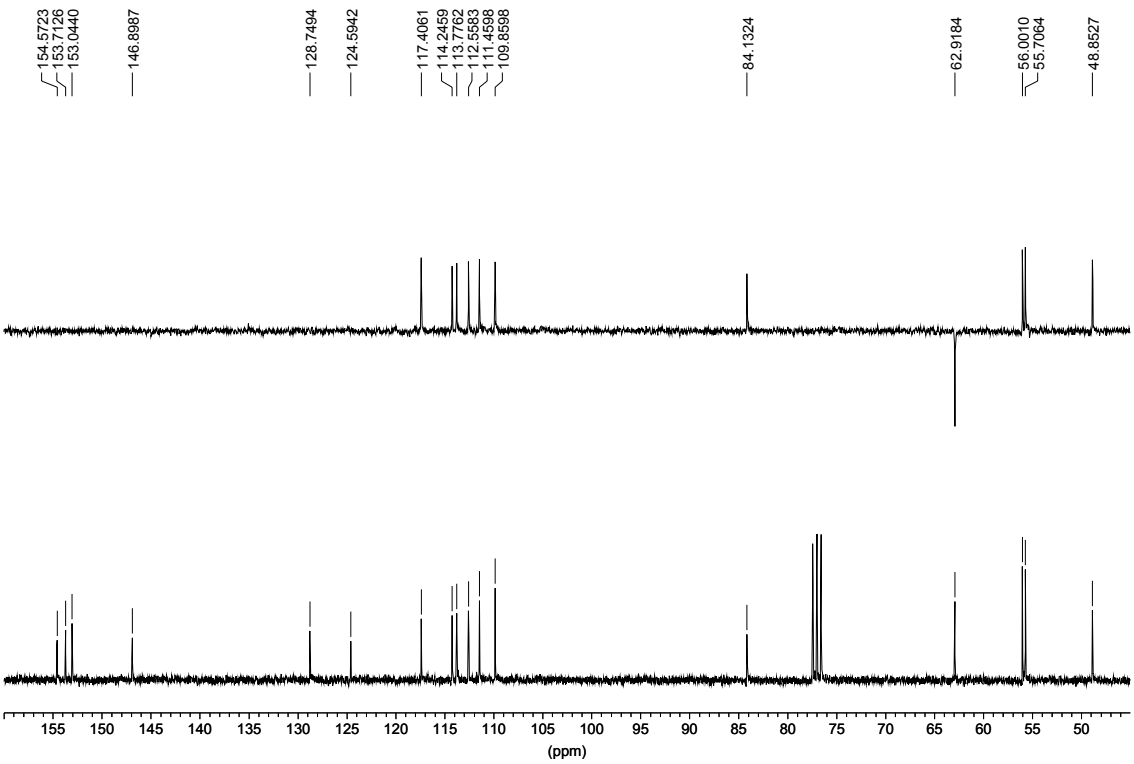
(2*S,3*R**)-3-Hidroxymethyl-5-methoxy-2-(5-methoxy-2-hydroxyphenyl)-2,3-dihydro-benzofuran (13*cis*).**



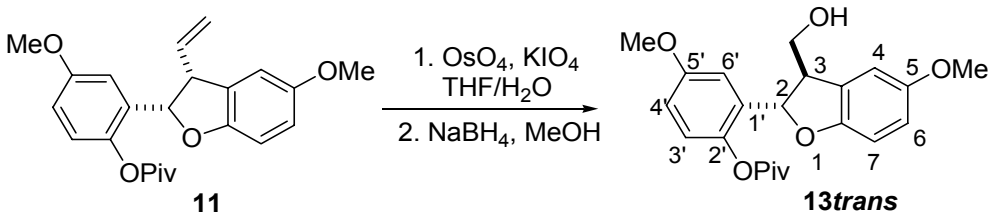
Compound **11** (187 mg, 0.49 mmol) was dissolved in THF/H_2O 3:2 (4mL) and cooled at 0ºC. The flask was protected from the light. OsO_4 (196 µL, 0.012 mmol, 2.5% in isopropanol) and $NaIO_4$ (419 mg, 1.96 mmol) were added. The mixture was stirred at 0ºC for 5 h, then water was added and extracted with Et_2O. The dried (Na_2SO_4) extract was concentrated *in vacuo*. The residue was dissolved in anhydrous Et_2O (4 mL), and added to a solution of $LiAlH_4$ (56 mg, 1.47 mmol) in EtO_2 (4 mL). The reaction mixture was stirred at r.t. for 30 minutes. Then, a saturated solution of NH_4Cl/H_2O (6 mL) was added, and the solution was extracted with CH_2Cl_2. The organic layer was dried over anhyd. Na_2SO_4, and the solvent removed *in vacuo*. Flash chromatography of the residue (hexane: Et_2O 4:6) afforded **13*cis*** (100 mg, 0.33 mmol, 68%) as a solid foam: IR (film) ν_{max} 3375, 2997, 2942, 2833, 1605, 1486, 1431, 1353, 1271, 1204, 1032, 972, 870, 807, 737 cm^{-1}; ^1H NMR

($CDCl_3$, 500 MHz) δ 6.89 (1H, d, *J*= 8.5 Hz, H-3'), 6.88 (1H, d, *J*= 2.6 Hz, H-6'), 6.86 (1H, d, *J*= 2.8 Hz, H-4), 6.80 (1H, d, *J*= 8.6 Hz, H-7), 6.78 (1H, dd, *J*= 8.6, *J*=2.8 Hz, H-6), 6.77 (1H, dd, *J*= 8.6, *J*= 2.6 Hz, H-4'), 6.02 (1H, d, *J*= 8.5 Hz, H-2), 3.85 (1H, m, H-3), 3.80 (3H, s, OCH_3), 3.76 (3H, s, OCH_3), 3.58 (1H, dd, *J*= 11.3, *J*= 5.3 Hz, H-1''), 3.53 (1H, dd, *J*= 11.3, *J*= 7.1 Hz, H-1''); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 154.57 (C, C-5'), 153.71 (C, C-7a), 153.04 (C, C-5), 146.90 (C, C-2'), 128.75 (C, C-1'), 124.59 (C, C-3a), 117.41 (CH, C-7), 114.24 (CH, C-4'), 113.78 (CH, C-6), 112.56 (CH, C-6'), 111.46 (CH, C-4), 109.86 (CH, C-3'), 84.13 (CH, C-2), 62.92 (CH_2, C-1"), 56.00 (CH_3, OCH_3), 55.71 (CH_3, OCH_3), 48.85 (CH, C-3). HRFABMS (*m/z*) calcd. for $C_{17}H_{18}O_5Na$ 325.1051 $[M+Na]^+$, found 325.1052.



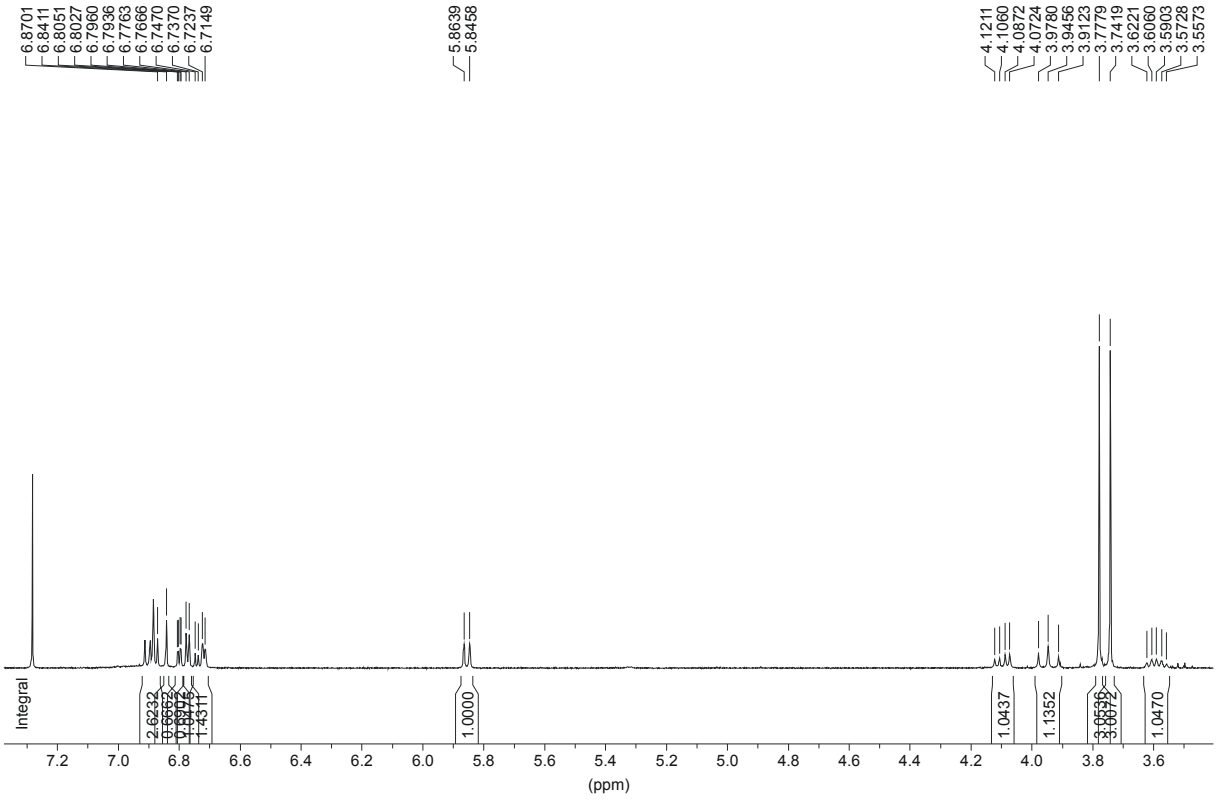


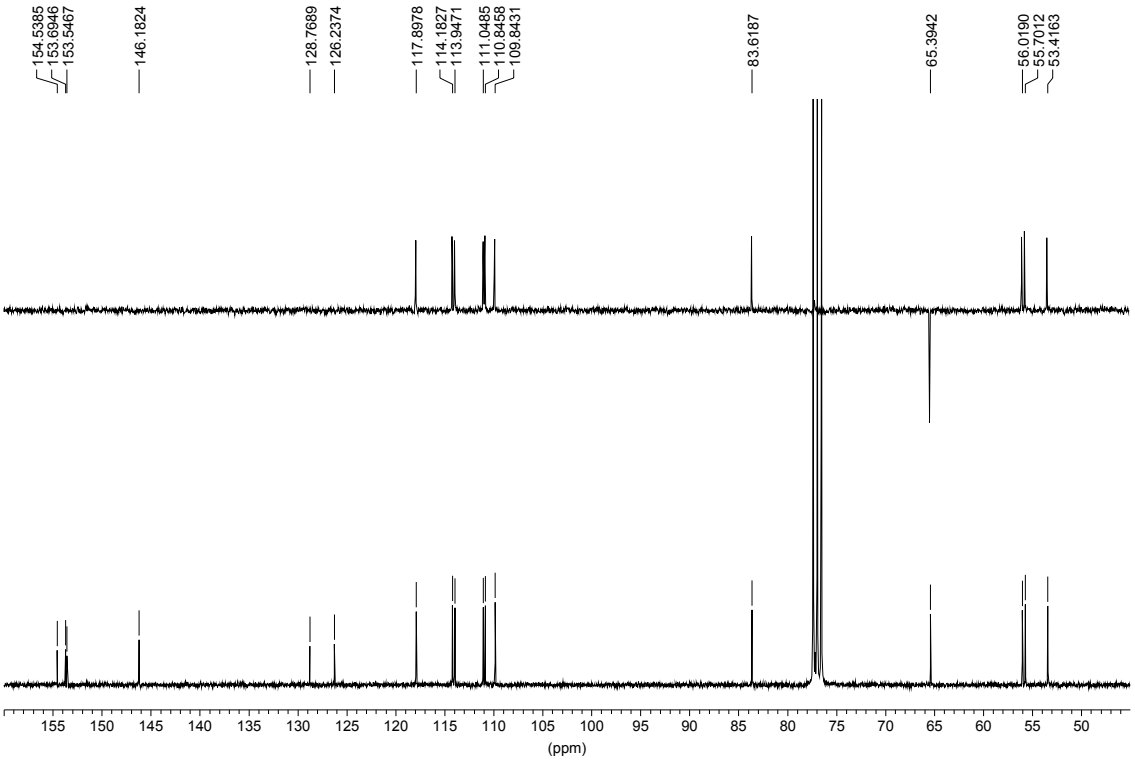
(2*S,3*S**)-3-Hydroxymethyl-5-methoxy-2-(5-methoxy-2-hydroxyphenyl)-2,3-dihydro-benzofuran (13*trans*).**



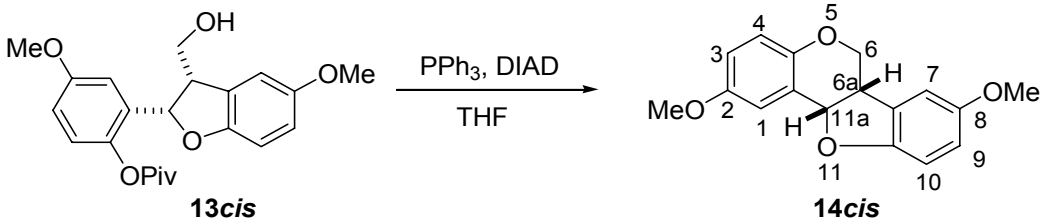
Compound **11** (449 mg, 1.18 mmol) was dissolved in THF/H_2O 3:2 (12 mL) and cooled at 0ºC. The flask was protected from the light. OsO_4 (474 μL, 0.029 mmol, 2.5% in isopropanol) and $NaIO_4$ (1 g, 4.71 mmol) were added. The mixture was stirred at 0ºC for 5 h, then water was added and extracted with Et_2O. The dried (Na_2SO_4) extract was concentrated *in vacuo*. The residue was dissolved in MeOH (10 mL) and the solution was cooled at 0ºC, then $NaBH_4$ (238 mg, 6.28 mmol) was added slowly. The mixture was allowed to warm to room temperature, and was stirred for 12 h. Then, a saturated solution of NH_4Cl/H_2O was added, and the solution was extracted with Et_2O. The organic layer was dried over anhyd. Na_2SO_4, and the solvent removed *in vacuo*. Flash chromatography of the residue (hexane:Et_2O 4:6) gave **13*trans*** (251 mg, 0.83 mmol, 70%) as a solid foam: IR (film) ν_{max} 3395, 2988, 2924, 2850, 1500, 1432, 1269, 1204, 1152, 1032, 986, 912, 743 cm^{-1} ; ^1H NMR ($CDCl_3$, 300 MHz) δ 6.90 (1H, d, *J*= 8.6 Hz, H-3'), 6.89 (1H, d, *J*= 3.0 Hz, H-4), 6.86 (1H, d, *J*= 8.8 Hz, H-7), 6.78 (1H, dd, *J*= 8.6, *J*= 2.6 Hz, H-4'), 6.75 (1H,

dd, *J*= 8.8, *J*= 3.0 Hz, H-6), 6.72 (1H, d, *J*= 2.6 Hz, H-6'), 5.86 (1H, d, *J*= 5.4 Hz, H-2), 4.10 (1H, dd, *J*= 10.1, *J*= 4.5 Hz, H-1"b), 3.94 (1H, t, *J*= 10.1 Hz, H-1"a), 3.78 (3H, s, OCH_3), 3.74 (3H, s, OCH_3), 3.58 (1H, ddd, *J*=10.1, *J*=5.4, *J*=4.5 Hz, H-3); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 154.54 (C, C-5'), 153.69* (C, C-7a), 153.55* (C, C-5), 146.18 (C, C-2'), 128.77 (C, C-1'), 126.24 (C, C-3a), 117.90 (CH, C-7), 114.18 (CH, C-4'), 113.95 (CH, C-6), 111.05 (CH, C-6'), 110.84 (CH, C-4), 109.84 (CH, C-3'), 83.62 (CH, C-2), 65.40 (CH_2, C-1"), 56.02 (CH_3, OCH_3), 55.70 (CH_3, OCH_3), 53.42 (CH, C-3). (*) may be interchanged; HRFABMS (*m/z*) calcd. for $C_{17}H_{18}O_5Na$ 325.1052 $[M+Na]^+$, found 325.1051.





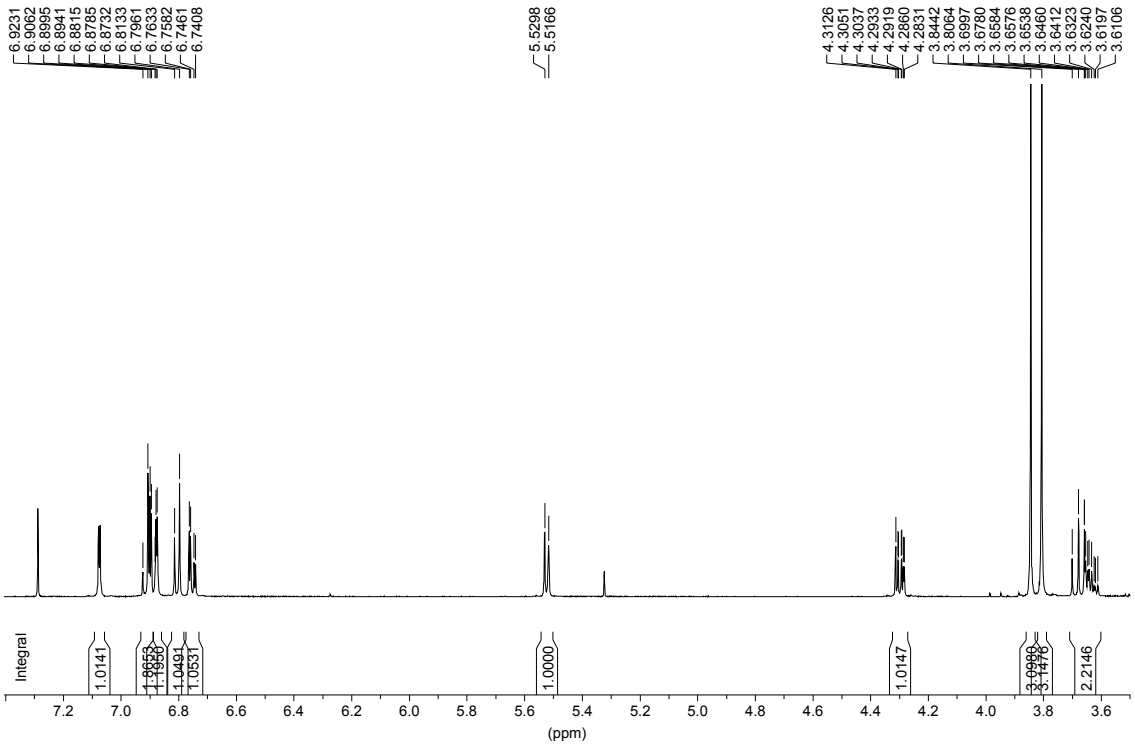
(±)-(*cis*)--2,8-dimethoxypterocarpan (14*cis*)

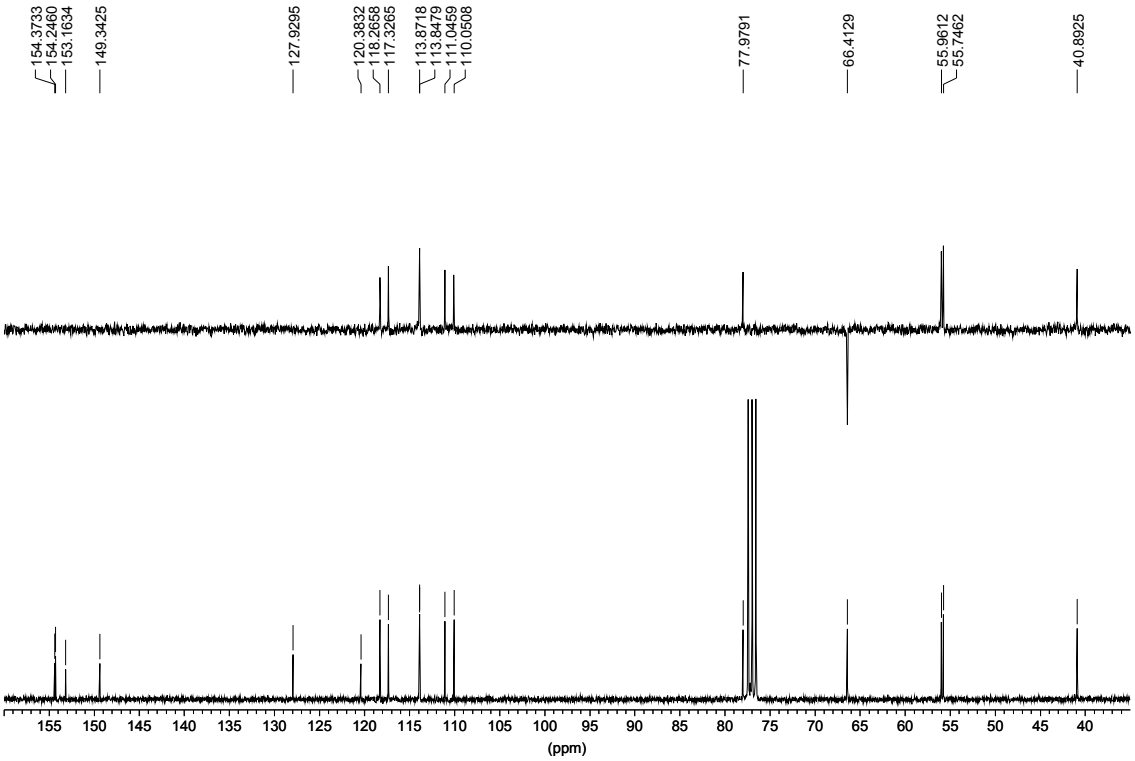


13*cis* **14*cis***

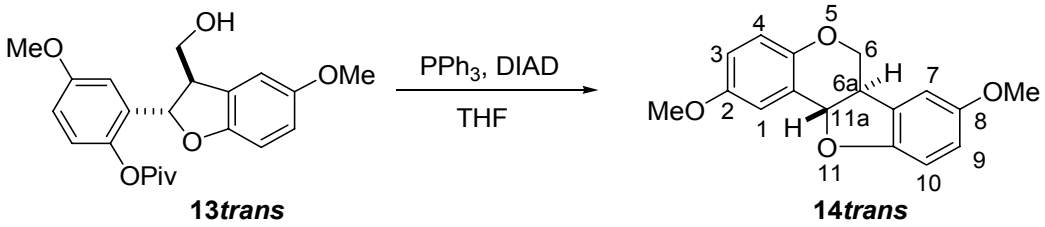
To a solution of **13*cis*** (35 mg, 0.11 mmol) in anhyd. THF (1 mL), PPh_3 (62 mg, 0.22 mmol) and DIAD (0.045 ml, 0.23 mmol), were added. After 30 min., the solvent was removed *in vacuo*. Flash chromatography (hexane:Et_2O 9:1) of the residue afforded **14cis** (24 mg, 0.08 mmol, 72%), as a white solid: m.p. 115-117ºC (hexane-Et_2O), IR (film) ν_{max} 2994, 2947, 2831, 1500, 1429, 1258, 1216, 1197, 1028, 865, 832, 805 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.07 (1H, d, *J*= 2.7 Hz, H-1), 6.90 (2H, m, H-3 y H-4), 6.87 (1H, d, *J*= 2.7 Hz, H-7),6.80 (1H, d, *J*= 8.6 Hz, H-10), 6.75 (1H, dd, *J*= 8.6, *J*= 2.7 Hz, H-9), 5.52 (1H, d, *J*= 6.6 Hz, H-11a), 4.29 (1H, dd, *J*= 10.5, *J*= 4.3 Hz, H-6), 3.83 (3H, s, OCH_3), 3.80 (3H, s, OCH_3), 3.68 (1H, t, *J*= 10.5 Hz, H-6'), 3.64 (1H, ddd, *J*= 10.8, *J*= 6.6, *J*= 4.3 Hz, H-6a); gNOESY-2D, NOEs observed: 3.64 (5.52); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 154.37 (C, C-2*), 154.25 (C, C-8*), 153.16 (C, C-10a), 149.34 (C, C-4a), 127.93 (C, C-

6b), 120.38 (C, C-11b), 118.27 (CH, C-4), 117.33 (CH, C-3), 113.87 (C, C-1*), 113.85 (CH, C-9*), 111.05 (CH, C-7), 110.05 (CH, C-10), 77.98 (CH, C-11a), 66.41 (CH_2, C-6), 55.96 (CH_3, OCH_3), 55.75 (CH_3, OCH_3), 40.89 (CH, C-6a). (*) may be interchanged; HRFABMS (*m/z*) calcd. for $C_{17}H_{16}O_4$ 284.1048 $[M]^+$, found 284.1050.





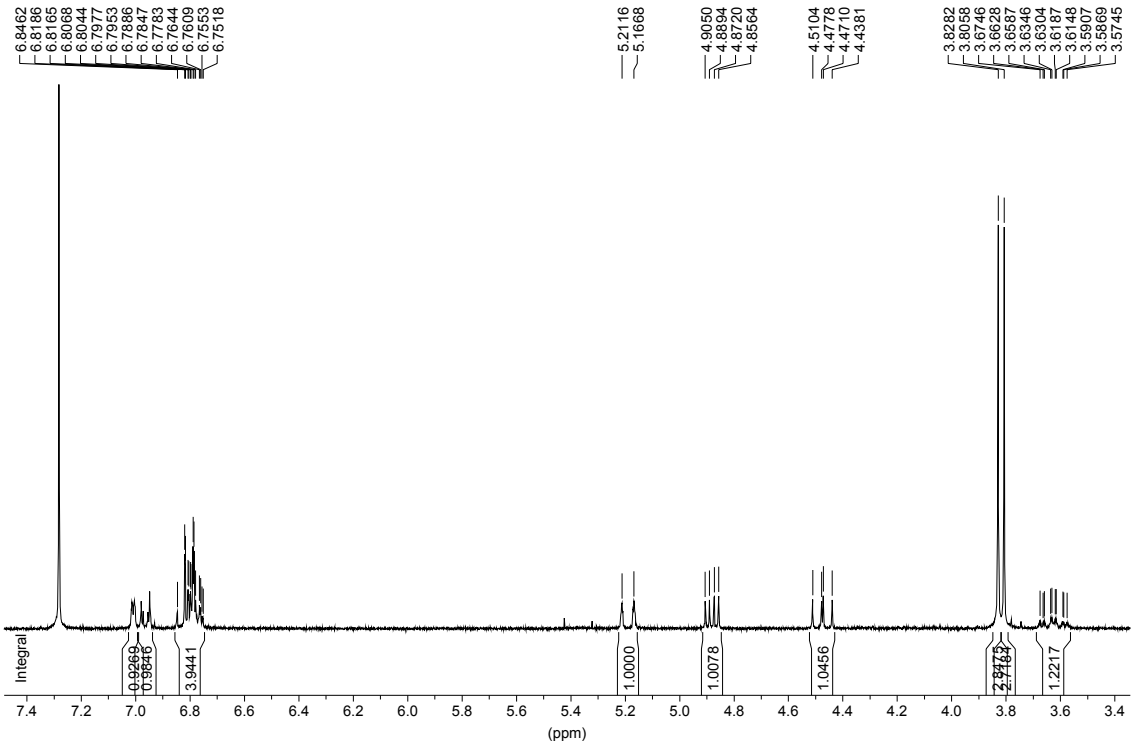
(±)-(*trans*)-2,8-dimethoxypterocarpan (14*trans*)

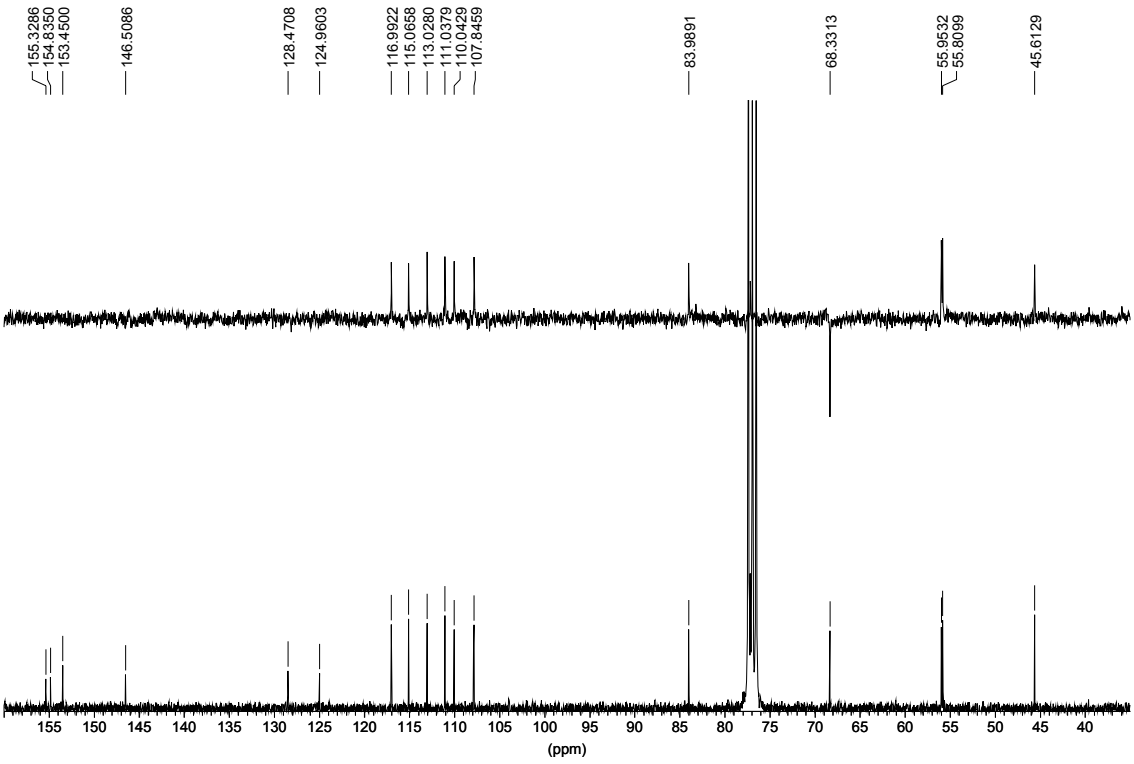


13*trans* **14*trans***

To a solution of **13*trans*** (10 mg, 0.03 mmol) in anhyd. THF (1 mL), PPh_3 (17 mg, 0.06 mmol) and DIAD (0.013 ml, 0.06 mmol), were added. After 30 min., the solvent was removed *in vacuo*. Flash chromatography (hexane:Et_2O 9:1) of the residue afforded **14*trans*** (6 mg, 0.02 mmol, 68%), as a white solid: m.p. 118-120ºC (hexane-Et_2O), IR (film) ν_{max} 2956, 2924, 2852, 2832, 1743, 1487, 1471, 1432, 1369, 1274, 1200, 1039 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.00 (1H, d, *J*= 2.7 Hz, H-7), 6.96 (1H, dd, *J*= 7.8, *J*= 2.7 Hz, H-9), 6.83-6.75 (4H, m, H-1, 3, 4, 10), 5.19 (1H, d, *J*= 13.4 Hz, H-11a), 4.88 (1H, dd, *J*= 9.9, *J*= 4.7 Hz, H-6), 4.47 (1H, dd, *J*= 11.9, *J*= 9.9 Hz, H-6'), 3.82 (3H, s, OCH_3), 3.80 (3H, s, OCH_3), 3.63 (1H, ddd, *J*= 13.4, *J*= 11.9, *J*= 4.7 Hz, H-6a); gNOESY-2D, NOEs observed: 3.63 (4.47, 4.88); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 155.33 (C, C-2*), 154.83 (C, C-8*), 153.45 (C, C-10a), 146.51 (C, C-4a), 128.47 (C, C-6b), 124.96 (C, C-11b), 116.99 (CH, C-4), 115.07 (CH, C-3), 113.03 (CH, C-1), 111.04 (CH, C-9), 110.04 (CH, C-10), 107.85 (CH, C-7), 83.99 (CH, C-11a), 68.33 (CH_2, C-6), 55.95 (CH_3, OCH_3), 55.81 (CH_3,

OCH_3), 45.61 (CH, C-6a). (*) may be interchanged; HRFABMS (*m/z*) calcd. for $C_{17}H_{16}O_4Na$ 307.0950 $[M+Na]^+$, found 307.0950.





Data for the X-ray structure analysis of 14*cis*: Crystal from Hexane/Et_2O: crystal dimensions 0.410 x 0.110 x 0.055mm; $C_{17}H_{16}O_4$ (M= 284.30); triclinic, space group P1, a= 4.7090(7), b= 8.2955(12), c= 9.1628(13)Å, α= 92.006(2)°, β= 94.865(2)°, γ= 104.989(3)°, V= 343.90(9)Å^3, Z= 1, Dx= 1,373Mg/m^3, μ(Mo+ Kα)= 0.098mm^{-1}.
λ= 0.71073Å (MoKα radiation, SMART APEX CCD single crystal diffractometer). Data collection at 273(2) K, ϕ and ω scans, 5.093<θ<46.474°. 1581 unique reflections of which 1206 were observed with I>2σ(I). Crystal structure and anisotropic least-squares refinement were carried out with SHELXL-97. The final cycle of full-matrix least-squares refinement based on 1206 reflections and 192 parameters converged to a final value of R1 (F^2>2σ(F^2)) = 0.030, wR2 (F^2>2σ(F^2)) = 0.0696. Residual electron density 0.09/-0.109eÅ^{-3}. Crystallographic data have been deposited with the Cambridge Structural Data Centre as supplementary publication number CCDC 260556.

Identification code	**14*cis***	
Empirical formula	C17 H16 O4	
Formula weight	284.30	
Temperature	273(2) K	
Wavelength	0.71073 Å	
Crystal system, space group	Triclinic, P1	
Unit cell dimensions	a = 4.7090(7) Å	alpha = 92.006(2)°
	b = 8.2955(12) Å	beta = 94.865(2)°
	c = 9.1628(13) Å	gamma = 104.989(3)°
Volume	343.90(9) Å^3	
Z, Calculated density	1, 1,373 Mg/m^3	
Absorption coefficient	0.098 mm^-1	
F (000)	150	
Crystal size	0.410 x 0.110 x 0.055 mm	
Theta range for data collection	5.093 to 46.474°	
Limiting indices	-5<=h<=5, -9<=k<=5, -10<=l<=10	
Reflections collected / unique	1581 / 1206 [R (int) = 0.0195]	
Refinement method	Full – matrix least-squares on F^2	
Data / restrains / parameters	1206/ 3 / 192	
Goodness-of-fit on F^2	1.006	
Final R indices [I>2sigma (I)]	R1 = 0.0300, wR2 = 0.0696	
R indices (all data)	R1 = 0.0321, wR2 = 0.0697	
Largest diff. Peak and hole	0.09 and -0.109 e.A^-3	

Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for **14*cis***. U (eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
O1	2457(1)	9774(1)	10244(1)	73.6(1)
O2	3859(1)	10024(1)	4341(2)	50.1(1)
O3	3283(1)	5744(1)	6107(2)	55.5(1)
O4	-2764(1)	4268(1)	635(1)	77.9(1)
C1	2817(1)	9921(1)	8779(1)	51.5(1)
C2	2136(1)	11158(1)	7954(1)	57.2(1)
C3	2602(1)	11176(1)	6486(1)	50.9(1)
C4	3661(1)	9967(1)	5832(1)	41.1(1)
C5	4369(1)	8719(1)	6635(1)	42.3(1)
C6	3952(1)	8733(1)	8119(1)	49.7(1)
C7	2783(1)	6267(1)	3665(1)	43.8(1)
C8	1407(1)	5974(1)	2246(1)	50.8(1)
C9	-1187(1)	4693(1)	1989(1)	53.6(1)
C10	-2353(1)	3759(1)	3124(1)	58.3(1)
C11	-972(1)	4065(1)	4527(1)	53.2(1)
C12	1598(1)	5322(1)	4770(1)	45.6(1)
C20	960(1)	10841(1)	10904(1)	78.2(1)
C21	6010(1)	9258(1)	3825(1)	48.4(1)
C22	5617(1)	7495(1)	4281(1)	47.6(1)
C23	-1612(1)	5114(1)	-583(1)	89.3(1)
C24	5429(1)	7347(1)	5943(1)	46.2(1)

Bond lengths [Å] and angles [°] for **14*cis***.

O(1) – C(1)	1.373(3)
O(1) – C(20)	1.416(4)
C(21) – O(2)	1.430(3)
C(21) – C(22)	1.505(4)
C(21) – H(21A)	0.9700
C(21) – H(21B)	0.9700
O(3) – C(12)	1.383(3)
O(3) – C(24)	1.469(3)
O(4) – C(9)	1.375(3)
O(4) – C(23)	1.412(4)
C(1) – C(6)	1.381(4)
C(1) – C(2)	1.382(4)
C(2) – C(3)	1.381(4)

C(2) – H(2)	0.9300
C(3) – C(4)	1.371(3)
C(3) – H(3)	0.9300
C(4) – O(2)	1.379(3)
C(4) – C(5)	1.383(3)
C(5) – C(6)	1.391(3)
C(5) – C(24)	1.498(4)
C(6) – H(6)	0.9300
C(7) – C(12)	1.370(3)
C(7) – C(8)	1.387(3)
C(7) – C(22)	1.505(3)
C(8) – C(9)	1.393(4)
C(8) – H(8)	0.9300
C(9) – C(10)	1.385(4)
C(10) – C(11)	1.375(3)
C(10) – H(10)	0.9300
C(11) – C(12)	1.373(3)
C(11) – H(11)	0.9300
C(20) – H(20A)	0.9600
C(20) – H(20B)	0.9600
C(20) – H(20C)	0.9600
C(22) – C(24)	1.540(4)
C(22) – H(22)	0.9800
C(23) – H(23A)	0.9600
C(23) – H(23B)	0.9600
C(23) – H(23C)	0.9600
C(24) – H(24)	0.9800
C(1) – O(1) – C(20)	117.2(3)
O(2) – C(21) – C(22)	113.0(2)
O(2) – C(21) – H(21A)	109.0
C(22) – C(21) – H(21A)	109.0
O(2) – C(21) – H(21B)	109.0
C(22) – C(21) – H(21B)	109.0
H(21A) – C(21) – H(21B)	107.8
C(12) – O(3) – C(24)	106.26(19)
C(9) – O(4) – C(23)	118.3(2)
O(1) – C(1) – C(6)	116.1(3)
O(1) – C(1) – C(2)	124.6(3)
C(6) – C(1) – C(2)	119.4(2)
C(3) – C(2) – C(1)	119.2(3)
C(3) – C(2) – H(2)	120.4
C(1) – C(2) – H(2)	120.4
C(4) – C(3) – C(2)	121.1(3)
C(4) – C(3) – H(3)	119.5
C(2) – C(3) – H(3)	119.5
C(3) C(4) – O(2)	116.8(2)
C(3) – C(4) – C(5)	120.8(2)
O(2) – C(4) – C(5)	122.3(2)
C(4) – C(5) – C(6)	117.7(3)
C(4) – C(5) – C(24)	122.2(2)

C(6) – C(5) – C(24)	120.1(2)
C(1) – C(6) – C(5)	121.9(3)
C(1) – C(6) – H(6)	119.1
C(5) – C(6) – H(6)	119.1
C(12) – C(7) – C(8)	120.5(2)
C(12) – C(7) – C(22)	108.8(2)
C(8) – C(7) – C(22)	130.7(2)
C(7) – C(8) – C(9)	117.9(3)
C(7) – C(8) – H(8)	121.0
C(9) – C(8) – H(8)	121.0
O(4) – C(9) – C(10)	115.6(2)
O(4) – C(9) – C(8)	123.8(3)
C(10) – C(9) – C(8)	120.6(3)
C(11) – C(10) – C(9)	120.9(3)
C(11) – C(10) – H(10)	119.5
C(9) – C(10) – H(10)	119.5
C(12) – C(11) – C(10)	118.1(3)
C(12) – C(11) – H(11)	120.9
C(10) – C(11) – H(11)	120.9
C(7) – C(12) – C(11)	122.0(3)
C(7) – C(12) – O(3)	113.1(2)
C(11) – C(12) – O(3)	124.9(2)
O(1) – C(20) – H(20A)	109.5
O(1) – C(20) – H(20B)	109.5
H(20A) – C(20) – H(20B)	109.5
O(1) – C(20) – H(20C)	109.5
H(20A) – C(20) – H(20C)	109.5
H(20B) – C(20) – H(20C)	109.5
C(4) – O(2) – C(21)	114.1(2)
C(21) – C(22) – C(7)	115.4(2)
C(21) – C(22) – C(24)	112.8(2)
C(7) – C(22) – C(24)	101.5(2)
C(21) – C(22) – H(22)	108.9
C(7) – C(22) – H(22)	108.9
C(24) – C(22) – H(22)	108.9
O(4) – C(23) – H(23A)	109.5
O(4) – C(23) – H(23B)	109.5
H(23A) – C(23) – H(23B)	109.5
O(4) – C(23) – H(23C)	109.5
H(23A) – C(23) – H(23C)	109.5
H(23B) – C(23) – H(23C)	109.5
O(3) – C(24) – C(5)	108.7(2)
O(3) – C(24) – C(22)	105.96(19)
C(5) – C(24) – C(22)	112.7(2)
O(3) – C(24) – H(24)	109.8
C(5) – C(24) – H(24)	109.8
C(22) – C(24) – H(24)	109.8

Anisotropic displacement parameters parameters (Å^2 x 10^3) for **14*cis***.The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a*b* U12]

	U11	U22	U33	U23	U13	U12
O1	92(2)	88(2)	47(1)	12(1)	19(1)	29(1)
O2	57(1)	50(1)	47(1)	10(1)	5(1)	18(1)
O3	62(1)	45(1)	59(1)	12(1)	1(1)	14(1)
O4	78(2)	71(2)	66(1)	3(1)	-6(1)	-10(1)
C1	48(2)	58(2)	46(2)	3(2)	4(1)	9(2)
C2	61(2)	53(2)	59(2)	-4(2)	8(2)	17(2)
C3	55(2)	43(2)	55(2)	9(1)	1(1)	16(1)
C4	39(1)	40(2)	42(2)	6(1)	5(1)	4(1)
C5	35(1)	44(2)	46(2)	8(2)	1(1)	8(1)
C6	48(2)	50(2)	50(2)	14(1)	3(1)	11(1)
C7	41(2)	38(2)	57(2)	6(1)	9(1)	16(1)
C8	54(2)	45(2)	55(2)	7(1)	11(1)	14(2)
C9	56(2)	40(2)	60(2)	-1(2)	-2(2)	8(1)
C10	54(2)	40(2)	76(2)	4(2)	4(2)	5(1)
C11	55(2)	37(2)	69(2)	14(2)	12(2)	11(1)
C12	47(2)	36(2)	56(2)	9(1)	5(1)	14(1)
C20	63(2)	116(1)	53(2)	-8(2)	11(2)	20(1)
C21	40(2)	51(2)	53(2)	6(1)	7(1)	7(1)
C22	34(1)	50(2)	60(2)	3(1)	7(1)	12(1)
C23	104(1)	87(1)	63(1)	9(2)	-7(2)	4(1)
C24	41(1)	41(2)	57(2)	7(1)	3(1)	13(1)

Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for **14*cis***.

	x	y	z	U(eq)
H2	1373	11968	8382	69
H3	2193	12021	5933	61
H6	4453	7919	8684	60
H8	2191	6613	1490	61
H10	-4094	2913	2935	70
H11	-1756	3439	5290	64
H20A	2018	11984	10821	117
H20B	841	10619	11921	117

H20C	-997	10642	10417	117
H21A	7966	9922	4201	58
H21B	5881	9254	2763	58
H22	7286	7091	4000	57
H23A	-1349	6294	-406	134
H23B	-2961	4723	-1444	134
H23C	257	4902	-727	134
H24	7363	7340	6426	55

Torsión angles [°] for **14*cis*.**

C(20) – O(1) – C(1) – C(6)	-172.3(2)
C(20) – O(1) – C(1) – C(2)	8.0(4)
O(1) – C(1) – C(2) – C(3)	179.9(2)
C(6) – C(1) – C(2) – C(3)	0.1(4)
C(1) – C(2) – C(3) – C(4)	1.6(4)
C(2) – C(3) – C(4) – O(2)	175.6(2)
C(2) – C(3) – C(4) – C(5)	-1.8(4)
C(3) – C(4) – C(5) – C(6)	0.4(3)
O(2) – C(4) – C(5) – C(6)	-176.9(2)
C(3) – C(4) – C(5) – C(24)	177.8(2)
O(2) – C(4) – C(5) – C(24)	0.5(3)
O(1) – C(1) – C(6) – C(5)	178.7(2)
C(2) – C(1) – C(6) – C(5)	-1.5(4)
C(4) – C(5) – C(6) – C(1)	1.3(4)
C(24) – C(5) – C(6) – C(1)	-176.2(2)
C(12) – C(7) – C(8) – C(9)	-0.3(4)
C(22) – C(7) – C(8) – C(9)	177.6(3)
C(23) – O(4) – C(9) – C(10)	-176.8(3)
C(23) – O(4) – C(9) – C(8)	3.7(5)
C(7) – C(8) – C(9) – O(4)	-179.8(3)
C(7) – C(8) – C(9) – C(10)	0.6(4)
O(4) – C(9) – C(10) – C(11)	179.9(3)
C(8) – C(9) – C(10) –C(11)	-0.5(4)
C(9) – C(10) – C(11) – C(12)	-0.1(4)
C(8) – C(7) – C(12) – C(11)	-0.2(4)
C(22) – C(7) – C(12) – C(11)	-178.5(2)
C(8) – C(7) – C(12) – O(3)	178.3(2)
C(22) – C(7) – C(12) – O(3)	0.0(3)
C(10) – C(11) – C(12) – C(7)	0.4(4)
C(10) – C(11) – C(12) – O(3)	-177.9(3)
C(24) – O(3) – C(12) – C(7)	13.2(3)
C(24) – O(3) – C(12) – C(11)	-168.3(2)
C(3) – C(4) – O(2) – C(21)	155.1(2)
C(5) – C(4) – O(2) – C(21)	-27.5(3)
C(22) – C(21) – O(2) – C(4)	53.2(3)

O(2) – C(21) – C(22) – C(7)	64.0(3)
O(2) – C(21) – C(22) – C(24)	-52.1(3)
C(12) – C(7) – C(22) – C(21)	-134.6(2)
C(8) – C(7) – C(22) – C(21)	47.3(4)
C(12) – C(7) – C(22) – C(24)	-12.3(3)
C(8) – C(7) – C(22) – C(24)	169.6(3)
C(12) – O(3) – C(24) – C(5)	100.9(2)
C(12) – O(3) – C(24) – C(22)	-20.5(3)
C(4) – C(5) – C(24) – O(3)	-117.3(2)
C(6) – C(5) – C(24) – O(3)	60.1(3)
C(4) – C(5) – C(24) – C(22)	-0.1(3)
C(6) – C(5) – C(24) – C(22)	177.3(2)
C(21) – C(22) – C(24) – O(3)	143.7(2)
C(7) – C(22) – C(24) – O(3)	19.6(3)
C(21) – C(22) – C(24) – C(5)	25.0(3)
C(7) – C(22) – C(24) – C(5)	-99.1(2)

Data for the X-ray structure analysis of 14*trans*: Crystal from Hexane/Et_2O: crystal dimensions 0.270 x 0.150 x 0.080mm; $C_{17}H_{16}O_4$ (M= 284.30); triclinic, space group P-1, a= 8.0941(8), b= 8.7487(8), c= 10.2094(10)Å, α= 78.617(2)°, β= 82.940(2)°, γ= 77.161(2)°, V= 688.65(11)Å^3, Z= 2, Dx= 1,371 Mg/m^3, μ(Mo+ Kα)= 0.097 mm^{-1}. λ= 0.71073Å (MoKα radiation, SMART APEX CCD single crystal diffractometer). Data collection at 273(2) K, ϕ and ω scans, 5.18<θ<47.62°. 3775 unique reflections of which 2407 were observed with I>2σ(I). Crystal structure and anisotropic least-squares refinement were carried out with SHELXL-97. The final cycle of full-matrix least-squares refinement based on 2407 reflections and 192 parameters converged to a final value of R1 (F^2>2σ(F^2)) = 0.057, wR2 (F^2>2σ(F^2)) = 0.1687. Residual electron density 0.364/-0.348eÅ^{-3}. Crystallographic data have been deposited with the Cambridge Structural Data Centre as supplementary publication number CCDC 260557.

Identification code	**14*trans***	
Empirical formula	C17 H16 O4	
Formula_weight	284.30	
Temperature	273(2) K	
Wavelength	0.71073 Å	
Crystal system, space group	Triclinic, P-1	
Unit cell dimensions	a = 8.0941(8) Å	alpha = 78.617(2) °
	b = 8.7487(8) Å	beta = 82.940(2) °
	c = 10.2094(10) Å	gamma = 77.161(2) °
Volume	688.65(11) Å^3	
Z, Calculated density	2, 1,371 Mg/m^3	
Absorption coefficient	0.097 mm^-1	
F (000)	300	
Crystal size	0.270 x 0.150 x 0.080 mm	
Theta range for data collection	5.18 to 47.62 °	
Limiting indices	-9<=h<=9, -10<=k<=10, -10<=l<=12	
Reflections collected / unique	3775 / 2407 [R (int) = 0.0247]	
Refinement method	Full – matrix least-squares on F^2	
Data / restrains / parameters	2407/ 0 / 192	
Goodness-of-fit on F^2	1.070	
Final R indices [I>2sigma (I)]	R1 = 0.0579, wR2 = 0.1687	
R indices (all data)	R1 = 0.0810, wR2 = 0.1901	
Largest diff. Peak and hole	0.364 and -0.348 e.A^-3	

Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for **14*trans***. U (eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
O1	15020(1)	5856(1)	6733(2)	60.4(1)
O2	8222(1)	8737(1)	6510(2)	60.3(1)
O3	10555(1)	6553(1)	3280(2)	49.2(1)
O4	4801(1)	7993(1)	552(2)	66.2(1)
C1	10874(1)	7315(1)	5468(1)	45.2(1)
C2	12561(1)	6610(1)	5586(1)	46.5(1)
C4	12397(1)	7286(1)	7758(1)	54.5(1)
C5	10699(1)	7980(1)	7656(1)	52.0(1)
C6	9930(1)	8003(1)	6529(1)	46.0(1)
C7	7673(1)	7569(1)	3176(1)	50.9(1)
C8	9167(1)	6855(1)	2526(1)	44.6(1)
C9	9195(1)	6503(1)	1274(1)	53.9(1)
C10	7691(1)	6911(1)	662(1)	56.1(1)
C11	6195(1)	7641(1)	1282(1)	52.7(1)
C12	6164(1)	7952(1)	2566(1)	57.8(1)
C20	15851(1)	5836(1)	7893(1)	67.3(1)
C21	7319(1)	8882(1)	5339(1)	54.9(1)
C22	8133(1)	7641(1)	4540(1)	61.6(1)
C23	9958(4)	7586(4)	4244(1)	62.7(1)
C24	3245(1)	8832(1)	1119(1)	70.6(1)

Bond lengths [Å] and angles [°] for **14*trans***.

O(1) – C(3)	1.376(3)
O(1) – C(20)	1.427(3)
O(2) – C(6)	1.390(3)
O(2) – C(21)	1.447(3)
O(3) – C(8)	1.388(3)
O(3) – C(23)	1.435(3)
O(4) – C(11)	1.373(3)
O(4) – C(24)	1.427(3)
C(1) – C(2)	1.378(3)
C(1) – C(6)	1.402(4)
C(1) – C(23)	1.483(4)
C(2) – C(3)	1.380(3)
C(2) – H(2)	0.9300
C(3) – C(4)	1.382(4)
C(4) – C(5)	1.381(4)
C(4) – H(4)	0.9300

C(5) – C(6)	1.369(4)
C(5) – H(5)	0.9300
C(7) – C(12)	1.384(4)
C(7) – C(8)	1.387(4)
C(7) – C(22)	1.501(4)
C(8) – C(9)	1.369(4)
C(9) – C(10)	1.381(4)
C(9) – H(9)	0.9300
C(10) – C(11)	1.379(4)
C(10) – H(10)	0.9300
C(11) – C(12)	1.386(4)
C(12) – H(12)	0.9300
C(20) – H(20A)	0.9600
C(20) – H(20B)	0.9600
C(20) – H(20C)	0.9600
C(21) – C(22)	1.476(4)
C(21) – H(21A)	0.9700
C(21) – H(21B)	0.9700
C(22) – C(23)	1.463(4)
C(22) – H(22)	0.9800
C(23) – H(23)	0.9800
C(24) – H(24A)	0.9600
C(24) – H(24B)	0.9600
C(24) – H(24C)	0.9600
C(3) – O(1) – C(20)	117.0(2)
C(6) – O(2) – C(21)	120.62(19)
C(8) – O(3) – C(23)	101.75(19)
C(11) – O(4) – C(24)	117.6(2)
C(2) – C(1) – C(6)	119.3(2)
C(2) – C(1) – C(23)	125.9(2)
C(6) – C(1) – C(23)	114.5(2)
C(1) – C(2) – C(3)	120.8(2)
C(1) – C(2) – H(2)	119.6
C(3) – C(2) – H(2)	119.6
O(1) – C(3) – C(2)	115.9(2)
O(1) – C(3) – C(4)	124.5(2)
C(2) – C(3) – C(4)	119.6(2)
C(5) – C(4) – C(3)	120.1(2)
C(5) – C(4) – H(4)	120.0
C(3) – C(4) – H(4)	120.0
C(6) – C(5) – C(4)	120.5(2)
C(6) – C(5) – H(5)	119.7
C(4) – C(5) – H(5)	119.7
C(5) – C(6) – O(2)	116.6(2)
C(5) – C(6) – C(1)	119.8(2)
O(2) – C(6) – C(1)	123.7(2)
C(12) – C(7) – C(8)	120.5(3)
C(12) – C(7) – C(22)	134.0(3)
C(8) – C(7) – C(22)	105.4(2)
C(9) – C(8) – C(7)	121.3(2)

C(9) – C(8) – O(3)	125.8(2)
C(7) – C(8) – O(3)	112.9(2)
C(8) – C(9) – C(10)	117.9(3)
C(8) – C(9) – H(9)	121.1
C(10) – C(9) – H(9)	121.1
C(11) – C(10) – C(9)	121.7(3)
C(11) – C(10) – H(10)	119.1
C(9) – C(10) – H(10)	119.1
O(4) – C(11) – C(10)	115.5(2)
O(4) – C(11) – C(12)	124.4(3)
C(10) – C(11) – C(12)	120.1(3)
C(7) – C(12) – C(11)	118.4(3)
C(7) – C(12) – H(12)	120.8
C(11) – C(12) – H(12)	120.8
O(1) – C(20) – H(20A)	109.5
O(1) – C(20) – H(20B)	109.5
H(20A) – C(20) – H(20B)	109.5
O(1) – C(20) – H(20C)	109.5
H(20A) – C(20) – H(20C)	109.5
H(20B) – C(20) – H(20C)	109.5
O(2) – C(21) – C(22)	111.0(2)
O(2) – C(21) – H(21A)	109.4
C(22) – C(21) – H(21A)	109.4
O(2) – C(21) – H(21B)	109.4
C(22) – C(21) – H(21B)	109.4
H(21A) – C(21) – H(21B)	108.0
C(23) – C(22) – C(21)	112.0(3)
C(23) – C(22) – C(7)	99.6(2)
C(21) – C(22) – C(7)	125.1(2)
C(23) – C(22) – H(22)	106.3
C(21) – C(22) – H(22)	106.3
C(7) – C(22) – H(22)	106.3
O(3) – C(23) – C(22)	107.2(2)
O(3) – C(23) – C(1)	118.8(2)
C(22) – C(23) – C(1)	112.9(2)
O(3) – C(23) – H(23)	105.7
C(22) – C(23) – H(23)	105.7
C(1) – C(23) – H(23)	105.7
O(4) – C(24) – H(24A)	109.5
O(4) – C(24) – H(24B)	109.5
H(24A) – C(24) – H(24B)	109.5
O(4) – C(24) – H(24C)	109.5
H(24A) – C(24) – H(24C)	109.5
H(24B) – C(24) – H(24C)	109.5

Anisotropic displacement parameters parameters (Å^2 x 10^3) for **14*trans***. The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a*b* U12]

	U11	U22	U33	U23	U13	U12
O1	44(1)	87(1)	53(1)	-31(1)	-12(1)	1(1)
O2	48(1)	80(1)	55(1)	-35(1)	-7(1)	4(1)
O3	42(1)	62(1)	46(1)	-23(1)	-6(1)	-1(1)
O4	46(1)	94(2)	61(1)	-33(1)	-15(1)	3(1)
C1	46(1)	49(2)	44(1)	-16(1)	-5(1)	-7(1)
C2	46(2)	53(2)	44(2)	-21(1)	-1(1)	-10(1)
C3	44(1)	53(2)	45(2)	-14(1)	-6(1)	-9(1)
C4	59(2)	67(2)	41(2)	-20(1)	-8(1)	-9(1)
C5	54(2)	61(2)	40(2)	-18(1)	1(1)	-4(1)
C6	45(1)	47(1)	47(2)	-14(1)	-4(1)	-6(1)
C7	46(2)	63(2)	45(2)	-21(1)	-6(1)	-3(1)
C8	39(1)	52(2)	44(1)	-14(1)	-5(1)	-5(1)
C9	45(2)	69(2)	48(2)	-26(1)	-2(1)	-1(1)
C10	54(2)	72(2)	45(2)	-26(1)	-6(1)	-4(1)
C11	46(2)	64(2)	50(2)	-18(1)	-11(1)	-3(1)
C12	43(2)	77(2)	54(2)	-28(1)	-2(1)	-1(1)
C20	53(2)	94(1)	58(2)	-26(2)	-19(1)	-2(2)
C21	48(2)	66(2)	52(2)	-24(1)	-8(1)	-1(1)
C22	51(2)	83(1)	52(2)	-27(1)	-6(1)	-2(1)
C23	51(2)	84(1)	56(2)	-38(2)	-8(1)	4(1)
C24	44(2)	98(1)	68(1)	-26(2)	-12(1)	3(1)

Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for **14*trans***.

	x	y	z	U(eq)
H2	13192	6149	4887	55
H4	12915	7295	8520	65
H5	10072	8436	8359	62
H9	10195	6005	850	65
H10	7686	6688	-191	67
H12	5153	8407	3007	69
H20A	15737	6907	8040	101
H20B	17035	5363	7760	101
H20C	15341	5226	8659	101
H21A	7305	9925	4791	66

H21B	6152	8786	5618	66
H22	8020	6619	5106	74
H23	10060	8654	3771	75
H24A	2885	8195	1937	106
H24B	2389	9047	497	106
H24C	3415	9818	1303	106

Torsión angles [°] for **14*trans*.**

C(6) – C(1) – C(2) – C(3)	-0.2(4)
C(23) – C(1) – C(2) – C(3)	172.8(2)
C(20) – O(1) – C(3) – C(2)	178.8(2)
C(20) – O(1) – C(3) – C(4)	0.5(4)
C(1) – C(2) – C(3) – O(1)	-179.4(2)
C(1) – C(2) – C(3) – C(4)	-1.1(4)
O(1) – C(3) – C(4) – C(5)	180.0(2)
C(2) – C(3) – C(4) – C(5)	1.9(4)
C(3) – C(4) – C(5) – C(6)	-1.3(4)
C(4) – C(5) – C(6) – O(2)	-179.5(2)
C(4) – C(5) – C(6) – C(1)	0.0(4)
C(21) – O(2) – C(6) – C(5)	177.3(2)
C(21) – O(2) – C(6) – C(1)	-2.2(4)
C(2) – C(1) – C(6) – C(5)	0.7(4)
C(23) – C(1) – C(6) – C(5)	-173.0(2)
C(2) – C(1) – C(6) – O(2)	-179.8(2)
C(23) – C(1) – C(6) – O(2)	6.5(4)
C(12) – C(7) – C(8) – C(9)	-0.3(4)
C(22) – C(7) – C(8) – C(9)	175.8(2)
C(12) – C(7) – C(8) – O(3)	-179.9(2)
C(22) – C(7) – C(8) – O(3)	-3.9(3)
C(23) – O(3) – C(8) – C(9)	162.1(3)
C(23) – O(3) – C(8) – C(7)	-18.3(3)
C(7) – C(8) – C(9) – C(10)	1.3(4)
O(3) – C(8) – C(9) – C(10)	-179.1(2)
C(8) – C(9) – C(10) – C(11)	-0.4(4)
C(24) – O(4) – C(11) – C(10)	-176.4(2)
C(24) – O(4) – C(11) – C(12)	4.5(4)
C(9) – C(10) – C(11) – O(4)	179.4(2)
C(9) – C(10) – C(11) – C(12)	-1.5(4)
C(8) – C(7) – C(12) – C(11)	-1.6(4)
C(22) – C(7) – C(12) – C(11)	-176.3(3)
O(4) – C(11) – C(12) – C(7)	-178.5(2)
C(10) – C(11) – C(12) – C(7)	2.5(4)
C(6) – O(2) – C(21) – C(22)	24.4(3)
O(2) – C(21) – C(22) – C(23)	-51.3(3)
O(2) – C(21) – C(22) – C(7)	-171.5(2)
C(12) – C(7) – C(22) – C(23)	-161.0(3)
C(8) – C(7) – C(22) – C(23)	23.7(3)

C(12) – C(7) – C(22) – C(21)	-35.4(5)
C(8) – C(7) – C(22) – C(21)	149.3(3)
C(8) – O(3) – C(23) – C(22)	34.2(3)
C(8) – O(3) – C(23) – C(1)	163.6(2)
C(21) – C(22) – C(23) – O(3)	-170.0(2)
C(7) – C(22) – C(23) – O(3)	-35.9(3)
C(21) – C(22) – C(23) – C(1)	57.3(4)
C(7) – C(22) – C(23) – C(1)	-168.6(2)
C(2) – C(1) – C(23) – O(3)	26.4(4)
C(6) – C(1) – C(23) – O(3)	-160.4(2)
C(2) – C(1) – C(23) – C(22)	153.1(3)
C(6) – C(1) – C(23) – C(22)	-33.7(4)