Supplementary material

A concise organocatalytic and enantioselective synthesis of isotetronic acids

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General Remarks: NMR analysis were carried out on spectrometers Bruker AC-200 FT (200 MHz for proton, 50.4 MHz for carbon), Bruker AC-250 FT (250 MHz for proton, 63 MHz for carbon), Bruker DPX-300 (300 MHz for proton, 75.5 MHz for carbon) and Bruker DPX-400 (400 MHz for proton, 100 MHz for carbon) by using deuterated chloroform as solvent. The chemical shifts (δ) for carbon and proton are given compared to the internal reference (TMS) and are expressed in ppm. Some mass spectra (low resolution) were obtained using a Thermo Quest Finnigan Trace GC-MS apparatus. Ionization was carried out by electronic impact (potential of ionization: 70 eV). Other mass spectra (low and high resolution) were obtained on a Micromass autospec-Q spectrometer. Ionization employed was the electronic impact mode [potential of ionization: 70 eV), and the LSIMS mode (potential of ionization: 35 keV, matrix: (3-nitrophenyl)methanol]. IR spectra were obtained on a Perkin-Elmer Paragon 1000 FT-IR spectrometer. The wavelengths (ν) are expressed in cm^{-1}.

General procedure for the preparation of the isotetronic acids : The α-ketoacid (1 mmol), the aldehyde (1 mmol) and the catalyst (10 to 30 mol%) in solution (or in suspension) in the desired solvent (1 mL) were stirred at room temperature for the period specified in Table 1. After removal of the solvent, the crude mixtures were purified by column chromatography

over silica gel (CH_2Cl_2-MeOH) to furnish the desired compounds. For reactions carried out in water, a small amount of CH_2Cl_2 (1 mL) is added to the reaction mixture to extract the products before chromatography over silica gel.

Characterization of the isotetronic acids:

(*S*)-3-hydroxy-5-isopropyl-4-methyfuran-2(*5H*)-one, **7a**: Pale yellow waxy solid; *R*f (CH_2Cl_2/MeOH, 98/2) = 0.3; HPLC: Welk O2 (hexane/EtOH, 90/10, flow rate 1.0 mL min^{-1}, λ = 247 nm): t_{minor} = 9.4, t_{major} = 10.0 min; ^{1}H NMR (300 MHz, $CDCl_3$), δ 6.02 (bs, 1H, OH), 4.69 (m, 1H, C*H*O), 2.14-2.04 (m, 1H, C*H*$(CH_3)_2$), 1.89 (s, 3H, C*H*$_3$C=C), 1.14 (d, *J* = 6.8 Hz, 3H, C*H*$_3$CH), 0.72 ppm (d, *J* = 6.8 Hz, 3H, C*H*$_3$CH); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 171.00, 138.03, 130.81, 85.84, 29.83, 19.35, 13.88, 9.68 ppm; MS (EI): *m*/*z* (%) = 156 (2), 85 (52), 43 (100); HRMS (LSIMS): calcd. for $C_8H_{12}O_3$ 156.078644, found: 156.078781.

Ethyl-2,5-dihydro-4-hydroxy-3-methyl-5-oxofuran-2-carboxylate, **7b**: Colorless oil; *R*f (CH_2Cl_2/MeOH, 99/1) = 0.2; HPLC: Welk O2 (hexane/EtOH, 97/3, flow rate 1.0 mL min^{-1}, λ = 238 nm): *t* = 33.4, *t* = 36.5 min; ^{1}H NMR (250 MHz, $CDCl_3$), δ 5.18 (s, 1H, C*H*O), 4.28 (m, 2H, C*H*$_2$CH$_3$), 1.98 (s, 3H, C*H*$_3$C=C), 1.30 ppm (t, J = 7.5 Hz, 3H, C*H*$_3$CH$_2$); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 170.30, 166.67, 138.54, 127.32, 78.81, 62.89, 14.39, 9.76 ppm; MS (LSIMS): *m*/*z* (%) = 373 (15) $[2M + H]^+$, 209 (15) $[M + Na]^+$, 187 (100) $[M + H]^+$; HRMS (LSIMS): calcd. for $C_8H_{11}O_5$ $[M + H]^+$: 187.060649, found: 187.060400.

(*S*)-3-hydroxy-4-methyl-5-phenylfuran-2(5H)-one, **7d**: White solid; M.p. 75 °C; *R*f (CH_2Cl_2/MeOH, 98/2) = 0.3; HPLC: Chiralcel AD-H® (hexane/*i*-PrOH, 90/10, flow rate 1.0 mL min^{-1}, λ = 230 nm): t_{minor} = 15.6, t_{major} = 12.8 min; ^{1}H NMR (300 MHz, $CDCl_3$), δ 7.41-7.39 (m, 2H, ArH), 7.25-7.22 (m, 3H, ArH), 5.64 (s, 1H, C*H*O), 5.50 (s, 1H, OH), 1.78 ppm (s, 3H, C*H*$_3$C=C); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 170.81, 137.49, 134.44, 131.49, 129.56, 129.00, 127.19, 83.51, 9.64 ppm; IR (KBr) ν_{max}/cm^{-1} 3530, 3443, 3359, 1735, 1700, 1687, 1457, 1310, 1213, 1165, 1150, 1054, 954, 779, 760, 699. MS (EI): *m*/*z* (%) = 190 (70), 145 (100); HRMS (LSIMS): calcd. for $C_{11}H_{10}O_3$ 190.062994, found: 190.063233.

(*S*)-3-hydroxy-4-methyl-5-(4-nitrophenyl)furan-2(5H)-one, **7e**: Orange solid; M.p. 85 °C; *R*f (CH_2Cl_2/MeOH, 98/2) = 0.25; HPLC: Welk O2 (hexane/EtOH, 90/10, flow rate 1.0 mL min^{-1}, λ = 254 nm): t_{minor} = 22.4, t_{major} = 25.2 min; ^{1}H NMR (300 MHz, $CDCl_3$), δ 8.26 (d, *J* = 8.7

Hz, 2H, ArH), 7.43 (d, J = 8.7 Hz, 2H, ArH), 5.95 (s, 1H, C*H*O), 5.74 (bs, 1H, OH), 1.80 ppm (s, 3H, CH_3C=C); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 169.74, 148.64, 141.70, 137.64, 130.02, 127.86, 124.27, 81.75, 9.50 ppm; IR (KBr) ν_{max}/cm^{-1} 3319, 1767, 1702, 1600, 1514, 1405, 1358, 1310, 1215, 1149, 1055, 1000, 979, 856, 829, 806, 774, 751, 700. MS (EI): m/z (%) = 235 (15), 190 (100), 116 (85), 49 (85); HRMS: calcd. for $C_{11}H_9NO_5$: 235.048073, found: 235.048006.

(*R*)-3-hydroxy-4-methyl-5-(perfluorophenyl)furan-2(5H)-one, **7f**: White solid; M.p. 148 °C; *R*f (CH_2Cl_2/MeOH, 98/2) = 0.25; HPLC: Welk O2 (hexane/EtOH, 96/4, flow rate 1.0 mL min^{-1}, λ = 254 nm): t_{minor} = 13.8, t_{major} = 15.6 min; ^{1}H NMR (250 MHz, $CDCl_3$), δ 6.05 (s, 1H, C*H*O), 1.86 ppm (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6, 146.0 ($^1J_{CF}$ = 250 Hz), 142.3 ($^1J_{CF}$ = 250 Hz), 138.5, 138.0 ($^1J_{CF}$ = 260 Hz), 127.6, 108.6, 73.3, 9.3 ppm; IR (KBr) ν_{max}/cm^{-1} 3349, 3201, 1710, 1689, 1676, 1656, 1531, 1508, 1429, 1362, 1315, 1289, 1214, 1165, 1135, 1056, 1029, 1009, 992, 967, 912, 831, 779, 752, 665. MS (ES$^-$): m/z (%) = 279.0 (100) [M – H]$^-$; HRMS (LSIMS): calcd. for [M + H]$^+$ $C_{11}H_6F_5O_3$: 281.023420, found: 281.023420.

(*S*)-5-(4-bromophenyl)-3-hydroxy-4-methylfuran-2(5H)-one, **7g**: Pale yellow solid; M.p. 139 °C; *R*f (CH_2Cl_2/MeOH, 99/1) = 0.3; HPLC: Welk O2 (hexane/EtOH, 96/4, flow rate 1.0 mL min^{-1}, λ = 254 nm): t_{minor} = 20.2, t_{major} = 28.6 min; ^{1}H NMR (250 MHz, $CDCl_3$), δ 7.52 (d, J = 8.5 Hz, 2H, ArH), 7.11 (d, J = 8.5 Hz, 2H, ArH), 5.29 (s, 1H, C*H*O), 1.75 ppm (s, 3H, CH_3); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 170.43, 137.69, 133.58, 132.24, 130.86, 128.81, 123.69, 82.63, 9.58 ppm. IR (KBr) ν_{max}/cm^{-1} 3526, 3455, 3348, 1748, 1706, 1687, 1489, 1437, 1412, 1366, 1305, 1287, 1213, 1194, 1154, 1068, 1012, 992, 974, 840, 827, 803, 773. MS (ES–): m/z (%) = 266.9 (100) [M – H]$^-$, 268.9 (75), 269.9 (20); HRMS (LSIMS): calcd. for [M + H]$^+$ $C_{11}H_{10}BrO_3$ 268.981330, found: 268.981814.

(*S*)-3-hydroxy-5-(4-methoxyphenyl)-4-methylfuran-2(5H)-one, **7h**: Pale yellow solid; M.p. 124 °C; *R*f (CH_2Cl_2/MeOH, 99/1) = 0.3; HPLC: Welk O2 (hexane/EtOH, 90/10, flow rate 1.0 mL min^{-1}, λ = 254 nm): t_{minor} = 26.3, t_{major} = 34.2 min; ^{1}H NMR (250 MHz, $CDCl_3$), δ 7.16 (d, J = 7.5 Hz, 2H, ArH), 6.90 (d, J = 7.5 Hz, 2H, ArH), 5.60 (s, 1H, C*H*O), 3.82 (s, 3H, OCH_3), 1.77 ppm (s, 3H, CH_3); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 170.93, 160.53, 137.76, 131.51, 128.83, 126.32, 114.38, 83.36, 55.34, 9.70 ppm. IR (KBr) ν_{max}/cm^{-1} 3319, 1752, 1705, 1611,

1514, 1458, 1438, 1412, 1362, 1304, 1283, 1258, 1210, 1174, 1150, 1030, 975, 835. MS (LSIMS+): *m*/*z* (%) = 243 (30) $[M + Na]^+$, 221.0 (100) $[M + H]^+$; HRMS (LSIMS), calcd. for $[M + H]^+$ $C_{12}H_{13}O_4$: 221.081384, found: 221.081886.

(*R*)-3-hydroxy-5-(perfluorophenyl)-4-phenylfuran-2(5H)-one, **7j**: White solid; M.p. 162 °C; *R*f (CH_2Cl_2/MeOH, 98/2) = 0.3; HPLC: Welk O2 (hexane/EtOH, 96/4, flow rate 1.0 mL min^{-1}, λ = 254 nm): t_{minor} = 13.5, t_{major} = 16.1 min; ^{1}H NMR (400 MHz, $CDCl_3$), δ 7.58 (d, J = 7.2 Hz, 2H, ArH), 7.38 (m, 3H, ArH), 6.62 ppm (s, 1H, C*H*O); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.7, 146.0 ($^1J_{CF}$ = 250 Hz), 142.4 ($^1J_{CF}$ = 260 Hz), 138.0 ($^1J_{CF}$ = 250 Hz), 137.9, 129.9, 129.4, 129.2, 127.1, 127.0, 109.7, 71.1 ppm. IR (KBr) ν_{max}/cm^{-1} 3289, 3218, 1757, 1528, 1505, 1404, 1337, 1307, 1294, 1157, 1134, 994, 950, 765, 697, 663. MS (LSIMS): *m*/*z* (%) = 343 (100) $[M + H]^+$, 365.0 (85) $[M + Na]^+$; HRMS (+TOF MS), calcd. for $[M + Na]^+$ $C_{16}H_7O_3F_5Na$: 365.0213, found: 365.214.

(*R*)-4-ethyl-3-hydroxy-5-(perfluorophenyl)furan-2(5H)-one, **7k**: White solid; M.p. 147 °C; *R*f (CH_2Cl_2/MeOH, 98/2) = 0.3; HPLC: Welk O2 (hexane/EtOH, 96/4, flow rate 1.0 mL min^{-1}, λ = 254 nm): t_{minor} = 13.3, t_{major} = 15.0 min; ^{1}H NMR (250 MHz, $CDCl_3$), δ 6.11 (s, 1H, C*H*O), 2.44 (qd, ^3J = 7.6 Hz, ^2J = 15.3 Hz, 1H, C*H*HCH$_3$), 2.08 (qd, ^3J = 7.6 Hz, ^2J = 15.3 Hz, 1H, CH*H*CH$_3$), 1.11 ppm (t, J = 8.5 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.10, 146.0 ($^1J_{CF}$ = 250 Hz), 142.3 ($^1J_{CF}$ = 250 Hz), 138.0 ($^1J_{CF}$ = 250 Hz), 138.0, 132.7, 108.9, 72.2, 18.2, 11.6 ppm. IR (KBr) ν_{max}/cm^{-1} 3218, 1731, 1680, 1670, 1654, 1529, 1506, 1360, 1338, 1312, 1260, 1164, 1135, 1072, 995, 945, 750, 668. MS (LSIMS): *m*/*z* (%) = 295 (100) $[M + H]^+$, 317.0 (55) $[M + Na]^+$; HRMS (+TOF MS), calcd. for $[M + Na]^+$ $C_{12}H_7O_3F_5Na$: 317.0213, found: 317.0205.

(*R*)-5-(tribromomethyl)-3-hydroxy-4-methylfuran-2(5H)-one, **9a**: The reaction affords a mixture of tribromo- **9a,** and dibromo-derivatives **9b**, in an approximately 2/1 ratio (GC-MS, of the reaction mixture given below). Whilst **9a** and **9b** display very close *R*f on silica TLC plates, they have been partially separated by column chromatography (GC-MS and HPLC chromatograms presented below) to afford **9a** in an analytically pure form. White solid; *R*f (CH_2Cl_2/MeOH, 98/2) = 0.2; HPLC: Chiralcel AD-H® (hexane/*i*-PrOH, 90/10, flow rate 1.0 mL min^{-1}, λ = 230 nm): t_{minor} = 8.9, t_{major} = 9.5 min; ^{1}H NMR (400 MHz, $CDCl_3$), δ 6.35 (s, 1H, OH), 5.30 (s, 1H, CHO), 2.10 ppm (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.8,

142.4, 128.4, 88.5, 39.2, 12.7 ppm. IR (KBr) ν_{max}/cm^{-1} 3287, 1760, 1699, 1437, 1409, 1357, 1325, 1277, 1209, 1141, 1069, 1031, 993, 822, 770, 740, 703. MS (LSIMS): *m/z* (%) = 387.0 (13) $[M + Na]^+$, 364.0 (10) $[M + H]^+$; HRMS (LSIMS), calcd. for $[M + Na]^+$ C_6H_5ONaBr: 384.7686, found: 384.7683.

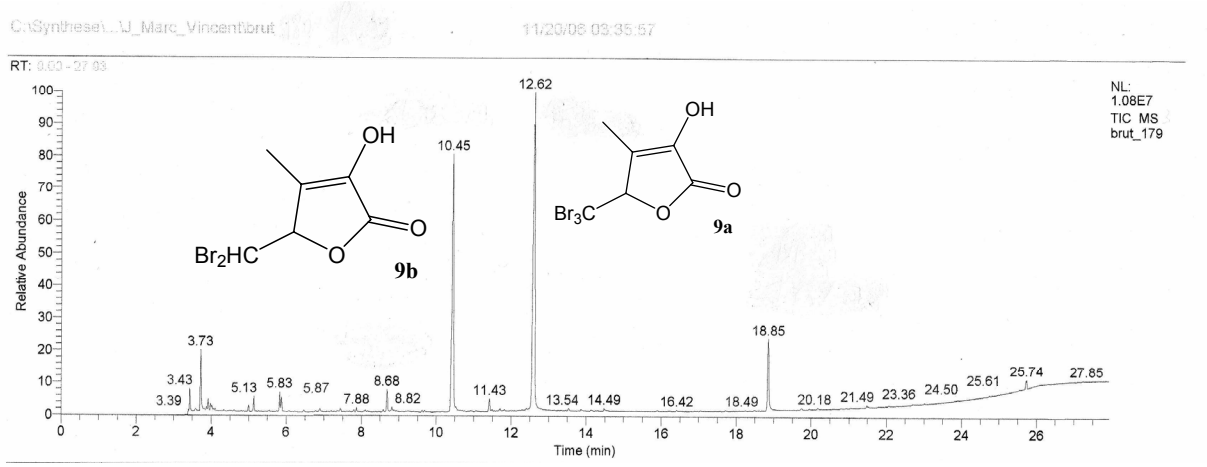


Figure 1. GC chromatogram of the reaction mixture.

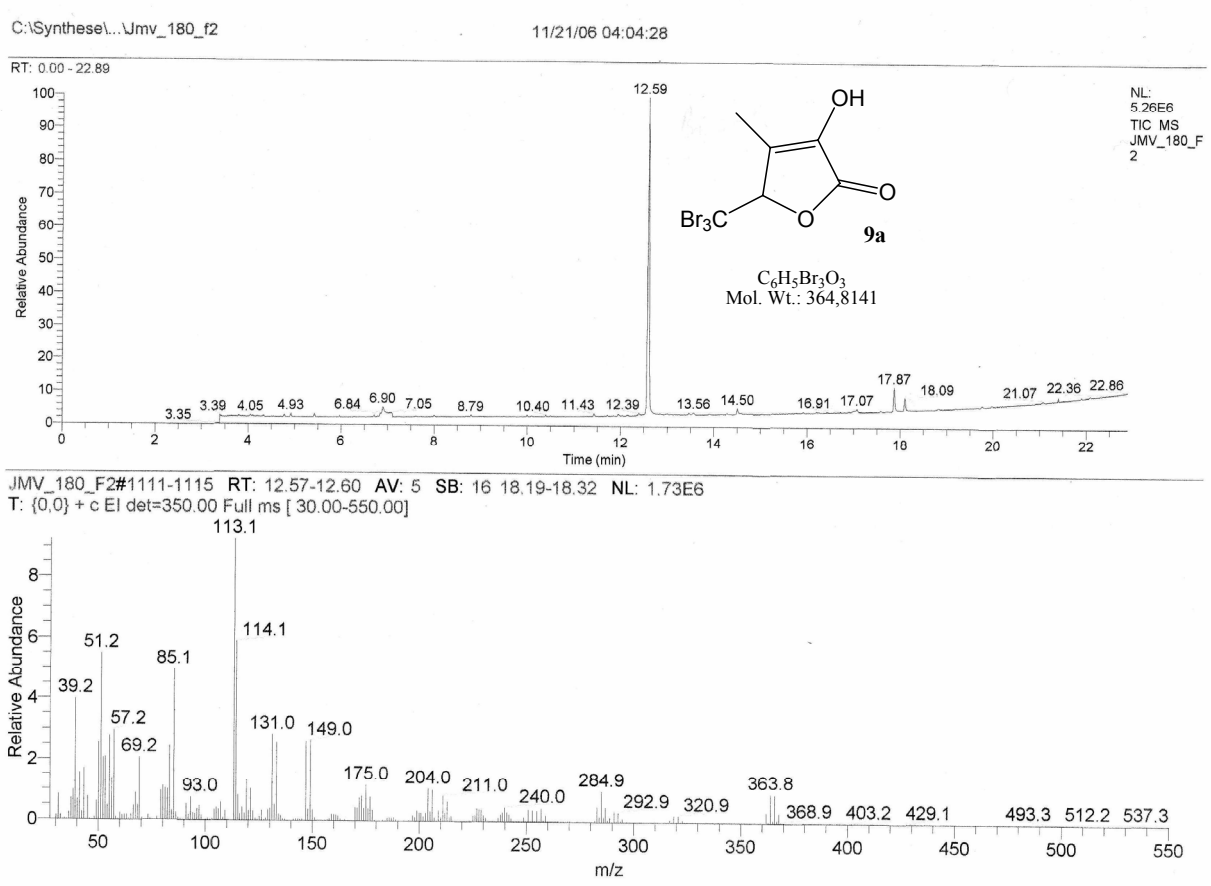
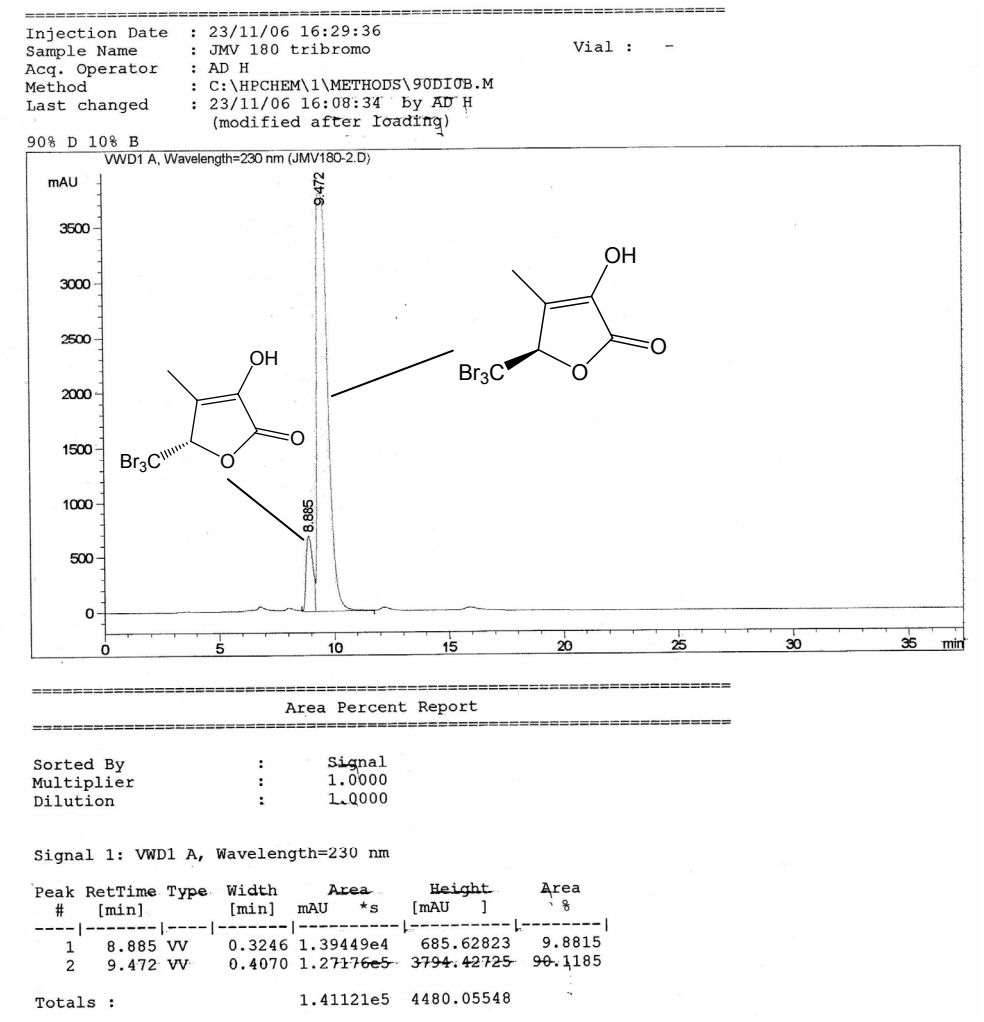


Figure2. GC chromatogram and MS spectrum of **9a** isolated after column chromatography.



Area Percent Report

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Dilution : 1.0000

Signal 1: VWD1 A, Wavelength=230 nm

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1	8.885	VV	0.3246	1.39449e4	685.62823	9.8815
2	9.472	VV	0.4070	1.27176e5	3794.42725	90.1185
Totals :				1.41121e5	4480.05548	

Figure 3. Chiral HPLC of **9a** obtained after column chromatography.

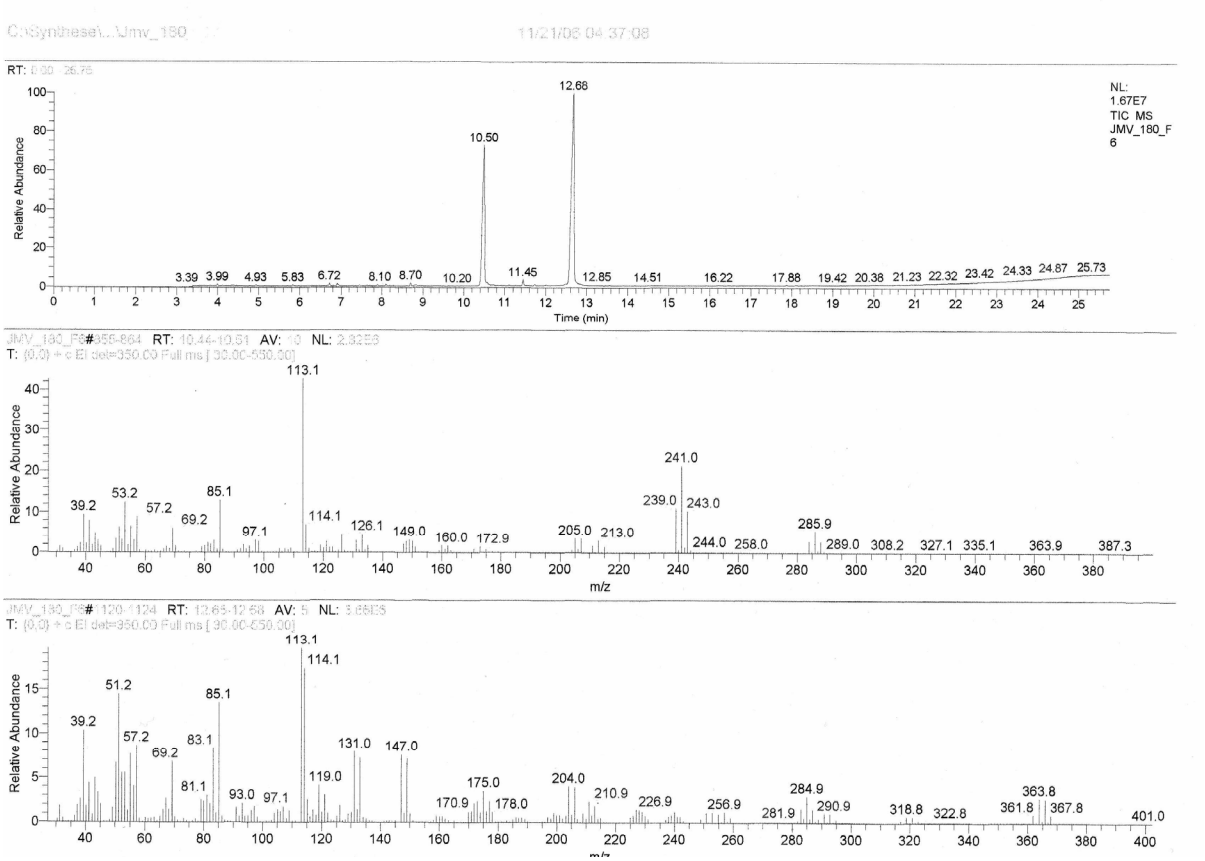

Figure 4. GC chromatogram and MS spectra of **9a** and **9b** mixture obtained after column chromatography.

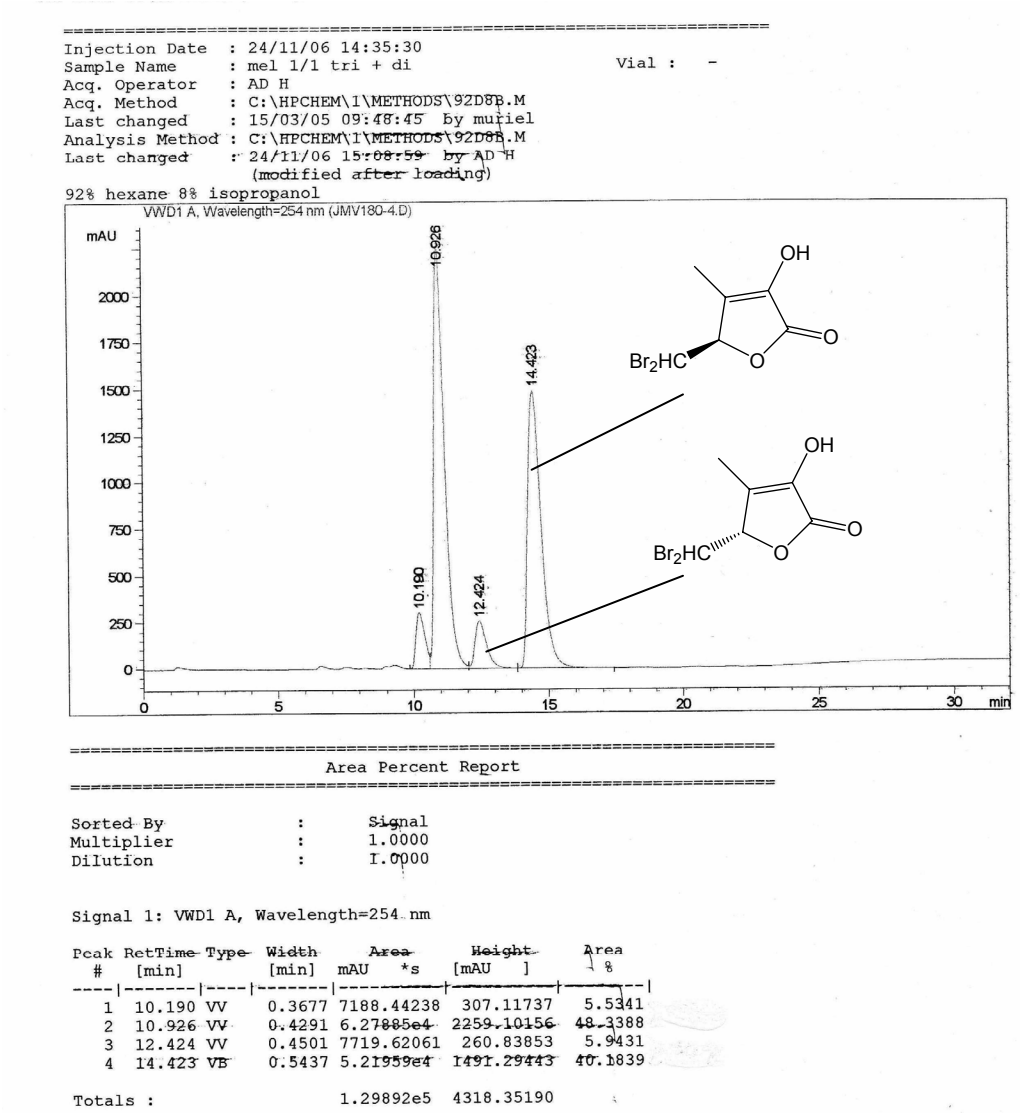

Figure 5. Chiral HPLC of **9a** and **9b** mixture obtained after column chromatography.

Representative HPLC chromatograms of isotetronic acids isolated after silica gel chromatography

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Acq. Operator   : welk
Method          : C:\HPCHEM\1\METHODS\96D-4C.M
Last changed    : 16/07/07 08:50:57  by welk
                  (modified after loading)
96 % Hexane 4 % Ethanol
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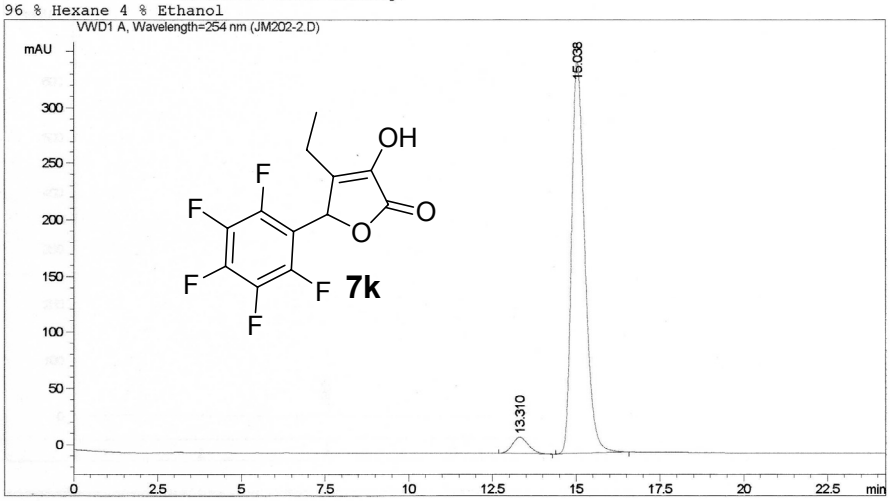


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Signal 1: VWD1 A, Wavelength=254 nm

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   2  15.038 PB    0.4244 9657.19336  349.41730  95.1591

Totals :                  1.01485e4   364.22381

 Results obtained with enhanced integrator!
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Instrument 1 16/07/07 09:18:21 welk Page 1 of 1

Data File C:\HPCHEM\1\DATA\JMV197-3.D Sample Name: JMV 197 + dichlo

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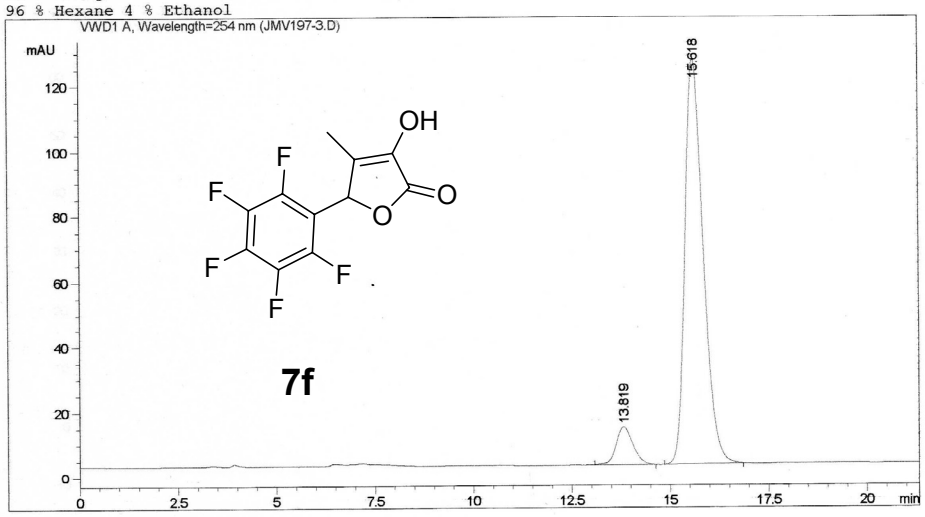

7f

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Dilution              :      1.0000

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   1  13.819 BB    0.4512  344.59238   11.60850   7.9190
   2  15.618 BB    0.4974 4006.84595  124.15592  92.0810

Totals :                  4351.43832  135.76442

 Results obtained with enhanced integrator!
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                        *** End of Report ***
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Instrument 1 10/07/07 09:45:24 welk Page 1 of 1

Data File C:\HPCHEM\1\DATA\CM033-1.D Sample Name: CM033

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90% D 10% B
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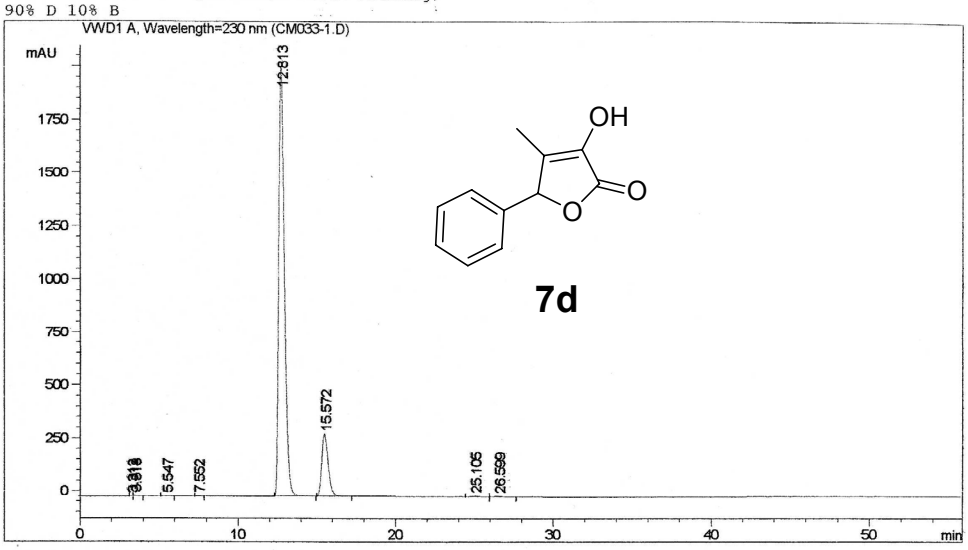

7d

Area Percent Report

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Multiplier            :      1.0000
Dilution              :      1.0000

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2	3.518	VB	0.2268	83.61907	5.08607	0.1402
3	5.547	BP	0.2396	52.14037	3.27573	0.0874
4	7.552	PV	0.2884	39.66379	2.08996	0.0665
5	12.813	PB	0.3872	5.07770e4	2024.80176	85.1054
6	15.572	BB	0.4422	8485.83008	294.75427	14.2228
7	25.105	BV	0.5451	109.46065	2.83473	0.1835
8	26.599	VB	0.5945	105.26464	2.56912	0.1764
Totals :				5.96636e4	2337.31361	

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 Results obtained with enhanced integrator!
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*** End of Report ***

Instrument 1 05/05/06 10:10:59 AD H Page 1 of 1

Data File C:\HPCHEM\1\DATA\JM203-1D.D Sample Name: JMV 203

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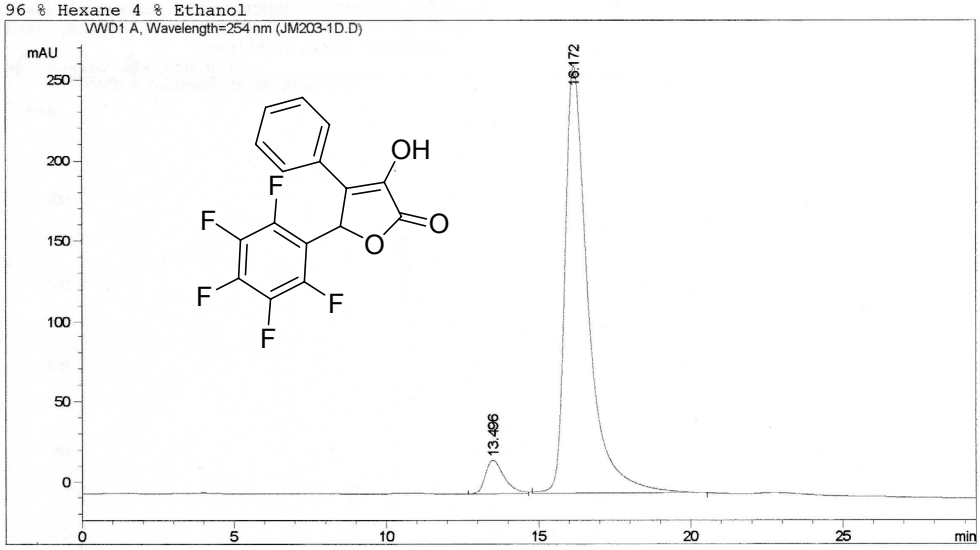


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Dilution              :      1.0000

Signal 1: VWD1 A, Wavelength=254 nm

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   1  13.496 BB    0.6719  943.68909   21.27355   6.2414
   2  16.172 BB    0.7918 1.41761e4   266.13364  93.7586

Totals :                  1.51198e4   287.40718

 Results obtained with enhanced integrator!
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                          *** End of Report ***
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Instrument 1 16/07/07 09:55:06 welk Page 1 of 1

HPLC Report

Reported by User: System Project Name: MURIEL

SAMPLE INFORMATION

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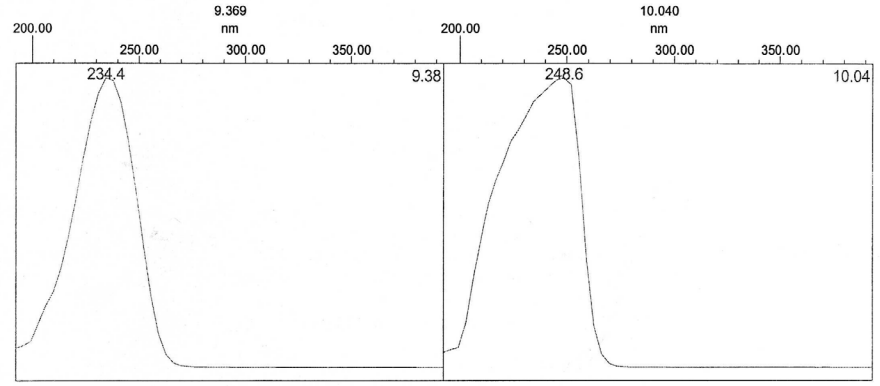
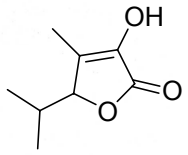
Vial:	1	Acq. Method Set:	90_10
Injection #:	3	Date Processed:	23/03/06 17:06:38
Injection Volume:	20.00 ul	Processing Method:	CM
Run Time:	200.0 Minutes	Channel Name:	Wvln Ch1
Sample Set Name:		Proc. Chnl. Descr.:	PDA 262.0 nm

Spectrum Index Plot



Peak Results

	RT	Height	% Area
1	9.369	61008	12.07
2	10.040	397369	87.93



7a

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VCD measurements. IR and VCD spectra were recorded with a ThermoNicolet Nexus 670 FTIR spectrometer equipped with a VCD optical bench.[1] In this optical bench, the light beam was focused by a BaF_2 lens (191 mm focal length) to the sample, passing an optical filter (depending on the studied spectral range), a BaF_2 wire grid polarizer (Specac), and a ZnSe photoelastic modulator (Hinds Instruments, Type II/ZS50). The light was then focused by a ZnSe lens (38.1 mm focal length) onto a 1x1 mm^2 HgCdTe (ThermoNicolet, MCTA* E6032) detector. IR and VCD spectra were recorded at a resolution of 4 cm^{-1}, by coadding 50 scans and 36000 scans (12h acquisition time), respectively. The sample was held in a variable path length cell with BaF_2 windows. IR and VCD spectra of **7f** were measured in $CDCl_3$ at a concentration of 0.025 M and at a path length of 250 μm. Baseline corrections of the VCD spectrum was performed by subtracting the VCD spectrum of (±)-**7f** recorded at the same concentration. In all experiments, the photoelastic modulator was adjusted for a maximum efficiency at 1400 cm^{-1}. Calculations were done with the standard ThermoNicolet software, using Happ and Genzel apodization, de-Haseth phase-correction and a zero-filling factor of one. Calibration spectra were recorded using a birefringent plate (CdSe) and a second BaF_2 wire grid polarizer, following the experimental procedure previously published.[2] Finally, in the presented IR spectra, the solvent absorption was subtracted out.

DFT calculations. The geometry optimizations, vibrational frequencies, absorption, and VCD intensities were calculated by Gaussian 03 program[3] on the CIS-IBM of the M3PEC-Mesocentre of the University Bordeaux I. Calculations of the optimized geometry of $\mathbf{7f_a}$ and $\mathbf{7f_b}$ conformers were performed at the density functional theory level using B3PW91 functional and cc-pVTZ basis set. Vibrational frequencies, IR, and VCD intensities were calculated at the same level of theory, utilizing the magnetic field perturbation method with gauge-invariant atomic orbitals.[4] For comparison to experiment, the calculated frequencies were scaled by 0.978 and the calculated intensities were converted to Lorentzian bands with half-width of 7 cm^{-1}.

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