A short olefin metathesis-based route to enantiomerically pure arylated dihydropyrans and α,β -unsaturated δ -valero lactones

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¹H-NMR of **4c** (400 MHz, CDCl₃)

^{13}C -NMR of **4c** (100 MHz, CDCl_3)

^1H -NMR of **4d** (400 MHz, CDCl_3)

HW 575. p2

^{13}C -NMR (APT) of **4d** (100 MHz, CDCl_3)

HW 574.62

^1H -NMR of **4e** (400 MHz, CDCl_3)

^{13}C -NMR (APT) of **4e** (100 MHz, CDCl_3)

¹H-NMR of **6d** (400 MHz, CDCl₃)

875 MHz

^{13}C -NMR (APT) of **6d** (100 MHz, CDCl_3)

¹H-NMR of **6e** (400 MHz, CDCl₃)

^{13}C -NMR (APT) of **6e** (100 MHz, CDCl_3)

HW 510.51

$^1\text{H-NMR}$ of **7c** (400 MHz, CDCl_3)

^{13}C -NMR (APT) of **7c** (100 MHz, CDCl_3)

1H-NMR of **7d** (500 MHz, CDCl₃)

^{13}C -NMR (APT) of **7d** (125 MHz, CDCl_3)

HW580-noe1_29May2002

Archive directory: /export/home/vnmr1/vnmrSYS/data
Sample directory: HW580-noe1_29May2002

Pulse Sequence: s2pul
Solvent: CDCl₃
Temp: 27.0 C / 300.1 K
File: PROTON
INOVA-600 "eden"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.888 sec
Width 6000.6 Hz
8 repetitions
OBSERVE H1, 599.8312089 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 23 sec

1H-NMR of **7e** (600 MHz, CDCl₃)

^{13}C -NMR of **7e** (125 MHz, CDCl_3)

^{13}C -NMR of **8c** (125 MHz, CDCl_3)

Spectroscopical data for ketones 4:

(R)-2-Allyloxy-1,2-bis-(3-methoxy-phenyl)-ethanone (4c). MS (EI): m/z 312 (M^+ , <5), 177 (70), 149 (40), 135 (70), 121 (100), 107 (20), 77 (40). IR (film): 2960 s, 2839 m, 1694 s, 1607 s, 1489 s, 1262 s, 1039 m, 784 s, 696 s cm^{-1} . $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 7.51 (m, 1H, Ph), 7.44 (m, 1H, Ph), 7.22-7.14 (2H, Ph), 6.98-6.92 (3H, Ph), 6.74 (m, 1H, Ph), 5.88 (dddd, 1H, $J = 17.1, 10.3, 5.8, 5.8$, $-\text{CH}=\text{CH}_2$), 5.56 (s, 1H, $-\text{CHO}$), 5.23 (dddd, 1H, $J = 17.1, 1.8, 1.8, 1.8$, $-\text{CH}=\text{CH}_2$), 5.15 (dddd, 1H, $J = 10.3, 1.8, 1.8, 1.8$, $-\text{CH}=\text{CH}_2$), 4.03 (ddd, 2H, $J = 5.8, 1.8, 1.8$, $-\text{CHHO}-$), 3.71 (3H, $-\text{OCH}_3$), 3.69 (3H, $-\text{OCH}_3$). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ 196.8 (0), 159.9 (0), 159.5 (0), 137.7 (0), 136.2 (0), 134.0 (1), 129.8 (1), 129.4 (1), 121.6 (1), 119.9 (1), 119.8 (1), 118.1 (2), 114.1 (1), 113.2 (1), 112.7 (1), 83.6 (1), 70.5 (2), 55.3 (3), 55.2 (3). $[\alpha]_{\text{D}}^{22} = -37.0$ ($c = 1.04$, CH_2Cl_2).

(R)-2-Allyloxy-1,2-bis-(2-chlorophenyl)-ethanone (4d). MS (EI): m/z 320/322 (M^+ , 20%/12%), 263 (100). IR (film): 3070 (m), 2922 (m), 1716 (s), 1590 (m), 1471 (m), 1435 (m), 762 (s) cm^{-1} . $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 7.50 (dd, 1H, $J = 7.5, 2.0$, Ar), 7.35 – 7.10 (7H, Ar), 6.12 (s, 1H, $\text{CHOCH}_2\text{CH}=\text{CH}_2$), 5.92 (dddd, 1H, $J = 17.1, 10.3, 5.8, 5.8$, $\text{CHOCH}_2\text{CH}=\text{CH}_2$), 5.26 (dm, 1H, $J = 17.1$, $=\text{CH}_2$), 5.20 (dm, 1H, $J = 10.3$, $=\text{CH}_2$), 4.15 – 4.05 (2H, OCH_2). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ 199.2 (0), 137.7 (0), 134.3 (0), 133.8 (1), 133.4 (0), 131.5 (1), 131.0 (0), 130.0 (1), 130.0 (1), 129.5 (1), 129.5 (1), 128.9 (1), 127.3 (1), 126.5 (1), 118.3 (2), 81.2 (1), 70.8 (2). $[\alpha]_{\text{D}}^{22} = -62.0$ ($c = 0.80$, CH_2Cl_2).

(R)-2-Allyloxy-1,2-bis-(4-bromophenyl)-ethanone (4e). MS (EI): m/z 409/410/411 (5%, M^+ , 1:2:1 isotope pattern), 227 (100). IR (film): 3087 (m), 2961 (m), 2862 (m), 1699 (s), 1683 (s), 1585 (s), 1108 (s), 801 (s). $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 7.84 (d, 2H, $J = 8.5$, Ar), 7.52 (d,

2H, $J = 8.5$, Ar), 7.45 (d, 2H, $J = 8.5$, Ar), 7.30 (d, 2H, $J = 8.5$, Ar), 5.90 (dddd, 1H, $J = 17.3$, 10.5, 5.8, 5.8, $\text{OCH}_2\text{CH=}$), 5.48 (s, 1H, CHOCH_2), 5.27 (dddd, 1H, $J = 17.3$, 1.7, 1.5, 1.5, $=\text{CH}_2$), 5.22 (dddd, 1H, $J = 10.5$, 1.5, 1.5, 1.5, 1.5, $=\text{CH}_2$), 4.09 (ddm, 1H, $J = 12.8$, 5.8, OCHHCH=), 4.05 (ddm, 1H, $J = 12.8$, 5.8, OCHHCH=). ^{13}C -NMR (100 MHz, CDCl_3): δ 196.1 (0), 135.0 (0), 133.5 (1), 133.2 (0), 132.0 (1), 131.8 (1), 130.7 (1), 128.7 (1), 128.7 (0), 122.7 (0), 118.5 (2), 83.8 (1), 70.8 (2). $[\alpha]_{\text{D}}^{20} = +1.5$ ($c = 1.35$, CH_2Cl_2).

Spectroscopical data for dienes 6:

(1R, 2S)-1-Allyloxy-1,2-bis-(3-methoxy-phenyl)-but-3-en-2-ol (6c). Anal. calcd. for $\text{C}_{21}\text{H}_{24}\text{O}_4$: C, 74.09 %; H, 7.11 %. Found: C, 74.20 %; H, 7.15 %. MS (EI): m/z 341 ($\text{M}^+ + 1$, <5), 282 (10), 177 (90), 149 (40), 135 (80), 121 (100), 77 (15). IR (film): 3498 (bm), 2956 (m), 2835 (m), 1601 (s), 1489 (s), 1258 (s), 1047 (s), 771 (s) cm^{-1} . ^1H -NMR (400 MHz, CDCl_3): δ 7.15-7.08 (2H, Ph), 6.90 (s, 1H, Ph), 6.85 (s, 1H, Ph), 6.76-6.67 (3H, Ph), 6.61 (s, 1H, Ph), 6.53 (dd, 1H, $J = 17.5$, 10.8, $-\text{CH}=\text{CH}_2$), 5.80 (dddd, 1H, $J = 17.3$, 10.5, 6.0, 5.0, $-\text{CH}=\text{CH}_2$), 5.37 (dm, 1H, $J = 17.3$, $=\text{CH}_2$), 5.25 (dm, 1H, $J = 10.8$, $=\text{CH}_2$), 5.17 (dm, 1H, $J = 17.3$, $=\text{CH}_2$), 5.12 (dm, 1H, $J = 10.5$, $=\text{CH}_2$), 4.50 (s, 1H, $-\text{CHO}-$), 3.96 (ddm, 1H, $J = 13.0$, 5.0, $-\text{OCHH}-$), 3.74 (ddm, 1H, $J = 13.0$, 6.0, $-\text{OCHH}-$), 3.68 (3H, $-\text{OCH}_3$), 3.66 (3H, $-\text{OCH}_3$), 2.68 (bs, 1H, $-\text{OH}$). ^{13}C -NMR (100 MHz, CDCl_3): δ 159.0 (0), 158.9 (0), 144.4 (0), 141.3 (1), 138.3 (0), 134.3 (1), 128.4 (1), 128.4 (1), 121.2 (1), 118.8 (1), 117.0 (2), 114.3 (2), 113.9 (1), 113.7 (1), 112.6 (1), 111.9 (1), 86.7 (1), 78.4 (0), 70.0 (2), 55.1 (3), 55.1 (3). $[\alpha]_{\text{D}}^{22} = 7.4$ ($c = 1.3$, CH_2Cl_2).

(1R, 2S)-1-Allyloxy-1,2-bis-(2-chloro-phenyl)-but-3-en-2-ol (6d). MS (EI): m/z 307/309/311 (M^+ -Allyl, 30%, 10:6:1 isotope pattern), 139/141 (100, 3:1 isotope pattern). IR (film): 3445 (s), 2930 (m), 1471 (m), 1439 (m), 1073 (s), 1038 (s), 754 (s) ^1H -NMR (400

MHz, CDCl₃): δ 7.68 (d, 1H, J = 7.5, Ar), 7.37 (dd, 1H, J = 7.8, 1.6, Ar), 7.20 (dd, 1H, J = 8.0, 1.2, Ar), 7.17-6.93 (6H, Ar, -CH=), 5.84 (dddd, 1H, J = 17.3, 10.5, 6.3, 5.2, -CH₂CH=), 5.67 (s, 1H, -CHAr), 5.35 (dd, 1H, J = 17.3, 1.0, -CH=CH₂), 5.27 (dd, 1H, J = 10.8, 1.0, -CH=CH₂), 5.20 (dm, 1H, J = 17.3, -CH₂CH=CH₂), 5.15 (dm, 1H, J = 10.5, -CH₂CH=CH₂), 3.93 (dd, 1H, J = 12.8, 5.3, -OCHH-), 3.81 (dd, 1H, J = 12.8, 6.3, -OCHH-), 3.25 (bs, 1H, HO-). ¹³C-NMR (100 MHz, CDCl₃): δ 142.3 (1), 139.8 (0), 135.0 (0), 134.9 (0), 134.0 (1), 131.7 (0), 130.9 (1), 130.4 (1), 129.0 (1), 128.7 (1), 128.7 (1), 128.4 (1), 126.0 (1), 125.9 (1), 117.7 (2), 115.4 (2), 78.9 (0), 78.3 (1), 70.2 (2). $[\alpha]_D^{24}$ = 34.8 (c = 0.85, CH₂Cl₂).

(1R, 2S)-1-Allyloxy-1,2-bis-(4-bromo-phenyl)-but-3-en-2-ol (6e). MS (EI): m/z 397/395/393 (M⁺-C₂H₃O, 50%, 1:2:1 isotope pattern), 227/225 (100, 1:1 isotope pattern). IR (film): 3445 (s), 2964 (m), 1487 (s), 1074 (s), 1011 (s). ¹H-NMR (400 MHz, CDCl₃): δ 7.31 (d, 2H, J = 8.5, Ar), 7.30 (d, 2H, J = 8.5, Ar), 7.12 (d, 2H, J = 8.5, Ar), 6.92 (d, 2H, J = 8.5, Ar), 6.44 (dd, 1H, J = 17.3, 10.8, -CH=CH₂), 5.75 (dddd, 1H, J = 17.1, 10.8, 6.3, 5.0, -CH₂CH=), 5.32 (dd, 1H, J = 17.3, 1.0, -CH=CH₂), 5.25 (dd, 1H, J = 10.8, 1.0, -CH=CH₂), 5.13 (dm, 1H, J = 17.3, -CH₂CH=CH₂), 5.12 (dm, 1H, J = 10.8, -CH₂CH=CH₂), 4.42 (s, 1H, -CHAr), 3.90 (dddd, 1H, J = 12.8, 5.0, 1.5, 1.5, -OCHH-), 3.68 (ddm, 1H, J = 12.8, 6.3, -OCHH-), 2.75 (bs, 1H, HO-). ¹³C-NMR (100 MHz, CDCl₃): δ 141.5 (0), 140.8 (1), 135.5 (0), 133.9 (1), 130.7 (1), 130.7 (1), 130.3 (1), 128.0 (1), 122.0 (0), 121.0 (0), 117.5 (2), 115.2 (2), 85.8 (1), 78.1 (0), 70.1 (2). $[\alpha]_D^{24}$ = 9.6 (c = 1.45, CH₂Cl₂).

Spectroscopical data for dihydropyrans 7:

(2R,3S)-2,3-Bis-(3-methoxy-phenyl)-3,6-dihydro-2H-pyran-3-ol (7c). MS (EI): m/z 313 ($M^+ + 1$, <5), 176 (95), 145 (100), 117 (20), 77 (10). IR (film): 3485 (bm), 2931 (m), 2834 (m), 1602 (s), 1489 (s), 1256 (s), 1045 (s), 774 (m) cm^{-1} . $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 7.19 (dd, 1H, $J = 8.0, 8.0$, Ar), 7.05 (dd, 1H, $J = 8.5, 8.0$, Ar), 6.78 (d, 1H, $J = 8.0$, Ar), 6.78 (d, 1H, $J = 8.5$, Ar), 6.73 (dd, 1H, $J = 8.5, 2.0$, Ar), 6.69 (s, 1H, Ar), 6.44 (d, 1H, $J = 8.0$, Ar), 6.38 (s, 1H, Ar), 6.13 (ddd, 1H, $J = 10.3, 3.5, 2.0$, $H4/H5$), 6.06 (ddd, 1H, $J = 10.3, 2.0, 2.0$, $H4/H5$), 4.63 (s, 1H, $H2$), 4.52 (ddd, 1H, $J = 16.8, 3.5, 2.0$, $H6$), 4.43 (dm, 1H, $J = 16.8$, $H6$), 3.67 (3H, $-\text{OCH}_3$), 3.60 (3H, $-\text{OCH}_3$), 2.39 (bs, 1H, $-\text{OH}$). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ 159.3 (0), 158.5 (0), 143.9 (0), 137.8 (0), 132.0 (1), 128.9 (1), 128.2 (1), 128.2 (1), 119.9 (1), 118.5 (1), 113.7 (1), 113.0 (1), 112.5 (1), 111.7 (1), 85.1 (1), 72.0 (0), 66.7 (2), 55.2 (3), 54.9 (3). $[\alpha]_{\text{D}}^{24} = +7.5$ ($c = 1.20$, CH_2Cl_2).

(2R,3S)-2,3-Bis-(2-chloro-phenyl)-3,6-dihydro-2H-pyran-3-ol (7d). MS (EI): m/z 303/305/307 ($M^+ - \text{OH}$, 60%, 10:6:1 isotope pattern), 145 (100). IR (film): 3468 (s), 2928 (s), 1471 (s), 1435 (s), 1120 (s), 751 (s) cm^{-1} . $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 7.73 (d, $J = 7.8$, Ar), 7.30–7.24 (2H, Ar), 7.21–7.11 (3H, Ar), 7.07–7.00 (2H, Ar), 6.20 (d, 1H, $J = 10.0$, $H4/5$), 6.08 (ddd, 1H, $J = 10.0, 3.2, 2.0$, $H4/5$), 5.68 (s, 1H, $H2$), 4.55 (dm, 1H, $J = 17.0$, $H6$), 4.50 (ddd, 1H, $J = 17.0, 3.5, 1.7$, $H6$), 2.56 (s, 1H, OH). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ 138.0 (0), 134.6 (0), 133.7 (0), 132.4 (1), 132.3 (0), 130.8 (1), 130.4 (1), 129.0 (1), 128.9 (1), 128.7 (1), 128.5 (1), 126.8 (1), 126.2 (1), 125.8 (1), 76.5 (1), 71.2 (0), 66.7 (2). $[\alpha]_{\text{D}}^{20} = +49.0$ ($c = 0.60$, CH_2Cl_2).

(2*R*,3*S*)-2,3-Bis-(4-bromo-phenyl)-3,6-dihydro-2*H*-pyran-3-ol (7e). MS (FAB): m/z 391/393/395 (M^+ -OH, 1:2:1 isotope pattern), 224/226 (1:1 isotope pattern), 183/185 (1:1 isotope pattern). IR (film): 3475 (m), 2931 (m), 1486 (s), 1122 (m), 1072 (s), 823 (s), 791 (s), 737 (s) cm^{-1} . ^1H -NMR (400 MHz, CDCl_3): δ 7.37 (d, 2H, $J = 8.5$, Ar-C2, meta), 7.27 (d, 2H, $J = 8.5$, Ar-C3, meta), 7.00 (d, 2H, $J = 8.5$, Ar-C2, ortho), 6.69 (d, 2H, $J = 8.5$, Ar-C3, ortho), 6.15 (ddd, 1H, $J = 10.3, 3.5, 1.8$, H4), 6.02 (ddd, 1H, $J = 10.3, 1.8, 1.8$, H5), 4.51 (ddd, 1H, $J = 17.0, 3.5, 1.8$, H6), 4.51 (s, 1H, H2), 4.42 (ddd, 1H, $J = 17.0, 1.8, 1.8$, H6), 2.36 (s, br., 1H, OH). ^{13}C -NMR (100 MHz, CDCl_3): δ 140.8 (0, C-Br, Ar-C2), 135.1 (0, C-Br, Ar-C3), 131.6 (1, C5), 131.0 (1, Ar-C2-meta), 130.3 (1, Ar-C3-meta), 129.3 (1, Ar-C3-ortho), 128.9 (1, C4), 127.9 (1, Ar-C2-ortho), 121.7 (0, ipso-C-Ar-C3), 121.4 (0, ipso-C-Ar-C2), 84.6 (1, C2), 71.6 (0, C3), 66.8 (2, C6). $[\alpha]_{\text{D}}^{20} = +94.4$ ($c = 0.70$, CH_2Cl_2).