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ENANTIOSELECTIVE SYNTHESIS OF MONO- AND DISUBSTITUTED 3,6-DIHYDRO-2*H*-PYRANS AND 5,6-DIHYDRO-PYRAN-2-ONES

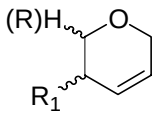
Irene Izzo,* Pasquale Del Gaudio, Carmela Della Monica, Maria Squitieri, and Francesco De Riccardis*

Department of Chemistry, University of Salerno, Via S. Allende –84081– Baronissi, (SA), Italy

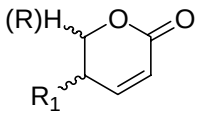
Abstract- An enantioselective synthesis of mono- and disubstituted 3,6-dihydro-2*H*-pyrans and 5,6-dihydropyran-2-ones was achieved *via* ring-closing olefin metathesis, employing Grubb's catalyst, and starting from ready available chiral building blocks.

Dihydro-2*H*-pyran and dihydropyran-2-one subunits are present in many biologically active natural products showing potent cytotoxic, antiviral, thrombopoietic activities. Some examples are: elactocin,[1] cytostatin,[2] leptomycins,[3] nafuredin,[4] pironetin,[5] and leustroducsins.[6] In addition these compounds could be useful building blocks for the synthesis of biologically active oxygen heterocycles *via* functionalization of double bond.[7] Recently many efforts have been directed towards stereoselective synthesis of 2,6-difunctionalised di- and tetrahydropyrans[8] and of α-hydroxyalkyldihydropyrans which have been used as key intermediates in the synthesis of higher-order sugars such as (+)-3-deoxy-D-*glycero*-D-*galacto*-2-nonulosonic acid (KDN), possessing oncofoetal antigen properties,[9] and 2-deoxy-β-KDO, the most potent inhibitor of the enzyme CMP-KDO synthetase.[10]

To date, however, there has been no demonstration of a general enantioselective method for the synthesis of stereochemically defined mono- and disubstituted 3,6-dihydro-2*H*-pyrans (**1**) and 5,6-dihydropyran-2-ones (**2**).[11]



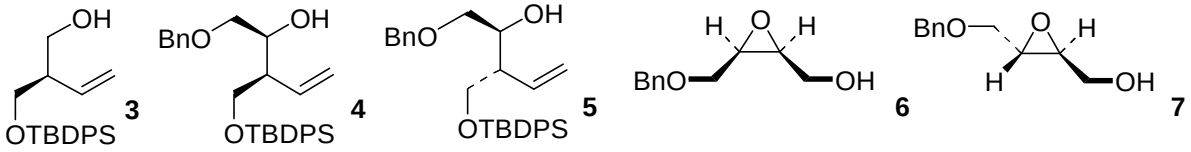
1



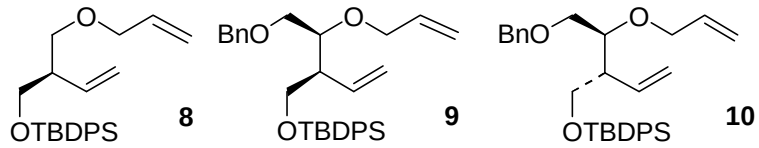
2

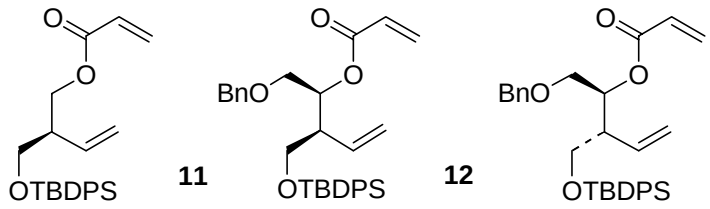
With the aim of finding the most convenient and useful access to the above reported substructures, we explored the potential of the ring-closing olefin metathesis on readily available derivatives of the

stereochemically pure starting materials (**3-5**). These valuable intermediates can be easily synthesized, in both the enantiomeric forms, through stereospecific oxirane ring opening[12] and straightforward functional groups transformation,[13] starting from *cis*- and *trans*-4-benzyloxy-2,3-epoxybutan-1-ols (**6** and **7**).[14]

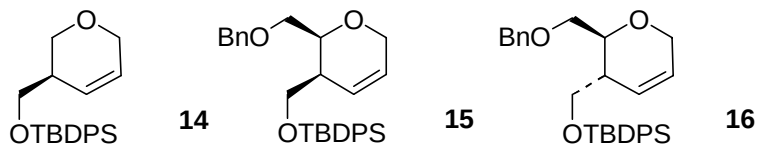


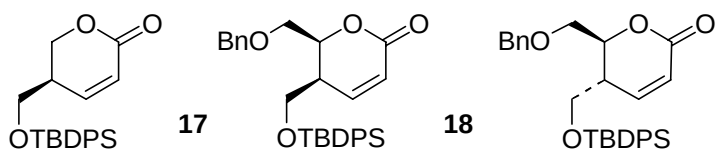
Treatment of derivatives (**3-5**) with allyl bromide[15] and acryloyl chloride [16] gave the allyl ethers (**8-10**) and the acryloyl esters (**11-13**) in excellent yields.





Allyl ethers (**8-10**) and acrylates (**11-13**) were exposed to Grubb's catalyst,[17] bis-(tricyclohexylphosphine)benzylidene ruthenium(IV) dichloride, $RuCl_2(CHC_6H_5)[P(C_6H_{11})_3]_2$, affording the expected mono- and disubstituted 3,6-dihydro-2*H*-pyrans (**14-16**) and 5,6-dihydropyran-2-ones (**17-19**) in high yields. No improvements in reaction times were observed adding to the reaction mixture titanium isopropoxide (0.3-3 equiv.), even though has been reported that its presence increases yields of α,β-unsatured γ- and δ-lactones and reduces the reaction times.[15,18]





In conclusion we have developed an efficient and general method for the enantioselective synthesis of orthogonally protected optically active mono- and disubstituted 3,6-dihydro-2*H*-pyrans and 5,6-dihydropyran-2-ones.

EXPERIMENTAL

Compounds (8-10). General procedure.

To a solution of alcohol (**4**) (0.143 g, 0.310 mmol) in CH_2Cl_2 (2 mL) at 0°C, Ag_2O (0.159 g, 0.931 mmol) was added. The mixture was stirred for 15 min at 0°C then allyl bromide (0.160 mL, 1.86 mmol). The resulting mixture was stirred at 0°C for 0.5 h and at rt for 18 h. Centrifugation afforded an organic phase which was concentraded in vacuo and purified by flash chromatography (silica gel, 10-30 % ethyl ether in petroleum ether) to give **9** as a colorless oil (0.155 g).

Compound (8): oil, 96% yield; $[\alpha]_D$ –4.8° (*c* = 1.0, $CHCl_3$); ^{1}H-NMR (400.13 MHz, $CDCl_3$) δ 1.06 (9 H, s, (C*H*$_3$)$_3$C-Si-), 2.56 (1 H, m, H-2), 3.52 (1 H, dd, *J* = 9.2, 3.0 Hz, H-1), 3.62 (1 H, dd, *J* = 9.2, 2.8 Hz, H'-1), 3.74 (2 H, m, -C*H*$_2$-OTBDPS), 3.99 (2 H, m, –OC*H*$_2$–CH=CH$_2$), 5.01-5.11 (3 H, d, H-4, H'-4 and –CH=C*H*H, overlapped), 5.18 (1 H, d, *J* = 17.2 Hz, –CH=CH*H*), 5.76 (1 H, m, H-3), 5.83 (1 H, m, –C*H*=CH$_2$), 7.35-7.42 (6 H, m, -C$_6$*H*$_5$), 7.67 (4 H, m, -C$_6$*H*$_5$); ^{13}C-NMR (100.06 MHz, $CDCl_3$), δ 19.9, 27.4 (× 3), 46.8, 64.6, 70.9, 72.6, 117.1, 117.2, 128.2 (× 4**)**, 130.1 (× 2), 134.3 (× 2), 135.6, 136.2 (× 4), 137.9. EIMS *m/z* 380; Anal. Calcd for $C_{24}H_{32}O_2Si$: C, 75.74; H, 8.47; Si, 7.38. Found: C, 75.89; H, 8.39; Si, 7.36.

Compound (9): oil, 95% yield; $[\alpha]_D$ –9.1° (*c* = 1.0, $CHCl_3$); ^{1}H-NMR (400.13 MHz, $CDCl_3$) δ 1.07 (9 H, s, (C*H*$_3$)$_3$C-Si-), 2.51 (1 H, m, H-3), 3.51 (1 H, dd, *J* = 10.5, 6.0 Hz, H-1), 3.67 (1 H, dd, *J* = 10.5, 5.2 Hz, H'-1), 3.75 (1 H, dd, *J* = 9.8, 4.5 Hz –C*H*HOTBDPS), 3.76 (1 H, m, H-2), 3.94 (1 H, dd, *J* = 9.8, 4.9 Hz -CH*H*-OTBDPS), 4.05 (1 H, dd, *J* = 12.6, 5.6 Hz, –OC*H*H-CH=CH$_2$), 4.25 (1 H, dd, *J* = 12.6, 5.5 Hz, -OCH*H*-CH=CH$_2$), 4.53 (2 H, s, OC*H*$_2$Ph), 5.11 (3 H, d, H-5, H'-5 and –CH=C*H*H, overlapped), 5.24 (1 H, d, *J* = 17.2 Hz, –CH=CH*H*), 5.90 (2 H, m, H-4 and –C*H*=CH$_2$), 7.34-7.41 (11 H, m, -C$_6$*H*$_5$), 7.69 (4 H, m, -C$_6$*H*$_5$); ^{13}C-NMR (100.06 MHz, $CDCl_3$), δ 19.3, 26.9 (× 3), 48.6, 64.0, 71.6 (× 2), 73.2, 77.7, 116.3, 117.1, 127.5 (× 7), 128.3 **(**× 2), 129.5 (× 2), 133.6, 133.7, 135.3, 135.6 (× 4), 137.0, 138.5. EIMS *m/z* 500; Anal. Calcd for $C_{32}H_{40}O_3Si$: C, 76.75; H, 8.05; Si, 5.61. Found: C, 76.72; H, 8.00; Si, 5.64.

Compound (10): oil, 78% yield; $[\alpha]_D$ –11.1° (*c* = 1.0, $CHCl_3$); ^{1}H-NMR (400.13 MHz, $CDCl_3$) δ 1.07 (9 H, s, (C*H*$_3$)$_3$C-Si), 2.51 (1 H, m, H-3), 3.51 (1 H, dd, *J* = 9.8, 5.0 Hz, H-1), 3.58 (1 H, dd, *J* = 10.0, 6.6 Hz –C*H*HOTBDPS), 3.61 (1 H, dd, *J* = 10.0, 5.7 Hz -CH*H*-OTBDPS), 3.84 (1 H, dd, *J* = 9.8, 8.7 Hz, H'-1), 3.98 (1 H, ddd, *J* = 8.7, 5.0, 3.3 Hz, H-2), 4.08 (1 H, dd, *J* = 12.8, 5.4 Hz, –OC*H*H-CH=CH$_2$), 4.25 (1 H, dd, *J* = 12.8, 5.5 Hz, -OCH*H*-CH=CH$_2$), 4.50 (1 H, d, *J* = 12.1 Hz, –OC*H*HPh), 4.56 (1 H, d, *J* = 12.1 Hz, –OCH*H*Ph), 5.02 (1 H, dd, *J* = 17.2, 1.9 Hz, H-5), 5.07 (1 H, dd, *J* = 10.5, 1.8 Hz, H'-5), 5.12 (1 H, d, *J* = 10.3 Hz, –OCH$_2$CH=C*H*H), 5.24 (1 H, d, *J* = 15.8 Hz, –OCH$_2$CH=CH*H*), 5.74 (1 H, m, H-4), 5.90 (1 H, m, –OCH$_2$C*H*=CH$_2$), 7.34-7.41 (11 H, m, -C$_6$*H*$_5$), 7.68 (4 H, m, -C$_6$*H*$_5$); ^{13}C-NMR (100.06 MHz, $CDCl_3$), δ 19.3, 26.9 (× 3), 49.0, 64.0, 72.1, 72.3, 73.2, 76.0, 116.1, 118.0, 127.5, 127.6 (× 6), 128.3 (× 2), 129.6 (×

2), 133.7 (× 2), 135.1, 135.6 (× 5), 138.5. EIMS *m/z* 500; Anal. Calcd for $C_{32}H_{40}O_3Si$: C, 76.75; H, 8.05; Si, 5.61. Found: C, 76.69; H, 8.01; Si, 5.61.

Compounds (11-13). General procedure.

To a solution of **4** (0.080 g, 0.174 mmol) in CH_2Cl_2 (2 mL) at –78°C, DMAP (0.004 g, 0.034 mmol), (*i*-Pr)$_2$NEt (0.210 mL, 1.21 mmol) and acryloyl chloride (0.056 mL, 0.694 mmol) were added. The resulting mixture was stirred at –20° for 18 h, quenched with HCl (2 mL, 2 M), washed with a saturated solution of $NaHCO_3$. The organic phase was dried (Na_2SO_4), filtered and concentrated in vacuo. The residue was purified by flash chromatography (silica gel 10-30% ethyl ether in petroleum ether) to give **12** as a colorless oil (0.092 g)

Compound (11): oil, 96% yield; $[\alpha]_D$ –4.1° (*c* = 1.0, $CHCl_3$); ^{1}H-NMR (400.13 MHz, $CDCl_3$) δ 1.07 (9 H, s, (C*H*$_3$)$_3$C-Si-), 2.66 (1 H, m, H-2), 3.73 (2 H, m, –C*H*$_2$OTBDPS), 4.34 (2 H, m, H-1, H'-1), 5.13 (1 H, d, *J* = 11.8 Hz, H-4), 5.14 (1 H, d, *J* = 16.0 Hz, H'-4), 5.79 (1 H, m, H-3), 5.80 (1 H, d, *J* = 10.4 Hz, –CH=C*H*H), 6.09 (1 H, dd, *J* = 17.2, 10.4 Hz, –C*H*=CH$_2$), 6.36 (1 H, d, *J* = 17.2 Hz, –CH=CH*H*), 7.36-7.43 (6 H, m, -C$_6$*H*$_5$), 7.67 (4 H, m, -C$_6$*H*$_5$); ^{13}C-NMR (100.06 MHz, $CDCl_3$), δ 19.3, 26.8 (× 3), 45.1, 63.7, 64.2, 117.4, 127.7 (× 4**)**, 128.5, 129.6 (× 2), 130.5, 133.5 (× 2), 135.6, (× 4), 135.8, 166.0. EIMS *m/z* 394; Anal. Calcd for $C_{24}H_{30}O_3Si$: C, 73.05; H, 7.66; Si, 7.12. Found: C, 73.00; H, 7.69; Si, 7.10.

Compound (12): oil, 96% yield; $[\alpha]_D$ –2.0° (*c* = 1.0, $CHCl_3$); ^{1}H-NMR (400.13 MHz, $CDCl_3$) δ 1.02 (9 H, s, (C*H*$_3$)$_3$C-Si-), 2.74 (1 H, m, H-3), 3.63 (1 H, dd, *J* = 10.9, 5.4 Hz, H-1), 3.67 (1 H, dd, *J* = 9.9, 4.2 Hz, –C*H*HOTBDPS), 3.70 (1 H, dd, *J* = 10.9, 2.9 Hz, H'-1), 3.76 (1 H, dd, *J* = 9.9, 4.9 Hz, –CH*H*OTBDPS), 4.43 (1 H, d, *J* = 12.0 Hz, –OC*H*HPh), 4.55 (1 H, d, *J* = 12.0 Hz, –OCH*H*Ph), 5.14 (1 H, d, *J* = 10.8 Hz, H-5), 5.15 (1 H, d, *J* = 16.8 Hz, H'-5), 5.34 (1 H, m, H-2), 5.81 (1 H, d, *J* = 10.7 Hz, –CH=C*H*H), 5.86 (1 H, m, H-3), 6.11 (1 H, dd, *J* = 17.3, 10.7 Hz, –C*H*=CH$_2$), 6.37 (1 H, d, *J* = 17.3 Hz, –CH=CH*H*), 7.33-7.43 (11 H, m, -C$_6$*H*$_5$), 7.62 (4 H, m, -C$_6$*H*$_5$); ^{13}C-NMR (100.06 MHz, $CDCl_3$), δ 19.2, 26.7 (× 3), 47.0, 63.6, 69.6, 72.1, 73.0, 118.2, 127.6 (× 7**)**, 128.3 (× 2), 128.6, 129.5 (× 2), 130.7, 133.3 (× 2), 134.0, 135.6, (× 4), 137.1, 166.1. EIMS *m/z* 514; Anal. Calcd for $C_{32}H_{38}O_4Si$: C, 74.67; H, 7.44; Si, 5.46. Found: C, 74.60; H, 7.37; Si, 5.45.

Compound (13): oil, 84% yield; $[\alpha]_D$ –7.7° (*c* = 1.0, $CHCl_3$); ^{1}H-NMR (400.13 MHz, $CDCl_3$) δ 1.07 (9 H, s, (C*H*$_3$)$_3$C-Si-), 2.71 (1 H, m, H-3), 3.60 (2 H, m, H-1 and H'-1), 3.73 (2 H, m, –C*H*$_2$OTBDPS), 4.50 (1 H, d, *J* = 12.0 Hz, –OC*H*HPh), 4.55 (1 H, d, *J* = 12.0 Hz, –OCH*H*Ph), 5.12 (1 H, d, *J* = 17.2 Hz, H-5), 5.14 (1 H, d, *J* = 10.3 Hz, H'-5), 5.56 (1 H, m, H-2), 5.76 (1 H, m, H-4), 5.83 (1 H, d, *J* = 10.0 Hz, –CH=C*H*H), 6.13 (1 H, dd, *J* = 17.2, 10.0 Hz, –C*H*=CH$_2$), 6.40 (1 H, d, *J* = 17.2 Hz, –CH=CH*H*), 7.36-7.43 (11 H, m, -C$_6$*H*$_5$), 7.65 (4 H, m, -C$_6$*H*$_5$); ^{13}C-NMR (100.06 MHz, $CDCl_3$), δ 19.2, 26.8 (× 3), 47.3, 63.7, 69.4, 71.2, 72.9, 118.8, 127.7 (× 7**)**, 128.4 (× 2), 128.6, 129.6 (× 2), 130.7, 133.3, 133.4, 134.6,

135.6, (× 4), 138.1, 165.5. EIMS *m/z* 514; Anal. Calcd for $C_{32}H_{38}O_4Si$: C, 74.67; H, 7.44; Si, 5.46. Found: C, 74.65; H, 7.41; Si, 5.45.

Compounds (14-16). General procedure.

To a solution of the allyl ether (**9**) (0.030 g, 0.060 mmol) in degassed CH_2Cl_2 (10 mL), Grubb's catalyst (0.010 g, 0.012 mmol) was added. The resulting mixture was stirred at reflux for 24 h. The mixture was then cooled to rt, concentrated in vacuo. The residue was purified by flash chromatography (silica gel, 50-100% CH_2Cl_2 in petroleum ether) to give **15** as a colorless oil (0.028 g).

Compound (14): oil, 98% yield; $[\alpha]_D$ +49.9° (*c* = 0.8, $CHCl_3$); ^{1}H-NMR (400.13 MHz, $CDCl_3$) δ 1.06 (9 H, s, (CH_3)$_3$C-Si-), 2.44 (1 H, m, H-3), 3.63 (2 H, m, -CH_2-OTBDPS), 3.77 (1 H, dd, *J* = 11.1, 5.8 Hz, H-2), 3.88 (1 H, dd, *J* = 11.1, 5.7 Hz, H'-2), 4.09 (2 H, m, H-6, H'-6), 5.69 (1 H, br d, *J* = 10.7 Hz, H-4 or H-5), 5.77 (1 H, d, *J* = 10.7 Hz, H-5 or H-4), 7.30-7.44 (6 H, m, -C_6H_5), 7.66 (4 H, m, -C_6H_5); ^{13}C-NMR (100.06 MHz, $CDCl_3$), δ 19.2, 26.8 (× 3), 37.8, 64.7, 65.6, 66.3, 125.3, 127.6 (× 4), 127.8, 129.6 (× 2), 133.7 (× 2), 135.6 (× 4); EIMS *m/z* 352; Anal. Calcd for $C_{22}H_{28}O_3Si$: C, 74.95; H, 8.01; Si, 7.97. Found: C, 74.89; H, 8.00; Si, 7.94.

Compound (15): oil, 100% yield; $[\alpha]_D$ +86.7° (*c* = 1.0, $CHCl_3$); ^{1}H-NMR (400.13 MHz, $CDCl_3$) δ 1.03 (9 H, s, (CH_3)$_3$C-Si-), 2.28 (1 H, m, H-3), 3.51 (1 H, dd, *J* = 10.4, 4.9 Hz, -C*H*H-OTBDPS), 3.72 (2 H, m, -CH_2-OBn), 3.80 (1 H, dd, *J* = 10.4, 8.2 Hz, -CH*H*-OTBDPS), 3.91 (1 H, m, H-2), 4.23 (2 H, m, H-6, H'-6), 4.49 (1 H, d, *J* = 12.3 Hz, C*H*H-Ph), 4.65 (1 H, d, *J* = 12.3 Hz, CH*H*-Ph), 5.71 (2 H, m, H-4, H-5), 7.29-7.44 (9 H, m, -C_6H_5), 7.63 (6 H, m, -C_6H_5); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 19.0, 26.7 (× 3), 39.6, 62.7, 66.3, 71.6, 73.4, 75.5, 125.6, 127.7 (× 8), 128.3 (× 2), 129.6 (× 2), 133.4 (× 2), 135.5 (× 4), 138.3; EIMS *m/z* 472; Anal. Calcd for $C_{30}H_{36}O_3Si$: C, 76.23; H, 7.68; Si, 5.94. Found: C, 76.20; H, 7.69; Si, 5.87.

Compound (16): oil, 70% yield; $[\alpha]_D$ +26.0° (*c* = 1.0, $CHCl_3$); ^{1}H-NMR (400.13 MHz, $CDCl_3$) δ 1.04 (9 H, s, (CH_3)$_3$C-Si-), 2.41 (1 H, m, H-3), 3.54 (2 H, m, -CH_2-OTBDPS), 3.64 (2 H, m, -CH_2-OBn), 3.76 (1 H, m, H-2), 4.16 (1 H, br d, *J* = 17.3 Hz, H-6), 4.26 (1 H, br d, *J* = 17.3 Hz, H'-6), 4.56 (2 H, br s, -CH_2-Ph), 5.73 (1 H, br d, *J* = 9.7 Hz, -H-4), 5.83 (2 H, br d, *J* = 9.7 Hz, H-5), 7.30-7.43 (9 H, m, -C_6H_5), 7.66 (4 H, m, -C_6H_5); ^{13}C-NMR (100.06 MHz, $CDCl_3$) δ 19.3, 26.8 (× 3), 38.8, 64.7, 64.8, 71.2, 73.4, 74.8, 126.0, 127.1, 127.5, 127.7 (× 6), 128.3 (× 2), 129.7 (× 2), 133.4, (× 2), 135.6 (× 4), 138.2; EIMS *m/z* 472; Anal. Calcd for $C_{30}H_{36}O_3Si$: C, 76.23; H, 7.68; Si, 5.94. Found: C, 76.25; H, 7.65; Si, 5.87.

Compounds (17-19). General procedure.

To a solution of the acrylate (**12**) (0.041 g, 0.080 mmol) in degassed CH_2Cl_2 (17 mL), Grubb's catalyst (0.023 g, 0.028 mmol) was added. The resulting mixture was stirred at reflux for 48-76 h. The mixture was

then cooled to rt, concentrated in vacuo. The residue was purified by flash chromatography (silica gel, 90-100% of CH_2Cl_2 in petroleum ether) to give **18** as a colorless oil (0.039 g).

Compound (17): oil, 95% yield; $[\alpha]_D$ +11.5° (*c* = 1.0, $CHCl_3$); ^{1}H-NMR (400.13 MHz, $CDCl_3$) δ 1.02 (9 H, s, (C*H*$_3$)$_3$C-Si), 2.73 (1 H, m, H-5), 3.68 (2 H, m, -C*H*$_2$-OTBDPS), 4.42 (2 H, m, H-6, H'-6), 6.01 (1 H, d, *J* = 9.8 Hz, H-3), 6.77 (1 H, dd, *J* = 9.8, 3.7 Hz, H-4), 7.38-7.47 (6 H, m, -C$_6$*H*$_5$), 7.62 (4 H, m, -C$_6$*H*$_5$); ^{13}C-NMR (100.06 MHz, $CDCl_3$) δ 19.2, 26.7 (× 3), 36.9, 62.5, 68.3, 122.0, 127.8 (× 4), 130.0 (× 2), 132.7, 132.8, 135.5 (× 4), 146.7, 163.5; EIMS *m/z* 366; IR ($CHCl_3$): υ = 1720 cm^{-1} (C=O); Anal. Calcd for $C_{22}H_{26}O_3Si$: C, 76.09; H, 7.15; Si, 7.66. Found: C, 76.04; H, 7.17; Si, 7.67.

Compound (18): oil, 90% yield; $[\alpha]_D$ +94.3° (*c* = 1.0, $CHCl_3$); ^{1}H-NMR (400.13 MHz, $CDCl_3$) δ 1.02 (9 H, s, (C*H*$_3$)$_3$C-Si), 2.70 (1 H, m, H-5), 3.66 (4 H, overlapped, C*H*$_2$-OBn, and C*H*$_2$-OTBDPS), 4.43 (1 H, d, *J* = 11.8 Hz, -C*H*H-Ph), 4.52 (1 H, d, *J* = 11.8 Hz, -CH*H*-Ph), 4.72 (1 H, m, H-6), 6.05 (1 H, br d, *J* = 9.5 Hz, H-3), 6.87 (1 H, dd, *J* = 9.5, 5.9 Hz, H-4), 7.29-7.39 (11 H, m, -C$_6$H$_5$), 7.60 (4 H, m, -C$_6$H$_5$); ^{13}C-NMR (100.06 MHz, $CDCl_3$) δ 19.0, 26.7 (× 3), 38.2, 60.9, 69.1, 73.5, 77.8, 121.9, 127.8 (× 7), 128.4 (× 2), 129.9 (× 2), 132.7 (× 2), 135.4 (× 4), 137.5, 146.9, 163.5; EIMS *m/z* 486; IR ($CHCl_3$): υ = 1720 cm^{-1} (C=O); Anal. Calcd for $C_{30}H_{34}O_4Si$: C, 74.04; H, 7.04; Si, 5.77. Found: C, 74.02; H, 7.10; Si, 5.77.

Compound (19): oil, 100% yield; $[\alpha]_D$ +43.6° (*c* = 1.0, $CHCl_3$); ^{1}H-NMR (400.13 MHz, $CDCl_3$) δ 1.04 (9 H, s, (C*H*$_3$)$_3$C-Si-), 2.89 (1 H, m, H-5), 3.56 (1 H, dd, *J* = 10.9, 3.8 Hz, -C*H*H-OBn), 3.67 (1 H, dd, *J* = 10.3, 1.9 Hz, -C*H*H-OTBDPS), 3.68 (1 H, br d, *J* = 10.9, -CH*H*-OBn), 3.80 (1 H, dd, *J* = 10.3, 5.0 Hz, -CH*H*-OTBDPS), 4.46 (1 H, d, *J* = 12.0 Hz, -C*H*H-Ph), 4.54 (1 H, d, *J* = 12.0 Hz, -CH*H*-Ph), 4.65 (1 H, m, H-6), 6.03 (1 H, dd, *J* = 10.0, 2.1 Hz, H-3), 6.78 (1 H, dd, *J* = 10.0, 3.1 Hz, H-4), 7.26-7.43 (11 H, m, -C$_6$H$_5$), 7.60 (4 H, m, -C$_6$H$_5$); ^{13}C-NMR (100.06 MHz, $CDCl_3$) δ 19.2, 26.8 (× 3), 37.8, 62.8, 69.2, 73.5, 78.0, 121.8, 127.6, 127.9 (× 6), 128.4 (× 2), 130.0 (× 2), 132.7, 132.8, 135.5 (× 4), 137.6, 147.6, 163.3. EIMS *m/z* 486; IR ($CHCl_3$): υ = 1730 cm^{-1} (C=O); Anal. Calcd for $C_{30}H_{34}O_4Si$: C, 74.04; H, 7.04; Si, 5.77. Found: C, 74.04; H, 7.07; Si, 5.66.

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