SUPPORTING INFORMATION
Direct C-Allylation of Aryl-Alkyl/Glycosyl Carbinols: Facile Synthesis of C-Linked Carbo- β^2 -/ γ^2 -/ δ^2 -Amino acids (Caas)

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General Information: Varian Gemini 200, 400 and 500 MHz/Bruker 300 MHz spectrometers with 7-10 mM solutions in deuteriochloroform, tetramethylsilane as internal standard. *J* values are given in Hz. Optical rotations were measured with a JASCO DIP-300 instrument and $[\alpha]_D$ values are in units of 10^{-1} deg $\text{cm}^2 \text{g}^{-1}$ at 25 °C. IR spectra were taken with a Perkin-Elmer 1310 spectrometer. Mass spectra were recorded on CEC-21-11013 or Finnigan Mat 1210 double focusing mass spectrometers operating at a direct inlet system and FABMS was measured using VG AUTOSPEC mass spectrometers at 5 or 7k resolution using perfluorokerosene as an internal reference. The software ACD/Name Version 1.0, developed by M/s Advanced Chemistry Development Inc., Toronto, Canada, assisted nomenclature used in the experimental section. Column chromatography was performed on silica gel (60-120 mesh). Energy minimized structures were obtained from SYBYL 6.8 programme (W. F. van Gunstern, H. J. C. Bernden, *Angew. Chem. Int. Ed.* **1990**, 29, 992-1023) on Silicon Graphics Workstation.

Allyltrimethylsilane, carbinols **1** and **2** are commercially available. (Aldrich Chemical Company).

1-(4-Methoxyphenyl) ethanol (3):

To a stirred suspension of Mg (0.064 g, 2.94 mmol) in dry THF (5 mL), MeI (0.18 mL, 2.93 mmol) was added at reflux. After 1 h, a solution of anisaldehyde (0.20 g, 1.47 mmol) in dry THF (5 mL) was added at the same temperature and stirred for 3 h at room temperature. The reaction mixture was quenched with aq. NH_4Cl (10 mL) and extracted with EtOAc (2 x 10 mL). Organic layer was washed with water (2 x 10 mL), brine (10 mL), dried (Na_2SO_4), concentrated in *vacuo* and residue purified by column

chromatography (60-120 mesh, silica gel 0.9:9.1, EtOAc: hexane) to afford **3** (0.198 g) in 89% yield as colorless syrup. ^1H NMR (CDCl_3 , 300 MHz): δ 1.20 (d, 3H, $J = 7.3$ Hz, $-\text{CH}_3$), 3.78 (s, 3H, OCH_3), 4.90 (d, 1H, $J = 7.5$ Hz, H-1), 6.78 (d, 2H, $J = 8.3$ Hz, Ar-H), 7.05 (d, 2H, $J = 8.3$ Hz, Ar-H); EIMS (m/z , %): 152 (M^+ , 100), 107 (65); IR (Neat): 2945, 1675, 1520, 1430 cm^{-1} .

1-(4-Methoxyphenyl)-2-methylpropan-1-ol (4):

To a stirred suspension of Mg (0.48 g, 22.05 mmol) in dry THF (10 mL), 2-chloropropane (1.72 g, 22.05 mmol) was added at reflux and stirred for 1 h. A solution of anisaldehyde (1.00 g, 7.35 mmol) in dry THF (10 mL) was added at the same temperature and stirred for 3 h at room temperature. The reaction mixture was worked up as described for **3** and purified by column chromatography (1:9, EtOAc:hexane) to afford **4** (1.2 g) in 88% yield as syrup. ^1H NMR (CDCl_3 , 200 MHz): δ 0.73 (d, 3H, $J = 7.0$ Hz, $-\text{CH}_3$), 0.96 (d, 3H, $J = 7.0$ Hz, $-\text{CH}_3$), 1.75-1.90 (m, 1H, H-2), 3.75 (s, 3H, OCH_3), 4.42 (d, 1H, $J = 7.3$ Hz, H-1), 6.80 (d, 2H, $J = 8.8$ Hz, Ar-H), 7.15 (d, 2H, $J = 8.8$ Hz, Ar-H); EIMS (m/z , %): 180 (M) (45), 107 (95), 91 (90); IR (Neat): 2966, 2361, 1737, 1457, 1344, 1152 cm^{-1} .

1-(4-Methoxyphenyl)-3-methylbutan-2-ol (5):

To a stirred suspension of Mg (0.76 g, 34.88 mmol) in dry THF (15 mL), 4-bromoanisole (4.36 mL, 34.88 mmol) was added at reflux and stirred for 1 h. A solution of valeraldehyde (1.00 g, 11.62 mmol) in dry THF (10 mL) was added at the same temperature and stirred for 2 h at room temperature. The reaction mixture was worked up as described for **3** and purified by column chromatography (1.2:8.8, EtOAc: hexane) to furnish **5** (2.0 g) in 89% yield as yellow liquid. ^1H NMR (CDCl_3 , 300 MHz): δ 0.93 (dd, 6H, $J = 2.3, 6.0$ Hz, 2 x CH_3), 1.40-1.50 (m, 1H, H-3), 1.55-1.75 (m, 2H, H-2, H-2'), 3.79 (s, 3H, OCH_3), 4.64 (t, 1H, $J = 5.3$ Hz, H-1), 6.82 (d, 2H, $J = 8.3$ Hz, Ar-H), 7.22 (d, 2H, $J = 8.3$ Hz, Ar-H); EIMS (m/z , %): 194 (M^+ , 56), 107 (100); IR (Neat): 3380, 2953, 1610, 1511, 1246 cm^{-1} .

1-(4-Methoxyphenyl)-2-phenylethanol (6):

To a stirred suspension of Mg (0.22 g, 9.99 mmol) in dry THF (5 mL), 4-bromoanisole (1.25 mL, 9.99 mmol) was added at reflux and stirred for 1 h. A solution of Phenyl acetaldehyde (0.80 g, 6.66 mmol) in dry THF (10 mL) was added at the same

temperature and stirred for 3 h at room temperature. The reaction mixture was worked up as described for **3** and purified by column chromatography (0.8:9.2, EtOAc: hexane) to afford **6** (1.20 g) in 78% yield as colorless syrup: ^1H NMR (CDCl_3 , 200 MHz): δ 2.85 (bs, 1H, OH), 2.95 (d, 2H, $J = 6.4$ Hz, H-2, H-2'), 3.80 (s, 3H, OCH_3), 4.80 (t, 1H, $J = 6.4$, H-1), 6.85 (d, 2H, $J = 8.8$ Hz, Ar-H), 7.10-7.35 (m, 7H, Ar-H); EIMS (m/z , %): 228 (M) (44), 151 (69), 107 (100); IR (Neat): 2930, 1640, 1520, 1420, 1250, 1157 cm^{-1} . **(R)-(3aR,5R,6S,6aR)-Tetrahydro-6-methoxy-2,2-dimethylfuro[2,3-d][1,3]dioxol-5-yl](4-methoxyphenyl)methanol (9)** and **(S)-(3aR,5R,6S,6aR)-tetrahydro-6-methoxy-2,2-dimethylfuro[2,3-d][1,3]dioxol-5-yl](4-methoxyphenyl) methanol (7)** :

To a stirred suspension of Mg (1.07 g, 49.01 mmol) in dry THF (20 mL), 4-bromoanisole (6.15 mL, 49.01 mmol) was added at reflux and stirred for 1 h. A solution of *(3aR, 5S, 6S, 6aR)-tetrahydro-6-methoxy-2,2-dimethylfuro[2,3-d][1,3] dioxol-5-carbaldehyde* (5.0 g, 24.50 mmol) in dry THF (25 mL) was added at the same temperature and stirred for 4 h at room temperature. The reaction mixture was worked up as described for **3** and purified by column chromatography (1:3, EtOAc:hexane). First eluted was **9** (1.11 g) in 14.7% yield as yellow syrup, $[\alpha]_{\text{D}}^{28} = +54.24$ (c 1.00, CHCl_3); ^1H NMR (CDCl_3 , 200 MHz): δ 1.30 (s, 3H, CH_3), 1.50 (s, 3H, CH_3), 3.55 (s, 3H, OCH_3), 3.80 (s, 3H, OCH_3), 3.90 (d, 1H, $J = 2.9$ Hz, H-3), 4.50 (m, 2H, H-4, H-2), 5.00 (d, 1H, $J = 10.0$ Hz, H-5), 5.78 (d, 1H, $J = 3.7$ Hz, H-1), 6.85 (d, 2H, $J = 8.8$ Hz, Ar-H), 7.10 (d, 2H, $J = 8.8$ Hz, Ar-H); ^{13}C NMR (CDCl_3 , 300 MHz): δ 26.4, 55.3, 72.0, 82.4, 84.5, 105.5, 112.3, 115.7, 127.3, 128.0, 129.2, 132.8, 159.4; FABMS (m/z , %): 310 (M^+ , 35), 173 (66), 137 (23), 107 (100); IR (Neat): 3376, 2953, 1610, 1511, 1246 cm^{-1} .

Second eluted was **7** (6.47 g) in 85.3% yield as yellow syrup, $[\alpha]_{\text{D}}^{28} = +69.86$ (c 1.00, CHCl_3); ^1H NMR (CDCl_3 , 200 MHz): δ 1.30 (s, 3H, CH_3), 1.45 (s, 3H, CH_3), 2.60 (bs, 1H, OH), 3.20 (d, 1H, $J = 3.2$ Hz, H-3), 3.17 (s, 3H, OCH_3), 3.80 (s, 3H, OCH_3), 4.12 (dd, 1H, $J = 3.2, 9.2$ Hz, H-4), 4.49 (d, 1H, $J = 4.0$ Hz, H-2), 4.90 (d, 1H, $J = 9.2$ Hz, H-5), 5.90 (d, 1H, $J = 4.0$ Hz, H-1), 6.85 (d, 2H, $J = 8.9$ Hz, Ar-H), 7.10 (d, 2H, $J = 8.9$ Hz, Ar-H); ^{13}C NMR (CDCl_3 , 300 MHz): δ 26.5, 55.2, 72.0, 82.5, 84.2, 105.6, 112.2, 115.8, 127.2, 128.0, 129.3, 132.8, 159.3; FABMS (m/z , %): 310 (M^+ , 57), 173 (100), 135 (42), 107 (100); IR (Neat): 3492, 2933, 1613, 1514, 1378, 1246 cm^{-1} .

(R)-(3aR,5R,6S,6aR)-6-(Benzyloxy)-tetrahydro-2,2-dimethylfuro[2,3-*d*][1,3]dioxol-5-yl] (4-methoxyphenyl)methanol (10) and (S)-(3aR,5R,6S,6aR)-6-(benzyloxy)-tetrahydro-2,2-dimethylfuro[2,3-*d*][1,3]dioxol-5-yl](4-methoxyphenyl) methanol (8) :

To a stirred suspension of Mg (0.59 g, 26.97 mmol) in dry THF (20 mL), 4-bromoanisole (3.37 mL, 26.97 mmol) was added at reflux and stirred for 1 h. A solution of (3aR, 5S, 6S, 6aR)-6-(benzyloxy)-tetrahydro-2,2-dimethylfuro[2,3-*d*] [1,3]dioxol-5-carbaldehyde (5.0 g, 17.98 mmol) in dry THF (25 mL) was added at the same temperature and stirred for 4 h at room temperature. The reaction mixture was worked up as described for **3** and purified by column chromatography (1.8:8.2, EtOAc: hexane). First eluted was **10** (0.72 g) in 12% yield as yellow syrup, $[\alpha]_D^{28} = -144.86$ (*c* 0.785, CHCl₃); ¹H NMR (CDCl₃, 300 MHz): δ 1.25 (s, 3H, CH₃), 1.42 (s, 3H, CH₃), 2.65 (bs, 1H, OH), 3.78 (s, 3H, OCH₃), 3.98 (d, 1H, *J* = 3.0 Hz, H-3), 4.15 (dd, 1H, *J* = 3.0, 6.8 Hz, H-4), 4.48 (d, 1H, *J* = 3.8 Hz, H-2), 4.50 (d, 1H, *J* = 7.5 Hz, BnCH), 4.70 (d, 1H, *J* = 7.5 Hz, BnCH), 4.90 (d, 1H, *J* = 6.8 Hz, H-5), 5.90 (d, 1H, *J* = 3.8 Hz, H-1), 6.80 (d, 2H, *J* = 6.5 Hz, Ar-H), 7.25-7.40 (m, 7H, Ar-H); ¹³C NMR (CDCl₃, 300 MHz): δ 26.2, 26.75, 55.2, 71.7, 82.1, 84.6, 105.3, 111.9, 113.5, 127.5, 127.93, 128.27, 128.47, 132.8, 137.1, 159.2; FABMS (*m/z*, %): 386 (M⁺, 44), 249 (60), 107 (95); IR (Neat): 3449, 2925, 1612, 1512, 1377, 1248 cm⁻¹.

Second eluted was **8** (5.31 g) in 88% yield as yellow syrup, $[\alpha]_D^{28} = -120.67$ (*c* 1.44, CHCl₃); ¹H NMR (CDCl₃, 300 MHz): δ 1.30 (s, 3H, CH₃), 1.50 (s, 3H, CH₃), 3.52 (d, 1H, *J* = 3.7 Hz, H-3), 3.80 (s, 3H, OCH₃), 4.20 (dd, 1H, *J* = 3.7, 8.3 Hz, H-4), 4.38 (d, 1H, *J* = 6.0 Hz, BnCH), 4.52 (d, 1H, *J* = 3.2 Hz, H-2), 4.54 (d, 1H, *J* = 7.5 Hz, BnCH), 4.98 (d, 1H, *J* = 7.5 Hz, H-5), 5.95 (d, 1H, *J* = 3.2 Hz, H-1), 6.80 (d, 2H, *J* = 9.0 Hz, Ar-H), 7.25-7.40 (m, 7H, Ar-H); ¹³C NMR (CDCl₃, 300 MHz): δ 26.19, 26.7, 55.17, 71.7, 82.0, 84.58, 105.1, 111.8, 113.68, 127.5, 127.9, 128.27, 128.47, 132.8, 137.0, 159.3; FABMS (*m/z*, %): 386 (M⁺, 85), 249 (25), 198 (55), 107 (92); IR (Neat): 3450, 2930, 1610, 1542, 1382, 1248 cm⁻¹.

(R)-((3aR,4R,6R,6aS)-Tetrahydro-4-(*tert.* butyldimethylsilanemethyl)-2,2-dimethyl-furo[3,4-*d*][1,3]dioxal-6-yl)(4-methoxyphenyl)methanol (12) and (S)-((3aR, 4R,

6R, 6aS)-tetrahydro-4-(tert. butyldimethylsilanemethyl)-2,2-dimethylfuro[3,4-d][1,3]di-oxal-6-yl)(4-methoxyphenyl)methanol (11):

To a stirred suspension of Mg (0.10 g, 4.74 mmol) in dry THF (5 mL), 4-bromoanisole (0.59 mL, 4.74 mmol) was added at reflux and stirred for 1 h. A solution of (3aR,4S,6R,6aR)-6-(tert. butyldimethylsilanemethyl)-tetrahydro-2,2-dimethyl furo [3,4-d] [1,3]dioxal-4-carbaldehyde (1.0 g, 3.16 mmol) in dry THF (10 mL) was added at the same temperature and stirred for 4 h at room temperature. The reaction mixture was worked up as described for **3** and purified by column chromatography (1:9, EtOAc:hexane). First eluted was **12** (0.13 g) in 13.3% yield as brown syrup. $[\alpha]_D^{28} = +57.86$ (*c* 2.5, CHCl₃); ¹H NMR (CDCl₃, 200 MHz): δ 0.10 (s, 6H, 2 x CH₃), 0.09 (s, 9H, 3 x CH₃), 1.25 (s, 3H, CH₃), 1.45 (s, 3H, CH₃), 3.80 (s, 3H, OCH₃), 3.95 (dd, 2H, *J* = 2.3, 6.0 Hz, CH₂), 4.05 (dd, 1H, *J* = 2.8, 4.5 Hz, H-1), 4.30 (t, 1H, *J* = 2.3 Hz, H-4), 4.55 (dd, 1H, *J* = 1.5, 6.0 Hz, H-2), 4.70 (d, 1H, *J* = 5.6 Hz, H-3), 4.85 (d, 1H, *J* = 2.8 Hz, H-1'), 6.85 (d, 2H, *J* = 9.0 Hz, Ar-H), 7.30 (d, 2H, *J* = 9.0 Hz, Ar-H); ¹³C NMR (CDCl₃, 300 MHz): δ 24.8, 25.6, 26.1, 55.0, 64.62, 72.35, 81.3, 83.3, 86.36, 113.35, 113.6, 127.85, 128.26, 133.5, 159.6; FABMS (*m/z*, %): 447 (M⁺+Na, 25), 287 (52), 107 (100); IR (Neat): 3494, 2932, 1614, 1514, 1251 cm⁻¹.

Second eluted was **11** (0.85 g) in 87% yield as brown syrup, $[\alpha]_D^{28} = -45.51$ (*c* 2.06, CHCl₃); ¹H NMR (CDCl₃, 300 MHz): δ 0.10 (s, 6H, 2 x CH₃), 0.09 (s, 9H, 3 x CH₃), 1.30 (s, 3H, CH₃), 1.60 (s, 3H, CH₃), 3.72 (dd, 1H, *J* = 3.8, 7.4 Hz, CH₂), 3.80 (s, 3H, OCH₃), 4.10 (dd, 1H, *J* = 3.8, 7.6 Hz, H-1), 4.29 (t, 1H, *J* = 2.7 Hz, H-4), 4.55 (dd, 1H, *J* = 1.5, 6.0 Hz, H-2), 4.75 (d, 1H, *J* = 6.0 Hz, H-3), 4.90 (d, 1H, *J* = 7.6 Hz, H-1'), 6.85 (d, 2H, *J* = 8.3 Hz, Ar-H), 7.40 (d, 2H, *J* = 9.0 Hz, Ar-H); ¹³C NMR (CDCl₃, 300 MHz): δ 24.78, 25.68, 26.3, 55.0, 64.58, 72.37, 81.23, 84.5, 86.25, 113.37, 113.57, 127.8, 128.28, 133.5, 159.6; FABMS (*m/z*, %): 447 (M⁺+Na, 40), 287 (32), 107 (100); IR (Neat): 3494, 2932, 1614, 1514, 1251 cm⁻¹.

4,4-Diphenyl but-1-ene (1a):

To a mixture of **1** (0.20 g, 1.08 mmol) and allyltrimethylsilane (0.24 g, 2.17 mmol) in CH₃CN (4 mL) was added ZrCl₄ (0.05 g, 0.21 mmol). After 15 min, solvent was evaporated from the reaction mixture, water (5 mL) was added to the residue and extracted with EtOAc (2 x 5 mL). Organic layer was dried (Na₂SO₄), evaporated and

residue purified by column chromatography (0.2:9.8, EtOAc:hexane) to afford **1a** (0.215 g) in 95% yield as syrup. ^1H NMR (CDCl_3 , 300 MHz): δ 2.80 (t, 2H, $J = 4.0$ Hz, H-3, H-3'), 3.95 (t, 1H, $J = 4.0$ Hz, H-4) 4.90-5.00 (m, 2H, H-1, H-1'), 5.60-5.75 (m, 1H, H-2), 7.10-7.35 (m, 10H, Ar-H); EIMS (m/z , %): 208 (M) (80), 131 (100); IR (Neat): 2950, 1675, 1510, 1452 cm^{-1} .

1-Methoxy-4-(pent-4-en-2-yl)benzene(3a):

To a mixture of **2** (0.20 g, 1.31 mmol) and allyltrimethylsilane (0.30 g, 2.63 mmol) in CH_3CN (5 mL) was added ZrCl_4 (0.06 g, 0.26 mmol) and stirred at room temperature for 25 min. The reaction mixture was worked up as described for **1a** and purified by column chromatography (0.2:9.8, EtOAc:hexane) to furnish **3a** (0.22 g) in 96% yield as syrup. ^1H NMR (CDCl_3 , 300 MHz): δ 1.20 (d, 3H, $J = 7.3$ Hz, $-\text{CH}_3$), 2.20-2.40 (m, 2H, H-3, H-3'), 2.70 (q, 1H, H-2), 3.78 (s, 3H, OCH_3), 4.90-5.00 (m, 2H, H-5, H-5'), 5.60-5.75 (m, 1H, H-4), 6.78 (d, 2H, $J = 8.3$ Hz, Ar-H), 7.05 (d, 2H, $J = 8.3$ Hz, Ar-H); EIMS (m/z , %): 176 (M^+ , 92), 107 (100); IR (Neat): 2950, 1675, 1510, 1452 cm^{-1} , HRMS (ESI): m/z calculated for $\text{C}_{12}\text{H}_{16}\text{O}$ (M^+) 176.1201, found 176.1200.

1-(Benzyloxy)-4-(2-methylhex-5-en-3-yl) benzene (4a) :

To a mixture of **4** (0.2 g, 1.11 mmol) and allyltrimethylsilane (0.25 g, 2.22 mmol) in CH_3CN (5 mL) was added ZrCl_4 (0.05 g, 0.22 mmol) and stirred at room temperature for 20 min. The reaction mixture was worked up as described for **1a** and purified by column chromatography (0.2:9.8, EtOAc:hexane) to give **4a** (0.216 g) in 96% yield as syrup. ^1H NMR (CDCl_3 , 200 MHz): δ 0.72 (d, 3H, $J = 7.3$ Hz, $-\text{CH}_3$), 0.95 (d, 3H, $J = 7.3$ Hz, $-\text{CH}_3$), 1.70-1.85 (m, 1H, H-2), 2.25-2.50 (m, 3H, H-3, H-4, H-4'), 3.75 (s, 3H, OCH_3), 4.80-4.95 (m, 2H, H-5, H-5'), 5.45-5.65 (m, 2H, H-6), 6.75 (d, 2H, $J = 8.0$ Hz, Ar-H), 6.98 (d, 2H, $J = 8.0$ Hz, Ar-H); EIMS (m/z , %): 204 (M^+ , 42), 107 (66), 97 (32); IR (Neat): 3438, 2957, 1642, 1512, 1148 cm^{-1} , HRMS (ESI): m/z calculated for $\text{C}_{14}\text{H}_{20}\text{O}$ (M^+) 204.5728, found 204.5723.

1-Methoxy-4-(6-methylhept-1-en-4-yl)benzene (5a):

To a mixture of **5** (0.20 g, 1.03 mmol) and allyltrimethylsilane (0.23 g, 2.06 mmol) in CH_3CN (5 mL) was added ZrCl_4 (0.04 g, 0.20 mmol) and stirred at room temperature for 30 min. The reaction mixture was worked up as described for **1a** and purified by column chromatography (0.2:9.8, EtOAc:hexane) to obtain **5a** (0.21 g) in 95% yield as

liquid. ^1H NMR (CDCl_3 , 200 MHz): δ 0.80 (t, 6H, $J = 4.1$ Hz, 2 x CH_3), 1.30-1.50 (m, 3H, H-5, H-5', H-6), 2.25 (t, 2H, $J = 4.1$ Hz, H-3, H-3'), 2.55-2.70 (m, 1H, H-4), 3.75 (s, 3H, OCH_3), 4.80-4.95 (m, 2H, H-1, H-1'), 5.50-5.70 (m, 1H, H-2), 6.75 (d, 2H, $J = 8.8$ Hz, Ar-H), 7.10 (d, 2H, $J = 8.8$ Hz, Ar-H); ^{13}C NMR (CDCl_3 , 300 MHz): δ 21.7, 23.5, 25.2, 42.0, 42.65, 45.4, 55.0, 113.5, 115.5, 128.4, 137.2, 157.7; EIMS (m/z , %): 218 (M^+ , 76), 107 (100); IR (Neat): 2955, 1611, 1513, 1466, 1248 cm^{-1} , HRMS (ESI): m/z calculated for $\text{C}_{15}\text{H}_{22}\text{O}$ (M^+) 218.1671, found 218.1665.

1-(2-(4-Methoxyphenyl)pent-4-enyl)benzene (6a):

To a mixture of **6** (0.20 g, 0.87 mmol) and allyltrimethylsilane (0.19 g, 1.75 mmol) in CH_3CN (2 mL) was added ZrCl_4 (0.04 g, 0.17 mmol) and stirred at room temperature for 25 min. The reaction mixture was worked up as described for **1a** and purified by column chromatography (0.3/9.7, EtOAc/hexane) to afford **6a** (0.209 g) in 95% yield as syrup. ^1H NMR (CDCl_3 , 200 MHz): δ 2.30-2.45 (m, 2H, H-3, H-3'), 2.75- 2.95 (m, 3H, H-1, H-1', H-2), 3.75 (s, 3H, OCH_3), 4.90-5.05 (m, 2H, H-4, H-4'), 5.55-5.75 (m, 1H, H-5), 6.75 (d, 2H, $J = 8.8$ Hz, Ar-H), 7.00 (d, 2H, $J = 8.8$ Hz, Ar-H), 7.10-7.35 (m, 5H, Ar-H); ^{13}C NMR (CDCl_3 , 300 MHz): δ 41.2, 43.5, 47.8, 55.2, 113.6, 116.2, 125.8, 128.9, 137.2, 137.8., 141.5, 157.8; EIMS (m/z , %): 252 (M^+ , 72), 145 (100), 107 (60); IR (Neat): 2910, 1625, 1542, 1423, 1247, 1130 cm^{-1} , HRMS (ESI): m/z calculated for $\text{C}_{18}\text{H}_{20}\text{O}$ (M^+) 252.1514, found 252.1510.

(3aR, 5R, 6S, 6aR)-tetrahydro-6-methoxy-5-((R)-1-(4-methoxyphenyl)butenyl)-2,2-dimethylfuro[3,2-d] [1,3]dioxol (7a):

To a mixture of **7** (5.00 g, 16.12 mmol) and allyltrimethylsilane (3.67 g, 32.25 mmol) in CH_3CN (15 mL), ZrCl_4 (0.76 g, 3.22 mmol) was added and stirred at room temperature for 40 min. Solvent was evaporated from the reaction mixture, water (10 mL) was added to the residue and extracted with EtOAc (2 x 25 mL). Organic layer was dried (Na_2SO_4), evaporated and residue purified by column chromatography (0.5:9.5, EtOAc:hexane) to furnish **7a** (4.04 g) in 75% yield as white solid, m. p. 64-66 $^\circ\text{C}$, $[\alpha]_{\text{D}}^{28} = +69.86$ (c 1.00, CHCl_3); ^1H NMR (CDCl_3 , 500 MHz): δ 1.32 (s, 3H, CH_3), 1.52 (s, 3H, CH_3), 2.25-2.45 (m, 1H, H-6), 2.70-2.87 (m, 1H, H-6'), 3.02-3.12 (m, 2H, H-5, H-3), 3.15 (s, 3H, OCH_3), 3.82 (s, 3H, OCH_3), 4.20 (dd, 1H, $J = 2.7, 10.9$ Hz, H-4), 4.45 (d, 1H, $J = 4.0$ Hz, H-2), 4.85 (dq, 1H, $J = 10.0, 1.8$ Hz, H-8), 4.92 (dq, 1H, $J =$

17.2, 1.8 Hz, H-8'), 5.55-5.65 (m, 1H, H-7), 5.95 (d, 1H, $J = 4.0$ Hz, H-1), 6.85 (d, 2H, $J = 9.0$ Hz, Ar-H), 7.15 (d, 2H, $J = 9.0$ Hz, Ar-H); ^{13}C NMR (CDCl_3 , 300 MHz): δ 158.2, 136.47, 133.05, 129.37, 115.93, 113.67, 111.28, 105.09, 84.17, 83.5, 81.26, 57.38, 55.16, 43.5, 37.6, 26.7, 26.16; FABMS (m/z , %): 334 (M^+ , 66), 173 (20), 161 (35), 107 (100); IR (Neat): 3430, 2957, 1634, 1512, 1249 cm^{-1} ; HRMS (ESI): m/z calculated for $\text{C}_{19}\text{H}_{26}\text{O}_5\text{Na}$ ($\text{M}^+ + \text{Na}$) 357.1677, found 357.1669.

(3aR, 5R, 6S, 6aR)-6-(Benzyloxy)-tetrahydro-5-((R)-1-(4-methoxyphenyl)but-3-enyl)-2,2-dimethyl-6-phenoxyfuro[3,2-d][1,3]dioxol (8a):

To a mixture of **8** (3.00 g, 7.77 mmol) and allyltrimethylsilane (1.77 g, 15.54 mmol) in CH_3CN (15 mL) was added ZrCl_4 (0.36 g, 1.55 mmol) and stirred at room temperature for 50 min. The reaction mixture was worked up as described for **1a** and purified by column chromatography (0.6:9.4, EtOAc:hexane) to give **8a** (2.45 g) in 77% yield as yellow syrup, $[\alpha]_{\text{D}}^{28} = -91.21$ (c 0.85, CHCl_3); ^1H NMR (CDCl_3 , 500 MHz): δ 1.30 (s, 3H, CH_3), 1.50 (s, 3H, CH_3), 2.35-2.45 (m, 1H, H-6), 2.75-2.85 (m, 1H, H-6'), 3.15 (td, 1H, $J = 10.5, 3.8$ Hz, H-5), 3.40 (d, 1H, $J = 3.0$ Hz, H-3), 3.80 (s, 3H, OCH_3), 4.10 (d, 1H, $J = 10.9$ Hz, Bn-CH), 4.30 (dd, 1H, $J = 3.0, 10.5$ Hz, H-4), 4.38 (d, 1H, $J = 10.9$ Hz, Bn-CH), 4.50 (d, 1H, $J = 3.6$ Hz, H-2), 4.85 (dq, 1H, $J = 10.4, 1.8$ Hz, H-8), 4.92 (dq, 1H, $J = 17.3, 1.8$ Hz, H-8'), 5.55-5.65 (m, 1H, H-7), 5.98 (d, 1H, $J = 3.6$ Hz, H-1), 6.80 (d, 2H, $J = 8.5$ Hz, Ar-H), 7.10 (d, 2H, $J = 8.5$ Hz, Ar-H) 7.20-7.40 (m, 5H, Ar-H); ^{13}C NMR (CDCl_3 , 300 MHz): δ 158.2, 136.35, 133.1, 129.38, 128.36, 127.7, 116.0, 113.69, 111.3, 105.0, 84.0, 81.86, 71.98, 55.18, 43.5, 38.0, 26.79, 26.2; FABMS (m/z , %): 410 (M^+ , 25), 161 (30), 121 (20), 91 (100); IR (Neat): 3449, 2924, 1636, 1459, 1249 cm^{-1} ; HRMS (ESI): m/z calculated for $\text{C}_{25}\text{H}_{34}\text{O}_5$ (M^+) 410.2093, found 410.2090.

(3aR, 5R, 6S, 6aR)-Tetrahydro-6-methoxy-5-((S)-1-(4-methoxyphenyl)but-3-enyl)-2,2-dimethylfuro[3,2-d][1,3]dioxol (9a):

To a mixture of **9** (0.50 g, 1.61 mmol) and allyltrimethylsilane (0.36 g, 3.22 mmol) in CH_3CN (4 mL) was added ZrCl_4 (0.07 g, 0.32 mmol) and stirred at room temperature for 45 min. The reaction mixture was worked up as described for **1a** and purified by column chromatography (0.6:9.4, EtOAc:hexane) to afford **9a** (0.38 g) in 72% yield as white solid. m. p. 73-75 $^\circ\text{C}$, $[\alpha]_{\text{D}}^{28} = -150.96$ (c 1.04, CHCl_3); ^1H NMR

(CDCl₃, 500 MHz): δ 1.30 (s, 3H, CH₃), 1.49 (s, 3H, CH₃), 2.27-2.40 (m, 2H, H-6, H-6'), 3.12 (ddd, 1H, J = 4.6, 9.6, 10.0 Hz, H-5), 3.45 (s, 3H, OCH₃), 3.73 (d, 1H, J = 3.0 Hz, H-3), 3.79 (s, 3H, OCH₃), 4.27 (dd, 1H, J = 3.0, 10.0 Hz, H-4), 4.48 (d, 1H, J = 3.6 Hz, H-2), 4.89 (dq, 1H, J = 10.0, 1.8 Hz, H-8), 4.93 (dq, 1H, J = 17.0, 1.8 Hz, H-8'), 5.55-5.65 (m, 1H, H-7), 5.82 (d, 1H, J = 3.6 Hz, H-1), 6.85 (d, 2H, J = 8.5 Hz, Ar-H), 7.15 (d, 2H, J = 8.5 Hz, Ar-H); ¹³C NMR (CDCl₃, 300 MHz): δ 158.07, 136.08, 133.75, 128.99, 115.98, 113.79, 111.0, 104.47, 83.8, 82.9, 81.09, 57.32, 55.1, 43.19, 37.19, 26.75, 26.23; FABMS (m/z , %): 334 (M⁺, 74), 173 (47), 161 (100), 107 (58); IR (Neat): 3430, 2957, 1634, 1512, 1249 cm⁻¹, HRMS (ESI): m/z calculated for C₁₈H₂₀O (M⁺) 252.1514, found 252.1511.

(3aR, 5R, 6S, 6aR)-6-(Benzyloxy)-tetrahydro-5-((S)-1-(4-methoxyphenyl)but-3-en-yl) -2,2-dimethyl-6-phenoxyfuro[3,2-d][1,3]dioxol (10a):

To a mixture of **10** (0.20 g, 0.51 mmol) and allyltrimethylsilane (0.11 g, 1.03 mmol) in CH₃CN (4 mL) was added ZrCl₄ (0.02 g, 0.10 mmol) and stirred at room temperature for 50 min. The reaction mixture was worked up as described for **1a** and purified by column chromatography (0.7:9.3, EtOAc:hexane) to furnish **6a** (0.15 g) in 72% yield as colorless syrup, $[\alpha]_D^{28}$ = -55.43 (c 1.0, CHCl₃); ¹H NMR (CDCl₃, 500 MHz): δ 1.25 (s, 3H, CH₃), 1.50 (s, 3H, CH₃), 2.45-2.65 (m, 2H, H-6, H-6'), 3.10 (ddd, 1H, J = 4.5, 9.4, 10.4 Hz, H-5), 3.65 (d, 1H, J = 3.2 Hz, H-3), 3.75 (s, 3H, OCH₃), 4.15 (d, 1H, J = 9.5 Hz, Bn-CH), 4.25 (dd, 1H, J = 3.2, 9.7 Hz, H-4), 4.35 (d, 1H, J = 9.5 Hz, Bn-CH), 4.45 (d, 1H, J = 3.4 Hz, H-2), 4.85 (dq, 1H, J = 10.2, 1.8 Hz, H-8), 4.90 (dq, 1H, J = 17.3, 1.8 Hz, H-8'), 5.50-5.65 (m, 1H, H-7), 5.90 (d, 1H, J = 3.4 Hz, H-1), 6.85 (d, 2H, J = 9.2 Hz, Ar-H), 7.15 (d, 2H, J = 8.2 Hz, Ar-H), 7.20-7.35 (m, 5H, Ar-H); ¹³C NMR (CDCl₃, 300 MHz): δ 158.2, 136.35, 133.1, 129.38, 128.36, 127.7, 116.0, 113.69, 111.3, 105.0, 84.0, 81.8, 71.98, 55.18, 43.54, 38.0, 26.79, 26.2; FABMS (m/z , %): 411 (M⁺+1, 30), 303 (65), 161 (82), 121 (20), 91 (100); IR (Neat): 3449, 2924, 1636, 1459, 1249 cm⁻¹, HRMS (ESI): m/z calculated for C₂₅H₃₄O₅ (M⁺) 410.2093, found 410.2088.

(3aR,4R,6R,6aS)-4-(tert. Butyldimethylsilanemethyl)-tetrahydro-6-((S)-1-(4-methoxyphenyl)but-3-enyl)-2,2-dimethylfuro[3,4-d][1,3]dioxal (11a):

To a mixture of **11** (0.10 g, 0.23 mmol), allyltrimethylsilane (0.05 g, 0.47 mmol) in CH₃CN (2 mL) was added ZrCl₄ (0.01 g, 0.04 mmol) and stirred at room temperature for 45 min. The reaction mixture was worked up as described for **1a** and purified by column chromatography (Silica gel, 60-120 mesh, 1:4, EtOAc:hexane) to give desilylated product (0.046 g) in 60% yield as liquid. It was dissolved in CH₂Cl₂ (2 mL), treated with TBDMSCl (0.02 g, 0.16 mmol) and imidazole (0.01 g, 0.22 mmol) and stirred for 20 min at room temperature. After completion of reaction (TLC analysis), it was diluted with water (5 mL) and extracted with CH₂Cl₂ (2 x 5 mL). The organic layer was washed with brine (2 x 5 mL), dried (Na₂SO₄) and evaporated. The residue was purified by column chromatography (0.2:9.8, EtOAc:hexane) to afford **11a** (0.064 g) in 95.5% yield as liquid, $[\alpha]_D^{28} = -62.08$ (*c* 1.47, CHCl₃); ¹H NMR (CDCl₃, 500 MHz): δ 0.10 (d, 3H, *J* = 4.00 Hz, 2 x CH₃), 0.09 (s, 9H, 3 x CH₃), 1.25 (s, 3H, CH₃), 1.55 (s, 3H, CH₃), 2.35-2.40 (m, 1H, H-2'), 2.75-2.85 (m, 1H, H-2''), 3.08 (td, 1H, *J* = 10.5, 3.8 Hz, H-1'), 3.65-3.75 (dd, 2H, *J* = 3.8, 11.0 Hz, CH₂OTBS), 3.80 (s, 3H, OCH₃), 4.05 (td, 1H, *J* = 3.8, 1.3 Hz, H-4), 4.15 (dd, 1H, *J* = 3.8, 10.6 Hz, H-1), 4.21 (dd, 1H, *J* = 3.8, 6.0 Hz, H-2), 4.69 (d, 1H, *J* = 6.0 Hz, H-3), 4.85 (dq, 1H, *J* = 10.5, 1.8 Hz, H-3'), 4.95 (dq, 1H, *J* = 17.6, 1.8 Hz, H-3''), 5.55-5.65 (m, 1H, H-4'), 6.80 (d, 2H, *J* = 8.5 Hz, Ar-H), 7.15 (d, 2H, *J* = 8.5 Hz, Ar-H); ¹³C NMR (CDCl₃, 300 MHz): δ 145.45, 138.25, 135.86, 122.38, 118.36, 115.7, 94.0, 91.69, 88.3, 82.0, 71.0, 62.8, 50.98, 47.18, 33.5, 32.0, 31.79; FABMS (*m/z*, %): 449 (*M*⁺+1, 24), 333 (42), 187 (44), 161 (100); IR (Neat): 3492, 2929, 1733, 1513, 1378, 1246 cm⁻¹; HRMS (ESI): *m/z* calculated for C₂₅H₄₀O₅ Si (*M*⁺) 448.2645, found 448.2641.

(3aR,4R,6R,6aS)-4-(tert. Butyldimethylsilanemethyl)-tetrahydro-6-((R)-1-(4-methoxyphenyl)but-3-enyl)-2,2-dimethylfuro[3,4-d][1,3]dioxal (12a):

To a mixture of **12** (0.10 g, 0.23 mmol) and allyltrimethylsilane (0.05 g, 0.47 mmol) in CH₃CN (2 mL) was added ZrCl₄ (0.01 g, 0.04 mmol) and stirred at room temperature for 60 min. The reaction mixture was worked up as described for **1a** and purified by column chromatography (Silica gel, 60-120 mesh, 1:3, EtOAc:hexane) to afford the desilylated product (0.05 g) in 65% yield as a liquid. To a stirred solution of the above alcohol in CH₂Cl₂ (2 mL), TBDMSCl (0.02 g, 0.14 mmol) and imidazole (0.01 g, 0.20 mmol) were added and stirred for 20 min. After completion of reaction,

the reaction mixture was diluted with water (5 mL) and extracted with CH₂Cl₂ (2 x 5 mL). The organic layer was washed with brine (2 x 5 mL), dried (Na₂SO₄) and evaporated. The residue was purified by column chromatography (0.2:9.8, EtOAc:hexane) to afford **12a** (0.064 g) in 89% yield as liquid, $[\alpha]_D^{28} = -44.02$ (*c* 1.20, CHCl₃); ¹H NMR (CDCl₃, 200 MHz): δ 0.10 (s, 6H, 2 x CH₃), 0.90 (s, 9H, 3 x CH₃), 1.25 (s, 3H, CH₃), 1.50 (s, 3H, CH₃), 2.50-2.65 (m, 2H, H-2', H-2''), 3.15 (ddd, 1H, *J* = 3.9, 9.0, 10.4 Hz, H-1'), 3.80 (s, 3H, OCH₃), 3.85 (dd, 2H, *J* = 4.2, 7.5 Hz, -CH₂OTBS), 4.05 (t, 1H, *J* = 3.2 Hz, H-4), 4.25-4.40 (m, 2H, H-1, H-2), 4.70 (d, 1H, *J* = 3.2 Hz, H-3), 4.83 (dq, 1H, *J* = 10.3, 1.8 Hz, H-3'), 4.92 (dq, 1H, *J* = 17.6, 1.8 Hz, H-3''), 5.45-5.60 (m, 1H, H-4'), 6.80 (d, 2H, *J* = 8.7 Hz, Ar-H), 7.10 (d, 2H, *J* = 8.7 Hz, Ar-H); ¹³C NMR (CDCl₃, 300 MHz): δ 145.6, 138.5, 135.26, 122.87, 118.1, 115.4, 94.28, 91.67, 88.19, 82.9, 71.28, 62.3, 50.1, 47.1, 33.6, 32.27, 31.38; FABMS (*m/z*, %): 449 (*M*⁺+1, 40), 333 (57), 187 (22), 161 (100); IR (Neat): 3492, 2929, 1733, 1513, 1378, 1246 cm⁻¹, HRMS (ESI): *m/z* calculated for C₂₅H₄₀O₅ Si (*M*⁺) 448.2645, found 448.2640.

(*R*)-3-((3*aR*, 5*R*, 6*S*, 6*aR*)-6-(Benzyloxy)-tetrahydro-2,2-dimethylfuro[3,2-*d*][1,3]dioxol-5-yl)-3-(4-methoxyphenyl)propanoic acid (14**):**

To a solution of **8a** (0.55 g, 1.34 mmol) in CH₂Cl₂ (10 mL) at -78 °C was introduced ozone *via* a pipette until blue color persisted. The solution was purged off excess ozone with a stream of nitrogen gas, added Me₂S (5 mL) and the reaction mixture warmed up to 25 °C. After 1 h, the reaction mixture was poured into H₂O (10 mL) and the organic layer separated. The aqueous layer was extracted with CH₂Cl₂ (2 x 10 mL), and the organic layer was washed with H₂O (10 mL), dried (Na₂SO₄) and evaporated to afford (*R*)-3-((3*aR*, 5*R*, 6*S*, 6*aR*)-6-(benzyloxy)-tetrahydro-2,2-dimethylfuro[2,3-*d*][1,3]dioxol-5-yl)-3-(4-methoxyphenyl)propanal (**13**), which was directly used for the next reaction.

To a stirred solution of the above aldehyde **13** (0.45 g, 1.09 mmol) in *tert.* butanol: water (3.5:1.0, 4.5 mL), sodium chlorite (0.14 g, 1.63 mmol) and H₂O₂ (0.61 mL, 5.46 mmol, 30% aq. soln.) were added and stirred at room temperature for 12 h. The reaction mixture was concentrated, residue dissolved in ethyl acetate (15 mL), washed with water (5 mL). Organic layer was dried (Na₂SO₄), evaporated and residue purified by column chromatography (3:7, EtOAc:hexane) to afford **14** (0.43 g) in 93%

yield as white foam. $[\alpha]_D^{28} = -74.80$ (c 0.90, CHCl_3); ^1H NMR (CDCl_3 , 300 MHz): δ 1.25 (s, 3H, CH_3), 1.48 (s, 3H, CH_3), 2.55 (dd, 1H, $J = 3.6, 10.8$ Hz, H-6'), 3.08 (dd, 1H, $J = 3.6, 15.8$ Hz, H-6), 3.36 (d, 1H, $J = 3.0$ Hz, H-3), 3.55 (ddd, 1H, $J = 3.0, 10.5$ Hz, H-5), 3.75 (s, 3H, OCH_3), 4.10 (s, 1H, CH), 4.20 (dd, 1H, $J = 3.0, 10.5$ Hz, H-4), 4.38 (s, 1H, CH), 4.42 (d, 1H, $J = 3.8$ Hz, H-2), 5.85 (d, 1H, $J = 3.8$ Hz, H-1), 6.75 (d, 2H, $J = 8.3$ Hz, Ar-H), 7.10 (d, 2H, $J = 8.3$ Hz, Ar-H) 7.20-7.35 (m, 5H, Ar-H); ^{13}C NMR (CDCl_3 , 300 MHz): δ 178.9, 159.26, 133.7, 129.8, 127.6, 127.3, 114.29, 112.8, 105.2, 84.6, 83.9, 72.5, 61.56, 39.28, 38.27, 26.95, 25.8; FABMS (m/z , %): 451 ($\text{M}^+ + \text{Na}$, 30), 249 (55), 197 (72), 107 (100); IR (Neat): 3449, 2930, 1704, 1513, 1379, 1249 cm^{-1} ; HRMS (ESI): m/z calculated for $\text{C}_{24}\text{H}_{29}\text{O}_7$ ($\text{M}^+ + 1$) 429.1913, found 429.1906.

Preparation of lactone (15):

To a solution of **14** (0.40 g, 0.93 mmol) in MeOH (7 mL) was added catalytic amount of Pd/C, passed H_2 gas and stirred for 12 h. The reaction mixture was filtered through sintered funnel, washed with MeOH (5 mL), concentrated and the residue purified by column chromatography (1:4, EtOAc:hexane) to afford **15** (0.27 g) in 92% yield as white solid. m. p. 183-185 $^\circ\text{C}$, $[\alpha]_D^{28} = -23.38$ (c 0.50, CHCl_3); ^1H NMR (CDCl_3 , 500 MHz): δ 1.33 (s, 3H, CH_3), 1.47 (s, 3H, CH_3), 2.70 (dd, 1H, $J = 5.0, 17.5$ Hz, H-6'), 2.96 (dd, 1H, $J = 13.7, 17.5$ Hz, H-6), 3.32 (ddd, 1H, $J = 1.7, 5.0, 13.7$ Hz, H-5), 4.58 (dd, 1H, $J = 1.7$ Hz, 2.9 Hz, H-4), 4.71 (d, 1H, $J = 3.8$ Hz, H-2), 4.83 (d, 1H, $J = 2.9$ Hz, H-3), 6.00 (d, 1H, $J = 3.8$ Hz, H-1), 6.89 (m, 2H, Ar-H), 7.29 (m, 2H, Ar-H); ^{13}C NMR (CDCl_3 , 300 MHz): δ 168.6, 159.0, 131.2, 128.7, 114.26, 112.4, 105.18, 84.44, 83.5, 75.08, 55.2, 38.0, 31.6, 29.65, 26.59, 26.2; ES+MS (m/z , %): 321 ($\text{M}^+ + 1$, 65), 246 (25), 202 (33), 179 (100); IR (Neat): 3464, 2956, 1740, 1519, 1380, 1215, 1081 cm^{-1} ; HRMS (ESI): m/z calculated for $\text{C}_{17}\text{H}_{21}\text{O}_6$ ($\text{M}^+ + 1$) 321.1338, found 321.1334.

(R)-3-((3aR, 5R, 6S, 6aR)-Tetrahydro-6-methoxy-2,2-dimethylfuro[3,2-d][1,3]dioxol-5-yl)-3-(4-methoxyphenyl)propanoic acid (17):

To a solution of **7a** (1.0 g, 2.99 mmol) in CH_2Cl_2 (15 mL) at -78 $^\circ\text{C}$ was introduced ozone *via* a pipette until blue color persisted. The solution was purged off excess ozone with a stream of N_2 , added Me_2S (5 mL) and the reaction mixture was

worked up as described for **13** to give (*R*)-3-((3*aR*, 5*R*, 6*S*, 6*aR*)-tetrahydro-6-methoxy-2,2-dimethylfuro[3,2-*d*][1,3]dioxol-5-yl)-3-(4-methoxyphenyl)propanal (**16**). The crude product was used as such for the next reaction.

To a stirred solution of **16** (0.80 g, 2.38 mmol) in *tert.* butanol: water (6:2.5, 8.5 mL), sodium chlorite (0.32 g, 3.57 mmol) and H₂O₂ (1.34 mL, 11.90 mmol, 30% aq. soln.) were added and stirred at room temperature for 12 h. The reaction mixture was worked up as described for **14**. The crude product was purified by column chromatography (3:7, EtOAc:hexane) to afford **17** (0.80 g) in 95% yield as white foam. m. p 142-145 °C, $[\alpha]_D^{28} = +66.24$ (*c* 0.725, CHCl₃); ¹H NMR (CDCl₃, 200 MHz): δ 1.25 (s, 3H, CH₃), 1.45 (s, 3H, CH₃), 2.60 (dd, 1H, *J* = 3.8, 10.3 Hz, H-6'), 3.00-3.15 (m, 2H, H-3, H-6), 3.16 (s, 3H, OCH₃), 3.52 (ddd, 1H, *J* = 4.0, 10.4 Hz, H-5), 3.80 (s, 3H, OCH₃), 4.10 (dd, 1H, *J* = 2.4, 10.4 Hz, H-4), 4.40 (d, 1H, *J* = 3.5 Hz, H-2), 5.82 (d, 1H, *J* = 3.5 Hz, H-1), 6.80 (d, 2H, *J* = 8.0 Hz, Ar-H), 7.15 (d, 2H, *J* = 8.0 Hz, Ar-H); ¹³C NMR (CDCl₃, 300 MHz): δ 26.1, 26.66, 55.0, 71.76, 81.95, 82.0, 84.5, 105.05, 113.59, 127.5, 128.2, 131.8, 137.1, 159.5; FABMS (*m/z*, %): 353 (M⁺+1, 25), 235 (20), 177 (30); IR (KBr): 3450, 2937, 1710, 1514, 1380, 1252 cm⁻¹;

***tert.* Butyl (S)-2-((3*aR*,5*R*,6*S*,6*aR*)-tetrahydro-6-methoxy-2,2-dimethylfuro [3,2-*d*][1, 3]dioxol-5-yl)-2-(4-methoxyphenyl)ethylcarbanate (**18**):**

To a cooled (0 °C) solution of **17** (0.50 g, 1.42 mmol) in acetone (5 mL), Et₃N (0.25 mL, 1.84 mmol) was added followed by dropwise addition of ethyl chloroformate (0.15 g, 1.42 mmol) in acetone (2 mL) for 30 min. After the completion of the reaction (15 min) as indicated by TLC, a chilled solution of NaN₃ (0.18 g, 2.84 mmol) in water (2 mL) was added. It was stirred for an additional 15 min at 0 °C and poured into ice water. The acyl azide was isolated by extraction with toluene (4 x 5 mL) and dried (Na₂SO₄). Toluene was concentrated to 1/5th of its volume and the acyl azide solution was added over 10 min to a vigorously stirred solution of *tert.* butanol (5 mL) and toluene while rapid reflux was maintained. After 8 h, again 2 equivalents of *tert.* butanol was added and reflux continued for additional 8 h. The reaction mixture was cooled to room temperature and concentrated to afford crude compound which was purified by column chromatography (0.5:9.5, EtOAc:hexane) to furnish **18** (0.37 g) in 63% yield as yellow syrup, $[\alpha]_D^{28} = +41.02$ (*c* 1.31, CHCl₃); ¹H NMR (CDCl₃, 200

MHz): δ 1.25 (s, 3H, CH₃), 1.35 (s, 9H, 3 x CH₃), 1.45 (s, 3H, CH₃), 3.05-3.20 (m, 5H, H-3, H-5, -OCH₃), 3.40-3.70 (m, 2H, H-6, H-6'), 3.75 (s, 3H, OCH₃), 4.20 (dd, 1H, J = 3.1, 10.1 Hz, H-4), 4.40 (d, 1H, J = 3.8 Hz, H-2), 4.95 (bs, 1H, NH), 5.90 (d, 1H, J = 3.8 Hz, H-1), 6.80 (d, 2H, J = 8.5 Hz, Ar-H), 7.10 (d, 2H, J = 8.5 Hz, Ar-H); ¹³C NMR (CDCl₃, 300 MHz): δ 158.2, 133.8, 129.37, 114.26, 104.5, 84.47, 83.9, 81.3, 57.0, 55.27, 42.57, 38.08, 28.7, 26.59, 25.6; FABMS (m/z , %): 446 (M⁺+Na, 5), 324 (M⁺-Boc, 46), 177 (60), 107 (30), 57 (100); IR (Neat): 3439, 2926, 1714, 1511, 1249 cm⁻¹; HRMS (ESI): m/z calculated for C₂₂H₃₄NO₇ (M⁺+1) 424.2335, found 424.2339.

(S)-methyl-2-(3aR,5R,6S,6aR)-tetrahydro-6-methoxy-2,2-dimethylfuro[3,2-d][1,3]dioxol-5-yl)-3-(pivalamido)propanoate (20):

A solution of NaIO₄ (1.517 g, 7.08 mmol) in CH₃CN:H₂O (2.8:4.8 mL) was treated with a solution of **18** (0.20 g, 0.472 mmol) in CCl₄ (2.8 mL) followed by RuCl₃ (5 mg) and NaHCO₃ (10 mg). The reaction mixture was stirred at room temperature for 8 h, treated with sat. aq. NaHCO₃ (25 mL) and washed with CH₂Cl₂ (2 x 20 mL). The aqueous layer was acidified with 10% aq. HCl to pH 2-3 in an ice-bath and extracted with EtOAc (4 x 20 mL). The organic layer was dried (Na₂SO₄) and concentrated *in vacuo*. The residue was purified by column chromatography (3.5:6.5, EtOAc:hexane) to afford (S)-2-((3aR, 5R, 6S, 6a R)-tetrahydro-6-methoxy-2,2-dimethylfuro[3,2-d][1,3]dioxol-5-yl)-3-(pivalamido)propanoic acid (**19**; 0.08 g) in 47% yield as syrup.

A solution of **19** (0.06 g, 0.16 mmol) in MeOH (2 mL) was admixed with ethereal diazomethane [prepared from 0.30 g of N-nitrosomethyl urea and 20% aq. KOH (10 mL)]. The reaction mixture was kept at 0 °C for 12 h, solvent evaporated and residue purified by column chromatography (1.4:8.6, EtOAc:hexane) to afford **20** (0.05 g) in 92% yield as yellow crystalline solid. m. p. 90-92° C, $[\alpha]_D^{28}$ = -32.08 (c 1.00, CHCl₃); ¹H NMR (CDCl₃, 500 MHz): δ 1.35 (s, 3H, CH₃), 1.45 (s, 9H, 3 x CH₃), 1.50 (s, 3H, CH₃), 2.95 (dt, 1H, J = 10.4, 5.5 Hz, H-5), 3.35 (s, 3H, OCH₃), 3.50-3.60 (m, 2H, CH₂), 3.70 (s, 3H, -COOCH₃), 3.80 (d, 1H, J = 2.7 Hz, H-3), 4.39 (dd, 1H, J = 2.7, 10.0 Hz, H-4), 4.55 (d, 1H, J = 3.6 Hz, H-2), 4.98 (bs, 1H, NH), 5.85 (d, 1H, J = 3.6 Hz, H-1); ¹³C NMR (CDCl₃, 300 MHz): δ 173.96, 162.10, 111.57, 104.77, 84.38, 81.74, 80.57, 57.78, 51.5, 44.19, 40.8, 29.6, 28.4, 27.3, 26.8, 26.26; ES+MS (m/z , %): 398 (M⁺+Na) (100), 376 (M⁺+1, 20), 320 (44), 275 (22); IR (Neat): 3387, 2932, 1716, 1517, 1370,

1253, 1166, 1080 cm^{-1} ; HRMS (ESI): m/z calculated for $\text{C}_{17}\text{H}_{30}\text{NO}_8$ ($\text{M}^+ + 1$) 376.1971, found 376.1969.

(R)-N-Benzyl-3-((3aR,5R,6S,6aR)-tetrahydro-6-methoxy-2,2-dimethylfuro[3,2-d][1,3]-dioxol-5-yl)-3-(4-methoxyphenyl)propan-1-amine (21):

To a stirred, cooled (0 °C) solution of **16** (0.80 g, 2.38 mmol) in CH_2Cl_2 (10 mL) was added benzyl amine (0.22 g, 2.38 mmol), anhydrous MgSO_4 (0.34 g, 2.85 mmol) and stirred at room temperature for 10 h. The reaction mixture was filtered off, precipitate washed with CH_2Cl_2 (10 mL) and the combined organic layers were evaporated. The residue was dissolved in MeOH (10 mL), cooled to 0 °C and treated with NaBH_4 (0.176 g, 4.76 mmol) and stirred at room temperature for 3 h. After the completion of the reaction, MeOH was evaporated and diluted with water (2 x 10 mL). It was extracted with EtOAc (2 x 10 mL), dried (Na_2SO_4) and evaporated. The residue was purified by column chromatography (1:4, EtOAc:hexane) to give **21** (0.86 g) in 85% yield as a red syrup, $[\alpha]_{\text{D}}^{28} = +40.86$ (c 1.00, CHCl_3); ^1H NMR (CDCl_3 , 300 MHz): δ 1.25 (s, 3H, CH_3), 1.47 (s, 3H, CH_3), 1.65-1.85 (m, 1H, -CH), 2.00-2.20 (m, 1H, -CH), 2.80-3.10 (m, 4H, H-3, H-5, H-6, H-6'), 3.05 (s, 3H, OCH_3), 3.65 (d, 2H, $J = 3.9$ Hz, $-\text{CH}_2$), 3.70 (s, 3H, OCH_3), 4.10 (dd, 1H, $J = 3.1, 10.8$ Hz, H-4), 4.40 (d, 1H, $J = 3.9$ Hz, H-2), 4.45 (bs, 1H, NH), 5.82 (d, 1H, $J = 3.9$ Hz, H-1), 6.75 (d, 2H, $J = 8.5$ Hz, Ar-H), 7.10 (d, 2H, $J = 8.5$ Hz, Ar-H), 7.20-7.35 (m, 5H, Ar-H); FABMS (m/z , %): 427 (M^+ , 33), 336 (20), 254 (60), 173 (20), 107 (100); IR (Neat): 3386, 2933, 1710, 1513, 1248 cm^{-1} ; HRMS (ESI): m/z calculated for $\text{C}_{25}\text{H}_{33}\text{NO}_5$ (M^+) 427.2359, found 427.2351.

tert. Butyl (R)-3-((3aR,5R,6S,6aR)-tetrahydro-6-methoxy-2,2-dimethylfuro[3, 2-d][1, 3]dioxol-5-yl)-3-(4-methoxyphenyl)propylcarbanate (23):

To a solution of **21** (0.80 g, 1.87 mmol) in MeOH (10 mL) was added catalytic amount of Pd/C, passed H_2 gas and stirred for 12 h. After completion of reaction, the reaction mixture was filtered through a sintered funnel, washed with MeOH (5 mL), concentrated under reduced pressure to give (R)-3-((3aR,5R,6S,6aR)-tetrahydro-6-methoxy-2,2-dimethylfuro[3,2-d][1,3]dioxol-5-yl)-3-(4-methoxyphenyl)propan-1-amine (**22**), which was directly used for the next reaction.

A stirred solution of **22** (0.62 g, 1.84 mmol) in dry THF (10 mL) was cooled to 0 °C and admixed with ice cooled Et₃N (0.511 mL, 3.67 mmol) and (Boc)₂O (0.481 g, 2.20 mmol). The reaction mixture was stirred at room temperature for 2 h, solvent evaporated and the residue was purified by column chromatography (1:4, EtOAc:hexane) to give **23** (0.69 g) in 86% yield as yellow syrup. $[\alpha]_D^{28} = +48.89$ (*c* 2.00, CHCl₃); ¹H NMR (CDCl₃, 200 MHz): δ 1.25 (s, 3H, CH₃), 1.35 (s, 9H, 3 x CH₃), 1.45 (s, 3H, CH₃), 1.65-1.85 (m, 1H, -CH), 2.00-2.20 (m, 1H, -CH), 2.85-3.05 (m, 4H, H-3, H-5, CH₂), 3.05 (s, 3H, OCH₃), 3.70 (s, 3H, OCH₃), 4.10 (dd, 1H, *J* = 3.1, 10.8 Hz, H-4), 4.40 (d, 1H, *J* = 3.9 Hz, H-2), 4.45 (bs, 1H, NH), 5.82 (d, 1H, *J* = 3.9 Hz, H-1), 6.75 (d, 2H, *J* = 8.5 Hz, Ar-H), 7.10 (d, 2H, *J* = 8.5 Hz, Ar-H); ¹³C NMR (CDCl₃, 300 MHz): δ 158.56, 134.84, 129.49, 115.2, 104.57, 84.7 83.49, 81.6, 57.18, 55.37, 42.57, 38.5, 34.8, 28.3, 26.6, 25.46; FABMS (*m/z*, %): 438 (M⁺, 45), 338 (95), 264 (30), 57 (100); IR (Neat): 3404, 2930, 1711, 1512, 1370, 1248, 1170 cm⁻¹; HRMS (ESI): *m/z* calculated for C₂₃H₃₆NO₇ (M⁺) 438.2491, found 438.2487.

***tert.* Butyl (S)-3-(methoxycarbonyl)-3-((3aR,5R,6S,6aR)-tetrahydro-6-methoxy-2,2-dimethylfuro[3,2-d][1,3]dioxol-5-yl)propylcarbamate (25):**

A solution of NaIO₄ (2.05 g, 9.58 mmol) in CH₃CN:H₂O (4.2:7.2 mL) was treated with a solution of **23** (0.30 g, 0.684 mmol) in CCl₄ (4.2 mL) followed by RuCl₃ (5 mg) and NaHCO₃ (15 mg). The reaction mixture was worked up as described for **19** and purified by column chromatography (3:7, EtOAc: hexane) to afford (*S*)-2-((3aR,5R,6S,6aR)-tetrahydro-6-methoxy-2,2-dimethylfuro[3,2-d][1,3]dioxol-5-yl)-4-(pivalamido)butanoic acid (**24**) (0.11 g) in 43% yield as a syrup.

A solution of **24** (0.10 g, 0.26 mmol) in MeOH (4 mL) was admixed with ethereal diazomethane [prepared from 0.30 g of N-nitrosomethyl urea and 20% aq. KOH (10 mL)]. The reaction mixture was stored at 0 °C for 12 h, evaporated and purified by column chromatography (1.4:8.6, EtOAc:hexane) to afford **25** (0.09 g) in 92% yield as yellow syrup. $[\alpha]_D^{28} = -38.00$ (*c* 1.00, CHCl₃); ¹H NMR (CDCl₃, 500 MHz): δ 1.35 (s, 3H, CH₃), 1.50 (s, 9H, 3 x -CH₃), 1.57 (s, 3H, -CH₃), 1.87-1.95 (m, 1H, -CH), 2.10-2.20 (m, 1H, CH), 2.85 (td, 1H, *J* = 9.3, 4.6 Hz, H-5), 3.35 (s, 3H, -OCH₃), 3.60-3.70 (m, 2H, CH₂), 3.72 (s, 3H, -COOCH₃), 3.75 (d, 1H, *J* = 3.6 Hz, H-3), 4.30 (dd, 1H, *J* = 3.6, 10.0 Hz, H-4), 4.55 (d, 1H, *J* = 3.6 Hz, H-2), 5.85 (d, 1H, *J* = 3.6

Hz, H-1); ^{13}C NMR (CDCl_3 , 300 MHz): δ 173.4, 162.7, 111.6, 104.77, 84.3, 81.77, 80.3, 57.80, 51.6, 42.51, 38.68, 29.68, 28.74, 28.0, 26.8, 26.3; ES+MS (m/z , %): 412 ($\text{M}^+ + \text{Na}$, 44), 390 ($\text{M}^+ + 1$, 70), 289 (100), 173 (40); IR (Neat): 3387, 2932, 1716, 1517, 1370, 1253, 1166 cm^{-1} ; HRMS (ESI): m/z calculated for $\text{C}_{18}\text{H}_{31}\text{NO}_8$ ($\text{M}^+ + 1$) 390.2050, found 390.2044.

(R)-4-((3aR, 5R,6S,6aR)-Tetrahydro-6-methoxy-2,2-dimethylfuro[3,2-d][1,3]dioxol-5-yl)-4-(4-methoxyphenyl)butan-1-ol (26):

To a stirred and cooled (0 °C) solution of **7a** (1.30 g, 3.89 mmol) in dry THF (10 mL) was added $\text{BH}_3\text{-DMS}$ (0.295 g, 3.89 mmol) dropwise and stirred at room temperature for 24 h. The reaction mixture was quenched with aq. 2N NaOH (6 mL) and H_2O_2 (1.5 mL). After 4 h, it was extracted with EtOAc (2 x 15 mL), organic layer was washed with water (2 x 10 mL), brine (10 mL) and dried (Na_2SO_4). It was evaporated and residue purified by column chromatography (3:7, EtOAc:hexane) to afford **26** (1.0 g) in 73% yield as white foam. $[\alpha]_{\text{D}}^{28} = +48.06$ (c 1.27, CHCl_3); ^1H NMR (CDCl_3 , 200 MHz): δ 1.20 (s, 3H, CH_3), 1.30-1.40 (m, 2H, CH_2), 1.48 (s, 3H, CH_3), 1.55-1.70 (m, 1H, -CH), 2.00-2.22 (m, 1H, -CH), 2.98 (m, 2H, H-3, H-5), 3.12 (s, 3H, OCH_3), 3.55 (m, 2H, $-\text{CH}_2$), 3.78 (s, 3H, OCH_3), 4.10 (dd, 1H, $J = 3.2, 10.8$ Hz, H-4), 4.39 (d, 1H, $J = 4.0$ Hz, H-2), 5.84 (d, 1H, $J = 4.0$ Hz, H-1), 6.80 (d, 2H, $J = 8.8$ Hz, Ar-H), 7.10 (d, 2H, $J = 8.8$ Hz, Ar-H); FABMS (m/z , %): 353 ($\text{M}^+ + 1$, 36), 179 (20), 173 (50); IR (Neat): 3376, 2953, 1610, 1511, 1246 cm^{-1} .

(3aR,5R,6S,6aR)-5-((R)-4-Azido-1-(4-methoxyphenyl)butyl)-tetrahydro-6-methoxy-2,2-dimethylfuro[3,2-d][1,3]dioxol (28):

A solution of **26** (1.00 g, 2.84 mmol) in CH_2Cl_2 (10 mL) containing Et_3N (0.79 mL, 5.68 mmol) was cooled to 0 °C, treated with $p\text{-TsCl}$ (0.64 g, 3.40 mmol) and stirred at room temperature for 10 h. Solvent was evaporated and residue obtained purified by column chromatography (1:4, EtOAc: hexane) to furnish (R)-4-((3aR,5R,6S,6aR)-tetrahydro-6-methoxy-2,2-dimethylfuro[3,2-d][1,3]dioxol-5-yl)-4-(4-methoxyphenyl)butyl-4-methylbenzenesulfonate (**27**) (1.39 g) in 97% yield, which was directly used for the next reaction.

A mixture of **27** (1.30 g, 2.56 mmol) and NaN_3 (0.41 g, 6.42 mmol) in DMF (5 mL) was stirred at 60 °C for 4 h. The reaction mixture was diluted with H_2O (5 mL)

and extracted with ether (2 x 15 mL). The organic layer was washed with brine (10 mL), dried (Na₂SO₄) and evaporated. The residue was purified by column chromatography (1.5:8.5, EtOAc:hexane) to obtain **28** (0.91 g) in 95% yield as white foam. $[\alpha]_D^{28} = +66.60$ (*c* 1.18, CHCl₃); ¹H NMR (CDCl₃, 200 MHz): δ 1.26 (s, 3H, CH₃), 1.35-1.73 (m, 6H, CH₃, CH₂, -CH), 2.00-2.20 (m, 1H, -CH), 2.85-3.05 (m, 3H, -CH₂, H-3), 3.10 (s, 3H, OCH₃), 3.20 (m, 1H, H-5), 3.78 (s, 3H, OCH₃), 4.10 (dd, 1H, *J* = 3.5, 10.4 Hz, H-4), 4.39 (d, 1H, *J* = 4.0 Hz, H-2), 5.83 (d, 1H, *J* = 4.0 Hz, H-1), 6.80 (d, 2H, *J* = 8.0 Hz, Ar-H), 7.10 (d, 2H, *J* = 8.0 Hz, Ar-H); FABMS (*m/z*, %): 377 (M⁺, 46), 204 (22), 173 (40), 107 (100); IR (Neat): 2967, 2130, 1610, 1511, 1248 cm⁻¹.

***tert.* Butyl (R)-4-((3aR, 5R, 6S, 6aR)-tetrahydro-6-methoxy-2,2-dimethylfuro[3,2-d][1,3]dioxol-5-yl)-4-(4-methoxyphenyl)butylcarbamate (30):**

To a solution of **28** (0.90 g, 2.38 mmol) in MeOH (4 mL) was added catalytic amount of Pd/C, passed H₂ gas and stirred for 12 h. After completion of reaction, the reaction mixture was filtered through sintered funnel, washed with MeOH (5 mL), concentrated under reduced pressure to give (*R*)-4-((3*aR*,5*R*,6*S*,6*aR*)-tetrahydro-6-methoxy-2,2-dimethylfuro[3,2-*d*][1,3]dioxol-5-yl)-4-(4-methoxyphenyl)butan-1-amine (**29**), which was directly used for the next reaction.

A stirred solution of **29** (0.80 g, 2.27 mmol) in dry THF (10 mL) was cooled to 0 °C and treated with Et₃N (0.634 mL, 4.55 mmol) and (Boc)₂O (0.546 g, 2.507 mmol). The reaction mixture was stirred at room temperature for 2 h, solvent evaporated and the residue obtained was purified by column chromatography (1:4, EtOAc:hexane) to furnish **30** (0.92 g) in 89% yield as white foam. $[\alpha]_D^{28} = +55.53$ (*c* 4.17, CHCl₃); ¹H NMR (CDCl₃, 300 MHz): δ 1.20-1.35 (m, 5H, CH₃, -CH₂), 1.38 (s, 9H, 3 x CH₃), 1.45 (s, 3H, CH₃), 1.50-1.65 (m, 1H, -CH), 2.00-2.15 (m, 1H, -CH), 2.85-3.10 (m, 4H, -CH₂, H-5, H-3), 3.12 (s, 3H, OCH₃), 3.78 (s, 3H, OCH₃), 4.08 (dd, 1H, *J* = 4.5, 10.5 Hz, H-4), 4.38 (d, 1H, *J* = 4.0 Hz, H-2), 4.50 (bs, 1H, NH), 5.84 (d, 1H, *J* = 4.0 Hz, H-1), 6.80 (d, 2H, *J* = 8.3 Hz, Ar-H), 7.10 (d, 2H, *J* = 8.3 Hz, Ar-H); ¹³C NMR (CDCl₃, 300 MHz): δ 158.5, 134.8, 129.49, 115.2, 104.57, 84.7, 83.49, 81.6, 57.18, 55.37, 42.57, 38.5, 34.8, 31.48, 28.3, 26.6, 25.46; FABMS (*m/z*, %): 452 (M⁺, 5), 352 (38), 278 (20), 173 (15), 57 (100); IR (Neat): 3386, 2933, 1710, 1513, 1248 cm⁻¹; HRMS (ESI): *m/z* calculated for C₂₄H₃₈NO₇ (M⁺) 452.2648, found 452.2645.

(S)-Methyl-2-((3aR,5R,6S,6aR)-tetrahydro-6-methoxy-2, 2-di methylfuro [3,2-d][1,3]dioxol-5-yl)-5-(pivalamido) pentanoate (32):

A solution of NaIO₄ (3.55 g, 16.6 mmol) in CH₃CN:H₂O (7.5:14 mL) was treated with a solution of **30** (0.50 g, 1.10 mmol) in CCl₄ (7.5 mL) followed by RuCl₃ (5 mg) and NaHCO₃ (25 mg). The reaction mixture was worked up as described for **19** and purified by column chromatography (3:7, EtOAc: hexane) to afford (S)-2-((3aR,5R,6S,6aR)-tetrahydro-6-methoxy-2,2-dimethylfuro[3,2-d][1,3] dioxol-5-yl)-4-(pivalamido)pentanoic acid (**131**) (0.11 g) in 43% yield as a syrup.

A solution of **131** (0.10 g, 0.25 mmol) in MeOH (4 mL) was admixed with ethereal diazomethane [prepared from 0.30 g of N-nitrosomethyl urea and 20% aq. KOH (10 mL)]. The reaction mixture was stored at 0 °C for 12 h, evaporated and purified by column chromatography (1.5:8.5, EtOAc:hexane) to afford **132** (0.09 g) in 87% yield as yellow syrup. $[\alpha]_D^{28} = -40.60$ (*c* 1.16, CHCl₃); ¹H NMR (CDCl₃, 500 MHz): δ 1.35 (s, 3H, CH₃), 1.42 (s, 9H, 3 x -CH₃), 1.48 (s, 3H, -CH₃), 1.50-1.62 (m, 2H, -CH₂), 1.65-1.75 (m, 1H, CH), 1.85-1.95 (m, 1H, CH), 2.80 (ddd, 1H, *J* = 4.5, 9.1, 13.6 Hz, H-5), 3.08-3.17 (m, 2H, CH₂), 3.33 (s, 3H, -OCH₃), 3.70 (s, 3H, -COOCH₃), 3.72 (d, 1H, *J* = 3.6 Hz, H-3), 4.28 (dd, 1H, *J* = 3.2, 10.0 Hz, H-4), 4.55 (d, 1H, *J* = 4.0 Hz, H-2), 4.57 (bs, 1H, NH), 5.85 (d, 1H, *J* = 4.0 Hz, H-1); ¹³C NMR (CDCl₃, 300 MHz): δ 172.3, 155.7, 111.7, 104.8, 84.4, 81.67, 80.58, 79.2, 57.8, 51.89, 45.0, 4.82, 28.3, 27.7, 26.8, 26.27; ES+MS (*m/z*, %): 426 (M⁺+Na, 100), 404 (M⁺+1, 45), 303 (60), 173 (33); IR (Neat): 3387, 2932, 1716, 1517, 1370, 1253, 1166 cm⁻¹; HRMS (ESI): *m/z* calculated for C₁₉H₃₄NO₈ (M⁺+1) 404.2284, found 404.2283.

^1H NMR (CDCl₃+300 MHz) spectrum of **5a**

^1H NMR (CDCl₃+200 MHz) spectrum of **6a**

^1H NMR (CDCl₃, 500 MHz) spectrum of **8a**

^1H NMR (CDCl₃+300 MHz) spectrum of **10a**

^1H NMR (CDCl₃, 500 MHz) spectrum of **11a**

^1H NMR (CDCl_3 +200 MHz) spectrum of **12a**

^1H NMR (CDCl_3 , 500 MHz) spectrum of **15**

^1H NMR (CDCl₃+200 MHz) spectrum of **17**

^1H NMR (CDCl₃, 200 MHz) spectrum of 18

^1H NMR (CDCl_3 +200 MHz) spectrum of **23**

^1H NMR (CDCl₃+200 MHz) spectrum of **26**

^1H NMR (CDCl₃+200 MHz) spectrum of **28**

S43

^1H NMR (CDCl_3 , 500 MHz) spectrum of **32**

^{13}C NMR (CDCl_3 , 300 MHz) spectrum of **8**

^{13}C NMR (CDCl_3 , 300 MHz) spectrum of 12

^{13}C NMR (CDCl_3 , 300 MHz) spectrum of **10a**

^{13}C NMR (CDCl_3 , 300 MHz) spectrum of 11a

^{13}C NMR (CDCl_3 , 300 MHz) spectrum of 12a

^{13}C NMR (CDCl_3 , 300 MHz) spectrum of 14

^{13}C NMR (CDCl₃, 300 MHz) spectrum of **15**

^{13}C NMR (CDCl_3 , 300 MHz) spectrum of 18

^{13}C NMR (CDCl_3 , 300 MHz) spectrum of 23

^{13}C NMR (CDCl_3 , 300 MHz) spectrum of 30

¹³C NMR (CDCl₃, 300 MHz) spectrum of **32**