Photochemical [2+2] Cycloaddition of Acetylene to Chiral 2(5*H*)-Furanones

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Supporting Information

S2 ORTEP diagrams for compounds **3b** and **3e**.

S3-S8 Full assignment of ¹H and ¹³C NMR spectra of compounds **1b**, **3a,b,d,e**, **4a,b,d,e**, **7**, **5b,c**,
6b,c, **8a** and **11a**.

Figure 1. Molecular structure of **3b** (ellipsoids at the 50% level).

Figure 2. Molecular structure of **3e** (ellipsoids at the 50%).

(1*R*,2*S*,5*R*)-menthyl [(5*S*)-2-oxo-2,5-dihydrofuran-5-yl]methyl carbonate (1b)

^1H NMR (400 MHz, CDCl_3) δ 7.44 (dd, $J_{4,3}=5.9$ Hz, $J_{4,5}=1.8$ Hz, 1H, H-4), 6.17 (dd, $J_{3,4}=5.9$ Hz, $J_{3,5}=2.2$ Hz, 1H, H-3), 5.21 (m, 1H, H-5), 4.47 (td, $J_{1',2'}=10.9$ Hz, $J_{1',6'\text{ax}}=10.9$ Hz, $J_{1',6'\text{eq}}=4.5$ Hz, 1H, H-1'), 4.35 (d, $J_{6,5}=4.5$ Hz, 2H, H-6), 2.00 (m, 1H, H-6'eq), 1.86 (m, 1H, H-1''), 1.64 (m, 2H, H-3'eq, H-4'ax), 1.43 (m, 1H, H-5'), 1.36 (m, 1H, H-2'), 1.02 (m, 2H, H-6'ax, H-4'eq), 0.88 (d, $J_{\text{Me},5'}=6.5$ Hz, 3H, CH_3), 0.85 (d, $J_{\text{Me},1''}=7.0$ Hz, 3H, CH_3), 0.84 (m, 1H, H-3'ax), 0.73 (d, $J_{\text{Me},1''}=7.0$ Hz, 3H, CH_3); ^{13}C NMR (62.5 MHz, CDCl_3) δ 172.0 (CO), 154.4 (CO), 152.1 (C-3), 123.4 (C-4), 80.5 (C-2), 79.2 (C-1'), 65.4 (C-1), 46.8 (C-2'), 40.6 (C-6'), 34.0 (C-3'), 31.4 (C-5'), 26.0 (C-1''), 23.3 (C-4'), 21.9 (CH_3), 20.6 (CH_3), 16.3 (CH_3).

(1*R*,4*S*,5*S*)-4-pivaloyloxymethyl-3-oxabicyclo[3.2.0]hept-6-en-2-one (3a)

^1H NMR (400 MHz, CDCl_3) δ 6.35 (dt, $J_{6,7}=2.7$ Hz, $J_{6,5}=0.5$ Hz, $J_{6,4}=0.5$ Hz, 1H, H-6), 6.30 (dd, $J_{7,6}=2.7$ Hz, $J_{7,1}=0.8$ Hz, 1H, H-7), 4.60 (dddd, $J_{4,8}=3.0$ Hz, $J_{4,8}=3.0$ Hz, $J_{4,5}=1.5$ Hz, $J_{4,6}=0.5$ Hz, 1H, H-4), 4.26 (dd, $J_{\text{gem}}=12.0$ Hz, $J_{8,4}=3.0$ Hz, 1H, H-8), 4.12 (dd, $J_{\text{gem}}=12.0$ Hz, $J_{8,4}=3.0$ Hz, 1H, H-8), 3.70 (dd, $J_{1,5}=3.5$ Hz, $J_{1,7}=0.8$ Hz, 1H, H-1), 3.45 (ddd, $J_{5,1}=3.5$ Hz, $J_{5,4}=1.5$ Hz, $J_{5,6}=0.5$ Hz, 1H, H-5), 1.20 (s, 9H, $(\text{CH}_3)_3\text{C}$); ^{13}C NMR (62.5 MHz, CDCl_3) δ 178.0 (CO), 174.6 (CO), 140.7 (C-6/C-7), 139.2 (C-6/C-7), 76.2 (C-4), 65.7 (C-8), 47.6 (C-1), 44.2 (C-5), 38.6 ($(\text{CH}_3)_3\text{C}$), 27.1 ($(\text{CH}_3)_3\text{C}$).

(1*S*,4*S*,5*R*)-4-pivaloyloxymethyl-3-oxabicyclo[3.2.0]hept-6-en-2-one (4a)

^1H NMR (400 MHz, CDCl_3) δ 6.34 (dd, $J_{6,7}=2.7$ Hz, $J_{6,5}=0.9$ Hz, 1H, H-6), 6.28 (dd, $J_{7,6}=2.7$ Hz, $J_{7,1}=0.9$ Hz, 1H, H-7), 4.61 (td, $J_{4,8}=7.2$ Hz, $J_{4,5}=7.2$ Hz, $J_{4,8}=4.8$ Hz, 1H, H-4), 4.30 (dd, $J_{\text{gem}}=11.8$ Hz, $J_{8,4}=4.8$ Hz, 1H, H-8), 4.22 (dd, $J_{\text{gem}}=11.8$ Hz, $J_{8,4}=7.2$ Hz, 1H, H-8), 3.70 (dd, $J_{1,5}=3.6$ Hz, $J_{1,7}=0.9$ Hz, 1H, H-1), 3.65 (ddd, $J_{5,4}=7.2$ Hz, $J_{5,1}=3.6$ Hz, $J_{5,6}=0.9$ Hz, 1H, H-5), 1.20 (s, 9H, $(\text{CH}_3)_3\text{C}$); ^{13}C NMR (62.5 MHz, CDCl_3) δ

178.1 (CO), 174.6 (CO), 139.7 (C-6/C-7), 138.7 (C-6/C-7), 75.3 (C-4), 63.2 (C-8), 47.6 (C-1), 43.4 (C-5), 38.8 ((CH₃)₃C), 27.1 ((CH₃)₃C).

(1R,2S,5R)-menthyl (1R,4S,5S)-2-oxo-3-oxabicyclo[3.2.0]hept-6-en-4-ylmethyl carbonate (3b)

¹H NMR (250 MHz, CDCl₃) δ 6.32 (dd, *J*_{6,7}=2.7 Hz, *J*_{6,5}=0.6 Hz, 1H, H-6), 6.28 (dd, *J*_{7,6}=2.7 Hz, *J*_{7,1}=1.1 Hz, 1H, H-7), 4.56 (td, *J*_{4,8}=3.9 Hz, *J*_{4,5}=1.6 Hz, 1H, H-4), 4.48 (td, *J*_{1',2'}=10.9 Hz, *J*_{1'6'ax}=10.9 Hz, *J*_{1'6'eq}=4.5 Hz, 1H, H-1'), 4.27 (dd, *J*_{gem}=11.6 Hz, *J*_{8,4}=3.9 Hz, 1H, H-8), 4.16 (dd, *J*_{gem}=11.6 Hz, *J*_{8,4}=3.9 Hz, 1H, H-8), 3.67 (dd, *J*_{1,5}=3.4 Hz, *J*_{1,7}=1.1 Hz, 1H, H-1), 3.43 (ddd, *J*_{5,1}=3.4 Hz, *J*_{5,4}=1.6 Hz, *J*_{5,6}=0.6 Hz, 1H, H-5), 2.01 (m, 1H, H-6'eq), 1.89 (m, 1H, H-1''), 1.64 (m, 2H, H-3'eq, H-4'ax), 1.44 (m, 1H, H-5'), 1.38 (m, 1H, H-2'), 1.01 (m, 2H, H-6'ax, H-4'eq), 0.88 (d, *J*_{Me,5'}=6.6 Hz, 3H, CH₃), 0.87 (d, *J*_{Me,1''}=7.2 Hz, 3H, CH₃), 0.84 (m, 1H, H-3'ax), 0.75 (d, *J*_{Me,1''}=7.0 Hz, 3H, CH₃); ¹³C NMR (62.5 MHz, CDCl₃) δ: 174.3 (CO), 154.4 (CO), 140.7 (C-6), 139.2 (C-7), 79.2 (C-1'), 76.1 (C-4), 67.7 (C-8), 47.2 (C-1), 46.8 (C-2'), 44.0 (C-5), 40.6 (C-6'), 34.0 (C-3'), 31.3 (C-5'), 26.1 (C-1''), 23.3 (C-4'), 21.9 (CH₃), 20.6 (CH₃), 16.3 (CH₃).

(1R,2S,5R)-menthyl (1S,4S,5R)-2-oxo-3-oxabicyclo[3.2.0]hept-6-en-4-ylmethyl carbonate (4b)

¹H NMR (250 MHz, CDCl₃) δ 6.34 (dd, *J*_{6,7}=2.7 Hz, *J*_{6,5}=1.0 Hz, 1H, H-6), 6.28 (dd, *J*_{7,6}=2.7 Hz, *J*_{7,1}=0.8 Hz, 1H, H-7), 4.63 (ddd, *J*_{4,8}=6.9 Hz, *J*_{4,5}=6.6 Hz, *J*_{4,8}=5.4 Hz, 1H, H-4), 4.50 (td, *J*_{1',2'}=10.9 Hz, *J*_{1'6'ax}=10.9 Hz, *J*_{1'6'eq}=4.5 Hz, 1H, H-1'), 4.33 (dd, *J*_{gem}=11.6 Hz, *J*_{8,4}=6.9 Hz, 1H, H-8), 4.26 (dd, *J*_{gem}=11.6 Hz, *J*_{8,4}=5.4 Hz, 1H, H-8), 3.69 (m, 1H, H-1), 3.65 (ddd, *J*_{5,4}=6.6 Hz, *J*_{5,1}=3.6 Hz, *J*_{5,6}=1.0 Hz, 1H, H-5), 2.03 (m, 1H, H-6'eq), 1.92 (m, 1H, H-1''), 1.65 (m, 2H, H-3'eq, H-4'ax), 1.44 (m, 1H, H-5'), 1.39 (m, 1H, H-2'), 1.02 (m, 2H, H-6'ax, H-4'eq), 0.89 (d, *J*_{Me,5'}=6.5 Hz, 3H, CH₃), 0.87 (d, *J*_{Me,1''}=7.0 Hz, 3H, CH₃), 0.84 (m,

1H, H-3'ax), 0.76 (d, $J_{\text{Me},1'}=7.0$ Hz, 3H, CH_3); ^{13}C NMR (62.5 MHz, CDCl_3) δ 173.6 (CO), 154.4 (CO), 139.8 (C-6), 138.5 (C-7), 79.1 (C-1'), 74.8 (C-4), 66.1 (C-8), 47.5 (C-1), 46.9 (C-2'), 43.2 (C-5), 40.6 (C-6'), 34.0 (C-3'), 31.3 (C-5'), 26.0 (C-1''), 23.2 (C-4'), 21.9 (CH_3), 20.6 (CH_3), 16.2 (CH_3).

(1R,4S,5S)-4-benzoyloxymethyl-3-oxabicyclo[3.2.0]hept-6-en-2-one (3c)

^1H NMR (400 MHz, CDCl_3) δ 7.98 (m, 2H, H-Ar), 7.55 (m, 1H, H-Ar), 7.42 (m, 2H, H-Ar), 6.37 (dd, $J_{6,7}=2.6$ Hz, $J_{6,5}=0.9$ Hz, 1H, H-6), 6.32 (dd, $J_{7,6}=2.6$ Hz, $J_{7,1}=0.9$ Hz, 1H, H-7), 4.72 (td, $J_{4,8}=3.2$ Hz, $J_{4,8}=3.2$ Hz, $J_{4,5}=1.5$ Hz, 1H, H-4), 4.50 (dd, $J_{\text{gem}}=12.0$ Hz, $J_{8,4}=3.2$ Hz, 1H, H-8), 4.44 (dd, $J_{\text{gem}}=12.0$ Hz, $J_{8,4}=3.2$ Hz, 1H, H-8), 3.72 (dd, $J_{1,5}=3.5$ Hz, $J_{1,7}=0.9$ Hz, 1H, H-1), 3.50 (ddd, $J_{5,1}=3.5$ Hz, $J_{5,4}=1.5$ Hz, $J_{5,6}=0.9$ Hz, 1H, H-5); ^{13}C NMR (62.5 MHz, CDCl_3) δ 174.6 (CO), 166.1 (CO), 140.7/139.2 (C-6/C-7), 133.5/129.6/129.2/128.6 (6C, C-Ar), 76.3 (C-4), 66.0 (C-8), 47.7 (C-1), 44.2 (C-5).

(1S,4S,5R)-4-benzoyloxymethyl-3-oxabicyclo[3.2.0]hept-6-en-2-one (4c)

^1H NMR (400 MHz, CDCl_3) δ 8.03 (m, 2H, H-Ar), 7.56 (m, 1H, H-Ar), 7.44 (m, 2H, H-Ar), 6.37 (d, $J_{6,7}=2.6$ Hz, 1H, H-6), 6.34 (d, $J_{7,6}=2.6$ Hz, 1H, H-7), 4.75 (ddd, $J_{4,8}=7.6$ Hz, $J_{4,5}=5.8$ Hz, $J_{4,8}=4.4$ Hz, 1H, H-4), 4.57 (dd, $J_{\text{gem}}=12.0$ Hz, $J_{8,4}=4.4$ Hz, 1H, H-8), 4.47 (dd, $J_{\text{gem}}=12.0$ Hz, $J_{8,4}=7.6$ Hz, 1H, H-8), 3.74 (m, 1H, H-1), 3.73 (d, $J_{5,1}=3.5$ Hz, 1H, H-5); ^{13}C NMR (62.5 MHz, CDCl_3) δ 173.8 (CO), 166.1 (CO), 139.7/138.7 (C-6/C-7), 133.4/129.7/129.3/128.4 (6C, C-Ar), 75.3 (C-4), 63.7 (C-8), 47.6 (C-1), 43.3 (C-5).

(1R,4S,5S)-5-methyl-4-pivaloyloxymethyl-3-oxabicyclo[3.2.0]hept-6-en-2-one (3e)

^1H NMR (400 MHz, CDCl_3) δ 6.38 (dd, $J_{6,7}=2.6$ Hz, $J_{6,1}=1.2$ Hz, 1H, H-6), 6.30 (dd, $J_{7,6}=2.6$ Hz, $J_{7,1}=0.8$ Hz, 1H, H-7), 4.54 (dd, $J_{4,8}=3.0$ Hz, $J_{4,8}=2.3$ Hz, 1H, H-4), 4.38 (dd, $J_{\text{gem}}=12.2$ Hz, $J_{8,4}=3.0$ Hz, 1H, H-8), 4.09 (dd, $J_{\text{gem}}=12.2$ Hz, $J_{8,4}=2.3$ Hz, 1H, H-8), 3.25 (s, 1H, H-1), 1.42 (s, 3H, CH_3), 1.18 (s, 9H, $(\text{CH}_3)_3\text{C}$); ^{13}C NMR (62.5 MHz, CDCl_3) δ 177.7 (CO), 175.3 (CO), 146.1 (C-6), 137.2 (C-7), 78.3 (C-4), 63.5 (C-8), 52.8 (C-1), 50.4 (C-5), 38.7 ($(\text{CH}_3)_3\text{C}$), 27.0 ($(\text{CH}_3)_3\text{C}$), 16.4 (CH_3 , CH_3).

(1*S*,4*S*,5*R*)-5-methy-4-pivaloyloxymethyl-3-oxabicyclo[3.2.0]hept-6-en-2-one (4e)

¹H NMR (250 MHz, CDCl₃) δ 6.33 (dd, $J_{6,7}$ =2.8 Hz, $J_{6,1}$ =0.9 Hz, 1H, H-6), 6.30 (dd, $J_{7,6}$ =2.8 Hz, $J_{7,1}$ =0.7 Hz, 1H, H-7), 4.33 (dd, $J_{4,8}$ =7.4 Hz, $J_{4,8}$ =4.7 Hz, 1H, H-4), 4.25 (dd, J_{gem} =11.7 Hz, $J_{8,4}$ =4.7 Hz, 1H, H-8), 4.19 (dd, J_{gem} =11.7 Hz, $J_{8,4}$ =7.4 Hz, 1H, H-8), 3.24 (s, 1H, H-1), 1.49 (s, 3H, CH₃), 1.21 (s, 9H, (CH₃)₃); ¹³C NMR (62.5 MHz, CDCl₃) δ 178.1 (CO), 174.1 (CO), 142.9 (C-7), 137.3 (C-6), 80.4 (C-4), 62.8 (C-8), 53.0 (C-1), 50.7 (C-5), 38.6 ((CH₃)₃C), 27.0 ((CH₃)₃C), 20.1 (CH₃).

(5*S*)-4-methyl-5-pivaloyloxymethyl-3-vinyl-2(5*H*)-furanone (7)

¹H NMR (250 MHz, CDCl₃) δ 6.37 (dd, $J_{1',2'b}$ =17.3 Hz, $J_{1',2'a}$ =10.4 Hz, 1H, H-1'), 6.26 (dd, $J_{2'b,1'}$ =17.3 Hz, J_{gem} =2.8 Hz, 1H, H-2'b), 5.48 (dd, $J_{2'a,1}$ =10.4 Hz, J_{gem} =2.8 Hz, 1H, H-2'a), 4.90 (dd, $J_{5,6}$ =4.0 Hz, $J_{5,6}$ =3.0 Hz, 1H, H-5), 4.40 (dd, J_{gem} =12.2 Hz, $J_{6,5}$ =3.0 Hz, 1H, H-6), 4.33 (dd, J_{gem} =12.2 Hz, $J_{6,5}$ =4.0 Hz, 1H, H-6), 2.06 (s, 3H, CH₃), 1.16 (s, 9H, (CH₃)₃C); ¹³C NMR (62.5 MHz, CDCl₃) δ 177.9 (CO), 171.2 (CO), 155.9 (C-4), 125.1 (C-3), 123.7 (C-1'), 121.2 (C-2'), 80.2 (C-5), 61.4 (C-6), 38.8 ((CH₃)₃C), 27.0 ((CH₃)₃C), 12.0 (CH₃).

(1*R*,2*S*,5*R*)-menthyl [(1*R*,4*S*,5*S*)-2-oxo-3-oxabicyclo[3.2.0]hept-4-yl]methyl carbonate (5b)

¹H NMR (400 MHz, CDCl₃) δ 4.53 (td, $J_{4,8}$ =3.8 Hz, $J_{4,8}$ =3.8 Hz, $J_{4,5}$ =0.8 Hz, 1H, H-4), 4.47 (td, $J_{1',2'}$ =10.9 Hz, $J_{1',6'ax}$ =10.9 Hz, $J_{1',6'eq}$ =4.5 Hz, 1H, H-1'), 4.21 (dd, J_{gem} =11.7 Hz, $J_{8,4}$ =3.8 Hz, 1H, H-8), 4.12 (dd, J_{gem} =11.7 Hz, $J_{8,4}$ =3.8 Hz, 1H, H-8), 3.13 (dddd, J =10.0 Hz, J =6.4 Hz, J =2.0 Hz, J =2.0 Hz, 1H, H-1), 3.02 (m, 1H, H-5), 2.53 (m, 1H, H-7), 2.39 (m, 1H, H-6), 2.14 (m, 2H, H-7, H-6), 2.02 (m, 1H, H-6'eq), 1.89 (m, 1H, H-1''), 1.65 (m, 2H, H-3'eq, H-4'ax), 1.43 (m, 1H, H-5'), 1.37 (m, 1H, H-2'), 1.02 (m, 2H, H-6'ax, H-4'eq), 0.89 (d, $J_{\text{Me},5'}$ =6.5 Hz, 3H, CH₃), 0.88 (d, $J_{\text{Me},1''}$ =7.0 Hz, 3H, CH₃), 0.88 (m, 1H, H-3'ax), 0.76 (d, $J_{\text{Me},1''}$ =7.0 Hz, 3H, CH₃); ¹³C NMR (62.5 MHz, CDCl₃) δ 179.7 (CO), 154.5 (CO), 82.2 (C-4), 79.1 (C-1'), 67.9 (C-8), 46.9 (C-2'), 40.5 (C-6'), 38.7 (C-1), 36.4 (C-5), 34.0 (C-3'), 31.4 (C-5'), 26.1 (C-1''), 24.8 (C-6), 23.6 (C-7), 23.3 (C-4'), 21.9 (CH₃), 20.6 (CH₃), 16.3 (CH₃).

(1R,2S,5R)-menthyl [(1S,4S,5R)-2-oxo-3-oxabicyclo[3.2.0]hept-4-yl]methyl carbonate (6b)

^1H NMR (400 MHz, CDCl_3) δ 4.63 (ddd, $J_{4,8}=7.3$ Hz, $J_{4,5}=5.9$ Hz, $J_{4,8}=4.7$ Hz, 1H, H-4), 4.52 (td, $J_{1',2'}=10.9$ Hz, $J_{1',6'\text{ax}}=10.9$ Hz, $J_{1',6'\text{eq}}=4.4$ Hz, 1H, H-1'), 4.40 (dd, $J_{\text{gem}}=11.7$ Hz, $J_{8,4}=7.3$ Hz, 1H, H-8), 4.23 (dd, $J_{\text{gem}}=11.7$ Hz, $J_{8,4}=4.7$ Hz, 1H, H-8), 3.24 (m, 1H, H-5), 3.14 (m, 1H, H-1), 2.51 (m, 1H, H-7), 2.26 (m, 1H, H-6), 2.11 (m, 2H, H-7, H-6), 2.03 (m, 1H, H-6'eq), 1.93 (m, 1H, H-1''), 1.66 (m, 2H, H-3'eq, H-4'ax), 1.45 (m, 1H, H-5'), 1.39 (m, 1H, H-2'), 1.03 (m, 2H, H-6'ax, H-4'eq), 0.90 (d, $J_{\text{Me},5'}=6.5$ Hz, 3H, CH_3), 0.88 (d, $J_{\text{Me},1''}=7.0$ Hz, 3H, CH_3), 0.88 (m, 1H, H-3'ax), 0.77 (d, $J_{\text{Me},1''}=7.0$ Hz, 3H, CH_3); ^{13}C NMR (62.5 MHz, CDCl_3) δ 179.3 (CO), 154.5 (CO), 79.1 (C-1'), 78.2 (C-4), 65.8 (C-8), 47.0 (C-2'), 40.7 (C-6'), 39.7 (C-1), 36.5 (C-5), 34.0 (C-3'), 31.4 (C-5'), 26.0 (C-1''), 23.3 (C-4'), 23.2 (C-7), 21.9 (CH_3), 20.7 (CH_3), 19.4 (C-6), 16.2 (CH_3).

(1R,4S,5S)-4-benzoyloxymethyl-3-oxabicyclo[3.2.0]heptan-2-one (5c)

^1H NMR (400 MHz, CDCl_3) δ 7.95 (m, 2H, H-Ar), 7.55 (m, 1H, H-Ar), 7.42 (m, 2H, H-Ar), 4.67 (ddd, $J_{4,8}=3.8$ Hz, $J_{4,8}=3.2$ Hz, $J_{4,5}=1.0$ Hz, 1H, H-4), 4.44 (dd, $J_{\text{gem}}=12.2$ Hz, $J_{8,4}=3.8$ Hz, 1H, H-8), 4.38 (dd, $J_{\text{gem}}=12.2$ Hz, $J_{8,4}=3.2$ Hz, 1H, H-8), 3.17 (m, 1H, H-1), 3.08 (m, 1H, H-5), 2.56 (m, 1H, H-7), 2.42 (m, 1H, H-6), 2.18 (m, 2H, H-6, H-7); ^{13}C NMR (62.5 MHz, CDCl_3) δ 179.9 (CO), 166.1 (CO), 133.4/129.6/129.1/128.6 (6C, C-Ar), 82.7 (C-4), 65.7 (C-8), 38.9 (C-1), 36.6 (C-5), 24.8 (C-6), 23.7 (C-7).

(1S,4S,5R)-4-benzoyloxymethyl-3-oxabicyclo[3.2.0]heptan-2-one (6c)

^1H NMR (400 MHz, CDCl_3) δ 8.02 (m, 2H, H-Ar), 7.60 (m, 1H, H-Ar), 7.44 (m, 2H, H-Ar), 4.76 (ddd, $J_{4,8}=7.0$ Hz, $J_{4,5}=5.9$ Hz, $J_{4,8}=4.7$ Hz, 1H, H-4), 4.54 (dd, $J_{\text{gem}}=12.0$ Hz, $J_{8,4}=7.0$ Hz, 1H, H-8), 4.51 (dd, $J_{\text{gem}}=12.0$ Hz, $J_{8,4}=4.7$ Hz, 1H, H-8), 3.31 (m, 1H, H-5), 3.17 (m, 1H, H-1), 2.54 (m, 1H, H-7), 2.34 (m, 1H, H-6), 2.15 (m, 2H, H-7, H-6); ^{13}C NMR (62.5 MHz, CDCl_3) δ 179.5 (CO), 166.2 (CO), 133.4/129.7/129.3/128.5 (6C, C-Ar), 78.7 (C-4), 63.5 (C-8), 39.8 (C-1), 36.6 (C-5), 23.3 (C-7), 19.5 (C-6).

(1*R*,1'*R*,4*S*,4'*S*,5*S*,5'*S*)-4,4'-[(1*R*,2*R*)-1,2-bis(trimethylsilyloxy)ethane-1,2-diyl]bis[3-oxabicyclo[3.2.0]hept-6-en-2-one] (8a)

^1H NMR (250 MHz, CDCl_3) δ 6.43 (dt, $J_{6,7}=2.7$ Hz, $J_{6,5}=0.8$ Hz, $J_{6,4}=0.8$ Hz, 2H, H-6), 6.21 (dd, $J_{7,6}=2.7$ Hz, $J_{7,1}=0.7$ Hz, 2H, H-7), 4.58 (ddd, $J_{4,8}=3.2$ Hz, $J_{4,5}=1.5$ Hz, $J_{4,6}=0.7$ Hz, 2H, H-4), 3.54 (dd, $J_{8,4}=3.2$ Hz, $J_{8,5}=1.0$ Hz, 2H, H-8), 3.50 (m, 4H, H-1, H-5), 0.15 (s, 18H, $(\text{CH}_3)_3\text{Si}$); ^{13}C NMR (62.5 MHz, CDCl_3) δ 174.9 (CO), 141.8 (C-6/C-7), 137.9 (C-6/C-7), 78.6 (C-4), 76.4 (C-8), 46.9 (C-5/C-1), 44.2 (C-5/C-1), 0.13 ($(\text{CH}_3)_3\text{Si}$).

(1*R*,1'*R*,4*S*,4'*S*,5*S*,5'*S*)-4,4'-[(1*R*,2*R*)-1,2-dihidroxyethane-1,2-diyl]bis[3-oxabicyclo[3.2.0]hept-6-en-2-one] (11a)

^1H NMR (acetone- d_6) δ 6.49 (dt, $J_{6,7}=2.7$ Hz, $J_{6,5}=0.8$ Hz, $J_{6,1}=0.8$ Hz, 2H, H-6), 6.29 (dd, $J_{7,6}=2.7$ Hz, $J_{7,1}=0.8$ Hz, 2H, H-7), 4.62 (dd, $J_{4,5}=1.4$ Hz, $J_{4,8}=0.7$ Hz, 2H, H-4), 3.73 (s, 2H, H-8), 3.66 (ddd, $J_{5,1}=3.4$ Hz, $J_{5,4}=1.4$ Hz, $J_{5,6}=0.8$ Hz, 2H, H-5), 3.57 (dd, $J_{1,5}=3.4$ Hz, $J_{1,7}=0.8$ Hz, 2H, H-1), 2.81 (m, 2H, OH); ^{13}C NMR (acetone- d_6) δ 174.3 (CO), 142.3 (C-6/C-7), 138.7 (C-6/C-7), 77.6 (C-4), 74.1 (C-8), 47.8 (C-5/C-1), 45.7 (C-5/C-1).