

## SUPPLEMENTARY MATERIAL

**General methods.** All reactions were run under N<sub>2</sub> atmosphere. Tetrahydrofuran (THF) was dried and distilled by the standard procedure before use. Solvents used in column chromatography were distilled prior to use. All other reagents used in the reactions were of the best commercial grade available. Column chromatography was carried out on silica gel 60 (230-400 mesh). All melting points were uncorrected. NMR spectra were recorded at 400, 300 or 200 MHz for <sup>1</sup>H and 100, 75, or 50.3 MHz for <sup>13</sup>C, with tetramethylsilane as internal standard for <sup>1</sup>H and the residual solvent signals as standard for <sup>13</sup>C. Chemical shifts are given in ppm. Mass spectra were obtained by EI (70 eV). IR spectra are given in cm<sup>-1</sup>.

**General procedure for the preparation of alkynyl carbene complexes 2.** Fischer carbene complexes were prepared by treatment of a 0.5 M solution of the corresponding acetylene in THF with n-butyllithium (1.1 eq.) in the presence of the metal hexacarbonyl (1 eq.) at -78° C. The mixture was stirred overnight and the metal acylate so formed was subsequently alkylated with methyl triflate (2 eq.) at -40° C. The reaction was then quenched with a saturated solution of Na<sub>2</sub>CO<sub>3</sub> and the aqueous layer was extracted twice with diethylether. The complexes **2** were purified by flash chromatography in hexane and recrystallized, when solids, in hexane at -20° C. The starting acetylenes were in turn prepared according to the Corey-Fuchs method<sup>1</sup> or by dehydration of the corresponding propargylic alcohols.<sup>2</sup> The preparation of most of the alkynyl carbene complexes **2** has already been reported.<sup>4</sup>

**General procedure for the reaction of enol ethers 5 with alkynyl carbene complexes 2.** Compounds **6** were prepared by reaction of 1 mmol of carbene neat with 10 mmol of the corresponding enol ether at rt, under nitrogen atmosphere. The progress of the reactions was followed by TLC. When the starting complex was consumed, the volatiles were removed by high vacuum (0.1 mm Hg). Flash chromatography of the crude reaction afforded the title compounds.

**Pentacarbonyl{[2,3,3a,5a-tetrahydro-4-(1-methyl-2-phenylethenyl)cyclobuta[b]furan-5-yl]methoxymethylene}tungsten(0) (6a).** It was prepared from **2a** according to the general procedure described above to afford, after flash chromatography with hexane:ether:dichloromethane (6:1:1), 0.37 g (0.64 mmol) of **6a** in 64% yield as a dark orange solid; m.p.= 92-94°C; <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>) δ 1.82-2.07 (m, 2H), 1.93 (s, 3H), 3.54 (dd, *J* = 7.7, 3.8 Hz, 1H), 3.90 (td, *J* = 8.9, 5.6 Hz, 1H), 4.17 (t, *J* = 7.9 Hz, 1H), 4.62 (s, 3H), 5.57 (d, *J* = 3.8 Hz, 1H), 6.92 (br s, 1H), 7.32-7.41 (m, 5H); <sup>13</sup>C NMR (50.3 MHz, CDCl<sub>3</sub>) δ 16.6 (CH<sub>3</sub>), 27.4 (CH<sub>2</sub>), 43.9 (CH), 66.6 (CH<sub>2</sub>), 68.2 (CH<sub>3</sub>), 79.1 (CH), 127.9 (CH), 128.3 (CH), 129.4 (CH), 131.2 (C), 136.2 (CH), 136.7 (C), 143.7 (C), 151.2 (C), 196.9 (C), 203.4 (C), 310.7 (C); IR (CH<sub>2</sub>Cl<sub>2</sub>) ν = 2066, 1937 cm<sup>-1</sup>. Anal. Calcd for C<sub>22</sub>H<sub>18</sub>O<sub>7</sub>W: C, 45.67; H, 3.14. Found: C, 45.42; H, 3.28.

**Pentacarbonyl{[4-(1-cyclopentenyl)-2,3,3a,5a-tetrahydrocyclobuta[b]furan-5-yl]methoxymethylene}tungsten(0) (6b).** It was prepared from **2b** according to the general procedure described above to afford, after flash chromatography with hexane:ether:dichloromethane (6:1:1), 0.45 g (0.85 mmol) of **6b** in 85% yield as a red solid; m.p.= 113-115°C; <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>) δ 1.70-2.04 (m, 4H), 2.28-2.53 (m, 4H), 3.31 (dd, *J* = 7.9, 3.6 Hz, 1H), 3.77-3.90 (m, 1H), 4.11 (t, *J* = 7.4 Hz, 1H), 4.56 (s, 3H), 5.54 (d, *J* = 3.6 Hz, 1H), 6.51 (m, 1H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 23.6 (CH<sub>2</sub>), 26.9 (CH<sub>2</sub>), 33.3 (CH<sub>2</sub>), 33.4 (CH<sub>2</sub>), 44.5 (CH), 66.2 (CH<sub>2</sub>), 68.0 (CH<sub>3</sub>), 80.0 (CH), 139.1 (C), 141.3 (C), 144.4 (CH), 148.4 (C), 197.2 (C), 203.2 (C), 305.6 (C); IR (CH<sub>2</sub>Cl<sub>2</sub>) ν = 2060, 1939 cm<sup>-1</sup>. Anal. Calcd for C<sub>18</sub>H<sub>16</sub>O<sub>7</sub>W: C, 40.91; H, 3.05. Found: C, 40.72; H, 2.97.

**Pentacarbonyl{[4-(1-cyclopentenyl)-2,3,3a,5a-tetrahydrocyclobuta[b]furan-5-yl]methoxymethylene}chromium(0) (6c).** It was prepared from **2c** according to the general procedure described above to afford, after flash chromatography with hexane:ether:dichloromethane (6:1:1), 0.37 g (0.93 mmol) of **6c** in 93% yield as a red solid; m.p.= 89-91°C; <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>) δ 1.72-2.03 (m, 4H), 2.19-2.49 (m, 4H), 3.40 (dd, *J* = 7.9, 3.3 Hz, 1H), 3.75-3.91 (m, 1H), 4.13 (t, *J* = 8.2 Hz, 1H), 4.73 (s, 3H), 5.61 (d, *J* = 3.3 Hz, 1H), 6.37 (m, 1H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 23.6 (CH<sub>2</sub>), 27.1 (CH<sub>2</sub>), 33.1 (CH<sub>2</sub>), 33.2 (CH<sub>2</sub>), 44.1 (CH), 65.5 (CH<sub>3</sub>), 66.5 (CH<sub>2</sub>), 80.1 (CH), 136.9 (C), 138.4 (C), 142.9 (CH), 146.1 (C), 216.2 (C), 223.8 (C), 334.3 (C); IR (CH<sub>2</sub>Cl<sub>2</sub>) ν = 2057, 1942 cm<sup>-1</sup>. Anal. Calcd for C<sub>18</sub>H<sub>16</sub>O<sub>7</sub>Cr: C, 54.54; H, 4.07. Found: C, 59.48; H, 4.18.

**Pentacarbonyl{[4-(1-cyclohexenyl)-2,3,3a,5a-tetrahydrocyclobuta[b]furan-5-yl]methoxymethylene}chromium(0) (6d).** It was prepared from **2d** according to the general procedure described above to afford, after flash chromatography with hexane:ether:dichloromethane (6:1:1), 0.24 g (0.58 mmol) of **6d** in 58% yield as a red oil; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 1.56-2.05 (m, 8H), 2.15-2.26 (m, 2H), 3.30-3.40 (m, 1H), 3.72-3.83 (m, 1H), 4.10 (t, *J* = 4.9 Hz, 1H), 4.64 (s, 3H), 5.51-5.53 (m, 1H), 6.21 (m, 1H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 21.4 (CH<sub>2</sub>), 22.2 (CH<sub>2</sub>), 26.2 (CH<sub>2</sub>), 26.3 (CH<sub>2</sub>), 27.4 (CH<sub>2</sub>), 43.2

<sup>1</sup> Corey, E. J.; Fusch, P. L. *Tetrahedron Lett.* **1972**, 3769.

<sup>2</sup> Brandsma, L. in *Preparative Acetylenic Chemistry*, Elsevier Science Publishers B. V., **1988**.

(CH), 65.6 (CH<sub>3</sub>), 66.8 (CH<sub>2</sub>), 79.6 (CH), 132.2 (C), 136.7 (CH), 139.3 (C), 145.8 (C), 216.1 (C), 223.8 (C), 339.0 (C); IR (CH<sub>2</sub>Cl<sub>2</sub>)  $\nu$  = 2056, 1938 cm<sup>-1</sup>. Anal. Calcd for C<sub>19</sub>H<sub>18</sub>CrO<sub>7</sub>: C, 55.60; H, 4.42. Found: C, 55.42; H, 4.58.

**Pentacarbonyl{[3,4,4a,6a-tetrahydro-5-(1-methylethenyl)-2H-cyclobuta[b]pyran-6-yl]methoxymethylene}tungsten(0) (6e).** It was prepared from **2e** according to the general procedure described above to afford, after flash chromatography with hexane:ether:dichloromethane (6:1:1), 0.41 g (0.79 mmol) of **6e** in 79% yield as a red solid; m.p. = 84-86°C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  1.54-1.82 (m, 3H), 1.75 (s, 3H), 2.04-2.14 (m, 1H), 2.95 (td,  $J$  = 4.8, 4.8 Hz, 1H), 3.68-3.84 (m, 2H), 4.59 (s, 3H), 5.10 (d,  $J$  = 4.8 Hz, 1H), 5.29 (br s, 2H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  20.4 (CH<sub>2</sub>), 20.6 (CH<sub>3</sub>), 38.1 (CH), 62.3 (CH<sub>2</sub>), 68.4 (CH<sub>3</sub>), 71.1 (CH), 122.2 (CH<sub>2</sub>), 138.3 (C), 144.2 (C), 154.9 (C), 196.7 (C), 203.4 (C), 311.9 (C); IR (CH<sub>2</sub>Cl<sub>2</sub>)  $\nu$  = 2068, 1939 cm<sup>-1</sup>. Anal. Calcd for C<sub>17</sub>H<sub>16</sub>O<sub>7</sub>W: C, 39.53; H, 3.12. Found: C, 39.70; H, 3.01.

**Pentacarbonyl{[3,4,4a,6a-tetrahydro-5-(1-methyl-2-phenylethenyl)-2H-cyclobuta[b]pyran-6-yl]methoxymethylene}chromium(0) (6f).** It was prepared from **2f** according to the general procedure described above to afford, after flash chromatography with hexane:ether:dichloromethane (6:1:1), 0.18 g (0.40 mmol) of **6f** in 40% yield as a dark red solid; m.p. = 113-115°C; <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>)  $\delta$  1.67-1.89 (m, 2H), 1.89 (s, 3H), 2.06-2.33 (m, 2H), 3.14 (td,  $J$  = 6.9, 4.6 Hz, 1H), 3.73-3.87 (m, 2H), 4.70 (s, 3H), 5.21 (d,  $J$  = 4.6 Hz, 1H), 6.69 (br s, 1H), 7.17-7.40 (m, 5H); <sup>13</sup>C NMR (50.3 MHz, CDCl<sub>3</sub>)  $\delta$  16.1 (CH<sub>3</sub>), 20.7 (CH<sub>2</sub>), 24.3 (CH<sub>2</sub>), 37.8 (CH), 62.8 (CH<sub>2</sub>), 65.8 (CH<sub>3</sub>), 71.5 (CH), 128.7 (CH), 128.3 (CH), 129.4 (CH), 131.1 (C), 135.1 (CH), 136.4 (C), 142.7 (C), 150.9 (C), 216.0 (C), 224.0 (C), 341.3 (C); IR (CH<sub>2</sub>Cl<sub>2</sub>)  $\nu$  = 2058, 1939 cm<sup>-1</sup>. Anal. Calcd for C<sub>23</sub>H<sub>20</sub>CrO<sub>7</sub>: C, 59.99; H, 4.38. Found: C, 60.02; H, 4.44.

**Pentacarbonyl{[3,4,4a,6a-tetrahydro-5-(2-phenylethenyl)-2H-cyclobuta[b]pyran-6-yl]methoxymethylene}chromium(0) (6g).** It was prepared from **2g** according to the general procedure described above to afford, after flash chromatography with hexane:ethyl acetate (5:1), 0.20 g (0.45 mmol) of **6g** in 45% yield as a dark red solid; m.p. = 110-112°C; <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>)  $\delta$  1.60-1.75 (m, 2H), 1.76-1.96 (m, 1H), 2.21-2.30 (m, 1H), 3.14 (td,  $J$  = 6.8, 4.9 Hz, 1H), 3.73-3.91 (m, 2H), 4.84 (s, 3H), 5.15 (d,  $J$  = 4.9 Hz, 1H), 7.01 (d,  $J$  = 16.2 Hz, 1H), 7.25 (d,  $J$  = 16.2 Hz, 1H), 7.39-7.47 (m, 3H), 7.51-7.56 (m, 2H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  20.7 (CH<sub>2</sub>), 23.6 (CH<sub>2</sub>), 37.2 (CH), 62.2 (CH<sub>2</sub>), 65.7 (CH<sub>3</sub>), 71.4 (CH), 121.9 (CH), 127.6 (CH), 128.9 (CH), 129.9 (CH), 135.6 (C), 142.8 (CH), 148.7 (C), 149.8 (C), 216.5 (C), 224.2 (C), 329.9 (C); IR (CH<sub>2</sub>Cl<sub>2</sub>)  $\nu$  = 2056, 1941 cm<sup>-1</sup>. Anal. Calcd for C<sub>22</sub>H<sub>18</sub>CrO<sub>7</sub>: C, 59.19; H, 4.07. Found: C, 59.29; H, 4.24.

**Pentacarbonyl{[5-(1-cyclopentenyl)-3,4,4a,6a-tetrahydro-2H-cyclobuta[b]pyran-6-yl]methoxymethylene}tungsten(0) (6h).** It was prepared from **2h** according to the general procedure described above to afford, after flash chromatography with hexane:ether:dichloromethane (4:1:1), 0.29 g (0.53 mmol) of **6h** in 53% yield as a dark red solid; m.p. = 93-95°C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  1.56-1.80 (m, 3H), 1.89-2.02 (m, 2H), 2.05-2.13 (m, 1H), 2.26-2.28 (m, 1H), 2.42-2.43 (m, 2H), 2.48-2.54 (m, 1H), 2.87 (td,  $J$  = 6.6, 5.0 Hz, 1H), 3.70-3.76 (m, 1H), 3.78-3.84 (m, 1H), 4.57 (s, 3H), 5.11 (d,  $J$  = 5.0 Hz, 1H), 6.38 (m, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  20.5 (CH<sub>2</sub>), 23.4 (CH<sub>2</sub>), 23.5 (CH<sub>2</sub>), 33.4 (CH<sub>2</sub>), 38.8 (CH), 62.0 (CH<sub>2</sub>), 67.9 (CH<sub>3</sub>), 71.6 (CH), 139.5 (C), 143.7 (CH), 144.7 (C), 152.2 (C), 197.2 (C), 203.3 (C), 305.4 (C); IR (THF)  $\nu$  = 2065, 1935 cm<sup>-1</sup>. Anal. Calcd for C<sub>19</sub>H<sub>18</sub>O<sub>7</sub>W: C, 42.06; H, 3.35. Found: C, 42.18; H, 3.48.

**Pentacarbonyl{[5-(1-cyclopentenyl)-3,4,4a,6a-tetrahydro-2H-cyclobuta[b]pyran-6-yl]methoxymethylene}chromium(0) (6i).** It was prepared from **2i** according to the general procedure described above to afford, after flash chromatography with hexane:ethyl acetate (5:1), 0.31 g (0.75 mmol) of **6i** in 75% yield as a red solid; m.p. = 85-87°C; <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>)  $\delta$  1.61-2.50 (m, 10H), 2.96 (td,  $J$  = 6.7, 4.6 Hz, 1H), 3.73-3.85 (m, 2H), 4.73 (s, 3H), 5.19 (d,  $J$  = 4.6, 1H), 6.24 (m, 1H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  20.5 (CH<sub>2</sub>), 23.6 (CH<sub>2</sub>), 33.1 (CH<sub>2</sub>), 33.3 (CH<sub>2</sub>), 38.3 (CH), 62.3 (CH<sub>2</sub>), 65.6 (CH<sub>3</sub>), 71.9 (CH), 138.7 (C), 139.7 (C), 141.8 (CH), 149.9 (C), 216.2 (C), 223.9 (C), 335.2 (C); IR (THF)  $\nu$  = 2058, 1939 cm<sup>-1</sup>. Anal. Calcd for C<sub>19</sub>H<sub>18</sub>CrO<sub>7</sub>: C, 55.60; H, 4.42. Found: C, 55.42; H, 4.58.

**Pentacarbonyl{[5-(1-cyclohexenyl)-3,4,4a,6a-tetrahydro-2H-cyclobuta[b]pyran-6-yl]methoxymethylene}chromium(0) (6j).** It was prepared from **2j** according to the general procedure described above to afford, after flash chromatography with hexane:ether:dichloromethane (6:1:1), 0.17 g (0.40 mmol) of **6j** in 40% yield as a red oil; <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>)  $\delta$  1.56-1.80 (m, 8H), 1.97-2.19 (m, 4H), 2.96 (td,  $J$  = 6.3, 4.6 Hz, 1H), 3.72-3.80 (m, 2H), 4.65 (s, 3H), 5.11 (d,  $J$  = 4.6, 1H), 6.07 (m, 1H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  20.6 (CH<sub>2</sub>), 21.4 (CH<sub>2</sub>), 24.2 (CH<sub>2</sub>), 26.1 (CH<sub>2</sub>), 26.2 (CH<sub>2</sub>), 37.6 (CH), 62.5 (CH<sub>2</sub>), 65.6 (CH<sub>3</sub>), 71.4 (CH), 132.7 (C), 135.9 (CH), 142.2 (C), 148.9 (C), 216.2 (C), 224.0 (C), 339.9 (C); IR (CH<sub>2</sub>Cl<sub>2</sub>)  $\nu$  = 2065, 1941 cm<sup>-1</sup>. Anal. Calcd for C<sub>20</sub>H<sub>20</sub>CrO<sub>7</sub>: C, 56.60; H, 4.75. Found: C, 56.48; H, 4.62.

**Pentacarbonyl{[3,4,4a,6a-tetrahydro-5-(1-methyl-3-(2-propenyloxy)-1-propenyl)-2H-cyclobuta[b]pyran-6-yl]methoxymethylene}chromium(0) (6k).** It was prepared from **2k** according to the general procedure described above to afford, after flash chromatography with hexane:ether:dichloromethane (6:1:1), 0.36 g (0.79 mmol) of **6k** in 79% yield as an

orange oil;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  1.45-1.85 (m, 3H), 1.60 (s, 3H), 2.10-2.20 (m, 2H), 2.95-3.05 (m, 1H), 3.74-3.78 (m, 2H), 3.97-4.02 (m, 2H), 4.10-4.15 (m, 2H), 4.64 (s, 3H), 5.05-5.13 (m, 1H), 5.15-5.39 (m, 2H), 5.78-6.01 (m, 2H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  14.4 ( $\text{CH}_3$ ), 20.6 ( $\text{CH}_2$ ), 24.0 ( $\text{CH}_2$ ), 37.6 ( $\text{CH}$ ), 62.7 ( $\text{CH}_2$ ), 65.8 ( $\text{CH}_3$ ), 66.6 ( $\text{CH}_2$ ), 71.4 ( $\text{CH}$ ), 71.6 ( $\text{CH}_2$ ), 117.5 ( $\text{CH}_2$ ), 131.6 (C), 133.0 ( $\text{CH}$ ), 134.3 ( $\text{CH}$ ), 140.9 (C), 150.8 (C), 215.9 (C), 223.9 (C), 341.9 (C); IR ( $\text{CH}_2\text{Cl}_2$ )  $\nu$  = 2064, 1935  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{21}\text{H}_{22}\text{CrO}_8$ : C, 55.50; H, 4.88. Found: C, 55.41; H, 4.78.

**General procedure for the preparation of polycycles 8.** A solution of complex **6** (0.5 mmol) in THF (25 mL) was refluxed under a nitrogen purge. The reaction was stopped when TLC revealed total consumption of the starting material. For reactions arising from chromium complexes, addition of hexane (50 mL) and exposure to sun light and air for 12 h, followed by flash chromatography afforded the title compounds. For tungsten complexes, the residue was loaded directly onto a silica gel column without exposure to light and air.

**2,3,3a,7b-Tetrahydro-7-methoxy-4-methyl-5-phenylbenzo[3,4]cyclobuta[1,2-*b*]furan-6-ol (8a).** It was prepared from **6a** according to the general procedure described above to afford, after flash chromatography with hexane:ether:dichloromethane (4:1:1), 125 mg (0.45 mmol) of **8a** in 89% yield as a light yellow solid; m.p. = 137-139°C; m.p. = 85-87°C;  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  1.74-2.00 (m, 2H), 1.91 (s, 3H), 3.72-3.85 (m, 1H), 4.04 (dd,  $J$  = 7.6, 3.5 Hz, 1H), 4.10 (s, 3H), 4.16 (t,  $J$  = 7.2 Hz, 1H), 5.32 (s, 1H), 5.64 (d,  $J$  = 3.5 Hz, 1H), 7.26-7.52 (m, 5H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  14.4 ( $\text{CH}_3$ ), 28.6 ( $\text{CH}_2$ ), 47.6 ( $\text{CH}$ ), 58.0 ( $\text{CH}_3$ ), 70.0 ( $\text{CH}$ ), 123.4 (C), 124.3 (C), 127.1 ( $\text{CH}$ ), 128.3 ( $\text{CH}$ ), 129.8 ( $\text{CH}$ ), 130.4 (C), 134.0 (C), 136.5 (C), 139.9 (C), 141.8 (C). Anal. Calcd for  $\text{C}_{18}\text{H}_{18}\text{O}_3$ : C, 76.56; H, 6.43. Found: C, 76.29; H, 6.36.

**2,3,5b,7,8,8a-Hexahydro-5-methoxy-1H-indeno[4',5':3,4]cyclobuta[1,2-*b*]furan-4-ol (8b).** It was prepared from **6b** according to the general procedure described above to afford, after flash chromatography with hexane:ether:dichloromethane (6:1:1), 89 mg (0.39 mmol) of **8b** in 77% yield as a white solid; m.p. = 155-157°C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.70-1.88 (m, 2H), 2.09 (hept,  $J$  = 7.2 Hz, 2H), 2.71 (t,  $J$  = 7.2 Hz, 2H), 2.83 (t,  $J$  = 7.2 Hz, 2H), 3.63-3.70 (m, 1H), 3.93 (dd,  $J$  = 7.8, 3.6 Hz, 1H), 4.01 (s, 3H), 4.10 (t,  $J$  = 8.0 Hz, 1H), 5.44 (s, 1H), 5.58 (d,  $J$  = 3.6 Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  26.0 ( $\text{CH}_2$ ), 28.8 ( $\text{CH}_2$ ), 28.9 ( $\text{CH}_2$ ), 29.4 ( $\text{CH}_2$ ), 47.7 ( $\text{CH}$ ), 58.1 ( $\text{CH}_3$ ), 66.8 ( $\text{CH}_2$ ), 80.5 ( $\text{CH}$ ), 124.2 (C), 130.3 (C), 132.0 (C), 132.9 (C), 140.0 (C), 140.7 (C). HRMS calcd for  $\text{C}_{14}\text{H}_{16}\text{O}_3$  232.1099, found 232.1096; LRMS (EI)  $m/z$  232 (75), 217 (100), 189 (27), 171 (7), 128 (8), 91 (5). Anal. Calcd for  $\text{C}_{14}\text{H}_{16}\text{O}_3$ : C, 72.38; H, 6.95. Found: C, 72.32; H, 6.94.

**(8c).** It is the same compound as **8b**. It was prepared from **6c** according to the general procedure described above to afford 65 mg (0.28 mmol) of **8c** in 56% yield.

**1,2,3,4,6a,8,9,9a-Octahydro-6-methoxynaphto[1',2':3,4]cyclobuta[1,2-*b*]furan-5-ol (8d).** It was prepared from **6d** according to the general procedure described above to afford, after flash chromatography with hexane:ether (3:1), 57 mg (0.23 mmol) of **8d** in 46% yield as a white solid; m.p. = 146-148°C;  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  1.62-1.93 (m, 6H), 2.57 (t,  $J$  = 5.9 Hz, 2H), 2.69 (t,  $J$  = 5.6 Hz, 2H), 3.62-3.73 (m, 1H), 3.95 (dd,  $J$  = 7.7, 3.5 Hz, 1H), 4.03 (s, 3H), 4.10 (t,  $J$  = 7.2 Hz, 1H), 5.47 (s, 1H), 5.57 (d,  $J$  = 3.5 Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  22.2 ( $\text{CH}_2$ ), 22.5 ( $\text{CH}_2$ ), 23.5 ( $\text{CH}_2$ ), 24.5 ( $\text{CH}_2$ ), 28.3 ( $\text{CH}_2$ ), 47.4 ( $\text{CH}$ ), 57.9 ( $\text{CH}_3$ ), 66.9 ( $\text{CH}_2$ ), 79.8 ( $\text{CH}$ ), 122.6 (C), 125.2 (C), 125.8 (C), 132.9 (C), 138.9 (C), 141.8 (C). Anal. Calcd for  $\text{C}_{15}\text{H}_{18}\text{O}_3$ : C, 73.15; H, 7.37. Found: C, 73.42; H, 7.50.

**3,4,4a,8a-Tetrahydro-8-methoxy-5-methyl-2H-benzo[3,4]cyclobuta[1,2-*b*]pyran-7-ol (8e).** It was prepared from **6e** according to the general procedure described above to afford, after flash chromatography with hexane:dichloromethane (5:1), 87 mg (0.40 mmol) of **8e** in 79% yield as a light yellow solid; m.p. = 88-90°C;  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  1.50-1.67 (m, 2H), 1.87-2.17 (m, 2H), 2.11 (s, 3H), 3.60 (td,  $J$  = 5.6, 5.1 Hz, 1H), 3.74-3.88 (m, 2H), 4.01 (s, 3H), 5.17 (d,  $J$  = 5.1 Hz, 1H), 5.35 (s, 1H), 6.71 (s, 1H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  16.1 ( $\text{CH}_3$ ), 19.5 ( $\text{CH}_2$ ), 22.6 ( $\text{CH}_2$ ), 41.3 ( $\text{CH}$ ), 57.7 ( $\text{CH}_3$ ), 61.5 ( $\text{CH}_2$ ), 71.9 ( $\text{CH}$ ), 117.4 ( $\text{CH}$ ), 125.9 (C), 127.3 (C), 136.4 (C), 140.5 (C), 144.1 (C). Anal. Calcd for  $\text{C}_{13}\text{H}_{16}\text{O}_3$ : C, 70.87; H, 7.33. Found: C, 70.96; H, 7.21.

**3,4,4a,8a-Tetrahydro-8-methoxy-5-methyl-6-phenyl-2H-benzo[3,4]cyclobuta[1,2-*b*]pyran-7-ol (8f).** It was prepared from **6f** according to the general procedure described above to afford, after flash chromatography with hexane:ethyl acetate (5:1), 89 mg (0.30 mmol) of **8f** in 60% yield as a light yellow solid; m.p. = 140-142°C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  1.51-1.82 (m, 2H), 1.88 (s, 3H), 1.91-2.24 (m, 2H), 3.66 (td,  $J$  = 5.7, 5.2 Hz, 1H), 3.77-3.99 (m, 2H), 4.06 (s, 3H), 5.23 (d,  $J$  = 5.2 Hz, 1H), 5.30 (s, 1H), 7.27-7.49 (m, 5H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  14.6 ( $\text{CH}_3$ ), 19.6 ( $\text{CH}_2$ ), 22.7 ( $\text{CH}_2$ ), 41.6 ( $\text{CH}$ ), 57.7 ( $\text{CH}_3$ ), 61.6 ( $\text{CH}_2$ ), 72.0 ( $\text{CH}$ ), 124.03 (C), 126.2 (C), 127.1 ( $\text{CH}$ ), 128.3 ( $\text{CH}$ ), 129.9 ( $\text{CH}$ ), 130.3 (C), 136.4 (C), 136.6 (C), 140.7 (C), 141.4 (C). HRMS calcd for  $\text{C}_{19}\text{H}_{20}\text{O}_3$  296.1412, found 296.1411; LRMS (EI)  $m/z$  296 (100), 282 (49), 267 (57), 239 (7), 165 (8). Anal. Calcd for  $\text{C}_{19}\text{H}_{20}\text{O}_3$ : C, 76.99; H, 6.81. Found: C, 77.14; H, 6.99.

**3,4,4a,8a-Tetrahydro-8-methoxy-6-phenyl-2H-benzo[3,4]cyclobuta[1,2-*b*]pyran-7-ol (8g).** It was prepared from **6g** according to the general procedure described above to afford, after flash chromatography with hexane:ethyl acetate (5:1), 79

mg (0.28 mmol) of **8g** in 56% yield as a yellow solid; m.p.= 130-132°C; <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>) δ 1.51-1.74 (m, 2H), 1.87-2.02 (m, 1H), 2.07-2.31 (m, 1H), 3.70 (td, *J* = 5.7, 5.0 Hz, 1H), 3.79-4.05 (m, 2H), 4.10 (s, 3H), 5.29 (d, *J* = 5.0 Hz, 1H), 6.72 (s, 1H), 7.28-7.61 (m, 5H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 19.4 (CH<sub>2</sub>), 23.4 (CH<sub>2</sub>), 42.3 (CH), 57.9 (CH<sub>3</sub>), 61.6 (CH<sub>2</sub>), 72.6 (CH), 116.7 (CH), 126.8 (CH), 127.0 (CH), 128.1 (CH), 129.2 (C), 130.0 (C), 138.2 (C), 138.3 (C), 141.2 (C), 142.6 (C). Anal. Calcd for C<sub>18</sub>H<sub>18</sub>O<sub>3</sub>: C, 76.56; H, 6.43. Found: C, 76.82; H, 6.18.

**1,2,3,5b,7,8,9,9a-Octahydro-5-methoxyindeno[4',5':3,4]cyclobuta[1,2-*b*]pyran-4-ol (8h)**. It was prepared from **6h** according to the general procedure described above to afford, after flash chromatography with hexane:ether:dichloromethane (4:1:1), 73 mg (0.30 mmol) of **8h** in 59% yield as a light yellow solid; m.p.= 110-112°C; <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>) δ 1.44-1.67 (m, 2H), 1.84-2.22 (m, 2H), 2.12 (dt, *J* = 7.1, 7.4 Hz, 2H), 2.73 (t, *J* = 7.4 Hz, 2H), 2.88 (t, *J* = 7.1 Hz, 2H), 3.60 (td, *J* = 5.7, 4.9 Hz, 1H), 3.71-3.93 (m, 2H), 4.01 (s, 3H), 5.22 (d, *J* = 4.9 Hz, 1H), 5.60 (br s, 1H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 19.5 (CH<sub>2</sub>), 22.7 (CH<sub>2</sub>), 26.0 (CH<sub>2</sub>), 28.9 (CH<sub>2</sub>), 29.4 (CH<sub>2</sub>), 41.5 (CH), 57.7 (CH<sub>3</sub>), 61.2 (CH<sub>2</sub>), 72.8 (CH), 126.0 (C), 132.2 (C), 132.4 (C), 132.7 (C), 140.3 (C), 140.8 (C). HRMS calcd for C<sub>15</sub>H<sub>18</sub>O<sub>3</sub> 246.1256, found 246.1256; LRMS (EI) *m/z* 246 (92), 231 (100), 217 (55), 203 (29), 161 (12). Anal. Calcd for C<sub>15</sub>H<sub>18</sub>O<sub>3</sub>: C, 75.13; H, 7.17. Found: C, 75.02; H, 7.48.

**(8i)**. Is the same compound as **8h**. It was prepared from **6i** according to the general procedure described above to afford 89 mg (0.36 mmol) of **8c** in 72% yield.

**2,3,4,6b,8,9,10a-Octahydro-6-methoxy-1H-naphto[1',2':3,4]cyclobuta[1,2-*b*]pyran-5-ol (8j)**. It was prepared from **6j** according to the general procedure described above to afford, after flash chromatography with hexane:ether:dichloromethane (4:1:1), 90 mg (0.35 mmol) of **8j** in 69% yield as a light yellow solid; m.p.= 114-116°C; <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>) δ 1.39-2.22 (m, 8H), 2.55 (t, *J* = 6.0 Hz, 2H), 2.70 (t, *J* = 6.0 Hz, 2H), 3.59 (td, *J* = 5.7, 5.0 Hz, 1H), 3.70-3.86 (m, 2H), 4.00 (s, 3H), 5.17 (d, *J* = 5.0 Hz, 1H), 5.47 (s, 1H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 19.6 (CH<sub>2</sub>), 22.3 (CH<sub>2</sub>), 22.6 (CH<sub>2</sub>), 23.5 (CH<sub>2</sub>), 24.8 (CH<sub>2</sub>), 41.4 (CH), 57.6 (CH<sub>3</sub>), 61.3 (CH<sub>2</sub>), 72.2 (CH), 124.4 (C), 125.6 (C), 125.9 (C), 135.3 (C), 139.8 (C), 141.4 (C). Anal. Calcd for C<sub>16</sub>H<sub>20</sub>O<sub>3</sub>: C, 73.81; H, 7.75. Found: C, 73.70; H, 7.63.

**3,4,4a,8a-Tetrahydro-8-methoxy-6-(2-propenyloxymethyl)-2H-benzo[3,4]cyclobuta[1,2-*b*]pyran-7-ol (8k)**. It was prepared from **6k** according to the general procedure described above to afford, after flash chromatography with hexane:ether:dichloromethane (4:1:1), 112 mg (0.39 mmol) of **8k** in 77% yield as a light yellow solid; m.p.= 158-160°C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 1.43-1.63 (m, 3H), 1.86-1.96 (m, 2H), 2.05-2.20 (m, 1H), 2.12 (s, 3H), 3.60 (dt, *J* = 5.2, 5.2 Hz, 1H), 3.71-3.84 (m, 2H), 3.99 (s, 3H), 4.06 (d, *J* = 5.7 Hz, 2H), 4.64 (s, 2H), 5.15 (d, *J* = 5.2 Hz, 1H), 5.20 (dd, *J* = 10.5, 1.5 Hz, 1H), 5.31 (dd, *J* = 17.4, 1.5 Hz, 1H), 5.69 (ddt, *J* = 17.4, 10.5, 5.7 Hz, 1H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 13.5 (CH<sub>3</sub>), 19.5 (CH<sub>2</sub>), 22.7 (CH<sub>2</sub>), 41.4 (CH), 57.7 (CH<sub>3</sub>), 61.5 (CH<sub>2</sub>), 64.3 (CH<sub>2</sub>), 71.1 (CH<sub>2</sub>), 71.8 (CH), 117.3 (CH<sub>2</sub>), 123.5 (C), 125.1 (C), 126.9 (C), 134.6 (CH), 136.3 (C), 141.0 (C), 143.7 (C). Anal. Calcd for C<sub>17</sub>H<sub>22</sub>O<sub>4</sub>: C, 70.31; H, 7.74. Found: C, 70.42; H, 7.68.