## Supporting Information

Synthesis of Substituted Tetralins and Benzosuberans via $\mathrm{BF}_{3} \cdot \mathrm{OEt}_{2}$ Mediated Formal (4+2) and (5+2) Stereocontrolled Cycloaddition of 4-Alkenols with Veratrol

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(1) ${ }^{1} \mathrm{H} \&{ }^{13} \mathrm{C}$ NMR spectroscopic data (pages $\mathrm{S}-3 \sim \mathrm{~S}-38$ )
(2) Additional scanned photocopies (pages S-39~S-351)
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## 1. Experimental section

1.1. General. All other reagents and solvents were obtained from commercial sources and used without further purification. Reactions were routinely carried out under an atmosphere of dry nitrogen with magnetic stirring. Products in organic solvents were dried with anhydrous magnesium sulfate before concentration in vacuo. Melting points were determined with a SMP3 melting apparatus. ${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ NMR spectra were recorded on a Varian INOVA- 400 spectrometer operating at 400 and at 100 MHz , respectively. Chemical shifts ( $\delta$ ) are reported in parts per million (ppm) and the coupling constants $(J)$ are given in Hertz. High resolution mass spectra (HRMS) were measured with a mass spectrometer Finnigan/Thermo Quest MAT 95XL. X-ray crystal structures were obtained with an Enraf-Nonius FR-590 diffractometer (CAD4, Kappa CCD). Elemental analyses were carried out with Heraeus Vario III-NCSH, Heraeus CHN-OS-Rapid Analyzer or Elementar Vario EL III.
1.2. A representative synthetic procedure of compounds 3a-t is as follows: $\mathrm{NaBH}_{4}$ ( 100 mg , 3.0 mmol ) was added to a solution of 1a-t ( 1.0 mmol ) in a co-solvent of THF ( 5 mL ) and MeOH ( 5 mL ) at $0^{\circ} \mathrm{C}$. The reaction mixture was stirred for 1 h at $0^{\circ} \mathrm{C}$ and the solvent was concentrated. The residue was diluted with water ( 10 mL ) and the mixture was extracted with $\mathrm{CH}_{2} \mathrm{Cl}_{2}(3 \times 20 \mathrm{~mL})$. The combined organic layers were washed with brine, dried, filtered and evaporated to afford crude product. Purification on silica gel (hexanes/EtOAc $=5 / 1 \sim 3 / 1$ ) afforded 3a-t.

1.2.1. 1-Phenyl-2-(toluene-4-sulfonyl)pent-4-en-1-ol (3a). According to the general procedure, reaction was performed in the presence of $\mathrm{NaBH}_{4}(100 \mathrm{mg}, 3.0 \mathrm{mmol})$ and $\mathbf{1 a}(314 \mathrm{mg}, 1.0 \mathrm{mmol})$ in a co-solvent of THF ( 5 mL ) and $\mathrm{MeOH}(5 \mathrm{~mL})$ at $0{ }^{\circ} \mathrm{C}$ for 1 h . Purification on silica gel (hexanes/EtOAc = 4/1) afforded 3a ( $92 \%$, 291 mg ). Colorless solid; $\mathrm{mp}=79-80^{\circ} \mathrm{C}$ (recrystallized from hexanes and EtOAc); HRMS (ESI, $\mathrm{M}^{+}+1$ ) calcd for $\mathrm{C}_{18} \mathrm{H}_{21} \mathrm{O}_{3} \mathrm{~S} 317.1212$, found 317.1218 ; ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 7.78(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 2 \mathrm{H}), 7.36-7.27(\mathrm{~m}, 7 \mathrm{H}), 5.25-5.15(\mathrm{~m}, 1 \mathrm{H}), 5.05(\mathrm{~d}, \mathrm{~J}$ $=8.4 \mathrm{~Hz}, 1 \mathrm{H}$ ), $4.72(\mathrm{dq}, J=1.2,10.4 \mathrm{~Hz}, 1 \mathrm{H}), 4.58(\mathrm{dq}, J=1.2,16.8 \mathrm{~Hz}, 1 \mathrm{H}), 4.20(\mathrm{br} \mathrm{s}, 1 \mathrm{H})$, 3.44-3.39 (m, 1H), 2.46 (s, 3H), 2.32-2.25 (m, 1H), 2.12-2.05 (m, 1H); ${ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): б 145.09, 139.44, 135.22, 133.04, 129.81 (2x), 128.82 ( $2 x$ ), 128.51 ( $3 x$ ), 127.31 ( $2 x$ ), 117.52, 73.08, 70.39, 31.11, 21.64; Anal. Calcd for $\mathrm{C}_{18} \mathrm{H}_{20} \mathrm{O}_{3} \mathrm{~S}: \mathrm{C}, 68.33$; $\mathrm{H}, 6.37$. Found: C, 68.58; H, 6.46.

1.2.2. 1-(4-Methoxyphenyl)-2-(toluene-4-sulfonyl)pent-4-en-1-ol (3b). According to the general procedure, reaction was performed in the presence of $\mathrm{NaBH}_{4}(100 \mathrm{mg}, 3.0 \mathrm{mmol})$ and 1b ( 344 mg , 1.0 mmol ) in a co-solvent of THF ( 5 mL ) and $\mathrm{MeOH}(5 \mathrm{~mL})$ at $0{ }^{\circ} \mathrm{C}$ for 1 h . Purification on silica gel (hexanes/EtOAc $=3 / 1$ ) afforded $3 \mathrm{~b}\left(93 \%, 322 \mathrm{mg}\right.$ ). Colorless oil; HRMS (ESI, $\mathrm{M}^{+}+1$ ) calcd for
$\mathrm{C}_{19} \mathrm{H}_{23} \mathrm{O}_{4} \mathrm{~S} 347.1317$, found $347.1315 ;{ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 7.79(\mathrm{~d}, J=8.0 \mathrm{~Hz}, 2 \mathrm{H}), 7.35$ (d, $J=8.0 \mathrm{~Hz}, 2 \mathrm{H}), 7.21(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 2 \mathrm{H}), 6.83(\mathrm{~d}, J=8.8 \mathrm{~Hz}, 2 \mathrm{H}), 5.27-5.17(\mathrm{~m}, 1 \mathrm{H}), 5.01(\mathrm{~d}, J=$ $8.4 \mathrm{~Hz}, 1 \mathrm{H}), 4.73(\mathrm{dq}, J=1.2,10.0 \mathrm{~Hz}, 1 \mathrm{H}), 4.59(\mathrm{dq}, J=1.2,16.8 \mathrm{~Hz}, 1 \mathrm{H}), 4.34(\mathrm{br} \mathrm{s}, 1 \mathrm{H}), 3.78(\mathrm{~s}$, 3H), 3.41-3.36 (m, 1H), $2.46(\mathrm{~s}, 3 \mathrm{H}), 2.30-2.23(\mathrm{~m}, 1 \mathrm{H}), 2.12-2.03(\mathrm{~m}, 1 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( 100 MHz , $\mathrm{CDCl}_{3}$ ): $\delta 159.73,145.07,135.28,133.15,131.65,129.81$ (2x), 128.84 (2x), 128.51 (2x), 117.45, 113.88 (2x), 72.69, 70.56, 55.26, 31.20, 21.66; Anal. Calcd for $\mathrm{C}_{19} \mathrm{H}_{22} \mathrm{O}_{4} \mathrm{~S}: \mathrm{C}, 65.87$; H, 6.40. Found: C, 65.55; H, 6.70.

1.2.3. 1-(4-Fluorophenyl)-2-(toluene-4-sulfonyl)pent-4-en-1-ol (3c). According to the general procedure, reaction was performed in the presence of $\mathrm{NaBH}_{4}(100 \mathrm{mg}, 3.0 \mathrm{mmol})$ and $\mathbf{1 c}(332 \mathrm{mg}$, 1.0 mmol ) in a co-solvent of THF ( 5 mL ) and $\mathrm{MeOH}(5 \mathrm{~mL})$ at $0^{\circ} \mathrm{C}$ for 1 h . Purification on silica gel (hexanes/EtOAc = 5/1) afforded 3c ( $86 \%, 287 \mathrm{mg}$ ). Colorless solid; $\mathrm{mp}=82-83^{\circ} \mathrm{C}$ (recrystallized from hexanes and EtOAc); HRMS (ESI, $\mathrm{M}^{+}+1$ ) calcd for $\mathrm{C}_{18} \mathrm{H}_{20} \mathrm{FO}_{3} \mathrm{~S} 335.1117$, found $335.1118 ;{ }^{1} \mathrm{H}$ NMR (400 MHz, $\mathrm{CDCl}_{3}$ ): $\delta 7.77$ (d, $\left.J=8.4 \mathrm{~Hz}, 2 \mathrm{H}\right), 7.36(\mathrm{~d}, J=8.0 \mathrm{~Hz}, 2 \mathrm{H}), 7.30-7.23(\mathrm{~m}, 2 \mathrm{H})$, 7.01-6.96 (m, 2H), 5.26-5.16 (m, 1H), $5.06(\mathrm{~d}, J=8.8 \mathrm{~Hz}, 1 \mathrm{H}), 4.74(\mathrm{dq}, J=1.2,10.0 \mathrm{~Hz}, 1 \mathrm{H}), 4.59$ (dq, $J=1.2,16.8 \mathrm{~Hz}, 1 \mathrm{H}$ ), $4.46(\mathrm{br} \mathrm{s}, 1 \mathrm{H}), 3.40-3.35(\mathrm{~m}, 1 \mathrm{H}), 2.46(\mathrm{~s}, 3 \mathrm{H}), 2.34-2.27(\mathrm{~m}, 1 \mathrm{H})$, 2.11-2.03 (m, 1H); ${ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 162.69(\mathrm{~d}, J=245.6 \mathrm{~Hz}), 145.27,135.34(\mathrm{~d}, J=$ 3.0 Hz ), 135.03, 132.83, 129.88 (2x), 129.01 (d, $J=7.6 \mathrm{~Hz}, 2 x$ ), 128.81 (2x), 117.70, 115.40 (d, $J=$ $21.3 \mathrm{~Hz}, 2 \mathrm{x})$, 72.37, 70.30, 31.05, 21.66.

1.2.4. 2-(Toluene-4-sulfonyl)-1-p-tolylpent-4-en-1-ol (3d). According to the general procedure, reaction was performed in the presence of $\mathrm{NaBH}_{4}(100 \mathrm{mg}, 3.0 \mathrm{mmol})$ and 1d ( $328 \mathrm{mg}, 1.0 \mathrm{mmol}$ ) in a co-solvent of THF ( 5 mL ) and $\mathrm{MeOH}(5 \mathrm{~mL})$ at $0^{\circ} \mathrm{C}$ for 1 h . Purification on silica gel (hexanes/EtOAc = 5/1) afforded 3d (93\%, 307 mg ). Colorless oil; HRMS (ESI, $\mathrm{M}^{+}+1$ ) calcd for $\mathrm{C}_{19} \mathrm{H}_{23} \mathrm{O}_{3} \mathrm{~S} 331.1368$, found 331.1366; ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 7.77(\mathrm{~d}, \mathrm{~J}=8.4 \mathrm{~Hz}, 2 \mathrm{H}), 7.33$ (d, $J=8.0 \mathrm{~Hz}, 2 \mathrm{H}), 7.17(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 2 \mathrm{H}), 7.09(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 2 \mathrm{H}), 5.30-5.20(\mathrm{~m}, 1 \mathrm{H}), 5.02(\mathrm{~d}, J=$ $8.4 \mathrm{~Hz}, 1 \mathrm{H}$ ), 4.75 (dq, $J=1.2,10.0 \mathrm{~Hz}, 1 \mathrm{H}$ ), 4.61 (dq, $J=1.2,16.8 \mathrm{~Hz}, 1 \mathrm{H}$ ), 4.32 (br s, 1H), 3.44-3.39 (m, 1H), $2.45(\mathrm{~s}, 3 \mathrm{H}), 2.31(\mathrm{~s}, 3 \mathrm{H}), 2.30-2.24(\mathrm{~m}, 1 \mathrm{H}), 2.14-2.07(\mathrm{~m}, 1 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR (100 $\mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 144.95,138.22,136.48,135.35,133.15$, 129.71 (2x), 129.12 (2x), 128.76 (2x), 127.11 (2x), 117.47, 72.82, 70.36, 31.07, 21.60, 21.08; Anal. Calcd for $\mathrm{C}_{19} \mathrm{H}_{22} \mathrm{O}_{3} \mathrm{~S}: \mathrm{C}, 69.06$; H , 6.71. Found: C, 69.38; H, 6.87.

1.2.5. 2-Methanesulfonyl-1-phenylpent-4-en-1-ol (3e). According to the general procedure, reaction was performed in the presence of $\mathrm{NaBH}_{4}(100 \mathrm{mg}, 3.0 \mathrm{mmol})$ and $\mathbf{1 e}(238 \mathrm{mg}, 1.0 \mathrm{mmol})$ in a co-solvent of THF ( 5 mL ) and $\mathrm{MeOH}(5 \mathrm{~mL})$ at $0{ }^{\circ} \mathrm{C}$ for 1 h . Purification on silica gel (hexanes/EtOAc = 5/1) afforded 3 e ( $87 \%, 209 \mathrm{mg}$ ). Colorless gum; HRMS (ESI, M ${ }^{+}+1$ ) calcd for $\mathrm{C}_{12} \mathrm{H}_{17} \mathrm{O}_{3} \mathrm{~S} 241.0899$, found 241.0902; ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 7.40-7.38(\mathrm{~m}, 4 \mathrm{H}), 7.35-7.29$ $(\mathrm{m}, 1 \mathrm{H}), 5.69(\mathrm{br} \mathrm{s}, 1 \mathrm{H}), 5.63-5.52(\mathrm{~m}, 1 \mathrm{H}), 5.03-4.95(\mathrm{~m}, 2 \mathrm{H}), 3.13(\mathrm{dt}, J=1.6,7.2 \mathrm{~Hz}, 1 \mathrm{H}), 2.94(\mathrm{~s}$, $3 \mathrm{H}), 2.87(\mathrm{~d}, J=2.8 \mathrm{~Hz}, 1 \mathrm{H}), 2.64(\mathrm{dt}, J=1.6,6.8 \mathrm{~Hz}, 2 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 139.90$, 134.72, 128.68 (2x), 128.07, 125.67 (2x), 117.70, 70.29, 70.22, 40.65, 27.05; Anal. Calcd for $\mathrm{C}_{12} \mathrm{H}_{16} \mathrm{O}_{3} \mathrm{~S}: \mathrm{C}, 59.97$; H, 6.71. Found: C, 60.21; H, 6.82.

1.2.6. 1-Naphthalen-2-yl-2-(toluene-4-sulfonyl)pent-4-en-1-ol (3f). According to the general procedure, reaction was performed in the presence of $\mathrm{NaBH}_{4}(100 \mathrm{mg}, 3.0 \mathrm{mmol})$ and $1 \mathrm{f}(364 \mathrm{mg}$, 1.0 mmol ) in a co-solvent of THF ( 5 mL ) and $\mathrm{MeOH}(5 \mathrm{~mL})$ at $0^{\circ} \mathrm{C}$ for 1 h . Purification on silica gel (hexanes/EtOAc = 5/1) afforded $3 f(90 \%, 329 \mathrm{mg})$. Colorless gum; HRMS (ESI, M ${ }^{+}+1$ ) calcd for $\mathrm{C}_{22} \mathrm{H}_{23} \mathrm{O}_{3} \mathrm{~S} 367.1368$, found 367.1369; ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 7.80-7.71$ ( $\mathrm{m}, 6 \mathrm{H}$ ), 7.50-7.45 (m, 2H), 7.38 (dd, $J=1.6,8.4 \mathrm{~Hz}, 1 \mathrm{H}), 7.24(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 2 \mathrm{H}), 5.37-5.27(\mathrm{~m}, 1 \mathrm{H}), 5.24(\mathrm{~d}, J=8.0$ $\mathrm{Hz}, 1 \mathrm{H}), 4.74(\mathrm{dq}, J=1.2,10.0 \mathrm{~Hz}, 1 \mathrm{H}), 4.63(\mathrm{dq}, J=1.2,16.8 \mathrm{~Hz}, 1 \mathrm{H}), 4.50(\mathrm{br} \mathrm{s}, 1 \mathrm{H}), 3.58-3.53$ $(\mathrm{m}, 1 \mathrm{H}), 2.43-2.36(\mathrm{~m}, 1 \mathrm{H}), 2.38(\mathrm{~s}, 3 \mathrm{H}), 2.26-2.19(\mathrm{~m}, 1 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $\left.100 \mathrm{MHz}, \mathrm{CDCl}_{3}\right)$ : $\delta 145.01$, 136.80, 135.36, 133.25, 133.07, 132.97, 129.68 (2x), 128.70 (2x), 128.46, 127.99, 127.60, 126.64, 126.30, 126.27, 124.28, 117.89, 72.99, 69.96, 30.97, 21.57.

1.2.7. 1-Biphenyl-4-yl-2-(toluene-4-sulfonyl)pent-4-en-1-ol (3g). According to the general procedure, reaction was performed in the presence of $\mathrm{NaBH}_{4}(100 \mathrm{mg}, 3.0 \mathrm{mmol})$ and $\mathbf{1 g}(390 \mathrm{mg}$, 1.0 mmol ) in a co-solvent of THF ( 5 mL ) and $\mathrm{MeOH}(5 \mathrm{~mL})$ at $0^{\circ} \mathrm{C}$ for 1 h . Purification on silica gel (hexanes/EtOAc $=5 / 1$ ) afforded $3 \mathrm{~g}(92 \%, 361 \mathrm{mg})$. Colorless gum; HRMS (ESI, M ${ }^{+}+1$ ) calcd for $\mathrm{C}_{24} \mathrm{H}_{25} \mathrm{O}_{3} \mathrm{~S} 393.1524$, found 393.1528 ; ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 7.77$ (d, $J=8.4 \mathrm{~Hz}, 2 \mathrm{H}$ ), 7.57-7.50 (m, 4H), 7.46-7.41 (m, 2H), 7.37-7.32 (m, 5H), 5.38-5.28 (m, 1H), 5.13 (d, J=8.0 Hz, 1H), 4.79 (dq, $J=1.2,10.0 \mathrm{~Hz}, 1 \mathrm{H}), 4.68(\mathrm{dq}, J=1.2,16.8 \mathrm{~Hz}, 1 \mathrm{H}), 4.20(\mathrm{br} \mathrm{s}, 1 \mathrm{H}), 3.51-3.46(\mathrm{~m}, 1 \mathrm{H})$, $2.43(\mathrm{~s}, 3 \mathrm{H}), 2.42-2.36(\mathrm{~m}, 1 \mathrm{H}), 2.25-2.17(\mathrm{~m}, 1 \mathrm{H}) ;{ }^{13} \mathrm{C} \operatorname{NMR}\left(100 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta 145.01,141.29$, 140.43, 138.48, 135.37, 133.06, 129.78 (2x), 128.75 (2x), 128.73 ( $2 x$ ), 127.59 ( $2 x$ ), 127.44, 127.13 (2x), 126.99 (2x), 117.75, 72.63, 70.19, 30.99, 21.60; Anal. Calcd for $\mathrm{C}_{24} \mathrm{H}_{24} \mathrm{O}_{3} \mathrm{~S}: \mathrm{C}, 73.44 ; \mathrm{H}, 6.16$. Found: C, 73.52; H, 6.23.

1.2.8. 2-Benzenesulfonyl-1-(4-methoxyphenyl)pent-4-en-1-ol (3h). According to the general procedure, reaction was performed in the presence of $\mathrm{NaBH}_{4}(100 \mathrm{mg}, 3.0 \mathrm{mmol})$ and $\mathbf{1 h}(330 \mathrm{mg}$, 1.0 mmol ) in a co-solvent of THF ( 5 mL ) and $\mathrm{MeOH}(5 \mathrm{~mL})$ at $0{ }^{\circ} \mathrm{C}$ for 1 h . Purification on silica gel (hexanes/EtOAc = 3/1) afforded $3 \mathrm{~h}\left(90 \%, 299 \mathrm{mg}\right.$ ). Colorless gum; HRMS (ESI, M ${ }^{+}+1$ ) calcd for $\mathrm{C}_{18} \mathrm{H}_{21} \mathrm{O}_{4} \mathrm{~S} 333.1161$, found 333.1162; ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 7.91-7.88(\mathrm{~m}, 2 \mathrm{H}), 7.67-7.63$ (m, 1H), 7.57-7.53 (m, 2H), $7.21(\mathrm{~d}, ~ J=8.8 \mathrm{~Hz}, 2 \mathrm{H}), 6.82(\mathrm{~d}, J=8.8 \mathrm{~Hz}, 2 \mathrm{H}), 5.30-5.19(\mathrm{~m}, 1 \mathrm{H})$, $5.04(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 1 \mathrm{H}), 4.75(\mathrm{dq}, J=1.2,10.0 \mathrm{~Hz}, 1 \mathrm{H}), 4.60(\mathrm{dq}, J=1.2,16.8 \mathrm{~Hz}, 1 \mathrm{H}), 4.20(\mathrm{br} \mathrm{s}$, $1 \mathrm{H})$, $3.77(\mathrm{~s}, 3 \mathrm{H}), 3.45-3.40(\mathrm{~m}, 1 \mathrm{H}), 2.32-2.25(\mathrm{~m}, 1 \mathrm{H}), 2.15-2.08(\mathrm{~m}, 1 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( 100 MHz , $\mathrm{CDCl}_{3}$ ): $\delta 159.65,138.52,133.84,133.00,131.56,129.09(2 x), 128.68(2 x), 128.40(2 x), 117.56$, 113.84 (2x), 72.54, 70.43, 55.21, 31.03.

1.2.9. 2-Benzenesulfonyl-1-(4-fluorophenyl)pent-4-en-1-ol (3i). According to the general procedure, reaction was performed in the presence of $\mathrm{NaBH}_{4}(100 \mathrm{mg}, 3.0 \mathrm{mmol})$ and $1 \mathrm{i}(318 \mathrm{mg}$, 1.0 mmol ) in a co-solvent of THF ( 5 mL ) and $\mathrm{MeOH}(5 \mathrm{~mL})$ at $0^{\circ} \mathrm{C}$ for 1 h . Purification on silica gel (hexanes/EtOAc = 5/1) afforded $\mathbf{3 i}\left(87 \%, 278 \mathrm{mg}\right.$ ). Colorless solid; mp $=106-107{ }^{\circ} \mathrm{C}$ (recrystallized from hexanes and EtOAc); HRMS (ESI, M ${ }^{+}+1$ ) calcd for $\mathrm{C}_{17} \mathrm{H}_{18} \mathrm{FO}_{3} \mathrm{~S} 321.0961$, found $321.0965 ;{ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 7.90-7.87(\mathrm{~m}, 2 \mathrm{H}), 7.69-7.64(\mathrm{~m}, 1 \mathrm{H}), 7.58-7.53(\mathrm{~m}, 2 \mathrm{H}), 7.30-7.25(\mathrm{~m}$, 2H), 7.01-6.95 (m, 2H), 5.28-5.18 (m, 1H), $5.09(\mathrm{~d}, J=8.0 \mathrm{~Hz}, 1 \mathrm{H}), 4.76(\mathrm{dq}, J=1.2,10.0 \mathrm{~Hz}, 1 \mathrm{H})$, 4.60 (dq, J = 1.2, $16.8 \mathrm{~Hz}, 1 \mathrm{H}$ ), 4.35 (br s, 1H), 3.44-3.39 (m, 1H), 2.36-2.29 (m, 1H), 2.16-2.08 (m, $1 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 162.64(\mathrm{~d}, J=245.6 \mathrm{~Hz}), 138.27,135.28(\mathrm{~d}, J=3.0 \mathrm{~Hz}), 134.01$, 132.70, 129.20 (2x), 128.93 (d, $J=8.3 \mathrm{~Hz}, 2 x$ ), $128.68(2 x), 117.84,115.40(d, J=21.3 \mathrm{~Hz}, 2 x$ ), 72.24, 70.22, 30.92; Anal. Calcd for $\mathrm{C}_{17} \mathrm{H}_{17} \mathrm{FO}_{3} \mathrm{~S}: \mathrm{C}, 63.73$; H, 5.35. Found: C, 63.87; H, 5.28.

1.2.10. 2-Methanesulfonyl-1-p-tolylpent-4-en-1-ol (3j). According to the general procedure, reaction was performed in the presence of $\mathrm{NaBH}_{4}(100 \mathrm{mg}, 3.0 \mathrm{mmol})$ and $1 \mathrm{j}(252 \mathrm{mg}, 1.0 \mathrm{mmol})$ in a co-solvent of THF ( 5 mL ) and $\mathrm{MeOH}(5 \mathrm{~mL})$ at $0{ }^{\circ} \mathrm{C}$ for 1 h . Purification on silica gel (hexanes/EtOAc = 5/1) afforded $3 \mathrm{j}\left(90 \%, 229 \mathrm{mg}\right.$ ). Colorless oil; HRMS (ESI, $\mathrm{M}^{+}+1$ ) calcd for $\mathrm{C}_{13} \mathrm{H}_{19} \mathrm{O}_{3} \mathrm{~S} 255.1055$, found 255.1056; ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 7.25-7.17$ (m, 5H), 5.72-5.62 (m, 1H), 5.01 (br s, 1H), 4.99 (br s, 1H), 4.90 (dq, J=1.6, 17.2 Hz, 1H), 3.30-3.25 (m, 1H), 2.97 (s, $3 \mathrm{H}), 2.48-2.32(\mathrm{~m}, 2 \mathrm{H}), 2.35(\mathrm{~s}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 138.61,137.11,133.17,129.46$ (2x), 126.87 (2x), 118.49, 72.74, 68.95, 44.00, 29.68, 21.12; Anal. Calcd for $\mathrm{C}_{13} \mathrm{H}_{18} \mathrm{O}_{3} \mathrm{~S}: \mathrm{C}, 61.39 ; \mathrm{H}$, 7.13. Found: C, 61.53; H, 7.34.
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1.2.11. 2-Benzenesulfonyl-1-biphenyl-4-ylpent-4-en-1-ol (3k). According to the general procedure, reaction was performed in the presence of $\mathrm{NaBH}_{4}(100 \mathrm{mg}, 3.0 \mathrm{mmol})$ and $\mathbf{1 k}(376 \mathrm{mg}$, $1.0 \mathrm{mmol})$ in a co-solvent of THF ( 5 mL ) and $\mathrm{MeOH}(5 \mathrm{~mL})$ at $0{ }^{\circ} \mathrm{C}$ for 1 h . Purification on silica gel (hexanes/EtOAc = 4/1) afforded $\mathbf{3 k}(92 \%, 348 \mathrm{mg})$. Colorless gum; HRMS (ESI, M ${ }^{+}+1$ ) calcd for $\mathrm{C}_{23} \mathrm{H}_{23} \mathrm{O}_{3} \mathrm{~S} 379.1368$, found 379.1370; ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 7.90-7.87$ (m, 2H), 7.67-7.62 (m, 1H), 7.60-7.50 (m, 6H), 7.46-7.42 (m, 2H), 7.38-7.33 (m, 3H), 5.39-5.29 (m, 1H), $5.16(d, J=$ $8.0 \mathrm{~Hz}, 1 \mathrm{H}), 4.80(\mathrm{dq}, J=1.6,10.4 \mathrm{~Hz}, 1 \mathrm{H}), 4.70(\mathrm{dq}, J=1.6,16.8 \mathrm{~Hz}, 1 \mathrm{H}), 4.33(\mathrm{br} \mathrm{s}, 1 \mathrm{H}), 3.52(\mathrm{dq}$, $J=1.6,11.6 \mathrm{~Hz}, 1 \mathrm{H}), 2.45-2.38(\mathrm{~m}, 1 \mathrm{H}), 2.29-2.22(\mathrm{~m}, 1 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR (100 MHz, CDCl $)^{2}$ : $\delta 141.34$, 140.43, 138.58, 138.42, 133.82, 132.97, 129.13 (2x), 128.78 (2x), 128.66 ( $2 x$ ), 127.55 ( $2 x$ ), 127.47, 127.19 (2x), 127.00 (2x), 117.93, 72.58, 70.19, 30.93; Anal. Calcd for $\mathrm{C}_{23} \mathrm{H}_{22} \mathrm{O}_{3} \mathrm{~S}: \mathrm{C}, 72.99 ; \mathrm{H}, 5.86$. Found: C, 72.80; H, 6.16.

1.2.12. 2-Benzenesulfonyl-1-phenylpent-4-en-1-ol (3I). According to the general procedure, reaction was performed in the presence of $\mathrm{NaBH}_{4}(100 \mathrm{mg}, 3.0 \mathrm{mmol})$ and $11(300 \mathrm{mg}, 1.0 \mathrm{mmol})$ in a co-solvent of THF ( 5 mL ) and $\mathrm{MeOH}(5 \mathrm{~mL})$ at $0{ }^{\circ} \mathrm{C}$ for 1 h . Purification on silica gel (hexanes/EtOAc = 4/1) afforded $\mathbf{3 I}\left(92 \%, 278 \mathrm{mg}\right.$ ). Colorless solid; mp $=106-107{ }^{\circ} \mathrm{C}$ (recrystallized from hexanes and EtOAc); HRMS (ESI, M ${ }^{+}+1$ ) calcd for $\mathrm{C}_{17} \mathrm{H}_{19} \mathrm{O}_{3} \mathrm{~S} 303.1055$, found $303.1057 ;{ }^{1} \mathrm{H}$ NMR (400 MHz, $\mathrm{CDCl}_{3}$ ): $\delta 7.90-7.87(\mathrm{~m}, 2 \mathrm{H}), 7.67-7.62(\mathrm{~m}, 1 \mathrm{H}), 7.56-7.52(\mathrm{~m}, 2 \mathrm{H}), 7.30-7.25(\mathrm{~m}$, $5 \mathrm{H}), 5.29-5.19(\mathrm{~m}, 1 \mathrm{H}), 5.09(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 1 \mathrm{H}), 4.74(\mathrm{dq}, J=1.2,11.2 \mathrm{~Hz}, 1 \mathrm{H}), 4.60(\mathrm{dq}, J=1.2$, $16.8 \mathrm{~Hz}, 1 \mathrm{H}), 4.20(\mathrm{br} \mathrm{s}, 1 \mathrm{H}), 3.49-3.44(\mathrm{~m}, 1 \mathrm{H}), 2.36-2.28(\mathrm{~m}, 1 \mathrm{H}), 2.18-2.11(\mathrm{~m}, 1 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 139.36,138.46,133.86,132.89,129.10(2 x), 128.65(2 x), 128.49,128.48(2 x)$, 127.18 (2x), 117.66, 72.91, 70.25, 30.93; Anal. Calcd for $\mathrm{C}_{17} \mathrm{H}_{18} \mathrm{O}_{3} \mathrm{~S}: \mathrm{C}, 67.52$; H, 6.00. Found: C, 67.67; H, 6.28.

1.2.13. 1-Phenyl-2-(toluene-3-sulfonyl)pent-4-en-1-ol (3m). According to the general procedure, reaction was performed in the presence of $\mathrm{NaBH}_{4}(100 \mathrm{mg}, 3.0 \mathrm{mmol})$ and $1 \mathrm{~m}(314 \mathrm{mg}, 1.0 \mathrm{mmol})$ in a co-solvent of THF ( 5 mL ) and $\mathrm{MeOH}(5 \mathrm{~mL})$ at $0{ }^{\circ} \mathrm{C}$ for 1 h . Purification on silica gel (hexanes/EtOAc = 4/1) afforded 3m (94\%, 297 mg ). Colorless gum; HRMS (ESI, M ${ }^{+}+1$ ) calcd for $\mathrm{C}_{18} \mathrm{H}_{21} \mathrm{O}_{3} \mathrm{~S} 317.1212$, found 317.1213 ; ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 7.70-7.67(\mathrm{~m}, 1 \mathrm{H}), 7.66(\mathrm{~s}$, $1 \mathrm{H}), 7.45-7.40(\mathrm{~m}, 2 \mathrm{H}), 7.31-7.25(\mathrm{~m}, 5 \mathrm{H}), 5.29-5.19(\mathrm{~m}, 1 \mathrm{H}), 5.09(\mathrm{~d}, J=8.0 \mathrm{~Hz}, 1 \mathrm{H}), 4.75(\mathrm{dq}, J=$ $1.6,10.4 \mathrm{~Hz}, 1 \mathrm{H}), 4.61(\mathrm{dq}, J=1.6,16.8 \mathrm{~Hz}, 1 \mathrm{H}), 4.20(\mathrm{br} \mathrm{s}, 1 \mathrm{H}), 3.48-3.43(\mathrm{~m}, 1 \mathrm{H}), 2.43(\mathrm{~s}, 3 \mathrm{H})$, 2.38-2.30 (m, 1H), 2.19-2.11 (m, 1H); ${ }^{13} \mathrm{C}$ NMR (100 MHz, CDCl ${ }_{3}$ ): $\delta 139.44,139.41,138.24$,
134.71, 133.02, 128.99, 128.94, 128.46, 128.45 (2x), 127.19 (2x), 125.80, 117.63, 72.88, 70.21, 30.97, 21.28; Anal. Calcd for $\mathrm{C}_{18} \mathrm{H}_{20} \mathrm{O}_{3} \mathrm{~S}: \mathrm{C}, 68.33$; $\mathrm{H}, 6.37$. Found: $\mathrm{C}, 68.23 ; \mathrm{H}, 6.48$.

1.2.14. 2-(4-Fluorobenzenesulfonyl)-1-phenylpent-4-en-1-ol (3n). According to the general procedure, reaction was performed in the presence of $\mathrm{NaBH}_{4}(100 \mathrm{mg}, 3.0 \mathrm{mmol})$ and $\mathbf{1 n}(318 \mathrm{mg}$, 1.0 mmol ) in a co-solvent of THF ( 5 mL ) and $\mathrm{MeOH}(5 \mathrm{~mL})$ at $0^{\circ} \mathrm{C}$ for 1 h . Purification on silica gel (hexanes/EtOAc = 5/1) afforded $3 n(90 \%, 288 \mathrm{mg})$. Colorless gum; HRMS (ESI, M ${ }^{+}+1$ ) calcd for $\mathrm{C}_{17} \mathrm{H}_{18} \mathrm{FO}_{3} \mathrm{~S} 321.0961$, found $321.0965 ;{ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 7.89-7.84(\mathrm{~m}, 2 \mathrm{H}), 7.31-7.23$ (m, 5H), 7.20-7.14 (m, 2H), 5.38-5.28 (m, 1H), 5.06 (d, $J=8.0 \mathrm{~Hz}, 1 \mathrm{H}$ ), 4.80 (dq, $J=1.2,10.0 \mathrm{~Hz}$, 1 H ), 4.68 (dq, $J=1.2,16.8 \mathrm{~Hz}, 1 \mathrm{H}$ ), 3.90 (br s, 1H), 3.50-3.45 (m, 1H), 2.38-2.26 (m, 1H), 2.25-2.19 (m, 1H); ${ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 165.66(\mathrm{~d}, J=254.7 \mathrm{~Hz}), 139.42,134.96(\mathrm{~d}, J=$ 3.0 Hz ), 132.78, $131.50(\mathrm{~d}, J=9.9 \mathrm{~Hz}, 2 x$ ), $128.45(2 x), 128.43,127.00(2 x), 117.87,116.25(\mathrm{~d}, J=$ $22.7 \mathrm{~Hz}, 2 \mathrm{x}), 72.73,70.28,30.76$.

1.2.15. 2-(4-Butylbenzenesulfonyl)-1-phenylpent-4-en-1-ol (30). According to the general procedure, reaction was performed in the presence of $\mathrm{NaBH}_{4}(100 \mathrm{mg}, 3.0 \mathrm{mmol})$ and 10 ( 356 mg , 1.0 mmol ) in a co-solvent of THF ( 5 mL ) and $\mathrm{MeOH}(5 \mathrm{~mL})$ at $0^{\circ} \mathrm{C}$ for 1 h . Purification on silica gel (hexanes/EtOAc = 5/1) afforded $30(95 \%, 340 \mathrm{mg})$. Colorless gum; HRMS (ESI, M ${ }^{+}+1$ ) calcd for $\mathrm{C}_{21} \mathrm{H}_{27} \mathrm{O}_{3} \mathrm{~S} 359.1681$, found 359.1687 ; ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 7.73(\mathrm{~d}, \mathrm{~J}=8.4 \mathrm{~Hz}, 2 \mathrm{H}), 7.27$ (d, $J=8.4 \mathrm{~Hz}, 2 \mathrm{H}$ ), 7.25-7.19 (m, 5H), 5.25-5.14 (m, 1H), 5.02 (d, $J=8.4 \mathrm{~Hz}, 1 \mathrm{H}), 4.68$ (dq, $J=1.2$, $10.0 \mathrm{~Hz}, 1 \mathrm{H}), 4.55(\mathrm{dq}, J=1.2,16.8 \mathrm{~Hz}, 1 \mathrm{H}), 4.00(\mathrm{br} \mathrm{s}, 1 \mathrm{H}), 3.43-3.38(\mathrm{~m}, 1 \mathrm{H}), 2.63(\mathrm{t}, J=8.0 \mathrm{~Hz}$, $2 \mathrm{H}), 2.31-2.24(\mathrm{~m}, 1 \mathrm{H}), 2.12-2.05(\mathrm{~m}, 1 \mathrm{H}), 1.60-1.53(\mathrm{~m}, 2 \mathrm{H}), 1.35-1.26(\mathrm{~m}, 2 \mathrm{H}), 0.89(\mathrm{t}, J=7.2 \mathrm{~Hz}$, $3 H) ;{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 149.70,139.42,135.41,132.97,129.00(2 \mathrm{x}), 128.62(2 \mathrm{x})$, 128.30 (2x), 128.27, 127.11 (2x), 72.78, 70.11, 35.40, 32.90, 30.86, 29.50, 22.05, 13.68.

1.2.16. 2-(Toluene-4-sulfonyl)-1-(4-trifluoromethylphenyl)pent-4-en-1-ol (3p). According to the general procedure, reaction was performed in the presence of $\mathrm{NaBH}_{4}(100 \mathrm{mg}, 3.0 \mathrm{mmol})$ and $\mathbf{1 p}$ $(382 \mathrm{mg}, 1.0 \mathrm{mmol})$ in a co-solvent of THF ( 5 mL ) and $\mathrm{MeOH}(5 \mathrm{~mL})$ at $0^{\circ} \mathrm{C}$ for 1 h . Purification on silica gel (hexanes/EtOAc $=5 / 1$ ) afforded $3 p\left(89 \%, 342 \mathrm{mg}\right.$ ). Colorless solid; mp $=103-104{ }^{\circ} \mathrm{C}$ (recrystallized from hexanes and EtOAc); HRMS (ESI, $\mathrm{M}^{+}+1$ ) calcd for $\mathrm{C}_{19} \mathrm{H}_{20} \mathrm{~F}_{3} \mathrm{O}_{3} \mathrm{~S}$ 385.1085, found $385.1087 ;{ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 7.65(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 2 \mathrm{H}), 7.49(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 2 \mathrm{H})$, $7.38(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 2 \mathrm{H}), 7.27(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 2 \mathrm{H}), 5.40-5.30(\mathrm{~m}, 1 \mathrm{H}), 5.14(\mathrm{~d}, J=7.2 \mathrm{~Hz}, 1 \mathrm{H}), 4.84$
(dq, $J=1.2,10.0 \mathrm{~Hz}, 1 \mathrm{H}$ ), 4.73 (dq, $J=1.2,16.8 \mathrm{~Hz}, 1 \mathrm{H}), 4.48(\mathrm{br} \mathrm{s}, 1 \mathrm{H}), 3.48-3.43(\mathrm{~m}, 1 \mathrm{H})$, 2.52-2.44 (m, 1H), $2.42(\mathrm{~s}, 3 \mathrm{H}), 2.29-2.21(\mathrm{~m}, 1 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 145.22,143.61$, 135.18, 132.63, 129.81 ( 2 x ), 128.53 ( 2 x ), 127.32 ( 2 x ), 125.31 ( $\mathrm{d}, \mathrm{J}=3.8 \mathrm{~Hz}, 2 \mathrm{x}$ ), 125.23 ( $\mathrm{d}, \mathrm{J}=3.7$ $\mathrm{Hz}, 2 \mathrm{x}), 118.32,71.91,69.45,30.58,21.53$.

1.2.17. 1-(3-Nitrophenyl)-2-(toluene-4-sulfonyl)pent-4-en-1-ol (3q). According to the general procedure, reaction was performed in the presence of $\mathrm{NaBH}_{4}(100 \mathrm{mg}, 3.0 \mathrm{mmol})$ and $1 \mathrm{q}(359 \mathrm{mg}$, $1.0 \mathrm{mmol})$ in a co-solvent of THF ( 5 mL ) and $\mathrm{MeOH}(5 \mathrm{~mL})$ at $0^{\circ} \mathrm{C}$ for 1 h . Purification on silica gel (hexanes/EtOAc $=5 / 1$ ) afforded $3 q\left(86 \%, 310 \mathrm{mg}\right.$ ). Colorless solid; $\mathrm{mp}=121-122{ }^{\circ} \mathrm{C}$ (recrystallized from hexanes and EtOAc); HRMS (ESI, M ${ }^{+}+1$ ) calcd for $\mathrm{C}_{18} \mathrm{H}_{20} \mathrm{NO}_{5} \mathrm{~S} 362.1062$, found 362.1063 ; ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 8.11-8.07(\mathrm{~m}, 2 \mathrm{H}), 7.69(\mathrm{~d}, \mathrm{~J}=8.4 \mathrm{~Hz}, 3 \mathrm{H}), 7.48(\mathrm{~d}$, $J=8.0 \mathrm{~Hz}, 1 \mathrm{H}), 7.31(\mathrm{~d}, J=8.0 \mathrm{~Hz}, 2 \mathrm{H}), 5.39-5.28(\mathrm{~m}, 1 \mathrm{H}), 5.19(\mathrm{dd}, J=4.0,7.2 \mathrm{~Hz}, 1 \mathrm{H}), 4.83(\mathrm{dq}$, $J=1.2,10.4 \mathrm{~Hz}, 1 \mathrm{H}), 4.70(\mathrm{dq}, J=1.2,17.2 \mathrm{~Hz}, 1 \mathrm{H}), 4.57(\mathrm{~d}, J=4.4 \mathrm{~Hz}, 1 \mathrm{H}), 3.50-3.45(\mathrm{~m}, 1 \mathrm{H})$, 2.51-2.45 (m, 1H), 2.43 (s, 3H), 2.27-2.19 (m, 1H); ${ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta$ 148.10, 145.48, 141.89, 134.88, 133.14, 132.42, 129.96 (2x), 129.40, 128.61 (2x), 123.12, 122.10, 118.51, 71.71, 69.23, 30.68, 21.60; Anal. Calcd for $\mathrm{C}_{18} \mathrm{H}_{19} \mathrm{NO}_{5} \mathrm{~S}: \mathrm{C}, 59.82 ; \mathrm{H}, 5.30$. Found: C, 59.95; H, 5.48.

1.2.18. 1-(4-Nitrophenyl)-2-(toluene-4-sulfonyl)pent-4-en-1-ol (3r). According to the general procedure, reaction was performed in the presence of $\mathrm{NaBH}_{4}(100 \mathrm{mg}, 3.0 \mathrm{mmol})$ and $\mathbf{1 r}(359 \mathrm{mg}$, 1.0 mmol ) in a co-solvent of THF ( 5 mL ) and $\mathrm{MeOH}(5 \mathrm{~mL})$ at $0^{\circ} \mathrm{C}$ for 1 h . Purification on silica gel (hexanes/EtOAc = 5/1) afforded $3 \mathbf{r}\left(72 \%, 260 \mathrm{mg}\right.$ ). Colorless solid; $\mathrm{mp}=142-143^{\circ} \mathrm{C}$ (recrystallized from hexanes and EtOAc); HRMS (ESI, M ${ }^{+}+1$ ) calcd for $\mathrm{C}_{18} \mathrm{H}_{20} \mathrm{NO}_{5} \mathrm{~S} 362.1062$, found 362.1063 ; ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 8.12(\mathrm{~d}, J=8.8 \mathrm{~Hz}, 2 \mathrm{H}), 7.69(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 2 \mathrm{H}), 7.47(\mathrm{~d}, J=8.8 \mathrm{~Hz}, 2 \mathrm{H})$, 7.31 (d, $J=8.0 \mathrm{~Hz}, 2 \mathrm{H}), 5.37-5.26(\mathrm{~m}, 1 \mathrm{H}), 5.21(\mathrm{~d}, J=7.2 \mathrm{~Hz}, 1 \mathrm{H}), 4.84(\mathrm{dq}, J=1.2,10.4 \mathrm{~Hz}, 1 \mathrm{H})$, 4.72 (dq, $J=1.2,17.2 \mathrm{~Hz}, 1 \mathrm{H}$ ), $4.53(\mathrm{brs}, 1 \mathrm{H}), 3.47-3.42(\mathrm{~m}, 1 \mathrm{H}), 2.49-2.41(\mathrm{~m}, 1 \mathrm{H}), 2.44(\mathrm{~s}, 3 \mathrm{H})$, 2.26-2.17 (m, 1H); ${ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta$ 146.84, 145.57, 134.88, 132.40, 130.86, 129.93 (2x), 128.65 (2x), $127.99(2 x), 123.52(2 x), 118.59,71.79,69.37,30.65,21.63$.

1.2.19. 1,2-Diphenylpent-4-en-1-ol (3s). According to the general procedure, reaction was performed in the presence of $\mathrm{NaBH}_{4}(100 \mathrm{mg}, 3.0 \mathrm{mmol})$ and $1 \mathrm{~s}(236 \mathrm{mg}, 1.0 \mathrm{mmol})$ in a co-solvent of THF ( 5 mL ) and $\mathrm{MeOH}(5 \mathrm{~mL})$ at $0{ }^{\circ} \mathrm{C}$ for 1 h . Purification on silica gel (hexanes/EtOAc $=5 / 1$ ) afforded $3 \mathrm{~s}\left(80 \%, 190 \mathrm{mg}\right.$ ). Colorless solid; $\mathrm{mp}=50-51^{\circ} \mathrm{C}$ (recrystallized
from hexanes and EtOAc); HRMS (ESI, $\mathrm{M}^{+}+1$ ) calcd for $\mathrm{C}_{17} \mathrm{H}_{19} \mathrm{O}$ 239.1436, found 239.1441; ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 7.37-7.14(\mathrm{~m}, 10 \mathrm{H}), 5.57-5.47(\mathrm{~m}, 1 \mathrm{H}), 5.01-5.83(\mathrm{~m}, 2 \mathrm{H}), 4.80(\mathrm{~d}, J=$ $8.0 \mathrm{~Hz}, 1 \mathrm{H}$ ), 3.00-2.95 (m, 1H), 2.39-2.24 (m, 2H), $1.80(\mathrm{br} \mathrm{s}, 1 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta$ $142.43,140.39,136.14,128.93(2 x), 128.45$ (2x), 128.26 ( $2 x$ ), 127.77, 126.95, 126.85 ( $2 x$ ), 116.23, 77.91, 53.95, 36.39.

1.2.20. 1-(4-Fluorophenyl)-2-phenylpent-4-en-1-ol (3t). According to the general procedure, reaction was performed in the presence of $\mathrm{NaBH}_{4}(100 \mathrm{mg}, 3.0 \mathrm{mmol})$ and $\mathbf{1 t}(254 \mathrm{mg}, 1.0 \mathrm{mmol})$ in a co-solvent of THF ( 5 mL ) and $\mathrm{MeOH}(5 \mathrm{~mL})$ at $0{ }^{\circ} \mathrm{C}$ for 1 h . Purification on silica gel (hexanes/EtOAc $=5 / 1$ ) afforded $3 \mathrm{t}\left(82 \%, 210 \mathrm{mg}\right.$ ). Colorless solid; $\mathrm{mp}=54-55^{\circ} \mathrm{C}$ (recrystallized from hexanes and EtOAc); HRMS (ESI, M ${ }^{+}+1$ ) calcd for $\mathrm{C}_{17} \mathrm{H}_{18} \mathrm{FO} 257.1342$, found 257.1345 ; ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 7.36-7.32(\mathrm{~m}, 2 \mathrm{H}), 7.30-7.19(\mathrm{~m}, 5 \mathrm{H}), 7.06-7.01(\mathrm{~m}, 2 \mathrm{H}), 5.59-5.48(\mathrm{~m}$, $1 \mathrm{H}), ~ 4.92-4.85(\mathrm{~m}, 2 \mathrm{H}), 4.78(\mathrm{~d}, J=7.2 \mathrm{~Hz}, 1 \mathrm{H}), 2.96-2.90(\mathrm{~m}, 1 \mathrm{H}), 2.39-2.26(\mathrm{~m}, 2 \mathrm{H}), 1.95(\mathrm{br} \mathrm{s}$, $1 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 162.18$ ( $\mathrm{d}, J=244.1 \mathrm{~Hz}$ ), $140.02,138.11$ ( $\mathrm{d}, J=3.1 \mathrm{~Hz}$ ), 135.92 , $128.85(2 x), 128.40(2 x), 128.15(d, J=8.3 \mathrm{~Hz}, 2 x), 126.94,116.27,114.96(d, J=21.2 \mathrm{~Hz}, 2 x)$, 77.02, 53.94, 36.20.
1.3. A representative synthetic procedure of compounds 4a-p is as follows: $\mathrm{NaBH}_{4}$ ( 100 mg , 3.0 mmol ) was added to a solution of $\mathbf{2 a - p}(1.0 \mathrm{mmol})$ in a co-solvent of THF ( 5 mL ) and MeOH ( 5 mL ) at $0^{\circ} \mathrm{C}$. The reaction mixture was stirred for 1 h at $0^{\circ} \mathrm{C}$ and the solvent was concentrated. The residue was diluted with water ( 10 mL ) and the mixture was extracted with $\mathrm{CH}_{2} \mathrm{Cl}_{2}(3 \times 20 \mathrm{~mL})$. The combined organic layers were washed with brine, dried, filtered and evaporated to afford crude product. Purification on silica gel (hexanes/EtOAc $=5 / 1 \sim 3 / 1$ ) afforded 4a-p.

1.3.1. 5-Methyl-1-phenyl-2-(toluene-4-sulfonyl)hex-4-en-1-ol (4a). According to the general procedure, reaction was performed in the presence of $\mathrm{NaBH}_{4}(100 \mathrm{mg}, 3.0 \mathrm{mmol})$ and $\mathbf{2 a}$ ( 342 mg , 1.0 mmol ) in a co-solvent of THF ( 5 mL ) and $\mathrm{MeOH}(5 \mathrm{~mL})$ at $0^{\circ} \mathrm{C}$ for 1 h . Purification on silica gel (hexanes/EtOAc $=5 / 1$ ) afforded $4 \mathbf{a}\left(90 \%, 310 \mathrm{mg}\right.$ ). Colorless solid; $\mathrm{mp}=84-85^{\circ} \mathrm{C}$ (recrystallized from hexanes and EtOAc); HRMS (ESI, $\mathrm{M}^{+}+1$ ) calcd for $\mathrm{C}_{20} \mathrm{H}_{25} \mathrm{O}_{3} \mathrm{~S} 345.1524$, found 345.1530 ; ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 7.76(\mathrm{~d}, J=8.0 \mathrm{~Hz}, 2 \mathrm{H}), 7.33(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 2 \mathrm{H}), 7.30-7.24(\mathrm{~m}, 5 \mathrm{H}), 5.07$ (d, $J=8.4 \mathrm{~Hz}, 1 \mathrm{H}), 4.50(\mathrm{br} \mathrm{s}, 1 \mathrm{H}), 4.43(\mathrm{brt}, J=6.8 \mathrm{~Hz}, 1 \mathrm{H}), 3.41-3.35(\mathrm{~m}, 1 \mathrm{H}), 2.45(\mathrm{~s}, 3 \mathrm{H})$, 2.29-2.21 (m, 1H), 2.02-1.94 (m, 1H), $1.38(\mathrm{~s}, 3 \mathrm{H}), 1.15(\mathrm{~s}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta$ 144.91, 139.68, 135.54, 134.14, 129.71 (2x), 128.73 ( $2 x$ ), 128.43 ( $2 x$ ), 128.34, 127.25 (2x), 119.19, 73.07, 70.94, 25.75, 25.46, 21.61, 17.27.

1.3.2. 1-(4-Methoxyphenyl)-5-methyl-2-(toluene-4-sulfonyl)hex-4-en-1-ol (4b). According to the general procedure, reaction was performed in the presence of $\mathrm{NaBH}_{4}(100 \mathrm{mg}, 3.0 \mathrm{mmol})$ and $\mathbf{2 b}$ ( $372 \mathrm{mg}, 1.0 \mathrm{mmol}$ ) in a co-solvent of THF ( 5 mL ) and $\mathrm{MeOH}(5 \mathrm{~mL})$ at $0^{\circ} \mathrm{C}$ for 1 h . Purification on silica gel (hexanes/EtOAc = 3/1) afforded 4b (92\%, 344 mg ). Colorless gum; HRMS (ESI, M ${ }^{+}+1$ ) calcd for $\mathrm{C}_{21} \mathrm{H}_{27} \mathrm{O}_{4} \mathrm{~S} 375.1630$, found 375.1632 ; ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 7.75(\mathrm{~d}, \mathrm{~J}=8.0 \mathrm{~Hz}$, $2 \mathrm{H}), 7.32(\mathrm{~d}, J=8.0 \mathrm{~Hz}, 2 \mathrm{H}), 7.20(\mathrm{~d}, J=8.8 \mathrm{~Hz}, 2 \mathrm{H}), 6.80(\mathrm{~d}, J=8.8 \mathrm{~Hz}, 2 \mathrm{H}), 5.03(\mathrm{~d}, J=8.8 \mathrm{~Hz}$, $1 \mathrm{H}), 4.48-4.44(\mathrm{~m}, 1 \mathrm{H}), 4.45(\mathrm{br} \mathrm{s}, 1 \mathrm{H}), 3.75(\mathrm{~s}, 3 \mathrm{H}), 3.38-3.33(\mathrm{~m}, 1 \mathrm{H}), 2.42(\mathrm{~s}, 3 \mathrm{H}), 2.29-2.18(\mathrm{~m}$, $1 \mathrm{H})$, 2.00-1.93 (m, 1H), $1.39(\mathrm{~d}, J=1.6 \mathrm{~Hz}, 3 \mathrm{H}), 1.16(\mathrm{~s}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 159.42$, $144.72,135.53,133.75,131.81,129.56$ (2x), 128.58 ( $2 x$ ), 128.31 ( $2 x$ ), 119.22, 113.65 ( $2 x$ ), 72.49 , 70.91, 55.11, 25.66, 25.36, 21.47, 17.21.

1.3.3. 5-Methyl-2-(toluene-4-sulfonyl)-1-p-tolylhex-4-en-1-ol (4c). According to the general procedure, reaction was performed in the presence of $\mathrm{NaBH}_{4}(100 \mathrm{mg}, 3.0 \mathrm{mmol})$ and $\mathbf{2 c}(356 \mathrm{mg}$, $1.0 \mathrm{mmol})$ in a co-solvent of THF ( 5 mL ) and $\mathrm{MeOH}(5 \mathrm{~mL})$ at $0{ }^{\circ} \mathrm{C}$ for 1 h . Purification on silica gel (hexanes/EtOAc = 6/1) afforded 4c (94\%, 337 mg ). Colorless gum; HRMS (ESI, M ${ }^{+}+1$ ) calcd for $\mathrm{C}_{21} \mathrm{H}_{27} \mathrm{O}_{3} \mathrm{~S} 359.1681$, found 359.1685 ; ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 7.74(\mathrm{~d}, \mathrm{~J}=8.4 \mathrm{~Hz}, 2 \mathrm{H}), 7.30$ (d, $J=8.0 \mathrm{~Hz}, 2 \mathrm{H}), 7.16$ (d, $J=8.0 \mathrm{~Hz}, 2 \mathrm{H}), 7.07(\mathrm{~d}, J=8.0 \mathrm{~Hz}, 2 \mathrm{H}), 5.03(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 1 \mathrm{H}), 4.47$ (br t, J=6.8 Hz, 1H), $4.00(\mathrm{br} \mathrm{s}, 1 \mathrm{H}), 3.40-3.35(\mathrm{~m}, 1 \mathrm{H}), 2.42(\mathrm{~s}, 3 \mathrm{H}), 2.29(\mathrm{~s}, 3 \mathrm{H}), 2.26-2.20(\mathrm{~m}$, $1 \mathrm{H}), 2.03-1.96(\mathrm{~m}, 1 \mathrm{H}), 1.38(\mathrm{~s}, 3 \mathrm{H}), 1.16(\mathrm{~s}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 144.68,137.86$, 136.67, 135.62, 133.79, 129.53 (2x), 128.92 (2x), 128.56 (2x), 126.99 (2x), 119.22, 72.70, 70.83, 25.61, 25.35, 21.47, 20.97, 17.19.

1.3.4. 1-Biphenyl-4-yl-5-methyl-2-(toluene-4-sulfonyl)hex-4-en-1-ol (4d). According to the general procedure, reaction was performed in the presence of $\mathrm{NaBH}_{4}(100 \mathrm{mg}, 3.0 \mathrm{mmol})$ and $\mathbf{2 d}$ $(418 \mathrm{mg}, 1.0 \mathrm{mmol})$ in a co-solvent of THF ( 5 mL ) and $\mathrm{MeOH}(5 \mathrm{~mL})$ at $0{ }^{\circ} \mathrm{C}$ for 1 h . Purification on silica gel (hexanes/EtOAc $=5 / 1$ ) afforded $4 d(88 \%, 370 \mathrm{mg})$. Colorless gum; HRMS (ESI, $\mathrm{M}^{+}+1$ ) calcd for $\mathrm{C}_{26} \mathrm{H}_{29} \mathrm{O}_{3} \mathrm{~S} 421.1837$, found 421.1841 ; ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 7.66(\mathrm{~d}, J=8.4 \mathrm{~Hz}$, $2 \mathrm{H}), 7.57-7.30(\mathrm{~m}, 11 \mathrm{H}), 5.15(\mathrm{~d}, J=8.0 \mathrm{~Hz}, 1 \mathrm{H}), 4.57-4.53(\mathrm{~m}, 1 \mathrm{H}), 3.80(\mathrm{br} \mathrm{s}, 1 \mathrm{H}), 3.49-3.44(\mathrm{~m}$, $1 \mathrm{H}), 2.42(\mathrm{~s}, 3 \mathrm{H}), 2.39-2.32(\mathrm{~m}, 1 \mathrm{H}), 2.16-2.08(\mathrm{~m}, 1 \mathrm{H}), 1.41(\mathrm{~d}, \mathrm{~J}=1.2 \mathrm{~Hz}, 3 \mathrm{H}), 1.22(\mathrm{~s}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C}$

NMR (100 MHz, $\mathrm{CDCl}_{3}$ ): $\delta 144.77,141.04,140.50,138.70,135.55,134.13,129.61$ (2x), 128.68 (2x), 128.57 ( $2 x$ ), 127.51 ( $2 x$ ), 127.30, 126.97 (2x), 126.89 (2x), 119.18, 72.57, 70.71, 25.54, 25.42, 21.49, 17.29.

1.3.5. 5-Methyl-1-naphthalen-2-yl-2-(toluene-4-sulfonyl)hex-4-en-1-ol (4e). According to the general procedure, reaction was performed in the presence of $\mathrm{NaBH}_{4}(100 \mathrm{mg}, 3.0 \mathrm{mmol})$ and $\mathbf{2 e}$ ( $392 \mathrm{mg}, 1.0 \mathrm{mmol}$ ) in a co-solvent of THF ( 5 mL ) and $\mathrm{MeOH}(5 \mathrm{~mL})$ at $0^{\circ} \mathrm{C}$ for 1 h . Purification on silica gel (hexanes/EtOAc $=5 / 1$ ) afforded $4 \mathbf{e}(88 \%, 347 \mathrm{mg})$. Colorless gum; HRMS (ESI, $\mathrm{M}^{+}+1$ ) calcd for $\mathrm{C}_{24} \mathrm{H}_{27} \mathrm{O}_{3} \mathrm{~S} 395.1681$, found $395.1685 ;{ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 7.68-7.70(\mathrm{~m}, 6 \mathrm{H})$, $7.47-7.43(\mathrm{~m}, 2 \mathrm{H}), 7.39(\mathrm{dd}, J=1.6,8.4 \mathrm{~Hz}, 1 \mathrm{H}), 7.19(\mathrm{~d}, J=8.0 \mathrm{~Hz}, 2 \mathrm{H}), 5.27(\mathrm{~d}, J=8.0 \mathrm{~Hz}, 1 \mathrm{H})$, 4.57-4.54 (m, 1H), $4.60(\mathrm{br} \mathrm{s}, 1 \mathrm{H}), 3.57-3.52(\mathrm{~m}, 1 \mathrm{H}), 2.41-2.35(\mathrm{~m}, 1 \mathrm{H}), 2.33(\mathrm{~s}, 3 \mathrm{H}), 2.18-2.11(\mathrm{~m}$, $1 \mathrm{H}), 1.31(\mathrm{~d}, J=0.8 \mathrm{~Hz}, 3 \mathrm{H}), 1.12(\mathrm{~s}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 144.63,136.95,135.54$, 134.12, 133.03, 132.85, 129.40 (2x), 128.41 (2x), 128.06, 127.78, 127.38, 126.35, 126.02, 125.97, 124.23, 119.00, 72.78, 70.31, 25.42, 25.23, 21.34, 17.20.

1.3.6. 2-Benzenesulfonyl-1-(4-methoxyphenyl)-5-methylhex-4-en-1-ol (4f). According to the general procedure, reaction was performed in the presence of $\mathrm{NaBH}_{4}(100 \mathrm{mg}, 3.0 \mathrm{mmol})$ and $\mathbf{2 f}$ ( $358 \mathrm{mg}, 1.0 \mathrm{mmol}$ ) in a co-solvent of THF ( 5 mL ) and $\mathrm{MeOH}(5 \mathrm{~mL})$ at $0^{\circ} \mathrm{C}$ for 1 h . Purification on silica gel (hexanes/EtOAc =5/1) afforded $\mathbf{4 f}(90 \%, 324 \mathrm{mg})$. Colorless gum; HRMS (ESI, $\mathrm{M}^{+}+1$ ) calcd for $\mathrm{C}_{20} \mathrm{H}_{25} \mathrm{O}_{4} \mathrm{~S} 361.1474$, found $361.1483 ;{ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 7.91-7.86(\mathrm{~m}, 2 \mathrm{H})$, 7.65-7.61 (m, 1H), 7.56-7.51 (m, 2H), 7.22-7.18 (m, 2H), $6.81(\mathrm{~d}, \mathrm{~J}=8.8 \mathrm{~Hz}, 2 \mathrm{H}), 5.06(\mathrm{~d}, J=8.4$ $\mathrm{Hz}, 1 \mathrm{H}), 4.48-4.43(\mathrm{~m}, 1 \mathrm{H}), 4.00(\mathrm{br} \mathrm{s}, 1 \mathrm{H}), 3.76(\mathrm{~s}, 3 \mathrm{H}), 3.41-3.36(\mathrm{~m}, 1 \mathrm{H}), 2.28-2.21(\mathrm{~m}, 1 \mathrm{H})$, 2.03-1.96 (m, 1H), $1.38(\mathrm{~d}, \mathrm{~J}=1.2 \mathrm{~Hz}, 3 \mathrm{H}), 1.16(\mathrm{~s}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 159.51$, $138.79,134.08,133.69,131.78,128.99$ (2x), 128.55 ( $2 x$ ), 128.34 ( $2 x$ ), 119.12, 113.77 ( $2 x$ ), 72.49, 70.95, 55.20, 25.70, 25.45, 17.27.

1.3.7. 2-Methanesulfonyl-1-(4-methoxyphenyl)-5-methylhex-4-en-1-ol (4g). According to the general procedure, reaction was performed in the presence of $\mathrm{NaBH}_{4}(100 \mathrm{mg}, 3.0 \mathrm{mmol})$ and $\mathbf{2 g}$ ( $296 \mathrm{mg}, 1.0 \mathrm{mmol}$ ) in a co-solvent of THF ( 5 mL ) and $\mathrm{MeOH}(5 \mathrm{~mL})$ at $0^{\circ} \mathrm{C}$ for 1 h . Purification on silica gel (hexanes/EtOAc $=5 / 1$ ) afforded $4 \mathrm{~g}(92 \%, 274 \mathrm{mg})$. Colorless gum; HRMS $\left(E S I, \mathrm{M}^{+}+1\right)$
calcd for $\mathrm{C}_{15} \mathrm{H}_{23} \mathrm{O}_{4} \mathrm{~S} 299.1317$, found 299.1320; ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 7.23(\mathrm{~d}, \mathrm{~J}=8.4 \mathrm{~Hz}$, 2H), 6.86 (d, $J=8.4 \mathrm{~Hz}, 2 \mathrm{H}$ ), $4.96(\mathrm{~d}, J=8.8 \mathrm{~Hz}, 1 \mathrm{H}), 4.95(\mathrm{brt}, J=6.8 \mathrm{~Hz}, 1 \mathrm{H}), 4.52(\mathrm{br} \mathrm{s}, 1 \mathrm{H})$, $3.77(\mathrm{~s}, 3 \mathrm{H}), 3.21-3.16(\mathrm{~m}, 1 \mathrm{H}), 2.94(\mathrm{~s}, 3 \mathrm{H}), 2.37-2.23(\mathrm{~m}, 2 \mathrm{H}), 1.58(\mathrm{~s}, 3 \mathrm{H}), 1.32(\mathrm{~s}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 159.60,134.70,132.44,128.12$ (2x), 119.04, 113.99 (2x), 72.52, 69.65, 55.21, 43.73, 25.60, 25.26, 17.47.

1.3.8. 1-(4-Fluorophenyl)-5-methyl-2-(toluene-4-sulfonyl)hex-4-en-1-ol (4h). According to the general procedure, reaction was performed in the presence of $\mathrm{NaBH}_{4}(100 \mathrm{mg}, 3.0 \mathrm{mmol})$ and $\mathbf{2 h}$ ( $360 \mathrm{mg}, 1.0 \mathrm{mmol}$ ) in a co-solvent of THF ( 5 mL ) and $\mathrm{MeOH}(5 \mathrm{~mL})$ at $0^{\circ} \mathrm{C}$ for 1 h . Purification on silica gel (hexanes/EtOAc $=5 / 1$ ) afforded $4 \mathrm{~h}(90 \%, 326 \mathrm{mg})$. Colorless solid; $\mathrm{mp}=88-89{ }^{\circ} \mathrm{C}$ (recrystallized from hexanes and EtOAc); HRMS (ESI, $\mathrm{M}^{+}+1$ ) calcd for $\mathrm{C}_{20} \mathrm{H}_{24} \mathrm{FO}_{3} \mathrm{~S}$ 363.1430, found 363.1436 ; ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 7.76(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 2 \mathrm{H}), 7.33(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 2 \mathrm{H})$, 7.30-7.25 (m, 2H), 7.00-6.94 (m, 2H), $5.09(\mathrm{~d}, ~ J=8.4 \mathrm{~Hz}, 1 \mathrm{H}), 4.49-4.45(\mathrm{~m}, 1 \mathrm{H}), 4.17(\mathrm{br} \mathrm{s}, 1 \mathrm{H})$, 3.39-3.34 (m, 1H), 2.44 (s, 3H), 2.30-2.22 (m, 1H), 2.04-1.96 (m, 1H), $1.41(\mathrm{~d}, \mathrm{~J}=1.2 \mathrm{~Hz}, 3 \mathrm{H}), 1.18$ (s, 3H); ${ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 162.40(\mathrm{~d}, J=244.9 \mathrm{~Hz}), 144.92,135.57(\mathrm{~d}, J=3.1 \mathrm{~Hz})$, $135.29,134.11,129.62(2 x), 128.84(d, J=8.3 \mathrm{~Hz}, 2 x), 128.55(2 x), 118.93$, 115.08 ( $d, J=21.3 \mathrm{~Hz}$, $2 x)$, 72.15, 70.68, 25.48, 25.32, 21.44, 17.18; Anal. Calcd for $\mathrm{C}_{20} \mathrm{H}_{23} \mathrm{FO}_{3} \mathrm{~S}: \mathrm{C}, 66.27 ; \mathrm{H}, 6.40$. Found: C, 66.38; H, 6.25.

1.3.9. 5-Methyl-1-(3-nitrophenyl)-2-(toluene-4-sulfonyl)hex-4-en-1-ol (4i). According to the general procedure, reaction was performed in the presence of $\mathrm{NaBH}_{4}(100 \mathrm{mg}, 3.0 \mathrm{mmol})$ and $\mathbf{2 i}$ $(387 \mathrm{mg}, 1.0 \mathrm{mmol})$ in a co-solvent of THF ( 5 mL ) and $\mathrm{MeOH}(5 \mathrm{~mL})$ at $0^{\circ} \mathrm{C}$ for 1 h . Purification on silica gel (hexanes/EtOAc = 3/1) afforded 4i (82\%, 319 mg ). Colorless solid; mp $=121-122{ }^{\circ} \mathrm{C}$ (recrystallized from hexanes and EtOAc); HRMS (ESI, M ${ }^{+}+1$ ) calcd for $\mathrm{C}_{20} \mathrm{H}_{24} \mathrm{NO}_{5} \mathrm{~S}$ 390.1375, found 390.1382; ${ }^{1} \mathrm{H}$ NMR (400 MHz, $\mathrm{CDCl}_{3}$ ): $\delta$ 8.07-8.05 (m, 2H), 7.69-7.66 (m, 3H), 7.47-7.43 (m, $1 \mathrm{H}), 7.28(\mathrm{~d}, J=8.0 \mathrm{~Hz}, 2 \mathrm{H}), 5.19(\mathrm{~d}, J=7.2 \mathrm{~Hz}, 1 \mathrm{H}), 4.57-4.52(\mathrm{~m}, 1 \mathrm{H}), 4.00(\mathrm{br} \mathrm{s}, 1 \mathrm{H}), 3.45-3.40$ $(\mathrm{m}, 1 \mathrm{H}), 2.40(\mathrm{~s}, 3 \mathrm{H}), 2.40-2.31(\mathrm{~m}, 1 \mathrm{H}), 2.18-2.11(\mathrm{~m}, 1 \mathrm{H}), 1.41(\mathrm{~d}, J=0.8 \mathrm{~Hz}, 3 \mathrm{H}), 1.22(\mathrm{~s}, 3 \mathrm{H})$; ${ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 147.95,145.22,142.12,135.31,135.11,133.07,129.78(2 \mathrm{x})$, 129.24, 128.48 ( $2 x$ ), 122.88, 122.02, 118.45, 71.63, 69.80, 25.42, 25.18, 21.48, 17.39.

1.3.10. 5-Methyl-1-(4-nitrophenyl)-2-(toluene-4-sulfonyl)hex-4-en-1-ol (4j). According to the general procedure, reaction was performed in the presence of $\mathrm{NaBH}_{4}(100 \mathrm{mg}, 3.0 \mathrm{mmol})$ and $\mathbf{2 j}$ $(387 \mathrm{mg}, 1.0 \mathrm{mmol})$ in a co-solvent of THF ( 5 mL ) and $\mathrm{MeOH}(5 \mathrm{~mL})$ at $0^{\circ} \mathrm{C}$ for 1 h . Purification on silica gel (hexanes/EtOAc = 3/1) afforded $4 \mathrm{j}\left(70 \%\right.$, 272 mg ). Colorless gum; HRMS (ESI, $\mathrm{M}^{+}+1$ ) calcd for $\mathrm{C}_{20} \mathrm{H}_{24} \mathrm{NO}_{5} \mathrm{~S} 390.1375$, found 390.1378 ; ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 8.11$ (d, $J=8.8 \mathrm{~Hz}$, $2 \mathrm{H}), 8.68(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 2 \mathrm{H}), 7.47(\mathrm{~d}, J=8.8 \mathrm{~Hz}, 2 \mathrm{H}), 7.30(\mathrm{~d}, J=8.0 \mathrm{~Hz}, 2 \mathrm{H}), 5.21(\mathrm{~d}, J=7.2 \mathrm{~Hz}$, $1 \mathrm{H}), 4.55-4.51(\mathrm{~m}, 1 \mathrm{H}), 4.50(\mathrm{br} \mathrm{s}, 1 \mathrm{H}), 3.42-3.37(\mathrm{~m}, 1 \mathrm{H}), 2.43(\mathrm{~s}, 3 \mathrm{H}), 2.39-2.32(\mathrm{~m}, 1 \mathrm{H})$, 2.19-2.11 (m, 1H), $1.43(\mathrm{~d}, J=1.2 \mathrm{~Hz}, 3 \mathrm{H}), 1.27(\mathrm{~s}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 147.20$, $135.45,135.17,130.86,129.82(2 x), 128.77,128.58(2 x), 127.92(2 x), 123.39$ ( $2 x$ ), 118.51, 71.79 , 70.06, $25.29(2 x), 21.60,17.52$.


### 1.3.11. 5-Methyl-2-(toluene-4-sulfonyl)-1-(4-trifluoromethylphenyl)hex-4-en-1-ol

According to the general procedure, reaction was performed in the presence of $\mathrm{NaBH}_{4}$ ( 100 mg , $3.0 \mathrm{mmol})$ and $\mathbf{2 k}(410 \mathrm{mg}, 1.0 \mathrm{mmol})$ in a co-solvent of THF ( 5 mL ) and $\mathrm{MeOH}(5 \mathrm{~mL})$ at $0^{\circ} \mathrm{C}$ for 1 h. Purification on silica gel (hexanes/EtOAc $=5 / 1$ ) afforded $\mathbf{4 k}(83 \%, 342 \mathrm{mg})$. Colorless solid; mp $=98-99{ }^{\circ} \mathrm{C}$ (recrystallized from hexanes and EtOAc); HRMS (ESI, $\mathrm{M}^{+}+1$ ) calcd for $\mathrm{C}_{21} \mathrm{H}_{24} \mathrm{~F}_{3} \mathrm{O}_{3} \mathrm{~S}$ 413.1398, found 413.1401 ; ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 7.66(\mathrm{~d}, J=8.0 \mathrm{~Hz}, 2 \mathrm{H}), 7.49(\mathrm{~d}, J=8.4$ $\mathrm{Hz}, 2 \mathrm{H}), 7.38(\mathrm{~d}, J=8.0 \mathrm{~Hz}, 2 \mathrm{H}), 7.27(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 2 \mathrm{H}), 5.15(\mathrm{~d}, J=7.6 \mathrm{~Hz}, 1 \mathrm{H}), 4.51$ (brt, $J=8.4$ $\mathrm{Hz}, 1 \mathrm{H}), 4.50(\mathrm{br} \mathrm{s}, 1 \mathrm{H}), 3.42-3.37(\mathrm{~m}, 1 \mathrm{H}), 2.42(\mathrm{~s}, 3 \mathrm{H}), 2.40-2.36(\mathrm{~m}, 1 \mathrm{H}), 2.19-2.11(\mathrm{~m}, 1 \mathrm{H}), 1.42$ (d, $J=0.8 \mathrm{~Hz}, 3 \mathrm{H}$ ), $1.26(\mathrm{~s}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 145.10,143.84,135.35,135.10$, 130.40, 130.09, 129.76 (2x), 128.52 (2x), 127.35 (2x), 125.19 (q, J = $3.8 \mathrm{~Hz}, 2 x$ ), 118.78, 72.03, 70.19, 25.45, 25.24, 21.53, 17.43; Anal. Calcd for $\mathrm{C}_{21} \mathrm{H}_{23} \mathrm{~F}_{3} \mathrm{O}_{3} \mathrm{~S}: \mathrm{C}, 61.15$; H, 5.62. Found: C, 61.30; H, 5.33.

1.3.12. 5,9-Dimethyl-1-phenyl-2-(toluene-4-sulfonyl)deca-4,8-dien-1-ol (4I). According to the general procedure, reaction was performed in the presence of $\mathrm{NaBH}_{4}(100 \mathrm{mg}, 3.0 \mathrm{mmol})$ and $\mathbf{2 l}$ $(410 \mathrm{mg}, 1.0 \mathrm{mmol})$ in a co-solvent of THF ( 5 mL ) and $\mathrm{MeOH}(5 \mathrm{~mL})$ at $0^{\circ} \mathrm{C}$ for 1 h . Purification on silica gel (hexanes/EtOAc $=5 / 1$ ) afforded $4 \mathrm{II}(80 \%, 330 \mathrm{mg})$. Colorless gum; HRMS (ESI, $\left.\mathrm{M}^{+}+1\right)$ calcd for $\mathrm{C}_{25} \mathrm{H}_{33} \mathrm{O}_{3} \mathrm{~S} 413.2150$, found $413.2155 ;{ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 7.78-7.75(\mathrm{~m}, 2 \mathrm{H})$,
7.34-7.24 (m, 7H), $5.07(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 1 \mathrm{H}), 4.97-4.93(\mathrm{~m}, 1 \mathrm{H}), 4.45-4.41(\mathrm{~m}, 1 \mathrm{H}), 4.00(\mathrm{br} \mathrm{s}, 1 \mathrm{H})$, 3.40-3.35 (m, 1H), 2.44 (s, 3H), 2.32-2.25 (m, 1H), 2.04-1.97 (m, 1H), 1.85-1.76 (m, 2H), 1.71-1.67 (m, 2H), $1.65(\mathrm{~d}, J=0.8 \mathrm{~Hz}, 3 \mathrm{H}), 1.55(\mathrm{~s}, 3 \mathrm{H}), 1.14(\mathrm{~s}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 144.91$, 139.68, 137.75, 135.43, 131.40, 129.70 ( $2 x$ ), 128.71 ( $2 x$ ), 128.40 ( $2 x$ ), 128.29, 127.21 ( $2 x$ ), 123.93, 118.79, 73.01, 71.00, 39.27, 26.08, 25.59, 25.54, 21.57, 17.59, 15.67; Anal. Calcd for $\mathrm{C}_{25} \mathrm{H}_{32} \mathrm{O}_{3} \mathrm{~S}: \mathrm{C}$, 72.78; H, 7.82. Found: C, 72.92; H, 8.02.


### 1.3.13. 5,9-Dimethyl-1-naphthalen-2-yl-2-(toluene-4-sulfonyl)deca-4,8-dien-1-ol (4m).

 According to the general procedure, reaction was performed in the presence of $\mathrm{NaBH}_{4}(100 \mathrm{mg}$, $3.0 \mathrm{mmol})$ and $\mathbf{2 m}(460 \mathrm{mg}, 1.0 \mathrm{mmol})$ in a co-solvent of THF ( 5 mL ) and $\mathrm{MeOH}(5 \mathrm{~mL})$ at $0^{\circ} \mathrm{C}$ for 1 h. Purification on silica gel (hexanes/EtOAc $=5 / 1$ ) afforded $4 \mathrm{~m}(82 \%, 379 \mathrm{mg})$. Colorless gum; HRMS (ESI, $\mathrm{M}^{+}+1$ ) calcd for $\mathrm{C}_{29} \mathrm{H}_{35} \mathrm{O}_{3} \mathrm{~S} 463.2307$, found 463.2309; ${ }^{1} \mathrm{H} \mathrm{NMR}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right.$ ): $\delta$ 7.79-7.70 (m, 6H), 7.49-7.44 (m, 2H), 7.39 (dd, $J=2.4,8.4 \mathrm{~Hz}, 1 \mathrm{H}$ ), $7.22(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 2 \mathrm{H}), 5.26$ $(\mathrm{d}, J=8.0 \mathrm{~Hz}, 1 \mathrm{H}), 4.94-4.89(\mathrm{~m}, 1 \mathrm{H}), 4.60(\mathrm{br} \mathrm{s}, 1 \mathrm{H}), 4.57-4.53(\mathrm{~m}, 1 \mathrm{H}), 3.54-3.49(\mathrm{~m}, 1 \mathrm{H})$, 2.42-2.38 (m, 1H), $2.38(\mathrm{~s}, 3 \mathrm{H}), 2.20-2.12(\mathrm{~m}, 1 \mathrm{H}), 1.78-1.72(\mathrm{~m}, 2 \mathrm{H}), 1.64(\mathrm{~s}, 3 \mathrm{H}), 1.64-1.56(\mathrm{~m}$, 2H), $1.52(\mathrm{~s}, 3 \mathrm{H}), 1.14(\mathrm{~s}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 144.82,138.07,137.06,135.62$, $133.18,133.00,131.41,129.59$ (2x), 128.59 (2x), 128.27, 127.92, 127.53, 126.46, 126.20, 126.14, 124.31, 123.91, 118.75, 72.94, 70.56, 39.23, 26.03, 25.59, 25.45, 21.50, 17.60, 15.81.

### 1.3.14. 1-(4-Fluorophenyl)-5,9-dimethyl-2-(toluene-4-sulfonyl)deca-4,8-dien-1-ol

According to the general procedure, reaction was performed in the presence of $\mathrm{NaBH}_{4}(100 \mathrm{mg}$, $3.0 \mathrm{mmol})$ and $\mathbf{2 n}(428 \mathrm{mg}, 1.0 \mathrm{mmol})$ in a co-solvent of THF ( 5 mL ) and $\mathrm{MeOH}(5 \mathrm{~mL})$ at $0^{\circ} \mathrm{C}$ for 1 h. Purification on silica gel (hexanes/EtOAc $=5 / 1$ ) afforded $\mathbf{4 n}(86 \%, 370 \mathrm{mg})$. Colorless gum; HRMS (ESI, M ${ }^{+}+1$ ) calcd for $\mathrm{C}_{25} \mathrm{H}_{32} \mathrm{FO}_{3} \mathrm{~S} 431.2056$, found 431.2052; ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta$ 7.78-7.73 (m, 2H), 7.34 (d, $J=8.4 \mathrm{~Hz}, 2 \mathrm{H}$ ), 7.30-7.25 (m, 2H), 7.00-6.94 (m, 2H), 5.07 (d, $J=8.4$ $\mathrm{Hz}, 1 \mathrm{H}), 4.97-4.93(\mathrm{~m}, 1 \mathrm{H}), 4.44(\mathrm{brt}, J=7.2 \mathrm{~Hz}, 1 \mathrm{H}), 4.40(\mathrm{br} \mathrm{s}, 1 \mathrm{H}), 3.36-3.31(\mathrm{~m}, 1 \mathrm{H}), 2.45(\mathrm{~s}$, $3 \mathrm{H}), 2.32-2.25(\mathrm{~m}, 1 \mathrm{H}), 2.04-1.96(\mathrm{~m}, 1 \mathrm{H}), 1.83-1.78(\mathrm{~m}, 2 \mathrm{H}), 1.71-1.65(\mathrm{~m}, 2 \mathrm{H}), 1.64(\mathrm{~d}, J=1.2 \mathrm{~Hz}$, 3H), 1.52 ( $\mathrm{s}, 3 \mathrm{H}$ ), $1.17(\mathrm{~s}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 162.55(\mathrm{~d}, J=245.6 \mathrm{~Hz}), 145.08$, $137.99,135.64$ ( $\mathrm{d}, J=3.0 \mathrm{~Hz}$ ), 135.32, 131.53, 129.78 ( $2 x$ ), 128.90 ( $\mathrm{d}, J=8.3 \mathrm{~Hz}, 2 x$ ), 128.71 (2x), 123.85, 118.65, 115.26 (d, J = 21.3 Hz, 2x), 72.32, 70.97, 39.29, 26.10, 25.60, 25.51, 21.59, 17.57, 15.74.


### 1.3.15. 1-(4-Methoxyphenyl)-5,9-dimethyl-2-(toluene-4-sulfonyl)deca-4,8-dien-1-ol (40).

According to the general procedure, reaction was performed in the presence of $\mathrm{NaBH}_{4}$ ( 100 mg , $3.0 \mathrm{mmol})$ and $\mathbf{2 0}(440 \mathrm{mg}, 1.0 \mathrm{mmol})$ in a co-solvent of THF ( 5 mL ) and $\mathrm{MeOH}(5 \mathrm{~mL})$ at $0^{\circ} \mathrm{C}$ for 1 h. Purification on silica gel (hexanes/EtOAc = 4/1) afforded 40 ( $86 \%, 380 \mathrm{mg}$ ). Colorless gum; HRMS (ESI, M ${ }^{+}+1$ ) calcd for $\mathrm{C}_{26} \mathrm{H}_{35} \mathrm{O}_{4} \mathrm{~S} 443.2256$, found 443.2261 ; ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta$ 7.77 (d, $J=8.4 \mathrm{~Hz}, 2 \mathrm{H}), 7.34(\mathrm{~d}, J=8.0 \mathrm{~Hz}, 2 \mathrm{H}), 7.21(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 2 \mathrm{H}), 6.81(\mathrm{~d}, J=8.8 \mathrm{~Hz}, 2 \mathrm{H})$, $5.03(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 1 \mathrm{H}), 4.98-4.93(\mathrm{~m}, 1 \mathrm{H}), 4.60(\mathrm{br} \mathrm{s}, 1 \mathrm{H}), 4.45(\mathrm{dt}, J=1.2,7.2 \mathrm{~Hz}, 1 \mathrm{H}), 3.77(\mathrm{br} \mathrm{s}$, $3 \mathrm{H}), 3.37-3.32(\mathrm{~m}, 1 \mathrm{H}), 2.45(\mathrm{~s}, 3 \mathrm{H})$, 2.30-2.22 (m, 1H), 2.01-1.94 (m, 1H), 1.86-1.77 (m, 2H), 1.72-1.62 (m, 2H), $1.62(\mathrm{~d}, \mathrm{~J}=1.2 \mathrm{~Hz}, 3 \mathrm{H}), 1.55(\mathrm{~s}, 3 \mathrm{H}), 1.16(\mathrm{~s}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 159.60,144.90,137.61,135.58,131.94,131.45,129.72(2 x), 128.77(2 x), 128.43(2 x), 123.98$, $118.97,113.83$ (2x), 72.66, 71.22, 55.24, 39.33, 26.14, 25.70, 25.63, 21.62, 17.61, 15.78.


### 1.3.16. 2-Methanesulfonyl-1-(4-methoxyphenyl)-5,9-dimethyldeca-4,8-dien-1-ol

According to the general procedure, reaction was performed in the presence of $\mathrm{NaBH}_{4}$ ( 100 mg , $3.0 \mathrm{mmol})$ and $\mathbf{2 p}(364 \mathrm{mg}, 1.0 \mathrm{mmol})$ in a co-solvent of THF ( 5 mL ) and $\mathrm{MeOH}(5 \mathrm{~mL})$ at $0^{\circ} \mathrm{C}$ for 1 h. Purification on silica gel (hexanes/EtOAc $=3 / 1$ ) afforded 4 p $(87 \%, 318 \mathrm{mg})$. Colorless gum; HRMS (ESI, $\mathrm{M}^{+}+1$ ) calcd for $\mathrm{C}_{20} \mathrm{H}_{31} \mathrm{O}_{4} \mathrm{~S} 367.1943$, found $367.1946 ;{ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta$ 7.18 (d, J=8.4 Hz, 2H), $6.80(\mathrm{~d}, J=8.8 \mathrm{~Hz}, 2 \mathrm{H}), 4.97(\mathrm{brt}, J=6.8 \mathrm{~Hz}, 1 \mathrm{H}), 4.91-4.87(\mathrm{~m}, 2 \mathrm{H}), 3.83$ (br s, 1H), $3.71(\mathrm{~s}, 3 \mathrm{H}), 3.15-3.11(\mathrm{~m}, 1 \mathrm{H}), 2.90(\mathrm{~s}, 3 \mathrm{H}), 2.32-2.17(\mathrm{~m}, 2 \mathrm{H}), 1.94-1.89(\mathrm{~m}, 2 \mathrm{H})$, $1.88-1.77(\mathrm{~m}, 2 \mathrm{H}), 1.60(\mathrm{~s}, 3 \mathrm{H}), 1.52(\mathrm{~s}, 3 \mathrm{H}), 1.26(\mathrm{~s}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 159.32$, 137.77, 132.44, 131.10, 128.01 (2x), 123.82, 118.91, 113.69 (2x), 72.29, 69.44, 54.92, 43.50, 39.26, 26.03, 25.37, 23.78, 17.36, 15.55.
1.4. A representative synthetic procedure of compounds $5 \mathrm{a}-\mathrm{x}$ is as follows: $\mathrm{BF}_{3} \cdot \mathrm{OEt}_{2}(57 \mathrm{mg}$, $0.4 \mathrm{mmol})$ was added to a solution of $3 \mathrm{a}-\mathbf{0}, 3 \mathrm{~s}-\mathrm{t}(0.2 \mathrm{mmol})$ and $7 \mathrm{a}-\mathbf{e}(0.3 \mathrm{mmol})$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}(5 \mathrm{~mL})$ at $25^{\circ} \mathrm{C}$. The reaction mixture was stirred at $25{ }^{\circ} \mathrm{C}$ for 20 h . The reaction mixture was concentrated and the residue was diluted with water $(10 \mathrm{~mL})$ and the mixture was extracted with $\mathrm{CH}_{2} \mathrm{Cl}_{2}(3 \times 20$ mL ). The combined organic layers were washed with brine, dried, filtered and evaporated to afford crude product under reduced pressure. Purification on silica gel (hexanes/EtOAc $=3 / 1$ ) afforded 5a-x.

1.4.1. 6,7-Dimethoxy-4-methyl-1-phenyl-2-(toluene-4-sulfonyl)-1,2,3,4-tetrahydronaphthalene (5a). According to the general procedure, reaction was performed in the presence of $\mathrm{BF}_{3} \cdot \mathrm{OEt}_{2}$ (57 $\mathrm{mg}, 0.4 \mathrm{mmol})$, $3 \mathrm{a}(63 \mathrm{mg}, 0.2 \mathrm{mmol})$ and $7 \mathbf{a}(41 \mathrm{mg}, 0.3 \mathrm{mmol})$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}(5 \mathrm{~mL})$ at $25^{\circ} \mathrm{C}$ for 20 h . Purification on silica gel (hexanes/EtOAc $=3 / 1$ ) afforded $5 \mathrm{a}(90 \%, 78 \mathrm{mg})$. Colorless solid; $\mathrm{mp}=$ $131-132{ }^{\circ} \mathrm{C}$ (recrystallized from hexanes and EtOAc); HRMS (ESI, M ${ }^{+}+1$ ) calcd for $\mathrm{C}_{26} \mathrm{H}_{29} \mathrm{O}_{4} \mathrm{~S}$ 437.1787, found 437.1791; ${ }^{1} \mathrm{H} \operatorname{NMR}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta 7.58$ (d, $J=8.0 \mathrm{~Hz}, 2 \mathrm{H}$ ), 7.18 (d, $J=8.0$ $\mathrm{Hz}, 2 \mathrm{H}), 7.14-7.09(\mathrm{~m}, 3 \mathrm{H}), 6.95-6.93(\mathrm{~m}, 2 \mathrm{H}), 6.76(\mathrm{~s}, 1 \mathrm{H}), 6.26(\mathrm{~s}, 1 \mathrm{H}), 4.55(\mathrm{~d}, \mathrm{~J}=8.0 \mathrm{~Hz}, 1 \mathrm{H})$, 3.86 (s, 3H), 3.84-3.76 (m, 1H), 3.59 (s, 3H), 2.97-2.92 (m, 1H), 2.45-2.34 (m, 1H), $2.39(\mathrm{~s}, 3 \mathrm{H})$, $1.73(\mathrm{q}, J=12.4 \mathrm{~Hz}, 1 \mathrm{H}), 1.39(\mathrm{~d}, J=7.2 \mathrm{~Hz}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C} \operatorname{NMR}\left(100 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta 147.58,147.51$, $144.39,144.15,135.47,133.00,129.83$, 129.49 ( $2 x$ ), $128.64(2 x), 128.59(2 x), 128.45(2 x), 126.40$, 112.78, 108.14, 67.56, 55.88, 55.67, 45.09, 32.75, 31.49, 21.53, 20.37.


### 1.4.2.

6,7-Dimethoxy-1-(4-methoxyphenyl)-4-methyl-2-(toluene-4-sulfonyl)-1,2,3,4-tetrahydronapht halene (5b). According to the general procedure, reaction was performed in the presence of $\mathrm{BF}_{3} . \mathrm{OEt}_{2}(57 \mathrm{mg}, 0.4 \mathrm{mmol}), \mathbf{3 b}(69 \mathrm{mg}, 0.2 \mathrm{mmol})$ and $7 \mathbf{a}(41 \mathrm{mg}, 0.3 \mathrm{mmol})$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}(5 \mathrm{~mL})$ at $25^{\circ} \mathrm{C}$ for 20 h . Purification on silica gel (hexanes/EtOAc $=3 / 1$ ) afforded $5 \mathrm{~b}(92 \%, 86 \mathrm{mg})$. Colorless solid; $m p=124-125{ }^{\circ} \mathrm{C}$ (recrystallized from hexanes and EtOAc); HRMS (ESI, $\mathrm{M}^{+}+1$ ) calcd for $\mathrm{C}_{27} \mathrm{H}_{31} \mathrm{O}_{5} \mathrm{~S} 467.1892$, found 467.1893 ; ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 7.55(\mathrm{~d}, J=8.0 \mathrm{~Hz}, 2 \mathrm{H}), 7.17$ (d, $J=8.0 \mathrm{~Hz}, 2 \mathrm{H}), 6.85(\mathrm{~d}, J=8.8 \mathrm{~Hz}, 2 \mathrm{H}), 6.75(\mathrm{~s}, 1 \mathrm{H}), 6.63(\mathrm{~d}, J=8.8 \mathrm{~Hz}, 2 \mathrm{H}), 6.24(\mathrm{~s}, 1 \mathrm{H}), 4.49$ (d, $J=8.4 \mathrm{~Hz}, 1 \mathrm{H}), 3.85(\mathrm{~s}, 3 \mathrm{H}), 3.84-3.74(\mathrm{~m}, 1 \mathrm{H}), 3.74(\mathrm{~s}, 3 \mathrm{H}), 3.59(\mathrm{~s}, 3 \mathrm{H}), 2.98-2.93(\mathrm{~m}, 1 \mathrm{H})$, 2.43-2.40 (m, 1H), $2.38(\mathrm{~s}, 3 \mathrm{H}), 1.72(\mathrm{q}, J=12.4 \mathrm{~Hz}, 1 \mathrm{H}), 1.39(\mathrm{~d}, J=6.4 \mathrm{~Hz}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR (100 $\mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 158.11,147.51,147.43,143.91,136.17,135.70,132.82,130.21,129.66$ (2x), $129.40(2 x), 128.52(2 x), 113.77(2 x), 112.66,108.15,67.63,55.86,55.67,55.12,44.56,32.68$, 31.63, 21.50, 20.54.


### 1.4.3.

1-(4-Fluorophenyl)-6,7-dimethoxy-4-methyl-2-(toluene-4-sulfonyl)-1,2,3,4-tetrahydronaphtha lene (5c). According to the general procedure, reaction was performed in the presence of $\mathrm{BF}_{3} \cdot \mathrm{OEt}_{2}$ ( $57 \mathrm{mg}, 0.4 \mathrm{mmol}$ ), 3c ( $67 \mathrm{mg}, 0.2 \mathrm{mmol}$ ) and $\mathbf{7 a}\left(41 \mathrm{mg}, 0.3 \mathrm{mmol}\right.$ ) in $\mathrm{CH}_{2} \mathrm{Cl}_{2}(5 \mathrm{~mL})$ at $25^{\circ} \mathrm{C}$ for 20 h . Purification on silica gel (hexanes/EtOAc $=3 / 1$ ) afforded $5 \mathrm{c}(89 \%, 81 \mathrm{mg})$. Colorless solid; mp $=120-121^{\circ} \mathrm{C}$ (recrystallized from hexanes and EtOAc); HRMS (ESI, M ${ }^{+}+1$ ) calcd for $\mathrm{C}_{26} \mathrm{H}_{28} \mathrm{FO}_{4} \mathrm{~S}$ 455.1692 , found $455.1697 ;{ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 7.55$ (d, $J=8.4 \mathrm{~Hz}, 2 \mathrm{H}$ ), 7.19 (d, $J=8.0$ $\mathrm{Hz}, 2 \mathrm{H}), 7.95-6.89(\mathrm{~m}, 2 \mathrm{H}), 6.83-6.77(\mathrm{~m}, 2 \mathrm{H}), 6.76(\mathrm{~s}, 1 \mathrm{H}), 6.19(\mathrm{~s}, 1 \mathrm{H}), 4.54(\mathrm{~d}, \mathrm{~J}=8.4 \mathrm{~Hz}, 1 \mathrm{H})$, $3.85(\mathrm{~s}, 3 \mathrm{H}), 3.76-3.70(\mathrm{~m}, 1 \mathrm{H}), 3.58(\mathrm{~s}, 3 \mathrm{H}), 2.98-2.92(\mathrm{~m}, 1 \mathrm{H}), 2.44-2.36(\mathrm{~m}, 1 \mathrm{H}), 2.39(\mathrm{~s}, 3 \mathrm{H})$, $1.72(\mathrm{q}, J=12.4 \mathrm{~Hz}, 1 \mathrm{H}), 1.39(\mathrm{~d}, J=6.8 \mathrm{~Hz}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C} \mathrm{NMR}\left(100 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta 161.42(\mathrm{~d}, J=$ 244.1 Hz ), 147.66, 147.51, 144.28, 140.02 ( $\mathrm{d}, \mathrm{J}=3.0 \mathrm{~Hz}$ ), 135.48, 132.86, $130.23(\mathrm{~d}, J=7.6 \mathrm{~Hz}$, $2 x)$, 130.13, $129.49(2 x), 128.50(2 x), 115.21(d, J=21.2 H z, 2 x), 112.58,108.22,67.60,55.85$, 55.66, 44.59, 32.68, 31.65, 21.49, 20.53.

1.4.4. 6,7-Dimethoxy-4-methyl-2-(toluene-4-sulfonyl)-1-p-tolyl-1,2,3,4-tetrahydronaphthalene (5d). According to the general procedure, reaction was performed in the presence of $\mathrm{BF}_{3} \cdot \mathrm{OEt}_{2}$ (57 $\mathrm{mg}, 0.4 \mathrm{mmol}), 3 \mathrm{~d}(66 \mathrm{mg}, 0.2 \mathrm{mmol})$ and $\mathbf{7 a}(41 \mathrm{mg}, 0.3 \mathrm{mmol})$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}(5 \mathrm{~mL})$ at $25^{\circ} \mathrm{C}$ for 20 h . Purification on silica gel (hexanes/EtOAc $=3 / 1$ ) afforded $5 \mathrm{~d}(88 \%, 79 \mathrm{mg})$. Colorless solid; $\mathrm{mp}=$ $77-78{ }^{\circ} \mathrm{C}$ (recrystallized from hexanes and EtOAc); HRMS (ESI, $\mathrm{M}^{+}+1$ ) calcd for $\mathrm{C}_{27} \mathrm{H}_{31} \mathrm{O}_{4} \mathrm{~S}$ 451.1943, found 451.1943; ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 7.56$ (d, $\left.J=8.4 \mathrm{~Hz}, 2 \mathrm{H}\right), 7.17(\mathrm{~d}, J=8.0$ $\mathrm{Hz}, 2 \mathrm{H}), 6.91(\mathrm{~d}, J=8.0 \mathrm{~Hz}, 2 \mathrm{H}), 6.82(\mathrm{~d}, J=8.0 \mathrm{~Hz}, 2 \mathrm{H}), 6.76(\mathrm{~s}, 1 \mathrm{H}), 6.27(\mathrm{~s}, 1 \mathrm{H}), 4.80(\mathrm{~d}, J=7.6$ $\mathrm{Hz}, 1 \mathrm{H}), 3.85(\mathrm{~s}, 3 \mathrm{H}), 3.84-3.75(\mathrm{~m}, 1 \mathrm{H}), 3.60(\mathrm{~s}, 3 \mathrm{H}), 2.98-2.92(\mathrm{~m}, 1 \mathrm{H}), 2.42-2.35(\mathrm{~m}, 1 \mathrm{H}), 2.39(\mathrm{~s}$, $3 \mathrm{H}), 2.25(\mathrm{~s}, 3 \mathrm{H}), 1.72(\mathrm{q}, J=12.4 \mathrm{~Hz}, 1 \mathrm{H}), 1.39(\mathrm{~d}, J=6.8 \mathrm{~Hz}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta$ 147.54, 147.47, 144.00, 141.16, 136.03, 135.58, 132.94, 130.03, 129.39 (2x), 129.10 ( $2 x$ ), 128.60 (2x), 128.46 (2x), 112.75, 108.15, 67.62, 55.88, 55.69, 44.80, 32.71, 31.54, 21.53, 20.96, 20.43.


### 1.4.5. 2-Methanesulfonyl-6,7-dimethoxy-4-methyl-1-phenyl-1,2,3,4-tetrahydronaphthalene

 (5e). According to the general procedure, reaction was performed in the presence of $\mathrm{BF}_{3} \cdot \mathrm{OEt}_{2}$ ( 57 $\mathrm{mg}, 0.4 \mathrm{mmol}), 3 \mathrm{e}(48 \mathrm{mg}, 0.2 \mathrm{mmol})$ and $7 \mathrm{a}(41 \mathrm{mg}, 0.3 \mathrm{mmol})$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}(5 \mathrm{~mL})$ at $25^{\circ} \mathrm{C}$ for 20 h . Purification on silica gel (hexanes/EtOAc $=3 / 1$ ) afforded $5 \mathrm{e}(82 \%, 59 \mathrm{mg})$. Colorless gum; HRMS $\left(\mathrm{ESI}, \mathrm{M}^{+}+1\right)$ calcd for $\mathrm{C}_{20} \mathrm{H}_{25} \mathrm{O}_{4} \mathrm{~S} 361.1474$, found $361.1478 ;{ }^{1} \mathrm{H} \mathrm{NMR}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right)$ : $\delta$ 7.36-7.32 (m, 2H), 7.30-7.22 (m, 3H), 6.79 (s, 1H), $6.20(\mathrm{~s}, 1 \mathrm{H}), 4.53(\mathrm{~d}, \mathrm{~J}=9.6 \mathrm{~Hz}, 1 \mathrm{H}), 3.87(\mathrm{~s}$,$3 \mathrm{H}), 3.56(\mathrm{~s}, 3 \mathrm{H}), 3.57-3.51(\mathrm{~m}, 1 \mathrm{H}), 3.10-3.04(\mathrm{~m}, 1 \mathrm{H}), 2.70-2.65(\mathrm{~m}, 1 \mathrm{H}), 2.19(\mathrm{~s}, 3 \mathrm{H}), 1.72(\mathrm{q}, \mathrm{J}=$ $12.4 \mathrm{~Hz}, 1 \mathrm{H}), 1.44(\mathrm{~d}, \mathrm{~J}=6.4 \mathrm{~Hz}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 147.68,147.34,143.66$, 132.65, 129.59, 129.32 (2x), 129.11 (2x), 127.49, 112.53, 108.37, 67.17, 55.78, 55.62, 46.78, 41.15, 32.10, 30.54, 21.03.

1.4.6. 6,7-Dimethoxy-4-methyl-2-(toluene-4-sulfonyl)-1,2,3,4-tetrahydro[1,2']binaphthalenyl (5f). According to the general procedure, reaction was performed in the presence of $\mathrm{BF}_{3} \cdot \mathrm{OEt}_{2}$ (57 $\mathrm{mg}, 0.4 \mathrm{mmol}), 3 \mathrm{f}(73 \mathrm{mg}, 0.2 \mathrm{mmol})$ and $\mathbf{7 a}(41 \mathrm{mg}, 0.3 \mathrm{mmol})$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}(5 \mathrm{~mL})$ at $25^{\circ} \mathrm{C}$ for 20 h . Purification on silica gel (hexanes/EtOAc $=3 / 1$ ) afforded $5 \mathrm{f}(83 \%, 81 \mathrm{mg})$. Colorless solid; $\mathrm{mp}=$ $148-149{ }^{\circ} \mathrm{C}$ (recrystallized from hexanes and EtOAc); HRMS (ESI, $\mathrm{M}^{+}+1$ ) calcd for $\mathrm{C}_{30} \mathrm{H}_{31} \mathrm{O}_{4} \mathrm{~S}$ 487.1943, found 487.1944; ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 7.69$ (d, $J=8.8 \mathrm{~Hz}, 1 \mathrm{H}$ ), $7.63(\mathrm{~d}, J=8.8$ $\mathrm{Hz}, 1 \mathrm{H}), 7.52(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 1 \mathrm{H}), 7.46-7.39(\mathrm{~m}, 4 \mathrm{H}), 7.33(\mathrm{~d}, J=1.2 \mathrm{~Hz}, 1 \mathrm{H}), 6.96$ (dd, $J=2.0,8.8$ $\mathrm{Hz}, 1 \mathrm{H}), 6.86(\mathrm{~d}, J=8.0 \mathrm{~Hz}, 2 \mathrm{H}), 6.81(\mathrm{~s}, 1 \mathrm{H}), 6.24(\mathrm{~s}, 1 \mathrm{H}), 4.67(\mathrm{~d}, J=8.8 \mathrm{~Hz}, 1 \mathrm{H}), 3.92-3.90(\mathrm{~m}$, $1 \mathrm{H}), 3.87(\mathrm{~s}, 3 \mathrm{H}), 3.49(\mathrm{~s}, 3 \mathrm{H}), 3.11-3.06(\mathrm{~m}, 1 \mathrm{H}), 2.60(\mathrm{dt}, J=4.0,12.4 \mathrm{~Hz}, 1 \mathrm{H}), 2.12(\mathrm{~s}, 3 \mathrm{H}), 1.84$ (q, $J=12.4 \mathrm{~Hz}, 1 \mathrm{H}), 1.46(\mathrm{~d}, J=6.8 \mathrm{~Hz}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C} \operatorname{NMR}\left(100 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta 147.68,147.51$, 143.92, 140.78, 135.82, 133.08, 132.97, 132.20, 129.69, 129.09 (2x), 128.47, 128.34, 128.18 (2x), $127.71,127.42,126.16,126.01,125.70,112.83,108.35,66.99,55.88,55.71,46.03,31.93(2 x)$, 21.28, 20.77.


### 1.4.7.

1-Biphenyl-4-yl-6,7-dimethoxy-4-methyl-2-(toluene-4-sulfonyl)-1,2,3,4-tetrahydronaphthalen $\mathbf{e}(5 \mathrm{~g})$. According to the general procedure, reaction was performed in the presence of $\mathrm{BF}_{3} \cdot \mathrm{OEt}_{2}$ $(57 \mathrm{mg}, 0.4 \mathrm{mmol}), \mathbf{3 g}(78 \mathrm{mg}, 0.2 \mathrm{mmol})$ and $7 \mathrm{a}(41 \mathrm{mg}, 0.3 \mathrm{mmol})$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}(5 \mathrm{~mL})$ at $25^{\circ} \mathrm{C}$ for 20 h. Purification on silica gel (hexanes/EtOAc $=3 / 1$ ) afforded $5 \mathrm{~g}(86 \%, 88 \mathrm{mg})$. Colorless solid; $m p=162-163{ }^{\circ} \mathrm{C}$ (recrystallized from hexanes and EtOAc); HRMS (ESI, $\mathrm{M}^{+}+1$ ) calcd for $\mathrm{C}_{32} \mathrm{H}_{33} \mathrm{O}_{4} \mathrm{~S}$ 513.2100, found 513.2107; ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 7.56(\mathrm{~d}, J=8.0 \mathrm{~Hz}, 2 \mathrm{H}), 7.53-7.50(\mathrm{~m}$, 2H), 7.44-7.40 (m, 2H), 7.35-7.33 (m, 1H), 7.33 (d, $J=8.4 \mathrm{~Hz}, 2 \mathrm{H}$ ), $7.14(\mathrm{~d}, J=8.0 \mathrm{~Hz}, 2 \mathrm{H}), 7.01$ (d, $J=8.4 \mathrm{~Hz}, 2 \mathrm{H}), 6.79(\mathrm{~s}, 1 \mathrm{H}), 6.29(\mathrm{~s}, 1 \mathrm{H}), 4.60(\mathrm{~d}, J=8.0 \mathrm{~Hz}, 1 \mathrm{H}), 3.87(\mathrm{~s}, 3 \mathrm{H}), 3.86-3.78(\mathrm{~m}, 1 \mathrm{H})$, $3.60(\mathrm{~s}, 3 \mathrm{H}), 3.03-2.98(\mathrm{~m}, 1 \mathrm{H}), 2.51-2.46(\mathrm{~m}, 1 \mathrm{H}), 2.31(\mathrm{~s}, 3 \mathrm{H}), 1.78(\mathrm{q}, \mathrm{J}=12.4 \mathrm{~Hz}, 1 \mathrm{H}), 1.42(\mathrm{~d}, J$ $=6.8 \mathrm{~Hz}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR (100 MHz, CDCl ${ }_{3}$ ): $\delta 147.64,147.49,144.02,143.08,140.56,139.30$, $135.75,132.97,129.75,129.42(2 x), 129.13$ (2x), 128.71 (2x), 128.47 (2x), 127.23, 127.04 (2x),
126.85 (2x), 112.72, 108.23, 67.46, 55.87, 55.71, 45.11, 32.44, 31.71, 21.48, 20.55. Single-crystal X-Ray diagram: crystal of compound $\mathbf{5 g}$ was grown by slow diffusion of EtOAc into a solution of compound 5 g in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ to yield colorless prisms. The compound crystallizes in the monoclinic crystal system, space group P 21/c, $a=12.1307(4) \AA, b=11.0079(3) \AA, c=20.0330(5) \AA, V=$ $2589.42(13) \AA^{3}, Z=4, d_{\text {calcd }}=1.315 \mathrm{mg} / \mathrm{cm}^{3}, F(000)=1088,2 \theta$ range $1.734 \sim 26.423^{\circ}, \mathrm{R}$ indices (all data) $R 1=0.0487, w R 2=0.1140$.


### 1.4.8.

## 2-Benzenesulfonyl-6,7-dimethoxy-1-(4-methoxyphenyl)-4-methyl-1,2,3,4-tetrahydronaphthal

 ene (5h). According to the general procedure, reaction was performed in the presence of $\mathrm{BF}_{3} \cdot \mathrm{OEt}_{2}$ $(57 \mathrm{mg}, 0.4 \mathrm{mmol})$, $\mathbf{3 h}(66 \mathrm{mg}, 0.2 \mathrm{mmol})$ and $7 \mathrm{a}(41 \mathrm{mg}, 0.3 \mathrm{mmol})$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}(5 \mathrm{~mL})$ at $25^{\circ} \mathrm{C}$ for 20 h. Purification on silica gel (hexanes/EtOAc $=3 / 1$ ) afforded $5 \mathrm{~h}(86 \%, 78 \mathrm{mg})$. Colorless solid; $m p=149-150{ }^{\circ} \mathrm{C}$ (recrystallized from hexanes and EtOAc ); HRMS (ESI, $\mathrm{M}^{+}+1$ ) calcd for $\mathrm{C}_{26} \mathrm{H}_{29} \mathrm{O}_{5} \mathrm{~S}$ 453.1736, found 453.1742; ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 7.66-7.64(\mathrm{~m}, 2 \mathrm{H}), 7.52-7.45(\mathrm{~m}, 1 \mathrm{H})$, $7.39-7.35(\mathrm{~m}, 2 \mathrm{H}), 6.84(\mathrm{~d}, J=8.8 \mathrm{~Hz}, 2 \mathrm{H}), 6.75(\mathrm{~s}, 1 \mathrm{H}), 6.61(\mathrm{~d}, J=8.8 \mathrm{~Hz}, 2 \mathrm{H}), 6.23(\mathrm{~s}, 1 \mathrm{H}), 4.51$ $(\mathrm{d}, J=8.4 \mathrm{~Hz}, 1 \mathrm{H}), 3.85(\mathrm{~s}, 3 \mathrm{H}), 3.83-3.76(\mathrm{~m}, 1 \mathrm{H}), 3.73(\mathrm{~s}, 3 \mathrm{H}), 3.58(\mathrm{~s}, 3 \mathrm{H}), 3.00-2.95(\mathrm{~m}, 1 \mathrm{H})$, $2.45(\mathrm{dt}, J=4.4,12.8 \mathrm{~Hz}, 1 \mathrm{H}), 1.75(\mathrm{q}, J=12.4 \mathrm{~Hz}, 1 \mathrm{H}), 1.40(\mathrm{~d}, J=6.8 \mathrm{~Hz}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR (100 $\mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 158.09,147.53,147.42,138.84,135.83,132.94,130.12,129.68$ (2x), 128.85, $128.73(2 x), 128.38(2 x), 113.81(2 x), 112.61,108.19,67.53,55.84,55.65,55.12,44.65,32.47$, 31.68, 20.59.

### 1.4.9.

2-Benzenesulfonyl-1-(4-fluorophenyl)-6,7-dimethoxy-4-methyl-1,2,3,4-tetrahydronaphthalen $\mathbf{e} \mathbf{( 5 i )}$. According to the general procedure, reaction was performed in the presence of $\mathrm{BF}_{3} \cdot \mathrm{OEt}_{2}$ (57 $\mathrm{mg}, 0.4 \mathrm{mmol}), 3 i(64 \mathrm{mg}, 0.2 \mathrm{mmol})$ and $7 \mathrm{a}(41 \mathrm{mg}, 0.3 \mathrm{mmol})$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}(5 \mathrm{~mL})$ at $25^{\circ} \mathrm{C}$ for 20 h . Purification on silica gel (hexanes/EtOAc = 3/1) afforded $5 \mathbf{i}(87 \%, 77 \mathrm{mg})$. Colorless solid; $\mathrm{mp}=$ $117-118{ }^{\circ} \mathrm{C}$ (recrystallized from hexanes and EtOAc); HRMS (ESI, $\mathrm{M}^{+}+1$ ) calcd for $\mathrm{C}_{25} \mathrm{H}_{26} \mathrm{FO}_{4} \mathrm{~S}$ 441.1536, found 441.1541; ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 7.67-7.65(\mathrm{~m}, 2 \mathrm{H}), 7.55-7.52(\mathrm{~m}, 1 \mathrm{H})$, 7.42-7.38 (m, 2H), 6.93-6.87 (m, 2H), 6.81-6.77 (m, 2H), $6.76(\mathrm{~s}, 1 \mathrm{H}), 6.18(\mathrm{~s}, 1 \mathrm{H}), 4.56(\mathrm{~d}, \mathrm{~J}=8.4$ $\mathrm{Hz}, 1 \mathrm{H}), 3.85(\mathrm{~s}, 3 \mathrm{H}), 3.79-3.73(\mathrm{~m}, 1 \mathrm{H}), 3.58(\mathrm{~s}, 3 \mathrm{H}), 3.00-2.94(\mathrm{~m}, 1 \mathrm{H}), 2.43(\mathrm{dt}, J=4.0,8.0 \mathrm{~Hz}$, $1 \mathrm{H}), 1.75(\mathrm{q}, J=12.4 \mathrm{~Hz}, 1 \mathrm{H}), 1.40(\mathrm{~d}, J=6.8 \mathrm{~Hz}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C} \mathrm{NMR}\left(100 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta 161.48(\mathrm{~d}, J$ $=244.5 \mathrm{~Hz}), 147.72,147.54,139.75(\mathrm{~d}, J=3.8 \mathrm{~Hz}), 138.67,133.21,132.81,130.30(\mathrm{~d}, J=7.6 \mathrm{~Hz}$, $2 x), 129.61,128.87(2 x), 128.40(2 x), 115.29(d, J=21.2 H z, 2 x), 112.55,108.28,67.56,55.87$,

1.4.10. 2-Methanesulfonyl-6,7-dimethoxy-4-methyl-1-p-tolyl-1,2,3,4-tetrahydronaphthalene (5j). According to the general procedure, reaction was performed in the presence of $\mathrm{BF}_{3} \cdot \mathrm{OEt}_{2}$ (57 $\mathrm{mg}, 0.4 \mathrm{mmol}$ ), $\mathbf{3 j}$ ( $51 \mathrm{mg}, 0.2 \mathrm{mmol}$ ) and $\mathbf{7 a}(41 \mathrm{mg}, 0.3 \mathrm{mmol})$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}(5 \mathrm{~mL})$ at $25^{\circ} \mathrm{C}$ for 20 h . Purification on silica gel (hexanes/EtOAc = 3/1) afforded $5 \mathrm{j}(84 \%, 63 \mathrm{mg})$. Colorless gum; HRMS $\left(\mathrm{ESI}, \mathrm{M}^{+}+1\right.$ ) calcd for $\mathrm{C}_{21} \mathrm{H}_{27} \mathrm{O}_{4} \mathrm{~S} 375.1630$, found $375.1633 ;{ }^{1} \mathrm{H} \mathrm{NMR}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta$ 7.15-7.10 (m, 4H), $6.79(\mathrm{~s}, 1 \mathrm{H}), 6.22(\mathrm{~s}, 1 \mathrm{H}), 4.48(\mathrm{~d}, ~ J=9.6 \mathrm{~Hz}, 1 \mathrm{H}), 3.86(\mathrm{~s}, 3 \mathrm{H}), 3.57(\mathrm{~s}, 3 \mathrm{H})$, 3.55-3.48 (m, 1H), 3.09-3.03 (m, 1H), 2.69-2.64 (m, 1H), $2.32(\mathrm{~s}, 3 \mathrm{H}), 2.20(\mathrm{~s}, 3 \mathrm{H}), 1.70(\mathrm{q}, \mathrm{J}=12.8$ $\mathrm{Hz}, 1 \mathrm{H}), 1.43(\mathrm{~d}, J=6.8 \mathrm{~Hz}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C} \operatorname{NMR}\left(100 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta 147.65,147.35,140.52,137.13$, 132.62, 129.86, 129.75 (2x), 129.15 (2x), 112.61, 108.41, 67.21, 55.78, 55.67, 46.41, 41.23, 32.10, 30.52, 21.03, 21.01.


### 1.4.11.

2-Benzenesulfonyl-1-biphenyl-4-yl-6,7-dimethoxy-4-methyl-1,2,3,4-tetrahydronaphthalene $\mathbf{( 5 k})$. According to the general procedure, reaction was performed in the presence of $\mathrm{BF}_{3} \cdot \mathrm{OEt}_{2}$ (57 $\mathrm{mg}, 0.4 \mathrm{mmol}), \mathbf{3 k}(76 \mathrm{mg}, 0.2 \mathrm{mmol})$ and $\mathbf{7 a}(41 \mathrm{mg}, 0.3 \mathrm{mmol})$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}(5 \mathrm{~mL})$ at $25^{\circ} \mathrm{C}$ for 20 h . Purification on silica gel (hexanes/EtOAc = 3/1) afforded 5k ( $89 \%$, 89 mg ). Colorless solid; $\mathrm{mp}=$ $175-176{ }^{\circ} \mathrm{C}$ (recrystallized from hexanes and EtOAc); HRMS (ESI, $\mathrm{M}^{+}+1$ ) calcd for $\mathrm{C}_{31} \mathrm{H}_{31} \mathrm{O}_{4} \mathrm{~S}$ 499.1943, found 499.1950; ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 7.68-7.66(\mathrm{~m}, 2 \mathrm{H}), 7.51-7.41(\mathrm{~m}, 5 \mathrm{H})$, 7.36-7.29 (m, 5H), $6.99(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 2 \mathrm{H}), 6.79(\mathrm{~s}, 1 \mathrm{H}), 6.28(\mathrm{~s}, 1 \mathrm{H}), 4.62(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 1 \mathrm{H})$, 3.92-3.89 (m, 1H), $3.87(\mathrm{~s}, 3 \mathrm{H}), 3.59(\mathrm{~s}, 3 \mathrm{H}), 3.06-3.00(\mathrm{~m}, 1 \mathrm{H}), 2.54-2.49(\mathrm{~m}, 1 \mathrm{H}), 1.81(\mathrm{q}, \mathrm{J}=12.4$ $\mathrm{Hz}, 1 \mathrm{H}$ ), $1.43(\mathrm{~d}, \mathrm{~J}=6.8 \mathrm{~Hz}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C} \operatorname{NMR}\left(100 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta 147.68,147.51,142.87,140.58$, 139.33, 138.84, 132.92, 129.67, 129.14 (2x), 128.77 (3x), 128.73 (2x), 128.40 ( $2 x$ ), 127.22, 127.10 (2x), 126.84 (2x), 112.70, 108.28, 67.44, 55.87, 55.71, 45.17, 32.30, 31.74, 21.59; Anal. Calcd for $\mathrm{C}_{31} \mathrm{H}_{30} \mathrm{O}_{4} \mathrm{~S}: \mathrm{C}, 74.67$; H, 6.06. Found: C, 74.88; H, 6.25.

1.4.12. 2-Benzenesulfonyl-6,7-dimethoxy-4-methyl-1-phenyl-1,2,3,4-tetrahydronaphthalene (5I). According to the general procedure, reaction was performed in the presence of $\mathrm{BF}_{3} \cdot \mathrm{OEt}_{2}$ (57 $\mathrm{mg}, 0.4 \mathrm{mmol}), 31(60 \mathrm{mg}, 0.2 \mathrm{mmol})$ and $7 \mathrm{a}(41 \mathrm{mg}, 0.3 \mathrm{mmol})$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}(5 \mathrm{~mL})$ at $25^{\circ} \mathrm{C}$ for 20 h . Purification on silica gel (hexanes/EtOAc = 3/1) afforded $5 \mathbf{I}(82 \%, 69 \mathrm{mg})$. Colorless solid; $\mathrm{mp}=$ $140-141{ }^{\circ} \mathrm{C}$ (recrystallized from hexanes and EtOAc); HRMS (ESI, $\mathrm{M}^{+}+1$ ) calcd for $\mathrm{C}_{25} \mathrm{H}_{27} \mathrm{O}_{4} \mathrm{~S}$ 423.1630, found 423.1632; ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 7.69-7.67(\mathrm{~m}, 2 \mathrm{H}), 7.52-7.46(\mathrm{~m}, 1 \mathrm{H})$, 7.39-7.35 (m, 2H), 7.13-7.05 (m, 3H), 6.95-6.90 (m, 2H), $6.77(\mathrm{~s}, 1 \mathrm{H}), 6.24(\mathrm{~s}, 1 \mathrm{H}), 4.57(\mathrm{~d}, \mathrm{~J}=8.0$ $\mathrm{Hz}, 1 \mathrm{H}$ ), 3.87-3.81 (m, 1H), $3.85(\mathrm{~s}, 3 \mathrm{H}), 3.58(\mathrm{~s}, 3 \mathrm{H}), 3.00-2.94(\mathrm{~m}, 1 \mathrm{H}), 2.42(\mathrm{dt}, J=4.4,12.8 \mathrm{~Hz}$, $1 \mathrm{H}), 1.77(\mathrm{q}, J=12.8 \mathrm{~Hz}, 1 \mathrm{H}), 1.40(\mathrm{~d}, J=6.8 \mathrm{~Hz}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 147.57$, 147.46, 144.03, 138.58, 133.14, 132.88, 129.72, 128.81 (2x), 128.59 ( 2 x ), 128.47 ( 2 x ), 128.46 ( 2 x ), $126.56,112.68,108.13,67.39,55.84,55.62,45.18,32.50,31.52,20.43$.


### 1.4.13.

6,7-Dimethoxy-4-methyl-1-phenyl-2-(toluene-3-sulfonyl)-1,2,3,4-tetrahydronaphthalene (5m). According to the general procedure, reaction was performed in the presence of $\mathrm{BF}_{3} . \mathrm{OEt}_{2}(57 \mathrm{mg}$, $0.4 \mathrm{mmol}), 3 \mathrm{~m}(63 \mathrm{mg}, 0.2 \mathrm{mmol})$ and $7 \mathrm{a}(41 \mathrm{mg}, 0.3 \mathrm{mmol})$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}(5 \mathrm{~mL})$ at $25^{\circ} \mathrm{C}$ for 20 h . Purification on silica gel (hexanes/EtOAc $=3 / 1$ ) afforded $5 \mathrm{~m}(86 \%, 75 \mathrm{mg})$. Colorless solid; $\mathrm{mp}=$ $149-150{ }^{\circ} \mathrm{C}$ (recrystallized from hexanes and EtOAc); HRMS (ESI, $\mathrm{M}^{+}+1$ ) calcd for $\mathrm{C}_{26} \mathrm{H}_{29} \mathrm{O}_{4} \mathrm{~S}$ 437.1787, found 437.1785; ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 7.51-7.49(\mathrm{~m}, 1 \mathrm{H}), 7.39(\mathrm{~s}, 1 \mathrm{H}), 7.29-7.24$ $(\mathrm{m}, 2 \mathrm{H}), 7.11-7.04(\mathrm{~m}, 3 \mathrm{H}), 6.94-6.90(\mathrm{~m}, 2 \mathrm{H}), 6.77(\mathrm{~s}, 1 \mathrm{H}), 6.23(\mathrm{~s}, 1 \mathrm{H}), 4.55(\mathrm{~d}, \mathrm{~J}=8.4 \mathrm{~Hz}, 1 \mathrm{H})$, $3.87-3.81(\mathrm{~m}, 1 \mathrm{H}), 3.85(\mathrm{~s}, 3 \mathrm{H}), 3.57(\mathrm{~s}, 3 \mathrm{H}), 3.01-2.95(\mathrm{~m}, 1 \mathrm{H}), 2.45(\mathrm{dt}, J=4.4,12.8 \mathrm{~Hz}, 1 \mathrm{H}), 2.30$ ( $\mathrm{s}, 3 \mathrm{H}$ ), $1.76(\mathrm{q}, J=12.8 \mathrm{~Hz}, 1 \mathrm{H}), 1.41(\mathrm{~d}, J=6.8 \mathrm{~Hz}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 147.54$, 147.42, 143.97, 138.93, 138.50, 133.94, 132.85, 129.81, 128.78, 128.62 (2x), 128.36, 128.29 ( $2 x$ ), $126.52,125.49,112.67,108.14,67.30,55.83,55.61,45.31,32.35,31.58,21.13,20.48$.


### 1.4.14.

## 2-(4-Fluorobenzenesulfonyl)-6,7-dimethoxy-4-methyl-1-phenyl-1,2,3,4-tetrahydronaphthalen

 $\mathbf{e}(\mathbf{5 n})$. According to the general procedure, reaction was performed in the presence of $\mathrm{BF}_{3} \cdot \mathrm{OEt}_{2}$ ( $57 \mathrm{mg}, 0.4 \mathrm{mmol}$ ), $3 \mathrm{n}\left(64 \mathrm{mg}, 0.2 \mathrm{mmol}\right.$ ) and $7 \mathrm{a}(41 \mathrm{mg}, 0.3 \mathrm{mmol})$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}(5 \mathrm{~mL})$ at $25^{\circ} \mathrm{C}$ for 20 h. Purification on silica gel (hexanes/EtOAc $=3 / 1$ ) afforded $5 n(80 \%, 70 \mathrm{mg})$. Colorless solid; $m p=174-175{ }^{\circ} \mathrm{C}$ (recrystallized from hexanes and EtOAc); HRMS (ESI, M ${ }^{+}+1$ ) calcd for$\mathrm{C}_{25} \mathrm{H}_{26} \mathrm{FO}_{4} \mathrm{~S} 441.1536$, found 441.1532 ; ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 7.65-7.62(\mathrm{~m}, 2 \mathrm{H}), 7.16-7.07$ (m, 3H), 7.03-6.98 (m, 2H), 6.94-6.91 (m, 2H), $6.77(\mathrm{~s}, 1 \mathrm{H}), 6.19(\mathrm{~s}, 1 \mathrm{H}), 4.53(\mathrm{~d}, \mathrm{~J}=8.8 \mathrm{~Hz}, 1 \mathrm{H})$, $3.85(\mathrm{~s}, 3 \mathrm{H}), 3.85-3.80(\mathrm{~m}, 1 \mathrm{H}), 3.56(\mathrm{~s}, 3 \mathrm{H}), 3.05-2.96(\mathrm{~m}, 1 \mathrm{H}), 2.49(\mathrm{dt}, J=4.0,12.8 \mathrm{~Hz}, 1 \mathrm{H}), 1.77$ ( $q, J=12.8 \mathrm{~Hz}, 1 \mathrm{H}$ ), $1.42(\mathrm{~d}, J=6.8 \mathrm{~Hz}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 165.35(\mathrm{~d}, \mathrm{~J}=253.9$ Hz), 147.65, 147.50, 143.75, 134.85 (d, $J=3.0 \mathrm{~Hz}), 132.69,131.20(\mathrm{~d}, J=9.1 \mathrm{~Hz}, 2 \mathrm{x}), 129.69$, 128.74 (2x), 128.53 ( $2 x$ ), 126.70, 116.04 ( $d, J=22.0 \mathrm{~Hz}, 2 x$ ), 112.64, 108.24, 67.57, 55.87, 55.64, 45.60, 32.26, 31.75, 20.64; Anal. Calcd for $\mathrm{C}_{25} \mathrm{H}_{25} \mathrm{FO}_{4} \mathrm{~S}: \mathrm{C}, 68.16$; H, 5.72. Found: C, 68.23; H, 5.93.


### 1.4.15.

2-(4-Butylbenzenesulfonyl)-6,7-dimethoxy-4-methyl-1-phenyl-1,2,3,4-tetrahydronaphthalene (50). According to the general procedure, reaction was performed in the presence of $\mathrm{BF}_{3} \cdot \mathrm{OEt}_{2}$ (57 $\mathrm{mg}, 0.4 \mathrm{mmol}), 30(72 \mathrm{mg}, 0.2 \mathrm{mmol})$ and $7 \mathrm{a}(41 \mathrm{mg}, 0.3 \mathrm{mmol})$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}(5 \mathrm{~mL})$ at $25^{\circ} \mathrm{C}$ for 20 h . Purification on silica gel (hexanes/EtOAc $=3 / 1$ ) afforded $50(86 \%, 82 \mathrm{mg})$. Colorless solid; $\mathrm{mp}=$ $119-120{ }^{\circ} \mathrm{C}$ (recrystallized from hexanes and EtOAc); HRMS (ESI, M ${ }^{+}+1$ ) calcd for $\mathrm{C}_{29} \mathrm{H}_{35} \mathrm{O}_{4} \mathrm{~S}$ 479.2256, found 479.2255 ; ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 7.58(\mathrm{~d}, \mathrm{~J}=8.4 \mathrm{~Hz}, 2 \mathrm{H}$ ), 7.17 ( $\mathrm{d}, \mathrm{J}=8.4$ $\mathrm{Hz}, 2 \mathrm{H}), 7.11-7.06(\mathrm{~m}, 3 \mathrm{H}), 6.93-6.91(\mathrm{~m}, 2 \mathrm{H}), 6.77(\mathrm{~s}, 1 \mathrm{H}), 6.24(\mathrm{~s}, 1 \mathrm{H}), 4.55(\mathrm{~d}, \mathrm{~J}=8.0 \mathrm{~Hz}, 1 \mathrm{H})$, $3.85(\mathrm{~s}, 3 \mathrm{H}), 3.84-3.79(\mathrm{~m}, 1 \mathrm{H}), 3.58(\mathrm{~s}, 3 \mathrm{H}), 3.00-2.94(\mathrm{~m}, 1 \mathrm{H}), 2.62(\mathrm{t}, \mathrm{J}=8.0 \mathrm{~Hz}, 2 \mathrm{H}), 2.43(\mathrm{dt}, J$ $=4.4,12.4 \mathrm{~Hz}, 1 \mathrm{H}), 1.76(\mathrm{q}, J=12.8 \mathrm{~Hz}, 1 \mathrm{H}), 1.60-1.54(\mathrm{~m}, 2 \mathrm{H}), 1.40(\mathrm{~d}, J=6.8 \mathrm{~Hz}, 3 \mathrm{H}), 1.38-1.30$ $(\mathrm{m}, 2 \mathrm{H}), 0.94(\mathrm{t}, \mathrm{J}=7.2 \mathrm{~Hz}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 148.91,147.53$, 147.43, 144.19, 135.70, 132.92, 129.84, 128.81 (2x), $128.58(2 x), 128.53(2 x), 128.39(2 x), 126.43,112.72,108.13$, $67.39,55.84,55.61,45.22,35.47,33.07,32.48,31.51,22.19,20.41,13.79$.

1.4.16. 8-Methyl-5-phenyl-6-(toluene-4-sulfonyl)-5,6,7,8-tetrahydronaphtho[2,3-d][1,3]dioxole (5p). According to the general procedure, reaction was performed in the presence of $\mathrm{BF}_{3} \cdot \mathrm{OEt}_{2}$ ( 57 $\mathrm{mg}, 0.4 \mathrm{mmol})$, $\mathbf{3 a}\left(63 \mathrm{mg}, 0.2 \mathrm{mmol}\right.$ ) and $\mathbf{7 b}(37 \mathrm{mg}, 0.3 \mathrm{mmol})$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}(5 \mathrm{~mL})$ at $25^{\circ} \mathrm{C}$ for 20 h . Purification on silica gel (hexanes/EtOAc $=3 / 1$ ) afforded $5 \mathrm{p}(86 \%, 72 \mathrm{mg})$. Colorless solid; $\mathrm{mp}=$ $124-125{ }^{\circ} \mathrm{C}$ (recrystallized from hexanes and EtOAc); HRMS (ESI, M ${ }^{+}+1$ ) calcd for $\mathrm{C}_{25} \mathrm{H}_{25} \mathrm{O}_{4} \mathrm{~S}$ 421.1474, found 421.1477; ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 7.57$ (d, $J=8.0 \mathrm{~Hz}, 2 \mathrm{H}$ ), 7.18 (d, $J=7.6$ $\mathrm{Hz}, 2 \mathrm{H}), 7.12-7.09(\mathrm{~m}, 3 \mathrm{H}), 6.94-6.91(\mathrm{~m}, 2 \mathrm{H}), 6.76(\mathrm{~s}, 1 \mathrm{H}), 6.27(\mathrm{~s}, 1 \mathrm{H}), 5.85(\mathrm{~d}, \mathrm{~J}=1.6 \mathrm{~Hz}, 1 \mathrm{H})$, 5.83 (d, $J=1.6 \mathrm{~Hz}, 1 \mathrm{H}), 4.51(\mathrm{~d}, J=7.6 \mathrm{~Hz}, 1 \mathrm{H}), 3.83-3.77(\mathrm{~m}, 1 \mathrm{H}), 2.92-2.87(\mathrm{~m}, 1 \mathrm{H}), 2.39(\mathrm{~s}, 3 \mathrm{H})$,
$2.38-2.33(\mathrm{~m}, 1 \mathrm{H}), 1.72(\mathrm{q}, J=12.4 \mathrm{~Hz}, 1 \mathrm{H}), 1.36(\mathrm{~d}, \mathrm{~J}=6.8 \mathrm{~Hz}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C} \mathrm{NMR}\left(100 \mathrm{MHz}, \mathrm{CDCl}_{3}\right):$ $\delta 146.40,146.05,144.31,144.20,135.38,134.31,130.91,129.53$ (2x), 128.64 (2x), 128.53 (4x), 126.45, 109.77, 105.17, 100.86, 67.46, 45.37, 32.72, 31.72, 21.54, 20.44. Single-crystal X-Ray diagram: crystal of compound 5 p was grown by slow diffusion of EtOAc into a solution of compound $\mathbf{5 p}$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ to yield colorless prisms. The compound crystallizes in the monoclinic crystal system, space group P 21/c, $a=10.8495(5) \AA, b=9.9471(15) \AA, c=19.6318(10) \AA, V=$ $2111.60(18) \AA^{3}, Z=4, d_{\text {calcd }}=1.323 \mathrm{mg} / \mathrm{cm}^{3}, F(000)=888,2 \theta$ range $2.082 \sim 26.463^{\circ}, R$ indices (all data) $\mathrm{R} 1=0.0989, w R 2=0.1760$.

1.4.17. 8-Methyl-5-phenyl-6-(toluene-3-sulfonyl)-5,6,7,8-tetrahydronaphtho[2,3-d][1,3]dioxole $(5 q)$. According to the general procedure, reaction was performed in the presence of $\mathrm{BF}_{3} \cdot \mathrm{OEt}_{2}$ ( 57 $\mathrm{mg}, 0.4 \mathrm{mmol})$, $3 \mathrm{a}(63 \mathrm{mg}, 0.2 \mathrm{mmol})$ and $7 \mathrm{~b}(37 \mathrm{mg}, 0.3 \mathrm{mmol})$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}(5 \mathrm{~mL})$ at $25^{\circ} \mathrm{C}$ for 20 h . Purification on silica gel (hexanes/EtOAc = 3/1) afforded $\mathbf{5 q}(87 \%, 73 \mathrm{mg})$. Colorless solid; $\mathrm{mp}=$ $154-155{ }^{\circ} \mathrm{C}$ (recrystallized from hexanes and EtOAc); HRMS (ESI, M ${ }^{+}+1$ ) calcd for $\mathrm{C}_{25} \mathrm{H}_{25} \mathrm{O}_{4} \mathrm{~S}$ 421.1474, found 421.1477; ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 7.52-7.49(\mathrm{~m}, 1 \mathrm{H}), 7.40(\mathrm{~s}, 1 \mathrm{H}), 7.30-7.25$ (m, 2H), 7.12-7.04 (m, 3H), 6.93-6.90 (m, 2H), $6.77(\mathrm{~s}, 1 \mathrm{H}), 6.25(\mathrm{~s}, 1 \mathrm{H}), 6.85(\mathrm{~d}, \mathrm{~J}=1.2 \mathrm{~Hz}, 1 \mathrm{H})$, $5.82(\mathrm{~d}, J=1.2 \mathrm{~Hz}, 1 \mathrm{H}), 4.52(\mathrm{~d}, J=8.0 \mathrm{~Hz}, 1 \mathrm{H}), 3.87-3.80(\mathrm{~m}, 1 \mathrm{H}), 2.96-2.90(\mathrm{~m}, 1 \mathrm{H}), 2.42(\mathrm{dt}, J=$ $4.4,12.8 \mathrm{~Hz}, 1 \mathrm{H}), 2.31(\mathrm{~s}, 3 \mathrm{H}), 1.75(\mathrm{q}, J=12.8 \mathrm{~Hz}, 1 \mathrm{H}), 1.37(\mathrm{~d}, J=6.8 \mathrm{~Hz}, 3 \mathrm{H})$; ${ }^{13} \mathrm{C}$ NMR ( 100 $\mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 146.39,146.03,143.96,139.01,138.47,134.19,134.00,130.94,128.82,128.69$, 128.60 (2x), 128.40 (2x), 126.59, 125.54, 109.69, 105.21, 100.85, 67.26, 45.61, 32.37, 31.84, 21.17, 20.57.


### 1.4.18.

## 6-(4-n-Butylbenzenesulfonyl)-8-methyl-5-phenyl-5,6,7,8-tetrahydronaphtho[2,3-d][1,3]dioxol

$\mathbf{e} \mathbf{( 5 r )}$. According to the general procedure, reaction was performed in the presence of $\mathrm{BF}_{3} \cdot \mathrm{OEt}_{2}(57$ $\mathrm{mg}, 0.4 \mathrm{mmol}), 30(72 \mathrm{mg}, 0.2 \mathrm{mmol})$ and $\mathbf{7 b}(37 \mathrm{mg}, 0.3 \mathrm{mmol})$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}(5 \mathrm{~mL})$ at $25^{\circ} \mathrm{C}$ for 20 h . Purification on silica gel (hexanes/EtOAc $=3 / 1$ ) afforded $5 \mathbf{r}(89 \%, 82 \mathrm{mg})$. Colorless solid; $\mathrm{mp}=$ $142-143{ }^{\circ} \mathrm{C}$ (recrystallized from hexanes and EtOAc); HRMS (ESI, M ${ }^{+}+1$ ) calcd for $\mathrm{C}_{28} \mathrm{H}_{31} \mathrm{O}_{4} \mathrm{~S}$ 463.1943, found 463.1945; ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 7.57$ ( $\mathrm{d}, J=8.4 \mathrm{~Hz}, 2 \mathrm{H}$ ), 7.17 ( $\mathrm{d}, \mathrm{J}=8.4$ $\mathrm{Hz}, 2 \mathrm{H}), 7.11-7.04(\mathrm{~m}, 3 \mathrm{H}), 6.92-6.90(\mathrm{~m}, 2 \mathrm{H}), 6.77(\mathrm{~s}, 1 \mathrm{H}), 6.26(\mathrm{~s}, 1 \mathrm{H}), 5.70(\mathrm{~d}, J=1.6 \mathrm{~Hz}, 1 \mathrm{H})$, $5.82(\mathrm{~d}, J=1.2 \mathrm{~Hz}, 1 \mathrm{H}), 4.51(\mathrm{~d}, J=8.0 \mathrm{~Hz}, 1 \mathrm{H}), 3.85-3.79(\mathrm{~m}, 1 \mathrm{H}), 2.94-2.89(\mathrm{~m}, 1 \mathrm{H}), 2.63(\mathrm{t}, \mathrm{J}=$
$8.0 \mathrm{~Hz}, 2 \mathrm{H}), 2.41(\mathrm{dt}, J=4.4,12.4 \mathrm{~Hz}, 1 \mathrm{H}), 1.69(\mathrm{q}, J=12.8 \mathrm{~Hz}, 1 \mathrm{H}), 1.62-1.53(\mathrm{~m}, 2 \mathrm{H}), 1.37(\mathrm{~d}, J=$ $6.8 \mathrm{~Hz}, 3 \mathrm{H}), 1.38-1.30(\mathrm{~m}, 2 \mathrm{H}), 0.95(\mathrm{t}, \mathrm{J}=7.2 \mathrm{~Hz}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 148.99$, $146.37,146.01,144.14,135.63,134.26,130.92,128.87$ (2x), 128.56 ( $2 x$ ), 128.53 ( $2 x$ ), 128.48 ( $2 x$ ), $126.51,109.72,105.17,100.83,67.34,45.52,35.52,33.12,32.49,31.75,22.23,20.48,13.83$.

1.4.19. 6,7-Dimethoxy-4-methyl-1,2-diphenyl-1,2,3,4-tetrahydronaphthalene (5s). According to the general procedure, reaction was performed in the presence of $\mathrm{BF}_{3} \cdot \mathrm{OEt}_{2}(57 \mathrm{mg}, 0.4 \mathrm{mmol}), 3 \mathbf{r}$ $(48 \mathrm{mg}, 0.2 \mathrm{mmol})$ and $7 \mathrm{a}(41 \mathrm{mg}, 0.3 \mathrm{mmol})$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}(5 \mathrm{~mL})$ at $25^{\circ} \mathrm{C}$ for 20 h . Purification on silica gel (hexanes/EtOAc = 3/1) afforded 5s ( $80 \%$, 57 mg ). Colorless solid; $\mathrm{mp}=140-141^{\circ} \mathrm{C}$ (recrystallized from hexanes and EtOAc); HRMS (ESI, M ${ }^{+}+1$ ) calcd for $\mathrm{C}_{25} \mathrm{H}_{27} \mathrm{O}_{2}$ 359.2011, found 359.2017; ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 7.19-7.08(\mathrm{~m}, 6 \mathrm{H}), 7.00-6.97(\mathrm{~m}, 2 \mathrm{H}), 6.89(\mathrm{~s}, 1 \mathrm{H})$, 6.87-6.85 (m, 2H), $6.22(\mathrm{~s}, 1 \mathrm{H}), 4.12(\mathrm{~d}, J=11.2 \mathrm{~Hz}, 1 \mathrm{H}), 3.92(\mathrm{~s}, 3 \mathrm{H}), 3.56(\mathrm{~s}, 3 \mathrm{H}), 3.21-3.15(\mathrm{~m}$, $1 \mathrm{H}), 3.06$ (dt, $J=2.4,12.8 \mathrm{~Hz}, 1 \mathrm{H}), 2.14$ (ddd, $J=2.8,5.2,12.8 \mathrm{~Hz}, 1 \mathrm{H}), 1.94(\mathrm{q}, J=12.8 \mathrm{~Hz}, 1 \mathrm{H})$, 1.42 ( $\mathrm{d}, \mathrm{J}=6.8 \mathrm{~Hz}, 3 \mathrm{H}$ ); ${ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 147.23,146.80,145.45,145.05,134.14$, 132.33, $129.26(2 x), 128.10(2 x), 127.83(2 x), 127.50(2 x), 125.97,125.87,112.99,108.94,55.84$, 55.65, 54.36, 50.37, 40.81, 33.53, 21.69; Anal. Calcd for $\mathrm{C}_{25} \mathrm{H}_{26} \mathrm{O}_{2}$ : C, 83.76; H, 7.31. Found: C, 83.89; H, 7.50. Single-crystal X-Ray diagram: crystal of compound $5 \mathbf{s}$ was grown by slow diffusion of EtOAc into a solution of compound $5 \mathbf{s}$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ to yield colorless prisms. The compound crystallizes in the monoclinic crystal system, space group P 21/c, $a=10.2155(13) \AA, b=18.822$ (2) $\AA, c=10.6623(15) \AA, V=1922.8(4) \AA^{3}, Z=4, d_{\text {calcd }}=1.238 \mathrm{mg} / \mathrm{cm}^{3}, F(000)=768,2 \theta$ range $2.126 \sim 26.390^{\circ}$, R indices (all data) $\mathrm{R} 1=0.0583$, $\mathrm{wR} 2=0.1024$.

1.4.20. 1-(4-Fluorophenyl)-6,7-dimethoxy-4-methyl-2-phenyl-1,2,3,4-tetrahydronaphthalene (5t). According to the general procedure, reaction was performed in the presence of $\mathrm{BF}_{3} \cdot \mathrm{OEt}_{2}$ (57 $\mathrm{mg}, 0.4 \mathrm{mmol}$ ), $3 \mathrm{t}(51 \mathrm{mg}, 0.2 \mathrm{mmol})$ and $7 \mathrm{a}(41 \mathrm{mg}, 0.3 \mathrm{mmol})$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}(5 \mathrm{~mL})$ at $25^{\circ} \mathrm{C}$ for 20 h . Purification on silica gel (hexanes/EtOAc = 3/1) afforded 5t ( $84 \%$, 63 mg ). Colorless solid; $\mathrm{mp}=$ $172-173{ }^{\circ} \mathrm{C}$ (recrystallized from hexanes and EtOAc); HRMS (ESI, $\mathrm{M}^{+}+1$ ) calcd for $\mathrm{C}_{25} \mathrm{H}_{26} \mathrm{FO}_{2}$ 377.1917, found 377.1924; ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 7.20-7.10(\mathrm{~m}, 3 \mathrm{H}), 6.97-6.95(\mathrm{~m}, 2 \mathrm{H})$, 6.88 (s, 1H), 6.81 (br s, 2H), $6.80(b r s, 2 H), 6.18(\mathrm{~s}, 1 \mathrm{H}), 4.10(\mathrm{~d}, ~ J=10.8 \mathrm{~Hz}, 1 \mathrm{H}), 3.91(\mathrm{~s}, 3 \mathrm{H})$, 3.57 (s, 3H), 3.21-3.12 (m, 1H), 2.98 (dt, $J=2.4,12.8 \mathrm{~Hz}, 1 \mathrm{H}), 2.14$ (ddd, $J=2.8,5.2,12.8 \mathrm{~Hz}, 1 \mathrm{H}$ ), 1.93 ( $\mathrm{q}, ~ J=12.8 \mathrm{~Hz}, 1 \mathrm{H}$ ), $\left.1.41(\mathrm{~d}, J=6.8 \mathrm{~Hz}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C} \mathrm{NMR} \mathrm{(100MHz,CDCl}_{3}\right): \delta 161.14(\mathrm{~d}, J=$ 242.6 Hz ), 147.37, 146.87, 144.79, 141.21 ( $\mathrm{d}, J=3.0 \mathrm{~Hz}$ ), 134.19, 132.01, 130.56 ( $\mathrm{d}, J=7.6 \mathrm{~Hz}$, $2 x), 128.11(2 x), 127.47(2 x), 126.11,114.66(d, J=21.3 \mathrm{~Hz}, 2 x), 112.83,109.07,55.86,55.68$,
53.69, 50.62, 40.70, 33.53, 21.71; Anal. Calcd for $\mathrm{C}_{25} \mathrm{H}_{25} \mathrm{FO}_{2}$ : C, 79.76; H, 6.69. Found: C, 79.62; H, 6.82. Single-crystal X-Ray diagram: crystal of compound 5 t was grown by slow diffusion of EtOAc into a solution of compound $5 \mathbf{t}$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ to yield colorless prisms. The compound crystallizes in the monoclinic crystal system, space group P 21/c, $a=10.3721$ (7) $\AA, b=18.7809$ (11) $\AA, c=10.7938$ (6) $\AA, V=1970.8(2) \AA^{3}, Z=4, d_{\text {calcd }}=1.269 \mathrm{mg} / \mathrm{cm}^{3}, F(000)=800,2 \theta$ range $2.095 \sim 26.383^{\circ}, R$ indices (all data) $\mathrm{R} 1=0.0556, \mathrm{wR} 2=0.1387$.


### 1.4.21.

5,7-Dimethoxy-4-methyl-1-phenyl-2-(toluene-4-sulfonyl)-1,2,3,4-tetrahydronaphthalene (5u). According to the general procedure, reaction was performed in the presence of $\mathrm{BF}_{3} \cdot \mathrm{OEt}_{2}(57 \mathrm{mg}$, $0.4 \mathrm{mmol})$, $\mathbf{3 a}(63 \mathrm{mg}, 0.2 \mathrm{mmol})$ and $\mathbf{7 c}(41 \mathrm{mg}, 0.3 \mathrm{mmol})$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}(5 \mathrm{~mL})$ at $25{ }^{\circ} \mathrm{C}$ for 20 h . Purification on silica gel (hexanes/EtOAc $=3 / 1$ ) afforded $5 \mathrm{u}(84 \%, 73 \mathrm{mg})$. Colorless solid; $\mathrm{mp}=$ $199-200{ }^{\circ} \mathrm{C}$ (recrystallized from hexanes and EtOAc); HRMS (ESI, $\mathrm{M}^{+}+1$ ) calcd for $\mathrm{C}_{26} \mathrm{H}_{29} \mathrm{O}_{4} \mathrm{~S}$ 437.1787, found 437.1789; ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 7.47$ ( $\mathrm{d}, \mathrm{J}=8.0 \mathrm{~Hz}, 2 \mathrm{H}$ ), 7.13 ( $\mathrm{d}, J=8.0$ $\mathrm{Hz}, 2 \mathrm{H}), 7.09-7.01(\mathrm{~m}, 3 \mathrm{H}), 6.79-6.76(\mathrm{~m}, 2 \mathrm{H}), 6.29(\mathrm{~d}, J=2.4 \mathrm{~Hz}, 1 \mathrm{H}), 5.68(\mathrm{~d}, J=2.4 \mathrm{~Hz}, 1 \mathrm{H})$, $4.39(\mathrm{~d}, \mathrm{~J}=8.4 \mathrm{~Hz}, 1 \mathrm{H}), 3.81(\mathrm{~s}, 3 \mathrm{H}), 3.63-3.58(\mathrm{~m}, 1 \mathrm{H}), 3.50(\mathrm{~s}, 3 \mathrm{H}), 3.29-3.23(\mathrm{~m}, 1 \mathrm{H}), 2.61$ (ddd, $J=4.4,6.8,11.2 \mathrm{~Hz}, 1 \mathrm{H}), 2.38(\mathrm{~s}, 3 \mathrm{H}), 2.00(\mathrm{ddd}, J=1.6,6.4,9.6 \mathrm{~Hz}, 1 \mathrm{H}), 1.43(\mathrm{~d}, J=6.8 \mathrm{~Hz}, 3 \mathrm{H})$; ${ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 158.26,158.21,143.58,142.61,139.27,136.61,129.37$ (2x), 129.31 ( $2 x$ ), 128.21 (4x), 126.64, 122.19, 105.66, 97.00, 65.98, 55.18, 54.96, 46.60, 29.72, 27.98, 22.05, 21.52. Single-crystal X-Ray diagram: crystal of compound $5 \mathbf{u}$ was grown by slow diffusion of EtOAc into a solution of compound $5 \mathbf{u}$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ to yield colorless prisms. The compound crystallizes in the monoclinic crystal system, space group P 21/c, $a=23.259(3) \AA, b=5.6619(4) \AA$, $c=17.6922(16) \AA, V=2155.0(3) \AA^{3}, Z=4, d_{\text {calcd }}=1.346 \mathrm{mg} / \mathrm{cm}^{3}, F(000)=928,2 \theta$ range $0.946 \sim 26.387^{\circ}, R$ indices (all data) $\mathrm{R} 1=0.0841, \mathrm{wR} 2=0.2079$.


### 1.4.22.

## 6,7,8-Trimethoxy-4-methyl-1-phenyl-2-(toluene-4-sulfonyl)-1,2,3,4-tetrahydronaphthalene

$(5 \mathrm{v})$. According to the general procedure, reaction was performed in the presence of $\mathrm{BF}_{3} \cdot \mathrm{OEt}_{2}$ (57 $\mathrm{mg}, 0.4 \mathrm{mmol}$ ), $3 \mathrm{a}(63 \mathrm{mg}, 0.2 \mathrm{mmol})$ and $7 \mathbf{d}(50 \mathrm{mg}, 0.3 \mathrm{mmol})$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}(5 \mathrm{~mL})$ at $25^{\circ} \mathrm{C}$ for 20 h . Purification on silica gel (hexanes/EtOAc $=3 / 1$ ) afforded $5 \mathrm{v}(80 \%, 75 \mathrm{mg})$. Colorless gum; HRMS (ESI, $\mathrm{M}^{+}+1$ ) calcd for $\mathrm{C}_{27} \mathrm{H}_{31} \mathrm{O}_{5} \mathrm{~S} 467.1892$, found 467.1898; ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 7.55$ (d,
$J=8.0 \mathrm{~Hz}, 2 \mathrm{H}), 7.18-7.12(\mathrm{~m}, 5 \mathrm{H}), 7.04-7.02(\mathrm{~m}, 2 \mathrm{H}), 5.98(\mathrm{~s}, 1 \mathrm{H}), 4.41(\mathrm{~d}, J=9.2 \mathrm{~Hz}, 1 \mathrm{H}), 3.90(\mathrm{~s}$, $3 \mathrm{H}), 3.90-3.83(\mathrm{~m}, 1 \mathrm{H}), 3.80(\mathrm{~s}, 3 \mathrm{H}), 3.52(\mathrm{~s}, 3 \mathrm{H}), 3.38-3.34(\mathrm{~m}, 1 \mathrm{H}), 2.37(\mathrm{~s}, 3 \mathrm{H}), 2.21(\mathrm{dt}, J=3.2$, $16.8 \mathrm{~Hz}, 1 \mathrm{H}), 2.08(\mathrm{dt}, J=5.6,16.8 \mathrm{~Hz}, 1 \mathrm{H}), 1.32(\mathrm{~d}, J=6.8 \mathrm{~Hz}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta$ $151.90,151.45,150.46,144.04,143.90,140.37,135.62,132.19,129.41$ (2x), 129.13 ( $2 x$ ), 128.59 (2x), 128.40 (2x), 126.48, 108.53, 64.08, 60.80, 60.57, 55.69, 45.31, 29.63, 26.64, 21.88, 21.51.


### 1.4.23.

## 6-Butoxy-7-methoxy-4-methyl-1-phenyl-2-(toluene-4-sulfonyl)-1,2,3,4-tetrahydronaphthalen

 e(5w) and
7-Butoxy-6-methoxy-4-methyl-1-phenyl-2-(toluene-4-sulfonyl)-1,2,3,4-tetrahydronaphthalen $\mathbf{e} \mathbf{( 5 x )}$. According to the general procedure, reaction was performed in the presence of $\mathrm{BF}_{3} \cdot \mathrm{OEt}_{2}$ ( $57 \mathrm{mg}, 0.4 \mathrm{mmol}$ ), 3a ( $63 \mathrm{mg}, 0.2 \mathrm{mmol}$ ) and $7 \mathbf{e}(54 \mathrm{mg}, 0.3 \mathrm{mmol})$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}(5 \mathrm{~mL})$ at $25^{\circ} \mathrm{C}$ for 20 h . Purification on silica gel (hexanes/EtOAc $=3 / 1$ ) afforded a mixture of 5 w and $5 \mathrm{x}(75 \%, 72 \mathrm{mg})$ with a ratio of $2: 1$. HRMS ( $\mathrm{ESI}, \mathrm{M}^{+}+1$ ) calcd for $\mathrm{C}_{29} \mathrm{H}_{35} \mathrm{O}_{4} \mathrm{~S} 479.2256$, found 479.2258 ; For major product: ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 7.58-7.56(\mathrm{~m}, 2 \mathrm{H}), 7.18(\mathrm{~d}, J=8.0 \mathrm{~Hz}, 2 \mathrm{H}), 7.14-7.08(\mathrm{~m}$, $3 \mathrm{H}), 6.95-6.93(\mathrm{~m}, 2 \mathrm{H}), 6.77(\mathrm{~s}, 1 \mathrm{H}), 6.25(\mathrm{~s}, 1 \mathrm{H}), 4.54(\mathrm{~d}, J=7.6 \mathrm{~Hz}, 1 \mathrm{H}), 4.01-3.94(\mathrm{~m}, 2 \mathrm{H})$, 3.78-3.66 (m, 2H), $3.57(\mathrm{~s}, 3 \mathrm{H}), 2.96-2.92(\mathrm{~m}, 1 \mathrm{H}), 2.42-2.35(\mathrm{~m}, 2 \mathrm{H}), 2.38(\mathrm{~s}, 3 \mathrm{H}), 1.83-1.70(\mathrm{~m}$, $2 \mathrm{H}), 1.52-1.43(\mathrm{~m}, 2 \mathrm{H}), 1.40-1.37(\mathrm{~m}, 2 \mathrm{H}), 0.96(\mathrm{t}, J=7.2 \mathrm{~Hz}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta$ $147.93,147.16,144.40,135.42,132.95,129.79,129.46(2 x), 128.72,128.62(4 x), 128.40(2 x)$, $126.35,113.26,109.87,68.77,67.55,55.81,45.09,32.75,31.46,31.28,21.52,20.37,19.19,13.86$. For minor product: ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 7.58-7.56(\mathrm{~m}, 2 \mathrm{H}), 7.18(\mathrm{~d}, J=8.0 \mathrm{~Hz}, 2 \mathrm{H})$, 7.14-7.08 (m, 3H), 6.95-6.93 (m, 2H), $6.76(\mathrm{~s}, 1 \mathrm{H}), 6.24(\mathrm{~s}, 1 \mathrm{H}), 4.52(\mathrm{~d}, J=6.8 \mathrm{~Hz}, 1 \mathrm{H}), 4.01-3.94$ (m, 2H), $3.83(\mathrm{~s}, 3 \mathrm{H}), 3.78-3.66(\mathrm{~m}, 2 \mathrm{H}), 2.96-2.92(\mathrm{~m}, 1 \mathrm{H}), 2.42-2.35(\mathrm{~m}, 2 \mathrm{H}), 2.38(\mathrm{~s}, 3 \mathrm{H})$, 1.83-1.70 (m, 2H), 1.52-1.43 (m, 2H), 1.40-1.37 (m, 2H), $0.86(\mathrm{t}, J=7.2 \mathrm{~Hz}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR (100 $\mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 147.90,146.95,144.12,135.42,132.82,129.87,129.46$ (2x), 128.96, $128.62(4 \mathrm{x})$, $128.40(2 x), 126.35,114.44,108.66,68.41,67.49,56.06,45.13,32.72,31.53,30.90,21.52,20.40$, 19.03, 13.78.
1.5. A representative synthetic procedure of compounds $6 \mathrm{a}-\mathrm{i}$ is as follows: $\mathrm{BF}_{3} \cdot \mathrm{OEt}_{2}(57 \mathrm{mg}$, $0.4 \mathrm{mmol})$ was added to a solution of $4 \mathbf{a}-\mathbf{g}(0.2 \mathrm{mmol})$ and $\mathbf{7 a - b}, 7 \mathbf{f}(0.3 \mathrm{mmol})$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}(5 \mathrm{~mL})$ at $25^{\circ} \mathrm{C}$. The reaction mixture was stirred at $25{ }^{\circ} \mathrm{C}$ for 20 h . The reaction mixture was concentrated and the residue was diluted with water $(10 \mathrm{~mL})$ and the mixture was extracted with $\mathrm{CH}_{2} \mathrm{Cl}_{2}(3 \times 20$ mL ). The combined organic layers were washed with brine, dried, filtered and evaporated to afford crude product under reduced pressure. Purification on silica gel (hexanes/EtOAc $=5 / 1 \sim 3 / 1$ ) afforded 6a-i.

1.5.1.

2,3-Dimethoxy-5,5-dimethyl-9-phenyl-8-(toluene-4-sulfonyl)-6,7,8,9-tetrahydro-5H-benzocycl oheptene (6a). According to the general procedure, reaction was performed in the presence of $\mathrm{BF}_{3} . \mathrm{OEt}_{2}(57 \mathrm{mg}, 0.4 \mathrm{mmol}), 4 \mathrm{a}(69 \mathrm{mg}, 0.2 \mathrm{mmol})$ and $7 \mathrm{a}(41 \mathrm{mg}, 0.3 \mathrm{mmol})$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}(5 \mathrm{~mL})$ at $25^{\circ} \mathrm{C}$ for 20 h . Purification on silica gel (hexanes/EtOAc =3/1) afforded $\mathbf{6 a}(82 \%, 76 \mathrm{mg})$. Colorless solid; $m p=191-192{ }^{\circ} \mathrm{C}$ (recrystallized from hexanes and EtOAc); HRMS (ESI, M ${ }^{+}+1$ ) calcd for $\mathrm{C}_{28} \mathrm{H}_{33} \mathrm{O}_{4} \mathrm{~S} 465.2100$, found 465.2102; ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 7.72$ (d, $J=8.4 \mathrm{~Hz}, 2 \mathrm{H}$ ), 7.28 (d, J=8.0 Hz, 2H), 7.23-7.20 (m, 2H), 7.17-7.13 (m, 1H), 6.98 (d, J=8.0 Hz, 2H), 6.91 (s, 1H), 6.45 (s, 1H), $4.97(\mathrm{~d}, \mathrm{~J}=2.4 \mathrm{~Hz}, 1 \mathrm{H}), 4.13-4.08(\mathrm{~m}, 1 \mathrm{H}), 3.90(\mathrm{~s}, 3 \mathrm{H}), 3.77(\mathrm{~s}, 3 \mathrm{H}), 2.42(\mathrm{~s}, 3 \mathrm{H})$, 2.19-2.10 (m, 1H), 1.94-1.86 (m, 1H), 1.69-1.58 (m, 1H), 1.51-1.45 (m, 1H), $1.34(\mathrm{~s}, 3 \mathrm{H}), 1.17(\mathrm{~s}$, $3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 148.11,146.90,144.40,144.29,139.15,135.28,129.62(2 \mathrm{x})$, 128.83 ( $2 x$ ), 128.31 (2x), $127.40(2 x)$, 126.69, 126.24, 116.51, 112.83, 69.62, 55.84, 55.71, 48.18, 40.02, 35.47, 32.94, 32.65, 22.01, 21.56; Anal. Calcd for $\mathrm{C}_{28} \mathrm{H}_{32} \mathrm{O}_{4} \mathrm{~S}: \mathrm{C}, 72.38 ; \mathrm{H}, 6.94$. Found: C, 72.50; H, 7.18. Single-crystal X-Ray diagram: crystal of compound $\mathbf{6 a}$ was grown by slow diffusion of EtOAc into a solution of compound $\mathbf{6 a}$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ to yield colorless prisms. The compound crystallizes in the orthorombic crystal system, space group P $212121, a=9.4078$ (8) $\AA, b=$ $9.4698(8) \AA, c=26.640(2) \AA, V=2373.3(4) \AA^{3}, Z=4, d_{\text {calcd }}=1.300 \mathrm{mg} / \mathrm{cm}^{3}, F(000)=992,2 \theta$ range $1.529 \sim 26.480^{\circ}$, $R$ indices (all data) $R 1=0.0368$, wR2 $=0.0806$.


### 1.5.2.

2,3-Dimethoxy-9-(4-methoxyphenyl)-5,5-dimethyl-8-(toluene-4-sulfonyl)-6,7,8,9-tetrahydro-5
H-benzocycloheptene (6b). According to the general procedure, reaction was performed in the presence of $\mathrm{BF}_{3} \cdot \mathrm{OEt}_{2}(57 \mathrm{mg}, 0.4 \mathrm{mmol}), 4 \mathrm{~b}(75 \mathrm{mg}, 0.2 \mathrm{mmol})$ and $7 \mathrm{a}(41 \mathrm{mg}, 0.3 \mathrm{mmol})$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}(5 \mathrm{~mL})$ at $25^{\circ} \mathrm{C}$ for 20 h . Purification on silica gel (hexanes/EtOAc = 3/1) afforded $\mathbf{6 b}(82 \%$, 81 mg ). Colorless solid; $\mathrm{mp}=123-124{ }^{\circ} \mathrm{C}$ (recrystallized from hexanes and EtOAc); HRMS (ESI, $\mathrm{M}^{+}+1$ ) calcd for $\mathrm{C}_{29} \mathrm{H}_{35} \mathrm{O}_{5} \mathrm{~S} 495.2205$, found 495.2209 ; ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 7.67(\mathrm{~d}, \mathrm{~J}=$ $8.4 \mathrm{~Hz}, 2 \mathrm{H}), 7.24(\mathrm{~d}, J=8.0 \mathrm{~Hz}, 2 \mathrm{H}), 6.90(\mathrm{~s}, 1 \mathrm{H}), 6.86(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 2 \mathrm{H}), 6.72(\mathrm{~d}, J=8.8 \mathrm{~Hz}, 2 \mathrm{H})$, 6.43 (s, 1H), 4.91 (d, J = $3.2 \mathrm{~Hz}, 1 \mathrm{H}$ ), 4.05-4.01 (m, 1H), 3.87 (s, 3H), 3.74 (s, 3H), 3.73 (s, 3H), $2.39(\mathrm{~s}, 3 \mathrm{H}), 2.21-2.13(\mathrm{~m}, 1 \mathrm{H}), 1.92-1.83(\mathrm{~m}, 1 \mathrm{H}), 1.73-1.67(\mathrm{~m}, 1 \mathrm{H}), 1.57-1.51(\mathrm{~m}, 1 \mathrm{H}), 1.33(\mathrm{~s}$, $3 \mathrm{H}), 1.18(\mathrm{~s}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 157.86,147.87,146.69,144.13,138.98,135.67$, 135.38, 129.44 (2x), 128.57 (2x), 128.43 (2x), 127.13, 116.14, 113.45 (2x), 112.60, 69.34, 55.71, $55.56,55.06,47.23,39.80,35.32,32.90,32.56,21.94,21.41$. Single-crystal X-Ray diagram: crystal of compound $\mathbf{6} \mathbf{b}$ was grown by slow diffusion of EtOAc into a solution of compound $\mathbf{6} \mathbf{b}$ in
$\mathrm{CH}_{2} \mathrm{Cl}_{2}$ to yield colorless prisms. The compound crystallizes in the orthorombic crystal system, space group $P 21 / c, a=10.4874(8) \AA, b=11.6664(8) \AA, c=24.139(2) \AA, V=2953.4(4) \AA^{3}, Z=4$, $d_{\text {calcd }}=1.112 \mathrm{mg} / \mathrm{cm}^{3}, F(000)=1056,2 \theta$ range $2.428 \sim 26.356^{\circ}$, R indices (all data) $\mathrm{R} 1=0.1542$, $w R 2=0.2103$.


### 1.5.3.

2,3-Dimethoxy-5,5-dimethyl-8-(toluene-4-sulfonyl)-9-p-tolyl-6,7,8,9-tetrahydro-5H-benzocycl oheptene (6c). According to the general procedure, reaction was performed in the presence of $\mathrm{BF}_{3} . \mathrm{OEt}_{2}(57 \mathrm{mg}, 0.4 \mathrm{mmol}), 4 \mathrm{c}(72 \mathrm{mg}, 0.2 \mathrm{mmol})$ and $7 \mathrm{a}(41 \mathrm{mg}, 0.3 \mathrm{mmol})$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}(5 \mathrm{~mL})$ at $25^{\circ} \mathrm{C}$ for 20 h . Purification on silica gel (hexanes/EtOAc $=5 / 1$ ) afforded $\mathbf{6 c}(80 \%, 76 \mathrm{mg})$. Colorless solid; $m p=158-159{ }^{\circ} \mathrm{C}$ (recrystallized from hexanes and EtOAc); HRMS (ESI, $\mathrm{M}^{+}+1$ ) calcd for $\mathrm{C}_{29} \mathrm{H}_{35} \mathrm{O}_{4} \mathrm{~S} 479.2256$, found 479.2258 ; ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 7.71(\mathrm{~d}, J=8.0 \mathrm{~Hz}, 2 \mathrm{H}), 7.27$ (d, J=8.0 Hz, 2H), 7.01 (d, J = $8.0 \mathrm{~Hz}, 2 \mathrm{H}$ ), 6.91 (s, 1H), 6.85 (d, J=8.4 Hz, 2H), 6.45 (s, 1H), 4.92 (d, $J=2.0 \mathrm{~Hz}, 1 \mathrm{H})$, 4.11-4.07 (m, 1H), $3.90(\mathrm{~s}, 3 \mathrm{H}), 3.77(\mathrm{~s}, 3 \mathrm{H}), 2.42(\mathrm{~s}, 3 \mathrm{H}), 2.28(\mathrm{~s}, 3 \mathrm{H})$, 2.20-2.12 (m, 1H), 1.94-1.87 (m, 1H), $1.70(\mathrm{dd}, J=9.2,14.8 \mathrm{~Hz}, 1 \mathrm{H}), 1.50(\mathrm{dd}, J=9.2,14.8 \mathrm{~Hz}$, $1 \mathrm{H}), 1.34(\mathrm{~s}, 3 \mathrm{H}), 1.18(\mathrm{~s}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C} \operatorname{NMR}\left(100 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta 147.98,146.78,144.27,141.09$, 139.08, 135.82, 135.31, 129.83 ( $2 x$ ), 128.93 ( $2 x$ ), 128.73 ( $2 x$ ), 127.27 (2x), 126.87, 116.36, 112.70, $69.55,55.78,55.64,47.79,39.96,35.41,32.95,32.59,21.91,21.52,20.77$.


### 1.5.4.

9-Biphenyl-4-yl-2,3-dimethoxy-5,5-dimethyl-8-(toluene-4-sulfonyl)-6,7,8,9-tetrahydro-5H-ben zocycloheptene (6d). According to the general procedure, reaction was performed in the presence of $\mathrm{BF}_{3} . \mathrm{OEt}_{2}(57 \mathrm{mg}, 0.4 \mathrm{mmol}), 4 \mathrm{~d}(84 \mathrm{mg}, 0.2 \mathrm{mmol})$ and $7 \mathrm{a}(41 \mathrm{mg}, 0.3 \mathrm{mmol})$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}(5 \mathrm{~mL})$ at $25^{\circ} \mathrm{C}$ for 20 h . Purification on silica gel (hexanes/EtOAc $=4 / 1$ ) afforded $\mathbf{6 d}(82 \%$, 89 mg ). Colorless gum; HRMS (ESI, M ${ }^{+}+1$ ) calcd for $\mathrm{C}_{34} \mathrm{H}_{37} \mathrm{O}_{4} \mathrm{~S} 541.2413$, found 541.2412 ; ${ }^{1} \mathrm{H}$ NMR (400 MHz, $\mathrm{CDCl}_{3}$ ): $\delta 7.72(\mathrm{~d}, \mathrm{~J}=8.4 \mathrm{~Hz}, 2 \mathrm{H}), 7.56-7.53(\mathrm{~m}, 2 \mathrm{H}), 7.45-7.40(\mathrm{~m}, 4 \mathrm{H}), 7.35-7.31$ (m, 1H), 7.28-7.26 (m, 2H), $7.05(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 2 \mathrm{H}), 6.94(\mathrm{~s}, 1 \mathrm{H}), 6.49(\mathrm{~s}, 1 \mathrm{H}), 5.02(\mathrm{~d}, J=3.2 \mathrm{~Hz}$, $1 \mathrm{H})$, 4.16-4.11 (m, 1H), $3.91(\mathrm{~s}, 3 \mathrm{H}), 3.77(\mathrm{~s}, 3 \mathrm{H}), 2.40(\mathrm{~s}, 3 \mathrm{H}), 2.26-2.18(\mathrm{~m}, 1 \mathrm{H}), 1.97-1.89(\mathrm{~m}$, $1 \mathrm{H}), 1.74(\mathrm{dd}, J=9.6,14.8 \mathrm{~Hz}, 1 \mathrm{H}), 1.58(\mathrm{dd}, J=9.6,14.8 \mathrm{~Hz}, 1 \mathrm{H}), 1.37(\mathrm{~s}, 3 \mathrm{H}), 1.22(\mathrm{~s}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR (100 MHz, $\mathrm{CDCl}_{3}$ ): $\delta 148.11,146.89,144.32,143.05,140.35,139.18,139.12,135.44,129.60$ (2x), 128.74 (4x), 127.99 (2x), 127.27, 126.86 (4x), 126.74, 116.31, 112.78, 69.55, 55.84, 55.71, 47.91, 39.98, 35.57, 33.03, 32.66, 22.03, 21.53.


### 1.5.5.

2,3-Dimethoxy-5,5-dimethyl-9-naphthalen-2-yl-8-(toluene-4-sulfonyl)-6,7,8,9-tetrahydro-5H-b enzocycloheptene (6e). According to the general procedure, reaction was performed in the presence of $\mathrm{BF}_{3} . \mathrm{OEt}_{2}(57 \mathrm{mg}, 0.4 \mathrm{mmol}), 4 \mathrm{e}(79 \mathrm{mg}, 0.2 \mathrm{mmol})$ and $7 \mathrm{a}(41 \mathrm{mg}, 0.3 \mathrm{mmol})$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}(5 \mathrm{~mL})$ at $25^{\circ} \mathrm{C}$ for 20 h . Purification on silica gel (hexanes/EtOAc $=4 / 1$ ) afforded $\mathbf{6 e}(78 \%$, 80 mg ). Colorless gum; HRMS (ESI, M ${ }^{+}+1$ ) calcd for $\mathrm{C}_{32} \mathrm{H}_{35} \mathrm{O}_{4} \mathrm{~S} 515.2256$, found $515.2260 ;{ }^{1} \mathrm{H}$ NMR (400 MHz, CDCl $)_{3}$ : $\delta 7.79-7.76(\mathrm{~m}, 1 \mathrm{H}), 7.73(\mathrm{~d}, J=8.8 \mathrm{~Hz}, 1 \mathrm{H}), 7.69(\mathrm{~d}, J=8.0 \mathrm{~Hz}, 2 \mathrm{H})$, 7.62-7.57 (m, 1H), 7.45-7.40 (m, 2H), 7.28 (dd, $J=2.0,8.8 \mathrm{~Hz}, 1 \mathrm{H}$ ), 7.25 (br s, 1H), 7.19 (d, J= 8.0 $\mathrm{Hz}, 2 \mathrm{H}), 6.96(\mathrm{~s}, 1 \mathrm{H}), 6.51(\mathrm{~s}, 1 \mathrm{H}), 5.17(\mathrm{~d}, \mathrm{~J}=3.2 \mathrm{~Hz}, 1 \mathrm{H}), 4.24-4.17(\mathrm{~m}, 1 \mathrm{H}), 3.92(\mathrm{~s}, 3 \mathrm{H}), 3.73(\mathrm{~s}$, $3 \mathrm{H}), 2.36(\mathrm{~s}, 3 \mathrm{H}), 2.28-2.19(\mathrm{~m}, 1 \mathrm{H}), 1.95-1.87(\mathrm{~m}, 1 \mathrm{H}), 1.73(\mathrm{dd}, J=9.6,14.8 \mathrm{~Hz}, 1 \mathrm{H}), 1.55(\mathrm{dd}, J$ $=9.6,14.8 \mathrm{~Hz}, 1 \mathrm{H}$ ), 1.38 (s, 3H), 1.23 (s, 3H); ${ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 148.13,146.93$, 144.34, 141.24, 139.28, 135.45, 132.98, 131.94, 129.51 (2x), 128.70 (2x), 128.08, 127.73, 127.36, 127.80, 126.69, 126.14, 125.80, 125.77, 116.31, 112.78, 69.47, 55.87, 55.69, 48.36, 40.02, 35.46, 33.03, 32.73, 22.23, 21.49; Anal. Calcd for $\mathrm{C}_{32} \mathrm{H}_{34} \mathrm{O}_{4} \mathrm{~S}: \mathrm{C}, 74.68 ; \mathrm{H}, 6.66$. Found: C, 74.87; H, 6.91 .


### 1.5.6.

## 8-Benzenesulfonyl-2,3-dimethoxy-9-(4-methoxyphenyl)-5,5-dimethyl-6,7,8,9-tetrahydro-5H-b

 enzocycloheptene (6f). According to the general procedure, reaction was performed in the presence of $\mathrm{BF}_{3} . \mathrm{OEt}_{2}(57 \mathrm{mg}, 0.4 \mathrm{mmol}), 4 \mathrm{f}(72 \mathrm{mg}, 0.2 \mathrm{mmol})$ and $7 \mathrm{a}(41 \mathrm{mg}, 0.3 \mathrm{mmol})$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ $(5 \mathrm{~mL})$ at $25^{\circ} \mathrm{C}$ for 20 h . Purification on silica gel (hexanes/EtOAc $=3 / 1$ ) afforded $6 \mathbf{f}(76 \%, 73 \mathrm{mg})$. Colorless solid; $m p=167-168{ }^{\circ} \mathrm{C}$ (recrystallized from hexanes and EtOAc); HRMS (ESI, $\mathrm{M}^{+}+1$ ) calcd for $\mathrm{C}_{28} \mathrm{H}_{33} \mathrm{O}_{5} \mathrm{~S} 481.2049$, found $481.2054 ;{ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 7.79-7.76(\mathrm{~m}, 2 \mathrm{H})$, 7.57-7.53 (m, 1H), 7.46-7.42 (m, 2H), $6.89(\mathrm{~s}, 1 \mathrm{H}), 6.87(\mathrm{~d}, J=8.8 \mathrm{~Hz}, 2 \mathrm{H}), 6.71(\mathrm{~d}, J=8.8 \mathrm{~Hz}, 2 \mathrm{H})$, $6.44(\mathrm{~s}, 1 \mathrm{H}), 4.94(\mathrm{~d}, \mathrm{~J}=3.6 \mathrm{~Hz}, 1 \mathrm{H}), 4.09-4.03(\mathrm{~m}, 1 \mathrm{H}), 3.87(\mathrm{~s}, 3 \mathrm{H}), 3.74(\mathrm{~s}, 3 \mathrm{H}), 3.73(\mathrm{~s}, 3 \mathrm{H})$, 2.24-2.16 (m, 1H), 1.91-1.84 (m, 1H), 1.75-1.69 (m, 1H), 1.60-1.53 (m, 1H), 1.33 (s, 3H), 1.19 (s, $3 \mathrm{H}) ;{ }^{13} \mathrm{C} \operatorname{NMR}\left(100 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta 157.93,147.91,146.73,139.04,138.49,135.41,133.21$, 128.82 ( $2 x$ ), 128.58 ( 4 x ), 127.13, 116.07, 113.53 (2x), 112.59, 69.34, 55.75, 55.62, 55.11, 47.17, 39.80, 35.37, 32.97, 32.57, 22.03; Anal. Calcd for $\mathrm{C}_{28} \mathrm{H}_{32} \mathrm{O}_{5} \mathrm{~S}: \mathrm{C}, 69.97$; H, 6.71. Found: C, 70.17; H, 6.96.

### 1.5.7.

8-Methanesulfonyl-2,3-dimethoxy-9-(4-methoxyphenyl)-5,5-dimethyl-6,7,8,9-tetrahydro-5H-b enzocycloheptene ( 6 g ). According to the general procedure, reaction was performed in the presence of $\mathrm{BF}_{3} \cdot \mathrm{OEt}_{2}(57 \mathrm{mg}, 0.4 \mathrm{mmol}), 4 \mathrm{~g}(60 \mathrm{mg}, 0.2 \mathrm{mmol})$ and $7 \mathrm{a}(41 \mathrm{mg}, 0.3 \mathrm{mmol})$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}(5 \mathrm{~mL})$ at $25^{\circ} \mathrm{C}$ for 20 h . Purification on silica gel (hexanes/EtOAc $=3 / 1$ ) afforded $\mathbf{6 g}(80 \%$, 67 mg ). Colorless gum; HRMS (ESI, M ${ }^{+}+1$ ) calcd for $\mathrm{C}_{23} \mathrm{H}_{31} \mathrm{O}_{5} \mathrm{~S} 419.1892$, found 419.1897; ${ }^{1} \mathrm{H}$ NMR (400 MHz, CDCl $)_{3}$ : $\delta 7.01$ (d, J= $8.4 \mathrm{~Hz}, 2 \mathrm{H}$ ), $6.97(\mathrm{~s}, 1 \mathrm{H}), 6.84(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 2 \mathrm{H}), 6.54$ (s, $1 \mathrm{H}), 4.92(\mathrm{~d}, \mathrm{~J}=3.6 \mathrm{~Hz}, 1 \mathrm{H}), 3.95-3.90(\mathrm{~m}, 1 \mathrm{H}), 3.90(\mathrm{~s}, 3 \mathrm{H}), 3.77(\mathrm{~s}, 3 \mathrm{H}), 3.75(\mathrm{~s}, 3 \mathrm{H}), 2.53(\mathrm{~s}, 3 \mathrm{H})$, 2.25-2.02 (m, 2H), $1.80(\mathrm{dd}, J=9.2,14.8 \mathrm{~Hz}, 1 \mathrm{H}), 1.64-1.55(\mathrm{~m}, 1 \mathrm{H}), 1.40(\mathrm{~s}, 3 \mathrm{H}), 1.19(\mathrm{~s}, 3 \mathrm{H}){ }^{13} \mathrm{C}$ NMR (100 MHz, $\mathrm{CDCl}_{3}$ ): $\delta 158.17$, 148.27, 147.12, 139.36, 135.54, 128.52 (2x), 126.71, 115.95, 113.82 (2x), 113.04, 68.94, 55.81, 55.78, 55.18, 47.90, 40.05, 38.54, 35.26, 33.10, 32.61, 22.29.


### 1.5.8.

8-Benzenesulfonyl-9-(4-methoxyphenyl)-5,5-dimethyl-6,7,8,9-tetrahydro-5H-1,3-dioxa-cyclo hepta[f]indene (6h). According to the general procedure, reaction was performed in the presence of $\mathrm{BF}_{3} \cdot \mathrm{OEt}_{2}(57 \mathrm{mg}, 0.4 \mathrm{mmol}), 4 \mathrm{f}(72 \mathrm{mg}, 0.2 \mathrm{mmol})$ and $\mathbf{7 b}(37 \mathrm{mg}, 0.3 \mathrm{mmol})$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}(5 \mathrm{~mL})$ at $25^{\circ} \mathrm{C}$ for 20 h . Purification on silica gel (hexanes/EtOAc $=3 / 1$ ) afforded $\mathbf{6 h}(85 \%, 79 \mathrm{mg})$. Colorless gum; HRMS (ESI, $\mathrm{M}^{+}+1$ ) calcd for $\mathrm{C}_{27} \mathrm{H}_{29} \mathrm{O}_{5} \mathrm{~S} 465.1736$, found 465.1739 ; ${ }^{1} \mathrm{H}$ NMR ( 400 MHz , $\mathrm{CDCl}_{3}$ ): $\delta 7.76-7.74(\mathrm{~m}, 2 \mathrm{H}), 7.57-7.53(\mathrm{~m}, 1 \mathrm{H}), 7.46-7.43(\mathrm{~m}, 2 \mathrm{H}), 6.91(\mathrm{~s}, 1 \mathrm{H}), 6.84(\mathrm{~d}, \mathrm{~J}=8.4 \mathrm{~Hz}$, $2 \mathrm{H}), 6.69(\mathrm{~d}, J=8.8 \mathrm{~Hz}, 2 \mathrm{H}), 6.45(\mathrm{~s}, 1 \mathrm{H}), 6.90(\mathrm{~d}, J=1.2 \mathrm{~Hz}, 1 \mathrm{H}), 5.88(\mathrm{~d}, J=1.2 \mathrm{~Hz}, 1 \mathrm{H}), 4.89(\mathrm{~d}$, $J=4.4 \mathrm{~Hz}, 1 \mathrm{H}), 4.12-4.01(\mathrm{~m}, 1 \mathrm{H}), 3.78(\mathrm{~s}, 3 \mathrm{H}), 2.32-2.24(\mathrm{~m}, 1 \mathrm{H}), 1.91-1.50(\mathrm{~m}, 3 \mathrm{H}), 1.35(\mathrm{~s}, 3 \mathrm{H})$, 1.19 (s, 3H); ${ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 158.00,147.11,145.63,140.54,138.86,134.48$, 133.13, 128.85 (2x), 128.75 (2x), 128.46 (3x), 113.57 (2x), 112.36, 108.96, 100.98, 68.60, 55.12, 47.17, 39.89, 35.35, 33.13, 32.69, 21.91.

1.5.9.

## 8-Benzenesulfonyl-2,3-dibutoxy-9-(4-methoxyphenyl)-5,5-dimethyl-6,7,8,9-tetrahydro-5H-be

nzocycloheptene (6i). According to the general procedure, reaction was performed in the presence of $\mathrm{BF}_{3} . \mathrm{OEt}_{2}(57 \mathrm{mg}, 0.4 \mathrm{mmol}), 4 \mathrm{f}(72 \mathrm{mg}, 0.2 \mathrm{mmol})$ and $7 \mathrm{f}(67 \mathrm{mg}, 0.3 \mathrm{mmol})$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ $(5 \mathrm{~mL})$ at $25^{\circ} \mathrm{C}$ for 20 h . Purification on silica gel (hexanes/EtOAc $=3 / 1$ ) afforded $6 \mathbf{i}(85 \%, 96 \mathrm{mg})$. Colorless solid; $m p=151-152^{\circ} \mathrm{C}$ (recrystallized from hexanes and EtOAc); HRMS (ESI, $\mathrm{M}^{+}+1$ ) calcd for $\mathrm{C}_{34} \mathrm{H}_{45} \mathrm{O}_{5} \mathrm{~S} 565.2988$, found 565.2989; ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 7.77-7.75(\mathrm{~m}, 2 \mathrm{H})$, $7.57-7.53(\mathrm{~m}, 1 \mathrm{H}), 7.46-7.42(\mathrm{~m}, 2 \mathrm{H}), 6.90(\mathrm{~s}, 1 \mathrm{H}), 6.87(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 2 \mathrm{H}), 6.71(\mathrm{~d}, J=8.0 \mathrm{~Hz}, 2 \mathrm{H})$, $6.45(\mathrm{~s}, 1 \mathrm{H}), 4.92(\mathrm{~d}, J=3.6 \mathrm{~Hz}, 1 \mathrm{H}), 4.07-4.04(\mathrm{~m}, 1 \mathrm{H}), 4.00(\mathrm{t}, J=6.4 \mathrm{~Hz}, 2 \mathrm{H}), 3.90-3.77(\mathrm{~m}, 2 \mathrm{H})$, 3.75 (s, 3H), 2.35-2.17 (m, 1H), 1.93-1.69 (m, 6H), 1.54-1.39 (m, 5H), 1.31 (s, 3H), 1.18 (s, 3H), $1.00(\mathrm{t}, \mathrm{J}=6.8 \mathrm{~Hz}, 3 \mathrm{H}), 0.92(\mathrm{t}, \mathrm{J}=6.4 \mathrm{~Hz}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C} \mathrm{NMR}\left(100 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta 157.98,148.08$, $147.13,139.22,138.68,135.48,133.17$, 128.82 ( $2 x$ ), 128.74 ( $2 x$ ), 128.70 ( $2 x$ ), 127.62, 118.69, $115.91,113.56$ (2x), 69.46, 69.25, 68.76, 55.18, 47.22, 39.73, 35.50, 33.06, 32.65, 31.50, 31.31, 22.14, 19.23, 19.19, 13.89, 13.84. Single-crystal X-Ray diagram: crystal of compound $\mathbf{6 i}$ was grown by slow diffusion of EtOAc into a solution of compound $\mathbf{6 i}$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ to yield colorless prisms. The compound crystallizes in the monoclinic crystal system, space group P 21/n, $a=10.3966$ (8) $\AA, b=$ $11.0245(10) \AA, c=26.053(2) \AA, V=2984.6(4) \AA^{3}, Z=4, d_{\text {calcd }}=1.257 \mathrm{mg} / \mathrm{cm}^{3}, F(000)=1216,2 \theta$ range $1.564 \sim 26.401^{\circ}, R$ indices (all data) $R 1=0.0665$, wR2 $=0.1384$.
1.6. A representative synthetic procedure of compounds 8a-c is as follows: $\mathrm{BF}_{3} \cdot \mathrm{OEt}_{2}(28 \mathrm{mg}$, $0.2 \mathrm{mmol})$ was added to a solution of 3 p-r ( 0.2 mmol ) in $\mathrm{CH}_{2} \mathrm{Cl}_{2}(5 \mathrm{~mL})$ at $25^{\circ} \mathrm{C}$. The reaction mixture was stirred at $25^{\circ} \mathrm{C}$ for 20 h . The reaction mixture was concentrated and the residue was diluted with water ( 10 mL ) and the mixture was extracted with $\mathrm{CH}_{2} \mathrm{Cl}_{2}(3 \times 20 \mathrm{~mL})$. The combined organic layers were washed with brine, dried, filtered and evaporated to afford crude product under reduced pressure. Purification on silica gel (hexanes/EtOAc $=5 / 1 \sim 3 / 1$ ) afforded 8a-c.


### 1.6.1. 5-Methyl-3-(toluene-4-sulfonyl)-2-(4-trifluoromethylphenyl)tetrahydrofuran

According to the general procedure, reaction was performed in the presence of $\mathrm{BF}_{3} \cdot \mathrm{OEt}_{2}(28 \mathrm{mg}$, 0.2 mmol ) and $3 \mathrm{p}(77 \mathrm{mg}, 0.2 \mathrm{mmol})$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}(5 \mathrm{~mL})$ at $25^{\circ} \mathrm{C}$ for 20 h . Purification on silica gel (hexanes/EtOAc = 5/1) afforded $8 \mathbf{a}\left(90 \%, 69 \mathrm{mg}\right.$ ). Colorless solid; $\mathrm{mp}=151-152{ }^{\circ} \mathrm{C}$ (recrystallized from hexanes and EtOAc); HRMS (ESI, $\mathrm{M}^{+}+1$ ) calcd for $\mathrm{C}_{19} \mathrm{H}_{20} \mathrm{~F}_{3} \mathrm{O}_{3} \mathrm{~S} 385.1085$, found 385.1088; ${ }^{1} \mathrm{H}$ NMR $\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta 7.33(\mathrm{~d}, J=8.8 \mathrm{~Hz}, 2 \mathrm{H}), 7.28(\mathrm{~d}, J=8.8 \mathrm{~Hz}, 2 \mathrm{H}), 7.17(\mathrm{~d}, J=8.8 \mathrm{~Hz}$, $2 \mathrm{H}), 7.03(\mathrm{~d}, J=8.8 \mathrm{~Hz}, 2 \mathrm{H}), 5.35(\mathrm{~d}, J=5.6 \mathrm{~Hz}, 1 \mathrm{H}), 4.85-4.80(\mathrm{~m}, 1 \mathrm{H}), 4.17-4.13(\mathrm{~m}, 1 \mathrm{H}), 3.08$ (ddd, $J=3.6,6.8,14.4 \mathrm{~Hz}, 1 \mathrm{H}), 2.35(\mathrm{~s}, 3 \mathrm{H}), 2.12(\mathrm{dt}, J=8.0,14.0 \mathrm{~Hz}, 1 \mathrm{H}), 1.35(\mathrm{~d}, J=6.4 \mathrm{~Hz}, 3 \mathrm{H})$; ${ }^{13} \mathrm{C}$ NMR (100 MHz, $\mathrm{CDCl}_{3}$ ): $\delta 144.03,140.32,136.04,129.93,129.47(2 x), 127.67,127.60(2 x)$, 127.46 (2x), 124.34 (q, $J=3.8 \mathrm{~Hz}, 2 x$ ), 79.49, 74.81, 68.01, 35.30, 21.72, 21.35. Single-crystal X-Ray diagram: crystal of compound $\mathbf{8 a}$ was grown by slow diffusion of EtOAc into a solution of compound $8 \mathbf{a}$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ to yield colorless prisms. The compound crystallizes in the orthorhombic crystal system, space group P $212121, a=5.6186(6) \AA, b=8.3590(8) \AA, c=37.132(3) \AA, V=$
$1743.9(3) \AA^{3}, Z=4, d_{\text {calcd }}=1.464 \mathrm{mg} / \mathrm{cm}^{3}, F(000)=800,2 \theta$ range $1.097 \sim 26.447^{\circ}, \mathrm{R}$ indices (all data) $\mathrm{R} 1=0.0461, w R 2=0.0961$.

1.6.2. 5-Methyl-2-(3-nitrophenyl)-3-(toluene-4-sulfonyl)tetrahydrofuran (8b). According to the general procedure, reaction was performed in the presence of $\mathrm{BF}_{3} \cdot \mathrm{OEt}_{2}(28 \mathrm{mg}, 0.2 \mathrm{mmol})$ and 3 q ( $72 \mathrm{mg}, 0.2 \mathrm{mmol}$ ) in $\mathrm{CH}_{2} \mathrm{Cl}_{2}(5 \mathrm{~mL})$ at $25^{\circ} \mathrm{C}$ for 20 h . Purification on silica gel (hexanes/EtOAc $=$ $5 / 1$ ) afforded $\mathbf{8 b}(92 \%, 66 \mathrm{mg})$. Colorless solid; $\mathrm{mp}=116-118^{\circ} \mathrm{C}$ (recrystallized from hexanes and EtOAc); HRMS (ESI, M ${ }^{+}+1$ ) calcd for $\mathrm{C}_{18} \mathrm{H}_{20} \mathrm{NO}_{5} \mathrm{~S} 362.1062$, found 362.1068 ; ${ }^{1} \mathrm{H}$ NMR ( 400 MHz , $\mathrm{CDCl}_{3}$ ): ס 8.06-8.03 (m, 1H), 7.84-7.82 (m, 1H), $7.76(\mathrm{brt}, J=2.0 \mathrm{~Hz}, 1 \mathrm{H}), 7.44(\mathrm{t}, \mathrm{J}=8.4 \mathrm{~Hz}, 1 \mathrm{H})$, 7.23 (d, $J=8.4 \mathrm{~Hz}, 2 \mathrm{H}), 7.09(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 2 \mathrm{H}), 5.41(\mathrm{~d}, J=6.0 \mathrm{~Hz}, 1 \mathrm{H}), 4.88-4.80(\mathrm{~m}, 1 \mathrm{H})$, $4.23-4.19(\mathrm{~m}, 1 \mathrm{H}), 3.02$ (ddd, $J=4.0,6.8,14.4 \mathrm{~Hz}, 1 \mathrm{H}), 2.33(\mathrm{~s}, 3 \mathrm{H}), 2.10(\mathrm{dt}, J=7.2,14.4 \mathrm{~Hz}, 1 \mathrm{H})$, $1.34(\mathrm{~d}, \mathrm{~J}=6.4 \mathrm{~Hz}, 3 \mathrm{H})$; ${ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 147.48,144.49,138.62,136.13,133.79$, 129.65 (2x), 128.73, 127.42 (2x), 122.72, 122.34, 79.09, 75.04, 67.60, 35.32, 21.56, 21.30; Anal. Calcd for $\mathrm{C}_{18} \mathrm{H}_{19} \mathrm{NO}_{5} \mathrm{~S}$ : C, 59.82 ; H, 5.30 . Found: C, $59.98 ; \mathrm{H}, 5.51$. Single-crystal X-Ray diagram: crystal of compound $\mathbf{8} \mathbf{b}$ was grown by slow diffusion of EtOAc into a solution of compound $\mathbf{8 b}$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ to yield colorless prisms. The compound crystallizes in the monoclinic crystal system, space group $\mathrm{P} 21 / \mathrm{n}, a=11.8500(15) \AA, b=10.4794(13) \AA, c=13.4988(17) \AA, V=1675.5(4) \AA^{3}, Z$ $=4, d_{\text {calcd }}=1.433 \mathrm{mg} / \mathrm{cm}^{3}, F(000)=760,2 \theta$ range $2.252 \sim 26.378^{\circ}$, $R$ indices (all data) $R 1=0.0484$, $\mathrm{wR} 2=0.0877$.

1.6.3. 5-Methyl-2-(4-nitrophenyl)-3-(toluene-4-sulfonyl)tetrahydrofuran (8c). According to the general procedure, reaction was performed in the presence of $\mathrm{BF}_{3} \cdot \mathrm{OEt}_{2}(28 \mathrm{mg}, 0.2 \mathrm{mmol})$ and 3 r ( $72 \mathrm{mg}, 0.2 \mathrm{mmol}$ ) in $\mathrm{CH}_{2} \mathrm{Cl}_{2}(5 \mathrm{~mL})$ at $25^{\circ} \mathrm{C}$ for 20 h . Purification on silica gel (hexanes/EtOAc $=$ $5 / 1$ ) afforded $8 \mathrm{c}\left(95 \%, 69 \mathrm{mg}\right.$ ). Colorless solid; $\mathrm{mp}=173-174^{\circ} \mathrm{C}$ (recrystallized from hexanes and EtOAc); HRMS (ESI, M ${ }^{+}+1$ ) calcd for $\mathrm{C}_{18} \mathrm{H}_{20} \mathrm{NO}_{5} \mathrm{~S} 362.1062$, found 362.1068 ; ${ }^{1} \mathrm{H}$ NMR ( 400 MHz , $\mathrm{CDCl}_{3}$ ): $\delta 8.00$ ( $\mathrm{d}, J=8.4 \mathrm{~Hz}, 2 \mathrm{H}$ ), 7.43 (d, $J=8.4 \mathrm{~Hz}, 2 \mathrm{H}$ ), $7.30(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 2 \mathrm{H}), 7.12(\mathrm{~d}, J=8.4$ $\mathrm{Hz}, 2 \mathrm{H}), 5.43$ (d, J = 6.0 Hz, 1H), 4.86-4.81 (m, 1H), 4.18-4.14 (m, 1H), 2.99-2.93 (m, 1H), 2.39 (s, 3 H ), 2.10-2.03 (m, 1H), $1.34(\mathrm{~d}, \mathrm{~J}=6.0 \mathrm{~Hz}, 3 \mathrm{H})$; ${ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): ס 144.68, 143.95, 136.10, 129.60 ( $2 x$ ), 128.27 ( $2 x$ ), 127.67 ( $2 x$ ), 122.76 (2x), 113.99, 79.36, 75.11, 68.04, 35.61, 21.68, 21.52.
1.7. A representative synthetic procedure of compounds $9 \mathrm{a}-\mathrm{g}$ is as follows: $\mathrm{BF}_{3} \cdot \mathrm{OEt}_{2}(28 \mathrm{mg}$, $0.2 \mathrm{mmol})$ was added to a solution of $\mathbf{4 a}, 4 \mathrm{~d}-\mathbf{e}$ and $\mathbf{4 h} \mathbf{- k}(0.2 \mathrm{mmol})$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}(5 \mathrm{~mL})$ at $25^{\circ} \mathrm{C}$. The
reaction mixture was stirred at $25^{\circ} \mathrm{C}$ for 20 h . The reaction mixture was concentrated and the residue was diluted with water ( 10 mL ) and the mixture was extracted with $\mathrm{CH}_{2} \mathrm{Cl}_{2}(3 \times 20 \mathrm{~mL})$. The combined organic layers were washed with brine, dried, filtered and evaporated to afford crude product under reduced pressure. Purification on silica gel (hexanes/EtOAc $=5 / 1 \sim 3 / 1$ ) afforded 9a-g.

1.7.1. 2,2-Dimethyl-6-phenyl-5-(toluene-4-sulfonyl)tetrahydropyran (9a). According to the general procedure, reaction was performed in the presence of $\mathrm{BF}_{3} \cdot \mathrm{OEt}_{2}(28 \mathrm{mg}, 0.2 \mathrm{mmol})$ and $\mathbf{4 a}$ ( $69 \mathrm{mg}, 0.2 \mathrm{mmol}$ ) in $\mathrm{CH}_{2} \mathrm{Cl}_{2}(5 \mathrm{~mL})$ at $25^{\circ} \mathrm{C}$ for 20 h . Purification on silica gel (hexanes/EtOAc $=$ $3 / 1$ ) afforded $9 \mathrm{a}(90 \%, 62 \mathrm{mg})$. Colorless solid; $\mathrm{mp}=148-149{ }^{\circ} \mathrm{C}$ (recrystallized from hexanes and EtOAc); HRMS (ESI, M ${ }^{+}+1$ ) calcd for $\mathrm{C}_{20} \mathrm{H}_{25} \mathrm{O}_{3} \mathrm{~S} 345.1524$, found $345.1523 ;{ }^{1} \mathrm{H}$ NMR ( 400 MHz , $\mathrm{CDCl}_{3}$ ): $\delta 7.25-7.20(\mathrm{~m}, 2 \mathrm{H}), 7.14(\mathrm{~d}, \mathrm{~J}=8.4 \mathrm{~Hz}, 2 \mathrm{H}), 7.09-7.04(\mathrm{~m}, 3 \mathrm{H}), 6.95(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 2 \mathrm{H})$, 5.09 (d, J = 2.8 Hz, 1H), 3.56-3.54 (m, 1H), 2.81-2.77 (m, 1H), 2.31 (s, 3H), 2.21-2.12 (m, 2H), 1.51-1.47 (m, 1H), $1.42(\mathrm{~s}, 3 \mathrm{H}), 1.28(\mathrm{~s}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C} \operatorname{NMR}\left(100 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta 142.80,138.70,138.46$, $128.97(2 x), 127.62(2 x), 127.52(2 x), 126.86,126.15(2 x), 72.83,71.01,62.88,31.37,31.09,21.58$, 21.47, 21.35; Anal. Calcd for $\mathrm{C}_{20} \mathrm{H}_{24} \mathrm{O}_{3} \mathrm{~S}: \mathrm{C}, 69.73 ; \mathrm{H}, 7.02$. Found: C, 69.62; H, 6.91. Single-crystal X-Ray diagram: crystal of compound 9a was grown by slow diffusion of EtOAc into a solution of compound 9 a in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ to yield colorless prisms. The compound crystallizes in the monoclinic crystal system, space group P 21/c, $a=6.0190(2) \AA, b=22.9167(10) \AA, c=13.0996(6) \AA, V=$ $1770.47(13) \AA^{3}, Z=4, d_{\text {calcd }}=1.292 \mathrm{mg} / \mathrm{cm}^{3}, F(000)=736,2 \theta$ range $1.777 \sim 26.462^{\circ}, R$ indices (all data) $R 1=0.0407, w R 2=0.1190$.

1.7.2. 6-(4-Fluorophenyl)-2,2-dimethyl-5-(toluene-4-sulfonyl)tetrahydropyran (9b). According to the general procedure, reaction was performed in the presence of $\mathrm{BF}_{3} \cdot \mathrm{OEt}_{2}(28 \mathrm{mg}, 0.2 \mathrm{mmol})$ and $4 \mathrm{~h}(72 \mathrm{mg}, 0.2 \mathrm{mmol})$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}(5 \mathrm{~mL})$ at $25^{\circ} \mathrm{C}$ for 20 h . Purification on silica gel (hexanes/EtOAc = 3/1) afforded 9b (92\%, 67 mg ). Colorless solid; $\mathrm{mp}=164-166^{\circ} \mathrm{C}$ (recrystallized from hexanes and EtOAc); HRMS (ESI, M ${ }^{+}+1$ ) calcd for $\mathrm{C}_{20} \mathrm{H}_{24} \mathrm{FO}_{3} \mathrm{~S} 363.1430$, found 363.1436 ; ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 7.18-7.14(\mathrm{~m}, 4 \mathrm{H}), 7.01(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 2 \mathrm{H}), 6.75-6.71(\mathrm{~m}, 2 \mathrm{H}), 5.05(\mathrm{~d}, J$ $=2.8 \mathrm{~Hz}, 1 \mathrm{H}), 3.52-3.50(\mathrm{~m}, 1 \mathrm{H}), 2.79-2.75(\mathrm{~m}, 1 \mathrm{H})$, $2.33(\mathrm{~s}, 3 \mathrm{H}), 2.24-2.11(\mathrm{~m}, 2 \mathrm{H}), 1.50-1.46(\mathrm{~m}$, $1 \mathrm{H}), 1.41(\mathrm{~s}, 3 \mathrm{H}), 1.28(\mathrm{~s}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C} \operatorname{NMR}\left(100 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta 161.88(\mathrm{~d}, J=243.3 \mathrm{~Hz}), 143.15$, $138.35,134.44(\mathrm{~d}, J=3.1 \mathrm{~Hz}), 129.02(2 x), 127.79(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 2 x), 127.42(2 x), 114.36(\mathrm{~d}, J=$ $22.0 \mathrm{~Hz}, 2 x$ ), $73.00,70.50,62.83,31.25,31.05,21.47,21.36(2 x)$; Anal. Calcd for $\mathrm{C}_{20} \mathrm{H}_{23} \mathrm{FO}_{3} \mathrm{~S}: \mathrm{C}$, 66.27; H, 6.40. Found: C, 66.38; H, 6.59.

1.7.3. 2,2-Dimethyl-6-(3-nitrophenyl)-5-(toluene-4-sulfonyl)tetrahydropyran (9c). According to the general procedure, reaction was performed in the presence of $\mathrm{BF}_{3} . \mathrm{OEt}_{2}(28 \mathrm{mg}, 0.2 \mathrm{mmol})$ and $4 \mathbf{i}(78 \mathrm{mg}, 0.2 \mathrm{mmol})$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}(5 \mathrm{~mL})$ at $25^{\circ} \mathrm{C}$ for 20 h . Purification on silica gel (hexanes/EtOAc $=$ $3 / 1$ ) afforded $9 \mathbf{c}(90 \%, 70 \mathrm{mg})$. Colorless solid; $\mathrm{mp}=185-186{ }^{\circ} \mathrm{C}$ (recrystallized from hexanes and EtOAc); HRMS (ESI, $\mathrm{M}^{+}+1$ ) calcd for $\mathrm{C}_{20} \mathrm{H}_{24} \mathrm{NO}_{5} \mathrm{~S} 390.1375$, found 390.1378 ; ${ }^{1} \mathrm{H}$ NMR ( 400 MHz , $\mathrm{CDCl}_{3}$ ): $\delta 7.90(\mathrm{dd}, J=0.8,8.4 \mathrm{~Hz}, 1 \mathrm{H}), 7.78(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 1 \mathrm{H}), 7.75(\mathrm{br} \mathrm{s}, 1 \mathrm{H}), 7.33(\mathrm{t}, J=8.0 \mathrm{~Hz}$, $1 \mathrm{H}), 7.14(\mathrm{~d}, J=8.0 \mathrm{~Hz}, 2 \mathrm{H}), 6.95(\mathrm{~d}, J=8.0 \mathrm{~Hz}, 2 \mathrm{H}), 5.14(\mathrm{~d}, J=3.2 \mathrm{~Hz}, 1 \mathrm{H}), 3.65-3.63(\mathrm{~m}, 1 \mathrm{H})$, 2.76-2.71 (m, 1H), $2.25(\mathrm{~s}, 3 \mathrm{H}), 2.23-2.08(\mathrm{~m}, 2 \mathrm{H}), 1.50-1.45(\mathrm{~m}, 1 \mathrm{H}), 1.40(\mathrm{~s}, 3 \mathrm{H}), 1.26(\mathrm{~s}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR (100 MHz, $\mathrm{CDCl}_{3}$ ): $\delta 147.32,143.53,140.84,137.92,132.58,129.21$ (2x), 128.64, 127.18 (2x), 121.80, 121.11, 73.35, 70.07, 61.76, 30.94, 30.88, 21.38, 21.09, 21.03; Anal. Calcd for $\mathrm{C}_{20} \mathrm{H}_{23} \mathrm{NO}_{5} \mathrm{~S}: \mathrm{C}, 61.68$; H, 5.95. Found: C, 61.85; H, 6.22.

1.7.4. 2,2-Dimethyl-6-(4-nitrophenyl)-5-(toluene-4-sulfonyl)tetrahydropyran (9d). According to the general procedure, reaction was performed in the presence of $\mathrm{BF}_{3} . \mathrm{OEt}_{2}(28 \mathrm{mg}, 0.2 \mathrm{mmol})$ and $4 \mathbf{j}(78 \mathrm{mg}, 0.2 \mathrm{mmol})$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}(5 \mathrm{~mL})$ at $25^{\circ} \mathrm{C}$ for 20 h . Purification on silica gel (hexanes/EtOAc $=$ $3 / 1$ ) afforded 9d (94\%, 73 mg ). Colorless solid; $\mathrm{mp}=217-218^{\circ} \mathrm{C}$ (recrystallized from hexanes and EtOAc); HRMS (ESI, M ${ }^{+}+1$ ) calcd for $\mathrm{C}_{20} \mathrm{H}_{24} \mathrm{NO}_{5} \mathrm{~S} 390.1375$, found $390.1380 ;{ }^{1} \mathrm{H}$ NMR ( 400 MHz , $\mathrm{CDCl}_{3}$ ): $\delta 7.90$ (d, $\left.J=9.2 \mathrm{~Hz}, 2 \mathrm{H}\right), 7.38(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 2 \mathrm{H}), 7.20(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 2 \mathrm{H}), 6.99(\mathrm{~d}, J=8.0$ $\mathrm{Hz}, 2 \mathrm{H}), 5.16(\mathrm{~d}, \mathrm{~J}=2.8 \mathrm{~Hz}, 1 \mathrm{H}), 3.59-3.56(\mathrm{~m}, 1 \mathrm{H}), 2.77-2.69(\mathrm{~m}, 1 \mathrm{H}), 2.32(\mathrm{~s}, 3 \mathrm{H}), 2.28-2.14(\mathrm{~m}$, 2H), 1.52-1.48 (m, 1H), 1.43 (s, 3H), $1.30(\mathrm{~s}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 146.89,146.25$, 144.00, 137.84, 129.20 (2x), 127.52 (2x), 127.10 (2x), 122.71 (2x), 73.46, 70.62, 52.23, 30.97 ( $2 x$ ), 21.48, 21.41, 21.38; Anal. Calcd for $\mathrm{C}_{20} \mathrm{H}_{23} \mathrm{NO}_{5} \mathrm{~S}: \mathrm{C}, 61.68$; H, 5.95. Found: C, 61.92; H, 6.20.

1.7.5. 2,2-Dimethyl-5-(toluene-4-sulfonyl)-6-(4-trifluoromethylphenyl)tetrahydropyran (9e). According to the general procedure, reaction was performed in the presence of $\mathrm{BF}_{3} . \mathrm{OEt}_{2}(28 \mathrm{mg}$, 0.2 mmol ) and $\mathbf{4 k}$ ( $82 \mathrm{mg}, 0.2 \mathrm{mmol}$ ) in $\mathrm{CH}_{2} \mathrm{Cl}_{2}(5 \mathrm{~mL})$ at $25^{\circ} \mathrm{C}$ for 20 h . Purification on silica gel (hexanes/EtOAc = 3/1) afforded 9e ( $90 \%, 74 \mathrm{mg}$ ). Colorless solid; $\mathrm{mp}=167-168{ }^{\circ} \mathrm{C}$ (recrystallized from hexanes and EtOAc); HRMS (ESI, $\mathrm{M}^{+}+1$ ) calcd for $\mathrm{C}_{21} \mathrm{H}_{24} \mathrm{~F}_{3} \mathrm{O}_{3} \mathrm{~S} 413.1398$, found 413.1401; ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 7.27$ (d, J= $8.8 \mathrm{~Hz}, 2 \mathrm{H}$ ), $7.24(\mathrm{~d}, J=8.8 \mathrm{~Hz}, 2 \mathrm{H}), 7.10(\mathrm{~d}, J=8.4 \mathrm{~Hz}$,
$2 \mathrm{H}), 6.93(\mathrm{~d}, J=8.0 \mathrm{~Hz}, 2 \mathrm{H}), 5.11(\mathrm{~d}, J=2.4 \mathrm{~Hz}, 1 \mathrm{H}), 3.58-3.56(\mathrm{~m}, 1 \mathrm{H}), 2.91-2.86(\mathrm{~m}, 1 \mathrm{H}), 2.29(\mathrm{~s}$, $3 \mathrm{H}), 2.27-2.15(\mathrm{~m}, 2 \mathrm{H}), 1.53-1.50(\mathrm{~m}, 1 \mathrm{H}), 1.44(\mathrm{~s}, 3 \mathrm{H}), 1.29(\mathrm{~s}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta$ 143.28 ( 2 x ), 142.65, 138.09, 129.12 (2x), 128.86, 127.25 ( 2 x ), $126.50(2 \mathrm{x}), 124.40(\mathrm{q}, J=3.7 \mathrm{~Hz}$, $2 x), 73.18,70.52,62.19,31.31,31.03,21.41,21.19,21.16$; Anal. Calcd for $\mathrm{C}_{21} \mathrm{H}_{23} \mathrm{~F}_{3} \mathrm{O}_{3} \mathrm{~S}: \mathrm{C}, 61.15$; H, 5.62. Found: C, 61.30; H, 5.54.

1.7.6. 6-Biphenyl-4-yl-2,2-dimethyl-5-(toluene-4-sulfonyl)tetrahydropyran (9f). According to the general procedure, reaction was performed in the presence of $\mathrm{BF}_{3} . \mathrm{OEt}_{2}(28 \mathrm{mg}, 0.2 \mathrm{mmol})$ and 4d ( $84 \mathrm{mg}, 0.2 \mathrm{mmol}$ ) in $\mathrm{CH}_{2} \mathrm{Cl}_{2}(5 \mathrm{~mL})$ at $25^{\circ} \mathrm{C}$ for 20 h . Purification on silica gel (hexanes/ EtOAc $=3 / 1$ ) afforded $9 f(82 \%, 69 \mathrm{mg})$. Colorless solid; $\mathrm{mp}=208-209^{\circ} \mathrm{C}$ (recrystallized from hexanes and EtOAc); HRMS (ESI, $\mathrm{M}^{+}+1$ ) calcd for $\mathrm{C}_{26} \mathrm{H}_{29} \mathrm{O}_{3} \mathrm{~S} 421.1837$, found $421.1842 ;{ }^{1} \mathrm{H}$ NMR ( 400 MHz , $\mathrm{CDCl}_{3}$ ): $\delta 7.52-7.43(\mathrm{~m}, 4 \mathrm{H}), 7.38-7.33(\mathrm{~m}, 1 \mathrm{H}), 7.27-7.22(\mathrm{~m}, 4 \mathrm{H}), 7.16(\mathrm{~d}, \mathrm{~J}=8.0 \mathrm{~Hz}, 2 \mathrm{H}), 6.91(\mathrm{~d}$, $J=8.0 \mathrm{~Hz}, 2 \mathrm{H}), 5.14(\mathrm{~d}, J=3.2 \mathrm{~Hz}, 1 \mathrm{H}), 3.61-3.59(\mathrm{~m}, 1 \mathrm{H})$, 2.94-2.89 (m, 1H), 2.30-2.17 (m, 2H), $2.23(\mathrm{~s}, 3 \mathrm{H}), 1.55-1.51(\mathrm{~m}, 1 \mathrm{H}), 1.46(\mathrm{~s}, 3 \mathrm{H}), 1.32(\mathrm{~s}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 142.69$, 140.89, 139.86, 138.59, 137.74, 128.95 (2x), 128.71 (2x), 127.43 (2x), 127.19, 126.89 ( $2 x$ ), 126.58 (2x), 126.27 (2x), 72.94, 70.81, 62.95, 31.53, 31.15, 21.50, 21.33 ( 2 x ); Anal. Calcd for $\mathrm{C}_{26} \mathrm{H}_{28} \mathrm{O}_{3} \mathrm{~S}$ : C, 74.25; H, 6.71. Found: C, 74.55; H, 6.82.

1.7.7. 2,2-Dimethyl-6-naphthalen-2-yl-5-(toluene-4-sulfonyl)tetrahydropyran (9g). According to the general procedure, reaction was performed in the presence of $\mathrm{BF}_{3} \cdot \mathrm{OEt}_{2}(28 \mathrm{mg}, 0.2 \mathrm{mmol})$ and $4 \mathbf{e}(79 \mathrm{mg}, 0.2 \mathrm{mmol})$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}(5 \mathrm{~mL})$ at $25{ }^{\circ} \mathrm{C}$ for 20 h . Purification on silica gel (hexanes/EtOAc = 3/1) afforded $9 \mathrm{~g}\left(84 \%, 66 \mathrm{mg}\right.$ ). Colorless solid; $\mathrm{mp}=192-193^{\circ} \mathrm{C}$ (recrystallized from hexanes and EtOAc); HRMS (ESI, $\mathrm{M}^{+}+1$ ) calcd for $\mathrm{C}_{24} \mathrm{H}_{27} \mathrm{O}_{3} \mathrm{~S} 395.1681$, found $395.1684 ;{ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 7.69-7.66(\mathrm{~m}, 3 \mathrm{H}), 7.44-7.38(\mathrm{~m}, 3 \mathrm{H}), 7.12(\mathrm{dd}, J=1.2,8.4 \mathrm{~Hz}, 1 \mathrm{H})$, $6.97(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 2 \mathrm{H}), 6.49(\mathrm{~d}, J=8.0 \mathrm{~Hz}, 2 \mathrm{H}), 5.24(\mathrm{~d}, J=2.4 \mathrm{~Hz}, 1 \mathrm{H}), 3.64-3.63(\mathrm{~m}, 1 \mathrm{H})$, $3.00-2.90(\mathrm{~m}, 1 \mathrm{H}), 2.40-2.22(\mathrm{~m}, 2 \mathrm{H}), 2.02(\mathrm{~s}, 3 \mathrm{H}), 1.57-1.54(\mathrm{~m}, 1 \mathrm{H}), 1.50(\mathrm{~s}, 3 \mathrm{H}), 1.34(\mathrm{~s}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR (100 MHz, $\mathrm{CDCl}_{3}$ ): $\delta 142.66,138.11,135.82,132.89,132.69,128.46$ (2x), 127.95, 127.21 (2x), 127.16 (2x), 125.67, 125.58, 125.11, 123.88, 73.06, 71.02, 62.61, 31.57, 31.18, 21.54, 21.22, 21.08; Anal. Calcd for $\mathrm{C}_{24} \mathrm{H}_{26} \mathrm{O}_{3} \mathrm{~S}: \mathrm{C}, 73.06 ; \mathrm{H}, 6.64$. Found: C, 73.18; H, 6.72.
1.8. A representative synthetic procedure of compounds $10 \mathrm{a}-\mathrm{b}$ is as follows: $\mathrm{BF}_{3} \cdot \mathrm{OEt}_{2}(57 \mathrm{mg}$, $0.4 \mathrm{mmol})$ was added to a solution of 4 I and $\mathbf{4 n}(0.2 \mathrm{mmol})$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}(5 \mathrm{~mL})$ at $25^{\circ} \mathrm{C}$. The reaction
mixture was stirred at $25^{\circ} \mathrm{C}$ for 20 h . The reaction mixture was concentrated and the residue was diluted with water ( 10 mL ) and the mixture was extracted with $\mathrm{CH}_{2} \mathrm{Cl}_{2}(3 \times 20 \mathrm{~mL})$. The combined organic layers were washed with brine, dried, filtered and evaporated to afford crude product under reduced pressure. Purification on silica gel (hexanes/EtOAc $=5 / 1 \sim 3 / 1$ ) afforded 10a-b.

1.8.1. 5,5,8a-Trimethyl-2-phenyl-3-(toluene-4-sulfonyl)octahydrochromene (10a). According to the general procedure, reaction was performed in the presence of $\mathrm{BF}_{3} \cdot \mathrm{OEt}_{2}(57 \mathrm{mg}, 0.4 \mathrm{mmol}$ ) and 41 ( $82 \mathrm{mg}, 0.2 \mathrm{mmol}$ ) in $\mathrm{CH}_{2} \mathrm{Cl}_{2}(5 \mathrm{~mL})$ at $25{ }^{\circ} \mathrm{C}$ for 20 h . Purification on silica gel (hexanes/EtOAc = 3/1) afforded 10a ( $76 \%$, 63 mg ). Colorless solid; mp $=224-225^{\circ} \mathrm{C}$ (recrystallized from hexanes and EtOAc); HRMS (ESI, $\mathrm{M}^{+}+1$ ) calcd for $\mathrm{C}_{25} \mathrm{H}_{33} \mathrm{O}_{3} \mathrm{~S} 413.2150$, found 413.2155 ; ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 7.22-7.20(\mathrm{~m}, 2 \mathrm{H}), 7.12-7.04(\mathrm{~m}, 5 \mathrm{H}), 6.96(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 2 \mathrm{H}), 5.17(\mathrm{~d}, J$ $=3.6 \mathrm{~Hz}, 1 \mathrm{H}), 3.73-3.70(\mathrm{~m}, 1 \mathrm{H}), 2.79(\mathrm{~d}, J=2.4 \mathrm{~Hz}, 1 \mathrm{H}), 2.31(\mathrm{~s}, 3 \mathrm{H}), 2.17(\mathrm{dd}, J=2.4,14.0 \mathrm{~Hz}$, 1 H ), $1.94(\mathrm{dt}, J=5.2,14.0 \mathrm{~Hz}, 1 \mathrm{H}), 1.81-1.55(\mathrm{~m}, 4 \mathrm{H}), 1.46-1.38(\mathrm{~m}, 2 \mathrm{H}), 1.33(\mathrm{~s}, 3 \mathrm{H}), 1.03(\mathrm{~s}, 3 \mathrm{H})$, 0.79 (s, 3H); ${ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 142.65,138.79,138.77,128.95$ ( 2 x ), 127.53 ( 2 x ), 127.37 (2x), 126.86, 126.47 (2x), 76.24, 70.53, 65.21, 47.34, 41.27, 39.77, 33.33, 31.53, 21.34, 21.11, 20.23, 20.06, 18.43; Anal. Calcd for $\mathrm{C}_{25} \mathrm{H}_{32} \mathrm{O}_{3} \mathrm{~S}: \mathrm{C}, 72.78 ; \mathrm{H}, 7.82$. Found: C, 72.62; H, 7.75. Single-crystal X-Ray diagram: crystal of compound 10a was grown by slow diffusion of EtOAc into a solution of compound 10 a in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ to yield colorless prisms. The compound crystallizes in the orthorhombic crystal system, space group P b c a, $a=16.0500$ ( 8 ) $\AA$, $b=11.2326(5) \AA, c=$ 24.8893(13) $\AA, V=4487.1(4) \AA^{3}, Z=8, d_{\text {calcd }}=1.221 \mathrm{mg} / \mathrm{cm}^{3}, F(000)=1776,2 \theta$ range $1.636 \sim 26.396^{\circ}$, $R$ indices (all data) $R 1=0.0687$, wR2 $=0.1145$.

1.8.2. 2-(4-Fluoro-phenyl)-5,5,8a-trimethyl-3-(toluene-4-sulfonyl)octahydrochromene (10b). According to the general procedure, reaction was performed in the presence of $\mathrm{BF}_{3} \cdot \mathrm{OEt}_{2}(57 \mathrm{mg}$, $0.4 \mathrm{mmol})$ and $4 \mathrm{n}(86 \mathrm{mg}, 0.2 \mathrm{mmol})$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}(5 \mathrm{~mL})$ at $25^{\circ} \mathrm{C}$ for 20 h . Purification on silica gel (hexanes/EtOAc = 3/1) afforded 10b ( $80 \%$, 69 mg ). Colorless solid; mp $=199-200{ }^{\circ} \mathrm{C}$ (recrystallized from hexanes and EtOAc); HRMS (ESI, M ${ }^{+}+1$ ) calcd for $\mathrm{C}_{25} \mathrm{H}_{32} \mathrm{FO}_{3} \mathrm{~S}$ 431.2056, found 431.2060; ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 7.18-7.13(\mathrm{~m}, 4 \mathrm{H}), 7.02(\mathrm{~d}, \mathrm{~J}=8.0 \mathrm{~Hz}, 2 \mathrm{H})$, 6.77-6.72 (m, 2H), $5.13(\mathrm{~d}, J=3.6 \mathrm{~Hz}, 1 \mathrm{H}), 3.69-3.66(\mathrm{~m}, 1 \mathrm{H}), 2.77(\mathrm{dt}, J=2.4,14.4 \mathrm{~Hz}, 1 \mathrm{H}), 2.34$ (s, 3H), 2.17 (dd, $J=2.8,14.0 \mathrm{~Hz}, 1 \mathrm{H}$ ), 1.93 (dt, $J=2.8,14.0 \mathrm{~Hz}, 1 \mathrm{H}), 1.80-1.54(\mathrm{~m}, 4 \mathrm{H}), 1.46-1.39$ (m, 2H), $1.33(\mathrm{~s}, 3 \mathrm{H}), 1.02(\mathrm{~s}, 3 \mathrm{H}), 0.78(\mathrm{~s}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C} \operatorname{NMR}\left(100 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta 161.95(\mathrm{~d}, \mathrm{~J}=243.4$ $\mathrm{Hz}), 143.07,138.69,133.56(\mathrm{~d}, J=3.8 \mathrm{~Hz}), 129.03(2 x), 128.13(\mathrm{~d}, J=7.6 \mathrm{~Hz}, 2 \mathrm{x}), 127.33(2 x)$, 114.35 ( $\mathrm{d}, \mathrm{J}=21.2 \mathrm{~Hz}, 2 x$ ), 76.47, 70.08, 65.23, 47.27, 41.28, 39.80, 33.38, 31.58, 21.40, 21.00,
20.26, 20.09, 18.46; Anal. Calcd for $\mathrm{C}_{25} \mathrm{H}_{31} \mathrm{FO}_{3} \mathrm{~S}: \mathrm{C}, 69.74 ; \mathrm{H}, 7.26$. Found: C, 69.86; $\mathrm{H}, 7.37$. Single-crystal X-Ray diagram: crystal of compound 10b was grown by slow diffusion of EtOAc into a solution of compound $\mathbf{1 0 b}$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ to yield colorless prisms. The compound crystallizes in the monoclinic crystal system, space group P 21/n, $a=15.2927$ (5) $\AA, b=18.9203$ (5) $\AA, c=22.9664$ (7) $\AA, V=6644.5(3) \AA^{3}, Z=12, d_{\text {calcd }}=1.291 \mathrm{mg} / \mathrm{cm}^{3}, F(000)=2760,2 \theta$ range $1.394 \sim 26.414^{\circ}, R$ indices (all data) R1 $=0.0514, \mathrm{wR} 2=0.1217$.



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Ambient temperature
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Kuo0601
Pulse Se
wdd

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07

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08
 398
129.934
-128.653 -$-146.838$
145.573
$0 カ \tau$
0 Z T
[ $\quad$
118.594

## *

$\qquad$
$\stackrel{\infty}{\stackrel{\infty}{\circ}}$

- <br> $\square$}
+ 

$-71.78$
-
$-118.594$
127.98
123.521



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09

\section*{meny

## meny <br> 

[^1]


113.60


${ }_{0}^{\circ} \cdot \angle$

$\qquad$
$-7.068$
7.051
wd

## －

end


Ambient temperature
Total 672 repetitions

as asind
ckeroony
mdd



Pulse Sequence: s2pul
UNITYplus-400 "unity $400^{\prime \prime}$
Date: Apr 212015
Solvent: CoC 13 .
Ambint temperature
Total 64 repetitions

-



69.75
18.75

.292
.284


Kuo 0404
Pulse


[^2]


mold



Pulse Sequence: s2pul
UNITYplus-400 unity 400 "
Date: Jun 152015
Solvent: coc 13
Ambient temperature
YU1040612


wdd
$0 乙 \tau$



 Ambient temperature
Total 64 repetitions Pulse Sequence: s2pul
UNITYplus-400 unity $400^{\prime \prime}$
Date: Jun 172015
Solvent: CDC13
Ambient temperature
Total 64 repetitions
stgotoins




19.10
31.01 $\sigma^{\circ} L$


7.471
7.467
7.779
-7.767
7.755
$[7.747$
$\stackrel{\rightharpoonup}{\omega}$
62.49
$$
\square
$$

wdd
wdd $2^{\circ} L$
$\qquad$ 7.196
$\qquad$

| e»əoads ( $\varepsilon_{\text {IJã }}$ 'ZHW 00t) yWN $H_{\downarrow}$戸† punodmo |
| :---: |
|  |

 dr90b0ins

bas asin




Yul040614
Pulse Seq

081










bas asind
عtgovotns

 Pulse Sequence: s2pul
UNITYplus-400 "unity 400 8t90botns




8t90b0ins

$\square \xrightarrow{\square} \begin{array}{r}133.072 \\ 129.782 \\ 129.237 \\ 128.479\end{array}$
$\Longrightarrow \begin{aligned} & \square \\ & 133.072 \\ & 129.782 \\ & 129.237 \\ & 128.479\end{aligned}$

$02 \tau$

$\qquad$
$-135.30$
00


(1)

8
$0 t$



72.000 .318

## $-147.202$ <br> 

$\qquad$ -135.445
-132.398
$-135.165$ 130.859
-129.820
-128.767
-128.577 -128.577
-127.918
$-118.510$
$00 \tau$

127.918
-123.392
$\square 71.785$

09


$\qquad$
$-21.595$
N $\qquad$ 17.524



<t90boins
 Ambient temperature
Total 136 repetitions Pulse Sequence: s2pul
UNITYplus-400 "unity 400
Date: Jun 16 " 2015
Solvent: CDC13 YU1040617
udd




wdd


Pulse Sequence: s2pu
UNITYplus-400 "unity 400
Date: Jun 252015
Solvent: CDC13
Ambient temperature
Yu1040624




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202000ISA







 .856
.848
.828

.778
767
.760
.
$10.16\left[\begin{array}{c}\omega \\ 0 \\ 0\end{array}\right.$

$\qquad$
$12.84-$
$31.80=0$





Solvent: cocl3
Ambient tenperature
Total 260 repetitions

かてboony


UNITYPlus-400 "unity400"
Date: May 72015
Solvent: CDC13
Ambient temperature



112.780
001
 - $\qquad$ 67.555
09



$\stackrel{\rightharpoonup}{0}$

$\qquad$ 32.753
31.487
02

$\qquad$ 21.526
wdd
$\longrightarrow-20.374$

Kuo0424
Pulse Se




wdd $02 \quad 00$ $\qquad$
112.658
108.148

$\stackrel{0}{\circ}$
$\qquad$
67.631
$\qquad$
55.669

$\longrightarrow 44.556$
$\square$
$\sim$
$\sim$ 32.677
21.504
120.541


Pulse Sequence: s2pul
UNITYplus-400 "unity 400
Date: Mar 162015
Solvent CDC13
Ambient temperature
Total 1056 repetitions
nos astind
nocoony
${ }^{\text {STOD }} 9 \mathrm{gl}$ (

$11.31\left[\begin{array}{c}\text { A } \\ 0\end{array}\right]$



10.96
$35.35-$
0
on
3.5


10.80 -
mm

$\qquad$


2.947
S
$\stackrel{\substack{\vec{~} \\ \dot{\infty} \\ \infty \\ \perp}}{ }$

$\longrightarrow-2.394$



路






$-130.268$ 130.192
129.570
08


$$
\|
$$

$\qquad$ 67.600
09



-115.311
-115.099
575

$\longrightarrow 108.224$

$$
7 \sqrt{.000} \begin{aligned}
& 77.318 \\
& 76.689
\end{aligned}
$$

$\qquad$
$\qquad$
$-44.594$
$0 t$

$\qquad$


~ $\sim^{2}-20.533$
wdd
$:$







081
1111
112.529
$-108.368$
001

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$75 \cdot \begin{gathered}.000 \\ 76.682\end{gathered}$
$-67.168$
$\qquad$
55.782
-55.616
$-46.784$
$\longrightarrow 41.152$
$\longrightarrow$
-
-30.540
$\longrightarrow 21.034$
und
 6260onx

astnd
uo0929


$$
\begin{aligned}
& 10.00-[ \\
& \text { in } \\
& \text { + } \\
& 42.07-[
\end{aligned}
$$


$=$

Solvent: CDC 13
Ambient temperature
Total 320 repetition
Pulse Sequence: s2pul
UNITYplus-400 "unity 400 "
Date: Apr 212015
Kuo 0331-1
Pulse Seq
Kuo0331-1

$0 t$
02
udd



$\qquad$

$-129.093$
128.464
-128.327
-128.175
$\lcm{-128.175}$
$\qquad$
$\qquad$
-
$09108 \tau$
 bas asınd
I-teqoony


















suo!7!7adə」 $950 \varepsilon 18701$

bas astnd
n-bてEoony











Ambient temperature
Pulse Sequence: s2pul
UNITYplus -400 "unity 400 "
udd


10.65

$\qquad$
 Ambient temperature
Total 64 repetitions UNITYplus-400 "unity 400
Date: Jul 23 20 2015
Solvent: CDC13
Ambient temperature Yin0717
Pulse
udd







UNITYplus-400 "unity 400 "
Date: Jul 152015
Solvent: coclir
Ambient temperature
Total 64 repetitions
عILoon>






5.848
5.827

$\qquad$ 22.81
10.71
25.38
33.12
$22.68-[$
$10.74-$
. 00 $\uparrow$
11.15
34.84

15

1.379
-1.362
32.77 -



wdd


 Ambient
Total 64 temperature
repetitions
Pulse Sequence: s2pul
UNITYplus-400 unity $400^{\prime \prime}$
Date: Jul 162015
Solvent: CoCl3
Ambient teoperature
Kuo0710








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wdd

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wdd
8



${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) spectra


Pulse Sequence: s2pul
UNITYplus-400 "unity 400 "
Date: May 82015
Solvent: coclu
Ambient temperature
Total 80 repetitions Kuo 0501
Pulse

Kuo 0501



udd








Yu1040612-1
Pulse Seque




Ambient temperature
Total 40 repetitions
Pulse
UNITYplus-400 "unity $400 "$
Date: Jun 172015
Solvent: CDC13
Ambient temperature
Yu1040612-1
Pulse Seque
 さ-てT9060



$-116.358$
$-112.704$

001

$\square$
$\qquad$
.
.817
.309


76.682
$\longrightarrow 69.548$

47.793
$-39.962$
-35.406
-32.950 $\longrightarrow-32.950$
$\stackrel{\square}{\square}$

$\qquad$ 35.406
32.95
$\qquad$



Yul040610
Nise Sequence: s2pul
"unity 40





















Pulse Sequence: s2pul
UNITYplus-400 "unity $400^{\prime \prime}$
Date: Ju1 2015
Solvent: cocis 1315
Ambient temperature
Yu1040630
Pulse Seq





$\qquad$

0 ZI

$$
122.718
$$||


 UNITYplus-400 "unity 400
Date: Aug 3015
Solvent: cDC13
Ambient temperature
Total 1408 repetitions abz $\angle 0$ onx
 ulse Sequence: s2pul
"unity 400 $\bigcirc \longrightarrow$





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19.89
29.01

.079
7.069
$\qquad$
$\qquad$
wdd




081

143.154
138.348
138.348
-134.460

- 134.429
$\longrightarrow \begin{array}{r}114.470 \\ -114.250\end{array}$

07

- 62.832
$-62.832$
$0 I$

1


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$02 T$
$\qquad$

## nem

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77.000
76.682
72.998
70.496

.017
.827
743 127.743
-127.417
wdd 02

$\qquad$
$\qquad$





180

$-147.324$

00 T

09

$\qquad$
30.941
-30.881
$\qquad$
$\qquad$
wdd
widd $02 \ldots \ldots \ldots \ldots$
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YU1040626
Pulse Sequ






081
097
$0 カ \tau$

$\qquad$
$\qquad$

$-21.329$
udd
0
00
09
1.
021
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Ambient temperature
Total 912 repetitions
UNITYplus-400 "unity 400
Date: Jun 22 2015
Solvent: CDC13
Ambient temperature
tover
Yul040615-2
Pulse Seque
Pulse Sequence: s2pul
${ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) spectra

nce: s2pul
unnity 400
2015






Ambient temperature
Total 1248 repetitions
 Yu1040614-2




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    $S$ asind
    Losoons

[^1]:    $0 t$

[^2]:    $\qquad$

