Supporting Information

Synthesis of Substituted Tetralins and Benzosuberans via BF₃·OEt₂ Mediated Formal (4+2) and (5+2) Stereocontrolled Cycloaddition of 4-Alkenols with Veratrol

Meng-Yang Chang* and Yu-Chieh Cheng

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S-100~S-103 (3р) <u>о</u> н о	S-104~S-107 (3q) <u>о</u> н о	S-108~S-110 (3r) <u>o</u> н o	S-111~S-114 (3s) он	S-115~S-118 (3t) oн
F ₃ C Me	O ₂ N S O Me	O ₂ N Me		F
S-119~S-122 (4a)	S-123~S-126 (4b)	S-127~S-129 (4c)	S-130~S-133 (4d) ^{Me}	S-134~S-137 (4e)
S Me		S Me Me	o Me	S Me Me
ОН	МеО	Ме	ОН	ОН
S-138~S-141 (4 f)	S-142~S-144 (4g)	S-145~S-148 (4h)	S-149~S-152 (4i) ^{Me}	S-153~S-155 (4j) Me
O Me	Me S Me	O Me	O Me	O Me
ОН	MeO	о не F		O H
S-156~S-158 (4k)	S-159~S-162 (4I)	S-163~S-166 (4m)	S-167~S-170 (4n)	S-171~S-174 (4o)
O Me O Me O OH	O Me Me O OH Me	O Me Me O OH Me	O Me Me O OH Me	O Me Me O OH Me
F₃C S-175~S-177 (4 p)	S-178~S-181 (5a)	S-182~S-185 (5b)	г S-186~S-189 (5с)	мео S-190~S-193 (5d)
Me 9 Me Me	Me , o	Me	Me	Me
MeO OH Me			F MeO MeO MeO	
S-194~S-197 (5e) Me, <i>,</i> o	S-198~S-201 (5f) Me	S-202~S-205 (5g) Me	S-206~S-209 (5h)	S-210~S-213 (5i)
MeO OMe	S ^O O ^S → Me	-Me	Meo Me	F - Me
	MeO OMe	MeO OMe	MeO OMe	MeO OMe

S-214~S-217 (5)	S-218~S-221 (5K)	S-222~S-225 (5I)	S-226~S-229 (5m)	5-230~S-233 (5n)
	ο	o	Me	r -
-Me	or Simon Me	O ^{r S}	O ^{'S}	os
Me MeO OMe				-Me
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S-234~S-237 (50)	S-238~S-241 (5p)	S-242~S-245 (5q)	S-246~S-249 (5r)	S-250~S-253 (5s)
Me	Me	Me	Me	
or Store	o s	o ^s	o s	Me
Me Me	Me		-Me	
				MeO OMe
MeO OMe	0_0 S-258~S-261 (5u)	S-262~S-265 (5v)	0_0 S-266~S-269	(5w + 5x)
	Me	Me	Me Me	
	s o	s o	s o	S, O
F Me	O Me	O ²⁻ -Me	0 ²	O ^r →→Me
MeO OMe	-OMe	-OMe		
0.070.0.070 (0.)	MeO	MeO OMe	MeO OC ₄ H ₉	C₄H ₉ O OMe
S-2/0~S-2/3 (6a)	S-2/4~S-2/7 (6b)	S-278~S-281 (6C)	S-282~S-285 (6d)	S-286~S-289 (6e)
S S	, s	, o	, o	o s
O Me Me	O Me	O Me	O Me Me	O Me
	MeO	Me		
MeO OMe S-290~S-293 (6f)	MeO OMe S-294~S-297 (6g)	MeO OMe S-298~S-301 (6h)	MeO OMe S-302~S-305 (6i)	MeO OMe S-306~S-309 (8a)
, p	Me	, p	, p	Me
S O Me	O Me Me	S O Me	O Me	s o
Mag	MeO	Me	Me	F ₃ C
MeO OMe	MeÓ ÔMe		C4H9O OC4H9	
S-310~S-313 (8b)	S-314~S-316 (8c)	S-317~S-320 (9a)	S-321~S-324 (9b)	S-325~S-328 (9c)
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O ₂ N O	0 ^{1/3}	0 Me	0 Me	O ₂ N Me
, O, Me	O ₂ N O ⁻ Ne	Me	F O Me	Me
S-329~S-331 (9d)	S-332~S-335 (9e) Me	S-336~S-339 (9f) Me	S-340~S-343 (9g) Me	S-344~S-347 (10a) ^{Me}
o s	, o	, o	, o	S H Me
Me Me	O Me	Ó Me	O Me	
O ₂ N We	F ₃ C	Me Me	Me	
S-348~S-351 (10b)				
, S, Me				
F O Me				
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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. ¹H and ¹³C NMR spectra were recorded on a Varian INOVA-400 spectrometer operating at 400 and at 100 MHz, respectively. Chemical shifts (δ) 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: NaBH₄ (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 °C. The reaction mixture was stirred for 1 h at 0 °C and the solvent was concentrated. The residue was diluted with water (10 mL) and the mixture was extracted with CH₂Cl₂ (3 x 20 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 NaBH₄ (100 mg, 3.0 mmol) and **1a** (314 mg, 1.0 mmol) in a co-solvent of THF (5 mL) and MeOH (5 mL) at 0 °C for 1 h. Purification on silica gel (hexanes/EtOAc = 4/1) afforded **3a** (92%, 291 mg). Colorless solid; mp = 79-80 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M⁺+1) calcd for C₁₈H₂₁O₃S 317.1212, found 317.1218; ¹H NMR (400 MHz, CDCl₃): δ 7.78 (d, *J* = 8.4 Hz, 2H), 7.36-7.27 (m, 7H), 5.25-5.15 (m, 1H), 5.05 (d, *J* = 8.4 Hz, 1H), 4.72 (dq, *J* = 1.2, 10.4 Hz, 1H), 4.58 (dq, *J* = 1.2, 16.8 Hz, 1H), 4.20 (br s, 1H), 3.44-3.39 (m, 1H), 2.46 (s, 3H), 2.32-2.25 (m, 1H), 2.12-2.05 (m, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 145.09, 139.44, 135.22, 133.04, 129.81 (2x), 128.82 (2x), 128.51 (3x), 127.31 (2x), 117.52, 73.08, 70.39, 31.11, 21.64; Anal. Calcd for C₁₈H₂₀O₃S: C, 68.33; 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 NaBH₄ (100 mg, 3.0 mmol) and **1b** (344 mg, 1.0 mmol) in a co-solvent of THF (5 mL) and MeOH (5 mL) at 0 °C for 1 h. Purification on silica gel (hexanes/EtOAc = 3/1) afforded **3b** (93%, 322 mg). Colorless oil; HRMS (ESI, M⁺+1) calcd for

C₁₉H₂₃O₄S 347.1317, found 347.1315; ¹H NMR (400 MHz, CDCl₃): δ 7.79 (d, J = 8.0 Hz, 2H), 7.35 (d, J = 8.0 Hz, 2H), 7.21 (d, J = 8.4 Hz, 2H), 6.83 (d, J = 8.8 Hz, 2H), 5.27-5.17 (m, 1H), 5.01 (d, J = 8.4 Hz, 1H), 4.73 (dq, J = 1.2, 10.0 Hz, 1H), 4.59 (dq, J = 1.2, 16.8 Hz, 1H), 4.34 (br s, 1H), 3.78 (s, 3H), 3.41-3.36 (m, 1H), 2.46 (s, 3H), 2.30-2.23 (m, 1H), 2.12-2.03 (m, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 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 C₁₉H₂₂O₄S: 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 NaBH₄ (100 mg, 3.0 mmol) and **1c** (332 mg, 1.0 mmol) in a co-solvent of THF (5 mL) and MeOH (5 mL) at 0 °C for 1 h. Purification on silica gel (hexanes/EtOAc = 5/1) afforded **3c** (86%, 287 mg). Colorless solid; mp = 82-83 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M⁺+1) calcd for C₁₈H₂₀FO₃S 335.1117, found 335.1118; ¹H NMR (400 MHz, CDCl₃): δ 7.77 (d, *J* = 8.4 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.30-7.23 (m, 2H), 7.01-6.96 (m, 2H), 5.26-5.16 (m, 1H), 5.06 (d, *J* = 8.8 Hz, 1H), 4.74 (dq, *J* = 1.2, 10.0 Hz, 1H), 4.59 (dq, *J* = 1.2, 16.8 Hz, 1H), 4.46 (br s, 1H), 3.40-3.35 (m, 1H), 2.46 (s, 3H), 2.34-2.27 (m, 1H), 2.11-2.03 (m, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 162.69 (d, *J* = 245.6 Hz), 145.27, 135.34 (d, *J* = 3.0 Hz), 135.03, 132.83, 129.88 (2x), 129.01 (d, *J* = 7.6 Hz, 2x), 128.81 (2x), 117.70, 115.40 (d, *J* = 21.3 Hz, 2x), 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 NaBH₄ (100 mg, 3.0 mmol) and **1d** (328 mg, 1.0 mmol) in a co-solvent of THF (5 mL) and MeOH (5 mL) at 0 °C for 1 h. Purification on silica gel (hexanes/EtOAc = 5/1) afforded **3d** (93%, 307 mg). Colorless oil; HRMS (ESI, M⁺+1) calcd for $C_{19}H_{23}O_3S$ 331.1368, found 331.1366; ¹H NMR (400 MHz, CDCl₃): δ 7.77 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.17 (d, *J* = 8.4 Hz, 2H), 7.09 (d, *J* = 8.4 Hz, 2H), 5.30-5.20 (m, 1H), 5.02 (d, *J* = 8.4 Hz, 1H), 4.75 (dq, *J* = 1.2, 10.0 Hz, 1H), 4.61 (dq, *J* = 1.2, 16.8 Hz, 1H), 4.32 (br s, 1H), 3.44-3.39 (m, 1H), 2.45 (s, 3H), 2.31 (s, 3H), 2.30-2.24 (m, 1H), 2.14-2.07 (m, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 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 $C_{19}H_{22}O_3S$: 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 NaBH₄ (100 mg, 3.0 mmol) and **1e** (238 mg, 1.0 mmol) in a co-solvent of THF (5 mL) and MeOH (5 mL) at 0 °C for 1 h. Purification on silica gel (hexanes/EtOAc = 5/1) afforded **3e** (87%, 209 mg). Colorless gum; HRMS (ESI, M⁺+1) calcd for $C_{12}H_{17}O_3S$ 241.0899, found 241.0902; ¹H NMR (400 MHz, CDCl₃): δ 7.40-7.38 (m, 4H), 7.35-7.29 (m, 1H), 5.69 (br s, 1H), 5.63-5.52 (m, 1H), 5.03-4.95 (m, 2H), 3.13 (dt, *J* = 1.6, 7.2 Hz, 1H), 2.94 (s, 3H), 2.87 (d, *J* = 2.8 Hz, 1H), 2.64 (dt, *J* = 1.6, 6.8 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 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 $C_{12}H_{16}O_3S$: 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 NaBH₄ (100 mg, 3.0 mmol) and **1f** (364 mg, 1.0 mmol) in a co-solvent of THF (5 mL) and MeOH (5 mL) at 0 °C for 1 h. Purification on silica gel (hexanes/EtOAc = 5/1) afforded **3f** (90%, 329 mg). Colorless gum; HRMS (ESI, M⁺+1) calcd for $C_{22}H_{23}O_3S$ 367.1368, found 367.1369; ¹H NMR (400 MHz, CDCl₃): δ 7.80-7.71 (m, 6H), 7.50-7.45 (m, 2H), 7.38 (dd, *J* = 1.6, 8.4 Hz, 1H), 7.24 (d, *J* = 8.4 Hz, 2H), 5.37-5.27 (m, 1H), 5.24 (d, *J* = 8.0 Hz, 1H), 4.74 (dq, *J* = 1.2, 10.0 Hz, 1H), 4.63 (dq, *J* = 1.2, 16.8 Hz, 1H), 4.50 (br s, 1H), 3.58-3.53 (m, 1H), 2.43-2.36 (m, 1H), 2.38 (s, 3H), 2.26-2.19 (m, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 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 NaBH₄ (100 mg, 3.0 mmol) and **1g** (390 mg, 1.0 mmol) in a co-solvent of THF (5 mL) and MeOH (5 mL) at 0 °C for 1 h. Purification on silica gel (hexanes/EtOAc = 5/1) afforded **3g** (92%, 361 mg). Colorless gum; HRMS (ESI, M⁺+1) calcd for $C_{24}H_{25}O_3S$ 393.1524, found 393.1528; ¹H NMR (400 MHz, CDCl₃): δ 7.77 (d, *J* = 8.4 Hz, 2H), 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 Hz, 1H), 4.68 (dq, *J* = 1.2, 16.8 Hz, 1H), 4.20 (br s, 1H), 3.51-3.46 (m, 1H), 2.43 (s, 3H), 2.42-2.36 (m, 1H), 2.25-2.17 (m, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 145.01, 141.29, 140.43, 138.48, 135.37, 133.06, 129.78 (2x), 128.75 (2x), 128.73 (2x), 127.59 (2x), 127.44, 127.13 (2x), 126.99 (2x), 117.75, 72.63, 70.19, 30.99, 21.60; Anal. Calcd for $C_{24}H_{24}O_3S$: C, 73.44; 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 NaBH₄ (100 mg, 3.0 mmol) and **1h** (330 mg, 1.0 mmol) in a co-solvent of THF (5 mL) and MeOH (5 mL) at 0 °C for 1 h. Purification on silica gel (hexanes/EtOAc = 3/1) afforded **3h** (90%, 299 mg). Colorless gum; HRMS (ESI, M⁺+1) calcd for C₁₈H₂₁O₄S 333.1161, found 333.1162; ¹H NMR (400 MHz, CDCl₃): δ 7.91-7.88 (m, 2H), 7.67-7.63 (m, 1H), 7.57-7.53 (m, 2H), 7.21 (d, *J* = 8.8 Hz, 2H), 6.82 (d, *J* = 8.8 Hz, 2H), 5.30-5.19 (m, 1H), 5.04 (d, *J* = 8.4 Hz, 1H), 4.75 (dq, *J* = 1.2, 10.0 Hz, 1H), 4.60 (dq, *J* = 1.2, 16.8 Hz, 1H), 4.20 (br s, 1H), 3.77 (s, 3H), 3.45-3.40 (m, 1H), 2.32-2.25 (m, 1H), 2.15-2.08 (m, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 159.65, 138.52, 133.84, 133.00, 131.56, 129.09 (2x), 128.68 (2x), 128.40 (2x), 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 NaBH₄ (100 mg, 3.0 mmol) and **1i** (318 mg, 1.0 mmol) in a co-solvent of THF (5 mL) and MeOH (5 mL) at 0 °C for 1 h. Purification on silica gel (hexanes/EtOAc = 5/1) afforded **3i** (87%, 278 mg). Colorless solid; mp = 106-107 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M⁺+1) calcd for C₁₇H₁₈FO₃S 321.0961, found 321.0965; ¹H NMR (400 MHz, CDCl₃): δ 7.90-7.87 (m, 2H), 7.69-7.64 (m, 1H), 7.58-7.53 (m, 2H), 7.30-7.25 (m, 2H), 7.01-6.95 (m, 2H), 5.28-5.18 (m, 1H), 5.09 (d, *J* = 8.0 Hz, 1H), 4.76 (dq, *J* = 1.2, 10.0 Hz, 1H), 4.60 (dq, *J* = 1.2, 16.8 Hz, 1H), 4.35 (br s, 1H), 3.44-3.39 (m, 1H), 2.36-2.29 (m, 1H), 2.16-2.08 (m, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 162.64 (d, *J* = 245.6 Hz), 138.27, 135.28 (d, *J* = 3.0 Hz), 134.01, 132.70, 129.20 (2x), 128.93 (d, *J* = 8.3 Hz, 2x), 128.68 (2x), 117.84, 115.40 (d, *J* = 21.3 Hz, 2x), 72.24, 70.22, 30.92; Anal. Calcd for C₁₇H₁₇FO₃S: 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 NaBH₄ (100 mg, 3.0 mmol) and **1**j (252 mg, 1.0 mmol) in a co-solvent of THF (5 mL) and MeOH (5 mL) at 0 °C for 1 h. Purification on silica gel (hexanes/EtOAc = 5/1) afforded **3**j (90%, 229 mg). Colorless oil; HRMS (ESI, M⁺+1) calcd for $C_{13}H_{19}O_3S$ 255.1055, found 255.1056; ¹H NMR (400 MHz, CDCl₃): δ 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, 3H), 2.48-2.32 (m, 2H), 2.35 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 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 $C_{13}H_{18}O_3S$: C, 61.39; H, 7.13. Found: C, 61.53; H, 7.34.



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 NaBH₄ (100 mg, 3.0 mmol) and **1k** (376 mg, 1.0 mmol) in a co-solvent of THF (5 mL) and MeOH (5 mL) at 0 °C for 1 h. Purification on silica gel (hexanes/EtOAc = 4/1) afforded **3k** (92%, 348 mg). Colorless gum; HRMS (ESI, M⁺+1) calcd for $C_{23}H_{23}O_3S$ 379.1368, found 379.1370; ¹H NMR (400 MHz, CDCl₃): δ 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 Hz, 1H), 4.80 (dq, *J* = 1.6, 10.4 Hz, 1H), 4.70 (dq, *J* = 1.6, 16.8 Hz, 1H), 4.33 (br s, 1H), 3.52 (dq, *J* = 1.6, 11.6 Hz, 1H), 2.45-2.38 (m, 1H), 2.29-2.22 (m, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 141.34, 140.43, 138.58, 138.42, 133.82, 132.97, 129.13 (2x), 128.78 (2x), 128.66 (2x), 127.55 (2x), 127.47, 127.19 (2x), 127.00 (2x), 117.93, 72.58, 70.19, 30.93; Anal. Calcd for $C_{23}H_{22}O_3S$: C, 72.99; 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 NaBH₄ (100 mg, 3.0 mmol) and **1I** (300 mg, 1.0 mmol) in a co-solvent of THF (5 mL) and MeOH (5 mL) at 0 °C for 1 h. Purification on silica gel (hexanes/EtOAc = 4/1) afforded **3I** (92%, 278 mg). Colorless solid; mp = 106-107 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M⁺+1) calcd for C₁₇H₁₉O₃S 303.1055, found 303.1057; ¹H NMR (400 MHz, CDCI₃): δ 7.90-7.87 (m, 2H), 7.67-7.62 (m, 1H), 7.56-7.52 (m, 2H), 7.30-7.25 (m, 5H), 5.29-5.19 (m, 1H), 5.09 (d, *J* = 8.4 Hz, 1H), 4.74 (dq, *J* = 1.2, 11.2 Hz, 1H), 4.60 (dq, *J* = 1.2, 16.8 Hz, 1H), 4.20 (br s, 1H), 3.49-3.44 (m, 1H), 2.36-2.28 (m, 1H), 2.18-2.11 (m, 1H); ¹³C NMR (100 MHz, CDCI₃): δ 139.36, 138.46, 133.86, 132.89, 129.10 (2x), 128.65 (2x), 128.49, 128.48 (2x), 127.18 (2x), 117.66, 72.91, 70.25, 30.93; Anal. Calcd for C₁₇H₁₈O₃S: 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 NaBH₄ (100 mg, 3.0 mmol) and **1m** (314 mg, 1.0 mmol) in a co-solvent of THF (5 mL) and MeOH (5 mL) at 0 °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 $C_{18}H_{21}O_3S$ 317.1212, found 317.1213; ¹H NMR (400 MHz, CDCl₃): δ 7.70-7.67 (m, 1H), 7.66 (s, 1H), 7.45-7.40 (m, 2H), 7.31-7.25 (m, 5H), 5.29-5.19 (m, 1H), 5.09 (d, *J* = 8.0 Hz, 1H), 4.75 (dq, *J* = 1.6, 10.4 Hz, 1H), 4.61 (dq, *J* = 1.6, 16.8 Hz, 1H), 4.20 (br s, 1H), 3.48-3.43 (m, 1H), 2.43 (s, 3H), 2.38-2.30 (m, 1H), 2.19-2.11 (m, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 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 C₁₈H₂₀O₃S: C, 68.33; H, 6.37. Found: C, 68.23; 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 NaBH₄ (100 mg, 3.0 mmol) and **1n** (318 mg, 1.0 mmol) in a co-solvent of THF (5 mL) and MeOH (5 mL) at 0 °C for 1 h. Purification on silica gel (hexanes/EtOAc = 5/1) afforded **3n** (90%, 288 mg). Colorless gum; HRMS (ESI, M⁺+1) calcd for C₁₇H₁₈FO₃S 321.0961, found 321.0965; ¹H NMR (400 MHz, CDCl₃): δ 7.89-7.84 (m, 2H), 7.31-7.23 (m, 5H), 7.20-7.14 (m, 2H), 5.38-5.28 (m, 1H), 5.06 (d, *J* = 8.0 Hz, 1H), 4.80 (dq, *J* = 1.2, 10.0 Hz, 1H), 4.68 (dq, *J* = 1.2, 16.8 Hz, 1H), 3.90 (br s, 1H), 3.50-3.45 (m, 1H), 2.38-2.26 (m, 1H), 2.25-2.19 (m, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 165.66 (d, *J* = 254.7 Hz), 139.42, 134.96 (d, *J* = 3.0 Hz), 132.78, 131.50 (d, *J* = 9.9 Hz, 2x), 128.45 (2x), 128.43, 127.00 (2x), 117.87, 116.25 (d, *J* = 22.7 Hz, 2x), 72.73, 70.28, 30.76.



1.2.15. 2-(4-Butylbenzenesulfonyl)-1-phenylpent-4-en-1-ol (3o). According to the general procedure, reaction was performed in the presence of NaBH₄ (100 mg, 3.0 mmol) and **1o** (356 mg, 1.0 mmol) in a co-solvent of THF (5 mL) and MeOH (5 mL) at 0 °C for 1 h. Purification on silica gel (hexanes/EtOAc = 5/1) afforded **3o** (95%, 340 mg). Colorless gum; HRMS (ESI, M⁺+1) calcd for $C_{21}H_{27}O_3S$ 359.1681, found 359.1687; ¹H NMR (400 MHz, CDCl₃): δ 7.73 (d, *J* = 8.4 Hz, 2H), 7.27 (d, *J* = 8.4 Hz, 2H), 7.25-7.19 (m, 5H), 5.25-5.14 (m, 1H), 5.02 (d, *J* = 8.4 Hz, 1H), 4.68 (dq, *J* = 1.2, 10.0 Hz, 1H), 4.55 (dq, *J* = 1.2, 16.8 Hz, 1H), 4.00 (br s, 1H), 3.43-3.38 (m, 1H), 2.63 (t, *J* = 8.0 Hz, 2H), 2.31-2.24 (m, 1H), 2.12-2.05 (m, 1H), 1.60-1.53 (m, 2H), 1.35-1.26 (m, 2H), 0.89 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 149.70, 139.42, 135.41, 132.97, 129.00 (2x), 128.62 (2x), 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 NaBH₄ (100 mg, 3.0 mmol) and **1p** (382 mg, 1.0 mmol) in a co-solvent of THF (5 mL) and MeOH (5 mL) at 0 °C for 1 h. Purification on silica gel (hexanes/EtOAc = 5/1) afforded **3p** (89%, 342 mg). Colorless solid; mp = 103-104 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M⁺+1) calcd for C₁₉H₂₀F₃O₃S 385.1085, found 385.1087; ¹H NMR (400 MHz, CDCl₃): δ 7.65 (d, *J* = 8.4 Hz, 2H), 7.49 (d, *J* = 8.4 Hz, 2H), 7.38 (d, *J* = 8.4 Hz, 2H), 7.27 (d, *J* = 8.4 Hz, 2H), 5.40-5.30 (m, 1H), 5.14 (d, *J* = 7.2 Hz, 1H), 4.84

(dq, J = 1.2, 10.0 Hz, 1H), 4.73 (dq, J = 1.2, 16.8 Hz, 1H), 4.48 (br s, 1H), 3.48-3.43 (m, 1H), 2.52-2.44 (m, 1H), 2.42 (s, 3H), 2.29-2.21 (m, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 145.22, 143.61, 135.18, 132.63, 129.81 (2x), 128.53 (2x), 127.32 (2x), 125.31 (d, J = 3.8 Hz, 2x), 125.23 (d, J = 3.7 Hz, 2x), 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 NaBH₄ (100 mg, 3.0 mmol) and **1q** (359 mg, 1.0 mmol) in a co-solvent of THF (5 mL) and MeOH (5 mL) at 0 °C for 1 h. Purification on silica gel (hexanes/EtOAc = 5/1) afforded **3q** (86%, 310 mg). Colorless solid; mp = 121-122 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M⁺+1) calcd for C₁₈H₂₀NO₅S 362.1062, found 362.1063; ¹H NMR (400 MHz, CDCI₃): δ 8.11-8.07 (m, 2H), 7.69 (d, *J* = 8.4 Hz, 3H), 7.48 (d, *J* = 8.0 Hz, 1H), 7.31 (d, *J* = 8.0 Hz, 2H), 5.39-5.28 (m, 1H), 5.19 (dd, *J* = 4.0, 7.2 Hz, 1H), 4.83 (dq, *J* = 1.2, 10.4 Hz, 1H), 4.70 (dq, *J* = 1.2, 17.2 Hz, 1H), 4.57 (d, *J* = 4.4 Hz, 1H), 3.50-3.45 (m, 1H), 2.51-2.45 (m, 1H), 2.43 (s, 3H), 2.27-2.19 (m, 1H); ¹³C NMR (100 MHz, CDCI₃): δ 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 C₁₈H₁₉NO₅S: C, 59.82; 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 NaBH₄ (100 mg, 3.0 mmol) and **1r** (359 mg, 1.0 mmol) in a co-solvent of THF (5 mL) and MeOH (5 mL) at 0 °C for 1 h. Purification on silica gel (hexanes/EtOAc = 5/1) afforded **3r** (72%, 260 mg). Colorless solid; mp = 142-143 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M⁺+1) calcd for $C_{18}H_{20}NO_5S$ 362.1062, found 362.1063; ¹H NMR (400 MHz, CDCl₃): δ 8.12 (d, *J* = 8.8 Hz, 2H), 7.69 (d, *J* = 8.4 Hz, 2H), 7.47 (d, *J* = 8.8 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 5.37-5.26 (m, 1H), 5.21 (d, *J* = 7.2 Hz, 1H), 4.84 (dq, *J* = 1.2, 10.4 Hz, 1H), 4.72 (dq, *J* = 1.2, 17.2 Hz, 1H), 4.53 (br s, 1H), 3.47-3.42 (m, 1H), 2.49-2.41 (m, 1H), 2.44 (s, 3H), 2.26-2.17 (m, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 146.84, 145.57, 134.88, 132.40, 130.86, 129.93 (2x), 128.65 (2x), 127.99 (2x), 123.52 (2x), 118.59, 71.79, 69.37, 30.65, 21.63.

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1.2.19. 1,2-Diphenylpent-4-en-1-ol (3s). According to the general procedure, reaction was performed in the presence of NaBH₄ (100 mg, 3.0 mmol) and **1s** (236 mg, 1.0 mmol) in a co-solvent of THF (5 mL) and MeOH (5 mL) at 0 °C for 1 h. Purification on silica gel (hexanes/EtOAc = 5/1) afforded **3s** (80%, 190 mg). Colorless solid; mp = 50-51 °C (recrystallized

from hexanes and EtOAc); HRMS (ESI, M⁺+1) calcd for $C_{17}H_{19}O$ 239.1436, found 239.1441; ¹H NMR (400 MHz, CDCl₃): δ 7.37-7.14 (m, 10H), 5.57-5.47 (m, 1H), 5.01-5.83 (m, 2H), 4.80 (d, J = 8.0 Hz, 1H), 3.00-2.95 (m, 1H), 2.39-2.24 (m, 2H), 1.80 (br s, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 142.43, 140.39, 136.14, 128.93 (2x), 128.45 (2x), 128.26 (2x), 127.77, 126.95, 126.85 (2x), 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 NaBH₄ (100 mg, 3.0 mmol) and **1t** (254 mg, 1.0 mmol) in a co-solvent of THF (5 mL) and MeOH (5 mL) at 0 °C for 1 h. Purification on silica gel (hexanes/EtOAc = 5/1) afforded **3t** (82%, 210 mg). Colorless solid; mp = 54-55 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M⁺+1) calcd for C₁₇H₁₈FO 257.1342, found 257.1345; ¹H NMR (400 MHz, CDCl₃): δ 7.36-7.32 (m, 2H), 7.30-7.19 (m, 5H), 7.06-7.01 (m, 2H), 5.59-5.48 (m, 1H), 4.92-4.85 (m, 2H), 4.78 (d, *J* = 7.2 Hz, 1H), 2.96-2.90 (m, 1H), 2.39-2.26 (m, 2H), 1.95 (br s, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 162.18 (d, *J* = 244.1 Hz), 140.02, 138.11 (d, *J* = 3.1 Hz), 135.92, 128.85 (2x), 128.40 (2x), 128.15 (d, *J* = 8.3 Hz, 2x), 126.94, 116.27, 114.96 (d, *J* = 21.2 Hz, 2x), 77.02, 53.94, 36.20.

1.3. A representative synthetic procedure of compounds 4a-p is as follows: NaBH₄ (100 mg, 3.0 mmol) was added to a solution of **2a-p** (1.0 mmol) in a co-solvent of THF (5 mL) and MeOH (5 mL) at 0 °C. The reaction mixture was stirred for 1 h at 0 °C and the solvent was concentrated. The residue was diluted with water (10 mL) and the mixture was extracted with CH₂Cl₂ (3 x 20 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 NaBH₄ (100 mg, 3.0 mmol) and **2a** (342 mg, 1.0 mmol) in a co-solvent of THF (5 mL) and MeOH (5 mL) at 0 °C for 1 h. Purification on silica gel (hexanes/EtOAc = 5/1) afforded **4a** (90%, 310 mg). Colorless solid; mp = 84-85 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M⁺+1) calcd for C₂₀H₂₅O₃S 345.1524, found 345.1530; ¹H NMR (400 MHz, CDCl₃): δ 7.76 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 8.4 Hz, 2H), 7.30-7.24 (m, 5H), 5.07 (d, *J* = 8.4 Hz, 1H), 4.50 (br s, 1H), 4.43 (br t, *J* = 6.8 Hz, 1H), 3.41-3.35 (m, 1H), 2.45 (s, 3H), 2.29-2.21 (m, 1H), 2.02-1.94 (m, 1H), 1.38 (s, 3H), 1.15 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 144.91, 139.68, 135.54, 134.14, 129.71 (2x), 128.73 (2x), 128.43 (2x), 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 NaBH₄ (100 mg, 3.0 mmol) and **2b** (372 mg, 1.0 mmol) in a co-solvent of THF (5 mL) and MeOH (5 mL) at 0 °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 $C_{21}H_{27}O_4S$ 375.1630, found 375.1632; ¹H NMR (400 MHz, CDCl₃): δ 7.75 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.20 (d, *J* = 8.8 Hz, 2H), 6.80 (d, *J* = 8.8 Hz, 2H), 5.03 (d, *J* = 8.8 Hz, 1H), 4.48-4.44 (m, 1H), 4.45 (br s, 1H), 3.75 (s, 3H), 3.38-3.33 (m, 1H), 2.42 (s, 3H), 2.29-2.18 (m, 1H), 2.00-1.93 (m, 1H), 1.39 (d, *J* = 1.6 Hz, 3H), 1.16 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 159.42, 144.72, 135.53, 133.75, 131.81, 129.56 (2x), 128.58 (2x), 128.31 (2x), 119.22, 113.65 (2x), 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 NaBH₄ (100 mg, 3.0 mmol) and **2c** (356 mg, 1.0 mmol) in a co-solvent of THF (5 mL) and MeOH (5 mL) at 0 °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 $C_{21}H_{27}O_3S$ 359.1681, found 359.1685; ¹H NMR (400 MHz, CDCl₃): δ 7.74 (d, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 7.07 (d, *J* = 8.0 Hz, 2H), 5.03 (d, *J* = 8.4 Hz, 1H), 4.47 (br t, *J* = 6.8 Hz, 1H), 4.00 (br s, 1H), 3.40-3.35 (m, 1H), 2.42 (s, 3H), 2.29 (s, 3H), 2.26-2.20 (m, 1H), 2.03-1.96 (m, 1H), 1.38 (s, 3H), 1.16 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 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 NaBH₄ (100 mg, 3.0 mmol) and **2d** (418 mg, 1.0 mmol) in a co-solvent of THF (5 mL) and MeOH (5 mL) at 0 °C for 1 h. Purification on silica gel (hexanes/EtOAc = 5/1) afforded **4d** (88%, 370 mg). Colorless gum; HRMS (ESI, M⁺+1) calcd for $C_{26}H_{29}O_3S$ 421.1837, found 421.1841; ¹H NMR (400 MHz, CDCl₃): δ 7.66 (d, *J* = 8.4 Hz, 2H), 7.57-7.30 (m, 11H), 5.15 (d, *J* = 8.0 Hz, 1H), 4.57-4.53 (m, 1H), 3.80 (br s, 1H), 3.49-3.44 (m, 1H), 2.42 (s, 3H), 2.39-2.32 (m, 1H), 2.16-2.08 (m, 1H), 1.41 (d, *J* = 1.2 Hz, 3H), 1.22 (s, 3H); ¹³C

NMR (100 MHz, CDCl₃): δ 144.77, 141.04, 140.50, 138.70, 135.55, 134.13, 129.61 (2x), 128.68 (2x), 128.57 (2x), 127.51 (2x), 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 NaBH₄ (100 mg, 3.0 mmol) and **2e** (392 mg, 1.0 mmol) in a co-solvent of THF (5 mL) and MeOH (5 mL) at 0 °C for 1 h. Purification on silica gel (hexanes/EtOAc = 5/1) afforded **4e** (88%, 347 mg). Colorless gum; HRMS (ESI, M⁺+1) calcd for C₂₄H₂₇O₃S 395.1681, found 395.1685; ¹H NMR (400 MHz, CDCl₃): δ 7.68-7.70 (m, 6H), 7.47-7.43 (m, 2H), 7.39 (dd, *J* = 1.6, 8.4 Hz, 1H), 7.19 (d, *J* = 8.0 Hz, 2H), 5.27 (d, *J* = 8.0 Hz, 1H), 4.57-4.54 (m, 1H), 4.60 (br s, 1H), 3.57-3.52 (m, 1H), 2.41-2.35 (m, 1H), 2.33 (s, 3H), 2.18-2.11 (m, 1H), 1.31 (d, *J* = 0.8 Hz, 3H), 1.12 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 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 NaBH₄ (100 mg, 3.0 mmol) and **2f** (358 mg, 1.0 mmol) in a co-solvent of THF (5 mL) and MeOH (5 mL) at 0 °C for 1 h. Purification on silica gel (hexanes/EtOAc = 5/1) afforded **4f** (90%, 324 mg). Colorless gum; HRMS (ESI, M⁺+1) calcd for C₂₀H₂₅O₄S 361.1474, found 361.1483; ¹H NMR (400 MHz, CDCl₃): δ 7.91-7.86 (m, 2H), 7.65-7.61 (m, 1H), 7.56-7.51 (m, 2H), 7.22-7.18 (m, 2H), 6.81 (d, *J* = 8.8 Hz, 2H), 5.06 (d, *J* = 8.4 Hz, 1H), 4.48-4.43 (m, 1H), 4.00 (br s, 1H), 3.76 (s, 3H), 3.41-3.36 (m, 1H), 2.28-2.21 (m, 1H), 2.03-1.96 (m, 1H), 1.38 (d, *J* = 1.2 Hz, 3H), 1.16 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 159.51, 138.79, 134.08, 133.69, 131.78, 128.99 (2x), 128.55 (2x), 128.34 (2x), 119.12, 113.77 (2x), 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 NaBH₄ (100 mg, 3.0 mmol) and **2g** (296 mg, 1.0 mmol) in a co-solvent of THF (5 mL) and MeOH (5 mL) at 0 °C for 1 h. Purification on silica gel (hexanes/EtOAc = 5/1) afforded **4g** (92%, 274 mg). Colorless gum; HRMS (ESI, M⁺+1)

calcd for $C_{15}H_{23}O_4S$ 299.1317, found 299.1320; ¹H NMR (400 MHz, CDCl₃): δ 7.23 (d, *J* = 8.4 Hz, 2H), 6.86 (d, *J* = 8.4 Hz, 2H), 4.96 (d, *J* = 8.8 Hz, 1H), 4.95 (br t, *J* = 6.8 Hz, 1H), 4.52 (br s, 1H), 3.77 (s, 3H), 3.21-3.16 (m, 1H), 2.94 (s, 3H), 2.37-2.23 (m, 2H), 1.58 (s, 3H), 1.32 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 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 NaBH₄ (100 mg, 3.0 mmol) and **2h** (360 mg, 1.0 mmol) in a co-solvent of THF (5 mL) and MeOH (5 mL) at 0 °C for 1 h. Purification on silica gel (hexanes/EtOAc = 5/1) afforded **4h** (90%, 326 mg). Colorless solid; mp = 88-89 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M⁺+1) calcd for C₂₀H₂₄FO₃S 363.1430, found 363.1436; ¹H NMR (400 MHz, CDCl₃): δ 7.76 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 8.4 Hz, 2H), 7.30-7.25 (m, 2H), 7.00-6.94 (m, 2H), 5.09 (d, *J* = 8.4 Hz, 1H), 4.49-4.45 (m, 1H), 4.17 (br s, 1H), 3.39-3.34 (m, 1H), 2.44 (s, 3H), 2.30-2.22 (m, 1H), 2.04-1.96 (m, 1H), 1.41 (d, *J* = 1.2 Hz, 3H), 1.18 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 162.40 (d, *J* = 244.9 Hz), 144.92, 135.57 (d, *J* = 3.1 Hz), 135.29, 134.11, 129.62 (2x), 128.84 (d, *J* = 8.3 Hz, 2x), 128.55 (2x), 118.93, 115.08 (d, *J* = 21.3 Hz, 2x), 72.15, 70.68, 25.48, 25.32, 21.44, 17.18; Anal. Calcd for C₂₀H₂₃FO₃S: C, 66.27; 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 NaBH₄ (100 mg, 3.0 mmol) and **2i** (387 mg, 1.0 mmol) in a co-solvent of THF (5 mL) and MeOH (5 mL) at 0 °C for 1 h. Purification on silica gel (hexanes/EtOAc = 3/1) afforded **4i** (82%, 319 mg). Colorless solid; mp = 121-122 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M⁺+1) calcd for C₂₀H₂₄NO₅S 390.1375, found 390.1382; ¹H NMR (400 MHz, CDCl₃): δ 8.07-8.05 (m, 2H), 7.69-7.66 (m, 3H), 7.47-7.43 (m, 1H), 7.28 (d, *J* = 8.0 Hz, 2H), 5.19 (d, *J* = 7.2 Hz, 1H), 4.57-4.52 (m, 1H), 4.00 (br s, 1H), 3.45-3.40 (m, 1H), 2.40 (s, 3H), 2.40-2.31 (m, 1H), 2.18-2.11 (m, 1H), 1.41 (d, *J* = 0.8 Hz, 3H), 1.22 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 147.95, 145.22, 142.12, 135.31, 135.11, 133.07, 129.78 (2x), 129.24, 128.48 (2x), 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 NaBH₄ (100 mg, 3.0 mmol) and **2j** (387 mg, 1.0 mmol) in a co-solvent of THF (5 mL) and MeOH (5 mL) at 0 °C for 1 h. Purification on silica gel (hexanes/EtOAc = 3/1) afforded **4j** (70%, 272 mg). Colorless gum; HRMS (ESI, M⁺+1) calcd for $C_{20}H_{24}NO_5S$ 390.1375, found 390.1378; ¹H NMR (400 MHz, CDCl₃): δ 8.11 (d, *J* = 8.8 Hz, 2H), 8.68 (d, *J* = 8.4 Hz, 2H), 7.47 (d, *J* = 8.8 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 5.21 (d, *J* = 7.2 Hz, 1H), 4.55-4.51 (m, 1H), 4.50 (br s, 1H), 3.42-3.37 (m, 1H), 2.43 (s, 3H), 2.39-2.32 (m, 1H), 2.19-2.11 (m, 1H), 1.43 (d, *J* = 1.2 Hz, 3H), 1.27 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 147.20, 135.45, 135.17, 130.86, 129.82 (2x), 128.77, 128.58 (2x), 127.92 (2x), 123.39 (2x), 118.51, 71.79, 70.06, 25.29 (2x), 21.60, 17.52.



1.3.11. 5-Methyl-2-(toluene-4-sulfonyl)-1-(4-trifluoromethylphenyl)hex-4-en-1-ol (4k). According to the general procedure, reaction was performed in the presence of NaBH₄ (100 mg, 3.0 mmol) and **2k** (410 mg, 1.0 mmol) in a co-solvent of THF (5 mL) and MeOH (5 mL) at 0 °C for 1 h. Purification on silica gel (hexanes/EtOAc = 5/1) afforded **4k** (83%, 342 mg). Colorless solid; mp = 98-99 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M⁺+1) calcd for C₂₁H₂₄F₃O₃S 413.1398, found 413.1401; ¹H NMR (400 MHz, CDCl₃): δ 7.66 (d, *J* = 8.0 Hz, 2H), 7.49 (d, *J* = 8.4 Hz, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 8.4 Hz, 2H), 5.15 (d, *J* = 7.6 Hz, 1H), 4.51 (br t, *J* = 8.4 Hz, 1H), 4.50 (br s, 1H), 3.42-3.37 (m, 1H), 2.42 (s, 3H), 2.40-2.36 (m, 1H), 2.19-2.11 (m, 1H), 1.42 (d, *J* = 0.8 Hz, 3H), 1.26 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 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 Hz, 2x), 118.78, 72.03, 70.19, 25.45, 25.24, 21.53, 17.43; Anal. Calcd for C₂₁H₂₃F₃O₃S: 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 NaBH₄ (100 mg, 3.0 mmol) and **2I** (410 mg, 1.0 mmol) in a co-solvent of THF (5 mL) and MeOH (5 mL) at 0 °C for 1 h. Purification on silica gel (hexanes/EtOAc = 5/1) afforded **4I** (80%, 330 mg). Colorless gum; HRMS (ESI, M⁺+1) calcd for $C_{25}H_{33}O_3S$ 413.2150, found 413.2155; ¹H NMR (400 MHz, CDCl₃): δ 7.78-7.75 (m, 2H),

7.34-7.24 (m, 7H), 5.07 (d, J = 8.4 Hz, 1H), 4.97-4.93 (m, 1H), 4.45-4.41 (m, 1H), 4.00 (br s, 1H), 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 (d, J = 0.8 Hz, 3H), 1.55 (s, 3H), 1.14 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 144.91, 139.68, 137.75, 135.43, 131.40, 129.70 (2x), 128.71 (2x), 128.40 (2x), 128.29, 127.21 (2x), 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 C₂₅H₃₂O₃S: 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 NaBH₄ (100 mg, 3.0 mmol) and **2m** (460 mg, 1.0 mmol) in a co-solvent of THF (5 mL) and MeOH (5 mL) at 0 °C for 1 h. Purification on silica gel (hexanes/EtOAc = 5/1) afforded **4m** (82%, 379 mg). Colorless gum; HRMS (ESI, M⁺+1) calcd for C₂₉H₃₅O₃S 463.2307, found 463.2309; ¹H NMR (400 MHz, CDCl₃): $\overline{0}$ 7.79-7.70 (m, 6H), 7.49-7.44 (m, 2H), 7.39 (dd, *J* = 2.4, 8.4 Hz, 1H), 7.22 (d, *J* = 8.4 Hz, 2H), 5.26 (d, *J* = 8.0 Hz, 1H), 4.94-4.89 (m, 1H), 4.60 (br s, 1H), 4.57-4.53 (m, 1H), 3.54-3.49 (m, 1H), 2.42-2.38 (m, 1H), 2.38 (s, 3H), 2.20-2.12 (m, 1H), 1.78-1.72 (m, 2H), 1.64 (s, 3H), 1.64-1.56 (m, 2H), 1.52 (s, 3H), 1.14 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): $\overline{0}$ 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 (4n). According to the general procedure, reaction was performed in the presence of NaBH₄ (100 mg, 3.0 mmol) and **2n** (428 mg, 1.0 mmol) in a co-solvent of THF (5 mL) and MeOH (5 mL) at 0 °C for 1 h. Purification on silica gel (hexanes/EtOAc = 5/1) afforded **4n** (86%, 370 mg). Colorless gum; HRMS (ESI, M⁺+1) calcd for $C_{25}H_{32}FO_3S$ 431.2056, found 431.2052; ¹H NMR (400 MHz, CDCl₃): δ 7.78-7.73 (m, 2H), 7.34 (d, *J* = 8.4 Hz, 2H), 7.30-7.25 (m, 2H), 7.00-6.94 (m, 2H), 5.07 (d, *J* = 8.4 Hz, 1H), 4.97-4.93 (m, 1H), 4.44 (br t, *J* = 7.2 Hz, 1H), 4.40 (br s, 1H), 3.36-3.31 (m, 1H), 2.45 (s, 3H), 2.32-2.25 (m, 1H), 2.04-1.96 (m, 1H), 1.83-1.78 (m, 2H), 1.71-1.65 (m, 2H), 1.64 (d, *J* = 1.2 Hz, 3H), 1.52 (s, 3H), 1.17 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 162.55 (d, *J* = 245.6 Hz), 145.08, 137.99, 135.64 (d, *J* = 3.0 Hz), 135.32, 131.53, 129.78 (2x), 128.90 (d, *J* = 8.3 Hz, 2x), 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 (4o). According to the general procedure, reaction was performed in the presence of NaBH₄ (100 mg, 3.0 mmol) and **2o** (440 mg, 1.0 mmol) in a co-solvent of THF (5 mL) and MeOH (5 mL) at 0 °C for 1 h. Purification on silica gel (hexanes/EtOAc = 4/1) afforded **4o** (86%, 380 mg). Colorless gum; HRMS (ESI, M⁺+1) calcd for $C_{26}H_{35}O_4S$ 443.2256, found 443.2261; ¹H NMR (400 MHz, CDCl₃): $\overline{0}$ 7.77 (d, J = 8.4 Hz, 2H), 7.34 (d, J = 8.0 Hz, 2H), 7.21 (d, J = 8.4 Hz, 2H), 6.81 (d, J = 8.8 Hz, 2H), 5.03 (d, J = 8.4 Hz, 1H), 4.98-4.93 (m, 1H), 4.60 (br s, 1H), 4.45 (dt, J = 1.2, 7.2 Hz, 1H), 3.77 (br s, 3H), 3.37-3.32 (m, 1H), 2.45 (s, 3H), 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 (d, J = 1.2 Hz, 3H), 1.55 (s, 3H), 1.16 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): $\overline{0}$ 159.60, 144.90, 137.61, 135.58, 131.94, 131.45, 129.72 (2x), 128.77 (2x), 128.43 (2x), 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 (4p). According to the general procedure, reaction was performed in the presence of NaBH₄ (100 mg, 3.0 mmol) and **2p** (364 mg, 1.0 mmol) in a co-solvent of THF (5 mL) and MeOH (5 mL) at 0 °C for 1 h. Purification on silica gel (hexanes/EtOAc = 3/1) afforded **4p** (87%, 318 mg). Colorless gum; HRMS (ESI, M⁺+1) calcd for $C_{20}H_{31}O_4S$ 367.1943, found 367.1946; ¹H NMR (400 MHz, CDCl₃): δ 7.18 (d, J = 8.4 Hz, 2H), 6.80 (d, J = 8.8 Hz, 2H), 4.97 (br t, J = 6.8 Hz, 1H), 4.91-4.87 (m, 2H), 3.83 (br s, 1H), 3.71 (s, 3H), 3.15-3.11 (m, 1H), 2.90 (s, 3H), 2.32-2.17 (m, 2H), 1.94-1.89 (m, 2H), 1.88-1.77 (m, 2H), 1.60 (s, 3H), 1.52 (s, 3H), 1.26 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 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 5a-x is as follows: $BF_3 \cdot OEt_2$ (57 mg, 0.4 mmol) was added to a solution of **3a-o**, **3s-t** (0.2 mmol) and **7a-e** (0.3 mmol) in CH_2CI_2 (5 mL) at 25 °C. The reaction mixture was stirred at 25 °C for 20 h. The reaction mixture was concentrated and the residue was diluted with water (10 mL) and the mixture was extracted with CH_2CI_2 (3 x 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 BF₃·OEt₂ (57 mg, 0.4 mmol), **3a** (63 mg, 0.2 mmol) and **7a** (41 mg, 0.3 mmol) in CH₂Cl₂ (5 mL) at 25 °C for 20 h. Purification on silica gel (hexanes/EtOAc = 3/1) afforded **5a** (90%, 78 mg). Colorless solid; mp = 131-132 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M⁺+1) calcd for C₂₆H₂₉O₄S 437.1787, found 437.1791; ¹H NMR (400 MHz, CDCl₃): δ 7.58 (d, *J* = 8.0 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 7.14-7.09 (m, 3H), 6.95-6.93 (m, 2H), 6.76 (s, 1H), 6.26 (s, 1H), 4.55 (d, *J* = 8.0 Hz, 1H), 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 (s, 3H), 1.73 (q, *J* = 12.4 Hz, 1H), 1.39 (d, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 147.58, 147.51, 144.39, 144.15, 135.47, 133.00, 129.83, 129.49 (2x), 128.64 (2x), 128.59 (2x), 128.45 (2x), 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 BF₃·OEt₂ (57 mg, 0.4 mmol), **3b** (69 mg, 0.2 mmol) and **7a** (41 mg, 0.3 mmol) in CH₂Cl₂ (5 mL) at 25 °C for 20 h. Purification on silica gel (hexanes/EtOAc = 3/1) afforded **5b** (92%, 86 mg). Colorless solid; mp = 124-125 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M⁺+1) calcd for $C_{27}H_{31}O_5S$ 467.1892, found 467.1893; ¹H NMR (400 MHz, CDCl₃): δ 7.55 (d, *J* = 8.0 Hz, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 6.85 (d, *J* = 8.8 Hz, 2H), 6.75 (s, 1H), 6.63 (d, *J* = 8.8 Hz, 2H), 6.24 (s, 1H), 4.49 (d, *J* = 8.4 Hz, 1H), 3.85 (s, 3H), 3.84-3.74 (m, 1H), 3.74 (s, 3H), 3.59 (s, 3H), 2.98-2.93 (m, 1H), 2.43-2.40 (m, 1H), 2.38 (s, 3H), 1.72 (q, *J* = 12.4 Hz, 1H), 1.39 (d, *J* = 6.4 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 158.11, 147.51, 147.43, 143.91, 136.17, 135.70, 132.82, 130.21, 129.66 (2x), 129.40 (2x), 128.52 (2x), 113.77 (2x), 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 BF₃·OEt₂ (57 mg, 0.4 mmol), **3c** (67 mg, 0.2 mmol) and **7a** (41 mg, 0.3 mmol) in CH₂Cl₂ (5 mL) at 25 °C for 20 h. Purification on silica gel (hexanes/EtOAc = 3/1) afforded **5c** (89%, 81 mg). Colorless solid; mp = 120-121 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M⁺+1) calcd for C₂₆H₂₈FO₄S 455.1692, found 455.1697; ¹H NMR (400 MHz, CDCl₃): δ 7.55 (d, *J* = 8.4 Hz, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.95-6.89 (m, 2H), 6.83-6.77 (m, 2H), 6.76 (s, 1H), 6.19 (s, 1H), 4.54 (d, *J* = 8.4 Hz, 1H), 3.85 (s, 3H), 3.76-3.70 (m, 1H), 3.58 (s, 3H), 2.98-2.92 (m, 1H), 2.44-2.36 (m, 1H), 2.39 (s, 3H), 1.72 (q, *J* = 12.4 Hz, 1H), 1.39 (d, *J* = 6.8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 161.42 (d, *J* = 244.1 Hz), 147.66, 147.51, 144.28, 140.02 (d, *J* = 3.0 Hz), 135.48, 132.86, 130.23 (d, *J* = 7.6 Hz, 2x), 130.13, 129.49 (2x), 128.50 (2x), 115.21 (d, *J* = 21.2 Hz, 2x), 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 BF₃·OEt₂ (57 mg, 0.4 mmol), **3d** (66 mg, 0.2 mmol) and **7a** (41 mg, 0.3 mmol) in CH₂Cl₂ (5 mL) at 25 °C for 20 h. Purification on silica gel (hexanes/EtOAc = 3/1) afforded **5d** (88%, 79 mg). Colorless solid; mp = 77-78 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M⁺+1) calcd for C₂₇H₃₁O₄S 451.1943, found 451.1943; ¹H NMR (400 MHz, CDCl₃): δ 7.56 (d, *J* = 8.4 Hz, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 6.91 (d, *J* = 8.0 Hz, 2H), 6.82 (d, *J* = 8.0 Hz, 2H), 6.76 (s, 1H), 6.27 (s, 1H), 4.80 (d, *J* = 7.6 Hz, 1H), 3.85 (s, 3H), 3.84-3.75 (m, 1H), 3.60 (s, 3H), 2.98-2.92 (m, 1H), 2.42-2.35 (m, 1H), 2.39 (s, 3H), 2.25 (s, 3H), 1.72 (q, *J* = 12.4 Hz, 1H), 1.39 (d, *J* = 6.8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 147.54, 147.47, 144.00, 141.16, 136.03, 135.58, 132.94, 130.03, 129.39 (2x), 129.10 (2x), 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 BF₃·OEt₂ (57 mg, 0.4 mmol), **3e** (48 mg, 0.2 mmol) and **7a** (41 mg, 0.3 mmol) in CH₂Cl₂ (5 mL) at 25 °C for 20 h. Purification on silica gel (hexanes/EtOAc = 3/1) afforded **5e** (82%, 59 mg). Colorless gum; HRMS (ESI, M⁺+1) calcd for C₂₀H₂₅O₄S 361.1474, found 361.1478; ¹H NMR (400 MHz, CDCl₃): δ 7.36-7.32 (m, 2H), 7.30-7.22 (m, 3H), 6.79 (s, 1H), 6.20 (s, 1H), 4.53 (d, *J* = 9.6 Hz, 1H), 3.87 (s, 3H), 3.56 (s, 3H), 3.57-3.51 (m, 1H), 3.10-3.04 (m, 1H), 2.70-2.65 (m, 1H), 2.19 (s, 3H), 1.72 (q, J = 12.4 Hz, 1H), 1.44 (d, J = 6.4 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 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 BF₃·OEt₂ (57 mg, 0.4 mmol), **3f** (73 mg, 0.2 mmol) and **7a** (41 mg, 0.3 mmol) in CH₂Cl₂ (5 mL) at 25 °C for 20 h. Purification on silica gel (hexanes/EtOAc = 3/1) afforded **5f** (83%, 81 mg). Colorless solid; mp = 148-149 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M⁺+1) calcd for C₃₀H₃₁O₄S 487.1943, found 487.1944; ¹H NMR (400 MHz, CDCl₃): δ 7.69 (d, *J* = 8.8 Hz, 1H), 7.63 (d, *J* = 8.8 Hz, 1H), 7.52 (d, *J* = 8.4 Hz, 1H), 7.46-7.39 (m, 4H), 7.33 (d, *J* = 1.2 Hz, 1H), 6.96 (dd, *J* = 2.0, 8.8 Hz, 1H), 6.86 (d, *J* = 8.0 Hz, 2H), 6.81 (s, 1H), 6.24 (s, 1H), 4.67 (d, *J* = 8.8 Hz, 1H), 3.92-3.90 (m, 1H), 3.87 (s, 3H), 3.49 (s, 3H), 3.11-3.06 (m, 1H), 2.60 (dt, *J* = 4.0, 12.4 Hz, 1H), 2.12 (s, 3H), 1.84 (q, *J* = 12.4 Hz, 1H), 1.46 (d, *J* = 6.8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 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 (2x), 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 e (5g). According to the general procedure, reaction was performed in the presence of BF₃·OEt₂ (57 mg, 0.4 mmol), **3g** (78 mg, 0.2 mmol) and **7a** (41 mg, 0.3 mmol) in CH₂Cl₂ (5 mL) at 25 °C for 20 h. Purification on silica gel (hexanes/EtOAc = 3/1) afforded **5g** (86%, 88 mg). Colorless solid; mp = 162-163 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M⁺+1) calcd for C₃₂H₃₃O₄S 513.2100, found 513.2107; ¹H NMR (400 MHz, CDCl₃): δ 7.56 (d, *J* = 8.0 Hz, 2H), 7.53-7.50 (m, 2H), 7.44-7.40 (m, 2H), 7.35-7.33 (m, 1H), 7.33 (d, *J* = 8.4 Hz, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 7.01 (d, *J* = 8.4 Hz, 2H), 6.79 (s, 1H), 6.29 (s, 1H), 4.60 (d, *J* = 8.0 Hz, 1H), 3.87 (s, 3H), 3.86-3.78 (m, 1H), 3.60 (s, 3H), 3.03-2.98 (m, 1H), 2.51-2.46 (m, 1H), 2.31 (s, 3H), 1.78 (q, *J* = 12.4 Hz, 1H), 1.42 (d, *J* = 6.8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 147.64, 147.49, 144.02, 143.08, 140.56, 139.30, 135.75, 132.97, 129.75, 129.42 (2x), 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 **5g** was grown by slow diffusion of EtOAc into a solution of compound **5g** in CH₂Cl₂ to yield colorless prisms. The compound crystallizes in the monoclinic crystal system, space group P 21/c, a = 12.1307(4) Å, b = 11.0079(3) Å, c = 20.0330(5) Å, V = 2589.42(13) Å³, Z = 4, $d_{calcd} = 1.315$ mg/cm³, F(000) = 1088, 2θ range 1.734~26.423°, R indices (all data) R1 = 0.0487, wR2 = 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 BF₃·OEt₂ (57 mg, 0.4 mmol), **3h** (66 mg, 0.2 mmol) and **7a** (41 mg, 0.3 mmol) in CH₂Cl₂ (5 mL) at 25 °C for 20 h. Purification on silica gel (hexanes/EtOAc = 3/1) afforded **5h** (86%, 78 mg). Colorless solid; mp = 149-150 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M⁺+1) calcd for C₂₆H₂₉O₅S 453.1736, found 453.1742; ¹H NMR (400 MHz, CDCl₃): δ 7.66-7.64 (m, 2H), 7.52-7.45 (m, 1H), 7.39-7.35 (m, 2H), 6.84 (d, *J* = 8.8 Hz, 2H), 6.75 (s, 1H), 6.61 (d, *J* = 8.8 Hz, 2H), 6.23 (s, 1H), 4.51 (d, *J* = 8.4 Hz, 1H), 3.85 (s, 3H), 3.83-3.76 (m, 1H), 3.73 (s, 3H), 3.58 (s, 3H), 3.00-2.95 (m, 1H), 2.45 (dt, *J* = 4.4, 12.8 Hz, 1H), 1.75 (q, *J* = 12.4 Hz, 1H), 1.40 (d, *J* = 6.8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 158.09, 147.53, 147.42, 138.84, 135.83, 132.94, 130.12, 129.68 (2x), 128.85, 128.73 (2x), 128.38 (2x), 113.81 (2x), 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 e (5i). According to the general procedure, reaction was performed in the presence of BF₃·OEt₂ (57 mg, 0.4 mmol), **3i** (64 mg, 0.2 mmol) and **7a** (41 mg, 0.3 mmol) in CH₂Cl₂ (5 mL) at 25 °C for 20 h. Purification on silica gel (hexanes/EtOAc = 3/1) afforded **5i** (87%, 77 mg). Colorless solid; mp = 117-118 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M⁺+1) calcd for C₂₅H₂₆FO₄S 441.1536, found 441.1541; ¹H NMR (400 MHz, CDCl₃): δ 7.67-7.65 (m, 2H), 7.55-7.52 (m, 1H), 7.42-7.38 (m, 2H), 6.93-6.87 (m, 2H), 6.81-6.77 (m, 2H), 6.76 (s, 1H), 6.18 (s, 1H), 4.56 (d, *J* = 8.4 Hz, 1H), 3.85 (s, 3H), 3.79-3.73 (m, 1H), 3.58 (s, 3H), 3.00-2.94 (m, 1H), 2.43 (dt, *J* = 4.0, 8.0 Hz, 1H), 1.75 (q, *J* = 12.4 Hz, 1H), 1.40 (d, *J* = 6.8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 161.48 (d, *J* = 244.5 Hz), 147.72, 147.54, 139.75 (d, *J* = 3.8 Hz), 138.67, 133.21, 132.81, 130.30 (d, *J* = 7.6 Hz, 2x), 129.61, 128.87 (2x), 128.40 (2x), 115.29 (d, *J* = 21.2 Hz, 2x), 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 BF₃·OEt₂ (57 mg, 0.4 mmol), **3j** (51 mg, 0.2 mmol) and **7a** (41 mg, 0.3 mmol) in CH₂Cl₂ (5 mL) at 25 °C for 20 h. Purification on silica gel (hexanes/EtOAc = 3/1) afforded **5j** (84%, 63 mg). Colorless gum; HRMS (ESI, M⁺+1) calcd for C₂₁H₂₇O₄S 375.1630, found 375.1633; ¹H NMR (400 MHz, CDCl₃): δ 7.15-7.10 (m, 4H), 6.79 (s, 1H), 6.22 (s, 1H), 4.48 (d, *J* = 9.6 Hz, 1H), 3.86 (s, 3H), 3.57 (s, 3H), 3.55-3.48 (m, 1H), 3.09-3.03 (m, 1H), 2.69-2.64 (m, 1H), 2.32 (s, 3H), 2.20 (s, 3H), 1.70 (q, *J* = 12.8 Hz, 1H), 1.43 (d, *J* = 6.8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 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 (**5k**). According to the general procedure, reaction was performed in the presence of BF₃·OEt₂ (57 mg, 0.4 mmol), **3k** (76 mg, 0.2 mmol) and **7a** (41 mg, 0.3 mmol) in CH₂Cl₂ (5 mL) at 25 °C for 20 h. Purification on silica gel (hexanes/EtOAc = 3/1) afforded **5k** (89%, 89 mg). Colorless solid; mp = 175-176 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M⁺+1) calcd for C₃₁H₃₁O₄S 499.1943, found 499.1950; ¹H NMR (400 MHz, CDCl₃): δ 7.68-7.66 (m, 2H), 7.51-7.41 (m, 5H), 7.36-7.29 (m, 5H), 6.99 (d, *J* = 8.4 Hz, 2H), 6.79 (s, 1H), 6.28 (s, 1H), 4.62 (d, *J* = 8.4 Hz, 1H), 3.92-3.89 (m, 1H), 3.87 (s, 3H), 3.59 (s, 3H), 3.06-3.00 (m, 1H), 2.54-2.49 (m, 1H), 1.81 (q, *J* = 12.4 Hz, 1H), 1.43 (d, *J* = 6.8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 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 (2x), 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 C₃₁H₃₀O₄S: 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

(51). According to the general procedure, reaction was performed in the presence of BF₃·OEt₂ (57 mg, 0.4 mmol), **3I** (60 mg, 0.2 mmol) and **7a** (41 mg, 0.3 mmol) in CH₂Cl₂ (5 mL) at 25 °C for 20 h. Purification on silica gel (hexanes/EtOAc = 3/1) afforded **5I** (82%, 69 mg). Colorless solid; mp = 140-141 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M⁺+1) calcd for C₂₅H₂₇O₄S 423.1630, found 423.1632; ¹H NMR (400 MHz, CDCl₃): δ 7.69-7.67 (m, 2H), 7.52-7.46 (m, 1H), 7.39-7.35 (m, 2H), 7.13-7.05 (m, 3H), 6.95-6.90 (m, 2H), 6.77 (s, 1H), 6.24 (s, 1H), 4.57 (d, *J* = 8.0 Hz, 1H), 3.87-3.81 (m, 1H), 3.85 (s, 3H), 3.58 (s, 3H), 3.00-2.94 (m, 1H), 2.42 (dt, *J* = 4.4, 12.8 Hz, 1H), 1.77 (q, *J* = 12.8 Hz, 1H), 1.40 (d, *J* = 6.8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 147.57, 147.46, 144.03, 138.58, 133.14, 132.88, 129.72, 128.81 (2x), 128.59 (2x), 128.47 (2x), 128.46 (2x), 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 BF₃·OEt₂ (57 mg, 0.4 mmol), **3m** (63 mg, 0.2 mmol) and **7a** (41 mg, 0.3 mmol) in CH₂Cl₂ (5 mL) at 25 °C for 20 h. Purification on silica gel (hexanes/EtOAc = 3/1) afforded **5m** (86%, 75 mg). Colorless solid; mp = 149-150 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M⁺+1) calcd for C₂₆H₂₉O₄S 437.1787, found 437.1785; ¹H NMR (400 MHz, CDCl₃): δ 7.51-7.49 (m, 1H), 7.39 (s, 1H), 7.29-7.24 (m, 2H), 7.11-7.04 (m, 3H), 6.94-6.90 (m, 2H), 6.77 (s, 1H), 6.23 (s, 1H), 4.55 (d, *J* = 8.4 Hz, 1H), 3.87-3.81 (m, 1H), 3.85 (s, 3H), 3.57 (s, 3H), 3.01-2.95 (m, 1H), 2.45 (dt, *J* = 4.4, 12.8 Hz, 1H), 2.30 (s, 3H), 1.76 (q, *J* = 12.8 Hz, 1H), 1.41 (d, *J* = 6.8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 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 (2x), 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 e (5n). According to the general procedure, reaction was performed in the presence of BF₃·OEt₂ (57 mg, 0.4 mmol), **3n** (64 mg, 0.2 mmol) and **7a** (41 mg, 0.3 mmol) in CH₂Cl₂ (5 mL) at 25 °C for 20 h. Purification on silica gel (hexanes/EtOAc = 3/1) afforded **5n** (80%, 70 mg). Colorless solid; mp = 174-175 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M⁺+1) calcd for $C_{25}H_{26}FO_4S$ 441.1536, found 441.1532; ¹H NMR (400 MHz, CDCl₃): δ 7.65-7.62 (m, 2H), 7.16-7.07 (m, 3H), 7.03-6.98 (m, 2H), 6.94-6.91 (m, 2H), 6.77 (s, 1H), 6.19 (s, 1H), 4.53 (d, *J* = 8.8 Hz, 1H), 3.85 (s, 3H), 3.85-3.80 (m, 1H), 3.56 (s, 3H), 3.05-2.96 (m, 1H), 2.49 (dt, *J* = 4.0, 12.8 Hz, 1H), 1.77 (q, *J* = 12.8 Hz, 1H), 1.42 (d, *J* = 6.8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 165.35 (d, *J* = 253.9 Hz), 147.65, 147.50, 143.75, 134.85 (d, *J* = 3.0 Hz), 132.69, 131.20 (d, *J* = 9.1 Hz, 2x), 129.69, 128.74 (2x), 128.53 (2x), 126.70, 116.04 (d, *J* = 22.0 Hz, 2x), 112.64, 108.24, 67.57, 55.87, 55.64, 45.60, 32.26, 31.75, 20.64; Anal. Calcd for C₂₅H₂₅FO₄S: 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 BF₃·OEt₂ (57 mg, 0.4 mmol), **30** (72 mg, 0.2 mmol) and **7a** (41 mg, 0.3 mmol) in CH₂Cl₂ (5 mL) at 25 °C for 20 h. Purification on silica gel (hexanes/EtOAc = 3/1) afforded **5o** (86%, 82 mg). Colorless solid; mp = 119-120 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M⁺+1) calcd for C₂₉H₃₅O₄S 479.2256, found 479.2255; ¹H NMR (400 MHz, CDCl₃): δ 7.58 (d, *J* = 8.4 Hz, 2H), 7.17 (d, *J* = 8.4 Hz, 2H), 7.17 (d, *J* = 8.4 Hz, 2H), 7.11-7.06 (m, 3H), 6.93-6.91 (m, 2H), 6.77 (s, 1H), 6.24 (s, 1H), 4.55 (d, *J* = 8.0 Hz, 1H), 3.85 (s, 3H), 3.84-3.79 (m, 1H), 3.58 (s, 3H), 3.00-2.94 (m, 1H), 2.62 (t, *J* = 8.0 Hz, 2H), 2.43 (dt, *J* = 4.4, 12.4 Hz, 1H), 1.76 (q, *J* = 12.8 Hz, 1H), 1.60-1.54 (m, 2H), 1.40 (d, *J* = 6.8 Hz, 3H), 1.38-1.30 (m, 2H), 0.94 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 148.91, 147.53, 147.43, 144.19, 135.70, 132.92, 129.84, 128.81 (2x), 128.58 (2x), 128.53 (2x), 128.39 (2x), 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 BF₃·OEt₂ (57 mg, 0.4 mmol), **3a** (63 mg, 0.2 mmol) and **7b** (37 mg, 0.3 mmol) in CH₂Cl₂ (5 mL) at 25 °C for 20 h. Purification on silica gel (hexanes/EtOAc = 3/1) afforded **5p** (86%, 72 mg). Colorless solid; mp = 124-125 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M⁺+1) calcd for C₂₅H₂₅O₄S 421.1474, found 421.1477; ¹H NMR (400 MHz, CDCl₃): δ 7.57 (d, *J* = 8.0 Hz, 2H), 7.18 (d, *J* = 7.6 Hz, 2H), 7.12-7.09 (m, 3H), 6.94-6.91 (m, 2H), 6.76 (s, 1H), 6.27 (s, 1H), 5.85 (d, *J* = 1.6 Hz, 1H), 5.83 (d, *J* = 1.6 Hz, 1H), 4.51 (d, *J* = 7.6 Hz, 1H), 3.83-3.77 (m, 1H), 2.92-2.87 (m, 1H), 2.39 (s, 3H),

2.38-2.33 (m, 1H), 1.72 (q, J = 12.4 Hz, 1H), 1.36 (d, J = 6.8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 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 **5p** was grown by slow diffusion of EtOAc into a solution of compound **5p** in CH₂Cl₂ to yield colorless prisms. The compound crystallizes in the monoclinic crystal system, space group P 21/c, a = 10.8495(5) Å, b = 9.9471(15) Å, c = 19.6318(10) Å, V =2111.60(18) Å³, Z = 4, $d_{calcd} = 1.323$ mg/cm³, F(000) = 888, 2θ range 2.082~26.463°, R indices (all data) R1 = 0.0989, wR2 = 0.1760.



1.4.17. 8-Methyl-5-phenyl-6-(toluene-3-sulfonyl)-5,6,7,8-tetrahydronaphtho[2,3-*d*][1,3]dioxole (5q). According to the general procedure, reaction was performed in the presence of BF₃·OEt₂ (57 mg, 0.4 mmol), **3a** (63 mg, 0.2 mmol) and **7b** (37 mg, 0.3 mmol) in CH₂Cl₂ (5 mL) at 25 °C for 20 h. Purification on silica gel (hexanes/EtOAc = 3/1) afforded **5q** (87%, 73 mg). Colorless solid; mp = 154-155 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M⁺+1) calcd for C₂₅H₂₅O₄S 421.1474, found 421.1477; ¹H NMR (400 MHz, CDCl₃): δ 7.52-7.49 (m, 1H), 7.40 (s, 1H), 7.30-7.25 (m, 2H), 7.12-7.04 (m, 3H), 6.93-6.90 (m, 2H), 6.77 (s, 1H), 6.25 (s, 1H), 6.85 (d, *J* = 1.2 Hz, 1H), 5.82 (d, *J* = 1.2 Hz, 1H), 4.52 (d, *J* = 8.0 Hz, 1H), 3.87-3.80 (m, 1H), 2.96-2.90 (m, 1H), 2.42 (dt, *J* = 4.4, 12.8 Hz, 1H), 2.31 (s, 3H), 1.75 (q, *J* = 12.8 Hz, 1H), 1.37 (d, *J* = 6.8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 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 e (5r).** According to the general procedure, reaction was performed in the presence of BF₃·OEt₂ (57 mg, 0.4 mmol), **3o** (72 mg, 0.2 mmol) and **7b** (37 mg, 0.3 mmol) in CH₂Cl₂ (5 mL) at 25 °C for 20 h. Purification on silica gel (hexanes/EtOAc = 3/1) afforded **5r** (89%, 82 mg). Colorless solid; mp = 142-143 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M⁺+1) calcd for C₂₈H₃₁O₄S 463.1943, found 463.1945; ¹H NMR (400 MHz, CDCl₃): δ 7.57 (d, *J* = 8.4 Hz, 2H), 7.17 (d, *J* = 8.4 Hz, 2H), 7.17 (d, *J* = 8.4 Hz, 2H), 7.11-7.04 (m, 3H), 6.92-6.90 (m, 2H), 6.77 (s, 1H), 6.26 (s, 1H), 5.70 (d, *J* = 1.6 Hz, 1H), 5.82 (d, *J* = 1.2 Hz, 1H), 4.51 (d, *J* = 8.0 Hz, 1H), 3.85-3.79 (m, 1H), 2.94-2.89 (m, 1H), 2.63 (t, *J* = 8.0 Hz, 1H), 3.85-3.79 (m, 1H), 2.94-2.89 (m, 1H), 2.63 (t, *J* = 8.0 Hz, 1H), 3.85-3.79 (m, 1H), 2.94-2.89 (m, 1H), 2.63 (t, *J* = 8.0 Hz, 1H), 3.85-3.79 (m, 1H), 2.94-2.89 (m, 1H), 2.63 (t, *J* = 8.0 Hz, 1H), 3.85-3.79 (m, 1H), 2.94-2.89 (m, 1H), 2.63 (t, *J* = 8.0 Hz, 1H), 3.85-3.79 (m, 1H), 2.94-2.89 (m, 1H), 2.63 (t, *J* = 8.0 Hz, 1H), 3.85-3.79 (m, 1H), 2.94-2.89 (m, 1H), 2.63 (t, *J* = 8.0 Hz, 1H), 3.85-3.79 (m, 1H), 2.94-2.89 (m, 1H), 2.63 (t, *J* = 8.0 Hz, 1H), 3.85-3.79 (m, 1H), 2.94-2.89 (m, 1H), 2.63 (t, *J* = 8.0 Hz, 1H), 3.85-3.79 (m, 1H), 2.94-2.89 (m, 2H), 2.63 (t, *J* = 8.0 Hz, 1H), 3.85-3.79 (m, 2H), 3

8.0 Hz, 2H), 2.41 (dt, J = 4.4, 12.4 Hz, 1H), 1.69 (q, J = 12.8 Hz, 1H), 1.62-1.53 (m, 2H), 1.37 (d, J = 6.8 Hz, 3H), 1.38-1.30 (m, 2H), 0.95 (t, J = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 148.99, 146.37, 146.01, 144.14, 135.63, 134.26, 130.92, 128.87 (2x), 128.56 (2x), 128.53 (2x), 128.48 (2x), 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 BF₃·OEt₂ (57 mg, 0.4 mmol), **3r** (48 mg, 0.2 mmol) and **7a** (41 mg, 0.3 mmol) in CH_2Cl_2 (5 mL) at 25 °C for 20 h. Purification on silica gel (hexanes/EtOAc = 3/1) afforded 5s (80%, 57 mg). Colorless solid; mp = 140-141 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M⁺+1) calcd for C₂₅H₂₇O₂ 359.2011, found 359.2017; ¹H NMR (400 MHz, CDCl₃): δ 7.19-7.08 (m, 6H), 7.00-6.97 (m, 2H), 6.89 (s, 1H), 6.87-6.85 (m, 2H), 6.22 (s, 1H), 4.12 (d, J = 11.2 Hz, 1H), 3.92 (s, 3H), 3.56 (s, 3H), 3.21-3.15 (m, 1H), 3.06 (dt, J = 2.4, 12.8 Hz, 1H), 2.14 (ddd, J = 2.8, 5.2, 12.8 Hz, 1H), 1.94 (q, J = 12.8 Hz, 1H), 1.42 (d, J = 6.8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 147.23, 146.80, 145.45, 145.05, 134.14, 132.33, 129.26 (2x), 128.10 (2x), 127.83 (2x), 127.50 (2x), 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 C₂₅H₂₆O₂: C, 83.76; H, 7.31. Found: C, 83.89; H, 7.50. Single-crystal X-Ray diagram: crystal of compound 5s was grown by slow diffusion of EtOAc into a solution of compound 5s in CH₂Cl₂ to yield colorless prisms. The compound crystallizes in the monoclinic crystal system, space group P 21/c, a = 10.2155(13) Å, b = 18.822(2)Å, c = 10.6623(15) Å, V = 1922.8(4) Å³, Z = 4, $d_{calcd} = 1.238$ mg/cm³, F(000) = 768, 2θ range 2.126~26.390°, R indices (all data) R1 = 0.0583, wR2 = 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 BF₃·OEt₂ (57 mg, 0.4 mmol), **3t** (51 mg, 0.2 mmol) and **7a** (41 mg, 0.3 mmol) in CH₂Cl₂ (5 mL) at 25 °C for 20 h. Purification on silica gel (hexanes/EtOAc = 3/1) afforded **5t** (84%, 63 mg). Colorless solid; mp = 172-173 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M⁺+1) calcd for C₂₅H₂₆FO₂ 377.1917, found 377.1924; ¹H NMR (400 MHz, CDCl₃): δ 7.20-7.10 (m, 3H), 6.97-6.95 (m, 2H), 6.88 (s, 1H), 6.81 (br s, 2H), 6.80 (br s, 2H), 6.18 (s, 1H), 4.10 (d, *J* = 10.8 Hz, 1H), 3.91 (s, 3H), 3.57 (s, 3H), 3.21-3.12 (m, 1H), 2.98 (dt, *J* = 2.4, 12.8 Hz, 1H), 2.14 (ddd, *J* = 2.8, 5.2, 12.8 Hz, 1H), 1.93 (q, *J* = 12.8 Hz, 1H), 1.41 (d, *J* = 6.8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 161.14 (d, *J* = 242.6 Hz), 147.37, 146.87, 144.79, 141.21 (d, *J* = 3.0 Hz), 134.19, 132.01, 130.56 (d, *J* = 7.6 Hz, 2x), 128.11 (2x), 127.47 (2x), 126.11, 114.66 (d, *J* = 21.3 Hz, 2x), 112.83, 109.07, 55.86, 55.68,

53.69, 50.62, 40.70, 33.53, 21.71; Anal. Calcd for C₂₅H₂₅FO₂: C, 79.76; H, 6.69. Found: C, 79.62; H, 6.82. Single-crystal X-Ray diagram: crystal of compound **5t** was grown by slow diffusion of EtOAc into a solution of compound **5t** in CH₂Cl₂ to yield colorless prisms. The compound crystallizes in the monoclinic crystal system, space group P 21/c, a = 10.3721(7) Å, b = 18.7809(11) Å, c = 10.7938(6) Å, V = 1970.8(2) Å³, Z = 4, $d_{calcd} = 1.269$ mg/cm³, F(000) = 800, 2θ range 2.095~26.383°, R indices (all data) R1 = 0.0556, wR2 = 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 BF₃·OEt₂ (57 mg, 0.4 mmol), **3a** (63 mg, 0.2 mmol) and **7c** (41 mg, 0.3 mmol) in CH₂Cl₂ (5 mL) at 25 °C for 20 h. Purification on silica gel (hexanes/EtOAc = 3/1) afforded 5u (84%, 73 mg). Colorless solid; mp = 199-200 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M⁺+1) calcd for C₂₆H₂₉O₄S 437.1787, found 437.1789; ¹H NMR (400 MHz, CDCl₃): δ 7.47 (d, J = 8.0 Hz, 2H), 7.13 (d, J = 8.0 Hz, 2H), 7.09-7.01 (m, 3H), 6.79-6.76 (m, 2H), 6.29 (d, J = 2.4 Hz, 1H), 5.68 (d, J = 2.4 Hz, 1H), 4.39 (d, J = 8.4 Hz, 1H), 3.81 (s, 3H), 3.63-3.58 (m, 1H), 3.50 (s, 3H), 3.29-3.23 (m, 1H), 2.61 (ddd, J = 4.4, 6.8, 11.2 Hz, 1H), 2.38 (s, 3H), 2.00 (ddd, J = 1.6, 6.4, 9.6 Hz, 1H), 1.43 (d, J = 6.8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 158.26, 158.21, 143.58, 142.61, 139.27, 136.61, 129.37 (2x), 129.31 (2x), 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 **5u** was grown by slow diffusion of EtOAc into a solution of compound 5u in CH₂Cl₂ to yield colorless prisms. The compound crystallizes in the monoclinic crystal system, space group P 21/c, a = 23.259(3) Å, b = 5.6619(4) Å, c = 17.6922(16) Å, V = 2155.0(3) Å³, Z = 4, $d_{calcd} = 1.346$ mg/cm³, F(000) = 928, 2θ range 0.946~26.387°, R indices (all data) R1 = 0.0841, wR2 = 0.2079.



1.4.22.

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

(5v). According to the general procedure, reaction was performed in the presence of $BF_3 \cdot OEt_2$ (57 mg, 0.4 mmol), **3a** (63 mg, 0.2 mmol) and **7d** (50 mg, 0.3 mmol) in CH_2Cl_2 (5 mL) at 25 °C for 20 h. Purification on silica gel (hexanes/EtOAc = 3/1) afforded **5v** (80%, 75 mg). Colorless gum; HRMS (ESI, M⁺+1) calcd for $C_{27}H_{31}O_5S$ 467.1892, found 467.1898; ¹H NMR (400 MHz, CDCl₃): δ 7.55 (d,

J = 8.0 Hz, 2H), 7.18-7.12 (m, 5H), 7.04-7.02 (m, 2H), 5.98 (s, 1H), 4.41 (d, J = 9.2 Hz, 1H), 3.90 (s, 3H), 3.90-3.83 (m, 1H), 3.80 (s, 3H), 3.52 (s, 3H), 3.38-3.34 (m, 1H), 2.37 (s, 3H), 2.21 (dt, J = 3.2, 16.8 Hz, 1H), 2.08 (dt, J = 5.6, 16.8 Hz, 1H), 1.32 (d, J = 6.8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 151.90, 151.45, 150.46, 144.04, 143.90, 140.37, 135.62, 132.19, 129.41 (2x), 129.13 (2x), 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 e (5x). According to the general procedure, reaction was performed in the presence of BF₃·OEt₂ (57 mg, 0.4 mmol), **3a** (63 mg, 0.2 mmol) and **7e** (54 mg, 0.3 mmol) in CH₂Cl₂ (5 mL) at 25 °C for 20 h. Purification on silica gel (hexanes/EtOAc = 3/1) afforded a mixture of **5w** and **5x** (75%, 72 mg) with a ratio of 2:1. HRMS (ESI, M^++1) calcd for C₂₉H₃₅O₄S 479.2256, found 479.2258; For major product: ¹H NMR (400 MHz, CDCl₃): δ 7.58-7.56 (m, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 7.14-7.08 (m, 3H), 6.95-6.93 (m, 2H), 6.77 (s, 1H), 6.25 (s, 1H), 4.54 (d, J = 7.6 Hz, 1H), 4.01-3.94 (m, 2H), 3.78-3.66 (m, 2H), 3.57 (s, 3H), 2.96-2.92 (m, 1H), 2.42-2.35 (m, 2H), 2.38 (s, 3H), 1.83-1.70 (m, 2H), 1.52-1.43 (m, 2H), 1.40-1.37 (m, 2H), 0.96 (t, J = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 147.93, 147.16, 144.40, 135.42, 132.95, 129.79, 129.46 (2x), 128.72, 128.62 (4x), 128.40 (2x), 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: ¹H NMR (400 MHz, CDCl₃): δ 7.58-7.56 (m, 2H), 7.18 (d, J = 8.0 Hz, 2H), 7.14-7.08 (m, 3H), 6.95-6.93 (m, 2H), 6.76 (s, 1H), 6.24 (s, 1H), 4.52 (d, J = 6.8 Hz, 1H), 4.01-3.94 (m, 2H), 3.83 (s, 3H), 3.78-3.66 (m, 2H), 2.96-2.92 (m, 1H), 2.42-2.35 (m, 2H), 2.38 (s, 3H), 1.83-1.70 (m, 2H), 1.52-1.43 (m, 2H), 1.40-1.37 (m, 2H), 0.86 (t, J = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 147.90, 146.95, 144.12, 135.42, 132.82, 129.87, 129.46 (2x), 128.96, 128.62 (4x), 128.40 (2x), 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 6a-i is as follows: $BF_3 \cdot OEt_2$ (57 mg, 0.4 mmol) was added to a solution of **4a-g** (0.2 mmol) and **7a-b**, **7f** (0.3 mmol) in CH_2Cl_2 (5 mL) at 25 °C. The reaction mixture was stirred at 25 °C for 20 h. The reaction mixture was concentrated and the residue was diluted with water (10 mL) and the mixture was extracted with CH_2Cl_2 (3 x 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 - 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 BF₃·OEt₂ (57 mg, 0.4 mmol), 4a (69 mg, 0.2 mmol) and 7a (41 mg, 0.3 mmol) in CH₂Cl₂ (5 mL) at 25 °C for 20 h. Purification on silica gel (hexanes/EtOAc = 3/1) afforded 6a (82%, 76 mg). Colorless solid; mp = 191-192 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M⁺+1) calcd for $C_{28}H_{33}O_4S$ 465.2100, found 465.2102; ¹H NMR (400 MHz, CDCl₃): δ 7.72 (d, J = 8.4 Hz, 2H), 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 (d, J = 2.4 Hz, 1H), 4.13-4.08 (m, 1H), 3.90 (s, 3H), 3.77 (s, 3H), 2.42 (s, 3H), 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 (s, 3H), 1.17 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 148.11, 146.90, 144.40, 144.29, 139.15, 135.28, 129.62 (2x), 128.83 (2x), 128.31 (2x), 127.40 (2x), 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 C₂₈H₃₂O₄S: C, 72.38; H, 6.94. Found: C, 72.50; H, 7.18. Single-crystal X-Ray diagram: crystal of compound **6a** was grown by slow diffusion of EtOAc into a solution of compound **6a** in CH₂Cl₂ to yield colorless prisms. The compound crystallizes in the orthorombic crystal system, space group P 21 21 21, a = 9.4078(8) Å, b = 9.4698(8) Å, c = 26.640(2) Å, V = 2373.3(4) Å³, Z = 4, $d_{calcd} = 1.300$ mg/cm³, F(000) = 992, 20 range 1.529~26.480°, R indices (all data) R1 = 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 BF₃·OEt₂ (57 mg, 0.4 mmol), **4b** (75 mg, 0.2 mmol) and **7a** (41 mg, 0.3 mmol) in CH₂Cl₂ (5 mL) at 25 °C for 20 h. Purification on silica gel (hexanes/EtOAc = 3/1) afforded **6b** (82%, 81 mg). Colorless solid; mp = 123-124 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^+ +1) calcd for C₂₉H₃₅O₅S 495.2205, found 495.2209; ¹H NMR (400 MHz, CDCl₃): δ 7.67 (d, *J* = 8.4 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 6.90 (s, 1H), 6.86 (d, *J* = 8.4 Hz, 2H), 6.72 (d, *J* = 8.8 Hz, 2H), 6.43 (s, 1H), 4.91 (d, *J* = 3.2 Hz, 1H), 4.05-4.01 (m, 1H), 3.87 (s, 3H), 3.74 (s, 3H), 3.73 (s, 3H), 2.39 (s, 3H), 2.21-2.13 (m, 1H), 1.92-1.83 (m, 1H), 1.73-1.67 (m, 1H), 1.57-1.51 (m, 1H), 1.33 (s, 3H), 1.18 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 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 **6b** was grown by slow diffusion of EtOAc into a solution of compound **6b** in CH₂Cl₂ to yield colorless prisms. The compound crystallizes in the orthorombic crystal system, space group P 21/c, a = 10.4874(8) Å, b = 11.6664(8) Å, c = 24.139(2) Å, V = 2953.4(4) Å³, Z = 4, $d_{calcd} = 1.112$ mg/cm³, F(000) = 1056, 2θ range 2.428~26.356°, R indices (all data) R1 = 0.1542, wR2 = 0.2103.



1.5.3.

2,3-Dimethoxy-5,5-dimethyl-8-(toluene-4-sulfonyl)-9-*p***-tolyl-6,7,8,9-tetrahydro-5***H***-benzocycl oheptene (6c).** According to the general procedure, reaction was performed in the presence of BF₃·OEt₂ (57 mg, 0.4 mmol), **4c** (72 mg, 0.2 mmol) and **7a** (41 mg, 0.3 mmol) in CH₂Cl₂ (5 mL) at 25 °C for 20 h. Purification on silica gel (hexanes/EtOAc = 5/1) afforded **6c** (80%, 76 mg). Colorless solid; mp = 158-159 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M⁺+1) calcd for C₂₉H₃₅O₄S 479.2256, found 479.2258; ¹H NMR (400 MHz, CDCl₃): δ 7.71 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 7.01 (d, *J* = 8.0 Hz, 2H), 6.91 (s, 1H), 6.85 (d, *J* = 8.4 Hz, 2H), 6.45 (s, 1H), 4.92 (d, *J* = 2.0 Hz, 1H), 4.11-4.07 (m, 1H), 3.90 (s, 3H), 3.77 (s, 3H), 2.42 (s, 3H), 2.28 (s, 3H), 2.20-2.12 (m, 1H), 1.94-1.87 (m, 1H), 1.70 (dd, *J* = 9.2, 14.8 Hz, 1H), 1.50 (dd, *J* = 9.2, 14.8 Hz, 1H), 1.34 (s, 3H), 1.18 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 147.98, 146.78, 144.27, 141.09, 139.08, 135.82, 135.31, 129.83 (2x), 128.93 (2x), 128.73 (2x), 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 BF₃·OEt₂ (57 mg, 0.4 mmol), **4d** (84 mg, 0.2 mmol) and **7a** (41 mg, 0.3 mmol) in CH₂Cl₂ (5 mL) at 25 °C for 20 h. Purification on silica gel (hexanes/EtOAc = 4/1) afforded **6d** (82%, 89 mg). Colorless gum; HRMS (ESI, M⁺+1) calcd for C₃₄H₃₇O₄S 541.2413, found 541.2412; ¹H NMR (400 MHz, CDCl₃): δ 7.72 (d, *J* = 8.4 Hz, 2H), 7.56-7.53 (m, 2H), 7.45-7.40 (m, 4H), 7.35-7.31 (m, 1H), 7.28-7.26 (m, 2H), 7.05 (d, *J* = 8.4 Hz, 2H), 6.94 (s, 1H), 6.49 (s, 1H), 5.02 (d, *J* = 3.2 Hz, 1H), 4.16-4.11 (m, 1H), 3.91 (s, 3H), 3.77 (s, 3H), 2.40 (s, 3H), 2.26-2.18 (m, 1H), 1.97-1.89 (m, 1H), 1.74 (dd, *J* = 9.6, 14.8 Hz, 1H), 1.58 (dd, *J* = 9.6, 14.8 Hz, 1H), 1.37 (s, 3H), 1.22 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 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 BF₃·OEt₂ (57 mg, 0.4 mmol), **4e** (79 mg, 0.2 mmol) and **7a** (41 mg, 0.3 mmol) in CH₂Cl₂ (5 mL) at 25 °C for 20 h. Purification on silica gel (hexanes/EtOAc = 4/1) afforded **6e** (78%, 80 mg). Colorless gum; HRMS (ESI, M⁺+1) calcd for C₃₂H₃₅O₄S 515.2256, found 515.2260; ¹H NMR (400 MHz, CDCl₃): δ 7.79-7.76 (m, 1H), 7.73 (d, *J* = 8.8 Hz, 1H), 7.69 (d, *J* = 8.0 Hz, 2H), 7.62-7.57 (m, 1H), 7.45-7.40 (m, 2H), 7.28 (dd, *J* = 2.0, 8.8 Hz, 1H), 7.25 (br s, 1H), 7.19 (d, *J* = 8.0 Hz, 2H), 6.96 (s, 1H), 6.51 (s, 1H), 5.17 (d, *J* = 3.2 Hz, 1H), 4.24-4.17 (m, 1H), 3.92 (s, 3H), 3.73 (s, 3H), 2.36 (s, 3H), 2.28-2.19 (m, 1H), 1.95-1.87 (m, 1H), 1.73 (dd, *J* = 9.6, 14.8 Hz, 1H), 1.55 (dd, *J* = 9.6, 14.8 Hz, 1H), 1.38 (s, 3H), 1.23 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 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 C₃₂H₃₄O₄S: C, 74.68; 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 BF₃·OEt₂ (57 mg, 0.4 mmol), **4f** (72 mg, 0.2 mmol) and **7a** (41 mg, 0.3 mmol) in CH₂Cl₂ (5 mL) at 25 °C for 20 h. Purification on silica gel (hexanes/EtOAc = 3/1) afforded **6f** (76%, 73 mg). Colorless solid; mp = 167-168 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M⁺+1) calcd for C₂₈H₃₃O₅S 481.2049, found 481.2054; ¹H NMR (400 MHz, CDCl₃): δ 7.79-7.76 (m, 2H), 7.57-7.53 (m, 1H), 7.46-7.42 (m, 2H), 6.89 (s, 1H), 6.87 (d, *J* = 8.8 Hz, 2H), 6.71 (d, *J* = 8.8 Hz, 2H), 6.44 (s, 1H), 4.94 (d, *J* = 3.6 Hz, 1H), 4.09-4.03 (m, 1H), 3.87 (s, 3H), 3.74 (s, 3H), 3.73 (s, 3H), 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, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 157.93, 147.91, 146.73, 139.04, 138.49, 135.41, 133.21, 128.82 (2x), 128.58 (4x), 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 C₂₈H₃₂O₅S: 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 (6g). According to the general procedure, reaction was performed in the presence of BF₃·OEt₂ (57 mg, 0.4 mmol), 4g (60 mg, 0.2 mmol) and 7a (41 mg, 0.3 mmol) in CH₂Cl₂ (5 mL) at 25 °C for 20 h. Purification on silica gel (hexanes/EtOAc = 3/1) afforded 6g (80%, 67 mg). Colorless gum; HRMS (ESI, M⁺+1) calcd for C₂₃H₃₁O₅S 419.1892, found 419.1897; ¹H NMR (400 MHz, CDCl₃): δ 7.01 (d, *J* = 8.4 Hz, 2H), 6.97 (s, 1H), 6.84 (d, *J* = 8.4 Hz, 2H), 6.54 (s, 1H), 4.92 (d, *J* = 3.6 Hz, 1H), 3.95-3.90 (m, 1H), 3.90 (s, 3H), 3.77 (s, 3H), 3.75 (s, 3H), 2.53 (s, 3H), 2.25-2.02 (m, 2H), 1.80 (dd, *J* = 9.2, 14.8 Hz, 1H), 1.64-1.55 (m, 1H), 1.40 (s, 3H), 1.19 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 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 BF₃·OEt₂ (57 mg, 0.4 mmol), 4f (72 mg, 0.2 mmol) and 7b (37 mg, 0.3 mmol) in CH₂Cl₂ (5 mL) at 25 °C for 20 h. Purification on silica gel (hexanes/EtOAc = 3/1) afforded 6h (85%, 79 mg). Colorless gum; HRMS (ESI, M⁺+1) calcd for C₂₇H₂₉O₅S 465.1736, found 465.1739; ¹H NMR (400 MHz, CDCl₃): δ 7.76-7.74 (m, 2H), 7.57-7.53 (m, 1H), 7.46-7.43 (m, 2H), 6.91 (s, 1H), 6.84 (d, *J* = 8.4 Hz, 2H), 6.69 (d, *J* = 8.8 Hz, 2H), 6.45 (s, 1H), 6.90 (d, *J* = 1.2 Hz, 1H), 5.88 (d, *J* = 1.2 Hz, 1H), 4.89 (d, *J* = 4.4 Hz, 1H), 4.12-4.01 (m, 1H), 3.78 (s, 3H), 2.32-2.24 (m, 1H), 1.91-1.50 (m, 3H), 1.35 (s, 3H), 1.19 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 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 BF₃·OEt₂ (57 mg, 0.4 mmol), 4f (72 mg, 0.2 mmol) and 7f (67 mg, 0.3 mmol) in CH₂Cl₂ (5 mL) at 25 °C for 20 h. Purification on silica gel (hexanes/EtOAc = 3/1) afforded 6i (85%, 96 mg). Colorless solid; mp = 151-152 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for C₃₄H₄₅O₅S 565.2988, found 565.2989; ¹H NMR (400 MHz, CDCl₃): δ 7.77-7.75 (m, 2H), 7.57-7.53 (m, 1H), 7.46-7.42 (m, 2H), 6.90 (s, 1H), 6.87 (d, J = 8.4 Hz, 2H), 6.71 (d, J = 8.0 Hz, 2H), 6.45 (s, 1H), 4.92 (d, J = 3.6 Hz, 1H), 4.07-4.04 (m, 1H), 4.00 (t, J = 6.4 Hz, 2H), 3.90-3.77 (m, 2H), 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 (t, J = 6.8 Hz, 3H), 0.92 (t, J = 6.4 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 157.98, 148.08, 147.13, 139.22, 138.68, 135.48, 133.17, 128.82 (2x), 128.74 (2x), 128.70 (2x), 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 6i was grown by slow diffusion of EtOAc into a solution of compound **6i** in CH₂Cl₂ to yield colorless prisms. The compound crystallizes in the monoclinic crystal system, space group P 21/n, a = 10.3966(8) Å, b = 11.0245(10) Å, c = 26.053(2) Å, V = 2984.6(4) Å³, Z = 4, $d_{calcd} = 1.257$ mg/cm³, F(000) = 1216, 2θ range 1.564~26.401°, R indices (all data) R1 = 0.0665, wR2 = 0.1384.

1.6. A representative synthetic procedure of compounds 8a-c is as follows: $BF_3 \cdot OEt_2$ (28 mg, 0.2 mmol) was added to a solution of **3p-r** (0.2 mmol) in CH_2CI_2 (5 mL) at 25 °C. The reaction mixture was stirred at 25 °C for 20 h. The reaction mixture was concentrated and the residue was diluted with water (10 mL) and the mixture was extracted with CH_2CI_2 (3 x 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 **8a-c**.



1.6.1. 5-Methyl-3-(toluene-4-sulfonyl)-2-(4-trifluoromethylphenyl)tetrahydrofuran (8a). According to the general procedure, reaction was performed in the presence of BF₃·OEt₂ (28 mg, 0.2 mmol) and **3p** (77 mg, 0.2 mmol) in CH₂Cl₂ (5 mL) at 25 °C for 20 h. Purification on silica gel (hexanes/EtOAc = 5/1) afforded **8a** (90%, 69 mg). Colorless solid; mp = 151-152 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M⁺+1) calcd for C₁₉H₂₀F₃O₃S 385.1085, found 385.1088; ¹H NMR (400 MHz, CDCl₃): δ 7.33 (d, *J* = 8.8 Hz, 2H), 7.28 (d, *J* = 8.8 Hz, 2H), 7.17 (d, *J* = 8.8 Hz, 2H), 7.03 (d, *J* = 8.8 Hz, 2H), 5.35 (d, *J* = 5.6 Hz, 1H), 4.85-4.80 (m, 1H), 4.17-4.13 (m, 1H), 3.08 (ddd, *J* = 3.6, 6.8, 14.4 Hz, 1H), 2.35 (s, 3H), 2.12 (dt, *J* = 8.0, 14.0 Hz, 1H), 1.35 (d, *J* = 6.4 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 144.03, 140.32, 136.04, 129.93, 129.47 (2x), 127.67, 127.60 (2x), 127.46 (2x), 124.34 (q, *J* = 3.8 Hz, 2x), 79.49, 74.81, 68.01, 35.30, 21.72, 21.35. Single-crystal X-Ray diagram: crystal of compound **8a** was grown by slow diffusion of EtOAc into a solution of compound **8a** in CH₂Cl₂ to yield colorless prisms. The compound crystallizes in the orthorhombic crystal system, space group P 21 21 21, *a* = 5.6186(6) Å, *b* = 8.3590(8) Å, *c* = 37.132(3) Å, *V* =

1743.9(3) Å³, Z = 4, $d_{calcd} = 1.464 \text{ mg/cm}^3$, F(000) = 800, 2θ range $1.097 \sim 26.447^\circ$, R indices (all data) R1 = 0.0461, wR2 = 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 BF₃·OEt₂ (28 mg, 0.2 mmol) and 3q (72 mg, 0.2 mmol) in CH₂Cl₂ (5 mL) at 25 °C for 20 h. Purification on silica gel (hexanes/EtOAc = 5/1) afforded **8b** (92%, 66 mg). Colorless solid; mp = 116-118 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M⁺+1) calcd for C₁₈H₂₀NO₅S 362.1062, found 362.1068; ¹H NMR (400 MHz, CDCl₃): δ 8.06-8.03 (m, 1H), 7.84-7.82 (m, 1H), 7.76 (br t, J = 2.0 Hz, 1H), 7.44 (t, J = 8.4 Hz, 1H), 7.23 (d, J = 8.4 Hz, 2H), 7.09 (d, J = 8.4 Hz, 2H), 5.41 (d, J = 6.0 Hz, 1H), 4.88-4.80 (m, 1H), 4.23-4.19 (m, 1H), 3.02 (ddd, J = 4.0, 6.8, 14.4 Hz, 1H), 2.33 (s, 3H), 2.10 (dt, J = 7.2, 14.4 Hz, 1H), 1.34 (d, J = 6.4 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 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 C₁₈H₁₉NO₅S: C, 59.82; H, 5.30. Found: C, 59.98; H, 5.51. Single-crystal X-Ray diagram: crystal of compound 8b was grown by slow diffusion of EtOAc into a solution of compound 8b in CH₂Cl₂ to yield colorless prisms. The compound crystallizes in the monoclinic crystal system, space group P 21/n, a = 11.8500(15) Å, b = 10.4794(13) Å, c = 13.4988(17) Å, V = 1675.5(4) Å³, Z = 4, d_{calcd} = 1.433 mg/cm³, F(000) = 760, 2 θ range 2.252~26.378°, R indices (all data) R1 = 0.0484, wR2 = 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 BF₃·OEt₂ (28 mg, 0.2 mmol) and **3r** (72 mg, 0.2 mmol) in CH₂Cl₂ (5 mL) at 25 °C for 20 h. Purification on silica gel (hexanes/EtOAc = 5/1) afforded **8c** (95%, 69 mg). Colorless solid; mp = 173-174 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M⁺+1) calcd for C₁₈H₂₀NO₅S 362.1062, found 362.1068; ¹H NMR (400 MHz, CDCl₃): δ 8.00 (d, *J* = 8.4 Hz, 2H), 7.43 (d, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 8.4 Hz, 2H), 7.12 (d, *J* = 8.4 Hz, 2H), 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, 3H), 2.10-2.03 (m, 1H), 1.34 (d, *J* = 6.0 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 144.68, 143.95, 136.10, 129.60 (2x), 128.27 (2x), 127.67 (2x), 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 9a-g is as follows: BF₃·OEt₂ (28 mg, 0.2 mmol) was added to a solution of 4a, 4d-e and 4h-k (0.2 mmol) in CH₂Cl₂ (5 mL) at 25 °C. The

reaction mixture was stirred at 25 °C for 20 h. The reaction mixture was concentrated and the residue was diluted with water (10 mL) and the mixture was extracted with CH_2Cl_2 (3 x 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 = 5/1~3/1) 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 BF₃-OEt₂ (28 mg, 0.2 mmol) and **4a** (69 mg, 0.2 mmol) in CH₂Cl₂ (5 mL) at 25 °C for 20 h. Purification on silica gel (hexanes/EtOAc = 3/1) afforded **9a** (90%, 62 mg). Colorless solid; mp = 148-149 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M⁺+1) calcd for C₂₀H₂₅O₃S 345.1524, found 345.1523; ¹H NMR (400 MHz, CDCl₃): δ 7.25-7.20 (m, 2H), 7.14 (d, *J* = 8.4 Hz, 2H), 7.09-7.04 (m, 3H), 6.95 (d, *J* = 8.4 Hz, 2H), 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 (s, 3H), 1.28 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 142.80, 138.70, 138.46, 128.97 (2x), 127.62 (2x), 127.52 (2x), 126.86, 126.15 (2x), 72.83, 71.01, 62.88, 31.37, 31.09, 21.58, 21.47, 21.35; Anal. Calcd for C₂₀H₂₄O₃S: C, 69.73; 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 **9a** in CH₂Cl₂ to yield colorless prisms. The compound crystallizes in the monoclinic crystal system, space group P 21/c, *a* = 6.0190(2) Å, *b* = 22.9167(10) Å, *c* = 13.0996(6) Å, *V* = 1770.47(13) Å³, *Z* = 4, *d*_{calcd} = 1.292 mg/cm³, *F*(000) = 736, 2*θ* range 1.777~26.462°, R indices (all data) R1 = 0.0407, wR2 = 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 BF₃·OEt₂ (28 mg, 0.2 mmol) and **4h** (72 mg, 0.2 mmol) in CH₂Cl₂ (5 mL) at 25 °C for 20 h. Purification on silica gel (hexanes/EtOAc = 3/1) afforded **9b** (92%, 67 mg). Colorless solid; mp = 164-166 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M⁺+1) calcd for C₂₀H₂₄FO₃S 363.1430, found 363.1436; ¹H NMR (400 MHz, CDCl₃): δ 7.18-7.14 (m, 4H), 7.01 (d, *J* = 8.4 Hz, 2H), 6.75-6.71 (m, 2H), 5.05 (d, *J* = 2.8 Hz, 1H), 3.52-3.50 (m, 1H), 2.79-2.75 (m, 1H), 2.33 (s, 3H), 2.24-2.11 (m, 2H), 1.50-1.46 (m, 1H), 1.41 (s, 3H), 1.28 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 161.88 (d, *J* = 243.3 Hz), 143.15, 138.35, 134.44 (d, *J* = 3.1 Hz), 129.02 (2x), 127.79 (d, *J* = 8.4 Hz, 2x), 127.42 (2x), 114.36 (d, *J* = 22.0 Hz, 2x), 73.00, 70.50, 62.83, 31.25, 31.05, 21.47, 21.36 (2x); Anal. Calcd for C₂₀H₂₃FO₃S: 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 BF₃·OEt₂ (28 mg, 0.2 mmol) and **4i** (78 mg, 0.2 mmol) in CH₂Cl₂ (5 mL) at 25 °C for 20 h. Purification on silica gel (hexanes/EtOAc = 3/1) afforded **9c** (90%, 70 mg). Colorless solid; mp = 185-186 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M⁺+1) calcd for C₂₀H₂₄NO₅S 390.1375, found 390.1378; ¹H NMR (400 MHz, CDCl₃): δ 7.90 (dd, *J* = 0.8, 8.4 Hz, 1H), 7.78 (d, *J* = 8.4 Hz, 1H), 7.75 (br s, 1H), 7.33 (t, *J* = 8.0 Hz, 1H), 7.14 (d, *J* = 8.0 Hz, 2H), 6.95 (d, *J* = 8.0 Hz, 2H), 5.14 (d, *J* = 3.2 Hz, 1H), 3.65-3.63 (m, 1H), 2.76-2.71 (m, 1H), 2.25 (s, 3H), 2.23-2.08 (m, 2H), 1.50-1.45 (m, 1H), 1.40 (s, 3H), 1.26 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 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 C₂₀H₂₃NO₅S: 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 BF₃·OEt₂ (28 mg, 0.2 mmol) and **4j** (78 mg, 0.2 mmol) in CH₂Cl₂ (5 mL) at 25 °C for 20 h. Purification on silica gel (hexanes/EtOAc = 3/1) afforded **9d** (94%, 73 mg). Colorless solid; mp = 217-218 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M⁺+1) calcd for C₂₀H₂₄NO₅S 390.1375, found 390.1380; ¹H NMR (400 MHz, CDCl₃): δ 7.90 (d, *J* = 9.2 Hz, 2H), 7.38 (d, *J* = 8.4 Hz, 2H), 7.20 (d, *J* = 8.4 Hz, 2H), 6.99 (d, *J* = 8.0 Hz, 2H), 5.16 (d, *J* = 2.8 Hz, 1H), 3.59-3.56 (m, 1H), 2.77-2.69 (m, 1H), 2.32 (s, 3H), 2.28-2.14 (m, 2H), 1.52-1.48 (m, 1H), 1.43 (s, 3H), 1.30 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 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 (2x), 21.48, 21.41, 21.38; Anal. Calcd for C₂₀H₂₃NO₅S: 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 BF₃·OEt₂ (28 mg, 0.2 mmol) and **4k** (82 mg, 0.2 mmol) in CH₂Cl₂ (5 mL) at 25 °C for 20 h. Purification on silica gel (hexanes/EtOAc = 3/1) afforded **9e** (90%, 74 mg). Colorless solid; mp = 167-168 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M⁺+1) calcd for C₂₁H₂₄F₃O₃S 413.1398, found 413.1401; ¹H NMR (400 MHz, CDCl₃): δ 7.27 (d, *J* = 8.8 Hz, 2H), 7.24 (d, *J* = 8.8 Hz, 2H), 7.10 (d, *J* = 8.4 Hz, 2H), 6.93 (d, J = 8.0 Hz, 2H), 5.11 (d, J = 2.4 Hz, 1H), 3.58-3.56 (m, 1H), 2.91-2.86 (m, 1H), 2.29 (s, 3H), 2.27-2.15 (m, 2H), 1.53-1.50 (m, 1H), 1.44 (s, 3H), 1.29 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 143.28 (2x), 142.65, 138.09, 129.12 (2x), 128.86, 127.25 (2x), 126.50 (2x), 124.40 (q, J = 3.7 Hz, 2x), 73.18, 70.52, 62.19, 31.31, 31.03, 21.41, 21.19, 21.16; Anal. Calcd for C₂₁H₂₃F₃O₃S: 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 BF₃·OEt₂ (28 mg, 0.2 mmol) and **4d** (84 mg, 0.2 mmol) in CH₂Cl₂ (5 mL) at 25 °C for 20 h. Purification on silica gel (hexanes/EtOAc = 3/1) afforded **9f** (82%, 69 mg). Colorless solid; mp = 208-209 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M⁺+1) calcd for C₂₆H₂₉O₃S 421.1837, found 421.1842; ¹H NMR (400 MHz, CDCl₃): δ 7.52-7.43 (m, 4H), 7.38-7.33 (m, 1H), 7.27-7.22 (m, 4H), 7.16 (d, *J* = 8.0 Hz, 2H), 6.91 (d, *J* = 8.0 Hz, 2H), 5.14 (d, *J* = 3.2 Hz, 1H), 3.61-3.59 (m, 1H), 2.94-2.89 (m, 1H), 2.30-2.17 (m, 2H), 2.23 (s, 3H), 1.55-1.51 (m, 1H), 1.46 (s, 3H), 1.32 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 142.69, 140.89, 139.86, 138.59, 137.74, 128.95 (2x), 128.71 (2x), 127.43 (2x), 127.19, 126.89 (2x), 126.58 (2x), 126.27 (2x), 72.94, 70.81, 62.95, 31.53, 31.15, 21.50, 21.33 (2x); Anal. Calcd for C₂₆H₂₈O₃S: 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 BF₃·OEt₂ (28 mg, 0.2 mmol) and **4e** (79 mg, 0.2 mmol) in CH₂Cl₂ (5 mL) at 25 °C for 20 h. Purification on silica gel (hexanes/EtOAc = 3/1) afforded **9g** (84%, 66 mg). Colorless solid; mp = 192-193 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M⁺+1) calcd for C₂₄H₂₇O₃S 395.1681, found 395.1684; ¹H NMR (400 MHz, CDCl₃): δ 7.69-7.66 (m, 3H), 7.44-7.38 (m, 3H), 7.12 (dd, *J* = 1.2, 8.4 Hz, 1H), 6.97 (d, *J* = 8.4 Hz, 2H), 6.49 (d, *J* = 8.0 Hz, 2H), 5.24 (d, *J* = 2.4 Hz, 1H), 3.64-3.63 (m, 1H), 3.00-2.90 (m, 1H), 2.40-2.22 (m, 2H), 2.02 (s, 3H), 1.57-1.54 (m, 1H), 1.50 (s, 3H), 1.34 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 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 C₂₄H₂₆O₃S: C, 73.06; H, 6.64. Found: C, 73.18; H, 6.72.

1.8. A representative synthetic procedure of compounds 10a-b is as follows: $BF_3 \cdot OEt_2$ (57 mg, 0.4 mmol) was added to a solution of **4I** and **4n** (0.2 mmol) in CH_2CI_2 (5 mL) at 25 °C. The reaction
mixture was stirred at 25 °C for 20 h. The reaction mixture was concentrated and the residue was diluted with water (10 mL) and the mixture was extracted with CH_2Cl_2 (3 x 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 = 5/1~3/1) 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 BF₃·OEt₂ (57 mg, 0.4 mmol) and **4I** (82 mg, 0.2 mmol) in CH_2CI_2 (5 mL) at 25 °C for 20 h. Purification on silica gel (hexanes/EtOAc = 3/1) afforded **10a** (76%, 63 mg). Colorless solid; mp = 224-225 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^+ +1) calcd for C₂₅H₃₃O₃S 413.2150, found 413.2155; ¹H NMR (400 MHz, CDCl₃): δ 7.22-7.20 (m, 2H), 7.12-7.04 (m, 5H), 6.96 (d, J = 8.4 Hz, 2H), 5.17 (d, J = 3.6 Hz, 1H), 3.73-3.70 (m, 1H), 2.79 (d, J = 2.4 Hz, 1H), 2.31 (s, 3H), 2.17 (dd, J = 2.4, 14.0 Hz, 1H), 1.94 (dt, J = 5.2, 14.0 Hz, 1H), 1.81-1.55 (m, 4H), 1.46-1.38 (m, 2H), 1.33 (s, 3H), 1.03 (s, 3H), 0.79 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 142.65, 138.79, 138.77, 128.95 (2x), 127.53 (2x), 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 C₂₅H₃₂O₃S: C, 72.78; 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 **10a** in CH₂Cl₂ to yield colorless prisms. The compound crystallizes in the orthorhombic crystal system, space group P b c a, a = 16.0500(8) Å, b = 11.2326(5) Å, c = 10.0500(8)24.8893(13) Å, V = 4487.1(4) Å³, Z = 8, d_{calcd} = 1.221 mg/cm³, F(000) = 1776, 2 θ range 1.636~26.396°, R indices (all data) R1 = 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 BF₃·OEt₂ (57 mg, 0.4 mmol) and **4n** (86 mg, 0.2 mmol) in CH₂Cl₂ (5 mL) at 25 °C for 20 h. Purification on silica gel (hexanes/EtOAc = 3/1) afforded **10b** (80%, 69 mg). Colorless solid; mp = 199-200 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M⁺+1) calcd for C₂₅H₃₂FO₃S 431.2056, found 431.2060; ¹H NMR (400 MHz, CDCl₃): δ 7.18-7.13 (m, 4H), 7.02 (d, *J* = 8.0 Hz, 2H), 6.77-6.72 (m, 2H), 5.13 (d, *J* = 3.6 Hz, 1H), 3.69-3.66 (m, 1H), 2.77 (dt, *J* = 2.4, 14.4 Hz, 1H), 2.34 (s, 3H), 2.17 (dd, *J* = 2.8, 14.0 Hz, 1H), 1.93 (dt, *J* = 2.8, 14.0 Hz, 1H), 1.80-1.54 (m, 4H), 1.46-1.39 (m, 2H), 1.33 (s, 3H), 1.02 (s, 3H), 0.78 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 161.95 (d, *J* = 243.4 Hz), 143.07, 138.69, 133.56 (d, *J* = 3.8 Hz), 129.03 (2x), 128.13 (d, *J* = 7.6 Hz, 2x), 127.33 (2x), 114.35 (d, *J* = 21.2 Hz, 2x), 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 C₂₅H₃₁FO₃S: C, 69.74; H, 7.26. Found: C, 69.86; H, 7.37. Single-crystal X-Ray diagram: crystal of compound **10b** was grown by slow diffusion of EtOAc into a solution of compound **10b** in CH₂Cl₂ to yield colorless prisms. The compound crystallizes in the monoclinic crystal system, space group P 21/n, a = 15.2927(5) Å, b = 18.9203(5) Å, c = 22.9664(7) Å, V = 6644.5(3) Å³, Z = 12, $d_{calcd} = 1.291$ mg/cm³, F(000) = 2760, 2θ range 1.394~26.414°, R indices (all data) R1 = 0.0514, wR2 = 0.1217.



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