Supporting Information

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Materials and Methods. All commercial products were used as received and reagents were stored under ambient conditions unless otherwise stated. The manipulation of solid reagents was conducted on the benchtop unless otherwise stated. Reactions were conducted under an ambient atmosphere unless otherwise stated. Reaction vessels were sealed with a septum. Reactions conducted at elevated temperatures were heated with an oil bath, or aluminum heating block for a 135mm diameter circular hot plate (Chemglass CG-1991-04). Temperatures were regulated using an external thermocouple. For TLC analysis, $R_f$ values are reported based on normal phase silica plates with fluorescent indicator and I$_2$ staining. In the evaluation of TBAF(Pin)$_2$, extracts were eluted through Waters Sep-Pack® Light Silica Cartridges (WAT023537).

Instrumental Information. NMR spectra were obtained on a Varian MR400 (400.53 MHz for $^1$H; 100.13 MHz for $^{13}$C; 376.87 MHz for $^{19}$F) spectrometer. All $^{13}$C NMR data presented are proton-decoupled $^{13}$C NMR spectra, unless noted otherwise. $^1$H and $^{13}$C NMR chemical shifts (δ) are reported in parts per million (ppm) relative to TMS with the residual solvent peak used as an internal reference. $^1$H and $^{19}$F NMR multiplicities are reported as follows: singlet (s), doublet (d), triplet (t), quartet (q), and multiplet (m).

(3S,8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl acetate; (3-acetoxy-5-cholestenel 1. Cholesterol (2 g, 5.18 mmol) was dissolved in dichloromethane (40 mL) while stirring. Pyridine (0.84 mL, 10.36 mmol) was added. To this mixture, acetic anhydride (0.98 mL, 10.36 mmol) was added dropwise. The reaction was stirred for 10 hours, before being dried under vacuum. The product was purified by flash chromatography (10 g, 1:9 EtOAc:Hexane) to yield a waxy white solid (1.7460 g, 79%). TLC $R_f$ = 0.45, 1:9 EtOAc:Hexane. Conformed with commercially available product (Alfa Aesar A15052).
(3S,5R,6R,8S,9S,10R,13R,14S,17R)-5-bromo-6-hydroxy-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)hexadecahydro-1H-cyclopenta[a]phenanthren-3-yl acetate; (3-acetoxy-5-bromocholestan-6-ol) 2. Compound 1 (25 g, 58.3 mmol) was dissolved in 1,4-dioxane (250 mL). A solution of perchloric acid (5.83 mL of 70% perchloric acid added to 25 mL of H₂O; 18.4 mL of resulting solution used) and water (12.5 mL) were added. The flask was wrapped in foil and cooled in a water-ice bath over 15 min. N-bromoacetamide (12.5 g, 90.6 mmol) was added in portions over 15 minutes. The mixture was removed from the ice bath and stirred for 30 minutes, and then cooled in a water-ice bath before being quenched with 150 mL of 10% sodium thiosulfate solution. The product was extracted from the aqueous layer with diethyl ether 3 times, combined organic washes were washed with a 10% sodium thiosulfate solution until the color had been removed (1-2x), with water (1x) and brine (1x). The organic layer was dried over sodium sulfate, the solvent was removed in vacuo and the material was purified by recrystallization from acetone and water to yield the product as a white solid (15.9 g, 52% yield). TLC Rₚ = 0.33, 1:9 EtOAc:Hexane. \(^1\)H-NMR (400.53 MHz, CDCl₃): δ 5.47 (1H, m, 3α-H), 4.17 (1H, s, 6-OH), 2.50 (1H, t, J = 12.01 Hz, 6-H). \(^1\)C-NMR (100.13 MHz, CDCl₃): δ 170.43, 86.68, 75.69, 72.08, 56.06, 55.65, 47.40, 42.67, 40.32, 39.47, 38.42, 38.39, 36.12, 35.73, 35.09, 34.54, 30.55, 28.18, 27.96, 26.33, 24.05, 23.79, 22.85, 22.59, 21.39, 18.70, 18.08, 12.20. HRMS (ESI+) [M+H]⁺ Calculated for C₂₉H₄₉BrO₃: 542.3203; Found: 542.3198.

(3S,5R,6R,8S,9S,10R,13R,14S,17R)-5-bromo-13-methyl-17-((R)-6-methylheptan-2-yl)hexadecahydro-6,10-(epoxymethano)cyclopenta[a]phenanthren-3-yl acetate; (3-acetoxy-5-bromo-6-19-oxidocholestane) 3. Compound 2 (7.7 g, 14.65 mmol) was added to a flame dried flask and suspended in cyclohexane (150 mL). To this solution, lead tetraacetate (8.12 g, 18.31 mmol), and iodine (1.90 g, 7.50 mmol) were added while stirring. The flask was then heated to reflux and stirred for 2 hours. The reaction mixture was cooled to room temperature and quenched 150 mL of 10% sodium thiosulfate solution. The product was extracted with diethyl ether 3 times, washed with additional 10% sodium thiosulfate solution until the color had been removed (1-2x), with water (1x), and with brine (1x). The organic layer was dried over sodium
sulfate, the solvent was removed in vacuo and the material was purified by recrystallization from hexane, yielding a clear pale-yellow residue (5.73 g, 75% yield). **TLC** $R_f = 0.51$, 1:4 EtOAc:Hexane. **$^1$H-NMR** (400.53 MHz, CDCl$_3$): $\delta$ 5.18 (1H, m, 3α-H), 4.04 (1H, d, $J = 4.51$ Hz, 6-H), 3.82 (2H, dd, $J = 8.28$, 70.81 Hz, 19-H), 2.02 (3H, s, 3β-OAc). **$^{13}$C-NMR** (100.13 MHz, CDCl$_3$): $\delta$ 170.30, 82.29, 74.53, 69.98, 67.47, 55.97, 54.32, 48.64, 45.81, 43.13, 41.30, 39.71, 39.47, 36.10, 35.72, 32.81, 28.26, 28.00, 26.86, 23.75, 23.46, 23.24, 22.81, 22.65, 22.56, 21.32, 18.60, 12.40. **HRMS** (ESI+) [M+NH$_4$]$^+$ Calculated for C$_{29}$H$_{47}$BrO$_3$: 540.3047; Found: 540.3041.

(3S,8S,9S,10S,13R,14S,17R)-10-(hydroxymethyl)-13-methyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl acetate; (3-acetoxy-19-hydroxy-5-cholestenyl) 4. Compound 3 (1.463 g, 2.79 mmol) was dissolved in a solution of acetic acid and water (15:1, 42.25 mL). Zinc powder was activated by being stirred under vacuum at 80 °C. The activated zinc (3.654 g, 55.88 mmol) was then added while stirring. The reaction was then stirred for 24 hours, and another portion of zinc powder (1.827 g, 27.94 mmol) was added. After another 24 hours, the reaction mixture was poured into 100 mL of dichloromethane and filtered. The filtrate was concentrated on a rotary evaporator with a KOH trap. The remaining residue was extracted with ethyl acetate, washed with a saturated solution of sodium bicarbonate (1x), and with brine (1x). The organic layer was dried over sodium sulfate, the solvent was removed in vacuo, and the material was purified by flash chromatography (100 g, 1:4 EtOAc:Hexane) yielding a white powder (0.4098g, 33% yield). **TLC** $R_f = 0.35$, 1:4 EtOAc:Hexane. **$^1$H-NMR** (400.53 MHz, CDCl$_3$): $\delta$ 5.77 (1H, d, $J = 5.03$ Hz, 6-H), 4.64 (1H, m, 3α-H), 3.72 (2H, dd, $J = 11.34$, 83.92 Hz, 19-H), 2.03 (3H, s, 3β-OAc). **$^{13}$C-NMR** (100.13 MHz, CDCl$_3$): $\delta$ 170.52, 134.47, 128.33, 73.39, 62.68, 57.55, 56.07, 50.28, 42.50, 41.57, 39.97, 39.49, 38.19, 36.15, 35.76, 33.36, 33.07, 31.22, 28.22, 28.08, 28.00, 24.06, 23.81, 22.81, 22.55, 21.75, 18.69, 12.20. **HRMS** (ESI+) [M+H]$^+$ Calculated for C$_{29}$H$_{48}$O$_3$: 445.3676; Found: 445.3673. [M+NH$_4$]$^+$ Calculated for C$_{29}$H$_{48}$O$_3$: 462.3942; Found: 462.3947. [M+Na]$^+$ Calculated for C$_{29}$H$_{48}$O$_3$: 467.3485.
(3S,8S,9S,10S,13R,14S,17R)-13-methyl-17-((R)-6-methylheptan-2-yl)-10-((tosyloxy)methyl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl acetate; (3-acetoxy-19-tosyloxy-5-cholesten) 5. Compound 4 (0.5620 g, 1.26 mmol) was dissolved in dichloromethane (4.14 mL). Dimethylaminopyridine (0.8492 g, 6.95 mmol), and tosyl chloride (1.2049 g, 6.32 mmol) were added. The mixture was stirred for 72 hours, extracted with dichloromethane, washed with ammonium chloride (1x), and with brine (1x). The organic layer was dried over sodium sulfate and purified by flash chromatography on Florosil gel (20 g, 1:9 EtOAc:Hexane) yielding a white solid (0.4025 g, 53% yield). TLC Rf = 0.46, 1:4 EtOAc:Hexane. 1H-NMR (400.53 MHz, CDCl3): δ 7.79 (2H, d, J = 8.03 Hz, OTs-H), 7.35 (2H, d, J = 8.03 Hz, OTs-H), 5.59 (1H, d, J = 4.73 Hz, 6-H), 4.58 (1H, m, 3α-H), 4.05 (2H, dd, J = 10.08, 40.65 Hz, 19-H), 2.46 (3H, s, OTs-CH3), 2.01 (3H, s, 3β-OAc). 13C-NMR (100.13 MHz, CDCl3): δ 170.47, 144.74, 133.20, 132.83, 129.80, 127.97, 127.93, 72.94, 69.70, 56.98, 55.98, 49.76, 42.25, 39.95, 39.75, 39.50, 37.93, 36.13, 35.75, 32.36, 31.25, 28.13, 28.01, 27.63, 24.02, 23.80, 22.83, 22.57, 21.68, 21.67, 21.36, 18.67, 11.84. HRMS (ESI+) [M+NH4]⁺ Calculated for C36H54O5S: 616.4030; Found: 616.4029.

(3S,8S,9S,10S,13R,14S,17R)-13-methyl-17-((R)-6-methylheptan-2-yl)-10-((tosyloxy)methyl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl acetate; (19-tosyloxycholesten-5-en-3-ol) 6. Compound 5 (0.7425 g, 1.24 mmol) was dissolved in a solution of dichloromethane and methanol (1:1, 63 mL). Potassium carbonate (0.3427 g, 2.48 mmol) was added, and the solution was stirred for 18 hours. The mixture was then extracted with additional dichloromethane and washed with water. The organic layer was isolated, and the solvent was removed in vacuo, yielding a white solid (0.5990 g, 87% yield). TLC Rf = 0.44, 1:1 EtOAc:Hexane. Used directly in the next reaction.
(3S,8S,9S,13R,14S,17R)-6-(iodomethyl)-13-methyl-17-((R)-6-methylheptan-2-yl)-
2,3,4,6,7,8,9,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-ol; 
(6-iodomethyl-19-norcholest-5(10)-ene-3-ol) 7. Compound 6 (0.5990 g, 1.08 mmol) was added to a
flame dried flask and dissolved in isopropanol (43 mL). Potassium iodide (0.3571 g, 2.151
mmol) was added, and the mixture was stirred at reflux for 7 hours. The product was extracted
with ethyl acetate and washed with sodium thiosulfate and water. The organic layer was then
dried over sodium sulfate, loaded onto Florosil, and then eluted through silica (10 g, DCM). The
collected fractions were isolated and dried in vacuo. The residue was resuspended in acetonitrile
(18 mL) and stirred at reflux for 2 hours. The mixture was then loaded onto Florosil and eluted
through silica a second time (10 g, DCM). The collected fractions were isolated and dried in vacuo. The residue was resuspended in acetonitrile (18 mL) and stirred at reflux for 2 hours. The mixture was then loaded onto Florosil and eluted
through silica a second time (10 g, DCM). The collected fractions were isolated and dried in vacuo, yielding a yellow solid (0.1200g, 22% yield). TLC Rf = 0.18, DCM. 1H-NMR (400.53
MHz, CDCl3): δ 3.98 (1H, m, 3α-H), 3.47 (1H, d, J = 9.96 Hz), 3.06 (1H, t, J = 10.36 Hz). 13C-
NMR (100.13 MHz, CDCl3): δ 133.98, 125.08, 66.54, 56.33, 54.66, 47.45, 43.11, 40.18, 39.51,
38.50, 36.15, 35.77, 33.35, 31.52, 30.44, 28.29, 28.02, 25.37, 24.15, 23.80, 23.63, 22.83, 22.56,
18.62, 12.30, 12.11. HRMS (ESI+) [M+H-H2O]⁺ Calculated for C27H45IO: 495.2482; Found:
Calculated for C27H45IO: 367.3348; Found: 367.3343.

(3S,8S,9S,13R,14S,17R)-6-(iodomethyl)-13-methyl-17-((R)-6-methylheptan-2-yl)-
2,3,4,6,7,8,9,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl
acetate; (3-acetoxy-6-iodomethyl-19-norcholest-5(10)-ene) 8. Compound 7 (0.2500 g, 0.488
mmol) was added to a flame dried flask and dissolved in dichloromethane (4.7 mL). The flask
was stirred and chilled to 0 °C. To this solution, dimethylaminopyridine (0.0655 g, 0.537 mmol),
pyridine (0.079 mL, 0.976 mmol) and acetic anhydride (0.092 mL, 0.976 mmol) were added.
The reaction was then allowed to come to room temperature and stirred for 18 hours. The mixture was then loaded directly onto silica, and purified by flash chromatography (10 g, 1:9
EtOAc:Hexane) yielding a yellow oil (0.2363 g, 87% yield). **TLC** \( R_f = 0.70, 1:4 \) EtOAc:Hexane. 

**\(^1H\)-NMR** (400.53 MHz, CDCl\(_3\)): \( \delta 4.97 \) (1H, m, 3\( \alpha \)-H), 3.42 (1H, d, \( J = 10.06 \) Hz, 6\( \beta \)-CH\(_2\)), \( \delta 2.04 \) (3\( H \), s, 3\( \beta \)-OAc). 

**\(^13C\)-NMR** (100.13 MHz, CDCl\(_3\)): \( \delta 170.87, 134.05, 124.94, 69.80, 56.31, 54.62, 47.26, 43.13, 43.09, 40.15, 39.50, 36.13, 35.78, 35.10, 33.33, 31.50, 28.30, 28.02, 27.37, 25.39, 24.50, 23.81, 22.56, 21.47, 18.62, 12.32, 11.89. 

**HRMS** (ESI+) [M+H]\(^+\) Calculated for C\(_{29}\)H\(_{47}\)IO\(_2\): 555.2694; Found: 555.2679. [M+NH\(_4\)]\(^+\) Calculated for C\(_{29}\)H\(_{47}\)IO\(_2\): 572.2959; Found: 572.2952. [M+Na]\(^+\) Calculated for C\(_{29}\)H\(_{47}\)IO\(_2\): 577.2513; Found: 577.2508.

(3S,8S,9S,13R,14S,17R)-13-methyl-17-((R)-6-methylheptan-2-yl)-6-((tosyloxy)methyl)-2,3,4,6,7,8,9,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl acetate; (3-acetoxy-6-tosyloxyethyl-19-norcholest-5(10)-ene) 9. Compound 8 (0.4328 g, 0.780 mmol) was dissolved in acetonitrile (10 mL). To the solution, silver p-toluenesulfonate (0.3267 g, 1.17 mmol) was added. The mixture was stirred at 80 °C for 18 hours. The reaction mixture was filtered through a sintered glass funnel. The filtrate was loaded onto Florosil gel and purified by flash chromatography (20 g, 1:9 EtOAc:Hexane). The product was isolated as an off-white solid (0.1881 g, 40% yield). **TLC** \( R_f = 0.20, 1:4 \) EtOAc:Hexane. 

**\(^1H\)-NMR** (400.53 MHz, CDCl\(_3\)): \( \delta 7.79 \) (2H, d, \( J = 8.28 \) Hz, OTs-H), 7.34 (2H, d, \( J = 8.22 \) Hz, OTs-H), 4.92 (1H, m, 3\( \alpha \)-H), 4.04 (1H, d, \( J = 9.69 \) Hz, 6\( \beta \)-CH\(_2\)), 3.84 (1H, t, \( J = 9.67 \) Hz, 6\( \beta \)-CH\(_2\)), 2.44 (3\( H \), s, OTs-CH\(_3\)), 2.02 (3\( H \), s, 3\( \beta \)-OAc). 

**\(^13C\)-NMR** (100.13 MHz, CDCl\(_3\)): \( \delta 170.82, 144.66, 135.49, 134.42, 129.83, 127.91, 123.96, 121.69, 67.57, 56.32, 55.80, 54.65, 48.92, 46.24, 42.99, 42.76, 40.56, 39.93, 39.48, 38.92, 36.09, 35.75, 33.66, 33.46, 28.00, 27.86, 25.69, 25.61, 24.88, 23.79, 22.82, 22.55, 21.43, 18.65, 12.02. 

**HRMS** (ESI+) [M+H]\(^+\) Calculated for C\(_{36}\)H\(_{54}\)O\(_5\)S: 599.3765; Found: 599.3759. [M+NH\(_4\)]\(^+\) Calculated for C\(_{36}\)H\(_{54}\)O\(_5\)S: 616.4030; Found: 616.4027. [M+Na]\(^+\) Calculated for C\(_{36}\)H\(_{54}\)O\(_5\)S: 621.3584; Found: 621.3581.

(3S,8S,9S,13R,14S,17R)-6-(fluoromethyl)-13-methyl-17-((R)-6-methylheptan-2-yl)-2,3,4,6,7,8,9,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl acetate; (3-acetoxy-6-fluoromethyl-19-norcholest-5(10)-ene) 10. Compound 9 (0.1881 g,
0.314 mmol) was dissolved in acetonitrile (2 mL). TBAF(pin)$_2$ (0.3126 g, 0.628 mmol) was added. The reaction mixture was stirred at reflux for 18 hours. The mixture was then cooled to room temperature and extracted with diethyl ether. It was then loaded onto Florosil gel, and purified by flash chromatography (20 g, 1:19 EtOAc:Hexane) yielding the product as an oily residue (0.0942 g, 67% yield). $^1$H-NMR (400.53 MHz, CDCl$_3$): $\delta$ 5.14 (1H, m, 3\(\alpha\)-H), 4.71 (2H, d, J = 44.03 Hz, 6-CH$_2$), 2.05 (3H, s, 3\(\beta\)-OAc). $^{13}$C-NMR (100.13 MHz, CDCl$_3$): $\delta$ 170.97, 144.97, 137.96, 124.20, 69.35, 56.22, 55.18, 46.97, 42.78, 42.05, 40.18, 39.50, 39.16, 37.47, 36.12, 35.77, 30.84, 28.34, 28.01, 26.64, 25.37, 23.97, 23.80, 22.85, 22.54, 21.49, 18.68, 12.21. $^{19}$F-NMR (376.87 MHz, CDCl$_3$): $\delta$ -225.68 (m). HRMS (ESI+) [M+NH$_4$]$^+$ Calculated for C$_{29}$H$_{47}$FO$_2$: 464.3898; Found 464.3892.

(3S,8S,9S,13R,14S,17R)-6-(fluoromethyl)-13-methyl-17-((R)-6-methylheptan-2-yl)-2,3,4,6,7,8,9,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-ol; (6-fluoromethyl-19-norcholest-5(10)-en-3-ol) 11. Compound 10 (0.0300 g, 0.067 mmol) was dissolved in a solution of dichloromethane and methanol (1:1, 0.67 mL). Potassium carbonate (0.0185g, 0.134 mmol) was added, and the solution was stirred for 18 hours. The mixture was then extracted with additional dichloromethane and washed with water and brine. The organic layer was dried over sodium sulfate. It was then loaded onto Florosil gel and purified by flash chromatography (20 g, 1:9 EtOAc:Hexane) affording the product as an oily residue (0.0182 g, 67% yield). $^1$H-NMR (400.53 MHz, CDCl$_3$): $\delta$ 4.72 (2H, d, J = 59.23 Hz, 6-CH$_2$), 4.09 (1H, m, 3\(\alpha\)-H). $^{13}$C-NMR (100.13 MHz, CDCl$_3$): $\delta$ 145.21, 137.75, 124.28, 105.52, 66.19, 56.23, 55.25, 46.93, 42.74, 40.19, 39.50, 39.19, 37.61, 36.14, 35.75, 34.28, 29.74, 28.33, 28.01, 25.43, 23.87, 23.79, 23.57, 22.82, 22.56, 18.64, 12.15. $^{19}$F-NMR (376.87 MHz, CDCl$_3$): $\delta$ -225.34 (m). HRMS (ESI+) [M+H-HF]$^+$ Calculated for C$_{27}$H$_{45}$FO: 385.3465; Found: 385.3461. [M+H-H$_2$O-HF]$^+$ Calculated for C$_{27}$H$_{45}$FO: 367.3348; Found: 367.3349.
Measured m/z of [M+H]+: 542.3203
Predicted value is 542.3203
Preparation of TBAF(Pin)$_2$ Substrates

4-phenylbutyl-1-$p$-toluenesulfonate. In a flame dried flask, 4-phenyl-1-butanol (0.5 g, 3.33 mmol) was dissolved in dichloromethane (13 mL). Triethylamine (1.011 g, 9.99 mmol), and dimethylaminopyridine (0.0203 g, 0.1665 mmol) were added while stirring. The mixture was then cooled to 0 °C, and $p$-toluenesulfonyl chloride (0.6978 g, 3.66 mmol) was added. The reaction was then stirred at room temperature for 2 hours. It was then quenched in a saturated solution of ammonium chloride, extracted with ethyl acetate, and washed with brine. The organic layer was then dried over sodium sulfate, loaded onto silica gel, and purified by flash chromatography (20g, 1:9 EtOAc:Hexane), to give the product as a colorless oil (0.6647 g, 66% yield). $^1$H-NMR (400.53 MHz, CDCl$_3$): δ 7.80 (2H, d, J = 8.35 Hz, OTs-$H$), 7.34 (2H, d, J = 8.34 Hz, OTs-$H$), 7.28 (2H, t, J = 7.57 Hz, Ph-$H$), 7.19 (1H, t, J = 7.33 Hz, Ph-$H$), 7.13 (2H, d, J = 7.05 Hz, Ph-$H$), 4.05 (2H, t, J = 5.98 Hz, CH$_2$), 2.58 (2H, t, J = 7.03 Hz, CH$_2$), 2.45 (3H, s, OTs-CH$_3$), 1.67 (4H, m). $^{13}$C-NMR (100.13 MHz, CDCl$_3$): δ 144.78, 141.59, 133.10, 129.89, 128.37, 127.87, 125.92, 70.48, 35.09, 28.34, 27.11, 21.65. HRMS (ESI+) [M+NH$_4$]$^+$ Calculated for C$_{17}$H$_{20}$O$_3$S: 322.1471; Found: 322.1470. [M+Na]$^+$ Calculated for C$_{17}$H$_{20}$O$_3$S: 327.1025; Found: 327.1024.

4-phenylbutyl-2-$p$-toluenesulfonate. In a flame dried flask, 4-phenyl-2-butanol (0.5 g, 3.33 mmol) was dissolved in dichloromethane (13 mL). Triethylamine (2.022 g, 19.98 mmol), and dimethylaminopyridine (0.0406 g, 0.333 mmol) were added while stirring. The mixture was then cooled to 0 °C, and $p$-toluenesulfonyl chloride (1.3956 g, 7.32 mmol) was added. The reaction was then stirred at room temperature for 24 hours. It was then quenched in a saturated solution of ammonium chloride, extracted with ethyl acetate, and washed with brine. The organic layer was then dried over sodium sulfate, loaded onto silica gel, and purified by flash chromatography (20g, 1:19 EtOAc:Hexane), to give the product as a colorless oil (0.537 g, 53% yield). $^1$H-NMR (400.53 MHz, CDCl$_3$): δ 7.81 (2H, d, J = 8.31 Hz, OTs-$H$), 7.34 (2H, d, J = 8.16 Hz, OTs-$H$), 7.26 (2H, t, J = 7.63 Hz, Ph-$H$), 7.19 (1H, t, J = 7.30 Hz, Ph-$H$), 7.08 (2H, d, J = 7.32 Hz, Ph-$H$), 4.67 (1H, m, 2-H), 2.56 (2H, m, CH$_2$), 2.45 (3H, s, OTs-CH$_3$), 1.89 (2H, m, CH$_2$), 1.32 (3H, d, J = 6.30 Hz, 1-CH$_3$). $^{13}$C-NMR (100.13 MHz, CDCl$_3$): δ 144.55, 140.83, 134.45, 129.81, 128.45, 128.28, 127.73, 126.06, 79.92, 38.16, 31.17, 21.66, 20.86. HRMS (ESI+) [M+NH$_4$]$^+$ Calculated for C$_{17}$H$_{20}$O$_3$S: 322.1471; Found: 322.1470. [M+Na]$^+$ Calculated for C$_{17}$H$_{20}$O$_3$S: 327.1025; Found: 327.1024.
4-(napthalen-2-yl oxy)-propyl-1-p-toluenesulfonate. In a flame dried flask, 2-(3-bromopropoxy)naphthalene (0.5 g, 1.886 mmol) was dissolved in acetonitrile (8 mL). To this solution, silver p-toluenesulfonate (0.7893 g, 2.829 mmol) was added. The reaction mixture was then stirred at 80 °C. After 48 hours, another aliquot of silver p-toluenesulfonate (0.7893 g, 2.829 mmol) was added. At 72 hours, the reaction mixture was vacuum filtered through a sintered glass funnel, and the filtrate was washed with ethyl acetate. The liquid was then loaded onto Florosil, and purified by flash chromatography (20 g, 1:9 EtOAc:Hexane), to give the product as white crystals (0.607 g, 90.3% yield).

$^{1}H$-NMR (400.53 MHz, CDCl₃): δ 7.75 (3H, t, J = 8.35 Hz), 7.70 (2H, d, J = 8.65 Hz, OTs-H), 7.45 (1H, t, J = 7.55 Hz), 7.35 (1H, t, J = 7.53 Hz), 7.16 (2H, d, J = 7.98 Hz, OTs-H), 7.00 (1H, d, J = 2.45 Hz), 6.97 (1H, dd, J = 2.44, 8.76 Hz), 4.30 (2H, t, J = 5.97 Hz, CH₂), 4.05 (2H, t, J = 5.82 Hz, CH₂), 2.25 (3H, s, OTs-CH₃), 2.18 (2H, m).

$^{13}C$-NMR (100.13 MHz, CDCl₃): δ 156.33, 144.75, 134.42, 132.67, 129.75, 129.27, 128.98, 127.78, 127.60, 126.72, 126.43, 123.72, 118.63, 106.52, 67.04, 62.91, 28.80, 21.45.


3-(p-toluenesulfonyl)cholest-5(6)-ene. Cholesterol (1 g, 2.586 mmol) was dissolved in pyridine (4 mL). To this solution, dimethylaminopyridine (0.032 g, 0.2586 mmol) and p-toluenesulfonyl chloride (1.23 g, 6.46 mmol) were added, and the reaction was stirred for 18 hours. The reaction was then diluted with ethyl acetate and quenched in a saturated solution of ammonium chloride. The organic layer was then washed with a solution of hydrochloric acid (0.6 M) twice, a saturated solution of sodium bicarbonate once, and brine once. The organic layer was then dried under vacuum, triturated in methanol, and collected on a sintered glass funnel, to afford the product as a white powder (1.2897 g, 92% yield).

$^{1}H$-NMR (400.53 MHz, CDCl₃): δ 7.79 (2H, d, J = 8.29 Hz, OTs-H), 7.33 (2H, d, J = 8.07 Hz, OTs-H), 5.30 (1H, d, J = 5.25 Hz, 6-H), 4.32 (1H, m, 3α-H), 2.44 (3H, s, OTs-CH₃).

$^{13}C$-NMR (100.13 MHz, CDCl₃): δ 144.36, 138.84, 134.68, 129.72, 127.62, 123.48, 82.39, 56.63, 56.08, 49.89, 42.27, 39.64, 39.49, 38.85, 36.87, 36.33, 36.15, 35.75, 31.84, 31.73, 28.62, 28.19, 28.00, 24.24, 23.79, 22.81, 22.55, 21.64, 20.98, 19.14, 18.69, 11.82. HRMS (ESI+) [M+NH₄]$^+$ Calculated for C₃₄H₅₂O₃S: 558.3975; Found: 558.3951.
Evaluation of TBAF(Pin)$_2$

**General Procedure:** In a 4 mL autosampler vial, starting material (0.2 mmol) was dissolved in acetonitrile (0.8 mL). While stirring, TBAF(Pin)$_2$ (0.1991 g, 0.4 mmol) was added. The reaction was then heated to 70 °C. After 2 hours, the reaction was allowed to come to room temperature, and an 80 μL extract was taken up, and placed in a syringe attached to a Waters Light Silica Sep-Pack. The extract was then eluted through the Sep-Pack with 3 mL of ethyl acetate, and then washed with another 3 mL of ethyl acetate. After elution, the solvent was removed under vacuum, the residue was resuspended in deuterated chloroform, and placed in an NMR tube. To these tubes, 0.1 mL of a solution of 4-fluorobenzonitrile (0.2 M) was added as an internal standard, and the tubes were sealed and shaken vigorously. The $^{19}$F-NMR signal of the resulting product was then integrated against that of the standard (δ -102.40 ppm) to obtain a percent yield. The process was then repeated, with the reactions being stopped after 18 hours.

<table>
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<th>Substrate</th>
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<th>% $^{19}$F-NMR Yield (2 hrs)</th>
<th>% $^{19}$F-NMR Yield (18 hrs)</th>
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