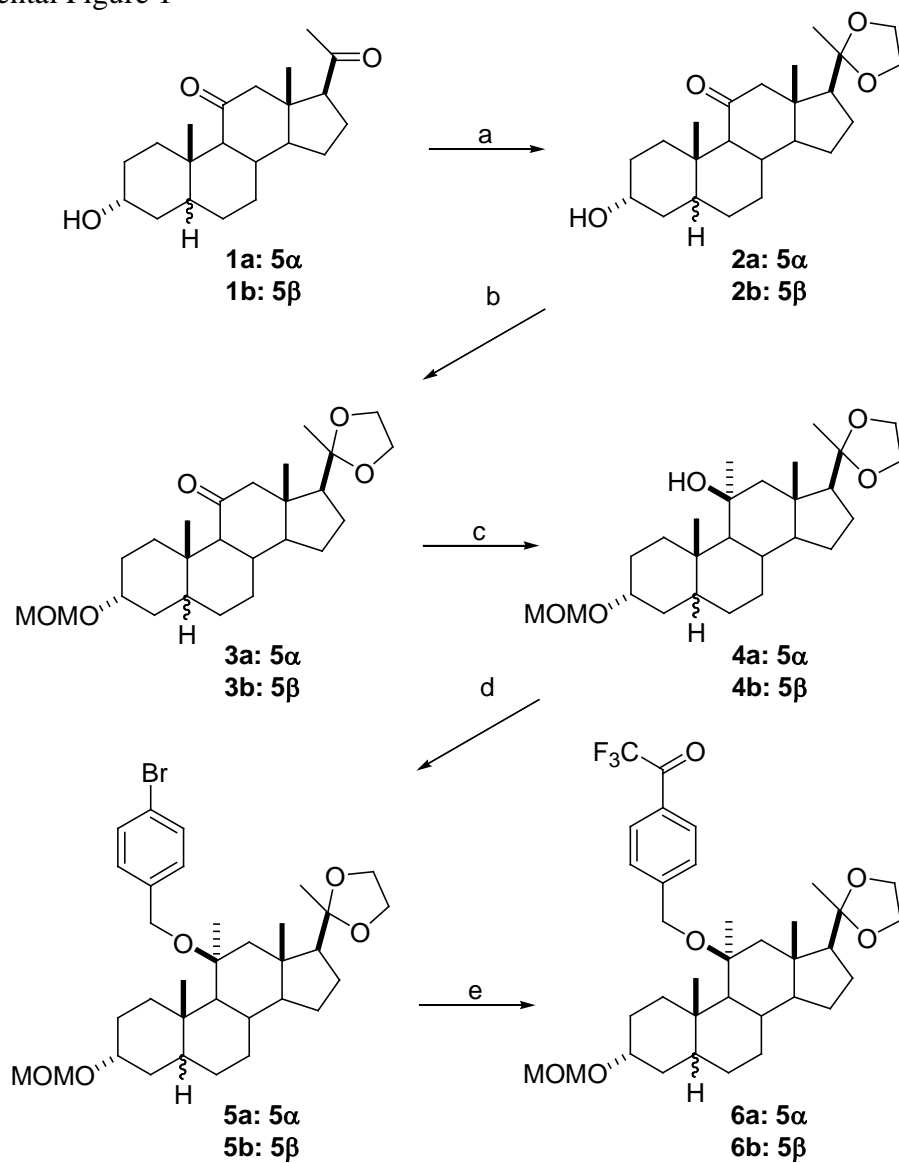
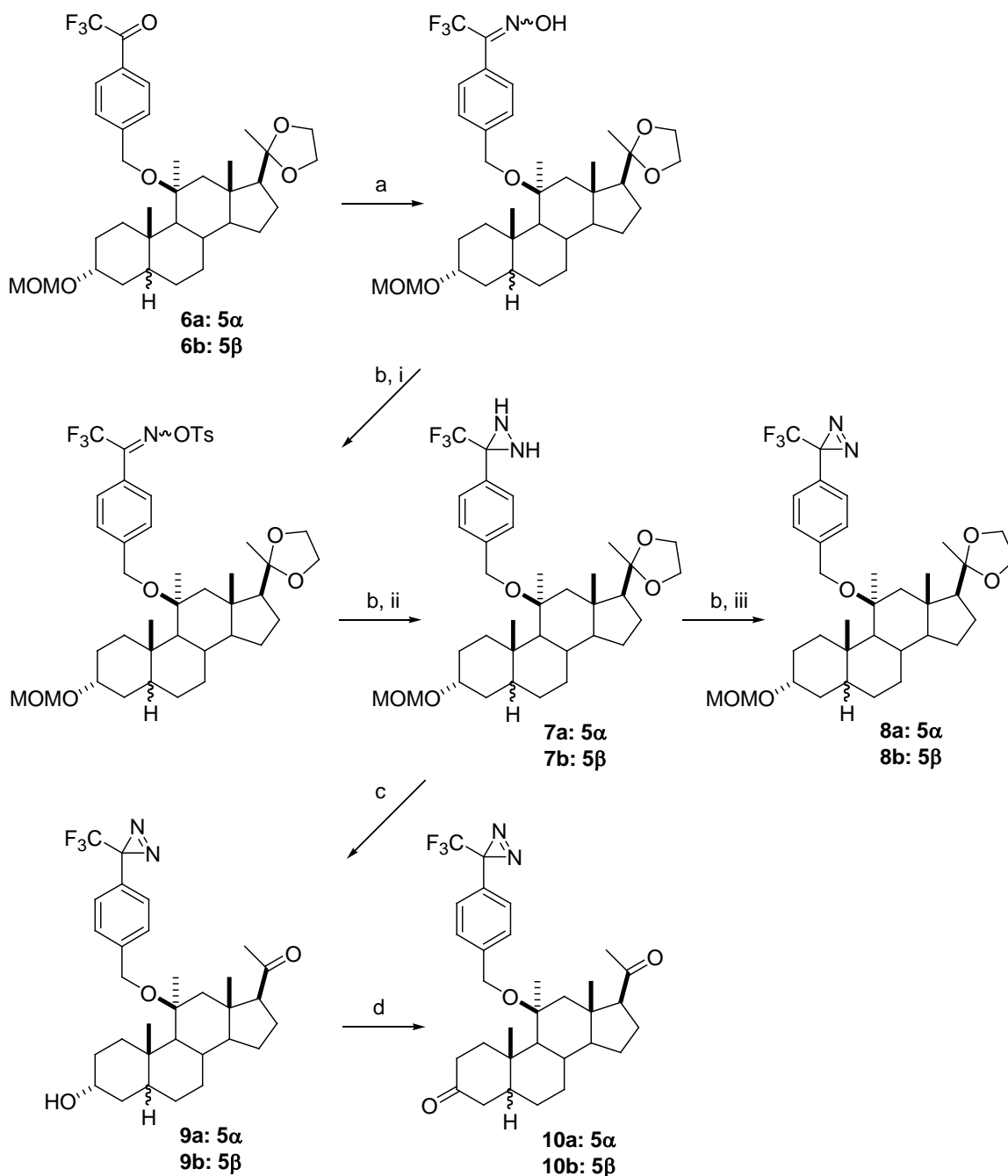


Supplemental Figure 1



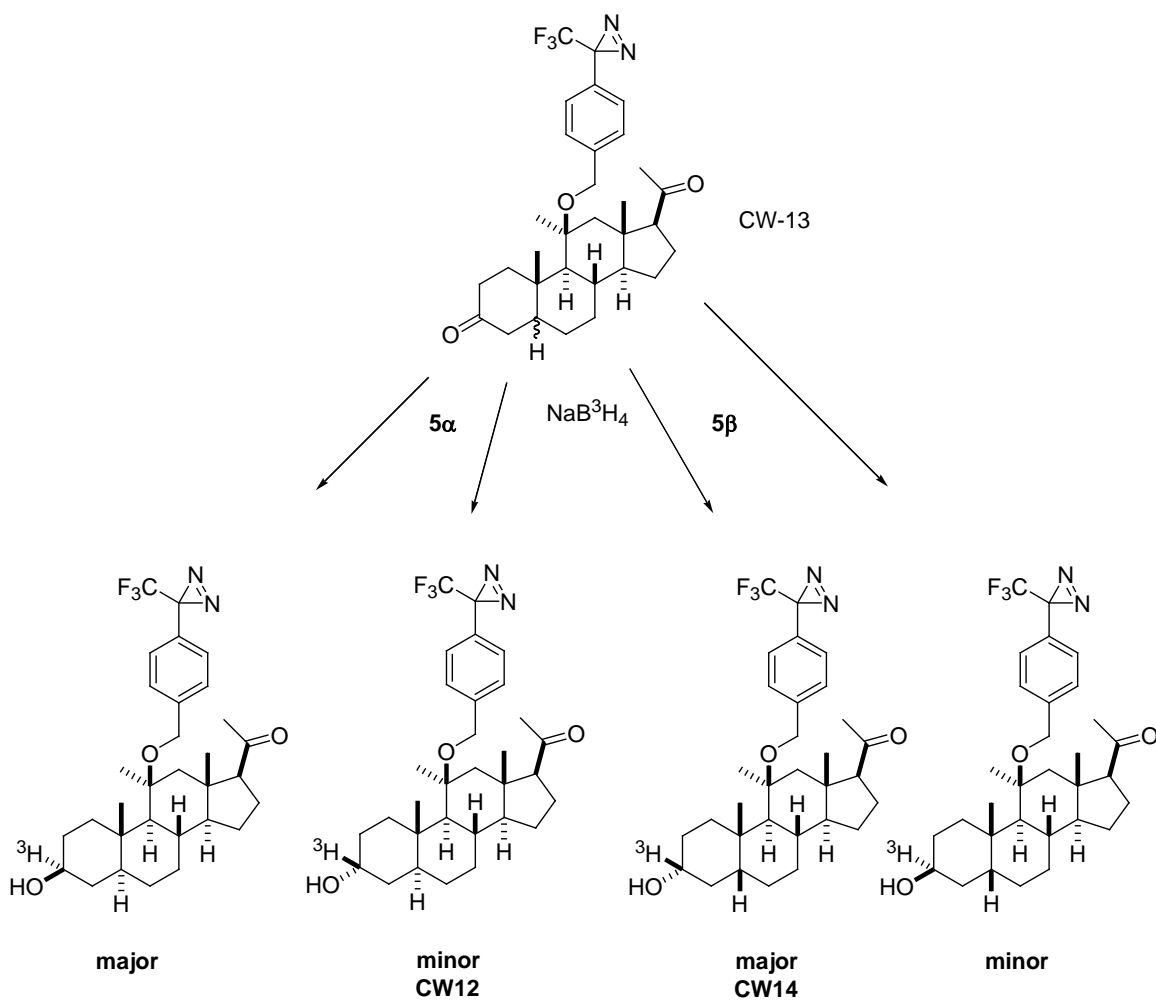
Reagents, conditions and yields: a) Ethylene glycol, PPTS, benzene, N₂, reflux, 12 h, (**2a**, 93%; **2b**, 88%); b) MOMCl, DIPEA, DMAP, CH₂Cl₂, room temperature, 15 min, (**3a**, 88%; **3b**, 81%); c) MeLi (1.6 M in ether), benzene, ether, N₂, room temperature, 12 h, (**4a**, 86%; **4b**, 84%); d) KH (ca. 35% in mineral oil), 4-bromobenzyl bromide, THF, reflux to room temperature, 12 h, (**5a**, 20% with 79% recovered **4a**; **5b**, 18% with 74% recovered **4b**); e) Mg turnings, N-trifluoroacetyl piperidine, THF, reflux to room temperature, 48 h, (**6a**, 73%; **6b**, 74%).

Supplemental Figure 2



Reagents, conditions and yields: a) $\text{H}_2\text{NOH}\cdot\text{HCl}$, NaAc, methanol, reflux, 12 h, (**5 α** , 45%, **5 β** , not purified) ; b, i) *p*-TsCl, Et_3N , DMAP, 0-5 $^\circ\text{C}$, 35 min, (**5 α** , 87%; **5 β** , not purified); b, ii) $\text{NH}_3(\text{liq.})$, CH_2Cl_2 , -78 $^\circ\text{C}$, 12 h, (**7a**, 98%; **7b**, not purified) ; b, iii) I_2 , Et_3N , methanol, room temperature, 1 h (**8a**, 98%; **8b**, 27% overall from **6b**) ; c) 10% $\text{HCl}(\text{aq.})$, THF, room temperature, 48 h, (**9a**, 95%; **9b**, 93%); d) PCC, CH_2Cl_2 , 0 $^\circ\text{C}$, 1 h, (**10a**, 98%; **10b**, 97%)

Supplemental Figure 3



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8 **CW12 (9a):** mp 63-65 °C (powder from EtOAc-hexanes); IR ν_{\max} 3401, 2923, 1702,
9 1345 cm^{-1} ; $^1\text{H NMR } \delta$ (CDCl_3) 7.35 (d, $J = 8.4$ Hz, 2H), 7.13 (d, $J = 8.1$ Hz, 2H), 4.42
10 (dd, $J_1 = 17.4$ Hz, $J_2 = 11.4$ Hz, 2H), 3.99 (s, 1H), 2.56 (d, $J = 14.4$ Hz, 1H), 2.41 (t, $J =$
11 9.0 Hz, 1H), 2.13 (s, 3H), 1.54 (s, 3H), 1.02 (s, 3H), 0.76 (s, 3H); $^{13}\text{C NMR } \delta$ (CDCl_3)
12 209.6, 141.1, 127.7 (2 x C), 127.6, 126.2 (2 x C), 122.0 (q, $J_{CF} = 272$ Hz), 80.2, 66.1,
13 64.5, 63.4, 62.5, 57.3, 48.2, 43.3, 40.3, 39.8, 36.3, 34.4, 33.8, 33.2, 31.4, 31.3, 29.1, 28.8,
14 28.2 (q, $J_{CF} = 32$ Hz), 25.0, 22.7, 14.8, 13.2. Anal.Calcd. for $\text{C}_{31}\text{H}_{41}\text{F}_3\text{N}_2\text{O}_3$: C, 68.11; H,
15 7.56; N, 5.12. Found: C, 68.31; H, 7.57. N, 4.98.
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19 **CW14 (9b):** mp: 78-80°C (from EtOAc-hexanes); IR ν_{\max} 3401, 2923, 1702, 1612, 1344,
20 1230 cm^{-1} ; $^1\text{H NMR } \delta$ (CDCl_3) 7.35 (d, $J = 8.4$ Hz, 2H), 7.12 (d, $J = 8.1$ Hz, 2H), 4.42 (s,
21 2H), 3.72 (m, 1H), 2.54 (d, $J = 14.4$ Hz, 1H), 2.41 (t, $J = 9.0$ Hz, 1H), 2.25 (d, $J = 14.7$
22 Hz, 1H), 2.13 (s, 3H), 1.52 (s, 3H), 1.14 (s, 3H), 0.74 (s, 3H); $^{13}\text{C NMR } \delta$ (CDCl_3)
23 209.6, 141.0, 127.7 (2 x C), 127.6, 126.2 (2 x C), 122.0 (q, $J_{CF} = 273$ Hz), 80.3, 71.9,
24 64.6, 62.3, 57.7, 50.4, 48.3, 47.1, 43.5, 38.5, 37.5, 37.2, 33.4, 32.1, 31.4, 29.1, 28.3 (q,
25 $J_{CF} = 32$ Hz), 28.2, 27.3, 26.9, 25.0, 22.7, 13.6. Anal.Calcd. for $\text{C}_{31}\text{H}_{41}\text{F}_3\text{N}_2\text{O}_3$: C, 68.11;
26 H, 7.56; N, 5.12. Found: C, 68.32; H, 7.73. N, 4.99.
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30 **Diketone precursor for [^3H]CW12 (10a):** mp 62-64 °C (powder from Et_2O); IR ν_{\max}
31 2923, 1705, 1610, 1463 cm^{-1} ; $^1\text{HNMR } \delta$ (CDCl_3) 7.35 (d, $J = 8.4$ Hz, 2H), 7.15 (d, $J =$
32 8.1 Hz, 2H), 4.44 (dd, $J_1 = 25.2$ Hz, $J_2 = 13.8$ Hz, 2H), 2.62 (d, $J = 14.4$ Hz, 1H), 2.14 (s,
33 3H), 1.51 (s, 3H), 1.24 (s, 3H), 0.80 (s, 3H); $^{13}\text{CNMR } \delta$ (CDCl_3): 211.9, 209.5, 140.7,
34 127.8 (3), 126.1 (2), 122.1 (q, $J_{CF} = 273$ Hz), 80.1, 64.3, 63.1, 62.6, 56.9, 49.1, 48.1,
35 44.9, 43.2, 41.0, 39.2, 38.3, 33.8, 32.8, 31.5, 31.4, 29.3, 28.3 (q, $J_{CF} = 32$ Hz), 25.1, 22.8,
36 14.9, 13.1. Anal.Calcd. for $\text{C}_{31}\text{H}_{39}\text{F}_3\text{N}_2\text{O}_3$: C, 68.36; H, 7.21; N, 5.14. Found: C, 68.87; H,
37 7.03. N, 4.94.
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40 **Diketone precursor for [^3H]CW14 (10b):** mp 72-74 °C (powder from Et_2O); IR ν_{\max} :
41 2923, 1705, 1610, 1463 cm^{-1} ; $^1\text{HNMR } \delta$ (CDCl_3) 7.35 (d, $J = 8.4$ Hz, 2H), 7.15 (d, $J =$
42 8.1 Hz, 2H), 4.44 (dd, $J_1 = 25.2$ Hz, $J_2 = 13.8$ Hz, 2H), 2.62 (d, $J = 14.4$ Hz, 1H), 2.14 (s,
43 3H), 1.51 (s, 3H), 1.24 (s, 3H), 0.80 (s, 3H); $^{13}\text{CNMR } \delta$ (CDCl_3): 211.9, 209.5, 140.7,
44 127.8 (3), 126.1 (2), 122.1 (q, $J_{CF} = 273$ Hz), 80.1, 64.3, 63.1, 62.6, 56.9, 49.1, 48.1,
45 44.9, 43.2, 41.0, 39.2, 38.3, 33.8, 32.8, 31.5, 31.4, 29.3, 28.3 (q, $J_{CF} = 32$ Hz), 25.1, 22.8,
46 14.9, 13.1. Anal.Calcd. for $\text{C}_{31}\text{H}_{39}\text{F}_3\text{N}_2\text{O}_3$: C, 68.36; H, 7.21; N, 5.14. Found: C, 68.53; H,
47 7.03. N, 4.94.
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