Supporting Information for:

Assessing the Regioselectivity OleD-Catalyzed Glycosylation with a Diverse Set of Acceptors

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Table of Contents

Daidzein 7-*O*-β-D-glucoside (**4**): ^{1}H NMR (DMSO-d6, 500 MHz): 9.55 (s, 1H), 8.40 (s, 1H), 8.04 (d, *J* = 9.0 Hz, 1H), 7.40 (d, *J* = 8.5 Hz, 2H), 7.23 (d, *J* = 2.5 Hz, 1H), 7.14 (dd, *J* = 9.0, 2.0 Hz, 1H), 6.81 (d, *J* = 8.5 Hz, 2H), 5.43 (d, *J* = 5.0 Hz, 1H), 5.14 (d, *J* = 4.5 Hz, 1H), 5.10 (d, *J* = 7.0 Hz, 1H), 5.08(d, *J* = 5.0 Hz, 1H), 4.61 (t, *J* = 5.5 Hz, 1H), 3.71 (m, 1H), 3.45 (m, 1H), 3.4-3.1 (m, 4H); ^{13}C NMR (DMSO-d6, 125 MHz): 180.1, 166.8, 162.6, 162.4, 158.7, 135.5(2C), 132.4, 129.1, 127.7, 123.9, 121.0, 120.4 (2C), 108.8, 105.4, 82.7, 82.0, 78.6, 75.1, 66.2; HRESIMS *m*/*z* 439.1003 $[M+Na]^{+}$ (cacld for $C_{21}H_{20}O_9Na$, 439.1000).

Daidzein 4'-*O*-β-D-glucoside (**5**): ^{1}H NMR (DMSO-d6, 500 MHz): 10.8 (s, 1H), 8.35 (s, 1H), 7.97 (d, *J* = 9.0 Hz, 1H), 7.50 (d, *J* = 8.5 Hz, 2H), 7.08 (d, *J* = 8.5 Hz, 2H), 6.94 (dd, *J* = 9.0, 2.5 Hz, 1H), 6.88 (d, *J* = 2.5 Hz, 1H), 5.32 (d, *J* = 5.0 Hz, 1H), 5.08 (d, *J* = 4.5 Hz, 1H), 5.01 (d, *J* = 5.5 Hz, 1H), 4.90 (d, *J* = 7.0 Hz, 1H), 4.56 (t, *J* = 5.0 Hz, 1H), 3.70 (m, 1H), 3.47 (m, 1H), 3.4-3.1 (m, 4H); ^{13}C NMR (DMSO-d6, 125 MHz): 179.9, 168.0, 162.8, 162.5, 158.7, 135.4(2C), 132.7, 130.9, 128.5, 122.0, 121.4(2C), 120.6, 107.6, 105.8, 82.5, 82.1, 78.7, 75.2, 66.2; HRESIMS *m*/*z* 439.1003 $[M+Na]^{+}$ (cacld for $C_{21}H_{20}O_9Na$, 439.1000).

Daidzein 7,4'-di-*O*-β-D-glucoside (**6**): ^{1}H NMR (DMSO-d6, 500 MHz): 8.46 (s, 1H), 8.05 (d, *J* = 9.0Hz, 1H), 7.52 (d, *J* = 8.5, 2H), 7.25 (d, *J* = 2.0, 1H), 7.15 (dd, *J* = 9.0, 2.0 Hz, 1H), 7.09 (d, *J* = 8.5, 2H), 5.11 (d, *J* = 7.0, 1H), 4.91 (d, *J* = 7.5, 1H), 3.80-3.10 (m, 10H); ^{13}C NMR (DMSO-d6, 125 MHz): 174.6, 161.5, 157.2, 157.0, 153.8, 130.0 (2C), 126.9, 125.3, 123.3, 116.0(2C), 118.4, 115.6, 103.4, 100.3, 100.0, 77.2, 77.0, 76.5, 76.4, 73.2, 73.1, 69.7, 69.6, 60.65, 60.60; HRESIMS *m*/*z* 601.1526 $[M+Na]^{+}$ (cacld for $C_{27}H_{30}O_{14}Na$, 601.1528).

Resveratrol 4'-*O*-β-D-glucoside (**8**): ^{1}H NMR (CD_3OD, 500 MHz): 7.47 (d, *J* = 9.0, 2H), 7.10 (d, *J* = 9.0, 2H), 7.02 (d, *J* = 16.5, 1H), 6.90 (d, *J* = 16.5, 1H), 6.488 (s, 1H), 6.484 (s, 1H), 6.2 (t, *J* = 2.0, 1H), 4.94 (d, *J* = 7.5, 1H), 3.92 (dd, *J* = 12.0, 2.0, 1H), 3.72 (dd, *J* = 12.0, 6.0, 1H), 3.52-3.36 (m, 4H); ^{13}C NMR (CD_3OD, 125 MHz): 159.9 (2C), 158.8, 141.1, 133.4, 129.0, 128.73 (2C), 128.69, 118.1 (2C), 106.1(2C), 103.1, 102.4, 78.3, 78.1, 75.1, 71.5, 62.7; HRESIMS *m*/*z* 413.1189 $[M+Na]^+$ (cacld for $C_{20}H_{22}O_8Na$, 413.1207).

Resveratrol 3-*O*-β-D-glucoside (**9**): ^{1}H NMR (CD_3OD, 500 MHz): 7.38 (d, *J* = 8.5, 2H), 7.03 (d, *J* = 16.0, 1H), 6.86 (d, *J* = 16.5, 1H), 6.80 (s, 1H), 6.77 (d, *J* = 8.5, 2H), 6.62 (s, 1H), 6.46 (t, *J* = 2.0, 1H), 4.90 (d, *J* = 7.5, 1H), 3.94 (dd, *J* = 12.0, 2.0, 1H), 3.72 (dd, *J* = 12.0, 6.0, 1H), 3.52-3.34 (m, 4H); ^{13}C NMR (CD_3OD, 125 MHz): 160.6, 159.7, 158.6, 141.6, 130.5, 130.1, 129.1(2C), 126.8, 116.6 (2C), 108.5, 107.2, 104.6, 102.6, 78.4, 78.2, 75.1, 71.6, 62.7; HRESIMS *m*/*z* 413.1204 $[M+Na]^+$ (cacld for $C_{20}H_{22}O_8Na$, 413.1207).

Resveratrol 3,4'-di-*O*-β-D-glucoside (**10**): ^{1}H NMR (CD_3OD, 500 MHz): 7.47 (d, *J* = 8.5, 2H), 7.09 (d, *J* = 9.0, 2H), 7.06 (d, *J* = 16.0, 1H), 6.94 (d, *J* = 16.0, 1H), 6.82 (s, 1H), 6.64 (s, 1H), 6.48 (t, *J* = 2.5, 1H), 4.93 (d, *J* = 7.5, 1H), 4.90 (d, *J* = 7.0, 1H), 3.94 (dd, *J* = 12.0, 2.0, 1H), 3.92 (dd, *J* = 12.0, 2.0, 1H), 3.72 (dd, *J* = 12.0, 5.0, 2H), 3.52-3.30 (m, 8H); ^{13}C NMR (CD_3OD, 125 MHz): 160.6, 159.8, 158.9, 141.3, 133.2, 129.6, 128.8(2C), 128.3, 118.1(2C), 108.7, 107.3, 104.5, 102.5, 102.4, 78.39, 78.32, 78.19, 78.13, 75.09, 75.06, 71.6, 71.5,62.73, 62.65; HRESIMS *m*/*z* 575.1730 $[M+Na]^+$ (cacld for $C_{26}H_{32}O_{13}Na$, 575.1736).

Resveratrol 3,5-di-*O*-β-D-glucoside (**11**): ^{1}H NMR (CD_3OD, 500 MHz): 7.40 (d, *J* = 9.0, 2H), 7.10 (d, *J* = 16.0, 1H), 6.977 (s, 1H), 6.973 (s, 1H), 6.92 (d, *J* = 16.0, 1H), 6.79 (d, *J* = 8.5, 2H), 6.78 (t, *J* = 2.0, 1H), 4.97 (d, *J* = 7.0, 2H), 3.97 (dd, *J* = 12.0, 2.0, 2H), 3.72 (dd, *J* = 12.0, 6.0, 2H), 3.60-3.36 (m, 8H); ^{13}C NMR (CD_3OD, 125 MHz): 160.3(2C), 158.7, 141.6, 130.7, 130.4, 129.2(2C), 126.4, 116.6(2C), 109.9, 107.3, 105.0, 102.4(2C), 78.4 (2C), 78.2(2C), 75.1(2C), 71.6(2C), 62.9(2C); HRESIMS *m*/*z* 575.1729 $[M+Na]^+$ (cacld for$C_{26}H_{32}O_{13}Na$, 575.1736).

10-hydroxycamptothecin 10-*O*-β-D-glucoside (15): ^{1}H NMR (DMSO, 500 MHz): 8.55 (s, 1H), 8.11 (d, *J* = 9.5 Hz, 1H), 7.63 (s, 1H), 7.59 (s, 1H), 7.30 (d, *J* = 9.5 Hz, 1H), 6.54 (s, 1H), 5.42 (m, 2H), 5.28 (m, 2H), 5.12 (d, *J* = 6.0 Hz, 1H), 4.64 (m, 1H), 3.77-3.16 (m, 6H), 1.88 (dd, *J* = 14.0, 7.0 Hz, 1H), 1.83 (dd, *J* = 14.0, 8.0 Hz, 1H), 0.87 (dd, *J* = 8.0, 7.0 Hz, 3H); ^{13}C NMR (DMSO, 125 MHz): 172.4, 156.7, 155.9, 150.6, 149.9, 145.6, 144.2, 130.33, 130.30, 130.1, 129.0, 123.0, 118.5, 110.4, 100.3, 96.2, 77.1, 76.6, 73.2, 72.4, 69.6, 65.2, 60.6, 50.3, 30.3, 7.8; HRESIMS *m*/*z* 549.1484 $[M+Na]^+$ (cacld for $C_{26}H_{26}N_2O_{10}Na$, 549.1480).

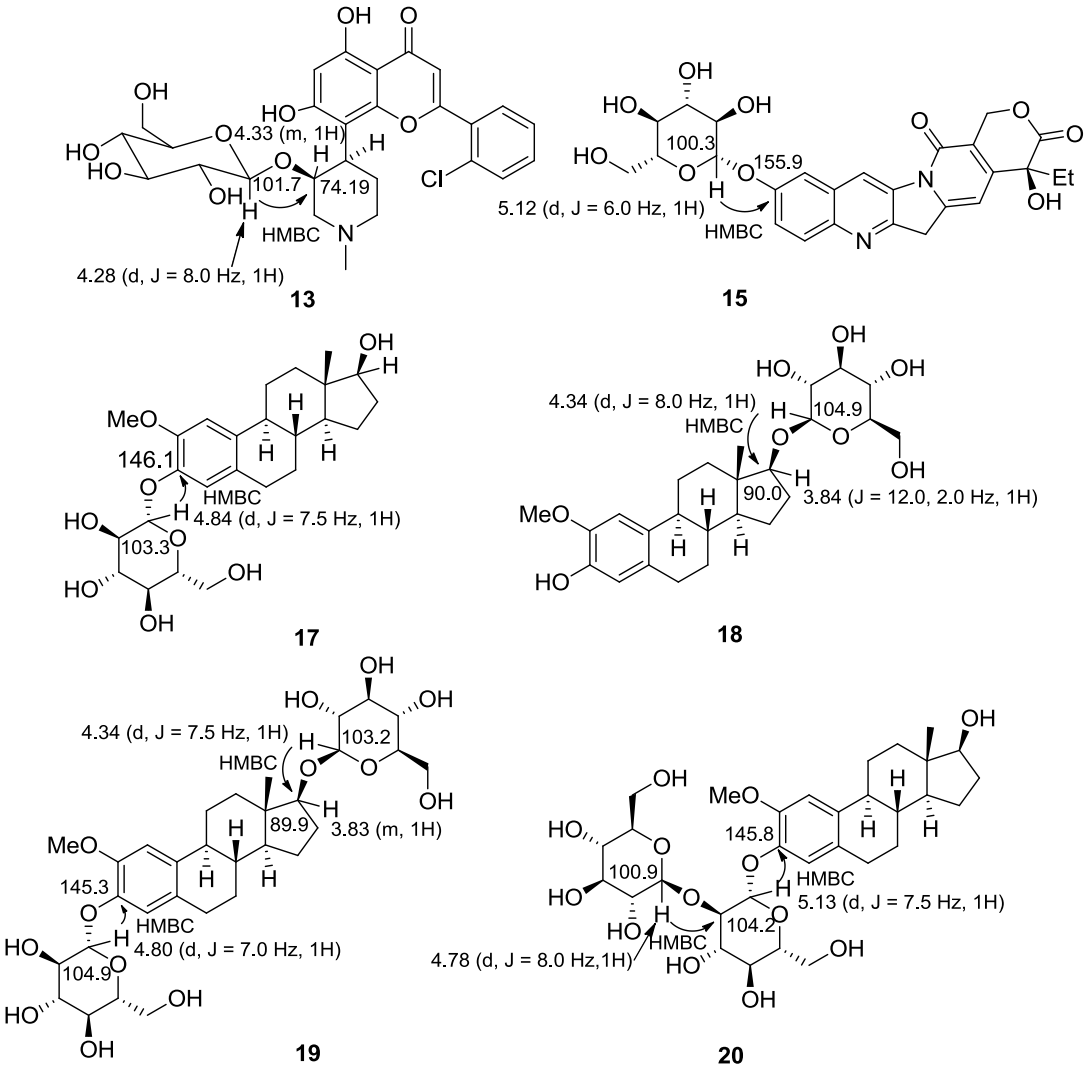


Figure S1. Key ^{1}H and ^{13}C NMR data and HMBC correlations of **13**, **15**, **17**, **18**, **19** and **20**.

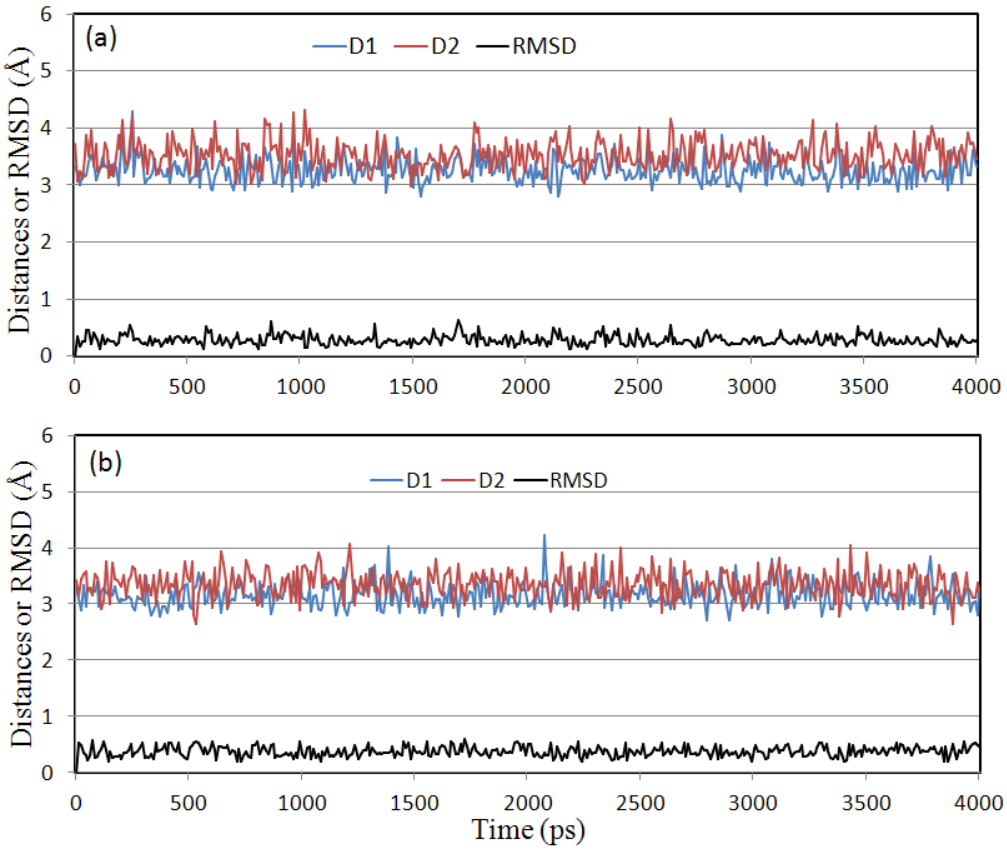


Figure S2. Plots of the MD-simulated internuclear distances and RMSD for atomic positions of the ligand *versus* the simulation time for OleD binding with compounds **3** (panel a) and **12** (panel b). Top: Trace D1 represents the internuclear distance between the oxygen of the hydroxyl group at position C4´ and the NE2 atom of the His19 side chain. Trace D2 represents the internuclear distance between the oxygen atom of the hydroxyl group at position C7 and the side chain of Asp179. Bottom: Trace D1 represents the internuclear distance between the oxygen of the hydroxyl group at position C3´ and the NE2 atom of His19 side chain. Trace D2 represents the internuclear distance between the oxygen atom of the carbonyl group and the hydroxyl group of Tyr114 side chain.

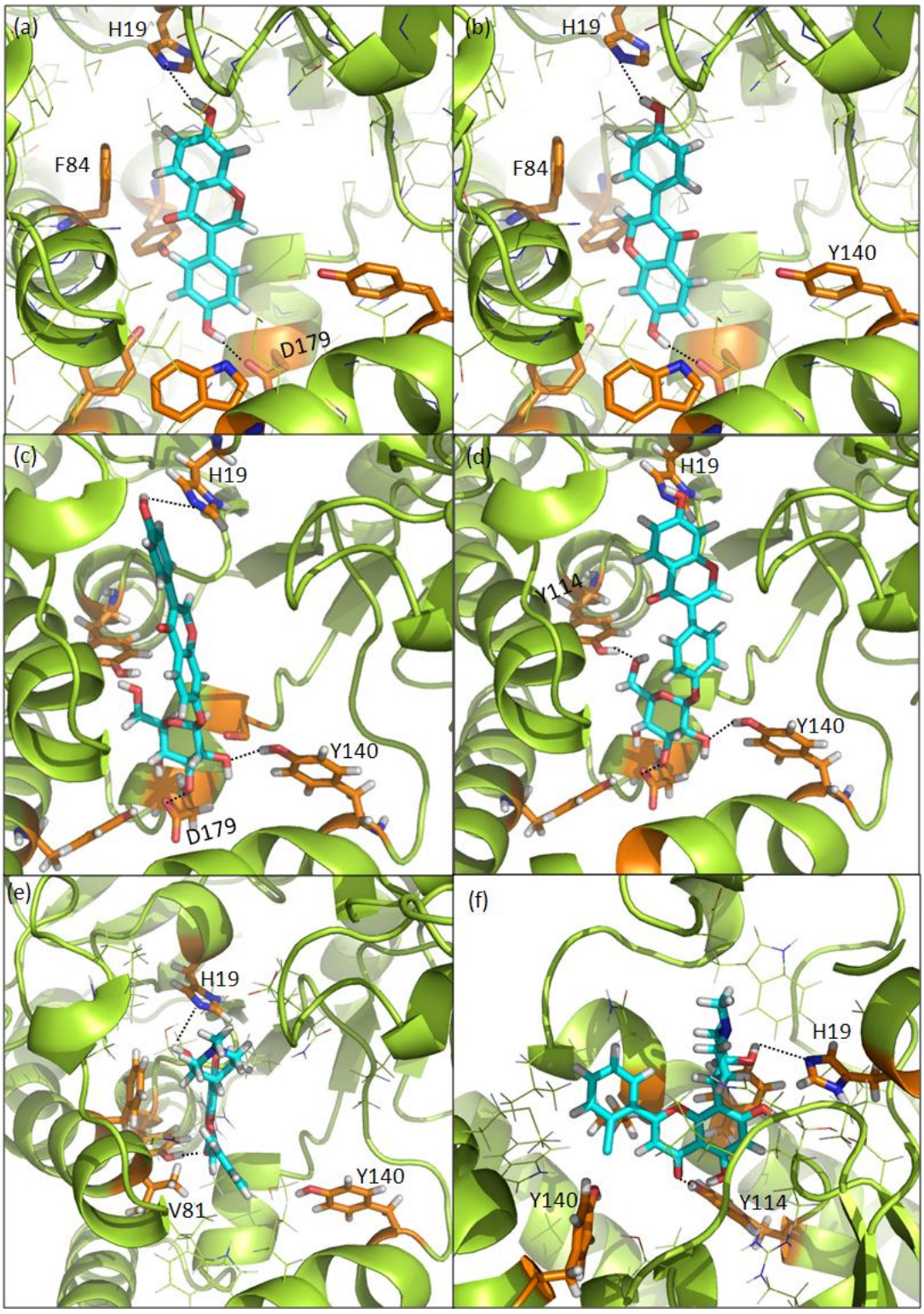


Figure S3. Ribbon view of the binding modes of compounds **3** (a, b), **4** (c), **5** (d) and **12** (e, f) with OleD.

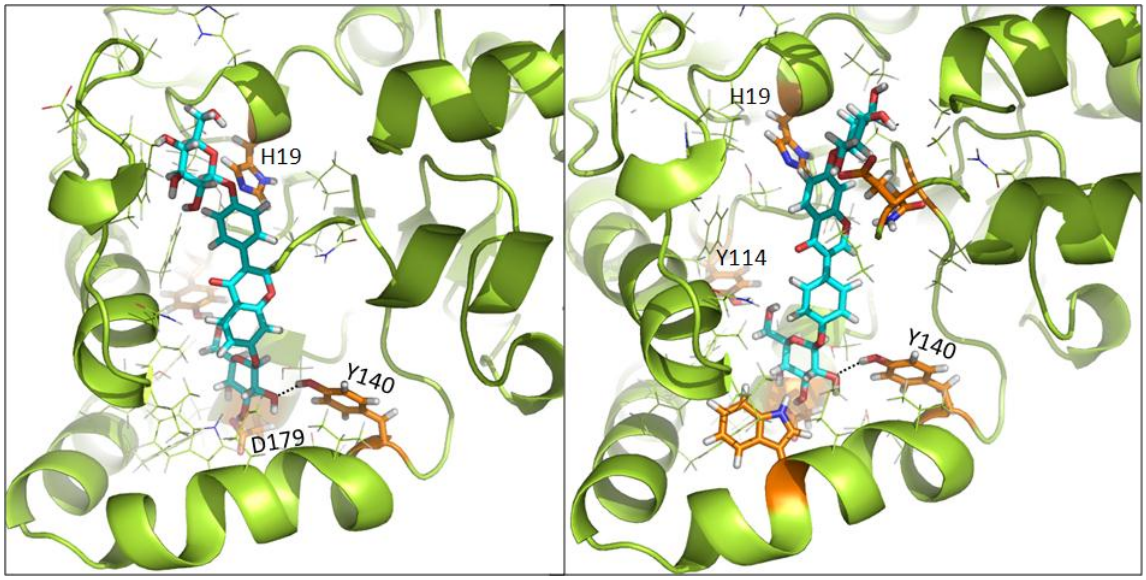


Figure S4. Ribbon view of the two binding modes of compound **6** with OleD.

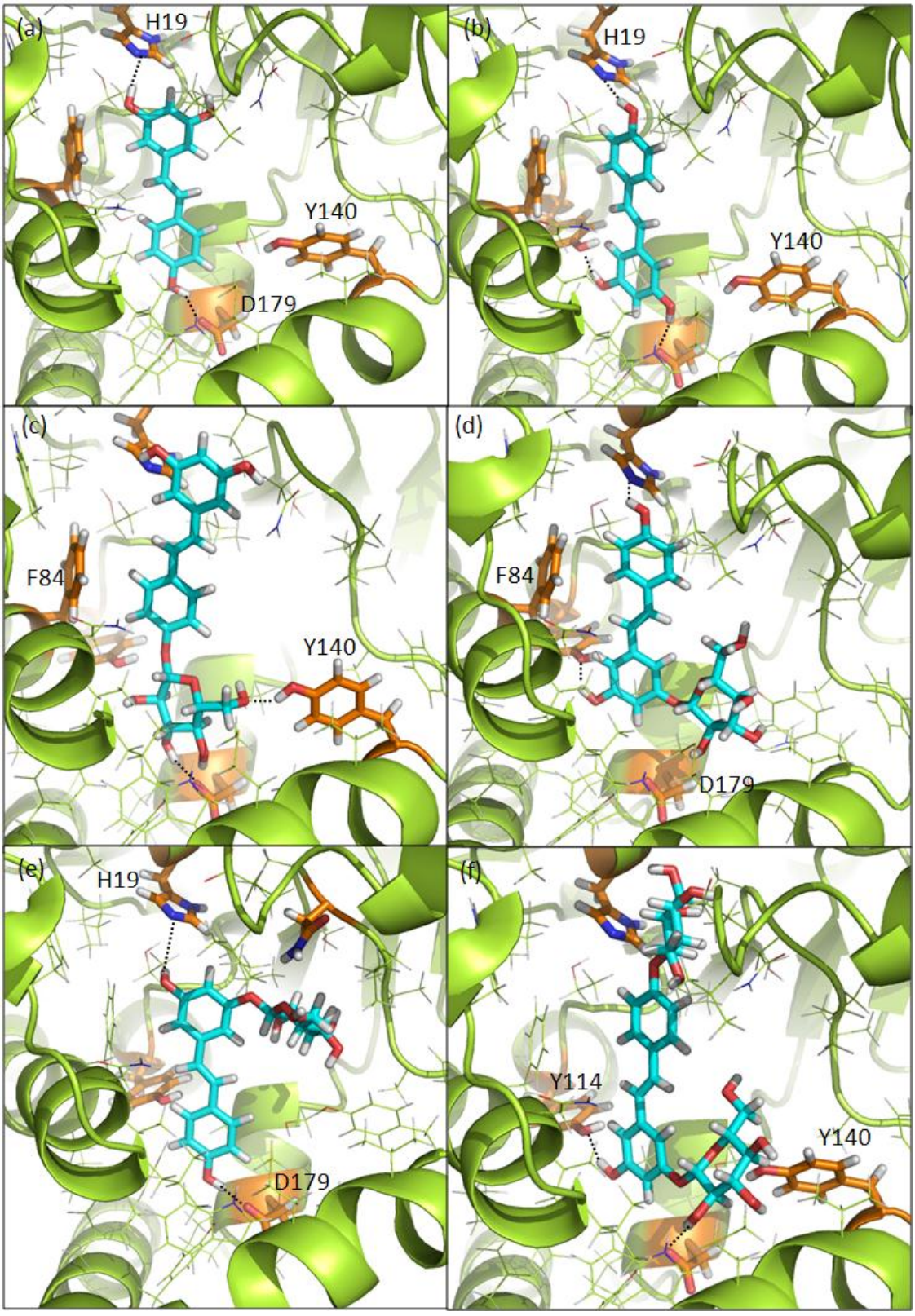


Figure S5. Ribbon view of the binding modes of compounds **7** (a, b), **8** (c), **9** (d, e), and **10** (f) with OleD.

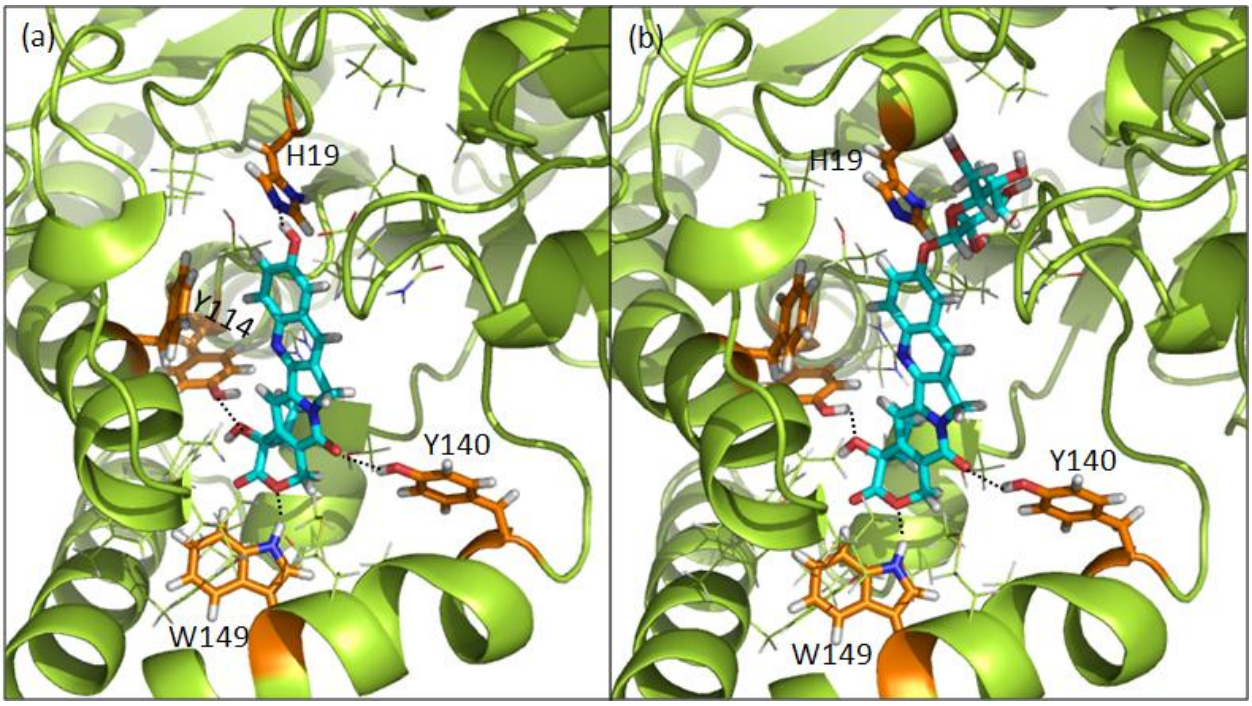


Figure S6. Ribbon view of the binding modes of compounds **14** (a) and **15** (b) with OleD.

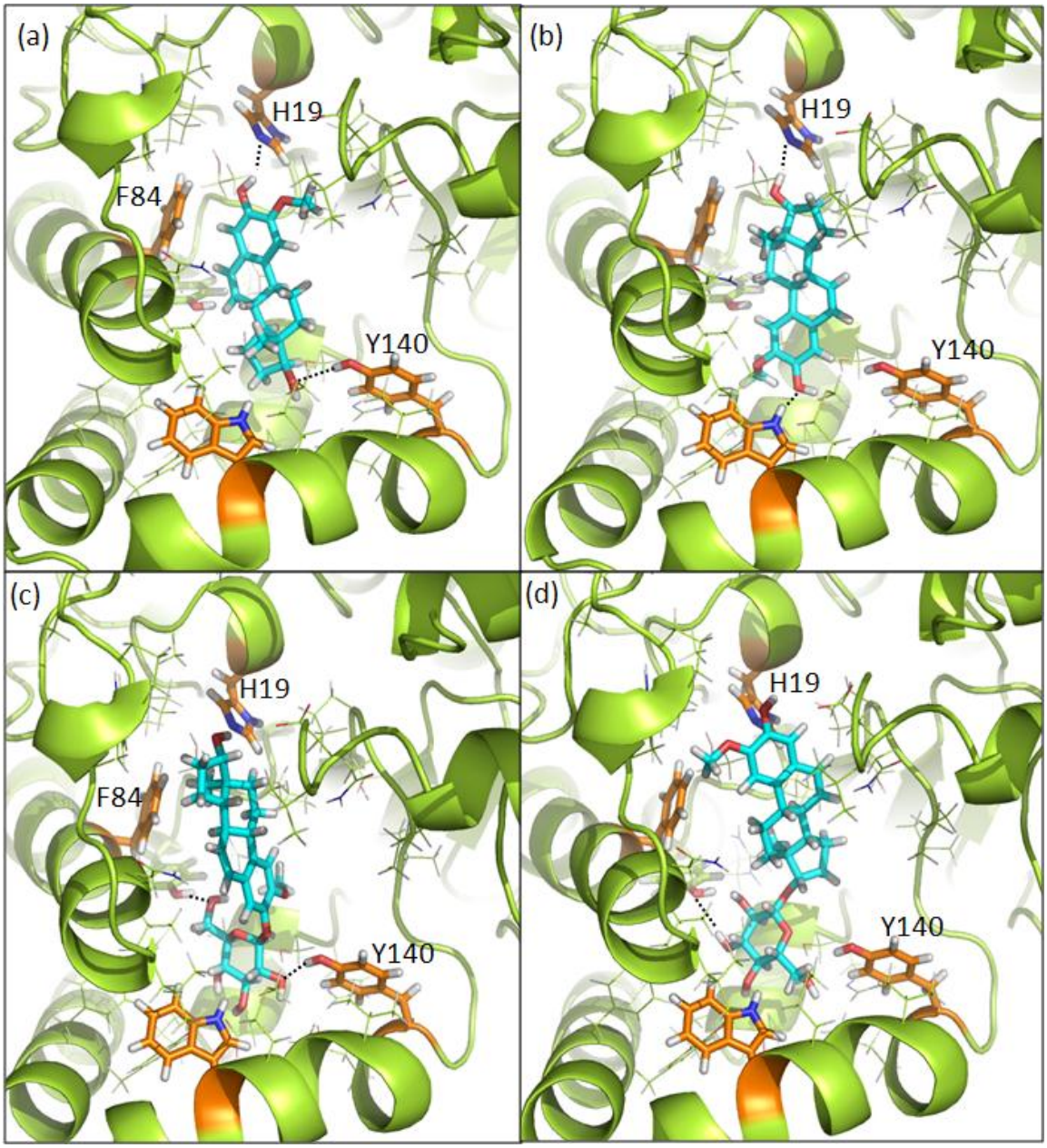


Figure S7. Ribbon view of the binding modes of compounds **16** (a, b), **17** (c), and **18** (d) with OleD.

Figure S8. ^{1}H (CD_3OD, 500 MHz)

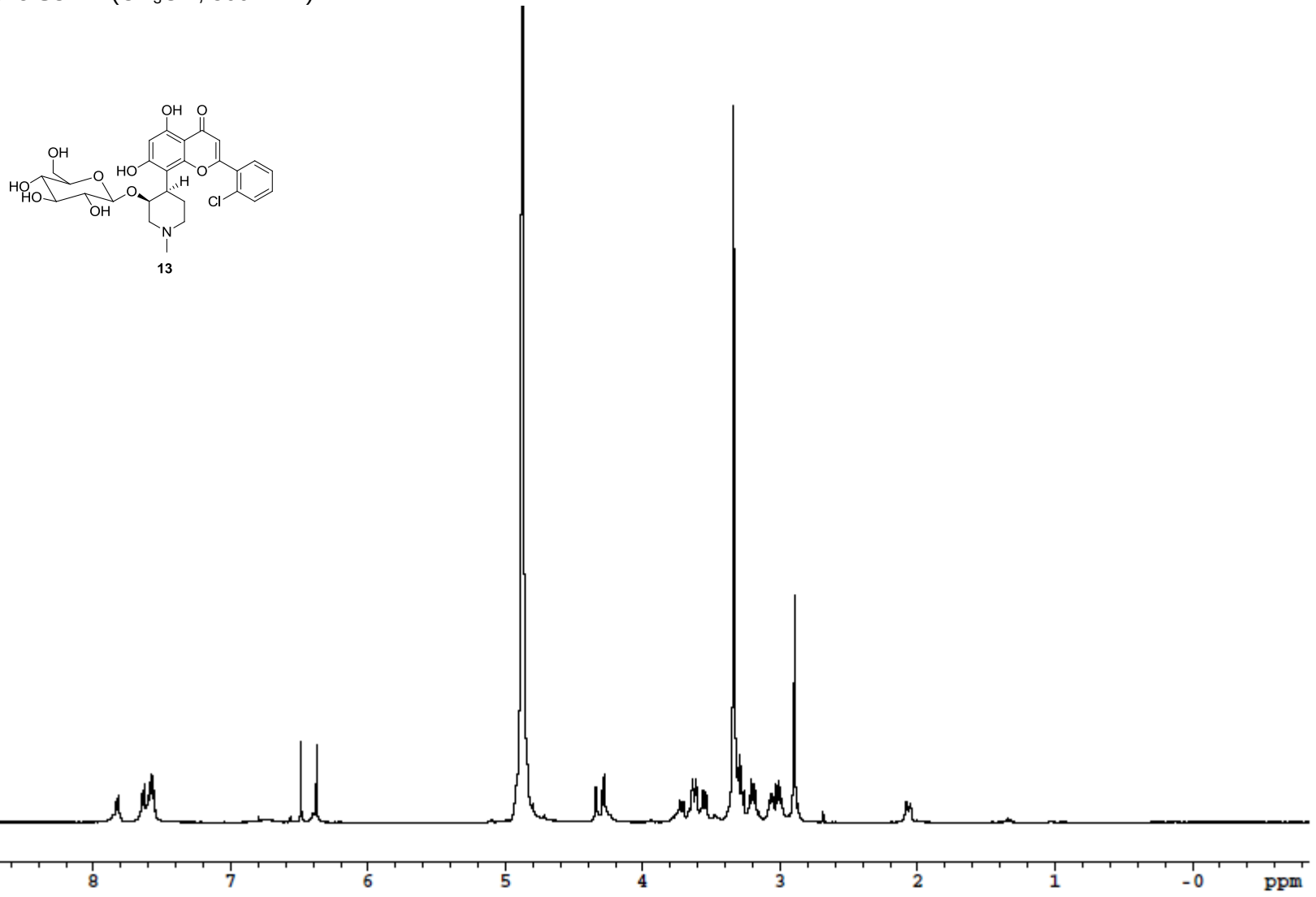
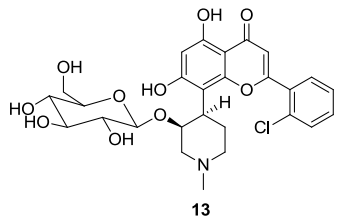
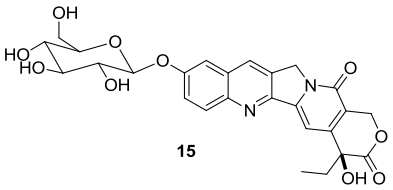


Figure S9. ^{13}C (CD_3OD, 125 MHz)



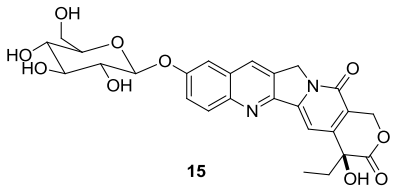
13

Figure S10. ^{1}H (DMSO, 500 MHz)



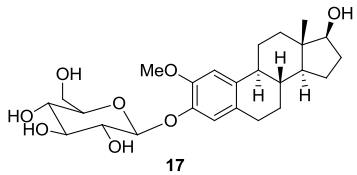
15

Figure S11. ^{13}C (DMSO, 125 MHz)



15

Figure S12. ^{1}H (CD_3OD, 500 MHz)



17

Figure S13. ^{13}C (CD_3OD, 100 MHz)

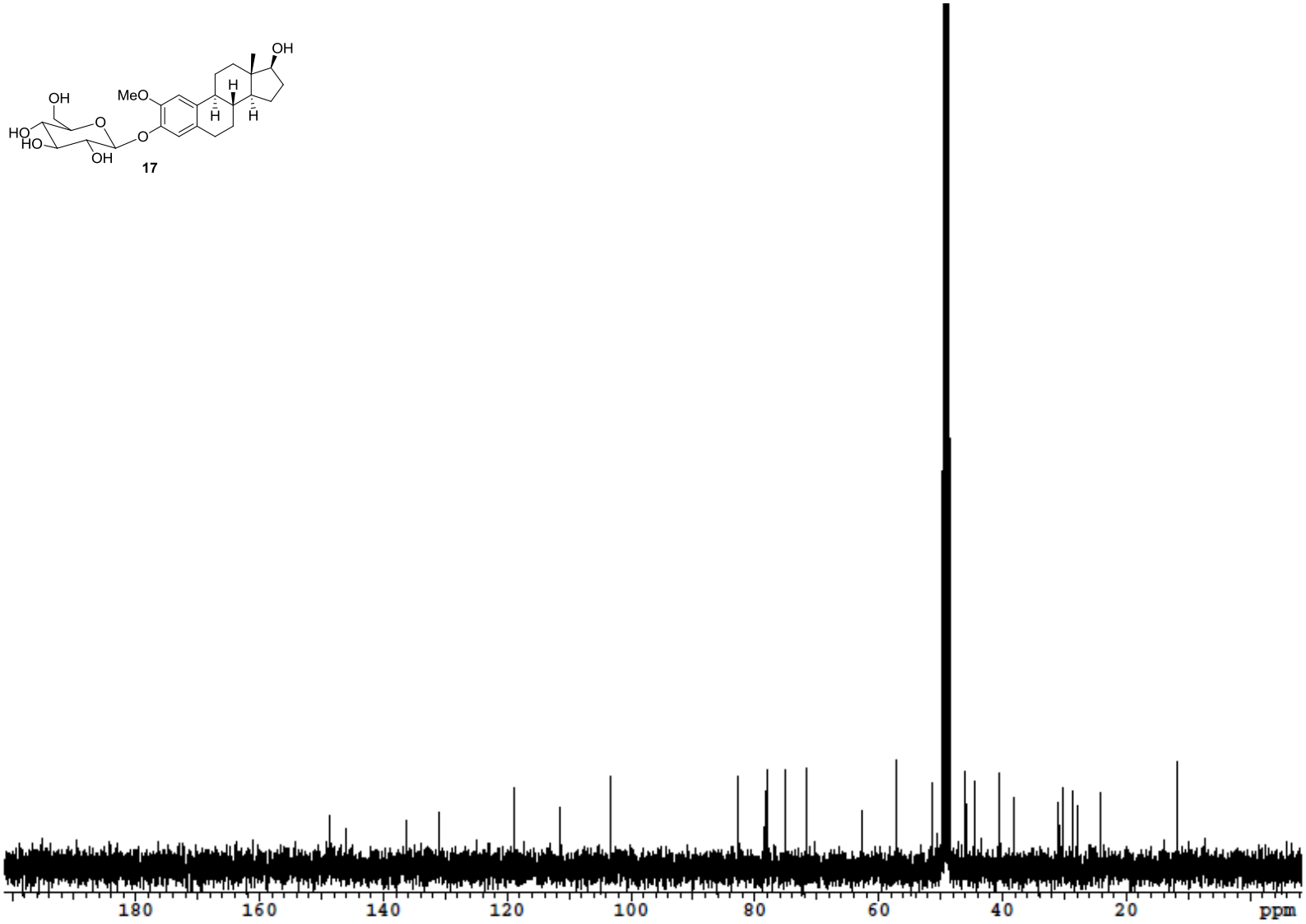
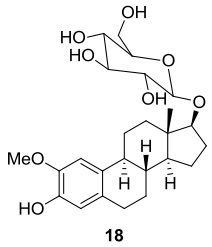


Figure S14. ^{1}H (CD_3OD, 500 MHz)



18

Figure S15. ^{13}C (CD_3OD, 125 MHz)

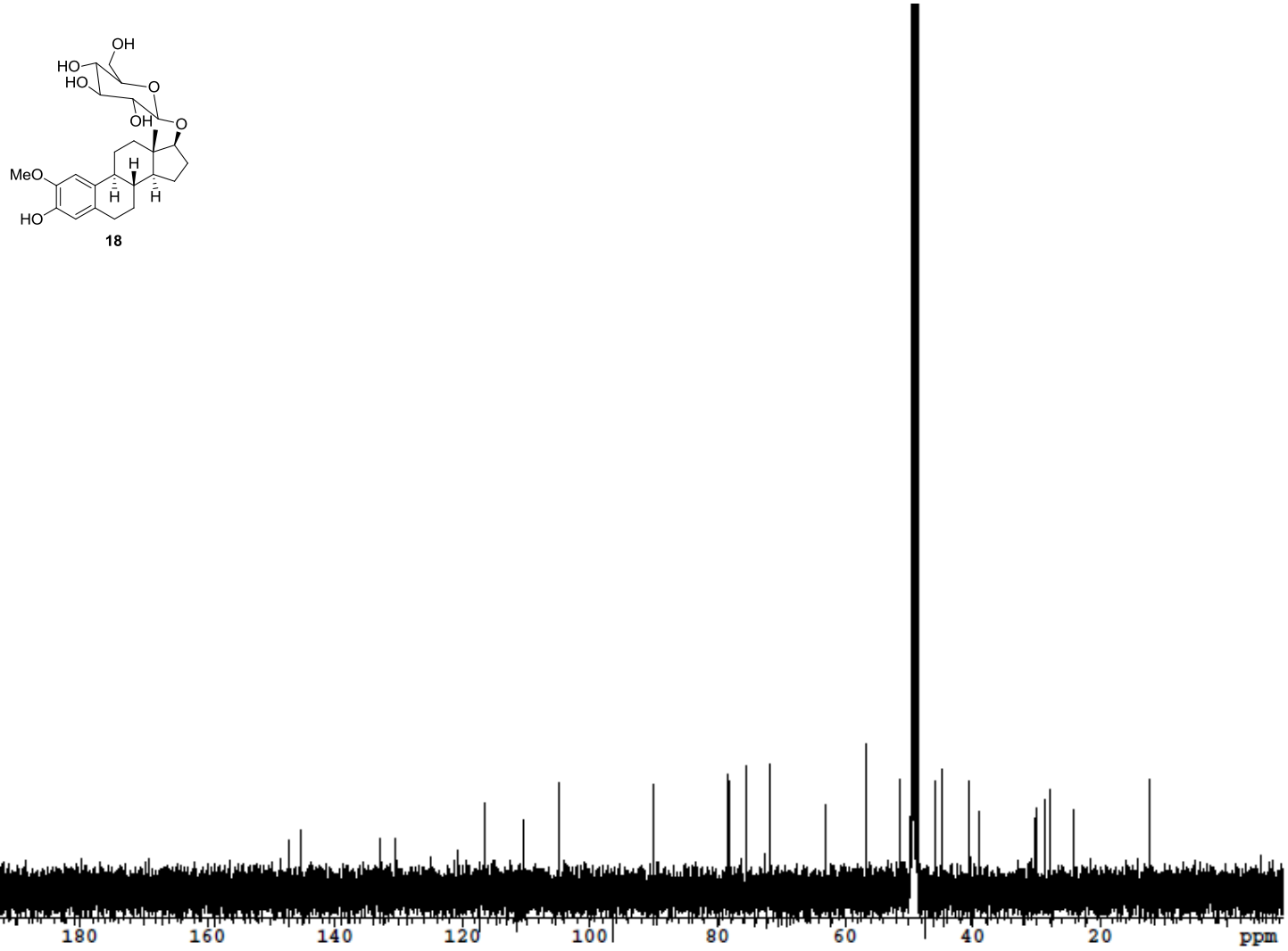


Figure S16. ^{1}H (CD_3OD, 500 MHz)

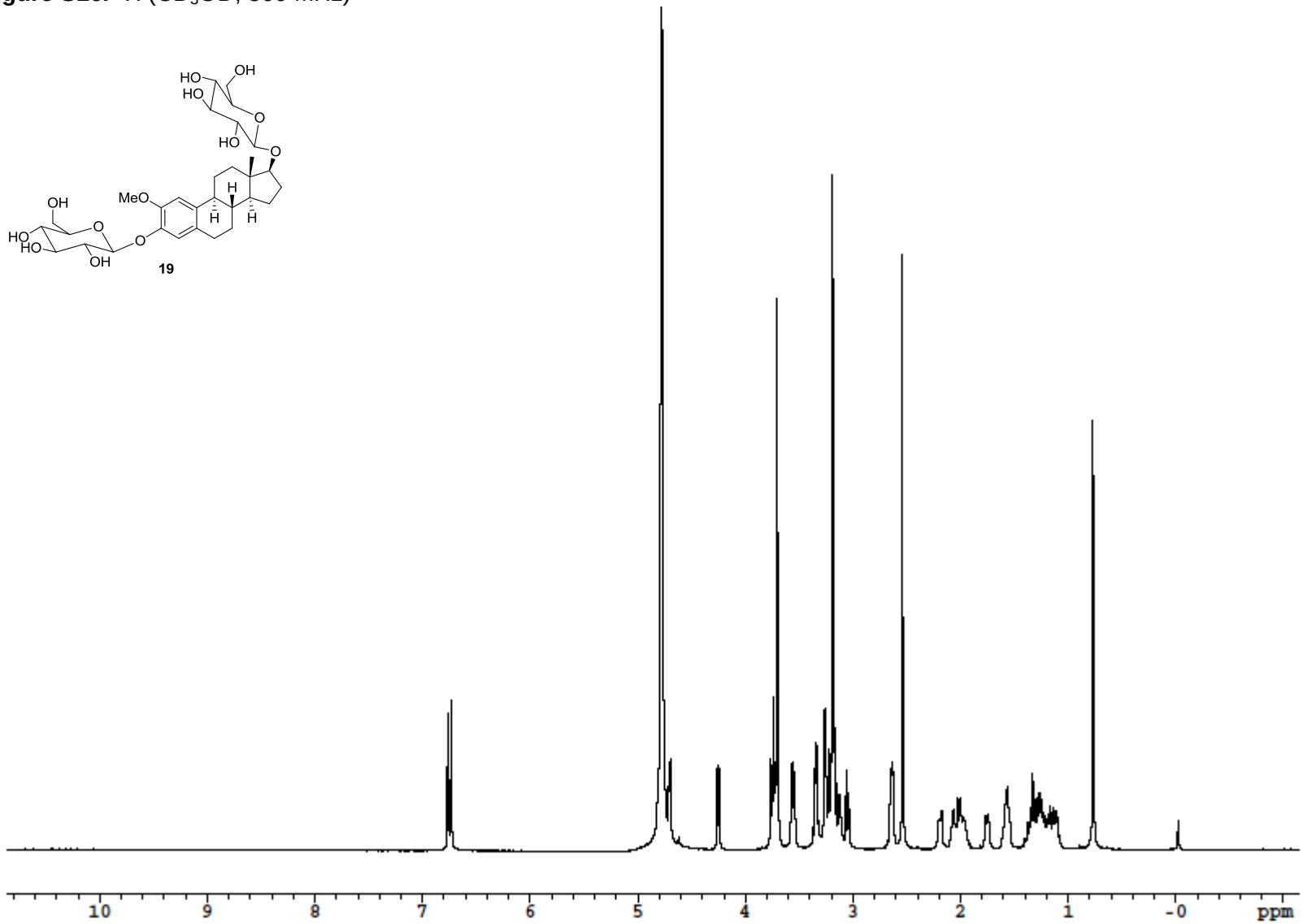
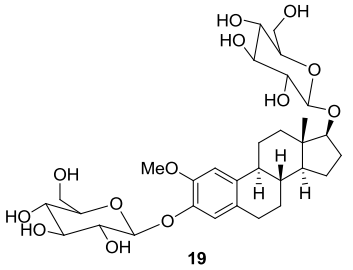


Figure S17. ^{13}C (CD_3OD, 125 MHz)



19

Figure S18. ^{1}H (CD_3OD, 500 MHz)

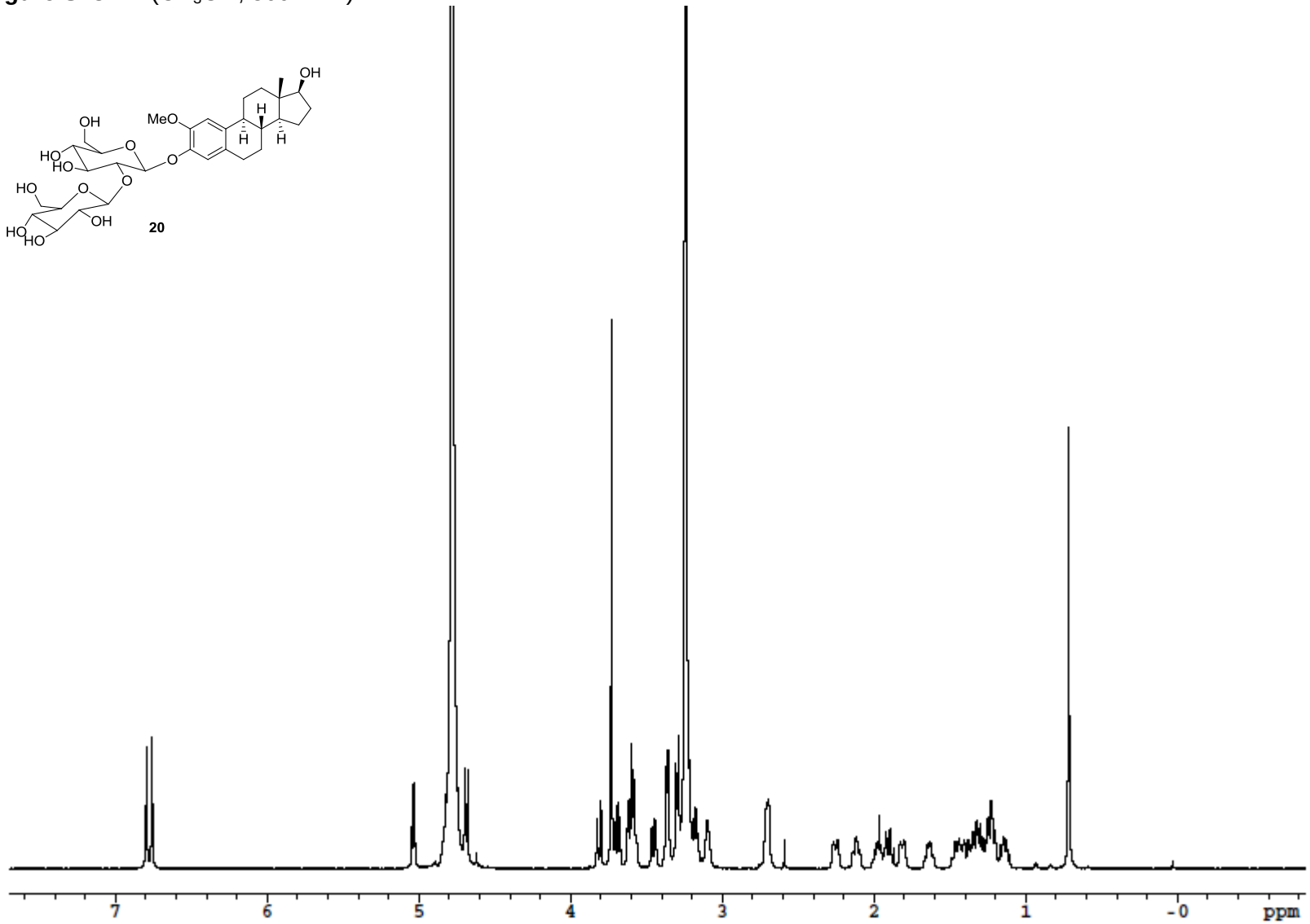


Figure S19. ^{13}C (CD_3OD, 125 MHz)