

Table S1 ^{13}C -NMR chemical shifts for oxyfunctionalization products (**6-27**)^a of (5 β)-3-oxo-bile acids (**1-5**).

Carbon	6	7	8	9	10	11	12	13	14	15	16
1	31.1	35.7	37.2	31.0	30.8	35.6	31.0	35.4	36.8	31.0	30.9
2	37.3	33.9	36.9	37.3	37.0	33.7	37.1	33.9	36.4	37.1	37.1
3	211.6	199.6	213.3	211.3	211.1	199.3	210.5	199.0	212.4	210.4	210.2
4	49.3	123.7	42.3	49.3	49.2	123.9	52.0	126.2	44.6	51.9	50.0
5	78.4	171.6	44.2	78.5	78.2	170.5	77.3	166.9	42.4	77.5	77.1
6	36.1	32.9	25.6	36.2	35.9	32.6	40.5	37.4	30.9	40.4	41.2
7	29.0	32.0	26.5	28.9	28.6	31.5	70.7	71.1	70.9	70.5	73.9
8	34.7	35.6	35.0	34.2	34.5	35.4	37.6	38.3	37.4	37.5	39.0
9	43.6	53.7	40.7	43.6	37.5	48.5	37.2	46.3	34.9	36.7	41.6
10	40.1	38.6	34.9	40.1	39.4	37.9	40.4	38.2	34.9	40.2	39.5
11	21.6	21.0	21.0	21.4	27.1	27.1	21.4	20.8	20.8	21.3	21.8
12	39.7	39.6	40.1	39.8	75.3	75.2	39.1	39.0	39.4	39.1	39.6
13	42.5	42.4	43.2	43.0	44.8	44.7	42.6	42.5	43.2	43.0	43.3
14	56.4	55.8	56.5	56.5	49.4	47.9	50.2	50.2	50.4	50.3	54.8
15	24.0	24.1	23.6	23.6	23.3	23.3	23.5	23.5	22.6	23.0	25.4
16	28.0	28.0	22.7	22.6	26.3	25.5	27.9	27.9	23.0	22.6	28.3
17	55.7	55.7	59.2	59.1	47.4	47.3	55.6	55.6	58.9	58.8	55.3
18	12.0	11.9	13.3	13.3	12.3	12.3	11.7	11.7	12.9	12.9	12.0
19	16.1	17.3	22.6	16.1	15.8	17.4	15.6	17.0	21.8	15.7	16.0
20	35.2	35.3	88.5	88.4	34.5	34.5	35.2	25.2	88.3	88.2	35.1
21	18.2	18.2	26.6	26.5	17.4	17.1	18.2	18.2	26.6	26.7	18.2
22	30.9	30.9 ^b	33.7	33.6	30.7	30.7 ^b	30.9	30.9 ^b	33.5	33.5	30.6 ^b
23	30.9	31.0 ^b	28.1	28.1	30.7	30.8 ^b	30.9	30.8 ^b	28.0	28.0	30.8 ^b
24	174.6	174.7	177.5	177.4	174.5	174.5	174.6	174.6	177.3	177.3	174.6
COO <u>C</u> H ₃	51.4	51.5			51.4	51.4	51.5	51.5			51.4
OCO <u>C</u> H ₃					170.3	170.3	170.0	170.5	170.1	169.9	170.5
OCO <u>C</u> H ₃						21.1			21.4	21.3	21.6

^a In ppm downfield from TMS

^b Assignments along a vertical column may be interchanged.

Table S1 (continued)

Carbon	17	18	19	20	21	22	23	26	27
1	36.1	35.5	30.7	30.8	35.4	30.8	36.0	37.2	39.2
2	36.8	33.8	37.1	36.9	33.8	36.9	33.8	35.6	37.1
3	211.2	198.9	209.6	210.2	198.7	210.2	198.7	214.3	213.7
4	42.6	125.0	50.1	51.9	126.5	51.8	126.8	42.3	42.9
5	43.9	165.8	77.3	77.1	165.8	77.5	166.6	44.0	44.3
6	32.3	38.1	41.4	40.4	37.3	40.4	36.5	25.8	34.4
7	72.6	75.2	73.6	70.3	70.6	70.2	70.4	26.5	74.9
8	39.1	39.0	41.8	37.1	41.0	40.3	41.9	33.6	42.6
9	39.4	50.5	38.6	32.4	38.2	36.6	37.2	40.2	39.9
10	34.2	37.8	39.6	39.8	34.4	39.6	34.4	35.0	33.9
11	21.3	20.8	21.7	27.1	27.0	26.0	25.4	21.0	21.4
12	39.8	75.1	39.8	74.9	74.8	74.8	75.1	39.7	40.1
13	43.9	45.5	43.8	42.6	44.9	45.4	45.5	43.2	43.8
14	55.1	43.3	55.4	43.2	43.1	43.3	43.3	56.5	55.7
15	24.9	21.8	25.0	22.8	22.8	22.6	21.8	24.1	26.7
16	22.9	22.2	23.0	26.3	25.5	22.3	22.2	23.6	23.2
17	58.1	50.8	58.2	47.3	47.3	50.3	50.8	59.2	58.2
18	13.2	13.5	13.3	12.2	12.2	13.5	13.5	13.3	13.4
19	26.6	21.6	16.1	15.4	17.4	15.5	21.6	22.8	22.7
20	88.2	88.2	88.2	34.6	34.6	87.4	87.4	88.6	88.4
21	13.6	26.8	26.8	17.5	16.9	25.8	25.8	26.5	26.4
22	27.5	33.6	33.6	30.7	30.8 ^b	30.8	30.8	39.1	39.4
23	32.2	28.0	28.0	30.7	30.7 ^b	27.8	27.8	28.1	28.1
24	174.4	177.3	177.4	174.5	174.5	174.5	174.5	176.9	177.3
COO <u>C</u> H ₃	51.6			51.5	51.5			51.5	51.5
O <u>C</u> OCH ₃	170.4	170.4	170.5	170.0	170.3	170.0	170.0		
				170.4	170.2	170.2	170.2		
OCO <u>C</u> H ₃	21.6	21.6	21.6	21.3	21.1	21.4	21.4		
				21.4	21.2	21.4	21.4		