## SUPPLEMENTAL MATERIALS AND METHODS

*Xf***DSF:** We isolated 1.3 mg of this acid from 3 L of *E. coli* culture and 3.2 mg of this acid from 3 liter of *E. herbicola* culture. RT = 22.8 min in the preparative HPLC isolation. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  = 6.35 (m, 1H), 5.80 (d, 1H, *J* = 11.5 Hz), 2.65 (m, 2H), 1.42 (m, 2H), 1.26 (m, 16 H), 0.88 (t, 3H, *J* = 7.0 Hz); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  = 171.2, 153.6, 118.8, 31.9, 29.59, 29.58, 29.5, 29.4, 29.3, 29.2, 29.1, 28.9, 22.7, 14.1; The methyl ester of this acid was synthesized by treatment of the isolate with 1.5 eq of trimethylsilyldiazomethane (TMSCH<sub>2</sub>N<sub>2</sub>) in benzene: MeOH 5:1. The methyl ester was isolated in 90% yield from this reaction. Mass analysis was conducted on the methyl ester (Fig. S6). GCMS (EI+): m/z (%): 240 (10) [M+], 209 (15), 143 (20), 113 (100); HRMS (EI+): C<sub>15</sub>H<sub>28</sub>O<sub>2</sub>: calcd. 240.2089, found 240.2090.

## Synthesis of 2(Z)-tetradecenoic acid

**Enoic ester:** Still-Gennari reagent (0.200 ml, 0.845 mmol, 1.1 equiv) was added to a solution of 18-c-6 (811 mg, 3.07 mmol, 4.0 equiv) in THF (12 ml) at room temperature. The mixture was taken to -78 °C, and a solution of potassium hexamethyldisilazide (KHMDS) in PhCH<sub>3</sub> (0.928 ml of a 0.91 M solution, 0.845 mmol, 1.1 equiv) was added dropwise over five minutes. The mixture turned light yellow, and was stirred at this temperature for fifteen minutes at which point a solution of dodecyl aldehyde (0.170 ml, 0.768 mmol, 1.0 equiv) in THF (5 ml) was added dropwise over ten minutes. The reaction mixture was stirred at -78°C for 2 h. The reaction was quenched by the addition of a saturated solution of NH<sub>4</sub>Cl (10 ml). The layers were separated, and the aqueous layer was extracted with EtOAc (3 x 15 ml). The combined organics were washed with brine (1 x 10 ml), dried over Na<sub>2</sub>SO<sub>4</sub>, and the volatiles were removed *in vacuo*. The crude oil was purified using flash column chromatography. The ester was isolated as a colorless

oil (169 mg, 86%): RF = 0.55 (100:1 Hexane:EtOAc); 1H NMR (500 MHz, CDCl<sub>3</sub>; Fig. S5 A) δ = 6.20 (m, 1H), 5.75 (d, 1H, *J* = 11.5 Hz), 4.16 (q, 2H, *J* = 7.0 Hz), 2.64 (m, 2H), 1.43 (quint, 2H, *J* = 7.0 Hz), 1.29 (m, 18H), 0.88 (t, 3H, *J* = 7.0 Hz) ppm; 13C NMR (125 MHz, CDCl<sub>3</sub>; Fig. S5 B) δ = 166.5, 150.7, 119.5, 59.7, 31.9, 29.59, 29.58, 29.5, 29.30, 29.27, 29.0, 28.9, 22.6, 14.2, 14.1 ppm; IR: v (cm-1) = 2924, 2854, 1722, 1181; LRMS (EI+): *m/z* (%): 254 (40) [M+], 209 (40), 127 (100), 99 (80);HRMS (EI+): C<sub>16</sub>H<sub>30</sub>O<sub>2</sub>: calcd. 254.2246, found 254.2246.

**Synthetic Xf DSF:** The ester (158.2 mg, 0.623 mmol, 1.0 equiv) was dissolved in THF (5 ml). Solid LiOH (89.7 mg, 3.74 mmol, 6.0 equiv) was dissolved in H<sub>2</sub>O (5 ml) and was added to the solution of the ester. The mixture was taken to 60 °C for 12 h at which point the reaction was complete by TLC. The mixture was acidified with a 10% solution of HCl to pH of 2.0 and extracted with EtOAc (4 x 15 ml). The combined organics were dried over Na<sub>2</sub>SO<sub>4</sub>, and the volatiles were removed *in vacuo*. The crude oil was purified by flash column chromatography. The isolable white solid was a 10:1 mixture of *Z:E* olefins which were separable with preparative reverse phased HPLC using the gradient shown in Table S2. *Xf*DSF (2(*Z*)-tetradecenoic acid) was isolated as a white solid (81.8 mg, 60%). RT = 19.2 min (Fig. S3 C); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>; Fig. S5 C)  $\delta$  = 6.36 (m, 1H), 5.78 (d, 1H, *J* = 11.5 Hz), 2.66 (q, 2H, *J* = 7.5 Hz), 1.44 (m, 2H), 1.29 (m, 16H), 0.88 (t, 3H, *J* = 6.5 Hz) ppm; <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>; Fig. S5 D)  $\delta$  = 171.4, 153.6, 118.8, 31.87, 29.59, 29.58, 29.5, 29.4, 29.3, 29.23, 29.18, 28.9, 22.6, 14.1 ppm; IR: v (cm-1) = 2924, 2854, 1700, 1639, 1233; LRMS (EI+): *m/z* (%): 226 (25) [M+], 166 (20), 99 (100), 86 (70); HRMS (EI+): C<sub>14</sub>H<sub>26</sub>O<sub>2</sub>: calcd. 226.1933, found 226.1931.

**Putative** *Xf***DSF:** RT = 19.3 min (Fig. S3 B); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ = 6.35 (m, 1H), 5.80 (d, 1H, *J* = 11.5 Hz), 2.65 (m, 2H), 1.45 (m, 2H), 1.26 (m, 16 H), 0.88 (t, 3H, *J* = 7.0 Hz); LRMS (EI+): *m/z* (%): 226 (15) [M+], 208 (10), 166 (25), 99 (100, 86 (70); HRMS (EI+):  $C_{14}H_{26}O_2$ : calcd. 226.1933, found 226.1929.