

### ***tert*-Butyldimethylsilyl ether-protected Zingerone**

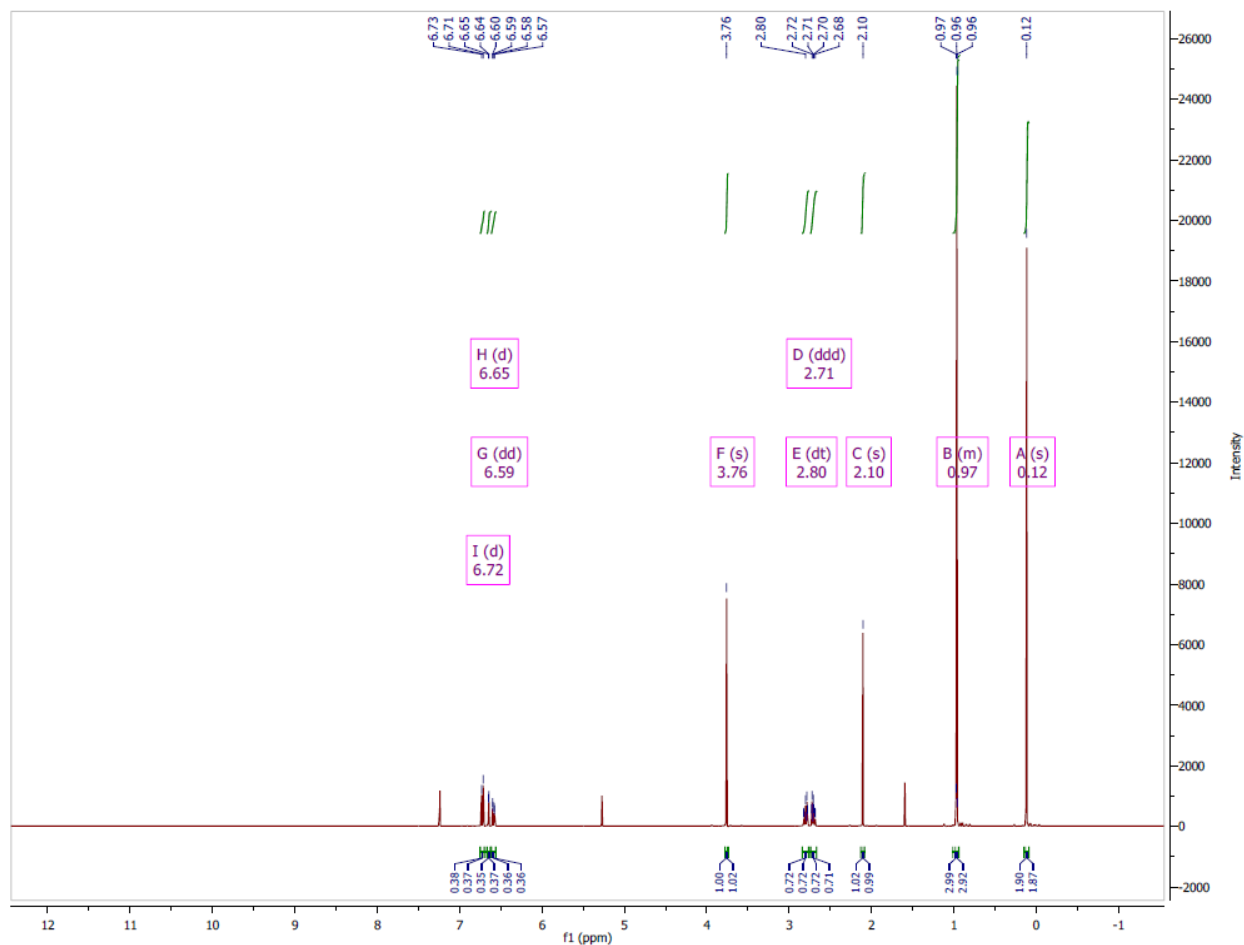
A 1-L round bottom flask was charged with zingerone (10 g, 51.5 mmol) and the solid was subsequently dissolved in dry methylene chloride (400 mL) with stirring at room temperature. To this mixture was added imidazole (7.01 g, 103.0 mmol) and the reaction stirred for ½ hour. To the reaction was then added *tert*-butyldimethylsilyl chloride (7.76 g, 51.5 mmol) in one portion and the reaction was left to stir overnight under an atmosphere of N<sub>2</sub> (g). The reaction was quenched by the addition of a saturated ammonium chloride solution (250 mL) and the aqueous layer was extracted with methylene chloride (2 x 100 mL). The combined organic layers were then washed with water (1 x 200 mL) and a saturated brine solution (2 x 200 mL). The organic layer was then dried over Na<sub>2</sub>SO<sub>4</sub>, decanted, and the excess solvent removed *in vacuo*. The crude oil was purified by column chromatography (silica gel; eluent: Methylene chloride) to yield the 16.75 g of pure product as a colorless oil (99% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 0.12 (6H, s, Si-CH<sub>3</sub>), 0.97 (9H, s, C-(CH<sub>3</sub>)<sub>3</sub>), 2.10 (3H, s, O=C-CH<sub>3</sub>), 2.71 (2H, ddd, J = 2.0, 6.3, and 9.3 Hz, -CH<sub>2</sub>-), 2.80 (2H, dt, J = 2.0 and 5.1 Hz, -CH<sub>2</sub>-), 3.76 (3H, s, -OCH<sub>3</sub>), 6.59 (1H, dd, J = 2.1 and 8.0 Hz, ArH), 6.65 (1H, d, J = 2.1 Hz, ArH), 6.72 (1H, d, J = 8.0 Hz, ArH); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ -4.44, 18.64, 25.94, 29.74, 30.39, 45.67, 55.72, 112.60, 120.44, 120.98, 134.62, 143.45, 150.95, 208.51; HRMS (ESI+) calcd for C<sub>17</sub>H<sub>29</sub>O<sub>3</sub>Si [M+H<sup>+</sup>]: 309.18800, found: 309.18830.

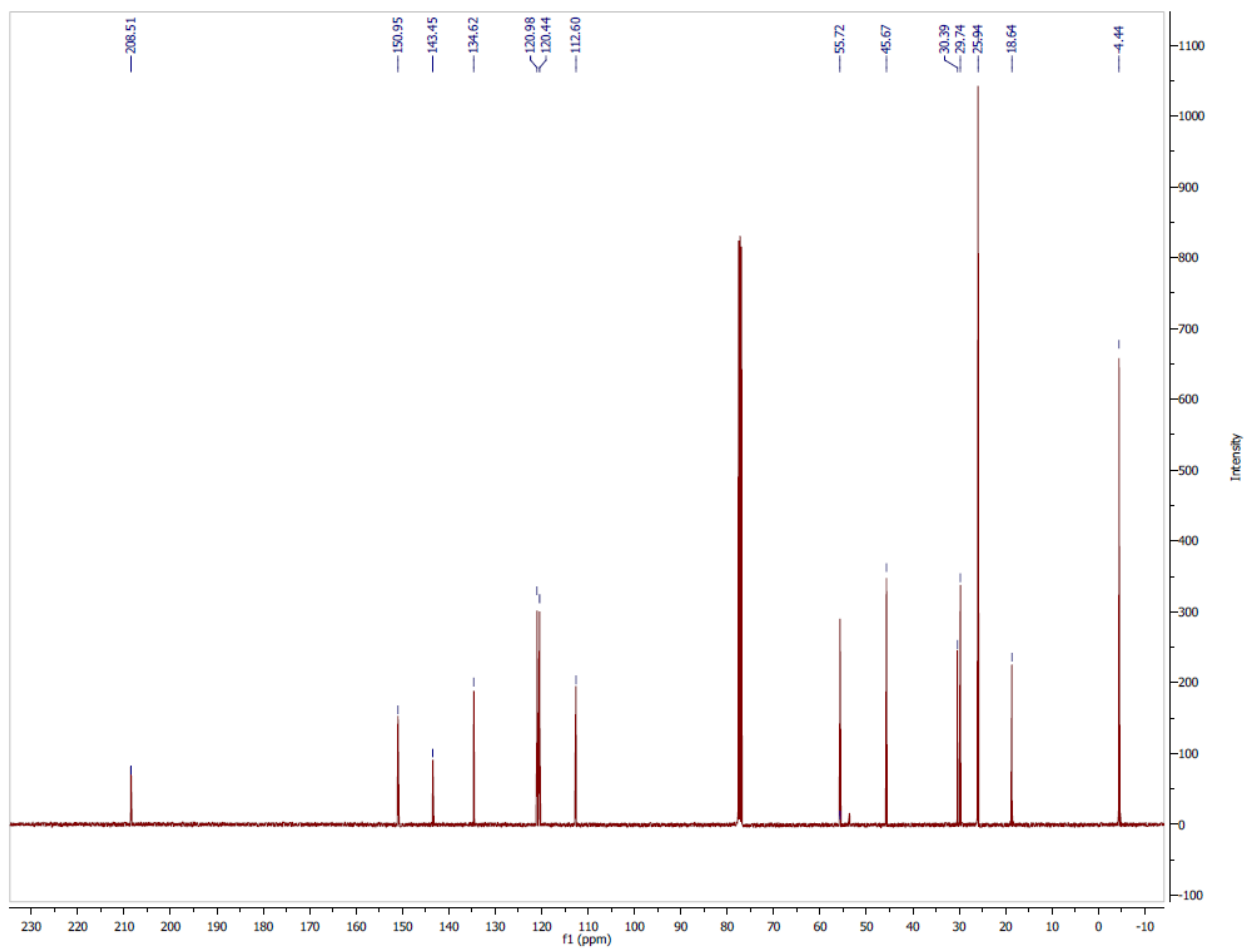
### **6-Gingerol**

A 100-mL oven-dried Schlenk flask was charged with diisopropylamine (0.82 mL, 5.81 mmol) and dissolved in dry tetrahydrofuran (20 mL). The reaction was then cooled to -78°C using a CO<sub>2</sub>(s)/acetone bath. To the cooled reaction was then added a 2.5 M solution of *n*-butyllithium in hexanes (2.5 mL, 5.55 mmol) and the reaction was allowed to stir for one hour to ensure formation of the lithium diisopropylamide salt. A solution of TBDMS-protected zingerone (1.7129 g, 5.55 mmol) in dry THF (10 mL) was subsequently added drop-wise *via* syringe to the reaction mixture. The reaction was stirred for three hours, and then a solution of distilled hexanal (0.68 mL, 5.55 mmol) in dry THF (10 mL) was added drop-wise *via* syringe to the reaction mixture. The reaction was then allowed to stir for three hours while warming from -78°C to 0°C. After three hours, the reaction was quenched with a dilution hydrochloric acid solution (25 mL). The reaction mixture was then further diluted with diethyl ether (50 mL), and the organic layer was extracted diethyl ether (3 x 15 mL). The combined organic layers were washed with a 1 M HCl solution (25 mL) and then washed with a brine solution (2 x 50 mL). The organic layer was then dried over MgSO<sub>4</sub>, filtered, and the excess solvent was removed *in vacuo*. The crude oil was purified by column chromatography (silica gel; eluent: 95/5 Hexanes/Ethyl acetate) to yield 1.5883 g of 6-gingerol as a slightly yellowish oil (70% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 0.87 (3H, t, J = 6.3 Hz, -CH<sub>3</sub>), 1.31 (4H, m, -CH<sub>2</sub>-), 1.42 (2H, m, -CH<sub>2</sub>-), 1.80 (2H, m, -CH<sub>2</sub>-), 2.72 (2H, m, Ph-CH<sub>2</sub>-), 2.81 (2H, dd, J = 5.3 and 12.3 Hz, -CH<sub>2</sub>-C=O), 3.83 (3H, s, -OCH<sub>3</sub>), 3.95 (1H, t, J = 6.9 Hz, -CH of the secondary alcohol), 6.67 (2H, m, ArH), 6.76 (1H, d, J = 8.0 Hz, ArH)

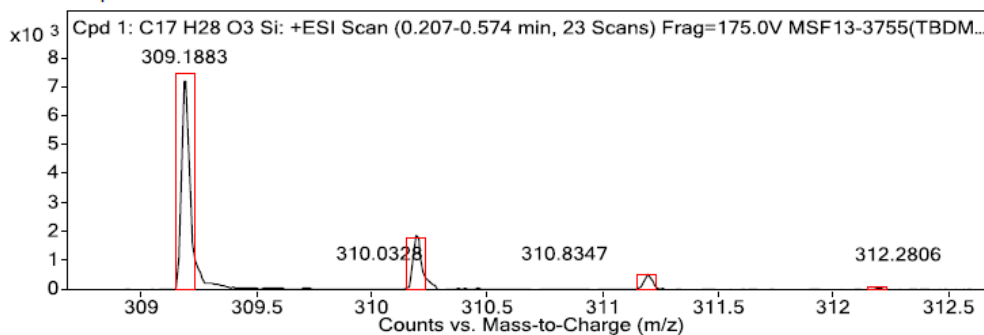
### **6-Shogaol**

A 50-mL round bottom flask was charged with 6-gingerol (1.0015 g, 3.40 mmol) and dissolved in 1,2-dimethoxyethane (20 mL). To the reaction mixture was added concentrated phosphoric acid (3 drops) and the mixture was then heated to 50°C. The reaction was allowed to stir over night under an atmosphere of N<sub>2</sub> (g). The reaction was then cooled to room temperature and diluted with diethyl ether (100 mL). The reaction was then washed with water (2 x 25 mL) and a saturated brine solution (2 x 25 mL) and the organic layer was then dried over MgSO<sub>4</sub>, filtered, and the remaining solvent removed *in vacuo*. The crude oil was purified by column chromatography (silica gel; eluent: Methylene chloride) to yield 0.5641 g of 6-shogaol as a yellow oil (60% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 0.87 (3H, t, J = 6.9 Hz, -CH<sub>3</sub>), 1.28 (4H, m, -CH<sub>2</sub>-), 1.43 (2H, dt, J = 7.3 and 14.6 Hz, -CH<sub>2</sub>-), 2.17 (2H, dd, J = 6.3 and 14.0 Hz), 2.83 (4H, tt, J = 5.9 and 12.0 Hz, -CH<sub>2</sub>- between Ph ring and ketone), 3.85 (3H, s, -OCH<sub>3</sub>), 5.50 (1H, bs, -OH), 6.07 (1H, dt, J = 1.5 and 15.9 Hz, =CH-), 6.67 (1H, dd, J = 2.0 and 8.0 Hz, =CH-), 6.69 (1H, d, J = 1.8 Hz, ArH), 6.79 (2H, m, ArH)





MS Zoomed Spectrum



MS Spectrum Peak List

Obs. m/z	Calc. m/z	Charge	Abund	Formula	Ion/Isotope	Tgt Mass Error (ppm)
309.18830	309.18800	1	7489.84	C <sub>17</sub> H <sub>28</sub> O <sub>3</sub> Si	(M+H) <sup>+</sup>	-0.7
310.03280	310.19060	1	61.44	C <sub>17</sub> H <sub>28</sub> O <sub>3</sub> Si	(M+H) <sup>+</sup>	509.12
310.83470	311.18900	1	60.53	C <sub>17</sub> H <sub>28</sub> O <sub>3</sub> Si	(M+H) <sup>+</sup>	1139.69
312.28060	312.19080	1	30.78	C <sub>17</sub> H <sub>28</sub> O <sub>3</sub> Si	(M+H) <sup>+</sup>	-287.41

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