

# **Discovery, Semisynthesis, Antiparasitic and Cytotoxic Evaluation of 14-Membered Resorcylic Acid Lactones and Their Derivatives**

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**References**

## I. General Experimental procedures

**Acetonide of Compounds 2–3, 5–8, and 16.** A mixture of **2** (48.0 mg), 2, 2-dimethoxypropane (4.5 mL), *p*-TsOH (10.0 mg) and acetone (10 mL) was stirred at room temperature for 1 h. Saturated aqueous NaHCO<sub>3</sub> (15 mL) was then added, and the reaction mixture was extracted with EtOAc (20 mL × 3). The organic solvents were removed with a high-vacuum pump, and the crude mixture was subjected to Sephadex LH-20 column chromatography with 1 L petroleum ether/CH<sub>2</sub>Cl<sub>2</sub>/MeOH (2:1:1, v/v/v) to obtain compound **18** (50.2 mg). Acetonide of compounds **3**, **5–8**, and **16** under the same reaction conditions gave the corresponding products **23**, **25**, **20**, **26**, **1**, and **17**, respectively. The known structures of **1**, **20**, **23**, **25**, and **26** were determined by comparing NMR data and MS spectrum with the literature.<sup>1</sup>

**Compound 17:** white, amorphous powder; [ $\alpha$ ]<sub>D</sub><sup>25</sup> +41.0 (*c* 0.13, MeOH); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz)  $\delta$  11.36 (1H, s, 2-OH), 6.64 (1H, dd, *J* = 16.1, 1.4 Hz, H-1'), 6.46 (1H, s, H-3), 5.99 (1H, ddd, *J* = 15.6, 8.2, 5.0 Hz, H-8'), 5.51 (1H, ddd, *J* = 16.1, 9.0, 3.7 Hz, H-2'), 5.44 (1H, ddt, *J* = 15.6, 8.6, 1.3 Hz, H-7'), 5.39 (1H, m, H-10'), 4.55 (1H, t, *J* = 8.6 Hz, H-6'), 4.19 (1H, m, H-4'), 3.91 (3H, s, 4-OCH<sub>3</sub>), 3.80 (1H, dd, *J* = 8.6, 2.5 Hz, H-5'), 2.87 (1H, m, Ha-3'), 2.56 (1H, m, Ha-9'), 2.43 (1H, m, Hb-9'), 2.36 (1H, m, Hb-3'), 1.43 (3H, s), 1.39 (6H, overlapped, -CH<sub>3</sub>×2); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz)  $\delta$  170.7 (C), 162.4 (C), 160.0 (C), 140.0 (C), 130.8 (CH), 130.4 (CH), 129.2 (CH), 128.9 (CH), 114.2 (C), 108.7 (C), 106.5 (C), 99.6 (CH), 81.0 (CH), 75.6 (CH), 71.4 (CH), 68.5 (CH), 56.5 (CH<sub>3</sub>), 37.2 (CH<sub>2</sub>), 37.2 (CH<sub>2</sub>), 27.3 (CH<sub>3</sub>), 27.1 (CH<sub>3</sub>), 19.4 (CH<sub>3</sub>); HRESIMS *m/z* 461.1338 [M + Na]<sup>+</sup> (calcd for C<sub>22</sub>H<sub>27</sub>O<sub>7</sub>ClNa, 461.1338); 95% yield.

**Compound 18:** white, amorphous powder; [ $\alpha$ ]<sub>D</sub><sup>25</sup> -23.2 (*c* 0.05, MeOH); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz)  $\delta$  11.72 (1H, s, 2-OH), 6.68 (1H, dd, *J* = 16.0, 2.1 Hz, H-1'), 6.48 (1H, s, H-3), 5.61 (1H, ddd, *J* = 16.0, 10, 2.5 Hz, H-2'), 5.24 (1H, m, H-10'), 5.30 (1H, m), 4.17 (2H, m), 3.92 (3H, s, 4-OCH<sub>3</sub>), 3.79 (1H, dd, *J* = 7.9, 1.8 Hz, H-5'), 2.94 (1H, m), 2.37 (1H, m), 2.01 (1H, m), 1.83 (1H, m), 1.62 (4H, overlapped), 1.42 (3H, s), 1.37 (3H, d, *J* = 6.4 Hz, H-11'), 1.36 (3H, s); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz)  $\delta$  170.8 (C), 162.9 (C), 160.0 (C), 139.8 (C), 132.1 (CH), 128.9 (CH), 114.6 (C), 107.7 (C), 106.1 (C), 99.7 (CH), 80.6 (CH), 73.9 (CH), 73.8 (CH), 69.4 (CH), 56.6 (CH<sub>3</sub>), 35.7 (CH<sub>2</sub>), 34.7 (CH<sub>2</sub>), 33.3 (CH<sub>2</sub>), 29.8 (CH<sub>2</sub>), 27.4 (CH<sub>3</sub>), 27.3 (CH<sub>3</sub>), 20.1 (CH<sub>3</sub>); HRESIMS *m/z* 463.1495 [M + Na]<sup>+</sup> (calcd for C<sub>22</sub>H<sub>29</sub>O<sub>7</sub>ClNa, 463.1494); 95% yield.

**Acylation of compounds 1–3 and 6–8.** To a solution of compound **1** (100 mg, 0.25 mmol) in

acetone (15 mL) was added excess anhydrous  $K_2CO_3$  and 5.0 mL of acetic anhydride, and the mixture was stirred at 40 °C for 12 h. When the reaction was completed, the solvent was removed in vacuo. Water (15 mL) was then added, and the reaction mixture was extracted with EtOAc (20 mL  $\times$  3). The organic solvents were removed under a vacuum, and the crude mixture was subjected to Sephadex LH-20 CC eluted with petroleum ether/ $CH_2Cl_2$ /MeOH (2:1:1, v/v/v) to obtain the compound **11** (98.8 mg). Acylation of compounds **2**, **3**, and **6–8** under the same reaction conditions gave the corresponding products **19**, **24**, **21**, **22**, **27**, and **12–15**, respectively. The known structures of **11** and **13** were determined by comparing NMR data and MS spectrum with the literature.<sup>2</sup>

**Compound 12:** white, amorphous powder;  $[\alpha]_D^{25} -56.8$  (*c* 0.12, MeOH);  $^1H$  NMR ( $CDCl_3$ , 500 MHz)  $\delta$  12.04 (1H, s, 2-OH), 7.07 (1H, d,  $J = 15.0$  Hz, H-1'), 6.40 (2H, overlapped, H-3, H-5), 6.14 (1H, m), 5.82 (1H, m), 5.69 (1H, m), 5.49 (1H, t,  $J = 8.2$  Hz), 5.39 (2H, overlapped), 5.01 (1H, m, H-10'), 3.81 (3H, s, 4-OCH<sub>3</sub>), 2.66 (1H, m), 2.47 (3H, overlapped), 2.05 (9H, -CH<sub>3</sub> $\times$ 3), 1.47 (3H, d,  $J = 6.3$  Hz, H-11');  $^{13}C$  NMR ( $CDCl_3$ , 125 MHz)  $\delta$  171.4 (C), 170.6 (C), 170.3 (C), 170.2 (C), 165.9 (C), 164.2 (C), 142.5 (C), 134.5 (CH), 132.9 (CH), 127.5 (CH), 126.0 (CH), 108.0 (C), 103.7 (CH), 100.2 (CH), 73.9 (CH), 73.8 (CH), 73.8 (CH), 71.1 (CH), 55.6 (CH<sub>3</sub>), 37.2 (CH<sub>2</sub>), 32.3 (CH<sub>2</sub>), 21.2 (CH<sub>3</sub>), 21.1 (CH<sub>3</sub>), 21.0 (CH<sub>3</sub>), 19.3 (CH<sub>3</sub>); HRESIMS  $m/z$  491.1921 [ $M + H$ ]<sup>+</sup> (calcd for  $C_{25}H_{31}O_{10}$ , 491.1912); 67% yield.

**Compound 14:** white, amorphous powder;  $[\alpha]_D^{25} +41.9$  (*c* 0.14, MeOH);  $^1H$  NMR ( $CDCl_3$ , 500 MHz)  $\delta$  6.82 (1H, d,  $J = 15.0$  Hz, H-1'), 6.72 (1H, d,  $J = 2.5$  Hz, H-5), 6.54 (1H, d,  $J = 2.5$  Hz, H-3), 6.02 (1H, m, H-8'), 5.94 (1H, ddd,  $J = 15.0, 9.0, 4.7$  Hz, H-2'), 5.62 (1H, dd,  $J = 15.5, 7.9$  Hz, H-7'), 5.46 (1H, m, H-10'), 5.31 (1H, m), 5.12 (2H, overlapped), 3.80 (3H, s, 4-OCH<sub>3</sub>), 2.95 (2H, overlapped), 2.55 (2H, overlapped), 2.58–2.28 (8H, -CH<sub>2</sub> $\times$ 4), 1.37 (3H, d,  $J = 6.1$ , H-11'), 1.23 (3H, t,  $J = 7.5$  Hz, -CH<sub>3</sub>), 1.10 (9H, -CH<sub>3</sub> $\times$ 3);  $^{13}C$  NMR ( $CDCl_3$ , 125 MHz)  $\delta$  173.8 (C), 173.5 (C), 173.4 (C), 172.7 (C), 165.6 (C), 161.3 (C), 150.8 (C), 139.1 (C), 133.8 (CH), 131.5 (CH), 126.6 (CH), 126.9 (CH), 117.7 (C), 110.5 (CH), 107.7 (CH), 73.6 (CH), 73.6 (CH), 72.9 (CH), 72.3 (CH), 55.7 (CH<sub>3</sub>), 37.8 (CH<sub>2</sub>), 37.8 (CH<sub>2</sub>), 27.8 (CH<sub>2</sub>), 27.7 (CH<sub>2</sub>), 27.6 (CH<sub>2</sub>), 27.6 (CH<sub>2</sub>), 20.1 (CH<sub>3</sub>), 9.3 (CH<sub>3</sub>), 9.2 (CH<sub>3</sub>), 9.0 (CH<sub>3</sub>), 9.0 (CH<sub>3</sub>); HRESIMS  $m/z$  611.2473 [ $M + Na$ ]<sup>+</sup> (calcd for  $C_{31}H_{40}O_{11}Na$ , 611.2463); 92% yield.

**Compound 15:** white, amorphous powder;  $[\alpha]_D^{25} -45.4$  (*c* 0.05, MeOH);  $^1H$  NMR ( $CDCl_3$ , 500

MHz)  $\delta$  7.66 (1H, d,  $J = 0.6$  Hz), 7.56 (1H, s), 7.49 (2H, d,  $J = 9.1$  Hz), 7.37 (1H, d,  $J = 3.2$  Hz), 7.19 (1H, m), 7.06 (2H, m), 6.97 (1H, m), 6.81 (1H, brs), 6.71 (1H, d,  $J = 1.8$  Hz), 6.58 (1H, m), 6.48 (1H, m), 6.41 (2H, overlapped), 6.20–6.05 (2H, overlapped), 5.80 (2H, overlapped), 5.69 (1H, m), 5.52 (1H, m), 5.23 (1H, m), 3.83 (3H, s, 4-OCH<sub>3</sub>), 2.88–2.76 (2H, overlapped), 2.56–2.38 (2H, overlapped), 1.29 (3H, d,  $J = 6.2$  Hz, H-11'); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz)  $\delta$  165.4 (C), 161.4 (C), 157.9 (C), 157.5 (C), 157.5 (C), 156.5 (C), 149.9 (C), 147.4, 146.9, 146.8, 146.8, 144.2, 144.1, 143.9, 143.9, 139.2, 134.6, 131.6, 129.2, 126.4, 119.9, 118.9, 118.9, 118.7, 118.0, 112.4, 112.1, 112.0, 112.0, 110.9, 107.9, 77.4 (CH), 74.0 (CH), 73.4 (CH), 71.9 (CH), 55.8 (CH<sub>3</sub>), 38.0 (CH<sub>2</sub>), 33.6 (CH<sub>2</sub>), 20.0 (CH<sub>3</sub>). HRESIMS  $m/z$  763.1634 [M + Na]<sup>+</sup> (calcd for C<sub>39</sub>H<sub>32</sub>O<sub>15</sub>Na, 763.1633); 85% yield.

**Compound 19:** white, amorphous powder; [ $\alpha$ ]<sub>D</sub><sup>25</sup> +15.1 ( $c$  0.05, MeOH); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz)  $\delta$  6.75 (1H, d,  $J = 15.9$  Hz, H-1'), 6.67 (1H, s, H-3), 5.94 (1H, m, H-2'), 5.27 (1H, m), 5.20 (1H, m), 4.98 (2H, overlapped), 3.90 (3H, s, 4-OCH<sub>3</sub>), 2.87 (1H, m), 2.47 (1H, m), 2.26 (3H, s, -CH<sub>3</sub>), 2.06 (3H, s, -CH<sub>3</sub>), 2.01 (6H, overlapped, -CH<sub>3</sub>×2), 1.70–1.35 (6H, overlapped), 1.32 (3H, d,  $J = 6.0$  Hz, H-11'); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz)  $\delta$  170.4 (C), 170.2 (C), 170.2 (C), 168.7 (C), 165.6 (C), 156.2 (C), 147.1 (C), 136.1, 132.9, 128.7, 120.4, 119.8, 105.7, 74.6 (CH), 71.9 (CH), 71.8 (CH), 70.0 (CH), 56.7 (CH<sub>3</sub>), 33.9 (CH<sub>2</sub>), 33.9 (CH<sub>2</sub>), 28.9 (CH<sub>2</sub>), 28.9 (CH<sub>2</sub>), 21.1 (CH<sub>3</sub>), 21.1 (CH<sub>3</sub>), 21.0 (CH<sub>3</sub>), 21.0 (CH<sub>3</sub>), 20.9 (CH<sub>3</sub>); HRESIMS  $m/z$  569.1788 [M + H]<sup>+</sup> (calcd for C<sub>27</sub>H<sub>34</sub>O<sub>11</sub>Cl, 569.1784); 87% yield.

**Compound 21:** white, amorphous powder; [ $\alpha$ ]<sub>D</sub><sup>25</sup> -8.5 ( $c$  0.08, MeOH); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz)  $\delta$  7.03 (1H, m), 6.80 (1H, d,  $J = 1.8$  Hz, H-5), 6.62 (1H, d,  $J = 15.9$  Hz, H-1'), 6.58 (1H, d,  $J = 1.8$  Hz, H-3), 6.22 (1H, d,  $J = 15.9$  Hz, H-7'), 5.99 (1H, m), 5.75 (1H, d,  $J = 2.4$  Hz, H-5'), 5.49 (1H, m), 5.29 (1H, m), 3.81 (3H, s, 4-OCH<sub>3</sub>), 2.62 (2H, m), 2.43 (2H, m), 2.26 (3H, s, -CH<sub>3</sub>), 2.12 (3H, s, -CH<sub>3</sub>), 2.09 (3H, s, -CH<sub>3</sub>), 1.42 (3H, d,  $J = 6.1$  Hz, H-11'); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz)  $\delta$  193.3 (C), 170.3 (C), 170.2 (C), 168.8 (C), 165.7 (C), 161.2 (C), 149.5 (C), 143.9 (CH), 143.9 (C), 138.3 (CH), 131.3 (CH), 128.4 (CH), 118.3 (C), 109.6 (CH), 107.7 (CH), 75.7 (CH), 72.9 (CH), 69.9 (CH), 55.8 (CH<sub>3</sub>), 39.0 (CH<sub>2</sub>), 32.8 (CH<sub>2</sub>), 21.1 (CH<sub>3</sub>), 21.0 (CH<sub>3</sub>), 20.8 (CH<sub>3</sub>), 20.7 (CH<sub>3</sub>); HRESIMS  $m/z$  511.1577 [M + Na]<sup>+</sup> (calcd for C<sub>25</sub>H<sub>28</sub>O<sub>10</sub>Na, 511.1575); 87% yield.

**Compound 22:** white, amorphous powder; [ $\alpha$ ]<sub>D</sub><sup>25</sup> +67.1 ( $c$  0.21, MeOH); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz)  $\delta$  7.96 (1H, dd,  $J = 4.0, 1.2$  Hz), 7.75 (1H, dd,  $J = 4.0, 1.2$  Hz), 7.67 (1H, dd,  $J = 4.0, 1.2$

Hz), 7.55 (3H, overlapped), 7.17 (1H, m), 7.07–6.99 (4H, overlapped), 6.73 (1H, d,  $J = 2.2$  Hz), 6.68 (1H, d,  $J = 15.8$  Hz), 6.42 (1H, d,  $J = 15.8$  Hz), 6.33 (1H, m), 6.05 (1H, d,  $J = 4.0$  Hz), 5.91 (1H, m), 5.32 (1H, m), 3.83 (3H, s, 4-OCH<sub>3</sub>), 2.82–2.68 (2H, overlapped), 2.46 (1H, m), 2.32 (1H, m), 1.06 (3H, d,  $J = 6.3$  Hz, H-11'); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz)  $\delta$  195.1 (C), 165.8 (C), 161.1 (C), 161.0 (C), 160.9 (C), 160.1 (C), 149.0 (C), 144.2, 138.7, 135.2, 134.6, 134.2, 134.1, 133.9, 133.2, 133.1, 132.6, 132.4, 130.4, 129.6, 129.2, 128.3, 128.2, 128.0, 119.1, 109.6 (CH), 107.7 (CH), 76.6 (CH), 73.3 (CH), 69.4 (CH), 55.9 (CH<sub>3</sub>), 39.8 (CH<sub>2</sub>), 34.1 (CH<sub>2</sub>), 20.5 (CH<sub>3</sub>). HRESIMS  $m/z$  715.0738 [M + Na]<sup>+</sup> (calcd for C<sub>34</sub>H<sub>28</sub>O<sub>10</sub>S<sub>3</sub>Na, 715.0737); 85% yield.

**Compound 24:** white, amorphous powder; [ $\alpha$ ]<sub>D</sub><sup>25</sup> –49.1 ( $c$  0.08, MeOH); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz)  $\delta$  7.04 (1H, m), 6.83 (2H, overlapped), 6.58 (1H, s, H-3), 6.26 (1H, d,  $J = 16.3$  Hz), 6.06 (1H, m), 5.45 (2H, overlapped), 5.34 (1H, m, H-10'), 3.83 (3H, s, 4-OCH<sub>3</sub>), 2.75 (1H, m), 2.65 (1H, m), 2.41 (2H, m), 2.29 (3H, s, -CH<sub>3</sub>), 2.11 (6H, overlapped, -CH<sub>3</sub>×2), 1.44 (3H, d,  $J = 6.2$  Hz, H-11'); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz)  $\delta$  194.0 (C), 170.3 (C), 170.0 (C), 169.4 (C), 164.9 (C), 161.7 (C), 151.2 (C), 144.6 (CH), 139.5 (C), 133.5 (CH), 131.7 (CH), 126.8 (CH), 117.0 (C), 111.2 (CH), 108.2 (CH), 75.0 (CH), 72.0 (CH), 70.6 (CH), 55.8 (CH<sub>3</sub>), 37.7 (CH<sub>2</sub>), 33.3 (CH<sub>2</sub>), 21.1 (CH<sub>3</sub>), 21.1 (CH<sub>3</sub>), 20.6 (CH<sub>3</sub>), 19.7 (CH<sub>3</sub>); HRESIMS  $m/z$  511.1575 [M + Na]<sup>+</sup> (calcd for C<sub>25</sub>H<sub>28</sub>O<sub>10</sub>Na, 511.1575); 87% yield.

**Compound 27:** white, amorphous powder; [ $\alpha$ ]<sub>D</sub><sup>25</sup> –55.7 ( $c$  0.13, MeOH); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz)  $\delta$  12.16 (1H, s, 2-OH), 6.95 (1H, d,  $J = 15.0$  Hz, H-1'), 6.49 (1H, dd,  $J = 11.5, 2.6$  Hz, H-7'), 6.37 (2H, overlapped, H-3, H-5), 6.23 (1H, td,  $J = 11.5, 2.6$  Hz, H-8'), 5.88 (1H, ddd,  $J = 15.0, 10.3, 4.3$  Hz, H-2'), 5.58 (1H, brs), 5.24 (2H, overlapped), 3.80 (3H, s, 4-OCH<sub>3</sub>), 3.55 (1H, m), 2.42 (3H, overlapped), 2.42 (3H, s, -CH<sub>3</sub>), 2.10 (3H, s, -CH<sub>3</sub>), 1.35 (3H, d,  $J = 6.0$ , H-11'); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz)  $\delta$  192.9 (C), 171.5 (C), 170.8 (C), 170.3 (C), 166.1 (C), 164.3 (C), 147.0 (CH), 143.0 (C), 133.9 (CH), 129.4 (CH), 126.0 (CH), 108.5 (C), 103.6 (CH), 100.2 (CH), 80.1 (CH), 74.0 (CH), 72.9 (CH), 55.6 (CH<sub>3</sub>), 36.9 (CH<sub>2</sub>), 33.3 (CH<sub>2</sub>), 21.2 (CH<sub>3</sub>), 20.9 (CH<sub>3</sub>), 20.8 (CH<sub>3</sub>); HRESIMS  $m/z$  447.1652 [M + H]<sup>+</sup> (calcd for C<sub>23</sub>H<sub>27</sub>O<sub>9</sub>, 447.1650); 65% yield.



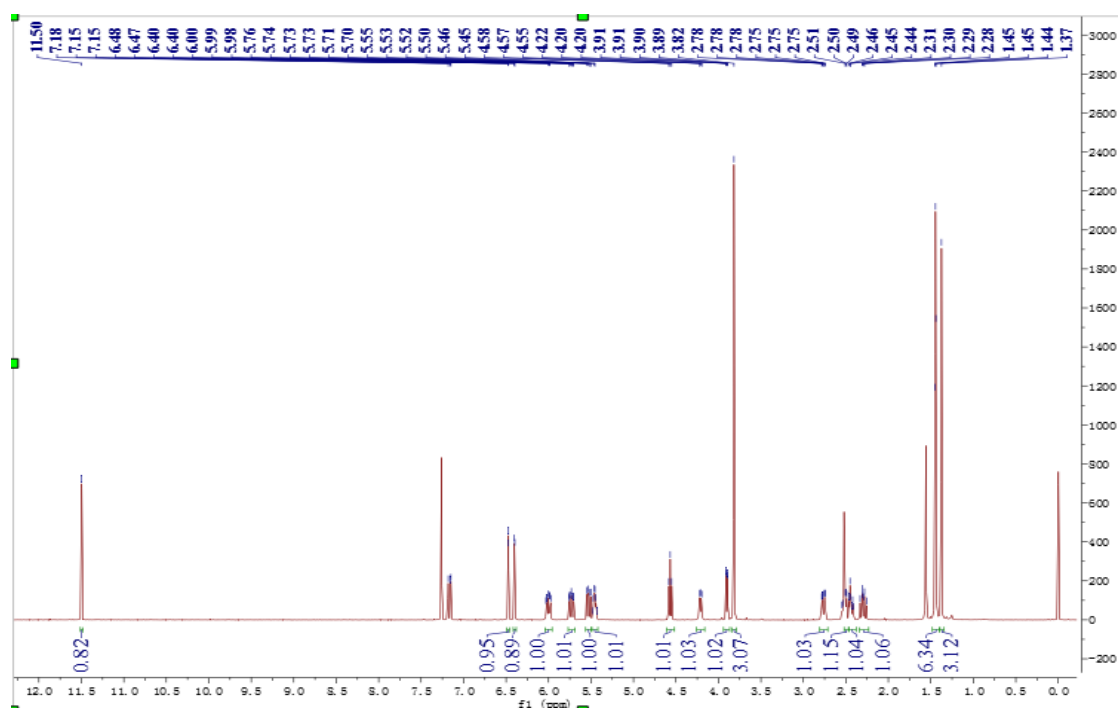


Figure S1.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of compound **1**.

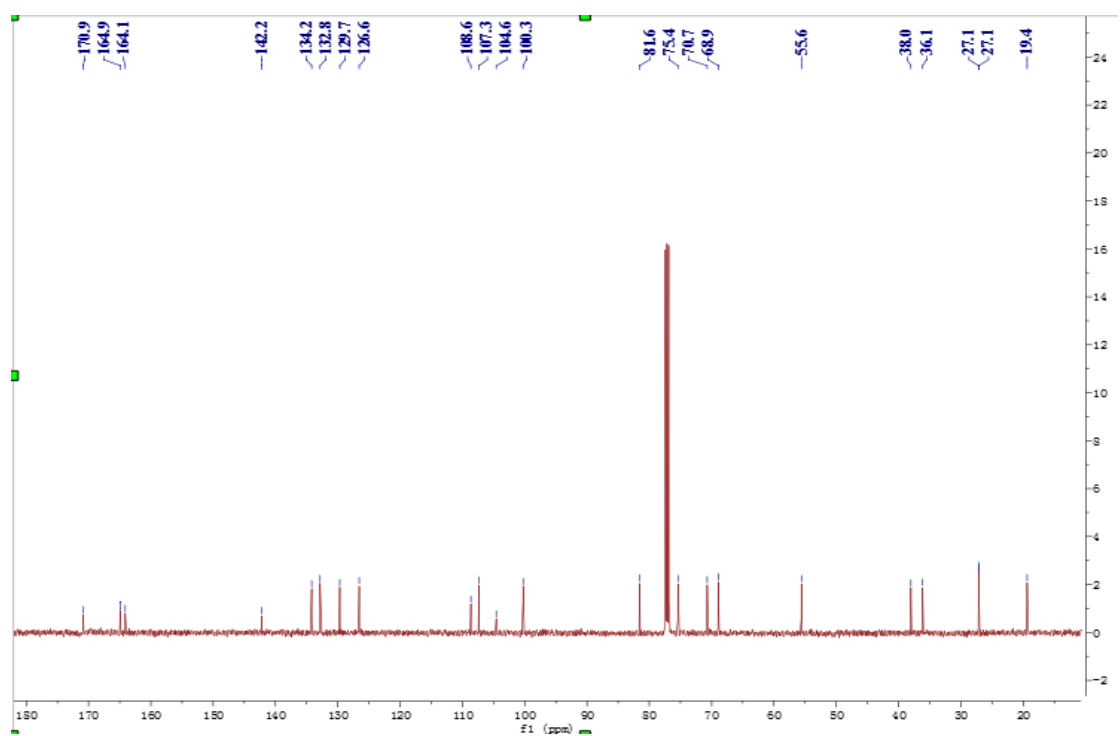
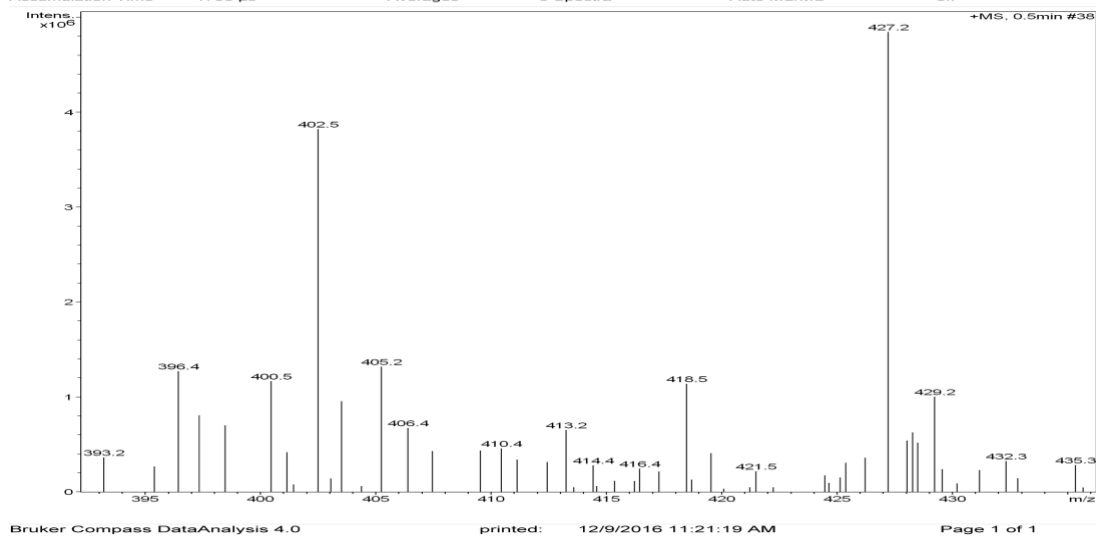


Figure S2.  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ) spectrum of compound **1**.

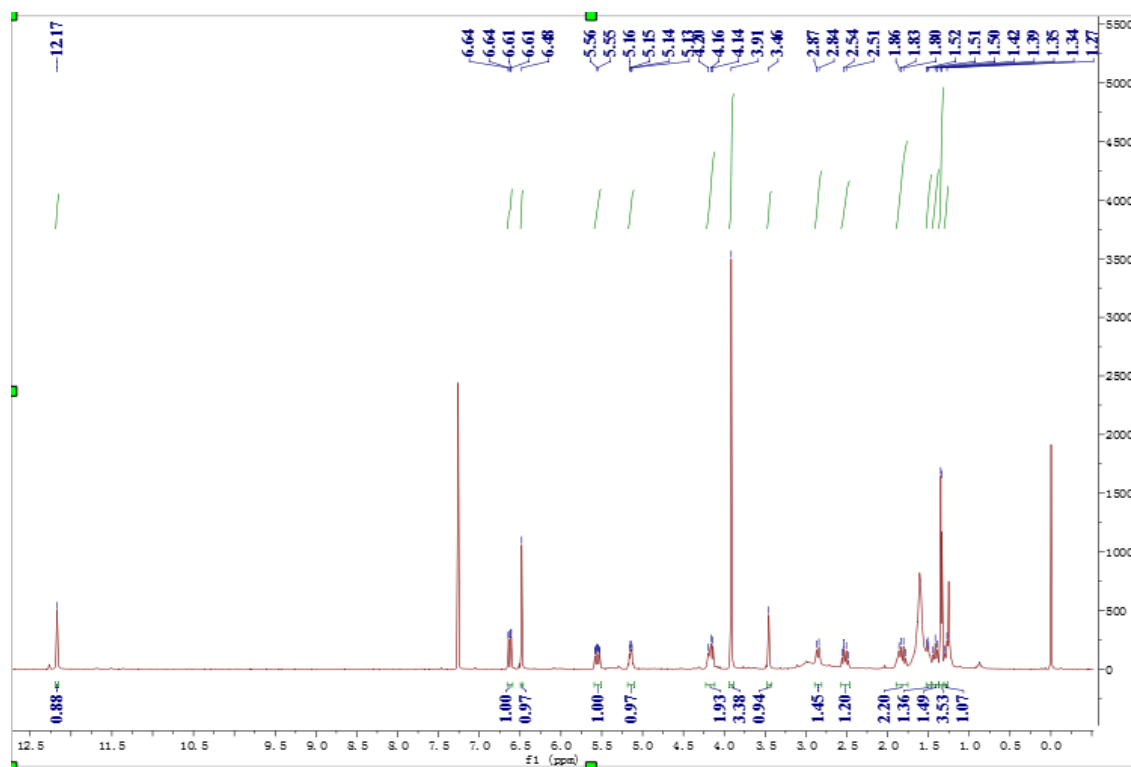
### Display Report

<b>Analysis Info</b>	D:\Data\WCY\20161202-ZXQ-4A.d	Acquisition Date	12/2/2016 12:59:55 PM
Analysis Name	20161001-MIX--G3-MSMS.m	Operator	bruker
Method	20161202-ZXQ-4A	Instrument	amaZon SL
Sample Name			
Comment			

<b>Acquisition Parameter</b>			
Ion Source Type	ESI	Ion Polarity	Positive
Mass Range Mode	Enhanced Resolution	Scan Begin	100 m/z
Capillary Exit	1758 $\mu$ s	Averages	n/a
Accumulation Time			5 Spectra
		Alternating Ion Polarity	off
		Scan End	1000 m/z
		Trap Drive	76.0
		Auto MS/MS	off



**Figure S3.** ESIMS spectrum of compound 1.



**Figure S4.**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of compound 2.

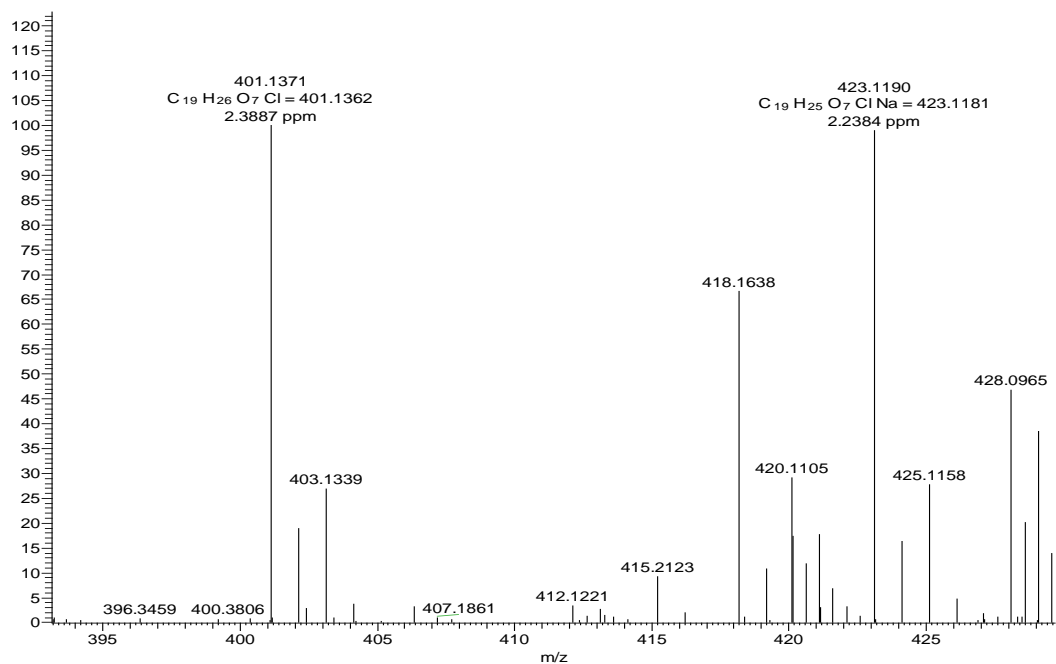


Figure S5. HRESIMS spectrum of compound 2.

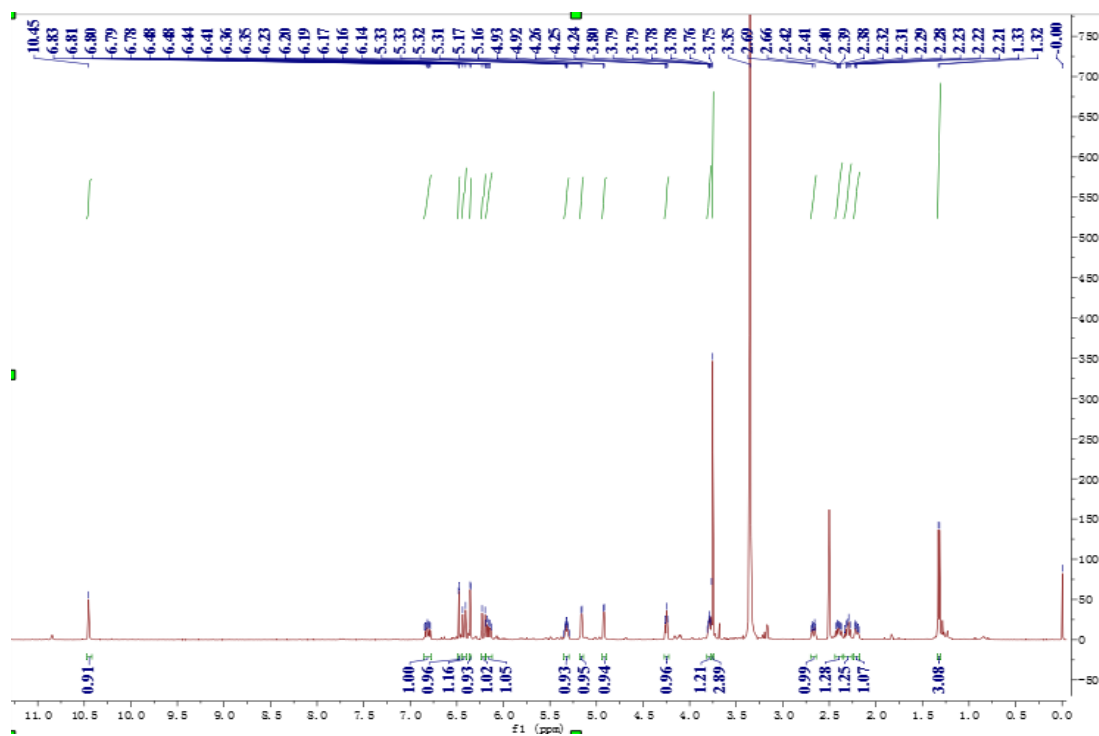


Figure S6. <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>) spectrum of compound 3.

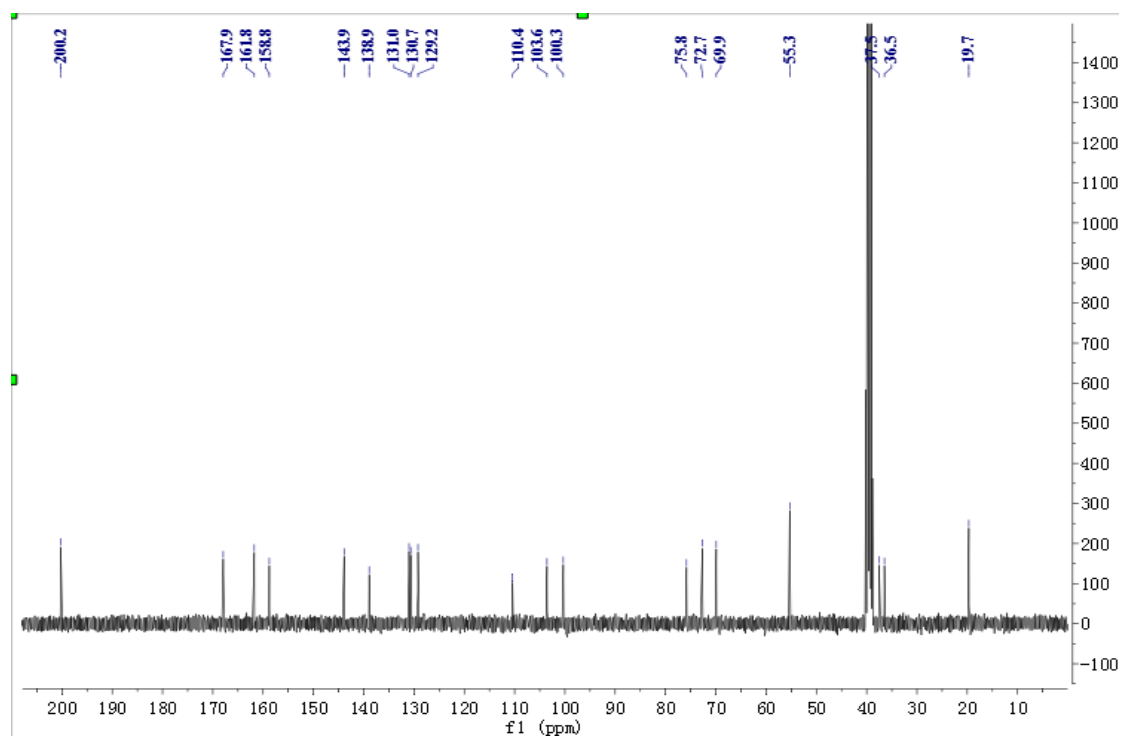


Figure S7.  $^{13}\text{C}$  NMR (125 MHz,  $\text{DMSO-}d_6$ ) spectrum of compound 3.

Display Report

<b>Analysis Info</b>		Acquisition Date	12/2/2016 12:48:23 PM
Analysis Name	D:\Data\WCY\20161202-ZXQ-4P-5.d	Operator	bruker
Method	20161001-MIX---G3-MSMS.m	Instrument	amazon SL
Sample Name	20161202-ZXQ-4P-5a		
Comment			

<b>Acquisition Parameter</b>		Ion Polarity	Positive	Alternating Ion Polarity	off
Ion Source Type	ESI	Scan Begin	100 m/z	Scan End	1000 m/z
Mass Range Mode	Enhanced	n/a	n/a	Trap Drive	76.0
Capillary Exit	RF-Guided	Averages	5 Spectra	Auto MS/MS	off
Accumulation Time	208 $\mu\text{s}$				

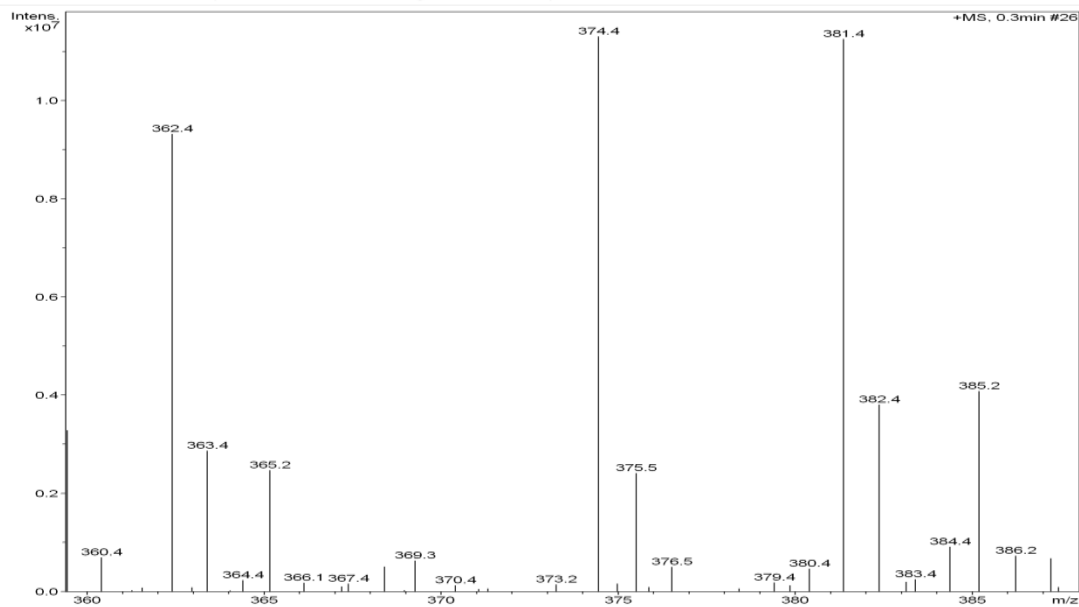


Figure S8. ESIMS spectrum of compound 3.

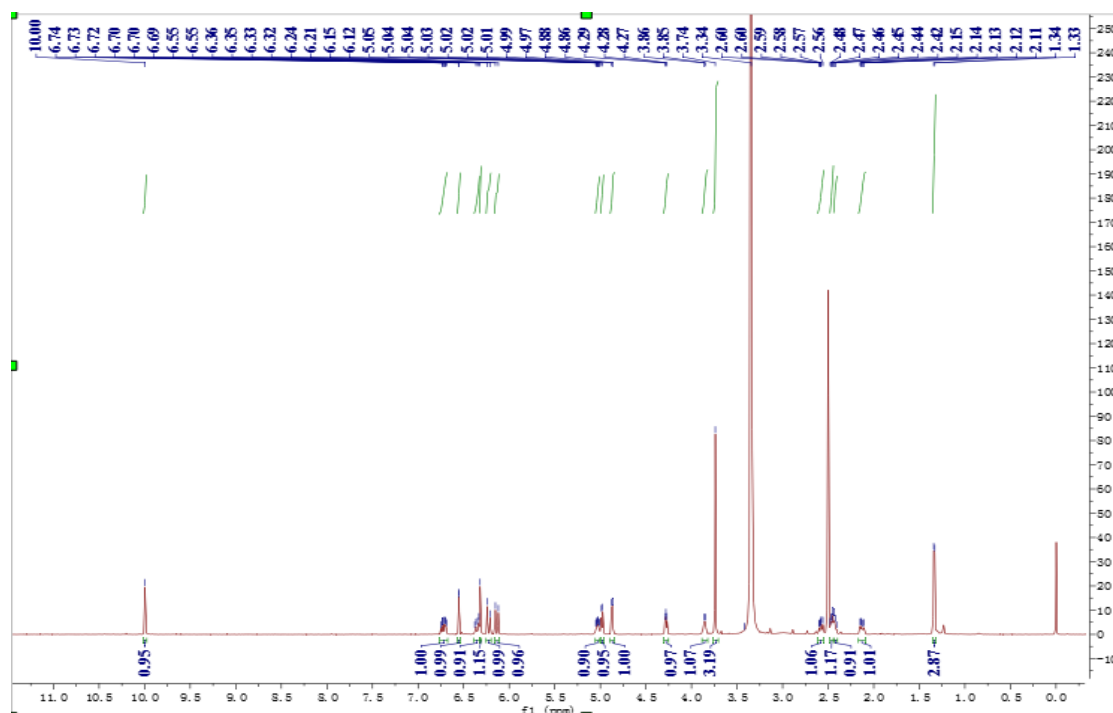


Figure S9.  $^1\text{H}$  NMR (500 MHz,  $\text{DMSO-}d_6$ ) spectrum of compound 4.

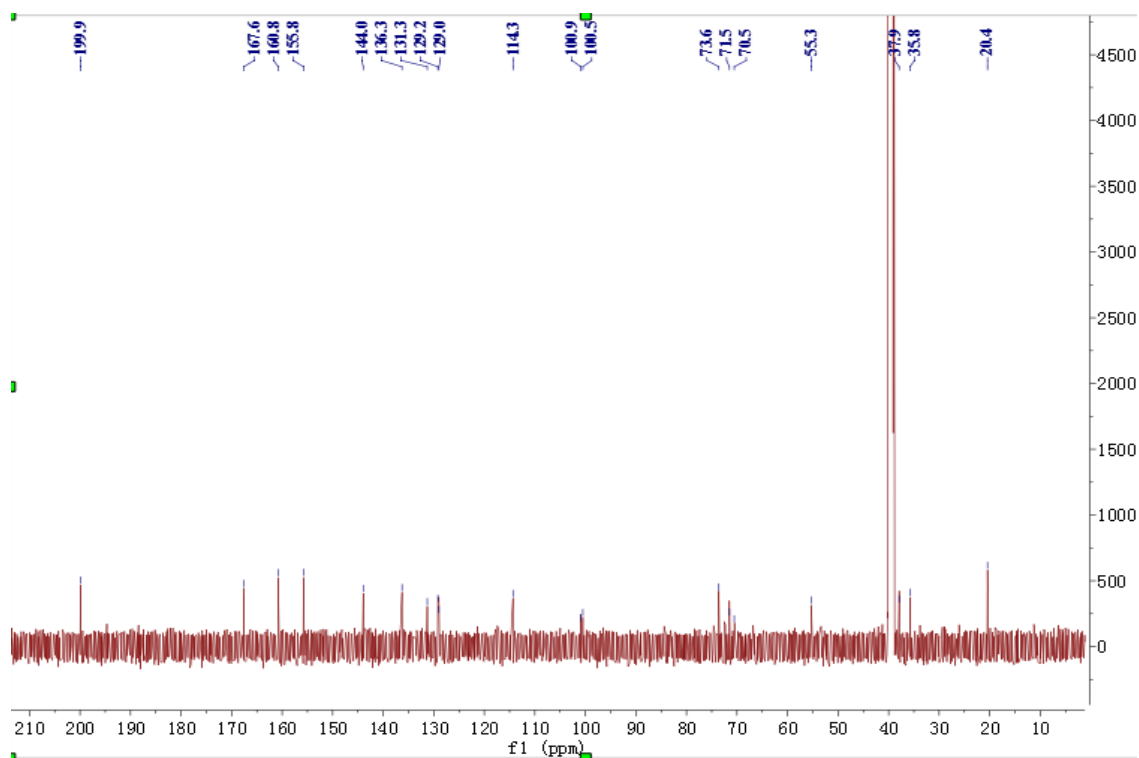
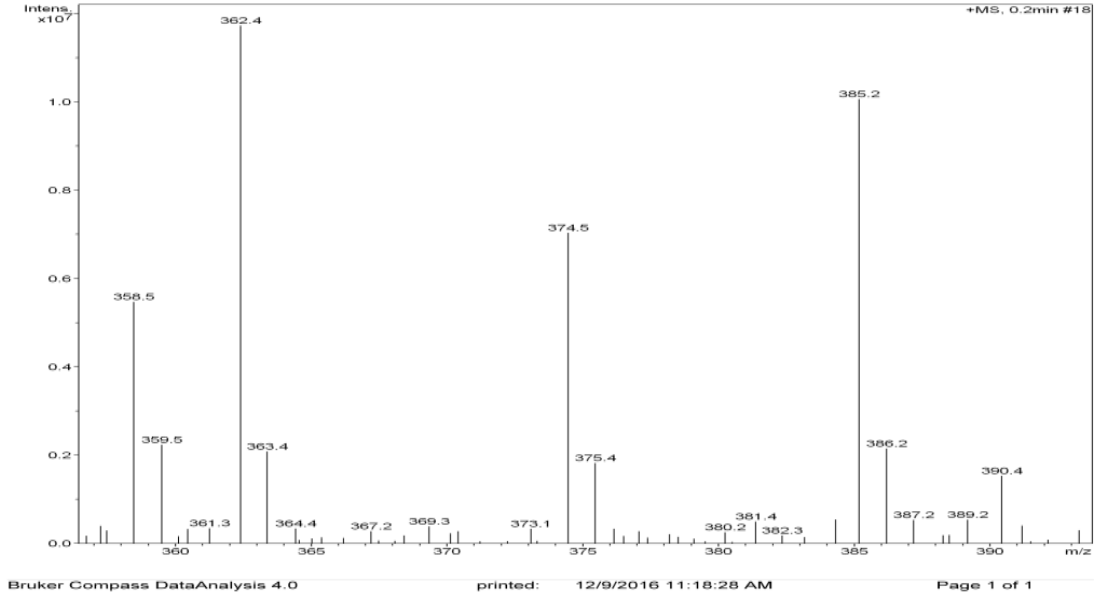


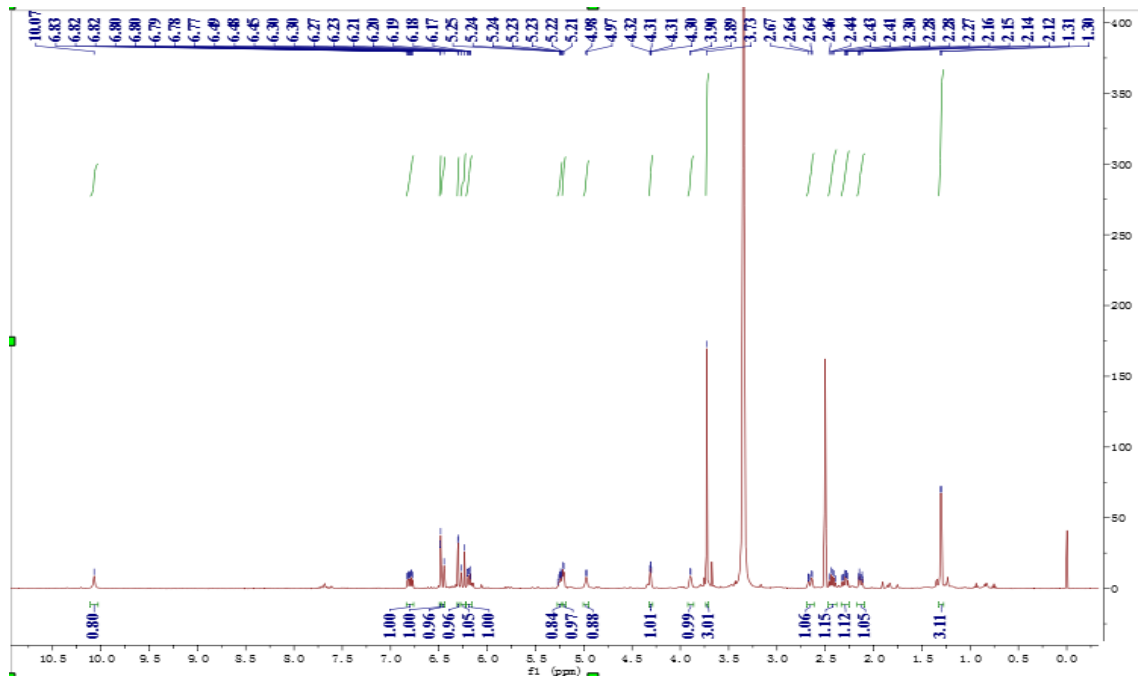
Figure S10.  $^{13}\text{C}$  NMR (125 MHz,  $\text{DMSO-}d_6$ ) spectrum of compound 4.

## Display Report

Analysis Info		Acquisition Date	
Analysis Name	D:\Data\WCY\20161202-ZXQ-4P-1.d	Acquisition Date	12/2/2016 12:39:21 PM
Method	20161001-MIX-G3-MSMS.m	Operator	bruker
Sample Name	20161202-ZXQ-4P-1	Instrument	amazon SL
Comment			
Acquisition Parameter			
Ion Source Type	ESI	Ion Polarity	Positive
Mass Range Mode	Enhanced MS	Scan Begin	n/a
Capillary Exit	144 µs	Averages	5 Spectra
Accumulation Time		Alternating Ion Polarity	off
		Scan End	1000 m/z
		Trap Drive	75.0
		Auto MS/MS	off



**Figure S11.** ESIMS spectrum of compound 4.



**Figure S12.** <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>) spectrum of compound 5.

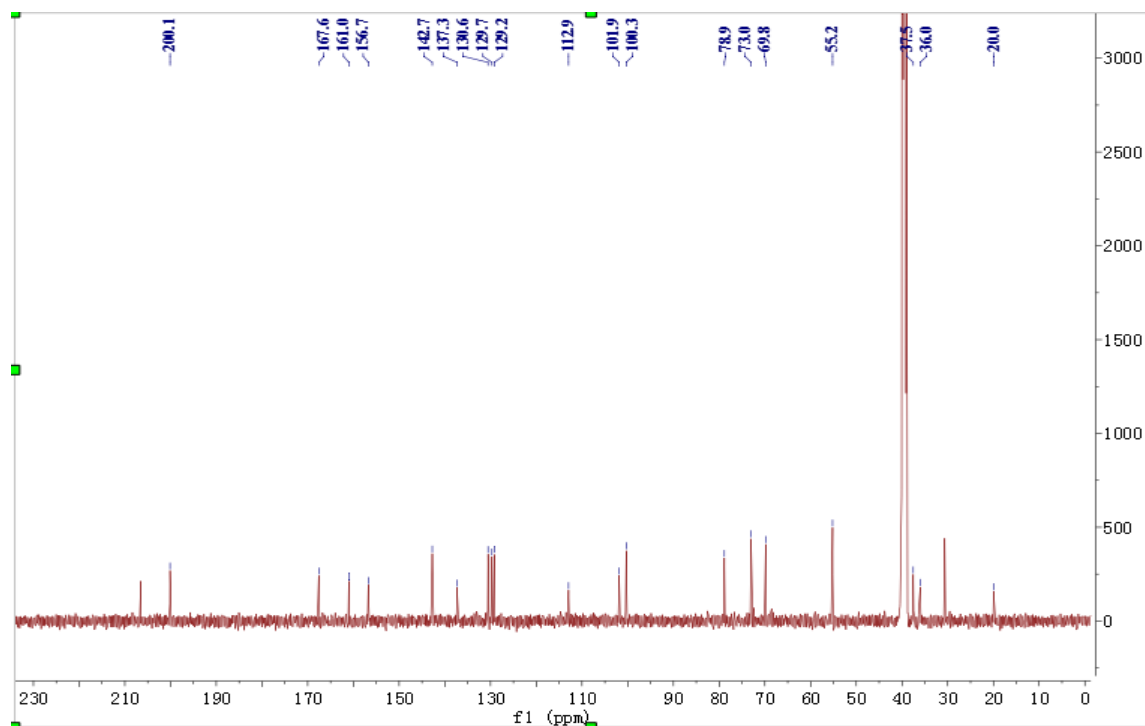


Figure S13.  $^{13}\text{C}$  NMR (125 MHz,  $\text{DMSO}-d_6$ ) spectrum of compound 5.

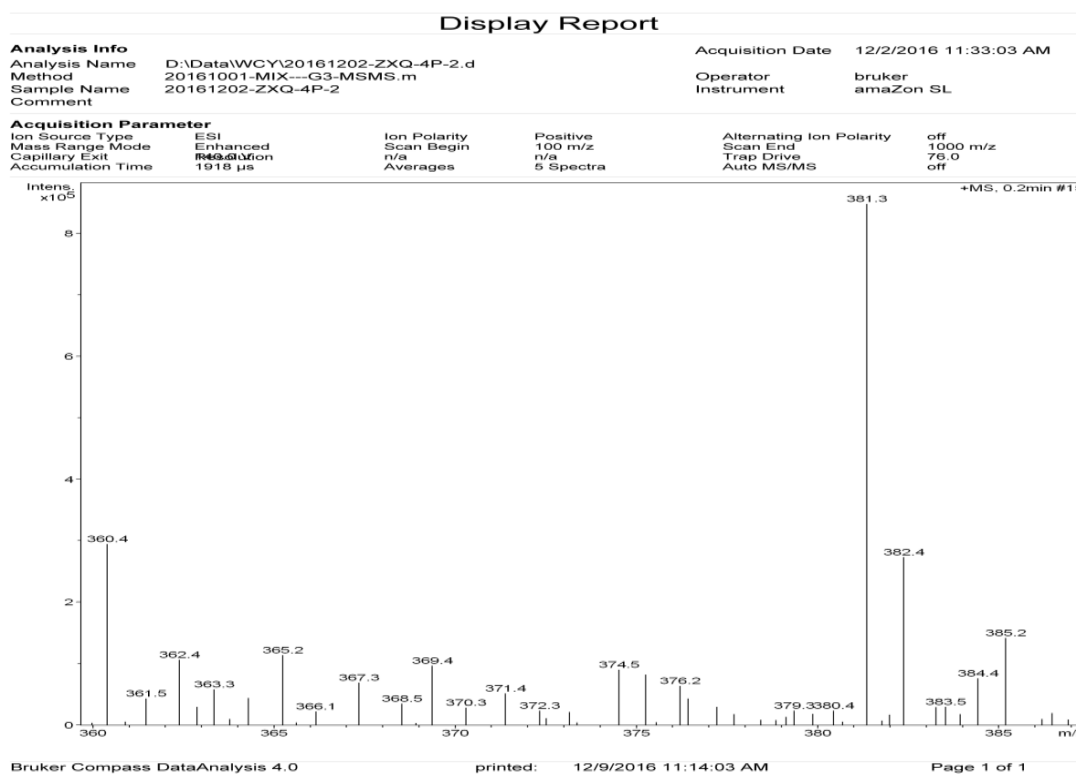


Figure S14. ESIMS spectrum of compound 5.

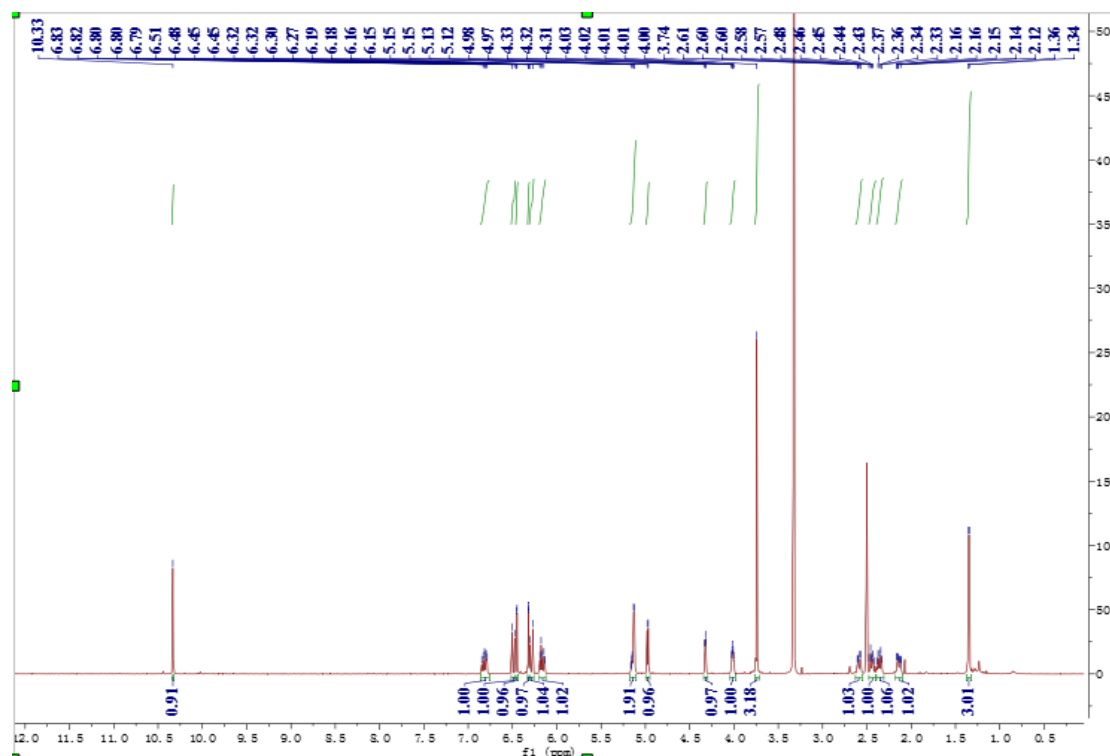


Figure S15.  $^1\text{H}$  NMR (500 MHz,  $\text{DMSO-}d_6$ ) spectrum of compound **6**.

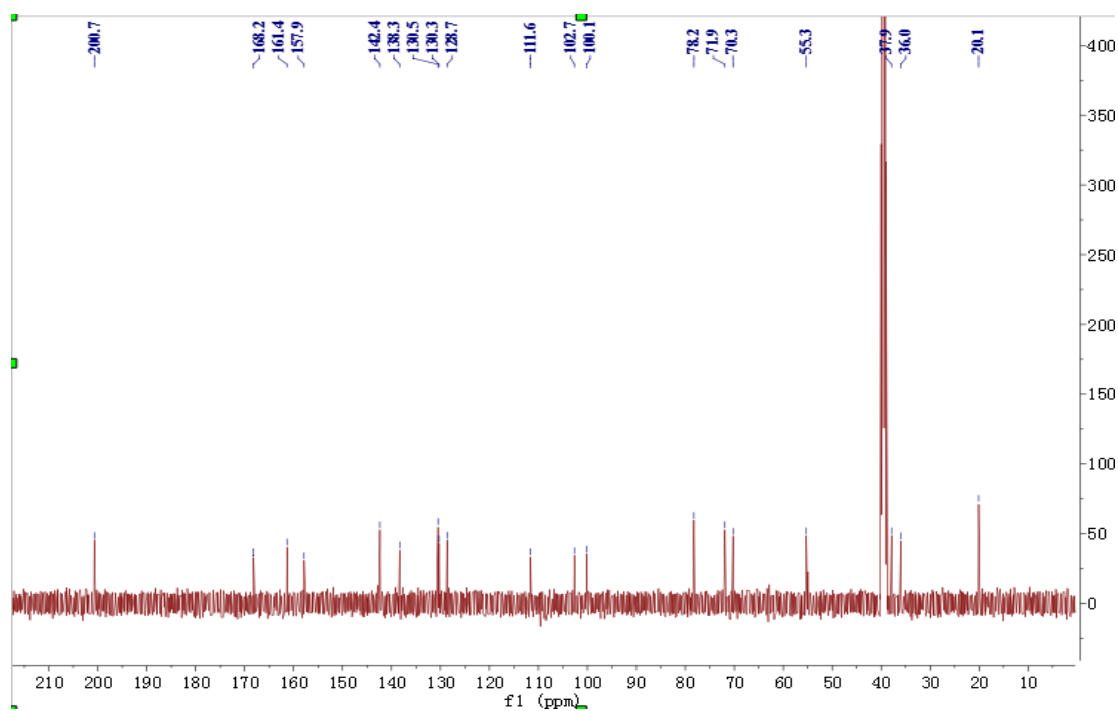


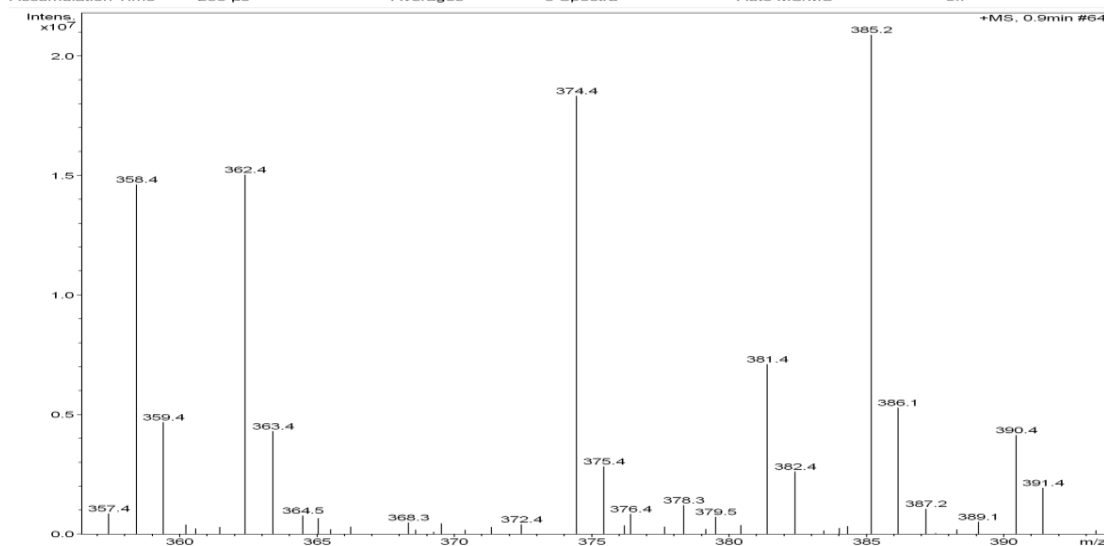
Figure S16.  $^{13}\text{C}$  NMR (125 MHz,  $\text{DMSO-}d_6$ ) spectrum of compound **6**.



## Display Report

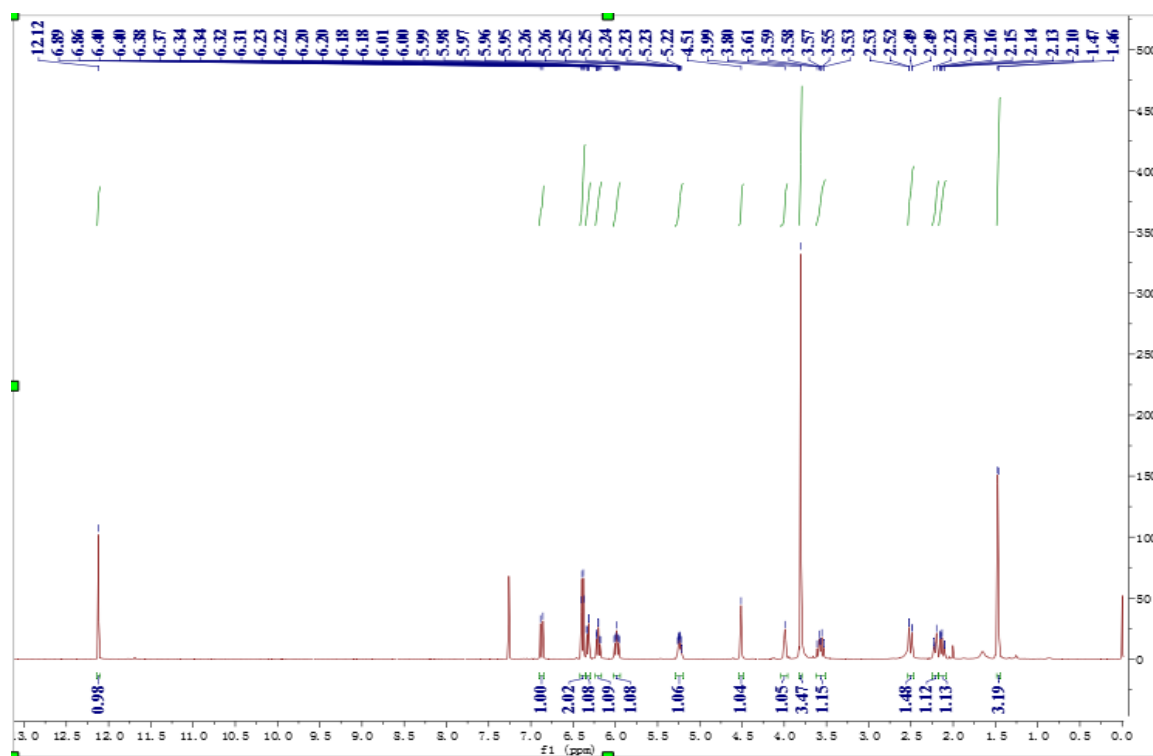
<b>Analysis Info</b> Analysis Name: D:\Data\WCY\20161202-ZXQ-4P-3.d Method: 20161001-MIX---G3-MSMS.m Sample Name: 20161202-ZXQ-6-CH3 Comment:	Acquisition Date: 12/2/2016 12:45:12 PM Operator: braker Instrument: amazon SL
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<b>Acquisition Parameter</b>	Ion Source Type: ESI	Ion Polarity: n/a	Positive 100 m/z	Alternating Ion Polarity: off
Mass Range Mode: Resolution	Enhanced Resolution: 253 $\mu$ s	Scan Begin: n/a	n/a	Scan End: 1000 m/z
Capillary Exit: Accumulation Time		Averages:	5 Spectra	Trap Drive: 76.0
				Auto MS/MS: off



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**Figure S17.** ESIMS spectrum of compound 6.

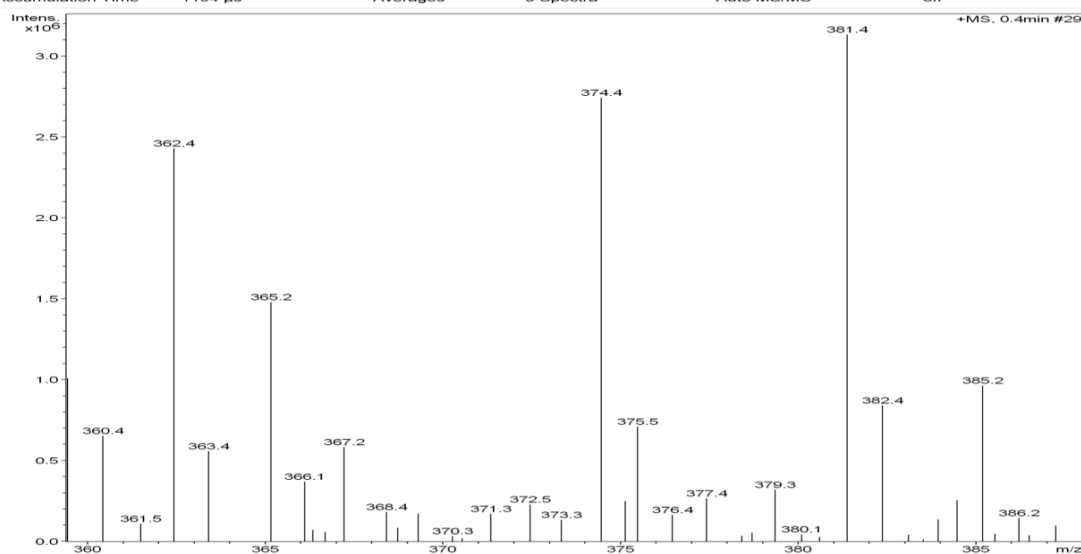


**Figure S18.** <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of compound 7.

## Display Report

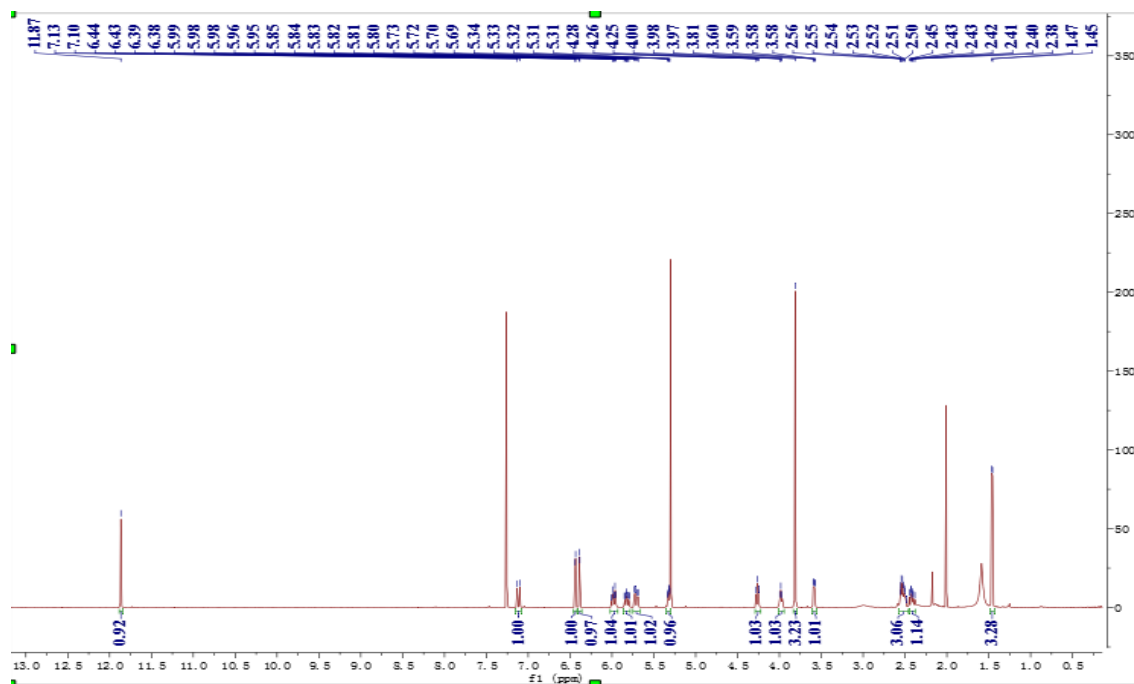
<b>Analysis Info</b>	Acquisition Date	12/2/2016 12:23:59 PM
Analysis Name	D:\Data\WCY\20161202-ZXQ-6.d	
Method	20161001-MIX--G3-MSMS.m	Operator
Sample Name	20161202-ZXQ-6	Instrument
Comment		bruker amaZon SL

<b>Acquisition Parameter</b>	Ion Source Type	Ion Polarity	Positive	Alternating Ion Polarity	off
Ion Source Type	ESI	Scan Begin	100 m/z	Scan End	1000 m/z
Mass Range Mode	Enhanced	n/a	n/a	Trap Drive	76.0
Capillary Exit	Resolution	Averages	5 Spectra	Auto MS/MS	off
Accumulation Time	1194 $\mu$ s				



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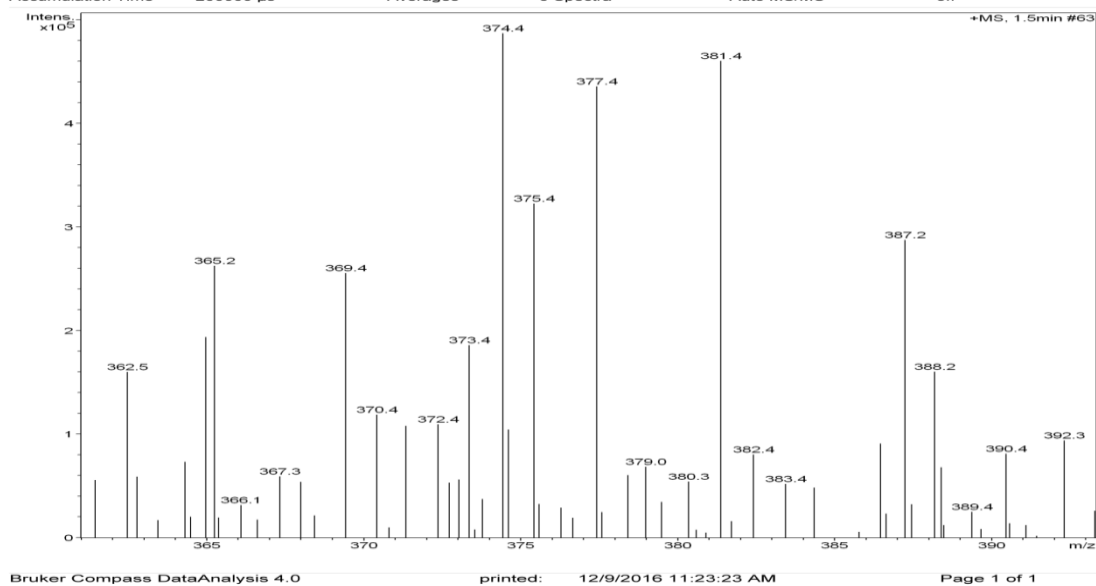
**Figure S19.** ESIMS spectrum of compound 7.



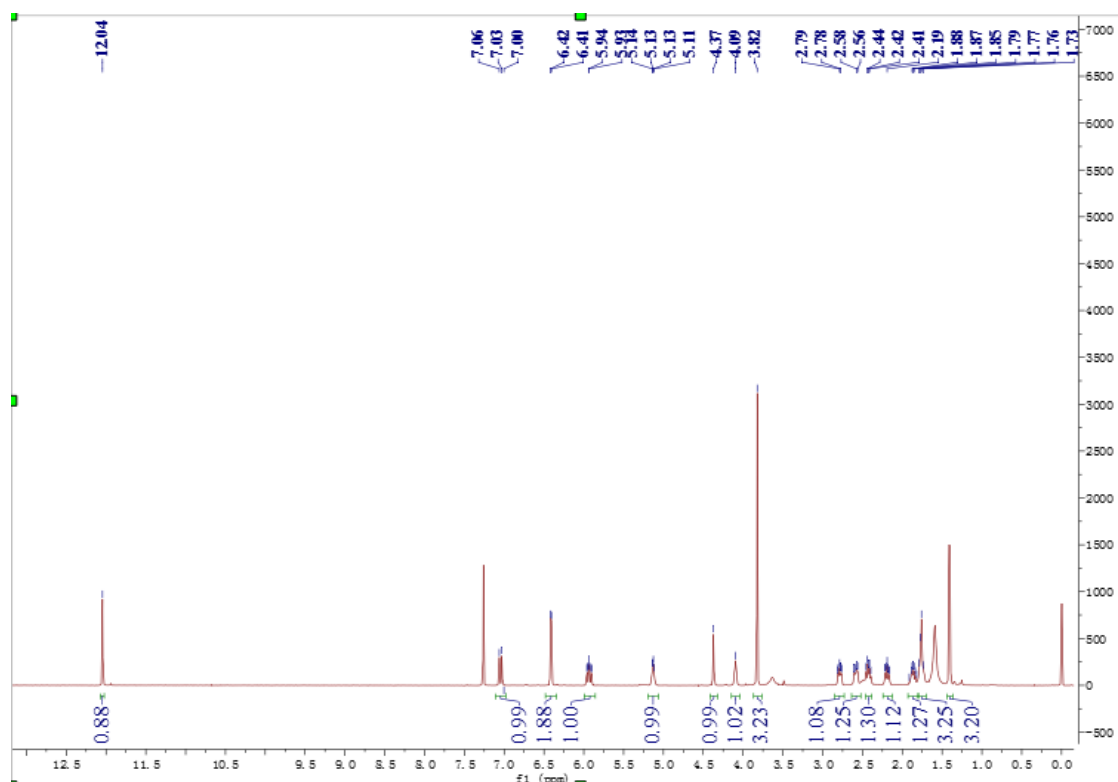
**Figure S20.** <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of compound 8.

## Display Report

<b>Analysis Info</b>		Acquisition Date	12/2/2016 11:56:29 AM
Analysis Name	D:\Data\WCY\20161202-ZXQ-4.d	Operator	bruker
Method	20161001-MIX---G3-MSMS.m	Instrument	amaZon SL
Sample Name	20161202-ZXQ-4		
Comment			
<b>Acquisition Parameter</b>			
Ion Source Type	ESI	Ion Polarity	Positive
Mass Range Mode	Enhanced Resolution	Scan Begin	100 m/z
Capillary Exit Accumulation Time	200000 µs	n/a	n/a
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		Alternating Ion Polarity	off
		Scan End	1000 m/z
		Trap Drive	76.0
		Auto MS/MS	off



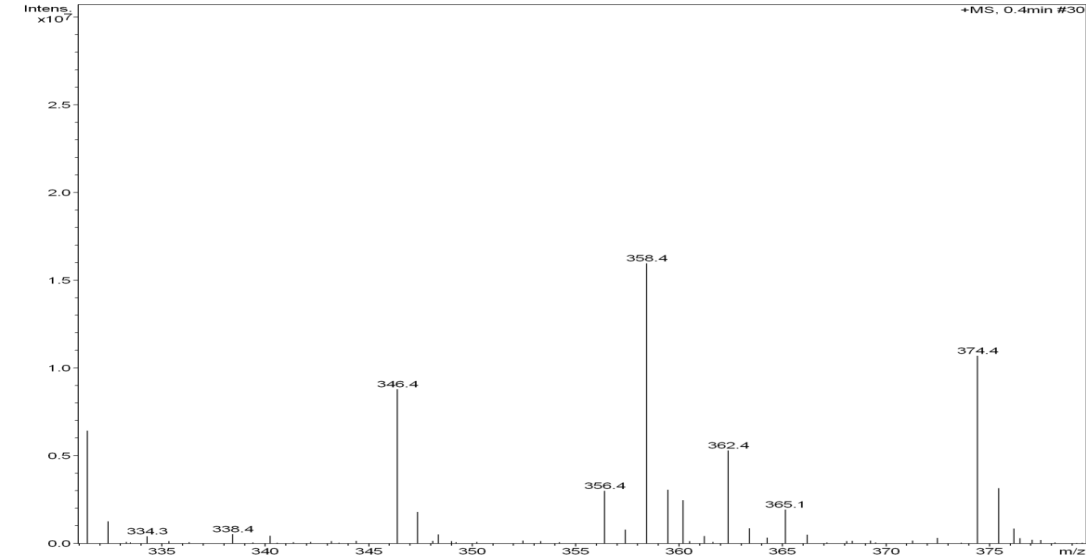
**Figure S21.** ESIMS spectrum of compound **8**.



**Figure S22.** <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of compound **9**.

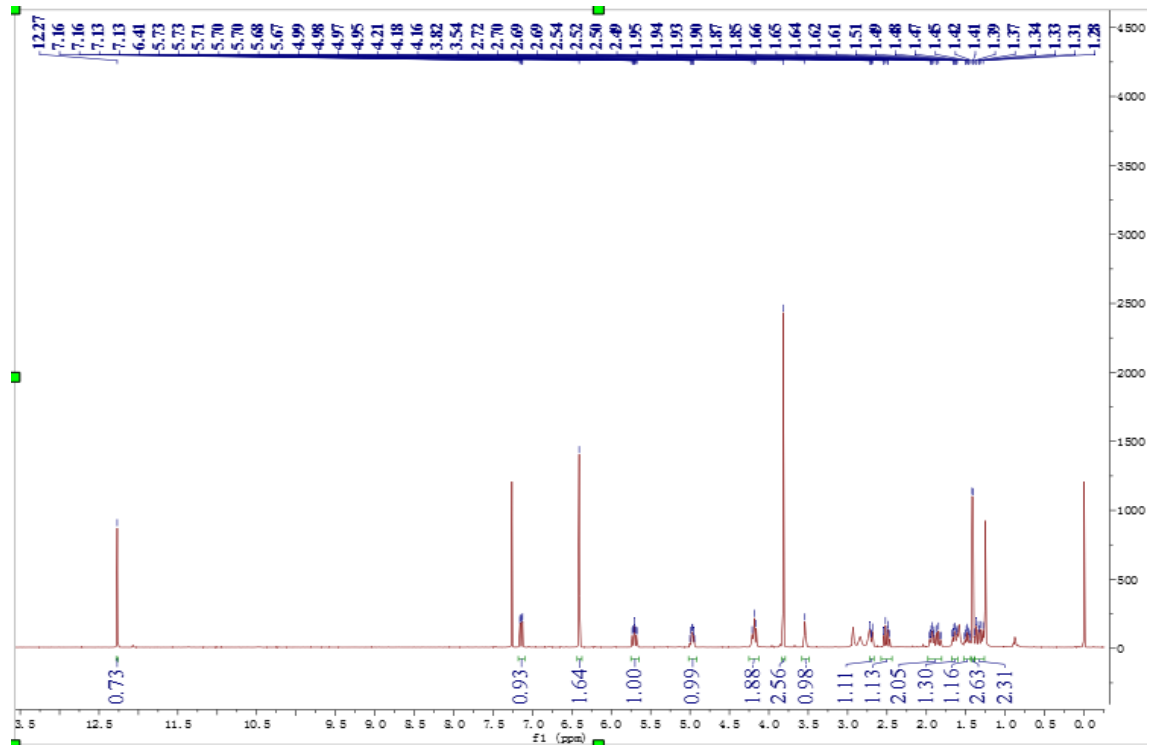
## Display Report

<b>Analysis Info</b>		Acquisition Date	12/2/2016 12:51:15 PM		
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Method	20161001-MIX-G3-MSMS.m	Instrument	amazon SL		
Sample Name	20161202-ZXQ-H311				
Comment					
<b>Acquisition Parameter</b>					
Ion Source Type	ESI	Ion Polarity	Positive	Alternating Ion Polarity	off
Mass Range Mode	Enhanced	Scan Begin	100 m/z	Scan End	1000 m/z
Capillary Exit	Resolution	n/a	n/a	Trap Drive	75.0
Accumulation Time	190 $\mu$ s	Averages	5 Spectra	Auto MS/MS	off



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**Figure S23.** ESIMS spectrum of compound 9.

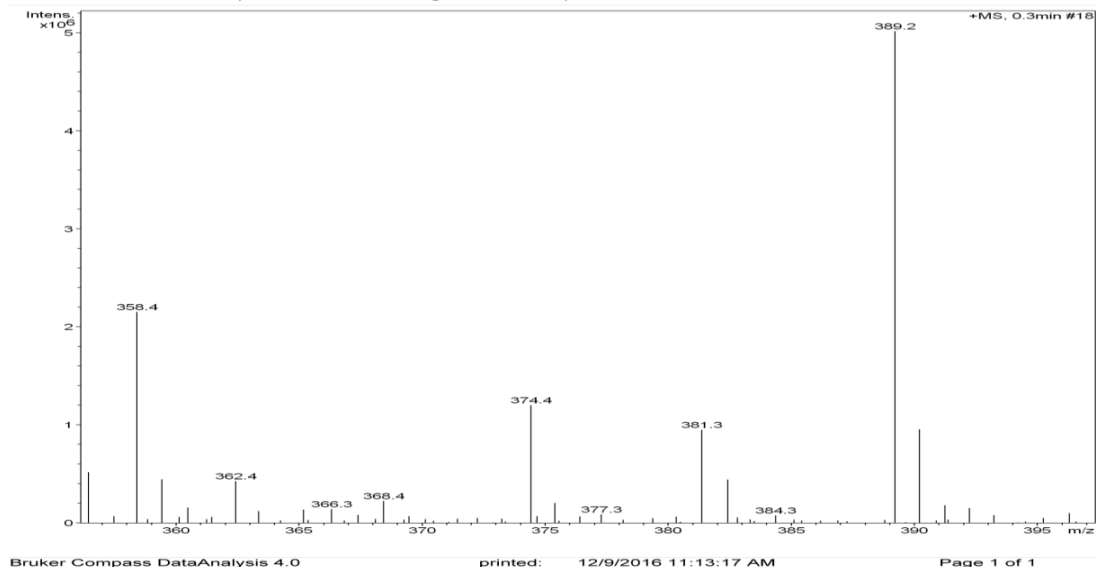


**Figure S24.**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of compound 10.

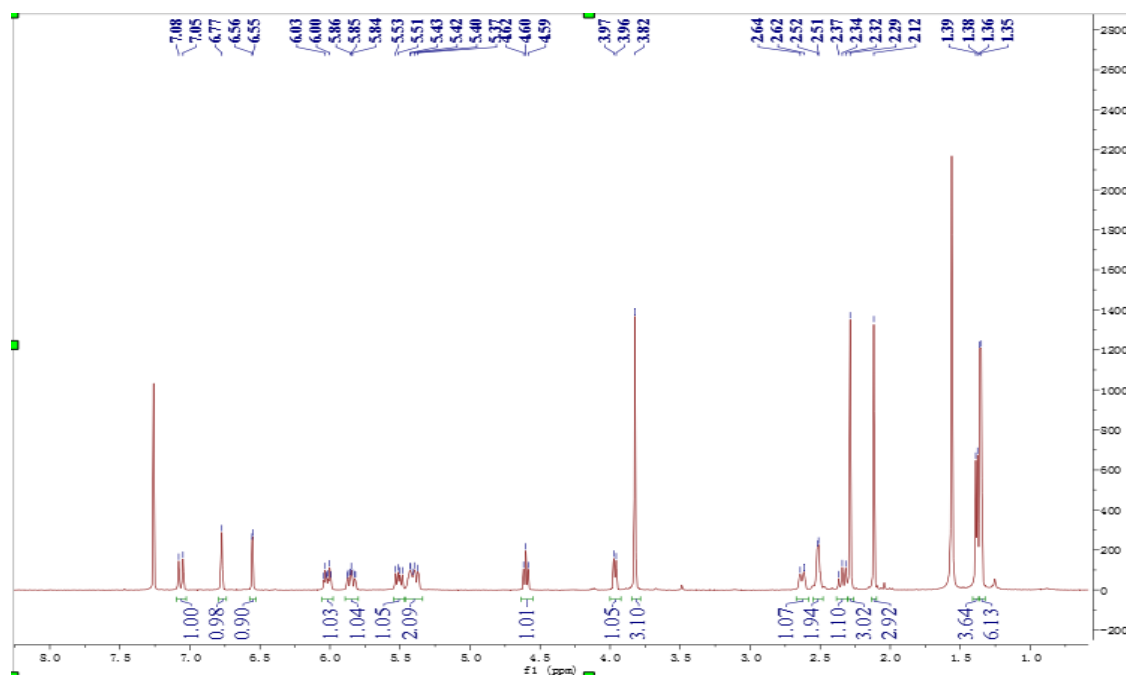
### Display Report

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Analysis Name	20161001-MIX---G3-MSMS.m	Operator	bruker
Method	20161202-ZXQ-H321	Instrument	amaZon SL
Sample Name			
Comment			

<b>Acquisition Parameter</b>			
Ion Source Type	ESI	Ion Polarity	Positive
Mass Range Mode	Enhanced Resolution	Scan Begin	100 m/z
Capillary Exit	n/a	Averages	n/a
Accumulation Time	1705 $\mu$ s		5 Spectra
		Alternating Ion Polarity	off
		Scan End	1000 m/z
		Trap Drive	76.0
		Auto MS/MS	off



**Figure S25.** ESIMS spectrum of compound **10**.



**Figure S26.** <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of compound **11**.

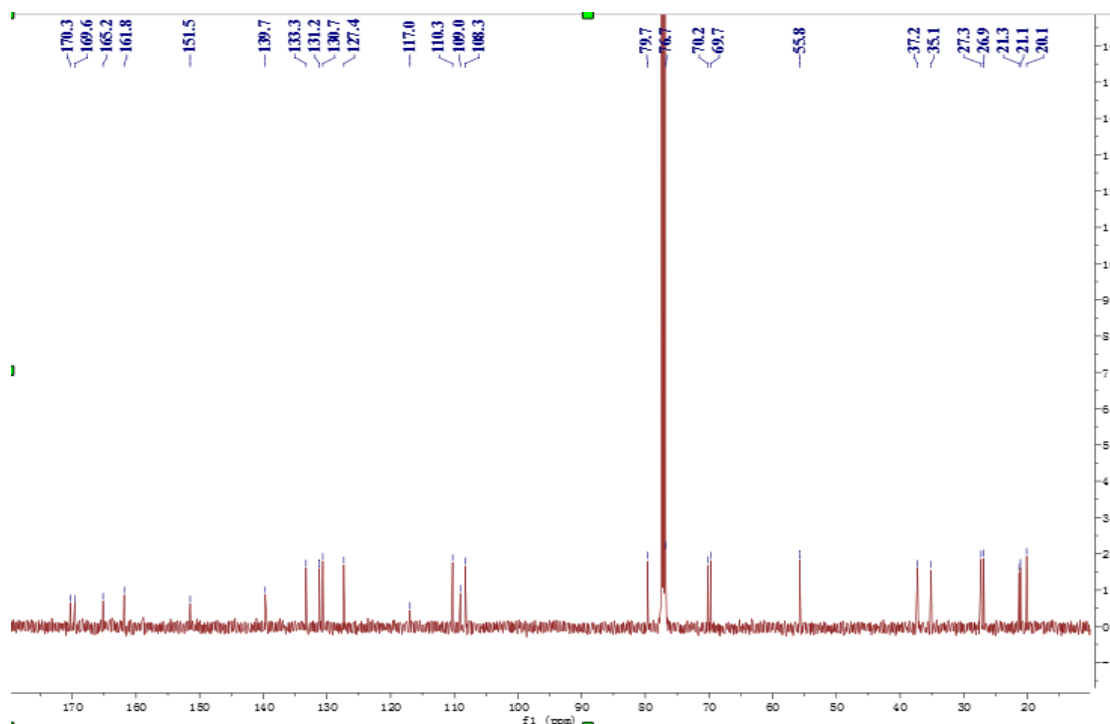


Figure S27.  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ) spectrum of compound **11**.

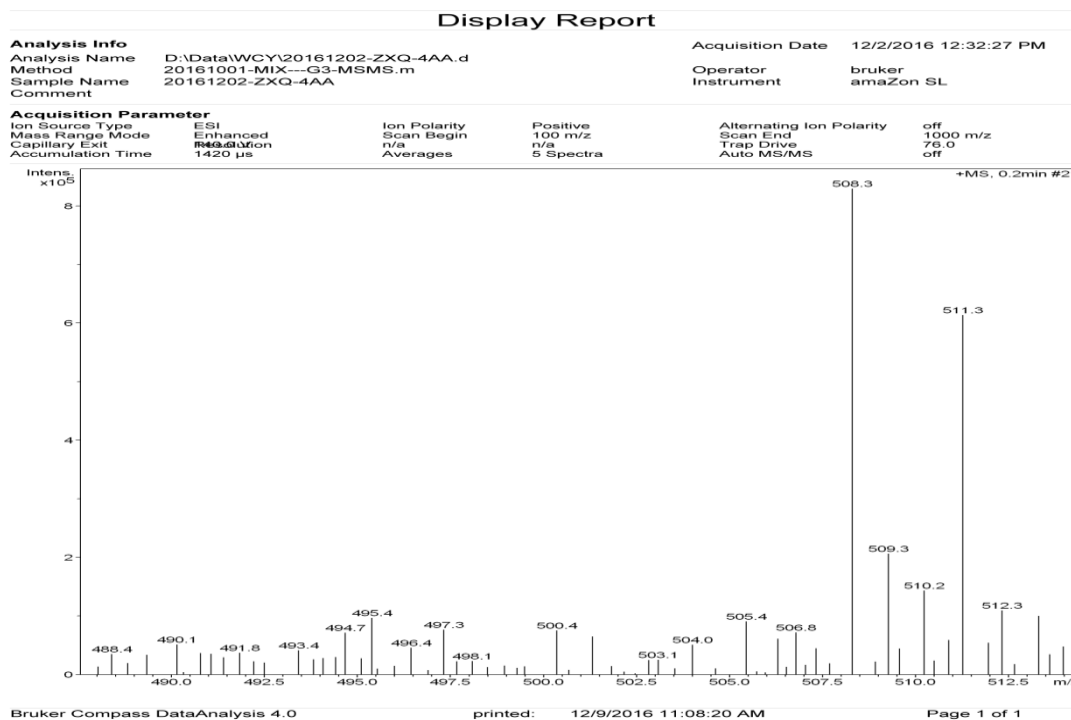
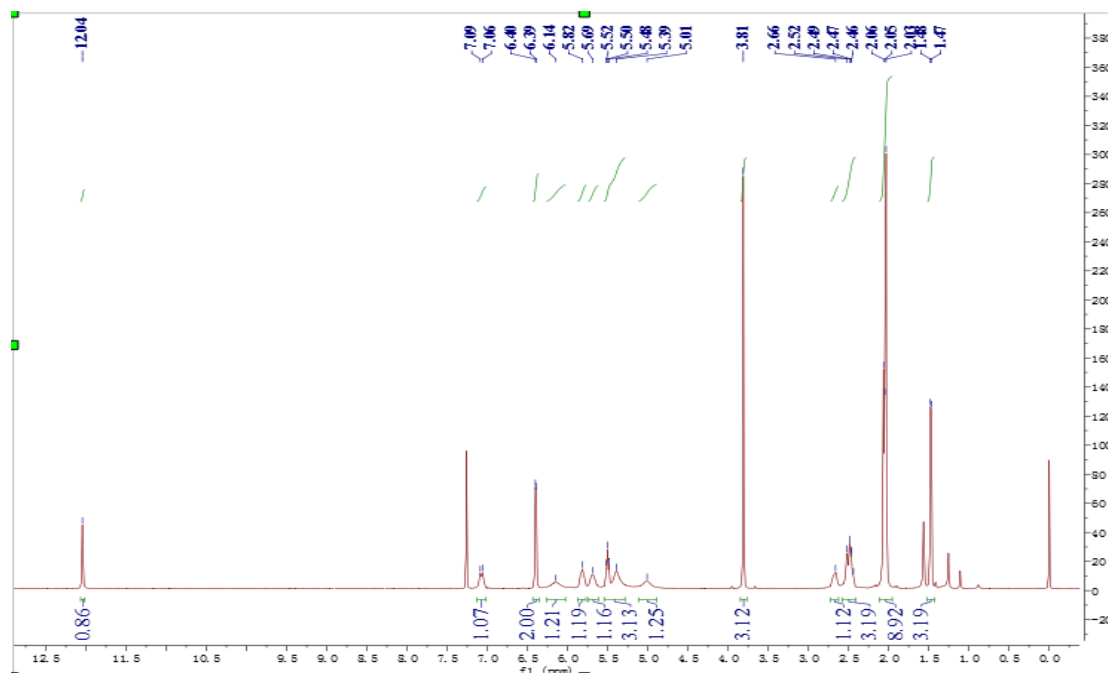
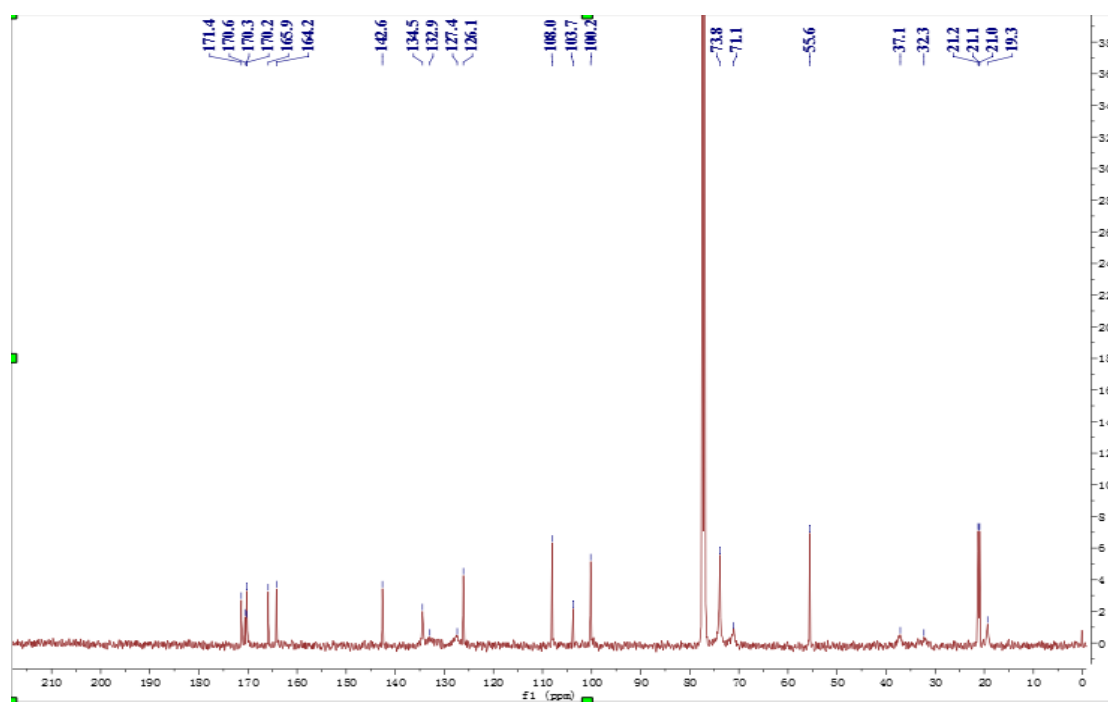


Figure S28. ESIMS spectrum of compound **11**.



**Figure S29.**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of compound **12**.



**Figure S30.**  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ) spectrum of compound **12**.

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T: FTMS + c ESI Full ms [150.00-2000.00]

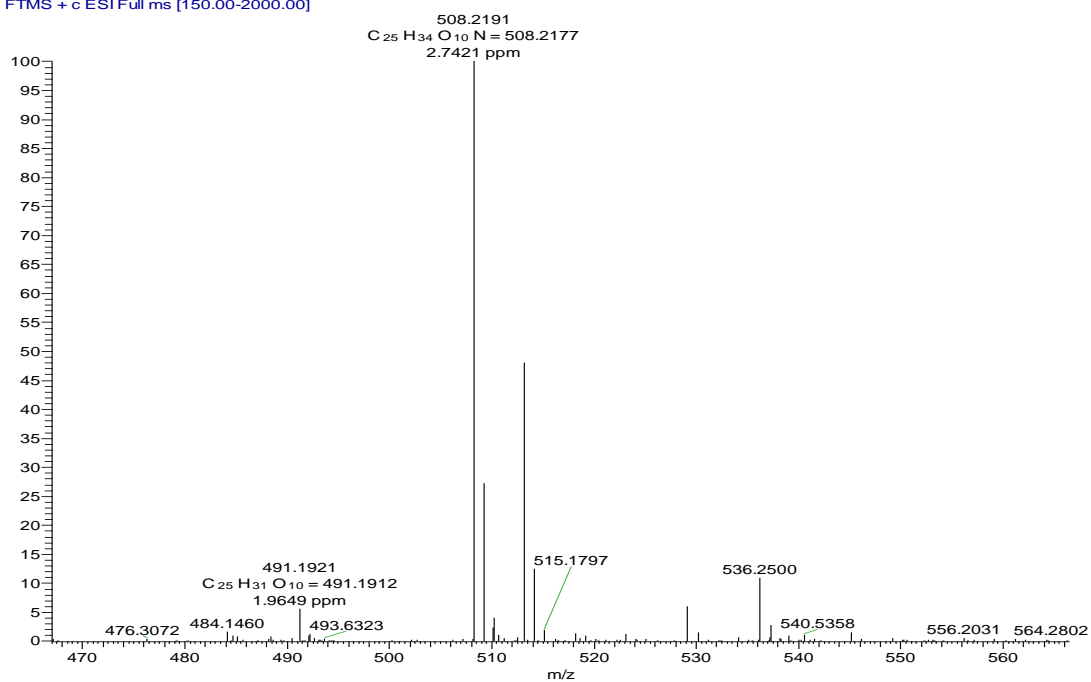


Figure S31. HRESIMS spectrum of compound 12.

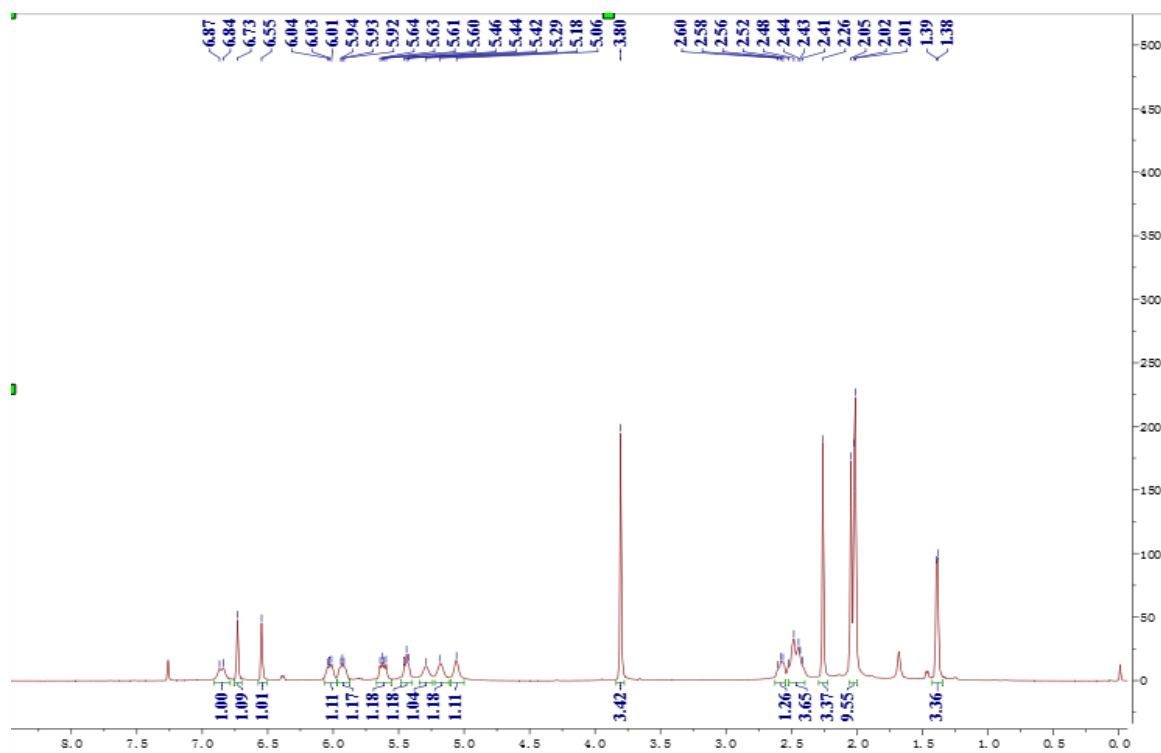
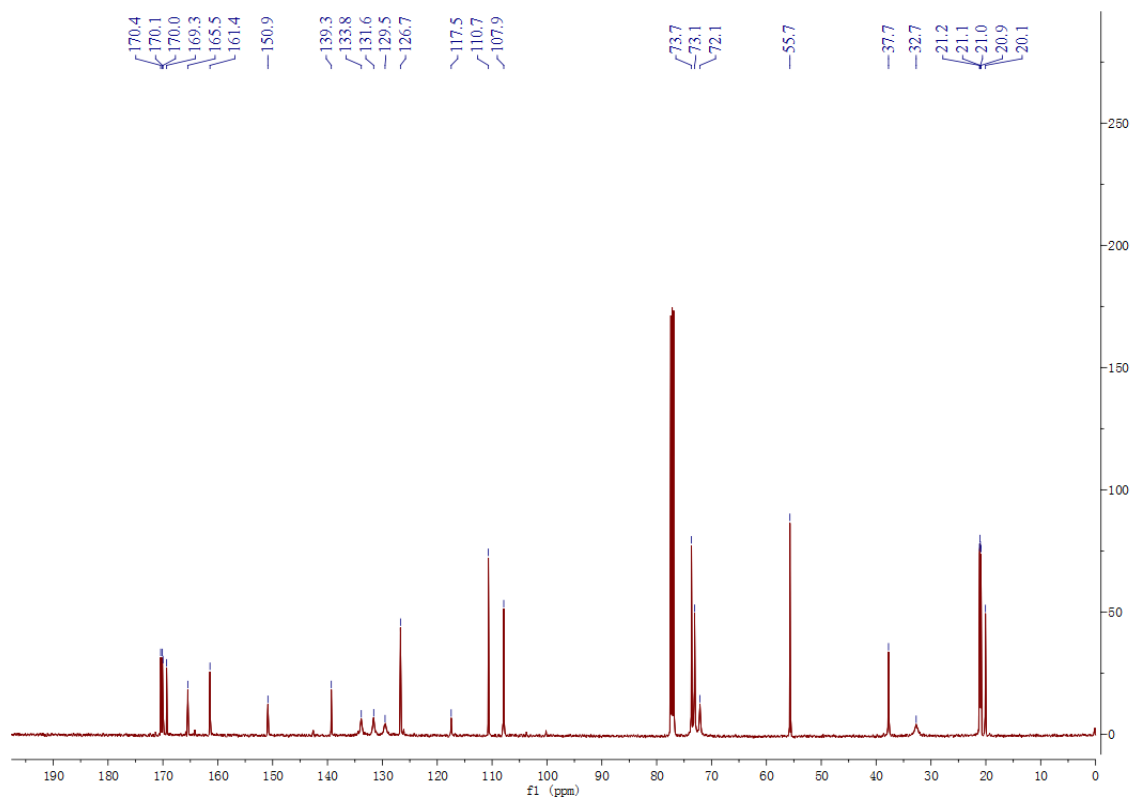
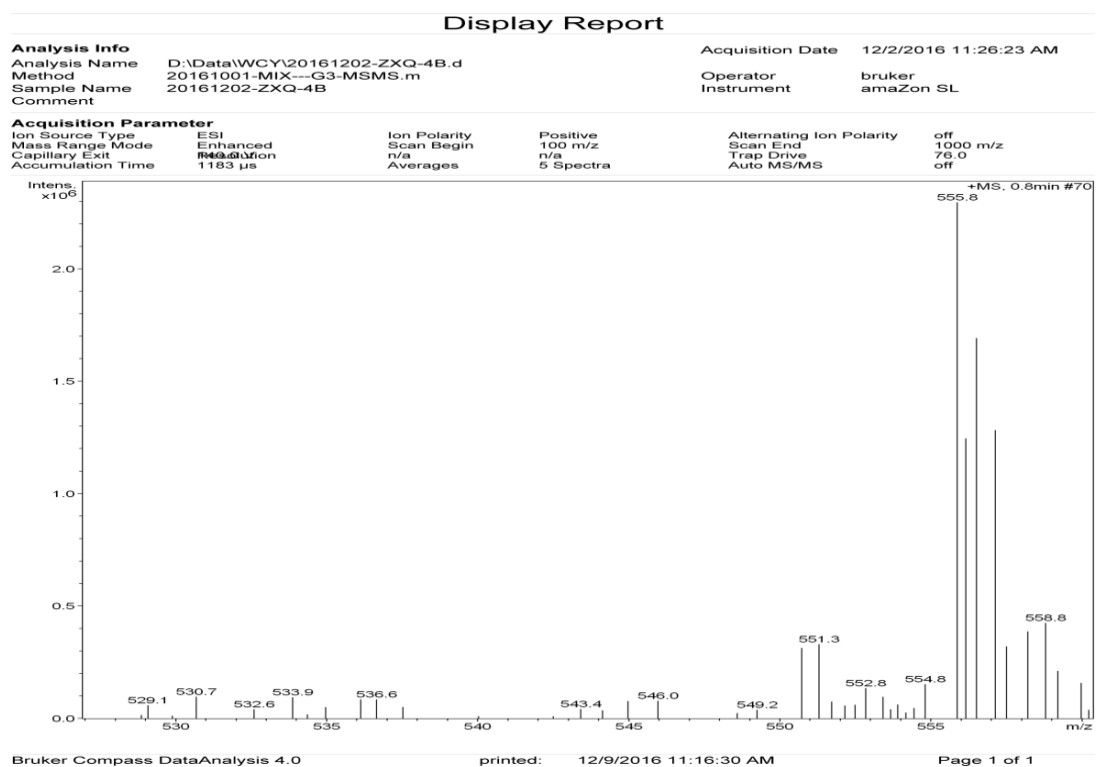


Figure S32. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of compound 13.





**Figure S33.**  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ) spectrum of compound **13**.



**Figure S34.** ESIMS spectrum of compound **13**.

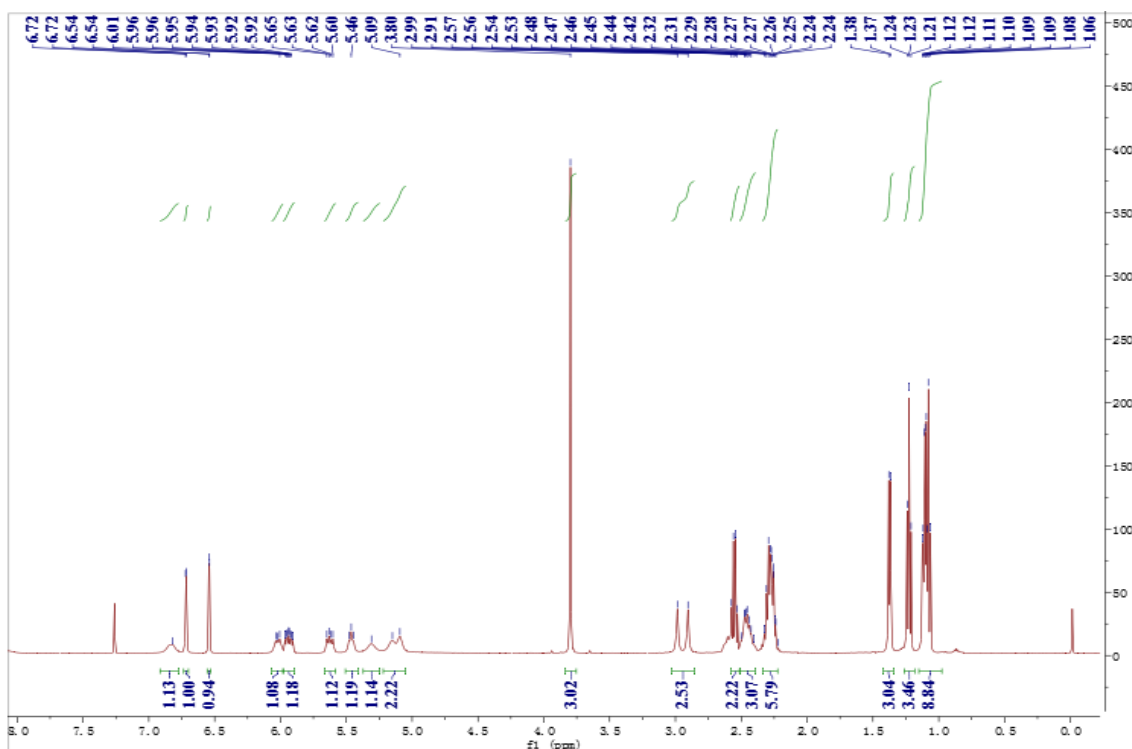


Figure S35.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of compound **14**.

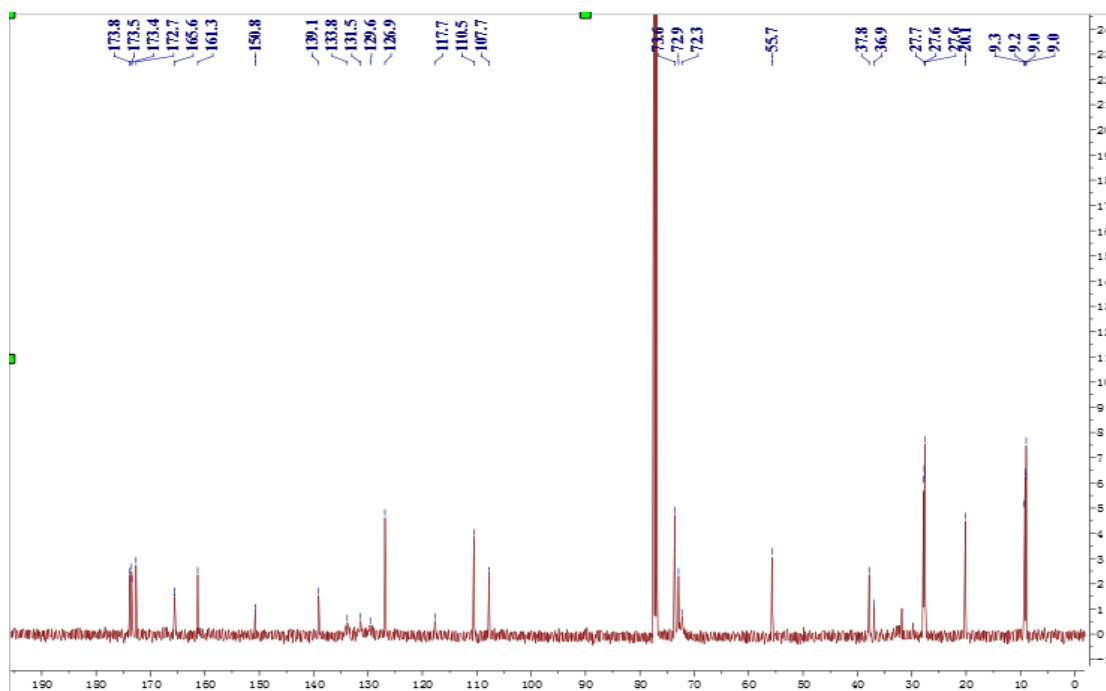


Figure S36.  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ) spectrum of compound **14**.

20160112-4c\_160108143815 #98 RT: 0.84 AV: 1 NL: 4.80E7  
T: FTMS + c ESI Full ms [150.00-2000.00]

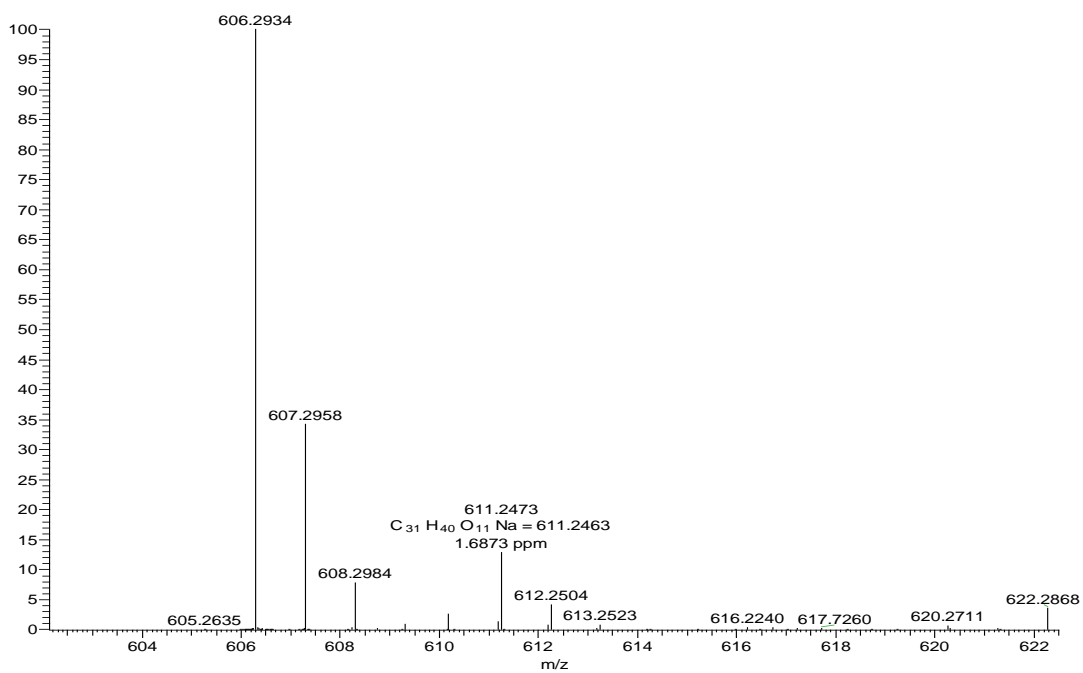


Figure S37. HRESIMS spectrum of compound 14.

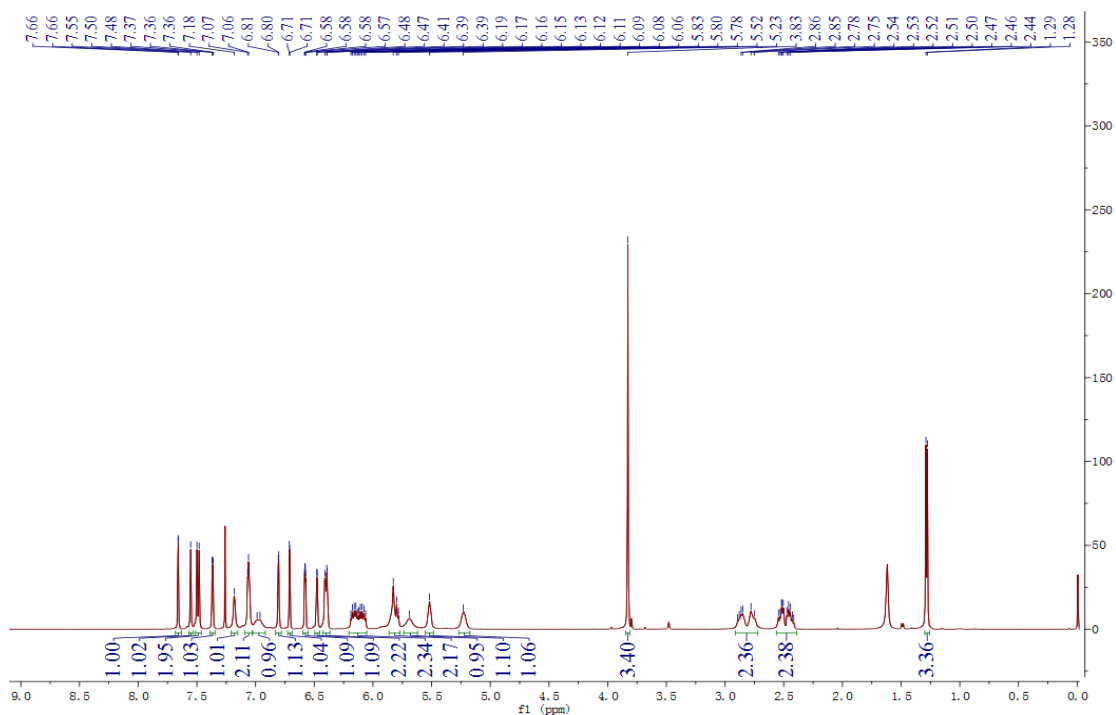
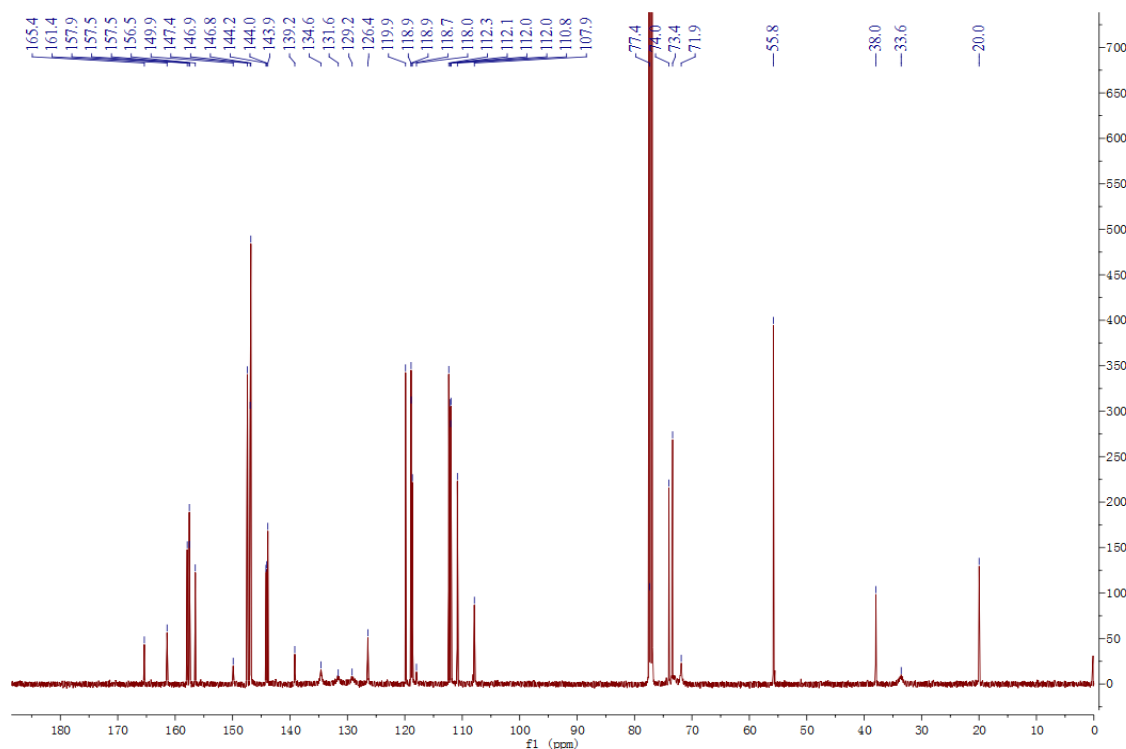
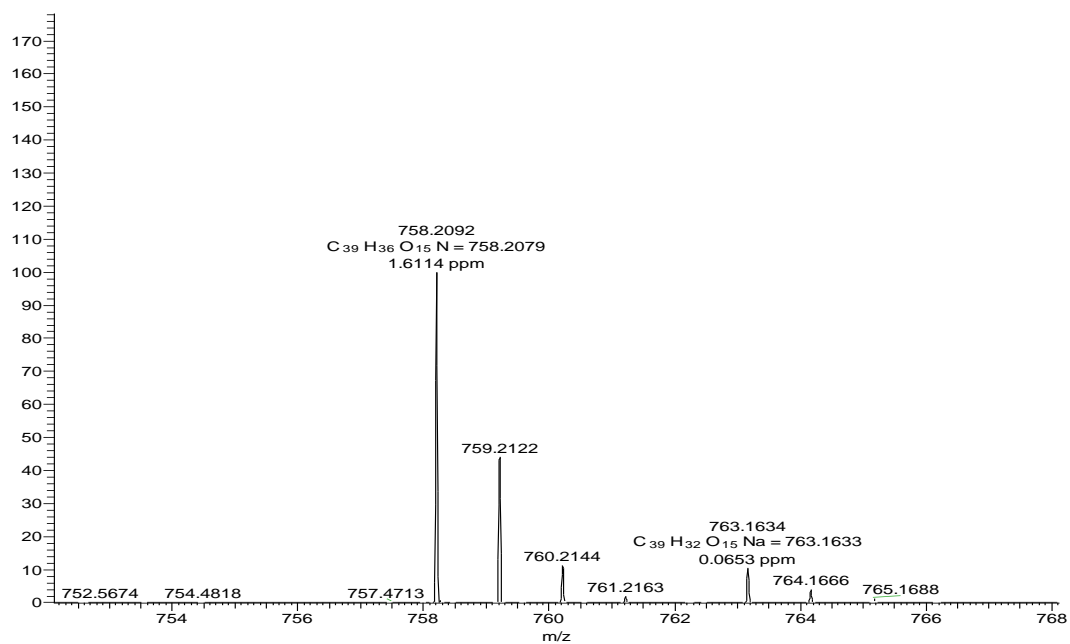


Figure S38. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of compound 15.



**Figure S39.**  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ) spectrum of compound **15**.

20170328-ZXQ4-FN\_170328134103 #30 RT: 0.25 AV: 1 NL: 1.46E7  
T: FTMS + p ESI Full ms [120.00-1000.00]



**Figure S40.** HRESIMS spectrum of compound **15**.

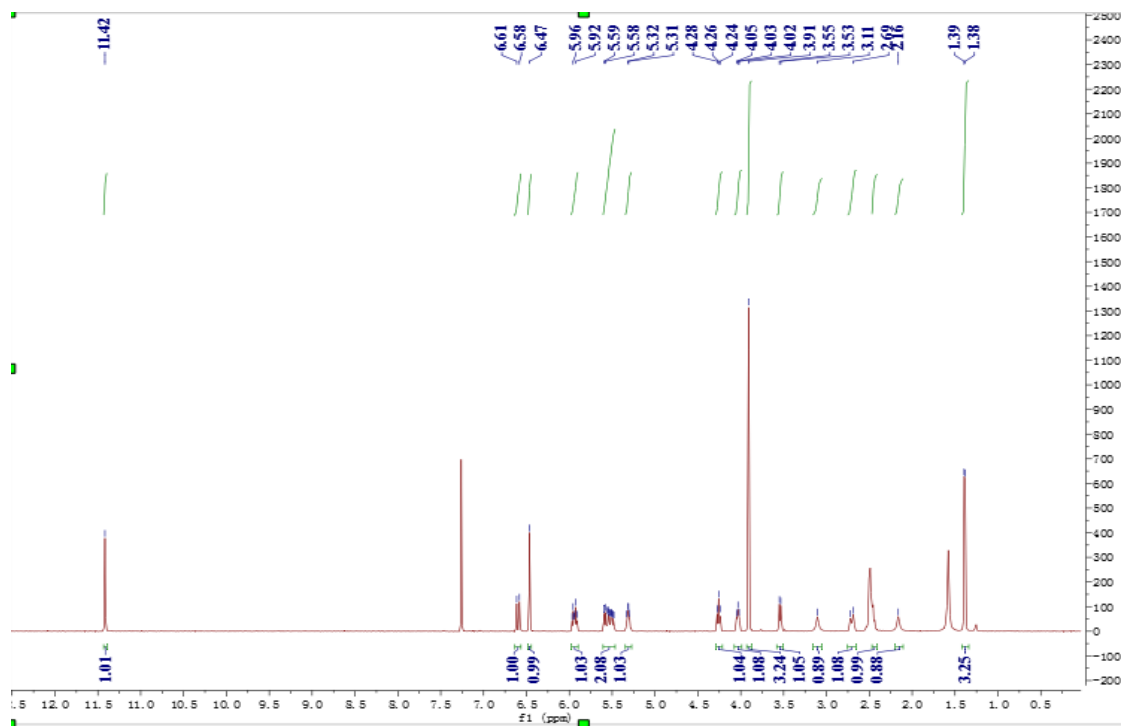


Figure S41.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of compound **16**.

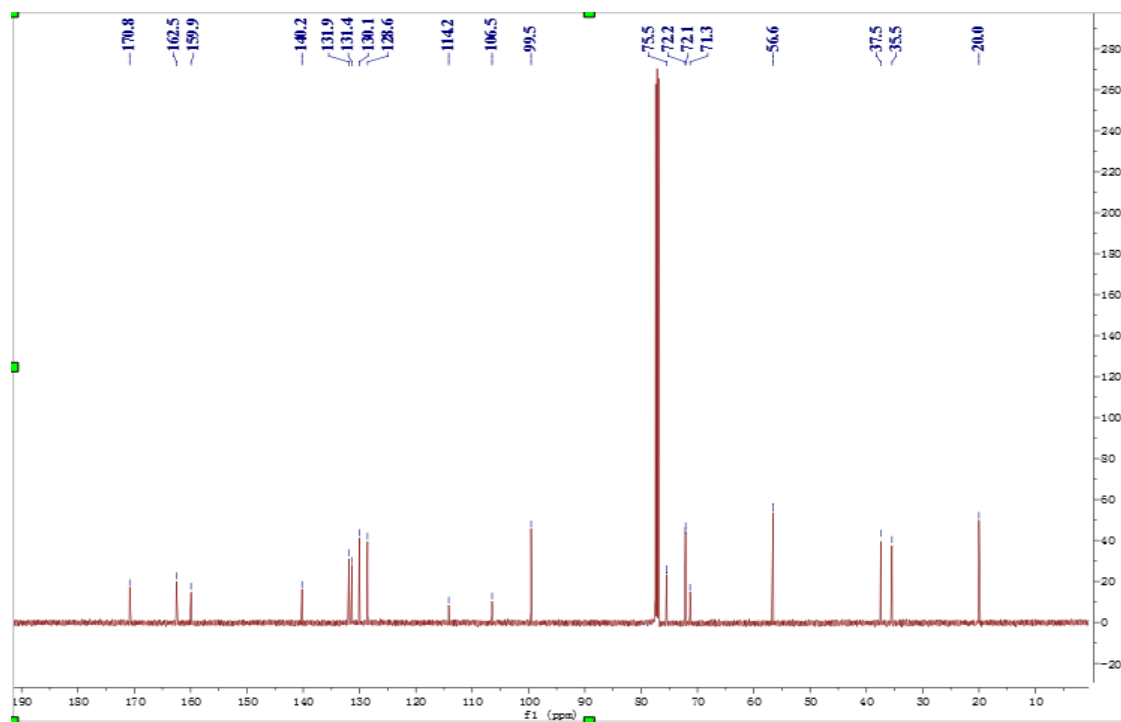


Figure S42.  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ) spectrum of compound **16**.

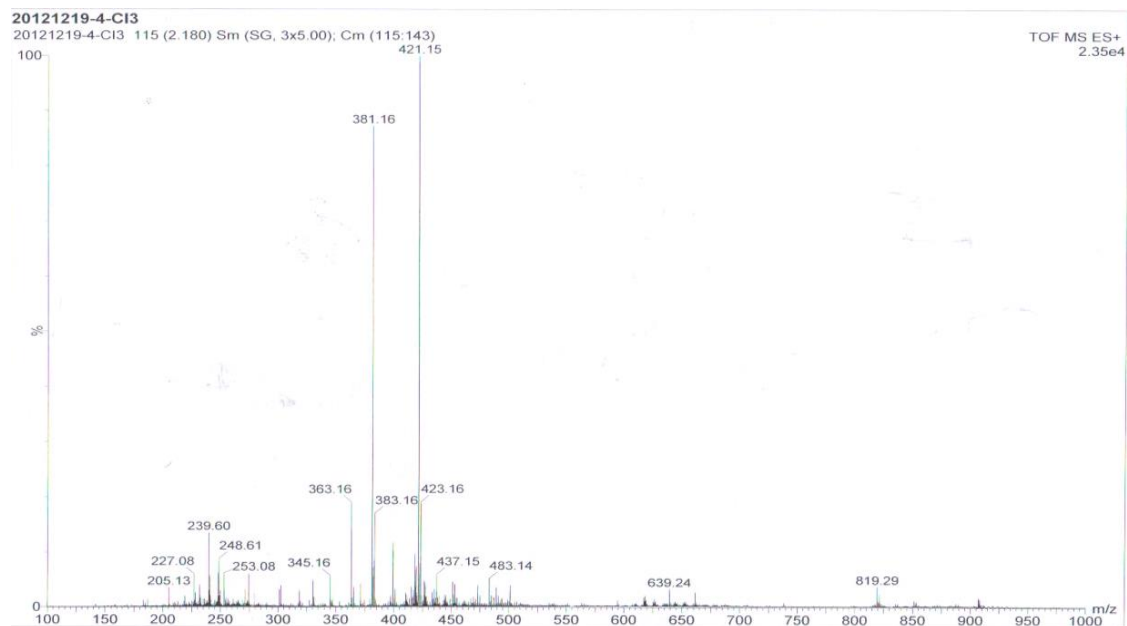


Figure S43. ESIMS spectrum of compound 16.

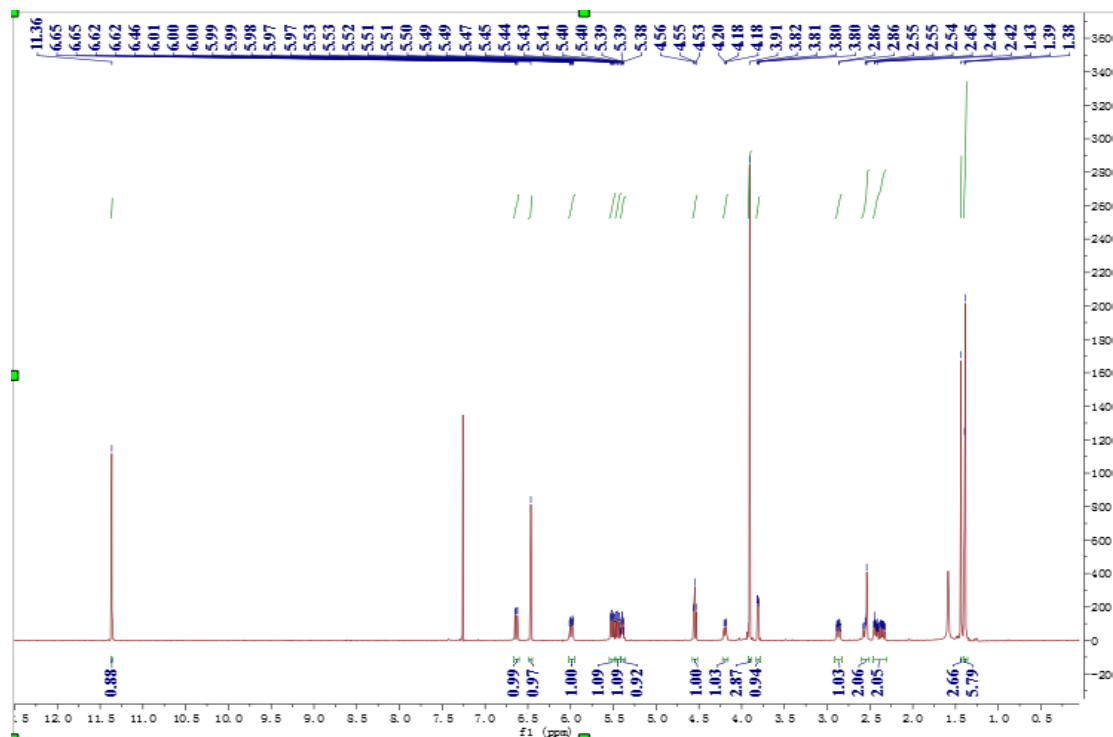


Figure S44.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of compound 17.

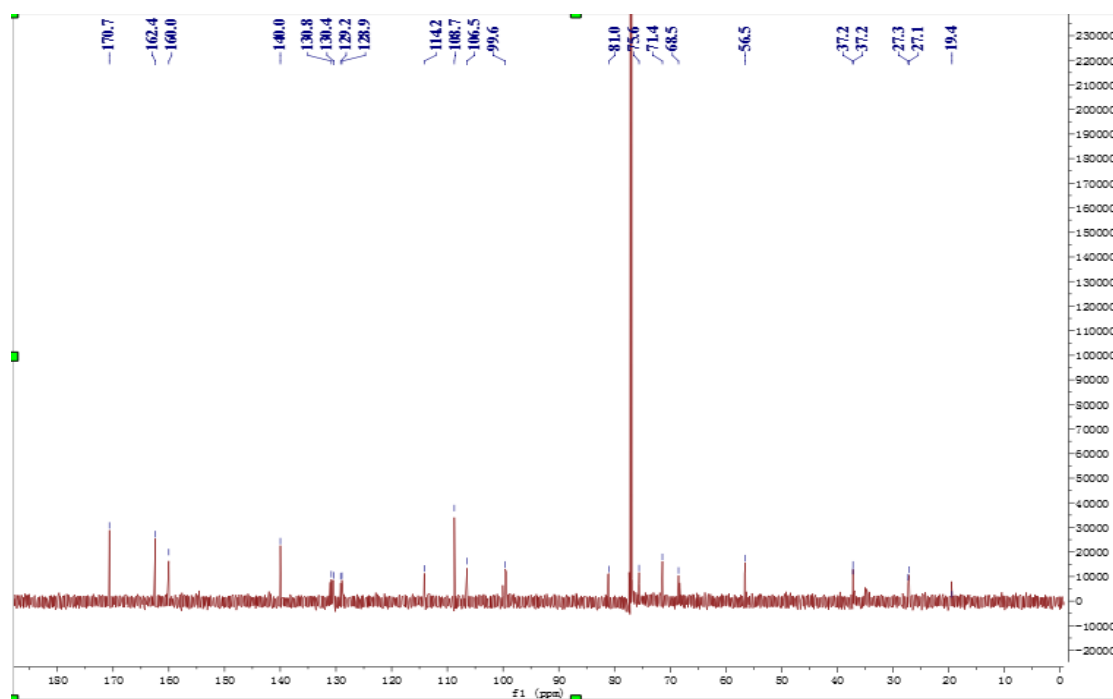


Figure S45.  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ) spectrum of compound 17.

20161118-4A-CL\_161118085603 #69 RT: 0.55 AV: 1 NL: 7.02E5  
 T: FTMS + p ESI Full ms [100.00-1000.00]

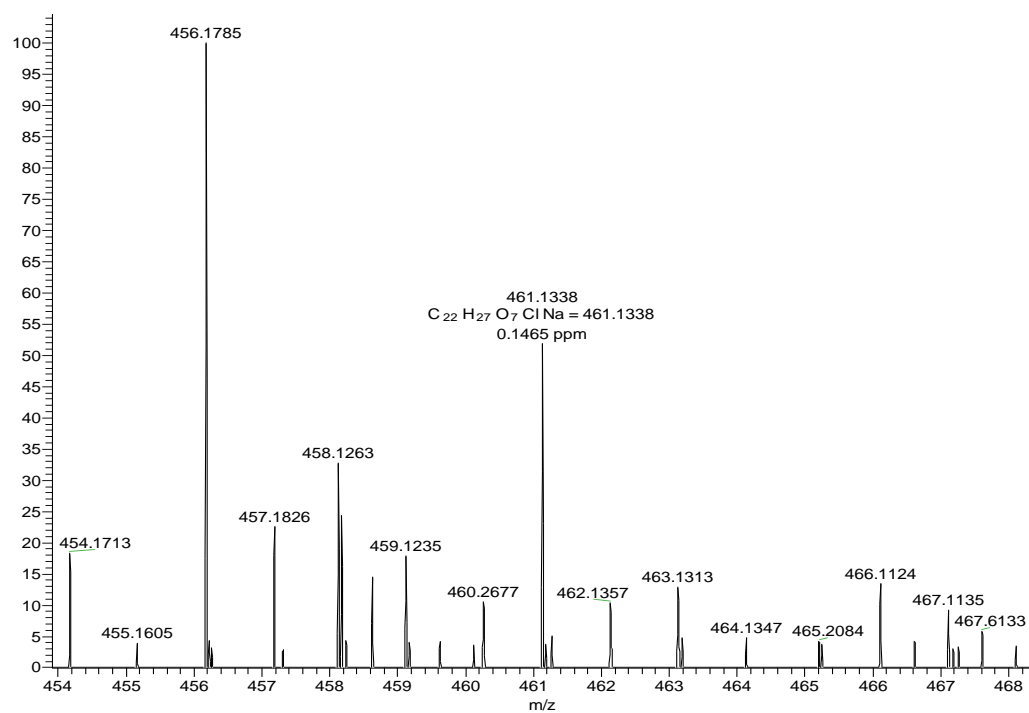


Figure S46. HRESIMS spectrum of compound 17.

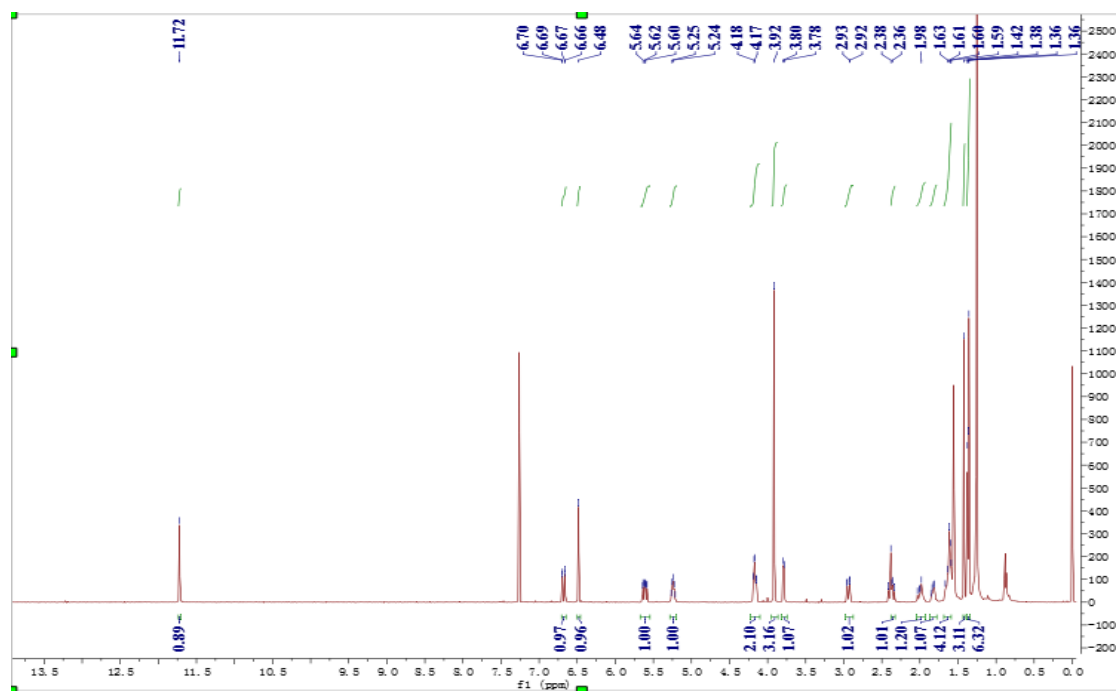


Figure S47.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of compound **18**.

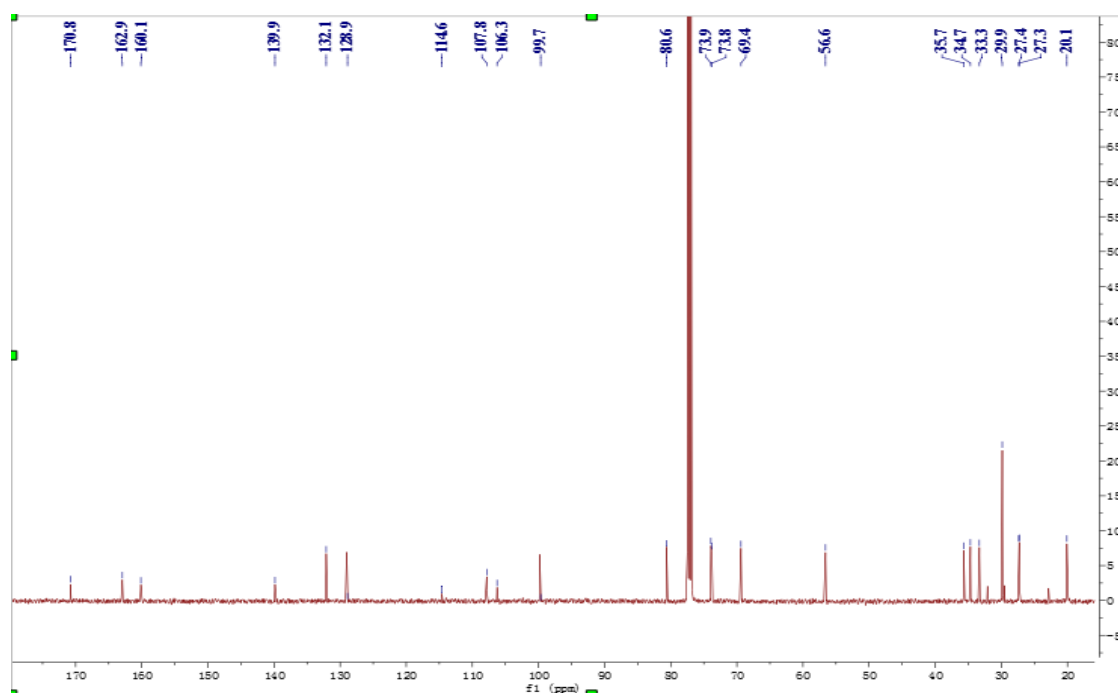


Figure S48.  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ) spectrum of compound **18**.



20161118-4-CL-HYA\_161118085603 #65 RT: 0.52 AV: 1 NL: 3.78E5  
T: FTMS + p ESI Full ms [100.00-1000.00]

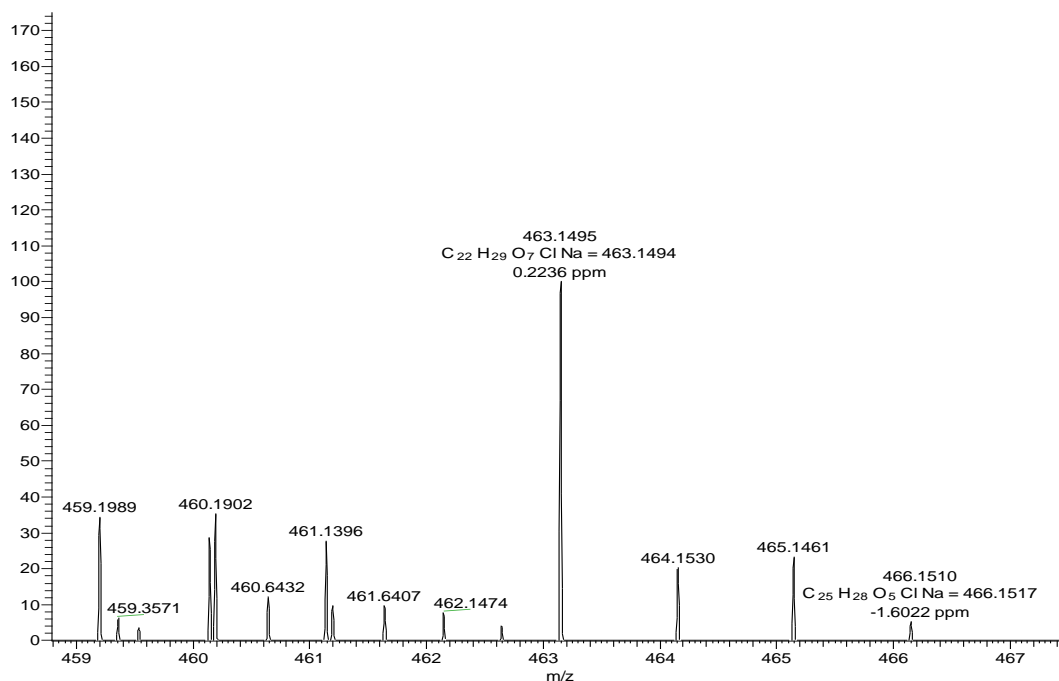


Figure S49. HRMSIMS spectrum of compound 18.

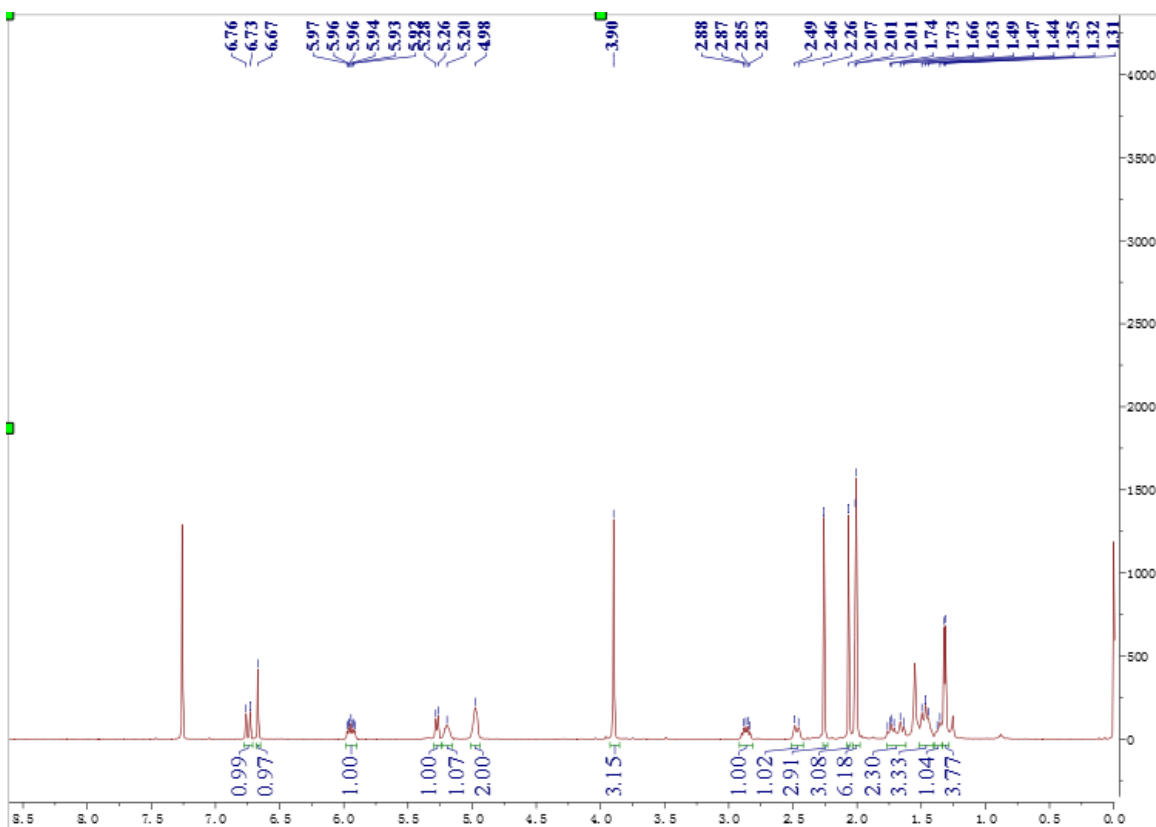
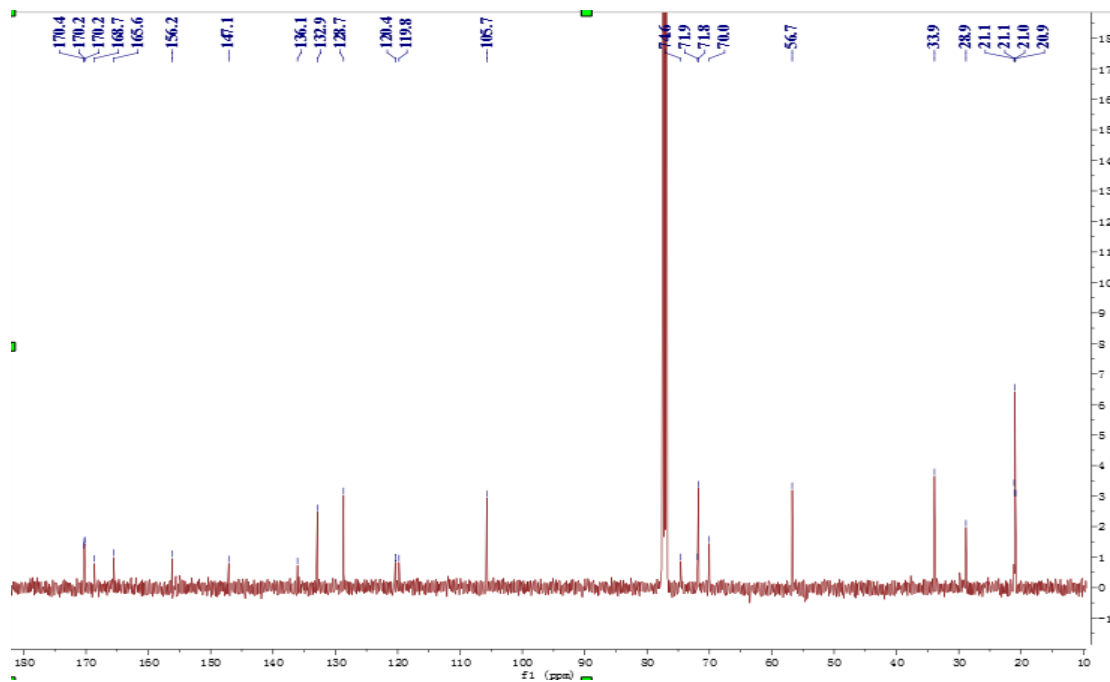
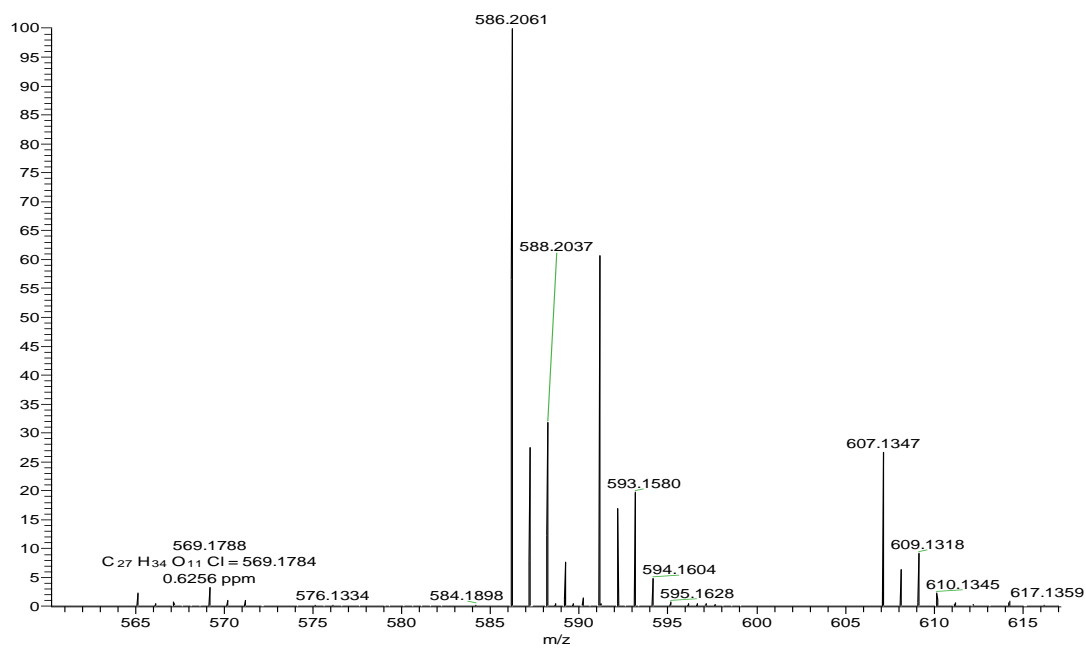


Figure S50. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of compound 19.



**Figure S51.**  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ) spectrum of compound **19**.

20161118-4-CL-HYB\_161118085603 #78 RT: 0.63 AV: 1 NL: 1.88E7  
 T: FTMS + p ESI Full ms [100.00-1000.00]



**Figure S52.** HRESIMS spectrum of compound **19**.

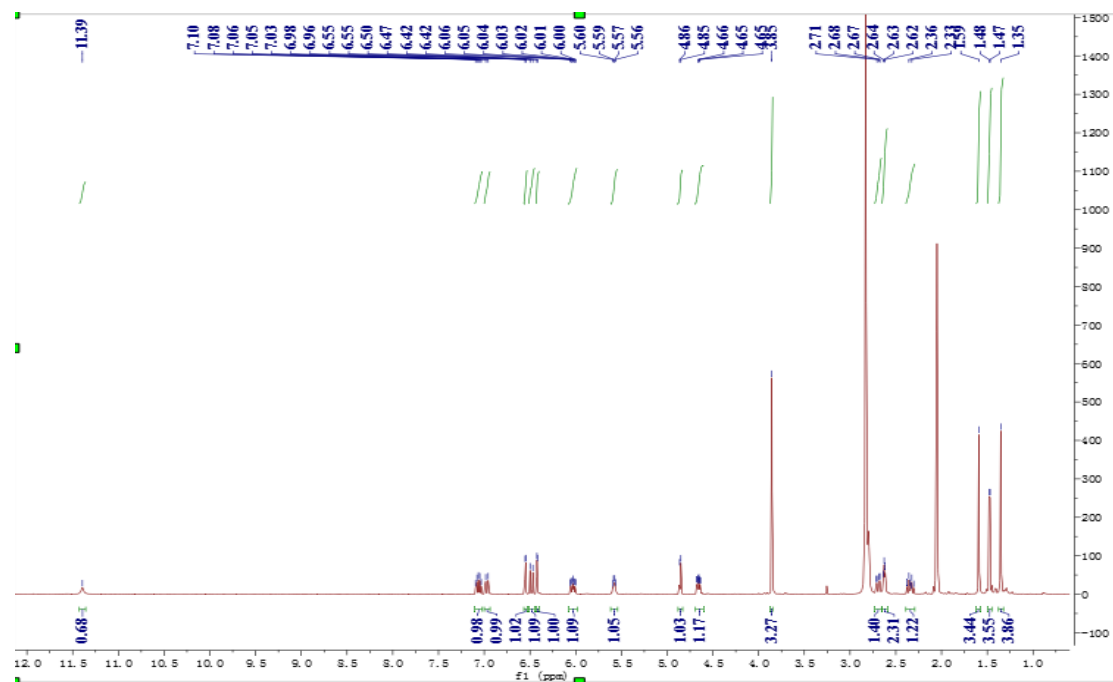


Figure S53.  $^1\text{H}$  NMR (500 MHz, Acetone- $d_6$ ) spectrum of compound **20**.

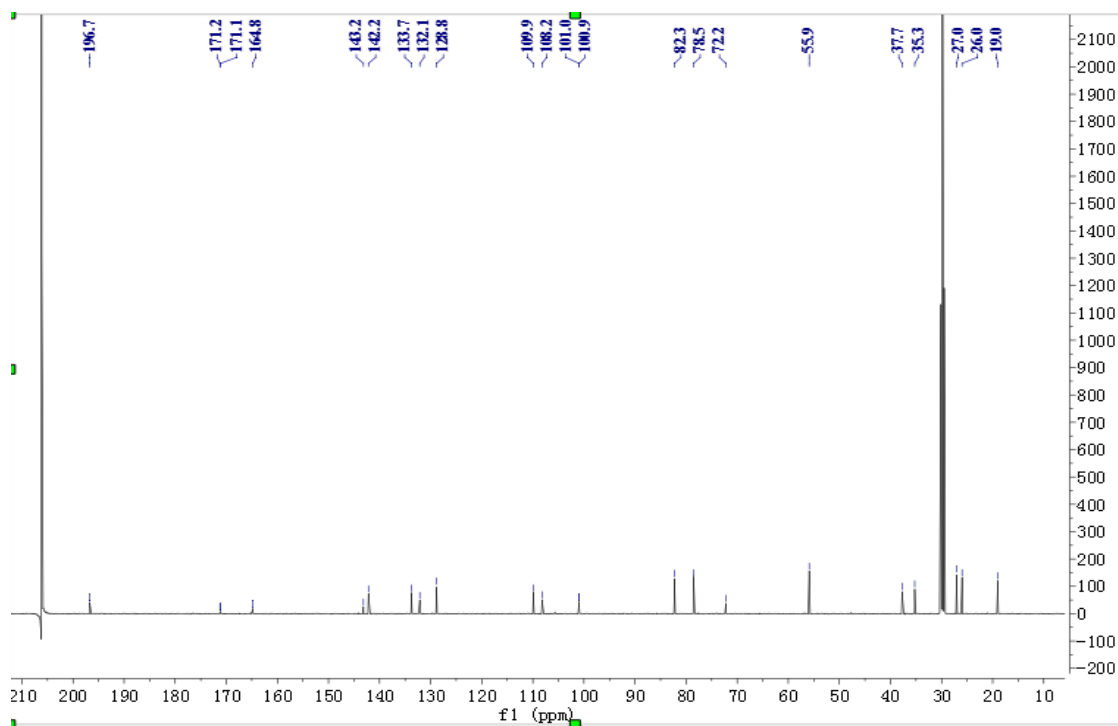
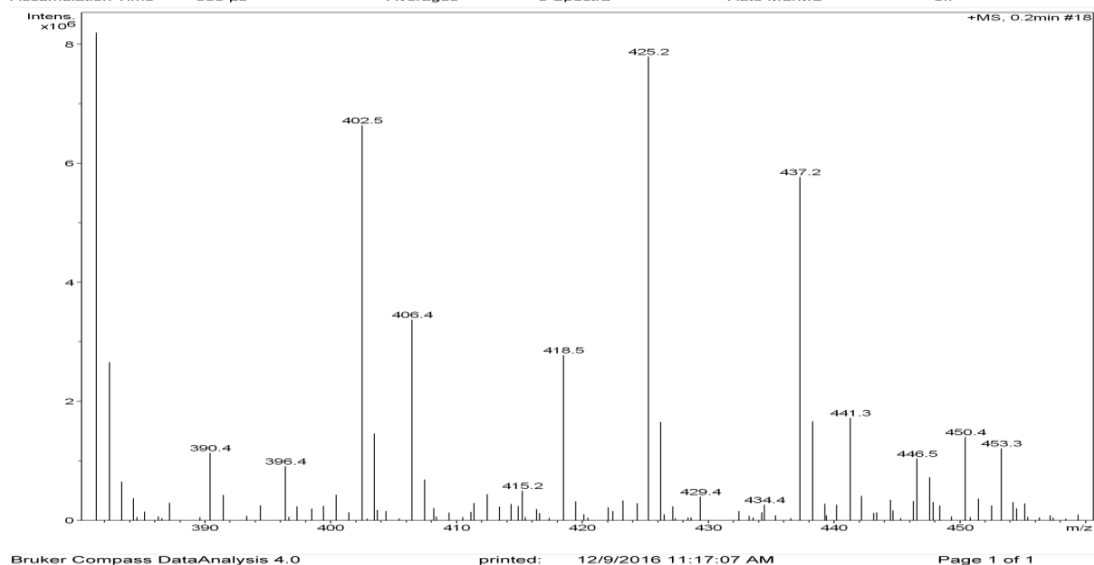


Figure S54.  $^{13}\text{C}$  NMR (125 MHz, Acetone- $d_6$ ) spectrum of compound **20**.

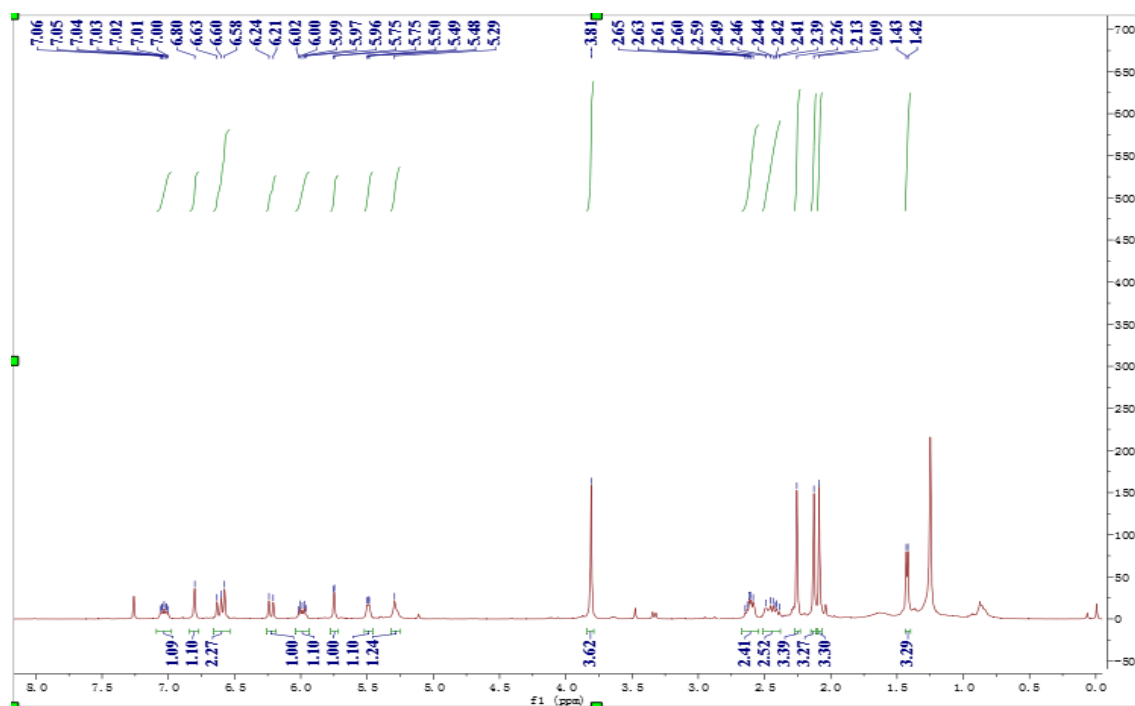
## Display Report

<b>Analysis Info</b>	D:\Data\WCY\20161202-ZXQ-4P-3a.d	Acquisition Date	12/2/2016 12:54:13 PM
Analysis Name	20161001-MIX--G3-MSMS.m	Operator	bruker
Method	20161202-ZXQ-4P-3a	Instrument	amazon SL
Sample Name			
Comment			

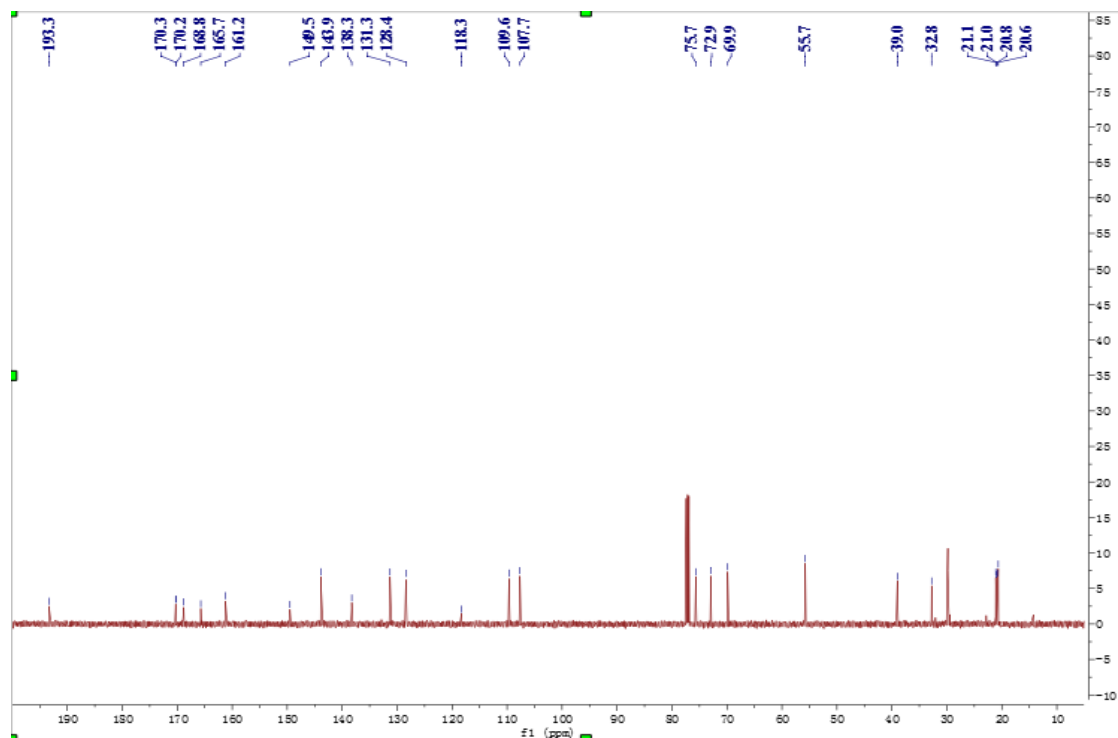
<b>Acquisition Parameter</b>			
Ion Source Type	ESI	Ion Polarity	Positive
Mass Range Mode	Enhanced	Scan Begin	100 m/z
Capillary Exit	RF @ 0.000	n/a	n/a
Accumulation Time	333 $\mu$ s	Averages	5 Spectra
		Alternating Ion Polarity	off
		Scan End	1000 m/z
		Trap Drive	76.0
		Auto MS/MS	off



**Figure S55.** ESIMS spectrum of compound **20**.

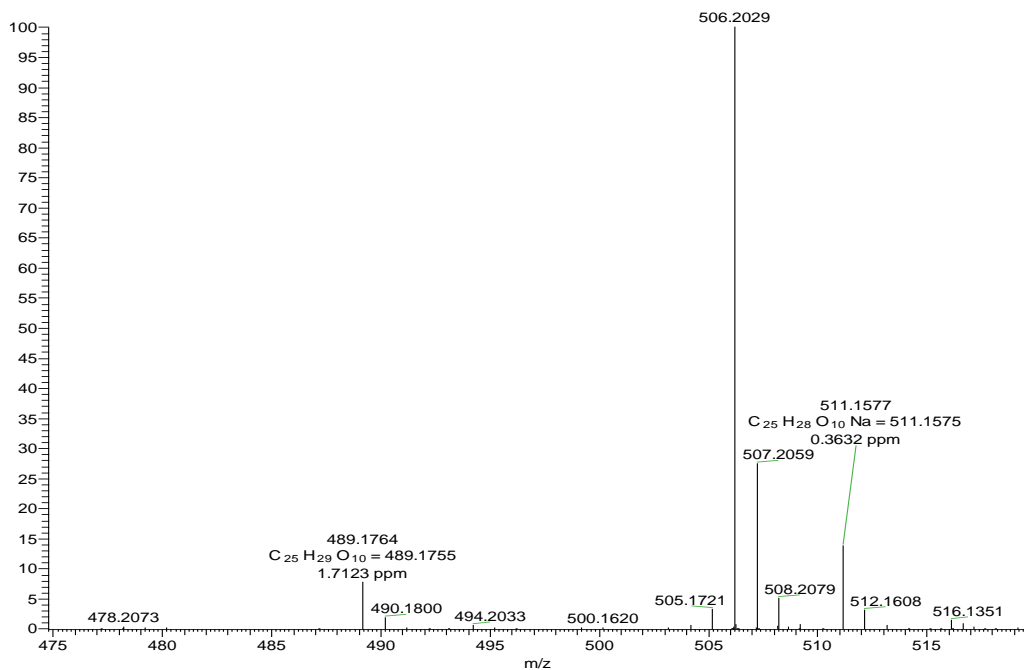


**Figure S56.**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of compound **21**.



**Figure S57.**  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ) spectrum of compound **21**.

20160112-4p-3b\_160108143815 #86 RT: 0.72 AV: 1 NL: 4.56E7  
 T: FTMS + c ESI Full ms [150.00-2000.00]



**Figure S58.** HRESIMS spectrum of compound **21**.

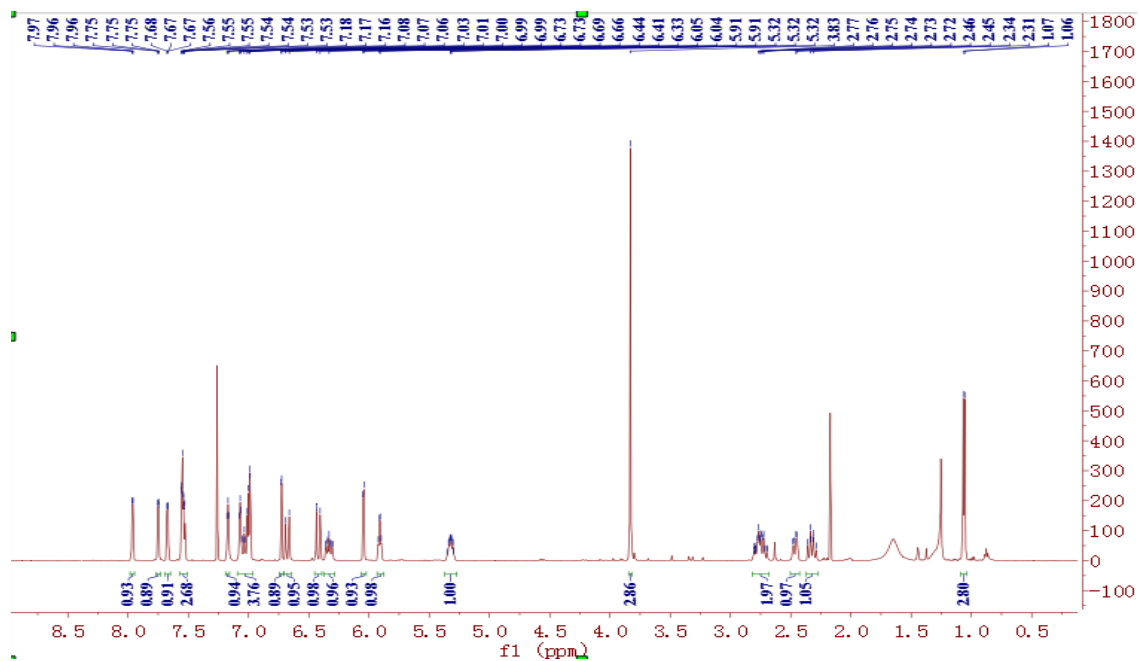


Figure S59.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of compound **22**.

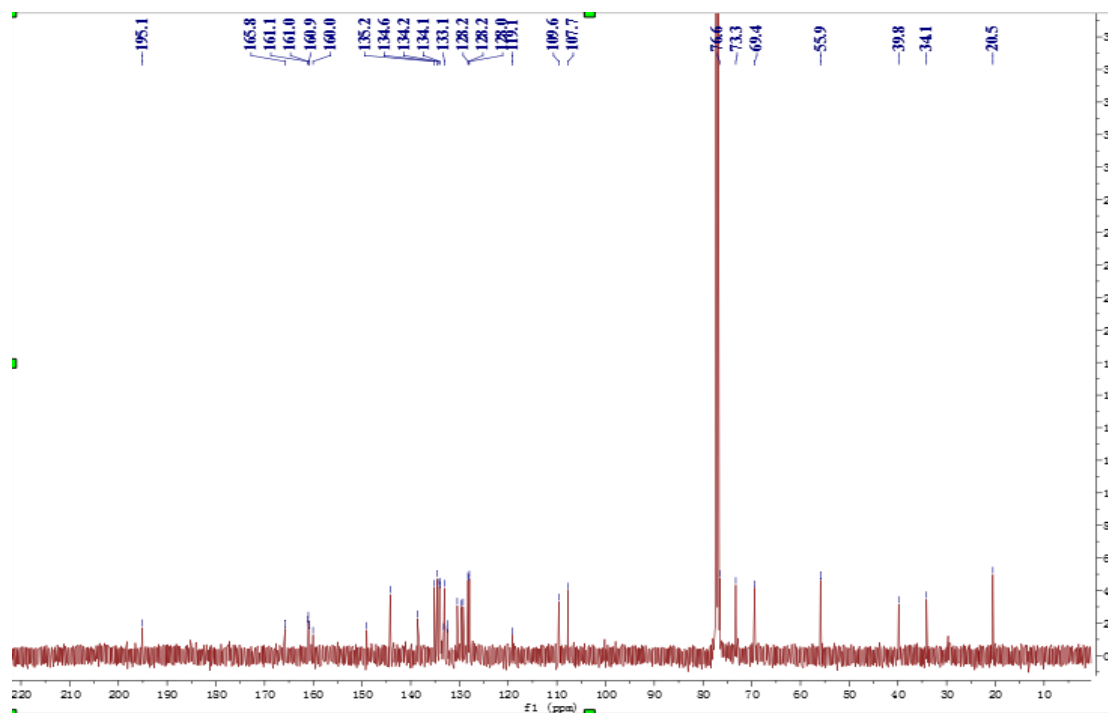


Figure S60.  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ) spectrum of compound **22**.

20170328-ZXQ4-SF\_170328134103 #86 RT: 0.68 AV: 1 NL: 1.32E7  
T: FTMS + p ESI Full ms [120.00-1000.00]

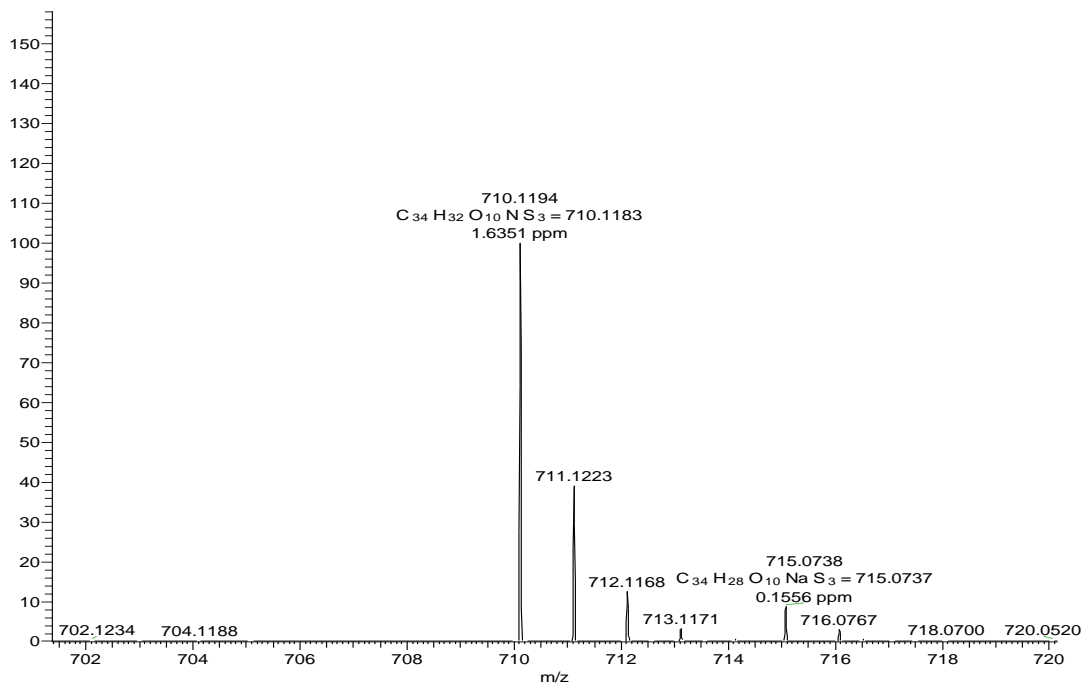


Figure S61. HRESIMS spectrum of compound 22.

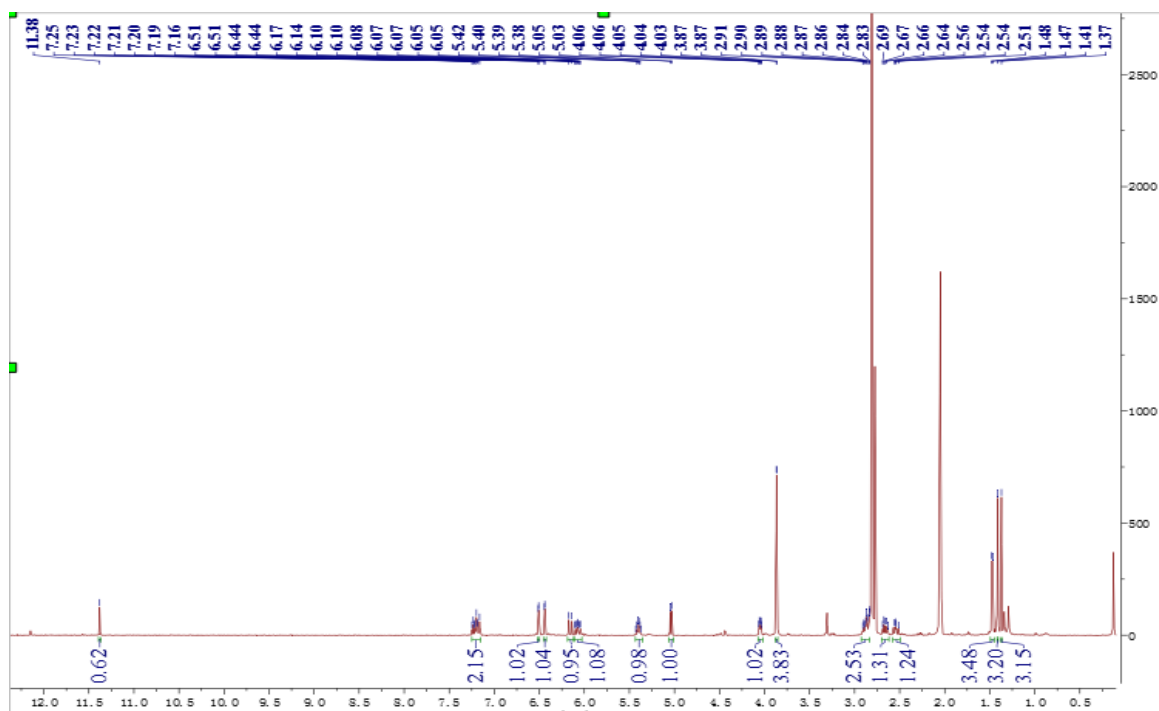


Figure S62.  $^1H$  NMR (500 MHz, Acetone- $d_6$ ) spectrum of compound 23.

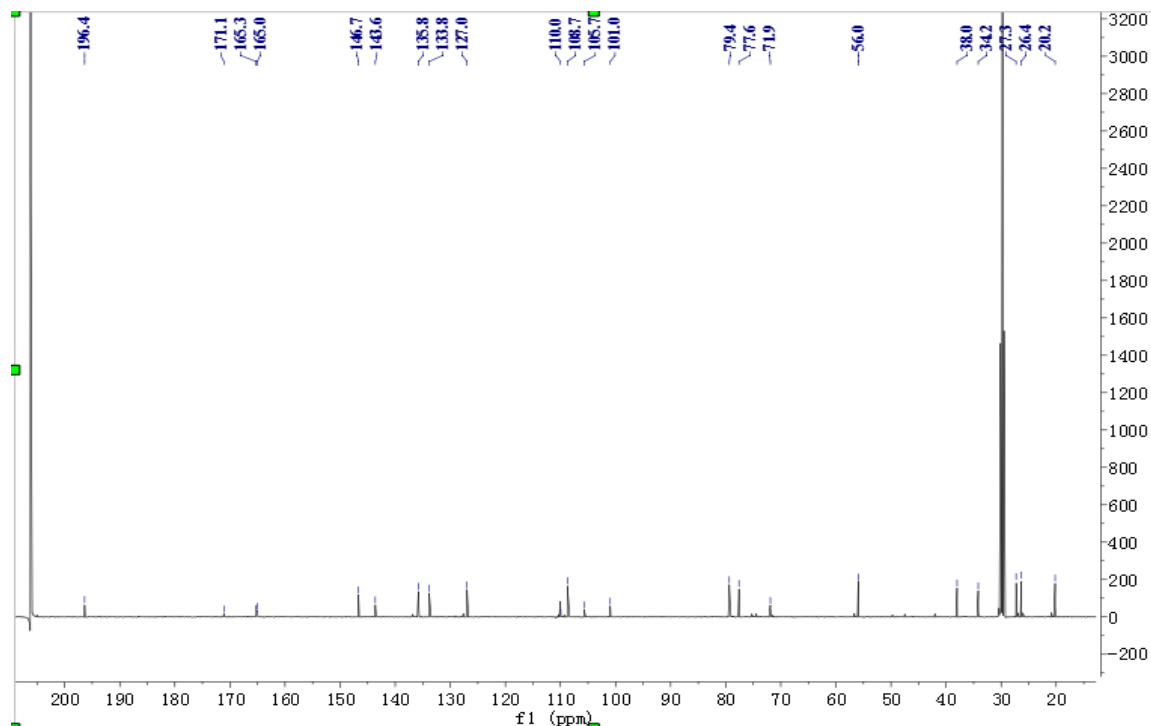


Figure S63.  $^{13}\text{C}$  NMR (125 MHz, Acetone- $d_6$ ) spectrum of compound **23**.

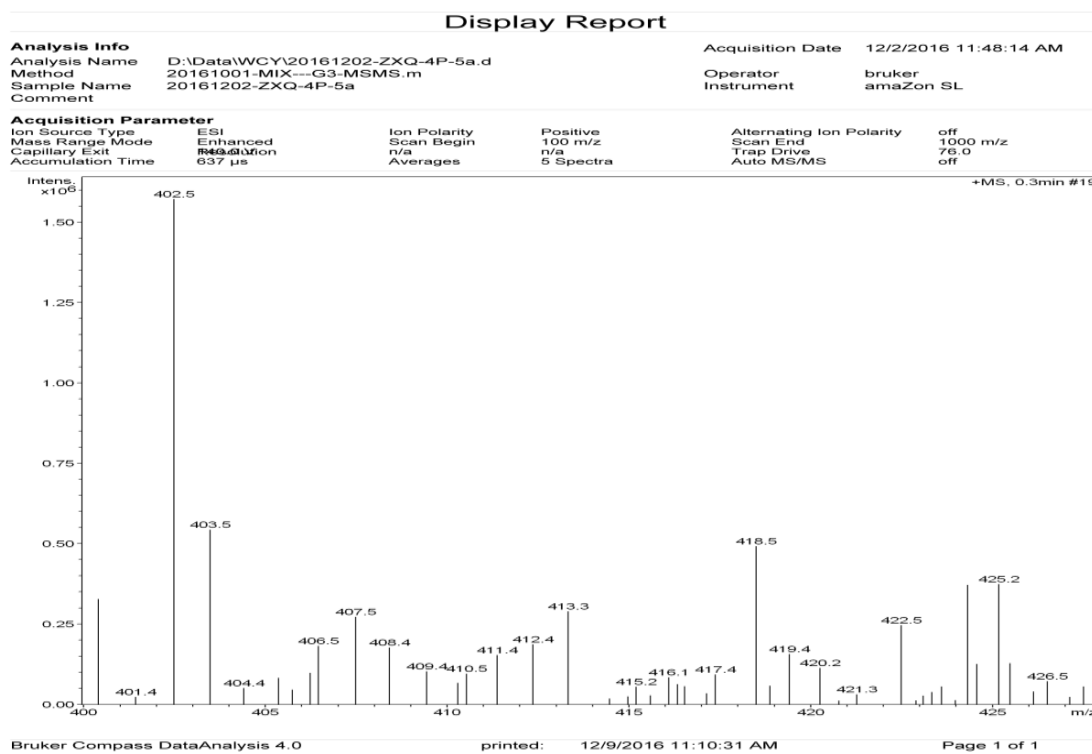
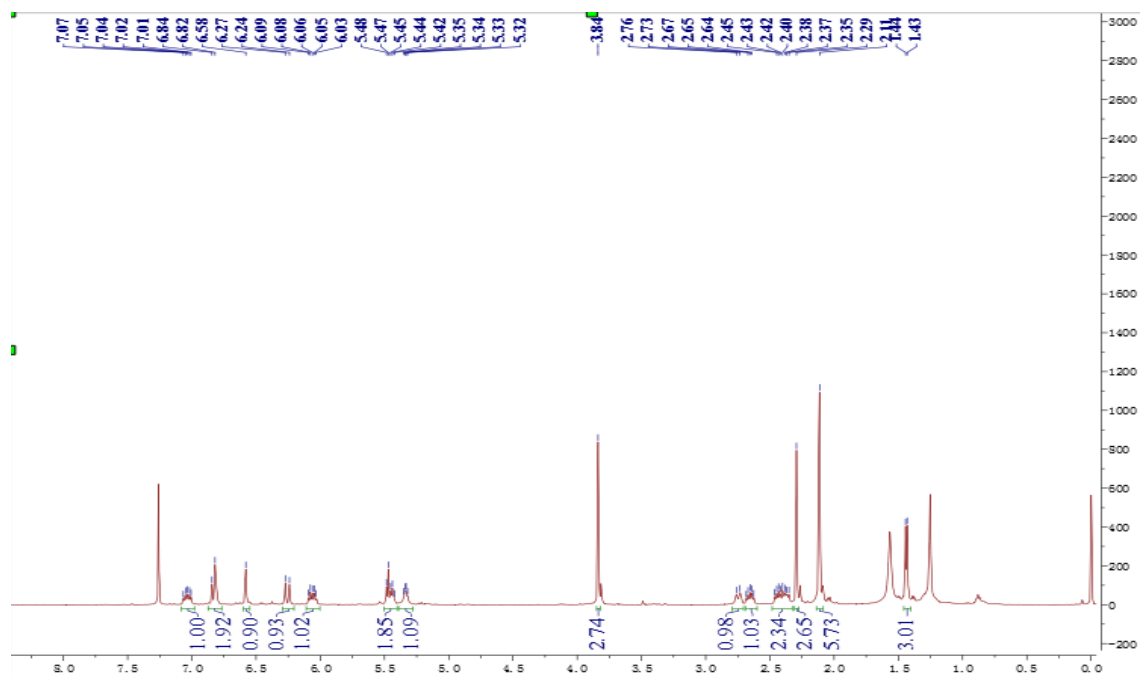
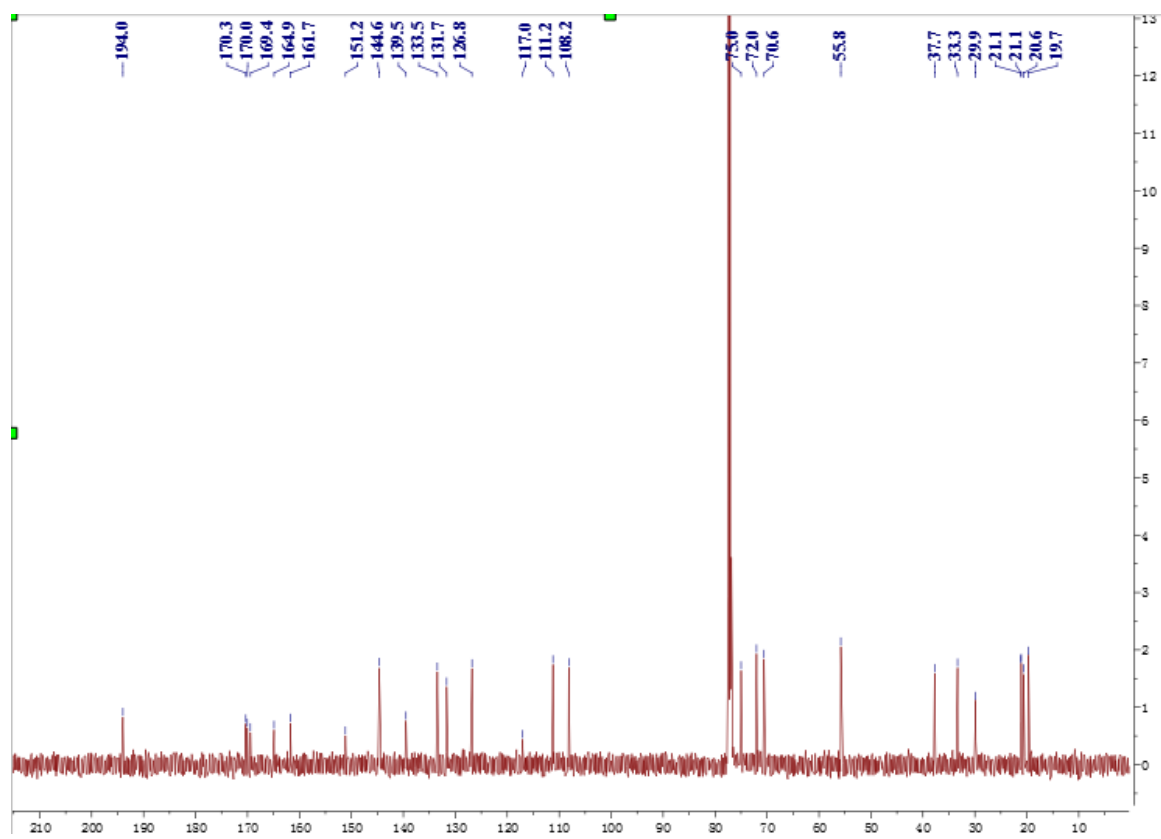


Figure S64. ESIMS spectrum of compound **23**.





**Figure S65.**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of compound **24**.



**Figure S66.**  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ) spectrum of compound **24**.

20161118-4P-5B\_161118085603 #26 RT: 0.21 AV: 1 NL: 3.86E7  
T: FTMS + p ESI Full ms [100.00-1000.00]

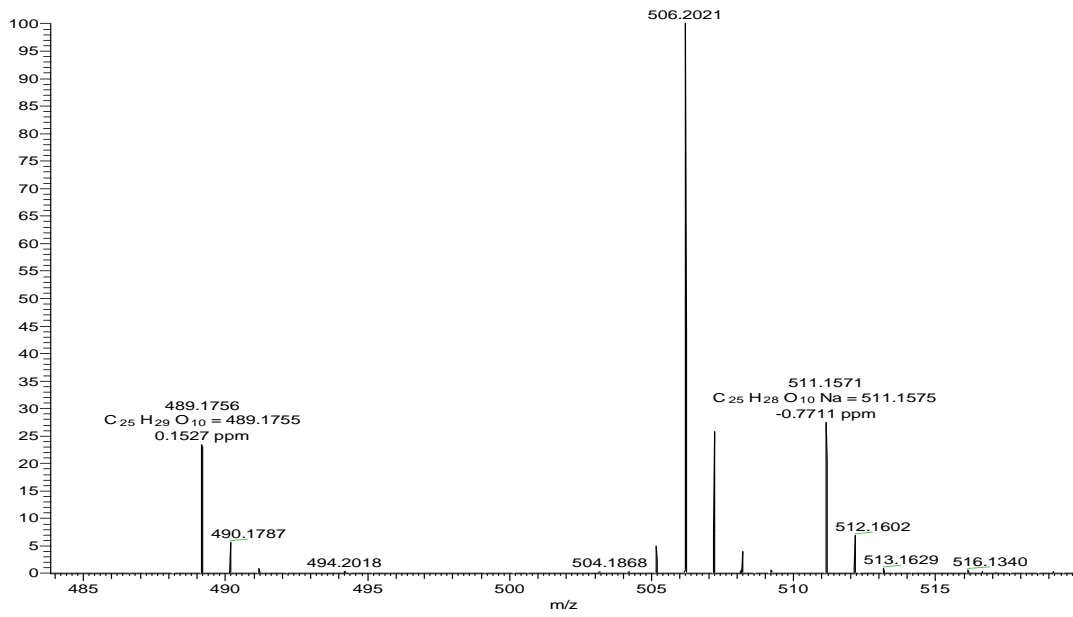


Figure S67. HRESIMS spectrum of compound 24.

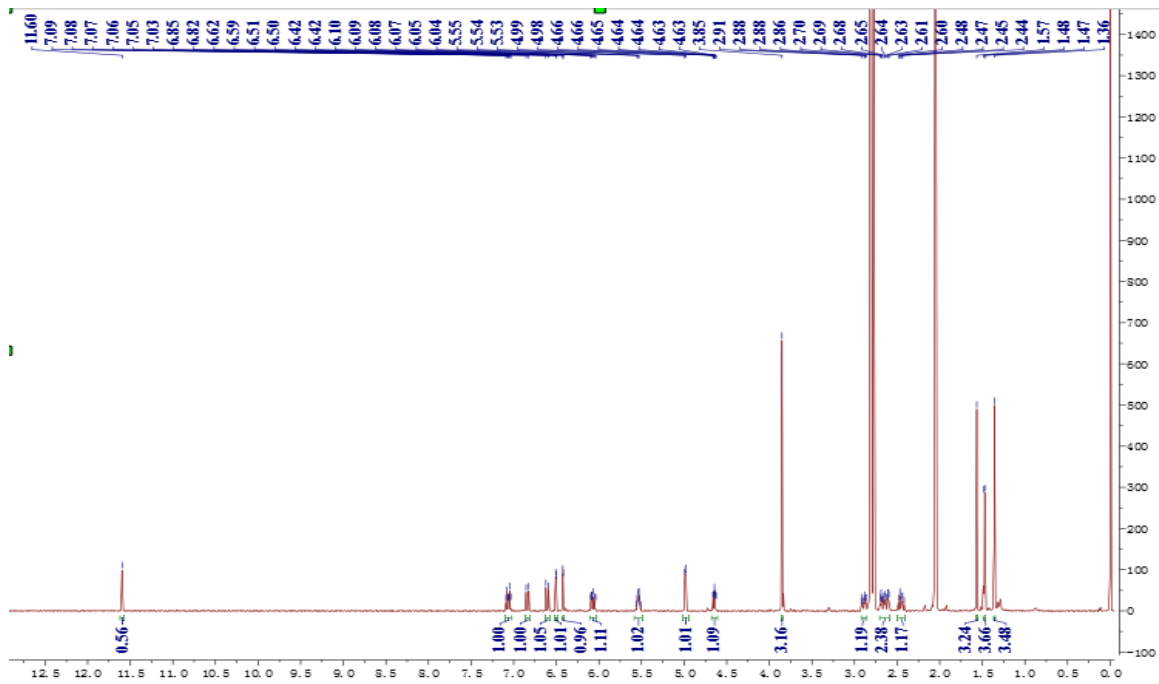
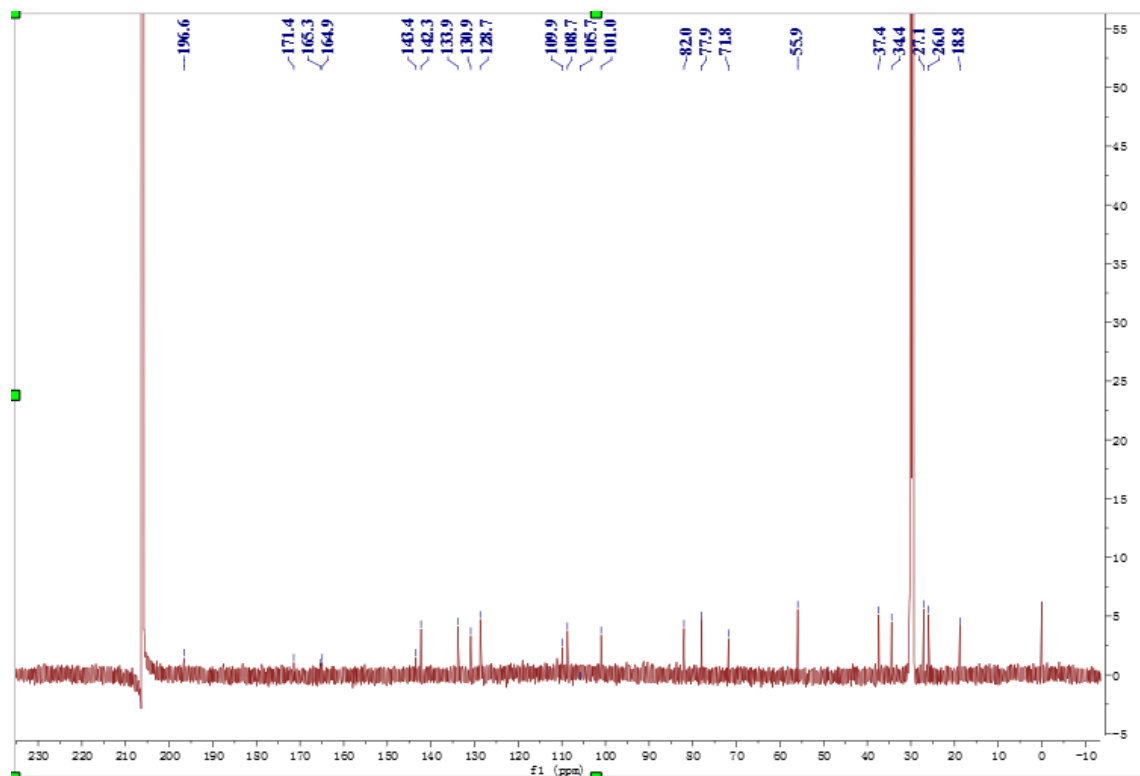


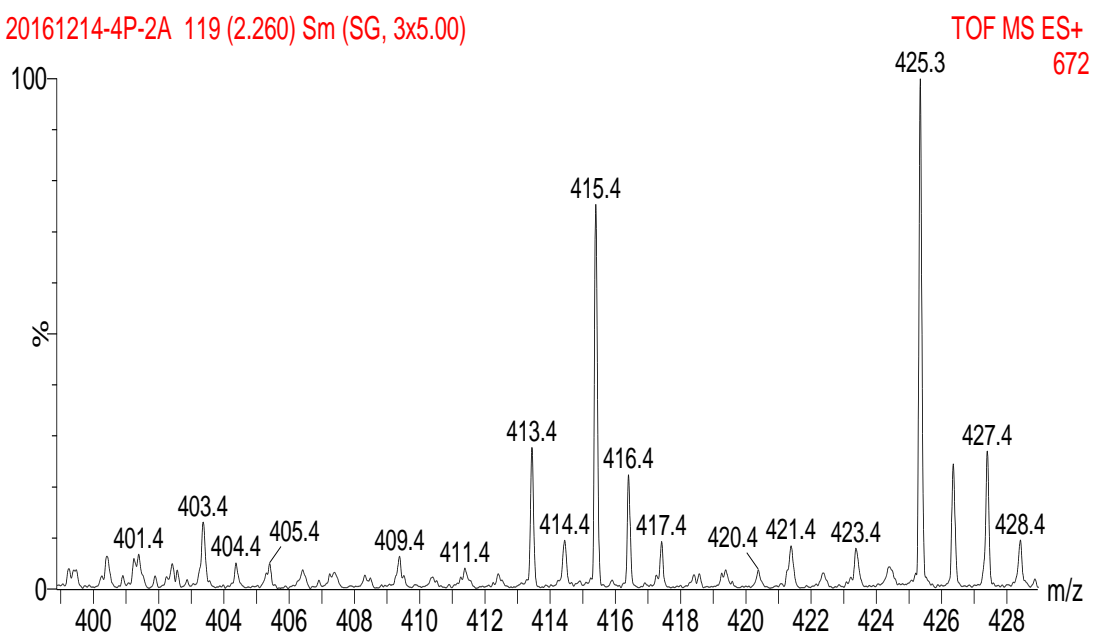
Figure S68. <sup>1</sup>H NMR (500 MHz, Acetone-*d*<sub>6</sub>) spectrum of compound 25.



**Figure S69.**  $^{13}\text{C}$  NMR (125 MHz, Acetone- $d_6$ ) spectrum of compound **25**.

20161214-4P-2A

20161214-4P-2A 119 (2.260) Sm (SG, 3x5.00)



**Figure S70.** ESIMS spectrum of compound **25**.

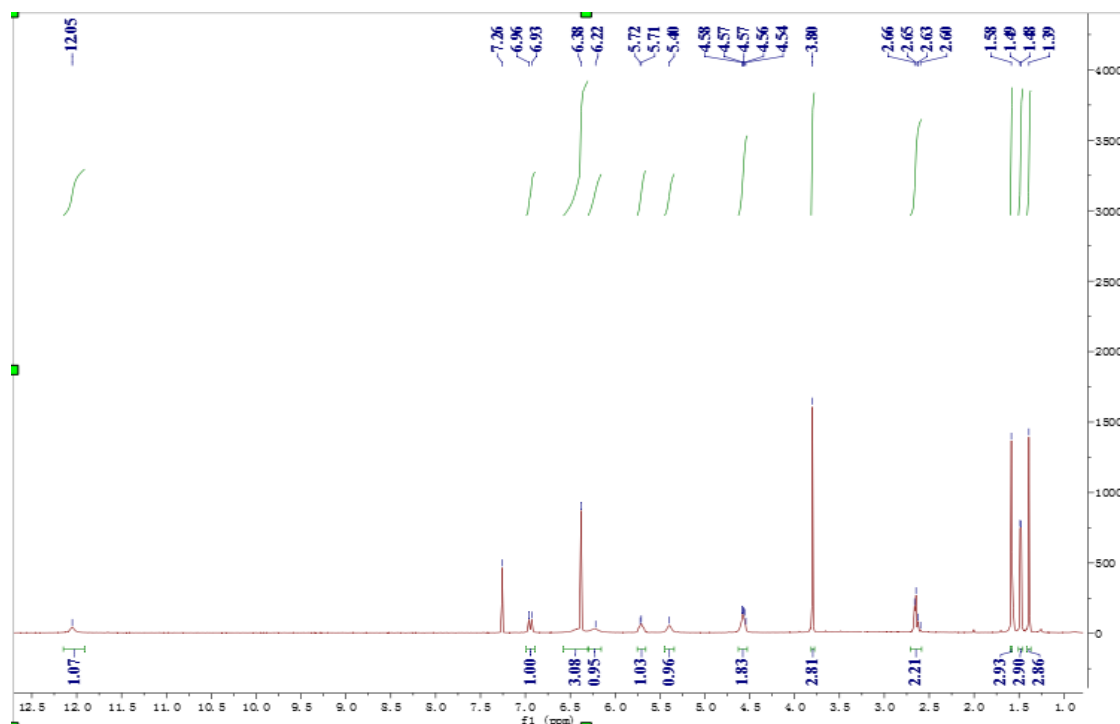


Figure S71.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of compound **26**.

### Display Report

Analysis Info		Acquisition Date	
Analysis Name	D:\Data\WCY\20161202-ZXQ-6a.d	Acquisition Date	12/2/2016 12:05:48 PM
Method	20161001-MIX---G3-MSMS.m	Operator	bruker
Sample Name	20161202-ZXQ-6a	Instrument	amaZon SL
Comment			
Acquisition Parameter			
Ion Source Type	ESI	Ion Polarity	Positive
Mass Range Mode	Enhanced	Scan Begin	100 m/z
Capillary Exit	RF-Gate	n/a	n/a
Accumulation Time	1684 $\mu\text{s}$	Averages	5 Spectra
		Alternating Ion Polarity	off
		Scan End	1000 m/z
		Trap Drive	76.0
		Auto MS/MS	off

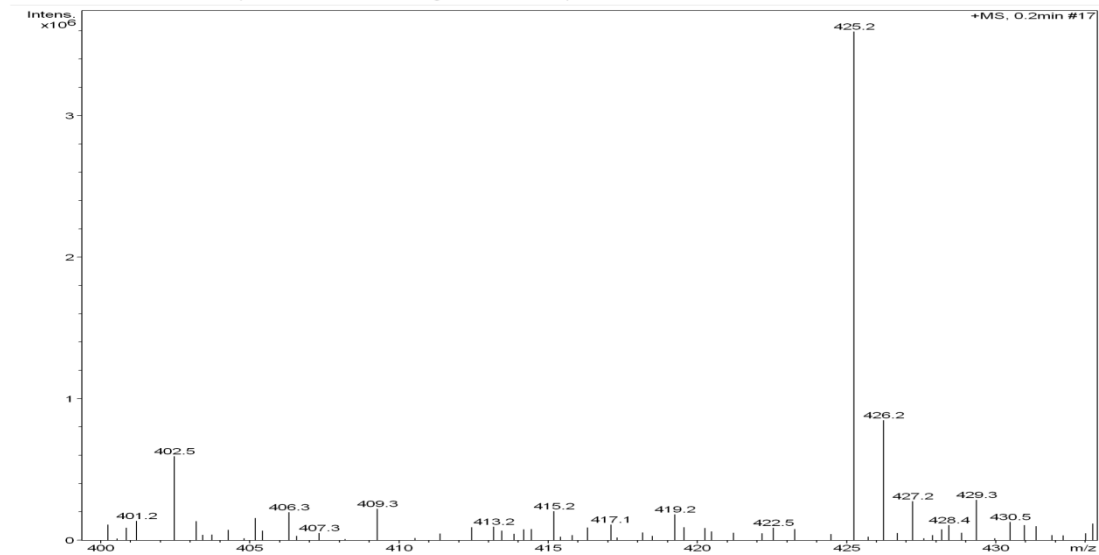


Figure S72. ESIMS spectrum of compound **26**.

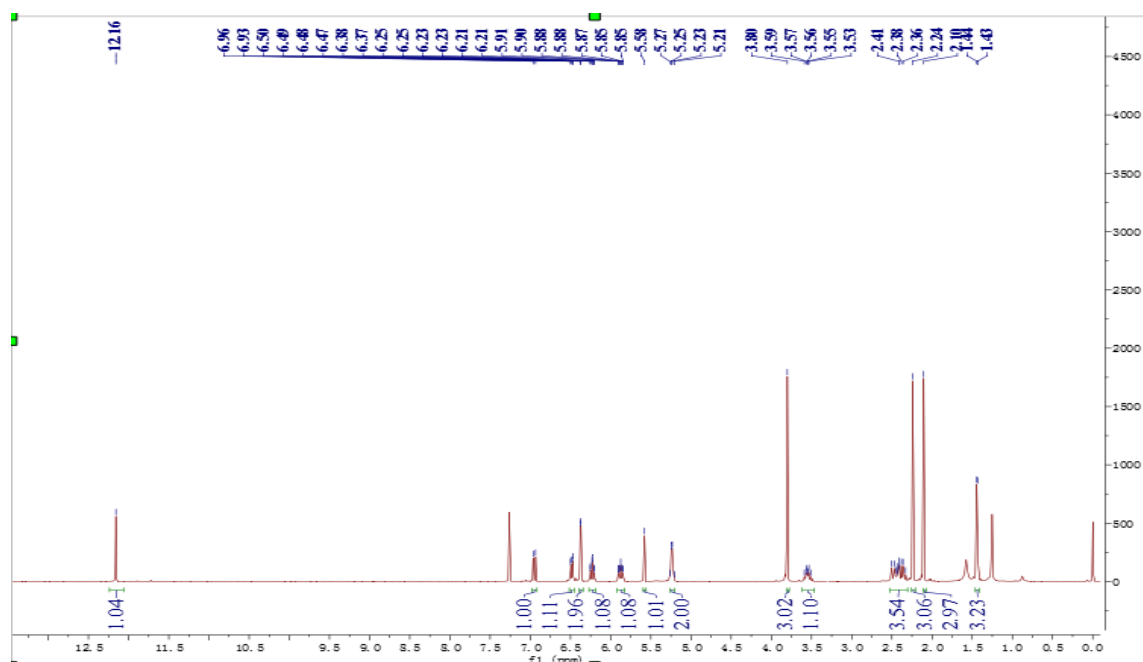


Figure S73.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of compound **27**.

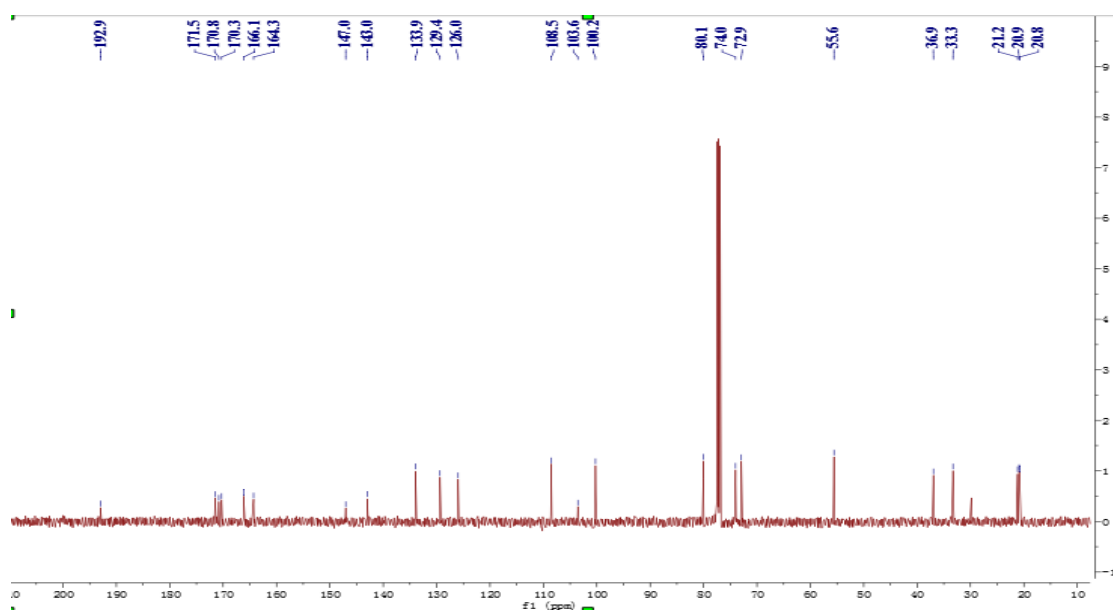
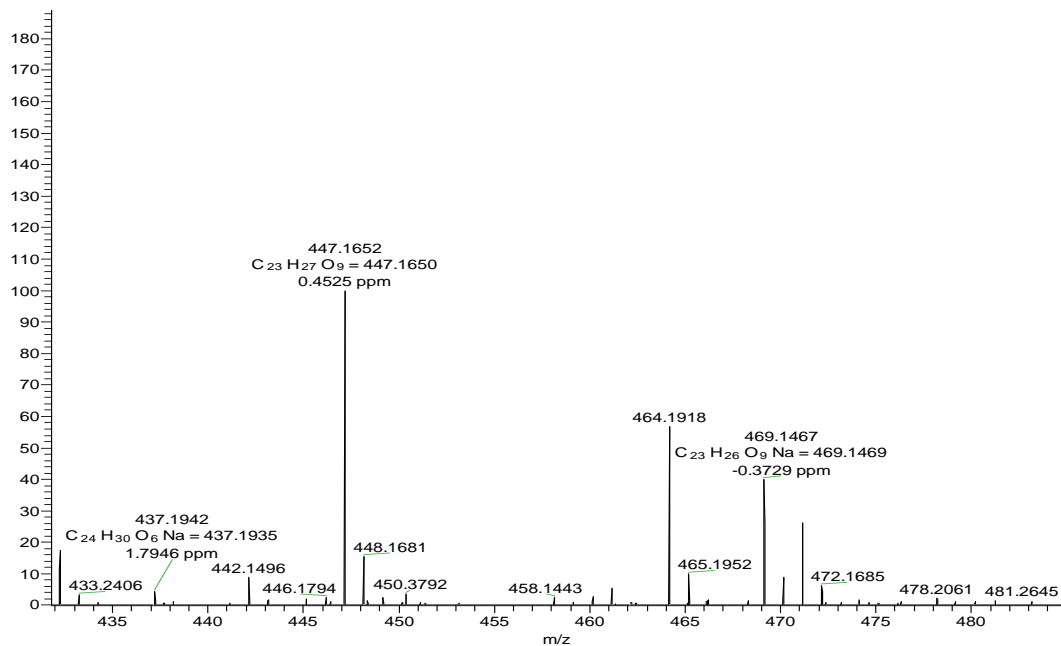


Figure S74.  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ) spectrum of compound **27**.



**Figure S75.** HRESIMS spectrum of compound **27**.

## References

1. Liu, Q. A. *et al.* Antifouling and fungicidal resorcylic acid lactones from the sea anemone-derived fungus *Cochliobolus lunatus*. *J. Agric. Food Chem.* **62**, 3183–3191 (2014).
2. Shao, C. L. *et al.* Potent antifouling resorcylic acid lactones from the gorgonian-derived fungus *Cochliobolus lunatus*. *J. Nat. Prod.* **74**, 629–633 (2011).