**Supporting Information**

**Coixlachryside B: A new benzoxazinoid glycoside from the roots of *Coix lachryma-jobi* var. *ma-yuen* (Gramineae)**

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**List of Supporting Information Page**

Characterization of Compounds**2**, **3** and **5**-**11**………………..…………………………….. S3

**Figure S1.** 1H NMR spectrum (700 MHz, DMSO-*d6*) of coixlachryside B (**1**) ……………. S6

**Figure S2.** 13C NMR spectrum (175 MHz, DMSO-*d6*) of coixlachryside B (**1**) …………… S7

**Figure S3.** DEPT135 spectrum of coixlachryside B (**1**) ………………………..………….. S8

**Figure S4.** 1H-1H COSY spectrum of coixlachryside B (**1**) ……….………………………. S9

**Figure S5.** HSQC spectrum of coixlachryside B (**1**) …………………….………………. S10

**Figure S6.** HMBC spectrum of coixlachryside B (**1**) ……………….……………..………. S11

**Figure S7.** HRESIMS spectrum of coixlachryside B (**1**) …………………………………. S12

**Figure S8.** CD spectrum of coixlachryside B (**1**) …………………………………………. S13

**Figure S9.** 1H NMR spectrum (700 MHz, methanol-*d4*) of 8*S*-tarennone (**2**) …………. S14

**Figure S10.** 13C NMR spectrum (175 MHz, methanol-*d4*) of 8*S*-tarennone (**2**) ………. S15

**Figure S11.** DEPT135 spectrum of 8*S*-tarennone (**2**) ………………………..………….. S16

**Figure S12.** 1H-1H COSY spectrum of 8*S*-tarennone (**2**) ……….………………………. S17

**Figure S13.** HSQC spectrum of 8*S*-tarennone (**2**) …………………….………………. S18

**Figure S14.** HMBC spectrum of 8*S*-tarennone (**2**) ……………….……………..………. S19

**Figure S15.** HRESIMS spectrum of 8*S*-tarennone (**2**) …………………………………. S20

Characterization of Compounds**2**, **3** and **5**-**11**

*(2R)-2-Hydroxy-7-methoxy-1,4(2H)-benzoxazin-3-one glucoside (HMBOA-Glc,* ***2****)*

White amorphous powder; [α]D25 +53.9º (*c* = 1.0, MeOH); CD (MeOH) λmax (Δε) 218 (+12.4) nm; 1H-NMR (700 MHz, DMSO-*d6*) δ 10.8 (1H, s, NH), 6.83 (1H, d, *J* = 9.1 Hz, H-5), 6.75 (1H, d, *J* = 2.8 Hz, H-8), 6.59 (1H, dd, *J* = 8.4, 2.8 Hz, H-6), 5.65 (1H, s, H-2), 4.55 (1H, d, *J* = 8.4 Hz, H-1'), 3.71 (1H, dd, *J* = 11.9, 2.1 Hz, Ha-6'), 3.70 (3H, s, OCH3), 3.43 (1H, dd, *J* = 11.9, 6.3 Hz, Hb-6'), 3.18 (1H, m, H-5'), 3.14 (1H, t, *J* = 9.1 Hz, H-3'), 3.01 (1H, t, *J* = 9.1 Hz, H-4'), 2.91 (1H, t, *J* = 9.1 Hz, H-2'); 13C-NMR (175 MHz, DMSO-*d6*) δ 159.2 (C-3), 155.0 (C-7), 140.5 (C-9), 119.1 (C-10), 115.2 (C-5), 108.1 (C-6), 103.2 (C-8), 102.1 (C-1'), 94.3 (C-2'), 76.9 (C-3'), 76.1 (C-5'), 72.6 (C-2'), 69.1 (C-4'), 60.5 (C-6'), 54.7 (OCH3); ESI-MS *m/z* 380 [M +Na]+, 356 [M – H]–.

*(2R)-2-Hydroxy-4,7-dimethoxy-1,4(2H)-benzoxazin-3-one glucoside (HDMBOA-Glc,* ***3****)*

White amorphous powder; [α]D25 +15.5º (*c* = 0.5, MeOH); CD (MeOH) λmax (Δε) 216 (+18.1) nm; 1H-NMR (700 MHz, CD3OD) δ 7.18 (1H, d, *J* = 8.4 Hz, H-5), 6.78 (1H, d, *J* = 2.1 Hz, H-8), 6.72 (1H, dd, *J* = 8.4, 2.1 Hz, H-6), 5.88 (1H, s, H-2), 4.67 (1H, d, *J* = 8.4 Hz, H-1'), 3.94 (3H, s, N-OCH3), 3.87 (1H, dd, *J* = 11.9, 2.1 Hz, Ha-6'), 3.78 (3H, s, 7-OCH3), 3.68 (1H, dd, *J* = 11.9, 4.9 Hz, b-6'), 3.32 (2H, m, H-3', 5'), 3.29 (1H, t, *J* = 9.1 Hz, H-4'), 3.17 (1H, t, *J* = 9.1 Hz, H-2'); 13C-NMR (175 MHz, CD3OD) δ 159.0 (C-3), 156.8 (C-7), 143.5 (C-9), 120.6 (C-10), 114.5 (C-5), 110.1 (C-6), 105.3 (C-8), 104.1 (C-1'), 98.4 (C-2), 78.5 (C-5'), 77.9 (C-3'), 74.7 (C-2'), 71.0 (C-4'), 63.4 (N-OCH3), 62.6 (C-6'), 56.2 (7-OCH3); ESI-MS *m/z* 410 [M + Na]+.

*8R-Evofolin B (****5****)*

White amorphous powder; [α]D25 ‒5.6º (*c* = 0.2, MeOH); CD (MeOH) λmax (Δε) 237 (‒2.22), 261 (+1.13), 305 (‒1.30) nm; 1H-NMR (700 MHz, CD3OD) δ 7.61 (1H, dd, *J* = 8.4, 2.4 Hz, H-6'), 7.56 (1H, d, *J* = 2.1 Hz, H-2'), 6.89 (1H, d, *J* = 2.1 Hz, H-2''), 6.80 (1H, d, *J* = 8.4 Hz, H-5'), 6.75 (1H, dd, *J* = 8.4, 2.1 Hz, H-6''), 6.72 (1H, d, *J* = 8.4 Hz, H-5''), 4.74 (1H, dd, *J* = 9.1, 5.6 Hz, H-2), 4.24 (1H, dd, *J* = 11.2, 9.1 Hz, Ha-3), 3.86 (3H, s, 3-OCH3), 3.82 (3H, s, 3'-OCH3), 3.70 (1H, dd, *J* = 11.5, 5.6 Hz, Hb-3); 13C-NMR (175 MHz, CD3OD) δ 199.6 (C-1), 153.1 (C-4'), 149.3 (C-3''), 148.9 (C-3'), 147.0 (C-4''), 130.4 (C-1'), 129.9 (C-1''), 125.2 (C-6'), 122.2 (C-6''), 116.6 (C-5''), 115.7 (C-5'), 112.7 (C-2''), 112.6 (C-2'), 65.5 (C-3), 56.4 (OCH3), 56.3 (OCH3), 56.3 (C-2); ESI-MS *m/z* 319 [M + H]+, 341 [M + Na]+, 317 [M – H]–; HRESIMS (positive) *m/z* 319.11843 [M + H]+ (calcd for C17H18O6, 319.11762).

*3,4,5-Trimethoxyphenylmethanol (****6****)*

Yellow powder; 1H-NMR (700 MHz, CD3OD) δ 6.67 (2H, s, H-2, 6), 4.54 (2H, s, H-7), 3.83 (6H, s, 3, 5-OCH3), 3.75 (3H, s, 4-OCH3); 13C-NMR (175 MHz, CD3OD) δ 154.5 (C-3, 5), 138.1 (C-4), 139.0 (C-1), 105.0 (C-2, 6), 65.3 (C-7), 61.1 (4-OCH3), 56.5 (3, 5-OCH3); ESI-MS *m/z* 199 [M + H]+, 221 [M + Na]+.

*α-Hydroxypropiosyringone (****7****)*

White amorphous powder; 1H-NMR (700 MHz, CD3OD) δ 7.32 (2H, s, H-2, 6), 5.19 (1H, q, *J* = 6.3 Hz, H-8), 3.90 (6H, s, 3, 5-OCH3), 1.41 (3H, d, *J* = 6.3 Hz, H-9); 13C-NMR (175 MHz, CD3OD) δ 201.9 (C-7), 149.1 (C-3, 5), 142.9 (C-4), 126.2 (C-1), 107.7 (C-2, 6), 70.0 (C-8), 56.9 (3, 5-OCH3), 22.1 (C-9); ESI-MS *m/z* 227 [M + H]+, 249 [M + Na]+, 225 [M – H]–.

*β-Hydroxypropiovanillone (****8****)*

Colorless amorphous powder; 1H-NMR (700 MHz, CD3OD) δ 7.57 (1H, dd, *J* = 8.4, 2.1 Hz, H-6), 7.54 (1H, d, *J* = 2.1 Hz, H-2), 6.86 (1H, d, *J* = 8.4 Hz, H-5), 3.94 (2H, t, *J* = 6.3 Hz, H-9), 3.90 (3H, s, 3-OCH3), 3.16 (2H, t, *J* = 6.3 Hz, H-8); 13C-NMR (175 MHz, CD3OD) δ 199.7 (C-7), 153.3 (C-4), 149.1 (C-3), 130.6 (C-1), 124.7 (C-6), 115.8 (C-5), 111.8 (C-2), 58.9 (C-9), 56.4 (3-OCH3), 41.6 (C-8); ESI-MS *m/z* 197 [M + H]+, 219 [M + Na]+, 195 [M - H]-.

*β-Hydroxypropiosyringone (****9****)*

Colorless amorphous powder; 1H-NMR (700 MHz, CD3OD) δ 7.31 (2H, s, H-2, 6), 3.95 (1H, t, *J* = 6.3 Hz, H-9), 3.90 (6H, s, 3, 5-OCH3), 3.18 (1H, t, *J* = 6.3 Hz, H-8); 13C-NMR (175 MHz, CD3OD) δ 199.6 (C-7), 149.0 (C-3, 5), 142.5 (C-4), 129.2 (C-1), 107.2 (C-2, 6), 58.9 (C-9), 56.8 (3, 5-OCH3), 41.7 (C-8); ESI-MS *m/z* 227 [M + H]+, 249 [M + Na]+, 225 [M - H]-.

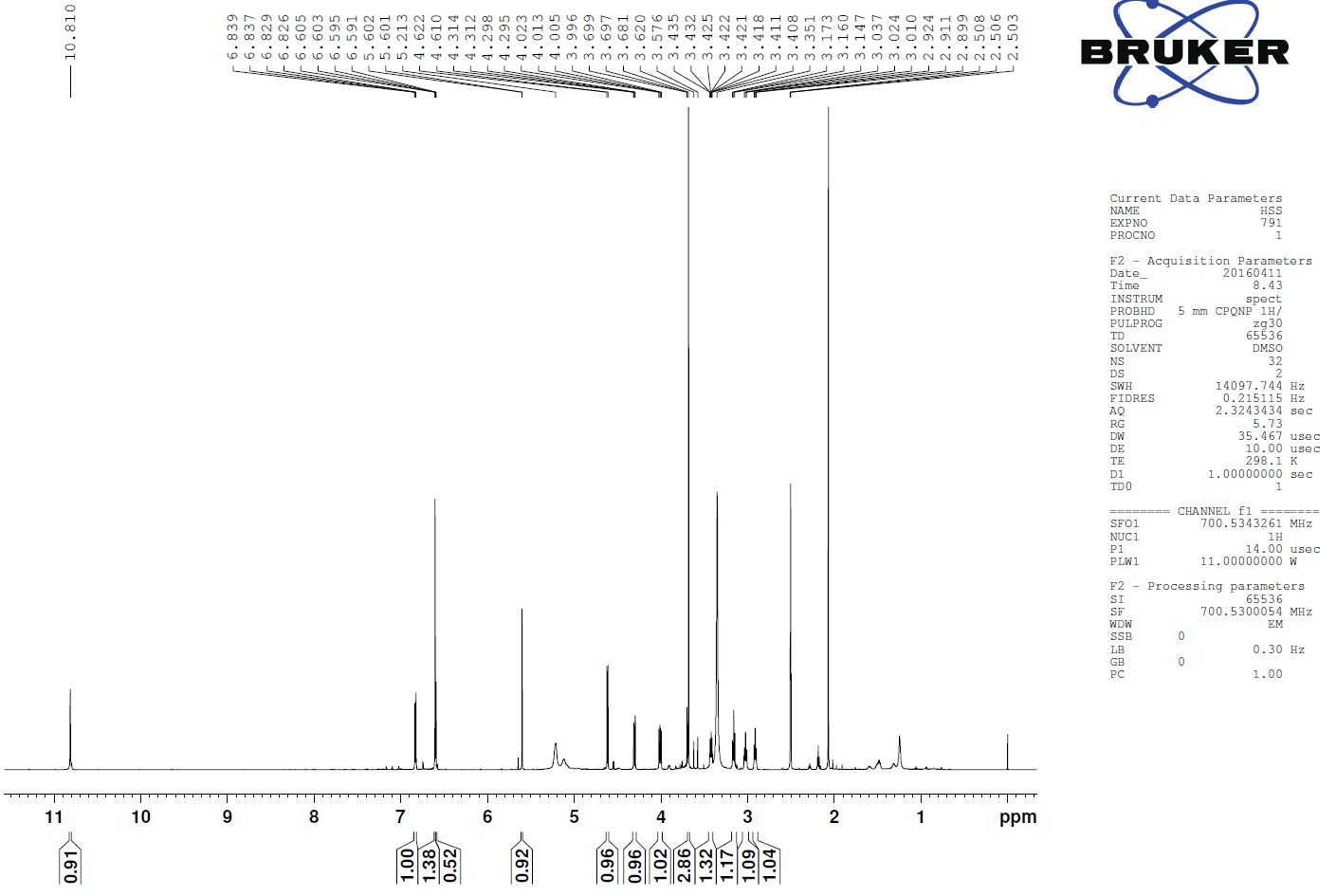
*1-O-Feruloylglycerol (****10****)*

White amorphous powder; 1H-NMR (700 MHz, CD3OD) δ 7.65 (1H, d, *J* = 16.1 Hz, H-7), 7.19 (1H, d, *J* = 2.1 Hz, H-2), 7.08 (1H, dd, *J* = 8.4, 2.1 Hz, H-6), 6.81 (1H, d, *J* = 8.4 Hz, H-5), 6.39 (1H, d, *J* = 16.1 Hz, H-8), 4.26 (1H, dd, *J* = 11.2, 4.2 Hz, Ha-1'), 4.17 (1H, dd, *J* = 11.2, 6.3 Hz, Hb-1'), 3.87 (1H, m, H-2'), 3.61 (2H, m, H-3'); 13C-NMR (175 MHz, CD3OD) δ 169.2 (C-9), 150.6 (C-4), 149.4 (C-3), 147.0 (C-7), 127.7 (C-1), 124.1 (C-6), 116.5 (C-5), 115.3 (C-8), 111.7 (C-2), 71.3 (C-2'), 66.6 (C-1'), 64.1 (C-3'), 56.3 (3-OCH3); ESI-MS *m/z* 269 [M + H]+, 291 [M + Na]+, 267 [M – H]–.

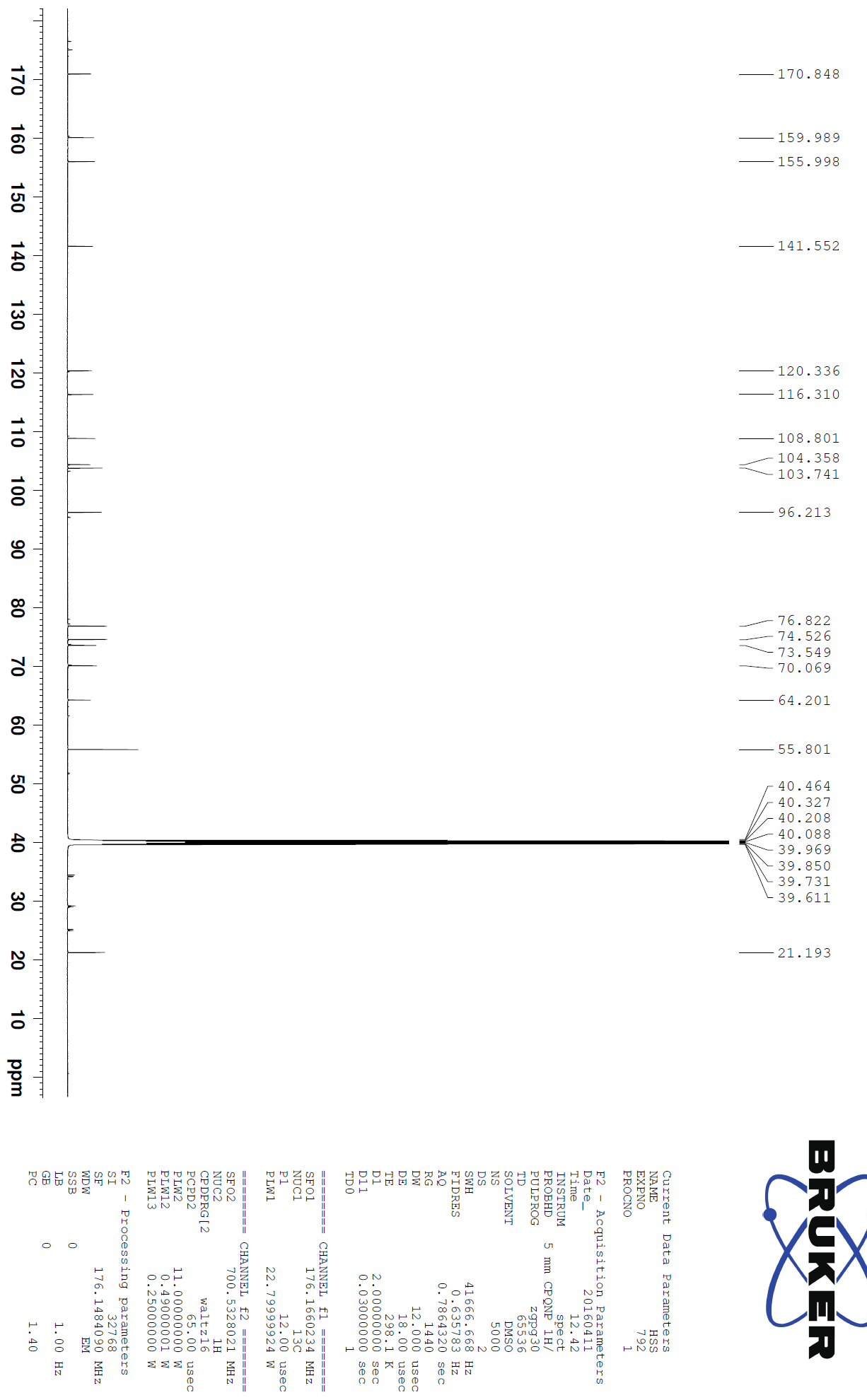
*10Z,13Z-nonadecadienoic acid (****11****)*

White amorphous powder; 1H-NMR (700 MHz, CDCl3) δ 5.36-5.29 (4H, m, H-10, 11, 13, 14), 2.74 (2H, t, *J* = 7.0 Hz, H-12), 2.32 (2H, t, *J* = 7.0 Hz, H-2), 2.02 (4H, dd, *J* = 14.0, 7.0 Hz, H-9, 15), 1.61 (2H, m, H-3), 1.35-1.23 (16H, m, H-4, 5, 6, 7, 8, 16, 17, 18), 0.86 (3H, t, *J* = 7.7 Hz, H-19); 13C-NMR (175 MHz, CDCl3) δ 179.9 (C-1), 130.2 (C-10), 130.0 (C-14), 128.1 (C-11), 127.9 (C-13), 34.1 (C-2), 31.5 (C-17), 29.6 (C-8), 29.4 (C-6, 7), 29.2 (C-16), 29.1 (C-5), 29.0 (C-4), 27.2 (C-15), 27.1 (C-9), 25.6 (C-12), 24.7 (C-3), 22.6 (C-18), 14.1 (C-19); ESI-MS *m/z* 295 [M + H]+, 317 [M + Na]+, 293 [M – H]–.

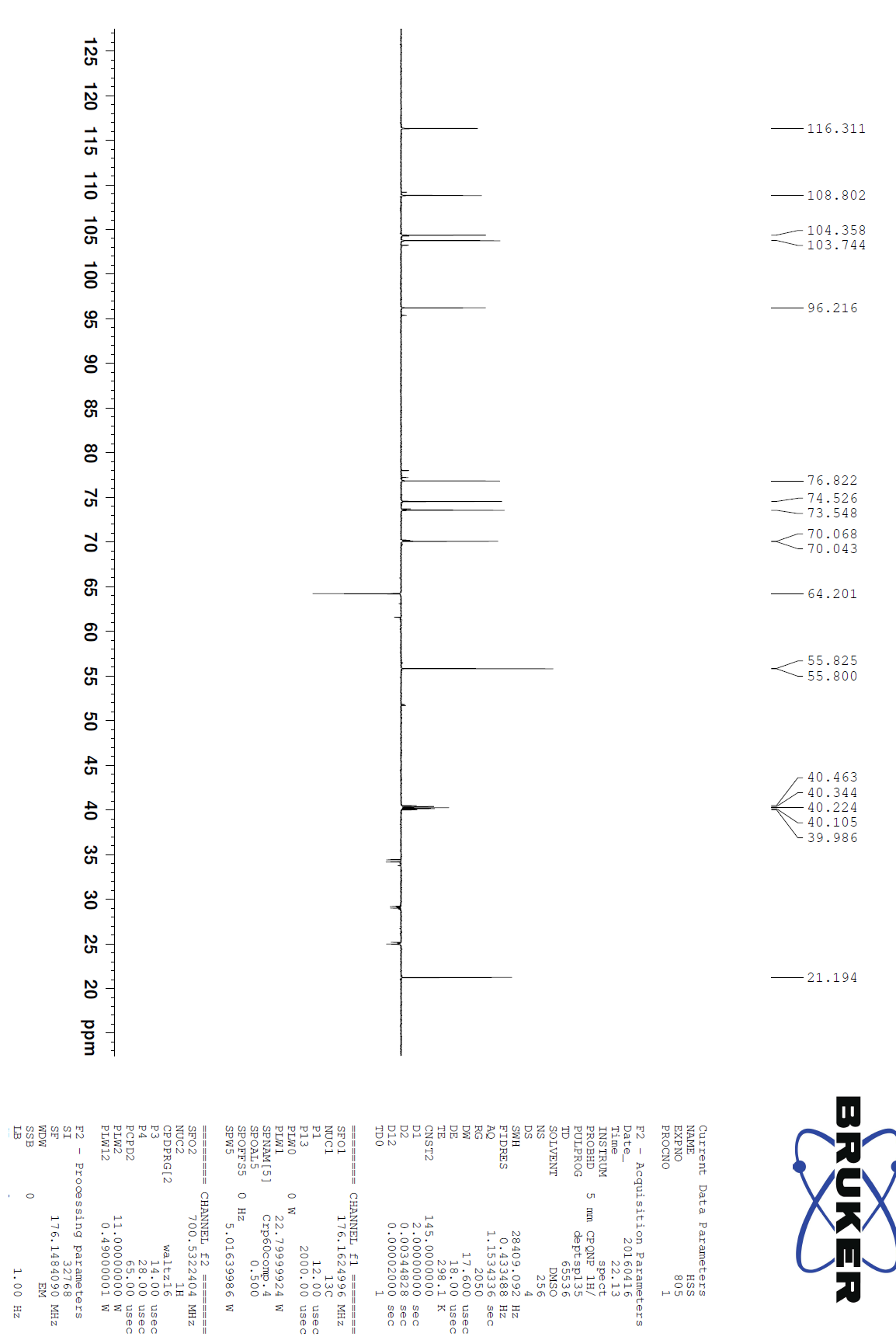
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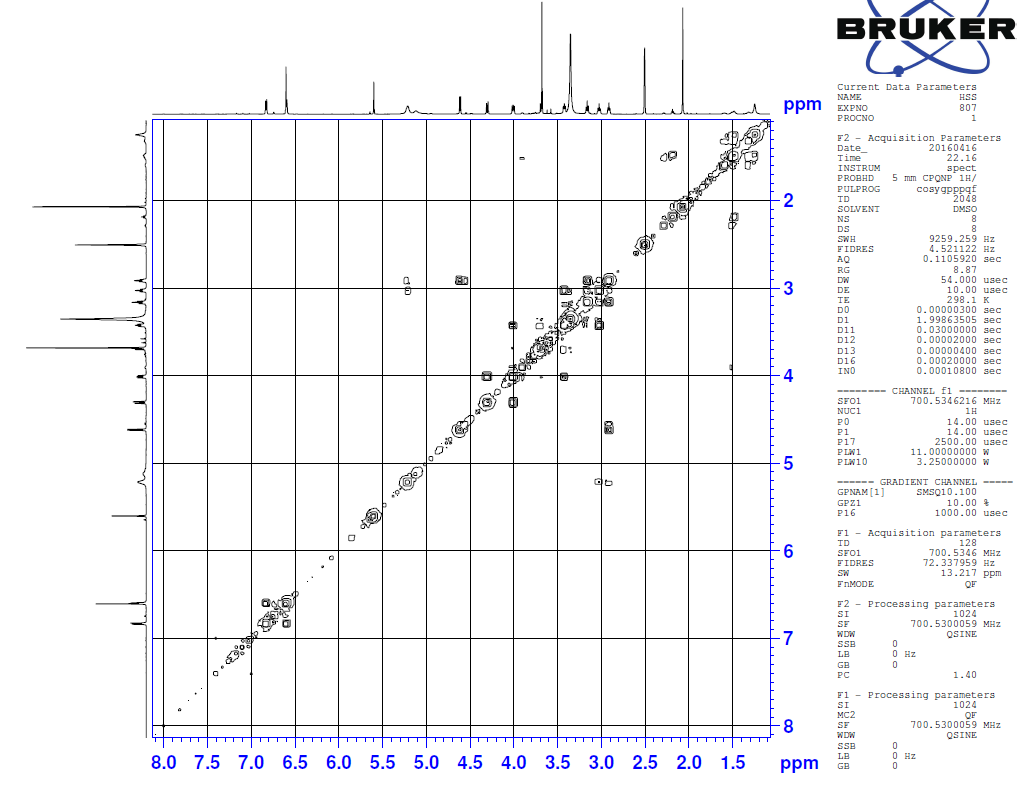
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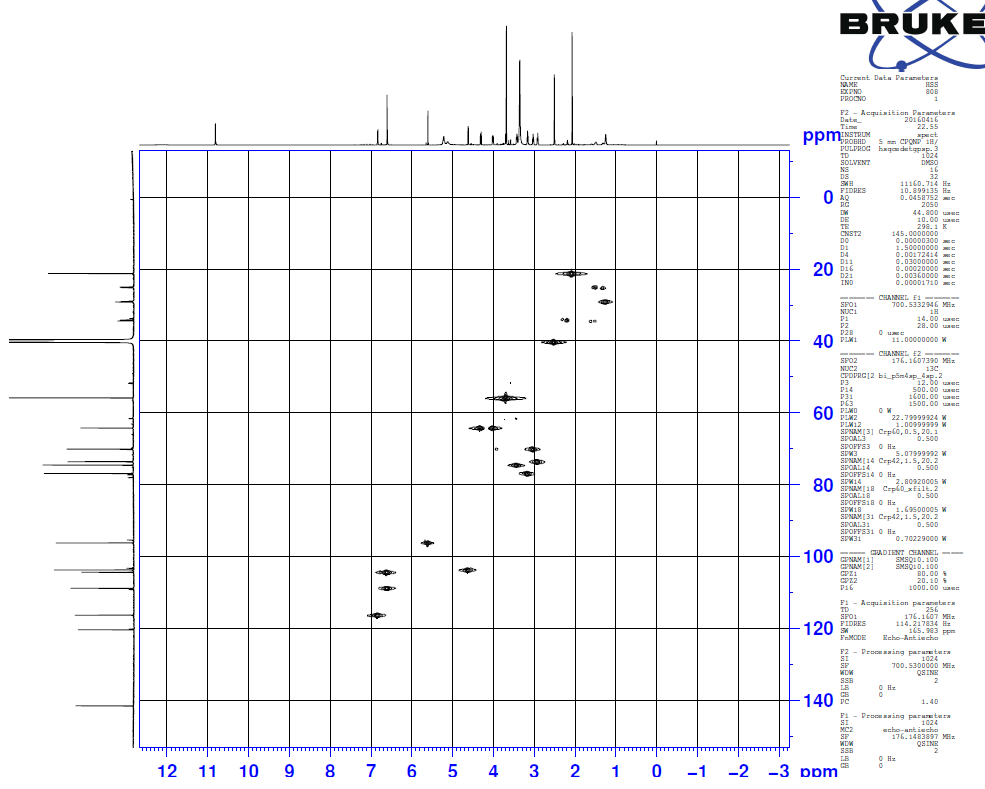
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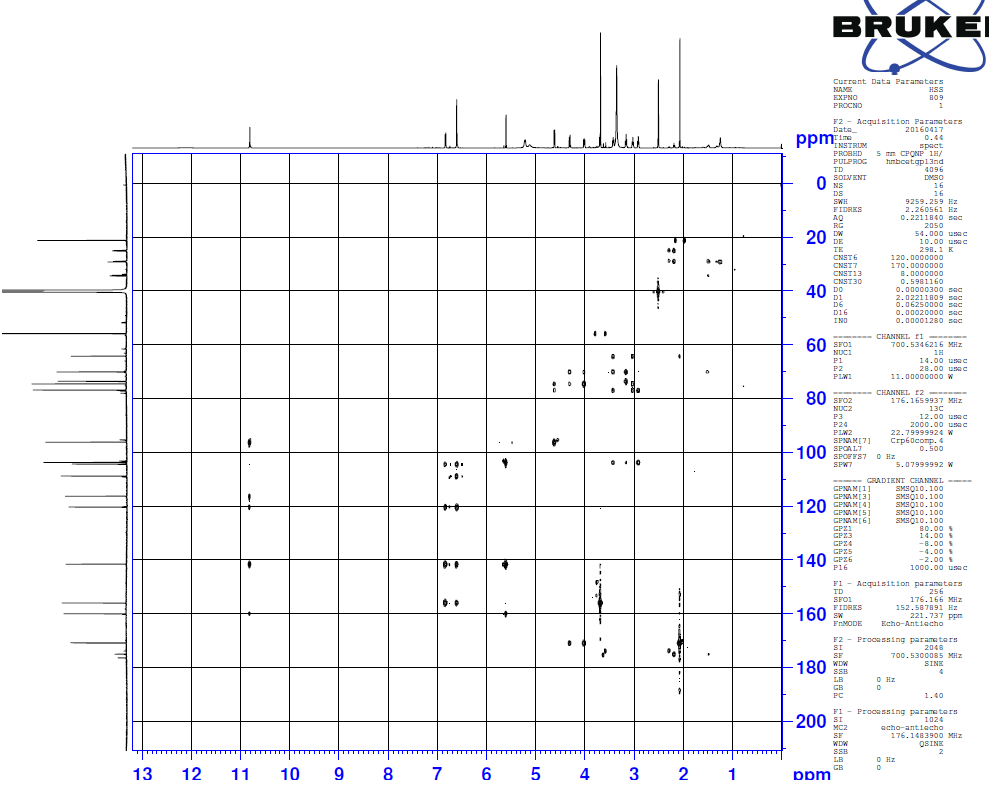
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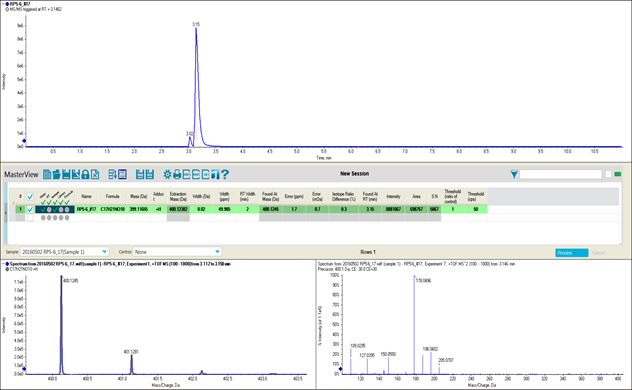
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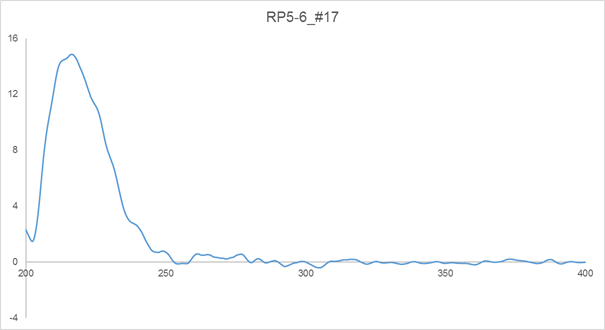
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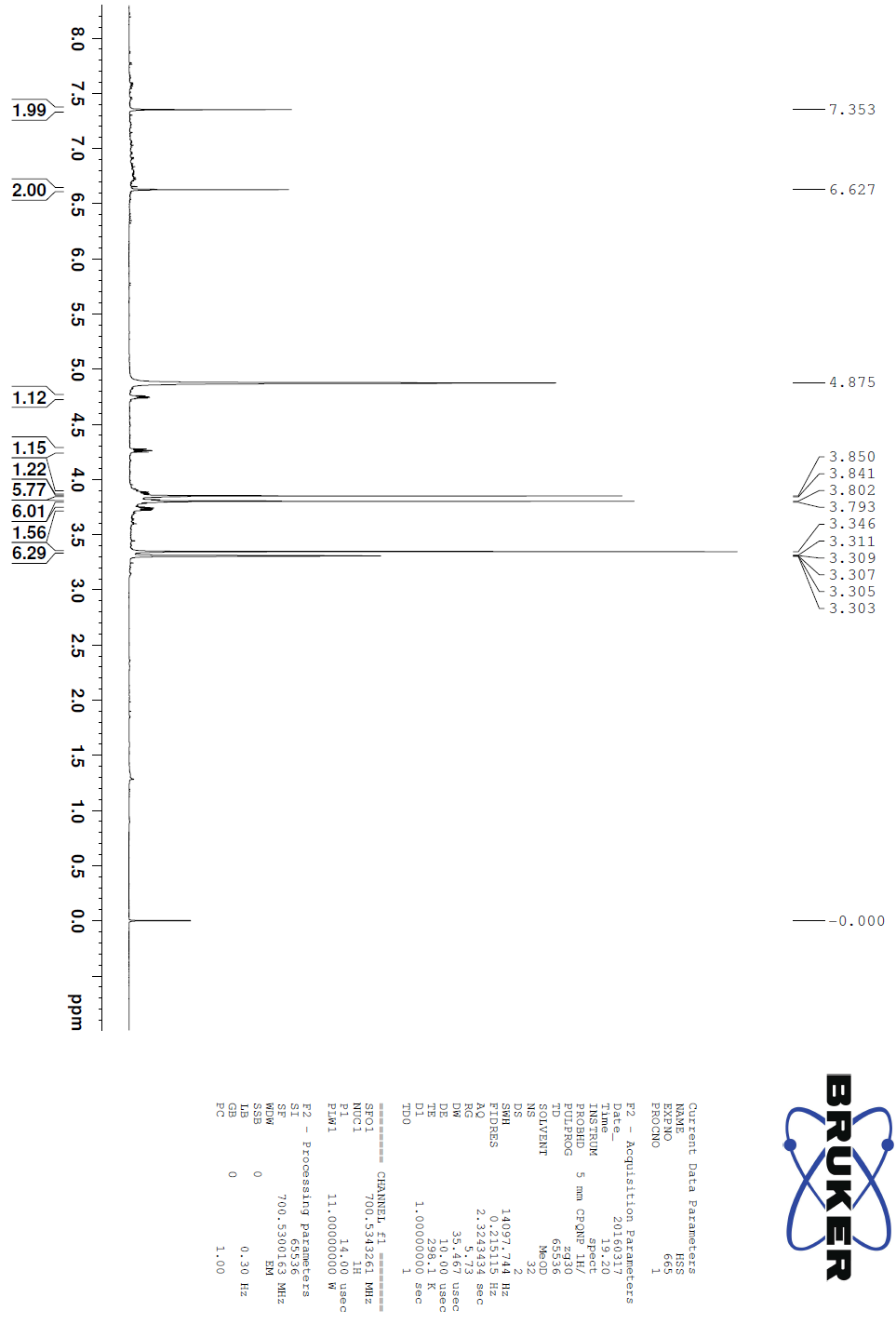
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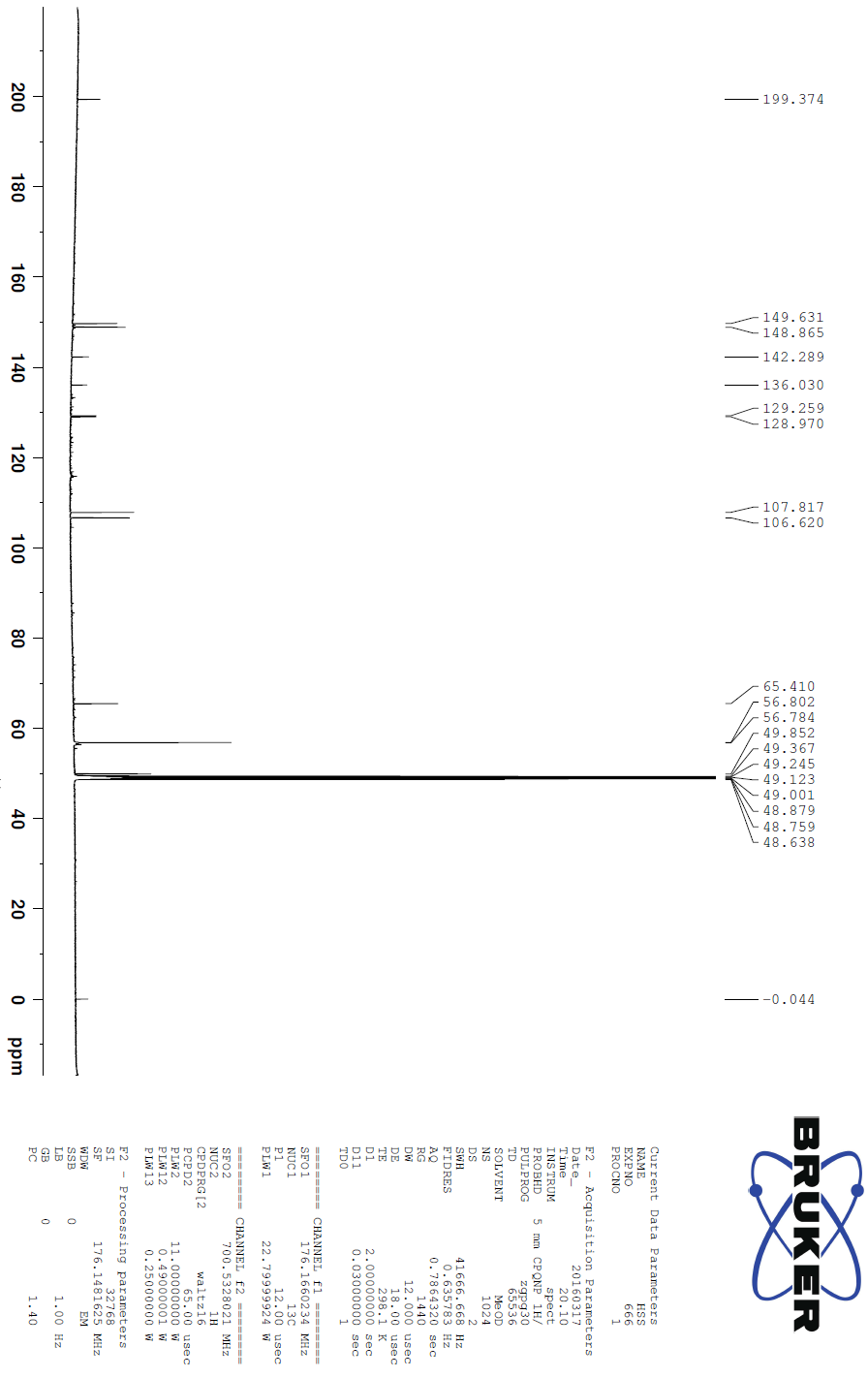
**Figure S8.**

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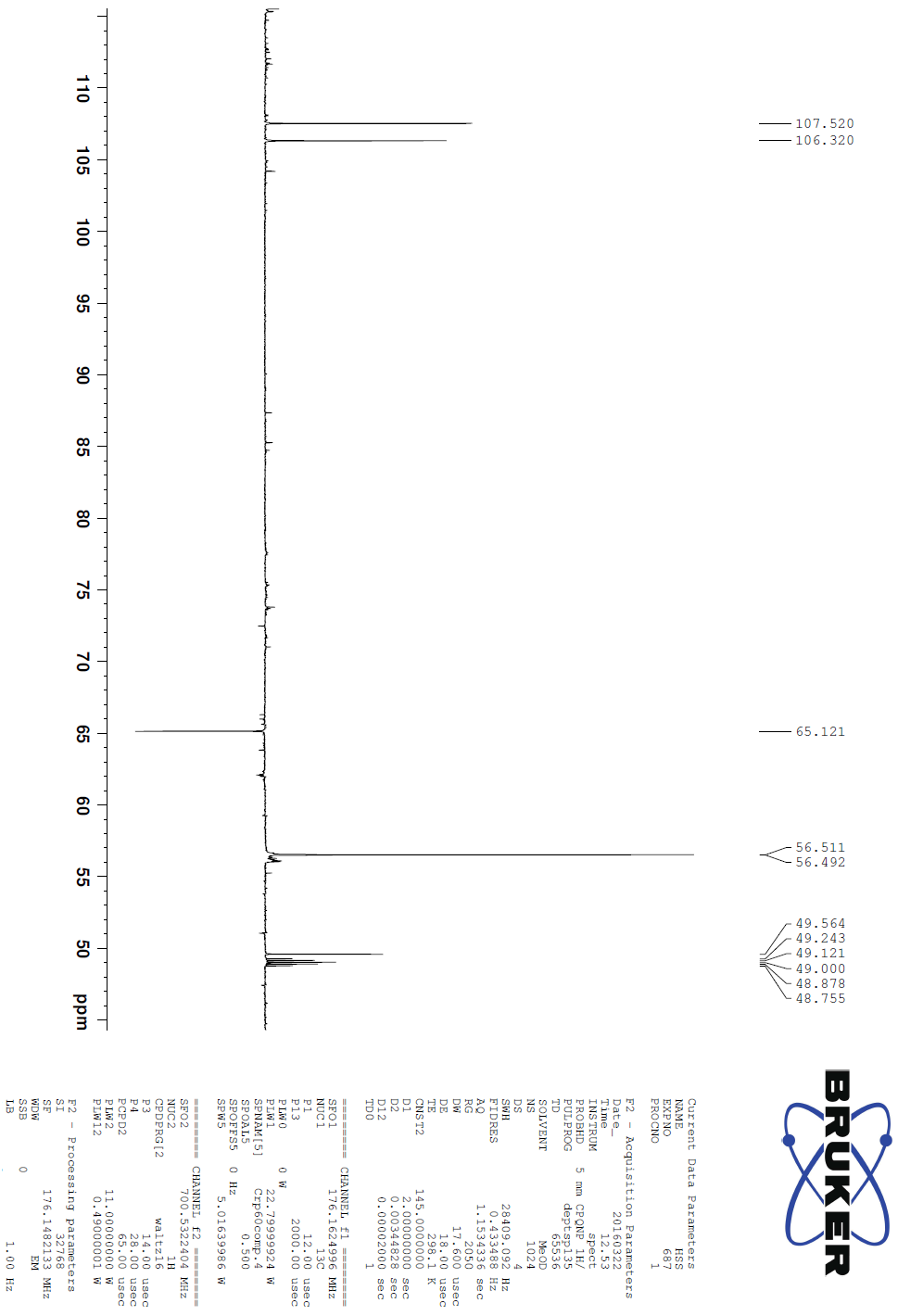
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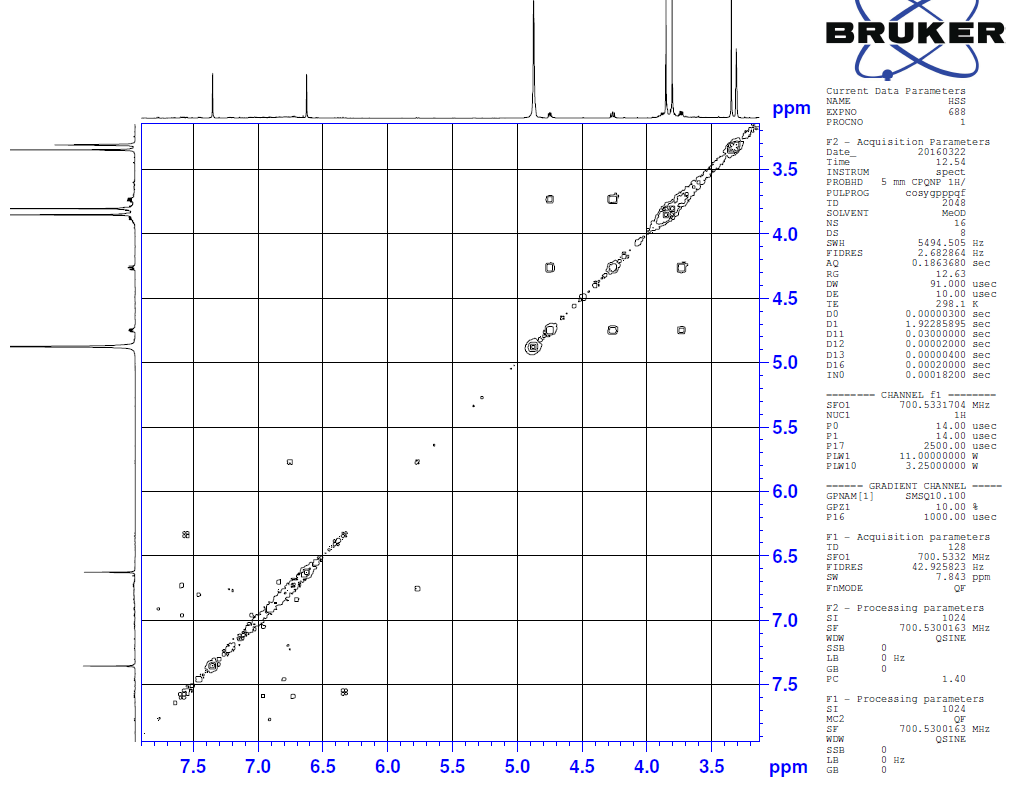
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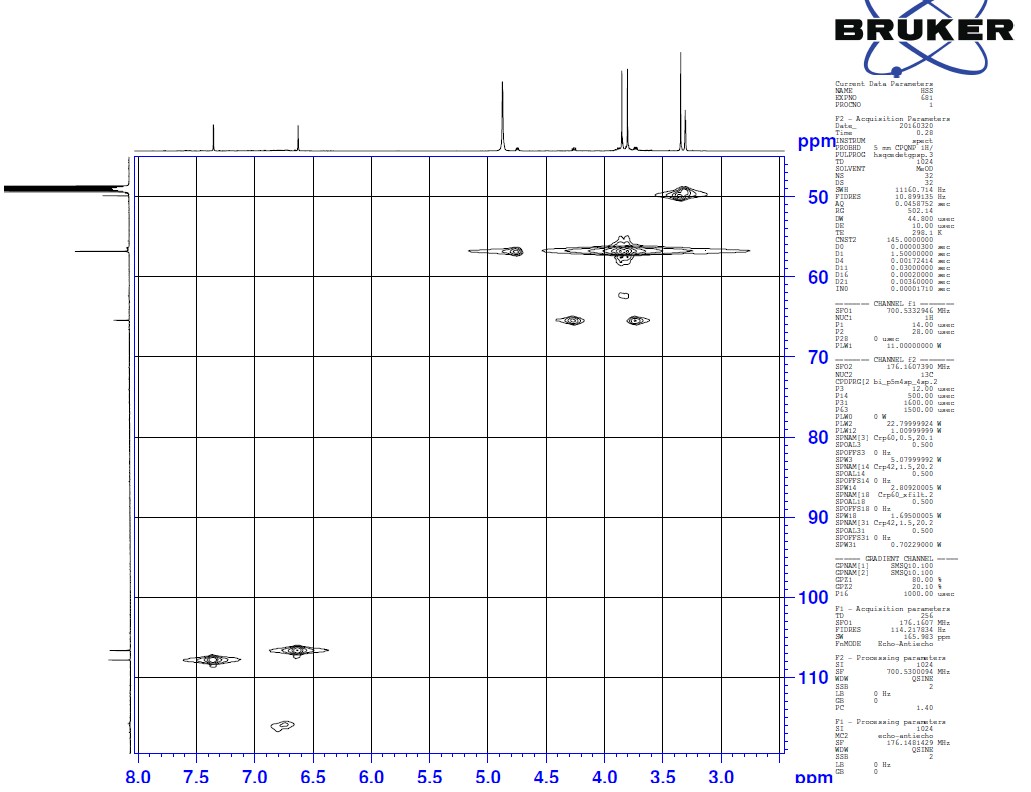
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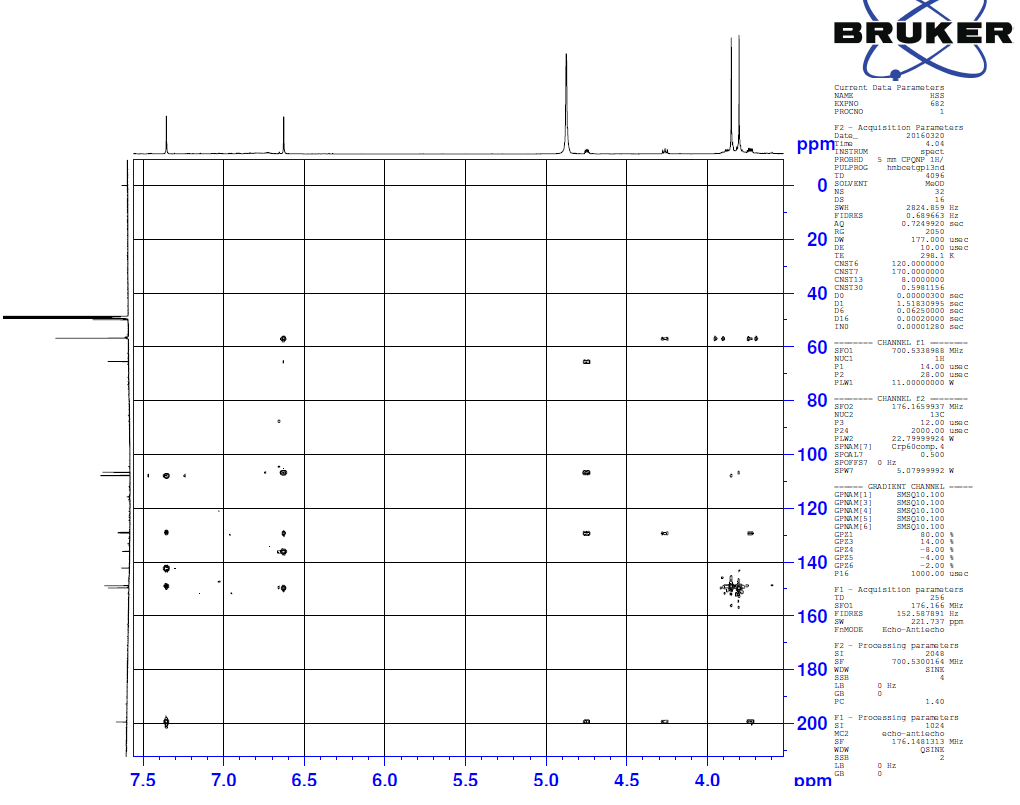
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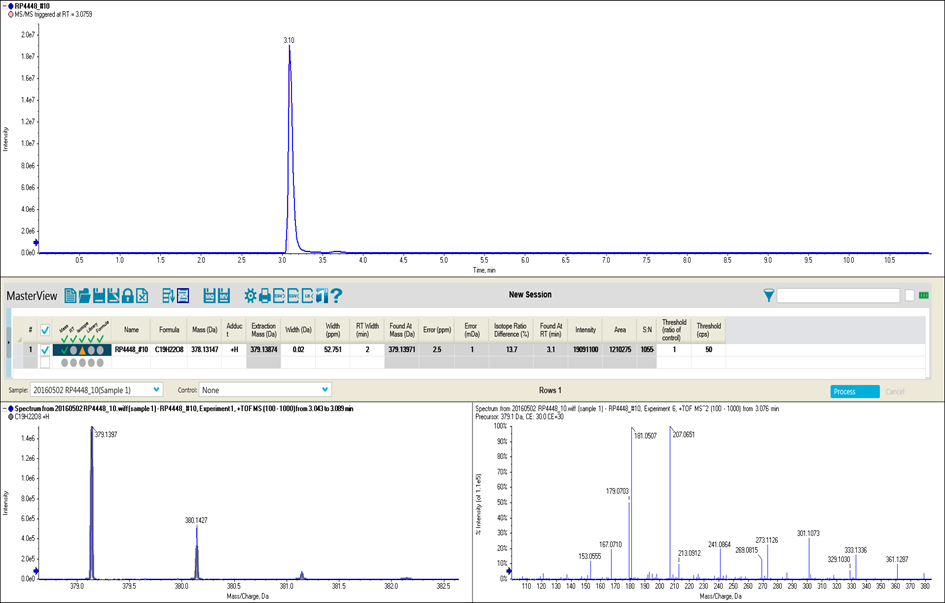
**Figure S13.**



**Figure S14.**



**Figure S15.**

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