

## **Palladium-Catalyzed Asymmetric Intramolecular Dearomative Heck Reaction of Pyrrole Derivatives**

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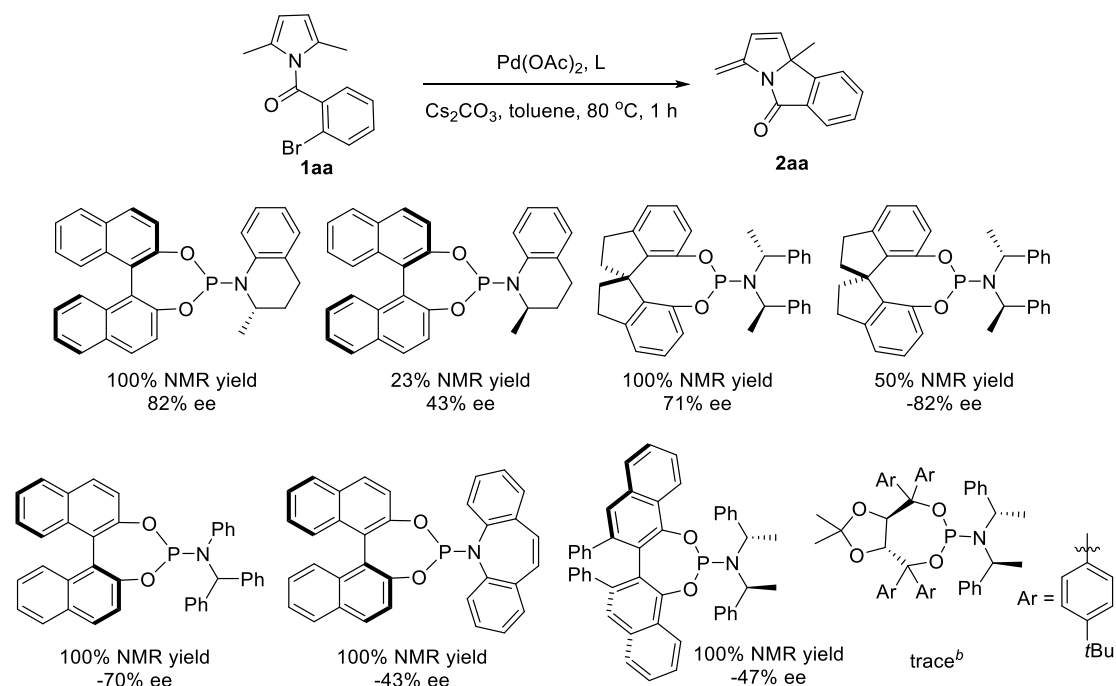
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**General Methods.** Unless stated otherwise, all reactions were carried out in flame-dried glassware under a dry argon atmosphere. All solvents were purified and dried according to standard methods prior to use.  $^1\text{H}$  and  $^{19}\text{F}$  NMR spectra were recorded on a Bruker or Agilent instrument (600 MHz or 400 MHz and 377 MHz, respectively) and internally referenced to tetramethylsilane signal or residual protio solvent signals and  $\text{CFCl}_3$ , respectively.  $^{13}\text{C}$  NMR spectra were recorded on a Bruker (101 MHz) or Agilent instrument (151 MHz or 101 MHz) and internally referenced to residual solvent signals. Data for  $^1\text{H}$  NMR are recorded as follows: chemical shift ( $\delta$ , ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, br = broad singlet, coupling constant (s) in Hz, integration). Data for  $^{13}\text{C}$  NMR and  $^{19}\text{F}$  NMR are reported in terms of chemical shift ( $\delta$ , ppm).

## Screening of chiral ligands.<sup>a</sup>



<sup>a</sup> Reaction conditions: **1aa** (0.2 mmol),  $\text{Pd}(\text{OAc})_2$  (0.01 mmol), ligand (0.024 mmol),  $\text{Cs}_2\text{CO}_3$  (0.24 mmol) in toluene (1.0 mL), 80 °C. <sup>b</sup> 8 h.

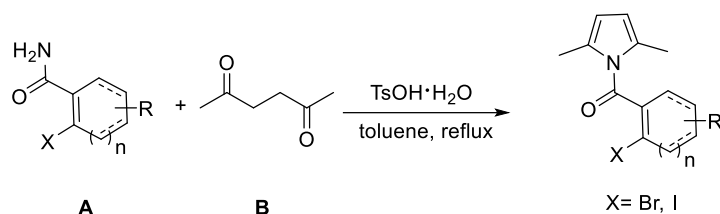
## Screening of palladium precursors.<sup>a</sup>

Reaction scheme showing the conversion of **1aa** to **2aa** using a palladium precursor [Pd] (5 mol %), ligand **L2** (12 mol %),  $\text{Cs}_2\text{CO}_3$ , toluene, 80 °C, t.

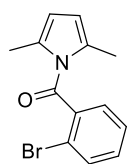
| Entry | [Pd]                                           | t (h) | <b>1aa</b> (%) <sup>b</sup> | <b>2aa</b> (%) <sup>b</sup> | ee (%) |
|-------|------------------------------------------------|-------|-----------------------------|-----------------------------|--------|
| 1     | $\text{Pd}(\text{OAc})_2$                      | 1     | -                           | 100                         | 87     |
| 2     | $\text{Pd}(\text{TFA})_2$                      | 1     | -                           | 98                          | 88     |
| 3     | $\text{Pd}(\text{dba})_2$                      | 5     | -                           | 100                         | 87     |
| 4     | $[\text{Pd}(\text{prenyl})\text{Cl}]_2$        | 5     | -                           | 97                          | 88     |
| 5     | $\text{Pd}(\text{MeCN})_2\text{Cl}_2$          | 6     | 25                          | 72                          | 84     |
| 6     | $[\text{Pd}(\text{C}_3\text{H}_5)\text{Cl}]_2$ | 6     | 5                           | 95                          | 86     |

<sup>a</sup> Reaction conditions: **1aa** (0.2 mmol), [Pd] (0.01 mmol), **L2** (0.024 mmol),  $\text{Cs}_2\text{CO}_3$  (0.24 mmol) in toluene (1.0 mL), 80 °C. <sup>b</sup> NMR yield.

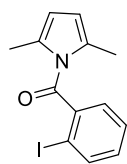
## General procedure for the preparation of pyrrole derivatives (1aa-1ao)



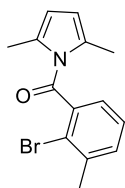
The synthesis of pyrrole derivatives was accomplished following the reported procedures<sup>1-2</sup>. The mixture of bromo- or iodobenzamide **A** (1.0 equiv) and TsOH·H<sub>2</sub>O (1.0 or 2.0 mol%) was dissolved in toluene. Then, 1,4-dione **B** (1.2 equiv) was added dropwise. The solution was heated in a flask equipped with a Dean–Stark apparatus for 5–8 h. After cooling to room temperature, the mixture was concentrated in vacuo. Purification by silica gel column chromatography (PE/EtOAc = 20:1) provided the desired pyrrole derivative.



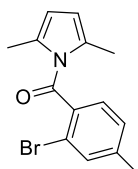
**1aa<sup>2</sup>**: white solid, 2.1 g, 75% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.64 (d, *J* = 7.6 Hz, 1H), 7.44–7.34 (m, 3H), 5.87 (s, 2H), 2.05 (s, 6H).



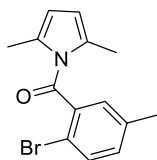
**1aa'**: white solid, 0.8 g, 25% yield, m.p. = 78–81 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.89 (d, *J* = 8.0 Hz, 1H), 7.45–7.37 (m, 2H), 7.19–7.15 (m, 1H), 5.87 (s, 2H), 2.04 (s, 6H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 170.2, 141.9, 140.1, 132.1, 131.0, 129.8, 128.3, 111.9, 93.5, 15.7. IR (film): ν<sub>max</sub> (cm<sup>-1</sup>) = 2919, 1684, 1585, 1539, 1453, 1355, 1315, 1219, 1165, 1022, 974, 904, 773, 734, 680, 597, 440. HRMS (ESI): Exact mass calcd. for C<sub>13</sub>H<sub>13</sub>INO ([M+H]<sup>+</sup>): 326.0036. Found: 326.0028.



**1ab:** white solid, 0.5 g, 17% yield, m.p. = 89-91 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.35 (d,  $J$  = 6.4 Hz, 1H), 7.28 (t,  $J$  = 7.6 Hz, 1H), 7.20 (dd,  $J$  = 7.6, 1.2 Hz, 1H), 5.85 (s, 2H), 2.45 (s, 3H), 2.05 (s, 6H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  169.1, 139.6, 139.1, 132.8, 131.2, 127.4, 127.2, 122.7, 111.8, 23.3, 15.6. IR (film):  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ) = 2923, 2344, 2302, 1684, 1581, 1543, 1449, 1393, 1357, 1322, 1231, 1035, 978, 834, 793, 750, 689, 596, 499. HRMS (ESI): Exact mass calcd. for  $\text{C}_{14}\text{H}_{15}\text{BrNO}$  ( $[\text{M}+\text{H}]^+$ ): 292.0332. Found: 292.0326.

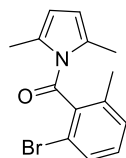


**1ac:** white solid, 3.5 g, 63% yield, m.p. = 93-95 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.46 (s, 1H), 7.31 (d,  $J$  = 7.6 Hz, 1H), 7.19 (dd,  $J$  = 7.6, 0.8 Hz, 1H), 5.85 (s, 2H), 2.39 (s, 3H), 2.05 (s, 6H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  169.0, 143.3, 135.5, 134.1, 131.0, 130.1, 128.4, 120.8, 111.6, 21.3, 15.4. IR (film):  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ) = 2923, 1682, 1596, 1544, 1440, 1360, 1318, 1222, 1046, 972, 909, 820, 785, 717, 669, 600, 523, 457. HRMS (ESI): Exact mass calcd. for  $\text{C}_{14}\text{H}_{15}\text{BrNO}$  ( $[\text{M}+\text{H}]^+$ ): 292.0332. Found: 292.0325.

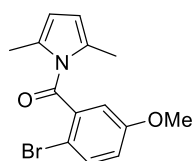


**1ad:** white solid, 0.4 g, 14% yield, m.p. = 86-88 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.46 (d,  $J$  = 8.4 Hz, 1H), 7.21 (d,  $J$  = 1.6 Hz, 1H), 7.13 (dd,  $J$  = 8.0, 1.6 Hz, 1H), 5.84 (s, 2H), 2.31 (s, 3H), 2.05 (s, 6H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  168.8, 138.0, 137.8, 133.2, 133.0, 130.9, 130.3, 117.2, 111.6, 20.7, 15.4. IR (film):  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ) = 2924,

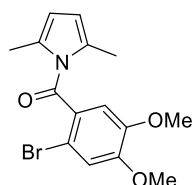
1740, 1683, 1537, 1456, 1390, 1356, 1313, 1261, 1091, 1021, 979, 808, 777, 673, 602, 509, 458. HRMS (ESI): Exact mass calcd. for  $C_{14}H_{15}BrNO$  ( $[M+H]^+$ ): 292.0332. Found: 292.0328.



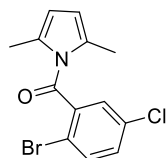
**1ae**: white solid, 0.3 g, 10% yield, m.p. = 87-89 °C.  $^1H$  NMR (600 MHz, DMSO, 80 °C)  $\delta$  7.56-7.55 (m, 1H), 7.36 (s, 1H), 7.35 (d,  $J$  = 1.8 Hz, 1H), 5.93 (s, 2H), 2.19 (s, 3H), 2.01 (s, 6H);  $^{13}C$  NMR (151 MHz, DMSO, 80 °C)  $\delta$  169.0, 139.2, 138.7, 132.8, 131.6, 131.1, 120.6, 113.7, 20.1, 16.3. IR (film):  $\nu_{max}$  ( $cm^{-1}$ ) = 2959, 1684, 1547, 1443, 1355, 1313, 1259, 1219, 1087, 1030, 974, 901, 781, 688, 583, 539, 496. HRMS (ESI): Exact mass calcd. for  $C_{14}H_{15}BrNO$  ( $[M+H]^+$ ): 292.0332. Found: 292.0327.



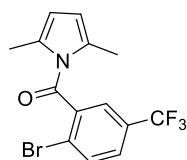
**1af**: white solid, 1.46 g, 25% yield.  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.47 (d,  $J$  = 8.8 Hz, 1H), 6.95 (d,  $J$  = 2.8 Hz, 1H), 6.90 (dd,  $J$  = 8.8, 3.2 Hz, 1H), 5.86 (s, 2H), 3.79 (s, 3H), 2.07 (s, 6H).



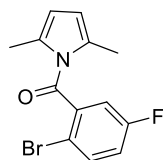
**1ag**: white solid, 0.7 g, 11% yield, m.p. = 107-109 °C.  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.05 (s, 1H), 6.95 (s, 1H), 5.86 (s, 2H), 3.93 (s, 3H), 3.87 (s, 3H), 2.07 (s, 6H);  $^{13}C$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  168.8, 151.7, 148.6, 130.7, 129.9, 115.9, 112.7, 112.5, 111.4, 56.4, 56.3, 15.1. IR (film):  $\nu_{max}$  ( $cm^{-1}$ ) = 2927, 1668, 1593, 1543, 1505, 1445, 1363, 1299, 1256, 1214, 1149, 1023, 983, 848, 784, 641, 602, 548. HRMS (ESI): Exact mass calcd. for  $C_{15}H_{17}BrNO_3$  ( $[M+H]^+$ ): 338.0386. Found: 338.0377.



**1ah**: white solid, 0.3 g, 10% yield, m.p. = 84-86 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.55 (d,  $J$  = 8.4 Hz, 1H), 7.41 (d,  $J$  = 2.4 Hz, 1H), 7.32 (dd,  $J$  = 8.4, 2.4 Hz, 1H), 5.88 (s, 2H), 2.07 (s, 6H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  167.4, 139.7, 134.8, 134.0, 132.2, 131.0, 129.8, 118.6, 112.3, 15.7. IR (film):  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ) = 2920, 1683, 1542, 1449, 1385, 1357, 1314, 1260, 1217, 1167, 1090, 1021, 979, 936, 892, 781, 697, 600, 503, 456. HRMS (ESI): Exact mass calcd. for  $\text{C}_{13}\text{H}_{12}\text{BrClNO}$  ( $[\text{M}+\text{H}]^+$ ): 311.9785. Found: 311.9782.

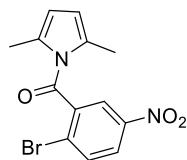


**1ai**: white solid, 0.6 g, 11% yield, m.p. = 84-86 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.78 (d,  $J$  = 8.4 Hz, 1H), 7.69 (d,  $J$  = 2.0 Hz, 1H), 7.61 (dd,  $J$  = 8.4, 2.0 Hz, 1H), 5.89 (s, 2H), 2.05 (s, 6H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  167.3, 139.3, 134.3, 131.0, 130.5 (q,  $J$  = 33.9 Hz), 128.6 (q,  $J$  = 3.6 Hz), 126.8 (q,  $J$  = 3.7 Hz), 124.7 (d,  $J$  = 1.4 Hz), 123.3 (q,  $J$  = 273.8 Hz), 112.6, 15.7;  $^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ )  $\delta$  -62.82 (s). IR (film):  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ) = 2928, 2344, 1687, 1598, 1547, 1417, 1354, 1309, 1221, 1167, 1111, 1073, 1024, 973, 931, 898, 838, 783, 708, 640, 597, 470, 437. HRMS (ESI): Exact mass calcd. for  $\text{C}_{14}\text{H}_{12}\text{BrF}_3\text{NO}$  ( $[\text{M}+\text{H}]^+$ ): 346.0049. Found: 346.0047.

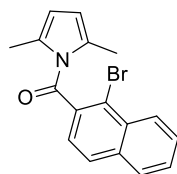


**1aj**: white solid, 0.7 g, 15% yield, m.p. = 62-64 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.58 (dd,  $J$  = 8.8, 4.8 Hz, 1H), 7.16 (dd,  $J$  = 8.0, 2.8 Hz, 1H), 7.11-7.06 (m, 1H), 5.87 (s, 2H), 2.07 (s, 6H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  167.4 (d,  $J$  = 1.8 Hz), 161.7 (d,  $J$  = 251.4 Hz), 139.81 (d,  $J$  = 6.9 Hz), 135.08 (d,  $J$  = 7.8 Hz), 130.9, 119.5 (d,  $J$  = 22.4 Hz), 117.1 (d,  $J$  = 24.4 Hz), 115.0 (d,  $J$  = 3.5 Hz), 112.2, 15.5;  $^{19}\text{F}$  NMR (377 MHz,

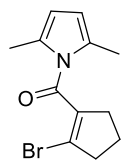
CDCl<sub>3</sub>)  $\delta$  -112.91 (m). IR (film):  $\nu_{\max}$  (cm<sup>-1</sup>) = 2965, 2345, 2302, 1681, 1541, 1462, 1408, 1358, 1318, 1261, 1209, 1089, 1042, 876, 793, 580, 521, 463. HRMS (ESI): Exact mass calcd. for C<sub>13</sub>H<sub>12</sub>BrFNO ([M+H]<sup>+</sup>): 296.0081. Found: 296.0077.



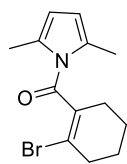
**1ak**: yellow solid, 1.2 g, 21% yield, m.p. = 117-119 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.28 (d, *J* = 2.0 Hz, 1H), 8.20 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.86 (d, *J* = 8.8 Hz, 1H), 5.91 (s, 2H), 2.06 (s, 6H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  166.4, 147.2, 139.8, 134.9, 130.9, 127.9, 126.3, 124.7, 112.9, 15.9. IR (film):  $\nu_{\max}$  (cm<sup>-1</sup>) = 2919, 1685, 1599, 1525, 1445, 1403, 1353, 1320, 1216, 1096, 1043, 977, 914, 841, 793, 734, 694, 600, 486, 451. HRMS (ESI): Exact mass calcd. for C<sub>13</sub>H<sub>12</sub>BrN<sub>2</sub>O<sub>3</sub> ([M+H]<sup>+</sup>): 323.0026. Found: 323.0026.



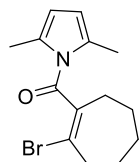
**1al**: white solid, 0.4 g, 6% yield, m.p. = 109-110 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.36 (d, *J* = 8.4 Hz, 1H), 7.88 (t, *J* = 7.6 Hz, 2H), 7.68-7.59 (m, 2H), 7.44 (d, *J* = 8.0 Hz, 1H), 5.88 (s, 2H), 2.05 (s, 6H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  169.4, 136.3, 134.9, 132.0, 131.2, 128.59, 128.55, 128.48, 128.37, 128.1, 125.3, 121.7, 112.0, 15.8. IR (film):  $\nu_{\max}$  (cm<sup>-1</sup>) = 2962, 1685, 1546, 1455, 1361, 1304, 1256, 1219, 1090, 1038, 926, 869, 790, 749, 569, 528. HRMS (ESI): Exact mass calcd. for C<sub>17</sub>H<sub>15</sub>BrNO ([M+H]<sup>+</sup>): 328.0332. Found: 328.0328.



**1am**<sup>2</sup>: white solid, 1.2 g, 32% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  5.82 (s, 2H), 2.82-2.74 (m, 4H), 2.25 (s, 6H), 2.11-2.03 (m, 2H).

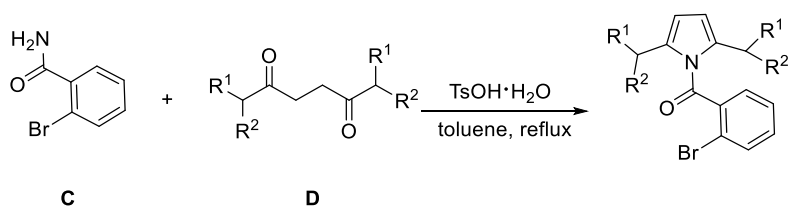


**1an<sup>2</sup>**: white solid, 0.3 g, 11% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 5.83 (s, 2H), 2.57-2.56 (m, 2H), 2.43-2.42 (m, 2H), 2.32 (s, 6H), 1.77-1.76 (m, 4H).

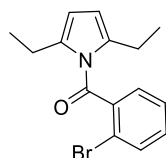


**1ao<sup>2</sup>**: white solid, 1.0 g, 48% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 5.82 (s, 2H), 2.84-2.81 (m, 2H), 2.46-2.44 (m, 2H), 2.31 (s, 6H), 1.80-1.76 (m, 4H), 1.69-1.66 (m, 2H).

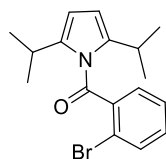
## General procedure for the preparation of pyrrole derivatives (1ba-1da)



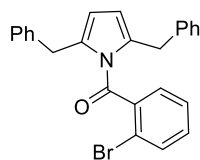
The mixture of 2-bromobenzamide **C** (1.0 equiv), 1,4-dione **D** (1.2 equiv) and TsOH·H<sub>2</sub>O (2.0 mol%) was dissolved in toluene. The solution was heated in a flask equipped with a Dean–Stark apparatus for 5–8 h. After cooling to room temperature, the mixture was concentrated in vacuo. Purification by silica gel column chromatography (PE/EtOAc = 20:1) provided the desired pyrrole derivative.



**1ba**: yellow oil, 0.9 g, 15% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.65–7.63 (m, 1H), 7.42–7.36 (m, 3H), 5.94 (s, 2H), 2.37 (q, *J* = 7.2 Hz, 4H), 1.12 (t, *J* = 7.2 Hz, 6H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 169.2, 138.2, 137.7, 133.9, 132.5, 130.6, 127.6, 121.2, 109.5, 22.1, 13.4. IR (film):  $\nu_{\text{max}}$  (cm<sup>-1</sup>) = 2969, 1690, 1587, 1534, 1433, 1378, 1313, 1203, 1156, 1021, 941, 903, 775, 741, 690, 643, 608, 456. HRMS (ESI): Exact mass calcd. for C<sub>15</sub>H<sub>17</sub>BrNO ([M+H]<sup>+</sup>): 306.0488. Found: 306.0482.

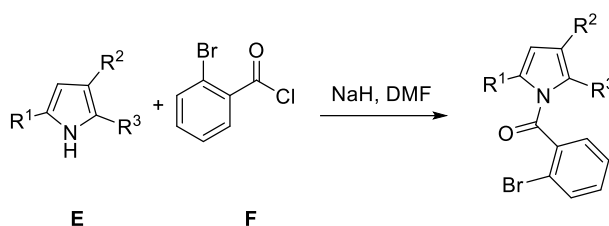


**1ca**: yellow oil, 0.2 g, 14% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.69–7.67 (m, 1H), 7.39–7.36 (m, 3H), 5.97 (s, 2H), 2.77–2.67 (m, 2H), 1.11 (s, 12H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 169.6, 142.7, 137.0, 134.6, 133.1, 131.8, 127.5, 122.2, 107.1, 26.6, 23.4. IR (film):  $\nu_{\text{max}}$  (cm<sup>-1</sup>) = 2964, 2927, 2870, 1694, 1584, 1521, 1461, 1387, 1307, 1264, 1202, 1026, 973, 911, 871, 783, 742, 686, 624, 526, 467. HRMS (ESI): Exact mass calcd. for C<sub>17</sub>H<sub>21</sub>BrNO ([M+H]<sup>+</sup>): 334.0801. Found: 334.0799.

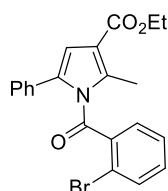


**1da**: yellow oil, 0.22 g, 25% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.56 (d,  $J$  = 8.0 Hz, 1H), 7.29 (dd,  $J$  = 7.6, 1.6 Hz, 1H), 7.24-7.14 (m, 7H), 7.02 (d,  $J$  = 6.8 Hz, 4H), 6.95 (dd,  $J$  = 7.6, 1.6 Hz, 1H), 5.79 (s, 2H), 3.75 (s, 4H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  168.8, 139.1, 137.3, 134.9, 133.6, 132.6, 130.9, 129.0, 128.4, 127.3, 126.4, 121.3, 112.9, 35.1. IR (film):  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ) = 3028, 2918, 2344, 1694, 1591, 1527, 1494, 1429, 1384, 1310, 1269, 1183, 1147, 1079, 1024, 915, 779, 700, 639, 465. HRMS (ESI): Exact mass calcd. for  $\text{C}_{25}\text{H}_{24}\text{BrN}_2\text{O}$  ( $[\text{M}+\text{NH}_4]^+$ ): 447.1067. Found: 447.1056.

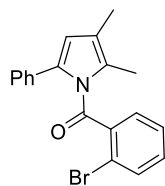
## General procedure for the preparation of pyrrole derivatives (1ea-1ga)



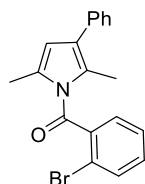
Substituted pyrrole **E** (1.0 equiv) was dissolved in DMF (0.5 M) at 0 °C. Sodium hydride (1.5 equiv) was added carefully. After 30 mins, 2-bromobenzoyl chloride **F** (1.5 equiv) was added dropwise. Then the reaction mixture was stirred at room temperature. After completion (monitored by TLC), the reaction mixture was quenched with saturated aqueous NH<sub>4</sub>Cl (10 mL) and the mixture was diluted with H<sub>2</sub>O (20 mL) and extracted with ethyl acetate (50 mL x 3). The combined ethyl acetate extract was washed with H<sub>2</sub>O (50 mL x 4), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and filtrated. After the solvent was concentrated under reduced pressure, the crude product was purified by silica gel column chromatography (PE/EtOAc = 20:1) to afford the desired product.



**1ea**: yellow solid, 1.1 g, 31% yield, m.p. = 89-91 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.35-7.33 (m, 1H), 7.13-7.04 (m, 8H), 6.63 (s, 1H), 4.33 (q, *J* = 7.2 Hz, 2H), 2.76 (s, 3H), 1.38 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 169.3, 165.1, 139.7, 136.0, 134.4, 133.8, 133.0, 132.5, 131.9, 128.2, 128.1, 127.4, 126.9, 122.2, 115.5, 112.9, 60.1, 14.5, 13.0. IR (film): ν<sub>max</sub> (cm<sup>-1</sup>) = 2959, 2322, 1687, 1579, 1540, 1433, 1392, 1358, 1317, 1224, 1169, 1024, 977, 909, 831, 752, 692, 602, 456. HRMS (ESI): Exact mass calcd. for C<sub>21</sub>H<sub>19</sub>BrNO<sub>3</sub> ([M+H]<sup>+</sup>): 412.0543. Found: 412.0535.

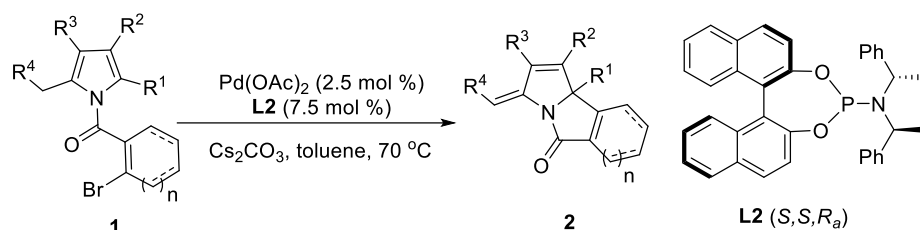


**1fa:** yellow oil, 0.8 g, 32% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.30 (dd,  $J = 7.2, 2.0$  Hz, 1H), 7.13-6.98 (m, 8H), 6.08 (s, 1H), 2.35 (s, 3H), 2.07 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  169.2, 137.4, 134.2, 133.7, 133.5, 132.1, 131.5, 129.6, 128.3, 127.8, 126.7, 126.6, 122.1, 119.1, 116.1, 12.2, 11.2. IR (film):  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ) = 2920, 1691, 1591, 1532, 1435, 1306, 1104, 1026, 909, 809, 750, 694, 633, 537, 459. HRMS (ESI): Exact mass calcd. for  $\text{C}_{19}\text{H}_{17}\text{BrNO}$  ( $[\text{M}+\text{H}]^+$ ): 354.0488. Found: 354.0481.

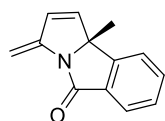


**1ga:** yellow solid, 1.6 g, 71% yield, m.p. = 64-66 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.67 (dd,  $J = 7.6, 1.2$  Hz, 1H), 7.50 (dd,  $J = 7.2, 2.0$  Hz, 1H), 7.45-7.34 (m, 6H), 7.26 (s, 1H), 6.10 (d,  $J = 0.8$  Hz, 1H), 2.14 (s, 3H), 2.10 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  168.9, 138.4, 135.6, 133.8, 132.5, 130.6, 130.5, 128.7, 128.5, 127.7, 126.5, 126.33, 126.26, 121.2, 113.4, 15.3, 14.1. IR (film):  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ) = 2922, 1689, 1588, 1547, 1433, 1394, 1326, 1192, 1122, 1038, 983, 916, 823, 764, 734, 692, 596, 534, 458. HRMS (ESI): Exact mass calcd. for  $\text{C}_{19}\text{H}_{17}\text{BrNO}$  ( $[\text{M}+\text{H}]^+$ ): 354.0488. Found: 354.0484.

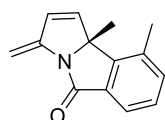
## General procedure for palladium-catalyzed dearomatization reaction



A flame-dried Schlenk tube was cooled to room temperature under argon. To this tube were added **1** (0.2 mmol), Pd(OAc)<sub>2</sub> (1.1 mg, 0.005 mmol), (S,S,R<sub>a</sub>)-**L2** (8.1 mg, 0.015 mmol), Cs<sub>2</sub>CO<sub>3</sub> (78.2 mg, 0.24 mmol) and toluene (1.0 mL). Then the reaction mixture was stirred at 70 °C. After completion (monitored by TLC), the reaction mixture was cooled to room temperature and diluted with ethyl acetate (3 mL). The mixture was filtered through celite, and the filtrate was concentrated under reduced pressure. The crude product was purified by silica gel column chromatography (PE/EtOAc = 20/1) to afford the desired product **2**.

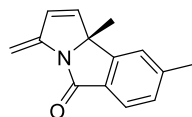


**2aa**<sup>2</sup>: white solid, 39.0 mg, 99% yield, 89% ee. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.83 (d, *J* = 7.6 Hz, 1H), 7.58 (td, *J* = 7.6, 0.8 Hz, 1H), 7.47-7.43 (m, 2H), 6.37 (dd, *J* = 5.6, 0.8 Hz, 1H), 6.11 (d, *J* = 5.6 Hz, 1H), 5.37 (s, 1H), 4.80 (s, 1H), 1.61 (s, 3H). [Daicel Chiralcel OD-H, *n*-hexane/2-propanol = 95/5, *v* = 1.0 mL·min<sup>-1</sup>, λ = 254 nm, *t* (major) = 7.94 min, *t* (minor) = 9.25 min]; [α]<sub>D</sub><sup>28</sup> = +62.6 (*c* = 0.5, CHCl<sub>3</sub>).

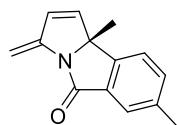


**2ab**: white solid, 41 mg, 97% yield, m.p. = 130-132 °C, 84% ee. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.67 (dd, *J* = 5.6, 2.8 Hz, 1H), 7.37-7.32 (m, 2H), 6.52 (d, *J* = 5.6 Hz, 1H), 6.13 (d, *J* = 5.6 Hz, 1H), 5.37 (s, 1H), 4.77 (s, 1H), 2.49 (s, 3H), 1.65 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 171.0, 149.0, 145.4, 134.82, 134.81, 132.6, 132.0, 130.0, 128.9, 122.8, 95.9, 77.5, 26.9, 18.4. IR (film): *v*<sub>max</sub> (cm<sup>-1</sup>) = 2925, 1769, 1688, 1604, 1480, 1449, 1326, 1190, 1154, 1119, 1080, 1035, 946, 836, 762, 566, 470. HRMS

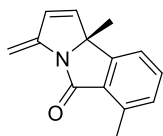
(ESI): Exact mass calcd. for  $C_{14}H_{14}NO$  ( $[M+H]^+$ ): 212.1070. Found: 212.1062. [Daicel Chiralcel OJ-H, *n*-hexane/2-propanol = 95/5,  $v = 1.0 \text{ mL} \cdot \text{min}^{-1}$ ,  $\lambda = 254 \text{ nm}$ ,  $t$  (major) = 9.84 min,  $t$  (minor) = 14.35 min];  $[\alpha]_D^{29} = +33.4$  ( $c = 0.5$ ,  $CHCl_3$ ).



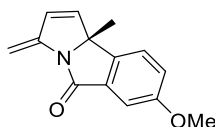
**2ac**: white solid, 40.3 mg, 95% yield, m.p. = 128-130 °C, 91% ee.  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.70 (d,  $J = 7.6 \text{ Hz}$ , 1H), 7.27-7.23 (m, 2H), 6.34 (d,  $J = 6.0 \text{ Hz}$ , 1H), 6.09 (d,  $J = 5.6 \text{ Hz}$ , 1H), 5.35 (s, 1H), 4.77 (s, 1H), 2.46 (s, 3H), 1.59 (s, 3H);  $^{13}C$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  171.6, 151.5, 146.3, 144.1, 136.3, 129.8, 129.6, 129.4, 125.0, 122.2, 96.2, 77.1, 28.4, 22.1. IR (film):  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ) = 2976, 1694, 1620, 1440, 1317, 1232, 1150, 1117, 939, 837, 776, 728, 686, 645, 526, 434. HRMS (ESI): Exact mass calcd. for  $C_{14}H_{14}NO$  ( $[M+H]^+$ ): 212.1070. Found: 212.1063. [Daicel Chiralcel OD-H, *n*-hexane/2-propanol = 95/5,  $v = 1.0 \text{ mL} \cdot \text{min}^{-1}$ ,  $\lambda = 254 \text{ nm}$ ,  $t$  (major) = 7.86 min,  $t$  (minor) = 9.56 min];  $[\alpha]_D^{29} = +62.6$  ( $c = 0.5$ ,  $CHCl_3$ ).



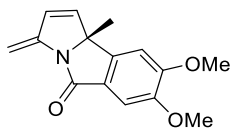
**2ad**: white solid, 40.2 mg, 95% yield, m.p. = 75-78 °C, 90% ee.  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.62 (s, 1H), 7.39 (d,  $J = 8.0 \text{ Hz}$ , 1H), 7.31 (d,  $J = 8.0 \text{ Hz}$ , 1H), 6.35 (d,  $J = 6.0 \text{ Hz}$ , 1H), 6.09 (d,  $J = 6.0 \text{ Hz}$ , 1H), 5.35 (s, 1H), 4.78 (s, 1H), 2.42 (s, 3H), 1.58 (s, 3H);  $^{13}C$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  171.6, 148.4, 146.2, 138.8, 136.5, 134.2, 132.2, 129.6, 125.3, 121.5, 96.3, 77.1, 28.4, 21.3. IR (film):  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ) = 2923, 2322, 1770, 1701, 1628, 1531, 1490, 1433, 1319, 1227, 1127, 1074, 1026, 828, 782, 731, 681, 642, 568. HRMS (ESI): Exact mass calcd. for  $C_{14}H_{14}NO$  ( $[M+H]^+$ ): 212.1070. Found: 212.1068. [Daicel Chiralcel OD-H, *n*-hexane/2-propanol = 99/1,  $v = 1.0 \text{ mL} \cdot \text{min}^{-1}$ ,  $\lambda = 254 \text{ nm}$ ,  $t$  (major) = 13.19 min,  $t$  (minor) = 15.54 min];  $[\alpha]_D^{29} = +32.7$  ( $c = 0.5$ ,  $CHCl_3$ ).



**2ae**: white solid, 38.1 mg, 91% yield, m.p. = 98-100 °C, 81% ee.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.43 (t,  $J$  = 7.2 Hz, 1H), 7.23 (d,  $J$  = 7.6 Hz, 1H), 7.18 (d,  $J$  = 7.2 Hz, 1H), 6.34 (d,  $J$  = 5.2 Hz, 1H), 6.09 (d,  $J$  = 5.6 Hz, 1H), 5.34 (s, 1H), 4.78 (s, 1H), 2.69 (s, 3H), 1.58 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  172.4, 151.7, 146.5, 139.7, 136.6, 132.8, 130.7, 129.6, 129.0, 119.2, 96.2, 76.4, 28.5, 17.9. IR (film):  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ) = 2922, 1768, 1692, 1634, 1598, 1478, 1422, 1318, 1271, 1229, 1178, 1126, 1096, 1036, 836, 784, 686, 466. HRMS (ESI): Exact mass calcd. for  $\text{C}_{14}\text{H}_{14}\text{NO}$  ( $[\text{M}+\text{H}]^+$ ): 212.1070. Found: 212.1065. [Daicel Chiralcel OD-H, *n*-hexane/2-propanol = 99/1,  $\nu$  = 1.0  $\text{mL}\cdot\text{min}^{-1}$ ,  $\lambda$  = 254 nm,  $t$  (major) = 8.66 min,  $t$  (minor) = 10.59 min];  $[\alpha]_{\text{D}}^{28}$  = -18.7 ( $c$  = 0.5,  $\text{CHCl}_3$ ).

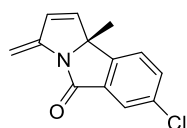


**2af<sup>2</sup>**: white solid, 40.3 mg, 89% yield, 84% ee.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.32 (d,  $J$  = 8.4 Hz, 1H), 7.29 (d,  $J$  = 2.4 Hz, 1H), 7.13 (dd,  $J$  = 8.4, 2.4 Hz, 1H), 6.35 (d,  $J$  = 5.2 Hz, 1H), 6.09 (d,  $J$  = 6.0 Hz, 1H), 5.35 (s, 1H), 4.79 (s, 1H), 3.85 (s, 3H), 1.58 (s, 3H). [Daicel Chiralcel OD-H, *n*-hexane/2-propanol = 99/1,  $\nu$  = 1.0  $\text{mL}\cdot\text{min}^{-1}$ ,  $\lambda$  = 254 nm,  $t$  (major) = 18.51 min,  $t$  (minor) = 22.59 min];  $[\alpha]_{\text{D}}^{24}$  = +33.3 ( $c$  = 0.5,  $\text{CHCl}_3$ ).

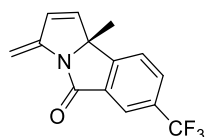


**2ag**: white oil, 49.6 mg, 96% yield, 82% ee.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.26 (s, 1H), 6.87 (s, 1H), 6.34 (d,  $J$  = 5.6 Hz, 1H), 6.09 (d,  $J$  = 5.6 Hz, 1H), 5.32 (s, 1H), 4.75 (s, 1H), 3.99 (s, 3H), 3.92 (s, 3H), 1.59 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  171.9, 153.9, 150.1, 146.4, 145.4, 136.3, 129.6, 123.8, 106.2, 103.5, 95.9, 76.9, 56.37, 56.30, 28.2. IR (film):  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ) = 2925, 2344, 2302, 1687, 1602, 1497, 1461, 1306, 1210,

1146, 1114, 1037, 983, 839, 772, 729, 645, 464. HRMS (ESI): Exact mass calcd. for  $C_{15}H_{16}NO_3$  ( $[M+H]^+$ ): 258.1125 Found: 258.1117. [Daicel Chiralcel OJ-H, *n*-hexane/2-propanol = 90/10,  $\nu = 1.0 \text{ mL} \cdot \text{min}^{-1}$ ,  $\lambda = 254 \text{ nm}$ ,  $t$  (major) = 22.93 min,  $t$  (minor) = 53.58 min];  $[\alpha]_D^{27} = +64.9$  ( $c = 0.5$ ,  $CHCl_3$ ).

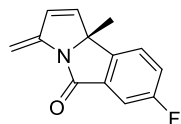


**2ah**: white solid, 32.9 mg, 71% yield, m.p. = 138-140 °C, 87% ee.  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.79 (s, 1H), 7.54 (d,  $J = 8.0 \text{ Hz}$ , 1H), 7.37 (d,  $J = 8.0 \text{ Hz}$ , 1H), 6.34 (d,  $J = 5.2 \text{ Hz}$ , 1H), 6.12 (d,  $J = 5.6 \text{ Hz}$ , 1H), 5.37 (s, 1H), 4.82 (s, 1H), 1.60 (s, 3H);  $^{13}C$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  169.9, 149.1, 145.8, 135.8, 135.0, 133.9, 133.3, 130.0, 125.2, 123.0, 97.1, 77.0, 28.4. IR (film):  $\nu_{max} (\text{cm}^{-1}) = 2922, 2326, 1693, 1639, 1464, 1420, 1319, 1258, 1231, 1179, 1114, 1071, 829, 788, 747, 692, 563$ . HRMS (ESI): Exact mass calcd. for  $C_{13}H_{11}ClNO$  ( $[M+H]^+$ ): 232.0524. Found: 232.0522. [Daicel Chiralcel OJ-H, *n*-hexane/2-propanol = 99/1,  $\nu = 1.0 \text{ mL} \cdot \text{min}^{-1}$ ,  $\lambda = 254 \text{ nm}$ ,  $t$  (major) = 15.10 min,  $t$  (minor) = 18.43 min];  $[\alpha]_D^{29} = +16.1$  ( $c = 0.5$ ,  $CHCl_3$ ).

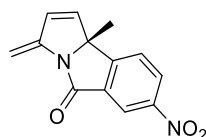


**2ai**: white solid, 45.2 mg, 85% yield, m.p. = 108-110 °C, 85% ee.  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  8.10 (s, 1H), 7.84 (d,  $J = 8.0 \text{ Hz}$ , 1H), 7.59 (d,  $J = 8.0 \text{ Hz}$ , 1H), 6.39 (d,  $J = 5.6 \text{ Hz}$ , 1H), 6.16 (d,  $J = 5.6 \text{ Hz}$ , 1H), 5.41 (d,  $J = 0.4 \text{ Hz}$ , 1H), 4.86 (s, 1H), 1.64 (s, 3H);  $^{13}C$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  169.8, 154.1, 145.7, 135.4, 133.0, 131.6 (q,  $J = 33.2 \text{ Hz}$ ), 130.4, 130.0 (q,  $J = 3.5 \text{ Hz}$ ), 123.7 (q,  $J = 273.6 \text{ Hz}$ ), 122.57 (q,  $J = 3.8 \text{ Hz}$ ), 122.55, 97.5, 77.3, 28.3;  $^{19}F$  NMR (377 MHz,  $CDCl_3$ )  $\delta$  -62.44 (s). IR (film):  $\nu_{max} (\text{cm}^{-1}) = 3064, 1707, 1626, 1578, 1437, 1316, 1268, 1231, 1170, 1113, 1062, 938, 838, 780, 727, 672, 631, 543$ . HRMS (ESI): Exact mass calcd. for  $C_{14}H_{11}F_3NO$  ( $[M+H]^+$ ): 266.0787. Found: 266.0781. [Daicel Chiralcel OJ-H, *n*-hexane/2-propanol = 99/1,  $\nu =$

1.0 mL·min<sup>-1</sup>,  $\lambda$  = 254 nm, t (major) = 10.42 min, t (minor) = 12.39 min];  $[\alpha]_D^{25}$  = +10.8 (c = 0.5, CHCl<sub>3</sub>).

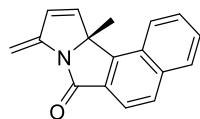


**2aj**: white solid, 30.1 mg, 70% yield, m.p. = 130-132 °C, 88% ee. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.48 (d,  $J$  = 7.2 Hz, 1H), 7.41 (dd,  $J$  = 8.0, 4.4 Hz, 1H), 7.30-7.26 (m, 1H), 6.36 (d,  $J$  = 5.6 Hz, 1H), 6.12 (d,  $J$  = 5.6 Hz, 1H), 5.37 (s, 1H), 4.82 (s, 1H), 1.60 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  170.2, 163.1 (d,  $J$  = 249.4 Hz), 146.6, 145.9, 136.1, 134.2 (d,  $J$  = 8.4 Hz), 129.9, 123.3 (d,  $J$  = 8.4 Hz), 120.7 (d,  $J$  = 23.8 Hz), 111.7 (d,  $J$  = 23.3 Hz), 97.0, 76.9, 28.5; <sup>19</sup>F NMR (377 MHz, CDCl<sub>3</sub>)  $\delta$  -112.42 (m). IR (film):  $\nu_{\max}$  (cm<sup>-1</sup>) = 1774, 1701, 1630, 1483, 1438, 1321, 1263, 1217, 1160, 1123, 1083, 1036, 937, 835, 781, 682, 643, 575. HRMS (ESI): Exact mass calcd. for C<sub>13</sub>H<sub>11</sub>FNO ([M+H]<sup>+</sup>): 216.0819. Found: 216.0817. [Daicel Chiralcel OD-H, *n*-hexane/2-propanol = 99/1,  $\nu$  = 1.0 mL·min<sup>-1</sup>,  $\lambda$  = 254 nm, t (major) = 11.03 min, t (minor) = 12.36 min];  $[\alpha]_D^{29}$  = +11.1 (c = 0.5, CHCl<sub>3</sub>).

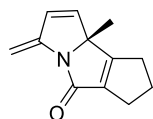


**2ak**: white solid, 9.0 mg, 19% yield, m.p. = 136-138 °C, 89% ee. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.66 (d,  $J$  = 2.0 Hz, 1H), 8.47 (dd,  $J$  = 8.0, 2.0 Hz, 1H), 7.63 (d,  $J$  = 8.0 Hz, 1H), 6.39 (d,  $J$  = 6.0 Hz, 1H), 6.19 (d,  $J$  = 5.6 Hz, 1H), 5.44 (s, 1H), 4.90 (s, 1H), 1.66 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  168.8, 156.4, 148.9, 145.4, 134.8, 134.0, 130.8, 128.1, 122.9, 120.9, 98.2, 77.3, 28.4. IR (film):  $\nu_{\max}$  (cm<sup>-1</sup>) = 2922, 2323, 1710, 1613, 1526, 1435, 1321, 1229, 1159, 1119, 1073, 1034, 943, 908, 850, 787, 730, 677, 642, 563, 483. HRMS (ESI): Exact mass calcd. for C<sub>13</sub>H<sub>11</sub>N<sub>2</sub>O<sub>3</sub> ([M+H]<sup>+</sup>): 243.0764. Found: 243.0762. [Daicel Chiralcel OD-H, *n*-hexane/2-propanol = 95/5,  $\nu$  = 1.0

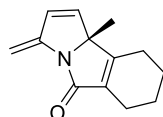
$\text{mL}\cdot\text{min}^{-1}$ ,  $\lambda = 254 \text{ nm}$ ,  $t$  (minor) = 25.68 min,  $t$  (major) = 29.68 min];  $[\alpha]_{\text{D}}^{27} = +25.1$  ( $c = 0.2$ ,  $\text{CHCl}_3$ ).



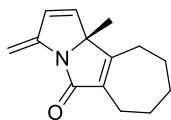
**2a1**: yellow oil, 44.0 mg, 89% yield, 79% ee.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.04-7.98 (m, 2H), 7.91 (d,  $J = 8.4 \text{ Hz}$ , 1H), 7.85 (d,  $J = 8.4 \text{ Hz}$ , 1H), 7.68-7.63 (m, 2H), 6.70 (d,  $J = 5.2 \text{ Hz}$ , 1H), 6.19 (d,  $J = 6.0 \text{ Hz}$ , 1H), 5.42 (s, 1H), 4.81 (s, 1H), 1.83 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  171.6, 149.9, 145.3, 136.3, 135.5, 130.3, 130.0, 129.72, 129.70, 128.2, 127.4, 127.2, 124.2, 120.9, 95.9, 77.8, 28.6. IR (film):  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ) = 1770, 1678, 1450, 1324, 1112, 831, 759, 729, 563. HRMS (ESI): Exact mass calcd. for  $\text{C}_{17}\text{H}_{14}\text{NO}$  ( $[\text{M}+\text{H}]^+$ ): 248.1070. Found: 248.1061. [Daicel Chiralcel OD-H,  $n$ -hexane/2-propanol = 99/1,  $\nu = 1.0 \text{ mL}\cdot\text{min}^{-1}$ ,  $\lambda = 254 \text{ nm}$ ,  $t$  (major) = 19.67 min,  $t$  (minor) = 23.98 min];  $[\alpha]_{\text{D}}^{31} = +109.8$  ( $c = 0.5$ ,  $\text{CHCl}_3$ ).



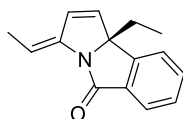
**2am<sup>2</sup>**: white solid, 36.4 mg, 97% yield, 91% ee.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.11 (d,  $J = 5.6 \text{ Hz}$ , 1H), 6.06 (d,  $J = 5.6 \text{ Hz}$ , 1H), 5.12 (s, 1H), 4.62 (s, 1H), 2.54-2.33 (m, 6H), 1.44 (s, 3H). [Daicel Chiralpak AD-H,  $n$ -hexane/2-propanol = 99/1,  $\nu = 1.0 \text{ mL}\cdot\text{min}^{-1}$ ,  $\lambda = 254 \text{ nm}$ ,  $t$  (minor) = 15.80 min,  $t$  (major) = 18.33 min];  $[\alpha]_{\text{D}}^{29} = +56.4$  ( $c = 0.5$ ,  $\text{CHCl}_3$ ).



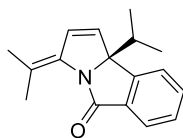
**2an<sup>2</sup>**: white solid, 36.3 mg, 90% yield, 96% ee.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.14 (d,  $J = 5.6 \text{ Hz}$ , 1H), 6.03 (d,  $J = 6.0 \text{ Hz}$ , 1H), 5.15 (s, 1H), 4.65 (s, 1H), 2.27-2.16 (m, 4H), 1.78-1.65 (m, 4H), 1.40 (s, 3H). [Daicel Chiralcel OJ-H,  $n$ -hexane/2-propanol = 99/1,  $\nu = 1.0 \text{ mL}\cdot\text{min}^{-1}$ ,  $\lambda = 254 \text{ nm}$ ,  $t$  (major) = 15.11 min,  $t$  (minor) = 21.45 min];  $[\alpha]_{\text{D}}^{29} = +5.8$  ( $c = 0.5$ ,  $\text{CHCl}_3$ ).



**2ao**<sup>2</sup>: white solid, 42.6 mg, 99% yield, 84% ee. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 6.16-6.14 (m, 1H), 6.02 (d, *J* = 5.6 Hz, 1H), 5.15 (d, *J* = 0.8 Hz, 1H), 4.63 (s, 1H), 2.46-2.28 (m, 4H), 1.86-1.80 (m, 1H), 1.74-1.58 (m, 4H), 1.54-1.48 (m, 1H), 1.40 (s, 3H). [Daicel Chiralcel OJ-H, *n*-hexane/2-propanol = 99/1, *v* = 1.0 mL·min<sup>-1</sup>, λ = 254 nm, *t* (major) = 9.33 min, *t* (minor) = 16.88 min]; [α]<sub>D</sub><sup>29</sup> = -17.0 (*c* = 0.5, CHCl<sub>3</sub>).

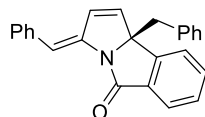


**2ba**: yellow oil, 39.7 mg, 88% yield, 85% ee. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.81 (d, *J* = 7.2 Hz, 1H), 7.55 (t, *J* = 7.6 Hz, 1H), 7.44-7.37 (m, 2H), 6.41 (d, *J* = 6.0 Hz, 1H), 6.25 (d, *J* = 5.6 Hz, 1H), 5.87 (q, *J* = 7.2 Hz, 1H), 1.89-1.83 (m, 5H), 0.73 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 172.5, 150.1, 140.7, 133.6, 133.1, 132.7, 128.5, 126.5, 124.9, 121.7, 108.2, 79.9, 33.7, 13.3, 8.5. IR (film): *v*<sub>max</sub> (cm<sup>-1</sup>) = 2322, 1770, 1703, 1615, 1441, 1335, 1297, 1250, 1209, 1101, 1055, 944, 835, 757, 672, 524. HRMS (ESI): Exact mass calcd. for C<sub>15</sub>H<sub>16</sub>NO ([M+H]<sup>+</sup>): 226.1226. Found: 226.1218. [Daicel Chiralpak AD-H, *n*-hexane/2-propanol = 98/2, *v* = 1.0 mL·min<sup>-1</sup>, λ = 254 nm, *t* (minor) = 12.92 min, *t* (major) = 19.85 min]; [α]<sub>D</sub><sup>28</sup> = +8.7 (*c* = 0.5, CHCl<sub>3</sub>).

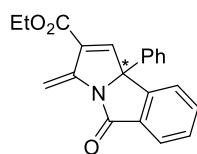


**2ca**: white solid, 15.0 mg, 59% yield, m.p. = 63-65 °C, 88% ee. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.78 (d, *J* = 7.6 Hz, 1H), 7.53 (t, *J* = 7.2 Hz, 1H), 7.43-7.40 (m, 2H), 6.41 (d, *J* = 6.0 Hz, 1H), 6.16 (d, *J* = 5.6 Hz, 1H), 2.16-2.12 (m, 4H), 1.87 (s, 3H), 0.85 (t, *J* = 7.2 Hz, 6H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 173.2, 149.3, 136.8, 133.5, 132.4, 131.4, 128.4, 124.9, 122.1, 120.0, 82.1, 36.7, 22.5, 20.0, 17.6, 17.5. IR (film): *v*<sub>max</sub> (cm<sup>-1</sup>) = 2921, 1704, 1674, 1607, 1461, 1439, 1358, 1294, 1256, 1205, 1113, 993, 836, 756, 711, 538. HRMS (ESI): Exact mass calcd. for C<sub>17</sub>H<sub>20</sub>NO ([M+H]<sup>+</sup>): 254.1539. Found:

254.1533. [Daicel Chiralpak AD-H, *n*-hexane/2-propanol = 99/1,  $\nu = 1.0 \text{ mL} \cdot \text{min}^{-1}$ ,  $\lambda = 254 \text{ nm}$ ,  $t$  (minor) = 15.88 min,  $t$  (major) = 27.01 min];  $[\alpha]_{\text{D}}^{26} = +112.5$  ( $c = 0.2$ ,  $\text{CHCl}_3$ ).

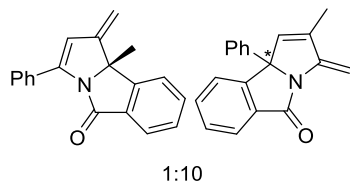


**2da**: white solid, 30.3 mg, 87% yield, m.p. = 54-56 °C, 29% ee.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.73 (d,  $J = 7.6 \text{ Hz}$ , 1H), 7.56 (t,  $J = 7.6 \text{ Hz}$ , 1H), 7.43-7.37 (m, 2H), 7.33-7.29 (m, 2H), 7.27-7.26 (m, 2H), 7.21-7.14 (m, 4H), 7.04-7.01 (m, 2H), 6.98 (s, 1H), 6.63 (d,  $J = 5.6 \text{ Hz}$ , 1H), 6.50 (dd,  $J = 6.0, 1.6 \text{ Hz}$ , 1H), 3.21 (AB,  $J_{AB} = 13.6 \text{ Hz}$ , 1H), 3.12 (BA,  $J_{BA} = 13.6 \text{ Hz}$ , 1H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  171.3, 149.0, 140.8, 136.9, 135.8, 134.9, 133.3, 132.6, 130.8, 128.8, 128.53, 128.51, 128.3, 127.9, 127.0, 126.6, 125.1, 122.3, 113.9, 79.6, 47.7. IR (film):  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ) = 2920, 2852, 1708, 1633, 1528, 1457, 1343, 1267, 1233, 1200, 1118, 1073, 1028, 907, 847, 790, 750, 690, 640, 568, 488. HRMS (ESI): Exact mass calcd. for  $\text{C}_{25}\text{H}_{20}\text{NO}$  ( $[\text{M}+\text{H}]^+$ ): 350.1539. Found: 350.1529. [Agilent 1260 Infinity Analytical SFC system Daicel Chiralcel OJ-H,  $\text{CO}_2$ /2-propanol = 80/20,  $\nu = 1.5 \text{ mL} \cdot \text{min}^{-1}$ ,  $\lambda = 214 \text{ nm}$ ,  $t$  (major) = 9.50 min,  $t$  (minor) = 10.19 min];  $[\alpha]_{\text{D}}^{25} = -5.8$  ( $c = 0.5$ ,  $\text{CHCl}_3$ ).

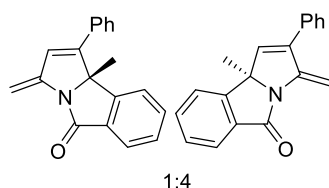


**2ea**: white solid, 27.1 mg, 40% yield, m.p. = 78-80 °C, 45% ee.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.87 (d,  $J = 7.2 \text{ Hz}$ , 1H), 7.59-7.52 (m, 3H), 7.50-7.46 (m, 1H), 7.42-7.40 (m, 2H), 7.33 (t,  $J = 7.6 \text{ Hz}$ , 2H), 7.29-7.26 (m, 1H), 5.74 (s, 1H), 5.71 (s, 1H), 4.29-4.24 (m, 2H), 1.32 (t,  $J = 7.2 \text{ Hz}$ , 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  171.9, 162.1, 149.1, 143.1, 141.5, 140.9, 133.6, 133.1, 131.7, 129.4, 129.2, 128.4, 125.5, 125.4, 123.2, 101.3, 78.8, 61.3, 14.3. IR (film):  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ) = 2980, 1716, 1600, 1457, 1334, 1300, 1250, 1176, 1133, 1058, 939, 863, 754, 695, 519, 476. HRMS (ESI): Exact mass calcd. for  $\text{C}_{21}\text{H}_{18}\text{NO}_3$  ( $[\text{M}+\text{H}]^+$ ): 332.1281. Found: 332.1267. [Daicel

Chiralcel OD-H, *n*-hexane/2-propanol = 98/2,  $\nu = 1.0 \text{ mL} \cdot \text{min}^{-1}$ ,  $\lambda = 254 \text{ nm}$ ,  $t$  (minor) = 15.54 min,  $t$  (major) = 18.12 min];  $[\alpha]_{\text{D}}^{20} = +26.2$  ( $c = 0.5$ ,  $\text{CHCl}_3$ ).



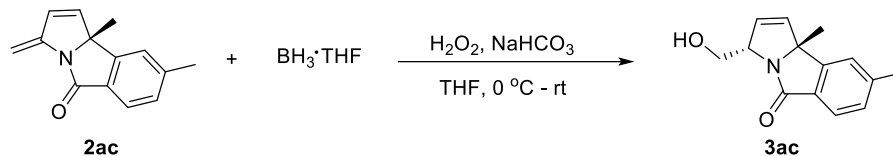
**2fa**: white solid, 47.9 mg, 88% yield, m.p. = 119-121 °C, minor: 86% ee, major: 66% ee. Two sets of signals were observed due to the existence of regioisomers (The ratio is about 1:10). The major one was marked with asterisk.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.84 (d,  $J = 7.6 \text{ Hz}$ , 1H), 7.53-7.36 (m, 6H), 7.30-7.22 (m, 3H), 6.48\* (s, 1H), 6.24 (s, 1H), 5.46\* (s, 1H), 5.09 (s, 1H), 5.01 (s, 1H), 4.79\* (s, 1H), 1.87\* (s, 3H), 1.78 (s, 1H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  171.9\*, 150.9\*, 147.6\*, 142.5\*, 138.3\*, 133.7, 133.2\*, 131.8\*, 130.3\*, 129.5, 128.85\*, 128.81\*, 128.2, 127.8\*, 125.4\*, 125.2\*, 123.1\*, 121.8, 116.6, 103.7, 94.8\*, 79.3\*, 30.5, 12.4\*. IR (film):  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ) = 2970, 2924, 1702, 1609, 1459, 1348, 1284, 1215, 1105, 1060, 1015, 945, 867, 759, 695, 629, 507. HRMS (ESI): Exact mass calcd. for  $\text{C}_{19}\text{H}_{16}\text{NO}$  ( $[\text{M}+\text{H}]^+$ ): 274.1226. Found: 274.1216. [Daicel Chiralcel OD-H, *n*-hexane/2-propanol = 95/5,  $\nu = 1.0 \text{ mL} \cdot \text{min}^{-1}$ ,  $\lambda = 254 \text{ nm}$ , major: ( $t_1 = 8.20 \text{ min}$ ,  $t_2 = 9.79 \text{ min}$ ); minor: ( $t_1 = 12.60 \text{ min}$ ,  $t_2 = 15.28 \text{ min}$ )];  $[\alpha]_{\text{D}}^{29} = +82.5$  ( $c = 0.5$ ,  $\text{CHCl}_3$ ).



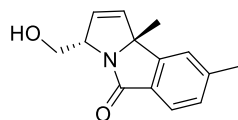
**2ga**: yellow oil, 53.2 mg, 97% yield, minor: 79% ee, major: 92% ee. Two sets of signals were observed due to the existence of regioisomers (The ratio is about 1:4). The major one was marked with asterisk.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.87 (d,  $J = 4.8 \text{ Hz}$ , 1H), 7.61-7.59 (m, 1H), 7.50-7.45 (m, 3H), 7.42-7.35 (m, 6H), 6.38\* (s, 1H), 6.17 (s, 1H), 5.56\* (s, 1H), 5.42 (s, 1H), 4.96\* (s, 1H), 4.88 (s, 1H), 1.81 (s, 1H), 1.69\* (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  171.5\*, 170.7, 151.1\*, 149.8, 149.7, 145.6\*,

145.1, 142.3\*, 133.4\*, 133.2\*, 133.0\*, 132.9, 132.2\*, 128.85, 128.80\*, 128.76, 128.70, 128.6\*, 128.3\*, 128.0\*, 127.5, 125.3\*, 125.2, 123.2, 121.8\*, 97.2\*, 96.8, 78.0, 75.1\*, 29.6, 28.5\*. IR (film):  $\nu_{\text{max}}$  (cm<sup>-1</sup>) = 2970, 2923, 1703, 1618, 1531, 1492, 1440, 1326, 1220, 1117, 1082, 1026, 839, 759, 691, 541, 492. HRMS (ESI): Exact mass calcd. for C<sub>19</sub>H<sub>16</sub>NO ([M+H]<sup>+</sup>): 274.1226. Found: 274.1217. [Agilent 1260 Infinity Analytical SFC system Daicel Chiralcel OJ-H, CO<sub>2</sub>/2-propanol = 95/5,  $\nu$  = 1.5 mL·min<sup>-1</sup>,  $\lambda$  = 214 nm, major: (t<sub>1</sub> = 17.03 min, t<sub>2</sub> = 17.95 min); minor: (t<sub>1</sub> = 15.30 min, t<sub>2</sub> = 20.87 min)];  $[\alpha]_{\text{D}}^{25}$  = +4.6 (c = 0.5, CHCl<sub>3</sub>).

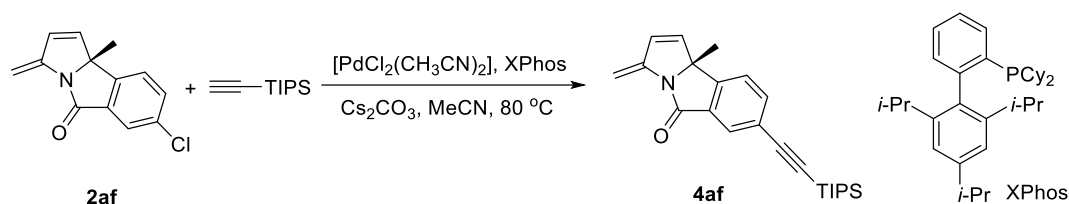
## Transformations of products



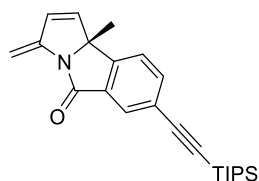
The transformation of **2ac** was accomplished following the reported procedures.<sup>3</sup>  $\text{BH}_3 \cdot \text{THF}$  (0.45 mL, 0.9 mol/L, 0.4 mmol, 2.0 equiv) was added to a cold solution (0 °C) of **2ac** (42.4 mg, 0.2 mmol, 1.0 equiv) in THF (3 mL), and the mixture was stirred at 0 °C for 2 h. Aqueous 30%  $\text{H}_2\text{O}_2$  (0.2 mL) and saturated aqueous  $\text{NaHCO}_3$  (0.2 mL) were added to the cold solution, and the mixture was stirred at room temperature overnight. The reaction was quenched with saturated aqueous  $\text{NH}_4\text{Cl}$  (1 mL) and diluted with ethyl acetate (3 mL). The mixture was filtered through celite, and the filtrate was concentrated under reduced pressure. The crude product was purified by silica gel column chromatography (PE/EtOAc = 10/1) to afford the desired product **3ac**.



**3ac**: white solid, 29.6 mg, 65% yield, m.p. = 115-117 °C, 86% ee.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.67 (d,  $J$  = 7.6 Hz, 1H), 7.27-7.24 (m, 2H), 6.24 (dd,  $J$  = 6.0, 2.4 Hz, 1H), 5.67 (d,  $J$  = 6.0 Hz, 1H), 5.53 (dd,  $J$  = 11.2, 3.6 Hz, 1H), 4.72 (d,  $J$  = 9.6 Hz, 1H), 4.05-3.98 (m, 1H), 3.90-3.83 (m, 1H), 2.47 (s, 3H), 1.54 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  172.4, 150.6, 143.6, 134.5, 130.0, 129.8, 129.6, 124.5, 121.8, 78.0, 67.2, 63.0, 26.6, 22.1. IR (film):  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ) = 3284, 2919, 2857, 1661, 1612, 1452, 1355, 1304, 1227, 1123, 1044, 1012, 942, 867, 828, 781, 714, 524, 429. HRMS (ESI): Exact mass calcd. for  $\text{C}_{14}\text{H}_{16}\text{NO}_2$  ( $[\text{M}+\text{H}]^+$ ): 230.1176. Found: 230.1168. [Daicel Chiralpak AD-H, *n*-hexane/2-propanol = 90/10,  $\nu$  = 1.0 mL $\cdot$ min $^{-1}$ ,  $\lambda$  = 254 nm,  $t$  (major) = 9.60 min,  $t$  (minor) = 11.16 min];  $[\alpha]_{\text{D}}^{26}$  = -104.7 ( $c$  = 0.5,  $\text{CHCl}_3$ ).

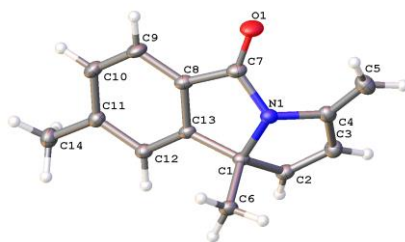


A flame-dried Schlenk tube was cooled to room temperature under argon. To this tube were added **2af** (23.1 mg, 0.1 mmol),  $[\text{PdCl}_2(\text{CH}_3\text{CN})_2]$  (2.2 mg, 0.05 mmol), XPhos (7.2 mg, 0.015 mmol),  $\text{Cs}_2\text{CO}_3$  (81.4 mg, 0.25 mmol) and  $\text{CH}_3\text{CN}$  (1.0 mL). Then the reaction mixture was stirred at room temperature for 10 min before the addition of (triisopropylsilyl)acetylene (27.4 mg, 0.15 mmol). After that, the mixture was stirred at 80 °C for 2 h. After completion, the mixture was filtered. The filtrate was concentrated under reduced pressure. The crude product was purified by silica gel column chromatography (PE/EtOAc) = 20/1) to afford **4af**.



**4af**: white solid, 32.6 mg, 90% yield, m.p. = 127-129 °C, 87% ee.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.93 (s, 1H), 7.67 (d,  $J$  = 7.6 Hz, 1H), 7.37 (d,  $J$  = 8.0 Hz, 1H), 6.34 (d,  $J$  = 5.6 Hz, 1H), 6.12 (d,  $J$  = 5.6 Hz, 1H), 5.37 (s, 1H), 4.82 (s, 1H), 1.59 (s, 3H), 1.13 (s, 21H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  170.6, 150.5, 145.9, 136.6, 135.9, 132.3, 130.0, 128.8, 124.5, 121.7, 105.7, 97.0, 92.5, 77.3, 28.4, 18.8, 11.4. IR (film):  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ) = 2932, 2861, 2151, 1704, 1630, 1459, 1424, 1319, 1224, 1127, 1070, 994, 927, 877, 841, 785, 725, 669, 599, 493, 451. HRMS (ESI): Exact mass calcd. for  $\text{C}_{24}\text{H}_{32}\text{NOSi}$  ( $[\text{M}+\text{H}]^+$ ): 378.2248. Found: 378.2234. [Daicel Chiralpak PC-2, *n*-hexane/2-propanol = 99/1,  $\nu$  = 1.0  $\text{mL}\cdot\text{min}^{-1}$ ,  $\lambda$  = 254 nm,  $t$  (major) = 6.42 min,  $t$  (minor) = 10.04 min];  $[\alpha]_{\text{D}}^{25}$  = -122.5 ( $c$  = 0.5,  $\text{CHCl}_3$ ).

## X-Ray crystal data of 2ac (CCDC 1870088)



Crystal data and structure refinement for mjl18347\_0m.

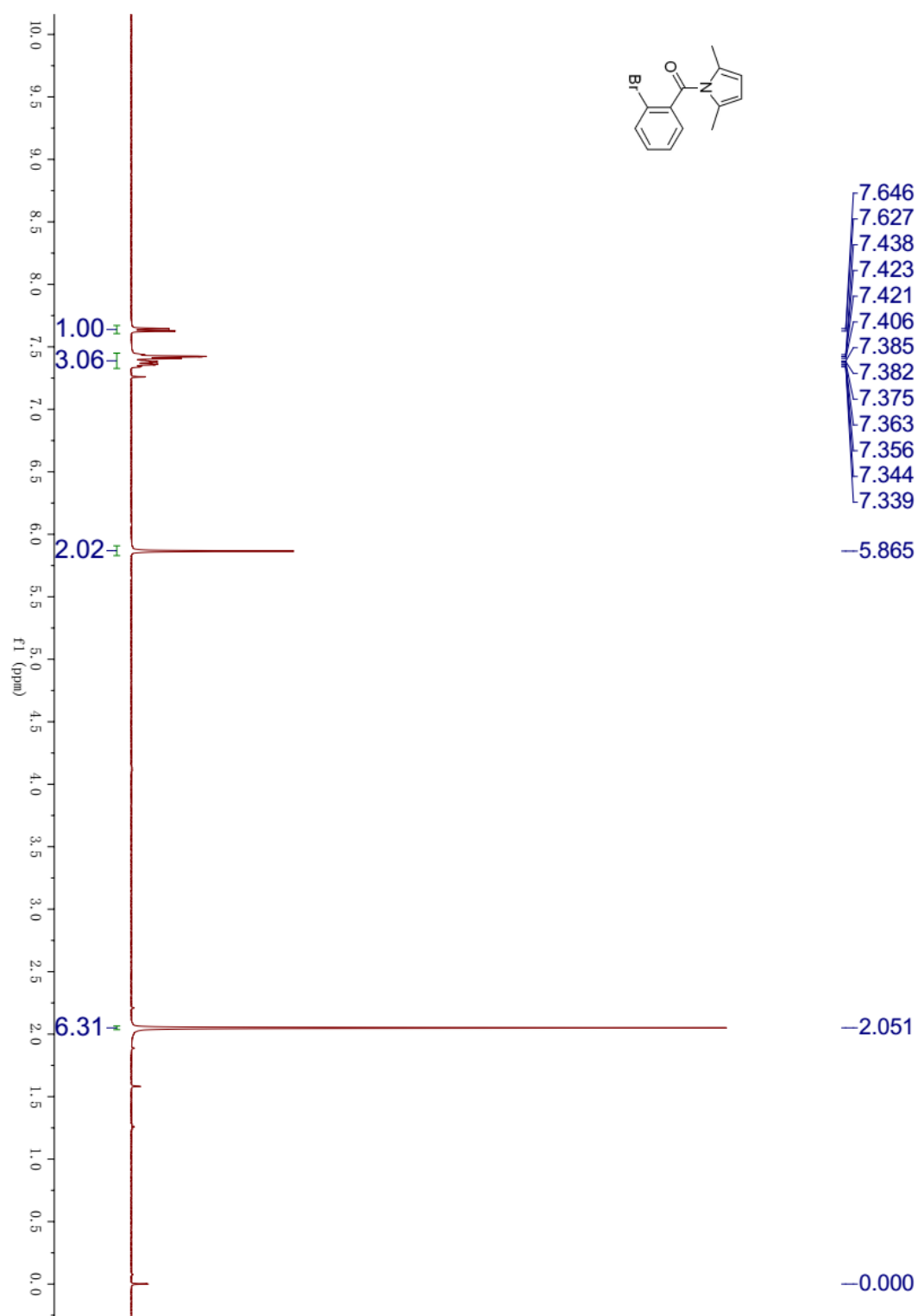
|                                   |                                               |          |
|-----------------------------------|-----------------------------------------------|----------|
| Identification code               | mjl18347_0m                                   |          |
| Empirical formula                 | C <sub>14</sub> H <sub>13</sub> N O           |          |
| Formula weight                    | 211.25                                        |          |
| Temperature                       | 169.99 K                                      |          |
| Wavelength                        | 1.34139 Å                                     |          |
| Crystal system                    | Orthorhombic                                  |          |
| Space group                       | P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub> |          |
| Unit cell dimensions              | a = 7.1848(2) Å                               | α = 90°. |
|                                   | b = 9.2538(2) Å                               | β = 90°. |
|                                   | c = 16.9186(4) Å                              | γ = 90°. |
| Volume                            | 1124.86(5) Å <sup>3</sup>                     |          |
| Z                                 | 4                                             |          |
| Density (calculated)              | 1.247 Mg/m <sup>3</sup>                       |          |
| Absorption coefficient            | 0.399 mm <sup>-1</sup>                        |          |
| F(000)                            | 448                                           |          |
| Crystal size                      | 0.12 x 0.1 x 0.05 mm <sup>3</sup>             |          |
| Theta range for data collection   | 4.547 to 54.929°.                             |          |
| Index ranges                      | -6 ≤ h ≤ 8, -11 ≤ k ≤ 11, -20 ≤ l ≤ 20        |          |
| Reflections collected             | 11814                                         |          |
| Independent reflections           | 2122 [R(int) = 0.0404]                        |          |
| Completeness to theta = 53.594°   | 98.7 %                                        |          |
| Absorption correction             | Semi-empirical from equivalents               |          |
| Max. and min. transmission        | 0.7508 and 0.5615                             |          |
| Refinement method                 | Full-matrix least-squares on F <sup>2</sup>   |          |
| Data / restraints / parameters    | 2122 / 0 / 147                                |          |
| Goodness-of-fit on F <sup>2</sup> | 1.084                                         |          |
| Final R indices [I > 2σ(I)]       | R1 = 0.0322, wR2 = 0.0881                     |          |
| R indices (all data)              | R1 = 0.0329, wR2 = 0.0888                     |          |
| Absolute structure parameter      | 0.08(10)                                      |          |
| Extinction coefficient            | n/a                                           |          |
| Largest diff. peak and hole       | 0.193 and -0.160 e.Å <sup>-3</sup>            |          |

## References

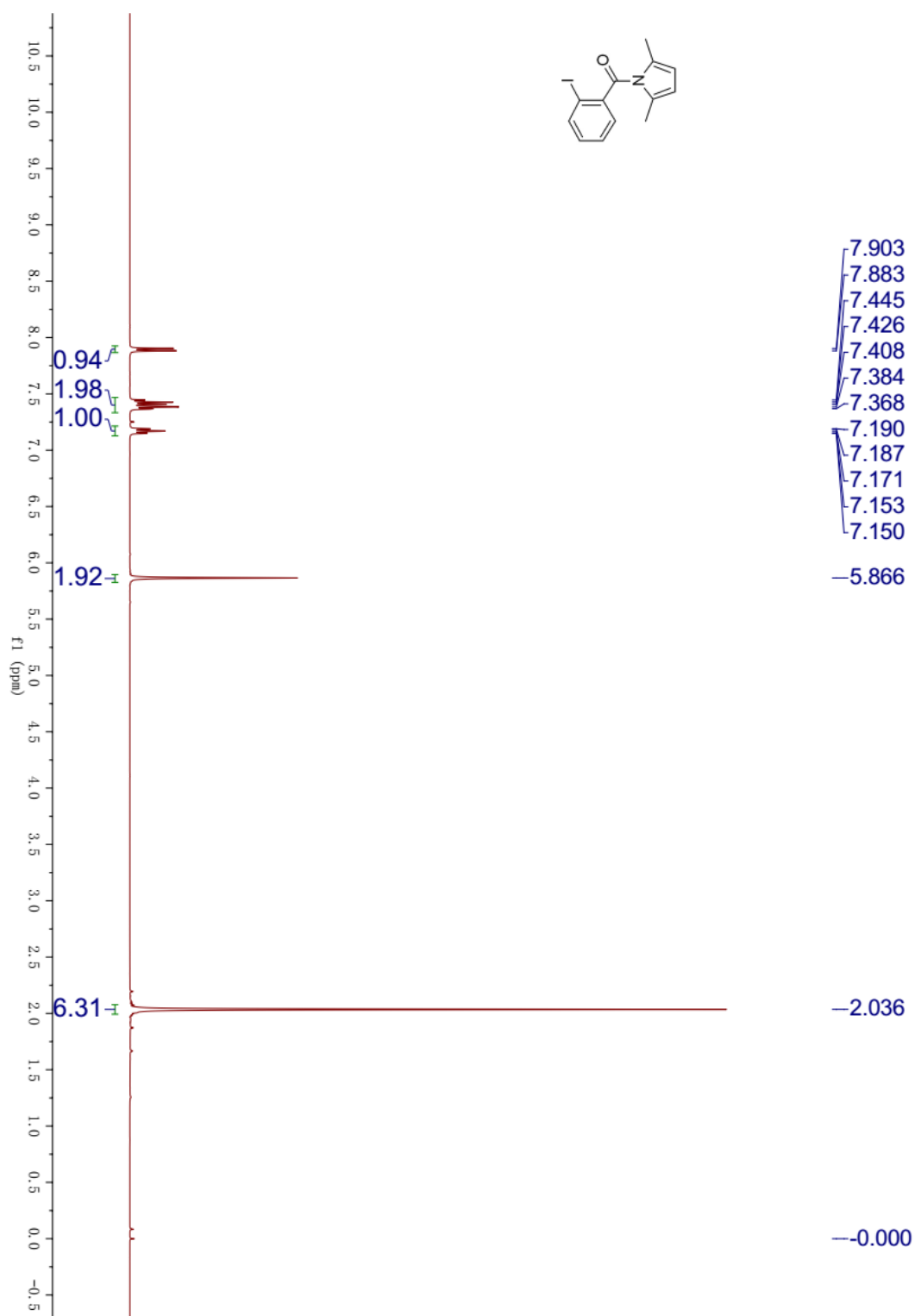
- [1] Ren, H.; Knochel, P. *Angew. Chem. Int. Ed.* **2006**, 45, 3462.
- [2] Ren, H.; Li, Z.; Knochel, P. *Chem. Asian J.* **2007**, 2, 416.
- [3] Jain, N.; Ciufolini, M. *Synlett* **2015**, 26, 631.

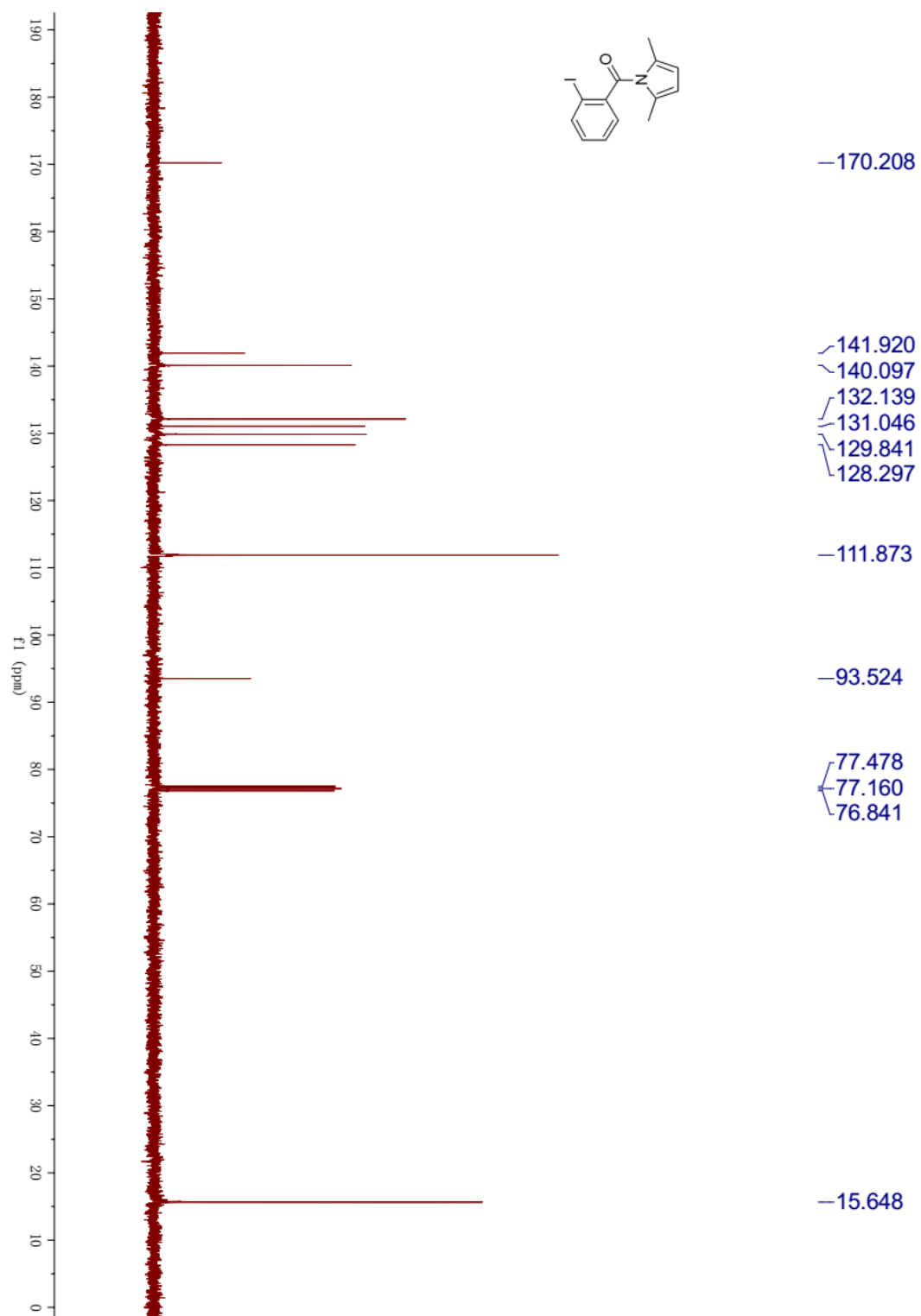
## Copies of NMR spectra and HPLC chromatographs

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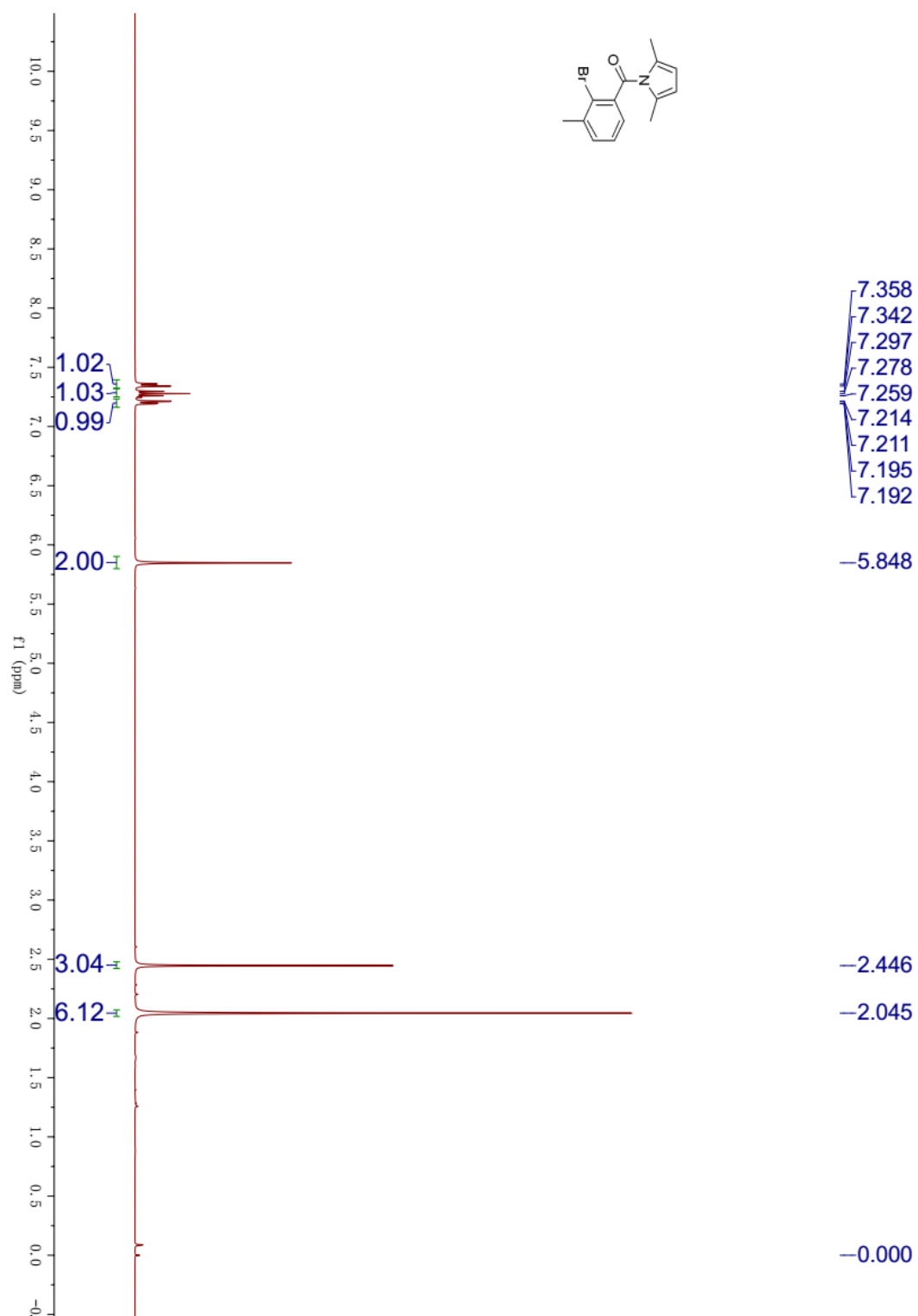


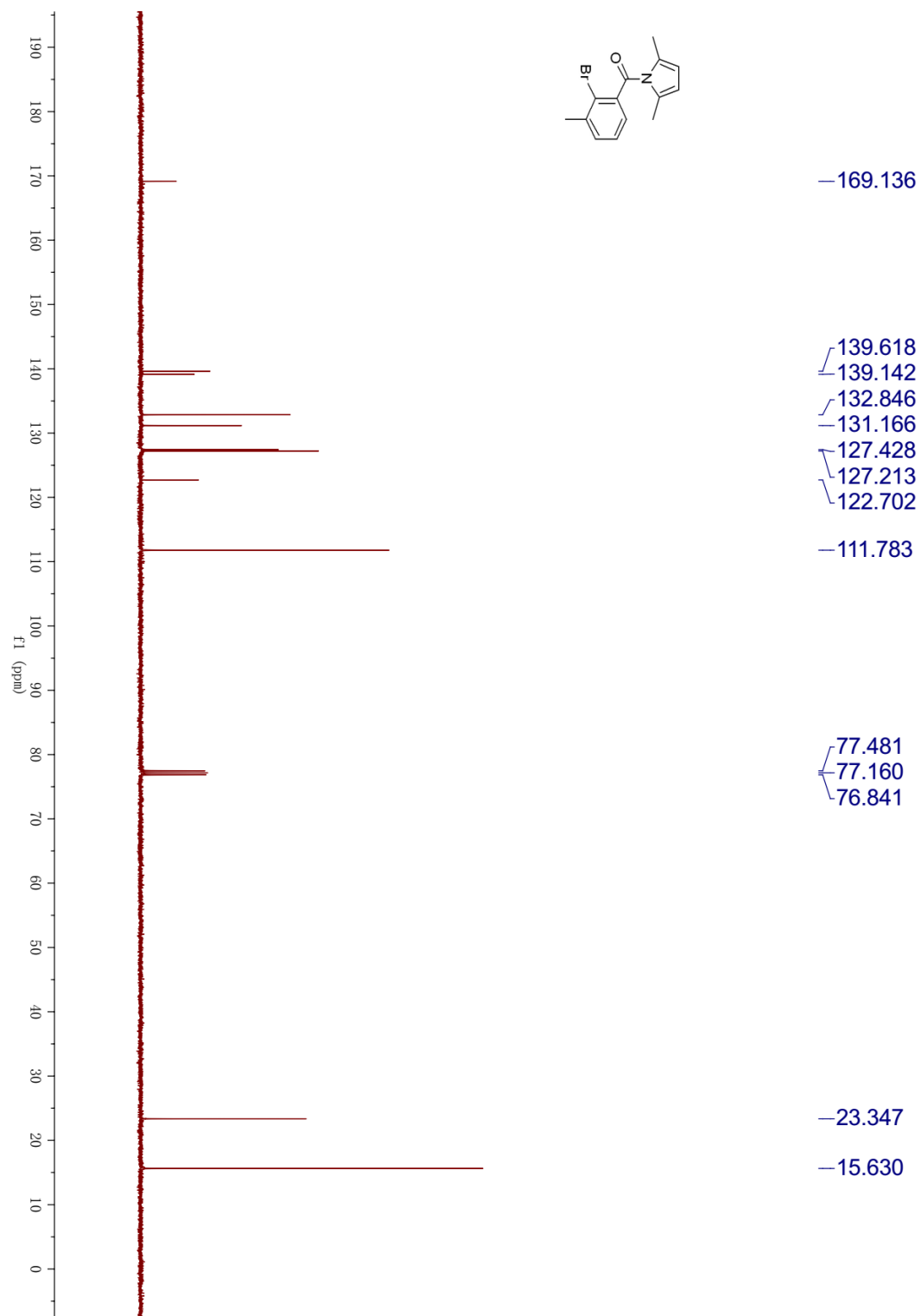
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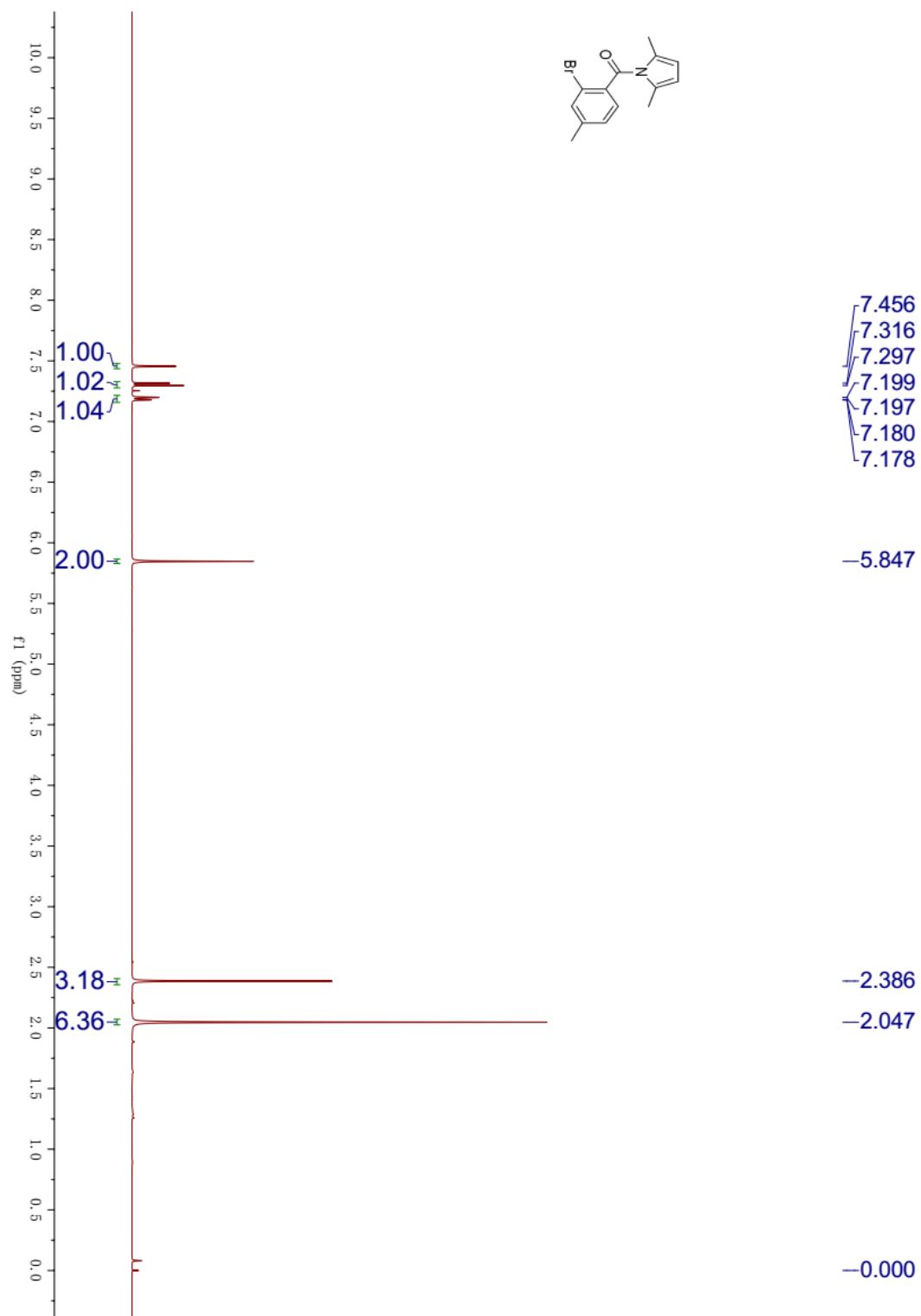


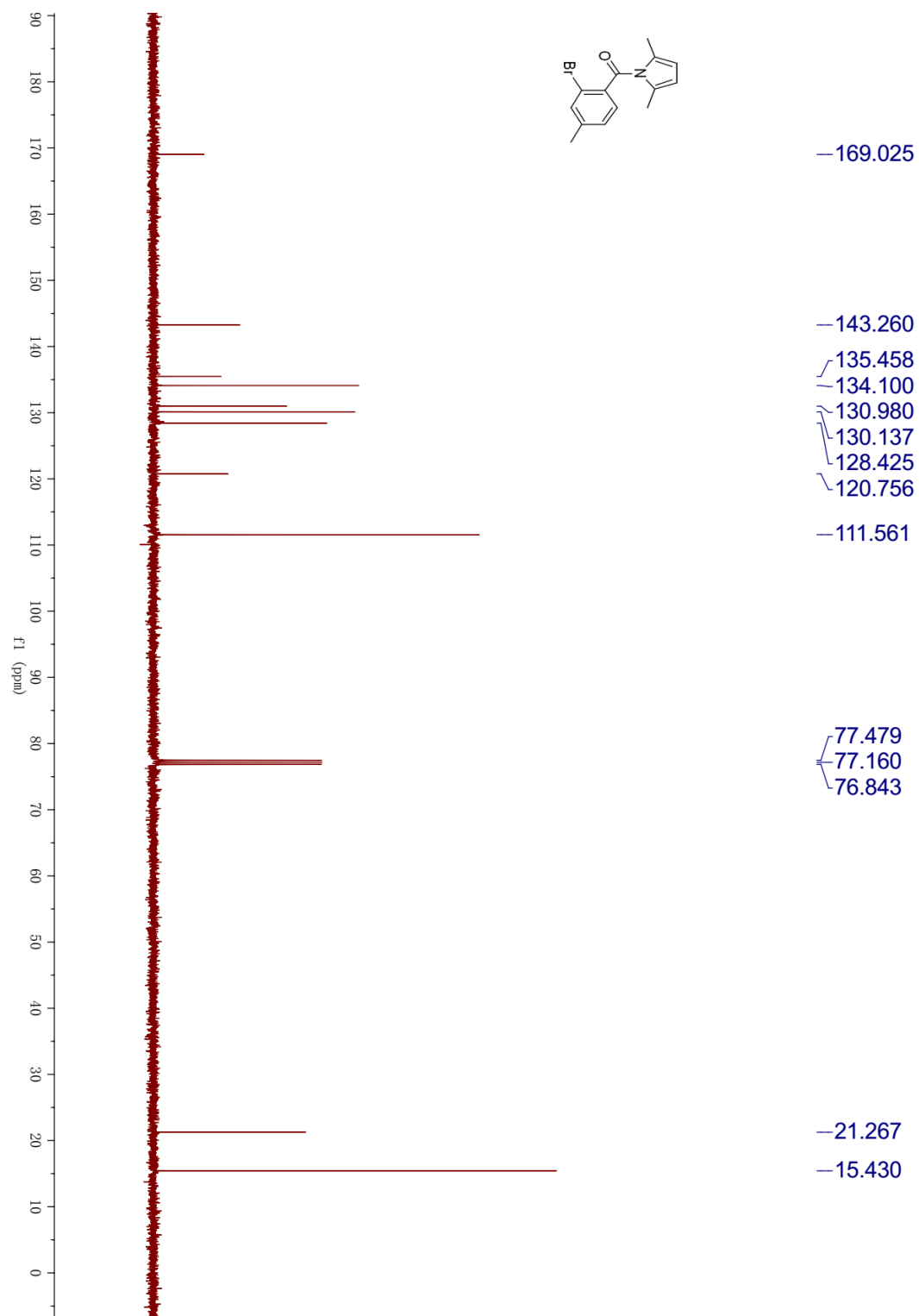
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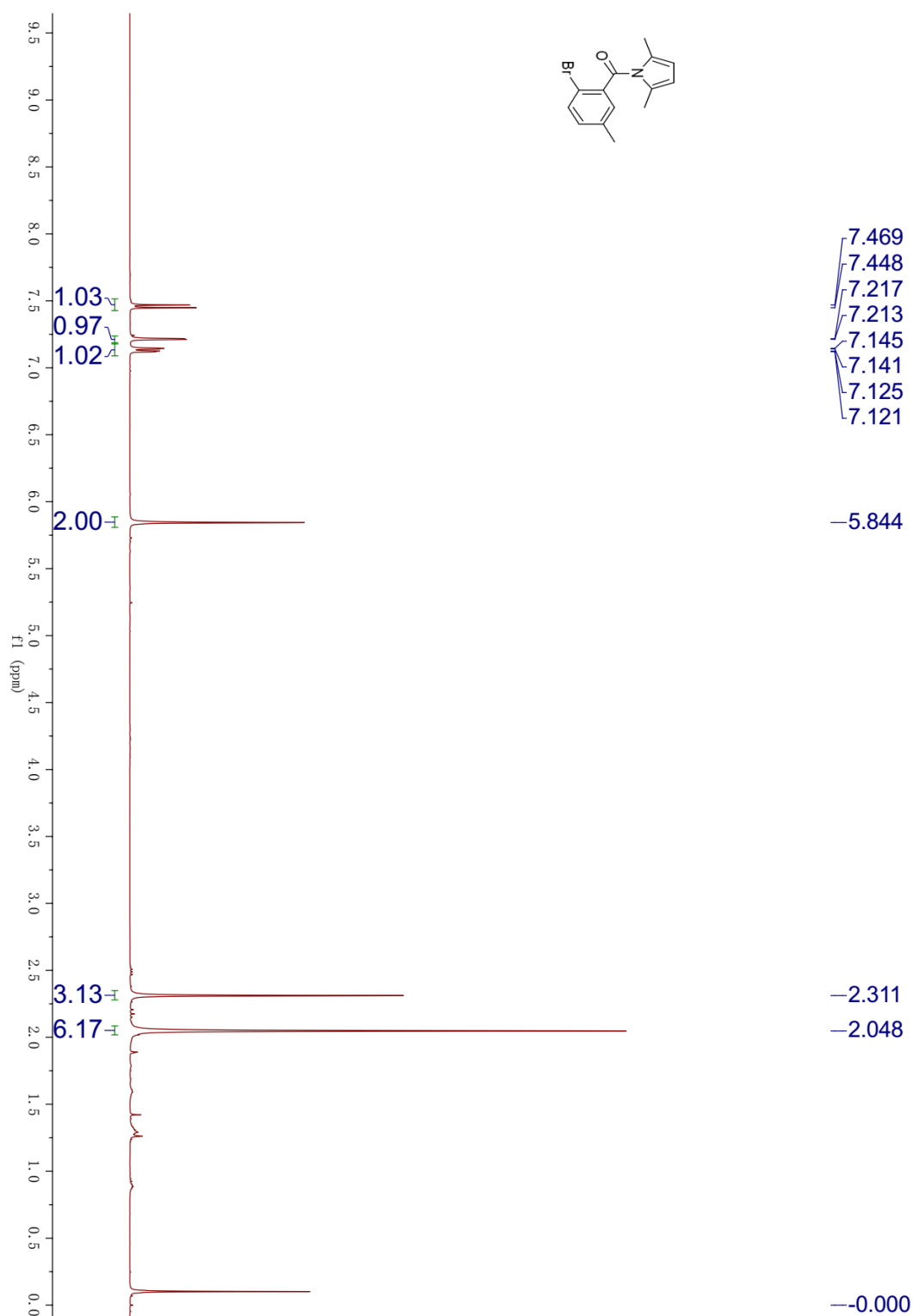


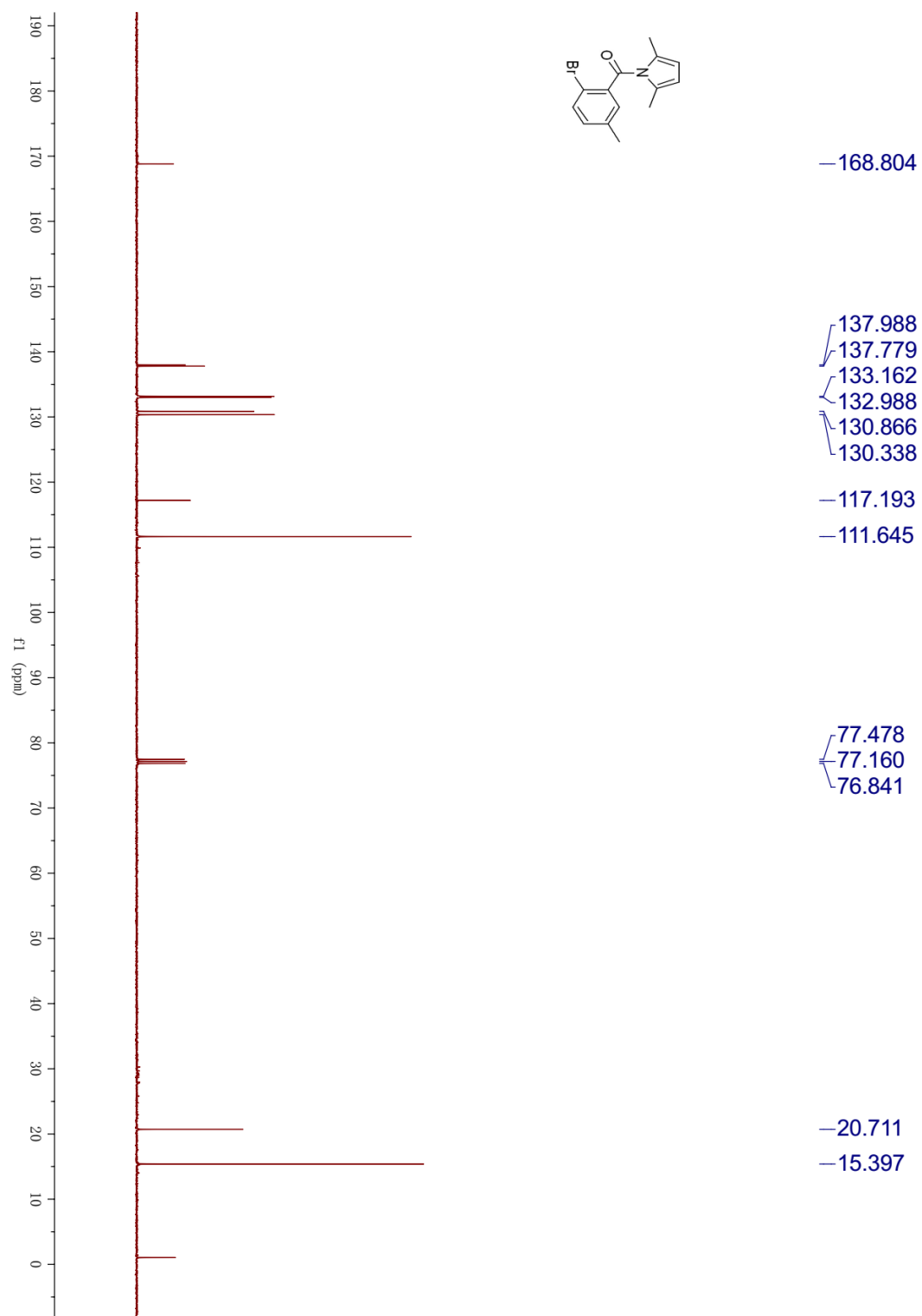
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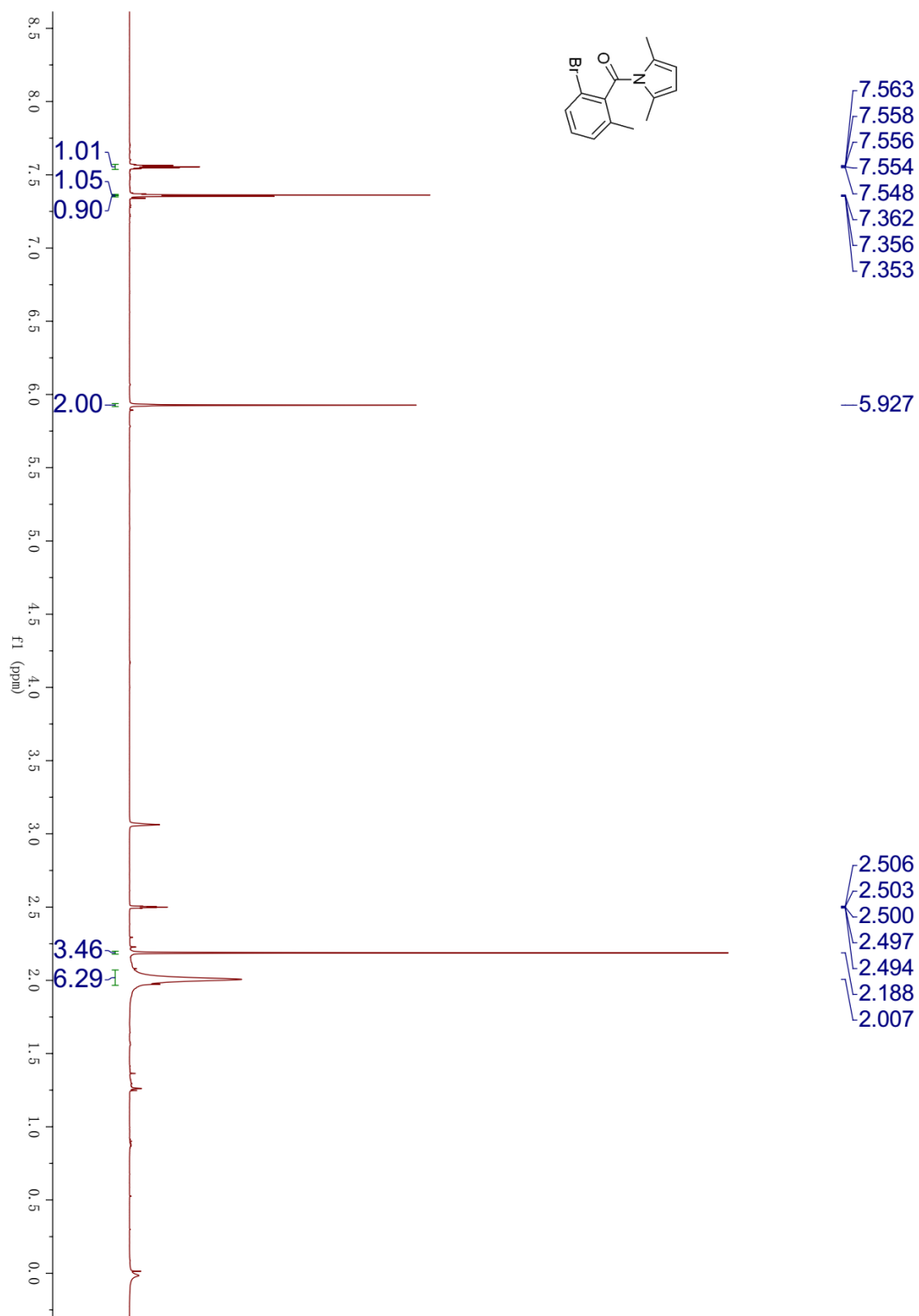


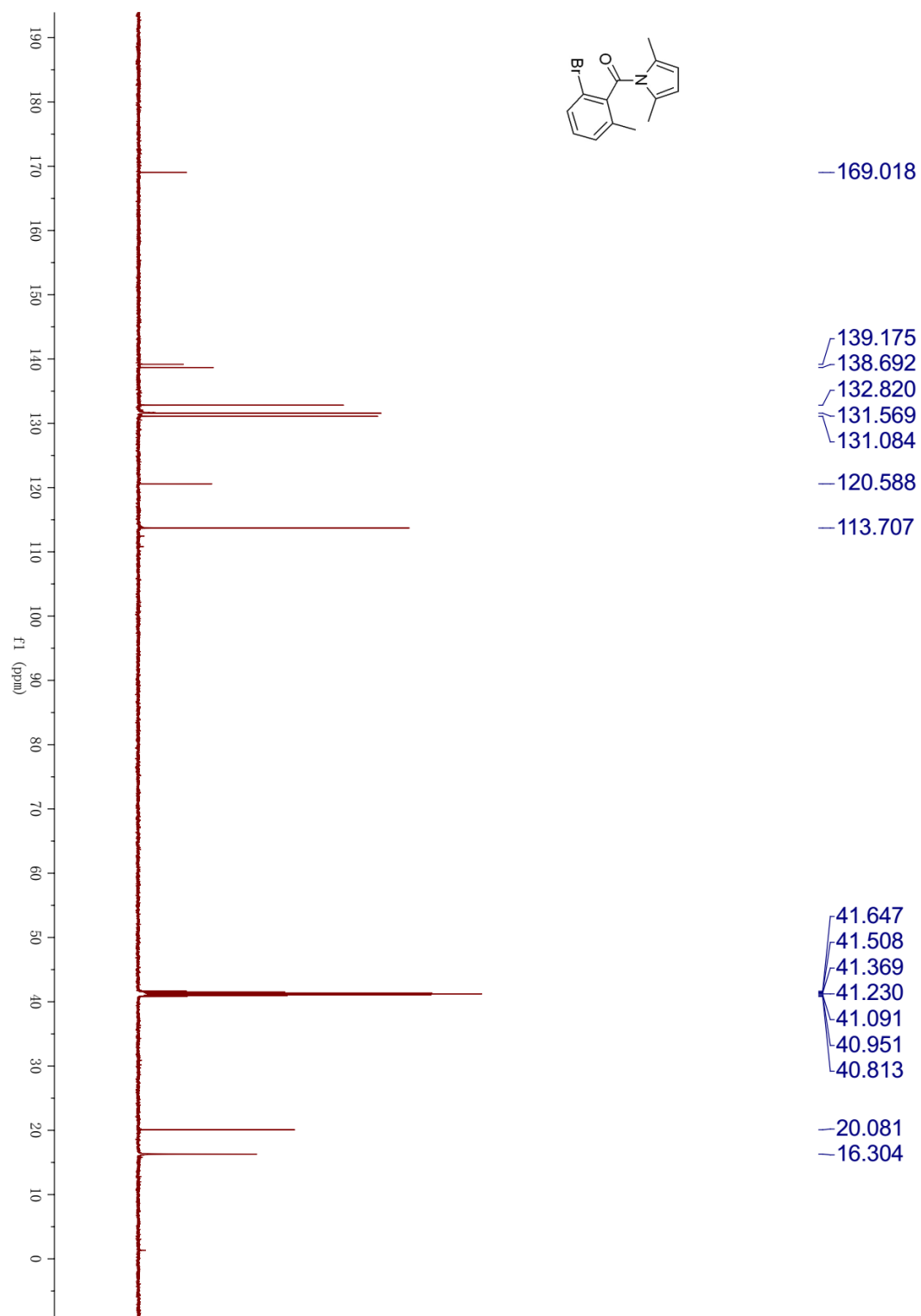
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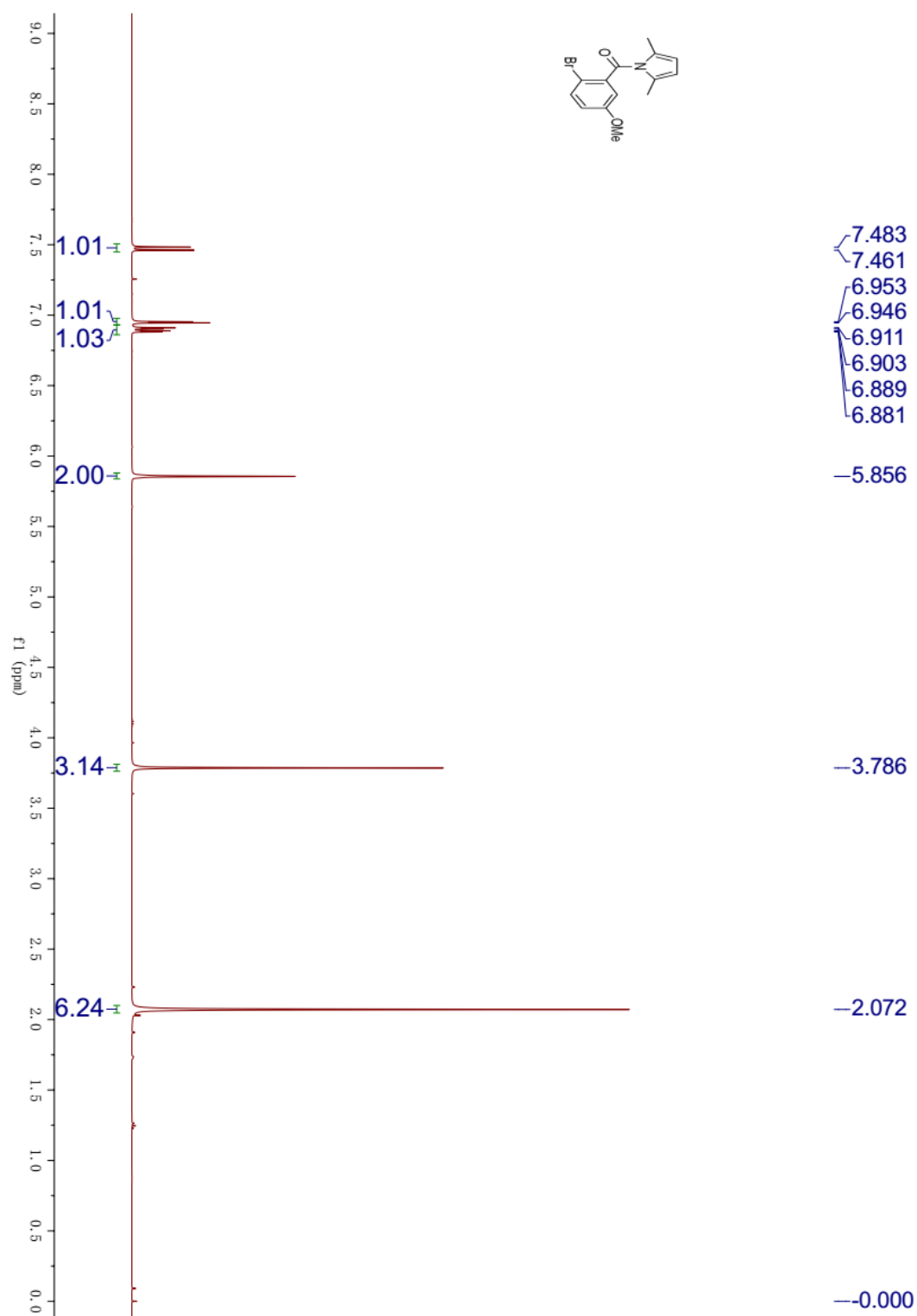


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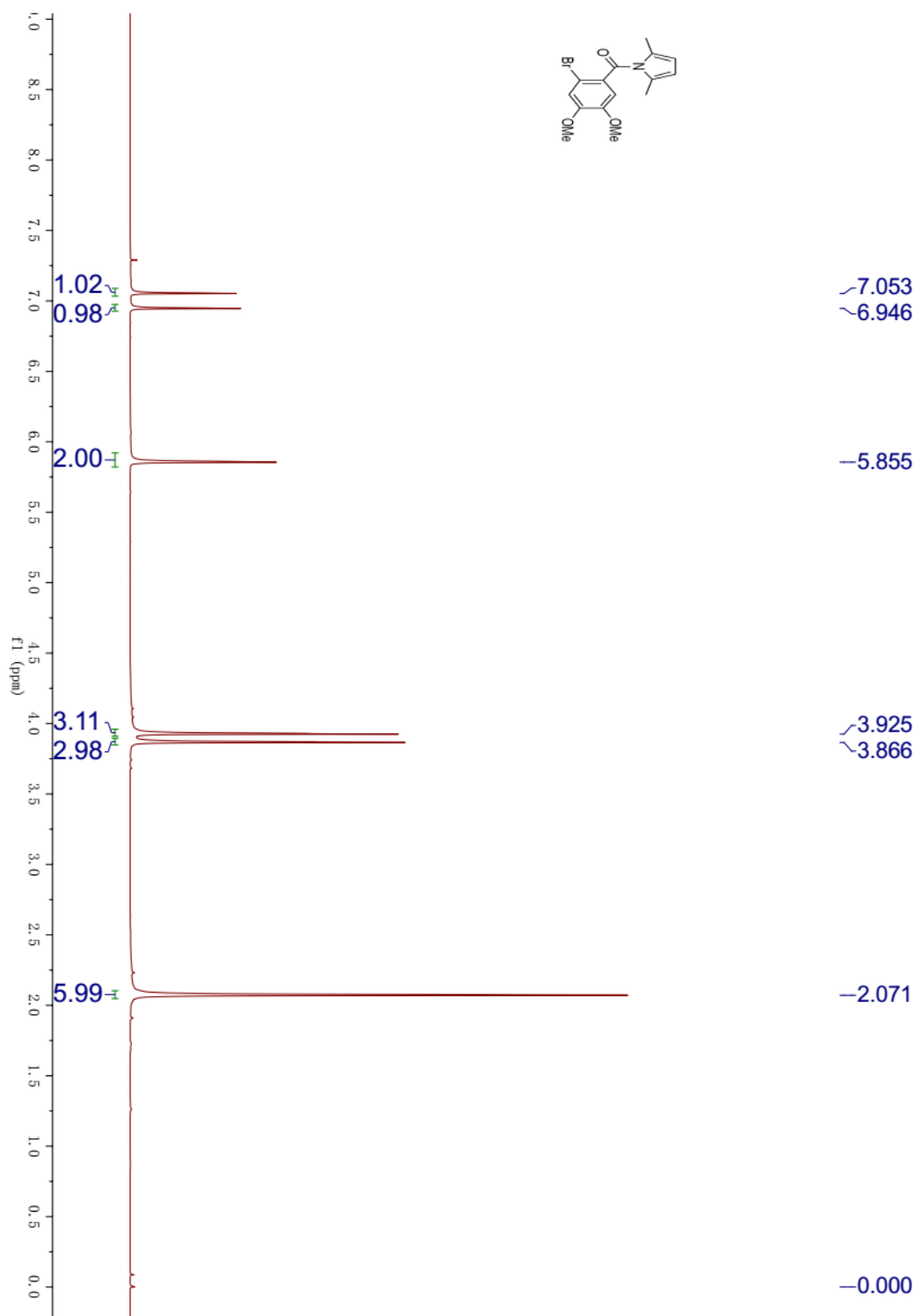


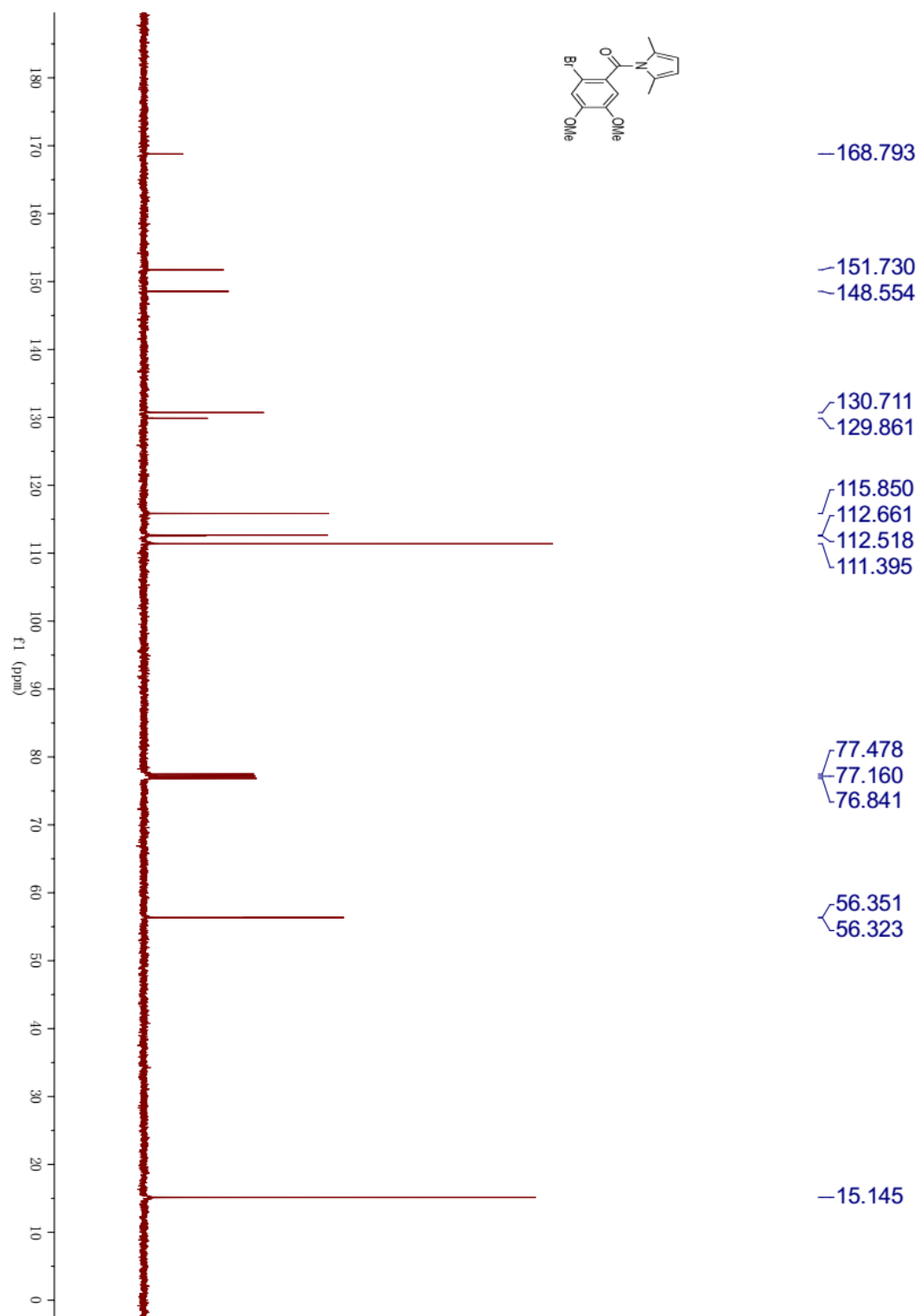


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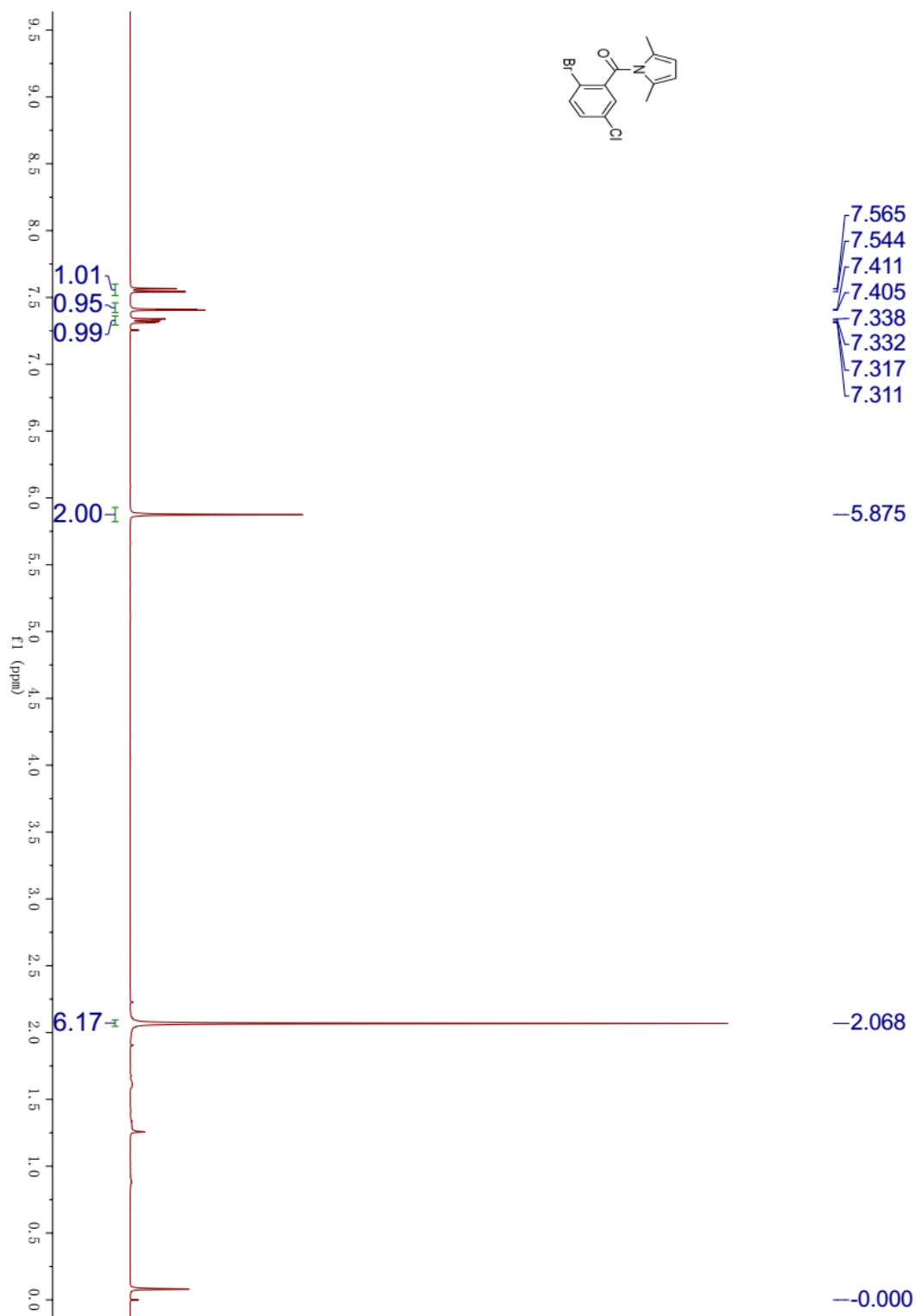


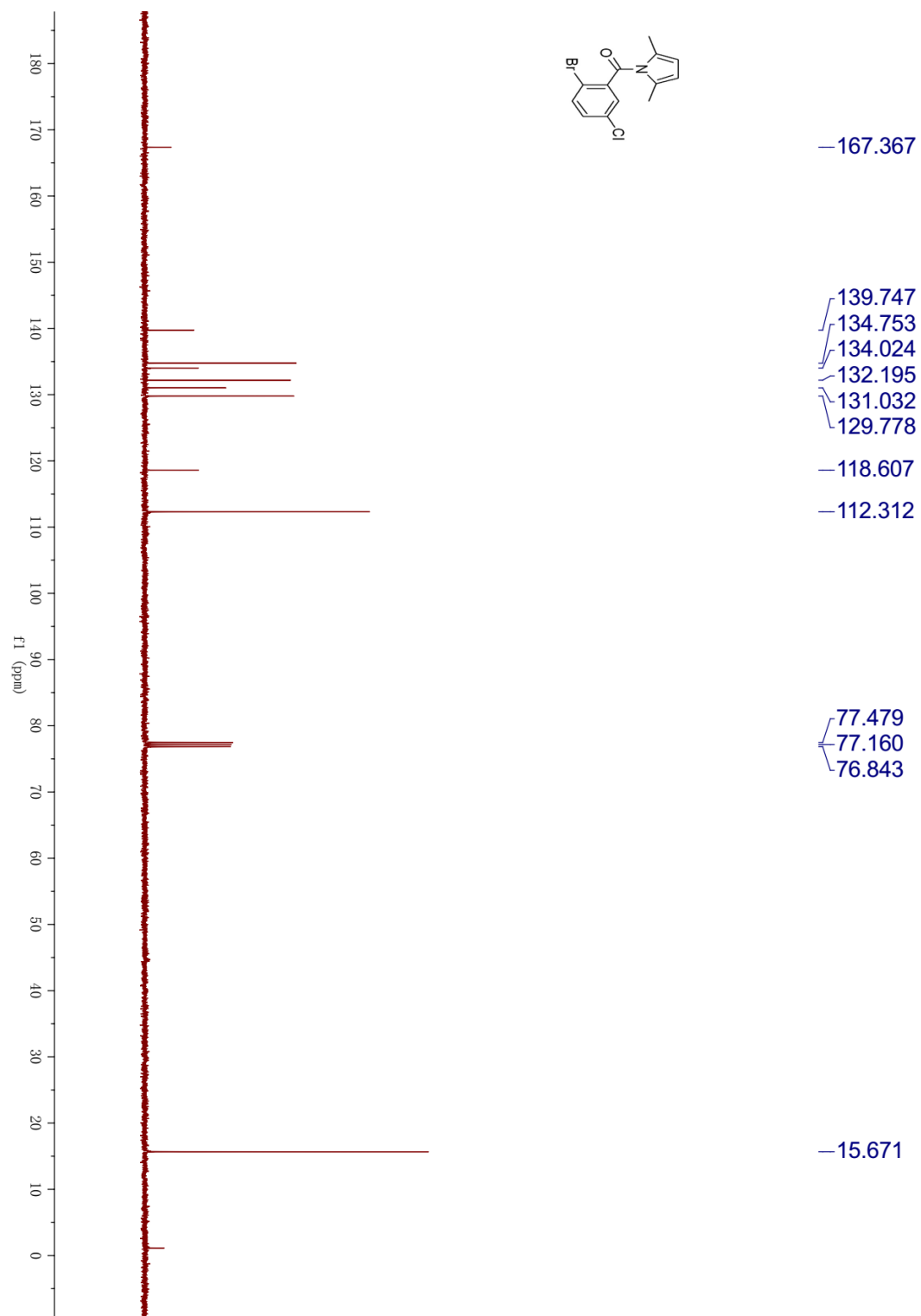
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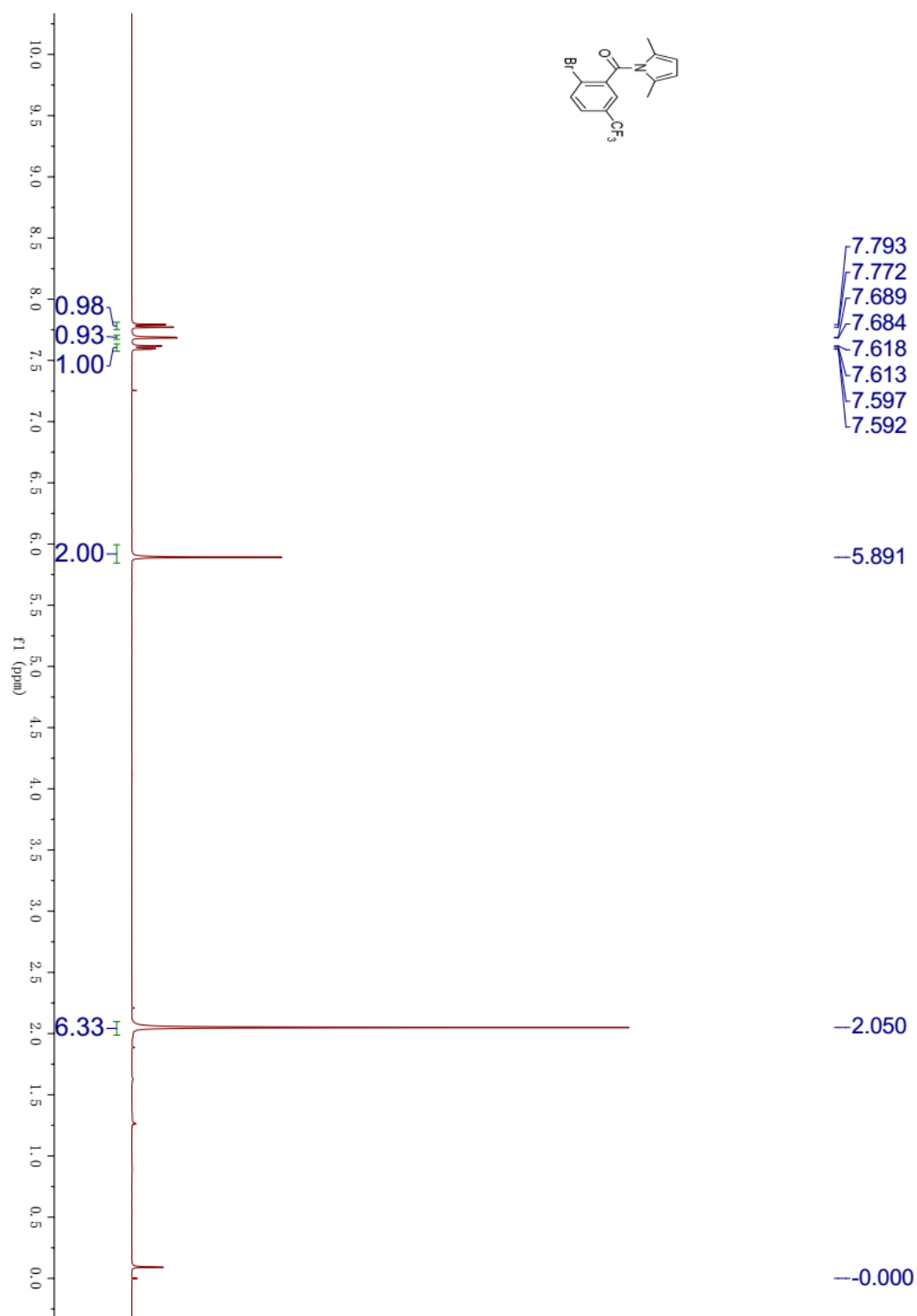


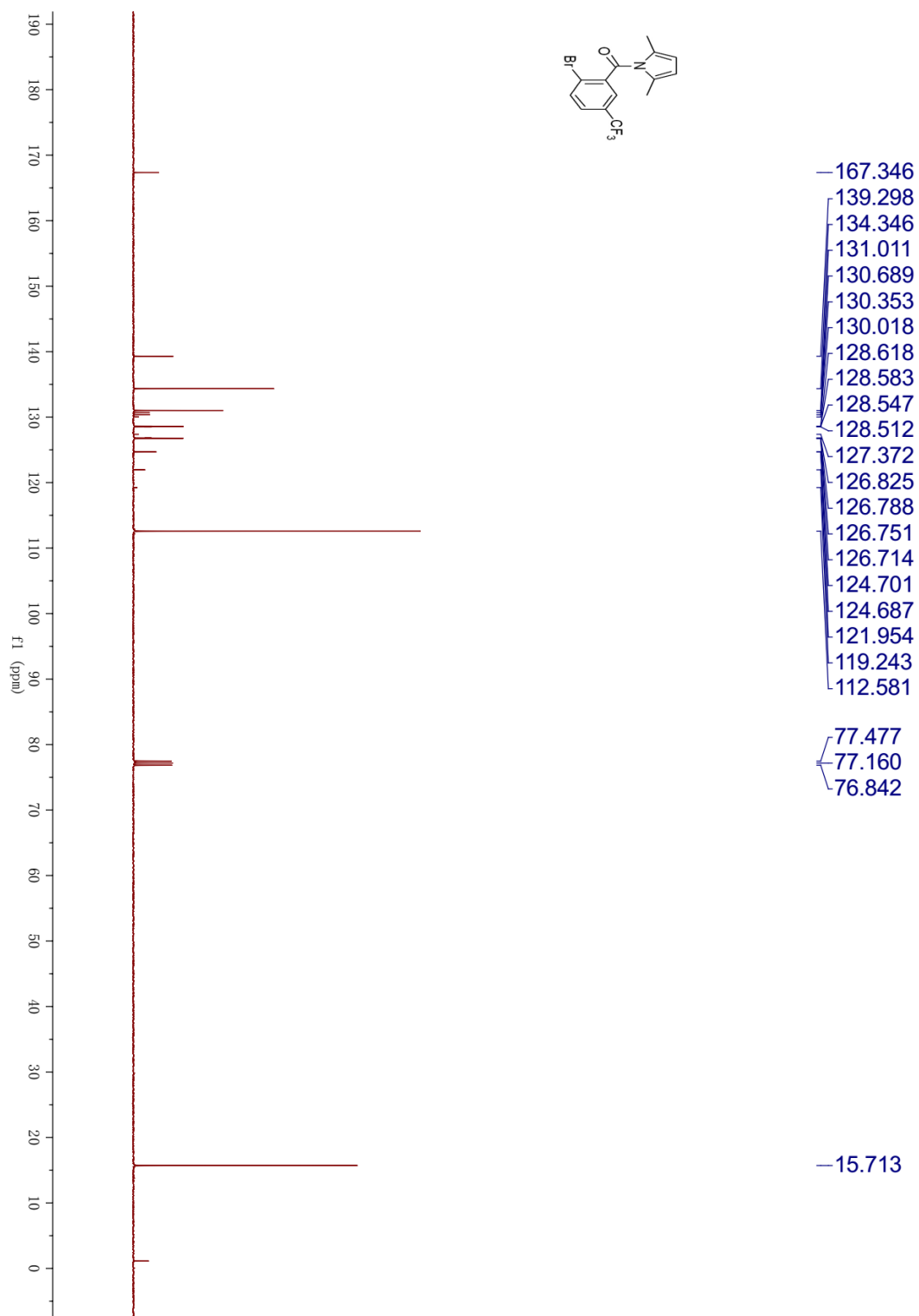
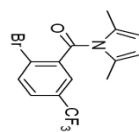
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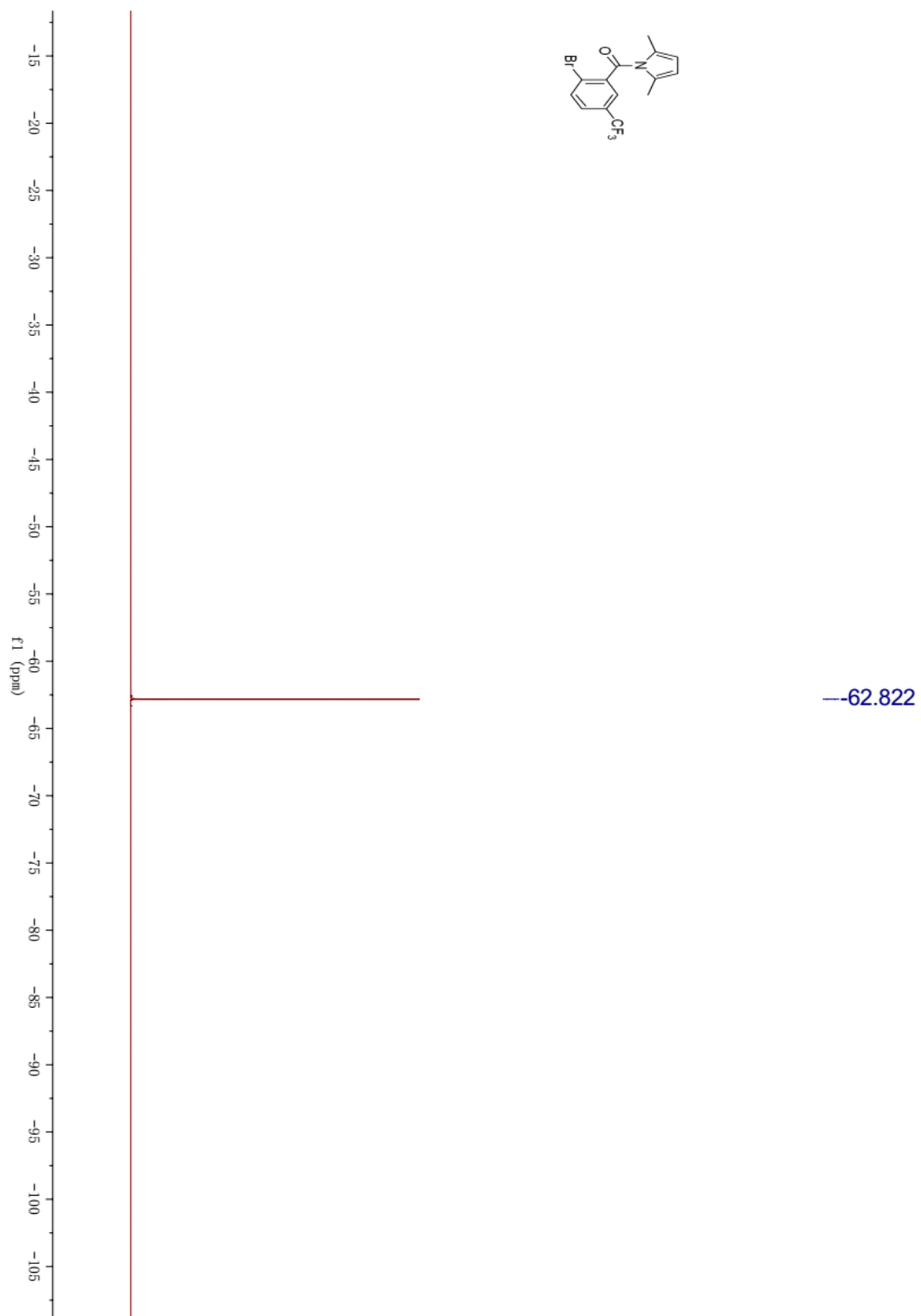
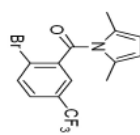




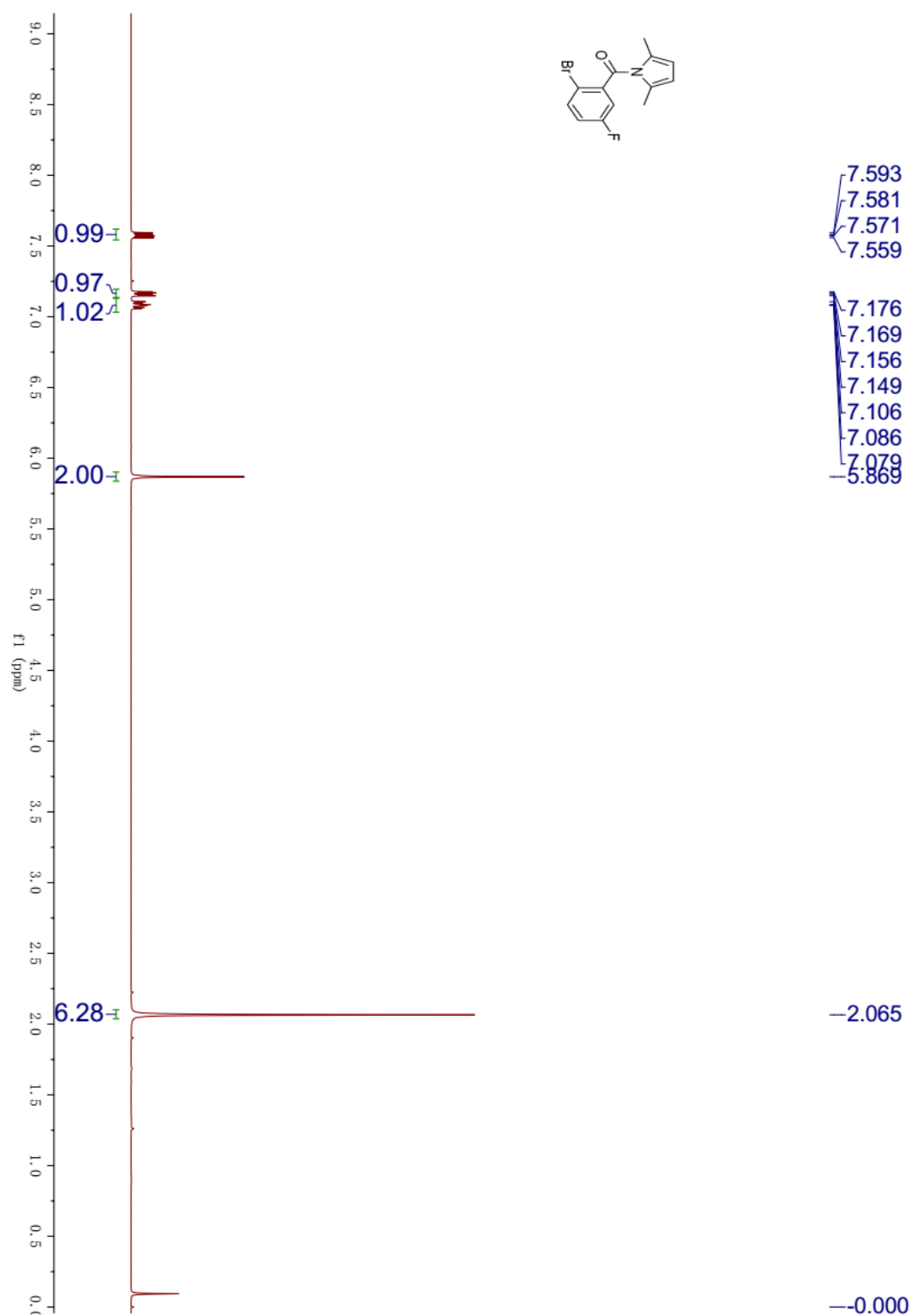
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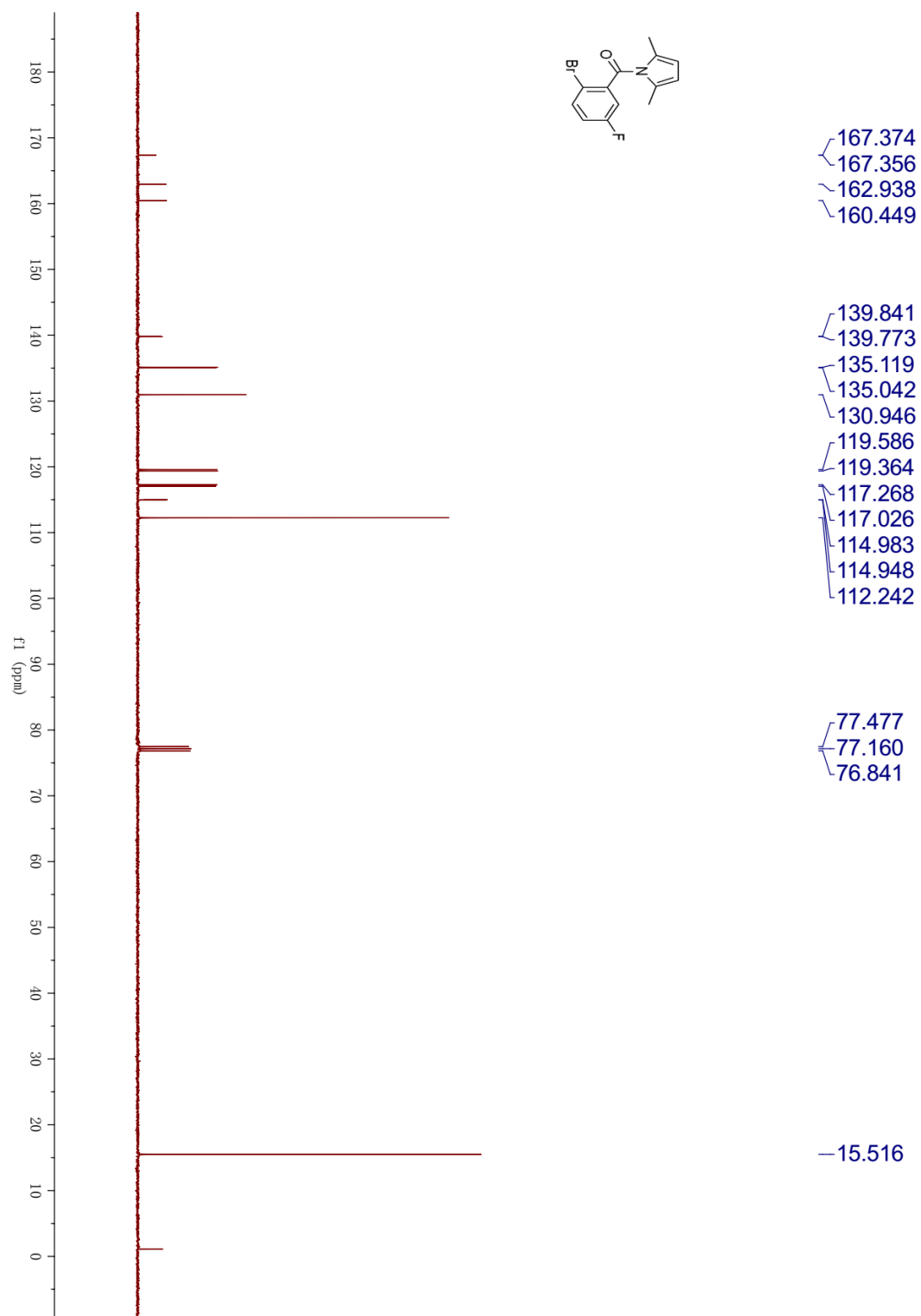


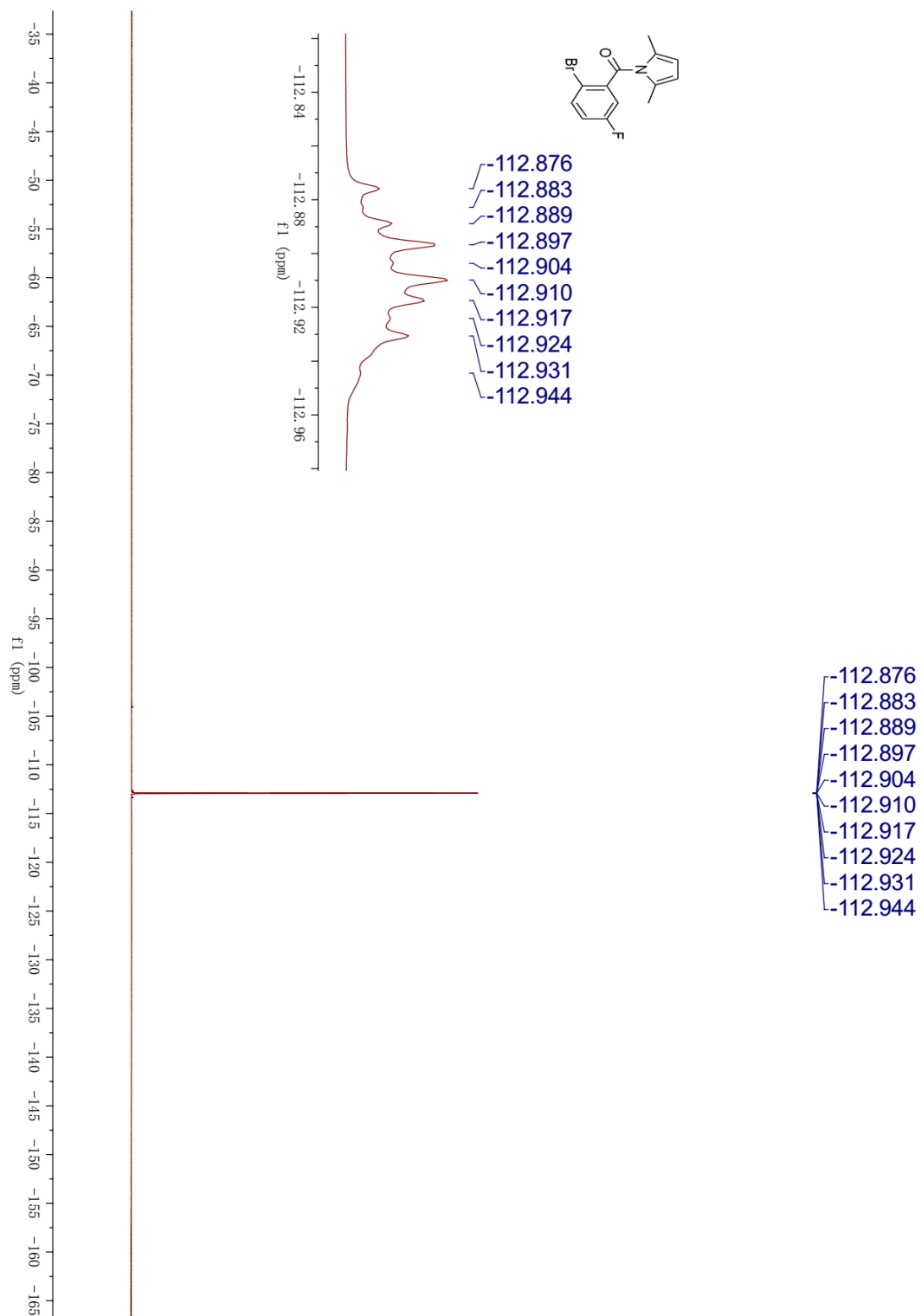
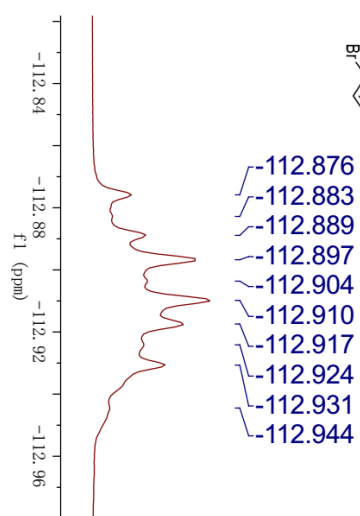
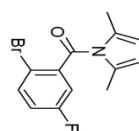




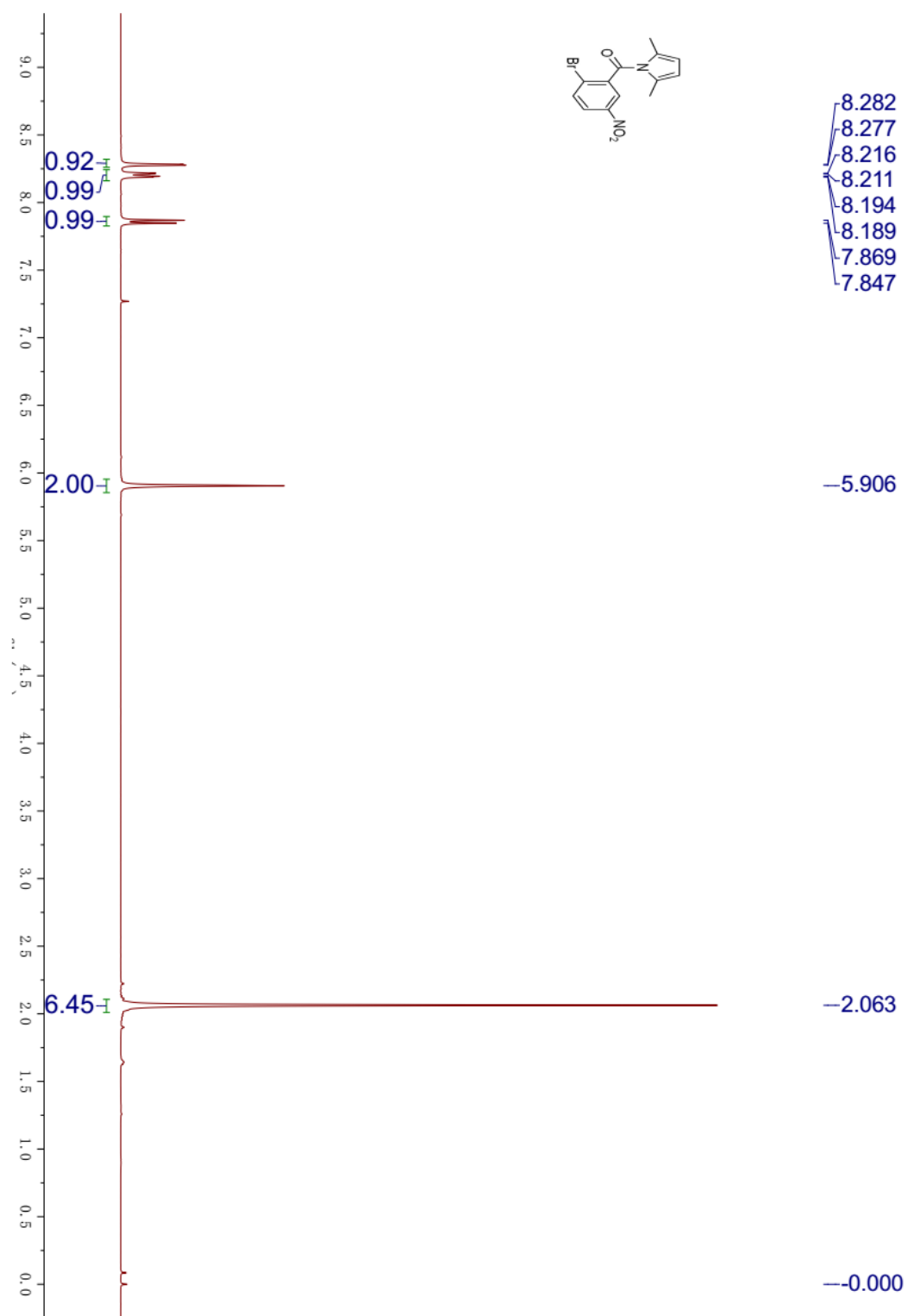
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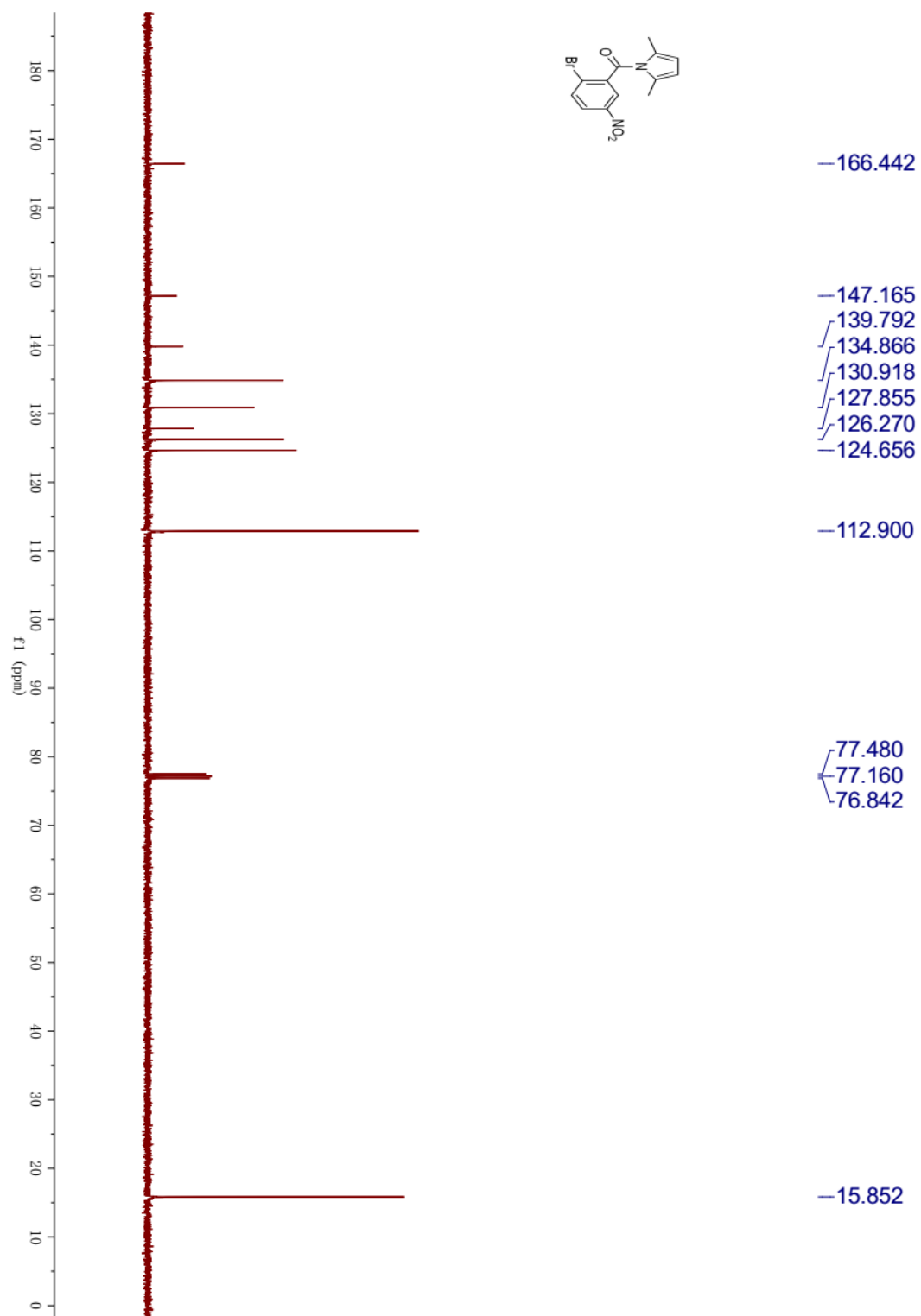




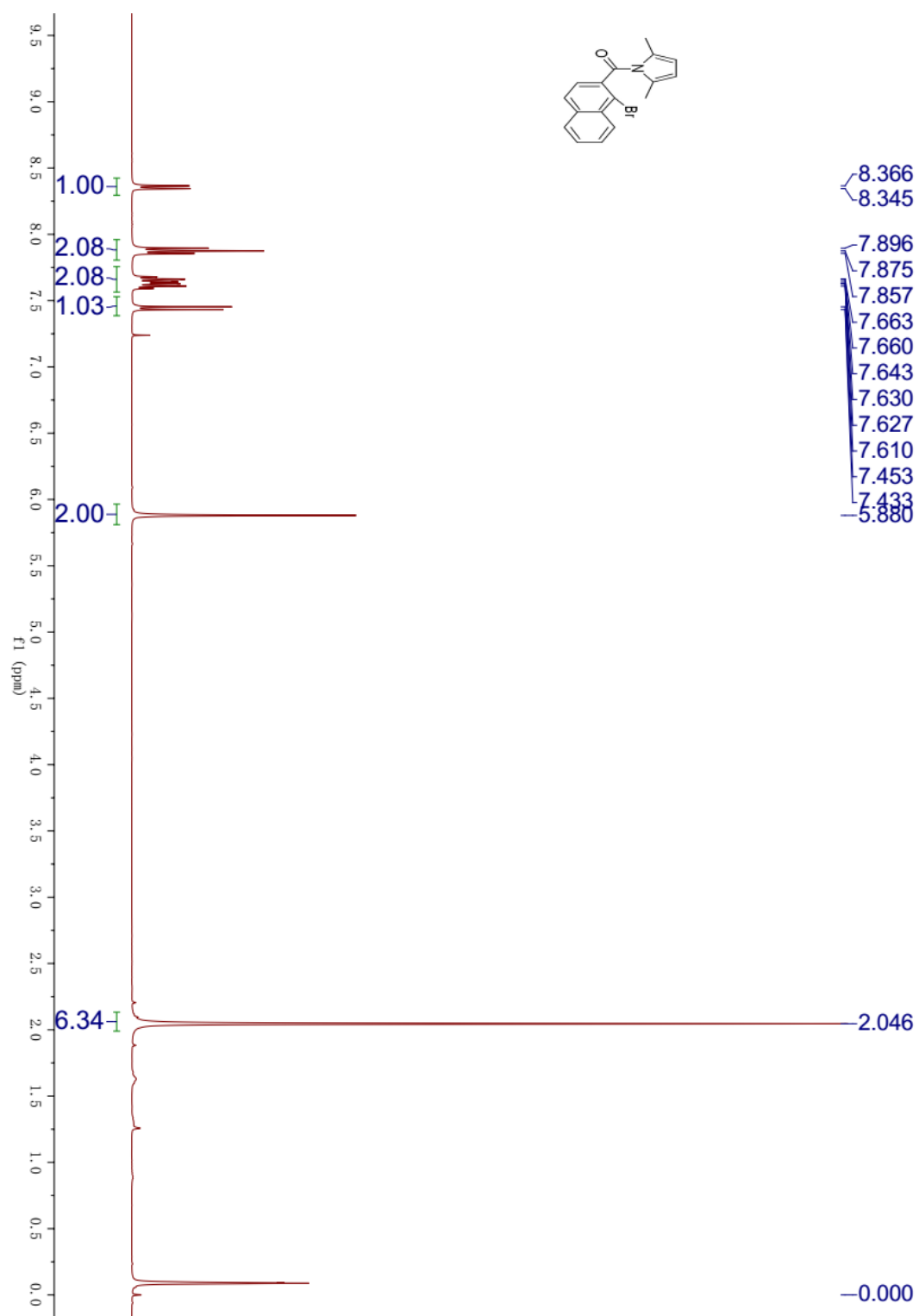


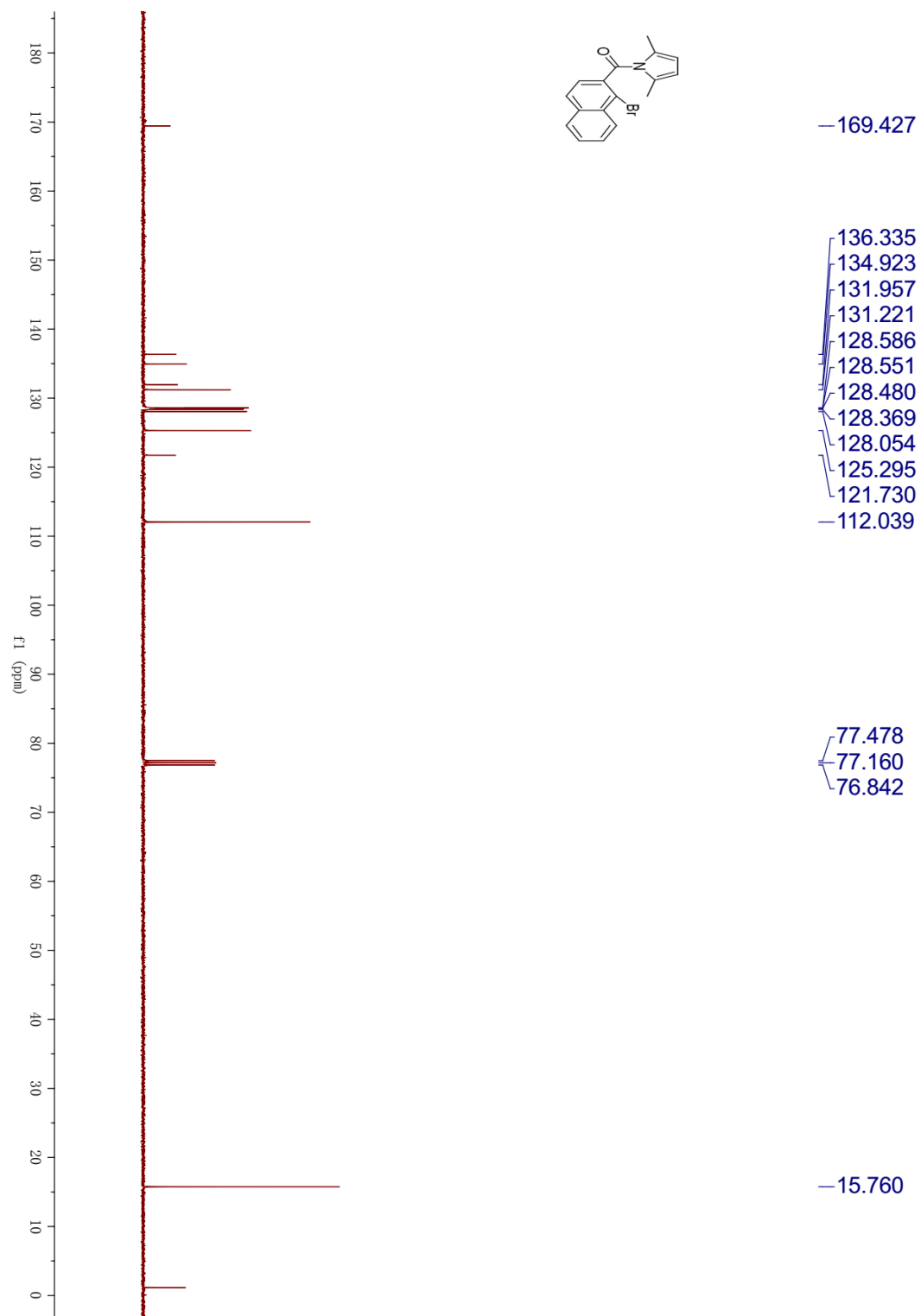
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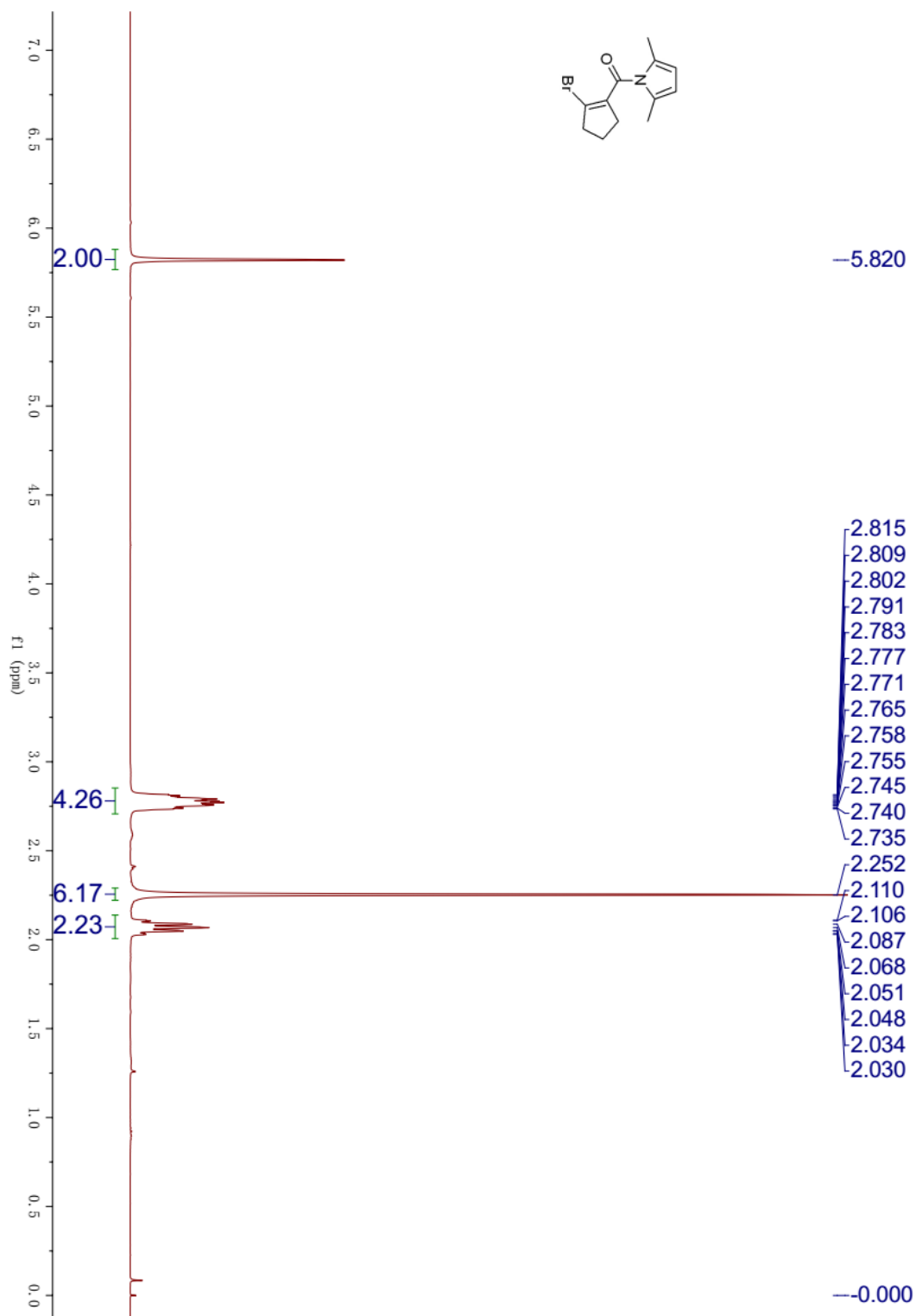


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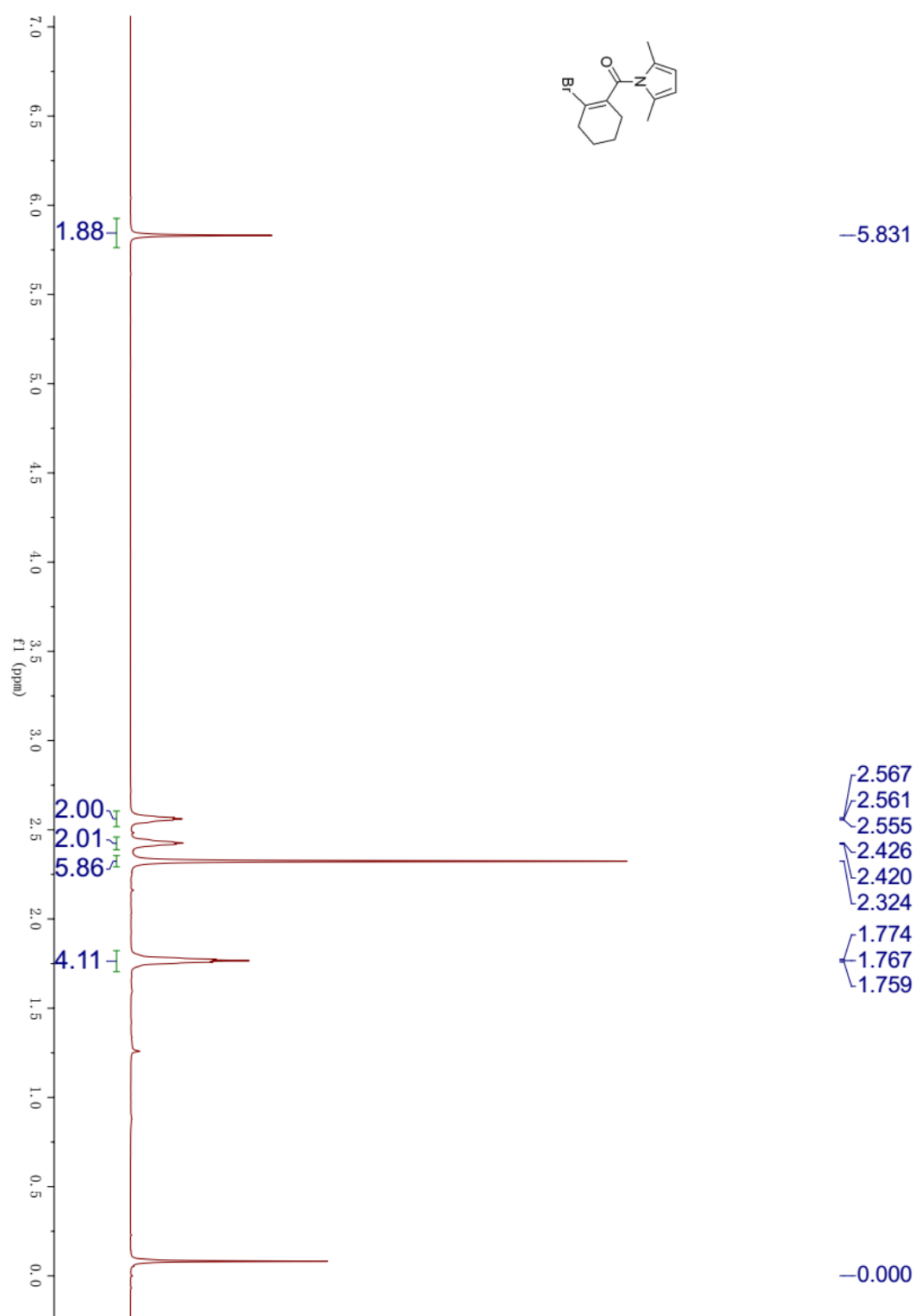




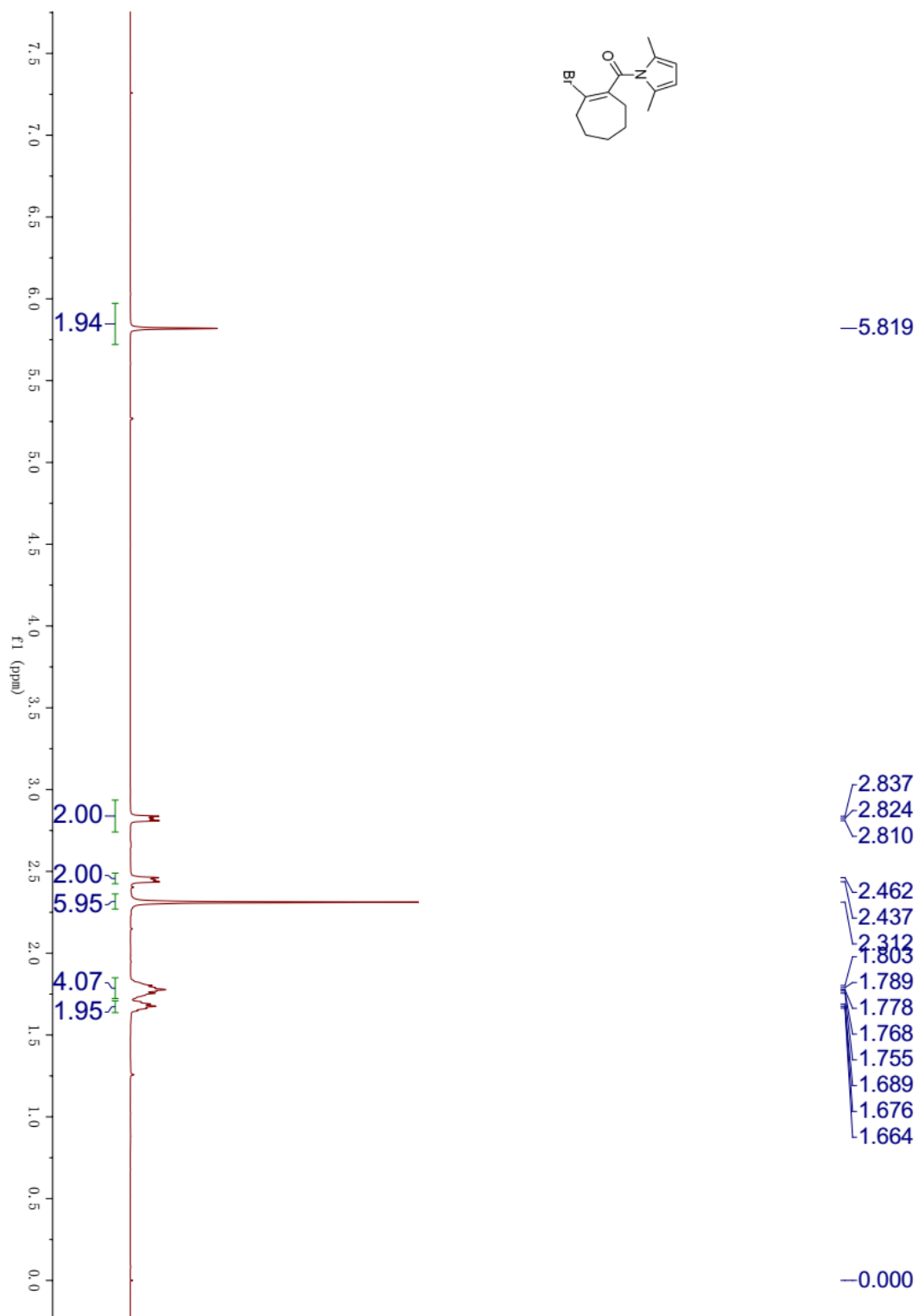
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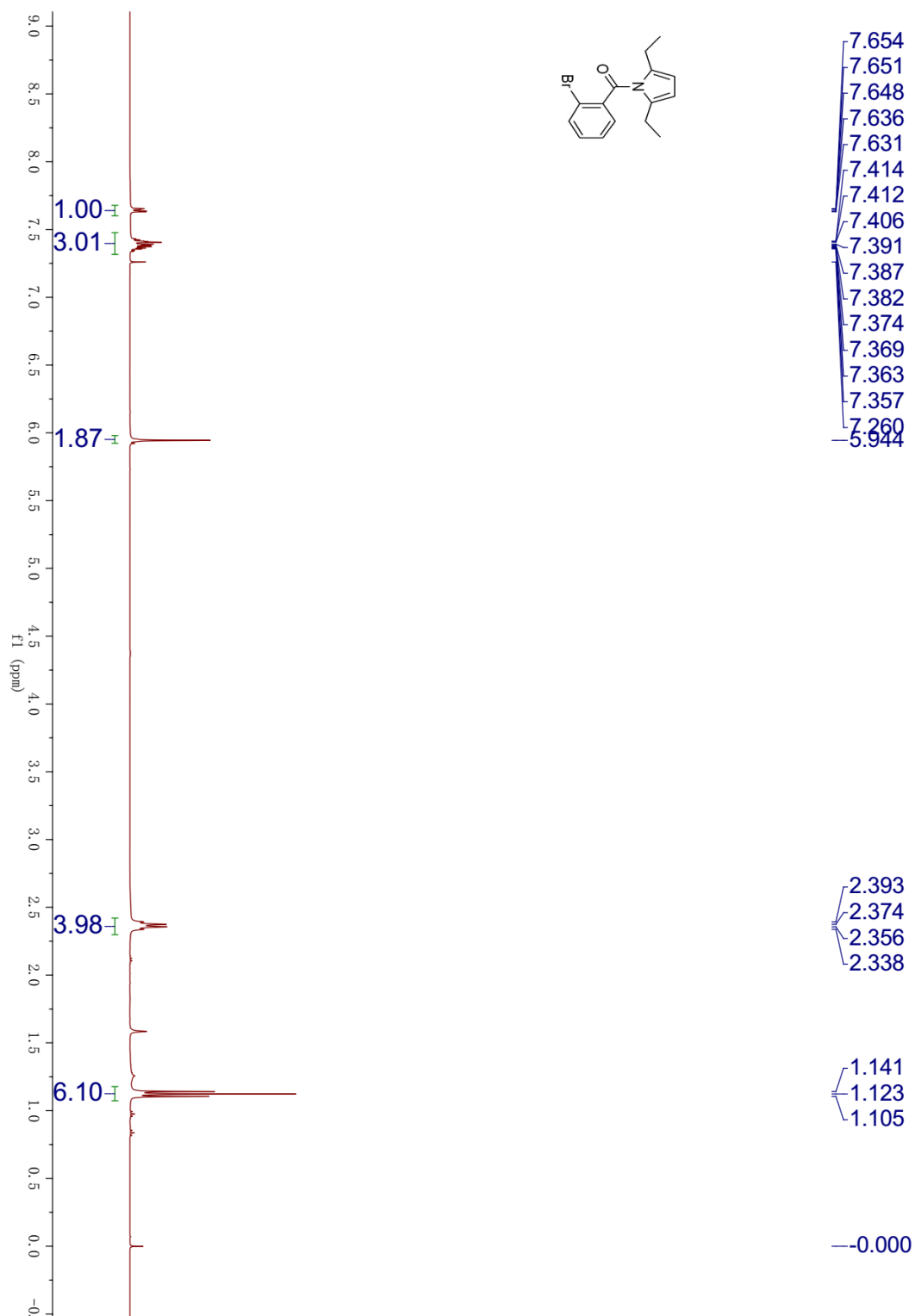
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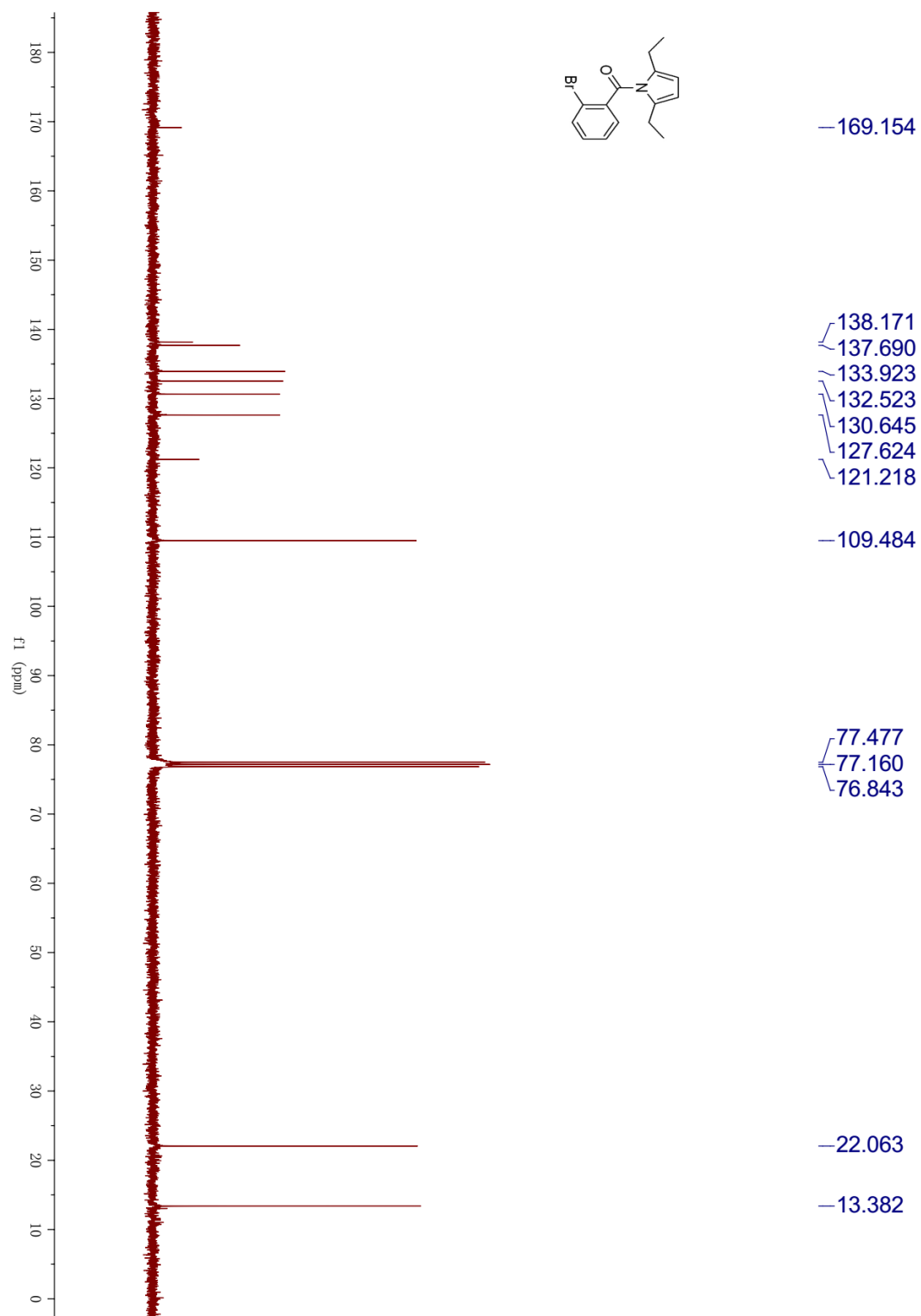


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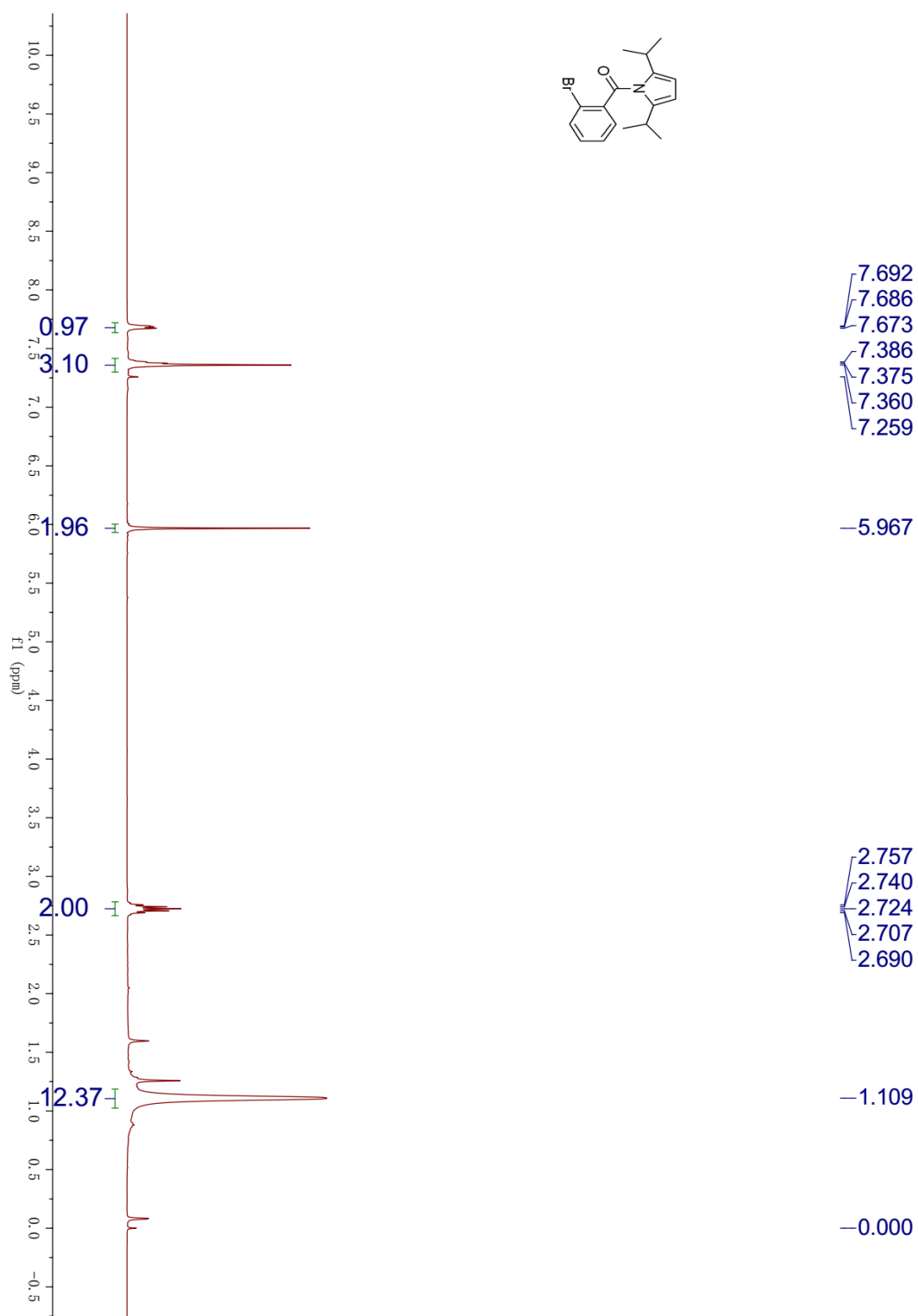


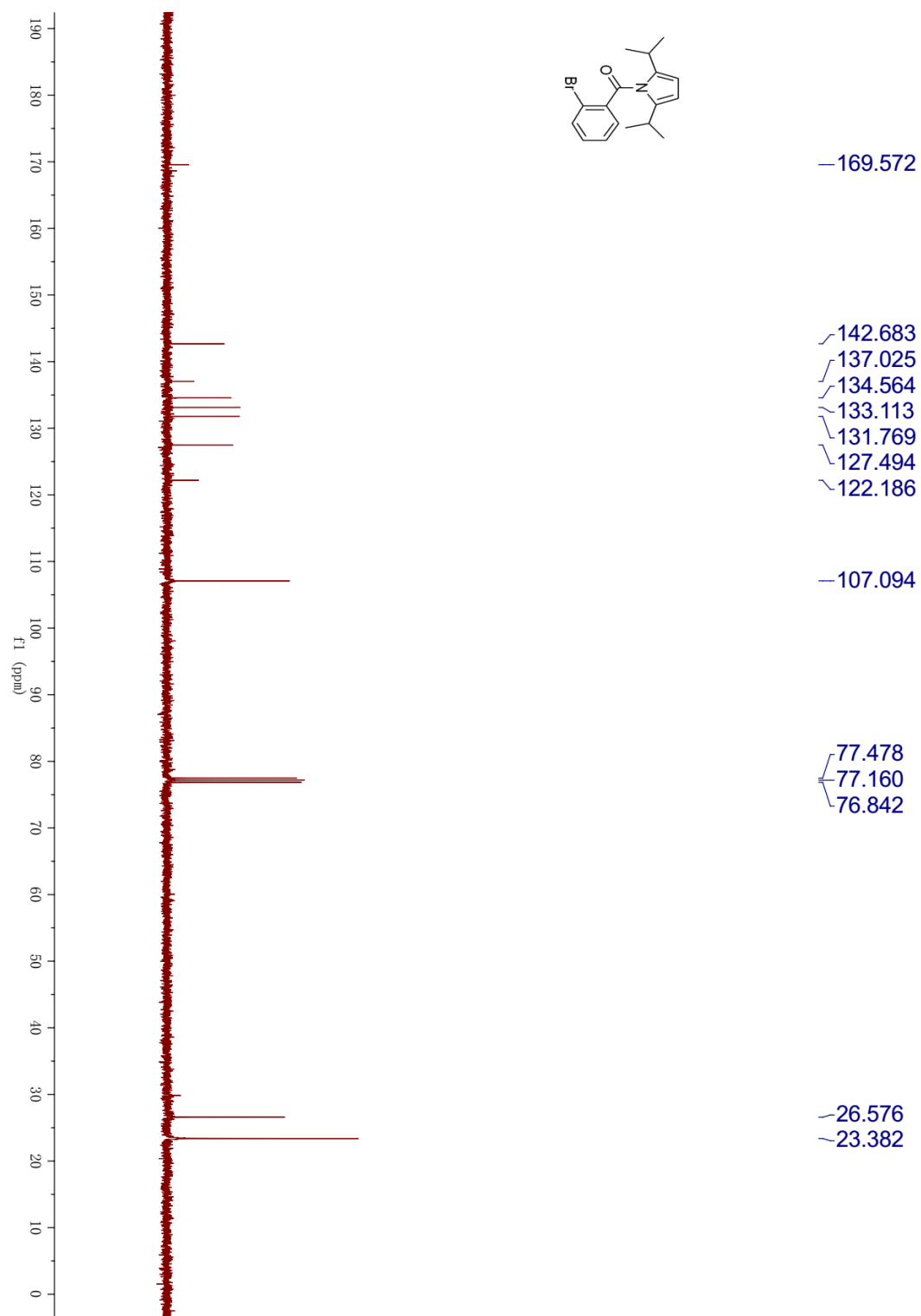
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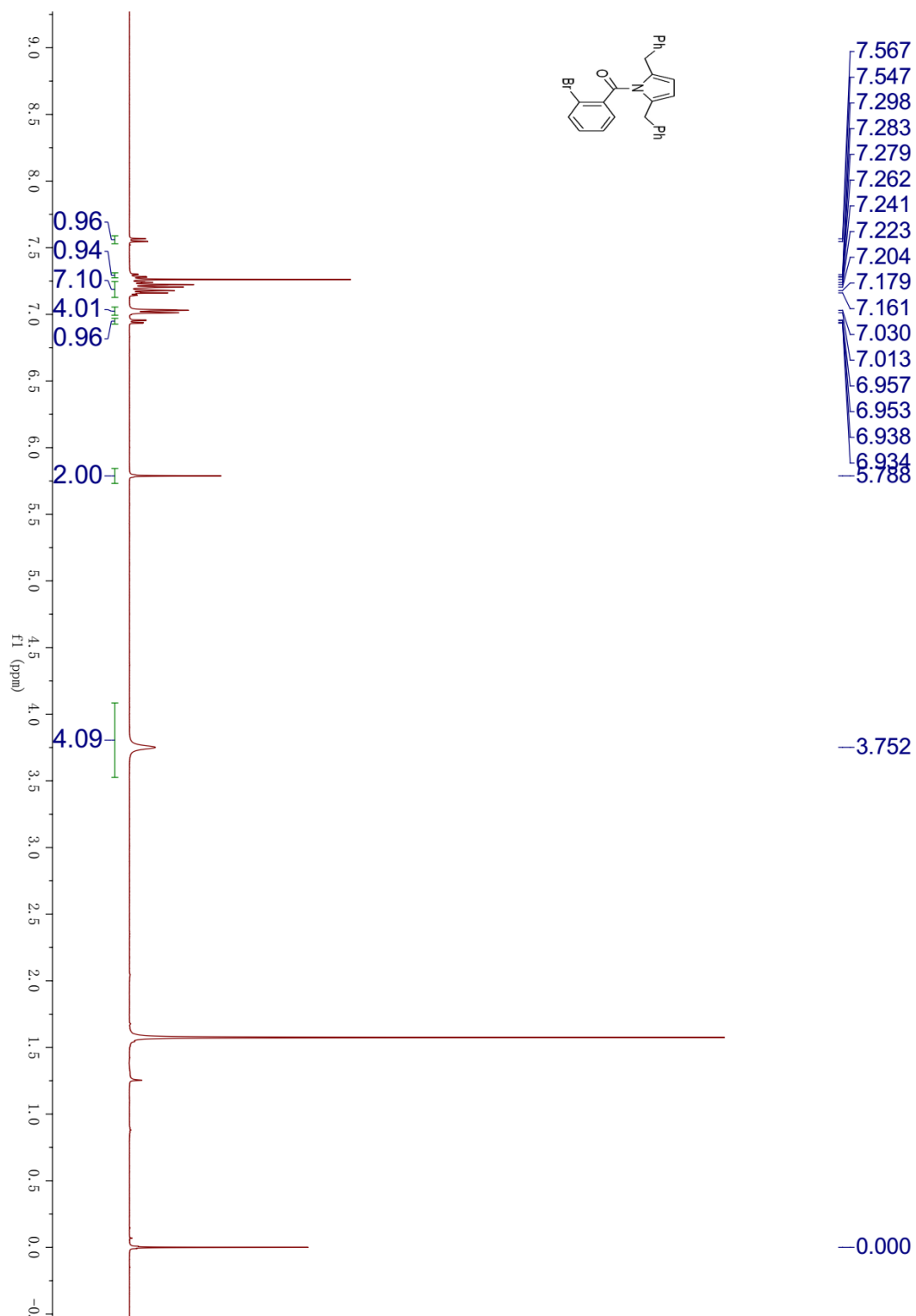


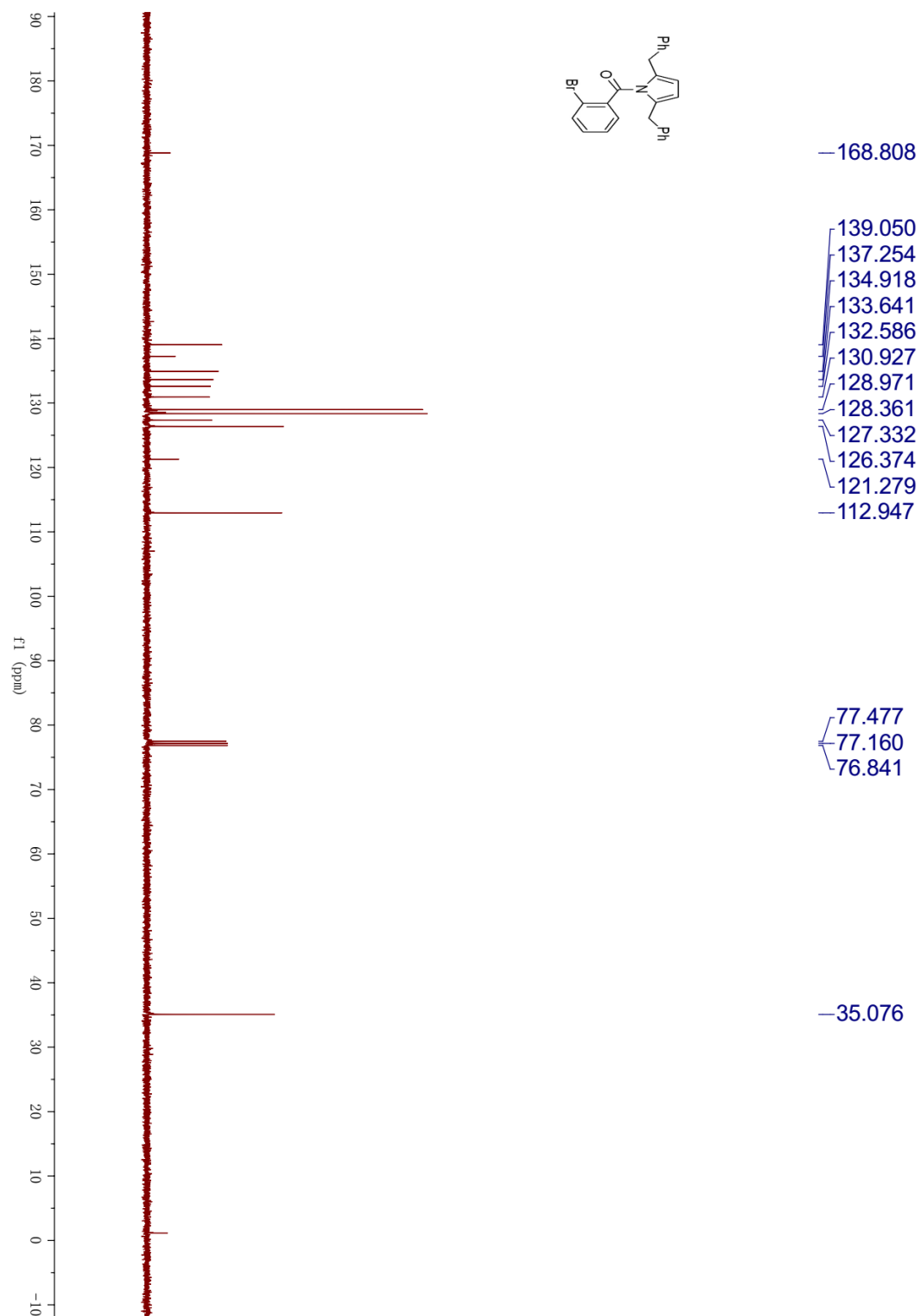
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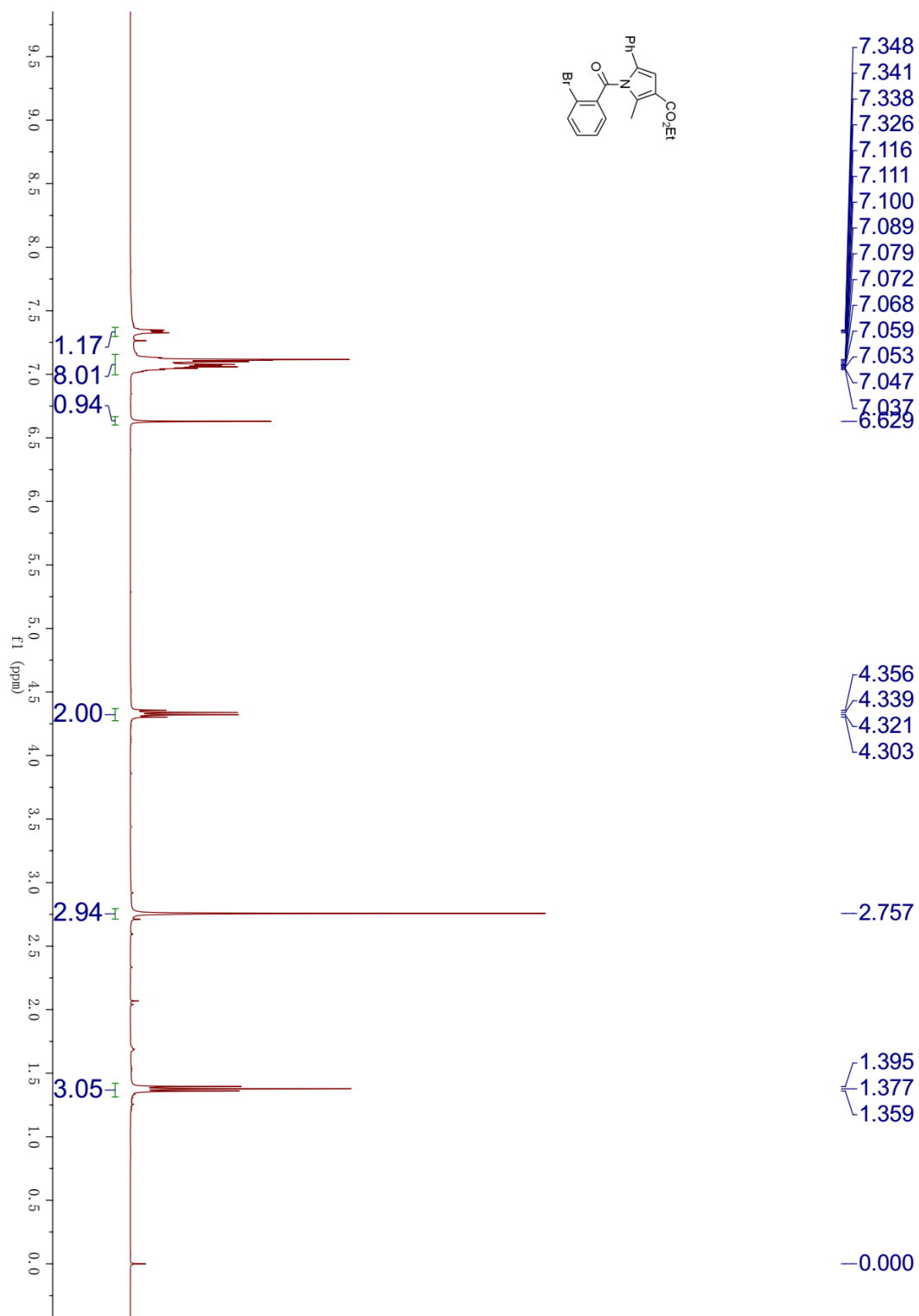


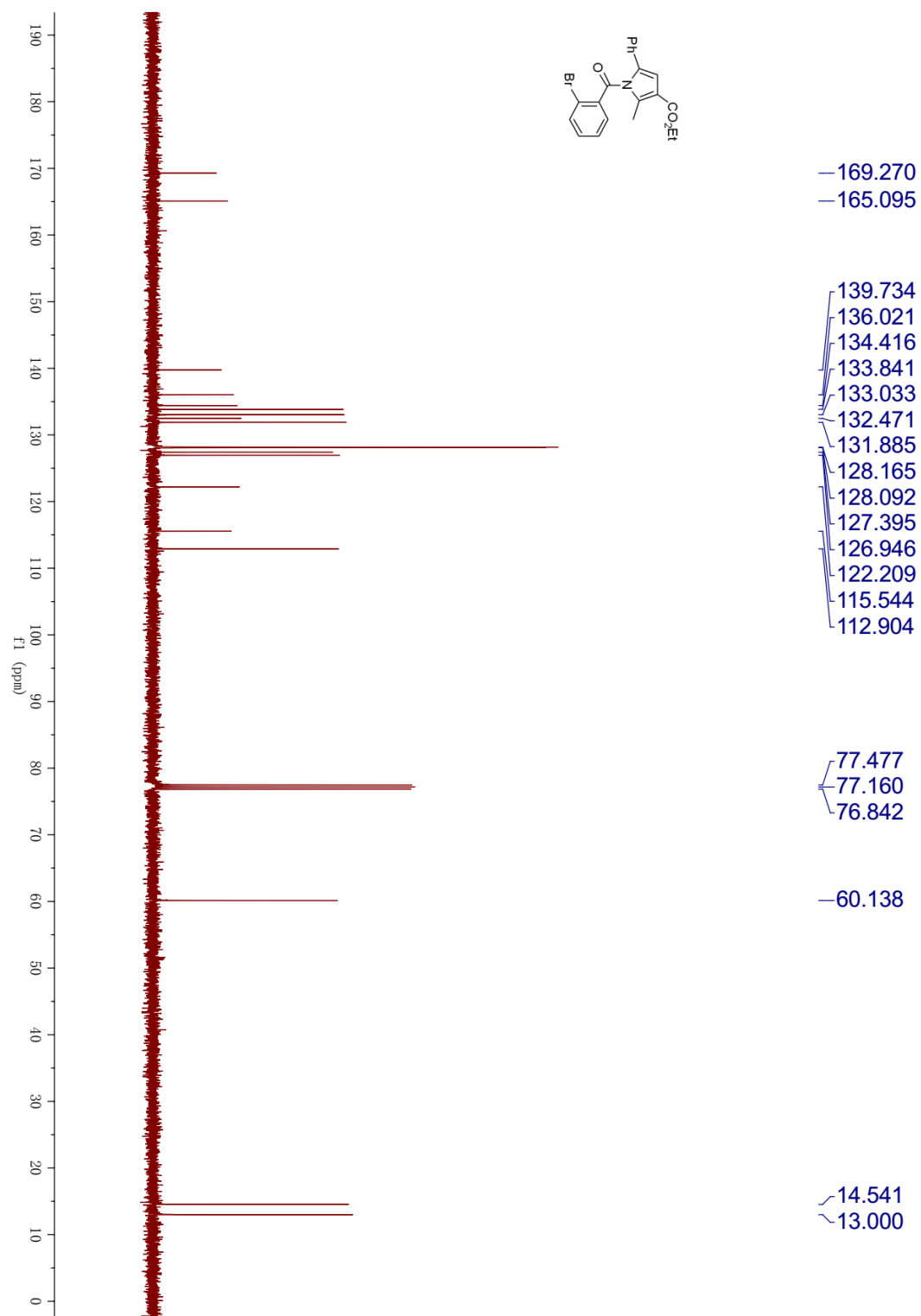
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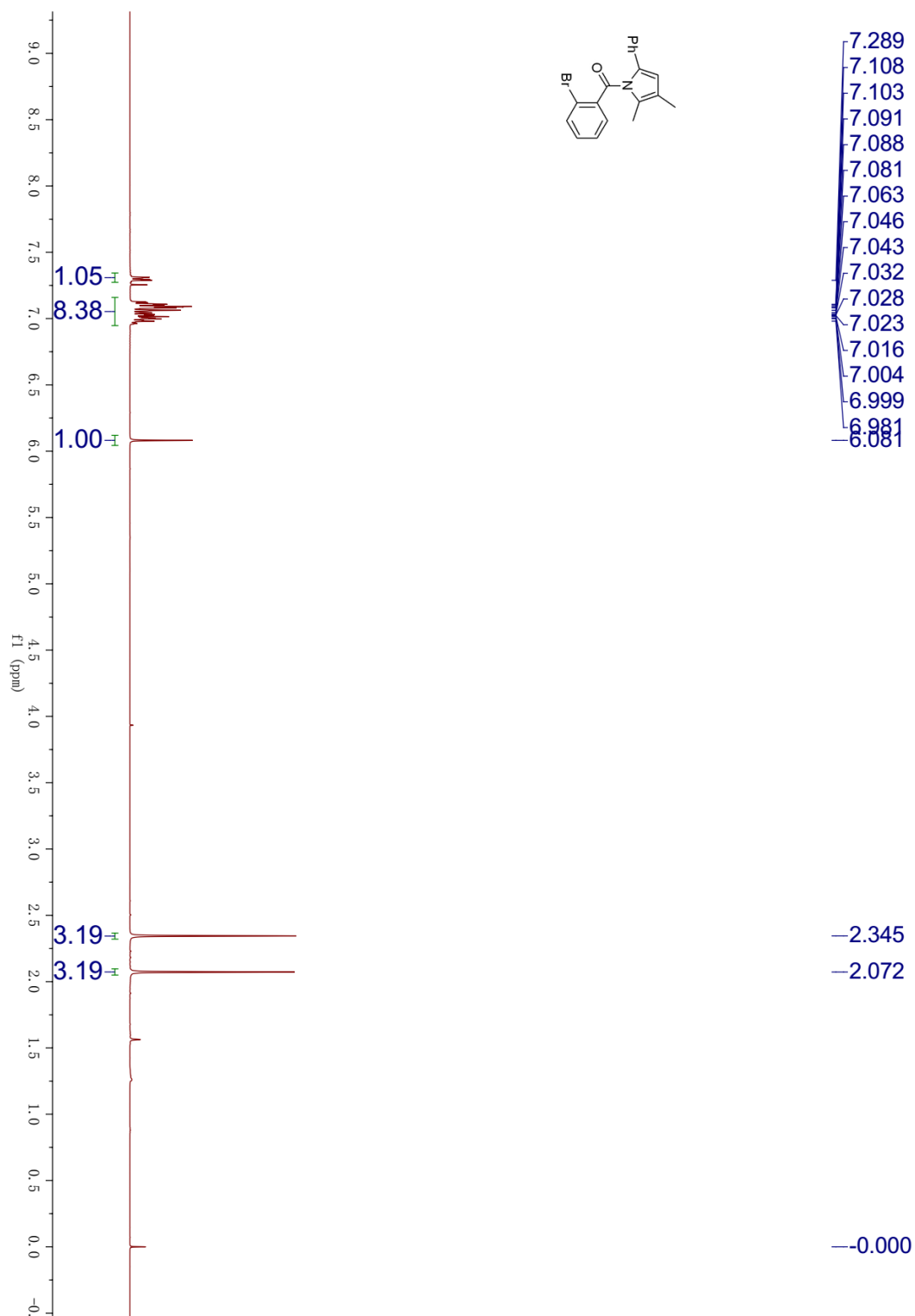


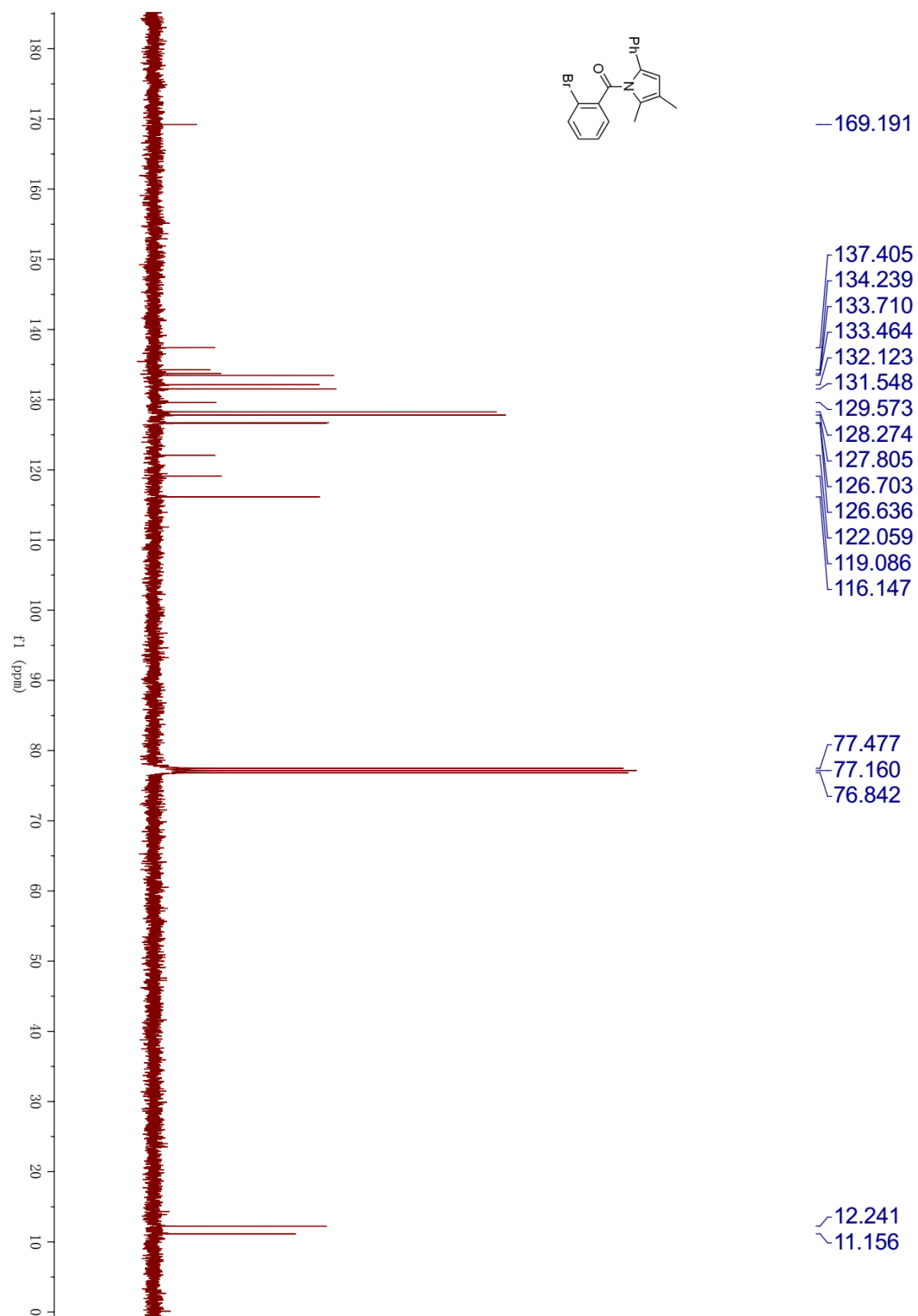
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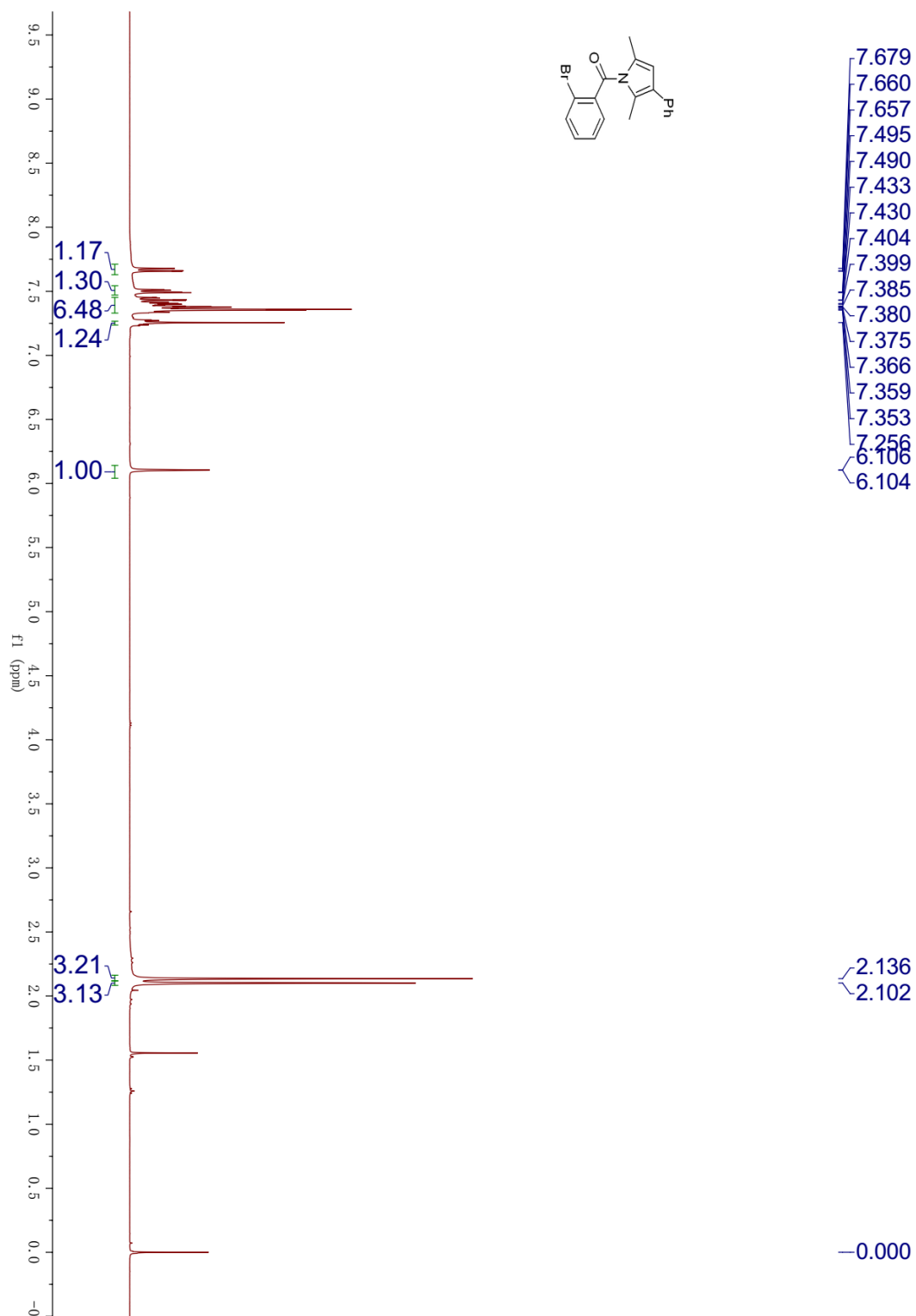


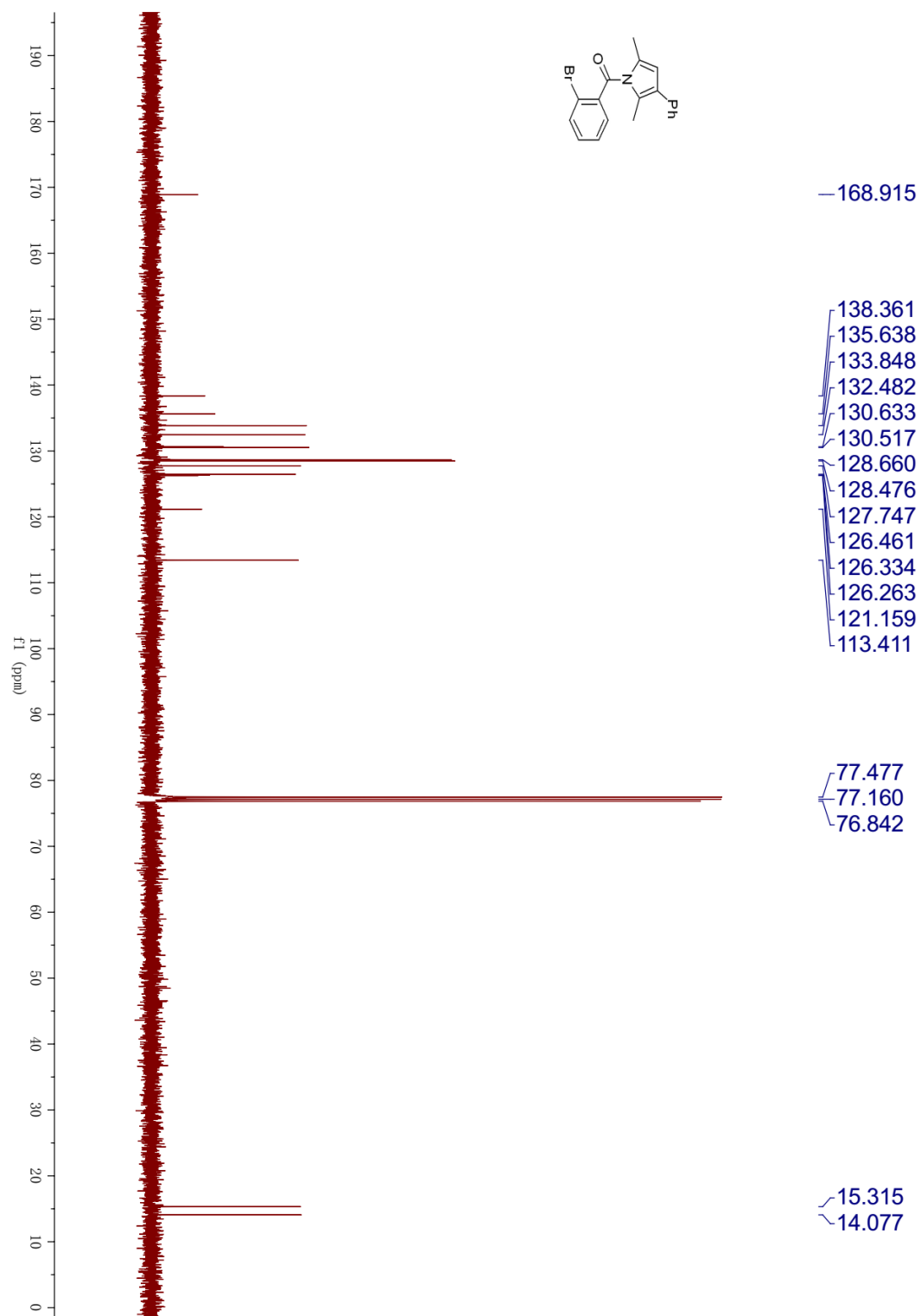
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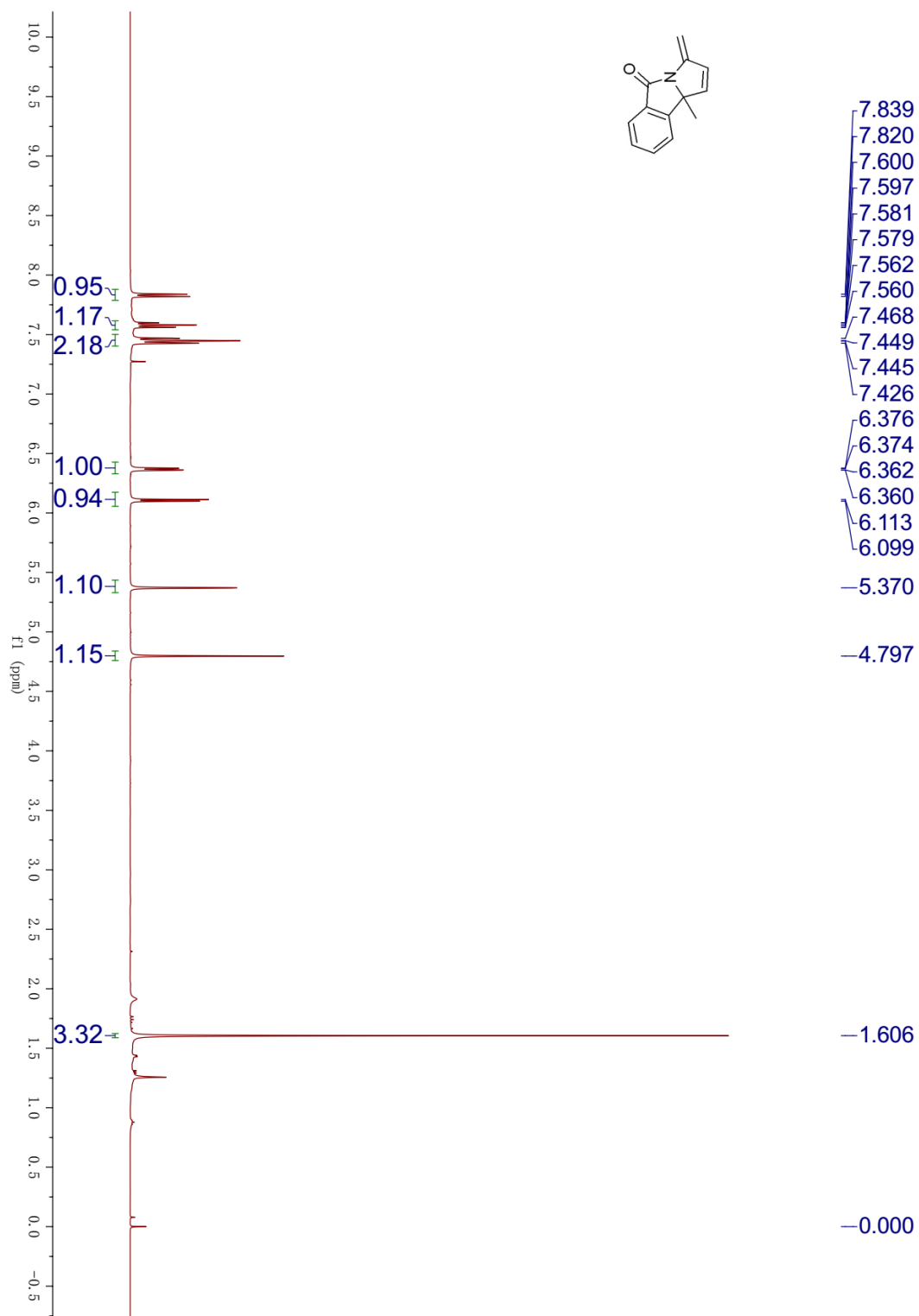


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2aa:



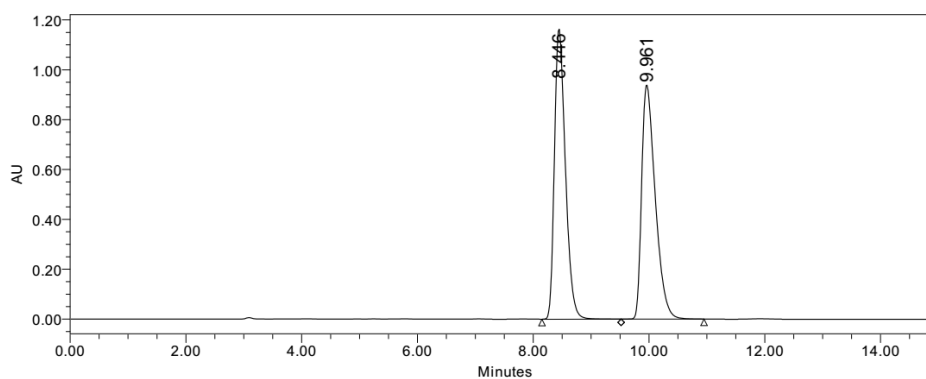
# HPLC of 2aa (racemic)



## Multi Sample Summary

### SAMPLE INFORMATION

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| Sample Name:      | yp-6-31-2-rac             | Acquired By:        | System          |
| Sample Type:      | Unknown                   | Sample Set Name:    | 1               |
| Vial:             | 1:A,2                     | Acq. Method Set:    | YP9505254       |
| Injection #:      | 1                         | Processing Method   | 1               |
| Injection Volume: | 10.00 ul                  | Channel Name:       | W2489 ChA       |
| Run Time:         | 15.0 Minutes              | Proc. Chnl. Descr.: | W2489 ChA 254nm |
| Date Acquired:    | 4/18/2018 12:26:56 PM CST |                     |                 |
| Date Processed:   | 7/18/2018 12:27:50 AM CST |                     |                 |



|   | RT    | Area     | % Area | Height  |
|---|-------|----------|--------|---------|
| 1 | 8.446 | 15323380 | 50.00  | 1164024 |
| 2 | 9.961 | 15324700 | 50.00  | 939728  |

Reported by User: System  
 Report Method: Multi Sample Summary  
 Report Method ID 1007  
 Page: 1 of 1

Project Name: yangping  
 Date Printed:  
 7/18/2018  
 12:28:53 AM PRC

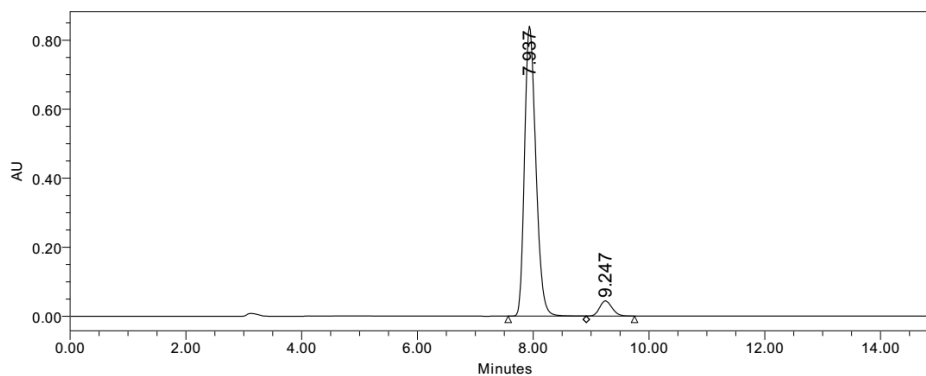
# HPLC of 2aa (chiral)



## Multi Sample Summary

### SAMPLE INFORMATION

|                   |                           |                     |                 |
|-------------------|---------------------------|---------------------|-----------------|
| Sample Name:      | yp-6-102                  | Acquired By:        | System          |
| Sample Type:      | Unknown                   | Sample Set Name:    | 1               |
| Vial:             | 1:A,2                     | Acq. Method Set:    | YP9505254       |
| Injection #:      | 1                         | Processing Method   | 1               |
| Injection Volume: | 10.00 ul                  | Channel Name:       | W2489 ChA       |
| Run Time:         | 15.0 Minutes              | Proc. Chnl. Descr.: | W2489 ChA 254nm |
| Date Acquired:    | 5/17/2018 4:56:06 PM CST  |                     |                 |
| Date Processed:   | 10/25/2018 9:07:28 AM CST |                     |                 |

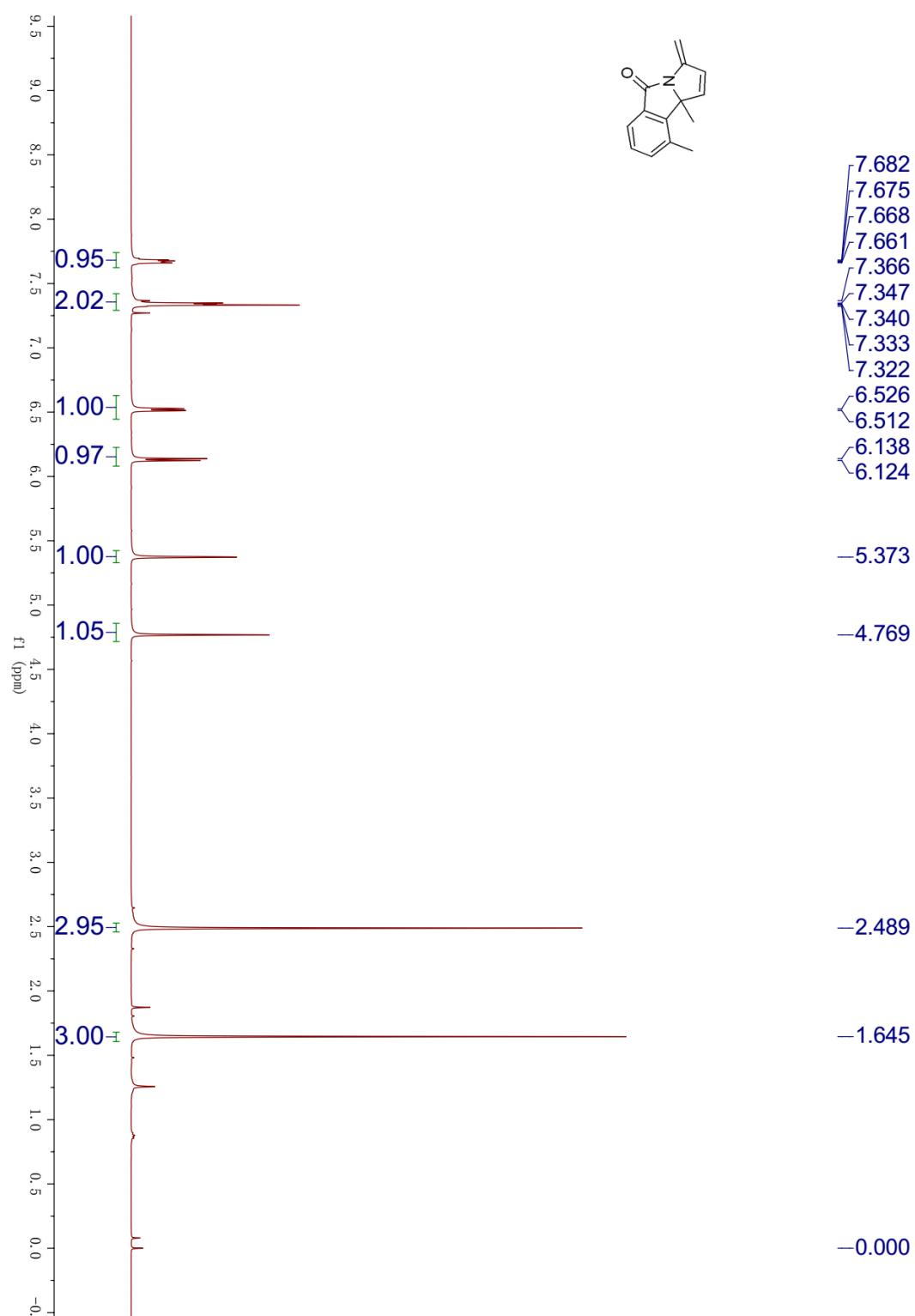


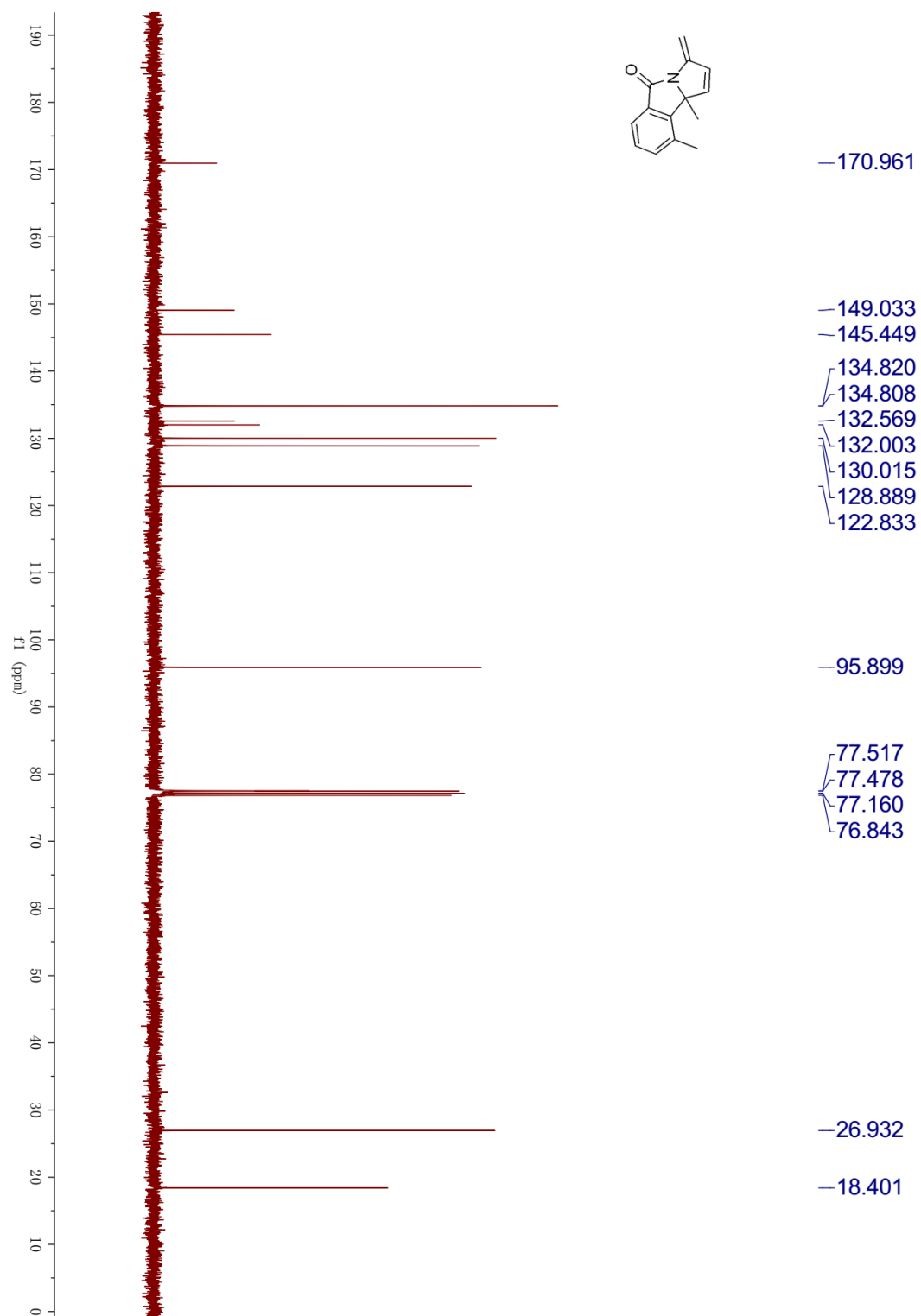
|   | RT    | Area     | % Area | Height |
|---|-------|----------|--------|--------|
| 1 | 7.937 | 11365603 | 94.47  | 840329 |
| 2 | 9.247 | 665071   | 5.53   | 44016  |

Reported by User: System  
 Report Method: Multi Sample Summary  
 Report Method ID 1007  
 Page: 1 of 1

Project Name: yangping  
 Date Printed:  
 10/25/2018  
 9:07:46 AM PRC

2ab:





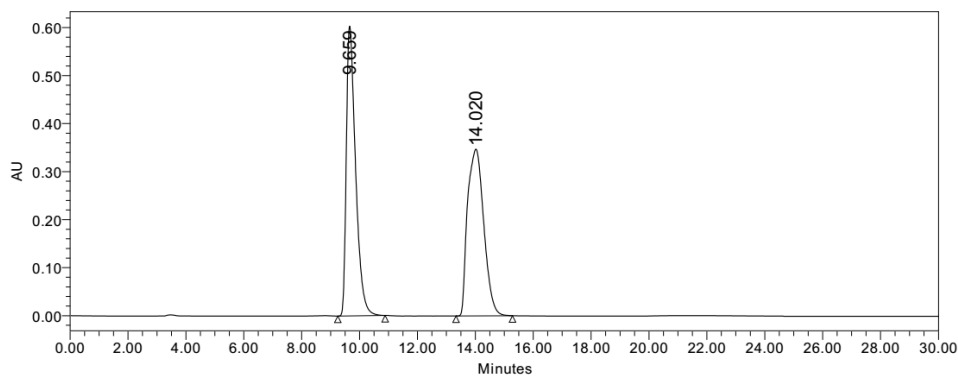
# HPLC of **2ab** (racemic)



## Multi Sample Summary

### SAMPLE INFORMATION

|                                            |              |                     |                 |
|--------------------------------------------|--------------|---------------------|-----------------|
| Sample Name:                               | yp-7-23-rac  | Acquired By:        | System          |
| Sample Type:                               | Unknown      | Sample Set Name:    | 1               |
| Vial:                                      | 1:A,2        | Acq. Method Set:    | YP9505254       |
| Injection #:                               | 1            | Processing Method   | 1               |
| Injection Volume:                          | 10.00 ul     | Channel Name:       | W2489 ChA       |
| Run Time:                                  | 30.0 Minutes | Proc. Chnl. Descr.: | W2489 ChA 254nm |
| Date Acquired: 5/23/2018 10:20:20 AM CST   |              |                     |                 |
| Date Processed: 10/25/2018 12:11:09 PM CST |              |                     |                 |



|   | RT     | Area     | % Area | Height |
|---|--------|----------|--------|--------|
| 1 | 9.659  | 13435094 | 49.84  | 604639 |
| 2 | 14.020 | 13520003 | 50.16  | 347229 |

Reported by User: System  
 Report Method: Multi Sample Summary  
 Report Method ID 1007  
 Page: 1 of 1

Project Name: yangping  
 Date Printed:  
 10/25/2018  
 12:11:42 PM PRC

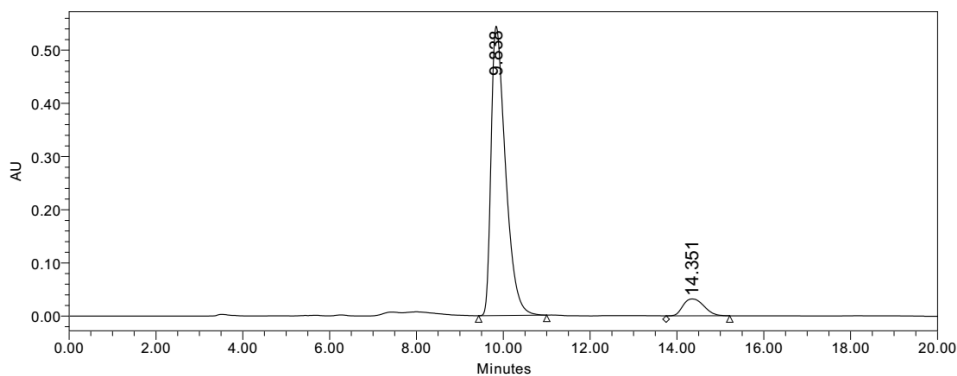
# HPLC of **2ab** (chiral)



## Multi Sample Summary

### SAMPLE INFORMATION

|                   |                           |                     |                 |
|-------------------|---------------------------|---------------------|-----------------|
| Sample Name:      | yp-7-28-2                 | Acquired By:        | System          |
| Sample Type:      | Unknown                   | Sample Set Name:    | 1               |
| Vial:             | 1:A,2                     | Acq. Method Set:    | YP9505254       |
| Injection #:      | 1                         | Processing Method   | 1               |
| Injection Volume: | 10.00 ul                  | Channel Name:       | W2489 ChA       |
| Run Time:         | 20.0 Minutes              | Proc. Chnl. Descr.: | W2489 ChA 254nm |
| Date Acquired:    | 5/23/2018 10:46:09 PM CST |                     |                 |
| Date Processed:   | 10/24/2018 2:17:42 PM CST |                     |                 |

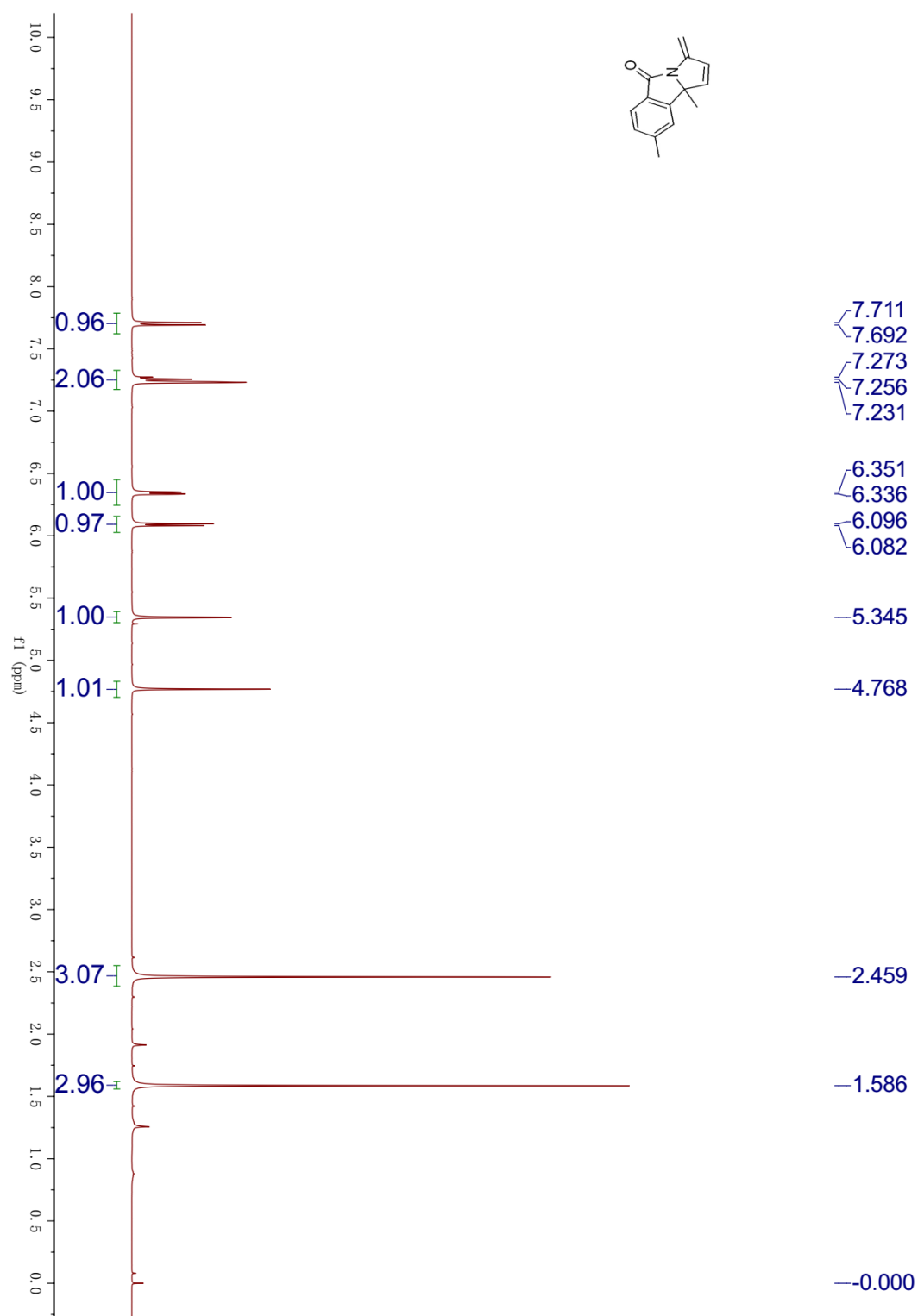


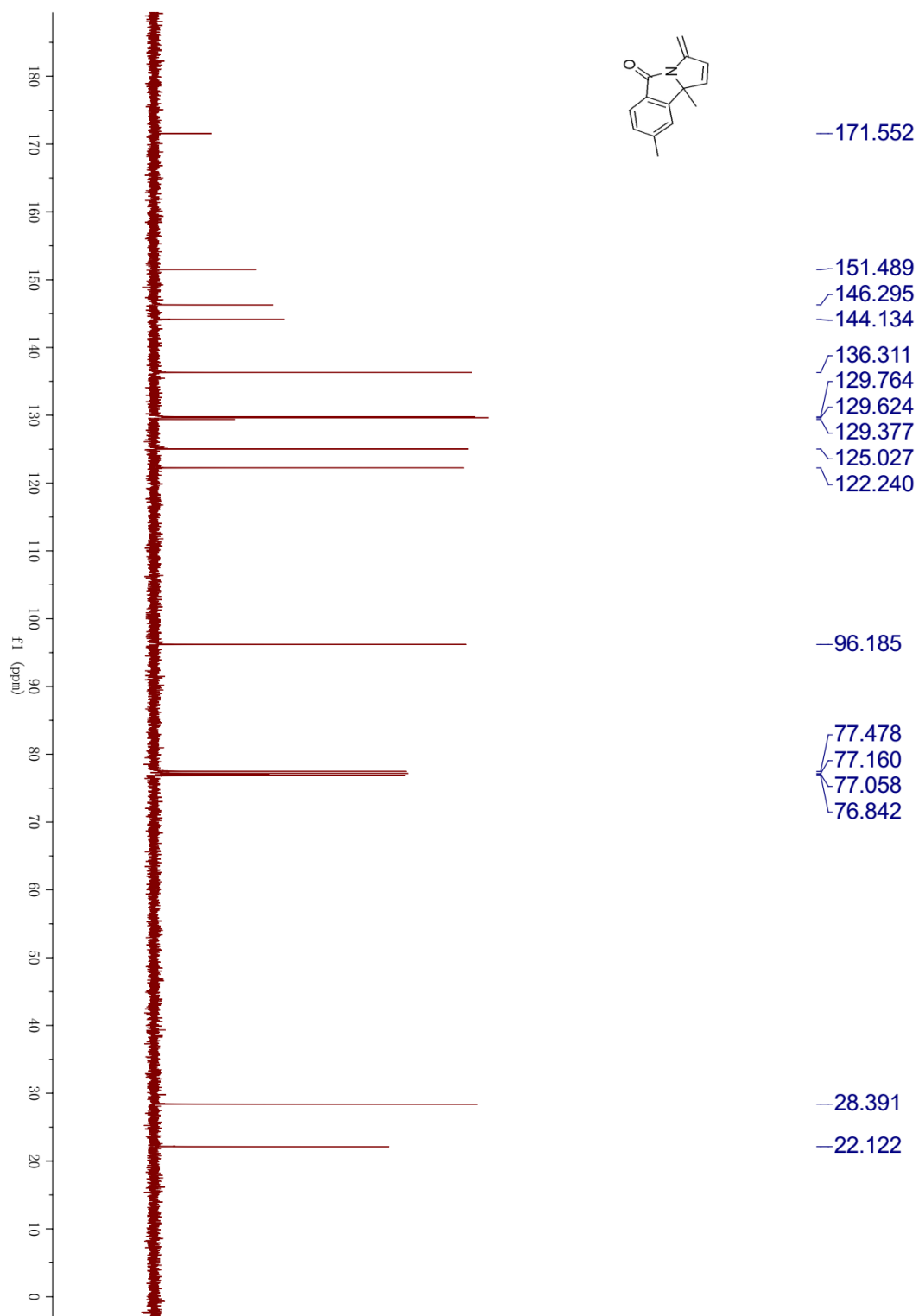
|   | RT     | Area     | % Area | Height |
|---|--------|----------|--------|--------|
| 1 | 9.838  | 12525164 | 92.17  | 544300 |
| 2 | 14.351 | 1063643  | 7.83   | 31823  |

Reported by User: System  
 Report Method: Multi Sample Summary  
 Report Method ID 1007  
 Page: 1 of 1

Project Name: yangping  
 Date Printed:  
 10/24/2018  
 2:18:11 PM PRC

2ac:





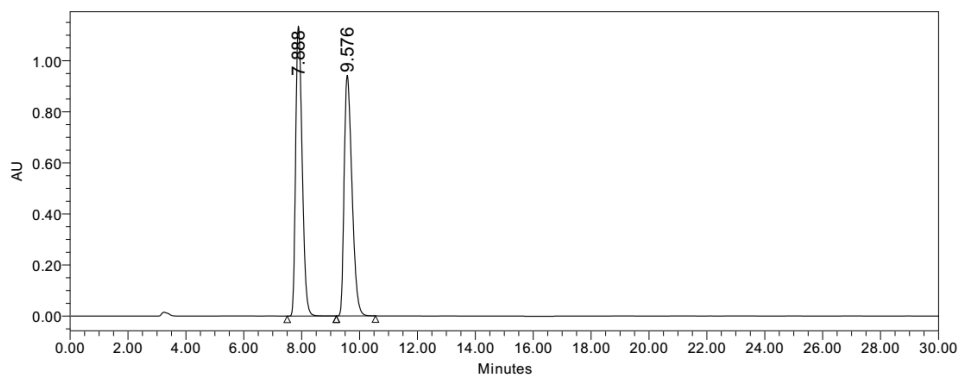
# HPLC of 2ac (racemic)



## Multi Sample Summary

### SAMPLE INFORMATION

|                   |                           |                     |                 |
|-------------------|---------------------------|---------------------|-----------------|
| Sample Name:      | yp-7-24-rac               | Acquired By:        | System          |
| Sample Type:      | Unknown                   | Sample Set Name:    | 1               |
| Vial:             | 1:A,3                     | Acq. Method Set:    | YP9505254       |
| Injection #:      | 1                         | Processing Method   | 1q              |
| Injection Volume: | 10.00 ul                  | Channel Name:       | W2489 ChA       |
| Run Time:         | 30.0 Minutes              | Proc. Chnl. Descr.: | W2489 ChA 254nm |
| Date Acquired:    | 5/23/2018 1:29:51 AM CST  |                     |                 |
| Date Processed:   | 7/18/2018 12:20:25 AM CST |                     |                 |



|   | RT    | Area     | % Area | Height  |
|---|-------|----------|--------|---------|
| 1 | 7.888 | 17724501 | 50.02  | 1135988 |
| 2 | 9.576 | 17710057 | 49.98  | 944521  |

Reported by User: System  
 Report Method: Multi Sample Summary  
 Report Method ID 1007  
 Page: 1 of 1

Project Name: yangping  
 Date Printed:  
 7/18/2018  
 12:21:06 AM PRC

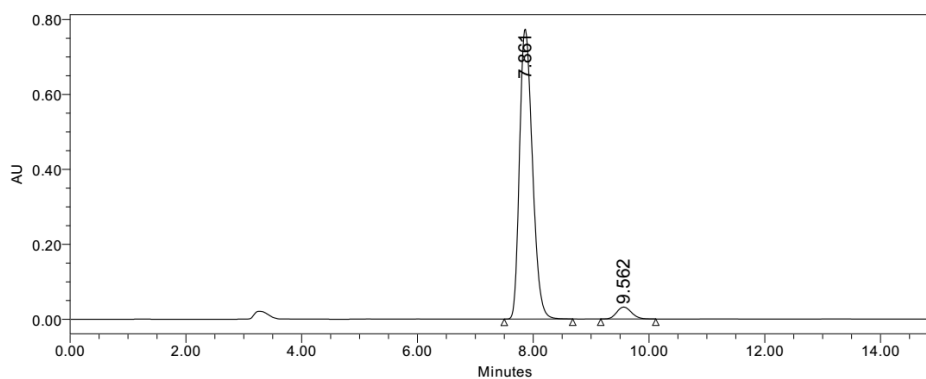
# HPLC of 2ac (chiral)



## Multi Sample Summary

### SAMPLE INFORMATION

|                   |                           |                     |                 |
|-------------------|---------------------------|---------------------|-----------------|
| Sample Name:      | yp-7-29-2                 | Acquired By:        | System          |
| Sample Type:      | Unknown                   | Sample Set Name:    | 1               |
| Vial:             | 1:A,2                     | Acq. Method Set:    | YP9505254       |
| Injection #:      | 1                         | Processing Method   | 1               |
| Injection Volume: | 10.00 ul                  | Channel Name:       | W2489 ChA       |
| Run Time:         | 15.0 Minutes              | Proc. Chnl. Descr.: | W2489 ChA 254nm |
| Date Acquired:    | 5/23/2018 8:41:05 PM CST  |                     |                 |
| Date Processed:   | 10/24/2018 8:19:00 AM CST |                     |                 |

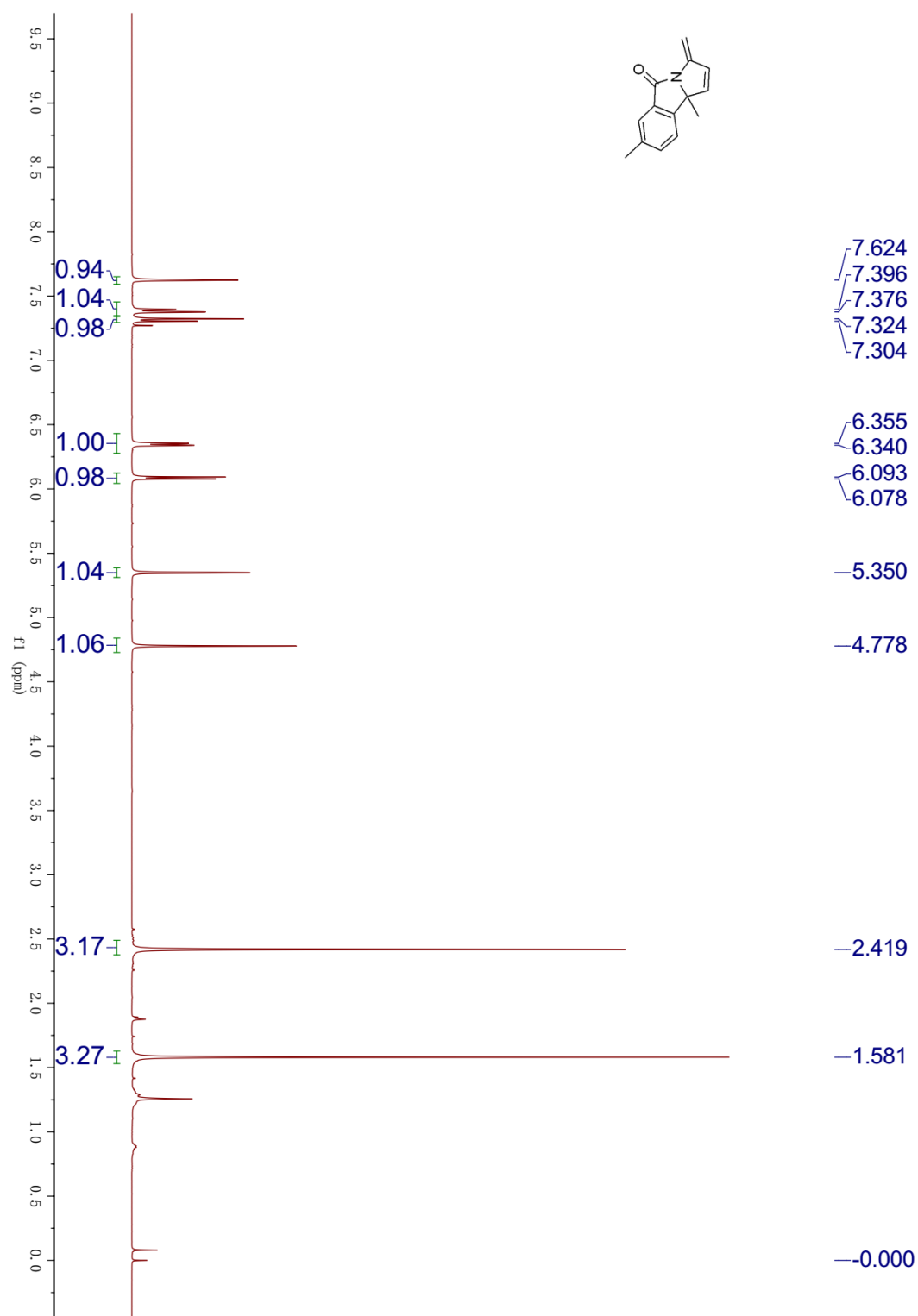


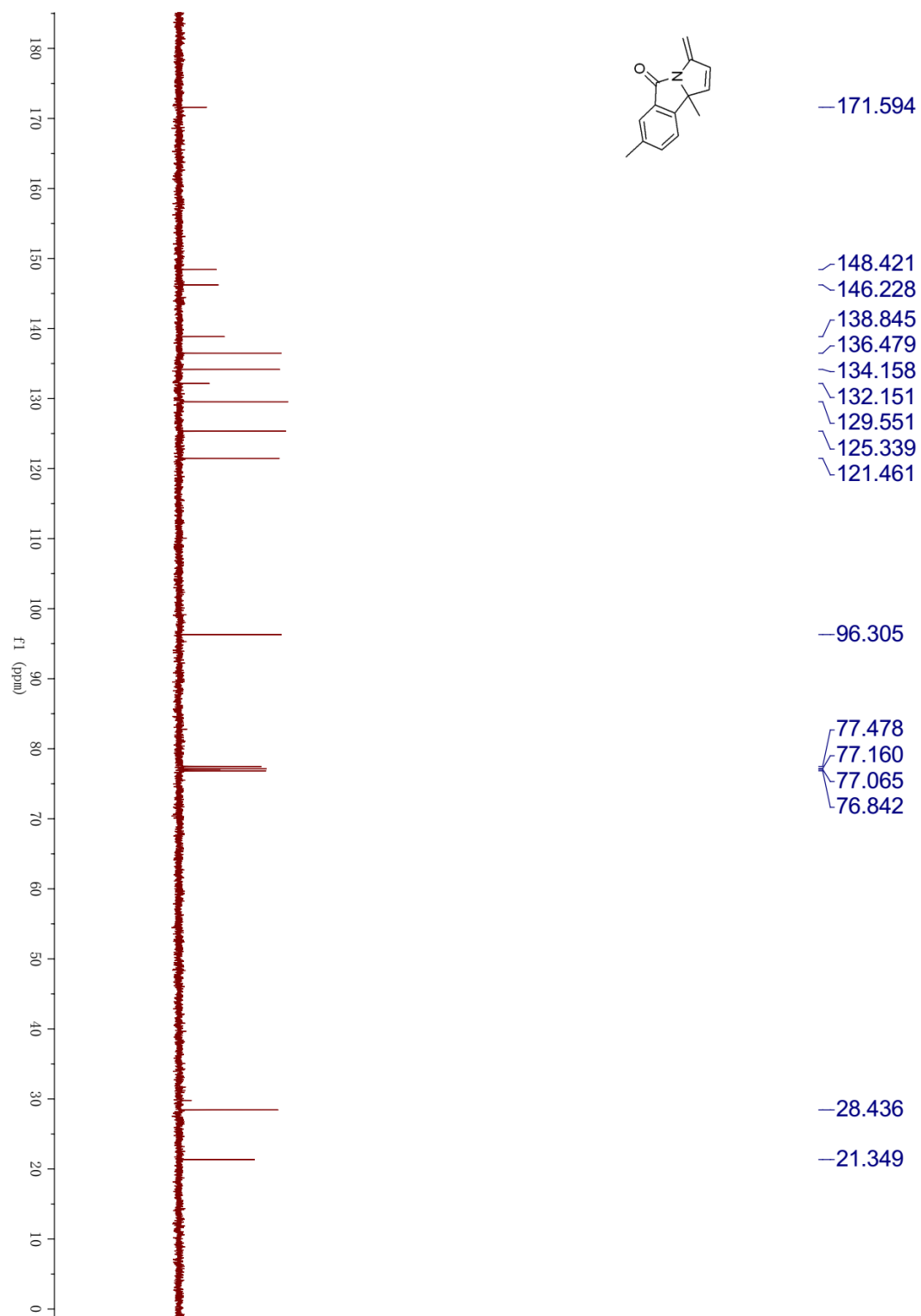
|   | RT    | Area     | % Area | Height |
|---|-------|----------|--------|--------|
| 1 | 7.861 | 11948487 | 95.45  | 774616 |
| 2 | 9.562 | 570060   | 4.55   | 32067  |

Reported by User: System  
 Report Method: Multi Sample Summary  
 Report Method ID 1007  
 Page: 1 of 1

Project Name: yangping  
 Date Printed:  
 10/24/2018  
 8:19:27 AM PRC

2ad:





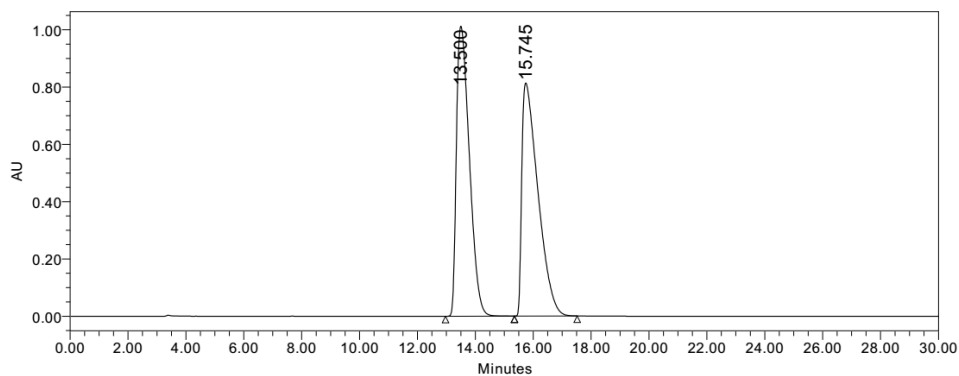
# HPLC of 2ad (racemic)



## Multi Sample Summary

### SAMPLE INFORMATION

|                   |                           |                     |                 |
|-------------------|---------------------------|---------------------|-----------------|
| Sample Name:      | yp-7-25-rac               | Acquired By:        | System          |
| Sample Type:      | Unknown                   | Sample Set Name:    | 1               |
| Vial:             | 1:A,4                     | Acq. Method Set:    | yp9901254       |
| Injection #:      | 1                         | Processing Method   | 1               |
| Injection Volume: | 10.00 ul                  | Channel Name:       | W2489 ChA       |
| Run Time:         | 30.0 Minutes              | Proc. Chnl. Descr.: | W2489 ChA 254nm |
| Date Acquired:    | 5/23/2018 8:53:51 AM CST  |                     |                 |
| Date Processed:   | 7/18/2018 12:16:51 AM CST |                     |                 |



|   | RT     | Area     | % Area | Height  |
|---|--------|----------|--------|---------|
| 1 | 13.500 | 31418258 | 49.95  | 1012343 |
| 2 | 15.745 | 31483204 | 50.05  | 813684  |

Reported by User: System  
 Report Method: Multi Sample Summary  
 Report Method ID 1007  
 Page: 1 of 1

Project Name: yangping  
 Date Printed:  
 7/18/2018  
 12:17:34 AM PRC

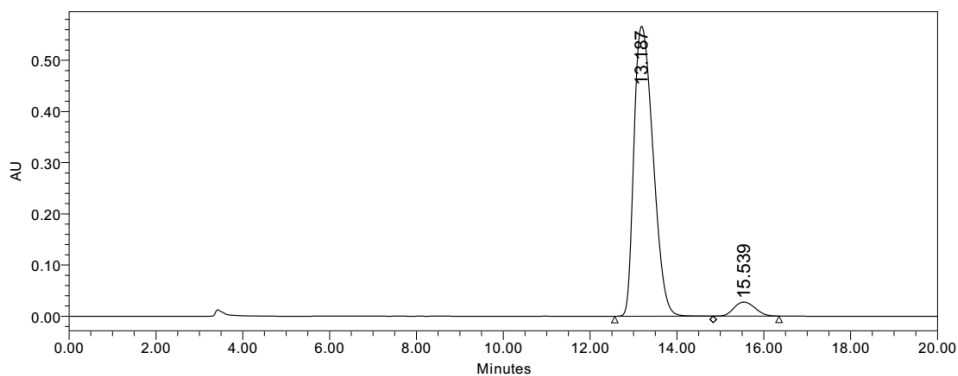
# HPLC of 2ad (chiral)



## Multi Sample Summary

### SAMPLE INFORMATION

|                   |                           |                     |                 |
|-------------------|---------------------------|---------------------|-----------------|
| Sample Name:      | yp-7-30-2                 | Acquired By:        | System          |
| Sample Type:      | Unknown                   | Sample Set Name:    | 1               |
| Vial:             | 1:A,2                     | Acq. Method Set:    | yp9901254       |
| Injection #:      | 1                         | Processing Method:  | 1               |
| Injection Volume: | 10.00 ul                  | Channel Name:       | W2489 ChA       |
| Run Time:         | 20.0 Minutes              | Proc. Chnl. Descr.: | W2489 ChA 254nm |
| Date Acquired:    | 5/24/2018 11:03:31 PM CST |                     |                 |
| Date Processed:   | 10/24/2018 8:20:27 AM CST |                     |                 |

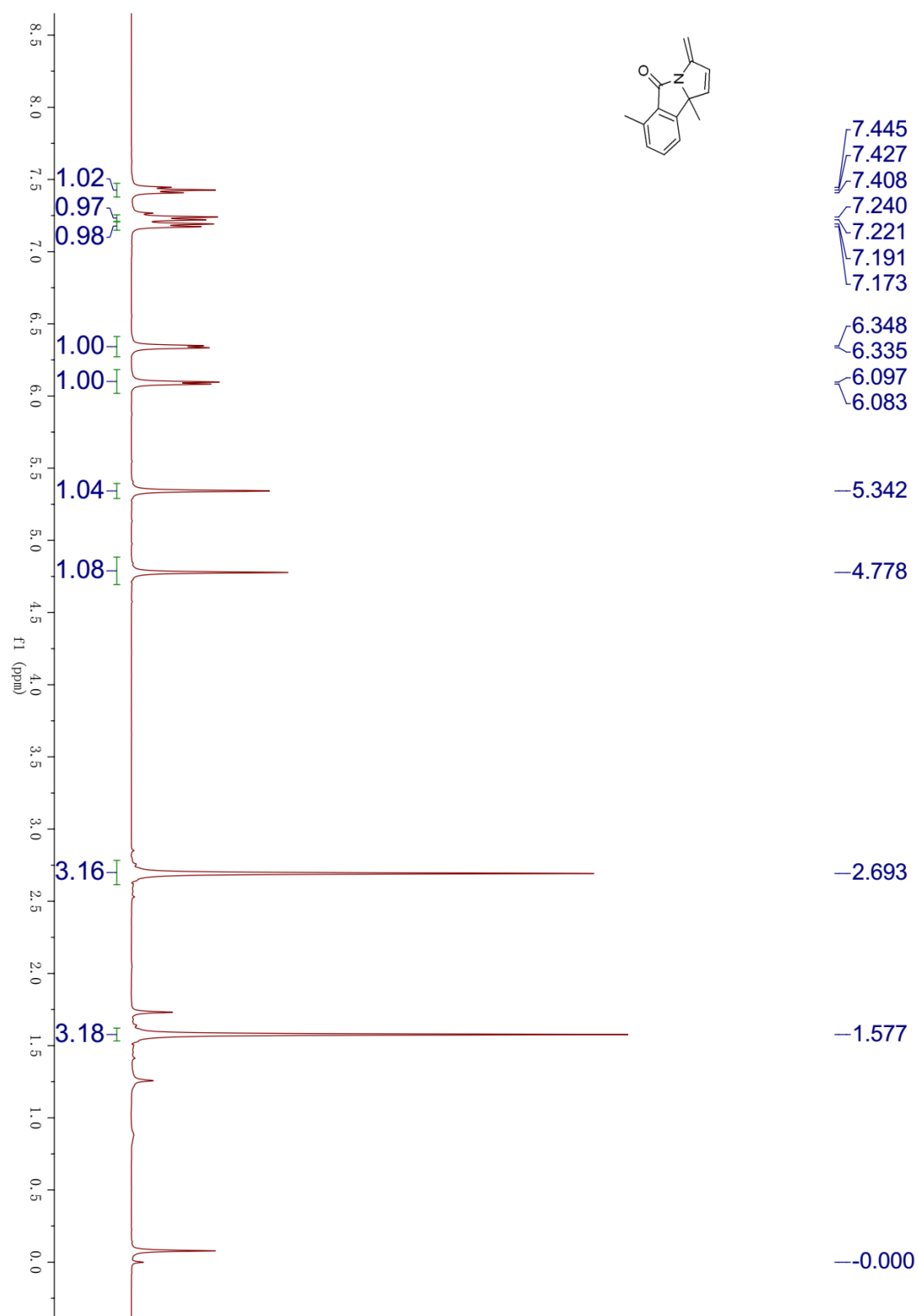


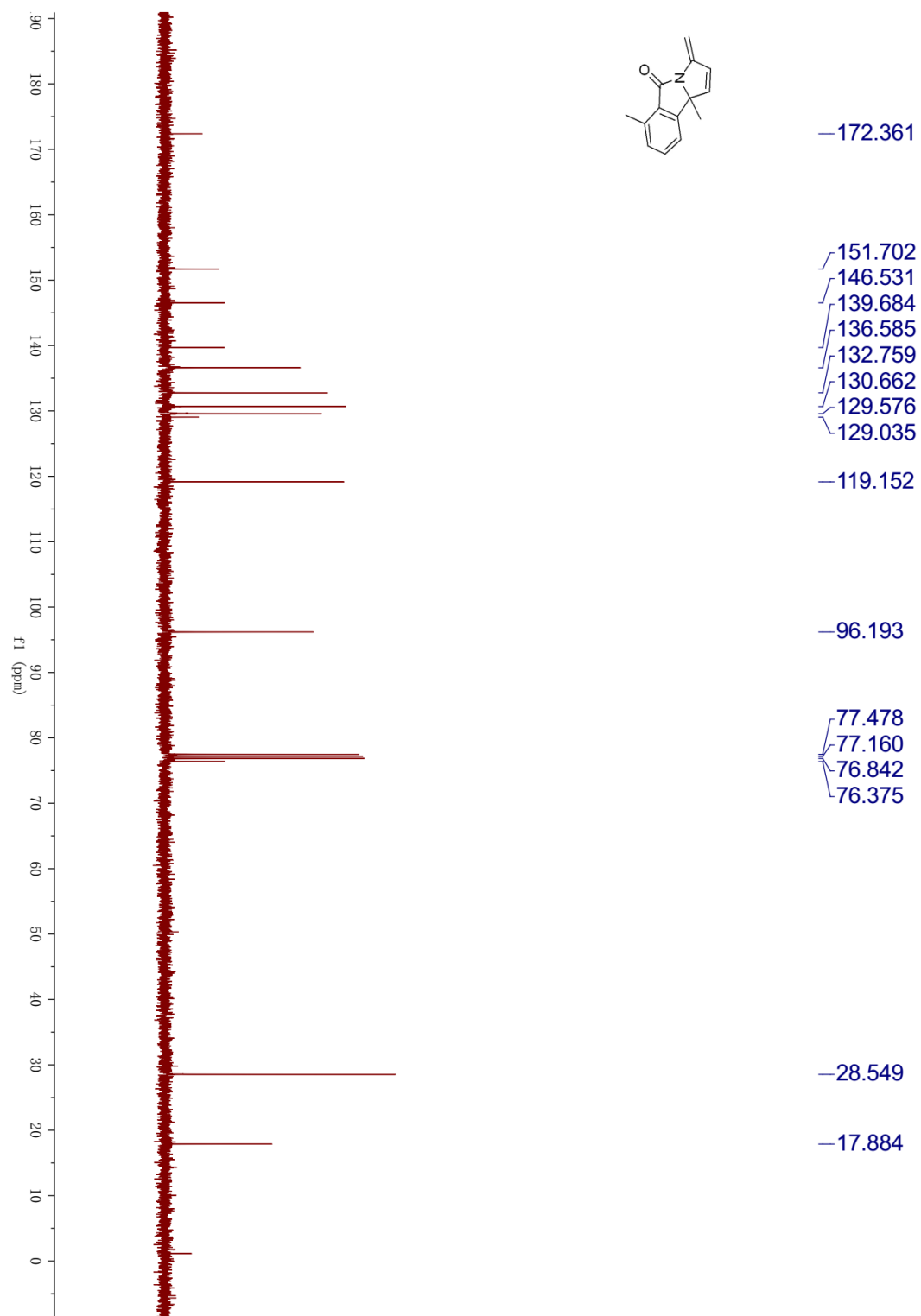
|   | RT     | Area     | % Area | Height |
|---|--------|----------|--------|--------|
| 1 | 13.187 | 17288672 | 94.90  | 566579 |
| 2 | 15.539 | 930059   | 5.10   | 27408  |

Reported by User: System  
 Report Method: Multi Sample Summary  
 Report Method ID 1007  
 Page: 1 of 1

Project Name: yangping  
 Date Printed:  
 10/24/2018  
 8:20:53 AM PRC

2ae:





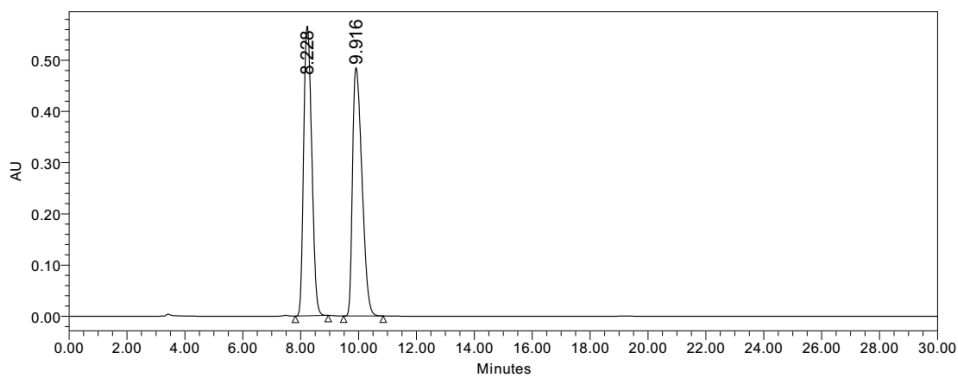
# HPLC of 2ae (racemic)



## Multi Sample Summary

### SAMPLE INFORMATION

|                   |                           |                     |                 |
|-------------------|---------------------------|---------------------|-----------------|
| Sample Name:      | yp-7-26-rac               | Acquired By:        | System          |
| Sample Type:      | Unknown                   | Sample Set Name:    | 1               |
| Vial:             | 1:A,5                     | Acq. Method Set:    | yp9901254       |
| Injection #:      | 1                         | Processing Method   | 1               |
| Injection Volume: | 10.00 ul                  | Channel Name:       | W2489 ChA       |
| Run Time:         | 30.0 Minutes              | Proc. Chnl. Descr.: | W2489 ChA 254nm |
| Date Acquired:    | 5/23/2018 9:24:14 AM CST  |                     |                 |
| Date Processed:   | 7/18/2018 12:14:05 AM CST |                     |                 |



|   | RT    | Area     | % Area | Height |
|---|-------|----------|--------|--------|
| 1 | 8.228 | 10966717 | 49.96  | 566150 |
| 2 | 9.916 | 10984301 | 50.04  | 485371 |

Reported by User: System  
 Report Method: Multi Sample Summary  
 Report Method ID 1007  
 Page: 1 of 1

Project Name: yangping  
 Date Printed:  
 7/18/2018  
 12:14:39 AM PRC

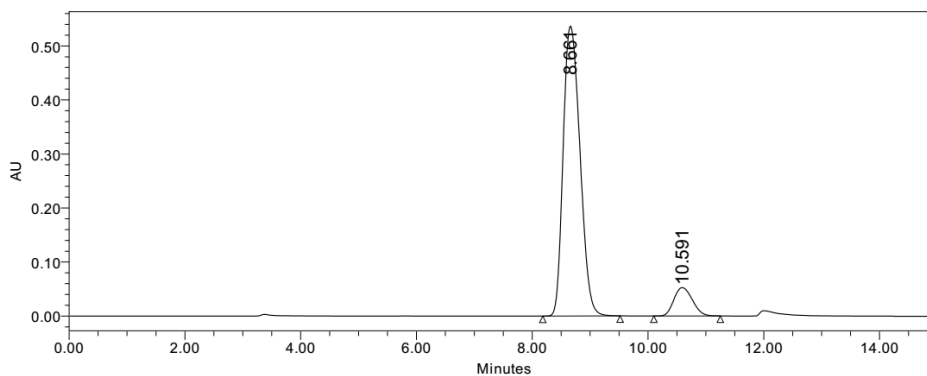
# HPLC of 2ae (chiral)



## Multi Sample Summary

### SAMPLE INFORMATION

|                   |                           |                     |                 |
|-------------------|---------------------------|---------------------|-----------------|
| Sample Name:      | yp-7-46-2                 | Acquired By:        | System          |
| Sample Type:      | Unknown                   | Sample Set Name:    | 1               |
| Vial:             | 1:A,2                     | Acq. Method Set:    | yp9901254       |
| Injection #:      | 1                         | Processing Method   | 1               |
| Injection Volume: | 10.00 ul                  | Channel Name:       | W2489 ChA       |
| Run Time:         | 15.0 Minutes              | Proc. Chnl. Descr.: | W2489 ChA 254nm |
| Date Acquired:    | 5/31/2018 6:52:19 PM CST  |                     |                 |
| Date Processed:   | 10/24/2018 8:21:51 AM CST |                     |                 |

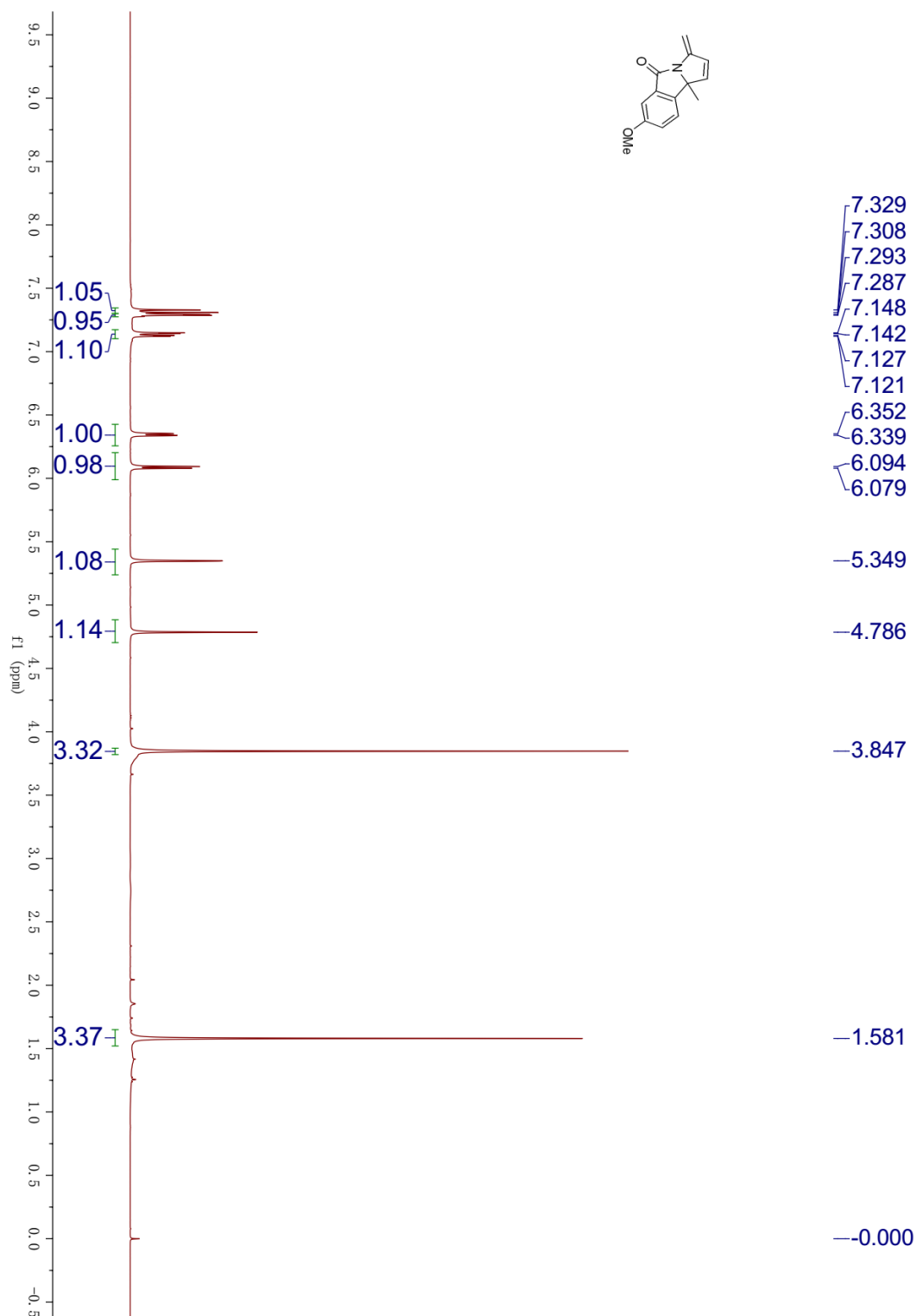


|   | RT     | Area     | % Area | Height |
|---|--------|----------|--------|--------|
| 1 | 8.661  | 10836021 | 90.25  | 536615 |
| 2 | 10.591 | 1170004  | 9.75   | 52538  |

Reported by User: System  
 Report Method: Multi Sample Summary  
 Report Method ID 1007  
 Page: 1 of 1

Project Name: yangping  
 Date Printed:  
 10/24/2018  
 8:22:17 AM PRC

2af:



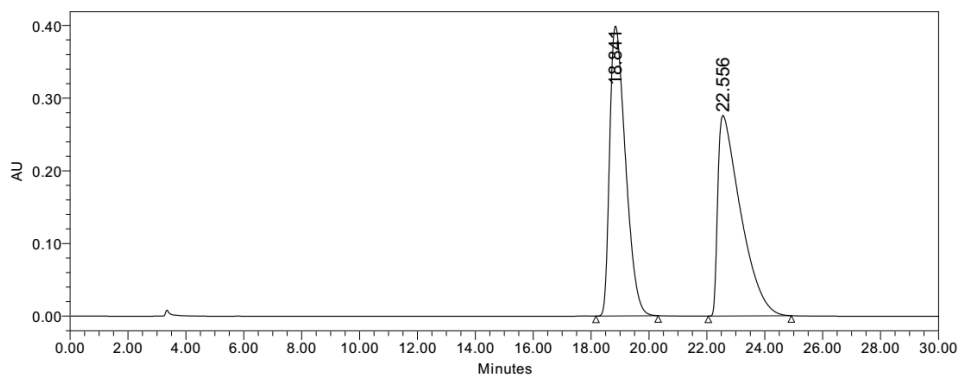
# HPLC of 2af (racemic)



## Multi Sample Summary

### SAMPLE INFORMATION

|                   |                           |                     |                 |
|-------------------|---------------------------|---------------------|-----------------|
| Sample Name:      | yp-7-51-2                 | Acquired By:        | System          |
| Sample Type:      | Unknown                   | Sample Set Name:    | 1               |
| Vial:             | 1:A,2                     | Acq. Method Set:    | yp9901254       |
| Injection #:      | 1                         | Processing Method   | 1               |
| Injection Volume: | 10.00 ul                  | Channel Name:       | W2489 ChA       |
| Run Time:         | 30.0 Minutes              | Proc. Chnl. Descr.: | W2489 ChA 254nm |
| Date Acquired:    | 6/1/2018 11:57:01 PM CST  |                     |                 |
| Date Processed:   | 7/18/2018 12:04:57 AM CST |                     |                 |



|   | RT     | Area     | % Area | Height |
|---|--------|----------|--------|--------|
| 1 | 18.841 | 15120675 | 49.99  | 398906 |
| 2 | 22.556 | 15127099 | 50.01  | 276055 |

Reported by User: System  
 Report Method: Multi Sample Summary  
 Report Method ID 1007  
 Page: 1 of 1

Project Name: yangping  
 Date Printed:  
 7/18/2018  
 12:05:57 AM PRC

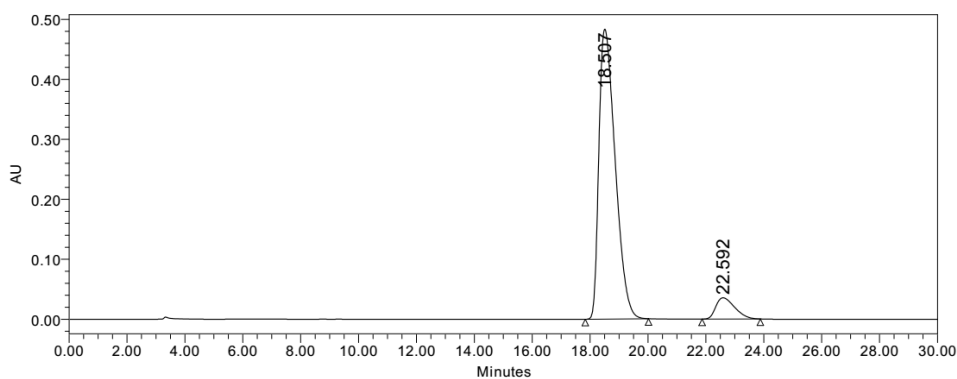
# HPLC of 2af (chiral)



## Multi Sample Summary

### SAMPLE INFORMATION

|                   |                           |                     |                 |
|-------------------|---------------------------|---------------------|-----------------|
| Sample Name:      | yp-7-56-2                 | Acquired By:        | System          |
| Sample Type:      | Unknown                   | Sample Set Name:    | 1               |
| Vial:             | 1:A,2                     | Acq. Method Set:    | yp9901254       |
| Injection #:      | 1                         | Processing Method   | 1               |
| Injection Volume: | 10.00 ul                  | Channel Name:       | W2489 ChA       |
| Run Time:         | 30.0 Minutes              | Proc. Chnl. Descr.: | W2489 ChA 254nm |
| Date Acquired:    | 6/2/2018 3:39:47 PM CST   |                     |                 |
| Date Processed:   | 10/24/2018 8:23:25 AM CST |                     |                 |

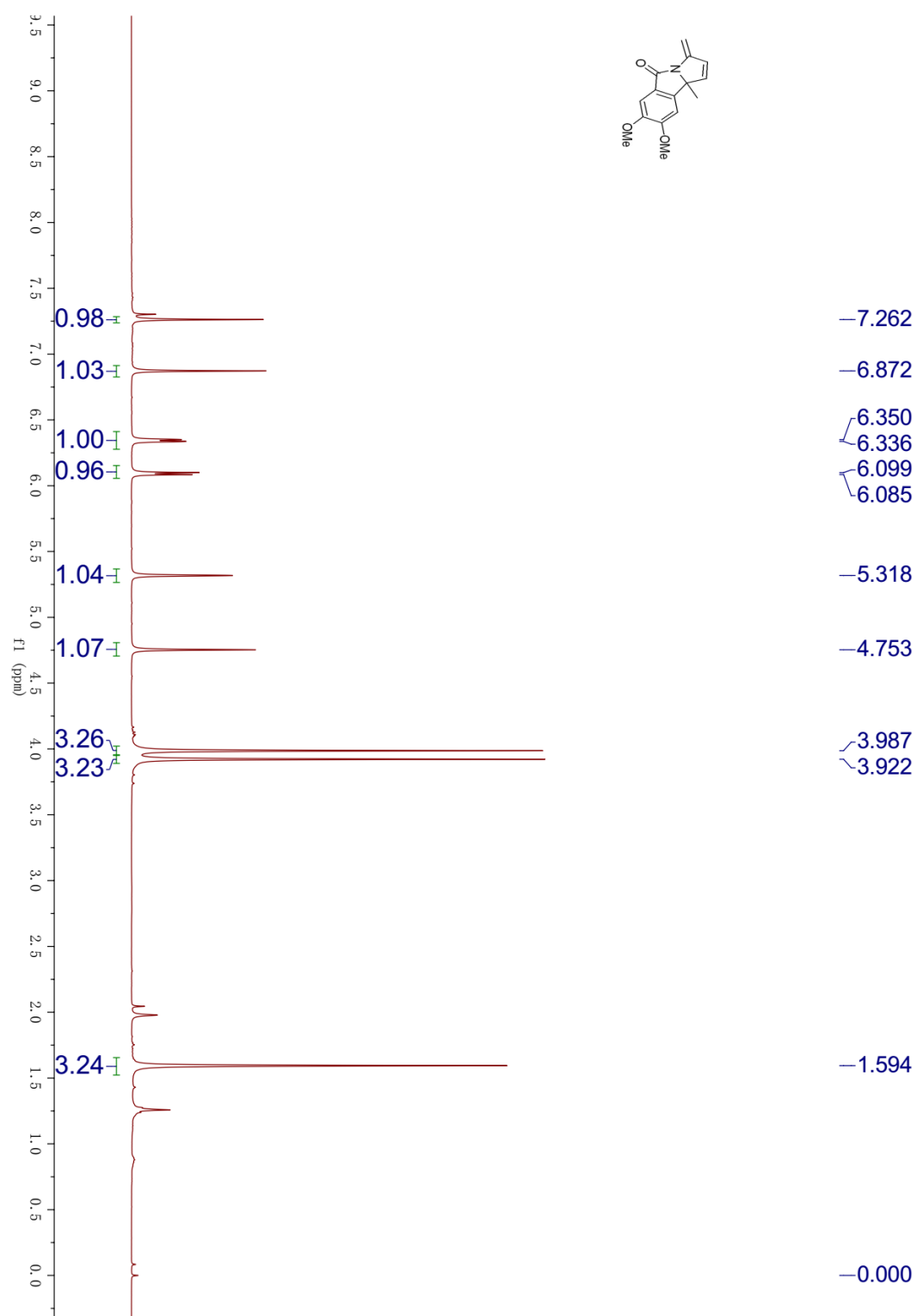


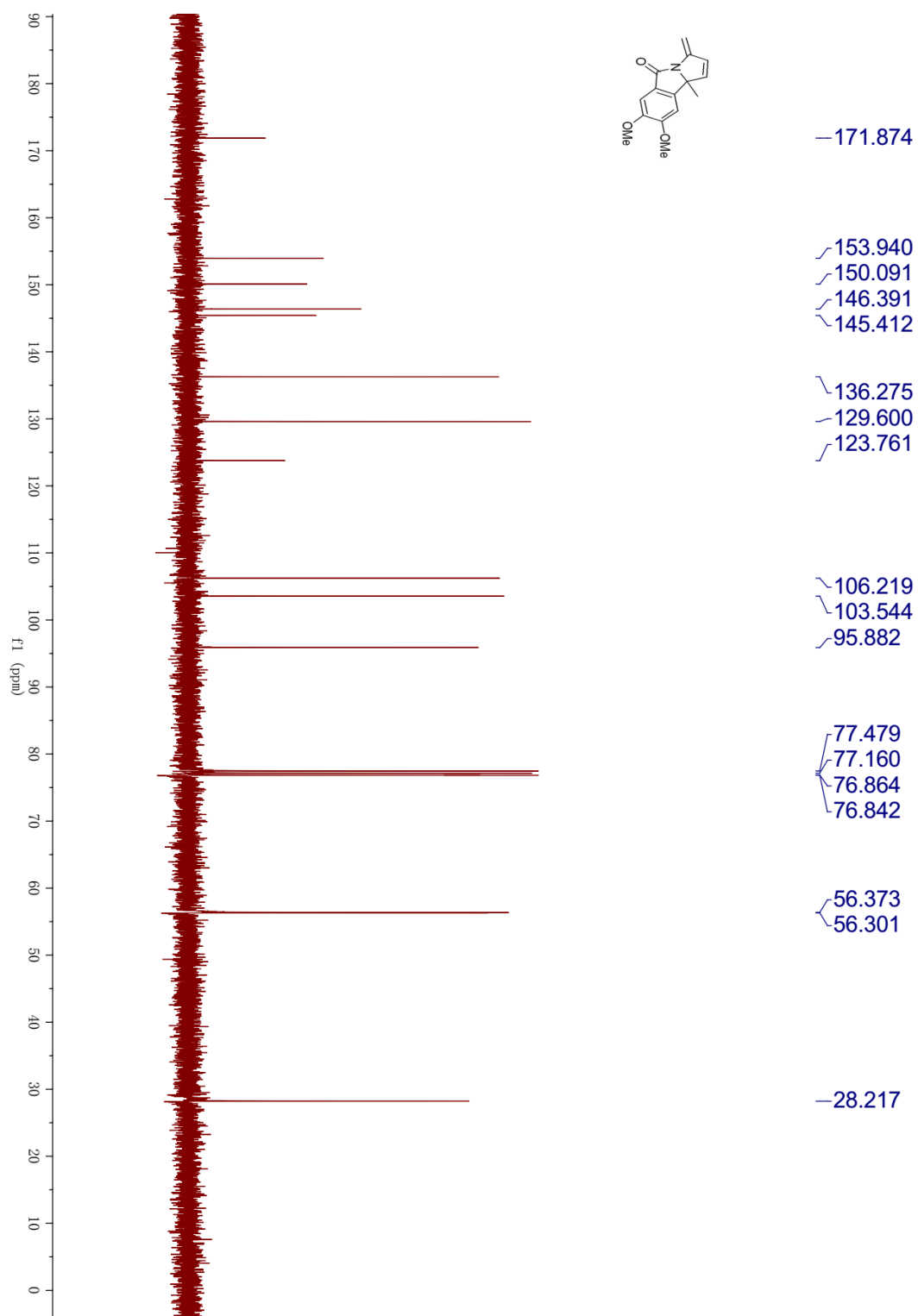
|   | RT     | Area     | % Area | Height |
|---|--------|----------|--------|--------|
| 1 | 18.507 | 18886973 | 92.10  | 483458 |
| 2 | 22.592 | 1619268  | 7.90   | 35547  |

Reported by User: System  
 Report Method: Multi Sample Summary  
 Report Method ID 1007  
 Page: 1 of 1

Project Name: yangping  
 Date Printed:  
 10/24/2018  
 8:24:00 AM PRC

2ag:





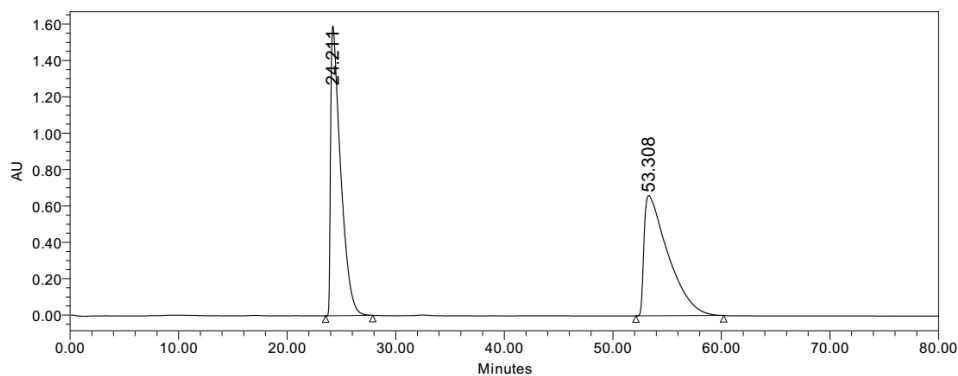
# HPLC of 2ag (racemic)



## Multi Sample Summary

### SAMPLE INFORMATION

|                   |                            |                     |                 |
|-------------------|----------------------------|---------------------|-----------------|
| Sample Name:      | YP-8-1-2                   | Acquired By:        | System          |
| Sample Type:      | Unknown                    | Sample Set Name:    | 1               |
| Vial:             | 1:A,2                      | Acq. Method Set:    | yp9010          |
| Injection #:      | 1                          | Processing Method   | 1               |
| Injection Volume: | 10.00 ul                   | Channel Name:       | W2489 ChA       |
| Run Time:         | 80.0 Minutes               | Proc. Chnl. Descr.: | W2489 ChA 254nm |
| Date Acquired:    | 6/17/2018 11:40:01 PM CST  |                     |                 |
| Date Processed:   | 10/25/2018 12:13:12 PM CST |                     |                 |



|   | RT     | Area      | % Area | Height  |
|---|--------|-----------|--------|---------|
| 1 | 24.211 | 102014577 | 50.11  | 1592085 |
| 2 | 53.308 | 101580442 | 49.89  | 661437  |

Reported by User: System  
 Report Method: Multi Sample Summary  
 Report Method ID 1007  
 Page: 1 of 1

Project Name: yangping  
 Date Printed:  
 10/25/2018  
 12:13:39 PM PRC

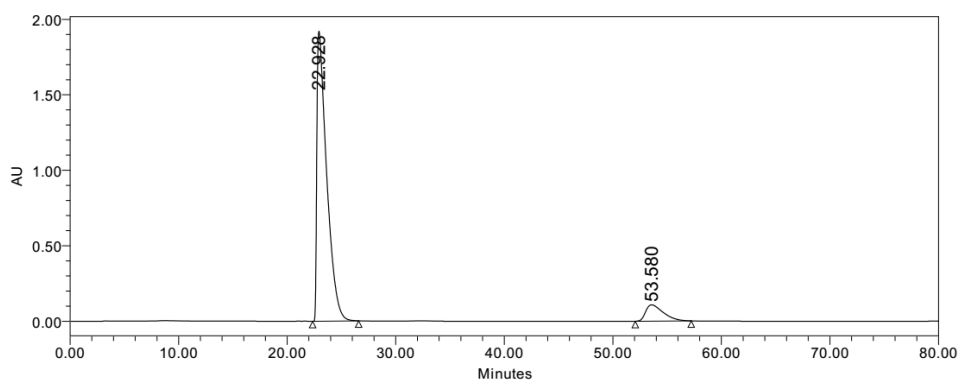
# HPLC of 2ag (chiral)



## Multi Sample Summary

### SAMPLE INFORMATION

|                   |                           |                     |                 |
|-------------------|---------------------------|---------------------|-----------------|
| Sample Name:      | yp-8-6-2                  | Acquired By:        | System          |
| Sample Type:      | Unknown                   | Sample Set Name:    | 1               |
| Vial:             | 1:A,2                     | Acq. Method Set:    | yp9010          |
| Injection #:      | 1                         | Processing Method   | 1               |
| Injection Volume: | 10.00 ul                  | Channel Name:       | W2489 ChA       |
| Run Time:         | 80.0 Minutes              | Proc. Chnl. Descr.: | W2489 ChA 254nm |
| Date Acquired:    | 6/19/2018 2:49:09 PM CST  |                     |                 |
| Date Processed:   | 10/24/2018 8:25:42 AM CST |                     |                 |

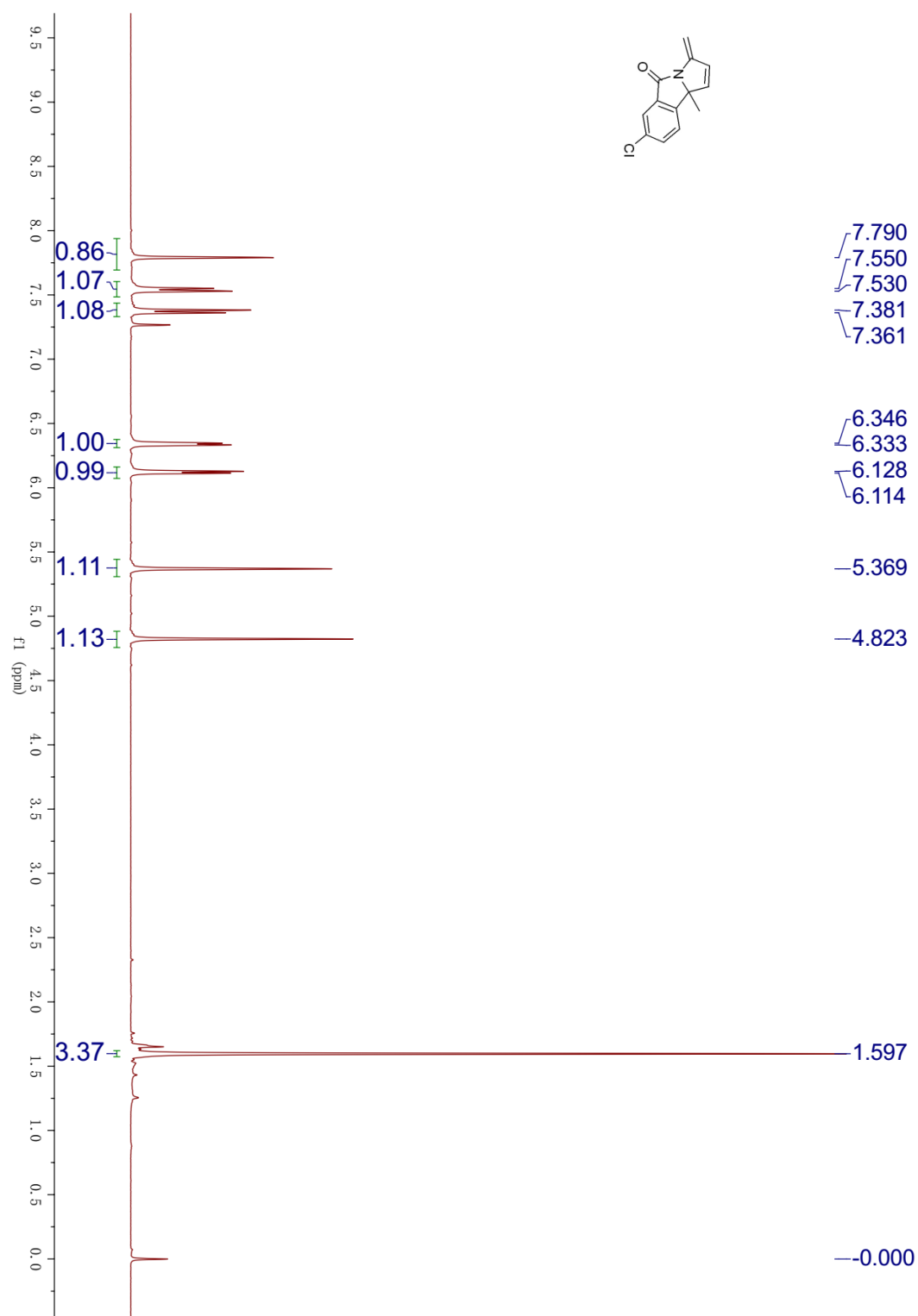


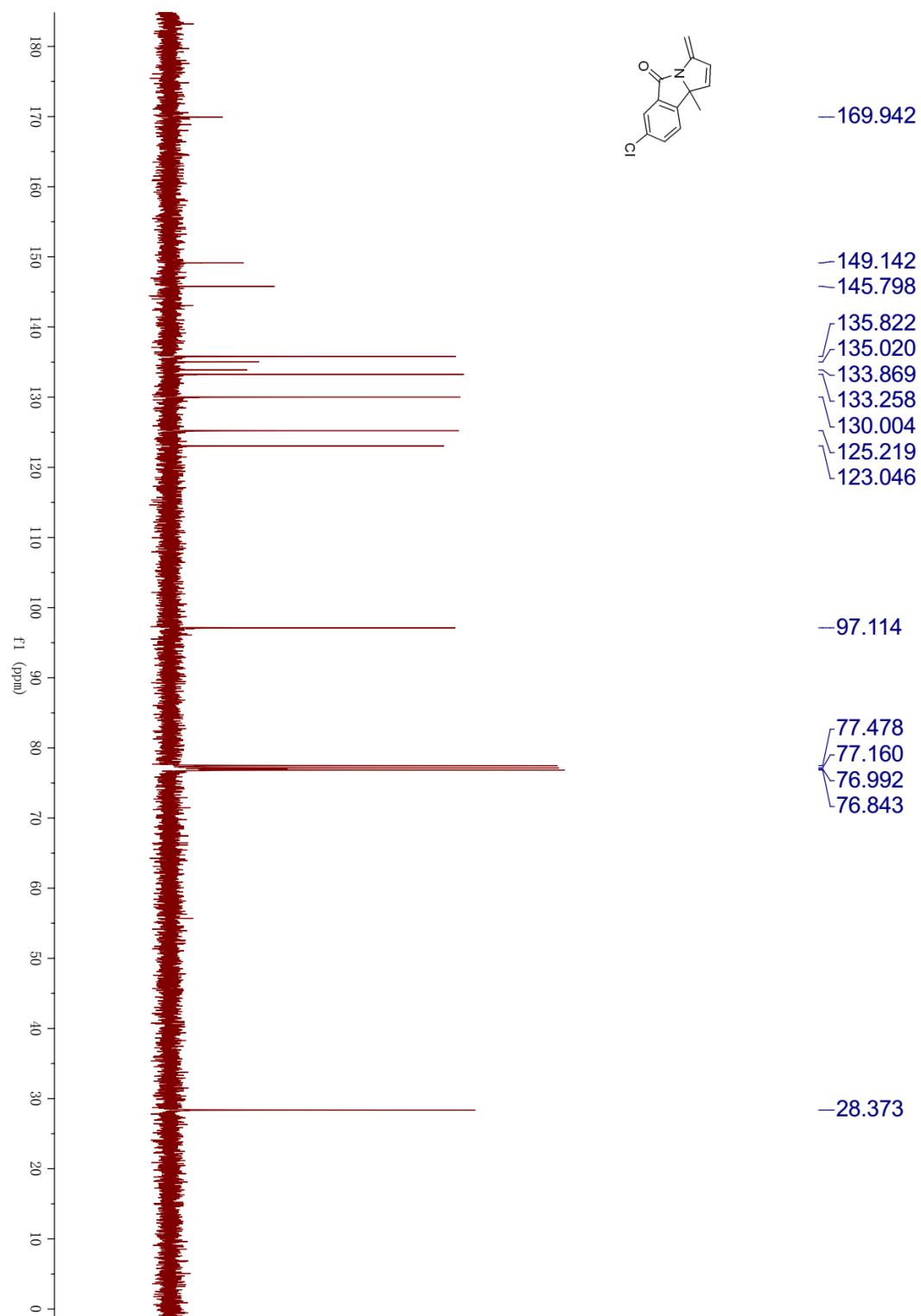
|   | RT     | Area      | % Area | Height  |
|---|--------|-----------|--------|---------|
| 1 | 22.928 | 120562804 | 90.82  | 1921298 |
| 2 | 53.580 | 12182178  | 9.18   | 107730  |

Reported by User: System  
 Report Method: Multi Sample Summary  
 Report Method ID 1007  
 Page: 1 of 1

Project Name: yangping  
 Date Printed:  
 10/24/2018  
 8:26:03 AM PRC

2ah:





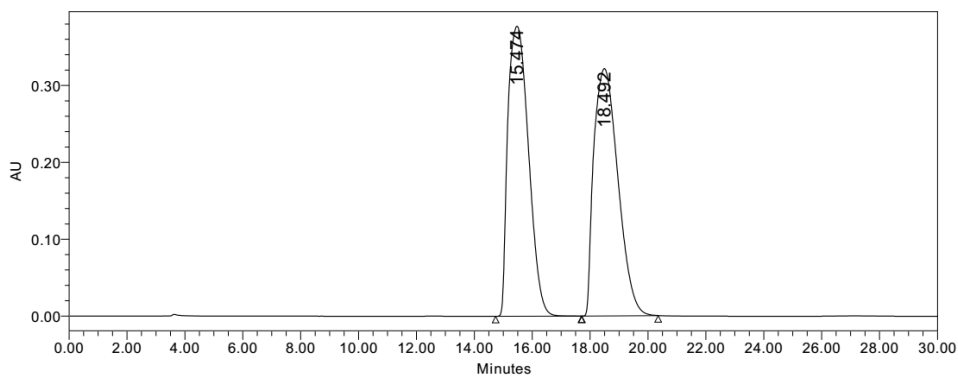
# HPLC of 2ah (racemic)



## Multi Sample Summary

### SAMPLE INFORMATION

|                   |                           |                     |                 |
|-------------------|---------------------------|---------------------|-----------------|
| Sample Name:      | yp-7-32-rac               | Acquired By:        | System          |
| Sample Type:      | Unknown                   | Sample Set Name:    | 1               |
| Vial:             | 1:A,2                     | Acq. Method Set:    | yp9901254       |
| Injection #:      | 1                         | Processing Method:  | 1               |
| Injection Volume: | 10.00 ul                  | Channel Name:       | W2489 ChA       |
| Run Time:         | 30.0 Minutes              | Proc. Chnl. Descr.: | W2489 ChA 254nm |
| Date Acquired:    | 5/25/2018 4:05:00 PM CST  |                     |                 |
| Date Processed:   | 7/18/2018 12:08:24 AM CST |                     |                 |



|   | RT     | Area     | % Area | Height |
|---|--------|----------|--------|--------|
| 1 | 15.474 | 18682645 | 50.11  | 377288 |
| 2 | 18.492 | 18601097 | 49.89  | 321705 |

Reported by User: System  
 Report Method: Multi Sample Summary  
 Report Method ID 1007  
 Page: 1 of 1

Project Name: yangping  
 Date Printed: 7/18/2018  
 12:09:05 AM PRC

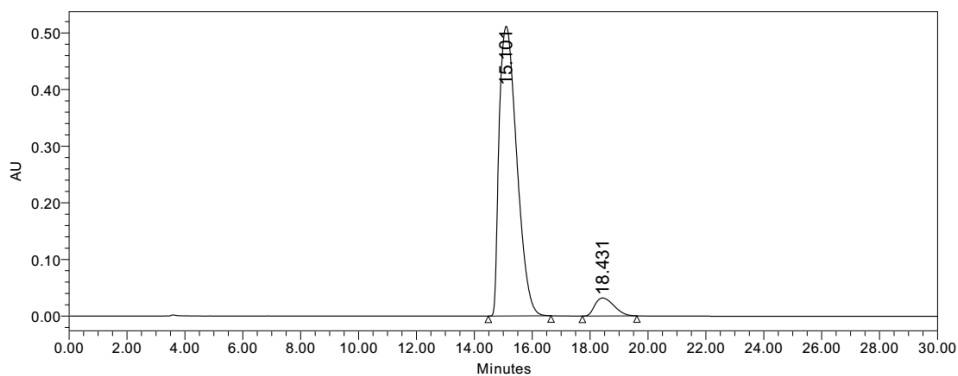
# HPLC of 2ah (chiral)



## Multi Sample Summary

### SAMPLE INFORMATION

|                   |                           |                     |                 |
|-------------------|---------------------------|---------------------|-----------------|
| Sample Name:      | yp-7-48-2                 | Acquired By:        | System          |
| Sample Type:      | Unknown                   | Sample Set Name:    | 1               |
| Vial:             | 1:A,2                     | Acq. Method Set:    | yp9901254       |
| Injection #:      | 1                         | Processing Method   | 1               |
| Injection Volume: | 10.00 ul                  | Channel Name:       | W2489 ChA       |
| Run Time:         | 30.0 Minutes              | Proc. Chnl. Descr.: | W2489 ChA 254nm |
| Date Acquired:    | 5/31/2018 11:37:00 PM CST |                     |                 |
| Date Processed:   | 10/24/2018 8:26:47 AM CST |                     |                 |

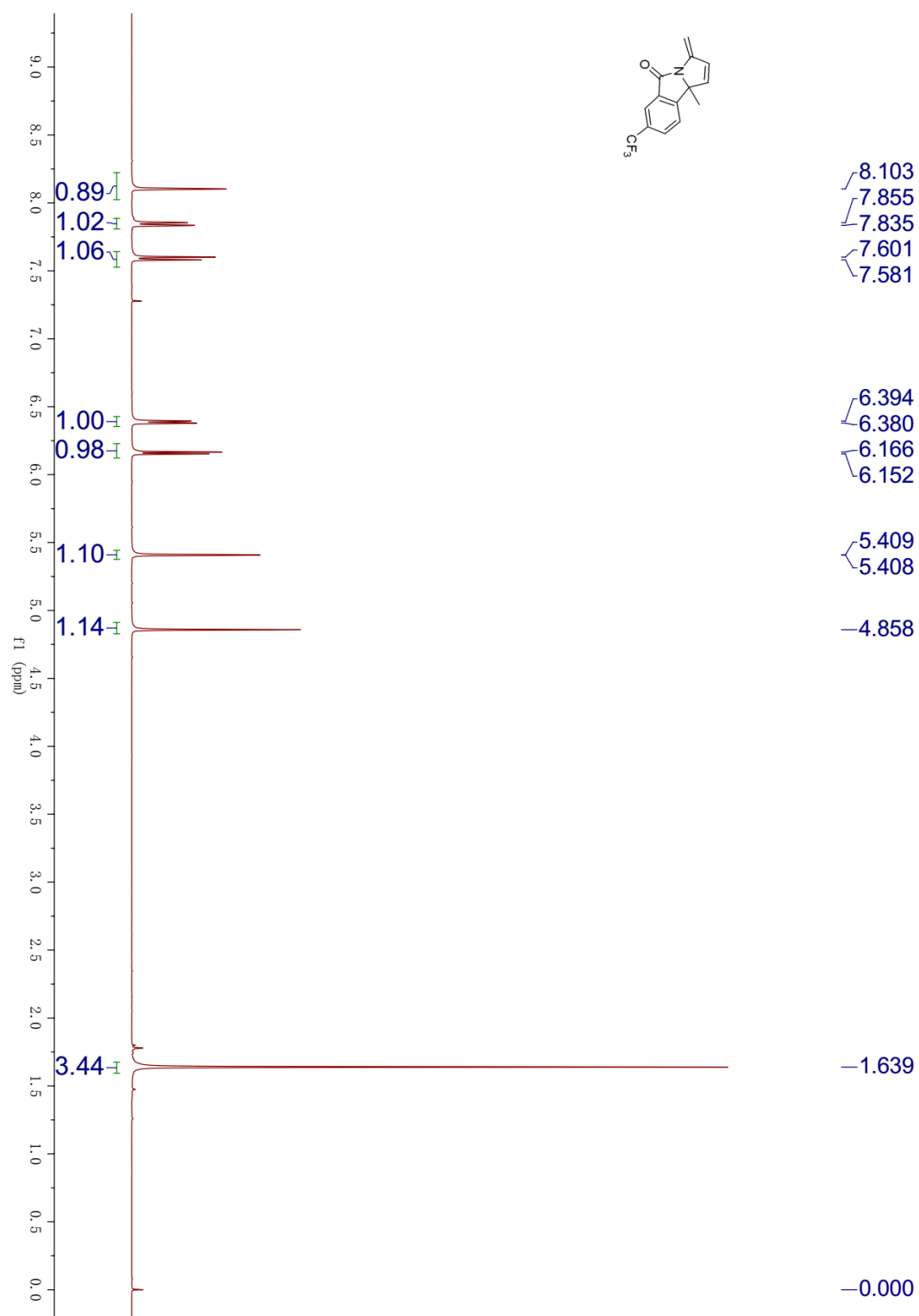


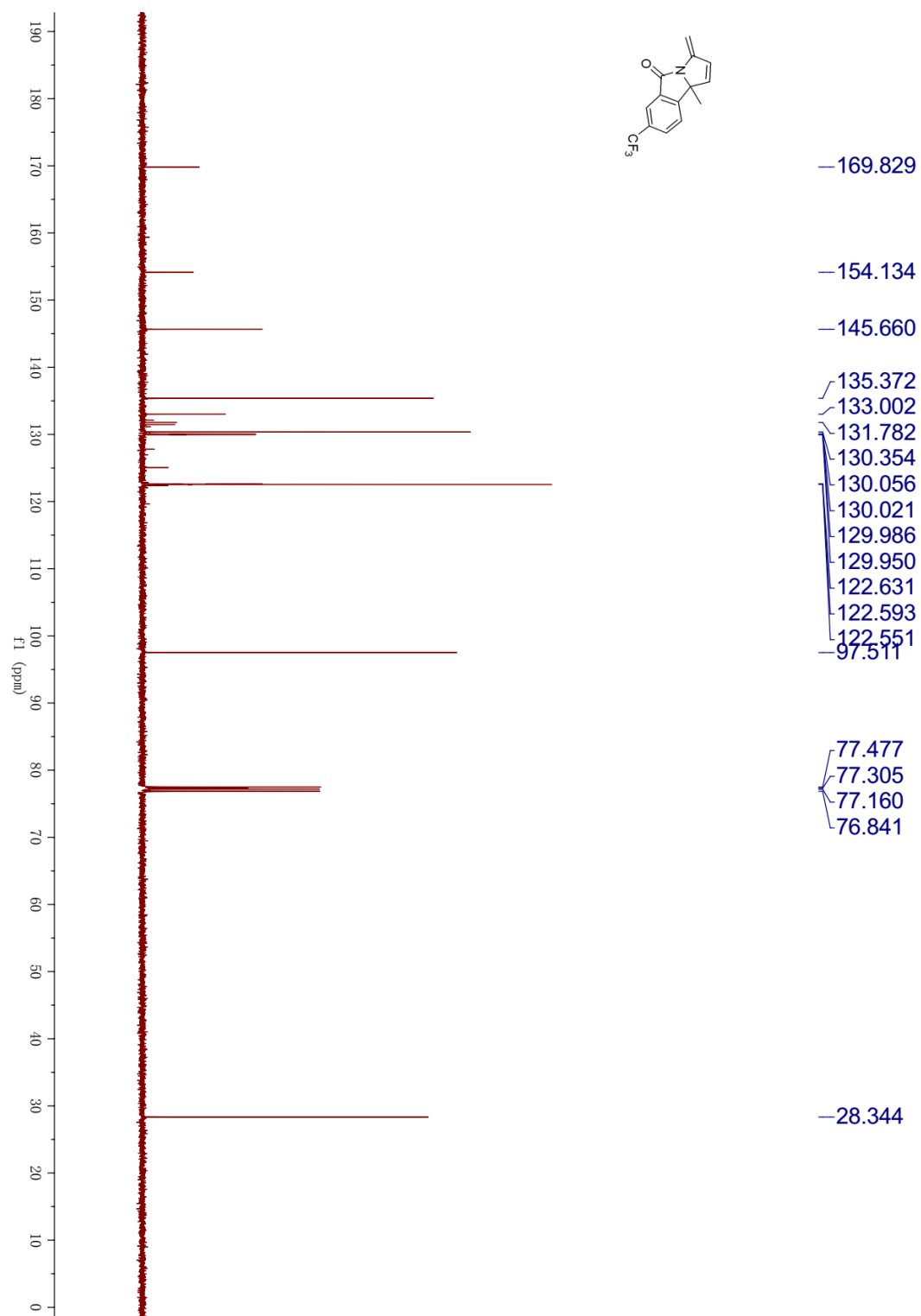
|   | RT     | Area     | % Area | Height |
|---|--------|----------|--------|--------|
| 1 | 15.101 | 21486106 | 93.64  | 511706 |
| 2 | 18.431 | 1460412  | 6.36   | 31758  |

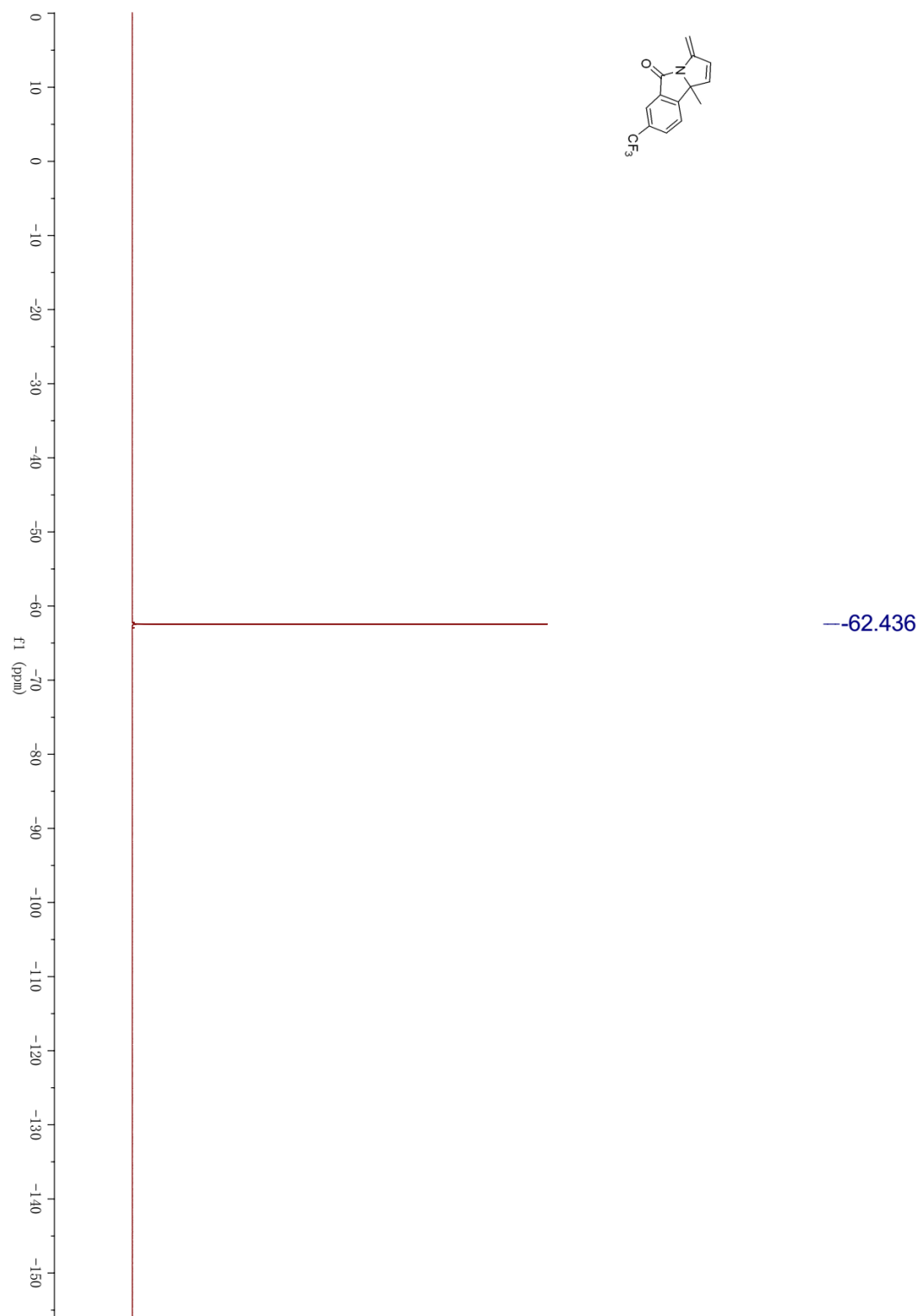
Reported by User: System  
 Report Method: Multi Sample Summary  
 Report Method ID 1007  
 Page: 1 of 1

Project Name: yangping  
 Date Printed:  
 10/24/2018  
 8:27:10 AM PRC

2ai:







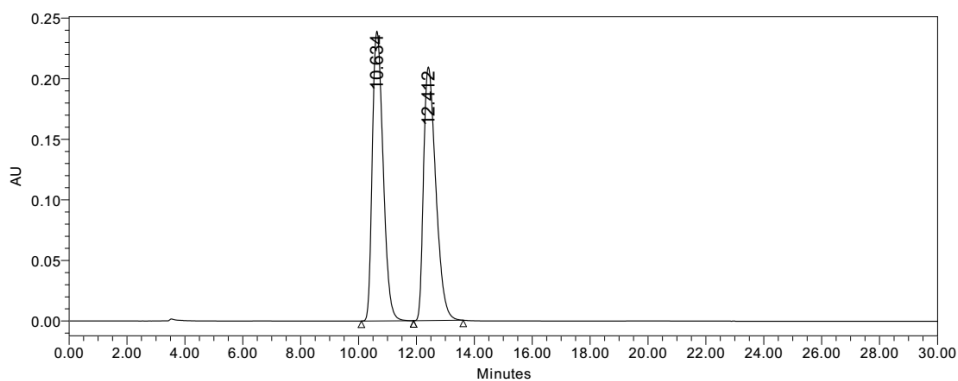
# HPLC of 2ai (racemic)



## Multi Sample Summary

### SAMPLE INFORMATION

|                                            |              |                     |                 |
|--------------------------------------------|--------------|---------------------|-----------------|
| Sample Name:                               | yp-7-53-2    | Acquired By:        | System          |
| Sample Type:                               | Unknown      | Sample Set Name:    | 1               |
| Vial:                                      | 1:A,2        | Acq. Method Set:    | yp9901254       |
| Injection #:                               | 1            | Processing Method   | 1               |
| Injection Volume:                          | 10.00 ul     | Channel Name:       | W2489 ChA       |
| Run Time:                                  | 30.0 Minutes | Proc. Chnl. Descr.: | W2489 ChA 254nm |
| Date Acquired: 6/2/2018 9:33:22 AM CST     |              |                     |                 |
| Date Processed: 10/25/2018 12:14:35 PM CST |              |                     |                 |



|   | RT     | Area    | % Area | Height |
|---|--------|---------|--------|--------|
| 1 | 10.634 | 6195211 | 50.15  | 239159 |
| 2 | 12.412 | 6159255 | 49.85  | 209379 |

Reported by User: System  
 Report Method: Multi Sample Summary  
 Report Method ID 1007  
 Page: 1 of 1

Project Name: yangping  
 Date Printed:  
 10/25/2018  
 12:14:58 PM PRC

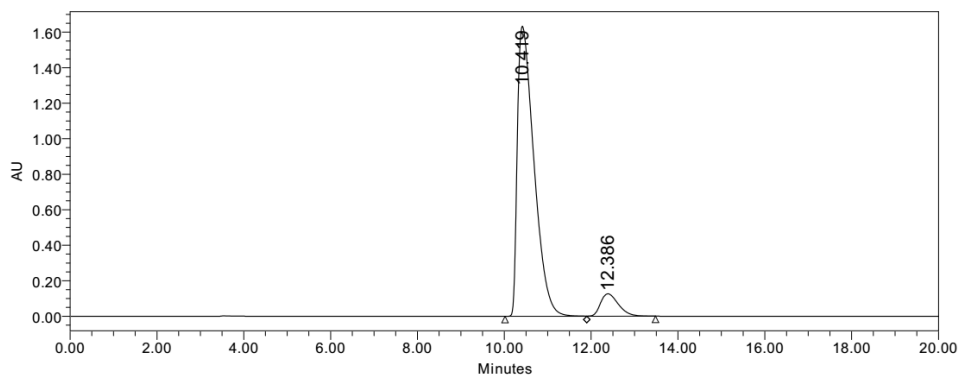
# HPLC of 2ai (chiral)



## Multi Sample Summary

### SAMPLE INFORMATION

|                   |                           |                     |                 |
|-------------------|---------------------------|---------------------|-----------------|
| Sample Name:      | yp-7-57-2                 | Acquired By:        | System          |
| Sample Type:      | Unknown                   | Sample Set Name:    | 1               |
| Vial:             | 1:A,2                     | Acq. Method Set:    | yp9901254       |
| Injection #:      | 1                         | Processing Method   | 1               |
| Injection Volume: | 10.00 ul                  | Channel Name:       | W2489 ChA       |
| Run Time:         | 20.0 Minutes              | Proc. Chnl. Descr.: | W2489 ChA 254nm |
| Date Acquired:    | 6/2/2018 11:38:08 PM CST  |                     |                 |
| Date Processed:   | 10/24/2018 8:28:32 AM CST |                     |                 |

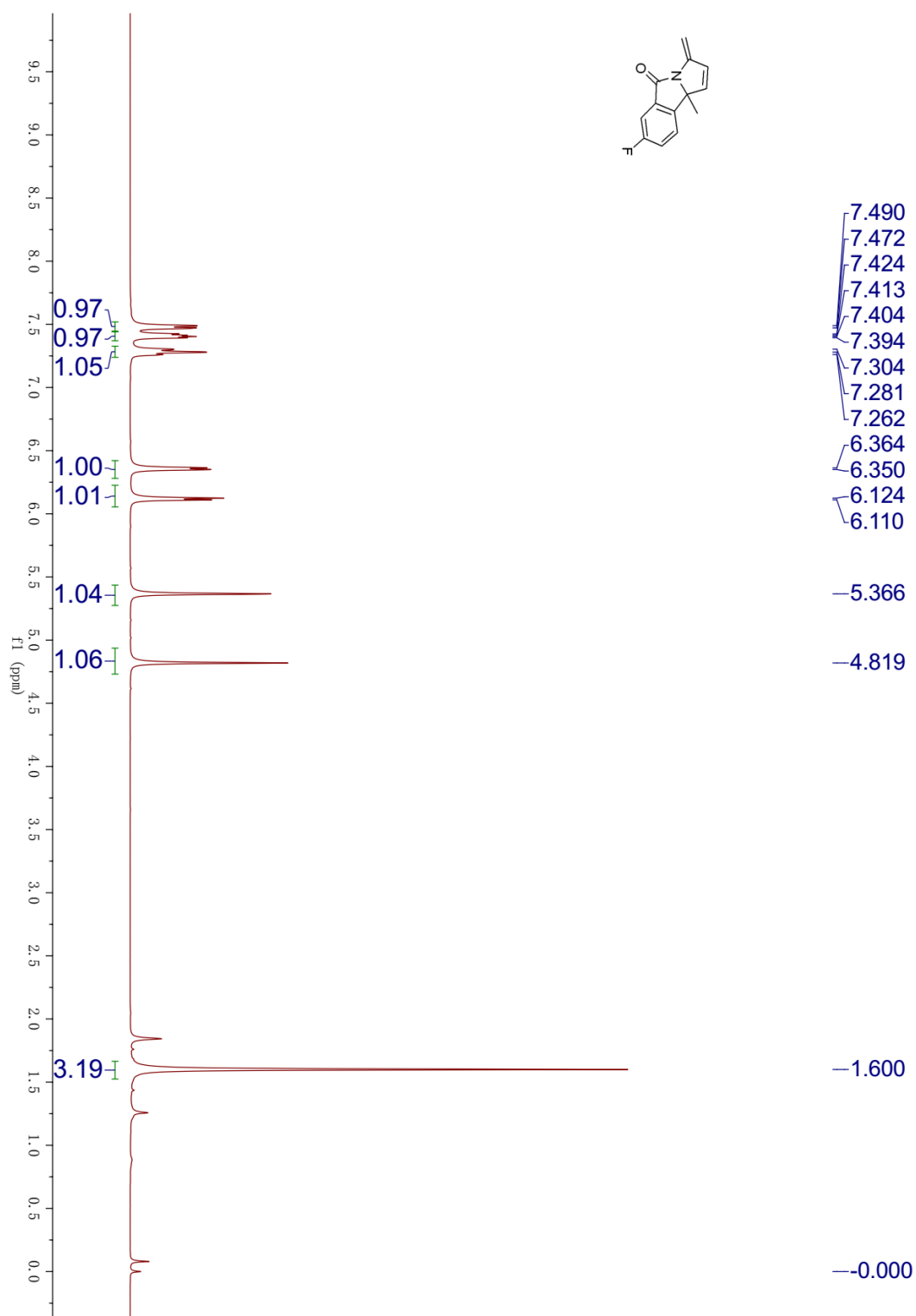


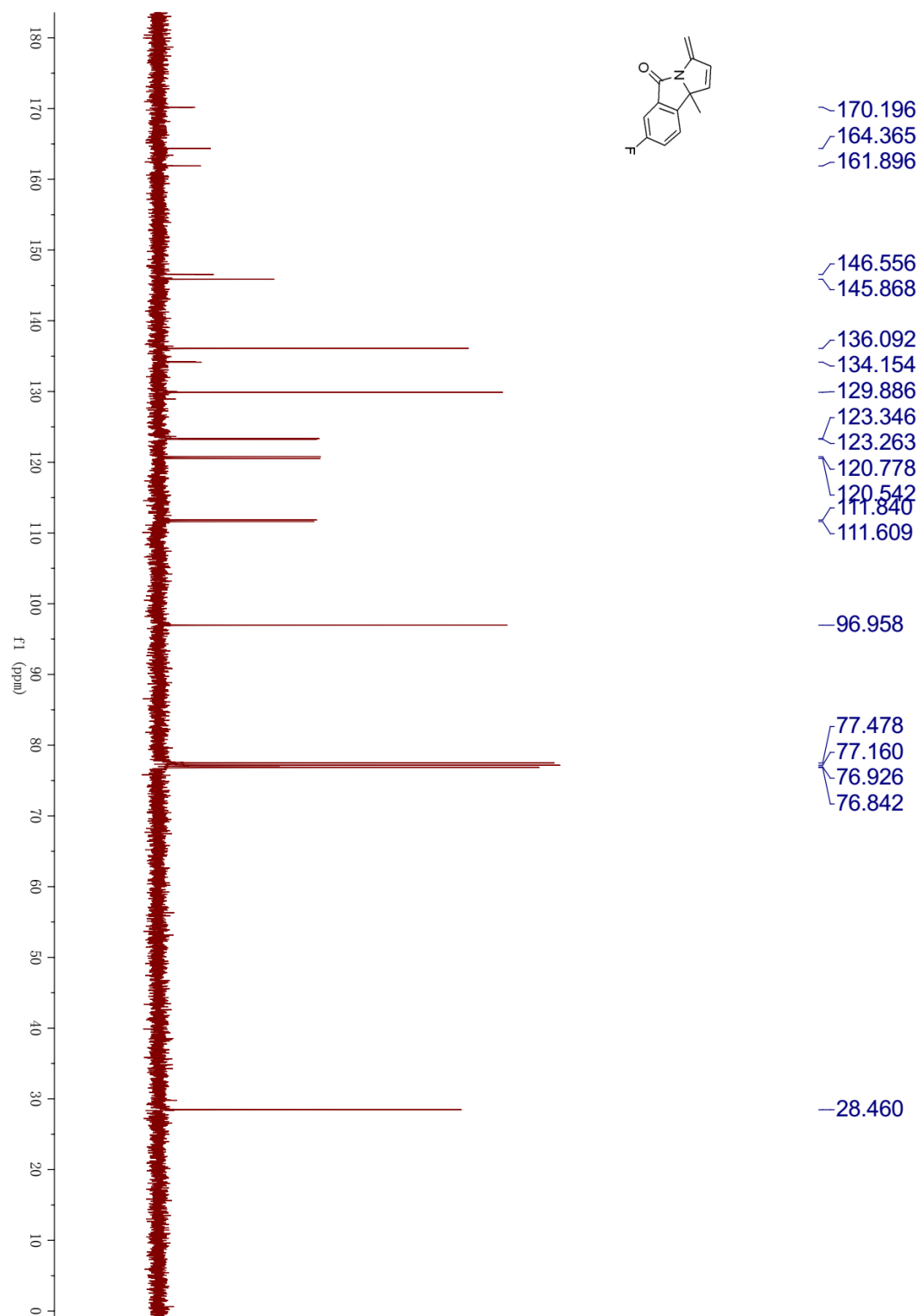
|   | RT     | Area     | % Area | Height  |
|---|--------|----------|--------|---------|
| 1 | 10.419 | 43461951 | 92.32  | 1633673 |
| 2 | 12.386 | 3615291  | 7.68   | 126154  |

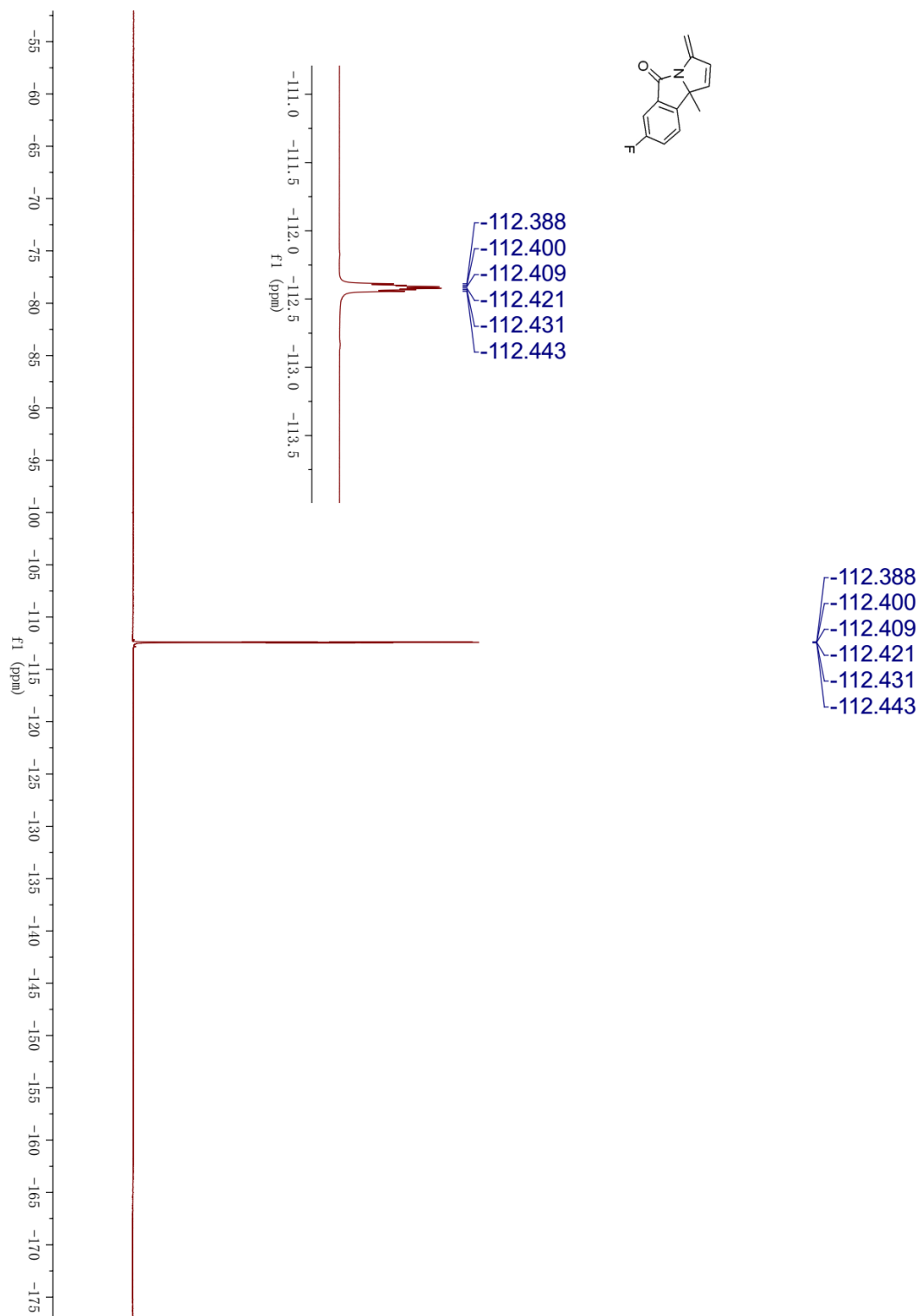
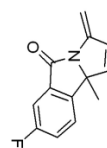
Reported by User: System  
 Report Method: Multi Sample Summary  
 Report Method ID 1007  
 Page: 1 of 1

Project Name: yangping  
 Date Printed:  
 10/24/2018  
 8:29:00 AM PRC

2aj:







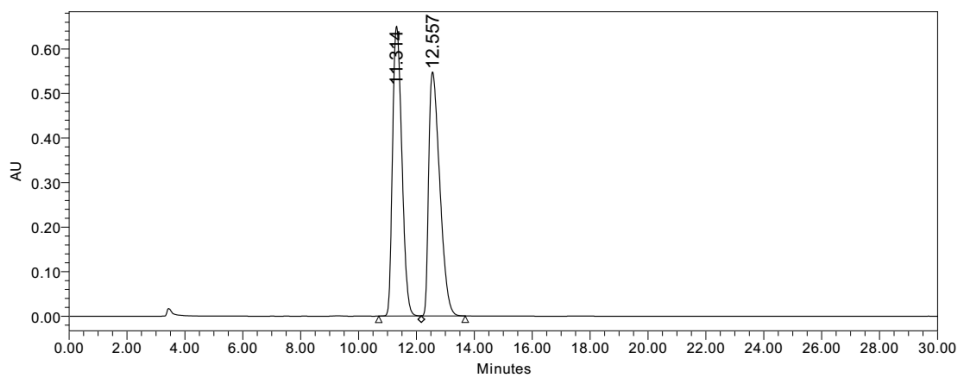
# HPLC of 2aj (racemic)



## Multi Sample Summary

### SAMPLE INFORMATION

|                   |                           |                     |                 |
|-------------------|---------------------------|---------------------|-----------------|
| Sample Name:      | yp-7-31-rac               | Acquired By:        | System          |
| Sample Type:      | Unknown                   | Sample Set Name:    | 1               |
| Vial:             | 1:A,2                     | Acq. Method Set:    | yp9901254       |
| Injection #:      | 1                         | Processing Method   | q               |
| Injection Volume: | 10.00 ul                  | Channel Name:       | W2489 ChA       |
| Run Time:         | 30.0 Minutes              | Proc. Chnl. Descr.: | W2489 ChA 254nm |
| Date Acquired:    | 5/25/2018 11:13:46 AM CST |                     |                 |
| Date Processed:   | 7/18/2018 12:11:14 AM CST |                     |                 |



|   | RT     | Area     | % Area | Height |
|---|--------|----------|--------|--------|
| 1 | 11.314 | 14532806 | 50.01  | 650646 |
| 2 | 12.557 | 14526184 | 49.99  | 548203 |

Reported by User: System  
 Report Method: Multi Sample Summary  
 Report Method ID 1007  
 Page: 1 of 1

Project Name: yangping  
 Date Printed:  
 7/18/2018  
 12:11:45 AM PRC

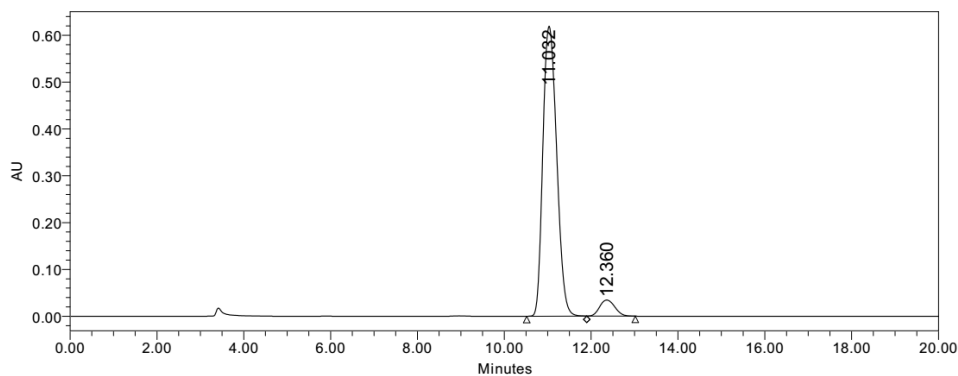
# HPLC of 2aj (chiral)



## Multi Sample Summary

### SAMPLE INFORMATION

|                                            |              |                     |                 |
|--------------------------------------------|--------------|---------------------|-----------------|
| Sample Name:                               | yp-7-47-2    | Acquired By:        | System          |
| Sample Type:                               | Unknown      | Sample Set Name:    | 1               |
| Vial:                                      | 1:A,2        | Acq. Method Set:    | yp9901254       |
| Injection #:                               | 1            | Processing Method:  | 1               |
| Injection Volume:                          | 10.00 ul     | Channel Name:       | W2489 ChA       |
| Run Time:                                  | 20.0 Minutes | Proc. Chnl. Descr.: | W2489 ChA 254nm |
| Date Acquired: 5/31/2018 1:25:32 PM CST    |              |                     |                 |
| Date Processed: 10/25/2018 10:30:55 AM CST |              |                     |                 |

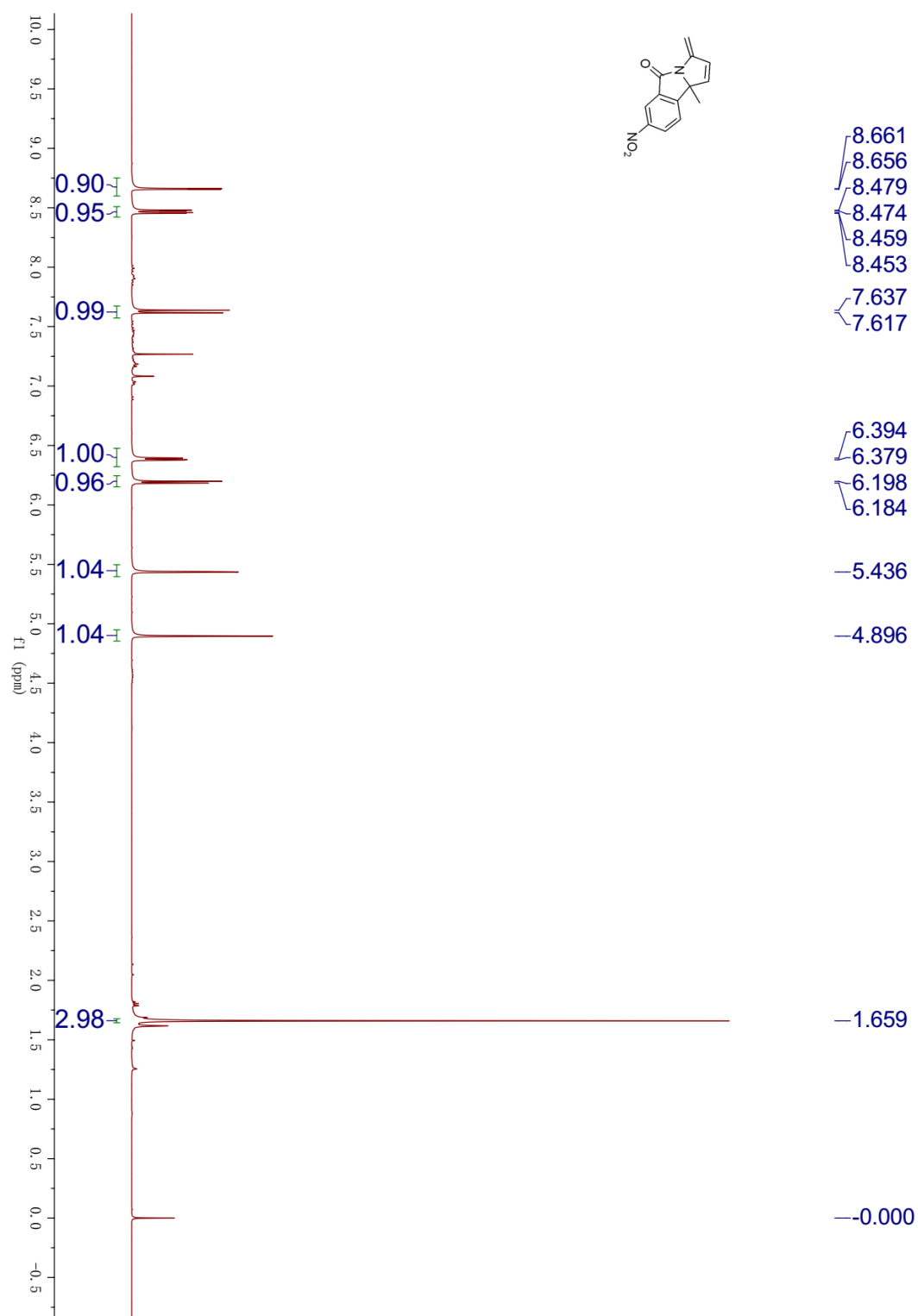


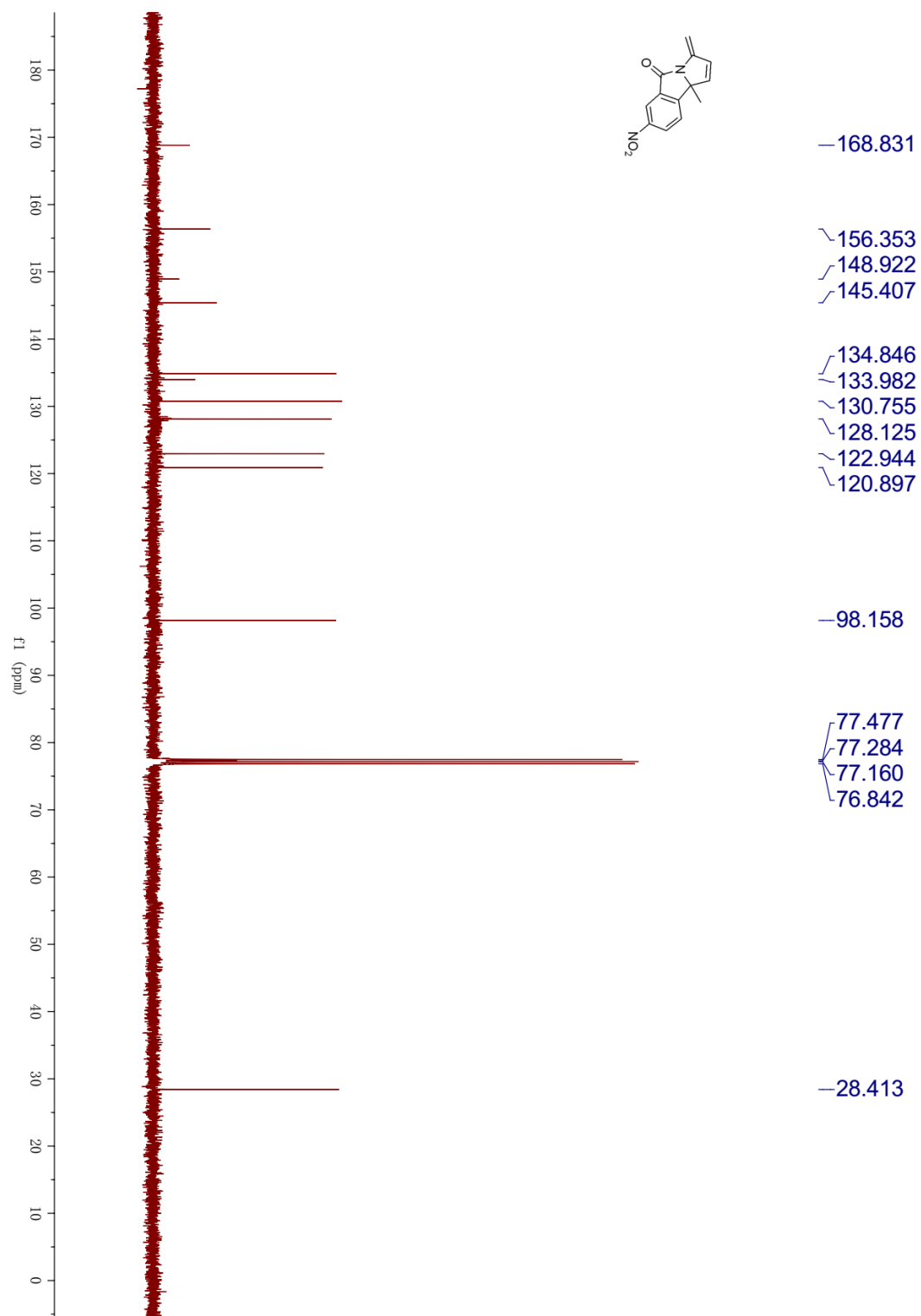
|   | RT     | Area     | % Area | Height |
|---|--------|----------|--------|--------|
| 1 | 11.032 | 13685737 | 94.21  | 619188 |
| 2 | 12.360 | 841689   | 5.79   | 34426  |

Reported by User: System  
 Report Method: Multi Sample Summary  
 Report Method ID 1007  
 Page: 1 of 1

Project Name: yangping  
 Date Printed:  
 10/25/2018  
 10:31:44 AM PRC

2ak:





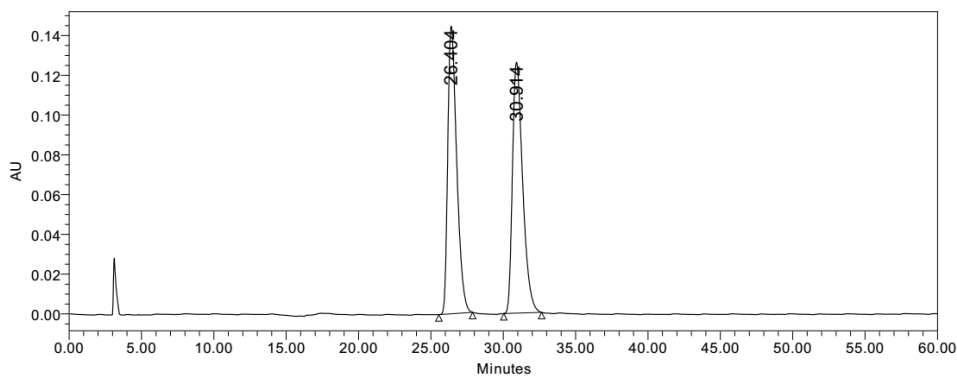
# HPLC of **2ak** (racemic)



## Multi Sample Summary

### SAMPLE INFORMATION

|                                           |              |                     |                 |
|-------------------------------------------|--------------|---------------------|-----------------|
| Sample Name:                              | yp-7-52-2    | Acquired By:        | System          |
| Sample Type:                              | Unknown      | Sample Set Name:    | 1               |
| Vial:                                     | 1:A,2        | Acq. Method Set:    | YP9505254       |
| Injection #:                              | 1            | Processing Method   | 1               |
| Injection Volume:                         | 10.00 ul     | Channel Name:       | W2489 ChA       |
| Run Time:                                 | 60.0 Minutes | Proc. Chnl. Descr.: | W2489 ChA 254nm |
| Date Acquired: 6/2/2018 10:05:46 PM CST   |              |                     |                 |
| Date Processed: 7/17/2018 11:55:04 PM CST |              |                     |                 |



|   | RT     | Area    | % Area | Height |
|---|--------|---------|--------|--------|
| 1 | 26.404 | 6214577 | 50.05  | 144655 |
| 2 | 30.914 | 6202042 | 49.95  | 126176 |

Reported by User: System  
 Report Method: Multi Sample Summary  
 Report Method ID 1007  
 Page: 1 of 1

Project Name: yangping  
 Date Printed: 7/17/2018  
 11:55:25 PM PRC

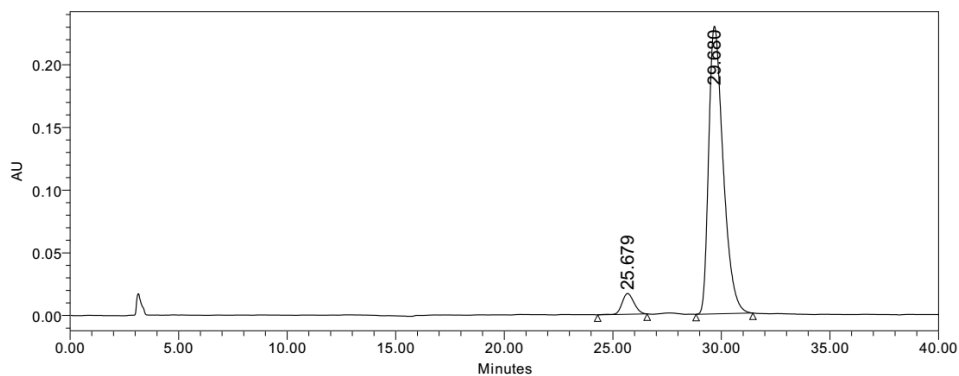
# HPLC of 2ak (chiral)



## Multi Sample Summary

### SAMPLE INFORMATION

|                   |                           |                     |                 |
|-------------------|---------------------------|---------------------|-----------------|
| Sample Name:      | yp-7-68-2                 | Acquired By:        | System          |
| Sample Type:      | Unknown                   | Sample Set Name:    | 1               |
| Vial:             | 1:A,2                     | Acq. Method Set:    | YP9505254       |
| Injection #:      | 1                         | Processing Method:  | 4761165         |
| Injection Volume: | 10.00 ul                  | Channel Name:       | W2489 ChA       |
| Run Time:         | 40.0 Minutes              | Proc. Chnl. Descr.: | W2489 ChA 254nm |
| Date Acquired:    | 6/6/2018 12:53:03 PM CST  |                     |                 |
| Date Processed:   | 10/24/2018 8:37:32 AM CST |                     |                 |

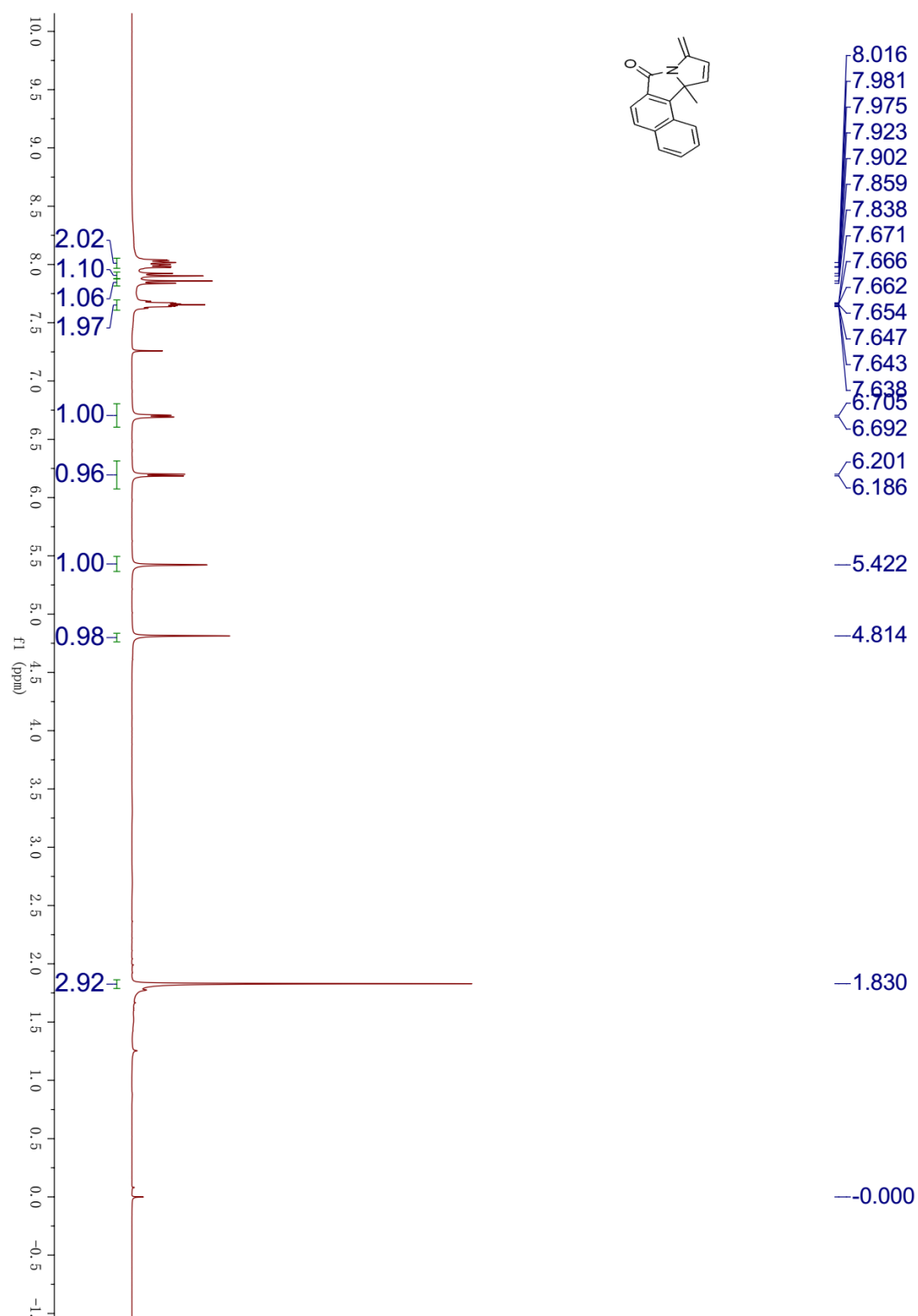


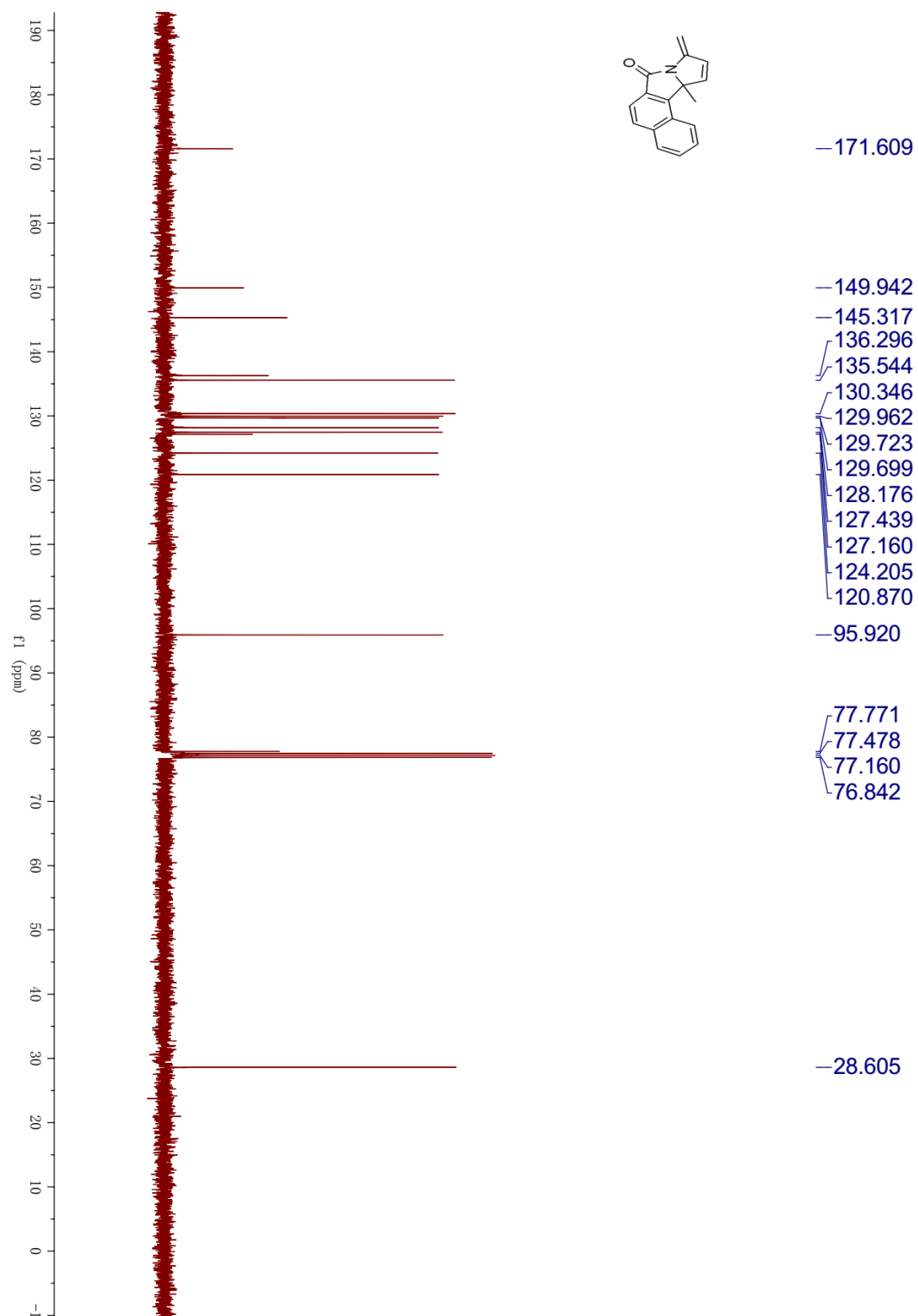
|   | RT     | Area     | % Area | Height |
|---|--------|----------|--------|--------|
| 1 | 25.679 | 631332   | 5.61   | 16528  |
| 2 | 29.680 | 10628158 | 94.39  | 229389 |

Reported by User: System  
 Report Method: Multi Sample Summary  
 Report Method ID 1007  
 Page: 1 of 1

Project Name: yangping  
 Date Printed:  
 10/24/2018  
 8:38:01 AM PRC

2al:





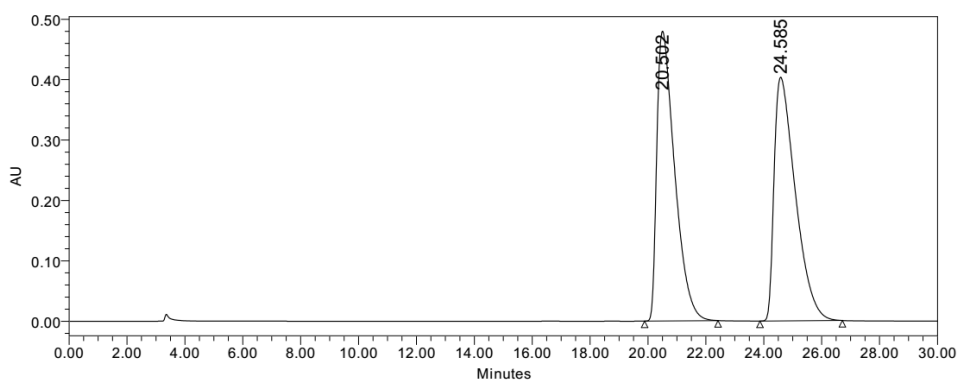
# HPLC of 2aI (racemic)



## Multi Sample Summary

### SAMPLE INFORMATION

|                   |                           |                     |                 |
|-------------------|---------------------------|---------------------|-----------------|
| Sample Name:      | yp-7-54-2                 | Acquired By:        | System          |
| Sample Type:      | Unknown                   | Sample Set Name:    | 1               |
| Vial:             | 1:A,2                     | Acq. Method Set:    | yp9901254       |
| Injection #:      | 1                         | Processing Method   | 1               |
| Injection Volume: | 10.00 ul                  | Channel Name:       | W2489 ChA       |
| Run Time:         | 30.0 Minutes              | Proc. Chnl. Descr.: | W2489 ChA 254nm |
| Date Acquired:    | 6/2/2018 1:27:21 AM CST   |                     |                 |
| Date Processed:   | 7/17/2018 11:50:44 PM CST |                     |                 |



|   | RT     | Area     | % Area | Height |
|---|--------|----------|--------|--------|
| 1 | 20.502 | 20535381 | 49.97  | 479822 |
| 2 | 24.585 | 20556559 | 50.03  | 403485 |

Reported by User: System  
 Report Method: Multi Sample Summary  
 Report Method ID 1007  
 Page: 1 of 1

Project Name: yangping  
 Date Printed:  
 7/17/2018  
 11:51:26 PM PRC

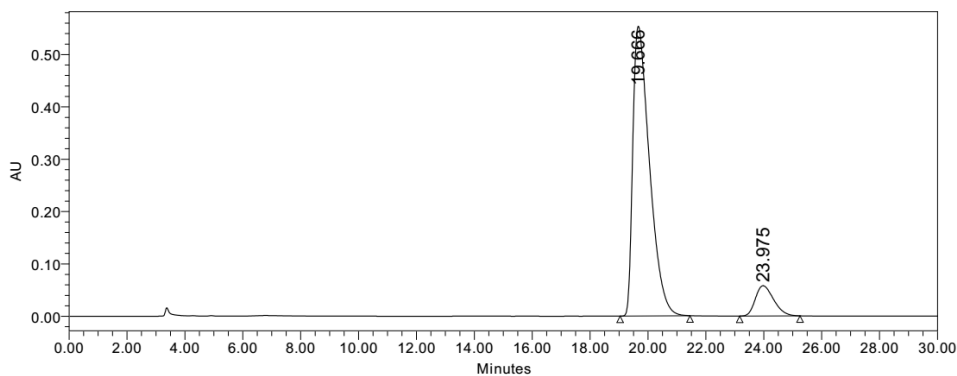
# HPLC of 2aI (chiral)



## Multi Sample Summary

### SAMPLE INFORMATION

|                   |                           |                     |                 |
|-------------------|---------------------------|---------------------|-----------------|
| Sample Name:      | yp-7-68-2                 | Acquired By:        | System          |
| Sample Type:      | Unknown                   | Sample Set Name:    | 1               |
| Vial:             | 1:A,2                     | Acq. Method Set:    | yp9901254       |
| Injection #:      | 1                         | Processing Method:  | 1               |
| Injection Volume: | 10.00 ul                  | Channel Name:       | W2489 ChA       |
| Run Time:         | 30.0 Minutes              | Proc. Chnl. Descr.: | W2489 ChA 254nm |
| Date Acquired:    | 6/5/2018 4:16:04 PM CST   |                     |                 |
| Date Processed:   | 10/24/2018 3:07:15 PM CST |                     |                 |

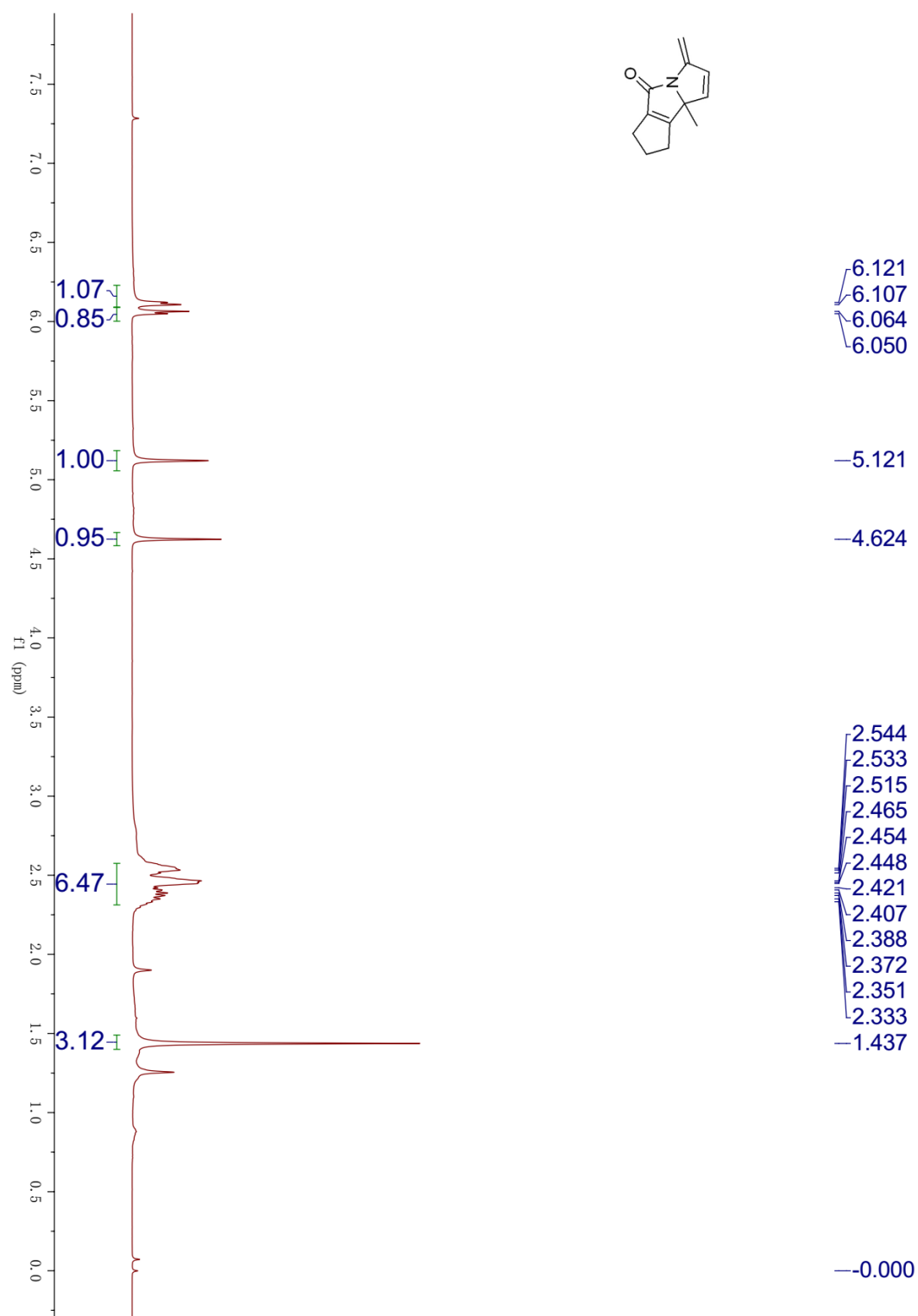


|   | RT     | Area     | % Area | Height |
|---|--------|----------|--------|--------|
| 1 | 19.666 | 22128106 | 89.71  | 553645 |
| 2 | 23.975 | 2537087  | 10.29  | 57871  |

Reported by User: System  
 Report Method: Multi Sample Summary  
 Report Method ID 1007  
 Page: 1 of 1

Project Name: yangping  
 Date Printed:  
 10/24/2018  
 3:07:54 PM PRC

2am:



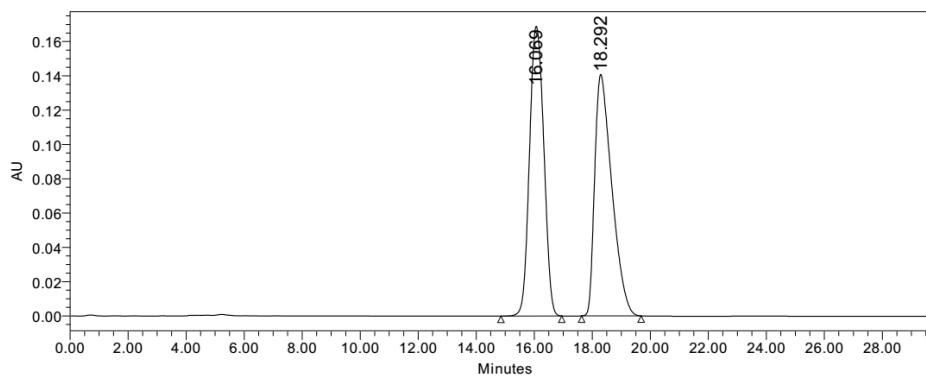
# HPLC of 2am (racemic)



## Multi Sample Summary

### SAMPLE INFORMATION

|                   |                           |                     |                 |
|-------------------|---------------------------|---------------------|-----------------|
| Sample Name:      | yp-7-82-2                 | Acquired By:        | System          |
| Sample Type:      | Unknown                   | Sample Set Name:    | 1               |
| Vial:             | 1:A,2                     | Acq. Method Set:    | yp9901254       |
| Injection #:      | 1                         | Processing Method   | 1               |
| Injection Volume: | 10.00 ul                  | Channel Name:       | W2489 ChA       |
| Run Time:         | 40.0 Minutes              | Proc. Chnl. Descr.: | W2489 ChA 254nm |
| Date Acquired:    | 6/8/2018 11:54:32 PM CST  |                     |                 |
| Date Processed:   | 7/17/2018 11:44:28 PM CST |                     |                 |



|   | RT     | Area    | % Area | Height |
|---|--------|---------|--------|--------|
| 1 | 16.069 | 5786955 | 49.99  | 169018 |
| 2 | 18.292 | 5788588 | 50.01  | 140873 |

Reported by User: System  
 Report Method: Multi Sample Summary  
 Report Method ID 1007  
 Page: 1 of 1

Project Name: yangping  
 Date Printed:  
 7/17/2018  
 11:46:49 PM PRC

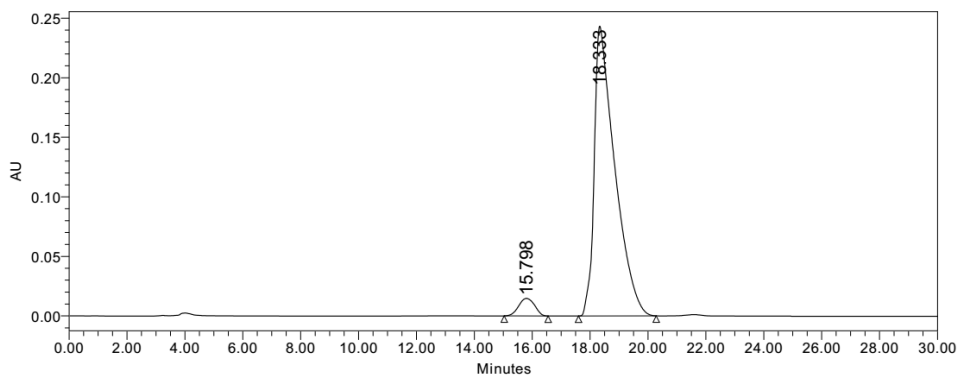
# HPLC of 2am (chiral)



## Multi Sample Summary

### SAMPLE INFORMATION

|                   |                           |                     |                 |
|-------------------|---------------------------|---------------------|-----------------|
| Sample Name:      | yp-7-85-2                 | Acquired By:        | System          |
| Sample Type:      | Unknown                   | Sample Set Name:    | 1               |
| Vial:             | 1:A,2                     | Acq. Method Set:    | yp9901254       |
| Injection #:      | 1                         | Processing Method   | 1               |
| Injection Volume: | 10.00 ul                  | Channel Name:       | W2489 ChA       |
| Run Time:         | 30.0 Minutes              | Proc. Chnl. Descr.: | W2489 ChA 254nm |
| Date Acquired:    | 6/9/2018 10:47:41 AM CST  |                     |                 |
| Date Processed:   | 10/24/2018 8:42:44 AM CST |                     |                 |

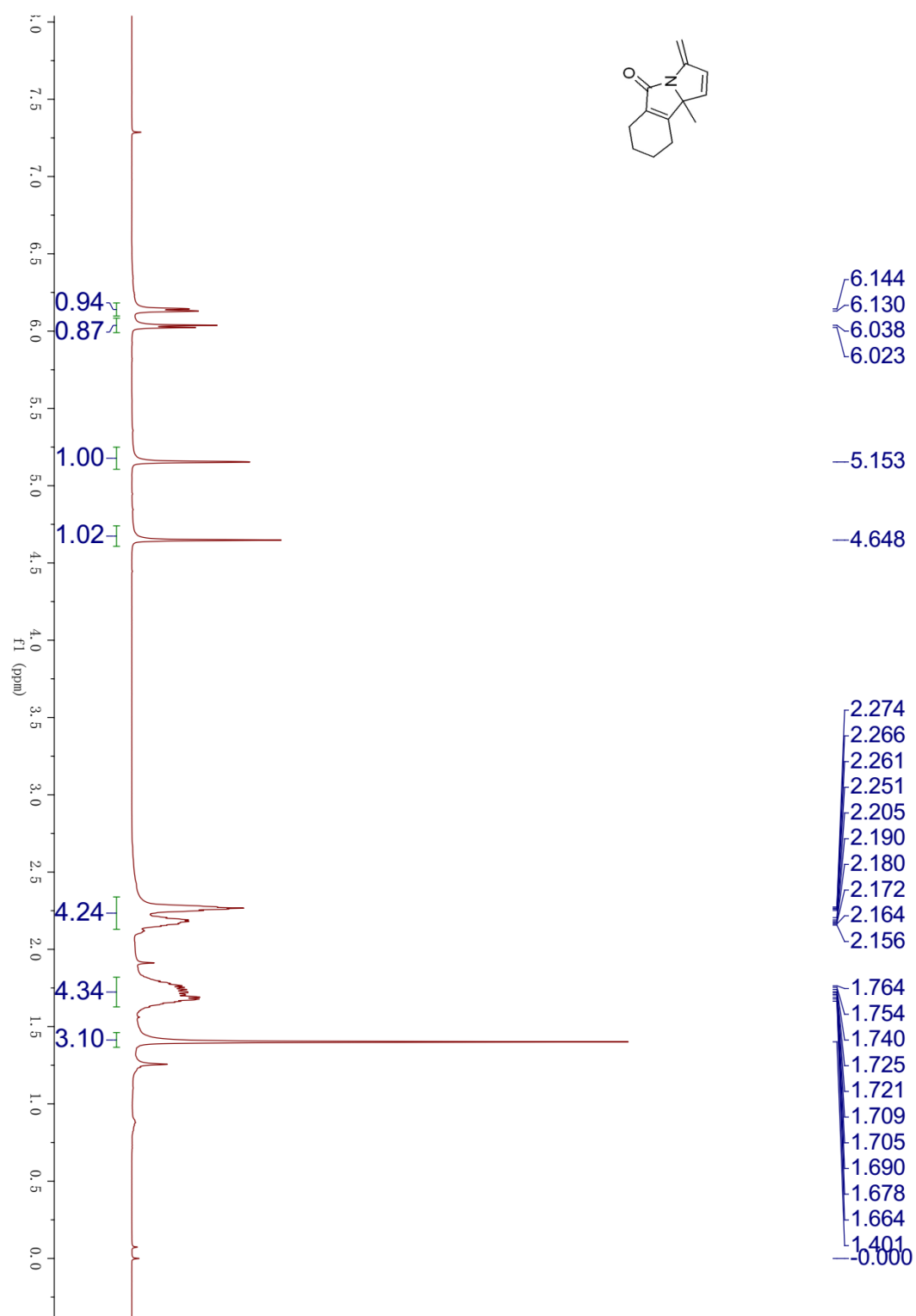


|   | RT     | Area     | % Area | Height |
|---|--------|----------|--------|--------|
| 1 | 15.798 | 565069   | 4.49   | 14734  |
| 2 | 18.333 | 12020054 | 95.51  | 243282 |

Reported by User: System  
 Report Method: Multi Sample Summary  
 Report Method ID 1007  
 Page: 1 of 1

Project Name: yangping  
 Date Printed:  
 10/24/2018  
 8:43:15 AM PRC

2an:



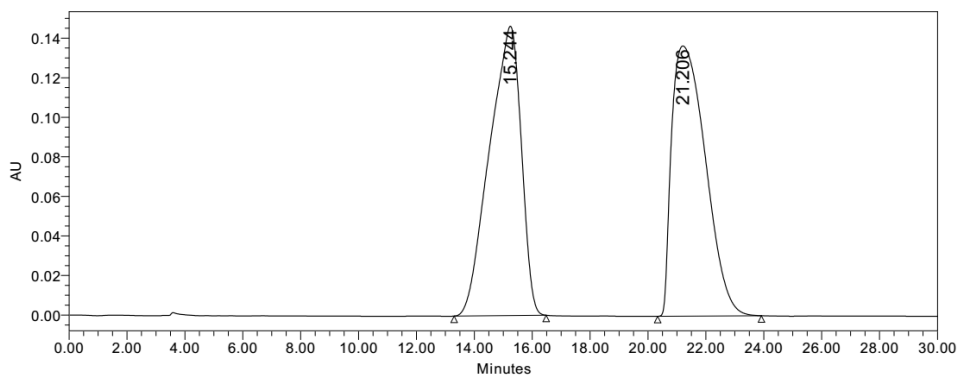
# HPLC of 2an (racemic)



## Multi Sample Summary

### SAMPLE INFORMATION

|                   |                           |                     |                 |
|-------------------|---------------------------|---------------------|-----------------|
| Sample Name:      | yp-7-83-2                 | Acquired By:        | System          |
| Sample Type:      | Unknown                   | Sample Set Name:    | 1               |
| Vial:             | 1:A,2                     | Acq. Method Set:    | yp9901254       |
| Injection #:      | 1                         | Processing Method   | 1               |
| Injection Volume: | 10.00 ul                  | Channel Name:       | W2489 ChA       |
| Run Time:         | 30.0 Minutes              | Proc. Chnl. Descr.: | W2489 ChA 254nm |
| Date Acquired:    | 6/9/2018 9:47:00 AM CST   |                     |                 |
| Date Processed:   | 7/17/2018 11:42:00 PM CST |                     |                 |



|   | RT     | Area     | % Area | Height |
|---|--------|----------|--------|--------|
| 1 | 15.244 | 11127235 | 50.06  | 146317 |
| 2 | 21.206 | 11098576 | 49.94  | 136612 |

Reported by User: System  
 Report Method: Multi Sample Summary  
 Report Method ID 1007  
 Page: 1 of 1

Project Name: yangping  
 Date Printed:  
 7/17/2018  
 11:42:40 PM PRC

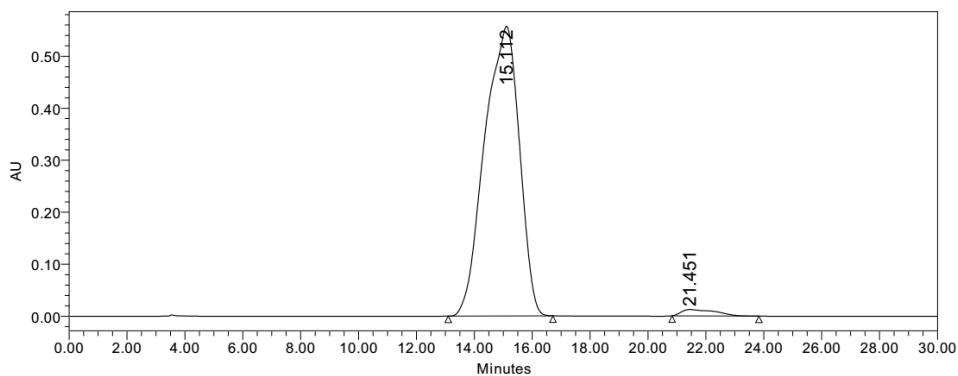
# HPLC of 2an (chiral)



## Multi Sample Summary

### SAMPLE INFORMATION

|                   |                           |                     |                 |
|-------------------|---------------------------|---------------------|-----------------|
| Sample Name:      | yp-7-87-2                 | Acquired By:        | System          |
| Sample Type:      | Unknown                   | Sample Set Name:    | 1               |
| Vial:             | 1:A,2                     | Acq. Method Set:    | yp9901254       |
| Injection #:      | 1                         | Processing Method   | 1               |
| Injection Volume: | 10.00 ul                  | Channel Name:       | W2489 ChA       |
| Run Time:         | 30.0 Minutes              | Proc. Chnl. Descr.: | W2489 ChA 254nm |
| Date Acquired:    | 6/9/2018 12:01:27 PM CST  |                     |                 |
| Date Processed:   | 10/24/2018 8:45:35 AM CST |                     |                 |

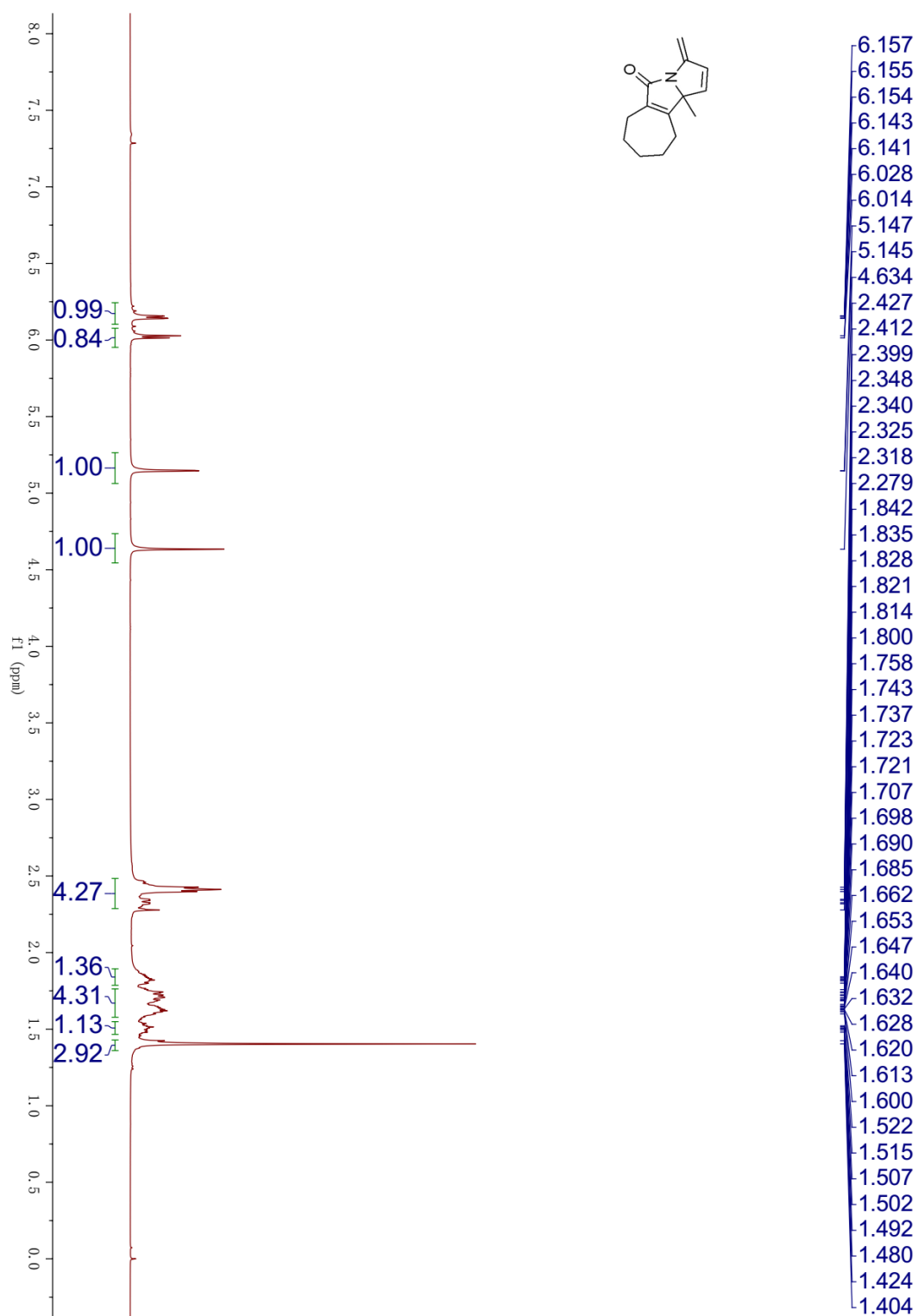


|   | RT     | Area     | % Area | Height |
|---|--------|----------|--------|--------|
| 1 | 15.112 | 46476373 | 97.87  | 557123 |
| 2 | 21.451 | 1010524  | 2.13   | 12235  |

Reported by User: System  
 Report Method: Multi Sample Summary  
 Report Method ID 1007  
 Page: 1 of 1

Project Name: yangping  
 Date Printed:  
 10/24/2018  
 8:46:10 AM PRC

2ao:



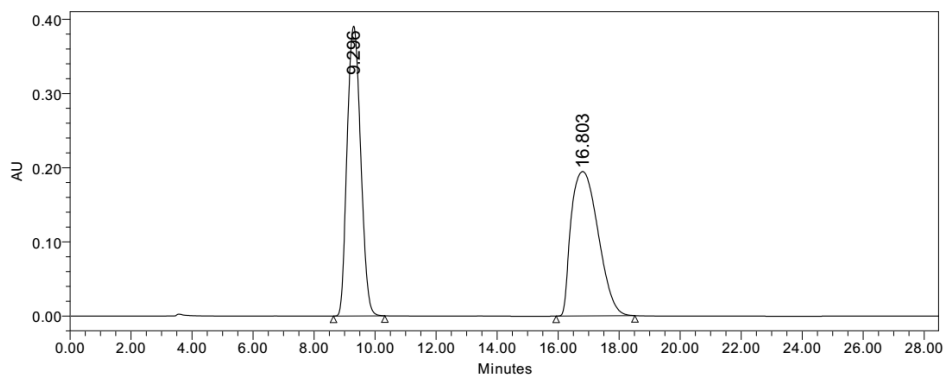
# HPLC of 2ao (racemic)



## Multi Sample Summary

### SAMPLE INFORMATION

|                   |                            |                     |                 |
|-------------------|----------------------------|---------------------|-----------------|
| Sample Name:      | yp-7-84-2                  | Acquired By:        | System          |
| Sample Type:      | Unknown                    | Sample Set Name:    | 1               |
| Vial:             | 1:A,4                      | Acq. Method Set:    | yp9901254       |
| Injection #:      | 1                          | Processing Method:  | 1               |
| Injection Volume: | 10.00 ul                   | Channel Name:       | W2489 ChA       |
| Run Time:         | 40.0 Minutes               | Proc. Chnl. Descr.: | W2489 ChA 254nm |
| Date Acquired:    | 6/8/2018 10:13:23 PM CST   |                     |                 |
| Date Processed:   | 10/25/2018 12:16:29 PM CST |                     |                 |



|   | RT     | Area     | % Area | Height |
|---|--------|----------|--------|--------|
| 1 | 9.296  | 12035995 | 50.10  | 390581 |
| 2 | 16.803 | 11990091 | 49.90  | 194668 |

Reported by User: System  
 Report Method: Multi Sample Summary  
 Report Method ID 1007  
 Page: 1 of 1

Project Name: yangping  
 Date Printed:  
 10/25/2018  
 12:17:01 PM PRC

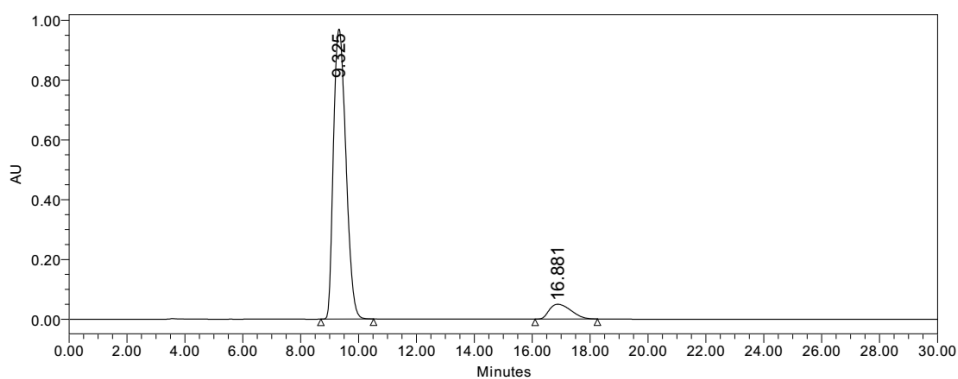
# HPLC of 2ao (chiral)



## Multi Sample Summary

### SAMPLE INFORMATION

|                   |                           |                     |                 |
|-------------------|---------------------------|---------------------|-----------------|
| Sample Name:      | yp-7-88-2                 | Acquired By:        | System          |
| Sample Type:      | Unknown                   | Sample Set Name:    | 1               |
| Vial:             | 1:A,2                     | Acq. Method Set:    | yp9901254       |
| Injection #:      | 1                         | Processing Method:  | 1               |
| Injection Volume: | 10.00 ul                  | Channel Name:       | W2489 ChA       |
| Run Time:         | 30.0 Minutes              | Proc. Chnl. Descr.: | W2489 ChA 254nm |
| Date Acquired:    | 6/9/2018 1:12:07 PM CST   |                     |                 |
| Date Processed:   | 10/24/2018 8:46:49 AM CST |                     |                 |

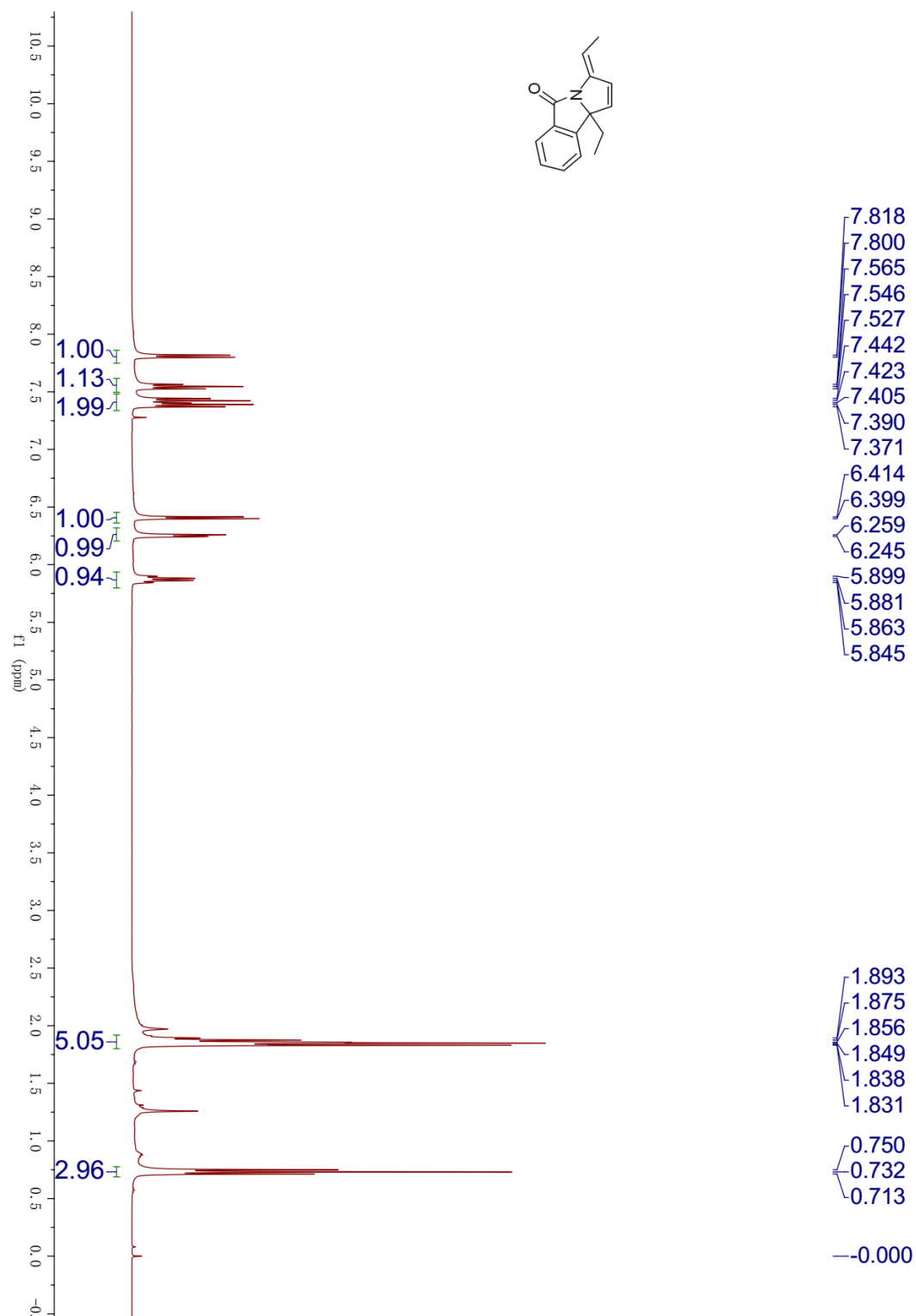


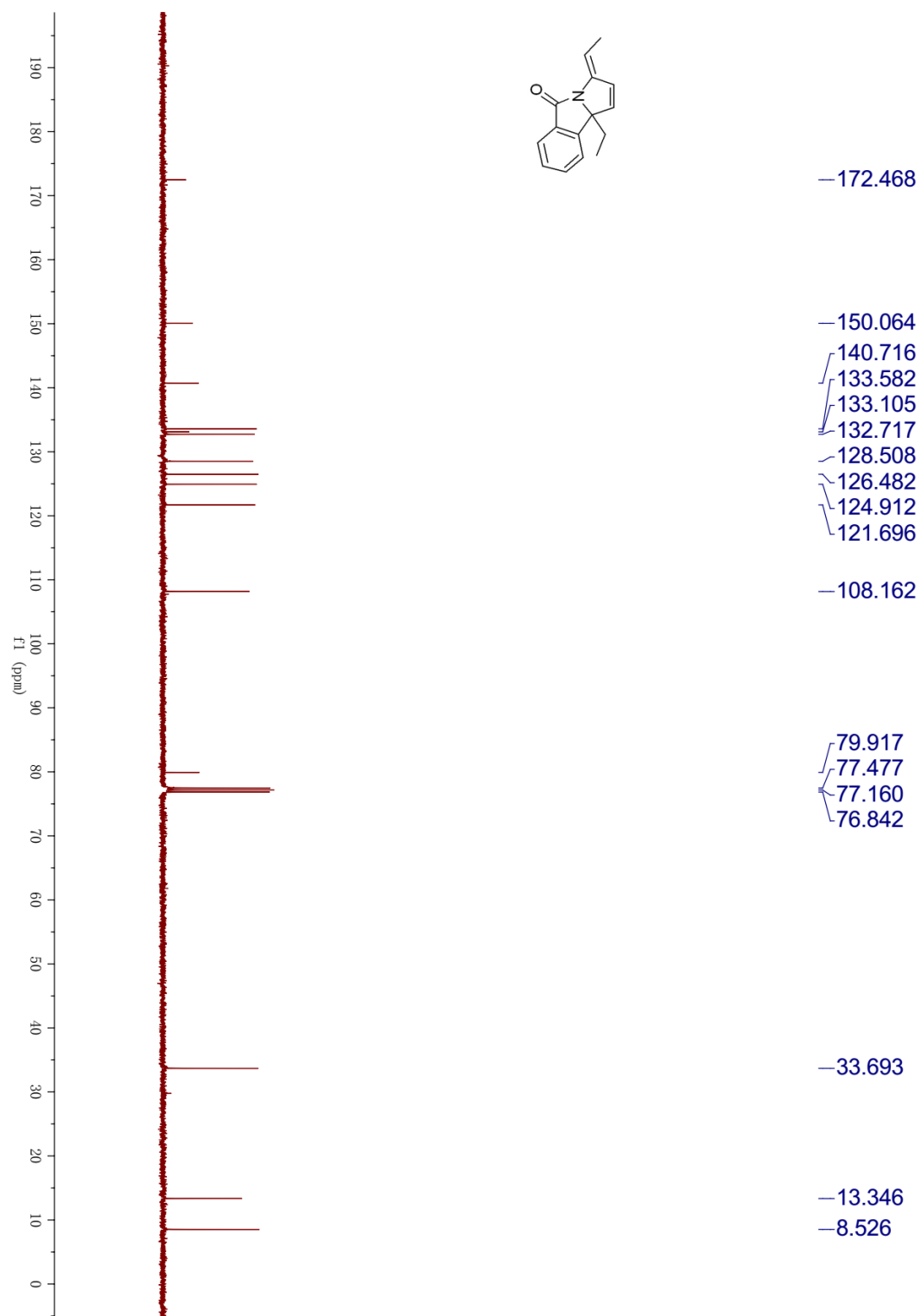
|   | RT     | Area     | % Area | Height |
|---|--------|----------|--------|--------|
| 1 | 9.325  | 28932736 | 91.75  | 970525 |
| 2 | 16.881 | 2601105  | 8.25   | 49742  |

Reported by User: System  
 Report Method: Multi Sample Summary  
 Report Method ID 1007  
 Page: 1 of 1

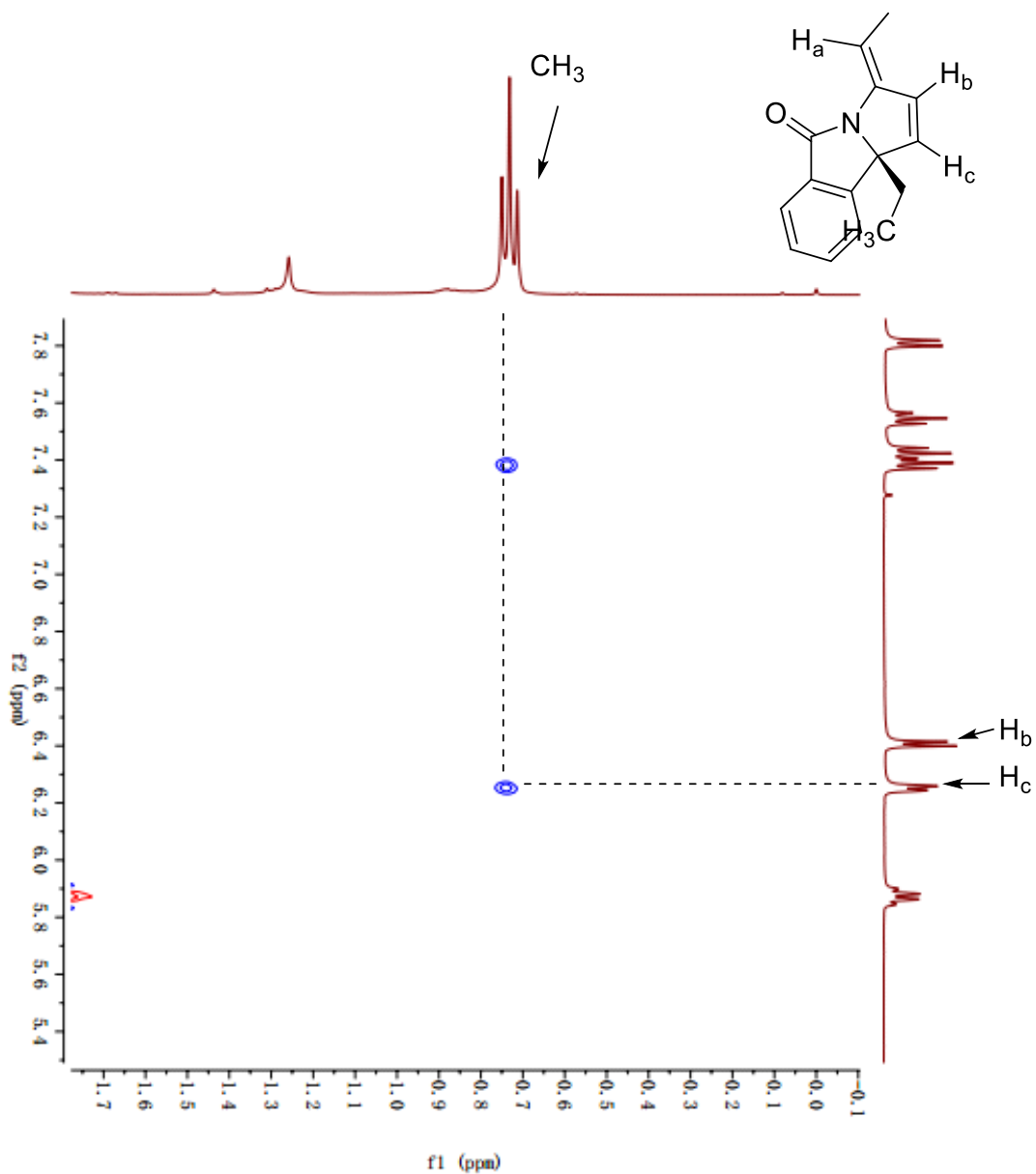
Project Name: yangping  
 Date Printed:  
 10/24/2018  
 8:47:26 AM PRC

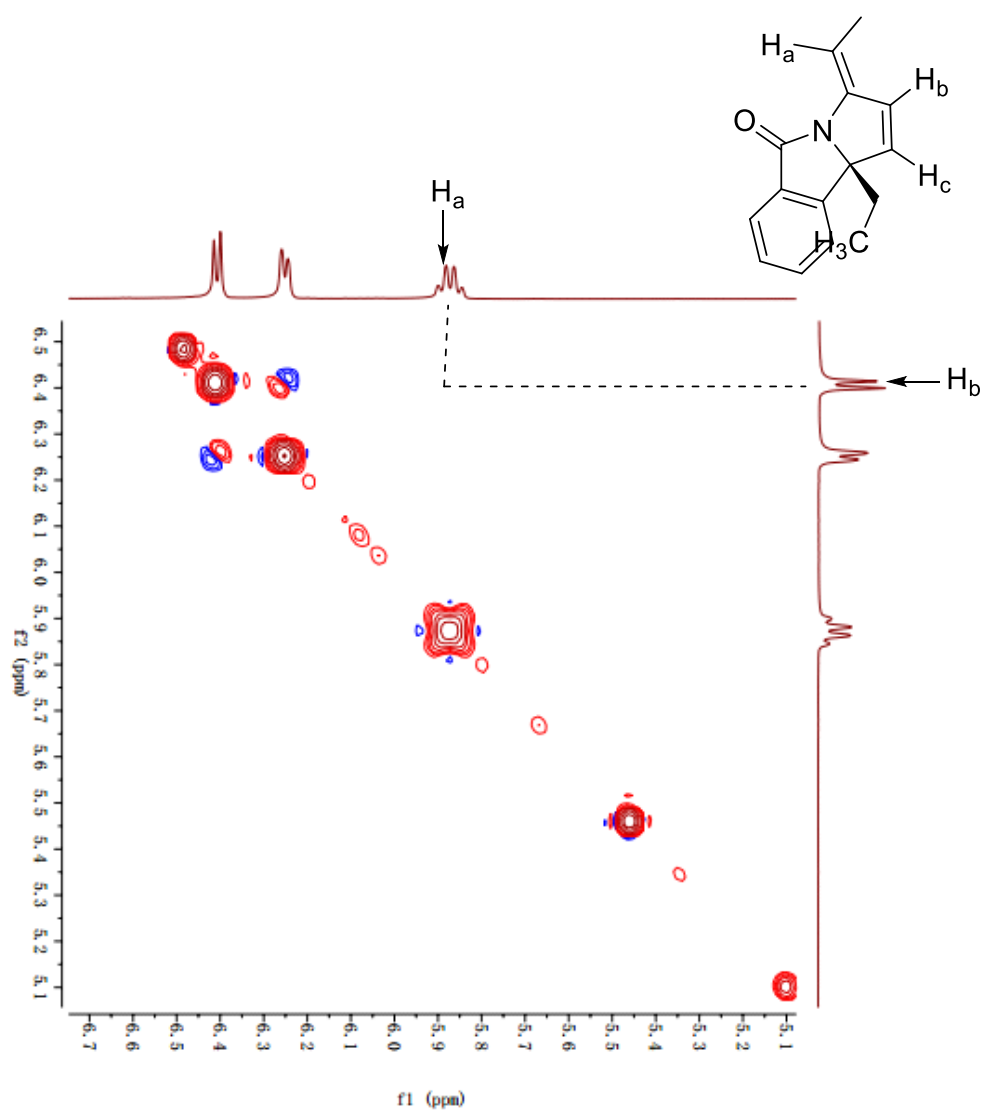
2ba:





NOESY NMR spectra of **2ba** (400 MHz, CDCl<sub>3</sub>)





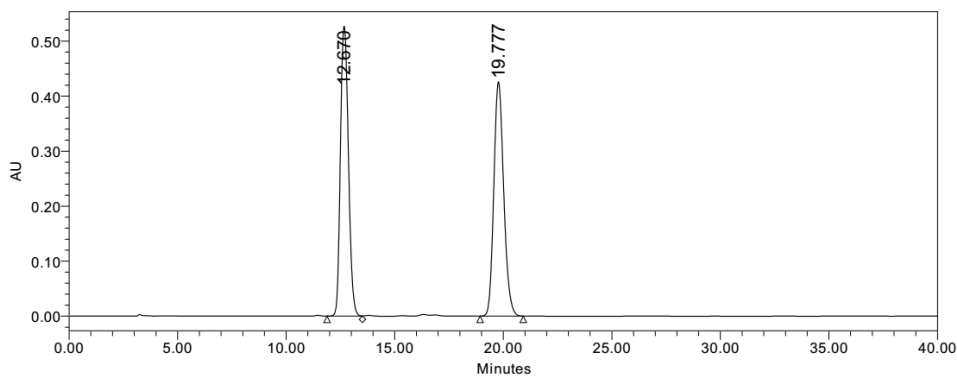
# HPLC of **2ba** (racemic)



## Multi Sample Summary

### SAMPLE INFORMATION

|                                            |              |                     |                 |
|--------------------------------------------|--------------|---------------------|-----------------|
| Sample Name:                               | YP-8-19-2    | Acquired By:        | System          |
| Sample Type:                               | Unknown      | Sample Set Name:    | 1               |
| Vial:                                      | 1:A,2        | Acq. Method Set:    | yp9802254       |
| Injection #:                               | 1            | Processing Method   | 1               |
| Injection Volume:                          | 10.00 ul     | Channel Name:       | W2489 ChA       |
| Run Time:                                  | 40.0 Minutes | Proc. Chnl. Descr.: | W2489 ChA 254nm |
| Date Acquired: 6/27/2018 3:42:20 PM CST    |              |                     |                 |
| Date Processed: 10/25/2018 12:17:46 PM CST |              |                     |                 |



|   | RT     | Area     | % Area | Height |
|---|--------|----------|--------|--------|
| 1 | 12.670 | 13491656 | 49.95  | 527199 |
| 2 | 19.777 | 13521080 | 50.05  | 426129 |

Reported by User: System  
 Report Method: Multi Sample Summary  
 Report Method ID 1007  
 Page: 1 of 1

Project Name: yangping  
 Date Printed:  
 10/25/2018  
 12:18:08 PM PRC

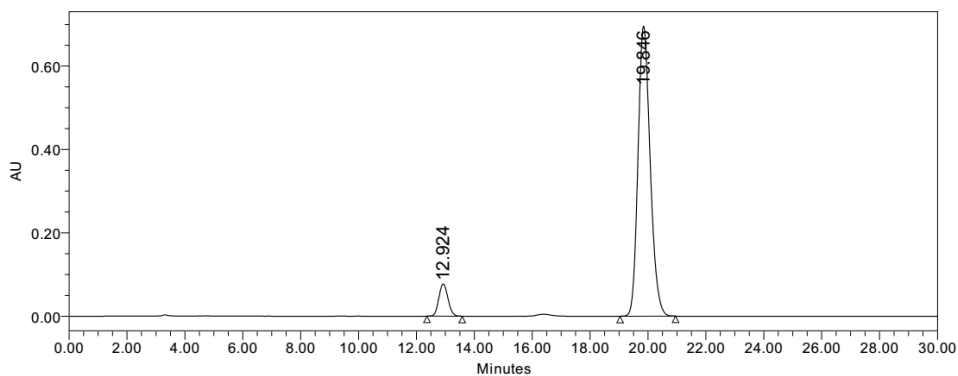
# HPLC of 2ba (chiral)



## Multi Sample Summary

### SAMPLE INFORMATION

|                   |                           |                     |                 |
|-------------------|---------------------------|---------------------|-----------------|
| Sample Name:      | yp-8-36-2-70              | Acquired By:        | System          |
| Sample Type:      | Unknown                   | Sample Set Name:    | 1               |
| Vial:             | 1:A,2                     | Acq. Method Set:    | yp9802254       |
| Injection #:      | 1                         | Processing Method   | 1               |
| Injection Volume: | 10.00 ul                  | Channel Name:       | W2489 ChA       |
| Run Time:         | 30.0 Minutes              | Proc. Chnl. Descr.: | W2489 ChA 254nm |
| Date Acquired:    | 7/4/2018 4:12:51 PM CST   |                     |                 |
| Date Processed:   | 10/24/2018 8:48:45 AM CST |                     |                 |

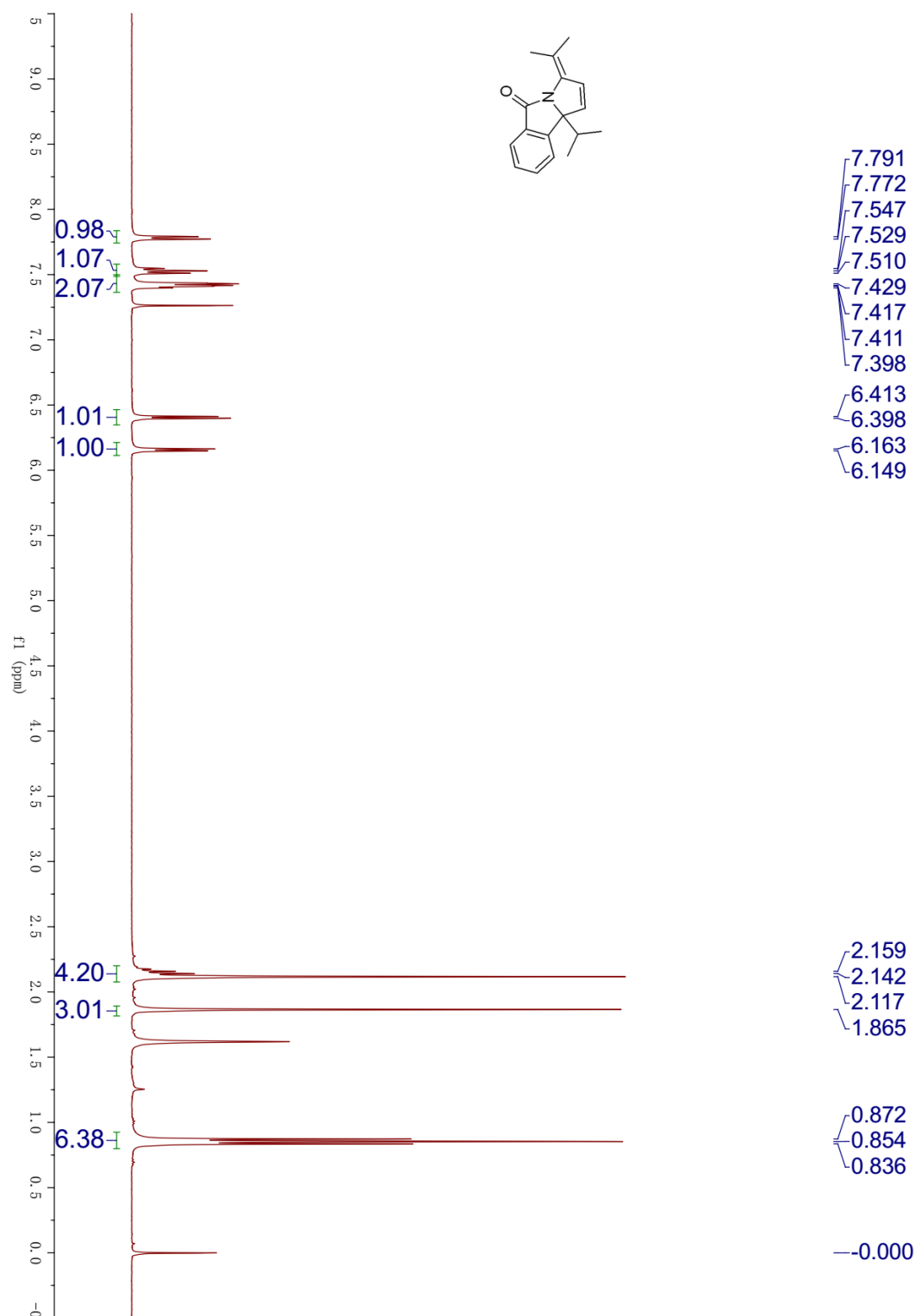


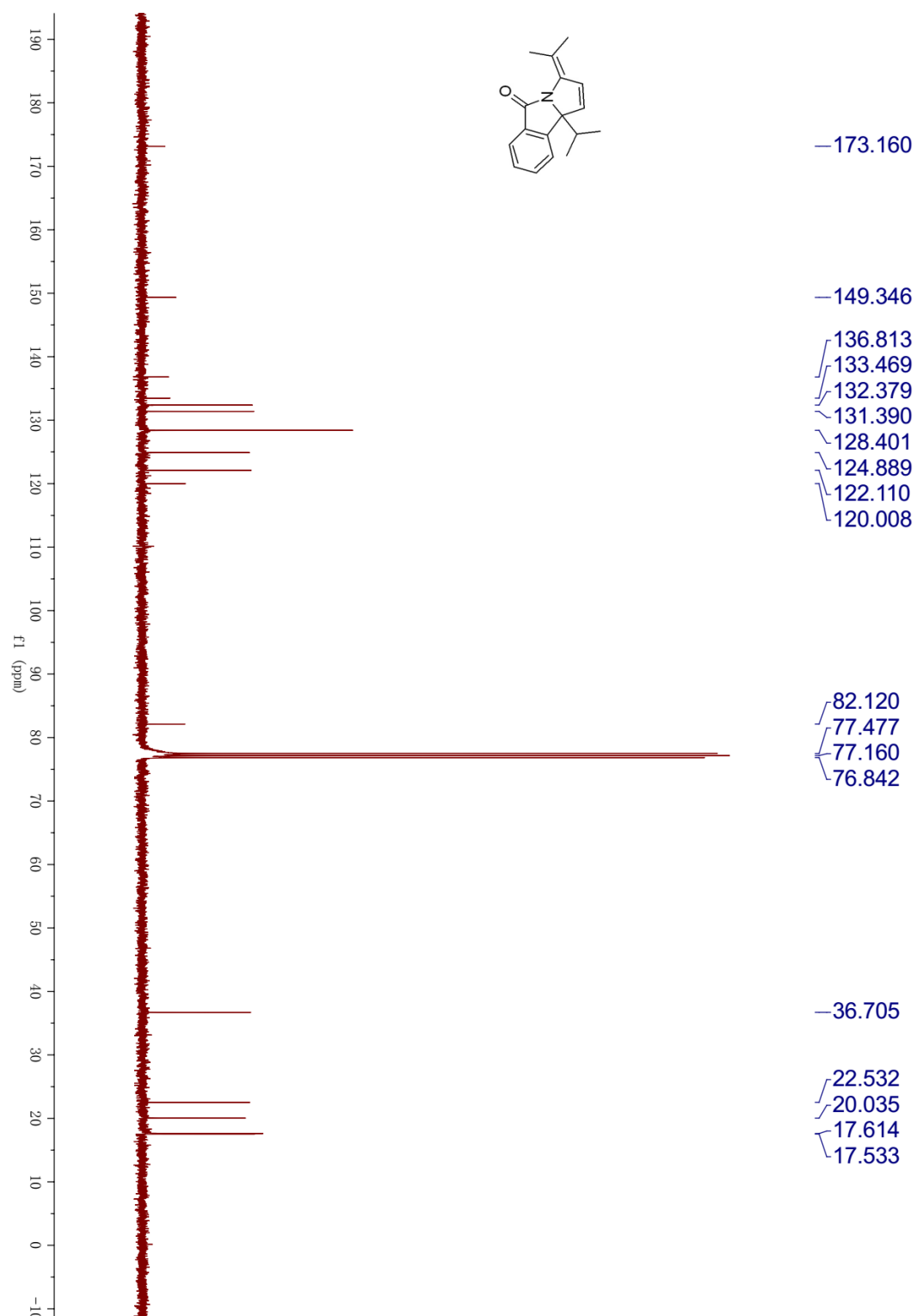
|   | RT     | Area     | % Area | Height |
|---|--------|----------|--------|--------|
| 1 | 12.924 | 1697722  | 7.72   | 77120  |
| 2 | 19.846 | 20291994 | 92.28  | 695674 |

Reported by User: System  
 Report Method: Multi Sample Summary  
 Report Method ID 1007  
 Page: 1 of 1

Project Name: yangping  
 Date Printed:  
 10/24/2018  
 8:49:17 AM PRC

2ca:





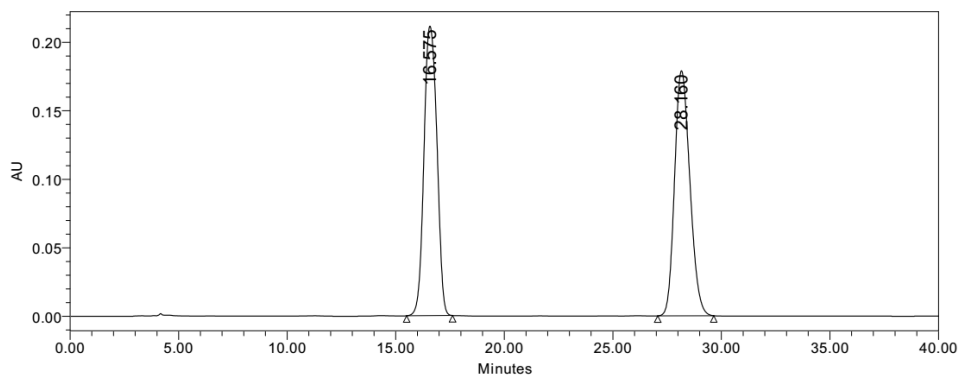
# HPLC of 2ca (racemic)



## Multi Sample Summary

### SAMPLE INFORMATION

|                   |                           |                     |                 |
|-------------------|---------------------------|---------------------|-----------------|
| Sample Name:      | YP-8-72-2                 | Acquired By:        | System          |
| Sample Type:      | Unknown                   | Sample Set Name:    | 1               |
| Vial:             | 1:A,2                     | Acq. Method Set:    | yp9901254       |
| Injection #:      | 1                         | Processing Method   | 11              |
| Injection Volume: | 10.00 ul                  | Channel Name:       | W2489 ChA       |
| Run Time:         | 40.0 Minutes              | Proc. Chnl. Descr.: | W2489 ChA 254nm |
| Date Acquired:    | 7/17/2018 10:41:40 AM CST |                     |                 |
| Date Processed:   | 7/17/2018 10:58:40 PM CST |                     |                 |



|   | RT     | Area    | % Area | Height |
|---|--------|---------|--------|--------|
| 1 | 16.575 | 8759471 | 50.00  | 211349 |
| 2 | 28.160 | 8760679 | 50.00  | 178902 |

Reported by User: System  
 Report Method: Multi Sample Summary  
 Report Method ID 1007  
 Page: 1 of 1

Project Name: yangping  
 Date Printed:  
 7/17/2018  
 10:59:14 PM PRC

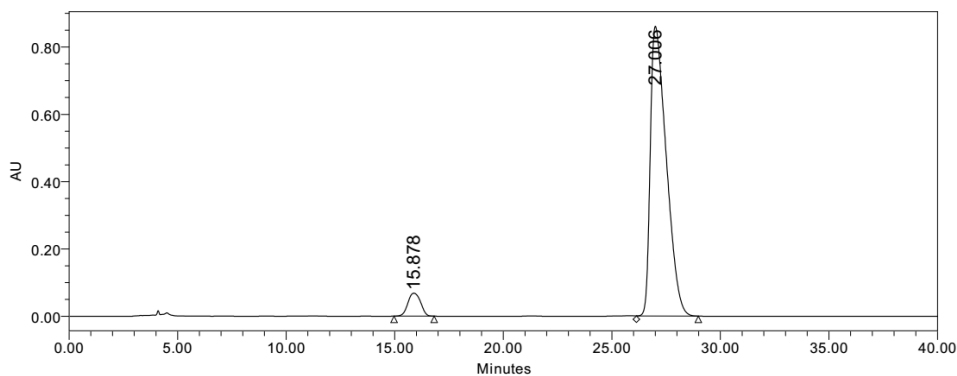
# HPLC of 2ca (chiral)



## Multi Sample Summary

### SAMPLE INFORMATION

|                   |                           |                     |                 |
|-------------------|---------------------------|---------------------|-----------------|
| Sample Name:      | YP-8-73-2                 | Acquired By:        | System          |
| Sample Type:      | Unknown                   | Sample Set Name:    | 1               |
| Vial:             | 1:A,3                     | Acq. Method Set:    | yp9901254       |
| Injection #:      | 1                         | Processing Method   | 1               |
| Injection Volume: | 10.00 ul                  | Channel Name:       | W2489 ChA       |
| Run Time:         | 40.0 Minutes              | Proc. Chnl. Descr.: | W2489 ChA 254nm |
| Date Acquired:    | 7/17/2018 11:22:05 AM CST |                     |                 |
| Date Processed:   | 10/24/2018 8:50:20 AM CST |                     |                 |

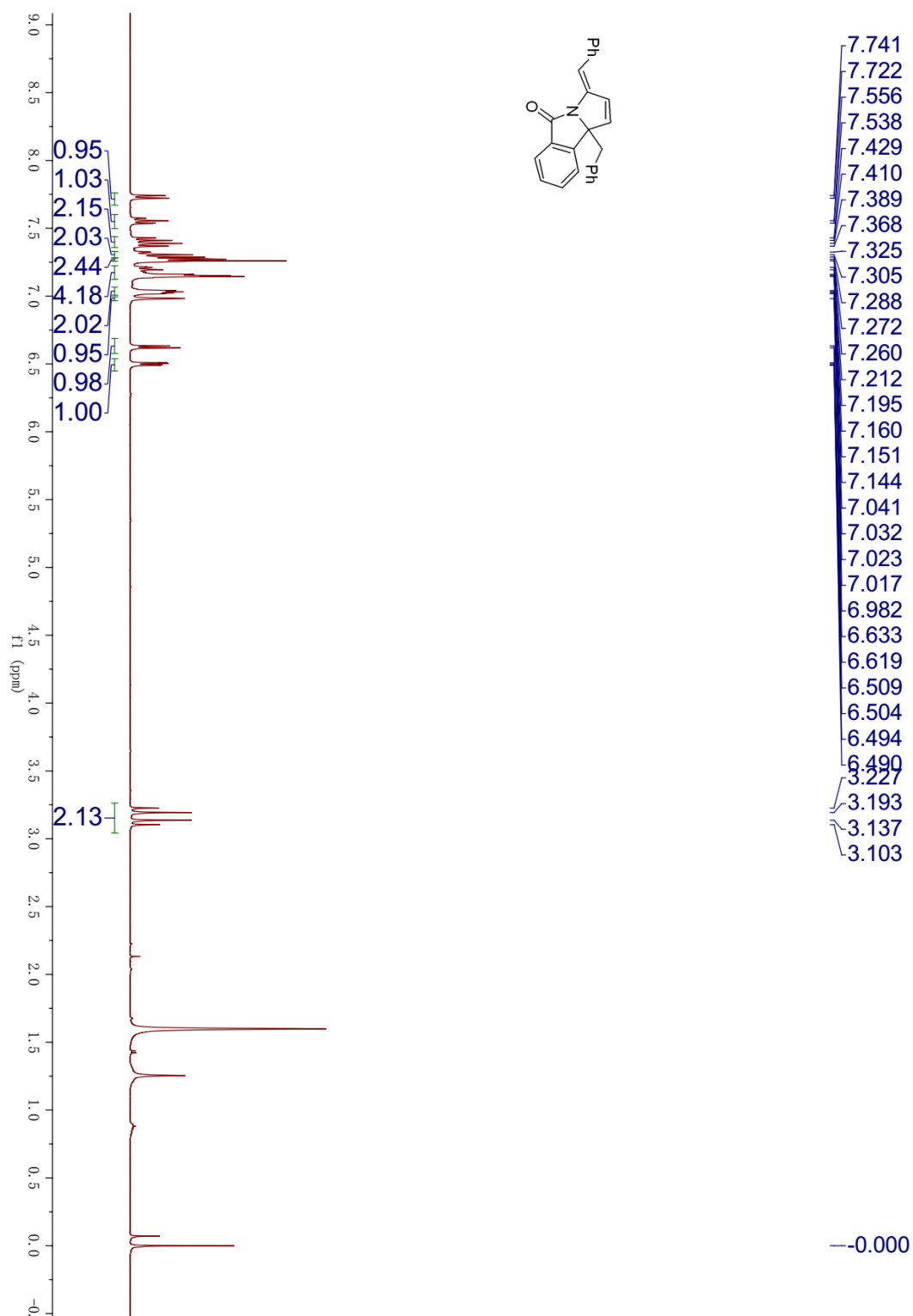


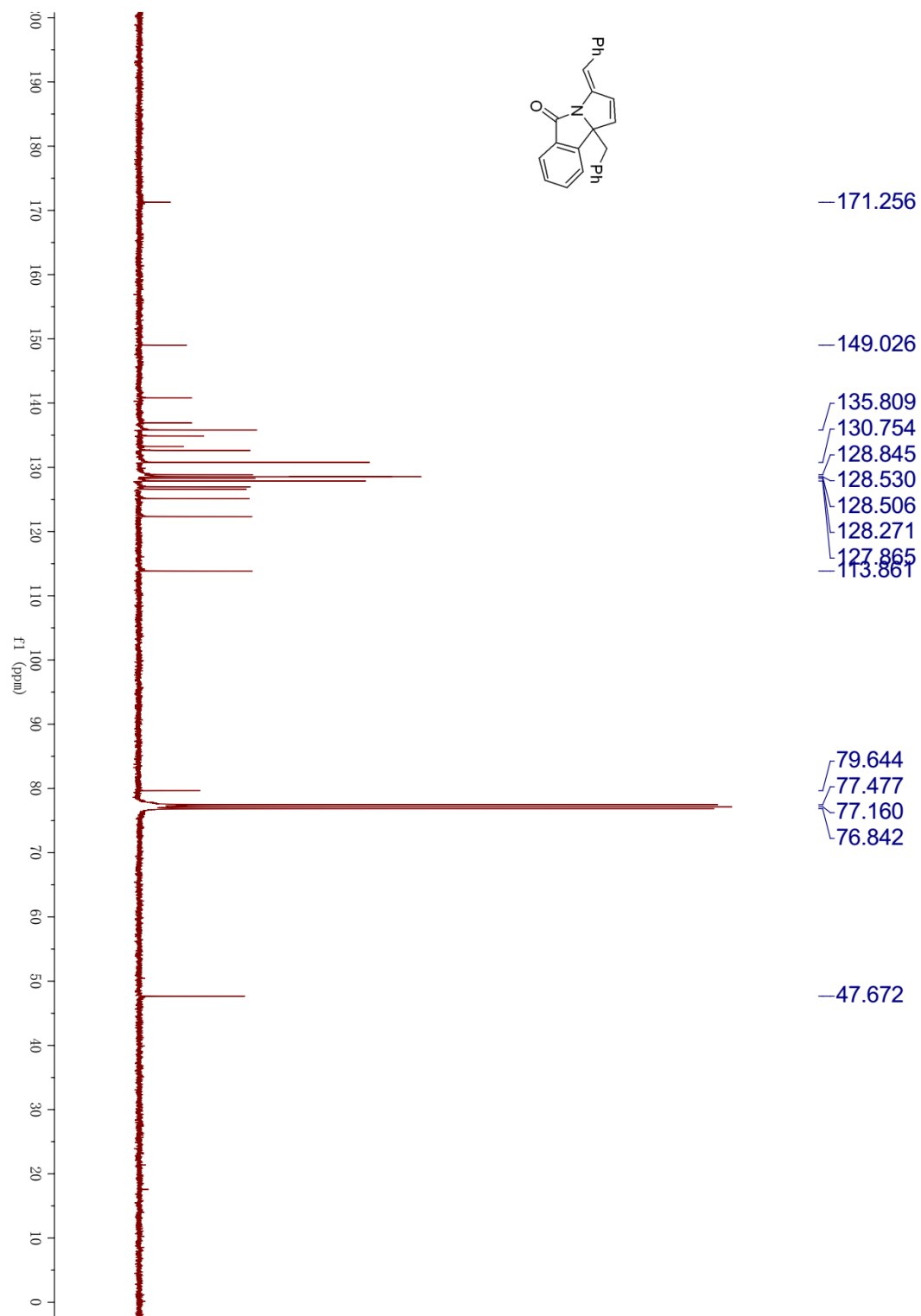
|   | RT     | Area     | % Area | Height |
|---|--------|----------|--------|--------|
| 1 | 15.878 | 2778394  | 5.95   | 68331  |
| 2 | 27.006 | 43887528 | 94.05  | 861137 |

Reported by User: System  
 Report Method: Multi Sample Summary  
 Report Method ID 1007  
 Page: 1 of 1

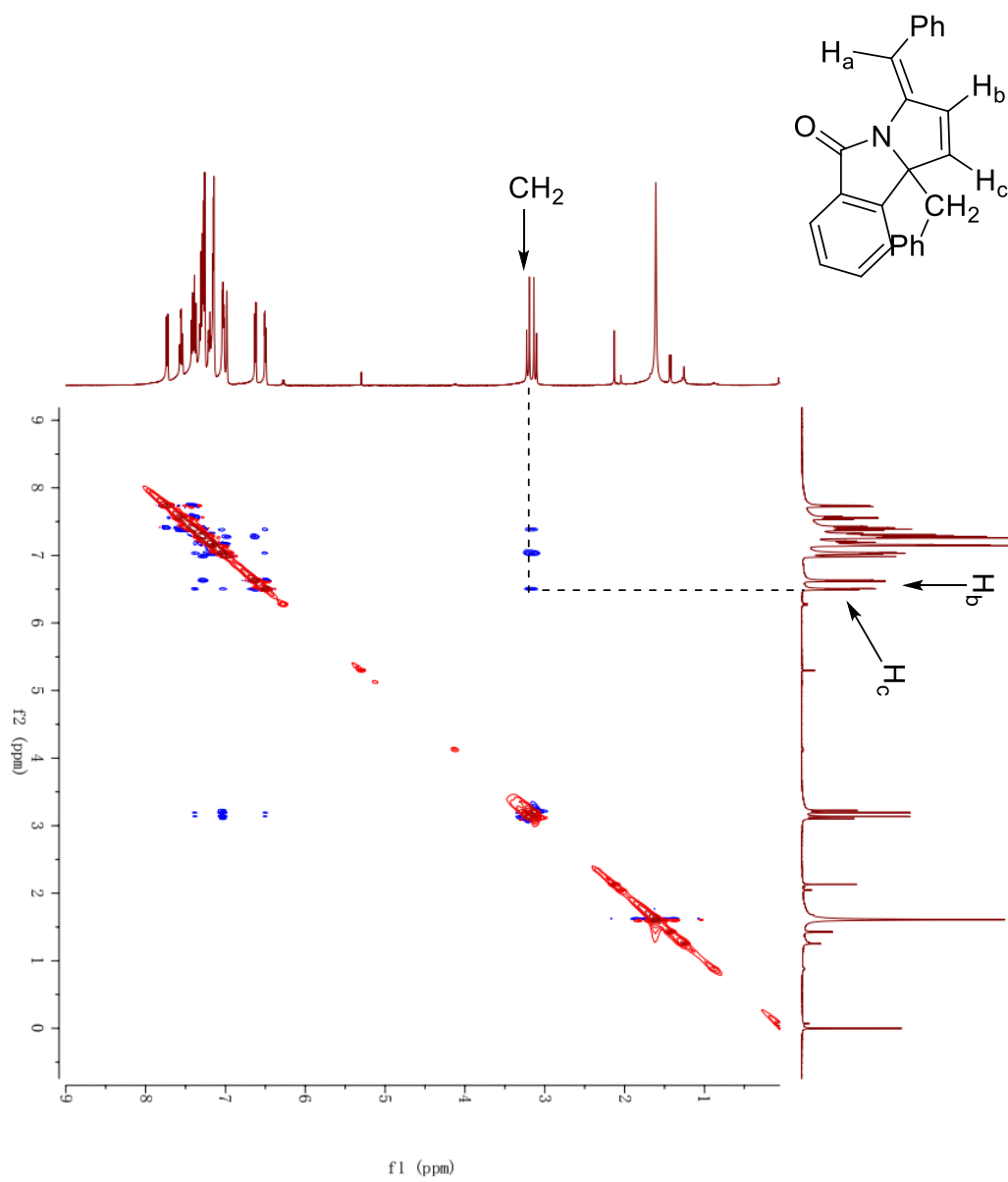
Project Name: yangping  
 Date Printed:  
 10/24/2018  
 8:51:00 AM PRC

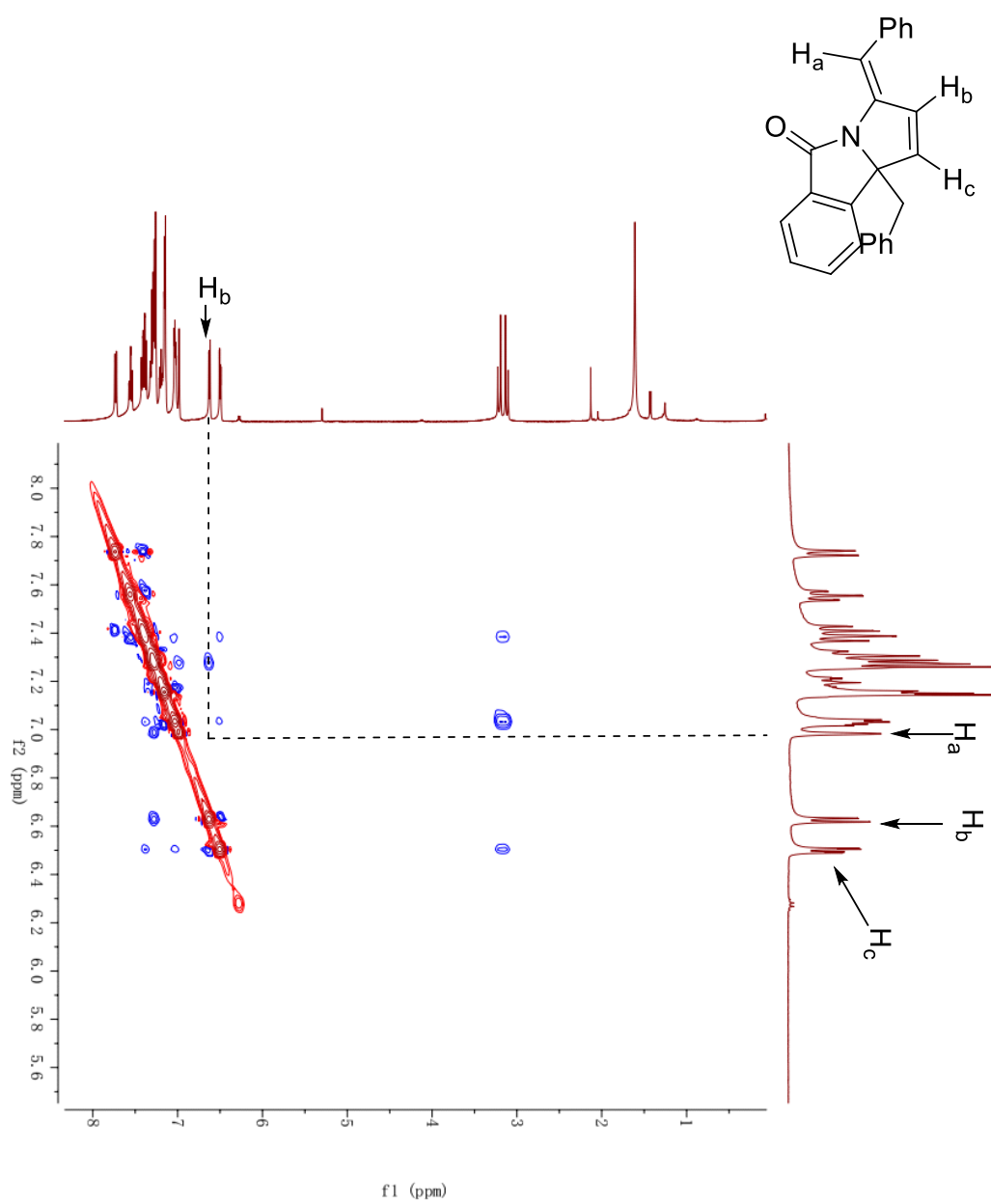
2da:





NOESY NMR spectra of **2da** (400 MHz, CDCl<sub>3</sub>)





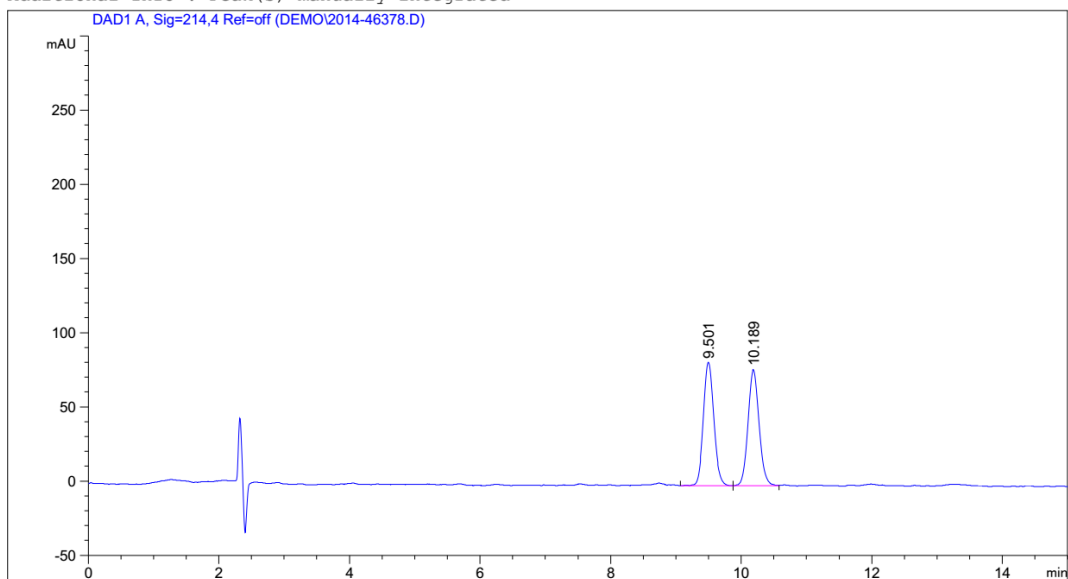
## HPLC of 2da (racemic)

Data File C:\CHEM32\1\DATA\DEMO\2014-46378.D

Sample Name: yp-8-60-rac-oj-h-8-2-1.5

```
=====
Acq. Operator   : 系统
Sample Operator : 系统
Acq. Instrument : SFC                      Location : Vial 62
Injection Date  : 16/07/2018 12:13:11      Inj Volume : 3.000 µl

Acq. Method     : C:\CHEM32\1\METHODS\AGILENT_SFC.M
Last changed    : 16/07/2018 12:10:37 by 系统
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\AGILENT_SFC.M
Last changed    : 16/07/2018 15:09:35 by 系统
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```



### Area Percent Report

```
=====
Sorted By      : Signal
Multiplier     : 1.0000
Dilution       : 1.0000
Use Multiplier & Dilution Factor with ISTDs
```

Signal 1: DAD1 A, Sig=214,4 Ref=off

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 9.501         | BB   | 0.1700      | 928.41376    | 83.33033     | 49.8770 |
| 2      | 10.189        | BV   | 0.1847      | 932.99408    | 78.48162     | 50.1230 |

Totals : 1861.40784 161.81195

Data File C:\CHEM32\1\DATA\DEMO\2014-46378.D  
Sample Name: yp-8-60-rac-oj-h-8-2-1.5

=====  
\*\*\* End of Report \*\*\*

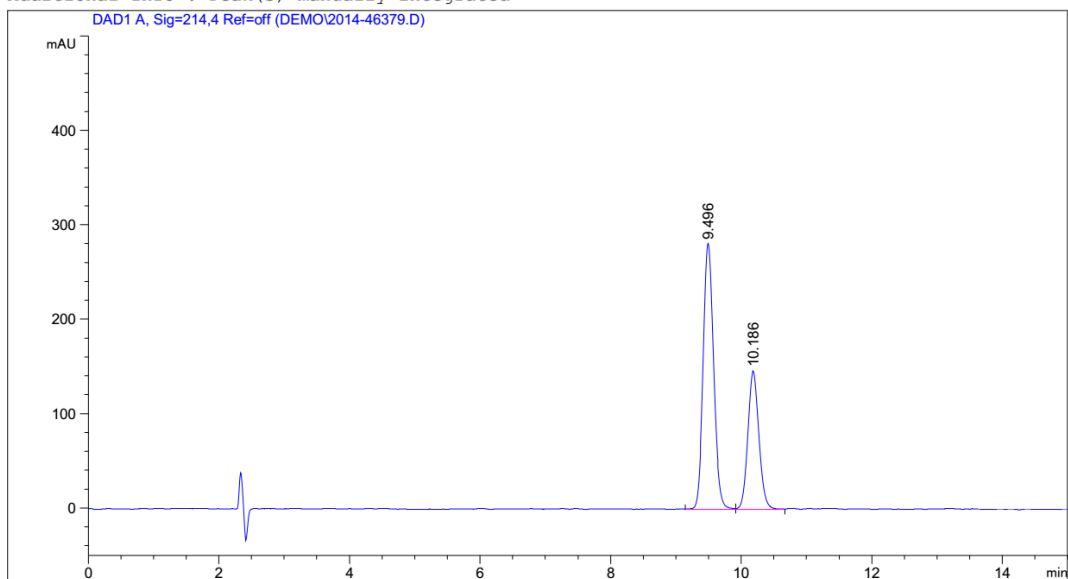
## HPLC of 2da (chiral)

Data File C:\CHEM32\1\DATA\DEMO\2014-46379.D

Sample Name: yp-8-60-chiral

```
=====
Acq. Operator   : 系统
Sample Operator : 系统
Acq. Instrument : SFC                      Location : Vial 64
Injection Date  : 16/07/2018 12:31:48      Inj Volume : 2.000 µl

Acq. Method     : C:\CHEM32\1\METHODS\AGILENT_SFC.M
Last changed    : 16/07/2018 12:29:53 by 系统
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\AGILENT_SFC.M
Last changed    : 16/07/2018 15:10:02 by 系统
                  (modified after loading)
Additional Info  : Peak(s) manually integrated
```



### Area Percent Report

```
=====
Sorted By      : Signal
Multiplier     : 1.0000
Dilution       : 1.0000
Use Multiplier & Dilution Factor with ISTDs
```

Signal 1: DAD1 A, Sig=214,4 Ref=off

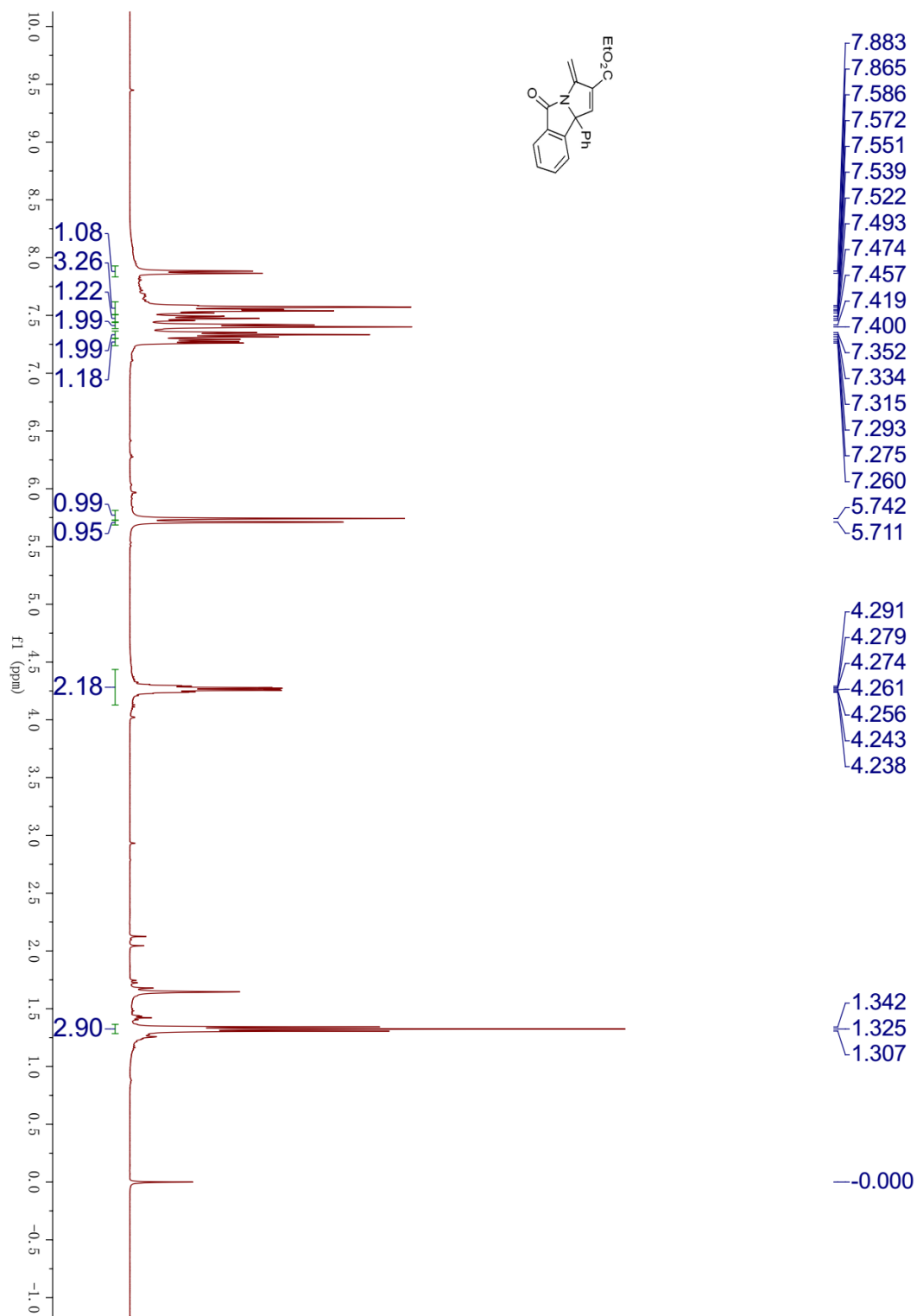
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 9.496         | BV   | 0.1714      | 3119.76172   | 281.38196    | 64.3395 |
| 2      | 10.186        | VB   | 0.1837      | 1729.14734   | 146.51035    | 35.6605 |

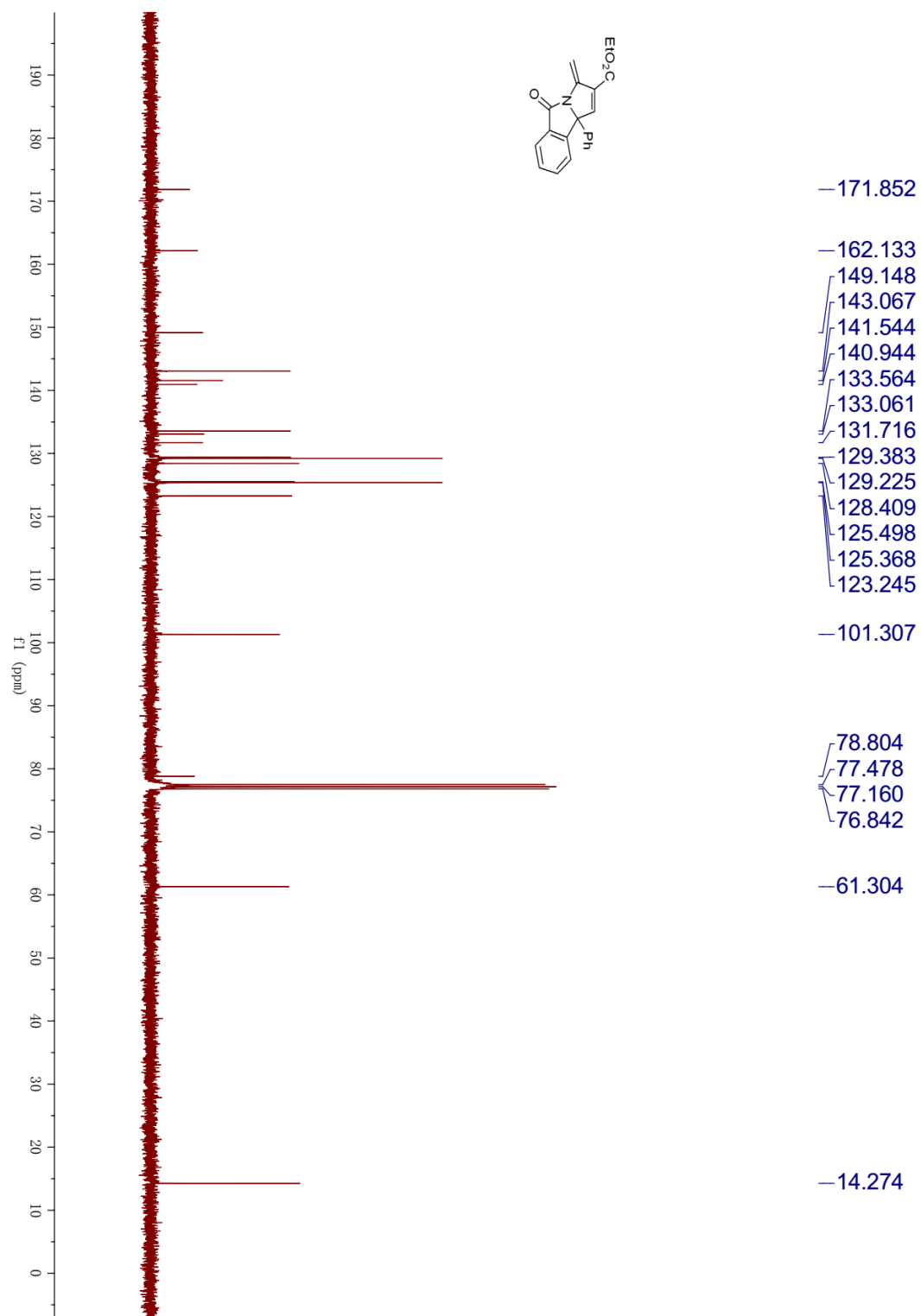
Totals : 4848.90906 427.89230

Data File C:\CHEM32\1\DATA\DEMO\2014-46379.D  
Sample Name: yp-8-60-chiral

=====  
\*\*\* End of Report \*\*\*

2ea:





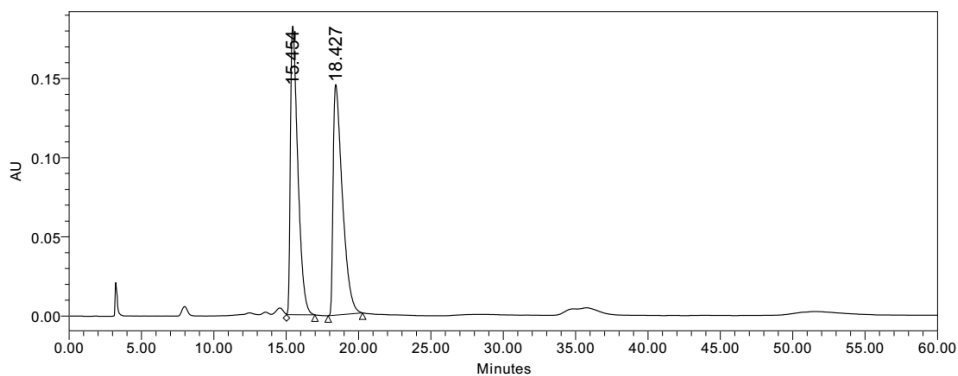
# HPLC of 2ea (racemic)



## Multi Sample Summary

### SAMPLE INFORMATION

|                   |                            |                     |                 |
|-------------------|----------------------------|---------------------|-----------------|
| Sample Name:      | yp-8-49-2                  | Acquired By:        | System          |
| Sample Type:      | Unknown                    | Sample Set Name:    | 1               |
| Vial:             | 1:A,2                      | Acq. Method Set:    | yp9802254       |
| Injection #:      | 1                          | Processing Method:  | 1               |
| Injection Volume: | 10.00 ul                   | Channel Name:       | W2489 ChA       |
| Run Time:         | 60.0 Minutes               | Proc. Chnl. Descr.: | W2489 ChA 254nm |
| Date Acquired:    | 7/7/2018 8:38:10 PM CST    |                     |                 |
| Date Processed:   | 10/25/2018 10:35:27 AM CST |                     |                 |



|   | RT     | Area    | % Area | Height |
|---|--------|---------|--------|--------|
| 1 | 15.454 | 6472764 | 50.07  | 182173 |
| 2 | 18.427 | 6453773 | 49.93  | 145516 |

Reported by User: System  
 Report Method: Multi Sample Summary  
 Report Method ID 1007  
 Page: 1 of 1

Project Name: yangping  
 Date Printed:  
 10/25/2018  
 10:35:48 AM PRC

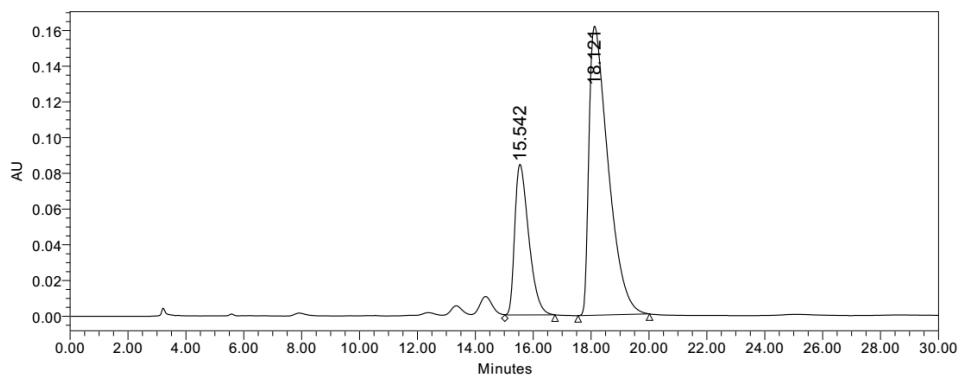
# HPLC of 2ea (chiral)



## Multi Sample Summary

### SAMPLE INFORMATION

|                   |                           |                     |                 |
|-------------------|---------------------------|---------------------|-----------------|
| Sample Name:      | yp-8-58-2                 | Acquired By:        | System          |
| Sample Type:      | Unknown                   | Sample Set Name:    | 1               |
| Vial:             | 1:A,2                     | Acq. Method Set:    | yp9802254       |
| Injection #:      | 1                         | Processing Method   | 1               |
| Injection Volume: | 10.00 ul                  | Channel Name:       | W2489 ChA       |
| Run Time:         | 30.0 Minutes              | Proc. Chnl. Descr.: | W2489 ChA 254nm |
| Date Acquired:    | 7/10/2018 10:16:57 PM CST |                     |                 |
| Date Processed:   | 10/24/2018 8:53:20 AM CST |                     |                 |

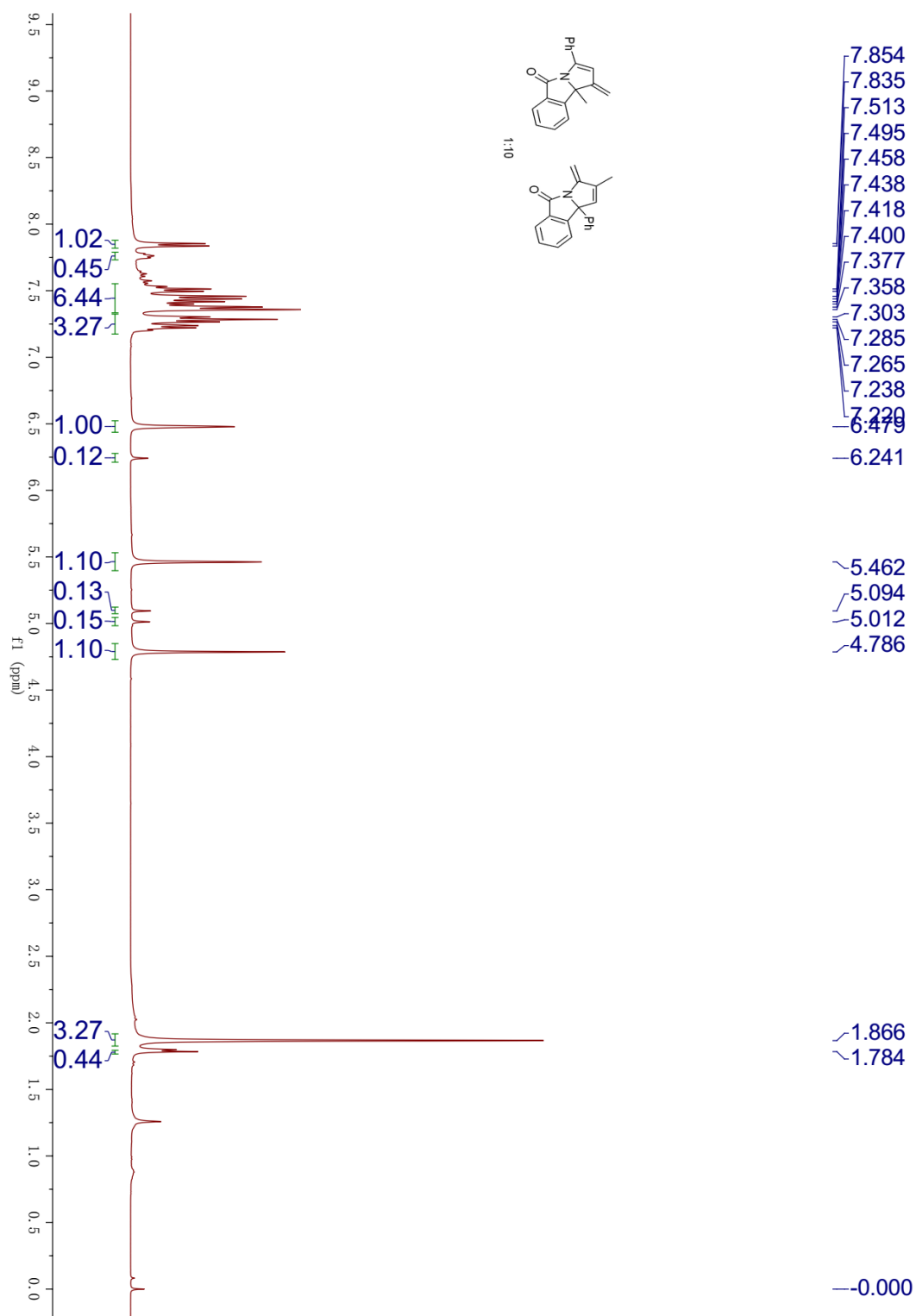


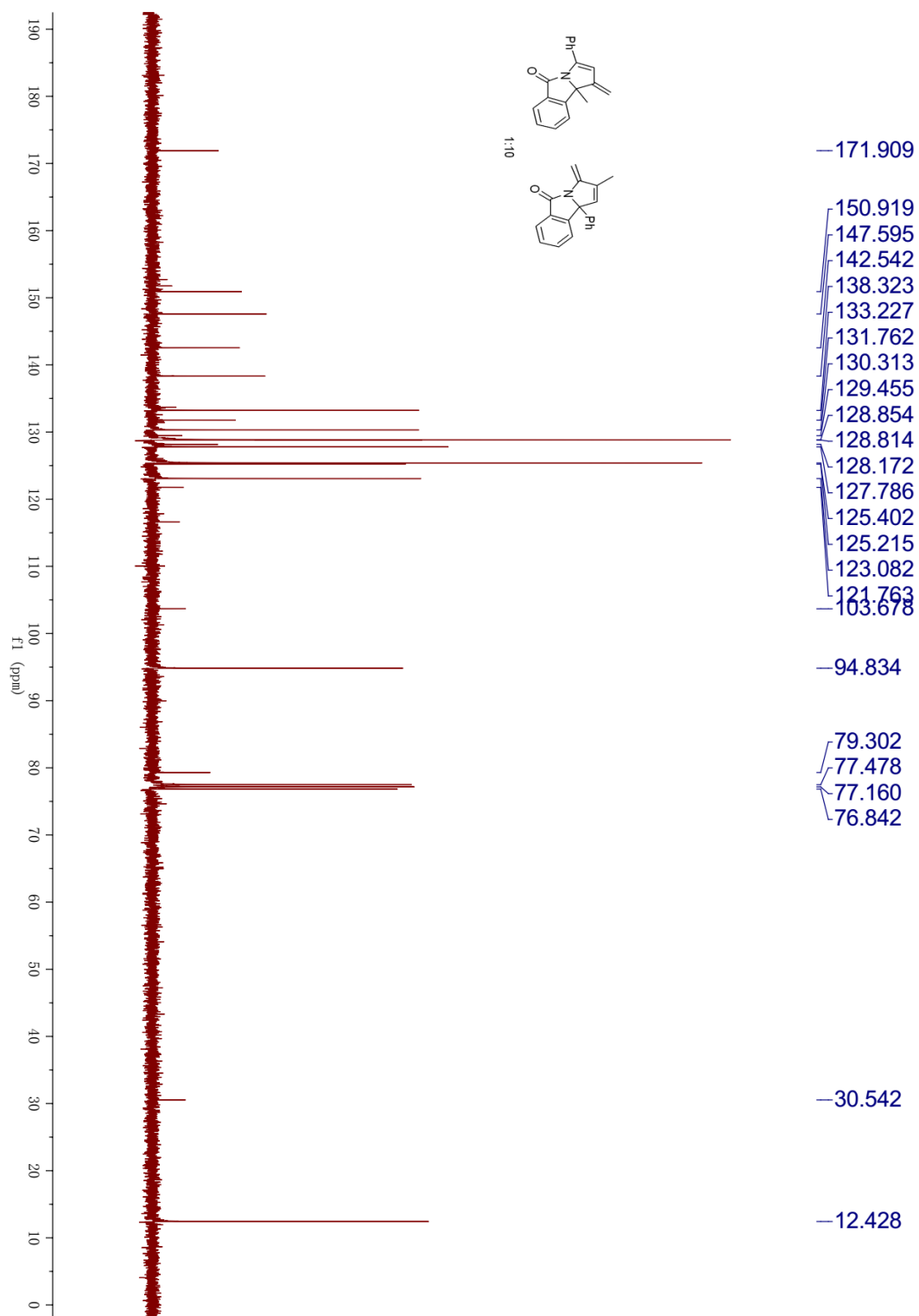
|   | RT     | Area    | % Area | Height |
|---|--------|---------|--------|--------|
| 1 | 15.542 | 2826243 | 27.49  | 84254  |
| 2 | 18.121 | 7455026 | 72.51  | 161804 |

Reported by User: System  
 Report Method: Multi Sample Summary  
 Report Method ID 1007  
 Page: 1 of 1

Project Name: yangping  
 Date Printed:  
 10/24/2018  
 8:53:52 AM PRC

2fa:





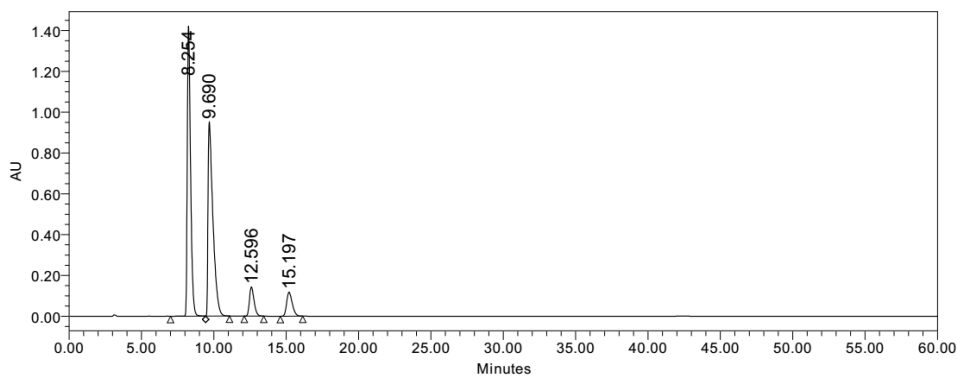
# HPLC of 2fa (racemic)



## Multi Sample Summary

### SAMPLE INFORMATION

|                   |                           |                     |                 |
|-------------------|---------------------------|---------------------|-----------------|
| Sample Name:      | YP-8-16-2                 | Acquired By:        | System          |
| Sample Type:      | Unknown                   | Sample Set Name:    | 1               |
| Vial:             | 1:A,2                     | Acq. Method Set:    | YP9505254       |
| Injection #:      | 1                         | Processing Method:  | 1               |
| Injection Volume: | 10.00 ul                  | Channel Name:       | W2489 ChA       |
| Run Time:         | 60.0 Minutes              | Proc. Chnl. Descr.: | W2489 ChA 254nm |
| Date Acquired:    | 6/27/2018 1:31:24 AM CST  |                     |                 |
| Date Processed:   | 7/17/2018 11:24:57 PM CST |                     |                 |



|   | RT     | Area     | % Area | Height  |
|---|--------|----------|--------|---------|
| 1 | 8.254  | 22397056 | 43.86  | 1421332 |
| 2 | 9.690  | 22320087 | 43.71  | 954120  |
| 3 | 12.596 | 3176905  | 6.22   | 143095  |
| 4 | 15.197 | 3171499  | 6.21   | 117270  |

Reported by User: System  
 Report Method: Multi Sample Summary  
 Report Method ID 1007  
 Page: 1 of 1

Project Name: yangping  
 Date Printed:  
 7/17/2018  
 11:26:13 PM PRC

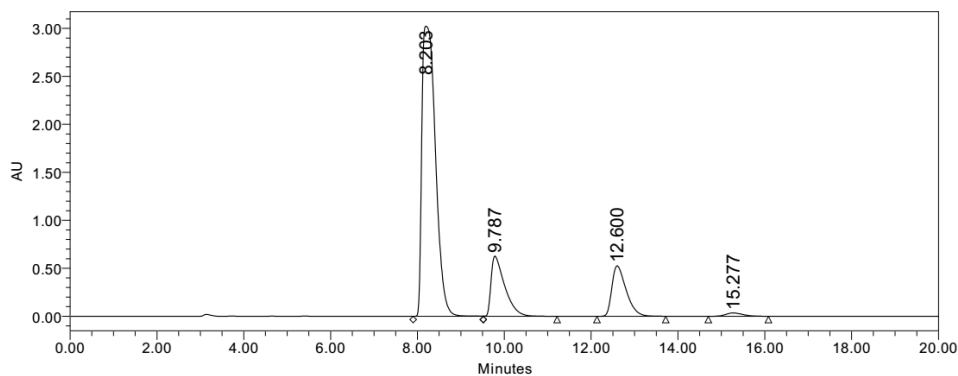
# HPLC of 2fa (chiral)



## Multi Sample Summary

### SAMPLE INFORMATION

|                   |                           |                     |                 |
|-------------------|---------------------------|---------------------|-----------------|
| Sample Name:      | YP-8-35-2                 | Acquired By:        | System          |
| Sample Type:      | Unknown                   | Sample Set Name:    | 1               |
| Vial:             | 1:A,2                     | Acq. Method Set:    | YP9505254       |
| Injection #:      | 1                         | Processing Method   | 1               |
| Injection Volume: | 10.00 ul                  | Channel Name:       | W2489 ChA       |
| Run Time:         | 20.0 Minutes              | Proc. Chnl. Descr.: | W2489 ChA 254nm |
| Date Acquired:    | 7/2/2018 11:55:18 PM CST  |                     |                 |
| Date Processed:   | 10/24/2018 8:56:25 AM CST |                     |                 |

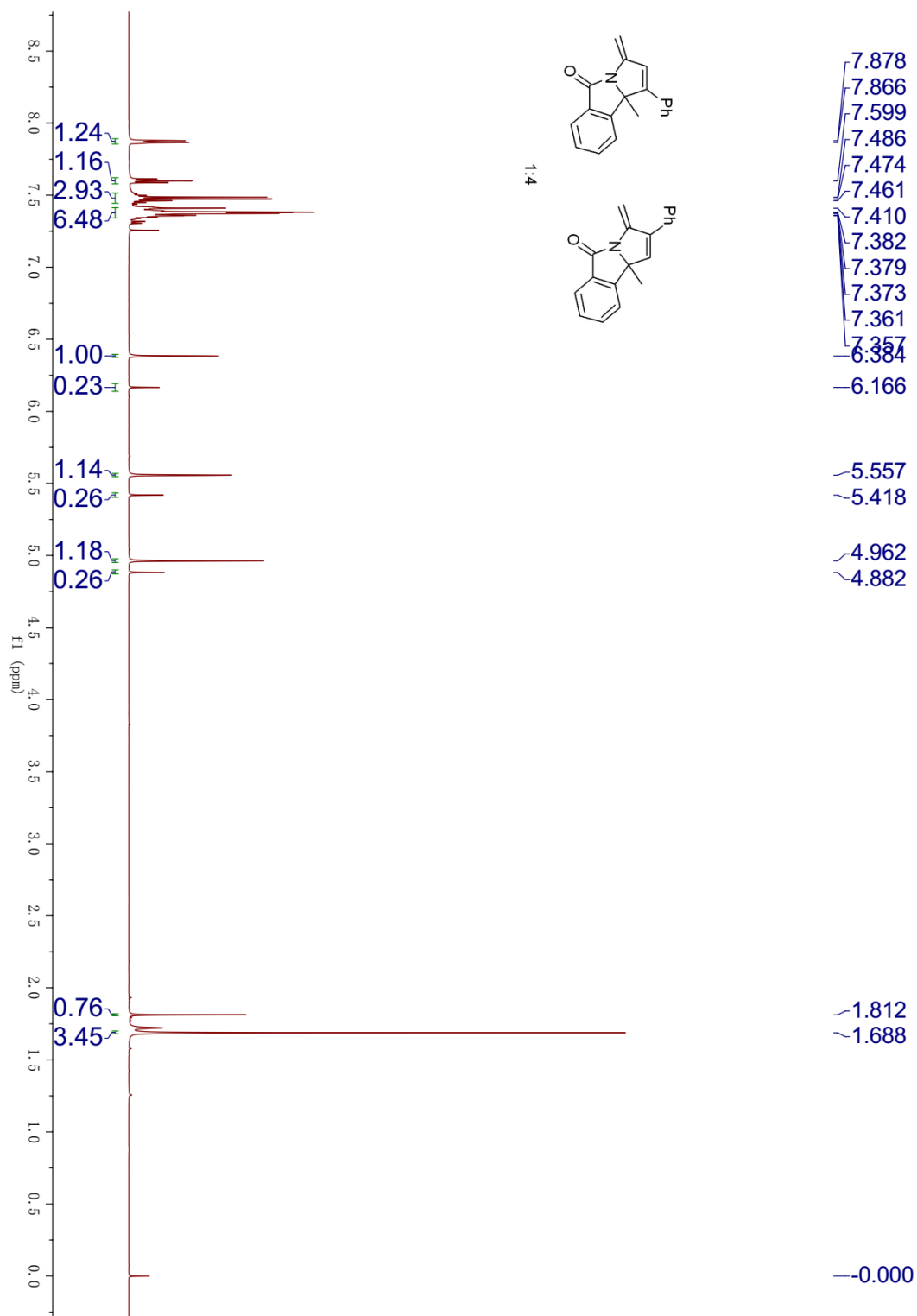


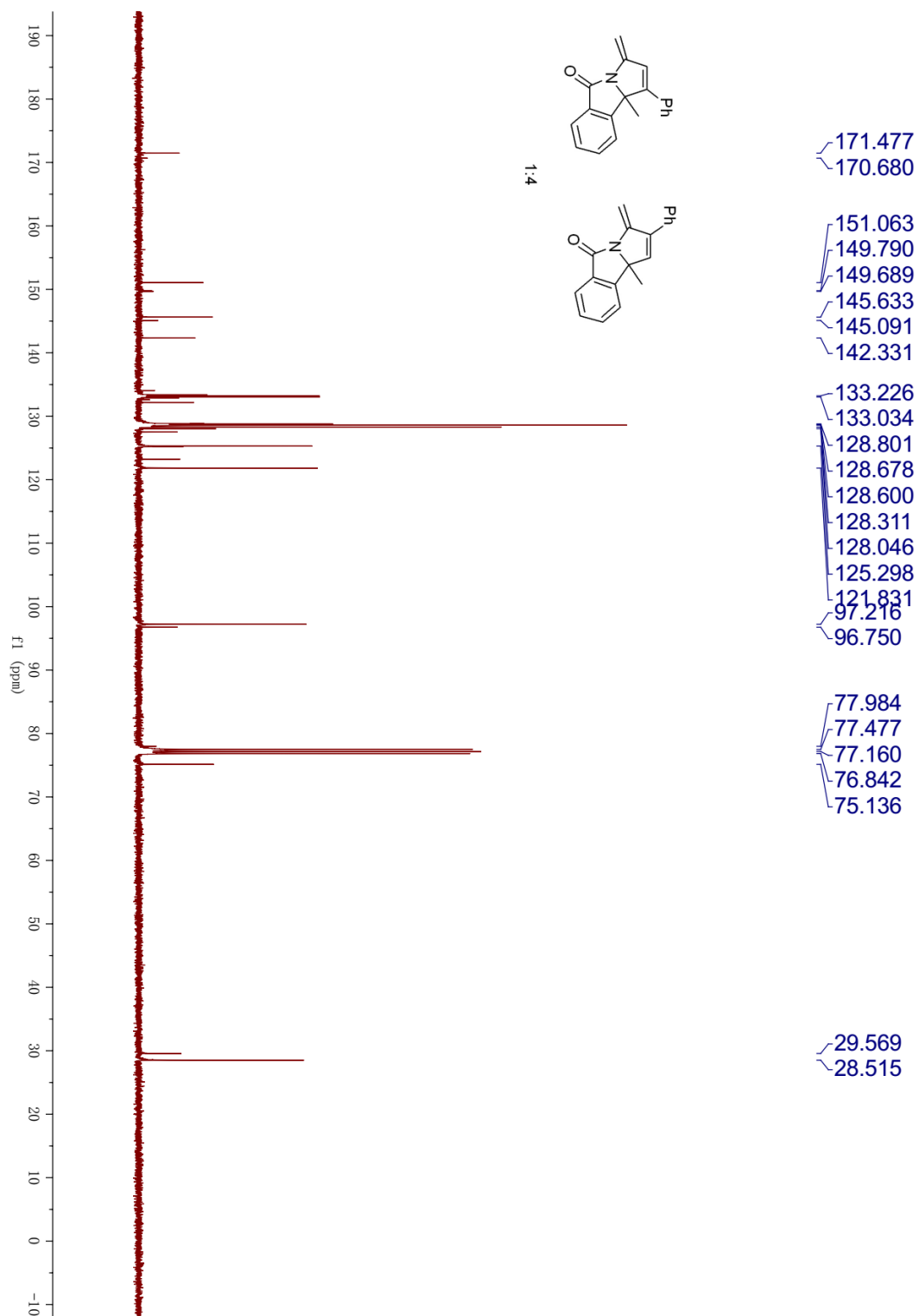
|   | RT     | Area     | % Area | Height  |
|---|--------|----------|--------|---------|
| 1 | 8.203  | 65994676 | 71.27  | 3023737 |
| 2 | 9.787  | 13687938 | 14.78  | 628036  |
| 3 | 12.600 | 11988600 | 12.95  | 525337  |
| 4 | 15.277 | 923932   | 1.00   | 34422   |

Reported by User: System  
 Report Method: Multi Sample Summary  
 Report Method ID 1007  
 Page: 1 of 1

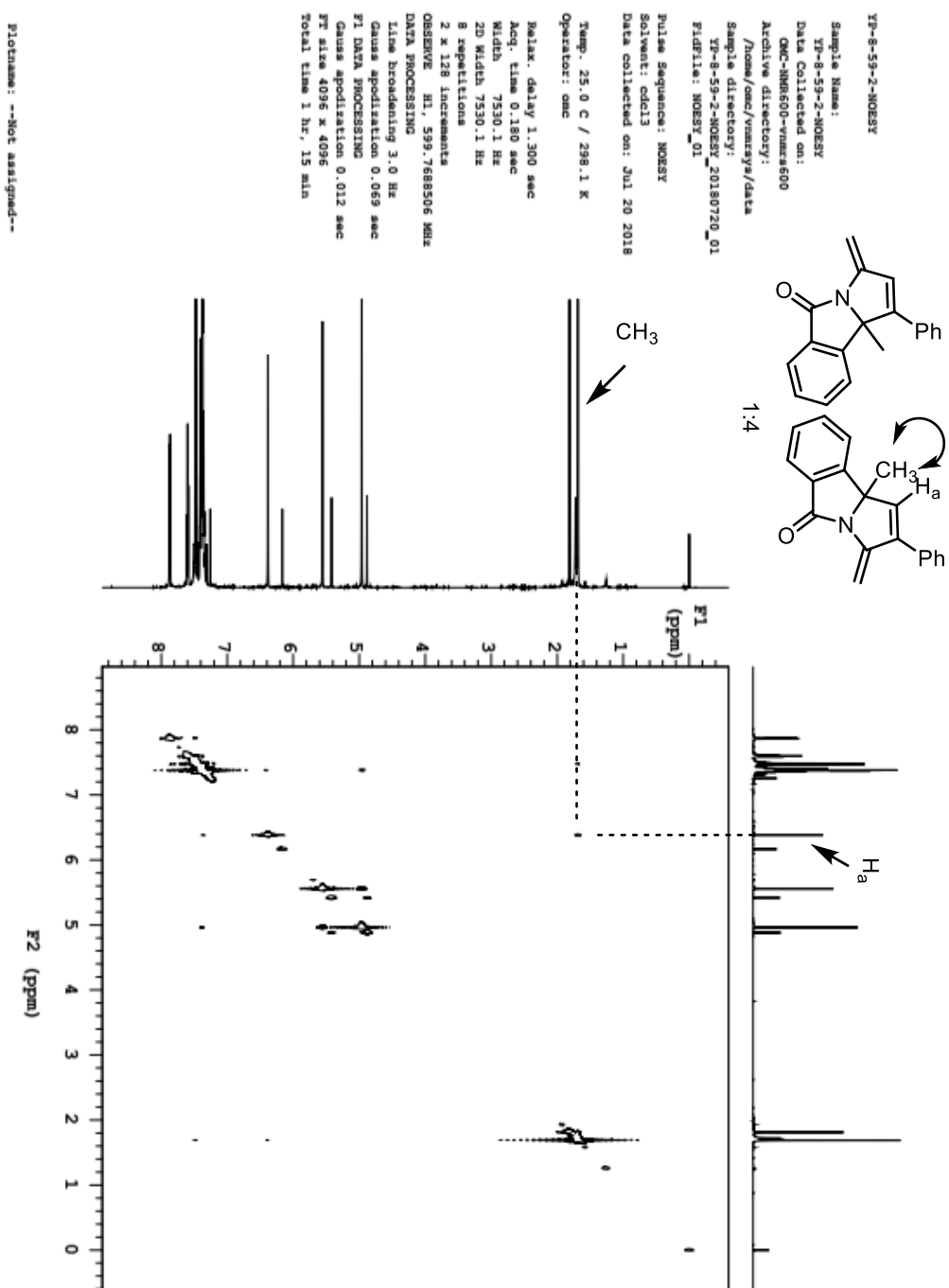
Project Name: yangping  
 Date Printed:  
 10/24/2018  
 8:57:00 AM PRC

2ga:





NOESY NMR spectra of **2ga** (600 MHz, CDCl<sub>3</sub>)



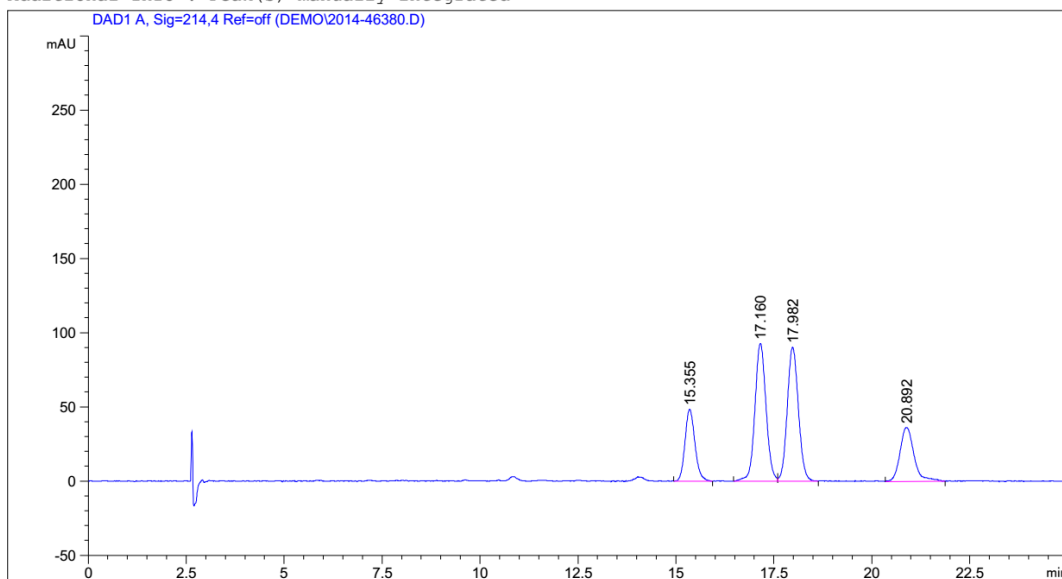
## HPLC of 2ga (racemic)

Data File C:\CHEM32\1\DATA\DEMO\2014-46380.D

Sample Name: yp-8-59-rac-oj-h-95-5-1.5

```
=====
Acq. Operator   : 系统
Sample Operator : 系统
Acq. Instrument : SFC                               Location : Vial 61
Injection Date  : 16/07/2018 13:12:57                Inj Volume : 5.000 µl

Acq. Method     : C:\CHEM32\1\METHODS\AGILENT_SFC.M
Last changed    : 16/07/2018 13:11:03 by 系统
                  (modified after loading)
Analysis Method  : C:\CHEM32\1\METHODS\AGILENT_SFC.M
Last changed    : 16/07/2018 15:10:37 by 系统
                  (modified after loading)
Additional Info  : Peak(s) manually integrated
```



### Area Percent Report

```
=====
Sorted By      : Signal
Multiplier     : 1.0000
Dilution       : 1.0000
Use Multiplier & Dilution Factor with ISTDs
```

Signal 1: DAD1 A, Sig=214,4 Ref=off

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 15.355        | BB   | 0.2737      | 854.20673    | 48.45715     | 15.9082 |
| 2      | 17.160        | BV   | 0.3003      | 1831.59460   | 92.79224     | 34.1105 |
| 3      | 17.982        | VB   | 0.3043      | 1780.90491   | 90.23550     | 33.1665 |
| 4      | 20.892        | BB   | 0.3596      | 902.88867    | 36.37937     | 16.8148 |

Data File C:\CHEM32\1\DATA\DEMO\2014-46380.D  
Sample Name: yp-8-59-rac-oj-h-95-5-1.5

Totals : 5369.59491 267.86425

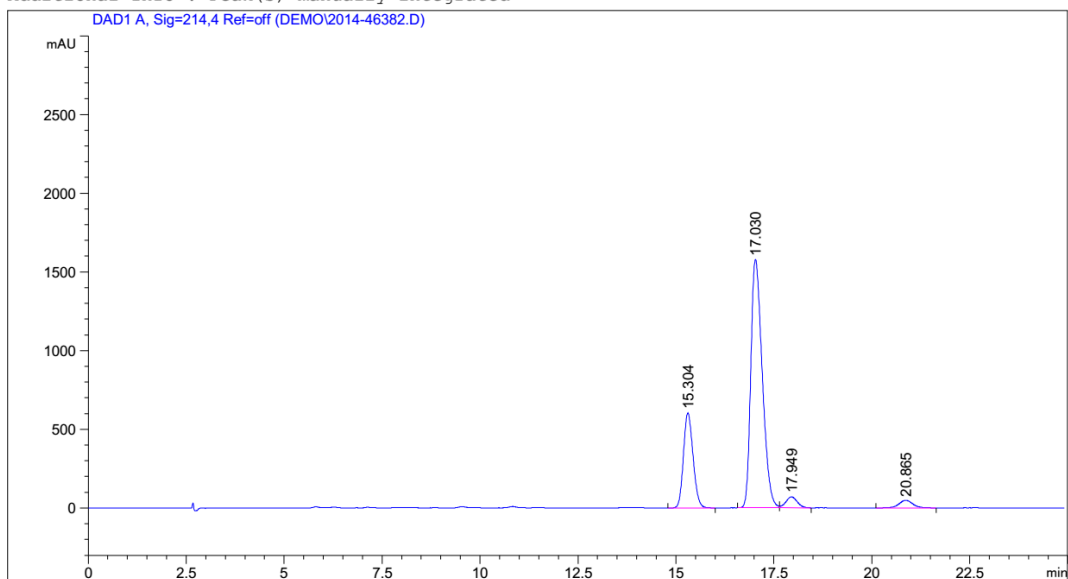
=====  
\*\*\* End of Report \*\*\*

## HPLC of 2ga (chiral)

Data File C:\CHEM32\1\DATA\DEMO\2014-46382.D

Sample Name: yp-8-59-chiral

```
=====
Acq. Operator   : 系统
Sample Operator : 系统
Acq. Instrument : SFC                               Location : Vial 63
Injection Date  : 16/07/2018 14:21:22                Inj Volume : 5.000 µl
Acq. Method     : C:\CHEM32\1\METHODS\AGILENT_SFC.M
Last changed    : 16/07/2018 14:19:21 by 系统
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\AGILENT_SFC.M
Last changed    : 16/07/2018 15:11:08 by 系统
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```



### Area Percent Report

```
=====
Sorted By      :      Signal
Multiplier     :      1.0000
Dilution       :      1.0000
Use Multiplier & Dilution Factor with ISTDs
```

Signal 1: DAD1 A, Sig=214,4 Ref=off

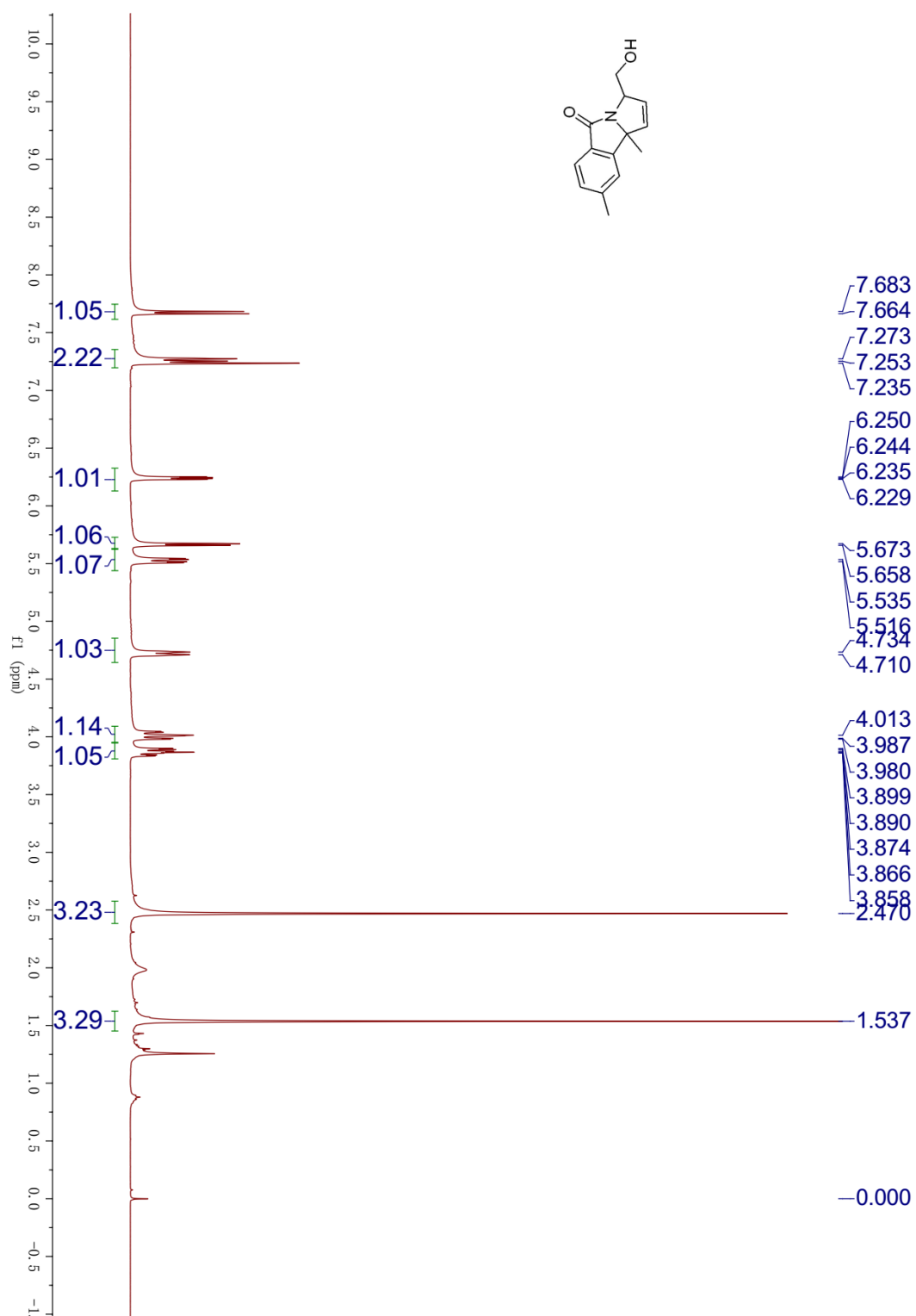
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area %  |
|--------|---------------|------|-------------|--------------|--------------|---------|
| 1      | 15.304        | BB   | 0.2653      | 1.02965e4    | 602.85693    | 22.9350 |
| 2      | 17.030        | BV   | 0.3143      | 3.19741e4    | 1578.59155   | 71.2207 |
| 3      | 17.949        | VB   | 0.3120      | 1405.91907   | 69.50964     | 3.1316  |
| 4      | 20.865        | BB   | 0.3724      | 1217.83032   | 48.92519     | 2.7127  |

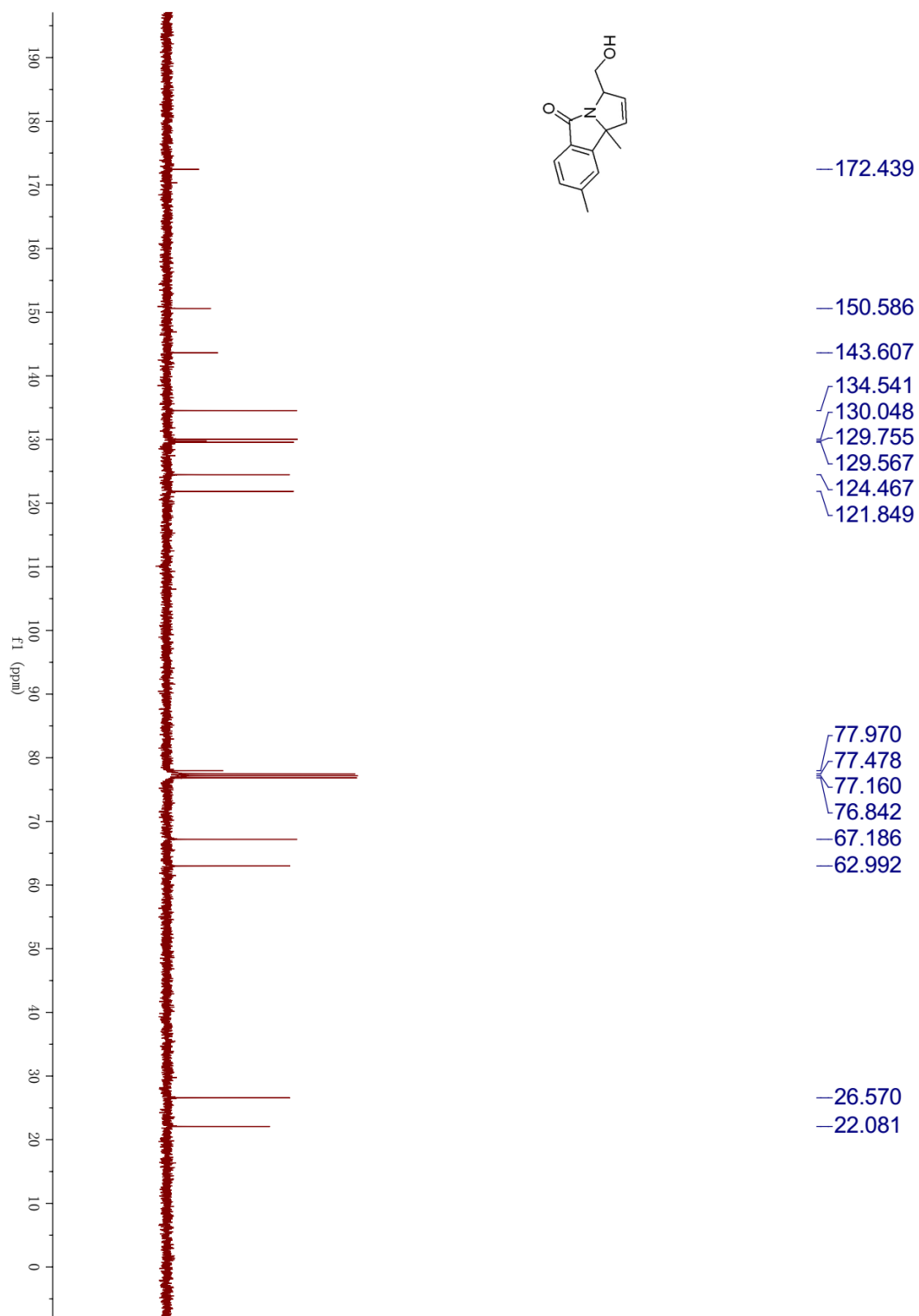
Data File C:\CHEM32\1\DATA\DEMO\2014-46382.D  
Sample Name: yp-8-59-chiral

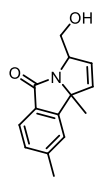
Totals : 4.48944e4 2299.88331

=====  
\*\*\* End of Report \*\*\*

3ac:



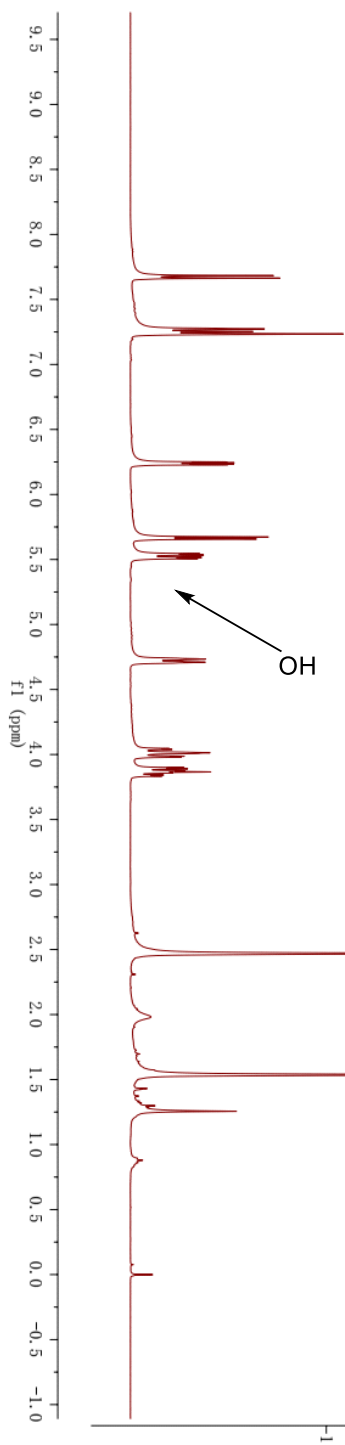




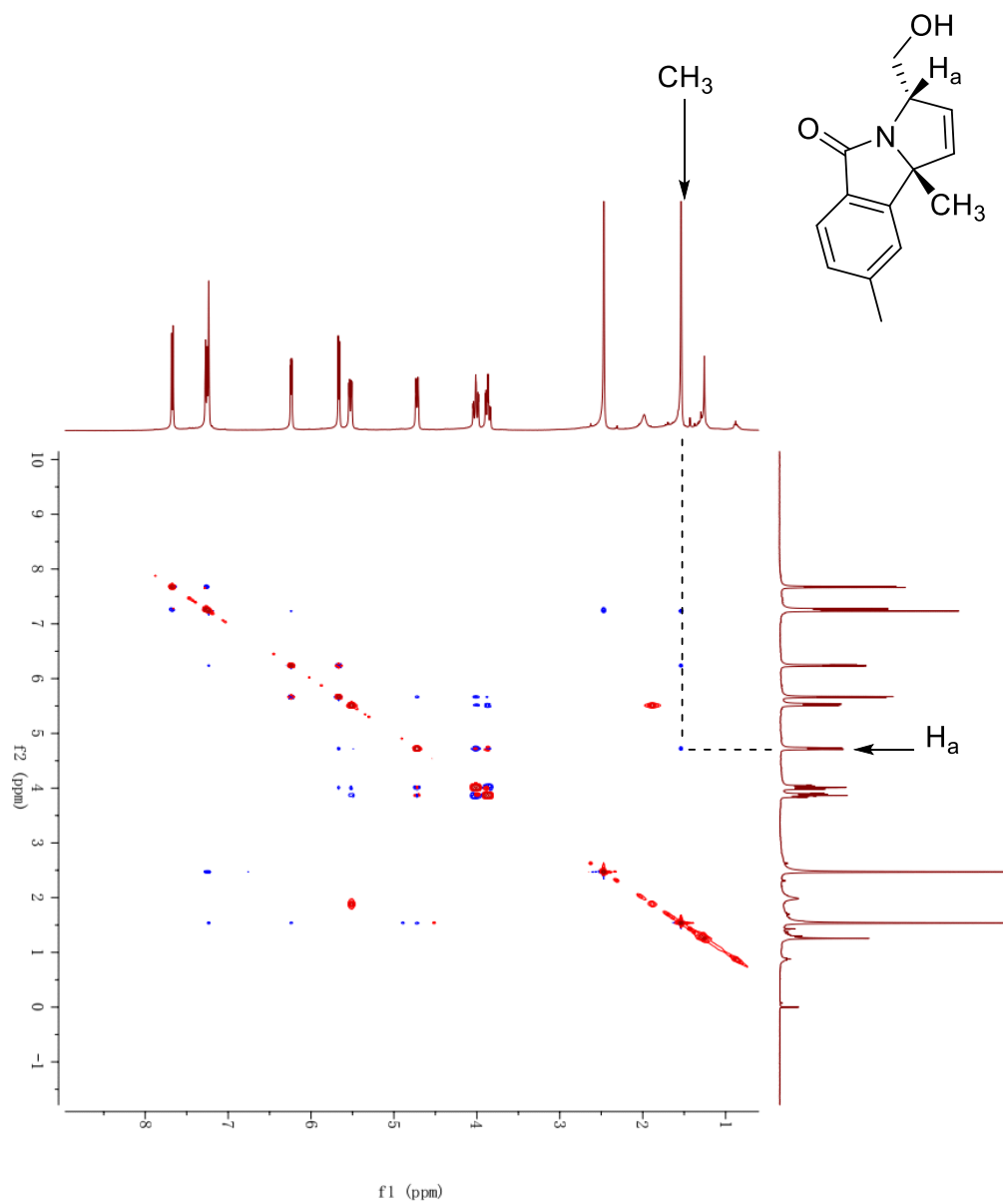
in CD<sub>3</sub>OD



in CDCl<sub>3</sub>



NOESY NMR spectra of **3ac** (400 MHz, CDCl<sub>3</sub>)



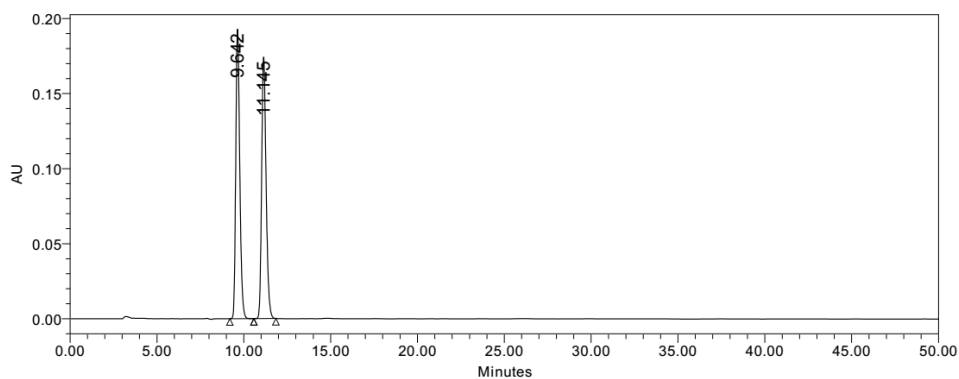
# HPLC of 3ac (racemic)



## Multi Sample Summary

### SAMPLE INFORMATION

|                   |                            |                     |                 |
|-------------------|----------------------------|---------------------|-----------------|
| Sample Name:      | yp-8-40-2-rac              | Acquired By:        | System          |
| Sample Type:      | Unknown                    | Sample Set Name:    | 1               |
| Vial:             | 1:A,2                      | Acq. Method Set:    | yp9010          |
| Injection #:      | 1                          | Processing Method   | 1               |
| Injection Volume: | 10.00 ul                   | Channel Name:       | W2489 ChA       |
| Run Time:         | 50.0 Minutes               | Proc. Chnl. Descr.: | W2489 ChA 254nm |
| Date Acquired:    | 7/6/2018 7:18:20 PM CST    |                     |                 |
| Date Processed:   | 10/25/2018 12:19:09 PM CST |                     |                 |



|   | RT     | Area    | % Area | Height |
|---|--------|---------|--------|--------|
| 1 | 9.642  | 3100787 | 50.02  | 193427 |
| 2 | 11.145 | 3097846 | 49.98  | 174416 |

Reported by User: System  
 Report Method: Multi Sample Summary  
 Report Method ID 1007  
 Page: 1 of 1

Project Name: yangping  
 Date Printed:  
 10/25/2018  
 12:19:32 PM PRC

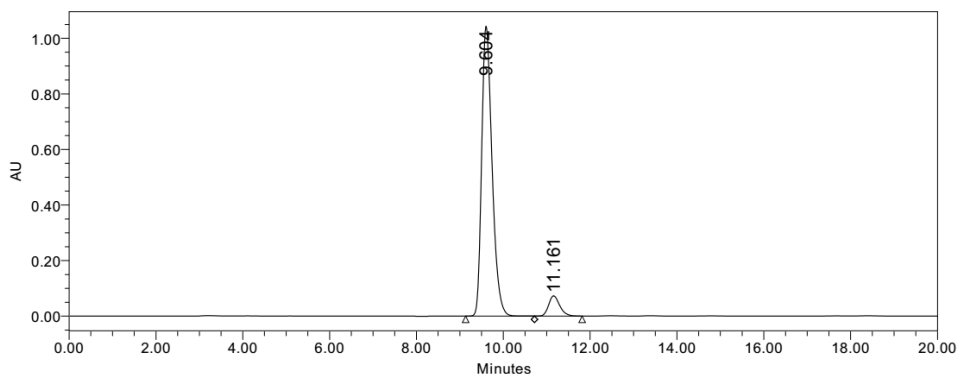
# HPLC of 3ac (chiral)



## Multi Sample Summary

### SAMPLE INFORMATION

|                   |                           |                     |                 |
|-------------------|---------------------------|---------------------|-----------------|
| Sample Name:      | yp-8-44-2                 | Acquired By:        | System          |
| Sample Type:      | Unknown                   | Sample Set Name:    | 1               |
| Vial:             | 1:A,2                     | Acq. Method Set:    | yp9010          |
| Injection #:      | 1                         | Processing Method:  | 1               |
| Injection Volume: | 10.00 ul                  | Channel Name:       | W2489 ChA       |
| Run Time:         | 20.0 Minutes              | Proc. Chnl. Descr.: | W2489 ChA 254nm |
| Date Acquired:    | 7/6/2018 8:39:44 PM CST   |                     |                 |
| Date Processed:   | 10/24/2018 1:17:57 PM CST |                     |                 |

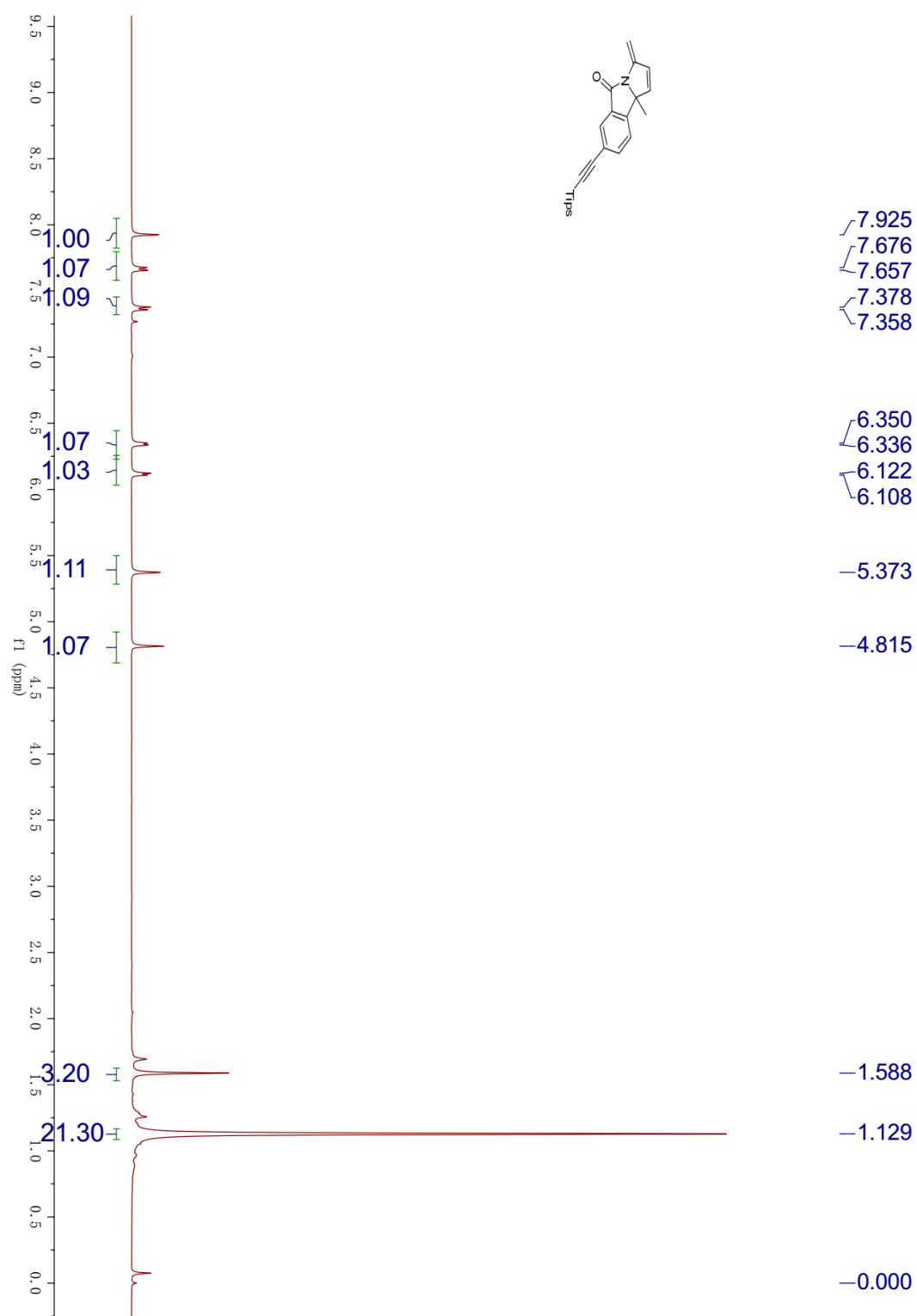


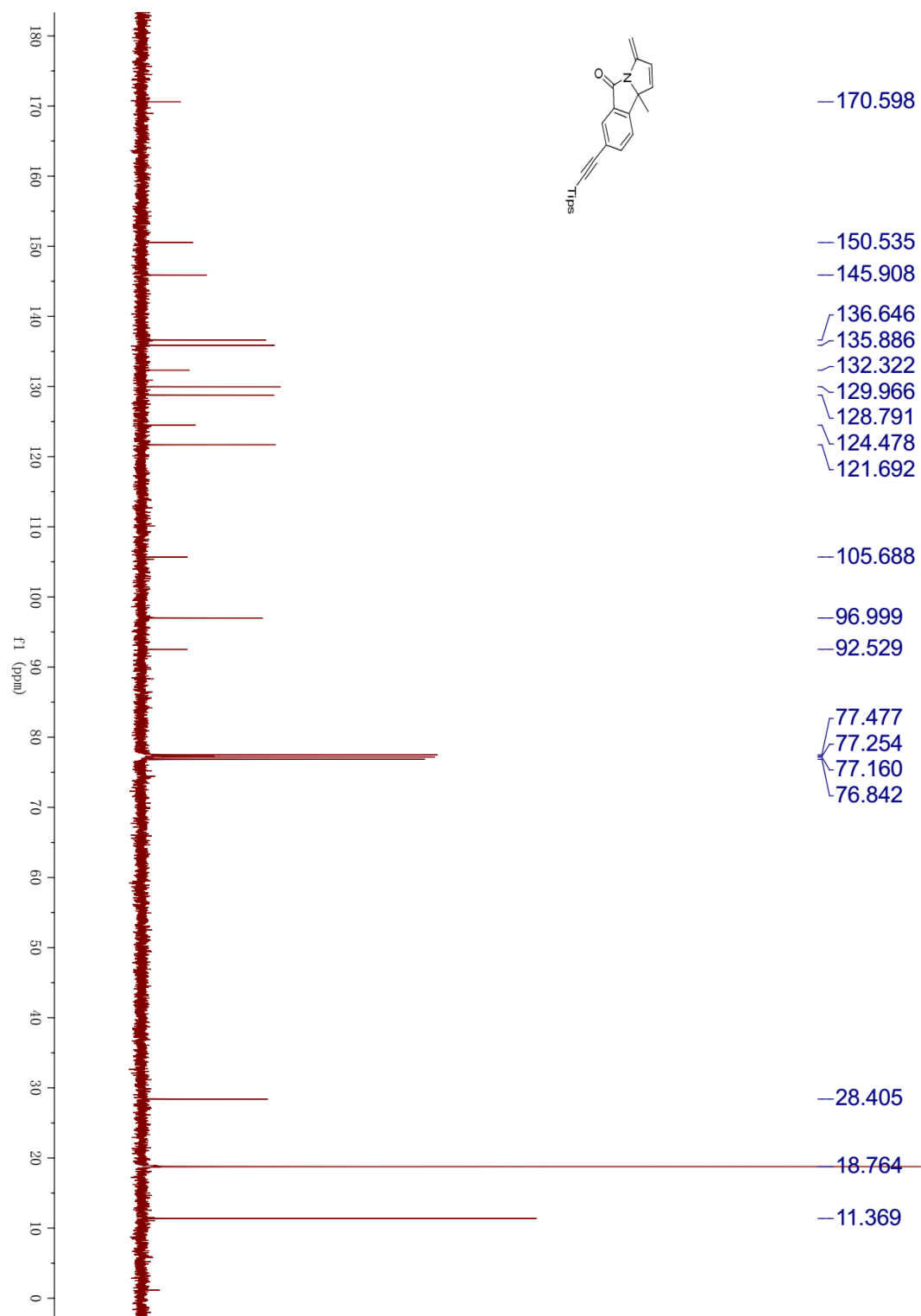
|   | RT     | Area     | % Area | Height  |
|---|--------|----------|--------|---------|
| 1 | 9.604  | 17325544 | 93.02  | 1043841 |
| 2 | 11.161 | 1300997  | 6.98   | 72827   |

Reported by User: System  
 Report Method: Multi Sample Summary  
 Report Method ID 1007  
 Page: 1 of 1

Project Name: yangping  
 Date Printed:  
 10/24/2018  
 1:18:18 PM PRC

4af:





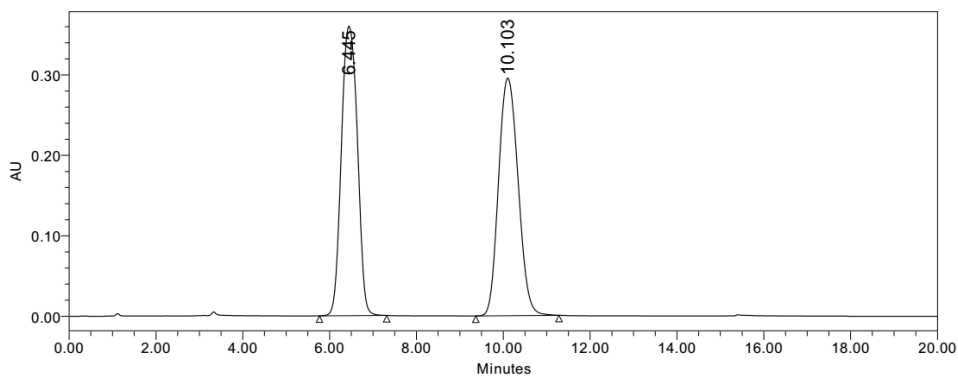
# HPLC of **4af** (racemic)



## Multi Sample Summary

### SAMPLE INFORMATION

|                   |                            |                     |                 |
|-------------------|----------------------------|---------------------|-----------------|
| Sample Name:      | yp-8-54-2                  | Acquired By:        | System          |
| Sample Type:      | Unknown                    | Sample Set Name:    | 1               |
| Vial:             | 1:A,2                      | Acq. Method Set:    | yp9901254       |
| Injection #:      | 1                          | Processing Method   | 1               |
| Injection Volume: | 10.00 ul                   | Channel Name:       | W2489 ChA       |
| Run Time:         | 20.0 Minutes               | Proc. Chnl. Descr.: | W2489 ChA 254nm |
| Date Acquired:    | 8/24/2018 4:21:57 PM CST   |                     |                 |
| Date Processed:   | 10/25/2018 12:20:15 PM CST |                     |                 |



|   | RT     | Area    | % Area | Height |
|---|--------|---------|--------|--------|
| 1 | 6.445  | 9254229 | 50.01  | 359922 |
| 2 | 10.103 | 9251073 | 49.99  | 295363 |

Reported by User: System  
 Report Method: Multi Sample Summary  
 Report Method ID 1007  
 Page: 1 of 1

Project Name: yangping  
 Date Printed:  
 10/25/2018  
 12:20:35 PM PRC

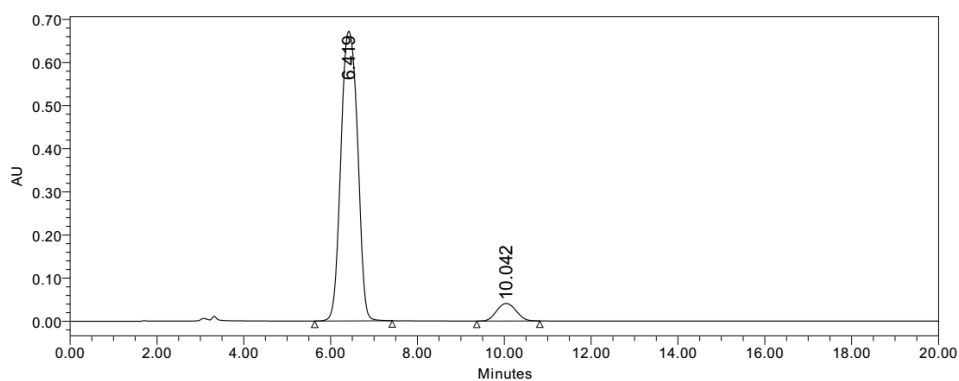
# HPLC of **4af** (chiral)



## Multi Sample Summary

### SAMPLE INFORMATION

|                   |                           |                     |                 |
|-------------------|---------------------------|---------------------|-----------------|
| Sample Name:      | yp-8-52-2                 | Acquired By:        | System          |
| Sample Type:      | Unknown                   | Sample Set Name:    | 1               |
| Vial:             | 1:A,3                     | Acq. Method Set:    | yp9901254       |
| Injection #:      | 1                         | Processing Method   | 1               |
| Injection Volume: | 10.00 ul                  | Channel Name:       | W2489 ChA       |
| Run Time:         | 20.0 Minutes              | Proc. Chnl. Descr.: | W2489 ChA 254nm |
| Date Acquired:    | 8/24/2018 4:42:22 PM CST  |                     |                 |
| Date Processed:   | 10/24/2018 1:16:12 PM CST |                     |                 |



|   | RT     | Area     | % Area | Height |
|---|--------|----------|--------|--------|
| 1 | 6.419  | 17949996 | 93.37  | 671711 |
| 2 | 10.042 | 1275524  | 6.63   | 40687  |

Reported by User: System  
 Report Method: Multi Sample Summary  
 Report Method ID 1007  
 Page: 1 of 1

Project Name: yangping  
 Date Printed:  
 10/24/2018  
 1:16:43 PM PRC