

## Supporting Information

**Title: An Efficient Copper-Catalyzed Synthesis of Anilines by Employing Aqueous Ammonia**

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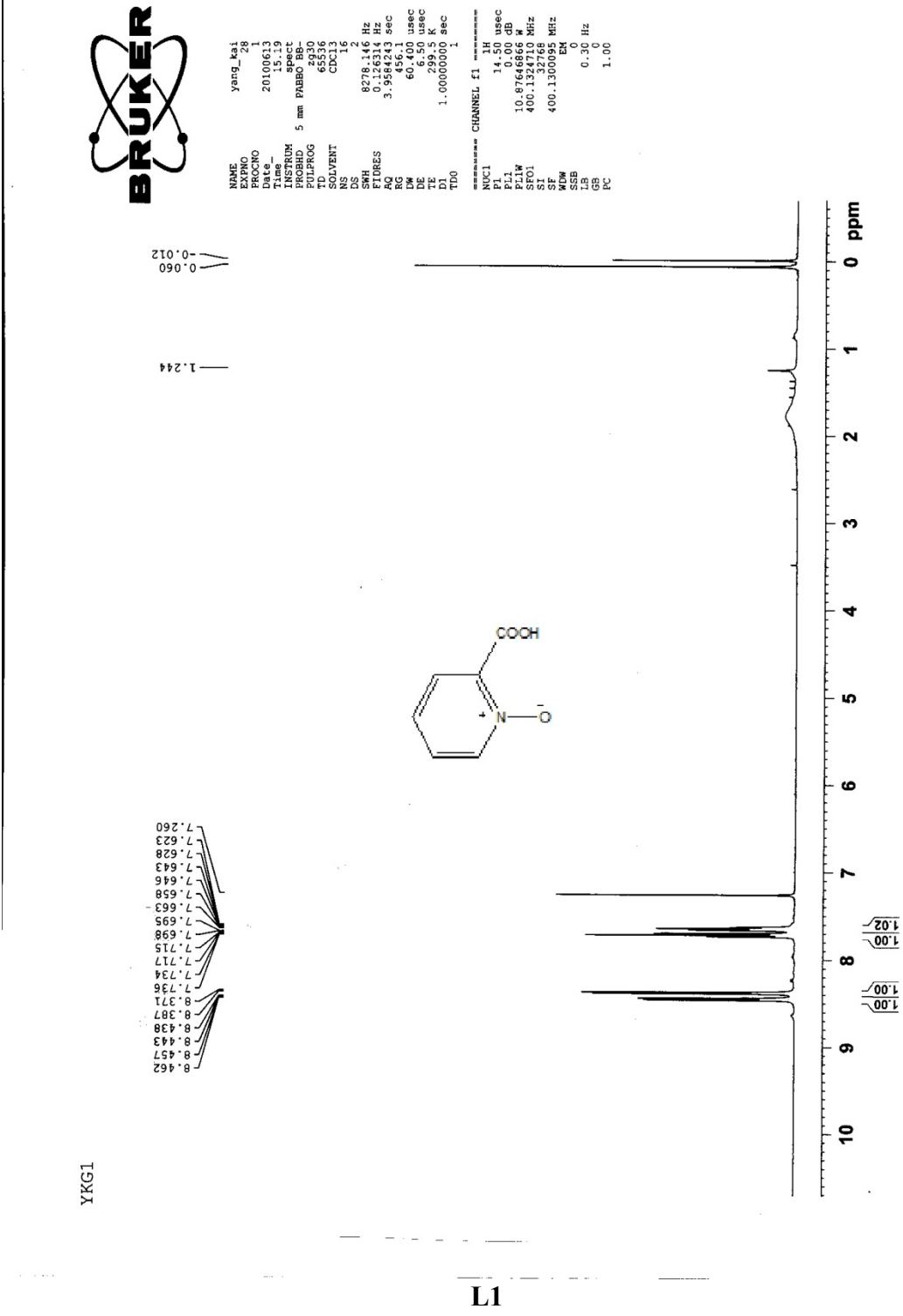
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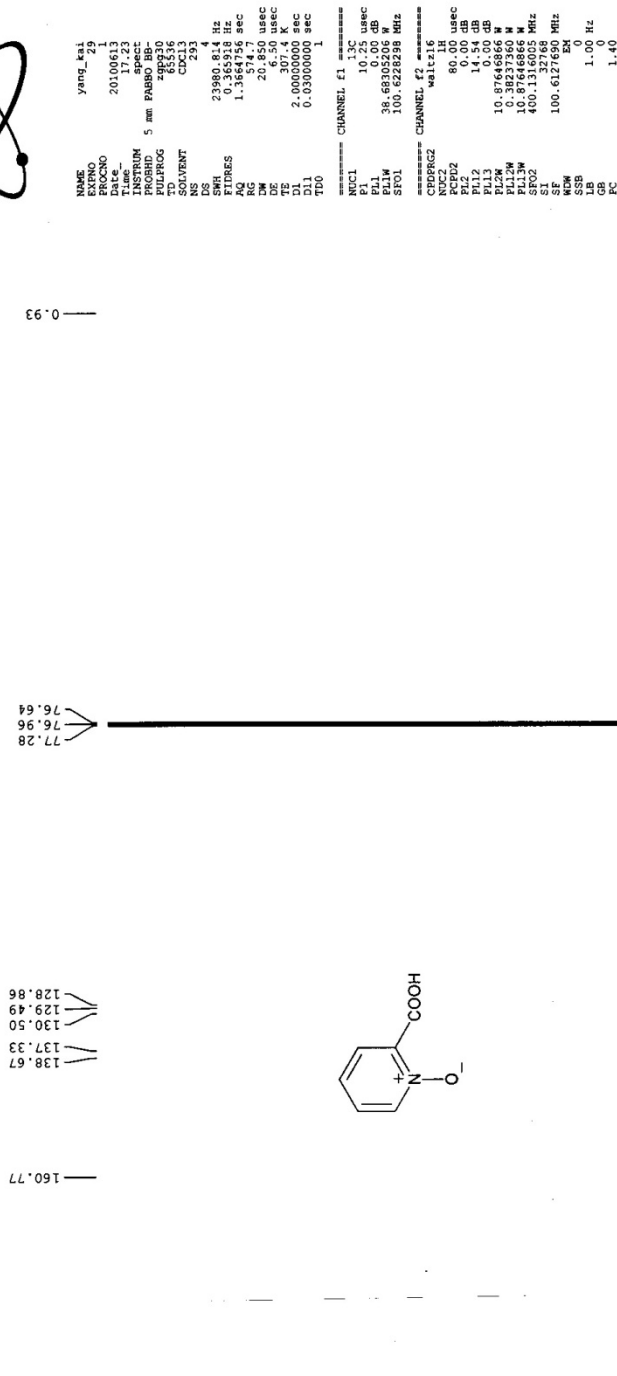
**1. General Experimental Methods:**  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded on Bruker Avance ARX- 400. Mass spectra were performed on Kompact Axima-CFR MALDI mass spectrometers. Optical rotations were recorded on a Perkin Elmer 341 polarimeter. Anhydrous solvents were obtained as follows: DMSO from  $\text{CaH}_2$ . All other solvents were reagent grade. All moisture sensitive reactions were carried out in flame dried flask under argon atmosphere.

2. Copies of <sup>1</sup>H and <sup>13</sup>C NMR of Ligands

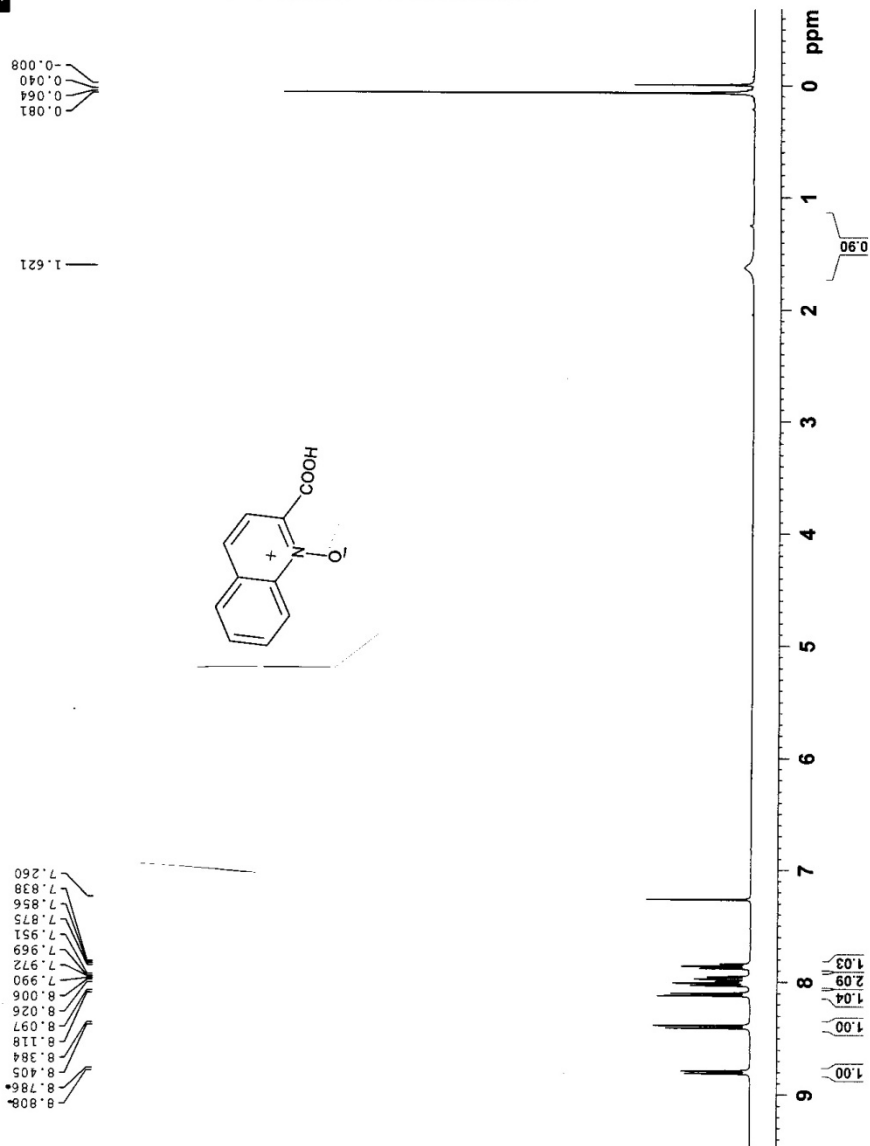
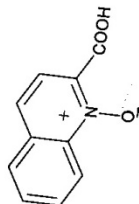




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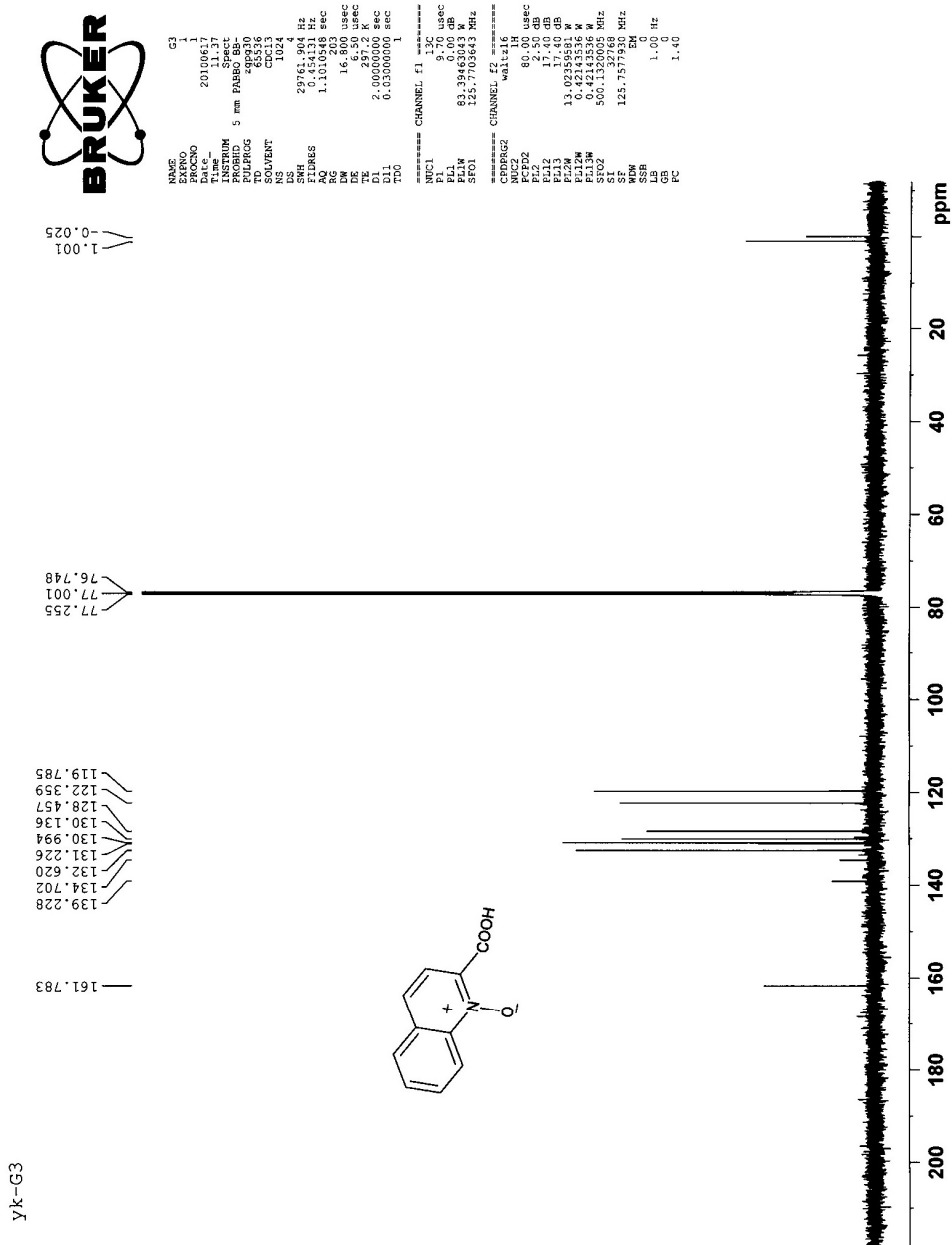


L1

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## L2



L2

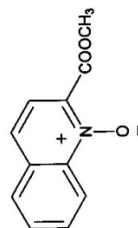


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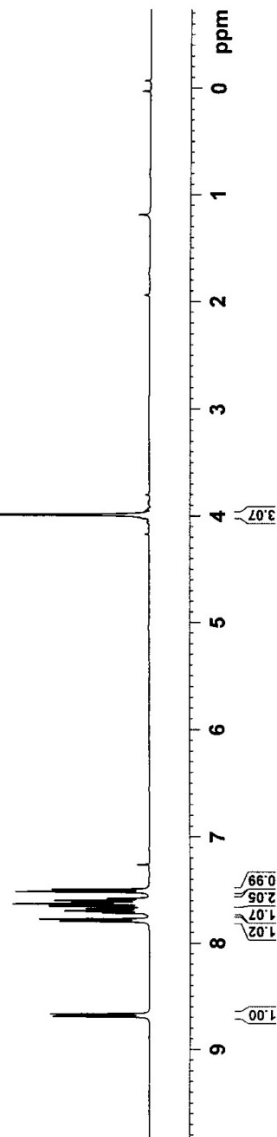
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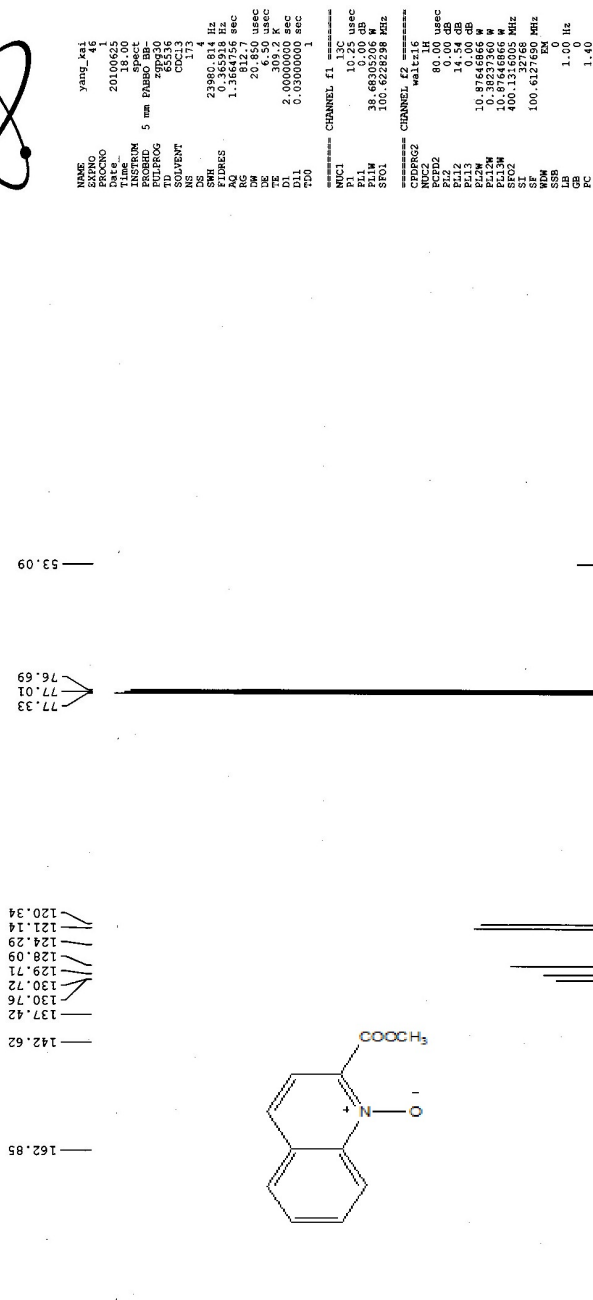
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L3



### L3

### 3. General Procedure A and B

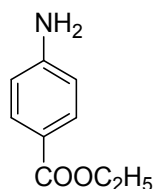
#### General Procedure A: the Coupling of Aryl Iodides with Aqueous Ammonia

A mixture of aryl iodide (1 mmol), aqueous ammonia (28%, 0.3 mL, 5.0 mmol), CuI (38 mg, 0.2 mmol), 2-carboxylic acid-quinoline-*N*-oxide (75.7 mg, 0.4 mmol), and K<sub>2</sub>CO<sub>3</sub> (346 mg, 2.5 mmol) in 2 mL of DMSO was heated at 50 °C for 23 h. Then the cooled mixture was partitioned between water and ethyl acetate. The organic layer was separated, and the aqueous layer was extracted with ethyl acetate (3 x 10 mL). The combined organic layers were washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated under vacuum. The residue was purified by chromatography on silicon gel with petroleum ether and ethyl acetate as eluent to provide the primary aryl amine.

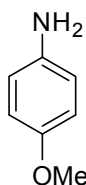
#### General Procedure B: the Coupling of Aryl and Heteroaryl Bromides with Aqueous Ammonia

A mixture of aryl iodide (1 mmol), aqueous ammonia (28%, 0.3 mL, 5.0 mmol), CuI (38 mg, 0.2 mmol), 2-carboxylic acid-quinoline-*N*-oxide (75.7 mg, 0.4 mmol), and K<sub>2</sub>CO<sub>3</sub> (346 mg, 2.5 mmol) in 2 mL of DMSO was heated at 80 °C for 23 h. Then the cooled mixture was partitioned between water and ethyl acetate. The organic layer was separated, and the aqueous layer was extracted with ethyl acetate (3 x 10 mL). The combined organic layers were washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated under vacuum. The residue was purified by chromatography on silicon gel with petroleum ether and ethyl acetate as eluent to provide the primary aryl amine.

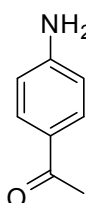
### 4. The Coupling of Aryl Iodides with Aqueous Ammonia: Table 2



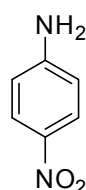
**Ethyl p-aminobenzoate (entry 1)**<sup>1</sup>: Following Procedure A, the crude oil was purified by flash chromatography on silica gel to provide 91% yield of the desired product as a white solid. Mp 88-90 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 1.36(t, *J* = 7.2 Hz, 3H), 4.04 (br s, 2H), 4.32 (d, *J* = 14.2 Hz, 2H), 6.64 (m, *J* = 11.0, 8.8 Hz, 2H), 7.85 (m, *J* = 9.0 Hz, 2H) ppm. MS (EI, *m/z*): 165 (M<sup>+</sup>). HRMS (ESI): C<sub>9</sub>H<sub>12</sub>NO<sub>2</sub> calculated [M+H]<sup>+</sup> 166.0868, found 166.0870.



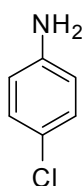
**4-Methoxyaniline (entry 2)<sup>2</sup>:** Following Procedure A, the crude oil was purified by flash chromatography on silica gel to provide 90% yield of the desired product as light yellow solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 3.44 (br s, 2H), 3.77 (s, 3H), 6.65 (d, *J* = 8.8 Hz, 2H), 6.71 (d, *J* = 8.8 Hz, 2H) ppm. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 55.7, 114.8, 116.4, 139.9, 152.8 ppm. MS (EI, *m/z*): 124 (*M*<sup>+</sup>+1). HRMS (ESI): C<sub>7</sub>H<sub>10</sub>NO calculated [*M*+H]<sup>+</sup> 124.0762, found 124.0759.



**4-aminoacetophenone (entry 3)<sup>1</sup>:** Following Procedure A, the crude oil was purified by flash chromatography on silica gel to provide 94% yield of the desired product as light yellow solid. Mp 103-105 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 2.25 (s, 3H), 4.23 (br s, 2H), 6.67 (d, *J* = 8.8 Hz, 2H), 7.83 (d, *J* = 8.8, 2H) ppm. MS (EI, *m/z*): 136 (*M*<sup>+</sup>+1). HRMS (ESI): C<sub>8</sub>H<sub>10</sub>NO calculated [*M*+H]<sup>+</sup> 136.0762, found 136.0765.

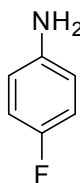


**4-Nitroaniline (entry 4)<sup>3</sup>:** Following Procedure A, the crude oil was purified by flash chromatography on silica gel to provide 89% yield of the desired product as pale yellow solid. Mp 146-149 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 3.33 (br s, 2H), 6.62 (d, *J* = 9.2 Hz, 2H), 7.11 (d, *J* = 9.2, 2H) ppm. MS (EI, *m/z*): 139 (*M*<sup>+</sup>+1). HRMS (ESI): C<sub>6</sub>H<sub>7</sub>N<sub>2</sub>O<sub>2</sub> calculated [*M*+H]<sup>+</sup> 139.0508, found 139.0505.

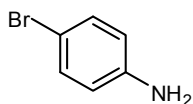


**4-Chloroaniline (entry 5)<sup>4</sup>:** Following Procedure A, the crude oil was purified by flash chromatography on silica gel to provide 92% yield of the desired product as white solid. Mp 70-72 °C. <sup>1</sup>H NMR (400 MHz,

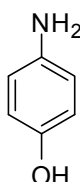
CDCl<sub>3</sub>):  $\delta$  4.38 (br s, 2H), 6.62 (d,  $J$  = 9.2, Hz, 2H), 8.06 (d,  $J$  = 9.2 Hz, 2H) ppm. MS (EI,  $m/z$ ): 128 ( $M^+$ +1). HRMS (ESI): C<sub>6</sub>H<sub>7</sub>NCl calculated [ $M+H$ ]<sup>+</sup> 128.0267, found 128.0263.



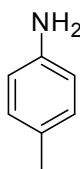
**4-Fluoroaniline (entry 6)**<sup>3</sup>: Following Procedure A, the crude oil was purified by flash chromatography on silica gel to provide 91% yield of the desired product as pale yellow oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  6.62 (m, 2H), 6.85 (t,  $J$  = 8.8 Hz, 2H) ppm. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  157.2, 155.4, 142.4, 115.9 ppm. MS (EI,  $m/z$ ): 112 ( $M^+$ +1). HRMS (ESI): C<sub>6</sub>H<sub>7</sub>NF calculated [ $M+H$ ]<sup>+</sup> 112.0563, found 112.0559.



**4-Bromoaniline (entry 7)**<sup>1</sup>: Following Procedure A, the crude oil was purified by flash chromatography on silica gel to provide 83% yield of the desired product as pale yellow solid. Mp 61-63 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  3.72 (br s, 2H), 6.58 (d,  $J$  = 8.8 Hz, 2H), 7.26 (d,  $J$  = 8.8 Hz, 2H) ppm. MS (EI,  $m/z$ ): 171 ( $M^+$ +1). HRMS (ESI): C<sub>6</sub>H<sub>7</sub>NBr calculated [ $M+H$ ]<sup>+</sup> 171.9762, found 171.9760.

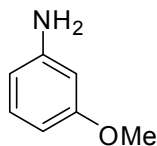


**4-Aminophenol (entry 8)**<sup>1</sup>: Following Procedure A, the crude oil was purified by flash chromatography on silica gel to provide 90% yield of the desired product as light yellow solid. Mp 181-183 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  3.43 (br s, 2H), 4.35 (br s, 1H), 6.62 (d,  $J$  = 8.8 Hz, 2H), 6.69 (d,  $J$  = 8.8 Hz, 2H) ppm. MS (EI,  $m/z$ ): 110 ( $M^+$ +1). HRMS (ESI): C<sub>6</sub>H<sub>8</sub>NO calculated [ $M+H$ ]<sup>+</sup> 110.0606, found 110.0603.

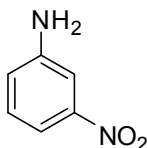


**4-Toluidine (entry 9)**<sup>1</sup>: Following Procedure A, the crude oil was purified by flash chromatography on silica gel to provide 94% yield of the desired product as colorless solid. Mp 42-44 °C. <sup>1</sup>H NMR (400

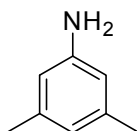
MHz, CDCl<sub>3</sub>):  $\delta$  2.27(s,3H ), 3.56 (br s, 2H), 6.63 (d,  $J$  = 8.4 Hz, 2H), 7.99 (d,  $J$ =8.4, 2H) ppm. MS (EI,  $m/z$ ): 108 ( $M^+$ +1). HRMS (ESI): C<sub>7</sub>H<sub>10</sub>N calculated [ $M+H$ ]<sup>+</sup> 108.0810, found 108.0813.



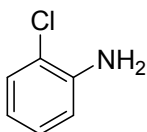
**4-Methoxyaniline (entry 10)<sup>2</sup>:** Following Procedure A, the crude oil was purified by flash chromatography on silica gel to provide 90% yield of the desired product as colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 3.77 (s, 3H), 6.25 (m, 1H), 6.30 (m, 1H), 6.34 (m, 1H ), 7.07 ( t,  $J$  = 8.0 Hz, 1H) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$ 160.3, 147.2, 130.0, 107.6, 103.8, 101.0, 55.0. MS (EI,  $m/z$ ): 124 ( $M^+$ +1). HRMS (ESI): C<sub>7</sub>H<sub>10</sub>NO calculated [ $M+H$ ]<sup>+</sup> 124.0762, found 124.0765.



**3-Nitroaniline (entry 11)<sup>1</sup>:** Following Procedure A, the crude oil was purified by flash chromatography on silica gel to provide 92% yield of the desired product as light yellow solid. Mp 112-115 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  3.92 (br s, 2H), 6.87 (ddd,  $J$  = 8.0, 2.4,0.8 Hz, 1H), 7.20 (t, 8.0 HZ, 1H ), 7.42( t, 2.0 HZ, 1H), 7.51 (ddd,  $J$  = 8.0, 2.4, 0.8 Hz, 2H) ppm. MS (EI,  $m/z$ ): 139 ( $M^+$ +1). HRMS (ESI): C<sub>6</sub>H<sub>7</sub>N<sub>2</sub>O<sub>2</sub> calculated [ $M+H$ ]<sup>+</sup> 139.0508, found 139.0510.



**3,5-Dimethoxyaniline (entry 12)<sup>1</sup>:** Following Procedure A, the crude oil was purified by flash chromatography on silica gel to provide 92% yield of the desired product as pale yellow oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  2.27 (s, 6H), 3.51 (br s, 2H), 6.37 (s, 2H), 6.47 (s, 1H) ppm; <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  21.2, 113.0, 120.4, 138.9, 146.3 ppm. MS (EI,  $m/z$ ): 122 ( $M^+$ +1). HRMS (ESI): C<sub>8</sub>H<sub>12</sub>N calculated [ $M+H$ ]<sup>+</sup> 122.0970, found 122.0966.



**2-chloroaniline (entry 13)**<sup>4</sup>: Following Procedure A, the crude oil was purified by flash chromatography on silica gel to provide 87% yield of the desired product as pale yellow oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  3.71 (brs, 2H), 6.54 (dd,  $J$  = 8.0, 8.0 Hz, 1H), 6.67 (t,  $J$  = 2.2 Hz, 1H), 7.17 (dd,  $J$  = 2.0, 1.8 Hz, 1H), 7.06 (t,  $J$  = 8.0 Hz, 1H) ppm. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  142.9, 129.3, 127.6, 119.2, 119.0, 115.8 ppm. MS (EI,  $m/z$ ): 128 ( $M^+$ +1). HRMS (ESI): C<sub>6</sub>H<sub>7</sub>NCl calculated [ $M+H$ ]<sup>+</sup> 128.0267, found 128.0270.

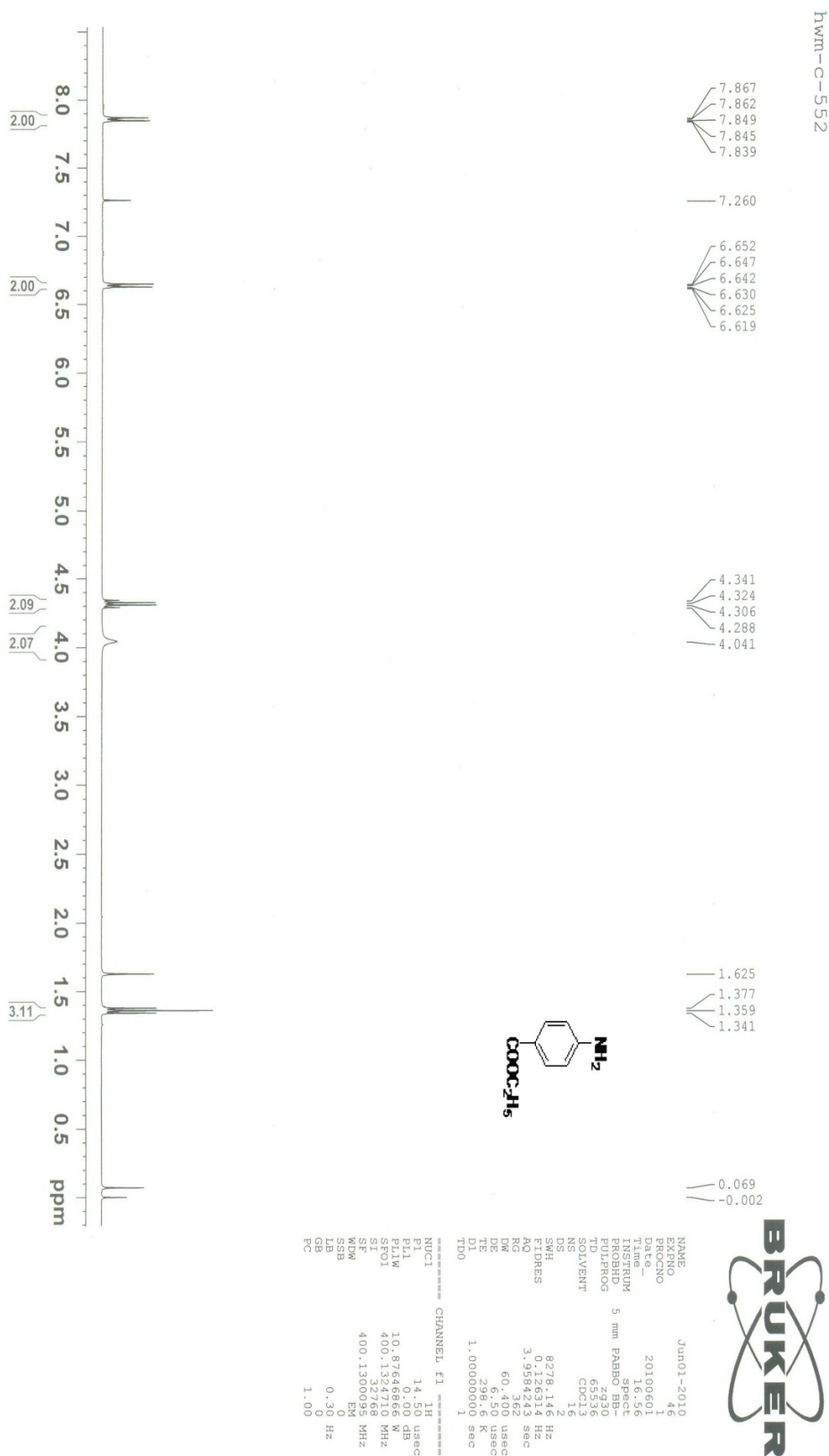


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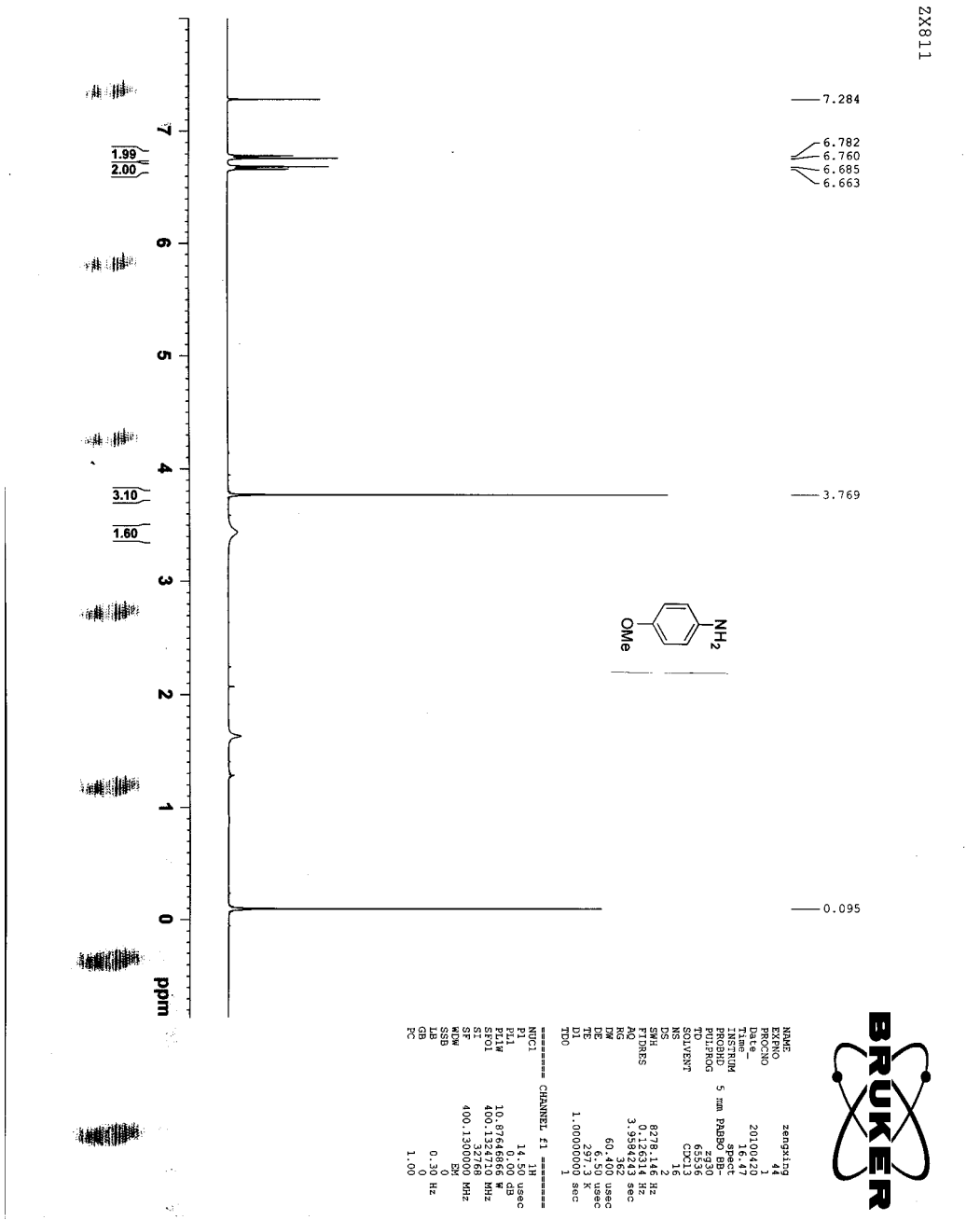


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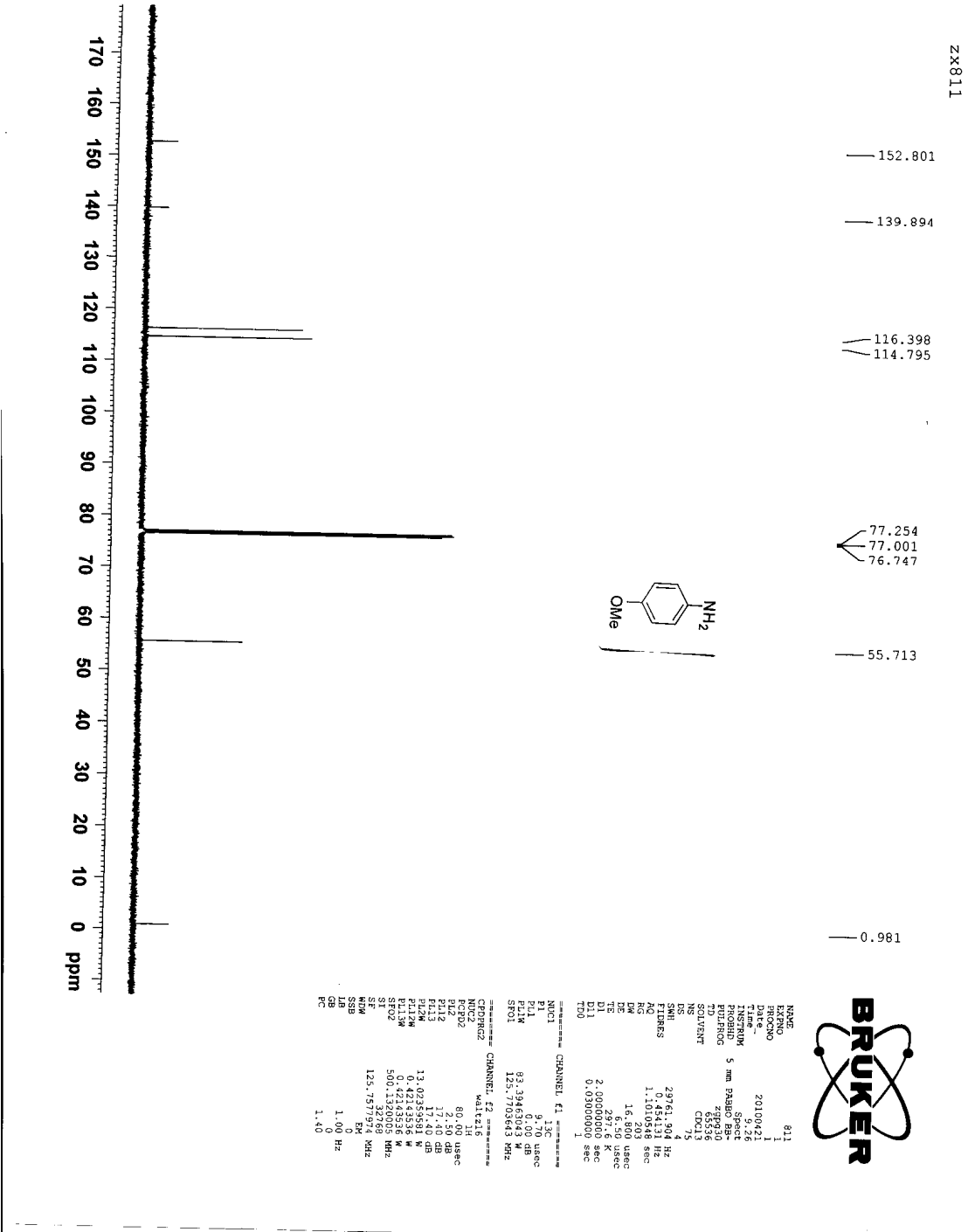


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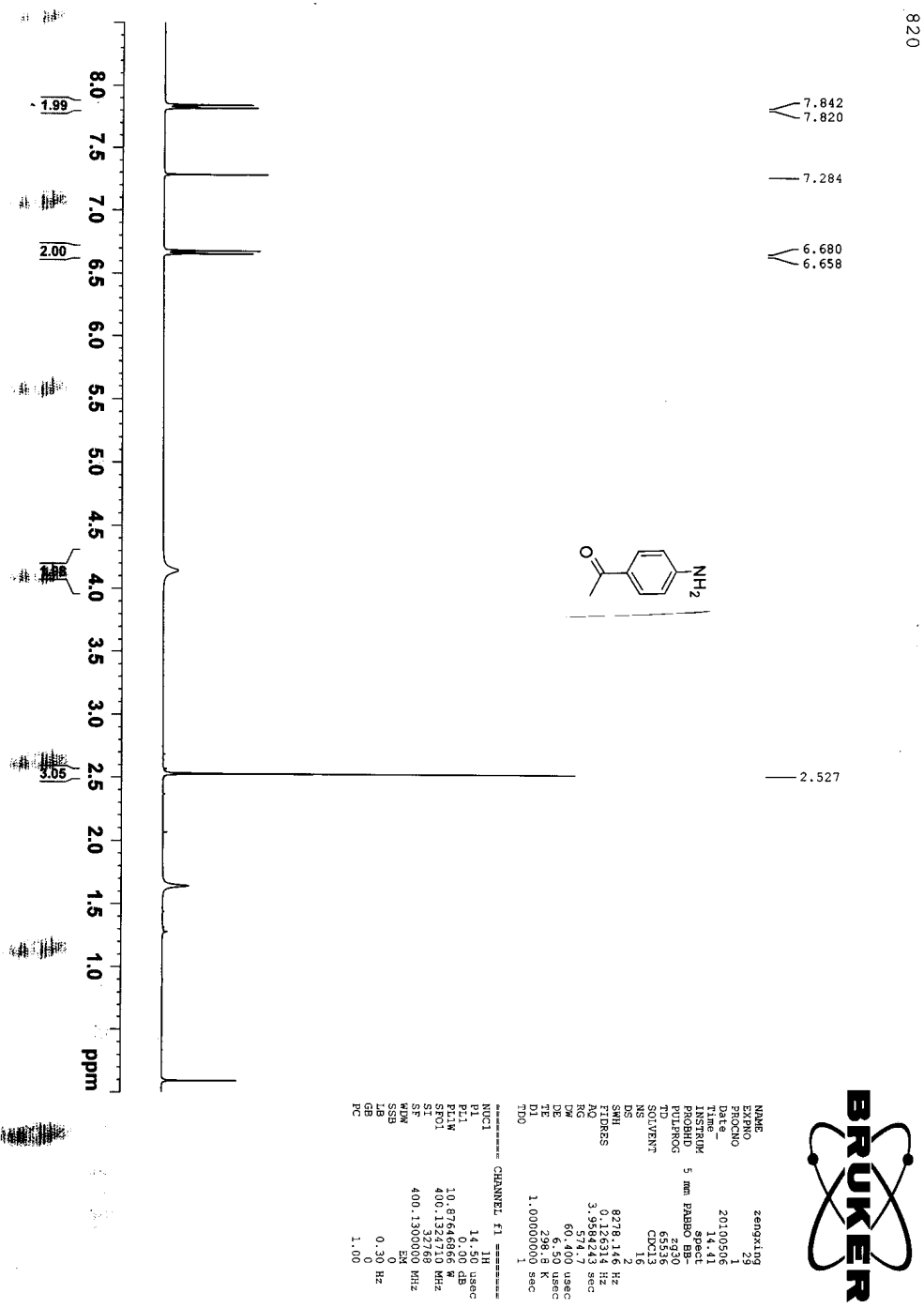


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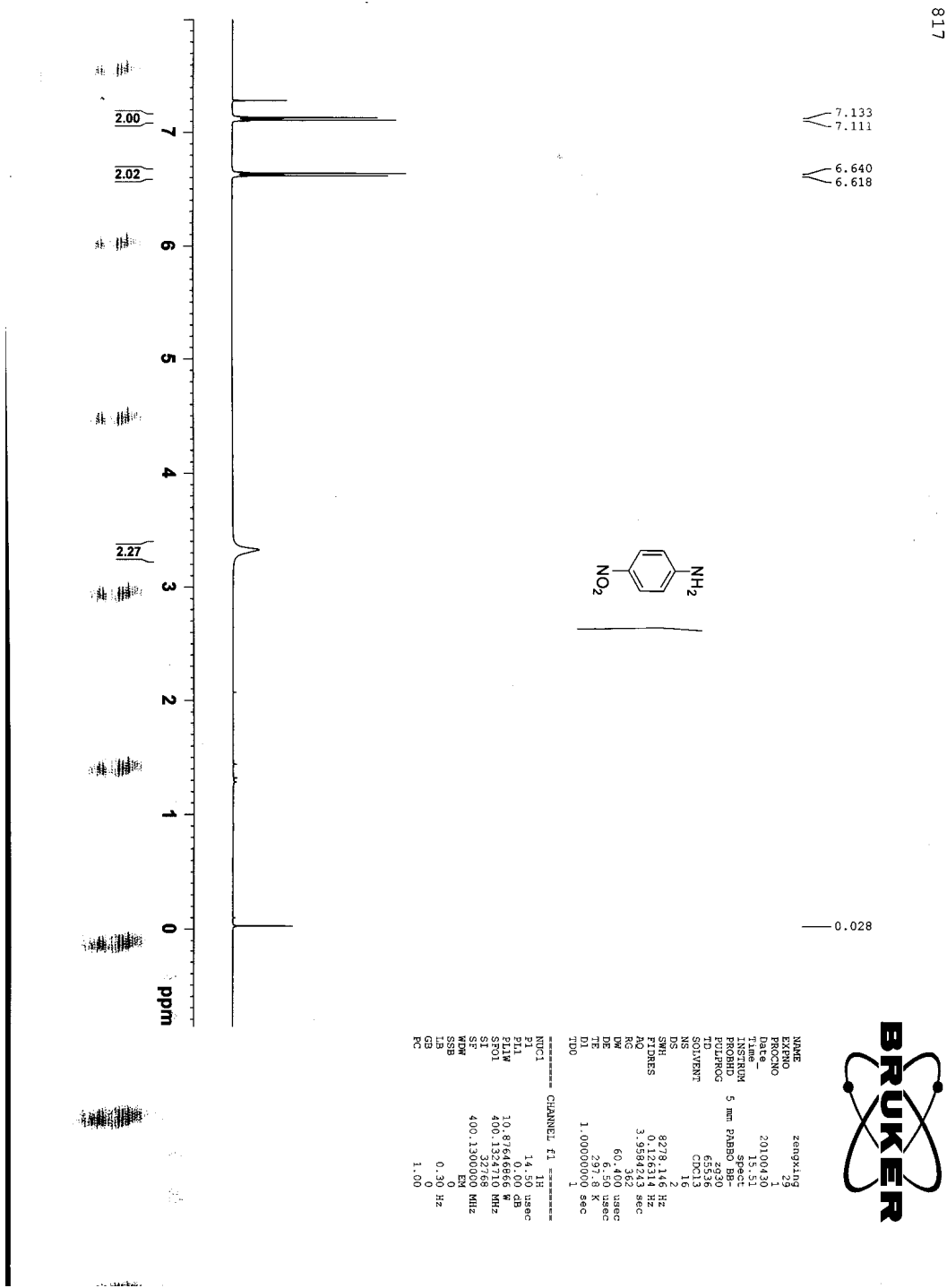


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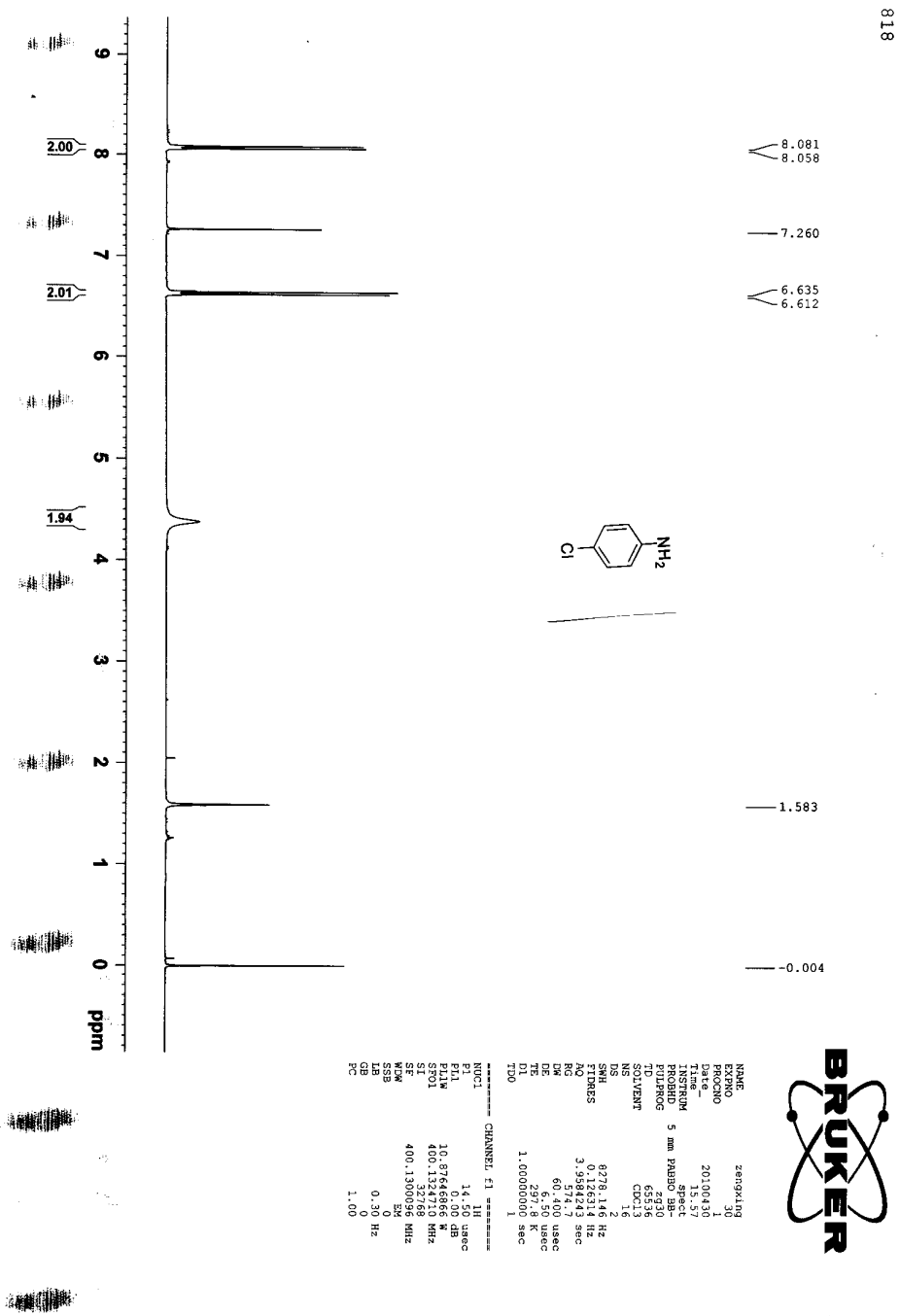


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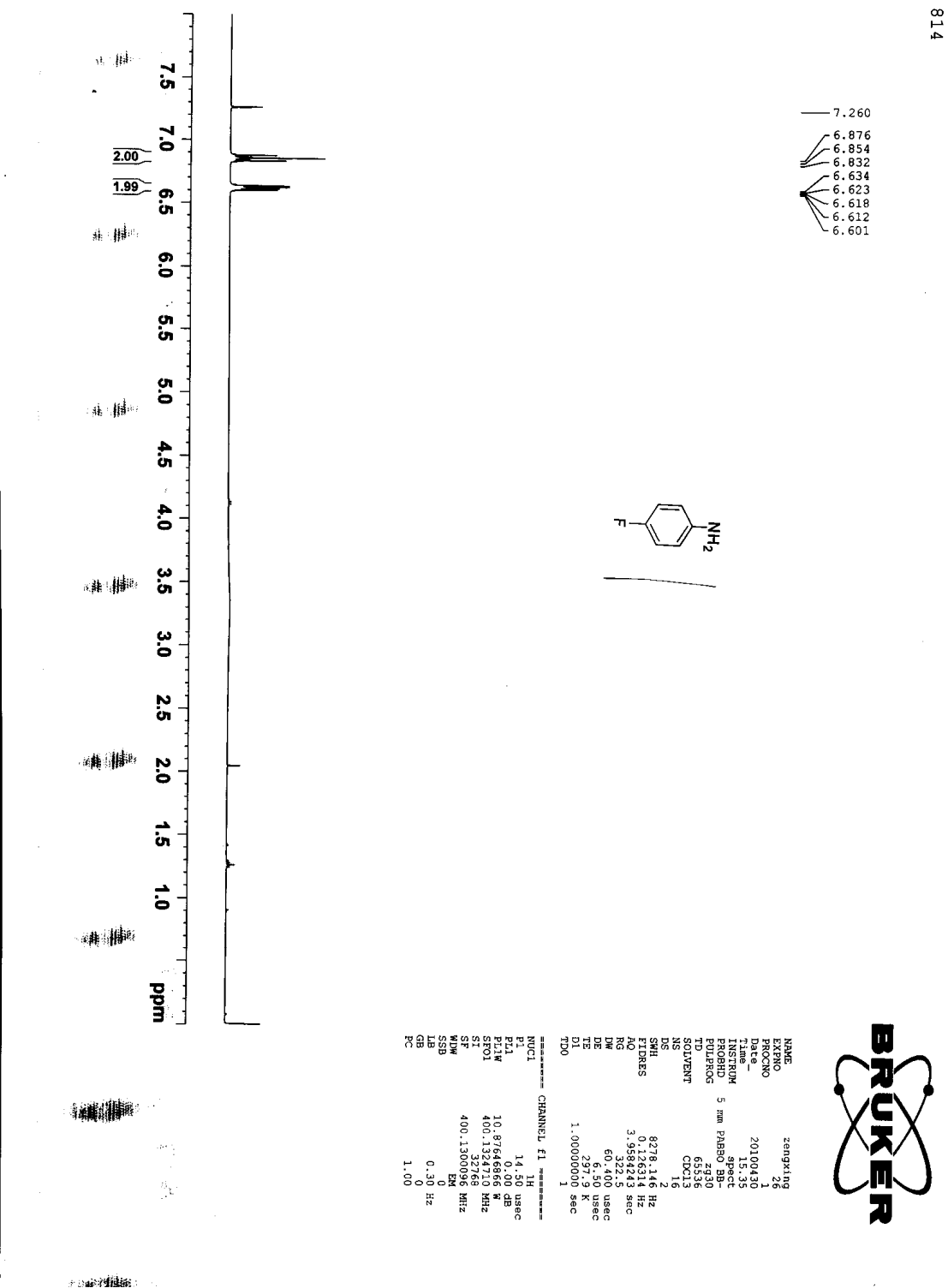
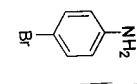
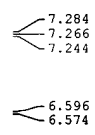


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S21

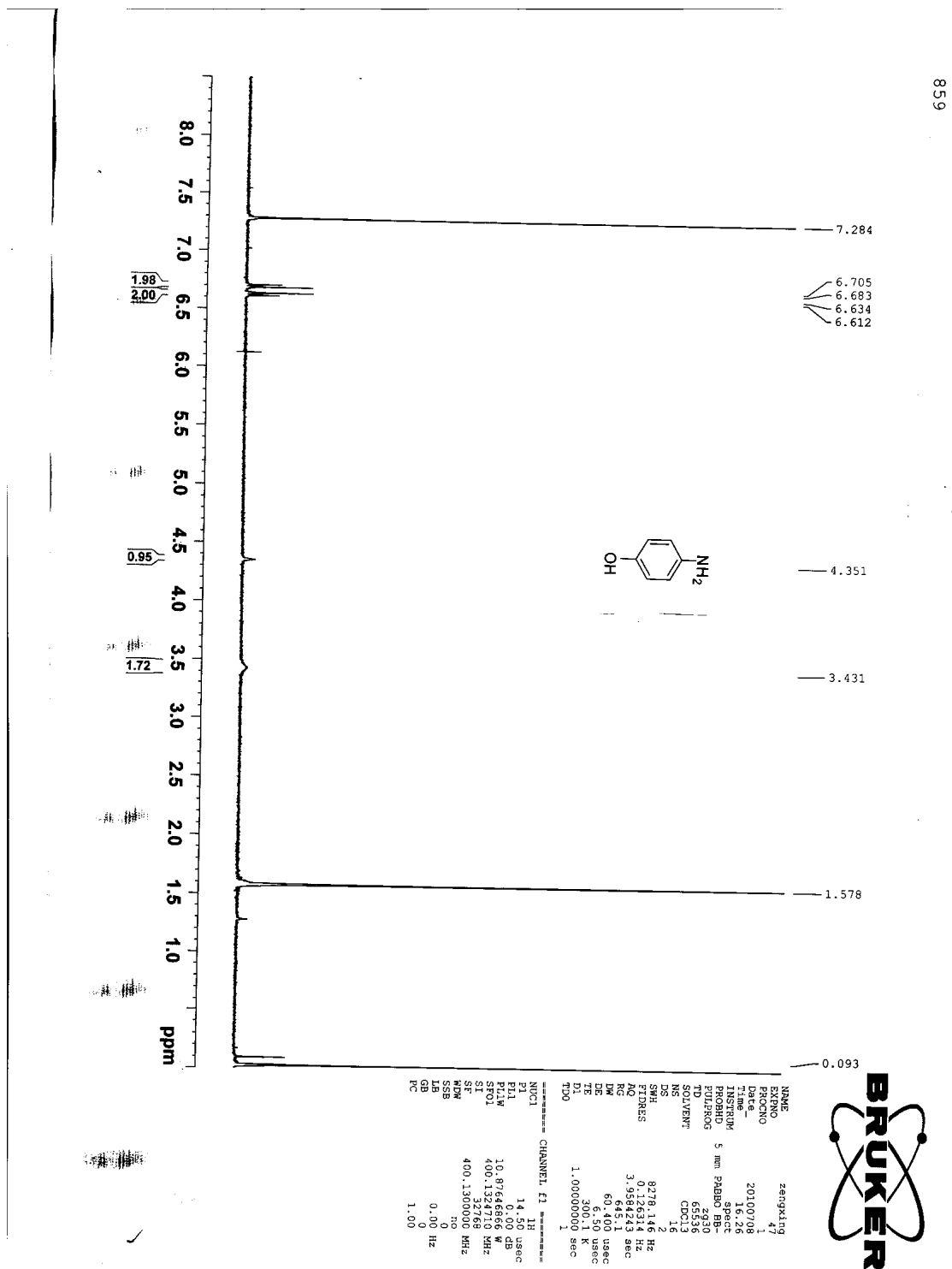


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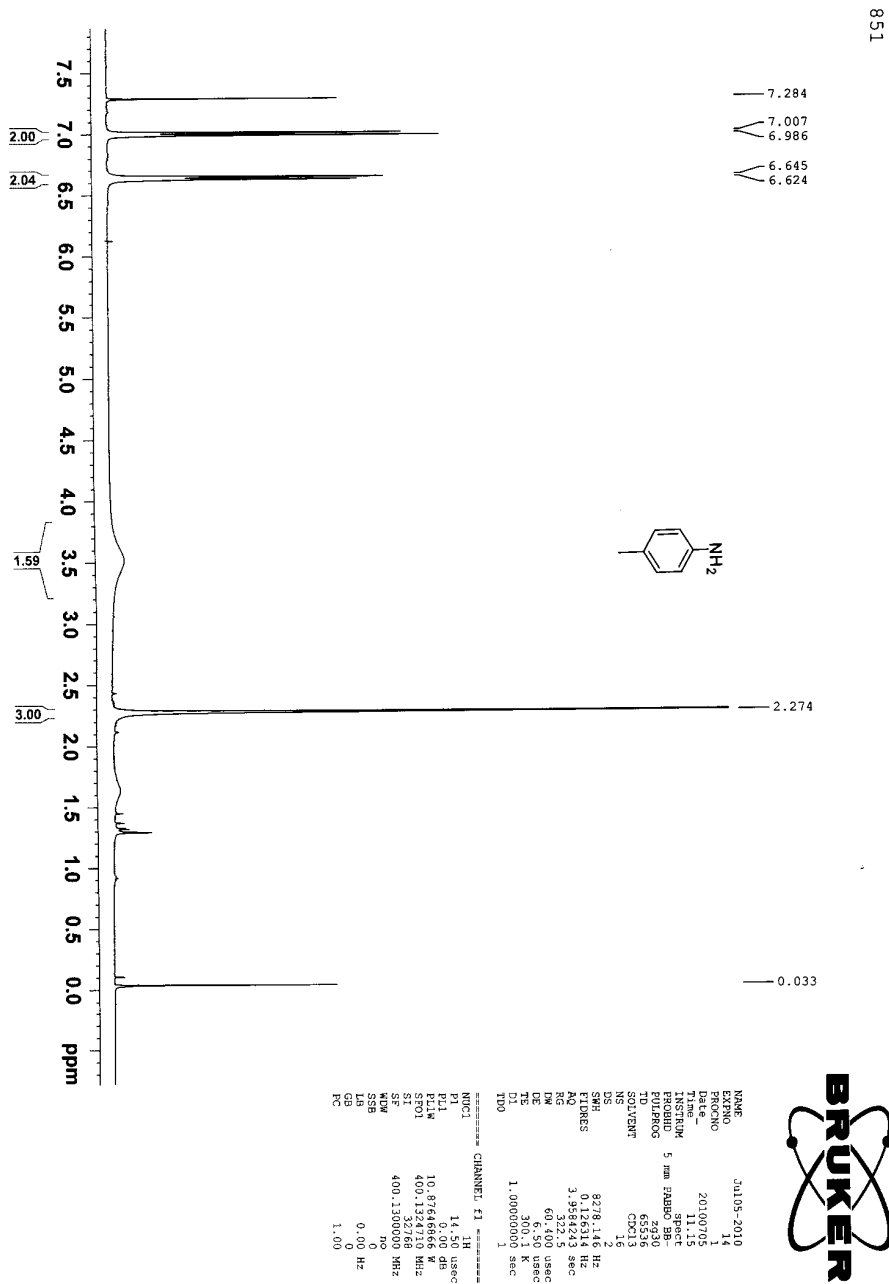


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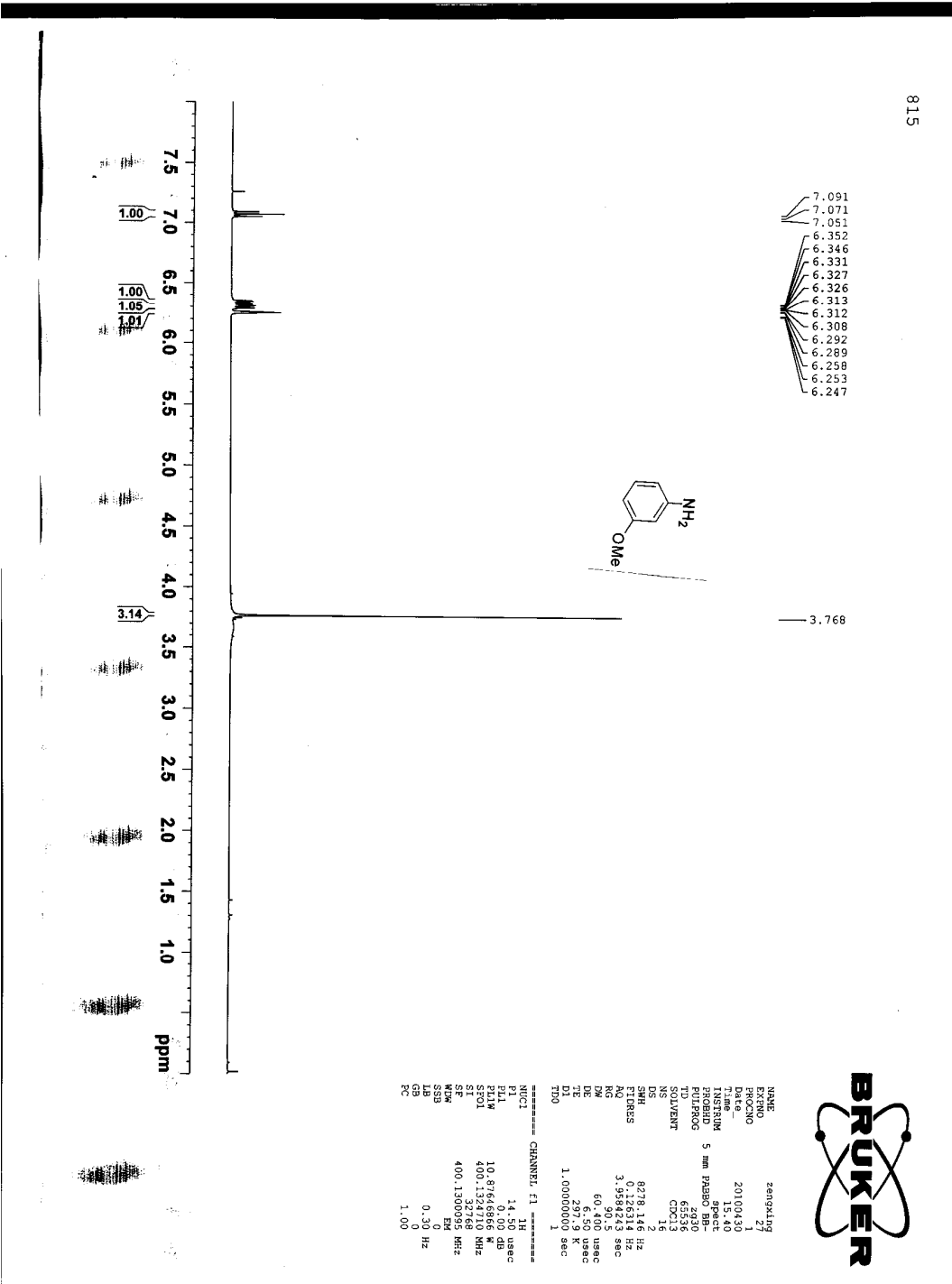


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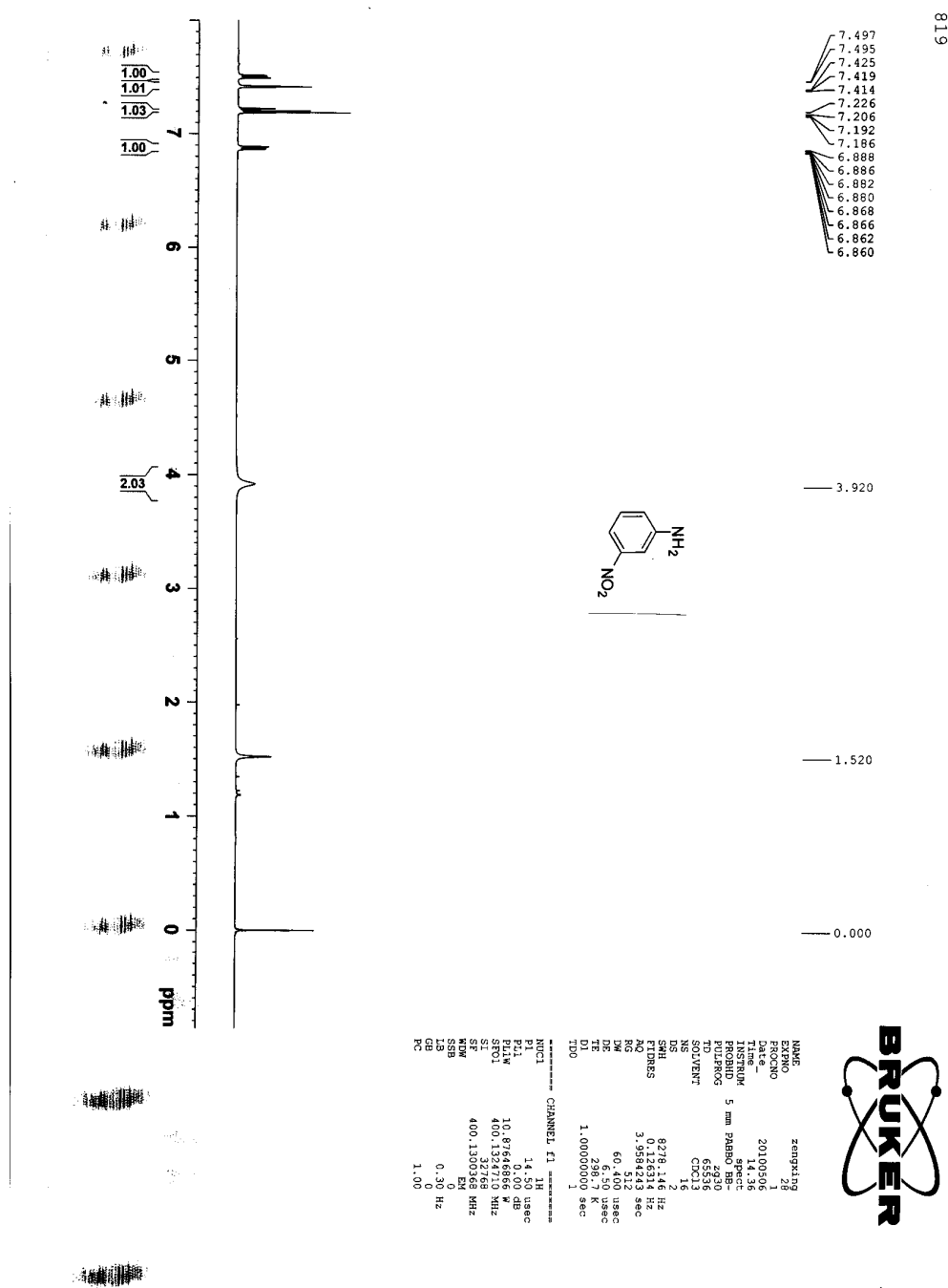


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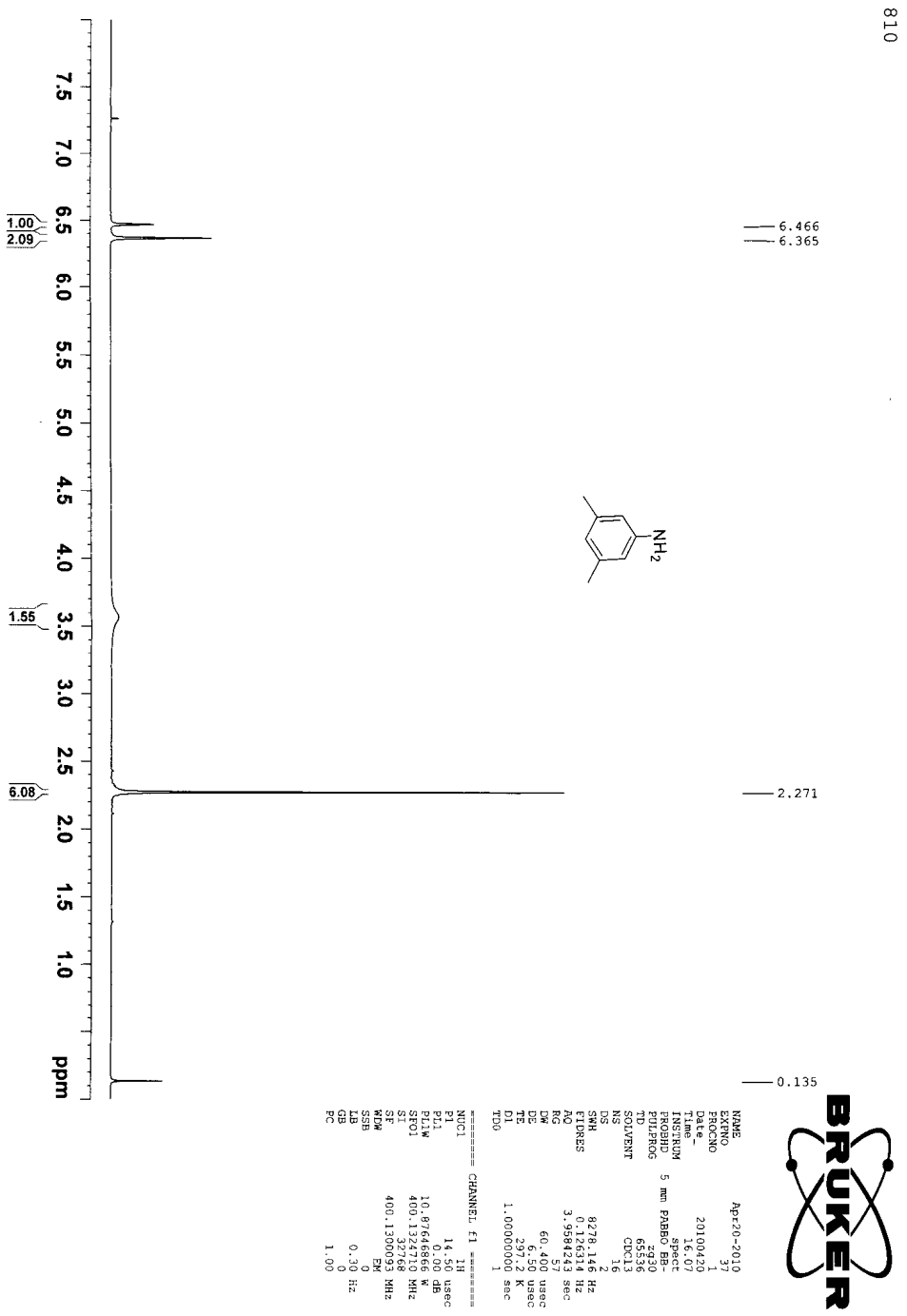
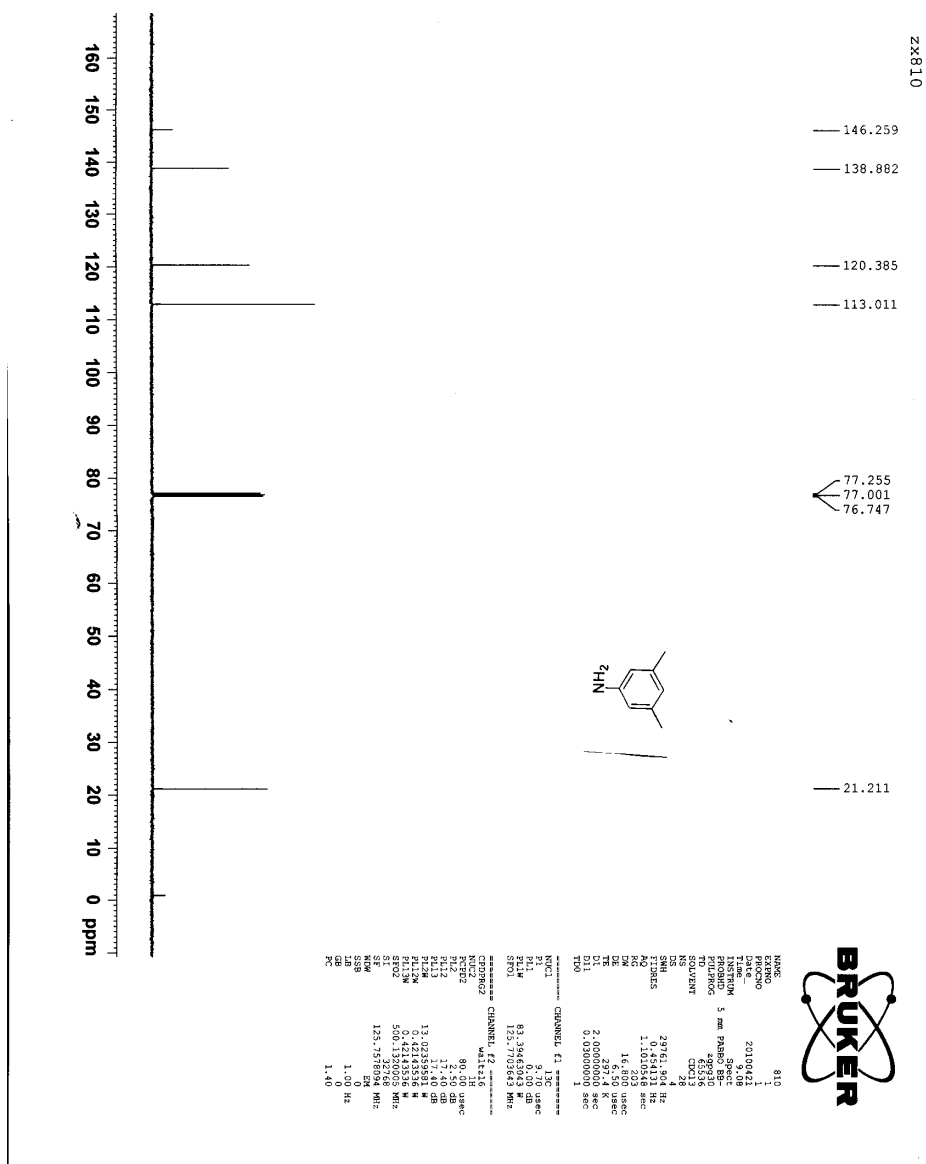


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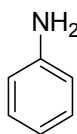
**Table 2, Entry 12**



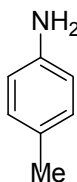


S28

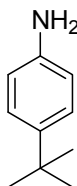
## 5. General Procedure B: Coupling of Aryl Bromides with Aqueous Ammonia: Table 3



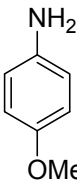
**Aniline (entry 1)<sup>1</sup>:** Following Procedure B, the crude oil was purified by flash chromatography on silica gel to provide 98% yield of the desired product as pale yellow oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 3.65 (br s, 2H), 6.70 (d, *J* = 8.4 Hz, 2H), 6.78 (t, *J* = 12.5 Hz, 1H), 7.17 (m, *J* = 16.0, 5.2 Hz, 2H) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 149.0, 129.6, 116.8, 114.8. MS (EI, *m/z*): 94 (*M*<sup>+</sup>+1). HRMS (ESI): C<sub>6</sub>H<sub>8</sub>N calculated [*M*+H]<sup>+</sup> 94.0657, found 94.0658.



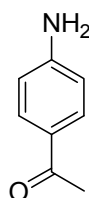
**4-Methoxyaniline (entry 2)<sup>1</sup>:** Following Procedure B, the crude oil was purified by flash chromatography on silica gel to provide 90% yield of the desired product as yellow solid. Mp 42-44 °C <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 2.25 (s, 3H), 3.52 (brs, 2H), 6.61 (d, *J* = 6.0 Hz, 2H), 6.97 (d, *J* = 6.0 Hz, 2H) ppm. MS (EI, *m/z*): 108 (*M*<sup>+</sup>+1). HRMS (ESI): C<sub>7</sub>H<sub>10</sub>N calculated [*M*+H]<sup>+</sup> 108.0810, found 108.0813.



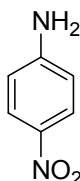
**4-tert-Butyl benzenamine (entry 3)<sup>5</sup>:** Following Procedure B, the crude oil was purified by flash chromatography on silica gel to provide 90% yield of the desired product as pale yellow oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 1.28 (s, 9H), 3.54 (br s, 2H), 6.64 (d, *J* = 6.8 Hz), 7.18 (d, *J* = 6.8 Hz) ppm; <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 1.003, 31.5, 33.9, 114.9, 126.0, 141.4, 143.8 ppm. MS (EI, *m/z*): 108 (*M*<sup>+</sup>+1). HRMS (ESI): C<sub>10</sub>H<sub>16</sub>N calculated [*M*+H]<sup>+</sup> 108.0810, found 108.0813.



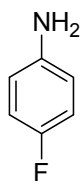
**4-Methoxyaniline (entry 4)<sup>1</sup>:** Following Procedure B, the crude oil was purified by flash chromatography on silica gel to provide 97% yield of the desired product as yellow solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 3.44 (br s, 2H), 3.77 (s, 3H), 6.67 (d, *J* = 6.4 Hz, 2H), 6.71 (d, *J* = 6.6 Hz, 2H) ppm. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 55.7, 114.8, 116.4, 139.9, 152.8 ppm. MS (EI, *m/z*): 124 (*M*<sup>+</sup>+1). HRMS (ESI): C<sub>7</sub>H<sub>10</sub>NO calculated [*M*+H]<sup>+</sup> 124.0762, found 124.0759.



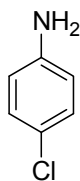
**4-Aminoacetophenone (entry 5)**<sup>2</sup>: Following Procedure B, the crude oil was purified by flash chromatography on silica gel to provide 93% yield of the desired product as pale yellow solid. Mp103-105 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 4.11 (br s, 2H), 6.65 (d, *J* = 6.8 Hz, 2H), 7.81 (d, *J* = 6.8 Hz, 2H) ppm. MS (EI, *m/z*): 136 (*M*<sup>+</sup>+1). HRMS (ESI): C<sub>8</sub>H<sub>10</sub>NO calculated [*M*+H]<sup>+</sup> 136.0762, found 136.0765.



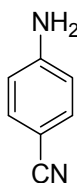
**p-Nitroaniline (entry 6)**<sup>3</sup>: Following Procedure B, the crude oil was purified by flash chromatography on silica gel to provide 96% yield of the desired product as pale yellow solid. Mp146-149 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 4.39 (br s, 2H), 6.62 (d, *J* = 7.0 Hz, 2H), 8.07 (d, *J* = 7.2 Hz, 2H) ppm. MS (EI, *m/z*): 139 (*M*<sup>+</sup>+1). HRMS (ESI): C<sub>6</sub>H<sub>7</sub>N<sub>2</sub>O<sub>2</sub> calculated [*M*+H]<sup>+</sup> 139.0508, found 139.0505.



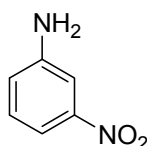
**4-Fluoroaniline (entry 7)**: Following Procedure B, the crude oil was purified by flash chromatography on silica gel to provide 96% yield of the desired product as pale yellow oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 3.53 (br s, 2H), 6.62 (m, *J* = 4.4, 2.0 Hz, 2H), 6.85 (m, *J* = 8.4, 8.8 Hz, 2H) ppm. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 157.2, 155.4, 142.4, 115.9 ppm. MS (EI, *m/z*): 112 (*M*<sup>+</sup>+1). HRMS (ESI): C<sub>6</sub>H<sub>7</sub>NF calculated [*M*+H]<sup>+</sup> 112.0563, found 112.0559.



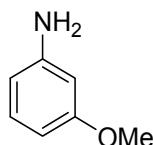
**p-Chloroaniline (entry 8)**<sup>4</sup>: Following Procedure B, the crude oil was purified by flash chromatography on silica gel to provide 88% yield of the desired product as white solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 3.65 (br s, 2H), 6.60 (dd, *J* = 7.8, 4.2 Hz, 2H), 7.10 (dd, *J* = 6.2, 8.5 Hz, 2H) ppm; <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 116.2, 123.2, 129.1, 144.9 ppm. MS (EI, *m/z*): 128 (*M*<sup>+</sup>+1). HRMS (ESI): C<sub>6</sub>H<sub>7</sub>NCl calculated [*M*+H]<sup>+</sup> 128.0267, found 128.0263.



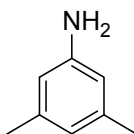
**4-Aminobenzonitrile (entry 9)<sup>1</sup>:** Following Procedure B, the crude oil was purified by flash chromatography on silica gel to provide 93% yield of the desired product as pale yellow solid. Mp 82-85 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 4.15 (brs, 2H), 6.64 (d, *J* = 6.8 Hz), 7.41 (d, *J* = 6.8 Hz) ppm; <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 100.3, 114.4, 120.0, 150.3 ppm. MS (EI, *m/z*): 119 (*M*<sup>+</sup>+1). HRMS (ESI): C<sub>7</sub>H<sub>7</sub>N<sub>2</sub> calculated [*M*+H]<sup>+</sup> 119.0609, found 119.0606.



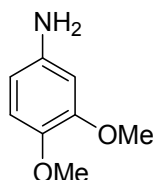
**3-Nitroaniline (entry 10)<sup>1</sup>:** Following Procedure B, the crude oil was purified by flash chromatography on silica gel to provide 95% yield of the desired product as pale yellow solid. Mp 112-115 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 3.99 (brs, 2H), 6.94 (dd, *J* = 10.4, 5.8 Hz, 1H), 7.27 (m, *J* = 8.0 Hz, 1H), 7.49 (t, *J* = 2.2 Hz, 1H), 7.57 (d, *J* = 0.8 Hz, 1H) ppm. MS (EI, *m/z*): 139 (*M*<sup>+</sup>+1). HRMS (ESI): C<sub>6</sub>H<sub>7</sub>N<sub>2</sub>O<sub>2</sub> calculated [*M*+H]<sup>+</sup> 139.0508, found 139.0510.



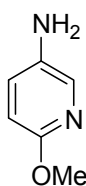
***m*-Methoxyaniline (entry 11)<sup>2</sup>:** Following Procedure B, the crude oil was purified by flash chromatography on silica gel to provide 93% yield of the desired product as pale yellow oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 3.65 (brs, 2H), 3.77 (s, 3H), 6.25 (t, *J* = 2 Hz), 6.31 (m, *J* = 8.2, 3.2, 4.2 Hz), 7.06 (t, *J* = 8.0 Hz) ppm; <sup>13</sup>C NMR (500 MHz, CDCl<sub>3</sub>): δ 55.08, 101.11, 103.99, 107.92, 130.09, 147.74, 160.78 ppm. MS (EI, *m/z*): 124 (*M*<sup>+</sup>+1). HRMS (ESI): C<sub>7</sub>H<sub>10</sub>NO calculated [*M*+H]<sup>+</sup> 124.0762, found 124.0765.



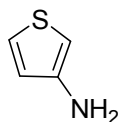
**3,5-Dimethoxyaniline (entry 12)<sup>1</sup>:** Following Procedure B, the crude oil was purified by flash chromatography on silica gel to provide 91% yield of the desired product as pale yellow oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 2.18 (s, 6H), 3.48 (br s, 2H), 6.29 (s, 2H), 6.38 (s, 1H) ppm; <sup>13</sup>C NMR (500 MHz, CDCl<sub>3</sub>): δ 21.3, 113.4, 120.4, 138.9, 146.3 ppm. MS (EI, *m/z*): 122 (*M*<sup>+</sup>+1). HRMS (ESI): C<sub>8</sub>H<sub>12</sub>N calculated [*M*+H]<sup>+</sup> 122.0970, found 122.0966.



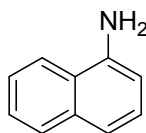
**4-Aminoveratrole (entry 13):** Following Procedure B, the crude oil was purified by flash chromatography on silica gel to provide 96% yield of the desired product as pale yellow solid. Mp. 85-87 °C  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  3.44 (br s, 2H), 3.80 (s, 3H), 3.83 (s, 3H), 6.23 (d,  $J$  = 8.4 Hz, 1H), 6.31 (d,  $J$  = 2.4 Hz, 1H), 6.70 (d,  $J$  = 1.2 Hz) ppm;  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  55.7, 56.6, 100.776, 106.4, 113.2, 140.6, 142.2, 149.9 ppm. MS (EI,  $m/z$ ): 154 ( $\text{M}^+$ +1). HRMS (ESI):  $\text{C}_8\text{H}_{12}\text{NO}_2$  calculated  $[\text{M}+\text{H}]^+ 154.0868$ , found 154.0871.



**5-Amino-2-methoxypyridine (entry 14)<sup>4</sup>:** Following Procedure B, the crude oil was purified by flash chromatography on silica gel to provide 95% yield of the desired product as pale yellow solid.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  3.39 (br s, 2H), 3.84 (s, 3H), 6.58 (d,  $J$  = 8.8 Hz, 1H), 7.01 (d,  $J$  = 8.9 Hz, 1H), 7.64 (d,  $J$  = 2.4 Hz, 1H) ppm;  $^{13}\text{C}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  53.3, 110.7, 127.6, 132.8, 136.6, 158.0 ppm. MS (EI,  $m/z$ ): 125 ( $\text{M}^+$ +1). HRMS (ESI):  $\text{C}_6\text{H}_9\text{N}_2\text{O}$  calculated  $[\text{M}+\text{H}]^+ 125.0715$ , found 125.0716.



**3-Thiophenamine (entry 15)<sup>1</sup>:** Following Procedure B, the crude oil was purified by flash chromatography on silica gel to provide 86% yield of the desired product as pale yellow oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  3.60 (br s, 2H), 6.17 (d,  $J$  = 3.0 Hz, 1H), 6.65 (d,  $J$  = 5.2 Hz, 1H), 7.13 (d,  $J$  = 5.2 Hz) ppm;  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  100.2, 121.1, 125.3, 145.1 ppm. MS (EI,  $m/z$ ): 100 ( $\text{M}^+$ +1). HRMS (ESI):  $\text{C}_4\text{H}_6\text{NS}$  calculated  $[\text{M}+\text{H}]^+ 100.0221$ , found 100.0221.



**1-Naphthalenamine (entry 16)<sup>1</sup>:** Following Procedure B, the crude oil was purified by flash chromatography on silica gel to provide 92% yield of the desired product as white solid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  4.14 (br s, 2H), 6.79 (t,  $J$  = 8.0 Hz, 1H), 7.33 (m,  $J$  = 6.4, 10.8 Hz, 2H), 7.48 (m,  $J$  = 4.8, 4.8 Hz, 2H), 7.81 (d,  $J$  = 2Hz, 2H) ppm;  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  , 109.7, 118.9, 120.7, 123.7,

124.8, 125.8, 126.3, 128.6, 134.4, 142.0 ppm. MS (EI,  $m/z$ ): 144 ( $M^{+}+1$ ). HRMS (ESI):  $C_{10}H_{10}N$   
calculated  $[M+H]^{+}$  144.0813, found 144.0812.

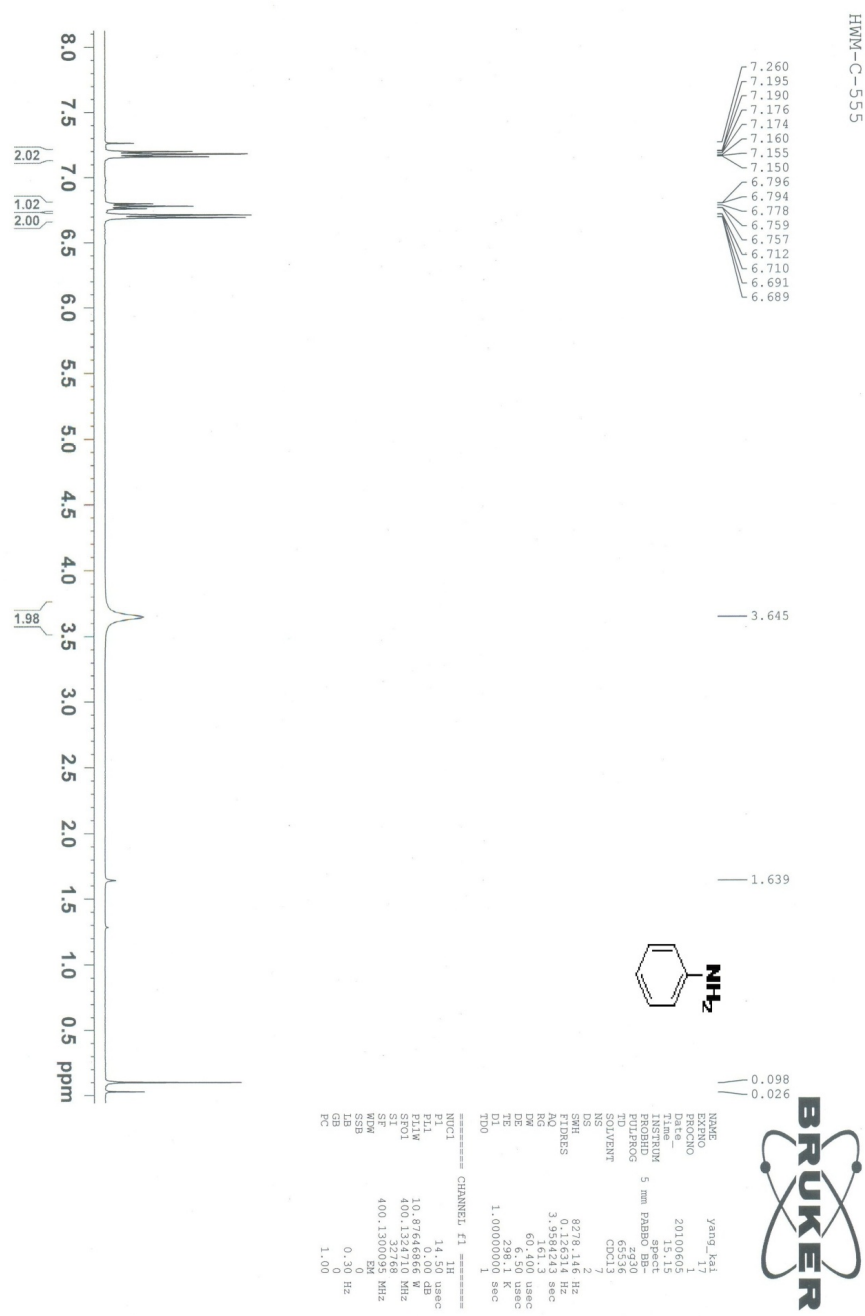


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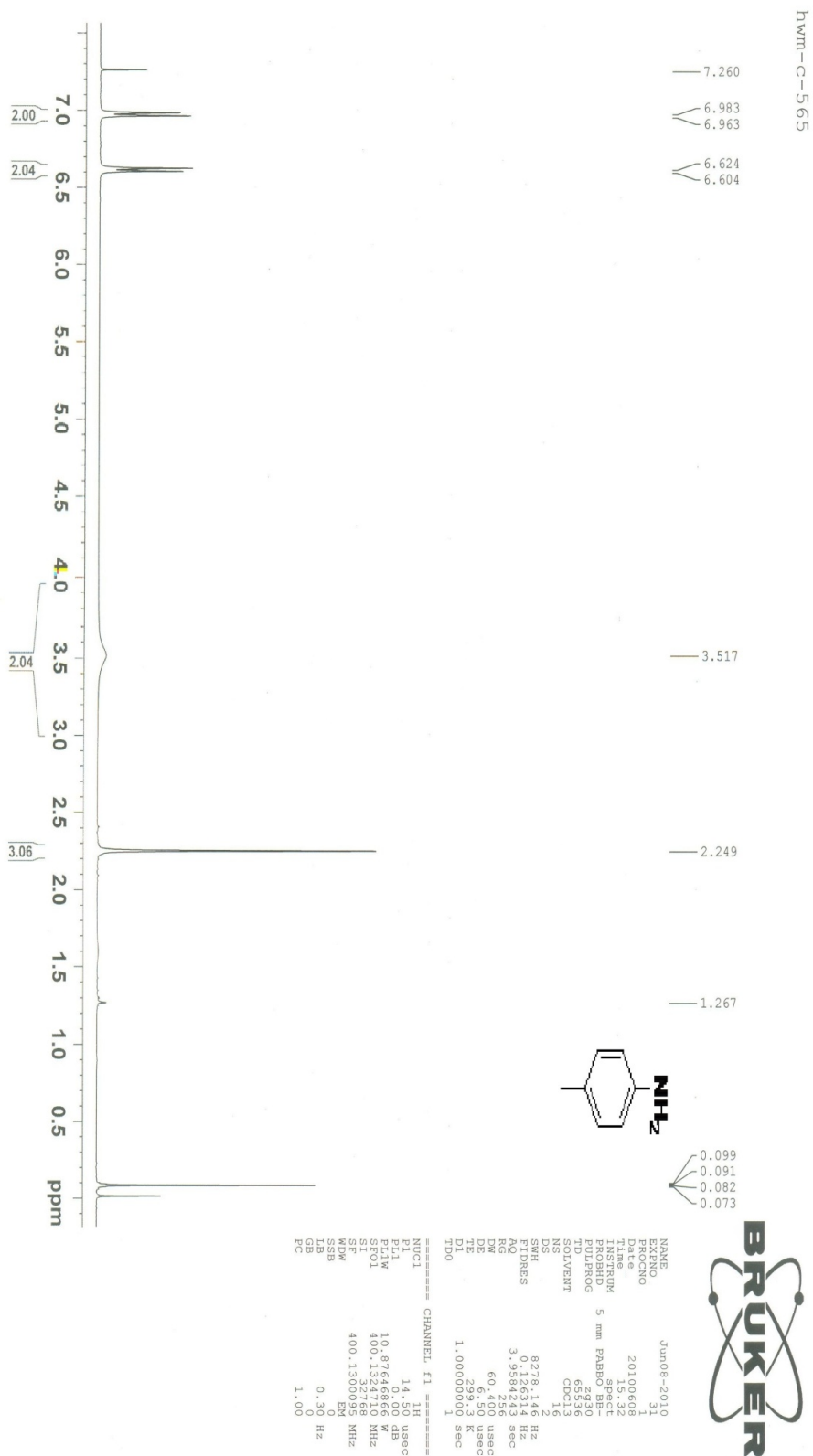


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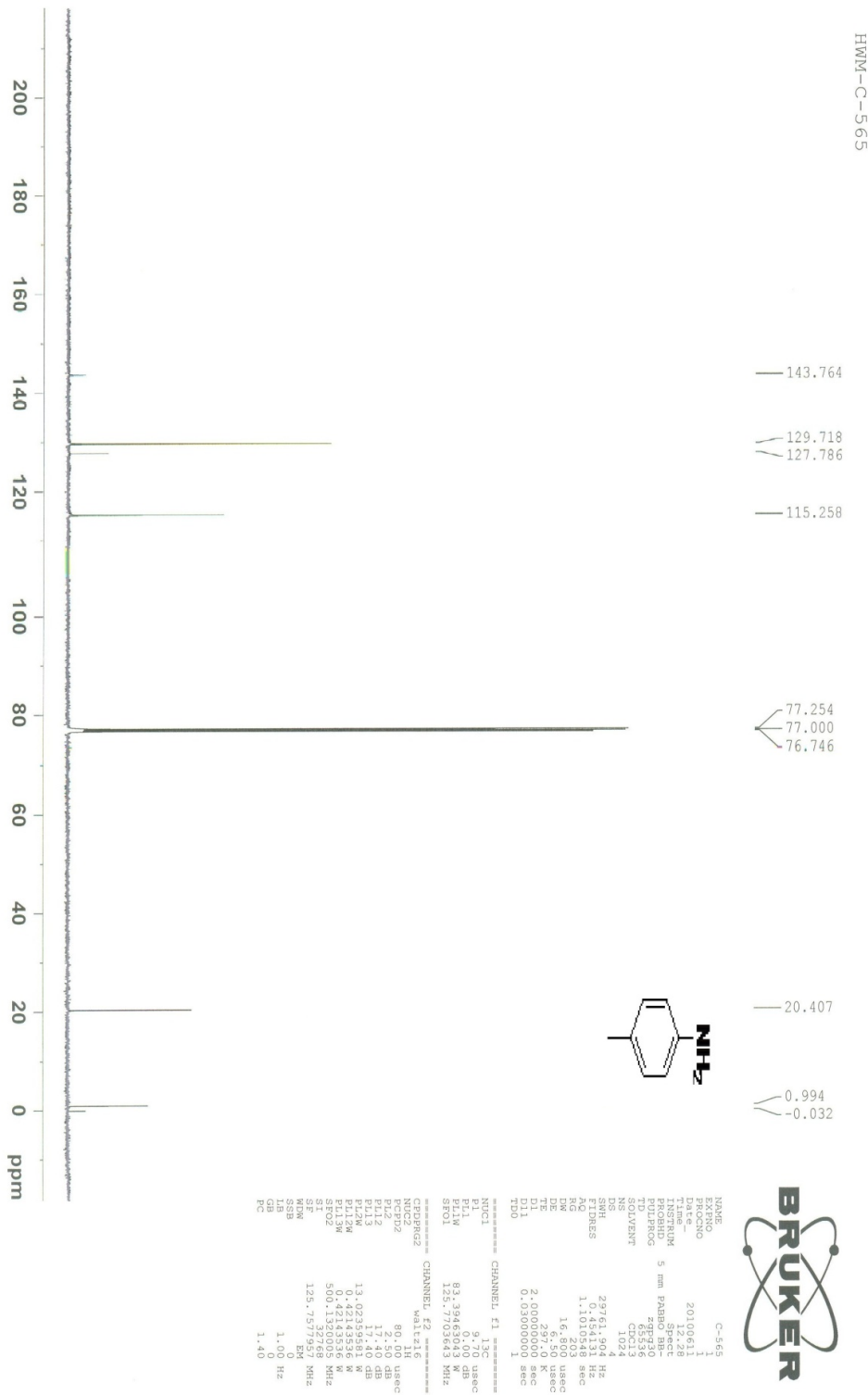


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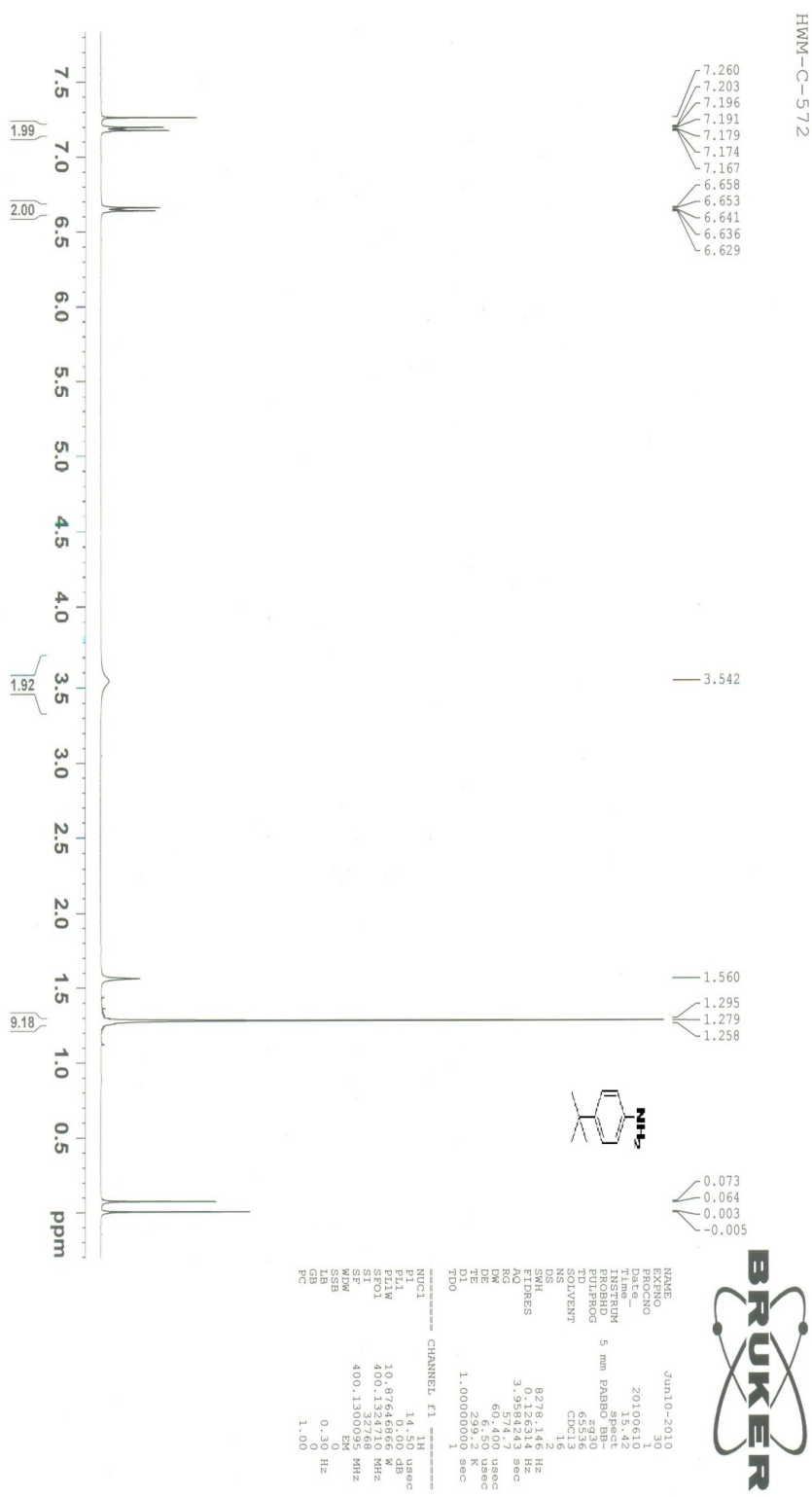


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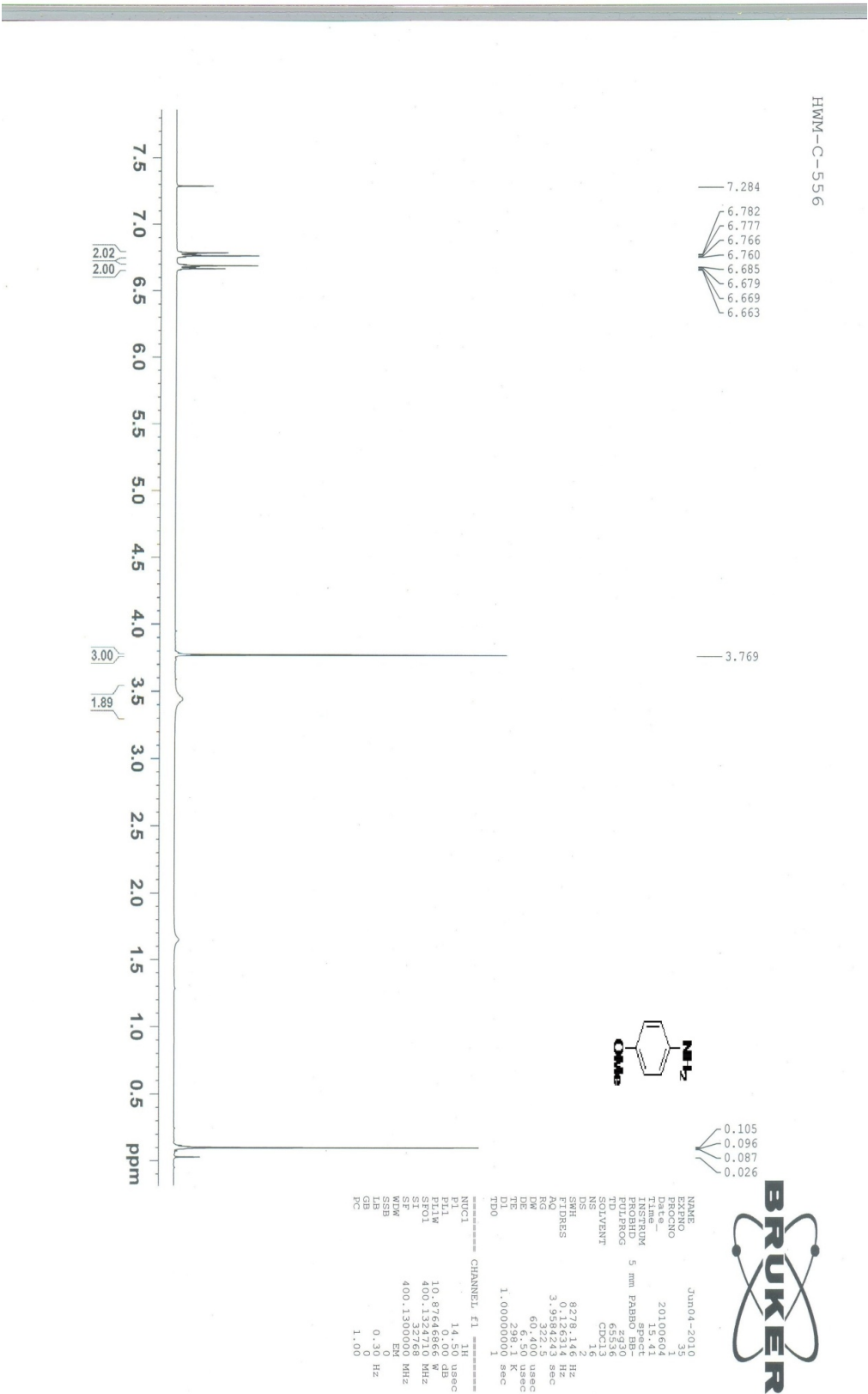


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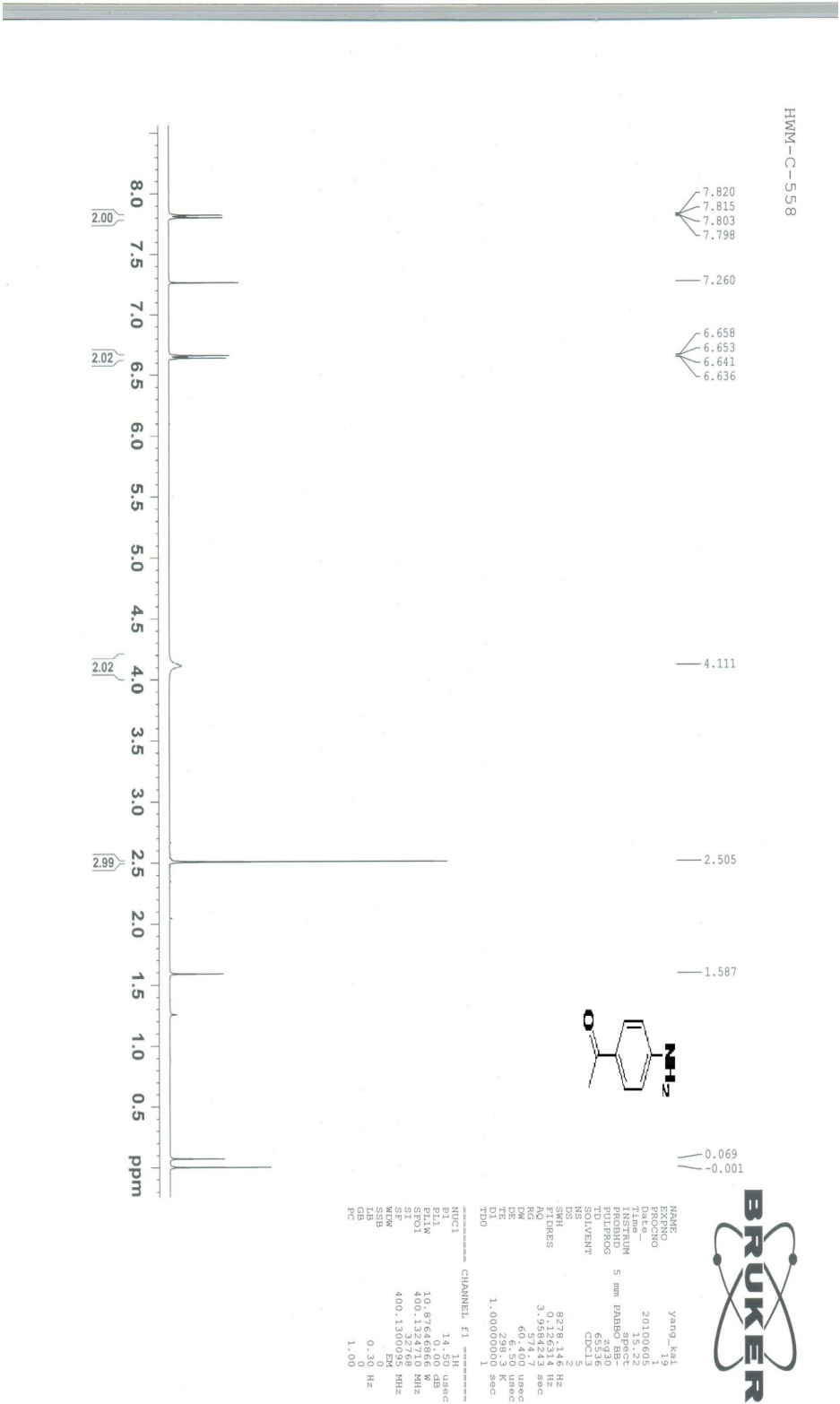


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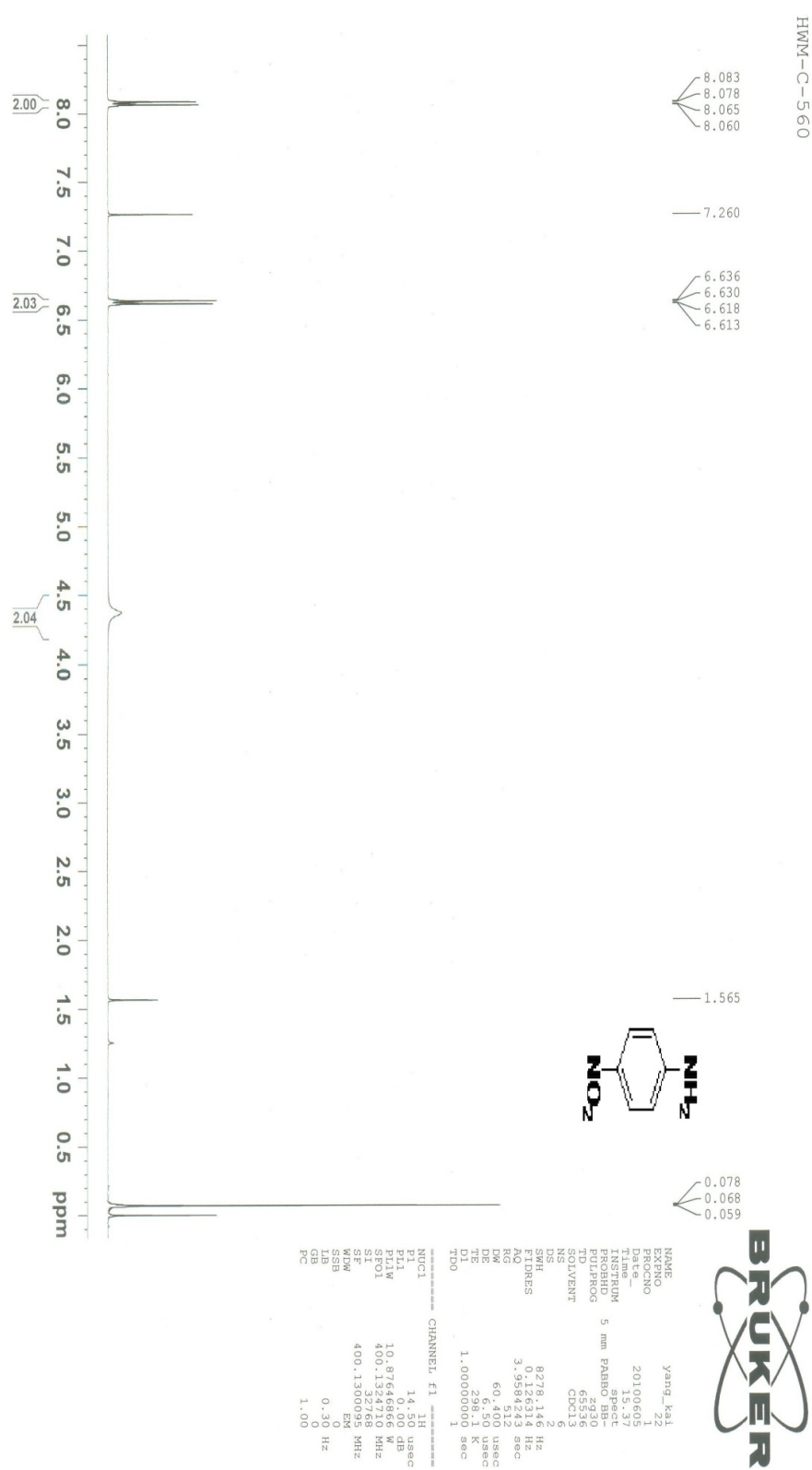


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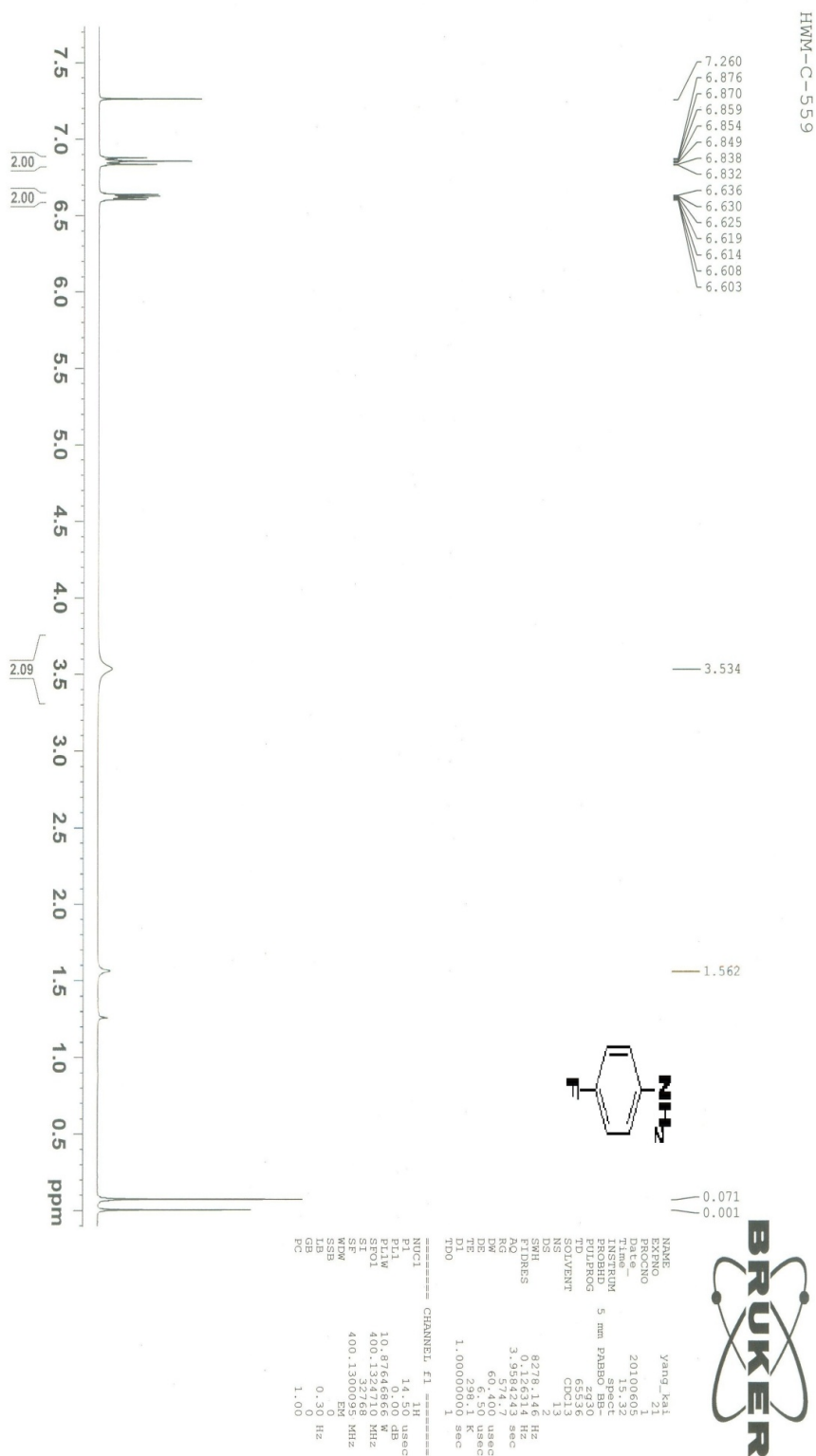


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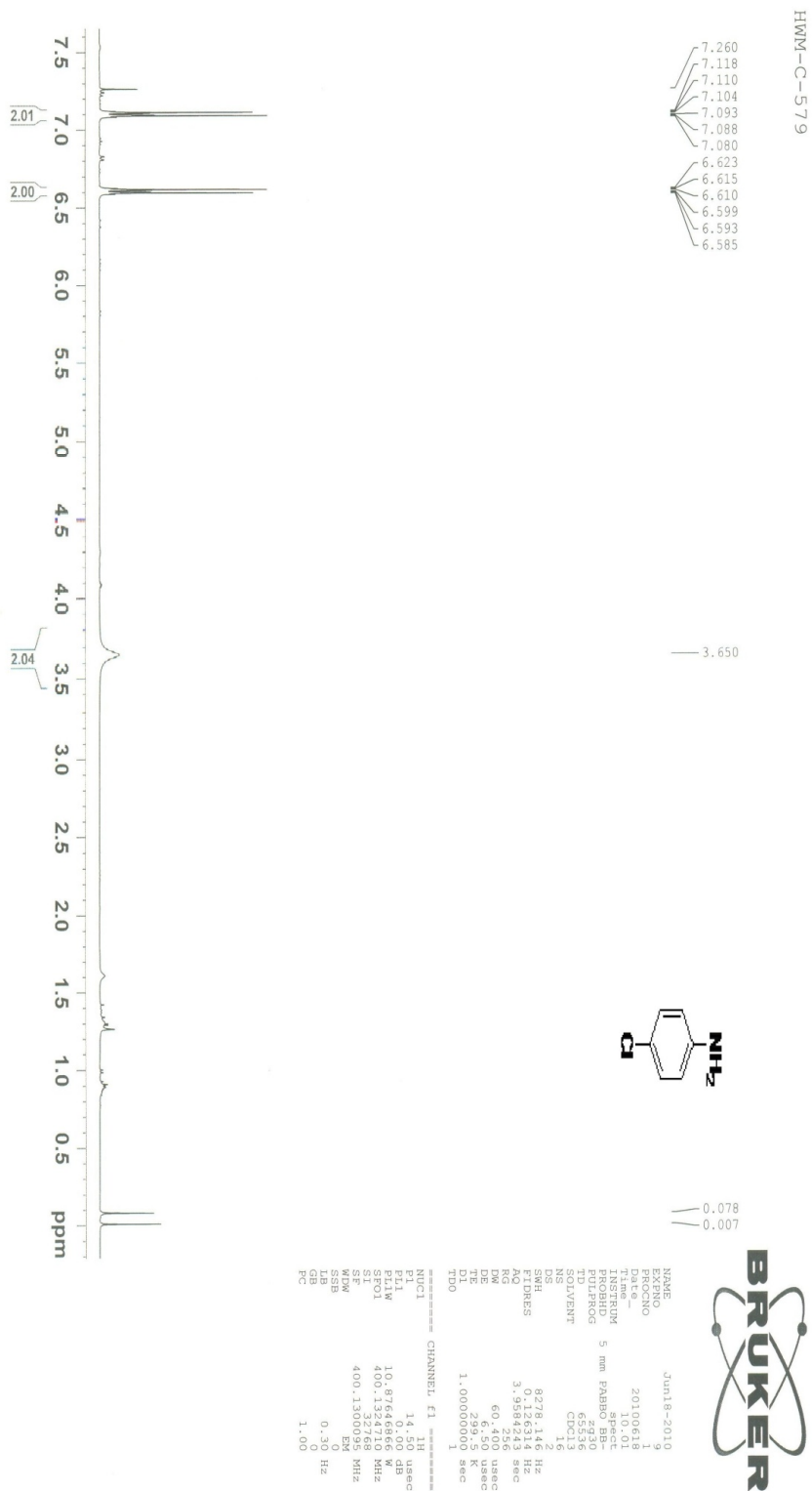
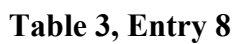


Table 3, Entry 8



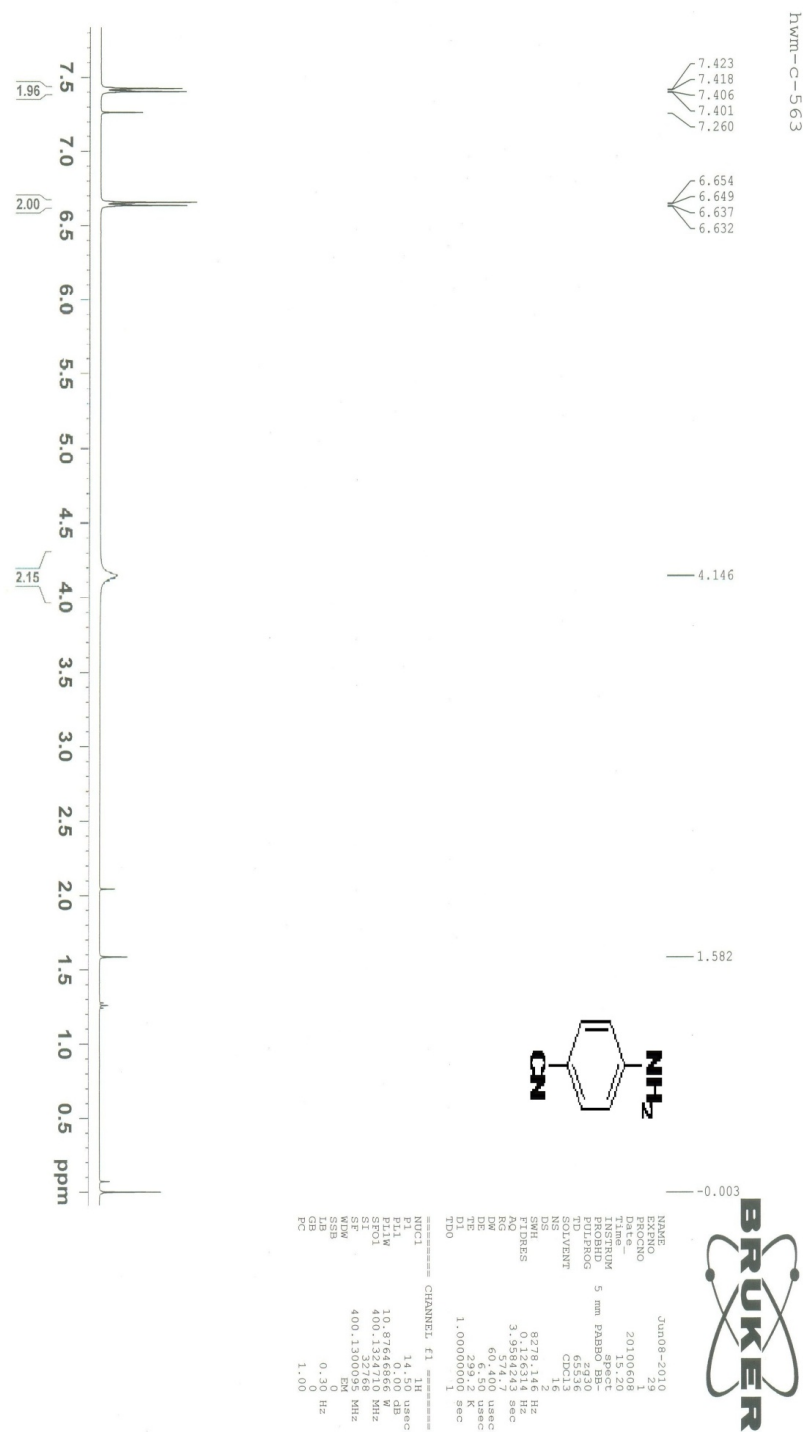


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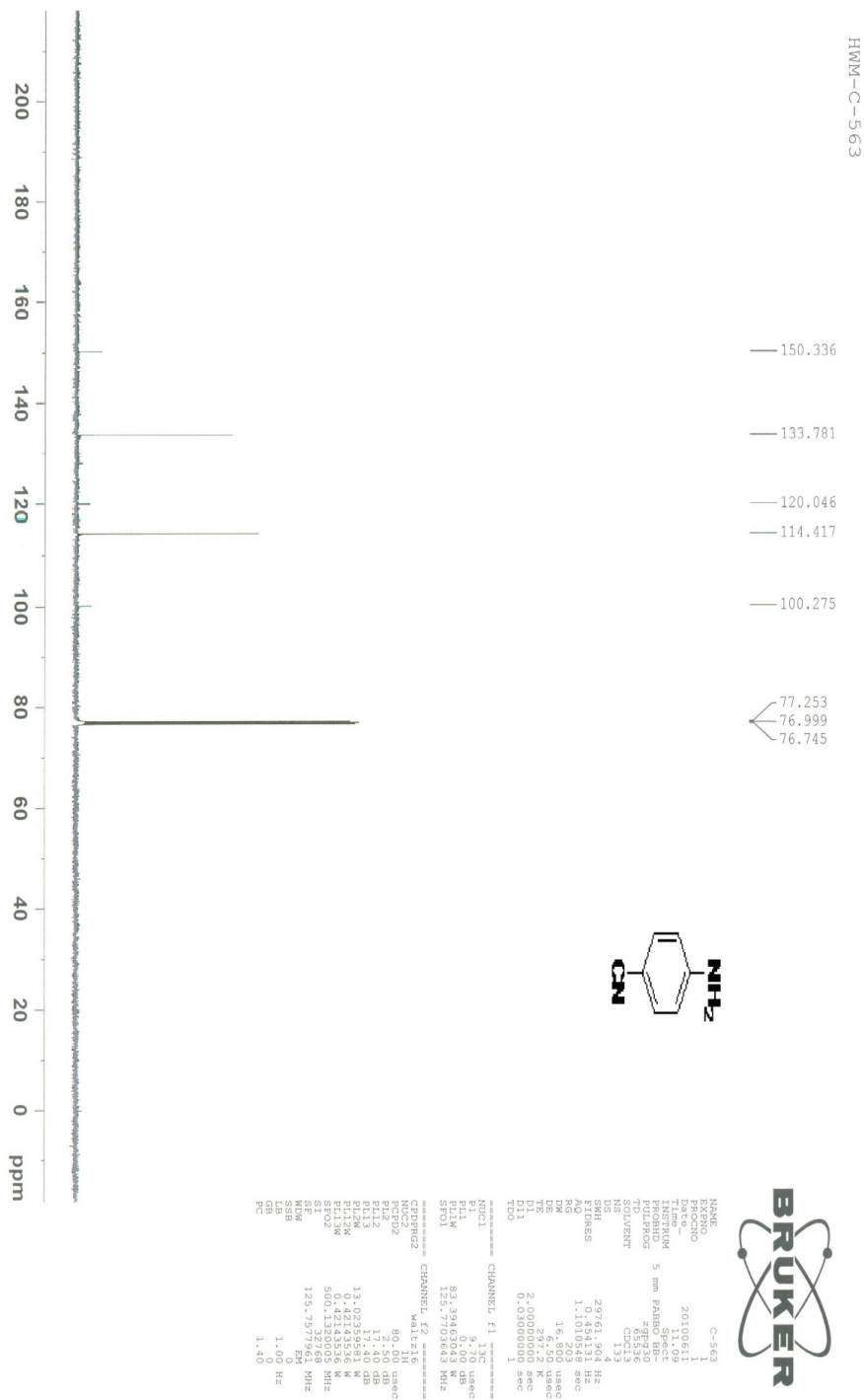


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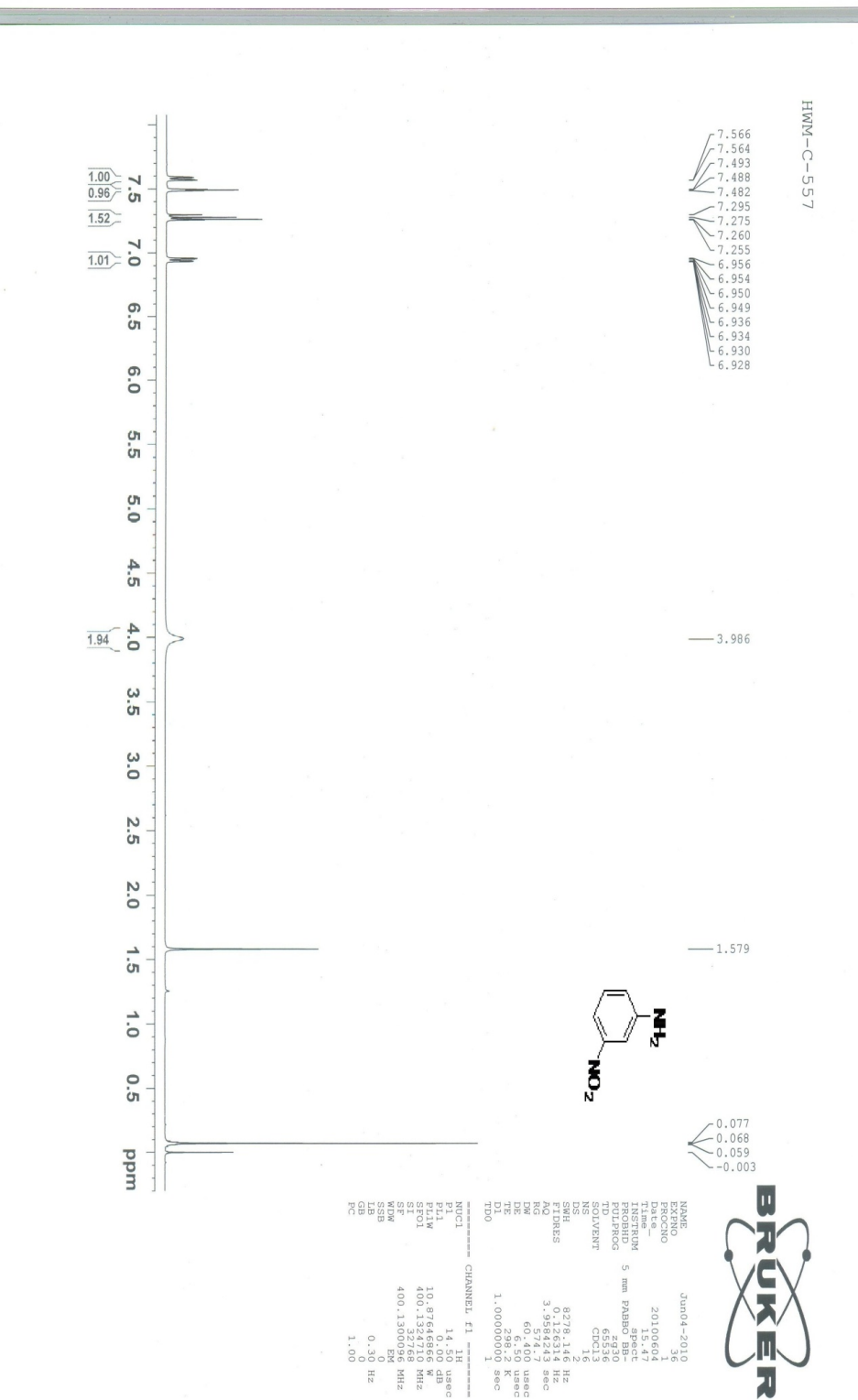


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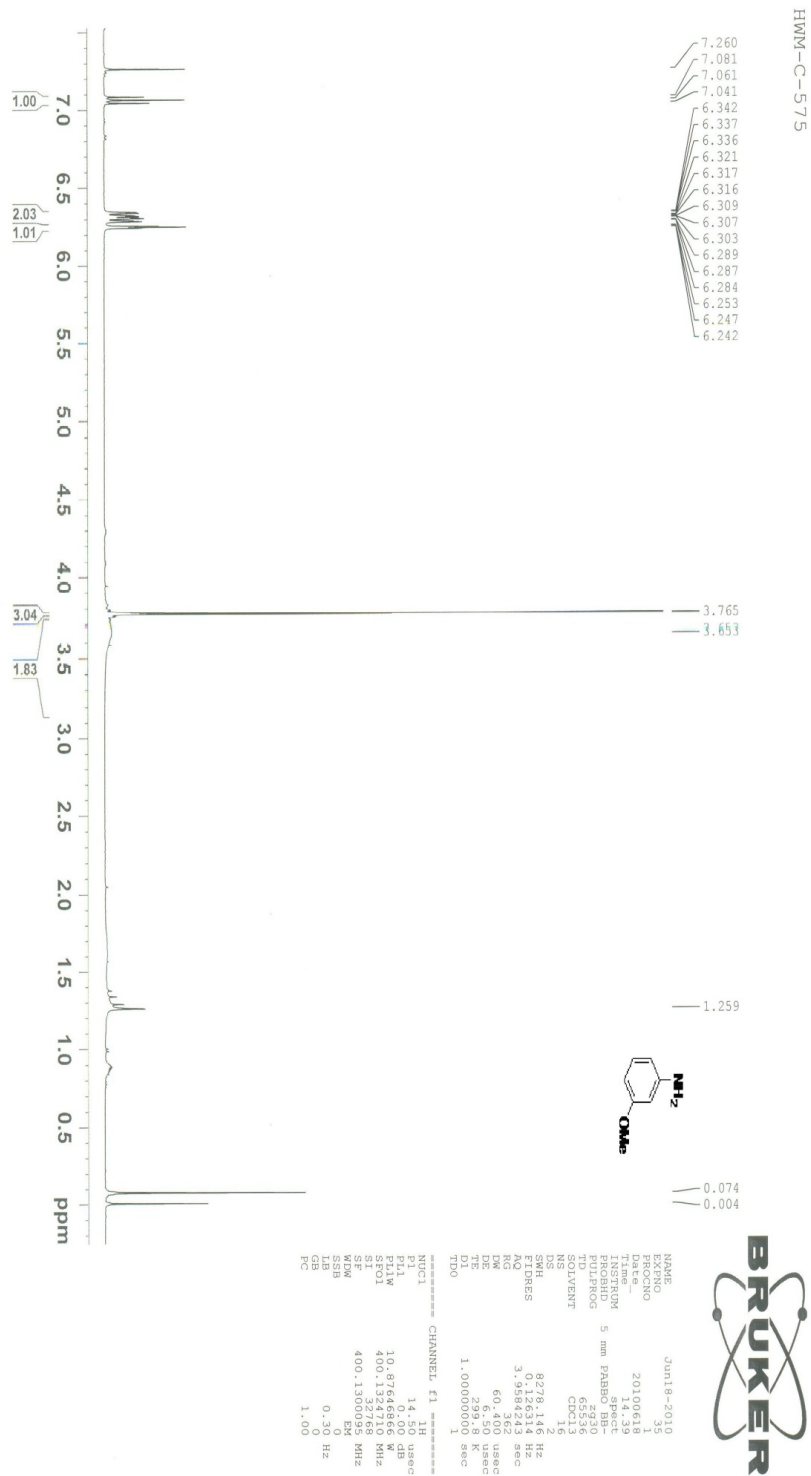


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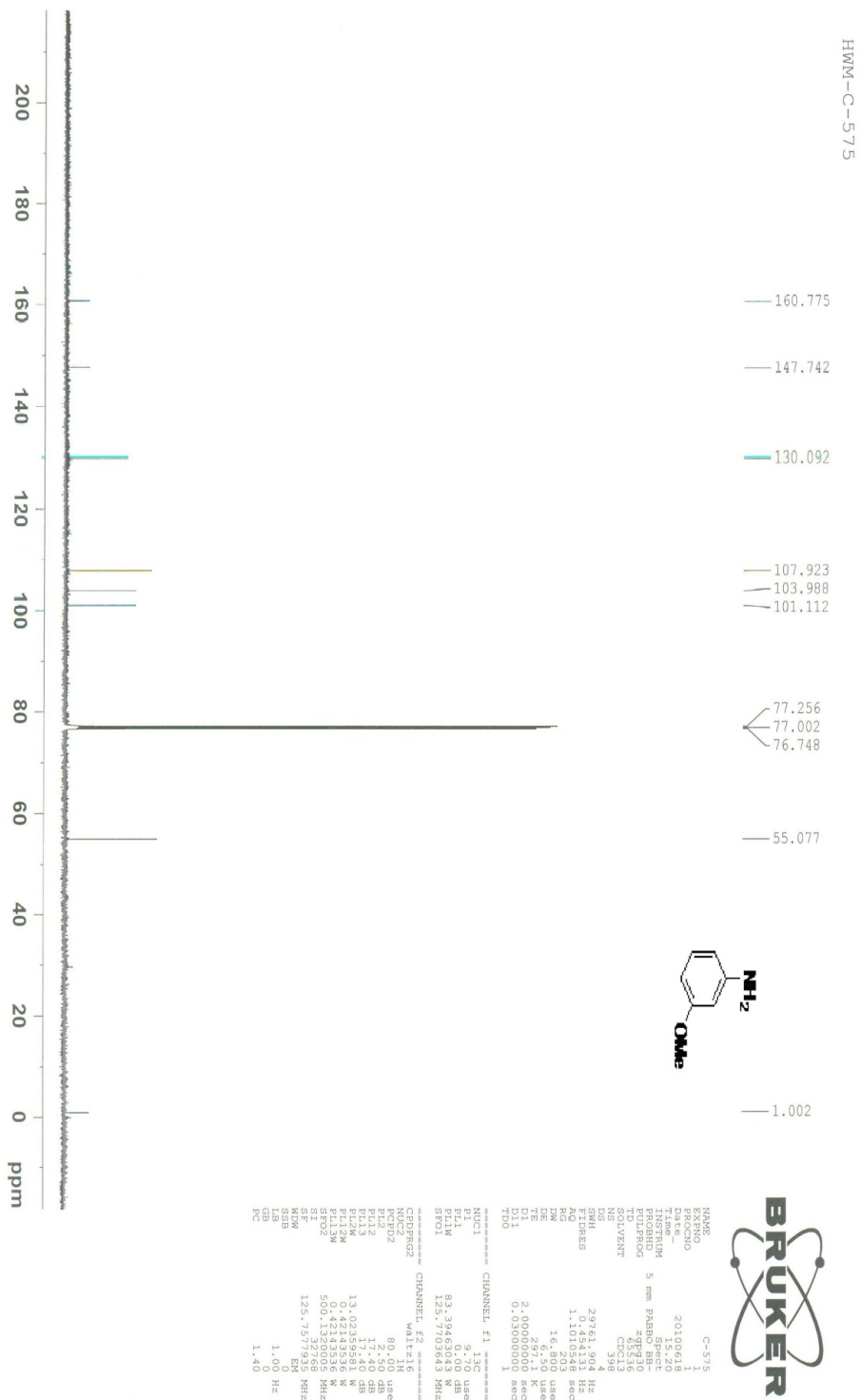


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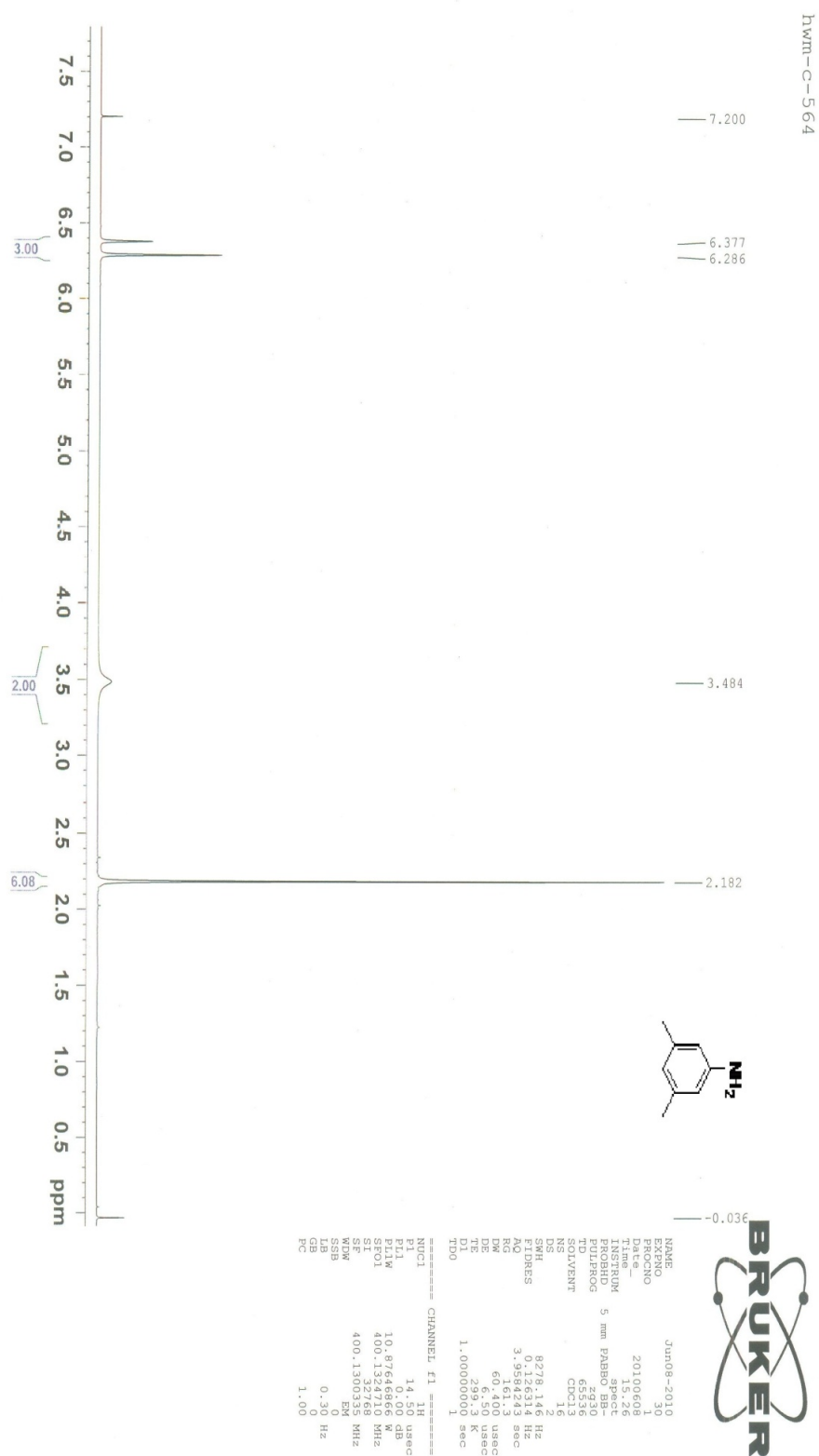


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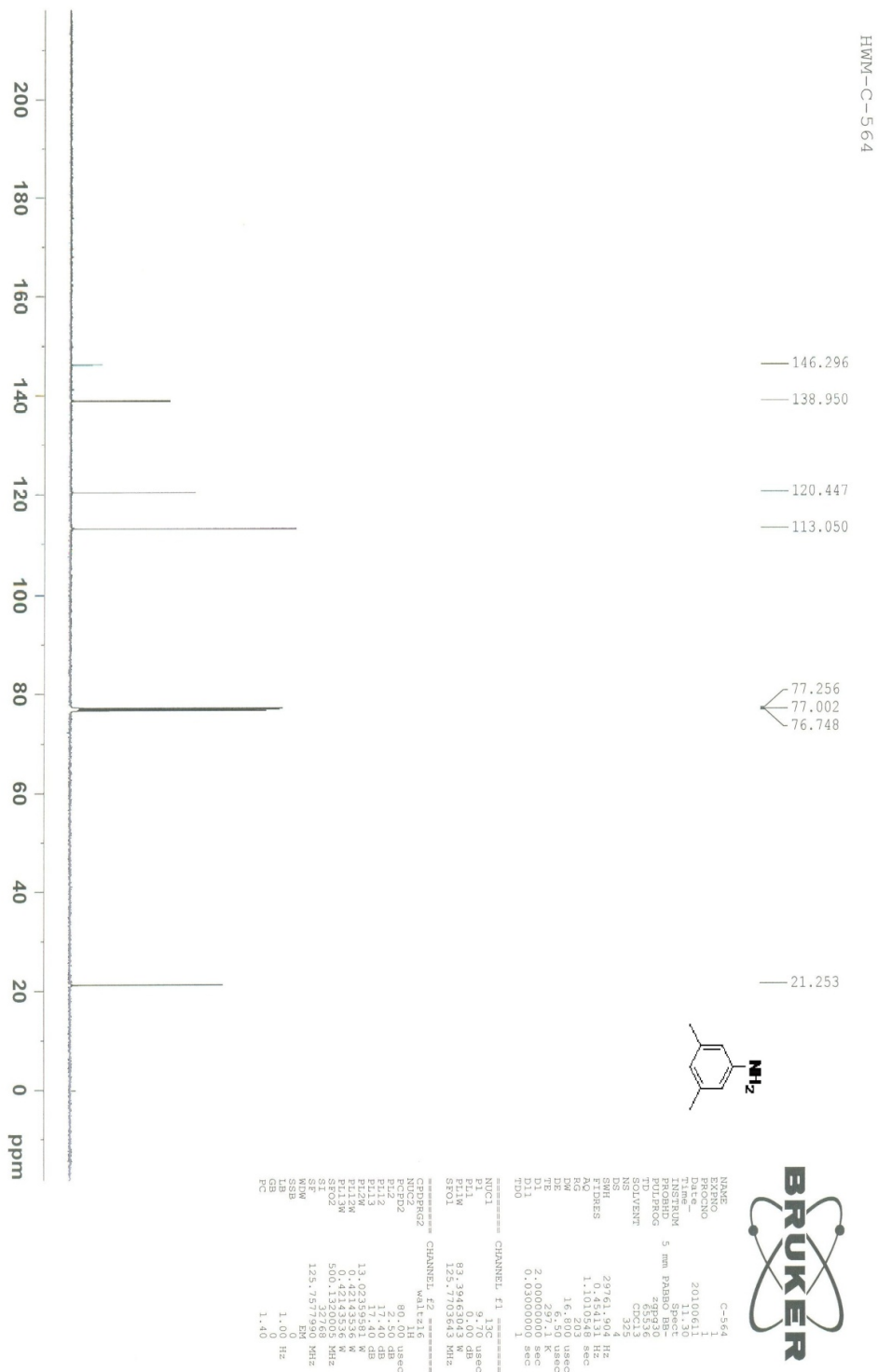


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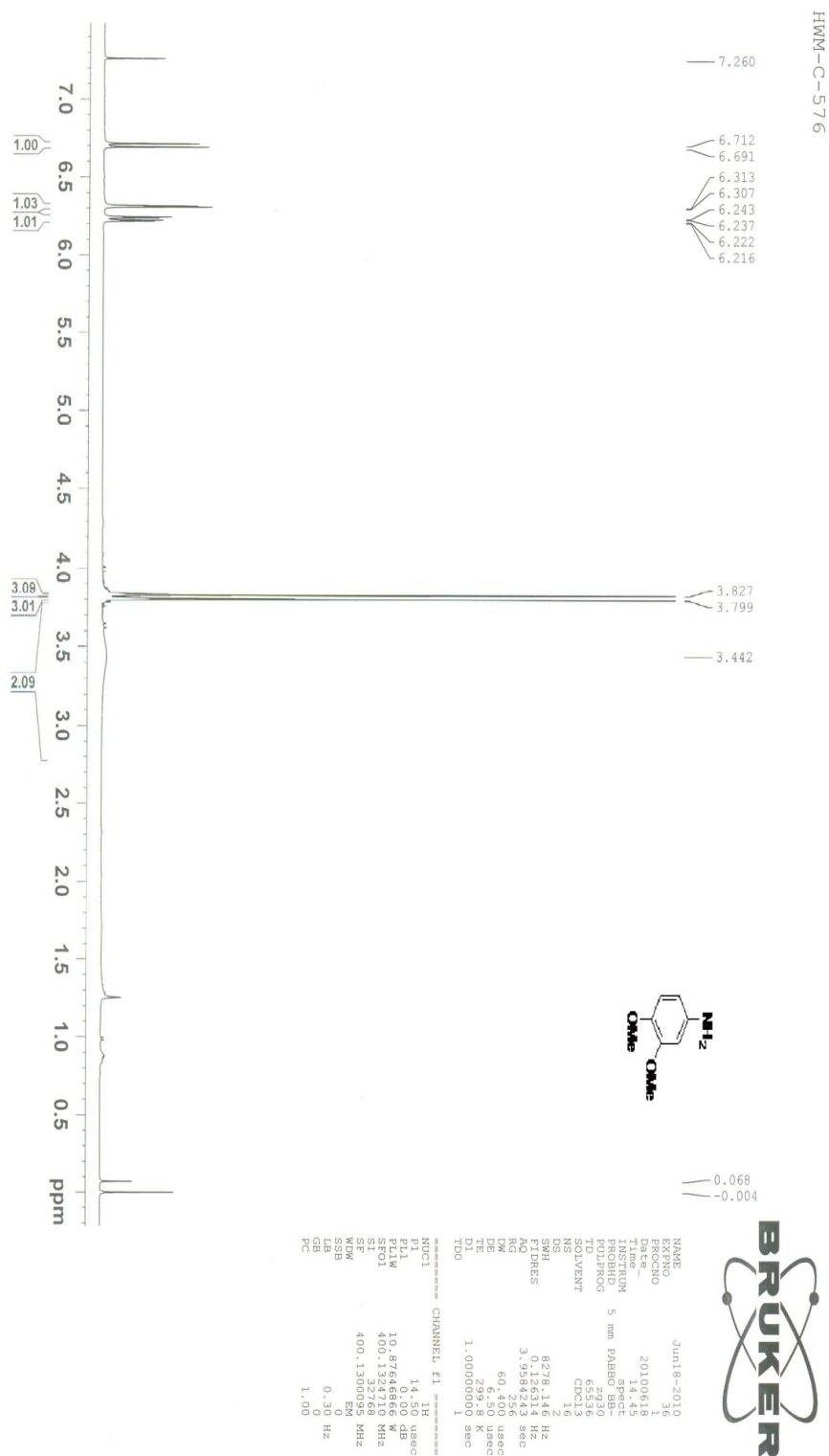


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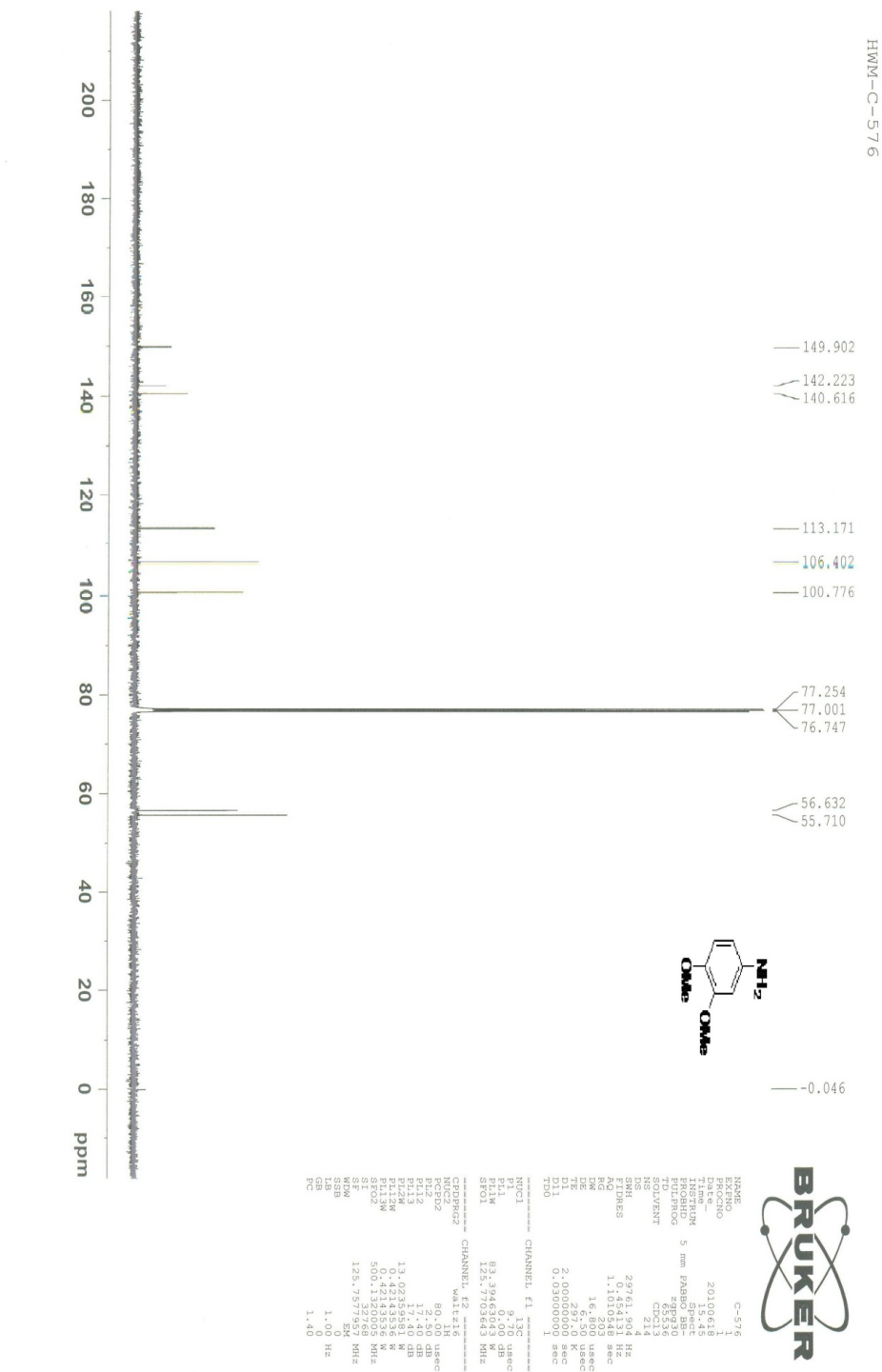


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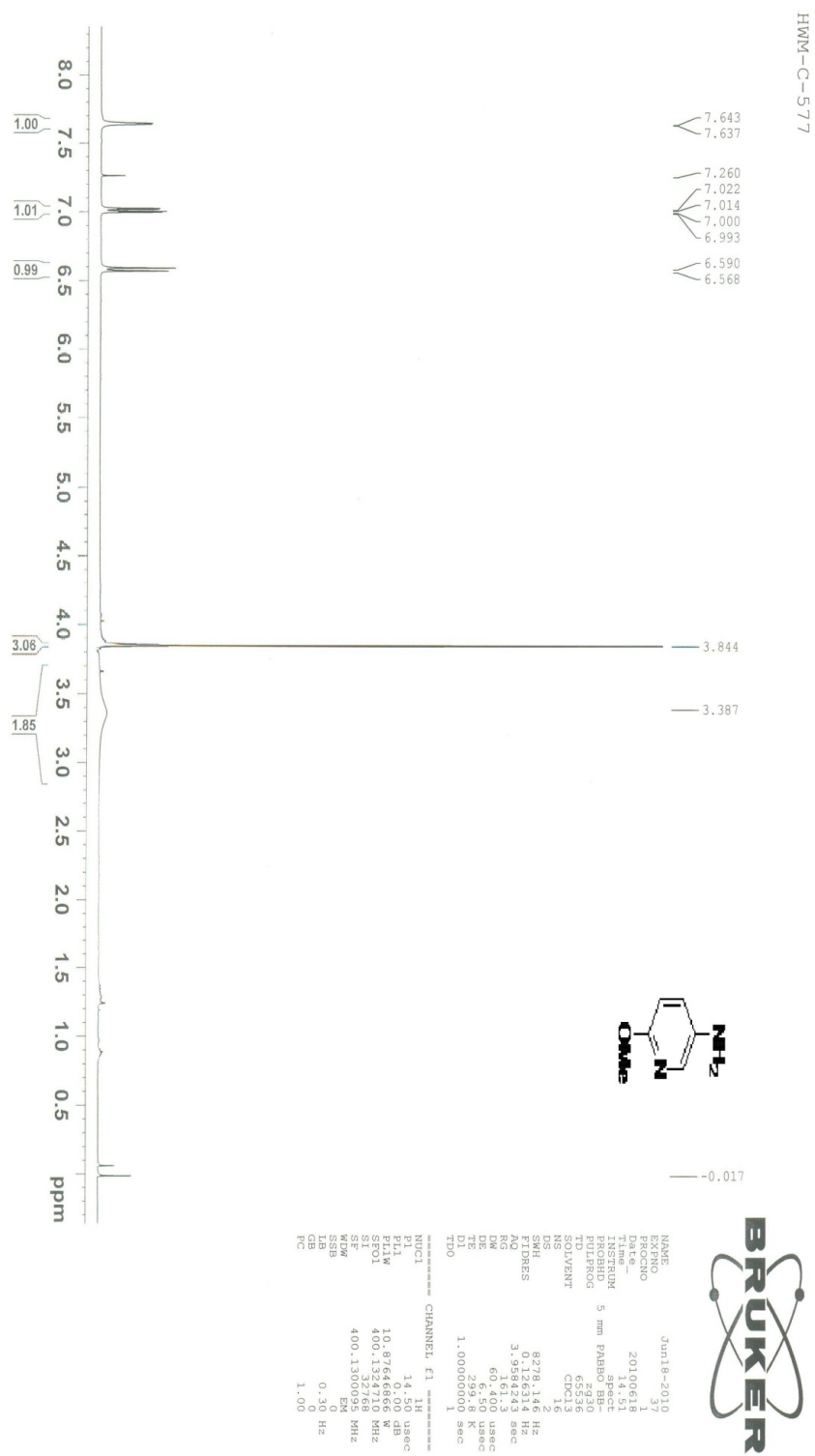


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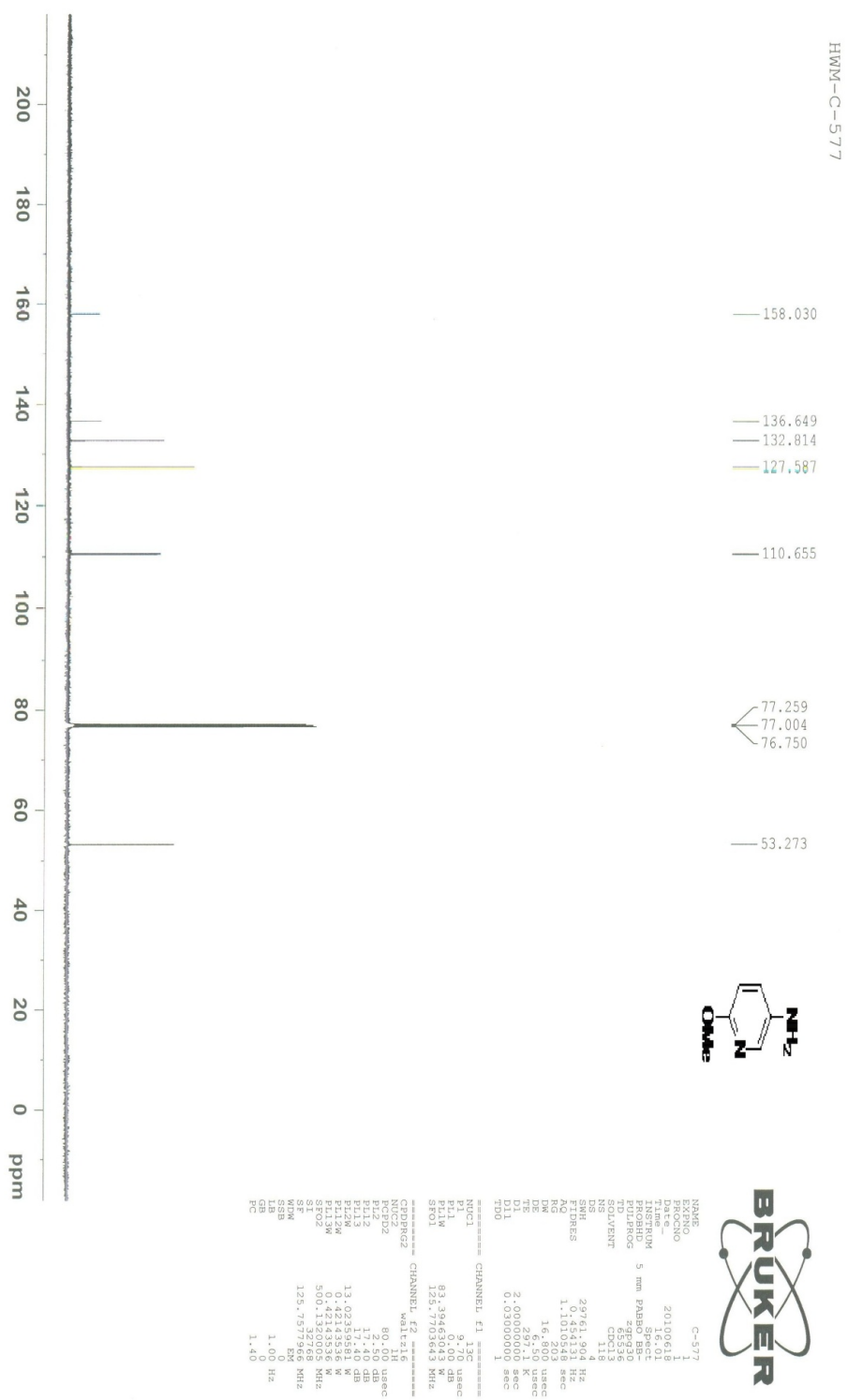


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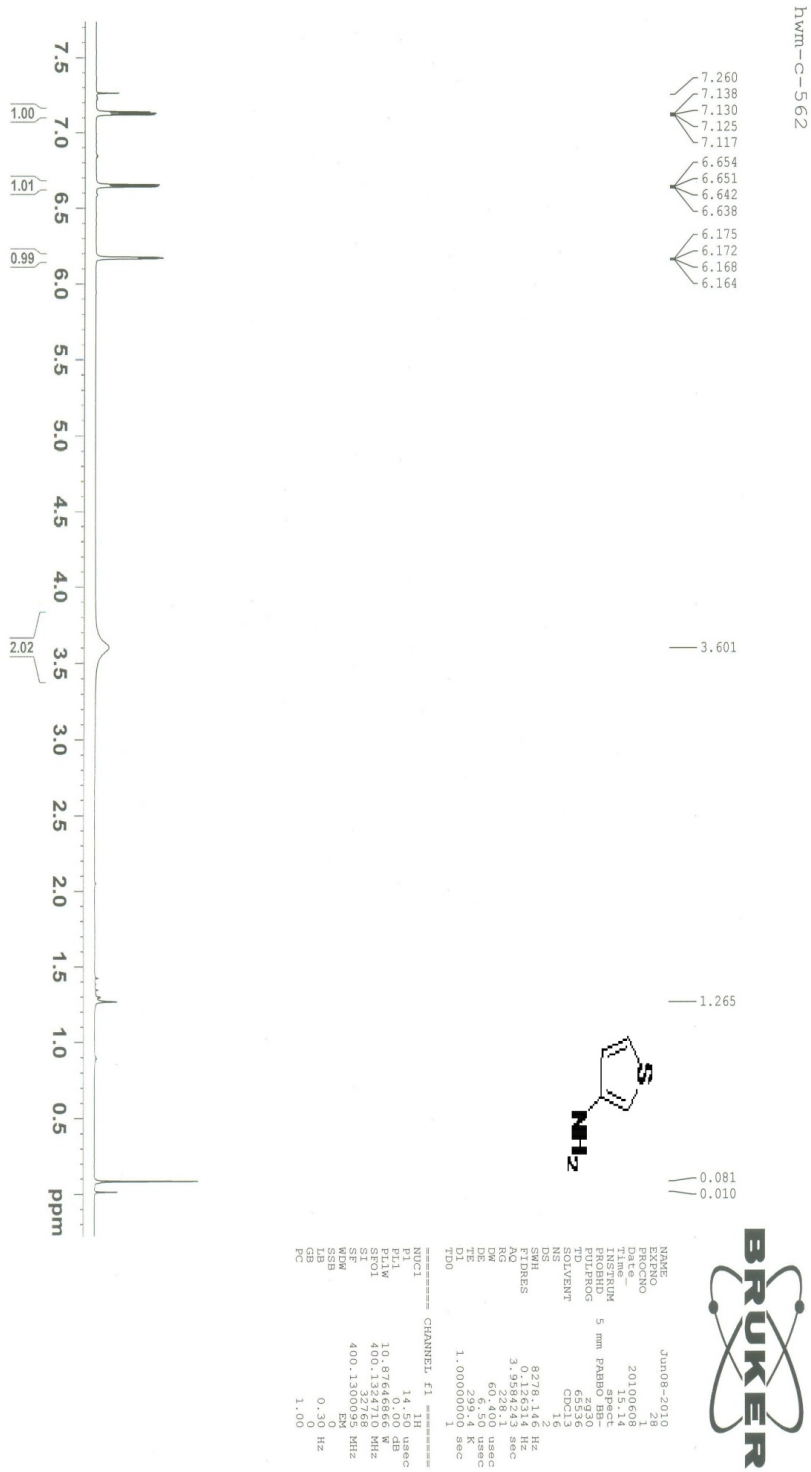


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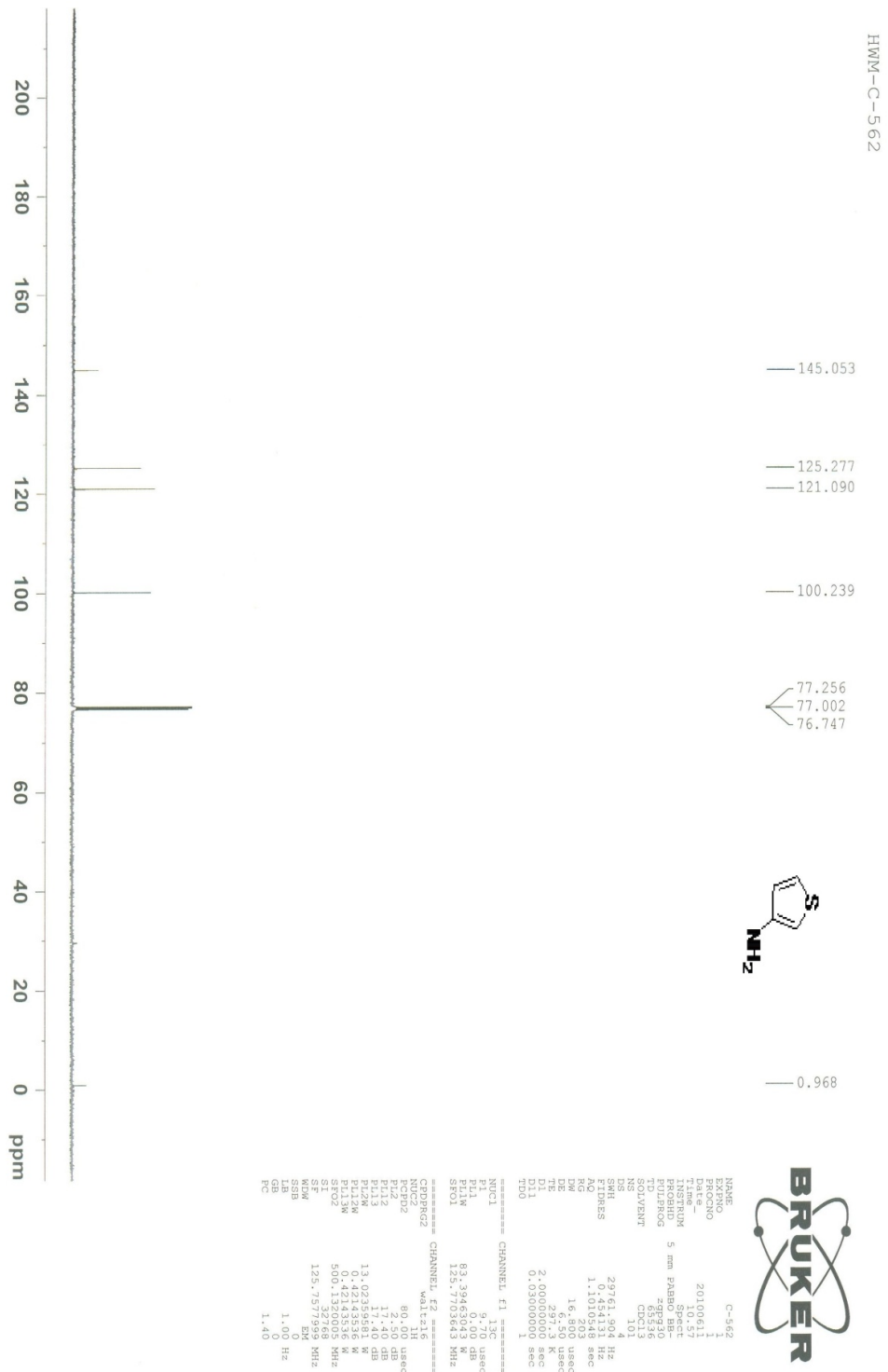


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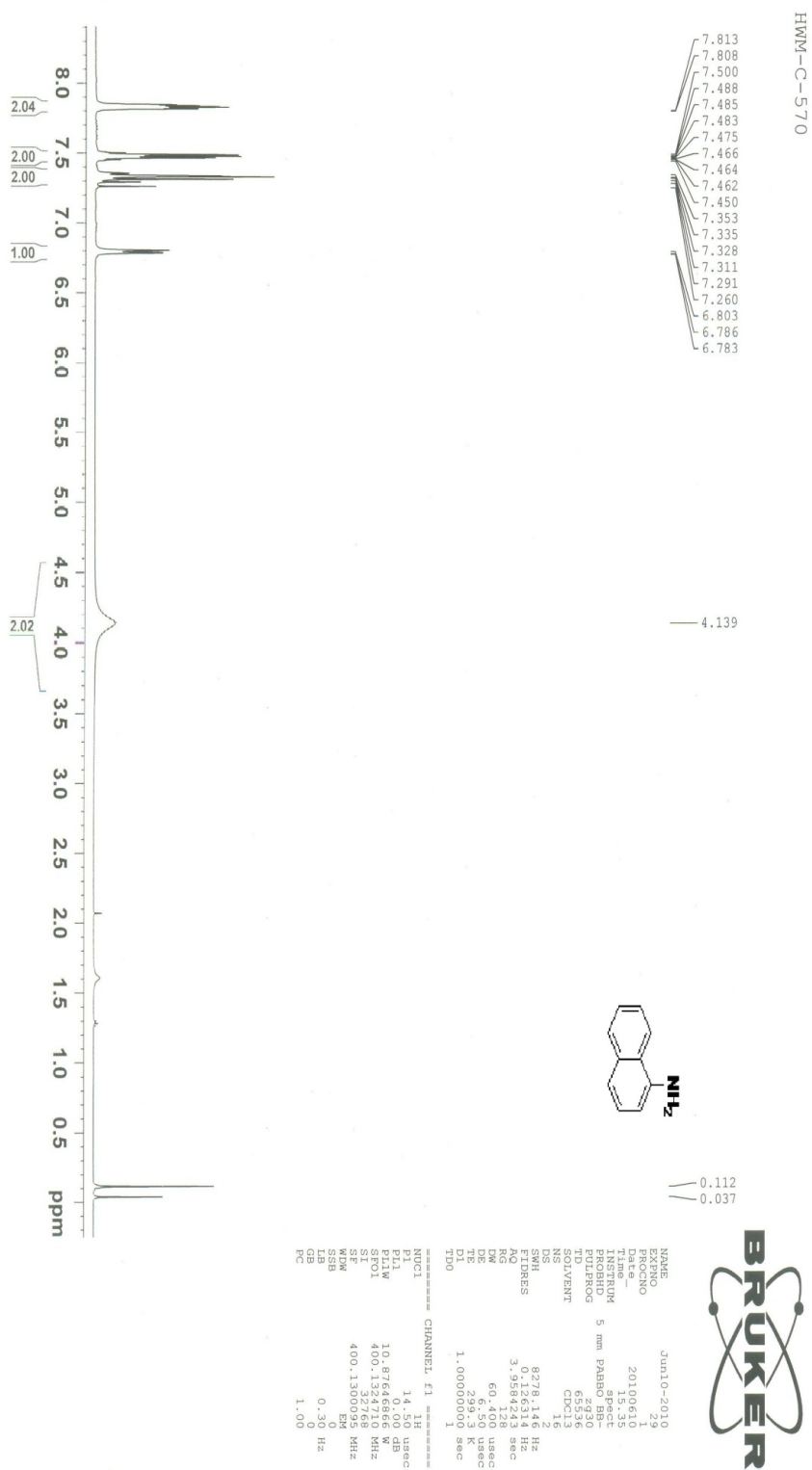


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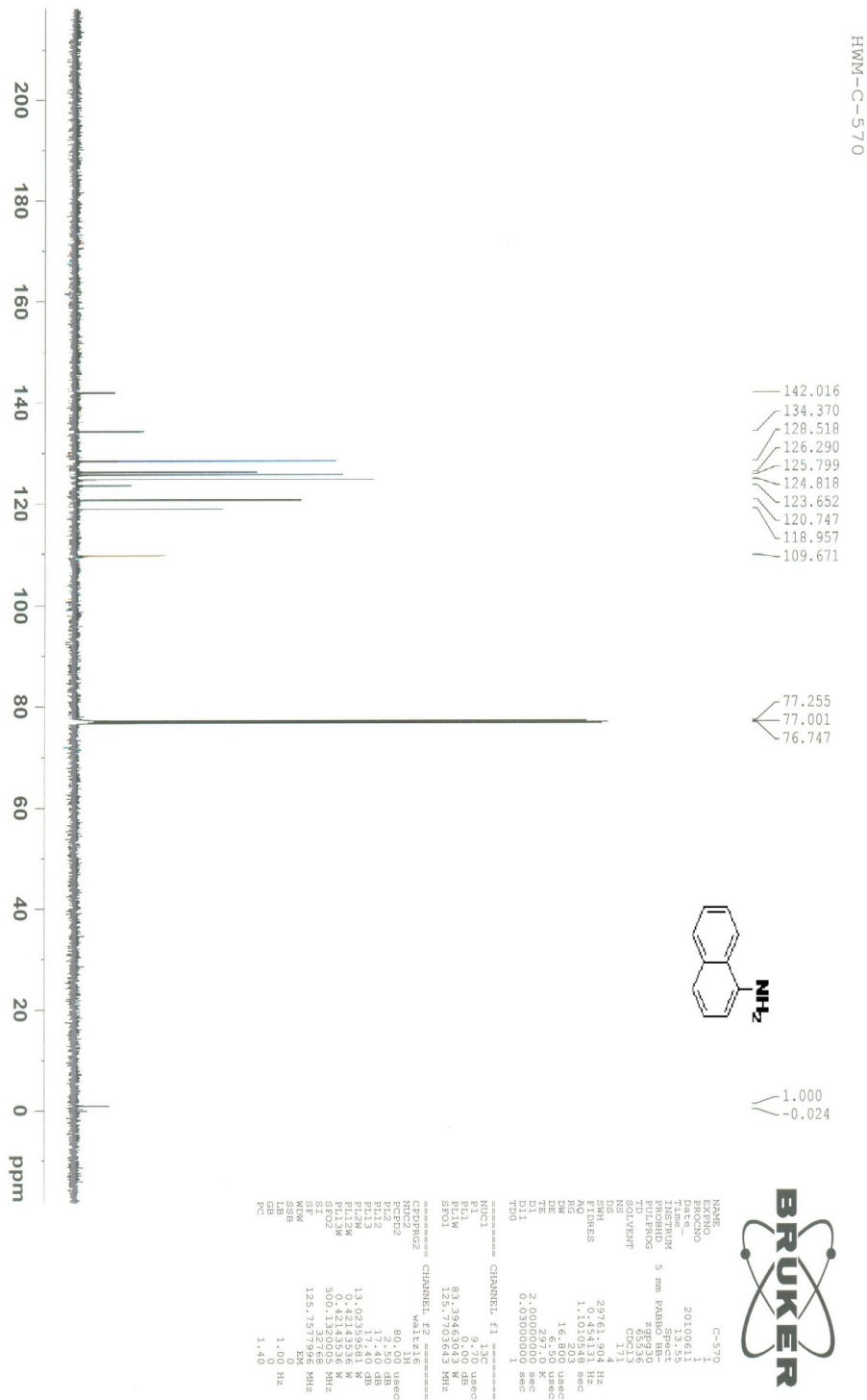


Table 3, Entry 16

## 6. Reference:

1. J. Kim, S. Chang, *Chem. Commun.* **2008**, 3052.
2. N. Xia, M. Taillefer, *Angew. Chem. Int. Ed.* **2009**, 48, 337.
3. Wu, F.; Darcel, C. *Eur. J. Org. Chem.* **2009**, 4753.
4. Wang, D.; Cai, Q.; Ding, K. *Adv. Synth. Catal.* **2009**, 351, 1722.
5. Stock, L. M.; Wasielewski, M. R. *J. Am. Chem. Soc.* **1977**, 99, 50-59.