

# **Allylic *Ethers* as Educts for Suzuki-Miyaura Couplings in Water at Room Temperature**

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## **Supporting Information**

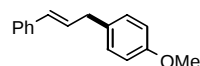
|                                |            |
|--------------------------------|------------|
| I. General Procedures          | (S2)       |
| II. Synthesis of allylic arene | (S2 – S8)  |
| III. One-pot reaction          | (S8)       |
| IV. Spectra data               | (S9 - S44) |

## General Information

PTS (Polyoxyethanyl- $\alpha$ -tocopheryl sebacate) was obtained from Zymes, LLC (PTS is also obtained from Sigma-Aldrich, catalog #698717), PdCl<sub>2</sub>(DPEphos) and PdCl<sub>2</sub>(D*t*-BPF) were purchased from Johnson Matthey. For TLC analyses precoated Kieselgel 60 F<sub>254</sub> plates (Merck, 0.25 mm thick) were used; for column chromatography Silica *Flash*® P60 (SiliCycle, 40-63  $\mu$ m) was used. Reactions were monitored using a Hewlett-Packard HP6890 gas chromatograph. <sup>1</sup>H and <sup>13</sup>C NMR spectra were obtained using a Varian UNITY INOVA 400 MHz NMR spectrometer. High resolution mass analyses were obtained using a VG70 double-focusing magnetic sector instrument (VG Analytical) for EI and a PE Sciex QStar Pulsar quadrupole/TOF instrument (API) for ESI.

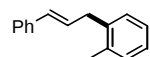
## General procedure

Allylic phenyl ether **1** (0.25 mmol), Arylboronic acid **2** (0.38 mmol), and PdCl<sub>2</sub>(DPEphos) (0.005 mmol, 3.6 mg) (or PdCl<sub>2</sub>(D*t*-BPF)) were sequentially added under air to a reaction tube equipped with a stir bar and a septum. PTS solution (0.8 mL, 2 wt %), and Et<sub>3</sub>N (0.75 mmol, 0.1 mL) were added by syringe and vigorously stirred for 5 – 22 h. After the reaction, the contents of the flask were diluted with brine and extracted with EtOAc. The solution obtained was dried over anhydrous MgSO<sub>4</sub>, filtered, and concentrated by rotary evaporation. The residue was purified by flash chromatography eluting with hexane/EtOAc to afford the product.



### 3a

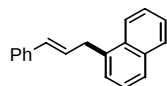
Following the general procedure, using **1a** (53 mg, 0.25 mmol), **2a** (58 mg, 0.38 mmol), PdCl<sub>2</sub>(DPEphos) (0.005 mmol, 3.6 mg), 2 wt % PTS solution (0.8 mL) and Et<sub>3</sub>N (0.75 mmol, 0.1 mL), yielded the allylic arene **3a** (55 mg, 99%), <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ : 3.47 (d, *J* = 6.5 Hz, 2H), 3.77 (s, 3H), 6.32 (ddt, *J* = 1.2, 6.7, 15.9 Hz, 1H), 6.42 (d, *J* = 15.9 Hz, 1H), 6.84 (d, *J* = 8.7 Hz, 2H), 7.12 (d, *J* = 8.3 Hz, 2H), 7.16-7.20 (m, 1H), 7.27 (t, *J* = 7.6 Hz, 2H), 7.34 (d, *J* = 7.6 Hz, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$ : 38.41, 55.22, 113.84, 126.05, 127.00, 128.44, 129.55, 129.61, 130.66, 132.10, 137.46, 157.99; HREIMS calcd for C<sub>16</sub>H<sub>16</sub>O(M<sup>+</sup>): 224.1201; found 224.1209.



### 3b

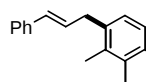
Following the general procedure, using **1a** (53 mg, 0.25 mmol), **2b** (51 mg, 0.38 mmol), PdCl<sub>2</sub>(DPEphos) (0.005 mmol, 3.6 mg), 2 wt % PTS solution (0.8 mL) and Et<sub>3</sub>N (0.75

mmol, 0.1 mL), yielded the allylic arene **3b** (51 mg, 99%),  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 2.32 (s, 3H), 3.51 (d,  $J$  = 4.8 Hz, 2H), 6.32-6.39 (m, 2H), 7.14-7.19 (m, 5H), 7.25-7.34 (m, 4H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 19.65, 37.07, 126.26, 126.30, 126.61, 127.24, 128.68, 128.72, 129.41, 130.41, 131.07, 136.61, 137.70, 138.42; HREIMS calcd for  $\text{C}_{16}\text{H}_{16}(\text{M}^+)$ : 208.1252; found 208.1259.



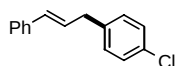
### 3c

Following the general procedure, using **1a** (53 mg, 0.25 mmol), **2c** (64 mg, 0.38 mmol),  $\text{PdCl}_2(\text{DPEphos})$  (0.005 mmol, 3.6 mg), 2 wt % PTS solution (0.8 mL) and  $\text{Et}_3\text{N}$  (0.75 mmol, 0.1 mL), yielded the allylic arene **3c** (53 mg, 87%),  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 3.99 (d,  $J$  = 4.8 Hz, 2H), 6.44-6.55 (m, 2H), 7.18 (t,  $J$  = 7.6 Hz, 1H), 7.39-7.53 (m, 8H), 7.76 (d,  $J$  = 8.2 Hz, 1H), 7.87 (d,  $J$  = 8.5 Hz, 1H), 8.10 (dd,  $J$  = 1.5, 8.2 Hz, 1H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 36.64, 124.24, 125.81, 125.87, 126.17, 126.32, 126.61, 127.31, 128.70, 128.93, 129.07, 131.51, 132.24, 134.08, 136.46, 137.65; HREIMS calcd for  $\text{C}_{19}\text{H}_{16}(\text{M}^+)$ : 244.1252; found 244.1246.



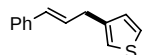
### 3d

Following the general procedure, using **1a** (53 mg, 0.25 mmol), **2d** (56 mg, 0.38 mmol),  $\text{PdCl}_2(\text{DPEphos})$  (0.005 mmol, 3.6 mg), 2 wt % PTS solution (0.8 mL) and  $\text{Et}_3\text{N}$  (0.75 mmol, 0.1 mL), yielded the allylic arene **3d** (55 mg, 99%),  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 2.23 (s, 3H), 2.30 (s, 3H), 3.56 (d,  $J$  = 3.6 Hz, 2H), 6.30-6.46 (m, 2H), 7.06 (brs, 3H), 7.18 (t,  $J$  = 7.2 Hz, 1H), 7.27 (t,  $J$  = 7.9 Hz, 2H), 7.33 (d,  $J$  = 7.2 Hz, 2H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 15.14, 20.67, 37.49, 125.49, 126.01, 126.95, 127.21, 128.13, 128.42, 128.92, 130.62, 134.96, 136.90, 137.54, 138.07; HREIMS calcd for  $\text{C}_{17}\text{H}_{18}(\text{M}^+)$ : 222.1408; found 222.1409.



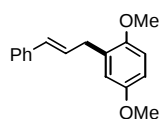
### 3e

Following the general procedure, using **1a** (53 mg, 0.25 mmol), **2e** (58 mg, 0.38 mmol),  $\text{PdCl}_2(\text{Dt-BPF})$  (0.015 mmol, 9.8 mg), 2 wt % PTS solution (0.8 mL) and  $\text{Et}_3\text{N}$  (0.75 mmol, 0.1 mL), yielded the allylic arene **3e** (42 mg, 74%),  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 3.49 (d,  $J$  = 6.7 Hz, 2H), 6.29 (dt,  $J$  = 6.8, 15.8 Hz, 1H), 6.42 (d,  $J$  = 15.8 Hz, 1H), 7.19 (d,  $J$  = 8.4 Hz, 2H), 7.26 (d,  $J$  = 7.9 Hz, 1H), 7.30 (d,  $J$  = 8.2 Hz, 2H), 7.32 (t,  $J$  = 7.3 Hz, 2H), 7.38 (d,  $J$  = 7.9 Hz, 2H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 38.58, 126.10, 127.23, 128.51, 129.98, 131.43, 131.90, 137.19, 138.53; HREIMS calcd for  $\text{C}_{15}\text{H}_{13}\text{Cl}(\text{M}^+)$ : 228.0706; found 228.0700.



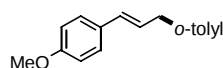
### 3f

Following the general procedure, using **1a** (53 mg, 0.25 mmol), **2f** (48 mg, 0.38 mmol), PdCl<sub>2</sub>(Dt-BPF) (0.015 mmol, 9.8 mg), 2 wt % PTS solution (0.8 mL) and Et<sub>3</sub>N (0.75 mmol, 0.1 mL), yielded the allylic arene **3f** (48 mg, 96%), <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ: 3.54 (d, *J* = 6.6 Hz, 2H), 6.35 (dt, *J* = 6.6, 15.8 Hz, 1H), 6.45 (d, *J* = 15.8 Hz, 1H), 7.02 (dd, *J* = 1.2, 4.9 Hz, 1H), 7.04-7.05 (m, 1H), 7.23-7.32 (m, 2H), 7.34 (d, *J* = 7.3 Hz, 2H), 7.40 (dd, *J* = 1.1, 8.3 Hz, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ: 33.79, 120.82, 125.54, 126.08, 127.11, 128.30, 128.47, 130.99, 137.35, 140.46; HREIMS calcd for C<sub>13</sub>H<sub>12</sub>S(M<sup>+</sup>): 200.0659; found 200.0663.



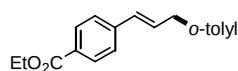
### 3g

Following the general procedure, using **1a** (53 mg, 0.25 mmol), **2g** (68 mg, 0.38 mmol), PdCl<sub>2</sub>(DPEphos) (0.015 mmol, 11 mg), 2 wt % PTS solution (0.8 mL) and Et<sub>3</sub>N (0.75 mmol, 0.1 mL), yielded the allylic arene **3g** (57 mg, 90%), *contaminated with p-dimethoxybenzene*. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ: 3.73 (s, 3H), 3.79 (s, 3H), 6.35 (dt, *J* = 6.5, 15.9 Hz, 1H), 6.43 (d, *J* = 15.9 Hz, 1H), 6.70-6.77 (m, 3H), 7.21 (t, *J* = 7.0 Hz, 1H), 7.26 (t, *J* = 8.1 Hz, 2H), 7.35 (d, *J* = 8.1 Hz, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ: 33.46, 55.63, 56.02, 111.22, 111.31, 116.22, 126.03, 126.88, 128.38, 128.56, 129.86, 130.83, 137.62, 151.52, 153.52; HREIMS calcd for C<sub>17</sub>H<sub>18</sub>O<sub>2</sub>(M<sup>+</sup>): 254.1306; found 254.1299.



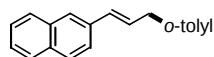
### 3h

Following the general procedure, using **1b** (60 mg, 0.25 mmol), **2b** (51 mg, 0.38 mmol), PdCl<sub>2</sub>(DPEphos) (0.015 mmol, 11 mg), 2 wt % PTS solution (0.8 mL) and Et<sub>3</sub>N (0.75 mmol, 0.1 mL), yielded the allylic arene **3h** (49 mg, 82%), <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ: 2.34 (s, 3H), 3.52 (dd, *J* = 1.1, 6.4 Hz, 2H), 3.80 (s, 3H), 6.20 (dt, *J* = 6.5, 15.8 Hz, 1H), 6.33 (d, *J* = 15.8 Hz, 1H), 6.84 (d, *J* = 8.8 Hz, 2H), 7.14-7.22 (m, 4H), 7.29 (d, *J* = 8.7 Hz, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ: 19.42, 36.81, 55.25, 113.86, 126.03, 126.30, 127.12, 129.15, 130.15, 130.20, 130.34, 136.38, 138.47, 158.75; HREIMS calcd for C<sub>17</sub>H<sub>18</sub>O(M<sup>+</sup>): 238.1357; found 238.1360.



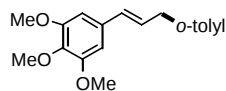
### 3i

Following the general procedure, using **1c** (70 mg, 0.25 mmol), **2b** (51 mg, 0.38 mmol), PdCl<sub>2</sub>(DPEphos) (0.005 mmol, 3.6 mg), 2 wt % PTS solution (0.8 mL) and Et<sub>3</sub>N (0.75 mmol, 0.1 mL), yielded the allylic arene **3i** (60 mg, 85%), <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ: 1.38 (t, *J* = 7.2 Hz, 3H), 2.33 (s, 3H), 3.56 (dd, *J* = 1.1, 6.2 Hz, 2H), 4.36 (q, *J* = 7.2 Hz, 2H), 3.80 (s, 3H), 6.38 (d, *J* = 15.9 Hz, 1H), 6.48 (dt, *J* = 6.2, 15.9 Hz, 1H), 7.15-7.18 (m, 4H), 7.38 (d, *J* = 8.3 Hz, 2H), 7.95 (d, *J* = 8.3 Hz, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ: 14.29, 19.40, 36.90, 60.80, 125.82, 126.13, 126.54, 128.78, 129.24, 129.78, 130.02, 130.26, 131.38, 136.35, 137.62, 141.85, 166.42; HREIMS calcd for C<sub>19</sub>H<sub>20</sub>O<sub>2</sub>(M<sup>+</sup>): 280.1463; found 280.1456.



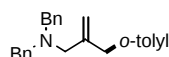
### 3j

Following the general procedure, using **1d** (65 mg, 0.25 mmol), **2b** (51 mg, 0.38 mmol), PdCl<sub>2</sub>(DPEphos) (0.005 mmol, 3.6 mg), 2 wt % PTS solution (0.8 mL) and Et<sub>3</sub>N (0.75 mmol, 0.1 mL), yielded the allylic arene **3j** (55 mg, 86%), <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ: 1.38 (t, *J* = 7.2 Hz, 3H), 2.33 (s, 3H), 3.56 (dd, *J* = 1.1, 6.2 Hz, 2H), 4.36 (q, *J* = 7.2 Hz, 2H), 2.36 (s, 3H), 3.59 (d, *J* = 5.5 Hz, 2H), 6.45 (dt, *J* = 6.0, 16.0 Hz, 1H), 6.52 (d, *J* = 16.0 Hz, 1H), 7.17-7.24 (m, 4H), 7.38-7.45 (m, 2H), 7.66 (s, 1H), 7.57 (dd, *J* = 1.7, 8.6 Hz, 1H), 7.73-7.78 (m, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ: 19.47, 36.97, 123.48, 125.52, 125.63, 126.11, 126.43, 127.58, 127.80, 128.03, 128.96, 129.25, 130.22, 130.92, 132.69, 133.60, 134.93, 136.42, 138.16; HREIMS calcd for C<sub>20</sub>H<sub>18</sub>(M<sup>+</sup>): 258.1408; found 258.1413.



### 3k

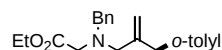
Following the general procedure, using **1e** (75 mg, 0.25 mmol), **2b** (51 mg, 0.38 mmol), PdCl<sub>2</sub>(DPEphos) (0.005 mmol, 3.6 mg), 2 wt % PTS solution (0.8 mL) and Et<sub>3</sub>N (0.75 mmol, 0.1 mL), yielded the allylic arene **3k** (67 mg, 90%), <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ: 2.33 (s, 3H), 3.53 (d, *J* = 4.8 Hz, 2H), 3.82 (s, 3H), 3.85 (s, 3H), 6.20-6.30 (m, 2H), 6.56 (s, 2H), 7.14-7.26 (m, 4H). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ: 19.40, 36.73, 55.97, 60.85, 102.95, 126.05, 126.41, 128.04, 129.28, 130.20, 133.21, 136.44, 137.27, 138.05, 153.19; HREIMS calcd for C<sub>19</sub>H<sub>22</sub>O<sub>3</sub>(M<sup>+</sup>): 298.1568; found 298.1572.



### 3l

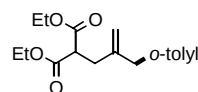
Following the general procedure, using **1f** (85 mg, 0.25 mmol), **2b** (68 mg, 0.5 mmol), PdCl<sub>2</sub>(DPEphos) (0.02 mmol, 14.4 mg), 2 wt % PTS solution (0.8 mL) and Et<sub>3</sub>N (0.75

mmol, 0.1 mL), yielded the allylic arene **3l** (70 mg, 82%),  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 2.25 (s, 3H), 3.06 (s, 2H), 3.45 (s, 2H), 3.59 (s, 4H), 4.58 (s, 1H), 5.14 (s, 1H), 7.04 (d,  $J$  = 7.1 Hz, 1H), 7.07-7.17 (m, 3H), 7.28 (t,  $J$  = 7.4 Hz, 2H), 7.35 (t,  $J$  = 7.4 Hz, 4H), 7.43 (d,  $J$  = 7.0 Hz, 4H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 19.56, 38.27, 58.17, 60.10, 113.95, 125.99, 126.36, 126.99, 128.40, 128.93, 130.22, 130.31, 136.94, 137.93, 139.78, 146.21; HRESI calcd for  $\text{C}_{25}\text{H}_{27}\text{N}(\text{MH}^+)$ : 342.2222; found 342.2218.



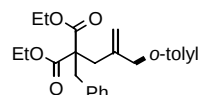
### 3m

Following the general procedure, using **1g** (84 mg, 0.25 mmol), **2b** (68 mg, 0.5 mmol),  $\text{PdCl}_2(\text{DPEphos})$  (0.02 mmol, 14.4 mg), 2 wt % PTS solution (0.8 mL) and  $\text{Et}_3\text{N}$  (0.75 mmol, 0.1 mL), yielded the allylic arene **3m** (76 mg, 90%),  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 1.26 (t,  $J$  = 7.1 Hz, 3H), 2.24 (s, 3H), 3.22 (s, 2H), 3.29 (s, 2H), 3.41 (s, 4H), 3.79 (s, 2H), 4.13 (q,  $J$  = 7.1 Hz, 2H), 4.60 (s, 1H), 5.05 (s, 1H), 7.06-7.13 (m, 4H), 7.23-7.26 (m, 1H), 7.32 (t,  $J$  = 7.0 Hz, 2H), 7.37 (d,  $J$  = 7.0 Hz, 2H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 14.43, 19.48, 38.04, 53.57, 57.85, 59.57, 60.28, 114.44, 125.94, 126.35, 127.20, 128.41, 129.07, 130.22, 136.98, 137.88, 139.16, 145.81, 171.63; HRESI calcd for  $\text{C}_{22}\text{H}_{27}\text{NO}_2(\text{MH}^+)$ : 338.2120; found 338.2115.



### 3n

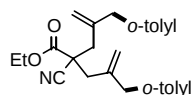
Following the general procedure, using **1h** (76 mg, 0.25 mmol), **2b** (51 mg, 0.38 mmol),  $\text{PdCl}_2(\text{DPEphos})$  (0.015 mmol, 11 mg), 2 wt % PTS solution (0.8 mL) and  $\text{Et}_3\text{N}$  (0.75 mmol, 0.1 mL), yielded the allylic arene **3n** (62 mg, 82%),  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 1.26 (t,  $J$  = 7.2 Hz, 6H), 2.24 (s, 3H), 2.65 (d,  $J$  = 6.8 Hz, 2H), 3.33 (s, 2H), 3.62 (t,  $J$  = 7.8 Hz, 1H), 4.19 (q,  $J$  = 7.2 Hz, 4H), 4.55 (d,  $J$  = 1.1 Hz, 1H), 4.85 (d,  $J$  = 1.1 Hz, 1H), 7.08-7.26 (m, 4H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 14.02, 19.24, 34.96, 40.04, 50.61, 61.40, 112.81, 125.86, 126.46, 129.91, 130.15, 136.79, 136.92, 143.95, 168.97; HREIMS calcd for  $\text{C}_{18}\text{H}_{24}\text{O}_4(\text{M}^+)$ : 304.1674; found 304.1666.



### 3o

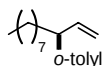
Following the general procedure, using **1i** (103 mg, 0.25 mmol), **2b** (68 mg, 0.5 mmol),  $\text{PdCl}_2(\text{DPEphos})$  (0.02 mmol, 14.4 mg), 2 wt % PTS solution (0.8 mL) and  $\text{Et}_3\text{N}$  (0.75 mmol, 0.1 mL), yielded the allylic arene **3o** (101 mg, 98%),  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 1.20 (t,  $J$  =

7.1 Hz, 6H), 2.24 (s, 3H), 2.71 (s, 2H), 3.26 (s, 2H), 3.37 (s, 2H), 4.13 (q,  $J$  = 7.1 Hz, 4H), 4.58 (s, 1H), 4.94 (s, 1H), 7.07-7.22 (m, 9H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 13.87, 19.28, 38.47, 38.67, 41.14, 58.26, 61.25, 114.51, 125.83, 126.37, 126.78, 128.05, 129.92, 129.98, 130.08, 136.28, 136.71, 137.27, 143.17, 171.06; HREIMS calcd for  $\text{C}_{25}\text{H}_{30}\text{O}_4(\text{M}^+)$ : 417.2042; found 417.2035.



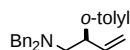
### 3p

Following the general procedure, using **1j** (77 mg, 0.25 mmol), **2b** (68 mg, 0.5 mmol),  $\text{PdCl}_2(\text{DPEphos})$  (0.02 mmol, 14.4 mg), 2 wt % PTS solution (0.8 mL) and  $\text{Et}_3\text{N}$  (0.75 mmol, 0.1 mL), yielded the allylic arene **3p** (55 mg, 72%),  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 1.32 (t,  $J$  = 7.2 Hz, 3H), 2.26 (s, 6H), 2.53 (d,  $J$  = 14.3 Hz, 2H), 2.74 (d,  $J$  = 14.3 Hz, 2H), 3.45 (dd,  $J$  = 6.5, 13.7 Hz, 4H), 4.25 (d,  $J$  = 7.2 Hz, 2H), 4.70 (s, 2H), 5.05 (s, 2H), 7.10-7.16 (m, 8H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 14.02, 19.37, 40.54, 44.06, 48.65, 62.79, 116.92, 119.62, 125.96, 126.60, 129.94, 130.25, 136.70, 136.95, 141.31, 168.63; HREIMS calcd for  $\text{C}_{27}\text{H}_{31}\text{NO}_2(\text{M}^+)$ : 401.2354; found 401.2355.



### 3q

Following the general procedure, using **1k** (60 mg, 0.25 mmol), **2b** (51 mg, 0.38 mmol),  $\text{PdCl}_2(\text{D}t\text{-BPF})$  (0.005 mmol, 3.2 mg), 2 wt % PTS solution (0.8 mL) and  $\text{Et}_3\text{N}$  (0.75 mmol, 0.1 mL), yielded the allylic arene **3q** (60 mg, 99%), contaminated with *E*-linear product.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 0.86 (t,  $J$  = 6.9 Hz, 3H), 1.24-1.33 (m, 14H), 2.32 (s, 3H), 3.47 (q,  $J$  = 7.3 Hz, 1H), 4.93-5.00 (m, 2H), 5.88 (ddd,  $J$  = 7.5, 10.2, 17.0 Hz, 1H), 7.07-7.18 (m, 4H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 14.11, 19.63, 22.66, 27.58, 29.31, 29.69, 31.87, 35.01, 44.95, 113.79, 125.72, 126.09, 126.30, 130.27, 135.78, 142.03, 142.58; HREIMS calcd for  $\text{C}_{18}\text{H}_{28}(\text{M}^+)$ : 244.2191; found 244.2197.



### 3r

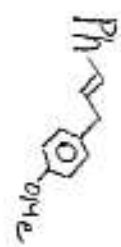
Following the general procedure, using **1l** (85 mg, 0.25 mmol), **2b** (68 mg, 0.5 mmol),  $\text{PdCl}_2(\text{D}t\text{-BPF})$  (0.005 mmol, 3.2 mg), 2 wt % PTS solution (0.8 mL) and  $\text{Et}_3\text{N}$  (0.75 mmol, 0.1 mL), yielded the allylic arene **3r** (60 mg, 71%), contaminated with *E*-linear product.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 2.22 (s, 3H), 2.69 (dd,  $J$  = 6.9, 12.8 Hz, 1H), 2.76 (dd,  $J$  = 6.9, 12.8 Hz, 1H), 3.53 (d, 4H), 3.84 (q,  $J$  = 7.2 Hz, 1H), 4.93 (dd,  $J$  = 1.1, 17.1 Hz, 1H), 4.98 (d,  $J$  = 10.2

Hz, 1H), 5.86-5.95 (m, 1H), 5.86-5.95 (m, 1H), 7.06-7.34 (m, 14H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 19.57, 43.49, 58.61, 58.73, 114.89, 125.92, 126.79, 127.22, 128.06, 128.13, 128.89, 130.22, 135.71, 139.60, 140.69, 140.80; HRESI calcd for  $\text{C}_{25}\text{H}_{27}\text{N}(\text{MH}^+)$ : 342.2222; found 342.2211.

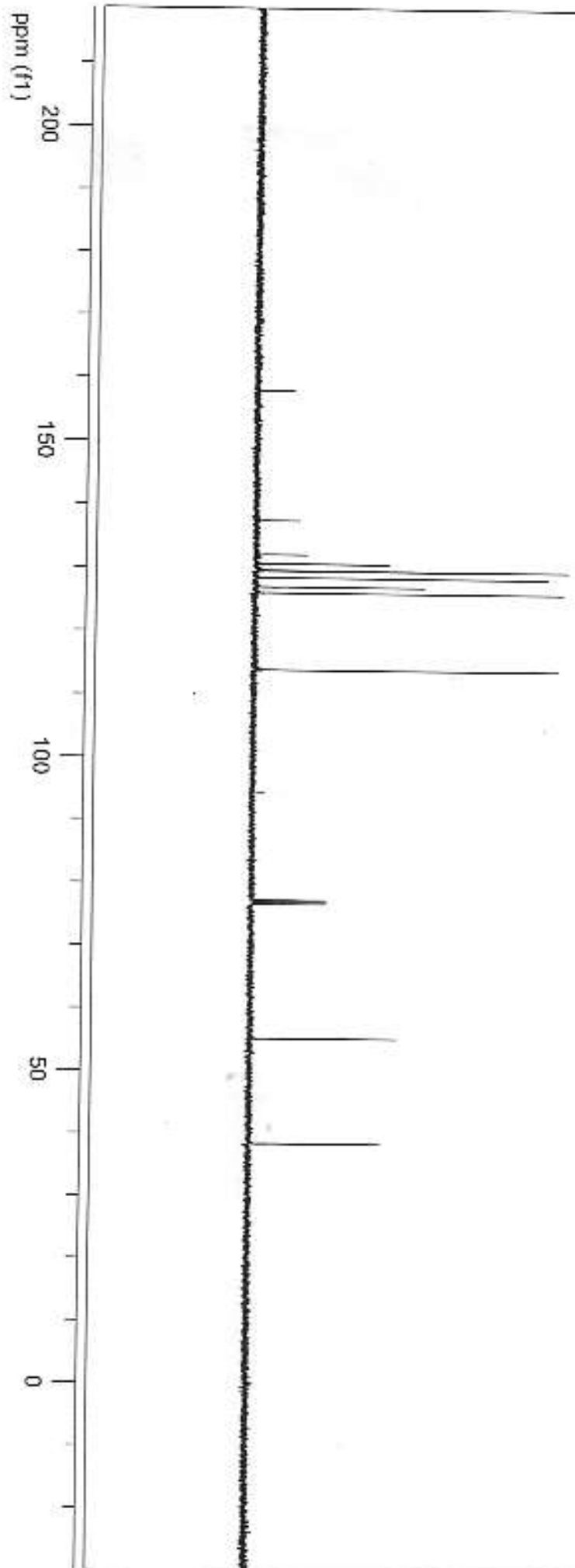
#### One-pot reaction (Scheme 3)

**4** (103 mg, 0.5 mmol), Dibenzylamine (99 mg, 0.5 mmol), Xantphos (2.9 mg, 0.005 mmol), and  $[\text{Pd}(\text{allyl})\text{Cl}]_2$  (0.9 mg, 0.0025 mmol) were sequentially added under Ar to a reaction tube equipped with a stir bar and a septum.

PTS solution (1 mL, 2 wt %) was added by syringe and vigorously stirred for 5 h. After the reaction, **2b** (138 mg, 1 mmol),  $\text{PdCl}_2(\text{DPEphos})$  (30 mg, 0.04 mmol), PTS solution (0.8 mL, 2 wt %), and  $\text{Et}_3\text{N}$  (0.2 mL, 1.5 mmol) were sequentially added to the reaction mixture. After vigorously stirred for 19 h, the contents of the flask were diluted with brine and extracted with EtOAc. The solution obtained was dried over anhydrous  $\text{MgSO}_4$ , filtered, and concentrated by rotary evaporation. The residue was purified by flash chromatography eluting with hexane/EtOAc to afford the product **3l** (130 mg, 76%).



3a

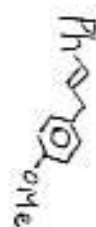


ppm (f1)

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5.0

0.0



3a

ppm (f1)

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150

100

50

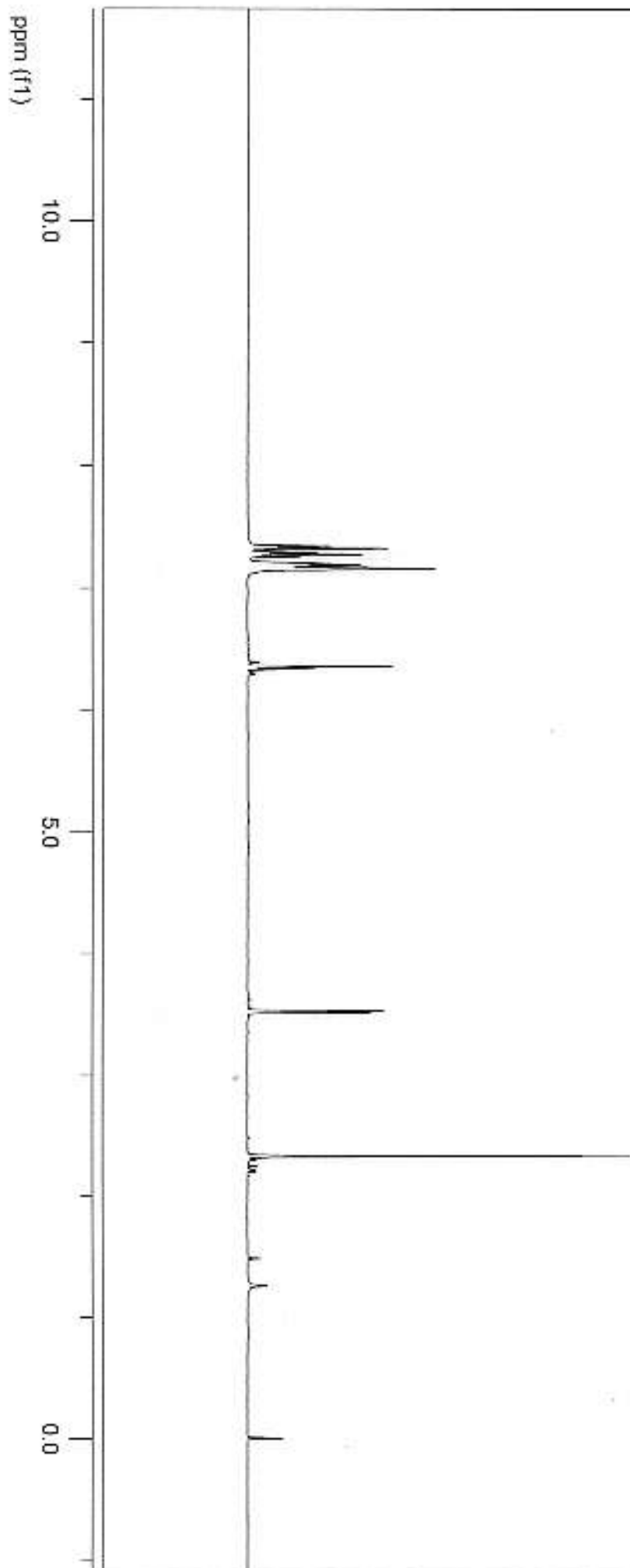
0

3b





**3b**



ppm (f1)

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100

50

0

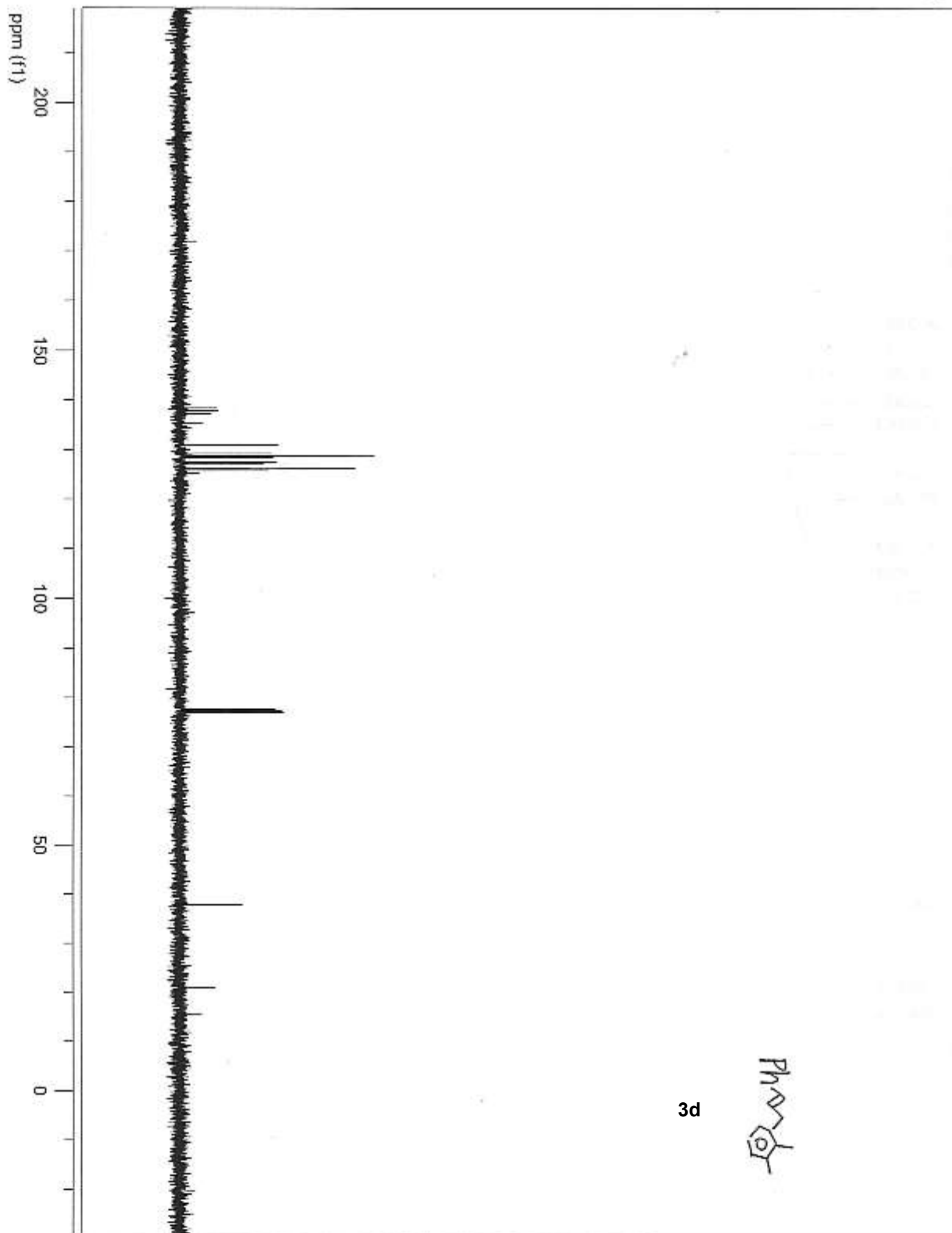
3c





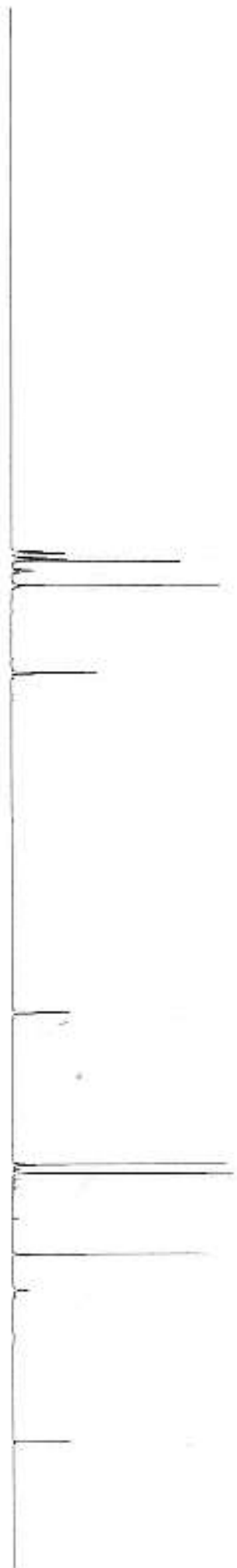


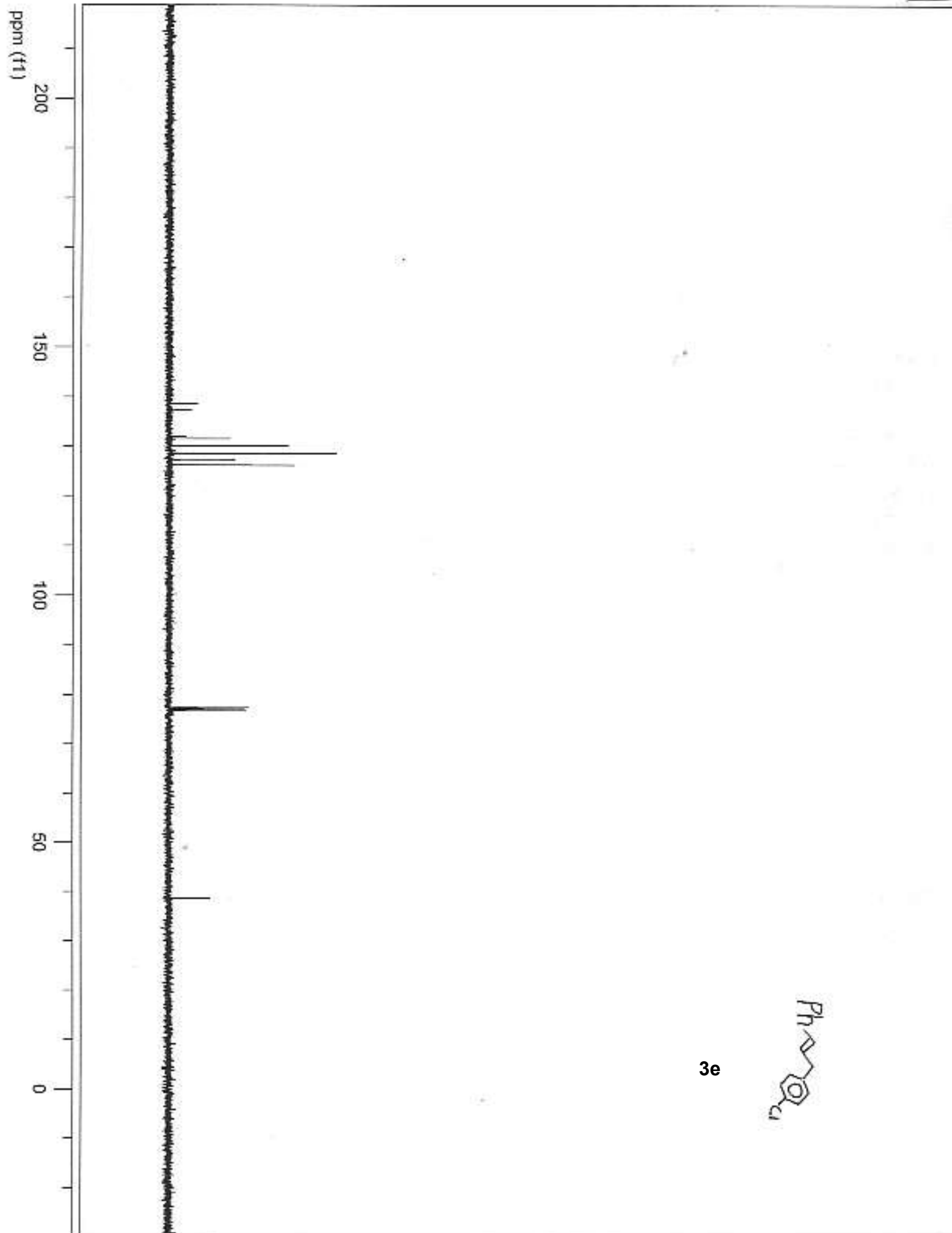
3d





**3d**







3e

ppm (f1)

10.0

5.0

0.0

ppm (f1)

200

150

100

50

0





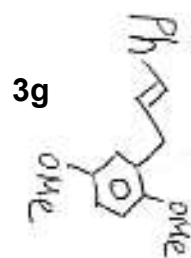
3f

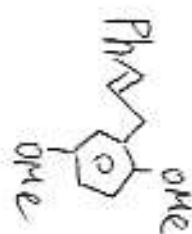
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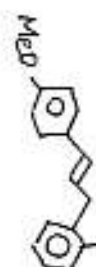
3g

ppm (f1)

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5.0

0.0



3h

ppm (f1)

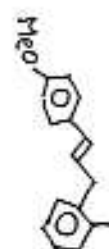
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150

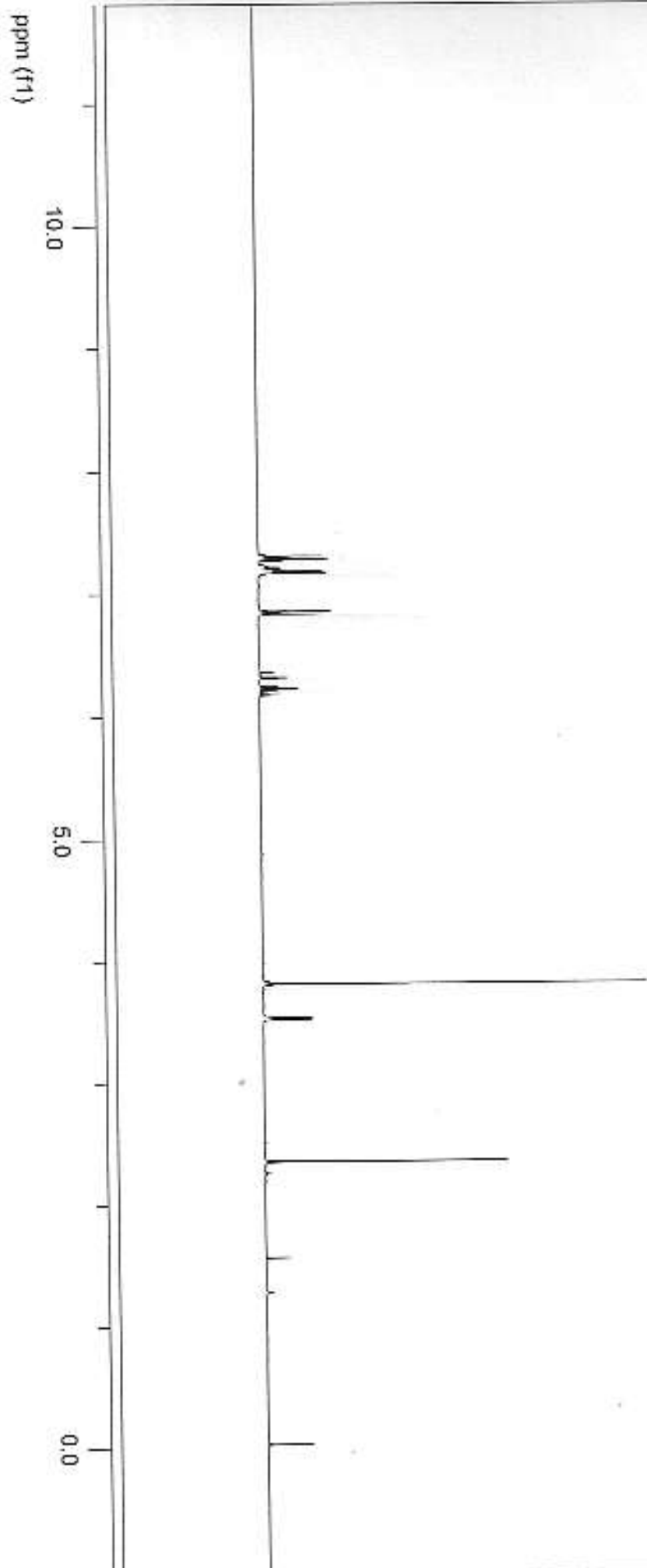
100

50

0



3h





3i

ppm (f1)

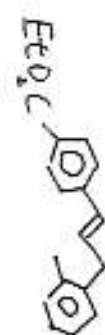
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150

100

50

0



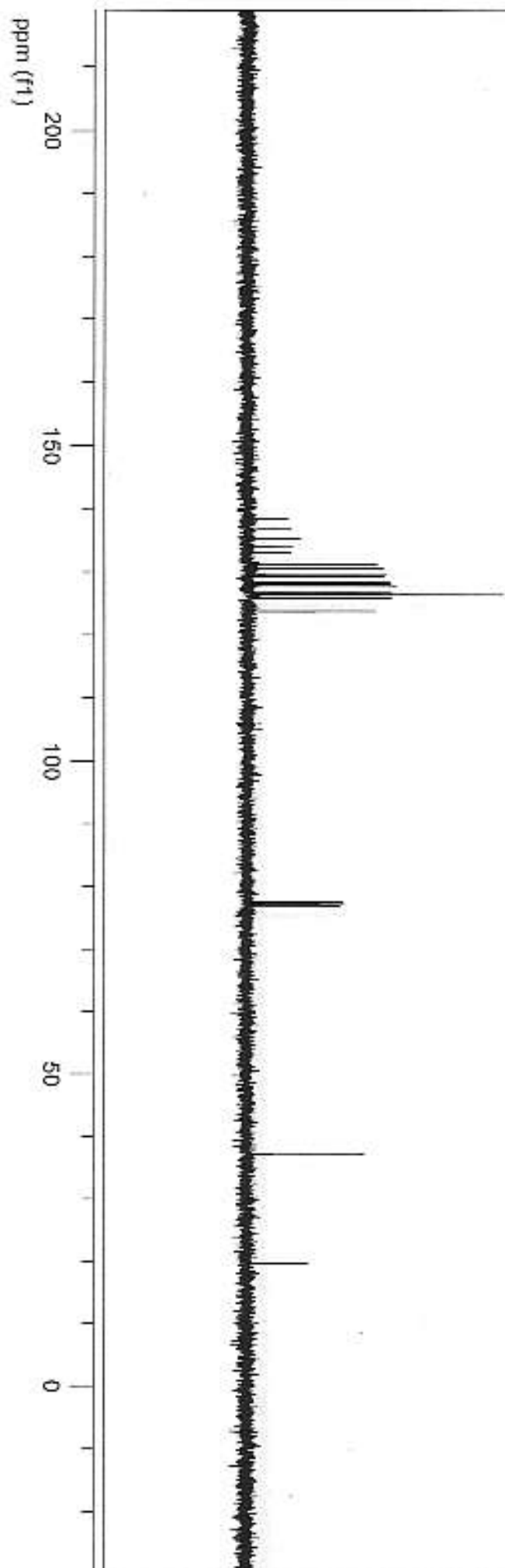
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ppm (f1)

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5.0

0.0



3j



ppm (f1)

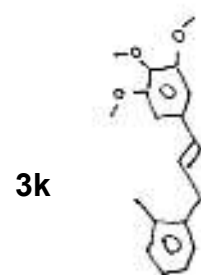
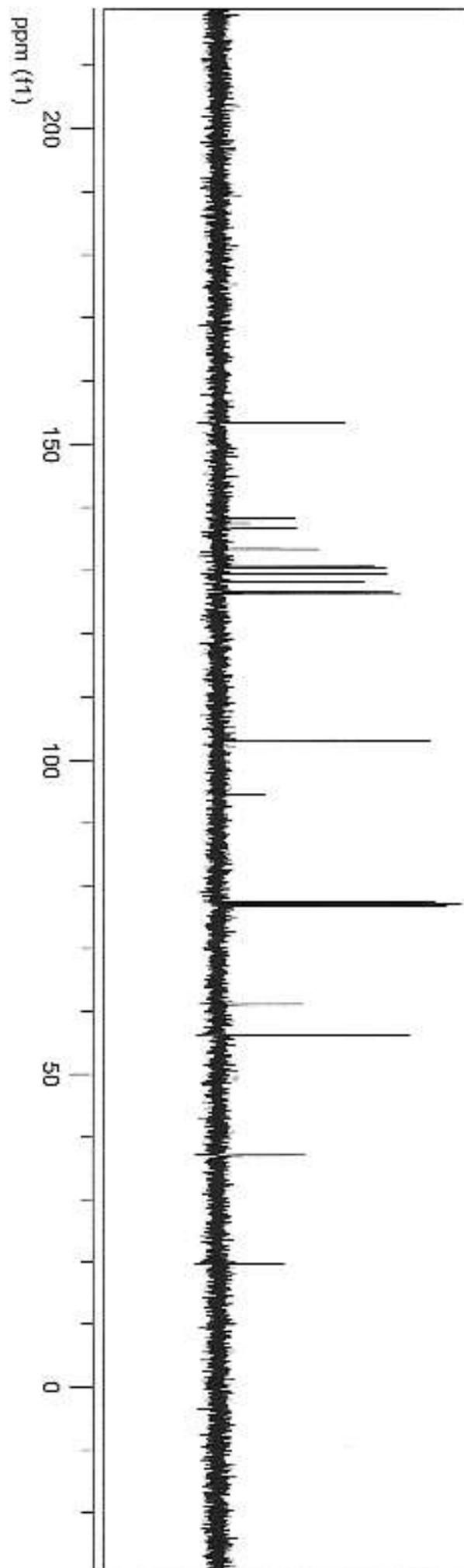
10.0

5.0

0.0

3j



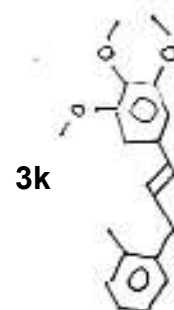


ppm (f1)

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5.0

0.0



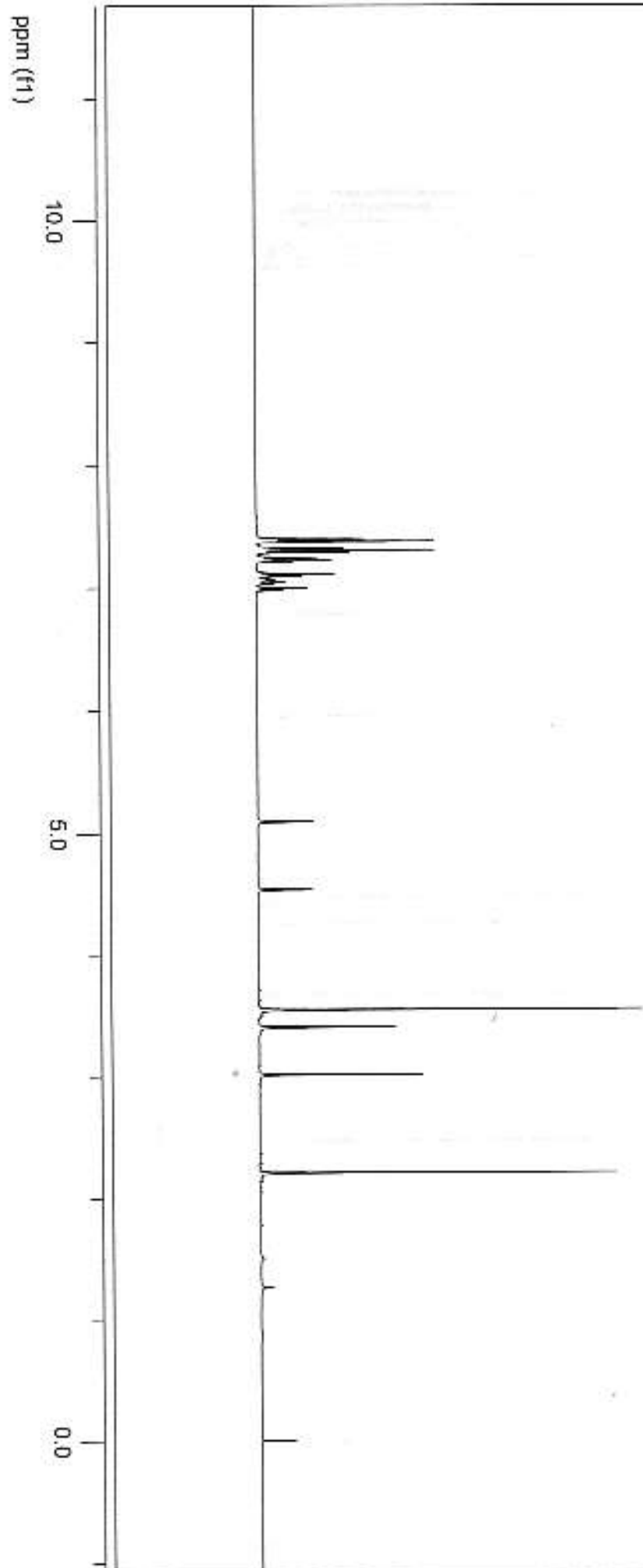


3l

ppm (f1)

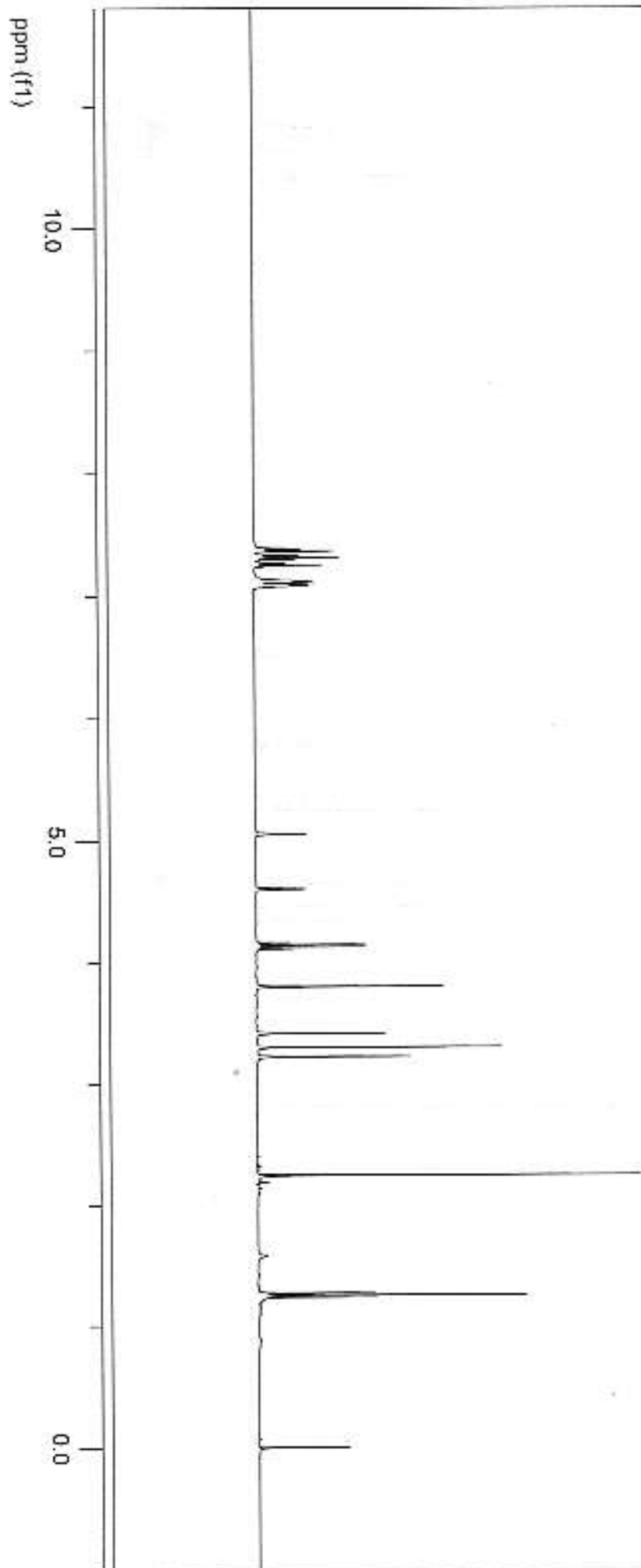


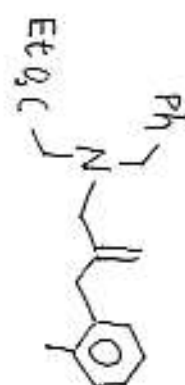
3l





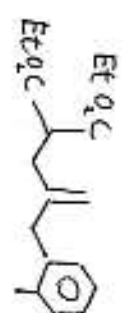
3m



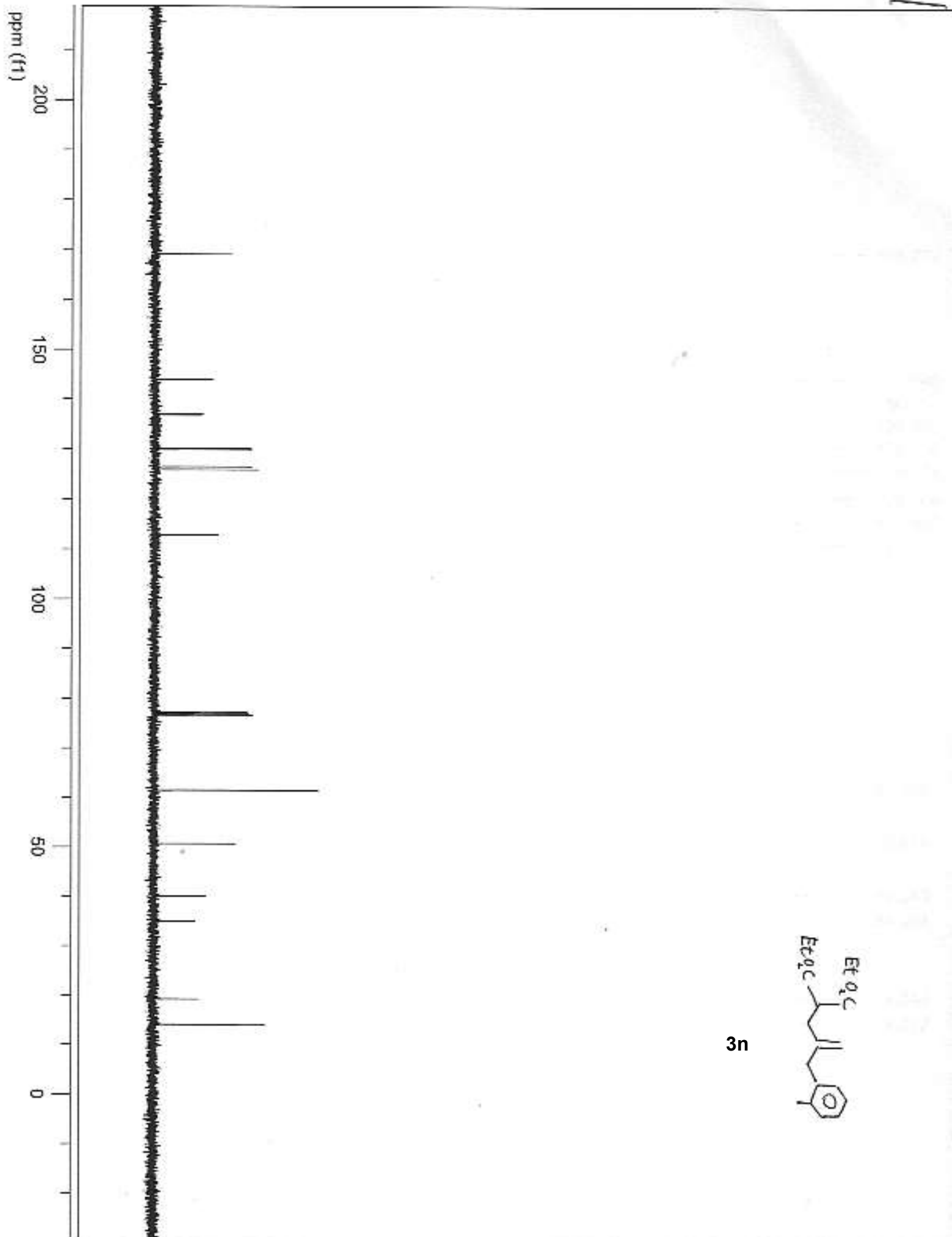


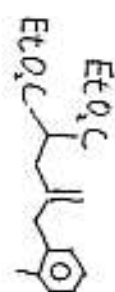
3m

ppm (f1)



3n





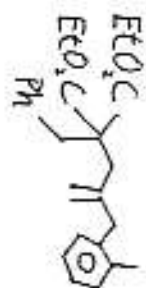
3n

ppm (f1)

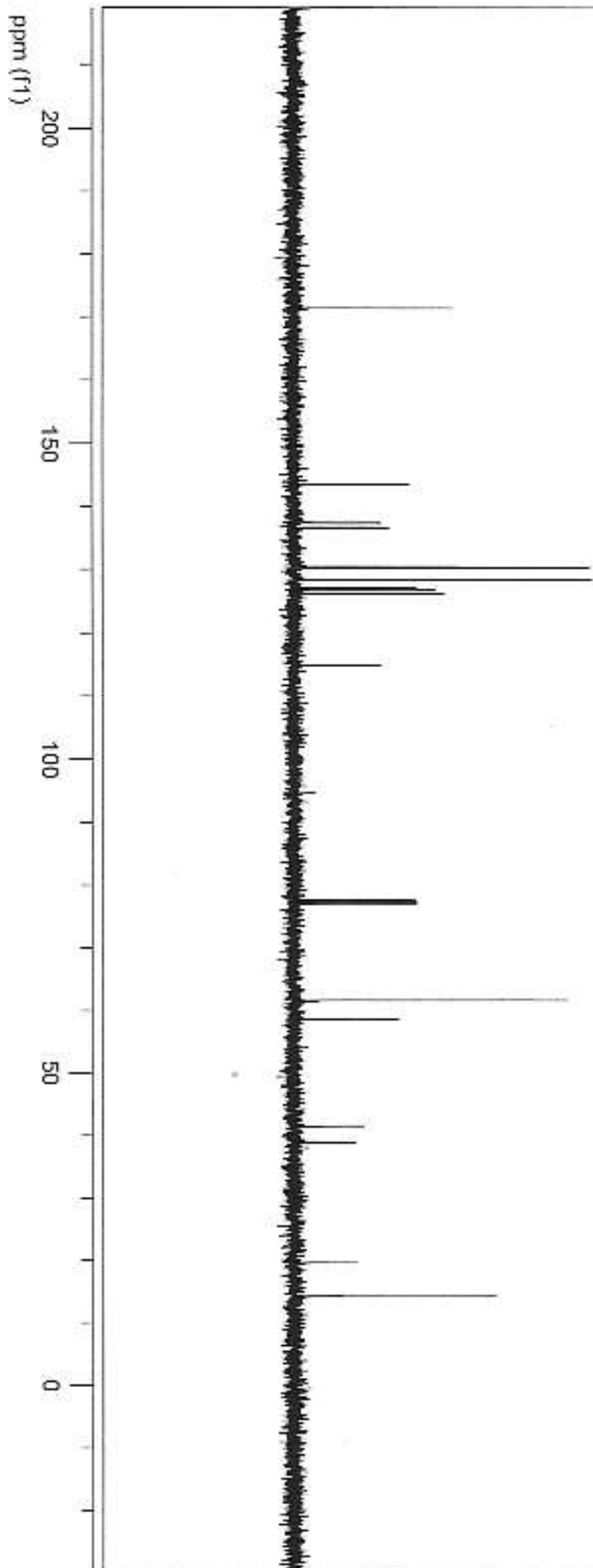
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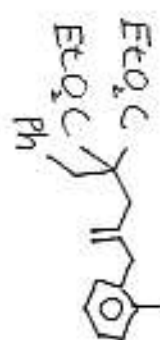
5.0

0.0

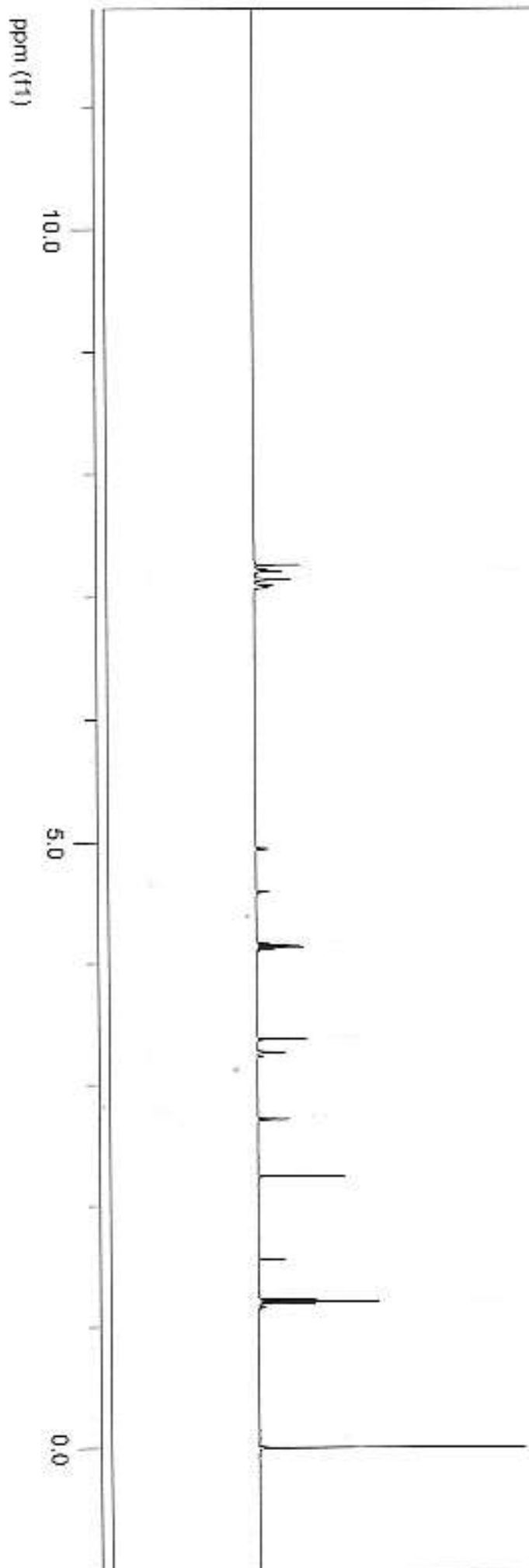


30





3o







ppm (f1)

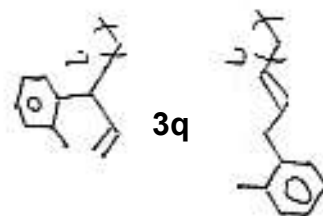
200

150

100

50

0

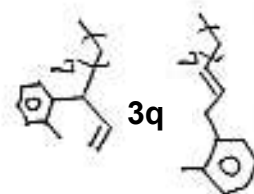


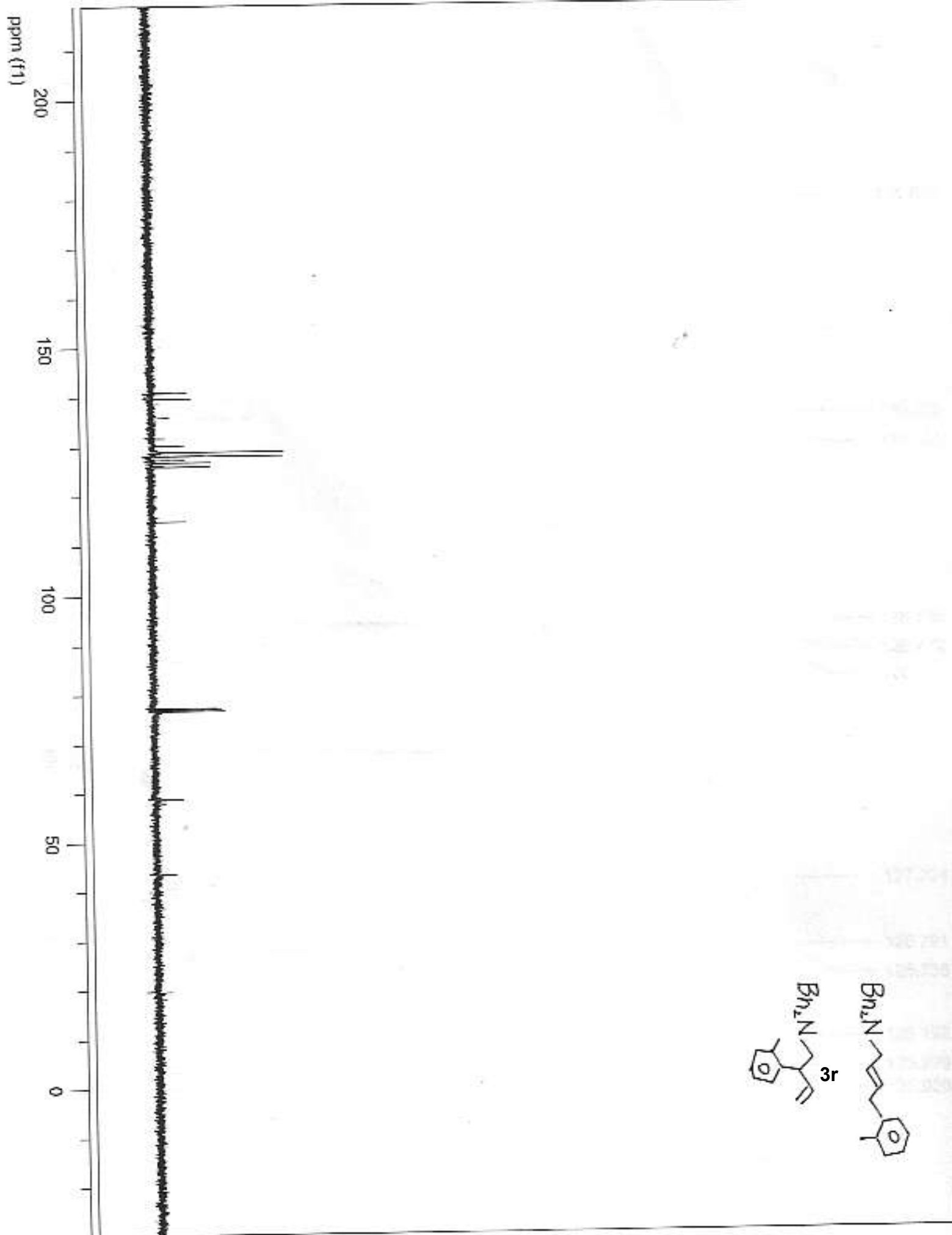
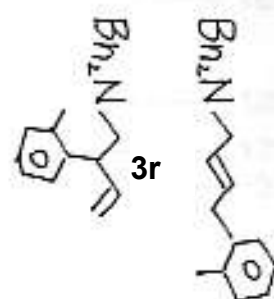
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5.0

0.0





ppm (f1)

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5.0

0.0

