

Supporting Information For

A Facile and Efficient Synthesis of Multisubstituted Pyrroles from Enaminoesters and Nitroolefins

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Context

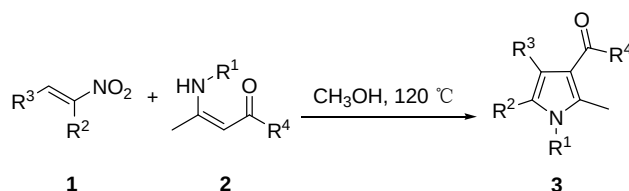
1. General information	-----S2
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General information:

Column chromatography was carried out on silica gel. ^1H NMR spectra were recorded on 400 MHz in CDCl_3 and ^{13}C NMR spectra were recorded on 100 MHz in CDCl_3 . Copies of their ^1H NMR, ^{13}C NMR spectra are provided. Unless otherwise stated, all solvents were purchased from commercial suppliers and used without further purification. The nitroolefins **1** and enaminoesters **2** were prepared according to the following literatures:

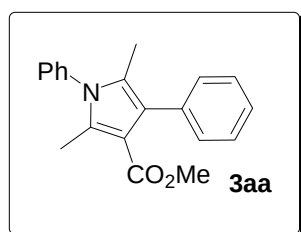
- (1) Alizadeh, A.; Khodaei, M. M.; Eshghi, A. *J. Org. Chem.* **2010**, *75*, 8295.
- (2) Würtz, S.; Rakshit, S.; Neumann, J. J.; Dröge, T.; Glorius, F. *Angew. Chem., Int. Ed.* **2008**, *47*, 7230.
- (3) Hebbache, H.; Hanka, Z.; Bruneau, C.; Renaud, J. L. *Synthesis*. **2009**, 2627.

Typical Procedure for Synthesis of Multisubstituted Pyrroles

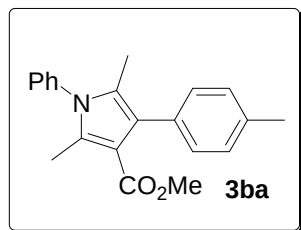


A round bottom flask (10 mL) was charged with nitroolefin **1** (0.3 mmol), enaminoesters **2** (1.5 eq), and CH_3OH (2.0 mL). The mixture was stirred at 120°C . After completion of the reaction (detected by TLC), the reaction mixture was cooled to room temperature. The solvent was removed by evaporation under reduced pressure. The residue was purified by chromatography on silica gel with hexane/ethyl acetate/triethyl amine as the eluent to afford the corresponding products **3**.

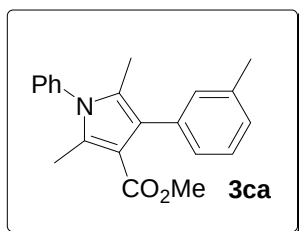
Spectroscopic data for products 3



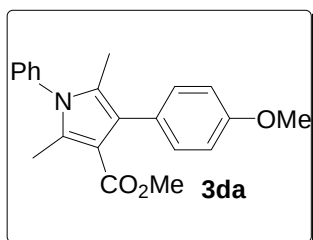
3aa¹: ^1H NMR (400 MHz, CDCl_3) δ 7.54-7.49 (m, 3H), 7.40-7.37 (m, 2H), 7.33-7.27 (m, 5H), 3.64 (s, 3H), 2.34 (s, 3H), 1.91 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 166.4, 137.8, 136.3, 135.8, 130.3, 129.4, 128.6, 128.3, 127.4, 126.9, 125.9, 122.3, 110.6, 50.5, 12.8, 11.3.



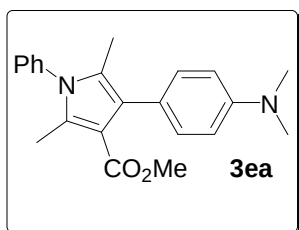
3ba: ^1H NMR (400 MHz, CDCl_3) δ 7.50-7.45 (m, 3H), 7.26-7.16 (m, 6H), 3.63 (s, 3H), 2.37 (s, 3H), 2.31 (s, 3H), 1.88 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 166.3, 137.8, 135.6, 135.3, 133.1, 130.1, 129.3, 128.5, 128.2, 126.7, 122.1, 110.6, 50.4, 21.2, 12.7, 11.2.



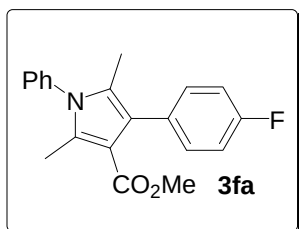
3ca: ^1H NMR (400 MHz, CDCl_3) δ 7.51-7.47 (m, 3H), 7.25-7.23 (m, 3H), 7.12-7.09 (m, 3H), 3.62 (s, 3H), 2.37 (s, 3H), 2.31 (s, 3H), 1.89 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 166.3, 137.8, 136.7, 136.0, 135.7, 130.9, 129.4, 128.5, 128.2, 127.4, 127.2, 126.8, 126.6, 122.2, 110.7, 50.4, 21.5, 12.7, 11.3. Anal. Calcd for $\text{C}_{21}\text{H}_{21}\text{NO}_2$: C 78.97, H 6.63, N 4.39; Found: C 79.09, H 7.18, N 4.18.



3da: ^1H NMR (400 MHz, CDCl_3) δ 7.54-7.50 (m, 3H), 7.28-7.25 (m, 4H), 6.96-6.94 (m, 2H), 3.86 (s, 3H), 3.67 (s, 3H), 2.34 (s, 3H), 1.91 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 166.4, 157.9, 137.8, 135.7, 131.4, 129.4, 128.6, 128.5, 128.3, 126.8, 121.9, 112.9, 110.7, 55.1, 50.5, 12.8, 11.3.

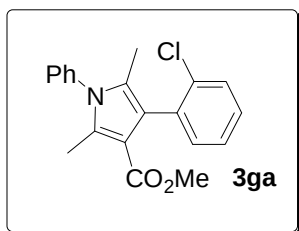


3ea: ^1H NMR (400 MHz, CDCl_3) δ 7.52-7.49 (m, 3H), 7.28-7.21 (m, 4H), 6.81-6.79 (m, 2H), 3.68 (s, 3H), 3.00 (s, 6H), 2.34 (s, 3H), 1.93 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 166.6, 148.8, 137.9, 135.5, 130.9, 129.4, 128.4, 128.3, 126.6, 124.3, 122.2, 111.9, 110.7, 50.5, 40.7, 12.8, 11.4.

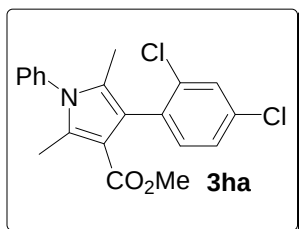


3fa: ^1H NMR (400 MHz, CDCl_3) δ 7.51-7.48 (m, 3H), 7.27-7.23 (m, 4H), 7.06-7.02 (t, $J = 9.2$ Hz, 2H), 3.62 (s, 3H), 2.31 (s, 3H), 1.85 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3)

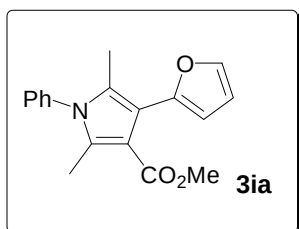
δ 166.1, 162.6 (d, $J_{CF} = 242.7$ Hz), 137.6, 135.9, 132.1, 131.8 (d, $J_{CF} = 7.8$ Hz), 129.4, 128.6, 128.2, 126.9, 121.3, 114.3 (d, $J_{CF} = 21$ Hz), 110.7, 50.4, 12.7, 11.1.



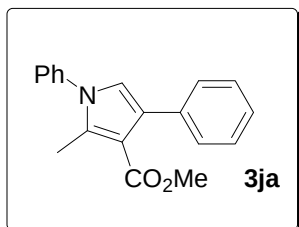
3ga: ^1H NMR (400 MHz, CDCl_3) δ 7.54-7.45 (m, 4H), 7.32-7.25 (m, 5H), 3.61 (s, 3H), 2.36 (s, 3H), 1.82 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 166.1, 137.6, 135.7, 134.8, 132.3, 129.4, 128.9, 128.6, 128.4, 128.2, 127.7, 127.3, 125.9, 119.4, 111.0, 50.5, 12.7, 11.2. Anal.Calcd for $\text{C}_{20}\text{H}_{18}\text{ClNO}_2$: C 70.69, H 5.34, N 4.12; Found: C 70.37, H 4.93, N 4.58.



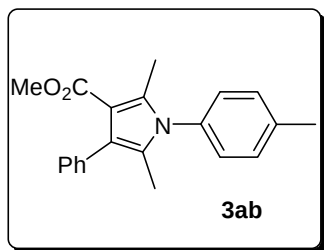
3ha: ^1H NMR (400 MHz, CDCl_3) δ 7.54-7.47 (m, 4H), 7.28-7.25 (m, 4H), 3.63 (s, 3H), 2.35 (s, 3H), 1.81 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 165.9, 137.5, 135.9, 135.5, 134.4, 133.1, 132.7, 129.5, 128.8, 128.7, 128.3, 128.2, 128.1, 127.5, 126.3, 118.3, 110.9, 50.6, 12.7, 11.1.



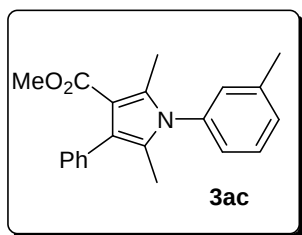
3ia: ^1H NMR (400 MHz, CDCl_3) δ 7.53-7.49 (m, 4H), 7.24-7.22 (m, 2H), 6.47 (s, 1H), 6.36 (s, 1H), 3.74 (s, 3H), 2.29 (s, 3H), 2.00 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 165.9, 149.2, 141.2, 137.4, 136.2, 129.5, 129.4, 128.8, 128.2, 111.7, 110.7, 110.5, 108.1, 50.8, 12.6, 11.5.



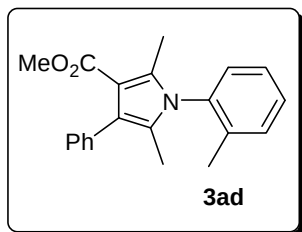
3ja: ^1H NMR (400 MHz, CDCl_3) δ 7.49-7.25 (m, 10H), 6.71 (s, 1H), 3.69 (s, 3H), 2.45 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 166.3, 138.9, 136.7, 135.4, 129.3, 129.1, 128.1, 127.7, 126.6, 126.3, 124.5, 120.9, 111.3, 50.6, 12.7.



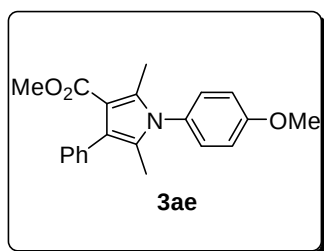
3ab: ^1H NMR (400 MHz, CDCl_3) δ 7.33-7.22 (m, 7H), 7.11-7.09 (d, $J = 7.6\text{Hz}$, 2H), 3.58 (s, 3H), 2.41 (s, 3H), 2.28 (s, 3H), 1.85 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 166.4, 138.6, 136.3, 135.9, 135.1, 130.3, 130.0, 127.9, 127.4, 126.9, 125.9, 122.1, 110.5, 50.42, 21.2, 12.7, 11.2.



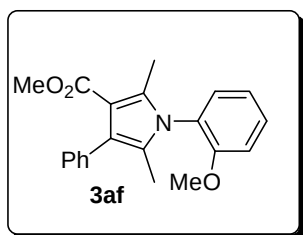
3ac: ^1H NMR (400 MHz, CDCl_3) δ 7.36-7.24 (m, 7H), 7.04 (m, 2H), 3.59 (s, 3H), 2.41 (s, 3H), 2.29 (s, 3H), 1.87 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 166.4, 139.5, 137.7, 136.4, 135.9, 130.4, 129.3, 129.2, 128.8, 127.4, 126.9, 125.9, 125.3, 122.2, 110.5, 50.4, 21.3, 12.8, 11.3.



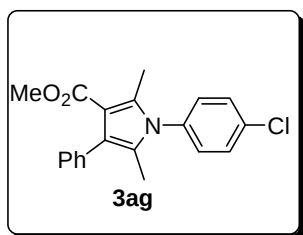
3ad: ^1H NMR (400 MHz, CDCl_3) δ 7.35-7.22 (m, 8H), 7.16-7.14 (d, $J = 7.6\text{ Hz}$, 2H), 3.59 (s, 3H), 2.19 (s, 3H), 1.97 (s, 3H), 1.77 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 166.4, 136.9, 136.6, 136.3, 135.5, 131.0, 130.4, 129.1, 128.6, 127.4, 127.0, 126.3, 125.9, 122.3, 110.4, 50.4, 17.2, 12.3, 10.8.



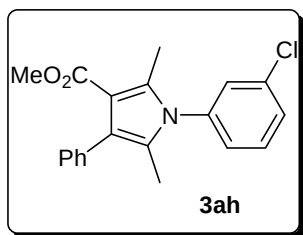
3ae: ^1H NMR (400 MHz, CDCl_3) δ 7.35-7.24 (m, 5H), 7.17-7.14 (m, 2H), 7.01-6.99 (m, 2H), 3.86 (s, 3H), 3.61 (s, 3H), 2.31 (s, 3H), 1.88 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 166.3, 159.4, 136.3, 136.1, 130.4, 130.3, 129.2, 127.3, 127.1, 125.8, 121.9, 114.5, 110.3, 55.4, 50.4, 12.6, 11.2.



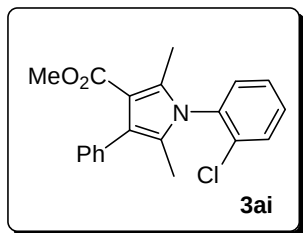
3af: ^1H NMR (400 MHz, CDCl_3) δ 7.43-7.41 (m, 1H), 7.36-7.32 (m, 4H), 7.25-7.24 (m, 1H), 7.19-7.17 (m, 1H), 7.08-7.04 (m, 2H), 3.79 (s, 3H), 3.61 (s, 3H), 2.28 (s, 3H), 1.85 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 166.4, 155.5, 136.5, 136.4, 130.4, 130.2, 129.9, 127.3, 127.2, 126.2, 125.7, 121.8, 120.8, 112.0, 110.2, 55.6, 50.3, 12.3, 10.7.



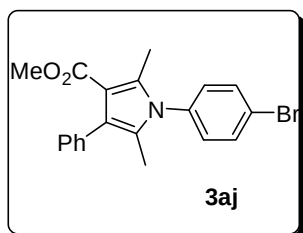
3ag: ^1H NMR (400 MHz, CDCl_3) δ 7.49-7.48 (d, J = 8.8 Hz, 2H), 7.37-7.33 (m, 2H), 7.28-7.25 (m, 3H), 7.21-7.18 (d, J = 8.4 Hz, 2H), 3.60 (s, 3H), 2.30 (s, 3H), 1.88 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 166.1, 136.2, 135.9, 135.6, 134.6, 130.2, 129.7, 129.5, 127.4, 126.7, 125.9, 122.5, 111.0, 50.4, 12.6, 11.2.



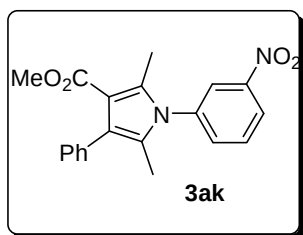
3ah: ^1H NMR (400 MHz, CDCl_3) δ 7.46-7.45 (m, 2H), 7.38-7.34 (m, 2H), 7.29-7.25 (m, 3H), 7.18-7.15 (m, 2H), 3.61 (s, 3H), 2.32 (s, 3H), 1.89 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 166.1, 138.9, 135.9, 135.6, 134.9, 130.4, 130.2, 128.9, 128.6, 127.4, 126.6, 126.6, 126.0, 122.6, 111.1, 50.4, 12.6, 11.2.



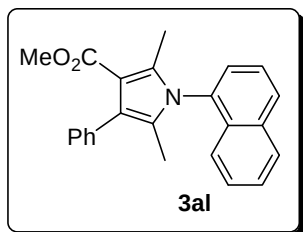
3ai: ^1H NMR (400 MHz, CDCl_3) δ 7.58-7.57 (m, 1H), 7.44-7.41 (m, 2H), 7.38-7.30 (m, 5H), 7.27-7.25 (m, 1H), 3.62 (s, 3H), 2.26 (s, 3H), 1.83 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 166.2, 136.1, 135.7, 135.6, 133.6, 130.4, 130.4, 130.3, 127.8, 127.7, 127.3, 126.6, 125.9, 122.4, 110.8, 50.4, 12.2, 10.6.



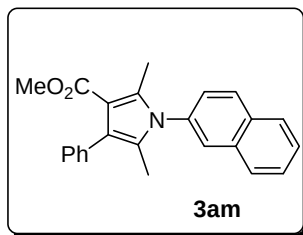
3aj: ^1H NMR (400 MHz, CDCl_3) δ 7.65-7.63 (d, $J=8.4$ Hz, 2H), 7.36-7.34 (m, 2H), 7.29-7.25 (m, 3H), 7.15-7.12 (d, $J=8.8$ Hz, 2H), 3.61 (s, 3H), 2.31 (s, 3H), 1.89 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 166.2, 136.8, 136.0, 135.6, 132.7, 130.3, 129.9, 127.5, 126.7, 126.1, 125.8, 122.6, 111.1, 50.5, 12.7, 11.3.



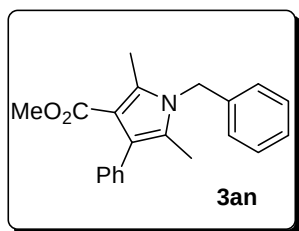
3ak: ^1H NMR (400 MHz, CDCl_3) δ 8.29-8.27 (d, $J=8.0$ Hz, 1H), 8.10 (s, 1H), 7.68-7.64 (t, $J=8.0$ Hz, 1H), 7.57-7.55 (m, 1H), 7.31-7.28 (m, 2H), 7.22-7.17 (m, 3H), 3.54 (s, 3H), 2.26 (s, 3H), 1.83 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 165.9, 148.7, 138.9, 135.6, 135.4, 134.4, 130.4, 130.2, 127.5, 126.5, 126.2, 123.5, 123.5, 123.2, 111.8, 50.6, 12.7, 11.3.



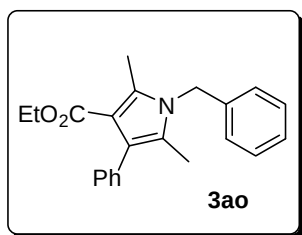
3al: ^1H NMR (400 MHz, CDCl_3) δ 7.99-7.94 (m, 2H), 7.61-7.50 (m, 4H), 7.46-7.38 (m, 4H), 7.29-7.24 (m, 2H), 3.65 (s, 3H), 2.21 (s, 3H), 1.78 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 166.4, 136.8, 136.2, 134.4, 134.2, 131.1, 130.4, 129.3, 128.2, 127.8, 127.6, 127.4, 126.8, 126.3, 125.9, 125.3, 122.7, 122.3, 110.6, 50.4, 12.3, 10.7.



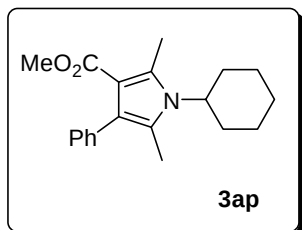
3am: ^1H NMR (400 MHz, CDCl_3) δ 7.97-7.87 (m, 3H), 7.74 (s, 1H), 7.58-7.56 (m, 2H), 7.38-7.22 (m, 6H), 3.62 (s, 3H), 2.35 (s, 3H), 1.91 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 166.3, 136.2, 136.0, 135.1, 133.2, 132.8, 130.3, 129.4, 127.9, 127.8, 127.4, 127.1, 127.0, 126.9, 125.9, 125.9, 122.4, 110.7, 50.4, 12.8, 11.3.



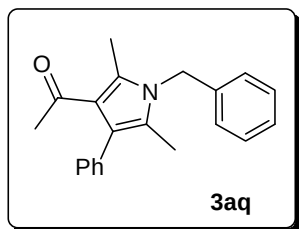
3an: ^1H NMR (400 MHz, CDCl_3) δ 7.36-7.32 (m, 4H), 7.28-7.25 (m, 4H), 6.97-6.95 (d, $J = 7.2$ Hz, 2H), 5.12 (s, 2H), 3.59 (s, 3H), 2.50 (s, 3H), 2.05 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 166.3, 136.9, 136.4, 135.1, 130.4, 128.9, 127.4, 127.3, 126.2, 125.8, 125.5, 122.6, 110.5, 50.3, 47.0, 11.5, 10.3.



3ao: ^1H NMR (400 MHz, CDCl_3) δ 7.36-7.32 (m, 4H), 7.29-7.25 (m, 4H), 6.98-6.96 (d, $J = 7.2$ Hz, 2H), 5.11 (s, 2H), 4.09-4.05 (q, $J = 6.8$ Hz, 2H), 2.51 (s, 3H), 2.04 (s, 3H), 1.03-0.99 (t, $J = 7.6$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 165.9, 136.9, 136.6, 135.0, 130.5, 128.8, 127.4, 127.3, 126.0, 125.8, 125.6, 122.6, 110.8, 59.0, 46.9, 13.8, 11.4, 10.3.

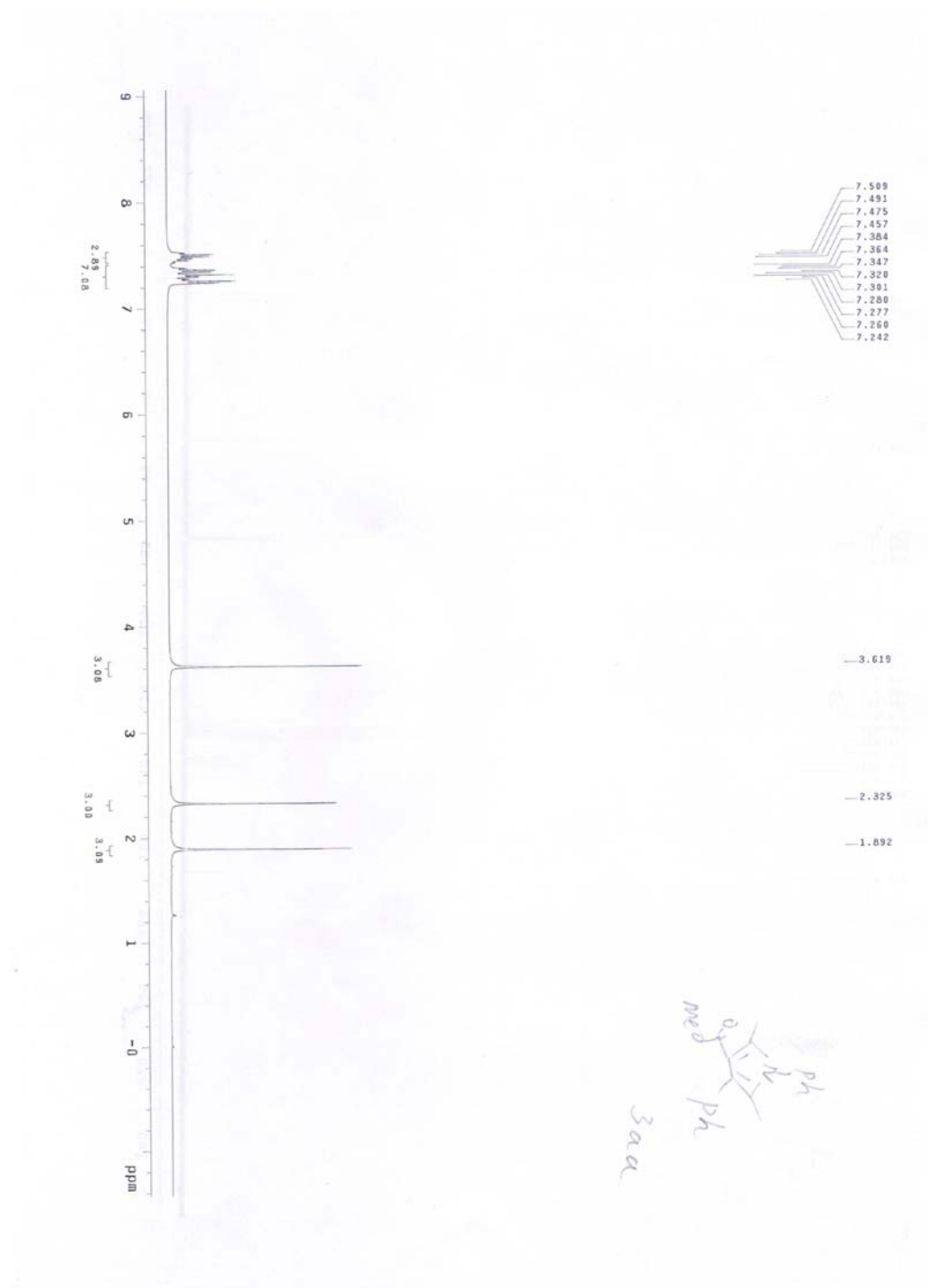
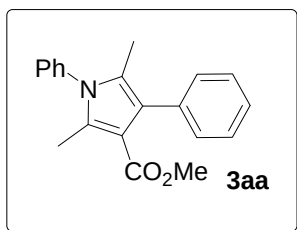


3ap: ^1H NMR (400 MHz, CDCl_3) δ 7.34-7.30 (m, 2H), 7.25-7.18 (m, 3H), 4.06 (m, 1H), 3.52 (s, 3H), 2.63 (s, 3H), 2.16 (s, 3H), 2.07-1.92 (m, 6H), 1.77-1.74 (m, 1H), 1.45-1.35 (m, 2H), 1.28-1.21 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 166.6, 136.9, 134.5, 130.5, 127.3, 125.7, 57.0, 50.3, 31.9, 26.6, 25.5.

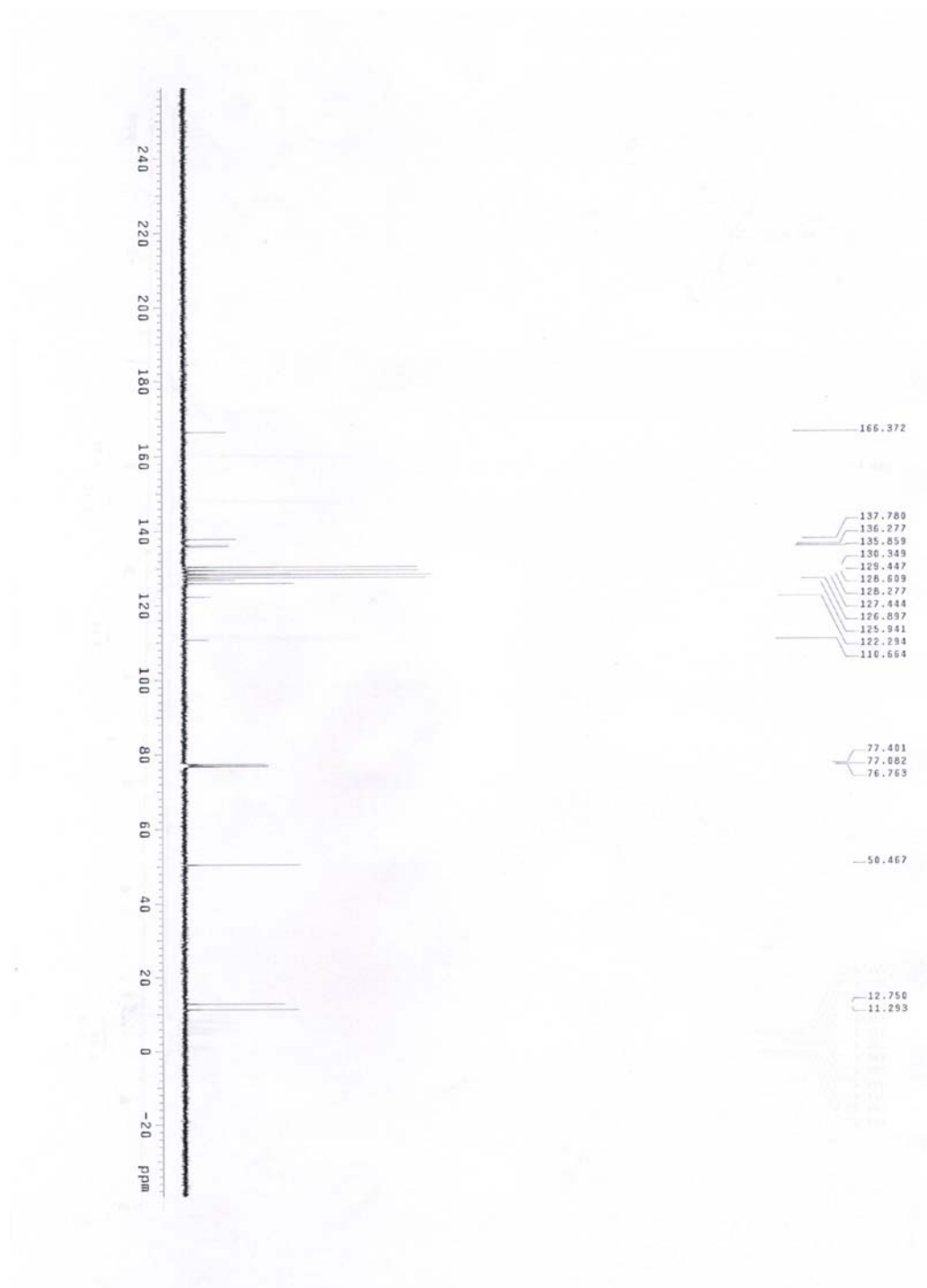
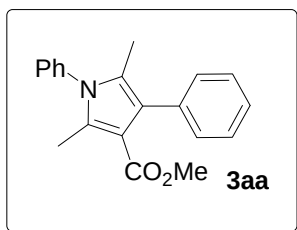


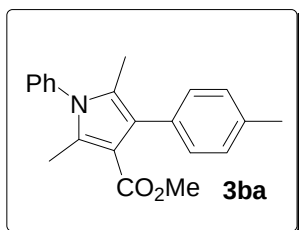
3aq: ^1H NMR (400 MHz, CDCl_3) δ 7.38-7.34 (m, 3H), 7.33-7.28 (m, 3H), 7.26-7.24 (m, 2H), 6.97-6.95 (d, $J = 6.4$ Hz, 2H), 5.10 (s, 2H), 2.46 (s, 3H), 1.99 (s, 3H), 1.89 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 197.3, 136.9, 136.7, 134.1, 130.5, 128.9, 128.1, 127.4, 126.5, 125.9, 125.6, 122.3, 121.6, 46.8, 31.0, 11.7, 10.2.

3aa:

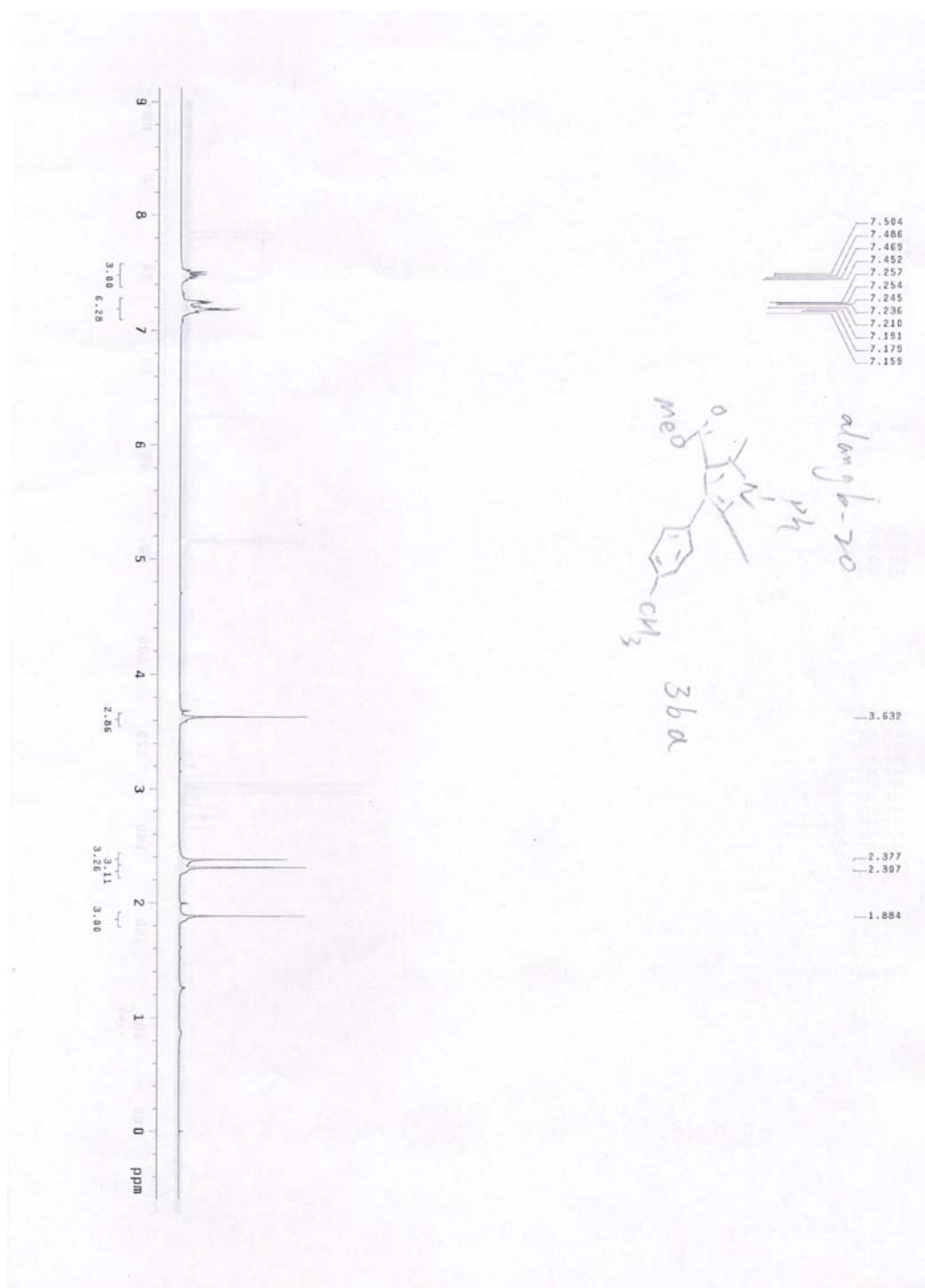


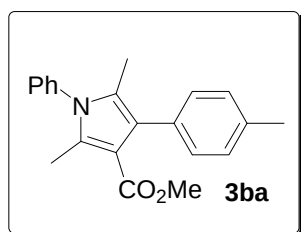
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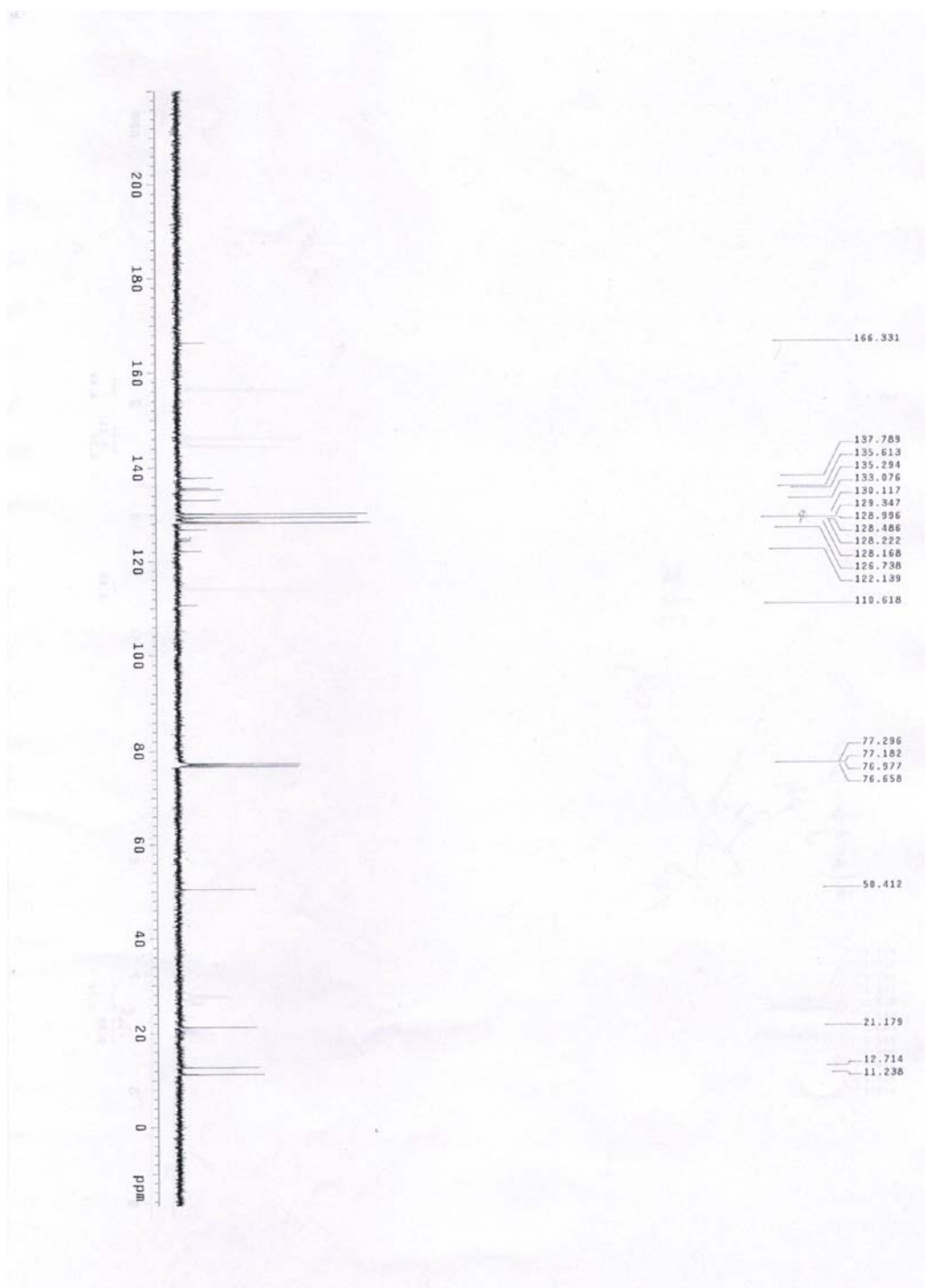


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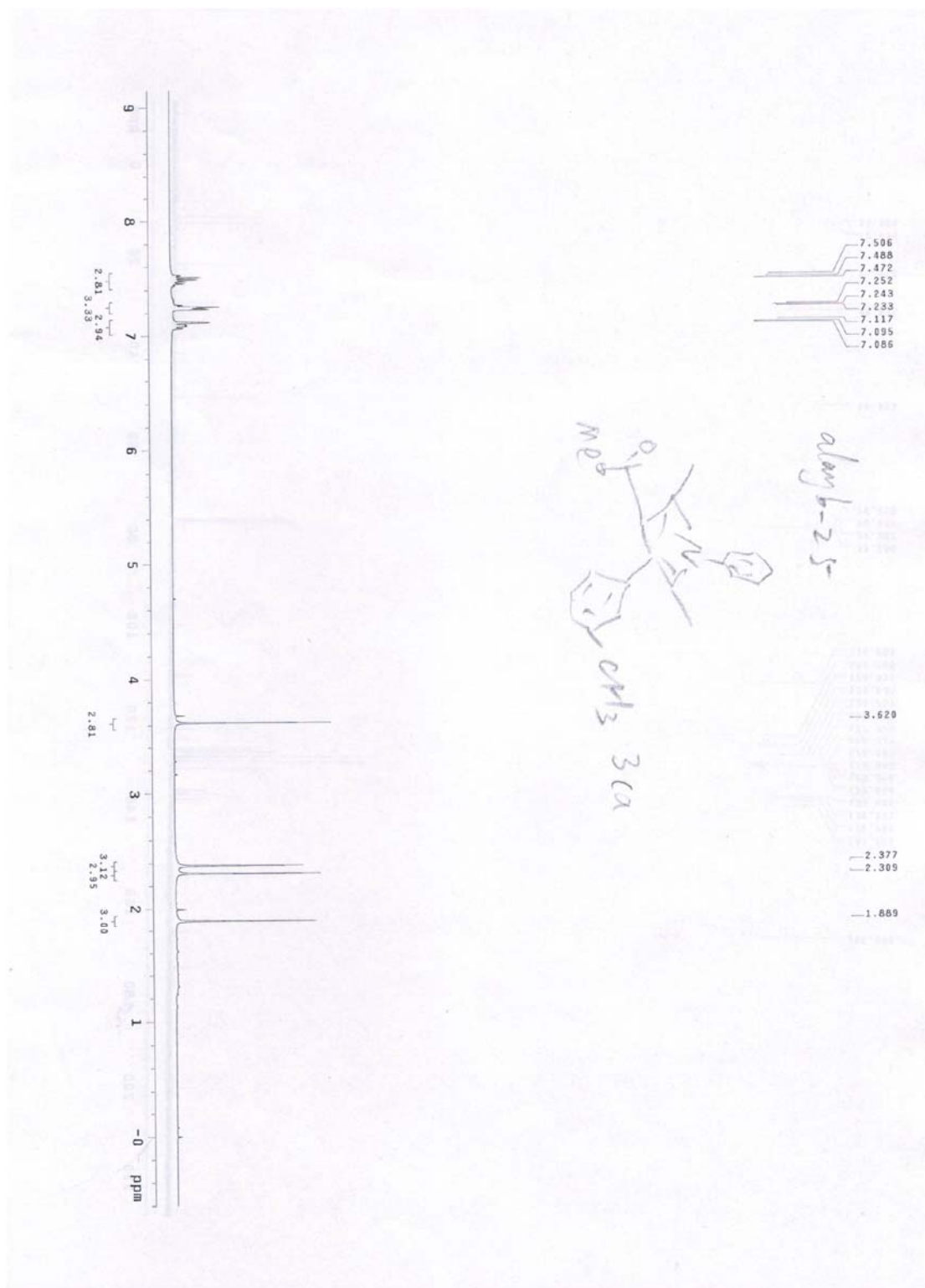
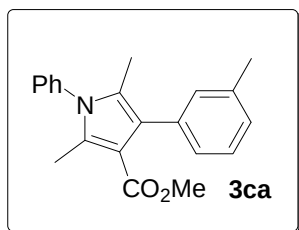




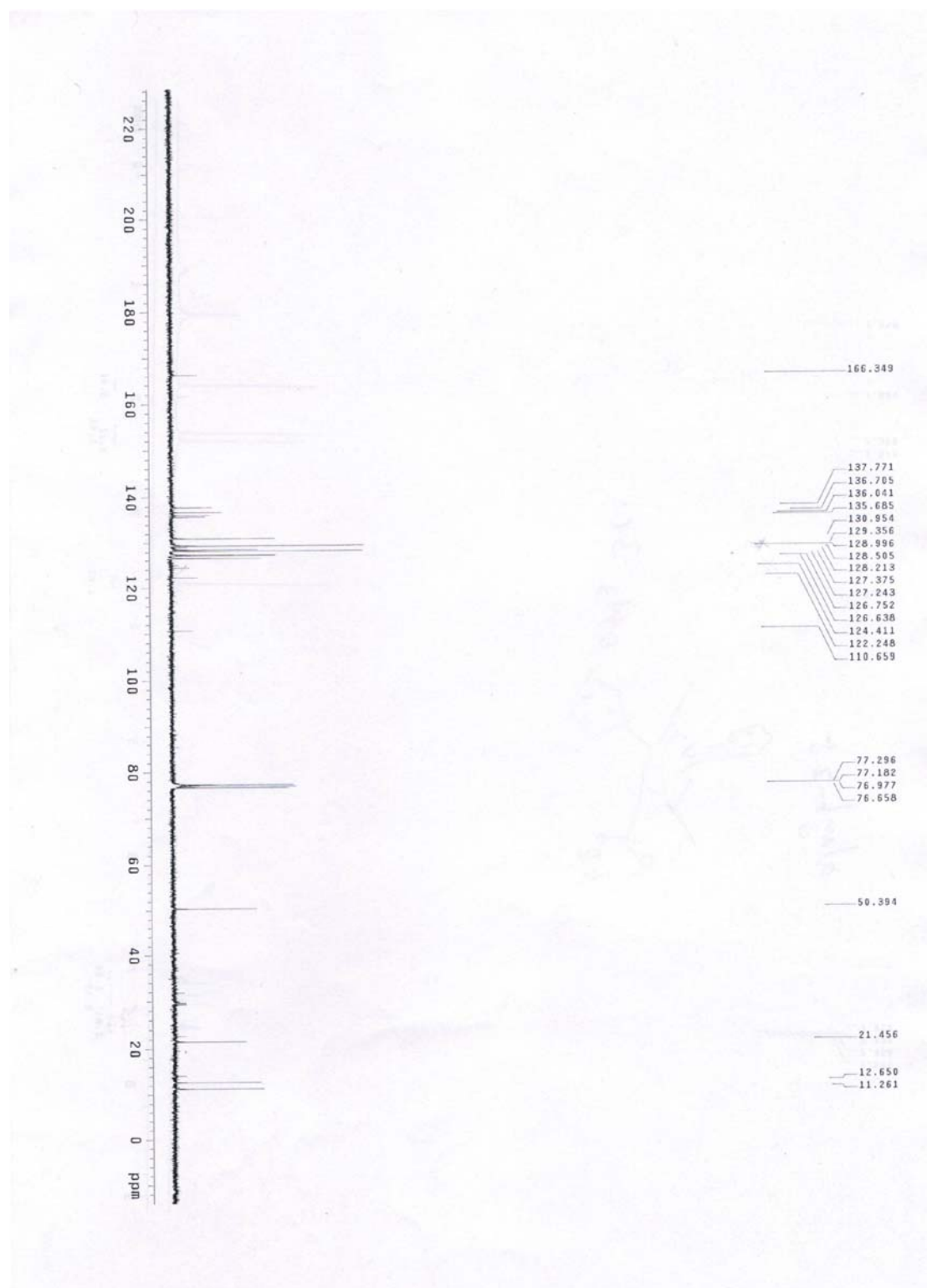
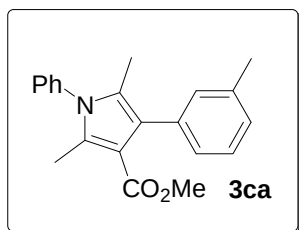
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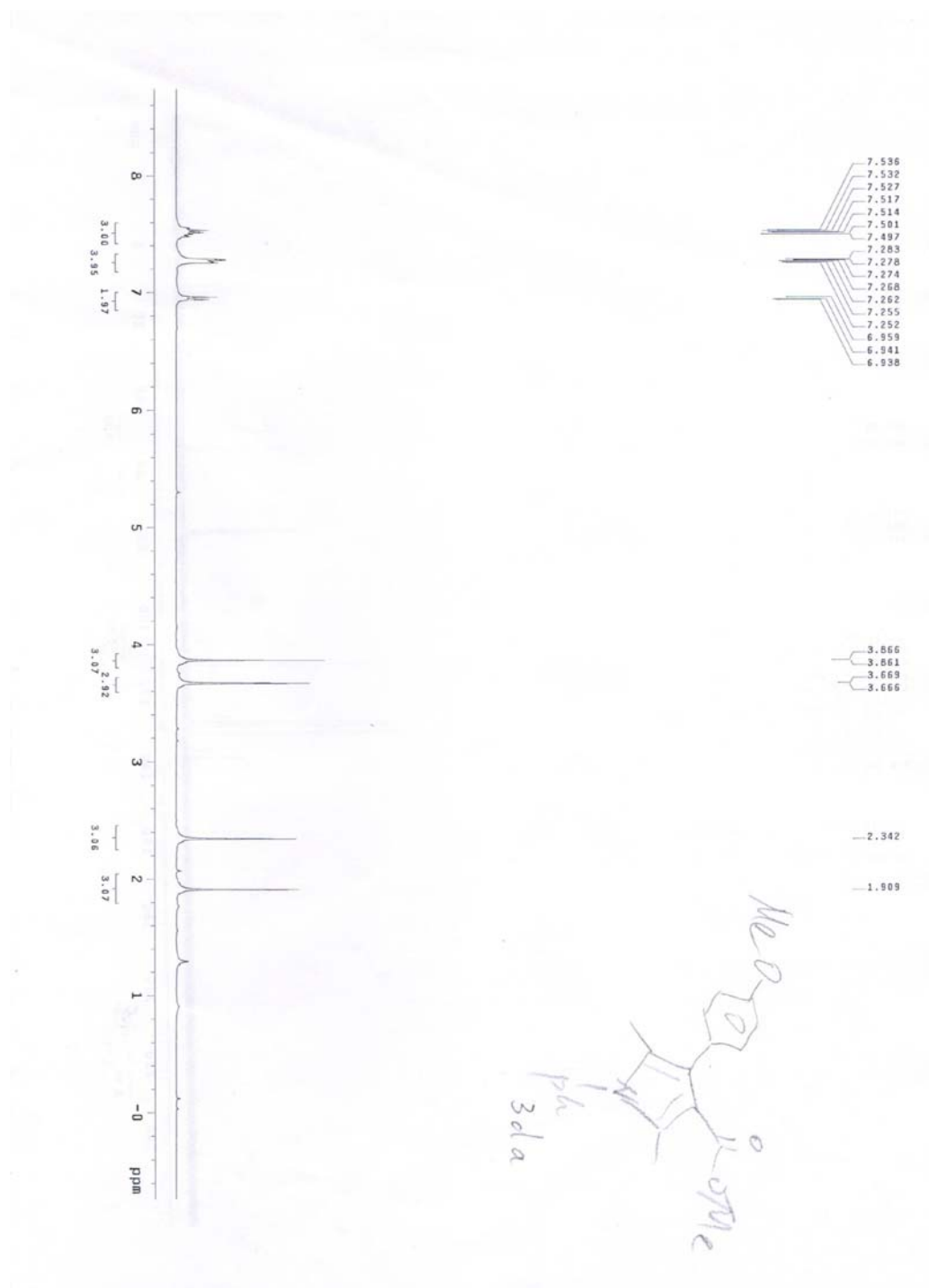
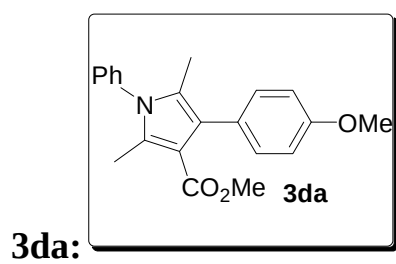


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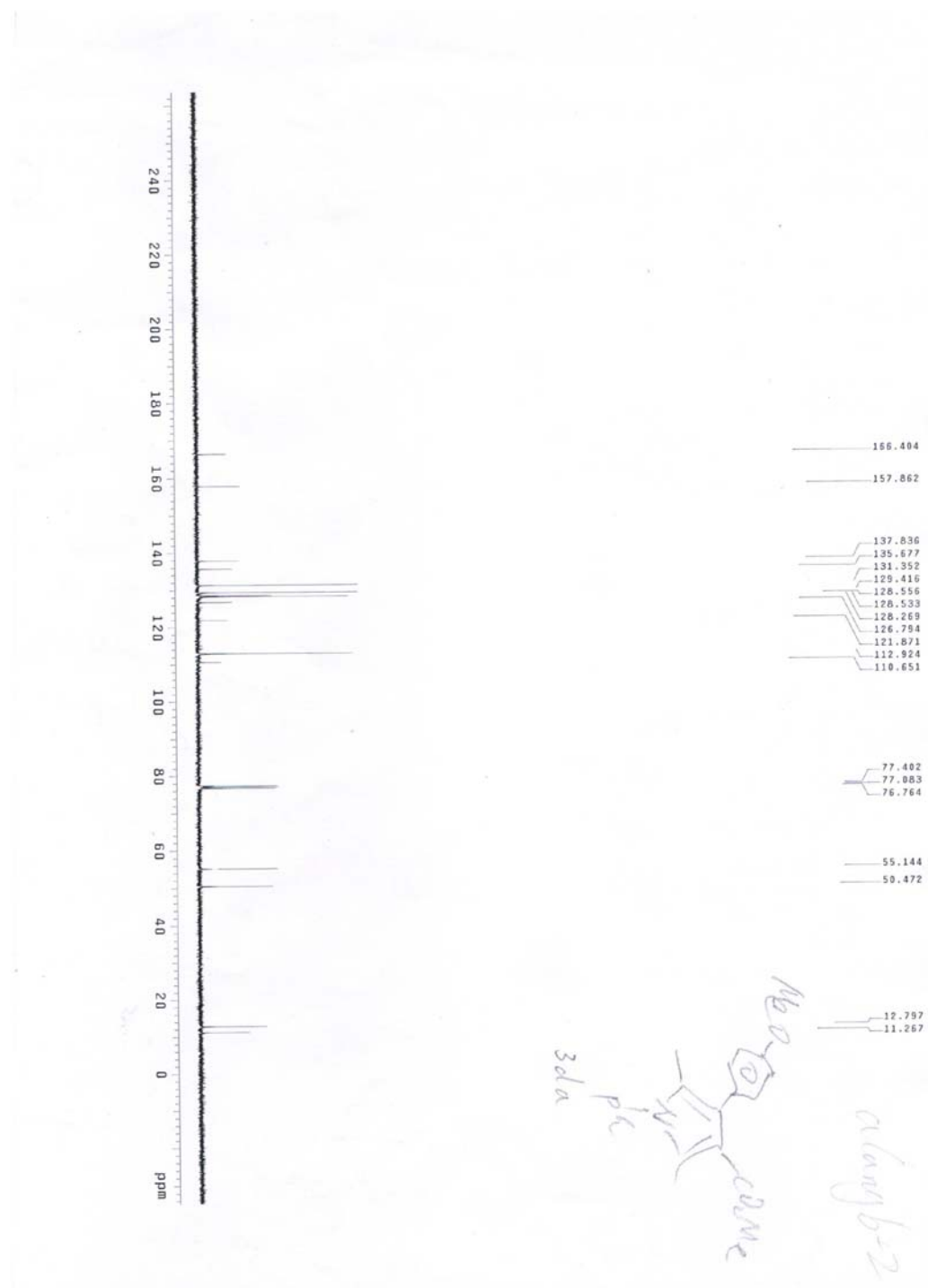
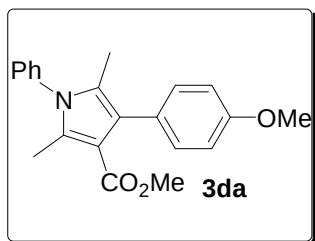


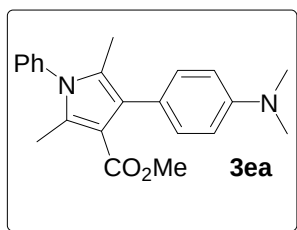
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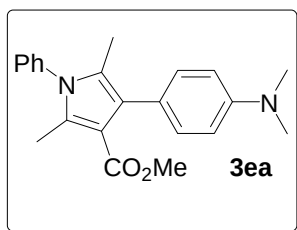
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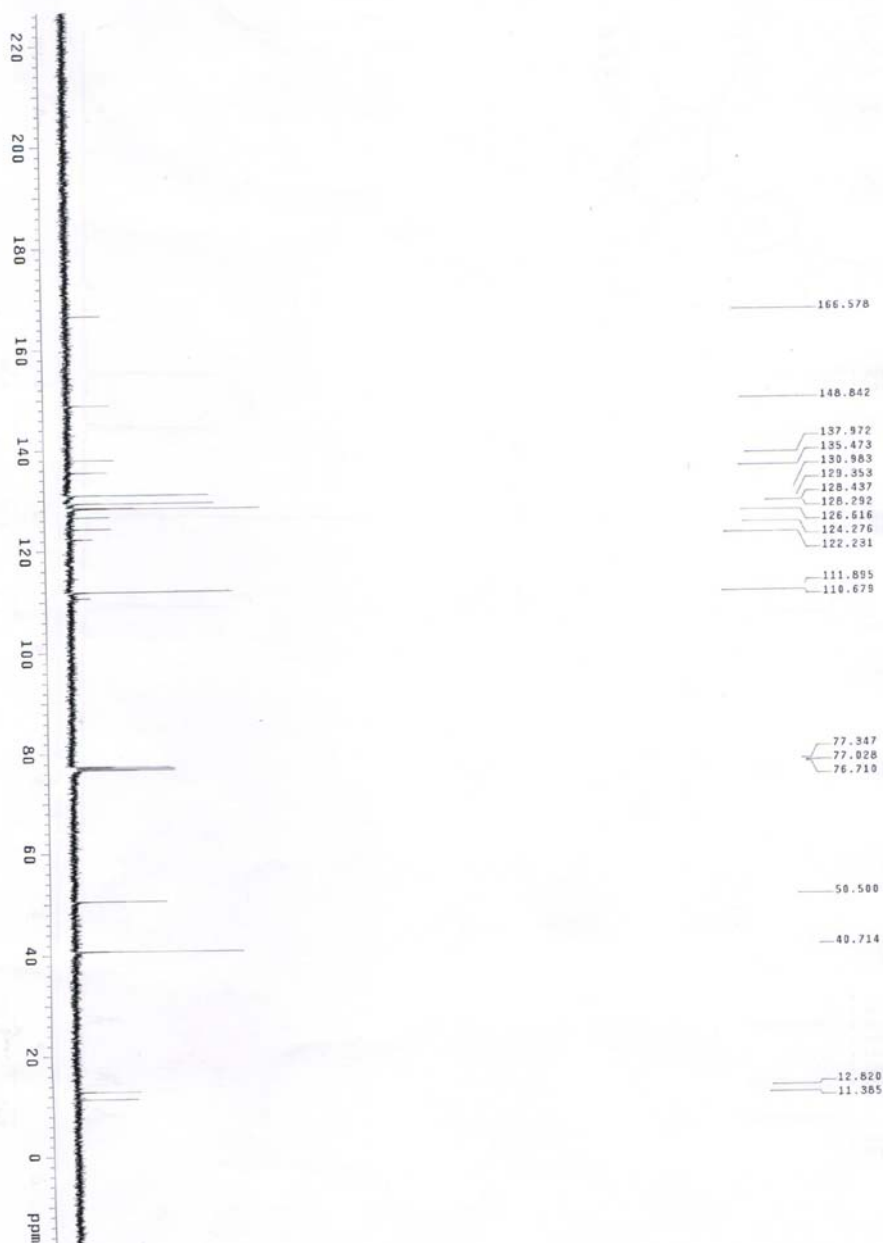


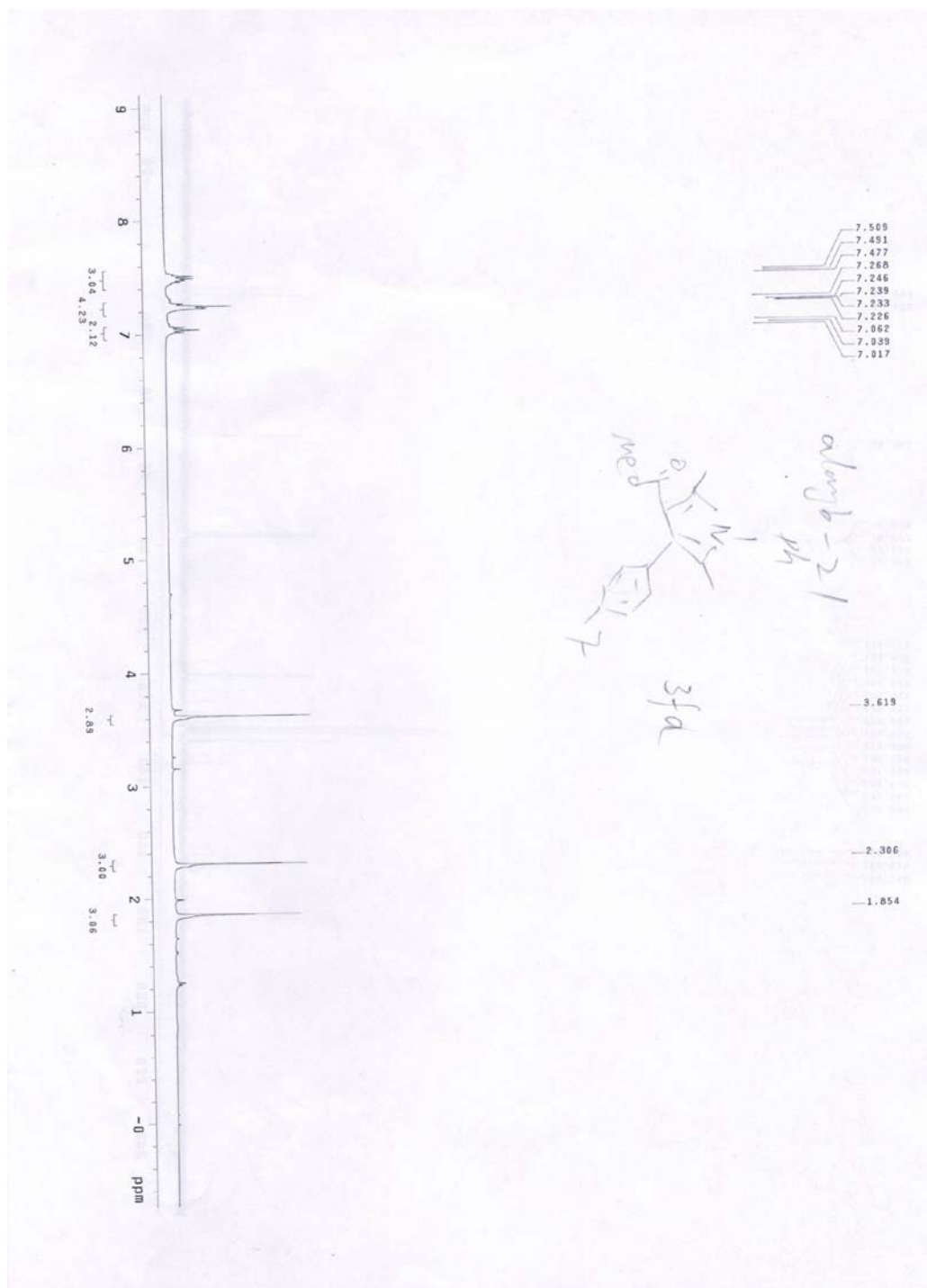
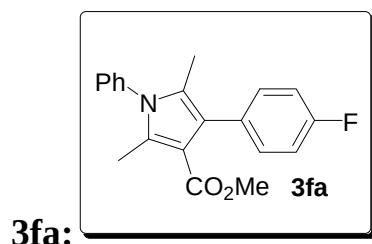
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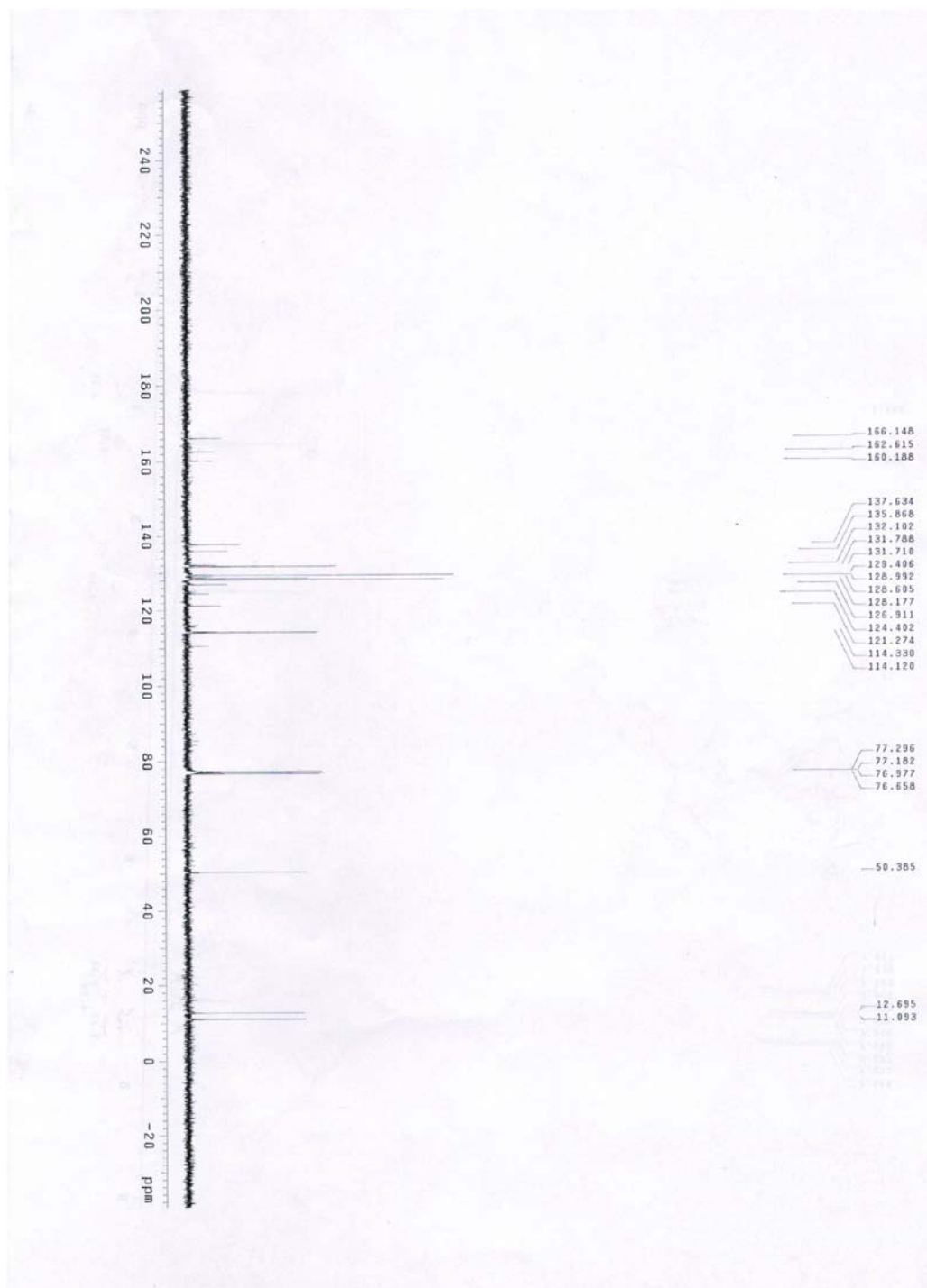
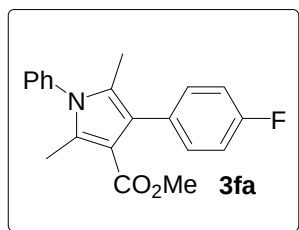


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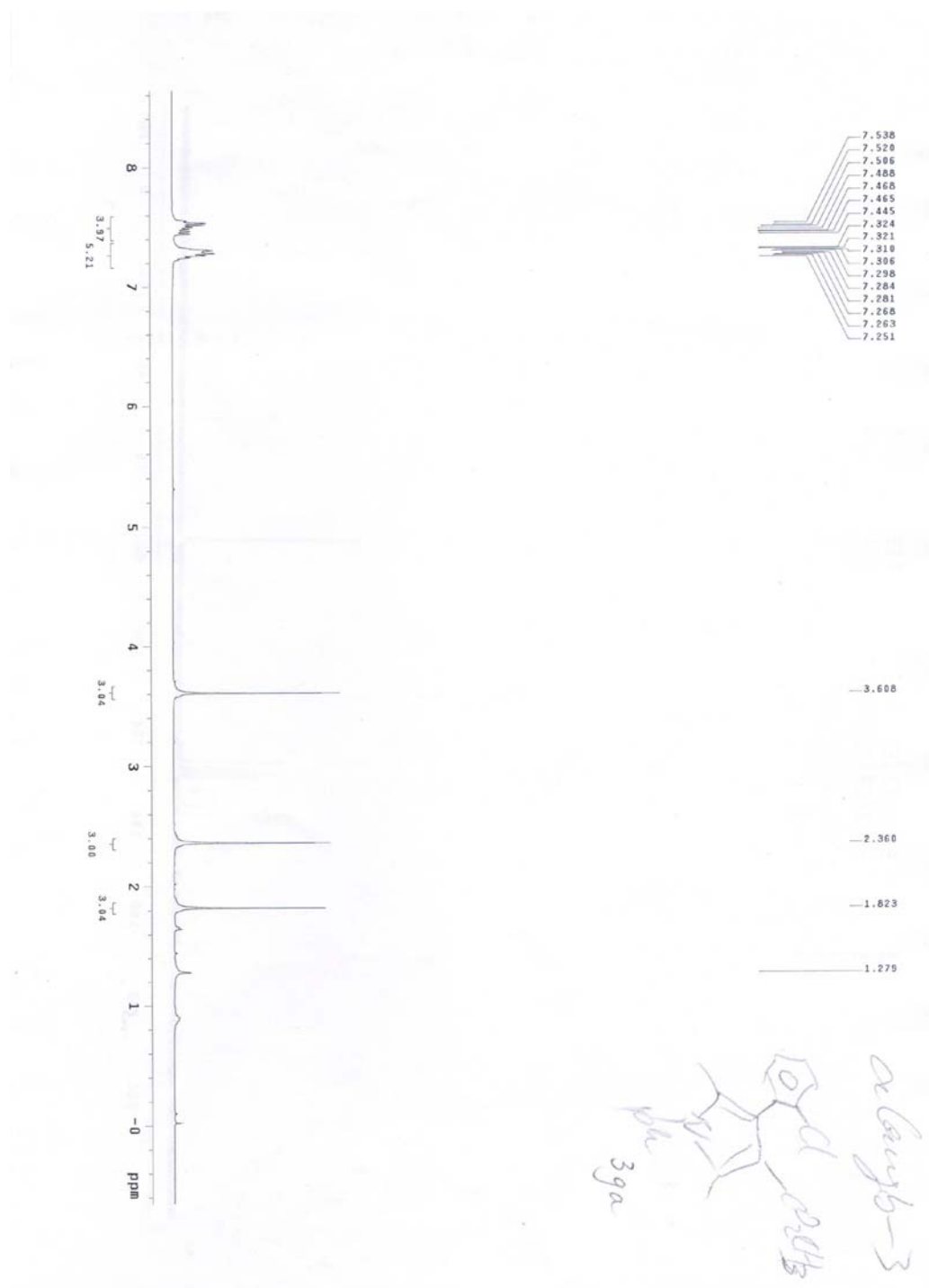
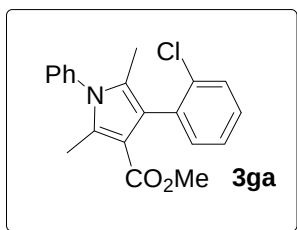


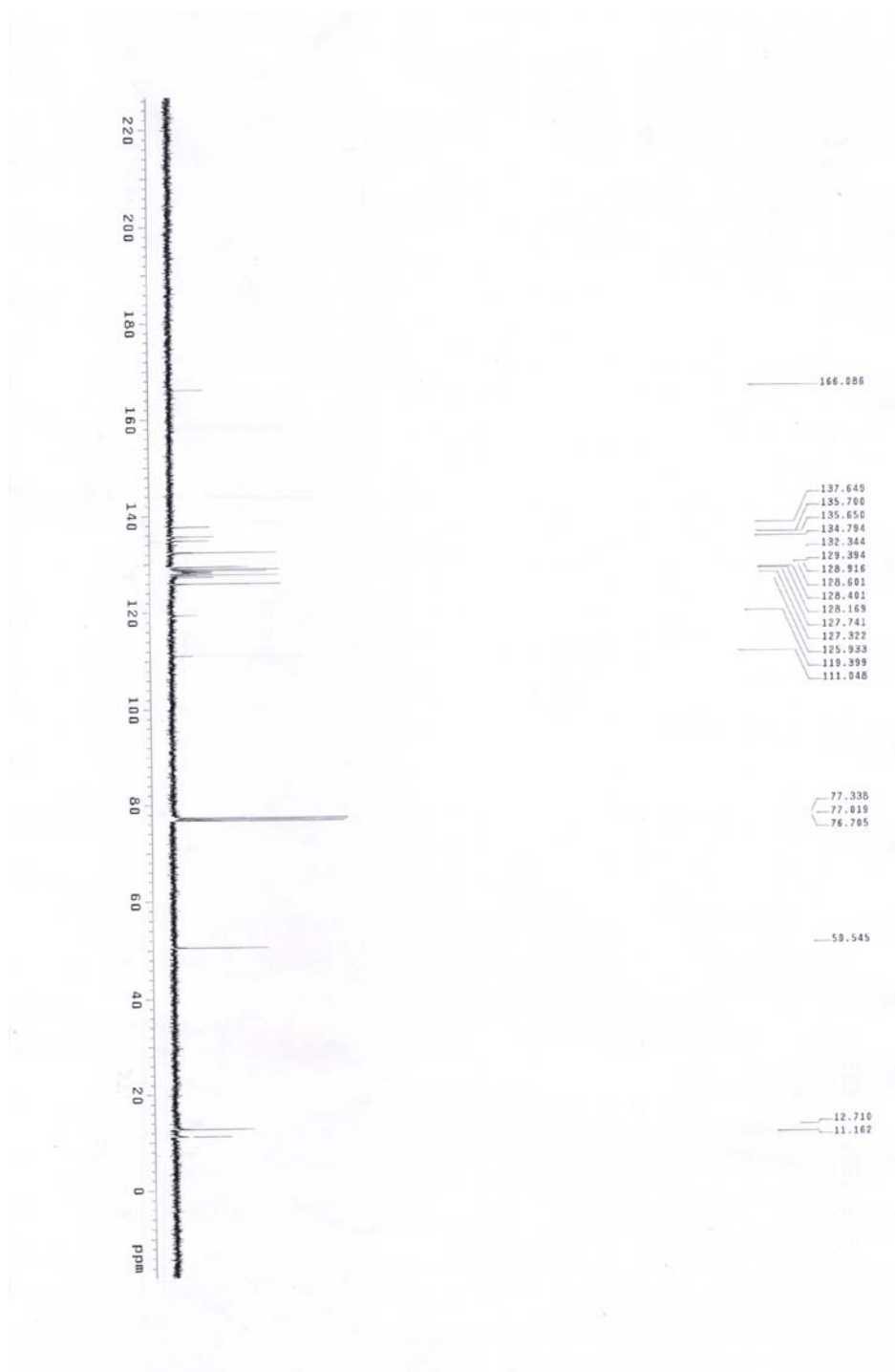
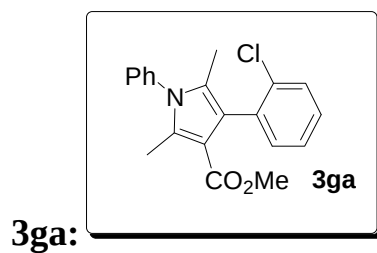


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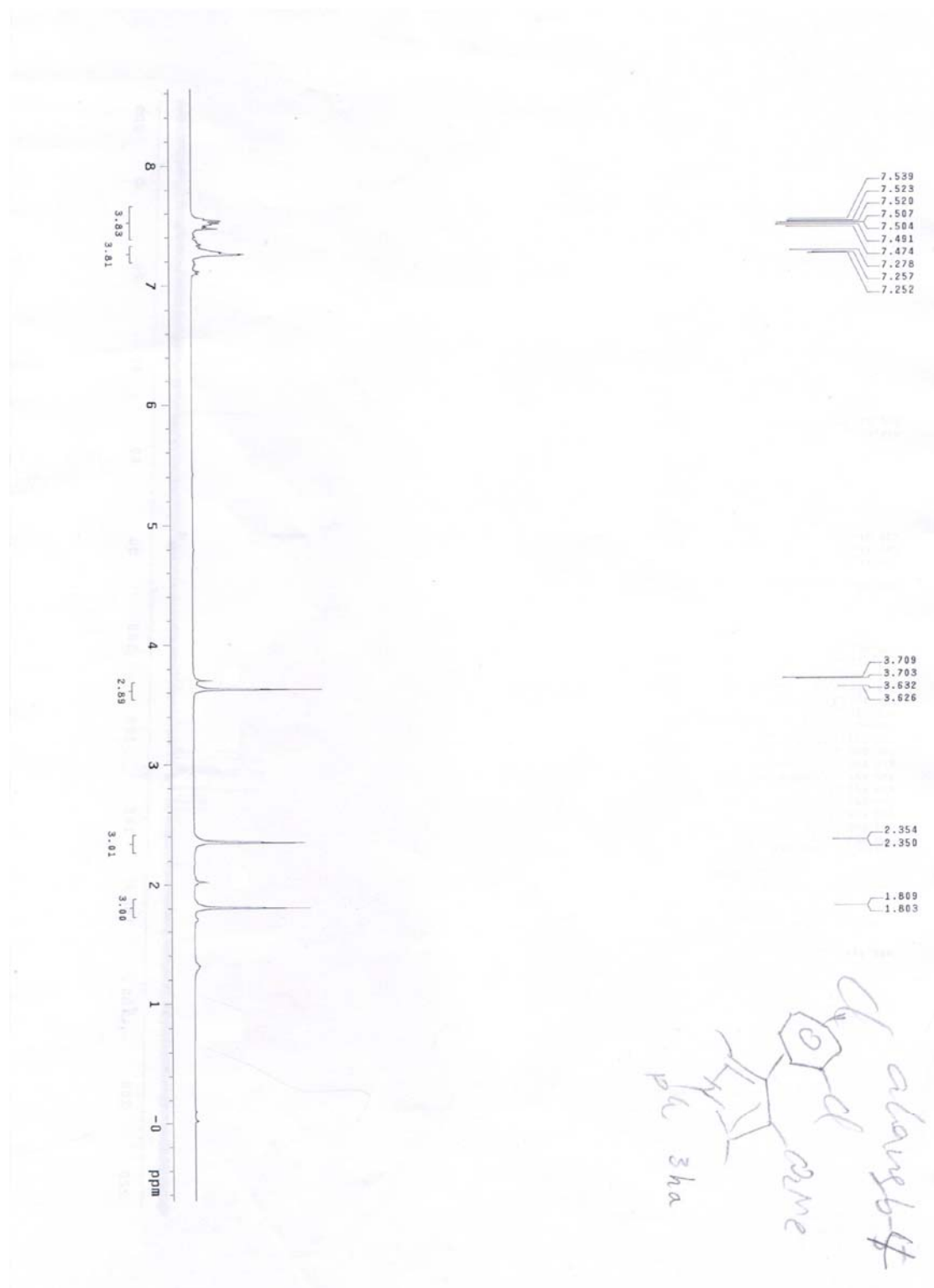
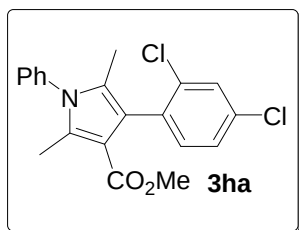


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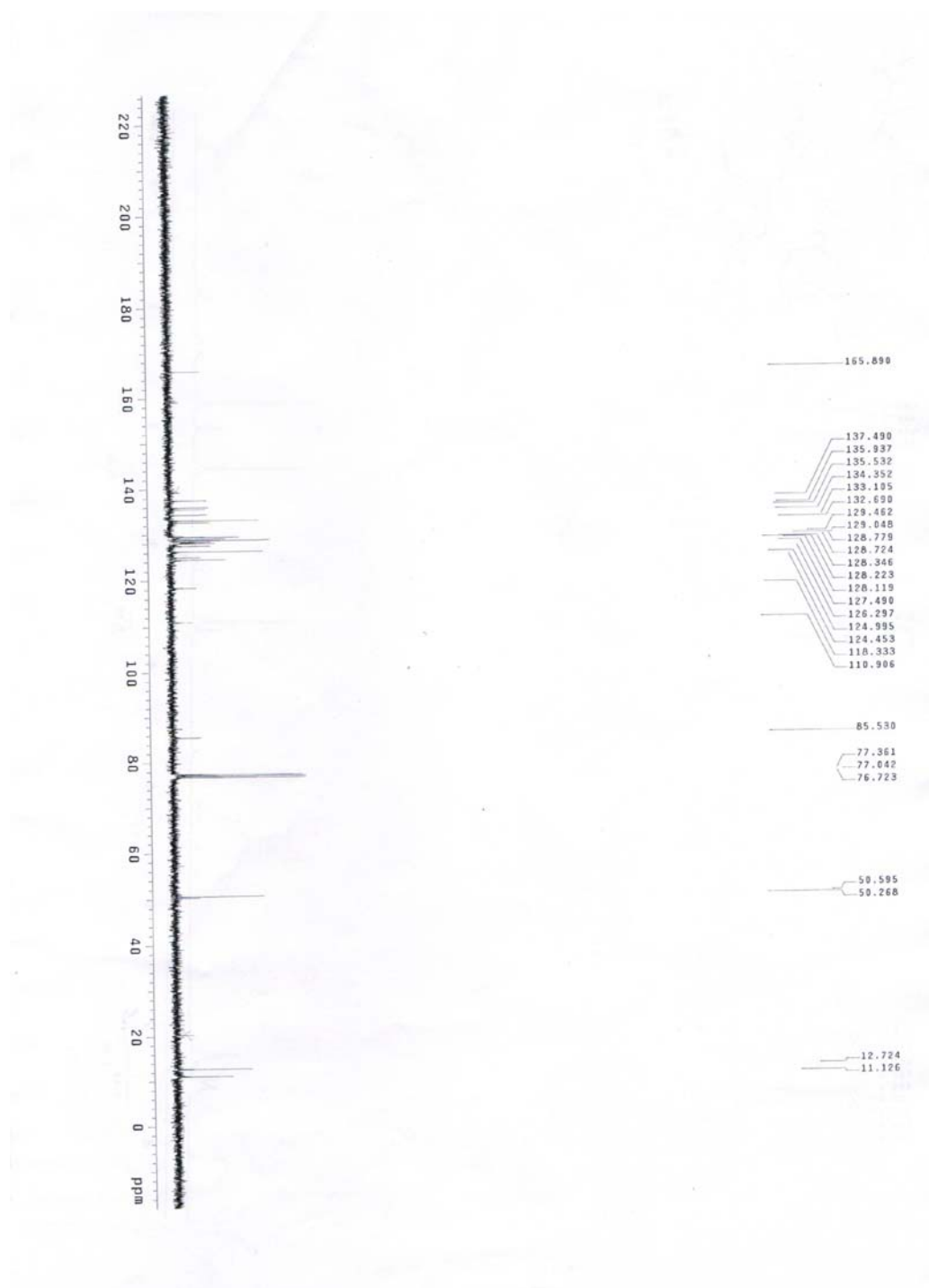
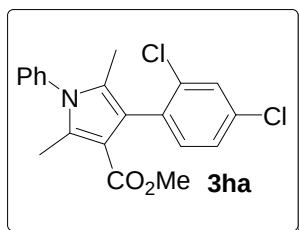




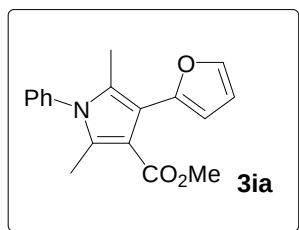
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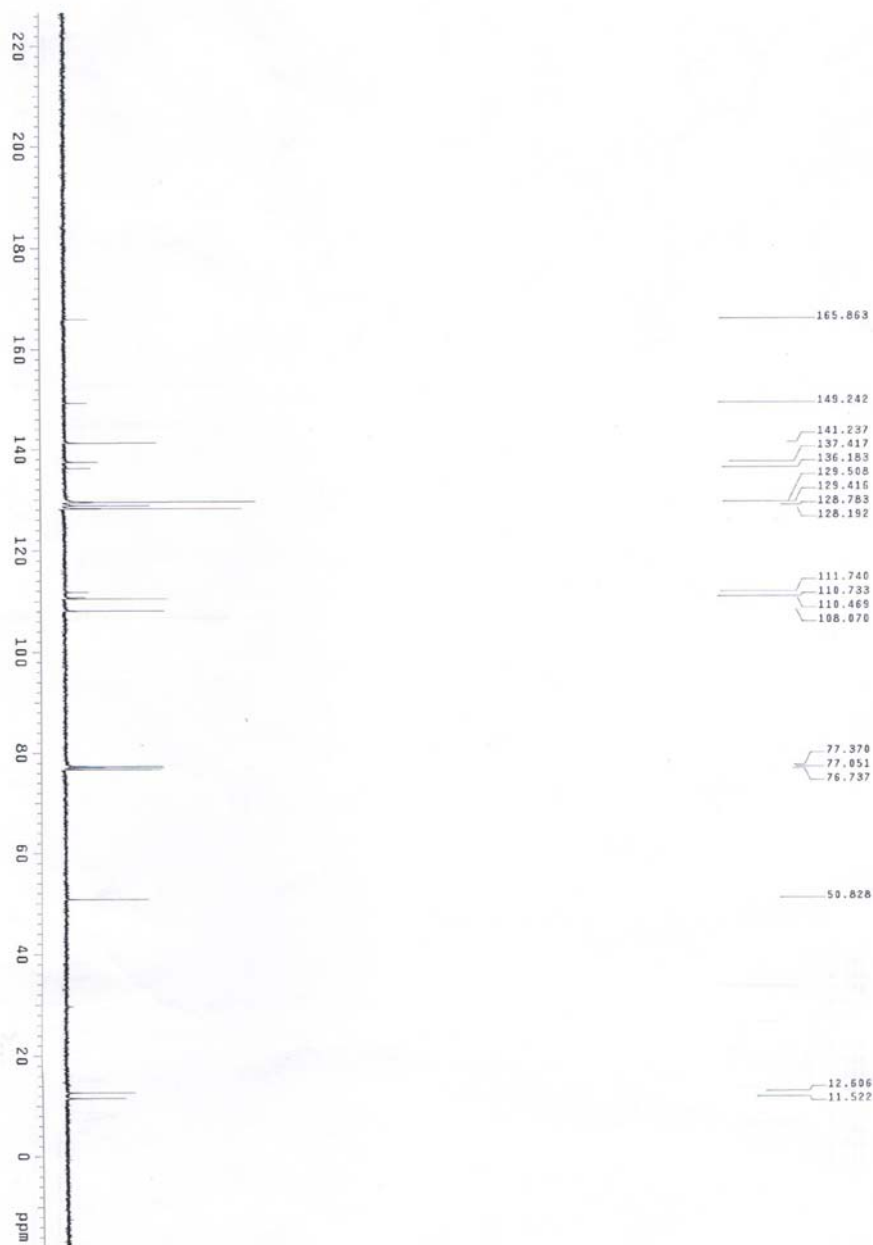
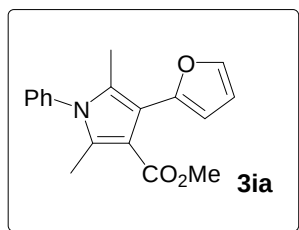
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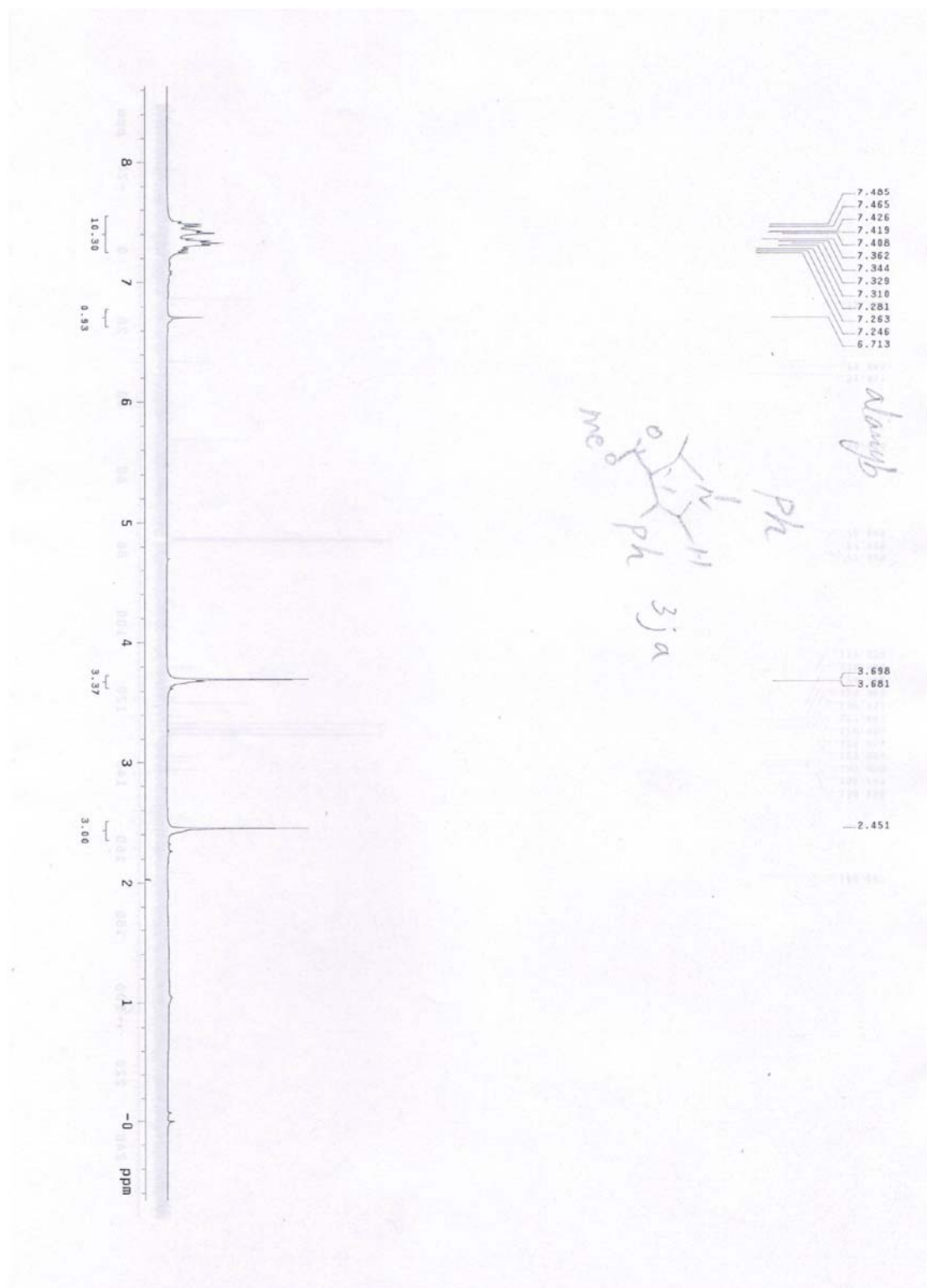
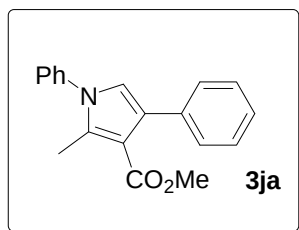
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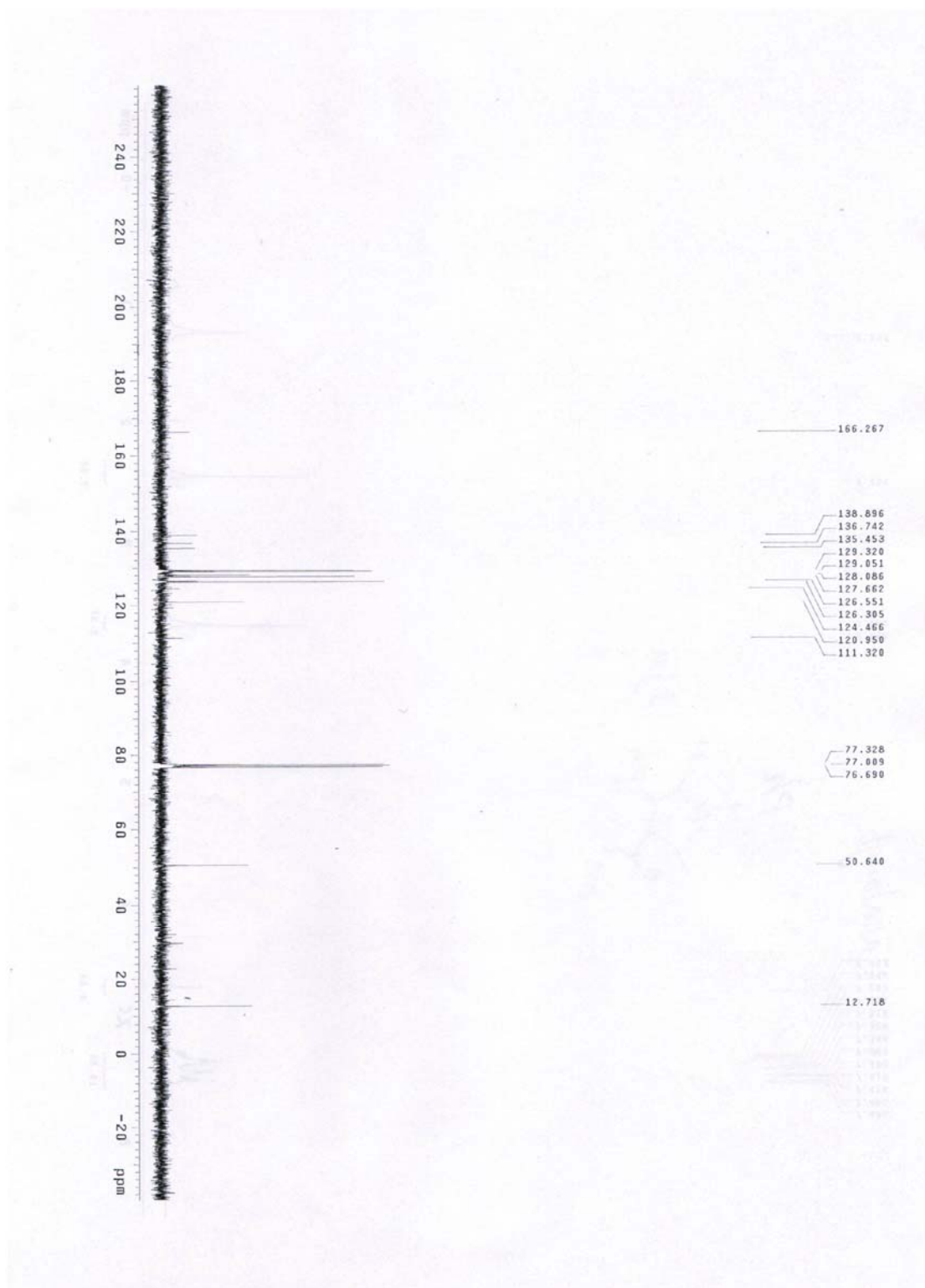
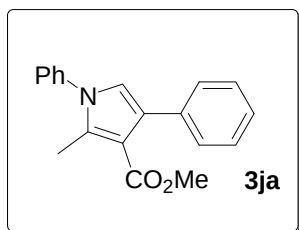
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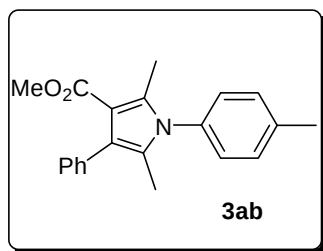


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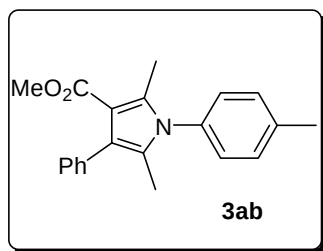
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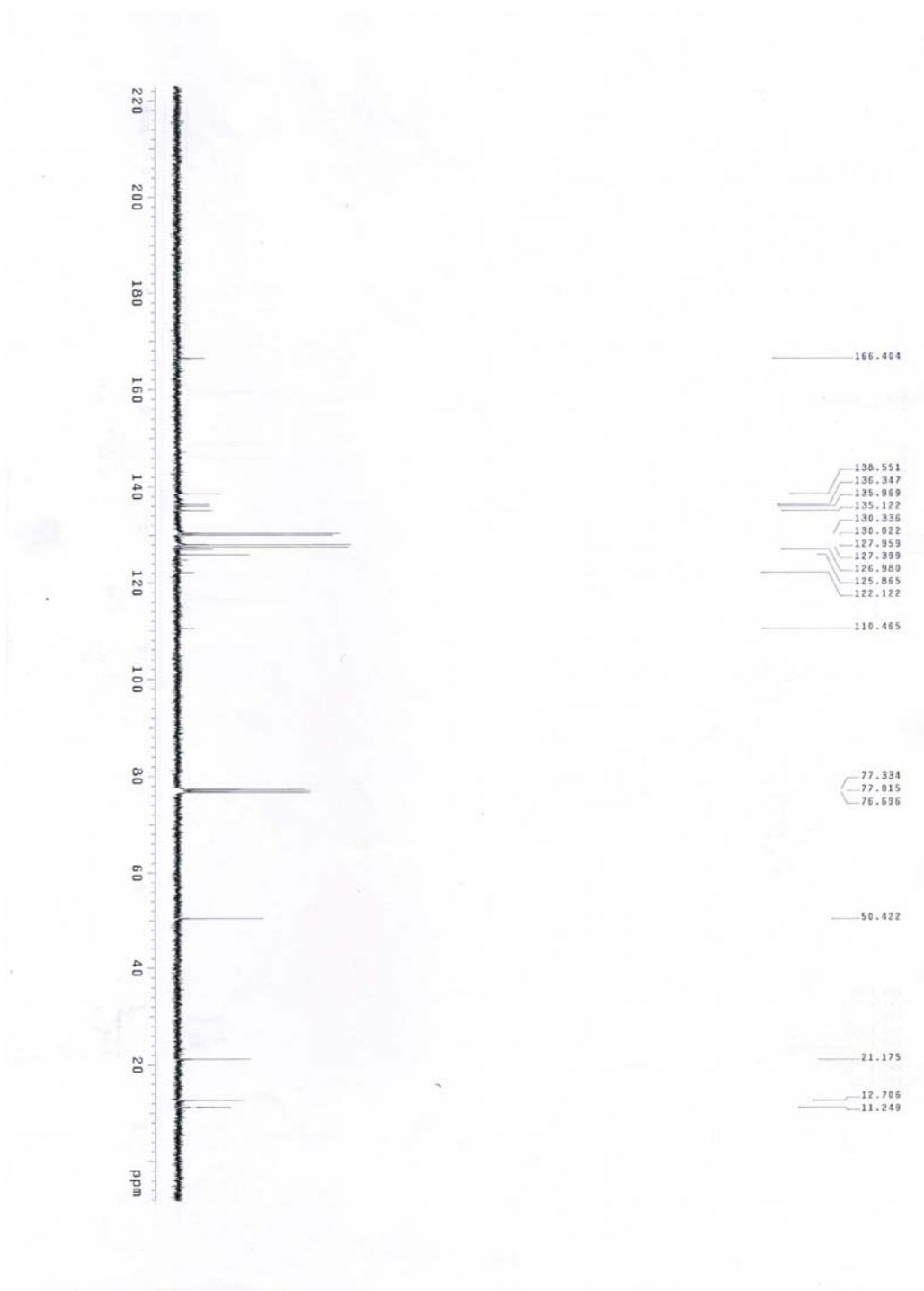


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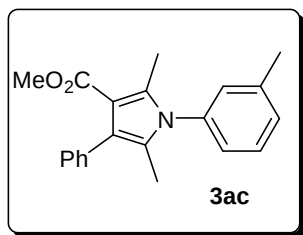




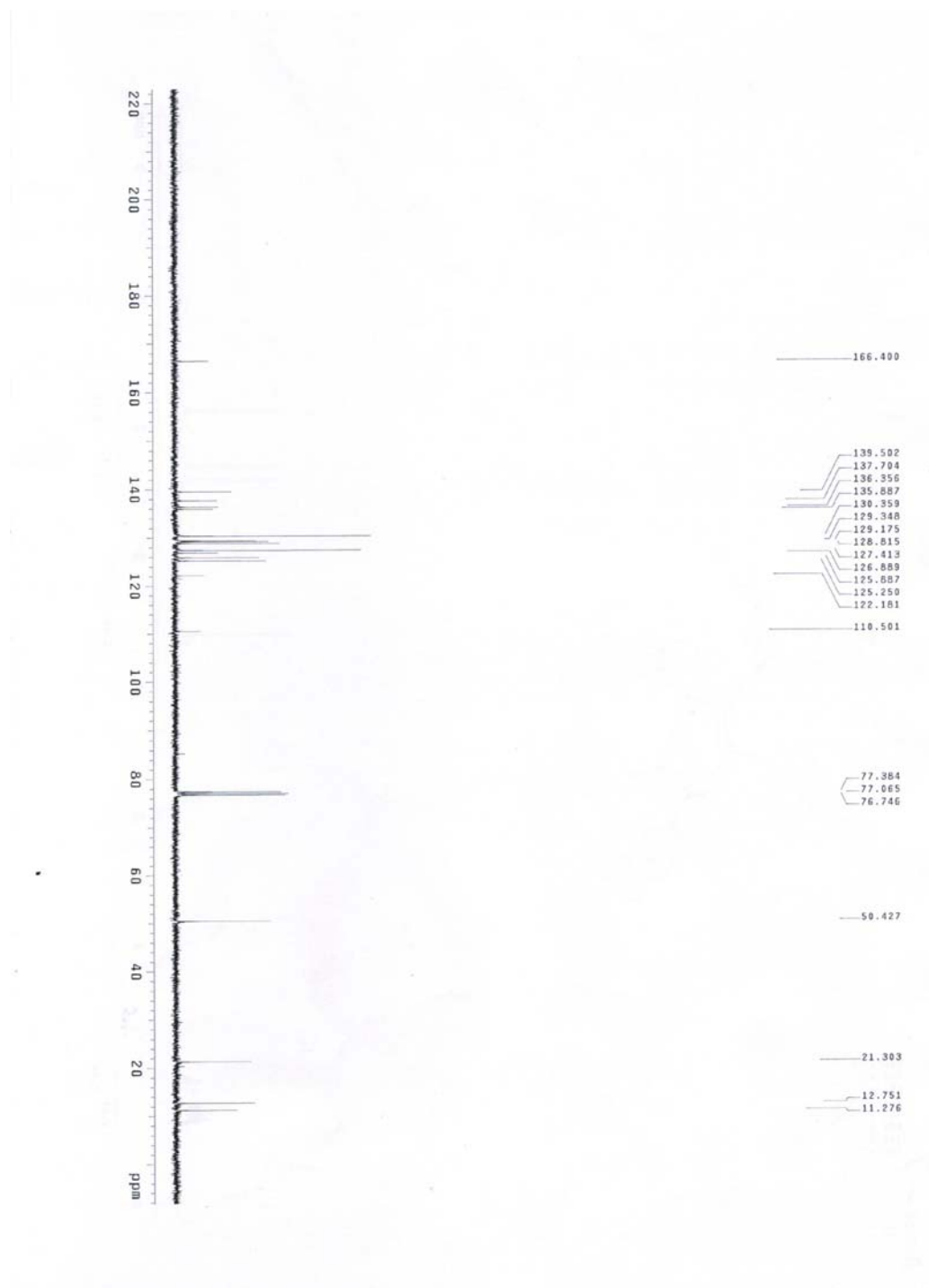
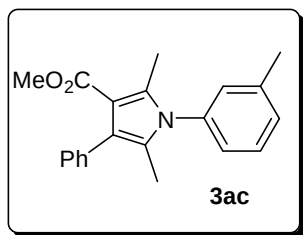
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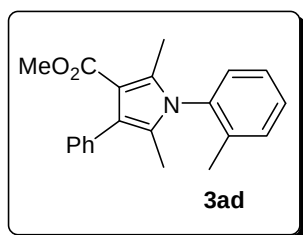
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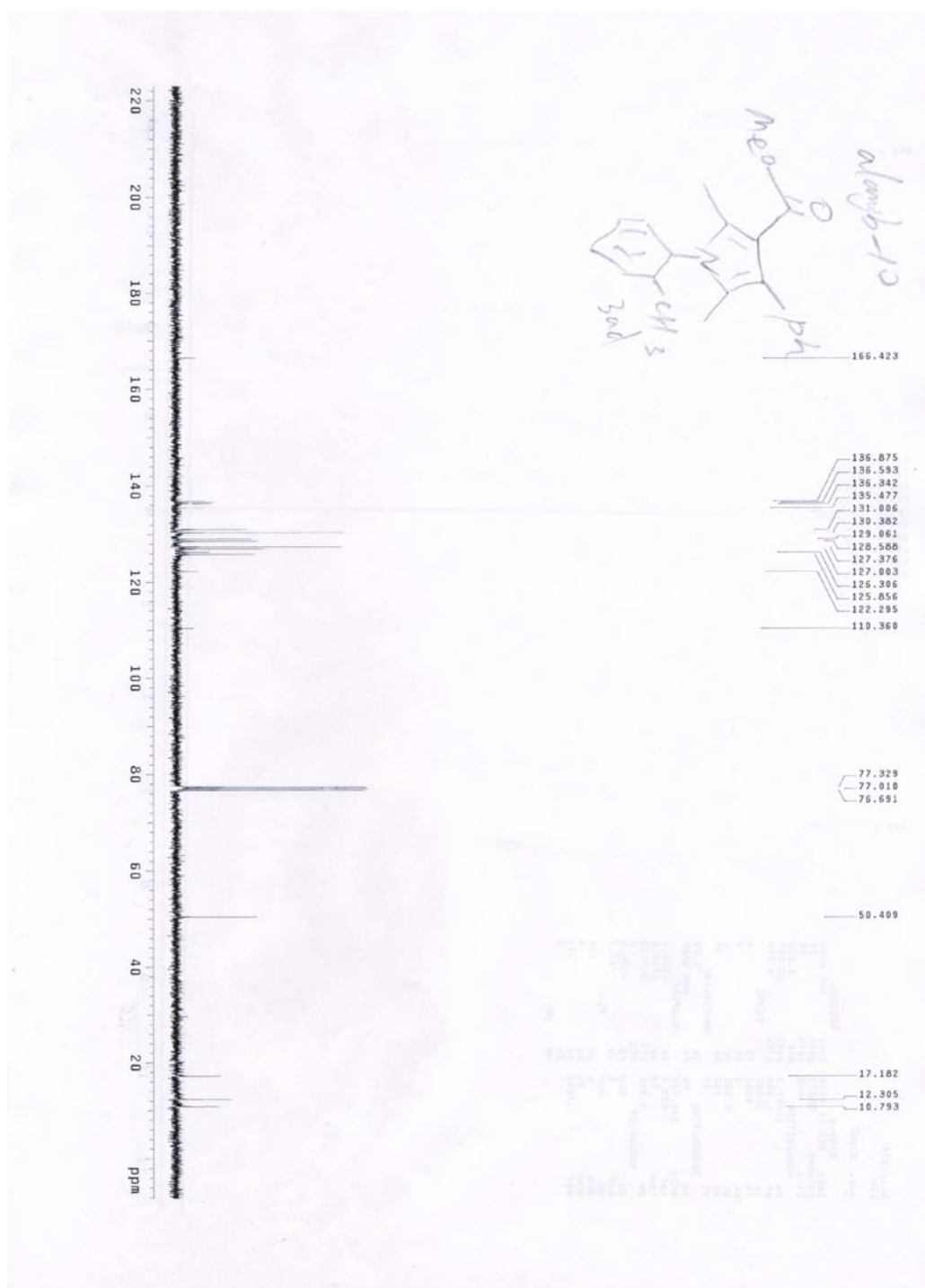
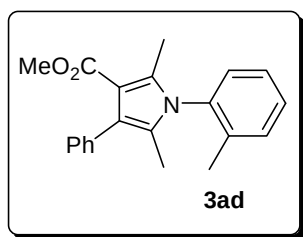
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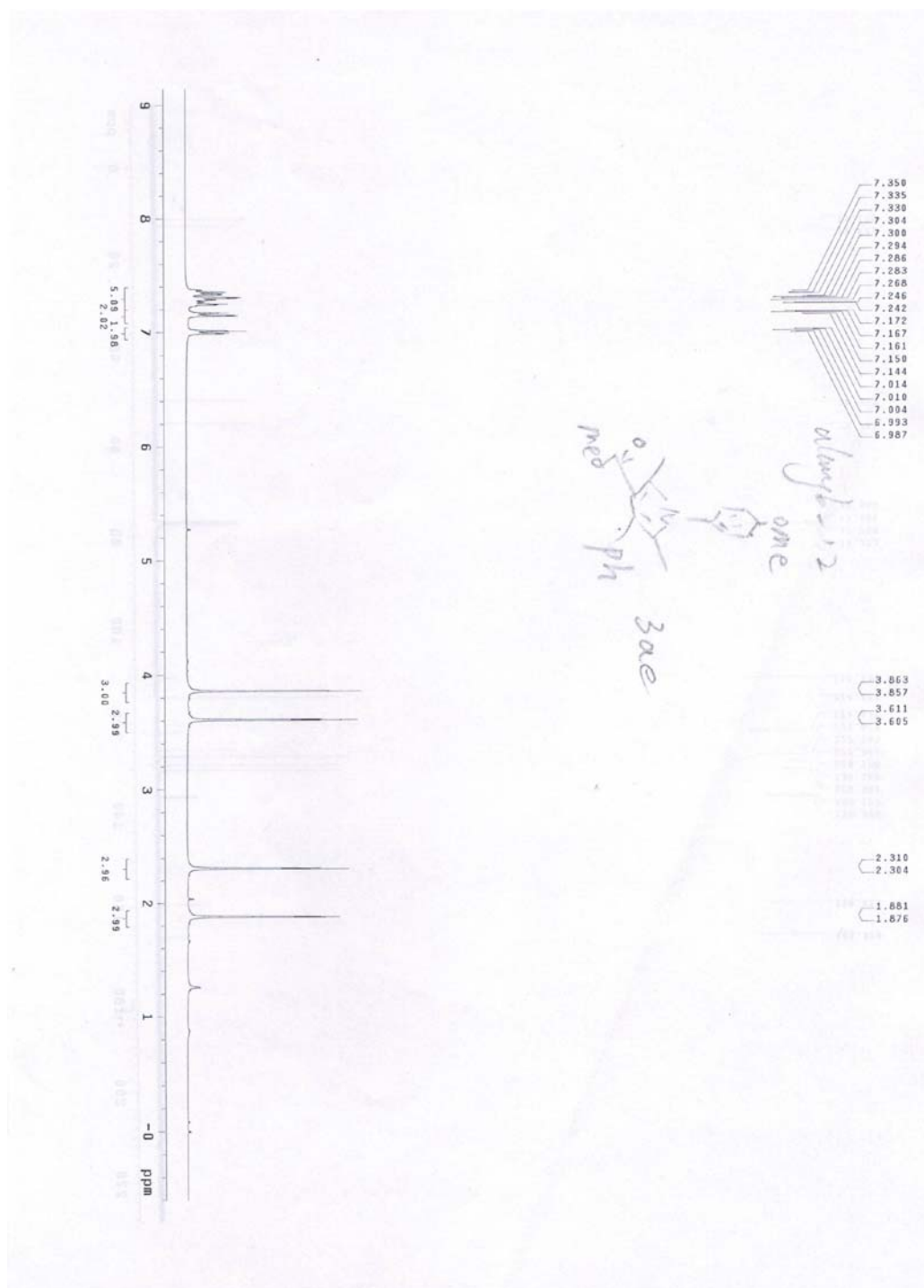
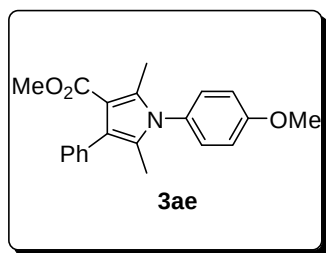
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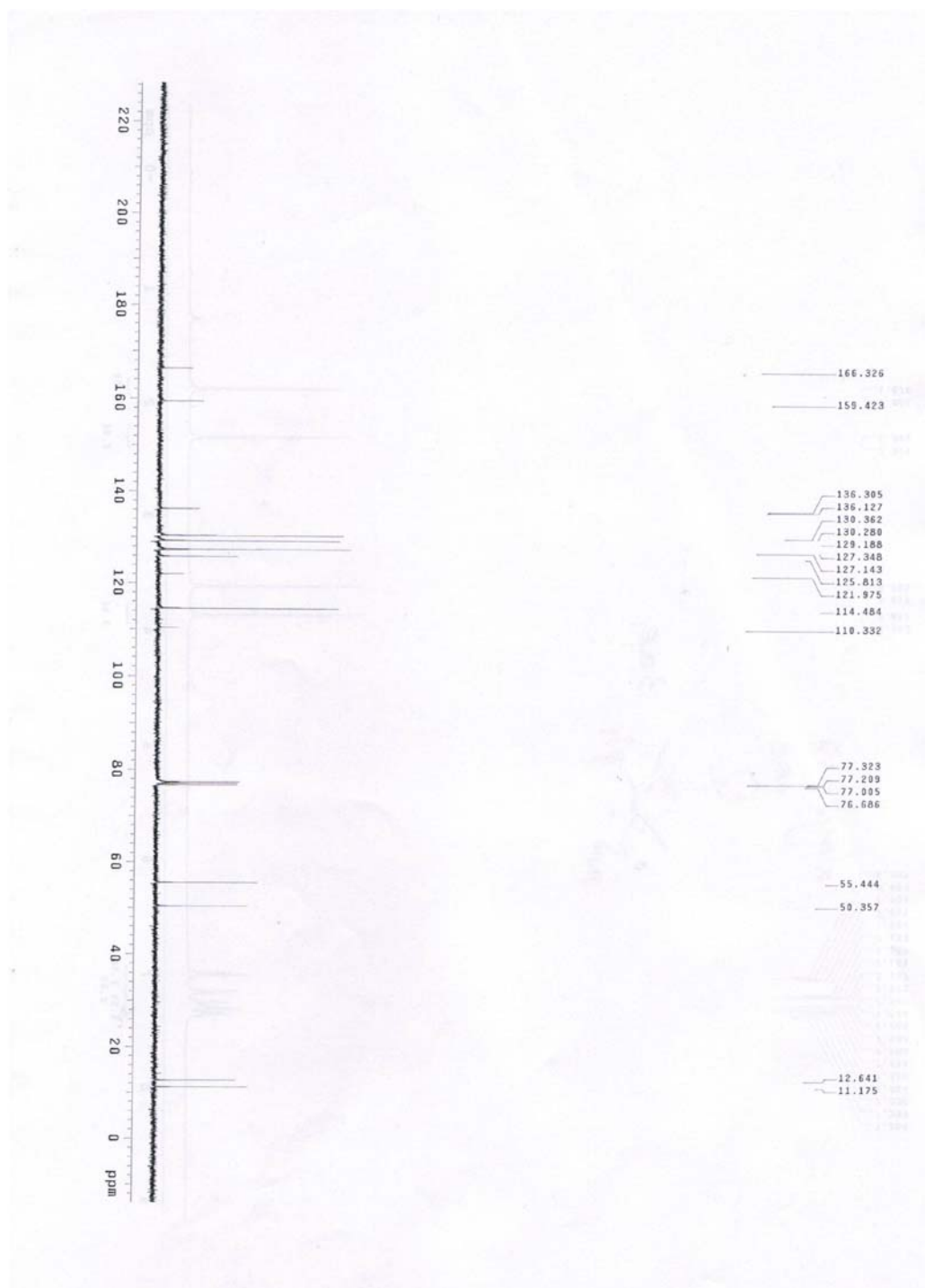
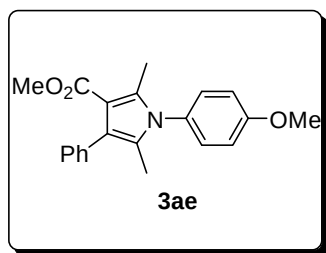
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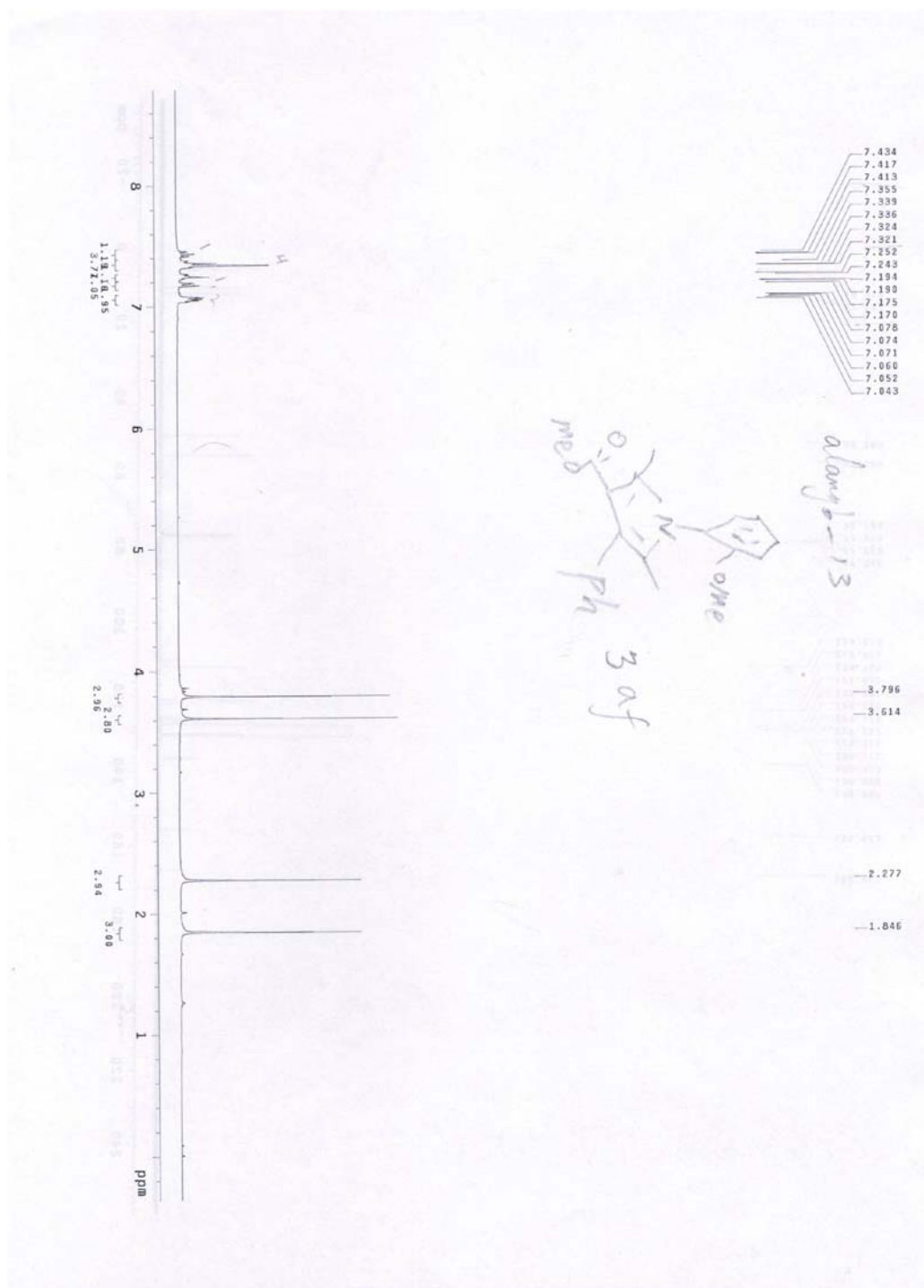
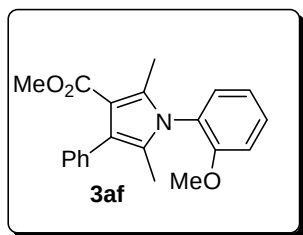
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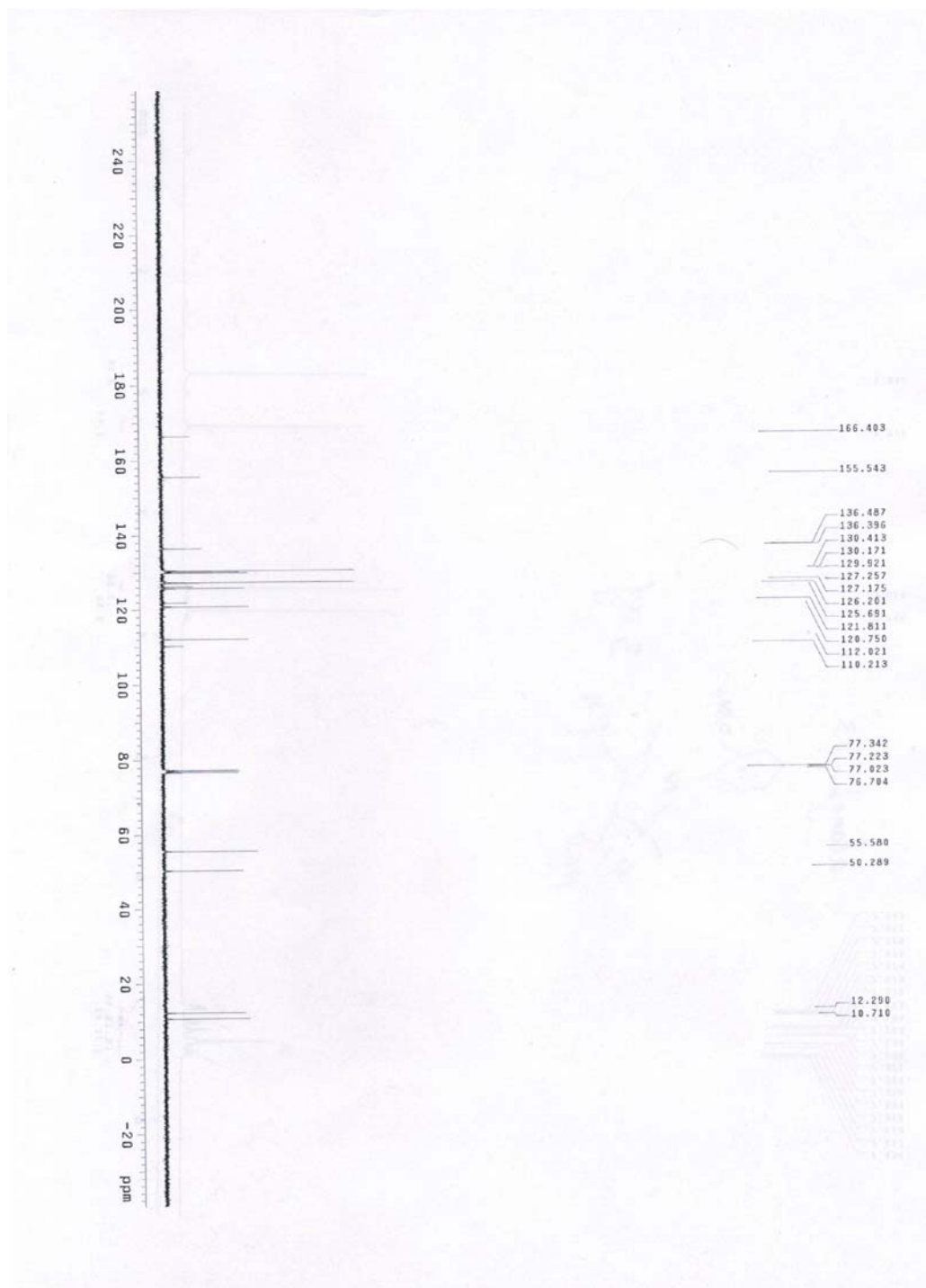
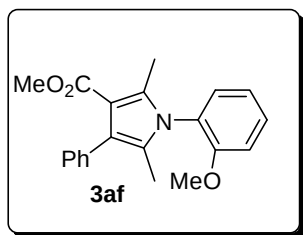
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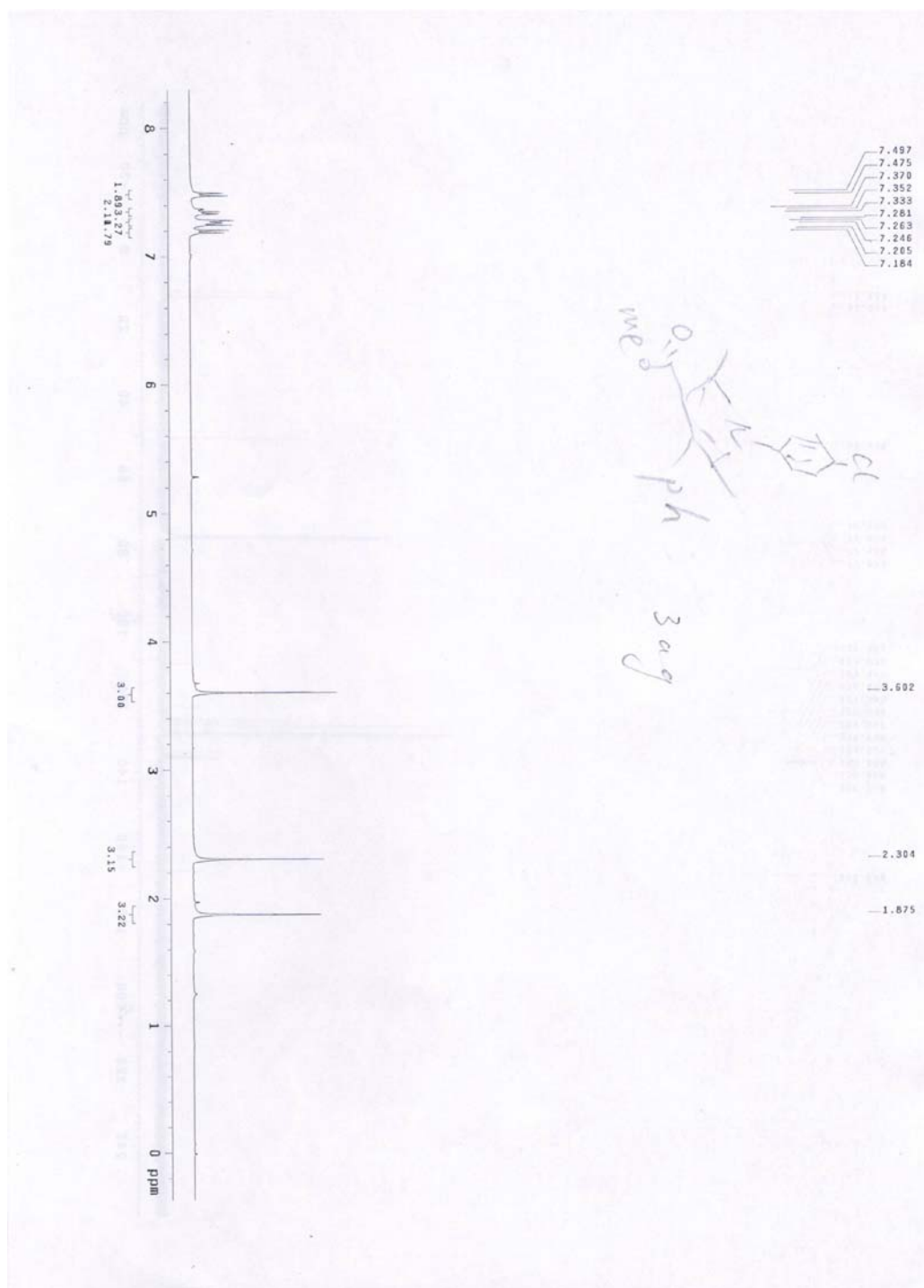
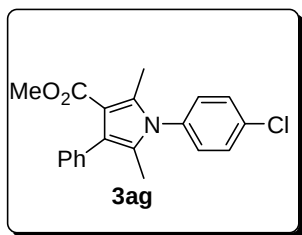
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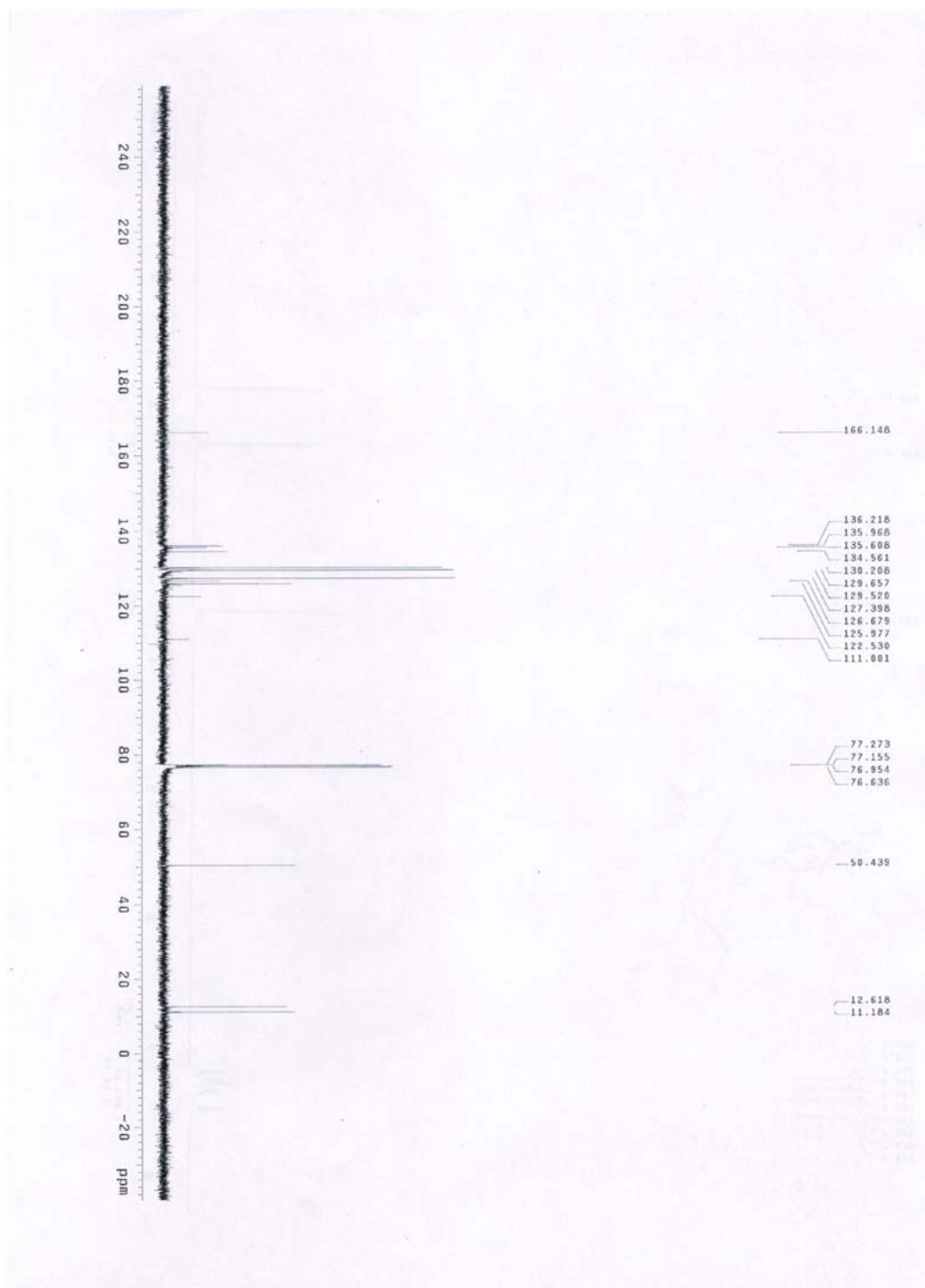
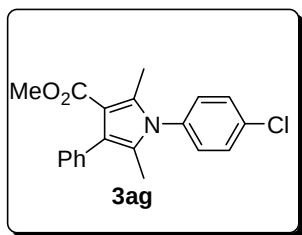
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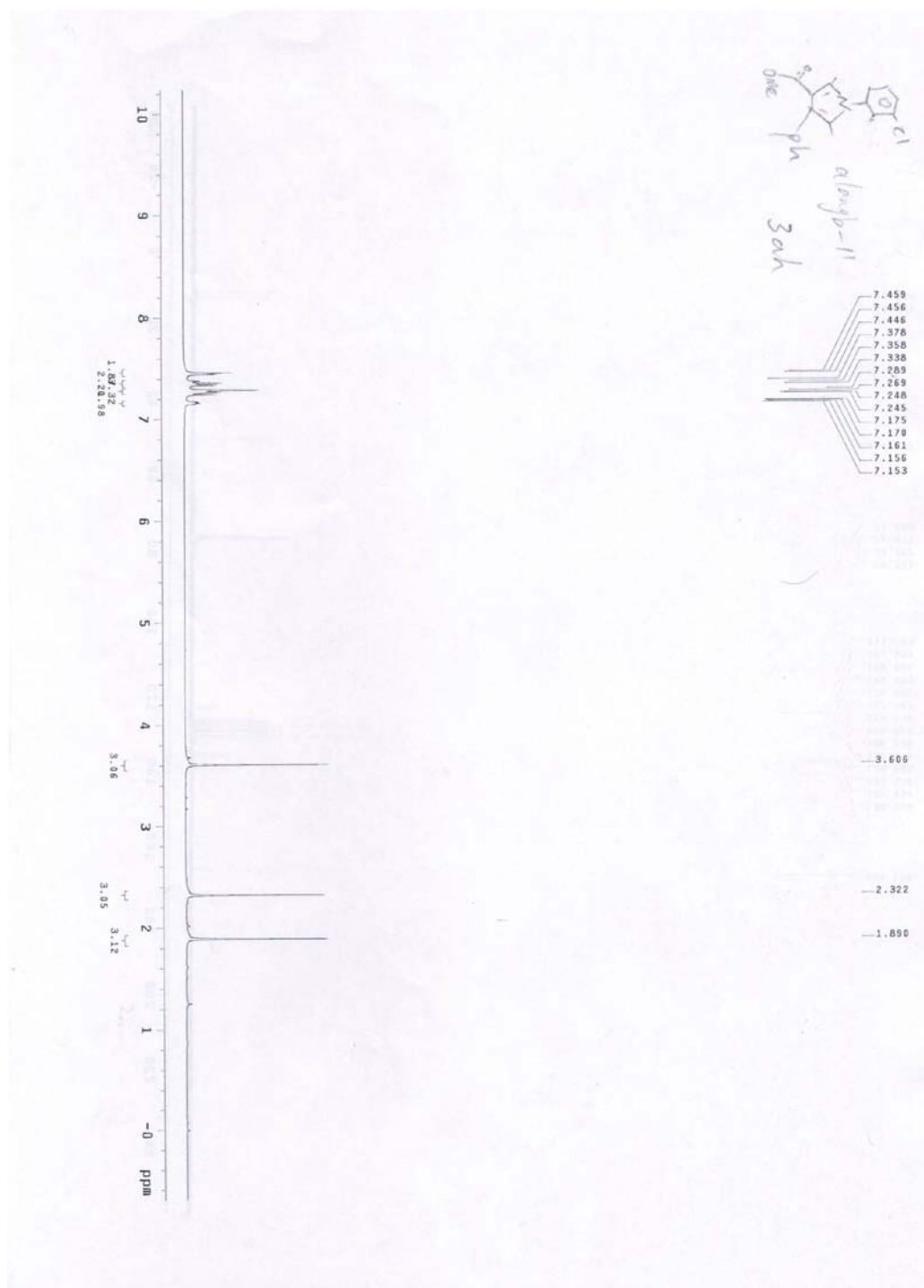
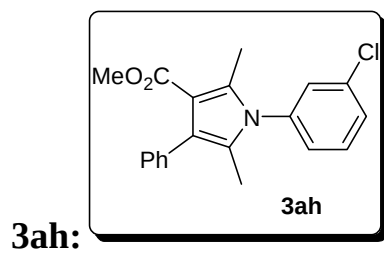


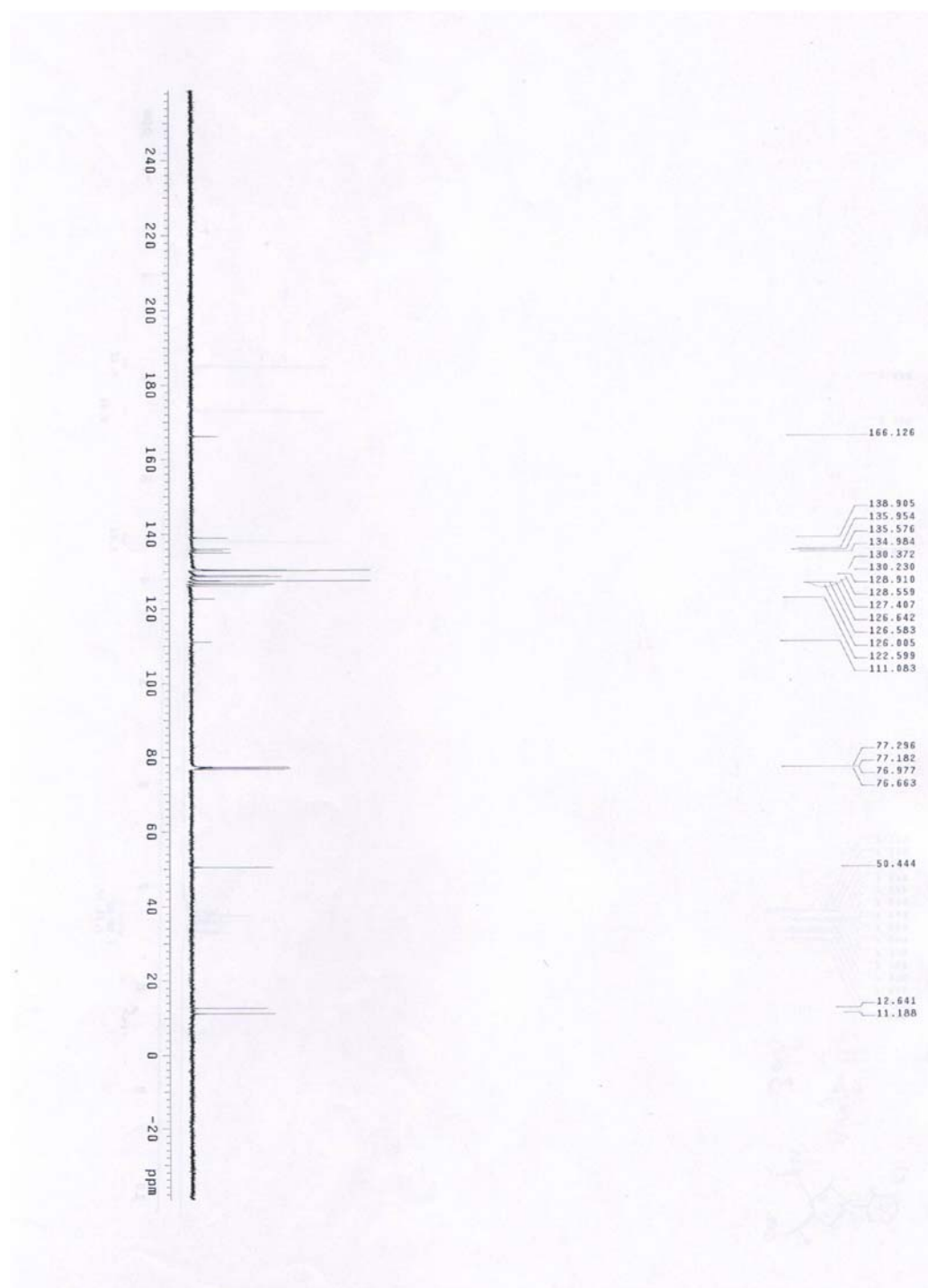
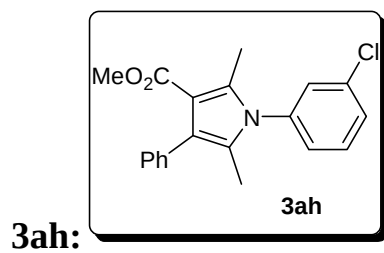
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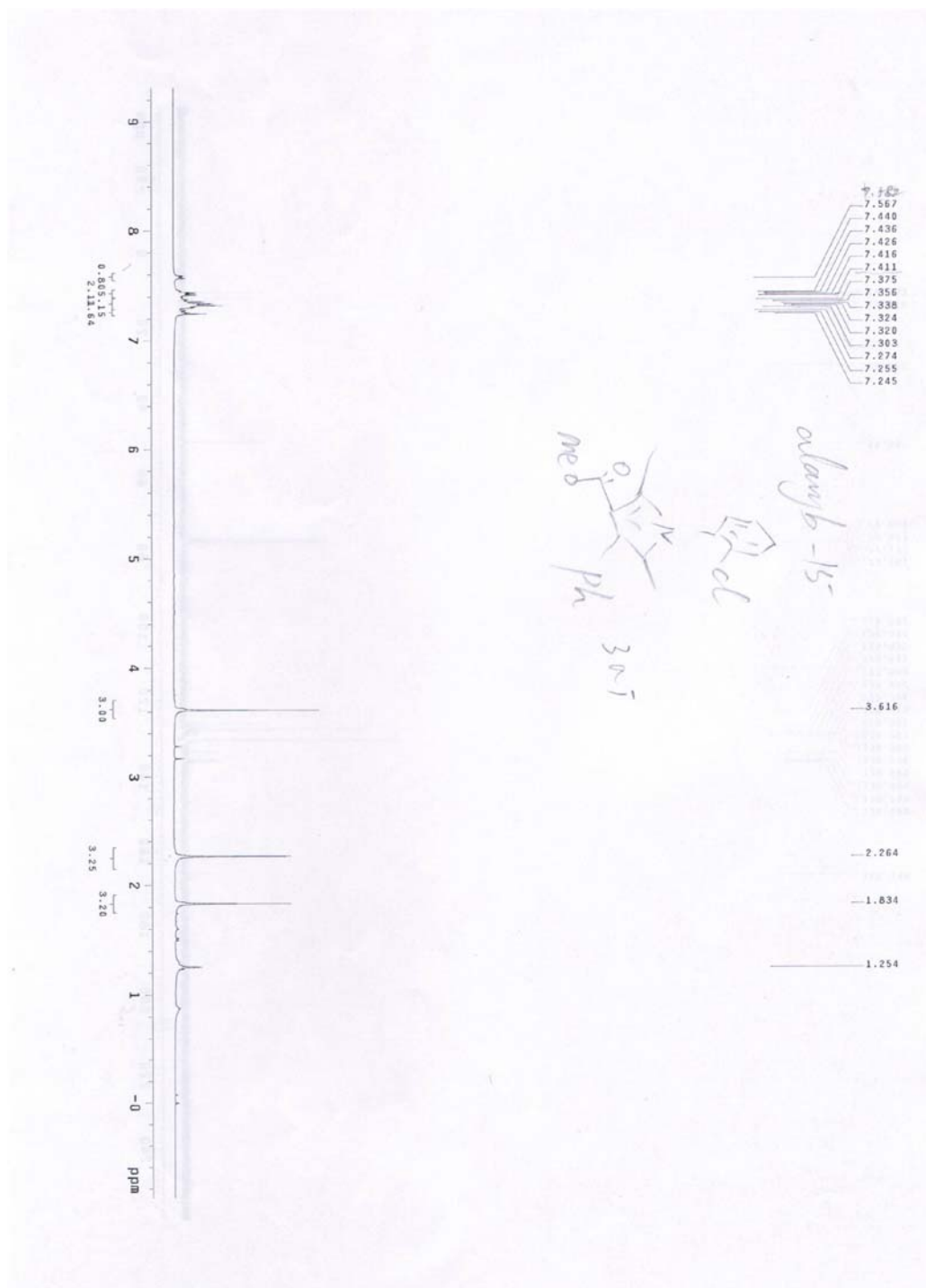
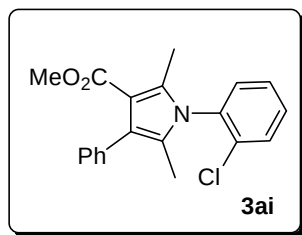
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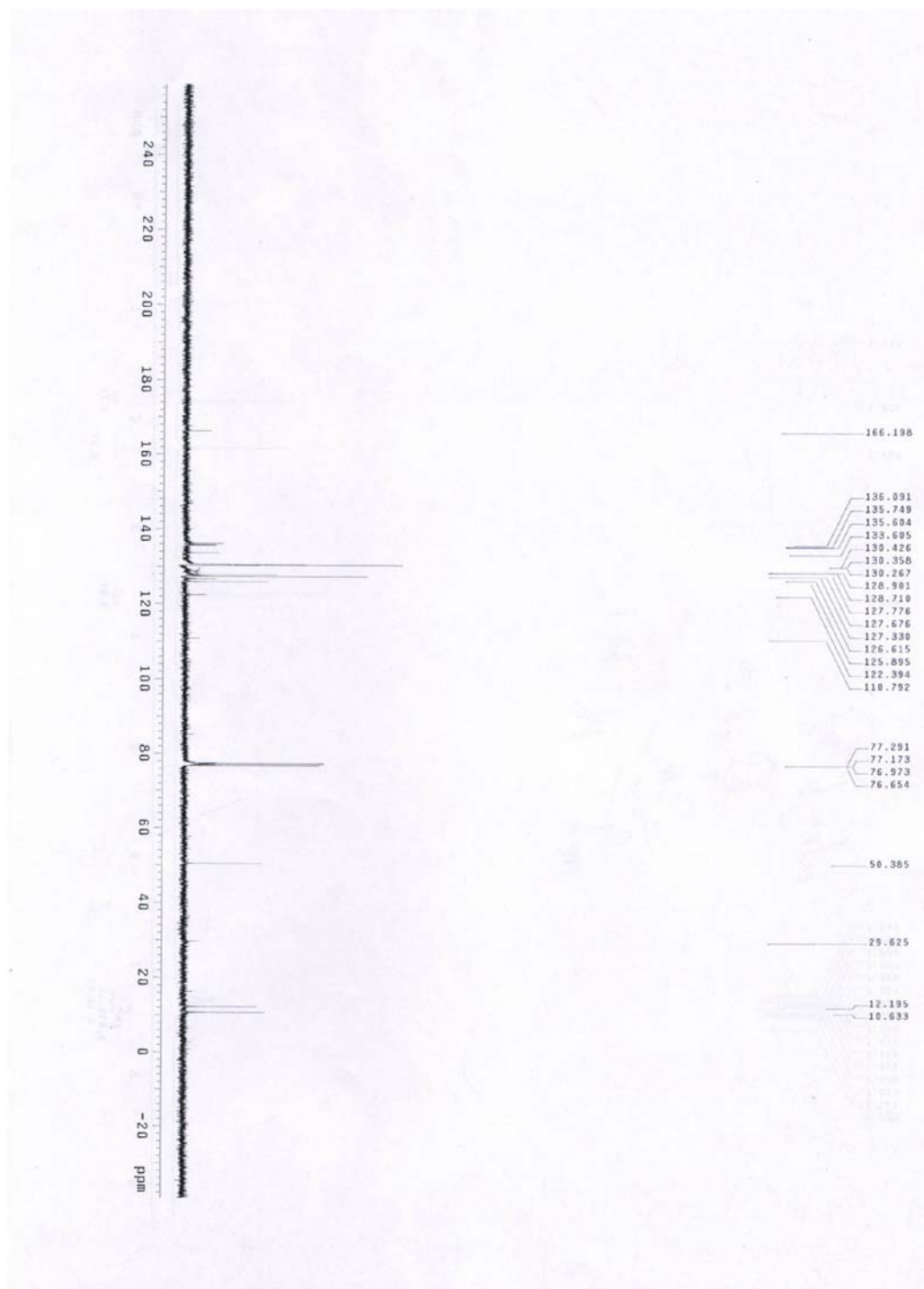
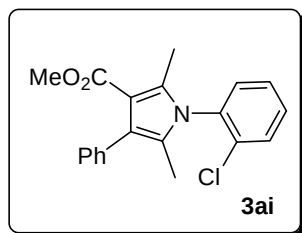




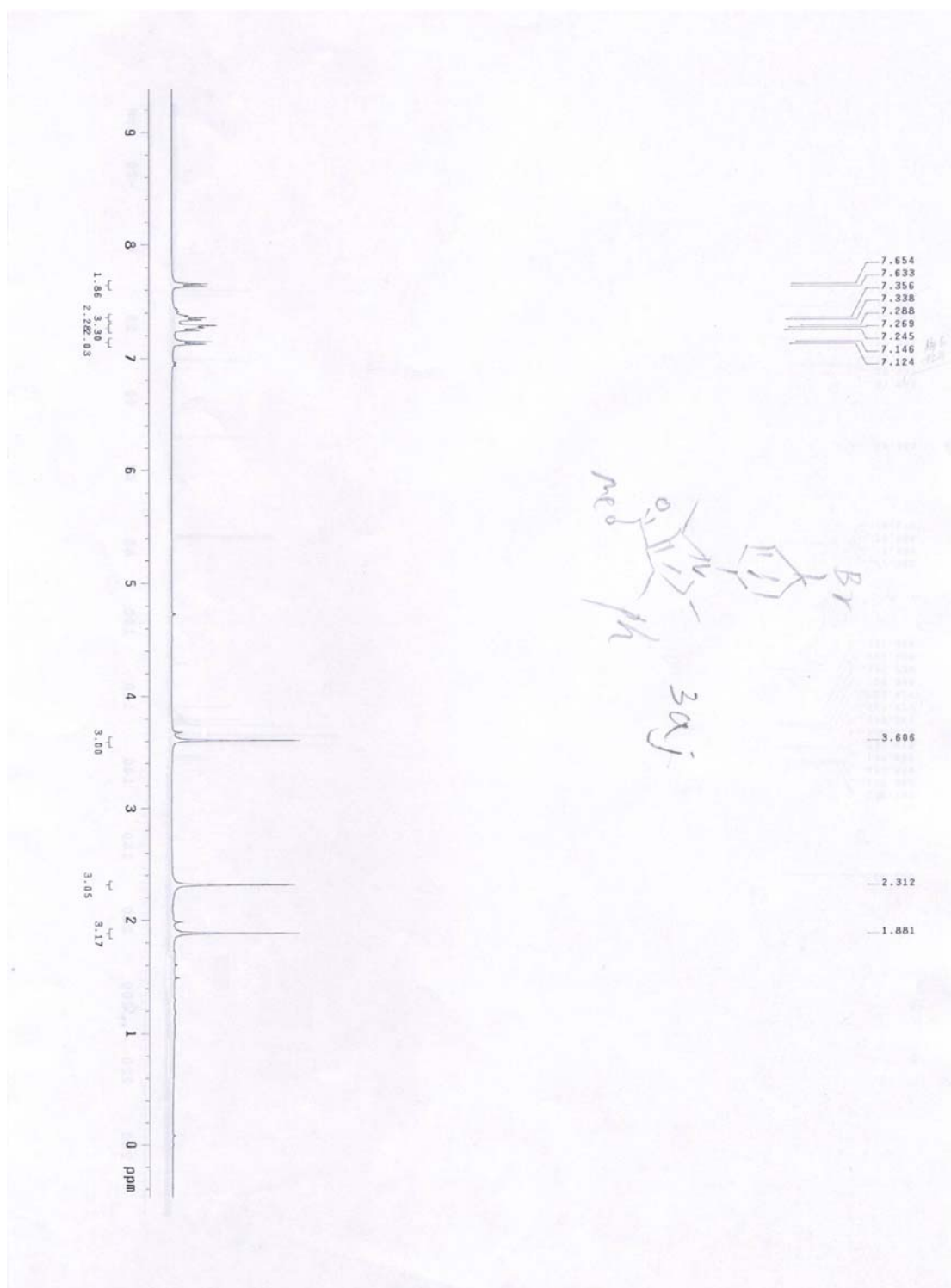
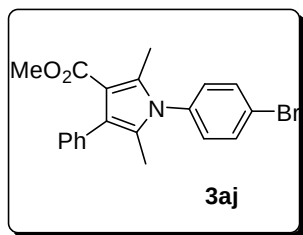
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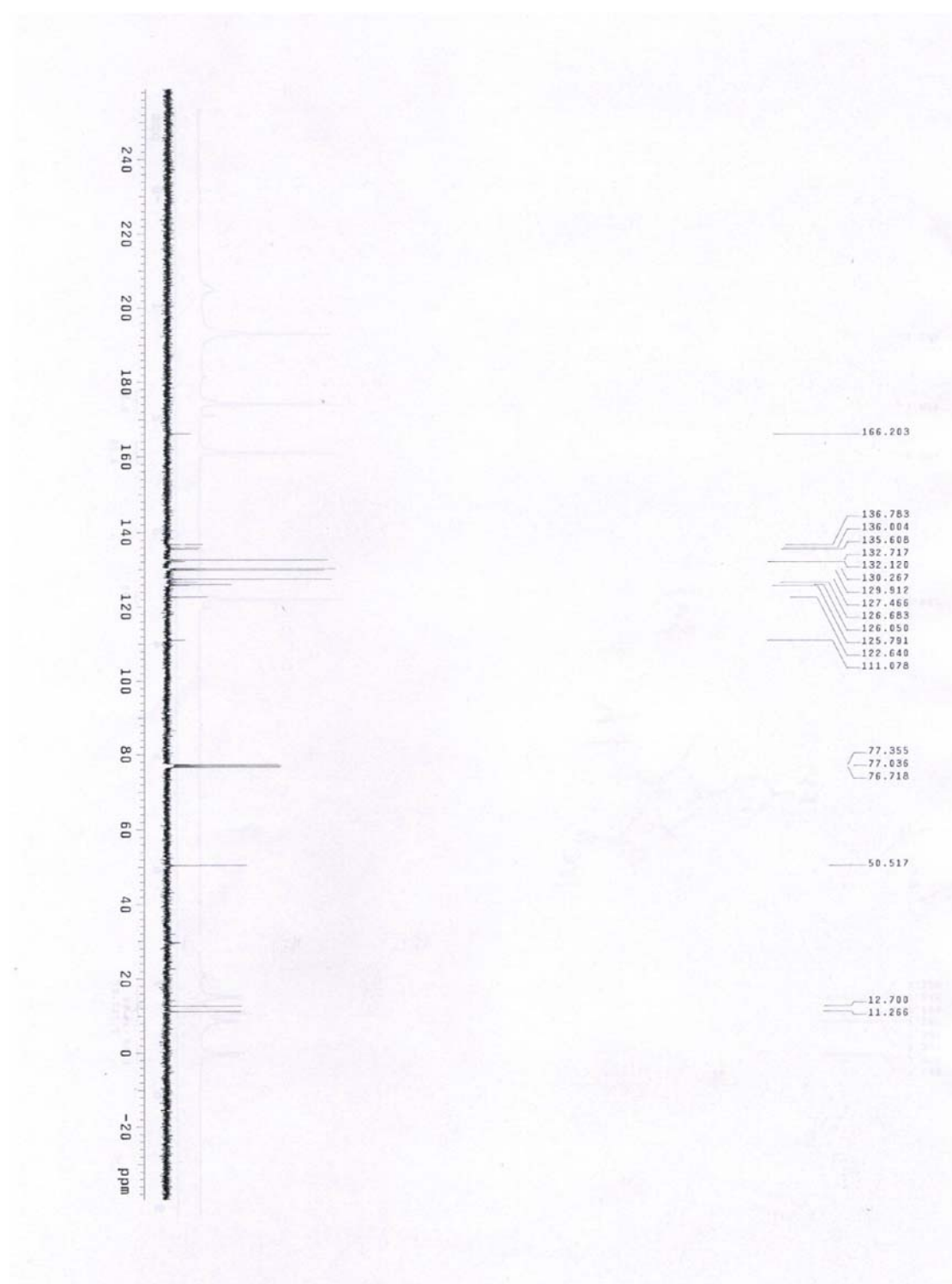
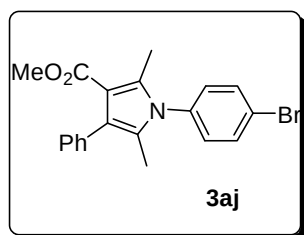
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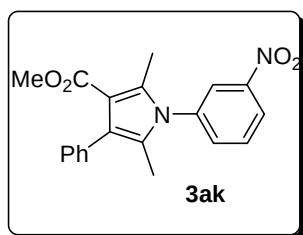


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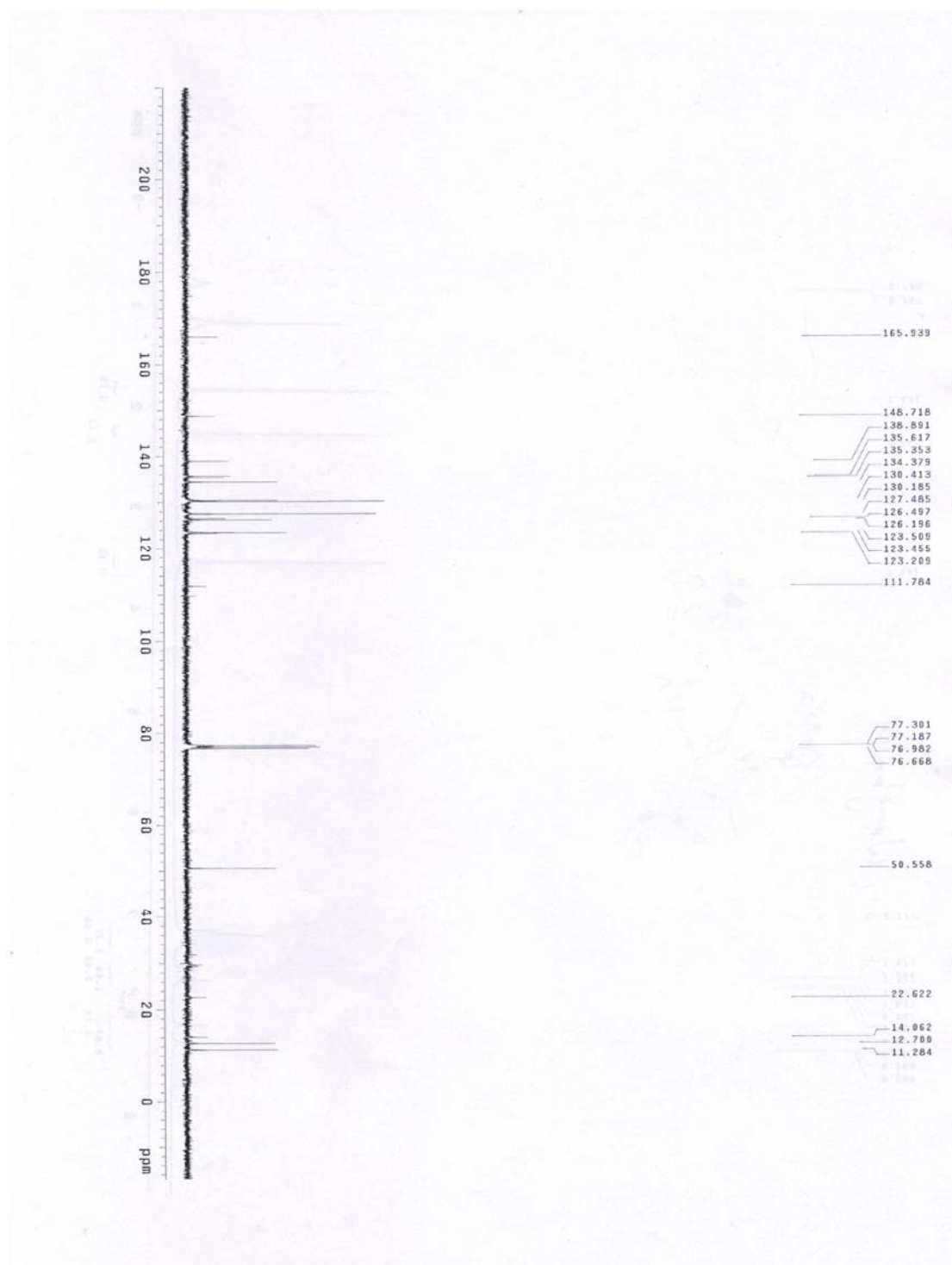
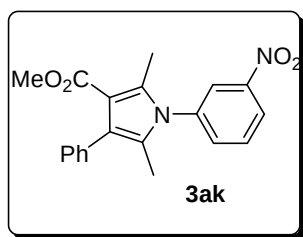


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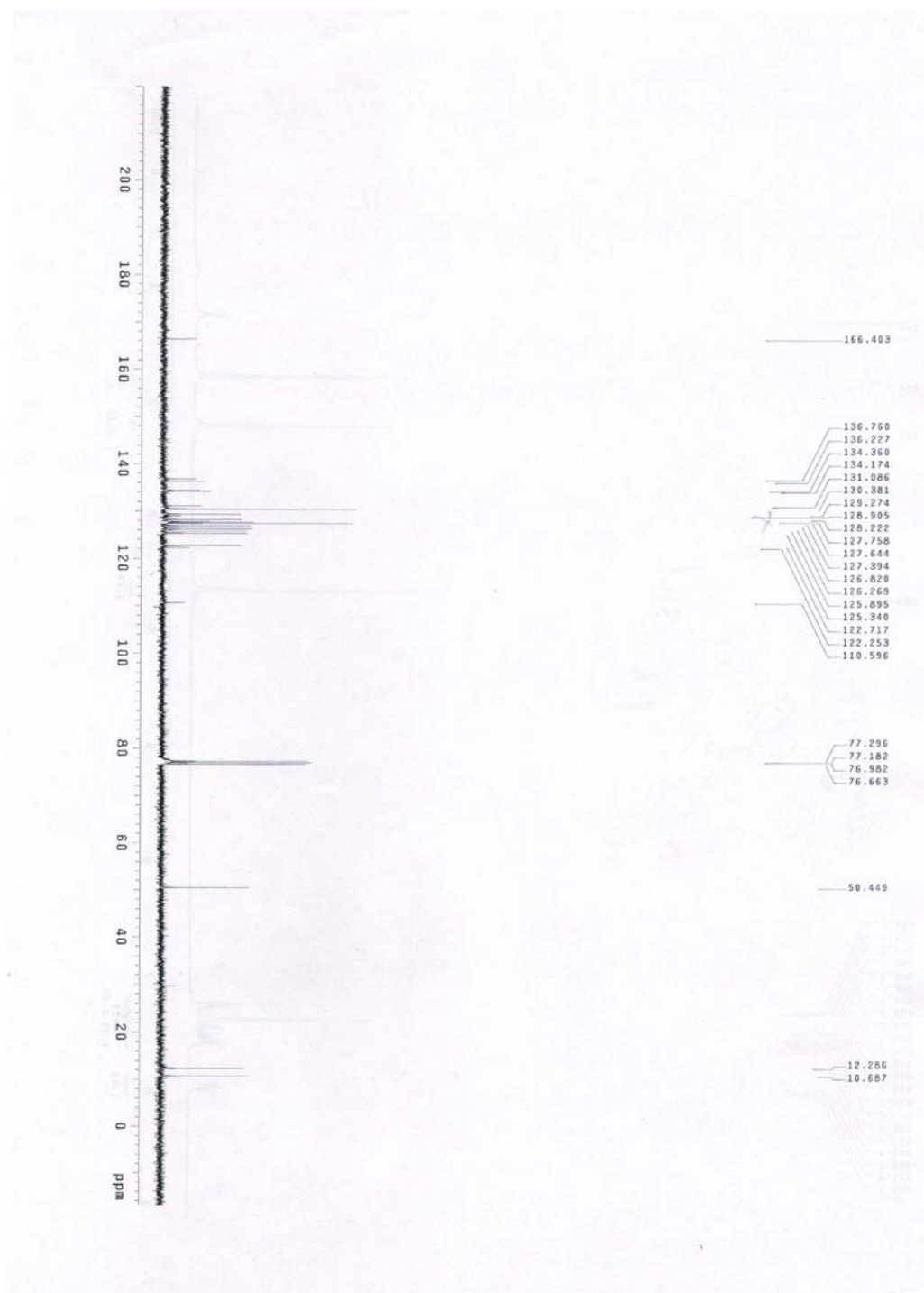
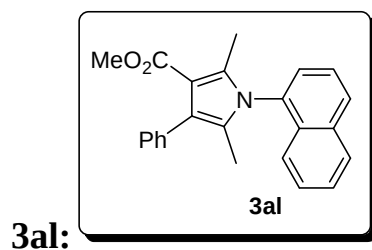


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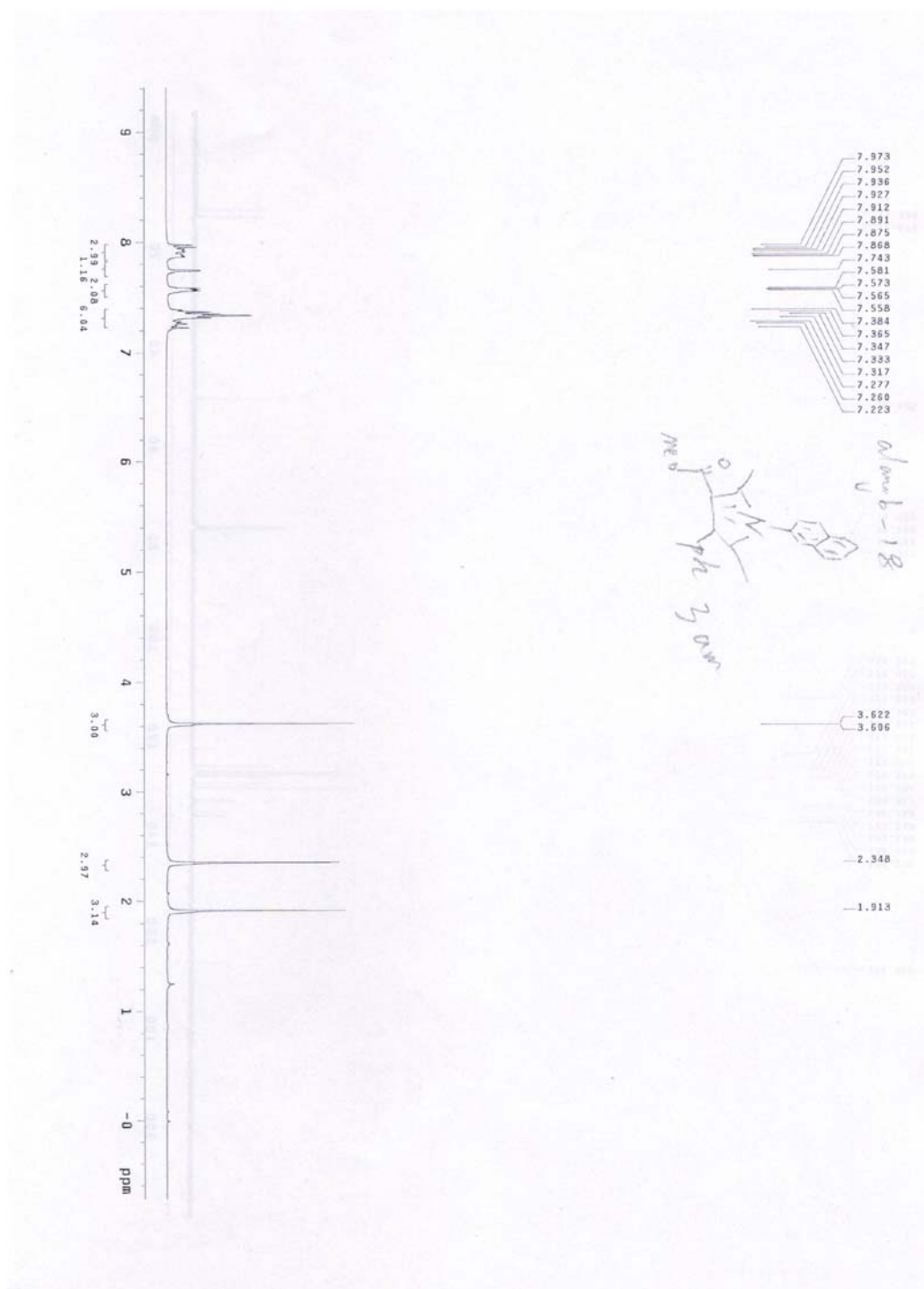
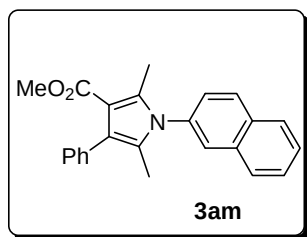


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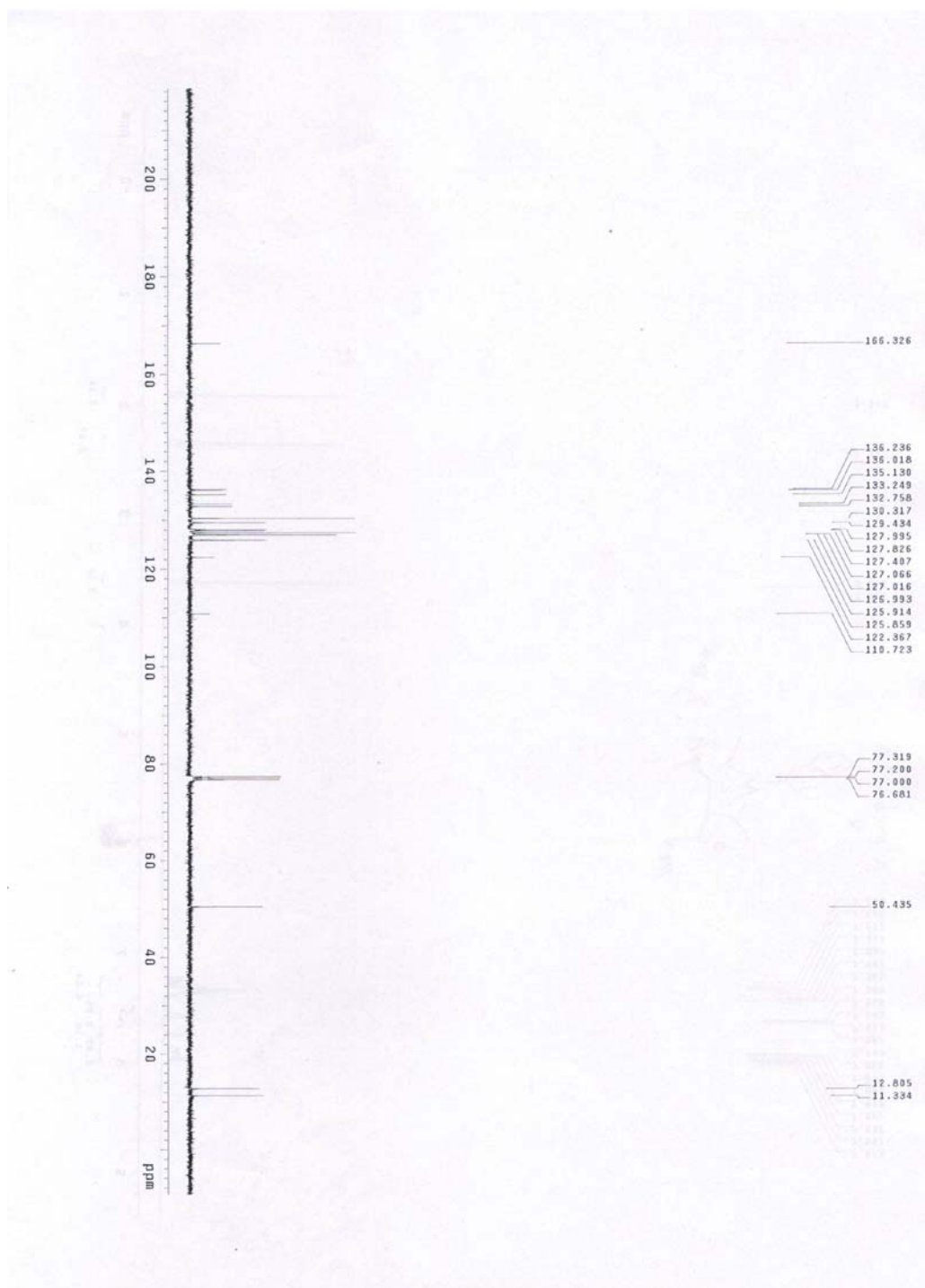
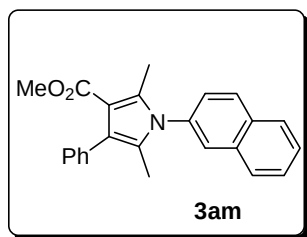




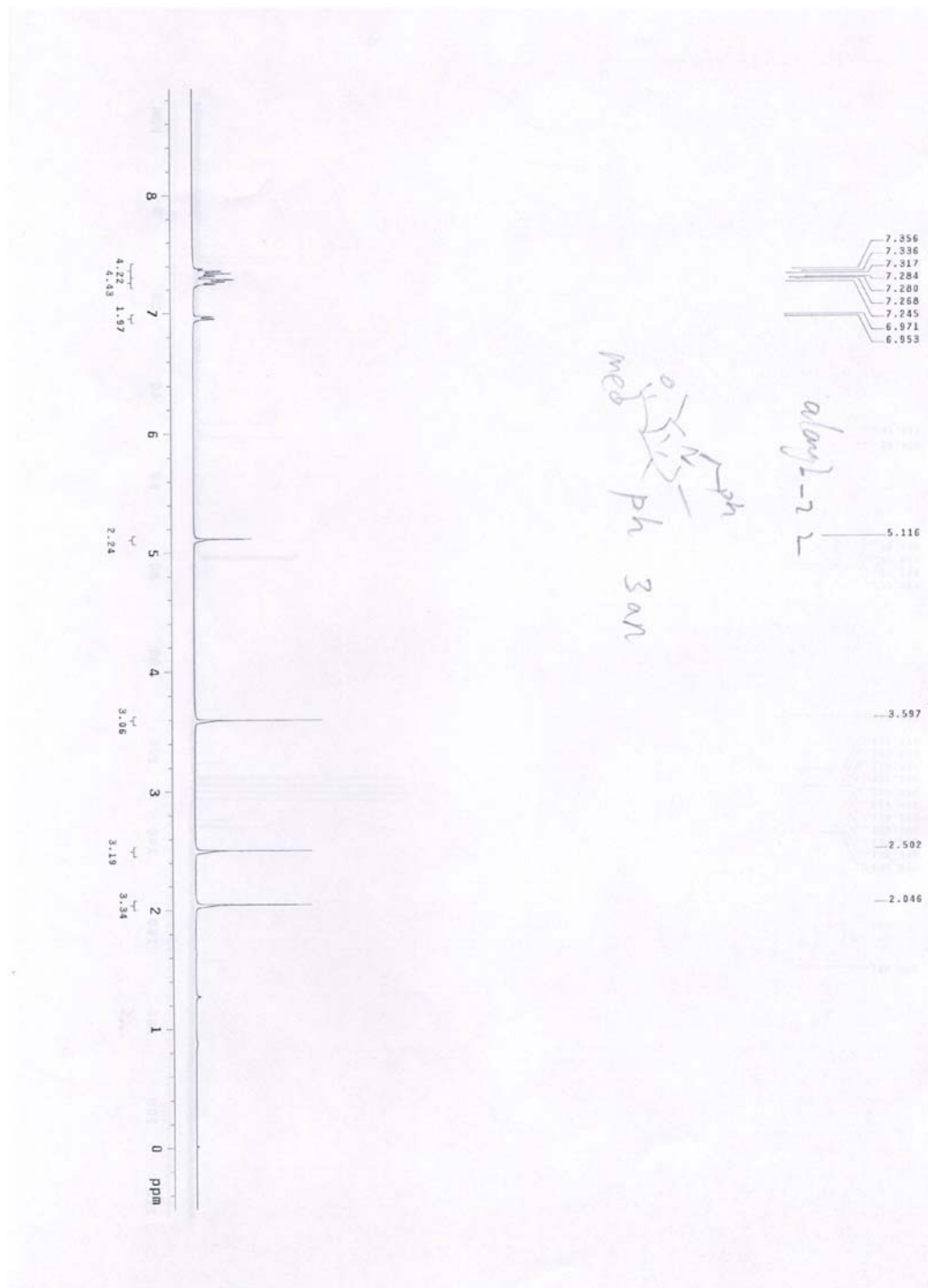
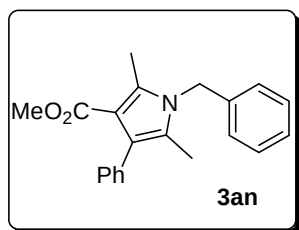
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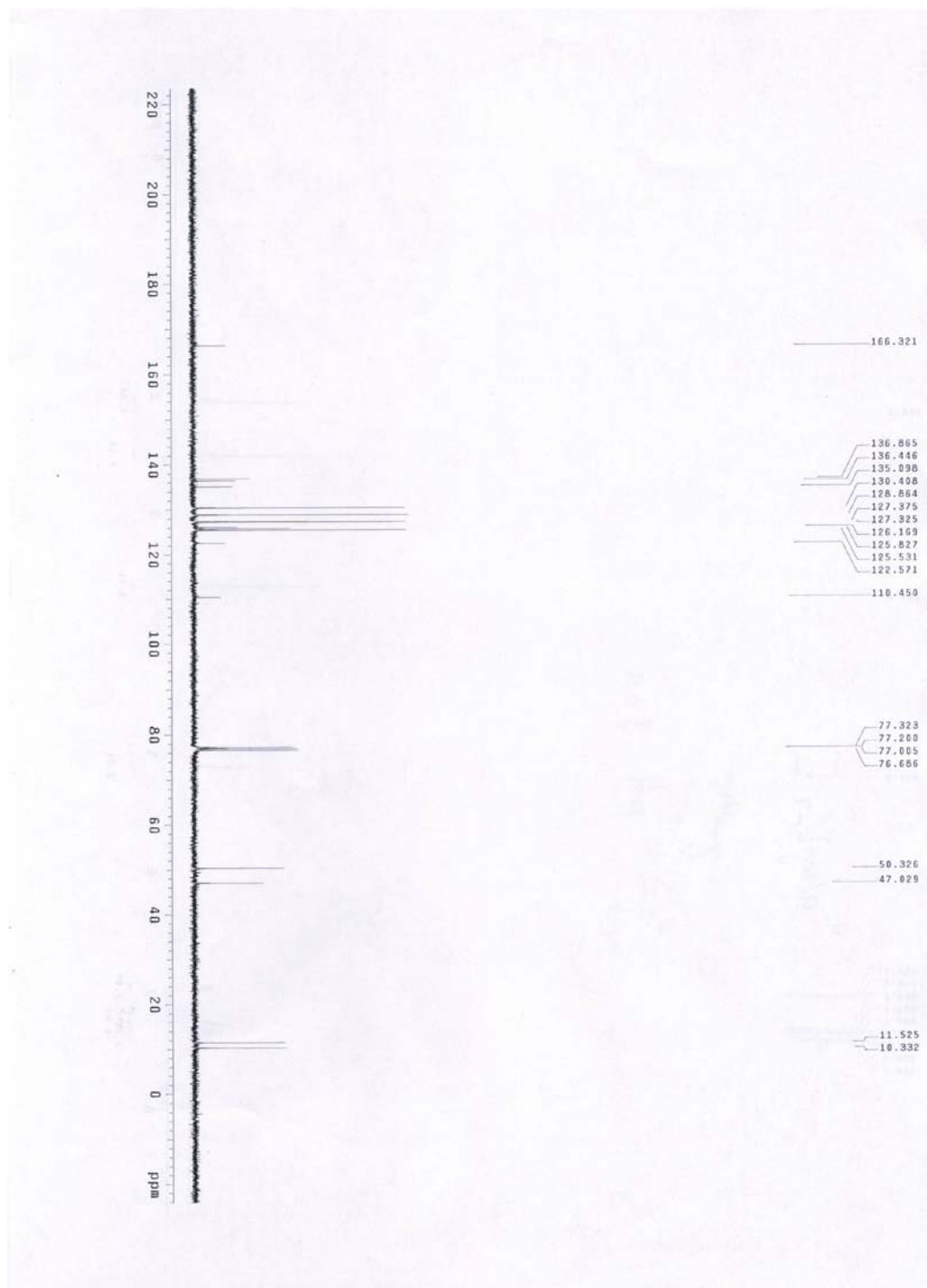
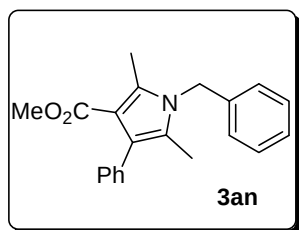
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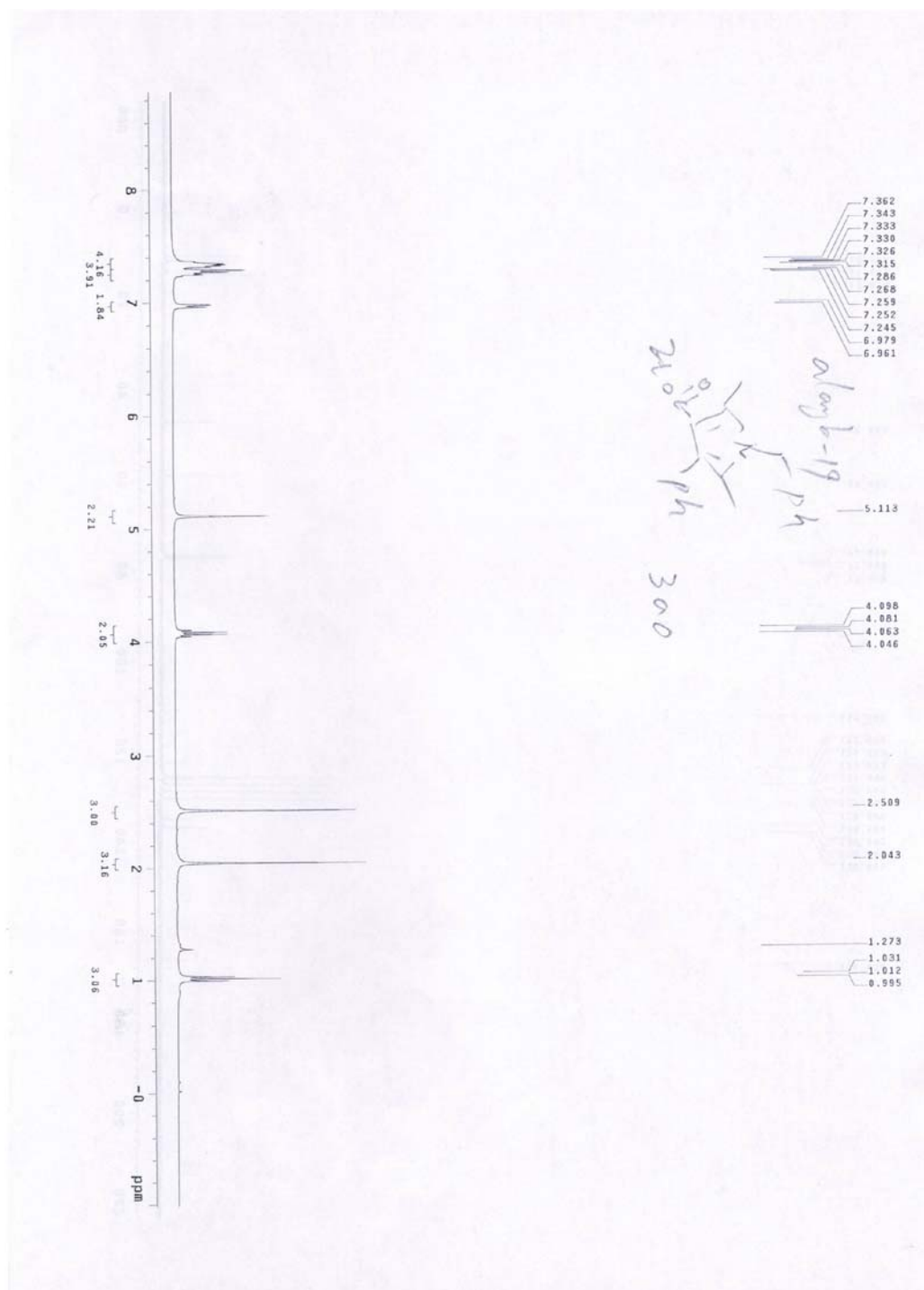
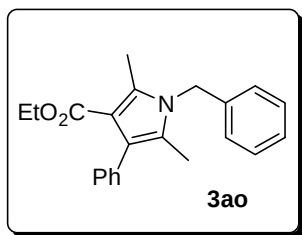
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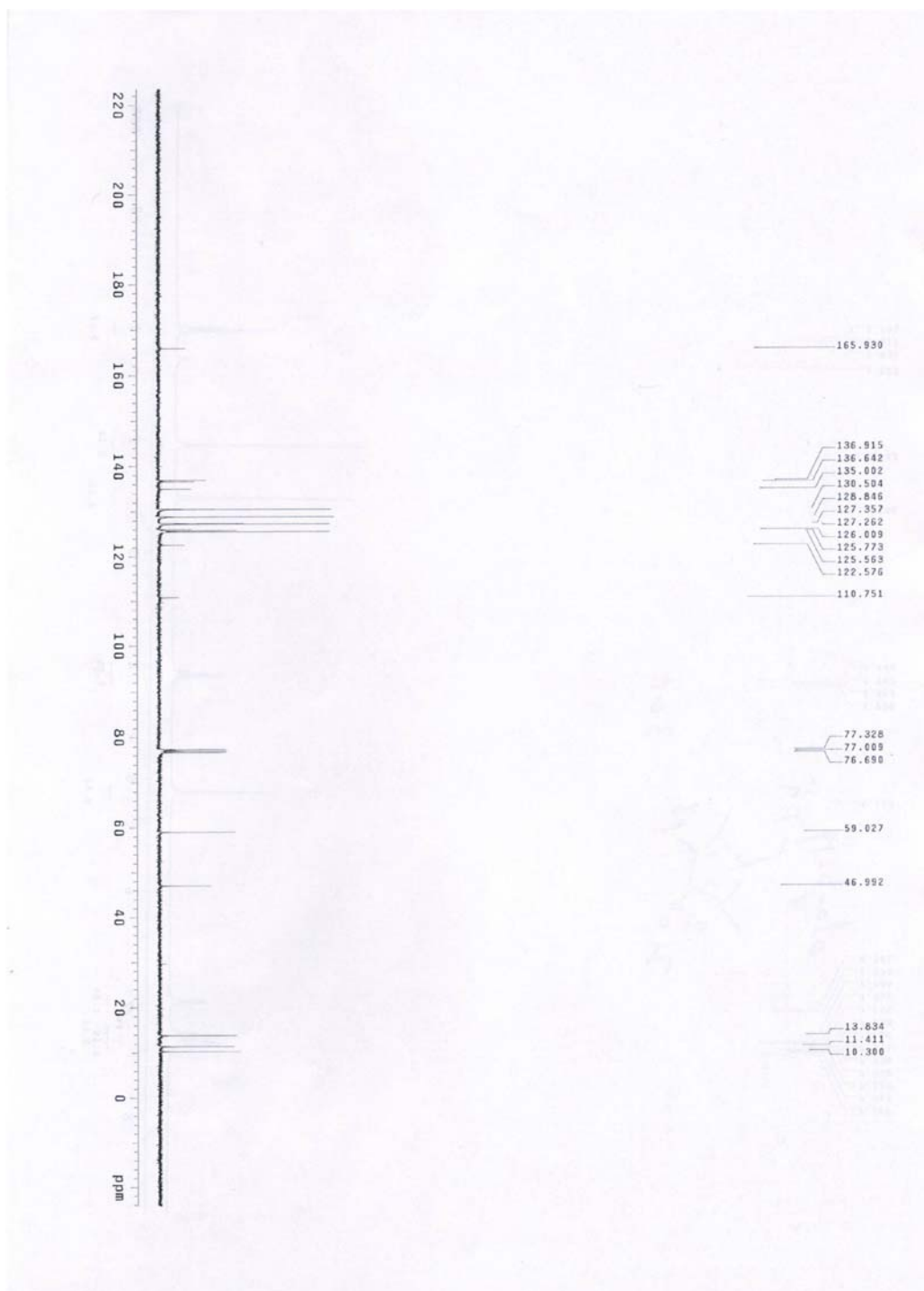
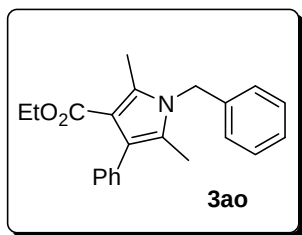
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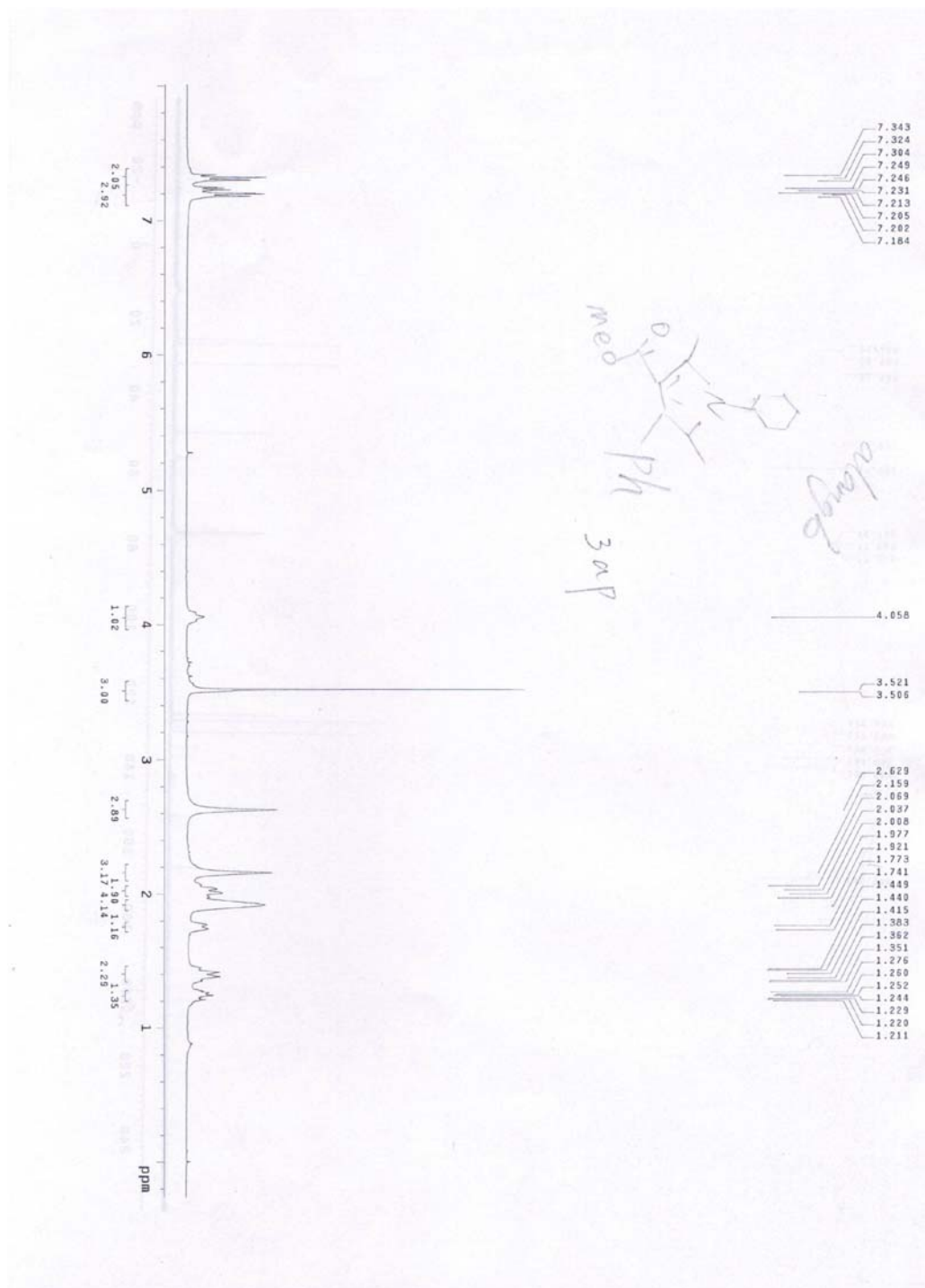
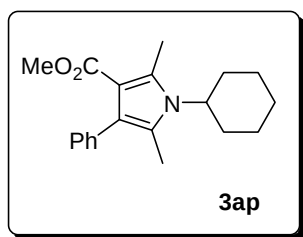
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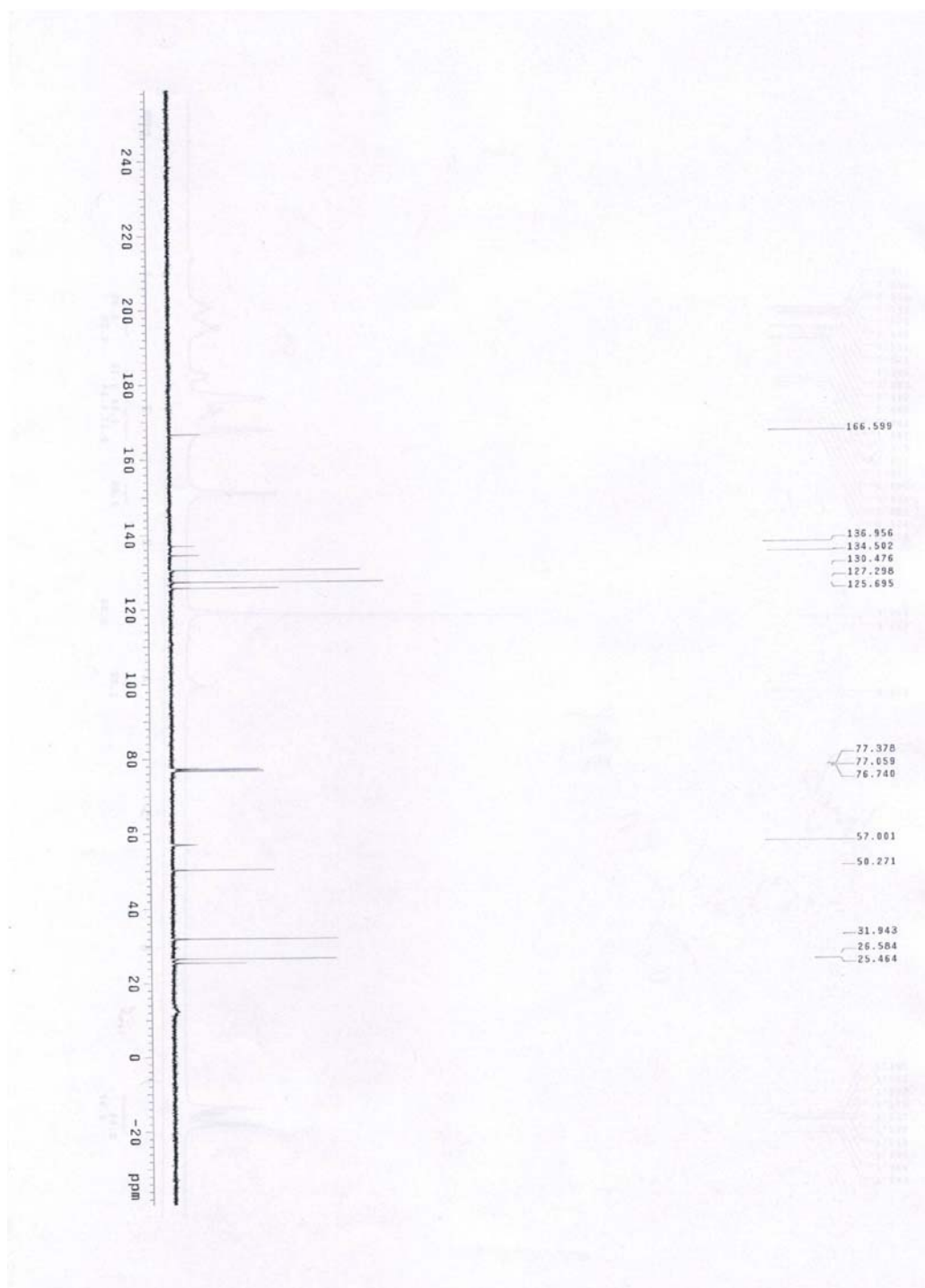
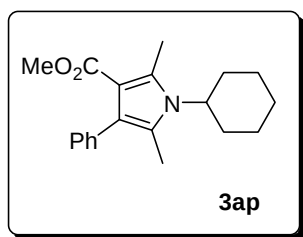
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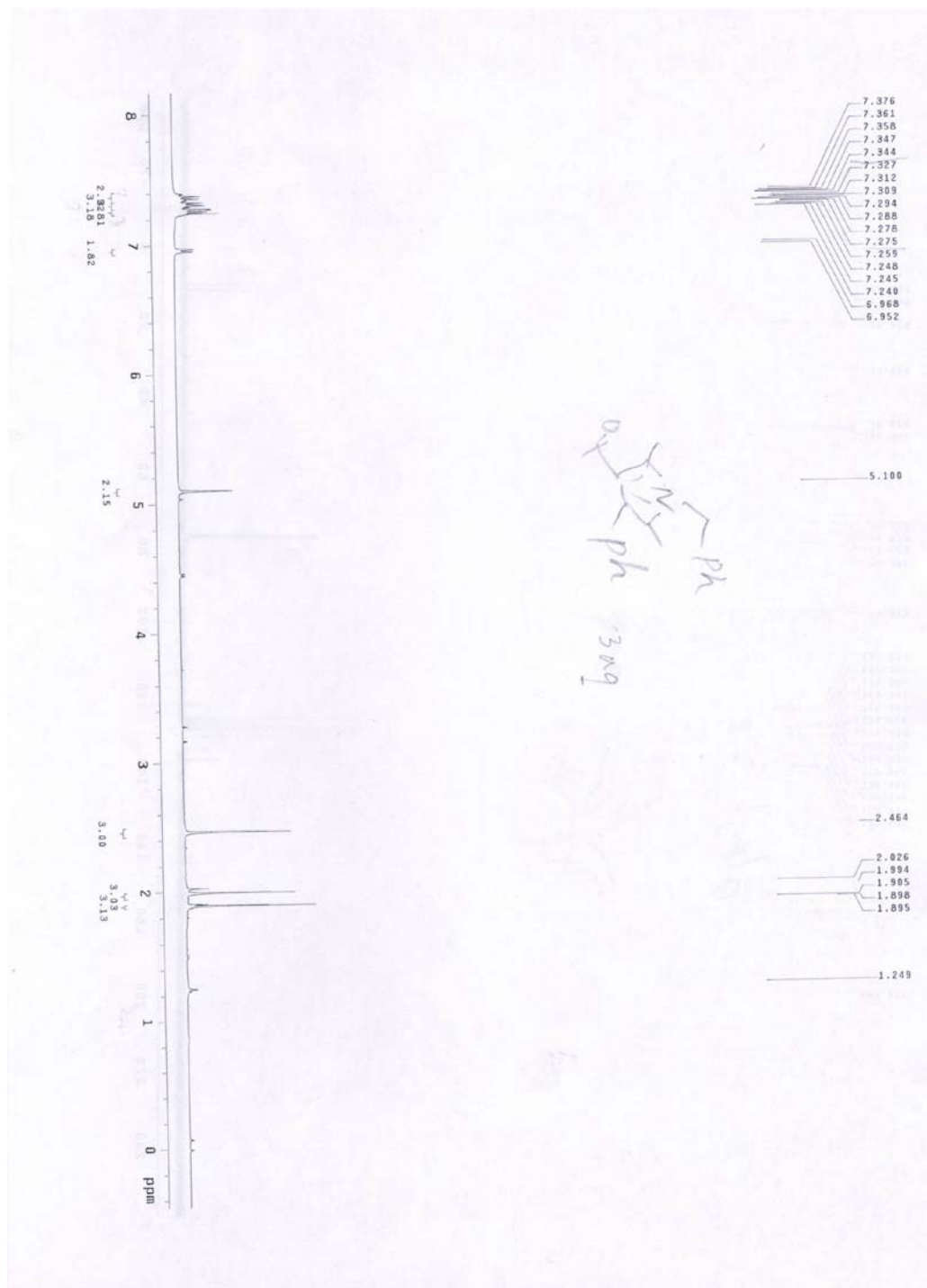
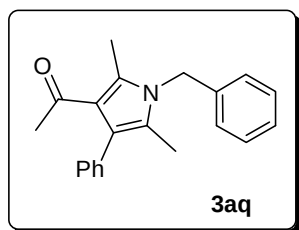
3ap:



3ap:



3aq:



3aq:

