

Electronic Supplementary Information

N- and O-Arylation of Pyridin-2-ones with Diaryliodonium Salts: Base-Dependent Orthogonal Selectivity under Metal-Free Conditions

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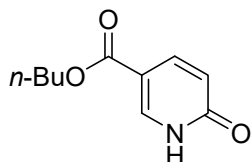
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Table of contents

1. General information	S2
2. Experimental procedures and characterization data	S2-S19
3. X-ray data of compounds 3ga , 4ga and 5	S20-S22
4. Comparison between the effects of FPh and ClPh	S23
5. References	S23
6. ¹ H and ¹³ C NMR spectra	S24-S64

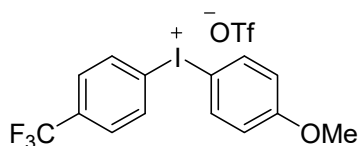
General. All melting points are not corrected. IR spectra were expressed in cm^{-1} (Shimadzu IR Affinity-1). ^1H NMR spectra were taken at 500 or 400 MHz, and ^{13}C NMR spectra were taken at 125 or 100 MHz (Varian NMR System 500PS SN / JEOL JNM-AL400). Chemical shift values of ^1H NMR are expressed in ppm relative to internal or external TMS. Abbreviations are as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad. A double-focusing magnetic sector mass spectrometer was used for low- and high-resolution EI-MS and FAB-MS (JEOL JMS-700N). A reflectron time-of-flight mass spectrometer was applied to low-resolution DART-MS (JEOL JMS-T100TD). The coupling products were isolated by silica gel column chromatography, while the iodonium salts were purified by alumina column chromatography prior to use if necessary. All reactions were performed under an argon atmosphere unless otherwise specified. Commercially available chemicals were purchased from Sigma-Aldrich, Tokyo Chemical Industry Co., Ltd., and Fujifilm Wako Pure Chemical Corporation. These chemicals were used as received. The known compounds such as pyridones **1g**¹, **1l**², iodonium salts **2a-b**³, **2c**⁴, **2d-e**³, **2f**⁵, **2g**⁶, **2h**³, **2i**⁷, **2j**⁸, **2k**⁷, and **2m**³ were prepared as previously reported. As the authentic samples for identification and yield calculation with ^1H NMR analysis, **3ak**⁹ and **4ab**¹⁰ were prepared as previously reported.

5-(*n*-Butoxycarbonyl)pyridin-2(1*H*)-one (**1e**)



A mixture of 6-hydroxynicotinic acid (696 mg, 5 mmol) and a catalytic amount of concentrated sulfuric acid (10 mol%) in *n*-butanol (2.0 mL) was heated for 3 h at 140 °C. After complete conversion, the mixture was cooled to room temperature and water and saturated Na_2CO_3 were added until the mixture reached pH 11-12. The resulting mixture was extracted with AcOEt. Concentration and purification through silica gel column chromatography (hexane/benzene = 1/2) gave 880 mg of the product (4.5 mmol, 90%) as white solids of mp 128-130 °C. ^1H NMR (400 MHz, CDCl_3): δ 0.97 (3H, t, J = 7.3 Hz), 1.40-1.49 (2H, m), 1.67-1.74 (2H, m), 4.28 (2H, t, J = 6.3 Hz), 6.59 (1H, d, J = 9.3 Hz), 8.02 (1H, dd, J = 2.4, 9.3 Hz), 8.21 (1H, d, J = 2.4 Hz), 12.9 (1H, brs). ^{13}C NMR (100 MHz, CDCl_3): δ 13.5 (CH_3), 19.0 (CH_2), 30.5 (CH_2), 64.8 (CH_2), 111.4 (C), 119.4 (CH), 139.7 (CH), 141.1 (CH), 164.1 (C), 165.8 (C). IR (ATR): 780, 1220, 1650, 1720, 2960 cm^{-1} . HRMS (EI) m/z (M^+) Calcd for $\text{C}_{10}\text{H}_{13}\text{NO}_3$: 195.0895. Found: 195.0892.

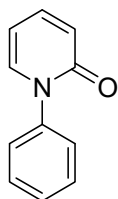
(4-(Trifluoromethyl)phenyl)(4-methoxyphenyl)iodonium triflate³ (2l)



MCPBA (82% active oxidant, 1.16 g, 5.5 mmol) and 1-iodo-4-(trifluoromethyl)benzene (1.36 g, 5 mmol) were dissolved in CH₂Cl₂ (25 mL), and TfOH (1.50 g, 10.0 mmol) was added at room temperature. After stirring at room temperature for 10 min, anisole (541 mg, 5.0 mmol) in CH₂Cl₂ (5 mL) was slowly added at 0 °C. The reaction mixture was stirred at 0 °C for 10 min and concentrated in vacuo at 0 °C. Et₂O (20 mL) was added, and then the mixture was stirred at room temperature for 10 min to precipitate off-white solids. After the flask was stored at 0 °C for 30 min, the solids were filtered off, washed with cold Et₂O, and dried under vacuum to give 2.07 g of the product (3.92 mmol, 78 %) as pale yellow solids of mp 151-152 °C. ¹H NMR (500 MHz, DMSO-*d*₆): δ 3.81 (3H, s), 7.10 (2H, d, *J* = 9.1 Hz), 7.91 (2H, d, *J* = 8.3 Hz), 8.22 (2H, d, *J* = 9.1 Hz), 8.39 (2H, d, *J* = 8.3 Hz). ¹³C NMR (100 MHz, DMSO-*d*₆): δ 55.8 (CH₃), 105.6 (C), 117.8 (CH), 120.9 (q, *J* = 321.9 Hz, C), 121.3 (C), 123.6 (q, *J* = 272.3 Hz, C), 128.4 (q, *J* = 3.3 Hz, CH), 131.9 (q, *J* = 32.3 Hz, C), 135.8 (CH), 137.7 (CH), 162.4 (C). ¹⁹F NMR (470 MHz, DMSO-*d*₆): δ -61.7 (3F), -77.8 (3F). IR (ATR): 1020, 1070, 1140, 1170, 1240 cm⁻¹. HRMS (FAB) *m/z* ([M-TfO]⁺) Calcd for C₁₄H₁₁F₃IO: 378.9807. Found: 378.9807.

General procedure for N-arylation of pyridin-2-ones with diaryliodonium salts. A screw cap test tube was charged with pyridin-2-one (**1a**) (47.5 mg, 0.5 mmol) and diphenyliodonium triflate (**2a**) (258 mg, 0.6 mmol). Then, the tube was evacuated and back-filled with argon. After fluorobenzene (1 mL) and diethylaniline (149 mg, 1.0 mmol) were added, a septum cap was replaced with a screw cap. The reaction mixture was stirred at 85 °C for 16 h. The mixture was cooled to room temperature and saturated Na₂CO₃ solution was added. The resulting mixture was extracted with AcOEt. The combined organic layers were dried over Na₂SO₄. Concentration and purification through silica gel column chromatography gave the desired product **3aa**.

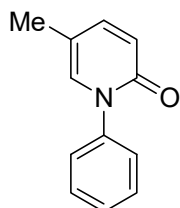
1-Phenylpyridin-2(1*H*)-one¹¹ (3aa)



Silica gel column chromatography (hexane/EtOAc = 1/2) gave 77 mg of the product (0.45 mmol,

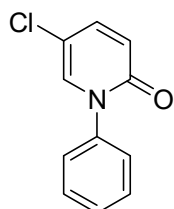
90%) as white solids of mp 126-128 °C. ¹H NMR (400 MHz, CDCl₃): δ 6.24 (1H, dt, *J* = 1.3, 6.8 Hz), 6.67 (1H, d, *J* = 9.2 Hz), 7.34 (1H, dd, *J* = 1.8, 6.8 Hz), 7.38-7.45 (4H, m), 7.48-7.52 (2H, m). ¹³C NMR (100 MHz, CDCl₃): δ 105.6 (CH), 121.4 (CH), 126.2 (CH), 128.1 (CH), 128.9 (CH), 137.7 (CH), 139.6 (CH), 140.6 (C), 162.0 (C). IR (ATR): 690, 760, 1530, 1580, 1650 cm⁻¹. EIMS *m/z*: 171 (M⁺).

5-Methyl-1-phenylpyridin-2(1*H*)-one¹² (3ba)



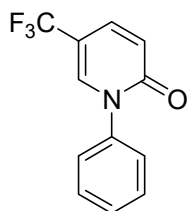
This reaction was conducted on 1 mmol scale. Silica gel column chromatography (hexane/EtOAc = 1/2) gave 163 mg of the product (0.88 mmol, 88%) as white solids of mp 107-109 °C. ¹H NMR (500 MHz, CDCl₃): δ 2.11 (3H, s), 6.61 (1H, d, *J* = 9.3 Hz), 7.11 (1H, s), 7.25-7.28 (1H, m), 7.37-7.42 (3H, m), 7.47-7.50 (2H, m). ¹³C NMR (100 MHz, CDCl₃): δ 16.9 (CH₃), 114.8 (C), 121.4 (CH), 126.6 (CH), 128.3 (CH), 129.3 (CH), 135.3 (CH), 141.1 (C), 142.6 (CH), 161.8 (C). IR (ATR): 830, 1140, 1490, 1610, 1670 cm⁻¹. EIMS *m/z*: 185 (M⁺).

5-Chloro-1-phenylpyridin-2(1*H*)-one¹³ (3ca)



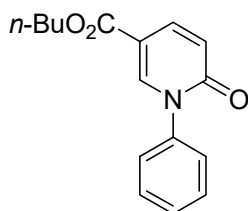
Silica gel column chromatography (hexane/EtOAc = 3/1) gave 91 mg of the product (0.44 mmol, 89%) as pale beige solids of mp 83-84 °C. ¹H NMR (400 MHz, CDCl₃): δ 6.64 (1H, d, *J* = 9.8 Hz), 7.34-7.53 (7H, m). ¹³C NMR (100 MHz, CDCl₃): δ 112.5 (C), 122.7 (CH), 126.4 (CH), 128.9 (CH), 129.5 (CH), 135.5 (CH), 140.2 (C), 140.9 (CH), 160.9 (C). IR (ATR): 690, 820, 1090, 1490, 1670 cm⁻¹. EIMS *m/z*: 205 (M⁺).

1-Phenyl-5-(trifluoromethyl)pyridin-2(1*H*)-one (3da)



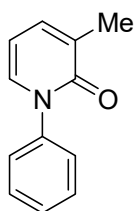
This reaction was conducted on 1 mmol scale. Silica gel column chromatography (hexane/EtOAc = 5/1) gave 215 mg of the product (0.90 mmol, 90%) as yellow solids of mp 57-58 °C. ¹H NMR (500 MHz, CDCl₃): δ 6.73 (1H, d, *J* = 9.8 Hz), 7.38 (2H, d, *J* = 7.3 Hz), 7.46-7.49 (1H, m), 7.52-7.55 (3H, m), 7.75 (1H, s). ¹³C NMR (125 MHz, CDCl₃): δ 109.5 (q, *J* = 35.3 Hz, C), 122.2 (CH), 123.1 (q, *J* = 269.0 Hz, C), 126.2 (CH), 129.0 (CH), 129.4 (CH), 135.2 (CH), 137.5 (q, *J* = 4.8 Hz, CH), 139.8 (C), 161.3 (C). IR (ATR): 690, 750, 1090, 1590, 1680 cm⁻¹. HRMS (EI): *m/z* (M⁺) Calcd for C₁₂H₈F₃NO: 239.0558. Found: 239.0559.

5-Butoxycarbonyl-1-phenylpyridin-2(1*H*)-one (3ea)



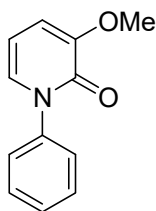
Silica gel column chromatography (hexane/EtOAc = 3/1) gave 128 mg of the product (0.47 mmol, 94%) as yellow solids of mp 63-64 °C. ¹H NMR (400 MHz, CDCl₃): δ 0.96 (3H, t, *J* = 7.3 Hz), 1.38-1.48 (2H, m), 1.67-1.74 (2H, m), 4.28 (2H, t, *J* = 6.8 Hz), 6.64 (1H, d, *J* = 9.8 Hz), 7.39 (2H, d, *J* = 7.8 Hz), 7.46-7.55 (3H, m), 7.93 (1H, dd, *J* = 2.0, 9.8 Hz), 8.22 (1H, d, *J* = 2.4 Hz). ¹³C NMR (100 MHz, CDCl₃): δ 13.6 (CH₃), 19.1 (CH₂), 30.6 (CH₂), 65.0 (CH₂), 110.2 (C), 120.6 (CH), 126.5 (CH), 129.1 (CH), 129.6 (CH), 139.0 (CH), 140.2 (C), 143.2 (CH), 162.3 (C), 164.3 (C). IR (ATR): 700, 800, 1110, 1650, 1710 cm⁻¹. HRMS (EI): *m/z* (M⁺) Calcd for C₁₆H₁₇NO₃: 271.1208. Found: 271.1208.

3-Methyl-1-phenylpyridin-2(1*H*)-one¹¹ (3fa)



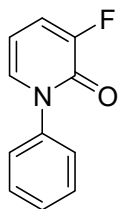
Silica gel column chromatography (hexane/EtOAc = 2/1) gave 66 mg of the product (0.36 mmol, 71%) as pale yellow solids of mp 118-120 °C. ¹H NMR (400 MHz, CDCl₃): δ 2.19 (3H, s), 6.17 (1H, t, *J* = 6.8 Hz), 7.23 (1H, d, *J* = 6.8 Hz), 7.27 (1H, d, *J* = 6.8 Hz), 7.37-7.43 (3H, m), 7.46-7.50 (2H, m). ¹³C NMR (100 MHz, CDCl₃): δ 17.2 (CH₃), 105.5 (CH), 126.6 (CH), 128.2 (CH), 129.2 (CH), 130.8 (C), 135.4 (CH), 136.9 (CH), 141.3 (C), 162.8 (C). IR (ATR): 700, 1070, 1490, 1590, 1650 cm⁻¹. EIMS *m/z*: 185 (M⁺).

3-Methoxy-1-phenylpyridin-2(1H)-one (3ga)



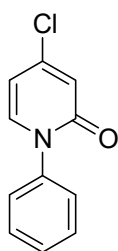
This reaction was conducted on 1 mmol scale. Silica gel column chromatography (EtOAc) gave 175 mg of the product (0.87 mmol, 87%) as white solids of mp 134-136 °C. ¹H NMR (400 MHz, CDCl₃): δ 3.86 (3H, s), 6.18 (1H, t, *J* = 7.3 Hz), 6.67 (1H, dd, *J* = 1.5, 7.3 Hz), 6.98 (1H, dd, *J* = 1.5, 6.8 Hz), 7.39-7.43 (3H, m), 7.47-7.51 (2H, m). ¹³C NMR (100 MHz, CDCl₃): δ 55.9 (CH₃), 104.8 (CH), 121.2 (CH), 126.5 (CH), 128.4 (CH), 129.0 (CH), 129.3 (CH), 140.9 (C), 150.5 (C), 158.0 (C). IR (ATR): 710, 1110, 1240, 1580, 1650 cm⁻¹. HRMS (EI): *m/z* (M⁺) Calcd for C₁₂H₁₁NO₂: 201.0790. Found: 201.0790.

3-Fluoro-1-phenylpyridin-2(1H)-one (3ha)



Silica gel column chromatography (hexane/EtOAc = 2/1) gave 83 mg of the product (0.44 mmol, 88%) as pink solids of mp 136-137 °C. ¹H NMR (400 MHz, CDCl₃): δ 6.16-6.20 (1H, m), 7.16-7.19 (2H, m), 7.40 (2H, d, *J* = 7.8 Hz), 7.45 (1H, t, *J* = 7.8 Hz), 7.52 (2H, t, *J* = 7.8 Hz). ¹³C NMR (100 MHz, CDCl₃): δ 103.7 (d, *J* = 5.8 Hz, CH), 120.2 (d, *J* = 17.4 Hz, CH), 126.4 (CH), 128.9 (CH), 129.5 (CH), 133.3 (d, *J* = 5.0 Hz, CH), 140.0 (C), 152.8 (d, *J* = 250.8 Hz, C), 156.3 (d, *J* = 25.7 Hz, C). IR (ATR): 750, 1110, 1490, 1610, 1660 cm⁻¹. HRMS (EI): *m/z* (M⁺) Calcd for C₁₁H₈FNO: 189.0590. Found: 189.0589.

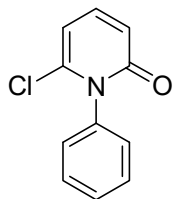
4-Chloro-1-phenylpyridin-2(1H)-one (3ia)



Silica gel column chromatography (hexane/EtOAc = 1/1) gave 91 mg of the product (0.44 mmol,

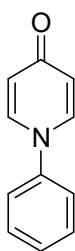
89%) as white solids of mp 131-132 °C. ¹H NMR (500 MHz, CDCl₃): δ 6.28 (1H, dd, *J* = 2.2, 7.3 Hz), 6.71 (1H, d, *J* = 2.2 Hz), 7.29 (1H, d, *J* = 7.3 Hz), 7.35 (2H, d, *J* = 7.3 Hz), 7.44 (1H, t, *J* = 7.3 Hz), 7.50 (2H, t, *J* = 7.3 Hz). ¹³C NMR (125 MHz, CDCl₃): δ 107.7 (CH), 119.9 (CH), 126.2 (CH), 128.6 (CH), 129.3 (CH), 137.9 (CH), 139.8 (C), 146.9 (C), 161.0 (C). IR (ATR): 690, 840, 1060, 1520, 1660 cm⁻¹. HRMS (EI) *m/z* Calcd for C₁₁H₈³⁵ClNO: 205.0294. Found: 205.0294.

6-Chloro-1-phenylpyridin-2(1*H*)-one (3ja)



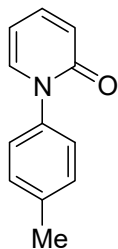
Silica gel column chromatography (hexane/benzene = 5/1) gave 34 mg of the product (0.17 mmol, 33%) yellow solids of mp 78-80 °C. ¹H NMR (400 MHz, CDCl₃): δ 6.74 (1H, d, *J* = 7.8 Hz), 7.04 (1H, d, *J* = 7.8 Hz), 7.15 (2H, d, *J* = 7.8 Hz), 7.23 (1H, t, *J* = 7.8 Hz), 7.41 (2H, t, *J* = 7.8 Hz), 7.62 (1H, t, *J* = 7.8 Hz). ¹³C NMR (100 MHz, CDCl₃): δ 109.1 (CH), 118.5 (CH), 121.0 (CH), 125.1 (CH), 129.8 (CH), 141.5 (CH), 149.2 (C), 153.7 (C), 163.2 (C). IR (ATR): 690, 790, 1140, 1200, 1580 cm⁻¹. HRMS (EI): *m/z* (M⁺) Calcd for C₁₁H₈³⁵ClNO: 205.0294. Found: 205.0295.

1-Phenylpyridin-4(1*H*)-one (3ka)



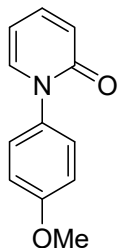
Silica gel column chromatography (hexane/EtOAc = 1/5) gave 56 mg of the product (0.33 mmol, 65%) as white solids of mp 125-127 °C. ¹H NMR (400 MHz, CDCl₃): δ 6.51 (2H, d, *J* = 7.8 Hz), 7.36 (2H, d, *J* = 7.8 Hz), 7.46 (1H, t, *J* = 7.8 Hz), 7.54 (2H, t, *J* = 7.8 Hz), 7.61 (2H, d, *J* = 7.8 Hz). ¹³C NMR (100 MHz, CDCl₃): δ 118.7 (CH), 122.8 (CH), 128.7 (CH), 130.3 (CH), 139.6 (CH), 143.1 (C), 178.9 (C). IR (ATR): 690, 860, 1030, 1490, 1630 cm⁻¹. HRMS (EI): *m/z* (M⁺) Calcd for C₁₁H₉NO: 171.0684. Found: 171.0684.

1-(4-Tolyl)pyridin-2(1H)-one¹⁴ (3ab)



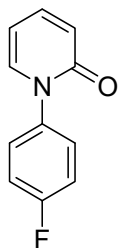
Silica gel column chromatography (hexane/EtOAc = 1/2) gave 78 mg of the product (0.42 mmol, 84%) as white solids of mp 135-137 °C. ¹H NMR (500 MHz, CDCl₃): δ 2.40 (3H, s), 6.22 (1H, t, *J* = 6.9 Hz), 6.65 (1H, d, *J* = 9.3 Hz), 7.25-7.33 (5H, m), 7.38 (1H, t, *J* = 7.1 Hz). ¹³C NMR (100 MHz, CDCl₃): δ 21.0 (CH₃), 105.7 (CH), 121.8 (CH), 126.3 (CH), 129.9 (CH), 138.2 (CH), 138.5 (C), 139.8 (CH), 162.6 (C). IR (ATR): 760, 1150, 1510, 1580, 1650 cm⁻¹. EIMS *m/z*: 185 (M⁺).

1-(4-Methoxyphenyl)pyridin-2(1H)-one¹¹ (3ac)



This reaction was conducted on 1 mmol scale. Silica gel column chromatography (hexane/EtOAc = 1/5) gave 181 mg of the product (0.90 mmol, 90%) as yellow solids of mp 101-103 °C. ¹H NMR (500 MHz, CDCl₃): δ 3.85 (3H, s), 6.22 (1H, t, *J* = 6.6 Hz), 6.65 (1H, d, *J* = 9.3 Hz), 6.99 (2H, d, *J* = 8.8 Hz), 7.29-7.33 (3H, m), 7.36-7.40 (1H, m). ¹³C NMR (100 MHz, CDCl₃): δ 55.5 (CH₃), 105.7 (CH), 114.5 (CH), 121.8 (CH), 127.6 (CH), 133.8 (C), 138.3 (CH), 139.8 (CH), 159.4 (C), 162.7 (C). IR (ATR): 760, 1030, 1240, 1510, 1660 cm⁻¹. EIMS *m/z*: 201 (M⁺).

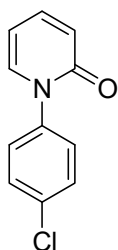
1-(4-Fluorophenyl)pyridin-2(1H)-one (3ad)



This reaction was conducted on 1 mmol scale. Silica gel column chromatography (hexane/EtOAc

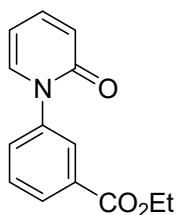
= 1/2) gave 166 mg of the product (0.88 mmol, 88%) as pale yellow solids of mp 142-143 °C. ¹H NMR (400 MHz, CDCl₃): δ 6.25 (1H, t, *J* = 6.8 Hz), 6.67 (1H, d, *J* = 8.8 Hz), 7.18 (2H, t, *J* = 8.8 Hz), 7.31 (1H, dd, *J* = 2.0, 6.8 Hz), 7.36-7.43 (3H, m). ¹³C NMR (100 MHz, CDCl₃): δ 106.0 (CH), 116.3 (d, *J* = 23.2 Hz, CH), 121.9 (CH), 128.4 (d, *J* = 9.1 Hz, CH), 136.9 (d, *J* = 2.5 Hz, C), 137.9 (CH), 140.0 (CH), 162.2 (d, *J* = 248.3 Hz, C), 162.4 (C). IR (ATR): 760, 1000, 1150, 1220, 1650 cm⁻¹. HRMS (EI): *m/z* (M⁺) Calcd for C₁₁H₈FNO: 189.0590. Found: 189.0590.

1-(4-Chlorophenyl)pyridin-2(1H)-one¹¹ (3ae)

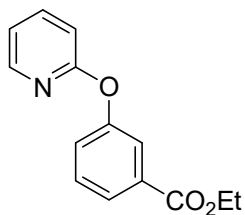


Silica gel column chromatography (hexane/EtOAc = 1/2) gave 75 mg of the product (0.36 mmol, 73%) as white solids of mp 133-134 °C. ¹H NMR (400 MHz, CDCl₃): δ 6.26 (1H, dt, *J* = 1.2, 6.8 Hz), 6.65-6.68 (1H, m), 7.30 (1H, dd, *J* = 2.0, 6.8 Hz), 7.33-7.36 (2H, m), 7.39-7.43 (1H, m), 7.45-7.49 (2H, m). ¹³C NMR (100 MHz, CDCl₃): δ 106.2 (CH), 122.0 (CH), 127.9 (CH), 129.5 (CH), 134.4 (C), 137.6 (CH), 139.3 (C), 140.1 (CH), 162.3 (C). IR (ATR): 760, 840, 1080, 1140, 1650 cm⁻¹. EIMS *m/z*: 205 (M⁺).

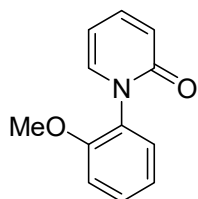
1-(3-Ethoxycarbonylphenyl)pyridin-2(1H)-one (3af)



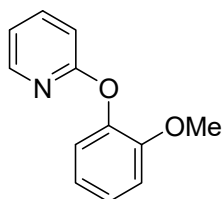
Silica gel column chromatography (hexane/EtOAc = 1/1) gave 103 mg of the product (0.42 mmol, 85%) as off-white solids of mp 91-92 °C. ¹H NMR (400 MHz, CDCl₃): δ 1.40 (3H, t, *J* = 7.3 Hz), 4.40 (2H, q, *J* = 7.3 Hz), 6.28 (1H, t, *J* = 6.8 Hz), 6.68 (1H, d, *J* = 9.3 Hz), 7.34-7.36 (1H, m), 7.40-7.45 (1H, m), 7.58 (1H, t, *J* = 7.8 Hz), 7.63-7.65 (1H, m), 8.05 (1H, s), 8.12 (1H, d, *J* = 7.8 Hz). ¹³C NMR (100 MHz, CDCl₃): δ 14.2 (CH₃), 61.3 (CH₂), 106.2 (CH), 122.0 (CH), 127.6 (CH), 129.4 (CH), 129.6 (CH), 131.1 (CH), 132.0 (C), 137.7 (CH), 140.1 (CH), 141.0 (C), 162.3 (C), 165.5 (C). IR (ATR): 760, 1240, 1590, 1650, 1720 cm⁻¹. HRMS (EI): *m/z* (M⁺) Calcd for C₁₄H₁₃NO₃: 243.0895. Found: 243.0894.

Ethyl 3-(pyridin-2-yloxy)benzoate¹⁵ (4af)

Silica gel column chromatography (hexane/Et₂O = 5/1, 2/1) gave 7 mg of the product (0.03 mmol, 3%) as a colorless oil. ¹H NMR (400 MHz, CDCl₃): δ 1.38 (3H, t, *J* = 7.3 Hz), 4.37 (2H, q, *J* = 7.3 Hz), 6.96 (1H, d, *J* = 8.3 Hz), 7.03 (1H, dd, *J* = 4.9, 6.3 Hz), 7.34-7.36 (1H, m), 7.48 (1H, t, *J* = 7.8 Hz), 7.70-7.74 (1H, m), 7.81-7.82 (1H, m), 7.90 (1H, d, *J* = 7.8 Hz), 8.19 (1H, dd, *J* = 1.5, 4.9 Hz). ¹³C NMR (100 MHz, CDCl₃): δ 14.2 (CH₃), 61.1 (CH₂), 111.7 (CH), 118.8 (CH), 122.3 (CH), 125.8 (CH), 125.9 (CH), 129.6 (CH), 132.2 (C), 139.6 (CH), 147.7 (CH), 154.1 (C), 163.4 (C), 166.0 (C). IR (ATR): 750, 1100, 1260, 1590, 1710 cm⁻¹. DART-MS *m/z*: 244 [M+H]⁺.

1-(2-Methoxyphenyl)pyridin-2(1H)-one¹⁶ (3ag)

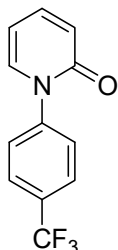
Silica gel column chromatography (hexane/EtOAc = 1/1) gave 75 mg of the product (0.37 mmol, 75%) as brown solids of mp 128-130 °C. ¹H NMR (400 MHz, CDCl₃): δ 3.82 (3H, s), 6.20 (1H, t, *J* = 6.8 Hz), 6.66 (1H, d, *J* = 9.3 Hz), 7.04-7.08 (2H, m), 7.24 (1H, dd, *J* = 2.0, 6.8 Hz), 7.26-7.28 (1H, m), 7.38-7.43 (2H, m). ¹³C NMR (100 MHz, CDCl₃): δ 55.8 (CH₃), 105.3 (CH), 112.4 (CH), 120.9 (CH), 121.8 (CH), 128.5 (CH), 129.7 (C), 130.3 (CH), 139.0 (CH), 139.9 (CH), 154.3 (C), 162.4 (C). IR (ATR): 760, 1110, 1500, 1580, 1660 cm⁻¹. EIMS *m/z*: 201 (M⁺).

2-(2-Methoxyphenoxy)pyridine¹⁷ (4ag)

Silica gel column chromatography (hexane/Et₂O = 4/1) gave 8 mg of the product (0.04 mmol, 8%) as white solids of mp 93-94 °C. ¹H NMR (400 MHz, CDCl₃): δ 3.77 (3H, s), 6.91-7.03 (4H, m), 7.14-7.16 (1H, m), 7.19-7.23 (1H, m), 7.64-7.69 (1H, m), 8.15 (1H, d, *J* = 3.4 Hz). ¹³C NMR

(100 MHz, CDCl₃): 55.8 (CH₃), 110.6 (CH), 112.8 (CH), 118.0 (CH), 121.1 (CH), 123.1 (CH), 126.0 (CH), 139.2 (CH), 142.6 (C), 147.6 (CH), 151.8 (C), 163.8 (C). IR (ATR): 750, 1020, 1110, 1240, 1270 cm⁻¹. DART-MS *m/z*: 202 [M+H]⁺.

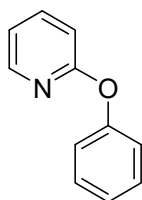
1-(4-(Trifluoromethyl)phenyl)pyridin-2(1*H*)-one (3ai)



Silica gel column chromatography (hexane/EtOAc = 1/2) gave 53 mg of the product (0.22 mmol, 44%) as white solids of mp 167-169 °C. ¹H NMR (400 MHz, CDCl₃): δ 6.28-6.31 (1H, m), 6.69 (1H, d, *J* = 9.3 Hz), 7.32 (1H, dd, *J* = 1.5, 6.8 Hz), 7.41-7.46 (1H, m), 7.55 (2H, d, *J* = 8.3 Hz), 7.78 (2H, d, *J* = 8.3 Hz). ¹³C NMR (125 MHz, CDCl₃): δ 106.4 (CH), 122.1 (CH), 123.6 (q, *J* = 271.8 Hz, C), 126.5 (q, *J* = 3.8 Hz, CH), 127.1 (CH), 130.6 (q, *J* = 33.4 Hz, C), 137.1 (CH), 140.2 (CH), 143.7 (C), 162.0 (C). IR (ATR): 760, 1070, 1140, 1580, 1650 cm⁻¹. HRMS (EI): *m/z* (M⁺) Calcd for C₁₂H₈F₃NO :239.0558. Found: 239.0557.

General procedure for O-arylation of pyridin-2-ones with diaryliodonium triflates. A screw cap test tube was charged with pyridin-2-one (**1a**) (95 mg, 1.0 mmol) and diphenyliodonium triflate (**2a**) (516 mg, 1.2 mmol). Then, the tube was evacuated and back-filled with argon. After chlorobenzene (2 mL) and quinoline (258 mg, 2.0 mmol) was added, a septum cap was replaced with a screw cap. The reaction mixture was stirred at 130 °C for 16 h. The mixture was cooled to room temperature and saturated Na₂CO₃ solution was added. The resulting mixture was extracted with AcOEt. The combined organic layers were dried over Na₂SO₄. Concentration and purification through silica gel column chromatography gave the desired product **4aa**.

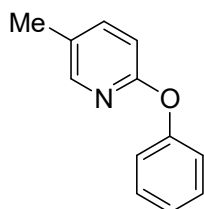
2-Phenoxypyridine¹⁸ (4aa)



Silica gel column chromatography (hexane/EtOAc = 16/1) gave 164 mg of the product (0.96 mmol, 96%) as a colorless oil. ¹H NMR (400 MHz, CDCl₃): δ 6.91 (1H, d, *J* = 8.3 Hz), 6.98-7.01

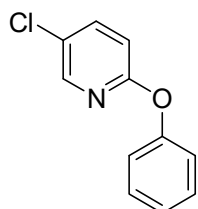
(1H, m), 7.13-7.16 (2H, m), 7.19-7.22 (1H, m), 7.39-7.43 (2H, m), 7.66-7.71 (1H, m), 8.21 (1H, dd, $J = 1.0, 4.9$ Hz). ^{13}C NMR (100 MHz, CDCl_3): δ 111.4 (CH), 118.3 (CH), 121.0 (CH), 124.5 (CH), 129.5 (CH), 139.3 (CH), 147.6 (CH), 154.1 (C), 163.6 (C). IR (ATR): 690, 750, 1240, 1590, 3060 cm^{-1} . EIMS m/z : 171 (M^+).

5-Methyl-2-phenoxy pyridine (4ba)



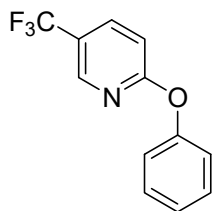
Silica gel column chromatography (hexane/EtOAc = 18/1) gave 170 mg of the product (0.92 mmol, 92%) as a yellow oil. ^1H NMR (500 MHz, CDCl_3): δ 2.28 (3H, s), 6.81 (1H, d, $J = 8.3$ Hz), 7.11 (2H, d, $J = 7.6$ Hz), 7.17 (1H, t, $J = 7.6$ Hz), 7.38 (2H, t, $J = 7.6$ Hz), 7.49 (1H, dd, $J = 2.0, 8.3$ Hz), 8.02 (1H, d, $J = 2.0$ Hz). ^{13}C NMR (100 MHz, CDCl_3): δ 17.4 (CH_3), 111.1 (CH), 120.8 (CH), 124.3 (CH), 127.8 (C), 129.7 (CH), 140.3 (CH), 147.5 (CH), 154.8 (C), 162.0 (C). IR (ATR): 690, 740, 1020, 1200, 1240, 1590, 3040 cm^{-1} . HRMS (EI) m/z Calcd for $\text{C}_{12}\text{H}_{11}\text{NO}$ (M^+): 185.0841. Found: 185.0837.

5-Chloro-2-phenoxy pyridine (4ca)



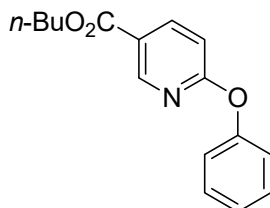
Silica gel column chromatography (hexane/benzene = 100/1) gave 179 mg of the product (0.87 mmol, 87%) as a colorless oil. ^1H NMR (400 MHz, CDCl_3): δ 6.88 (1H, d, $J = 8.3$ Hz), 7.12-7.14 (2H, m), 7.23 (1H, t, $J = 7.8$ Hz), 7.39-7.43 (2H, m), 7.64 (1H, dd, $J = 2.9, 8.3$ Hz), 8.13 (1H, d, $J = 2.9$ Hz). ^{13}C NMR (100 MHz, CDCl_3): δ 112.4 (CH), 121.1 (CH), 125.0 (CH), 125.8 (C), 129.7 (CH), 139.2 (CH), 146.1 (CH), 153.9 (C), 162.2 (C). IR (ATR): 690, 760, 1110, 1240, 1580, 3070 cm^{-1} . HRMS (EI) m/z (M^+) Calcd for $\text{C}_{11}\text{H}_8^{35}\text{ClNO}$: 205.0294; Found: 205.0296.

5-(Trifluoromethyl)-2-phenoxy pyridine (4da)



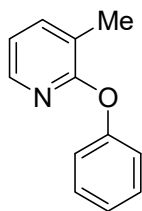
Silica gel column chromatography (hexane/EtOAc = 50/1) gave 175 mg of the product (0.73 mmol, 73%) as a colorless oil. ^1H NMR (400 MHz, CDCl_3): δ 7.01 (1H, d, J = 8.8 Hz), 7.15-7.17 (2H, m), 7.25-7.29 (1H, m), 7.44 (2H, t, J = 7.8 Hz), 7.90 (1H, dd, J = 2.4, 8.8 Hz), 8.45 (1H, s). ^{13}C NMR (100 MHz, CDCl_3): δ 111.3 (CH), 121.5 (CH), 121.5 (q, J = 33.9 Hz, C), 123.7 (q, J = 270.6 Hz, C), 125.5 (CH), 129.8 (CH), 136.6 (q, J = 3.3 Hz, CH), 145.5 (q, J = 4.1 Hz, CH), 153.2 (C), 165.9 (C). IR (ATR): 690, 740, 780, 1260, 1280, 1480, 1590, 3040 cm^{-1} . HRMS (EI) m/z (M^+) Calcd for $\text{C}_{12}\text{H}_8\text{F}_3\text{NO}$: 239.0558; Found: 239.0561.

Butyl 6-phenoxy pyridine-3-carboxylate (4ea)



Silica gel column chromatography (hexane/benzene = 16/1) gave 237 mg the product (0.87 mmol, 87%) as a pale yellow oil. ^1H NMR (400 MHz, CDCl_3): δ 0.97 (3H, t, J = 7.3 Hz), 1.41-1.51 (2H, m), 1.70-1.77 (2H, m), 4.32 (2H, t, J = 6.3 Hz), 6.94 (1H, d, J = 8.3 Hz), 7.15-7.17 (2H, m), 7.24-7.28 (1H, m), 7.42-7.46 (2H, m), 8.28 (1H, dd, J = 2.4, 8.8 Hz), 8.84 (1H, d, J = 2.4 Hz). ^{13}C NMR (100 MHz, CDCl_3): δ 13.6 (CH_3), 19.1 (CH_2), 30.6 (CH_2), 64.9 (CH_2), 110.7 (CH), 121.5 (CH + C), 125.4 (CH), 129.8 (CH), 140.6 (CH), 150.4 (CH), 153.4 (C), 165.2 (C), 166.5 (C). IR (ATR): 690, 750, 1250, 1470, 1590, 1720, 2960 cm^{-1} . HRMS (EI) m/z (M^+) Calcd for $\text{C}_{16}\text{H}_{17}\text{NO}_3$: 271.1208. Found: 271.1199.

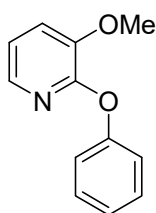
3-Methyl-2-phenoxy pyridine (4fa)



Silica gel column chromatography (hexane/EtOAc = 16/1) gave 167 mg of the product (0.90

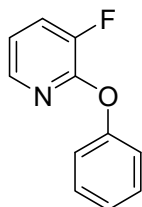
mmol, 90%) as a pale yellow oil. ^1H NMR (400 MHz, CDCl_3): δ 2.35 (3H, s), 6.91 (1H, dd, J = 4.9, 7.3 Hz), 7.11 (2H, dd, J = 1.0, 8.8 Hz), 7.16-7.19 (1H, m), 7.37-7.41 (2H, m), 7.53 (1H, dd, J = 1.0, 7.3 Hz), 8.00 (1H, d, J = 4.9 Hz). ^{13}C NMR (100 MHz, CDCl_3): δ 15.7 (CH_3), 118.5 (CH), 120.9 (CH), 121.8 (C), 124.1 (CH), 129.3 (CH), 139.6 (CH), 144.6 (CH), 154.4 (C), 161.7 (C). IR (ATR): 690, 730, 750, 1210, 1580, 3060 cm^{-1} . HRMS (EI) m/z (M^+) Calcd for $\text{C}_{12}\text{H}_{11}\text{NO}$: 185.0841; Found: 185.0842.

3-Methoxy-2-phenoxy pyridine (4ga)



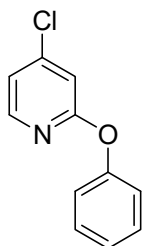
Silica gel column chromatography (hexane/EtOAc = 5/1) gave 162 mg of the product (0.81 mmol, 81%) as pale yellow solids of mp 105-107 $^{\circ}\text{C}$. ^1H NMR (400 MHz, CDCl_3): δ 3.95 (3H, s), 6.98 (1H, dd, J = 4.9, 8.3 Hz), 7.14-7.23 (4H, m), 7.37-7.41 (2H, m), 7.73 (1H, dd, J = 1.5, 4.9 Hz). ^{13}C NMR (100 MHz, CDCl_3): δ 55.6 (CH_3), 118.9 (CH), 121.0 (CH), 124.3 (CH), 129.3 (CH), 137.5 (CH), 144.7 (C), 153.4 (C), 154.1 (C). IR (ATR): 690, 790, 1010, 1210, 1480, 1580, 3010 cm^{-1} . HRMS (EI) m/z (M^+) Calcd for $\text{C}_{12}\text{H}_{11}\text{NO}_2$: 201.0790; Found: 201.0790.

3-Fluoro-2-phenoxy pyridine (4ha)



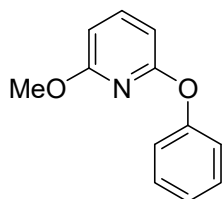
Silica gel column chromatography (hexane/EtOAc = 16/1) gave 171 mg of the product (0.90 mmol, 90%) as a yellow oil. ^1H NMR (400 MHz, CDCl_3): δ 6.98-7.02 (1H, m), 7.18 (2H, d, J = 7.8 Hz), 7.23 (1H, t, J = 7.8 Hz), 7.42 (2H, t, J = 7.8 Hz), 7.45-7.50 (1H, m), 7.93 (1H, dd, J = 1.5, 4.9 Hz). ^{13}C NMR (100 MHz, CDCl_3): δ 119.1 (d, J = 1.7 Hz, CH), 121.1 (CH), 124.5 (d, J = 15.7 Hz, CH), 125.0 (CH), 129.6 (CH), 141.9 (d, J = 5.8 Hz, CH), 148.0 (d, J = 259.9 Hz, C), 152.4 (d, J = 10.8 Hz, C), 153.5 (C). IR (ATR): 690, 790, 1110, 1200, 1590, 3070 cm^{-1} . HRMS (EI) m/z Calcd for $\text{C}_{11}\text{H}_8\text{FNO}$ (M^+): 189.0590. Found: 189.0588.

4-Chloro-2-phenoxypyridine (4ia)



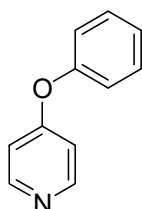
Silica gel column chromatography (hexane/EtOAc = 20/1) gave 168 mg of the product (0.82 mmol, 82%) as a colorless oil. ^1H NMR (500 MHz, CDCl_3): δ 6.92 (1H, d, J = 1.5 Hz), 7.00 (1H, dd, J = 1.7, 5.4 Hz), 7.13 (2H, d, J = 7.6 Hz), 7.23 (1H, t, J = 7.6 Hz), 7.42 (2H, t, J = 7.6 Hz), 8.09 (1H, d, J = 5.4 Hz). ^{13}C NMR (125 MHz, CDCl_3): δ 111.4 (CH), 118.9 (CH), 121.2 (CH), 125.0 (CH), 129.6 (CH), 146.1 (C), 148.2 (CH), 153.4 (C), 164.4 (C). IR (ATR): 690, 760, 1090, 1220, 1490 cm^{-1} . HRMS (EI) m/z Calcd for $\text{C}_{11}\text{H}_8^{35}\text{ClNO}$: 205.0294. Found: 205.0294.

2-Methoxy-6-phenoxypyridine¹⁷ (4la)



This reaction was conducted on 0.25 mmol scale. Silica gel column chromatography (hexane/benzene = 10/1) gave 35 mg the product (0.17 mmol, 70%) as a yellow oil. ^1H NMR (500 MHz, CDCl_3): δ 3.81 (3H, s), 6.30 (1H, d, J = 7.8 Hz), 6.44 (1H, d, J = 7.8 Hz), 7.15 (2H, d, J = 8.1 Hz), 7.17-7.20 (1H, m), 7.38 (2H, t, J = 8.1 Hz), 7.53 (1H, t, J = 7.8 Hz). ^{13}C NMR (100 MHz, CDCl_3): δ 53.4 (CH_3), 101.4 (CH), 104.2 (CH), 121.1 (CH), 124.5 (CH), 129.6 (CH), 141.4 (CH), 154.4 (C), 162.5 (C), 163.5 (C). IR (ATR): 690, 790, 1040, 1200, 1230, 1570, 3060 cm^{-1} . EIMS m/z : 201 (M^+).

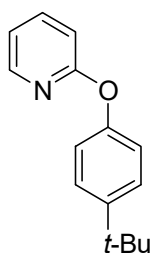
4-Phenoxypyridine (4ka)



Silica gel column chromatography (hexane/EtOAc = 2/1) gave 142 mg of the product (0.83 mmol, 83%) as a colorless oil. ^1H NMR (400 MHz, CDCl_3): δ 6.83-6.85 (2H, m), 7.10-7.12 (2H, m),

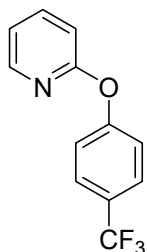
7.24-7.28 (1H, m), 7.44 (2H, t, $J = 7.8$ Hz), 8.46-8.48 (2H, m). ^{13}C NMR (100 MHz, CDCl_3): δ 112.1 (CH), 120.9 (CH), 125.5 (CH), 130.2 (CH), 151.5 (CH), 154.0 (C), 164.8 (C). IR (ATR): 690, 800, 1210, 1260, 1480, 1570, 3030 cm^{-1} . HRMS (EI) m/z (M^+) Calcd for $\text{C}_{11}\text{H}_9\text{NO}$: 171.0684; Found: 171.0687.

2-(4-*tert*-Butylphenoxy)pyridine¹⁹ (4ah)



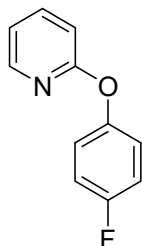
Silica gel column chromatography (hexane/EtOAc = 16/1) gave 216 mg of the product (0.95 mmol, 95%) as white solids of mp 110-112 °C. ^1H NMR (400 MHz, CDCl_3): δ 1.33 (9H, s), 6.89 (1H, d, $J = 8.3$ Hz), 6.96-7.00 (1H, m), 7.05-7.09 (2H, m), 7.39-7.43 (2H, m), 7.65-7.69 (1H, m), 8.21 (1H, dd, $J = 2.0, 4.9$ Hz). ^{13}C NMR (100 MHz, CDCl_3): δ 31.2 (CH_3), 34.1 (C), 111.2 (CH), 118.1 (CH), 120.4 (CH), 126.4 (CH), 139.2 (CH), 147.1 (C), 147.6 (CH), 151.6 (C), 163.8 (C). IR (ATR): 770, 840, 1210, 1590, 3060 cm^{-1} . EIMS m/z : 227 (M^+).

2-[4-(Trifluoromethyl)phenoxy]pyridine¹⁹ (4ai)



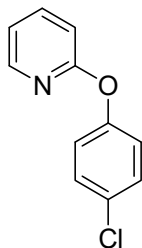
Silica gel column chromatography (hexane/EtOAc = 16/1) gave 239 mg of the product (0.99 mmol, 99%) as colorless oil. ^1H NMR (400 MHz, CDCl_3): δ 7.00 (1H, d, $J = 8.3$ Hz), 7.05-7.08 (1H, m), 7.24-7.26 (2H, m), 7.66 (2H, d, $J = 8.3$ Hz), 7.73-7.77 (1H, m), 8.22 (1H, d, $J = 3.4$ Hz). ^{13}C NMR (100 MHz, CDCl_3): δ 112.2 (CH), 119.3 (CH), 121.1 (CH), 124.1 (q, $J = 272.3$ Hz, C), 126.4 (q, $J = 32.3$ Hz, C), 126.9 (q, $J = 3.3$ Hz, CH), 139.8 (CH), 147.7 (CH), 157.0 (C), 162.8 (C). IR (ATR): 780, 850, 1120, 1240, 1470, 1570, 3070 cm^{-1} . EIMS m/z : 239 (M^+).

2-(4-Fluorophenoxy)pyridine¹⁷ (4ad)



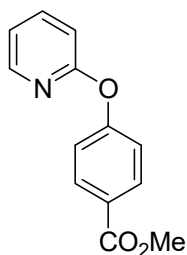
Silica gel column chromatography (hexane/EtOAc = 10/1) gave 172 mg of the product (0.91 mmol, 91%) as a yellow oil. ¹H NMR (400 MHz, CDCl₃): δ 6.91 (1H, d, *J* = 8.3 Hz), 7.00 (1H, dd, *J* = 4.9, 6.8 Hz), 7.06-7.13 (4H, m), 7.67-7.71 (1H, m), 8.18-8.19 (1H, m). ¹³C NMR (100 MHz, CDCl₃): δ 111.4 (CH), 116.3 (d, *J* = 23.2 Hz, CH), 118.5 (CH), 122.8 (d, *J* = 8.3 Hz, CH), 139.5 (CH), 147.7 (CH), 149.9 (C), 159.7 (d, *J* = 242.5 Hz, C), 163.8 (C). IR (ATR): 780, 880, 1190, 1220, 1270, 1590, 3060 cm⁻¹. EIMS *m/z*: 189 (M⁺).

2-(4-Chlorophenoxy)pyridine¹⁹ (4ae)



Silica gel column chromatography (hexane/EtOAc = 16/1) gave 197 mg of the product (0.96 mmol, 96%) as colorless oil. ¹H NMR (400 MHz, CDCl₃): δ 6.94 (1H, d, *J* = 8.3 Hz), 7.00-7.03 (1H, m), 7.09 (2H, d, *J* = 8.8 Hz), 7.36 (2H, d, *J* = 8.8 Hz), 7.69-7.73 (1H, m), 8.19 (1H, d, *J* = 3.4 Hz). ¹³C NMR (100 MHz, CDCl₃): δ 111.6 (CH), 118.7 (CH), 122.6 (CH), 129.6 (CH), 129.8 (C), 139.6 (CH), 147.6 (CH), 152.6 (C), 163.3 (C). IR (ATR): 770, 840, 1080, 1240, 1580, 3060 cm⁻¹. EIMS *m/z*: 205 (M⁺).

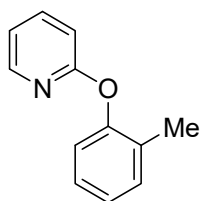
2-[4-(Methoxycarbonyl)phenoxy]pyridine¹⁷ (4aj)



This reaction was conducted on 0.25 mmol scale. Silica gel column chromatography (hexane/

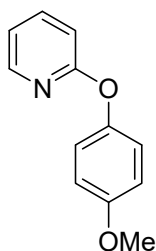
benezene = 1/4) gave 55 mg of the product (0.24 mmol, 96%) as a yellow oil. ^1H NMR (400 MHz, CDCl_3): δ 3.92 (3H, s), 6.98 (1H, d, $J = 8.3$ Hz), 7.07 (1H, dd, $J = 5.4, 6.8$ Hz), 7.18 (2H, d, $J = 8.8$ Hz), 7.72-7.76 (1H, m), 8.09 (2H, d, $J = 8.8$ Hz), 8.22-8.24 (1H, m). ^{13}C NMR (100 MHz, CDCl_3): δ 52.0 (CH_3), 112.4 (CH), 119.3 (CH), 120.4 (CH), 126.1 (C), 131.5 (CH), 139.8 (CH), 147.9 (CH), 158.4 (C), 162.9 (C), 166.6 (C). IR (ATR): 770, 850, 1190, 1220, 1260, 1590, 3070 cm^{-1} . EIMS m/z : 229 (M^+).

2-(2-Methylphenoxy)pyridine¹⁹ (4ak)

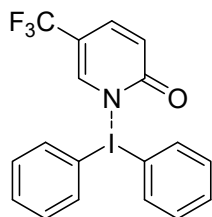


Silica gel column chromatography (hexane/EtOAc = 16/1) gave 184 mg of the product (0.99 mmol, 99%) as yellow oil. ^1H NMR (400 MHz, CDCl_3): δ 2.18 (3H, s), 6.85 (1H, d, $J = 8.3$ Hz), 6.94-6.97 (1H, m), 7.06 (1H, d, $J = 8.3$ Hz), 7.14 (1H, t, $J = 7.3$ Hz), 7.22-7.29 (2H, m), 7.64-7.69 (1H, m), 8.17-8.19 (1H, m). ^{13}C NMR (100 MHz, CDCl_3): δ 16.2 (CH_3), 110.6 (CH), 117.9 (CH), 121.7 (CH), 125.1 (CH), 127.1 (CH), 130.7 (C), 131.3 (CH), 139.3 (CH), 147.8 (CH), 152.2 (C), 163.7 (C). IR (ATR): 710, 770, 1240, 1470, 1570, 3060 cm^{-1} . EIMS m/z : 185 (M^+).

2-(4-Methoxyphenoxy)pyridine¹⁷ (4ac)



This reaction was conducted on 0.5 mmol scale. Silica gel column chromatography (hexane/EtOAc = 5/1) gave 3 mg of the product (0.015 mmol, 3%) as a yellow oil. ^1H NMR (500 MHz, CDCl_3): δ 3.82 (3H, s), 6.87 (1H, d, $J = 8.3$ Hz), 6.92-6.97 (3H, m), 7.06-7.08 (2H, m), 7.65-7.67 (1H, m), 8.18 (1H, dd, $J = 1.7, 4.9$ Hz). ^{13}C NMR (125 MHz, CDCl_3): δ 55.5 (CH_3), 111.0 (CH), 114.7 (CH), 118.0 (CH), 122.3 (CH), 139.2 (CH), 147.3 (C), 147.6 (CH), 156.5 (C), 164.2 (C). IR (ATR): 780, 880, 1030, 1200, 1230, 1590, 3060 cm^{-1} . EIMS m/z : 201 (M^+).

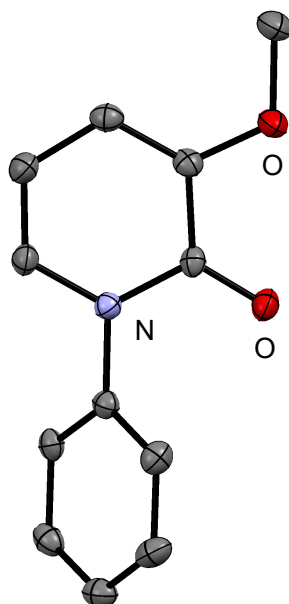
Diphenyliodonium 2-oxo-5-(trifluoromethyl)-2H-pyridin-1-ide (5)

Na (690 mg, 30 mmol) was added to MeOH (40 mL) at 0 °C and dissolved. To the solution was added 5-(trifluoromethyl)-2-pyridone (4.89 g, 30 mmol), and the reaction mixture was stirred at room temperature for 12 h. MeOH was removed to give 5.52 g of sodium 2-oxo-5-(trifluoromethyl)-2H-pyridin-1-ide (29.8 mmol, 99%) as white solids of mp 114-115 °C. ¹H NMR (500 MHz, DMSO-*d*₆): δ 5.87 (1H, d, *J* = 8.8 Hz), 7.18 (1H, dd, *J* = 2.2, 8.8 Hz), 7.91 (1H, d, *J* = 2.2 Hz). ¹³C NMR (125 MHz, DMSO-*d*₆): δ 106.0 (q, *J* = 31.5 Hz, C), 113.6 (CH), 126.5 (q, *J* = 268.0 Hz, C), 133.2 (q, *J* = 2.9 Hz, CH), 145.7 (q, *J* = 4.8 Hz, CH), 173.8 (C). ¹⁹F NMR (470 MHz, DMSO-*d*₆): δ -57.5. IR (ATR): 840, 1110, 1480, 3080 cm⁻¹. HRMS (FAB) *m/z* Calcd for C₆H₄F₃NONa [M+H]⁺: 186.0143. Found: 186.0146. Anal. Calcd for C₆H₃F₃NONa·1/2H₂O: C, 37.13; H, 2.08; N, 7.22. Found: C, 37.37; H, 2.05; N, 7.18.

A reaction flask was charged with diphenyliodonium triflate (860 mg, 2.0 mmol), and CH₂Cl₂ (135 mL) was added. To the solution was added 1.1 M aqueous solution of sodium 2-oxo-5-(trifluoromethyl)-2H-pyridin-1-ide (3.70 g, 20 mmol), and the reaction mixture was stirred at 0 °C for 12 h. The resulting mixture was extracted with CH₂Cl₂. The organic layers were washed with H₂O and concentrated. Et₂O (50 mL) was added and the mixture was stirred at room temperature for 30 min to precipitate solids. The solids were filtrated, washed with Et₂O, and dried in vacuo to give 755 mg of the product (1.70 mmol, 85% yield) as white solids of mp 143-144 °C. ¹H NMR (500 MHz, DMSO-*d*₆): δ 5.85 (1H, d, *J* = 9.1 Hz), 7.17 (1H, dd, *J* = 2.9, 9.1 Hz), 7.46 (4H, t, *J* = 7.6 Hz), 7.58 (2H, t, *J* = 7.6 Hz), 7.79 (1H, d, *J* = 2.0 Hz), 8.18 (4H, d, *J* = 7.6 Hz). ¹³C NMR (125 MHz, DMSO-*d*₆): δ 106.2 (q, *J* = 32.4 Hz, C), 113.4 (CH), 119.9 (C), 126.3 (q, *J* = 268.9 Hz, C), 131.0 (CH), 131.1 (CH), 133.0 (q, *J* = 1.9 Hz, CH), 134.8 (CH), 145.3 (q, *J* = 3.8 Hz, CH), 172.7 (C). ¹⁹F NMR (470 MHz, DMSO-*d*₆): δ -57.7. IR (ATR): 840, 1100, 1320, 1500, 1600 cm⁻¹. HRMS (FAB⁺) *m/z* Calcd for C₁₂H₁₀I [M-(5-CF₃-C₅H₃NO)]⁺: 280.9827. Found: 280.9826. HRMS (FAB⁻) *m/z* Calcd for C₆H₃F₃NO [M-(Ph₂I)]⁻: 162.0167. Found: 162.0171. Anal. Calcd for C₁₈H₁₃F₃INO: C, 48.78; H, 2.96; N, 3.16. Found: C, 48.53; H, 2.98; N, 3.17.

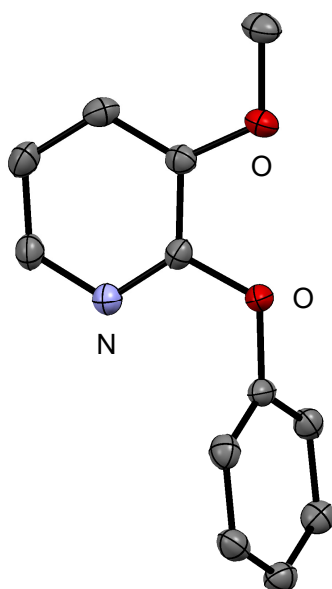
Compound 3ga (CCDC 1999363)

Bond precision:		C-C = 0.0031 Å	Wavelength=0.71075
Cell:	a=6.571(3)	b=12.434(5)	c=12.168(6)
	alpha=90	beta=93.376(7)	gamma=90
Temperature: 93 K			
	Calculated	Reported	
Volume	992.5(8)	992.4(8)	
Space group	P 21/c	P 1 21/c 1	
Hall group	-P 2ybc	-P 2ybc	
Moiety formula	C12 H11 N O2	C12 H11 N O2	
Sum formula	C12 H11 N O2	C12 H11 N O2	
Mr	201.22	201.22	
Dx,g cm-3	1.347	1.347	
Z	4	4	
Mu (mm-1)	0.092	0.092	
F000	424.0	424.0	
F000'	424.20		
h,k,lmax	8,16,15	8,15,15	
Nref	2284	2275	
Tmin,Tmax	0.991,0.998	0.886,0.998	
Tmin'	0.980		
Correction method= # Reported T Limits: Tmin=0.886 Tmax=0.998 AbsCorr =			
MULTI-SCAN			
Data completeness= 0.996		Theta(max)= 27.492	
R(reflections)= 0.0693(1776)		wR2(reflections)= 0.1506(2275)	
S = 1.189		Npar= 136	



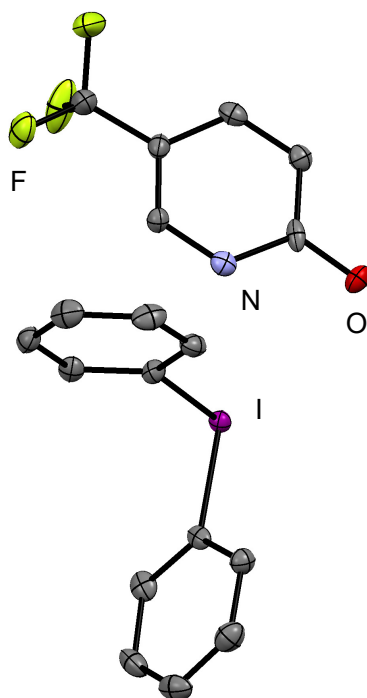
Compound 4ga (CCDC 1999364)

Bond precision:		C-C = 0.0032 Å	Wavelength=0.71075
Cell:	a=9.935(5)	b=7.985(4)	c=13.410(7)
	alpha=90	beta=110.758(9)	gamma=90
Temperature: 93 K			
	Calculated	Reported	
Volume	994.8(9)	994.8(9)	
Space group	P 21/n	P 1 21/n 1	
Hall group	-P 2yn	-P 2yn	
Moiety formula	C12 H11 N O2	C12 H11 N O2	
Sum formula	C12 H11 N O2	C12 H11 N O2	
Mr	201.22	201.22	
Dx, g cm-3	1.344	1.343	
Z	4	4	
Mu (mm-1)	0.092	0.092	
F000	424.0	424.0	
F000'	424.20		
h,k,lmax	12,10,17	12,10,17	
Nref	2278	2276	
Tmin,Tmax	0.989,0.998	0.854,0.998	
Tmin'	0.986		
Correction method= # Reported T Limits: Tmin=0.854 Tmax=0.998 AbsCorr =			
MULTI-SCAN			
Data completeness=	0.999	Theta(max)= 27.446	
R(reflections)=	0.0617(1494)	wR2(reflections)= 0.1373(2276)	
S =	1.090	Npar= 136	

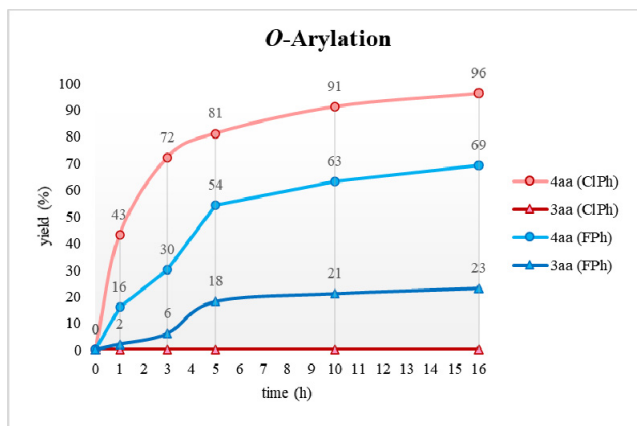
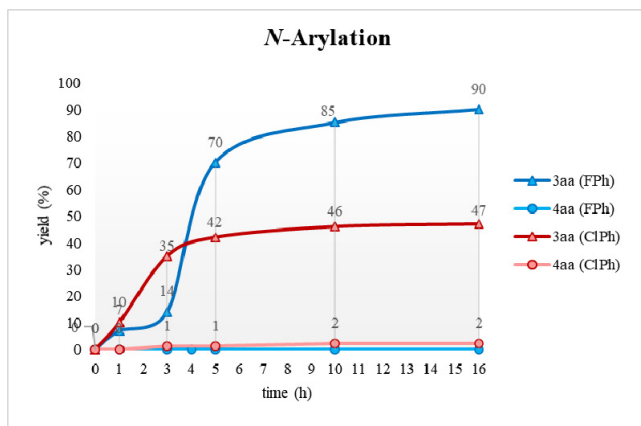
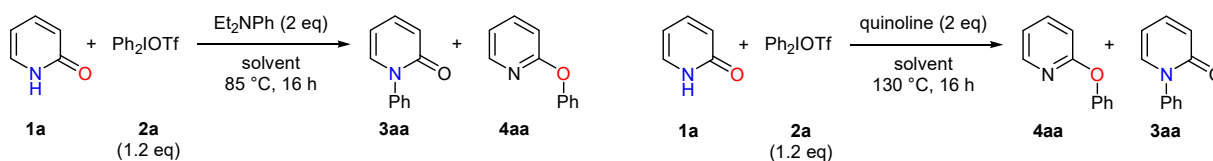


Compound 5 (CCDC 1999366)

Bond precision:		C-C = 0.0071 Å	Wavelength=0.71075
Cell:	a=6.0218(15)	b=15.569(4)	c=17.415(4)
	alpha=90	beta=91.278(5)	gamma=90
Temperature: 93 K			
	Calculated	Reported	
Volume	1632.3(7)	1632.3(7)	
Space group	P 21/n	P 1 21/n 1	
Hall group	-P 2yn	-P 2yn	
Moiety formula	C12 H10 I, C6 H3 F3 N O	C18 H13 F3 I N O	
Sum formula	C18 H13 F3 I N O	C18 H13 F3 I N O	
Mr	443.19	443.21	
Dx,g cm-3	1.804	1.803	
Z	4	4	
Mu (mm-1)	1.998	1.998	
F000	864.0	864.0	
F000'	862.56		
h,k,lmax	7,20,22	7,20,22	
Nref	3733	3666	
Tmin,Tmax	0.887,0.942	0.833,0.942	
Tmin'	0.819		
Correction method= # Reported T Limits: Tmin=0.833 Tmax=0.942 AbsCorr =			
MULTI-SCAN			
Data completeness= 0.982	Theta(max)= 27.475		
R(reflections)= 0.0417(3118)	wR2(reflections)= 0.1059(3666)		
S = 1.274	Npar= 217		



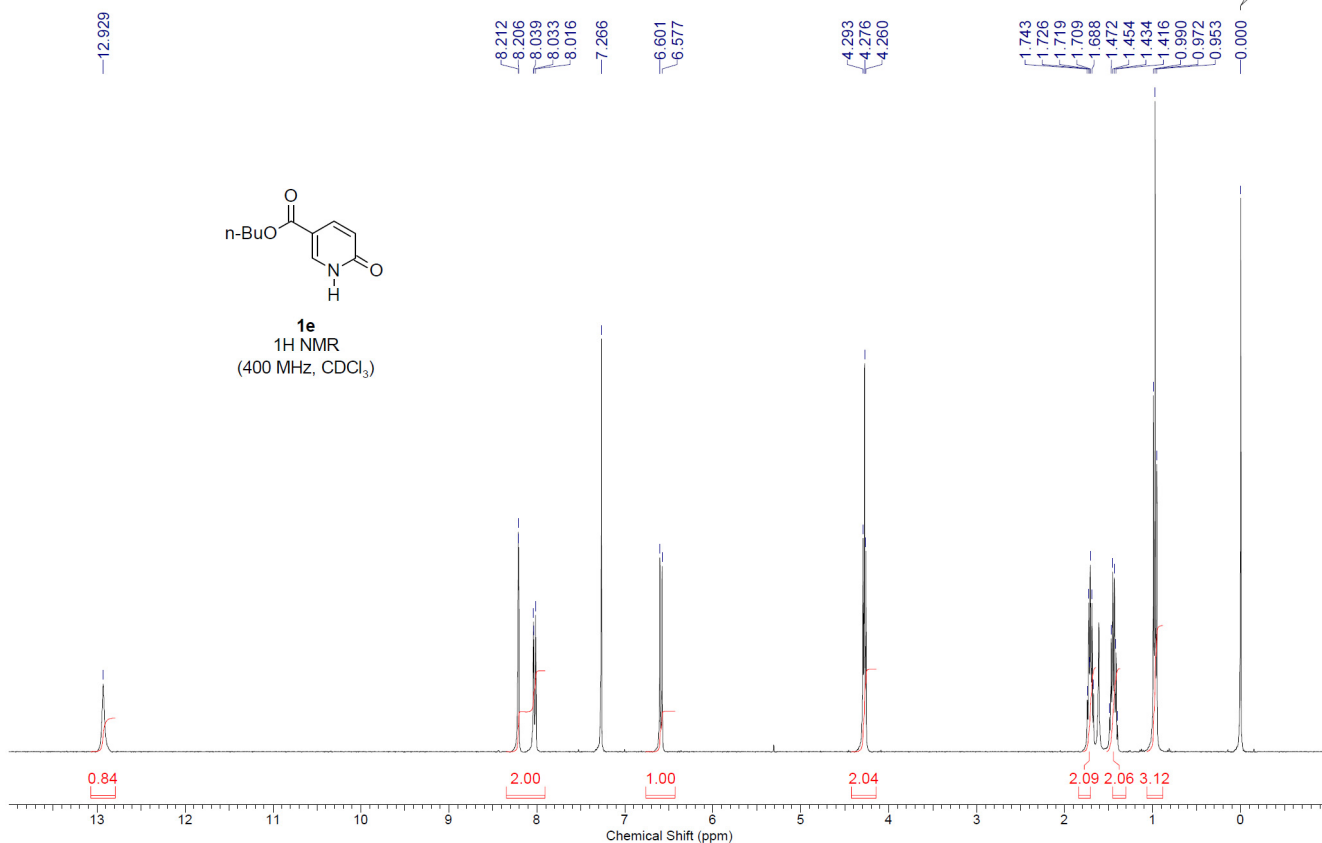
Comparison between the effects of FPh and ClPh



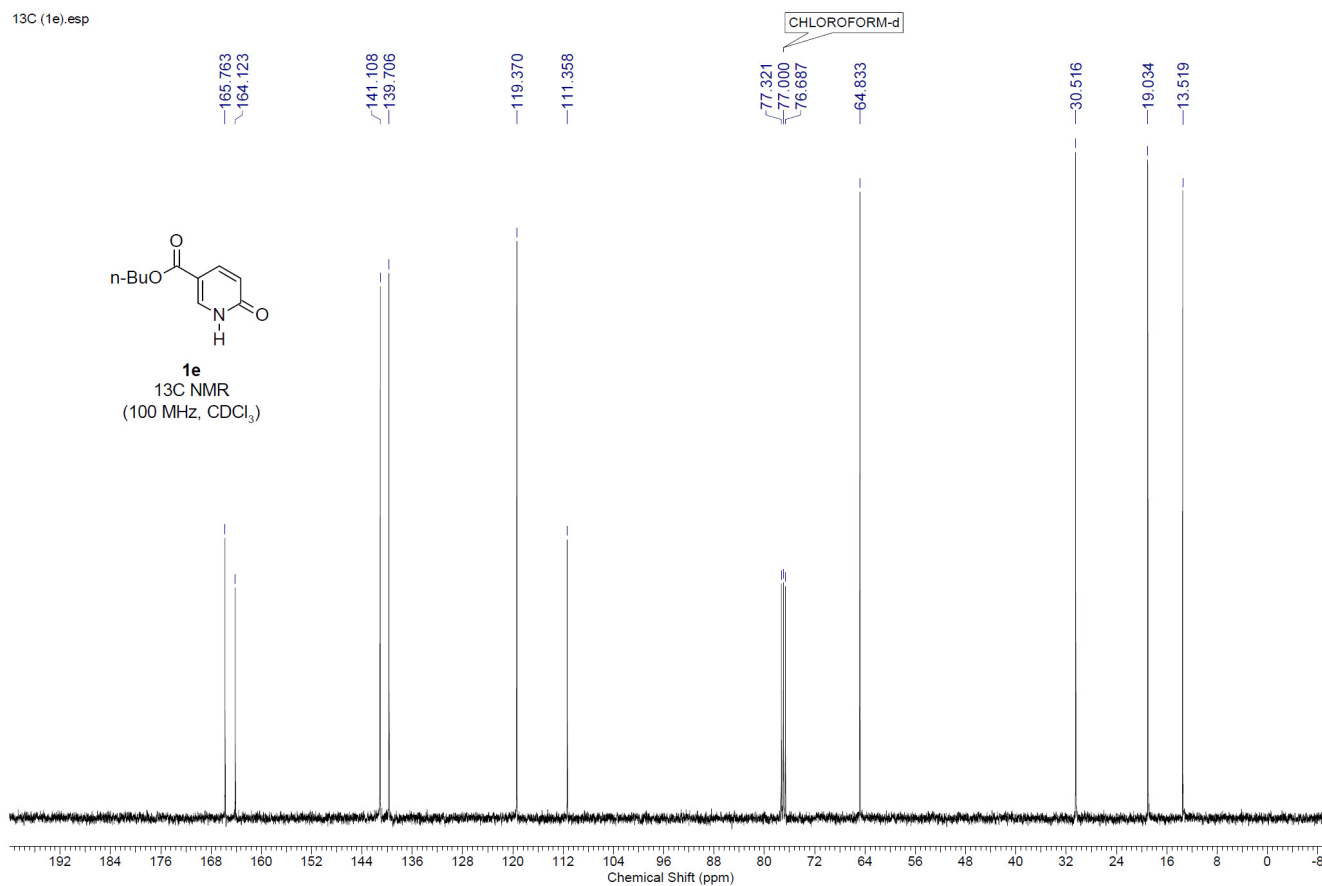
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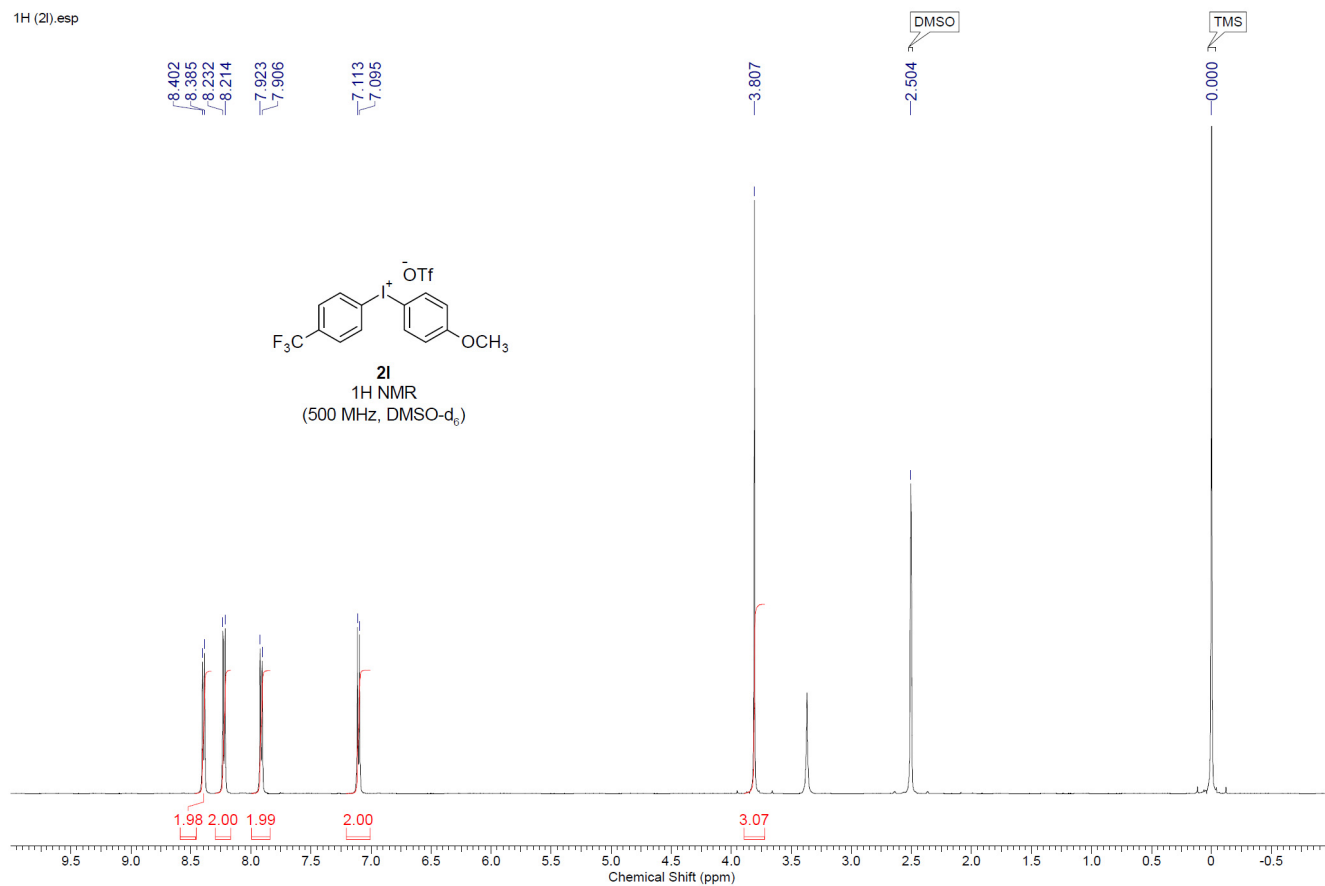
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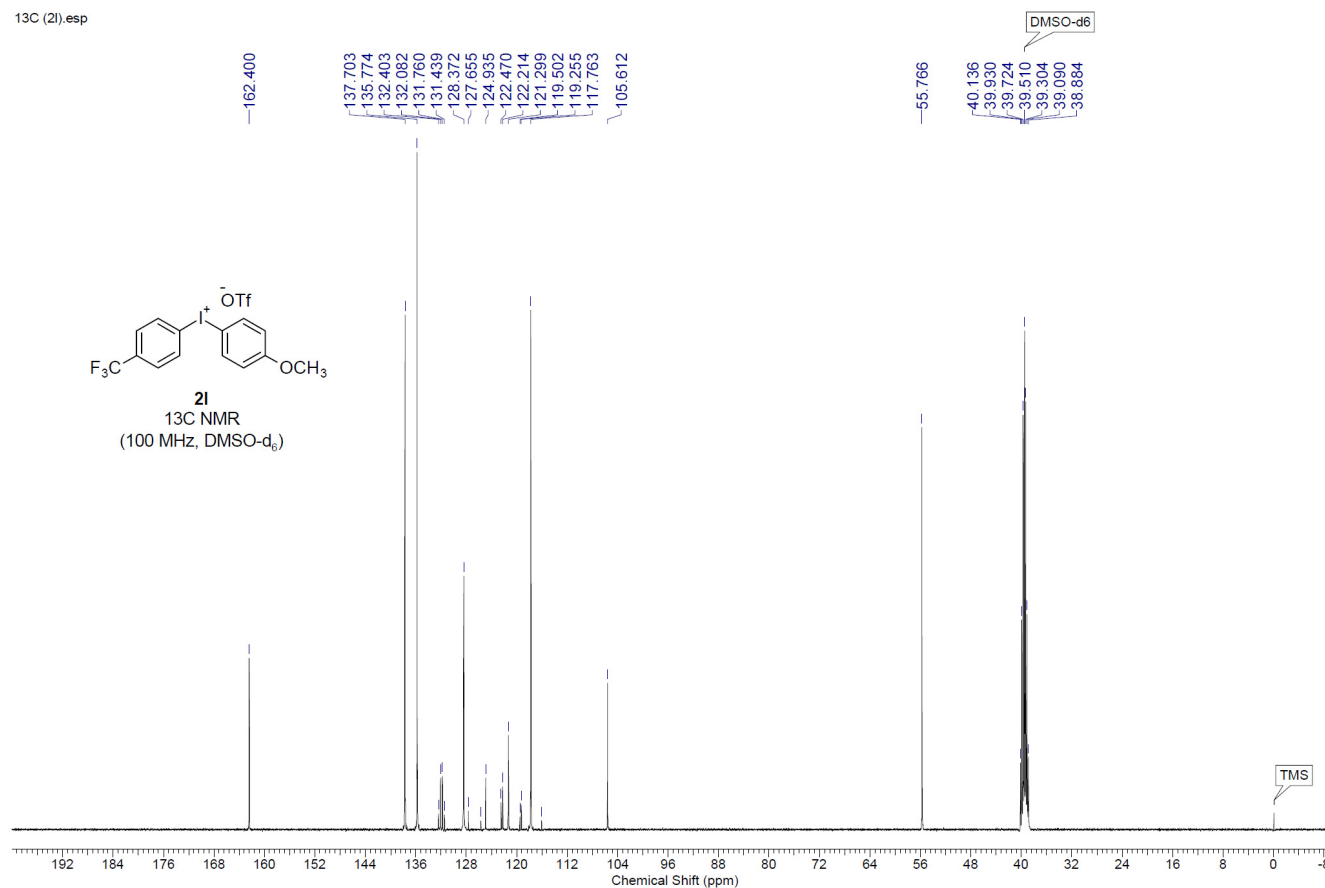
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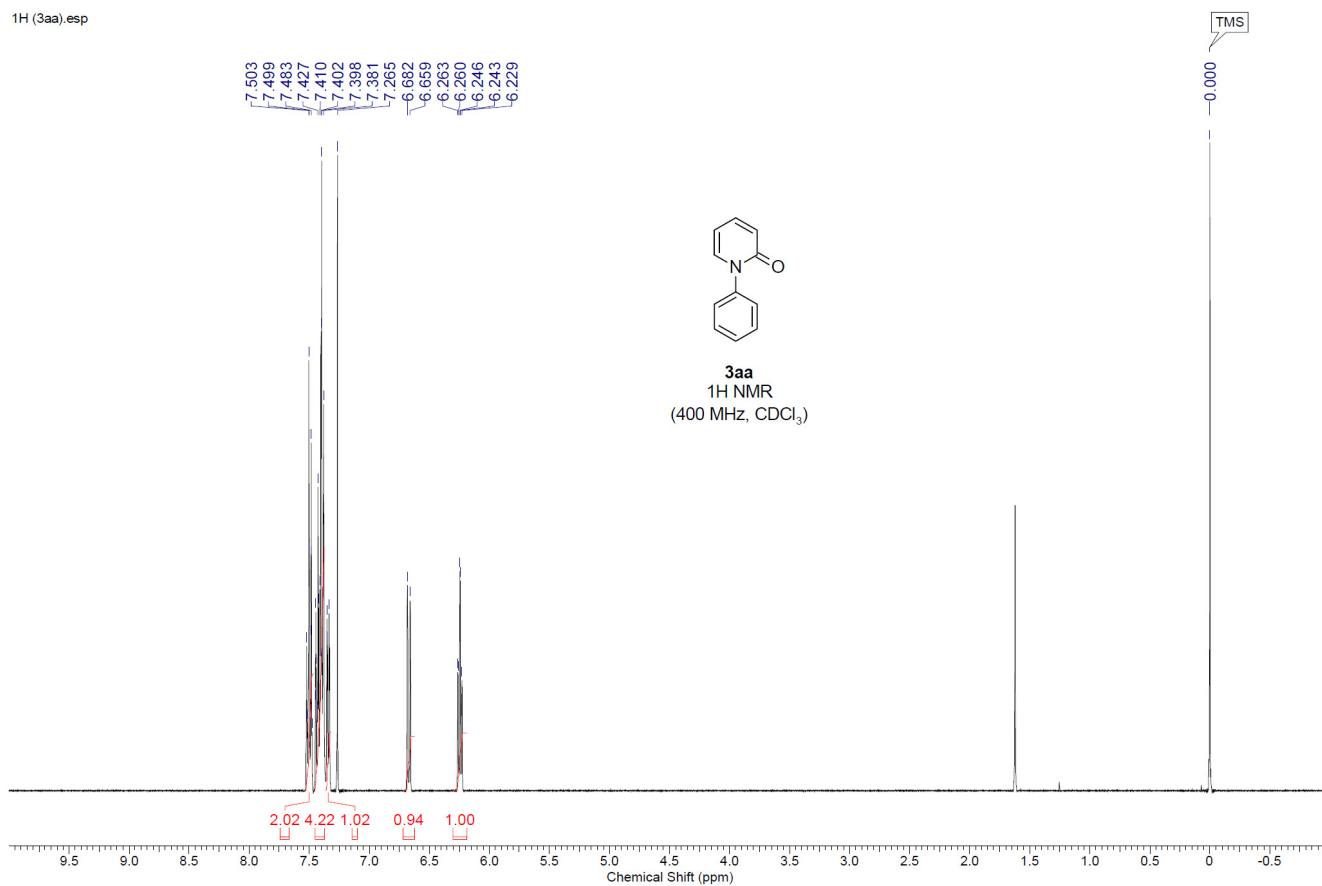
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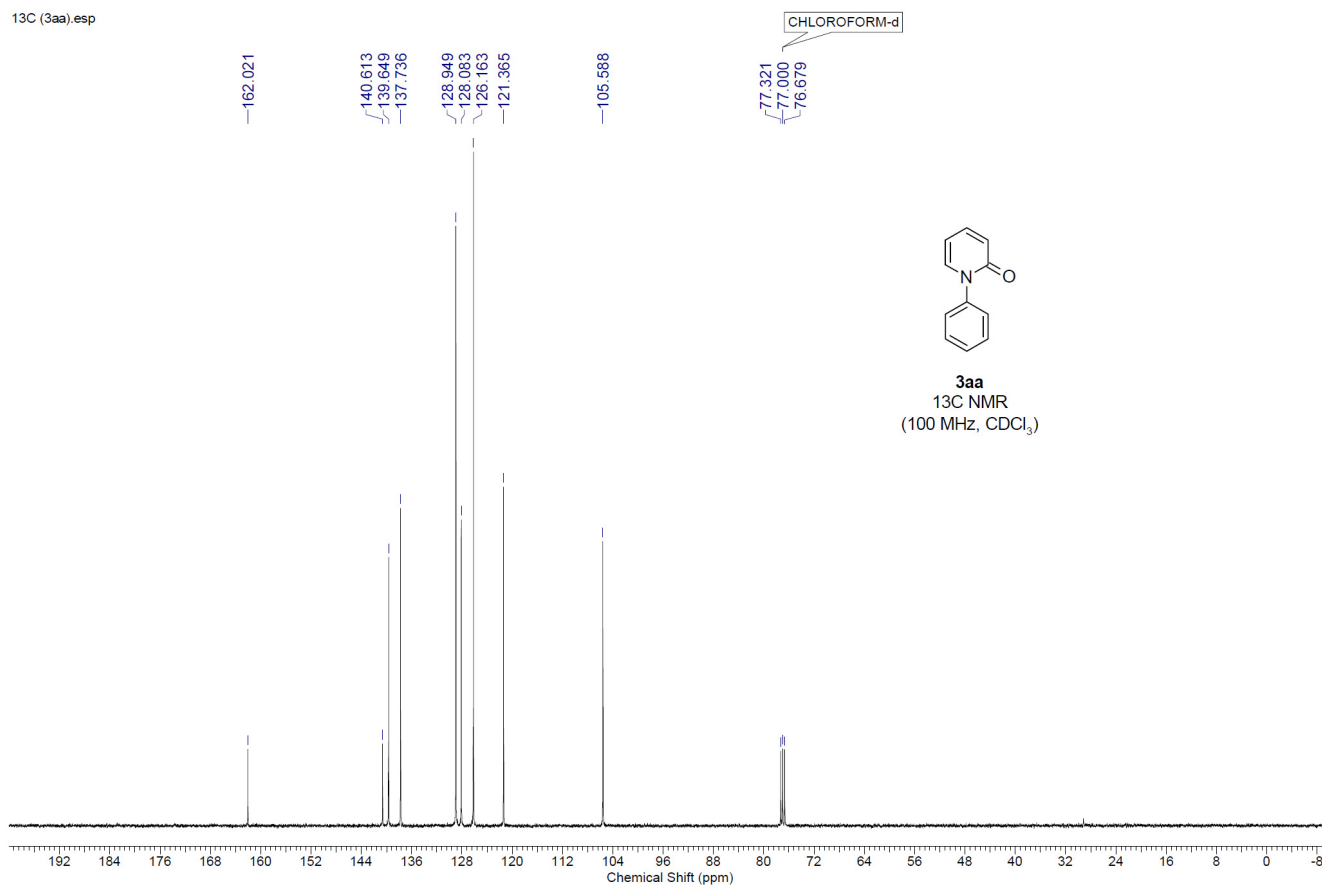
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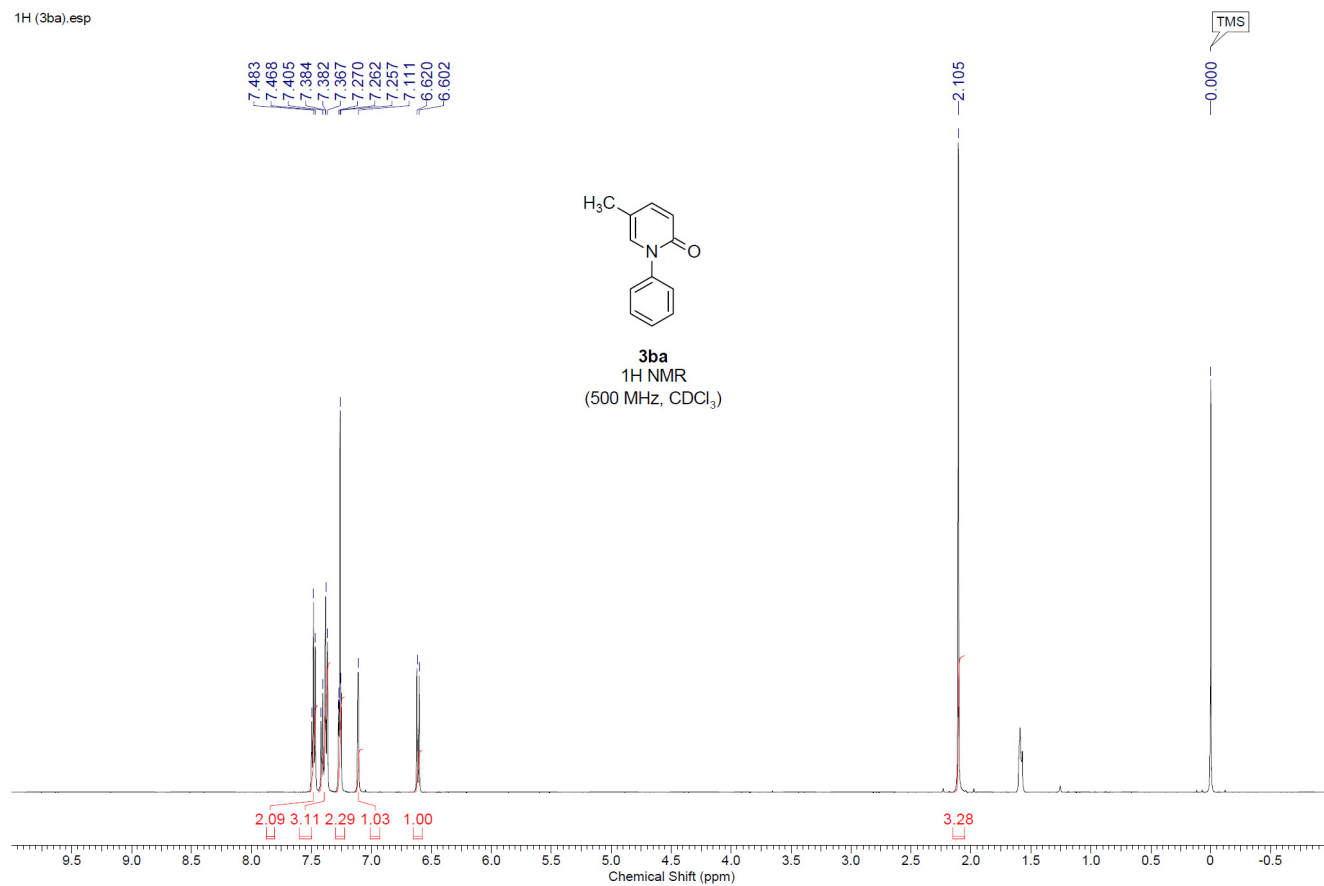
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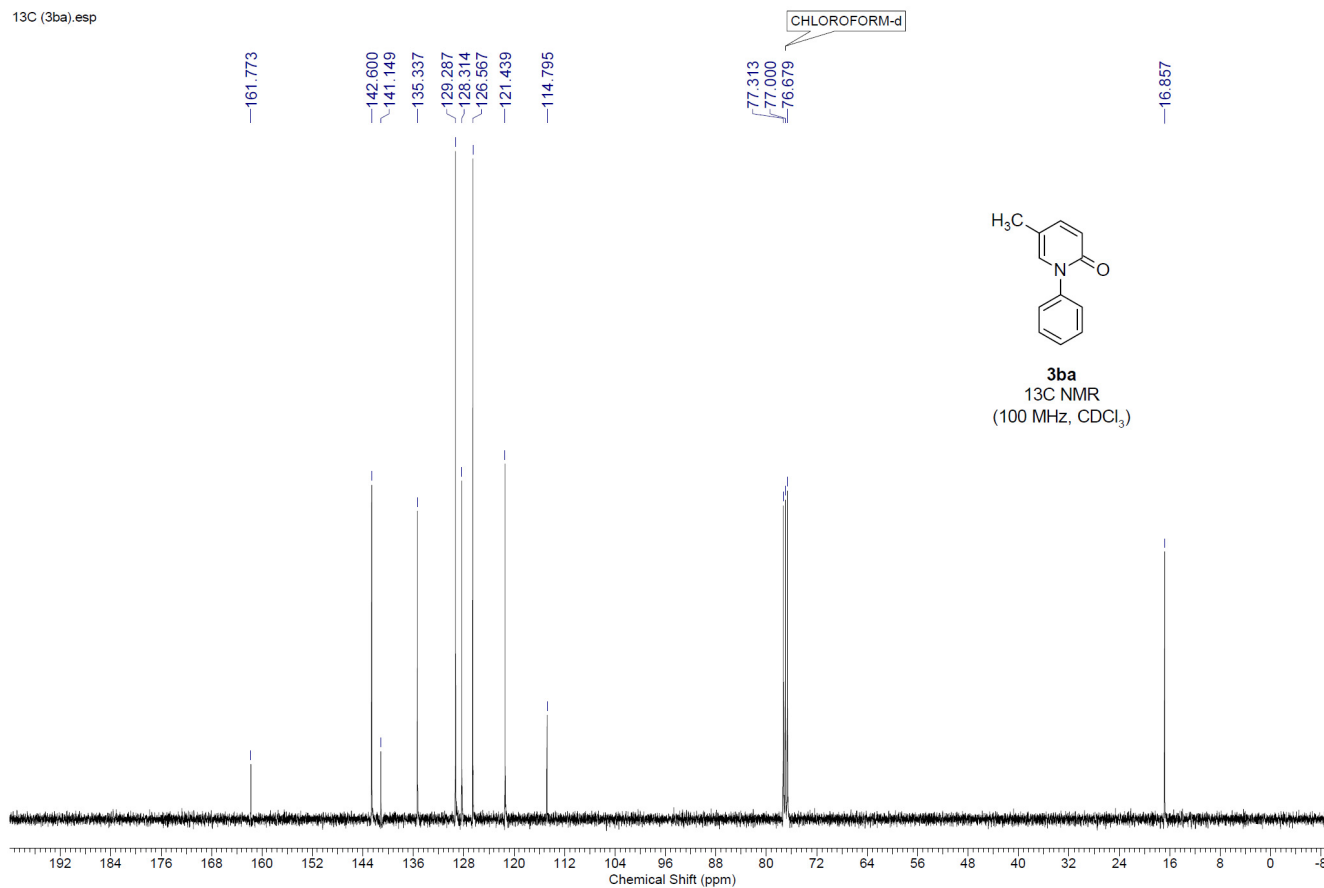
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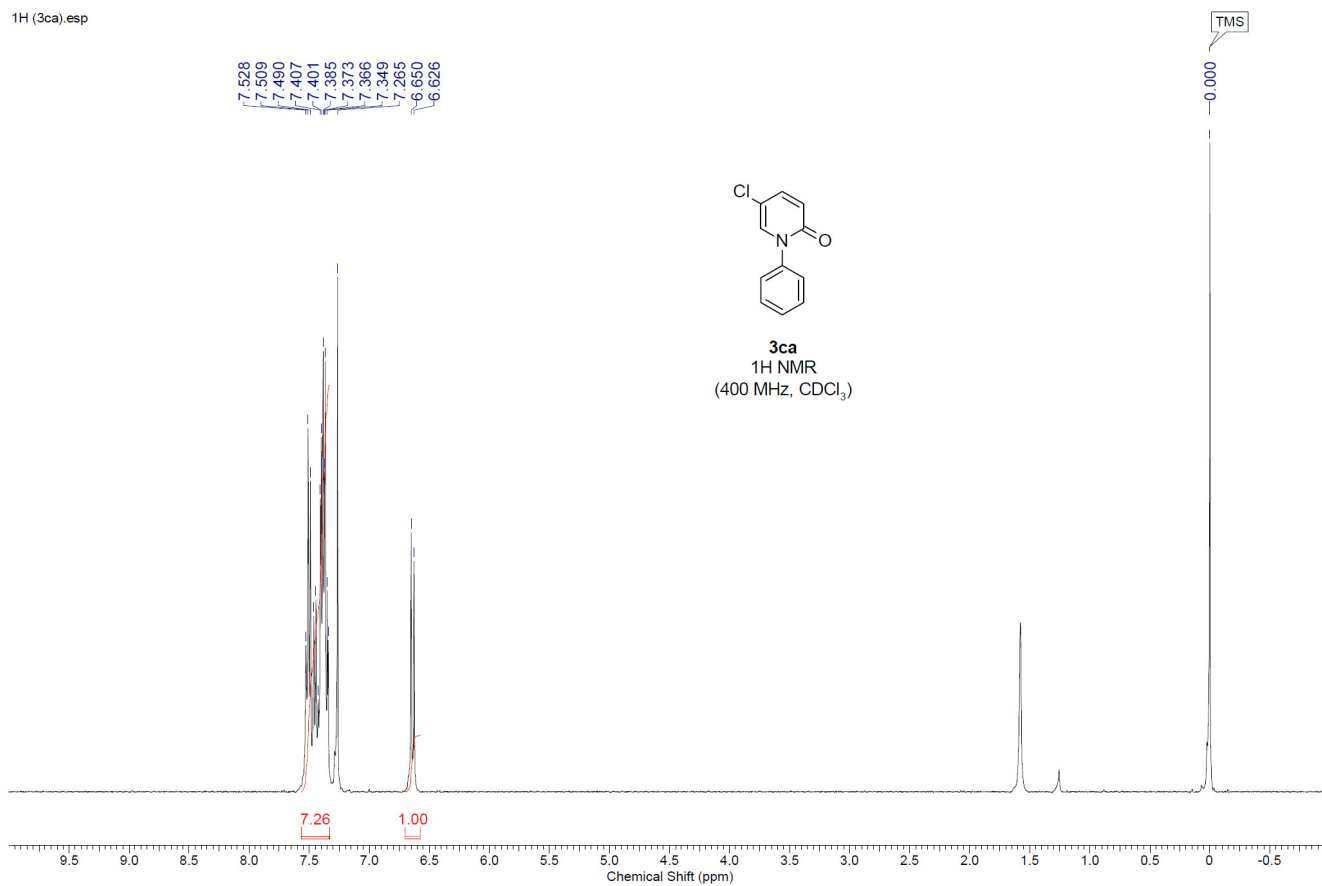
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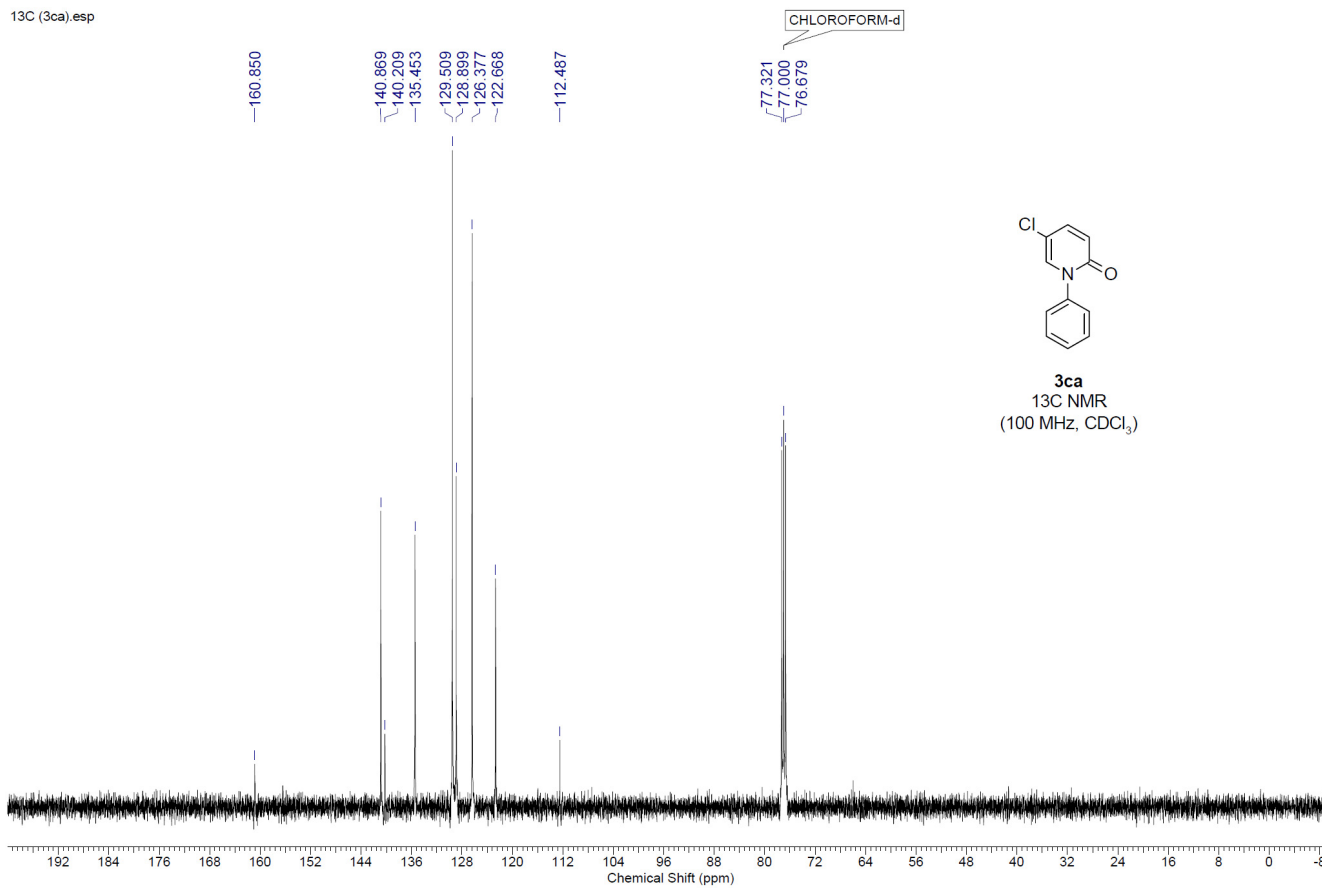
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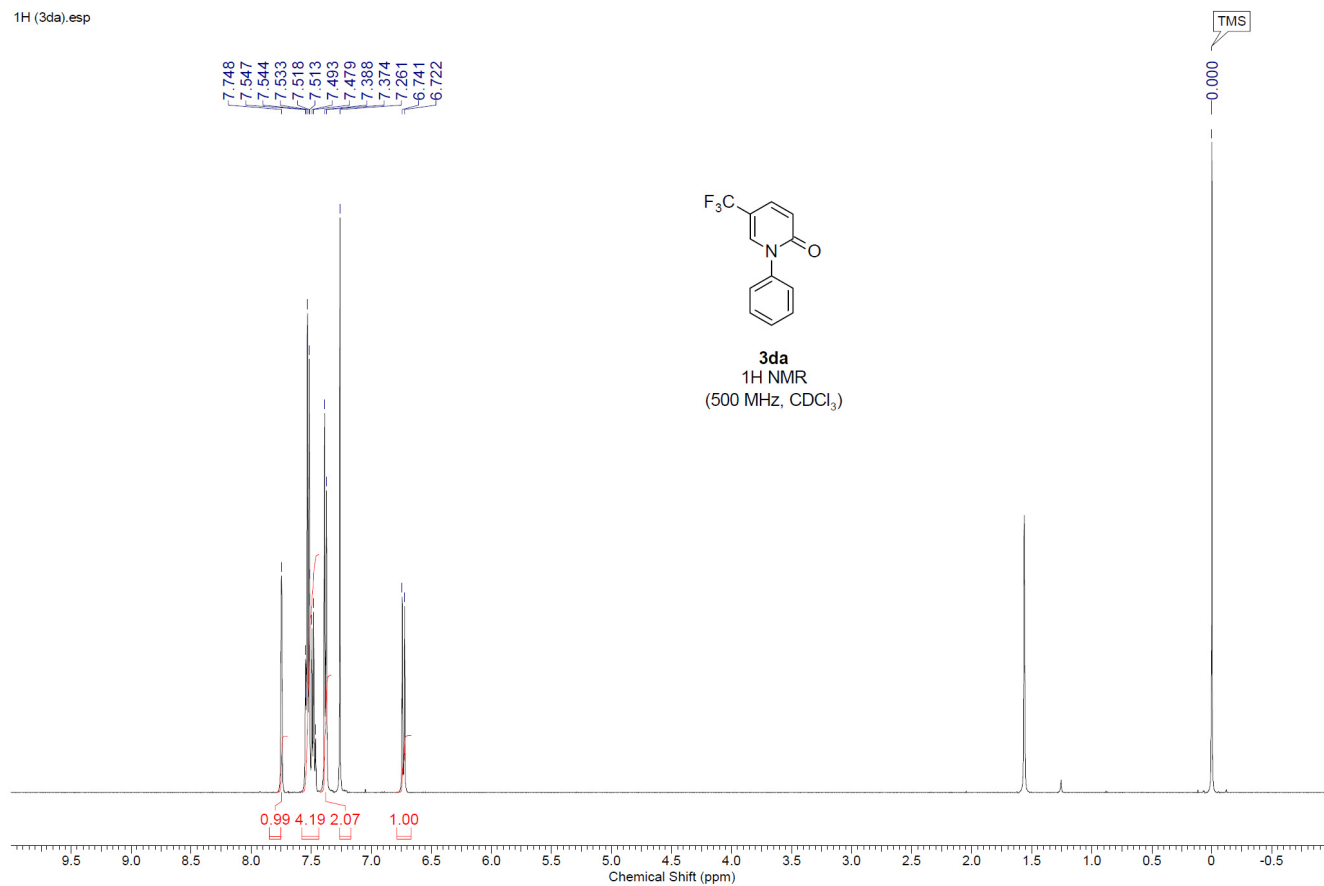
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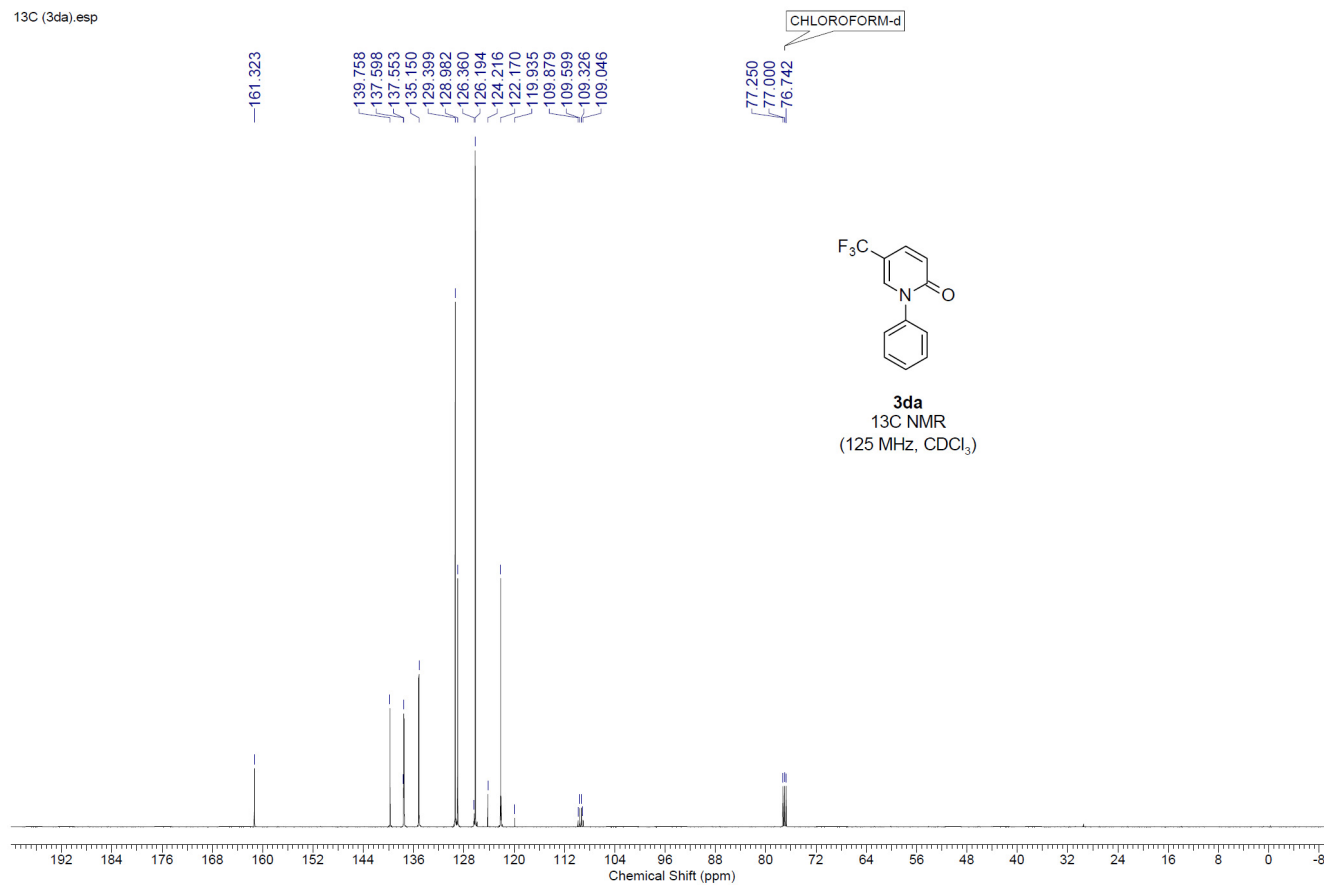
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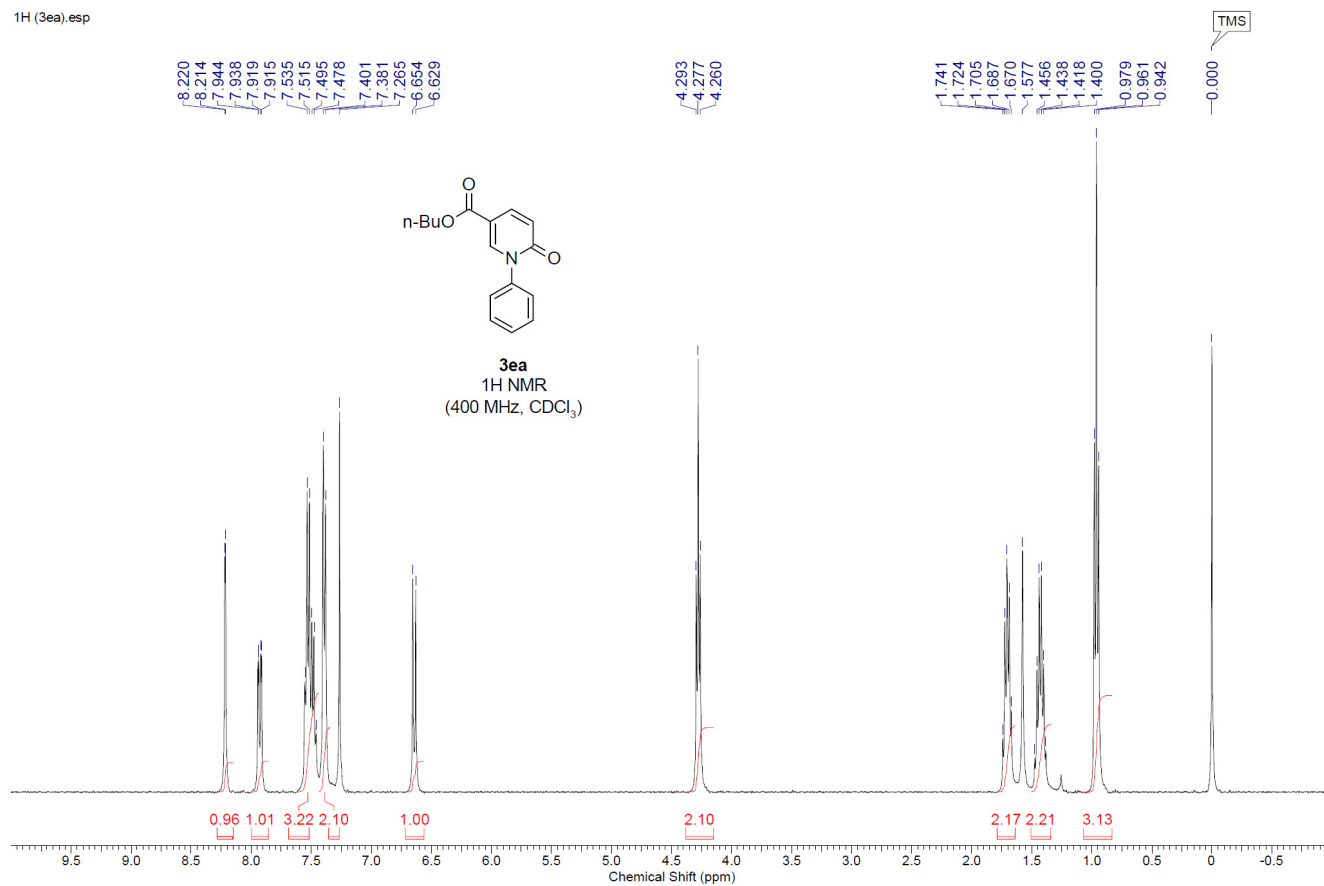
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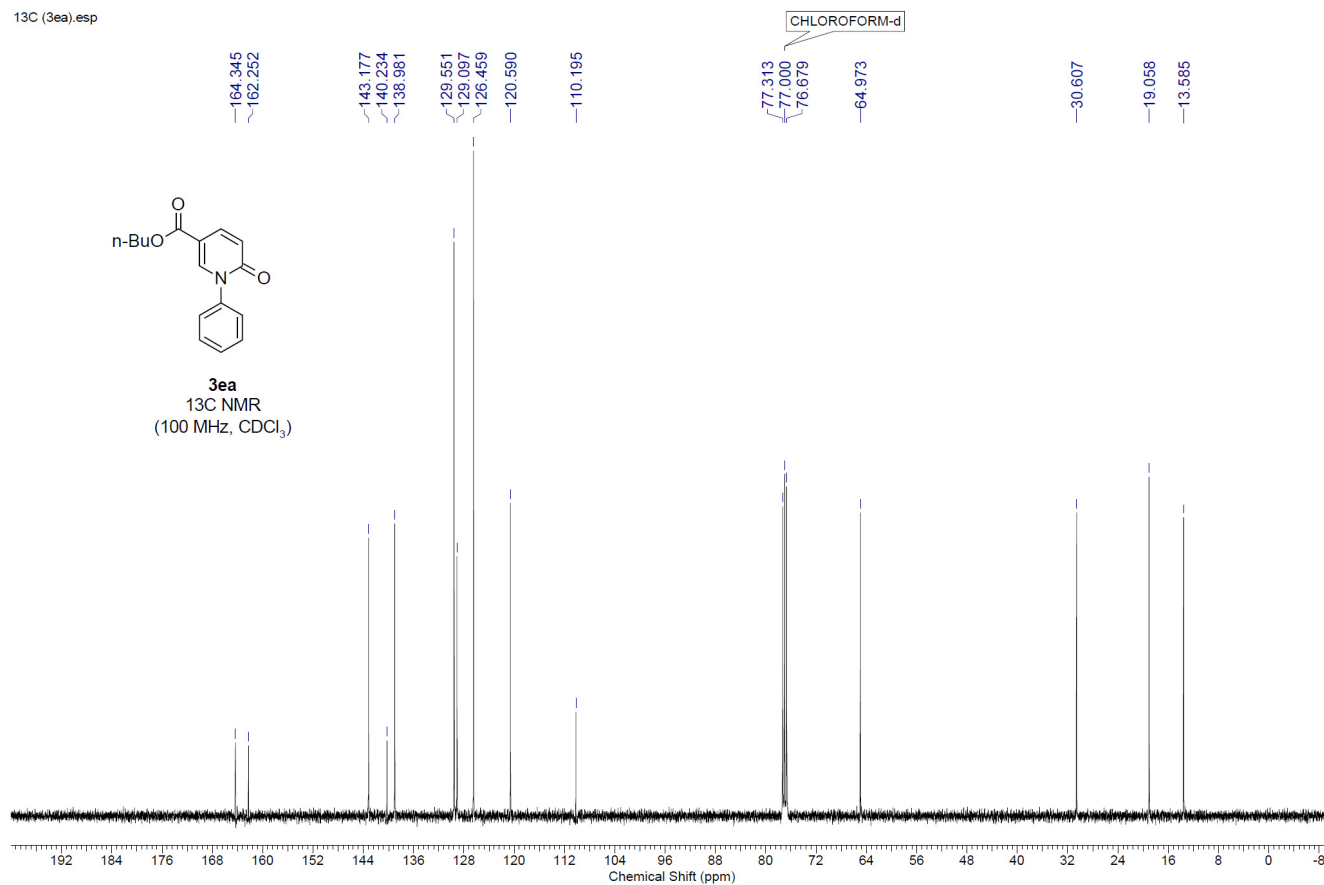
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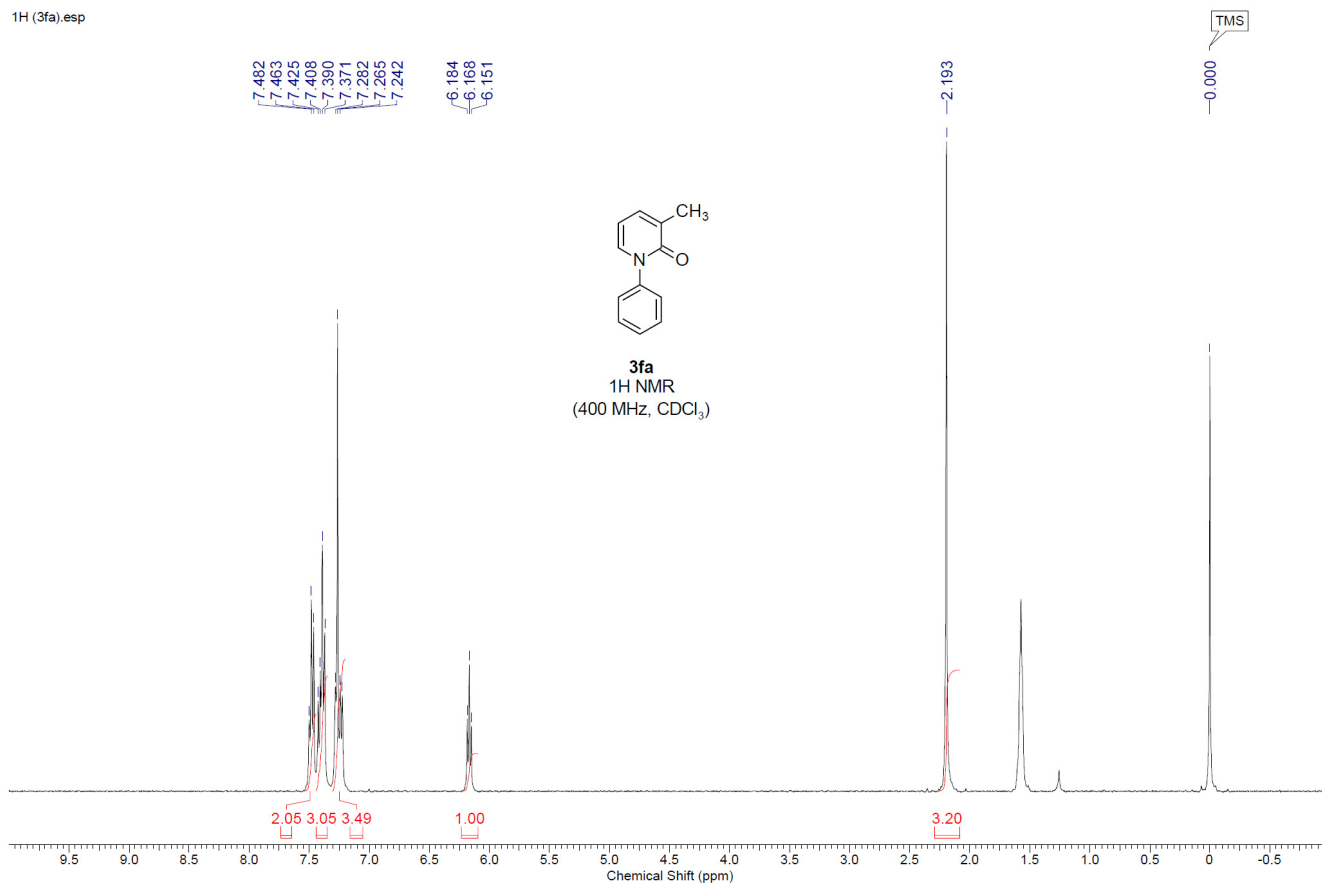
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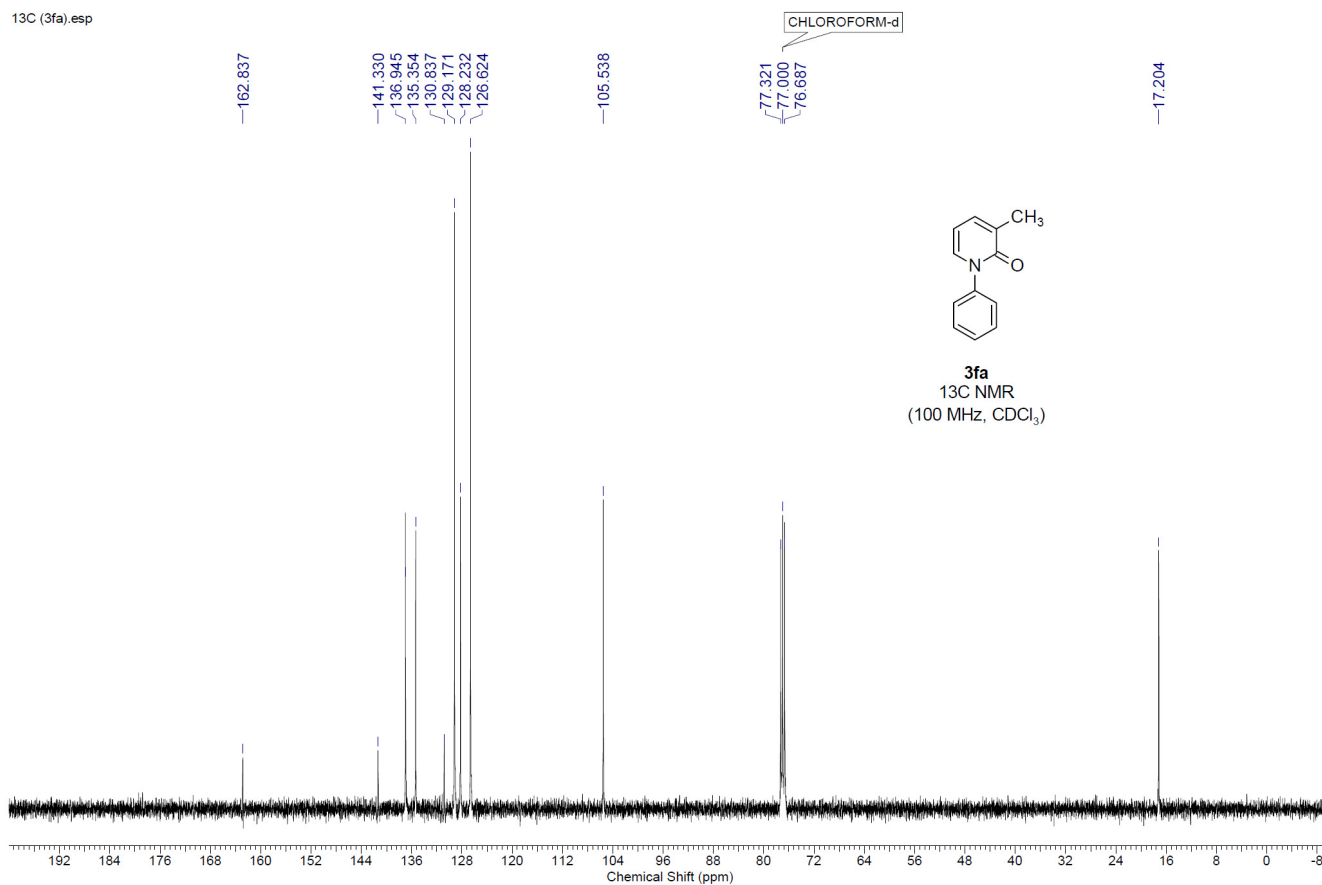
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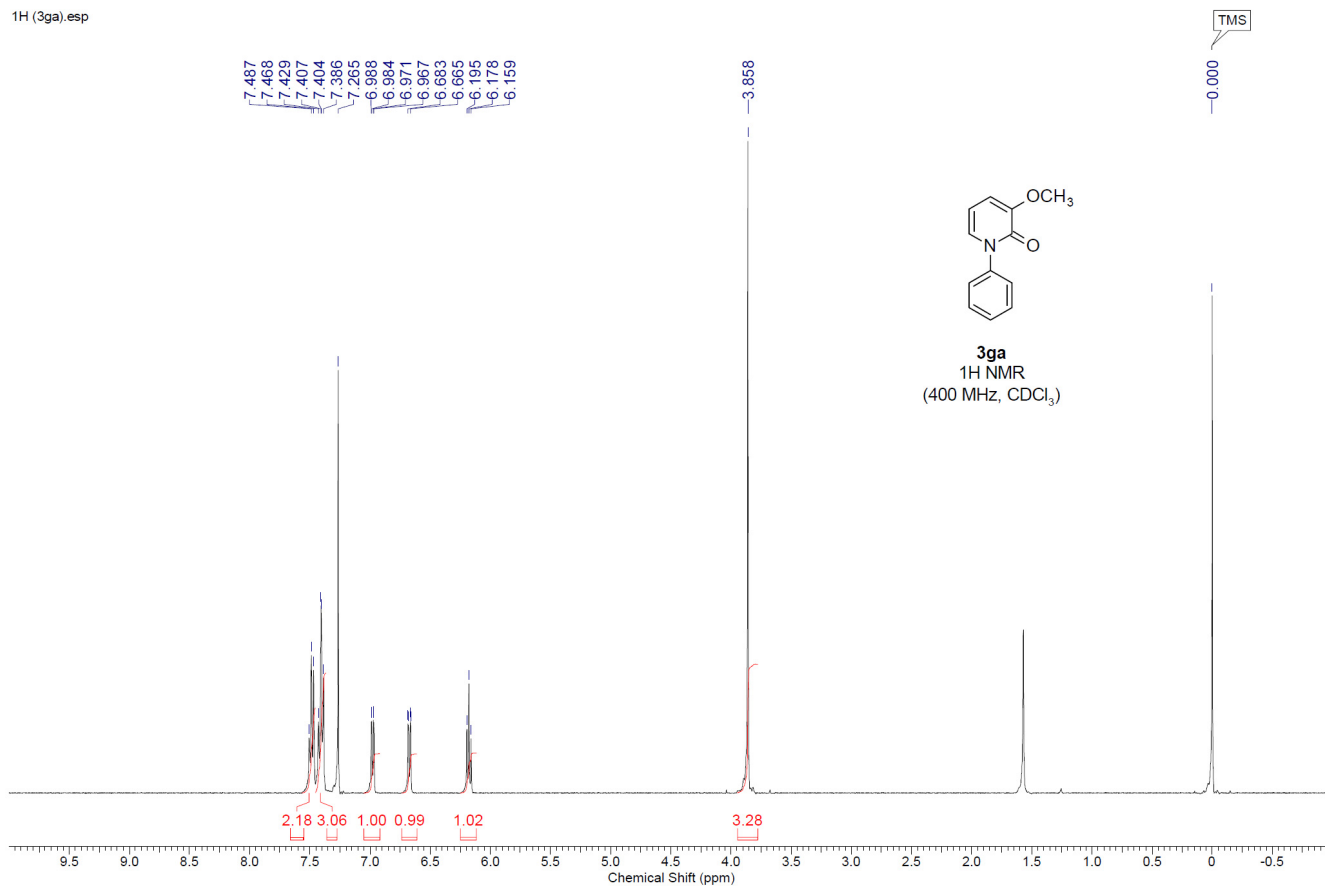
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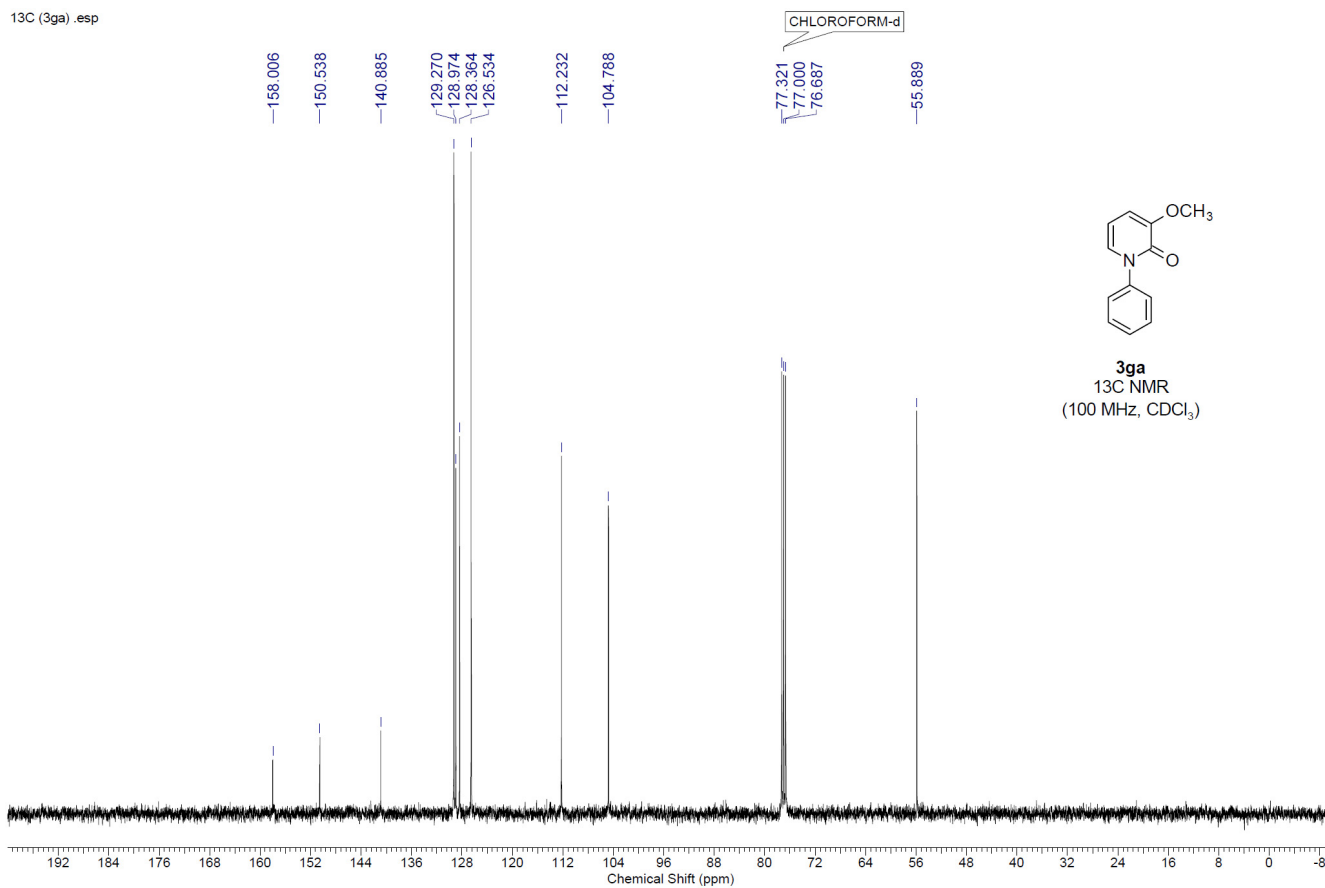
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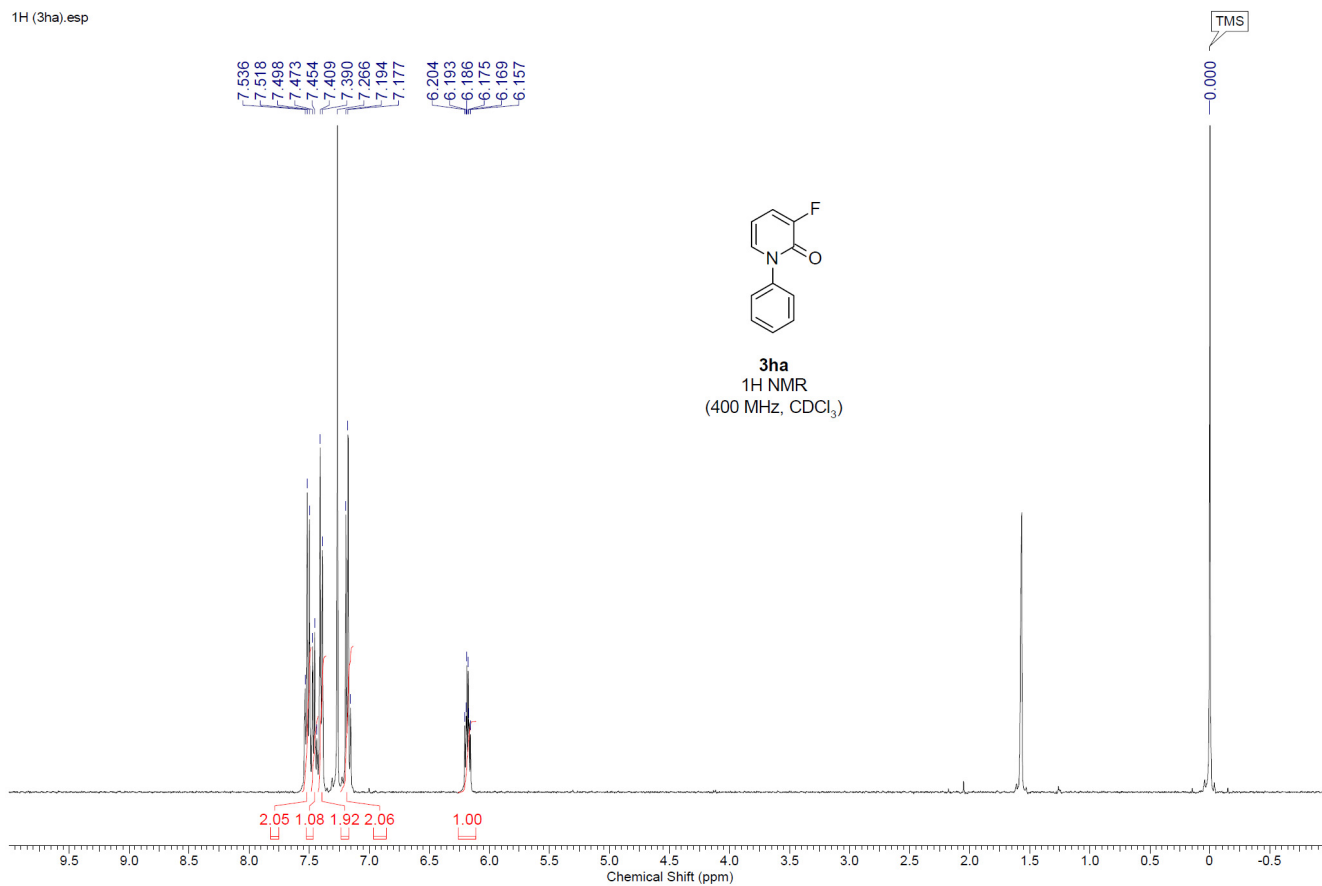
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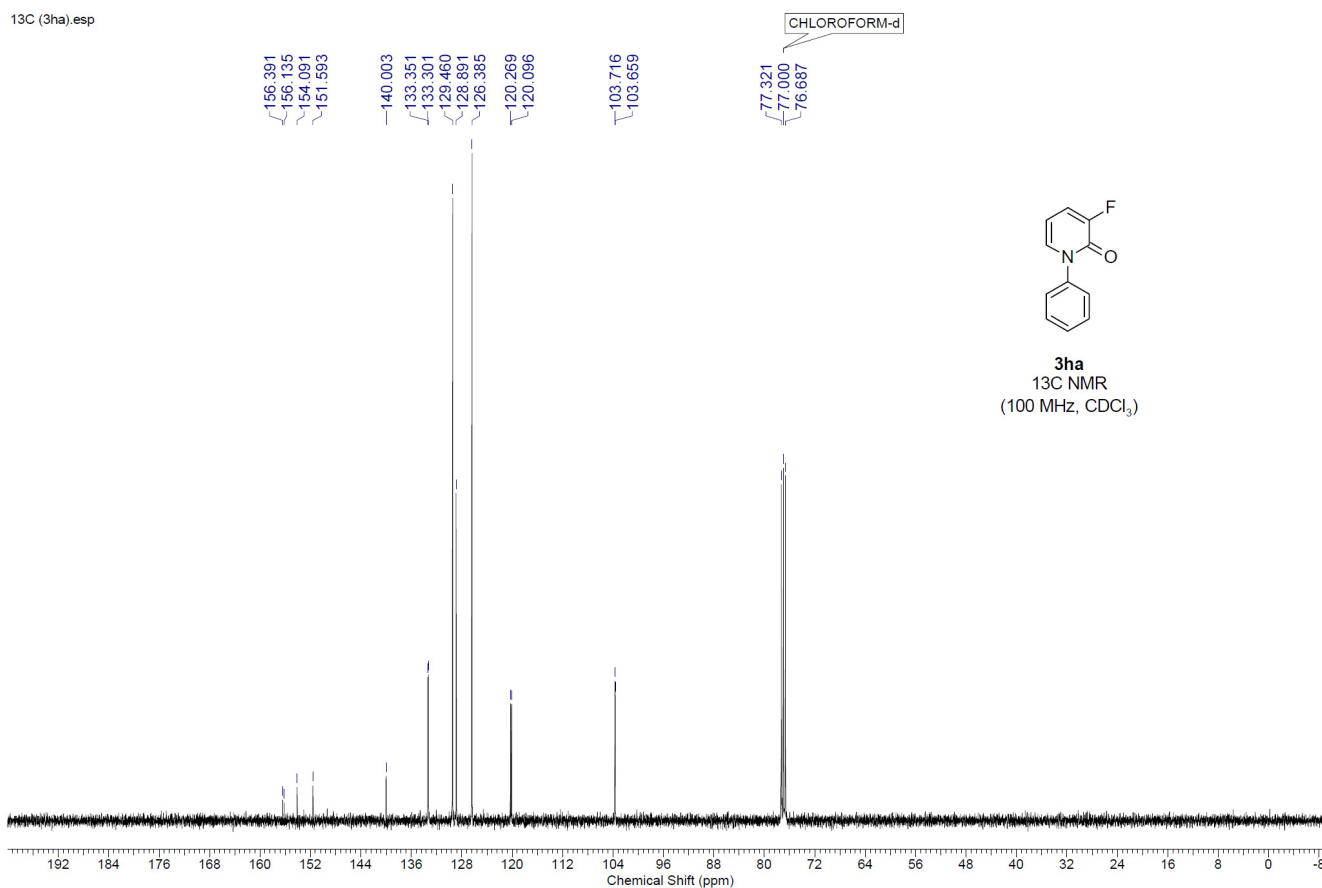
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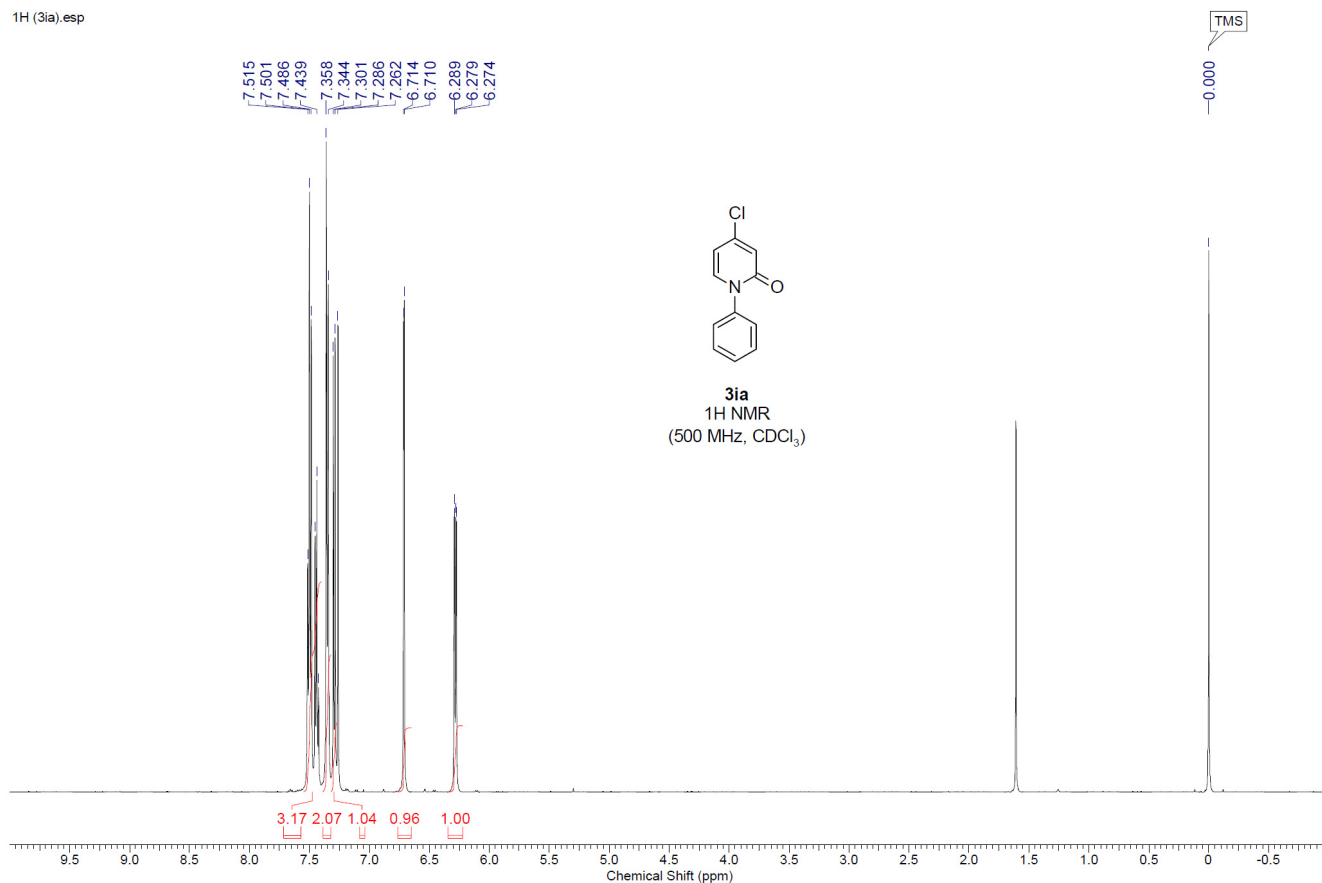
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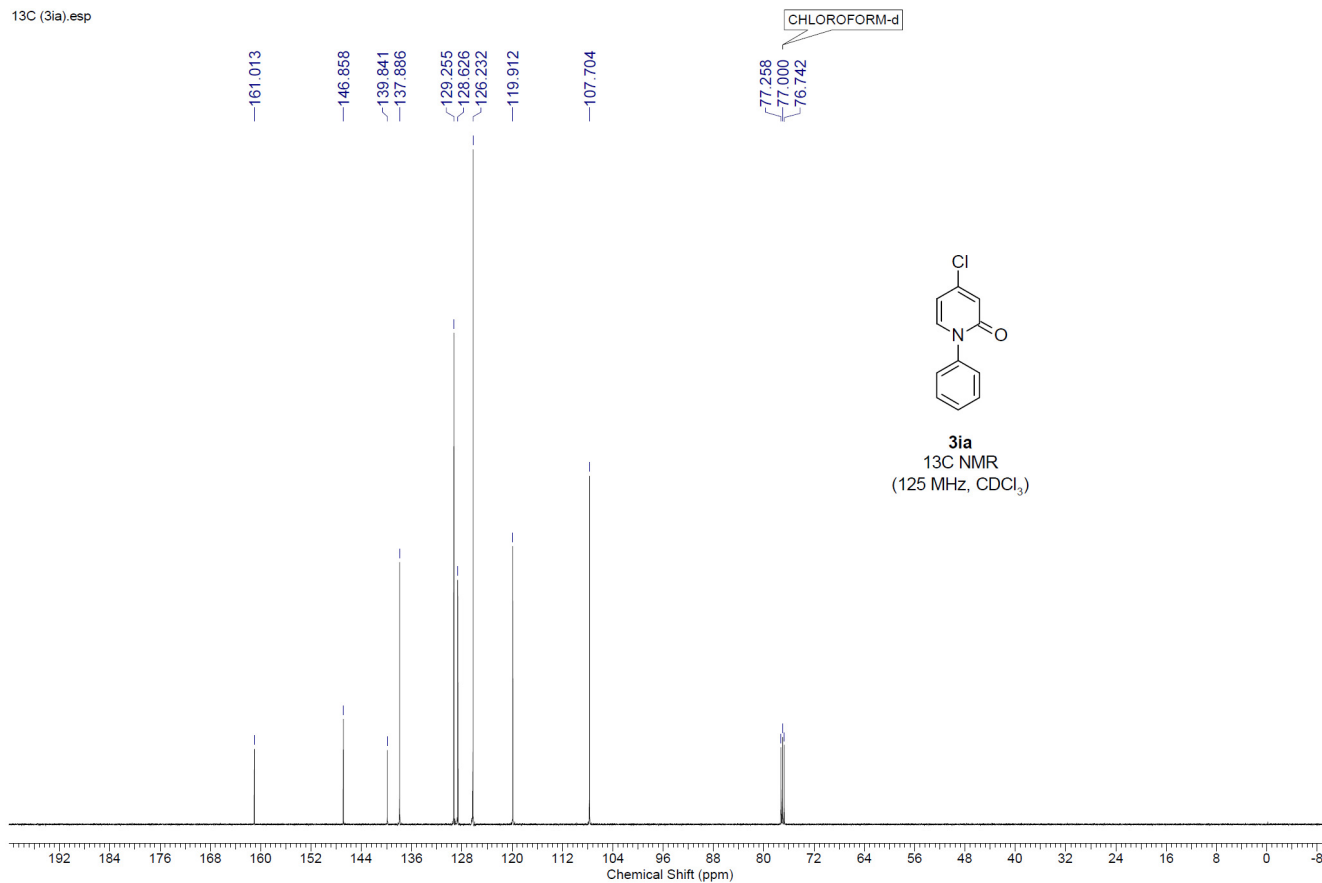
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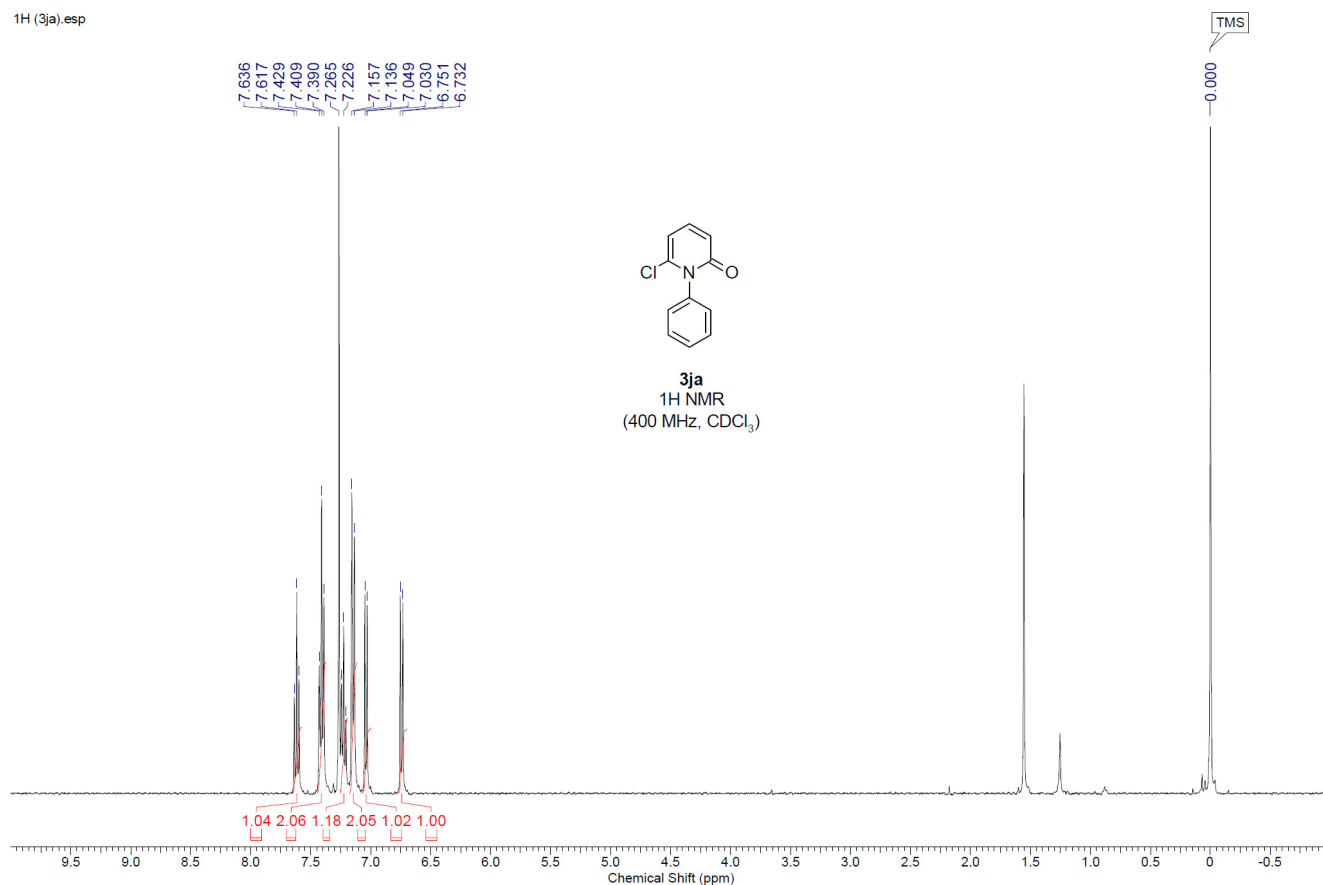
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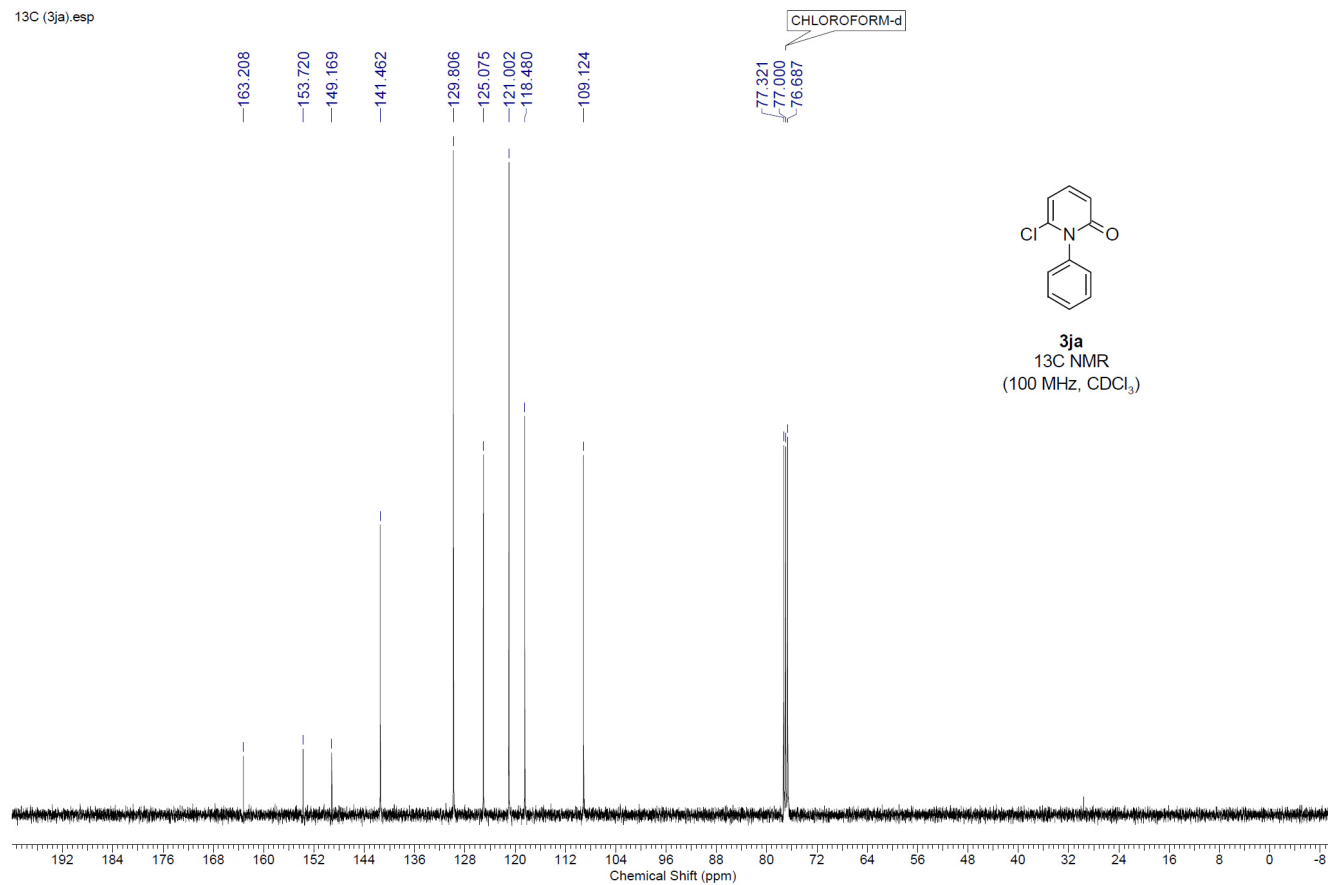
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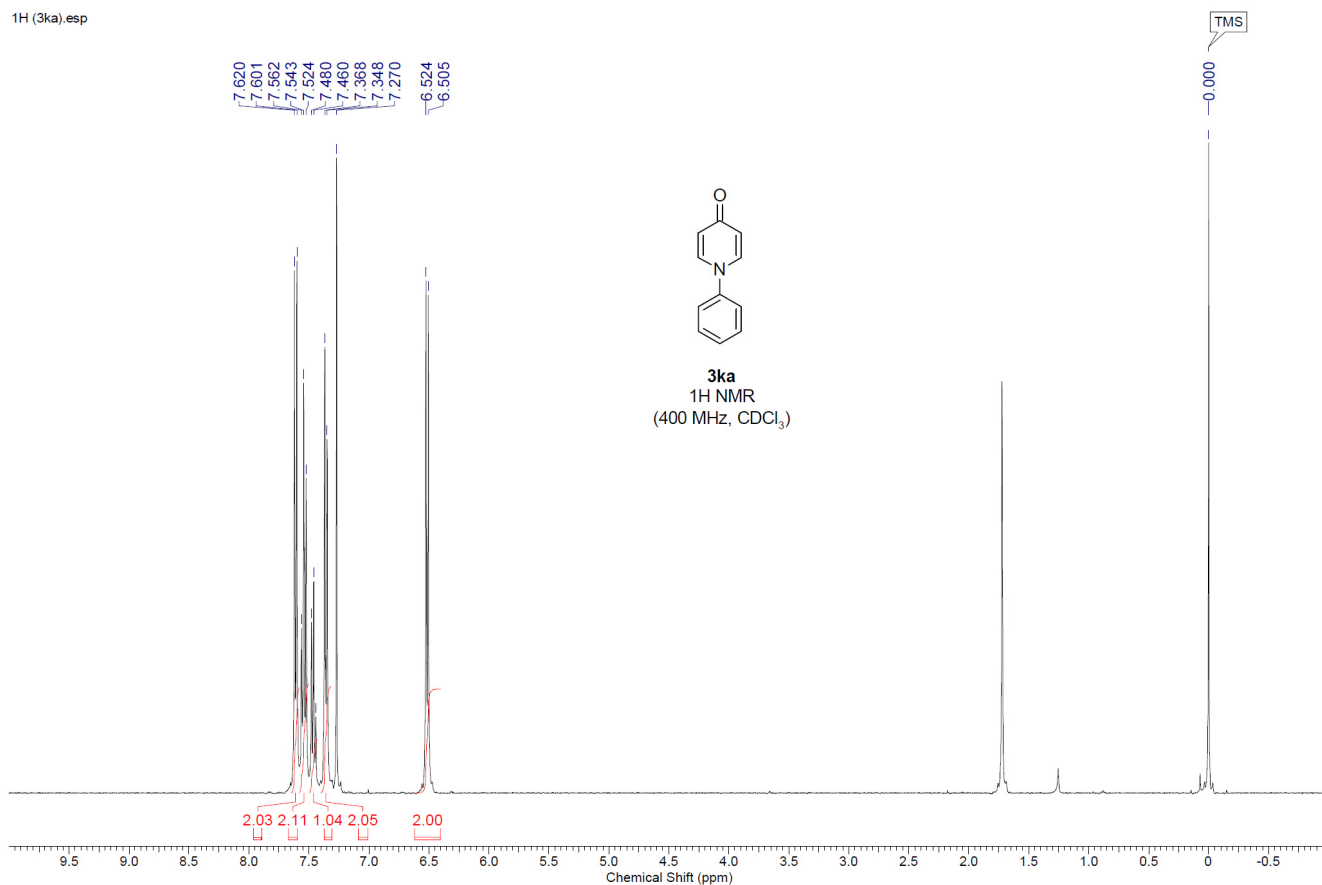
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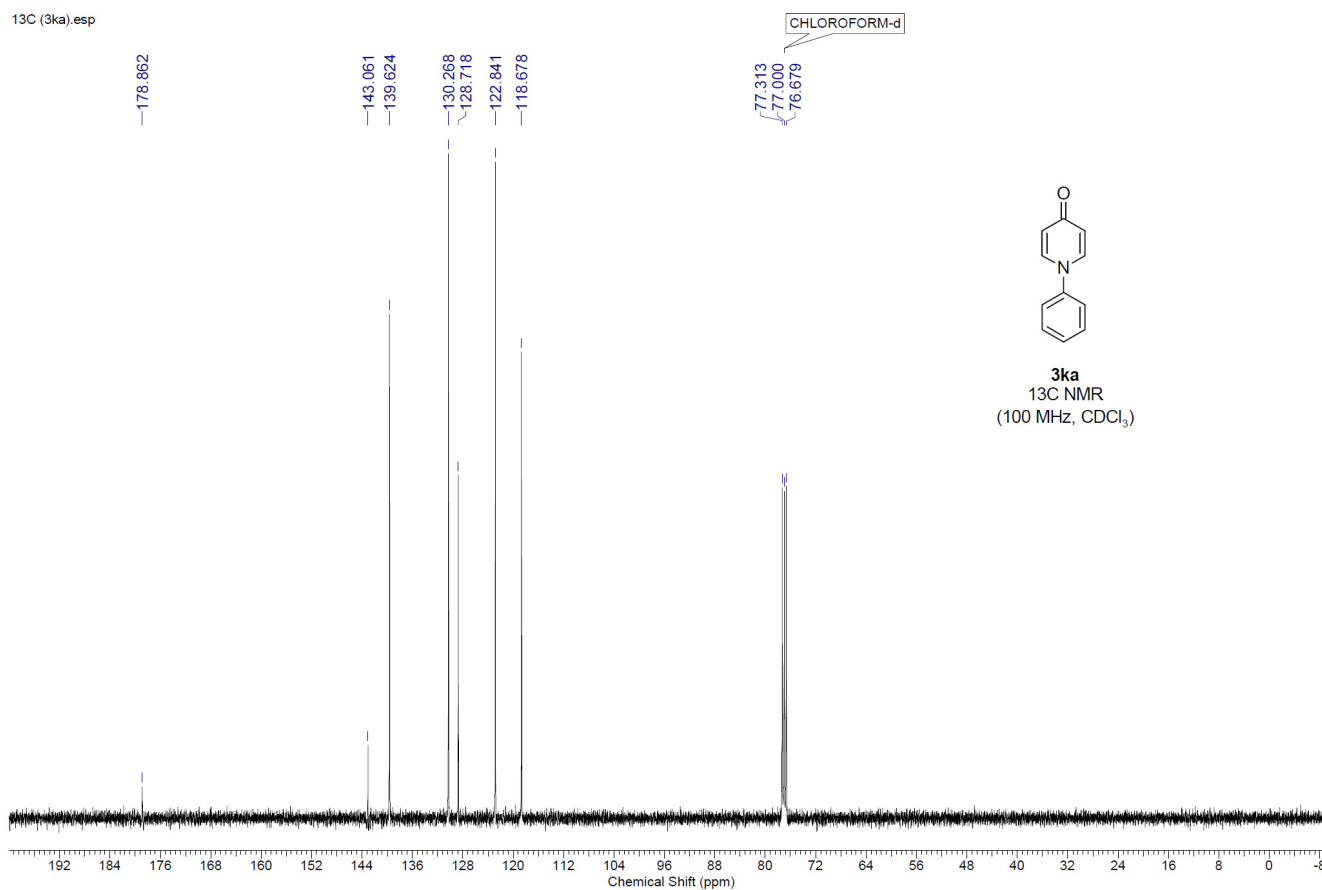
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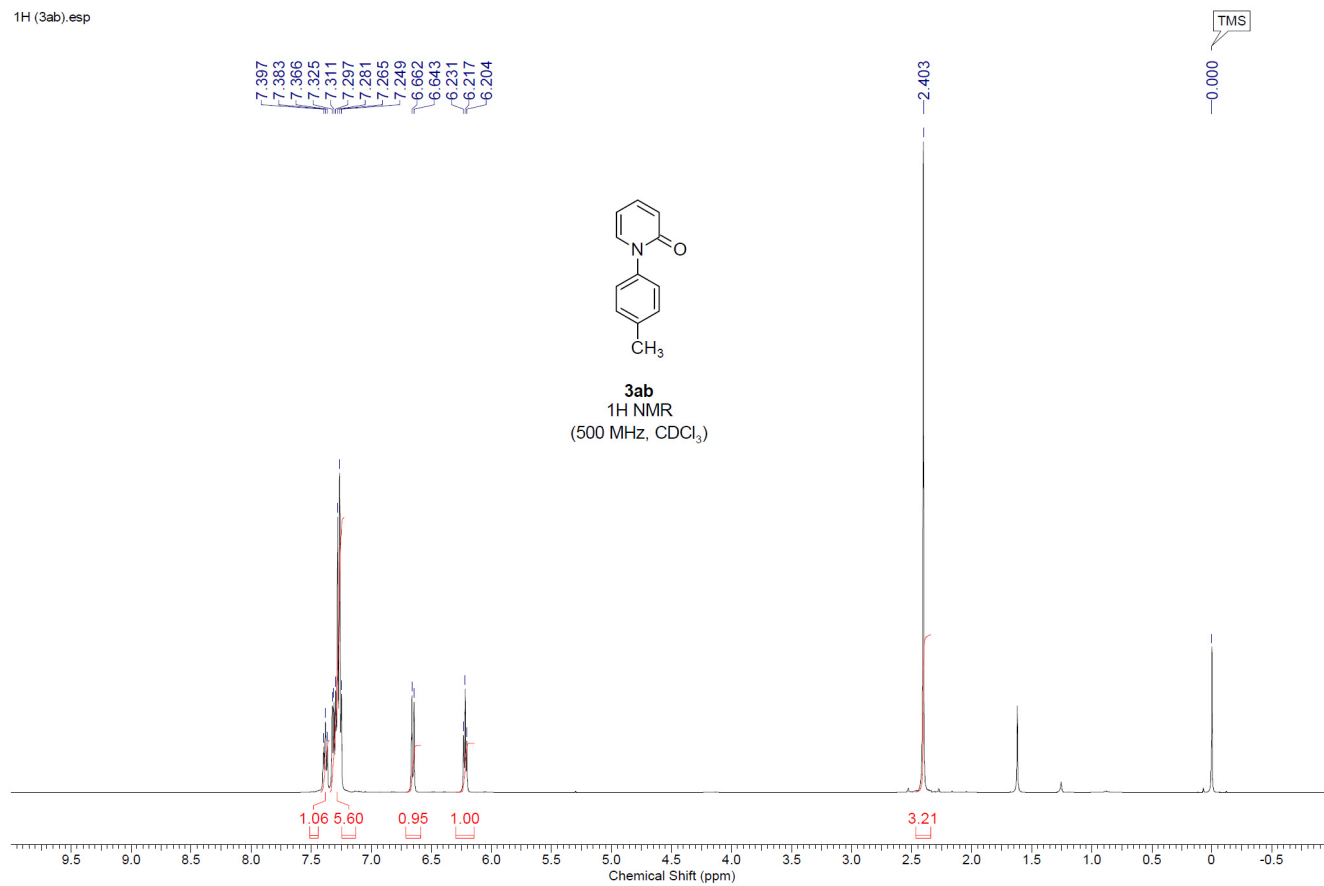
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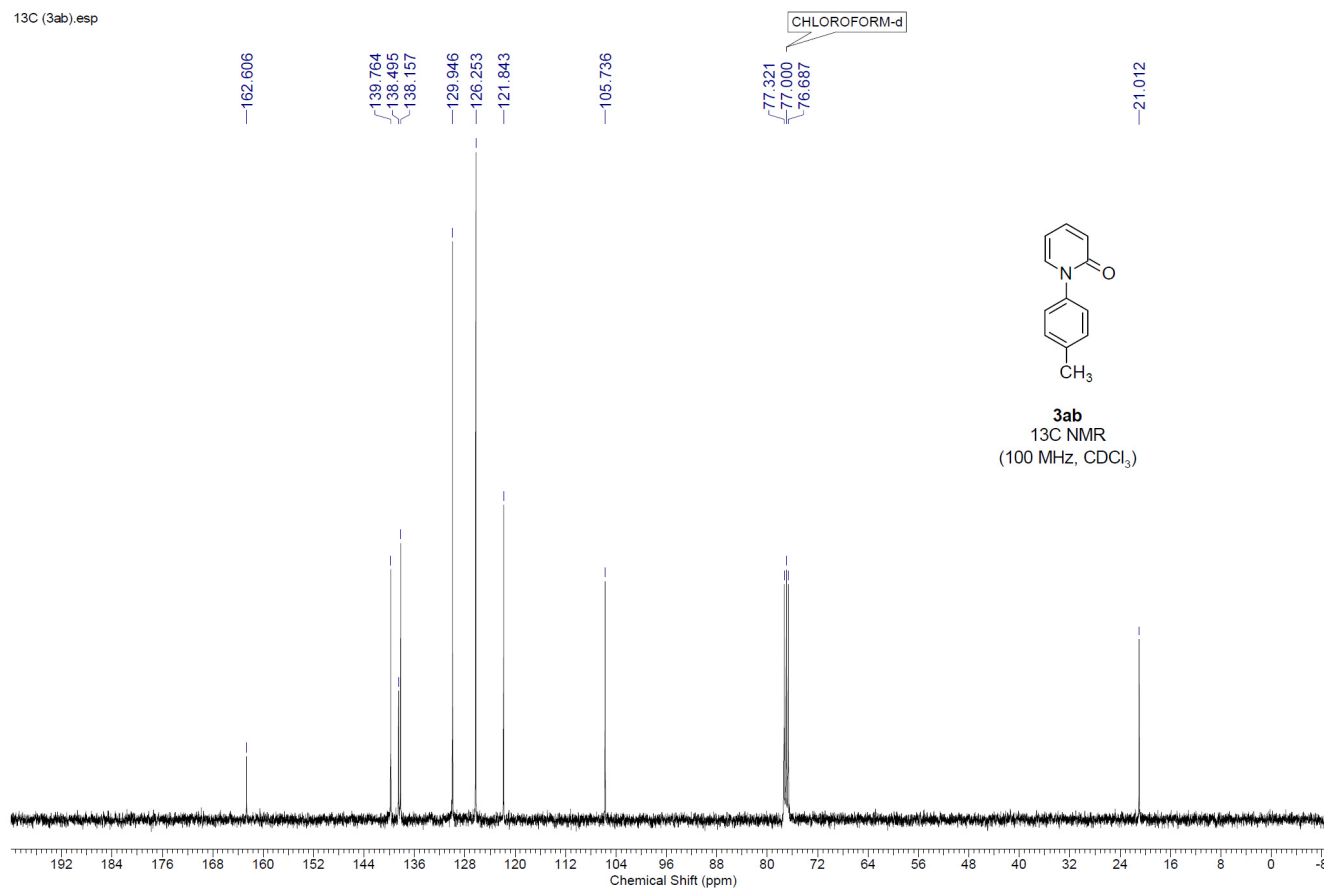
13C (3ka).esp



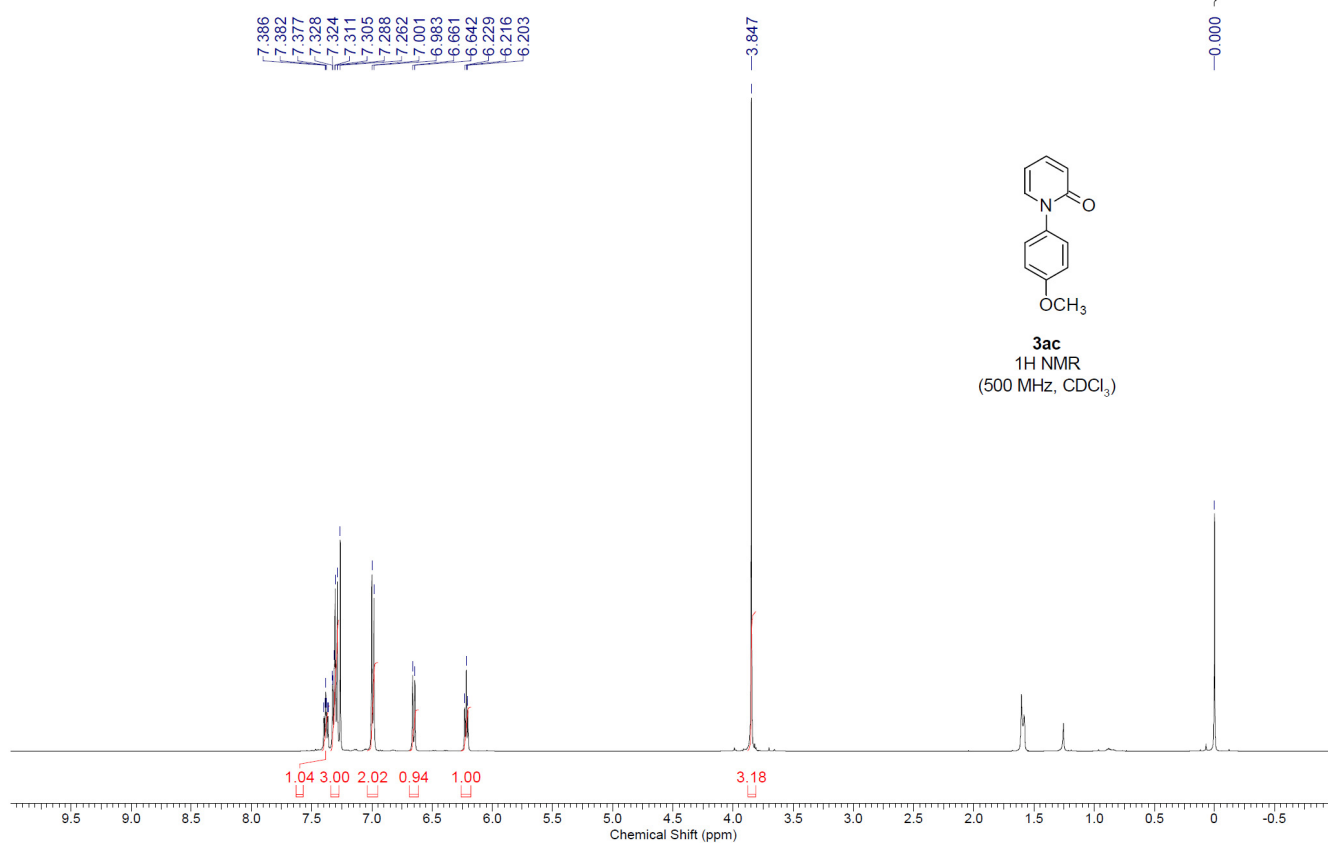
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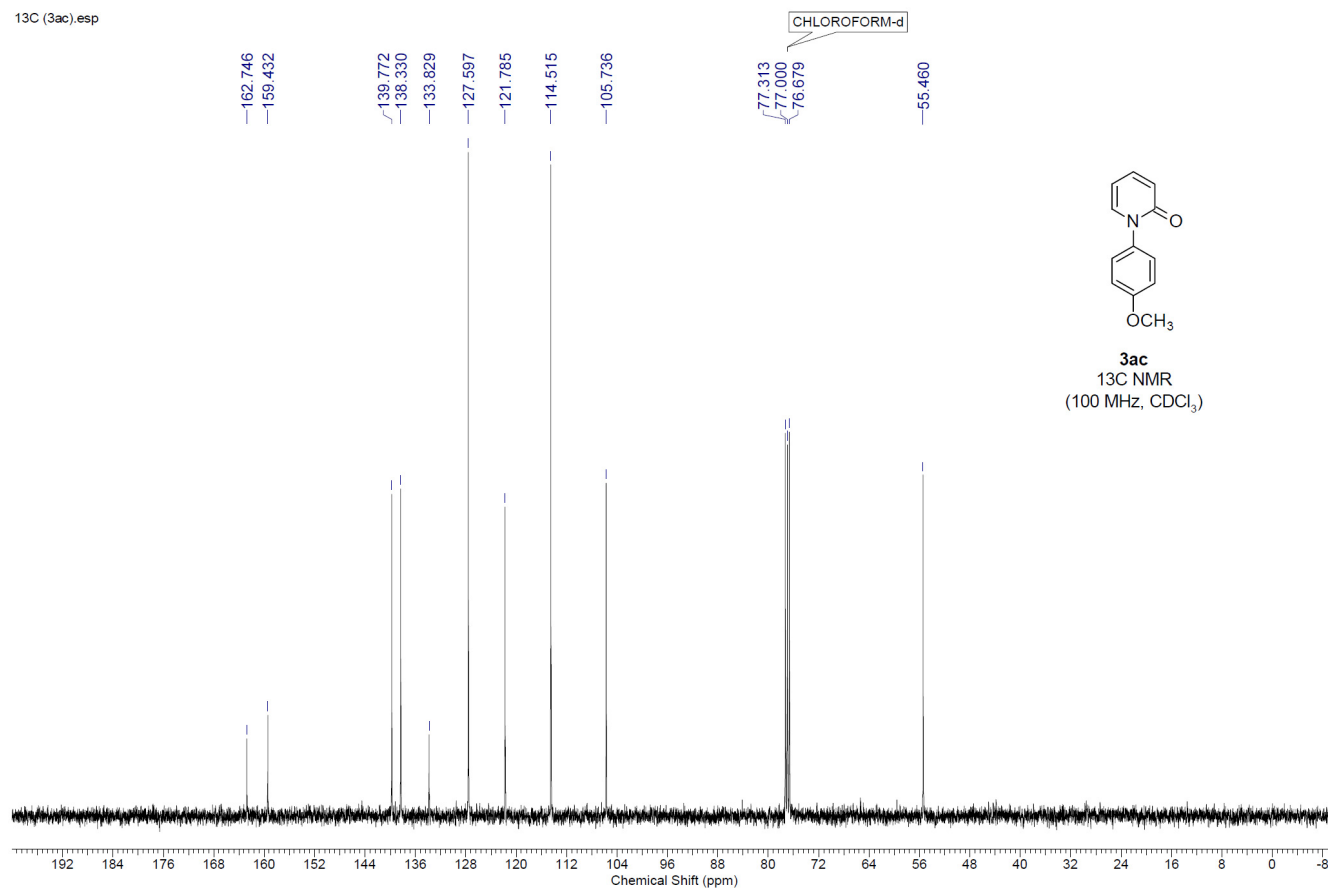
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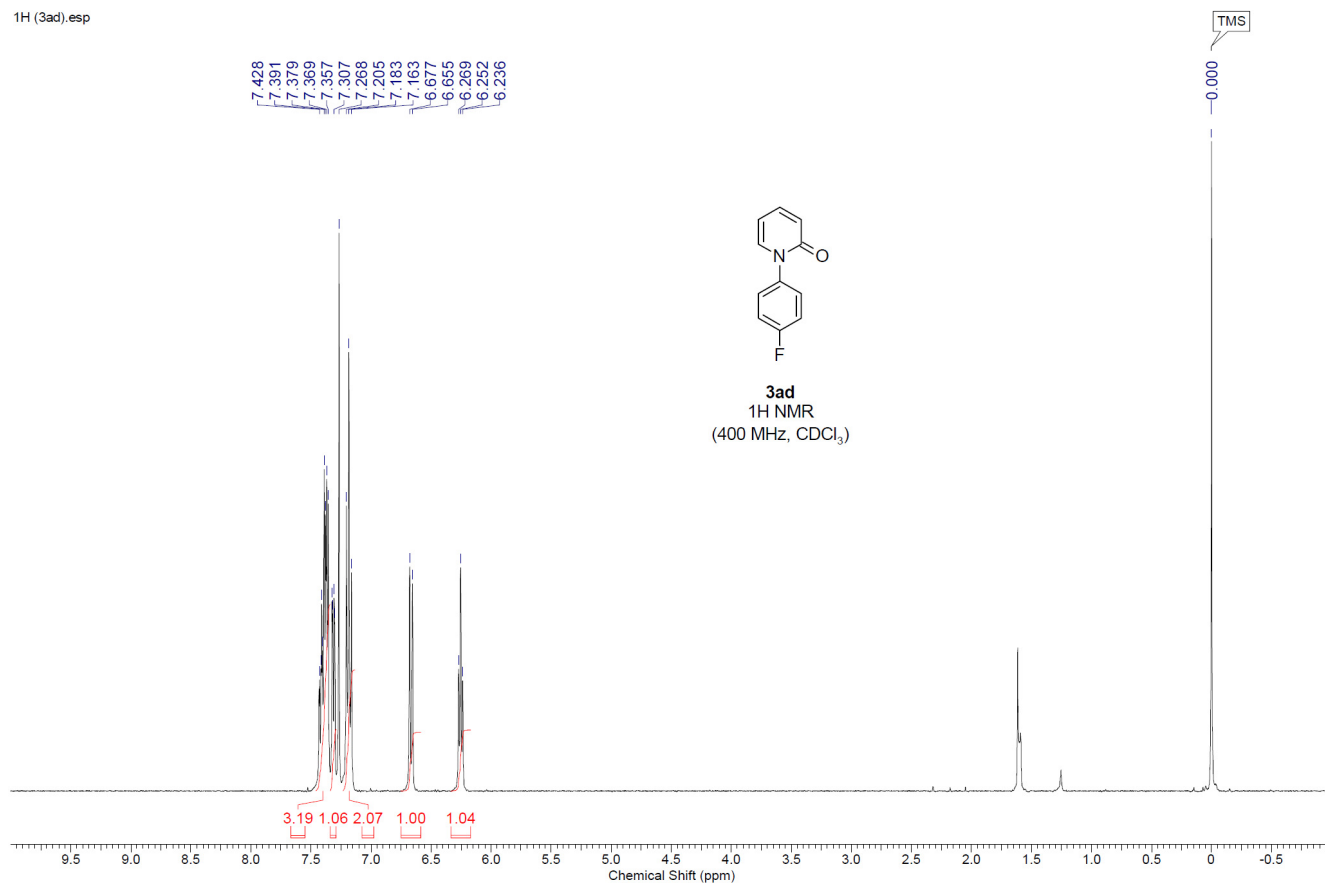
1H (3ac).esp



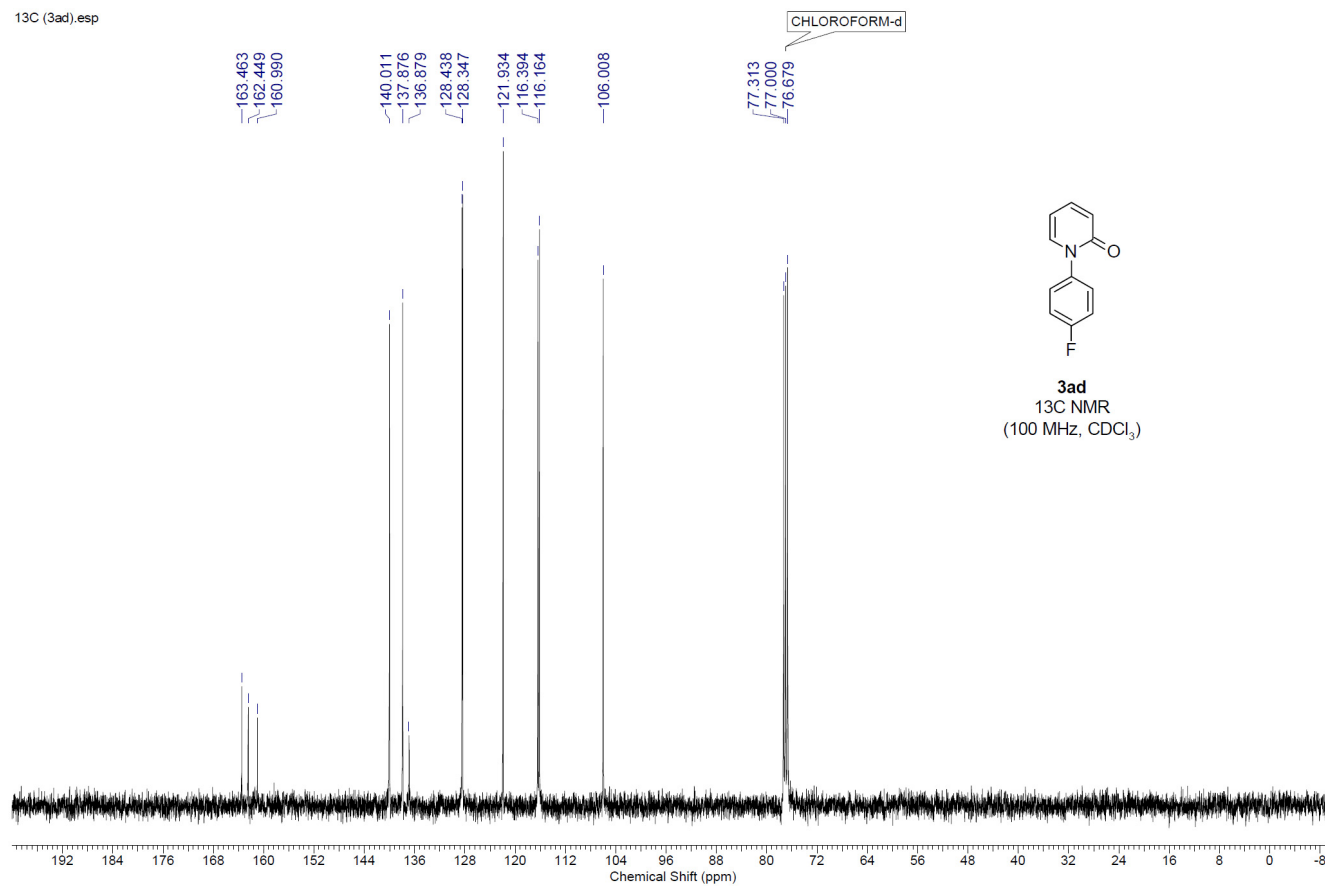
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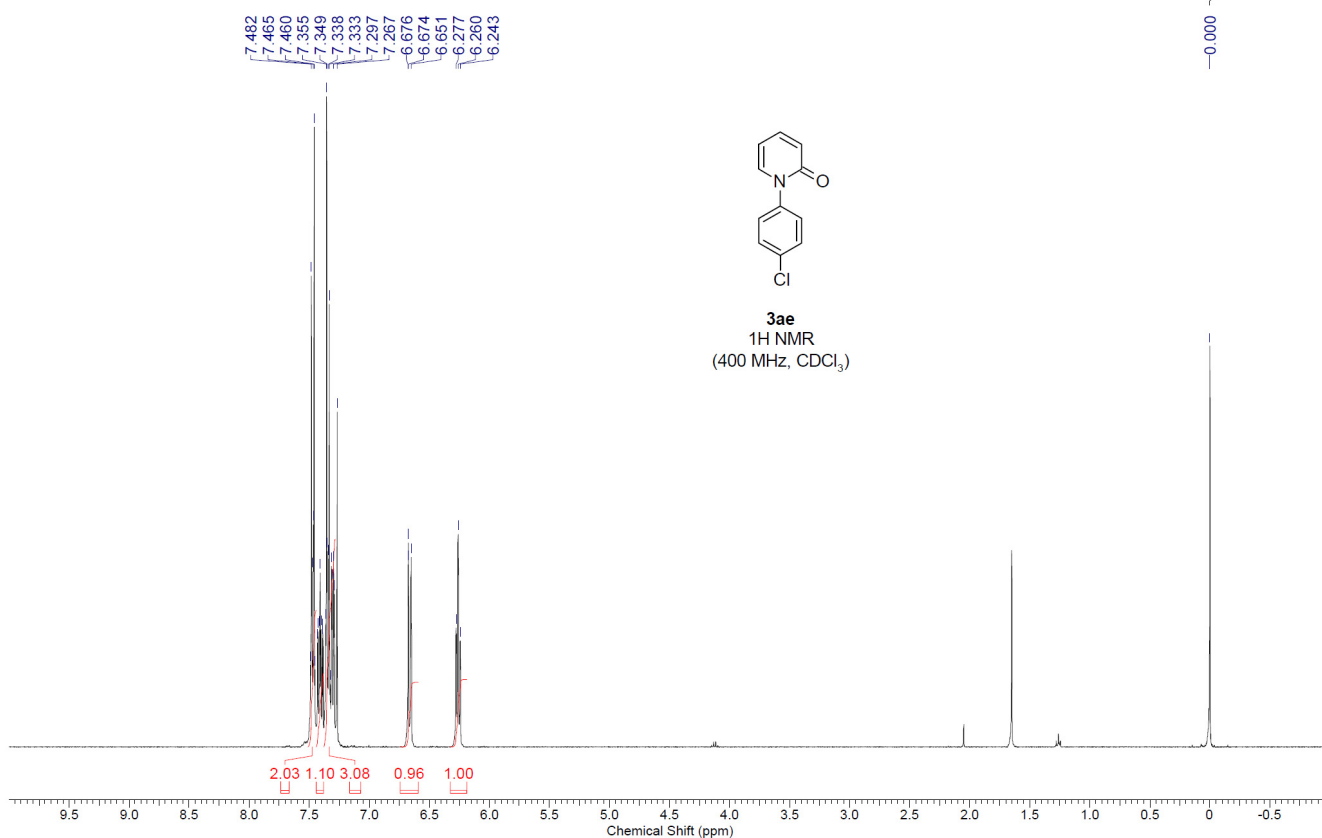
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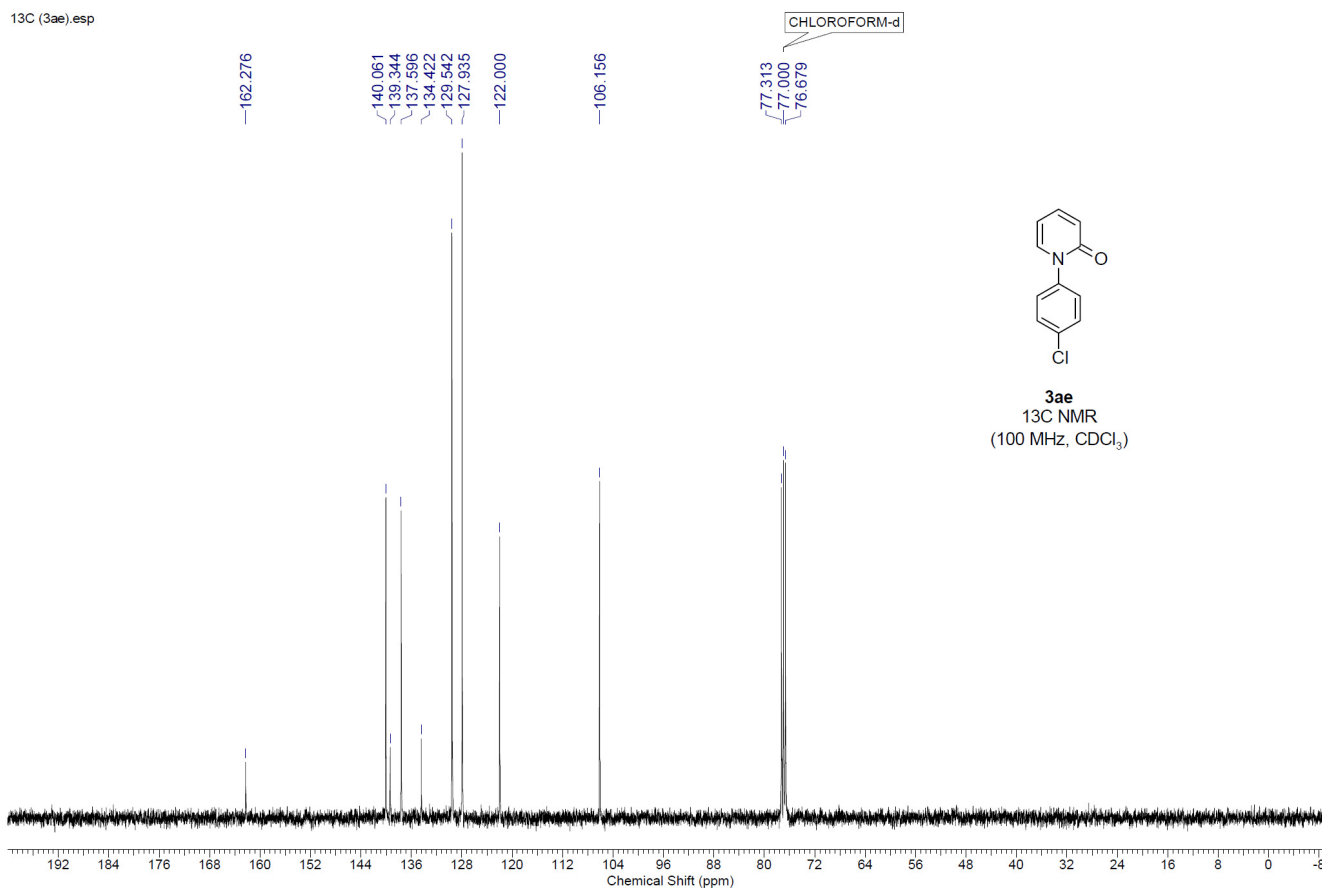
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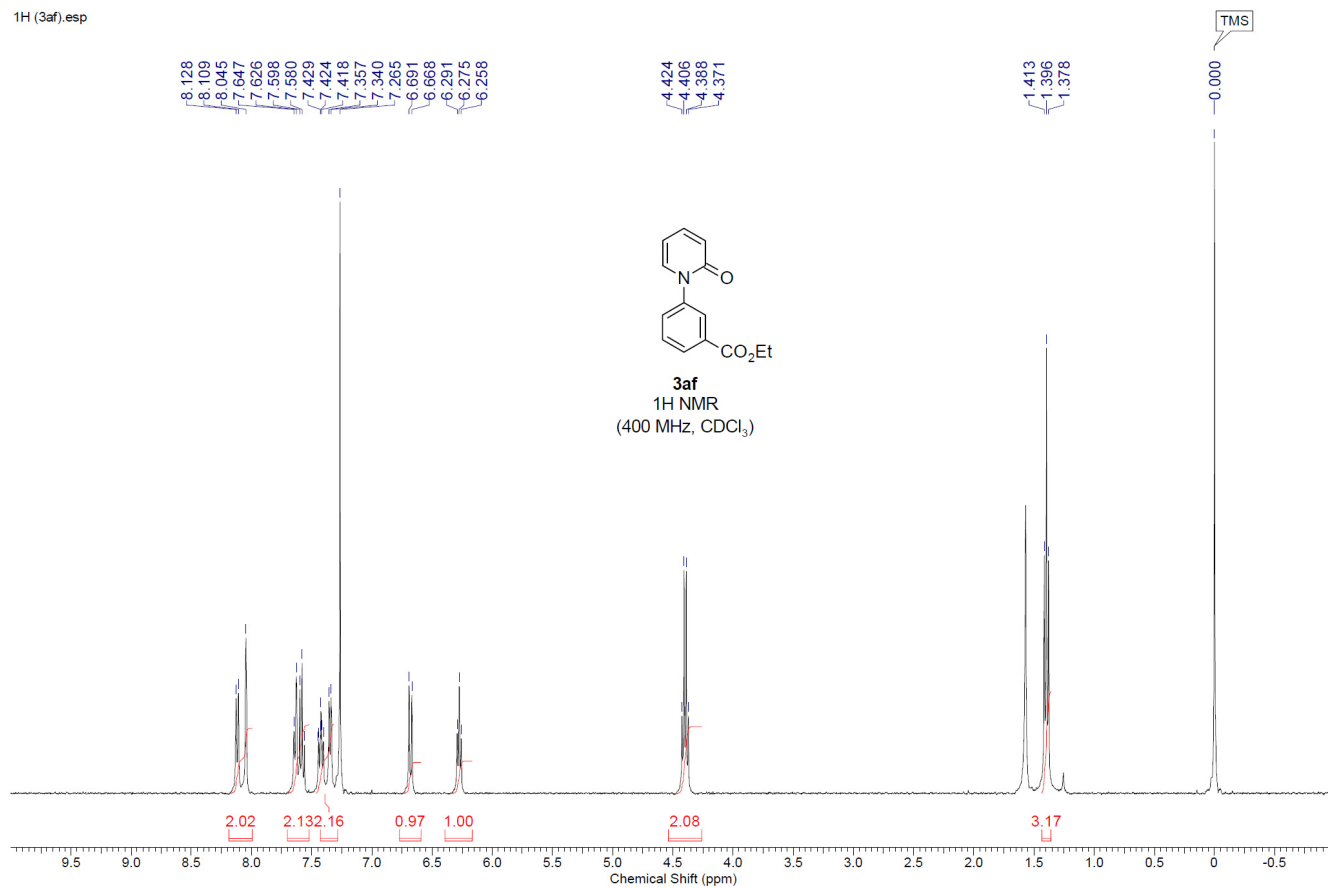
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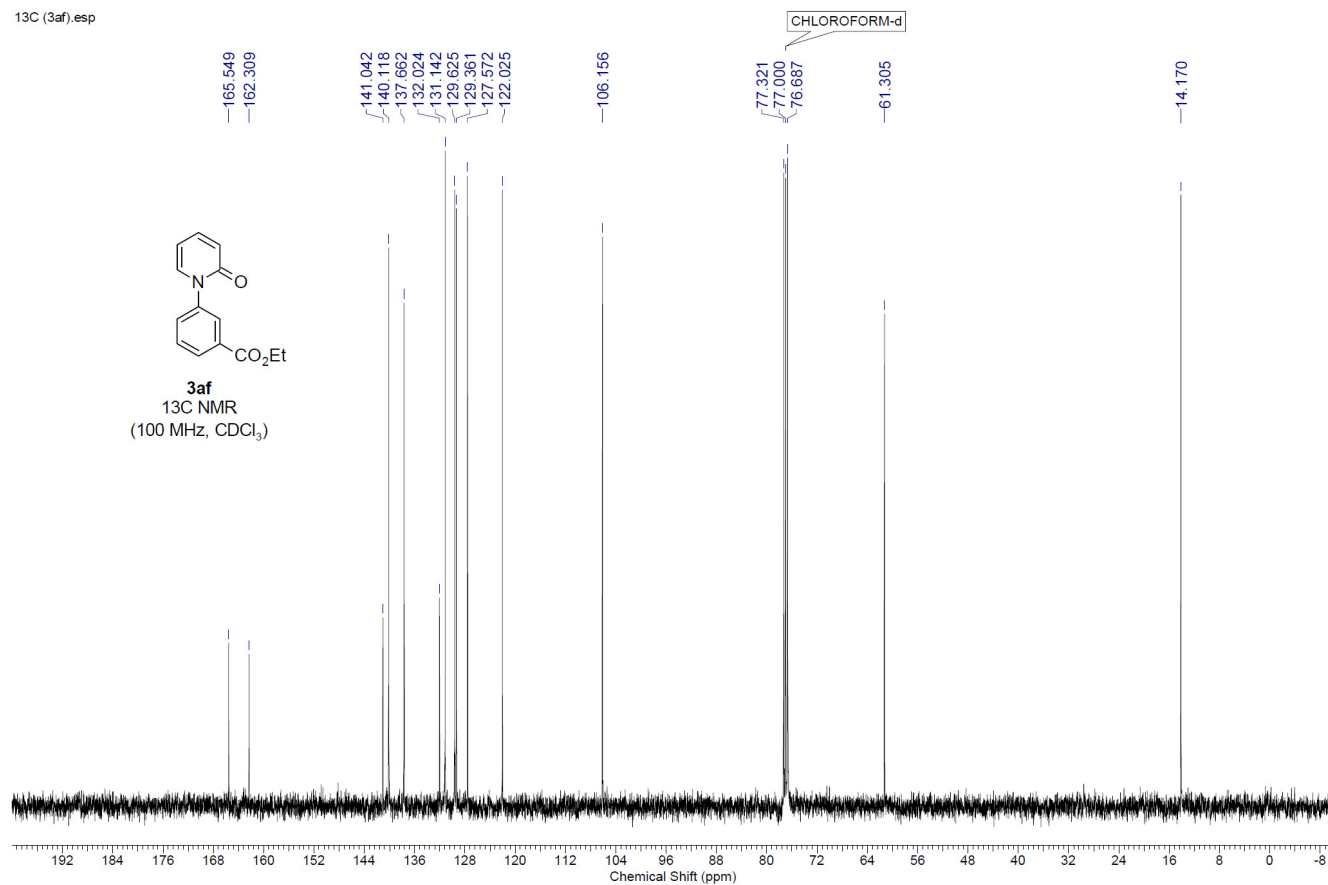
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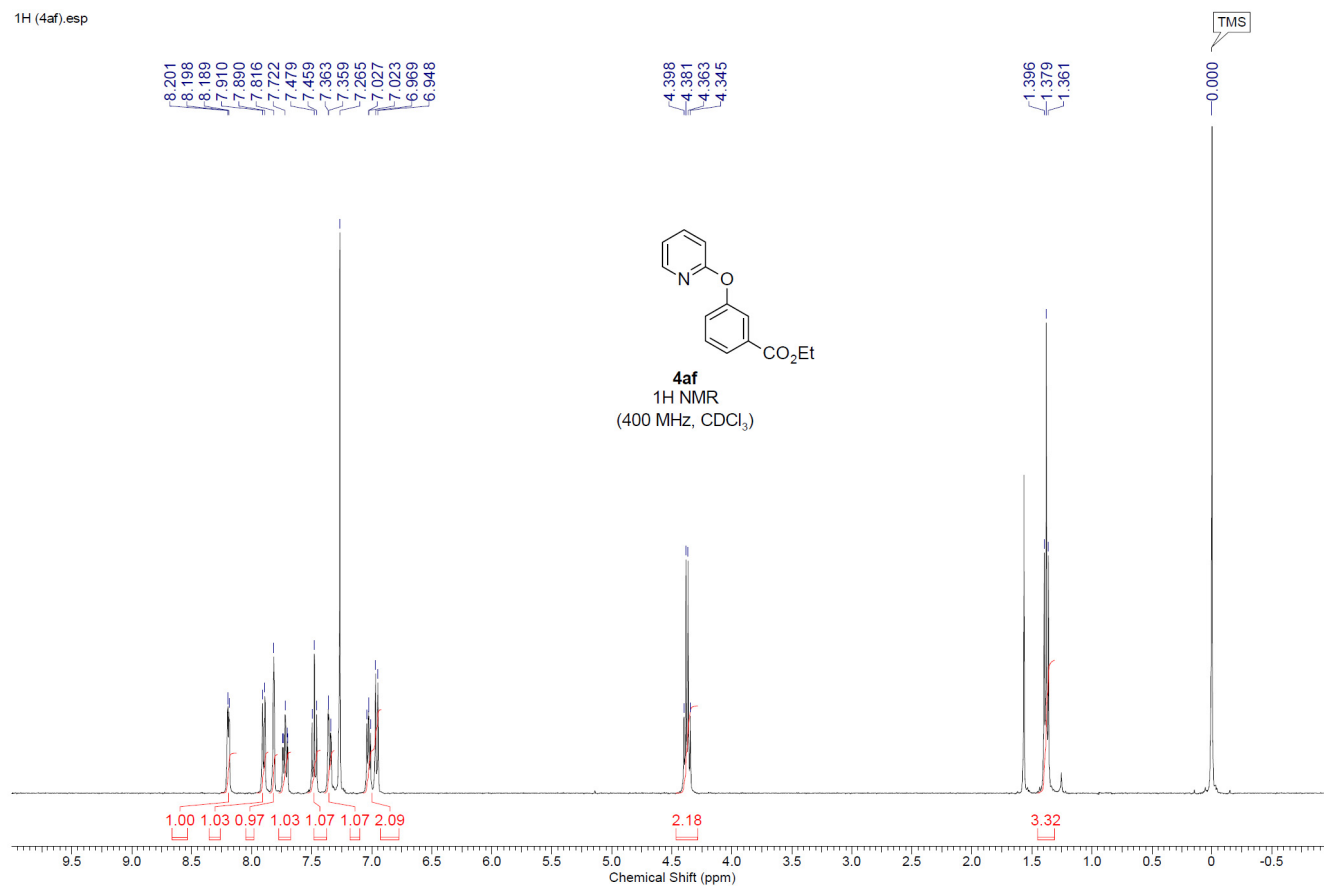
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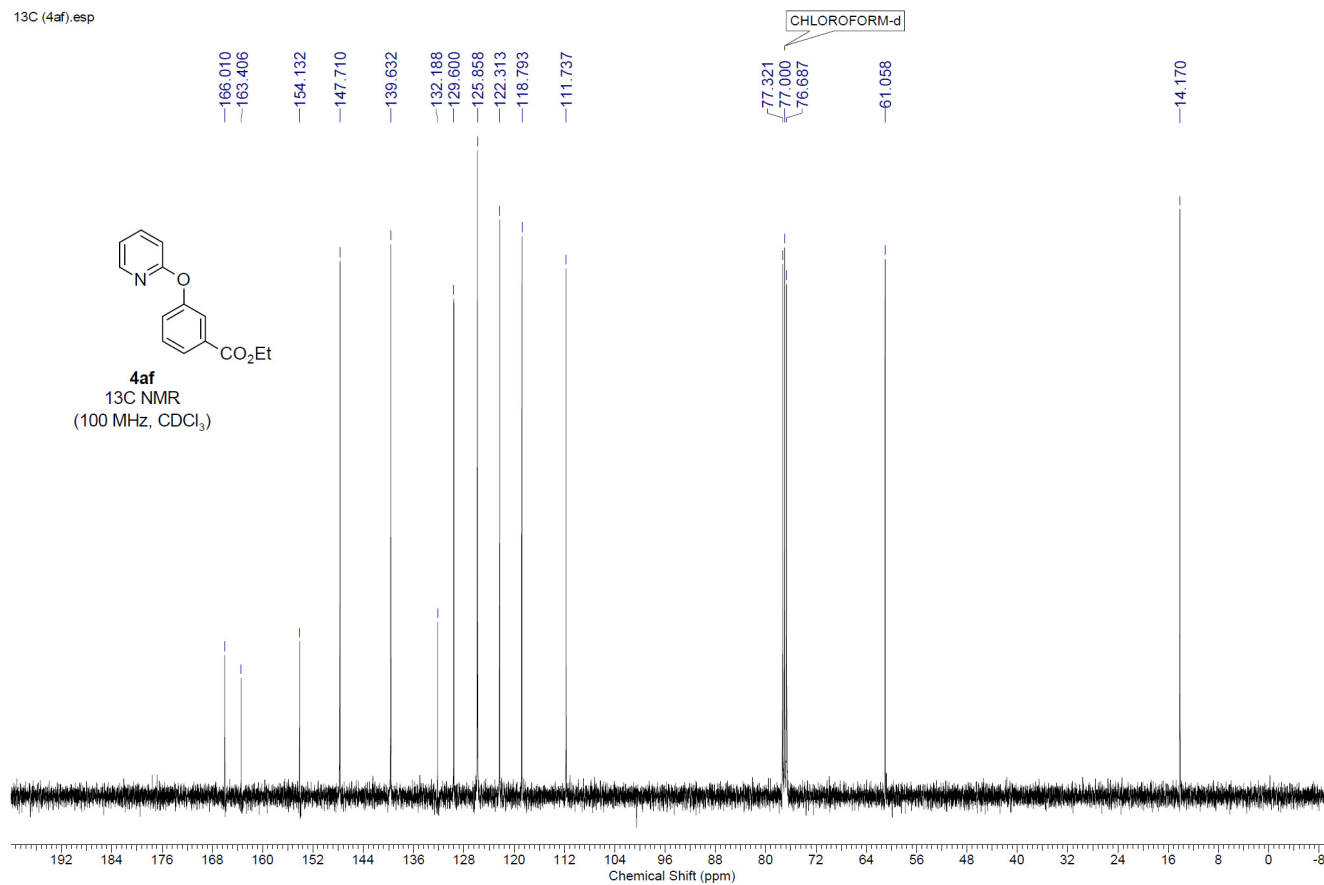
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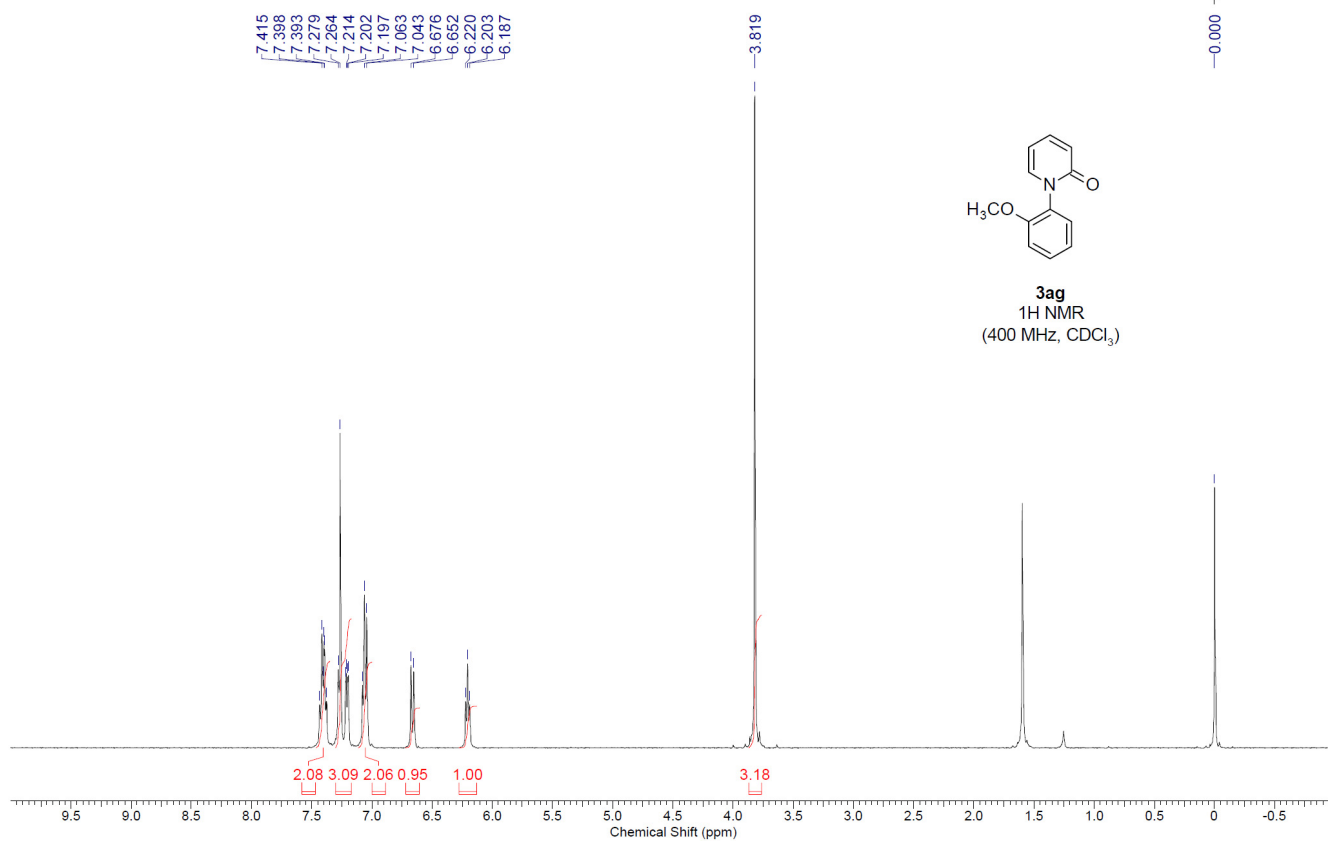
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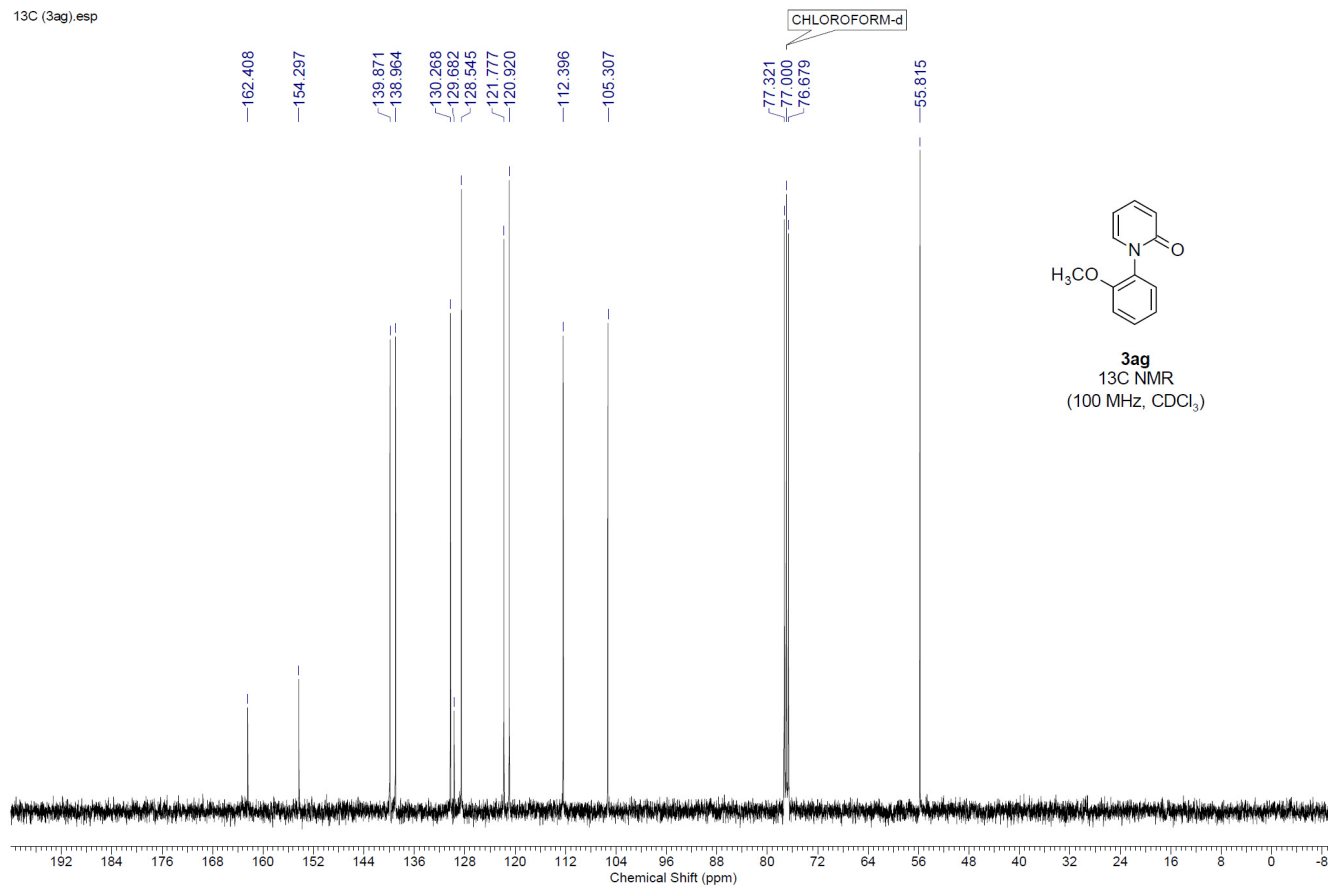
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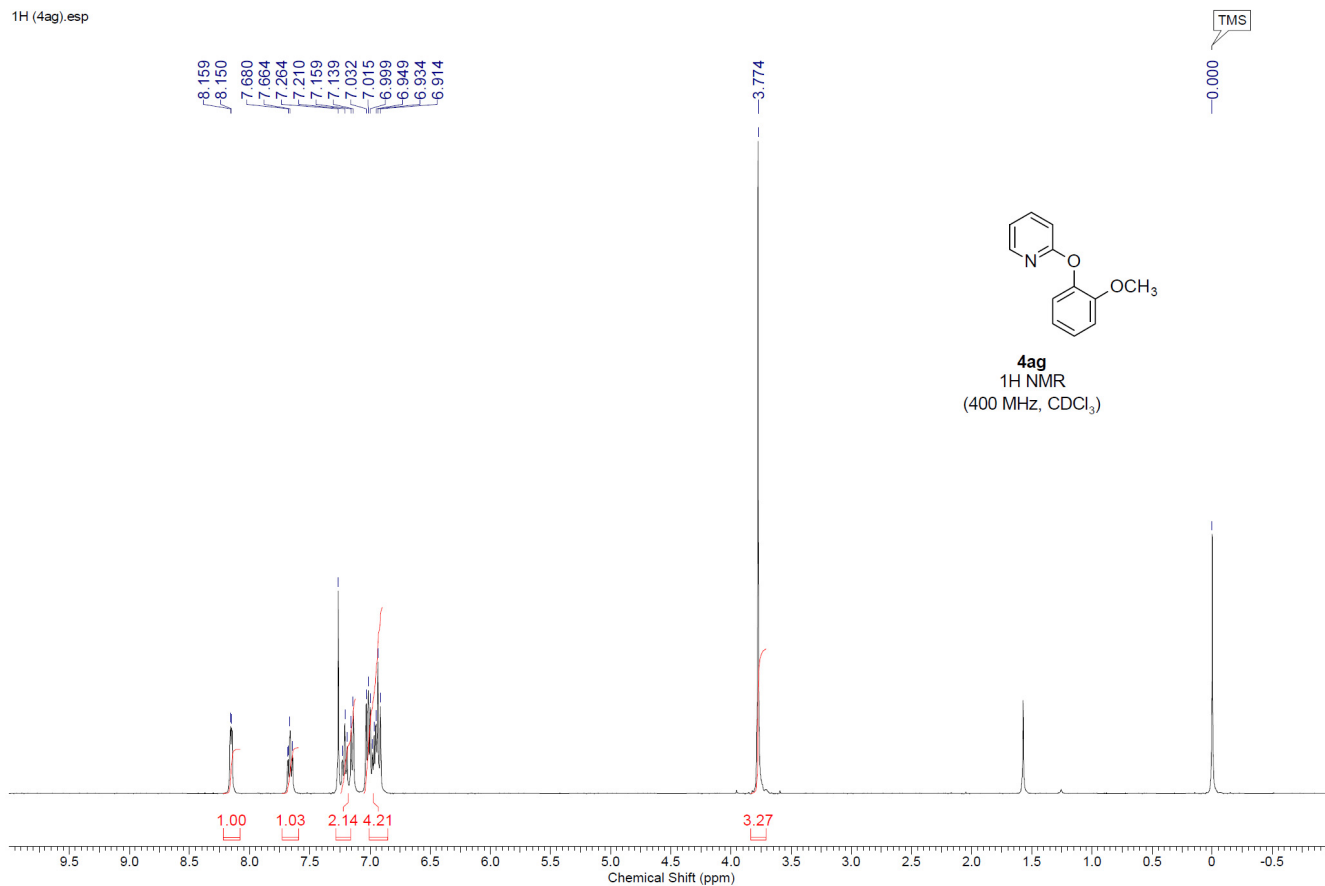
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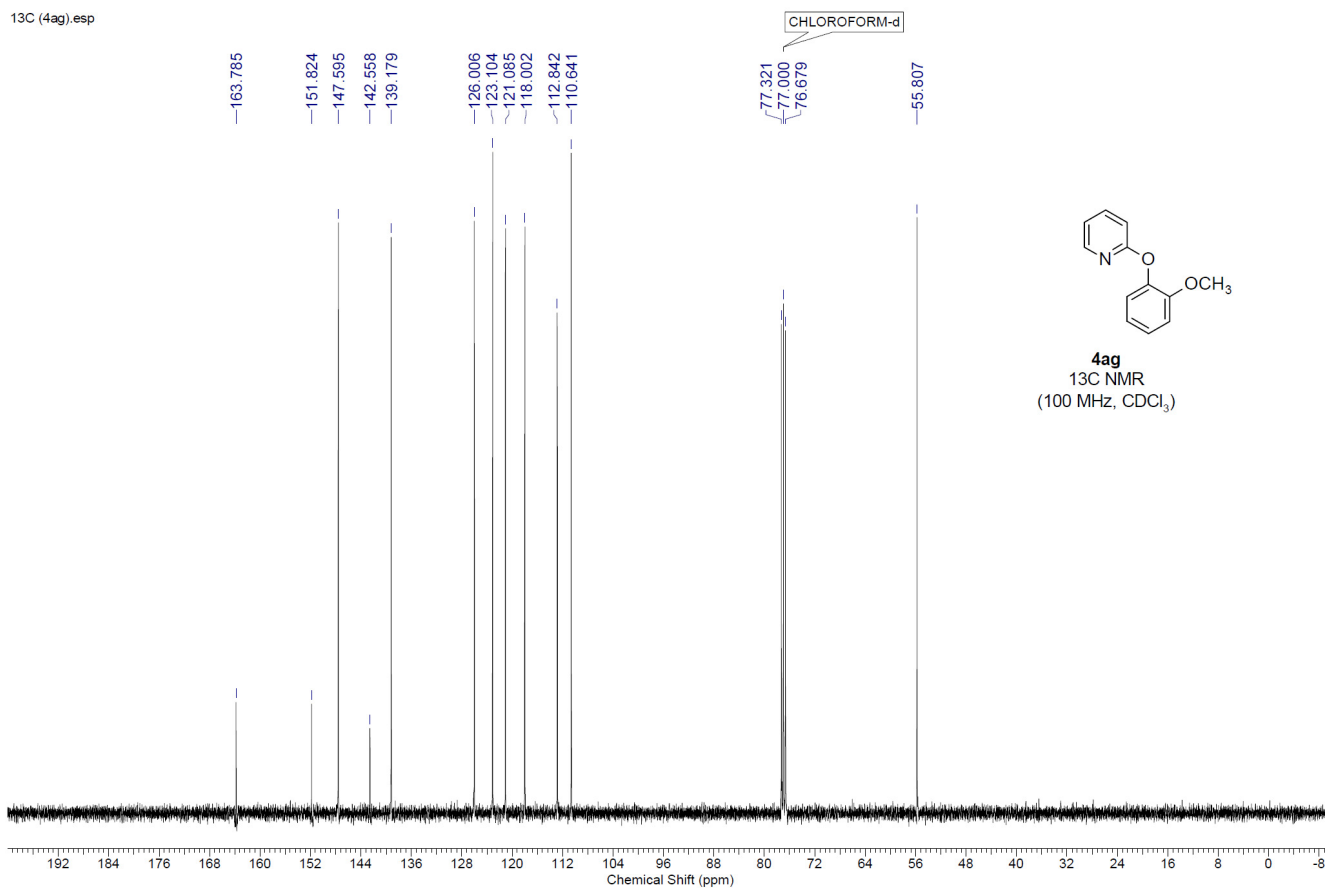
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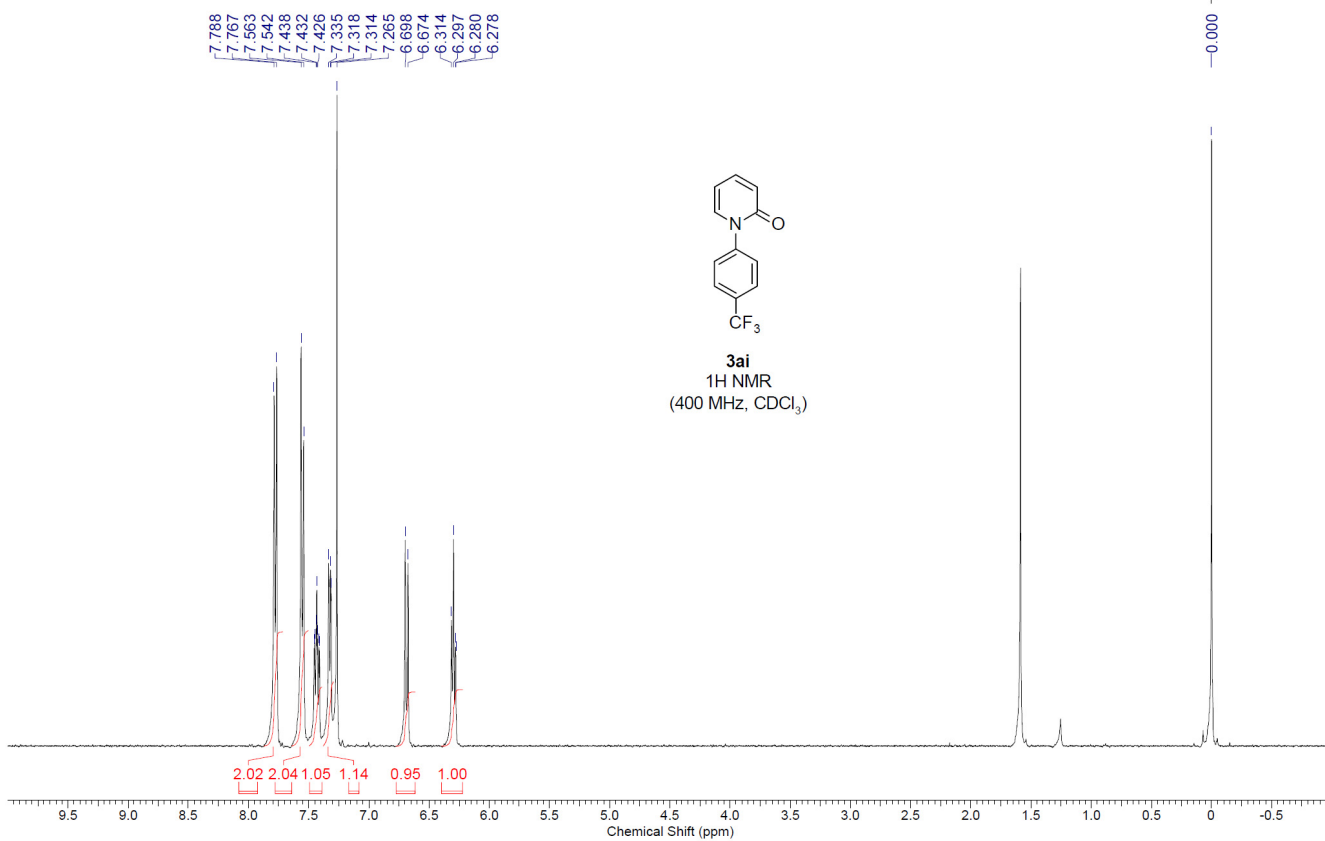
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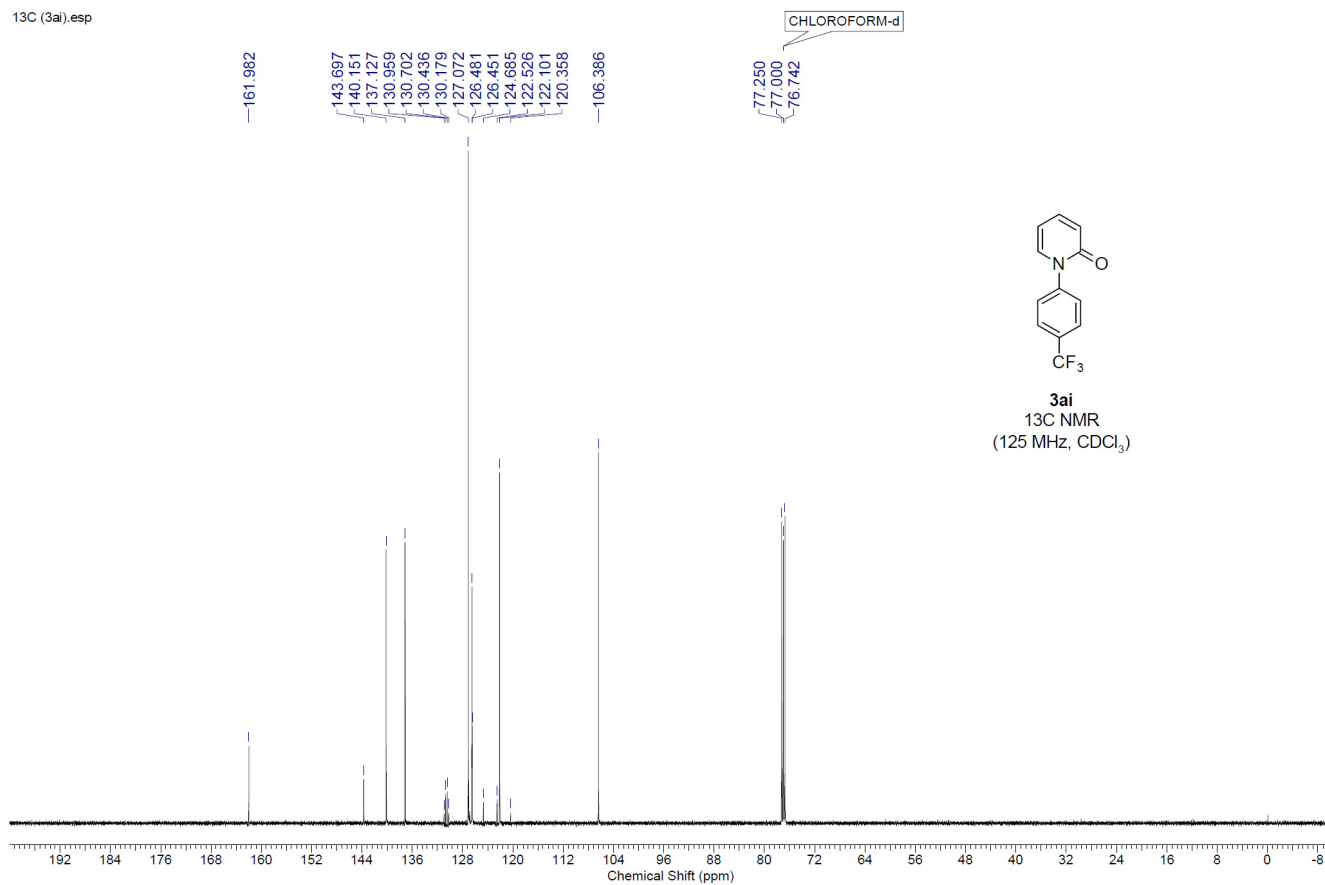
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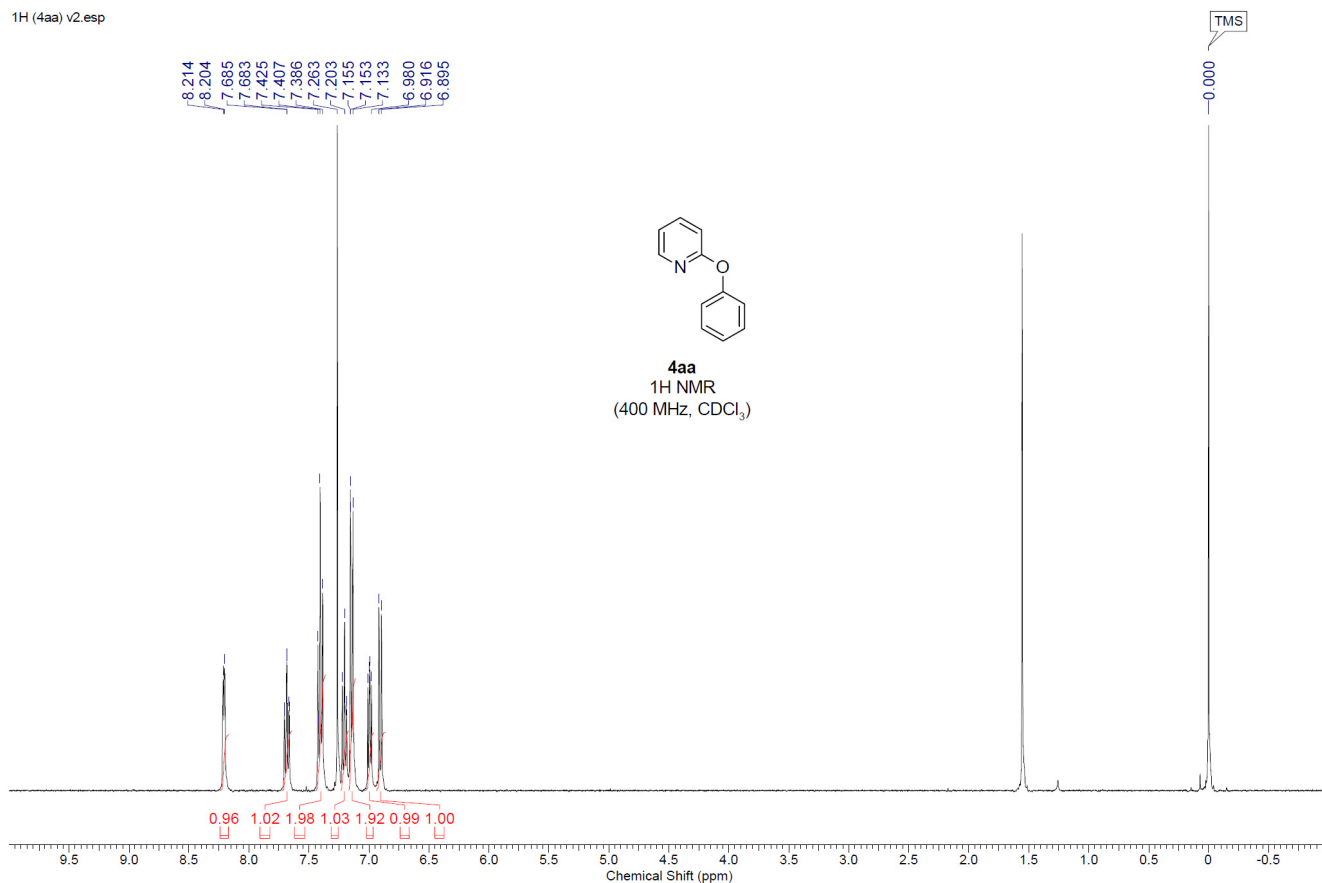
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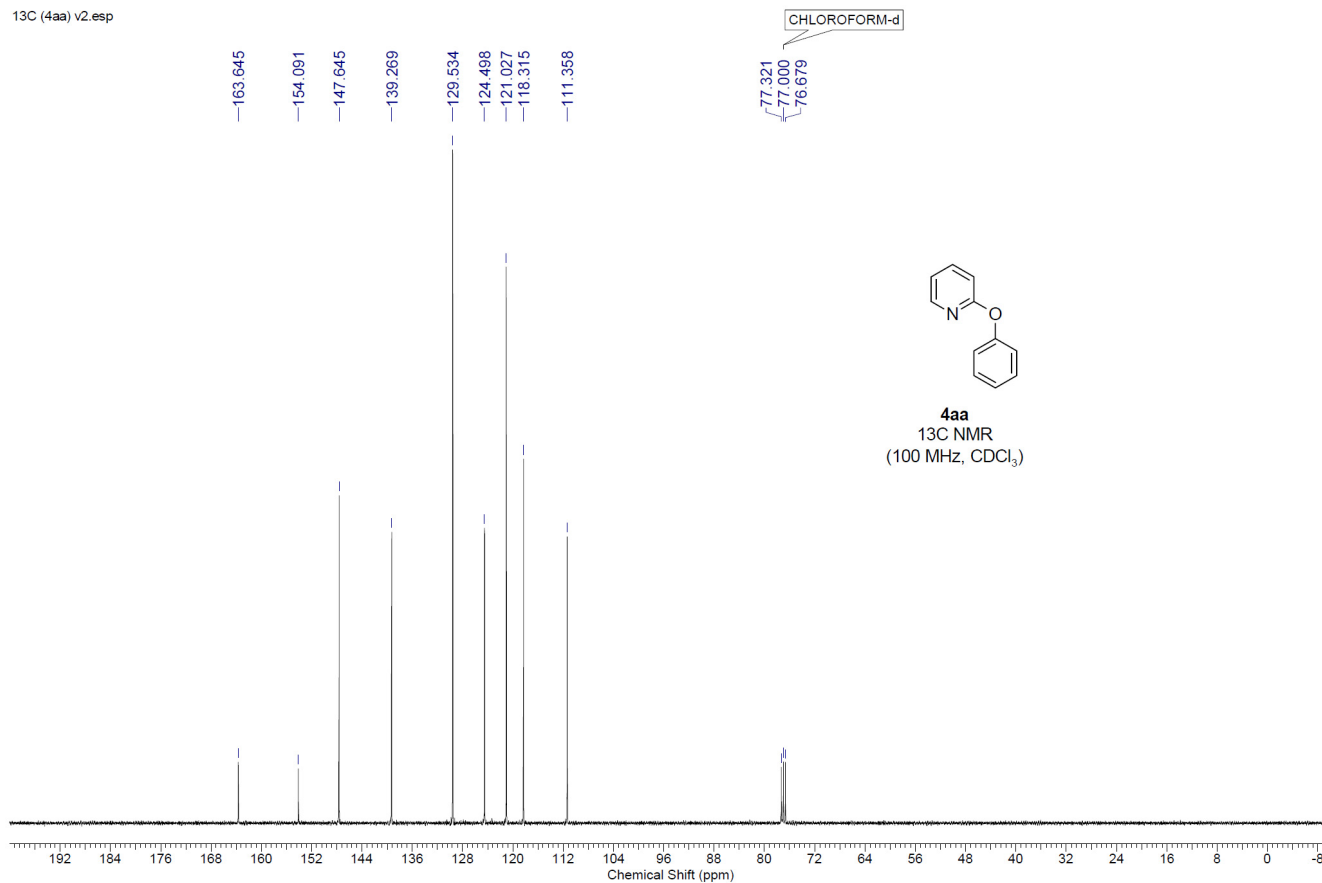
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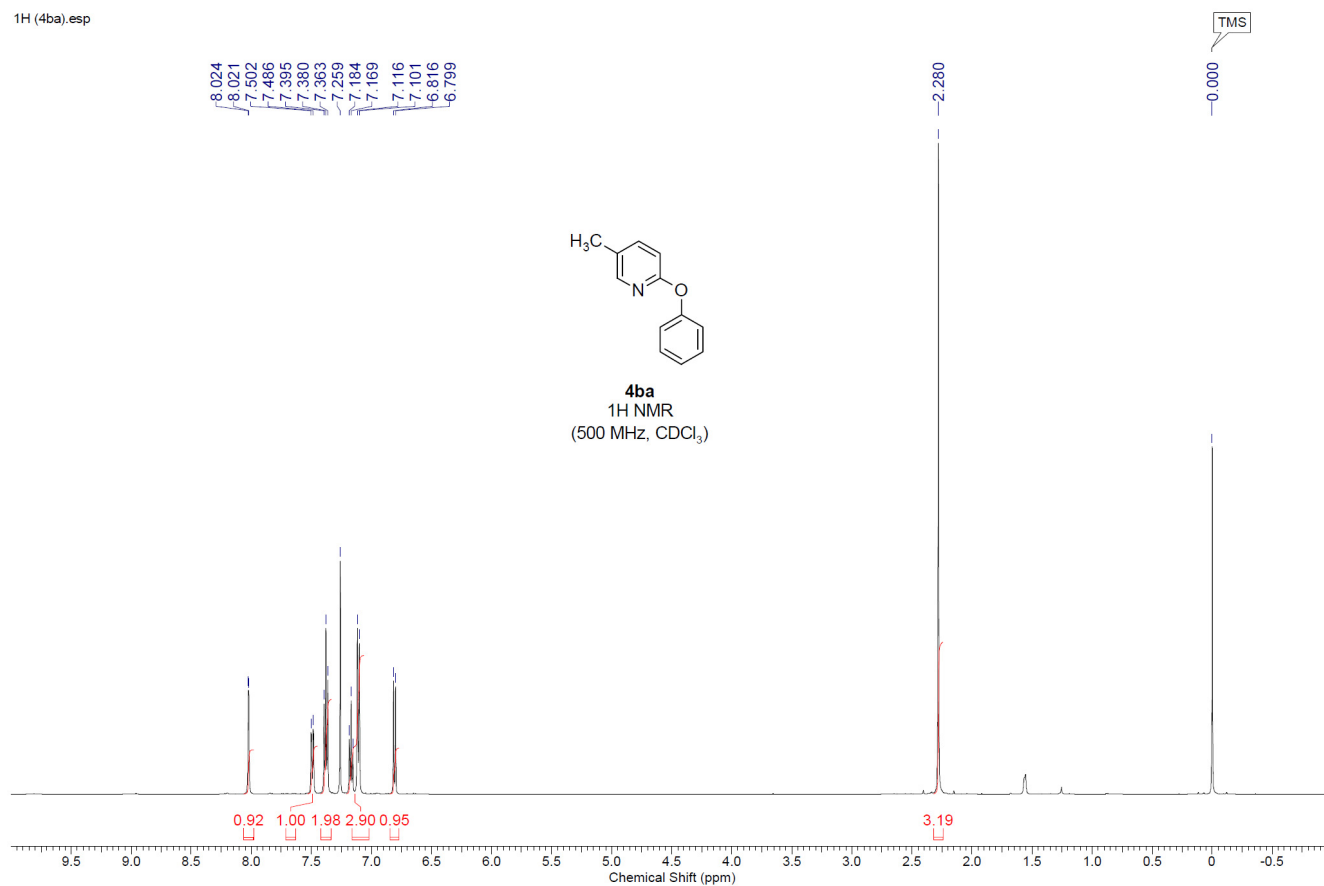
1H (4aa) v2.esp



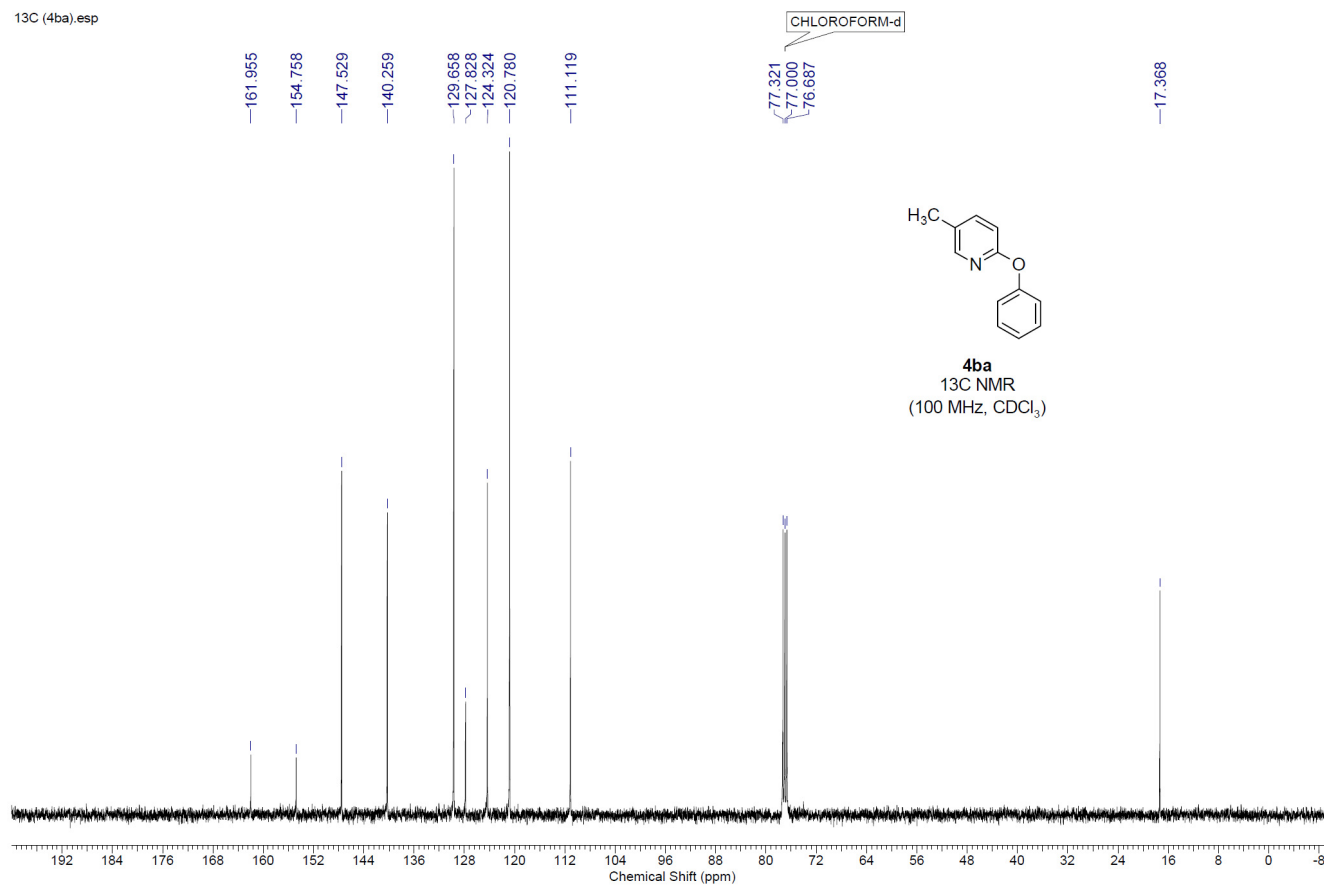
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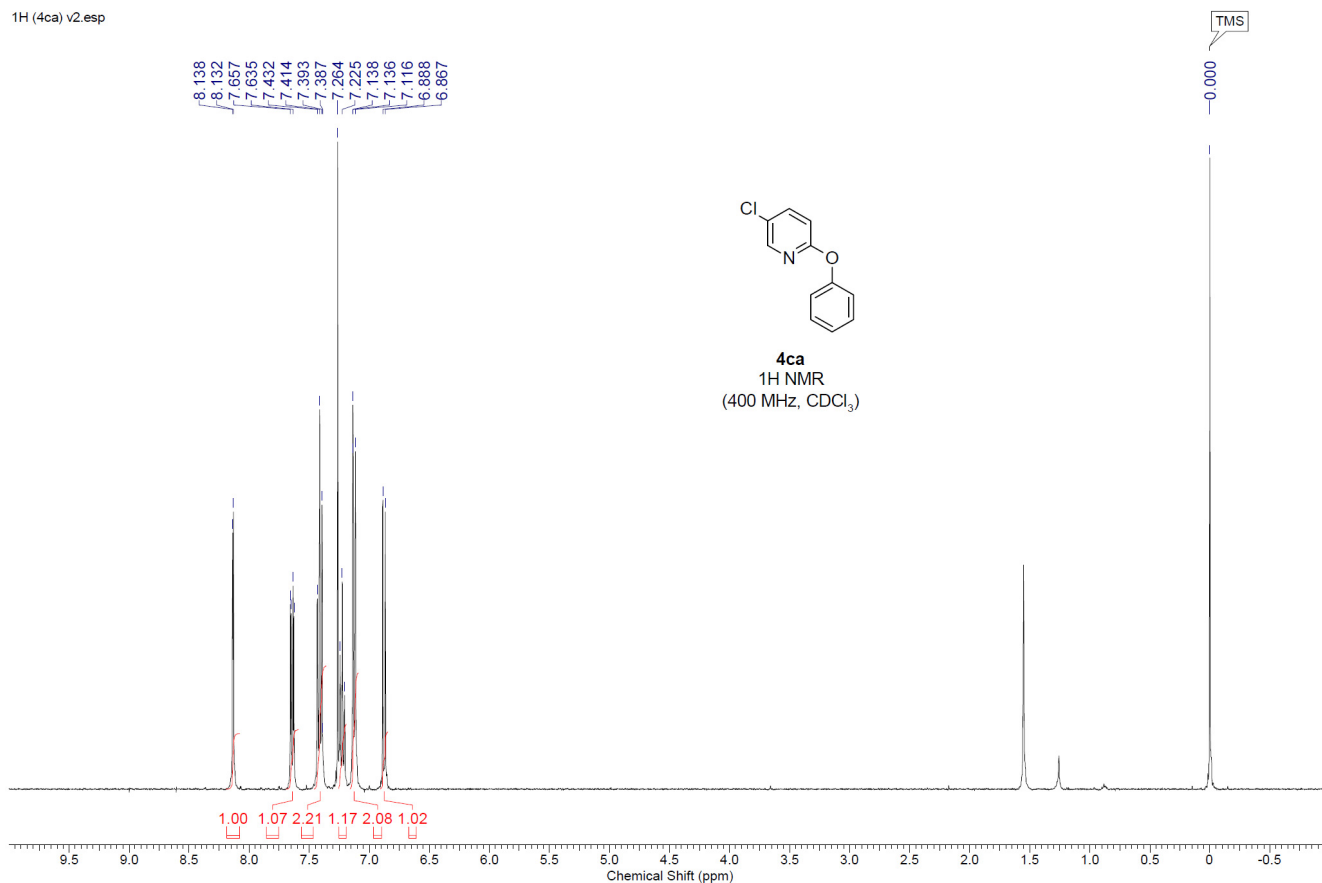
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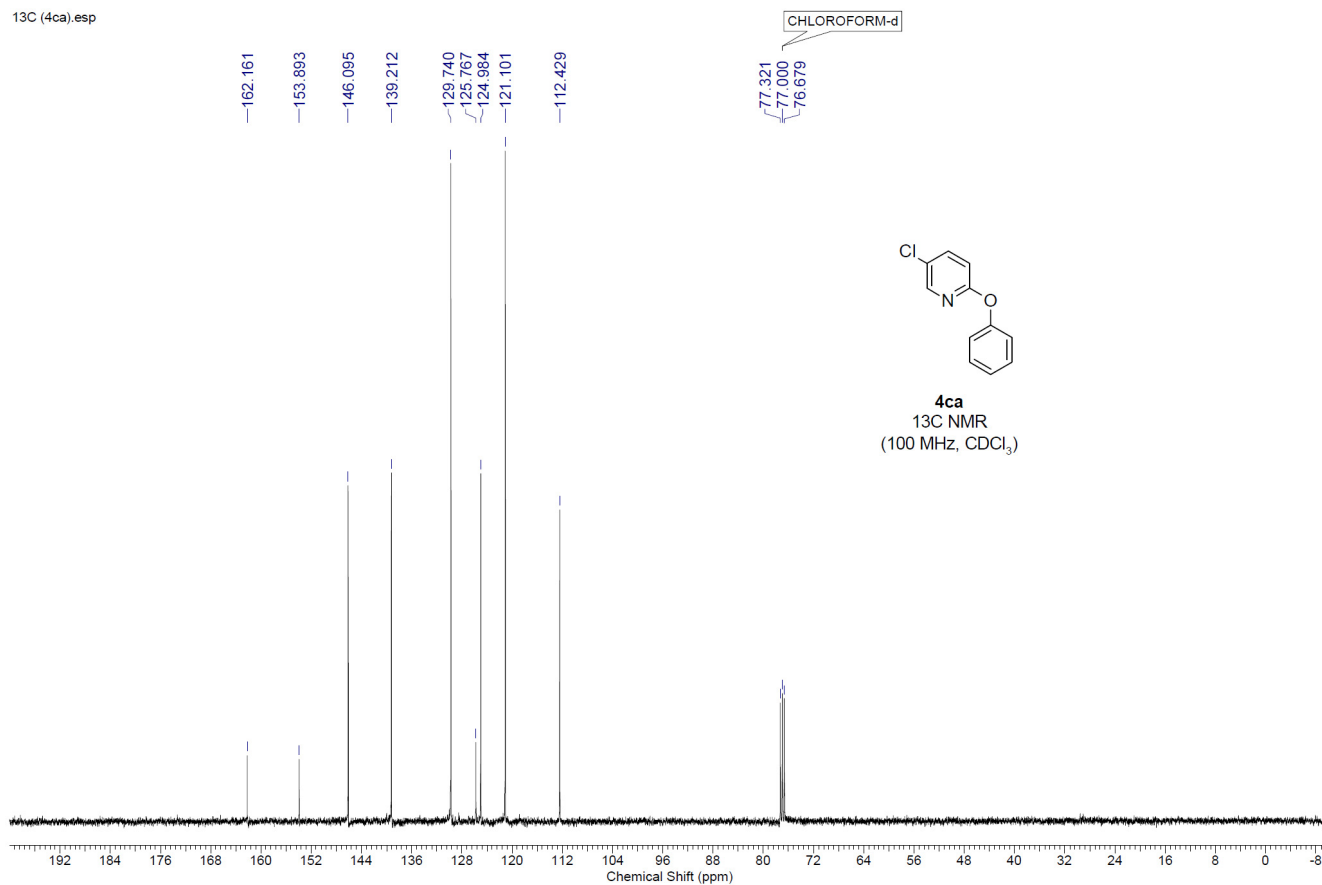
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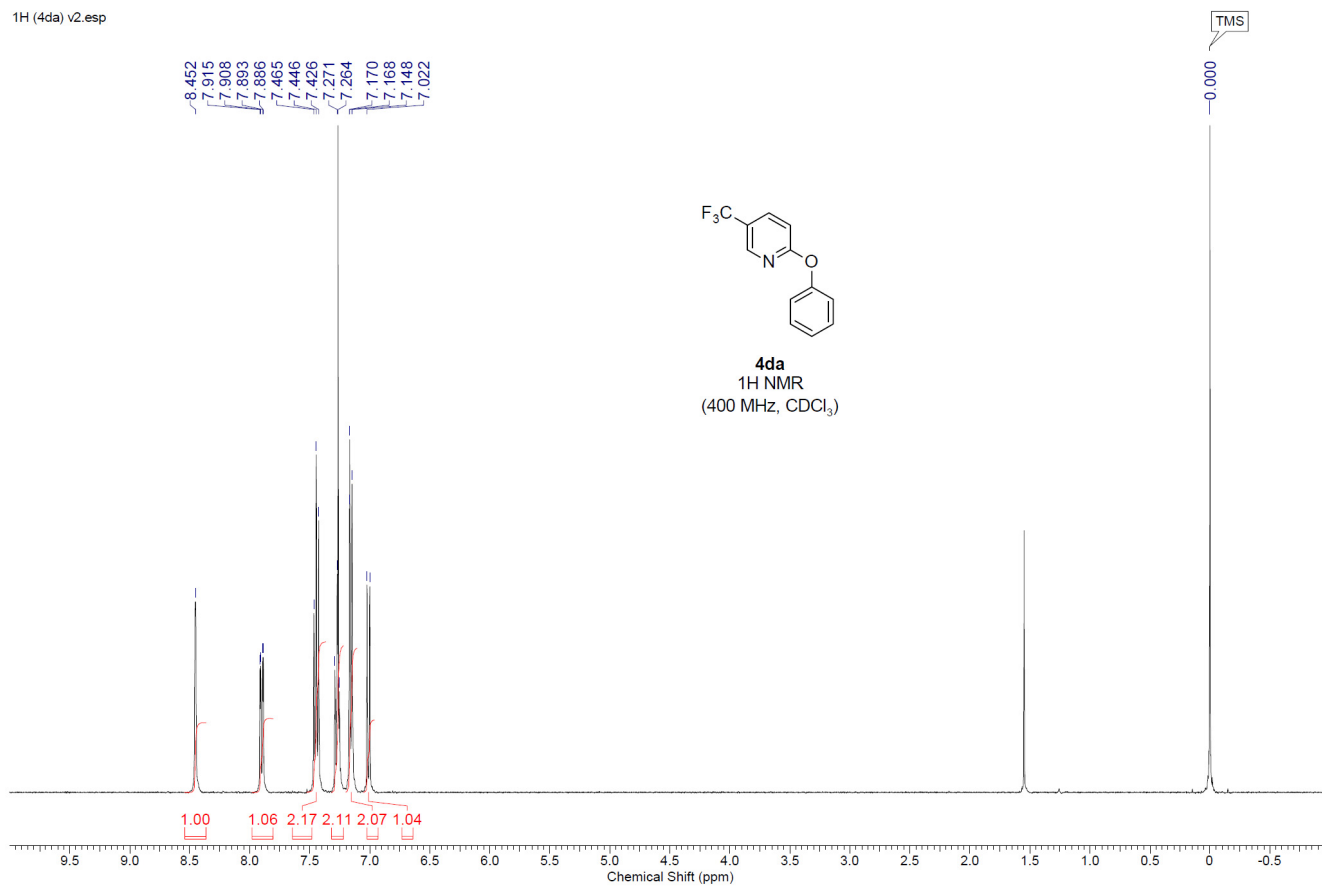
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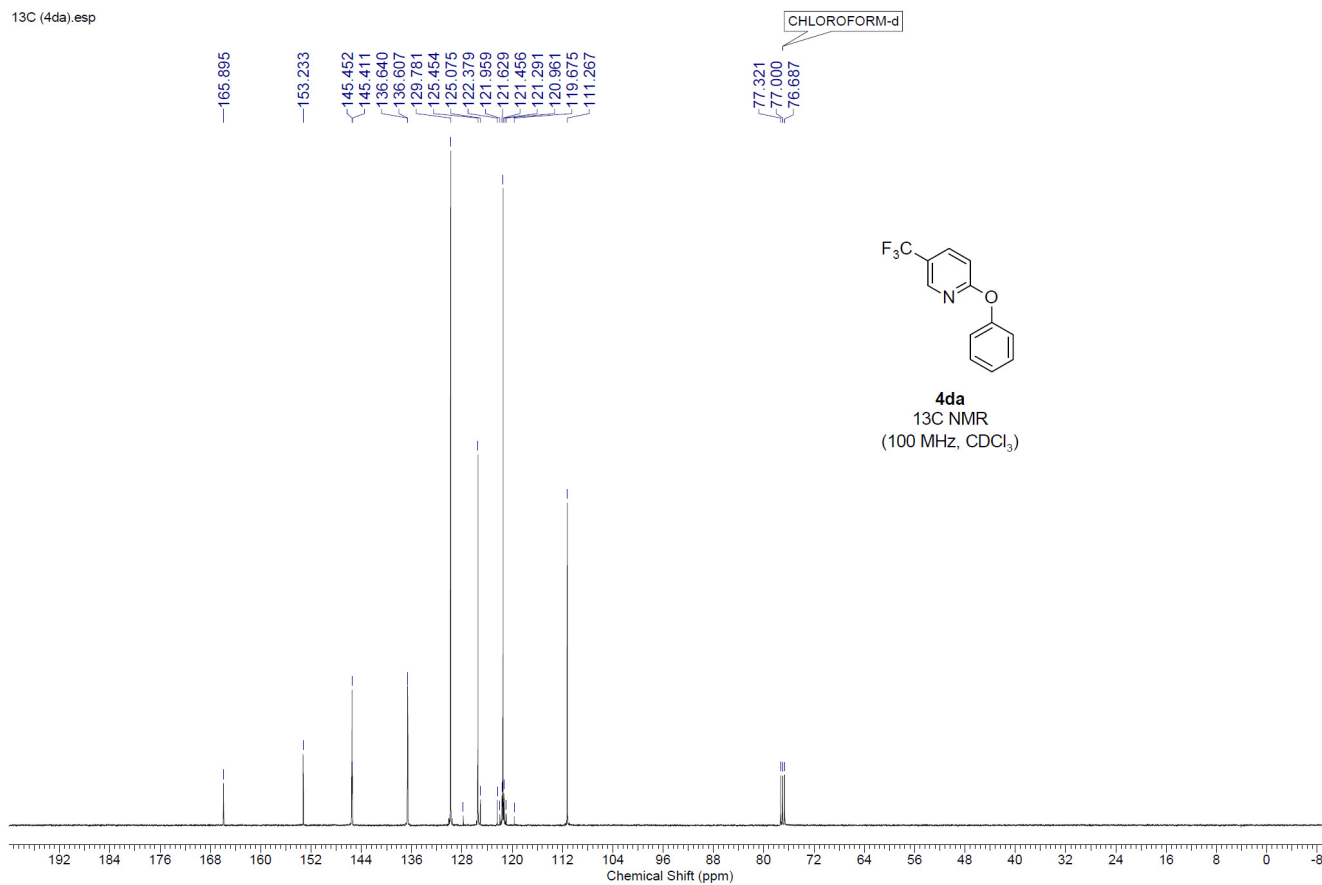
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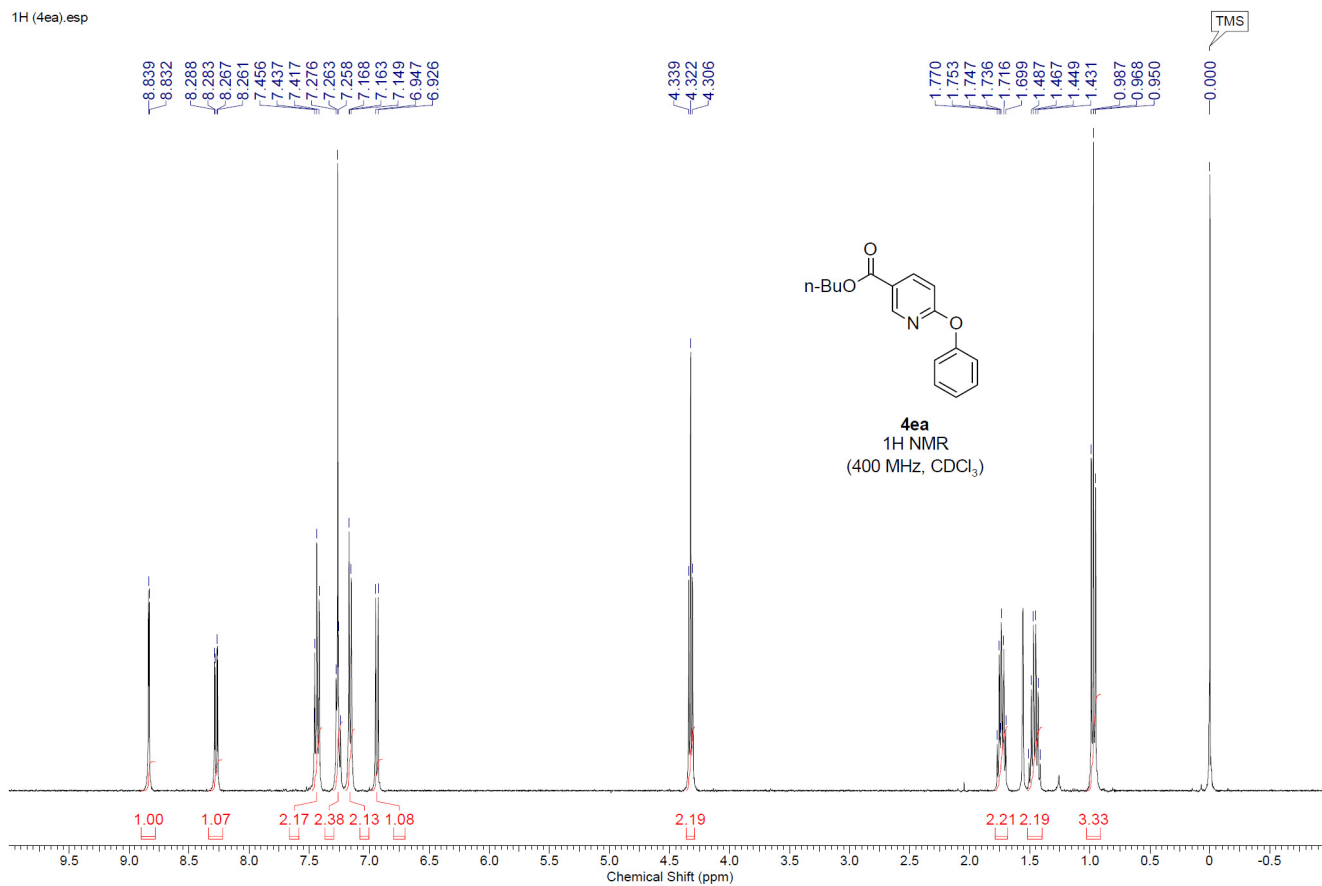
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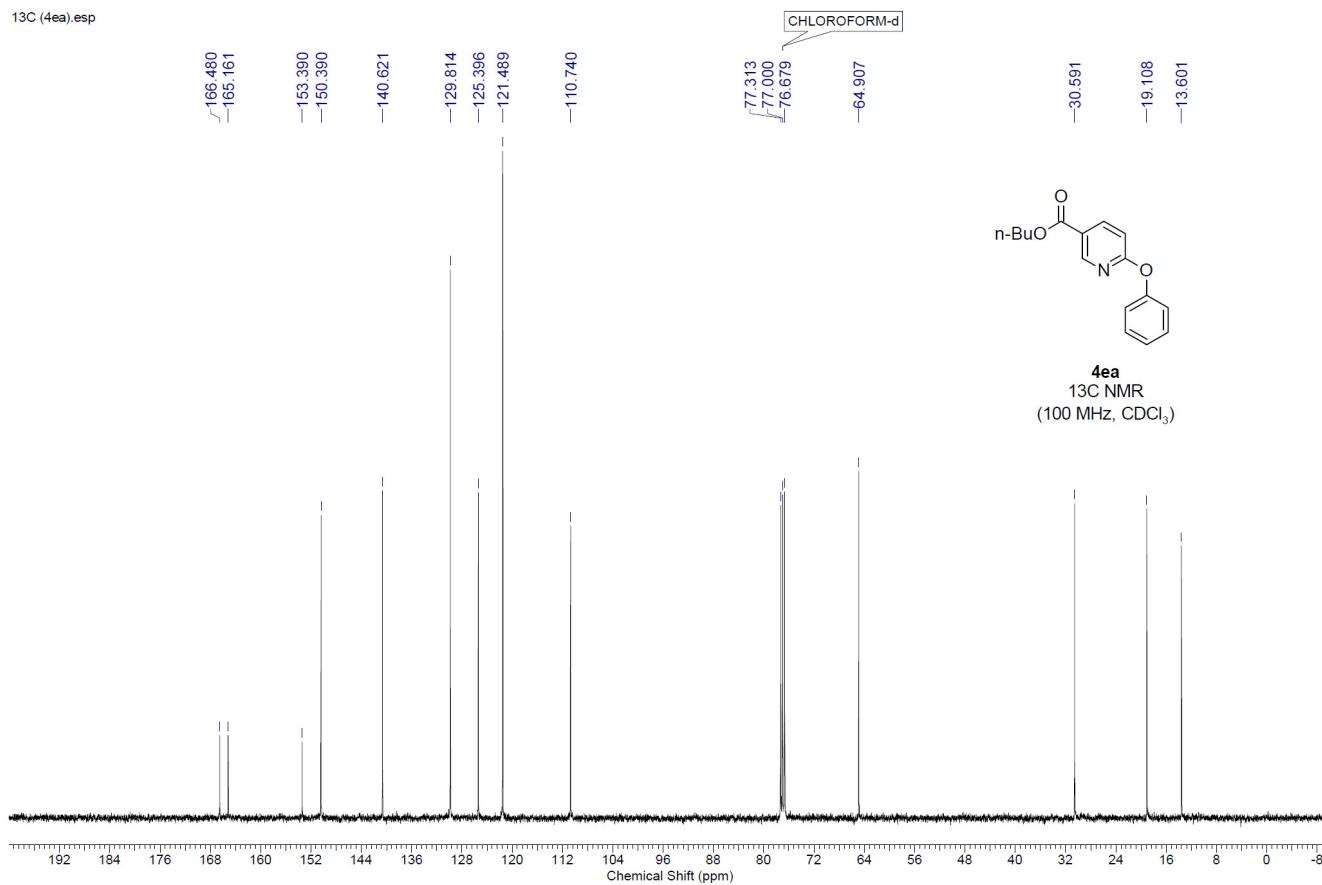
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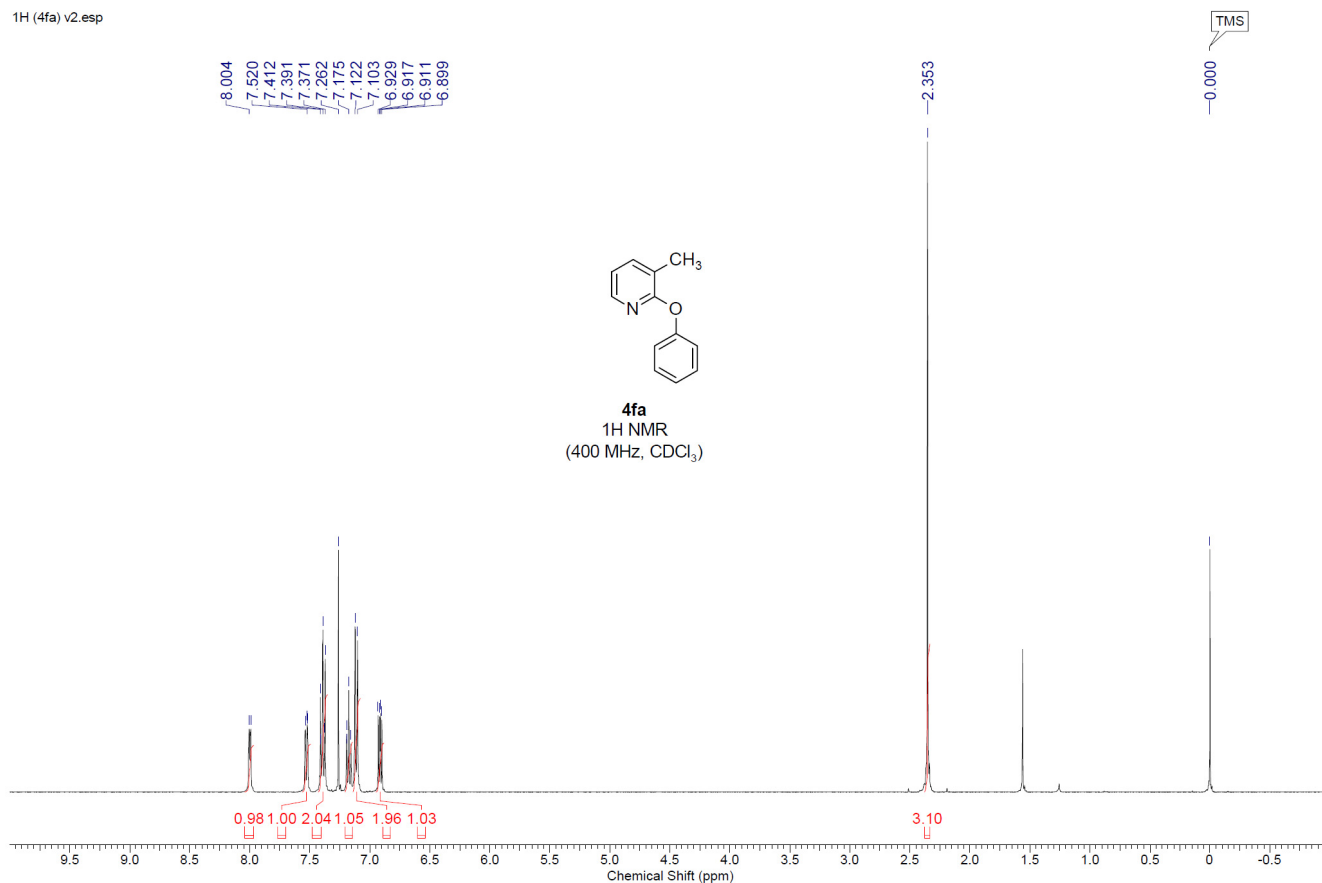
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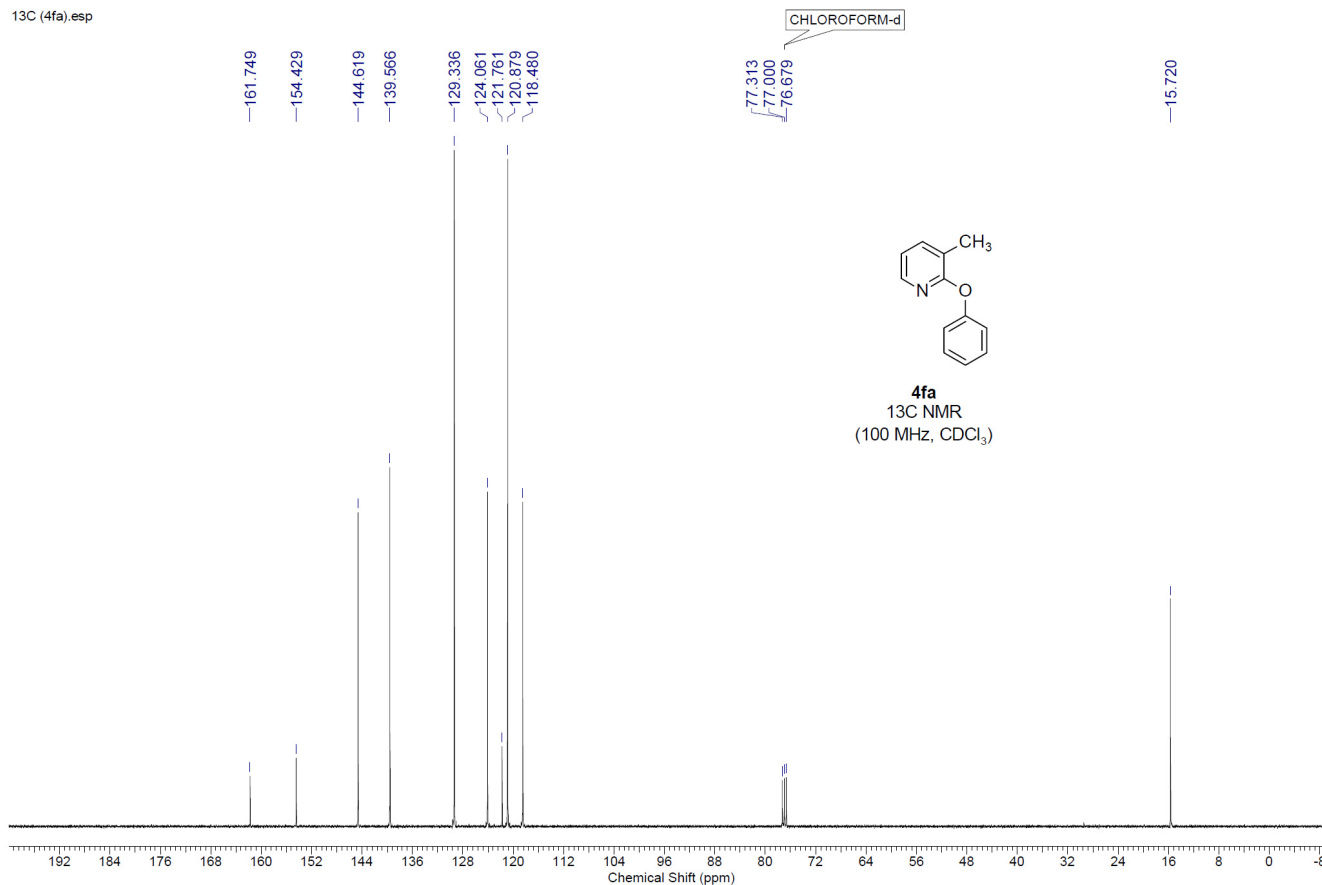
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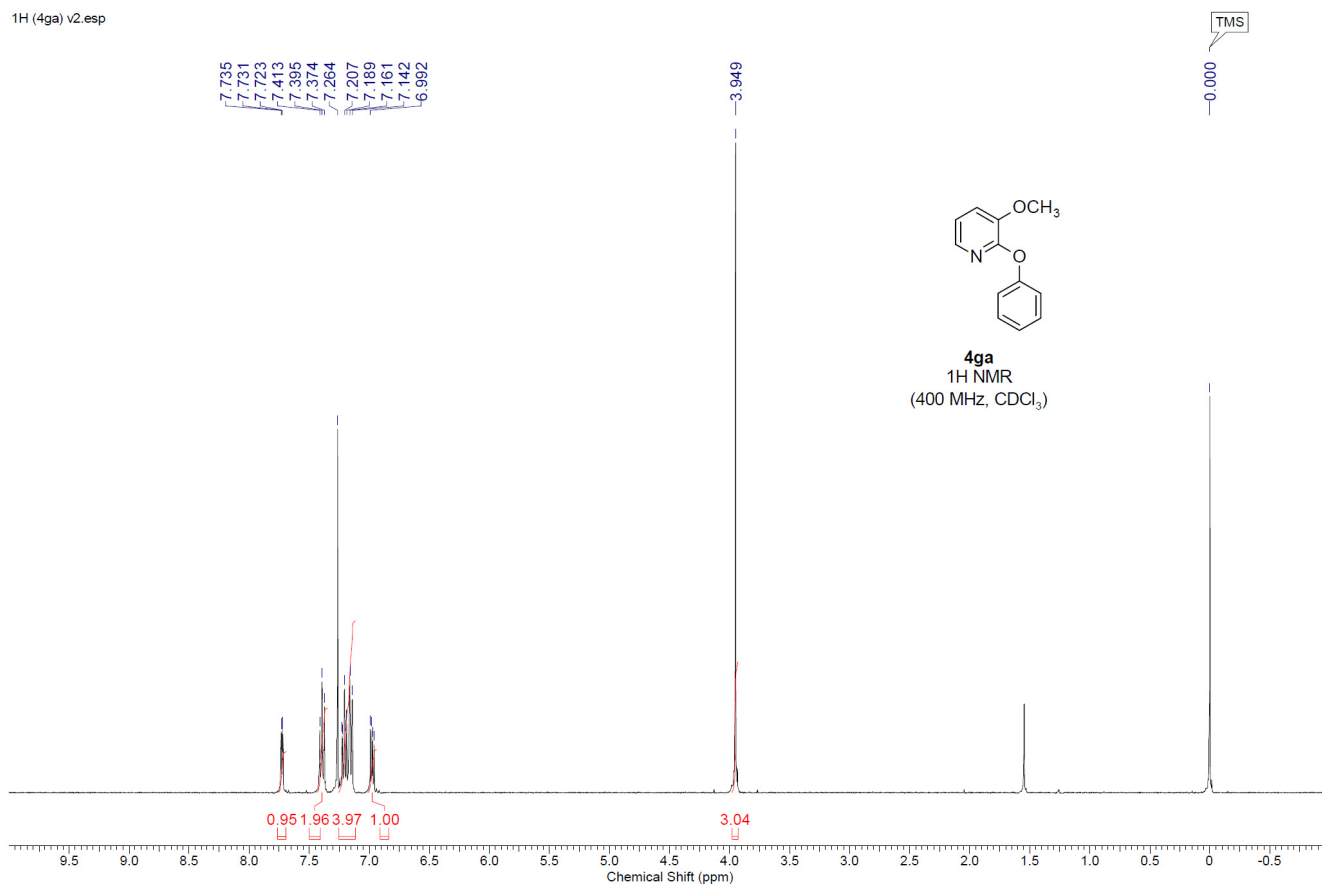
1H (4fa) v2.esp



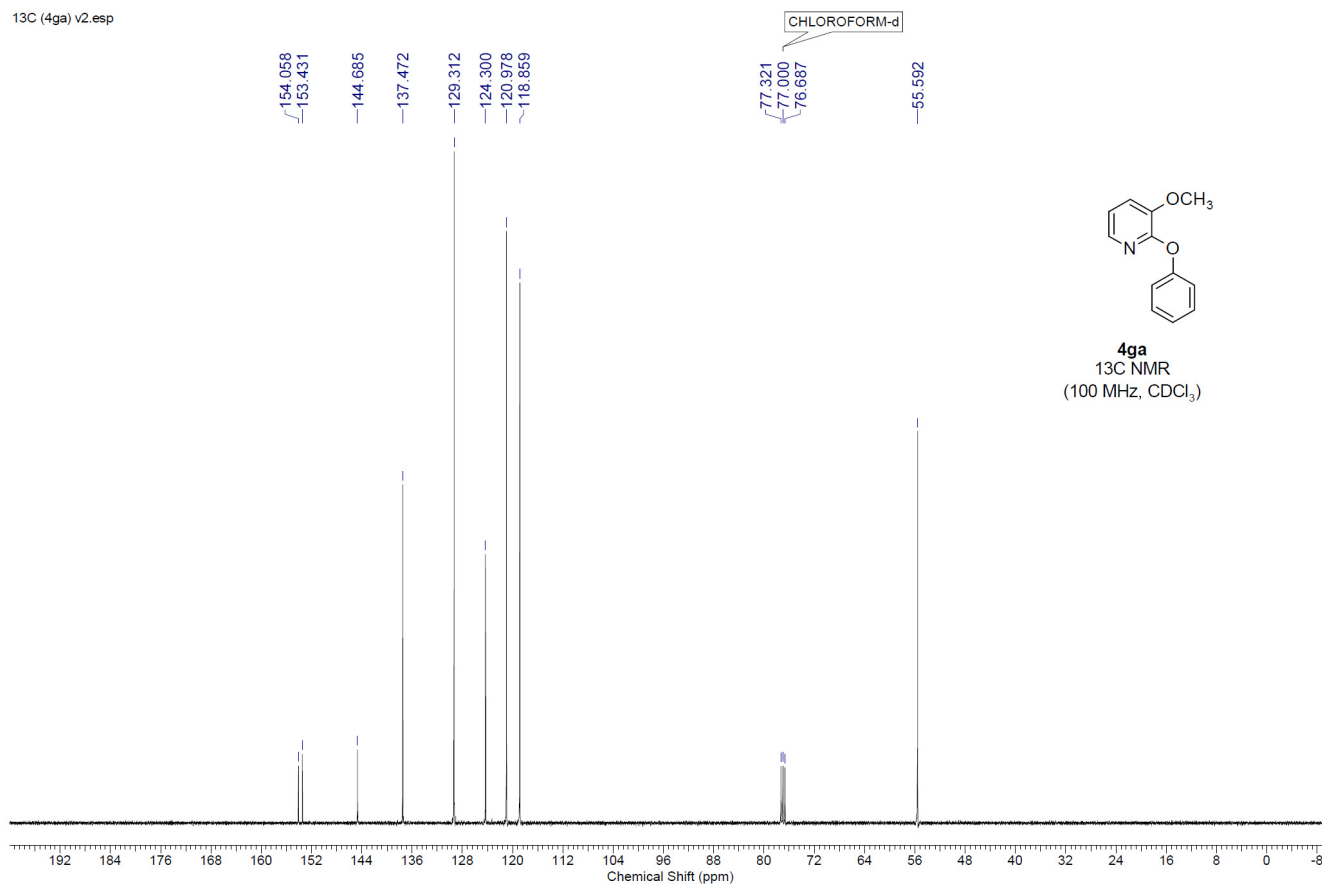
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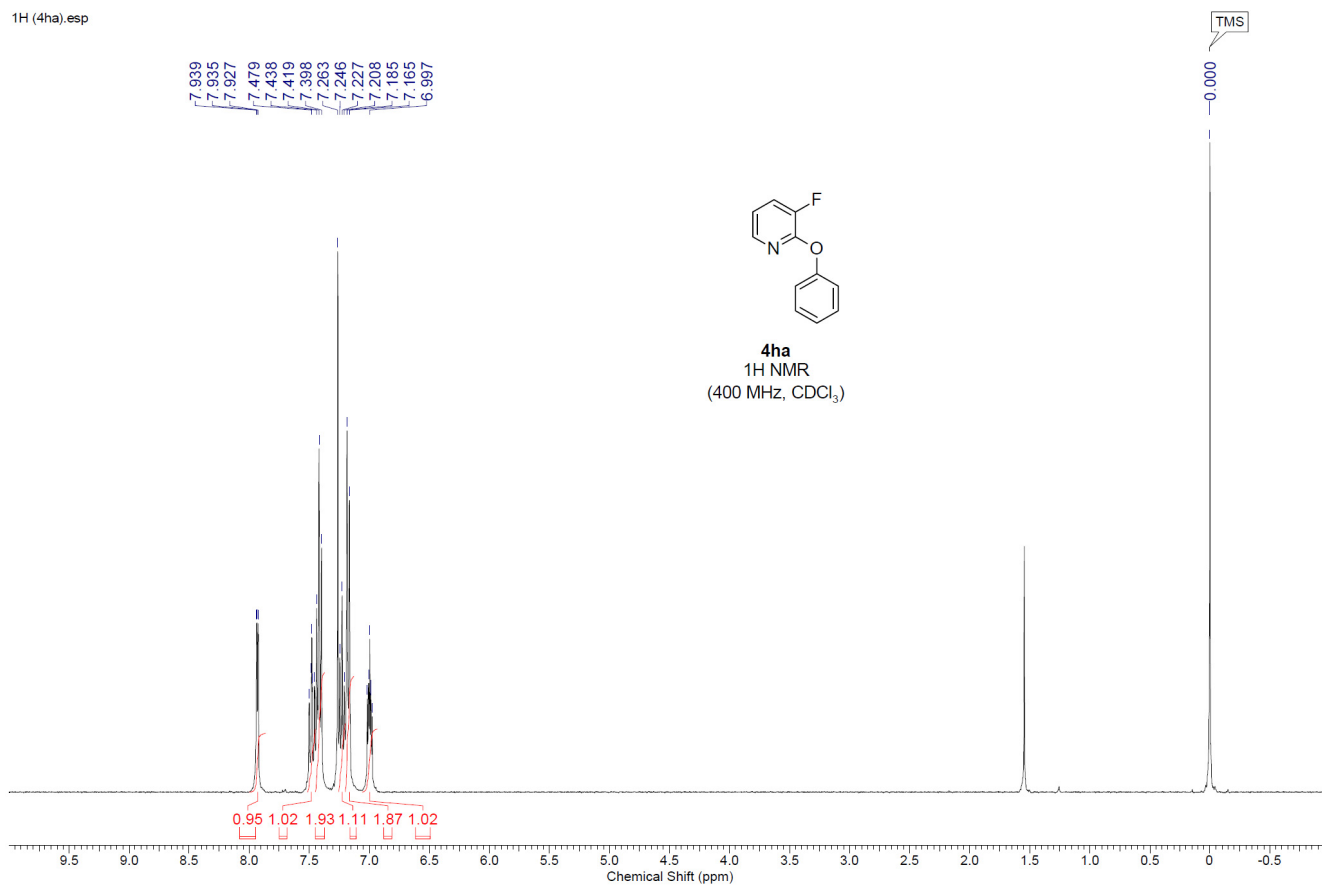
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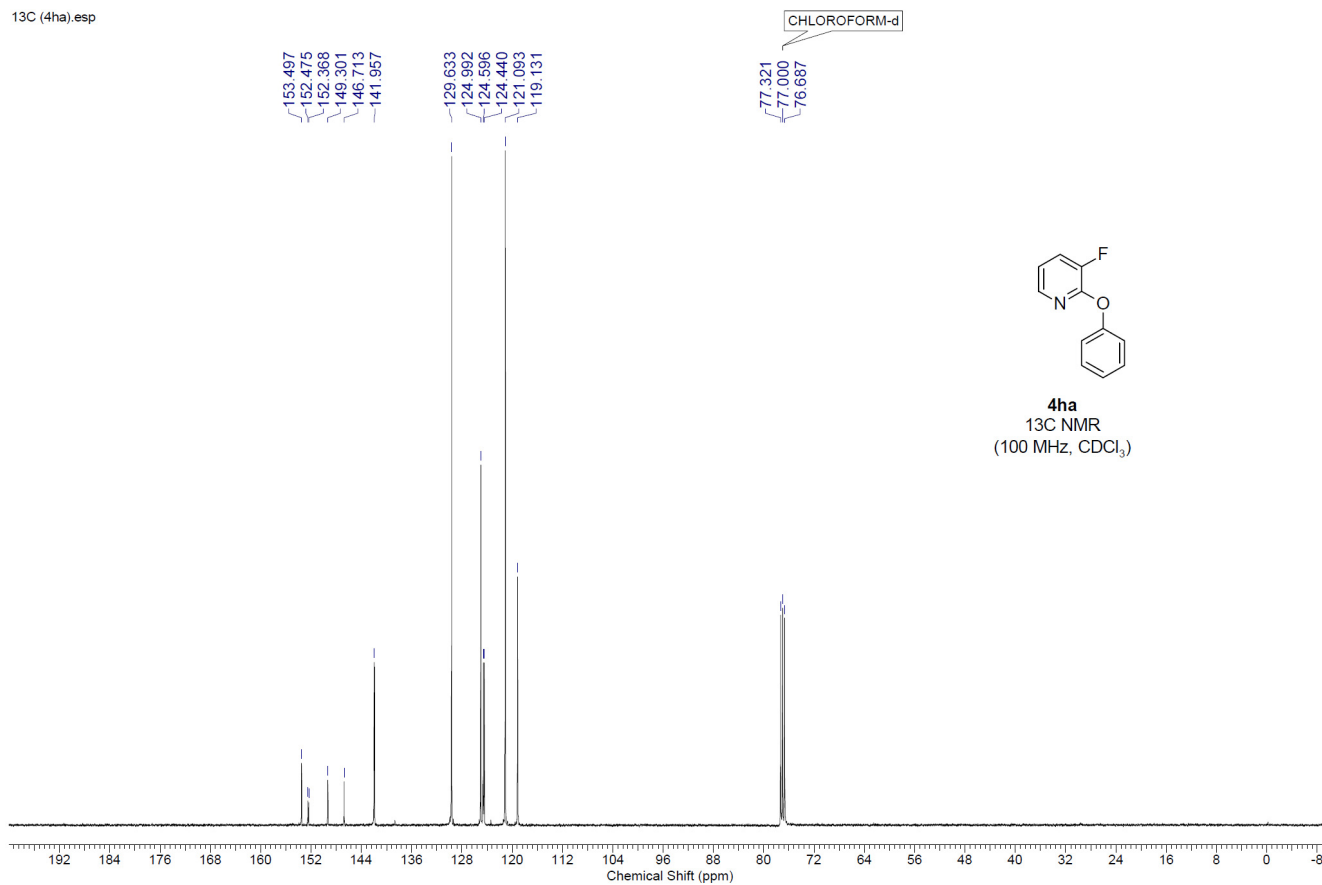
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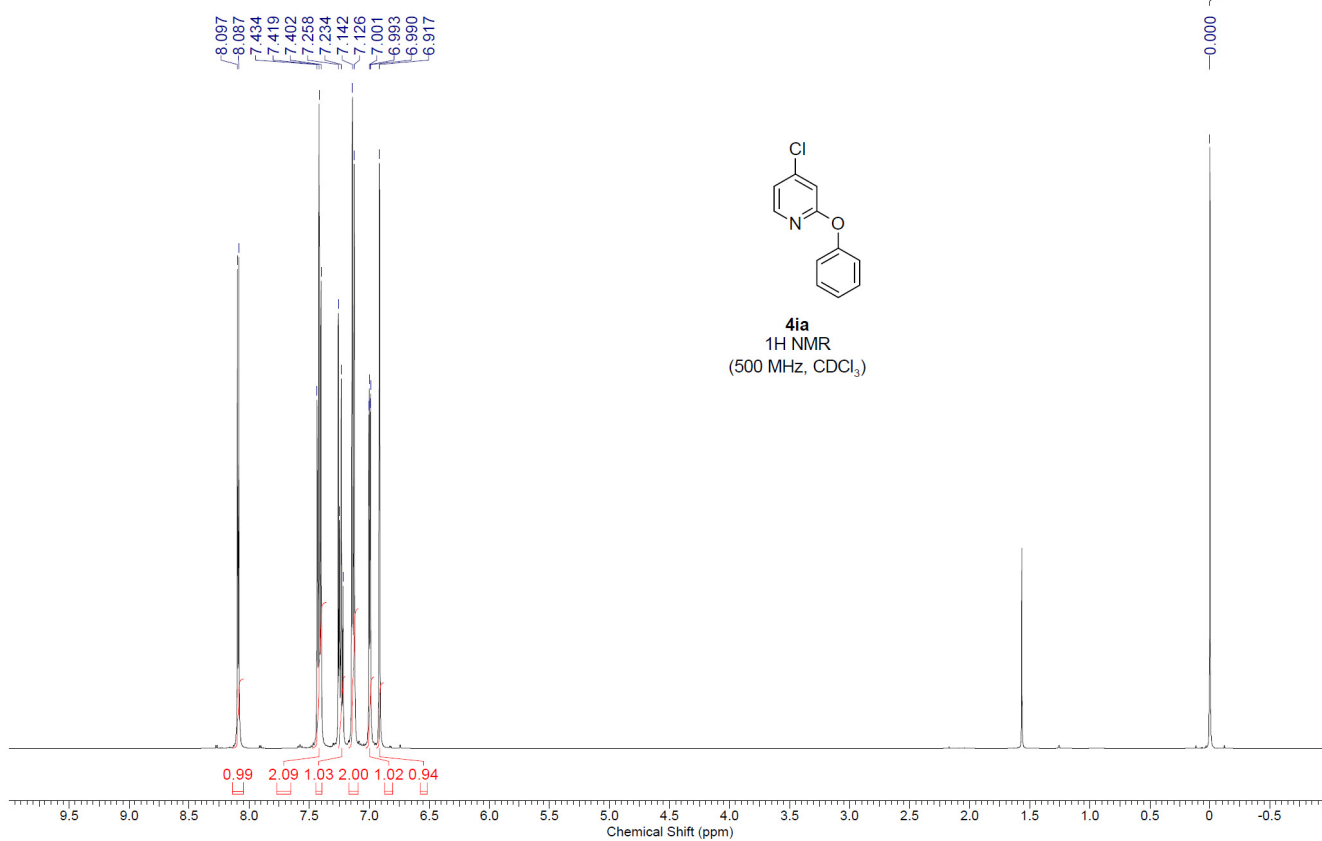
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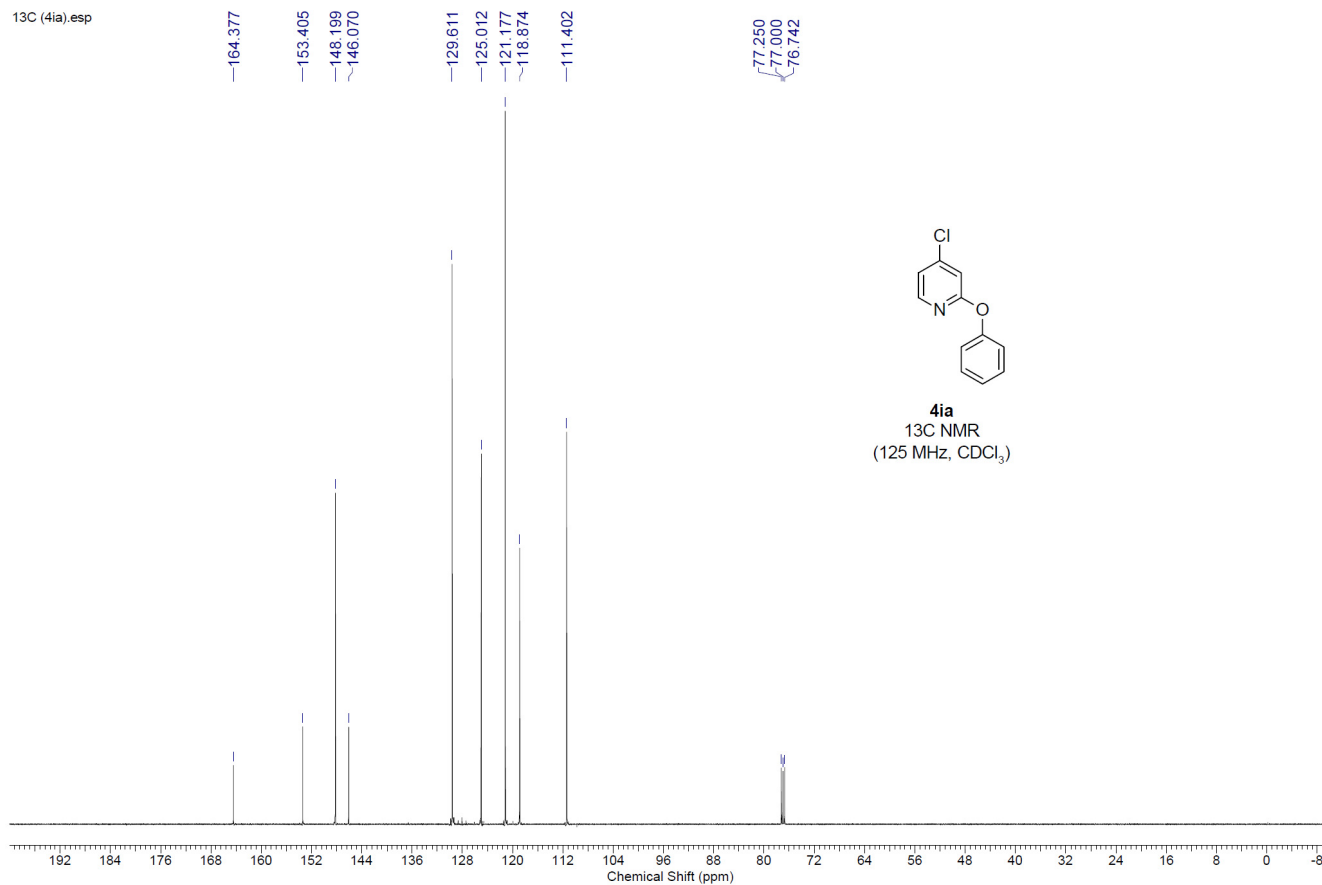
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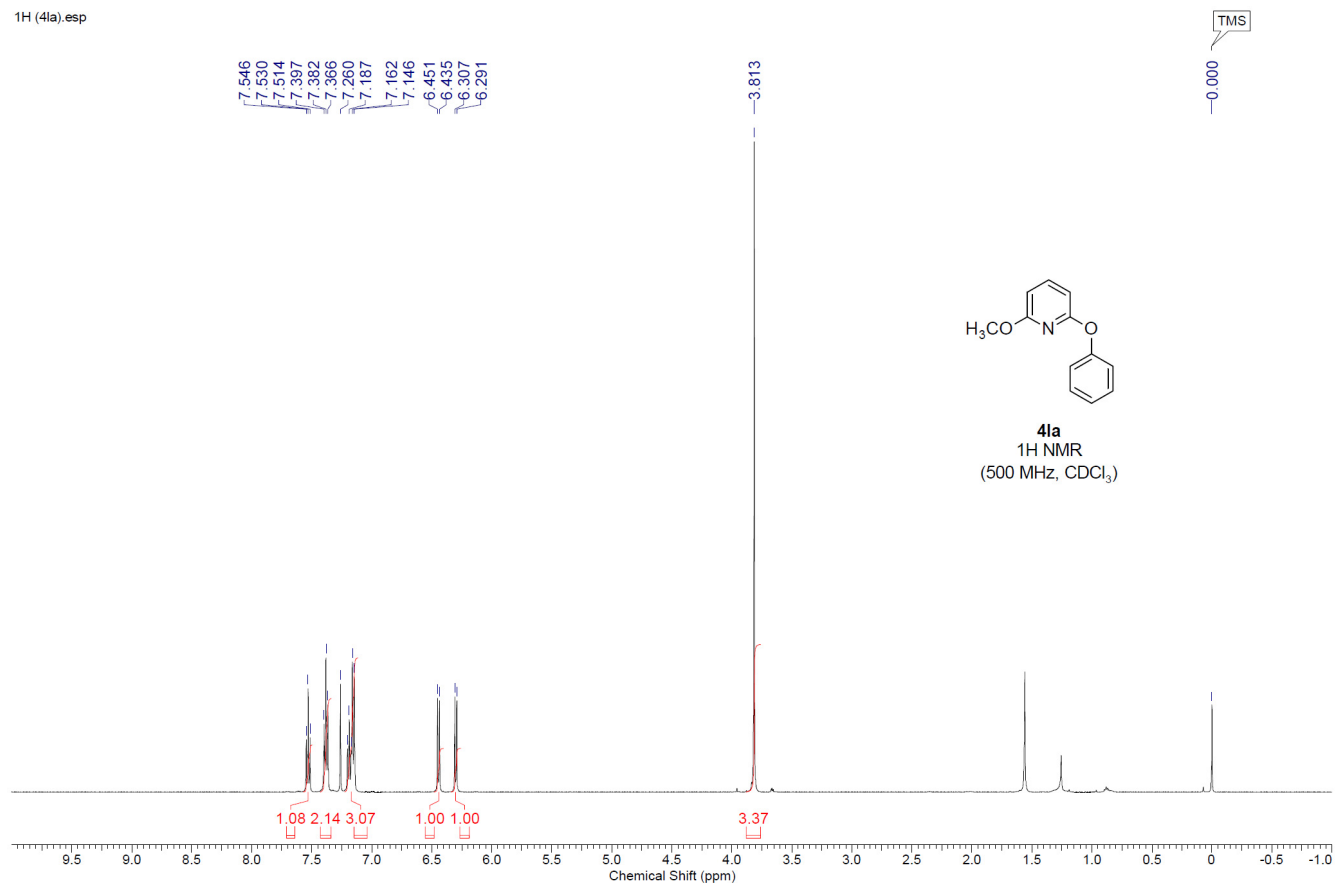
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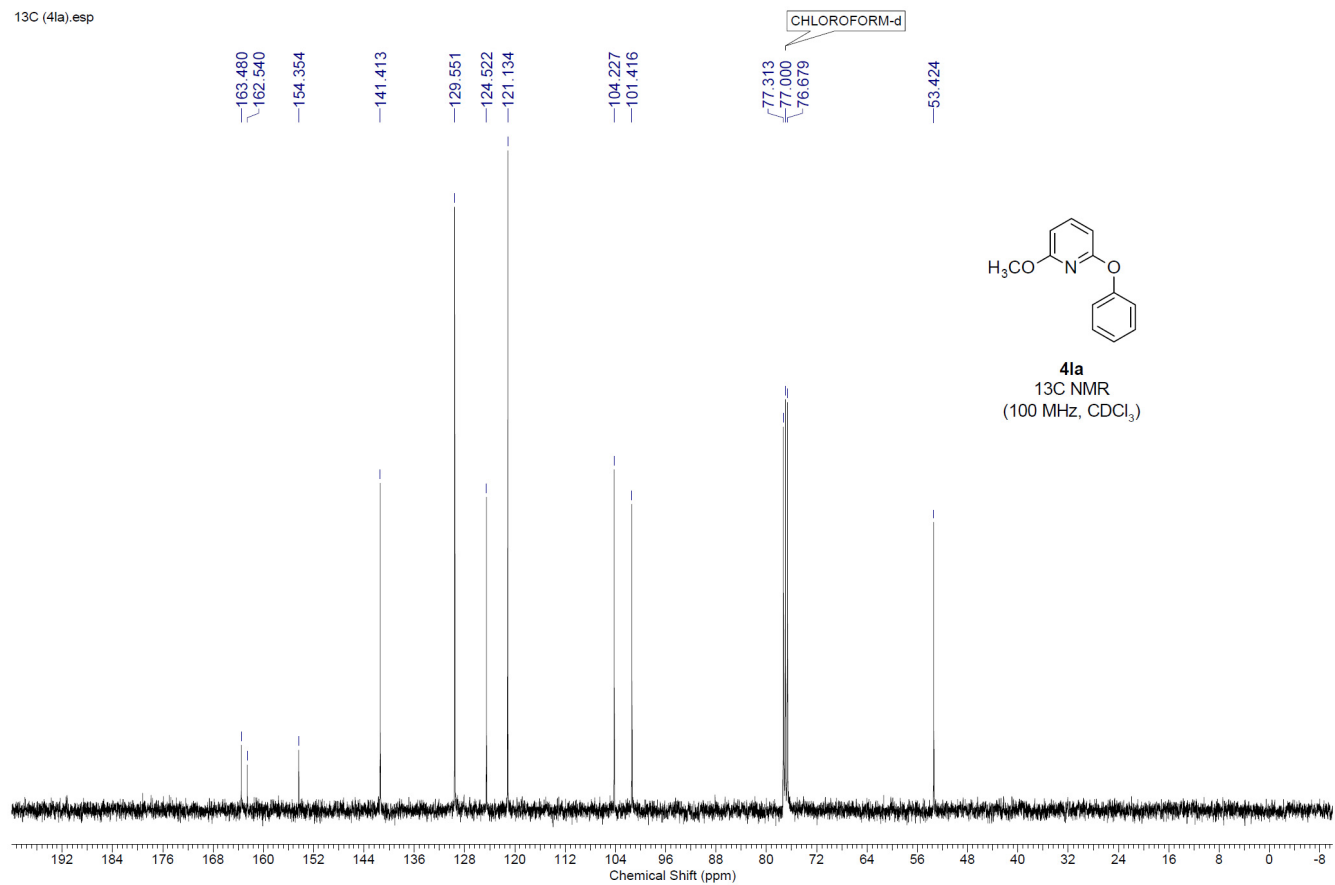
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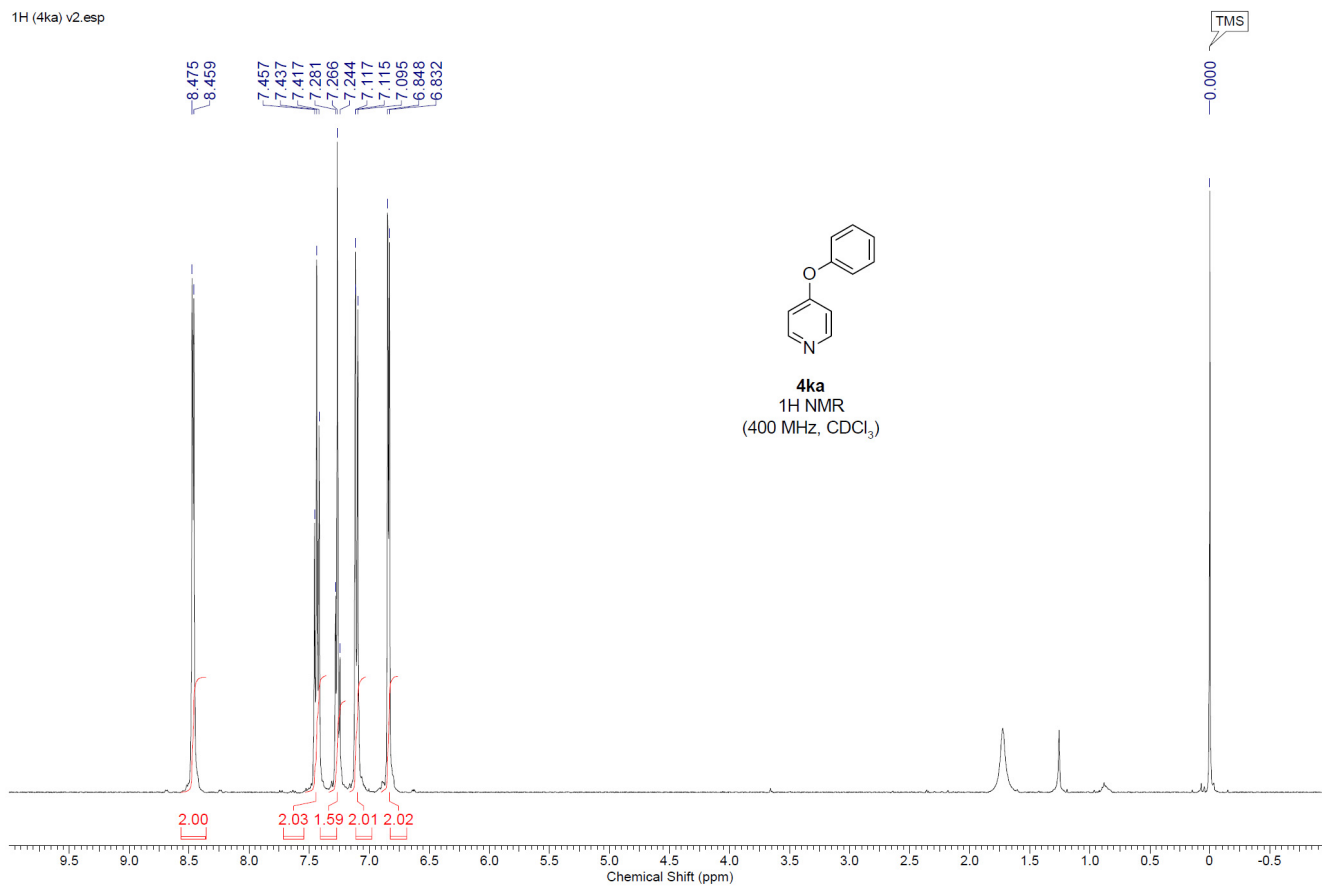
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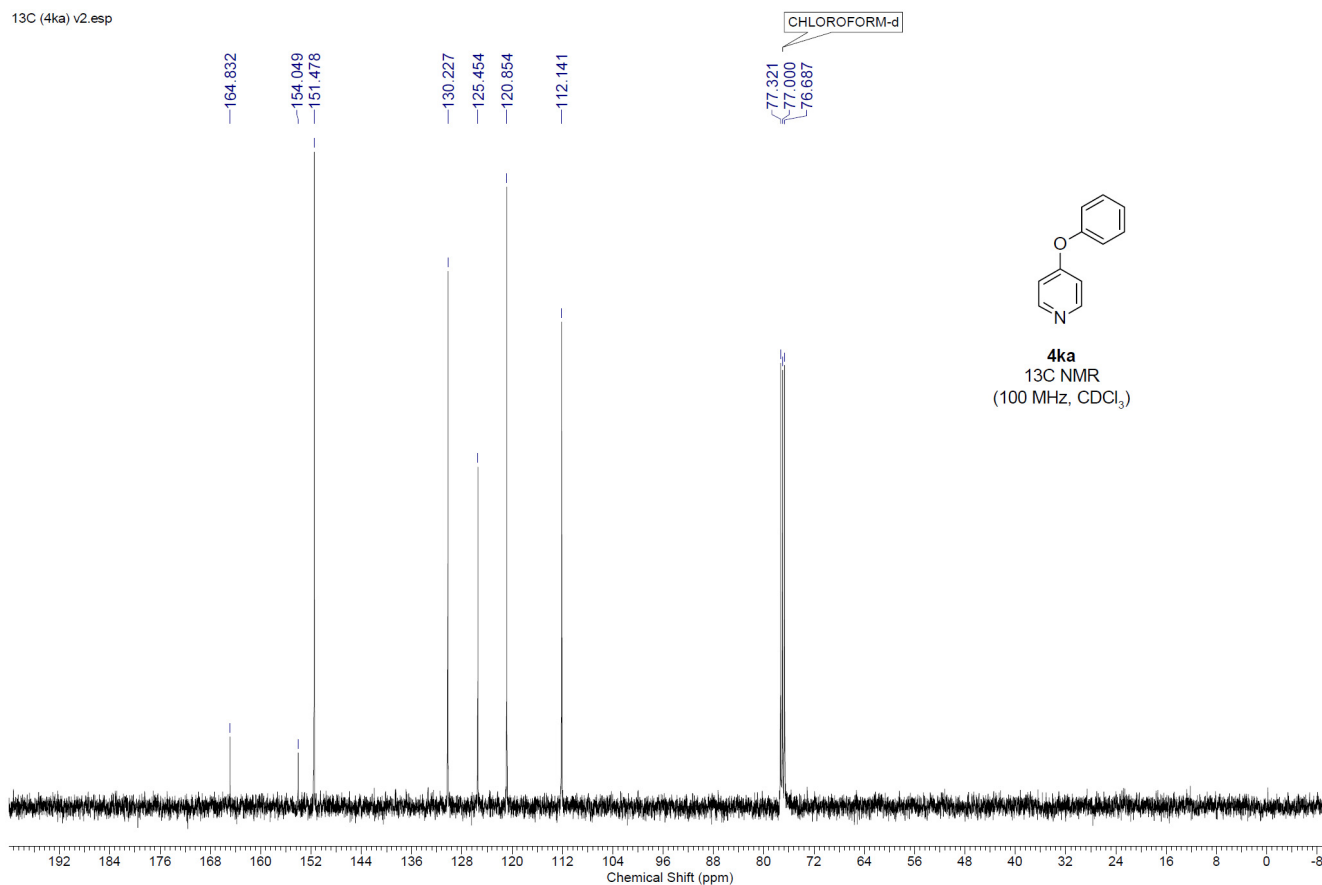
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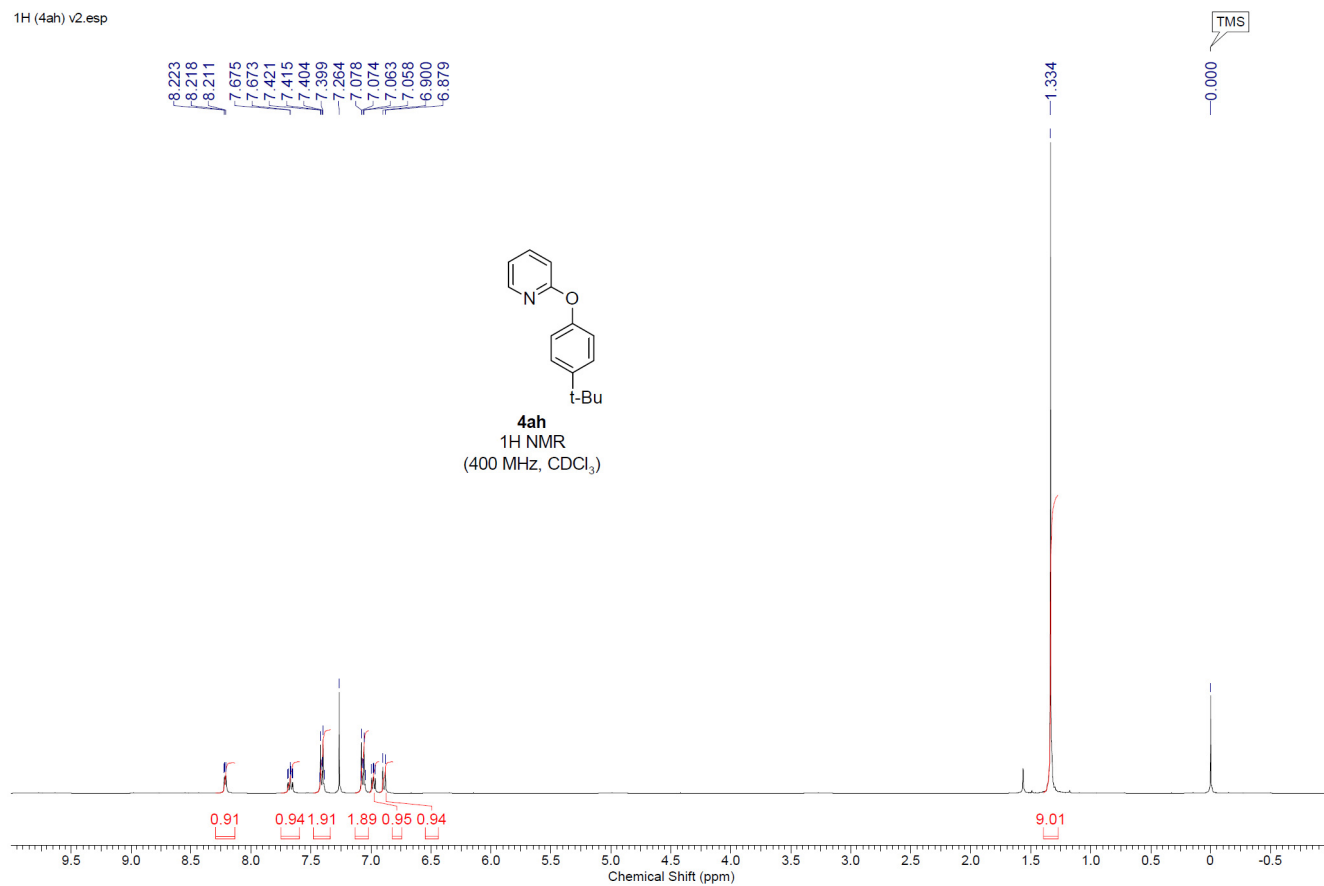
1H (4ka) v2.esp



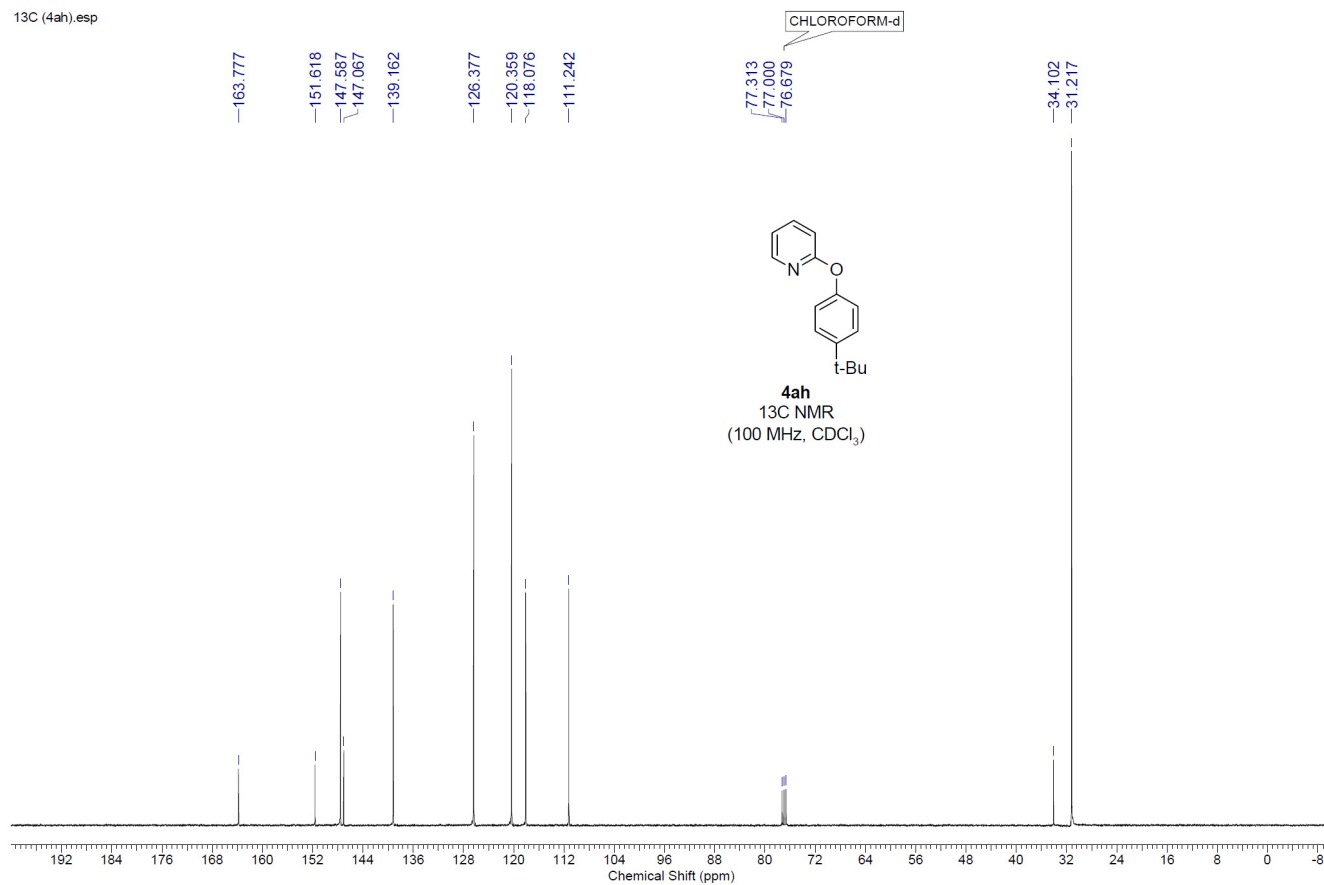
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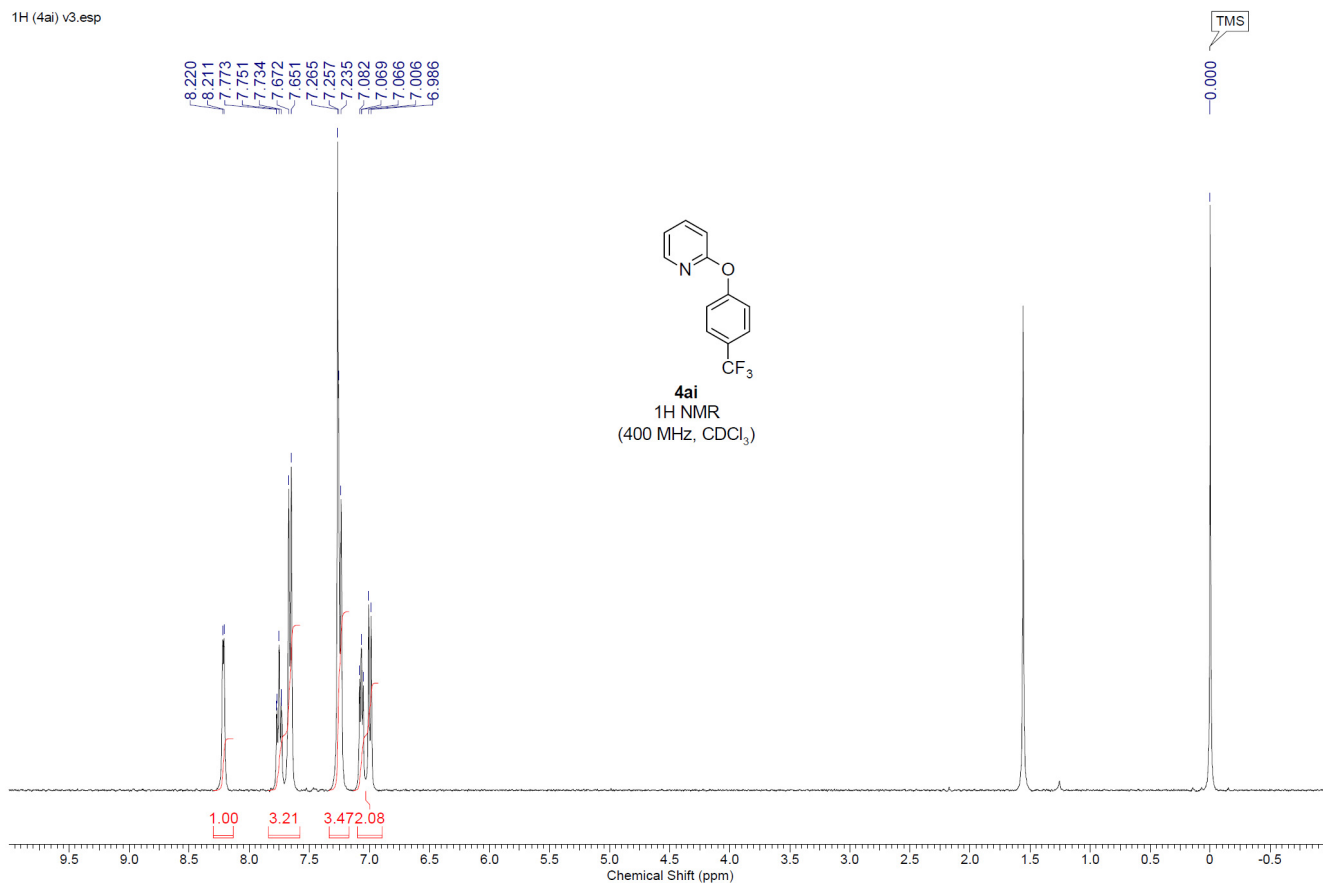
1H (4ah) v2.esp



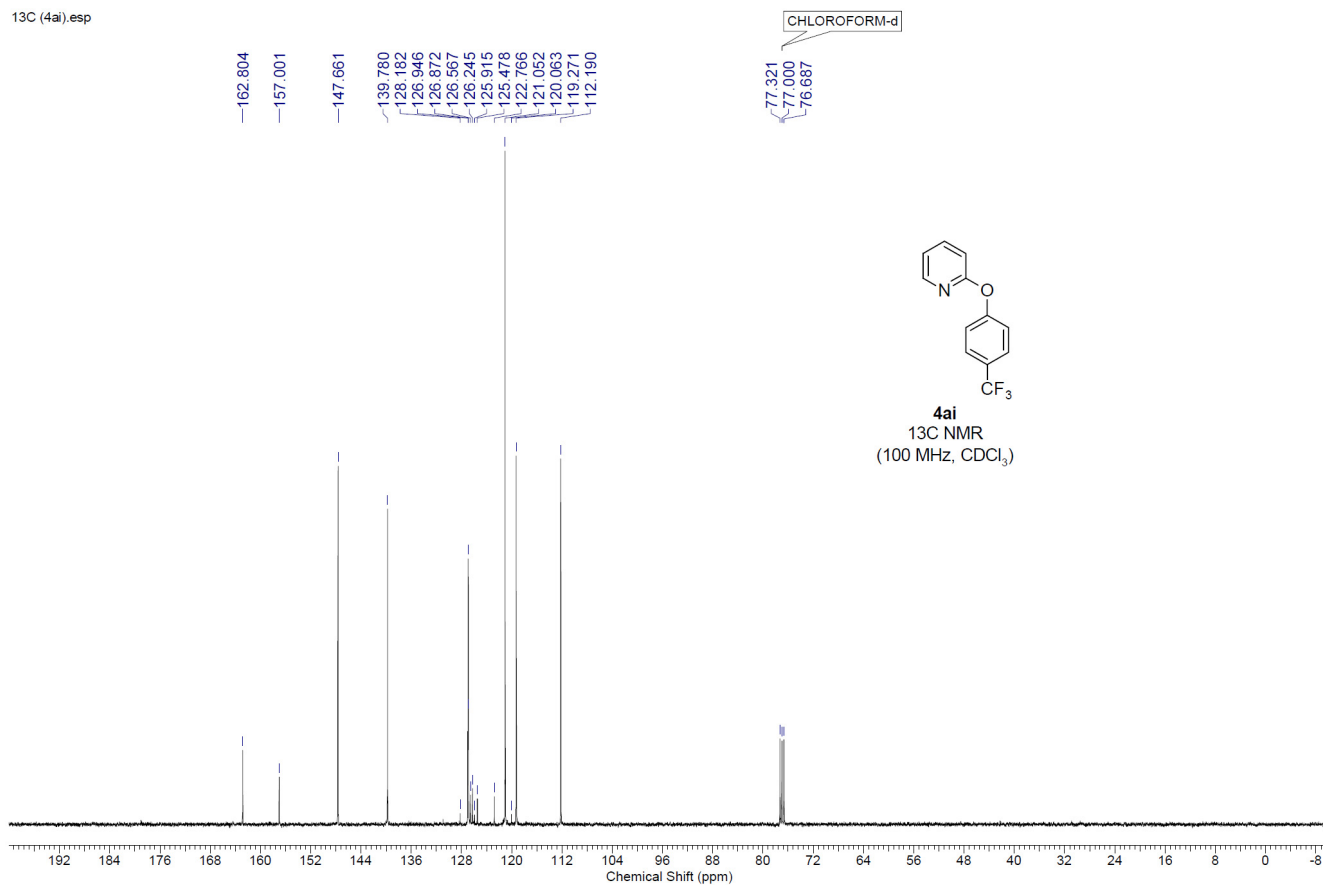
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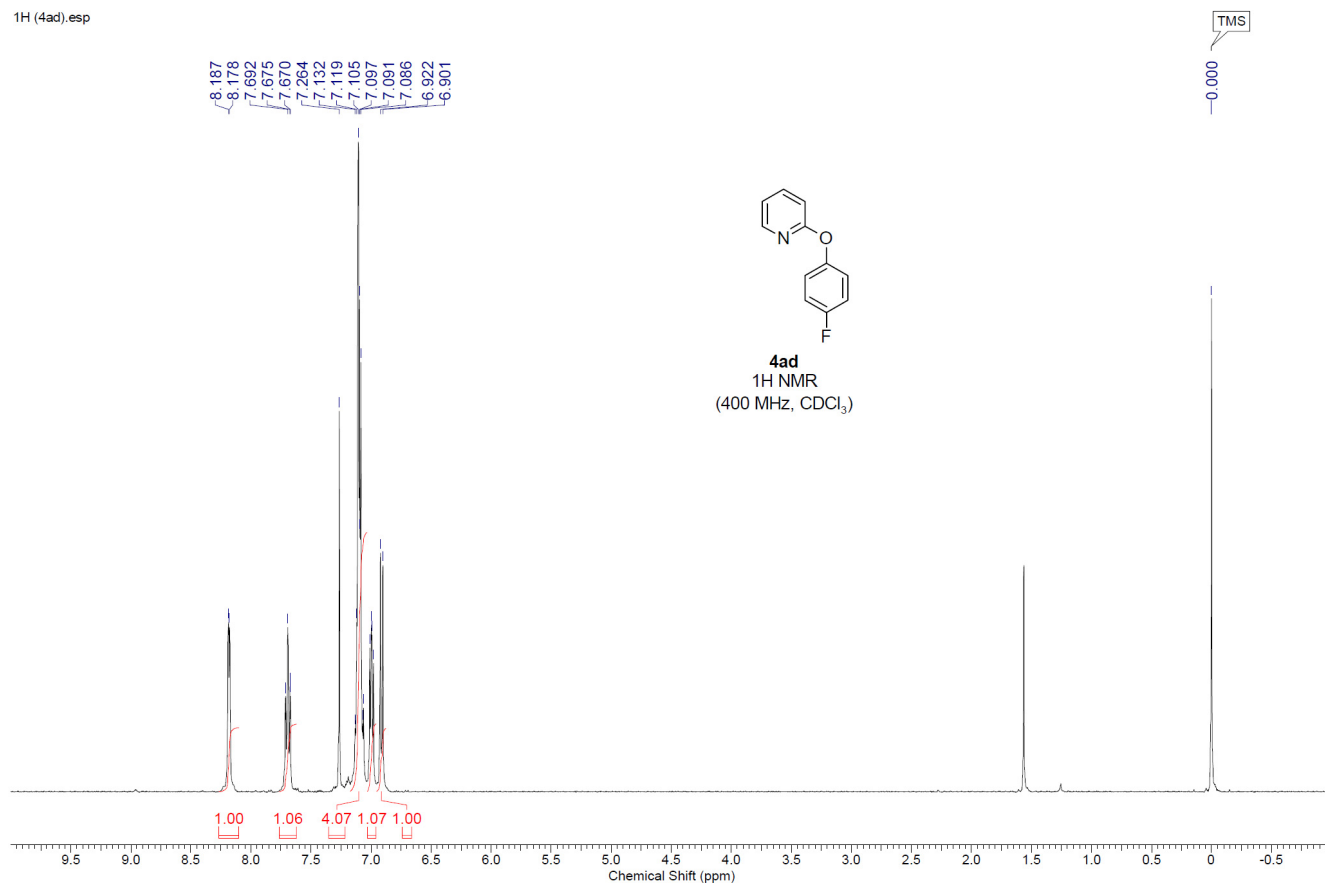
1H (4ai) v3.esp



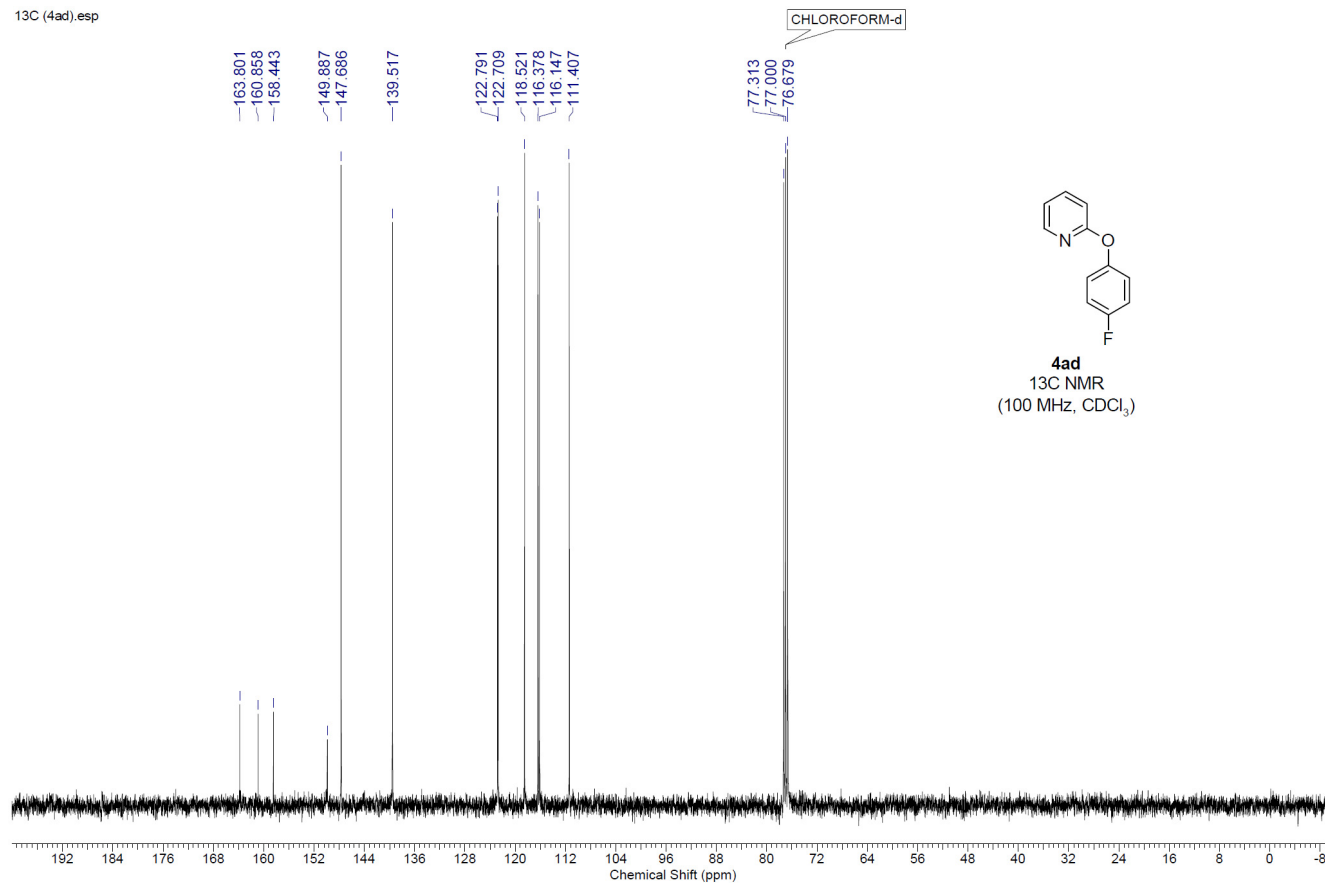
13C (4ai).esp



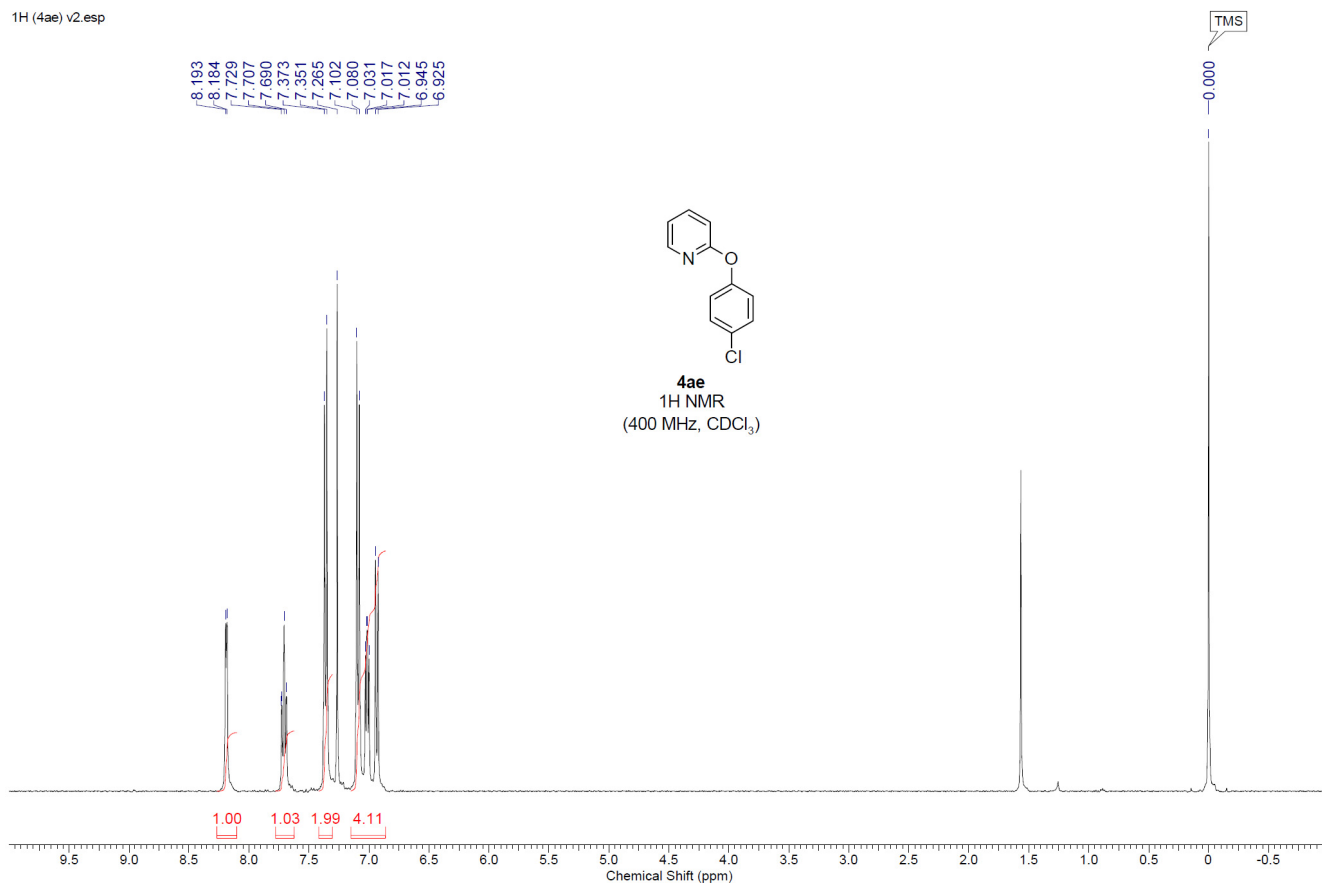
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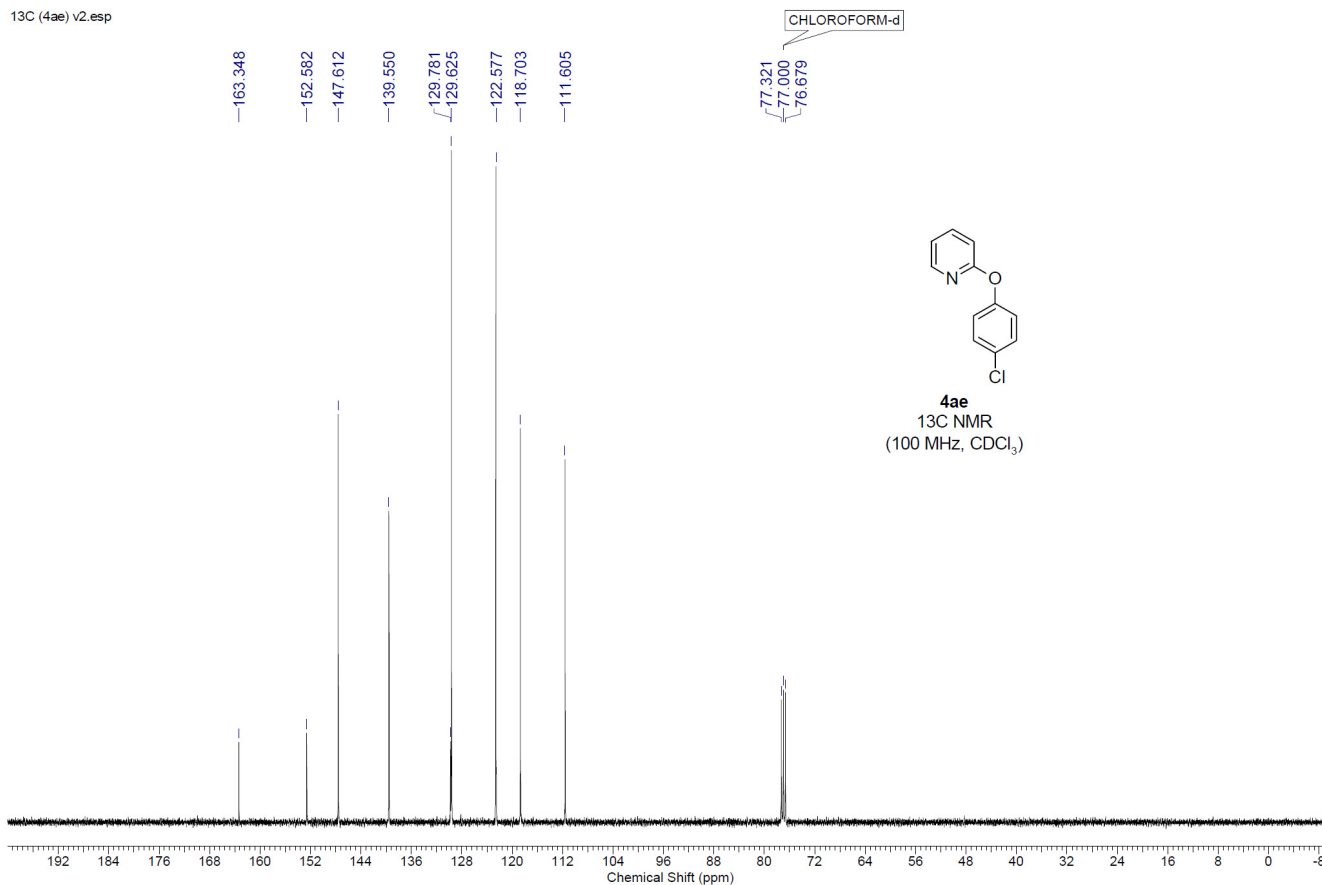
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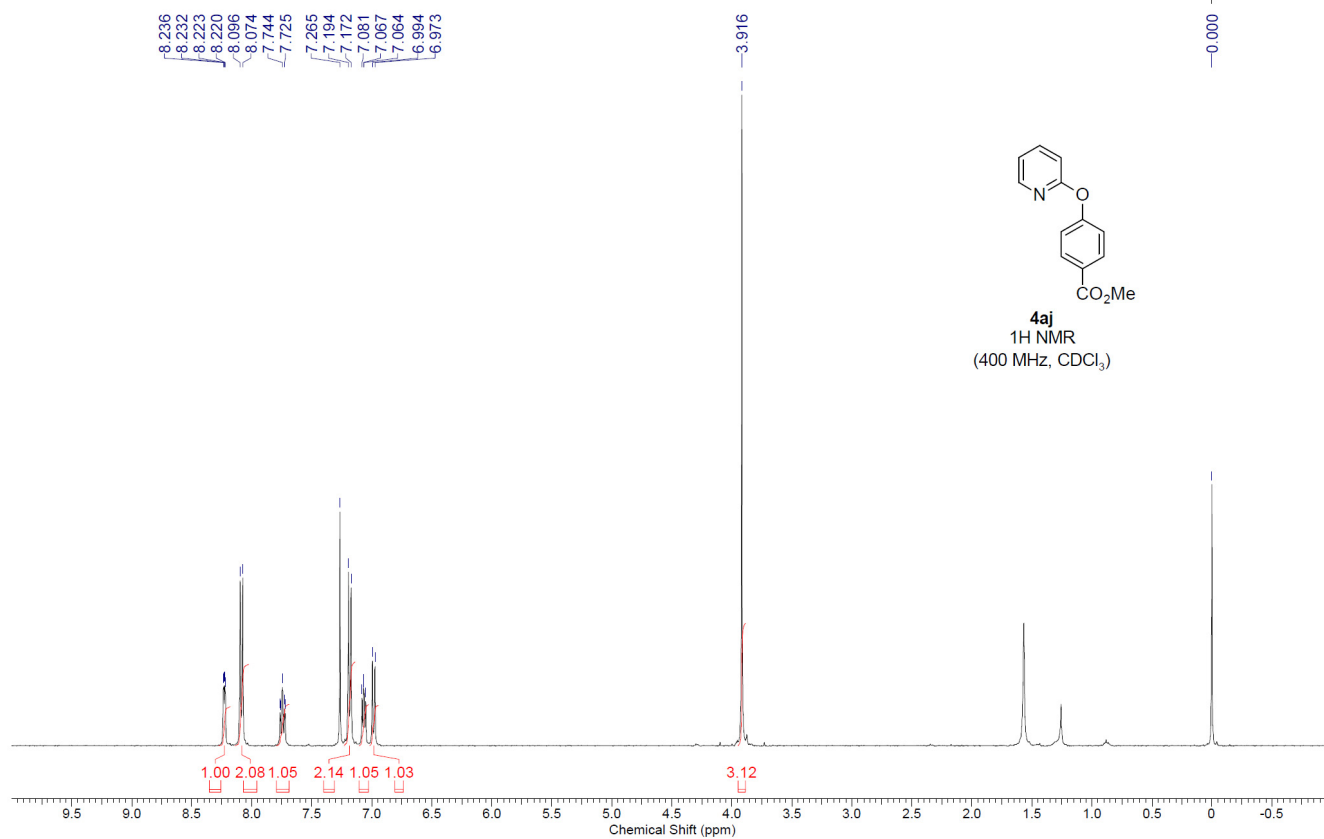
1H (4ae) v2.esp



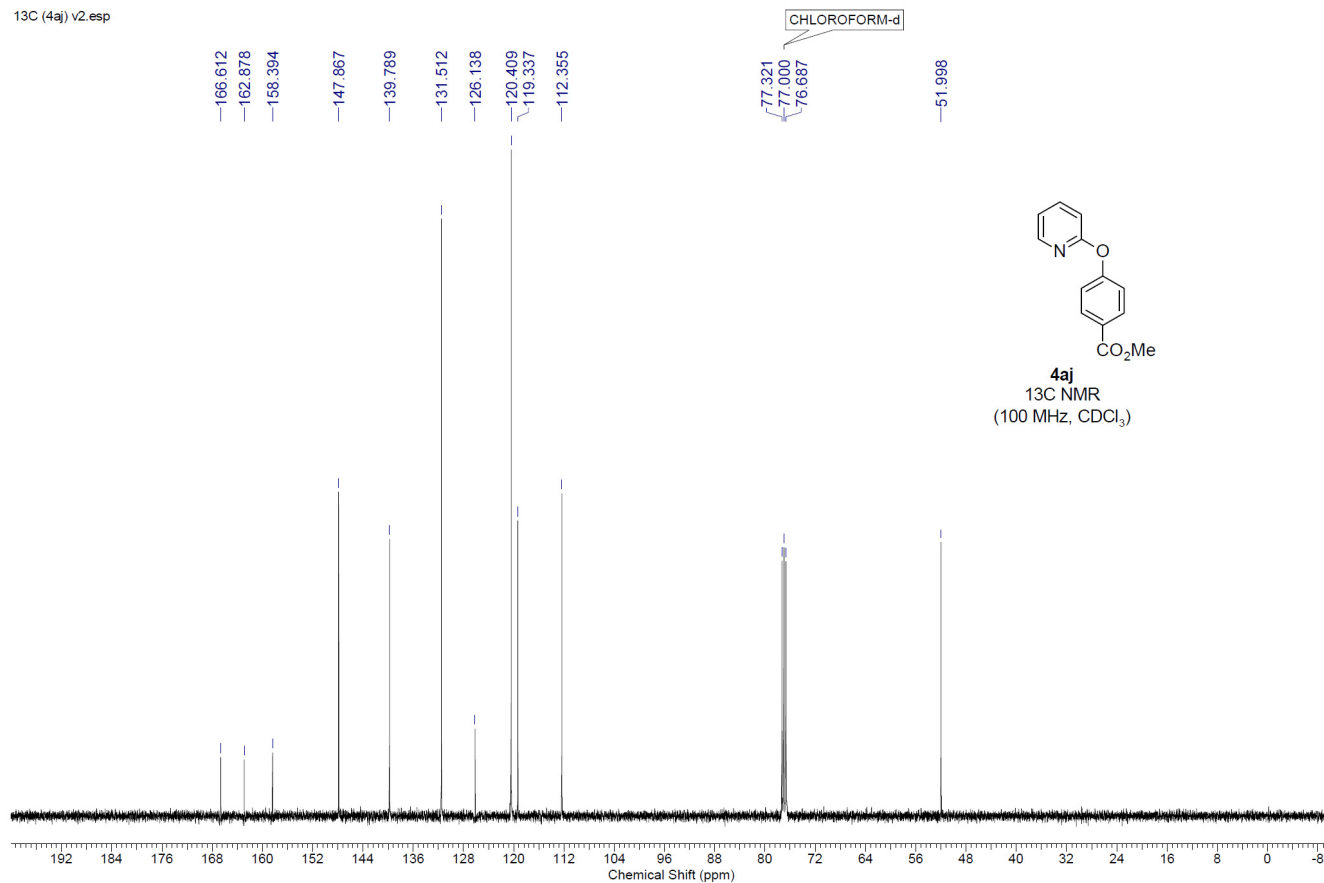
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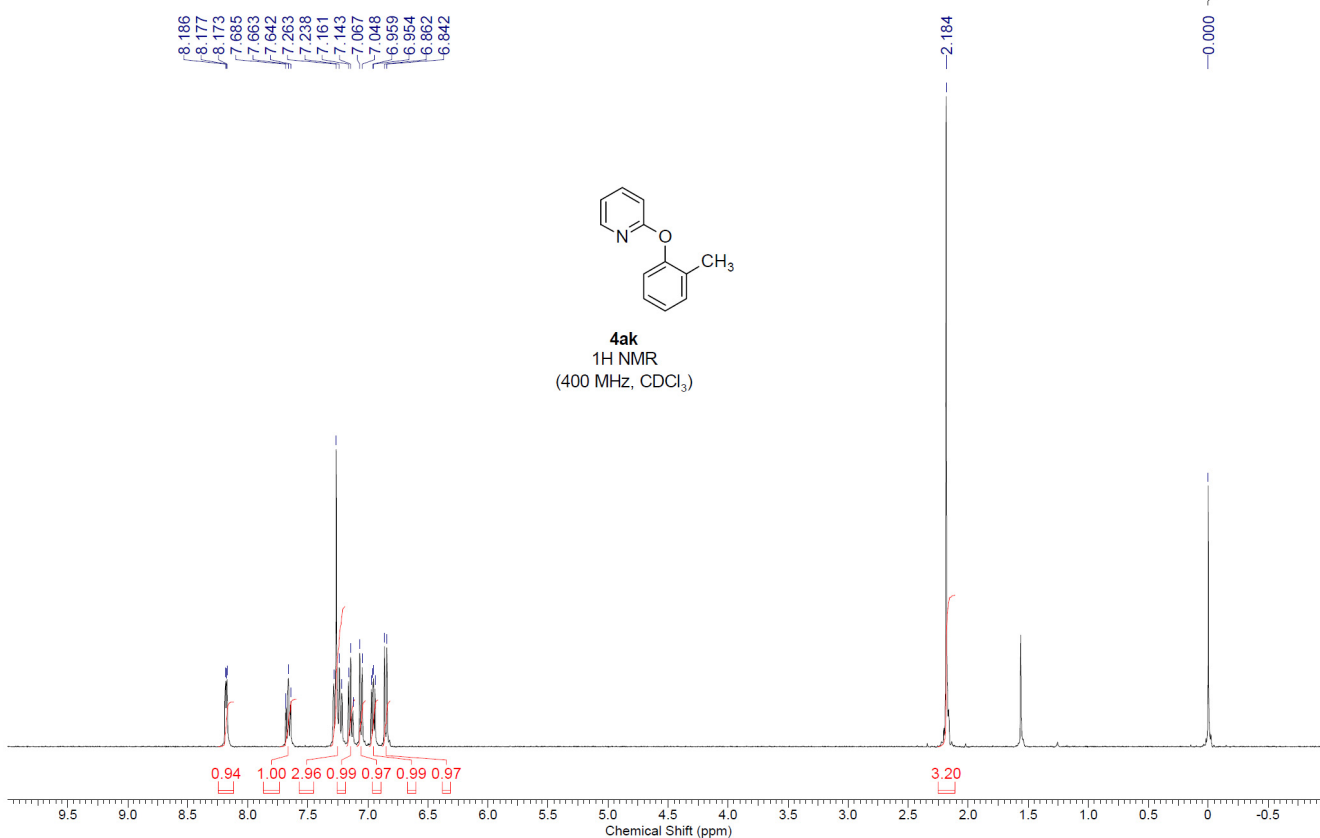
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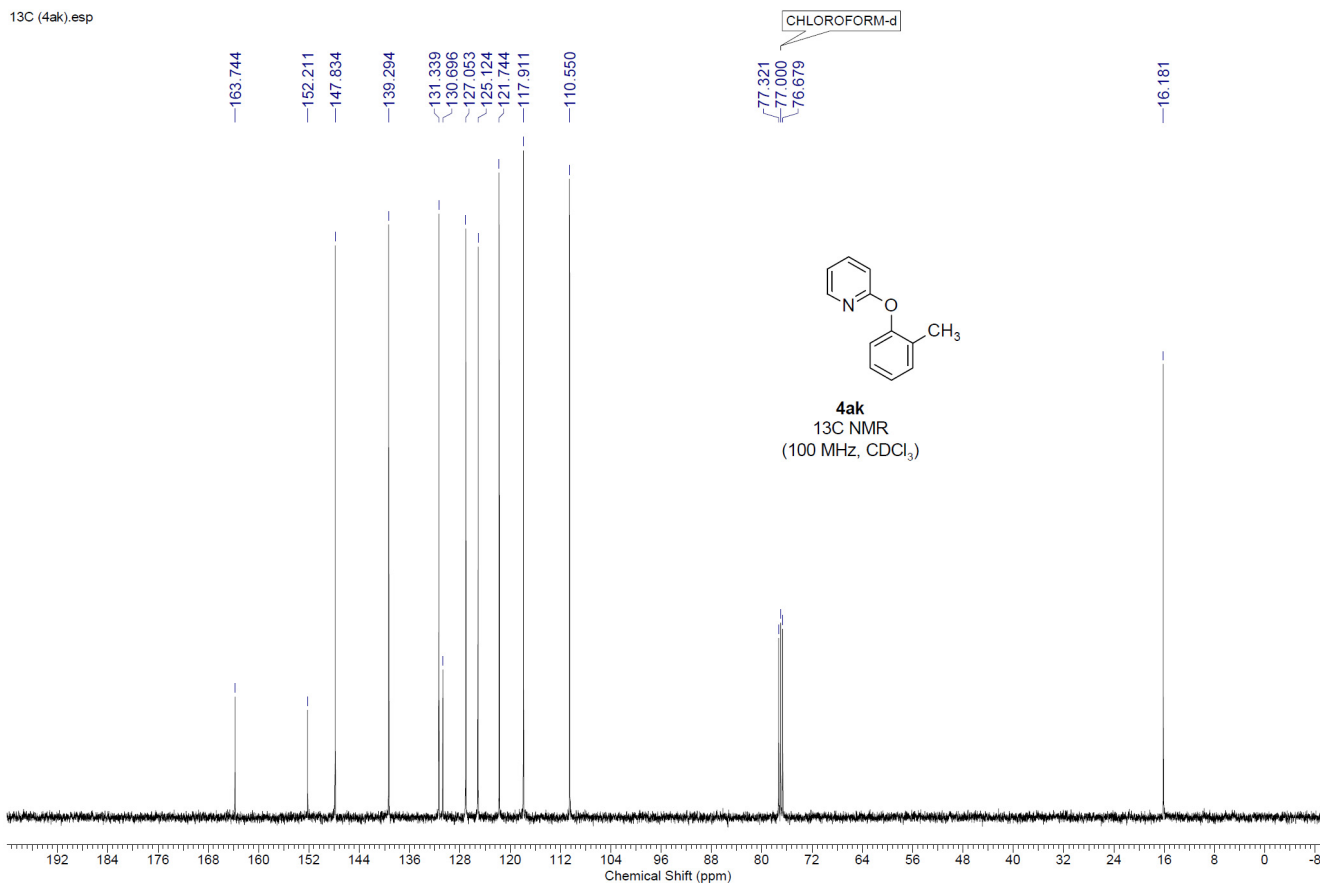
13C (4aj) v2.esp



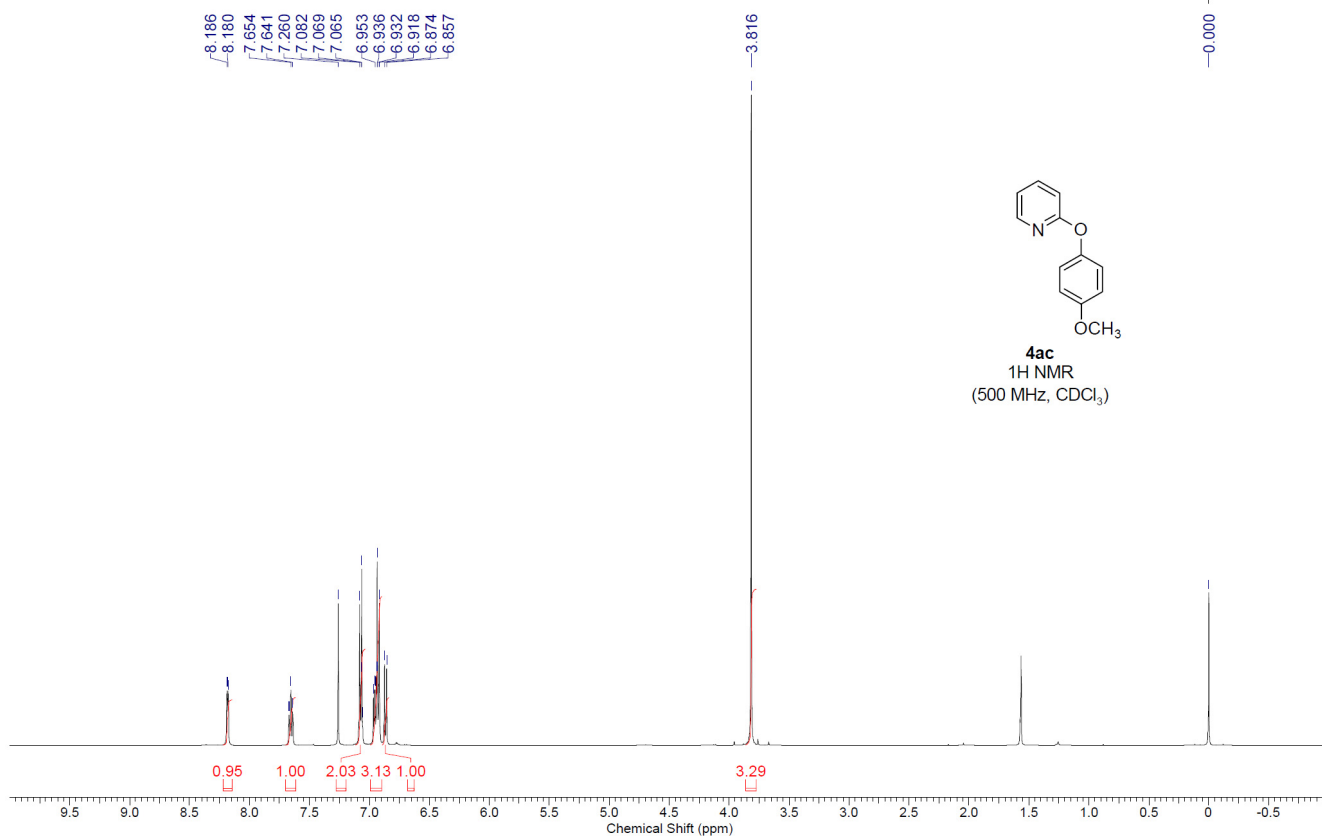
1H (4ak) v2.esp



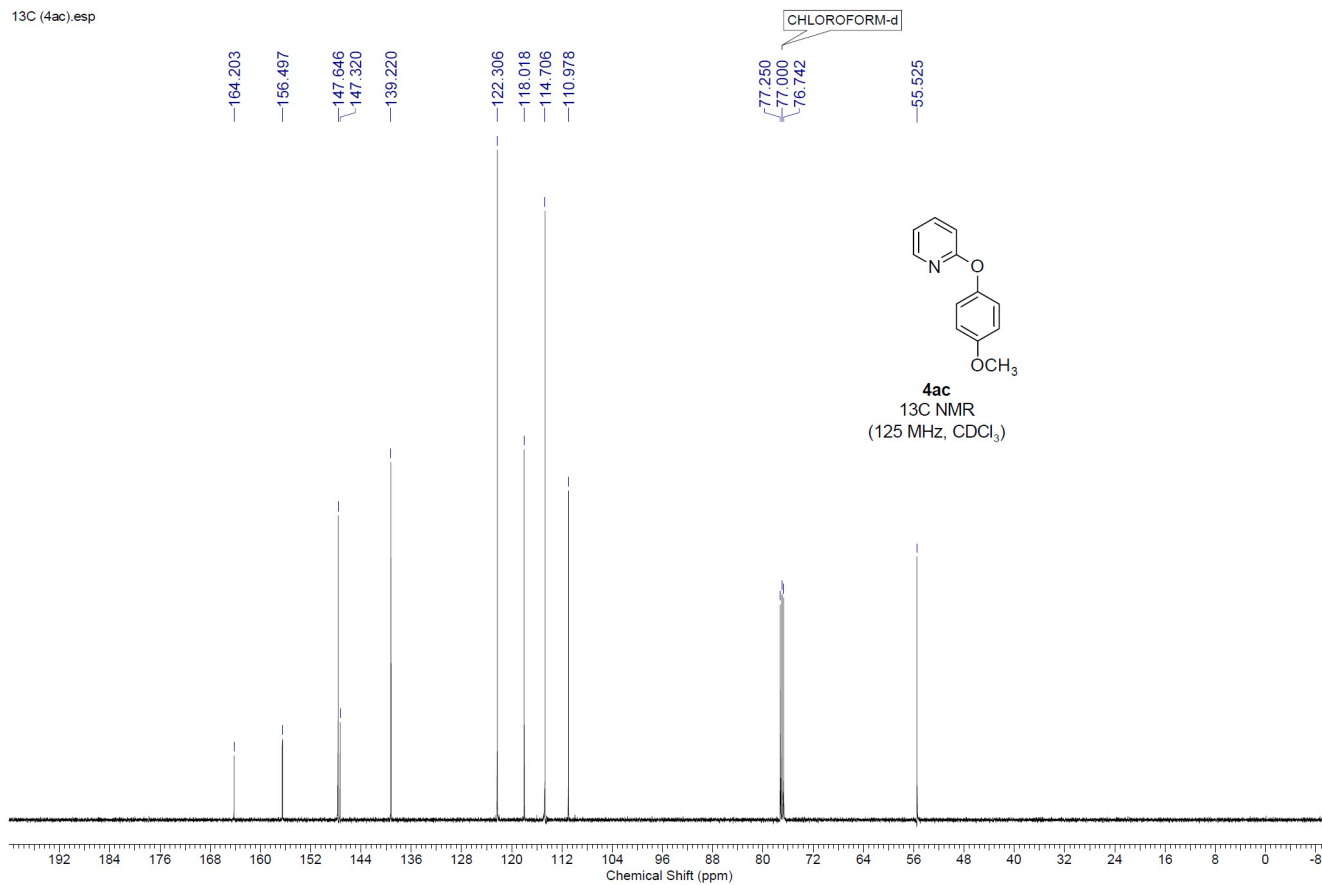
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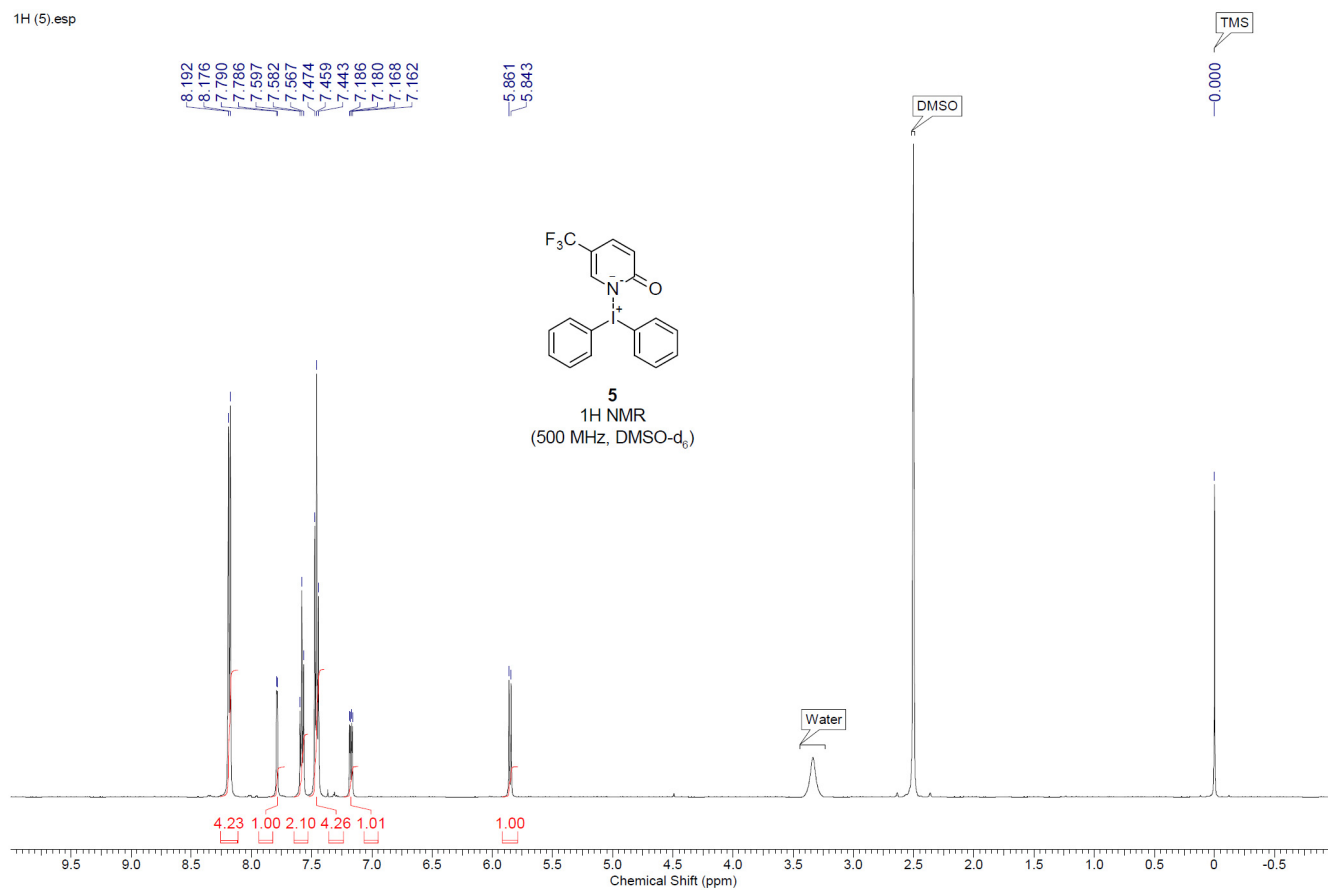
1H (4ac).esp



13C (4ac).esp



1H (5).esp



13C (5).esp

