Electronic Supplementary Material (ESI) for Green Chemistry.

Synthesis of 6,7-Dihydro-5H-cyclopenta[*b*]pyridin-5-one analogues through Manganese-Catalyzed Oxidation of the CH_2 Adjacent to Pyridine Moiety in Water

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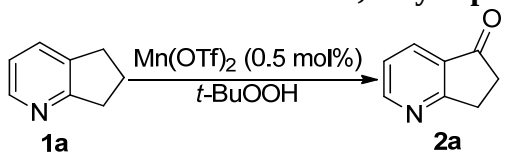
General

General: Unless otherwise stated, all reactions were carried out under air atmosphere in oven-dried and/or flame-dried glassware with magnetic stirring. Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification. All solvents employed in the reactions were distilled from appropriate drying agent prior to use. Organic solutions were concentrated under reduced pressure on a Büchi rotary evaporator. Reactions were monitored by thin layer chromatography using 0.25 mm E. Merck silica gel precoated glass plates (0.25 mm thickness, 60F-254, E. Merck) using UV light to visualize the course of reaction. ^{1}H NMR and ^{13}C NMR spectra were recorded at room temperature in $CDCl_3$ on 400 MHz instrument with tetramethylsilane (TMS) as internal standard. Flash column chromatography was performed on silica gel (200-300 mesh). Mass spectra (EI) were recorded on a Finnigan MAT 8200 at 70 eV in the EI mode. High resolution mass spectra were determined on a Thermo Scientific Orbitrap Elite, and amples were dissolved in CH_3OH. The $Mn(OTf)_2$ was bought from Sigma-Aldrich. The possible metallic impurities in $Mn(OTf)_2$ were tested using ICP. Co content is 4.82 ppm. Fe content is 6.05 ppm, and Pd content is only 0.96 ppm. Cu was not detected.

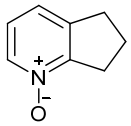
1. Reaction parameter optimization for the oxidation of 2,3-Cyclopentenopyridine 1a



1a **2a**

Entry	Catalyst	Oxidant	Solvent	Temp. [°C]	Yield [%]
1	$Mn(OTf)_2$	H_2O_2	MeCN	25(24h)	n.d
2	$Mn(OTf)_2$	O_2	MeCN	25(24h)	n.d
3	$Mn(OTf)_2$	AcOOH	MeCN	25(24h)	2,3-cyclopentenopyridine N-Oxide
4	$Mn(OTf)_2$	M-CPBA	MeCN	25(24h)	2,3-cyclopentenopyridine N-Oxide
5	$Mn(OTf)_2$	*t*-BuOOH	Methanol	25(24h)	n.d
6	$Mn(OTf)_2$	*t*-BuOOH	Alcohol	25(24h)	n.d
7	$Mn(OTf)_2$	*t*-BuOOH	Isobutanol	25(24h)	n.d

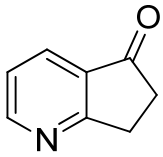
nd: no detected

2,3-cyclopentenopyridine N-Oxide: 

2. The oxidation reactions

General Oxidation Procedure A

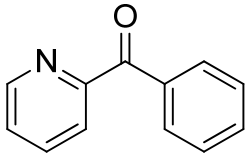
6,7-dihydro-5H-cyclopenta[*b*]pyridin-5-one **2a**:



A 25 mL round-bottom flask was subsequently charged with 2,3-Cyclopenteno pyridine (0.50 mmol), $Mn(OTf)_2$ (0.0025 mmol), *t*-BuOOH (65% in H_2O, 2.5mmol), H_2O (2.5 mL) and then stirred at 25°C for 24h. The reaction was then extracted with ethyl acetate (3×10 mL). Organic layer was dried over anhydrous Na_2SO_4, and evaporated in vacuo. The resulting residue was finally purified by flash column chromatography (Ethyl acetate/Petroleum ethe = from1:5 to 1:1). This gave the title compound in 88% yield. Off-white solid; mp: 62-63°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 8.82-8.77 (m, 1H), 8.00 (d, *J* = 7.7 Hz, 1H), 7.34-7.28 (m, 1H), 3.27 (dd, *J* = 8.0, 4.0 Hz, 2H), 2.81-2.74 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm: 204.88, 174.36, 155.72, 131.91, 130.33, 122.47,35.78, 28.73. HRMS (ESI) for C_8H_8NO $[M+H]^+$, calcd: 134.0606, found:134.0598.

The processing method of the large experiment in detail
A 500 mL round-bottom flask was subsequently charged with 2,3-cyclopenteno pyridine (25 mmol), $Mn(OTf)_2$ (0.125 mmol), *t*-BuOOH (65% in H_2O, 125mmol), H_2O (125 mL) and then stirred at 25°C for 72h. The saturation sodium thiosulfate aqueous solution was added to the reaction system until the KI-starch test paper did not change its color. The reaction was then extracted with ethyl acetate (3×100 mL). Organic layer was dried over anhydrous Na_2SO_4, and evaporated in vacuo. The resulting residue was finally purified by flash column chromatography (Ethyl acetate/Petroleum ethe = from1:5 to 1:1). This gave the title compound in 68% yield.

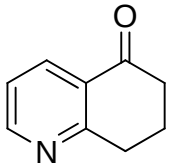
General Oxidation Procedure B
2-Benzoylpyridine **2h**:



A 25 mL round-bottom flask was subsequently charged with 2-Benzylpyridine (0.5 mmol), $Mn(OTf)_2$ (0.0025 mmol), *t*-BuOOH (65% in H_2O, 2.5mmol), *tert*-butanol (2.5 mL) and then stirred at 50°C for 48h. The reaction mixture was evaporated in vacuo. The resulting residue was purified by flash column chromatography (Ethyl acetate/Petroleum ethe = 1:5). This gave the title compound in 87% yield. Colorless solid; mp: 41-43°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 8.60 (d, *J* = 4.7 Hz, 1H), 8.01-7.93 (m, 2H), 7.91 (d, *J* = 7.8 Hz, 1H), 7.76 (d, *J* = 1.6 Hz, 1H), 7.47 (s, 1H), 7.37 (d, *J* = 7.9 Hz, 2H), 7.34 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm: 193.84, 155.16, 148.56, 137.03, 136.32, 132.90, 130.99, 128.15, 126.13, 124.60. HRMS (ESI) for $C_{12}H_{10}NO$ $[M+H]^+$, calcd: 184.0762, found: 184.0758.

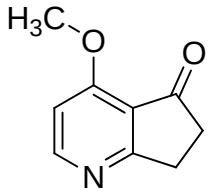
The compounds 2b, 2d, 2e, 2f, 2g were prepared according to general oxidation procedure A.

7,8-dihydroquinolin-5(6H)-one **2b**



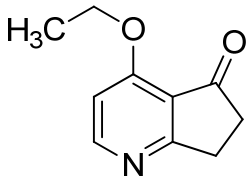
Compound **2b** was isolated in 77% yield. Colorless solid; mp: 208-212°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 8.61 (dd, *J* = 4.8, 1.8 Hz, 1H), 8.21 (dd, *J* = 7.9, 1.8 Hz, 1H), 7.24-7.20 (m, 1H), 3.10 (t, *J* = 6.2 Hz, 2H), 2.66-2.60 (m, 2H), 2.18-2.10 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm: 196.91, 162.68, 152.49, 134.02, 127.18, 121.24, 37.55, 31.54, 20.85. HRMS (ESI) for $C_9H_{10}NO$ $[M+H]^+$, calcd: 148.0762, found: 148.0759.

4-methoxy-6,7-dihydro-5H-cyclopenta[*b*]pyridin-5-one **2d**



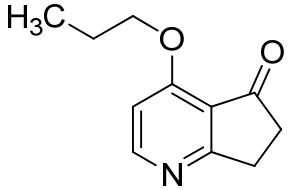
Compound **2d** was isolated in 83% yield. White solid; mp: 103-105°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 8.54 (dd, *J* = 5.8, 3.0 Hz, 1H), 6.72-6.64 (m, 1H), 3.95 (d, *J* = 2.5 Hz, 3H), 3.12 (td, *J* = 6.0, 3.0 Hz, 2H), 2.66 (td, *J* = 6.1, 3.3 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm: 202.89, 177.01, 164.18, 157.24, 119.53, 105.26, 56.10, 35.89, 28.59. HRMS (ESI) for $C_9H_{10}NO_2$ $[M+H]^+$, calcd: 164.0712, found:164.0703.

4-ethoxy-6,7-dihydro-5H-cyclopenta[*b*]pyridin-5-one **2e**



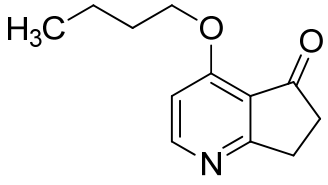
Compound **2e** was isolated in 82% yield. Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 8.55 (d, *J* = 5.9 Hz, 1H), 6.70 (d, *J* = 5.9 Hz, 1H), 4.26 (q, *J* = 7.0 Hz, 2H), 3.21-3.12 (m, 2H), 2.74-2.66 (m, 2H), 1.51 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm: 202.67, 177.13, 163.55, 157.02, 119.64, 105.86, 64.81, 35.92, 28.59, 14.18. HRMS (ESI) for $C_{10}H_{12}NO_2$ $[M+H]^+$, calcd: 178.0868, found: 178.0867.

4-propoxy-6,7-dihydro-5H-cyclopenta[*b*]pyridin-5-one **2f**



Compound **2f** was isolated in 81% yield. White solid; mp: 161-162°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 8.55 (d, *J* = 5.9 Hz, 1H), 6.70 (d, *J* = 5.9 Hz, 1H), 4.26 (q, *J* = 7.0 Hz, 2H), 3.21-3.12 (m, 2H), 2.74-2.66 (m, 2H), 1.51 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm: 203.0, 177.53, 164.24, 157.43, 120.17, 106.42, 71.00, 36.39, 29.06, 22.46, 10.70. HRMS (ESI) for $C_{11}H_{14}NO_2$ $[M+H]^+$, calcd: 192.1025, found: 192.1032.

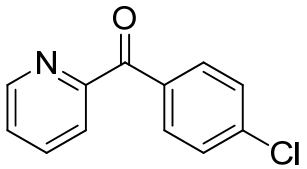
4-butoxy-6,7-dihydro-5H-cyclopenta[*b*]pyridin-5-one **2g**



Compound **2g** was isolated in 73% yield. Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 8.53 (d, *J* = 5.9 Hz, 1H), 6.69 (d, *J* = 5.9 Hz, 1H), 4.15 (t, *J* = 6.7 Hz, 2H), 3.19-3.09 (m, 2H), 2.72-2.63 (m, 2H), 1.90-1.79 (m, 2H), 1.55-1.44 (m, 2H), 0.96 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm: 202.50, 177.02, 163.75, 156.92, 119.67, 105.93, 68.86, 35.90, 30.54, 28.55, 18.99, 13.70. HRMS (ESI) for $C_{12}H_{16}NO_2$ $[M+H]^+$, calcd: 206.1181, found: 206.1171.

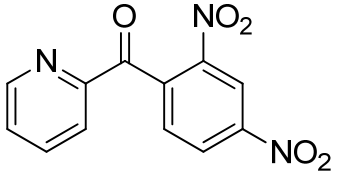
The compounds **2i**, **2j**, **2k**, **2l**, **2m, 2n, 2o** were prepared according to general oxidation procedure B.

(4-chlorophenyl)(pyridin-2-yl)methanone **2i**



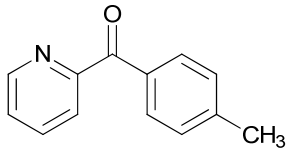
Compound **2i** was isolated in 86% yield. White solid; mp: 65-66°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 8.68 (d, *J* = 4.4 Hz, 1H), 8.09-8.00 (m, 3H), 7.87 (td, *J* = 7.7, 1.7 Hz, 1H), 7.49-7.39 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm: 192.29, 154.68, 148.49, 139.34, 137.16, 134.61, 132.50, 128.43, 126.39, 124.63. HRMS (ESI) for $C_{12}H_9ClNO$ $[M+H]^+$, calcd: 218.0373, found: 218.0364.

(2,4-dinitrophenyl)(pyridin-2-yl)methanone **2j**



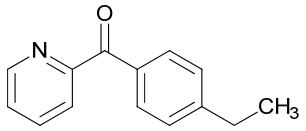
Compound **2j** was isolated in 31% yield. White solid; mp: 146-147°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 9.02 (s, 1H), 8.61 (d, *J* = 8.3 Hz, 1H), 8.48 (d, *J* = 4.6 Hz, 1H), 8.29 (d, *J* = 7.8 Hz, 1H), 7.94 (t, *J* = 7.7 Hz, 1H), 7.77 (d, *J* = 8.3 Hz, 1H), 7.48 (dd, *J* = 7.4, 4.9 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm: 191.53, 151.81, 149.31, 148.58, 141.21, 137.46, 130.69, 128.38, 127.79, 122.74, 119.11. HRMS (ESI) for $C_{12}H_8N_3O_5$ $[M+H]^+$, calcd: 274.0464, found: 274.0460.

pyridin-2-yl(p-tolyl)methanone **2k**



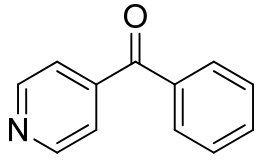
Compound **2k** was isolated in 80% yield. Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 8.74-8.67 (m, 1H), 8.03-7.95 (m, 3H), 7.90-7.82 (m, 1H), 7.45 (ttd, *J* = 4.8, 2.4, 1.2 Hz, 1H), 7.28 (d, *J* = 7.5 Hz, 2H), 2.41 (d, *J* = 1.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm: 193.56, 155.42, 148.50, 143.79, 136.99, 133.66, 131.15, 128.90, 126.00, 124.52, 21.73. HRMS (ESI) for $C_{13}H_{12}NO$ $[M+H]^+$, calcd: 198.0919, found: 198.0919.

(4-ethylphenyl)(pyridin-2-yl)methanone **2l**



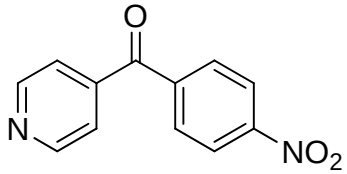
Compound **2l** was isolated in 81% yield. Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 8.73-8.65 (m, 1H), 7.99 (d, *J* = 8.1 Hz, 3H), 7.85 (dd, *J* = 11.3, 4.2 Hz, 1H), 7.43 (dd, *J* = 6.8, 5.6 Hz, 1H), 7.29 (d, *J* = 7.9 Hz, 2H), 2.69 (q, *J* = 7.6 Hz, 2H), 1.24 (td, *J* = 7.6, 0.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm: 193.56, 155.41, 149.94, 148.50, 137.01, 133.85, 131.26, 127.76, 126.01, 124.54, 29.05, 15.24. HRMS (ESI) for $C_{14}H_{14}NO$ $[M+H]^+$, calcd: 212.1075, found: 212.1079.

4-Benzoylpyridine **2m**



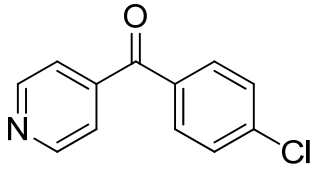
Compound **2k** was isolated in 72% yield. White solid; mp: 68-70°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 8.77 (d, *J* = 5.7 Hz, 2H), 7.78 (d, *J* = 7.5 Hz, 2H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.54 (d, *J* = 5.7 Hz, 2H), 7.47 (t, *J* = 7.6 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm: 195.49, 150.75, 144.78, 136.32, 133.91, 130.52, 129.05, 123.25. HRMS (ESI) for $C_{12}H_{10}NO$ $[M+H]^+$, calcd: 184.0762, found: 184.0759.

(4-nitrophenyl)(pyridin-4-yl)methanone **2n**



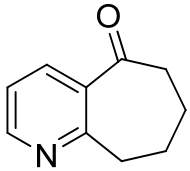
Compound **2l** was isolated in 70% yield. White solid; mp: 121-123°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 8.84 (d, *J* = 4.2 Hz, 2H), 8.34 (d, *J* = 7.9 Hz, 2H), 7.96 (d, *J* = 8.5 Hz, 2H), 7.60-7.54 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm: 193.92, 151.24, 150.91, 143.29, 141.27, 131.36, 124.32, 123.09. HRMS (ESI) for $C_{12}H_9N_2O_3$ $[M+H]^+$, calcd: 229.0613, found: 229.0618.

(4-chlorophenyl)(pyridin-4-yl)methanone **2o**



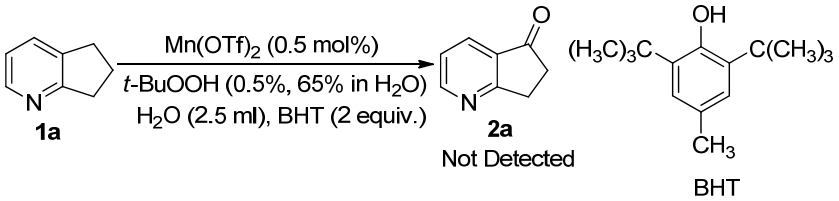
Compound 2m was isolated in 70% yield. White solid; mp: 108-110°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 8.80 (d, *J* = 4.3 Hz, 2H), 7.75 (d, *J* = 8.2 Hz, 2H), 7.53 (d, *J* = 4.5 Hz, 2H), 7.47 (d, *J* = 8.2 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm: 193.85, 150.48, 143.99, 140.17, 134.22, 131.46, 129.04, 122.65. HRMS (ESI) for $C_{12}H_9ClNO$ $[M+H]^+$, calcd: 218.0373, found: 218.0368.

The oxidation procedure of 1c forming compound **2c**.



A 25 mL round-bottom flask was subsequently charged with 2,3-cycloheptenopyridine (0.5 mmol), $Mn(OTf)_2$ (0.0025 mmol), *t*-BuOOH (65% in H_2O, 2.5 mmol), *tert*-butanol (2.5 mL) and then stirred at 50°C for 24 h. The reaction mixture was evaporated in vacuo. The resulting residue was purified by flash column chromatography (Ethyl acetate/Petroleum ethe = 1:5). This gave the title compound in 41% yield. Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 8.55 (dd, *J* = 4.8, 1.8 Hz, 1H), 7.96 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.20 (d, *J* = 4.9 Hz, 1H), 7.18 (s, 1H), 3.16-3.10 (m, 2H), 2.74 (dd, *J* = 7.2, 5.3 Hz, 2H), 1.95-1.87 (m, 2H), 1.87-1.79 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm: 203.35, 160.18, 150.78, 135.66, 132.94, 120.84, 39.87, 34.87, 23.05, 20.43. HRMS (ESI) for $C_{10}H_{12}NO$ $[M+H]^+$, calcd: 162.0919, found: 162.0928.

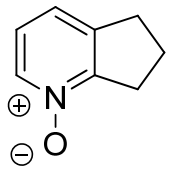
The oxidation reaction of **1a** with BHT



A 25 mL round-bottom flask was subsequently charged with 2,3-Cyclopenteno pyridine **1a** (0.50 mmol), $Mn(OTf)_2$ (0.0025 mmol), BHT (1 mmol), H_2O (2.5 mL) and then added *t*-BuOOH (65% in H_2O, 2.5mmol), stirred at 25°C for 24h.

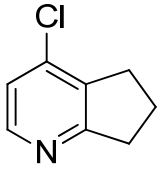
3. The synthesis of some substrates

The synthesis of 2,3-Cyclopentenopyridine N-Oxide



Under air, CH_3COOOH(126 mmol, 30% in H_2O) was added slowly to a 25 °C solution of 2,3-cycloheptenopyridine (1c, 42 mmol) in 100 mL CH_2Cl_2 in a 250 mL 2-L flask, and then stirred for 48h. 100 mL H_2O was added to the reaction mixture. Then anhydrous K_2CO_3 was slowly added to the reaction mixture until no bubbles up. The mixture was then extracted with CH_2Cl_2 (5×100 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated on a rotary evaporator. This gave the title compound in 98% yield. White solid; mp 120-122 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 8.11 (d, *J* = 3.8 Hz, 1H), 7.15 (dd, *J* = 23.3, 5.8 Hz, 2H), 3.22 (s, 2H), 3.04 (t, *J* = 7.0 Hz, 2H), 2.35-2.11 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm: 153.08, 142.22, 137.18, 123.80, 122.75, 77.51, 77.20, 76.88, 31.49, 29.45, 21.94. GC-MS: 135.0, 118.0, 104.0, 91.0, 77.0, 63.0, 51.0, 39.0, 27.1, 15.1.

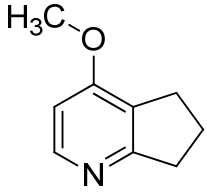
The synthesis of 4-Chloro-6,7-dihydro-5H-cyclopenta[*b*]pyridine



Under argon, $POCl_3$ (81.4 mmol) was added slowly to a 25 °C solution of 2,3-Cyclopentenopyridine N-Oxide (40.7 mmol) in anhydrous 1,2-dichloroethane (100 mL) in a 250 mL 2-L flask that was placed in an ice bath. The reaction mixture was stirred for 20 min at room temperature. The reaction vessel was then fitted with a condenser and heat to reflux for 5 h. Next, the reaction mixture was allowed to room temperature and poured into a mixture of ice and water slowly. Then, anhydrous K_2CO_3 was slowly added to the reaction mixture until no bubbles up. The mixture was then extracted with CH_2Cl_2 (3×150 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated on a rotary evaporator. The resulting residue was purified by flash column chromatography (Ethyl acetate/Petroleum ethe = 1:5). This gave the title compound in 85% yield. Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 8.15 (d, *J* = 5.0 Hz, 1H), 6.96 (d, *J* = 4.8 Hz, 1H), 3.01 (t, *J* = 7.7 Hz, 2H), 2.92 (t, *J* = 7.5 Hz, 2H), 2.08 (dd, *J* = 15.4, 7.7 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm: 167.17, 148.44, 140.59, 135.68, 121.30, 34.95, 29.86, 21.92. HRMS (ESI) for C_8H_9ClN $[M+H]^+$, calcd: 154.0424, found: 154.0422.

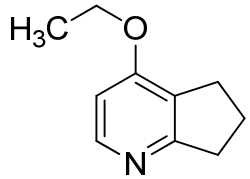
Ref. G. C. Fu, R. P. Wurz, E. C. Lee, J. C. Ruble, *Adv. Synth. Catal.* 2007, 349, 2345-2352.

The synthesis of 4-Methoxy-6,7-dihydro-5H-cyclopenta[*b*]pyridine



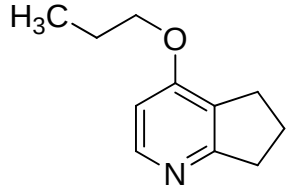
A 150 mL thick wall pressure bottle was charged with 20 mL CH_3OH and Na (7.5 mmol) was added. After the Na reacted completely, the 4-chloro-6,7-dihydro-5H-cyclopenta[*b*]pyridine (1.5 mmol) was added, and screwed on the sieve, and then stirred at 100°C for 24 h. The reaction mixture was evaporated in vacuo. 20 mL H_2O was added to the resulting residue and the mixture was then extracted with CH_2Cl_2 (3×100 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated on a rotary evaporator and purified by flash column chromatography (Ethyl acetate/Petroleum ethe= 1:3). This gave the title compound in 91% yield. yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 8.20 (d, *J* = 5.7 Hz, 1H), 6.51 (d, *J* = 5.8 Hz, 1H), 3.79 (s, 3H), 2.94 (t, *J* = 7.7 Hz, 2H), 2.81 (t, *J* = 7.5 Hz, 2H), 2.09-1.99 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm: 166.83, 162.30, 149.77, 124.23, 103.86, 77.42, 77.10, 76.78, 54.98, 34.50, 27.32, 22.48. HRMS (ESI) for $C_9H_{12}NO$ $[M+H]^+$, calcd: 150.0919, found: 150.0937.

4-Ethoxy-6,7-dihydro-5H-cyclopenta[*b*]pyridine



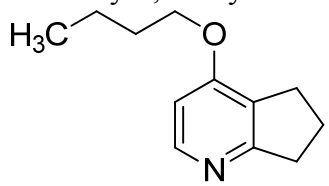
Compound 1f was isolated in 89% yield. Colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 8.14 (d, *J* = 5.8 Hz, 1H), 6.44 (d, *J* = 5.8 Hz, 1H), 3.99 (q, *J* = 7.0 Hz, 2H), 2.90 (t, *J* = 7.7 Hz, 2H), 2.78 (t, *J* = 7.4 Hz, 2H), 2.01 (dd, *J* = 15.2, 7.6 Hz, 2H), 1.33 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm: 166.77, 161.62, 149.56, 124.31, 104.51, 63.27, 34.51, 27.37, 22.45, 14.51. HRMS (ESI) for $C_{10}H_{14}NO$ $[M+H]^+$, calcd: 164.1075, found: 164.1079.

4-Propoxy-6,7-dihydro-5H-cyclopenta[*b*]pyridine



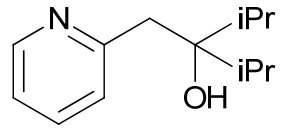
Compound 1g was isolated in 92% yield. Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 8.15 (d, *J* = 5.7 Hz, 1H), 6.47 (d, *J* = 5.8 Hz, 1H), 3.90 (t, *J* = 6.5 Hz, 2H), 2.92 (t, *J* = 7.7 Hz, 2H), 2.80 (t, *J* = 7.4 Hz, 2H), 2.02 (p, *J* = 7.6 Hz, 2H), 1.82-1.68 (m, 2H), 0.97 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm: 166.74, 161.81, 149.54, 124.39, 104.60, 69.17, 34.49, 27.33, 22.38 (d, *J* = 15.4 Hz), 10.32. HRMS (ESI) for $C_{11}H_{16}NO$ $[M+H]^+$, calcd: 178.1232, found: 178.1221.

4-Butoxy-6,7-dihydro-5H-cyclopenta[*b*]pyridine



Compound 1h was isolated in 90% yield. Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 8.13 (d, *J* = 4.9 Hz, 1H), 6.45 (d, *J* = 5.2 Hz, 1H), 3.92 (t, *J* = 5.9 Hz, 2H), 2.90 (t, *J* = 7.6 Hz, 2H), 2.78 (t, *J* = 7.2 Hz, 2H), 2.00 (dd, *J* = 9.9, 5.0 Hz, 2H), 1.77-1.62 (m, 2H), 1.49-1.32 (m, 2H), 0.90 (dt, *J* = 11.5, 5.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm: 166.69, 161.79, 149.53, 124.36, 104.55, 67.42, 34.47, 30.96, 27.33, 22.43, 19.10, 13.70. HRMS (ESI) for $C_{12}H_{18}NO$ $[M+H]^+$, calcd: 192.1388, found: 192.1365.

2,4-Dimethyl-3-(2-pyridinylmethyl)pentan-3-ol

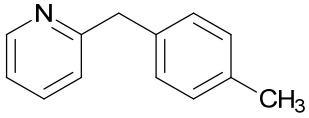


To a stirred solution of 2-methylpyridine (8 mL, 80.8 mmol) in dry THF (120 mL), under Ar-atmosphere was added BuLi (34 mL, 2.5 M in hexanes, 85mmol) dropwise at -78 °C. After 1 h stirring at -78 °C/-50 °C, diisopropylketone (13 mL, 91.4 mmol) was added and the mixture was stirred further at -50 °C for 2 h. The reaction was then quenched with water (50 mL) and extracted three times with ethyl acetate (3 × 100mL). The combined organic fractions were dried over $MgSO_4$ and filtered over a pad of Celite. The solvent was removed under reduced pressure and the resulting residue was finally purified via column chromatography (Ethyl acetate/Petroleum ethe= 1:10).

2,4-Dimethyl-3-(2-pyridinylmethyl)pentan-3-ol was isolated in 91% yield. Colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 8.35 (d, *J* = 4.6 Hz, 1H), 7.52 (tt, *J* = 7.7, 2.4 Hz, 1H), 7.10 (d, *J* = 6.9 Hz, 1H), 7.06-6.98 (m, 1H), 6.23 (d, *J* = 1.0 Hz, 1H), 2.83 (d, *J* = 2.0 Hz, 2H), 1.92-1.77 (m, 2H), 0.83 (td, *J*

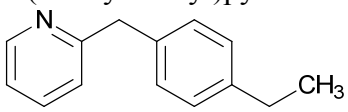
= 6.7, 2.1 Hz, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm: 161.74, 147.76, 136.74, 124.52, 120.98, 78.02, 38.11, 35.14, 18.12, 17.88.

2-(4-methylbenzyl)pyridine



A 50 mL RBF was subsequently charged with palladium(II) trifluoroacetate (42mg, 0.125 mmol), 1-bromo-4-methylbenzene (0.43, 2.5 mmol), 2,4-dimethyl-3-(2-pyridylmethyl)pentan-3-ol (0.621 g, 3 mmol), Cs_2CO_3 (1.22 g, 3.75 mmol), o-xylene (6 mL) and tricyclohexylphosphine (70mg, 0.25 mmol). The resulting mixture was replaced with Ar for 3 times and stirred at reflux under a Ar-atmosphere for 6 h. After cooling down to room temperature, the mixture was filtered over a pad of Celite. The solvent was removed under reduced pressure and the crude residue was finally purified via column chromatography (Ethyl acetate/Petroleum ethe= 1:5).
2-(4-methylbenzyl)pyridine was isolated in 85% yield. Colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 8.52-8.47 (m, 1H), 7.50 -7.40 (m, 1H), 7.13 (d, *J* = 7.9 Hz, 2H), 7.10-6.96 (m, 4H), 4.08 (s, 2H), 2.27 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm: 161.33, 149.34, 136.50 (d, J = 6.2 Hz), 135.84, 129.33, 129.05, 123.03, 121.17, 44.39, 21.09. HRMS (ESI) for $C_{13}H_{14}N$ $[M+H]^+$, calcd: 184.1126, found: 184.1129.

2-(4-ethylbenzyl)pyridine



2-(4-ethylbenzyl)pyridine was isolated in 87% yield. Colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 8.54-8.47 (m, 1H), 7.50-7.41 (m, 1H), 7.17 (d, *J* = 8.0 Hz, 2H), 7.10 (d, *J* = 8.0 Hz, 2H), 7.04 (d, *J* = 7.8 Hz, 1H), 7.02-6.96 (m, 1H), 4.10 (s, 2H), 2.58 (q, *J* = 7.6 Hz, 2H), 1.18 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm: 161.31, 149.35, 142.24, 136.77, 136.45, 129.09, 128.12, 123.07, 121.16, 44.43, 28.52, 15.67. HRMS (ESI) for $C_{14}H_{16}N$ $[M+H]^+$, calcd: 198.1283, found: 198.1290.

4.

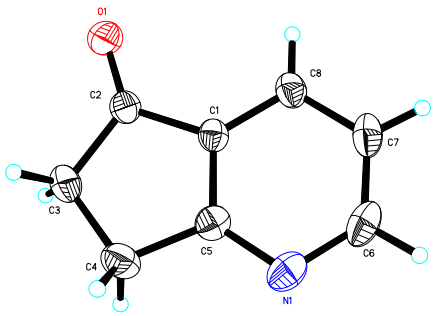


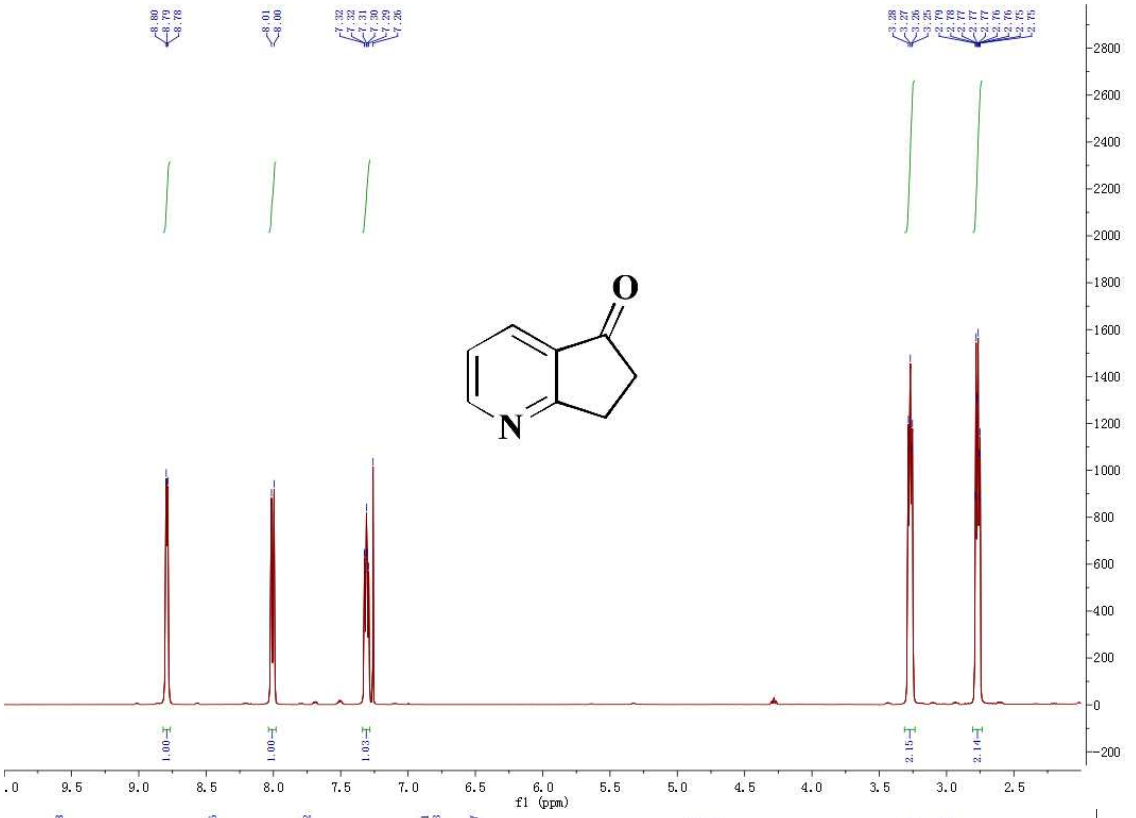
Figure 1 Molecular structure of **2a**.

Table 2 Crystal data and structure refinement for **2a**

Empirical formula	C8 H7 N O	
Formula weight	133.15	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P b c a	
Unit cell dimensions	a = 7.5044(13) Å	α= 90°.

	b = 11.9291(19) Å	β= 90°.
	c = 14.8473(19) Å	γ = 90°.
Volume	1329.1(4) $Å^3$	
Z	8	
Density (calculated)	1.331 Mg/m^3	
Absorption coefficient	0.089 mm^{-1}	
F(000)	560	
Crystal size	0.211 x 0.165 x 0.123 mm^3	
Theta range for data collection	3.416 to 25.492°.	
Index ranges	-7<=h<=9, -9<=k<=14, -17<=l<=17	
Reflections collected	4238	
Independent reflections	1228 [R(int) = 0.0483]	
Completeness to theta = 25.242°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.63215	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1228 / 0 / 92	
Goodness-of-fit on F^2	1.085	
Final R indices [I>2sigma(I)]	R1 = 0.0552, wR2 = 0.1269	
R indices (all data)	R1 = 0.0693, wR2 = 0.1383	
Extinction coefficient	0.26(2)	
Largest diff. peak and hole	0.269 and -0.316 $e.Å^{-3}$	

5. ^{1}H and ^{13}C NMR spectra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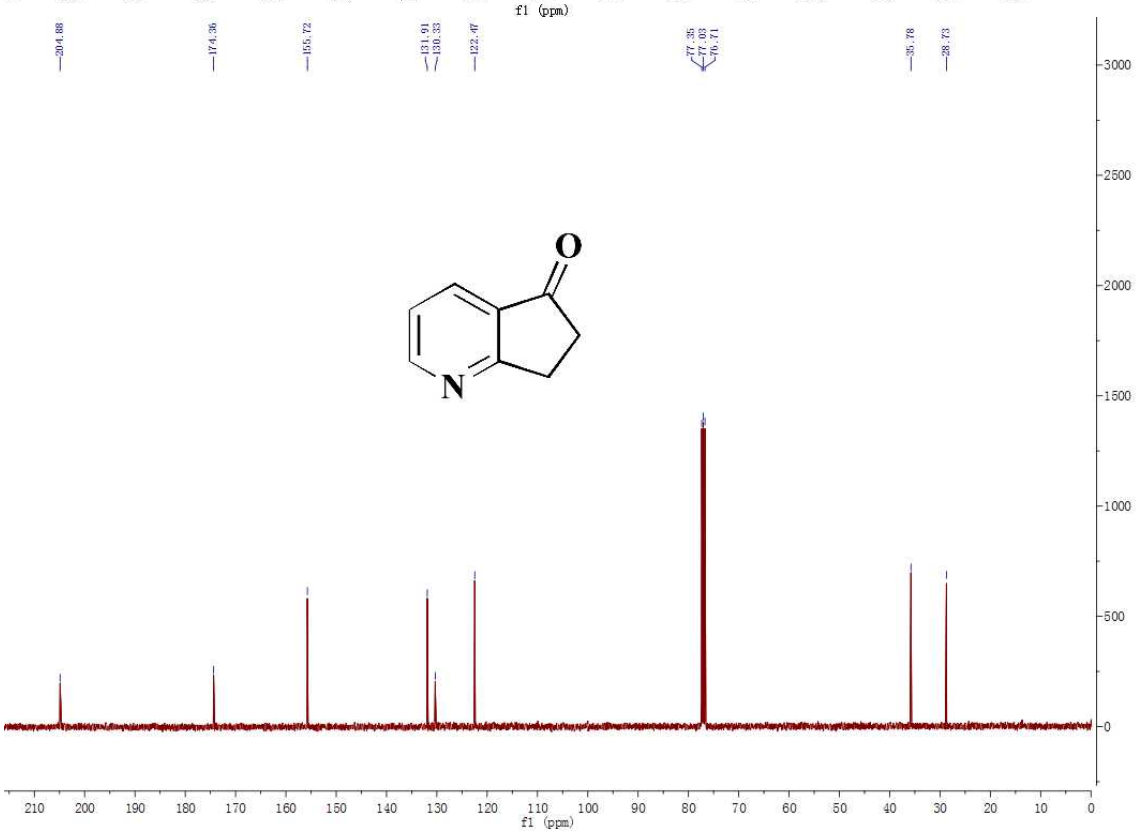
8.00
7.32
7.31
7.30
7.29
7.26
3.28
3.27
3.26
3.25
2.79
2.78
2.77
2.77
2.77
2.77
2.76
2.75
2.75
O
N
1.00
1.00
1.03
2.15
2.14
f1 (ppm)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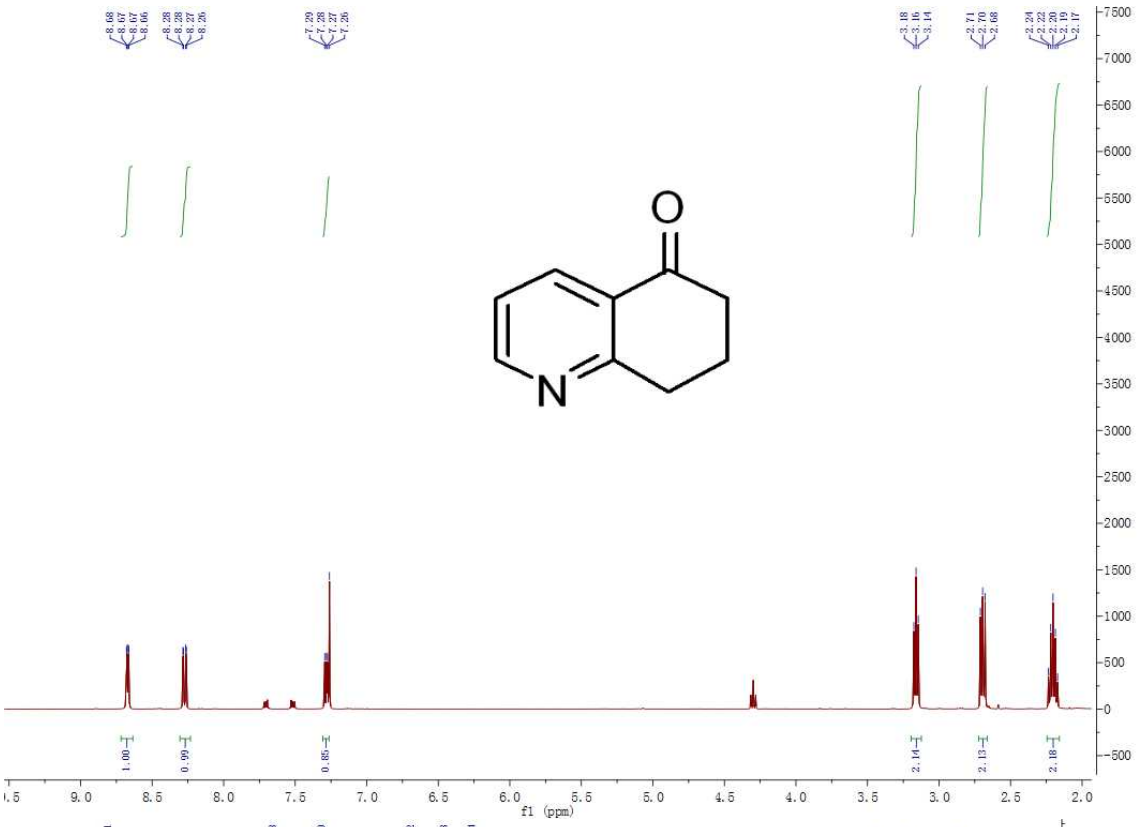
35.78
28.73
O
N
f1 (ppm)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8.28
8.27
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7.28
7.27
7.26
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3.16
3.14
2.71
2.70
2.68
2.24
2.22
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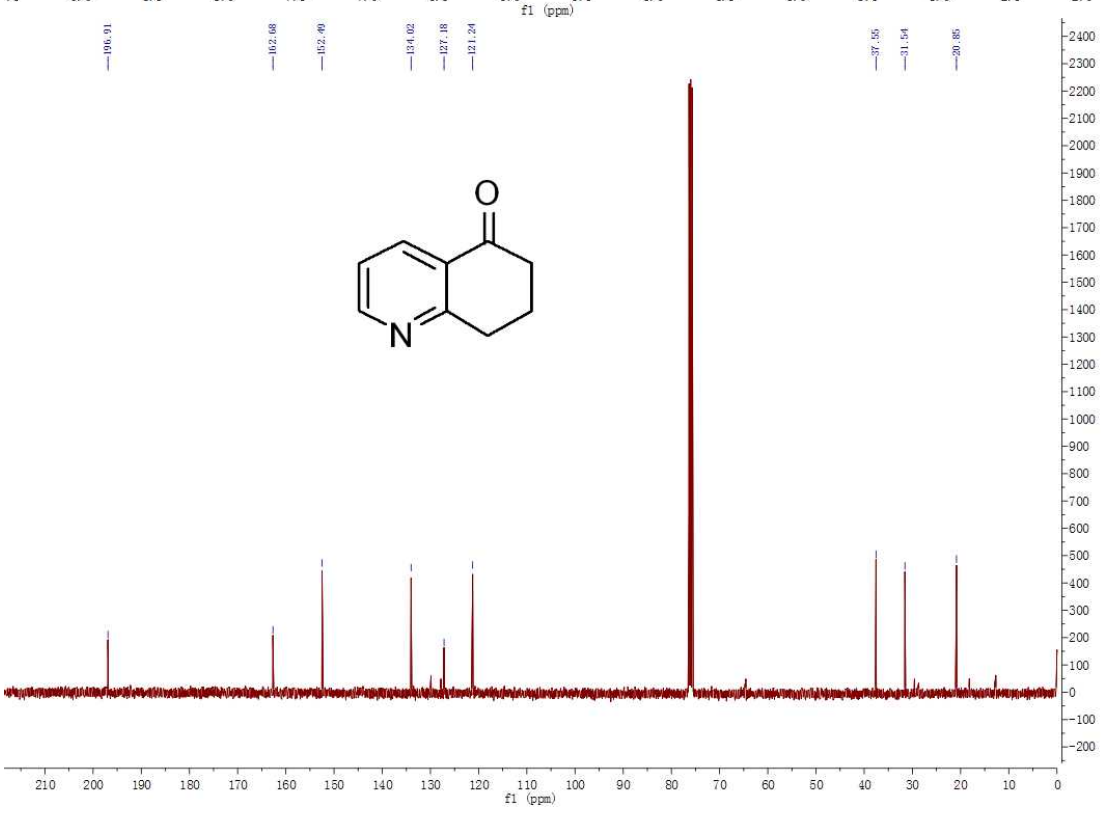
2.18
f1 (ppm)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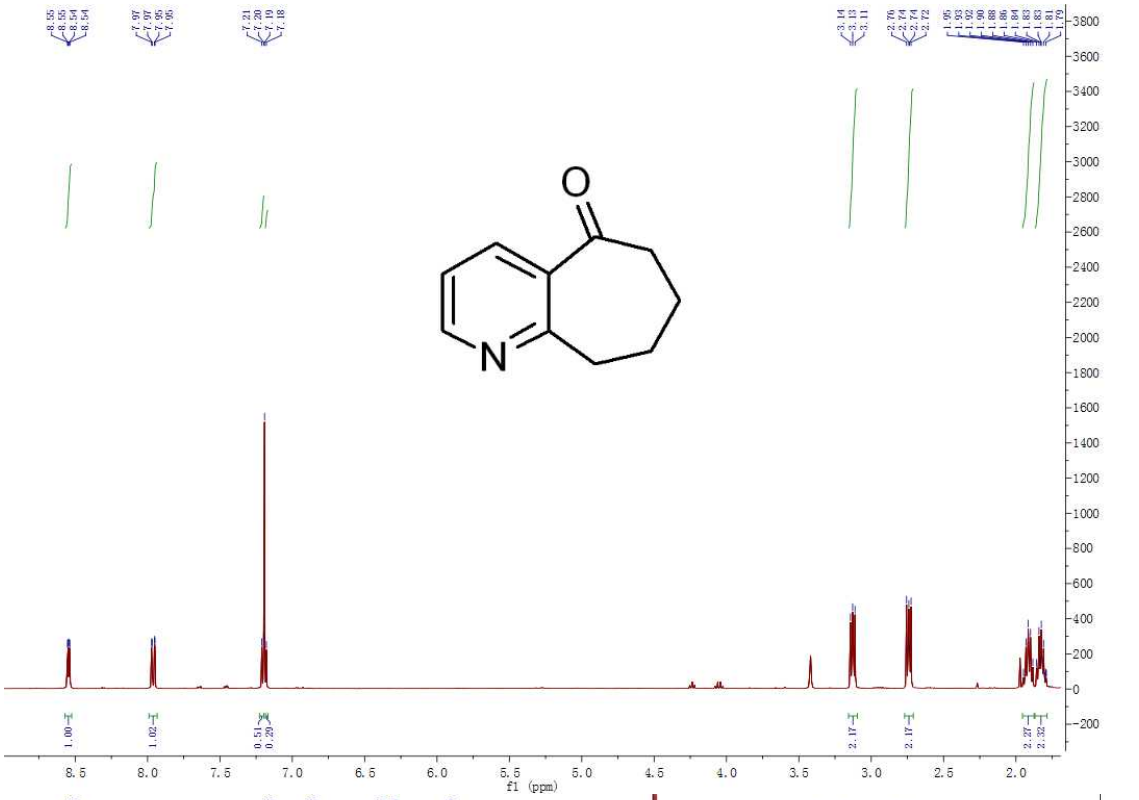
N
f1 (ppm)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1.92
1.90
1.88
1.86
1.84
1.83
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1.79
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N
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2.17
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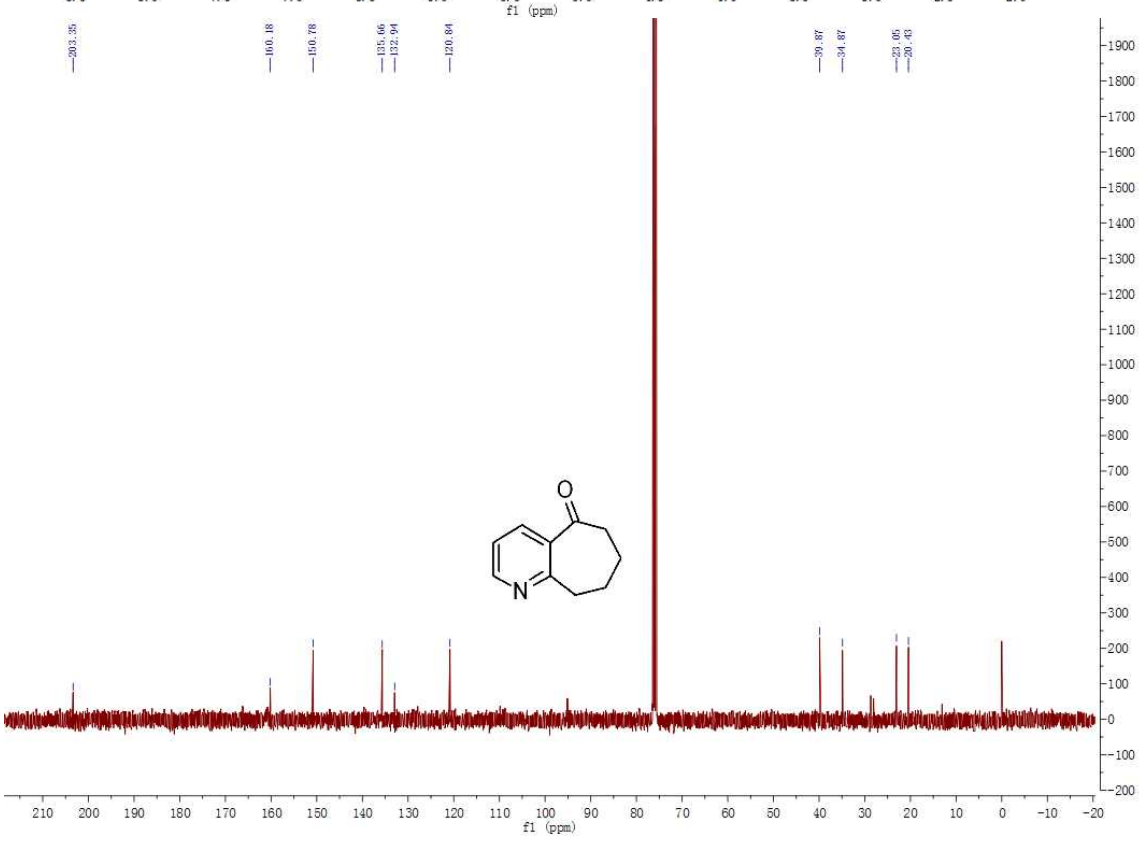
2.32
f1 (ppm)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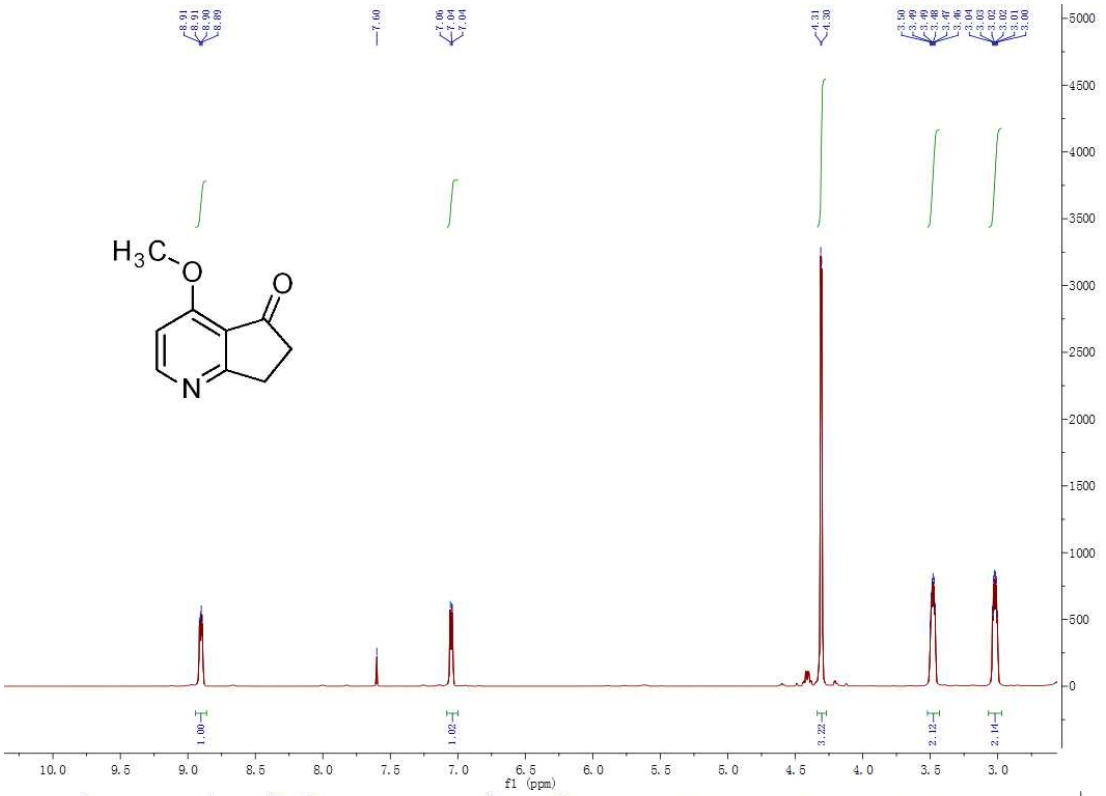
O
N
f1 (ppm)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7.04
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4.30
3.50
3.49
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3.46
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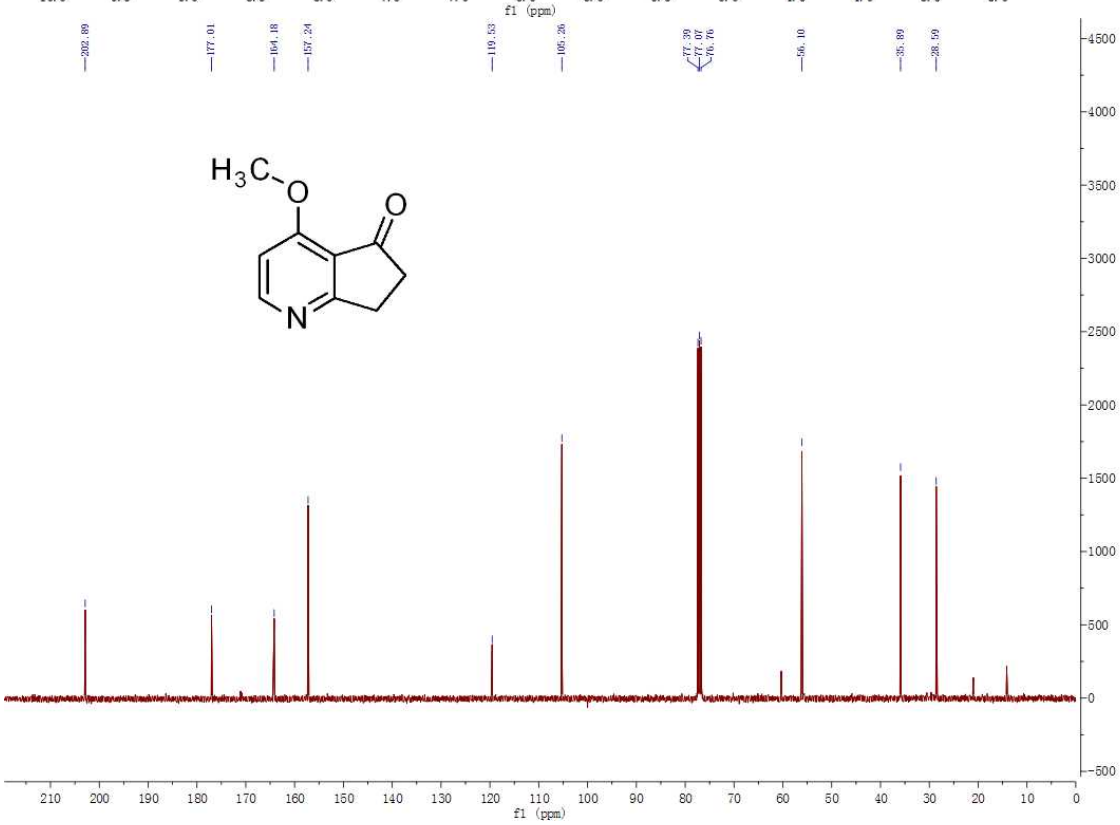
2.14
f1 (ppm)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H3C
O
O
N
f1 (ppm)


8.56
8.55
7.26
6.71
6.69
4.29
4.27
4.25
4.23
3.17
3.16
3.14
2.71
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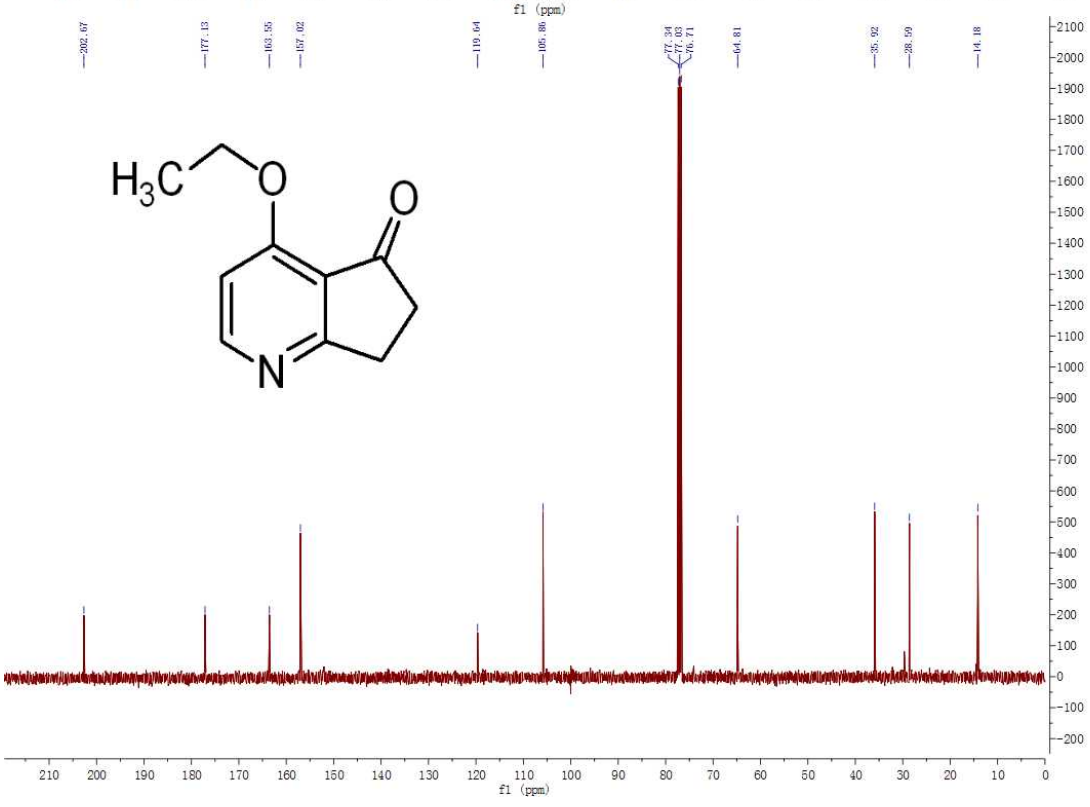
2.17
2.17
2.12
3.17
f1 (ppm)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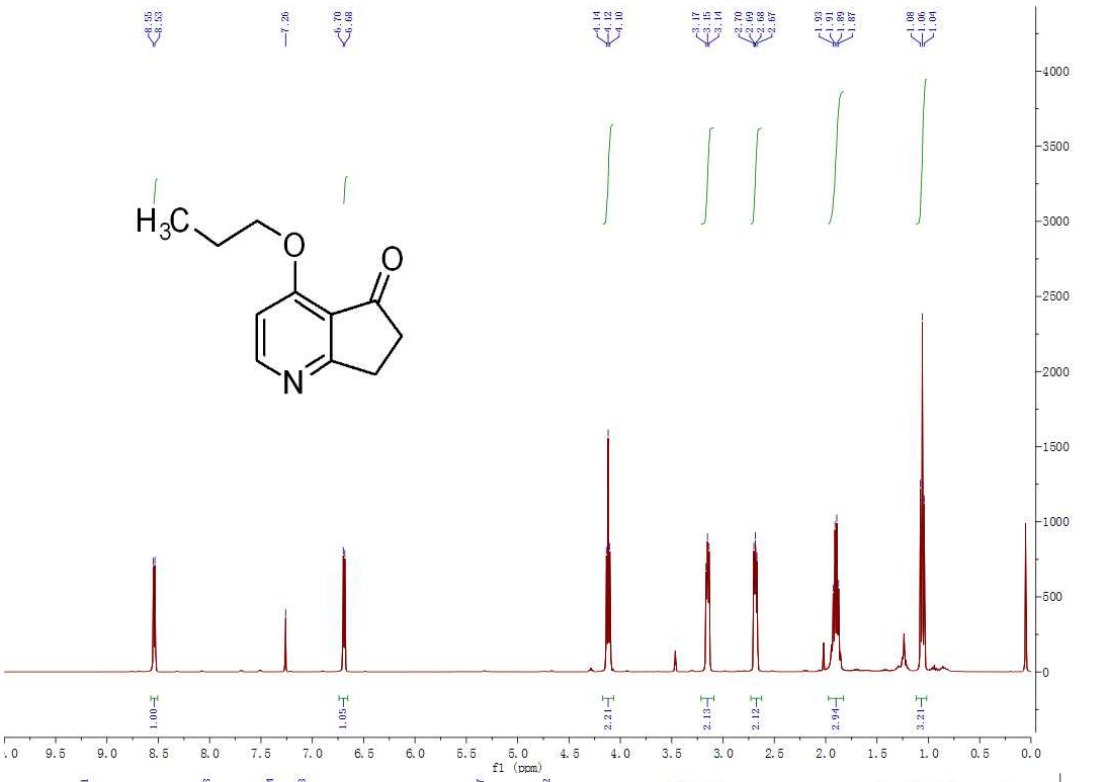
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3.14
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2.13
2.12
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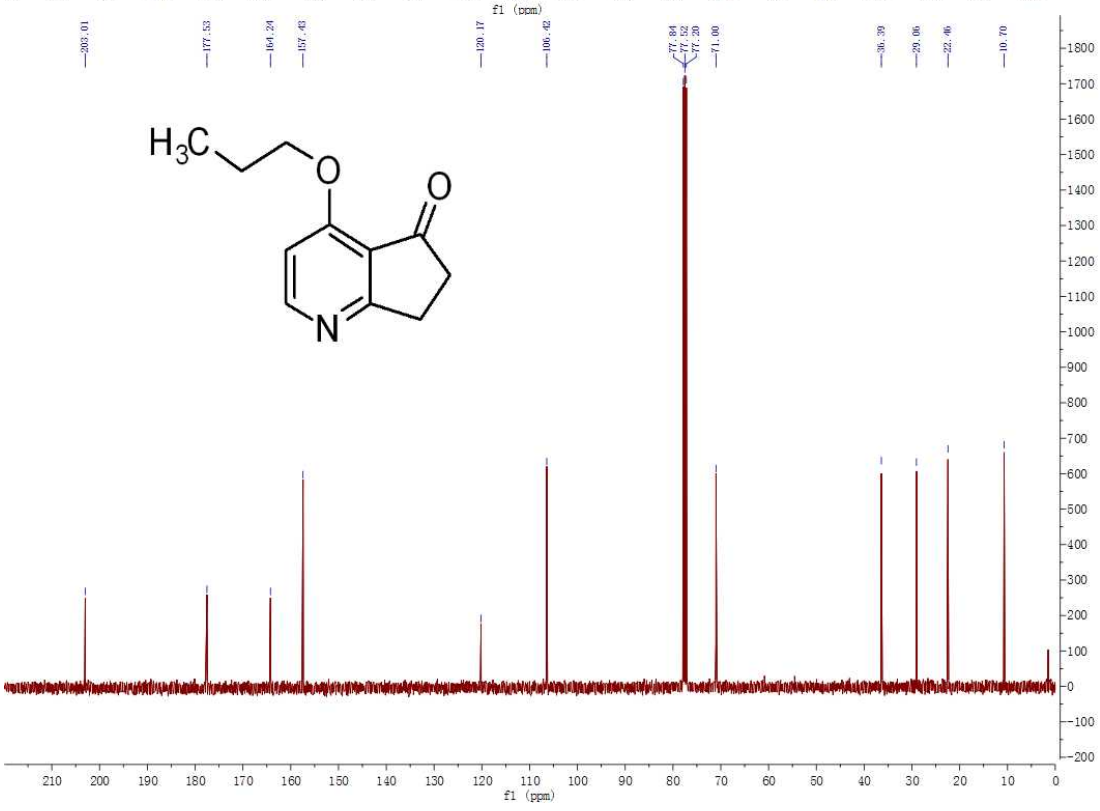
3.21
f1 (ppm)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71.00
36.39
29.06
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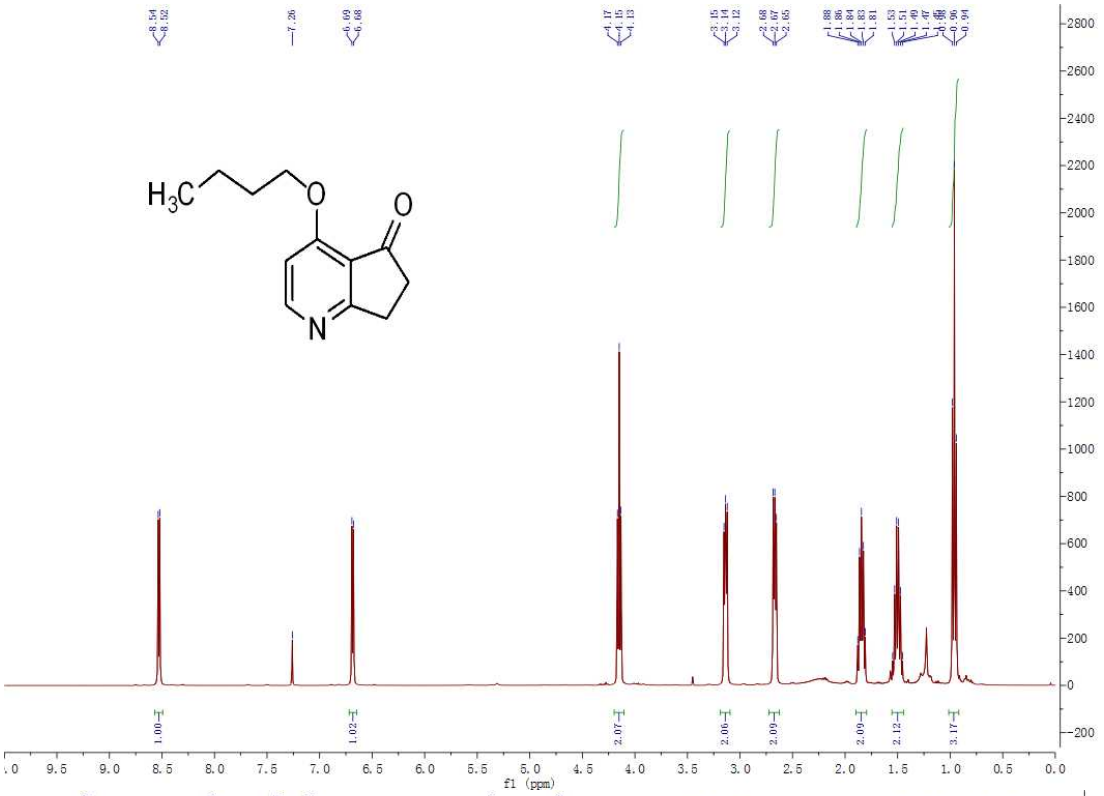
10.70
f1 (ppm)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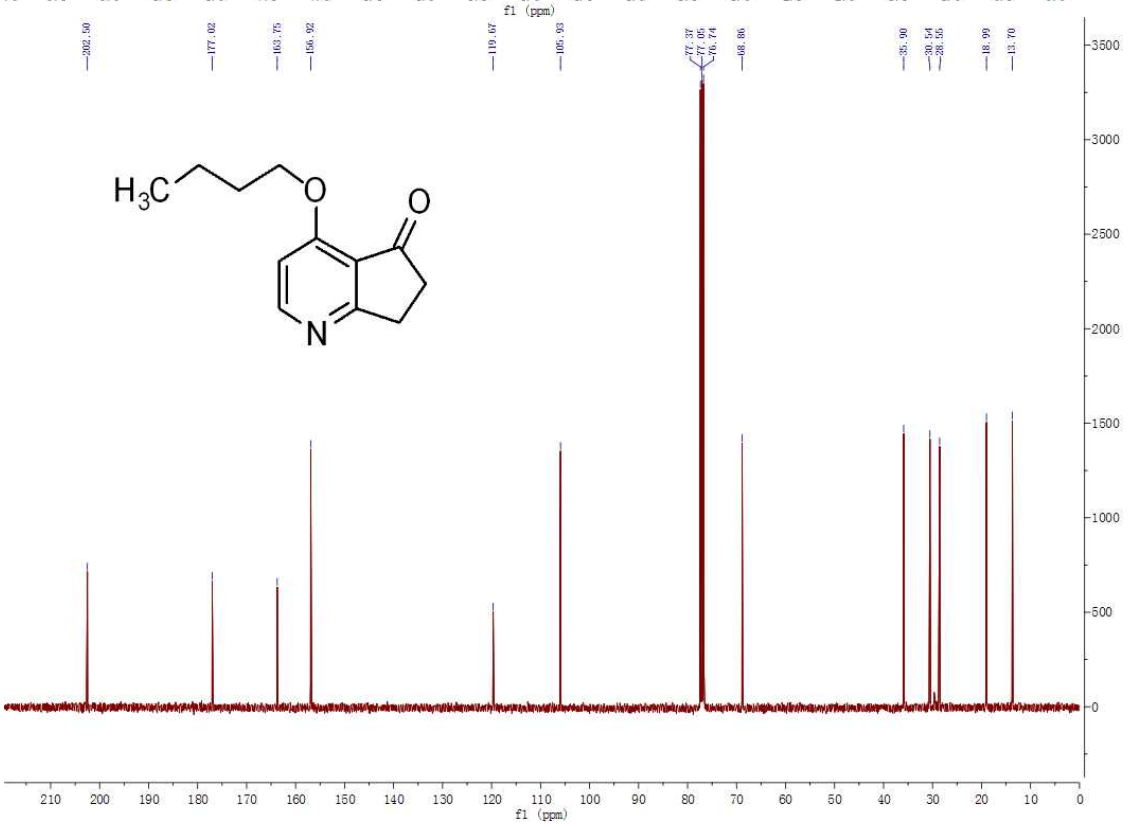
8.52
7.26
6.69
6.68
4.17
4.15
4.13
3.15
3.14
3.12
2.68
2.67
2.65
1.88
1.86
1.84
1.83
1.81
1.53
1.51
1.49
1.47
0.96
0.94
H3C
O
O
N
1.00
1.02
2.07
2.06
2.09
2.09
2.12
3.17
f1 (ppm)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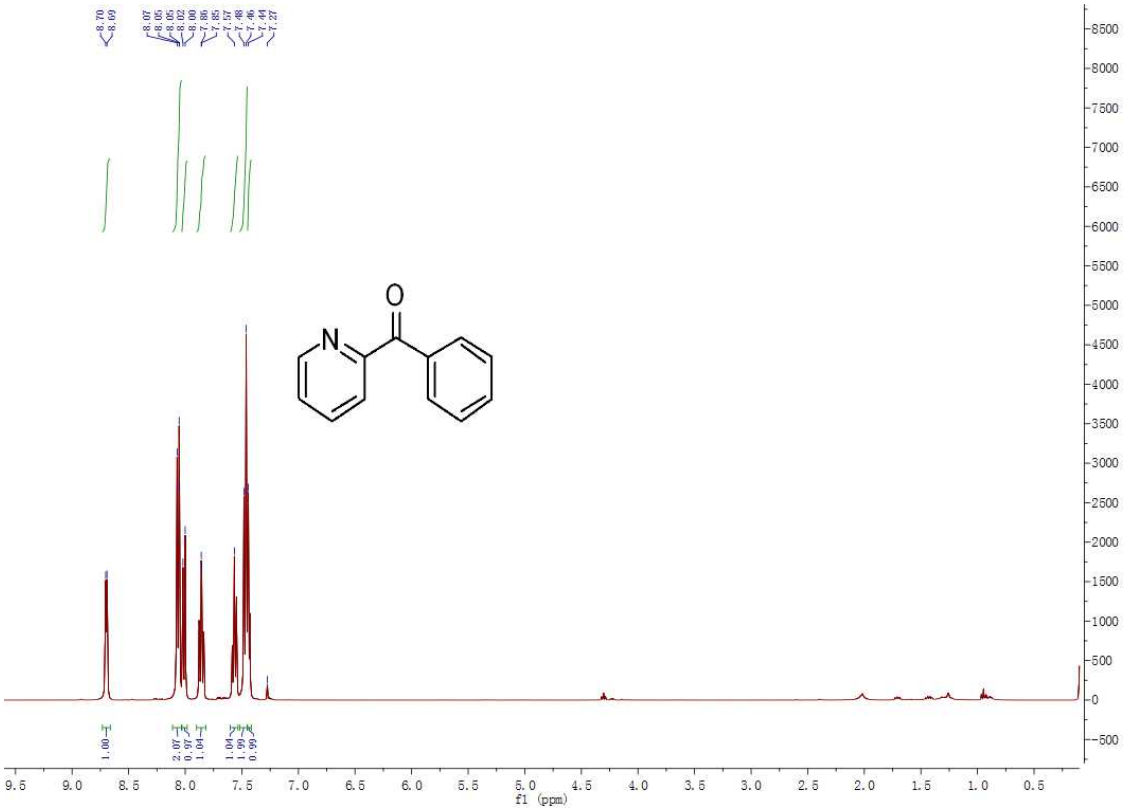
163.75
156.92
119.67
105.93
77.37
77.05
76.74
68.86
35.90
30.54
28.55
18.99
13.70
H3C
O
O
N
f1 (ppm)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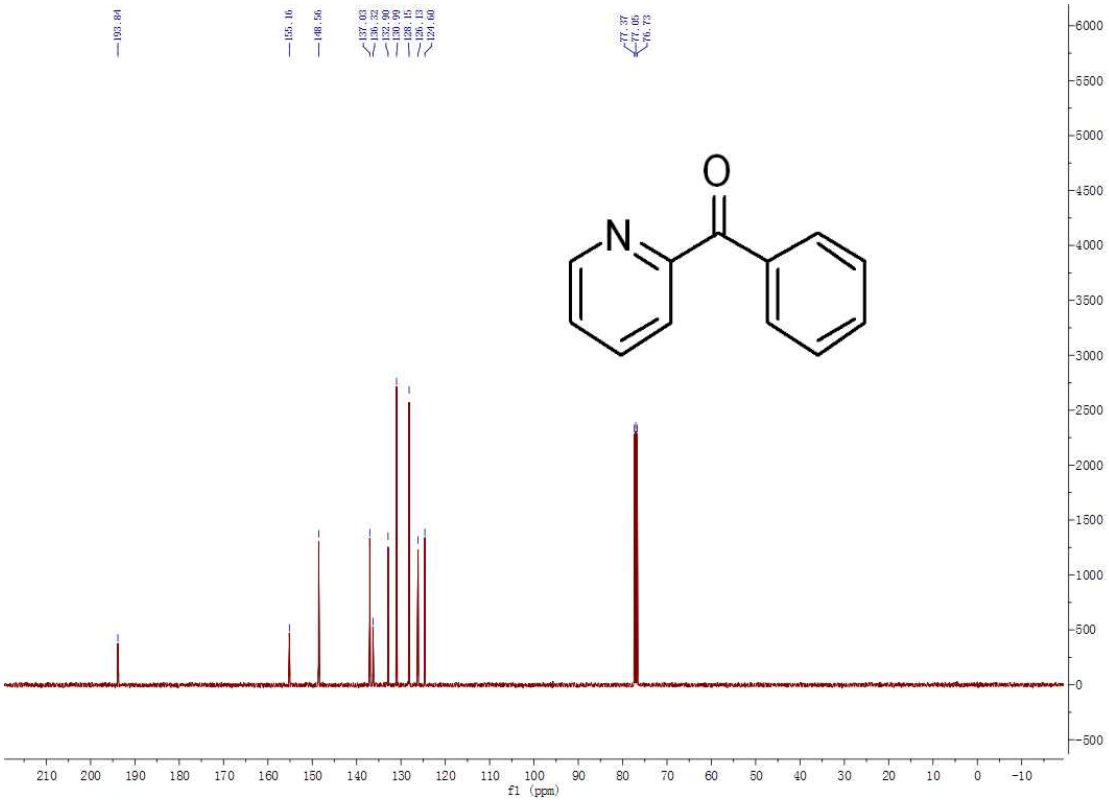
8.07
8.05
8.05
8.02
8.00
7.66
7.65
7.57
7.48
7.46
7.44
7.27
1.00
2.07
0.97
1.04
1.04
1.99
0.99
f1 (ppm)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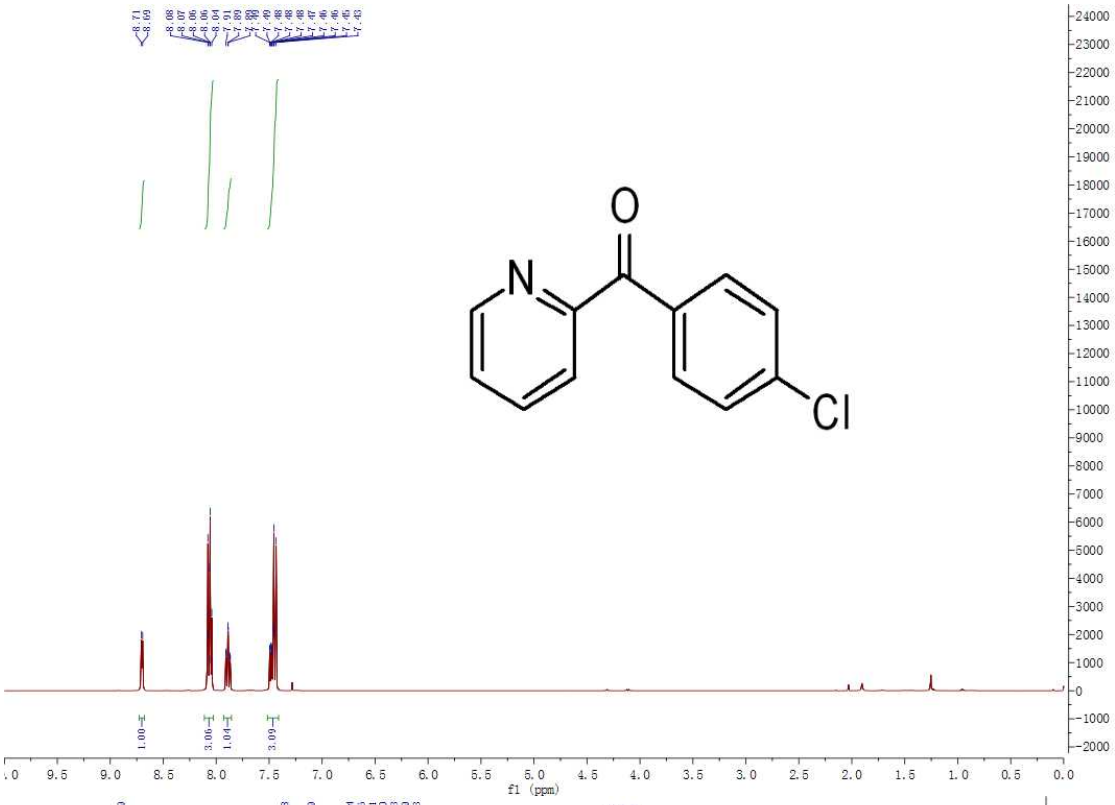
132.90
130.99
128.15
126.13
124.60
77.37
77.05
76.73
f1 (ppm)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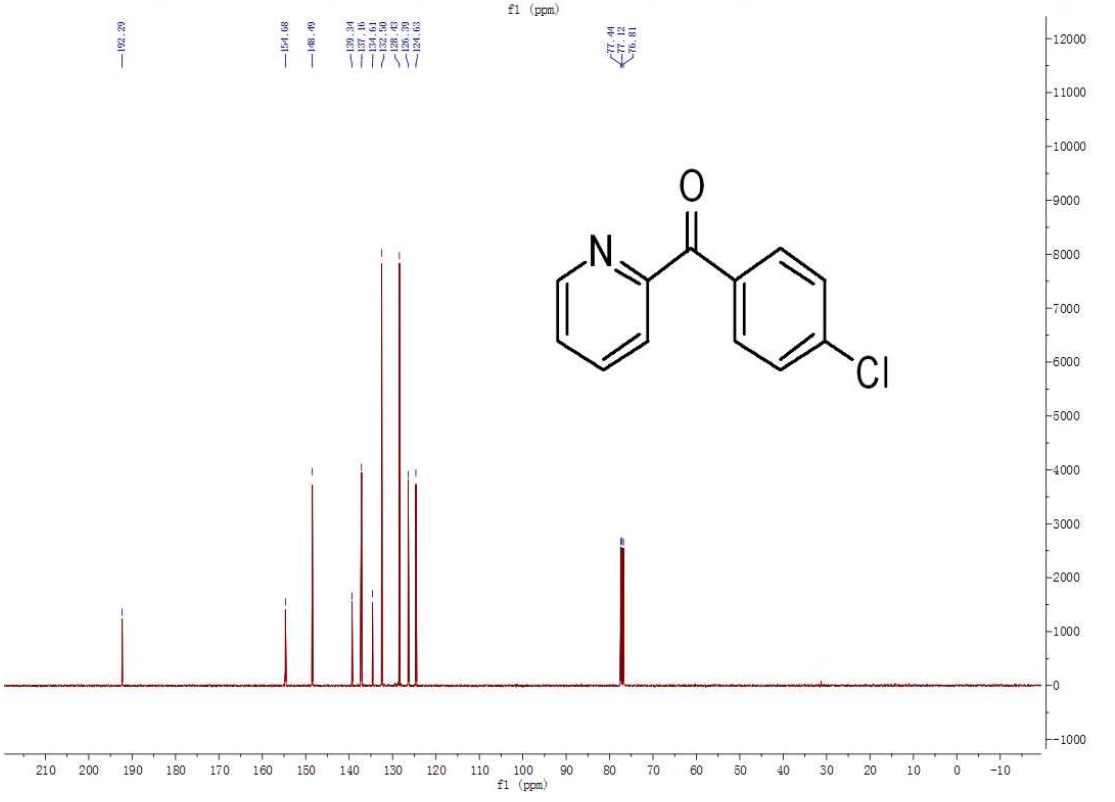
8.07
8.06
8.06
8.04
7.91
7.89
7.89
7.49
7.48
7.48
7.47
7.47
7.46
7.46
7.45
7.43
O
N
Cl
1.00
3.06
1.04
3.09
f1 (ppm)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154.68
148.49
139.34
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132.58
128.43
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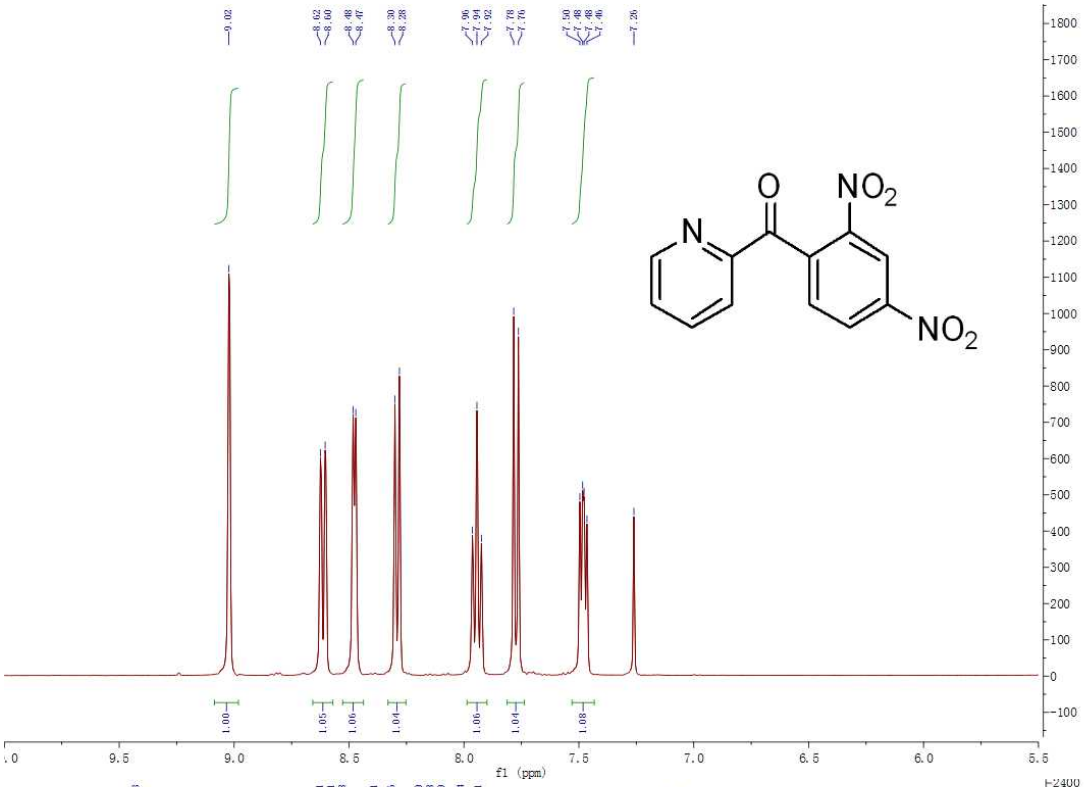
124.63
77.44
77.12
76.81
O
N
Cl
f1 (ppm)


9.02
8.62
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8.47
8.30
8.28
7.96
7.94
7.92
7.78
7.76
7.50
7.48
7.48
7.46
7.26
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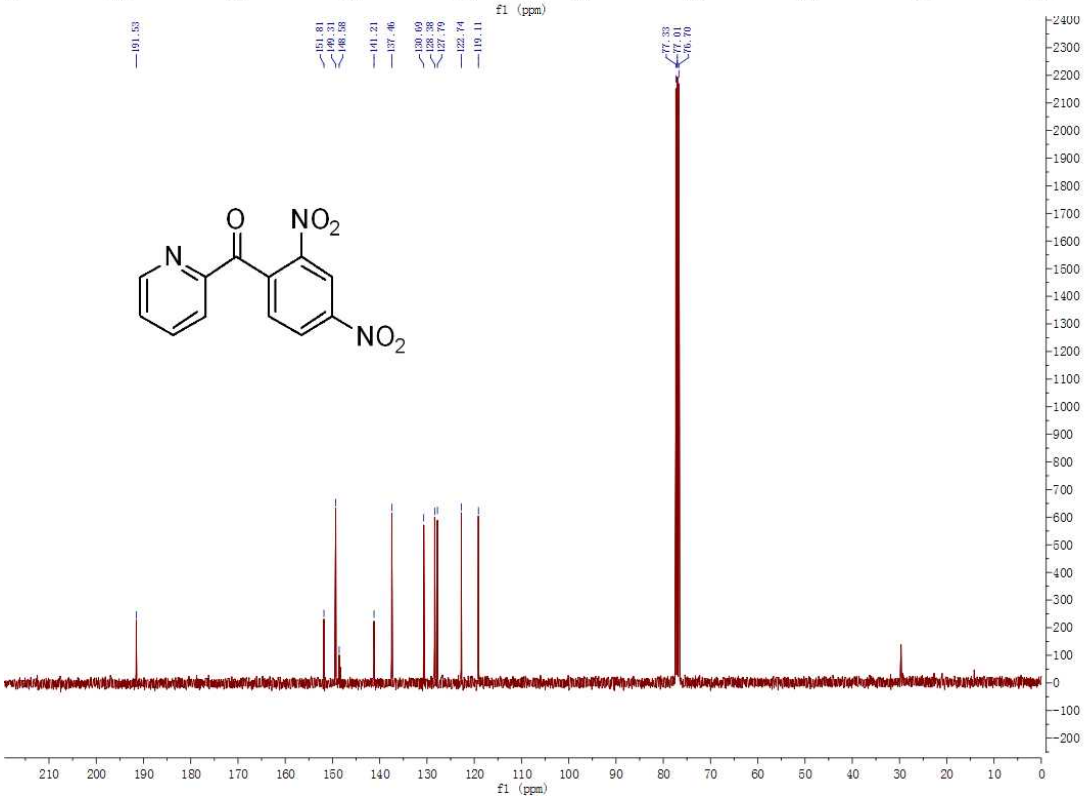
N
NO2
1.00
1.05
1.06
1.04
1.06
1.04
1.08
f1 (ppm)


191.53
151.81
149.31
148.58
141.21
137.46
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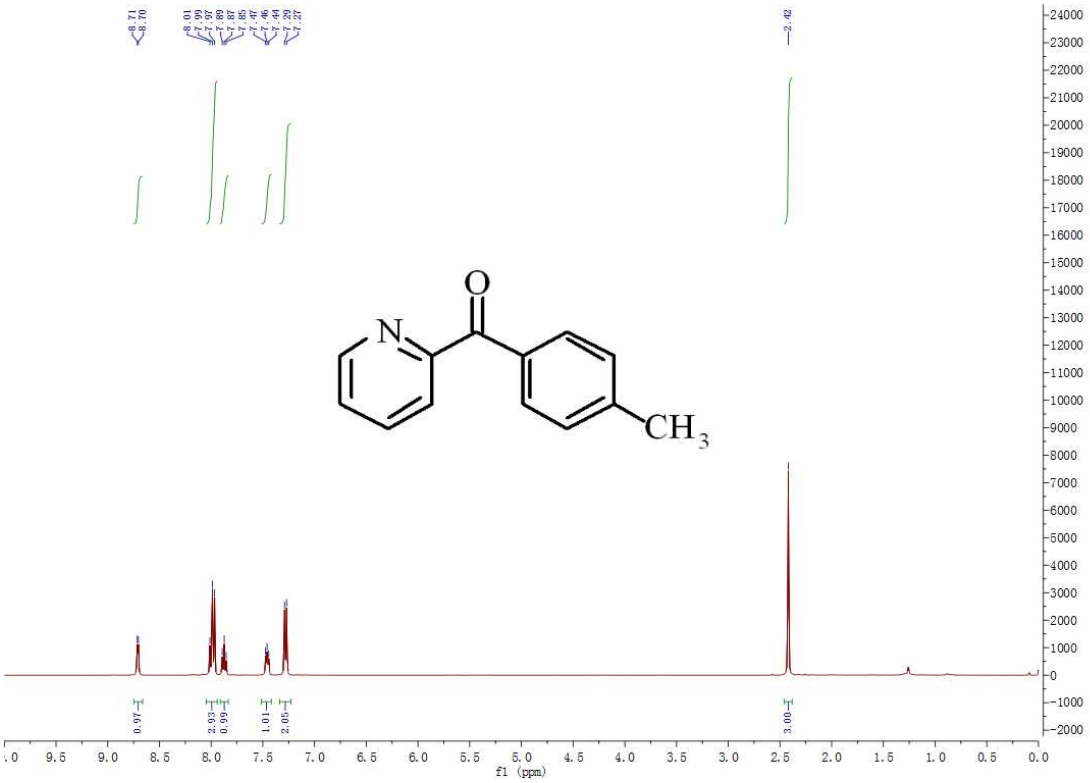
128.38
127.79
122.74
119.11
77.33
77.01
76.70
O
NO2
N
NO2
f1 (ppm)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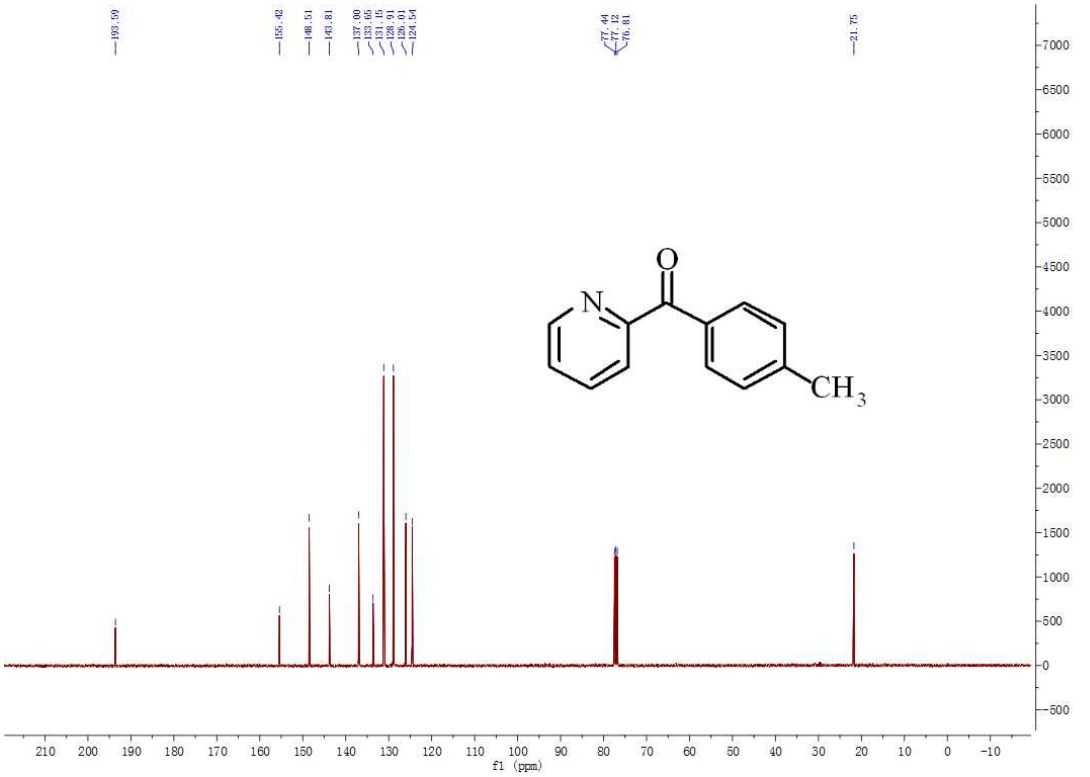
8.70
8.01
7.99
7.97
7.89
7.87
7.86
7.47
7.46
7.44
7.39
7.37
2.42
O
N
CH3
0.97
2.93
0.99
1.01
2.05
3.00
f1 (ppm)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145.81
137.00
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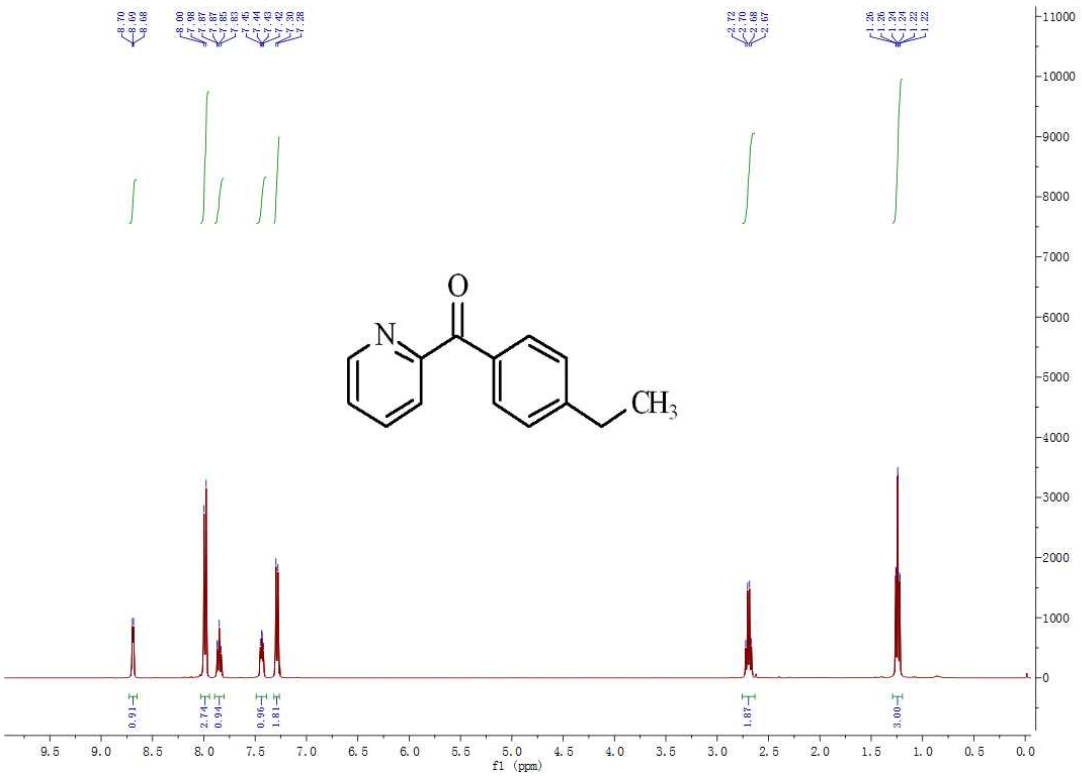
131.15
128.91
126.01
124.54
77.44
77.12
76.81
21.75
O
N
CH3
f1 (ppm)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8.69
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8.00
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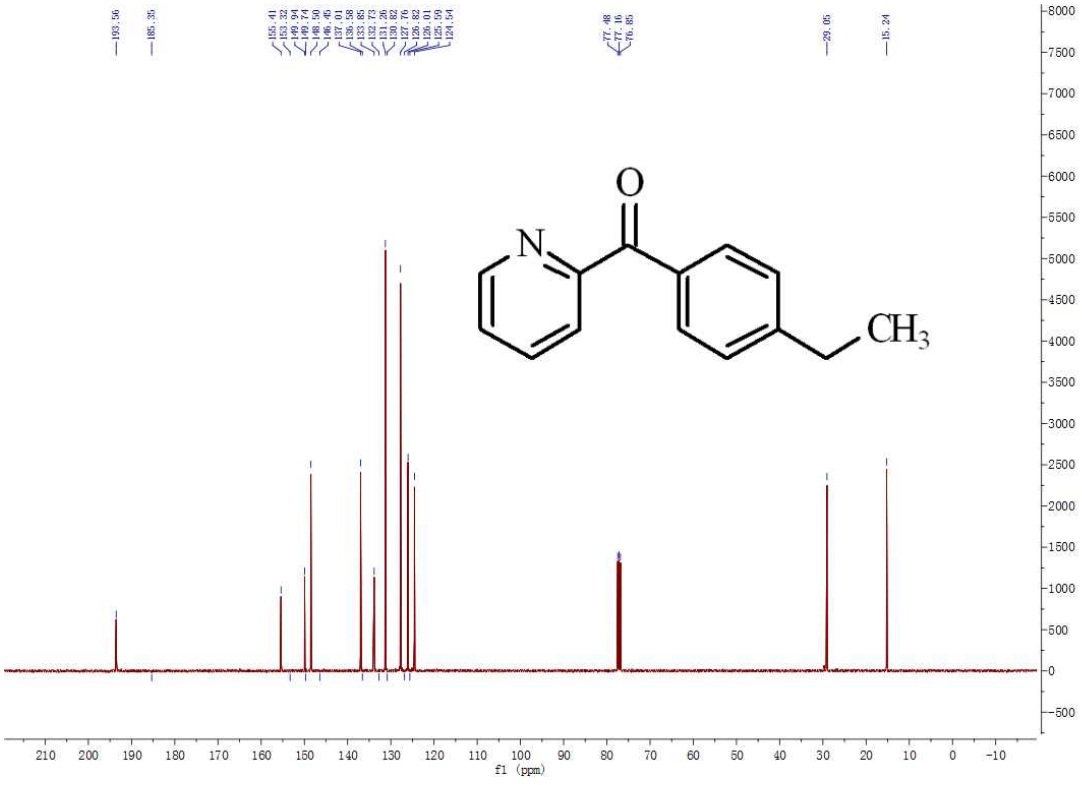
7.97
7.87
7.85
7.83
7.45
7.44
7.43
7.42
7.30
7.28
2.72
2.70
2.68
2.67
1.26
1.24
1.22
1.22
O
N
CH3
0.91
2.74
0.94
0.96
1.81
1.87
3.00
f1 (ppm)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153.32
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148.90
146.46
137.01
136.58
133.85
132.73
131.26
130.82
127.76
126.82
126.01
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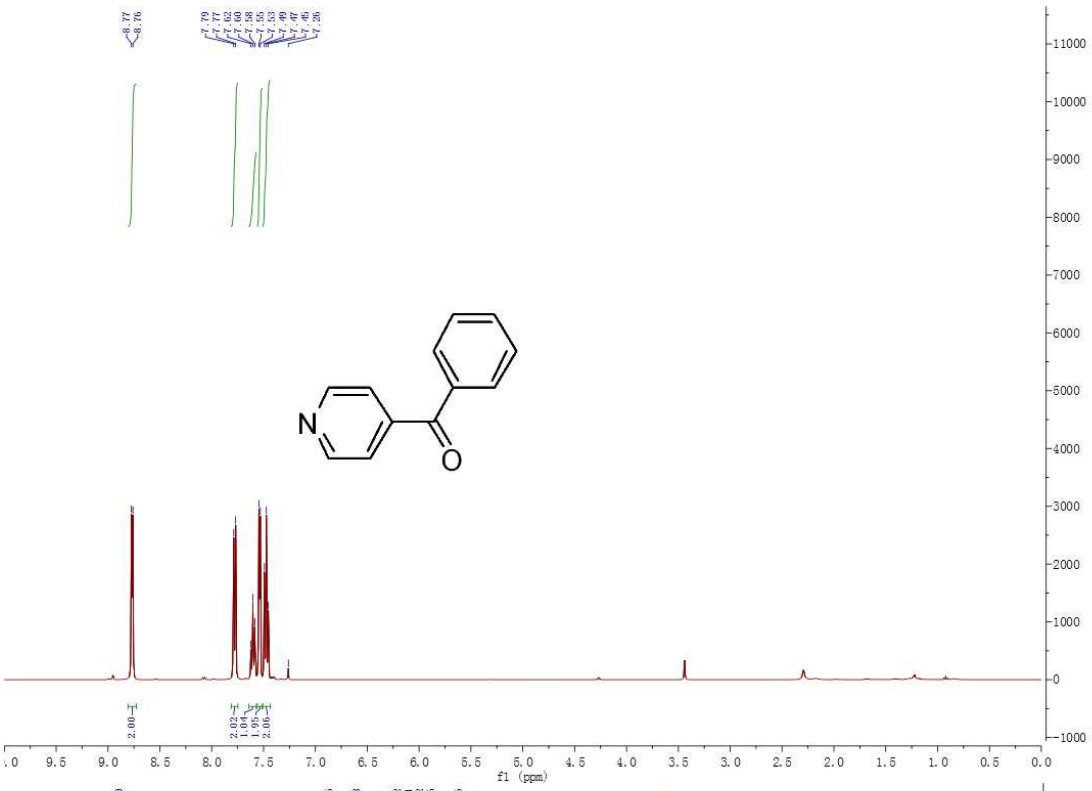
124.54
77.48
77.16
76.85
29.05
15.24
O
N
CH3
f1 (ppm)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8.76
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7.77
7.62
7.60
7.58
7.55
7.53
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7.45
7.26
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O
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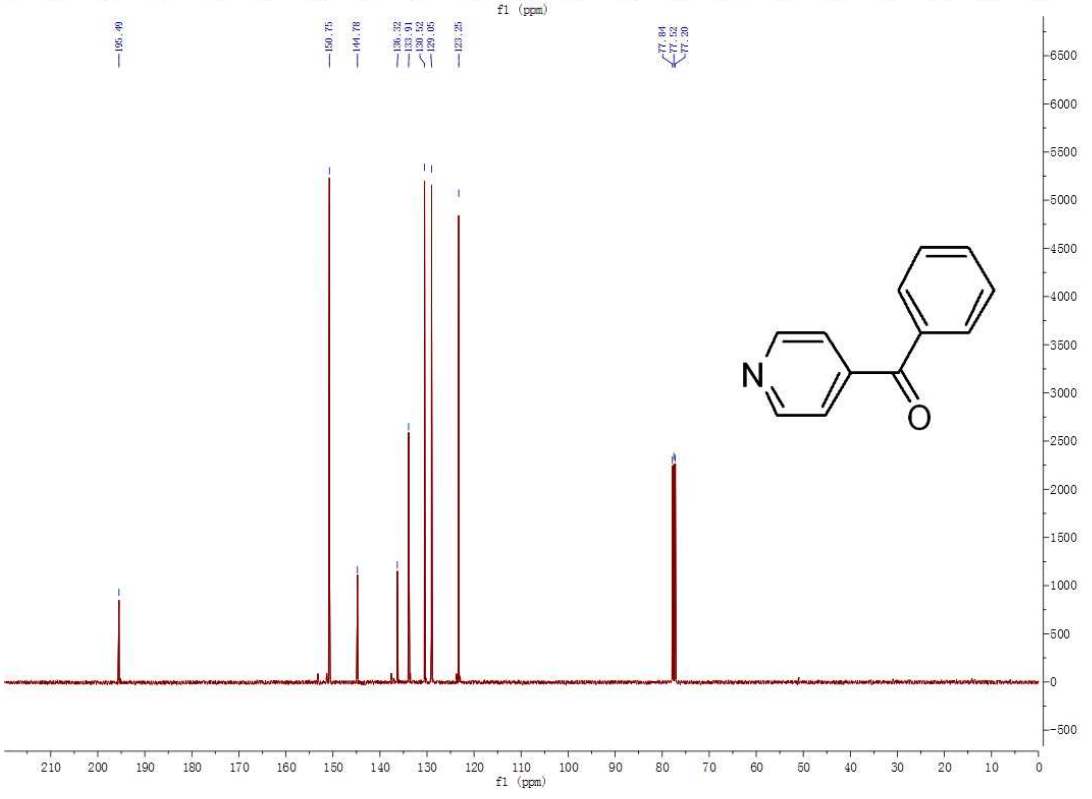
2.02
1.04
1.95
2.06
f1 (ppm)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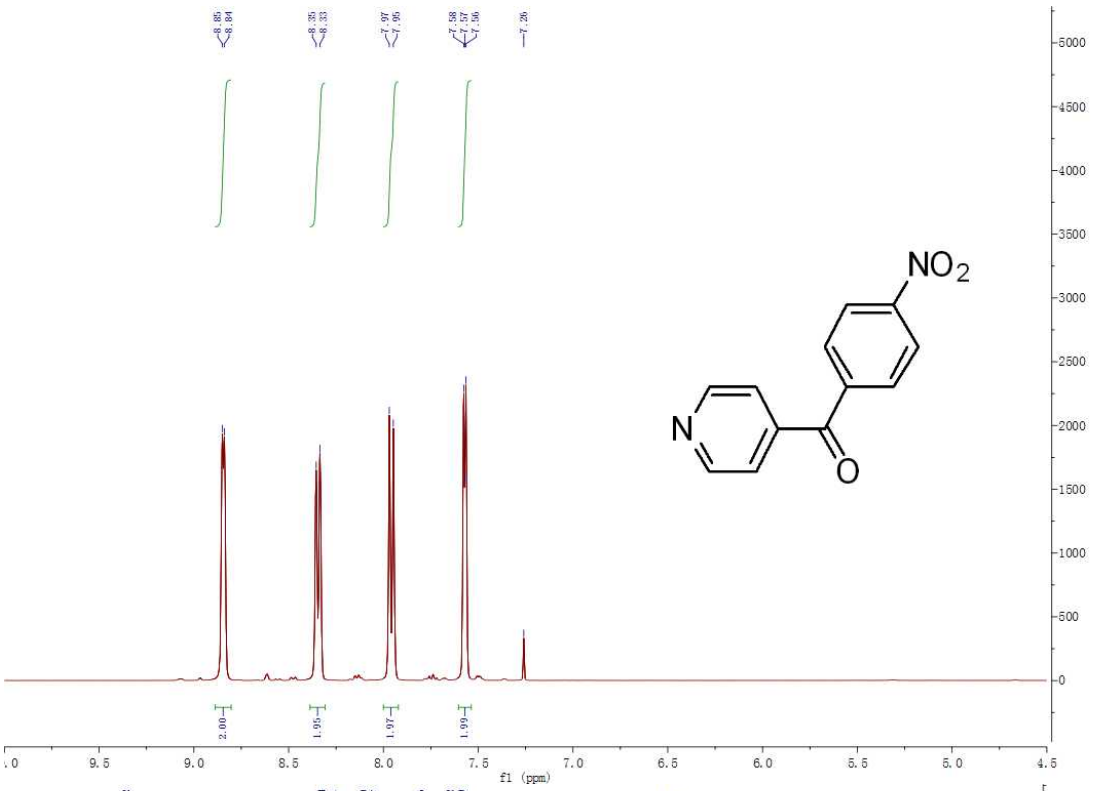
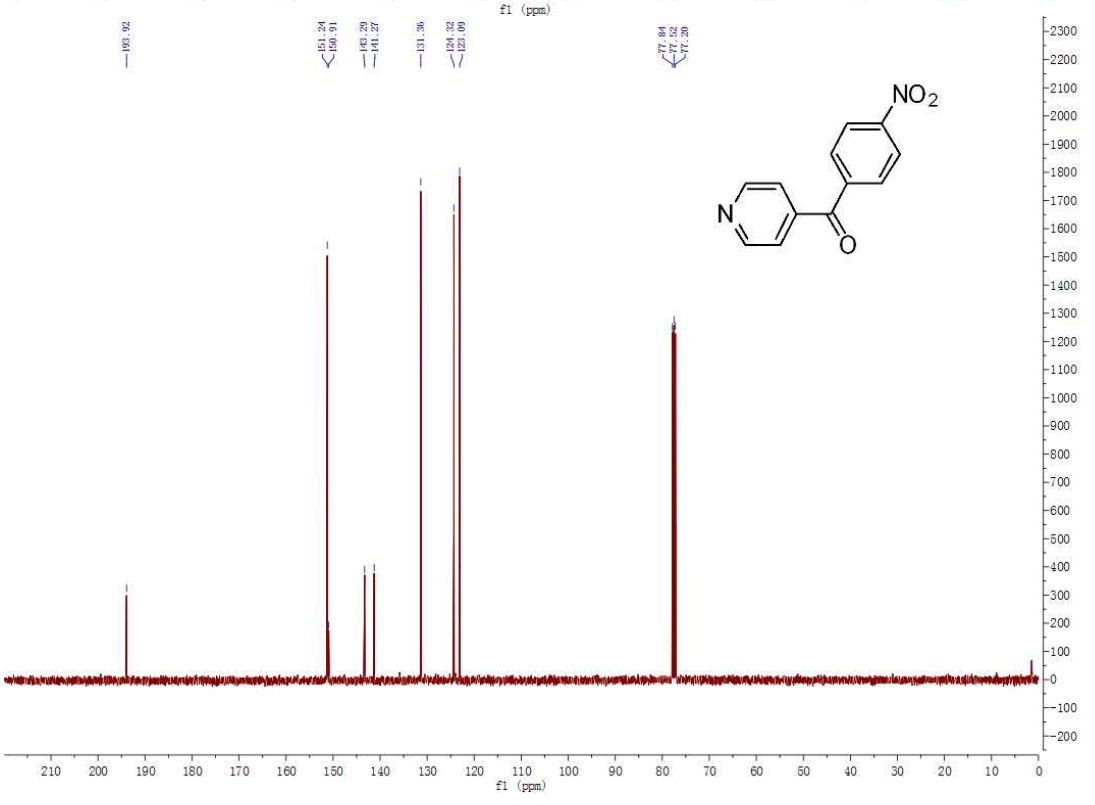
130.52
129.05
123.25
77.84
77.52
77.20
N
O
f1 (ppm)


8.85
8.84
8.35
8.33
7.97
7.96
7.58
7.57
7.56
7.26
NO2
N
O
2.00
1.95
1.97
1.99
f1 (ppm)


193.92
151.24
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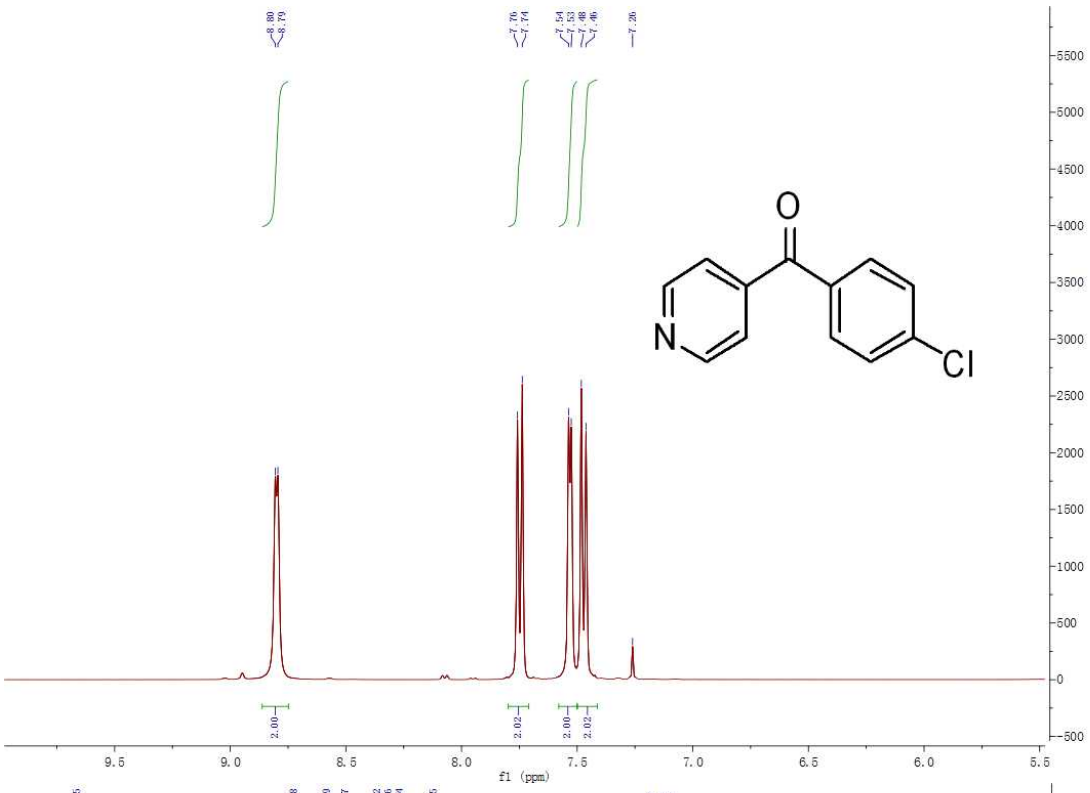
145.29
141.27
131.36
124.32
123.09
77.84
77.52
77.20
NO2
N
O
f1 (ppm)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8.79
7.76
7.74
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7.46
7.26
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N
Cl
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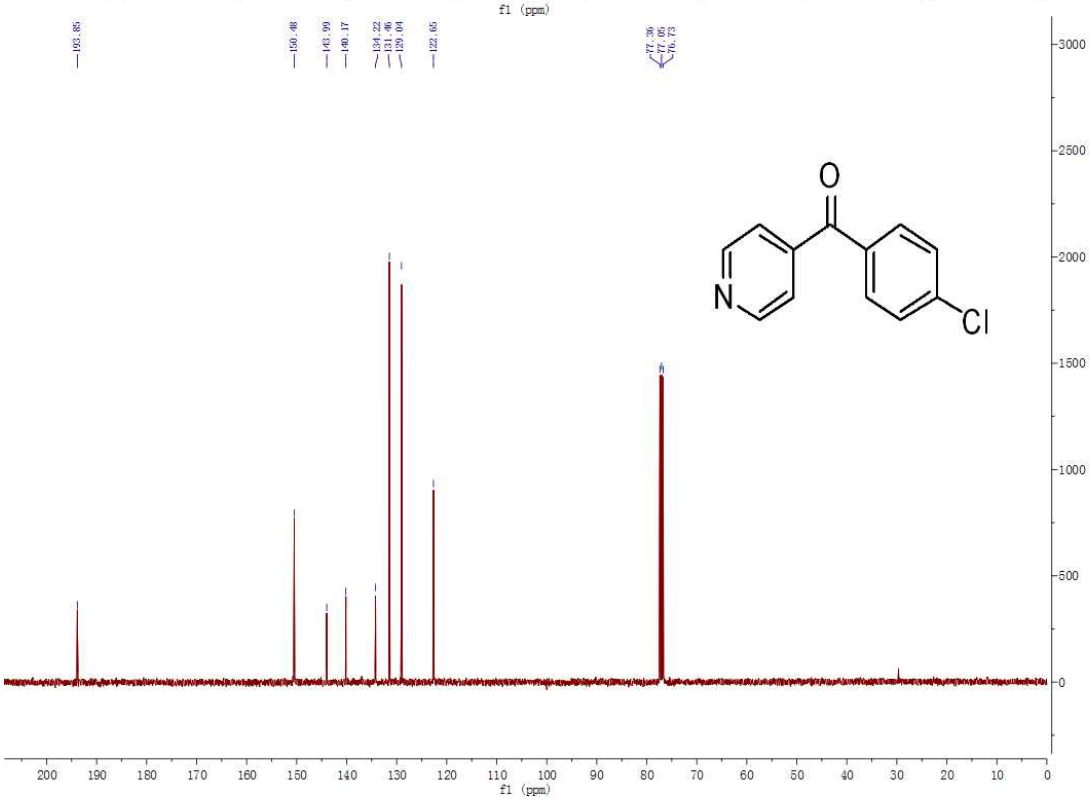
2.00
2.02
f1 (ppm)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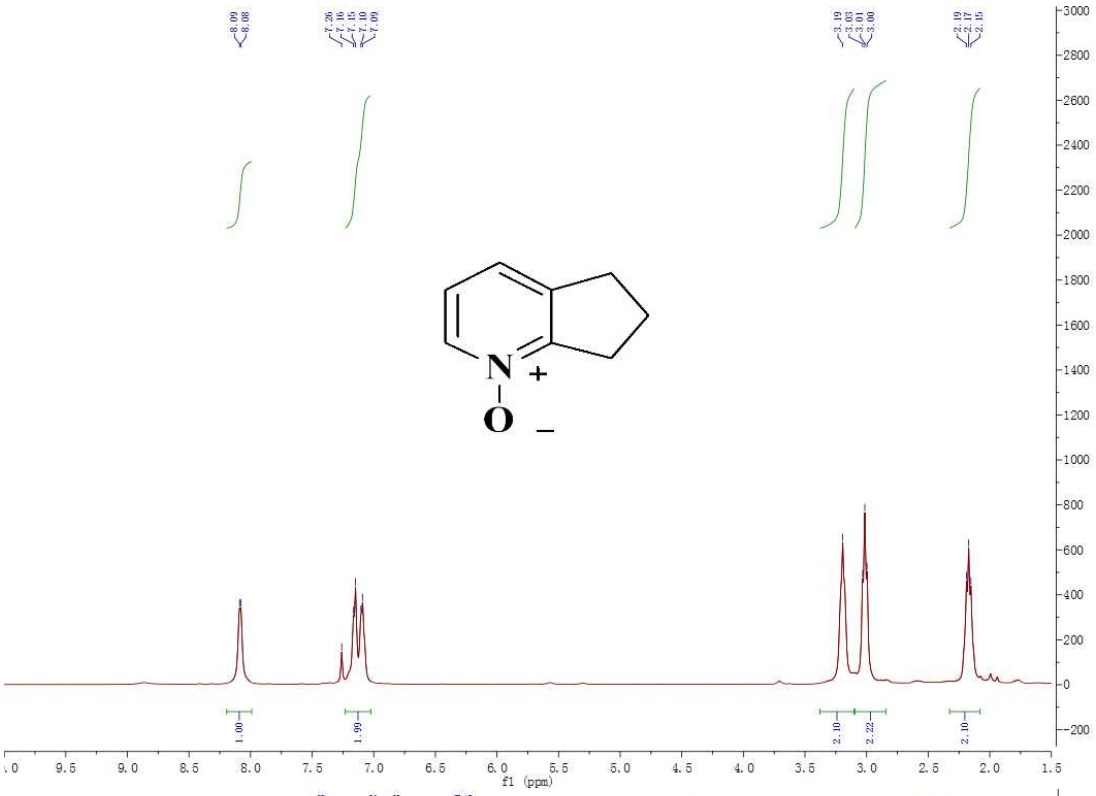
122.65
77.36
77.05
76.73
O
N
Cl
f1 (ppm)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7.26
7.16
7.15
7.10
7.09
3.19
3.03
3.01
3.00
2.19
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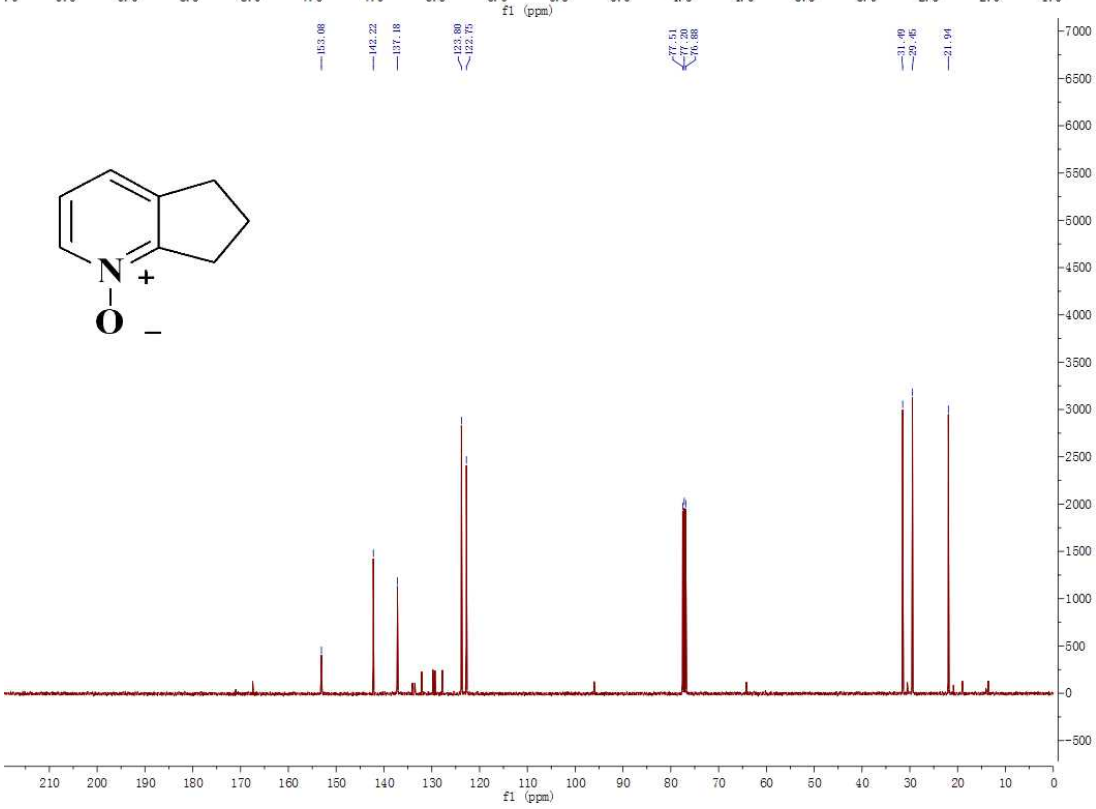
1.99
2.10
2.22
2.10
f1 (ppm)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142.22
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77.51
77.20
76.88
31.49
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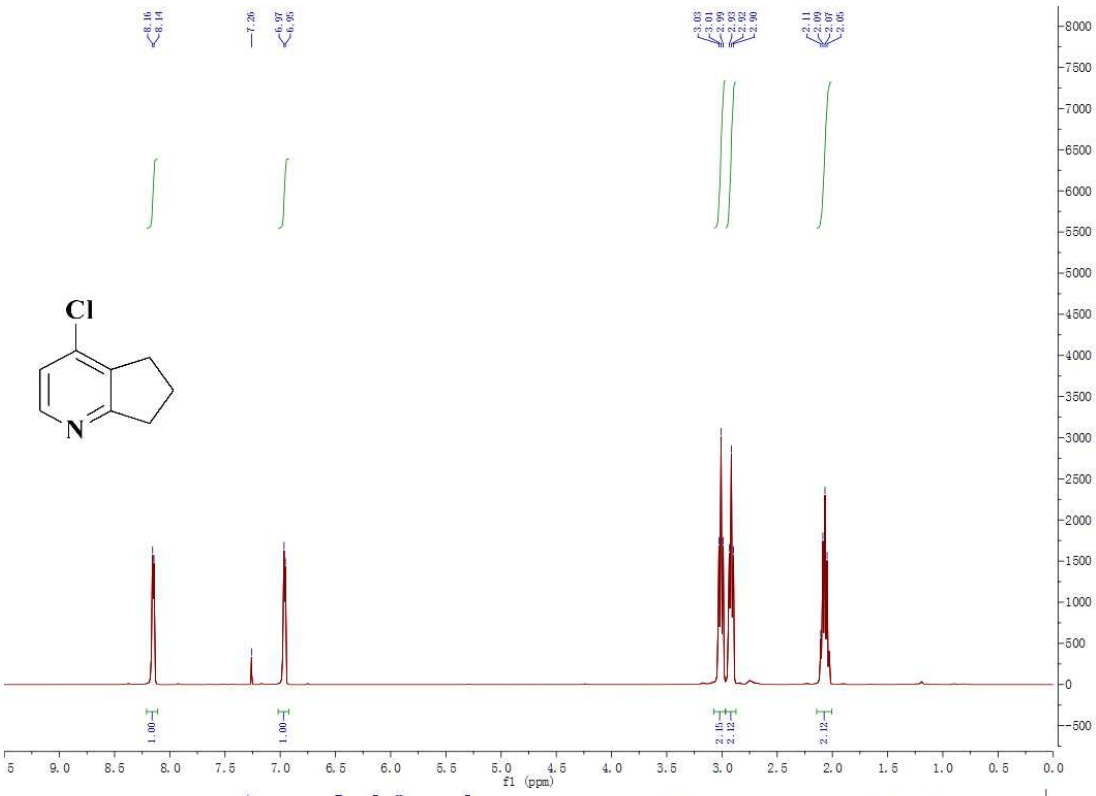
21.94
f1 (ppm)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8.14
7.26
6.97
6.95
3.03
3.01
2.99
2.95
2.92
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2.07
2.05
Cl
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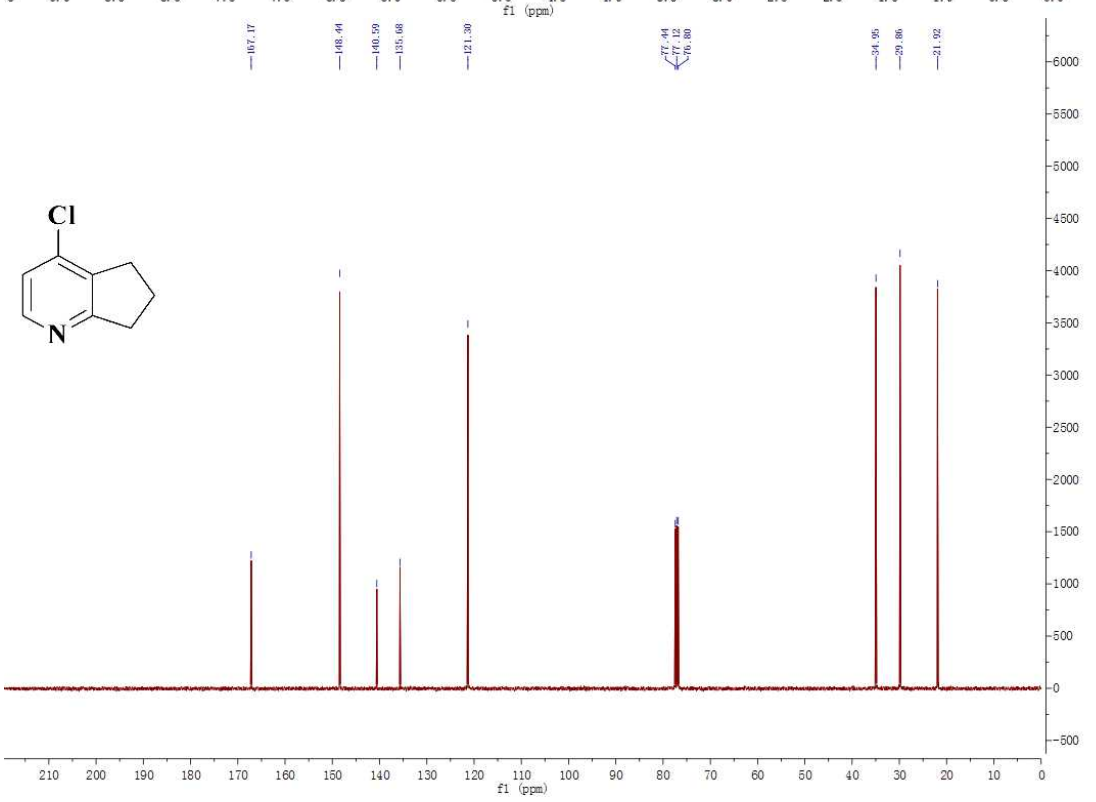
1.00
2.15
2.12
2.12
f1 (ppm)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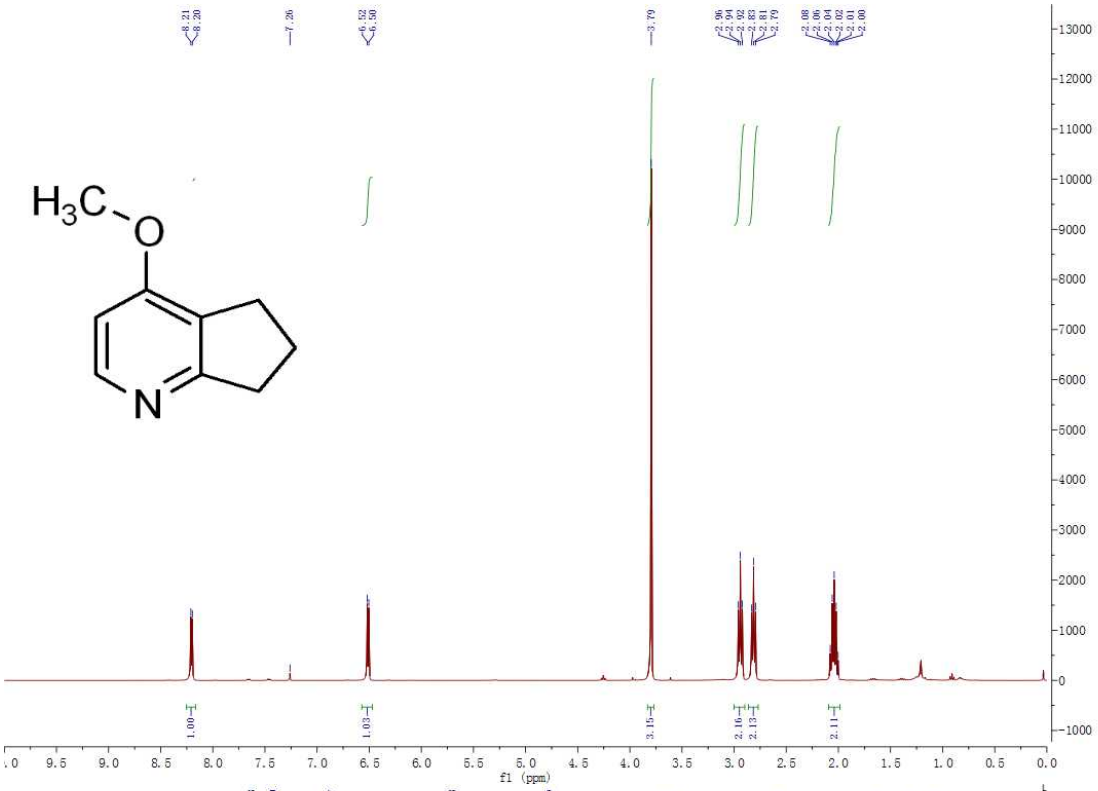
77.12
76.80
34.95
29.86
21.92
Cl
N
f1 (ppm)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2.94
2.92
2.83
2.81
2.79
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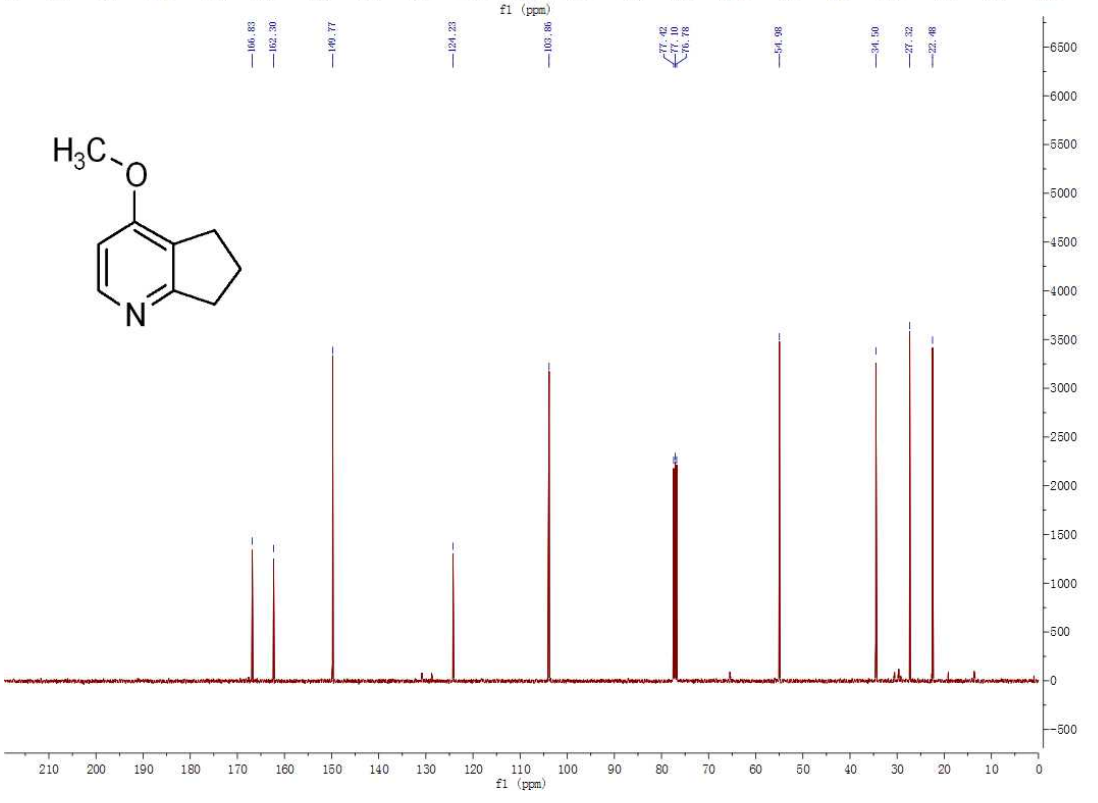
3.15
2.16
2.13
2.11
f1 (ppm)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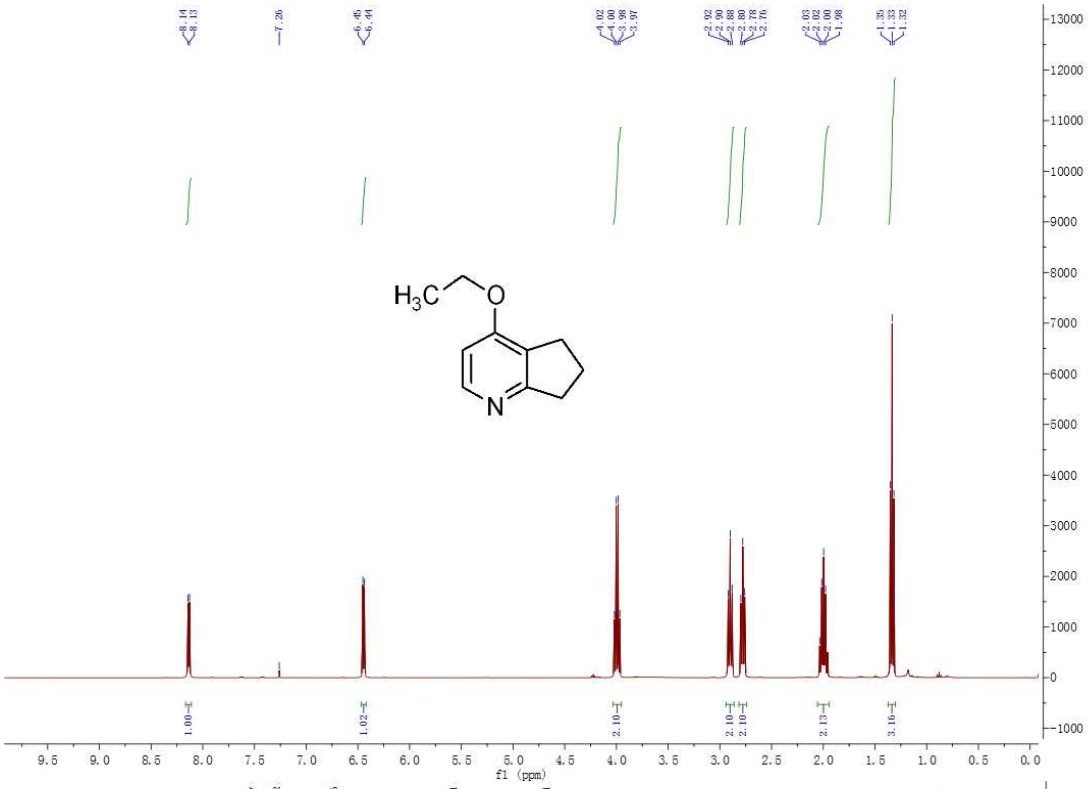
76.78
54.98
34.50
27.32
22.48
f1 (ppm)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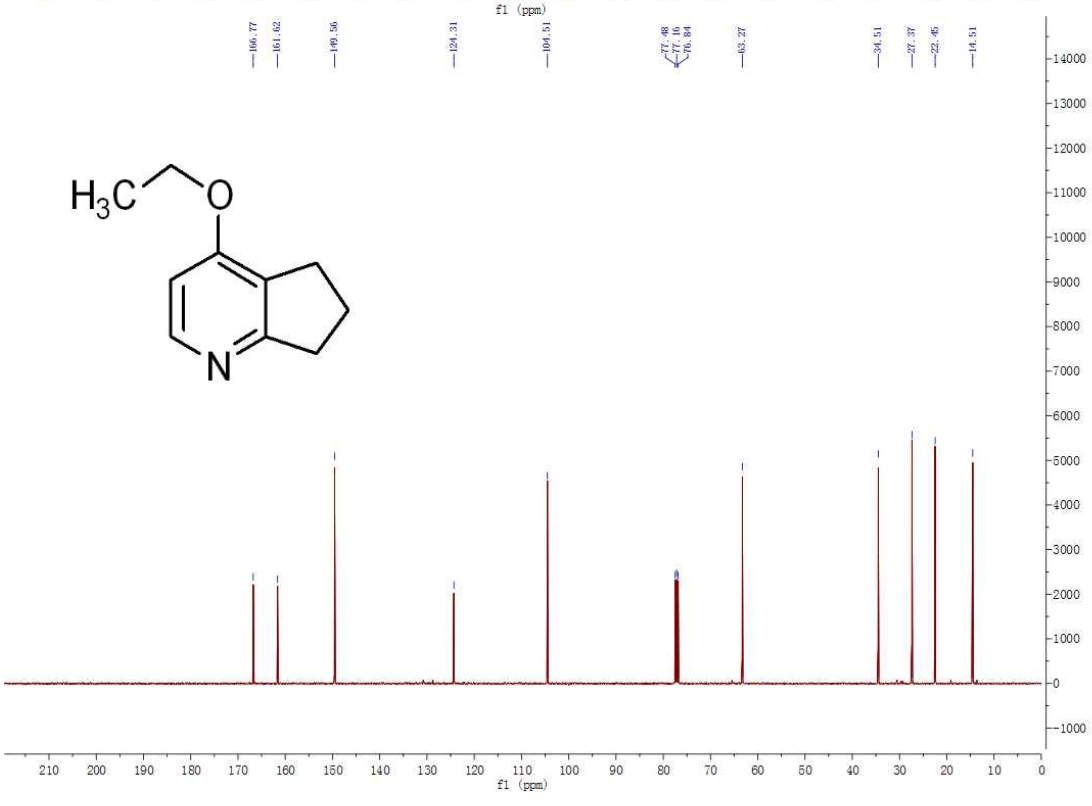
6.44
4.02
4.00
3.98
3.97
2.92
2.89
2.88
2.80
2.78
2.76
2.03
2.02
2.00
1.98
1.35
1.33
1.32
H3C
O
N
1.00
1.02
2.10
2.10
2.10
2.13
3.16
f1 (ppm)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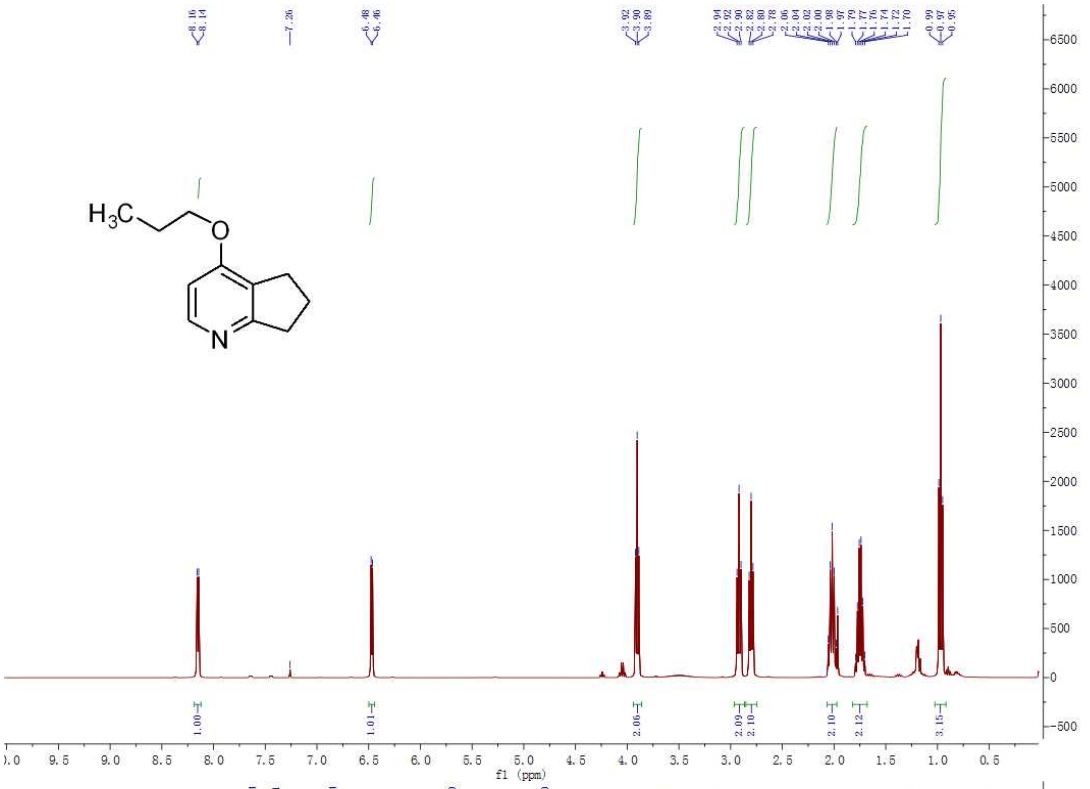
76.84
63.27
34.51
27.37
22.45
14.51
H3C
O
N
f1 (ppm)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6.46
3.92
3.90
3.89
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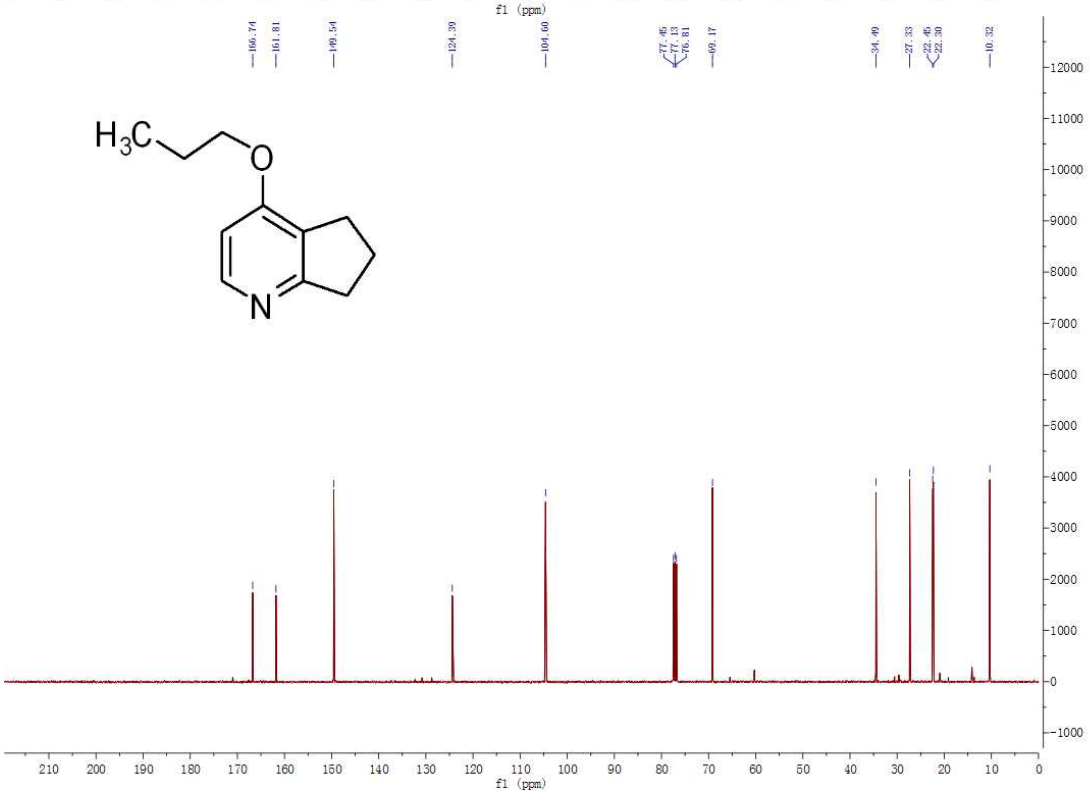
2.92
2.90
2.82
2.80
2.78
2.06
2.04
2.02
2.00
1.98
1.97
1.79
1.77
1.76
1.74
1.72
1.70
0.99
0.97
0.95
H3C
O
N
1.00
1.01
2.06
2.09
2.10
2.10
2.12
3.15
f1 (ppm)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104.60
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77.13
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69.17
34.49
27.33
22.45
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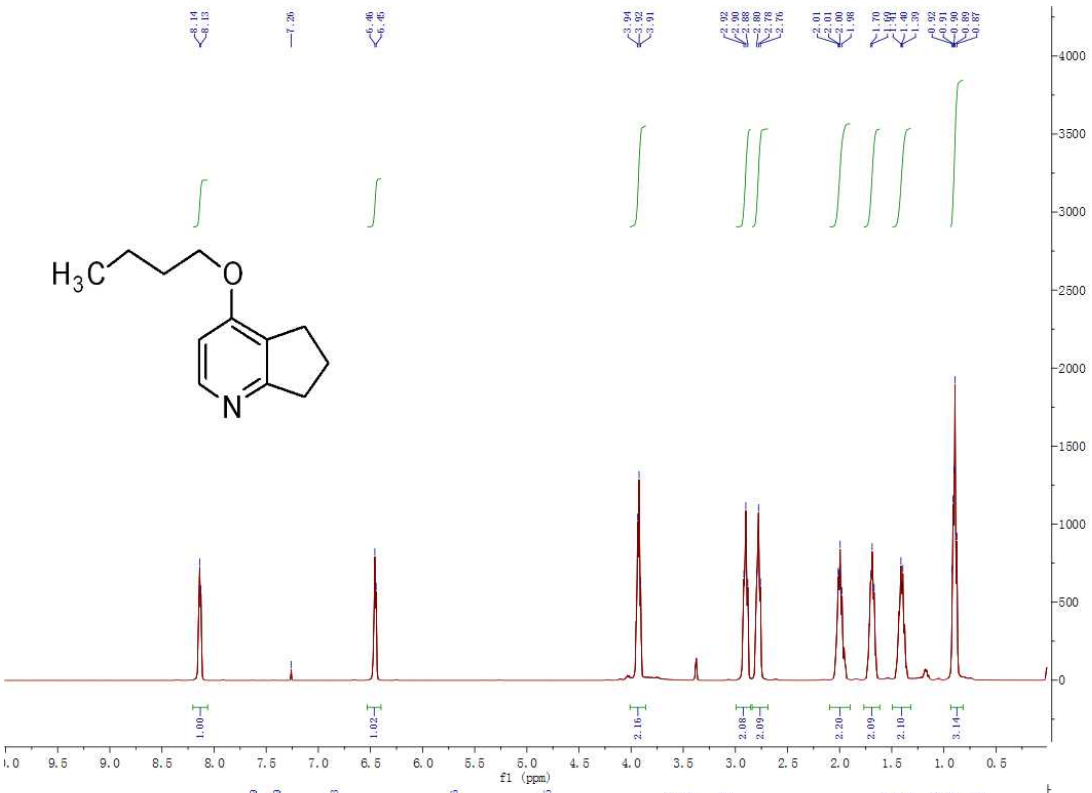
10.32
H3C
O
N
f1 (ppm)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2.88
2.80
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2.76
2.01
2.01
2.00
1.98
1.70
1.69
1.41
1.40
1.39
0.92
0.91
0.90
0.89
0.87
H3C
O
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1.02
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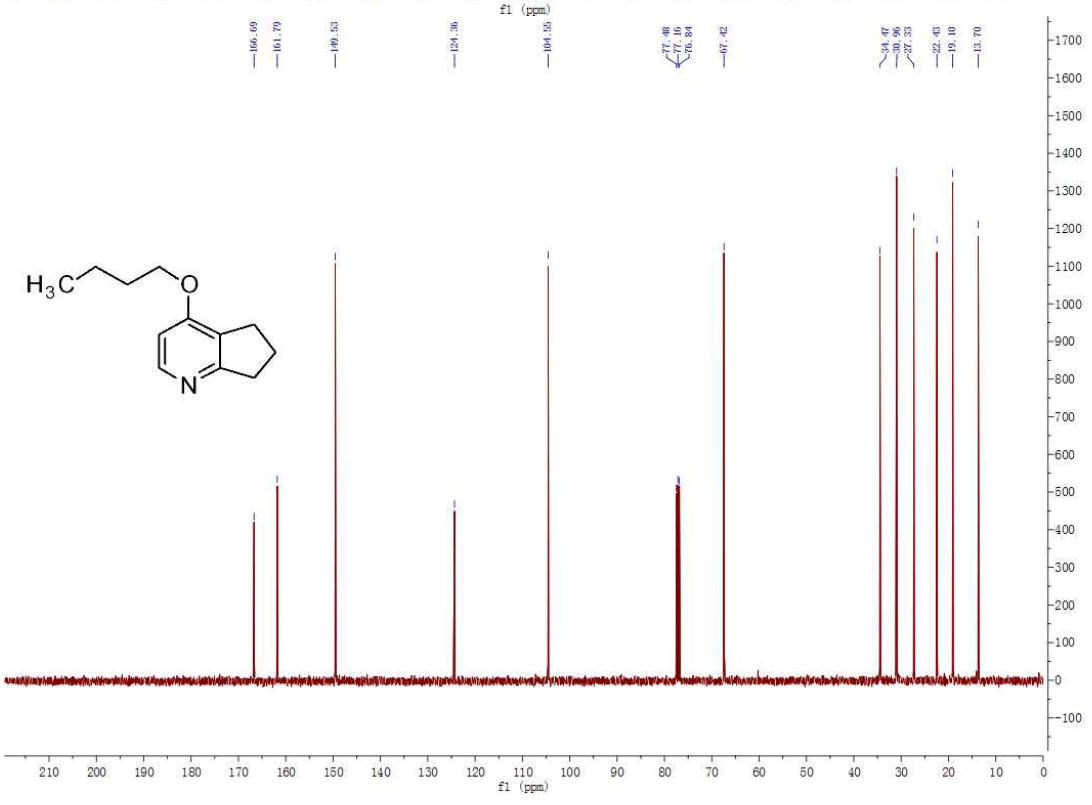
2.08
2.09
2.20
2.09
2.10
3.14
f1 (ppm)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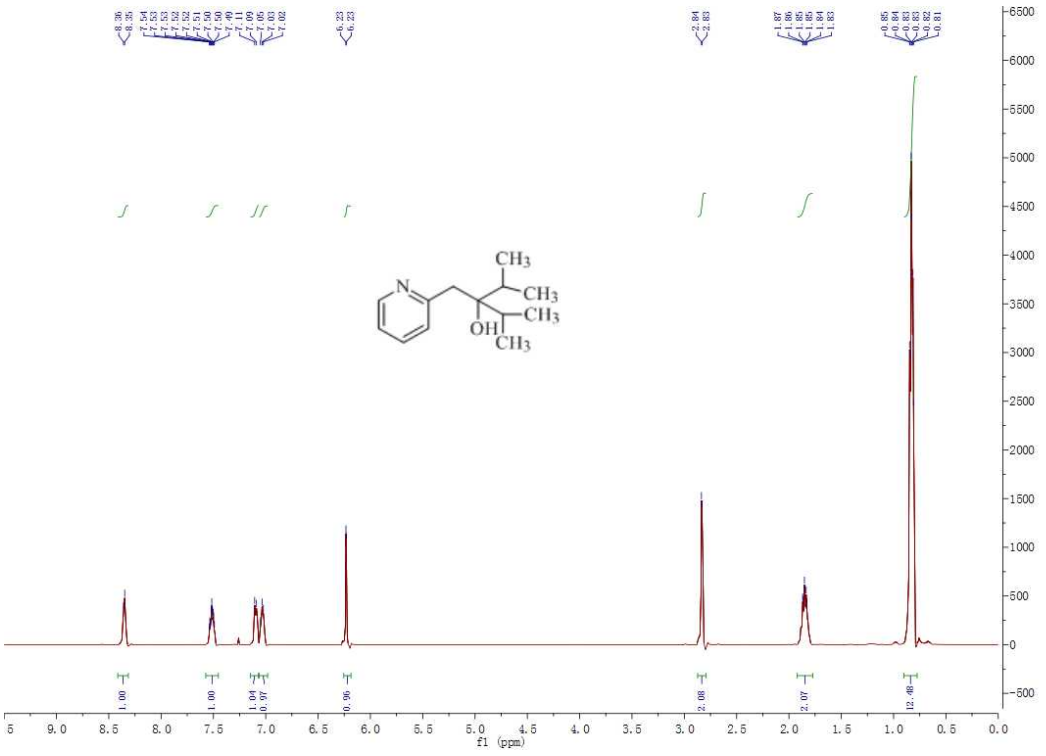
27.33
22.43
19.10
13.70
H3C
O
N
f1 (ppm)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7.51
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7.50
7.49
7.49
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7.09
7.05
7.03
7.02
6.23
6.23
2.84
2.83
1.87
1.86
1.85
1.85
1.84
1.83
0.85
0.84
0.83
0.83
0.82
0.81
CH3
CH3
CH3
OH
CH3
N
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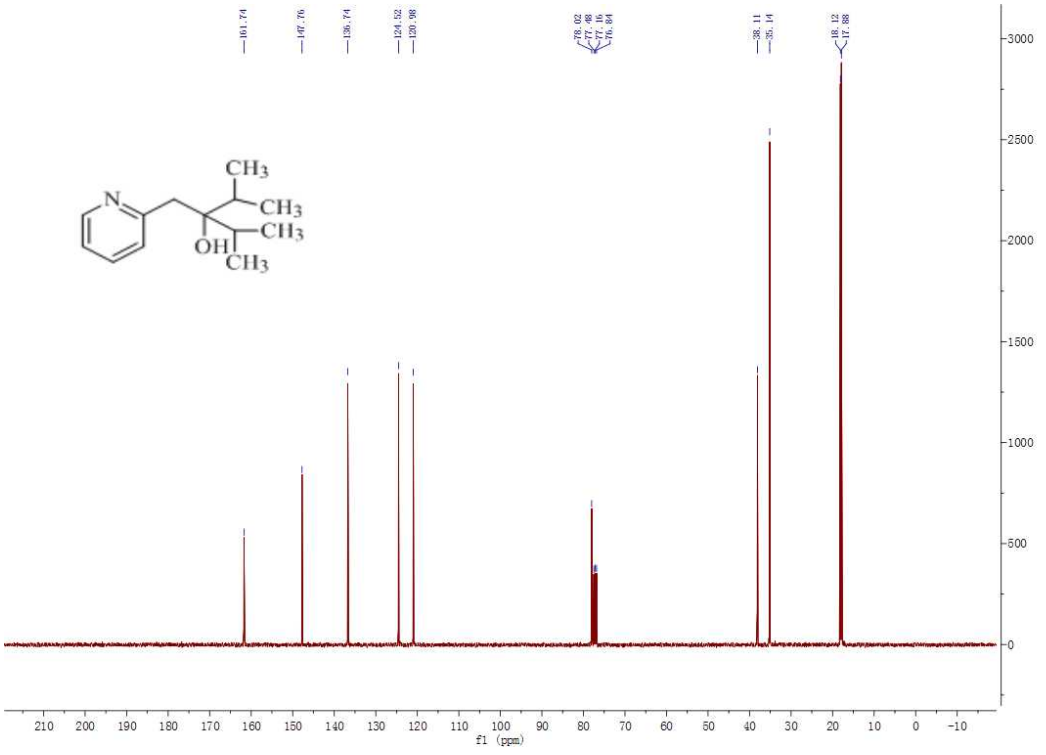
1.00
1.04
0.97
0.96
2.08
2.07
12.48
f1 (ppm)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136.74
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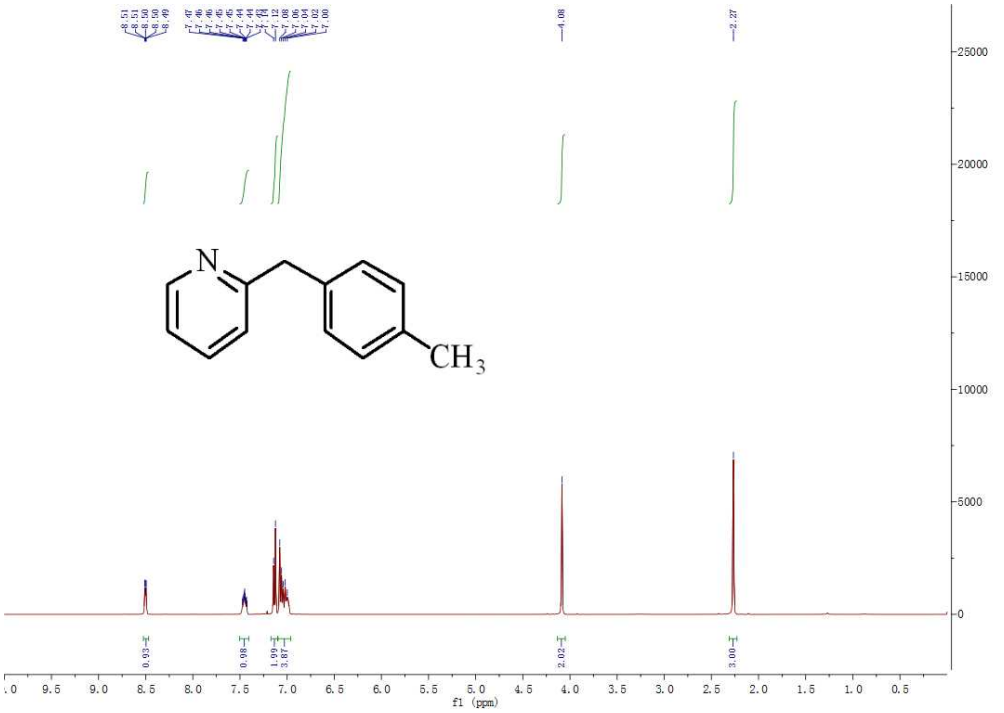
120.98
78.02
77.48
77.16
76.84
38.11
35.14
18.12
17.88
CH3
CH3
CH3
OH
CH3
N
f1 (ppm)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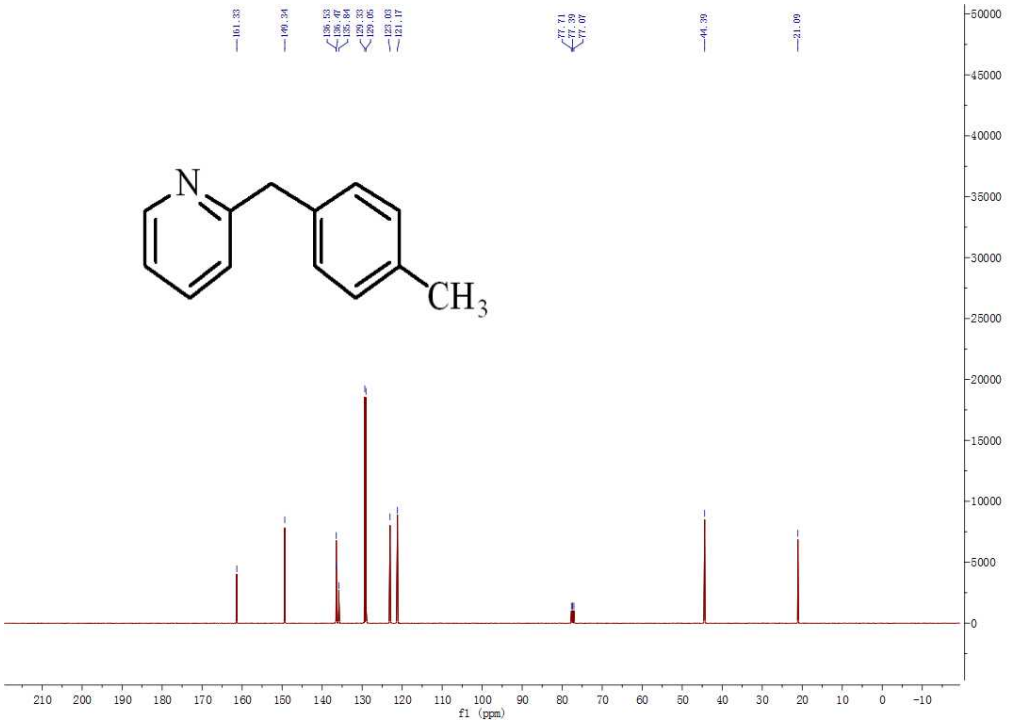
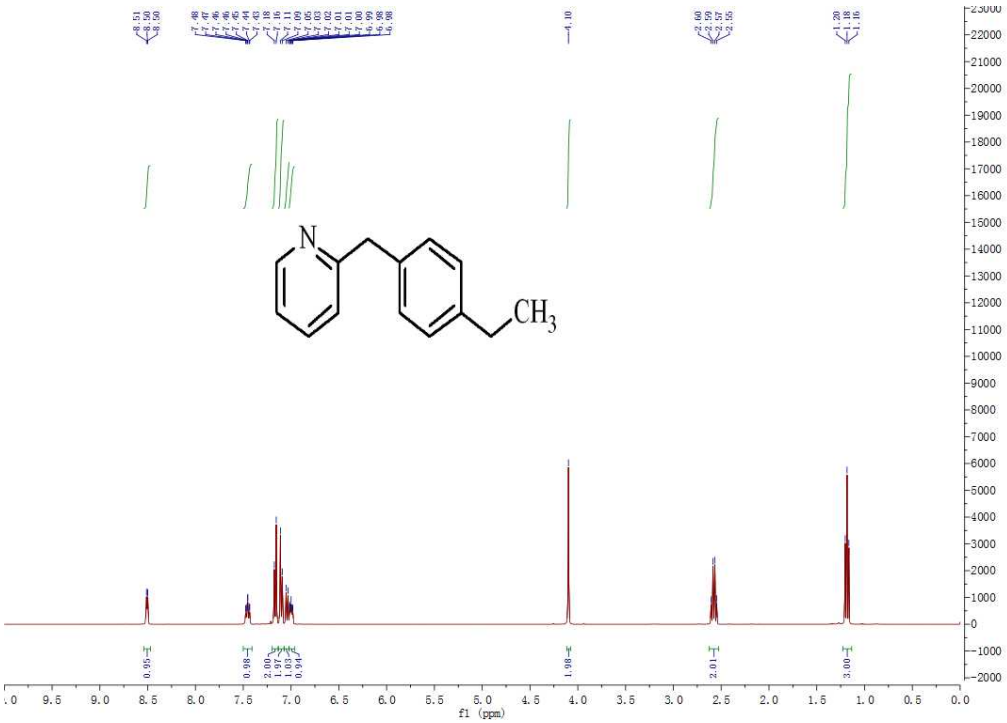
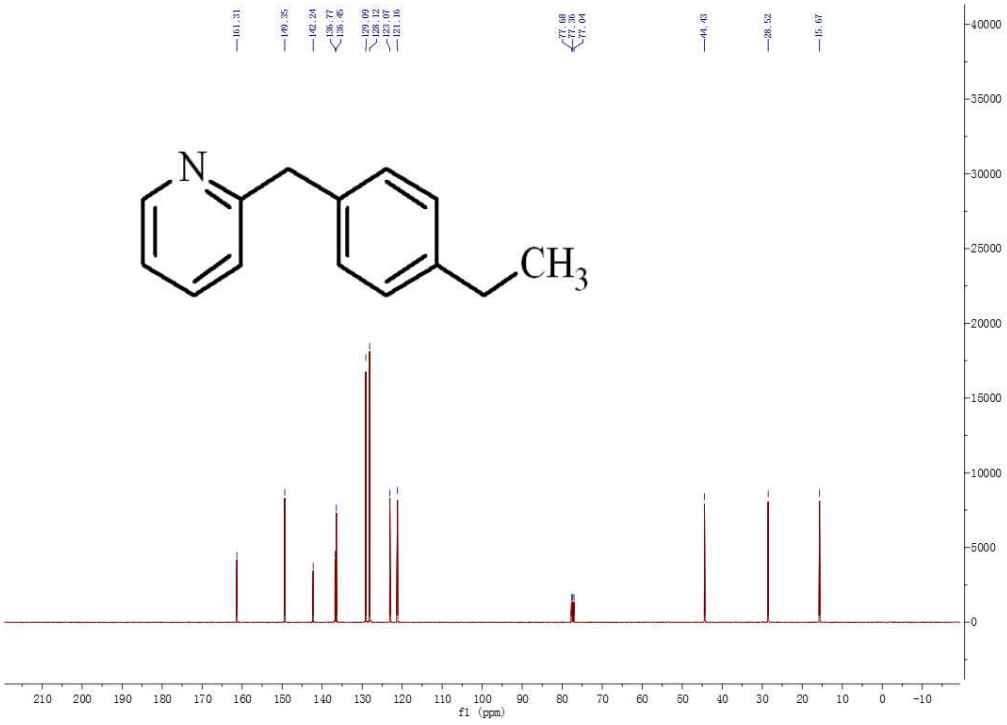
7.45
7.44
7.12
7.08
7.06
7.04
7.02
7.00
4.08
2.27
N
CH3
25000
20000
15000
10000
5000
0
0.93
0.98
1.97
3.87
2.03
3.00
f1 (ppm)


161.33
149.34
136.53
136.47
135.84
129.33
129.05
123.03
121.17
77.71
77.39
77.07
44.39
21.09
N
CH3
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
f1 (ppm)


8.51
8.50
8.50
7.48
7.47
7.46
7.46
7.45
7.44
7.43
7.18
7.11
7.10
7.05
7.03
7.02
7.01
7.01
7.00
6.99
6.98
4.10
2.60
2.59
2.57
2.55
1.20
1.18
1.16
N
CH3
0.95
0.98
2.00
1.97
1.03
0.94
1.98
2.01
3.00
f1 (ppm)


161.31
149.35
142.24
136.77
136.46
129.09
128.12
123.07
121.16
77.68
77.36
77.04
44.43
28.52
15.67
N
CH3
f1 (ppm)