Supporting Information

Palladium-Catalyzed Heck-type Reaction of Oximes with Allylic Alcohols: Synthesis of Pyridines and Azafluorenones

Meifang Zheng, Pengquan Chen, Wanqing Wu, Huanfeng Jiang *

School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510640, China

E-mail: jianghf@scut.edu.cn; Fax and Tel.: (+86) 20-87112906

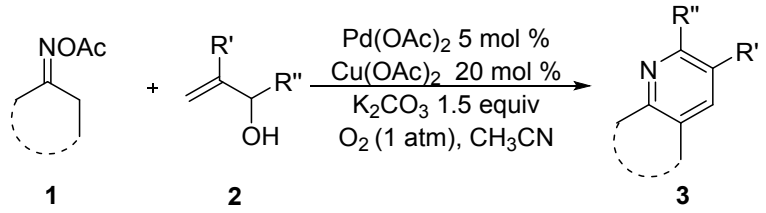
Lists of Contents

General Information

^{1}H and ^{13}C NMR spectra were recorded on BRUKER DRX-400 spectrometer using $CDCl_3$ as solvent and TMS as an internal standard. Gas chromatograph mass spectra were obtained with a SHIMADZU model GCMS-QP5000 spectrometer. High-resolution mass spectra (ESI) were obtained with a LCMS-IT-TOF mass spectrometer. Unless otherwise stated, all reagents and solvents were purchased from commercial suppliers and used without further purification. Oxime acetates were synthesized according to the literature procedure.

General Procedure for the Synthesis of Pyridines

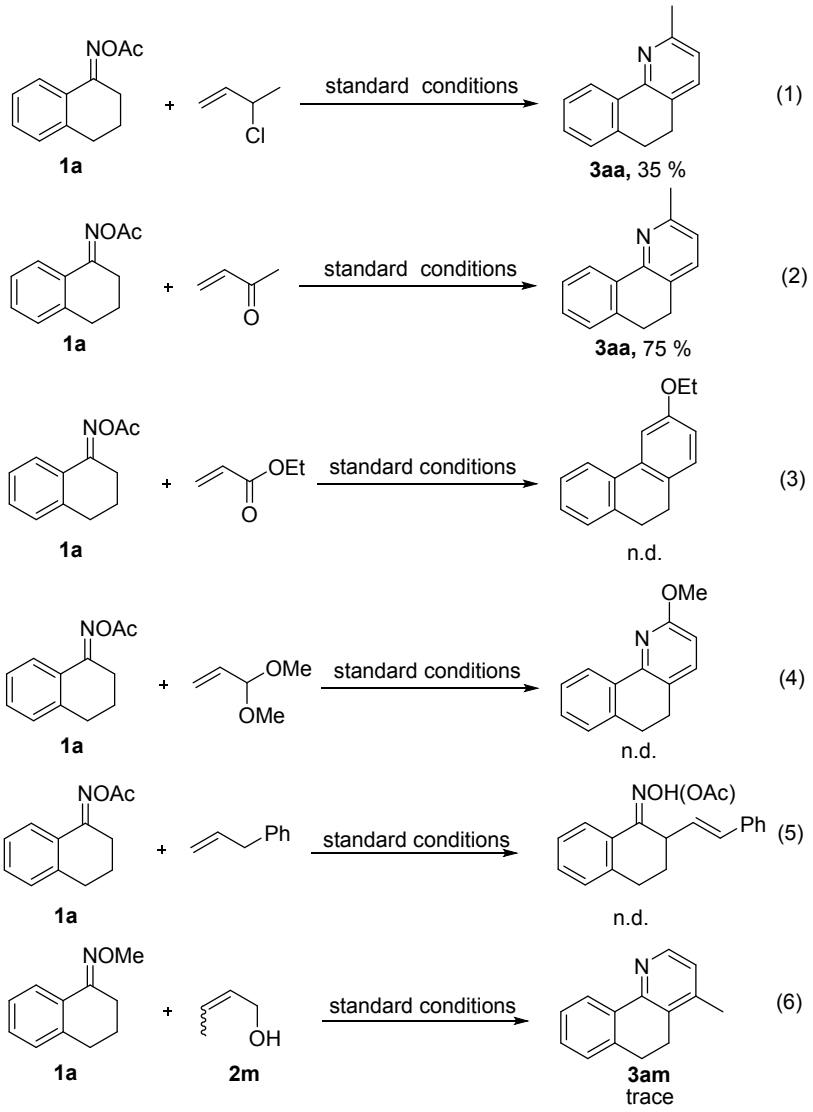
To a tube was added oxime **1** (0.5 mmol), allylic alcohols **2** (1.0 mmol), $Pd(OAc)_2$ (0.025 mmol), $Cu(OAc)_2$ (0.1 mmol), K_2CO_3 (0.75 mol) and CH_3CN (1 mL). The mixture was stirred at 80 ^{o}C for overnight. After the reaction was finished, the reaction mixture was cooled to room temperature, diluted in diethyl ether, and washed with NaCl aqueous solution. The aqueous phase was re-extracted with diethyl ether. The combined organic extracts were dried over $MgSO_4$ and concentrated in vacuum, and the resulting residue was purified by silica gel column chromatography using light petroleum ether/ethyl acetate as eluent to afford the desired products.



Control Experiments

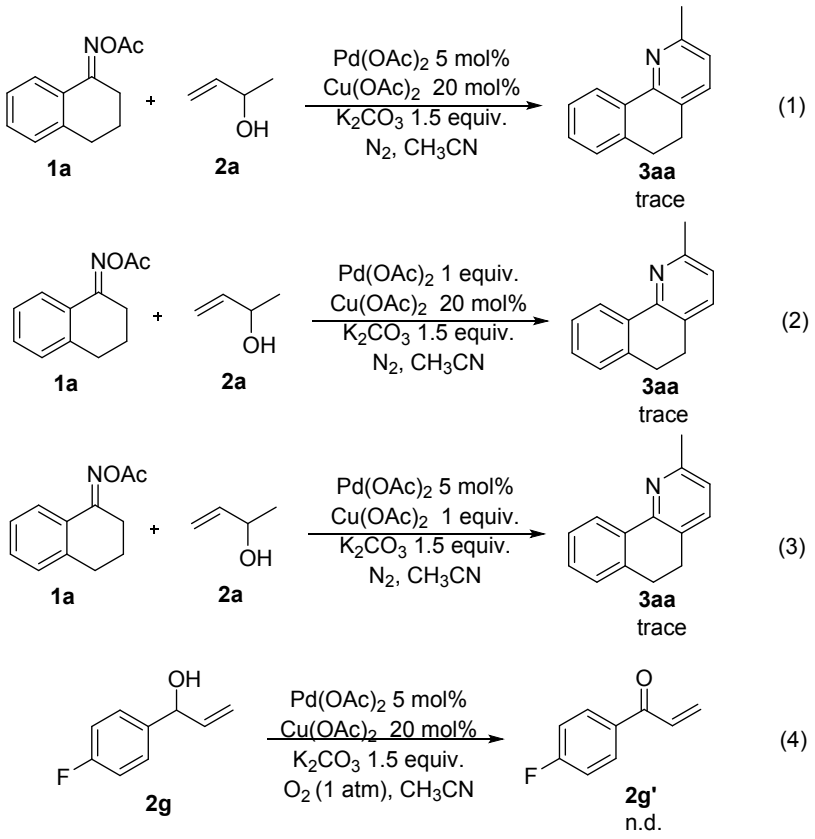
To gain more insight into the mechanism of this oxidative cyclization, several control experiments were conducted. To a tube were added oxime (0.5 mmol), $Pd(OAc)_2$ (0.025 mmol), $Cu(OAc)_2$ (0.1 mmol), K_2CO_3 (0.75 mol), CH_3CN (1 mL) and other alkenes (1.0 mmol) accordingly. The reaction was operated at 80 ^{o}C and stirred for overnight. After the reaction was finished, the reaction mixture was cooled to room temperature, diluted in diethyl ether, and washed with NaCl aqueous solution. The aqueous phase was re-extracted with diethyl ether. The combined organic extracts were dried over $MgSO_4$ and concentrated in vacuum, and the resulting residue was purified by silica gel column chromatography using light petroleum ether/ethyl acetate as eluent to afford the desired products.

The desired product **3aa** was obtained only in relatively low yield when 3-chlorobut-1-ene was added [eqn (1)] and but-3-en-2-one with good yield of 75% [eqn (2)]. However, with the addition of ethyl acrylate [eqn (3)], 3,3-dimethoxyprop-1-ene [eqn (4)] and allylbenzene [eqn (5)], no corresponding Heck reaction products were obtained.



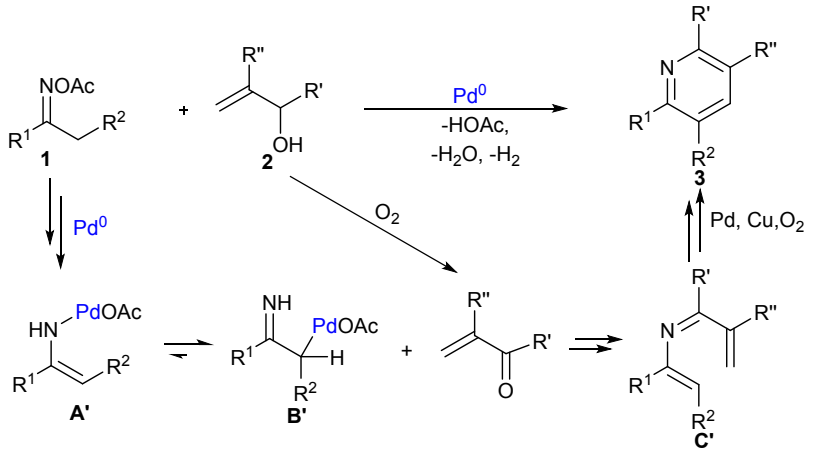
Scheme 1. Scope of alkenes

Next, we tried to explore the role of dioxygen (Scheme 2). When the reaction was carried out in N_2 atmosphere, only trace amount of **3aa** was detected by GC-MS [eqn (2)]. Increasing the amount of [Pd] and [Cu] catalysts did not improve the yield of **3aa** [eqn (2) and (3)].



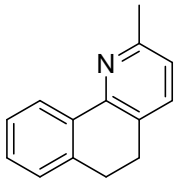
Scheme 2. Control experiments

Based on the experimental results and previous reports, herein, an alternative mechanism is proposed (Scheme 3). Firstly, the oxidative addition of the oxime N-O bond to Pd(0) species easily transformed to palladium enamide intermediate **A'**. Subsequent tautomerization affords the enamine-derived amido-Pd(II) species **B'**. Further condesation of **B'** with vinyl ketone results in imine species **C'**. Finally, the cyclization oxidation of intermediate **C'** gives the pyridine product **3**.



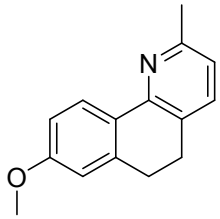
Scheme 3. Possible mechanism

Characterization Data for Products



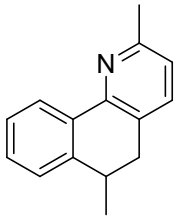
2-Methyl-5,6-dihydrobenzo[*h*]quinoline (3aa)

Pale yellow oil. Yield (84.8 mg, 87%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (d, *J* = 7.6 Hz, 1H), 7.36 (m, 2H), 7.28 (t, *J* = 7.3 Hz, 1H), 7.21 (d, *J* = 7.3 Hz, 1H), 6.98 (d, *J* = 7.6 Hz, 1H), 2.90 (s, 4H), 2.59 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.3, 151.7, 138.2, 136.0, 134.7, 128.9, 128.7, 127.7, 127.1, 125.0, 121.8, 28.3, 27.7, 24.4. IR (KBr) ν (cm^{-1}): 3483, 3407, 3243, 3271, 3068, 2967, 1630, 1437, 1366, 613, 483. ESI-HRMS calcd for $[M + H]^+$ $C_{14}H_{14}N$, 196.1121; found, 196.1121.



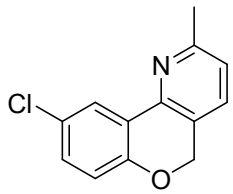
8-Methoxy-2-methyl-5,6-dihydrobenzo[*h*]quinoline (3ba)

Pale yellow solid; mp: 60-62 °C. Yield (70.9 mg, 63%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, *J* = 8.6 Hz, 1H), 7.33 (d, *J* = 7.6 Hz, 1H), 6.89 (m, 2H), 6.74 (s, 1H), 3.83 (s, 3H), 2.86 (s, 4H), 2.57 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.3, 156.2, 151.8, 140.0, 135.7, 127.9, 127.6, 126.6, 120.9, 113.1, 112.5, 55.3, 28.7, 27.8, 24.4. IR (KBr) ν (cm^{-1}): 3519, 3442, 3304, 3172, 3127, 3075, 1432, 1375, 754. ESI-HRMS calcd for $[M + H]^+$ $C_{15}H_{16}NO$, 226.1226; found, 226.1231.



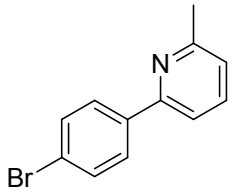
2,6-Dimethyl-5,6-dihydrobenzo[*h*]quinoline (3ca)

Pale yellow oil. Yield (82.5 mg, 79%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (d, *J* = 6.9 Hz, 1H), 7.35 (m, 3H), 7.25 (d, *J* = 5.7 Hz, 1H), 6.98 (d, *J* = 7.6 Hz, 1H), 3.04 (d, *J* = 13.0 Hz, 2H), 2.66 (m, 1H), 2.60 (s, 3H), 1.22 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.2, 151.3, 143.0, 136.6, 129.2, 127.4, 127.0, 126.3, 125.2, 121.9, 35.3, 32.4, 24.4, 20.2. IR (KBr) ν (cm^{-1}): 3589, 3518, 3444, 3304, 3171, 3129, 3073, 1704, 1433, 1370, 660 ESI-HRMS calcd for $[M + H]^+$ $C_{15}H_{16}N$, 210.1277; found, 210.1280.



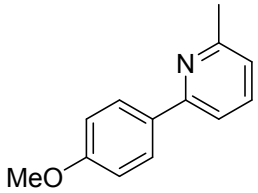
9-Chloro-2-methyl-5*H*-chromeno[4,3-*b*]pyridine (3da)

Pale yellow solid; mp 87-89 °C. Yield (68.1 mg, 59%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (s, 1H), 7.31 (d, *J* = 7.7 Hz, 1H), 7.22 (d, *J* = 8.5 Hz, 1H), 7.06 (d, *J* = 7.7 Hz, 1H), 6.88 (d, *J* = 8.5 Hz, 1H), 7, 5.18 (s, 2H), 2.60 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.5, 154.8, 146.8, 132.4, 130.7, 127.5, 124. 124.6, 122.9, 122.5, 118.3, 67.91, 24.5. IR (KBr) ν (cm^{-1}): 3648, 3519, 3443, 3305, 3127, 3075, 2925, 1704, 1434, 1375, 659. ESI-HRMS calcd for $[M + H]^+$ $C_{13}H_{11}ClNO$, 232.0524, 233.0554, 234.0494; found, 232.0524, 233.0556, 234.0497.



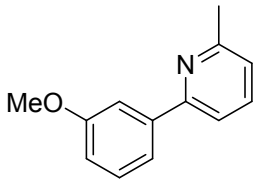
2-(4-Bromophenyl)-6-methylpyridine (3ea)

Pale yellow solid; mp 73-75 °C. Yield (109.9 mg, 89%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.4 Hz, 2H), 7.59 (m, 3H), 7.47 (d, *J* = 7.9 Hz, 1H), 7.09 (d, *J* = 7.6 Hz, 1H), 2.61 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.6, 155.7, 138.6, 137.0, 133.40, 132.7, 131.8, 128.6, 123.2, 122.0, 117.3, 24.7. IR (KBr) ν (cm^{-1}): 3518, 3444, 3304, 3129, 3073, 1705, 1433, 1370, 1204, 660. ESI-HRMS calcd for $[M + H]^+$ $C_{12}H_{11}BrN$, 248.0069, 249.0101, 250.0052; found, 248,0074, 249.0101, 250.0050.



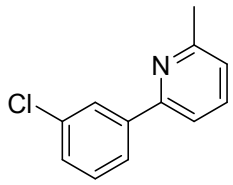
2-(4-Methoxyphenyl)-6-methylpyridine (3fa)

Pale yellow oil. Yield (79.6 mg, 80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.1 Hz, 2H), 7.59 (t, *J* = 7.7 Hz, 1H), 7.45 (d, *J* = 7.9 Hz, 1H), 7.04 (d, *J* = 7.6 Hz, 1H), 6.98 (d, *J* = 8.2 Hz, 2H), 3.85 (s, 3H), 2.61 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.3, 158.2, 156.6, 136.9, 132.3, 128.3, 120.9, 116.9, 114.1, 55.3, 24.7. IR (KBr) ν(cm^{-1}): 3651, 3519, 3444, 3242, 3128, 3072, 2920, 1708, 1436, 1368, 566. ESI-HRMS calcd for $[M + H]^+$ $C_{13}H_{14}NO$, 200.1070; found, 200.1069.



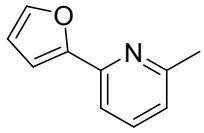
2-(3-Methoxyphenyl)-6-methylpyridine (3ga)

Pale yellow oil. Yield (68.6mg, 69%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.4 Hz, 2H), 7.61 (t, *J* = 7.6 Hz, 1H), 7.46 (d, *J* = 7.8 Hz, 1H), 7.01 (m, 3H), 3.86 (s, 3H), 2.62 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.0, 157.0, 155.5, 135.8, 133.8, 131.2, 129.7, 122.1, 121.2, 121.1, 111.4, 55.6, 24.7. IR (KBr) ν (cm^{-1}): 3587, 3518, 3443, 3304, 3127, 3075, 2972, 1433, 1374, 660. ESI-HRMS calcd for $[M + H]^+$ $C_{13}H_{14}NO$, 200.1070; found, 200.1072.



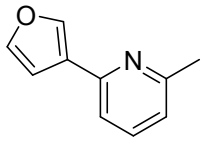
2-(3-Chlorophenyl)-6-methylpyridine (3ha)

Pale yellow oil. Yield (58.9 mg, 58%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (s, 1H), 7.88 (d, *J* = 6.6 Hz, 1H), 7.67 (t, *J* = 7.7 Hz, 1H), 7.52 (d, *J* = 7.8 Hz, 1H), 7.40 (d, *J* = 6.6 Hz, 2H), 7.15 (d, *J* = 7.6 Hz, 1H), 2.66 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.6, 155.4, 141.4, 137.1, 134.8, 129.9, 128.7, 127.2, 125.1, 122.2, 117.7, 24.6. IR (KBr) ν (cm^{-1}): 3650, 3519, 3444, 3303, 3129, 3073, 2850, 1706, 1433, 1370, 662. ESI-HRMS calcd for $[M + H]^+$ $C_{12}H_{11}ClN$, 204.0575, 205.0596, 206.0597; found, 204.0570, 205.0607, 206.0547.



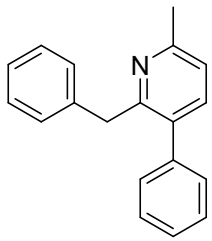
2-(Furan-2-yl)-6-methylpyridine (3ia)

Pale yellow oil. Yield (44.5 mg, 56%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (d, *J* = 4.8 Hz, 1H), 7.52 (s, 2H), 7.05 (s, 1H), 6.98 (d, *J* = 4.5 Hz, 1H), 6.52 (d, *J* = 1.4 Hz, 1H), 2.4 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.6, 149.2, 149.1, 147.91, 143.18, 123.0, 119.4, 112.0, 108.5, 21.2. IR (KBr) ν (cm^{-1}): 3589, 3518, 3444, 3304, 3129, 3073, 2923, 1705, 1434, 1370, 661, 563. ESI-HRMS calcd for $[M + H]^+$ $C_{10}H_{10}NO$, 160.0757; found, 160.0759.



2-(Furan-3-yl)-6-methylpyridine (3ja)

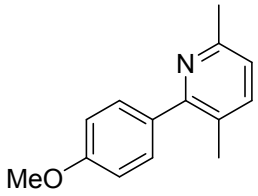
Pale yellow oil. Yield (58.8 mg, 74%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (t, *J* = 7.7 Hz, 1H), 7.50 (m, 2H), 7.03 (m, 2H), 6.51 (s, 1H), 2.60 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.4, 143.3, 136.9, 121.6, 115.8, 111.9, 108.6, 24.6. IR (KBr) ν (cm^{-1}): 3652, 3520, 3442, 3240, 3127, 3074, 2931, 1707, 1438, 1364, 566. ESI-HRMS calcd for $[M + H]^+$ $C_{10}H_{10}NO$, 160.0757; found, 160.0751.



2-Benzyl-6-methyl-3-phenylpyridine (3ka)

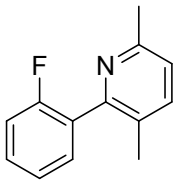
Pale yellow oil. Yield (99.7 mg, 77%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 7.3 Hz, 2H), 7.39 (t, *J* = 7.6 Hz, 2H), 7.29 (m, 5H), 7.22 (d, *J* = 14.9 Hz, 1H), 4.09 (s, 2H), 2.48 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.0, 146.2, 138.8, 134.2, 128.9, 128.8, 128.6, 128.4, 127.8, 126.4, 125.46, 33.0, 14.1.

IR (KBr) ν (cm^{-1}): 3450, 3373, 3301, 3128, 3072, 1590, 1435, 1367, 648, 590, 510. ESI-HRMS calcd for $[M + H]^+$ $C_{19}H_{18}N$, 260.1434; found, 260.1438.



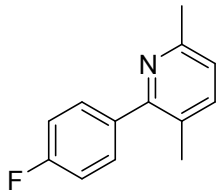
2-(4-Methoxyphenyl)-3,6-dimethylpyridine (3la)

Pale yellow oil. Yield (89.4 mg, 84%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.44 (t, *J* = 8.6 Hz, 3H), 6.98 (m, 3H), 3.84 (s, 3H), 2.55 (s, 3H), 2.29 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.3, 157.6, 155.3, 138.8, 133.5, 130.3, 127.3, 121.3, 113.6, 55.3, 24.2, 19.7. IR (KBr) ν (cm^{-1}): 3587, 3519, 3443, 3305, 3174, 3074, 1438, 1364, 782, 653, 554. ESI-HRMS calcd for $[M + H]^+$ $C_{14}H_{16}NO$, 214.1226; found, 214.1230.



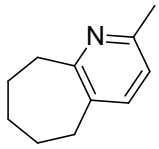
2-(2-Fluorophenyl)-3,6-dimethylpyridine (3ma)

Pale yellow oil. Yield (71.4 mg, 71%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 7.8 Hz, 1H), 7.37 (m, 2H), 7.22 (t, *J* = 7.4 Hz, 1H), 7.10 (m, 2H), 2.56 (s, 3H), 2.17 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.9, 158.5, 155.5, 153.3 138.2, 131.3, 131.3, 129.9, 129.8, 129.3, 128.7, 128.5, 124.4, 124.4, 122.4, 115.7, 115.5, 24.1, 18.4, 18.4. IR (KBr) ν (cm^{-1}): 3586, 3519, 3443, 3305, 3173, 3127, 3074, 1436, 1374, 816, 756. ESI-HRMS calcd for $[M + H]^+$ $C_{13}H_{13}FN$, 202.1027; found, 202.1028.



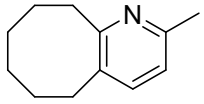
2-(4-Fluorophenyl)-3,6-dimethylpyridine (3na)[1]

Pale yellow oil. Yield (89.4 mg, 84%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 7.8 Hz, 1H), 7.38 (m, 2H), 7.23 (t, *J* = 7.5 Hz, 1H), 7.11 (m, 2H), 2.57 (s, 3H), 2.18 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.9, 158.5, 155.5, 153.3, 138.2, 131.3, 129.9, 129.3, 128.6, 124.4, 122.4 , 115.7, 115.5, 24.1, 18.4. IR (KBr) ν (cm^{-1}): 3518, 3305, 3170, 3127, 3075, 1703, 1430, 1375, 660. *m/z* (EI): 201.



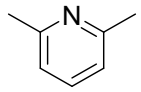
2-Methyl-6,7,8,9-tetrahydro-5*H*-cyclohepta[*b*]pyridine (3oa)[2]

Pale yellow oil. Yield (49.9 mg, 62%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (s, 1H), 6.87 (d, *J* = 7.5 Hz, 1H), 3.02 (m, 2H), 2.73 (m, 2H), 2.49 (s, 3H), 1.85 (m, 2H), 1.66 (m, 4H). ^{13}C NMR (101 MHz, CDCl3) δ 162.4, 154.2, 137.1, 135.0, 120.6, 39.1, 34.8, 32.5, 28.1, 26.5, 23.7. IR (KBr) ν (cm^{-1}): 3518, 3305, 3170, 3127, 3075, 1703, 1430, 1375, 660. *m/z* (EI): 161.



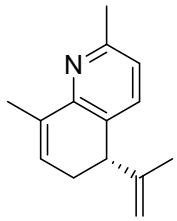
2-Methyl-5,6,7,8,9,10-hexahydrocycloocta[*b*]pyridine (3pa)

Pale yellow oil. Yield (43.1 mg, 49%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.27 (d, *J*=6.1, 1H), 6.92 (d, *J*=7.6, 1H), 2.95 (m, 2H), 2.73 (m, 2H), 2.51 (s, 3H), 1.78 (m, 2H), 1.67 (m, 2H), 1.38 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.1, 155.2, 137.1, 132.9, 121.1, 34.4, 32.2, 31.5, 30.7, 26.0, 25.9, 23.9. IR (KBr) ν (cm^{-1}): 3519, 3444, 3381, 3172, 3128, 3073, 1706, 1434, 1370, 662. ESI-HRMS calcd for $[M + H]^+$ $C_{12}H_{18}N$, 176.1434; found, 176.1438.



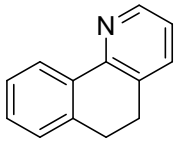
2,6-Dimethylpyridine (3qa)

Colorless oil. Yield (27.8 mg, 52%). ^{1}H NMR (400 MHz, CDCl3) δ 7.43 (m, 1H), 6.93 (m, 2H), 2.51 (s, 6H). ^{13}C NMR (101 MHz, CDCl3) δ 157.6, 136.5, 120.1, 24.4. IR (KBr) ν (cm^{-1}): 3519, 3444, 3381, 3172, 3128, 3073, 1706, 1434, 1370, 662. *m/z* (EI) 107.



(S)-2,8-Dimethyl-5-(prop-1-en-2-yl)-5,6-dihydroquinoline (3ra)

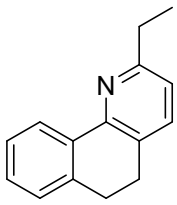
Pale yellow oil. Yield (42.8 mg, 43%). ^{1}H NMR (400 MHz, CDCl3) δ 7.23 (d, J = 7.7 Hz, 1H), 6.91 (d, J = 7.7 Hz, 1H), 6.05 (s, 1H), 4.90 (s, 1H), 4.75 (s, 1H), 3.56 (t, J = 8.7 Hz, 1H), 2.52 (s, 3H), 2.39 (m, , 2H), 2.14 (s, 3H), 1.71 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.3, 153.5, 146.1, 134.6, 129.3, 127.6, 121.0, 113.6, 45.5, 29.7, 27.7, 24.2, 19.7, 18.2. IR (KBr) ν (cm^{-1}): 3519, 3444, 3381, 3172, 3128, 3073, 1706, 1434, 1370, 662. ESI-HRMS calcd for $[M + H]^+$ $C_{14}H_{18}N$, 200.1434; found, 200.1433.



5,6-Dihydrobenzo[*h*]quinoline (3ab)

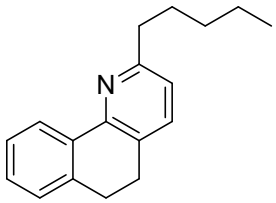
Pale yellow oil. Yield (68.8 mg, 76%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (d, *J* = 4.1 Hz, 1H), 8.32 (d, *J* = 7.5 Hz, 1H), 7.51 (d, *J* = 7.4 Hz, 1H), 7.36 (d, *J* = 7.5 Hz, 1H), 7.31 (s, 1H), 7.24 (m, 2H), 7.14 (d, *J* = 6.5 Hz, 1H), 2.94 (s, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.5, 147.6, 138.2, 135.8, 132.0, 129.2,

127.8, 127.2, 125.0, 122.3, 28.1, 28.0. IR (KBr) ν (cm^{-1}): 3518, 3303, 3129, 3073, 2967, 1433, 1370, 661, 582. ESI-HRMS calcd for $[M + H]^+$ $C_{13}H_{12}N$, 182.0964; found, 182.0970.



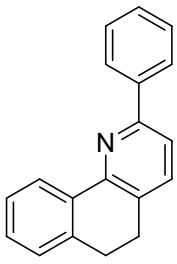
2-Ethyl-5,6-dihydrobenzo[*h*]quinoline (3ac)

Pale yellow oil. Yield (85.7 mg, 82%). ^1H NMR (400 MHz, $CDCl_3$) δ 8.42 (d, *J* = 7.6 Hz, 1H), 7.44 (d, *J* = 7.7 Hz, 1H), 7.39 (t, *J* = 7.4 Hz, 1H), 7.32 (t, *J* = 7.2 Hz, 1H), 7.24 (d, *J* = 7.3 Hz, 1H), 7.03 (d, *J* = 7.7 Hz, 1H), 2.91 (m, 6H), 1.40 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.4, 151.6, 138.2, 136.0, 128.8, 127.7, 127.1, 125.1, 120.5, 31.2, 28.3, 27.7, 13.9. IR (KBr) ν (cm^{-1}): 3587, 3518, 3443, 3304, 3127, 3075, 2972, 1433, 1374, 660. ESI-HRMS calcd for $[M + H]^+$ $C_{15}H_{16}N$, 210.1277; found, 210.1278.



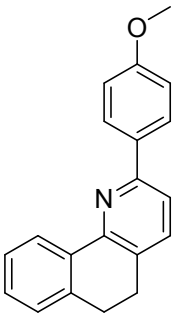
2-Pentyl-5,6-dihydrobenzo[*h*]quinoline (3ad)

Pale yellow oil. Yield (110.4 mg, 88%). ^1H NMR (400 MHz, $CDCl_3$) δ 8.37 (d, *J* = 7.5 Hz, 1H), 7.39 (d, *J* = 7.6 Hz, 1H), 7.35 (t, *J* = 7.5 Hz, 1H), 7.28 (t, *J* = 7.3 Hz, 1H), 7.20 (d, *J* = 7.4 Hz, 1H), 6.97 (d, *J* = 7.7 Hz, 1H), 2.90 (s, 4H), 2.83 (t, *J* = 7.7 Hz, 2H), 1.80 (m, 2H), 1.38 (m, 4H), 0.91 (t, *J* = 6.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.4, 151.6, 138.1, 135.9, 128.8, 127.6, 127.1, 125.1, 121.1, 31.6, 29.5, 28.2, 27.7, 22.6, 14.1. IR (KBr) ν (cm^{-1}): 3651, 3519, 3444, 3242, 3128, 3072, 2920, 1708, 1436, 1368, 566. ESI-HRMS calcd for $[M + H]^+$ $C_{15}H_{16}N$, 252.1745; found, 252.1747.



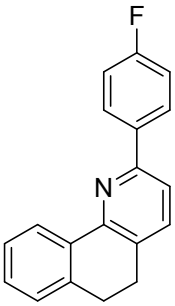
2-Phenyl-5,6-dihydrobenzo[*h*]quinoline (3ae)

Pale yellow solid; mp 103-105 °C. Yield (93.4 mg, 75%). ^1H NMR (400 MHz, $CDCl_3$) δ 8.53 (d, *J* = 7.4 Hz, 1H), 8.14 (d, *J* = 7.3 Hz, 2H), 7.57 (m, 2H), 7.49 (t, *J* = 7.4 Hz, 2H), 7.40 (m, 3H), 7.33 (d, *J* = 7.9 Hz, 1H), 2.97 (s, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.1, 152.1, 139.7, 138.2, 136.4, 134.9, 130.3, 129.1, 128.7, 128.2, 127.8, 127.1, 126.8, 125.3, 118.7, 28.2, 27.8. IR (KBr) ν (cm^{-1}): ESI-HRMS calcd for $[M + H]^+$ $C_{19}H_{16}N$, 258.1277; found, 258.1283.



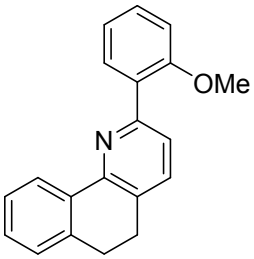
2-(4-Methoxyphenyl)-5,6-dihydrobenzo[*h*]quinoline (3af)

Pale yellow solid; mp 121-123 °C. Yield (101.9 mg, 71%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (d, *J* = 7.6 Hz, 1H), 8.02 (d, *J* = 8.6 Hz, 2H), 7.45 (s, 2H), 7.31 (t, *J* = 7.4 Hz, 1H), 7.24 (t, *J* = 7.3 Hz, 1H), 7.16 (d, *J* = 7.7 Hz, 1H), 6.93 (d, *J* = 8.6 Hz, 2H), 3.79 (s, 3H), 2.88 (s, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.3, 154.8, 151.8, 138.2, 136.3, 134.0, 132.4, 129.6, 129.0, 128.0, 127.7, 127.1, 125.2, 118.0, 114.0, 55.4, 28.2, 27.8. IR (KBr) ν (cm^{-1}): 3516, 3440, 3240, 3126, 3074, 1512, 1400, 1360, 1248, 1176, 1031, 822, 752. ESI-HRMS calcd for $[M + H]^+$ $C_{20}H_{18}NO$, 288.1383; found, 288.1386.



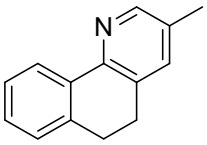
2-(4-Fluorophenyl)-5,6-dihydrobenzo[*h*]quinoline (3ag)

Pale yellow solid; mp 134-136 °C. Yield (108.6 mg, 79%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (d, *J* = 7.3 Hz, 1H), 8.12 (s, 2H), 7.55 (m, 2H), 7.36 (m, 3H), 7.17 (t, *J* = 8.6 Hz, 2H), 2.97 (s, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.0, 138.3, 136.7, 130.4, 129.3, 128.7, 128.6, 127.8, 127.2, 125.4, 118.6, 115.6, 115.42, 28.1, 27.8. IR (KBr) ν (cm^{-1}): 3589, 3518, 3445, 3303, 3128, 3073, 2929, 1584, 1435, 1368, 661, 513. ESI-HRMS calcd for $[M + H]^+$ $C_{19}H_{15}FN$, 276.1183; found, 276.1180.



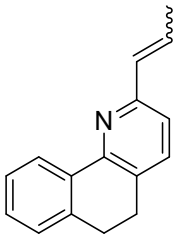
2-(2-Methoxyphenyl)-5,6-dihydrobenzo[*h*]quinoline (3ah)

Pale yellow solid; mp 131-133 °C. Yield (47.4 mg, 33%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (d, *J* = 7.6 Hz, 1H), 8.02 (d, *J* = 7.6 Hz, 1H), 7.73 (d, *J* = 7.9 Hz, 1H), 7.51 (d, *J* = 7.9 Hz, 1H), 7.36 (m, 2H), 7.29 (t, *J* = 7.3 Hz, 1H), 7.22 (d, *J* = 7.3 Hz, 1H), 7.13 (d, *J* = 7.4 Hz, 1H), 7.01 (d, *J* = 8.3 Hz, 1H), 3.88 (s, 3H), 2.97 (s, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.2, 153.7, 151.9, 138.0, 135.2, 135.0, 131.4, 129.8, 129.6, 129.5, 128.8, 127.7, 127.0, 125.2, 123.6, 121.1, 111.5, 55.7, 28.2, 27.8. IR (KBr) ν (cm^{-1}): 3650, 3519, 3444, 3303, 3228, 3073, 2939, 1434, 1369, 663, 586. *m/z* (EI): 287.



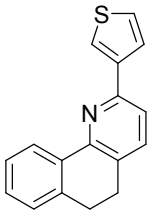
3-Methyl-5,6-dihydrobenzo[*h*]quinoline (3ai)

Pale yellow oil. Yield (72.1 mg, 74%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (s, 1H), 8.26 (d, *J* = 7.5 Hz, 1H), 7.32 (m, 3H), 7.21 (d, *J* = 7.2 Hz, 1H), 2.90 (s, 4H), 2.33 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.8, 137.9, 136.6, 128.8, 127.8, 127.2, 124.7, 28.1, 28.0, 18.2. IR (KBr) ν (cm^{-1}): 3592, 3518, 3446, 3300, 3132, 3069, 2965, 1709, 1436, 1368, 662, 571. ESI-HRMS calcd for $[M + H]^+$ $C_{14}H_{14}N$, 196.1121; found, 196.1126.



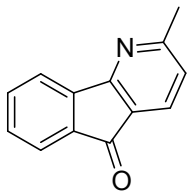
2-(Prop-1-en-1-yl)-5,6-dihydrobenzo[h]quinoline (3aj)

Pale yellow oil. Yield (49.7 mg, 45%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (d, *J* = 7.2 Hz, 1H), 7.41 (d, *J* = 7.7 Hz, 1H), 7.35 (t, *J* = 7.4 Hz, 1H), 7.30 (d, *J* = 7.2 Hz, 1H), 7.21 (d, *J* = 7.2 Hz, 1H), 7.06 (d, *J* = 7.7 Hz, 1H), 6.86 (m, 1H), 6.55 (d, *J* = 15.4 Hz, 1H), 2.91 (s, 4H), 1.95 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.1, 138.2, 136.0, 131.4, 129.8, 128.9, 127.7, 127.0, 125.1, 119.4, 28.2, 27.9, 18.3. IR (KBr) ν (cm^{-1}): 3649, 3519, 3444, 3241, 3128, 3073, 1595, 1435, 1369, 759, 698. ESI-HRMS calcd for $[M + H]^+$ $C_{16}H_{16}N$, 222.1277; found, 222.1284.



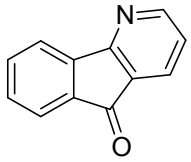
2-(Thiophen-3-yl)-5,6-dihydrobenzo[*h*]quinoline (3ak)

Pale yellow solid; mp 145-147 °C. Yield (86.8mg, 66%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (d, *J* = 7.6 Hz, 1H), 7.97 (s, 1H), 7.77 (d, *J* = 4.0 Hz, 1H), 7.50 (d, *J* = 7.5 Hz, 1H), 7.45 (d, *J* = 7.6 Hz, 1H), 7.38 (t, *J* = 7.1 Hz, 2H), 7.31 (t, *J* = 7.3 Hz, 1H), 7.22 (s, 1H), 2.95 (s, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.5, 138.2, 136.3, 134.7, 130.0, 129.1, 127.7, 127.1, 126.4, 126.0, 125.2, 122.9, 118.6, 28.2, 27.8. IR (KBr) ν (cm^{-1}): 3587, 3519, 3443, 3305, 3174, 3074, 1438, 1364, 782, 653, 554. ESI-HRMS calcd for $[M + H]^+$ $C_{17}H_{14}NS$, 264.0841; found, 264.0842.



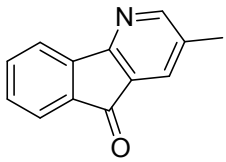
2-Methyl-5*H*-indeno[1,2-*b*]pyridin-5-one (4a)[3]

Pale yellow solid; mp 140-143 °C. Yield (43.9mg, 45%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 7.3 Hz, 1H), 7.78 (d, *J* = 7.6 Hz, 1H), 7.70 (d, *J* = 7.3 Hz, 1H), 7.57 (t, *J* = 7.2 Hz, 1H), 7.41 (t, *J* = 7.3 Hz, 1H), 7.05 (d, *J* = 7.6 Hz, 1H), 2.64 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.8, 165.2, 164.4, 143.5, 135.2, 135.0, 131.6, 130.8, 125.9, 124.0, 122.7, 120.9, 25.0. IR (KBr) ν (cm^{-1}): 3651, 3592, 3518, 3301, 3132, 3069, 2925, 1708, 1436, 1368, 663, 571. *m/z* (EI): 195.



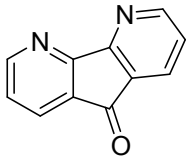
5*H*-Indeno[1,2-*b*]pyridin-5-one (4b)

Pale yellow solid; mp 138-141 °C. Yield (60.6 mg, 67%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (d, *J* = 3.4 Hz, 1H), 7.89 (m, 2H), 7.73 (d, *J* = 7.4 Hz, 1H), 7.61 (t, *J* = 7.5 Hz, 1H), 7.44 (t, *J* = 7.4 Hz, 1H), 7.22 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.7, 165.0, 153.8, 143.4, 135.4, 134.8, 131.6, 131.1, 124.2, 123.4, 121.1. IR (KBr) ν (cm^{-1}): 3587, 3518, 3443, 3305, 3127, 3074, 2921, 1717, 1437, 1365, 741, 662, 560. ESI-HRMS calcd for $[M + H]^+$ $C_{12}H_8NO$, 182.0600; found, 182.0595.



3-Methyl-5*H*-indeno[1,2-*b*]pyridin-5-one (4c)[3]

Pale yellow solid; mp 137-140 °C. Yield (45.8 mg, 47%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (s, 1H), 7.82 (d, *J* = 6.8 Hz, 1H), 7.71 (d, *J* = 7.1 Hz, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.41 (d, *J* = 7.2 Hz, 1H), 2.39 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.2, 135.3, 132.0, 130.5, 124.1, 120.6, 18.6. IR (KBr) ν (cm^{-1}): 3590, 3518, 3445, 3302, 3130, 3071 2924, 1710, 1435, 1369, 821, 747, 660. *m/z* (EI): 195.



5*H*-Cyclopenta[2,1-*b*:3,4-*b*']dipyridin-5-one (4d)[4]

Pale yellow solid; mp 210-212 °C. Yield (35.5 mg, 39%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.82 (d, *J* = 4.9 Hz, 2H), 8.01 (d, *J* = 7.5 Hz, 2H), 7.37 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.6, 163.4, 155.2, 131.5, 129.4, 124.8. IR (KBr) ν (cm^{-1}): 3651, 3519, 3444, 3242, 3128, 3072, 2920, 1708, 1436, 1368, 566. ESI-HRMS calcd for $[M + H]^+$ $C_{11}H_7N_2O$, 183.0553; found, 183.0553.

References

1 L. Ackermann, H. K. Potukuchi, A. R. Kapdi and C. Schulzke, *Chem. Eur. J.*, 2010, **16**, 3300.

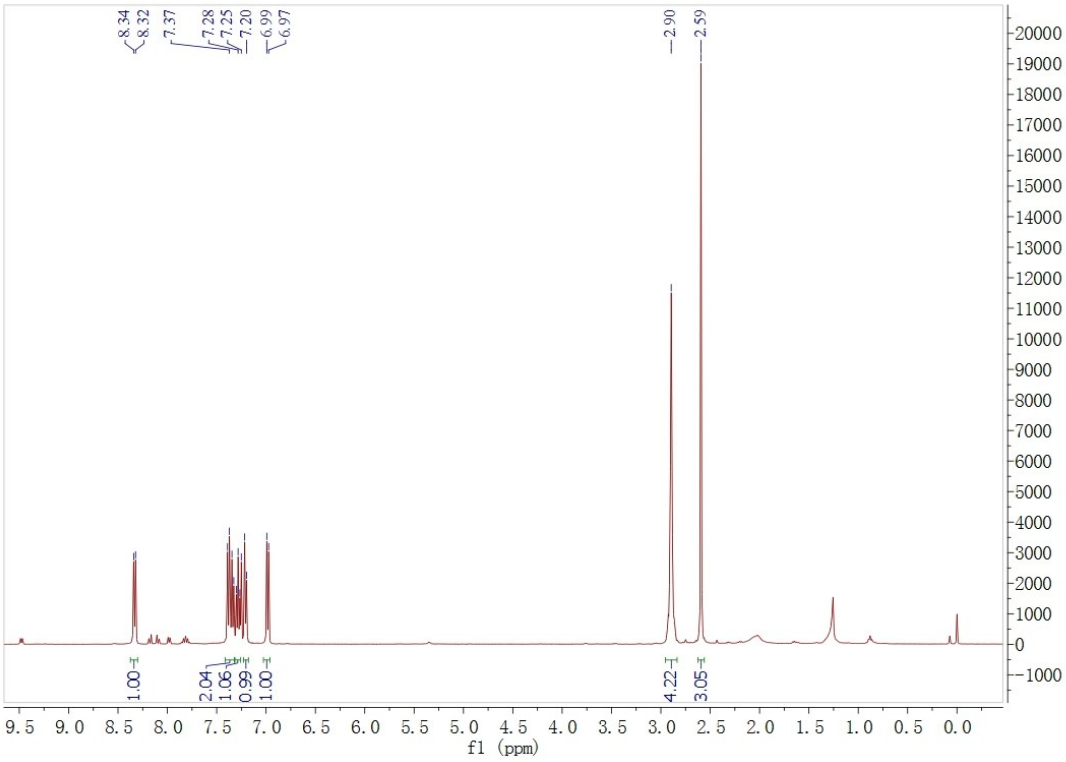
2 D. Craig, F. Painaa and S. C. Smith, *Chem. Commun.*, 2008, **44**, 3408.

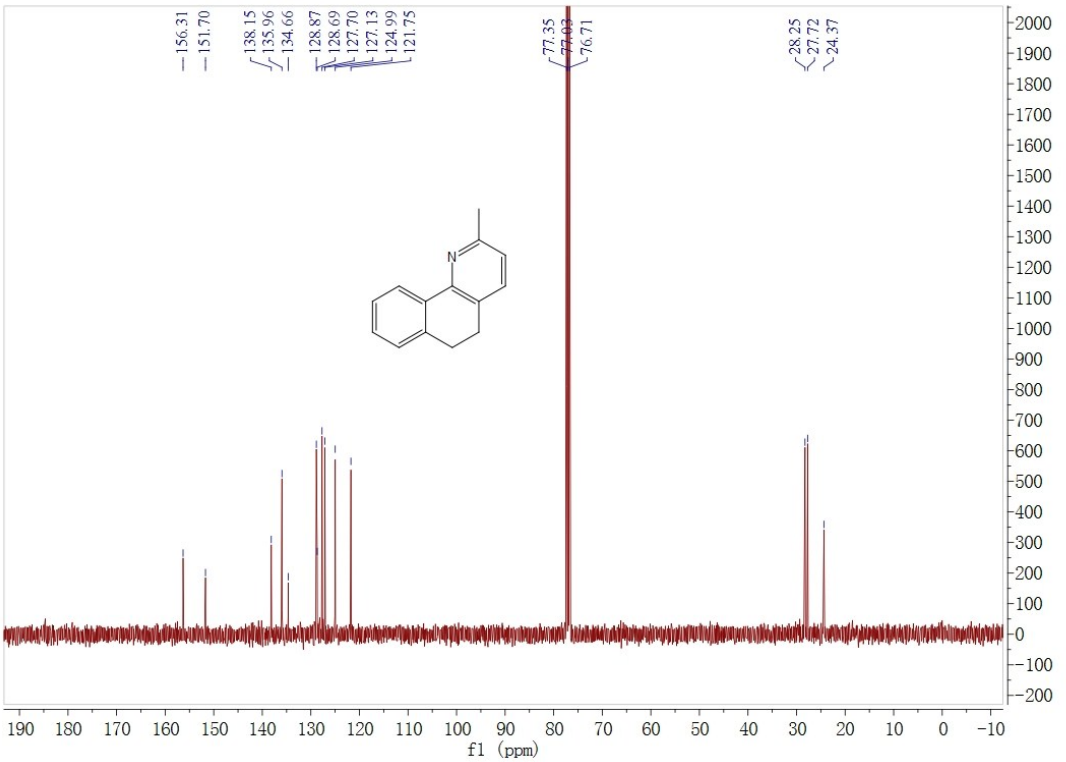
3 N. Mokato, *J. Chem. Soc.*, 1991, **12**, 3371.

4 M. Jean-Paul, *Eur. J. Org. Chem.*, 2001, **10**, 1821.

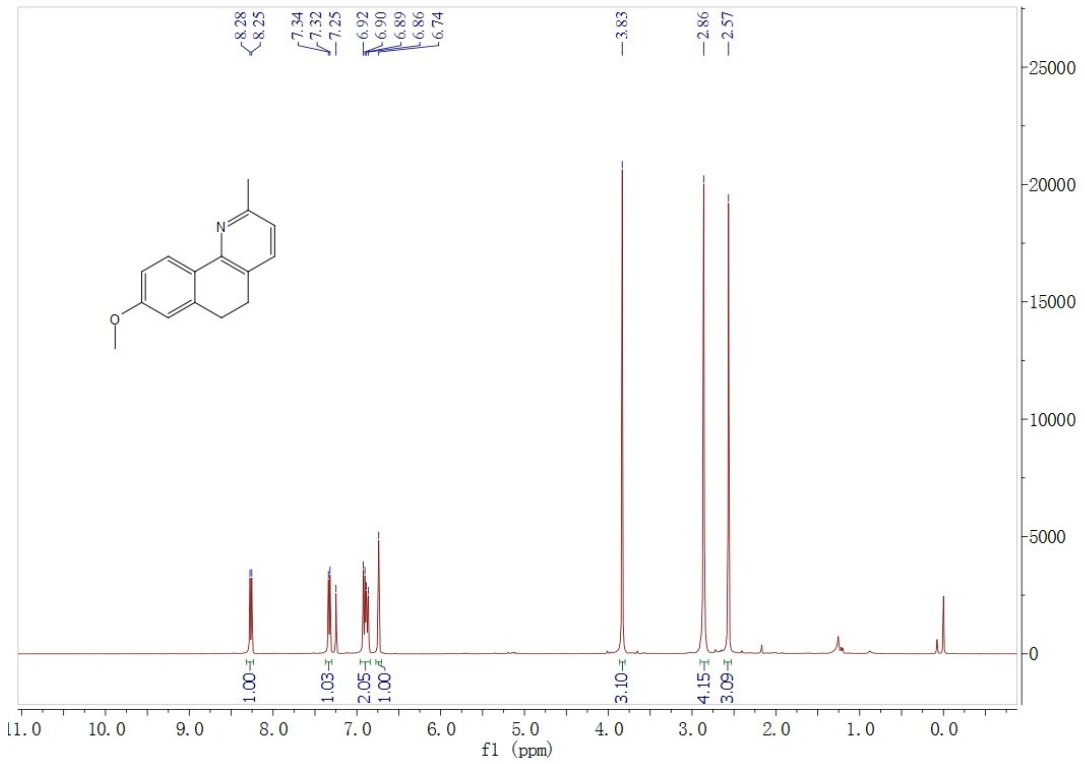
NMR Spectra for Compounds

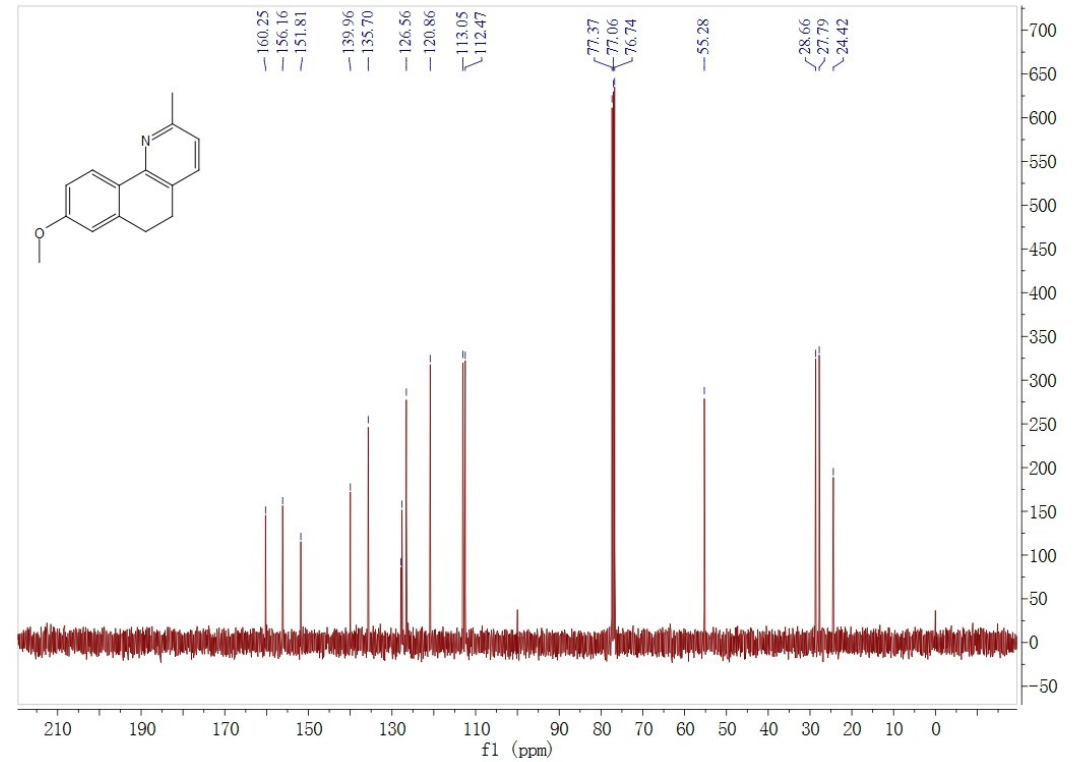
3aa


8.34
8.32
7.37
7.28
7.25
7.20
6.99
6.97
2.90
2.59
1.00
2.04
1.06
0.99
1.00
4.22
3.05
f1 (ppm)

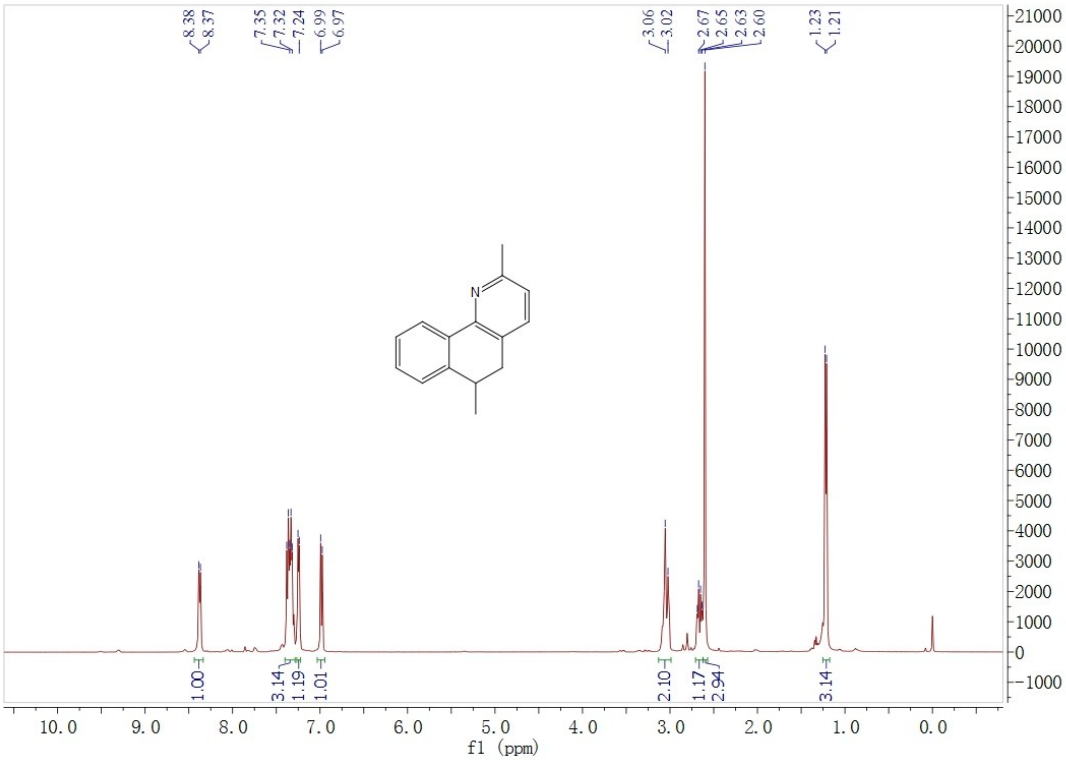

156.31
151.70
138.15
135.96
134.66
128.87
128.69
127.70
127.13
124.99
121.75
77.35
77.03
76.71
28.25
27.72
24.37
N
f1 (ppm)

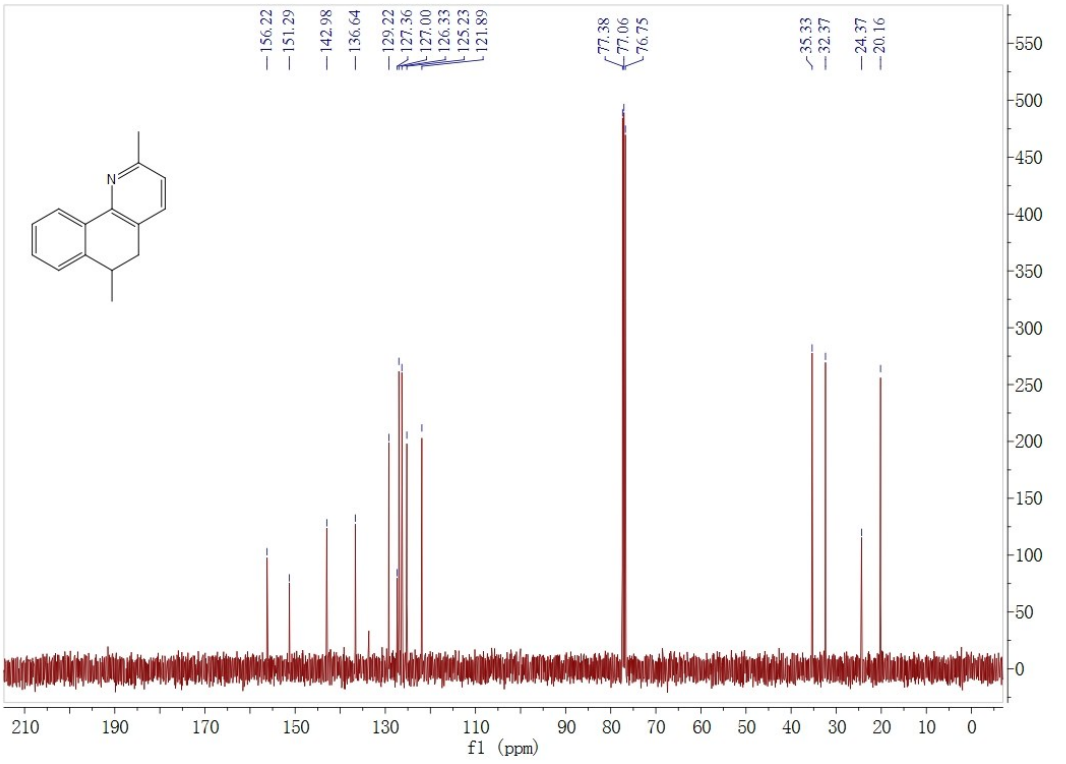
3ba


8.28
8.25
7.34
7.32
7.25
6.92
6.90
6.89
6.86
6.74
3.83
2.86
2.57
1.00
1.03
2.05
1.00
3.10
4.15
3.09
f1 (ppm)

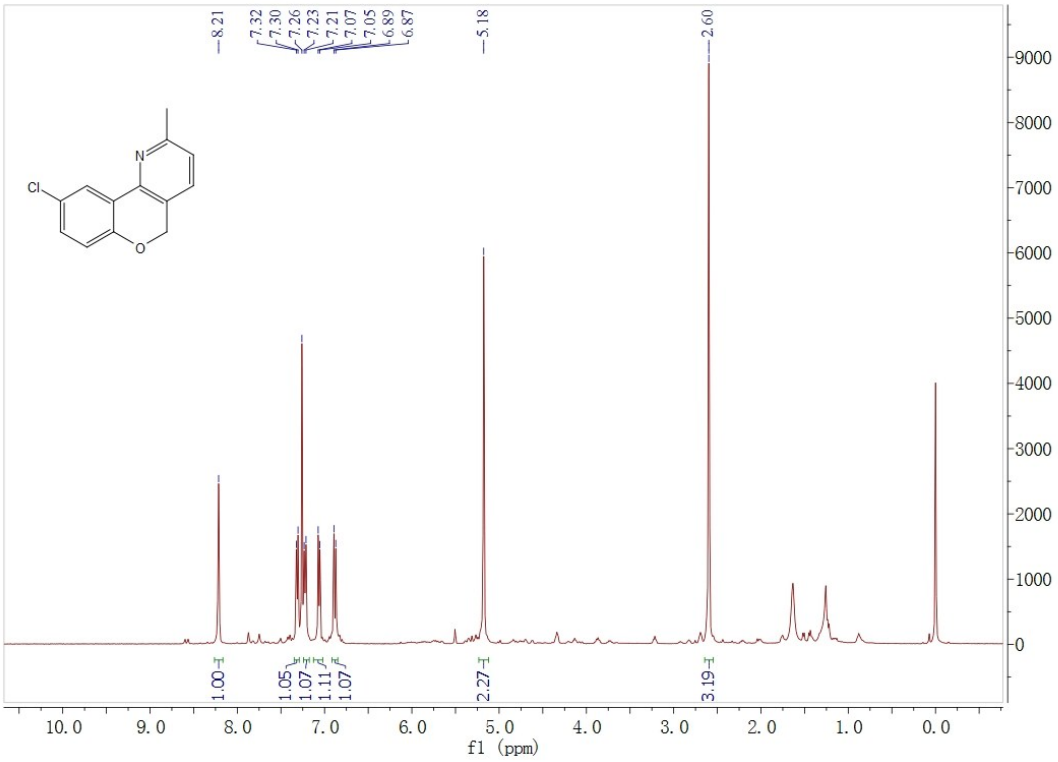

160.25
156.16
151.81
139.96
135.70
126.56
120.86
113.05
112.47
77.37
77.06
76.74
55.28
28.66
27.79
24.42
f1 (ppm)

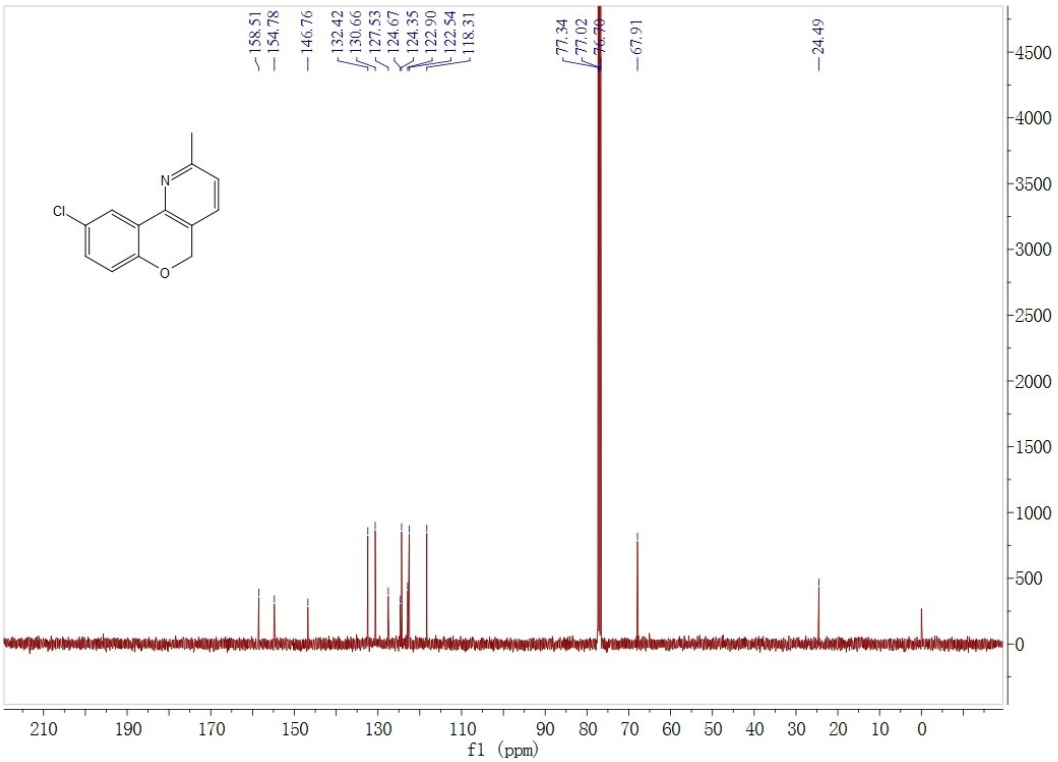
3ca


8.38
8.37
7.35
7.32
7.24
6.99
6.97
3.06
3.02
2.67
2.65
2.63
2.60
1.23
1.21
1.00
3.14
1.19
1.01
2.10
1.17
2.94
3.14
f1 (ppm)

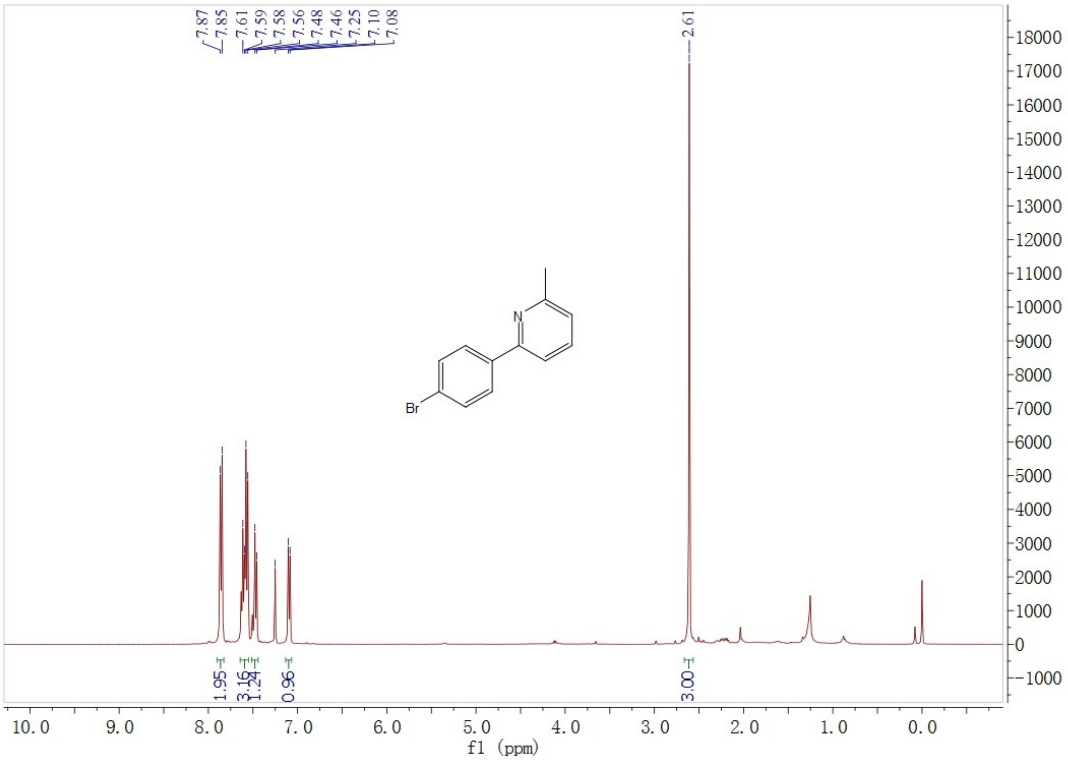

156.22
151.29
142.98
136.64
129.22
127.36
127.00
126.33
125.23
121.89
77.38
77.06
76.75
35.33
32.37
24.37
20.16
f1 (ppm)

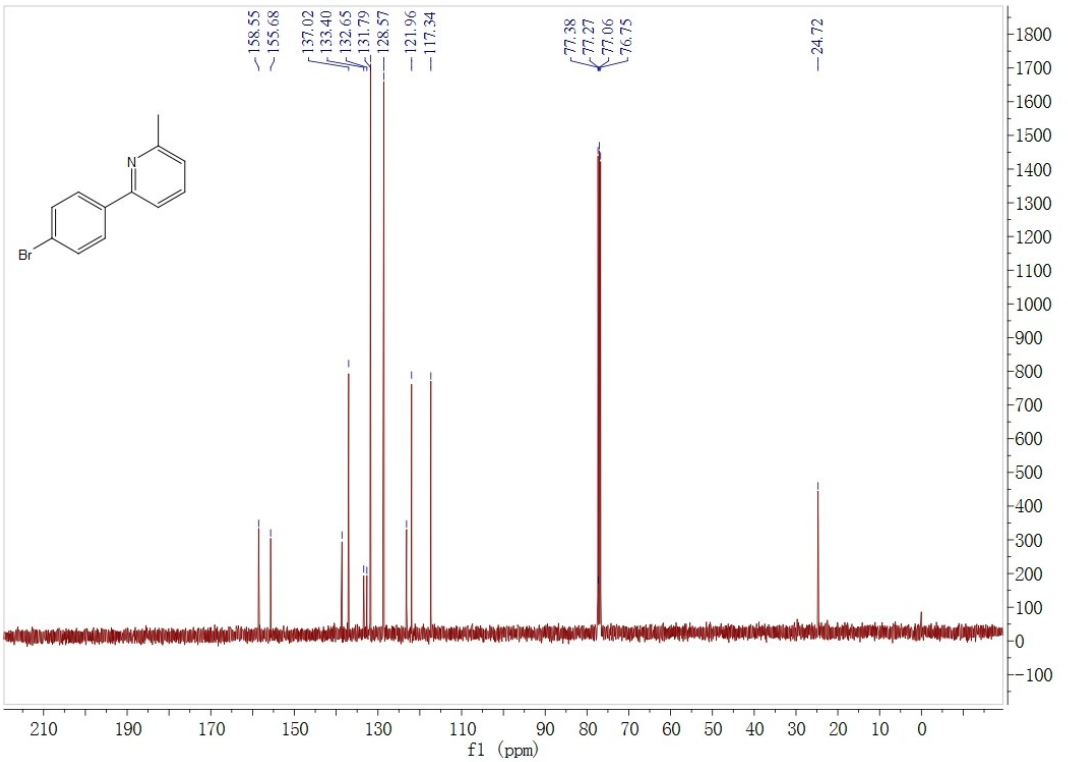
3da


8.21
7.32
7.30
7.26
7.23
7.21
7.07
7.05
6.89
6.87
5.18
2.60
Cl
N
O
1.00
1.05
1.07
1.11
1.07
2.27
3.19
f1 (ppm)

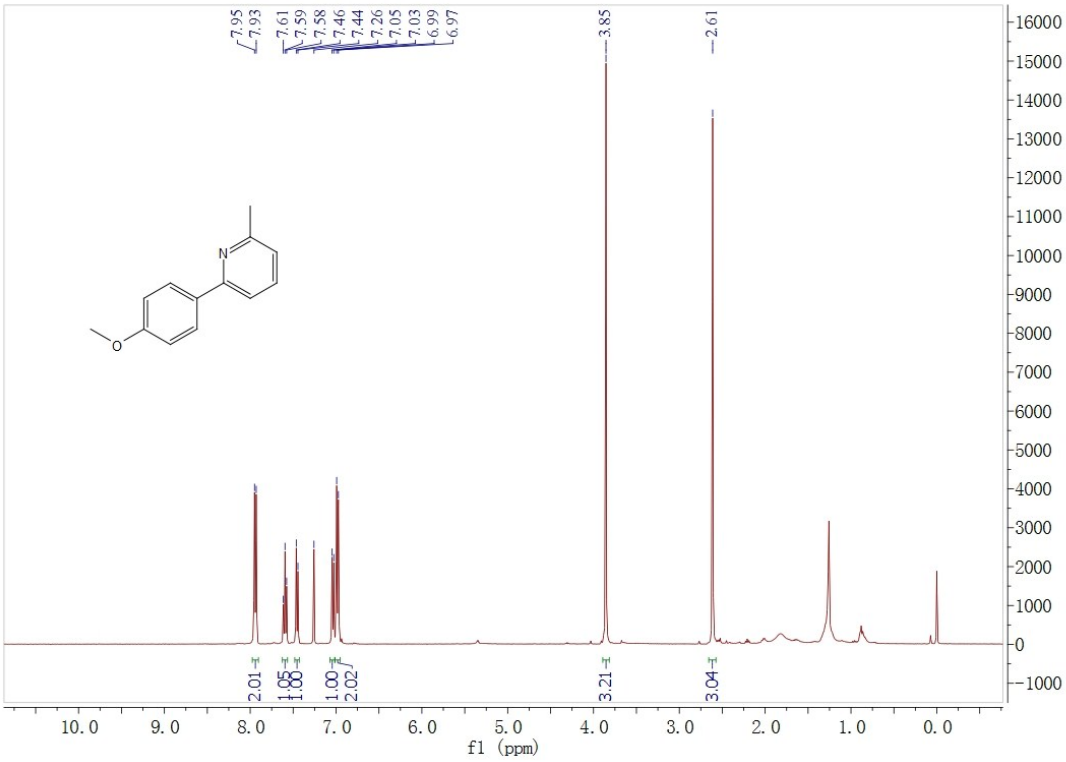

158.51
154.78
146.76
132.42
130.66
127.53
124.67
124.35
122.90
122.54
118.31
77.34
77.02
76.70
67.91
24.49
Cl
N
O
f1 (ppm)

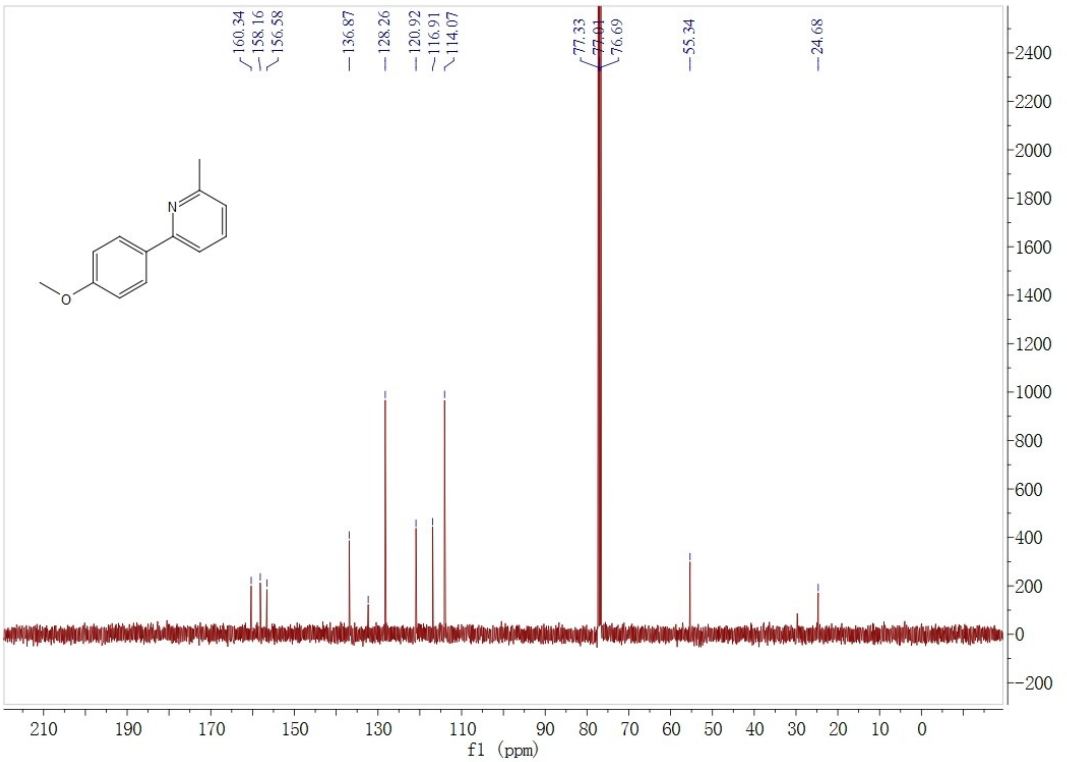
3ea


7.87
7.85
7.61
7.59
7.58
7.56
7.48
7.46
7.25
7.10
7.08
2.61
N
Br
1.95
3.15
1.24
0.96
3.00
f1 (ppm)

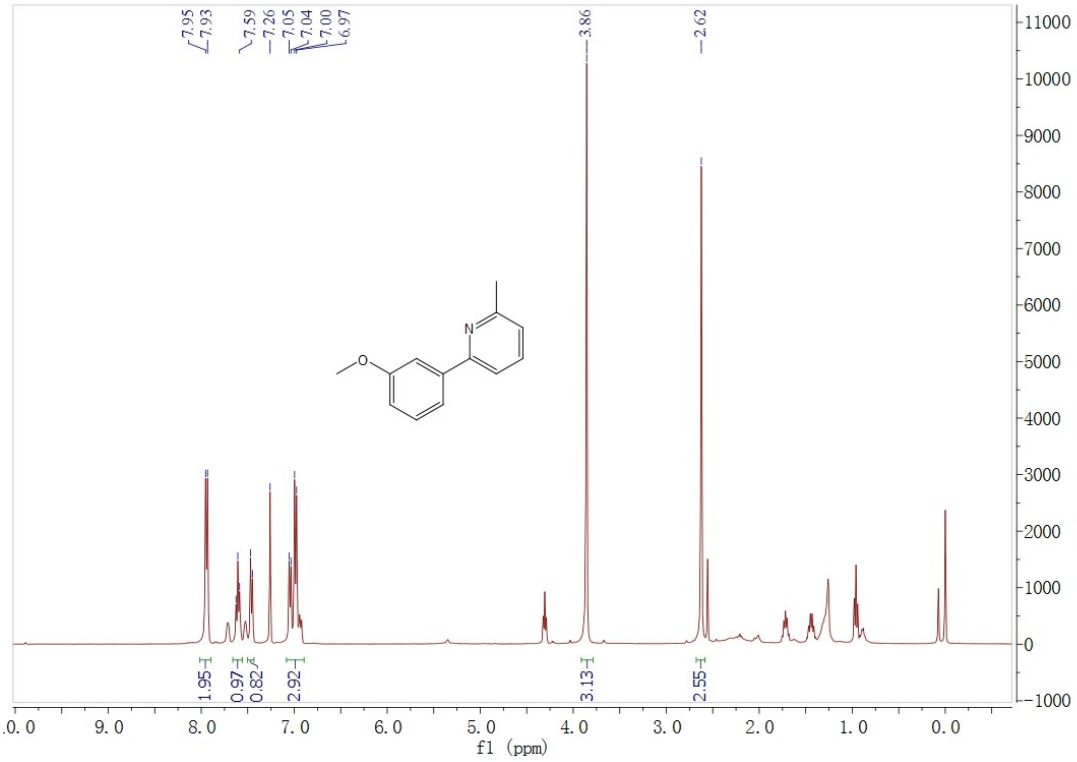

158.55
155.68
137.02
133.40
132.65
131.79
128.57
121.96
117.34
77.38
77.27
77.06
76.75
24.72
N
Br
f1 (ppm)

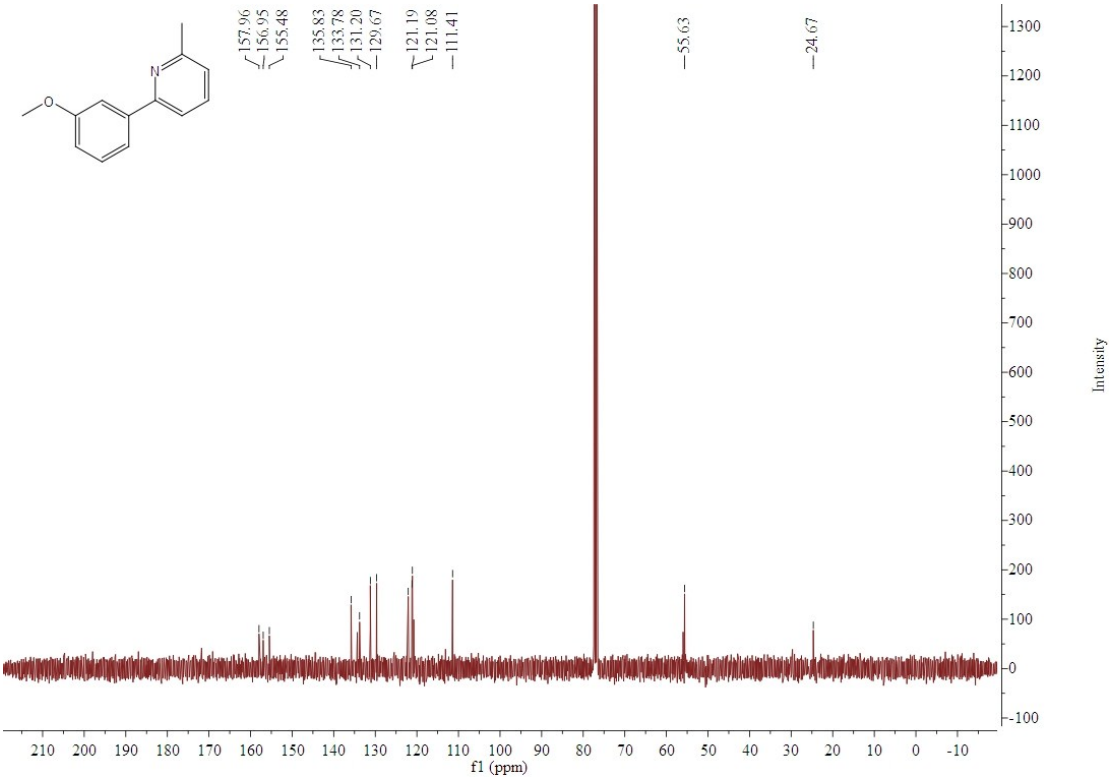
3fa


7.95
7.93
7.61
7.59
7.58
7.46
7.44
7.26
7.05
7.03
6.99
6.97
3.85
2.61
2.01
1.05
1.08
1.00
2.02
3.21
3.04
f1 (ppm)

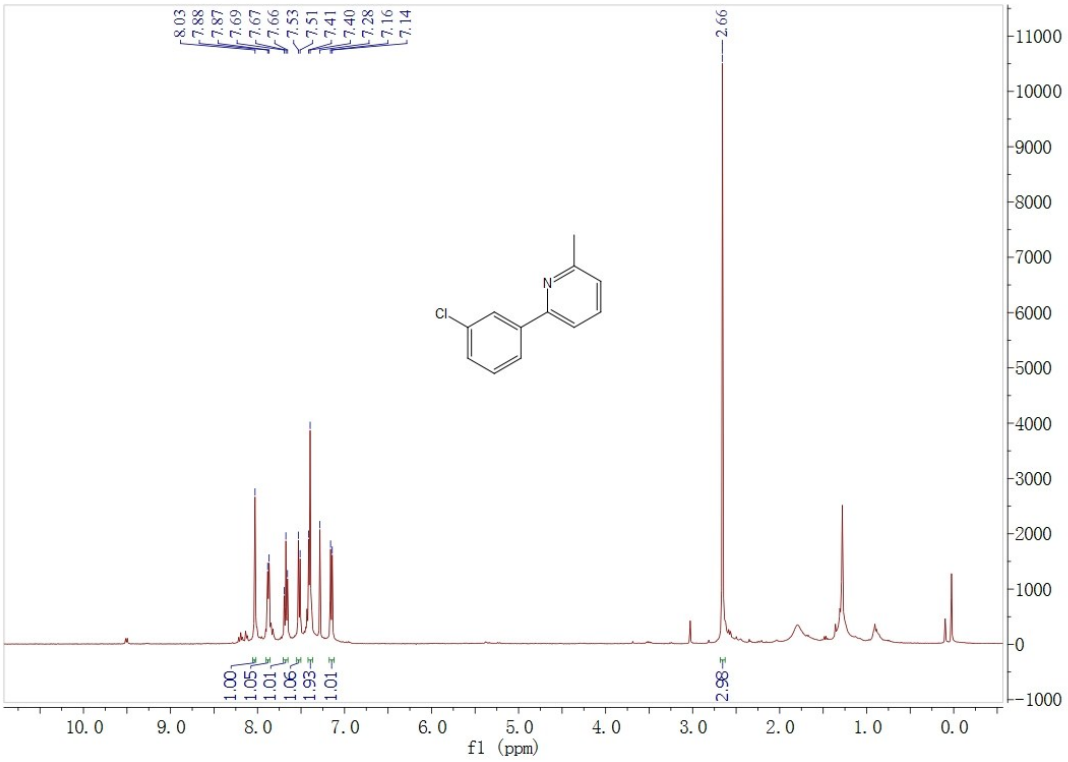

160.34
158.16
156.58
136.87
128.26
120.92
116.91
114.07
77.33
77.01
76.69
55.34
24.68
f1 (ppm)

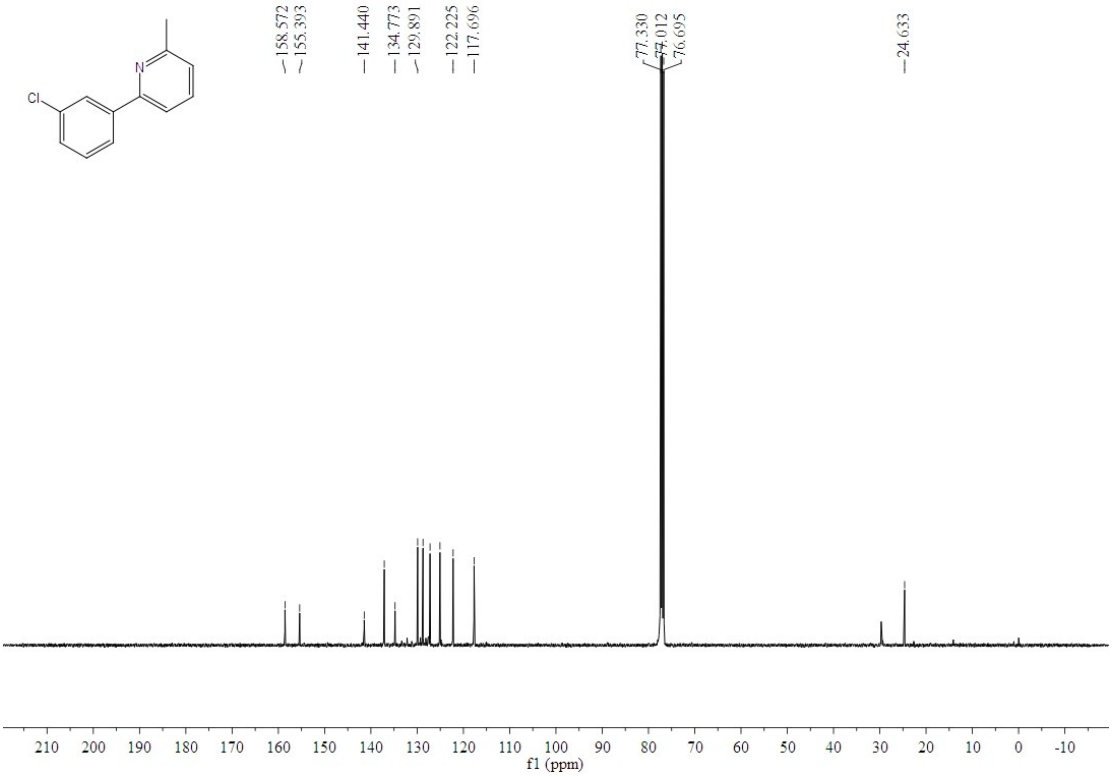
3ga


7.95
7.93
7.59
7.26
7.05
7.04
7.00
6.97
3.86
2.62
1.95
0.97
0.82
2.92
3.13
2.55
f1 (ppm)

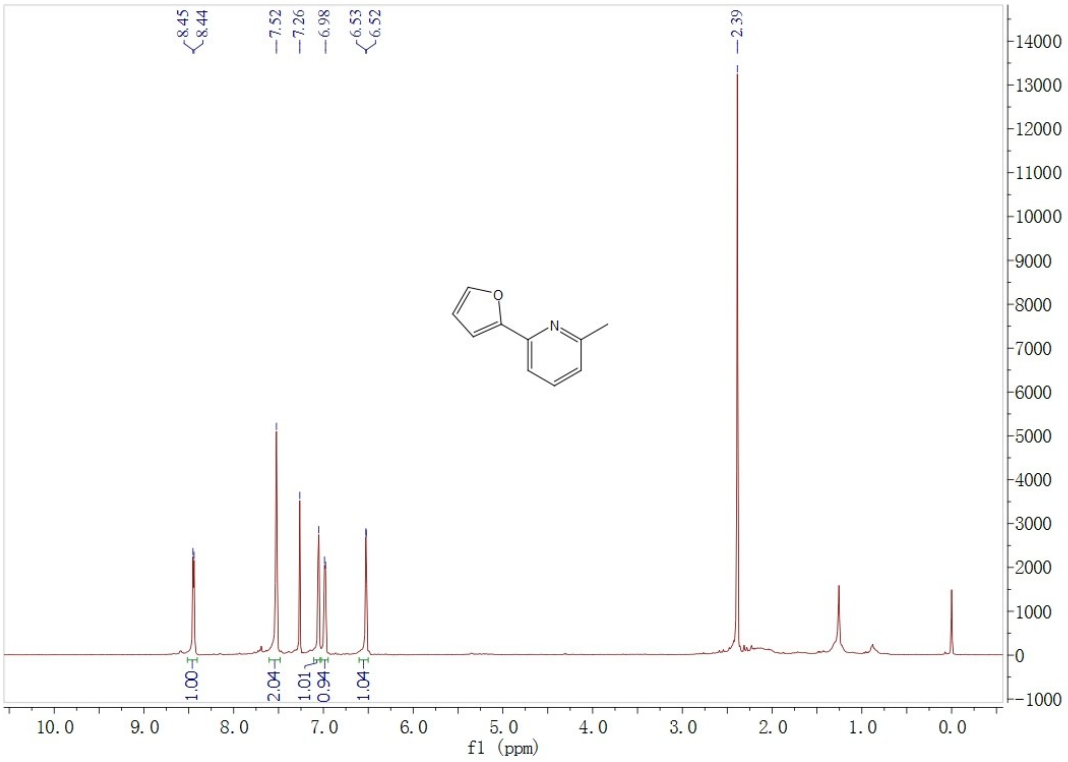

157.96
156.95
155.48
135.83
133.78
131.20
129.67
121.19
121.08
111.41
55.63
24.67
Intensity
f1 (ppm)

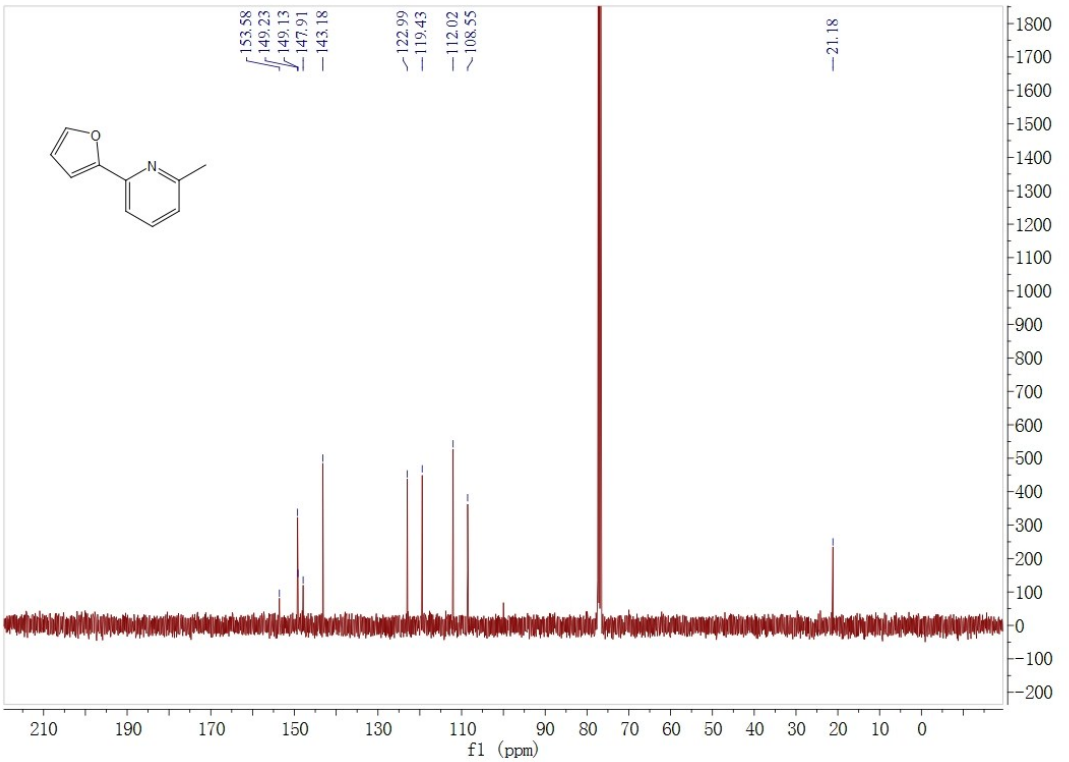
3ha


8.03
7.88
7.87
7.69
7.67
7.66
7.53
7.51
7.41
7.40
7.28
7.16
7.14
2.66
1.00
1.05
1.01
1.06
1.93
1.01
2.98
Cl
N
f1 (ppm)

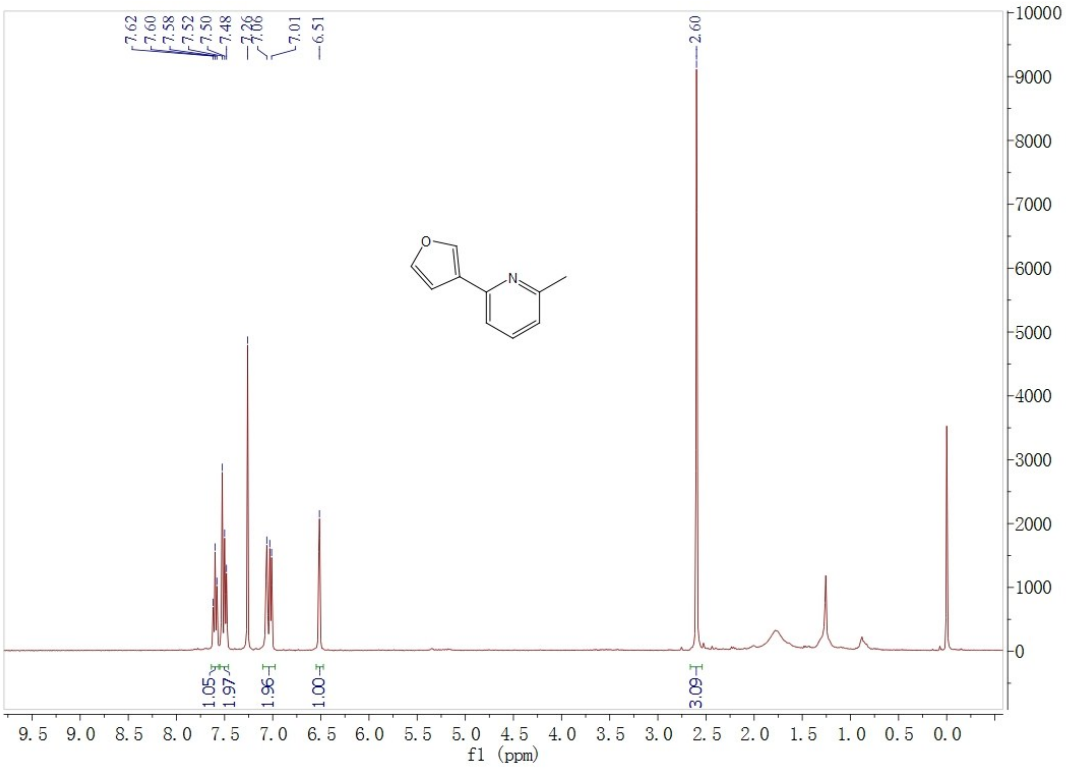

158.572
155.393
141.440
134.773
129.891
122.225
117.696
77.330
77.012
76.695
24.633
Cl
N
f1 (ppm)

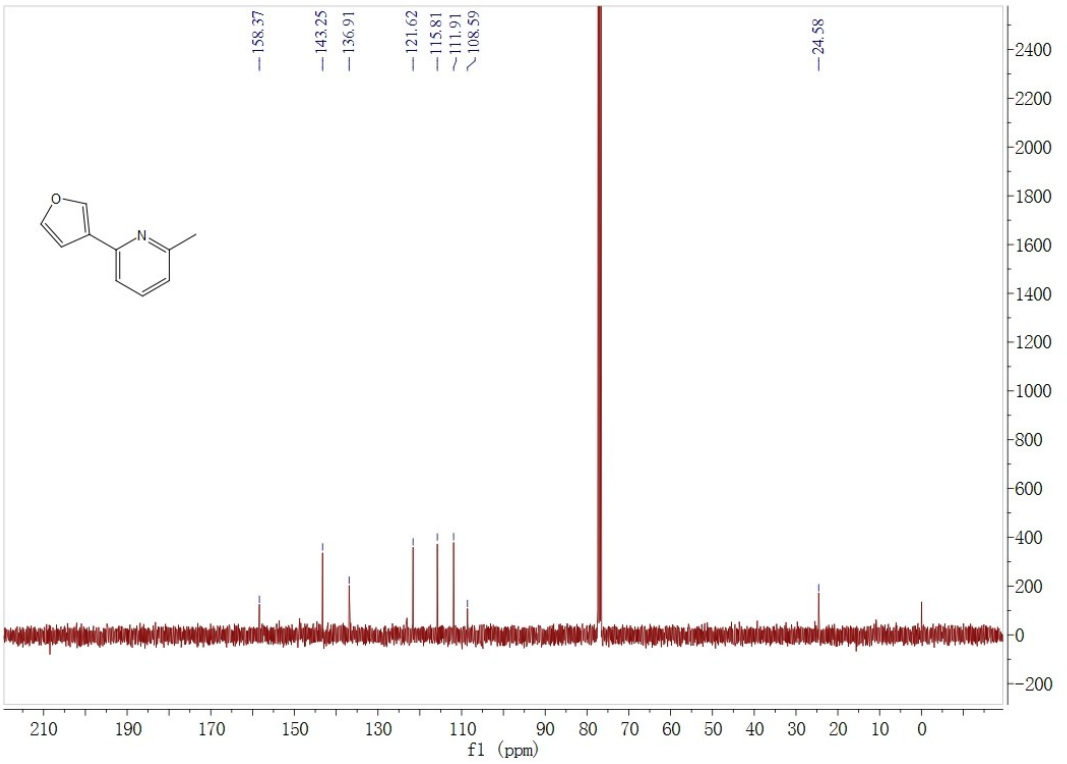
3ia


8.45
8.44
7.52
7.26
6.98
6.53
6.52
2.39
1.00
2.04
1.01
0.94
1.04
f1 (ppm)

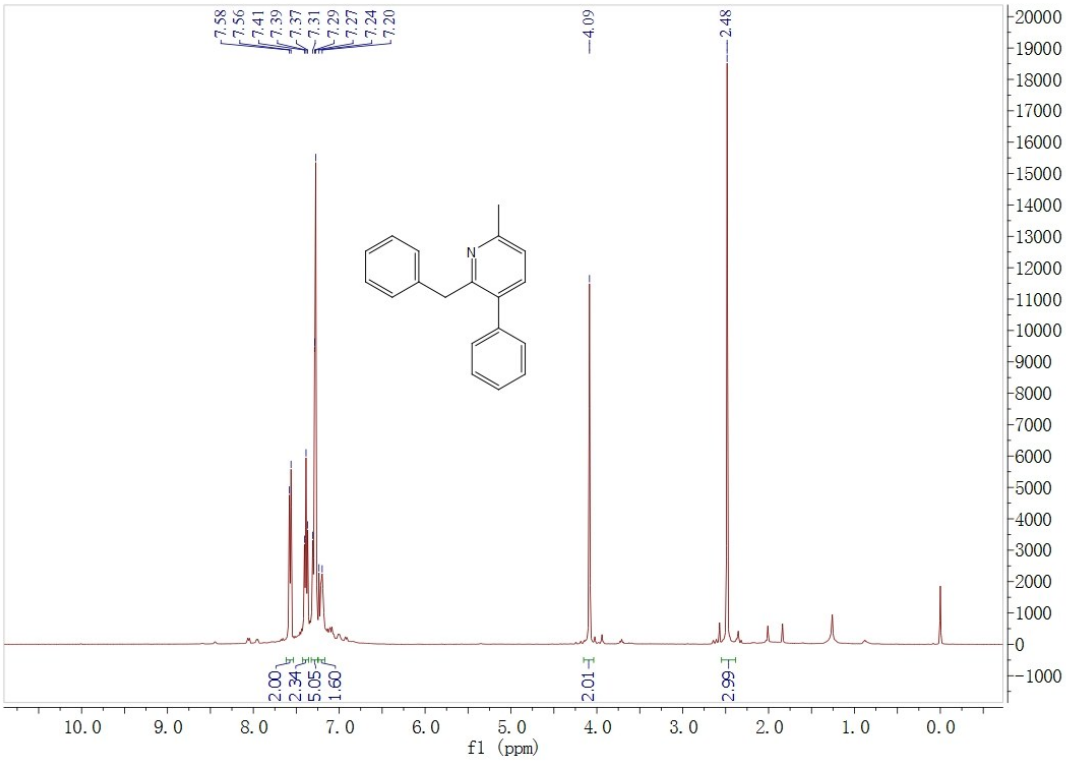

153.58
149.23
149.13
147.91
143.18
122.99
119.43
112.02
108.55
21.18
f1 (ppm)

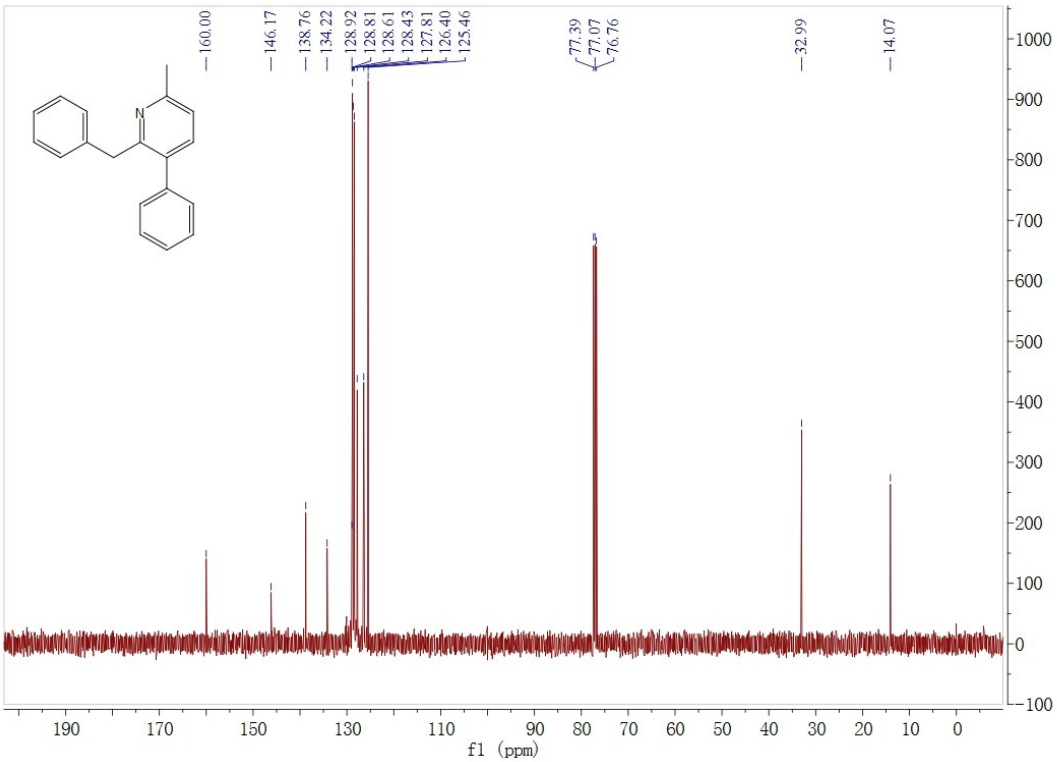
3ja


7.62
7.60
7.58
7.52
7.50
7.48
7.26
7.06
7.01
6.51
2.60
1.05
1.97
1.96
1.00
3.09
f1 (ppm)

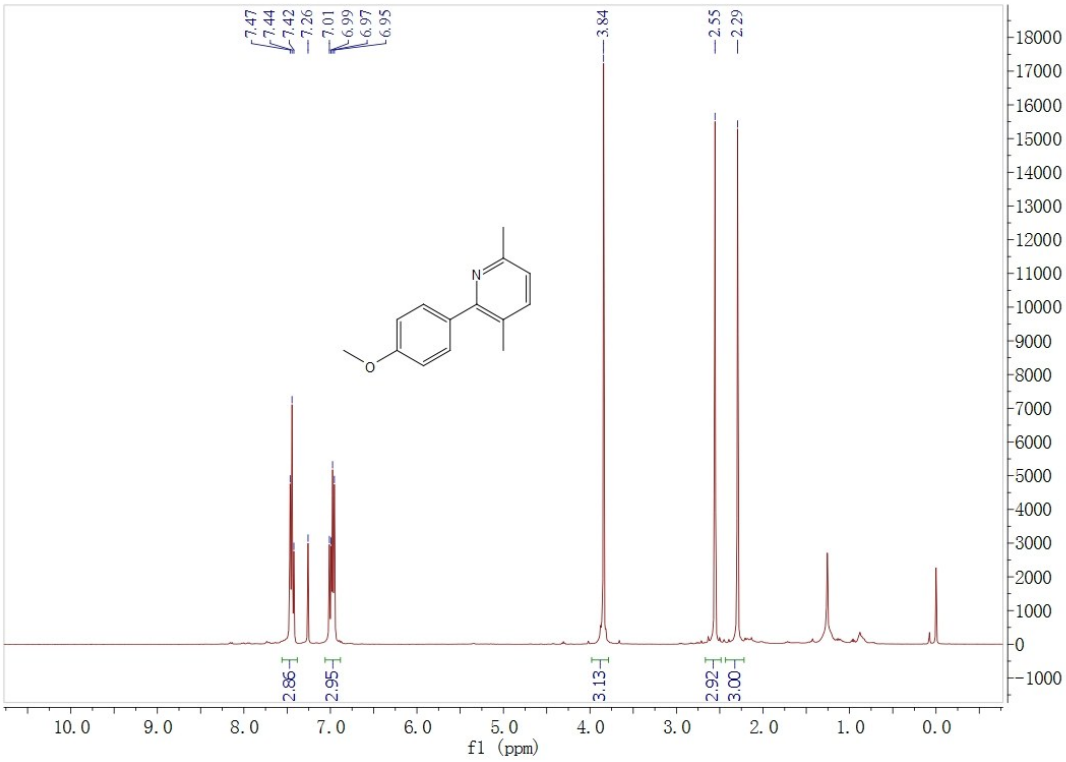

158.37
143.25
136.91
121.62
115.81
111.91
108.59
24.58
f1 (ppm)

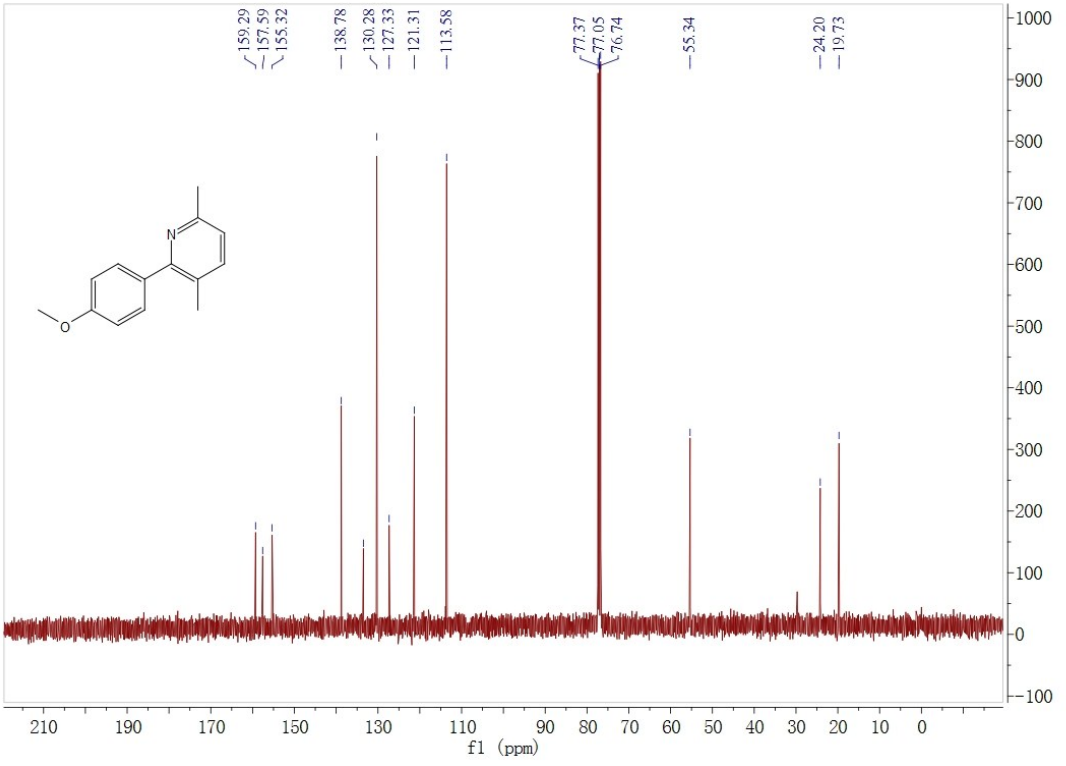
3ka


7.58
7.56
7.41
7.39
7.37
7.31
7.29
7.27
7.24
7.20
4.09
2.48
2.00
2.34
5.05
1.60
2.01
2.99
f1 (ppm)

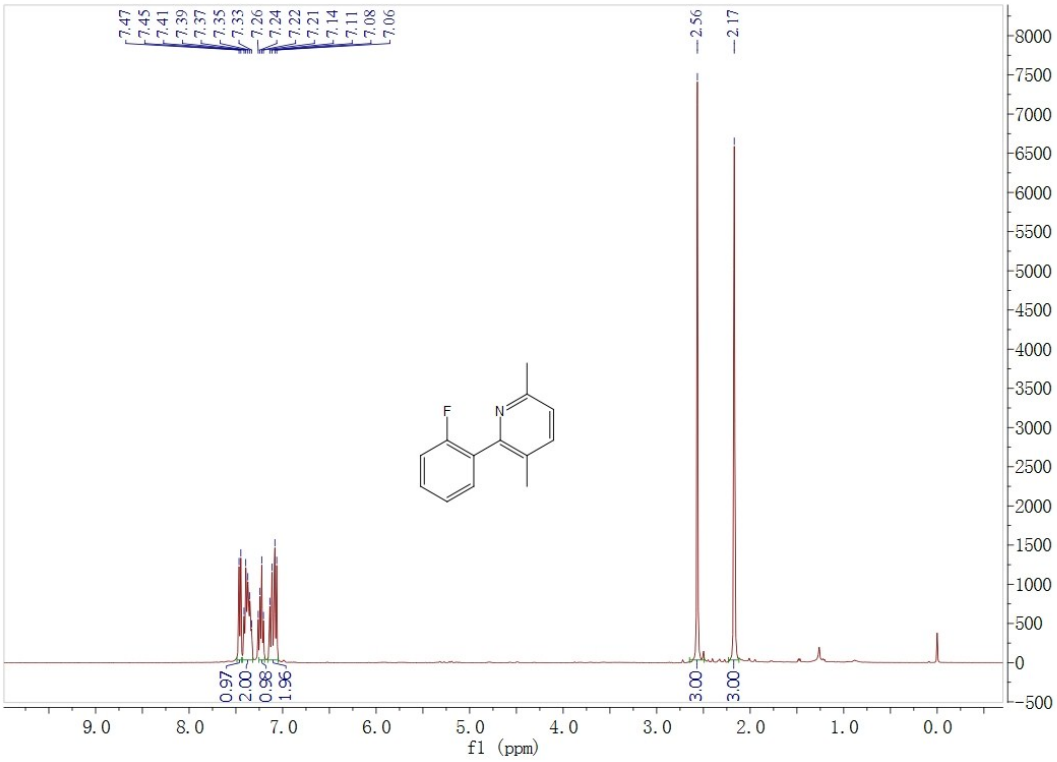

160.00
146.17
138.76
134.22
128.92
128.81
128.61
128.43
127.81
126.40
125.46
77.39
77.07
76.76
32.99
14.07
f1 (ppm)

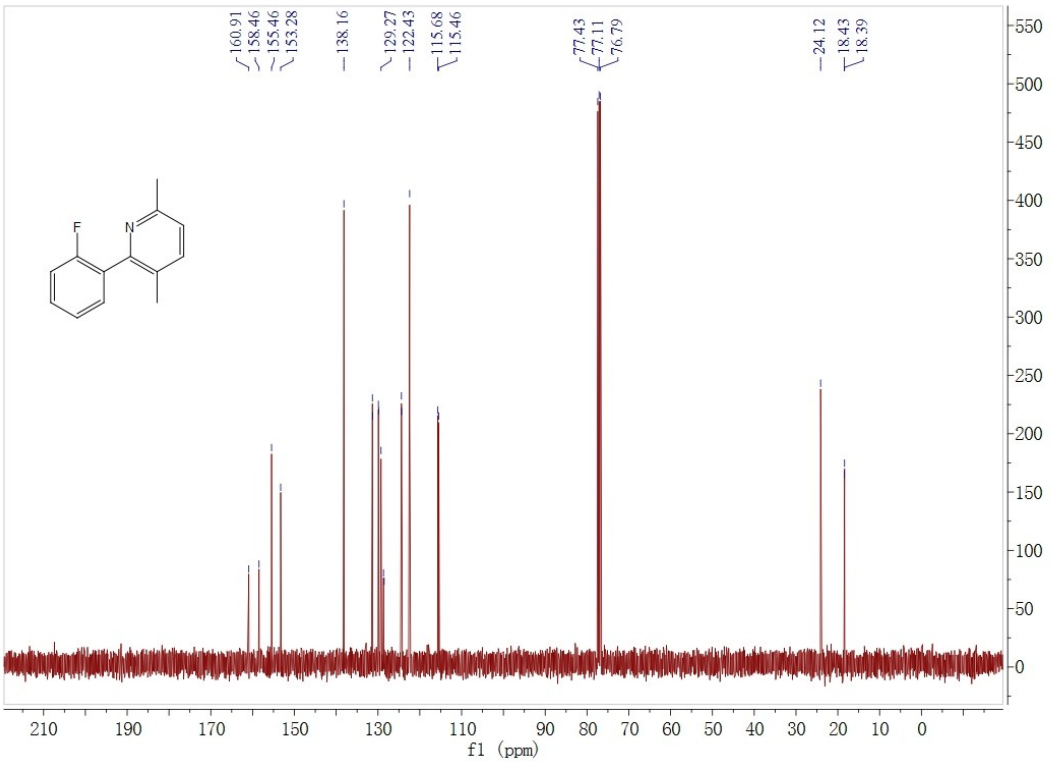
3la


7.47
7.44
7.42
7.26
7.01
6.99
6.97
6.95
3.84
2.55
2.29
2.86
2.95
3.13
2.92
3.00
f1 (ppm)

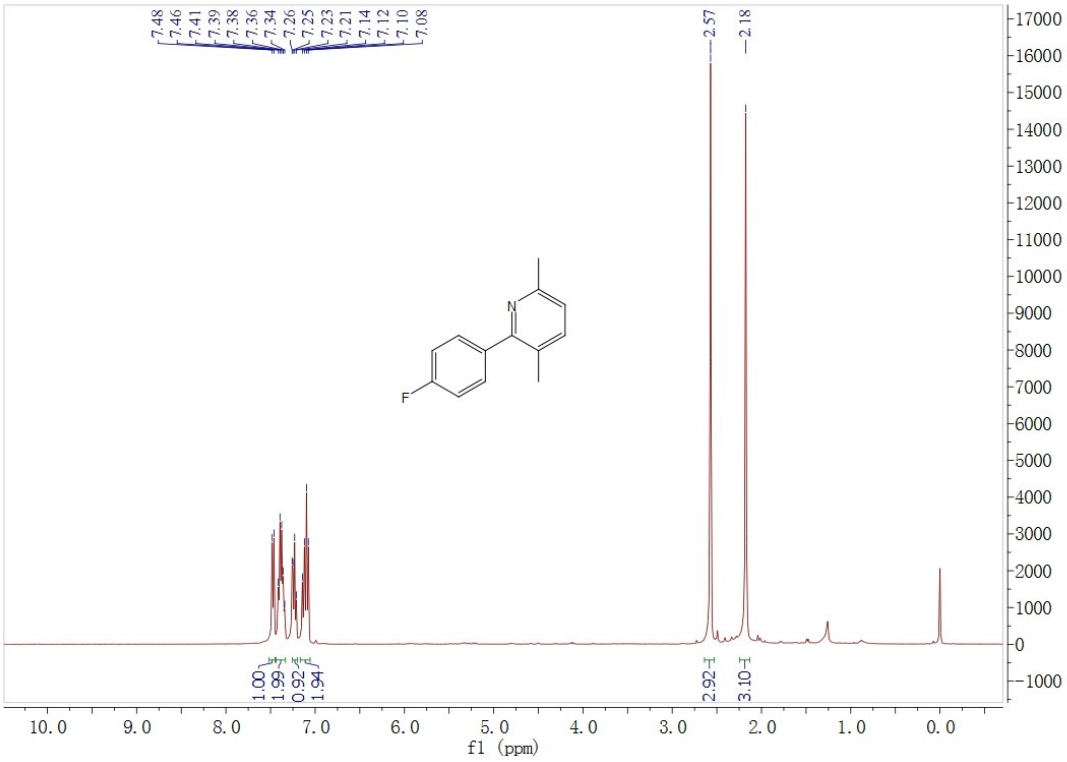

159.29
157.59
155.32
138.78
130.28
127.33
121.31
113.58
77.37
77.05
76.74
55.34
24.20
19.73
f1 (ppm)

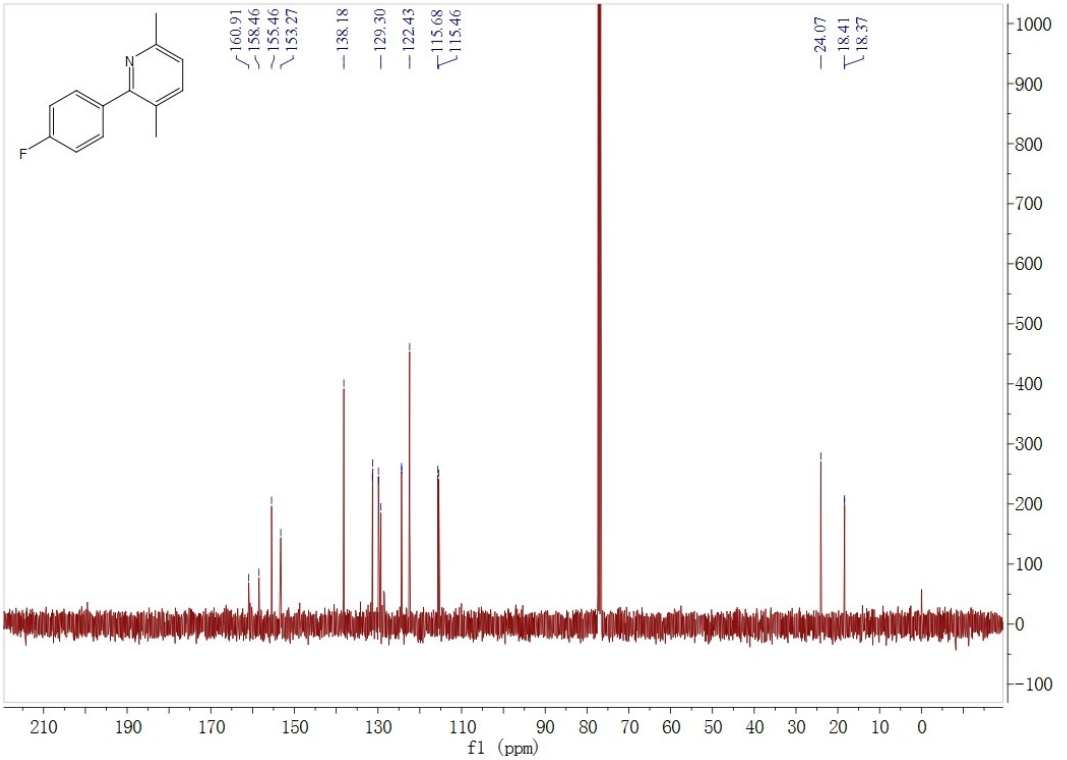
3ma


7.47
7.45
7.41
7.39
7.37
7.35
7.33
7.26
7.24
7.22
7.21
7.14
7.11
7.08
7.06
2.56
2.17
F
N
0.97
2.00
0.98
1.96
3.00
3.00
f1 (ppm)

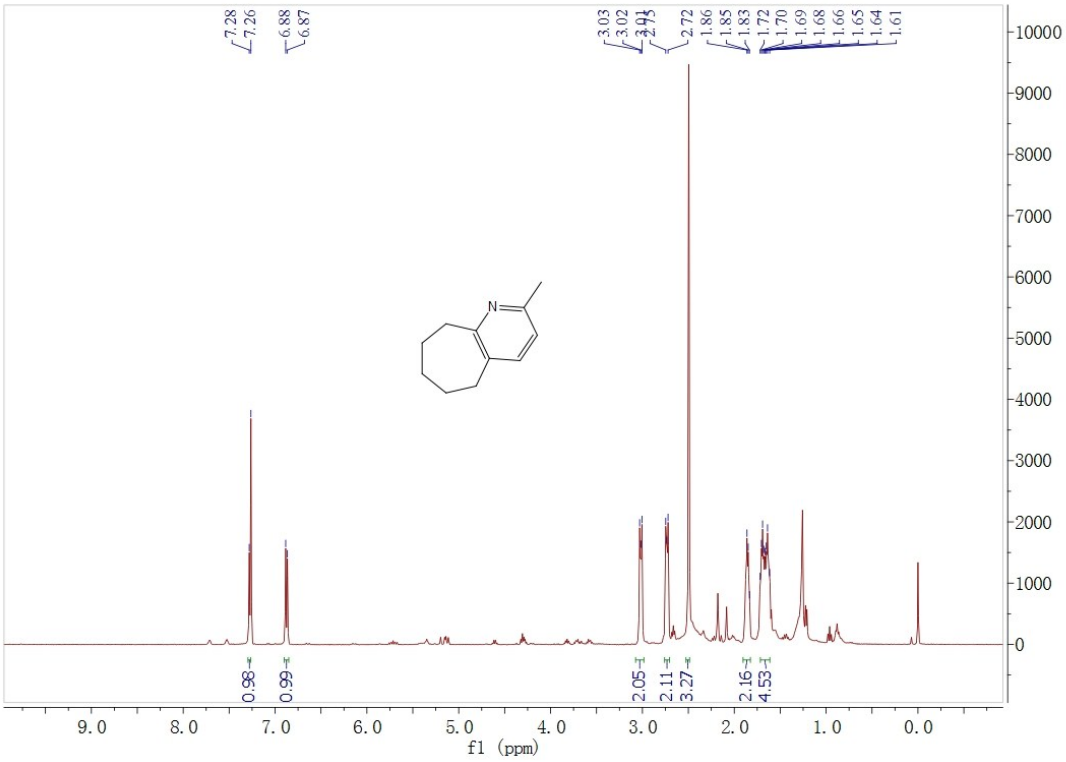

160.91
158.46
155.46
153.28
138.16
129.27
122.43
115.68
115.46
77.43
77.11
76.79
24.12
18.43
18.39
F
N
f1 (ppm)

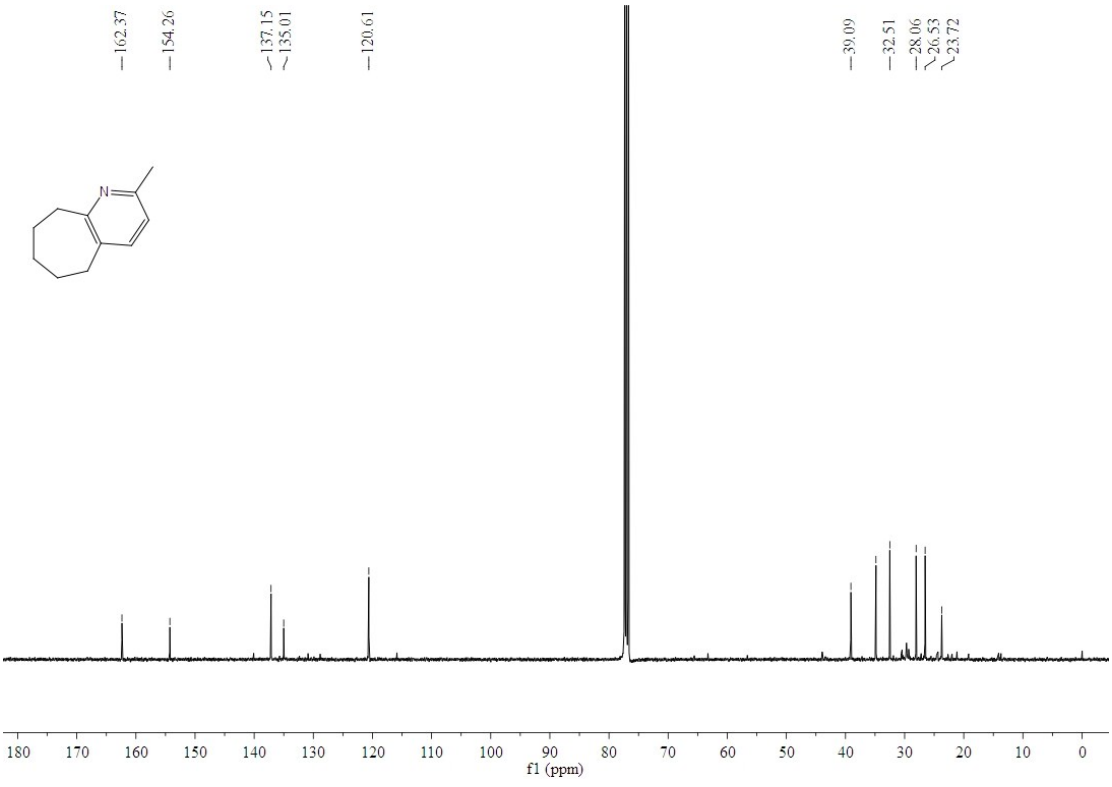
3na


7.48
7.46
7.41
7.39
7.38
7.36
7.34
7.26
7.25
7.23
7.21
7.14
7.12
7.10
7.08
2.57
2.18
1.00
1.99
0.92
1.94
2.92
3.10
N
F
f1 (ppm)

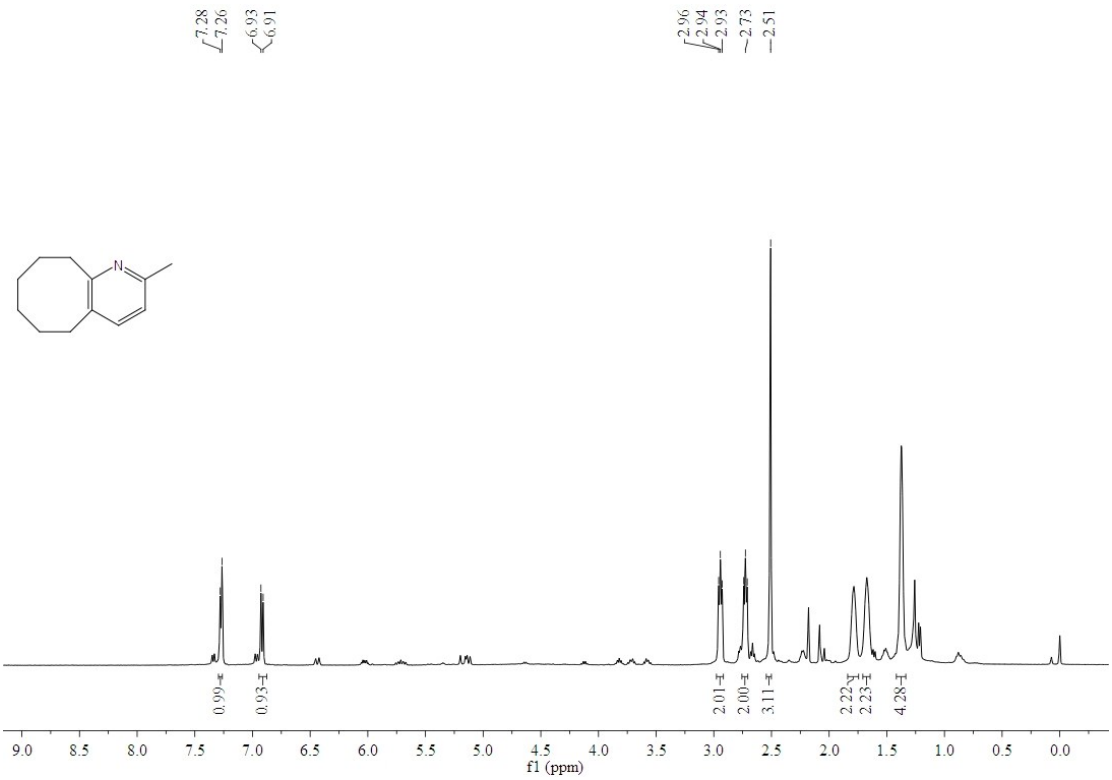

160.91
158.46
155.46
153.27
138.18
129.30
122.43
115.68
115.46
24.07
18.41
18.37
N
F
f1 (ppm)

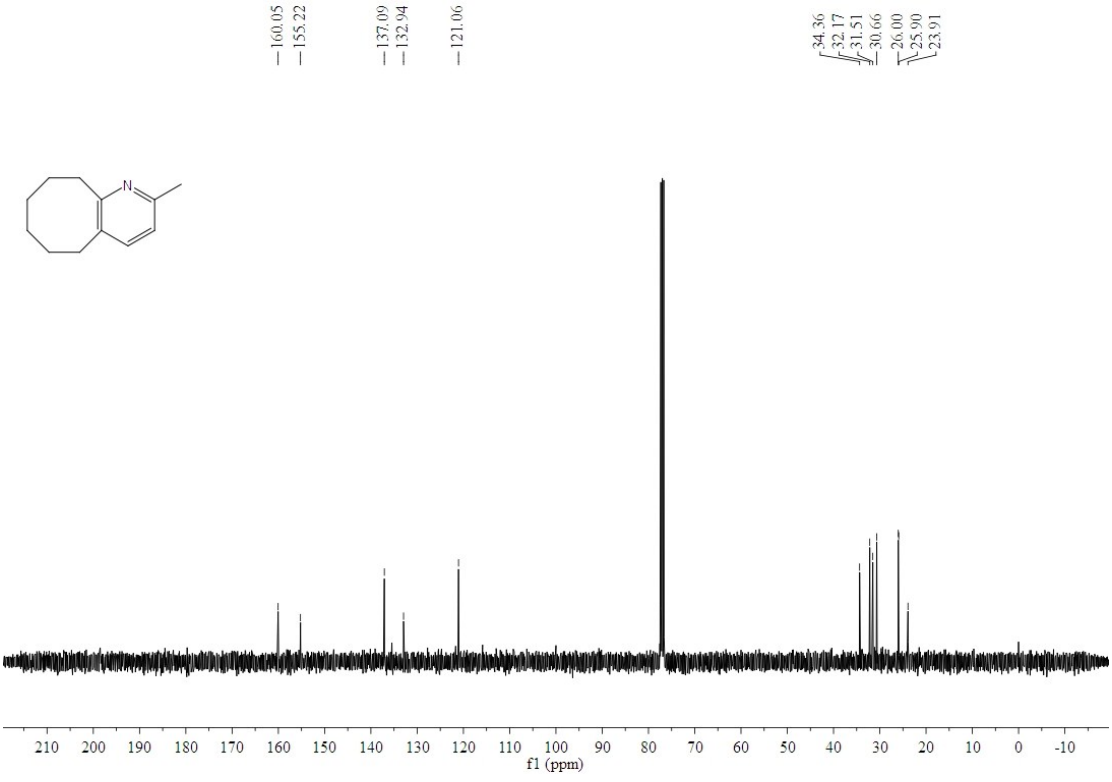
3oa


7.28
7.26
6.88
6.87
3.03
3.02
2.72
1.86
1.85
1.83
1.72
1.70
1.69
1.68
1.66
1.65
1.64
1.61
0.98
0.99
2.05
2.11
3.27
2.16
4.53
f1 (ppm)

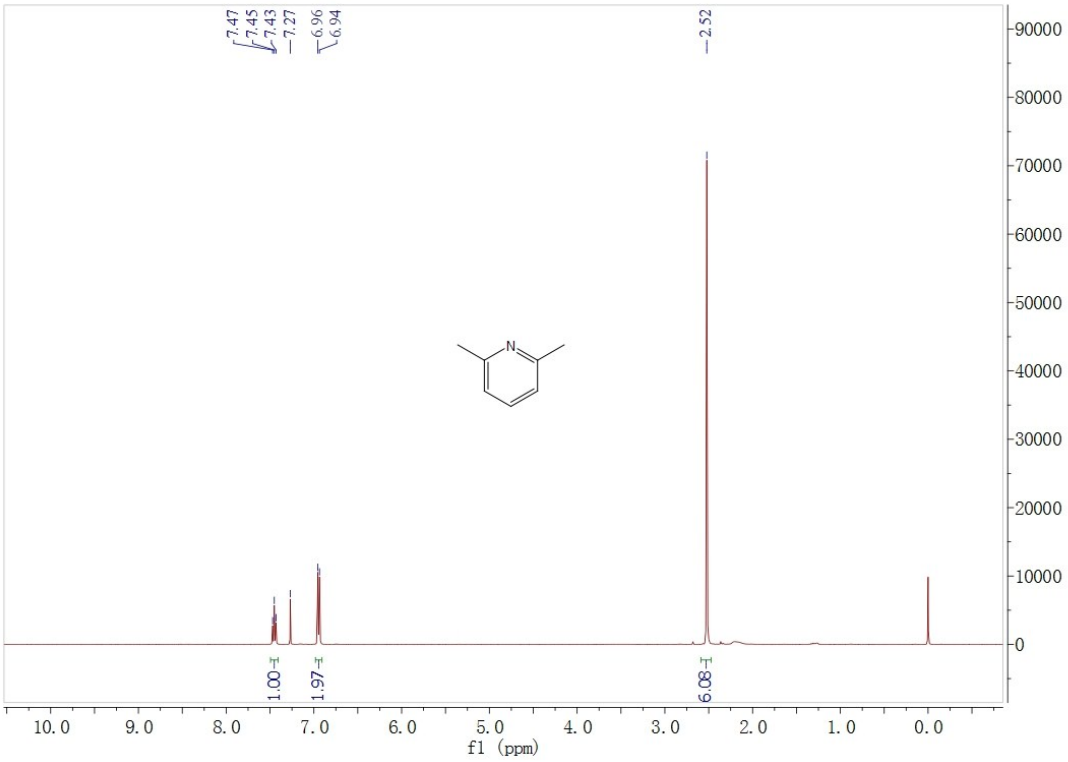

162.37
154.26
137.15
135.01
120.61
39.09
32.51
28.06
26.53
23.72
f1 (ppm)

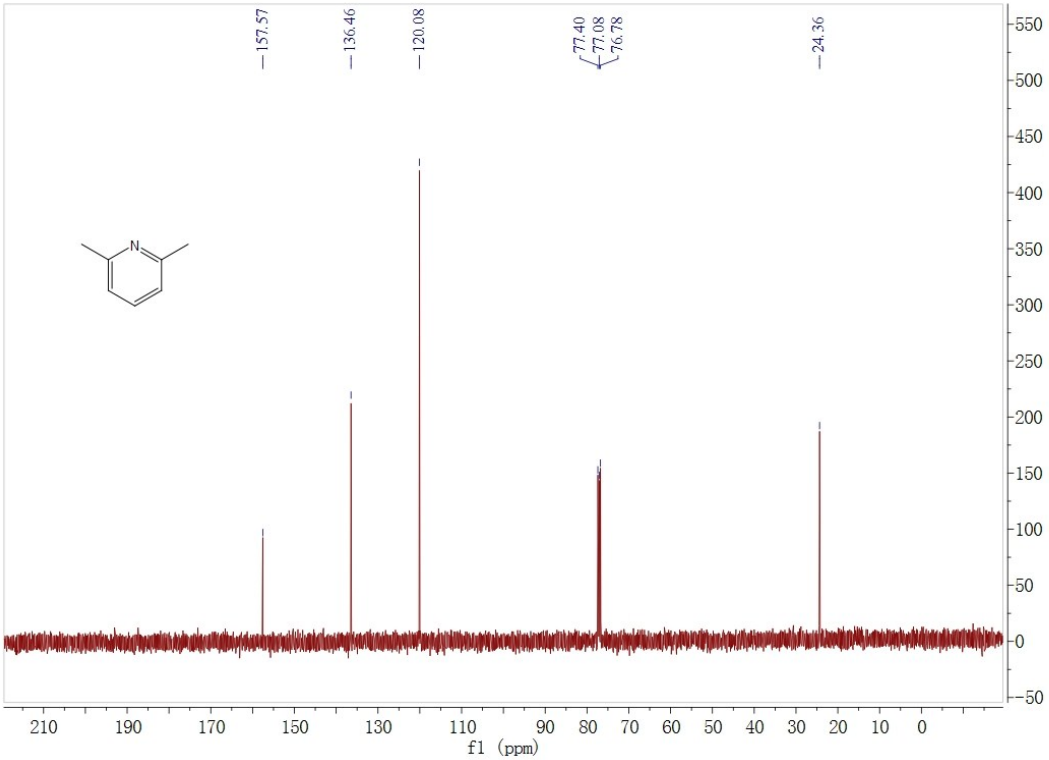
3pa


7.28
7.26
6.93
6.91
2.96
2.94
2.93
2.73
2.51
0.99
0.93
2.01
2.00
3.11
2.22
2.23
4.28
f1 (ppm)

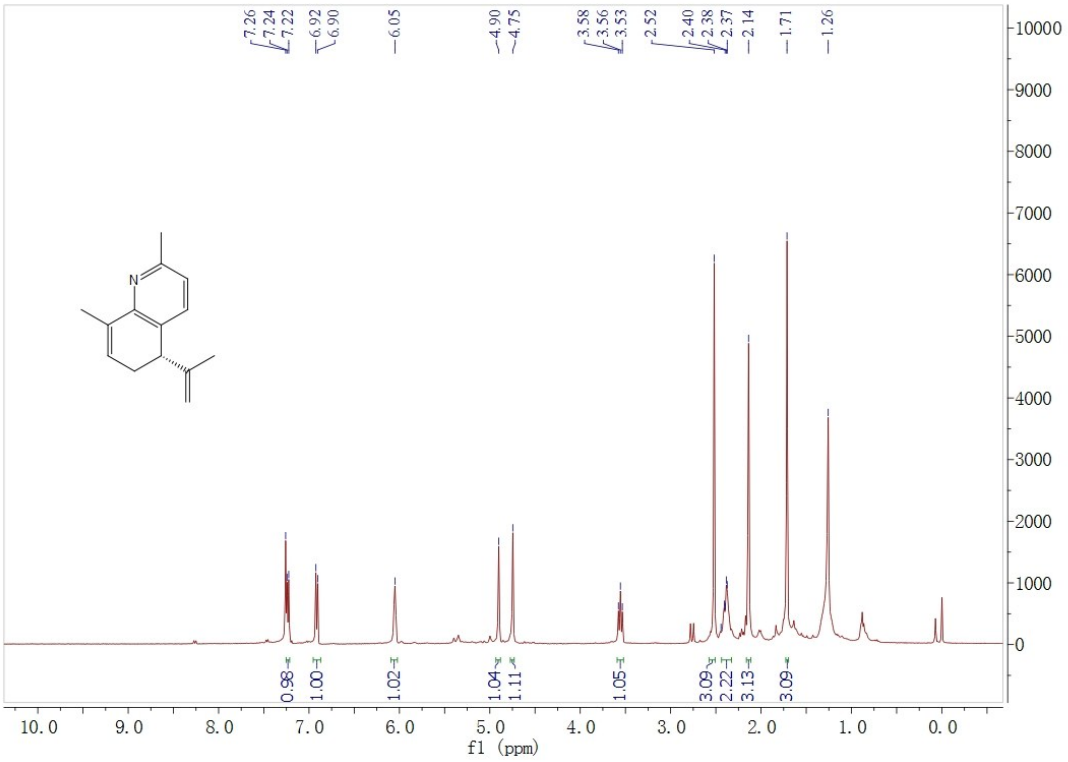

160.05
155.22
137.09
132.94
121.06
34.36
32.17
31.51
30.66
26.00
25.90
23.91
f1 (ppm)

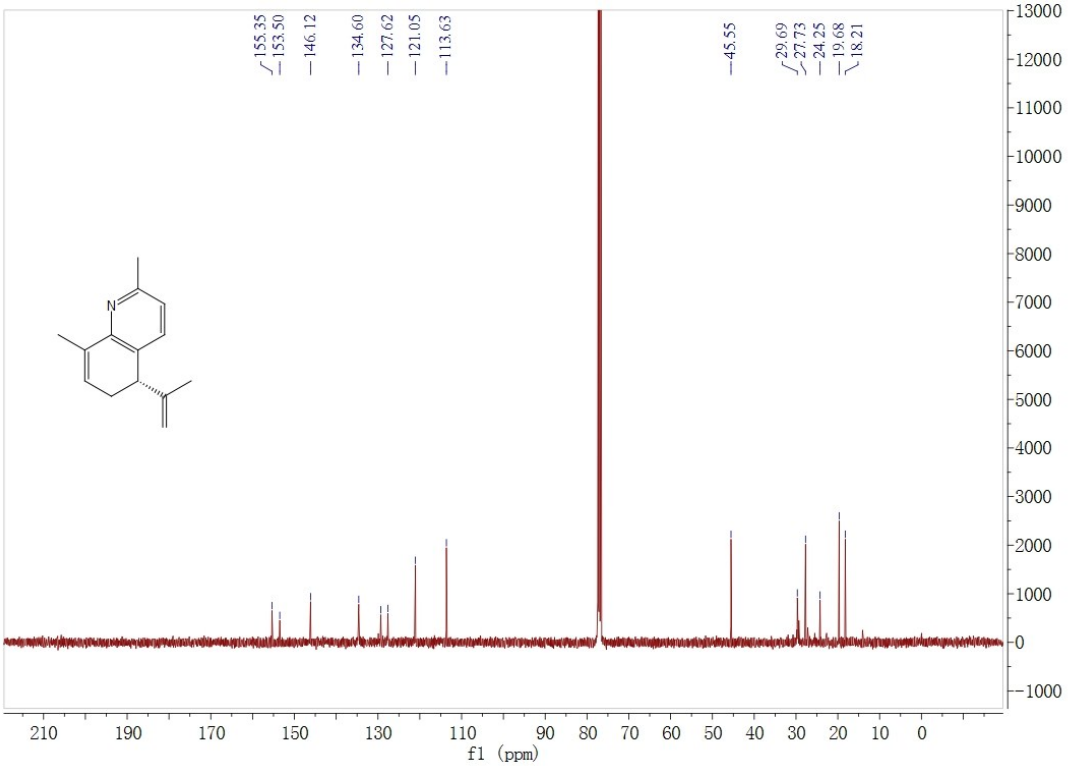
3qa


7.47
7.45
7.43
7.27
6.96
6.94
2.52
1.00
1.97
6.08
f1 (ppm)

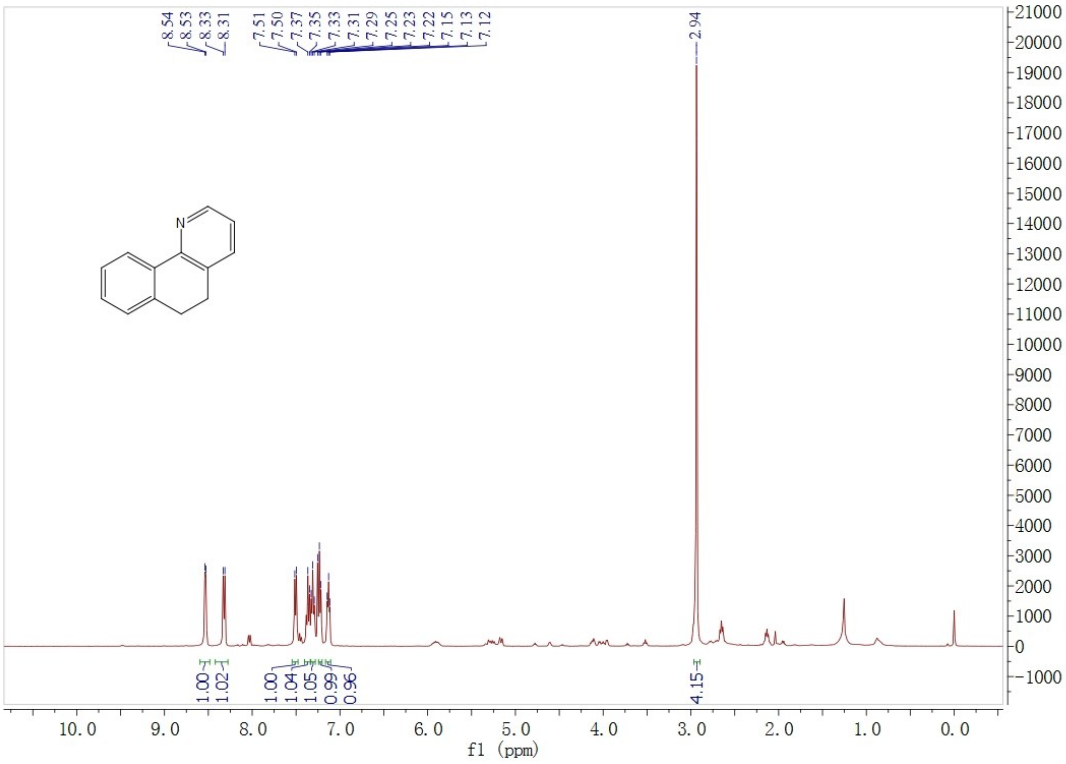

157.57
136.46
120.08
77.40
77.08
76.78
24.36
f1 (ppm)

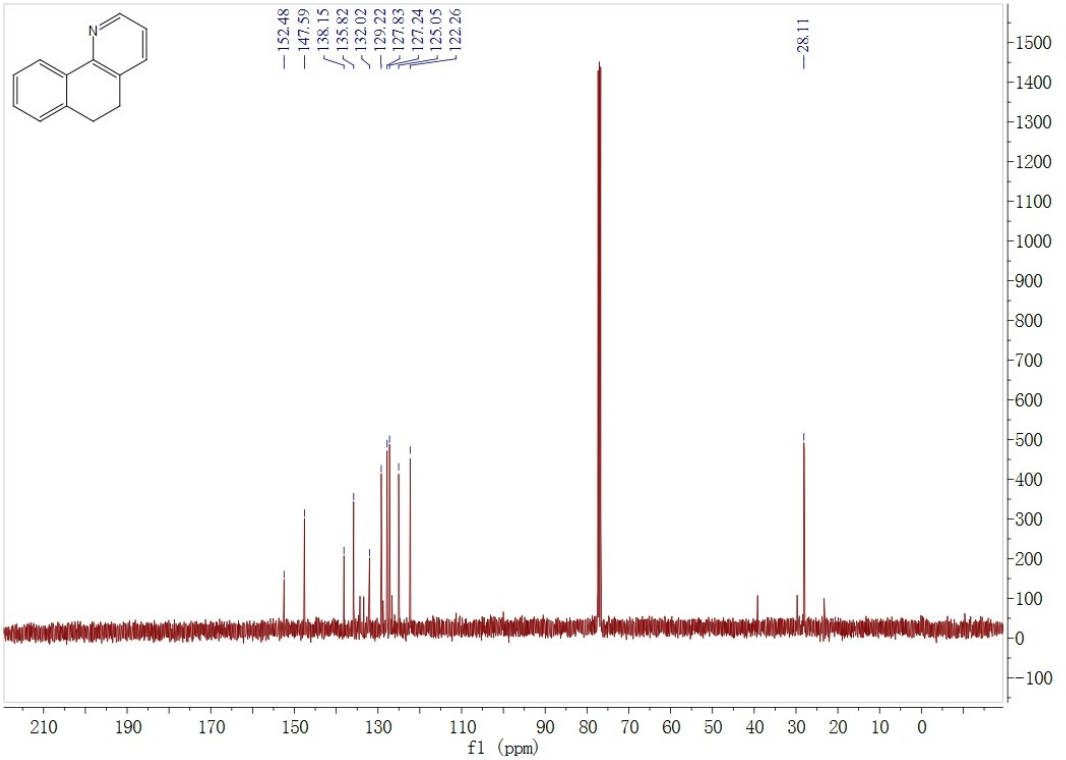
3ra


7.26
7.24
7.22
6.92
6.90
6.05
4.90
4.75
3.58
3.56
3.53
2.52
2.40
2.38
2.37
2.14
1.71
1.26
0.98
1.00
1.02
1.04
1.11
1.05
3.09
2.22
3.13
3.09
f1 (ppm)

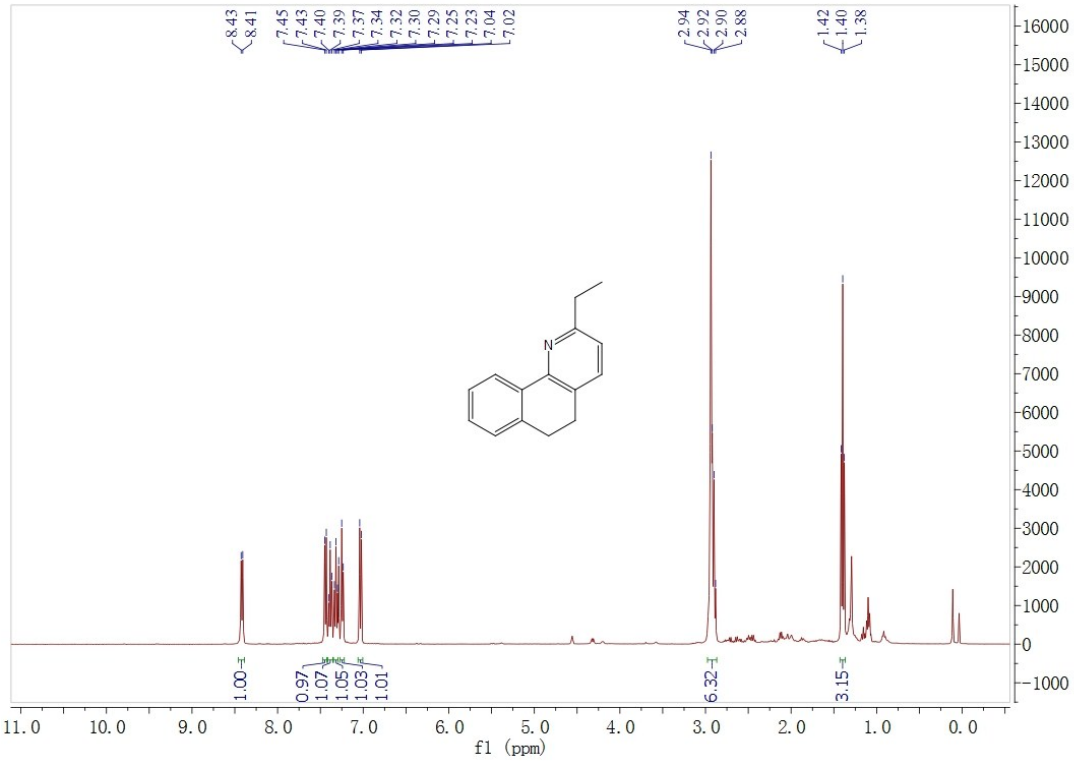

155.35
153.50
146.12
134.60
127.62
121.05
113.63
45.55
29.69
27.73
24.25
19.68
18.21
f1 (ppm)

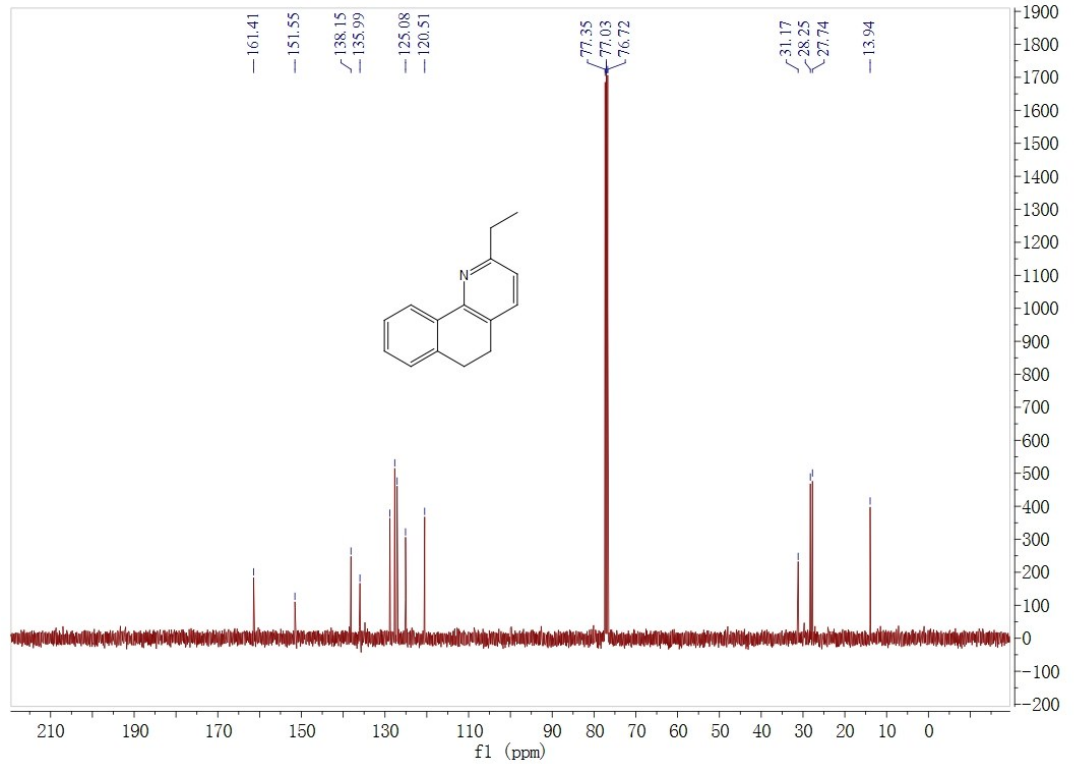
3ab


8.54
8.53
8.33
8.31
7.51
7.50
7.37
7.35
7.33
7.31
7.29
7.25
7.23
7.22
7.15
7.13
7.12
2.94
1.00
1.02
1.00
1.04
1.05
0.99
0.96
4.15
f1 (ppm)

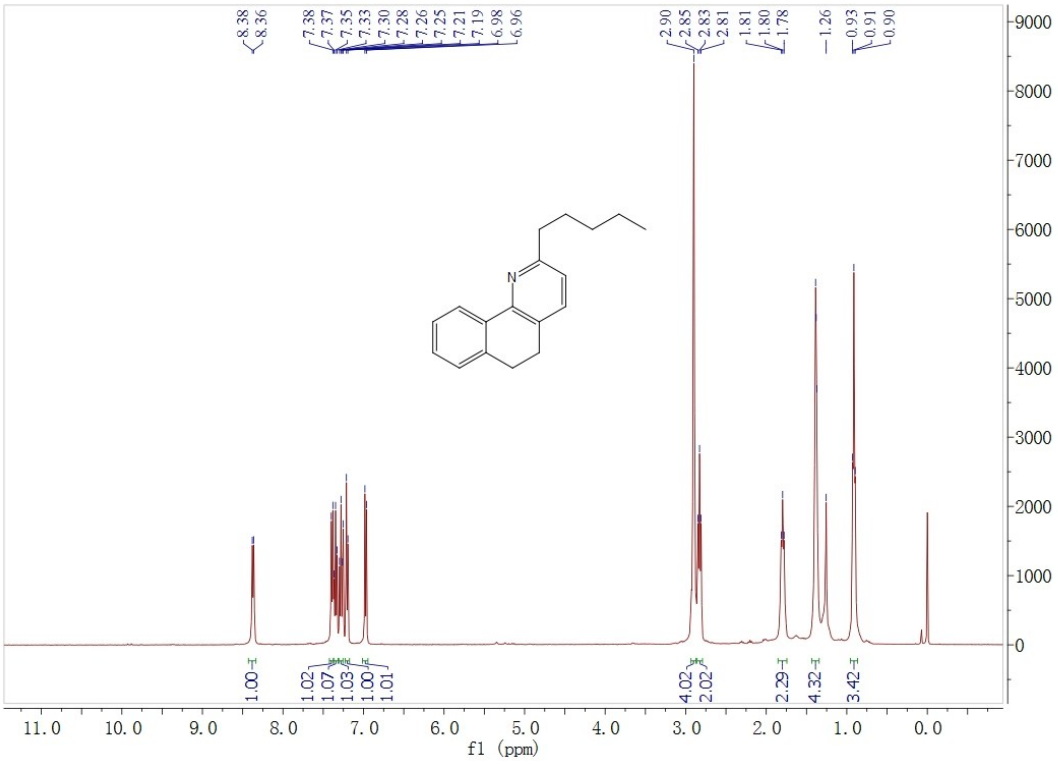

152.48
147.59
138.15
135.82
132.02
129.22
127.83
127.24
125.05
122.26
28.11
f1 (ppm)

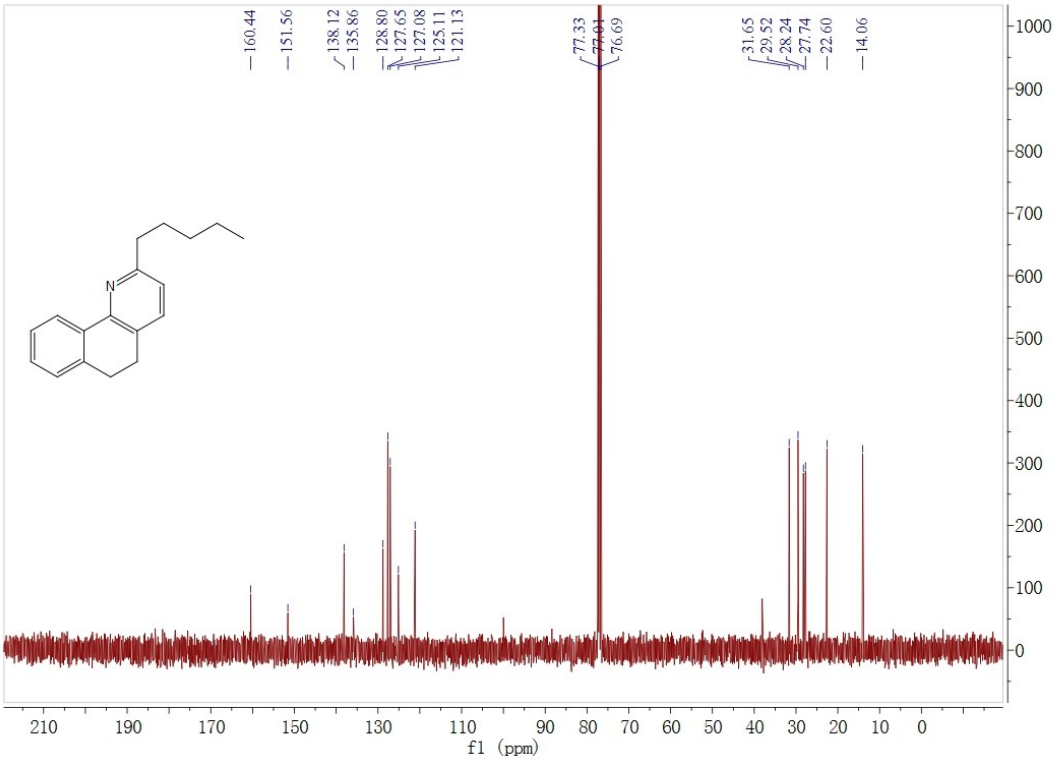
3ac


8.43
8.41
7.45
7.43
7.40
7.39
7.37
7.34
7.32
7.30
7.29
7.25
7.23
7.04
7.02
2.94
2.92
2.90
2.88
1.42
1.40
1.38
1.00
0.97
1.07
1.05
1.03
1.01
6.32
3.15
f1 (ppm)

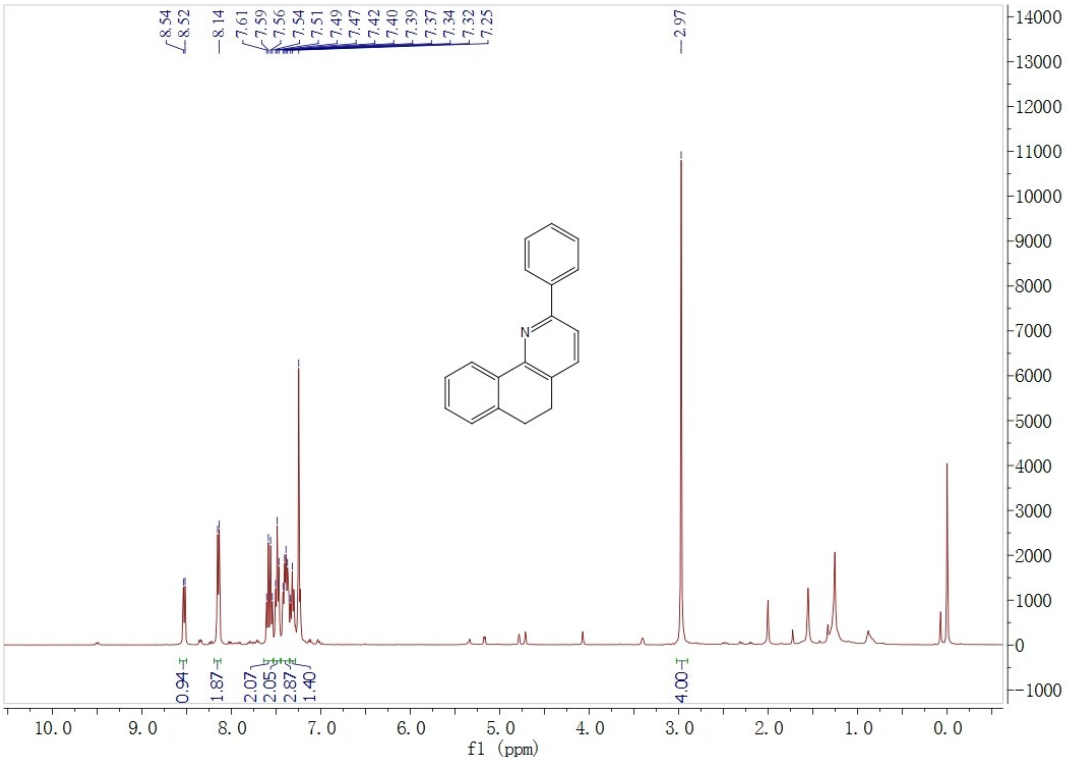

161.41
151.55
138.15
135.99
125.08
120.51
77.35
77.03
76.72
31.17
28.25
27.74
13.94
f1 (ppm)

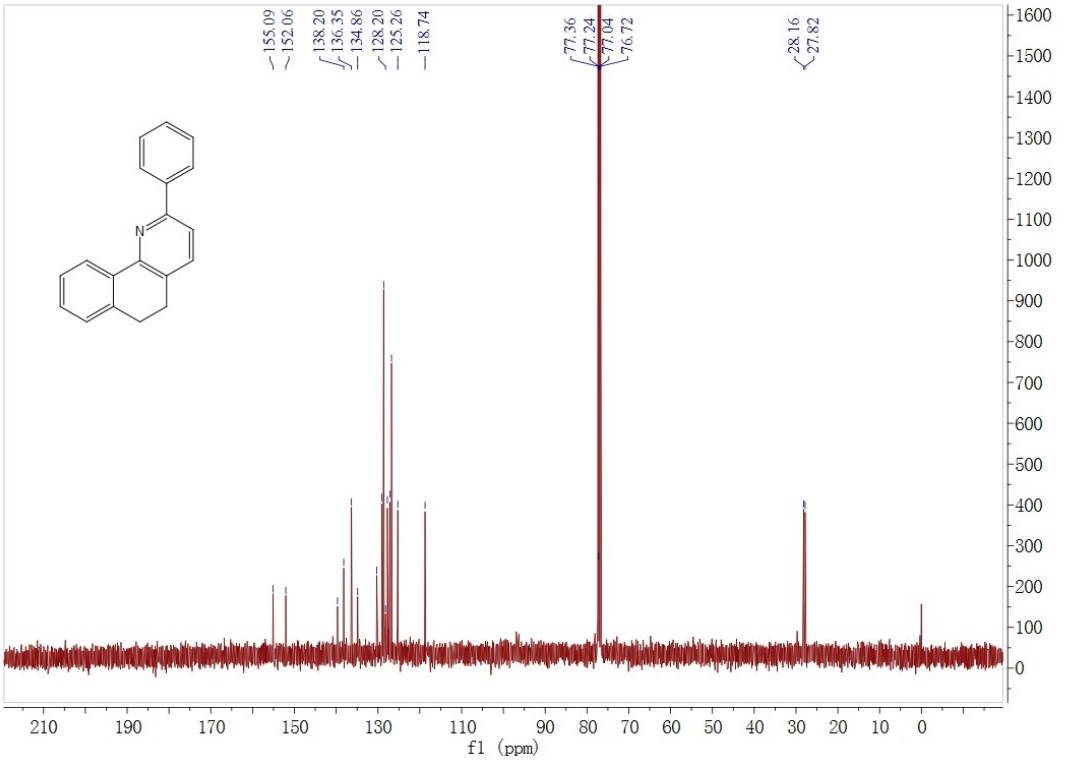
3ad


8.38
8.36
7.38
7.37
7.35
7.33
7.30
7.28
7.26
7.25
7.21
7.19
6.98
6.96
2.90
2.85
2.83
2.81
1.81
1.80
1.78
1.26
0.93
0.91
0.90
N
1.00
1.02
1.07
1.03
1.00
1.01
4.02
2.02
2.29
4.32
3.42
f1 (ppm)

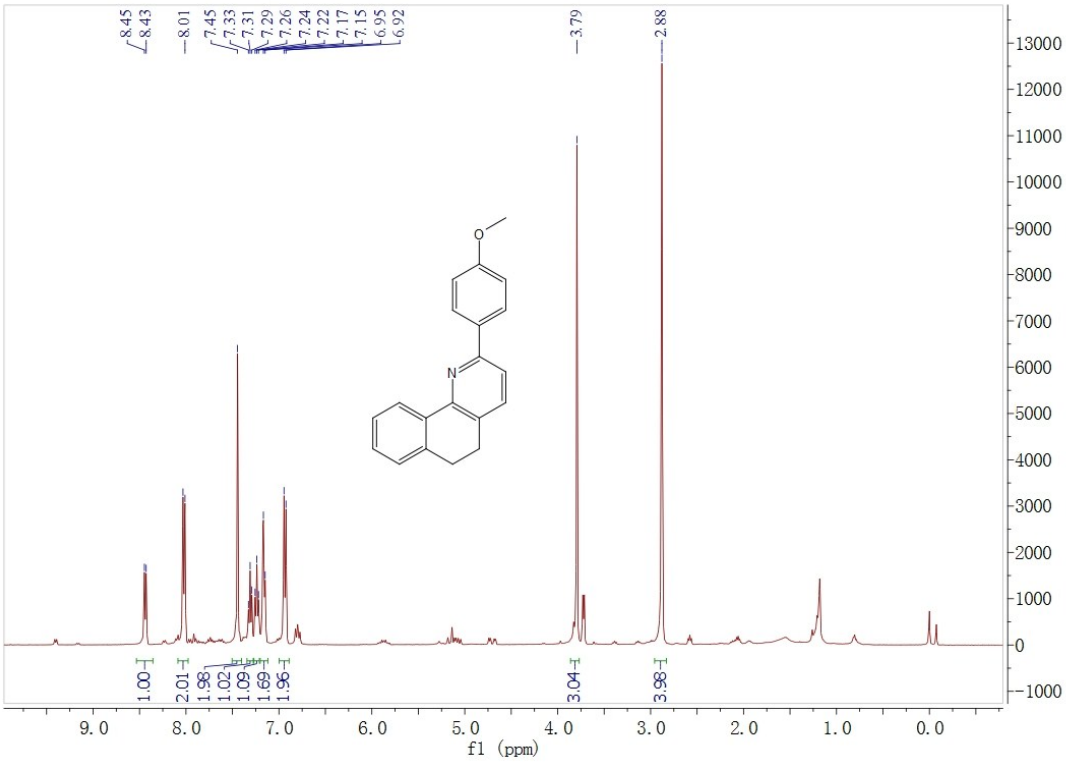

160.44
151.56
138.12
135.86
128.80
127.65
127.08
125.11
121.13
77.33
77.01
76.69
31.65
29.52
28.24
27.74
22.60
14.06
N
f1 (ppm)

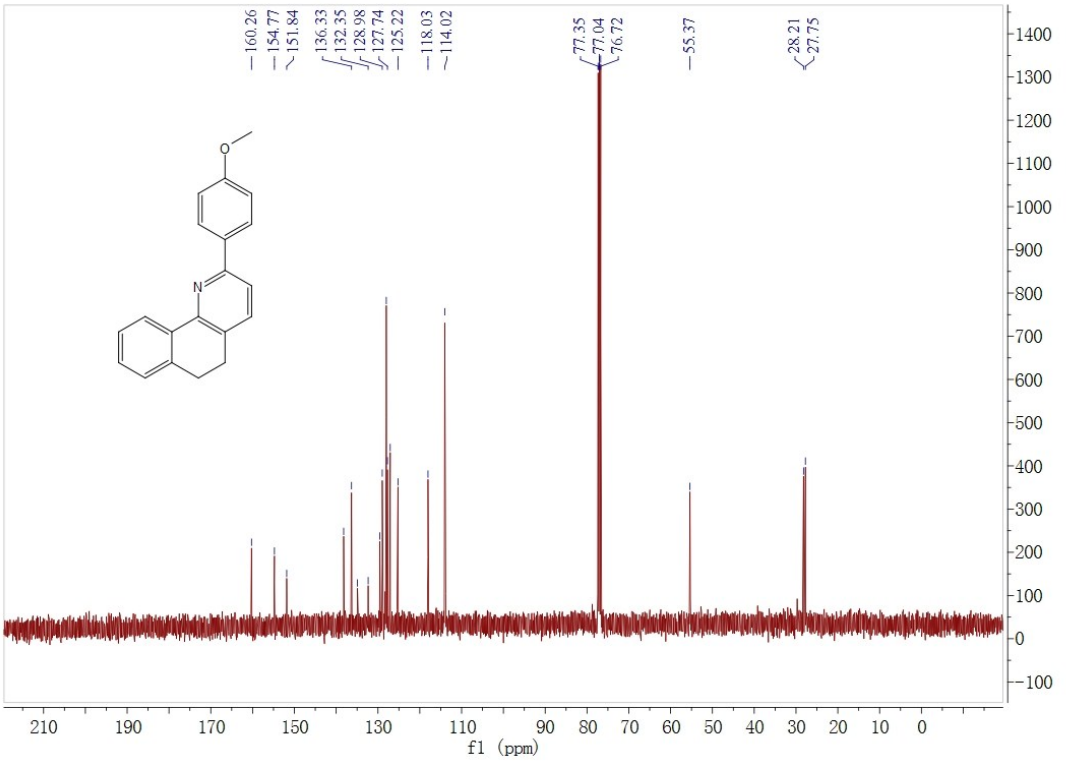
3ae


8.54
8.52
8.14
7.61
7.59
7.56
7.54
7.51
7.49
7.47
7.42
7.40
7.39
7.37
7.34
7.32
7.25
2.97
0.94
1.87
2.07
2.05
2.87
1.40
4.00
N
f1 (ppm)

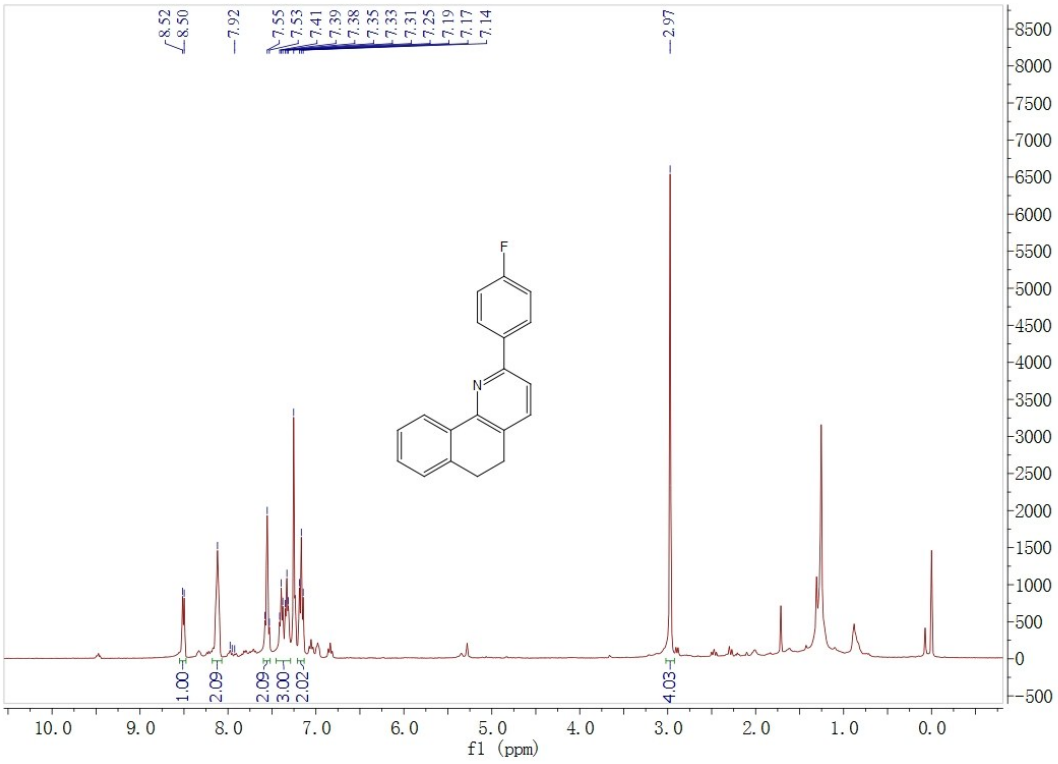

155.09
152.06
138.20
136.35
134.86
128.20
125.26
118.74
77.36
77.24
77.04
76.72
28.16
27.82
N
f1 (ppm)

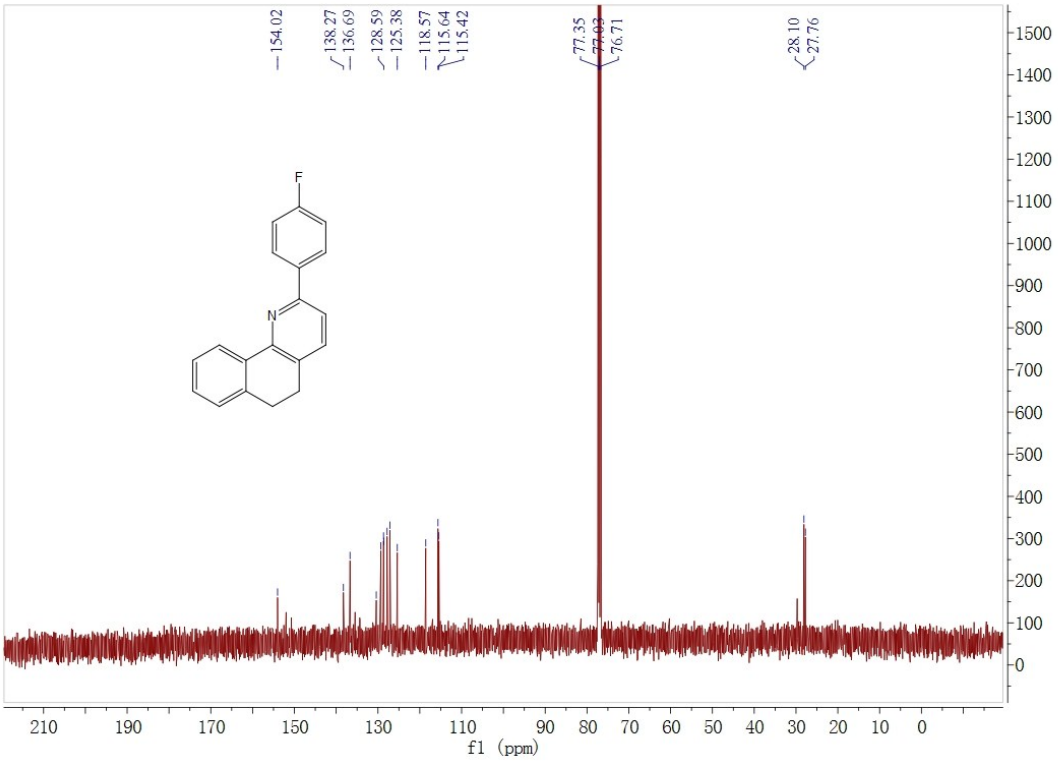
3af


8.45
8.43
8.01
7.45
7.33
7.31
7.29
7.26
7.24
7.22
7.17
7.15
6.95
6.92
3.79
2.88
O
N
1.00
2.01
1.98
1.02
1.05
1.69
1.96
3.04
3.98
f1 (ppm)

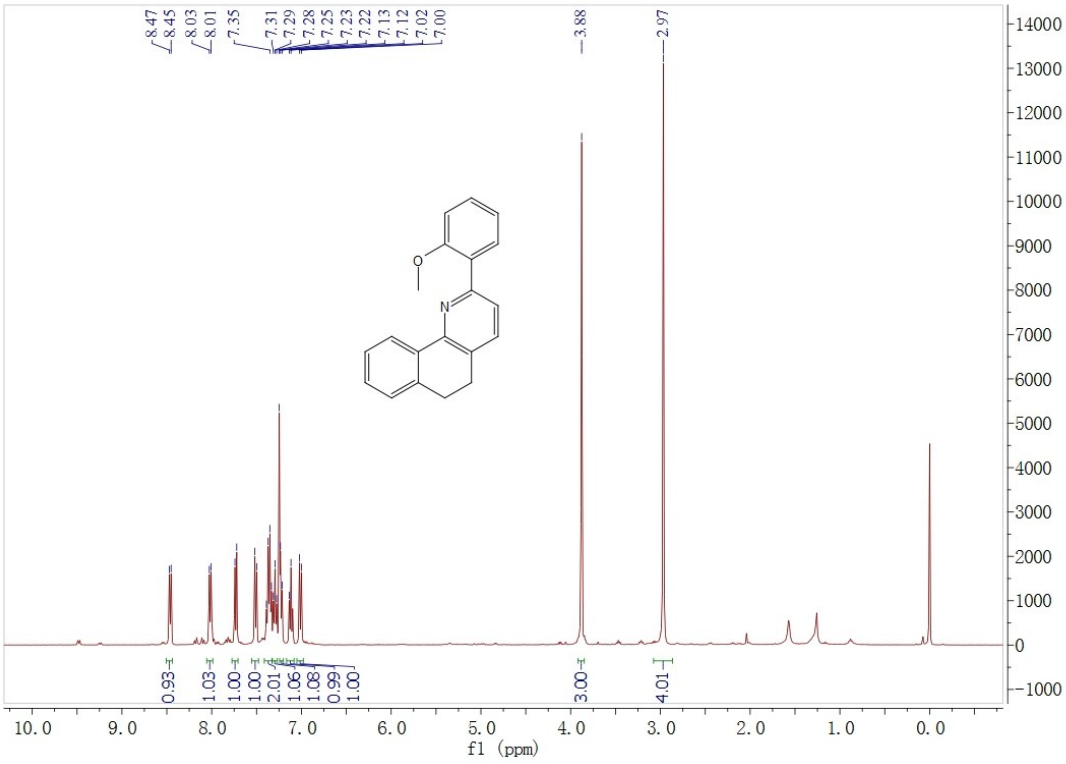

160.26
154.77
151.84
136.33
132.35
128.98
127.74
125.22
118.03
114.02
77.35
77.04
76.72
55.37
28.21
27.75
O
N
f1 (ppm)

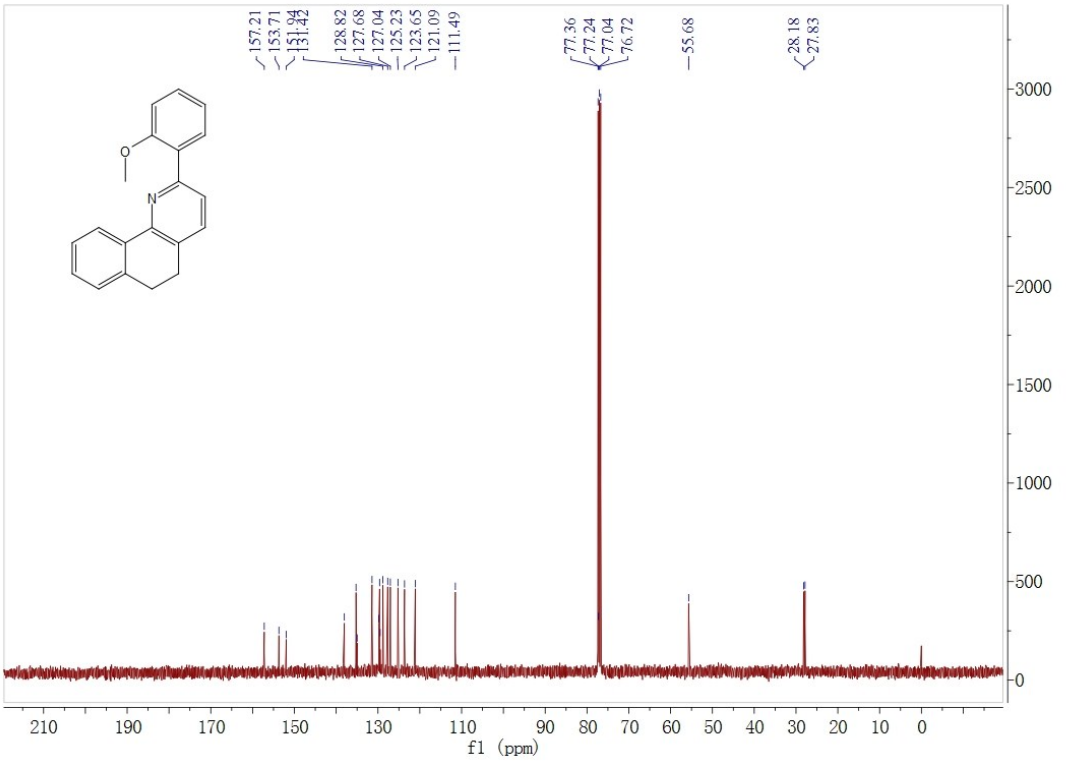
3ag


8.52
8.50
7.92
7.55
7.53
7.41
7.39
7.38
7.35
7.33
7.31
7.25
7.19
7.17
7.14
2.97
F
N
1.00
2.09
2.09
3.00
2.02
4.03
f1 (ppm)

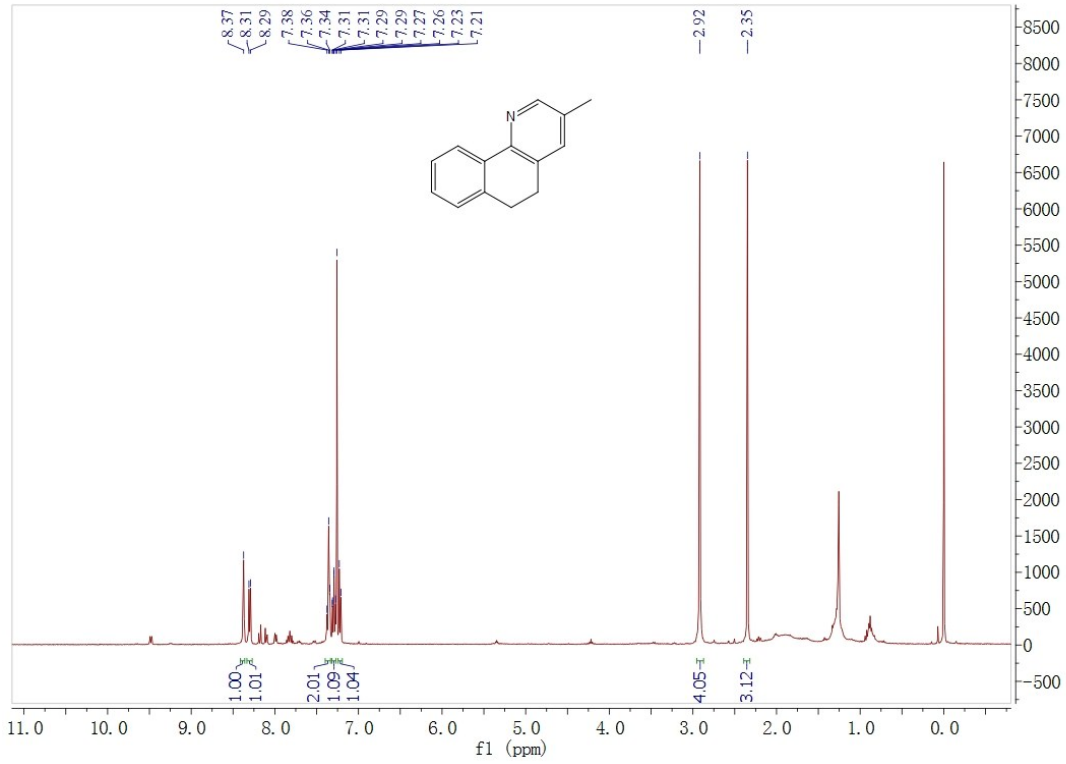

154.02
138.27
136.69
128.59
125.38
118.57
115.64
115.42
77.35
77.03
76.71
28.10
27.76
F
N
f1 (ppm)

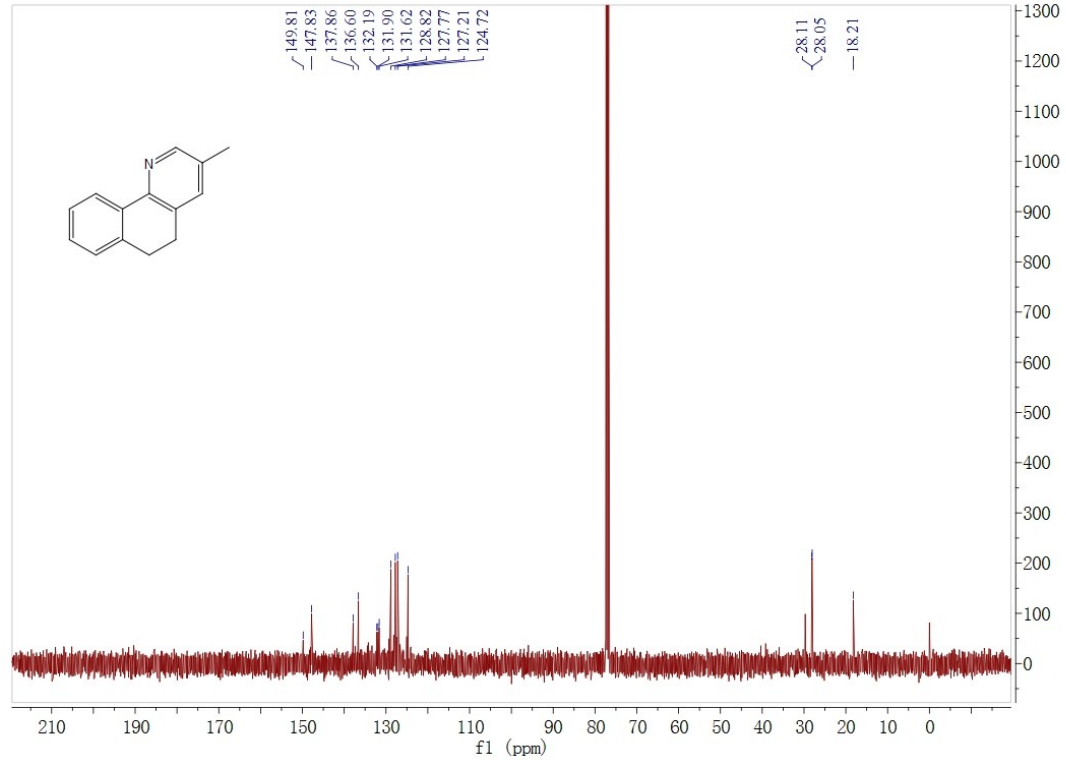
3ah


8.47
8.45
8.03
8.01
7.35
7.31
7.29
7.28
7.25
7.23
7.22
7.13
7.12
7.02
7.00
3.88
2.97
0.93
1.03
1.00
1.00
2.01
1.06
1.08
0.99
1.00
3.00
4.01
f1 (ppm)

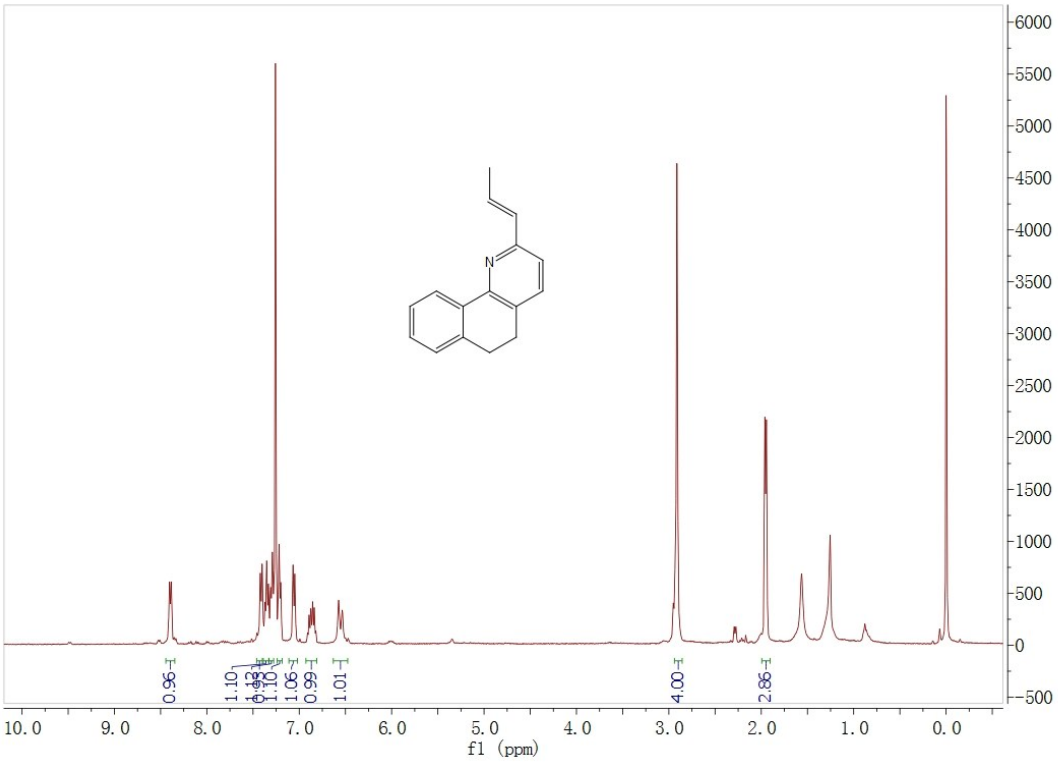

157.21
153.71
131.94
131.42
128.82
127.68
127.04
125.23
123.65
121.09
111.49
77.36
77.24
77.04
76.72
55.68
28.18
27.83
f1 (ppm)

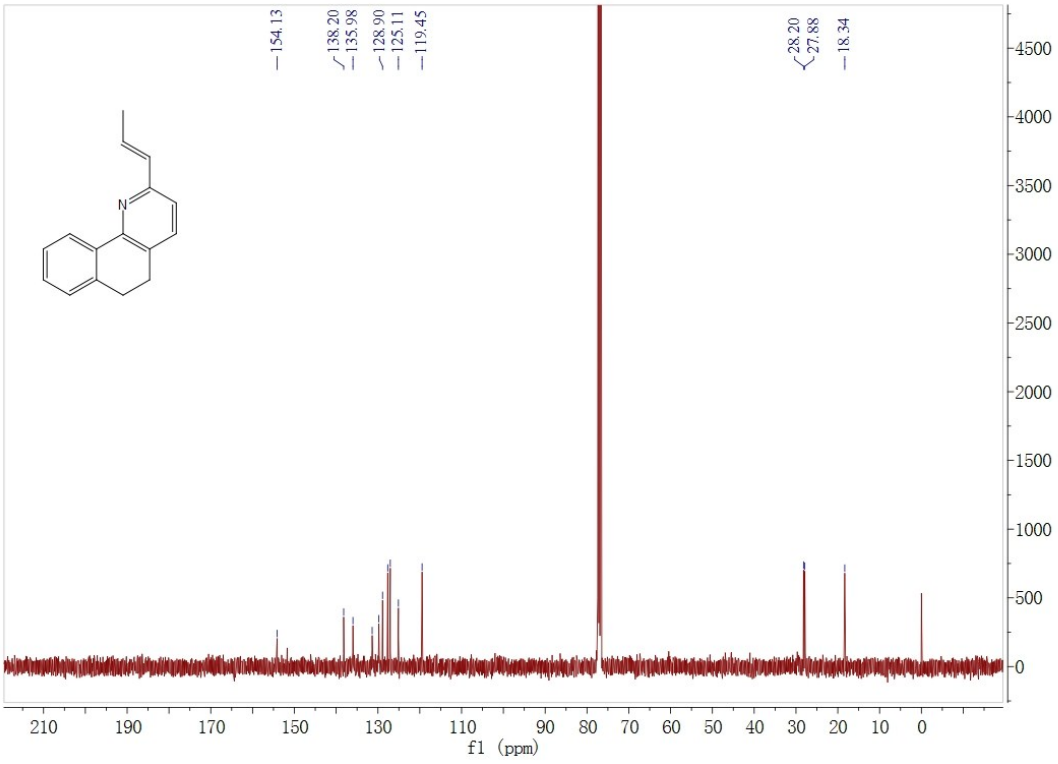
3ai


8.37
8.31
8.29
7.38
7.36
7.34
7.31
7.31
7.29
7.29
7.27
7.26
7.23
7.21
2.92
2.35
1.00
1.01
2.01
1.09
1.04
4.05
3.12
f1 (ppm)

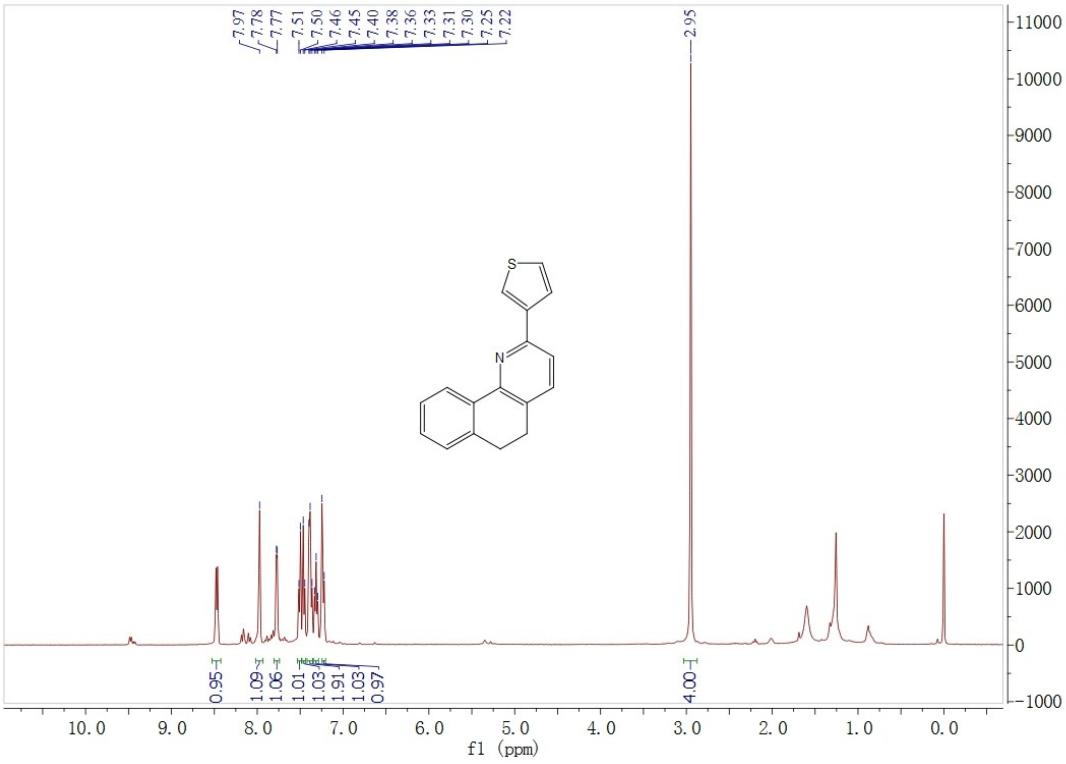

149.81
147.83
137.86
136.60
132.19
131.90
131.62
128.82
127.77
127.21
124.72
28.11
28.05
18.21
f1 (ppm)

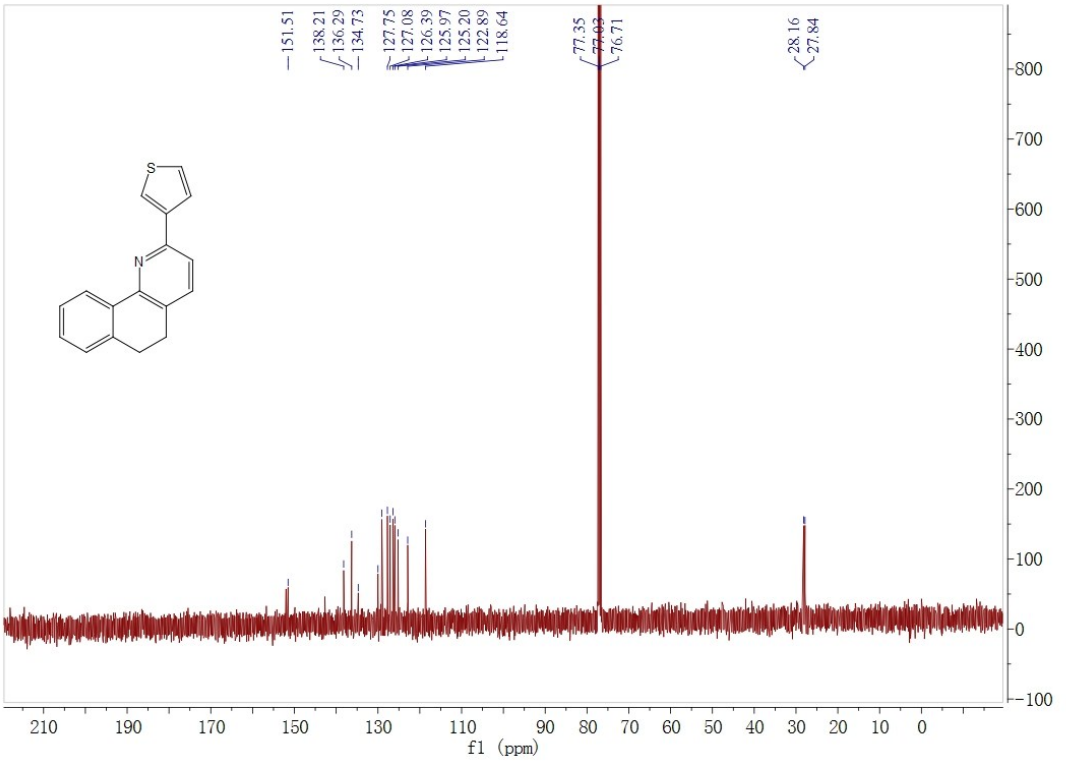
3aj


0.96
1.10
1.10
1.05
0.99
1.01
4.00
2.86
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)
N

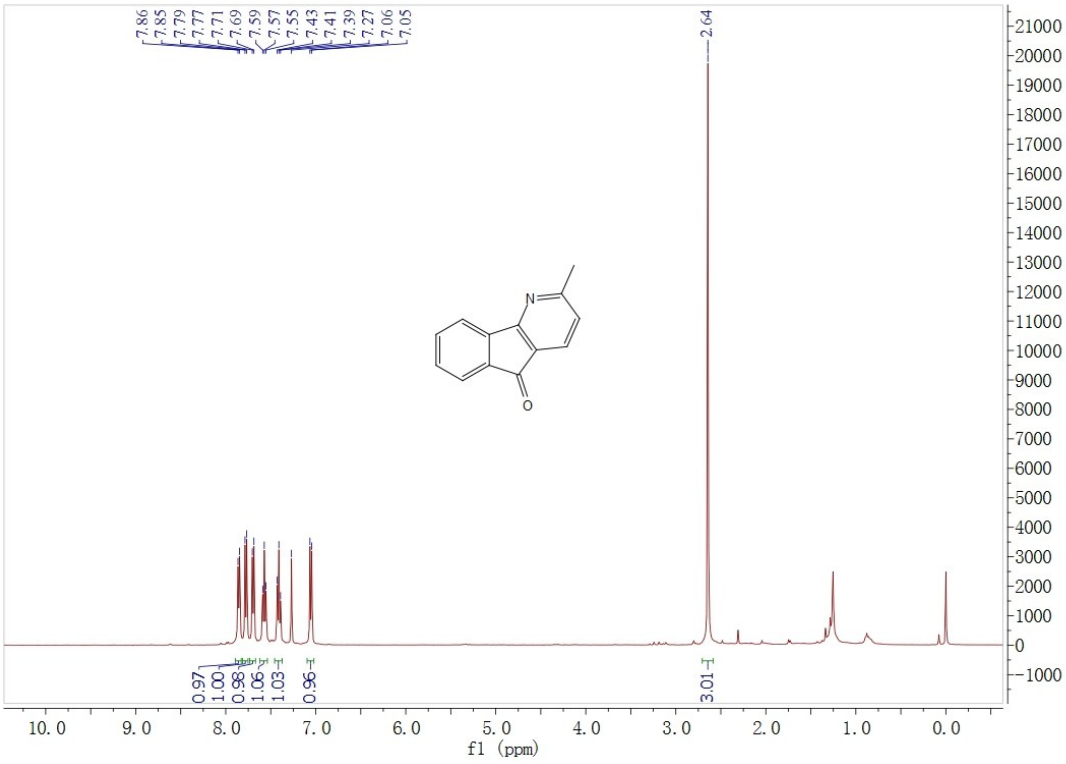

154.13
138.20
135.98
128.90
125.11
119.45
28.20
27.88
18.34
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
N

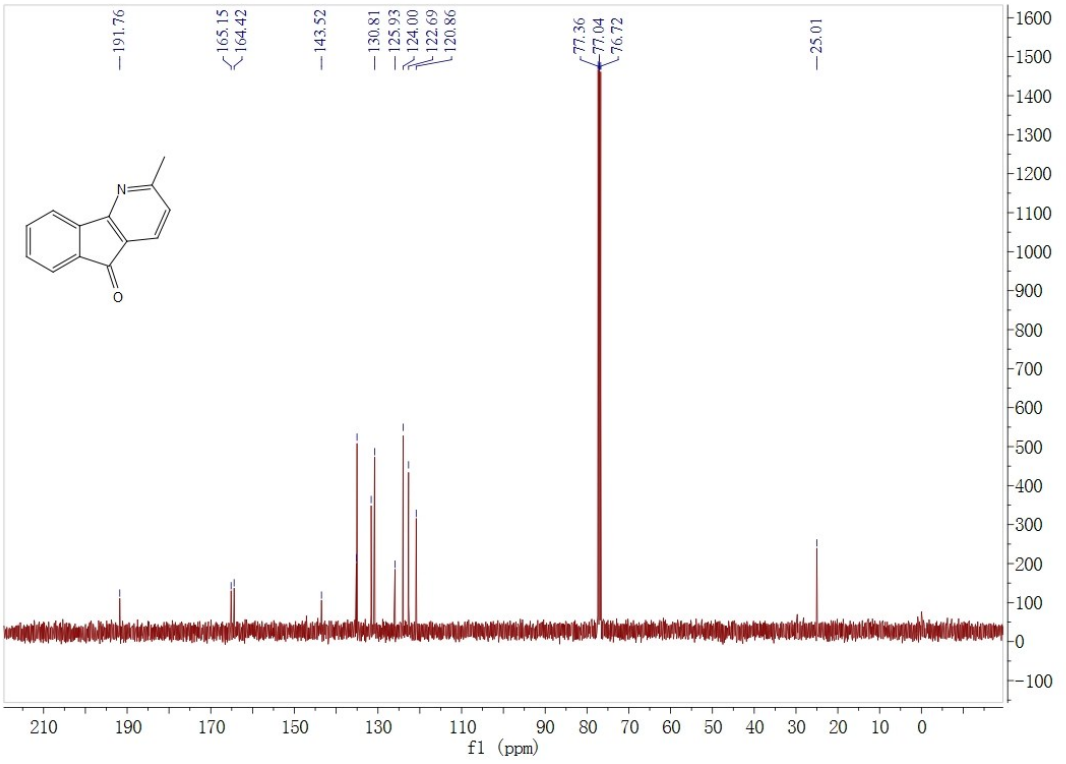
3ak


7.97
7.78
7.77
7.51
7.50
7.46
7.45
7.40
7.38
7.36
7.33
7.31
7.30
7.25
7.22
2.95
S
N
0.95
1.09
1.06
1.01
1.03
1.91
1.03
0.97
4.00
f1 (ppm)

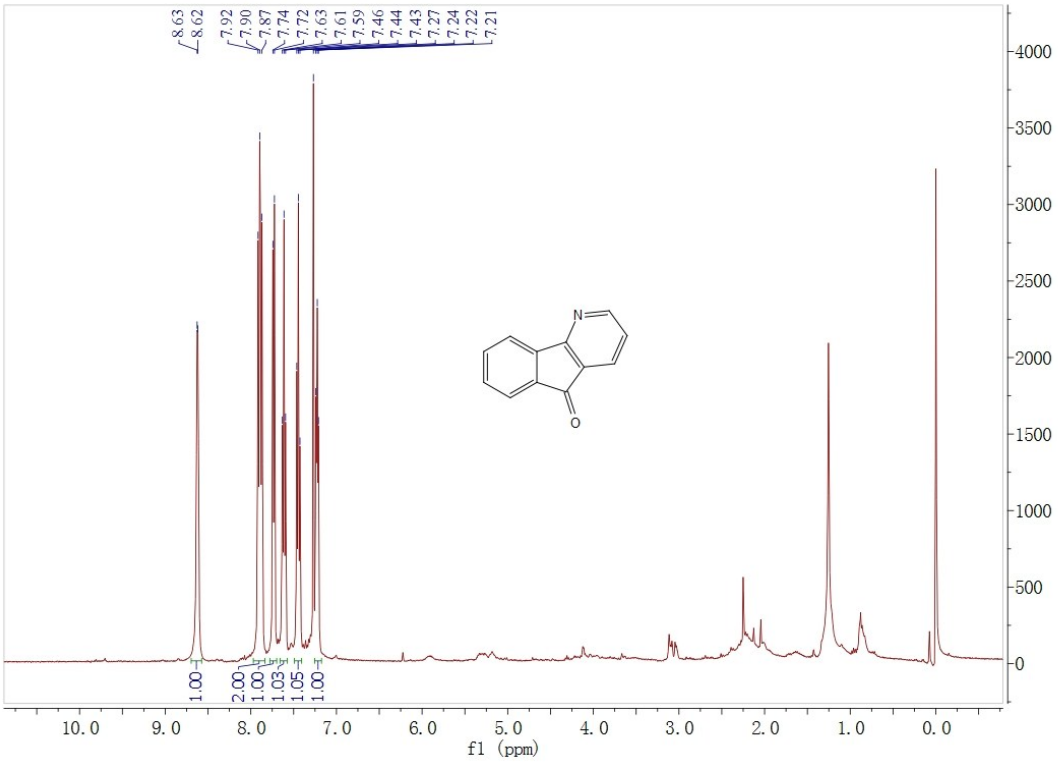

151.51
138.21
136.29
134.73
127.75
127.08
126.39
125.97
125.20
122.89
118.64
77.35
77.03
76.71
28.16
27.84
S
N
f1 (ppm)

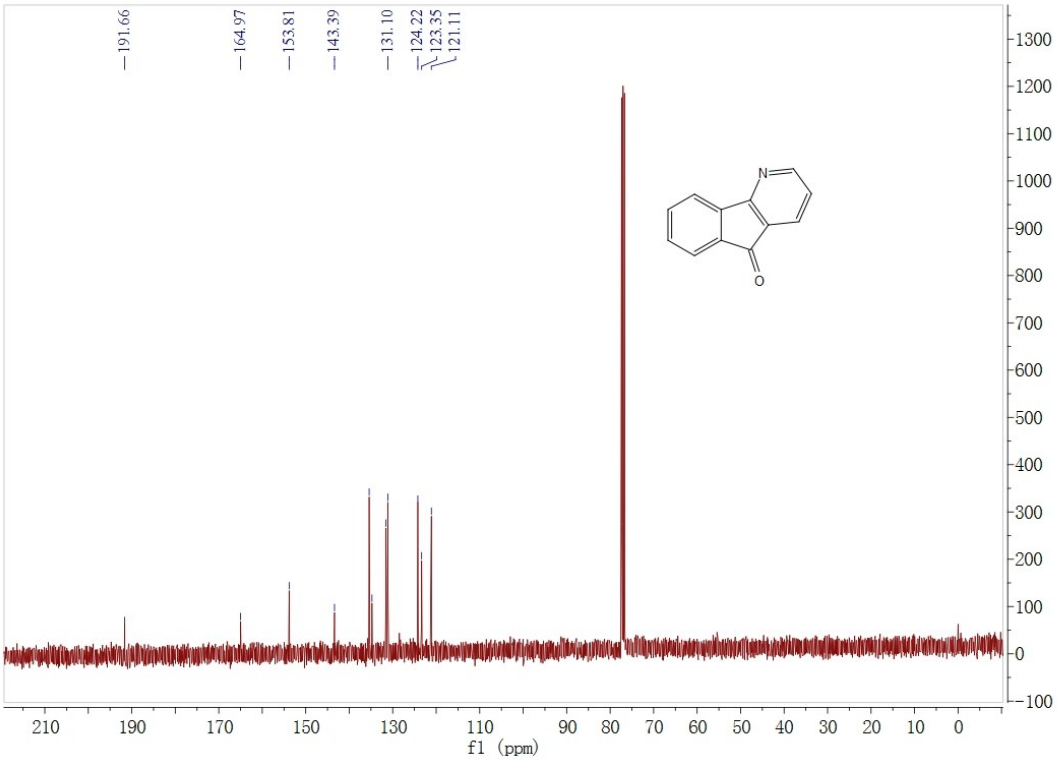
4a


7.86
7.85
7.79
7.77
7.77
7.71
7.69
7.59
7.57
7.55
7.43
7.41
7.39
7.27
7.06
7.05
2.64
0.97
1.00
0.98
1.06
1.03
0.96
3.01
f1 (ppm)

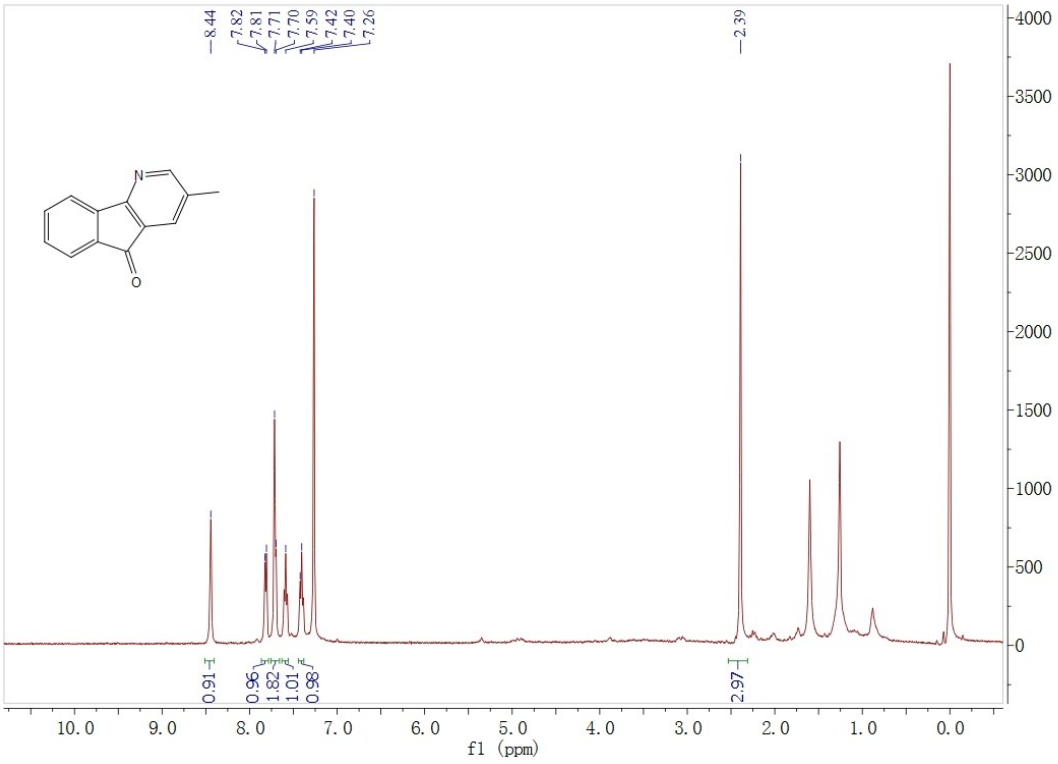

191.76
165.15
164.42
143.52
130.81
125.93
124.00
122.69
120.86
77.36
77.04
76.72
25.01
f1 (ppm)

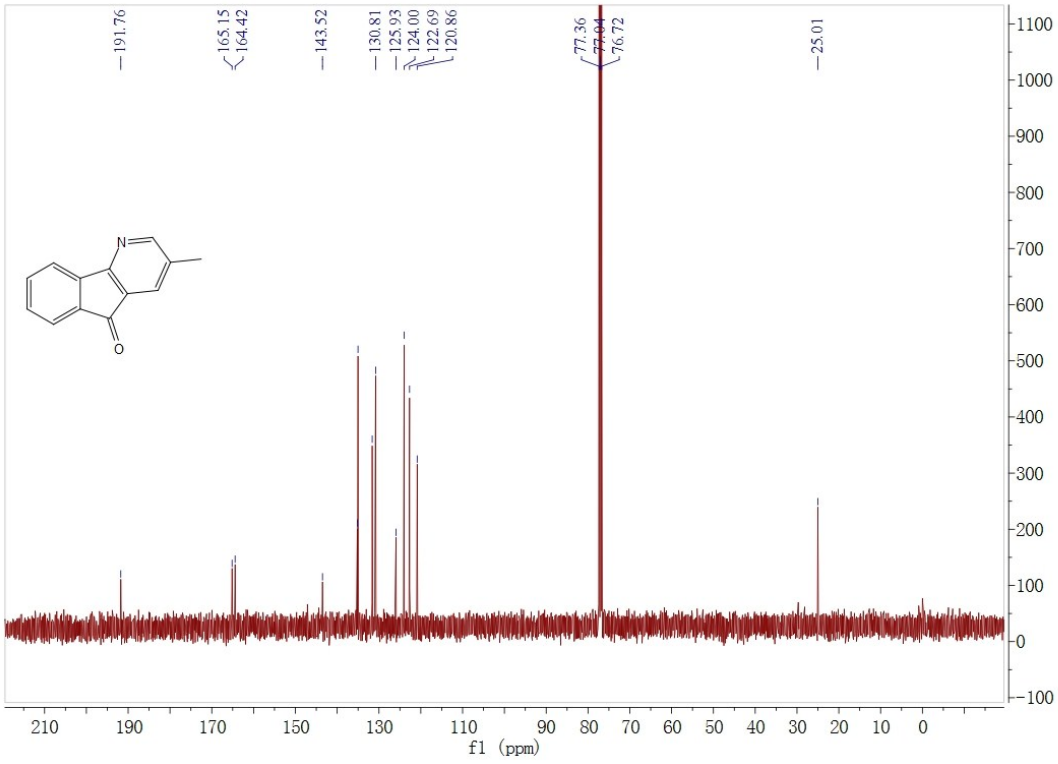
4b


8.63
8.62
7.92
7.90
7.87
7.74
7.72
7.63
7.61
7.59
7.46
7.44
7.43
7.27
7.24
7.22
7.21
1.00
2.00
1.00
1.03
1.05
1.00
N
O
f1 (ppm)

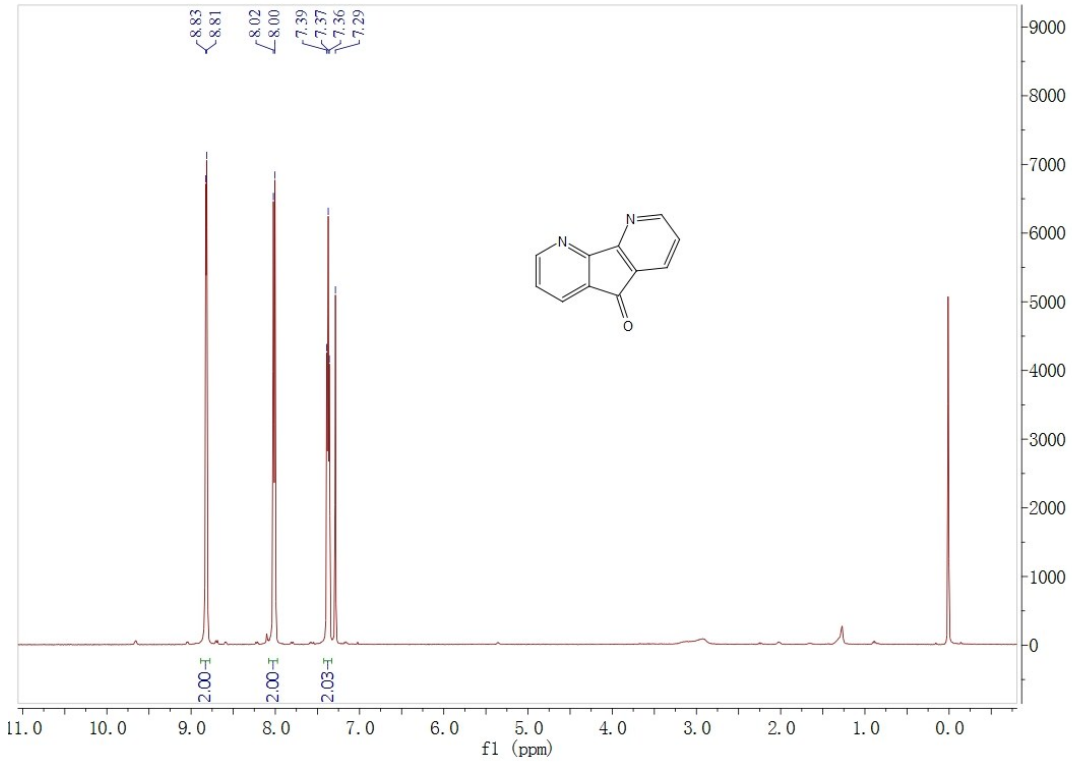

191.66
164.97
153.81
143.39
131.10
124.22
123.35
121.11
N
O
f1 (ppm)

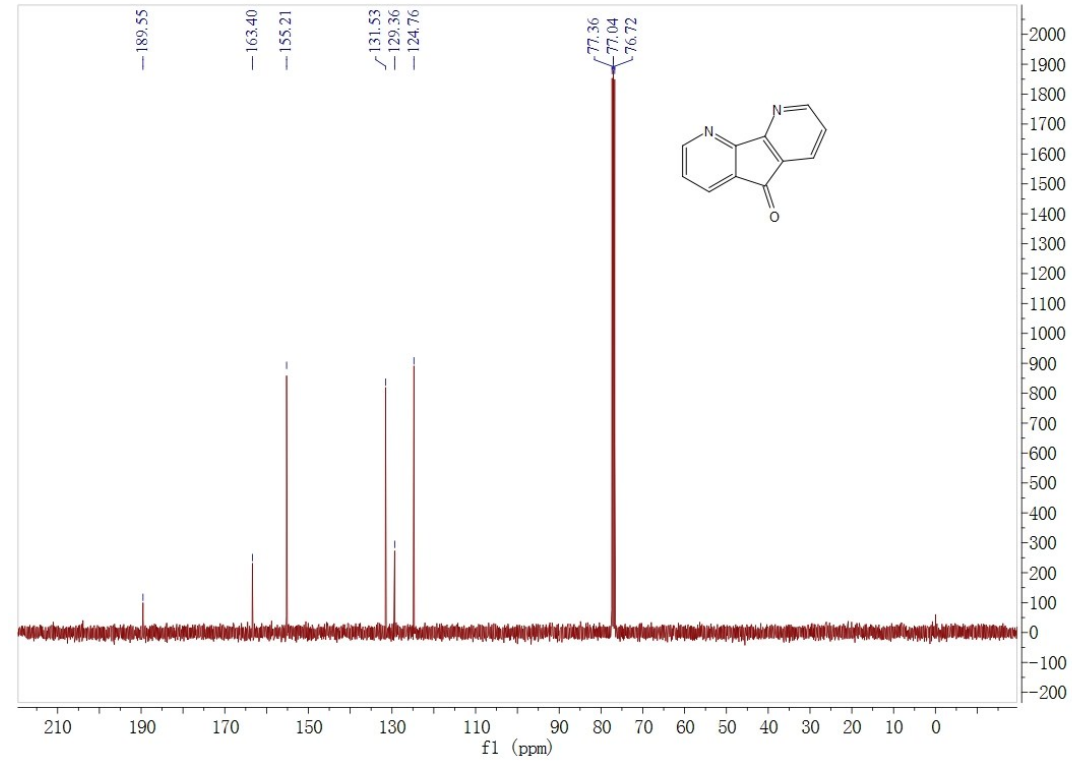
4c


8.44
7.82
7.81
7.71
7.70
7.59
7.42
7.40
7.26
2.39
0.91
0.95
1.82
1.01
0.98
2.97
f1 (ppm)


191.76
165.15
164.42
143.52
130.81
125.93
124.00
122.69
120.86
77.36
77.04
76.72
25.01
f1 (ppm)

4d


8.83
8.81
8.02
8.00
7.39
7.37
7.36
7.29
2.00
2.00
2.03
f1 (ppm)


189.55
163.40
155.21
131.53
129.36
124.76
77.36
77.04
76.72
f1 (ppm)