Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Ammonium iodide-promoted cyclization of ketones with DMSO and ammonium acetate for synthesis of substituted pyridines

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General Information

^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Advance 400 spectrometer in $CDCl_3$ at 400 MHz and 100 MHz, respectively. The chemical shifts were referenced to signals at 7.26 and 77.0 ppm, respectively. Proton coupling patterns were described as singlet (s), doublet (d), triplet (t), quartet (q) and multiplet (m). Mass spectra were recorded on a Shimadzu GCMS-QP5050A spectrometer at an ionization voltage of 70 eV equipped with a DB-WAX capillary column (internal diameter: 0.25 mm, length: 30 m). GC-MS was obtained using electron ionization. High resolution mass spectra (HRMS) were recorded on a MAT95XP high resolution mass spectrometer. Melting points were measured on an Electrothemal SGW-X4 microscopy digital melting point apparatus and were uncorrected. TLC was performed using commercially prepared 100-400 mesh silica gel plates (GF254), and visualization was effected at 254 nm. All substrates were purchased commercially without further purification and all solvents were dried with molecular sieves.

Typical procedure for the synthesis of substituted pyridines

A mixture of ammonium iodide (0.5 mmol), ammonium acetate (1 mmol), DMSO (2 mL) and ketones (1 mmol) were added into a 10 mL sealed tube successively. Subsequently, the reaction was carried out at 130 °C under magnetic stirring for 14 h. After cooling down, the reaction mixture was diluted with ethyl acetate and washed with $Na_2S_2O_3$ solutions and water for many times. The obtained top organic layer was dried with anhydrous $MgSO_4$. After drying, the mixture was concentrated under vacuum, and the crude residue was purified by silica gel column chromatography to afford the desired pure product.

Preliminary mechanistic studies

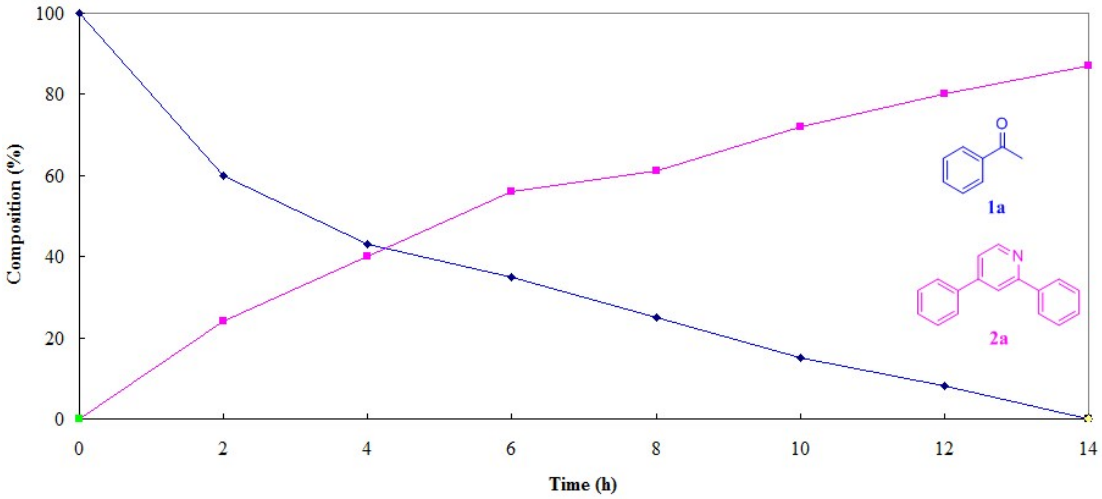
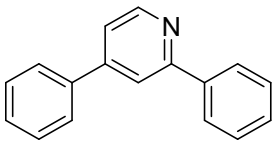


Figure S-1. Reaction profile of cyclization of ketones

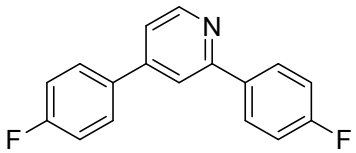
A single factor parallel experimental method was adopted to obtain the reaction profile. The reaction was carried out at 130 °C under magnetic stirring for 2 h, 4 h, 6 h, 8 h, 10 h, 12 h and 14 h. A small amount of (*E*)-1,3-diphenylbut-2-en-1-one could be detected when the reaction was performed at 2 h, 4 h and 6 h.

Analytical Data for the obtained products



2,4-diphenylpyridine (2a)[1]

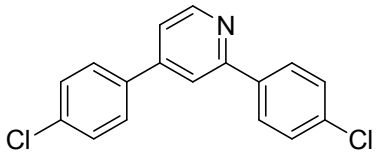
Brown liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.73 (d, *J* = 5.0 Hz, 1H), 8.05 (d, *J* = 7.4 Hz, 2H), 7.92 (s, 1H), 7.68 (d, *J* = 7.2 Hz, 2H), 7.51-7.42 (m, 7H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.0, 150.0, 149.3, 139.4, 138.5, 129.1, 129.0, 128.7, 127.0, 127.0, 120.2, 118.7.



2,4-bis(4-fluorophenyl)pyridine (2b)[1]

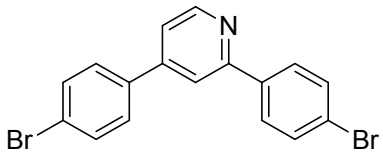
Orange solid; mp 81-83 °C (mp 83-85 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.69 (d, *J* = 5.0 Hz, 1H), 8.04-8.00 (m, 2H), 7.80 (s, 1H), 7.66-7.62 (m, 2H), 7.37 (d, *J* = 4.8 Hz, 1H), 7.20-7.14 (m,

4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.8, 164.6, 162.3, 162.2, 157.0, 150.0, 148.3, 135.4, 135.4, 134.4, 134.4, 128.8, 128.7, 120.0, 118.1, 116.2, 116.0, 115.8, 115.5.



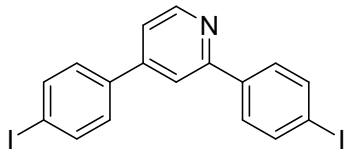
2,4-bis(4-fluorophenyl)pyridine (**2c**)[1]

Orange solid; mp 102-104 °C (mp 103-105 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.71 (d, *J* = 5.1 Hz, 1H), 7.98 (d, *J* = 8.5 Hz, 2H), 7.82 (s, 1H), 7.59 (d, *J* = 8.5 Hz, 2H), 7.48-7.44 (m, 4H), 7.39 (d, *J* = 5.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.9, 150.2, 148.2, 137.6, 136.7, 135.4, 135.3, 129.3, 128.9, 128.3, 128.2, 120.2, 118.1.



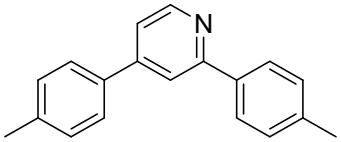
2,4-bis(4-bromophenyl)pyridine (**2d**)[1]

Orange solid; mp 135-137 °C (mp 136-138 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.72 (d, *J* = 5.0 Hz, 1H), 7.92 (d, *J* = 8.3 Hz, 2H), 7.83 (s, 1H), 7.64-7.60 (m, 4H), 7.53 (d, *J* = 8.4 Hz, 2H), 7.41 (d, *J* = 5.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.0, 150.3, 148.3, 138.0, 137.2, 132.3, 131.9, 128.6, 128.5, 123.7, 123.6,120.2, 118.1.



2,4-bis(4-iodophenyl)pyridine (**2e**)[2]

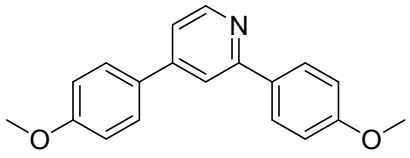
Off-white solid; mp 168-170 °C (mp 171-173 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.71 (d, *J* = 5.0 Hz, 1H), 7.84-7.76 (m, 7H), 7.39 (d, *J* = 8.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.0, 150.2, 148.4, 138.6, 138.3, 137.9, 137.7, 128.7, 128.7, 120.2, 118.0, 95.6, 95.4.



2,4-di-*p*-tolylpyridine (**2f**)[1]

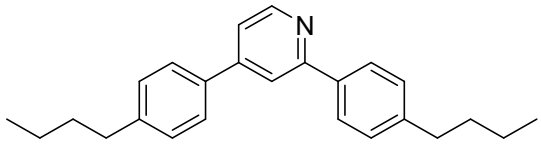
Off-white solid; mp 103-105 °C (mp 105-107 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.68 (d, J = 5.0 Hz, 1H), 7.94 (d, J = 8.0 Hz, 2H), 7.87 (s, 1H), 7.57 (d, J = 8.0 Hz, 2H), 7.37 (d, J = 4.0 Hz, 1H),

7.28 (d, J = 7.7 Hz, 4H), 2.40 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.9, 149.9, 149.0, 139.0, 138.9, 136.7, 135.6, 129.8, 129.4, 126.8, 119.7, 118.1, 21.2.



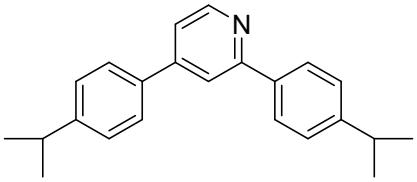
2,4-bis(4-methoxyphenyl)pyridine (**2g**)[1]

Off-white solid; mp 130-132 °C (mp 133-135 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.64 (d, *J* = 5.0 Hz, 1H), 8.00 (d, *J* = 8.6 Hz, 2H), 7.82 (s, 1H), 7.63 (d, *J* = 8.6 Hz, 2H), 7.34 (d, *J* = 5.0 Hz, 1H), 7.01 (d, *J* = 8.6 Hz, 4H), 3.85 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.4, 157.5, 149.8, 148.6, 132.1, 130.8, 128.2, 128.2, 119.0, 117.4, 114.4, 114.1, 55.3.



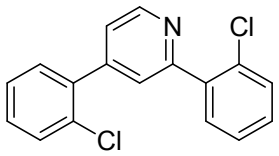
2,4-bis(4-butylphenyl)pyridine (**2h**)

Brown liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.67 (d, *J* = 5.1 Hz, 1H), 7.95 (d, *J* = 8.0 Hz, 2H), 7.89 (s, 1H), 7.59 (d, *J* = 8.0 Hz, 2H), 7.38 (d, *J* = 4.0 Hz, 1H), 7.29 (d, *J* = 7.9 Hz, 4H), 2.66 (t, *J* = 7.7 Hz, 4H), 1.67-1.60 (m, 4H), 1.42-1.34 (m, 4H), 0.95-0.92 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.0, 149.9, 149.0, 144.0, 143.9, 137.0, 135.8, 129.1, 128.8, 126.8, 119.7, 118.2, 35.4, 35.3, 33.5, 22.3, 13.9; HRMS (ESI) m/z: calcd for $C_{25}H_{30}N$ $[M+H]^+$, 344.2371; found 344.2373.



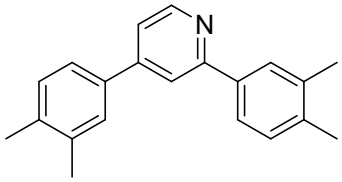
2,4-bis(4-isopropylphenyl)pyridine (**2i**)

Orange solid; mp 72-74 °C (not reported); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.70 (d, *J* = 5.1 Hz, 1H), 7.97 (d, *J* = 8.1 Hz, 2H), 7.91 (s, 1H), 7.63 (d, *J* = 8.1 Hz, 2H), 7.42 (d, *J* = 3.9 Hz, 1H), 7.38-7.35 (m, 4H), 3.02-2.95 (m, 2H), 1.30 (dd, *J* = 6.8, 2.0 Hz, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.0, 150.0, 149.9, 149.8, 149.2, 137.0, 136.0, 127.2, 127.0, 126.8, 119.8, 118.3, 33.9, 33.9, 23.9; HRMS (ESI) m/z: calcd for $C_{23}H_{26}N$ $[M+H]^+$, 316.2061; found 316.2060.



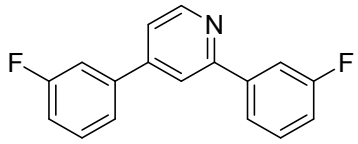
2,4-bis(2-chlorophenyl)pyridine (**2j**)[1]

Light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.78 (d, *J* = 4.9 Hz, 1H), 7.75 (s, 1H), 7.66 (d, *J* = 7.1 Hz, 1H), 7.51-7.47 (m, 2H), 7.39-7.34 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.7, 149.3, 146.9, 139.0, 137.7, 132.2, 131.6, 131.0, 130.2, 130.1, 129.7, 129.6, 127.1, 127.0, 125.4, 122.9.



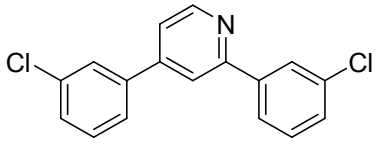
2,4-bis(3,4-dimethylphenyl)pyridine (**2k**)[2]

Brown solid; mp 72-74 °C (mp 75-77 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.66 (d, *J* = 4.9 Hz, 1H), 7.85 (d, *J* = 9.4 Hz, 2H), 7.74 (d, *J* = 7.8 Hz, 1H), 7.44 (s, 1H), 7.40 (d, *J* = 7.8 Hz, 1H), 7.36 (d, *J* = 4.2 Hz, 1H), 7.22 (d, *J* = 7.8 Hz, 2H), 2.34-2.30 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.9, 149.7, 149.1, 137.7, 137.5, 137.2, 137.0, 136.9, 136.0, 130.3, 129.9, 128.1, 128.1, 124.3, 124.3, 119.6, 118.2, 19.8, 19.5, 19.5.



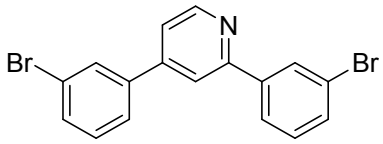
2,4-bis(3-fluorophenyl)pyridine (**2l**)

Light yellow solid; mp 86-88 °C (not reported); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.73 (d, *J* = 5.0 Hz, 1H), 7.86 (s, 1H), 7.82-7.77 (m, 2H), 7.48-7.42 (m, 4H), 7.37 (d, *J* = 9.7 Hz, 1H), 7.14 (dd, *J* = 17.9, 9.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.5, 164.4, 162.1, 162.00, 156.8, 156.8, 150.2, 148.2, 148.2, 141.5, 141.4, 140.5, 140.4, 130.8, 130.7, 130.3, 130.2, 122.7, 122.7, 122.5, 122.5, 120.6, 118.6, 116.1, 116.1, 115.9, 115.9, 114.2, 114.1, 113.9, 113.9; HRMS (ESI) m/z: calcd for $C_{17}H_{12}F_2N$ $[M+H]^+$, 268.0937; found 268.0932.



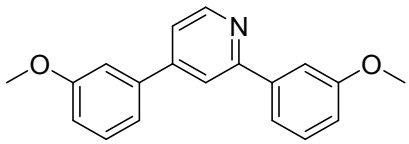
2,4-bis(3-chlorophenyl)pyridine (2m)[1]

Red-brown solid; mp 91-93 °C (mp 95-97 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.72 (d, *J* = 4.8 Hz, 1H), 8.05 (s, 1H), 7.91 (d, *J* = 5.8 Hz, 1H), 7.83 (s, 1H), 7.64 (s, 1H), 7.53 (d, *J* = 4.3 Hz, 1H), 7.43-7.35 (m, 5H); ^{13}C NMR (100MHz, $CDCl_3$): δ 156.7, 150.3, 148.0, 140.9, 140.0, 135.1, 134.9, 130.4, 130.0, 129.1, 127.2, 127.1, 125.2, 125.0, 120.6, 118.5.



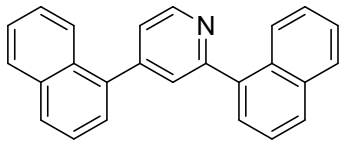
2,4-bis(3-bromophenyl)pyridine (2n)[1]

Red-brown solid; mp 88-90 °C (mp 89-91 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.72 (d, *J* = 4.9 Hz, 1H), 8.20 (s, 1H), 7.95 (d, *J* = 7.7 Hz, 1H), 7.81 (d, *J* = 7.3 Hz, 2H), 7.59-7.54 (m, 3H), 7.41-7.32 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.5, 150.3, 147.9, 141.1, 140.3, 132.0, 132.0, 130.6, 130.2, 130.0, 130.0, 125.7, 125.5, 123.2, 123.0, 120.6, 118.5.



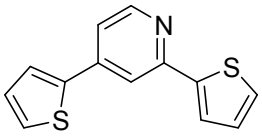
2,4-bis(3-methoxyphenyl)pyridine (2o)[1]

Brown oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.71 (d, *J* = 4.9 Hz, 1H), 7.89 (s, 1H), 7.63 (s, 1H), 7.59 (d, *J* = 7.5 Hz, 1H), 7.43-7.37 (m, 3H), 7.26 (d, *J* = 7.5 Hz, 1H), 7.19 (s, 1H), 6.98 (d, *J* = 8.2 Hz, 2H), 3.88 (d, *J* = 9.9 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.1, 160.0, 157.8, 149.9, 149.1, 140.9, 139.9, 130.1, 129.7, 120.4, 119.4, 119.4, 118.9, 115.1, 114.2, 112.8, 112.1, 55.3.



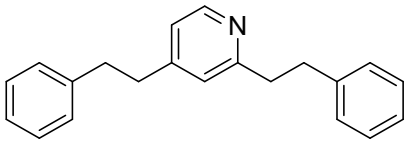
2,4-di(naphthalen-1-yl)pyridine (2p)[1]

Yellow solid; mp 110-112 °C (mp 112-114 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.88 (d, *J* = 4.9 Hz, 1H), 8.25 (d, *J* = 6.4 Hz, 1H), 7.97 (d, *J* = 7.9 Hz, 1H), 7.88 (d, *J* = 6.7 Hz, 4H), 7.73 (s, 1H), 7.67 (d, *J* = 7.0 Hz, 1H), 7.54-7.45 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.2, 149.4, 149.1, 138.2, 137.3, 133.9, 133.7, 131.1, 130.7, 129.0, 128.8, 128.5, 128.3, 127.6, 126.9, 126.6, 126.5, 126.2, 126.1, 125.8, 125.5, 125.3, 125.2, 125.1, 123.3.



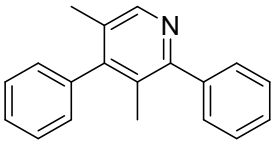
2,4-di(thiophen-2-yl)pyridine (**2q**)

Dark-brown solid; mp 58-60 °C (not reported); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.53 (d, *J* = 5.0 Hz, 1H), 7.82 (s, 1H), 7.66 (d, *J* = 2.4 Hz, 1H), 7.54 (d, *J* = 2.4 Hz, 1H), 7.42 (t, *J* = 4.7 Hz, 2H), 7.34 (d, *J* = 5.1 Hz, 1H), 7.14 (dd, *J* = 9.6, 5.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.1, 150.0, 144.4, 142.2, 141.1, 128.4, 128.0, 127.8, 127.2, 125.5, 124.8, 118.3, 115.0; HRMS (ESI) m/z: calcd for $C_{13}H_{10}NS_2$ $[M+H]^+$, 244.0252; found 244.0249.



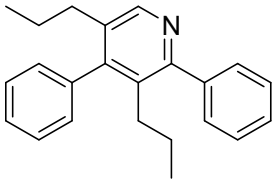
2,4-diphenethylpyridine (**2r**)

Brown oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.24 (s, 1H), 7.28-7.22 (m, 6H), 7.19 (d, *J* = 5.8 Hz, 2H), 7.09 (d, *J* = 7.3 Hz, 2H), 6.98 (d, *J* = 7.2 Hz, 2H), 4.06 (s, 2H), 3.99 (s, 2H), 2.49 (s, 2H), 2.06 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.8, 148.2, 145.4, 139.7, 138.7, 132.4, 132.2, 128.5, 128.5, 128.3, 127.7, 126.1, 126.1, 37.1, 34.6, 23.0, 15.5; HRMS (ESI) m/z: calcd for $C_{21}H_{22}N$ $[M+H]^+$, 288.1750; found 288.1747.



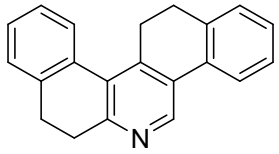
3,5-dimethyl-2,4-diphenylpyridine (**2v**)[3]

Orange solid; mp 78-80 °C (mp 84-85 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.44 (s, 1H), 7.53-7.36 (m, 8H), 7.16 (d, *J* = 7.5 Hz, 2H), 2.02 (d, *J* = 17.5 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.9, 150.6, 147.5, 141.2, 138.8, 129.8, 129.0, 128.7, 128.3, 128.0, 128.0, 127.6, 127.4, 17.9, 17.4.



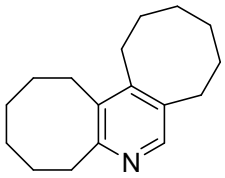
2,4-diphenyl-3,5-dipropylpyridine (**2w**)

Light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.42 (s, 1H), 7.49-7.34 (m, 8H), 7.19 (d, *J* = 6.9 Hz, 2H), 2.33 (dd, *J* = 16.4, 9.6 Hz, 4H), 1.49-1.40 (m, 2H), 1.19-1.09 (m, 2H), 0.80 (t, *J* = 7.3 Hz, 3H), 0.46 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.1, 149.9, 147.1, 141.5, 138.0, 134.5, 133.4, 128.7, 128.7, 128.1, 128.0, 127.4, 127.3, 33.0, 31.8, 24.0, 23.8, 14.1, 14.0; HRMS (ESI) m/z: calcd for $C_{23}H_{26}N$ $[M+H]^+$, 316.2068; found 316.2060.



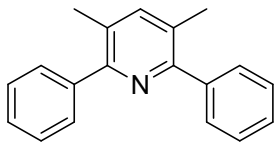
7,8,13,14-tetrahydrodibenzo[a,i]phenanthridine (**2x**)

Off-white solid; mp 162-164 °C (not reported); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.45 (s, 1H), 8.25 (d, *J* = 7.6 Hz, 1H), 7.53 (d, *J* = 4.3 Hz, 1H), 7.38-7.27 (m, 5H), 7.21 (d, *J* = 7.5 Hz, 1H), 3.25 (t, *J* = 6.9 Hz, 2H), 2.79 (d, *J* = 8.3 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.3, 146.1, 140.8, 140.5, 137.5, 135.4, 132.5, 132.2, 128.6, 128.5, 128.0, 127.9, 127.0, 126.0, 125.1, 29.4, 28.4, 27.4, 26.7; HRMS (ESI) m/z: calcd for $C_{21}H_{18}N$ $[M+H]^+$, 284.1439; found 284.1434.



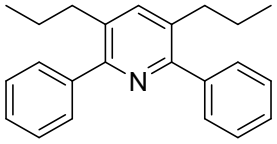
1,2,3,4,5,6,9,10,11,12,13,14-dodecahydrodicycloocta[b,d]pyridine (**2y**)[5]

Orange oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12 (s, 1H), 2.96-2.93 (t, *J* = 6.2 Hz, 2H), 2.85-2.79 (m, 4H), 2.73-2.70 (t, *J* = 6.0 Hz, 2H), 1.78-1.77 (m, 2H), 1.69 (s, 6H), 1.43 (s, 4H), 1.32-1.29 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.1, 147.1, 146.9, 135.1, 132.5, 35.6, 32.3, 30.8, 30.8, 30.4, 30.0, 26.6, 26.5, 26.3, 25.8, 25.5.



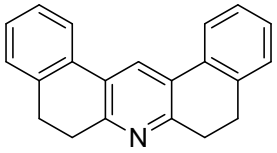
3,5-dimethyl-2,6-diphenylpyridine (**3a**)[4]

Light yellow solid; mp 130-132 °C (not reported); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 (d, *J* = 7.0 Hz, 4H), 7.46 (s, 1H), 7.41 (t, *J* = 7.3 Hz, 4H), 7.36-7.32 (m, 2H), 2.36 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.7, 141.1, 140.6, 129.2, 129.1, 128.0, 127.6, 19.6.



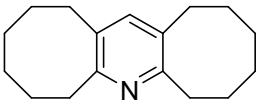
2,6-diphenyl-3,5-dipropylpyridine (3b)[4]

Off-white solid; mp 122-124 °C (not reported); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 (d, *J* = 7.3 Hz, 5H), 7.41-7.33 (m, 6H), 2.64 (t, *J* = 7.6 Hz, 4H), 1.61-1.55 (m, 4H), 0.89 (t, *J* = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.8, 140.8, 138.6, 133.8, 129.1, 128.0, 127.5, 34.2, 24.1, 14.0.



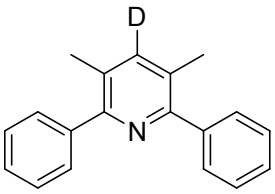
5,6,8,9-tetrahydrodibenzo[a,j]acridine (3c)[4]

Off-white solid; mp 116-118 °C (not reported); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.52 (d, *J* = 7.6 Hz, 2H), 7.37 (t, *J* = 7.4 Hz, 2H), 7.30-7.26 (m, 3H), 7.20 (d, *J* = 7.0 Hz, 2H), 2.91 (s, 8H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.3, 137.8, 135.2, 135.0, 130.5, 128.6, 127.6, 127.0, 124.9, 28.2, 27.8.



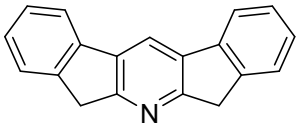
1,2,3,4,5,6,8,9,10,11,12,13-dodecahydrodicycloocta[b,e]pyridine (3d)[5]

Light yellow solid; mp 106-108 °C (mp 108-109 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.07 (s, 1H), 2.94-2.91 (t, *J* = 6.0 Hz, 4H), 2.72-2.69 (t, *J* = 6.2 Hz, 4H), 1.77 (s, 4H), 1.67 (s, 4H), 1.36 (s, 8H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.8, 137.3, 133.6, 34.0, 32.3, 31.4, 30.8, 26.0, 25.9.



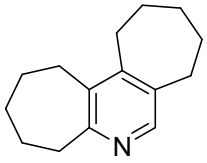
3,5-dimethyl-6-D-2,6-diphenylpyridine (3f)

Light yellow solid; mp 133-135 °C (not reported); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58 (d, *J* = 7.2 Hz, 4H), 7.41 (t, *J* = 7.2 Hz, 4H), 7.36-7.32 (m, 2H), 2.36 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.7, 140.6, 129.2, 129.0, 128.0, 127.6, 19.5; HRMS (ESI) m/z: calcd for $C_{19}H_{17}DN$ $[M+H]^+$, 261.1501; found 261.1497.



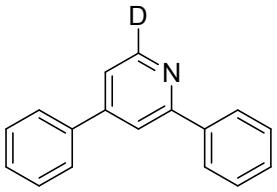
5,7-dihydrodiindeno[2,1-*b*: 1',2'-***e***]**pyridine** (**2a'**)

Brown solid; mp 162-164 °C (not reported); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.26 (d, *J* = 7.4 Hz, 2H), 7.89 (s, 1H), 7.54 (d, *J* = 7.4 Hz, 2H), 7.47 (t, *J* = 7.3 Hz, 2H), 7.39 (t, *J* = 7.3 Hz, 2H), 3.86 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.3, 143.9, 141.1, 135.1, 129.1, 128.2, 127.2, 125.0, 121.0, 34.5; HRMS (ESI) m/z: calcd for $C_{19}H_{14}N$ $[M+H]^+$, 256.1118; found 256.1121.



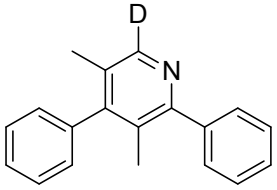
1,2,3,4,5,8,9,10,11,12-decahydrodicyclohepta[b,d]pyridine (**2b'**)[5]

Dark-brown liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 (s, 1H), 3.03 (t, *J* = 5.0 Hz, 2H), 2.84 (d, *J* = 8.2 Hz, 4H), 2.74 (t, *J* = 5.0 Hz, 2H), 1.83 (s, 4H), 1.69-1.58 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.3, 149.3, 144.6, 136.4, 134.7, 38.8, 32.8, 32.1, 32.0, 29.2, 28.1, 28.0, 27.2, 26.8, 26.5.



2,4-Diphenyl-6-D-pyridine (**2c'**)

Brown liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04 (d, *J* = 7.1 Hz, 2H), 7.92 (s, 1H), 7.68 (d, *J* = 6.9 Hz, 2H), 7.50-7.44 (m, 7H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.1, 149.3, 139.5, 138.5, 129.1, 129.0, 128.7, 127.0, 127.0, 120.1, 118.8; HRMS (ESI) m/z: calcd for $C_{17}H_{13}DN$ $[M+H]^+$, 233.1186; found 233.1184.



3,5-dimethyl-6-D-2,4-diphenylpyridine (**2d'**)

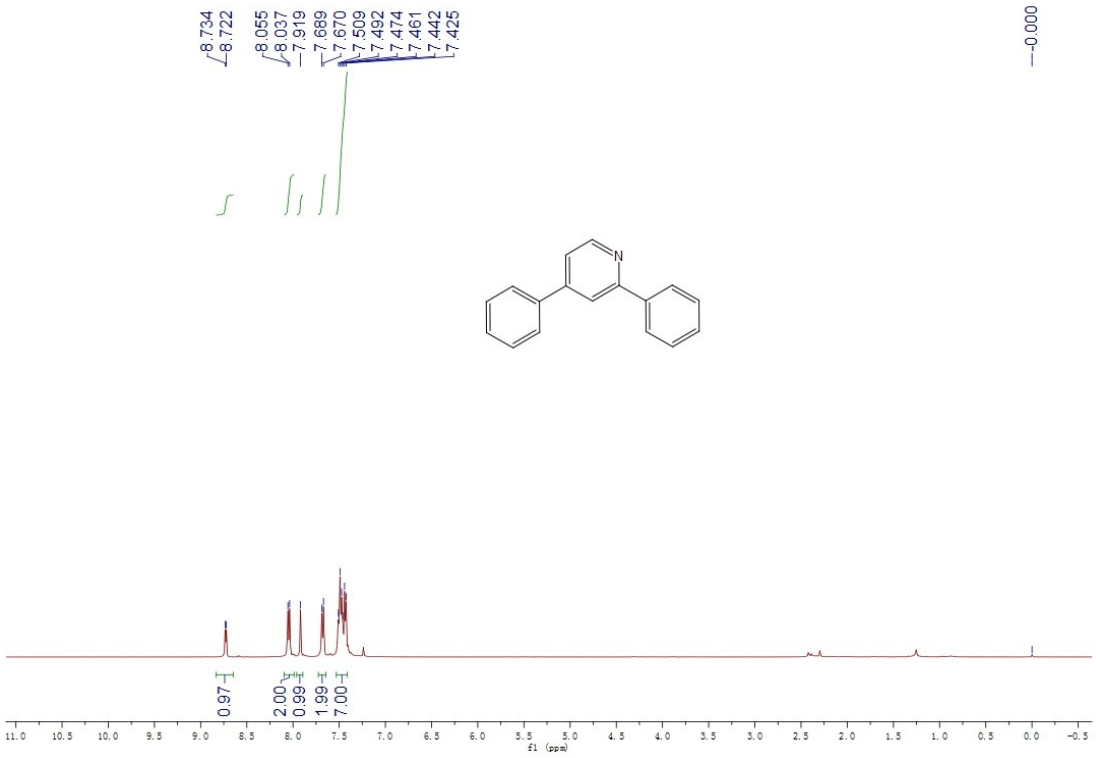
Light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53-7.37 (m, 8H), 7.16 (d, *J* = 6.9 Hz, 2H), 2.04 (s, 3H), 2.00 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.9, 150.6, 147.5, 141.2, 138.8, 129.8,

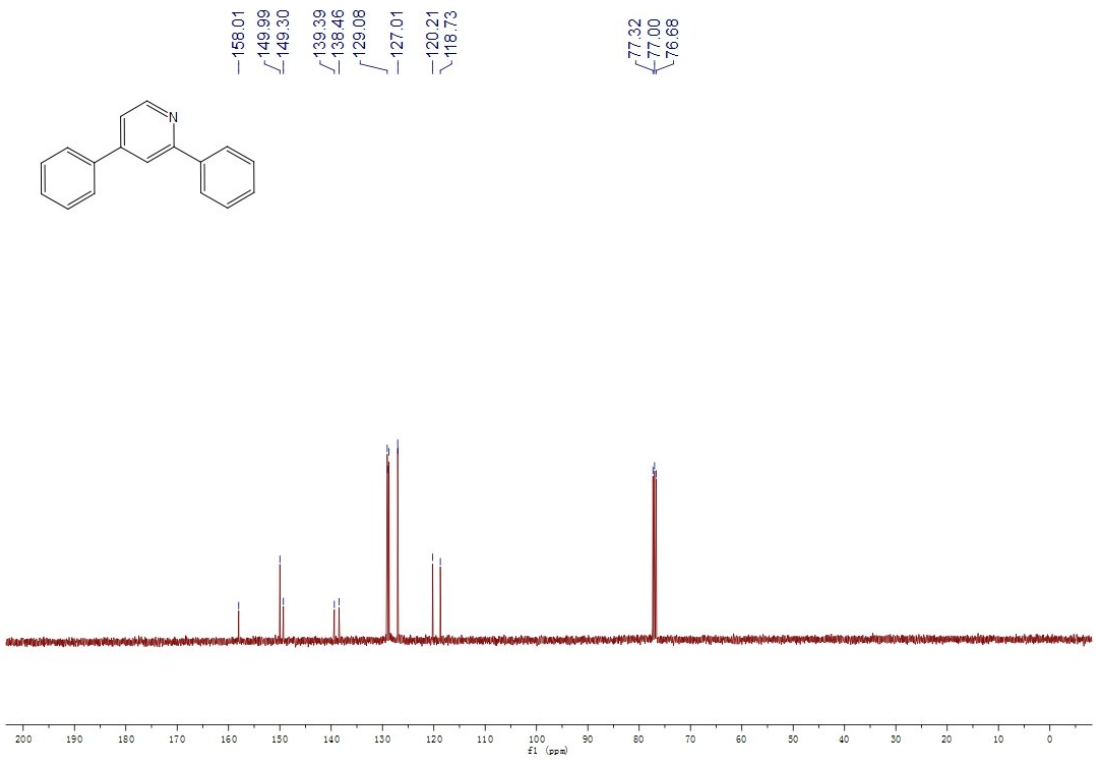
129.7, 129.1, 128.8, 128.4, 128.0, 128.0, 127.6, 127.4, 17.9, 17.4, 17.4; HRMS (ESI) m/z: calcd for $C_{19}H_{17}DN$ $[M+H]^+$, 261.1496; found 261.1497.

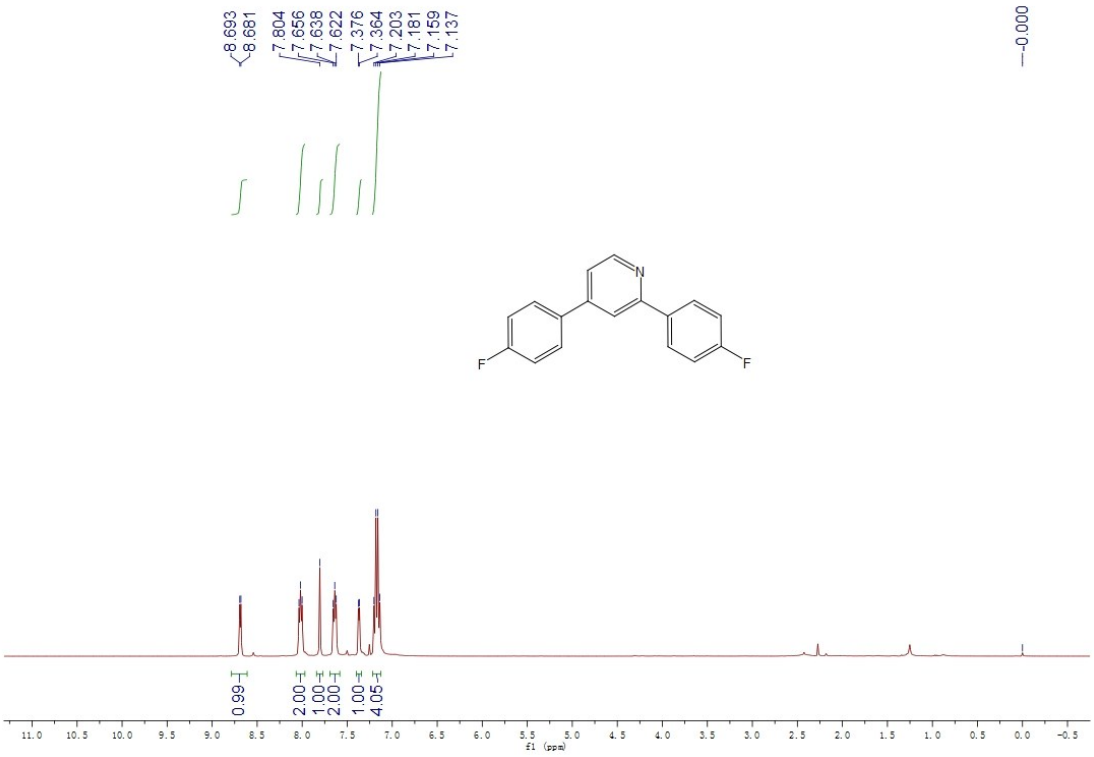
References

1. Y. Bai, L. C. Tang, H. W. Huang and G. J. Deng, *Org. Biomol. Chem.,* 2015, **13**, 4404.
2. J. Liu, C. X. Wang, L. S. Wu, F. Liang and G. S. Huang, *Synthesis,* 2010, **24**, 4228.
3. K. R. Roesch, H. M. Zhang and R. C. Larock, *J. Org. Chem.,* 2001, **66**, 8042.
4. M. N. Zhao, R. R. Hui, Z. H. Ren, Y. Y. Wang and Z. H. Guan, *Org. Lett.,* 2014, **16**, 3082.
5. K. V. V. K. Mohan, N. Narender and S. J. Kulkarni, *Microporous Mesoporous Mater.,* 2007, **106**, 229.

NMR spectra of the obtained products



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F
F
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2.00
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2.00
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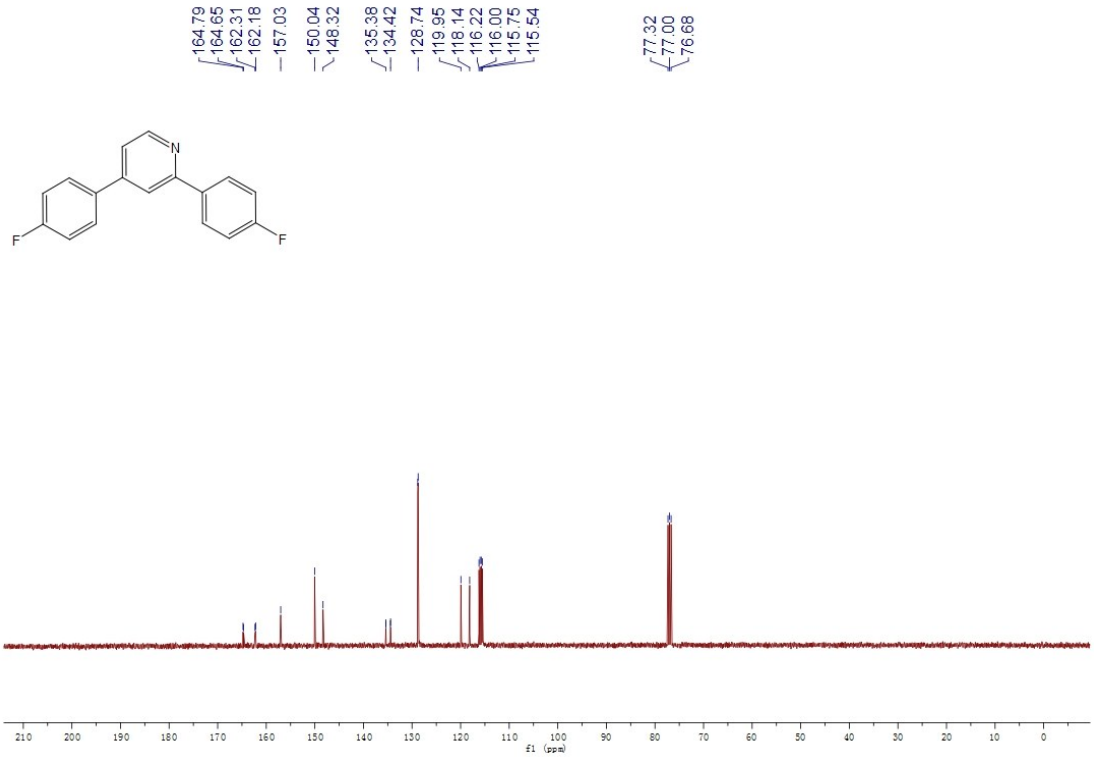
4.05
f1 (ppm)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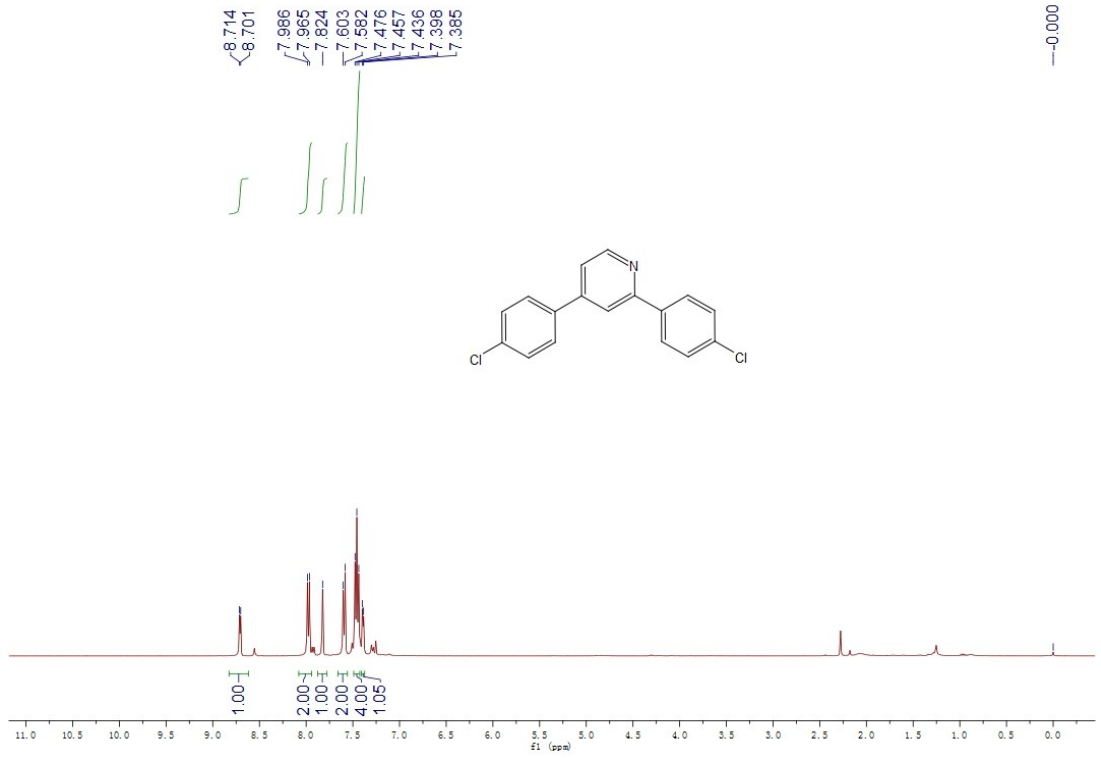
f1 (ppm)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Cl
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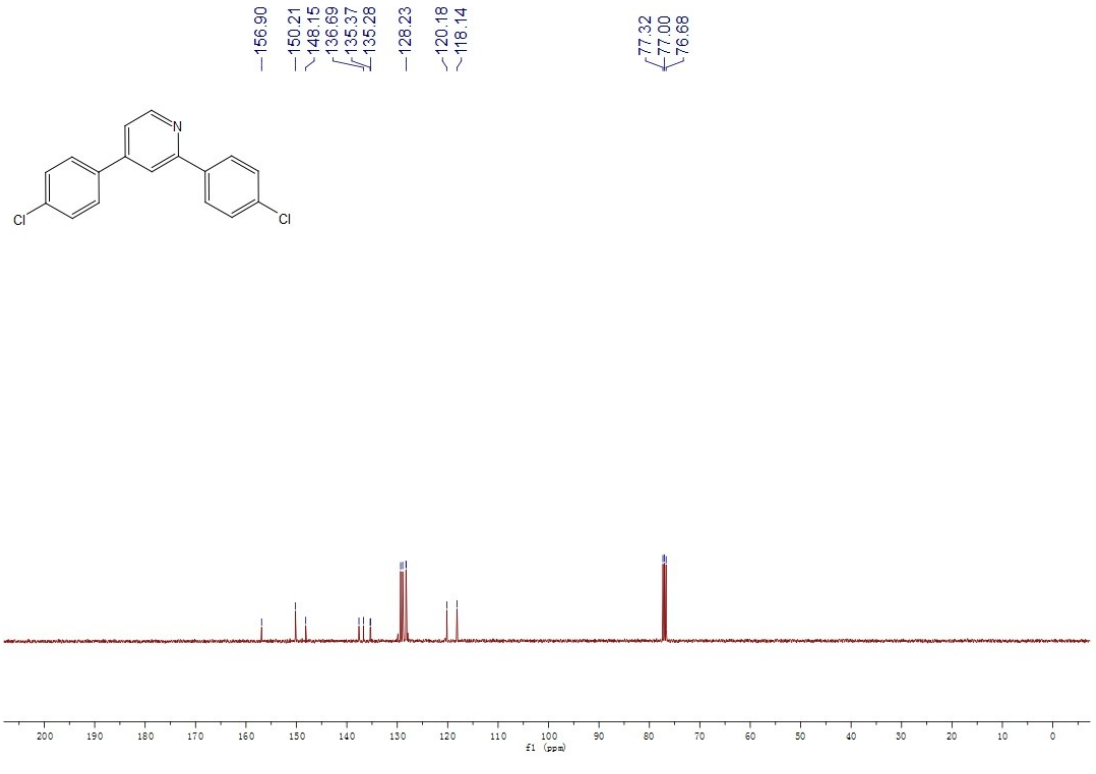
f1 (ppm)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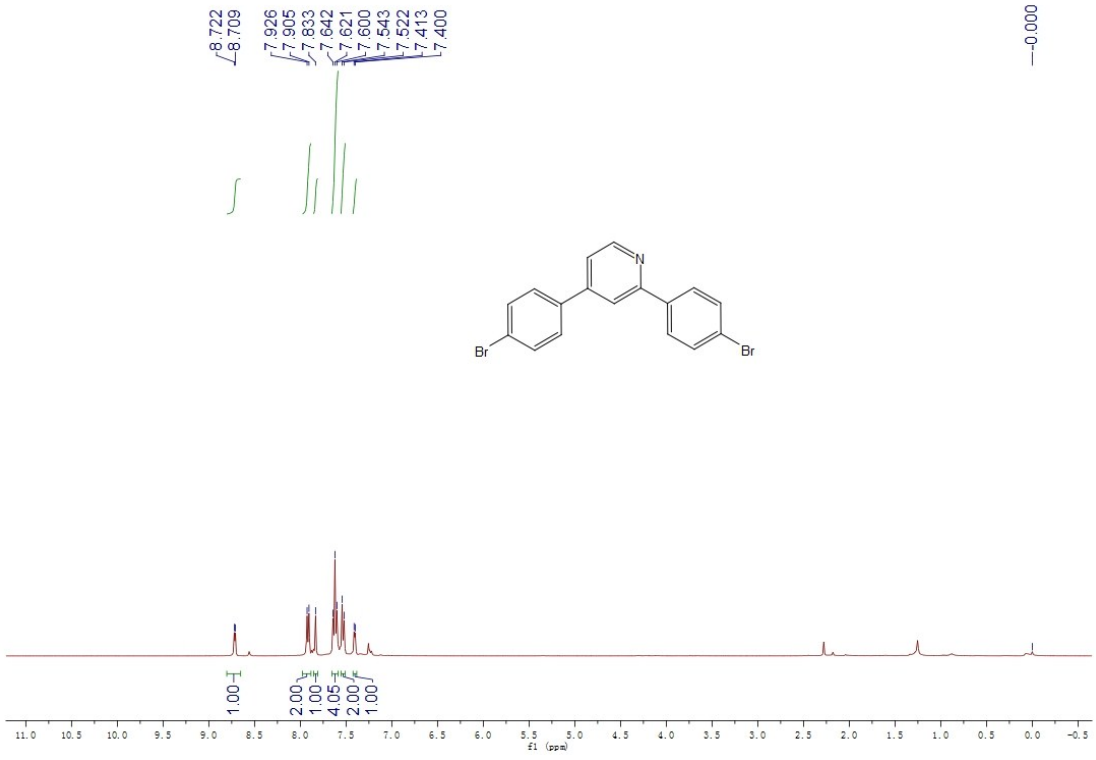
Cl
Cl
f1 (ppm)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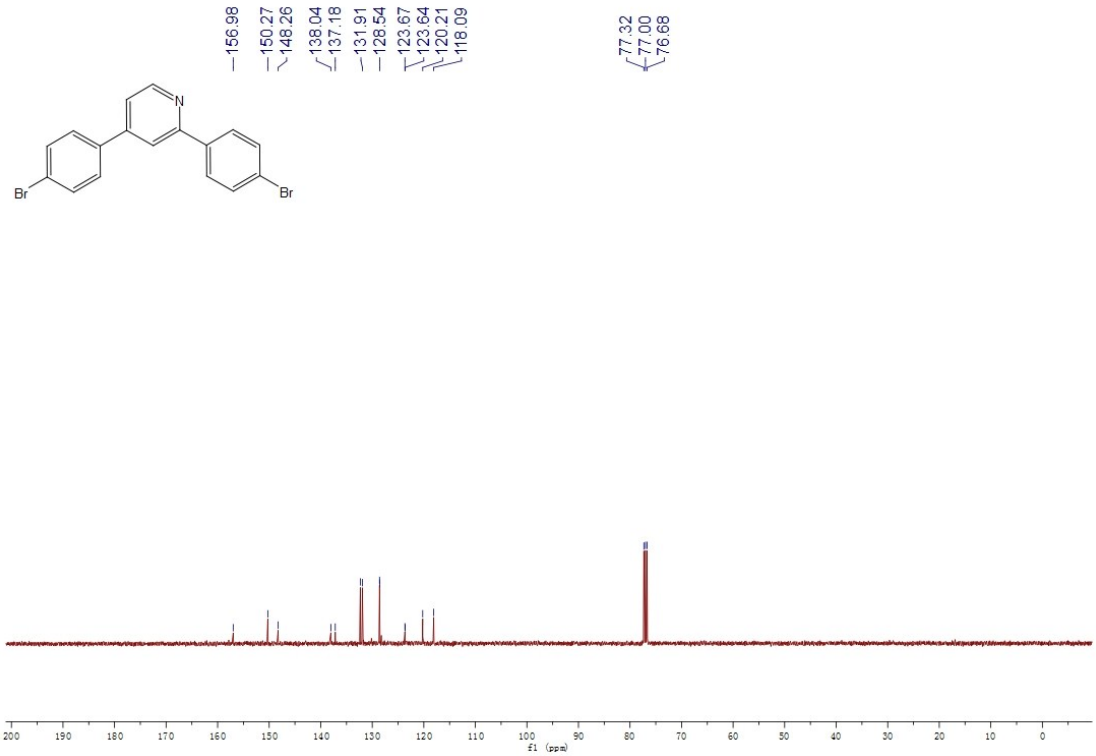
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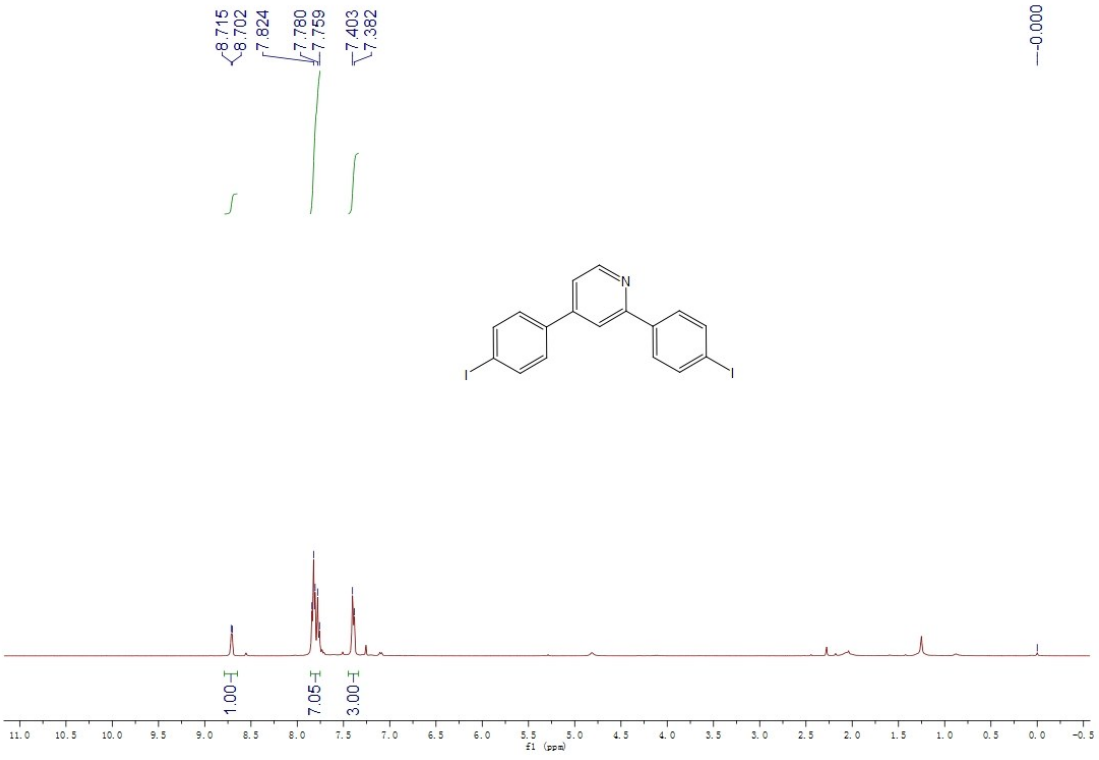
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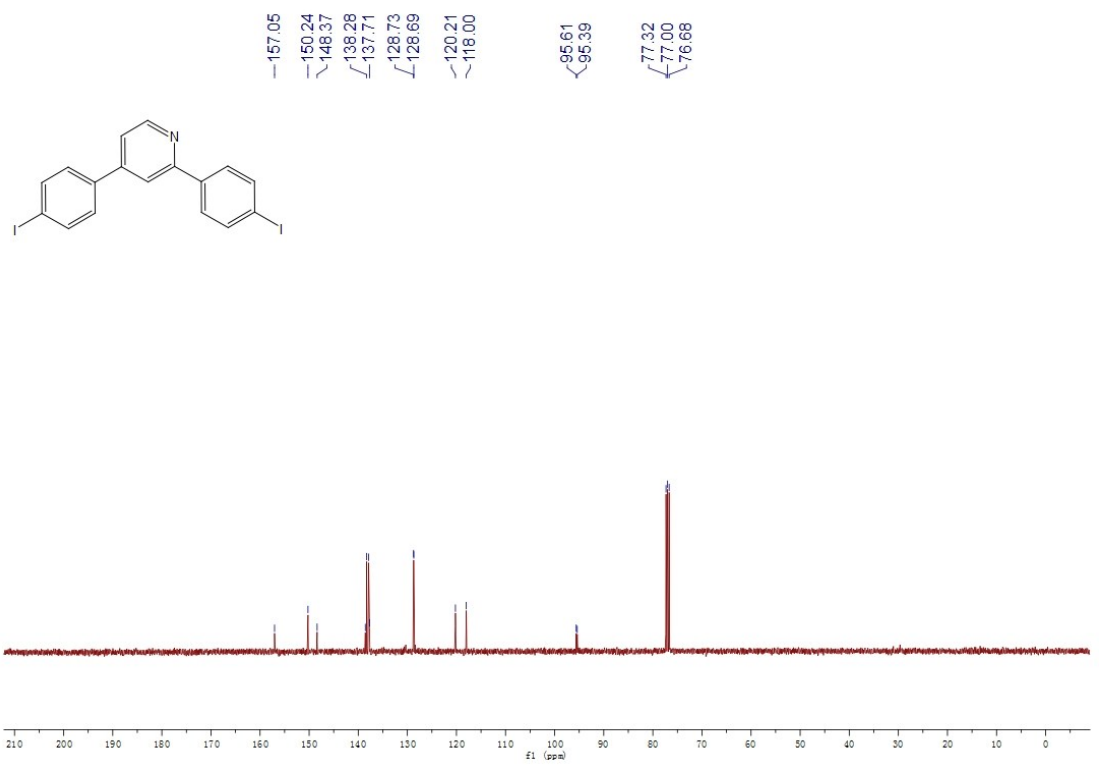
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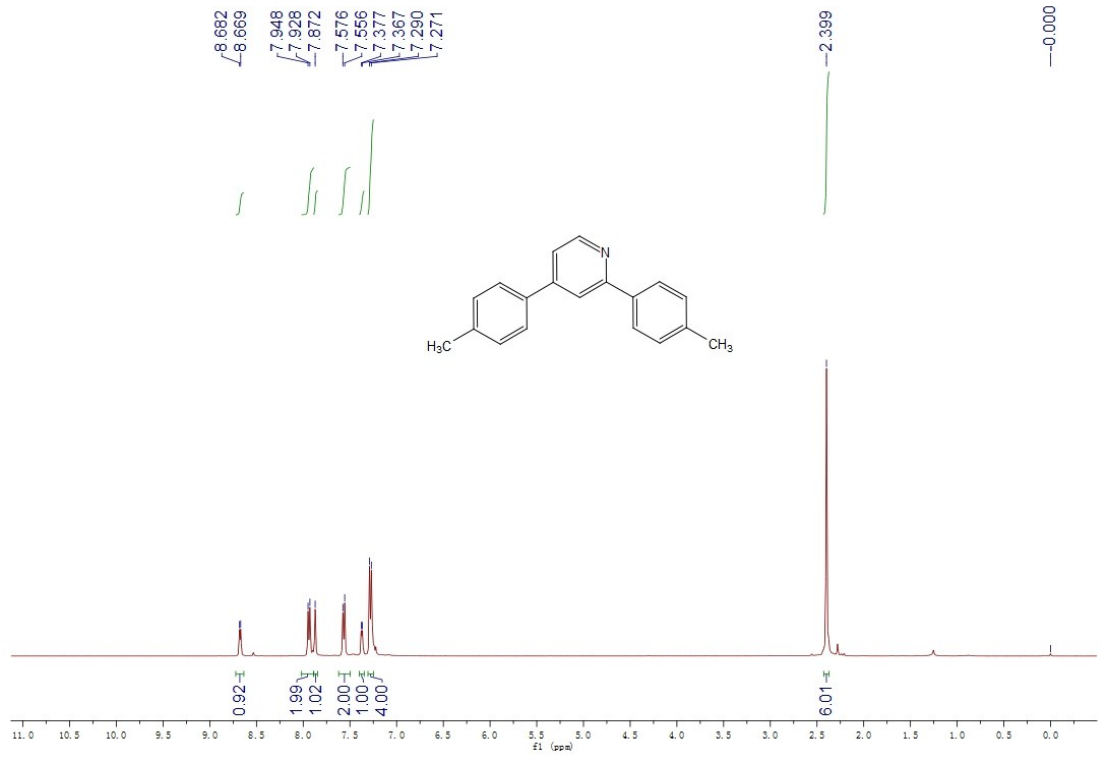
f1 (ppm)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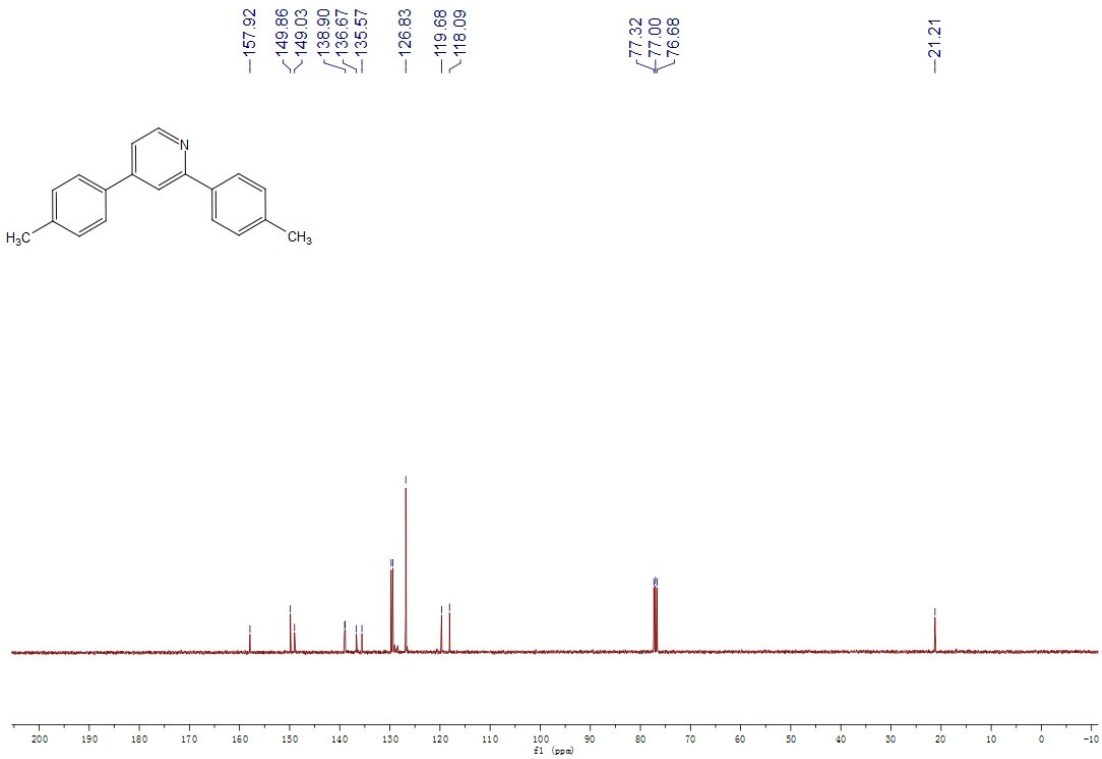
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f1 (ppm)


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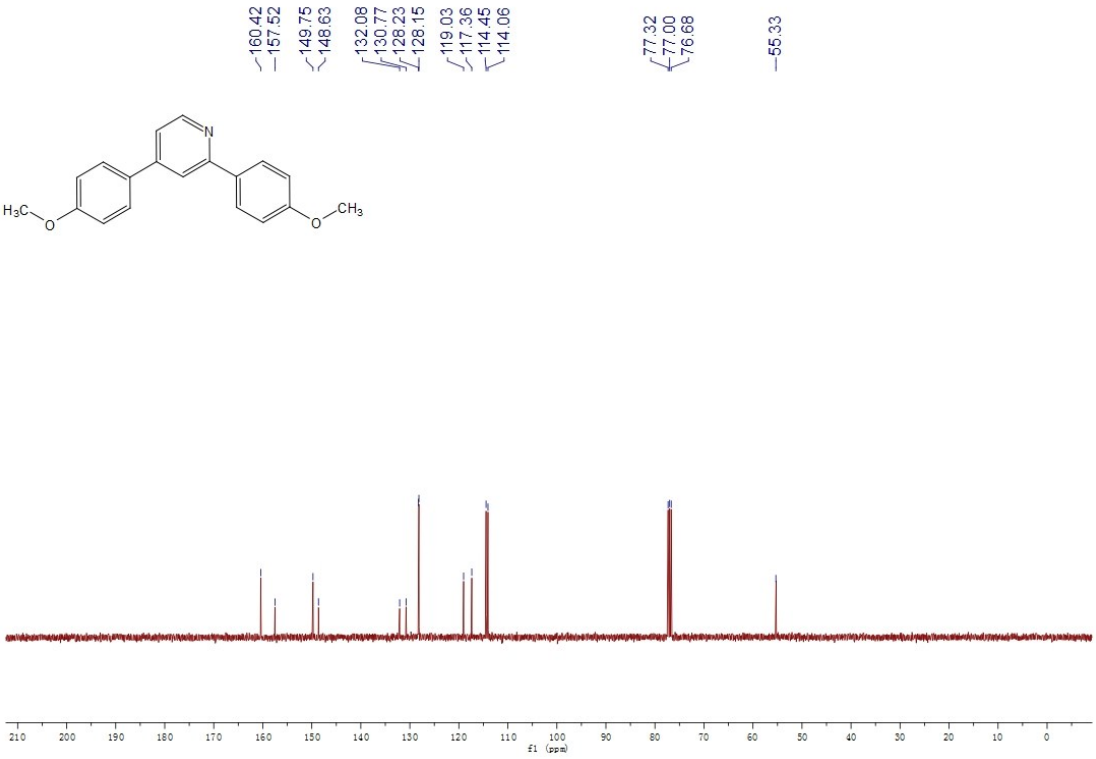
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H3C
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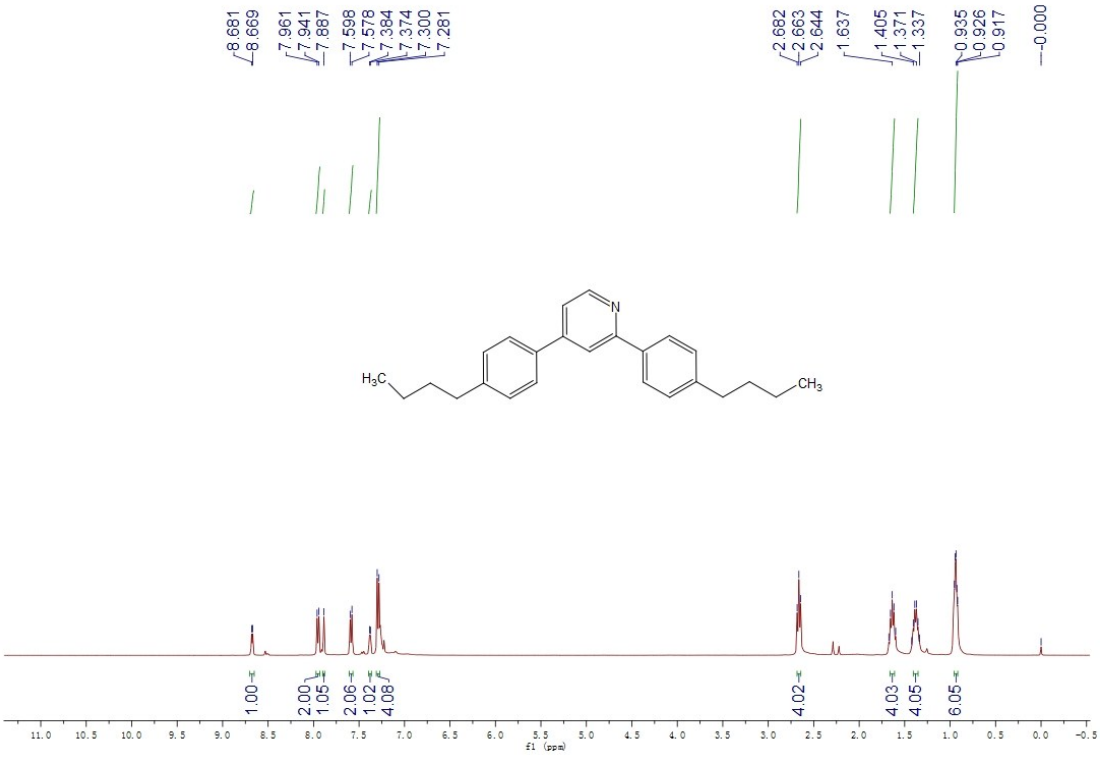
O
CH3
f1 (ppm)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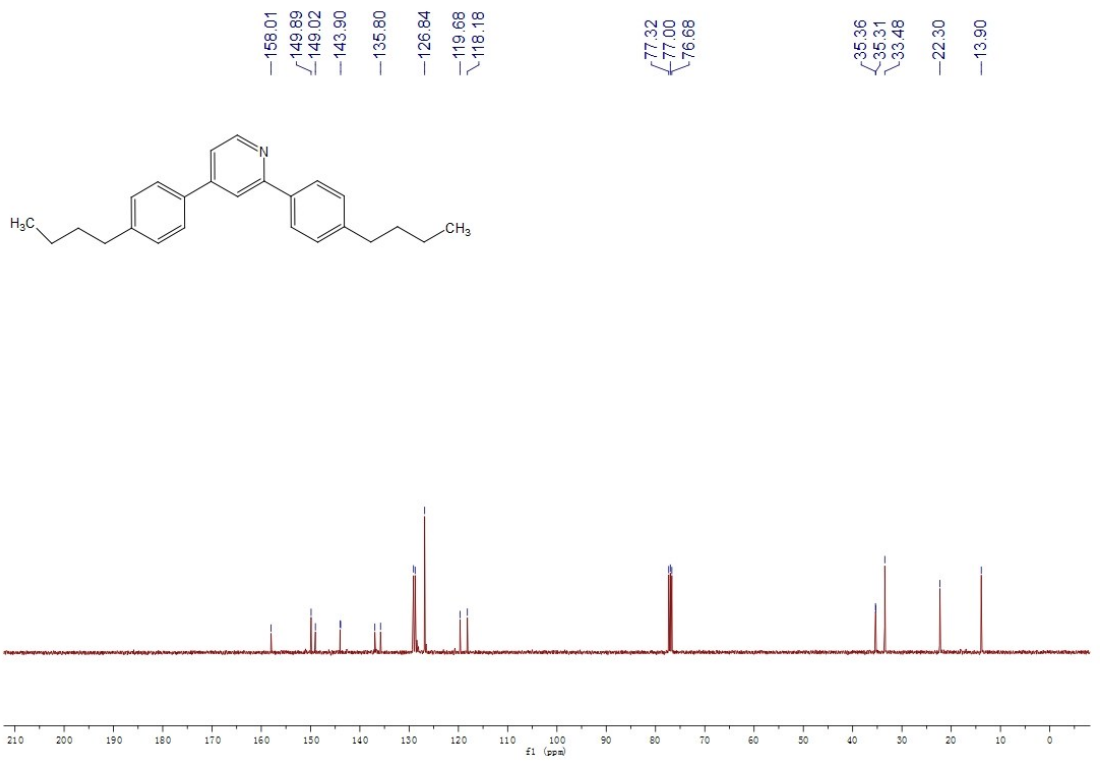
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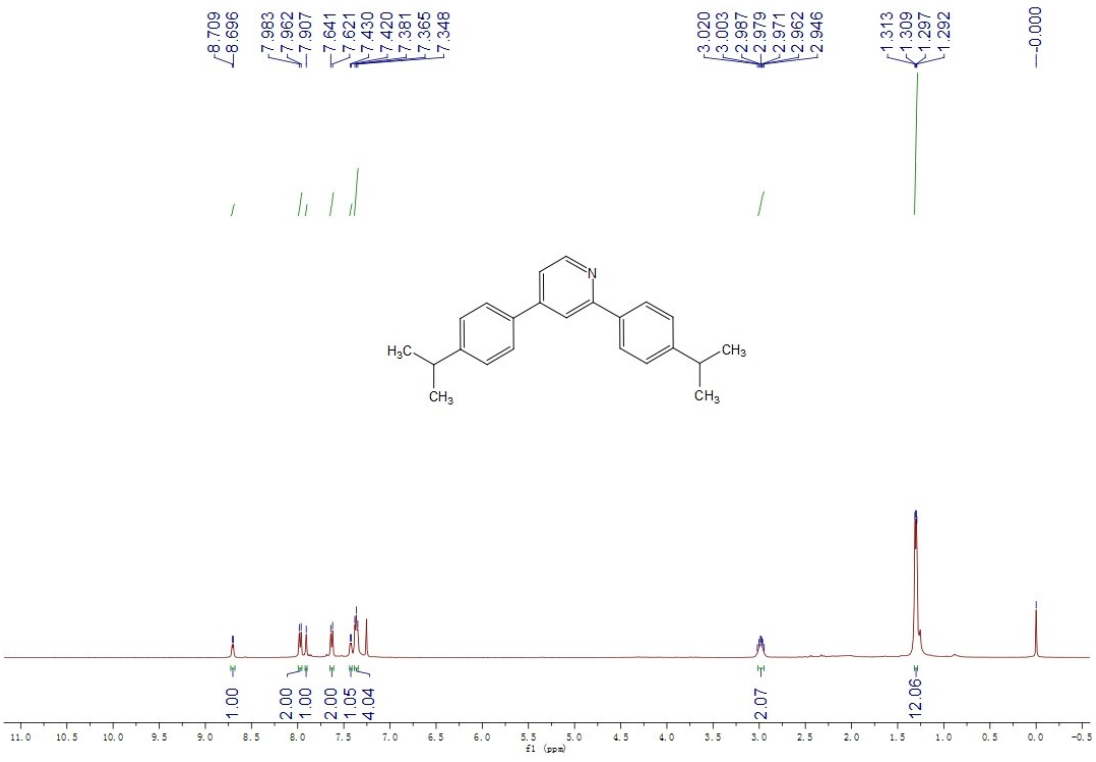
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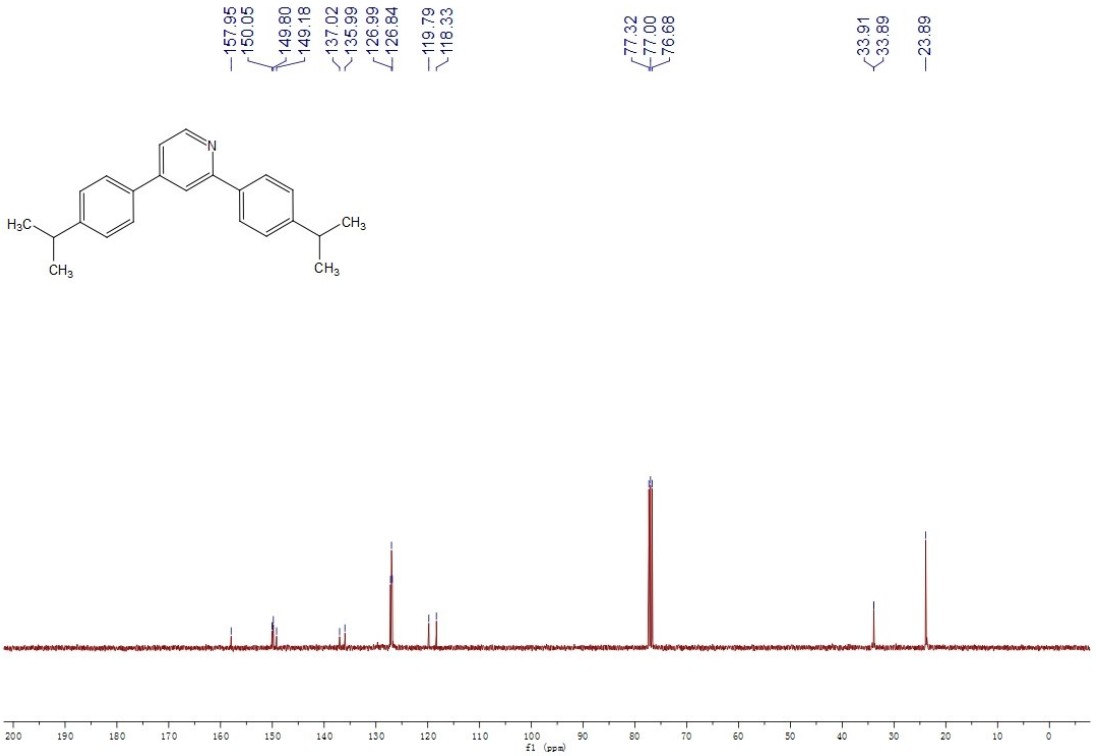
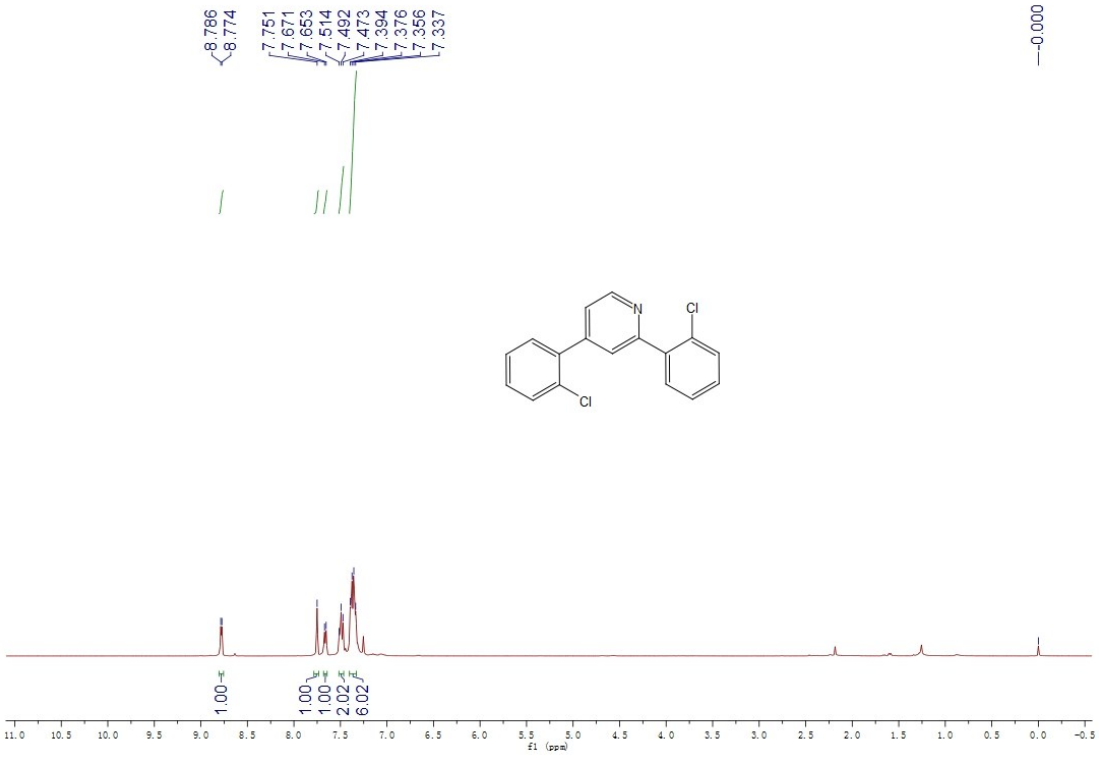
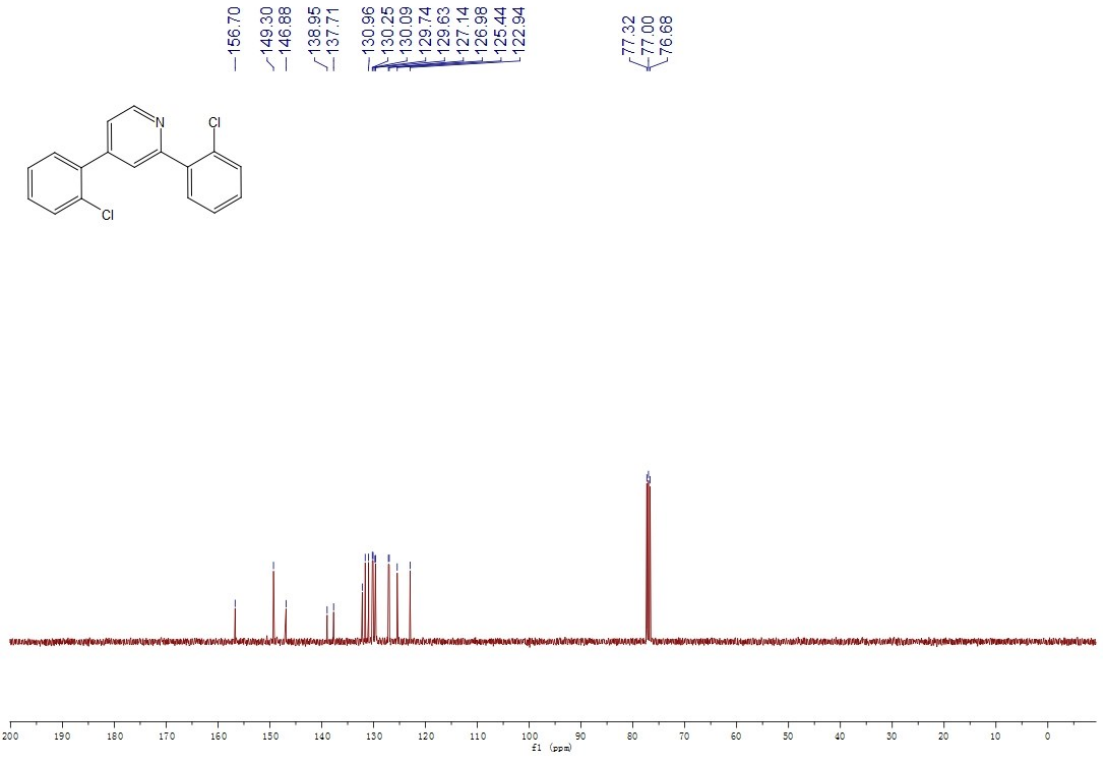
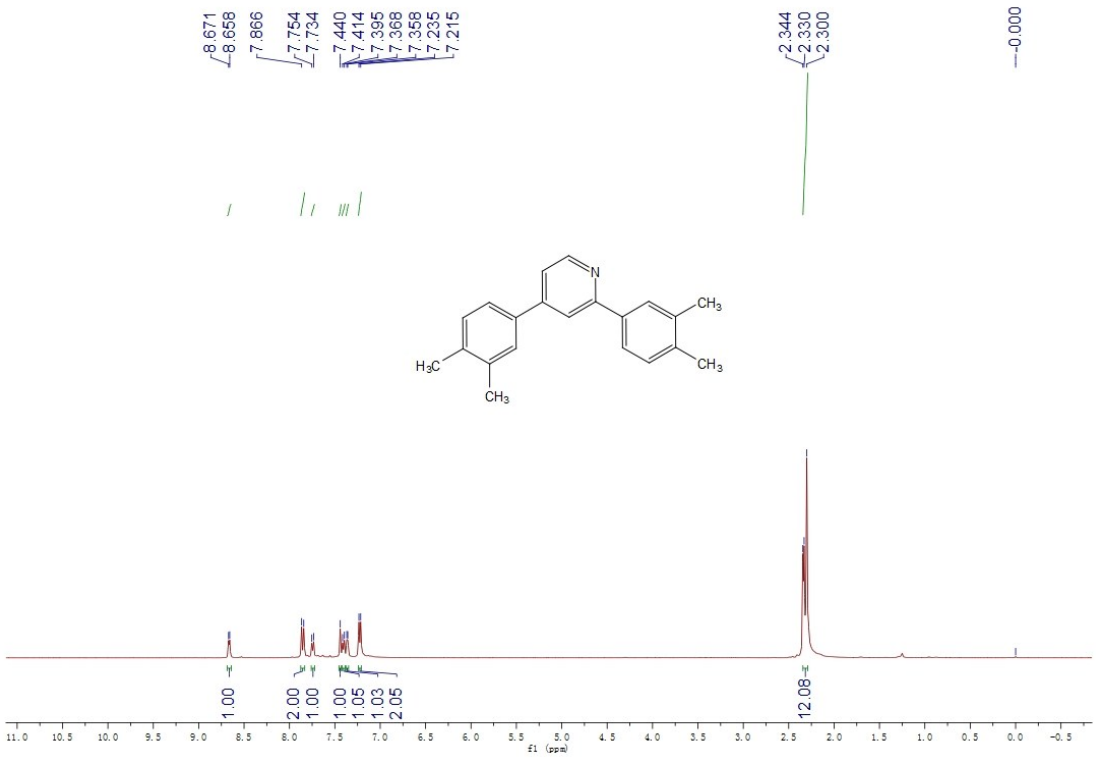
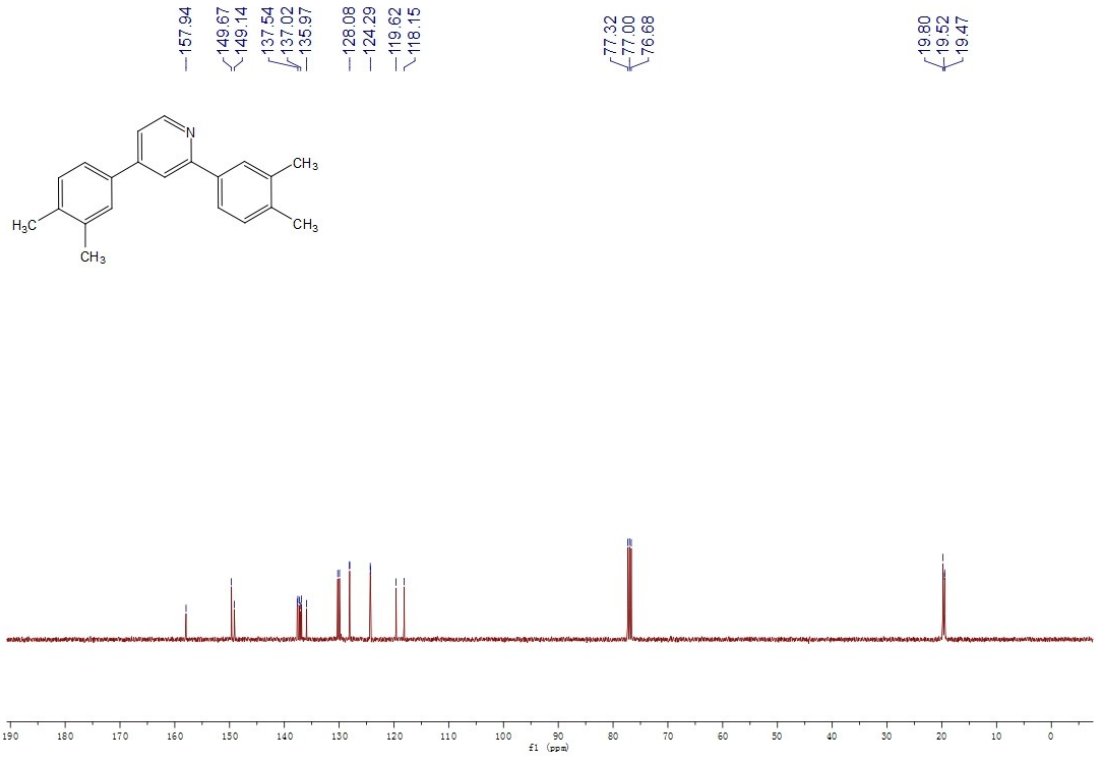
H3C
CH3
CH3
CH3
1.00
2.00
1.00
2.00
1.05
4.04
2.07
12.06
f1 (ppm)

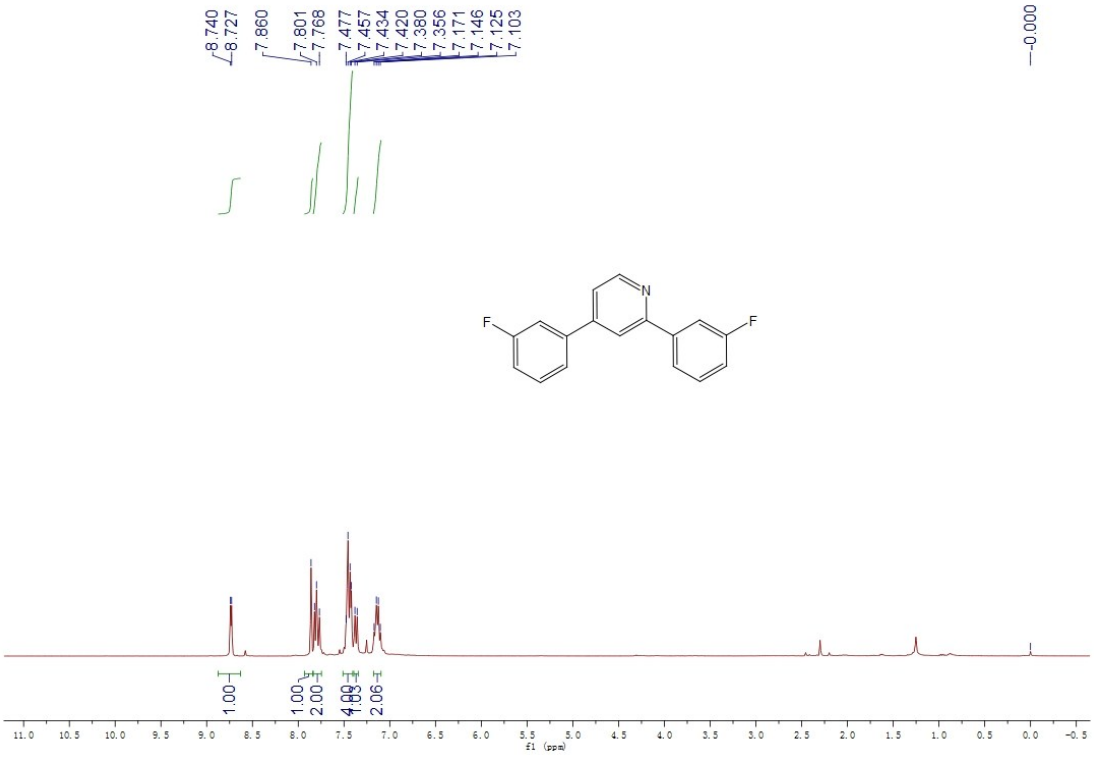

157.95
150.05
149.80
149.18
137.02
135.99
126.99
126.84
119.79
118.33
77.32
77.00
76.68
33.91
33.89
23.89
N
H3C
CH3
CH3
CH3
f1 (ppm)

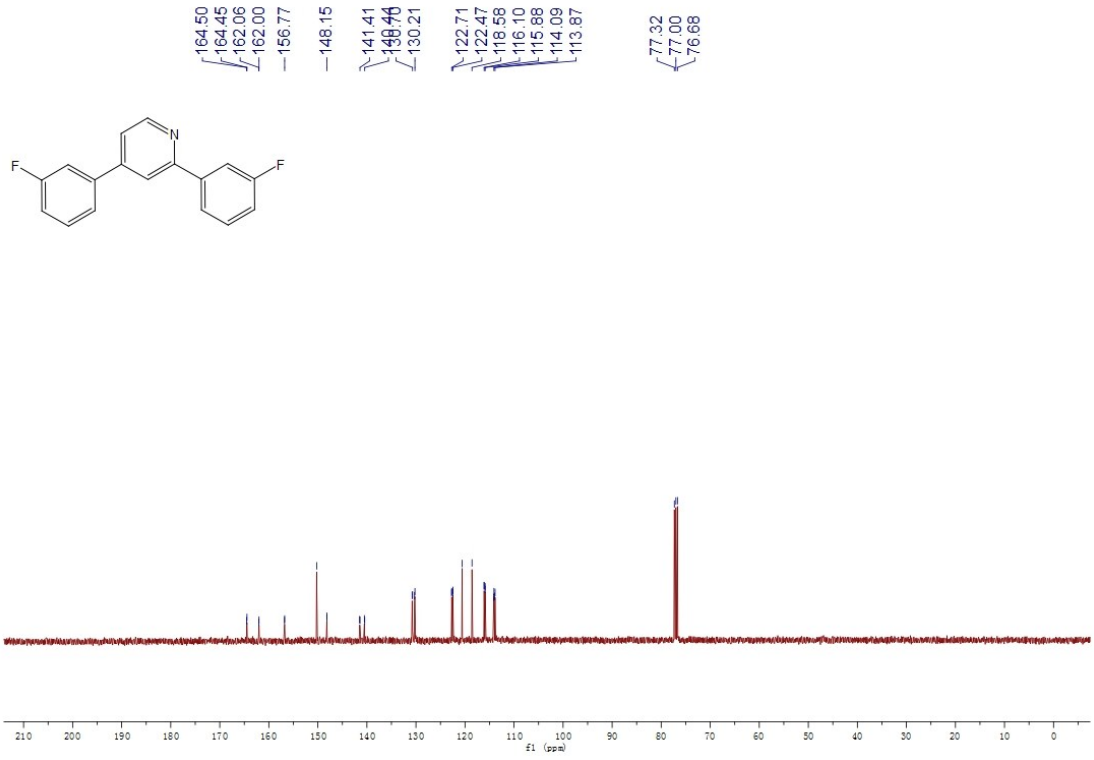

8.786
8.774
7.751
7.671
7.653
7.514
7.492
7.473
7.394
7.376
7.356
7.337
0.000
N
Cl
Cl
1.00
1.00
1.00
2.02
6.02
f1 (ppm)

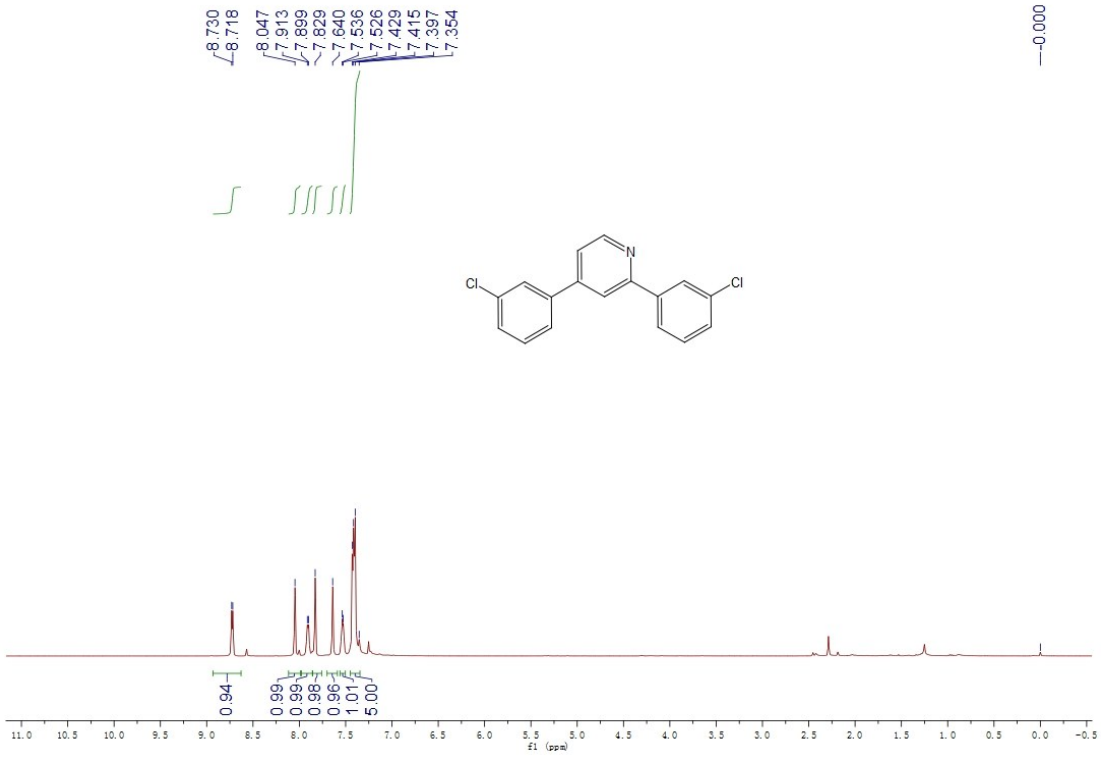

156.70
149.30
146.88
138.95
137.71
130.96
130.25
130.09
129.74
129.63
127.14
126.98
125.44
122.94
77.32
77.00
76.68
N
Cl
Cl
f1 (ppm)

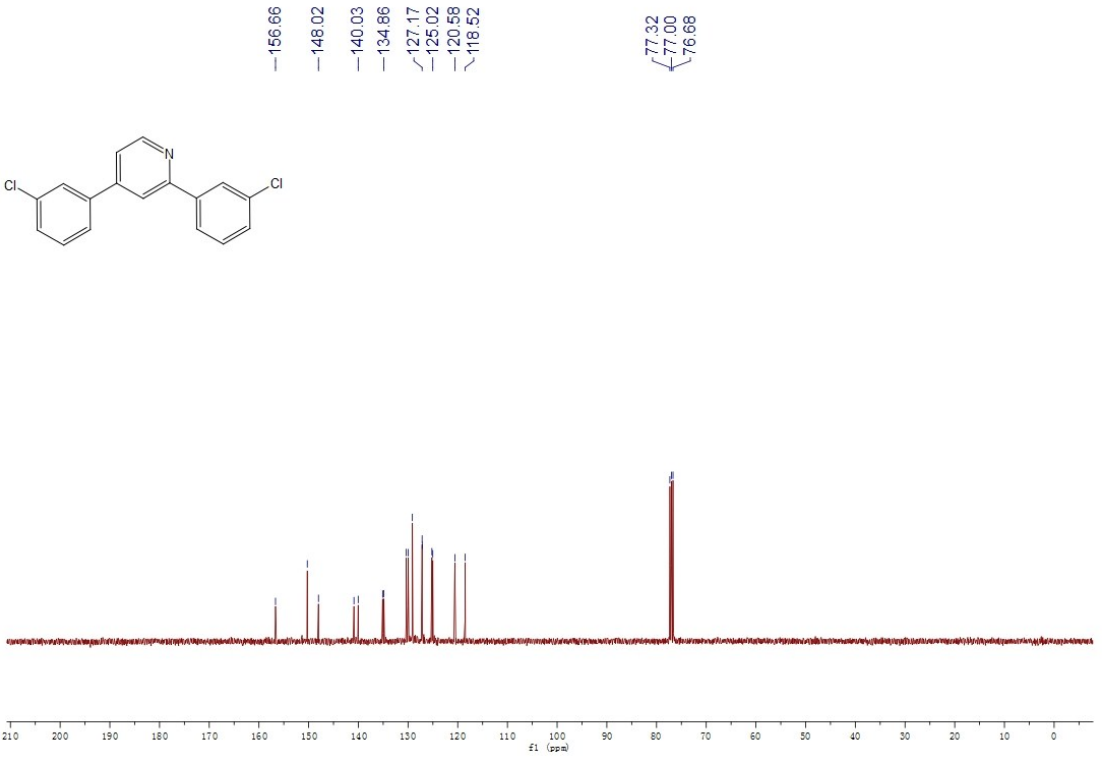

8.671
8.658
7.866
7.754
7.734
7.440
7.414
7.395
7.368
7.358
7.235
7.215
2.344
2.330
2.300
0.000
N
CH3
CH3
H3C
CH3
1.00
2.00
1.00
1.00
1.05
1.03
2.05
12.08
f1 (ppm)

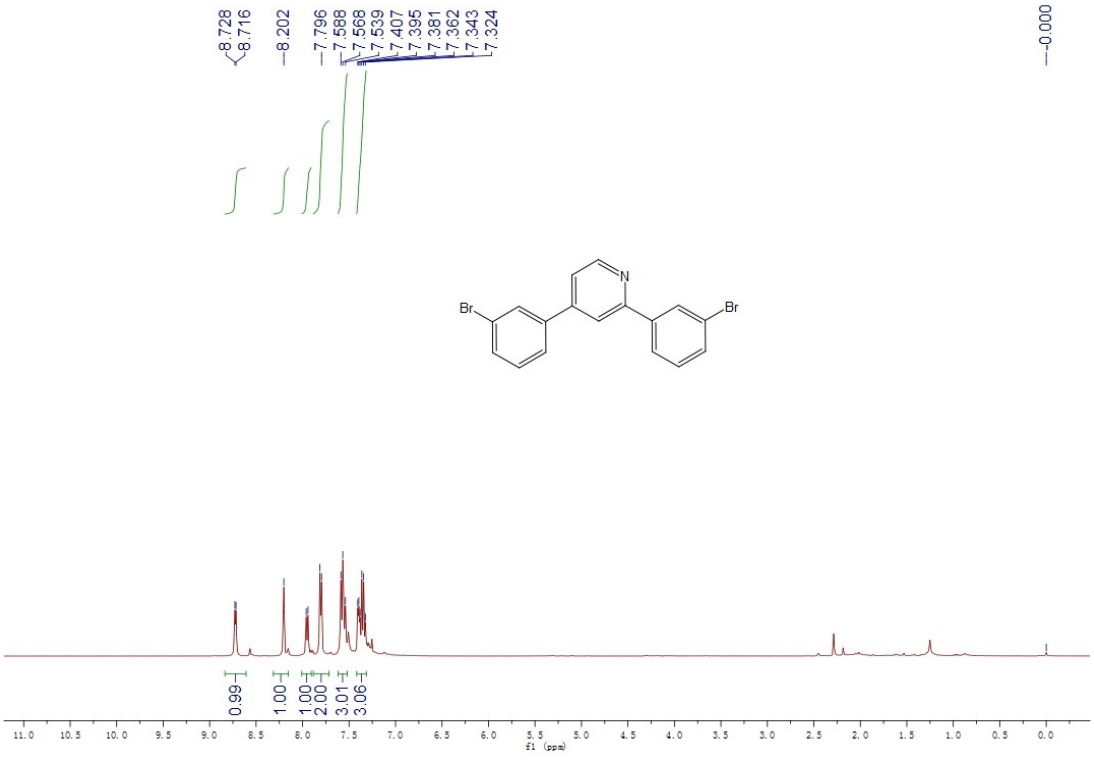

157.94
149.67
149.14
137.54
137.02
135.97
128.08
124.29
119.62
118.15
77.32
77.00
76.68
19.80
19.52
19.47
N
CH3
CH3
H3C
CH3
f1 (ppm)

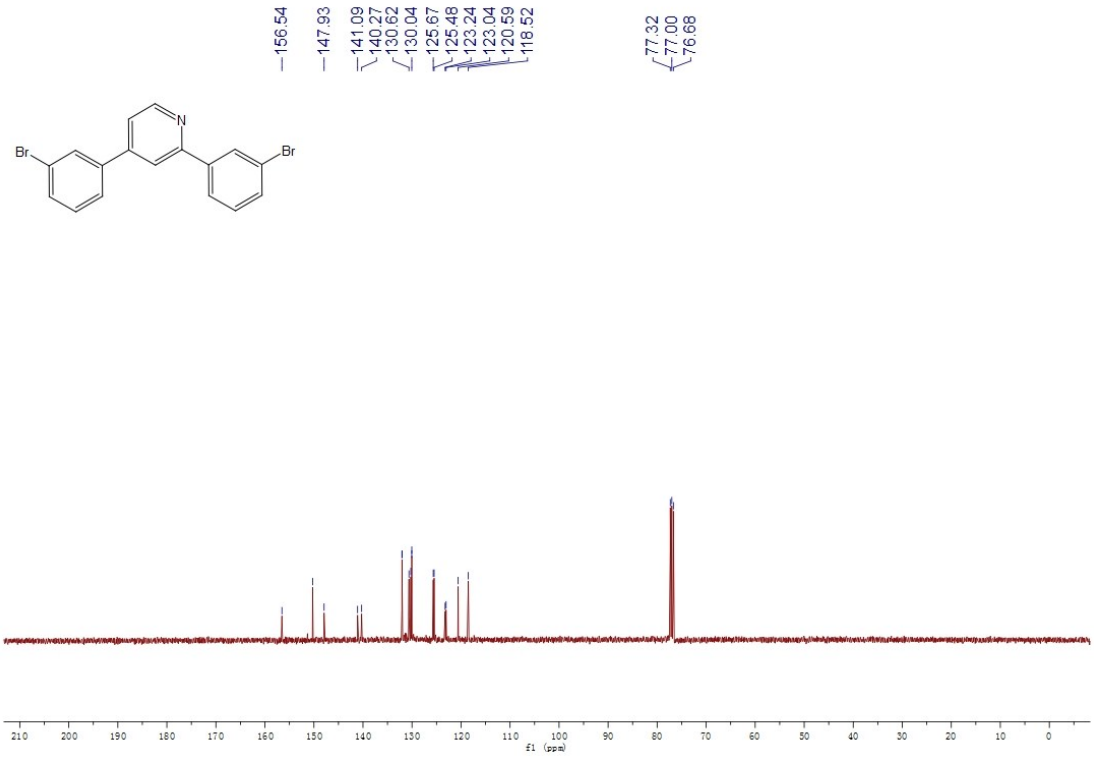

8.740
8.727
7.860
7.801
7.768
7.477
7.457
7.434
7.420
7.380
7.356
7.171
7.146
7.125
7.103
0.000
F
N
F
1.00
1.00
2.00
2.06
f1 (ppm)

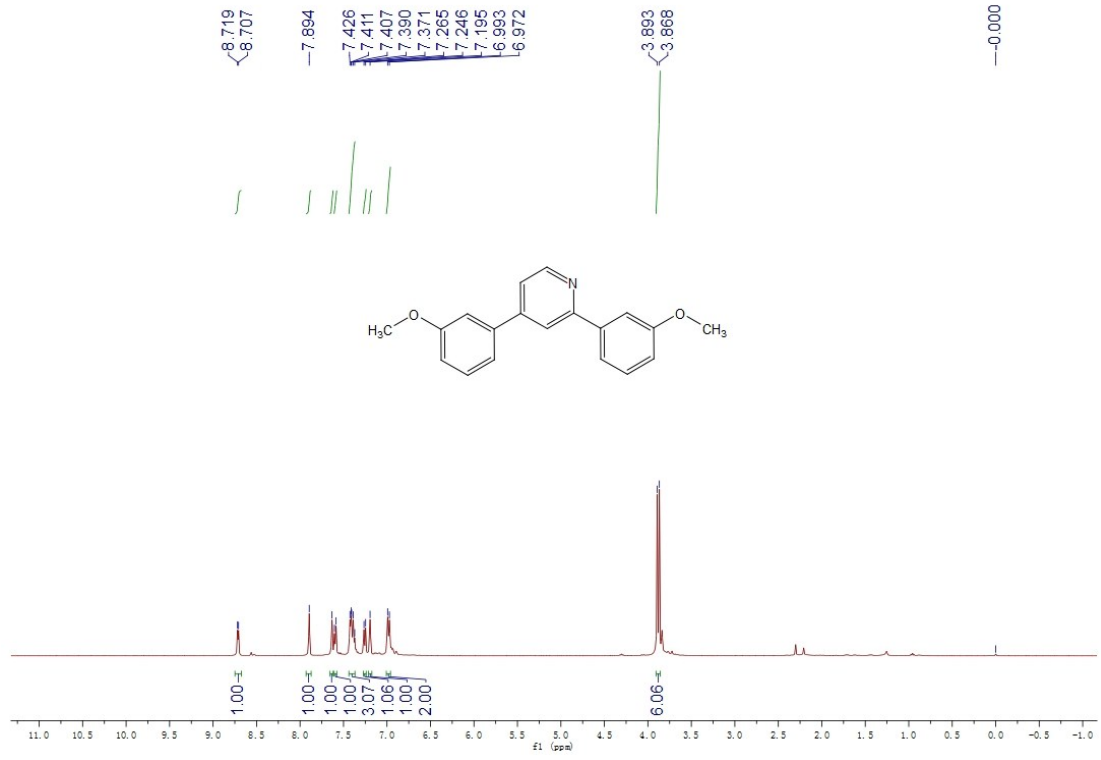

164.50
164.45
162.06
162.00
156.77
148.15
141.41
130.21
122.71
122.47
118.58
116.10
115.88
114.09
113.87
77.32
77.00
76.68
F
N
F
f1 (ppm)

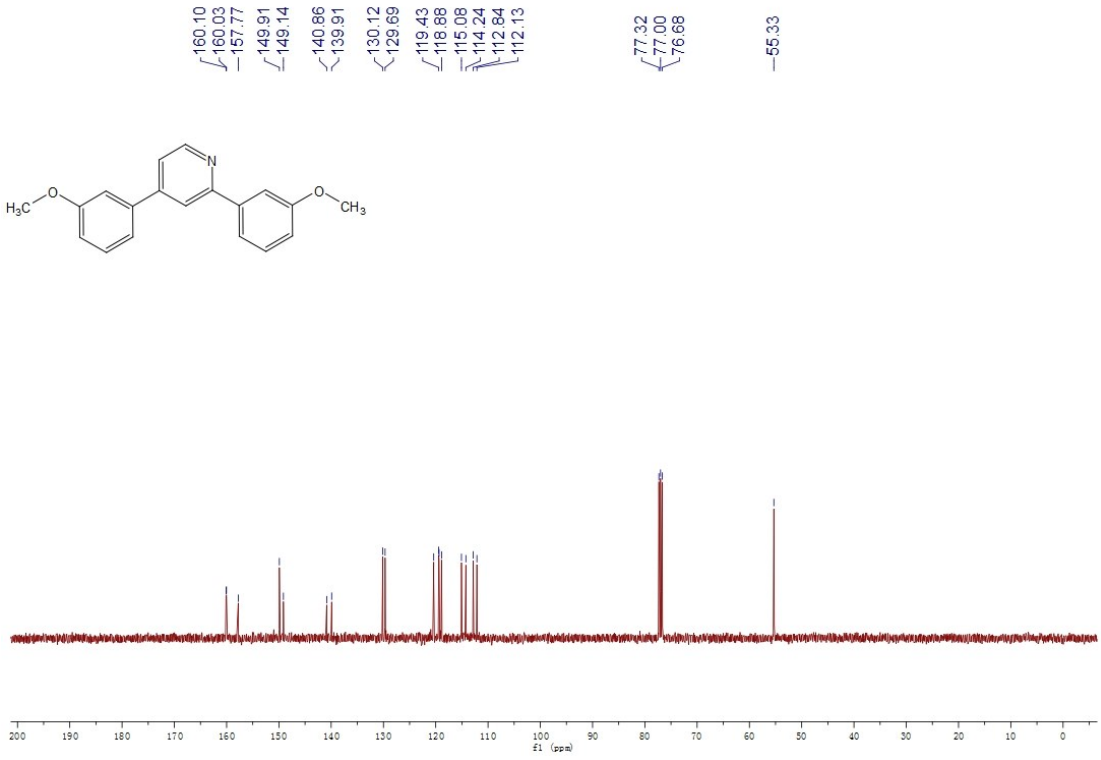

8.730
8.718
8.047
7.913
7.899
7.829
7.640
7.536
7.526
7.429
7.415
7.397
7.354
0.000
N
Cl
Cl
0.94
0.99
0.99
0.98
0.96
1.01
5.00
f1 (ppm)

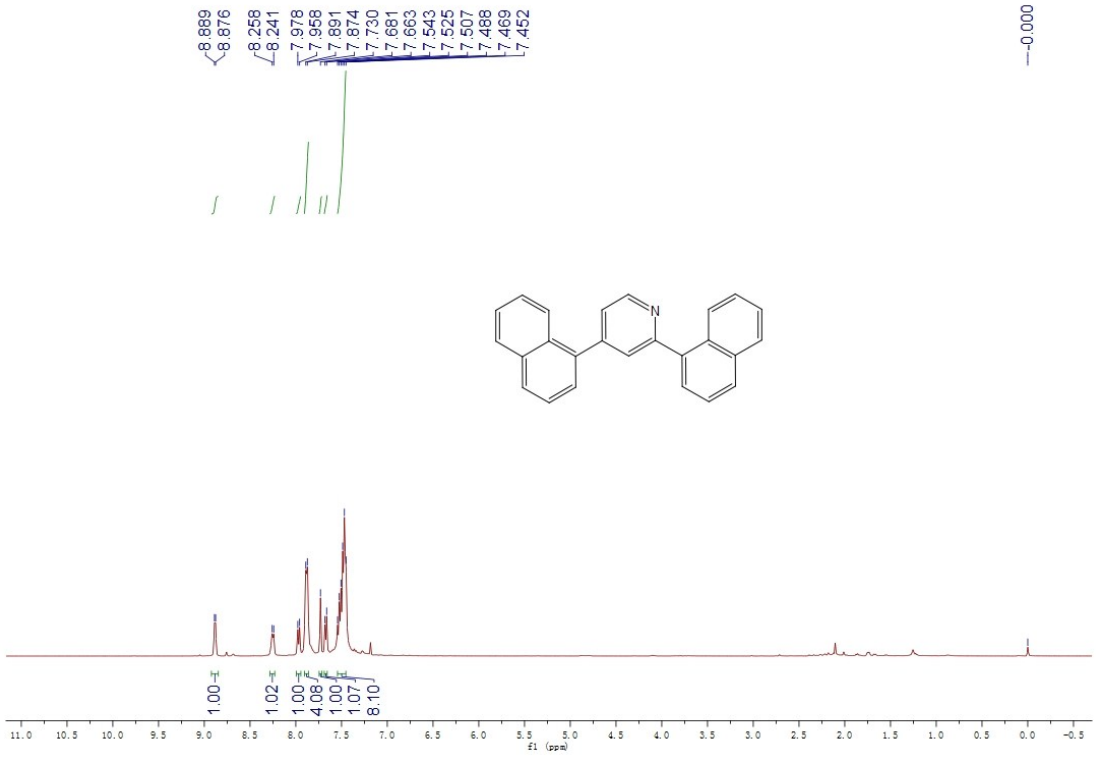

156.66
148.02
140.03
134.86
127.17
125.02
120.58
118.52
77.32
77.00
76.68
N
Cl
Cl
f1 (ppm)

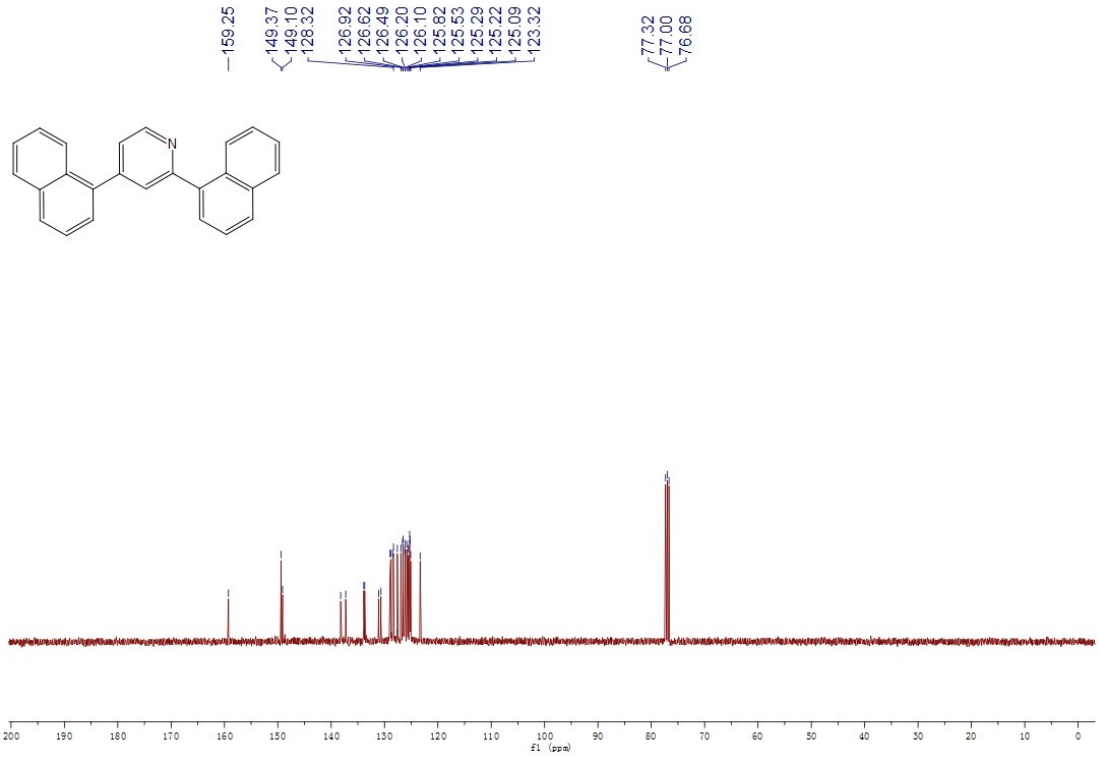

8.728
8.716
8.202
7.796
7.588
7.568
7.539
7.407
7.395
7.381
7.362
7.343
7.324
0.000
Br
Br
N
0.99
1.00
1.00
2.00
3.01
3.06
f1 (ppm)

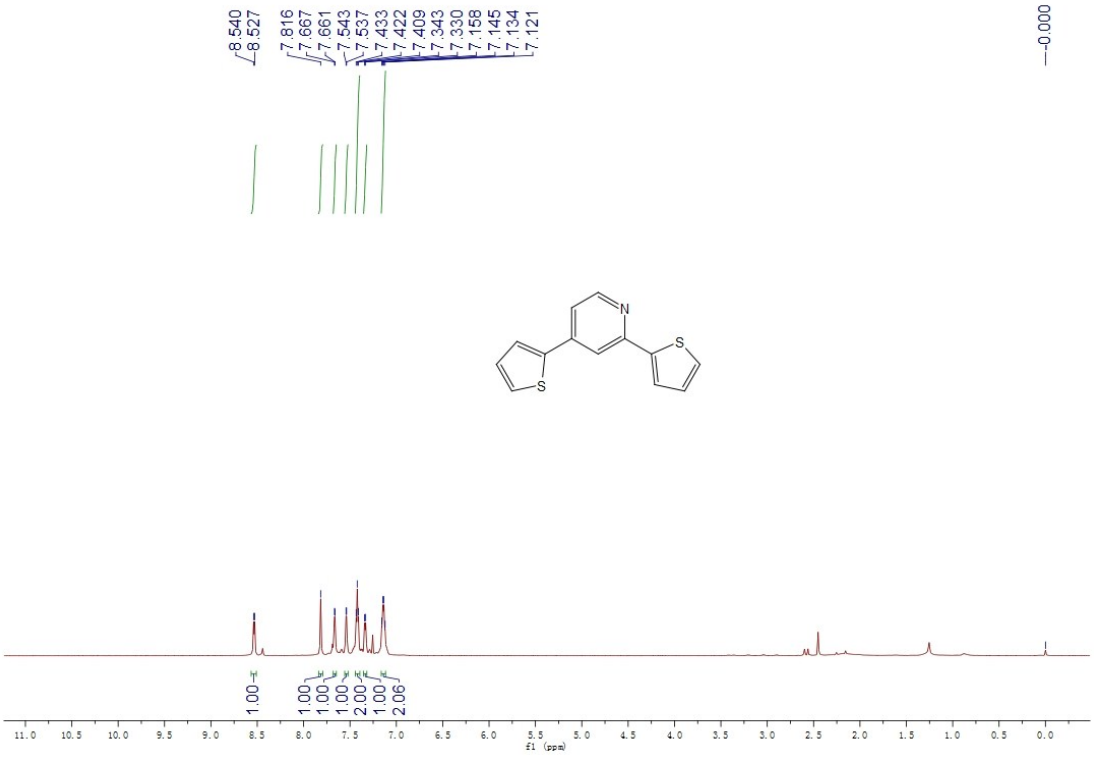

156.54
147.93
141.09
140.27
130.62
130.04
125.67
125.48
123.24
123.04
120.59
118.52
77.32
77.00
76.68
Br
Br
N
f1 (ppm)

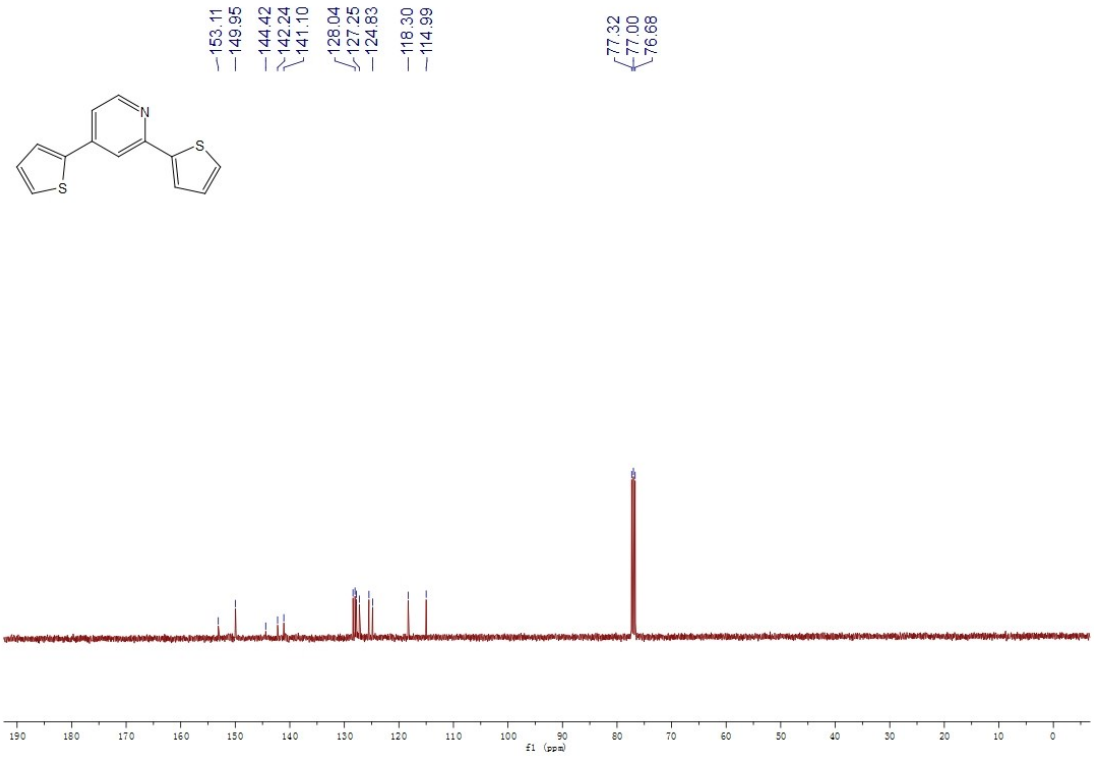

8.719
8.707
7.894
7.426
7.411
7.407
7.390
7.371
7.265
7.246
7.195
6.993
6.972
3.893
3.868
0.000
N
H3C
O
O
CH3
1.00
1.00
1.00
1.00
3.07
1.06
1.00
2.00
6.06
f1 (ppm)


160.10
160.03
157.77
149.91
149.14
140.86
139.91
130.12
129.69
119.43
118.88
115.08
114.24
112.84
112.13
77.32
77.00
76.68
55.33
N
H3C
O
O
CH3
f1 (ppm)

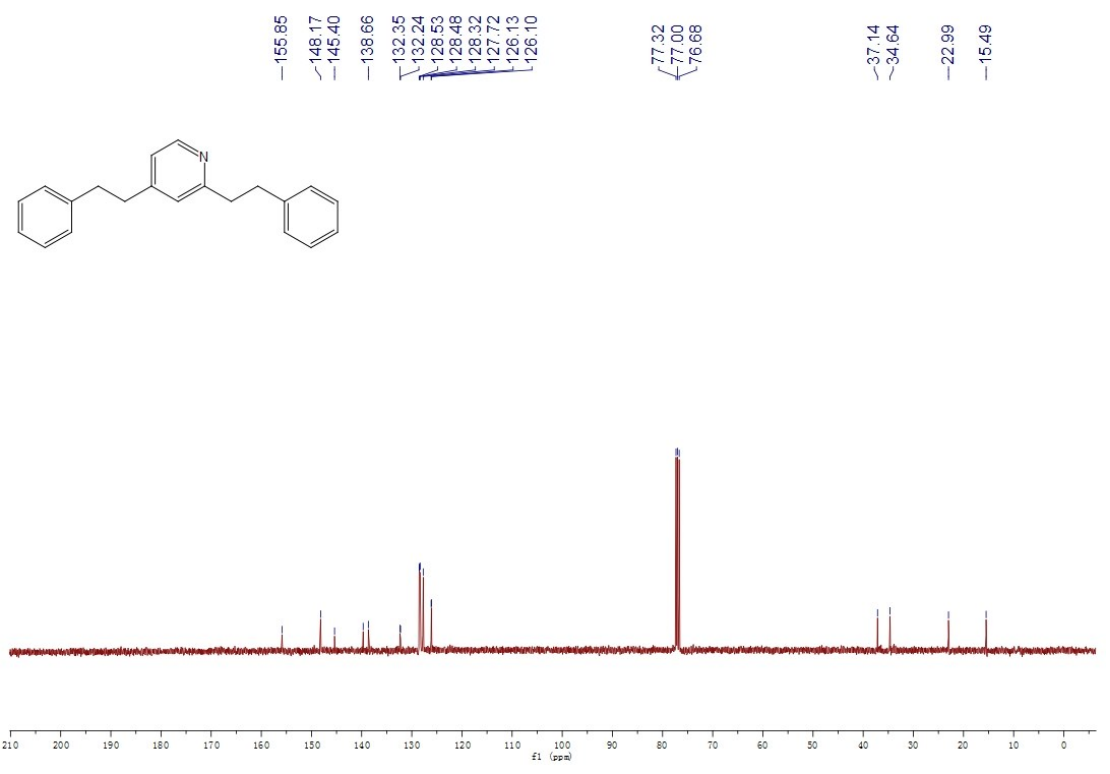

8.889
8.876
8.258
8.241
7.978
7.958
7.891
7.874
7.730
7.681
7.663
7.543
7.525
7.507
7.488
7.469
7.452
0.000
N
1.00
1.02
1.00
4.08
1.00
1.07
8.10
f1 (ppm)

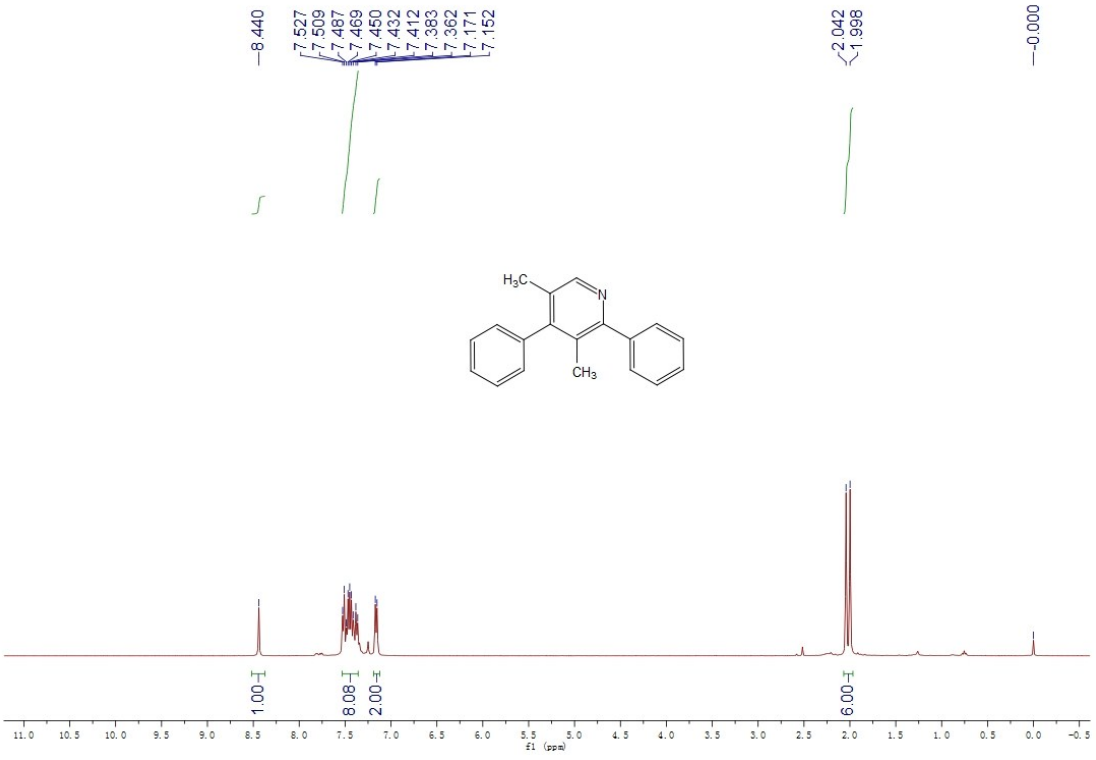

159.25
149.37
149.10
128.32
126.92
126.62
126.49
126.20
126.10
125.82
125.53
125.29
125.22
125.09
123.32
77.32
77.00
76.68
N
f1 (ppm)

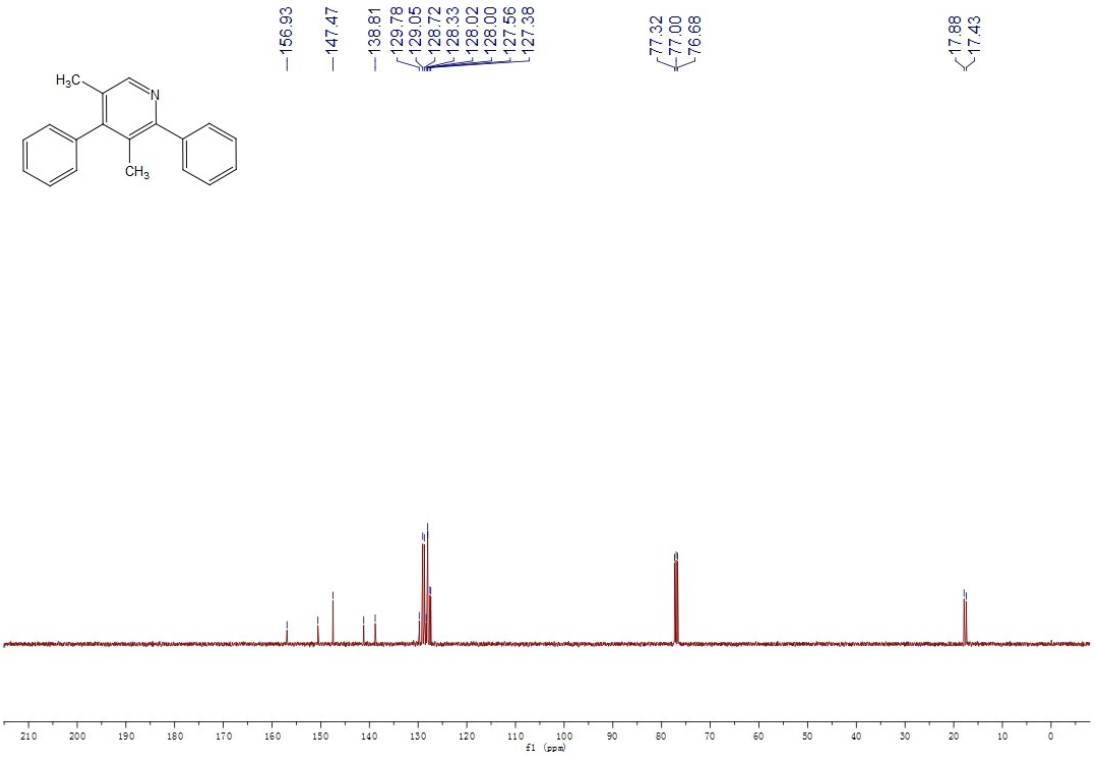

8.540
8.527
7.816
7.667
7.661
7.543
7.537
7.433
7.422
7.409
7.343
7.330
7.158
7.145
7.134
7.121
0.000
N
S
S
1.00
1.00
1.00
1.00
2.00
1.00
2.06
f1 (ppm)

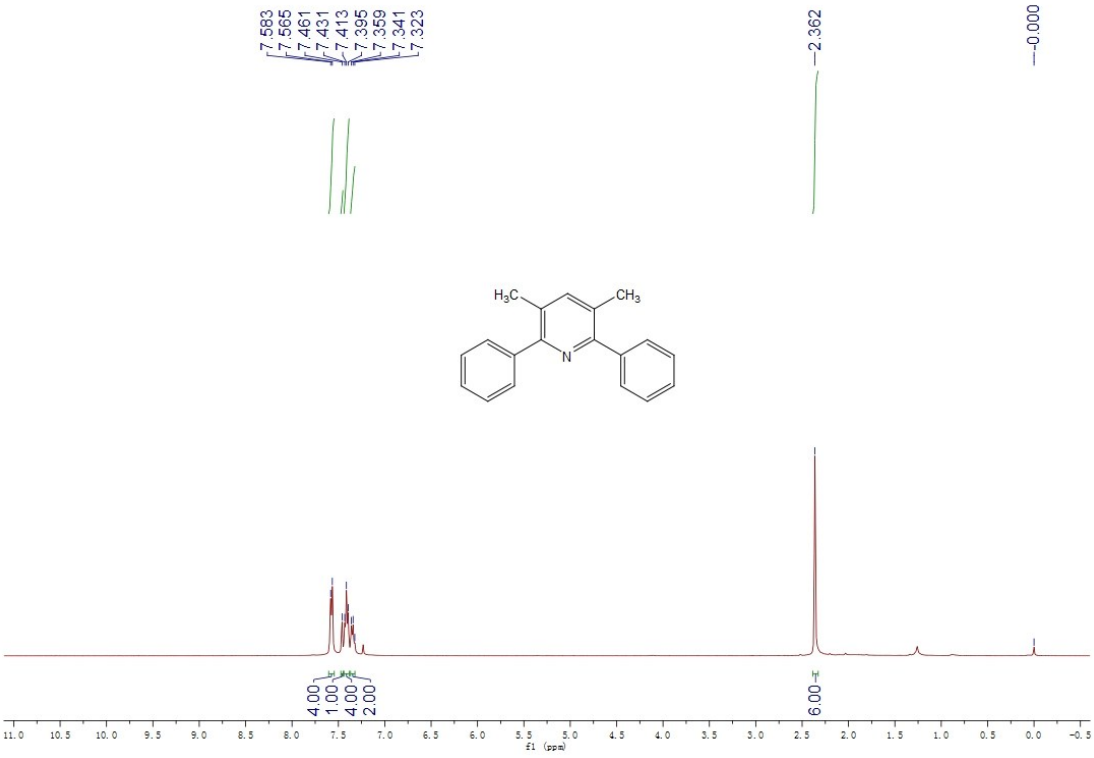

153.11
149.95
144.42
142.24
141.10
128.04
127.25
124.83
118.30
114.99
77.32
77.00
76.68
N
S
S
f1 (ppm)

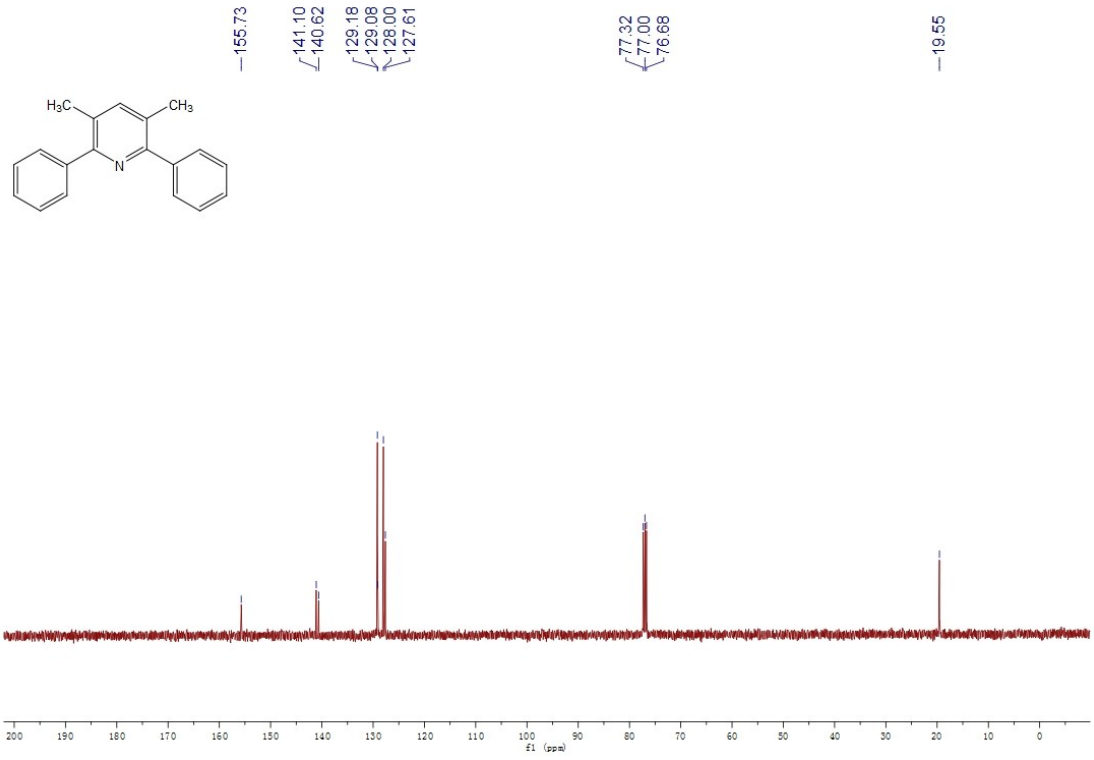

8.236
7.279
7.261
7.243
7.224
7.195
7.181
7.104
7.086
6.985
6.967
4.060
3.993
2.491
2.059
0.000
N
0.97
6.00
2.04
2.00
2.00
2.01
2.00
2.05
2.08
f1 (ppm)

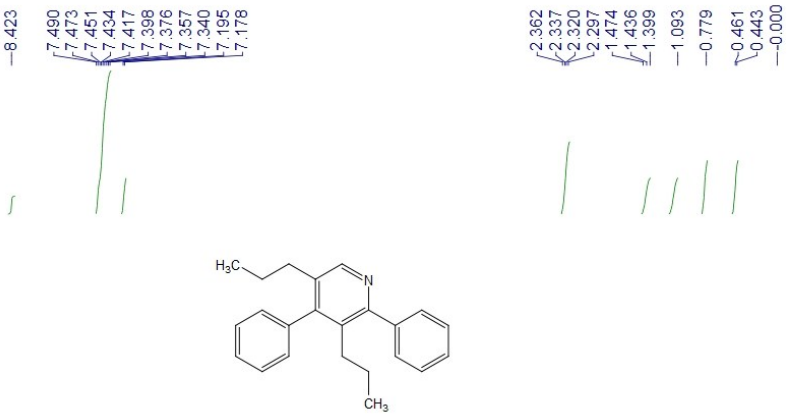

155.85
148.17
145.40
138.66
132.35
132.24
128.53
128.48
128.32
127.72
126.13
126.10
77.32
77.00
76.68
37.14
34.64
22.99
15.49
N
f1 (ppm)

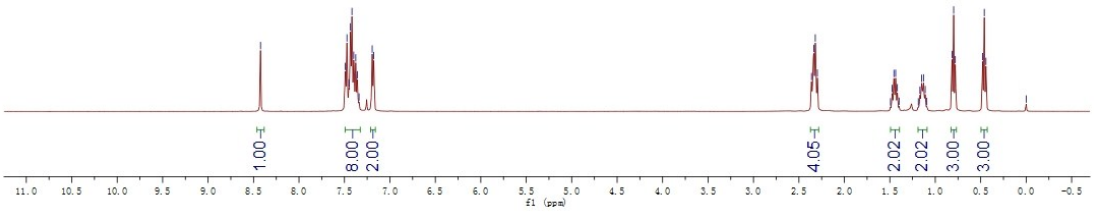

8.440
7.527
7.509
7.487
7.469
7.450
7.432
7.412
7.383
7.362
7.171
7.152
2.042
1.998
0.000
H3C
N
CH3
1.00
8.08
2.00
6.00
f1 (ppm)

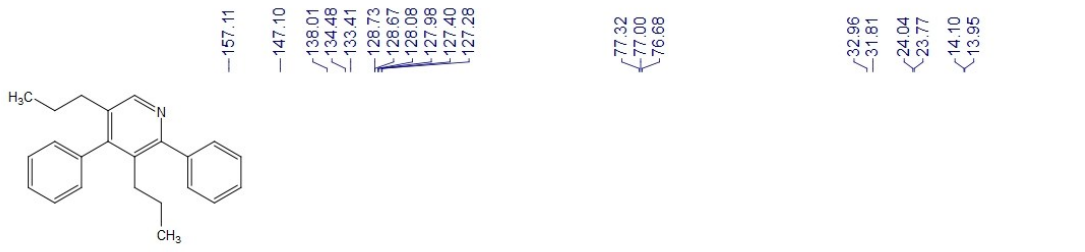

156.93
147.47
138.81
129.78
129.05
128.72
128.33
128.02
128.00
127.56
127.38
77.32
77.00
76.68
17.88
17.43
H3C
N
CH3
f1 (ppm)

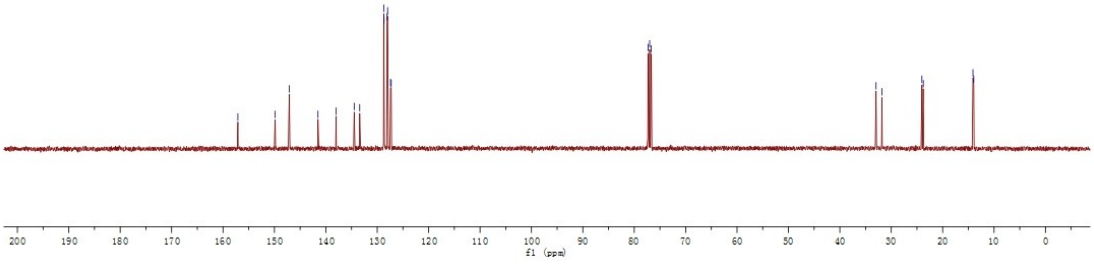

7.583
7.565
7.461
7.431
7.413
7.395
7.359
7.341
7.323
2.362
0.000
H3C
CH3
N
4.00
1.00
4.00
2.00
6.00
f1 (ppm)

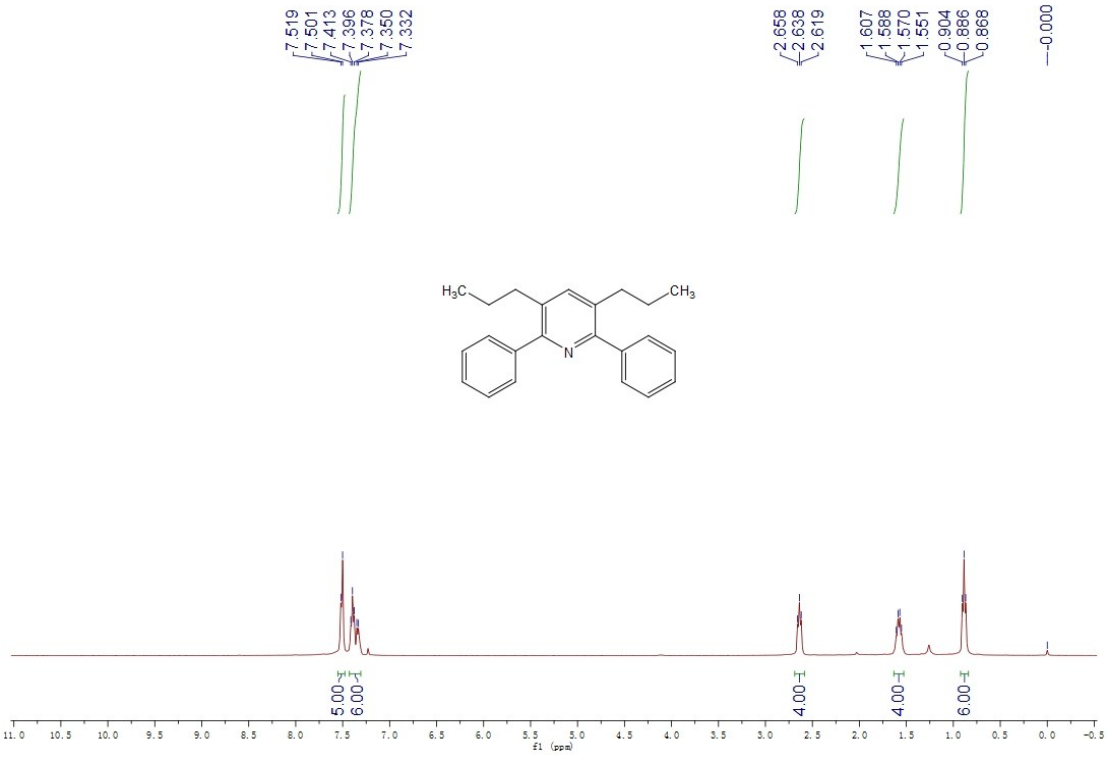

155.73
141.10
140.62
129.18
129.08
128.00
127.61
77.32
77.00
76.68
19.55
H3C
CH3
N
f1 (ppm)

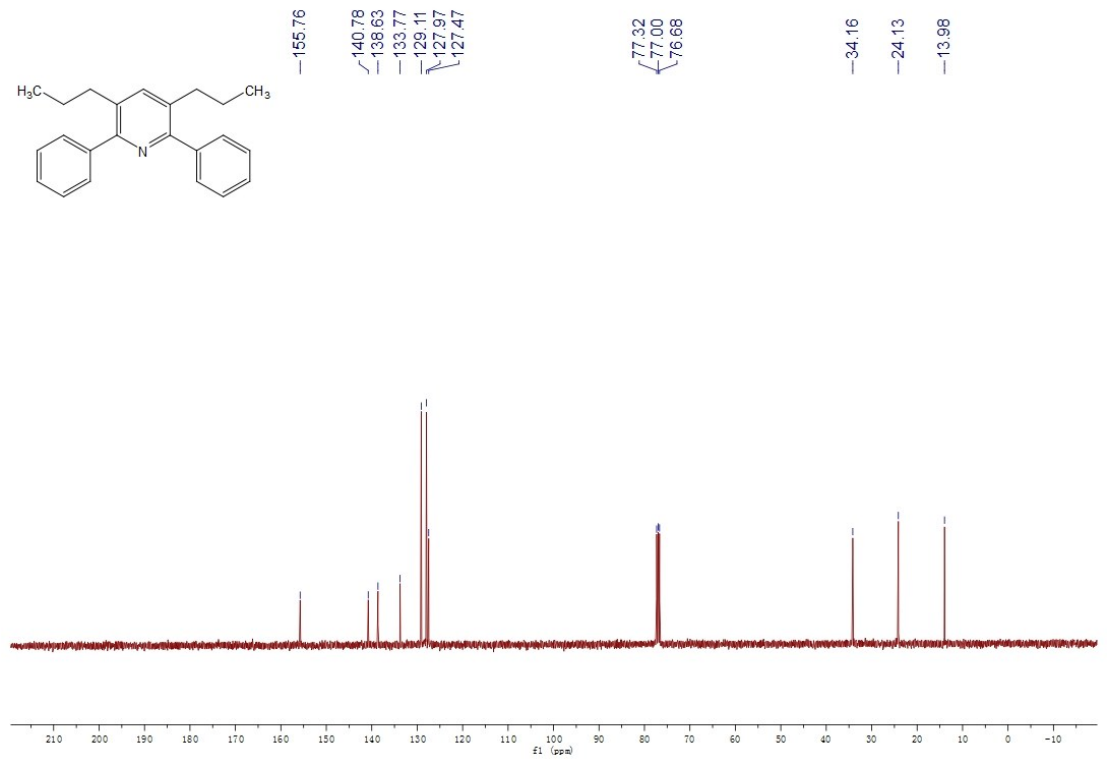

8.423
7.490
7.473
7.451
7.434
7.417
7.398
7.376
7.357
7.340
7.195
7.178
2.362
2.337
2.320
2.297
1.474
1.436
1.399
1.093
0.779
0.461
0.443
0.000
H3C
N
CH3

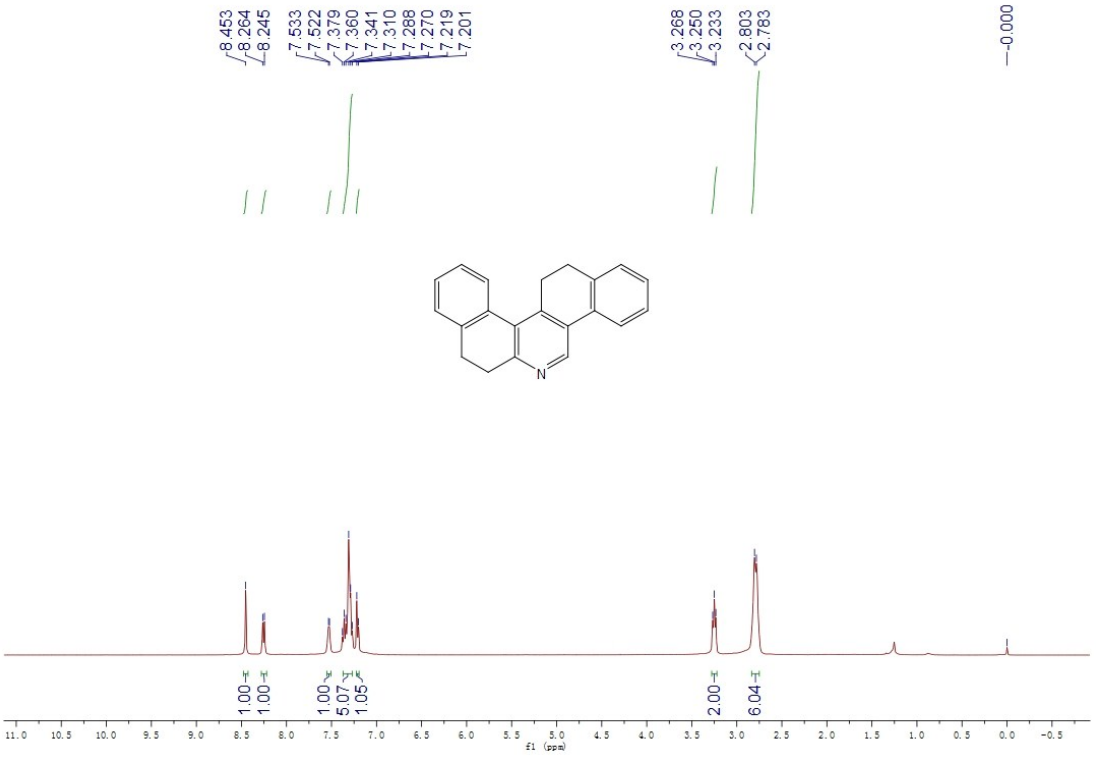

1.00
8.00
2.00
4.05
2.02
2.02
3.00
3.00
f1 (ppm)

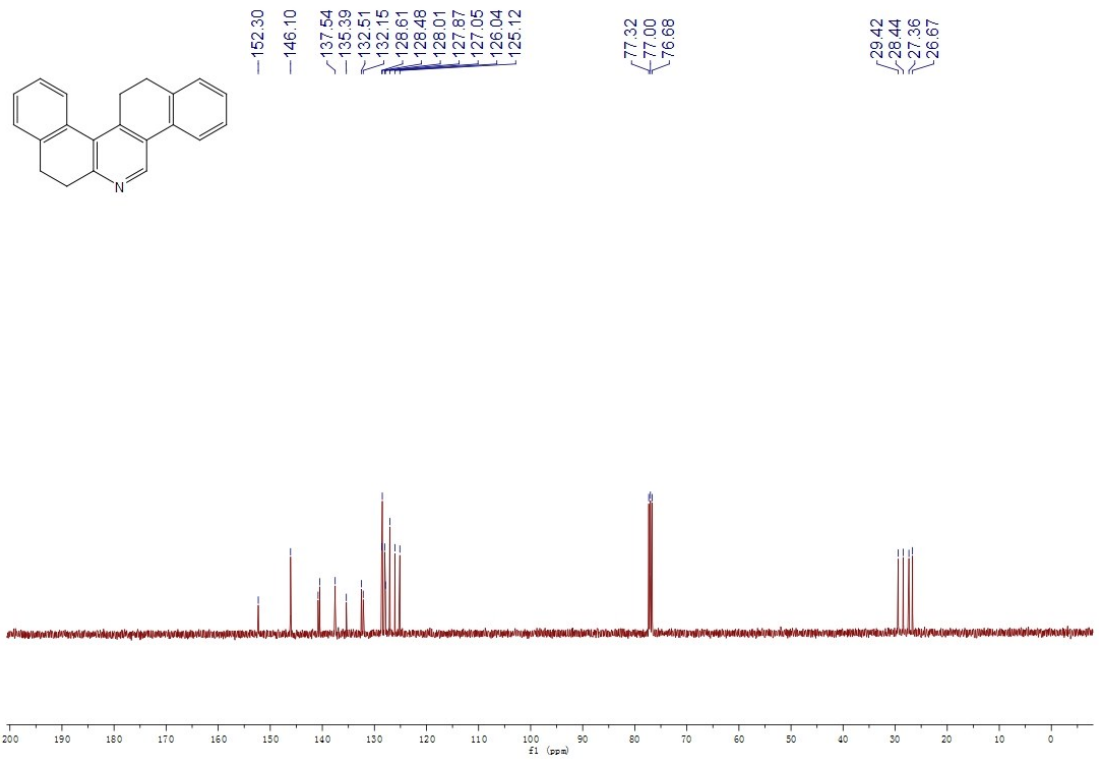

157.11
147.10
138.01
134.48
133.41
128.73
128.67
128.08
127.98
127.40
127.28
77.32
77.00
76.68
32.96
31.81
24.04
23.77
14.10
13.95
H3C
N
CH3

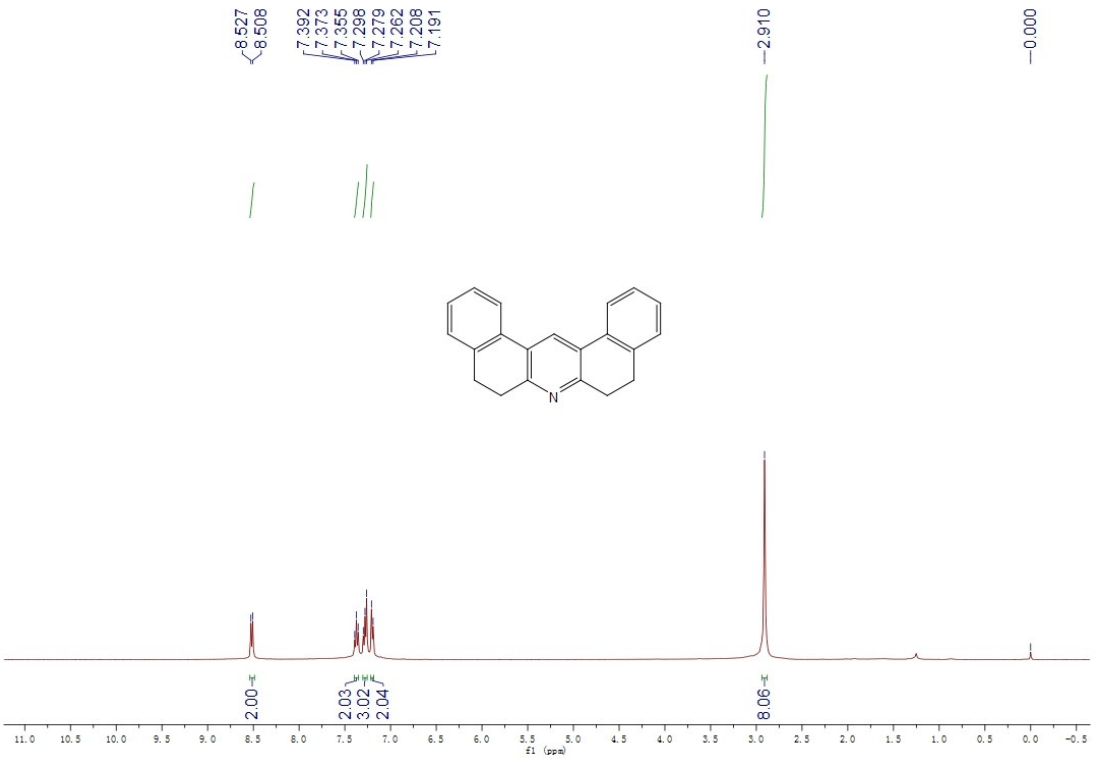

f1 (ppm)

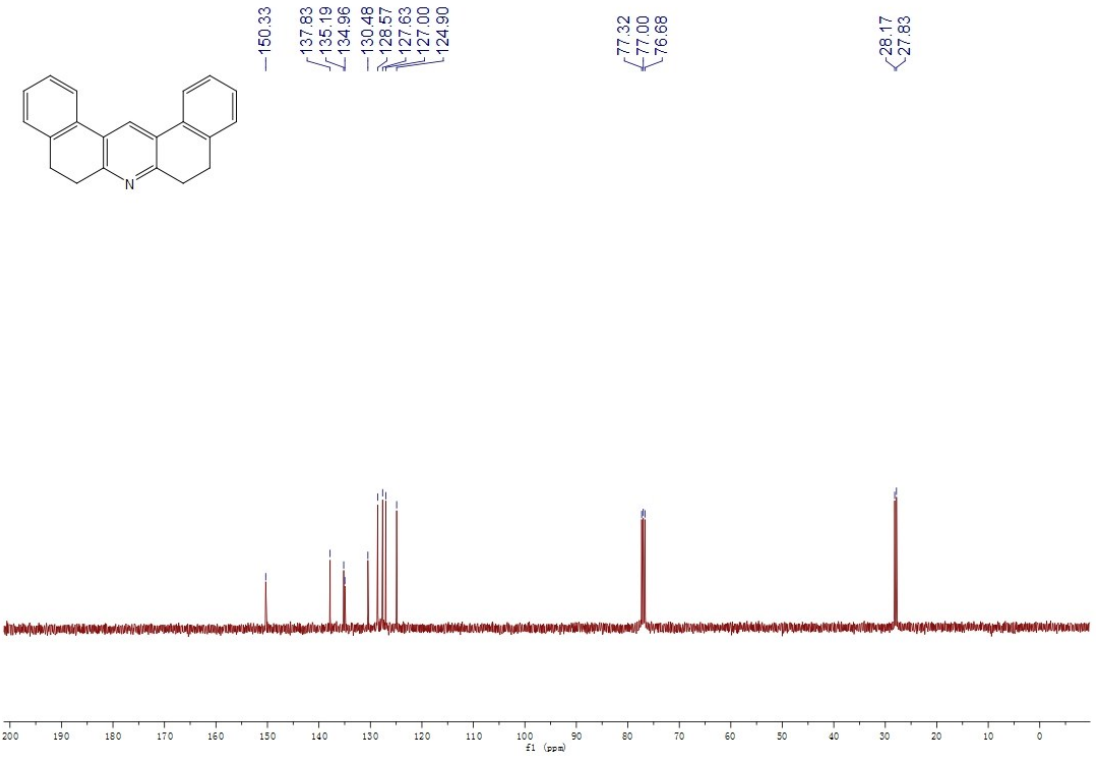

7.519
7.501
7.413
7.396
7.378
7.350
7.332
2.658
2.638
2.619
1.607
1.588
1.570
1.551
0.904
0.886
0.868
0.000
H3C
CH3
N
5.00
6.00
4.00
4.00
6.00
f1 (ppm)

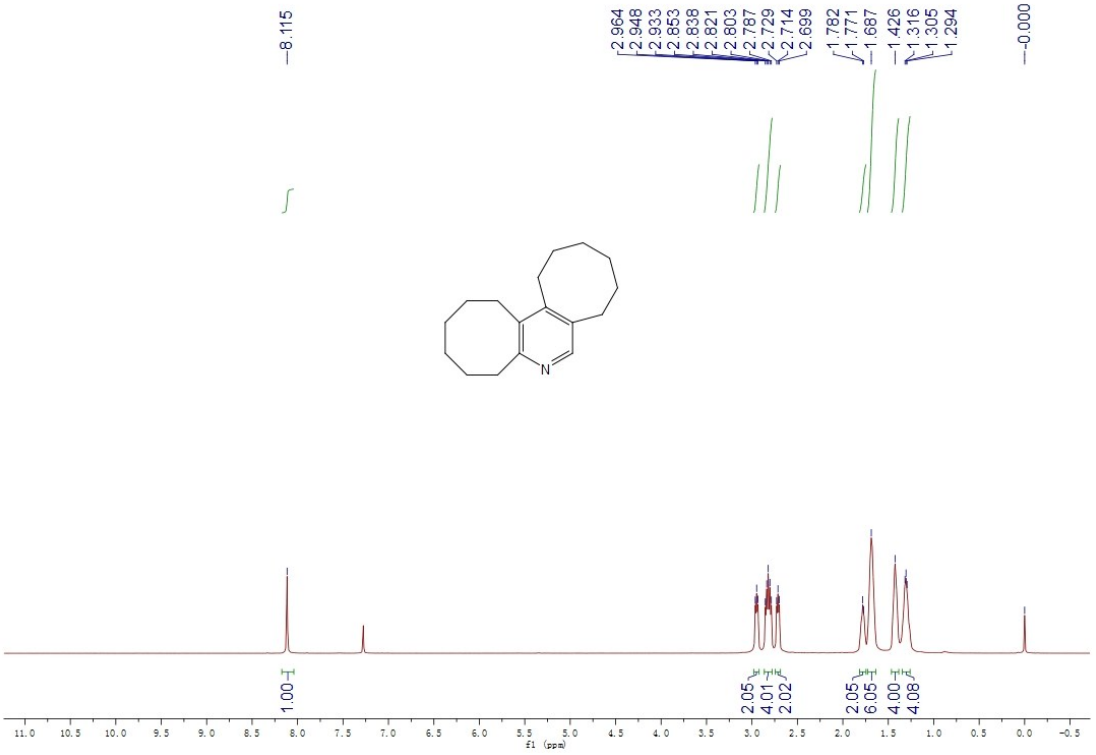

155.76
140.78
138.63
133.77
129.11
127.97
127.47
77.32
77.00
76.68
34.16
24.13
13.98
H3C
CH3
N
f1 (ppm)

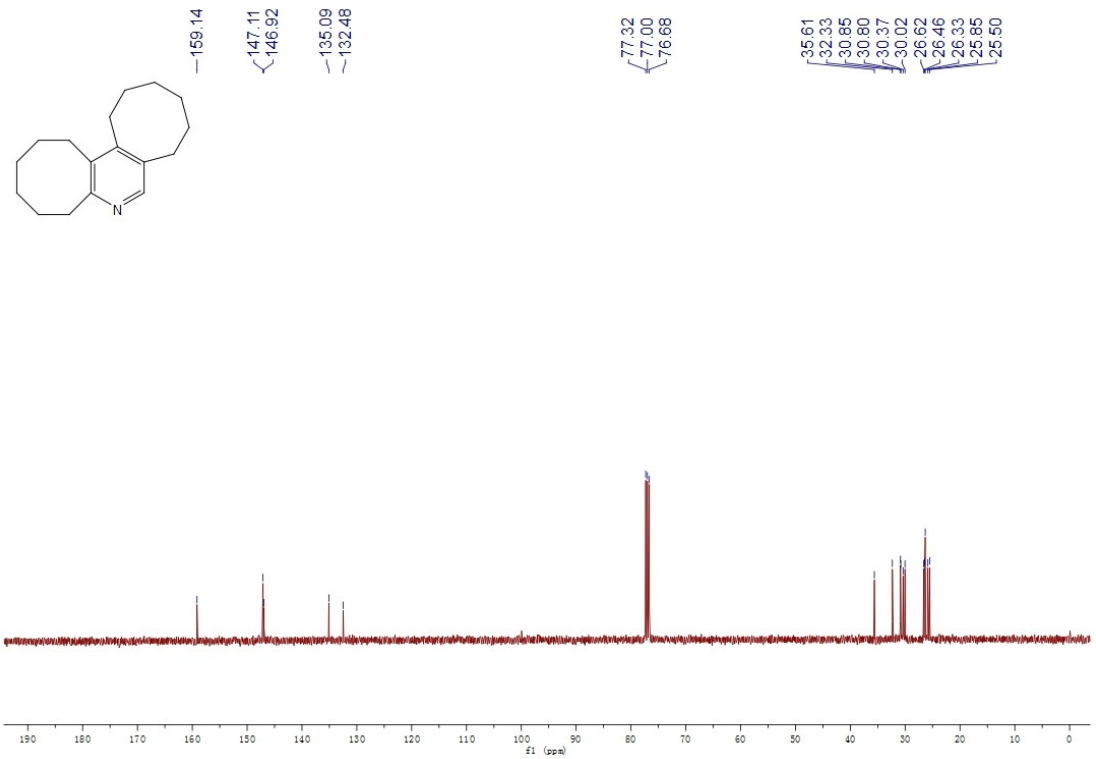

8.453
8.264
8.245
7.533
7.522
7.379
7.360
7.341
7.310
7.288
7.270
7.219
7.201
3.268
3.250
3.233
2.803
2.783
0.000
N
1.00
1.00
1.00
5.07
1.05
2.00
6.04
f1 (ppm)

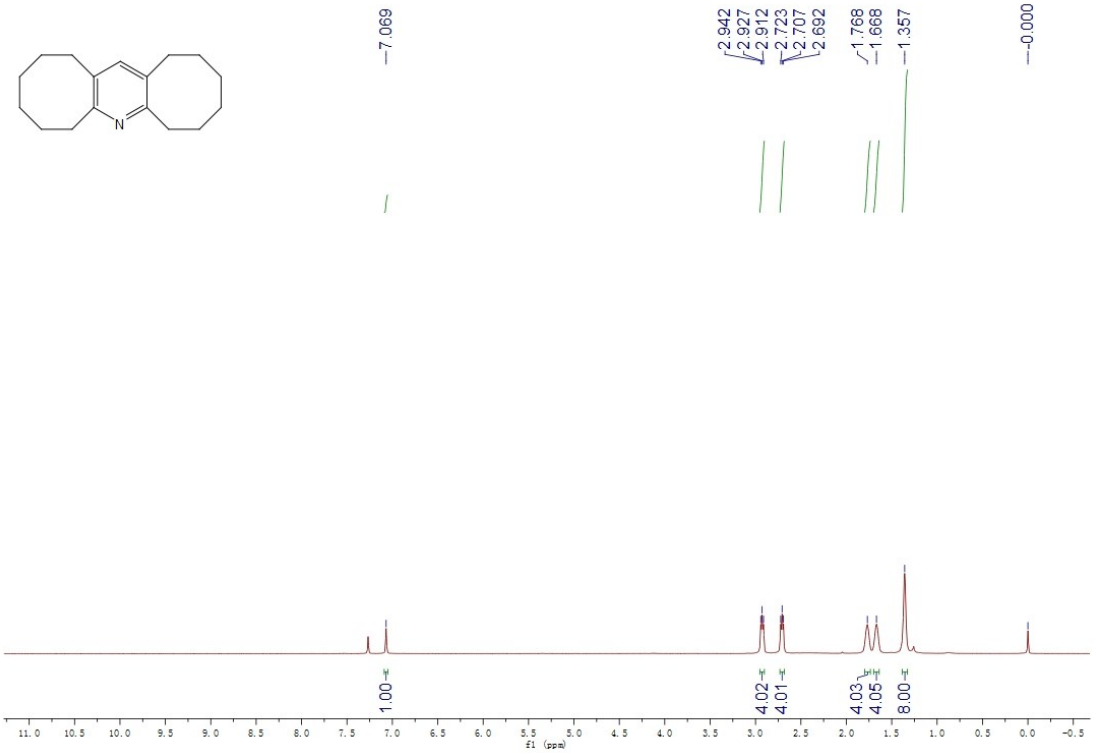

152.30
146.10
137.54
135.39
132.51
132.15
128.61
128.48
128.01
127.87
127.05
126.04
125.12
77.32
77.00
76.68
29.42
28.44
27.36
26.67
N
f1 (ppm)

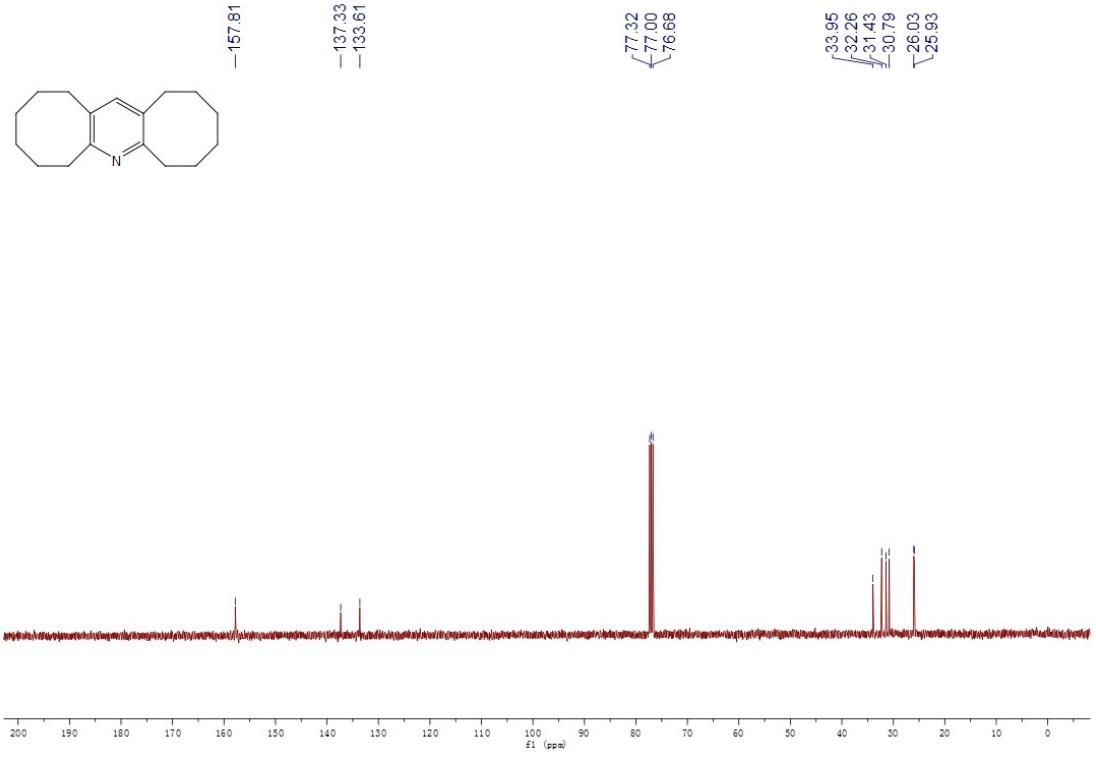

8.527
8.508
7.392
7.373
7.355
7.298
7.279
7.262
7.208
7.191
2.910
0.000
N
2.00
2.03
3.02
2.04
8.06
f1 (ppm)

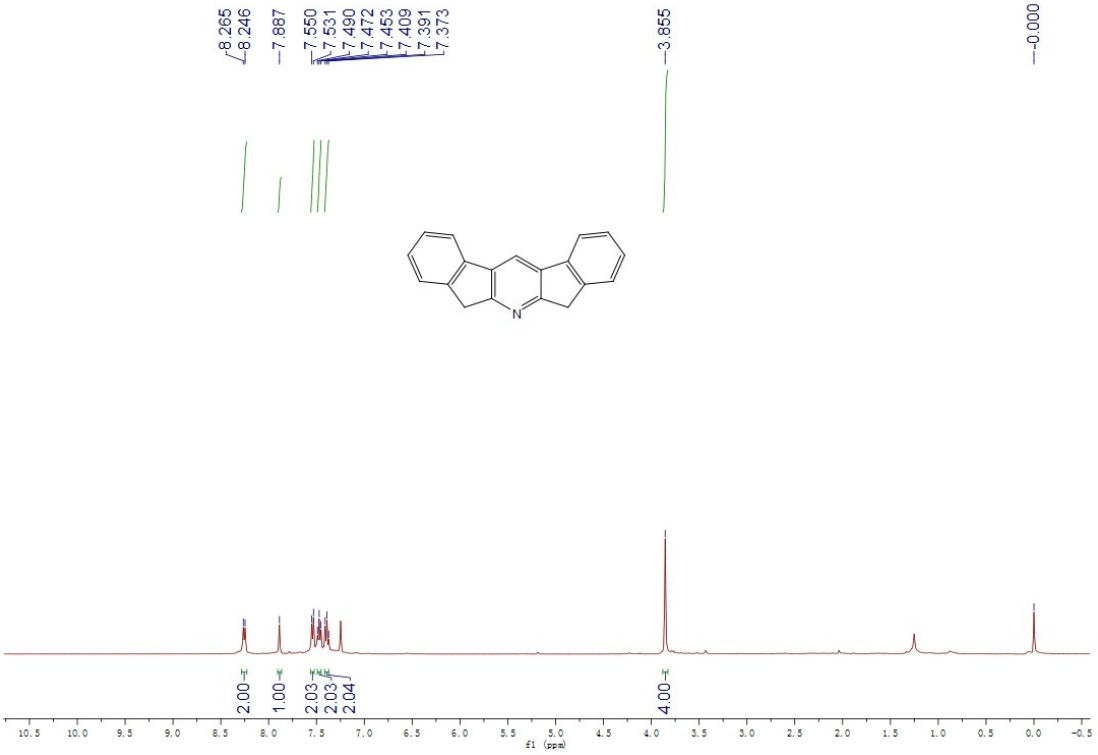

150.33
137.83
135.19
134.96
130.48
128.57
127.63
127.00
124.90
77.32
77.00
76.68
28.17
27.83
N
f1 (ppm)

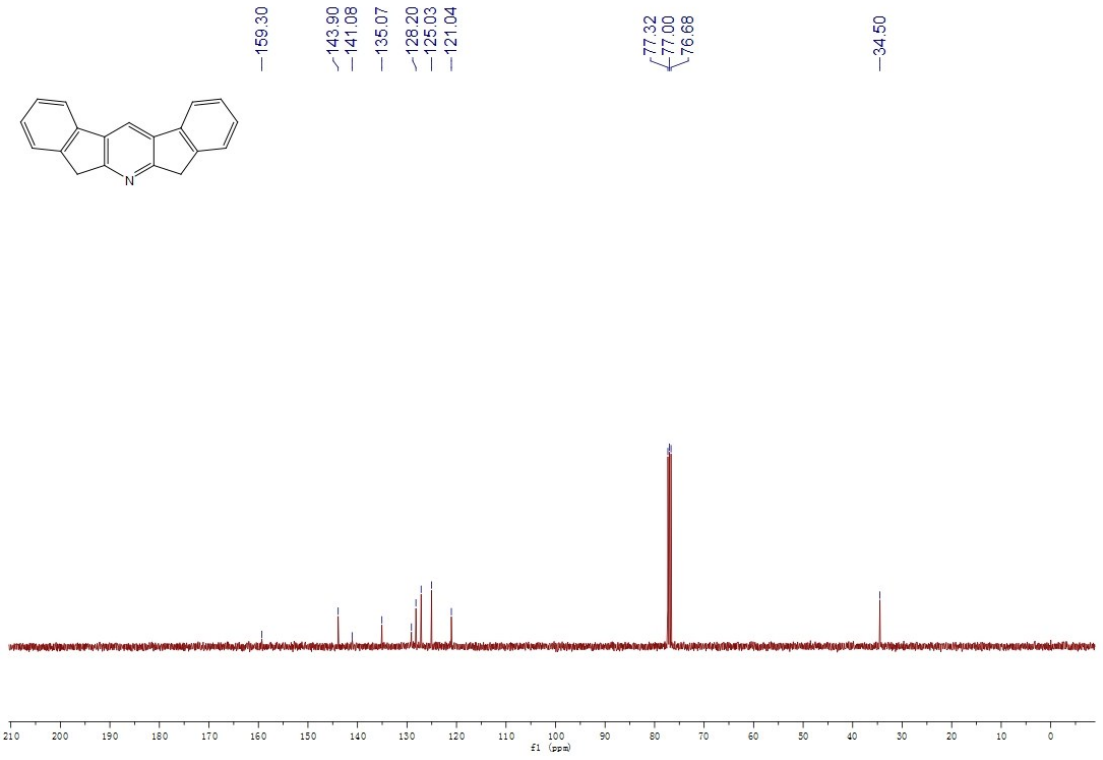

8.115
2.964
2.948
2.933
2.853
2.838
2.821
2.803
2.787
2.729
2.714
2.699
1.782
1.771
1.687
1.426
1.316
1.305
1.294
0.000
N
1.00
2.05
4.01
2.02
2.05
6.05
4.00
4.08
f1 (ppm)

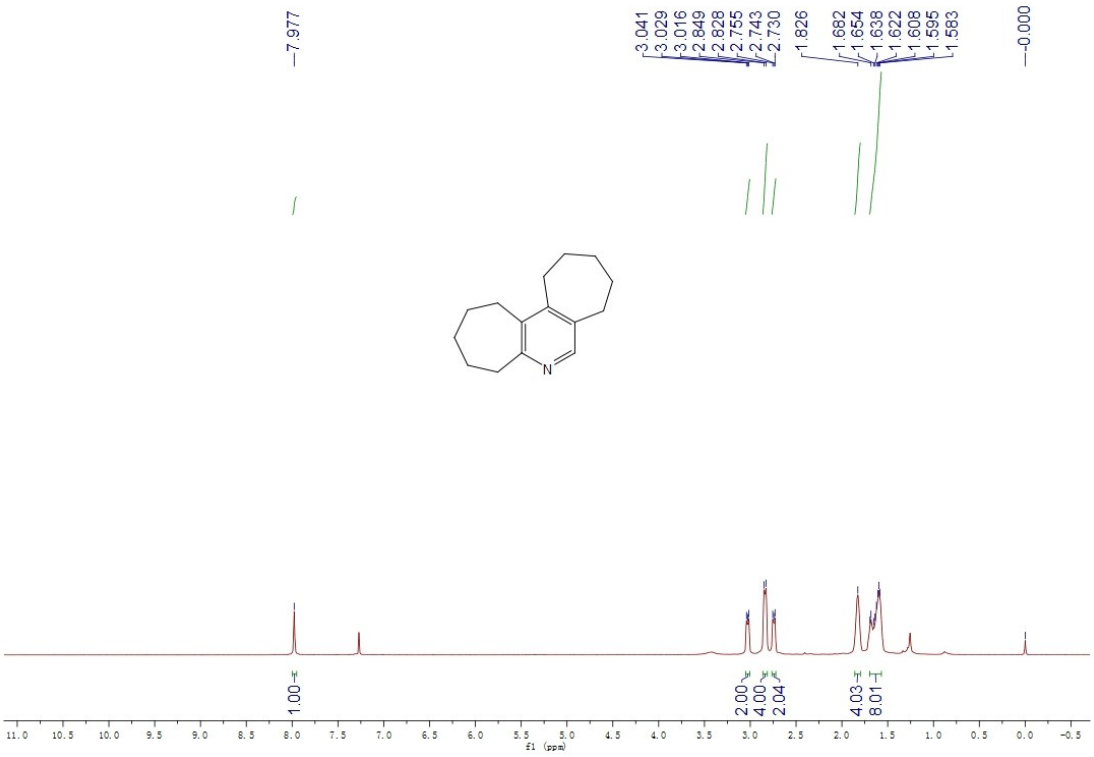

159.14
147.11
146.92
135.09
132.48
77.32
77.00
76.68
35.61
32.33
30.85
30.80
30.37
30.02
26.62
26.46
26.33
25.85
25.50
N
f1 (ppm)

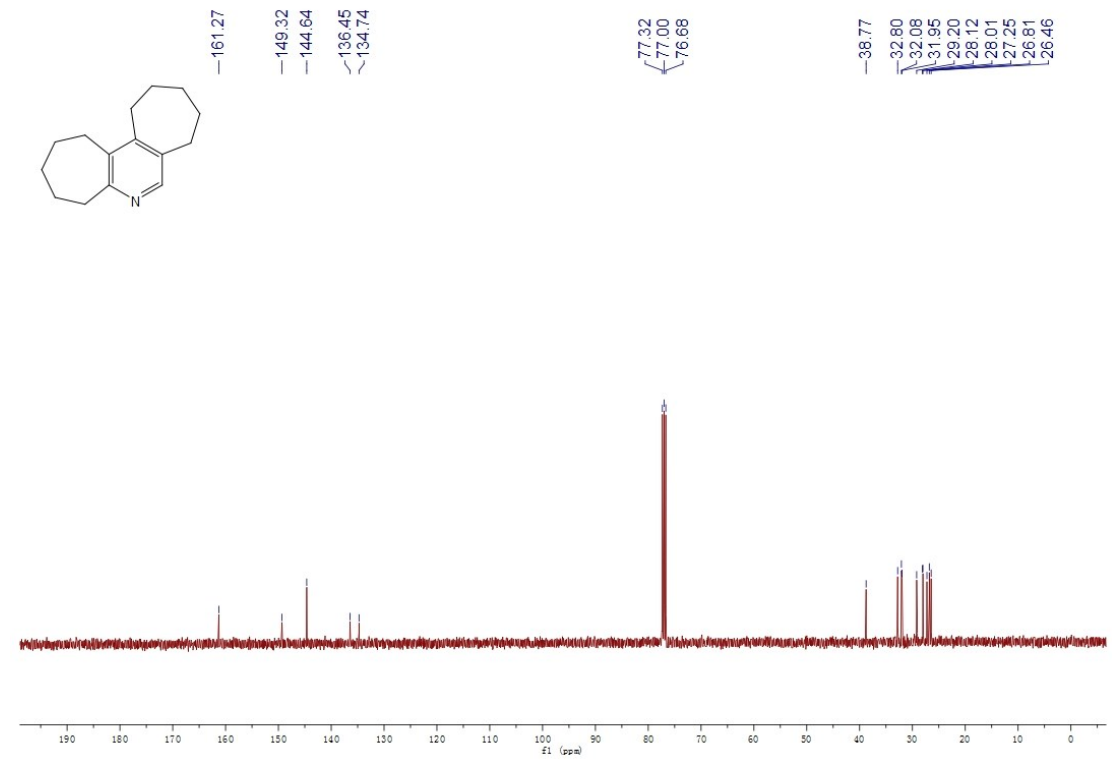

7.069
2.942
2.927
2.912
2.723
2.707
2.692
1.768
1.668
1.357
0.000
1.00
4.02
4.01
4.03
4.05
8.00
f1 (ppm)

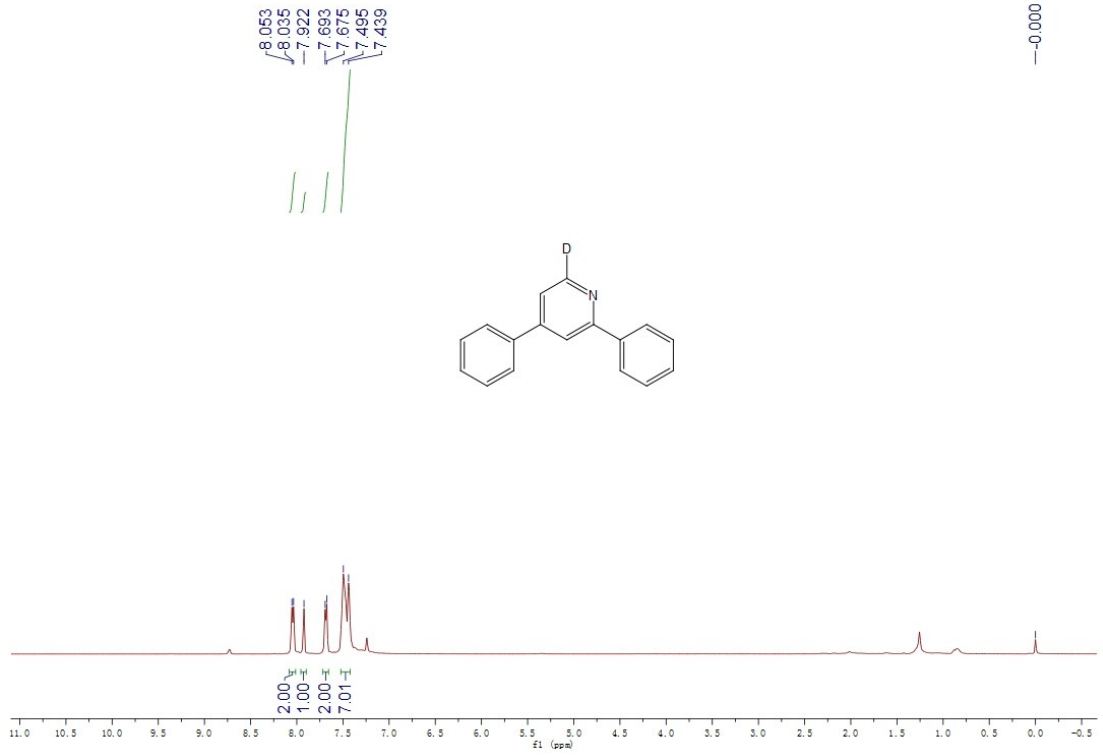

157.81
137.33
133.61
77.32
77.00
76.68
33.95
32.26
31.43
30.79
26.03
25.93
f1 (ppm)

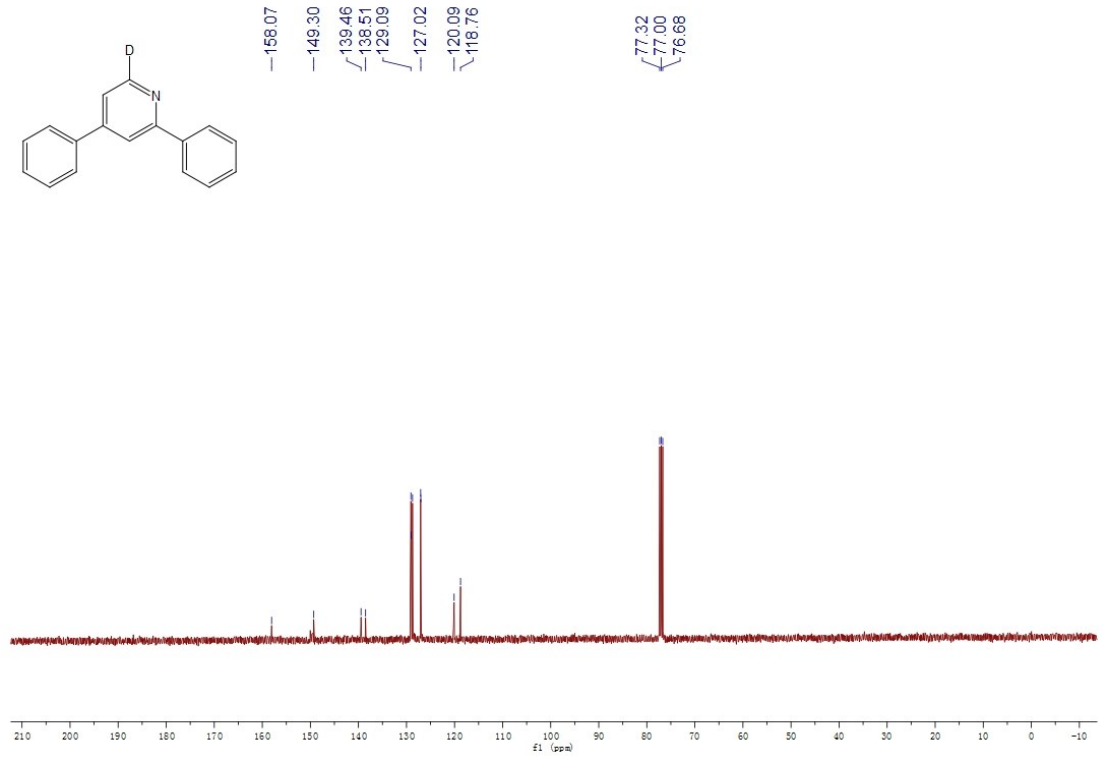

8.265
8.246
7.887
7.550
7.531
7.490
7.472
7.453
7.409
7.391
7.373
3.855
0.000
N
2.00
1.00
2.03
2.03
2.04
4.00
f1 (ppm)

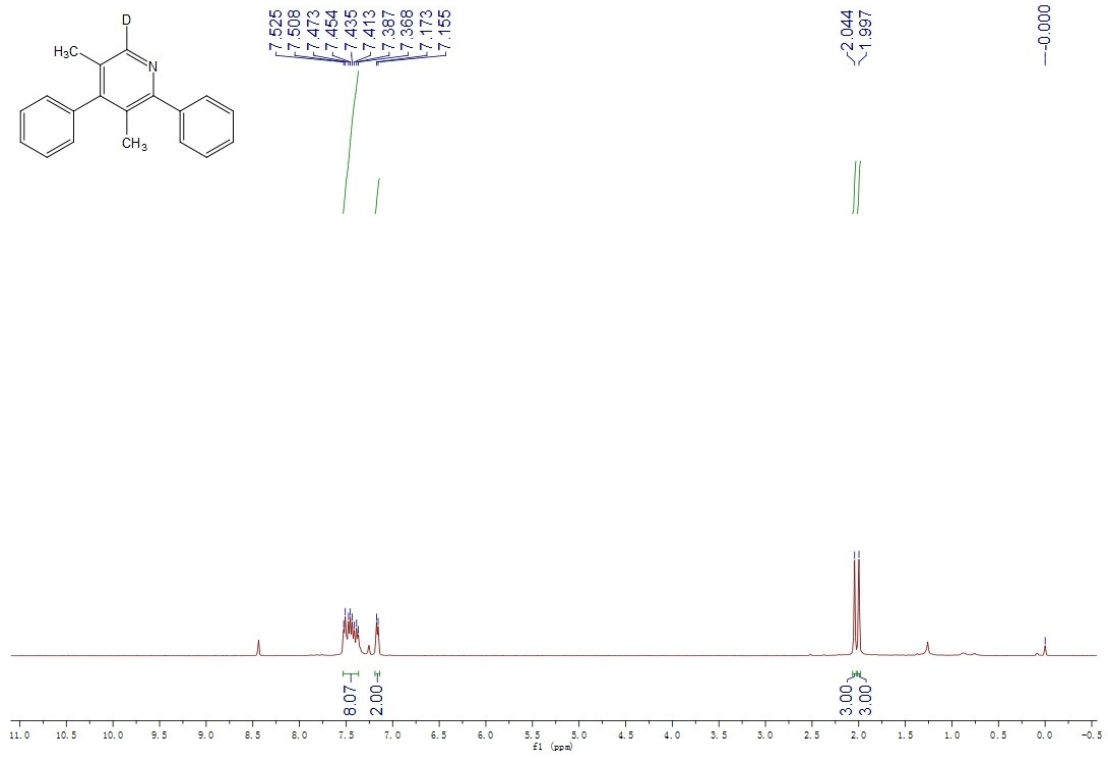

159.30
143.90
141.08
135.07
128.20
125.03
121.04
77.32
77.00
76.68
34.50
N
f1 (ppm)

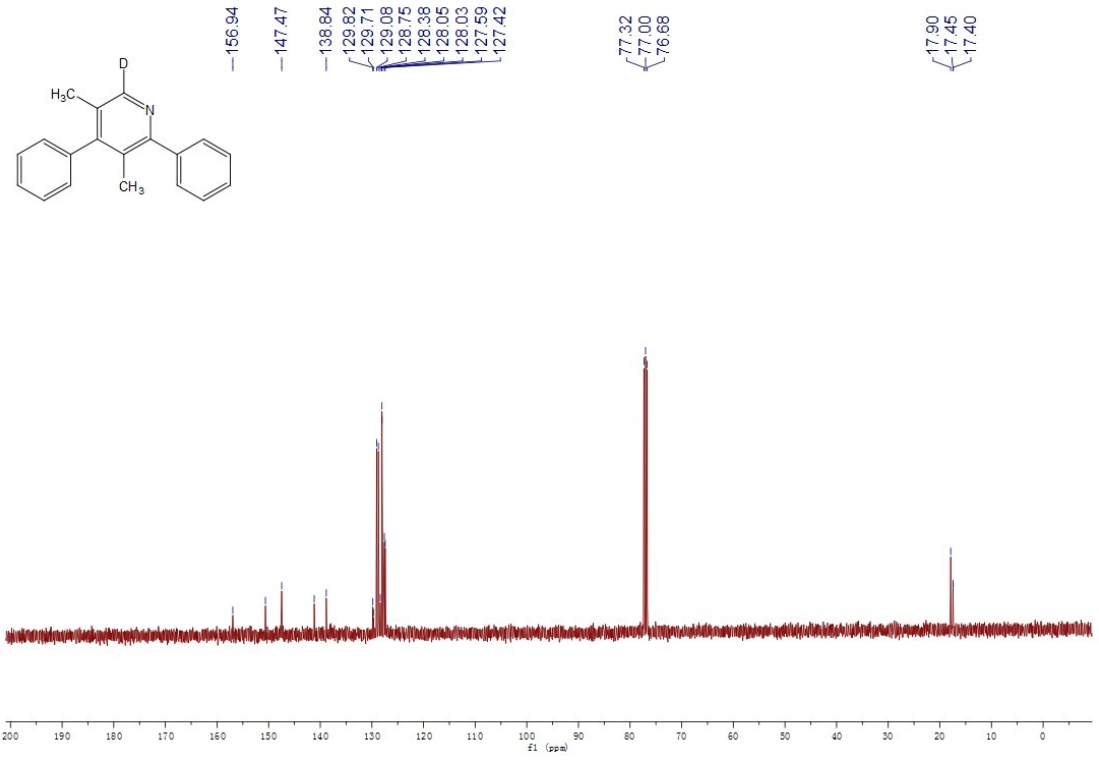

7.977
3.041
3.029
3.016
2.849
2.828
2.755
2.743
2.730
1.826
1.682
1.654
1.638
1.622
1.608
1.595
1.583
0.000
N
1.00
2.00
4.00
2.04
4.03
8.01
f1 (ppm)

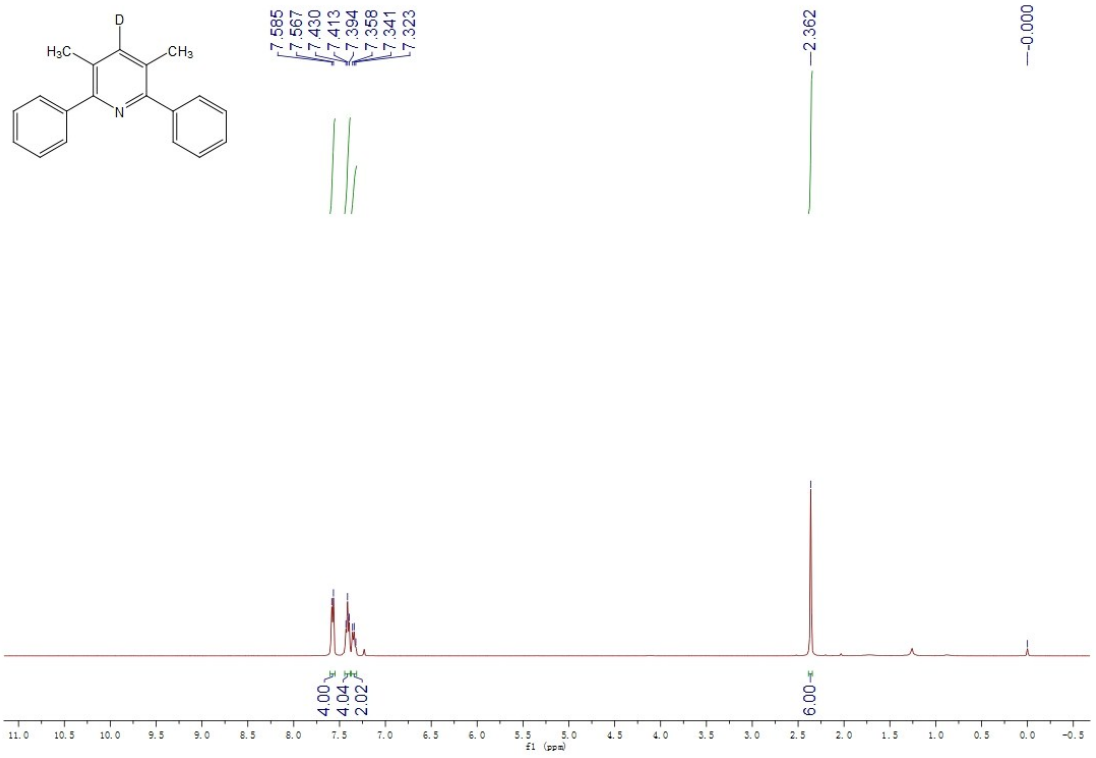

161.27
149.32
144.64
136.45
134.74
77.32
77.00
76.68
38.77
32.80
32.08
31.95
29.20
28.12
28.01
27.25
26.81
26.46
N
f1 (ppm)

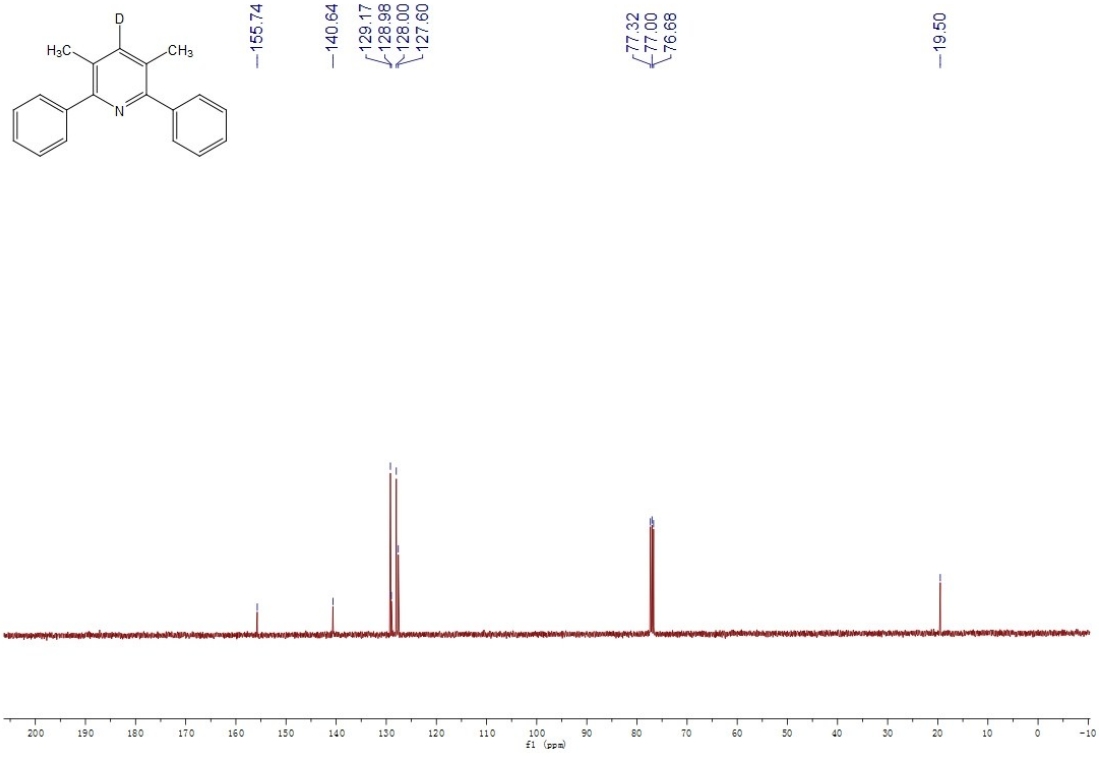

8.053
8.035
7.922
7.693
7.675
7.495
7.439
0.000
D
N
2.00
1.00
2.00
7.01
f1 (ppm)


158.07
149.30
139.46
138.51
129.09
127.02
120.09
118.76
77.32
77.00
76.68
D
N
f1 (ppm)


D
H3C
N
CH3
7.525
7.508
7.473
7.454
7.435
7.413
7.387
7.368
7.173
7.155
2.044
1.997
0.000
8.07
2.00
3.00
3.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


D
H3C
N
CH3
156.94
147.47
138.84
129.82
129.71
129.08
128.75
128.38
128.05
128.03
127.59
127.42
77.32
77.00
76.68
17.90
17.45
17.40
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


D
H3C
CH3
N
7.585
7.567
7.430
7.413
7.394
7.358
7.341
7.323
2.362
0.000
4.00
4.04
2.02
6.00
f1 (ppm)


D
H3C
CH3
N
155.74
140.64
129.17
128.98
128.00
127.60
77.32
77.00
76.68
19.50
f1 (ppm)