Electronic Supplementary Material (ESI) for RSC Advances.

Supporting materials

Heterogeneously copper-catalyzed oxidative synthesis of imidazo[1,2-*a*]pyridines using 2-aminopyridines and ketones under ligand- and additive-free conditions

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General information

All reagents were purchased from commercial suppliers and used without further purification. Metal salts and catalyst supports were commercially available and were used directly. All experiments were carried out under air. Flash chromatography was carried out with Merck silica gel 60 (200-300 mesh). Analytical TLC was performed with Merck silica gel 60 F254 plates, and the products were visualized by UV detection. ^{1}H NMR and ^{13}C NMR (400 and 100 MHz respectively) spectra were recorded in $CDCl_3$. Chemical shifts (δ) are reported in ppm using TMS as internal standard, and spin-spin coupling constants (J) are given in Hz.

Preparation of $CuCl_2$/nano-TiO_2

Support nano-TiO_2 powder (1g, particle size ≤ 30 nm, BET surface area ≥ 120 m^2/g, anatase) was added to a 50 mL round-bottom flask. A solution of $CuCl_2$-$2H_2O$ (0.108g) in acetone (10 mL) was added to nano-TiO_2 powder, and additional acetone (10 mL) was added to wash down the sides of the flask. Then the flask was submerged into an ultrasound bath for 3h at room temperature and stirred for further 20h at room temperature. After that, the acetone was distilled under reduced pressure on a rotary evaporator at 50 ^{o}C for more than 2h. Finally, the dried pale green powder was obtained.

Characterization of $CuCl_2$/nano-TiO_2

The Inductive Coupled Plasma Optical Emission Spectrum (ICP-OES) showed that the content of catalyst is Cu% = 3.16%

BET surface area: 65.0286 m^2/g

Pore volume (BJH Adsorption): 0.2792 cm^3/g

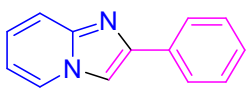
Pore size (BJH Adsorption): 16.1826 nm

General procedure for $CuCl_2$/nano-TiO_2-catalyzed cyclization

$CuCl_2$/nano-TiO_2 (12 mg, 0.8 mol%), 2-aminopyridine (0.6 mmol), ketone (0.5 mmol) and EtOH (0.6 mL) were added to a flask with a bar. The flask was stirred at 70 ^oC for 24h under air. After cooling to room temperature, the mixture was diluted with ethyl acetate and filtered. The filtrate was removed under reduced pressure to get the crude product, which was further purified by silica gel chromatography (petroleum/ethyl acetate = 3/1 as eluent) to yield corresponding product. The identity and purity of the products was confirmed by ^1H and ^{13}C NMR spectroscopic analysis.

Spectrum data of the products

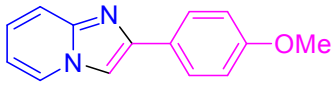
2-phenylH-imidazo[1,2-*a*]pyridine (3a)[1]



White solid, isolated yield 87%.^1H NMR (400MHz, $CDCl_3$): δ = 8.08(d, 1H, J = 5.6 Hz), 7.96(d, 2H, J = 5.2 Hz), 7.84(s, 1H), 7.61(d, 1H, J = 9.2

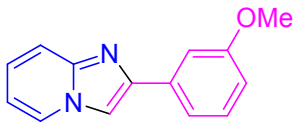
Hz), 7.43(t, 2H, J = 7.6 Hz), 7.33(t, 1H, J = 6.8 Hz), 6.75(m,1H); ^{13}C NMR (100MHz, $CDCl_3$): δ = 145.8, 145.6, 133.7, 128.7, 127.9, 126.0, 125.5, 124.6, 117.5, 112.4, 108.1.

2-(4-methoxyphenyl)H-imidazo[1,2-*a*]pyridine (3b)[1]



White solid, isolated yield 85%.^{1}H NMR (400MHz, $CDCl_3$): δ = 7.92(d, 1H, J = 6.8 Hz), 7.83(d, 2H, J = 7.2 Hz), 7.62(s, 1H), 7.56(d, 1H, J = 8 Hz), 7.06(t, 1H, J = 1.2 Hz), 6.93(d, 2H, J = 7.2 Hz), 6.62(t, 1H, J = 6.8 Hz), 3.78(s, 3H); ^{13}C NMR (100MHz, $CDCl_3$): δ = 159.3, 145.3, 145.2, 127.0, 126.2, 125.3, 124.2, 116.8, 113.9, 111.9, 107.1, 55.0.

2-(3-methoxyphenyl)H-imidazo[1,2-*a*]pyridine (3c)[1]



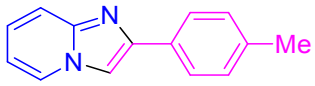
White solid, isolated yield 84%.^{1}H NMR (400MHz, $CDCl_3$): δ = 7.98(d, 1H, J = 6.4 Hz), 7.75(s, 1H), 7.53(d, 1H, J = 10 Hz), 7.52(s, 1H), 7.30(d, 1H, J = 7.2 Hz), 7.22(t, 1H, J = 7.2 Hz), 6.85(m,1H), 6.66(m, 1H), 3.84(s, 3H); ^{13}C NMR (100MHz, $CDCl_3$): δ = 159.9, 145.5, 145.4, 135.1, 129.5, 125.5, 124.5, 118.3, 117.2, 113.9, 112.2, 110.8, 108.3, 55.2.

2-(2-methoxyphenyl)H-imidazo[1,2-*a*]pyridine (3d)[2]

Yellow oil, isolated yield 69%.^{1}H NMR (400MHz, $CDCl_3$): δ = 8.41(d,

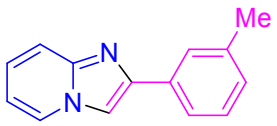
1H, *J* = 8 Hz), 8.15(s, 1H), 8.04(d, 1H, *J* = 6.8 Hz), 7.59(d, 1H, *J* = 9.2 Hz), 7.28(m,1H), 7.10(d, 2H, J = 6.4 Hz), 6.96(t, 1H, *J* = 8 Hz), 6.66(m,1H), 3.08(s, 3H); ^{13}C NMR (100MHz, $CDCl_3$): δ = 156.6, 144.2, 140.9, 128.6, 125.5, 124.2, 122.2, 120.8, 116.9, 112.4, 111.7, 110.7, 55.2.

2-p-tolylH-imidazo[1,2-*a*]pyridine (3e)[1]



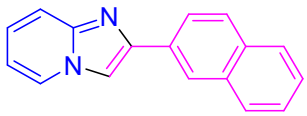
White solid, isolated yield 88%.^{1}H NMR (400MHz, $CDCl_3$): δ = 8.06(d, 1H, *J* = 6.4 Hz), 7.84(d, 2H, *J* = 8.4 Hz), 7.79(s, 1H), 7.61(d, 1H, *J* = 8.8 Hz), 7.24(d, 2H, J = 8 Hz), 7.13(m, 1H), 6.73(t,1H, *J* = 6.4 Hz), 2.38(s, 3H); ^{13}C NMR (100MHz, $CDCl_3$): δ = 145.9, 145.6, 137.7, 130.9, 129.4, 125.8,125.5, 124.4, 117.4, 112.1, 107.7, 21.2.

2-m-tolylH-imidazo[1,2-*a*]pyridine (3f)[3]



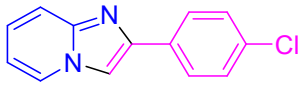
White solid, isolated yield 82%.^{1}H NMR (400MHz, $CDCl_3$): δ = 7.95(d, 1H, *J* = 6.8 Hz), 7.81(s, 1H), 7.72-7.67(m, 2H), 7.58(d, 1H, *J* = 8.4 Hz), 7.29(t, 1H, J = 7.6 Hz), 7.12-7.03(m, 2H), 6.65-6.62(m,1H), 2.39(s, 3H); ^{13}C NMR (100MHz, $CDCl_3$): δ = 145.5, 145.3, 128.4, 128.5, 128.4, 126.9, 125.4, 124.3, 122.8, 117.1, 112.1, 107.9, 21.2.

2-(naphthalen-2-yl)H-imidazo[1,2-*a*]pyridine (3g)[5]



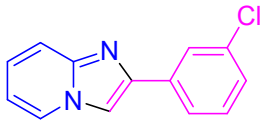
White solid, isolated yield 91%.^{1}H NMR (400MHz, $CDCl_3$): δ = 8.49(s, 1H), 7.92-7.88(m, 3H), 7.84-7.77(m, 3H), 7.62(d, 1H, J = 8.8 Hz), 7.46-7.44(m, 2H), 7.18-7.14(t, 1H, J = 8 Hz), 6.63 (t, 1H, J = 6.8 Hz); ^{13}C NMR (100MHz, $CDCl_3$): δ = 145.6, 145.4, 13.6, 133.0, 128.2, 128.1, 127.5, 126.1, 125.8, 125.5, 124.6, 124.5, 124.0, 117.2, 112.2, 108.5.

2-(4-chlorophenyl)H-imidazo[1,2-*a*]pyridine (3h)[2]



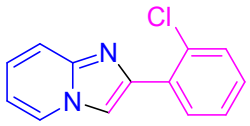
Yellow solid, isolated yield 92%.^{1}H NMR (400MHz, *d*-DMSO): δ = 8.52(d, 1H, J = 6.4 Hz), 7.99(d, 2H, J = 8.8 Hz), 7.59(d, 1H, J = 8.8 Hz), 7.49(d, 2H, J = 8.8 Hz), 7.26(t, 1H, J = 8 Hz), 6.90(t, 1H, J = 6.8 Hz); ^{13}C NMR (100MHz, *d*-DMSO): δ = 150.0, 145.2, 133.6, 126.5, 126.4, 124.2, 121.7, 116.1, 112.2, 111.7, 107.0.

2-(3-chlorophenyl)H-imidazo[1,2-*a*]pyridine (3i)[2]



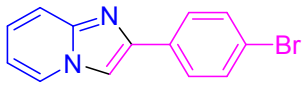
Yellow solid, isolated yield 88%.^{1}H NMR (400MHz, *d*-DMSO): δ = 8.54(d, 1H, J = 6.8 Hz), 8.51(s, 1H), 8.04(s, 1H), 7.94(d, 1H, J = 8 Hz), 7.61(d, 1H, J = 9.2 Hz), 7.47(d, 1H, J = 8 Hz), 7.39(d, 1H, J = 0.8 Hz), 7.28(t, 1H, J = 7.8 Hz), 6.94-6.91(m, 1H); ^{13}C NMR (100MHz, *d*-DMSO): δ = 144.8, 142.8, 136.1, 133.6, 130.6, 127.4, 126.9, 125.3, 125.1, 124.0, 116.7, 112.5, 109.9.

2-(2-chlorophenyl)H-imidazo[1,2-*a*]pyridine (3j)[4]



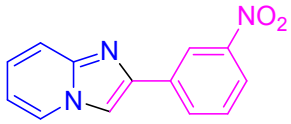
White solid, isolated yield 70%.^{1}H NMR (400MHz, $CDCl_3$): δ = 8.29-8.27(m, 1H), 8.24(s, 1H), 8.08(d, 1H, J = 6.8 Hz), 7.60(d, 1H, J = 8.8 Hz), 7.44-7.42(m, 1H), 7.35(s, 1H), 7.22(t, 1H, J = 8 Hz) 6.74-6.71(m,1H); ^{13}C NMR (100MHz, $CDCl_3$): δ = 144.4, 141.6, 132.2, 131.6, 130.8, 128.5, 126.9, 125.7, 124.8, 117.4, 112.3.

2-(4-bromophenyl)H-imidazo[1,2-*a*]pyridine (3k)[1]



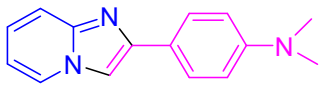
White solid, isolated yield 85%.^{1}H NMR (400MHz, $CDCl_3$): δ = 8.07(d, 1H, J = 6.4 Hz), 7.81-7.52(m, 6H), 7.17(t, 1H, J = 7.6 Hz), 6.77(t, 1H, J = 6.4 Hz); ^{13}C NMR (100MHz, $CDCl_3$): δ = 145.7, 144.6, 132.7, 131.8, 127.5, 124.9, 121.8, 117.5, 112.6, 108.2.

2-(3-nitrophenyl)H-imidazo[1,2-*a*]pyridine (3l)[4]



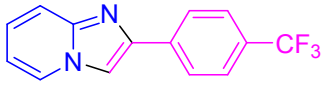
Yellow solid, isolated yield 72%.^{1}H NMR (400MHz, *d*-DMSO): δ = 8.78(s, 1H), 8.66(s, 1H), 8.58(s, 1H), 8.41(s, 1H), 8.17(s, 1H), 7.75(s, 1H) 7.65(d, 1H, J = 7.8 Hz), 7.34(s, 1H), 6.98(s, 1H); ^{13}C NMR (100MHz, *d*-DMSO): δ = 148.4, 144.8, 141.6, 135.4, 131.7, 130.4, 127.2, 125.9, 122.2, 119.7, 116.7, 112.9, 110.6.

4-(H-imidazo[1,2-*a*]pyridin-2-yl)-N,N-dimethylbenzenamine (3m)[6]



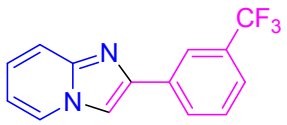
Yellow solid, isolated yield 65%.^{1}H NMR (400MHz, *d*-DMSO): δ = 8.46(d, 1H, J = 6.8 Hz), 8.18(s, 1H), 7.79(d, 2H, J = 8.8 Hz), 7.53(d, 1H, J = 9.2 Hz), 7.21-7.19(m, 1H), 6.84(t, 1H, J = 6.8 Hz), 6.78(d, 2H, J = 8.8 Hz), 2.94(s, 6H); ^{13}C NMR (100MHz, *d*-DMSO): δ = 150.0, 145.2, 144.6, 126.5, 126.4, 124.2, 121.8, 116.1, 112.2, 111.7, 107.0, 40.1.

2-(4-(trifluoromethyl)phenyl)H-imidazo[1,2-*a*]pyridine (3n)[6]



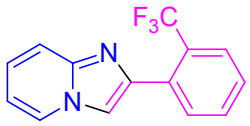
White solid, isolated yield 86%.^{1}H NMR (400MHz, $CDCl_3$): δ = 8.10(d, 1H, J = 6.8 Hz), 8.04(d, 2H, J = 8 Hz), 7.89(s, 1H), 7.68-7.62(m, 3H), 7.19(t, 1H, J = 1.2 Hz), 6.81-6.77(m, 1H); ^{13}C NMR (100MHz, $CDCl_3$): δ = 145.8, 144.3, 137.3 129.8, 129.5, 126.1, 125.7, 125.6, 125.5, 125.2, 122.9, 117.8, 112.8, 108.9.

2-(3-(trifluoromethyl)phenyl)H-imidazo[1,2-*a*]pyridine (3o)[6]



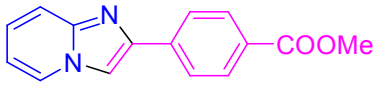
White solid, isolated yield 72%.^{1}H NMR (400MHz, $CDCl_3$): δ = 8.19(s, 1H), 8.04-7.99(m, 2H), 7.82-7.78(m, 1H), 7.58-7.50(m, 3H), 7.13-7.11(m, 1H), 6.71-6.67(m, 1H); ^{13}C NMR (100MHz, $CDCl_3$): δ = 145.6, 144.1, 134.6, 131.1., 130.8, 129.0, 128.9, 125.6, 125.5, 125.0, 124.3, 122.8, 122.6, 117.4, 112.6, 108.5.

2-(2-(trifluoromethyl)phenyl)H-imidazo[1,2-*a*]pyridine (3p)[6]



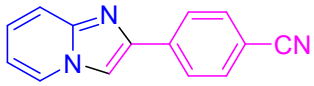
White solid, isolated yield 64%.^{1}H NMR (400MHz, $CDCl_3$): δ = 8.07(d, 1H, J = 6.8 Hz), 7.95(d, 1H, J = 8 Hz), 7.77(s, 1H), 7.72(d, 1H, J = 7.6 Hz), 7.60-7.55(m, 2H), 7.41(t, 1H, J = 7.6 Hz), 7.14-7.1(m, 1H), 6.73(t, 1H, J = 6.8 Hz); ^{13}C NMR (100MHz, $CDCl_3$): δ = 144.7, 142.3, 133.3, 132.4, 131.6, 127.6, 125.9, 125.8, 125.6, 124.7, 117.6, 112.4, 111.3.

methyl 4-(H-imidazo[1,2-*a*]pyridin-2-yl)benzoate (3q)[6]



White solid, isolated yield 81%.^{1}H NMR (400MHz, $CDCl_3$): δ = 8.11-8.10(m, 3H), 8.01(d, 2H, J = 8.4 Hz), 7.92(s, 1H), 7.63-7.61(m, 1H), 7.18(t, 1H, J = 1.2 Hz), 6.80-6.77(m, 1H), 3.92(s, 3H); ^{13}C NMR (100MHz, $CDCl_3$): δ = 166.9, 145.8, 144.5, 138.2, 130.0, 129.3, 125.7, 125.6, 125.1, 117.7, 112.7, 109.2, 52.1.

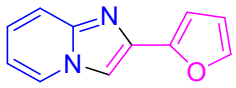
4-(H-imidazo[1,2-*a*]pyridin-2-yl)benzonitrile (3r)[6]



White solid, isolated yield 90%.^{1}H NMR (400MHz, $CDCl_3$): δ = 8.09(d, 1H, J = 6.8 Hz), 8.00-7.98(m, 2H), 7.89(s, 1H), 7.65-7.63(m, 2H), 7.59(d, 1H, J = 9.2 Hz), 7.18(t, 1H, J = 6.8 Hz), 6.80-6.76(m, 1H); ^{13}C NMR (100MHz, $CDCl_3$): δ = 145.8, 143.5, 138.2, 132.4, 126.2, 125.7, 125.4,

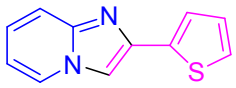
118.9, 117.7, 112.9, 110.8, 109.5.

2-(furan-2-yl)H-imidazo[1,2-*a*]pyridine (3s)[4]



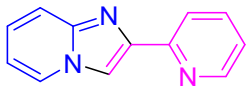
Gray solid, isolated yield 78%.^{1}H NMR (400MHz, $CDCl_3$): δ = 7.97(d, 1H, J = 6.8 Hz), 7.68(s, 1H), 7.52-7.49(m, 1H), 7.40-7.39(m, 1H), 7.15(t, 1H, J = 8 Hz), 6.85-6.82(m, 1H), 6.66-6.63(m, 1H), 6.44-6.43(m, 1H); ^{13}C NMR (100MHz, $CDCl_3$): δ = 149.4, 145.4, 141.8, 137.7, 125.5, 124.8, 117.1, 112.3, 111.4, 107.7, 106.4.

2-(thiophen-2-yl)H-imidazo[1,2-*a*]pyridine (3t)[4]



White solid, isolated yield 86%.^{1}H NMR (400MHz, $CDCl_3$): δ = 7.91(d, 1H, J = 6.8 Hz), 7.61(s, 1H), 7.49(d, 1H, J = 6.8 Hz), 7.37-7.36(m, 1H), 7.26-7.24(m, 1H), 7.01-6.99(m, 2H), 6.65-6.60(m, 1H); ^{13}C NMR (100MHz, $CDCl_3$): δ = 145.1, 140.5, 137.3, 127.5, 125.2, 124.8, 124.6, 123.4, 116.9, 112.2, 107.2.

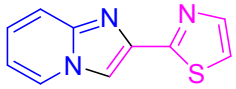
2-(pyridin-2-yl)H-imidazo[1,2-*a*]pyridine (3u)[5]



White solid, isolated yield 74%.^{1}H NMR (400MHz, $CDCl_3$): δ = 8.61-8.60(m, 1H), 8.23-8.09(m, 3H), 7.75(t, 1H, J = 6 Hz), 7.61(d, 1H, J = 9.2 Hz), 7.20-7.14(m, 2H), 7.63(t, 1H, J = 6.8 Hz); ^{13}C NMR (100MHz, $CDCl_3$): δ = 152.6, 149.1, 145.3, 145.2, 136.5, 125.7, 124.7, 122.4, 120.1,

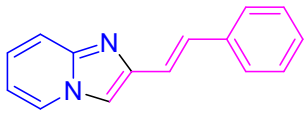
117.4, 112.4, 110.6.

2-(thiazol-2-yl)H-imidazo[1,2-*a*]pyridine (3v)[6]



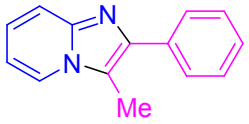
Yellow solid, isolated yield 71%.^{1}H NMR (400MHz, $CDCl_3$): δ = 8.11-8.08(m, 2H), 7.83(s, 1H), 7.85(s, 1H), 7.33(s, 1H), 7.17-7.16(m, 1H), 6.79-6.75(m, 1H); ^{13}C NMR (100MHz, $CDCl_3$): δ = 163.4, 145.3, 143.5, 140.2, 125.9, 119.1, 117.7, 113.1, 109.4.

(E)-2-styrylH-imidazo[1,2-*a*]pyridine (4a)[6]



White solid, isolated yield 78%.^{1}H NMR (400MHz, $CDCl_3$): δ = 8.04(d, 1H, J = 6.4 Hz), 7.58-7.54(m, 5H), 7.35(t, 2H, J = 7.5 Hz), 7.26(t, 1H, J = 7.5 Hz), 7.17-7.13(m, 2H), 6.74(t, 1H, J = 6.8 Hz); ^{13}C NMR (100MHz, $CDCl_3$): δ = 145.7, 144.1, 137.3, 130.5, 128.6, 127.7, 126.5, 125.4, 124.9, 119.9, 117.1, 112.2, 110.5.

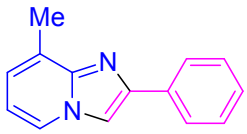
3-methyl-2-phenylH-imidazo[1,2-*a*]pyridine (4b)[6]



White solid, isolated yield 84%.^{1}H NMR (400MHz, $CDCl_3$): δ = 7.85(d, 1H, J = 6.8 Hz), 7.80-7.77(m, 2H), 7.62(d, 1H, J = 9.2 Hz), 7.47-7.43(m, 2H), 7.33(t, 1H, J = 8.8 Hz), 7.16-7.12(m, 1H), 6.82-6.78(m, 1H), 2.60(s, 3H); ^{13}C NMR (100MHz, $CDCl_3$): δ = 144.3, 142.3, 134.8, 128.4, 128.3,

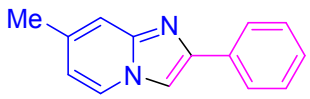
127.2, 123.4, 122.7, 117.3, 115.8, 111.9, 9.5.

8-methyl-2-phenylH-imidazo[1,2-*a*]pyridine (4c)[4]



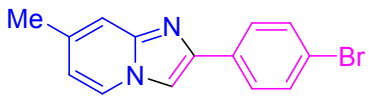
White solid, isolated yield 83%.^{1}H NMR (400MHz, $CDCl_3$): δ = 7.98-7.92(m, 3H), 7.79(s, 1H), 7.43(t, 2H, J = 7.6 Hz), 7.34(t, 1H, J = 2 Hz), 6.93(t, 1H, J = 8.8 Hz), 6.64(t, 1H, J = 6.8 Hz), 2.67(s, 3H); ^{13}C NMR (100MHz, $CDCl_3$): δ = 146.1, 145.1, 134.1, 128.6, 127.7, 127.4, 126.1, 123.3, 123.2, 112.2, 108.5, 17.0.

7-methyl-2-phenylH-imidazo[1,2-*a*]pyridine (4d)[3]



White solid, isolated yield 80%.^{1}H NMR (400MHz, $CDCl_3$): δ = 7.95-7.87(m, 3H), 7.69(s, 1H), 7.41(t, 2H, J = 7.2 Hz), 7.34(s, 1H), 7.32(t, 1H, J = 12 Hz), 6.53-6.51(m, 1H), 2.34(s, 3H); ^{13}C NMR (100MHz, $CDCl_3$): δ = 146.1, 145.5, 135,6, 133.9, 128.7, 127.8, 125.9, 124.8, 115.8, 114.9, 107.6, 21.4.

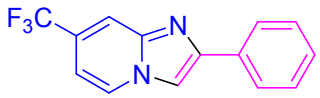
2-(4-bromophenyl)-7-methylH-imidazo[1,2-*a*]pyridine (4e)[5]



White solid, isolated yield 78%.^{1}H NMR (400MHz, $CDCl_3$): δ = 7.89(d, 1H, J = 6.8 Hz), 7.75(d, 2H, J = 8.8 Hz), 7.67(s, 1H), 7.49(d, 2H, J = 8 Hz), 7.33(s, 1H), 6.56-6.54(m, 1H), 2.35(s, 3H); ^{13}C NMR (100MHz,

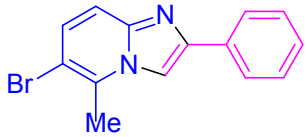
$CDCl_3$): δ = 146.1, 144.2, 135.8, 132.9, 131.6, 127.3, 124.7, 121.5, 115.7, 115.1, 107.6, 21.3.

2-phenyl-7-(trifluoromethyl)H-imidazo[1,2-*a*]pyridine (4f)[6]



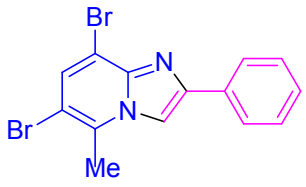
White solid, isolated yield 75%.^{1}H NMR (400MHz, $CDCl_3$): δ = 8.45(s, 1H), 7.95-7.89(m, 3H), 7.69(s, 1H), 7.46-7.26(m, 4H); ^{13}C NMR (100MHz, $CDCl_3$): δ = 147.7, 145.3, 152.9, 128.8, 128.6, 126.1, 124.5, 124.4, 120.5, 120.4, 118.1, 109.2.

6-bromo-5-methyl-2-phenylH-imidazo[1,2-*a*]pyridine (4g)[5]



White solid, isolated yield 61%.^{1}H NMR (400MHz, $CDCl_3$): δ = 7.90(d, 2H, J = 6.8 Hz), 7.64(s, 1H), 7.47-7.36(m, 3H), 7.32-7.24(m, 2H), 2.64(s, 3H); ^{13}C NMR (100MHz, $CDCl_3$): δ = 146.3, 133.7, 133.3, 132.8, 128.9, 128.8, 128.2, 125.9, 115.4, 107.5, 106.8, 18.5.

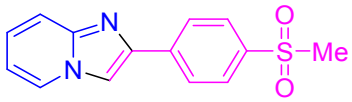
6,8-dibromo-5-methyl-2-phenylH-imidazo[1,2-*a*]pyridine (4h)[5]



White solid, isolated yield 55%.^{1}H NMR (400MHz, $CDCl_3$): δ = 7.94(d, 2H, J = 6.8 Hz), 7.73(s, 1H), 7.57(s, 1H), 7.42-7.40(m, 2H), 7.33(d, 1H, J = 6 Hz) 2.66(s, 3H); ^{13}C NMR (100MHz, $CDCl_3$): δ = 146.9, 142.8, 132.9,

132.2, 130.5, 128.7, 128.4, 126.2, 108.7, 108.5, 106.4, 18.4.

2-(4-(methylsulfonyl)phenyl)H-imidazo[1,2-*a*]pyridine (5)[3]

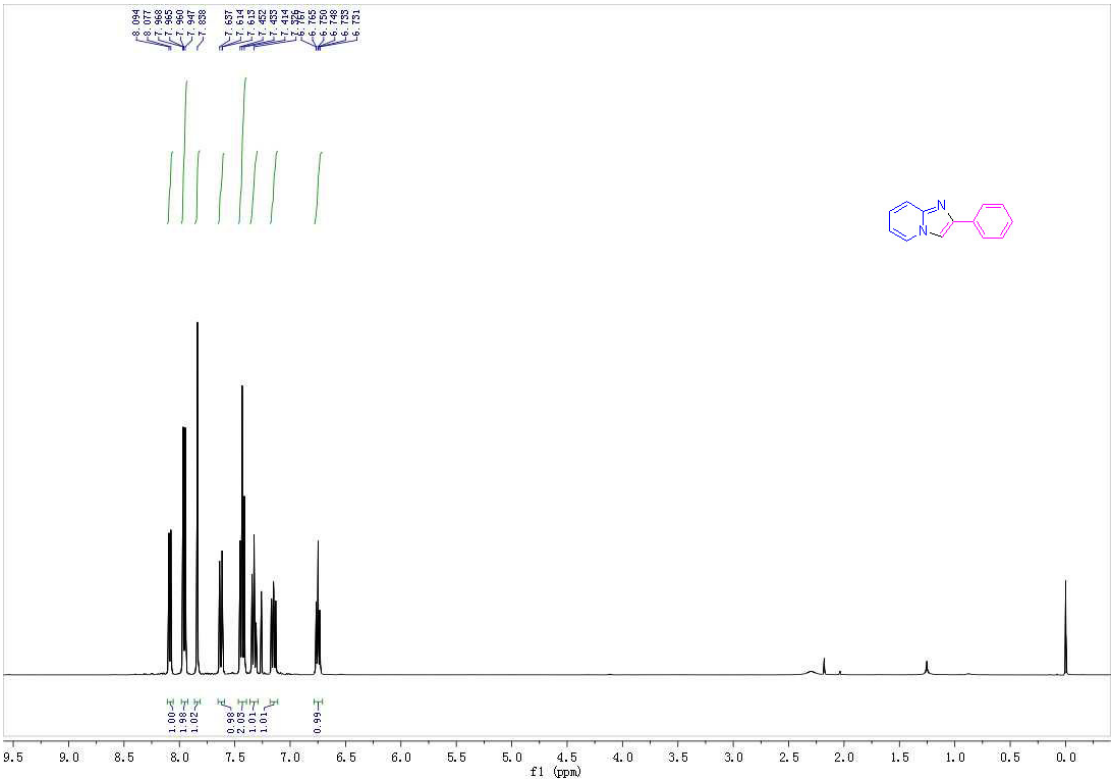


White solid, isolated yield 56%.^{1}H NMR (400MHz, $CDCl_3$): δ = 8.15-8.12(m, 3H), 8.06-8.02(m, 3H), 7.64-7.62(d, 1H, J = 9.2 Hz), 7.25-7.23(m, 1H), 6.85-6.82(m, 1H), 3.09(s, 3H); ^{13}C NMR (100MHz, $CDCl_3$): δ = 145.7, 143.9, 139.1,128.9, 127.7, 127.6, 126.4, 117.6, 112.9, 109.7, 44.1.

Reference

1. C. He, J. Hao, H. Xu, Y. Mo, H. Liu, J. Han and A. Lei, *Chem. Commun*., 2012, **48**, 11073
2. S. Santra, A. K. Bagdi, A. Majee and A. Hajra, *Adv. Synth. Catal*. 2013, **355**, 1065.
3. A. K. Bagdi, M. Rahman, S, Santra, A. Majee and Alakananda Hajra, *Adv. Synth. Catal*. 2013, **355**, 1741.
4. D. C. Mohan, R. R. Donthiri, S, N. Rao and Ss Adimurthy, *Adv. Synth. Catal*. 2013, **355**, 2217.
5. Z.-J. Cai, S.-Y. Wang and S.-J. Ji, *Adv. Synth. Catal*. 2013, **355**, 2686.
6. Y. Zhang, Z. Chen, W. Wu, Y. Zhang and W. Su, *J. Org. Chem.*, 2013, **78**, 12494.

Copy of ^{1}H NMR and ^{13}C NMR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7.947
7.838
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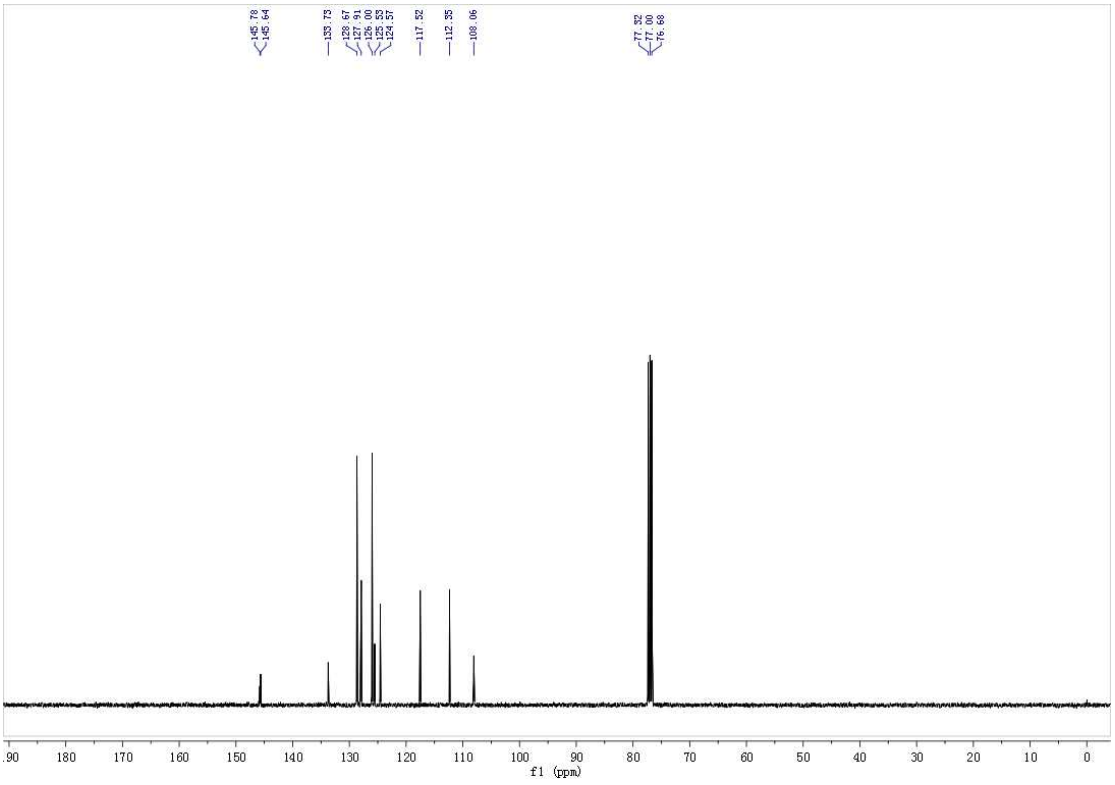
7.614
7.615
7.453
7.433
7.414
6.765
6.750
6.738
6.733
6.731
1.00
1.98
1.02
0.98
2.05
1.01
1.01
0.99
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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145.64
133.73
128.67
127.91
126.00
125.53
124.57
117.52
112.35
108.06
77.32
77.00
76.68
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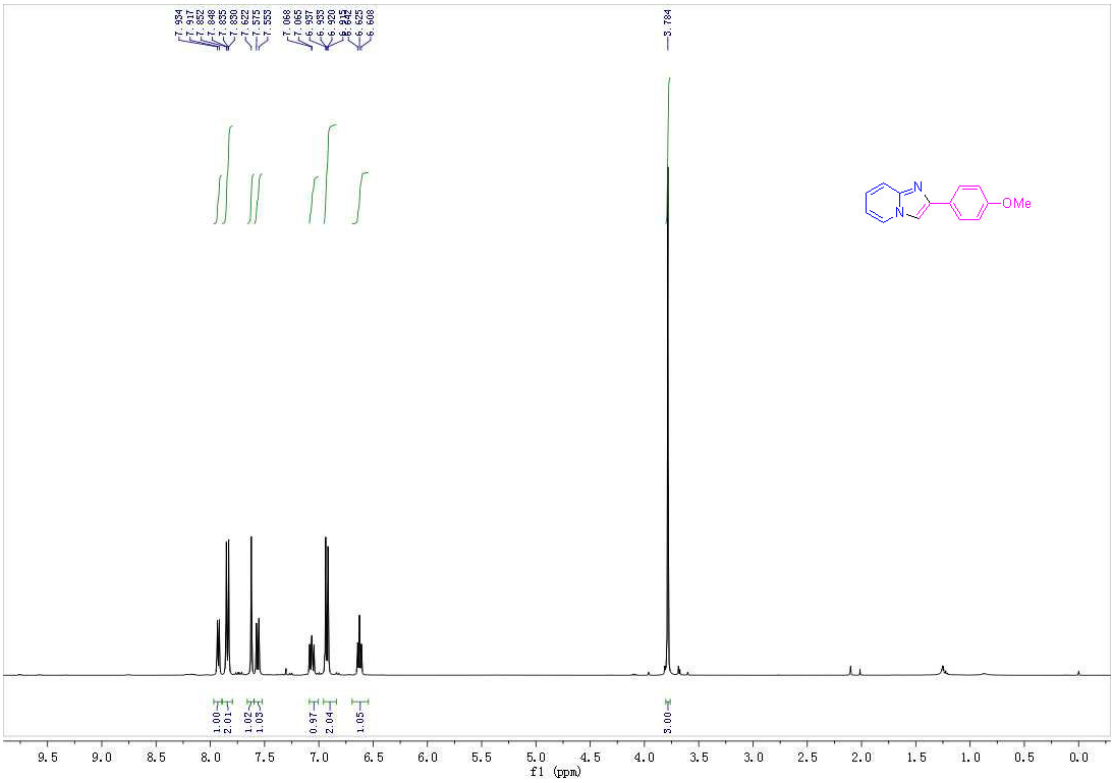
f1 (ppm)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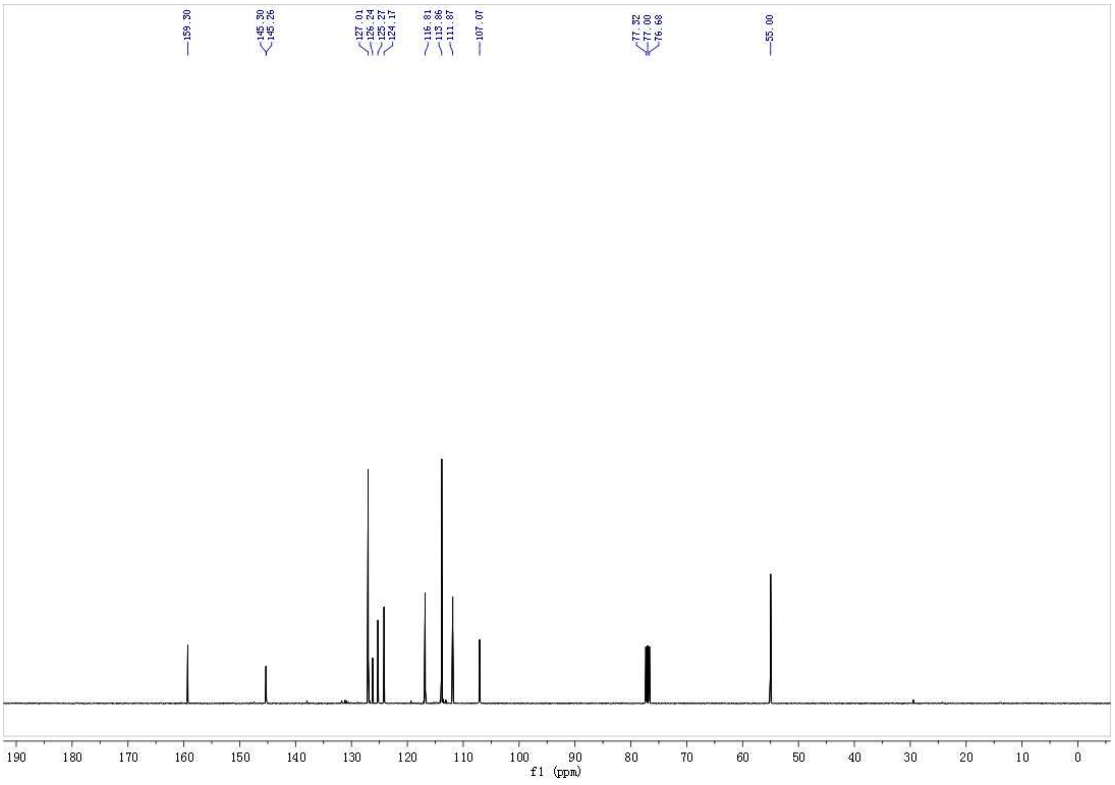
7.852
7.848
7.835
7.690
7.622
7.575
7.553
7.068
7.065
6.957
6.953
6.950
6.845
6.842
6.675
6.673
6.608
3.784
OMe
1.00
2.01
1.02
1.05
0.97
2.04
1.05
3.00
f1 (ppm)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145.30
145.26
127.01
126.24
125.27
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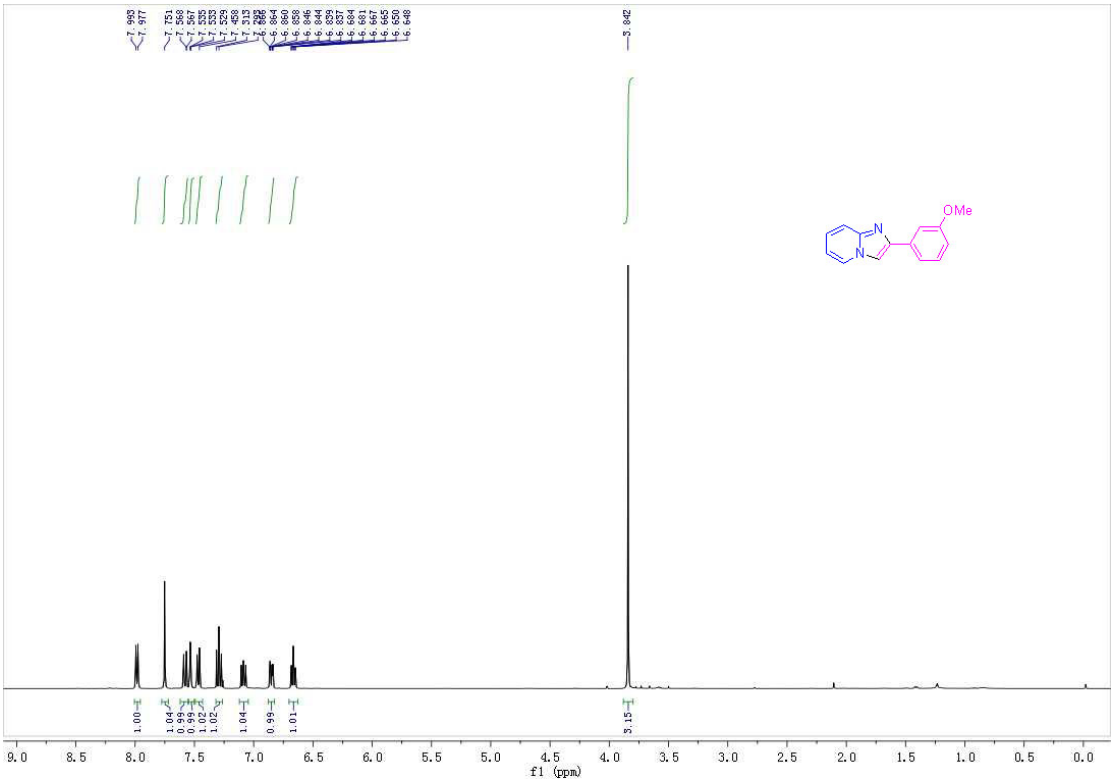
113.86
111.87
107.07
77.32
77.00
76.68
55.60
f1 (ppm)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7.535
7.533
7.329
7.313
6.864
6.860
6.858
6.846
6.844
6.839
6.837
6.684
6.681
6.667
6.665
6.650
6.648
3.842
OMe
N
N
1.00
1.04
0.99
1.02
1.02
1.04
0.99
1.01
3.15
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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3.0
2.5
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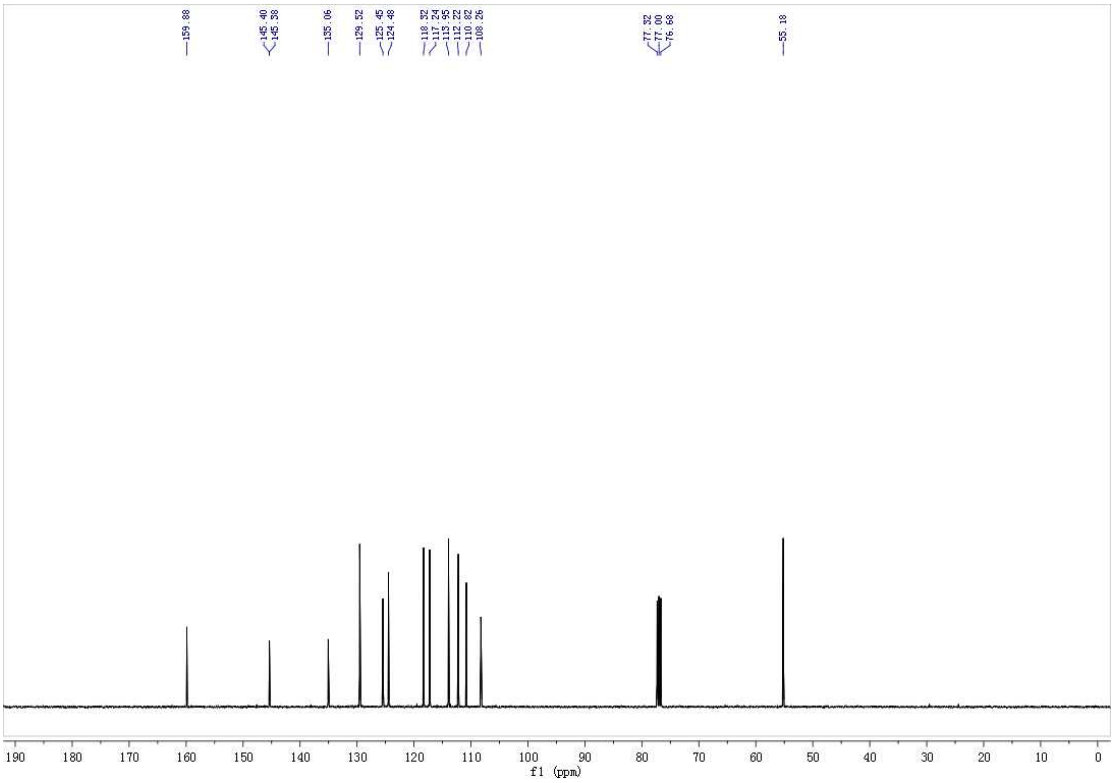
1.0
0.5
0.0
f1 (ppm)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125.45
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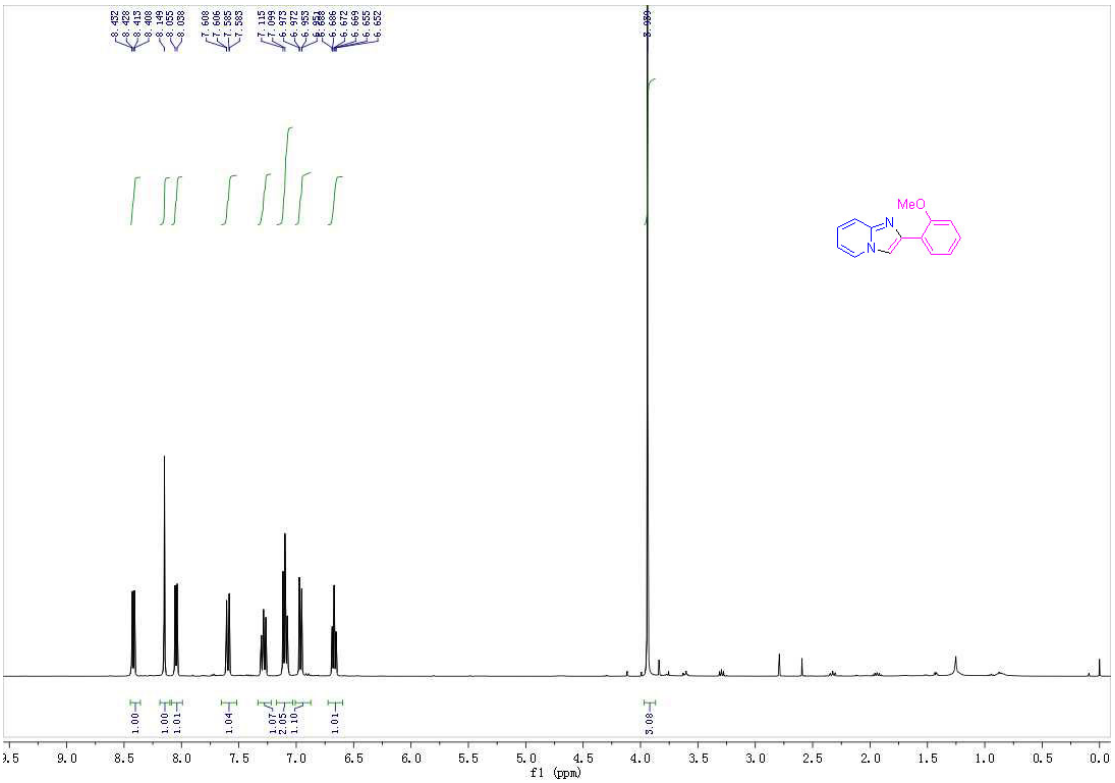
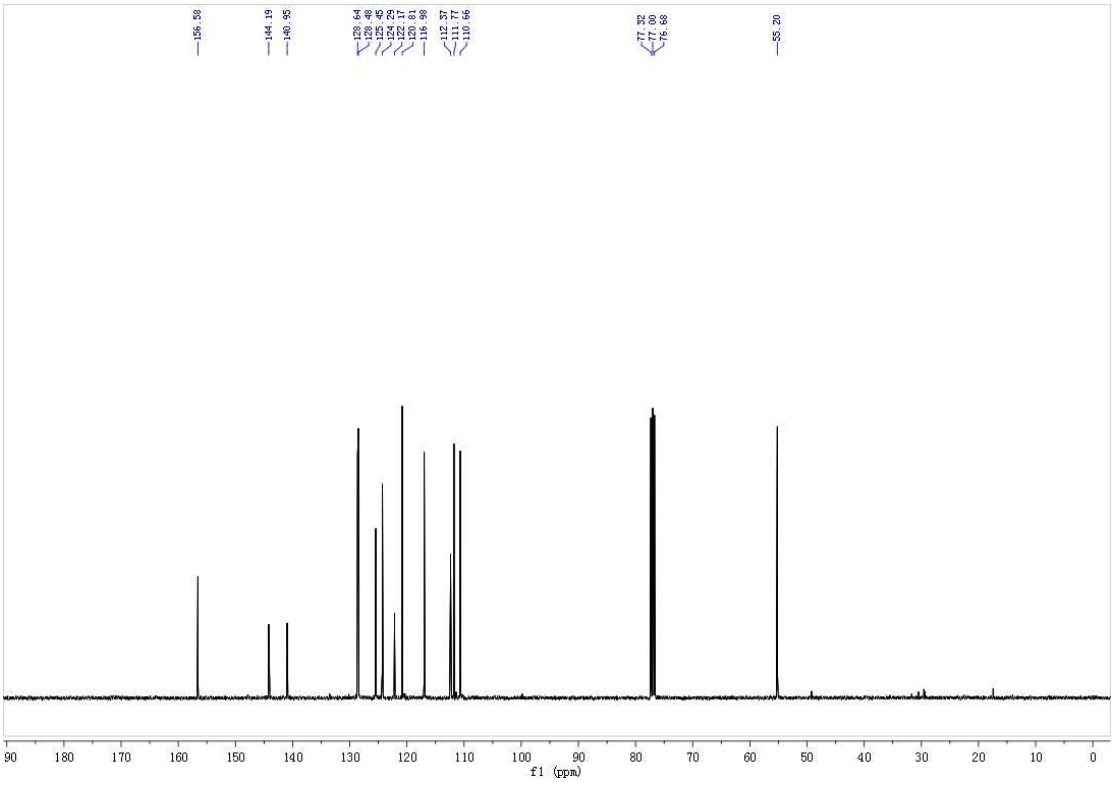
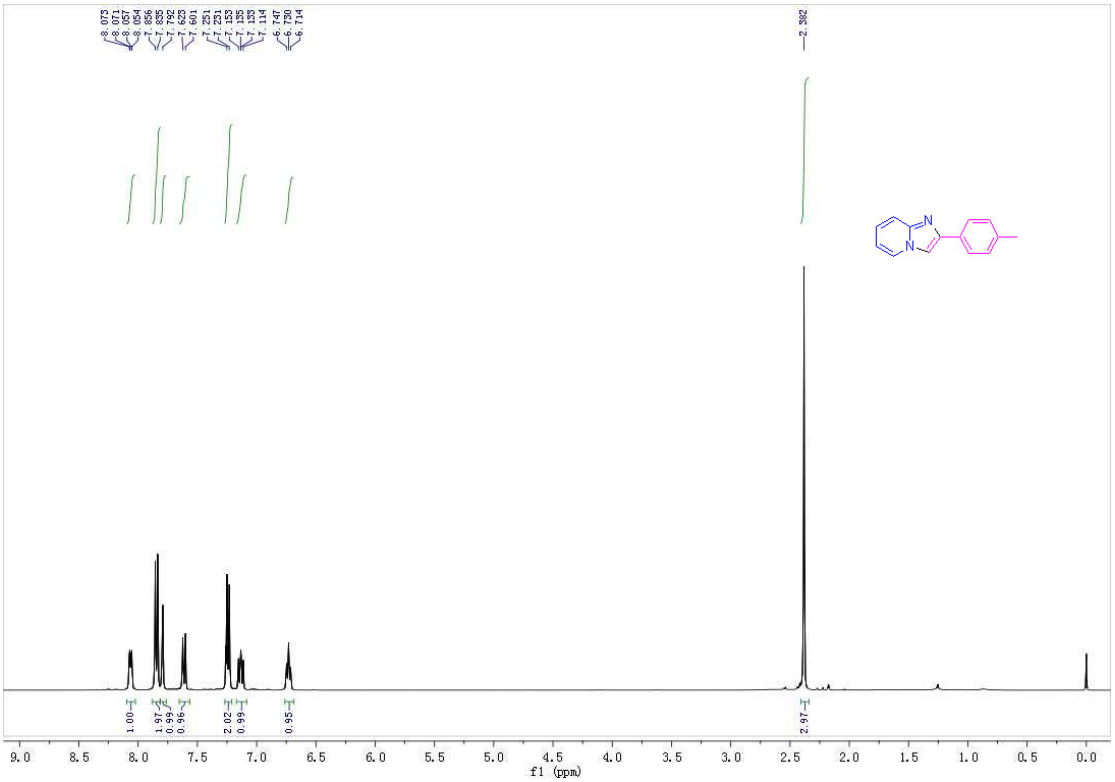
118.32
117.24
115.95
112.22
110.82
108.26
77.32
77.00
76.68
55.18
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


MeO
N
N
f1 (ppm)


f1 (ppm)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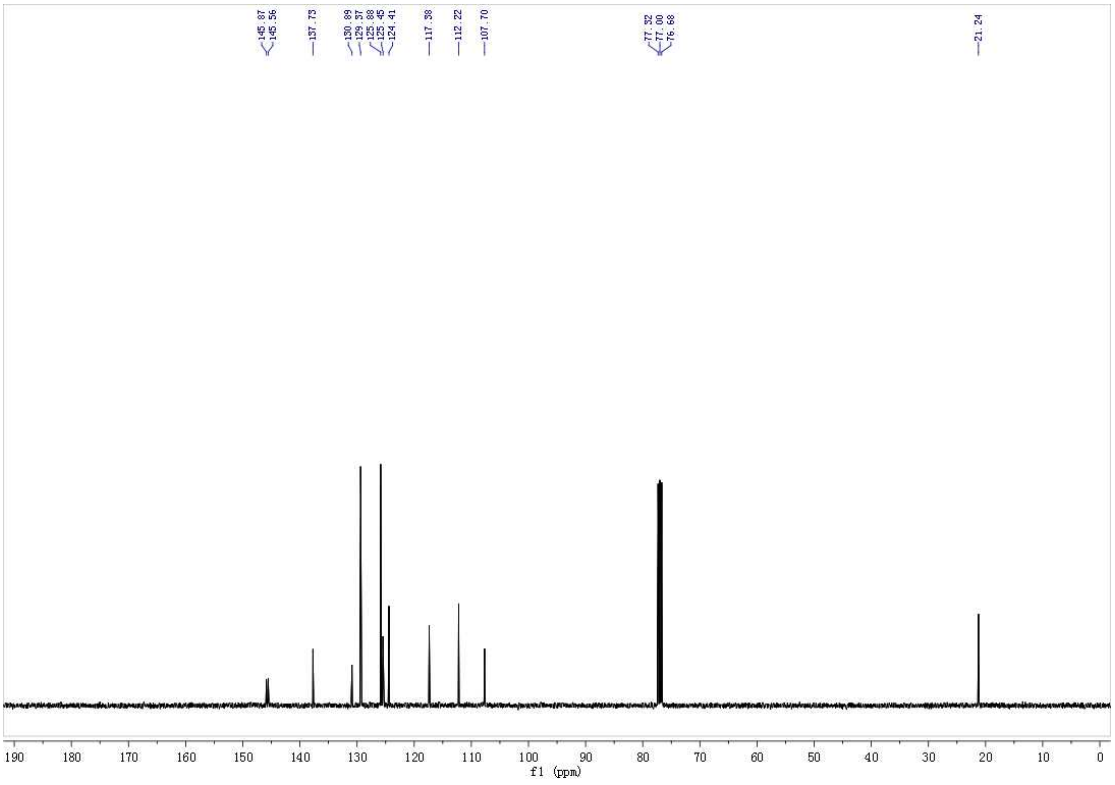
7.835
7.792
7.623
7.611
7.251
7.153
7.135
7.114
6.747
6.730
6.714
2.382
1.00
1.97
0.99
0.96
2.02
0.99
0.95
2.97
f1 (ppm)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145.56
137.73
130.99
129.97
125.88
125.45
124.41
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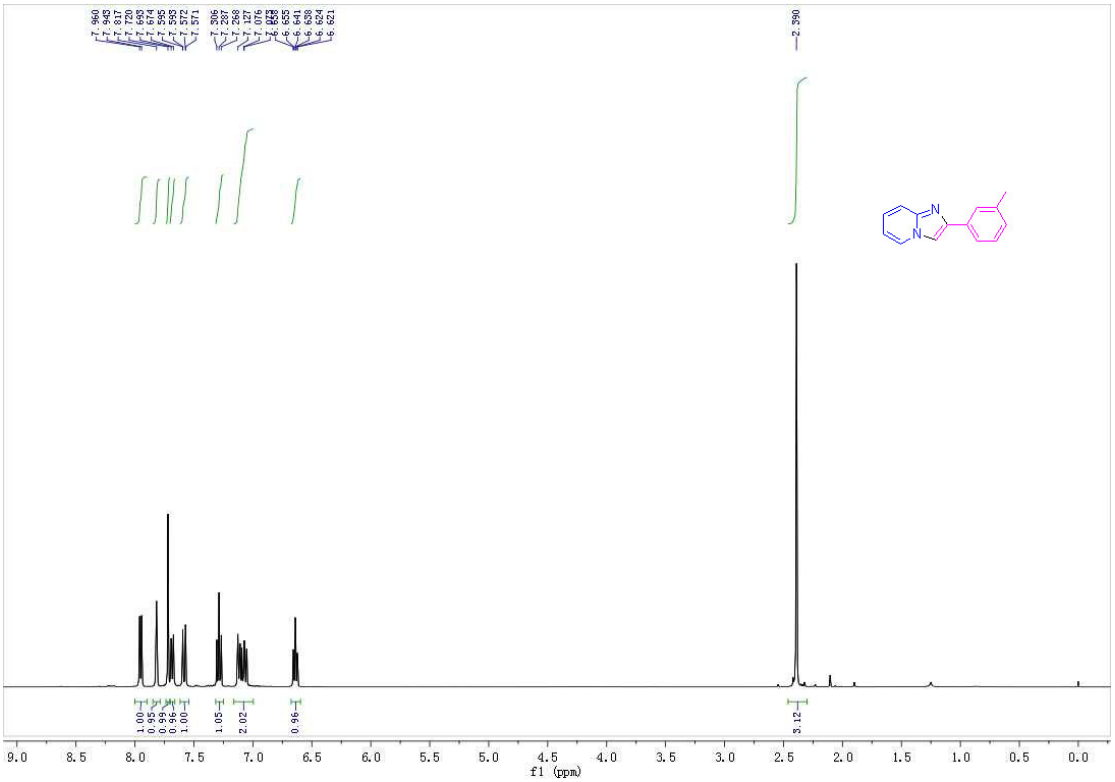
112.22
107.70
77.32
77.00
76.68
21.24
f1 (ppm)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7.571
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7.287
7.268
7.237
7.076
6.655
6.641
6.638
6.624
6.621
2.590
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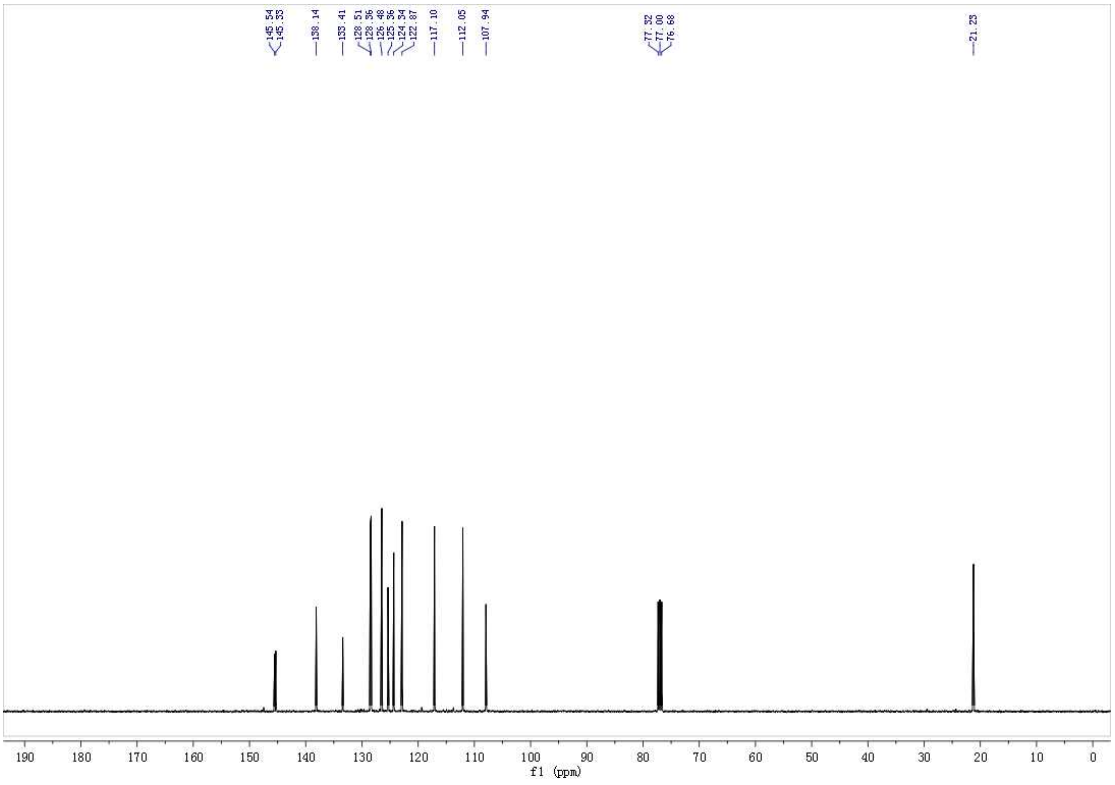
0.95
0.93
0.96
1.00
1.05
2.02
0.96
3.12
f1 (ppm)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133.41
128.51
128.36
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123.36
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122.67
117.10
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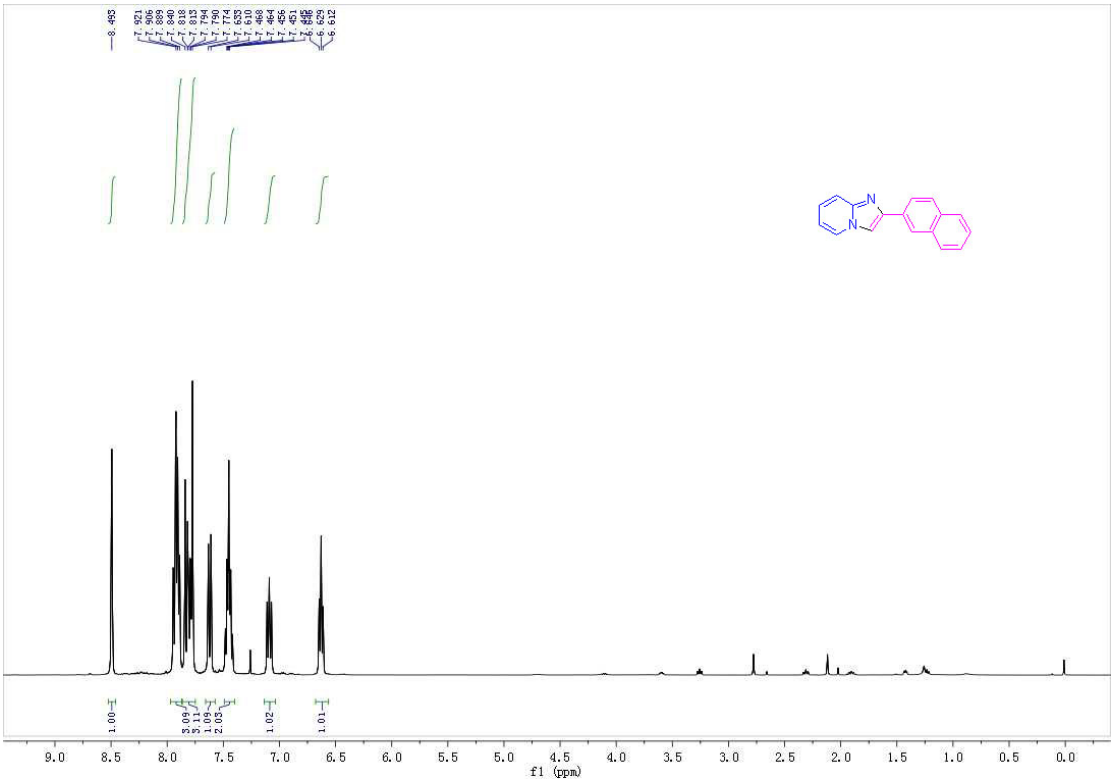
77.00
76.68
21.23
f1 (ppm)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7.468
7.464
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7.451
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6.612
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3.11
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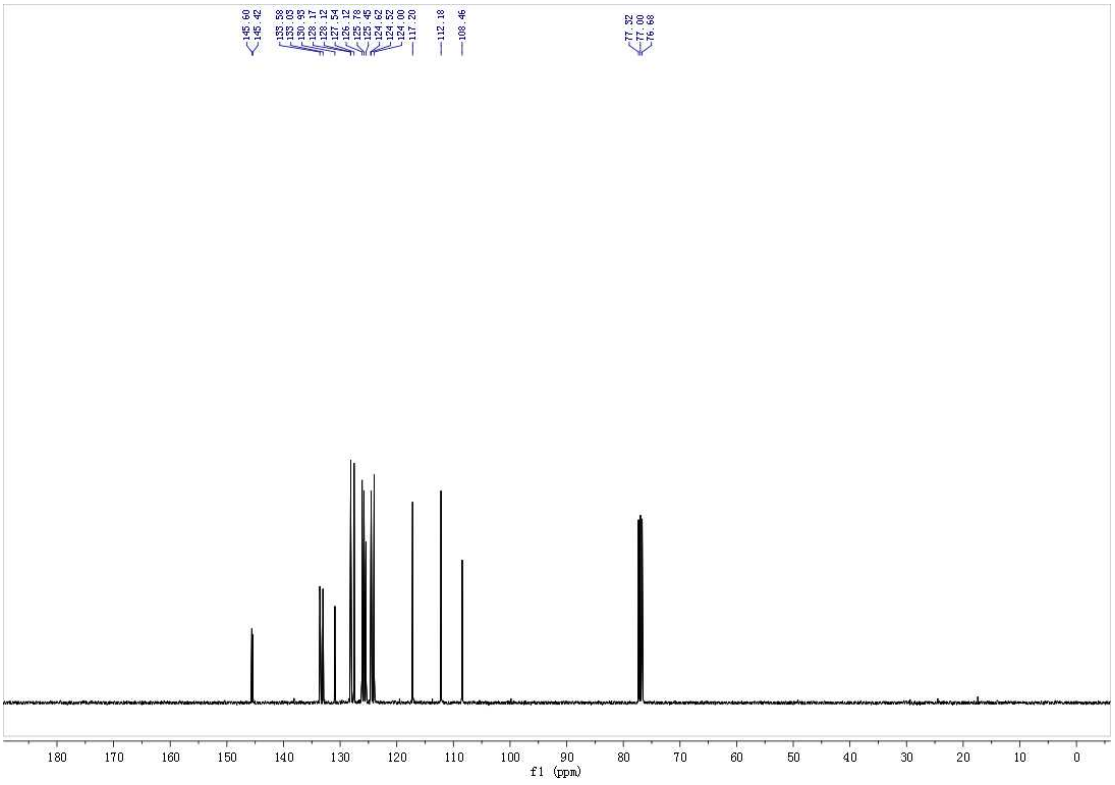
2.05
1.02
1.01
f1 (ppm)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127.54
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125.78
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124.53
124.00
117.20
112.18
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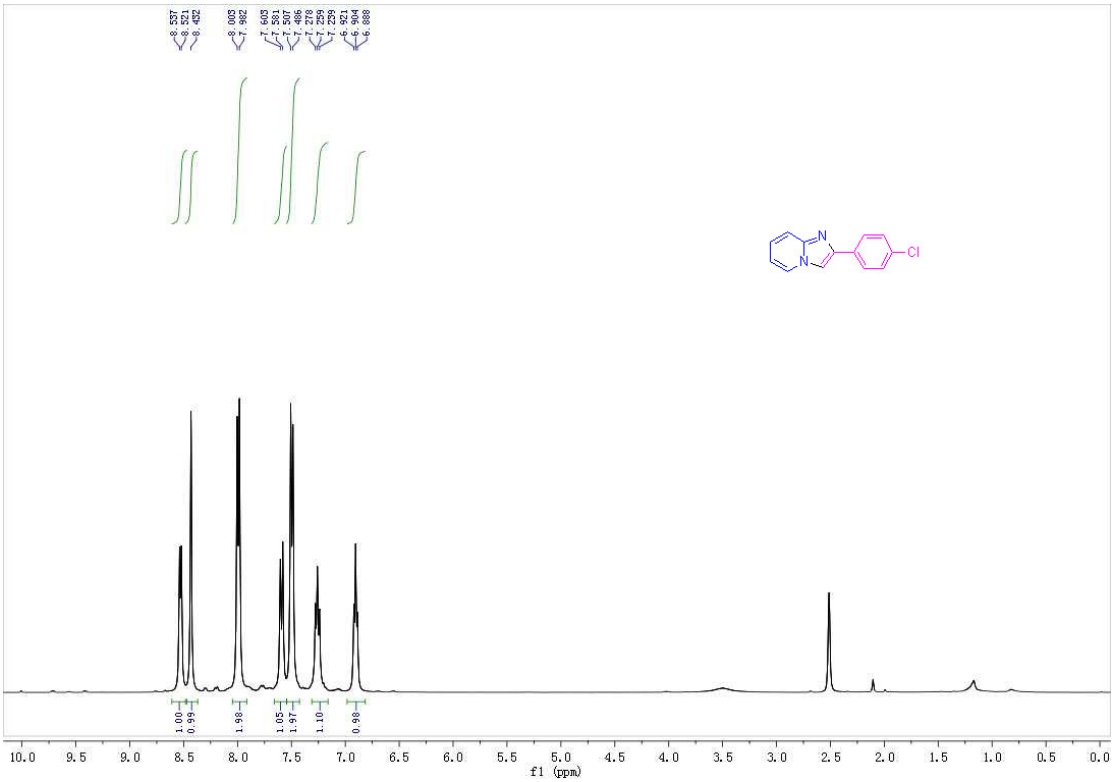
77.32
77.00
76.68
f1 (ppm)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7.259
7.236
6.921
6.904
6.888
N
N
Cl
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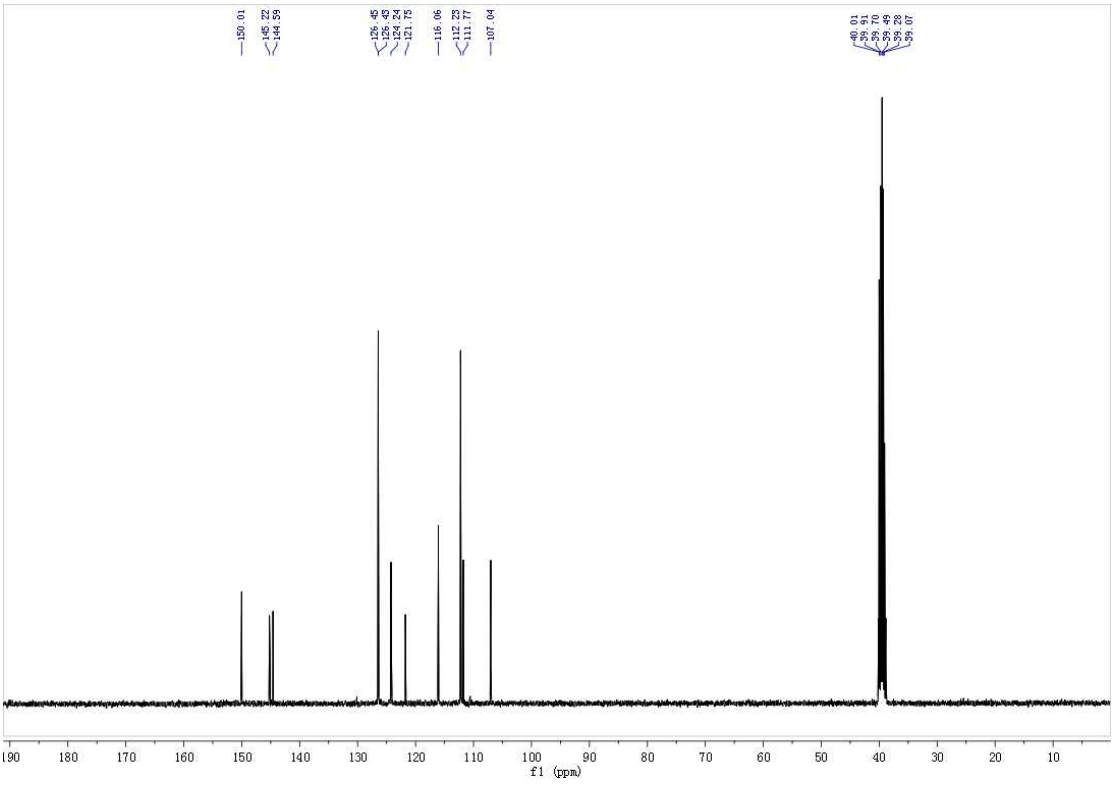
0.99
1.98
1.05
1.97
1.10
0.98
f1 (ppm)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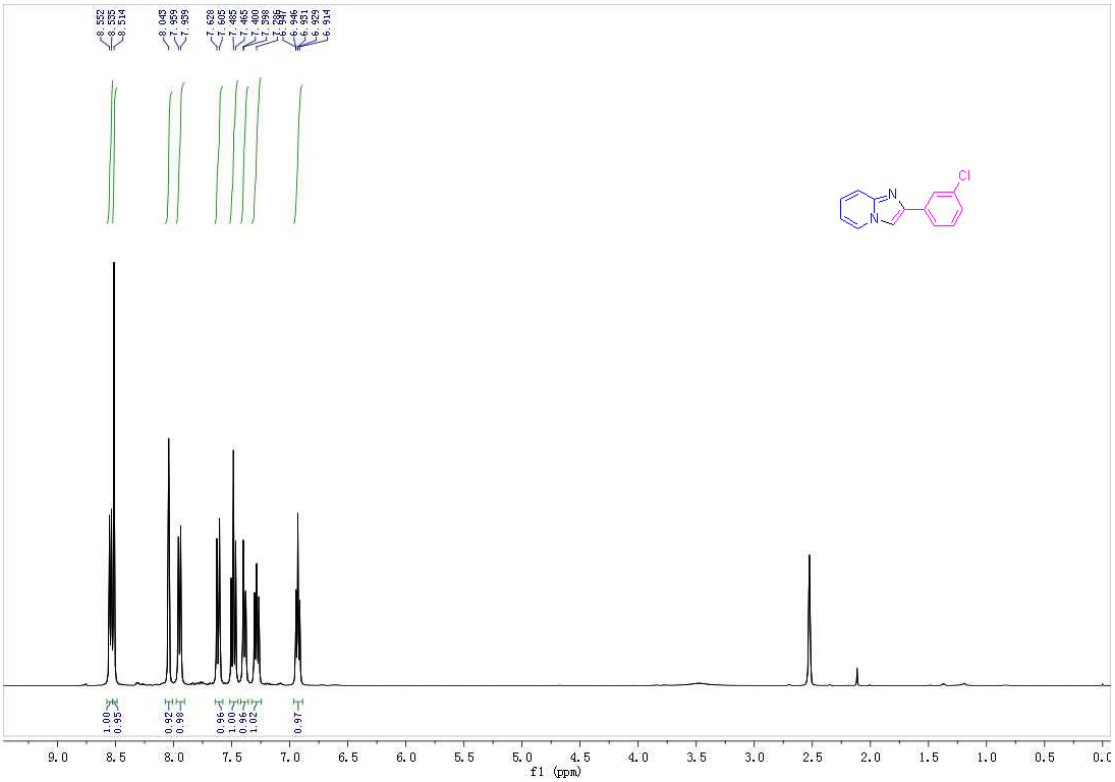
39.28
39.07
f1 (ppm)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6.931
6.929
6.914
Cl
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0.98
0.96
1.00
0.96
1.02
0.97
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8.0
7.5
7.0
6.5
6.0
5.5
5.0
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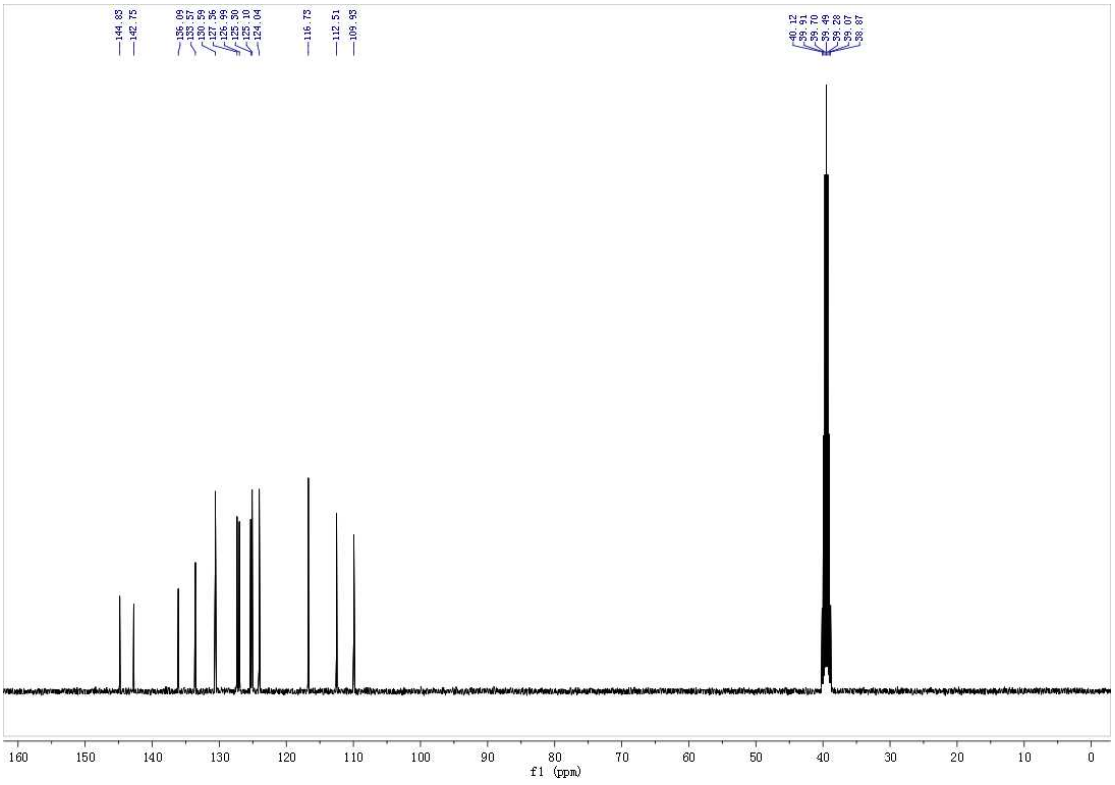
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126.93
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124.04
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112.51
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39.91
39.70
39.49
39.28
39.07
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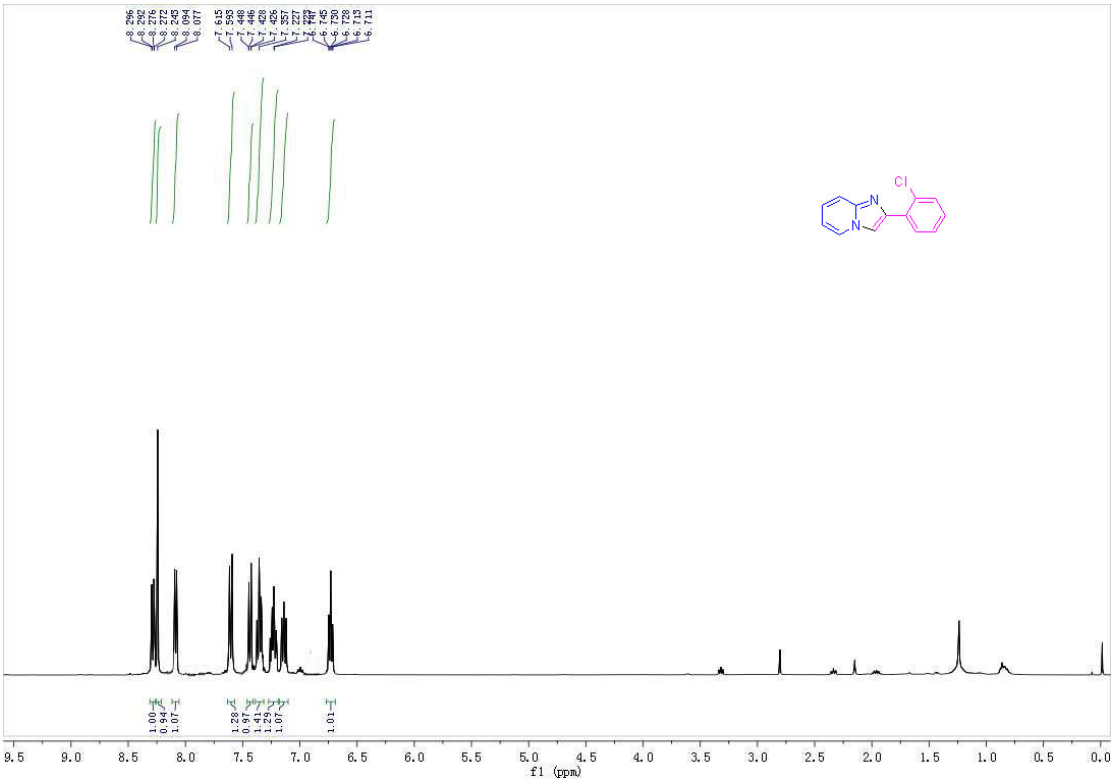
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7.357
7.227
6.745
6.730
6.713
6.711
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1.29
1.07
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7.0
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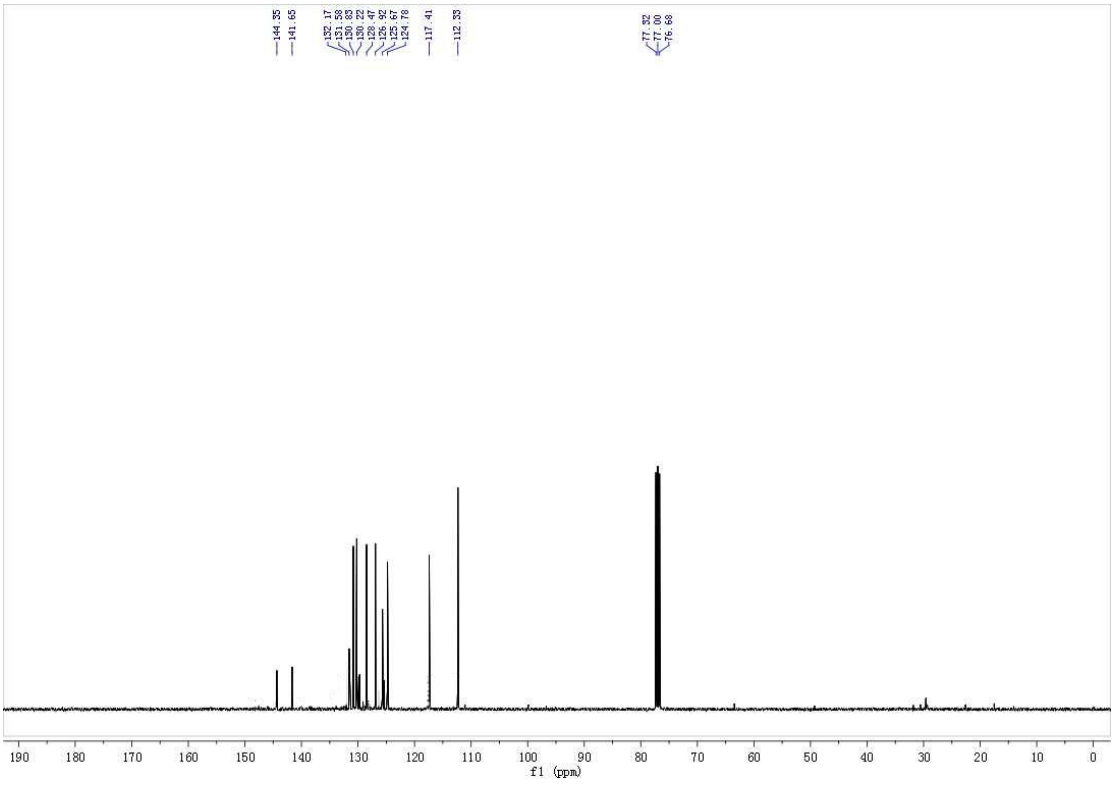
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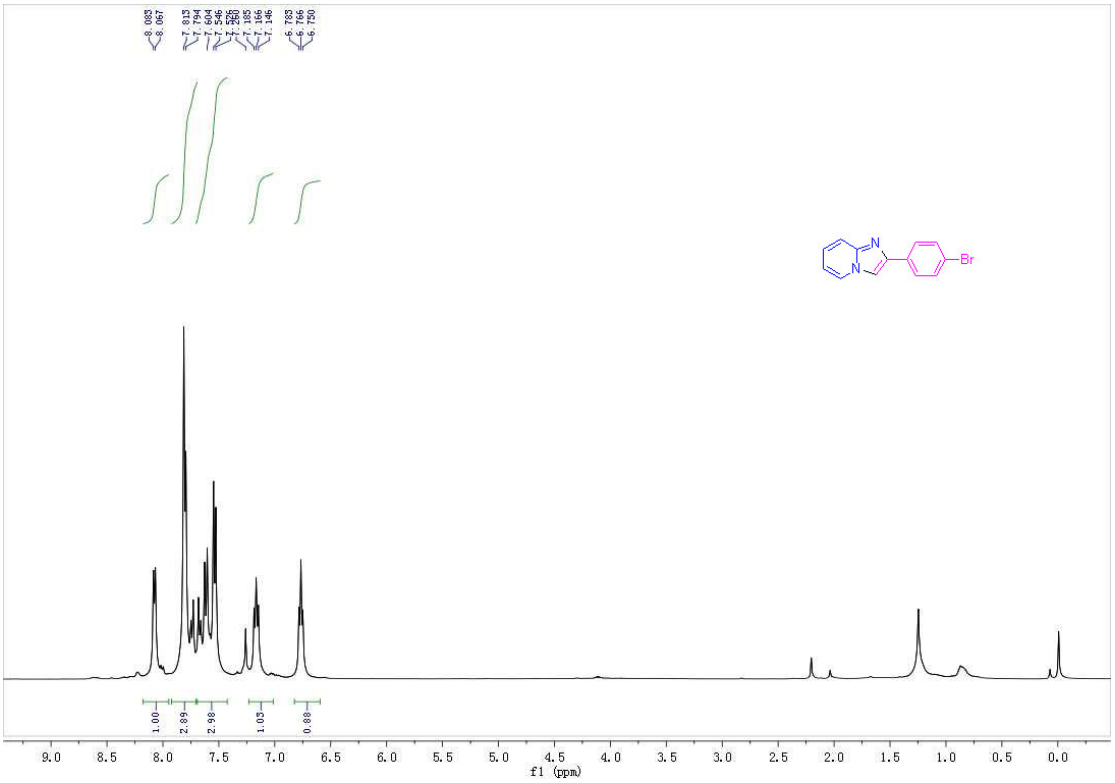
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N
Br
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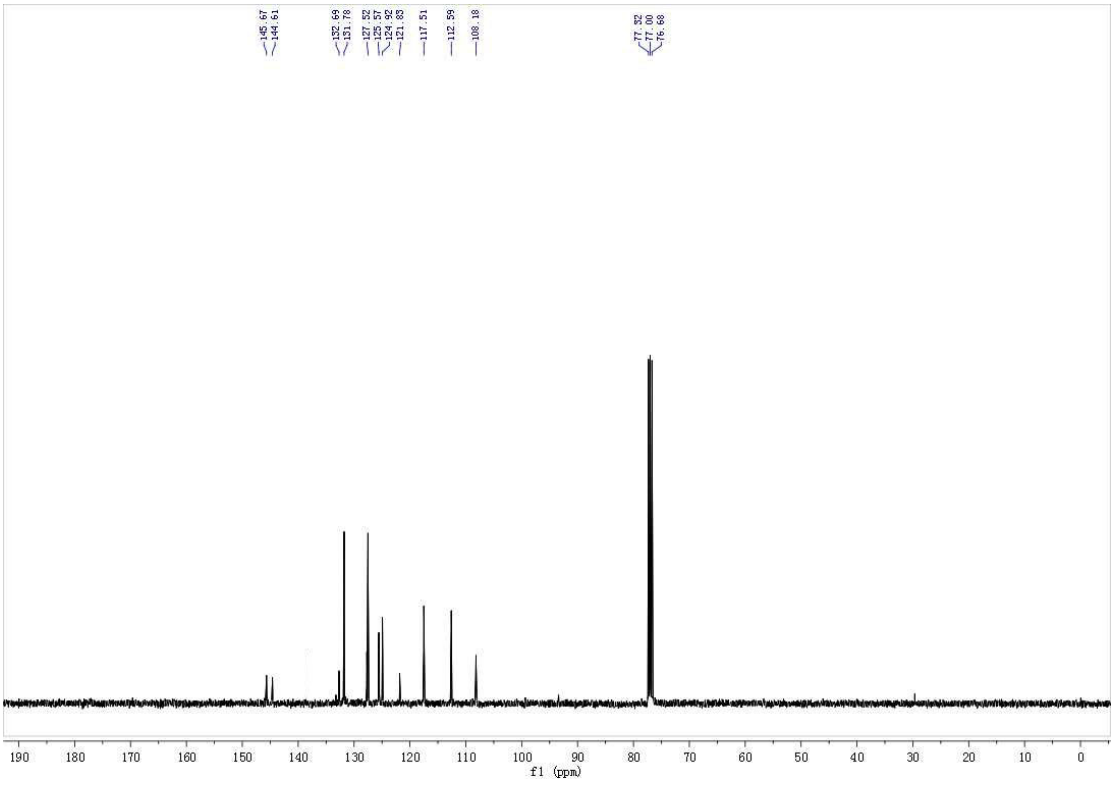
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180
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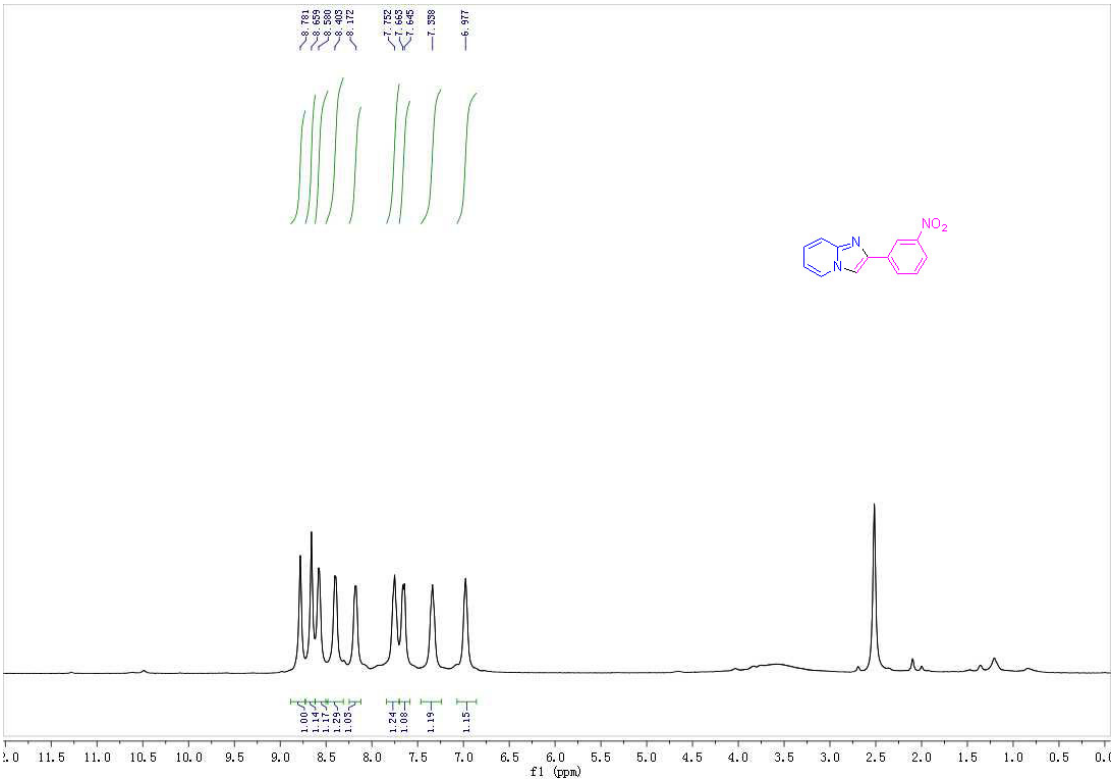
f1 (ppm)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7.645
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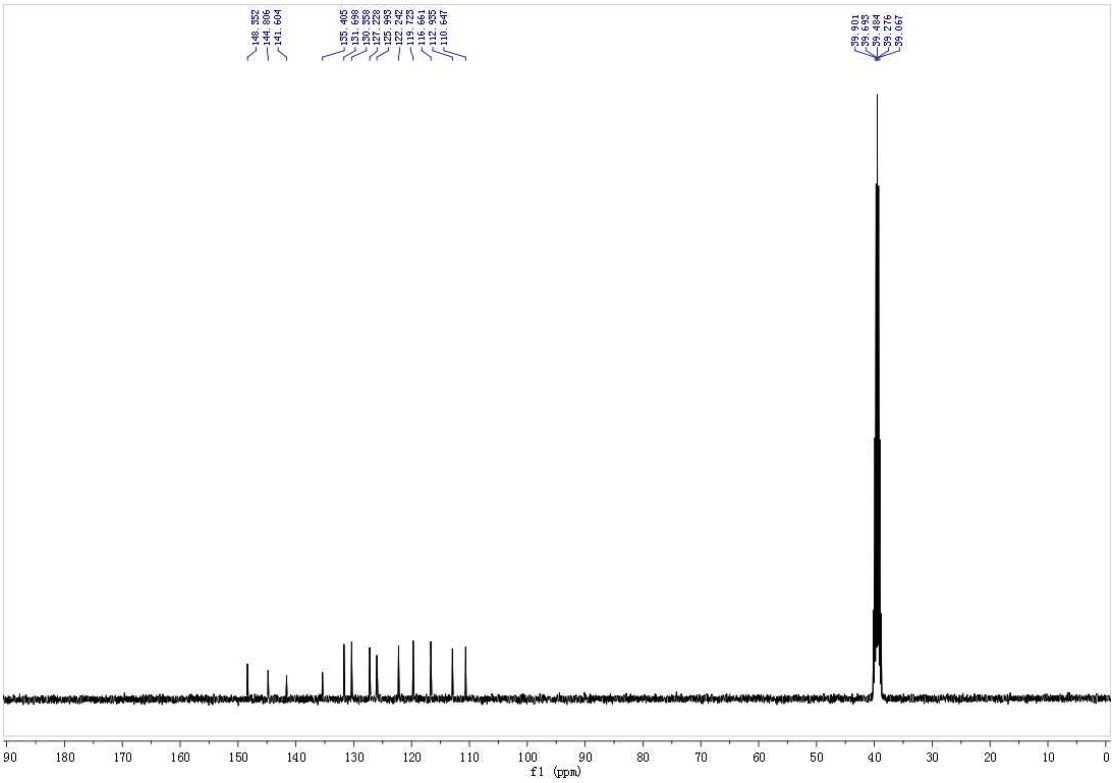
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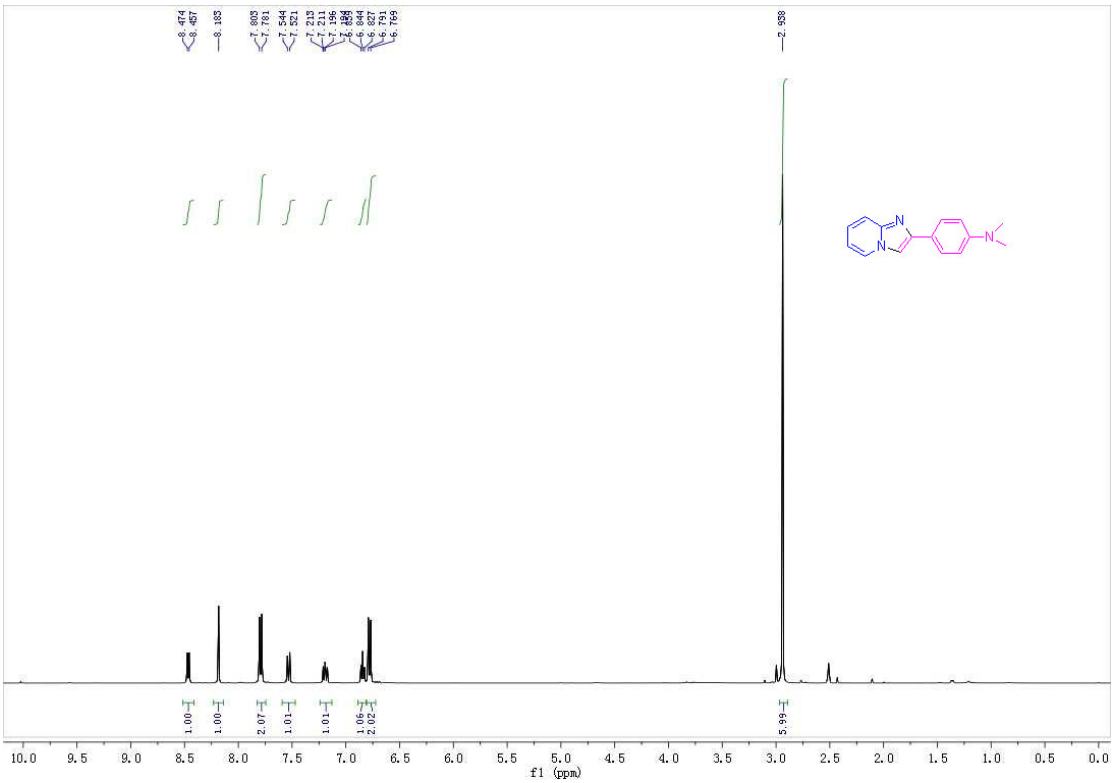
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7.194
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6.827
6.791
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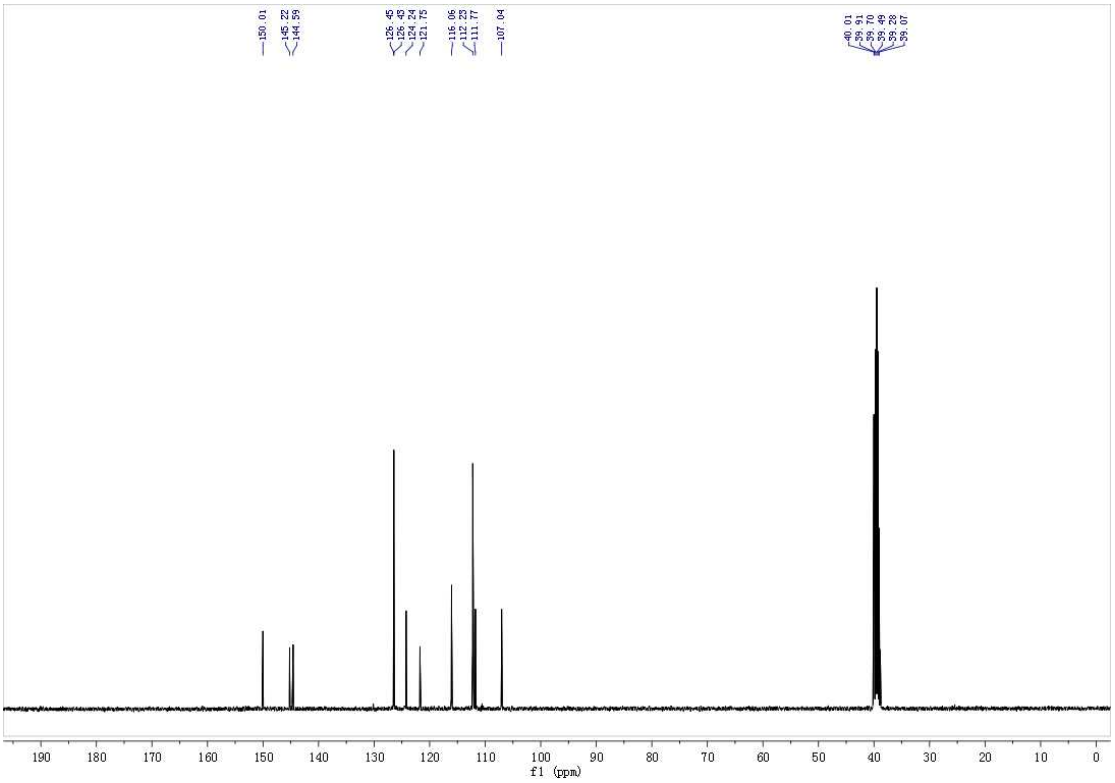
1.00
2.07
1.01
1.01
1.06
2.02
5.99
f1 (ppm)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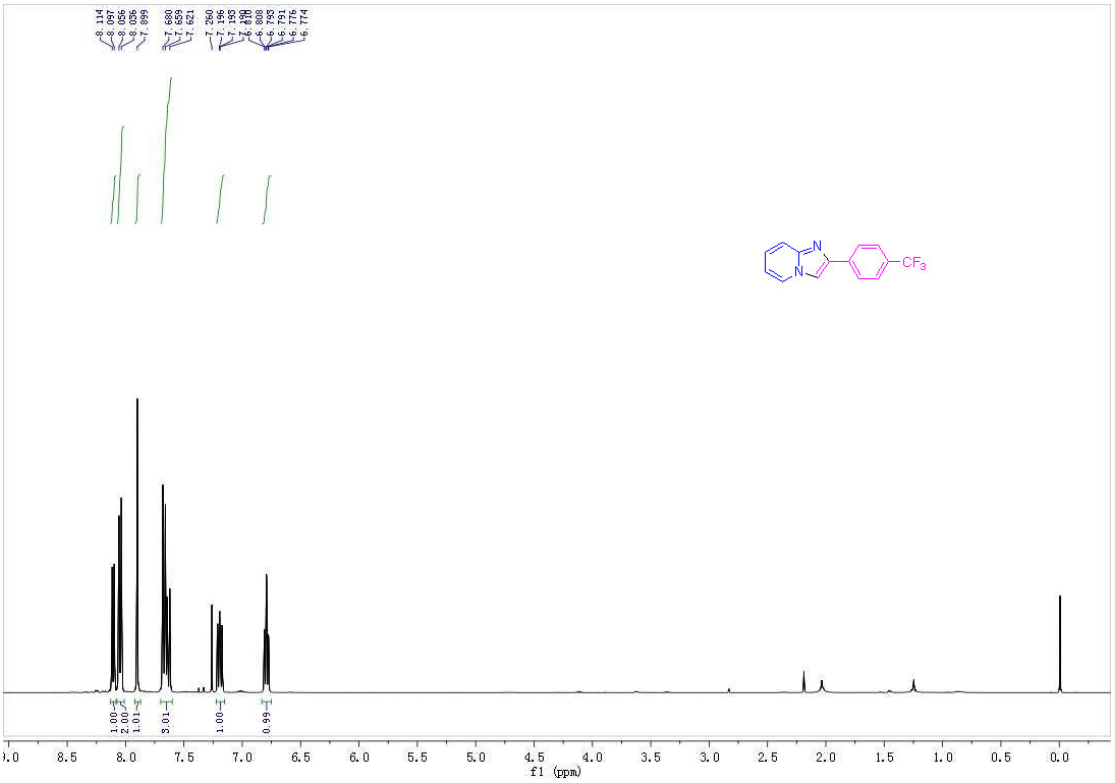
39.07
f1 (ppm)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7.621
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6.793
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1.01
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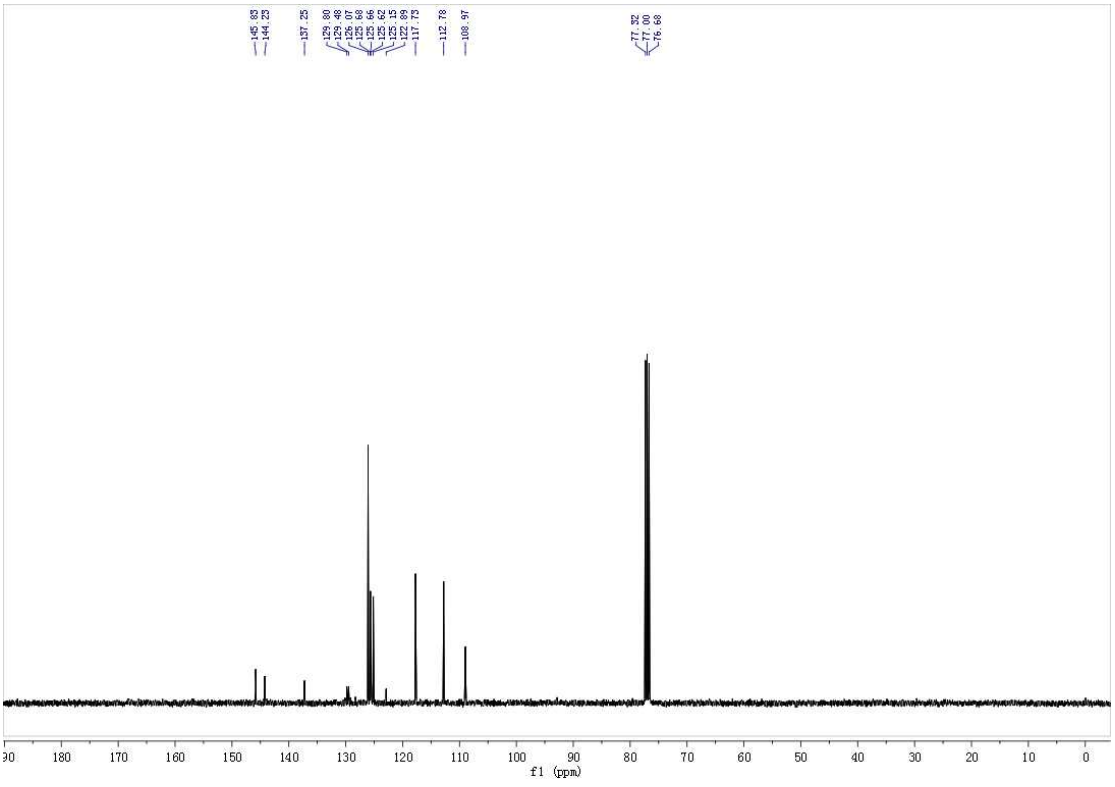
0.99
f1 (ppm)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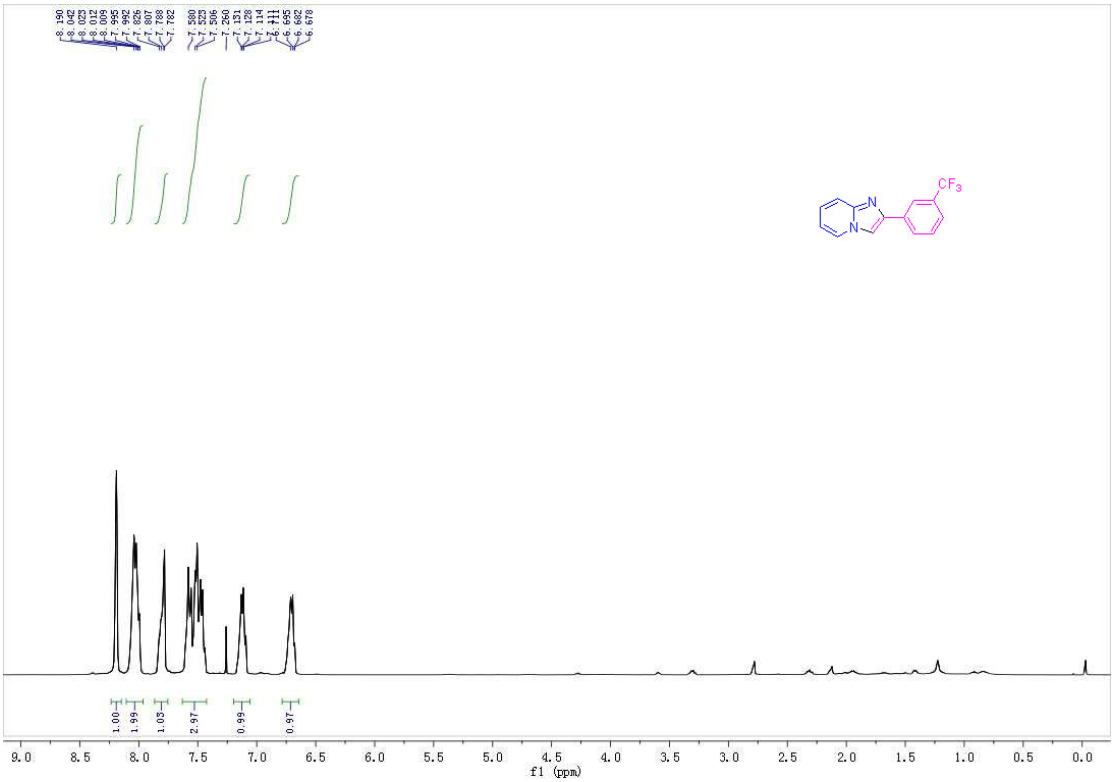
f1 (ppm)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7.992
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7.523
7.506
7.260
7.151
7.138
7.114
6.695
6.682
6.678
CF3
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N
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1.03
2.97
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0.97
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7.0
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6.0
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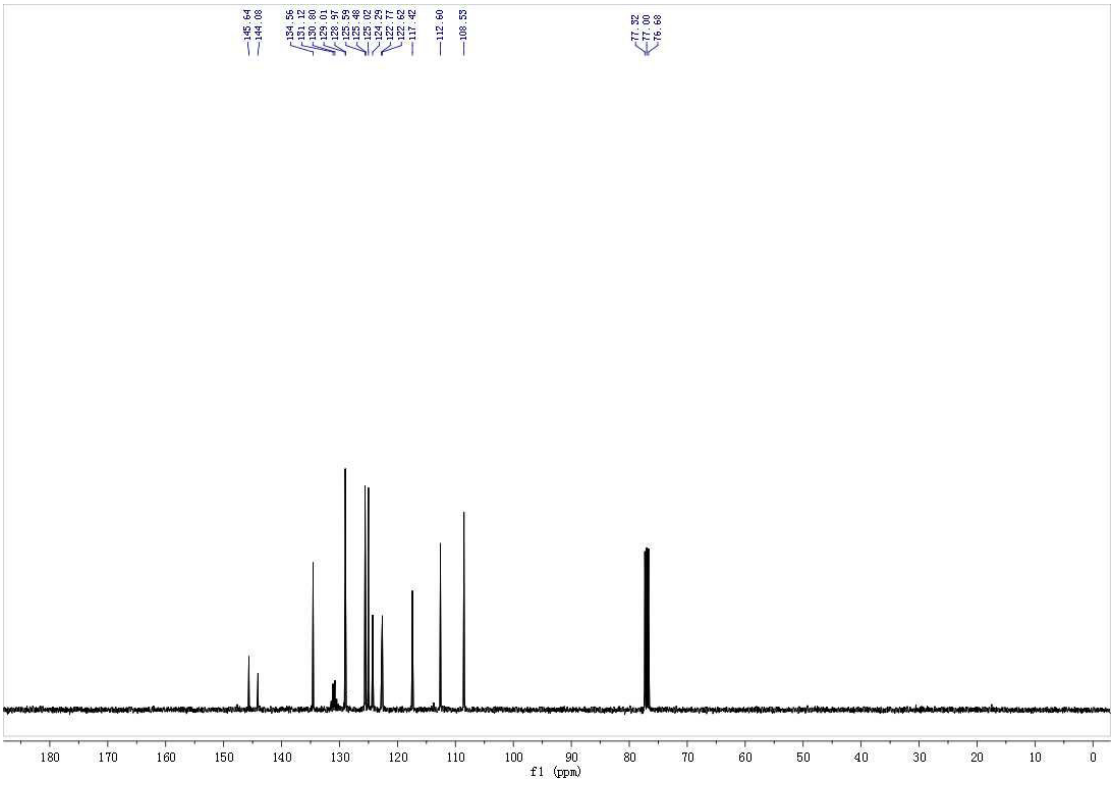
f1 (ppm)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125.02
124.29
122.77
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117.42
112.60
108.53
77.32
77.00
76.68
180
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130
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110
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90
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50
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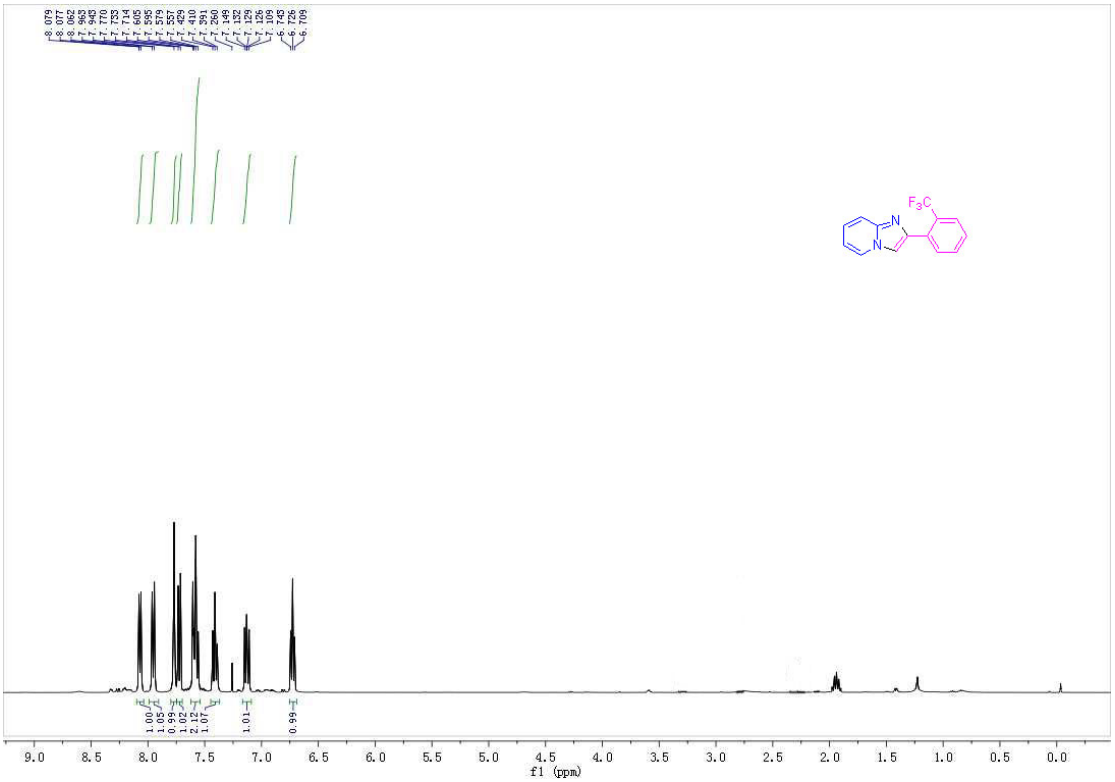
f1 (ppm)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7.391
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7.149
7.132
7.129
7.126
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6.745
6.726
6.709
F3C
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1.02
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7.0
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6.0
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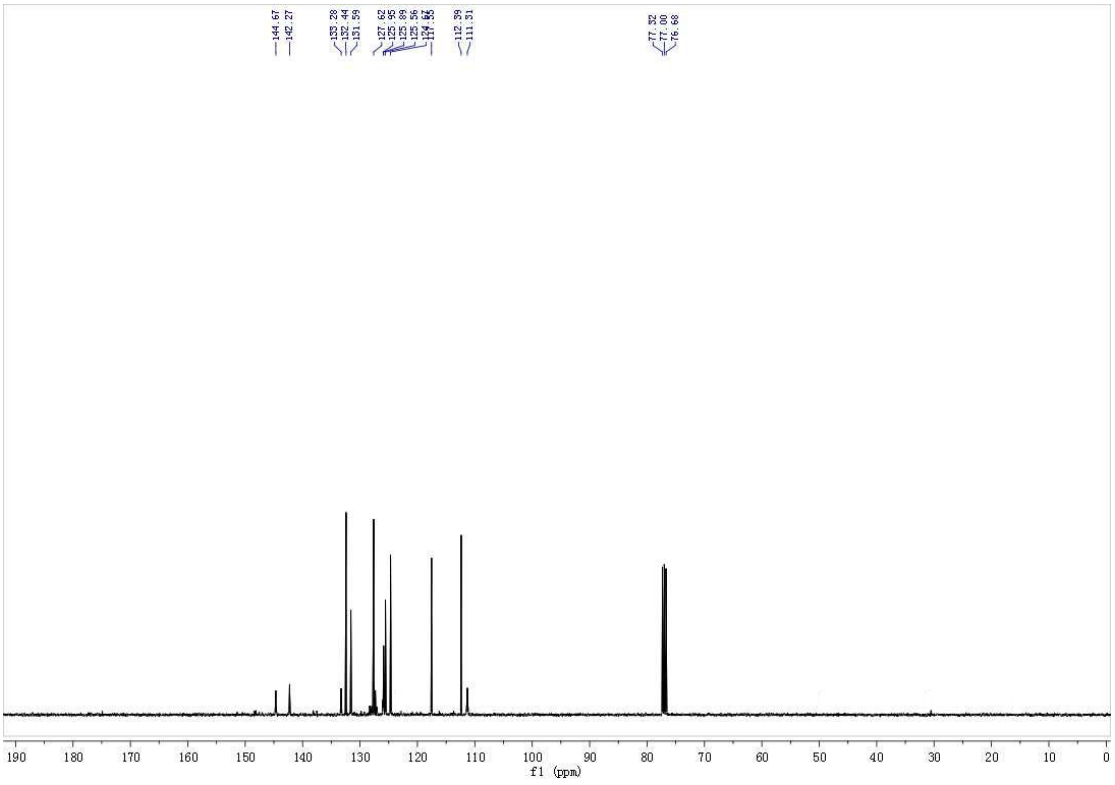
0.0
f1 (ppm)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76.68
190
180
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100
90
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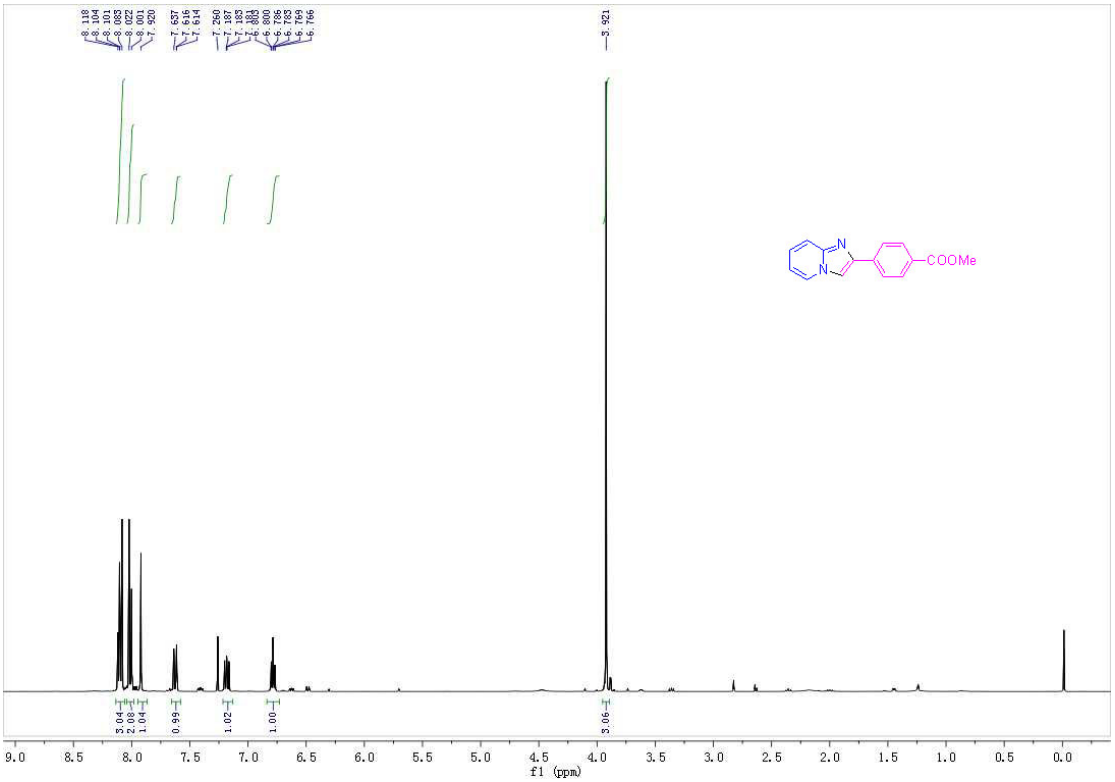
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7.614
7.260
7.187
7.183
6.803
6.800
6.795
6.783
6.769
6.766
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COOMe
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2.08
1.04
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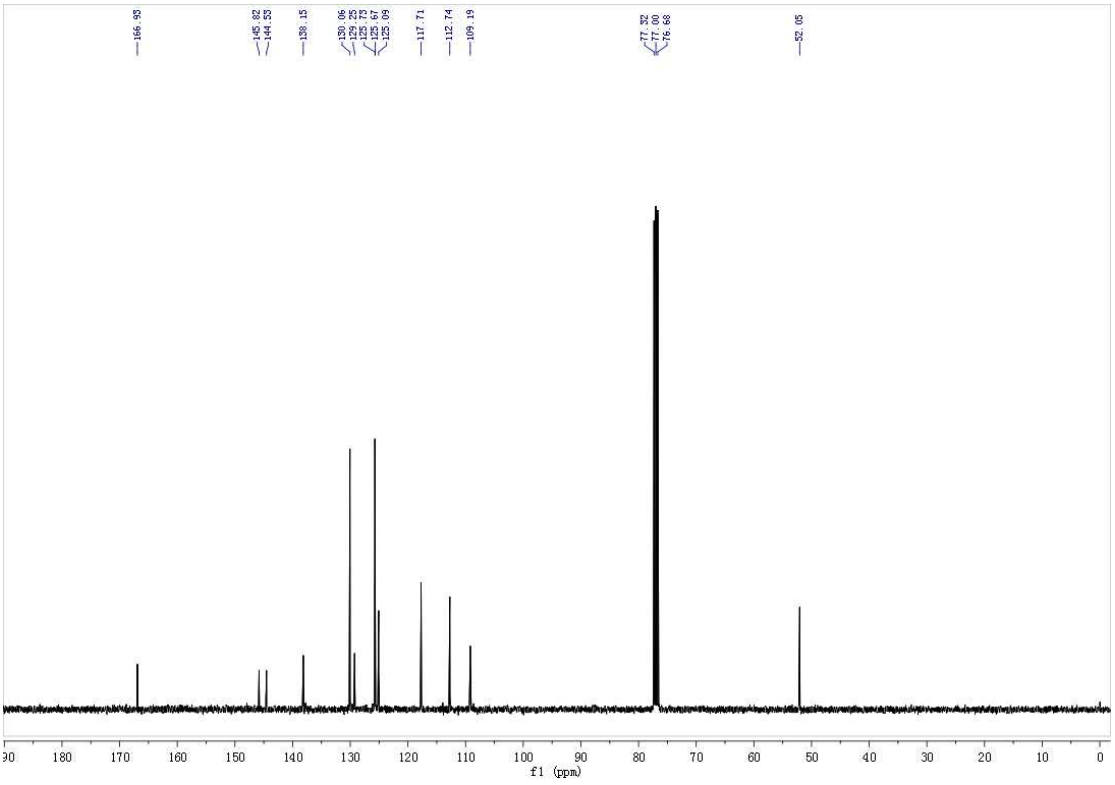
1.02
1.00
3.06
f1 (ppm)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77.00
76.68
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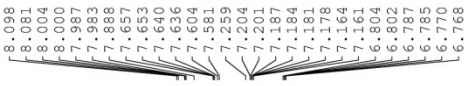
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8.004
8.000
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7.657
7.653
7.640
7.636
7.604
7.581
7.259
7.204
7.201
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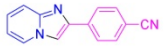
6.768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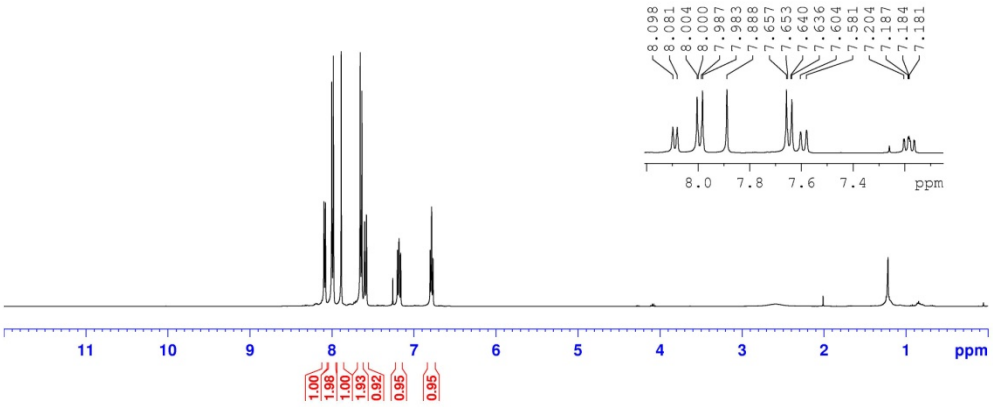
CN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7.581
7.204
7.187
7.184
7.181
8.0
7.8
7.6
7.4
ppm
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10
9
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6
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2
1
ppm
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1.00
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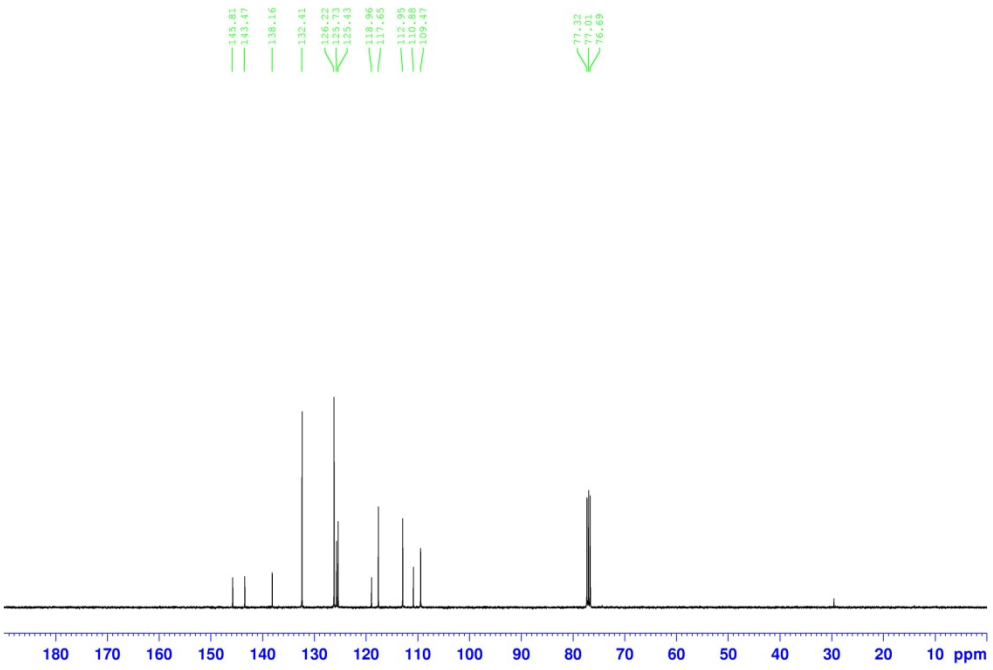
0.95
0.95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118.96
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110.88
109.47
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77.01
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140
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120
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90
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70
60
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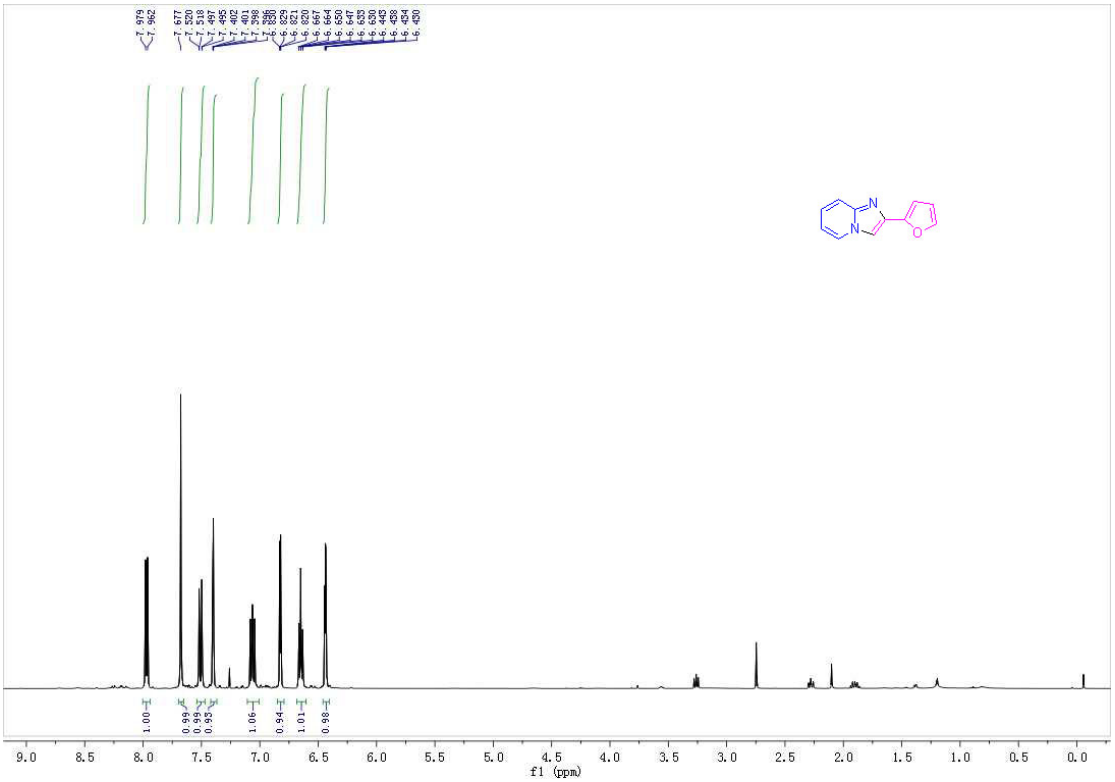
30
20
10
ppm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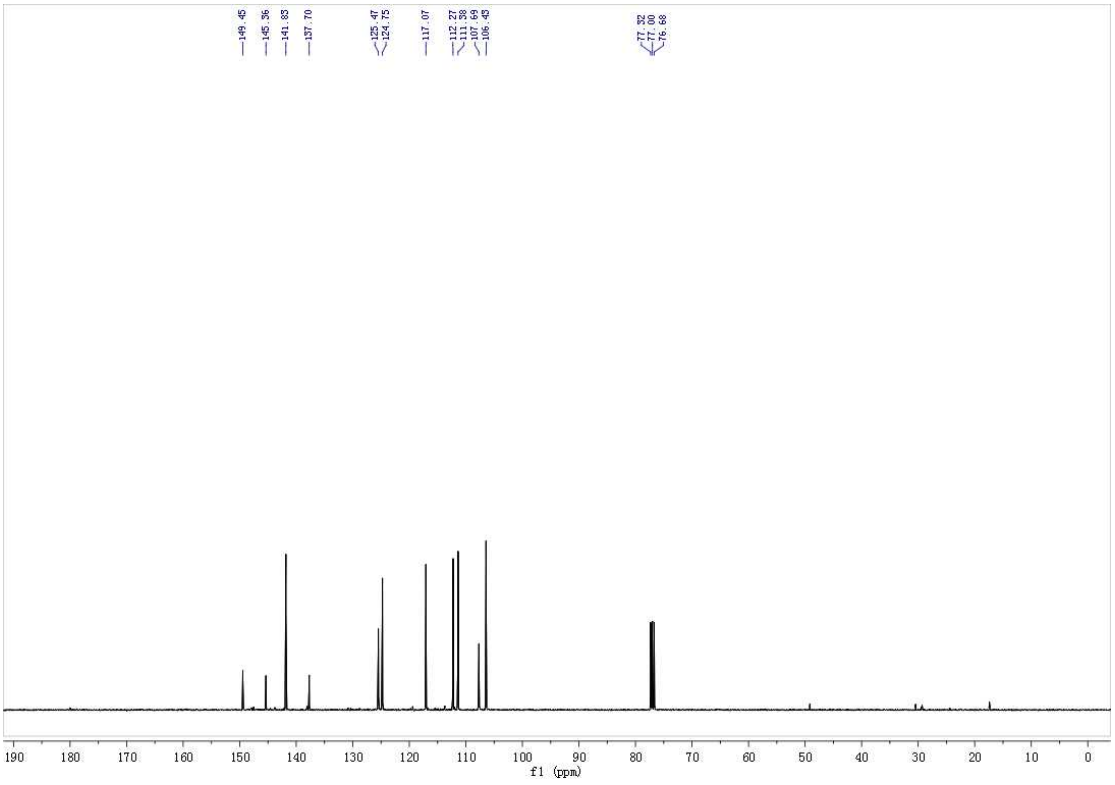
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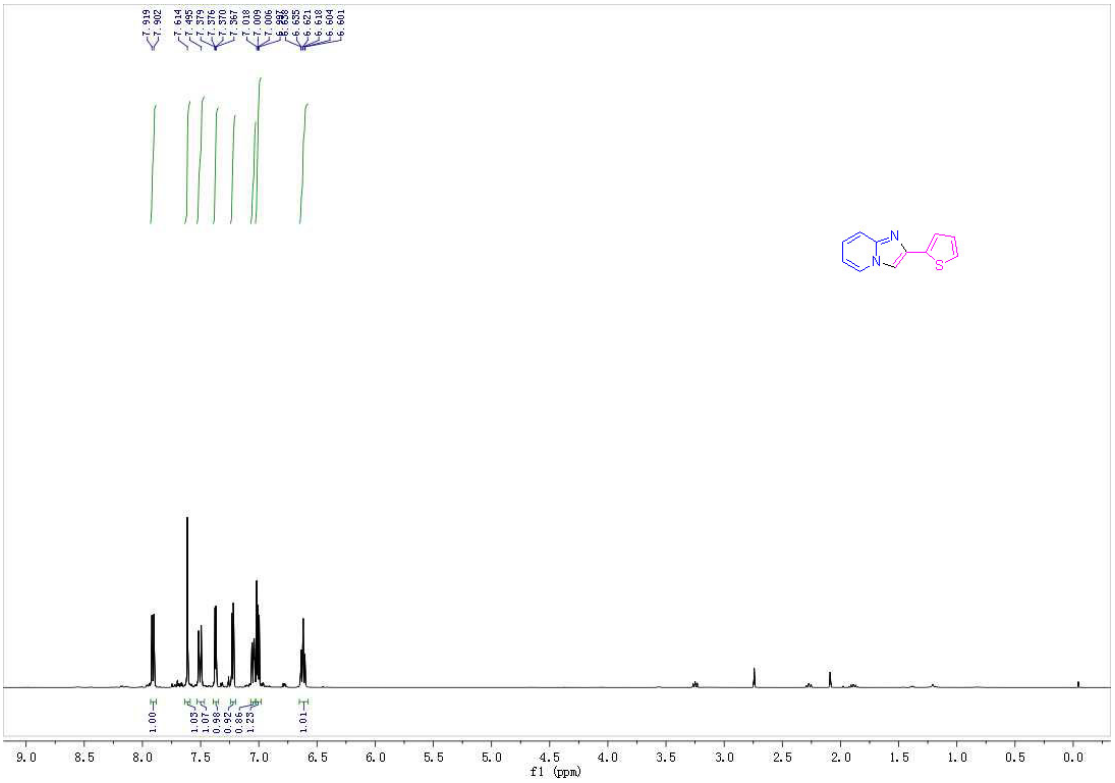
76.68
f1 (ppm)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6.621
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1.01
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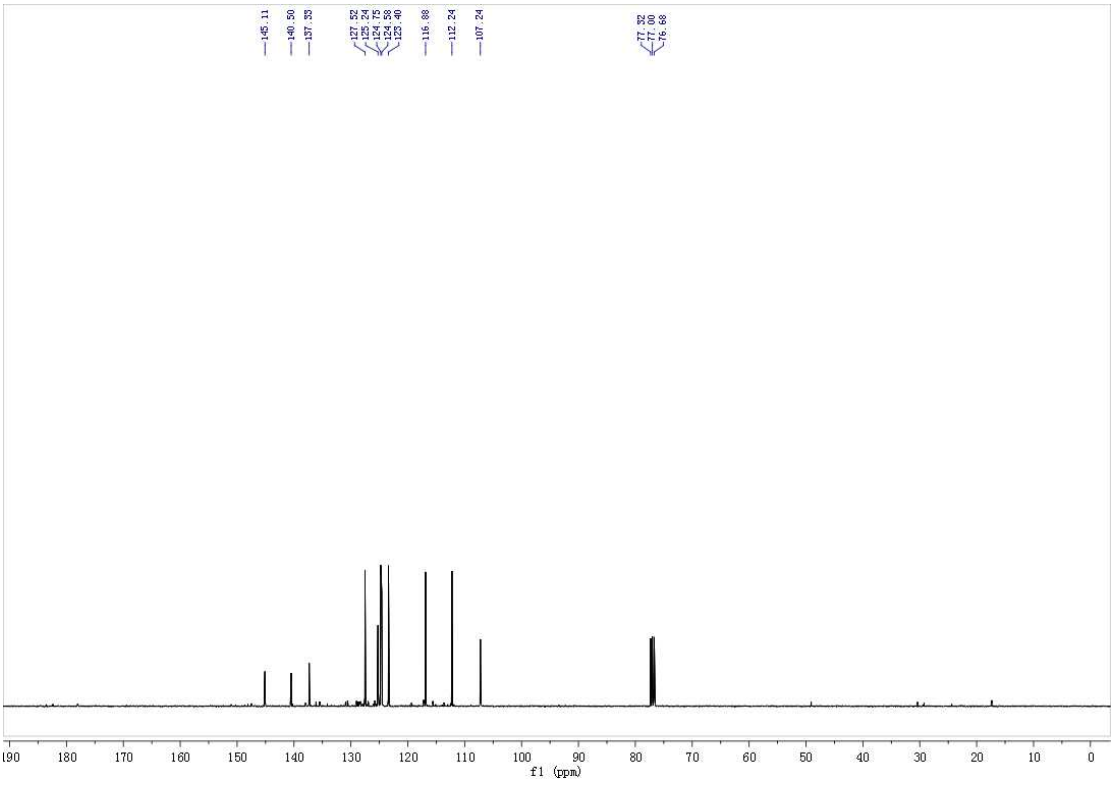
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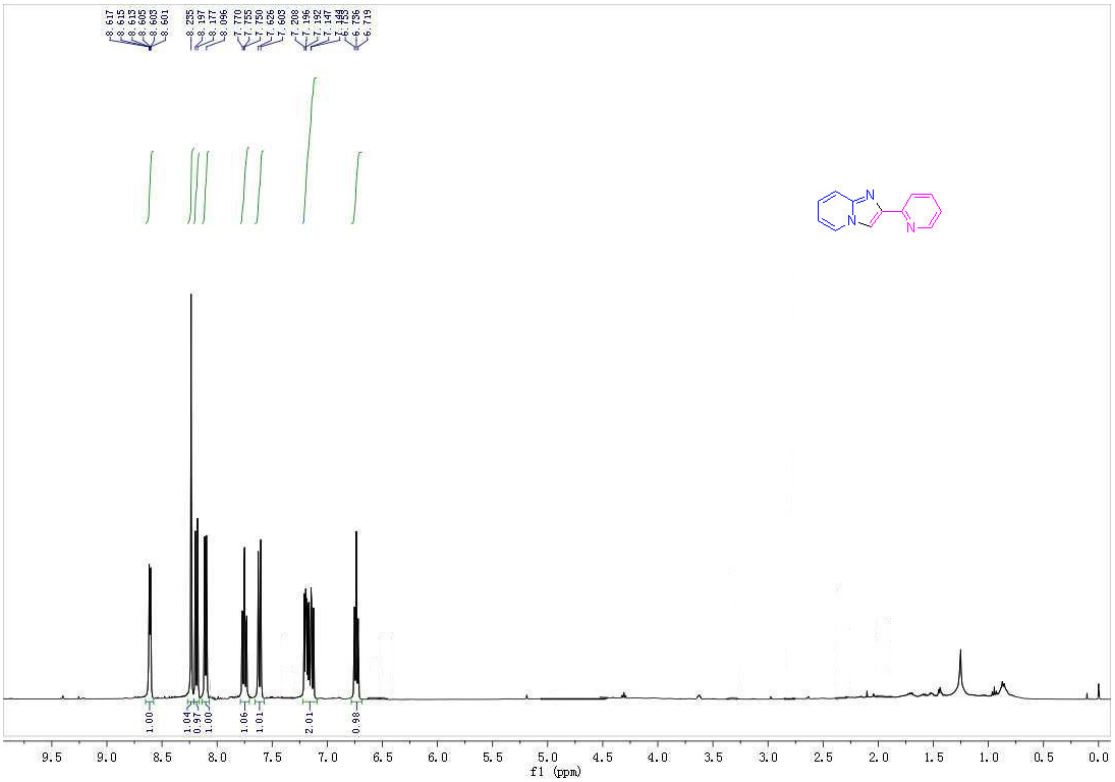
76.68
f1 (ppm)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7.603
7.208
7.196
7.192
7.147
7.143
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1.00
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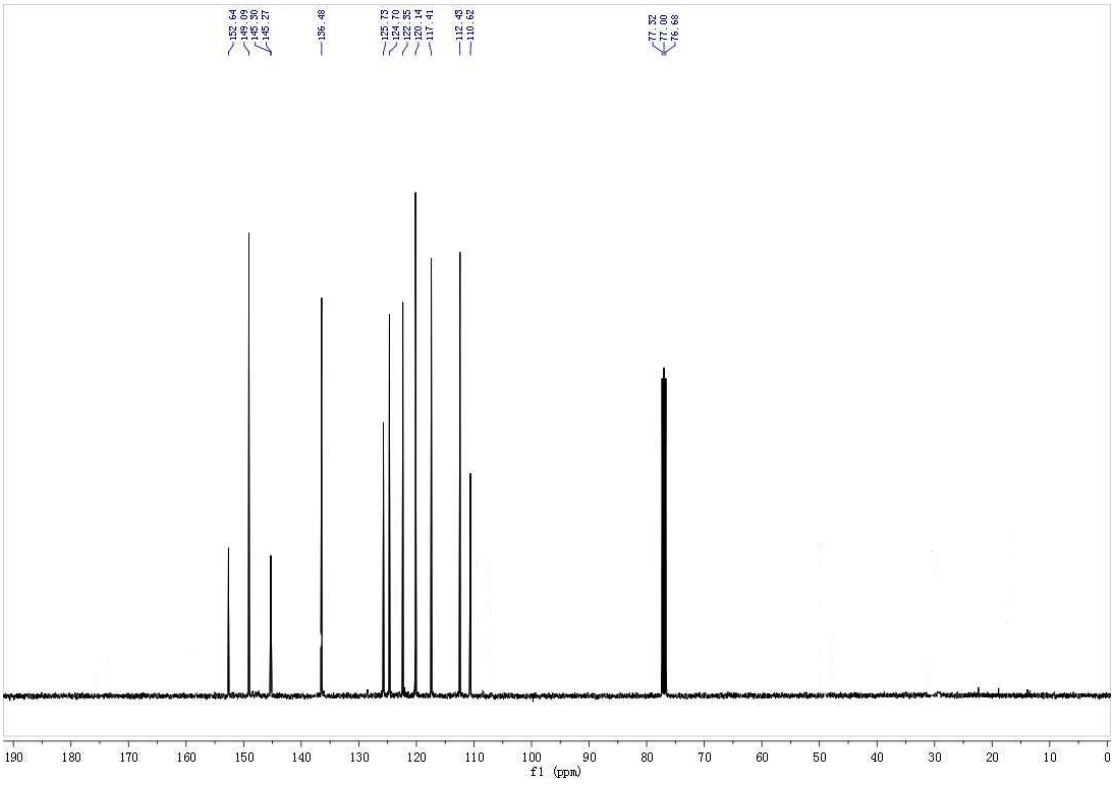
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112.48
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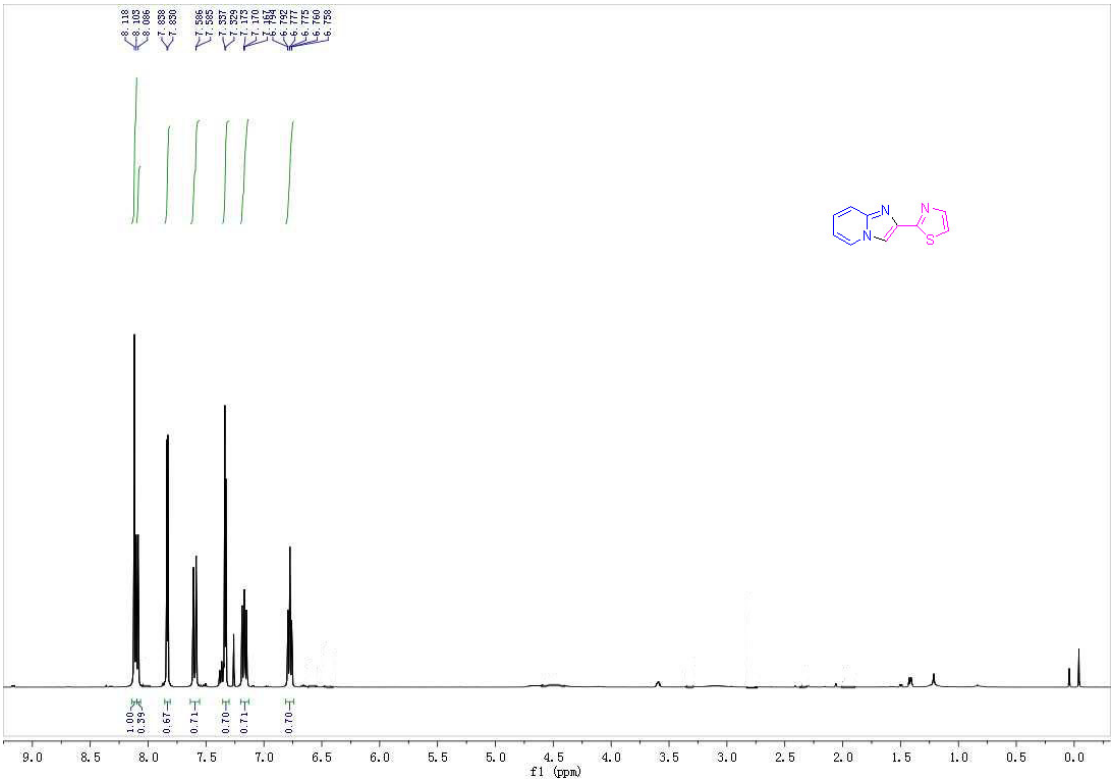
76.68
f1 (ppm)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7.170
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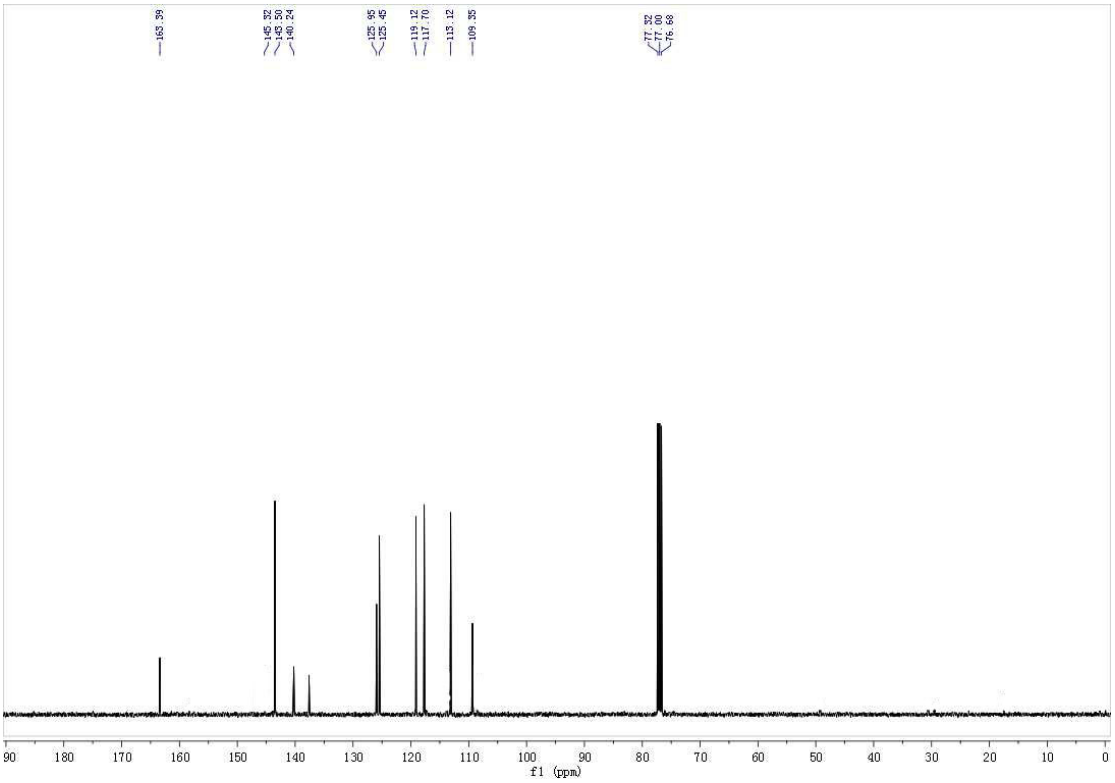
0.70
f1 (ppm)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117.70
113.12
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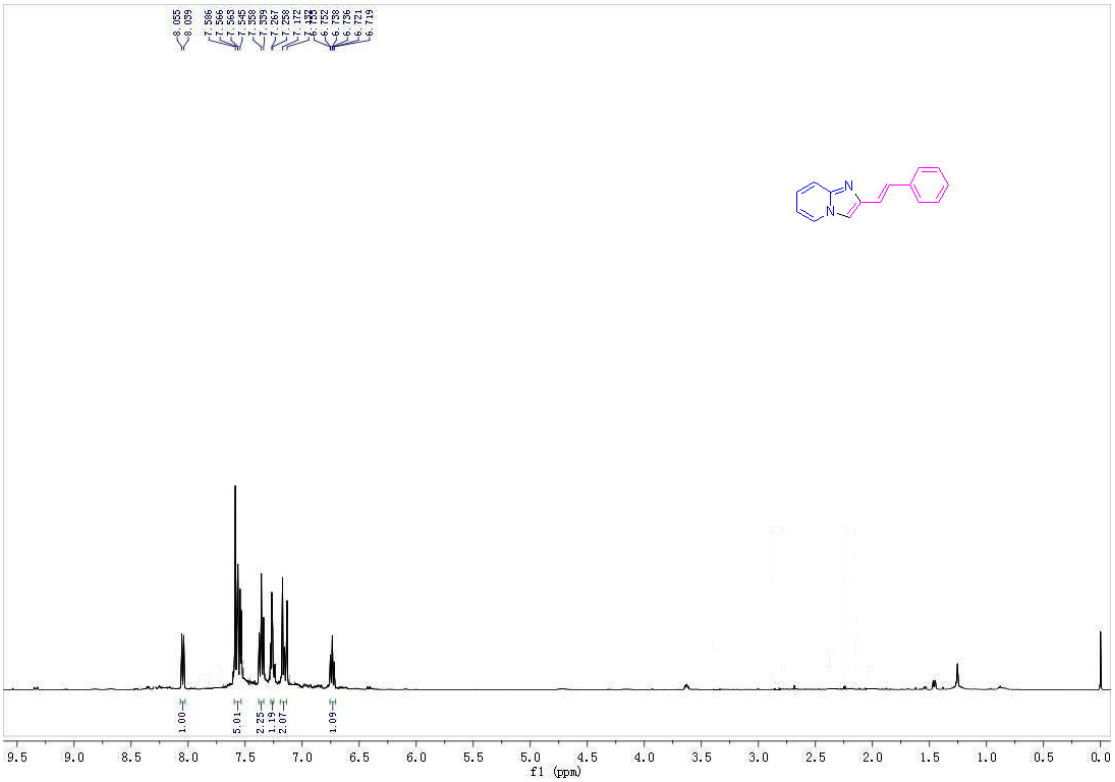
77.00
76.68
f1 (ppm)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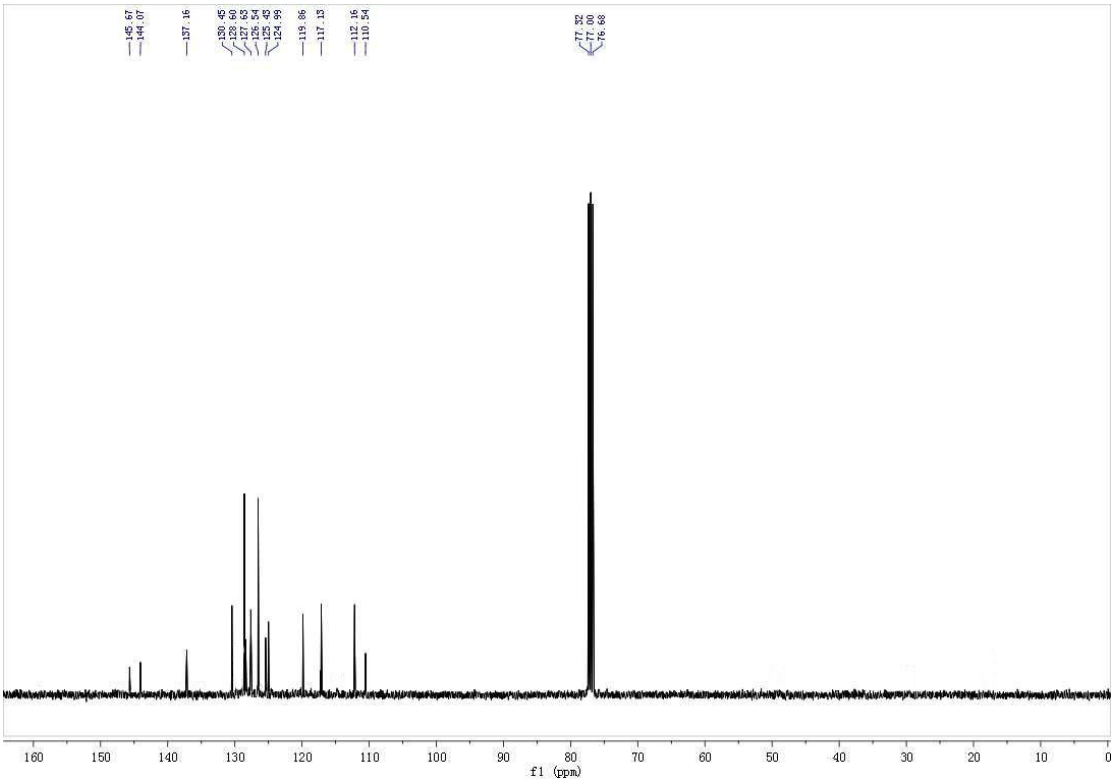
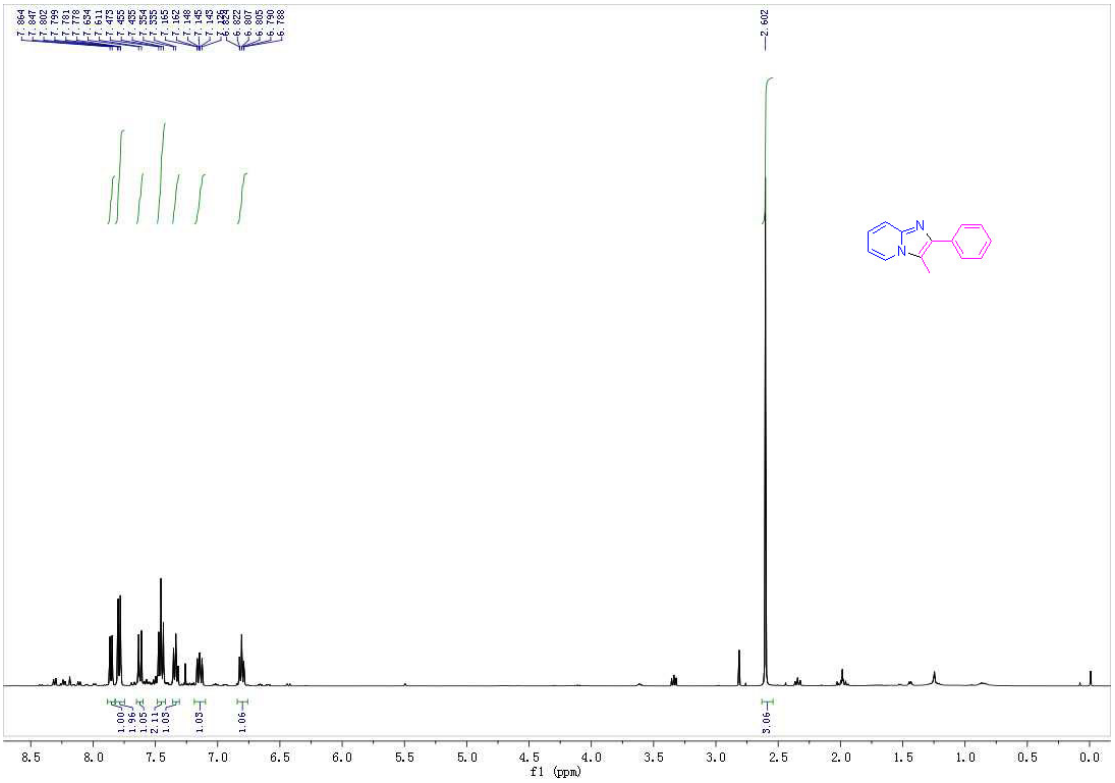
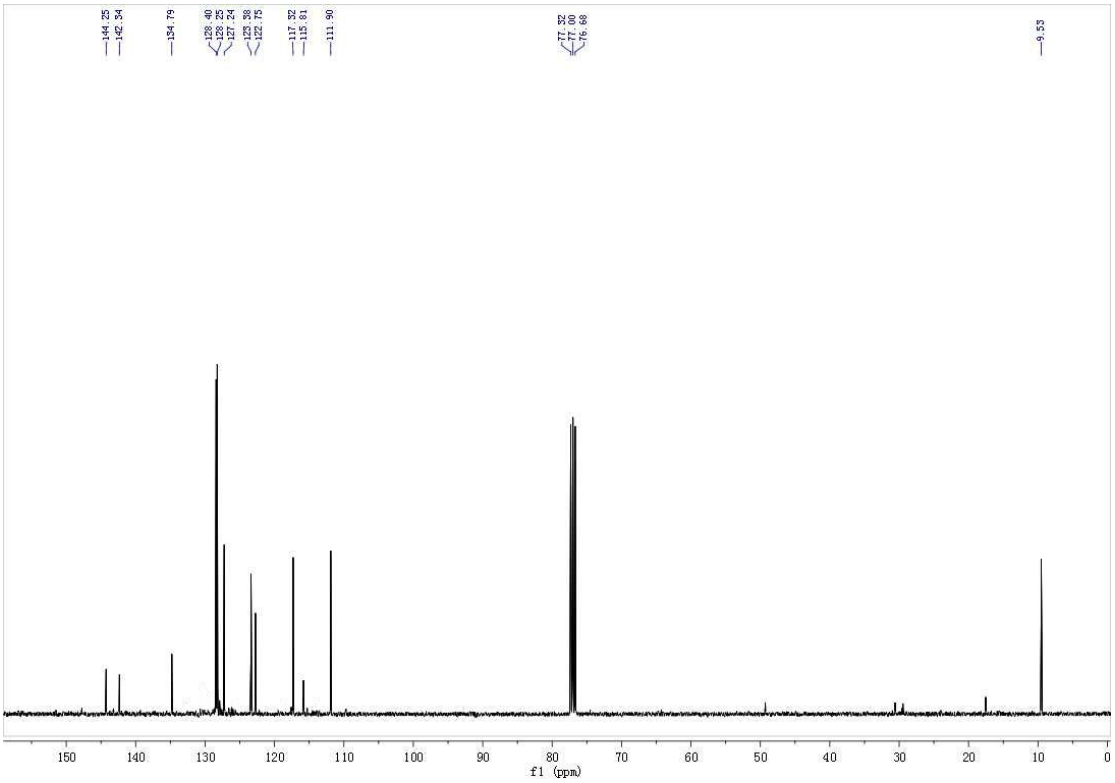
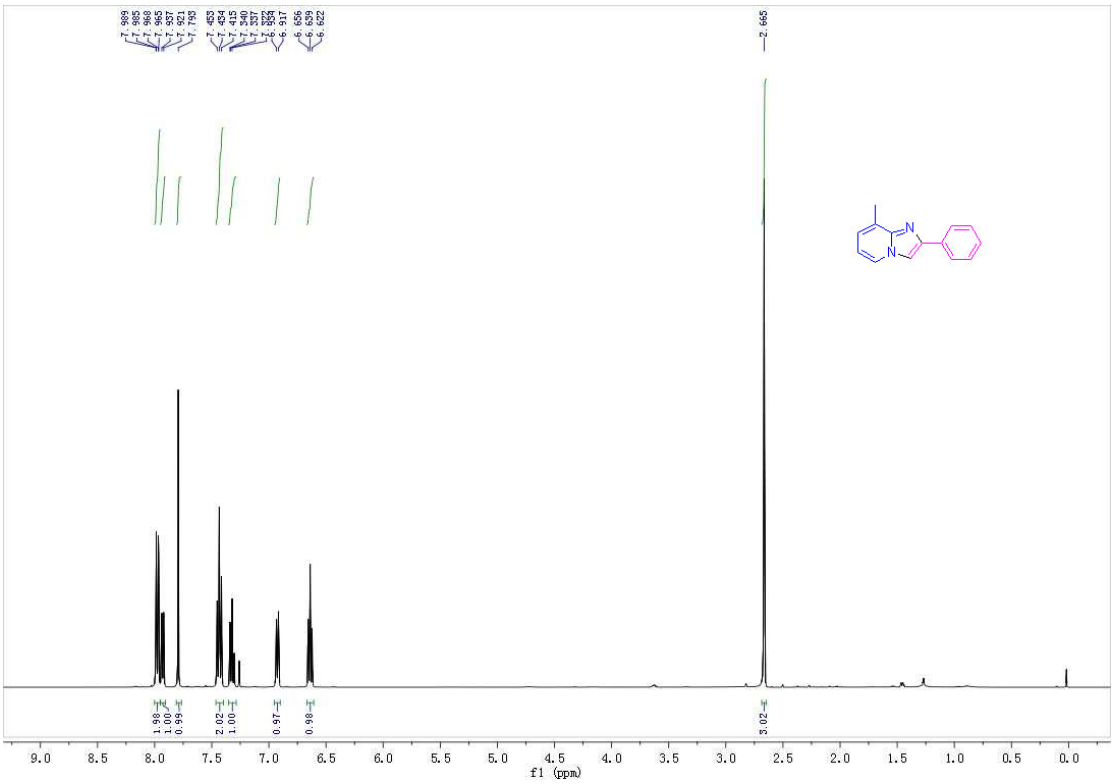
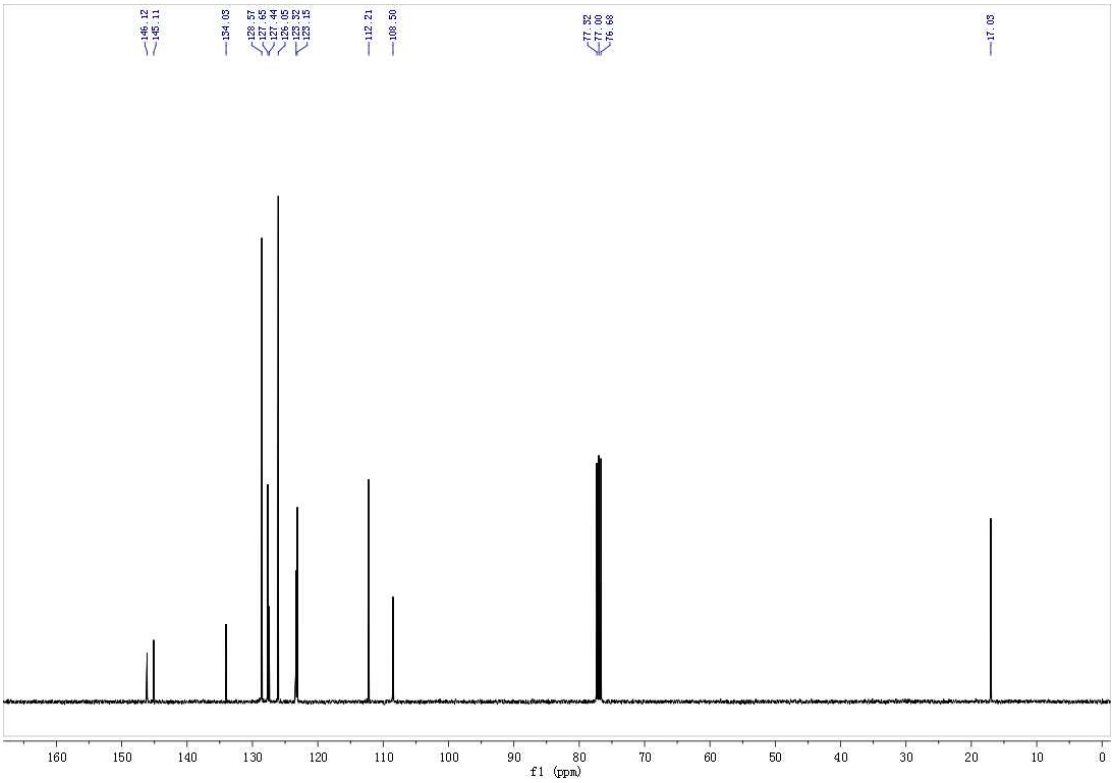
5.01
2.25
1.19
2.07
1.09
f1 (ppm)

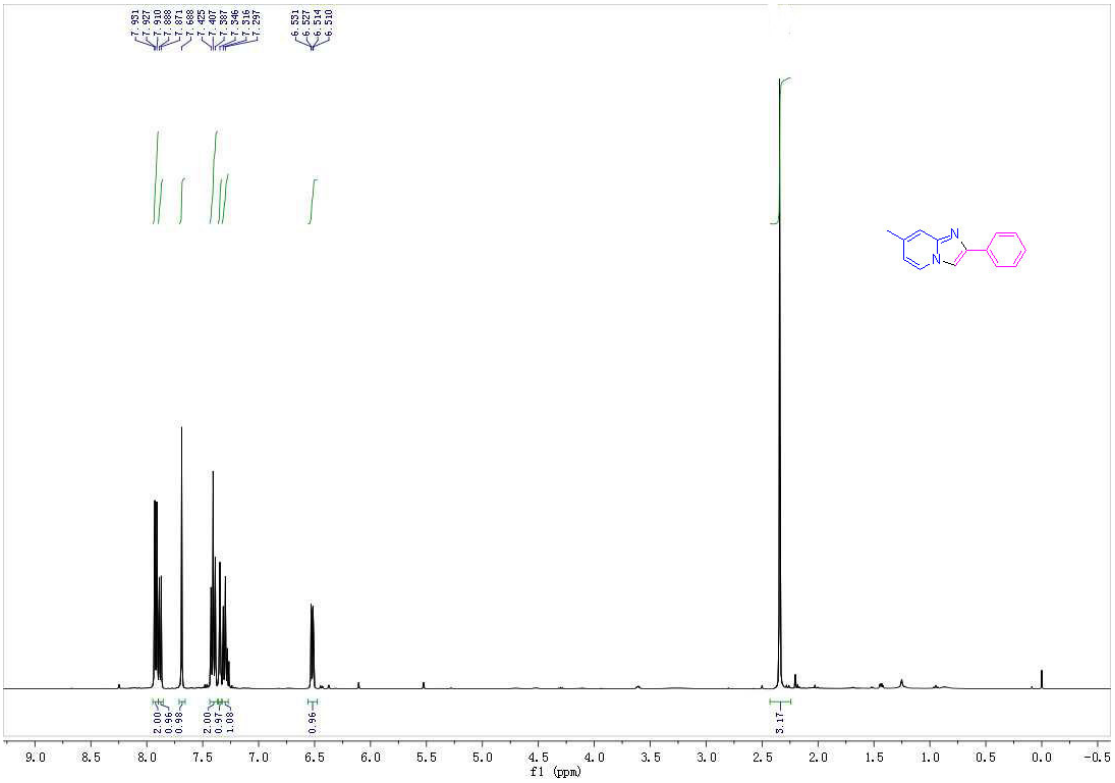

145.67
144.07
137.16
130.45
128.60
127.63
126.54
125.45
124.99
119.86
117.13
112.16
110.54
77.32
77.00
76.68
f1 (ppm)

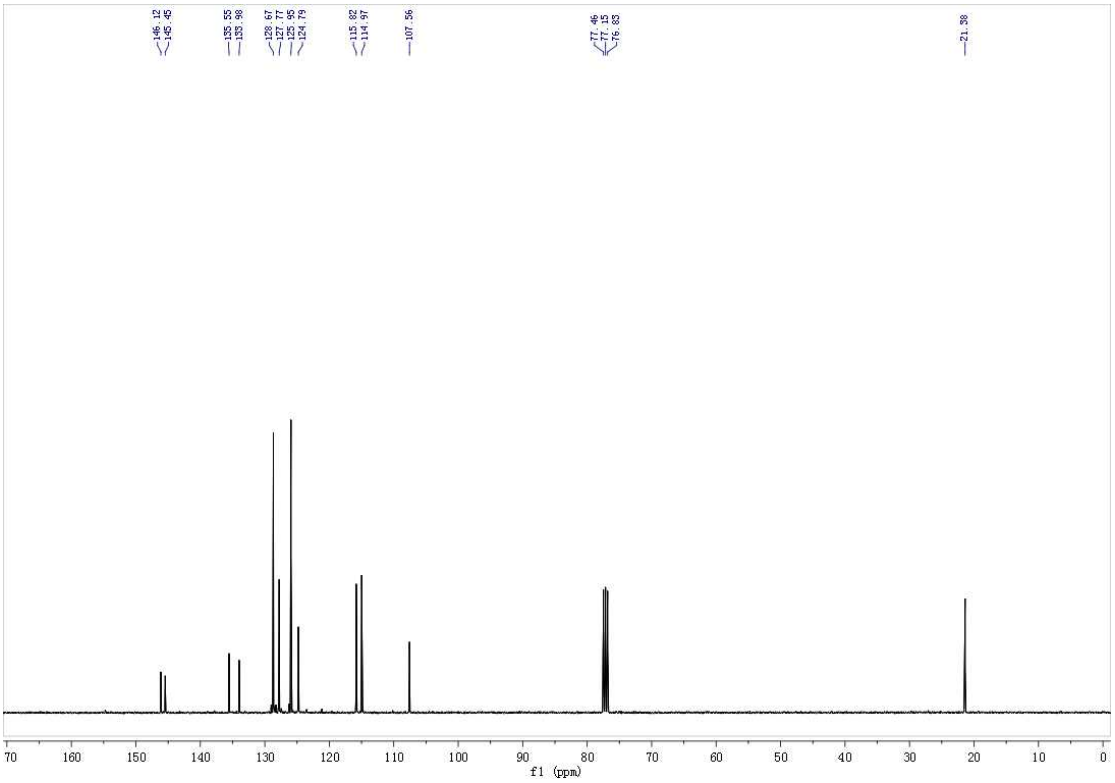

2.602
1.00
1.96
1.05
2.11
1.05
1.03
1.06
3.06
f1 (ppm)

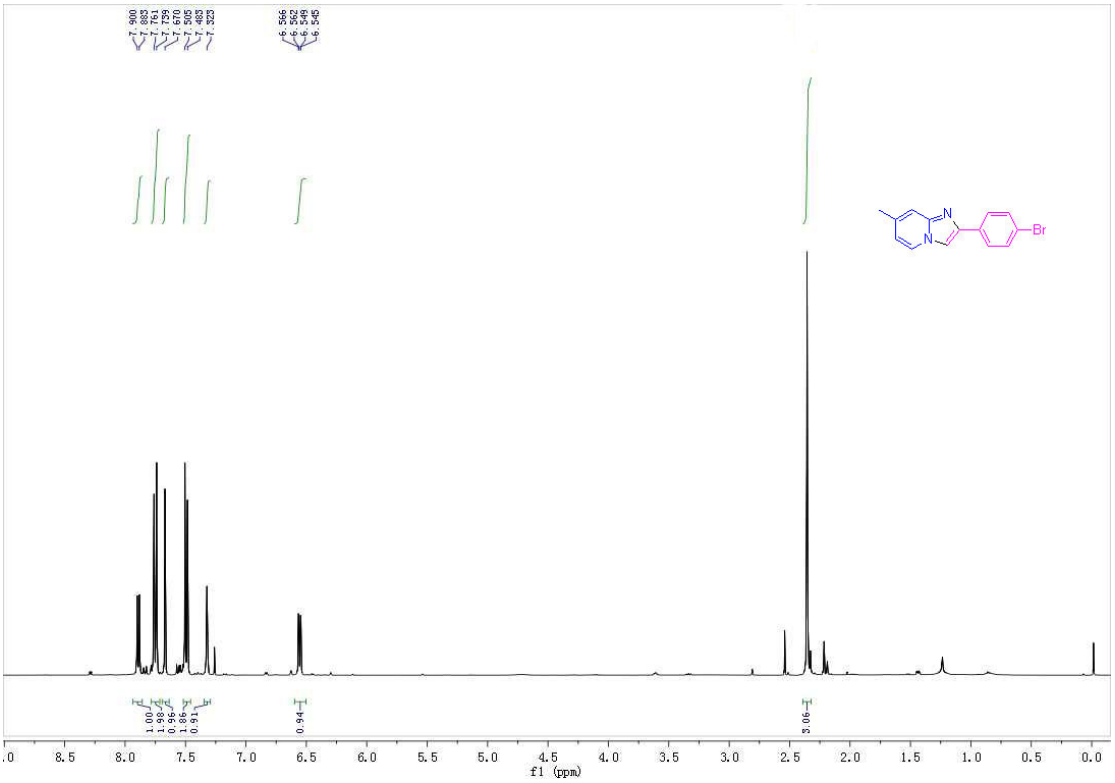

144.25
142.34
134.79
128.40
128.05
127.24
123.38
122.75
117.32
115.01
111.90
77.32
77.00
76.68
9.53
f1 (ppm)

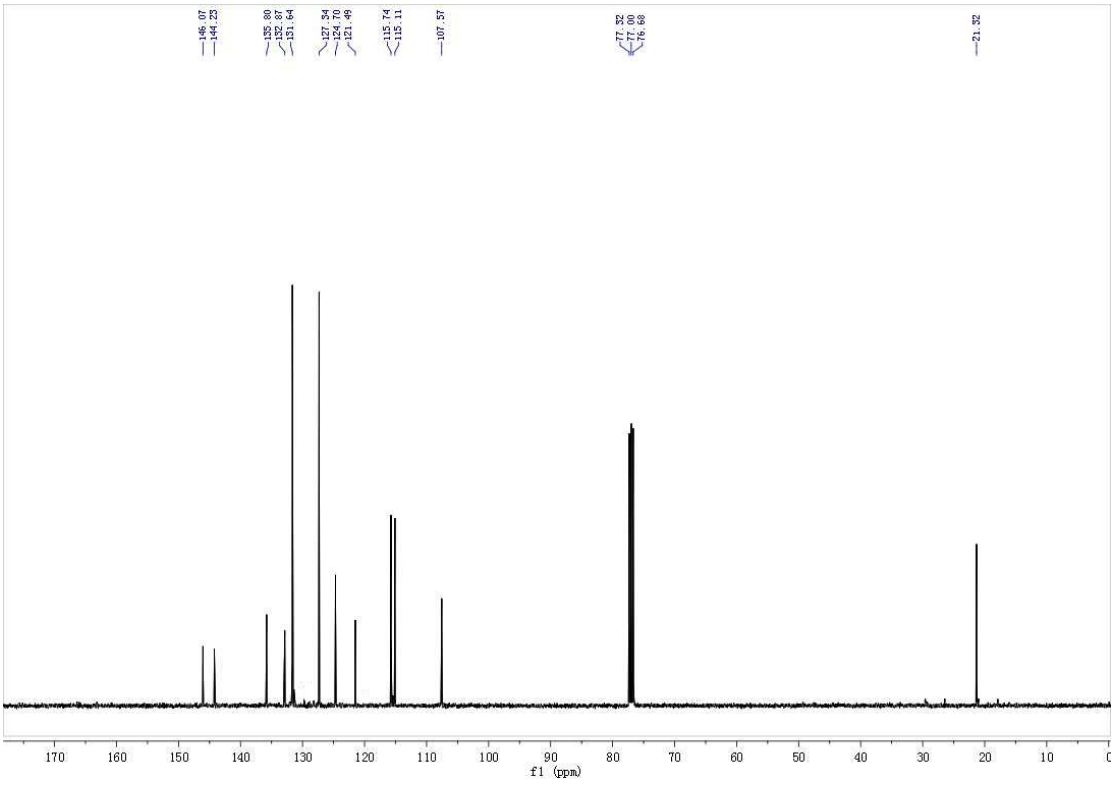

7.989
7.985
7.968
7.965
7.957
7.921
7.793
7.483
7.454
7.435
7.340
7.337
6.956
6.917
6.656
6.639
6.622
2.665
1.98
1.00
0.93
2.02
1.05
0.97
0.98
3.02
f1 (ppm)

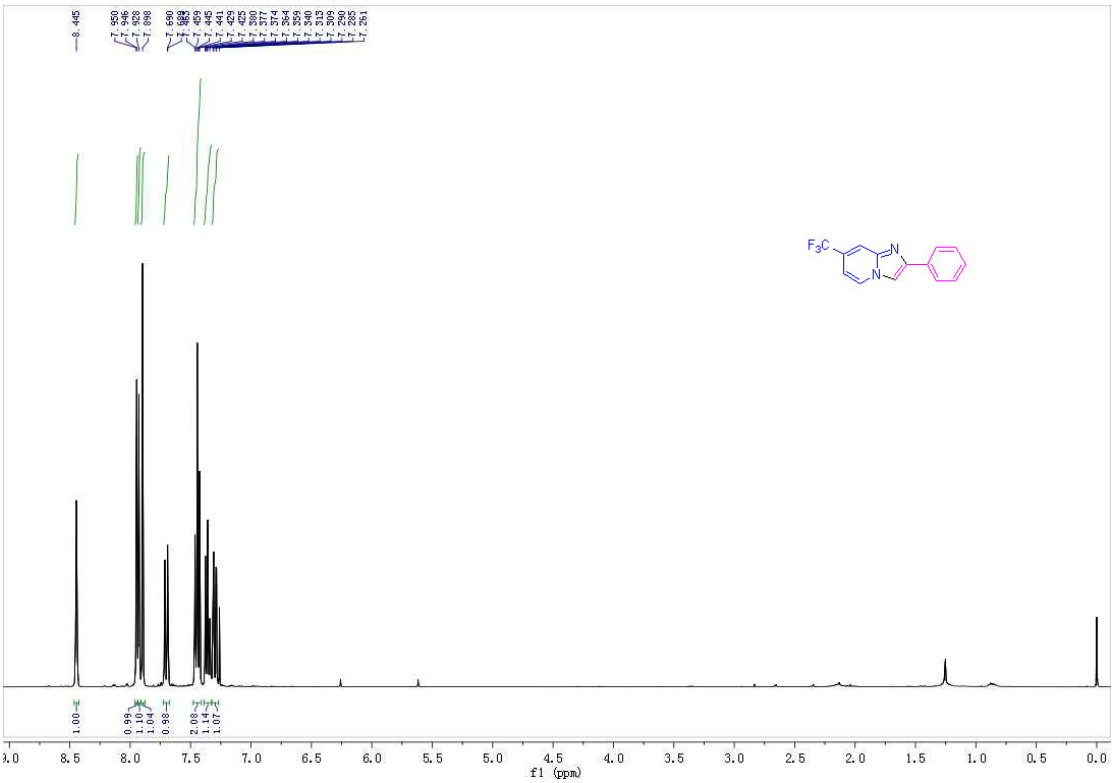

146.12
145.11
134.03
128.97
127.65
127.44
126.05
123.32
123.15
112.21
108.50
77.32
77.00
76.68
17.03
f1 (ppm)

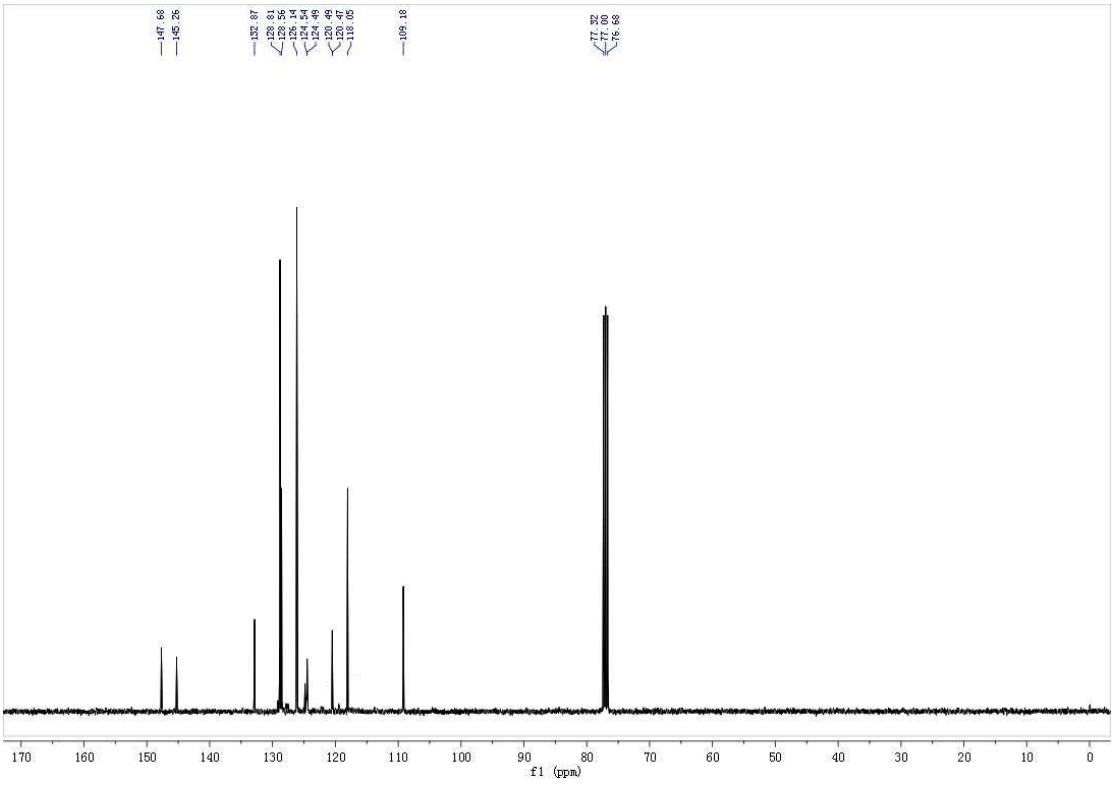

7.931
7.927
7.910
7.888
7.887
7.881
7.688
7.425
7.407
7.387
7.366
7.316
7.297
6.531
6.527
6.514
6.510
2.00
0.98
0.98
2.00
0.97
1.08
0.96
3.17
f1 (ppm)

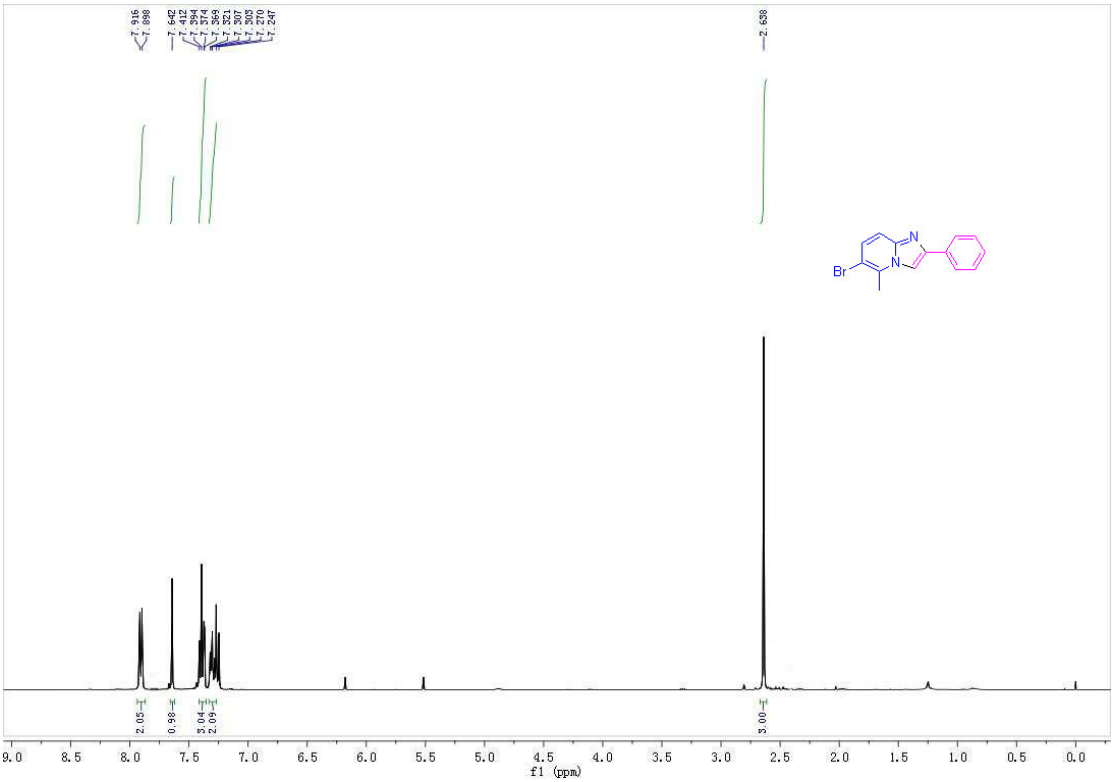

146.12
145.45
135.55
133.98
128.67
127.77
125.65
124.79
115.82
114.97
107.56
77.46
77.15
76.83
21.38
f1 (ppm)

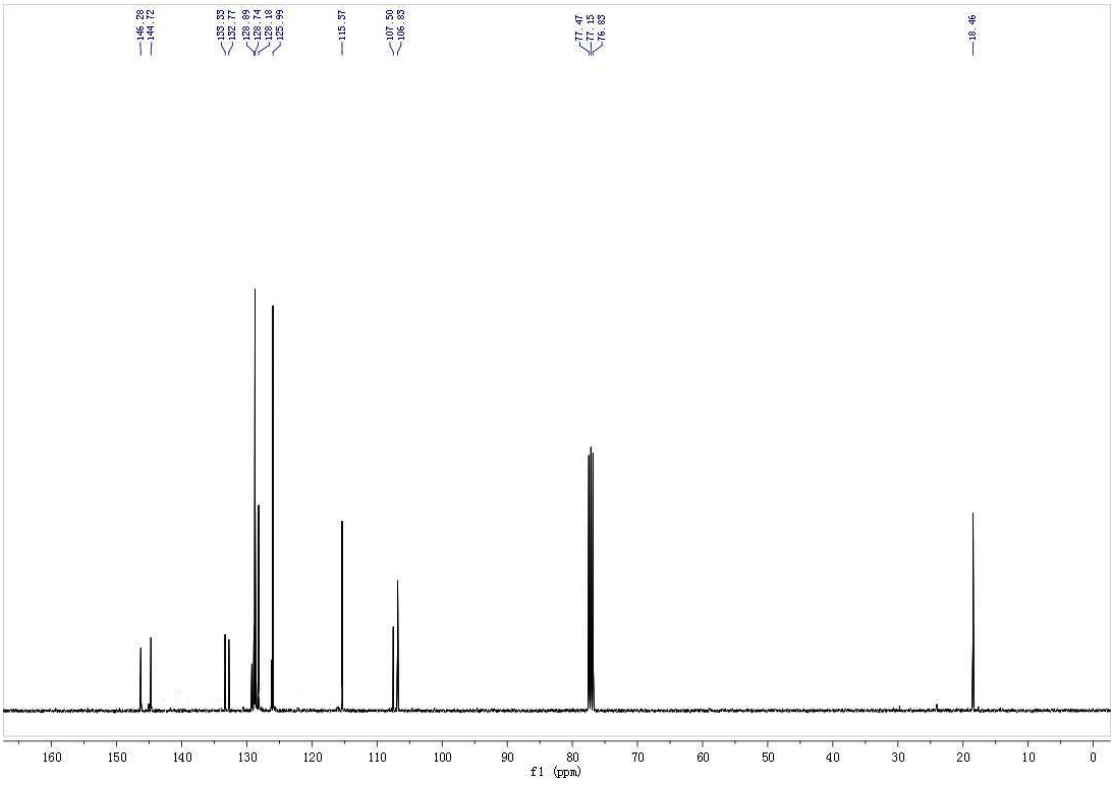

7.900
7.883
7.761
7.739
7.679
7.505
7.483
7.323
6.566
6.562
6.548
6.545
1.00
1.98
0.96
1.86
0.91
0.94
3.06
Br
f1 (ppm)

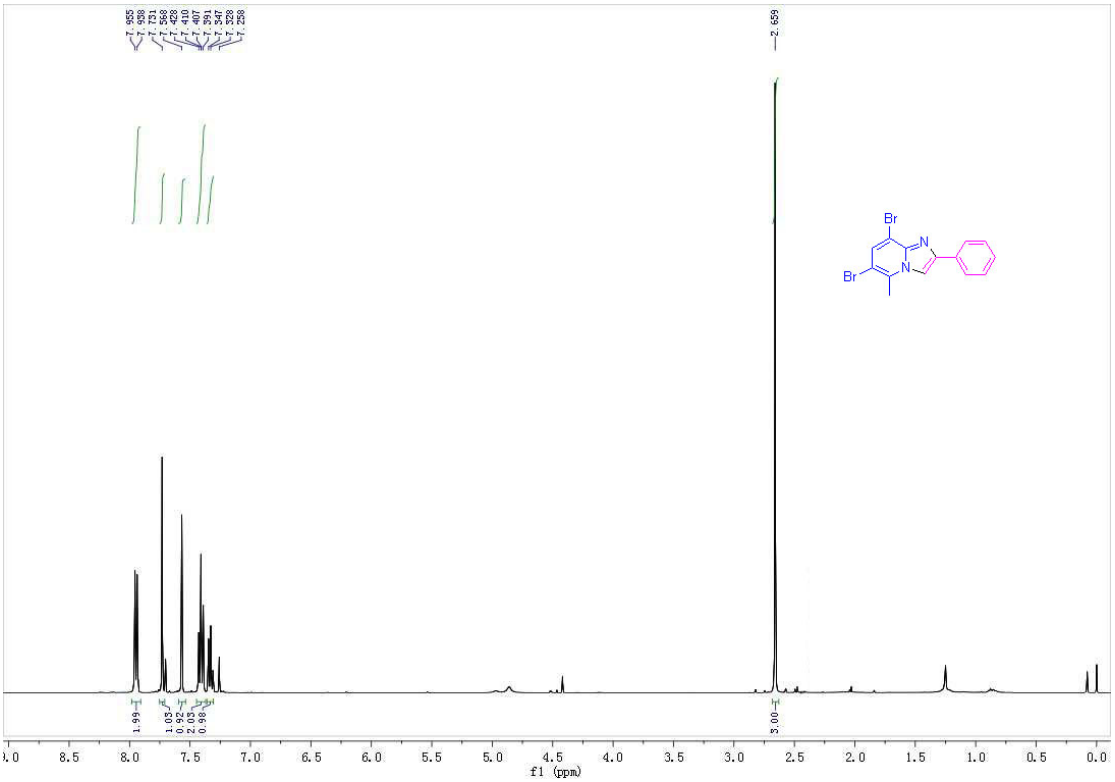

146.07
144.23
135.80
132.87
131.64
127.34
124.70
121.46
115.74
115.11
107.57
77.32
77.00
76.68
21.32
f1 (ppm)

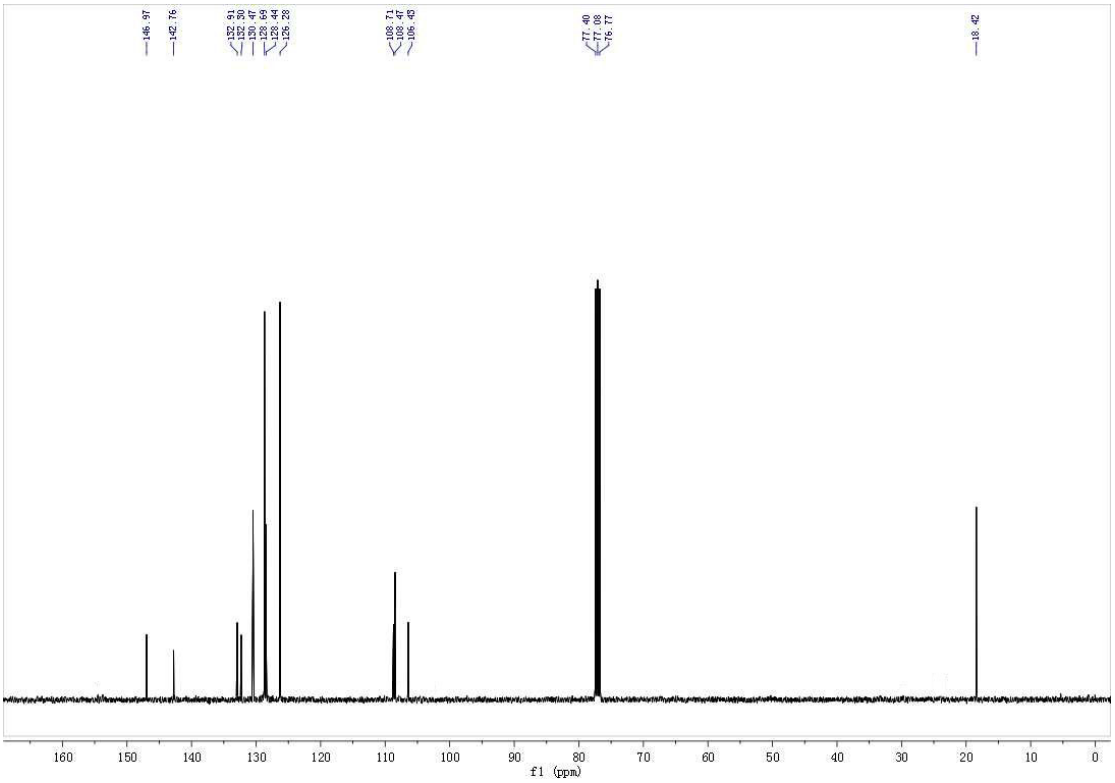

8.445
7.950
7.946
7.898
7.894
7.690
7.459
7.445
7.441
7.429
7.425
7.380
7.377
7.374
7.364
7.359
7.340
7.313
7.305
7.290
7.285
7.261
F3C
N
N
1.00
0.99
1.10
1.04
0.98
2.00
1.14
1.07
f1 (ppm)

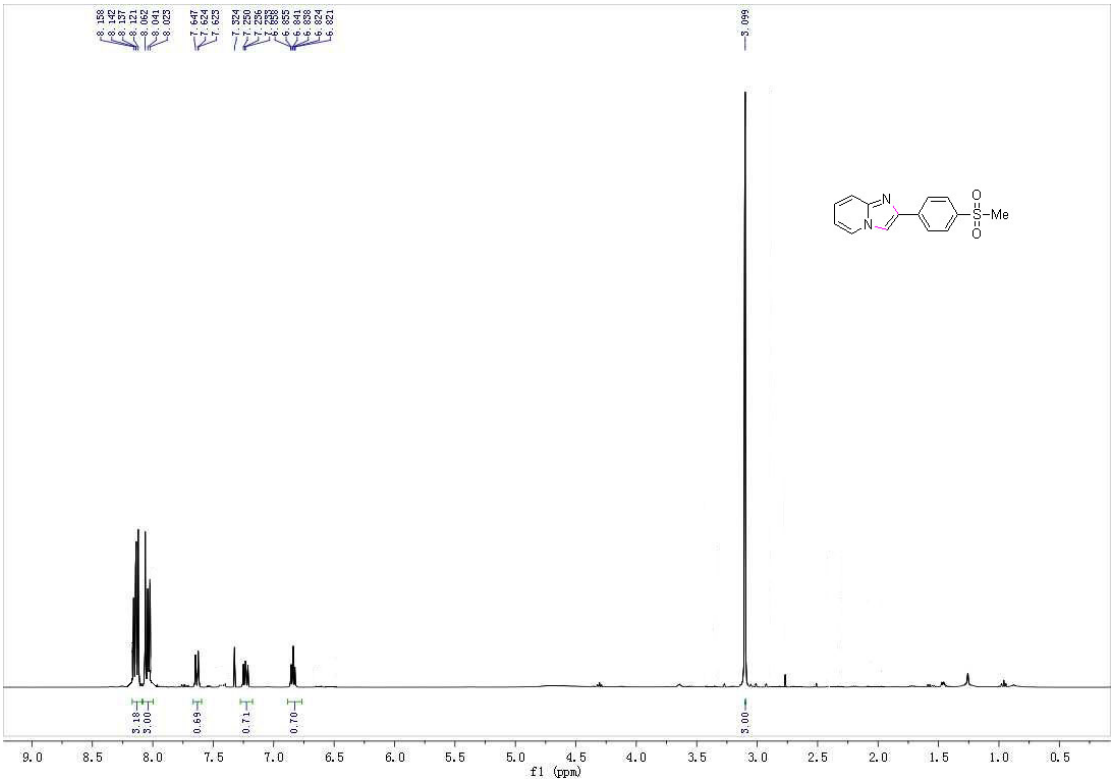

147.68
145.26
132.87
128.81
128.56
125.14
124.84
124.49
120.49
120.47
118.05
109.18
77.32
77.00
76.68
f1 (ppm)

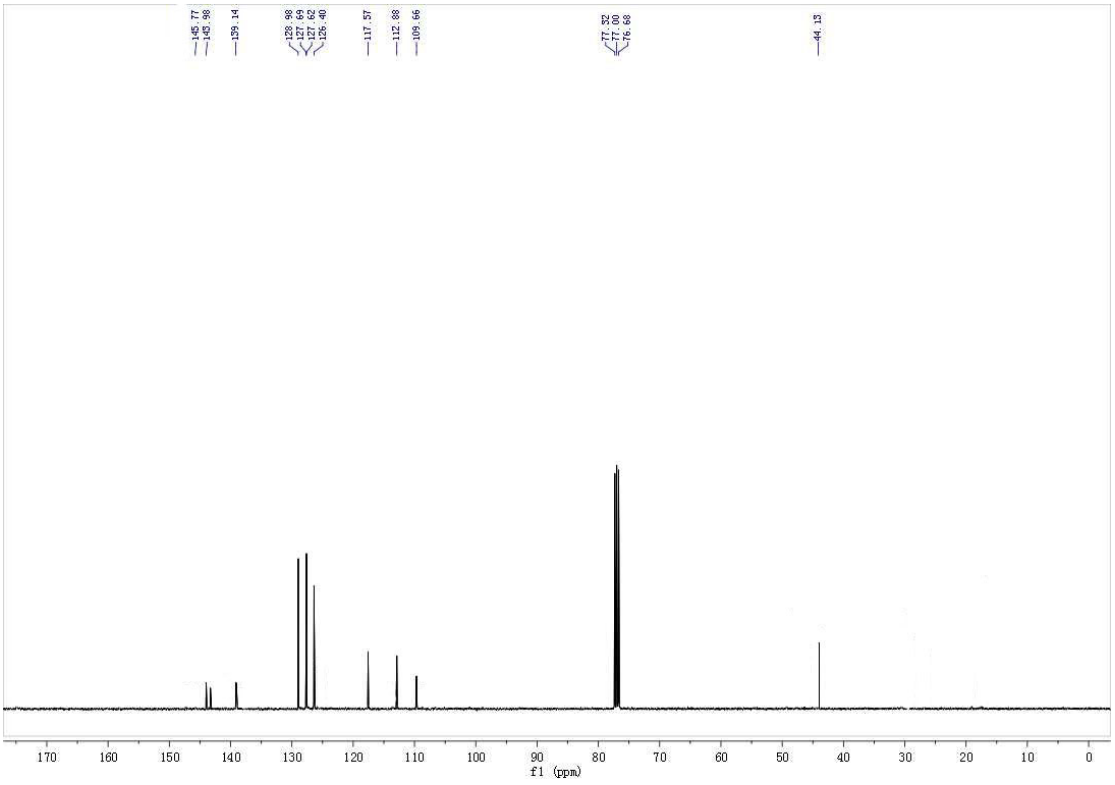

7.916
7.898
7.642
7.412
7.394
7.374
7.369
7.321
7.307
7.305
7.270
7.247
2.638
Br
N
2.05
0.98
3.04
2.09
3.00
f1 (ppm)


146.28
144.72
133.53
132.17
128.89
128.74
128.18
125.99
115.57
107.50
106.83
77.47
77.15
76.83
18.46
f1 (ppm)


7.955
7.938
7.731
7.568
7.428
7.410
7.407
7.391
7.341
7.328
7.258
2.659
Br
Br
N
N
1.99
1.05
0.92
2.15
0.98
3.00
f1 (ppm)


146.97
142.76
132.91
132.30
130.47
129.66
128.44
126.28
108.71
108.47
106.43
77.40
77.08
76.77
18.42
f1 (ppm)


8.158
8.142
8.137
8.121
8.062
8.041
8.025
7.647
7.624
7.623
7.334
7.250
7.236
6.855
6.841
6.838
6.824
6.821
3.099
3.18
3.00
0.69
0.71
0.70
3.00
Me
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
f1 (ppm)


145.77
145.96
139.14
128.98
127.69
127.62
126.40
117.57
112.88
109.66
77.32
77.00
76.68
44.13
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)