Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information

A Unique Annulation of 7-Azaindoles with Alkenyl Esters to Produce π-Conjugated 7-Azaindole Derivatives

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1. General Methods

NMR data were obtained for ^{1}H at 400 MHz or 600 MHz, and for ^{13}C at 101 MHz. Chemical shifts were reported in ppm from tetramethylsilane with the solvent resonance as the internal standard in $CDCl_3$ solution. ESI HRMS was recorded on a Waters SYNAPT G2 and Water XEVO G2 Q-ToF. UV detection was monitored at 220 nm. TLC was performed on glass-backed silica plates. Column chromatography was performed on silica gel (200-300 mesh), eluting with ethyl acetate and petroleum ether. All 7-azaindoles were commercially available. *N*-substituted 7-azaindoles were prepared according to the literature procedures.[1] Some electron-rich alkenes (**2a**, **2b**, **2c**, **2d**) were commercially available. Other electron-rich alkenes were prepared according to the literature procedures.[2]

2. General Procedure for Synthesis of Annulated 7-Azaindole Derivatives and Characterization Data

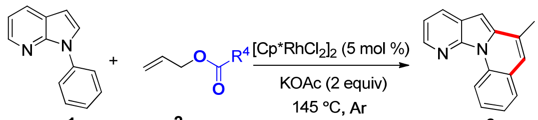
a. Synthesis of annulated 7-azaindole derivatives: 1-phenyl-1H-pyrrolo[2,3-b]pyridine **1a** (0.1 mmol, 19.4 mg), isopropenyl acetate **2a** (0.8 mL, 7 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 5.0 mol %) and KOAc (38.8 mg, 2 equiv) were stirred in seal tube at 145 °C for 80 h. After completion, the reaction mixture was purified by flash chromatography eluting with ethyl acetate and petroleum ether (1:200) to give the product **3aa** as a yellow solid (18.6 mg, 80%).

b. Synthesis of C-3 alkylated 7-azaindole derivative **4**: 6-methylpyrido[3',2':4,5]pyrrolo[1,2-a] quinoline **3aa** (0.05 mmol, 11.6 mg), nitorstyrene (14.9 mg, 2 equiv), $AlCl_3$ (2 mg, 0.3 equiv) were stirred in 0.6 mL DCM at room temperature for 36 h under air. After completion, the reaction mixture was purified by flash chromatography eluting with ethyl acetate and petroleum ether (1:40) to give the product **4** as a yellow solid (12.4 mg, 65%).

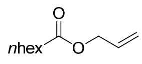
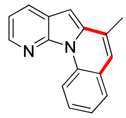
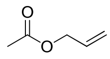
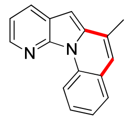
c. Synthesis of C-3 arylated 7-azaindole derivative **5**: 6-methylpyrido[3',2':4,5]pyrrolo[1,2-a] quinoline **3aa** (0.05 mmol, 11.6 mg), 1, 4-benzoquinone (10.8 mg, 2 equiv), 1,1'-binaphthyl-2,2'-diyl hydrogen-phosphate (1.7 mg, 0.1 equiv) were stirred in 0.6 mL DCM at room temperature for 6 h under air. After completion, the reaction mixture was purified by flash chromatography eluting with ethyl acetate and petroleum ether (1:8) to give the product **5** as a yellow solid (13.6 mg, 80%).

d. Synthesis of C-3 iodo-7-azaindole derivative **6**: 6-methylpyrido[3',2':4,5]pyrrolo[1,2-a] quinoline **3aa** (0.05 mmol, 11.6 mg), N-iodosuccinimide (12.3 mg, 1.1 equiv), KOH (8.4 mg, 3 equiv) were stirred in 0.6 mL CH_3CN at room temperature for 6 h under air. After completion, the reaction mixture was purified by flash chromatography eluting with ethyl acetate and petroleum ether (1:200) to give the product **6** as a yellow solid (17.5 mg, 98%).

SI 1 Scope of allyl acetates



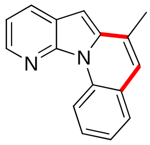
1a + **2** → **3aa**

entry	alkene **2**	product **3**[b]	entry	alkene **2**	product **3**[b]
1	 **2j**	 **3aa**, 25%	2	 **2k**	 **3aa**, 28%

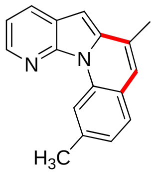
[a] General reaction conditions unless otherwise specified: 0.1 mmol of **1a**, 0.8 mL of **2**, 5 mol % of $[Cp^*RhCl_2]_2$, 2 equiv of KOAc, 145 °C, Ar atmosphere. [b] Isolated yield.

Allyl acetate **2j** and **2k** as coupling partners were also tolerated, giving **3aa** in 25% and 28% yields, respectively.

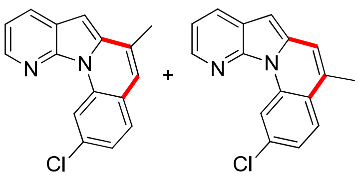
6-methylpyrido[3',2':4,5]pyrrolo[1,2-a]quinoline (**3aa**). 80 h, yellow solid, 80% yield; ^{1}H NMR (600 MHz, $CDCl_3$): δ 10.12 (d, J = 8.4 Hz, 1H), 8.57 (dd, J = 4.4, 1.2 Hz, 1H), 8.12 (dd, J = 7.9, 1.2 Hz, 1H), 7.63 (dd, J = 11.4, 4.1 Hz, 1H), 7.59 (d, J = 7.6 Hz, 1H), 7.37–7.30 (m, 2H), 7.03 (s, 1H), 6.67 (s, 1H), 2.47 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 145.4, 140.5, 136.2, 134.0, 127.2, 127.1, 126.2, 125.8, 122.7, 122.6, 122.3, 121.0, 116.9, 116.6, 90.9, 17.1 ppm. ESI HRMS: calcd. for $C_{16}H_{12}N_2$+H 233.1079, found 233.1071.



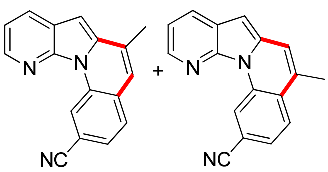
2,6-dimethylpyrido[3',2':4,5]pyrrolo[1,2-a]quinolone (**3ba**). 75 h, yellow solid, 94% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.95 (s, 1H), 8.57–8.55 (m, 1H), 8.11–8.08 (m, 1H), 7.45 (d, J = 8 Hz, 1H), 7.32–7.29 (m, 1H), 7.14 (d, J = 7.6 Hz, 1H), 6.98 (s, 1H), 6.62(s, 1H), 2.62 (s, 3H), 2.43 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 145.4, 140.3, 137.5, 136.4, 134.0, 126.9, 126.0, 124.5, 123.4, 122.6, 121.0, 120.3, 117.0, 116.5, 90.6, 21.2, 17.0 ppm. ESI HRMS: calcd. for $C_{17}H_{14}N_2$+H 247.1235, found 247.1236.



2-chloro-6-methylpyrido[3',2':4,5]pyrrolo[1,2-a]quinolone (**3ca**);
2-chloro-5-methylpyrido[3',2':4,5]pyrrolo[1,2-a]quinolone (**3ca'**); (**3ca/3ca'** = 5:1). 60 h, yellow solid, 71% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.17 (s, 1H), 8.55 (d, J = 4.4 Hz, 1H), 8.09 (d, J = 8 Hz, 1H), 7.49–7.44 (m, 1H), 7.34–7.30 (m, 1H), 7.27–7.26 (m, 1H), 6.93 (s, 1H), 6.64 (s, 1H), 2.43 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 146.4, 141.9, 136.8, 135.3, 133.6, 128.5, 128.3, 128.0, 127.1, 124.0, 123.6, 122.7, 122.2, 122.0, 119.3, 117.9, 117.9, 116.7, 92.6, 92.5, 18.5, 18.1 ppm. ESI HRMS: calcd. for $C_{16}H_{11}ClN_2$+H 267.0689, found 267.0690.

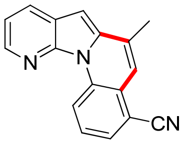


6-methylpyrido[3',2':4,5]pyrrolo[1,2-a]quinoline-2-carbonitrile (**3da**);
5-methylpyrido[3',2':4,5]pyrrolo[1,2-a]quinoline-2-carbonitrile (**3da'**); (**3da/3da'** = 1.4:1). 90 h, yellow solid, 61% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.29 (d, J = 18.8 Hz, 1H), 8.51–8.46 (m, 2H), 8.07– 8.01 (m, 2H), 7.57 (d, J = 8 Hz, 1H), 7.45–7.39 (m, 3H), 7.32–7.28 (m, 2H), 7.09 (s, 1H),6.82 (s, 1H), 6.60 (s, 1H), 6.48 (s, 1H), 2.39 (s, 6H) ppm; ^{13}C

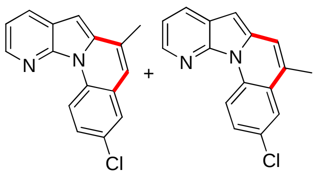


NMR (101 MHz, $CDCl_3$): δ 146.3, 146.0, 142.6, 141.9, 136.1, 135.5, 134.8, 134.3, 130.8, 130.0, 128.7, 128.4, 127.4, 127.3, 127.0, 126.0, 125.9, 124.8, 122.2, 122.1, 121.8, 121.7, 121.0, 119.4, 119.2, 118.2, 118.2, 111.3, 110.4, 93.9, 93.7, 19.2, 18.2 ppm. ESI HRMS: calcd. for $C_{17}H_{11}N_3$+H 258.1031, found 258.1038.

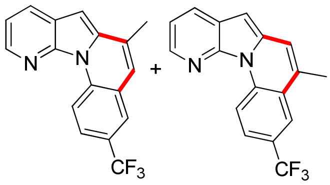
6-methylpyrido[3',2':4,5]pyrrolo[1,2-a]quinoline-4-carbonitrile (**3da''**). 90 h, yellow solid, 36% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.32–10.30 (m, 1H), 8.56–8.54 (m, 1H), 8.14–8.12 (m, 1H), 7.58–7.54 (m. 2H), 7.36–7.33 (m, 1H), 7.31 (s, 1H), 6.71 (s, 1H), 2.48 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 146.5, 142.5, 136.1, 135.1, 130.9, 128.9, 127.6, 127.6, 125.4, 122.3, 122.0, 119.4, 118.3, 117.7, 108.9, 93.8, 18.3 ppm. ESI HRMS: calcd. for $C_{17}H_{11}N_3$+Na 280.0851, found 280.0855.



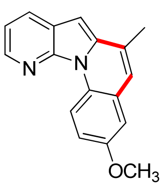
3-chloro-6-methylpyrido[3',2':4,5]pyrrolo[1,2-a]quinolone (**3ea**);
3-chloro-5-methylpyrido[3',2':4,5]pyrrolo[1,2-a]quinolone (**3ea'**); (**3ea/3ea'** = 3:2). 80 h, yellow solid, 74% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.03 (d, J = 9.2 Hz, 1H), 9.97 (d, J = 8.8 Hz, 1H), 8.53–8.51 (m, 1H), 8.48–8.47 (m, 1H), 8.09–8.07 (m, 1H), 8.04–8.02 (m, 1H), 7.61–7.60 (m, 1H),7.54–7.51 (m, 1H), 7.49–7.45 (m, 2H), 7.31–7.27 (m. 2H), 7.07 (s, 1H), 6.82 (s, 1H), 6.60 (s, 1H), 6.49 (s, 1H), 2.41 (s, 2H), 2.40 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 146.2, 145.9, 141.8, 141.2, 136.6, 135.3, 133.3, 130.3, 128.5, 128.3, 128.2, 128.0, 127.8, 126.2, 125.5, 125.1, 124.0, 122.3, 121.9, 119.5, 119.2, 118.9, 117.8, 92.8, 92.5, 19.2, 18.1 ppm. ESI HRMS: calcd. for $C_{16}H_{11}ClN_2$+H 267.0689, found 267.0692, 269.0668.



6-methyl-3-(trifluoromethyl)pyrido[3',2':4,5]pyrrolo[1,2-a]quinoline (**3fa**);
5-methyl-3-(trifluoromethyl)pyrido[3',2':4,5]pyrrolo[1,2-a]quinolone (**3fa'**); (**3fa/3fa'** = 3:2). 75 h, yellow solid, 73%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.18 (d, J = 8.8 Hz, 1H), 10.12 (d, J = 8.8 Hz, 1H), 8.54 (d, J = 4.4 Hz, 1H), 8.49 (d, J = 4.4 Hz, 1H), 8.09 (d, J = 8 Hz, 1H), 8.04 (d, J = 8 Hz, 1H), 7.88 (s, 1H), 7.82–7.75 (m, 3H), 7.34–7.29 (m, 2H), 7.08 (s, 1H), 6.91 (s, 1H), 6.62 (s, 1H), 6.50 (s, 1H), 2.46 (s, 2H), 2.43–2.40 (m, 4H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 146.5, 146.2, 142.1, 141.4, 137.9, 136.7, 135.4, 130.6, 128.5, 128.1, 125.7, 125.6, 125.3 (q, J = 4 Hz), 125.0 (q, J = 22.5 Hz), 124.4 (q, J = 3.5 Hz), 124.1 (q, J = 4 Hz), 123.9, 123.4, 122.9, 122.6, 122.5, 122.1, 121.4 (q, J = 3.9 Hz), 119.1, 118.4, 118.2, 118.1, 93.5, 93.1, 19.2, 18.1 ppm. ESI HRMS: calcd. for $C_{17}H_{11}F_3N_2$+Na 323.0772, found 323.0764.

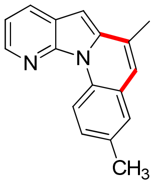


3-methoxy-6-methylpyrido[3',2':4,5]pyrrolo[1,2-a]quinoline (**3ga**). 50 h, yellow solid, 50% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.02 (d, J = 9.2 Hz, 1H), 8.55–8.53 (m, 1H), 8.12–8.10 (m, 1H), 7.31–7.28 (m, 1H), 7.23–7.16 (m, 1H), 7.06–7.05 (m, 1H), 6.98 (s, 1H), 6.65(s, 1H), 3.93–3.91 (m, 3H), 2.49–2.47 (m, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 154.3, 145.0, 140.5, 135.8, 128.5, 127.1, 126.4, 123.9, 122.4, 120.7, 118.1, 116.3, 114.3, 109.2, 90.5, 54.5, 17.1 ppm. ESI HRMS:

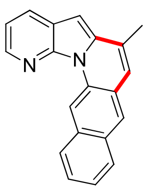


calcd. for $C_{17}H_{14}N_2O$+H 263.1184, found 263.1183.

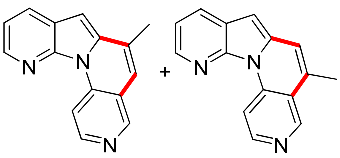
3,6-dimethylpyrido[3',2':4,5]pyrrolo[1,2-a]quinoline (**3ha**). 90 h, yellow solid, 68% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.94 (d, *J*= 8.4 Hz, 1H), 8.56–8.54 (m, 1H), 8.08(d, *J* = 8 Hz, 1H), 7.40 (d, *J* = 8.8 Hz, 1H), 7.32 –7.26(m, 2H), 6.91(s, 1H), 6.60(s, 1H), 2.46(s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 170.0, 150.2, 143.8, 142.9, 142.3, 136.7, 134.0, 130.7, 128.9, 128.0, 127.8, 126.5, 126.1, 124.6, 122.5, 116.8, 108.5, 94.0, 64.4, 45.3, 42.5, 30.3, 27.5, 18.9, 13.5 ppm. ESI HRMS: calcd. for $C_{17}H_{14}N_2$+H 247.1235, found 247.1233.



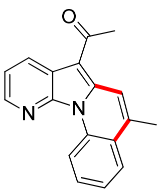
6-methylbenzo[g]pyrido[3',2':4,5]pyrrolo[1,2-a]quinolone (**3ia**). 80 h, yellow solid, 99% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.41 (s, 1H), 8.61 (d, *J* = 4.4 Hz, 1H), 8.12 (d, *J* = 8.4 Hz, 1H), 8.05 (d, *J* = 7.6 Hz, 1H), 7.89–7.84 (m, 2H), 7.52 (t, *J* = 8 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 1H), 7.31–7.26 (m, 1H), 6.97 (s, 1H), 6.61–6.60 (m, 1H), 2.38 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 147.4, 142.2, 137.0, 133.3, 132.9, 129.8, 128.3, 128.1, 127.4, 127.0, 126.0, 125.8, 124.8, 124.3, 123.9, 122.1, 117.4, 114.7, 94.0, 18.1 ppm. ESI HRMS: calcd. for $C_{20}H_{14}N_2$+H 283.1235, found 283.1237.



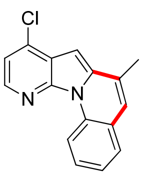
6-methylpyrido[3',2':4,5]pyrrolo[1,2-a][1,6]naphthyridine (**3ja**);
4-methylpyrido[3',2':4,5]pyrrolo[1,2-a][1,6]naphthyridine (**3ja'**); (**3ja/3ja'** = 2:1). 100 h, yellow solid, 30% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.84 (d, *J* = 5.2 Hz, 1H), 9.78 (d, *J* = 5.6 Hz, 1H), 8.97 (s, 1H), 8.81 (s, 1H), 8.74 (d, *J* = 5.2 Hz, 1H), 8.68 (d, *J* = 5.6 Hz, 1H), 8.57 (d, *J* = 4 Hz, 1H), 8.52 (d, *J* = 4.4 Hz, 1H), 8.12 (d, *J* = 7.6 Hz, 1H), 8.06 (d, *J* = 8 Hz, 1H), 7.69–7.64 (m, 1H), 7.54–7.53(m, 1H), 7.47–7.44 (m, 1H), 7.37–7.31 (m, 2H), 7.13 (s, 1H), 7.01 (s, 1H), 6.71 (s, 1H), 6.57 (s, 1H), 2.55 (s, 2H), 2.47 (s, 4H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 149.2, 148.8, 148.3, 146.8, 146.7, 142.5, 141.8, 139.5, 136.7, 135.3, 132.1, 132.0, 131.9, 129.9, 128.8, 128.6, 128.5, 128.4, 128.3, 122.5, 120.4, 119.3, 119.2, 118.5, 118.5, 111.8, 111.7, 94.2, 94.0, 18.6, 18.2 ppm. ESI HRMS: calcd. for $C_{15}H_{11}N_3$+H 234.1031, found 234.1023.



1-(5-methylpyrido[3',2':4,5]pyrrolo[1,2-a]quinolin-7-yl)ethanone (**3ka'**). 80 h, yellow solid, 77% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.37 (d, *J* = 8.8 Hz, 1H), 8.51 (d, *J* = 3.2 Hz, 1H), 8.46 (d, *J* = 7.6 Hz, 1H), 8.37 (s, 1H), 7.85 (d, *J* = 8 Hz, 1H), 7.74 (t, *J* = 7.6 Hz, 1H), 7.48 (t, *J* = 7.2 Hz, 1H), 7.42–7.39 (m, 1H), 2.75 (s, 3H) 2.64 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 193.0, 146.6, 141.9, 139.8, 139.0, 135.0, 130.1, 128.8, 124.7, 124.6, 124.4, 121.2, 119.7, 119.5, 117.9, 105.2, 31.7, 20.0 ppm. ESI HRMS: calcd. for $C_{18}H_{14}N_2O$+H 275.1184, found 275.1186.

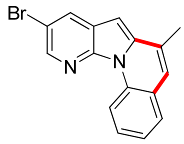


8-chloro-6-methylpyrido[3',2':4,5]pyrrolo[1,2-a]quinolone (**3ma**). 80 h, yellow solid, 55% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.04 (d, *J* = 8 Hz, 1H), 8.43 (d, *J* = 5.2 Hz, 1H), 7.64–7.59 (m, 2H), 7.38–7.35 (m, 2H), 7.08 (s, 1H), 6.77 (s, 1H), 4.94 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 141.5, 137.6, 135.1, 134.8, 128.4, 127.4, 126.7, 124.4, 123.8, 123.8, 121.4, 118.0, 117.6, 90.4, 18.1 ppm. ESI HRMS:



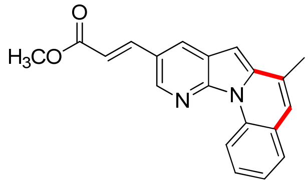
calcd. for $C_{16}H_{11}ClN_2$+H 267.0689, found 267.0693, 267.0664.

9-bromo-6-methylpyrido[3',2':4,5]pyrrolo[1,2-a]quinoline (**3na**). 80 h, yellow solid, 60% yield;



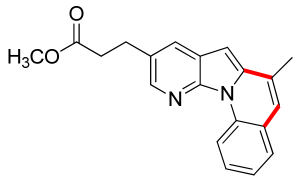
^{1}H NMR (400 MHz, $CDCl_3$): δ 9.82 (d, *J* = 8.4 Hz, 1H), 8.42 (s, 1H), 8.06 (s, 1H), 7.51–7.46 (m, 2H), 7.26–7.24 (m, 1H), 6.93 (s, 1H), 6.42 (s, 1H), 2.33 (s, 3H) ppm; ^{13}CNMR (101 MHz,$CDCl_3$): δ 144.5, 141.8, 138.4, 134.6, 129.8, 128.4, 127.4, 126.5, 124.4, 123.6, 123.6, 117.8, 113.7, 91.3, 18.1 ppm. ESI HRMS: calcd. for $C_{16}H_{11}BrN_2$+H 311.0184, found 311.01753, 313.0160.

(E)-methyl 3-(6-methylpyrido[3',2':4,5]pyrrolo[1,2-a]quinolin-9-yl)acrylate (**3oa**). 90 h, yellow



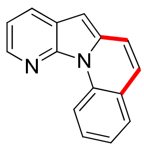
solid, 92% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.99 (d, *J* = 12 Hz, 1H), 8.66 (s, 1H), 8.20 (s, 1H), 7.89 (d, *J* = 16 Hz, 1H), 7.63–7.56 (m, 2H), 7.34 (t, *J* = 7.2 Hz, 1H), 7.02 (s, 1H), 6.59 (t, *J* = 19.6 Hz, 2H), 3.85 (s, 3H), 2.44 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 167.4, 146.9, 143.1, 142.1, 138.5, 134.6, 128.4, 127.4, 126.7, 126.7, 124.2, 124.1, 123.8, 121.9, 118.0, 117.1, 92.4, 51.7, 18.1 ppm. ESI HRMS: calcd. for $C_{20}H_{16}N_2O_2$+H 317.1290, found 317.1284.

methyl 3-(6-methylpyrido[3',2':4,5]pyrrolo[1,2-a]quinolin-9-yl)propanoate (**3pa**). 90 h, yellow



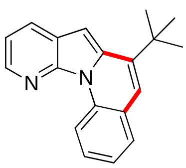
solid, 82% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.03 (d, *J* = 8.4 Hz, 1H), 8.40 (s, 1H), 7.92 (s, 1H), 7.61–7.55 (m, 2H), 7.31 (t, *J* = 6.8 Hz, 1H), 7.00 (s, 1H), 6.58 (s, 1H), 3.67 (s, 3H), 3.17–3.13 (m, 2H), 2.76–2.72 (m, 2H), 2.44 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 173.1, 145.5, 142.1, 137.6, 135.0, 129.6, 128.2, 127.4, 127.3, 126.8, 123.6, 123.6, 123.2, 122.0, 118.0, 117.7, 91.8, 91.6, 51.7, 36.2, 28.5, 18.1 ppm. ESI HRMS: calcd. for $C_{20}H_{18}N_2O_2$+H 319.1447, found 319.1447.

pyrido[3',2':4,5]pyrrolo[1,2-a]quinoline (**3ab**). 75 h, yellow solid, 42% yield; ^{1}H NMR (600 MHz,



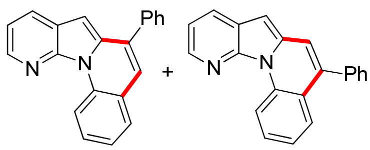
$CDCl_3$): δ 10.12 (d, *J* = 8.4 Hz, 1H), 8.56 (d, *J* = 4.1 Hz, 1H), 8.10 (d, *J* = 7.8 Hz, 1H), 7.66 (t, *J* = 7.8 Hz, 1H), 7.62 (d, *J* = 7.6 Hz, 1H), 7.37–7.29 (m, 3H), 7.19 (d, *J* = 9.4 Hz, 1H), 6.66 (s, 1H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 146.1, 141.6, 136.1, 135.8, 129.2, 128.2, 128.0, 125.4, 123.5, 123.4, 122.2, 118.8, 118.2, 117.7, 93.6 ppm. ESI HRMS: calcd. for $C_{15}H_{10}N_2$+H 219.0922, found 219.0915.

6-(tert-butyl)pyrido[3',2':4,5]pyrrolo[1,2-a]quinolone (**3ac**). 90 h, yellow oil, 45% yield; ^{1}H NMR



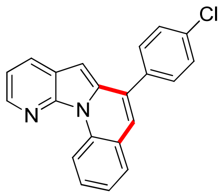
(400 MHz, $CDCl_3$): δ 10.20 (d, *J* = 8.8 Hz, 1H), 8.57–8.56 (m, 1H), 8.14–8.12 (m, 1H), 7.64–7.61 (m, 2H), 7.35–7.30 (m, 2H), 7.15 (s, 1H), 6.95 (s, 1H), 1.61–1.56 (m, 9H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 145.6, 141.6, 139.0, 134.9, 128.6, 128.0, 123.5, 123.3, 121.6, 121.2, 117.9, 117.6, 95.9, 35.5, 29.8 ppm. ESI HRMS: calcd. for $C_{19}H_{18}N_2$+H 275.1548, found 275.1540.

6-phenylpyrido[3',2':4,5]pyrrolo[1,2-a]quinoline (**3ad**);
5-phenylpyrido[3',2':4,5]pyrrolo[1,2-a]quinoline (**3ad'**); (**3ad**/**3ad**' = 18:1). 90 h, yellow solid, 44% yield; ^{1}H NMR (600 MHz, $CDCl_3$): δ 10.19 (d, *J* = 8.8 Hz, 1H), 8.59 (dd, *J* = 4.4, 1.1 Hz, 1H),



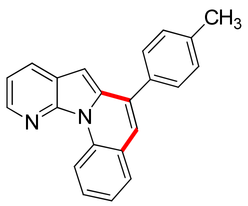
8.08 (dd, J = 7.8, 1.1 Hz, 1H), 7.73 (d, J = 7.3 Hz, 2H), 7.67 (dt, J = 7.1, 3.5 Hz, 2H), 7.53 (t, J = 7.5 Hz, 2H), 7.47 (t, J = 7.4 Hz, 1H), 7.37 (t, J = 7.4 Hz, 1H), 7.32 (dd, J = 7.8, 4.6 Hz, 1H), 7.19 (s, 1H), 6.75 (s, 1H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ146.5, 141.8, 138.3, 135.9, 135.4, 132.2, 129.0, 128.7, 128.5, 128.3, 128.2, 124.3, 123.7, 123.5, 122.0, 118.1, 117.7, 94.3 ppm. ESI HRMS: calcd. for $C_{21}H_{14}N_2$+H 295.1235, found 295.1239.

6-(4-chlorophenyl)pyrido[3',2':4,5]pyrrolo[1,2-a]quinolone (**3ae**). 90 h, yellow solid, 38% yield;



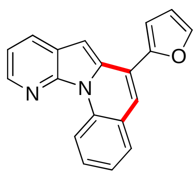
^{1}H NMR (400 MHz, $CDCl_3$): δ 10.18 (d, J = 8.4 Hz, 1H), 8.60–8.58 (m, 1H), 8.09–8.07 (m, 1H), 7.70–7.65 (m, 4H), 7.49 (d, J = 8.4 Hz, 2H), 7.38–7.31 (m, 2H), 7.16 (s, 1H), 6.70 (s, 1H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 146.5, 142.0, 136.7, 135.6, 135.4, 134.2, 131.0, 129.8, 129.3, 128.9, 128.4, 128.2, 124.5, 123.6, 123.5, 122.0, 118.1, 117.9, 94.2 ppm. ESI HRMS: calcd. for $C_{21}H_{13}ClN_2$+H 329.0846, found 329.0838, 331.0824.

6-(p-tolyl)pyrido[3',2':4,5]pyrrolo[1,2-a]quinolone (**3af**). 90 h, yellow solid, 42% yield;



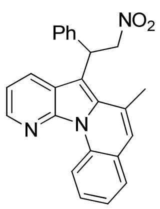
^{1}H NMR (400 MHz, $CDCl_3$): δ 10.18 (d, J = 8.8Hz, 1H), 8.59–8.58 (m, 1H), 8.09–8.07 (m, 1H), 7.69–7.66 (m, 2H), 7.66–7.62 (m, 2H), 7.38–7.30 (m, 4H), 7.18(s, 1H), 6.76 (s, 1H), 2.47 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 146.5, 141.8, 138.2, 136.1, 135.4, 135.4, 132.2, 129.4, 128.9, 128.3, 128.3, 128.1, 124.1, 123.8, 123.5, 122.1, 118.1, 117.7, 94.3, 21.3 ppm. ESI HRMS: calcd. for $C_{22}H_{16}N_2$+H 309.1392, found 309.1382.

6-(furan-2-yl)pyrido[3',2':4,5]pyrrolo[1,2-a]quinoline (**3ag**). 50 h, yellow solid, 35% yield;

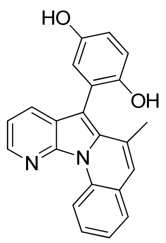


^{1}H NMR (400 MHz, $CDCl_3$): δ 10.20 (d, J = 8.4 Hz, 1H), 8.60-8.58 (m, 1H), 8.15 (d, J = 1.6 Hz, 1H), 7.70-7.64 (m, 2H), 7.62 (d, 1.6Hz, 1H), 7.61 (s, 1H), 7.38-7.33 (m, 2H), 7.19 (s, 1H), 6.99 (d, 3.6 Hz, 1H), 6.62-6.61 (m, 1H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 150.9, 146.3, 142.4, 142.0, 135.3, 132.8, 129.3, 128.5, 128.4, 123.6, 123.1, 122.1, 122.0, 120.9, 118.1, 117.9, 111.6, 108.6, 94.4 ppm. ESI HRMS: calcd. for C19H13N2O 285.1028, found 285.1026.

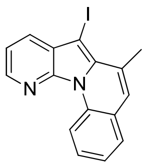
6-methyl-7-(2-nitro-1-phenylethyl)pyrido[3',2':4,5]pyrrolo[1,2-a]quinolone (**4**). 36 h, yellow solid, 65% yield;



^{1}H NMR (400 MHz, $CDCl_3$): δ 10.24 (d, J = 8.8 Hz, 1H), 8.56–8.54 (m, 1H), 7.78–7.75 (m, 1H), 7.64–7.62 (m, 1H), 7.60–7.56(m, 1H), 7.36–7.27 (m, 4H), 7.25–7.24 (m, 1H), 7.23–7.18 (m, 1H), 7.07 (s, 1H), 6.15 (t, J = 8 Hz, 1H), 5.42–5.37 (m, 1H), 5.27–5.22 (m, 1H), 2.80 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 146.1, 142.1, 139.6, 135.2, 134.1, 129.0, 128.8, 127.6, 127.5, 127.2, 127.1, 126.5, 123.6, 123.3, 120.5, 118.4, 117.5, 103.5, 99.9, 79.2, 40.0, 22.1 ppm. ESI HRMS: calcd. for $C_{24}H_{19}N_3O_2$+H 382.1556, found 382.1543.



2-(6-methylpyrido[3',2':4,5]pyrrolo[1,2-a]quinolin-7-yl)benzene-1,4-diol (**5**). 24 h, yellow solid, 80% yield; ^{1}H NMR (400 MHz, DMSO): δ 10.12 (d, J = 8.4 Hz, 1H), 8.82 (s, 1H), 8.60 (s, 1H), 8.49 (s, 1H), 7.80 (d, J = 7.6Hz, 1H), 7.73–7.71 (m, 1H), 7.69–7.65 (m, 1H), 7.42–7.38 (m, 2H), 7.15 (s, 1H), 6.80–6.78 (m, 1H), 6.71–6.68 (m, 2H), 2.16 (s, 3H) ppm; ^{13}C NMR (101 MHz, DMSO): δ 149.7, 149.2, 145.2, 142.6, 134.9, 132.7, 128.8, 128.6, 128.0, 127.8, 124.8, 124.0, 123.7, 123.0, 121.8, 119.4, 118.4, 117.7, 116.4, 116.0, 105.7, 19.7 ppm. ESI HRMS: calcd. for $C_{22}H_{16}N_2O_2$+H 341.1290, found 341.1288.

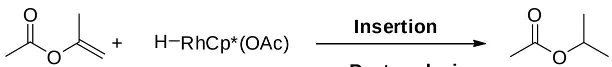


7-iodo-6-methylpyrido[3',2':4,5]pyrrolo[1,2-a]quinolone (**6**). 1.5 h, yellow solid, 98% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.14 (d, *J* = 8.4 Hz, 1H), 8.56–8.55 (m, 1H), 7.99–7.97 (m, 1H), 7.61–7.57 (m, 1H), 7.55–7.53 (m, 1H), 7.40–7.38 (m, 1H), 7.34–7.30 (m, 1H), 7.06 (s, 1H), 2.92 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 146.2, 143.0, 135.8, 134.4, 129.8, 128.5, 127.2, 127.1, 126.7, 125.7, 123.8, 123.4, 118.5, 118.2, 48.1, 22.5 ppm. ESI HRMS: calcd. for $C_{16}H_{11}IN_2$+H 359.0045, found 359.0039.

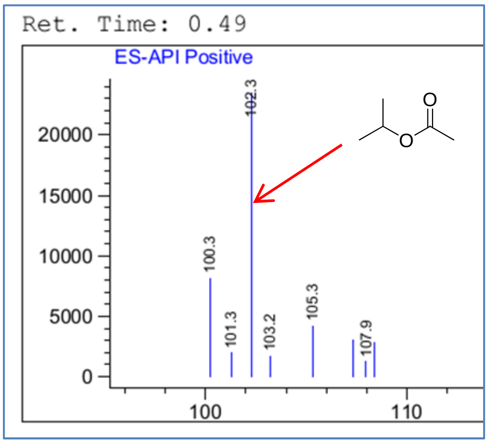
3. Mechanism Study

a. Parallel experiments

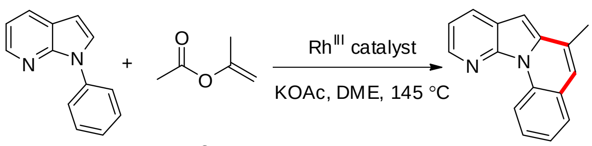
1) Alkyl acetate was detected.



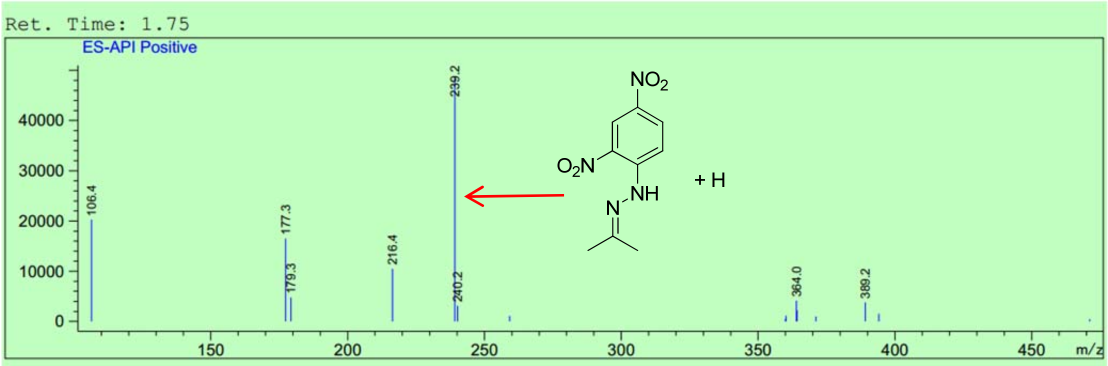
Alkyl acetate was detected by LCMS, which might be the possibility of H-Rh species reacts with isopropenyl acetate and followed by protonolysis of Rh-C bond.



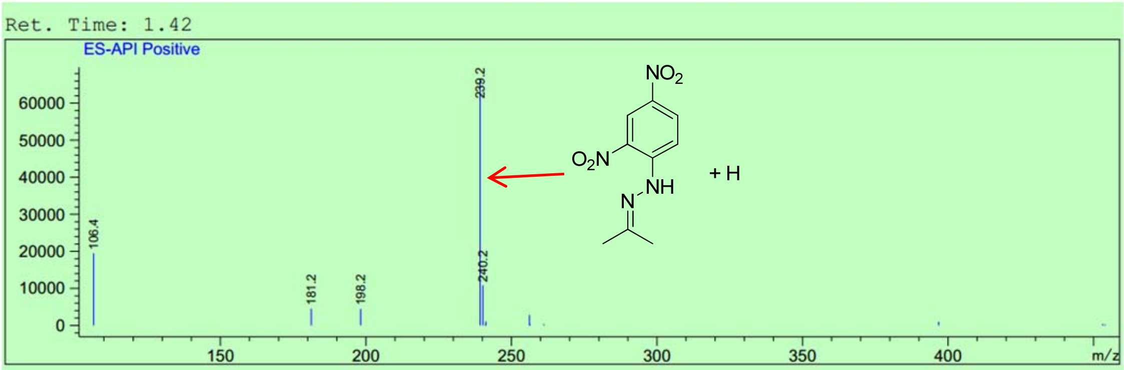
2) Acetone was detected



1-phenyl-1H-pyrrolo[2,3-b]pyridine **1a** (0.1 mmol, 19.4 mg), isopropenyl acetate **2a** (0.5 mL), [Cp*$RhCl_2$]$_2$ (3.1 mg, 5.0 mol %), KOAc (19.4 mg, 2 equiv) were stirred in seal tube at 145 °C for 80 h. After completion 2,4-dinitrophenylhydrazine (19.8 mg, 1.0 equiv) was added in the mixture to stir for another 6 h. As a result, the released acetone was trapped by 2,4-dinitrophenylhydrazine. The corresponding product 1-(2,4-dinitrophenyl)-2-(propan-2-ylidene)hydrazine was detected by LCMS.



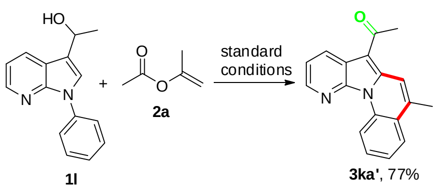
To illustrate the relationship between substrates and the released acetone, we took another reaction: Isopropenyl acetate **2a** (0.5 mL), $[Cp^*RhCl_2]_2$ (3.1 mg, 5.0 mol %), KOAc (19.4 mg, 2 equiv) were stirred in seal tube at 145 °C for 80 h without **1a**. After completion 2,4-dinitrophenylhydrazine (19.8 mg, 1.0 equiv) was added in the mixture to stir for another 6 h. As a result, we also trapped the released acetone.



These results indicates that the formation of acetone without any relation with substrate **1a**. Acetone would be formed from the decomposition or hydrolysis of the vinyl acetate when isopropenyl acetate **2a** was applied in these standard conditions, which is still unclear right now.

Moreover, hydroxyl group in subatrate **1l** can be oxidized in the reaction, probably due to the decomposed products of alkyl acetate could act as the oxidant.

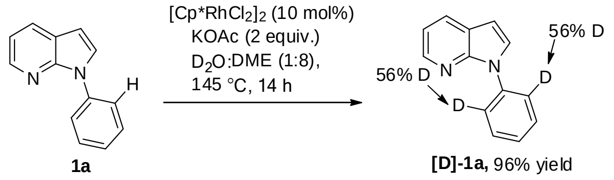
SI 2. 1l reacted with **2a** under standard conditions:

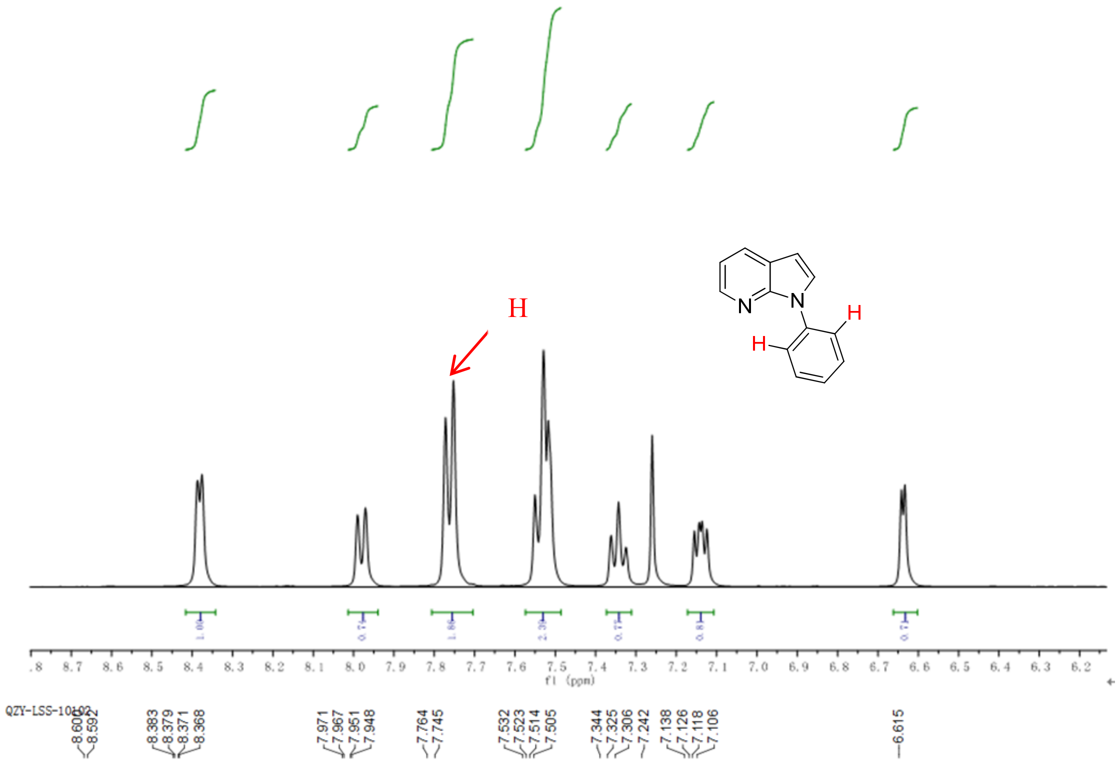


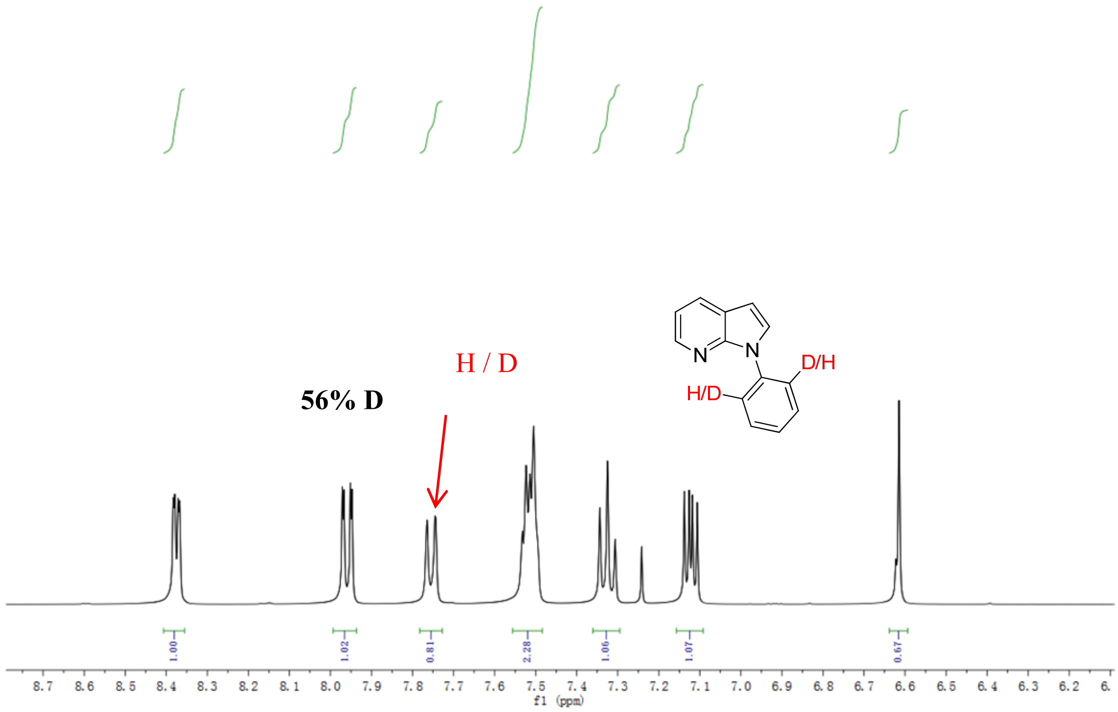
b. Kinetic Isotopic Effects

Deuterium-labeling experiments were carried out to study the mechanism of this coupling reaction. 1-phenyl-1H-pyrrolo[2,3-b]pyridine **1a** (0.1 mmol, 19.4 mg), $[Cp^*RhCl_2]_2$ (6.2 mg, 10 mol %) and KOAc (38.8 mg, 2 equiv.) were stirred using D_2O:DME (0.1 mL:0.8 mL) as solvent in seal tube at 145 °C for 14 h. After completion, the reaction mixture was purified by flash chromatography eluting with ethyl acetate and petroleum ether (1:40) to give the product (18.6 mg, 96% yield).

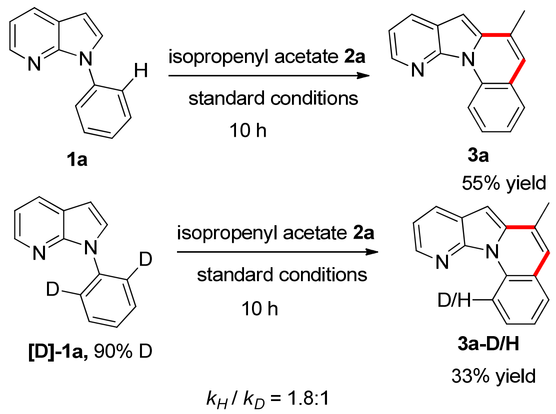
The deuterium rate was obtained from ^{1}H NMR.







To investigate the mechanism of this reaction, the standard substrate **1a** and [D]-**1a** were stirred in the parallel reaction under standard conditions for 10 h. According to the isolated yields and deuterated ratio, the DKIE of 1.8 was observed thus indicating that C-H bond cleavage might be involved in the rate-determining step.

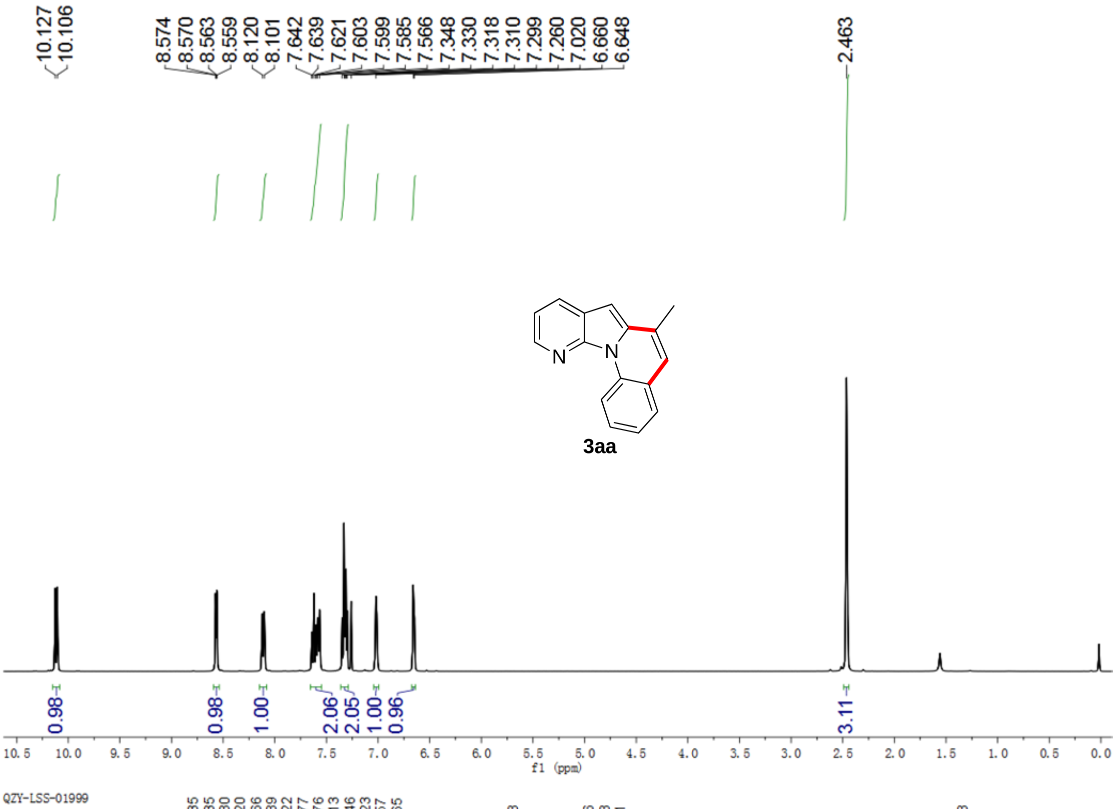


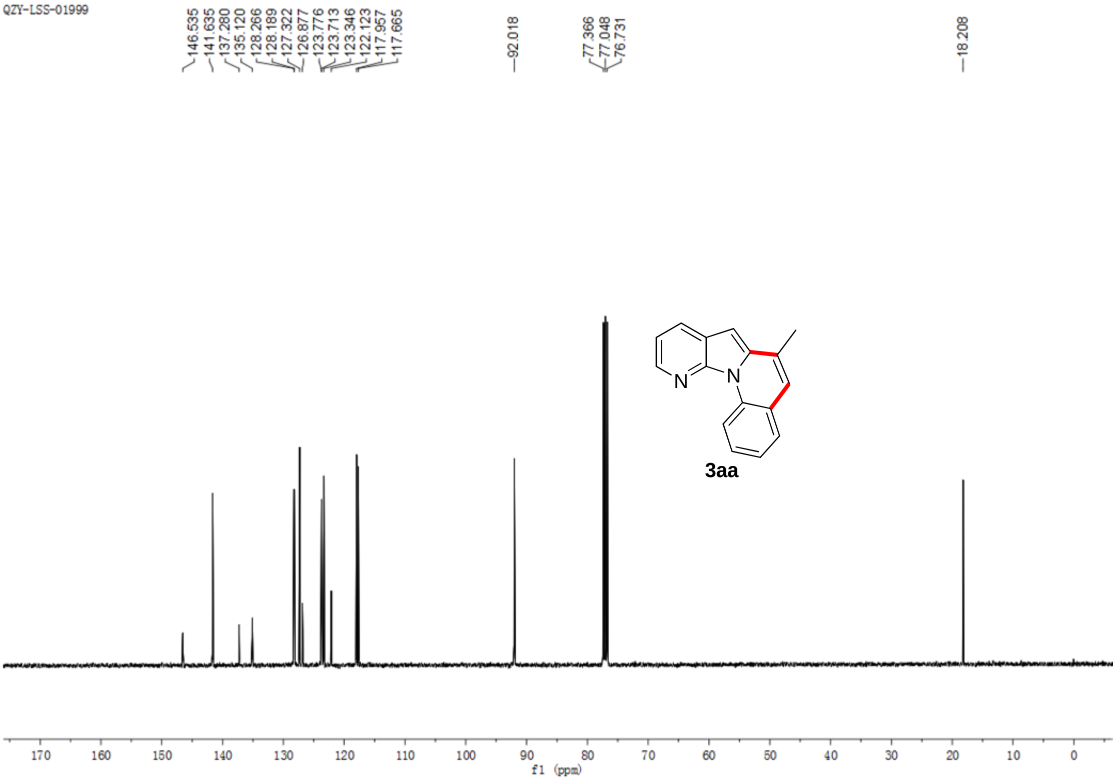
Reference

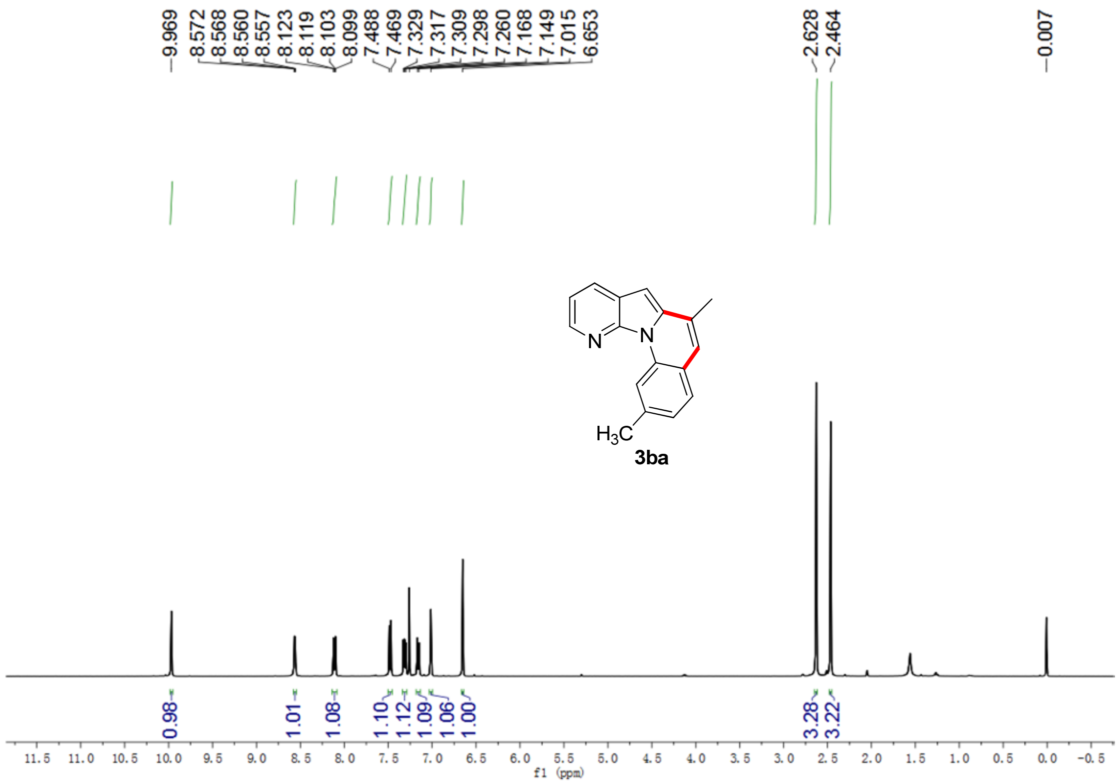
[1] G. Qian, X. Hong, B. Liu, H. Mao, B. Xu, *Org. Lett.* **2014**, *16*, 5294.

[2] L. J. Goossen, J. Paetzold, D. Koley, *Chem. Commun*. **2003**, 706.

4. NMR Spectra of Annulation 7-Azaindole Derivatives and Structure Determination

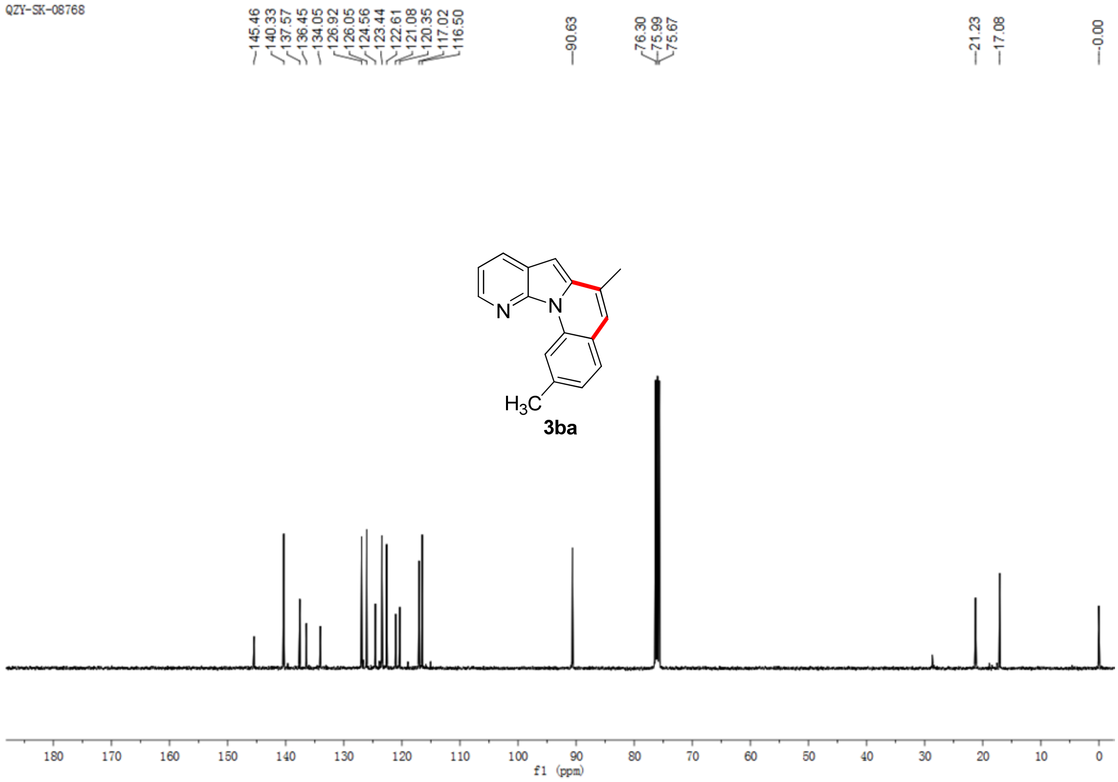




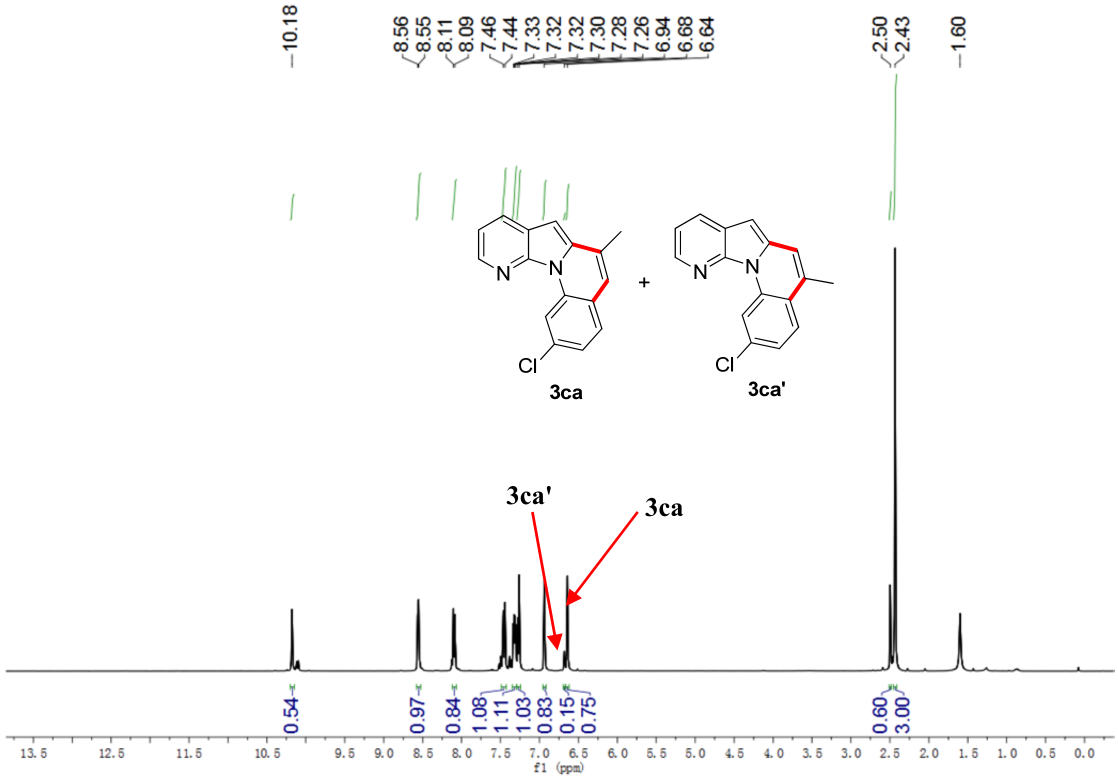


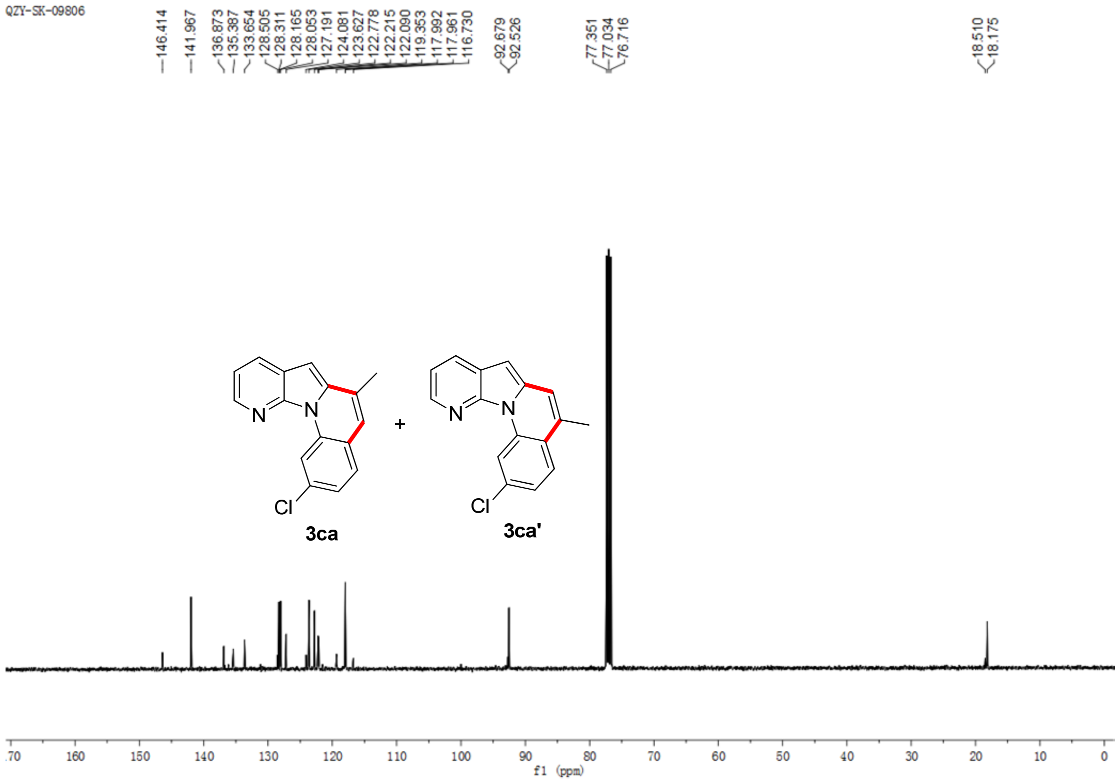
9.969
8.572
8.568
8.560
8.557
8.123
8.119
8.103
8.099
7.488
7.469
7.329
7.317
7.309
7.298
7.260
7.168
7.149
7.015
6.653
2.628
2.464
0.007
N
N
H3C
3ba
0.98
1.01
1.08
1.10
1.12
1.09
1.06
1.00
3.28
3.22
f1 (ppm)

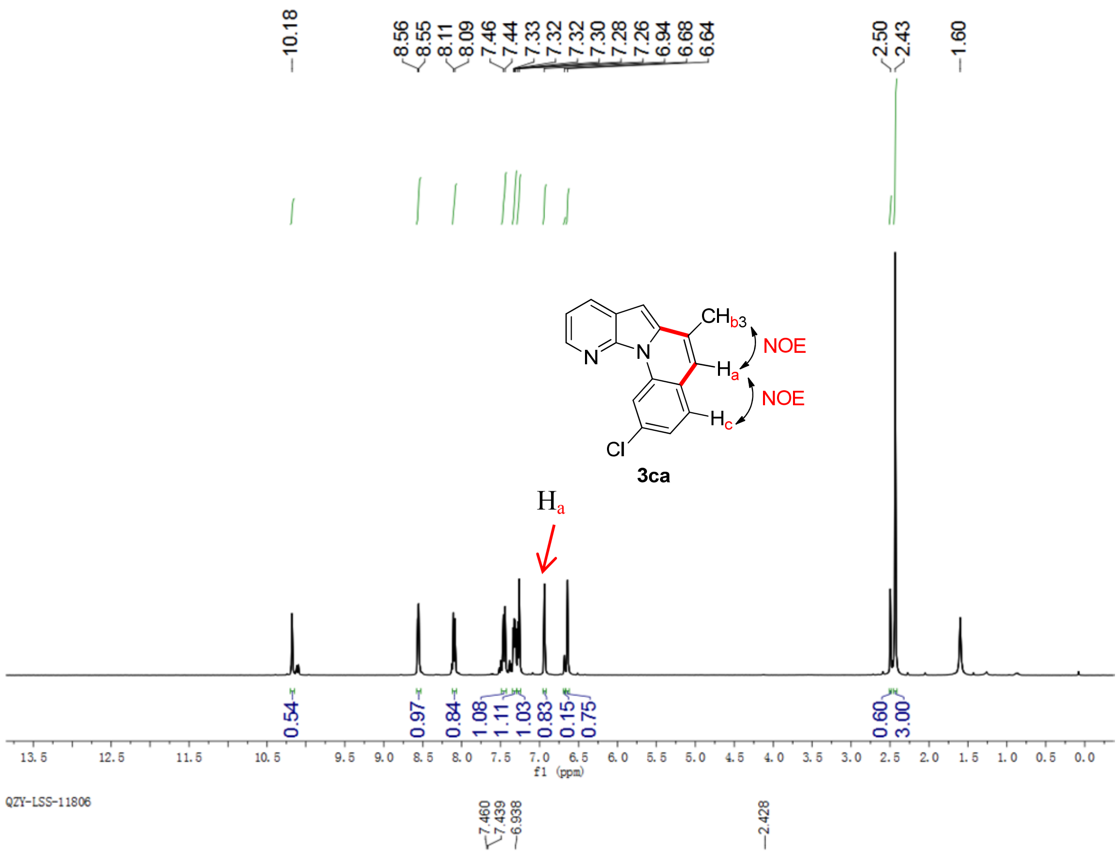
QZY-SK-08768



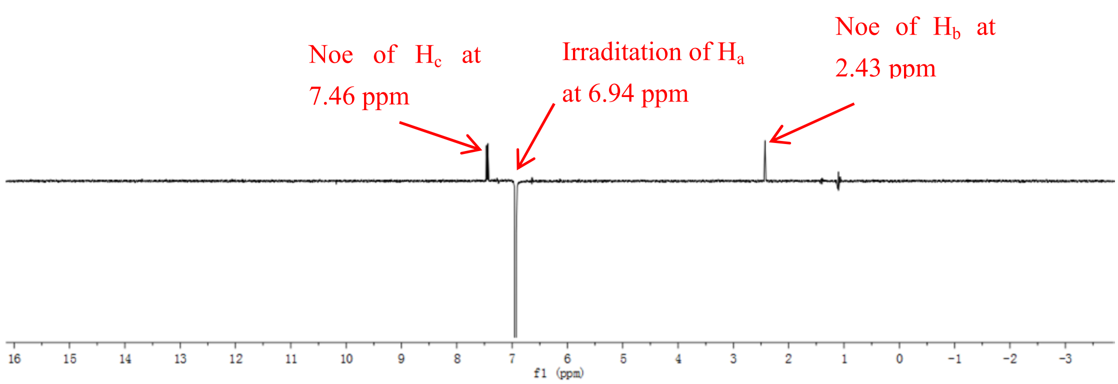
145.46
140.33
137.57
136.45
134.05
126.92
126.05
124.56
123.44
122.61
121.08
120.35
117.02
116.50
90.63
76.30
75.99
75.67
21.23
17.08
0.00
N
N
H3C
3ba
f1 (ppm)


10.18
8.56
8.55
8.11
8.09
7.46
7.44
7.33
7.32
7.32
7.30
7.28
7.26
6.94
6.68
6.64
2.50
2.43
1.60
N
N
Cl
3ca
+
N
N
Cl
3ca'
3ca'
3ca
0.54
0.97
0.84
1.08
1.11
1.03
0.83
0.15
0.75
0.60
3.00
f1 (ppm)

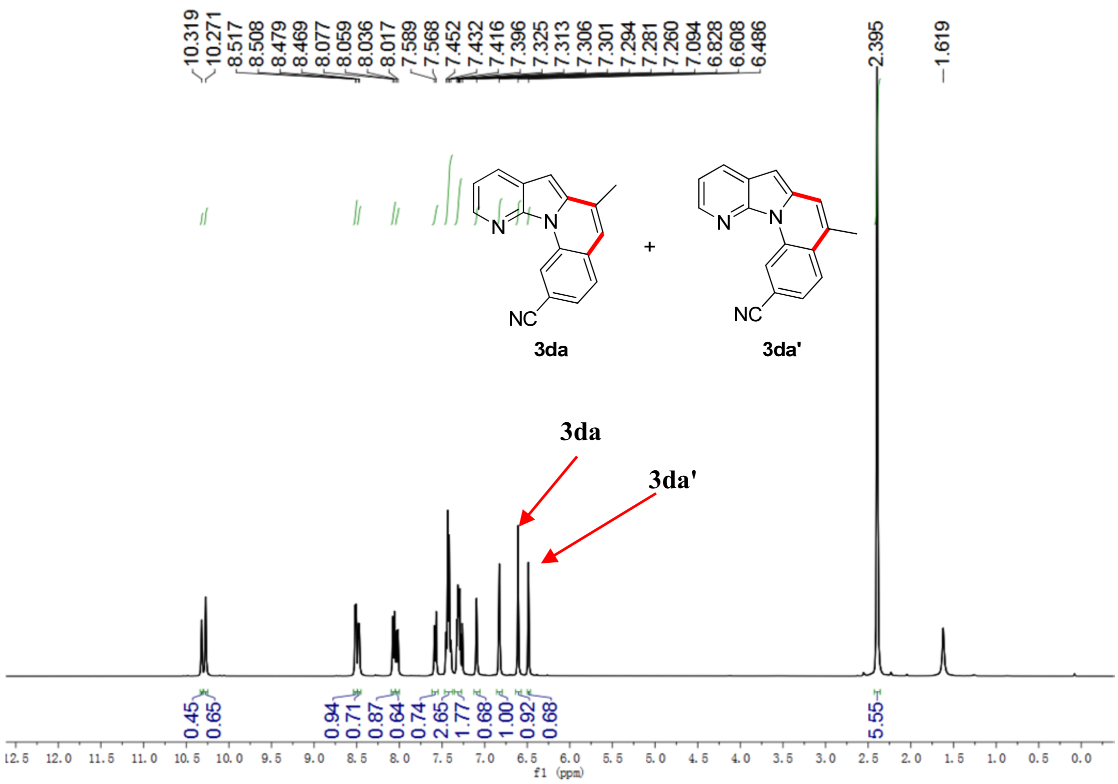

QZY-SK-09806
146.414
141.967
136.873
135.387
133.654
128.505
128.311
128.165
128.053
127.191
124.081
123.627
122.778
122.215
122.090
119.353
117.992
117.961
116.730
92.679
92.526
77.351
77.034
76.716
18.510
18.175
N
N
Cl
3ca
+
N
N
Cl
3ca'
f1 (ppm)

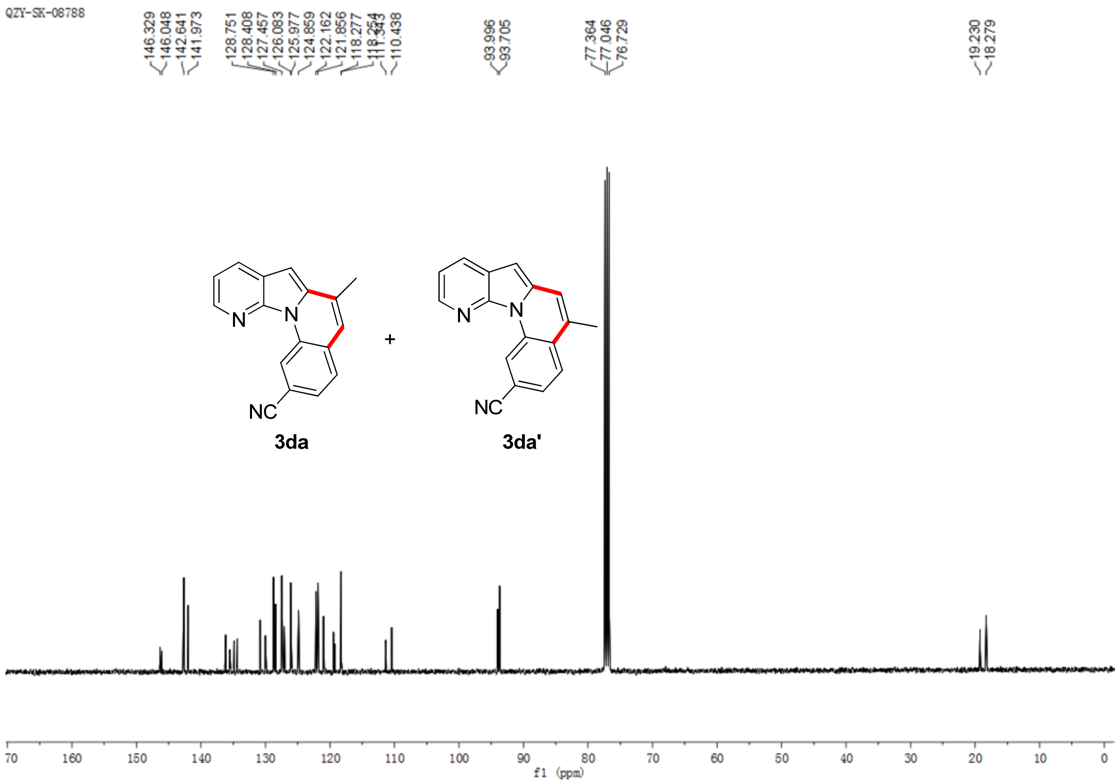


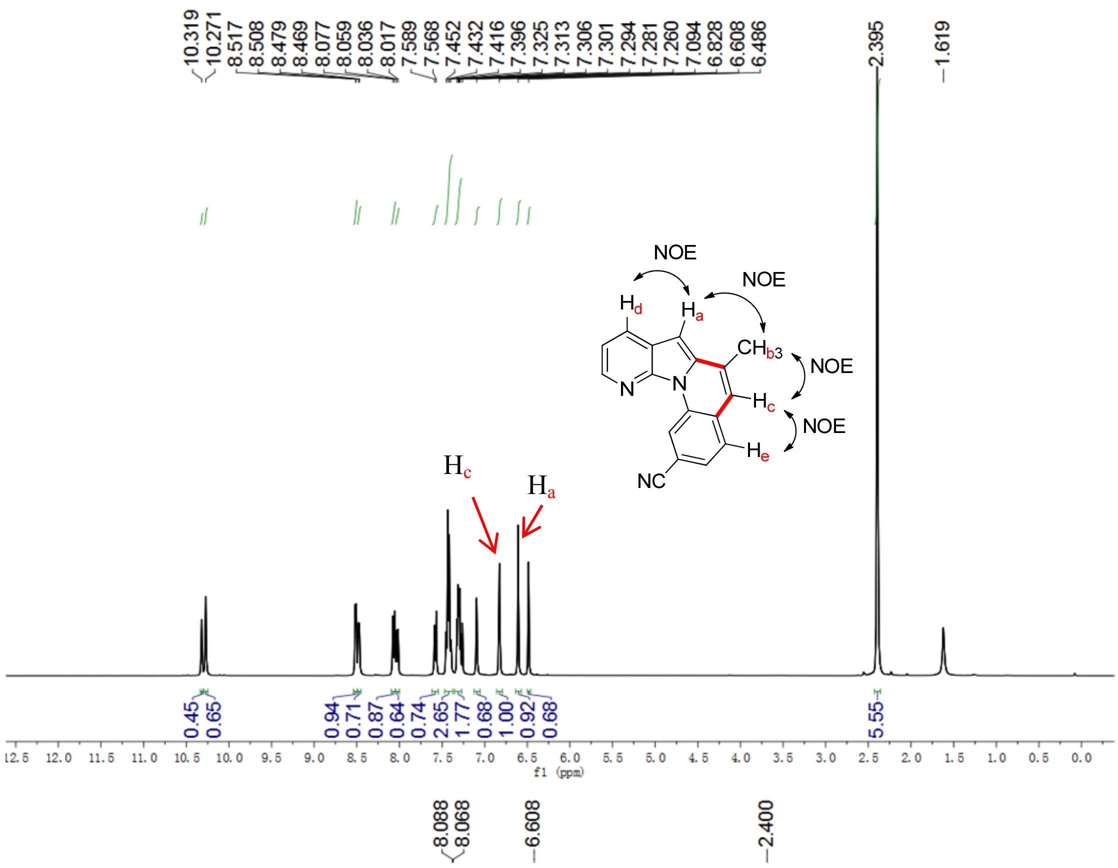
10.18
8.56
8.55
8.11
8.09
7.46
7.44
7.33
7.32
7.32
7.30
7.28
7.26
6.94
6.68
6.64
2.50
2.43
1.60
CH_{b3}
NOE
H_a
NOE
H_c
N
N
Cl
3ca
H_a
0.54
0.97
0.84
1.08
1.11
1.03
0.83
0.15
0.75
0.60
3.00
f1 (ppm)
QZY-LSS-11806
7.460
7.439
6.938
2.428

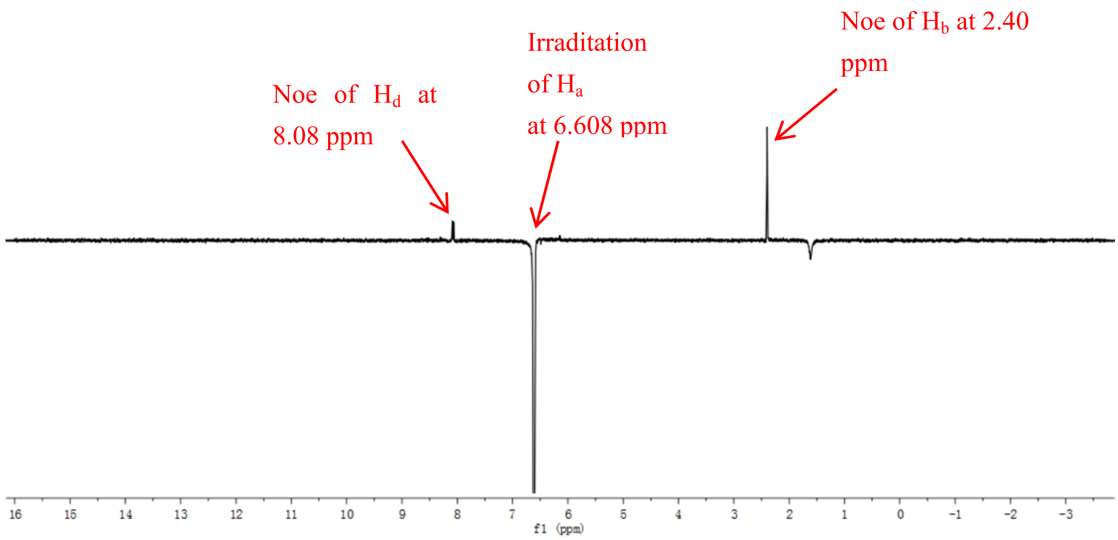


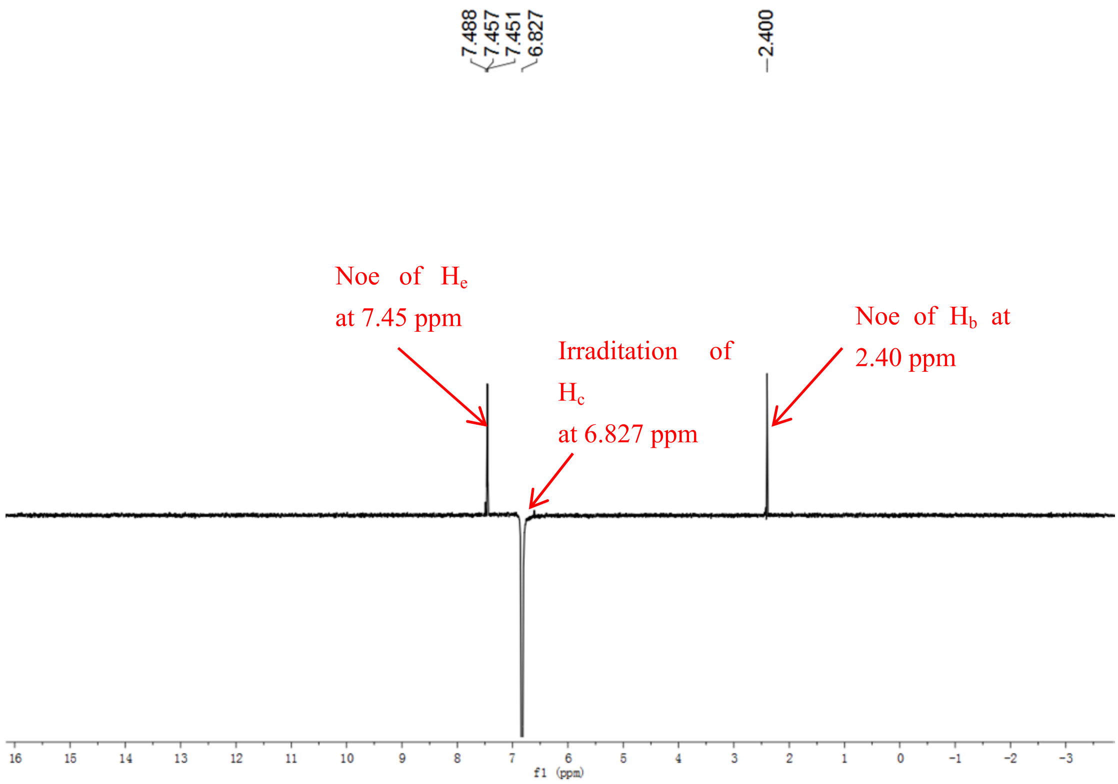
Noe of H_c at 7.46 ppm
Irraditation of H_a at 6.94 ppm
Noe of H_b at 2.43 ppm
f1 (ppm)

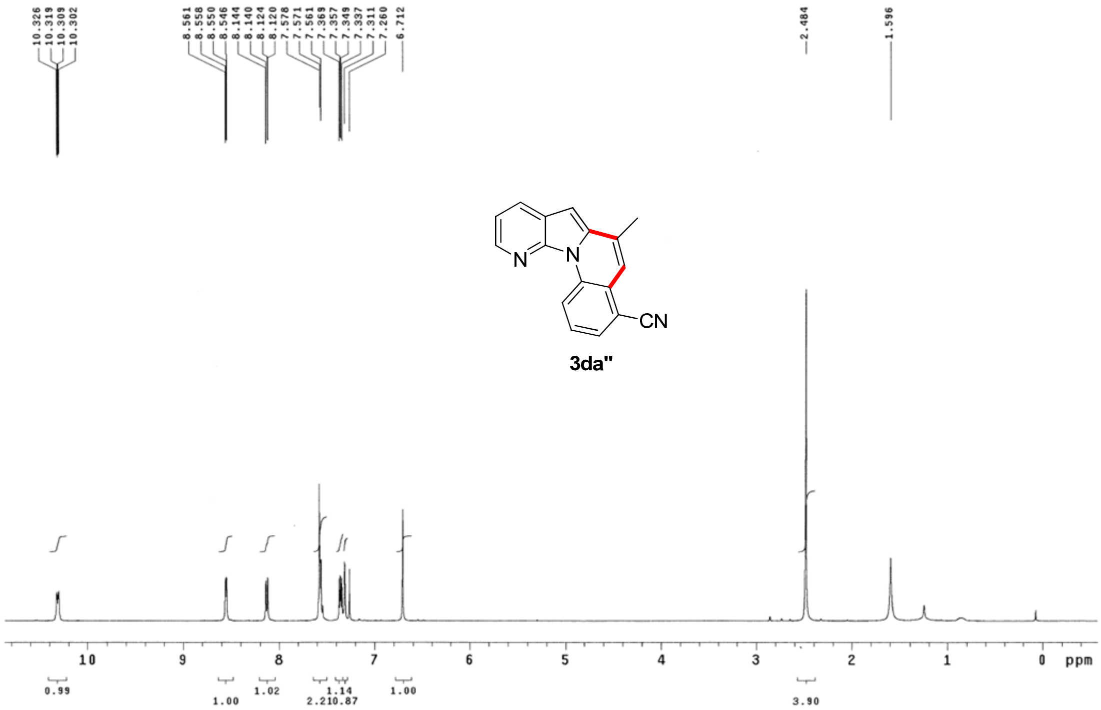

10.319
10.271
8.517
8.508
8.479
8.469
8.077
8.059
8.036
8.017
7.589
7.568
7.452
7.432
7.416
7.396
7.325
7.313
7.306
7.301
7.294
7.281
7.260
7.094
6.828
6.608
6.486
2.395
1.619
N
N
NC
3da
+
3da'
3da
3da'
0.45
0.65
0.94
0.71
0.87
0.64
0.74
2.65
1.77
0.68
1.00
0.92
0.68
5.55
f1 (ppm)
QZY-SK-08788

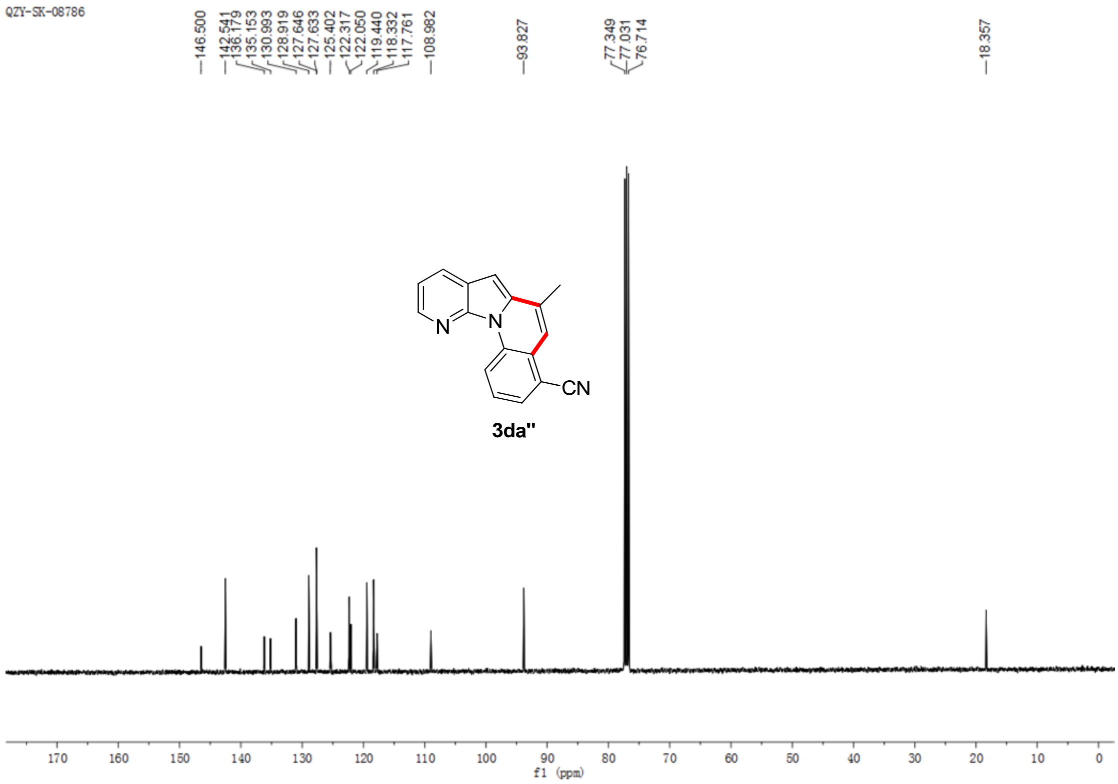

146.329
146.048
142.641
141.973
128.751
128.408
127.457
126.083
125.977
124.859
122.162
121.856
118.277
110.438
93.996
93.705
77.364
77.046
76.729
19.230
18.279
N
N
NC
3da
+
3da'
f1 (ppm)

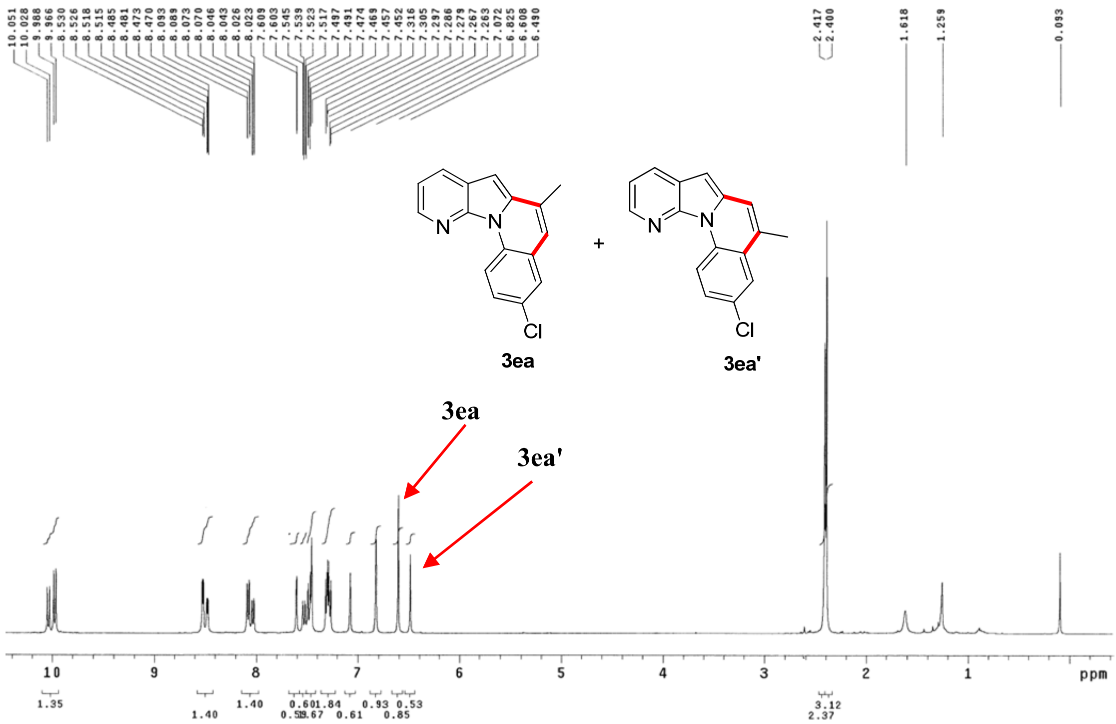

10.319
10.271
8.517
8.508
8.479
8.469
8.077
8.059
8.036
8.017
7.589
7.568
7.452
7.432
7.416
7.396
7.325
7.313
7.306
7.301
7.294
7.281
7.260
7.094
6.828
6.608
6.486
2.395
1.619
NOE
NOE
NOE
NOE
H_d
H_a
CH_{b3}
H_c
H_e
N
N
NC
H_c
H_a
0.45
0.65
0.94
0.71
0.87
0.64
0.74
2.65
1.77
0.68
1.00
0.92
0.68
5.55
f1 (ppm)
8.088
8.068
6.608
2.400

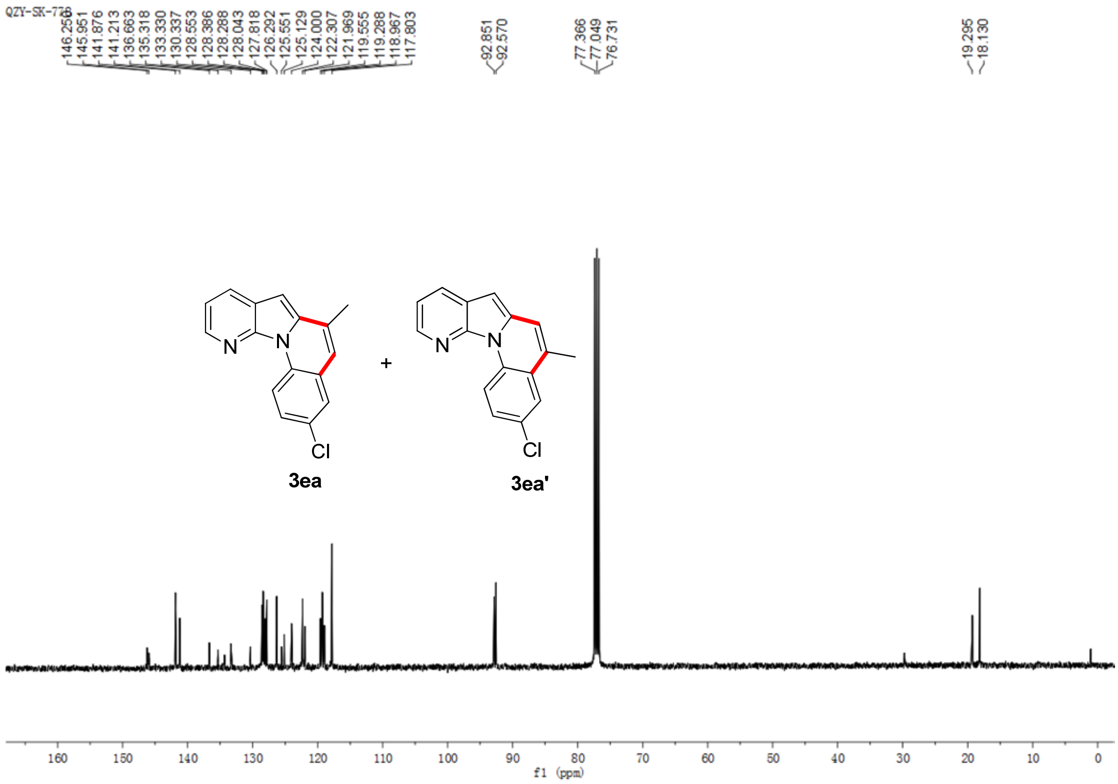

Noe of H_d at 8.08 ppm
Irradiation of H_a at 6.608 ppm
Noe of H_b at 2.40 ppm
f1 (ppm)

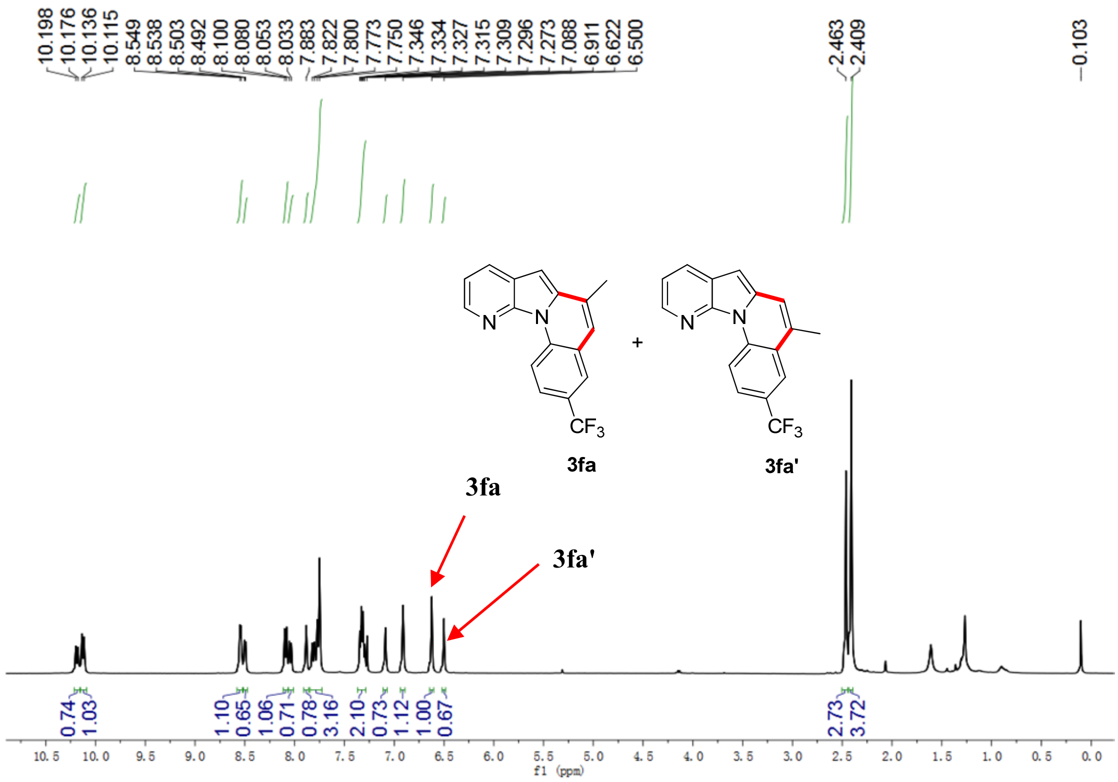

7.488
7.457
7.451
6.827
2.400
Noe of H_e at 7.45 ppm
Irraditation of H_c at 6.827 ppm
Noe of H_b at 2.40 ppm
f1 (ppm)

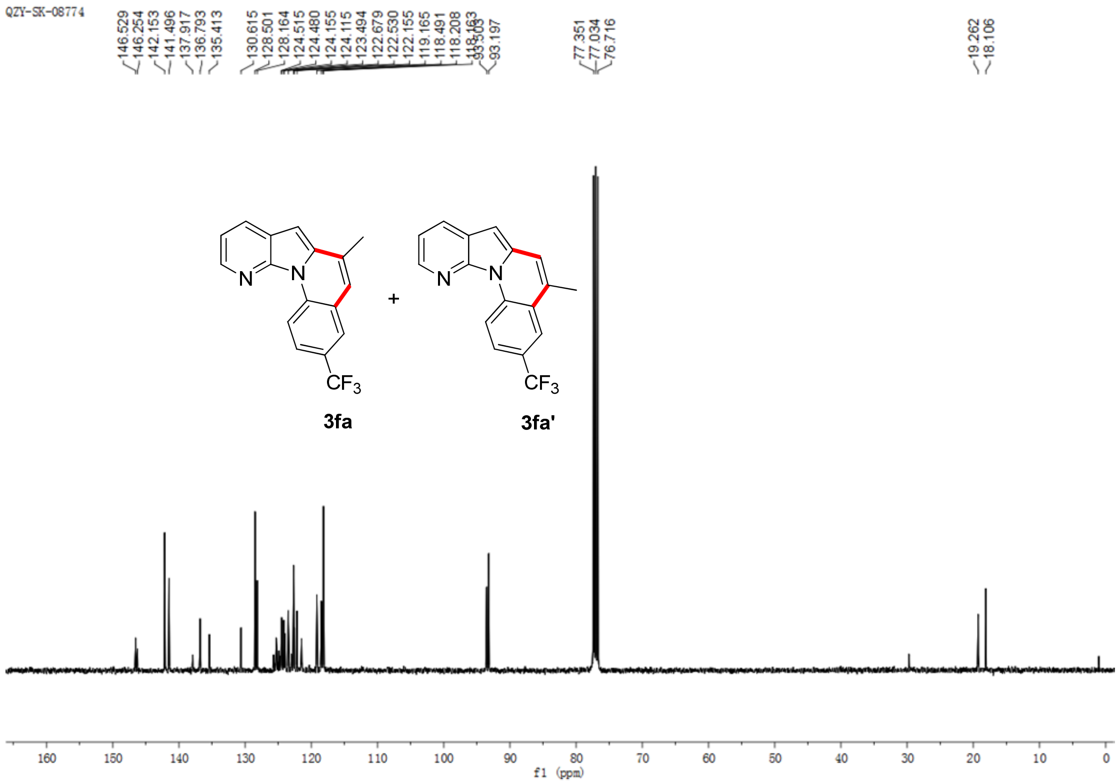

10.326
10.319
10.309
10.302
8.561
8.558
8.550
8.546
8.144
8.140
8.124
8.120
7.578
7.571
7.561
7.369
7.357
7.349
7.337
7.311
7.260
6.712
2.484
1.596
N
N
CN
3da''
ppm
0.99
1.00
1.02
2.21
0.87
1.14
1.00
3.90

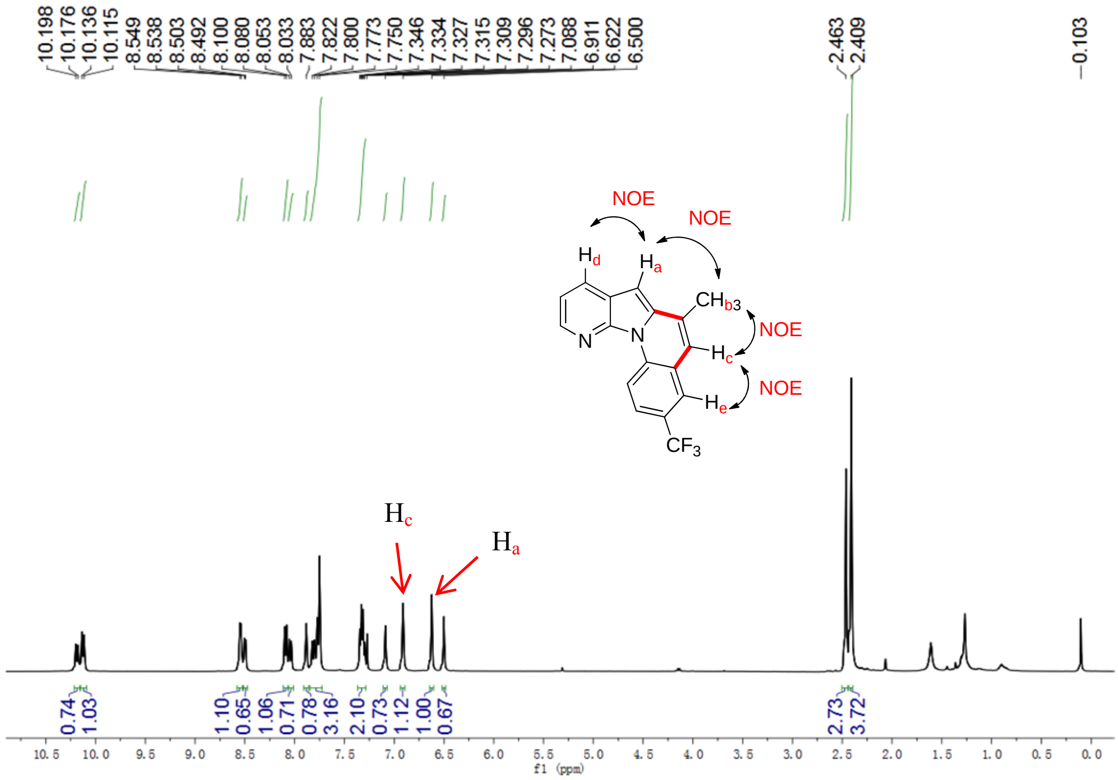

QZY-SK-08786
146.500
142.541
136.179
135.153
130.993
128.919
127.646
127.633
125.402
122.317
122.050
119.440
118.332
117.761
108.982
93.827
77.349
77.031
76.714
18.357
CN
N
3da''
f1 (ppm)

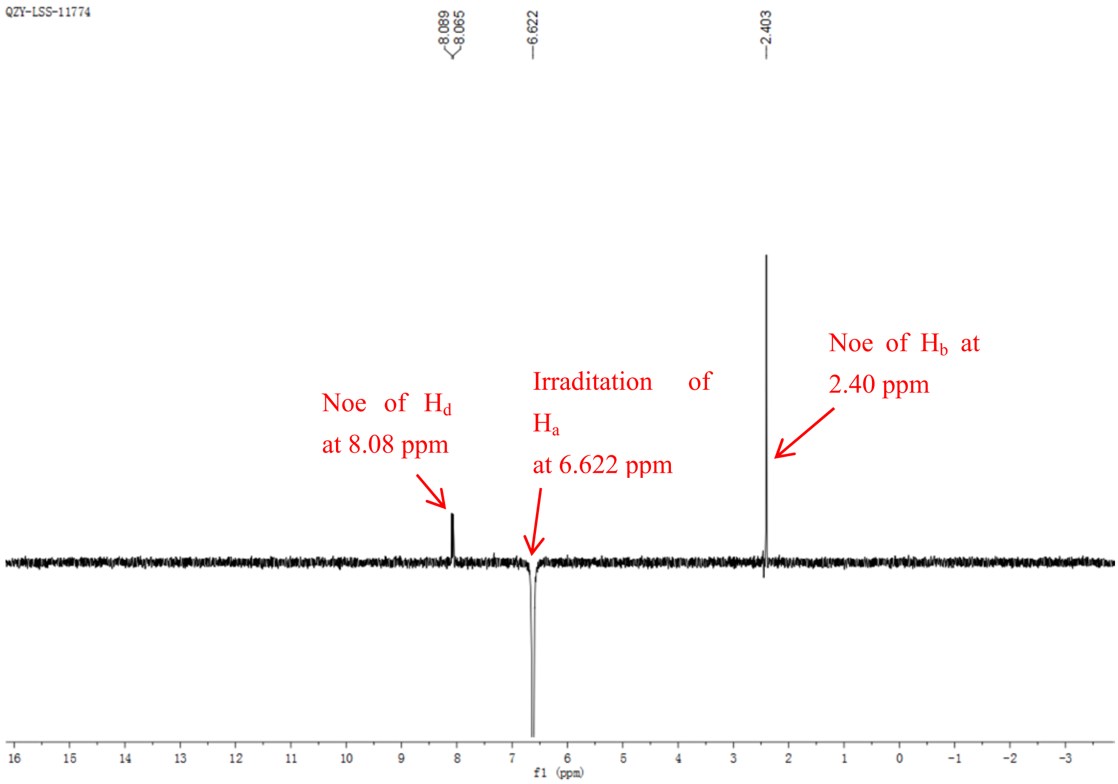

10.051
10.028
9.988
9.966
2.417
2.400
1.618
1.259
0.093
N
Cl
3ea
3ea'
ppm

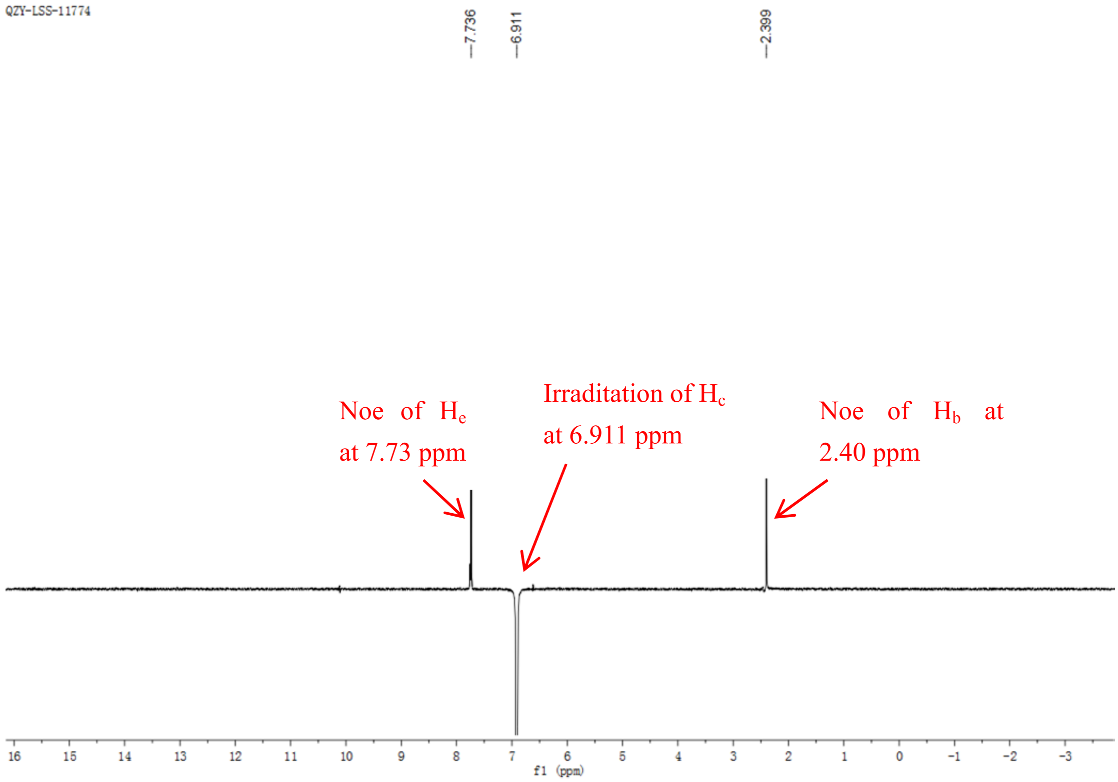

QZY-SK-77
146.258
145.951
141.876
141.213
136.663
135.318
133.330
130.337
128.553
128.386
128.288
128.043
127.818
126.292
125.551
125.129
124.000
122.307
121.969
119.555
119.288
118.967
117.803
92.851
92.570
77.366
77.049
76.731
19.295
18.130
N
N
Cl
3ea
+
N
N
Cl
3ea'
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

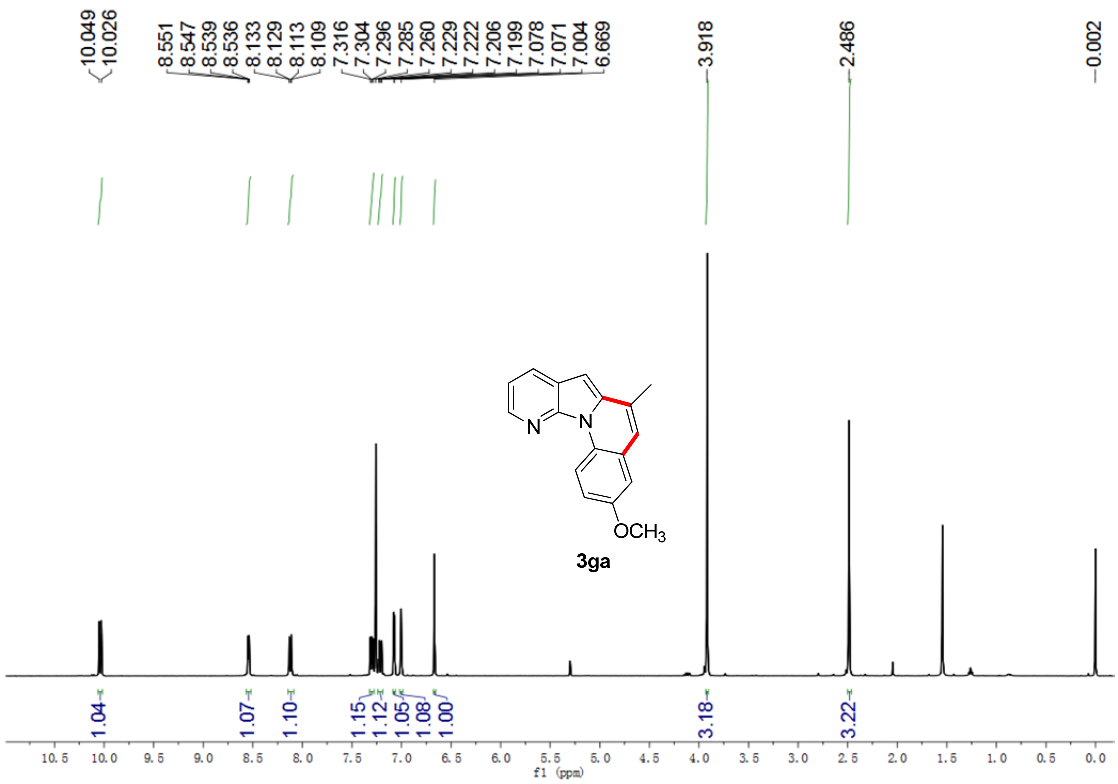

10.198
10.176
10.136
10.115
8.549
8.538
8.503
8.492
8.100
8.080
8.053
8.033
7.883
7.822
7.800
7.773
7.750
7.346
7.334
7.327
7.315
7.309
7.296
7.273
7.088
6.911
6.622
6.500
2.463
2.409
-0.103
N
N
CF3
3fa
+
N
N
CF3
3fa'
3fa
3fa'
0.74
1.03
1.10
0.65
1.06
0.71
0.78
3.16
2.10
0.73
1.12
1.00
0.67
2.73
3.72
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
f1 (ppm)

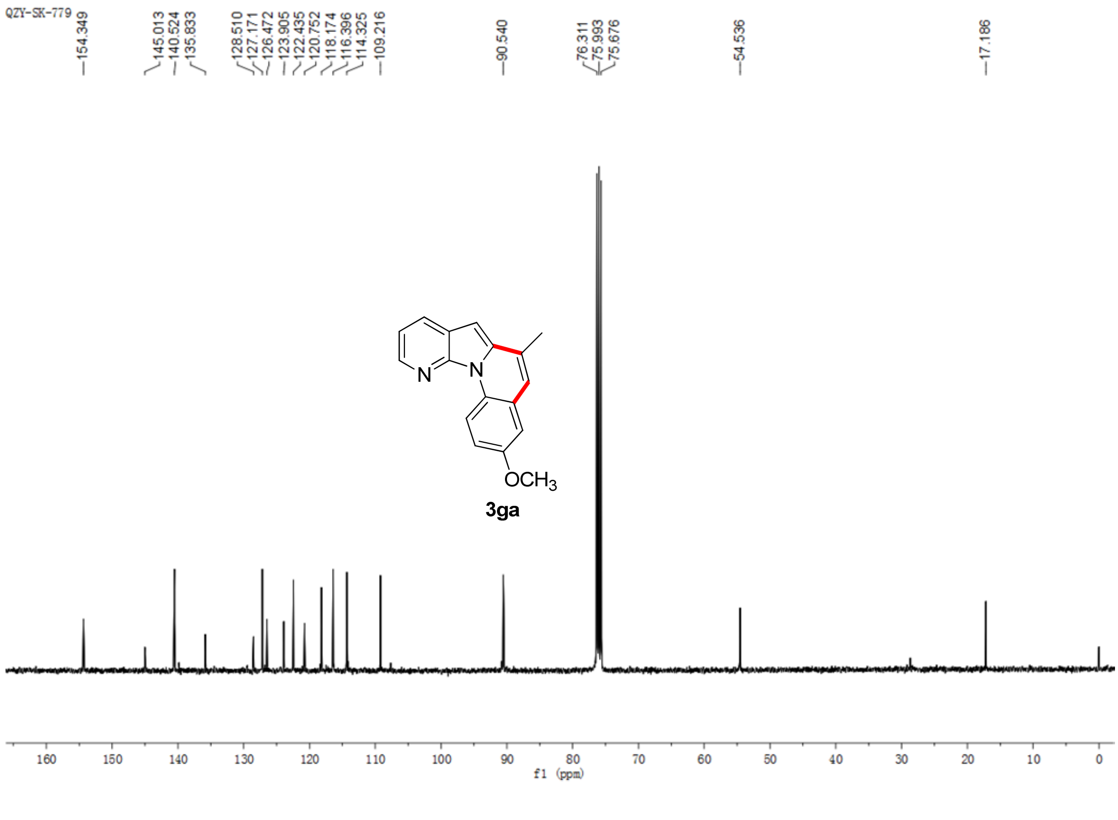

QZY-SK-08774
146.529
146.254
142.153
141.496
137.917
136.793
135.413
130.615
128.501
128.164
124.515
124.480
124.155
124.115
123.494
122.679
122.530
122.155
119.165
118.491
118.208
93.197
77.351
77.034
76.716
19.262
18.106
N
N
CF3
+
N
N
CF3
3fa
3fa'
f1 (ppm)

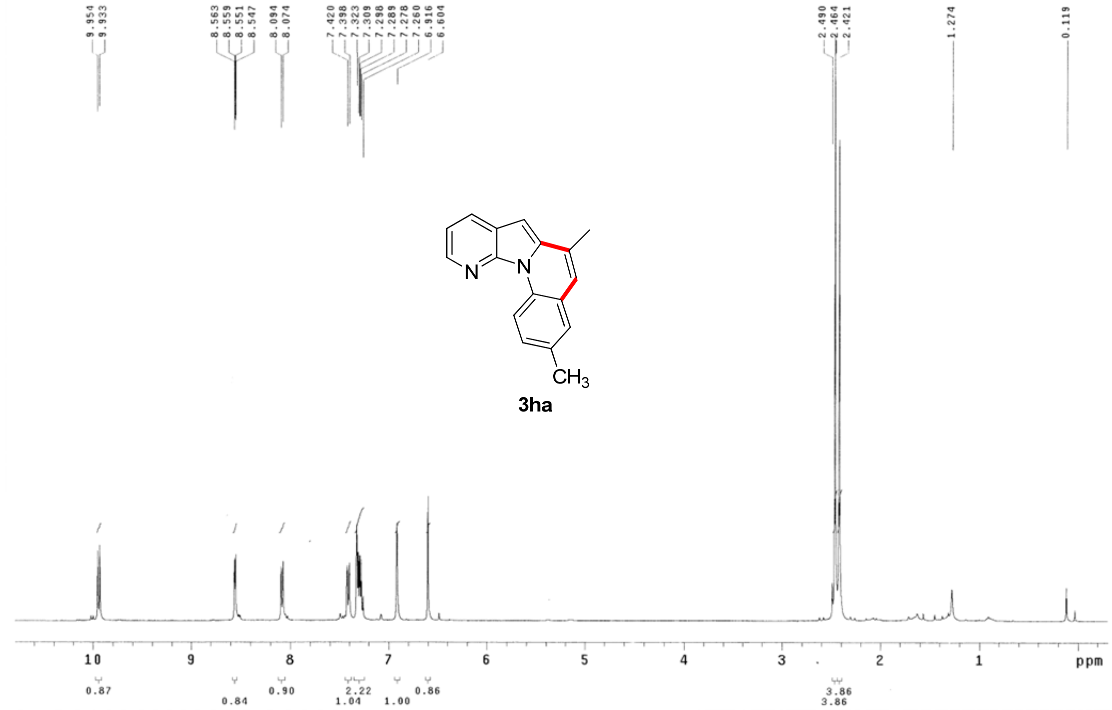

10.198
10.176
10.136
10.115
8.549
8.538
8.503
8.492
8.100
8.080
8.053
8.033
7.883
7.822
7.800
7.773
7.750
7.346
7.334
7.327
7.315
7.309
7.296
7.273
7.088
6.911
6.622
6.500
2.463
2.409
-0.103
NOE
NOE
NOE
NOE
Hd
Ha
CHb3
Hc
He
N
N
CF3
Hc
Ha
0.74
1.03
1.10
0.65
1.06
0.71
0.78
3.16
2.10
0.73
1.12
1.00
0.67
2.73
3.72
f1 (ppm)

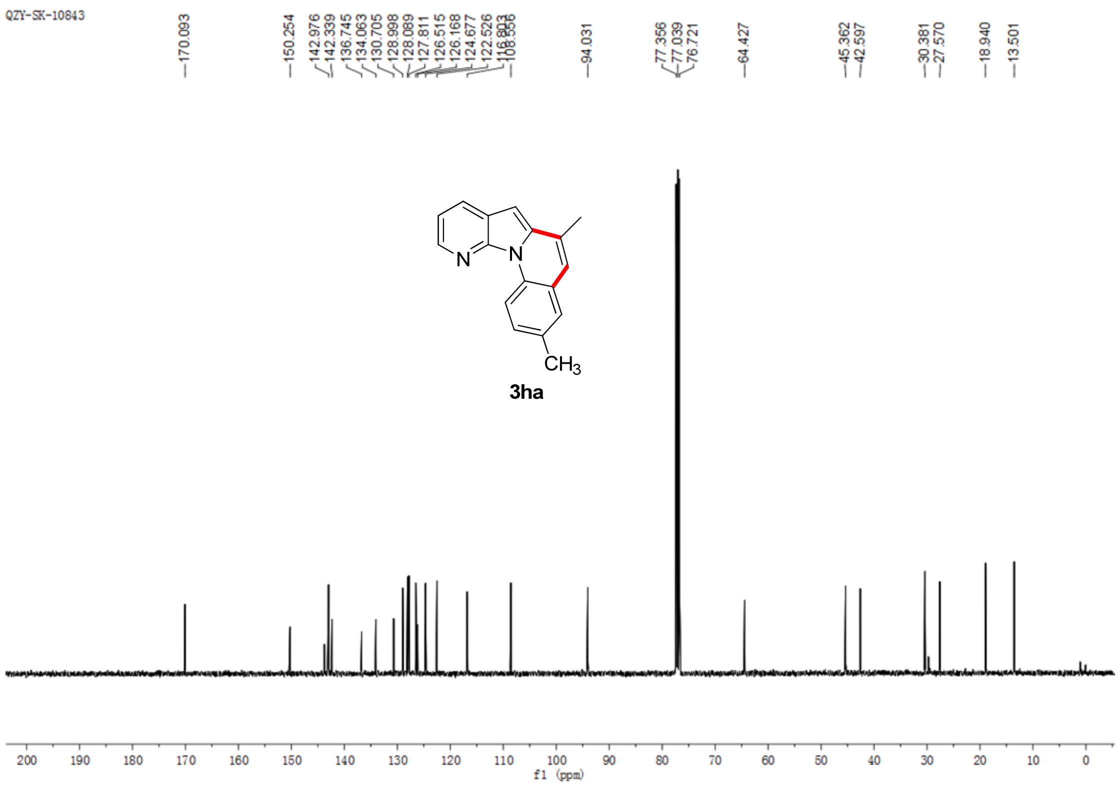

QZY-LSS-11774
8.089
8.065
6.622
2.403
Noe of H_d at 8.08 ppm
Irraditation of H_a at 6.622 ppm
Noe of H_b at 2.40 ppm
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

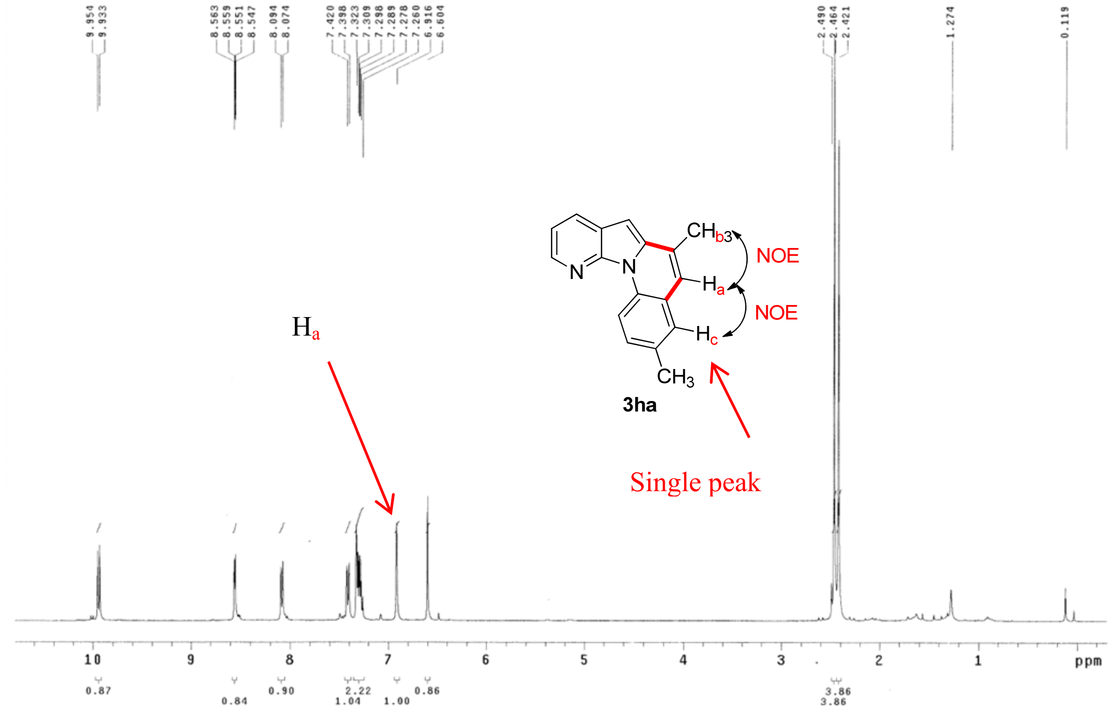

QZY-LSS-11774
7.736
6.911
2.399
Noe of H_e at 7.73 ppm
Irraditation of H_c at 6.911 ppm
Noe of H_b at 2.40 ppm
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

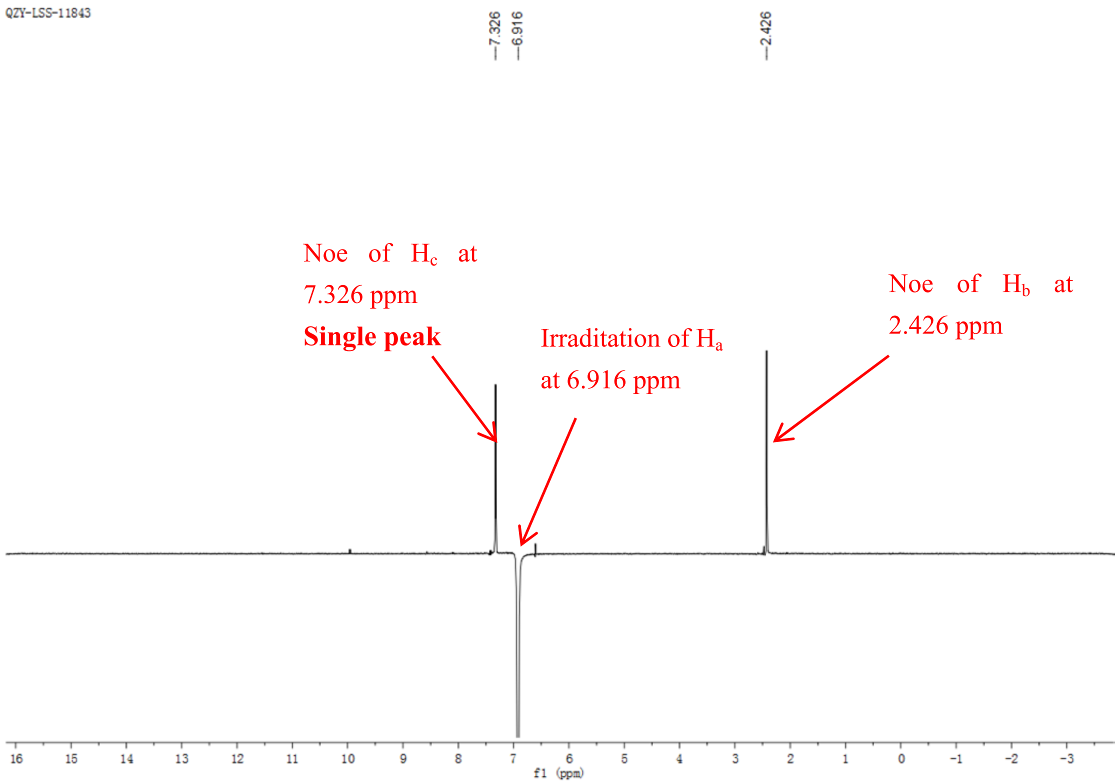

10.049
10.026
8.551
8.547
8.539
8.536
8.133
8.129
8.113
8.109
7.316
7.304
7.296
7.285
7.260
7.229
7.222
7.206
7.199
7.078
7.071
7.004
6.669
3.918
2.486
-0.002
1.04
1.07
1.10
1.15
1.12
1.05
1.08
1.00
3.18
3.22
N
N
OCH3
3ga
f1 (ppm)

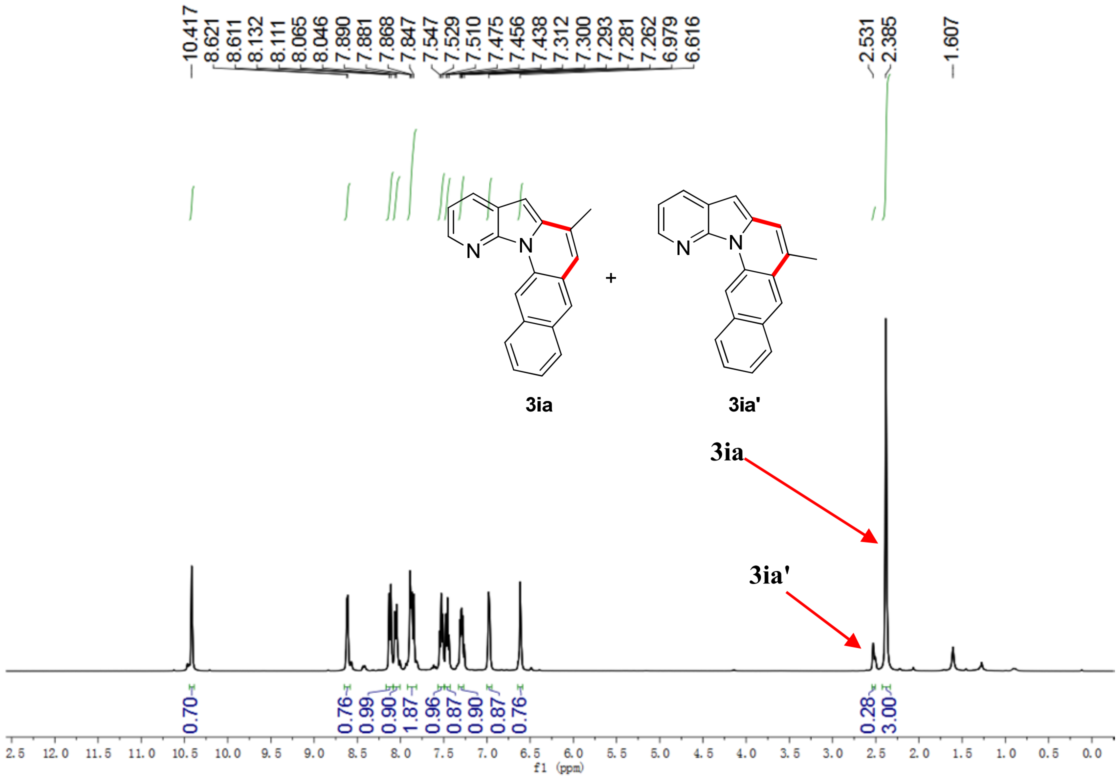

QZY-SK-779
154.349
145.013
140.524
135.833
128.510
127.171
126.472
123.905
122.435
120.752
118.174
116.396
114.325
109.216
90.540
76.311
75.993
75.676
54.536
17.186
N
N
OCH3
3ga
f1 (ppm)

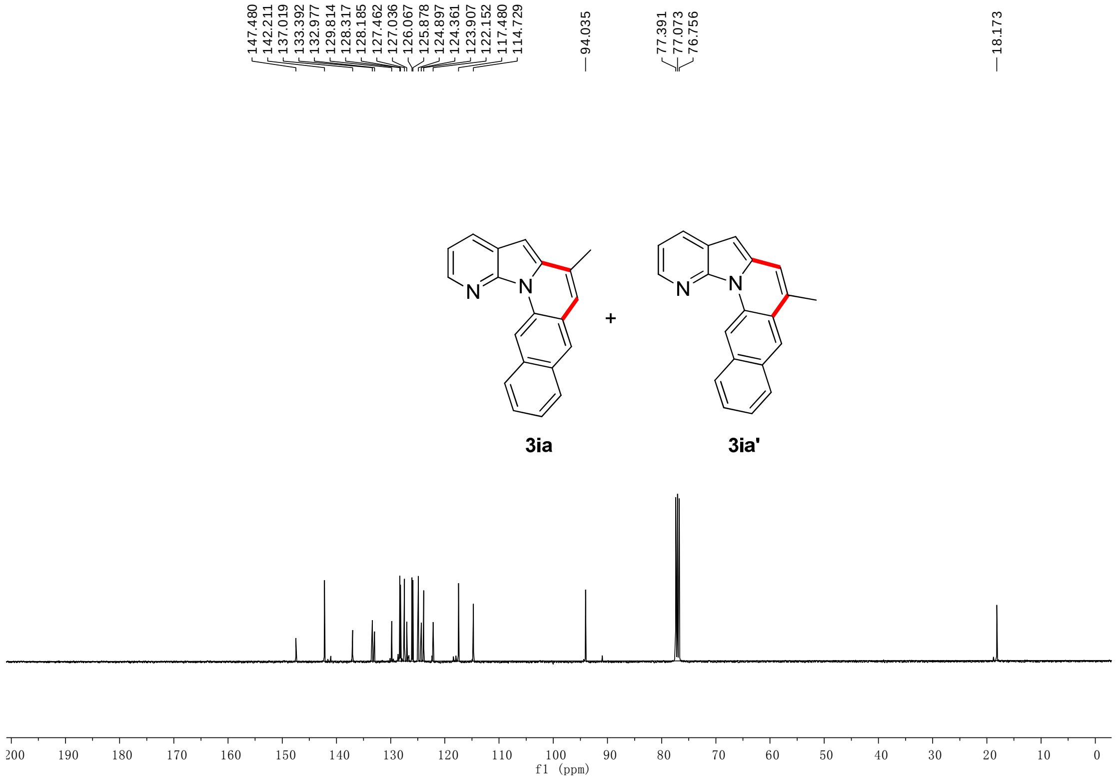

ppm

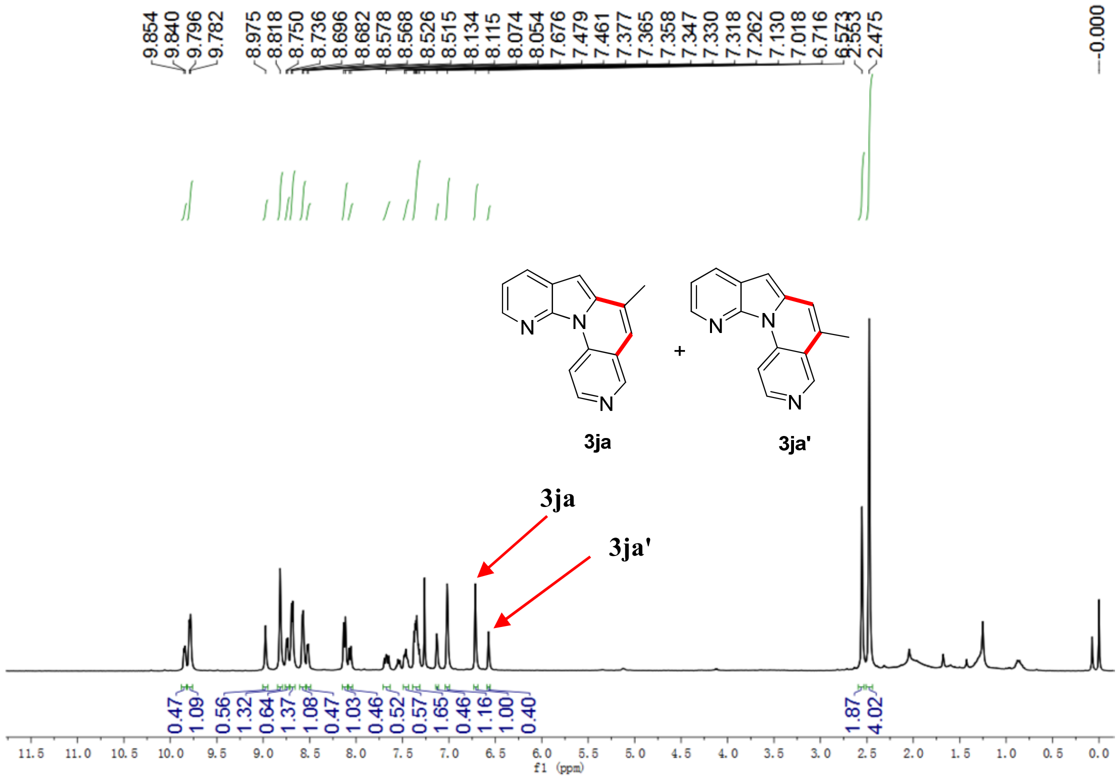

QZY-SK-10843
f1 (ppm)

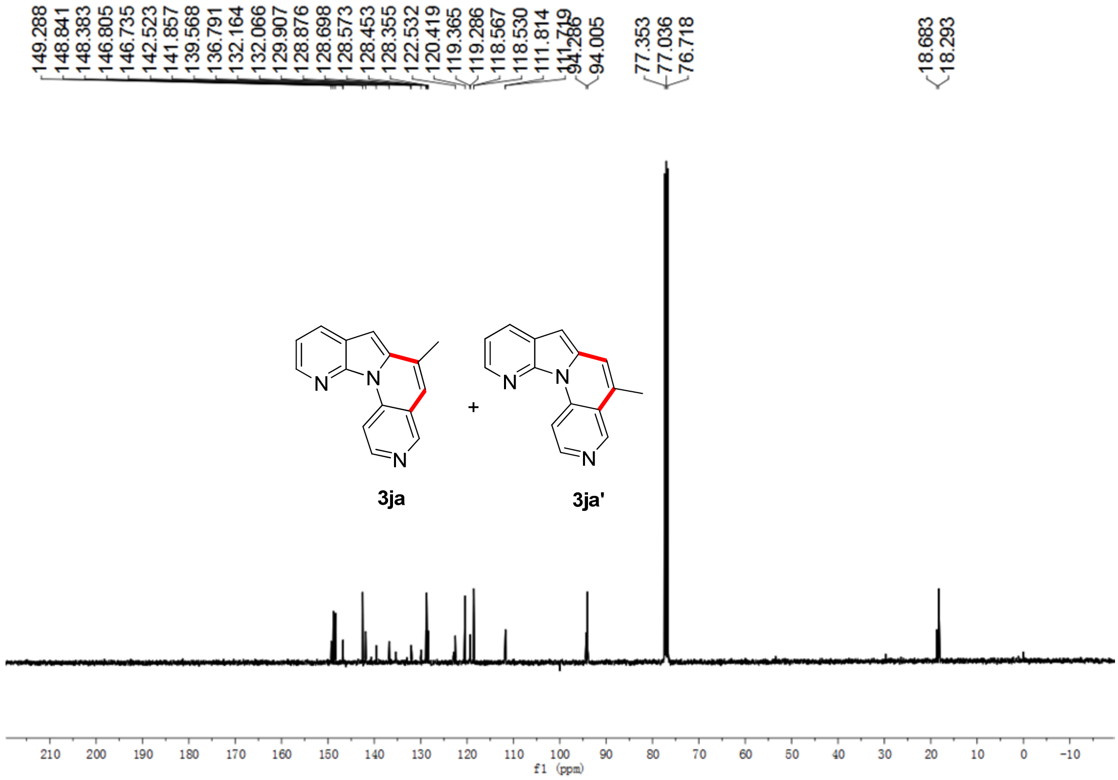

NOE
NOE
3ha
Single peak
ppm

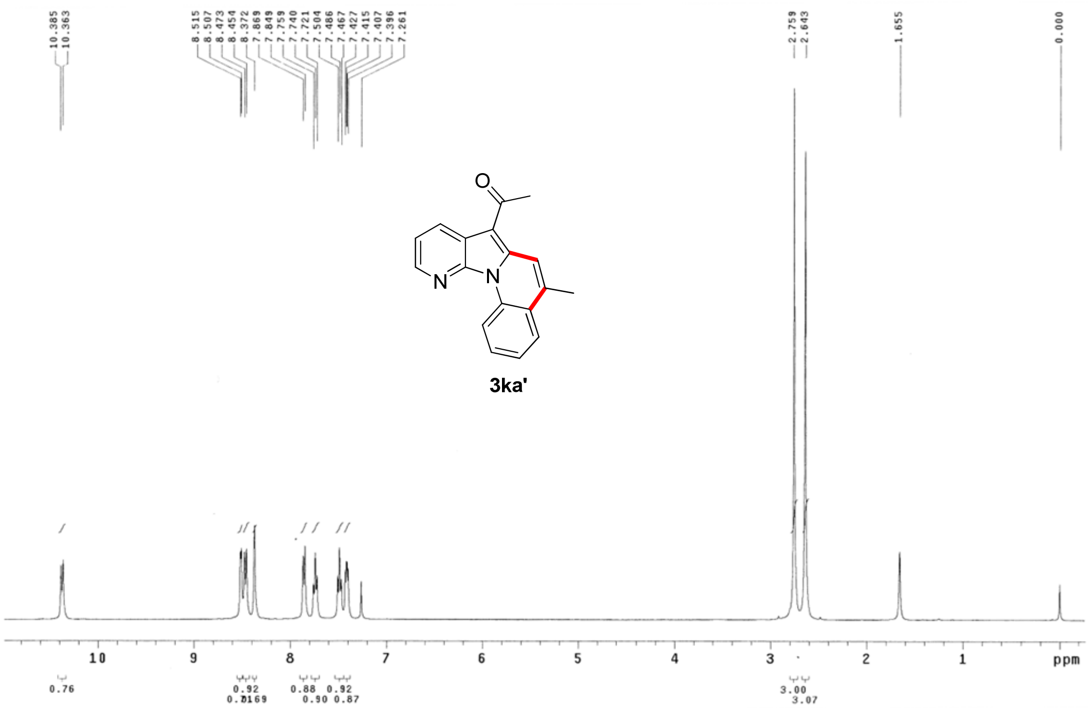

QZY-LSS-11843
Noe of Hc at 7.326 ppm
Single peak
Irraditation of Ha at 6.916 ppm
Noe of Hb at 2.426 ppm
f1 (ppm)

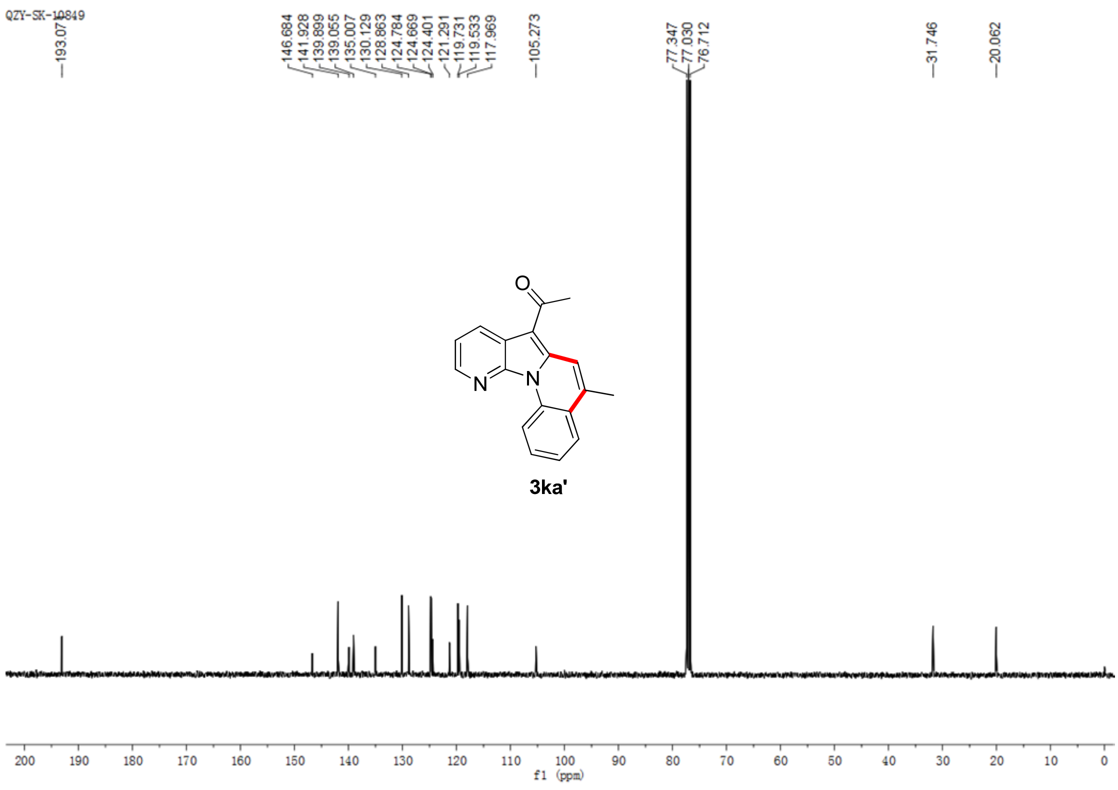

3ia
3ia'
3ia
3ia'

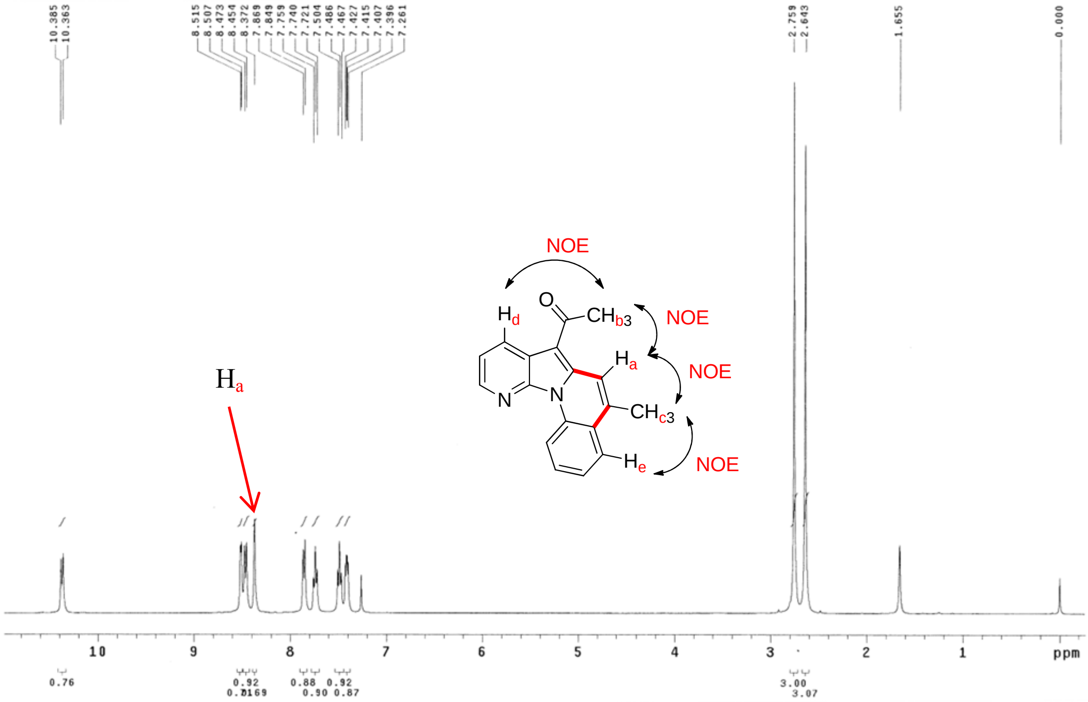

3ia
3ia'


9.854
9.840
9.796
9.782
8.975
8.818
8.750
8.736
8.696
8.682
8.578
8.568
8.526
8.515
8.134
8.115
8.074
8.054
7.676
7.479
7.461
7.377
7.365
7.358
7.347
7.330
7.318
7.262
7.130
7.018
6.716
6.573
2.553
2.475
0.000
N
N
N
3ja
+
3ja'
0.47
1.09
0.56
1.32
0.64
1.37
1.08
0.47
1.03
0.46
0.52
0.57
1.65
0.46
1.16
1.00
0.40
1.87
4.02
f1 (ppm)

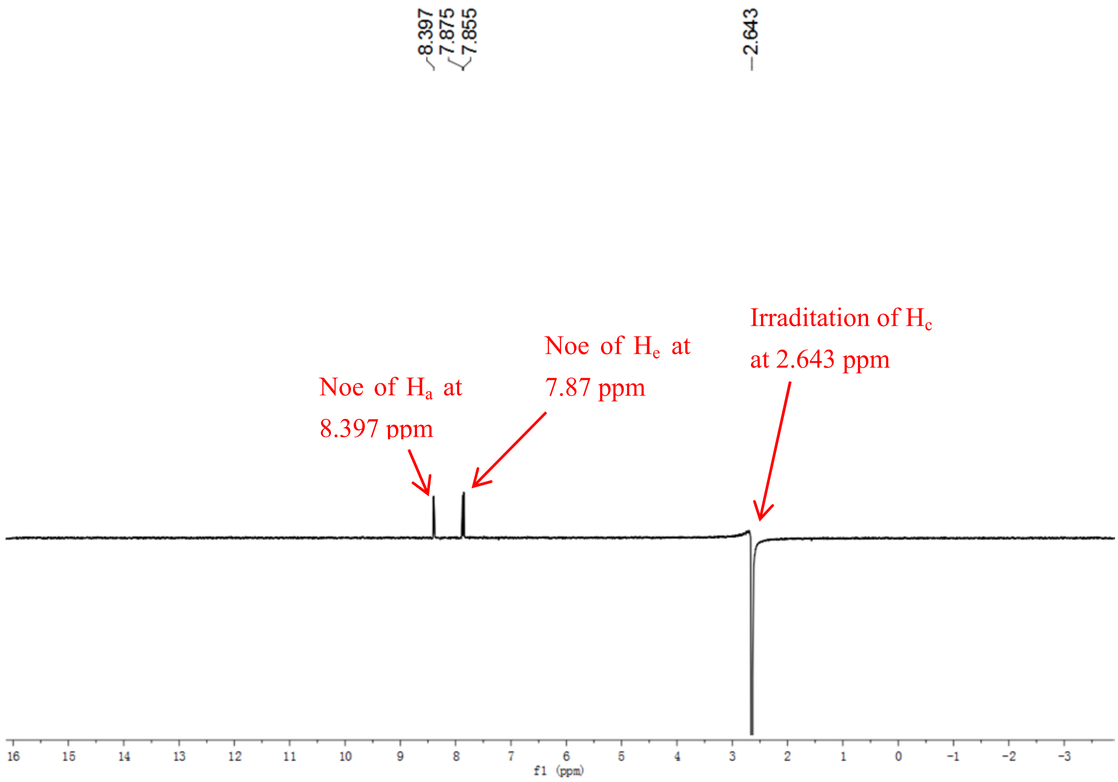

149.288
148.841
148.383
146.805
146.735
142.523
141.857
139.568
136.791
132.164
132.066
129.907
128.876
128.698
128.573
128.453
128.355
122.532
120.419
119.365
119.286
118.567
118.530
111.814
111.719
94.286
94.005
77.353
77.036
76.718
18.683
18.293
N
N
3ja
+
3ja'
f1 (ppm)


10.385
10.363
8.515
8.507
8.473
8.454
8.372
7.869
7.849
7.759
7.740
7.721
7.504
7.486
7.467
7.427
7.415
7.407
7.396
7.261
2.759
2.643
1.655
0.000
N
O
3ka'
ppm

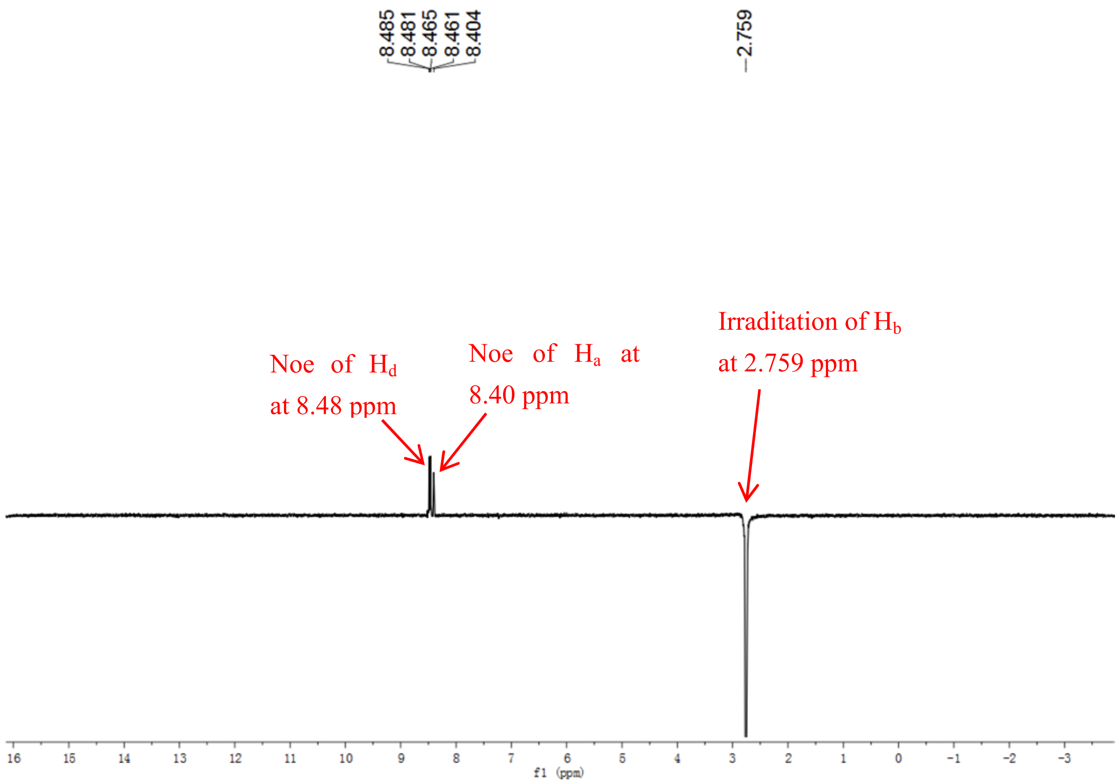

QZY-SK-10849
193.07
146.684
141.928
139.899
139.055
135.007
130.129
128.863
124.784
124.669
124.401
121.291
119.731
119.533
117.969
105.273
77.347
77.030
76.712
31.746
20.062
N
O
3ka'
f1 (ppm)

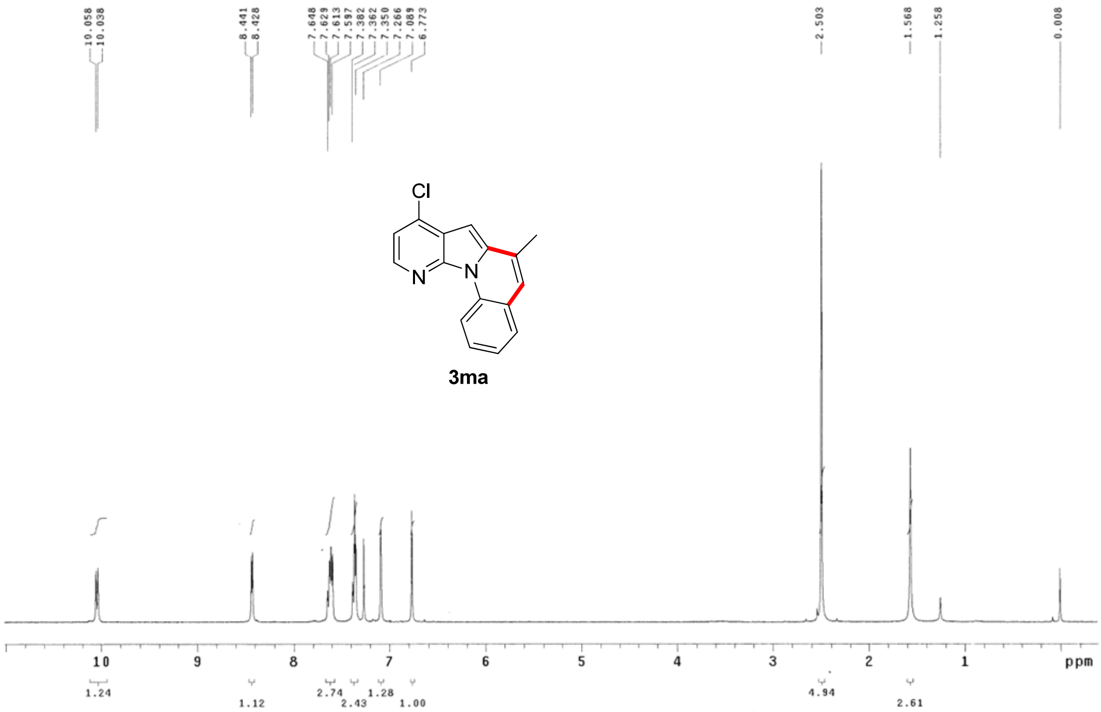


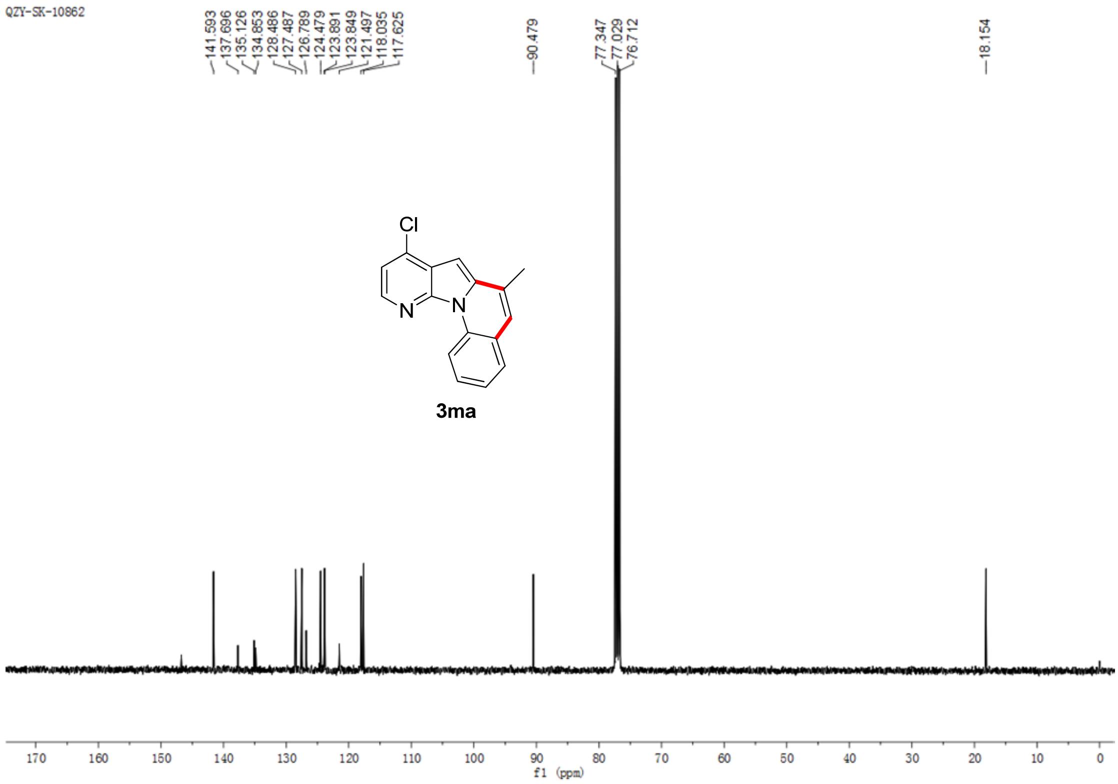
Ha
NOE
O
CHb3
Hd
Ha
N
N
CHc3
He
ppm

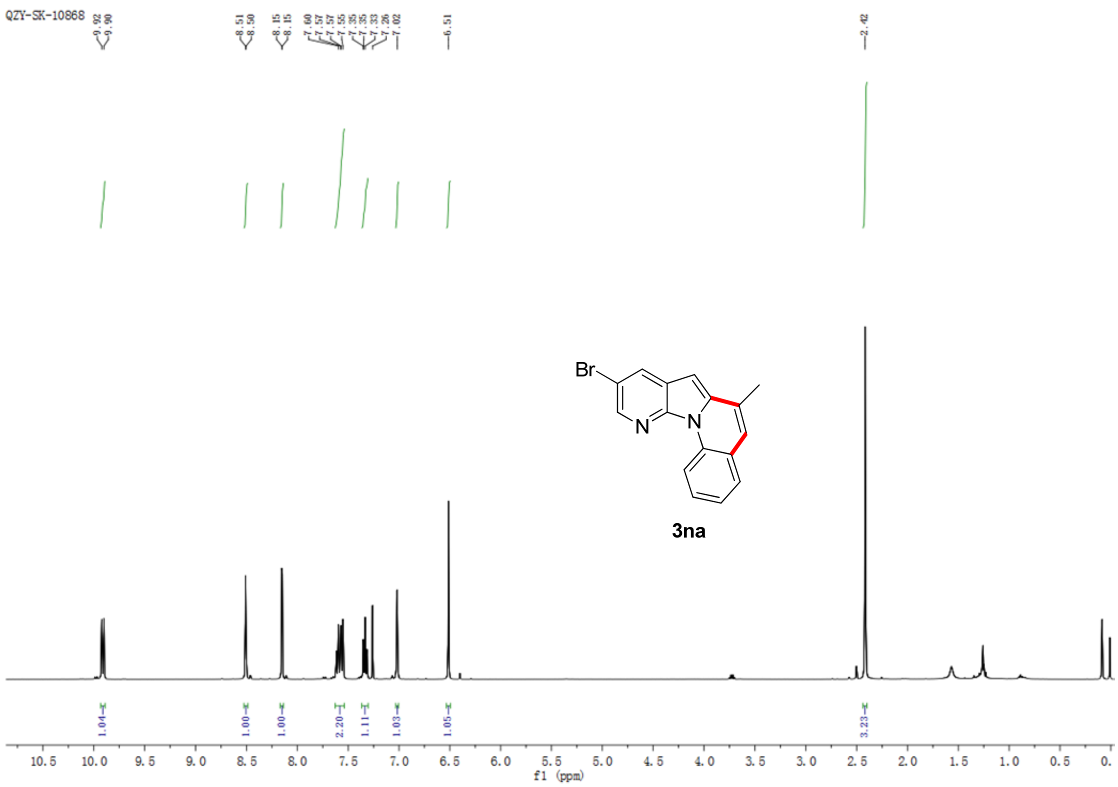


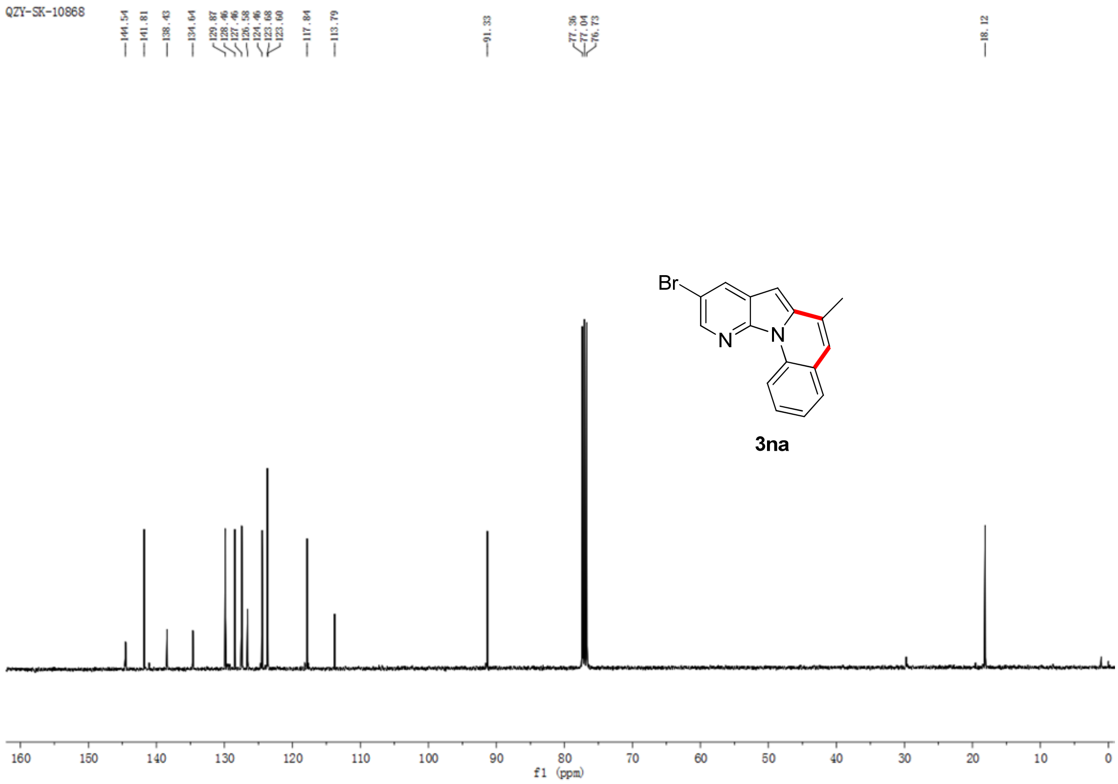
8.397
7.875
7.855
2.643
Irraditation of Hc at 2.643 ppm
Noe of He at 7.87 ppm
Noe of Ha at 8.397 ppm
f1 (ppm)

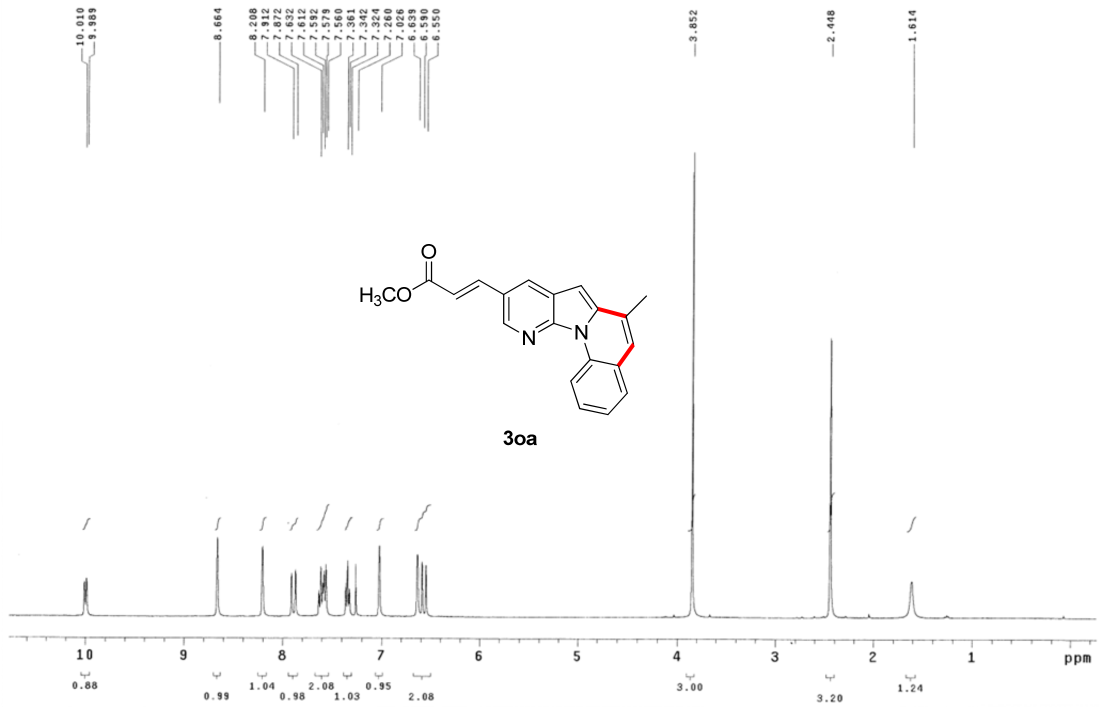

8.485
8.481
8.465
8.461
8.404
2.759
Noe of H$_d$ at 8.48 ppm
Noe of H$_a$ at 8.40 ppm
Irraditation of H$_b$ at 2.759 ppm
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

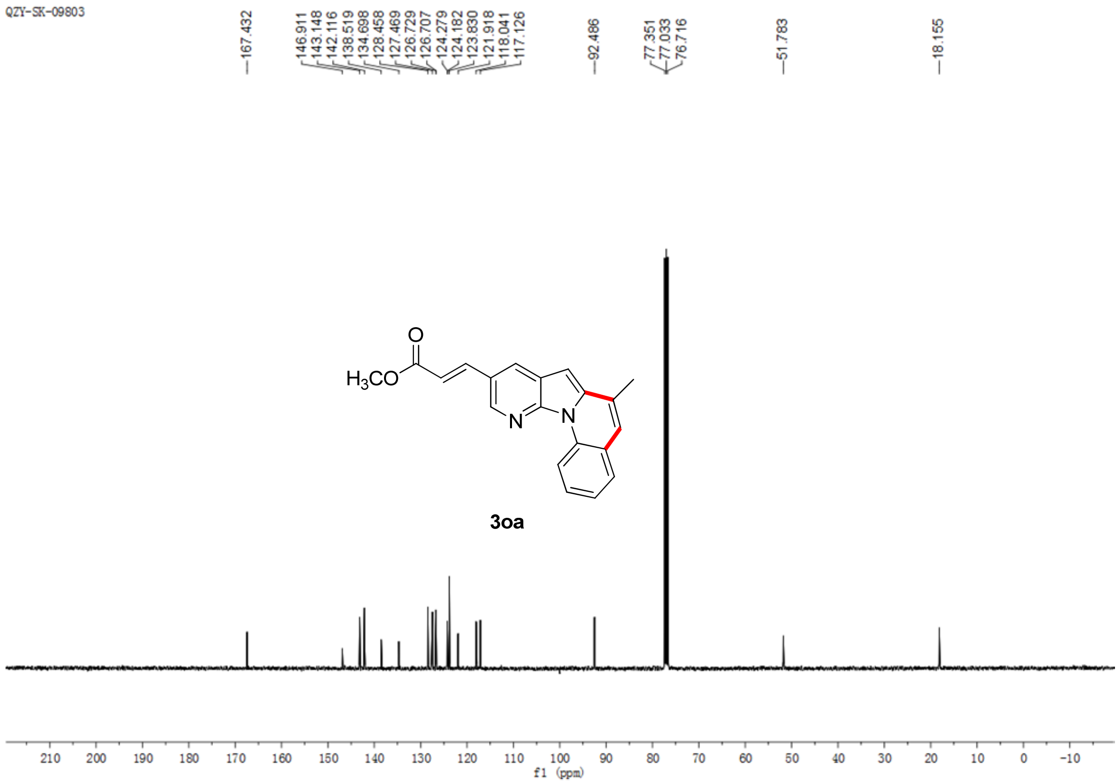

10.058
10.038
8.441
8.428
7.648
7.629
7.613
7.597
7.382
7.362
7.350
7.266
7.089
6.773
2.503
1.568
1.258
0.008
Cl
N
N
3ma
10 9 8 7 6 5 4 3 2 1 ppm
1.24
1.12
2.74
2.43
1.28
1.00
4.94
2.61

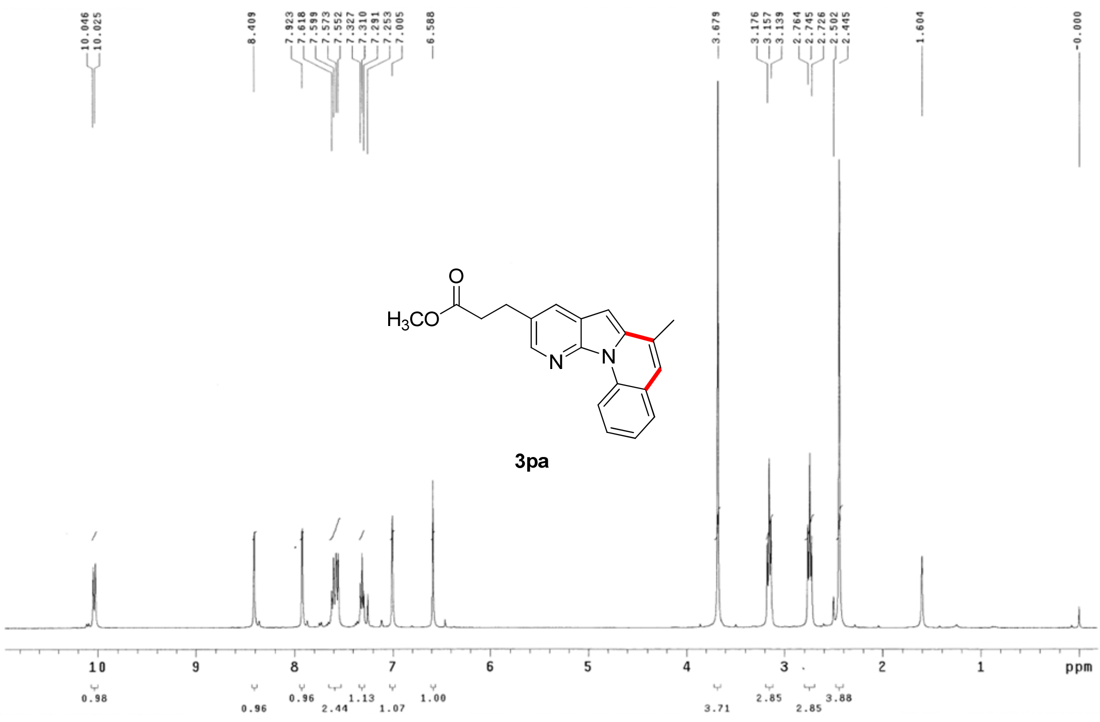

QZY-SK-10862
141.593
137.696
135.126
134.853
128.486
127.487
126.789
124.479
123.891
123.849
121.497
118.035
117.625
90.479
77.347
77.029
76.712
18.154
Cl
N
N
3ma
f1 (ppm)

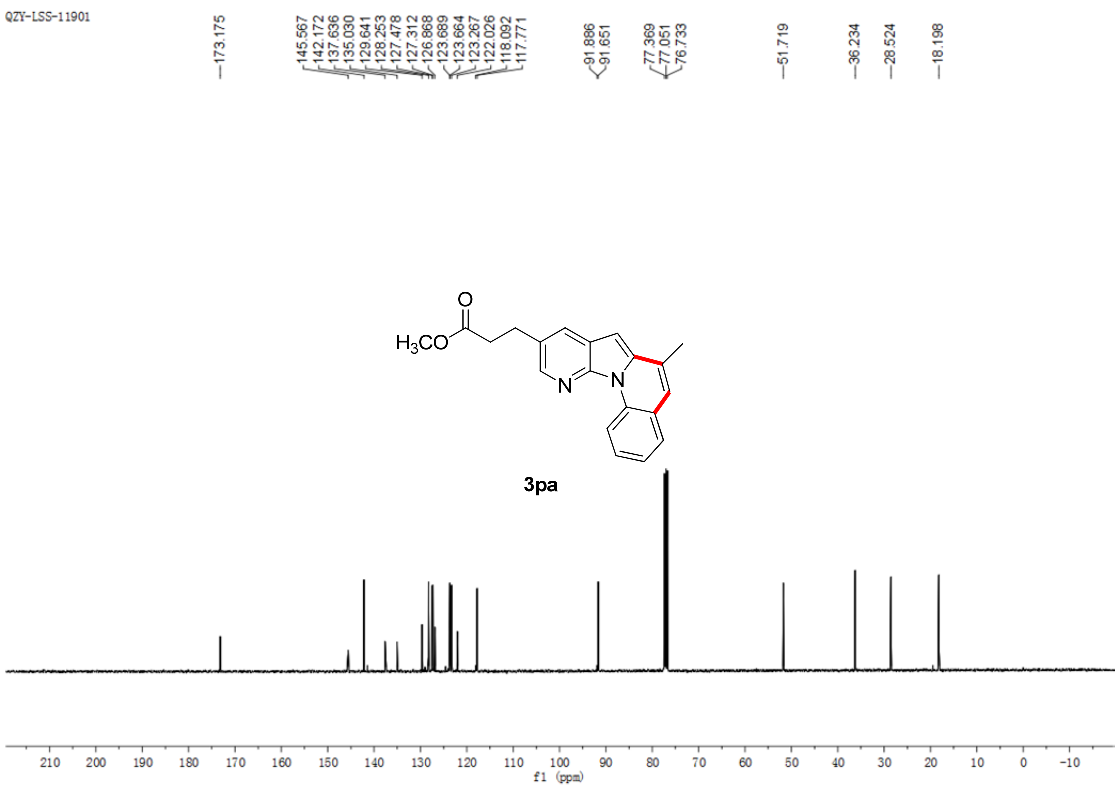

QZY-SK-10868
9.92
9.90
8.51
8.50
8.15
8.15
7.60
7.57
7.57
7.55
7.35
7.35
7.33
7.26
7.02
6.51
2.42
Br
N
N
3na
1.04
1.00
1.00
2.20
1.11
1.03
1.05
3.23
f1 (ppm)

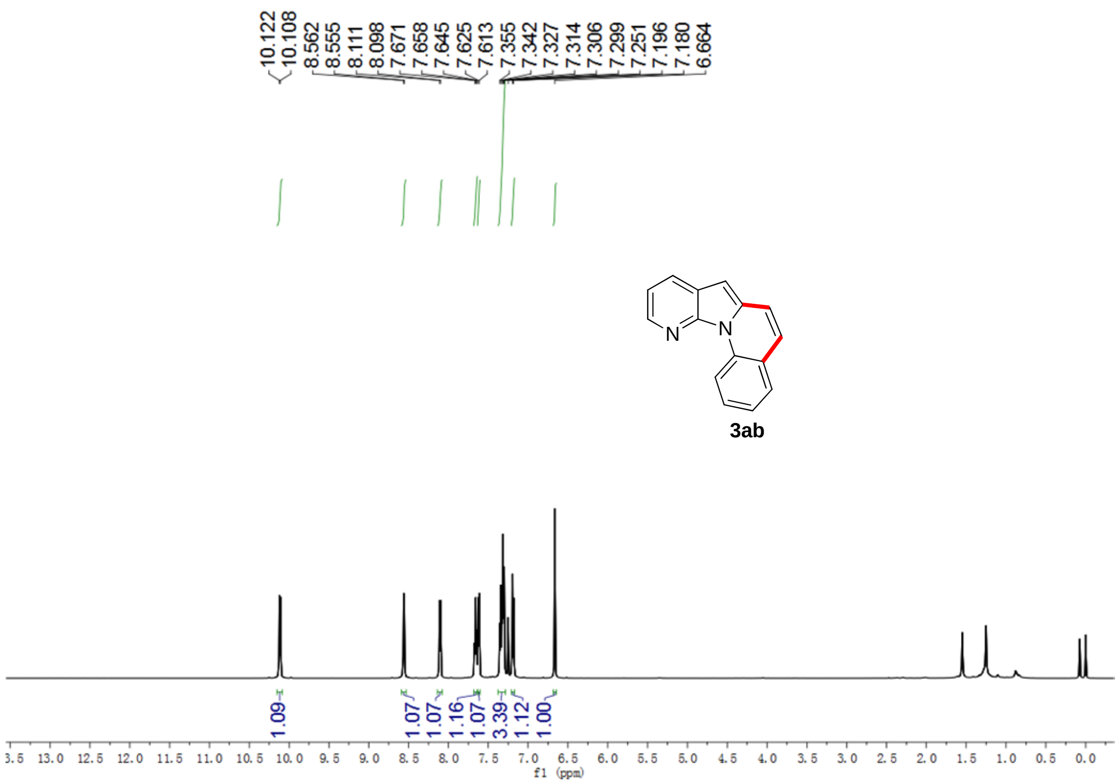

QZY-SK-10868
144.54
141.81
138.43
134.64
129.87
128.46
127.46
126.58
124.46
123.68
123.60
117.84
113.79
91.33
77.36
77.04
76.73
18.12
Br
N
N
3na
f1 (ppm)

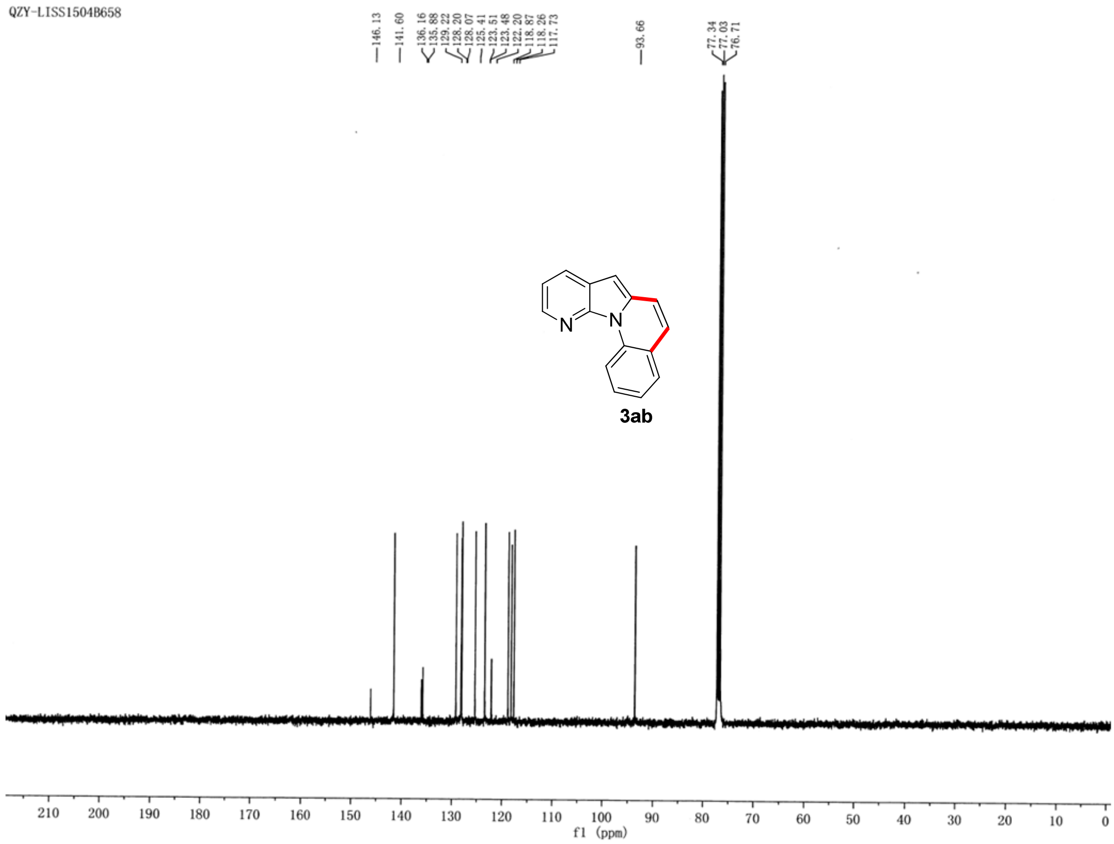

10.010
9.989
8.664
8.208
7.912
7.872
7.632
7.612
7.592
7.579
7.560
7.361
7.342
7.324
7.260
7.026
6.639
6.590
6.550
3.852
2.448
1.614
O
H3CO
N
N
3oa
ppm
0.88
0.99
1.04
0.98
2.08
1.03
0.95
2.08
3.00
3.20
1.24

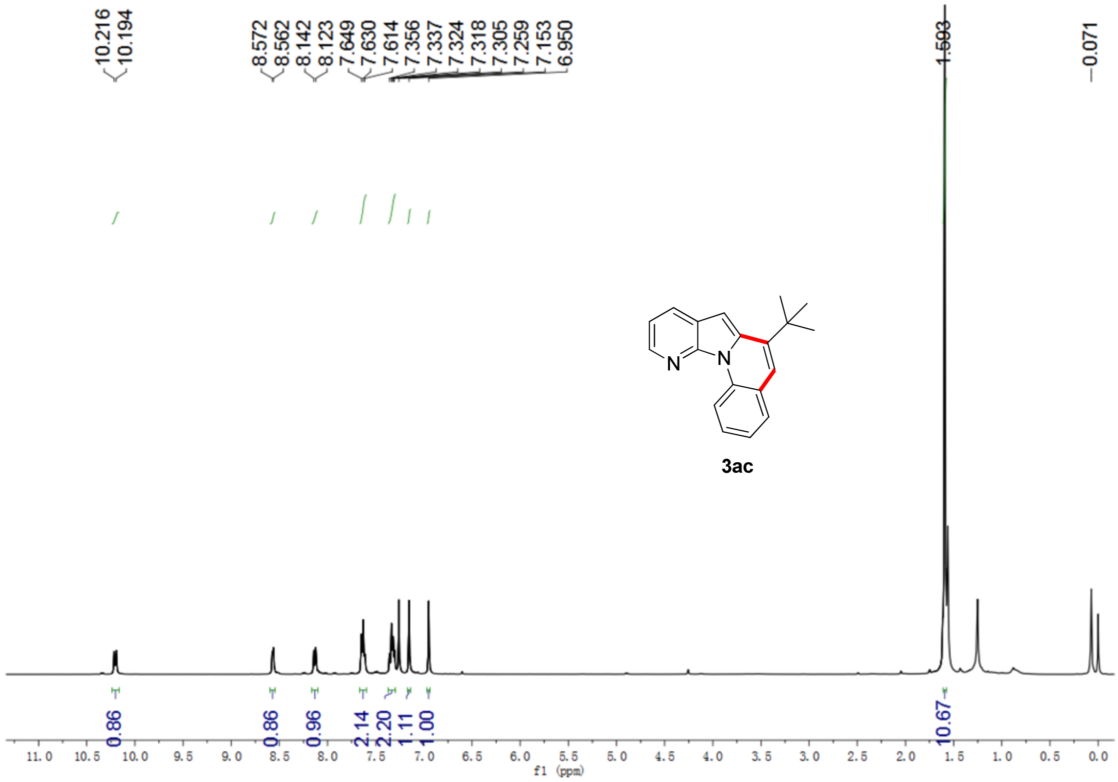

QZY-SK-09803
167.432
146.911 143.148 142.116 138.519 134.698 128.458 127.469 126.729 126.707 124.279 124.182 123.830 121.918 118.041 117.126
92.486
77.351 77.033 76.716
51.783
18.155
H3CO
O
N
N
3oa
f1 (ppm)

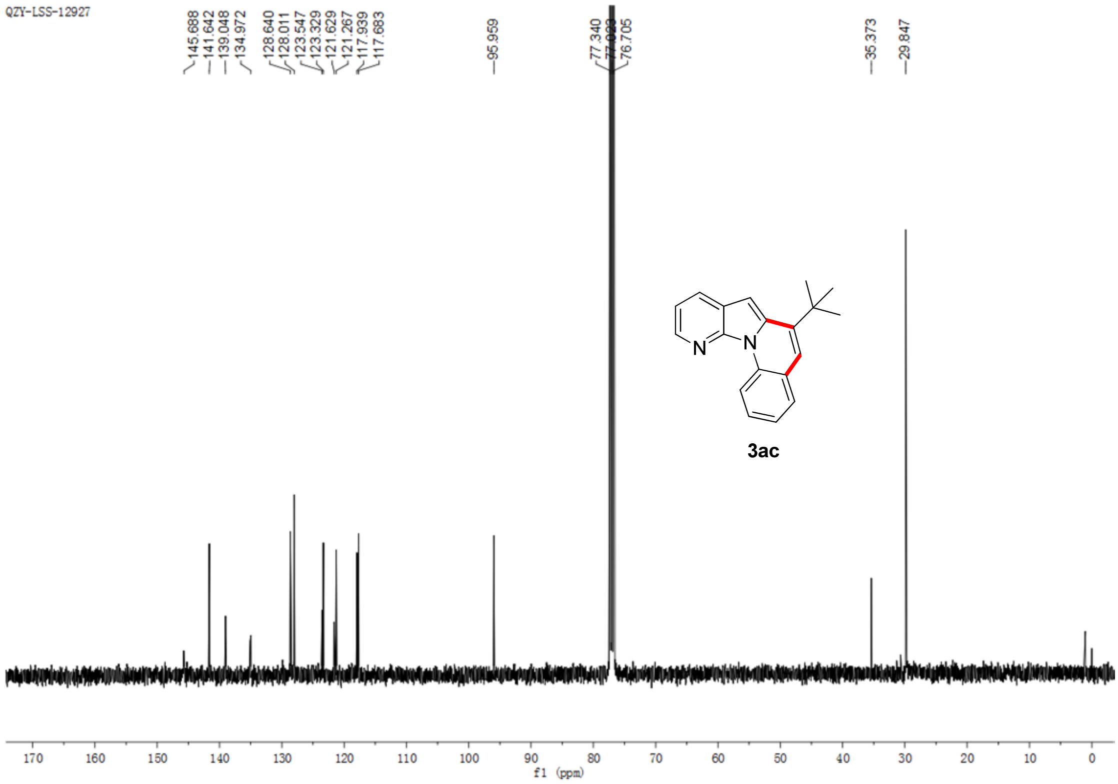

10.046 10.025
8.409
7.923 7.618 7.599 7.573 7.552 7.327 7.310 7.291 7.253 7.005
6.588
3.679
3.176 3.157 3.139 2.764 2.745 2.726 2.502 2.445
1.604
-0.000
H3CO
O
N
N
3pa
ppm
0.98 0.96 0.96 2.44 1.13 1.07 1.00 3.71 2.85 2.85 3.88

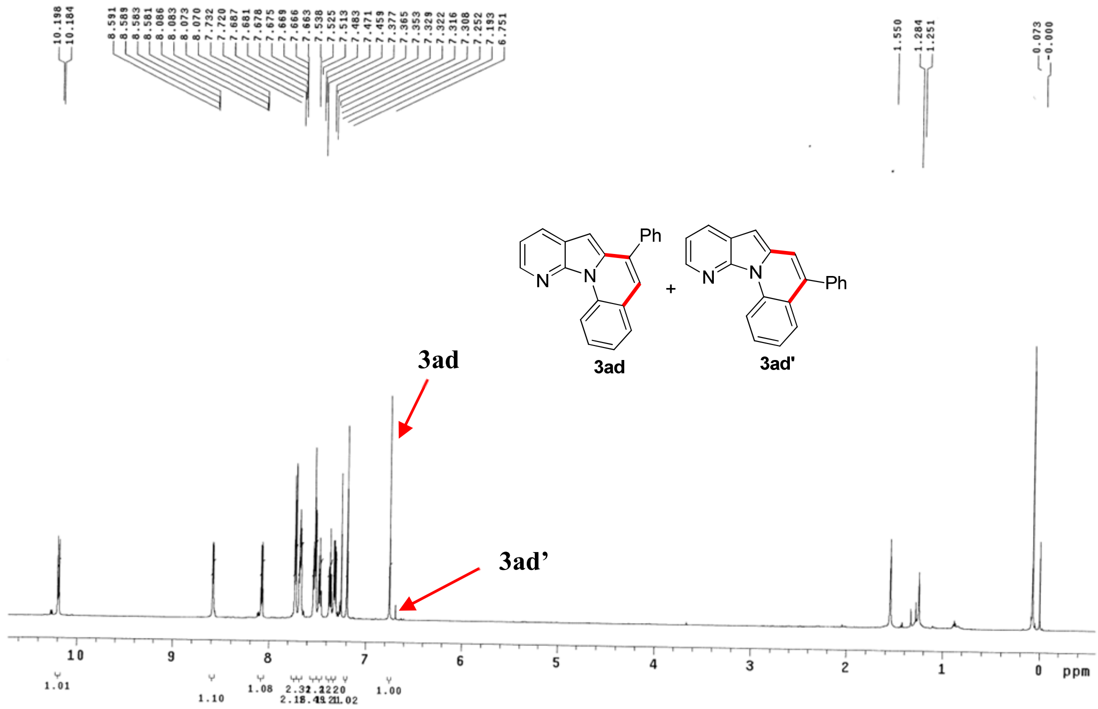

QZY-LSS-11901
173.175
145.567
142.172
137.636
135.030
129.641
128.253
127.478
127.312
126.868
123.689
123.664
123.267
122.026
118.092
117.771
91.886
91.651
77.369
77.051
76.733
51.719
36.234
28.524
18.198
O
H_3CO
N
N
3pa
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

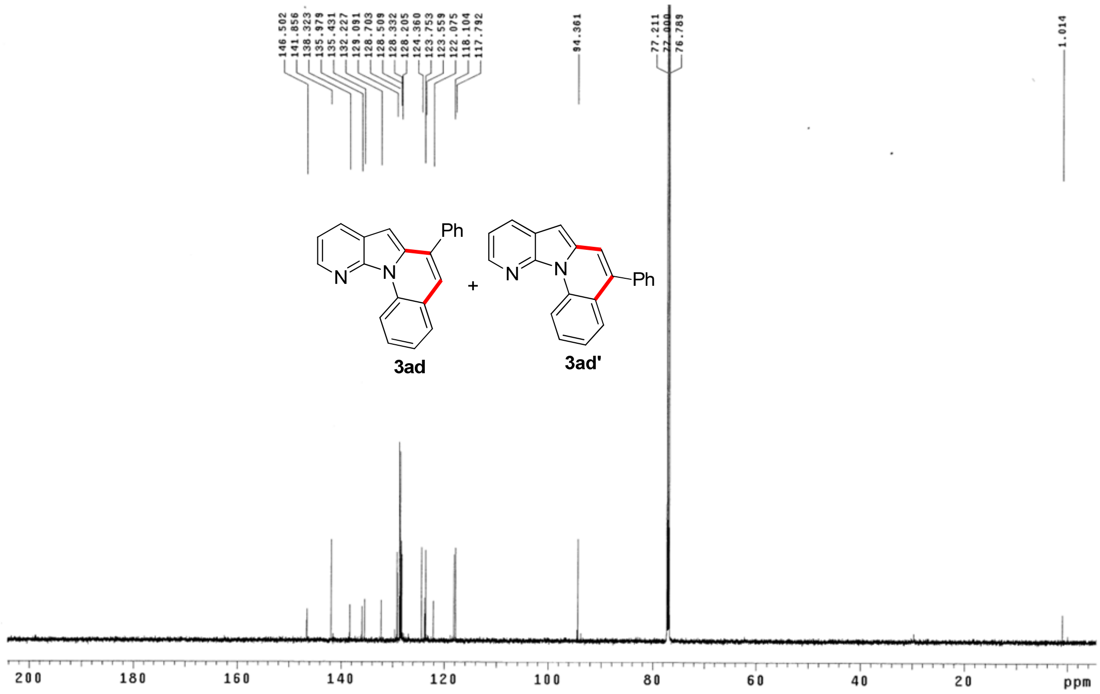

10.122
10.108
8.562
8.555
8.111
8.098
7.671
7.658
7.645
7.625
7.613
7.355
7.342
7.327
7.314
7.306
7.299
7.251
7.196
7.180
6.664
N
N
3ab
1.09
1.07
1.07
1.16
1.07
3.39
1.12
1.00
13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

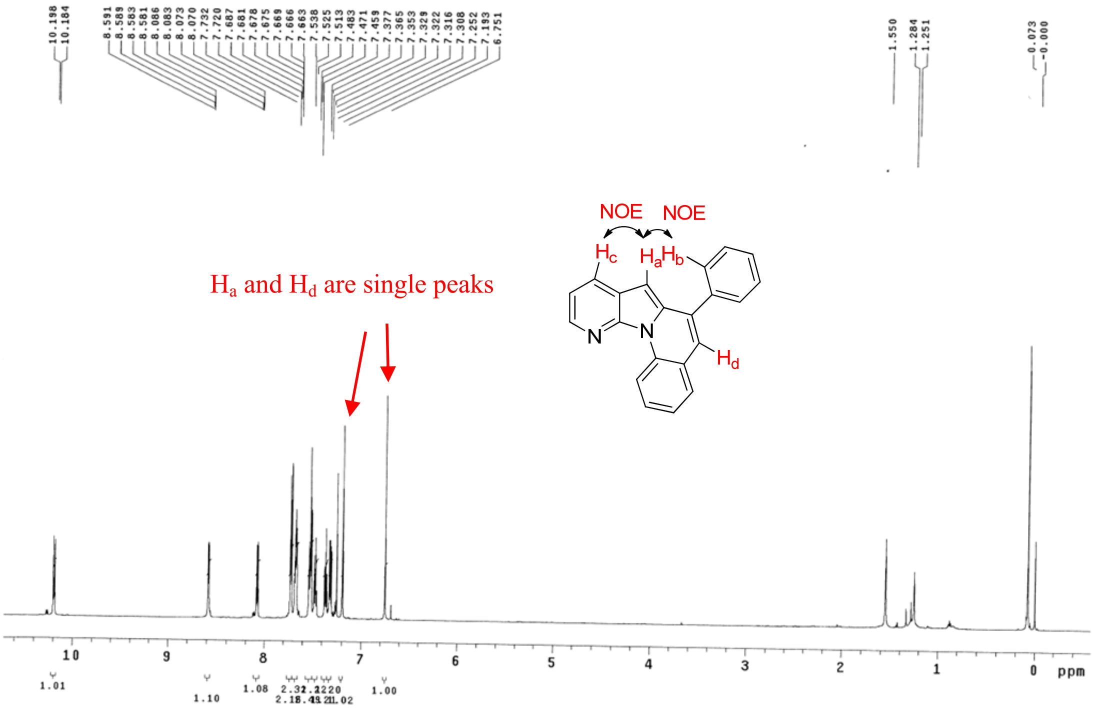

QZY-LISS1504B658
146.13
141.60
136.16
135.88
129.22
128.20
128.07
125.41
123.51
123.48
122.20
118.87
118.26
117.73
93.66
77.34
77.03
76.71
N
N
3ab
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

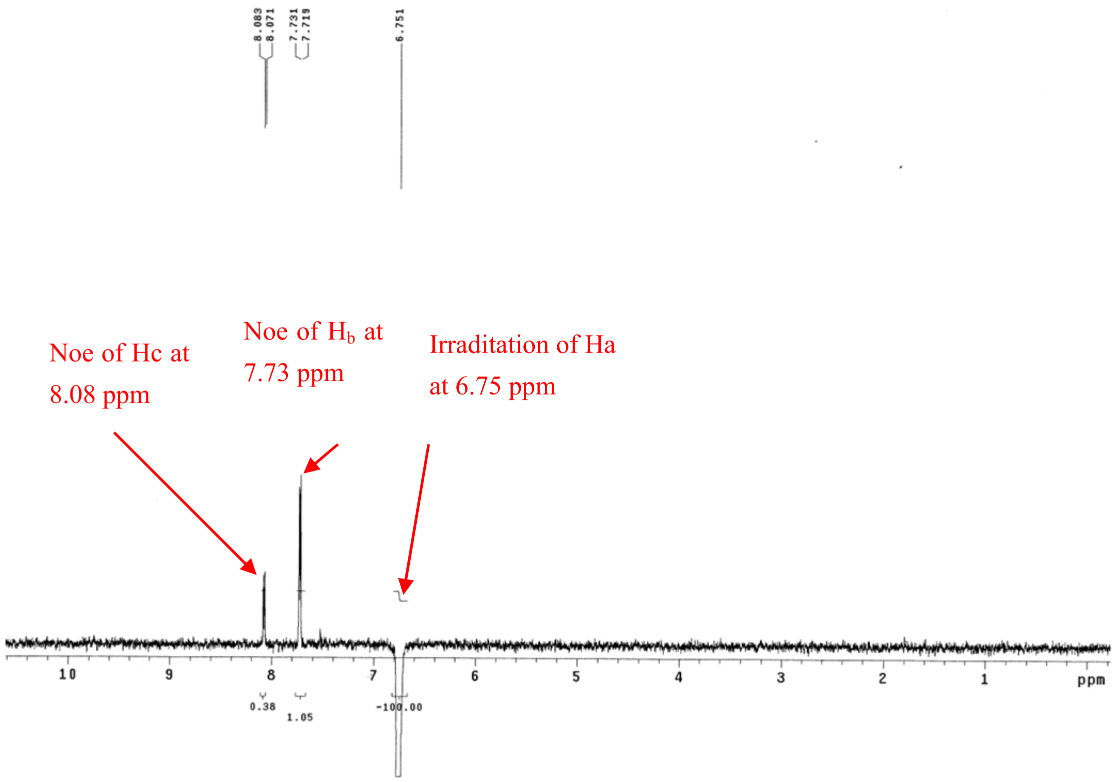

10.216
10.194
8.572
8.562
8.142
8.123
7.649
7.630
7.614
7.356
7.337
7.324
7.318
7.305
7.259
7.153
6.950
1.593
-0.071
N
N
3ac
0.86
0.86
0.96
2.14
2.20
1.11
1.00
10.67
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

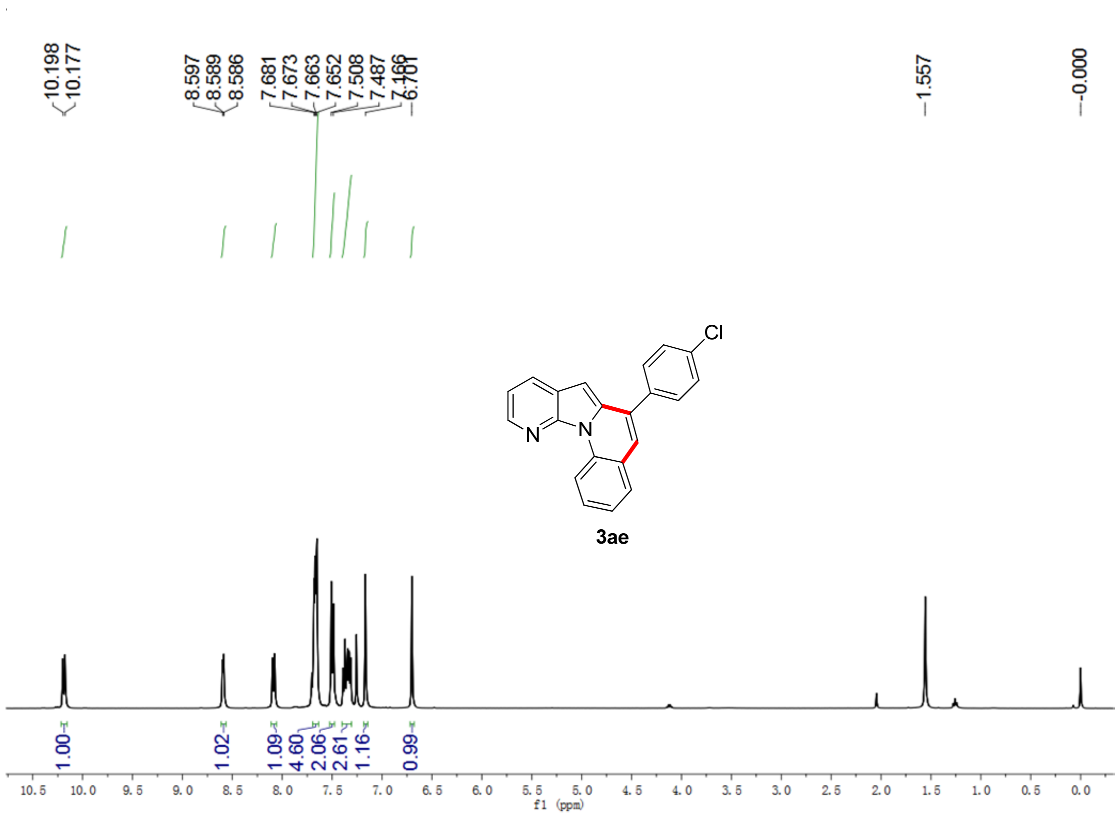

QZY-LSS-12927
145.688
141.642
139.048
134.972
128.640
128.011
123.547
123.329
121.629
121.267
117.939
117.683
95.959
77.340
76.705
35.373
29.847
N
N
3ac
f1 (ppm)

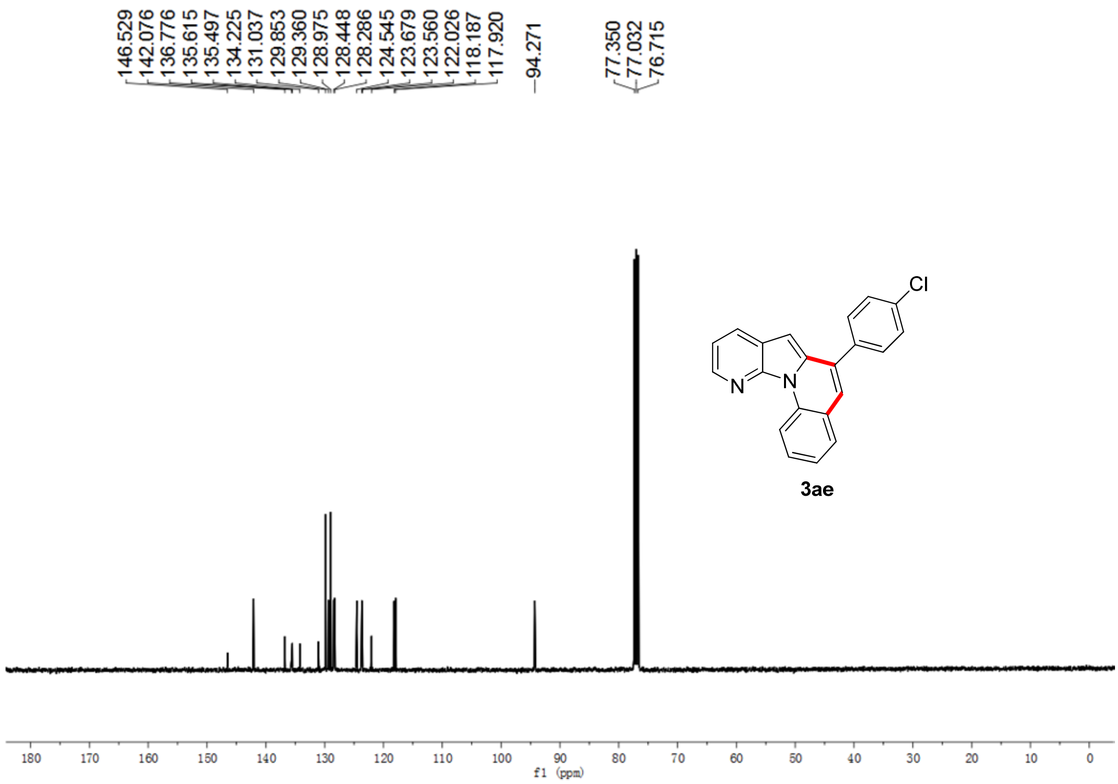

10.198
10.184
8.591
8.589
8.583
8.581
8.086
8.083
8.073
8.070
7.732
7.720
7.687
7.681
7.678
7.675
7.669
7.666
7.663
7.538
7.525
7.513
7.483
7.471
7.459
7.377
7.365
7.353
7.329
7.322
7.316
7.308
7.252
7.193
6.751
1.550
1.284
1.251
0.073
-0.000
Ph
N
N
+
Ph
3ad
3ad'
3ad
3ad'
1.01
1.10
1.08
1.00
ppm

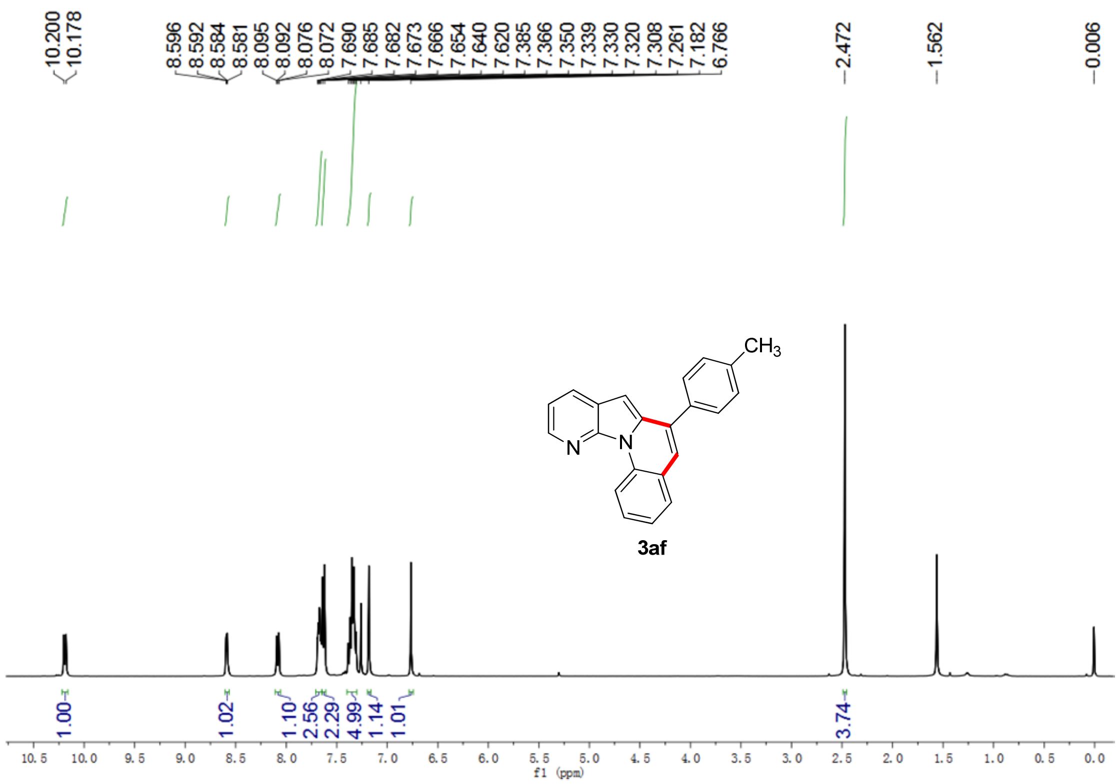

146.502
141.856
138.323
135.979
135.431
132.227
129.091
128.703
128.509
128.332
128.205
124.360
123.753
123.559
122.075
118.104
117.792
94.361
77.211
77.000
76.789
1.014
Ph
N
N
+
Ph
N
N
3ad
3ad'
200
180
160
140
120
100
80
60
40
20
ppm

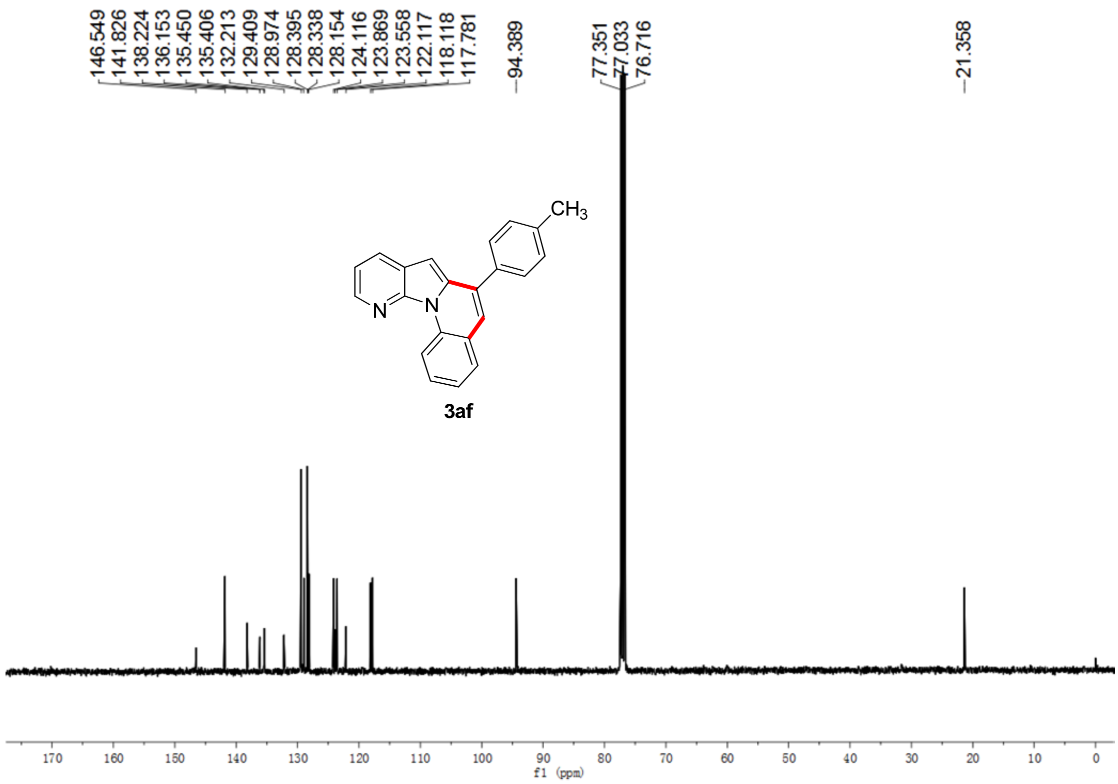

10.198
10.184
8.591
8.589
8.583
8.581
8.086
8.083
8.073
8.070
7.732
7.720
7.687
7.681
7.678
7.675
7.669
7.666
7.663
7.538
7.525
7.513
7.483
7.471
7.459
7.377
7.365
7.353
7.329
7.322
7.316
7.308
7.252
7.193
6.751
1.550
1.284
1.251
0.073
-0.000
NOE
NOE
Hc
Ha
Hb
Hd
N
N
Ha and Hd are single peaks
10
9
8
7
6
5
4
3
2
1
0
ppm
1.01
1.10
1.08
1.00

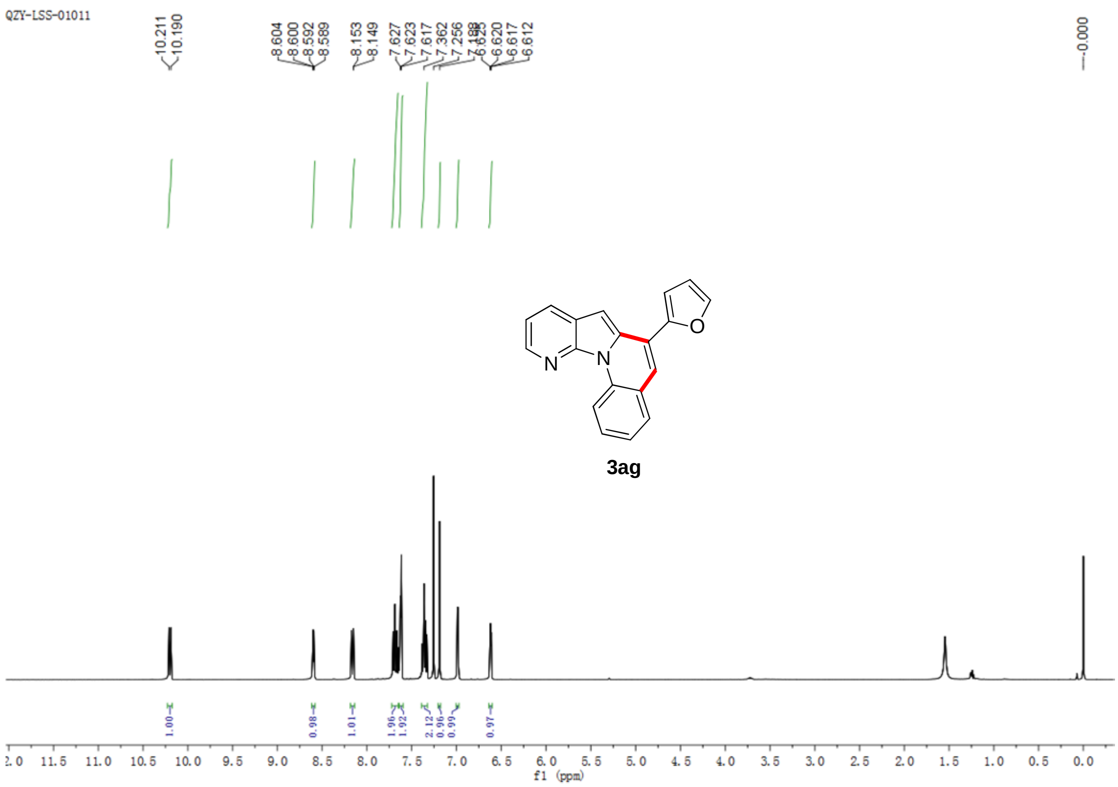

Noe of Hc at 8.08 ppm
Noe of H_b at 7.73 ppm
Irraditation of Ha at 6.75 ppm

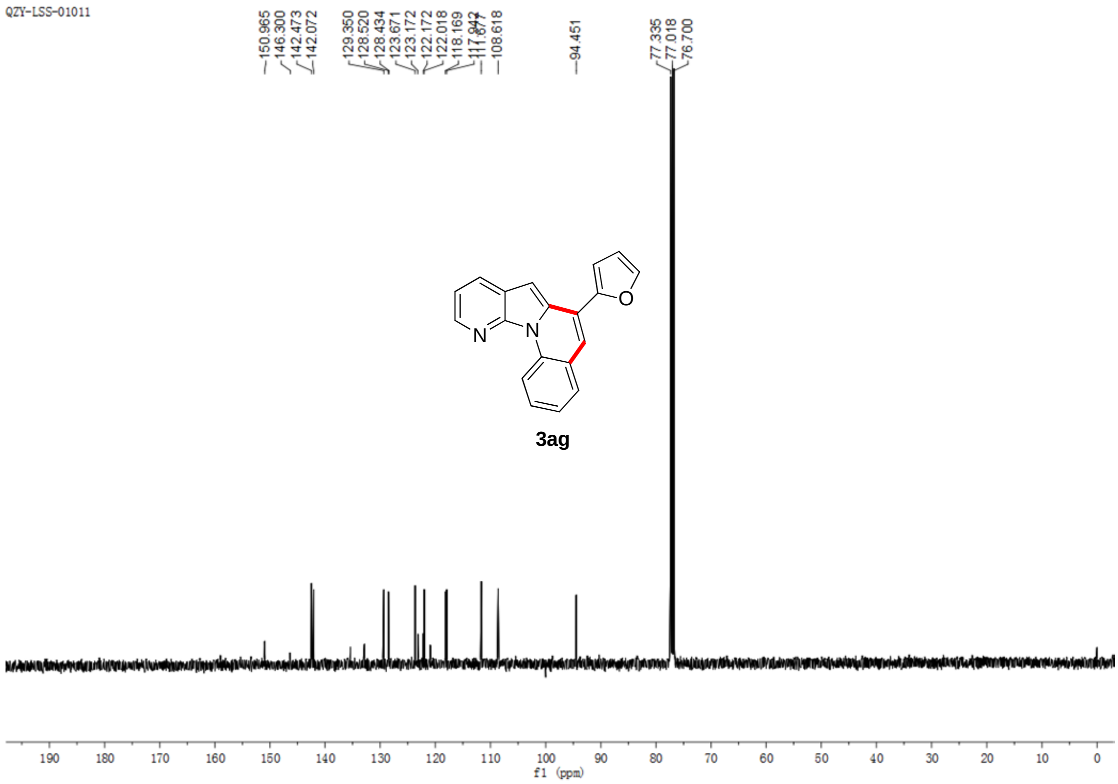

Cl
N
N
3ae


146.529
142.076
136.776
135.615
135.497
134.225
131.037
129.853
129.360
128.975
128.448
128.286
124.545
123.679
123.560
122.026
118.187
117.920
94.271
77.350
77.032
76.715
Cl
N
N
3ae
f1 (ppm)

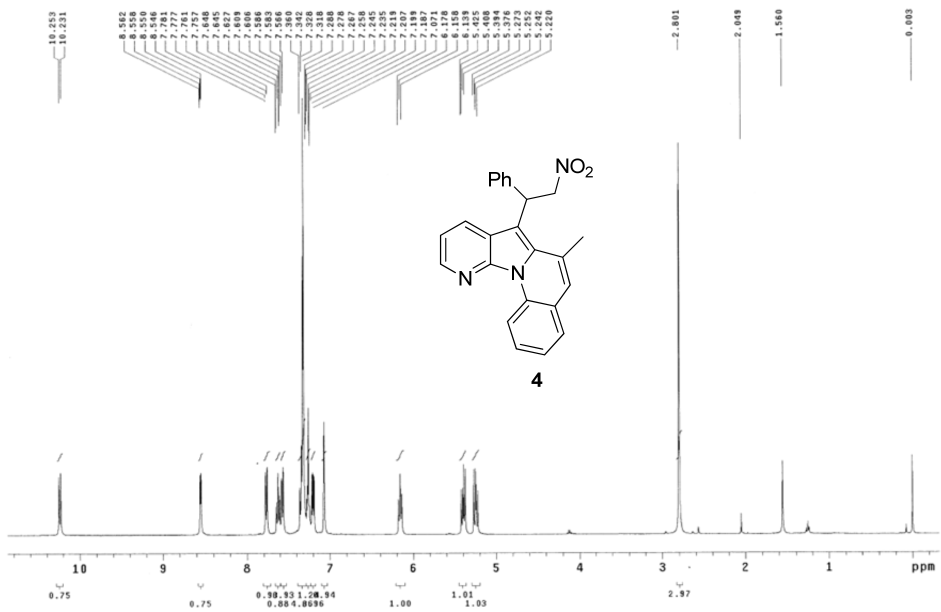

10.200
10.178
8.596
8.592
8.584
8.581
8.095
8.092
8.076
8.072
7.690
7.685
7.682
7.673
7.666
7.654
7.640
7.620
7.385
7.366
7.350
7.339
7.330
7.320
7.308
7.261
7.182
6.766
2.472
1.562
0.006
CH_3
N
N
3af
1.00
1.02
1.10
2.56
2.29
4.99
1.14
1.01
3.74
f1 (ppm)


146.549
141.826
138.224
136.153
135.450
135.406
132.213
129.409
128.974
128.395
128.338
128.154
124.116
123.869
123.558
122.117
118.118
117.781
94.389
77.351
77.033
76.716
21.358
CH3
N
N
3af
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

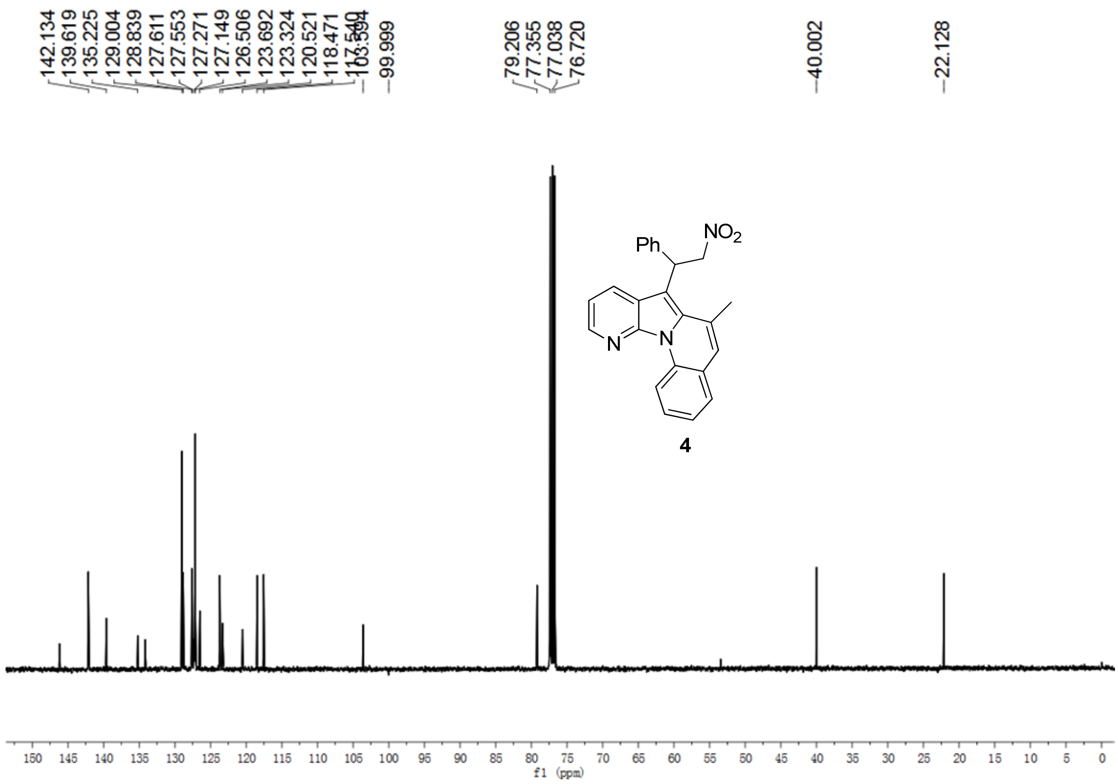

QZY-LSS-01011
10.211
10.190
8.604
8.600
8.592
8.589
8.153
8.149
7.627
7.623
7.617
7.362
7.256
7.188
6.625
6.620
6.617
6.612
0.000
O
N
N
3ag
f1 (ppm)


QZY-LSS-01011
150.965
146.300
142.473
142.072
129.350
128.520
128.434
123.671
123.172
122.172
122.018
118.169
111.677
108.618
94.451
77.335
77.018
76.700
N
N
O
f1 (ppm)

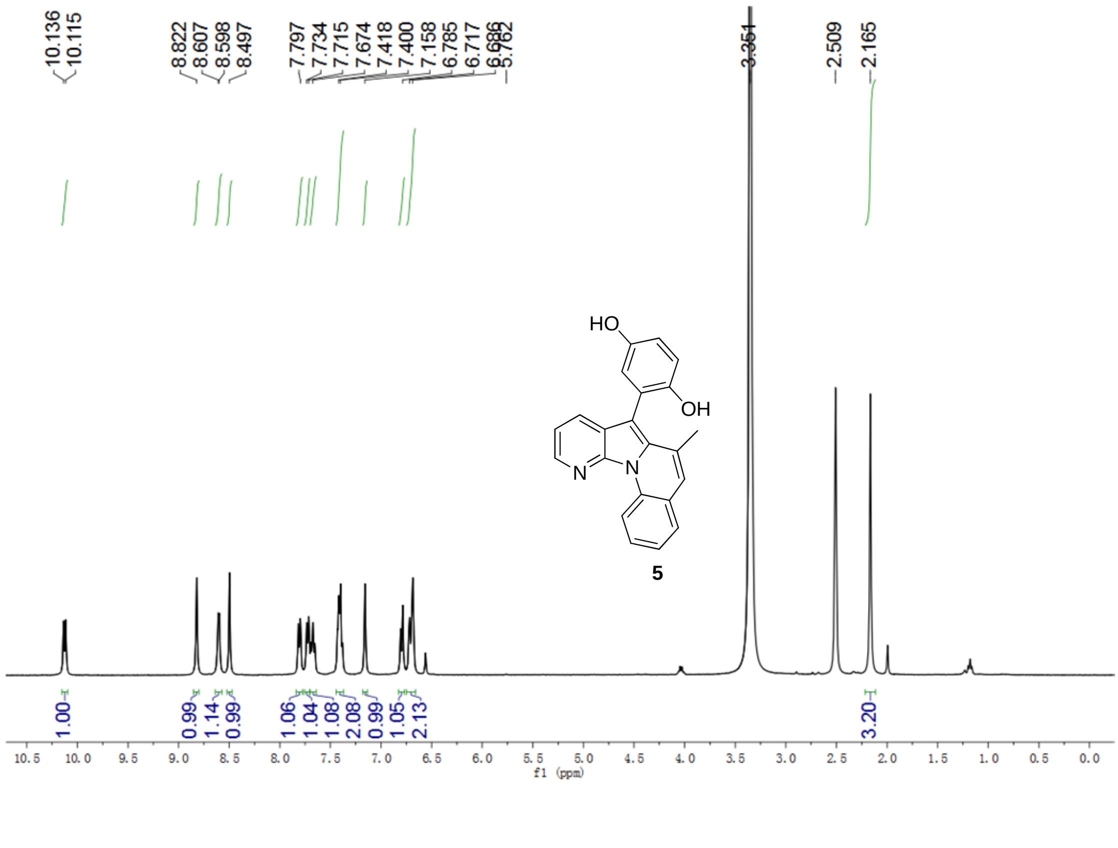
3ag


10.253
10.231
2.801
2.049
1.560
0.003
Ph
NO_2
N
N
ppm
0.75
0.75
1.00
1.01
1.03
2.97

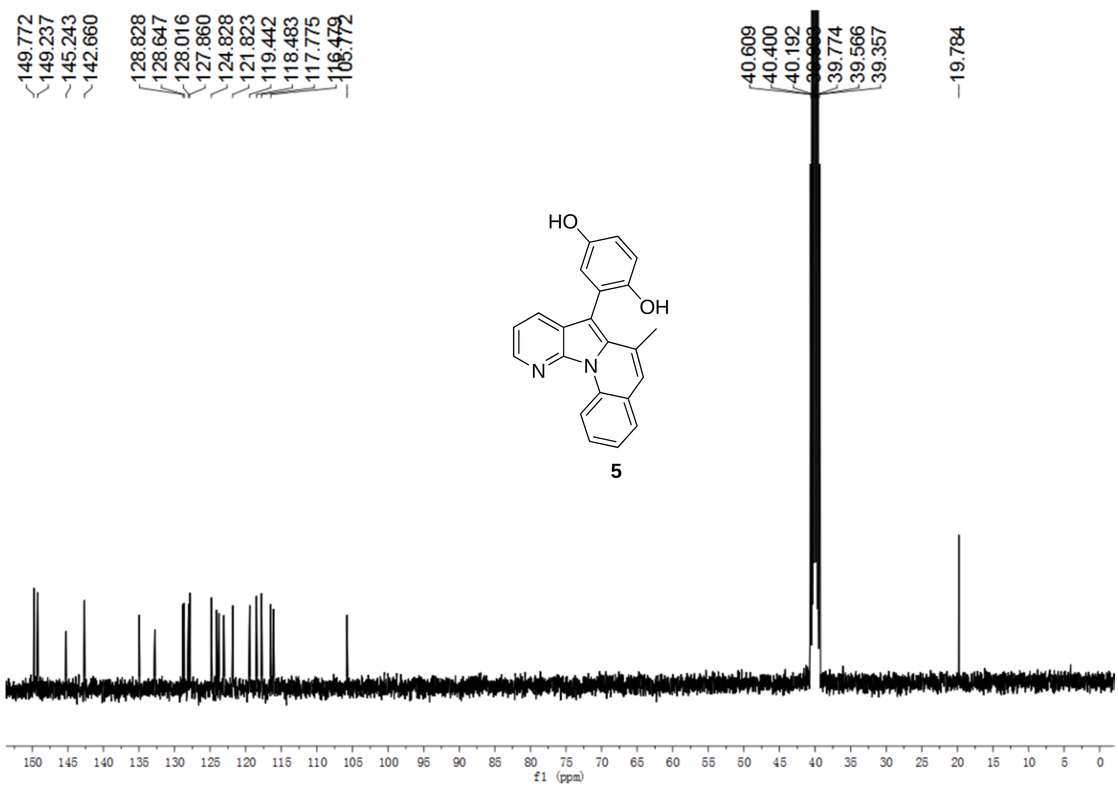
4

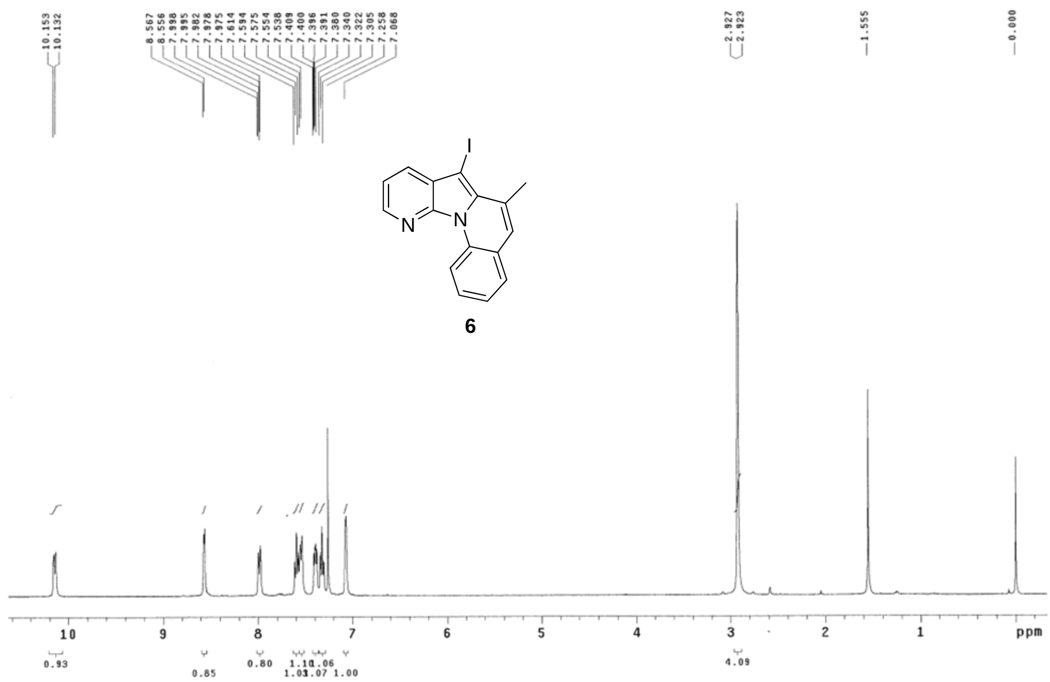


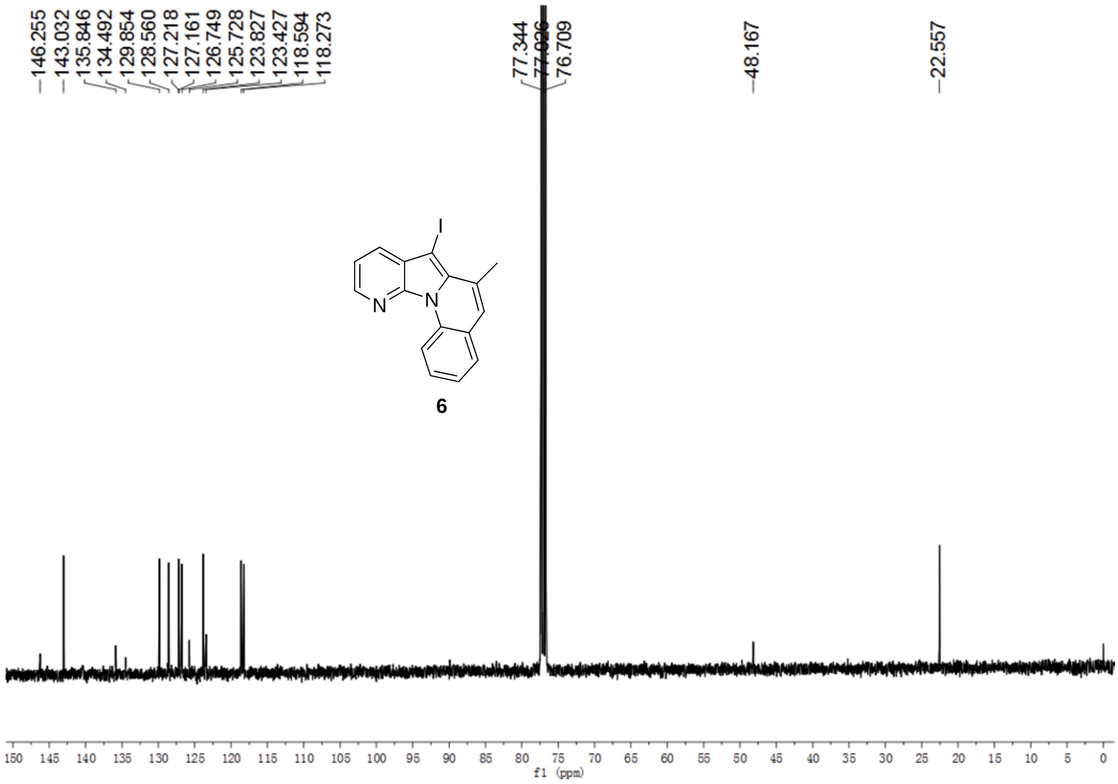
4



5


149.772
149.237
145.243
142.660
128.828
128.647
128.016
127.860
124.828
121.823
119.442
118.483
117.775
116.479
105.772
40.609
40.400
40.192
39.774
39.566
39.357
19.784
HO
OH
N
N
5
f1 (ppm)


10.153
10.132
8.567
8.556
7.998
7.995
7.982
7.978
7.975
7.614
7.594
7.575
7.554
7.538
7.409
7.400
7.396
7.391
7.380
7.340
7.322
7.305
7.258
7.068
2.927
2.923
1.555
0.000
I
N
N
6
ppm
0.93
0.85
0.80
1.10
1.06
1.01
1.07
1.00
4.09


146.255
143.032
135.846
134.492
129.854
128.560
127.218
127.161
126.749
125.728
123.827
123.427
118.594
118.273
77.344
77.026
76.709
48.167
22.557
I
N
N
6
f1 (ppm)