Supporting Information

Rhodium(III)-catalyzed C–C coupling of 7-azaindoles with vinyl acetates and allyl acetates

Shuai-Shuai Li,[a,b,c] Cheng-Qi Wang,[a] Hui Lin,[a] Xiao-Mei Zhang,[b] and Lin Dong*[a]

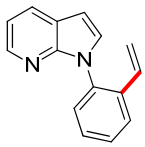
Table of Contents

1. General Methods

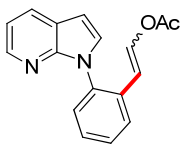
NMR data were obtained for ^{1}H at 400 MHz or 600 MHz, and for ^{13}C at 100 MHz or 151 MHz. Chemical shifts were reported in ppm from tetramethylsilane with the solvent resonance as the internal standard in $CDCl_3$ solution. ESI HRMS was recorded on a Waters SYNAPT G2 and Water XEVO G2 Q-ToF. UV detection 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 and electron-rich alkenes were commercially available. *N*-substituted 7-azaindoles were prepared according to the literature procedures.[1]

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

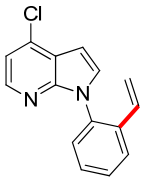
1-phenyl-1H-pyrrolo[2,3-b]pyridine **1a** (0.1 mmol, 19.4 mg), vinyl acetate **2a** (0.5 mL) and $Cp^*Rh(CH_3CN)_3(SbF_6)_2$ (2.5 mg, 3.0 mol %) were stirred in dioxane (1.0 mL) in seal tube at 130 °C for 30 h. After completion, the reaction mixture was purified by flash chromatography eluting with ethyl acetate and petroleum ether (1:50) to give the product **3aa** as colorless oil (8.3 mg, 38%), ethyl acetate and petroleum ether (1:10) to give the product **4aa** as colorless oil (16.6 mg, 60%).



1-(2-vinylphenyl)-1H-pyrrolo[2,3-b]pyridine (**3aa**). 30 h, 48% yield; ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.39 – 8.31 (m, 1H), 7.99 (dd, *J* = 7.8, 1.0 Hz, 1H), 7.76 (d, *J* = 6.9 Hz, 1H), 7.48 – 7.40 (m, 3H), 7.30 (d, *J* = 3.5 Hz, 1H), 7.12 (dd, *J* = 7.8, 4.7 Hz, 1H), 6.63 (d, *J* = 3.5 Hz, 1H), 6.33 (dd, *J* = 17.5, 11.0 Hz, 1H), 5.72 (d, *J* = 17.5 Hz, 1H), 5.18 (d, *J* = 11.1 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.5, 143.8, 135.8, 135.1, 132.2, 129.9, 128.9, 128.6, 128.5, 128.4, 126.3, 120.5, 116.4, 116.3, 100.8 ppm. ESI HRMS: calcd. for $C_{15}H_{12}N_2$+H 221.1079, found 221.1086.

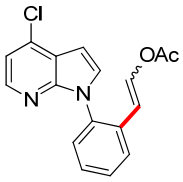


(E)-2-(1H-pyrrolo[2,3-b]pyridin-1-yl)styryl acetate (**4aa**); (Z)-2-(1H-pyrrolo[2,3-b] pyridin-1-yl)styryl acetate (**4aa'**); (**4aa**:**4aa'** = **5**:**4**). 30 h, 60% yield; ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.33 (t, *J* = 3.8 Hz, 2H), 8.03 – 7.96 (m, 3H), 7.77 (d, *J* = 12.7 Hz, 1H), 7.66 (d, *J* = 6.2 Hz, 1H), 7.46 (dd, *J* = 11.0, 7.5 Hz, 2H), 7.41 (dd, *J* = 15.7, 6.0 Hz, 4H), 7.28 (t, *J* = 3.1 Hz, 2H), 7.13 (dt, *J* = 11.0, 6.9 Hz, 3H), 6.63 (dd, *J* = 20.7, 3.4 Hz, 2H), 6.01 (d, *J* = 12.7 Hz, 1H), 5.35 (d, *J* = 7.4 Hz, 1H), 2.09 (s, 3H), 2.08 (s, 3H) ppm. ESI HRMS: calcd. for $C_{17}H_{14}N_2O_2$+H 279.1134, found 279.1124.

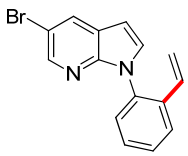


4-chloro-1-(2-vinylphenyl)-1H-pyrrolo[2,3-b]pyridine (**3ba**). 30 h, 25% yield; ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.21 (d, *J* = 5.1 Hz, 1H), 7.77 – 7.73 (m, 1H), 7.46 (dd, *J* = 10.8, 4.3 Hz, 1H), 7.43 (td, *J* = 7.5, 1.4 Hz, 1H), 7.38 (dd, *J* = 7.7, 1.1 Hz, 1H), 7.33 (d, *J* = 3.5 Hz, 1H), 7.15 (d, *J* = 5.1 Hz, 1H), 6.74 (d, *J* = 3.5 Hz, 1H), 6.27 (dd, *J* = 17.5, 11.0 Hz, 1H), 5.72 (d, *J* = 17.5 Hz, 1H), 5.19 (d, *J* = 11.1 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.0, 144.2, 136.2, 135.4, 135.2, 131.9, 130.4, 128.8, 128.6, 128.4, 126.4, 119.8, 116.7, 116.5, 99.4 ppm. ESI HRMS: calcd. for $C_{15}H_{11}ClN_2$+H 255.0689, found 255.0693.

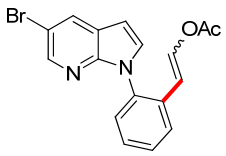
(E)-2-(4-chloro-1H-pyrrolo[2,3-b]pyridin-1-yl)styryl acetate (**4ba**); (Z)-2-(4-chloro -1H-pyrrolo[2,3-b]pyridin-1-yl)styryl acetate (**4ba'**); (**4ba:4ba' = 9:1**). 30 h, 68% yield; ^{1}H NMR



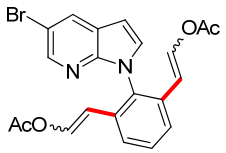
(400 MHz, $CDCl_3$): δ 8.21 (d, *J* = 5.1 Hz, 1H), 8.01 (d, *J* = 7.7 Hz, 1H), 7.48 (dd, *J* = 7.8, 4.0 Hz, 1H), 7.44 (s, 2H), 7.33 (d, *J* = 3.2 Hz, 1H), 7.19 – 7.13 (m, 2H), 6.73 (d, *J* = 3.2 Hz, 1H), 5.30 (d, *J* = 7.4 Hz, 1H), 2.22 (s, 1H), 2.12 (s, 3H) ppm. ESI HRMS: calcd. for $C_{17}H_{13}ClN_2O_2$+Na 335.0563, found 335.0558, 337.0560.



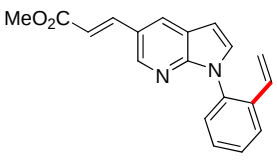
5-bromo-1-(2-vinylphenyl)-1H-pyrrolo[2,3-b]pyridine (**3ca**). 24 h, 14% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.34 (d, *J* = 1.5 Hz, 1H), 8.11 (d, *J* = 1.7 Hz, 1H), 7.75 (d, *J* = 7.3 Hz, 1H), 7.44 (dt, *J* = 14.5, 7.2 Hz, 2H), 7.37 (d, *J* = 6.9 Hz, 1H), 7.30 (d, *J* = 3.4 Hz, 1H), 6.58 (d, *J* = 3.4 Hz, 1H), 6.26 (dd, *J* = 17.5, 11.0 Hz, 1H), 5.72 (d, *J* = 17.5 Hz, 1H), 5.19 (d, *J* = 11.0 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.3, 135.3, 135.1, 131.9, 131.3, 131.0, 128.7, 128.6, 128.3, 126.4, 122.1, 116.6, 112.3, 100.4 ppm. ESI HRMS: calcd. for $C_{15}H_{11}BrN_2$+H 299.0184, found 299.0174, 301.0181.



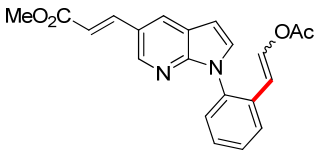
(E)-2-(5-bromo-1H-pyrrolo[2,3-b]pyridin-1-yl)styryl acetate (**4ca**); (Z)-2-(5-bromo-1H-pyrrolo[2,3-b]pyridin-1-yl)styryl acetate (**4ca'**); (**4ca:4ca' = 1:2**). 24 h, 70% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.34 (s, 1H), 8.10 (d, *J* = 6.5 Hz, 1H), 8.00 (d, *J* = 7.7 Hz, 1H), 7.77 (d, *J* = 12.8 Hz, 1H), 7.66 (d, *J* = 7.2 Hz, 1H), 7.51 – 7.44 (m, 1H), 7.42 (d, *J* = 4.0 Hz, 3H), 7.38 (dd, *J* = 13.5, 7.0 Hz, 1H), 7.29 (s, 2H), 7.16 (d, *J* = 7.4 Hz, 1H), 6.60 (d, *J* = 3.3 Hz, 1H), 6.56 (d, *J* = 3.3 Hz, 1H), 5.94 (d, *J* = 12.7 Hz, 1H), 5.29 (d, *J* = 7.3 Hz, 1H), 2.12 (s, 3H), 2.09 (s, 2H) ppm. ESI HRMS: calcd. for $C_{17}H_{13}BrN_2O_2$+Na 379.0058, found 379.0066, 381.0049.



(1E,1'E)-(2-(5-bromo-1H-pyrrolo[2,3-b]pyridin-1-yl)-1,3-phenylene)bis(ethene-2,1-diyl) diacetate (**5**); (1Z,1'Z)-(2-(5-bromo-1H-pyrrolo[2,3-b]pyridine-1-yl)-1,3-phenylene)bis(ethene-2,1-diyl) diacetate (**5'**); (**5:5' = 2:1**). 24 h, 8% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.33 (s, 2H), 7.99 (t, *J* = 7.6 Hz, 2H), 7.77 (d, *J* = 12.8 Hz, 1H), 7.66 (d, *J* = 5.0 Hz, 1H), 7.49 – 7.37 (m, 6H), 7.28 (s, 2H), 7.13 (dd, *J* = 10.7, 6.9 Hz, 3H), 6.65 (d, *J* = 3.2 Hz, 1H), 6.61 (d, *J* = 3.2 Hz, 1H), 6.01 (d, *J* = 12.8 Hz, 1H), 5.35 (d, *J* = 7.3 Hz, 1H), 2.09 (s, 2H), 2.08 (s, 4H) ppm. ESI HRMS: calcd. for $C_{21}H_{17}BrN_2O_4$+Na 463.0269, found 463.0279, 465.0264.

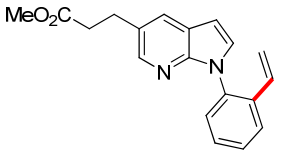


(E)-methyl3-(1-(2-vinylphenyl)-1H-pyrrolo[2,3-b]pyridin-5-yl)acrylate (**3da**). 12 h, 20% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.49 (s, 1H), 8.17 (s, 1H), 7.84 (d, *J* = 16.0 Hz, 1H), 7.76 (d, *J* = 7.3 Hz, 1H), 7.49 – 7.37 (m, 3H), 7.33 (d, *J* = 3.2 Hz, 1H), 6.67 (d, *J* = 3.2 Hz, 1H), 6.50 (d, *J* = 16.0 Hz, 1H), 6.29 (dd, *J* = 17.5, 11.0 Hz, 1H), 5.73 (d, *J* = 17.4 Hz, 1H), 5.20 (d, *J* = 11.0 Hz, 1H), 3.83 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.4, 149.2, 144.8, 143.1, 135.3, 135.0, 131.9, 131.3, 128.7, 128.6, 128.3, 127.7, 126.4, 123.3, 120.6, 116.6, 116.3, 101.5, 51.6 ppm. ESI HRMS: calcd. for $C_{19}H_{16}N_2O_2$+H 305.1290, found 305.1281.

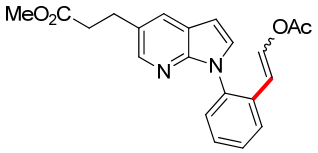


(2E)-methyl3-(1-(2-(2-acetoxyvinyl)phenyl)-1H-pyrrolo[2,3-b]pyridin-5-yl)acrylate (**4da**); (2Z)-methyl3-(1-(2-(2-acetoxyvinyl)phenyl)-1H-pyrrolo[2,3-b]pyridin-5-yl)acrylate (**4da'**); (**4da:4da' = 1.1:1**). 12 h, 75% yield; ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.49 (s, 2H), 8.17 (dd, *J* = 9.4,

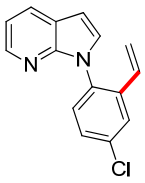
1.3 Hz, 2H), 8.01 (d, *J* = 7.8 Hz, 1H), 7.86 (d, *J* = 4.0 Hz, 1H), 7.83 (d, *J* = 4.0 Hz, 1H), 7.78 (d, *J* = 12.7 Hz, 1H), 7.67 (d, *J* = 7.4 Hz, 1H), 7.48 (dd, *J* = 11.2, 4.9 Hz, 1H), 7.43 (dd, *J* = 16.7, 9.1 Hz, 4H), 7.39 (t, *J* = 7.6 Hz, 1H), 7.32 (t, *J* = 3.4 Hz, 2H), 7.16 (d, *J* = 7.4 Hz, 1H), 6.69 (d, *J* = 3.5 Hz, 1H), 6.66 (d, *J* = 3.5 Hz, 1H), 6.51 (d, *J* = 3.3 Hz, 1H), 6.49 (d, *J* = 3.3 Hz, 1H), 5.97 (d, *J* = 12.8 Hz, 1H), 5.32 (d, *J* = 7.4 Hz, 1H), 3.82 (s, 6H), 2.11 (s, 3H), 2.09 (s, 3H) ppm. ESI HRMS: calcd. for $C_{21}H_{18}N_2O_4$+ H 363.1345, found 363.1354.



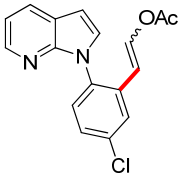
Methyl3-(1-(2-vinylphenyl)-1H-pyrrolo[2,3-b]pyridin-5-yl)propanoate (**3ea**). 12 h, 20% yield; ^{1}H NMR (600 MHz,$CDCl_3$): δ 8.19 (d, *J* = 1.0 Hz, 1H), 7.82 (s, 1H), 7.74 (d, *J* = 7.1 Hz, 1H), 7.42 (ddd, *J* = 21.7, 11.9, 4.4 Hz, 3H), 7.28 – 7.25 (m, 1H), 6.57 (d, *J* = 3.4 Hz, 1H), 6.32 (dd, *J* = 17.5, 11.0 Hz, 1H), 5.72 (d, *J* = 17.5 Hz, 1H), 5.18 (d, *J* = 11.1 Hz, 1H), 3.68 (s, 3H), 3.07 (t, *J* = 7.7 Hz, 2H), 2.69 (t, *J* = 7.7 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.1, 147.6, 144.2, 135.8, 135.0, 132.2, 130.2, 128.5, 128.4, 128.3, 128.3, 126.3, 120.4, 116.2, 100.4, 51.6, 36.2, 28.2 ppm. ESI HRMS: calcd. for $C_{19}H_{18}N_2O_2$+H 307.1447, found 307.1440.



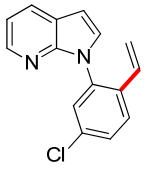
(E)-methyl3-(1-(2-(2-acetoxyvinyl)phenyl)-1H-pyrrolo[2,3-b]pyridin-5-yl)propanoate (**4ea**); (Z)-methyl3-(1-(2-(2-acetoxyvinyl)phenyl)-1H -pyrrolo[2,3-b]pyridin-5-yl)propanoate (**4ea'**); (**4ea**:**4ea'** = **2**:**1**). 12 h, 32% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19 (s, 2H), 8.02 – 7.98 (m, 1H), 7.85 – 7.80 (m, 2H), 7.78 (d, *J* = 12.8 Hz, 1H), 7.67 – 7.63 (m, 1H), 7.43 (ddd, *J* = 15.5, 10.4, 6.7 Hz, 6H), 7.26 (d, *J* = 3.2 Hz, 2H), 7.15 (d, *J* = 7.4 Hz, 1H), 6.59 (d, *J* = 3.5 Hz, 1H), 6.55 (d, *J* = 3.5 Hz, 1H), 6.01 (d, *J* = 12.8 Hz, 1H), 5.35 (d, *J* = 7.4 Hz, 1H), 3.68 (s, 6H), 3.07 (td, *J* = 7.7, 2.5 Hz, 4H), 2.69 (td, *J* = 7.7, 3.1 Hz, 4H), 2.10 (s, 3H), 2.09 (s, 3H) ppm. ESI HRMS: calcd. for $C_{21}H_{20}N_2O_4$+H 365.1501, found 365.1501.



1-(4-chloro-2-vinylphenyl)-1H-pyrrolo[2,3-b]pyridine (**3fa**). 24 h, 40% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.32 (d, *J* = 4.4 Hz, 1H), 7.99 (d, *J* = 7.7 Hz, 1H), 7.71 (s, 1H), 7.37 (q, *J* = 8.7 Hz, 2H), 7.25 (d, *J* = 3.8 Hz, 1H), 7.13 (dd, *J* = 7.7, 4.7 Hz, 1H), 6.64 (d, *J* = 3.4 Hz, 1H), 6.26 (dd, *J* = 17.5, 11.0 Hz, 1H), 5.73 (d, *J* = 17.5 Hz, 1H), 5.24 (d, *J* = 11.0 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.9, 135.7, 133.3, 130.2, 128.7, 128.5, 128.0, 127.5, 125.3, 119.5, 116.5, 115.6, 100.2 ppm. ESI HRMS: calcd. for $C_{15}H_{11}ClN_2$+H 255.0689, found 255.0683, 257.0665.

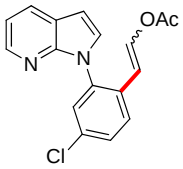


(E)-5-chloro-2-(1H-pyrrolo[2,3-b]pyridin-1-yl)styryl acetate (**4fa**); (Z)-5-chloro-2-(1H-pyrrolo[2,3-b]pyridin-1-yl)styryl acetate (**4fa'**); (**4fa:4fa' = 1.5:1**). 24 h, 50% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.32 (s, 2H), 7.98 (t, *J* = 7.5 Hz, 3H), 7.78 (d, *J* = 12.8 Hz, 1H), 7.63 (s, 1H), 7.38 (d, *J* = 7.4 Hz, 2H), 7.33 (d, *J* = 8.5 Hz, 2H), 7.25 (s, 2H), 7.18 (d, *J* = 7.4 Hz, 1H), 7.16 – 7.09 (m, 2H), 6.65 (d, *J* = 3.3 Hz, 1H), 6.62 (d, *J* = 3.3 Hz, 1H), 5.94 (d, *J* = 12.8 Hz, 1H), 5.28 (d, *J* = 7.4 Hz, 1H), 2.14 (s, 2H), 2.09 (s, 3H) ppm. ESI HRMS: calcd. for $C_{17}H_{13}ClN_2O_2$+Na 335.0563, found 335.0558, 337.0592.

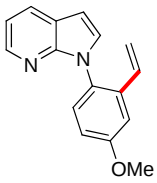


1-(5-chloro-2-vinylphenyl)-1H-pyrrolo[2,3-b]pyridine (**3ga**). 30 h, 43% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.34 (d, *J* = 4.2 Hz, 1H), 7.98 (d, *J* = 7.7 Hz, 1H), 7.67 (d, *J* = 8.3

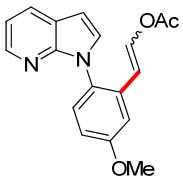
Hz, 1H), 7.41 (d, *J* = 11.8 Hz, 2H), 7.25 (d, *J* = 1.6 Hz, 1H), 7.13 (dd, *J* = 7.5, 4.8 Hz, 1H), 6.64 (d, *J* = 3.2 Hz, 1H), 6.27 (dd, *J* = 17.5, 11.1 Hz, 1H), 5.70 (d, *J* = 17.5 Hz, 1H), 5.20 (d, *J* = 11.0 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.4, 144.0, 136.7, 133.7, 133.7, 131.4, 129.5, 129.1, 128.7, 128.6, 127.4, 120.5, 116.7, 116.7, 101.4 ppm. ESI HRMS: calcd. for $C_{15}H_{11}ClN_2$+H 255.0689, found 255.0684, 257.0638.



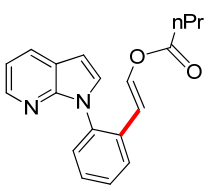
(E)-4-chloro-2-(1H-pyrrolo[2,3-b]pyridin-1-yl)styryl acetate (**4ga**); (Z)-4-chloro-2-(1H-pyrrolo[2,3-b]pyridin-1-yl)styryl acetate (**4ga'**); (**4ga**:**4ga'** = **2**:**1**). 30 h, 50% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.33 (d, *J* = 3.0 Hz, 2H), 7.98 (t, *J* = 7.5 Hz, 2H), 7.93 (d, *J* = 8.6 Hz, 1H), 7.75 (d, *J* = 12.8 Hz, 1H), 7.57 (d, *J* = 8.4 Hz, 1H), 7.47 (s, 1H), 7.40 (dd, *J* = 13.9, 9.1 Hz, 3H), 7.24 (d, *J* = 3.9 Hz, 2H), 7.14 (dt, *J* = 12.2, 4.0 Hz, 3H), 6.65 (d, *J* = 3.4 Hz, 1H), 6.61 (d, *J* = 3.4 Hz, 1H), 5.95 (d, *J* = 12.8 Hz, 1H), 5.30 (d, *J* = 7.4 Hz, 1H), 2.09 (s, 2H), 2.07 (s, 3H) ppm. ESI HRMS: calcd. for $C_{17}H_{13}ClN_2O_2$+ Na 335.0563, found 335.0557.



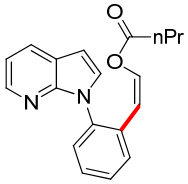
1-(4-methoxy-2-vinylphenyl)-1H-pyrrolo[2,3-b]pyridine (**3ha**). 24 h, 25% yield; ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.32 (d, *J* = 4.0 Hz, 1H), 7.97 (d, *J* = 7.8 Hz, 1H), 7.31 (d, *J* = 8.6 Hz, 1H), 7.25 (d, *J* = 3.7 Hz, 1H), 7.23 (d, *J* = 2.7 Hz, 1H), 7.10 (dd, *J* = 7.8, 4.7 Hz, 1H), 6.96 (dd, *J* = 8.6, 2.8 Hz, 1H), 6.60 (d, *J* = 3.4 Hz, 1H), 6.23 (dd, *J* = 17.5, 11.0 Hz, 1H), 5.69 (d, *J* = 17.5 Hz, 1H), 5.16 (d, *J* = 11.0 Hz, 1H), 3.89 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.5, 148.8, 143.8, 136.4, 132.1, 130.1, 129.6, 129.0, 128.9, 120.4, 116.4, 116.2, 114.3, 110.9, 100.5, 55.6 ppm. ESI HRMS: calcd. for $C_{16}H_{14}N_2O$+H 251.1184, found 251.1174.



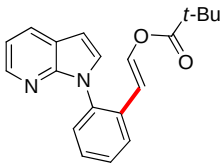
(E)-5-methoxy-2-(1H-pyrrolo[2,3-b]pyridin-1-yl)styryl acetate (**4ha**); (Z)-5-methoxy-2-(1H-pyrrolo[2,3-b]pyridin-1-yl)styryl acetate (**4ha'**); (**4ha:4ha' = 1.2:1**). 24 h, 66% yield; ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.34 – 8.31 (m, 2H), 8.00 – 7.96 (m, 2H), 7.75 (d, *J* = 12.7 Hz, 1H), 7.58 (d, *J* = 2.9 Hz, 1H), 7.35 (d, *J* = 8.6 Hz, 1H), 7.29 (d, *J* = 8.6 Hz, 1H), 7.25 – 7.24 (m, 2H), 7.13 (dd, *J* = 7.5, 4.9 Hz, 2H), 7.12 – 7.09 (m, 2H), 6.97 (d, *J* = 2.9 Hz, 1H), 6.94 (d, *J* = 2.9 Hz, 1H), 6.93 (d, *J* = 2.8 Hz, 1H), 6.62 (d, *J* = 3.5 Hz, 1H), 6.59 (d, *J* = 3.5 Hz, 1H), 5.92 (d, *J* = 12.8 Hz, 1H), 5.25 (d, *J* = 7.4 Hz, 1H), 3.89 (s, 2H), 3.88 (s, 3H), 2.13 (s, 2H), 2.07 (s, 3H) ppm. ESI HRMS: calcd. for $C_{18}H_{16}N_2O_3$+H 309.1239, found 309.1229.



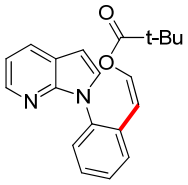
(E)-2-(1H-pyrrolo[2,3-b]pyridin-1-yl)styrylbutyrate (**4ab**). 36 h, 24% yield; ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.34 (d, *J* = 3.8 Hz, 1H), 8.00 (d, *J* = 7.0 Hz, 1H), 7.80 (d, *J* = 12.7 Hz, 1H), 7.66 (d, *J* = 6.8 Hz, 1H), 7.41 (dt, *J* = 12.0, 4.3 Hz, 3H), 7.29 (d, *J* = 3.4 Hz, 1H), 7.13 (dd, *J* = 7.8, 4.7 Hz, 1H), 6.65 (d, *J* = 3.4 Hz, 1H), 6.00 (d, *J* = 12.8 Hz, 1H), 2.31 (t, *J* = 7.4 Hz, 2H), 1.64 (dd, *J* = 14.8, 7.4 Hz, 2H), 0.93 (t, *J* = 7.4 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.4, 148.4, 143.9, 137.6, 135.9, 132.1, 129.7, 129.0, 128.8, 128.6, 128.2, 126.4, 120.5, 116.4, 110.6, 101.1, 35.7, 18.0, 13.5 ppm. ESI HRMS: calcd. for $C_{19}H_{18}N_2O_2$+H 307.1447, found 307.1440.



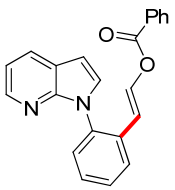
(Z)-2-(1H-pyrrolo[2,3-b]pyridin-1-yl)styryl butyrate (**4ab'**). 36 h, 16% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.33 (d, *J* = 4.4 Hz, 1H), 8.03 (d, *J* = 7.4 Hz, 1H), 7.98 (d, *J* = 7.7 Hz, 1H), 7.44 (dt, *J* = 8.6, 4.9 Hz, 3H), 7.29 (d, *J* = 3.3 Hz, 1H), 7.18 (d, *J* = 7.4 Hz, 1H), 7.12 (dd, *J* = 7.6, 4.8 Hz, 1H), 6.62 (d, *J* = 3.3 Hz, 1H), 5.33 (d, *J* = 7.4 Hz, 1H), 2.35 (t, *J* = 7.4 Hz, 2H), 1.69 (dd, *J* = 14.8, 7.4 Hz, 2H), 0.98 (t, *J* = 7.4 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.0, 148.3, 143.8, 136.1, 135.1, 131.3, 130.5, 129.8, 129.0, 128.4, 128.1, 128.0, 120.6, 116.4, 106.7, 100.9, 35.8, 18.0, 13.6 ppm. ESI HRMS: calcd. for $C_{19}H_{18}N_2O_2$+H 307.1447, found 307.1437.



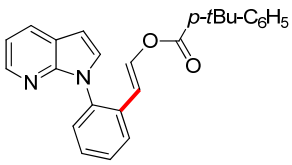
(E)-2-(1H-pyrrolo[2,3-b]pyridin-1-yl)styryl pivalate (**4ac**). 48 h, 31% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.34 (d, *J* = 4.5 Hz, 1H), 8.00 (d, *J* = 7.7 Hz, 1H), 7.78 (d, *J* = 12.8 Hz, 1H), 7.67 (d, *J* = 6.2 Hz, 1H), 7.43 – 7.37 (m, 3H), 7.30 (d, *J* = 3.4 Hz, 1H), 7.13 (dd, *J* = 7.7, 4.7 Hz, 1H), 6.66 (d, *J* = 3.4 Hz, 1H), 6.04 (d, *J* = 12.8 Hz, 1H), 1.19 (s, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 175.3, 148.4, 143.9, 138.1, 135.7, 132.1, 129.7, 128.9, 128.8, 128.5, 128.1, 126.4, 120.5, 116.4, 110.4, 101.04, 38.6, 26.8 ppm. ESI HRMS: calcd. for $C_{20}H_{20}N_2O_2$+Na 343.1422, found 343.1418.



(Z)-2-(1H-pyrrolo[2,3-b]pyridin-1-yl)styryl pivalate (**4ac'**). 48 h, 6% yield; ^{1}H NMR (600 MHz,$CDCl_3$): δ 8.33 (d, *J* = 4.3 Hz, 1H), 8.11 (d, *J* = 7.8 Hz, 1H), 7.99 (d, *J* = 7.7 Hz, 1H), 7.46 (dd, *J* = 14.7, 7.1 Hz, 2H), 7.43 – 7.39 (m, 1H), 7.30 (d, *J* = 3.4 Hz, 1H), 7.19 (d, *J* = 7.4 Hz, 1H), 7.12 (dd, *J* = 7.8, 4.7 Hz, 1H), 6.63 (d, *J* = 3.4 Hz, 1H), 5.30 (d, *J* = 7.4 Hz, 1H), 1.32 (s, 9H) ppm. ESI HRMS: calcd. for $C_{20}H_{20}N_2O_2$+Na 343.1422, found 343.1418

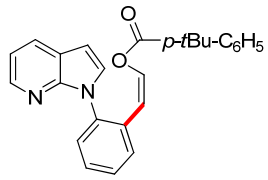


(E)-2-(1H-pyrrolo[2,3-b]pyridin-1-yl)styryl benzoate (**4ad**). 48 h, 50% yield; ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.38 (dd, *J* = 4.6, 1.3 Hz, 1H), 8.23 (d, *J* = 7.9 Hz, 1H), 8.17 (dd, *J* = 8.1, 0.9 Hz, 2H), 8.04 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.69 (t, *J* = 7.5 Hz, 1H), 7.61 – 7.54 (m, 4H), 7.53 – 7.50 (m, 1H), 7.49 (d, *J* = 7.3 Hz, 1H), 7.38 (d, *J* = 3.5 Hz, 1H), 7.17 (dd, *J* = 7.8, 4.7 Hz, 1H), 6.69 (d, *J* = 3.5 Hz, 1H), 5.53 (d, *J* = 7.3 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.2, 143.9, 136.3, 135.4, 133.8, 131.4, 130.7, 130.1, 129.9, 129.0, 128.7, 128.5, 128.2, 128.1, 120.6, 116.5, 107.9, 101.0 ppm. ESI HRMS: calcd. for $C_{22}H_{16}N_2O_2$+H 341.1290, found 341.1282.

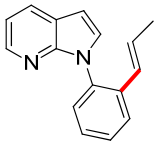


(E)-2-(1H-pyrrolo[2,3-b]pyridin-1-yl)styryl 4-(tert-butyl)benzoate (**4ae**). 48 h, 39% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.35 (d, *J* = 4.2 Hz, 1H), 8.06 – 7.99 (m, 2H), 7.95 (d, *J* = 8.3 Hz, 2H), 7.74 (d, *J* = 6.9 Hz, 1H), 7.46 – 7.40 (m, 5H), 7.32 (d, *J* = 3.4 Hz, 1H), 7.14 (dd, *J* = 7.7, 4.7 Hz, 1H), 6.67 (d, *J* = 3.4 Hz, 1H), 6.19 (d, *J* = 12.7 Hz, 1H), 1.31 (s, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.4, 157.5, 148.4, 143.9, 138.0, 135.9, 132.1, 129.9, 129.8, 129.0, 128.8, 128.6, 128.2, 126.5, 125.7, 125.4, 120.5, 116.4, 111.1, 101.1 ppm. ESI HRMS: calcd. for $C_{26}H_{24}N_2O_2$+H 397.1916, found 397.1909.

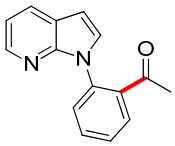
(Z)-2-(1H-pyrrolo[2,3-b]pyridin-1-yl)styryl 4-(tert-butyl)benzoate (**4ae'**). 48 h, 6% yield; ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.33 (d, *J* = 4.6 Hz, 1H), 8.19 (d, *J* = 7.8 Hz, 1H), 8.05 (d, *J* = 8.4 Hz, 2H), 7.98



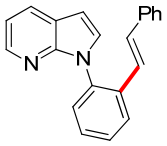
(dd, J = 7.8, 1.1 Hz, 1H), 7.53 (t, J = 8.3 Hz, 3H), 7.49 (d, J = 7.1 Hz, 1H), 7.44 (dd, J = 13.5, 7.3 Hz, 2H), 7.33 (d, J = 3.5 Hz, 1H), 7.11 (dd, J = 7.8, 4.7 Hz, 1H), 6.63 (d, J = 3.5 Hz, 1H), 5.45 (d, J = 7.3 Hz, 1H), 1.37 (s, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.1, 157.6, 148.3, 143.8, 136.1, 135.5, 131.5, 130.7, 130.0, 129.9, 128.9, 128.4, 128.1, 128.1, 125.8, 125.7, 120.5, 116.4, 107.4, 100.9, 35.2, 31.0 ppm. ESI HRMS: calcd. for $C_{26}H_{24}N_2O_2$+H 397.1916, found 397.1909.



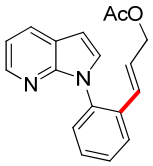
(E)-1-(2-(prop-1-en-1-yl)phenyl)-1H-pyrrolo[2,3-b]pyridine (**3af**). 24 h, 25% yield ; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.33 (d, J = 4.4 Hz, 1H), 7.99 (d, J = 7.7 Hz, 1H), 7.67 (d, J = 7.5 Hz, 1H), 7.38 (dd, J = 13.4, 5.7 Hz, 3H), 7.29 (d, J = 3.3 Hz, 1H), 7.11 (dd, J = 7.7, 4.7 Hz, 1H), 6.62 (d, J = 3.3 Hz, 1H), 6.26 – 6.14 (m, 1H), 5.98 (d, J = 15.7 Hz, 1H), 1.71 (d, J = 6.5 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.5, 142.8, 134.4, 134.1, 129.0, 127.8, 127.4, 127.3, 127.3, 126.4, 125.3, 125.1, 119.4, 115.2, 99.6, 17.7 ppm. ESI HRMS: calcd. for $C_{16}H_{14}N_2$+H 235.1235, found 235.1240.



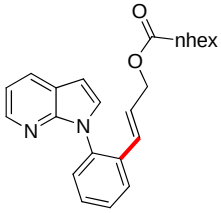
1-(2-(1H-pyrrolo[2,3-b]pyridin-1-yl)phenyl)ethanone (**6**). 48 h, 30% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.31 (d, J = 4.6 Hz, 1H), 7.98 (d, J = 7.8 Hz, 1H), 7.76 (d, J = 7.7 Hz, 1H), 7.64 (t, J = 7.6 Hz, 1H), 7.50 (t, J = 7.9 Hz, 2H), 7.34 (d, J = 3.5 Hz, 1H), 7.13 (dd, J = 7.7, 4.7 Hz, 1H), 6.68 (d, J = 3.5 Hz, 1H), 1.97 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 200.6, 148.0, 143.9, 137.6, 135.7, 132.2, 129.3, 129.0, 128.8, 128.0, 127.8, 120.9, 116.9, 102.2, 28.4 ppm. ESI HRMS: calcd. for $C_{15}H_{12}N_2O$+Na 259.0847, found 259.0845.



E)-1-(2-styrylphenyl)-1H-pyrrolo[2,3-b]pyridine (**3ag**). 48 h, 24% yield; ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.36 (d, J = 4.2 Hz, 1H), 8.03 (d, J = 7.8 Hz, 1H), 7.88 (d, J = 7.8 Hz, 1H), 7.50 – 7.42 (m, 3H), 7.35 (d, J = 3.6 Hz, 1H), 7.25 (s, 4H), 7.19 (dd, J = 8.5, 4.0 Hz, 1H), 7.13 (dd, J = 7.8, 4.7 Hz, 1H), 7.07 (d, J = 16.3 Hz, 1H), 6.72 (d, J = 16.2 Hz, 1H), 6.66 (d, J = 3.6 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.5, 143.9, 137.0, 136.0, 134.7, 130.8, 130.1, 129.0, 128.5, 128.3, 128.2, 127.7, 126.5, 126.4, 123.9, 120.6, 116.4, 100.9, 29.6 ppm. ESI HRMS: calcd. for $C_{21}H_{16}N_2$+H 297.1392, found 297.1398.

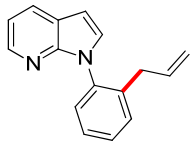


(E)-3-(2-(1H-pyrrolo[2,3-b]pyridin-1-yl)phenyl)allyl acetate (**4ah**). 24 h, 8% yield ; ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.33 (d, J = 4.5 Hz, 1H), 8.00 (d, J = 7.8 Hz, 1H), 7.74 – 7.71 (m, 1H), 7.45 – 7.41 (m, 3H), 7.28 (d, J = 3.5 Hz, 1H), 7.13 (dd, J = 7.8, 4.7 Hz, 1H), 6.64 (d, J = 3.5 Hz, 1H), 6.24 (s, 2H), 4.53 (d, J = 2.5 Hz, 2H), 1.97 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.6, 148.5, 143.9, 136.0, 133.7, 129.9, 129.0, 129.0, 128.5, 128.4, 126.7, 125.6, 120.5, 116.4, 101.0, 64.7, 20.8 ppm. ESI HRMS: calcd. for $C_{18}H_{16}N_2O_2$+Na 315.1109, found 315.1118.

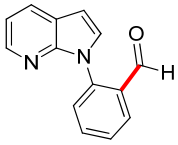


(E)-3-(2-(1H-pyrrolo[2,3-b]pyridin-1-yl)phenyl)allylheptanoate (**4ai**). 24 h, 11% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.33 (d, J = 4.3 Hz, 1H), 7.99 (d, J = 7.7 Hz, 1H), 7.72 (d, J = 4.4 Hz, 1H), 7.43 (d, J = 9.4 Hz, 3H), 7.28 (d, J = 3.3 Hz, 1H), 7.12 (dd, J = 7.5, 4.9 Hz, 1H), 6.64 (d, J = 3.2 Hz, 1H), 6.24 (s, 2H), 4.54

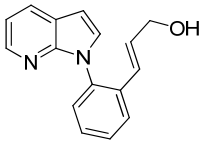
(s, 2H), 2.21 (t, *J* = 7.5 Hz, 2H), 1.52 (dd, *J* = 13.9, 6.8 Hz, 2H), 1.25 (s, 6H), 0.87 (t, *J* = 6.3 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.4, 148.1, 143.9, 129.9, 129.0, 128.7, 128.6, 128.5, 128.4, 126.7, 125.8, 116.4, 101.0, 64.5, 34.2, 31.4, 28.7, 24.8, 22.4, 14.0 ppm. ESI HRMS: calcd. for $C_{23}H_{26}N_2O_2$+H 363.2073, found 363.2071.



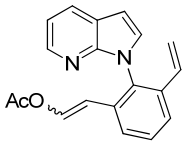
1-(2-allylphenyl)-1H-pyrrolo[2,3-b]pyridine (**8**). 24 h, 70% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.32 (d, *J* = 4.3 Hz, 1H), 7.98 (d, *J* = 7.8 Hz, 1H), 7.47 – 7.38 (m, 2H), 7.35 (s, 2H), 7.29 – 7.22 (m, 1H), 7.10 (dd, *J* = 7.7, 4.7 Hz, 1H), 6.61 (d, *J* = 3.4 Hz, 1H), 5.82 – 5.69 (m, 1H), 4.92 (d, *J* = 9 .8 Hz, 1H), 4.80 (d, *J* = 17.0 Hz, 1H), 3.18 (d, *J* = 6.3 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.3, 143.7, 137.8, 136.8, 136.3, 130.4, 129.5, 128.7, 128.6, 127.2, 120.4, 116.2, 100.6, 35.9 ppm. ESI HRMS: calcd. for $C_{16}H_{14}N_2$+H 235.1235, found 235.1228.



2-(1H-pyrrolo[2,3-b]pyridin-1-yl)benzaldehyde (**9**). 2 h, 70% yield; ^{1}H NMR (600 MHz, $CDCl_3$): δ 9.72 (s, 1H), 8.32 (d, *J* = 3.8 Hz, 1H), 8.14 (d, *J* = 7.7 Hz, 1H), 8.01 (d, *J* = 7.7 Hz, 1H), 7.75 (t, *J* = 7.5 Hz, 1H), 7.57 (t, *J* = 7.5 Hz, 1H), 7.49 (d, *J* = 7.8 Hz, 1H), 7.46 (d, *J* = 2.8 Hz, 1H), 7.19 – 7.15 (m, 1H), 6.73 (d, *J* = 2.8 Hz, 1H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$): δ 189.3, 148.9, 144.2, 140.0, 134.7, 131.6, 129.4, 129.2, 128.6, 128.0, 127.6, 120.7, 117.3, 102.6 ppm. ESI HRMS: calcd. for $C_{14}H_{10}N_2O$+H 223.0871, found 223.0873.



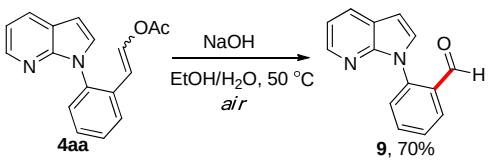
(E)-3-(2-(1H-pyrrolo[2,3-b]pyridin-1-yl)phenyl)prop-2-en-1-ol (**10**). 2 h, 99% yield; ^{1}H NMR (400 MHz, $CDCL_3$): δ 8.31 (d, *J* = 4.3 Hz, 1H), 7.99 (d, *J* = 7.7 Hz, 1H), 7.71 (d, *J* = 6.8 Hz, 1H), 7.47 – 7.36 (m, 4H), 7.28 (d, *J* = 3.1 Hz, 1H), 7.12 (dd, *J* = 7.3, 4.7 Hz, 1H), 6.63 (d, *J* = 3.0 Hz, 1H), 6.35 – 6.26 (m, 1H), 6.21 (d, *J* = 16.1 Hz, 1H), 4.11 (d, *J* = 4.7 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.4, 143.8, 135.8, 134.2, 131.1, 129.8, 129.0, 128.6, 128.4, 128.4, 126.7, 126.2, 120.5, 116.4, 101.0, 63.5 ppm. ESI HRMS: calcd. for $C_{16}H_{14}N_2O$+H 251.1184, found 251.1174.



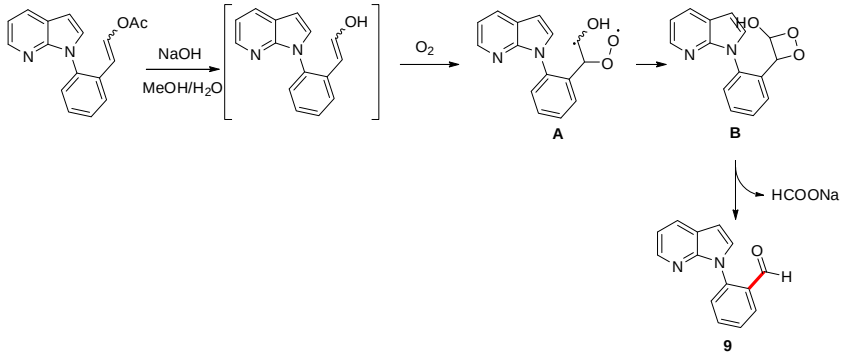
(E)-2-(1H-pyrrolo[2,3-b]pyridin-1-yl)-3-vinylstyryl acetate (**11**); (Z)-2-(1H-pyrrolo[2,3-b]pyridin-1-yl)-3-vinylstyryl acetate (**11'**); (**11**:**11'** = 3:1). 48 h, 15% yield; ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.32 (d, *J* = 3.8 Hz, 1H), 8.02 (d, *J* = 8.2 Hz, 1H), 8.00 – 7.96 (m, 1H), 7.73 (d, *J* = 12.7 Hz, 1H), 7.67 – 7.61 (m, 1H), 7.57 (d, *J* = 7.6 Hz, 1H), 7.49 (t, *J* = 7.7 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 1H), 7.16 (s, 1H), 7.15 – 7.11 (m, 1H), 7.08 (d, *J* = 7.2 Hz, 1H), 6.68 (d, *J* = 13.5 Hz, 1H), 6.05 – 5.94 (m, 1H), 5.76 – 5.64 (m, 2H), 5.10 (d, *J* = 11.0 Hz, 1H), 5.01 (d, *J* = 7.3 Hz, 1H), 2.21 (s, 1H), 2.05 (s, 3H) ppm. ESI HRMS: calcd. for $C_{19}H_{16}N_2O_2$+H 305.1290, found 305.1288.

3. Mechanism Study

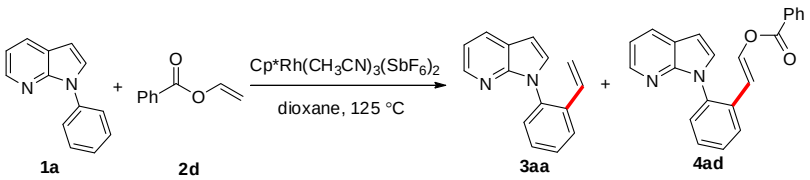
SI 1. A plausible mechanism about the generation of benzaldehyde **9**.



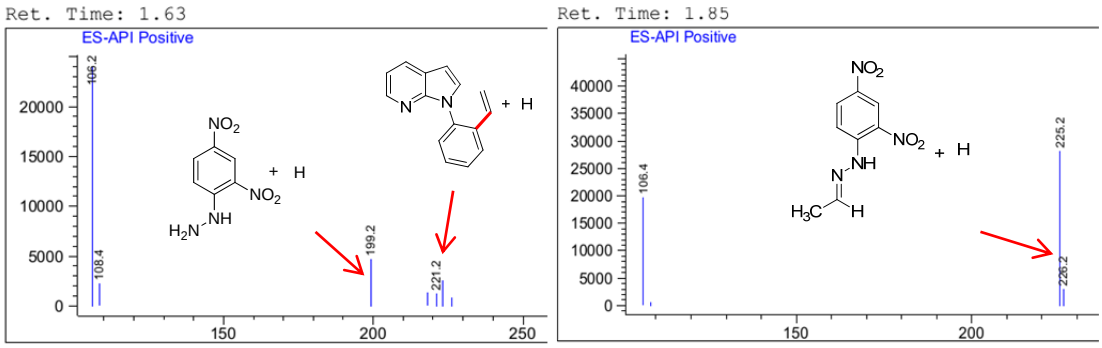
From the evidence that we had obtained we proposed a plausible mechanism. The enol as the hydrolysis product from **4aa** was oxidized to the radical **A** by molecular oxygen in air. Dioxetane intermediate **B** is produced subsequently, followed by the generation of benzaldehyde **9.**[2]



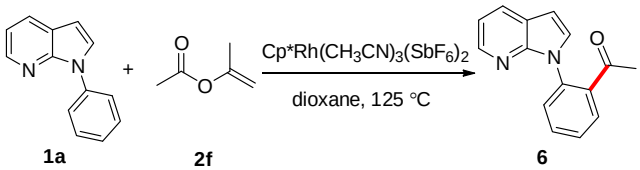
SI 2. Plausible Reaction Mechanism



1-phenyl-1H-pyrrolo[2,3-b]pyridine **1a** (0.1 mmol, 19.4 mg), vinyl benzoate **2d** (10 equiv, 140 uL), $Cp^*Rh(CH_3CN)_3(SbF_6)_2$ (4.2 mg, 5.0 mol %) were stirred in dioxane (1.0 mL) in seal tube at 130 °C for 48 h. After completion, in order to investigate acetaldehyde, 2,4-dinitrophenylhydrazine (31.7 mg, 1.6 equiv) was added in the mixture to stir another 6 h. The corresponding product 1-(2,4-dinitrophenyl)-2-ethylidenehydrazine was detected by LCMS. These data indicated that acetaldehyde was released in the reaction.

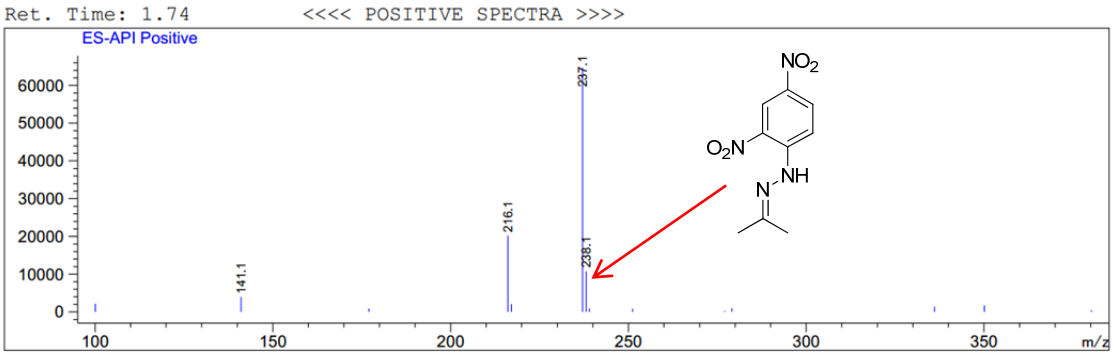


SI 3. Plausible Reaction Mechanism of **6**

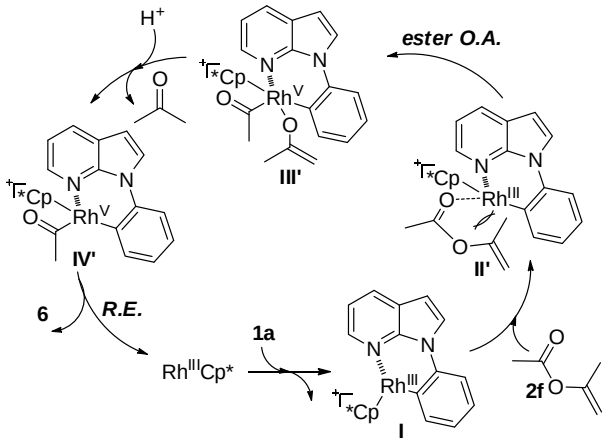


1-phenyl-1H-pyrrolo[2,3-b]pyridine **1a** (0.1 mmol, 19.4 mg), isopropenyl acetate **2f** (0.5 mL), $Cp^*Rh(CH_3CN)_3(SbF_6)_2$ (4.2 mg, 5.0 mol %) were stirred in dioxane (1.0 mL) in seal tube at 130 °C for 48 h. After completion, in order to investigate the acetone, 2,4-dinitrophenylhydrazine (19.8 mg, 1.0 equiv) was added in the mixture to stir another 6 h. The corresponding product 1-(2,4-dinitrophenyl)-2-(propan-2-ylidene)hydrazine was detected by LCMS. The data indicated

that acetone was released during the formation of the carbonyl product **6.**



When substituents on vinyl were applied to the system, the methyl or phenyl group might block the coordination with alkene to give the rhodacycle species **II'**. Then **II'** would subsequently be involved in an ester oxidative addition generating the rhodacycle species **III'**. With treatment of proton, **IV'** is isolated through the loss of acetone. Finally, the reductive elimination is followed to lead **6**, and the catalytically active Rh(III) is regenerated.[3] However, mechanistic details of producing of the product **6** are not clear right now and further investigation of the catalytic mechanism is underway in our laboratory.



Plausible reaction mechanism.

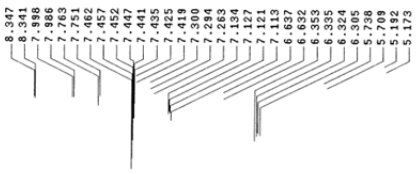
Refference

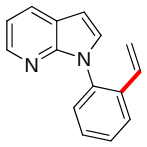
[1] G. Qian, X. Hong, B. Liu, H. Mao, B. Xu, *Org. Lett.* **2014**, *16*, 5294.

[2] B. Hu, Y.-F. Li, Z.-J. Li, X.-B. Meng, *Org. Biomol. Chem.* **2013**, *11*, 4138.

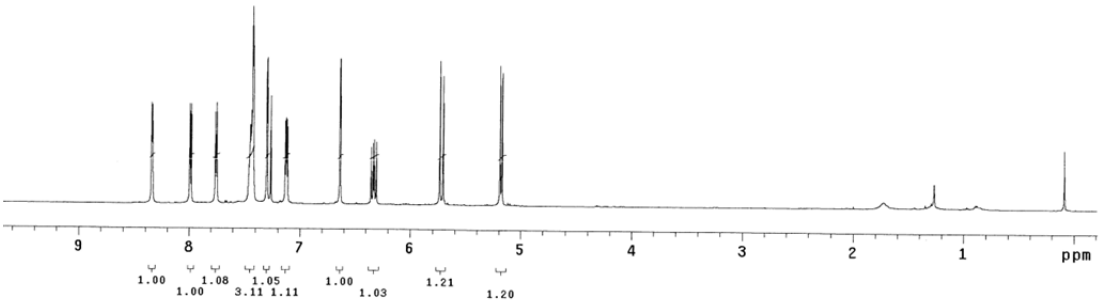
[3] P. Mamone, G. Danoun, L. J. Gooßen, *Angew. Chem. Int. Ed.*, **2013**, *52*, 6704.

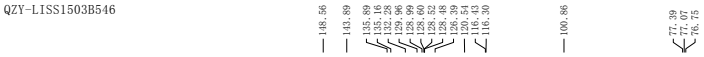
4. NMR Spectra of 7-Azaindole Derivatives and Structure Determination

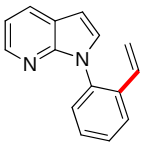

8.347
8.341
7.998
7.986
7.763
7.751
7.462
7.457
7.452
7.447
7.441
7.435
7.425
7.419
7.300
7.294
7.263
7.134
7.127
7.121
7.113
6.637
6.632
6.335
6.330
6.324
6.305
5.738
5.709
5.132
5.173
0.087



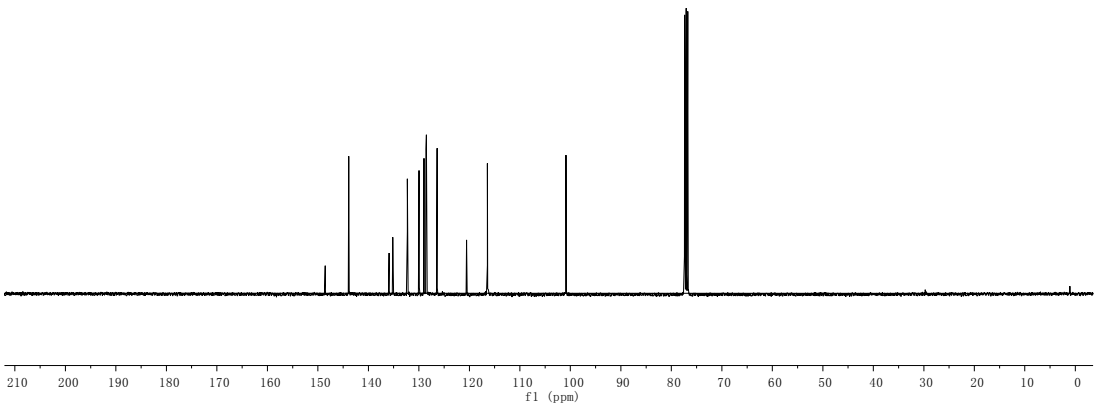
3aa

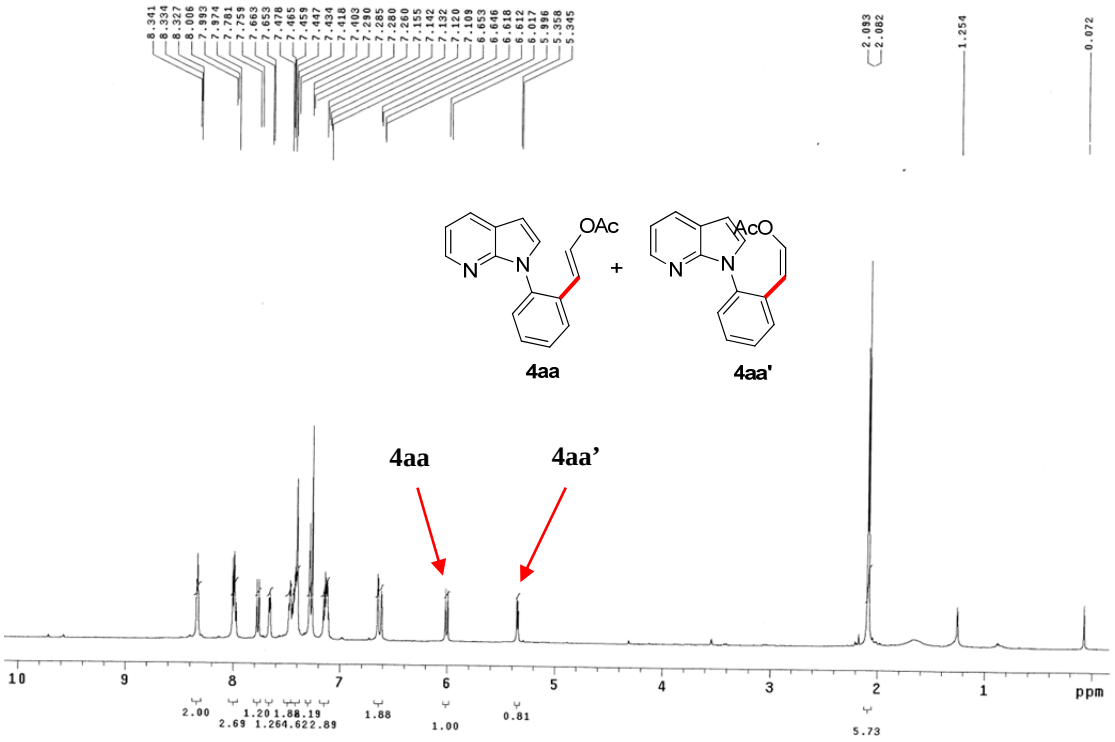

9
8
7
6
5
4
3
2
1
ppm
1.00
1.00
1.08
3.11
1.05
1.11
1.00
1.03
1.21
1.20

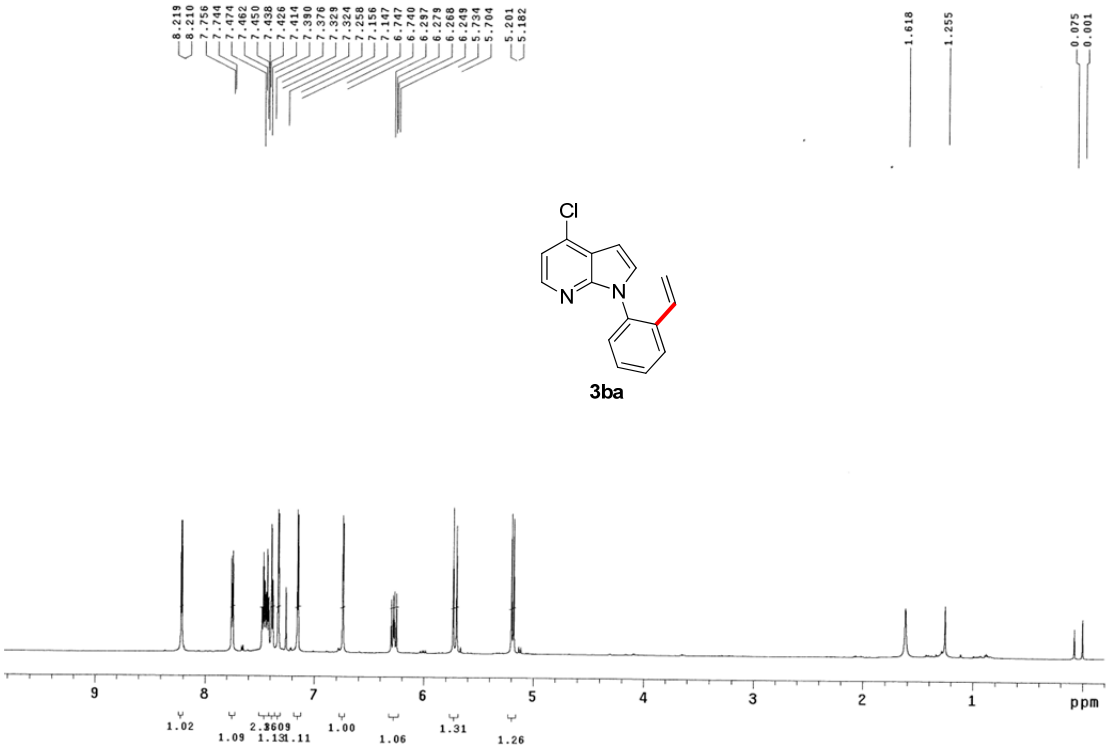

QZY-LISS1503B546
148.56
143.89
135.69
131.45
132.28
129.96
128.99
128.60
128.52
128.48
126.39
120.54
110.43
116.30
100.86
77.39
77.07
76.75

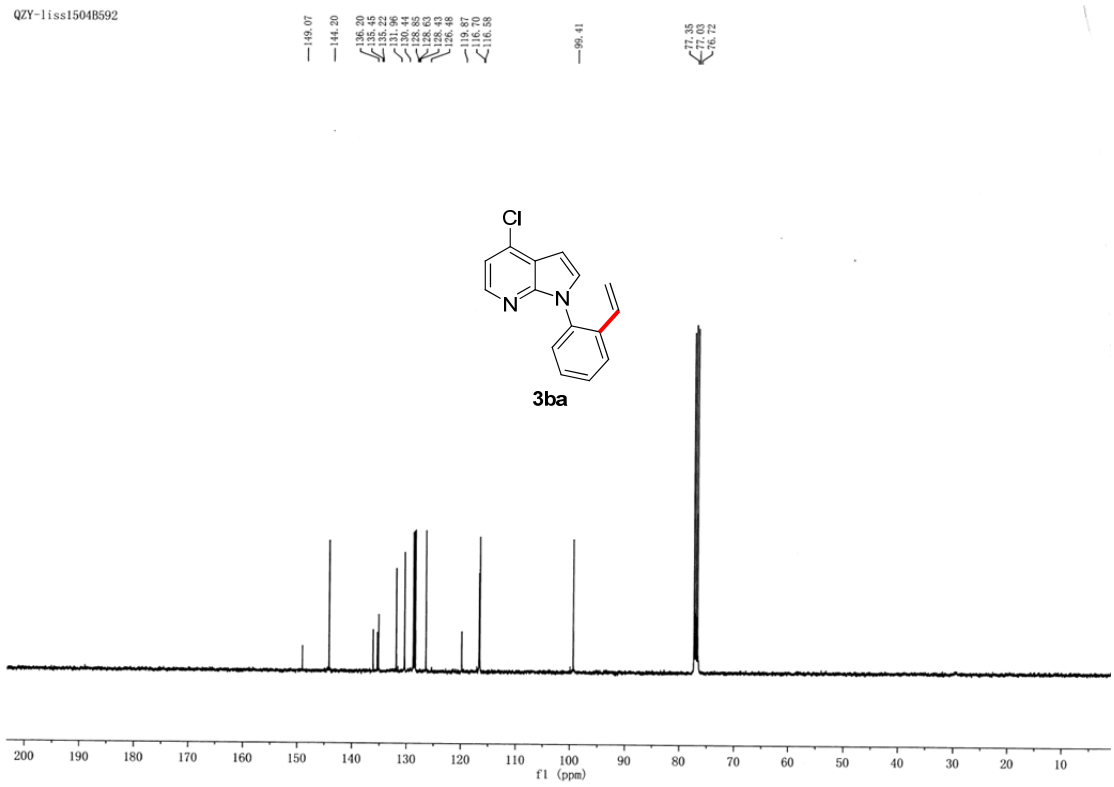


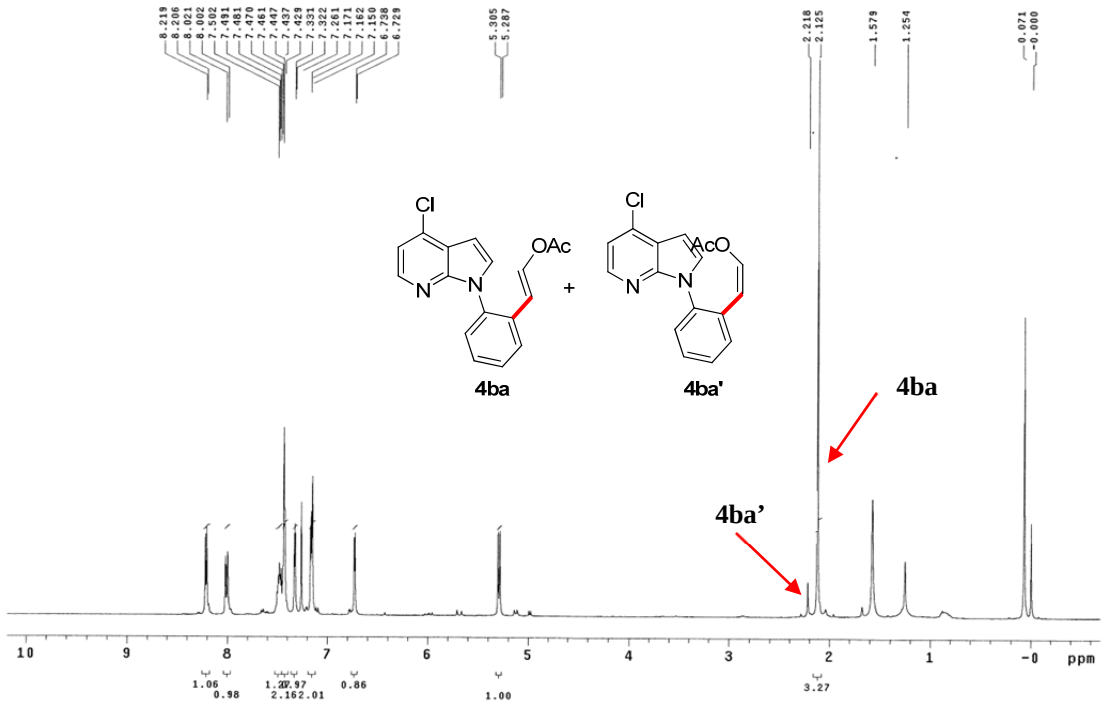
3aa

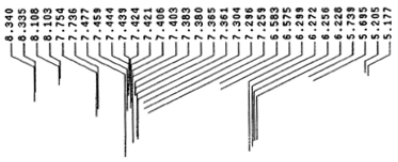

210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

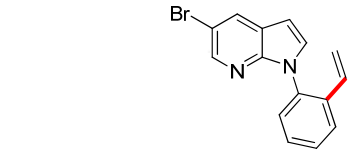

8.341
8.334
8.327
8.006
7.993
7.974
7.781
7.758
7.663
7.653
7.478
7.465
7.459
7.447
7.434
7.418
7.403
7.280
7.280
7.260
7.155
7.142
7.132
7.120
7.109
6.653
6.646
6.618
6.612
6.017
5.996
5.358
5.345
2.093
2.082
1.254
0.072
OAc
AcO
N
N
+
4aa
4aa'
4aa
4aa’
10
9
8
7
6
5
4
3
2
1
ppm
2.00
1.20
1.88
8.19
2.69
1.26
4.62
2.89
1.88
1.00
0.81
5.73


8.219
8.210
7.756
7.744
7.474
7.462
7.450
7.438
7.426
7.414
7.390
7.376
7.329
7.324
7.258
7.156
7.147
6.747
6.740
6.297
6.279
6.268
6.249
5.734
5.704
5.201
5.182
1.618
1.255
0.075
0.001
Cl
N
N
3ba
9
8
7
6
5
4
3
2
1
ppm
1.02
1.09
2.36
1.13
09
1.11
1.00
1.06
1.31
1.26

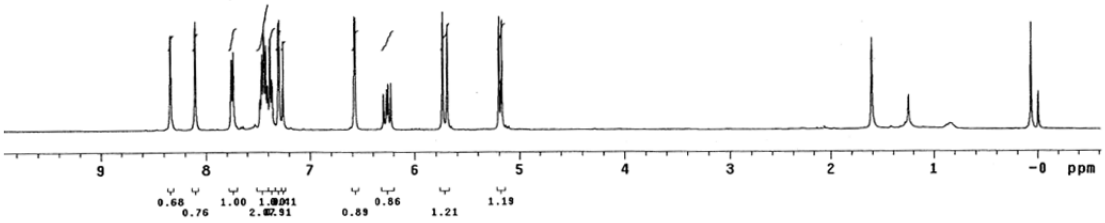

QZY-liss1504B592
Cl
N
N
3ba
f1 (ppm)

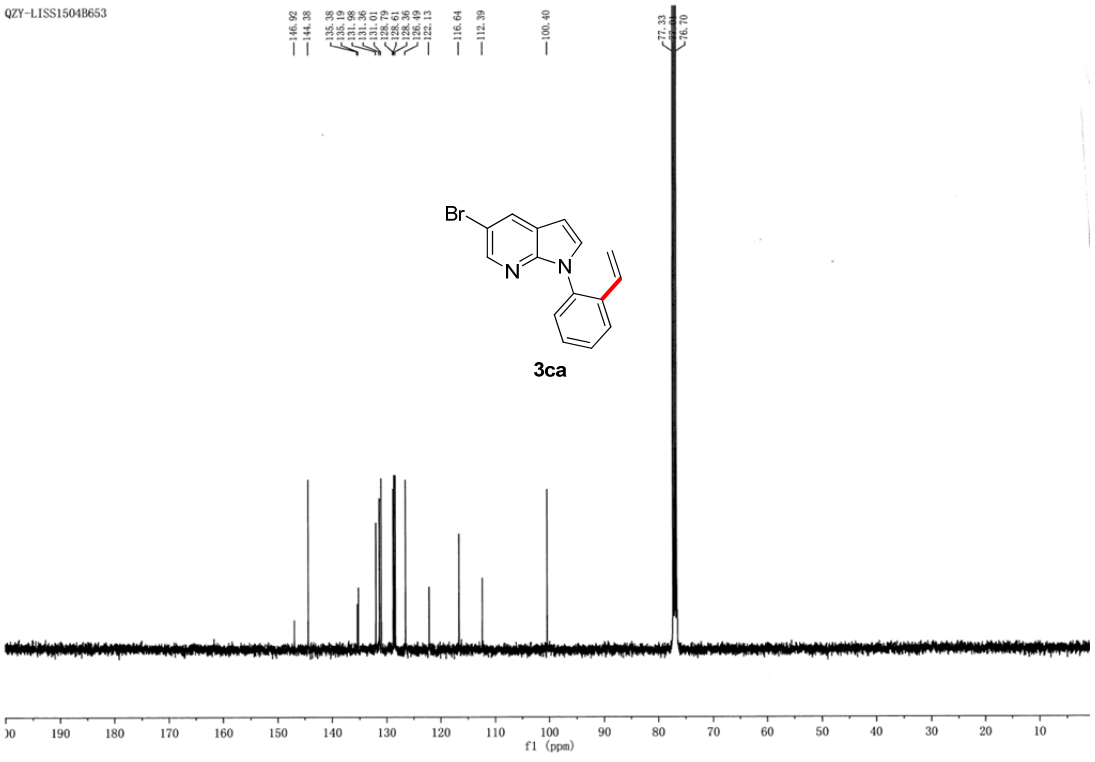

Cl
OAc
+
Cl
AcO
4ba
4ba'
4ba
4ba'
ppm

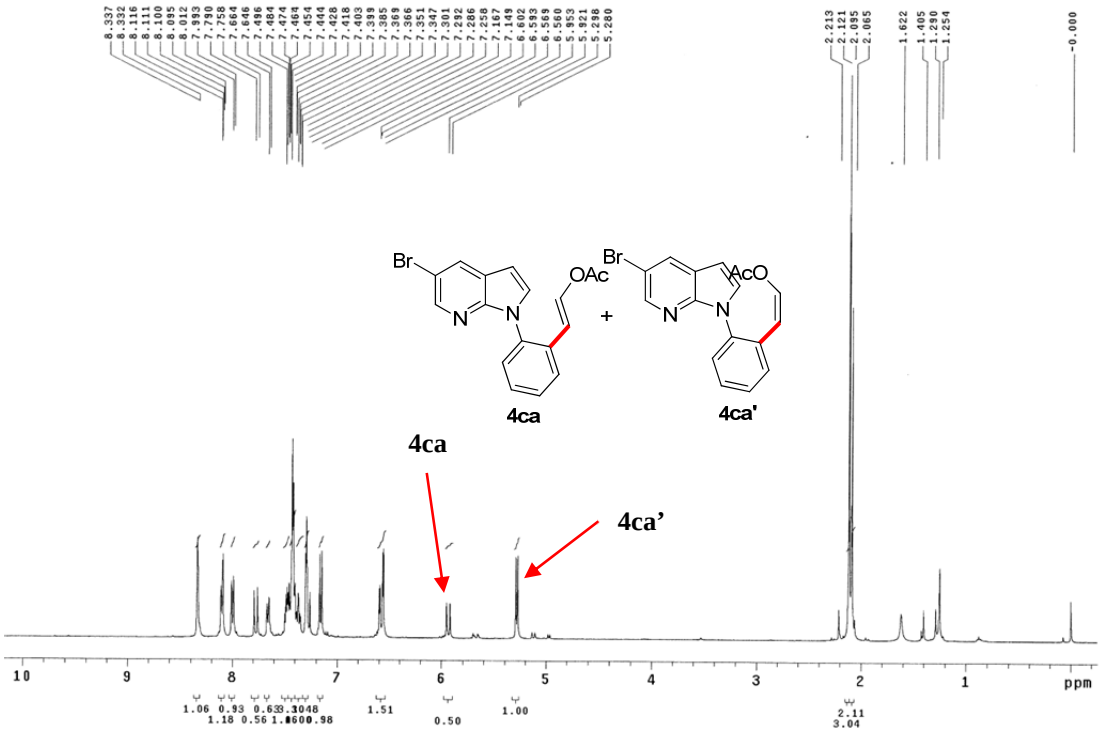


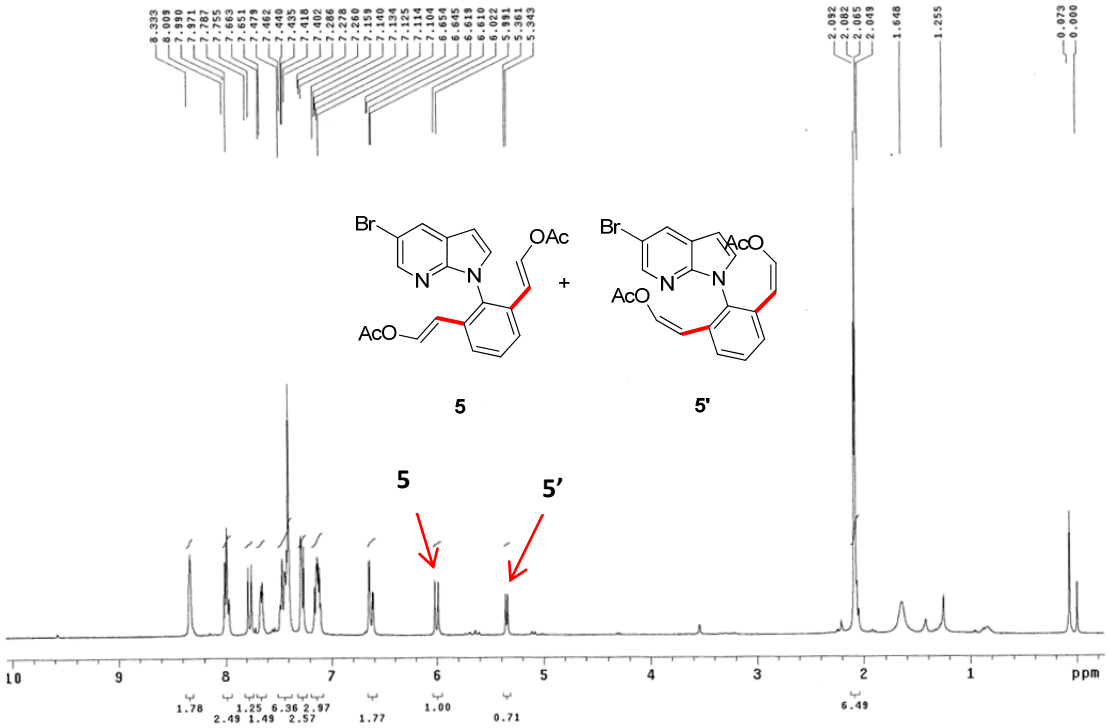

Br
N
N

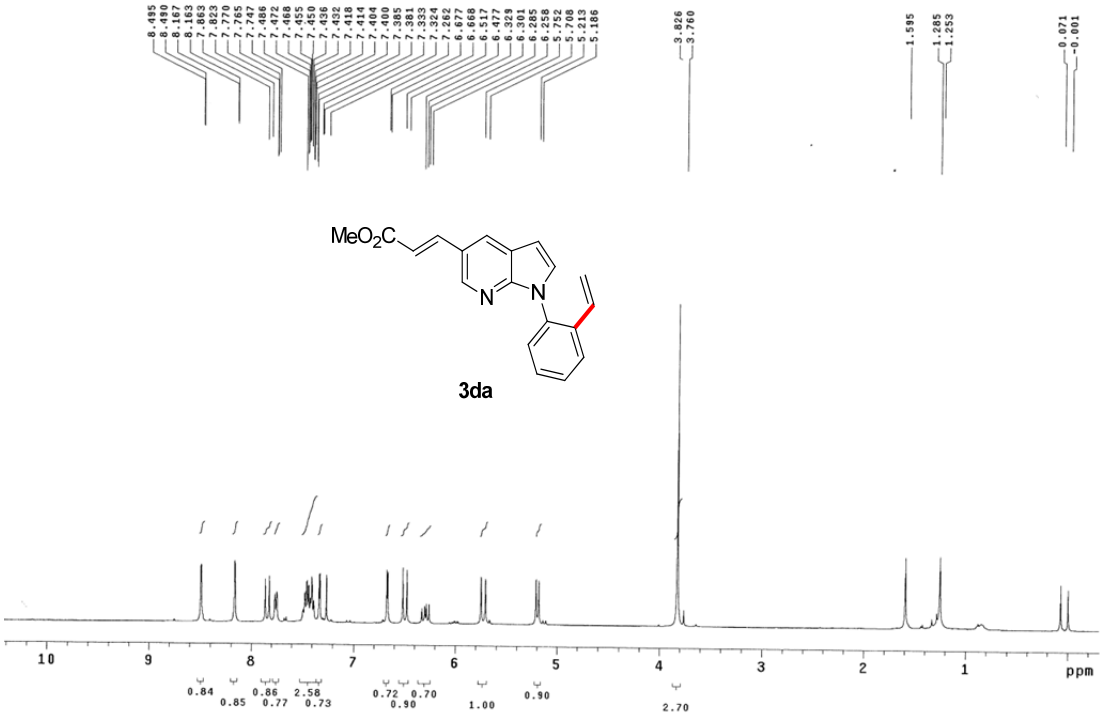
3ca

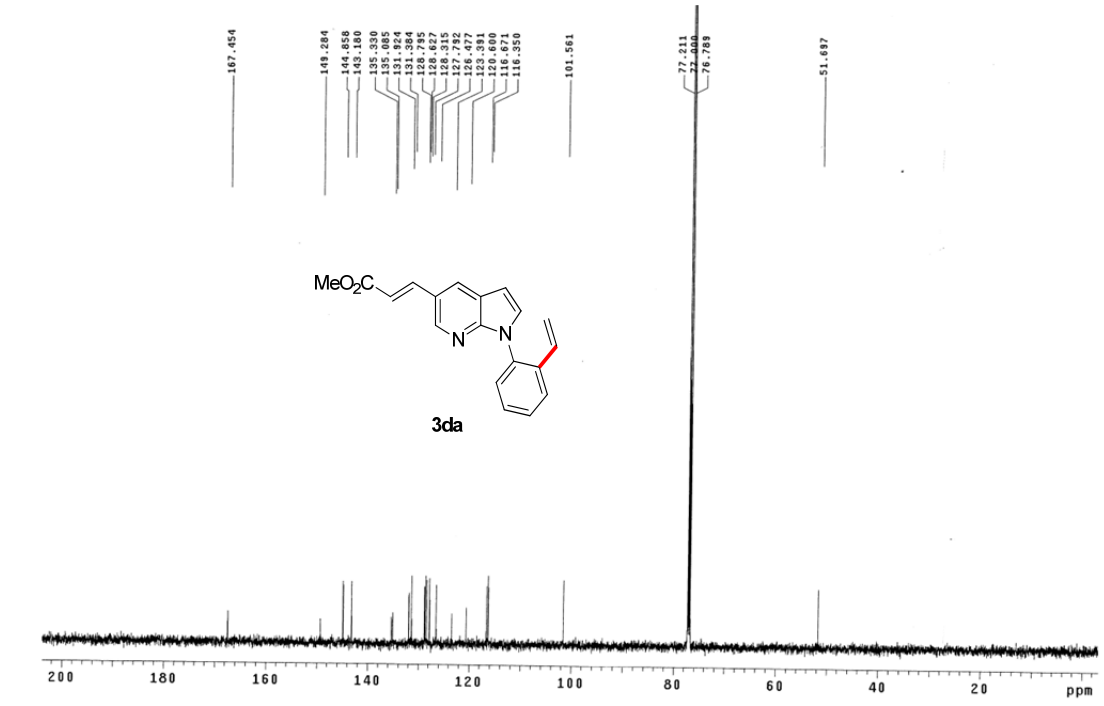

9
8
7
6
5
4
3
2
1
-0 ppm
0.68
0.76
1.00
0.89
0.86
1.21
1.19

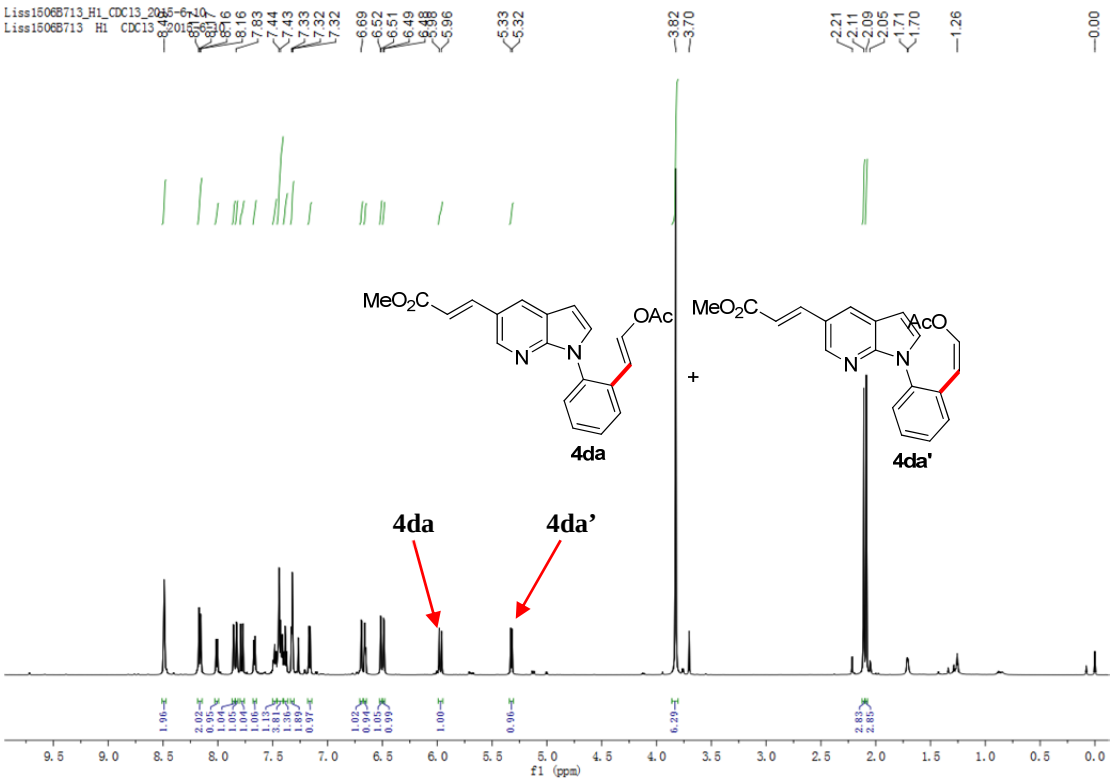

QZY-LISS1504B653
146.92
144.38
135.38
135.19
131.98
131.36
131.01
128.79
128.61
128.36
126.49
122.13
116.64
112.39
100.40
77.33
77.01
76.70
Br
N
N
3ca
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

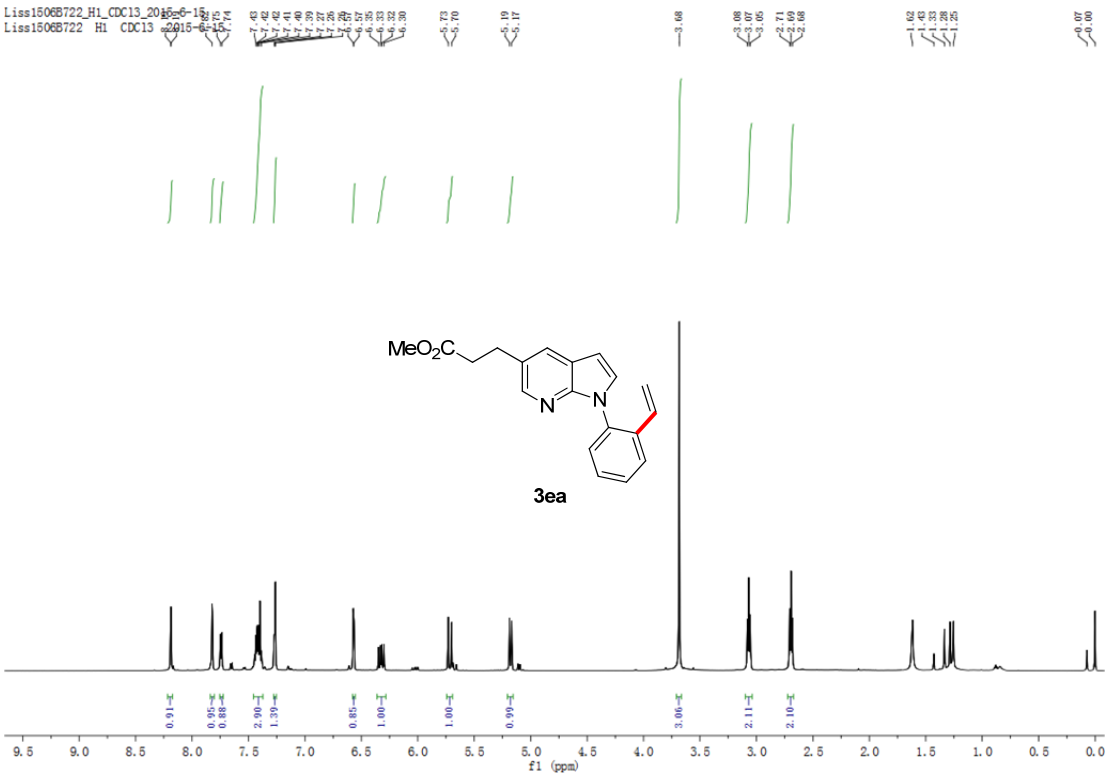

Br
OAc
+
Br
AcO
N
N
4ca
4ca'
4ca
4ca'
ppm

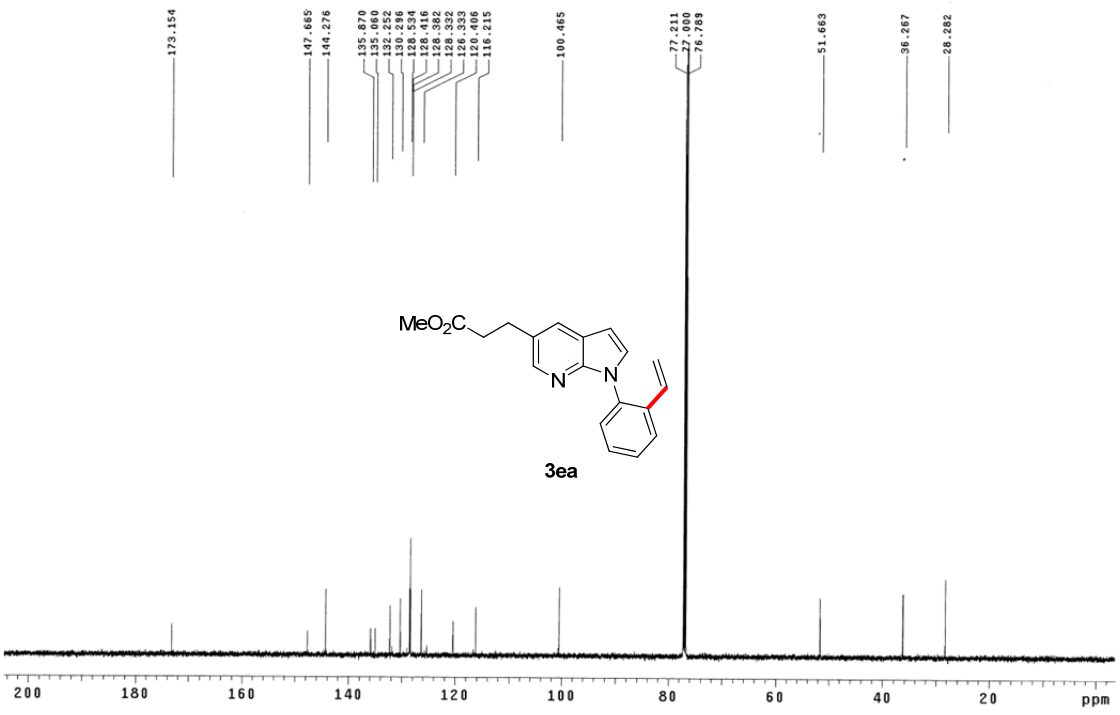

Br
OAc
AcO
+
Br
AcO
AcO
N
N
5
5'
5
5'
ppm

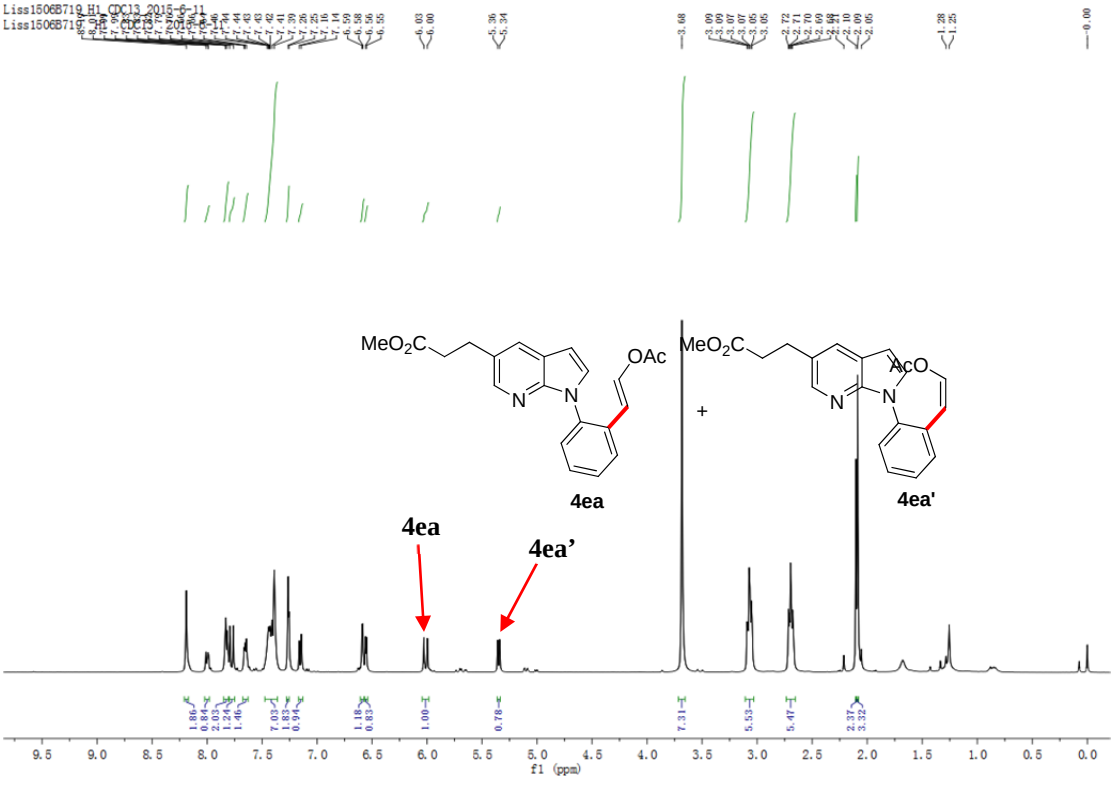

8.495
8.490
8.167
8.163
7.863
7.853
7.770
7.765
7.747
7.486
7.472
7.468
7.455
7.450
7.436
7.432
7.418
7.414
7.404
7.400
7.385
7.381
7.353
7.324
7.262
6.677
6.668
6.517
6.477
6.329
6.301
6.285
6.258
5.752
5.708
5.213
5.186
3.826
3.760
1.595
1.285
1.253
0.071
-0.001
MeO2C
N
N
3da
10
9
8
7
6
5
4
3
2
1
ppm
0.84
0.85
0.86
0.77
2.58
0.73
0.72
0.90
0.70
1.00
0.90
2.70

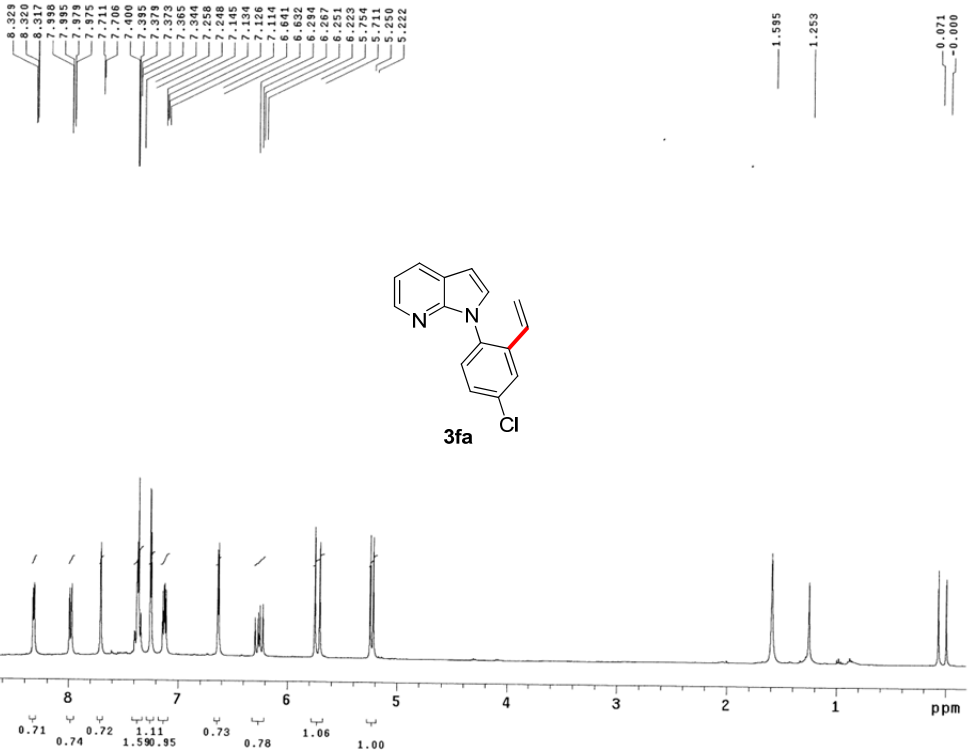

167.454
149.284
144.858
143.180
135.330
135.085
131.924
131.384
128.795
128.627
128.315
127.792
126.477
123.381
120.660
116.671
116.350
101.561
77.211
77.000
76.789
51.697
MeO2C
N
N
3da
200
180
160
140
120
100
80
60
40
20
ppm

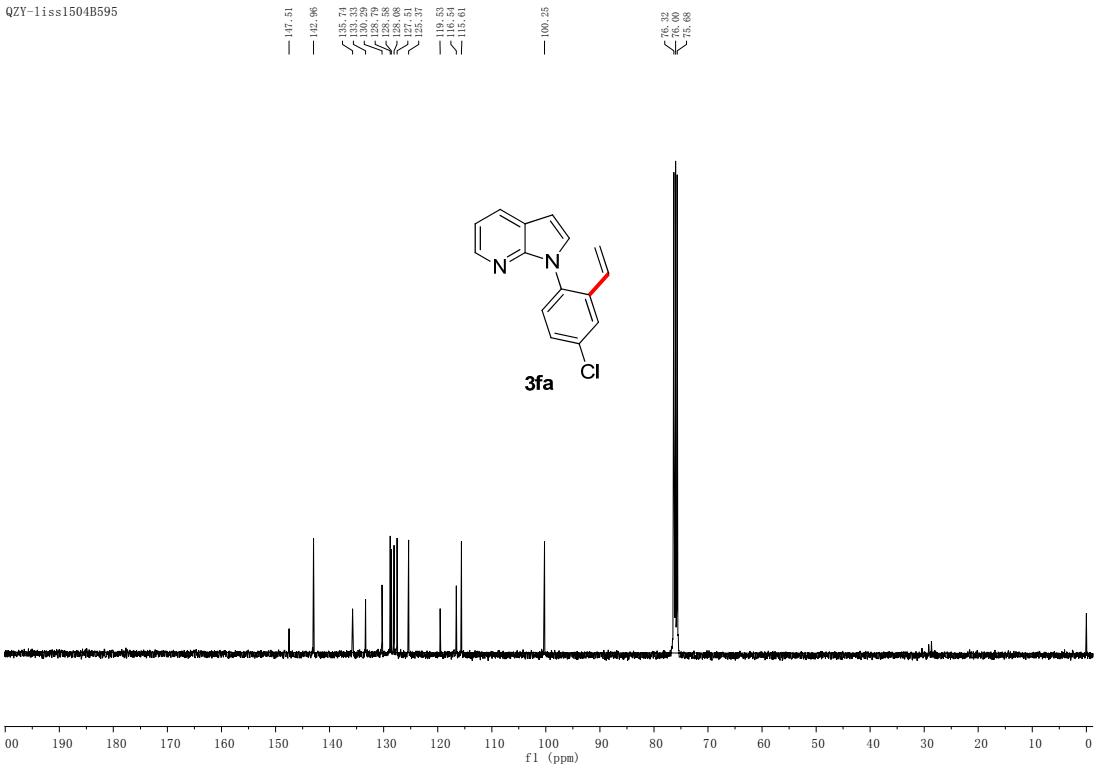

Liss1506B713_H1_CDC13_2015-6-10
Liss1506B713 H1 CDC13
MeO2C
OAc
N
4da
MeO2C
AcO
N
4da'
+
4da
4da'
f1 (ppm)

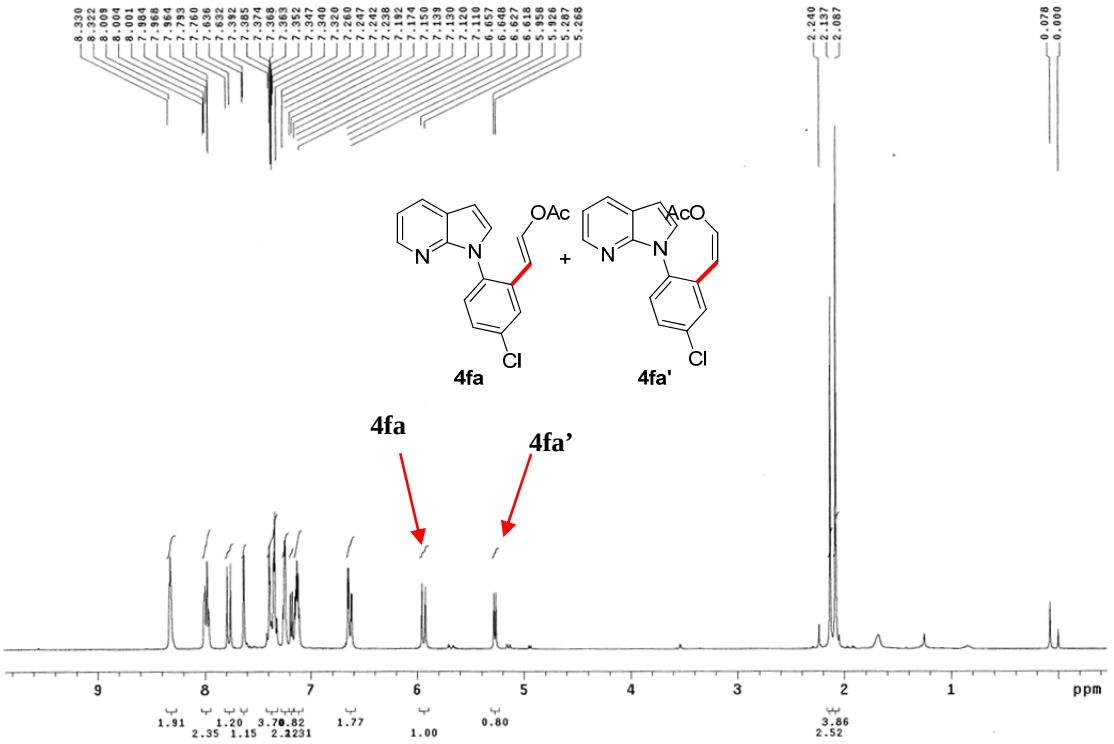

Liss1506B722_H1_CDC13_2015-6-15
Liss1506B722 H1 CDC13
MeO2C
N
3ea
f1 (ppm)

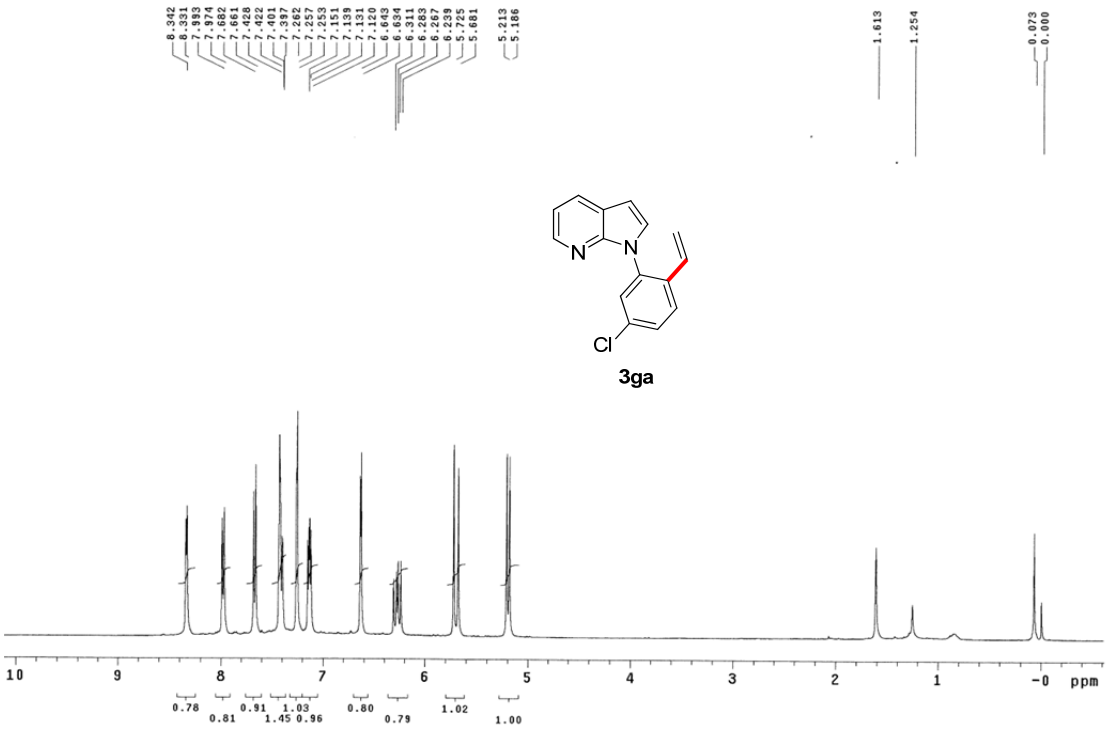

173.154
147.665
144.276
135.870
135.060
132.252
130.296
128.534
128.416
128.382
128.333
126.333
120.406
116.215
100.465
77.211
77.000
76.789
51.663
36.267
28.282
MeO2C
N
N
3ea
200
180
160
140
120
100
80
60
40
20
ppm

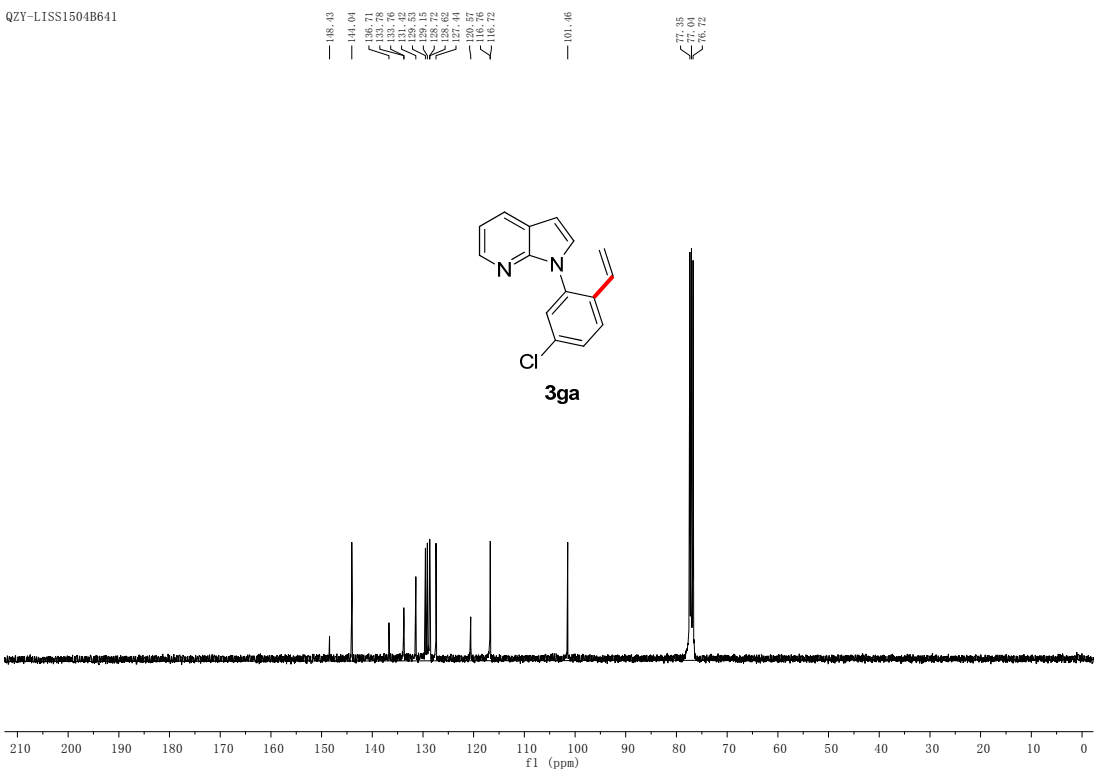

MeO2C
OAc
N
N
4ea
MeO2C
AcO
N
N
4ea'
+
4ea
4ea'
f1 (ppm)

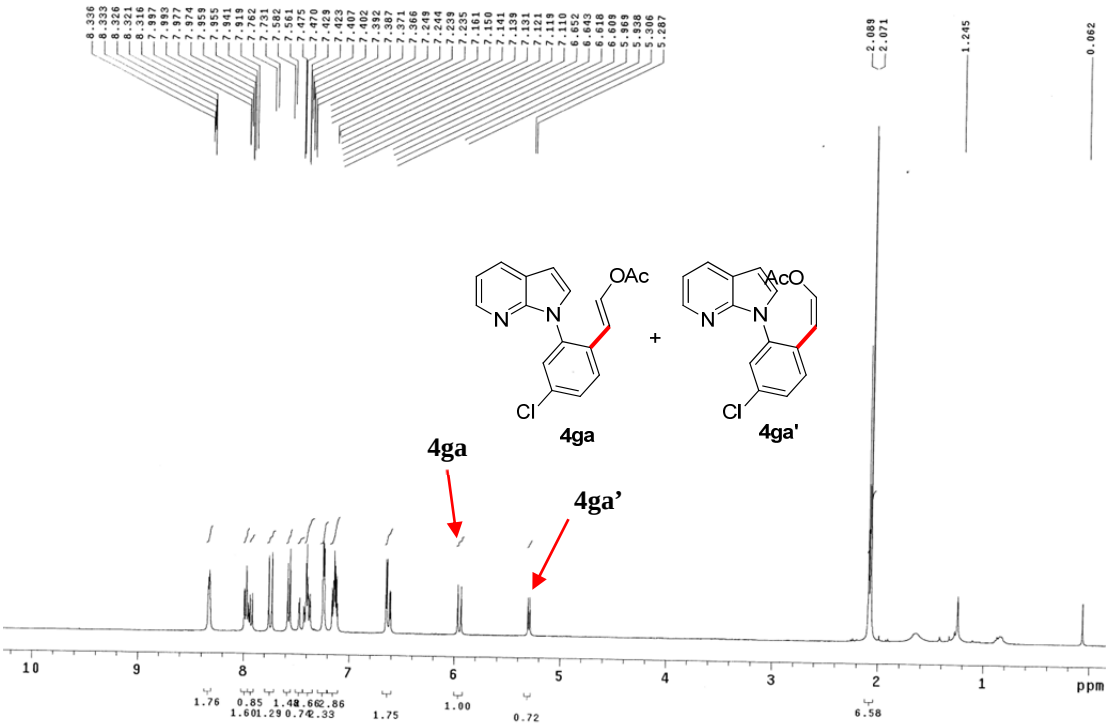

8.329
8.320
8.317
7.998
7.995
7.979
7.975
7.711
7.706
7.400
7.395
7.379
7.373
7.365
7.344
7.258
7.248
7.145
7.134
7.126
7.114
6.641
6.632
6.267
6.251
6.223
5.754
5.711
5.250
5.222
1.595
1.253
0.071
-0.000
N
N
Cl
3fa
9
8
7
6
5
4
3
2
1
ppm
0.71
0.74
0.72
1.11
1.59
0.95
0.73
0.78
1.06
1.00

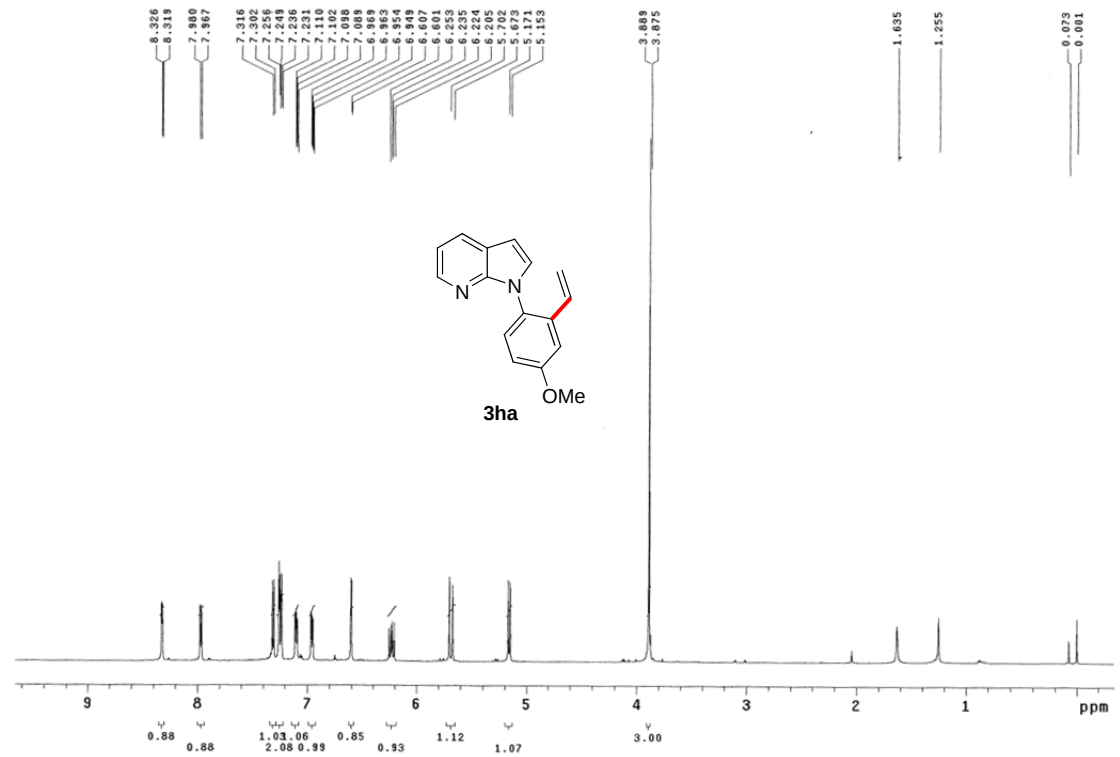

QZY-1iss1504B595
147.51
142.96
135.74
133.33
130.29
128.79
128.58
128.08
127.51
125.57
119.53
116.54
115.61
100.25
76.32
76.00
75.68
N
N
Cl
3fa
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

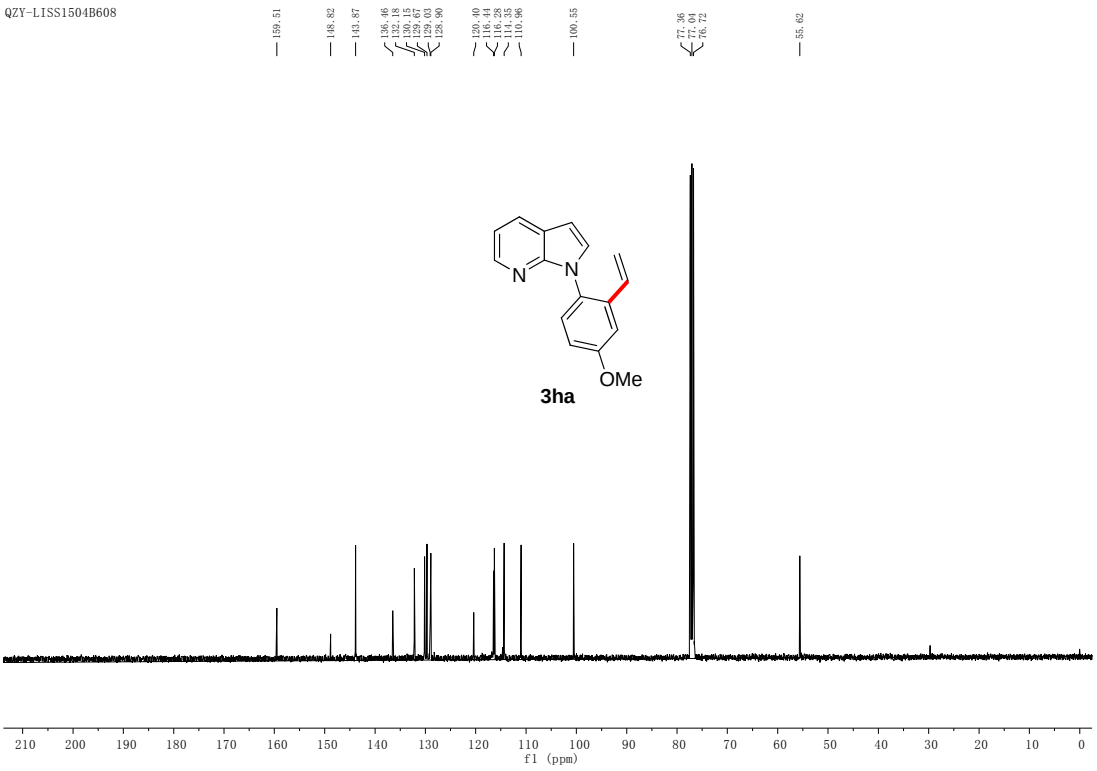

OAc
AcO
N
N
Cl
4fa
4fa'
4fa
4fa’
ppm

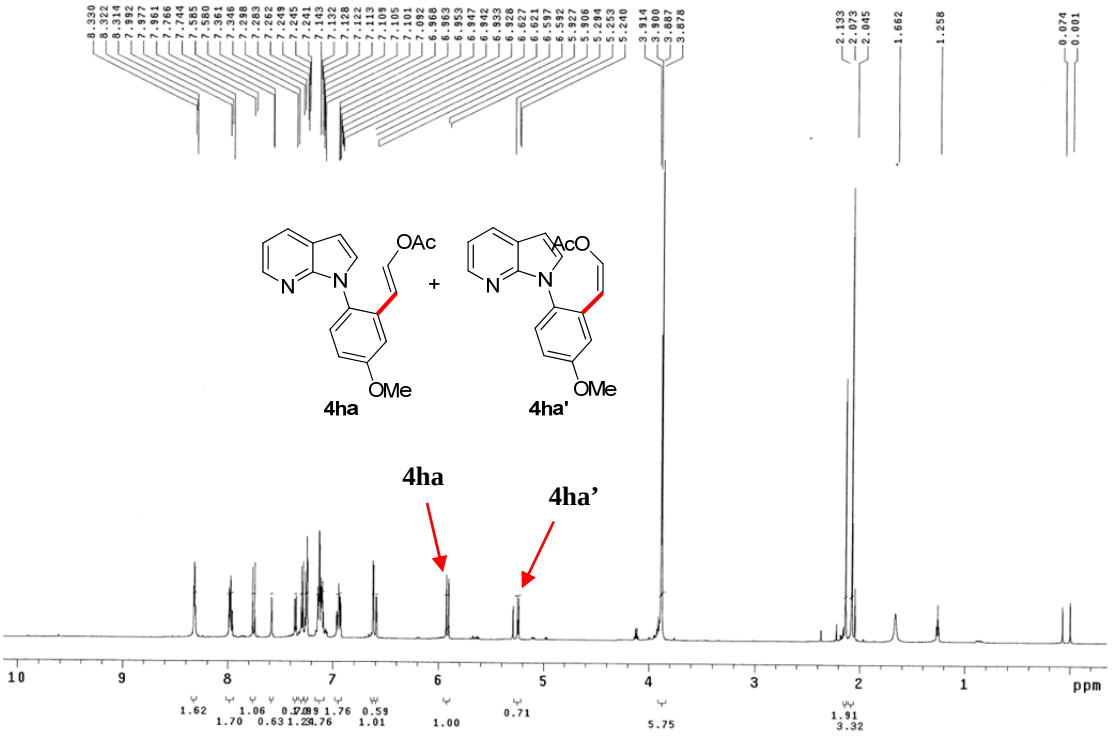

N
N
Cl
3ga
ppm

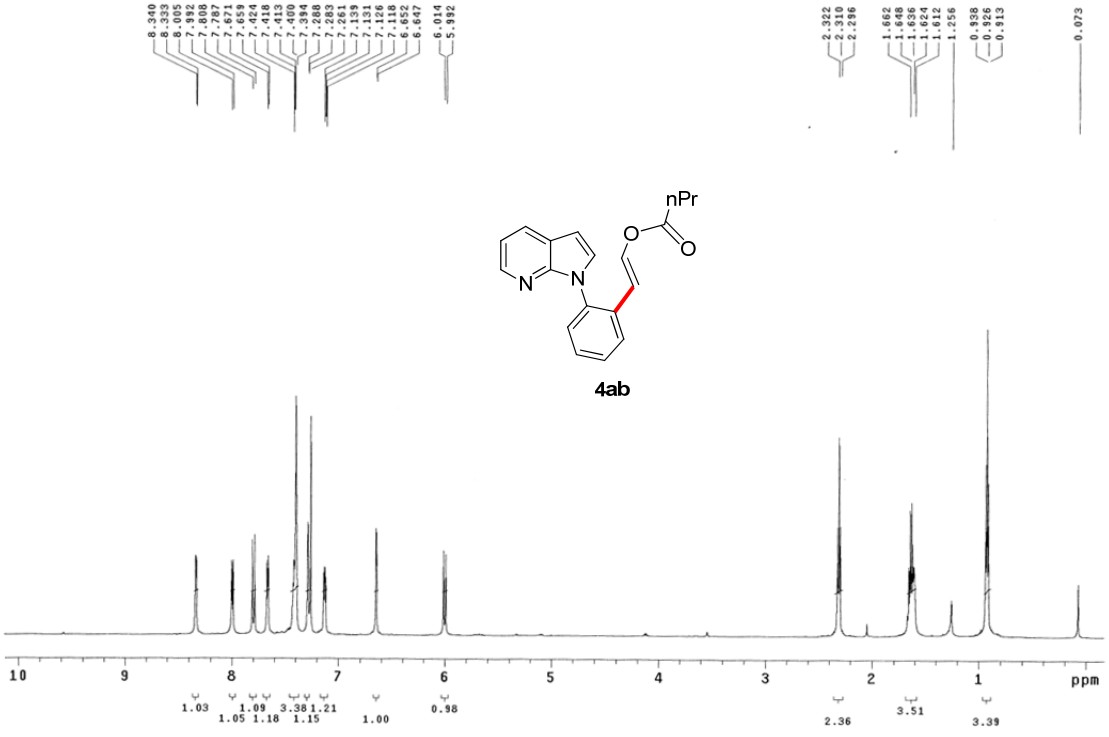

QZY-LISS1504B641
108.43
144.04
136.71
133.78
133.76
131.42
129.53
129.15
128.72
128.62
127.44
120.57
116.76
116.72
101.46
77.35
77.04
76.72
3ga
f1 (ppm)

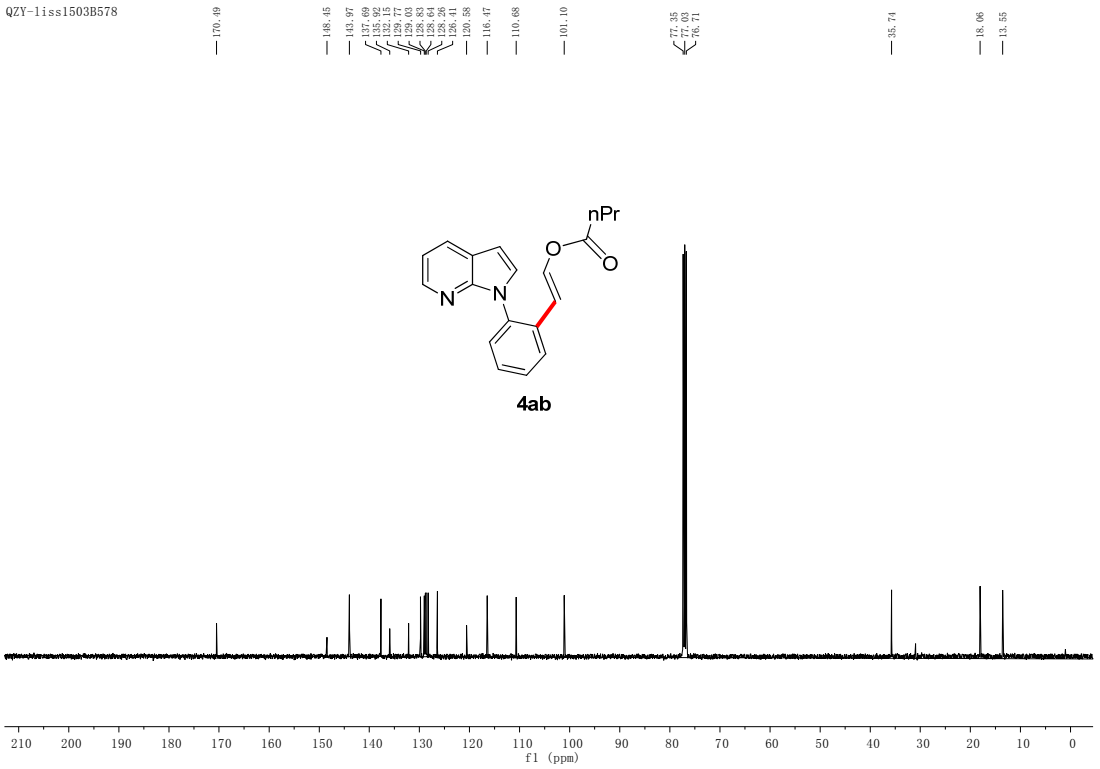

2.088
2.071
1.245
0.062
OAc
AcO
4ga
4ga'
4ga
4ga’
ppm

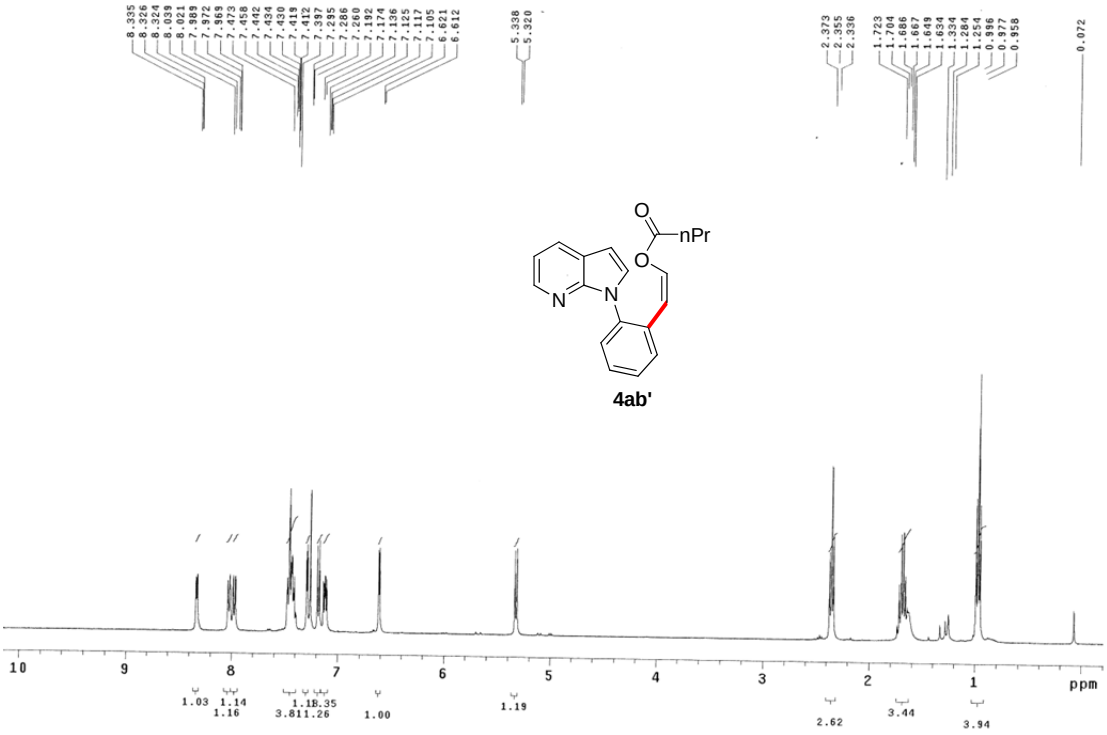

8.326
8.319
7.980
7.967
7.316
7.302
7.256
7.248
7.236
7.231
7.110
7.102
7.098
7.089
6.969
6.963
6.954
6.949
6.607
6.601
6.253
6.235
6.224
6.205
6.702
5.673
5.171
5.153
3.889
3.875
1.635
1.255
0.073
0.001
N
N
OMe
3ha
9
8
7
6
5
4
3
2
1
ppm
0.88
0.88
1.03
1.06
2.08
0.99
0.85
0.93
1.12
1.07
3.00

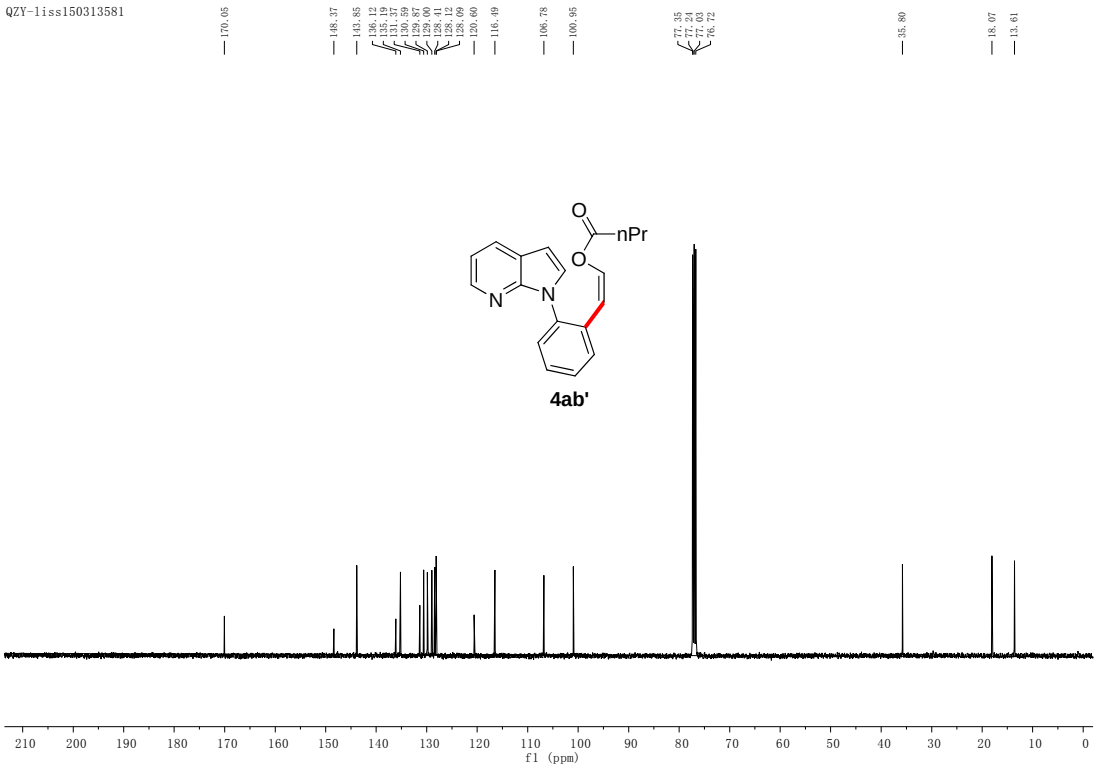

QZY-LISS1504B608
159.51
148.82
143.87
136.46
132.18
130.15
129.67
129.03
128.90
120.40
116.44
116.28
114.35
110.96
100.55
77.36
77.04
76.72
55.62
N
N
OMe
3ha
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

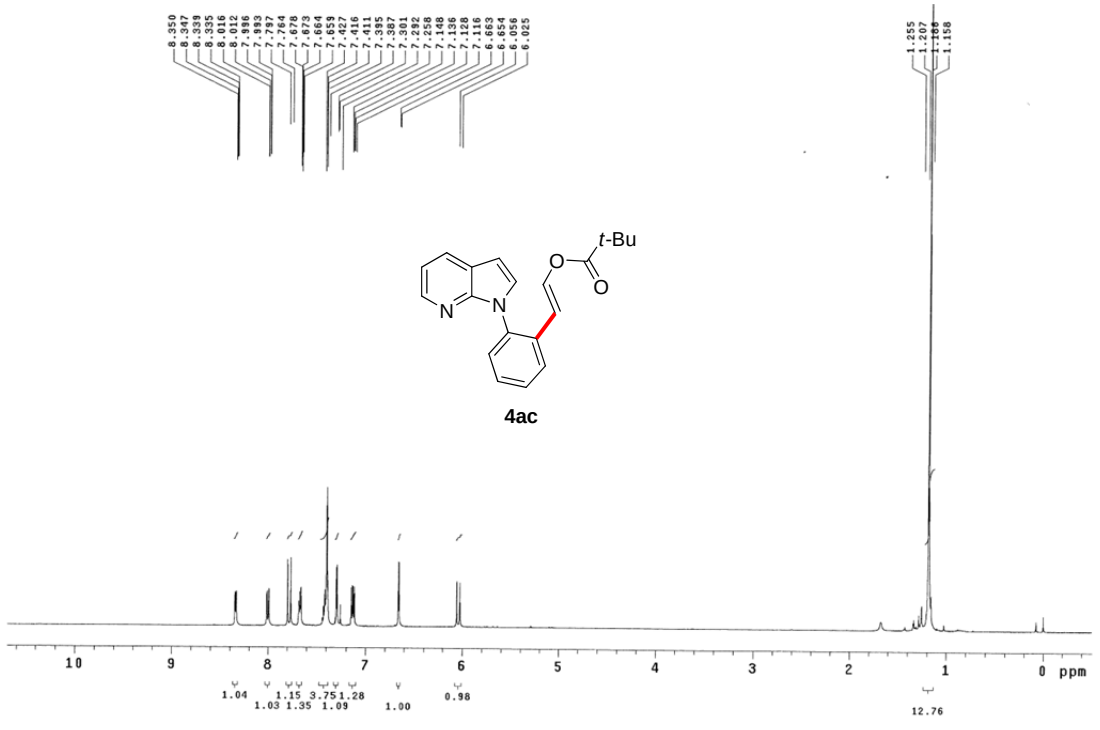

OAc
AcO
OMe
OMe
4ha
4ha'
4ha
4ha'
ppm

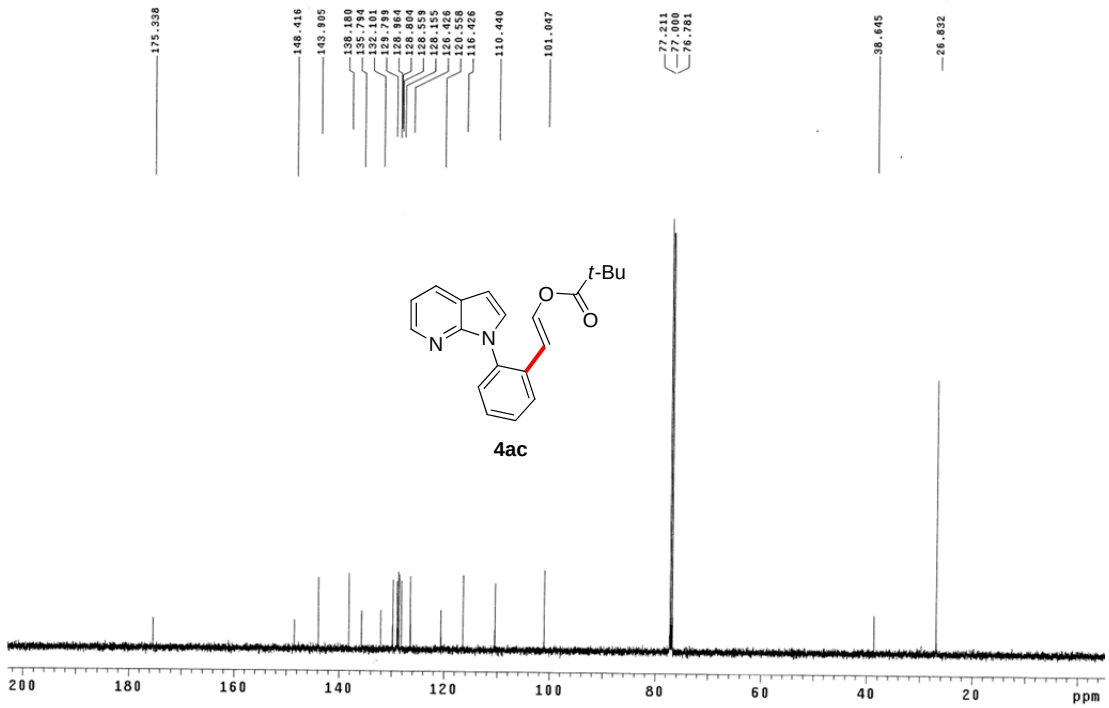

nPr
O
O
4ab
ppm


QZY-liss1503B578
170.49
148.45
143.97
137.69
135.92
132.15
129.77
129.63
128.83
128.64
128.26
126.41
120.58
116.47
110.68
101.10
77.35
77.03
76.71
35.74
18.06
13.55
nPr
O
O
N
N
4ab
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

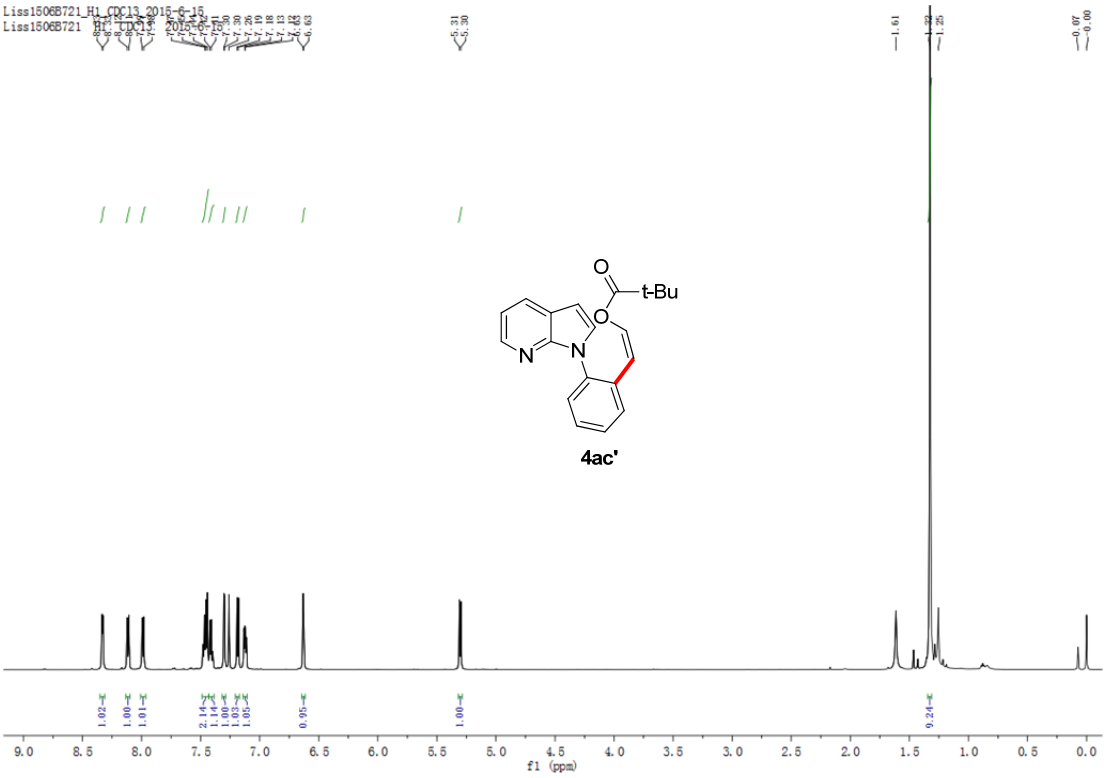

8.335
8.326
8.324
8.039
8.021
7.989
7.972
7.969
7.473
7.458
7.442
7.434
7.430
7.418
7.412
7.397
7.295
7.286
7.260
7.192
7.174
7.156
7.125
7.117
7.105
6.621
6.612
5.338
5.320
2.373
2.355
2.336
1.723
1.704
1.686
1.667
1.649
1.634
1.334
1.284
1.254
0.996
0.977
0.958
0.072
O
nPr
O
N
N
4ab'
10
9
8
7
6
5
4
3
2
1
ppm
1.03
1.14
1.16
1.18
1.35
3.81
1.26
1.00
1.19
2.62
3.44
3.94


QZY-liss150313581
170.05
148.37
143.85
136.12
135.19
131.37
130.59
129.87
129.00
128.41
128.21
128.09
120.60
116.49
106.78
100.95
77.35
77.04
76.72
35.80
18.07
13.61
nPr
O
O
N
N
4ab'
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.350
8.347
8.339
8.335
8.016
8.012
7.996
7.993
7.797
7.794
7.764
7.678
7.673
7.664
7.659
7.427
7.416
7.411
7.395
7.387
7.301
7.292
7.258
7.148
7.136
7.128
7.116
6.663
6.654
6.056
6.025
1.255
1.207
1.168
1.158
t-Bu
O
O
N
N
4ac
10
9
8
7
6
5
4
3
2
1
0 ppm
1.04
1.03
1.15
1.35
3.75
1.09
1.28
1.00
0.98
12.76

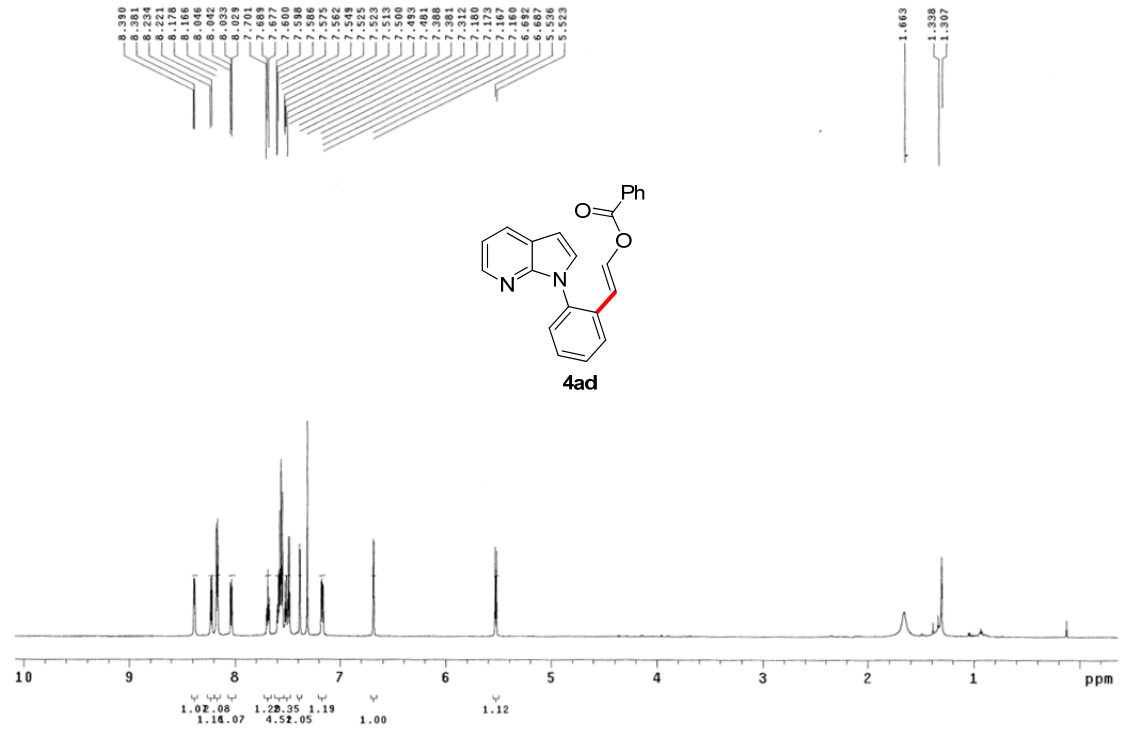

175.338
148.416
143.905
138.180
135.794
132.101
129.799
128.984
128.604
128.155
126.426
120.558
116.426
110.440
101.047
77.211
77.000
76.781
38.645
26.832
t-Bu
O
O
N
N
200
180
160
140
120
100
80
60
40
20
ppm

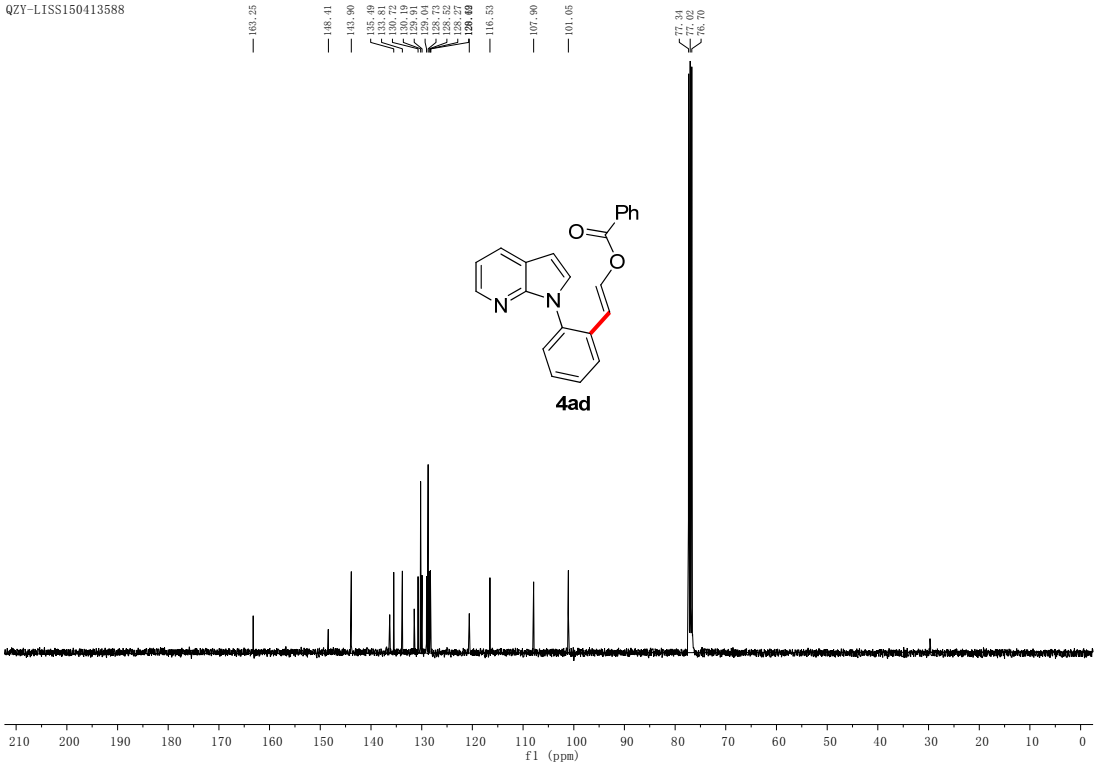
4ac

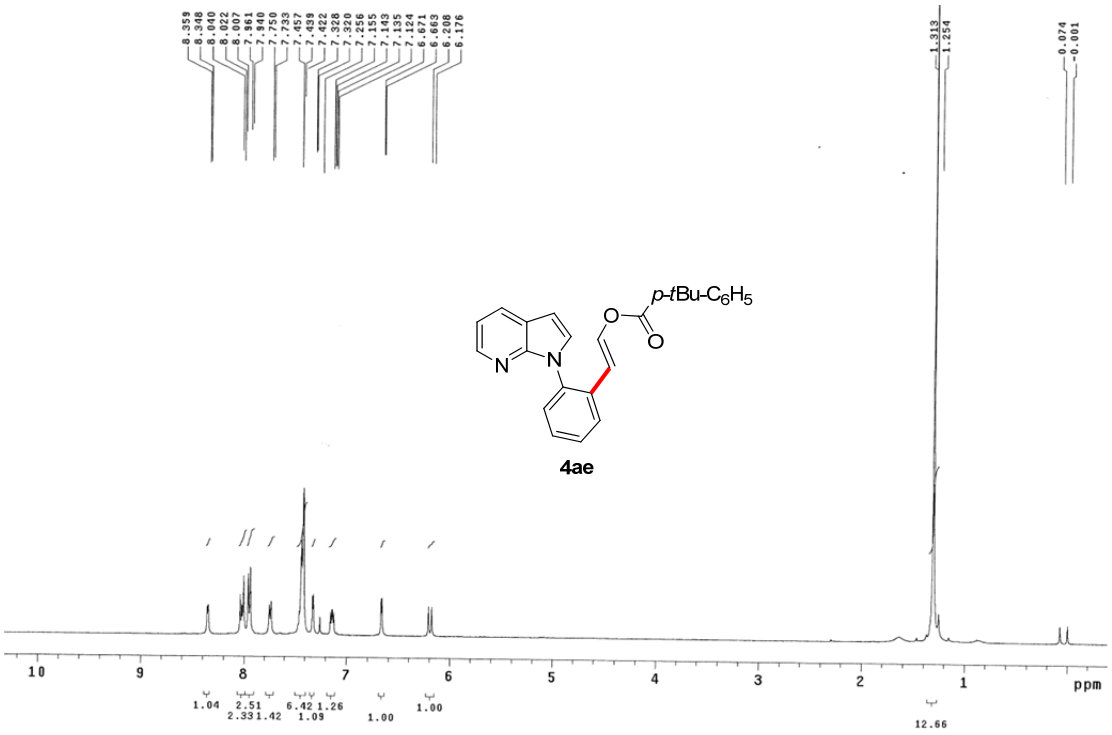

Liss1506B721_H1_CDCl3_2015-6-15
Liss1506B721 H1 CDCl3 2015-6-15
5.31
5.30
1.61
1.32
1.25
0.07
0.00
1.02
1.00
1.01
2.14
1.14
1.00
1.03
1.05
0.95
1.00
9.24
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

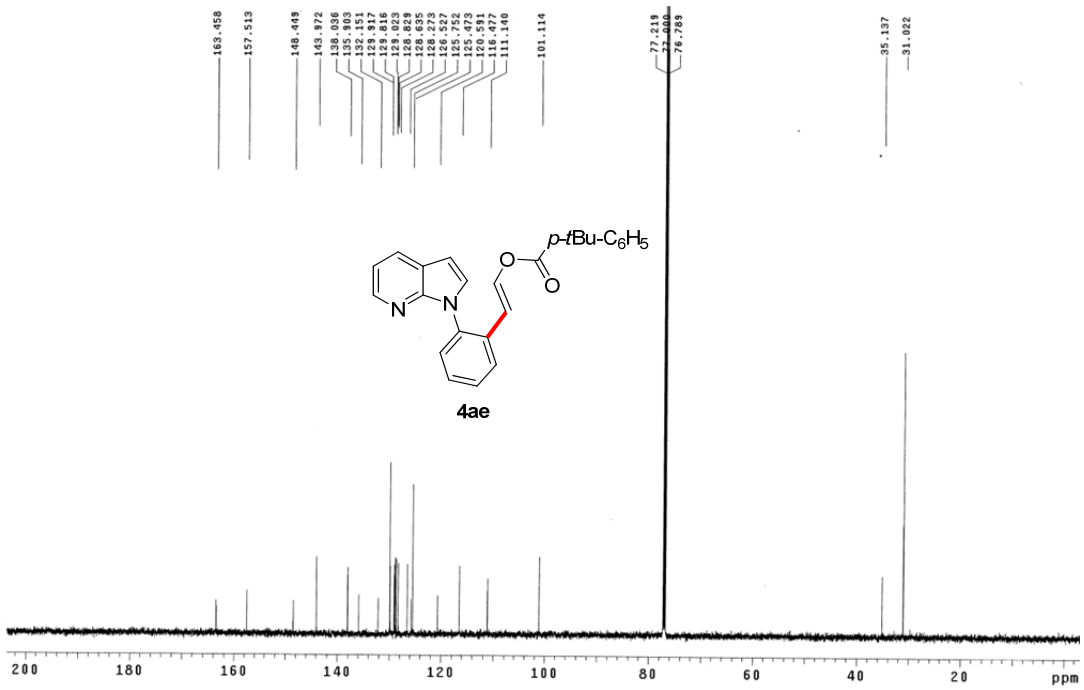
O
t-Bu
O
N
N

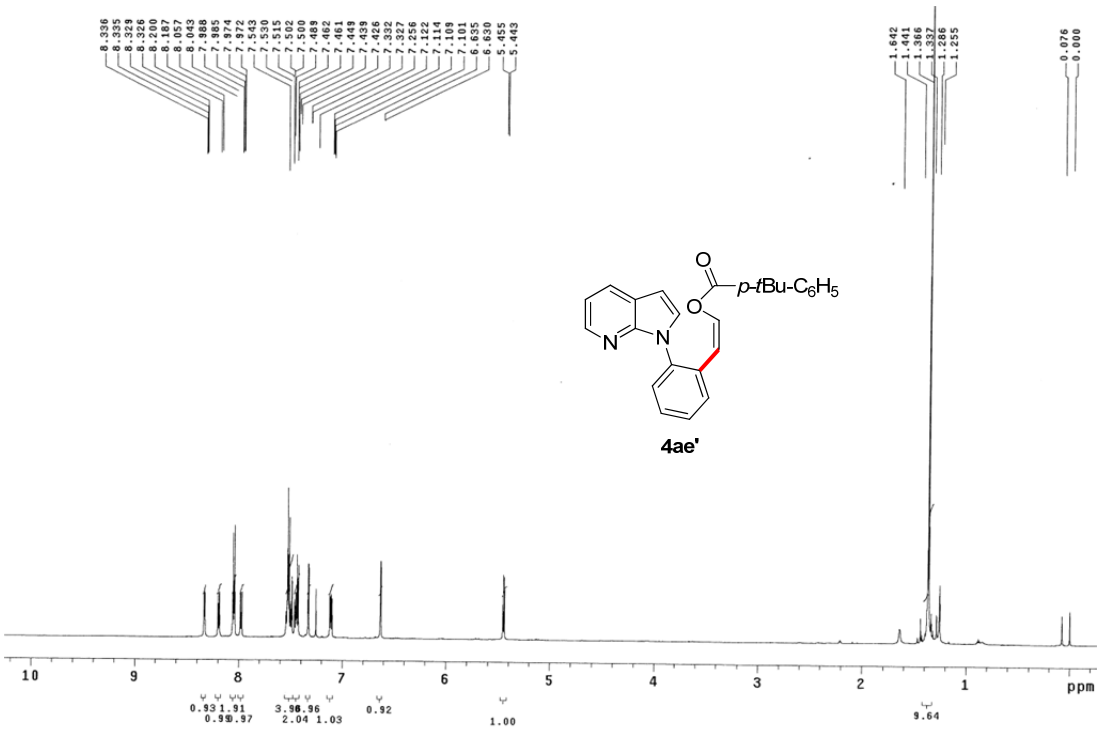
4ac'

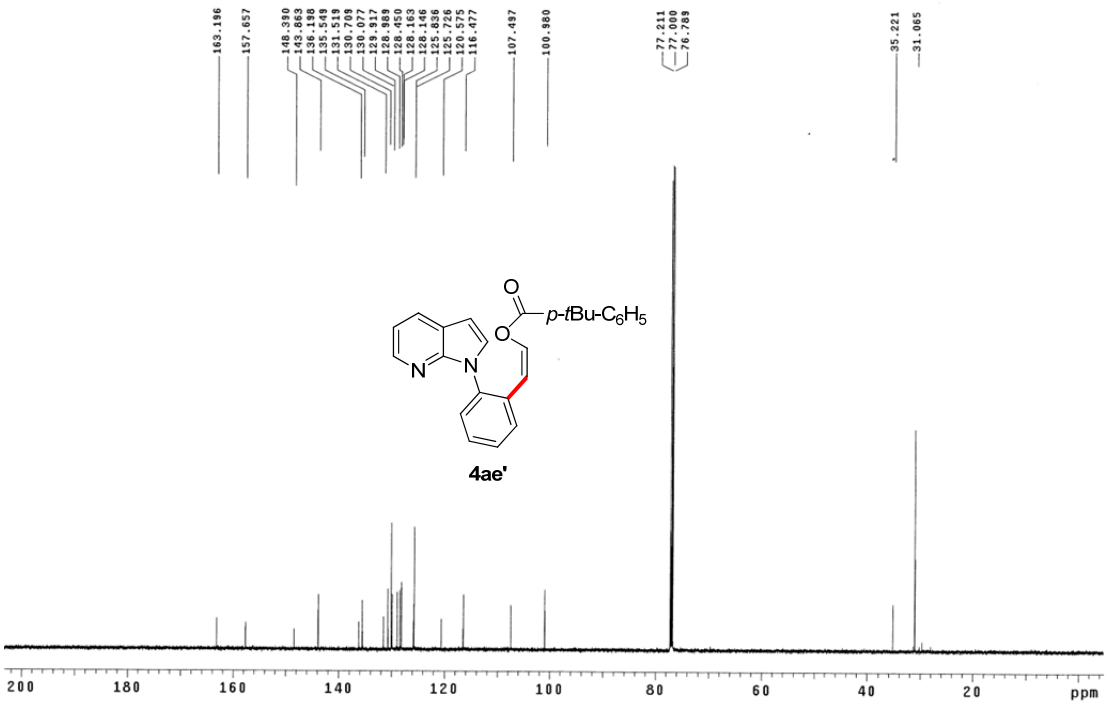

8.330
8.301
8.234
8.221
8.178
8.166
8.046
8.042
8.033
8.028
7.701
7.689
7.677
7.600
7.598
7.586
7.575
7.562
7.548
7.525
7.523
7.513
7.500
7.493
7.481
7.388
7.381
7.312
7.180
7.173
7.167
7.160
6.692
6.687
5.536
5.523
1.663
1.338
1.307
Ph
O
O
N
N
4ad
10
9
8
7
6
5
4
3
2
1
ppm
1.02
2.08
1.16
4.07
1.22
2.35
4.52
2.05
1.19
1.00
1.12

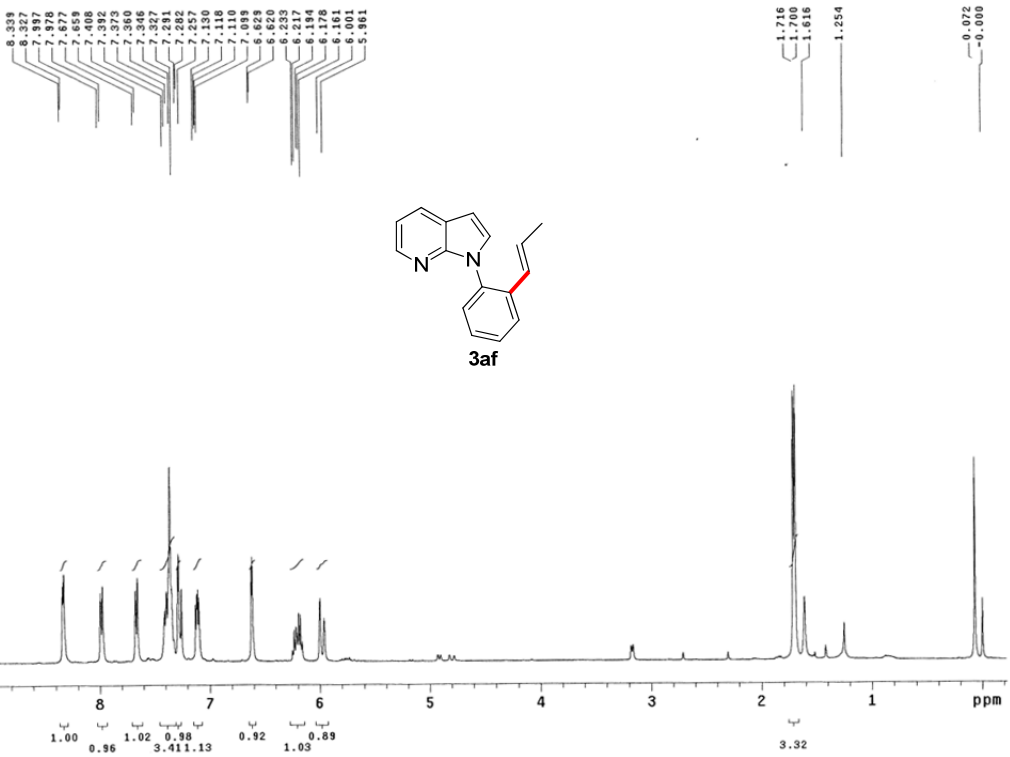

QZY-LISS150413588
163.25
148.41
143.90
135.49
133.81
130.72
130.19
129.91
129.04
128.73
128.52
128.27
116.53
107.90
101.05
77.34
77.02
76.70
Ph
O
O
N
N
4ad
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

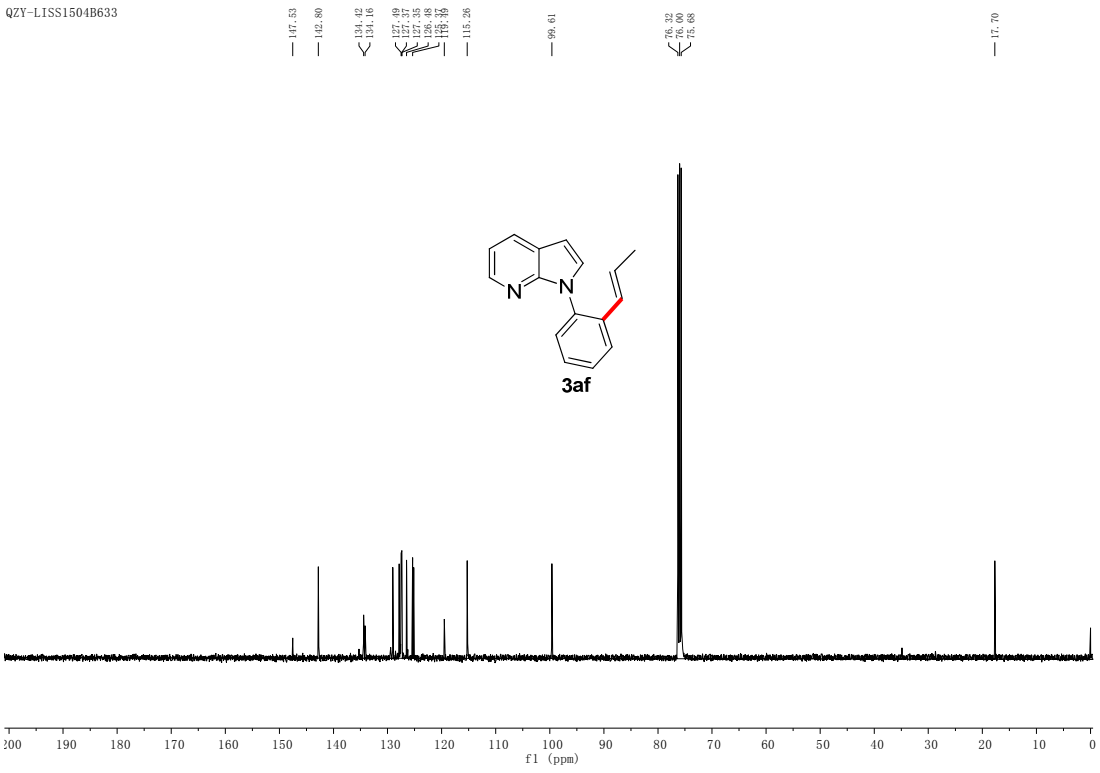

p-tBu-C6H5
4ae
ppm

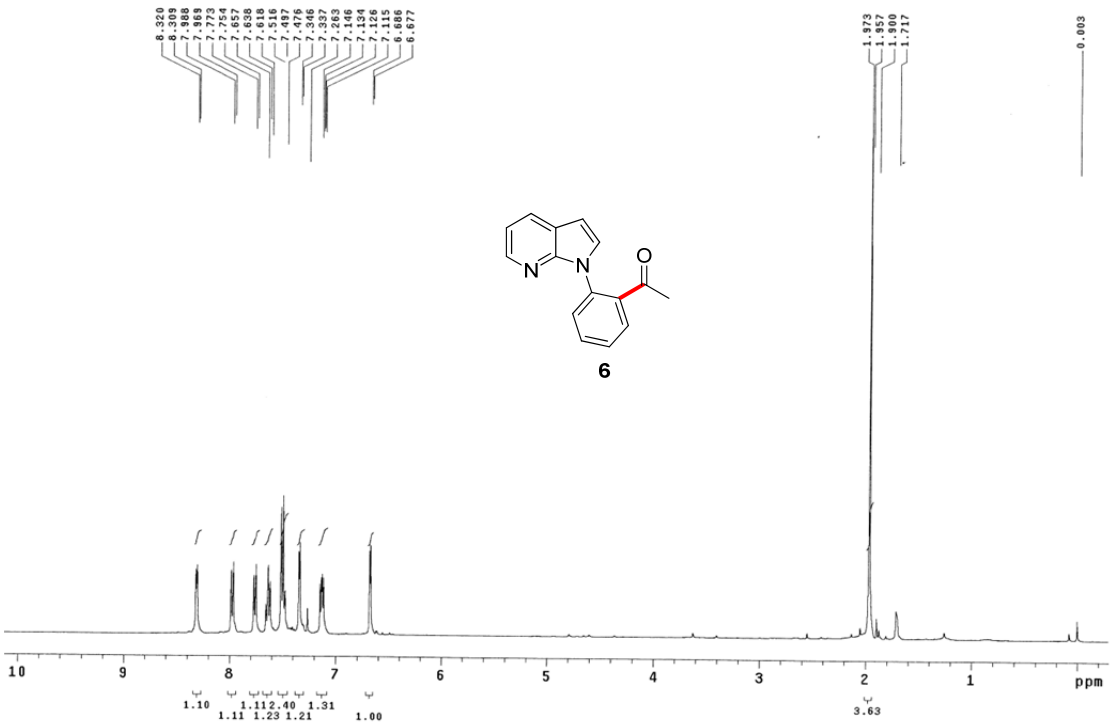

p-tBu-C6H5
4ae
ppm


8.336
8.335
8.329
8.328
8.200
8.187
8.057
8.043
7.988
7.985
7.974
7.972
7.543
7.530
7.515
7.502
7.500
7.489
7.462
7.461
7.449
7.439
7.426
7.332
7.327
7.256
7.122
7.114
7.109
7.101
6.635
6.630
5.455
5.443
1.642
1.441
1.366
1.337
1.266
1.255
0.076
0.000
p-tBu-C6H5
4ae'
10
9
8
7
6
5
4
3
2
1
ppm
0.93 1.91
0.98 0.97
3.96 0.96
2.04 1.03
0.92
1.00
9.64

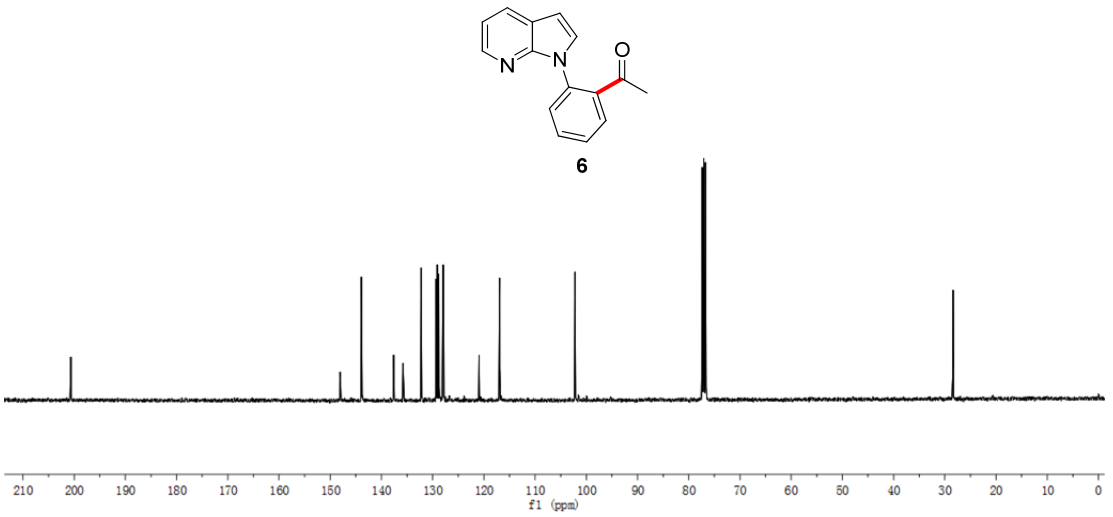

163.196
157.657
148.390
143.663
136.188
135.540
131.519
130.709
130.077
129.917
128.889
128.450
126.163
125.446
125.436
125.726
120.575
116.477
107.497
100.980
77.211
77.000
76.789
35.221
31.065
p-tBu-C6H5
4ae'
200
180
160
140
120
100
80
60
40
20
ppm

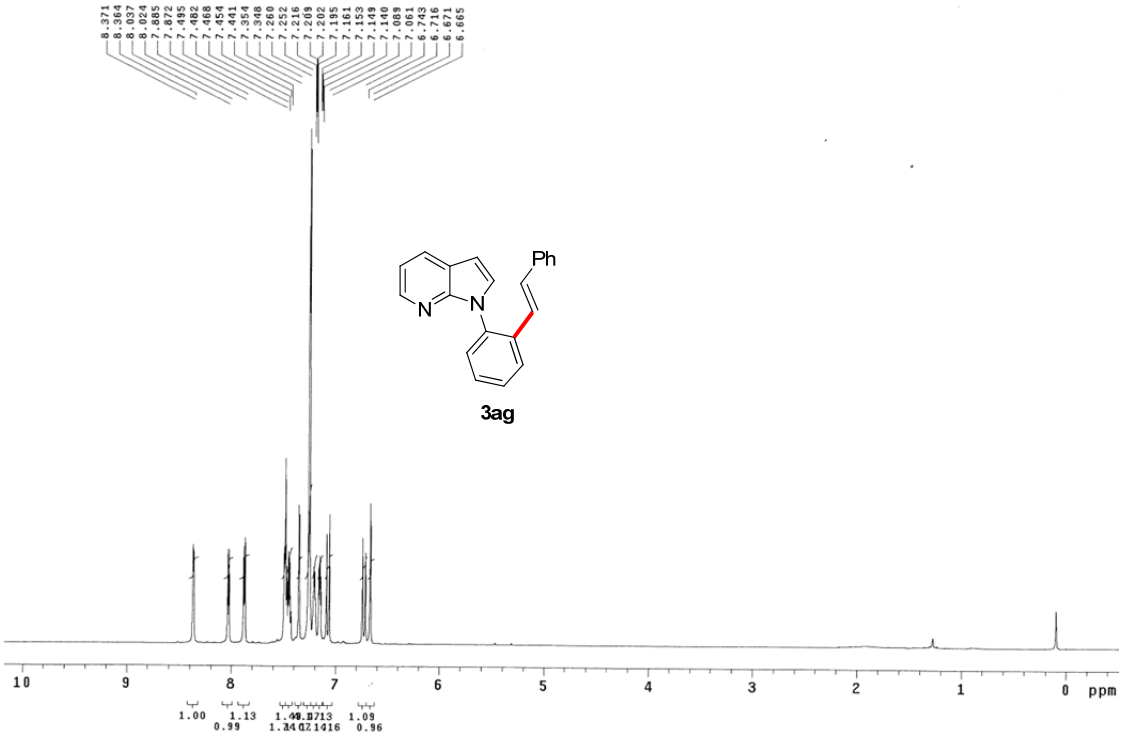

8.339
8.327
7.997
7.978
7.677
7.659
7.408
7.392
7.373
7.360
7.345
7.327
7.291
7.282
7.257
7.130
7.118
7.110
7.099
6.629
6.620
6.233
6.217
6.194
6.178
6.161
6.001
5.981
1.716
1.700
1.616
1.254
0.072
0.000
3af
9
8
7
6
5
4
3
2
1
ppm
1.00
0.96
1.02
0.98
3.41
1.13
0.92
1.03
0.89
3.32

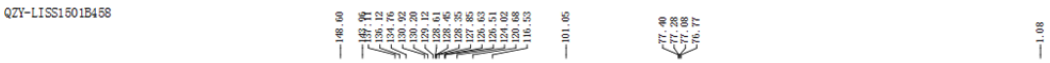

QZY-LISS1504B633
147.53
142.80
134.42
134.16
127.49
127.37
127.35
126.48
120.39
115.26
99.61
76.32
76.00
75.68
17.70
3af
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

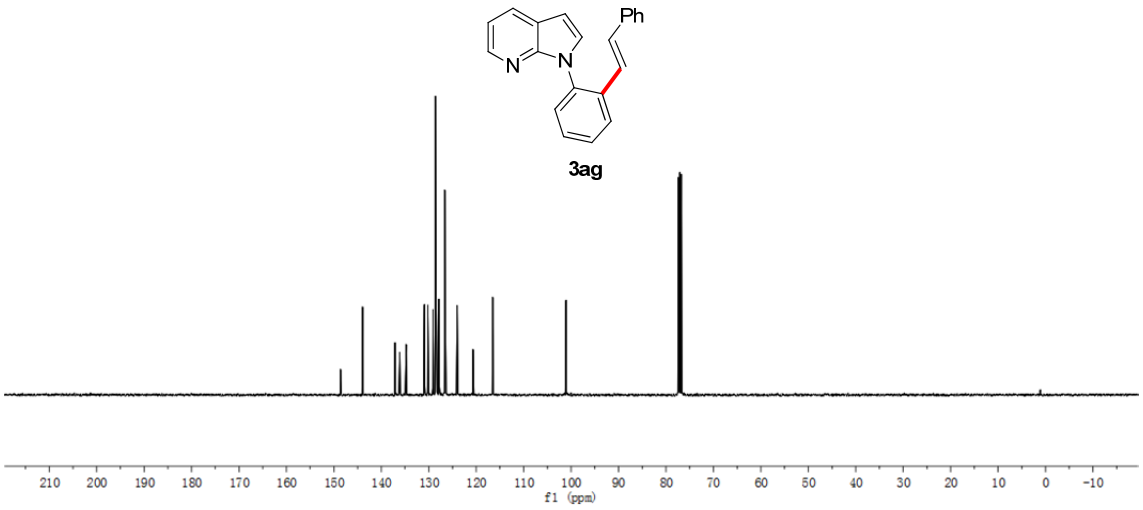

8.320
8.309
7.988
7.965
7.773
7.754
7.657
7.638
7.618
7.516
7.497
7.476
7.346
7.337
7.263
7.146
7.134
7.126
7.115
6.686
6.677
1.973
1.957
1.900
1.717
0.003
N
N
O
6
10
9
8
7
6
5
4
3
2
1
ppm
1.10
1.11
1.12
1.23
2.40
1.21
1.31
1.00
3.63

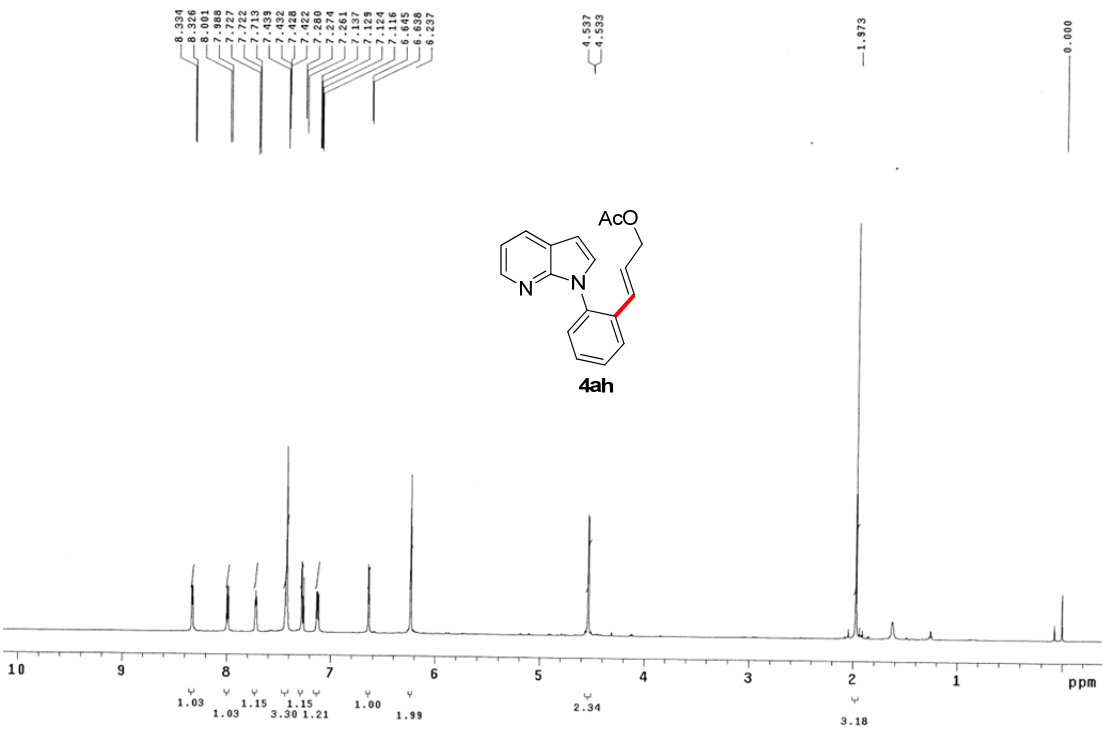

QZY-LISS1504B644
200.646
148.049
143.910
132.232
129.318
129.087
128.813
127.996
120.946
116.933
102.201
77.378
77.060
76.742
28.397

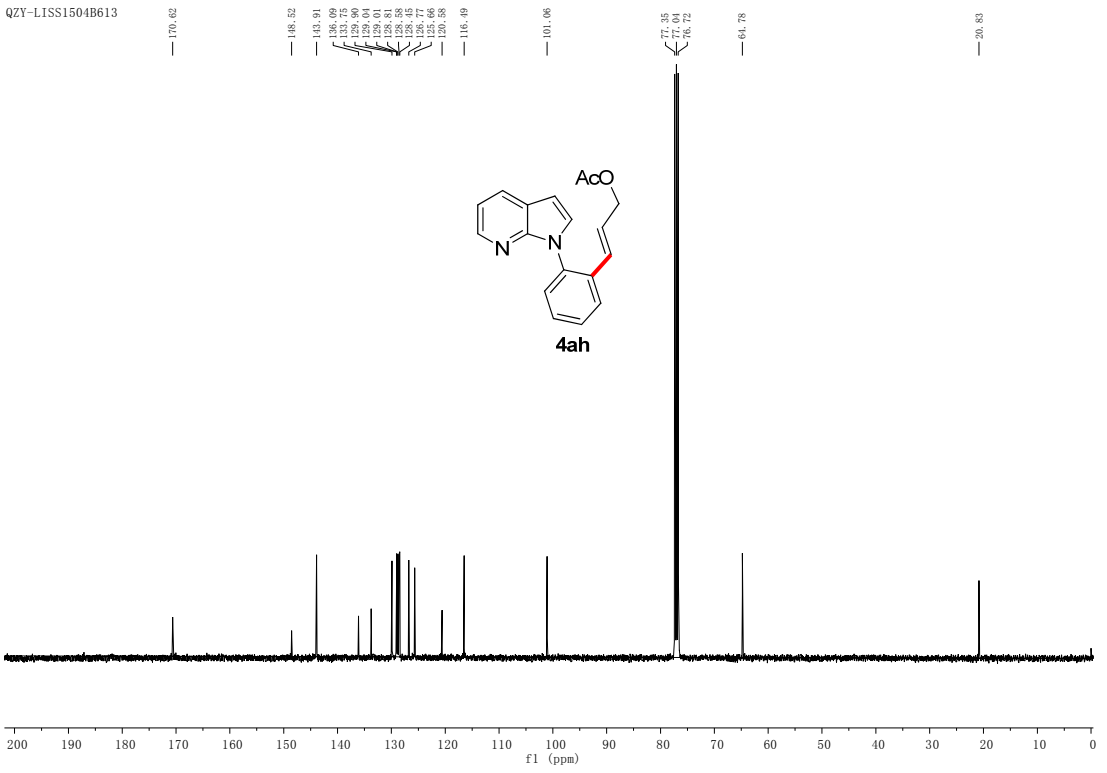

N
N
O
6
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

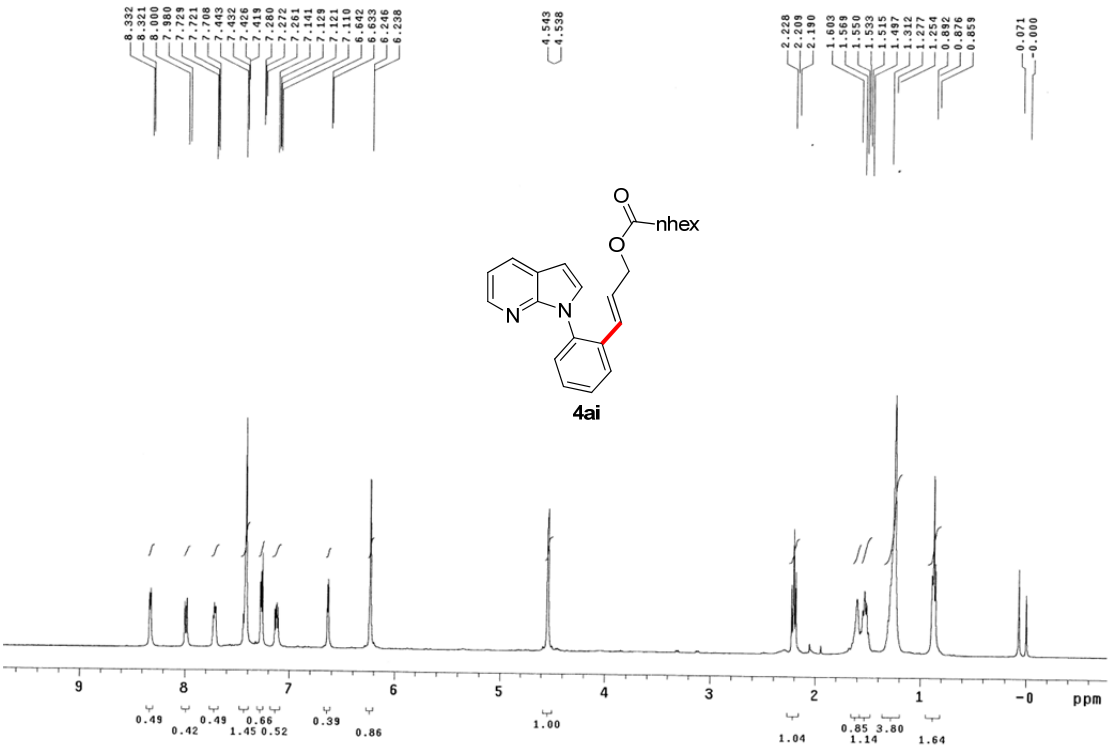

Ph
N
N
3ag
10
9
8
7
6
5
4
3
2
1
0
ppm

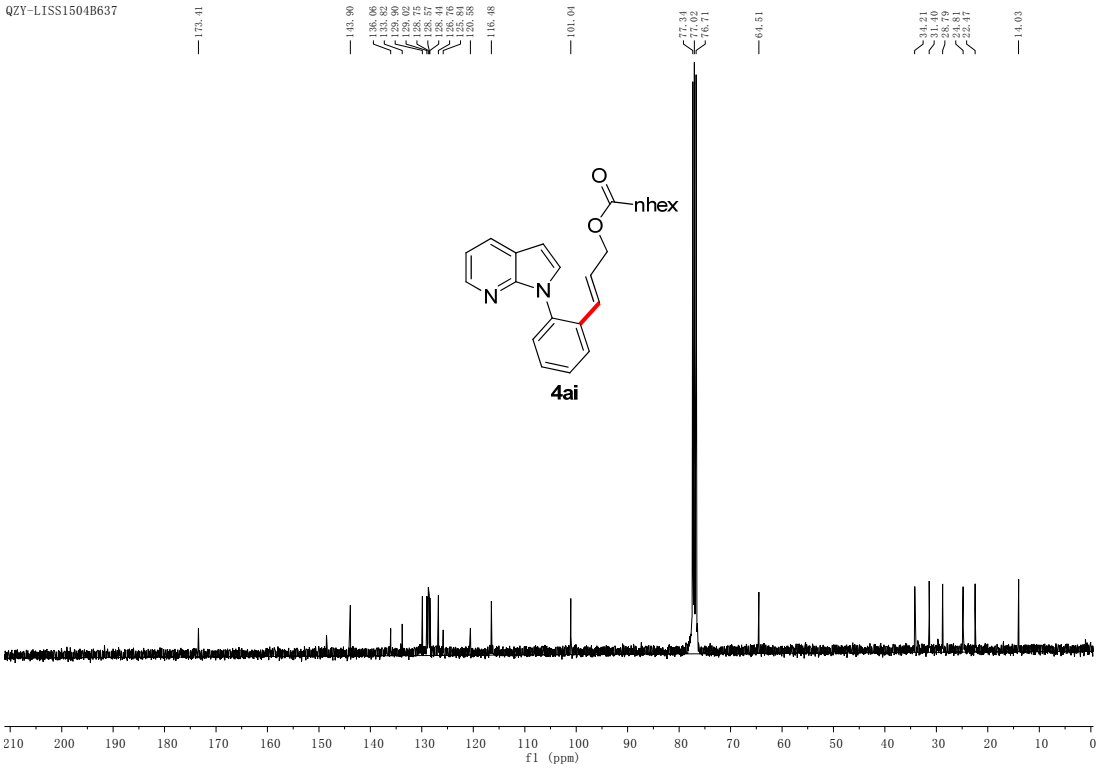

QZY-LISS1501B458

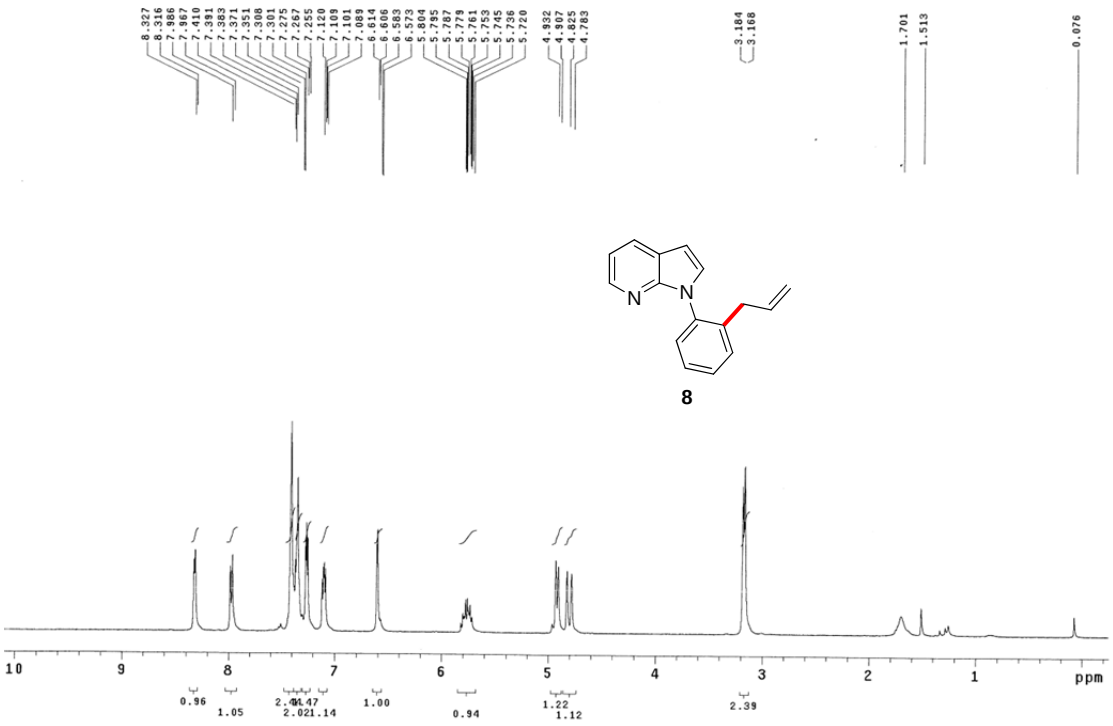

Ph
N
N
3ag
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

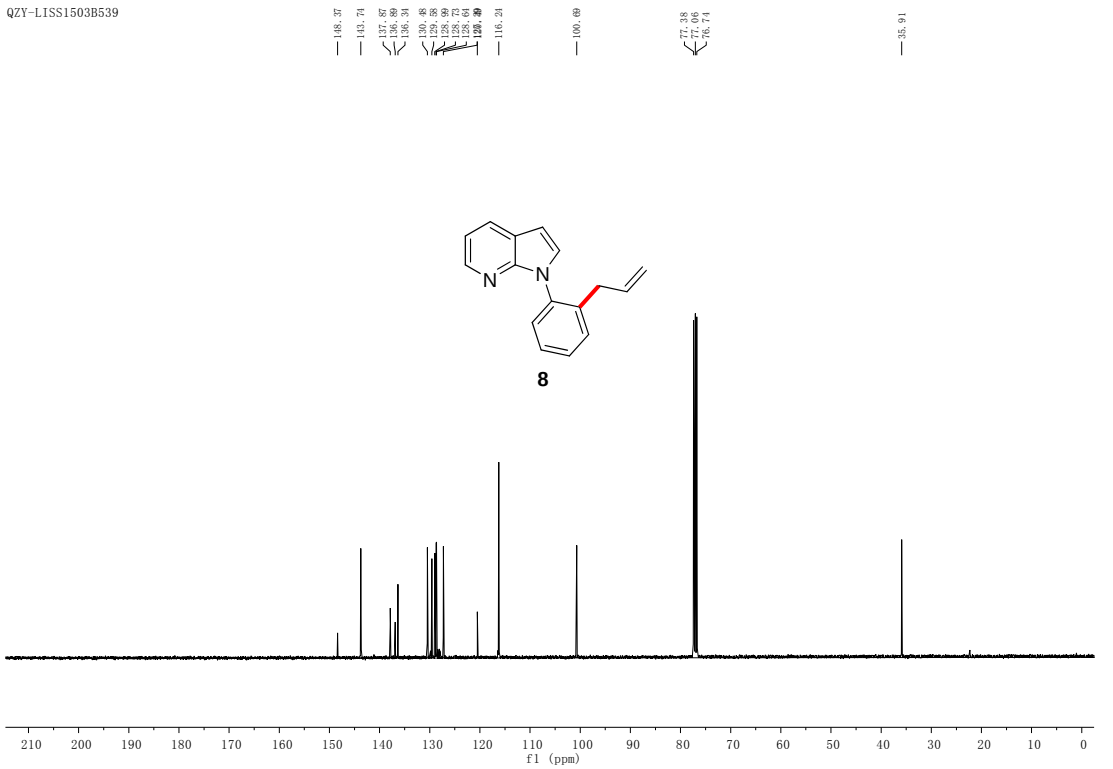

8.334
8.326
8.001
7.988
7.727
7.722
7.713
7.438
7.432
7.428
7.422
7.280
7.274
7.261
7.137
7.129
7.124
7.114
6.645
6.638
6.237
4.537
4.533
1.973
0.000
AcO
N
N
4ah
10
9
8
7
6
5
4
3
2
1
ppm
1.03
1.03
1.15
1.15
3.30
1.21
1.00
1.99
2.34
3.18

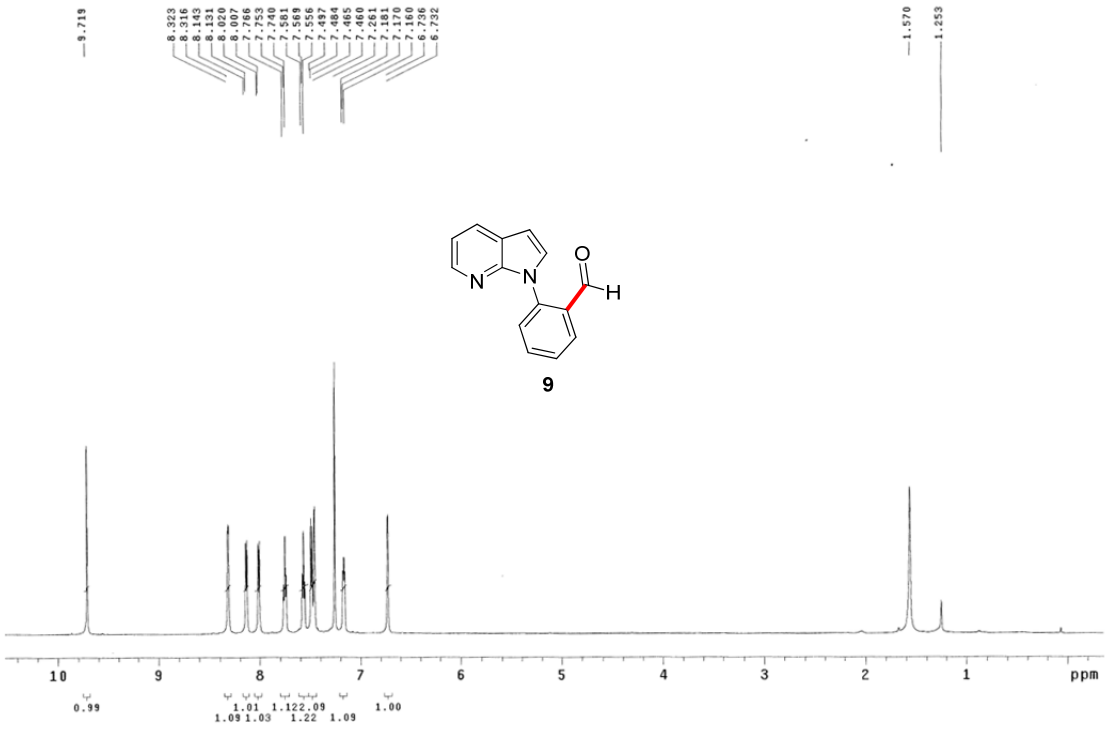

QZY-LISS1504B613
170.62
148.52
143.91
136.09
133.75
129.90
129.04
129.01
128.81
128.58
128.45
126.77
125.66
120.58
116.49
101.06
77.35
77.04
76.72
64.78
20.83
AcO
N
N
4ah
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

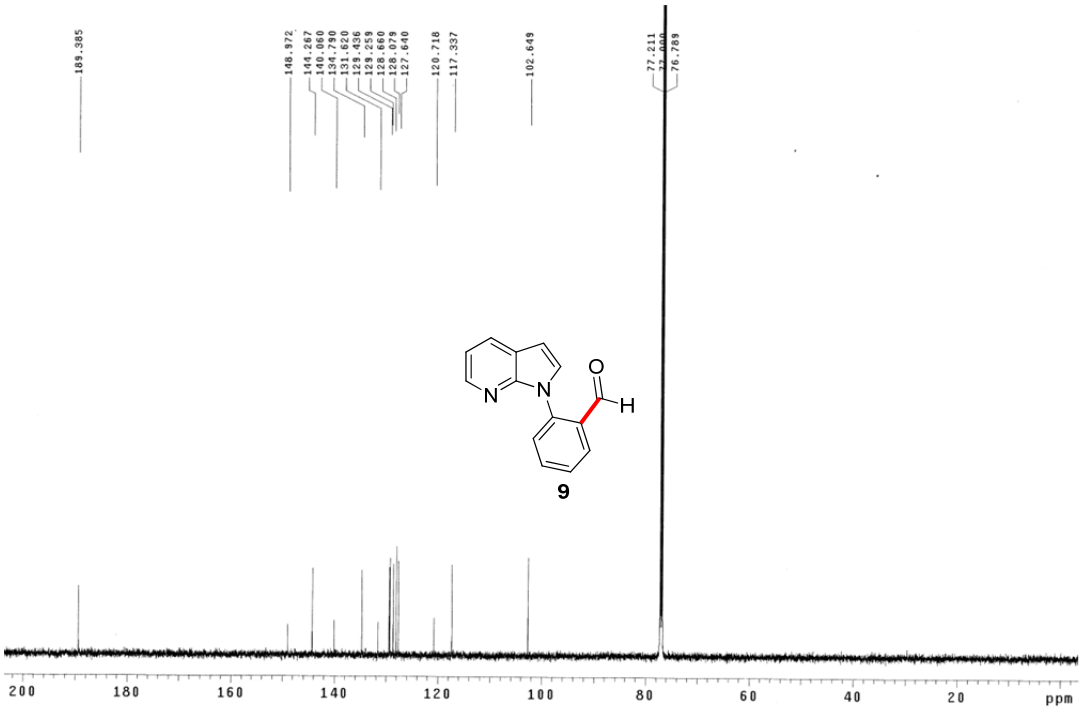

8.332
8.321
8.000
7.980
7.729
7.721
7.708
7.443
7.432
7.426
7.419
7.280
7.272
7.261
7.141
7.129
7.121
7.110
6.642
6.633
6.246
6.238
4.543
4.538
2.228
2.209
2.190
1.603
1.569
1.550
1.533
1.515
1.497
1.312
1.277
1.254
0.892
0.876
0.859
0.071
-0.000
nhex
4ai
9
8
7
6
5
4
3
2
1
-0
ppm
0.49
0.42
0.49
1.45
0.66
0.52
0.39
0.86
1.00
1.04
0.85
1.14
3.80
1.64

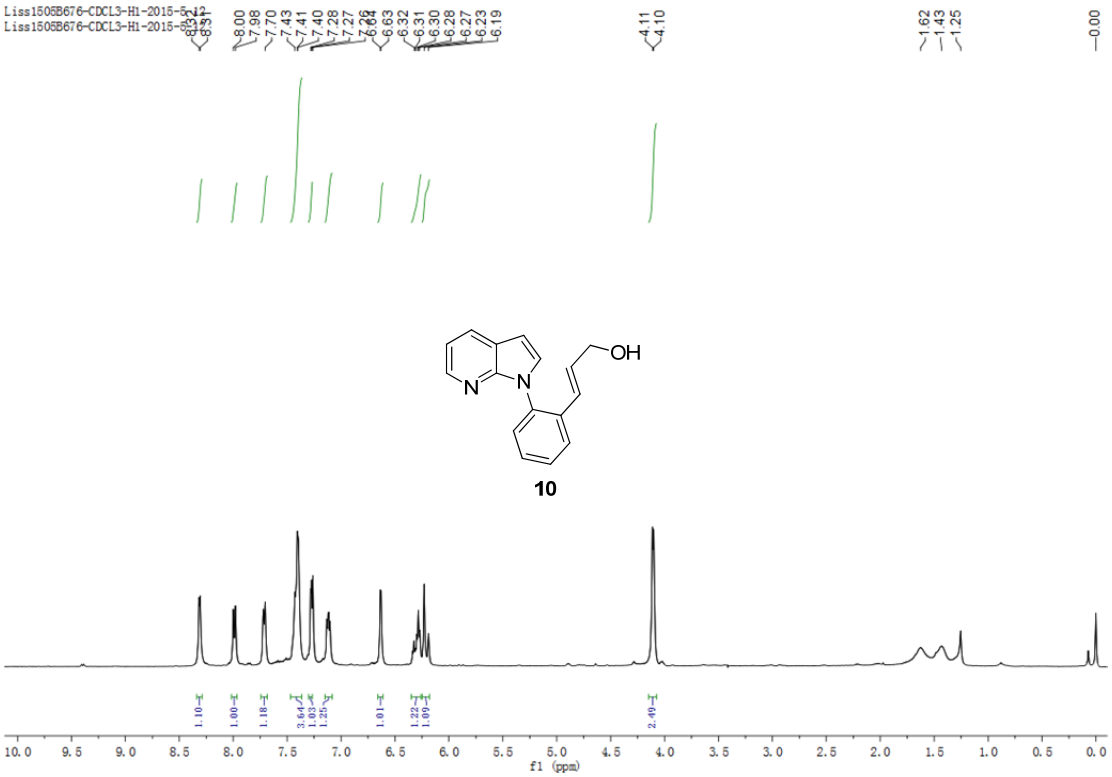

QZY-LISS1504B637
173.41
143.90
136.06
133.82
129.90
129.02
128.75
128.57
128.44
126.76
125.81
120.58
116.48
101.04
77.34
77.02
76.71
64.51
34.21
31.40
28.79
24.81
22.47
14.03
nhex
4ai
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

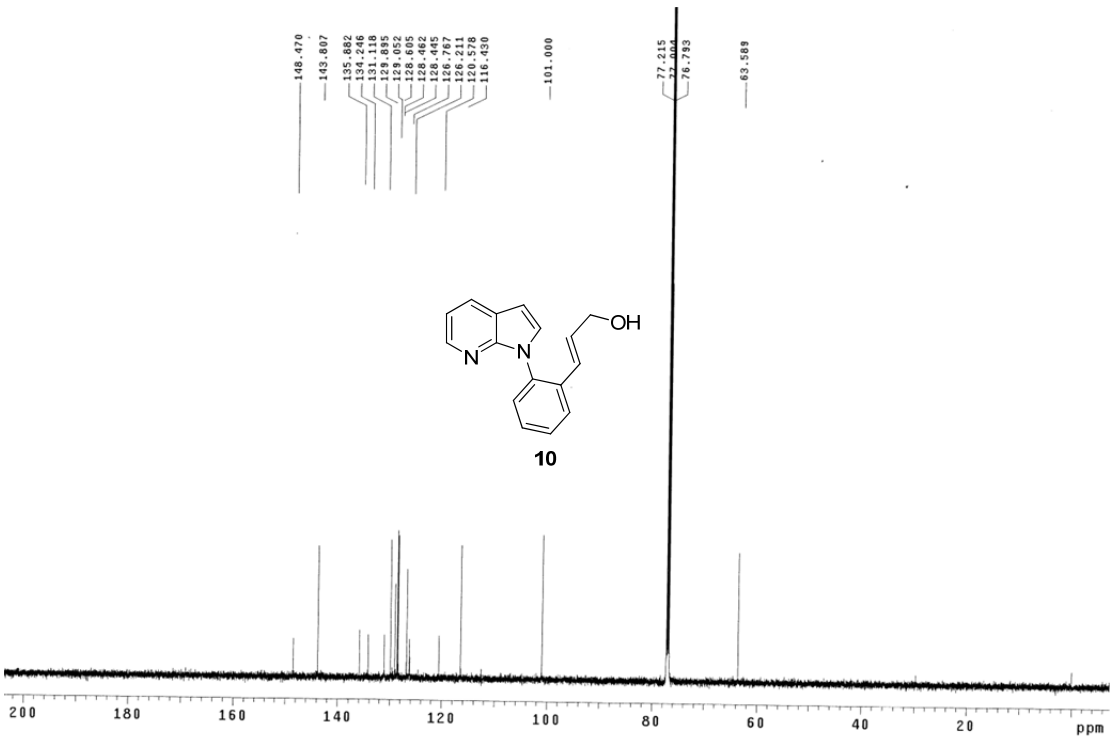

8.327
8.316
7.965
7.957
7.410
7.391
7.383
7.371
7.351
7.308
7.301
7.275
7.262
7.255
7.120
7.109
7.101
7.089
6.614
6.606
6.583
6.573
5.804
5.795
5.787
5.779
5.761
5.753
5.745
5.736
5.720
4.932
4.907
4.825
4.783
3.184
3.168
1.701
1.513
0.076
N
N
8
10
9
8
7
6
5
4
3
2
1
ppm
0.96
1.05
2.41
2.47
2.021.14
1.00
0.94
1.22
1.12
2.39

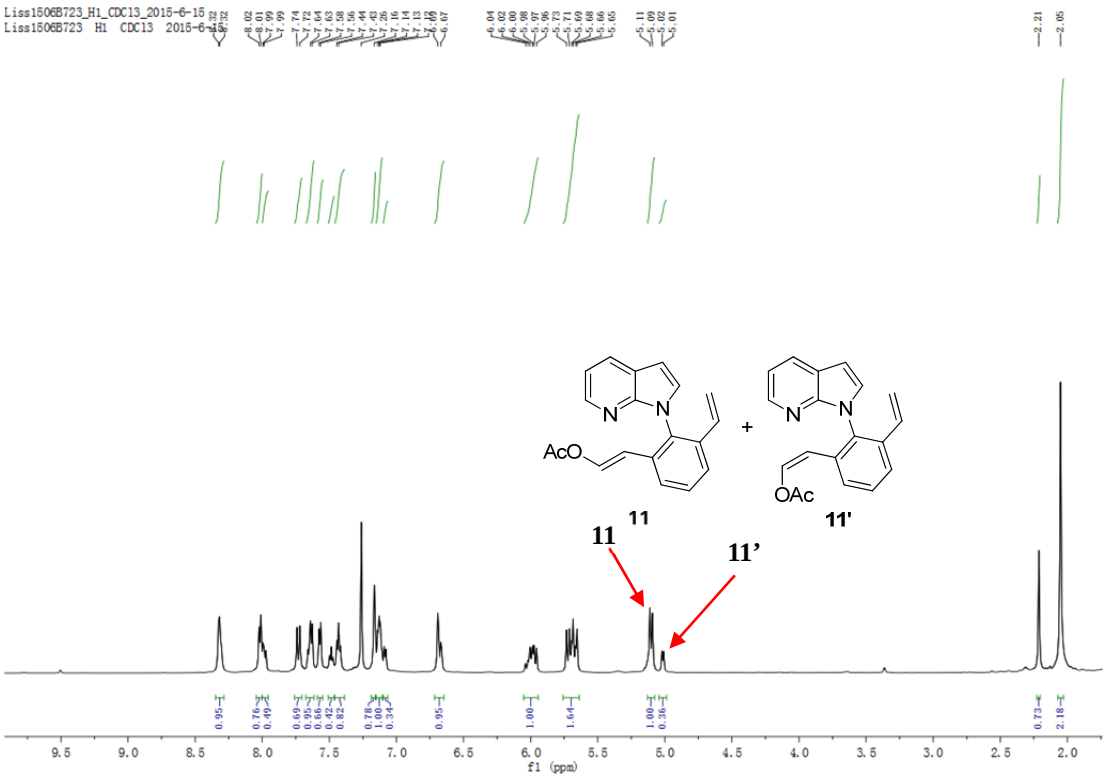

QZY-LISS1503B539
148.37
143.74
137.67
134.99
136.39
130.48
129.88
128.99
128.73
116.24
100.69
77.38
77.06
76.74
35.91
N
N
8
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


9.719
8.323
8.316
8.143
8.131
8.020
8.007
7.766
7.753
7.740
7.581
7.568
7.556
7.497
7.484
7.465
7.460
7.261
7.181
7.170
7.160
6.736
6.732
1.570
1.253
O
N
N
H
9
10
9
8
7
6
5
4
3
2
1
ppm
0.99
1.09
1.01
1.03
1.12
1.22
2.09
1.09
1.00


183.385
146.972
144.267
140.060
134.790
131.620
128.436
128.258
128.060
128.079
127.640
120.718
117.337
102.649
77.211
77.000
76.789
O
N
N
H
9
200
180
160
140
120
100
80
60
40
20
ppm


OH
N
N
10
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)


OH
N
N
10
200 180 160 140 120 100 80 60 40 20
ppm


Liss1506B723_H1_CDC13_2015-6-15
Liss1506B723 H1 CDC13 2015-6-15
AcO
OAc
11
11'
11
11'
f1 (ppm)