

Supporting Information for
One-pot construction of fused polycyclic heteroarenes involving
7-azaindoles and α,β -unsaturated ketones

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Table of Contents

1. General Methods	S2
2. General Procedure for Synthesis of Alkylated Products and Aza-Fused 7-Azaindole Derivatives and Characterization Data	S2-S9
3. Mechanism Study	S9-S13
4. NMR Spectra of Alkylated Products and Aza-Fused 7-Azaindole Derivatives and Structure Determination	S14-S48

1. General Methods

NMR data were obtained for ^1H at 400 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 alkynes were commercially available. *N*-substituted 7-azaindoles were prepared according to the literature procedures.^[1]

2. General Procedure for Synthesis of Alkylated Products and Aza-Fused 7-Azaindole Derivatives and Characterization Data

a. General Procedure for Synthesis of Alkylated Products

1-phenyl-1*H*-pyrrolo[2,3-*b*]pyridine **1a** (19.4 mg, 0.10 mmol), ethyl vinyl ketone **2a** (16.8 mg, 0.20 mmol), $[\text{Cp}^*\text{Rh}(\text{CH}_3\text{CN})_3(\text{SbF}_6)_2]$ (1.7 mg, 2 mol %) and HOAc (3 μL , 0.5 equiv.) were stirred in toluene (1.0 mL) at 60 °C for 13 h. After completion, the reaction mixture was purified by flash chromatography eluting with ethyl acetate and petroleum ether (1:20) to give the product **4a** as light yellow oil (25.8 mg, 93%).

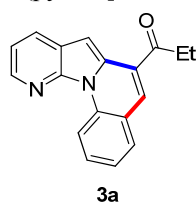
b. General Procedure for Synthesis of Aza-Fused 7-Azaindole Derivatives

1-phenyl-1*H*-pyrrolo[2,3-*b*]pyridine **1a** (19.4 mg, 0.10 mmol), ethyl vinyl ketone **2a** (16.8 mg, 0.20 mmol), $[\text{Cp}^*\text{Rh}(\text{CH}_3\text{CN})_3(\text{SbF}_6)_2]$ (1.7 mg, 2 mol %) and $\text{Cu}(\text{OAc})_2$ (54.6 mg, 3 equiv.) were stirred in toluene (1.0 mL) at 130 °C for 21 h. After completion, the reaction mixture was purified by flash chromatography eluting with ethyl acetate and petroleum ether (1:40) to give the product **3a** as orange solid (14.2 mg, 52%).

1-(pyrido[3',2':4,5]pyrrolo[1,2-*a*]quinolin-6-yl)propan-1-one **3a** (27.4 mg, 0.1 mmol), benzaldehyde (21.2 mg, 0.2 mmol) and NaOH (50 μL , 6 mol/L) were stirred in MeOH (1 mL) at 50 °C for 36 h. After completion, the reaction mixture was purified by flash chromatography eluting with ethyl acetate and petroleum ether (1:40) to give the product **5** as yellow solid (32.6 mg, 90%).

(*E*)-2-methyl-3-phenyl-1-(pyrido[3',2':4,5]pyrrolo[1,2-*a*]quinolin-6-yl)prop-2-en-1-one **5** (32.6 mg, 0.09 mmol) and AlCl_3 (48 mg, 0.4 equiv.) were stirred in DCM (1 mL) at room temperature for 48 h. After completion, the reaction mixture was purified by flash chromatography eluting with ethyl acetate and petroleum ether (1:50) to give the product **6** as yellow solid (20.2 mg, 62%) and product **7** as yellow solid (9.8 mg, 30%)

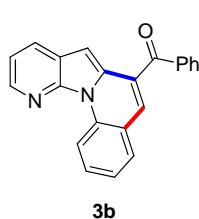
1-(pyrido[3',2':4,5]pyrrolo[1,2-*a*]quinolin-6-yl)propan-1-one (**3a**). Orange solid, 21 h, 52% yield;



^1H NMR (400 MHz, CDCl_3): δ 10.12 (d, $J = 8.4$ Hz, 1H), 8.55 (d, $J = 4.0$ Hz, 1H), 8.13 (d, $J = 7.6$ Hz, 1H), 7.82 (s, 1H), 7.72-7.69 (m, 1H), 7.63-7.61 (m, 2H), 7.33-7.28 (m, 2H), 3.07 (q, $J = 7.2$ Hz, 2H), 1.28 (t, $J = 7.2$ Hz, 3H) ppm;
 ^{13}C NMR (100 MHz, CDCl_3): δ 199.3, 145.7, 142.2, 137.2, 132.0, 131.7, 130.9, 129.8, 129.0, 126.7, 123.5, 122.6, 121.5, 118.3, 118.0, 97.2, 32.1, 8.5

ppm. ESI HRMS: calcd. for C₁₈H₁₄N₂O+Na 297.1004, found 297.1009.

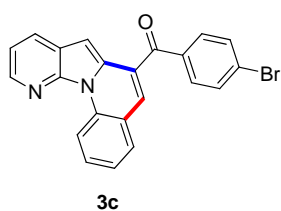
phenyl(pyrido[3',2':4,5]pyrrolo[1,2-a]quinolin-6-yl)methanone (**3b**). Orange solid, 17 h, 50% yield;



¹H NMR (400 MHz, CDCl₃): δ 10.2 (d, *J* = 8.8 Hz, 1H), 8.60-8.59 (m, 1H), 8.16-8.14 (m, 1H), 7.92 (d, *J* = 7.2 Hz, 2H), 7.78-7.74 (m, 1H), 7.65-7.62 (m, 2H), 7.54-7.51 (m, 3H), 7.37-7.33 (m, 2H), 7.24 (d, *J* = 3.6 Hz, 1H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ 194.5, 145.9, 142.4, 137.9, 137.0, 132.8, 132.8, 132.0, 131.8, 129.9, 129.8, 129.0, 128.5, 127.7, 123.7, 122.3, 121.7, 118.4, 118.1, 96.3 ppm. ESI HRMS: calcd. for C₂₂H₁₄N₂O+Na 345.1004, found

345.0995.

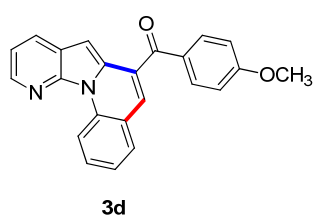
(4-bromophenyl)(pyrido[3',2':4,5]pyrrolo[1,2-a]quinolin-6-yl)methanone (**3c**). Orange solid, 23 h,



56% yield; ¹H NMR (400 MHz, CDCl₃): δ 10.22 (d, *J* = 8.4 Hz, 1H), 8.61 (d, *J* = 3.6 Hz, 1H), 8.16 (d, *J* = 8.0 Hz, 1H), 7.80-7.77 (m, 3H), 7.68-7.65 (m, 3H), 7.51 (s, 1H), 7.39-7.35 (m, 2H), 7.25-7.21 (m, 1H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ 193.4, 145.9, 142.5, 137.0, 136.6, 132.5, 132.0, 132.0, 131.9, 131.3, 129.9, 129.0, 128.0, 127.4, 123.8, 122.3, 121.6, 118.4, 118.2, 96.3 ppm. ESI HRMS: calcd. for

C₂₂H₁₃BrN₂O+Na 423.0109, found 423.0108, 425.0101.

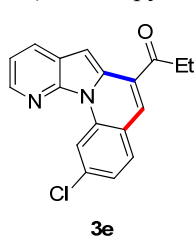
(4-methoxyphenyl)(pyrido[3',2':4,5]pyrrolo[1,2-a]quinolin-6-yl)methanone (**3d**). Orange solid, 70



h, 44% yield; ¹H NMR (400 MHz, CDCl₃): δ 10.21 (d, *J* = 8.8 Hz, 1H), 8.60 (d, *J* = 3.6 Hz, 1H), 8.13 (d, *J* = 7.6 Hz, 1H), 7.96 (d, *J* = 8.8 Hz, 2H), 7.76 (t, *J* = 8.0 Hz, 1H), 7.67 (d, *J* = 7.6 Hz, 1H), 7.48 (s, 1H), 7.39-7.33 (m, 2H), 7.07 (s, 1H), 7.00 (d, *J* = 8.8 Hz, 2H), 3.91 (s, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ 193.1, 163.7, 146.0, 142.3, 136.8, 133.1, 132.4, 131.4, 130.2, 130.0, 129.5, 128.9,

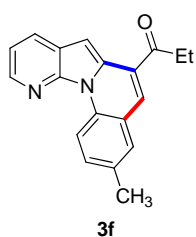
128.6, 123.7, 122.2, 121.9, 118.4, 118.1, 113.8, 95.9, 55.5 ppm. ESI HRMS: calcd. for C₂₃H₁₆N₂O₂+H 353.1290, found 353.1308.

1-(2-chloropyrido[3',2':4,5]pyrrolo[1,2-a]quinolin-6-yl)propan-1-one (**3e**). Orange solid, 35 h, 60%



yield; ¹H NMR (400 MHz, CDCl₃): δ 10.17 (s, 1H), 8.55-8.54 (m, 1H), 8.11 (d, *J* = 8.0 Hz, 1H), 7.71 (s, 1H), 7.57 (s, 1H), 7.49 (d, *J* = 8.4 Hz, 1H), 7.34-7.31 (m, 1H), 7.23 (d, *J* = 8.4 Hz, 1H), 3.04 (q, *J* = 7.2 Hz, 2H), 1.28 (t, *J* = 7.2 Hz, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ 199.0, 145.5, 142.5, 137.8, 137.4, 131.3, 130.4, 129.7, 129.1, 126.7, 123.9, 122.6, 119.9, 118.3, 118.3, 97.8, 32.1, 8.4 ppm. ESI HRMS: calcd. for C₁₈H₁₃ClN₂O+H 309.0795, found 309.0787,

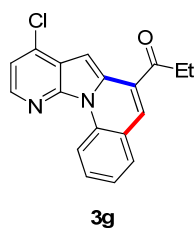
311.0755.



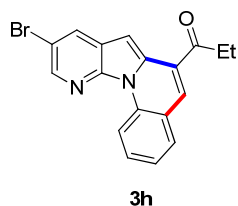
1-(3-methylpyrido[3',2':4,5]pyrrolo[1,2-a]quinolin-6-yl)propan-1-one (**3f**). Light orange solid, 22 h, 66% yield; ¹H NMR (400 MHz, CDCl₃): δ 9.99 (d, *J* = 8.4 Hz, 1H), 8.56-8.55 (m, 1H), 8.15 (d, *J* = 8.0 Hz, 1H), 7.82-7.80 (m, 1H), 7.62 (s, 1H), 7.54-7.51 (m, 1H), 7.43 (s, 1H), 7.33-7.30 (m, 1H), 3.10-3.05 (m, 2H), 2.45 (s, 3H), 1.29 (t, *J* = 7.2 Hz, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃):

δ 199.4, 145.5, 142.1, 135.2, 133.1, 133.0, 131.7, 131.0, 129.7, 128.9, 126.7, 122.5, 121.5, 118.1, 117.8, 96.9, 32.2, 20.8, 8.5 ppm. ESI HRMS: calcd. for $C_{19}H_{16}N_2O+H$ 289.1341, found 289.1331.

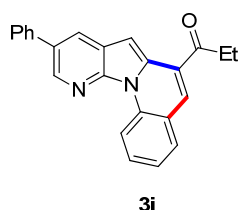
1-(8-chloropyrido[3',2':4,5]pyrrolo[1,2-a]quinolin-6-yl)propan-1-one (**3g**). Light orange solid, 35 h, 70% yield; 1H NMR (400 MHz, $CDCl_3$): δ 10.01 (d, $J = 5.6$ Hz, 1H), 8.39 (d, $J = 3.2$ Hz, 1H), 7.84 (s, 1H), 7.71-7.67 (m, 2H), 7.64 (d, $J = 4.8$ Hz, 1H), 7.35-7.32 (m, 2H), 3.08 (q, $J = 4.8$ Hz, 2H), 1.30 (t, $J = 4.8$ Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.9, 145.8, 142.1, 136.8, 136.0, 132.1, 132.0, 131.4, 129.9, 126.5, 124.0, 121.9, 121.6, 118.3, 117.9, 95.6, 32.1, 8.4 ppm. ESI HRMS: calcd. for $C_{18}H_{13}ClN_2O+H$ 309.0795, found 309.0783, 311.0749.



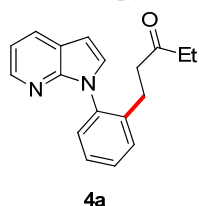
1-(9-bromopyrido[3',2':4,5]pyrrolo[1,2-a]quinolin-6-yl)propan-1-one (**3h**). Light orange solid, 35 h, 46% yield; 1H NMR (400 MHz, $CDCl_3$): δ 9.99 (d, $J = 5.2$ Hz, 1H), 8.53 (s, 1H), 8.22 (s, 1H), 7.91 (s, 1H), 7.75-7.69 (m, 2H), 7.56 (s, 1H), 7.39-7.36 (m, 1H), 3.11 (q, $J = 4.8$ Hz, 2H), 1.30 (t, $J = 4.8$ Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.1, 143.8, 142.6, 136.8, 132.9, 132.3, 131.6, 130.7, 130.0, 126.5, 124.1, 123.9, 121.5, 118.2, 114.1, 96.6, 32.1, 8.4 ppm. ESI HRMS: calcd. for $C_{18}H_{13}BrN_2O+H$ 353.0290, found 353.0280, 355.0259.



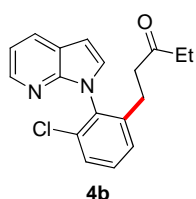
1-(9-phenylpyrido[3',2':4,5]pyrrolo[1,2-a]quinolin-6-yl)propan-1-one (**3i**). Orange solid, 21 h, 43% yield; 1H NMR (400 MHz, $CDCl_3$): δ 10.1 (s, 1H), 8.77 (s, 1H), 8.27 (s, 1H), 7.83 (s, 1H), 7.73-7.69 (m, 3H), 7.64 (s, 2H), 7.50 (t, $J = 4.8$ Hz, 2H), 7.40 (t, $J = 4.8$ Hz, 1H), 7.32 (t, $J = 4.8$ Hz, 1H), 3.08 (q, $J = 4.8$ Hz, 2H), 1.29 (t, $J = 4.8$ Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.2, 145.1, 141.6, 139.2, 137.1, 132.3, 132.1, 131.4, 131.0, 129.9, 129.0, 127.5, 127.3, 126.9, 126.7, 123.6, 122.5, 121.5, 118.2, 97.5, 32.1, 8.5 ppm. ESI HRMS: calcd. for $C_{24}H_{18}N_2O+H$ 351.1497, found 351.1484.



1-(2-(1*H*-pyrrolo[2,3-*b*]pyridin-1-yl)phenyl)pentan-3-one (**4a**). Light yellow oil, 13 h, 93% yield; 1H NMR (400 MHz, $CDCl_3$): δ 8.18 (d, $J = 4.4$ Hz, 1H), 7.83 (d, $J = 7.6$ Hz, 1H), 7.25 (d, $J = 3.6$ Hz, 2H), 7.22-7.14 (m, 3H), 6.97-6.93 (m, 1H), 6.50-6.49 (m, 1H), 2.58 (t, $J = 7.6$ Hz, 2H), 2.33 (t, $J = 7.6$ Hz, 2H), 2.01 (q, $J = 7.2$ Hz, 2H), 0.74 (t, $J = 7.6$ Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 210.1, 148.5, 143.7, 139.2, 136.9, 130.2, 129.4, 129.1, 128.9, 127.3, 120.4, 116.3, 101.1, 42.4, 35.6, 25.7, 7.6 ppm. ESI HRMS: calcd. for $C_{18}H_{18}N_2O+Na$ 301.1317, found 301.1325.

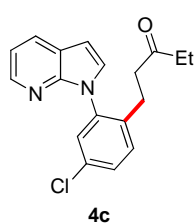


1-(3-chloro-2-(1*H*-pyrrolo[2,3-*b*]pyridin-1-yl)phenyl)pentan-3-one (**4b**). Light yellow oil, 39 h, 73% yield; 1H NMR (400 MHz, $CDCl_3$): δ 8.31 (d, $J = 4.0$ Hz, 1H), 7.99 (d, $J = 6.8$ Hz, 1H), 7.42 (d, $J = 7.6$ Hz, 1H), 7.37-7.30 (m, 2H), 7.20 (d, $J = 3.6$ Hz, 1H), 7.13-7.10 (m, 1H), 6.69 (d, $J = 3.6$ Hz, 1H), 2.71-2.64 (m, 1H), 2.61-2.54 (m, 1H), 2.47 (t, $J = 7.6$ Hz, 2H), 2.21-2.10 (m, 2H), 0.88 (t, $J = 7.6$ Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 209.9, 148.2, 143.8, 142.6, 134.5, 134.4, 129.9,



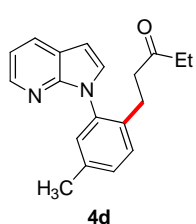
129.2, 128.9, 128.5, 128.2, 120.3, 116.5, 101.7, 42.4, 35.7, 26.0, 7.6 ppm. ESI HRMS: calcd. for $C_{18}H_{17}ClN_2O+H$ 313.1108, found 313.1095, 315.1076.

1-(4-chloro-2-(1*H*-pyrrolo[2,3-*b*]pyridin-1-yl)phenyl)pentan-3-one (**4c**). Light yellow oil, 12 h, 96%



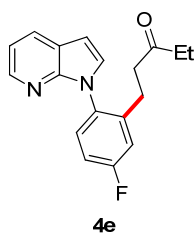
$C_{18}H_{17}ClN_2O+Na$ 335.0927, found 335.0920, 337.0916.

1-(4-methyl-2-(1*H*-pyrrolo[2,3-*b*]pyridin-1-yl)phenyl)pentan-3-one (**4d**). Yellow oil, 17 h, 87%



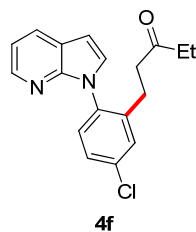
ESI HRMS: calcd. for $C_{19}H_{20}N_2O+Na$ 315.1473, found 315.1474.

1-(5-fluoro-2-(1*H*-pyrrolo[2,3-*b*]pyridin-1-yl)phenyl)pentan-3-one (**4e**). Yellow oil, 11 h, 95%

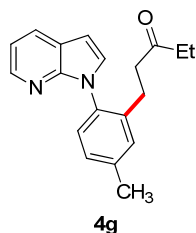


114.1 (d, $J = 22.4$ Hz), 101.3, 41.9, 35.7, 25.5, 7.6 ppm. ESI HRMS: calcd. for $C_{18}H_{17}FN_2O+Na$ 319.1223, found 319.1219.

1-(5-chloro-2-(1*H*-pyrrolo[2,3-*b*]pyridin-1-yl)phenyl)pentan-3-one (**4f**). Light yellow oil, 11 h, 78%



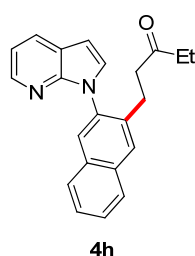
ESI HRMS: calcd. for $C_{18}H_{17}ClN_2O+Na$ 335.0927, found 335.0930, 337.0916.



1-(5-methyl-2-(1*H*-pyrrolo[2,3-*b*]pyridin-1-yl)phenyl)pentan-3-one (**4g**). Light yellow oil, 15 h, 84% yield; 1H NMR (400 MHz, $CDCl_3$): δ 8.23 (d, $J = 3.6$ Hz, 1H), 7.89 (d, $J = 7.2$ Hz, 1H), 7.19 (d, $J = 3.2$ Hz, 1H), 7.13-1.07 (m, 3H), 7.03-7.00 (m, 1H), 6.55 (d, $J = 2.8$ Hz, 1H), 2.58 (t, $J = 7.2$ Hz, 2H), 2.38 (t, $J =$

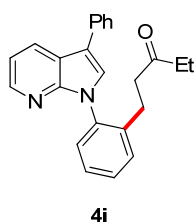
8.0 Hz, 2H), 2.33 (s, 3H), 2.07 (q, $J = 7.2$ Hz, 2H), 0.81 (t, $J = 7.6$ Hz, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ 210.3, 148.5, 143.6, 138.8, 138.7, 134.1, 130.7, 129.4, 128.9, 128.6, 127.9, 120.3, 116.1, 100.8, 42.5, 35.6, 25.6, 21.1, 7.63 ppm. ESI HRMS: calcd. for $\text{C}_{19}\text{H}_{20}\text{N}_2\text{O}+\text{H}$ 293.1654, found 293.1649.

1-(3-(1*H*-pyrrolo[2,3-*b*]pyridin-1-yl)naphthalen-2-yl)pentan-3-one (**4h**). Brown solid, 33 h, 71% yield;



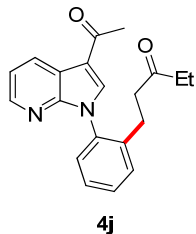
^1H NMR (400 MHz, CDCl_3): δ 8.30 (d, $J = 4.4$ Hz, 1H), 7.99 (d, $J = 7.6$ Hz, 1H), 7.84-7.77 (m, 4H), 7.51-7.43 (m, 2H), 7.35 (d, $J = 3.6$ Hz, 1H), 7.12-7.09 (m, 1H), 6.66 (d, $J = 3.2$ Hz, 1H), 2.84 (t, $J = 7.6$ Hz, 2H), 2.49 (t, $J = 7.6$ Hz, 2H), 2.14 (q, $J = 7.2$ Hz, 2H), 0.87 (t, $J = 7.2$ Hz, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ 210.3, 148.8, 143.8, 136.9, 135.4, 133.4, 132.3, 129.7, 129.0, 128.8, 127.8, 127.7, 127.3, 126.8, 126.1, 120.5, 116.4, 101.2, 42.4, 35.7, 26.0, 7.7 ppm. ESI HRMS: calcd. for $\text{C}_{22}\text{H}_{20}\text{N}_2\text{O}+\text{Na}$ 351.1473, found 351.1468.

1-(2-(3-phenyl-1*H*-pyrrolo[2,3-*b*]pyridin-1-yl)phenyl)pentan-3-one (**4i**). Light yellow oil, 20 h, 77% yield;



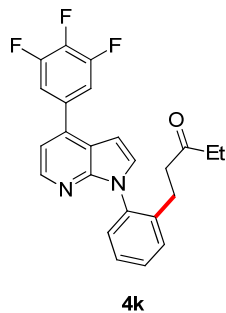
^1H NMR (400 MHz, CDCl_3): δ 8.38 (d, $J = 3.6$ Hz, 1H), 8.32 (d, $J = 7.6$ Hz, 1H), 7.71 (d, $J = 7.6$ Hz, 2H), 7.52-7.48 (m, 3H), 7.43-7.41 (m, 2H), 7.39-7.33 (m, 3H), 7.22-7.19 (m, 1H), 2.79 (t, $J = 7.2$ Hz, 2H), 2.55 (t, $J = 8.0$ Hz, 2H), 2.20 (q, $J = 7.2$ Hz, 2H), 0.91 (t, $J = 7.2$ Hz, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ 210.3, 149.0, 144.1, 139.2, 136.6, 134.5, 130.2, 129.0, 129.0, 128.9, 128.5, 127.4, 127.1, 126.5, 126.4, 118.6, 116.7, 116.6, 42.5, 35.7, 25.7, 7.7 ppm. ESI HRMS: calcd. for $\text{C}_{24}\text{H}_{22}\text{N}_2\text{O}+\text{Na}$ 377.1630, found 377.1636.

1-(2-(3-acetyl-1*H*-pyrrolo[2,3-*b*]pyridin-1-yl)phenyl)pentan-3-one (**4j**). Light pink solid, 17 h, 93% yield;



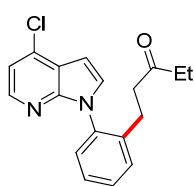
^1H NMR (400 MHz, CDCl_3): δ 8.71 (d, $J = 7.6$ Hz, 1H), 8.36 (d, $J = 4.4$ Hz, 1H), 7.99 (s, 1H), 7.48-7.43 (m, 2H), 7.41-7.36 (m, 1H), 7.32-7.25 (m, 2H), 2.68 (t, $J = 6.8$ Hz, 2H), 2.58-2.54 (m, 5H), 2.20 (q, $J = 7.2$ Hz, 2H), 0.90 (t, $J = 7.2$ Hz, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ 209.8, 193.1, 149.1, 145.2, 139.0, 135.6, 135.6, 131.3, 130.1, 129.7, 128.6, 127.4, 118.9, 118.3, 116.5, 42.2, 35.7, 27.2, 25.1, 7.6 ppm. ESI HRMS: calcd. for $\text{C}_{20}\text{H}_{20}\text{N}_2\text{O}_2+\text{Na}$ 343.1422, found 343.1420.

1-(2-(4-(3,4,5-trifluorophenyl)-1*H*-pyrrolo[2,3-*b*]pyridin-1-yl)phenyl)pentan-3-one (**4k**). Yellow oil, 20 h, 78% yield;



^1H NMR (400 MHz, CDCl_3): δ 8.36 (d, $J = 4.8$ Hz, 1H), 7.41-7.34 (m, 6H), 7.30 (d, $J = 7.6$ Hz, 1H), 7.11 (d, $J = 4.8$ Hz, 1H), 6.77 (d, $J = 3.6$ Hz, 1H), 2.71 (t, $J = 7.2$ Hz, 2H), 2.55 (t, $J = 7.6$ Hz, 2H), 2.21 (q, $J = 7.2$ Hz, 2H), 0.91 (t, $J = 7.2$ Hz, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ 210.2, 152.7 (dd, $J_1 = 4.1$ Hz, $J_2 = 10.1$ Hz), 150.2 (dd, $J_1 = 4.0$ Hz, $J_2 = 9.9$ Hz), 149.1, 144.1, 141.1 (t, $J = 15.2$ Hz), 139.1, 139.0, 138.6 (t, $J = 17.1$ Hz), 136.6, 134.9-134.7 (m), 130.5, 130.1, 129.2, 128.8, 127.3, 118.0, 115.2, 112.6 (dd, $J_1 = 6.1$ Hz, $J_2 = 15.9$ Hz), 99.7, 42.5, 35.8, 25.4, 7.6 ppm. ESI HRMS: calcd. for $\text{C}_{24}\text{H}_{19}\text{F}_3\text{N}_2\text{O}+\text{Na}$ 431.1347, found 431.1346.

1-(2-(4-chloro-1*H*-pyrrolo[2,3-*b*]pyridin-1-yl)phenyl)pentan-3-one (**4i**). Light yellow oil, 32 h, 81%

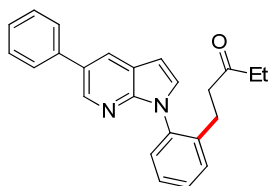


4i

yield; ¹H NMR (400 MHz, CDCl₃): δ 8.16 (d, *J* = 5.2 Hz, 1H), 7.41-7.35 (m, 2H), 7.33-7.30 (m, 2H), 7.25 (d, *J* = 7.6 Hz, 1H), 7.11 (d, *J* = 5.2 Hz, 1H), 6.72 (d, *J* = 3.6 Hz, 1H), 2.66 (t, *J* = 7.2 Hz, 2H), 2.46 (t, *J* = 7.6 Hz, 2H), 2.17 (q, *J* = 7.2 Hz, 2H), 0.88 (t, *J* = 7.2 Hz, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ 210.1, 149.0, 144.0, 139.1, 136.4, 136.3, 130.2, 130.0, 129.2, 128.7,

127.3, 119.8, 116.5, 99.6, 42.3, 35.8, 25.5, 7.6 ppm. ESI HRMS: calcd. for C₁₈H₁₇ClN₂O+Na 335.0927, found 335.0928, 337.0923.

1-(2-(5-phenyl-1*H*-pyrrolo[2,3-*b*]pyridin-1-yl)phenyl)pentan-3-one (**4m**). Light yellow oil, 11 h,

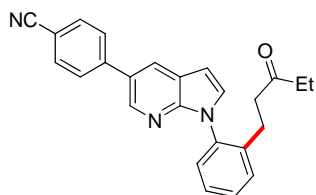


4m

94% yield; ¹H NMR (400 MHz, CDCl₃): δ 8.45 (d, *J* = 2.0 Hz, 1H), 8.05 (d, *J* = 2.0 Hz, 1H), 7.52 (d, *J* = 7.2 Hz, 2H), 7.38-7.34 (m, 2H), 7.31-7.30 (m, 2H), 7.28-7.21 (m, 4H), 6.58 (d, *J* = 3.2 Hz, 1H), 2.65 (t, *J* = 8.0 Hz, 2H), 2.41 (t, *J* = 8.0 Hz, 2H), 2.07 (q, *J* = 7.2 Hz, 2H), 0.79 (t, *J* = 7.2 Hz, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ 210.3, 148.1,

143.1, 139.5, 139.2, 136.8, 130.2, 130.1, 129.0, 128.9, 128.9, 127.5, 127.4, 127.4, 127.1, 120.5, 101.4, 42.5, 35.8, 25.7, 7.7 ppm. ESI HRMS: calcd. for C₂₄H₂₂N₂O+H 355.1810, found 355.1794.

4-(1-(2-(3-oxopentyl)phenyl)-1*H*-pyrrolo[2,3-*b*]pyridin-5-yl)benzonitrile (**4n**). Light yellow solid,

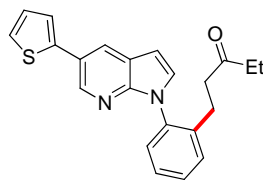


4n

46 h, 75% yield; ¹H NMR (400 MHz, CDCl₃): δ 8.53 (d, *J* = 2.0 Hz, 1H), 8.18 (d, *J* = 2.0 Hz, 1H), 7.76-7.71 (m, 4H), 7.44-7.41 (m, 2H), 7.39-7.35 (m, 2H), 7.33-7.31 (m, 1H), 6.72 (d, *J* = 3.6 Hz, 1H), 2.73 (t, *J* = 7.6 Hz, 2H), 2.53 (t, *J* = 7.6 Hz, 2H), 2.21 (q, *J* = 7.2 Hz, 2H), 0.90 (t, *J* = 7.6 Hz, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ

210.1, 148.5, 144.1, 142.8, 139.1, 136.5, 132.7, 130.9, 130.1, 129.2, 128.7, 128.1, 127.8, 127.7, 127.4, 120.5, 118.9, 110.6, 101.6, 42.4, 35.8, 25.5, 7.69 ppm. ESI HRMS: calcd. for C₂₅H₂₁N₃O+Na 402.1582, found 402.1585.

1-(2-(5-(thiophen-2-yl)-1*H*-pyrrolo[2,3-*b*]pyridin-1-yl)phenyl)pentan-3-one (**4o**). Light yellow oil,

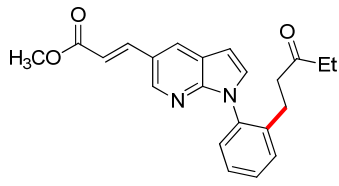


4o

20 h, 76% yield; ¹H NMR (400 MHz, CDCl₃): δ 8.57 (s, 1H), 8.14 (s, 1H), 7.43-7.39 (m, 5H), 7.37-7.29 (m, 3H), 6.65 (d, *J* = 3.2 Hz, 1H), 2.73 (t, *J* = 7.6 Hz, 2H), 2.48 (t, *J* = 7.6 Hz, 2H), 2.17 (q, *J* = 7.6 Hz, 2H), 0.88 (t, *J* = 7.2 Hz, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ 210.2, 147.9, 142.6, 140.4, 139.1, 136.8, 130.2, 129.0, 128.8, 127.3,

126.7, 126.5, 125.1, 120.4, 119.8, 101.3, 42.4, 35.7, 25.7, 7.7 ppm. ESI HRMS: calcd. for C₂₂H₂₀N₂OS+Na 383.1194, found 383.1199.

(*E*)-methyl 3-(1-(2-(3-oxopentyl)phenyl)-1*H*-pyrrolo[2,3-*b*]pyridin-5-yl)acrylate (**4p**). Light

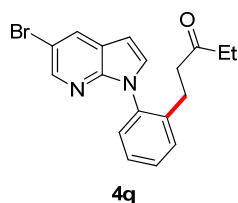


4p

yellow oil, 17 h, 82% yield; ¹H NMR (400 MHz, CDCl₃): δ 8.46 (d, *J* = 1.2 Hz, 1H), 8.16 (d, *J* = 1.6 Hz, 1H), 7.83 (d, *J* = 16.0 Hz, 1H), 7.42-7.27 (m, 5H), 6.68 (d, *J* = 3.2 Hz, 1H), 6.49 (d, *J* = 1.6 Hz, 1H), 3.82 (s, 3H), 2.69 (t, *J* = 8.0 Hz, 2H), 2.49 (t, *J* = 8.0 Hz, 2H), 2.19 (q, *J* = 7.2 Hz, 2H), 0.89 (t, *J* = 7.2 Hz, 3H) ppm; ¹³C

NMR (100 MHz, CDCl₃): δ 210.1, 167.4, 149.2, 144.7, 143.1, 139.0, 136.3, 131.0, 130.2, 129.2, 128.7, 127.9, 127.4, 123.3, 120.5, 116.4, 101.8, 51.7, 42.4, 35.8, 25.5, 7.6 ppm. ESI HRMS: calcd. for C₂₂H₂₂N₂O₃+Na 385.1528, found 385.1521.

1-(2-(5-bromo-1*H*-pyrrolo[2,3-*b*]pyridin-1-yl)phenyl)pentan-3-one (**4q**). Light yellow oil, 21 h, 92%

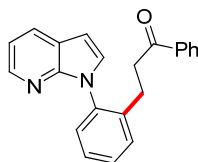


4q

yield; ¹H NMR (400 MHz, CDCl₃): δ 8.22 (d, *J* = 2.0 Hz, 1H), 8.01 (d, *J* = 2.0 Hz, 1H), 7.33-7.24 (m, 3H), 7.21 (d, *J* = 3.6 Hz, 1H), 7.18 (d, *J* = 7.6 Hz, 1H), 6.50 (d, *J* = 3.2 Hz, 1H), 2.59 (t, *J* = 7.2 Hz, 2H), 2.39 (t, *J* = 8.0 Hz, 2H), 2.11 (q, *J* = 7.6 Hz, 2H), 0.82 (t, *J* = 7.6 Hz, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ 210.1, 146.8, 144.2, 139.1, 136.3, 131.1, 130.9, 130.2, 129.2, 128.7, 127.3, 122.0, 112.3, 100.6, 42.4, 35.8, 25.5, 7.68 ppm.

ESI HRMS: calcd. for C₁₈H₁₇BrN₂O+Na 379.0422, found 379.0421, 381.0400.

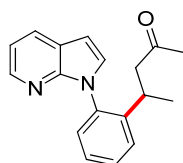
3-(2-(1*H*-pyrrolo[2,3-*b*]pyridin-1-yl)phenyl)-1-phenylpropan-1-one (**4r**). Yellow oil, 21 h, 86%



4r

yield; ¹H NMR (400 MHz, CDCl₃): δ 8.30 (d, *J* = 4.4 Hz, 1H), 7.97 (d, *J* = 7.6 Hz, 1H), 7.63 (d, *J* = 7.6 Hz, 2H), 7.47-7.41 (m, 3H), 7.38-7.28 (m, 5H), 7.10-7.06 (m, 1H), 6.63 (d, *J* = 3.6 Hz, 1H), 3.02 (t, *J* = 7.2 Hz, 2H), 2.87 (t, *J* = 8.0 Hz, 2H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ 198.8, 148.4, 143.6, 139.1, 136.8, 136.2, 132.7, 130.2, 129.3, 128.9, 128.8, 128.8, 128.3, 127.7, 127.2, 120.3, 116.2, 101.0, 39.2, 26.3 ppm. ESI HRMS: calcd. for C₂₂H₁₈N₂O+H 327.1497, found 327.1482.

(*R*)-4-(2-(1*H*-pyrrolo[2,3-*b*]pyridin-1-yl)phenyl)pentan-2-one (**4s**). Light yellow oil, 28 h, 84%

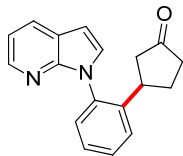


4s

yield; ¹H NMR (400 MHz, CDCl₃): δ 8.27 (d, *J* = 4.0 Hz, 1H), 7.97 (d, *J* = 7.6 Hz, 1H), 7.46-7.41 (m, 3H), 7.34-7.29 (m, 2H), 7.09-7.06 (m, 1H), 6.64 (d, *J* = 3.2 Hz, 1H), 2.97-2.82 (m, 2H), 2.49-2.45 (m, 1H), 1.88-1.73 (m, 3H), 1.13 (d, *J* = 6.8 Hz, 3H) ppm; ¹³C NMR (100 MHz, DMSO): δ 207.3, 148.9, 144.8, 143.4, 136.3, 131.0, 129.3, 129.3, 127.3, 127.1, 120.3, 116.7, 101.0, 50.8, 30.1, 29.3, 21.9 ppm. ESI HRMS: calcd. for C₁₈H₁₈N₂O+H 279.1497, found

279.1530.

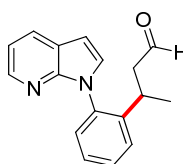
(*R*)-3-(2-(1*H*-pyrrolo[2,3-*b*]pyridin-1-yl)phenyl)cyclopentanone (**4t**). Light yellow oil, 21 h, 86%



4t

yield; ¹H NMR (400 MHz, DMSO): δ 8.20 (d, *J* = 4.4 Hz, 1H), 8.07 (d, *J* = 8.0 Hz, 1H), 7.67-7.64 (m, 2H), 7.53 (t, *J* = 7.6 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 1H), 7.30 (d, *J* = 7.6 Hz, 1H), 7.17-7.14 (m, 1H), 6.71 (d, *J* = 3.2 Hz, 1H), 3.10-3.02 (m, 1H), 2.29-2.12 (m, 3H), 2.02-1.92 (m, 3H) ppm; ¹³C NMR (100 MHz, DMSO): δ 217.6, 148.8, 143.6, 141.9, 137.2, 130.8, 129.4, 129.3, 129.3, 127.5,

127.4, 120.3, 116.8, 101.4, 45.8, 38.5, 37.1, 30.6 ppm. ESI HRMS: calcd. for C₁₈H₁₆N₂O+H 277.1341, found 277.1334.

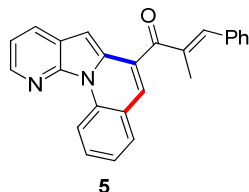


4u

(*R*)-3-(2-(1*H*-pyrrolo[2,3-*b*]pyridin-1-yl)phenyl)butanal (**4u**). Brown oil, 48 h, 66% yield; ¹H NMR (400 MHz, CDCl₃): δ 9.44 (s, 1H), 8.28 (s, 1H), 7.99 (d, *J* = 8.0 Hz, 1H), 7.49-7.42 (m, 2H), 7.37-7.28 (m, 3H), 7.12-7.09 (m, 1H), 6.66 (d, *J* = 3.2 Hz, 1H), 3.09-3.04 (m, 1H), 2.82-2.70 (m, 1H), 2.53-2.47 (m, 1H),

1.19 (d, $J = 5.2$ Hz, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ 201.7, 148.8, 143.7, 136.1, 129.6, 129.3, 129.1, 129.0, 127.3, 126.9, 120.4, 116.4, 101.1, 51.2, 28.3, 22.1 ppm. ESI HRMS: calcd. for $\text{C}_{17}\text{H}_{16}\text{N}_2\text{O}+\text{H}$ 265.1341, found 265.1334.

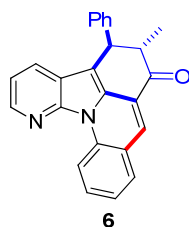
(E)-2-methyl-3-phenyl-1-(pyrido[3',2':4,5]pyrrolo[1,2-a]quinolin-6-yl)prop-2-en-1-one (**5**). Yellow solid, 24 h, 90% yield; ^1H NMR (400 MHz, CDCl_3): δ 8.61-8.59 (m, 1H),



8.16-8.14 (m, 1H), 7.78-7.74 (m, 1H), 7.70-7.68 (m, 1H), 7.52 (s, 1H), 7.46-7.43 (m, 4H), 7.41-7.38 (m, 2H), 7.37-7.34 (m, 3H), 7.06 (s, 1H), 2.37 (s, 3H) ppm; ^{13}C NMR (150 MHz, CDCl_3): δ 196.9, 146.0, 142.6, 142.3, 137.1, 136.6, 135.5, 133.2, 131.2, 129.9, 129.4, 129.0, 128.9, 128.9, 128.8, 128.5, 123.7, 122.2, 121.9, 118.3, 118.0, 95.5, 14.0 ppm.

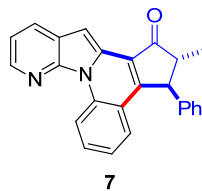
ESI HRMS: calcd. for $\text{C}_{25}\text{H}_{18}\text{N}_2\text{O}+\text{H}$ 363.1497, found 363.1484.

6-methyl-5-phenyl-5H-pyrido[3',2':4,5]pyrrolo[3,2,1-de]acridin-7(6H)-one (**6**). Yellow solid, 24 h, 62% yield; ^1H NMR (400 MHz, CDCl_3): δ 10.24 (d, $J = 8.8$ Hz, 1H), 8.60 (d, $J = 4.4$ Hz, 1H), 8.21 (d, $J = 7.6$ Hz, 1H), 7.72 (t, $J = 8.0$ Hz, 1H), 7.56 (d, $J = 7.6$ Hz, 1H), 7.50 (s, 1H), 7.39-7.36 (m, 1H), 7.26-7.17 (m, 5H), 5.01 (d, $J = 7.2$ Hz, 1H), 3.21 (q, $J = 7.6$ Hz, 1H), 0.91 (d, $J = 7.6$ Hz, 3H) ppm; ^{13}C NMR



(100 MHz, CDCl_3): δ 205.9, 157.0, 146.2, 142.3, 139.2, 138.6, 132.5, 129.4, 129.1, 128.7, 127.3, 127.0, 126.8, 123.5, 122.8, 120.0, 119.0, 118.1, 94.7, 48.7, 47.4, 12.0 ppm. ESI HRMS: calcd. for $\text{C}_{25}\text{H}_{18}\text{N}_2\text{O}+\text{H}$ 363.1497, found 363.1477.

2-methyl-3-phenyl-2,3-dihydro-1H-cyclopenta[c]pyrido[3',2':4,5]pyrrolo[1,2-a]quinolin-1-one (**7**).



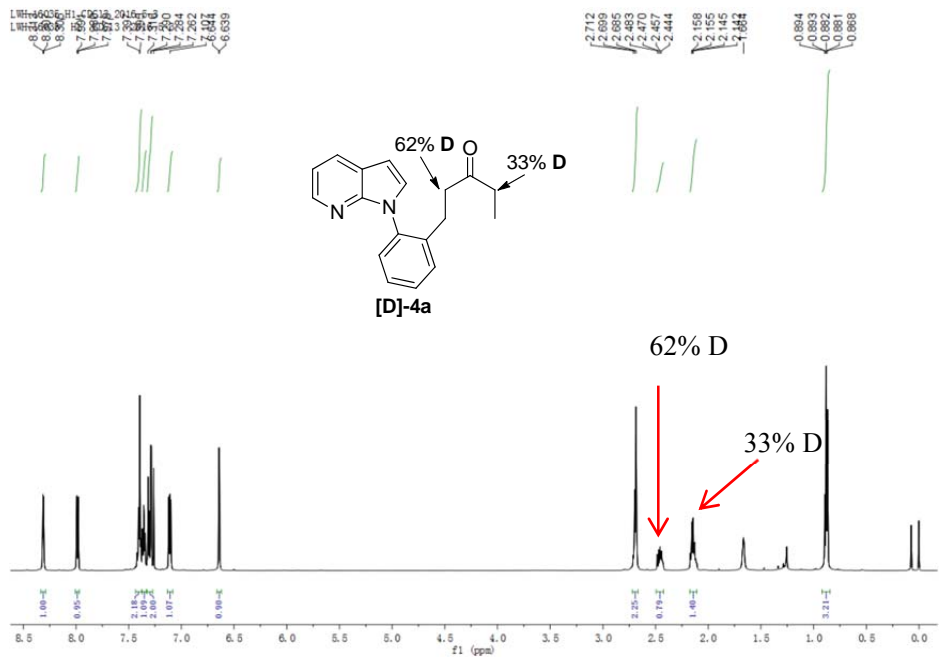
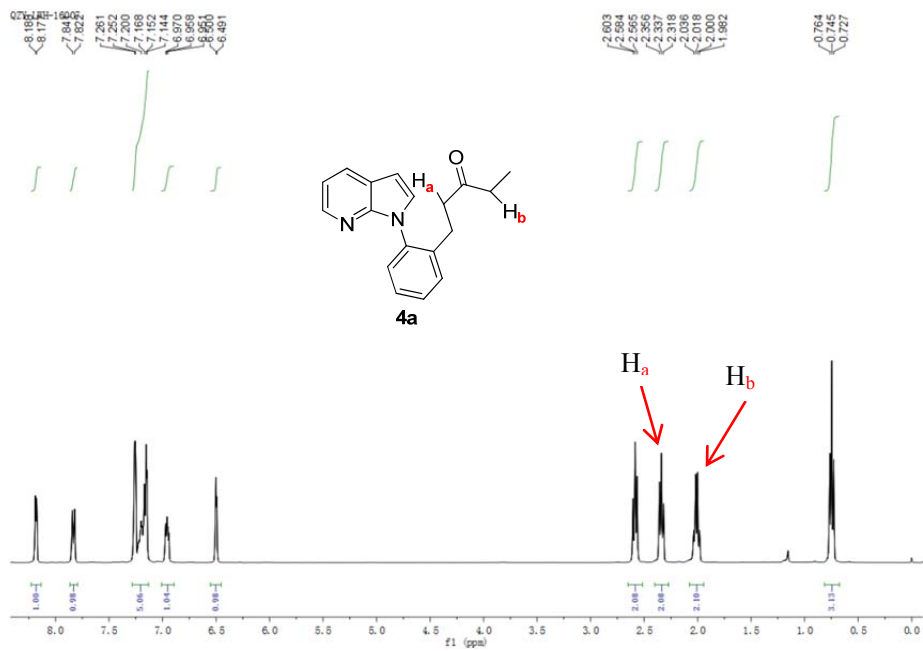
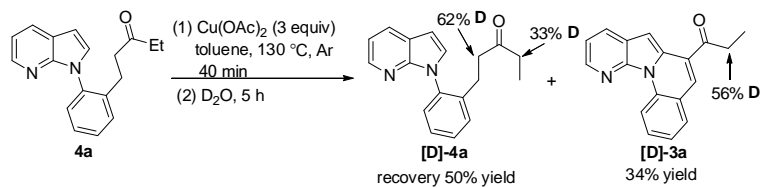
Yellow solid, 24 h, 30% yield; ^1H NMR (400 MHz, CDCl_3): δ 10.27 (d, $J = 8.8$ Hz, 1H), 8.60-8.59 (m, 1H), 8.23-8.21 (m, 1H), 7.76-7.72 (m, 1H), 7.52 (s, 1H), 7.47-7.45 (m, 1H), 7.40-7.36 (m, 1H), 7.35-7.31 (m, 2H), 7.29-7.27 (m, 1H), 7.23-7.21 (m, 2H), 7.19-7.15 (m, 1H), 4.34 (d, $J = 2.8$ Hz, 1H), 2.70-2.66 (m, 1H), 1.50 (d, $J = 7.6$ Hz, 3H) ppm; ^{13}C NMR (151 MHz,

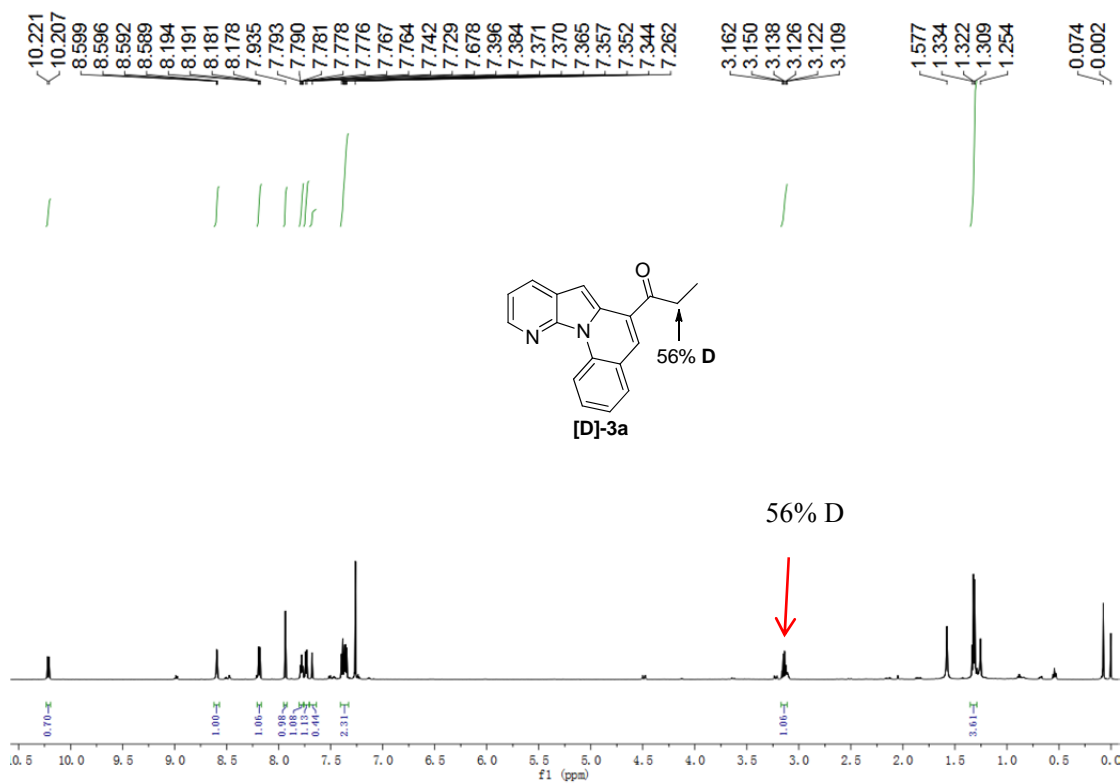
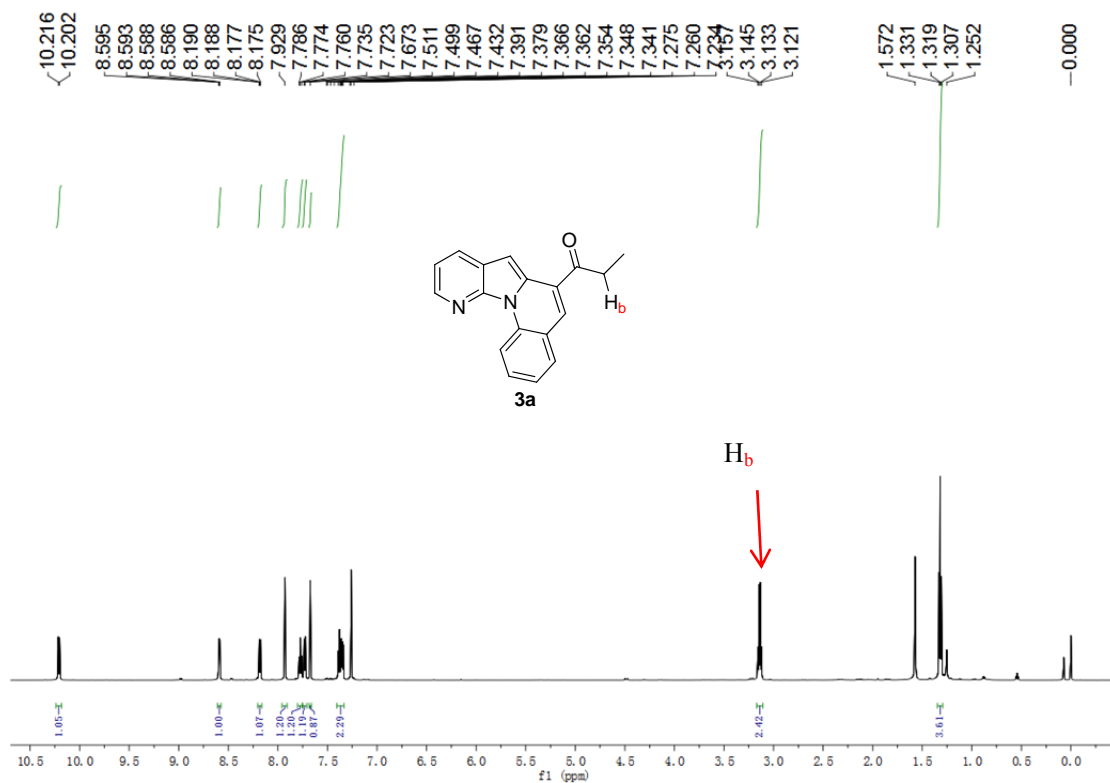
CDCl_3): δ 205.7, 156.7, 146.0, 142.4, 142.3, 138.6, 132.5, 129.3, 129.1, 127.1, 127.1, 127.1, 123.3, 122.7, 120.0, 118.9, 118.1, 94.6, 53.6, 53.3, 15.8 ppm. ESI HRMS: calcd. for $\text{C}_{25}\text{H}_{18}\text{N}_2\text{O}+\text{H}$ 363.1497, found 363.1477.

[1] Qian, G.; Hong, X.; Liu, B.; Mao, H.; Xu, B. *Org. Lett.* **2014**, *16*, 5294-5297.

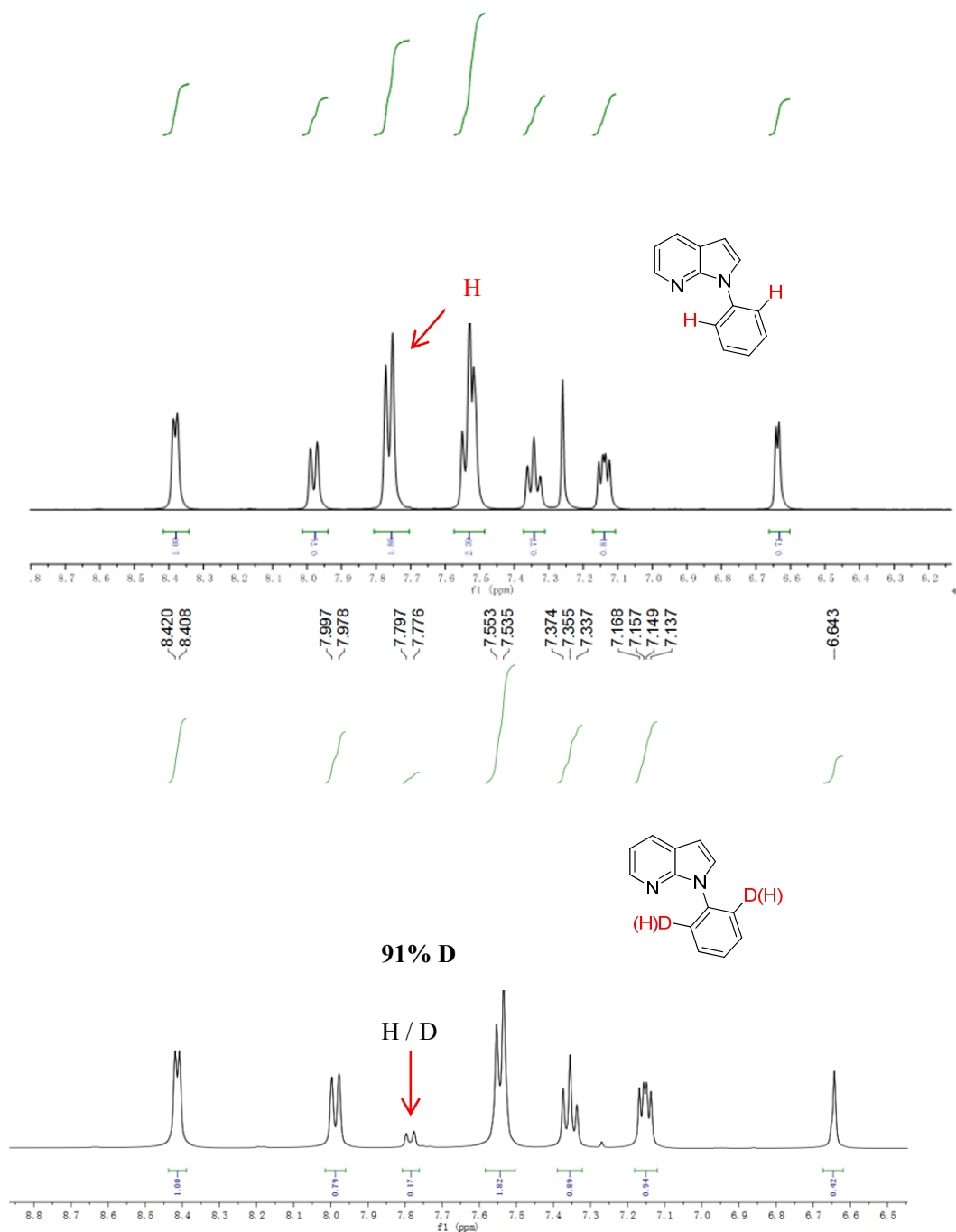
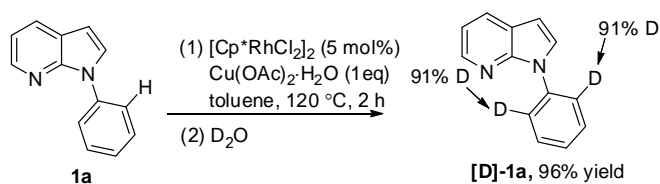
3. Mechanism Study

1. Deuterium-labeling experiments were carried out to study the mechanism of the copper-catalyzed annulation process. **4a** and $\text{Cu}(\text{OAc})_2$ (3 equiv.) were stirred in toluene at 130°C for 40 min, then D_2O was added and stirred for 5 h. The deuterium was obtained from ^1H NMR. From the results we could draw the conclusion that α -position of carbonyl group could be activated by $\text{Cu}(\text{OAc})_2$ in this reaction system. No reaction occurred when we added TEMPO to the reaction, which implies that the annulation from **4a** to **3a** involves copper-catalyzed radical process.



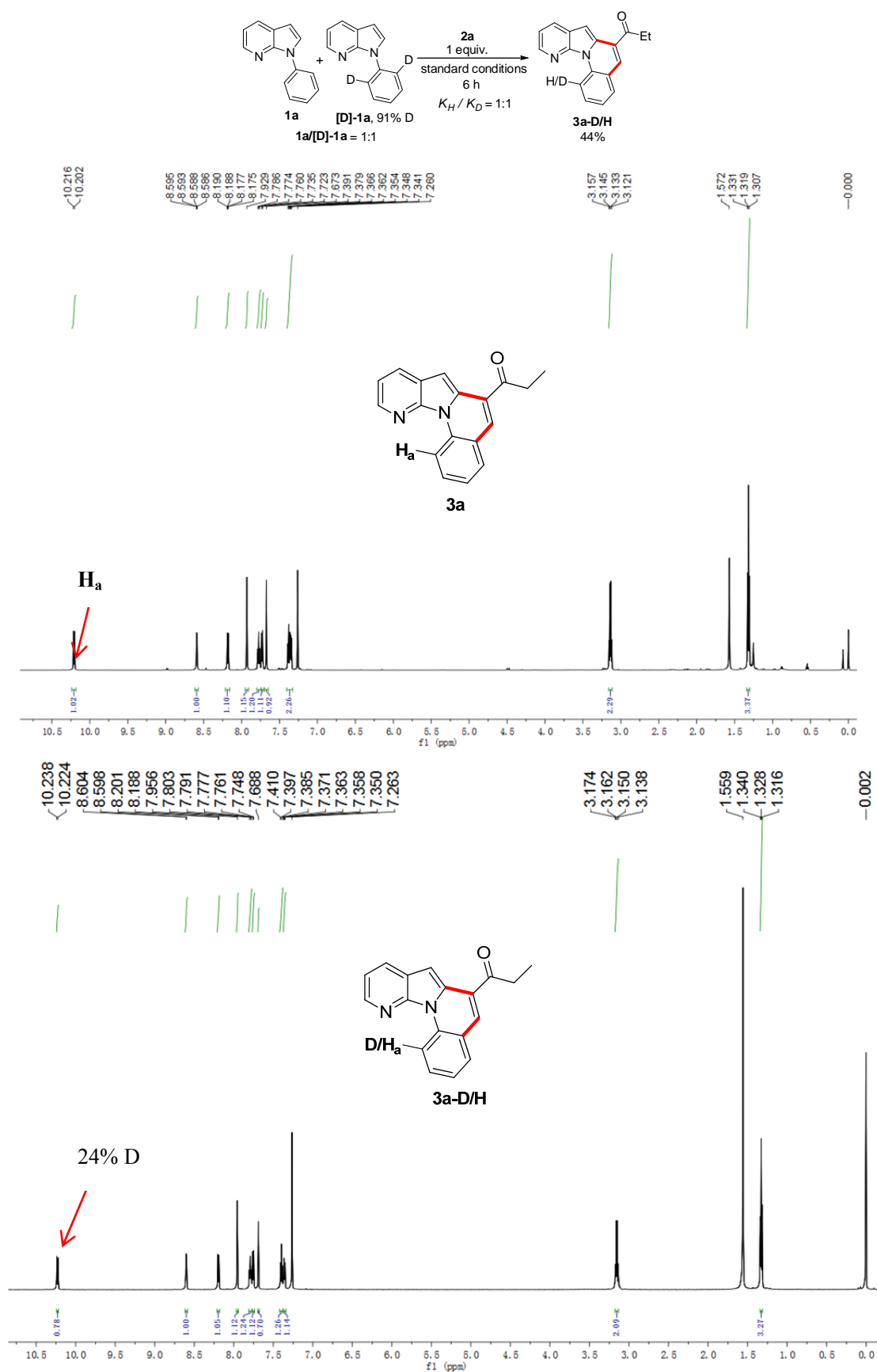


2. Deuterium-labeling experiments were carried out to study the mechanism of this coupling reaction. **1a** was stirred in the absence of α,β -unsaturated ketones for 3 h under standard conditions, then D_2O was added and stirred for 6 h. The deuterium rate was obtained from 1H NMR.

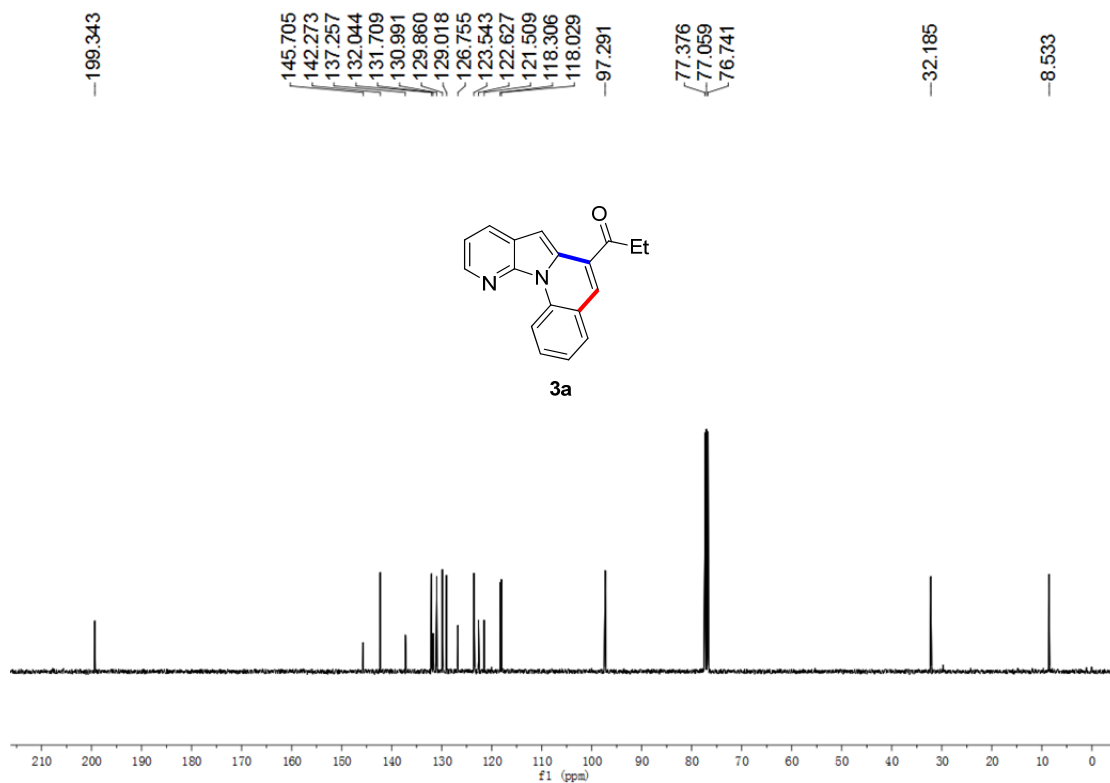
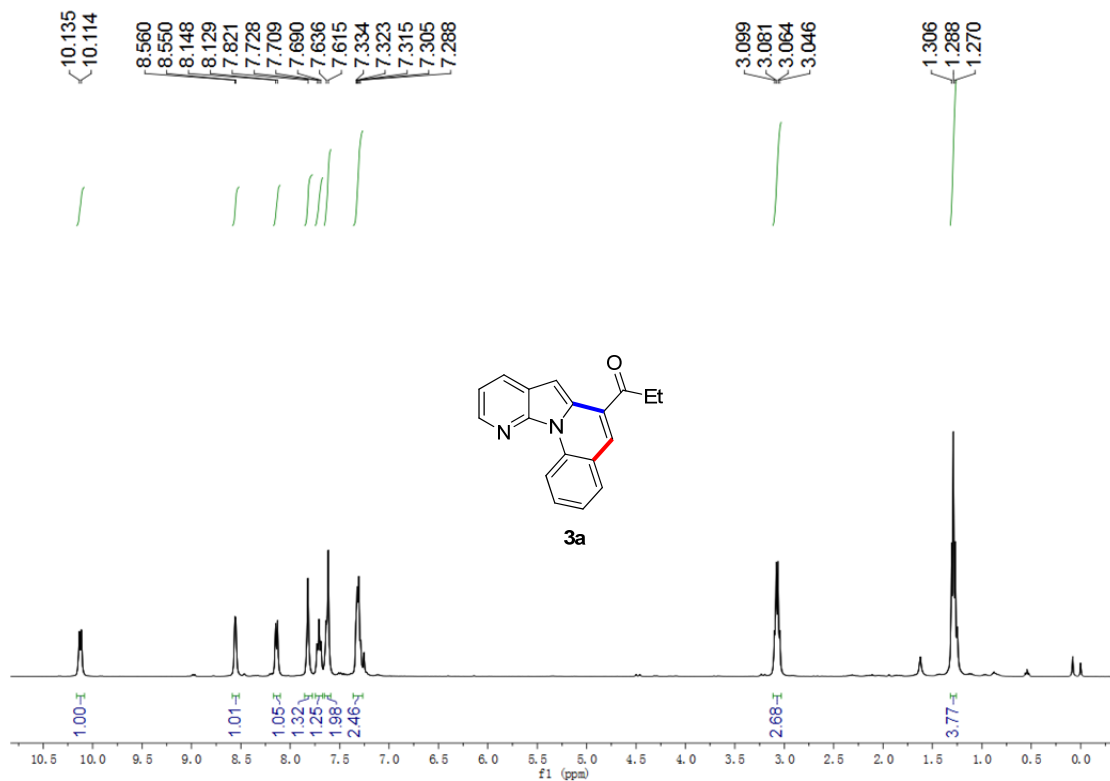


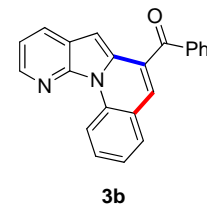
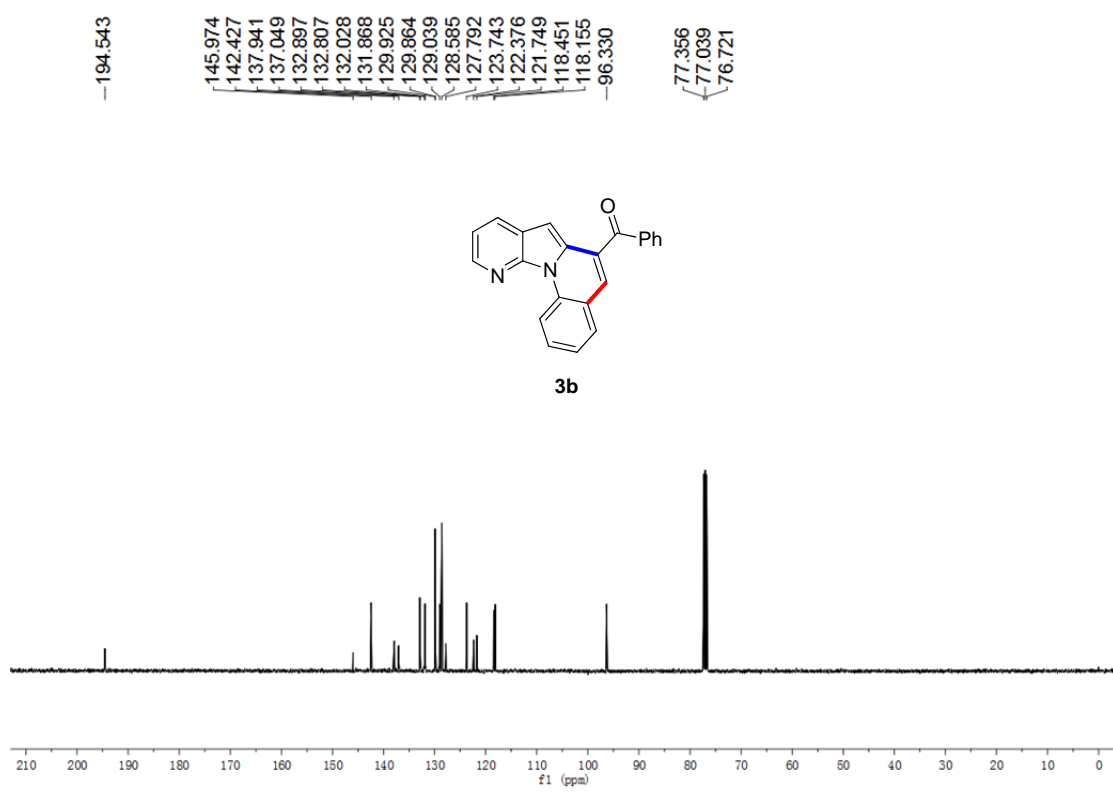
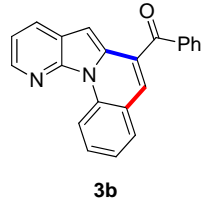
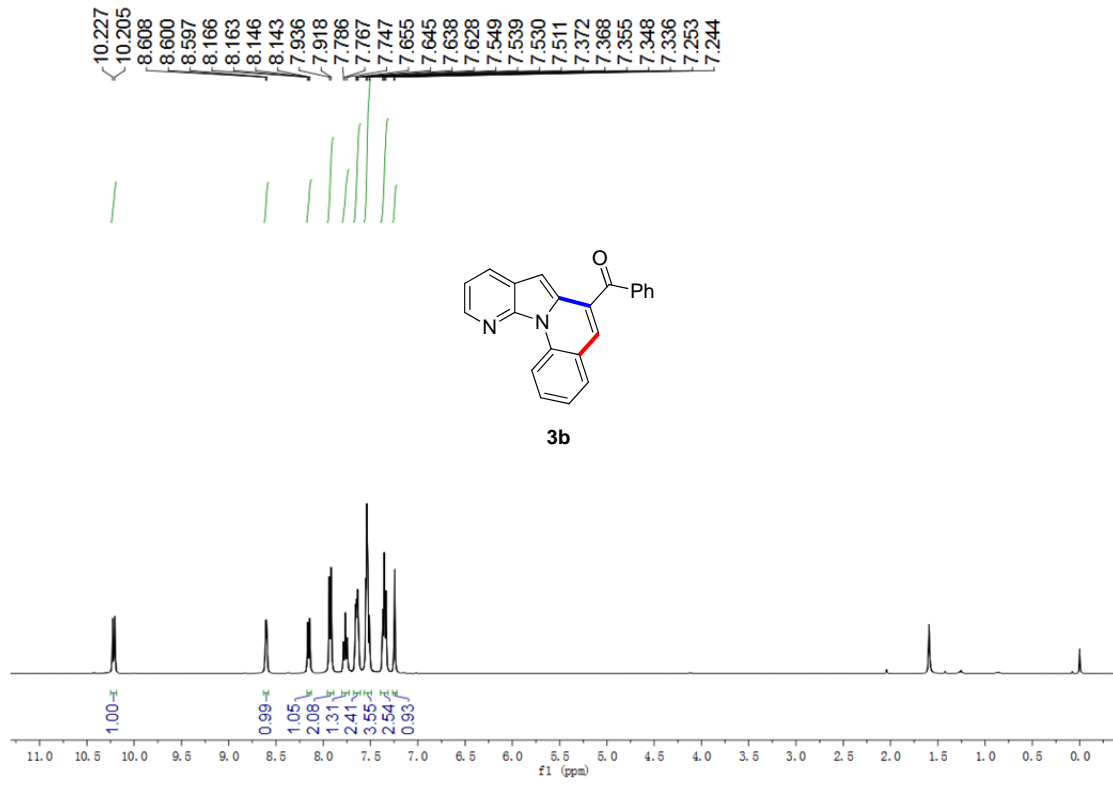
3. The deuterium kinetic isotopic effect was determined to be 1, thus indicates that the cleavage

of ortho C–H bond might be reversible and not involved in the rate-determining step.

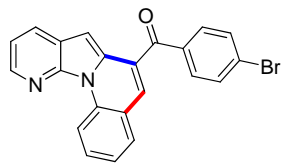


4. NMR Spectra of Alkylated Products and Aza-Fused 7-Azaindole Derivatives and Structure Determination

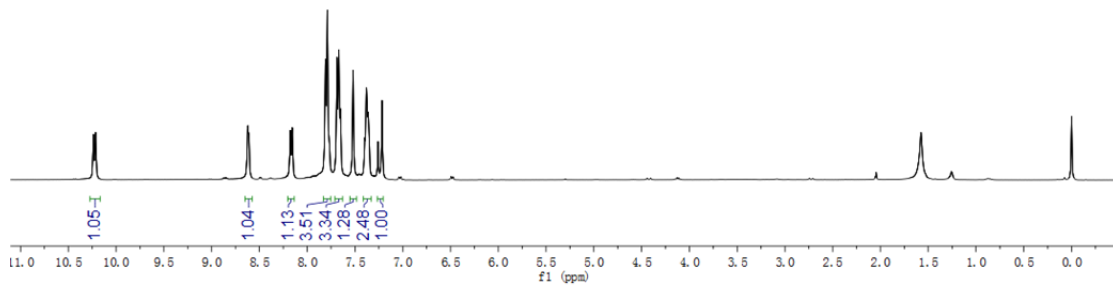




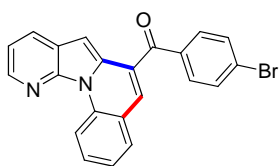
10.236
10.215
8.621
8.612
8.176
8.156
7.808
7.788
7.772
7.688
7.668
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7.519
7.397
7.380
7.363
7.354
7.259
7.217



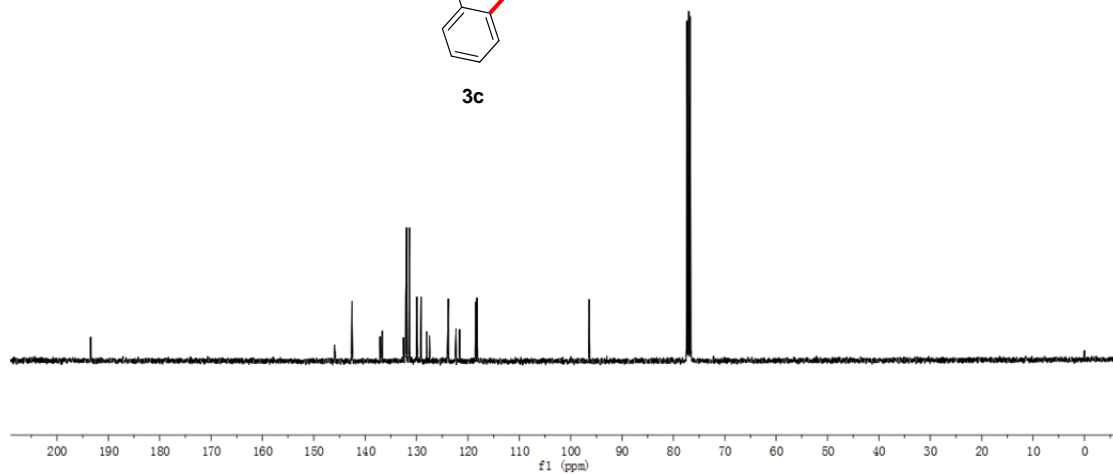
3c

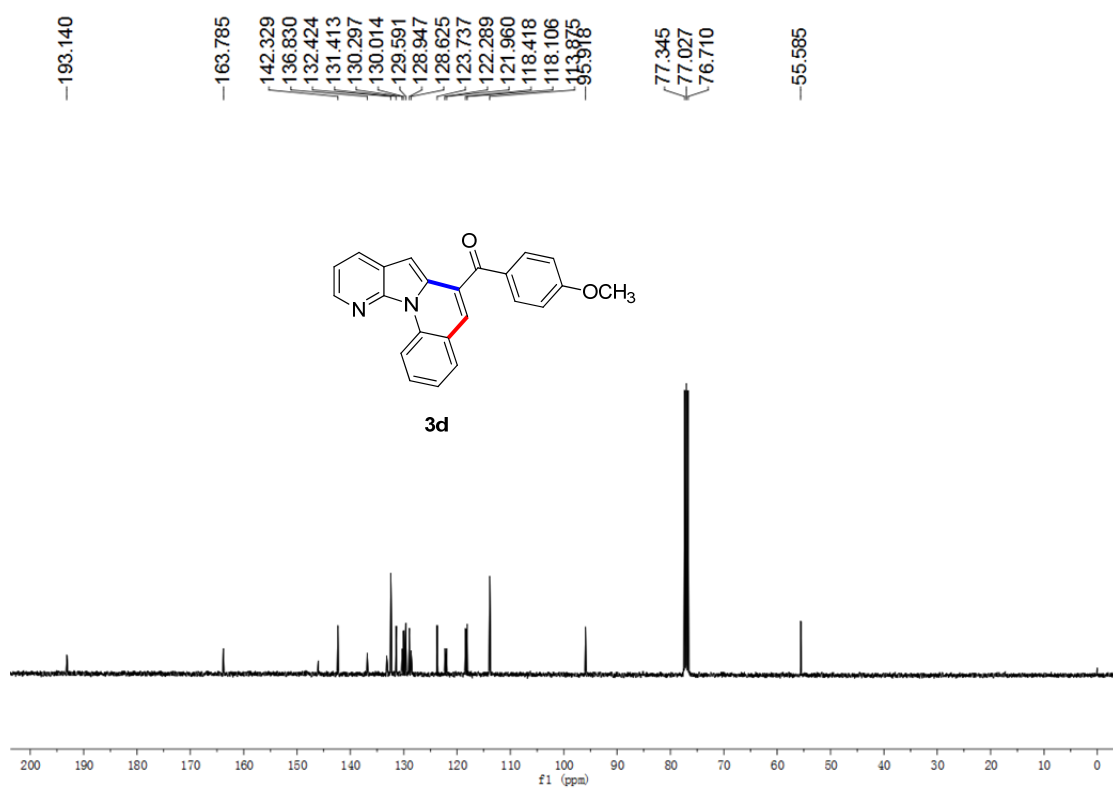
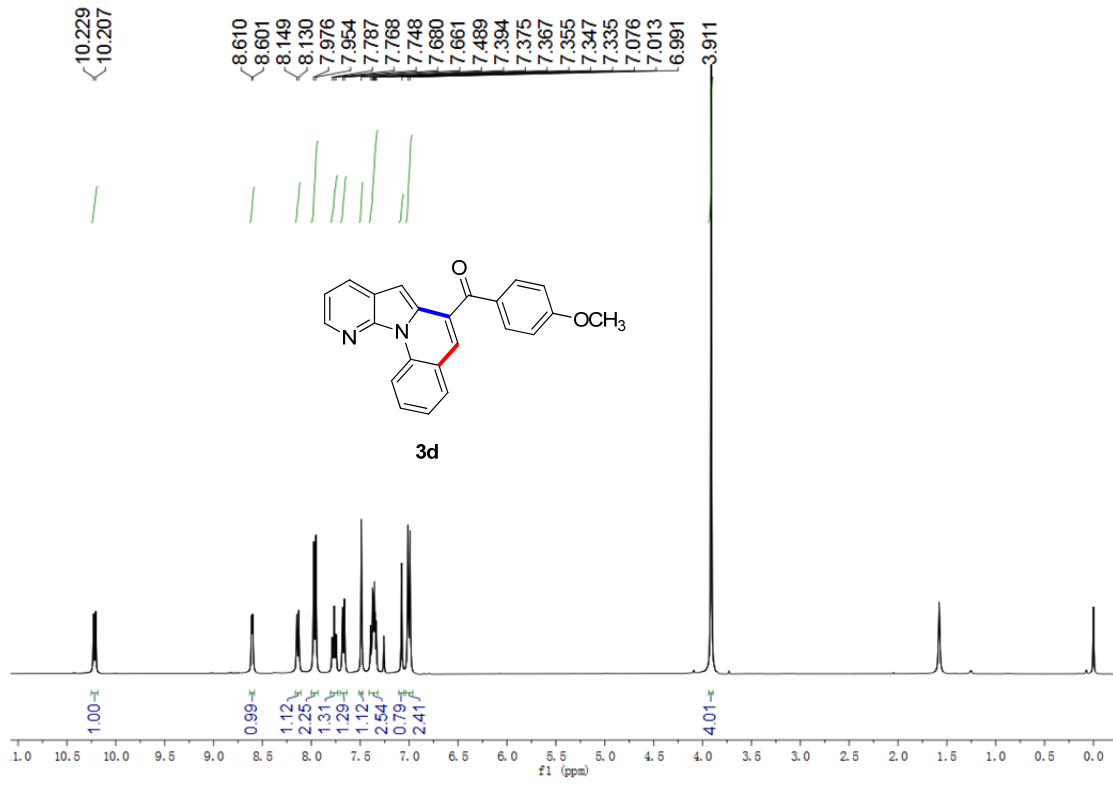


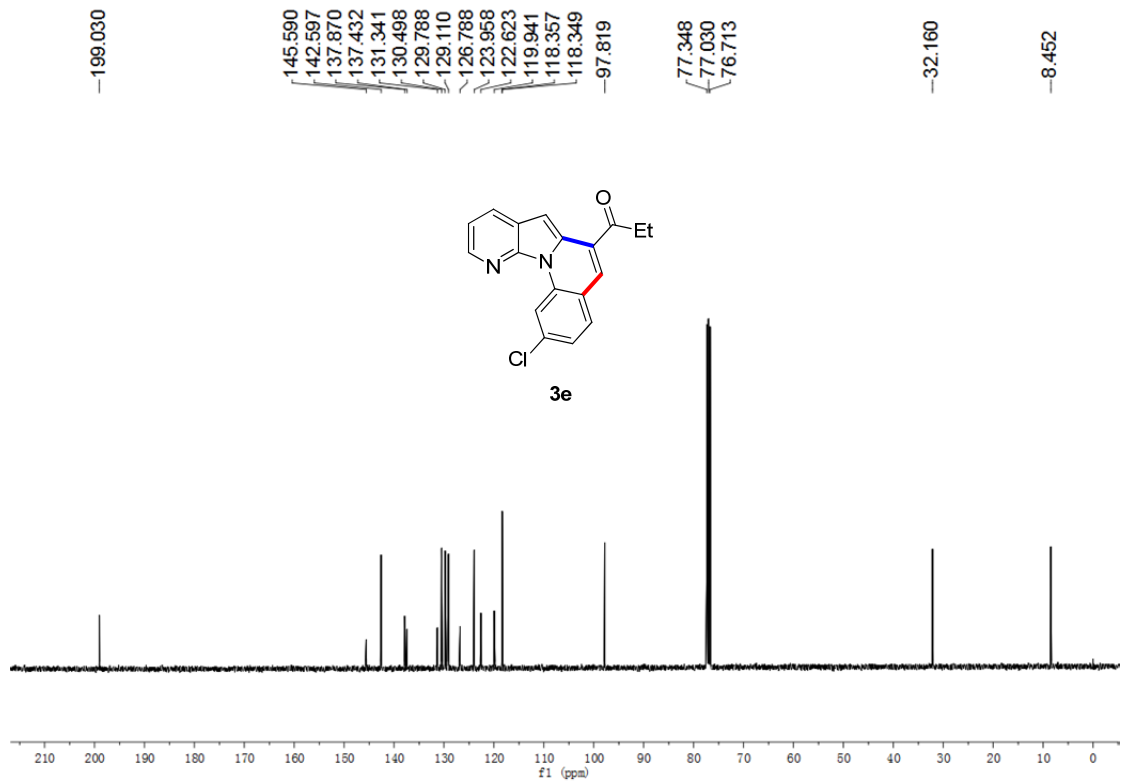
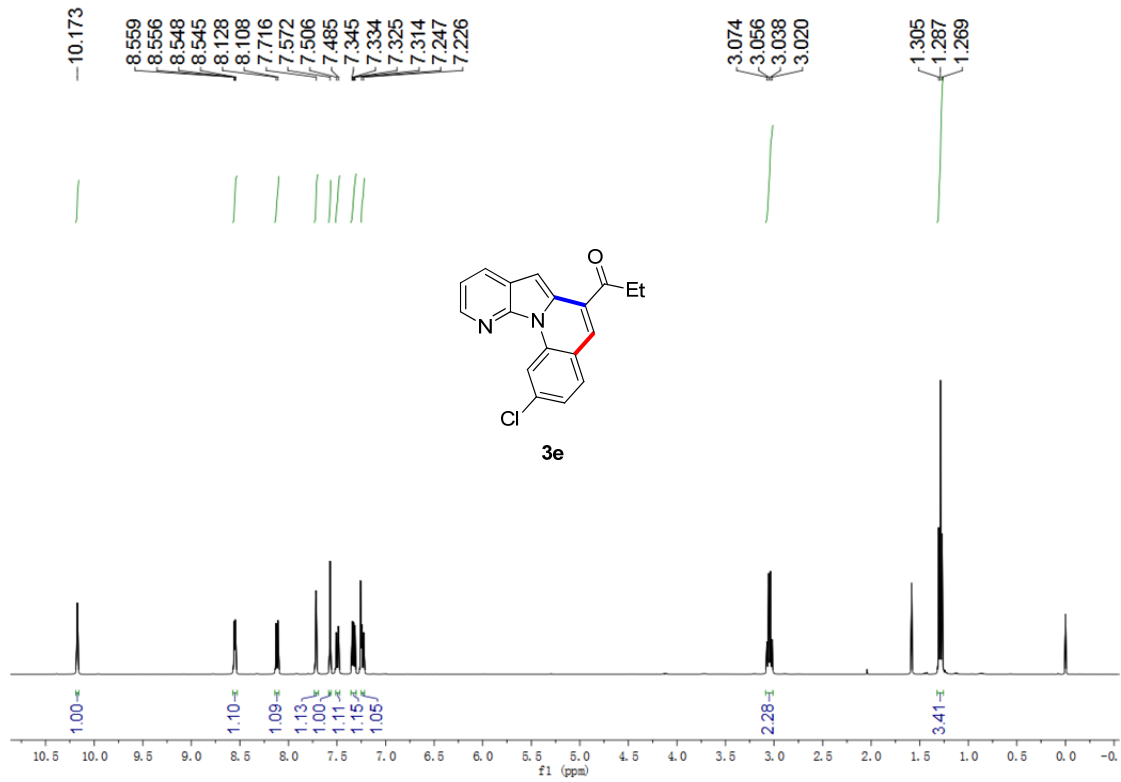
193.422
145.960
142.571
137.098
136.653
132.533
132.089
132.051
131.926
131.389
129.919
129.095
128.030
127.460
123.839
122.314
121.614
118.499
118.236
96.385
77.345
77.028
76.710

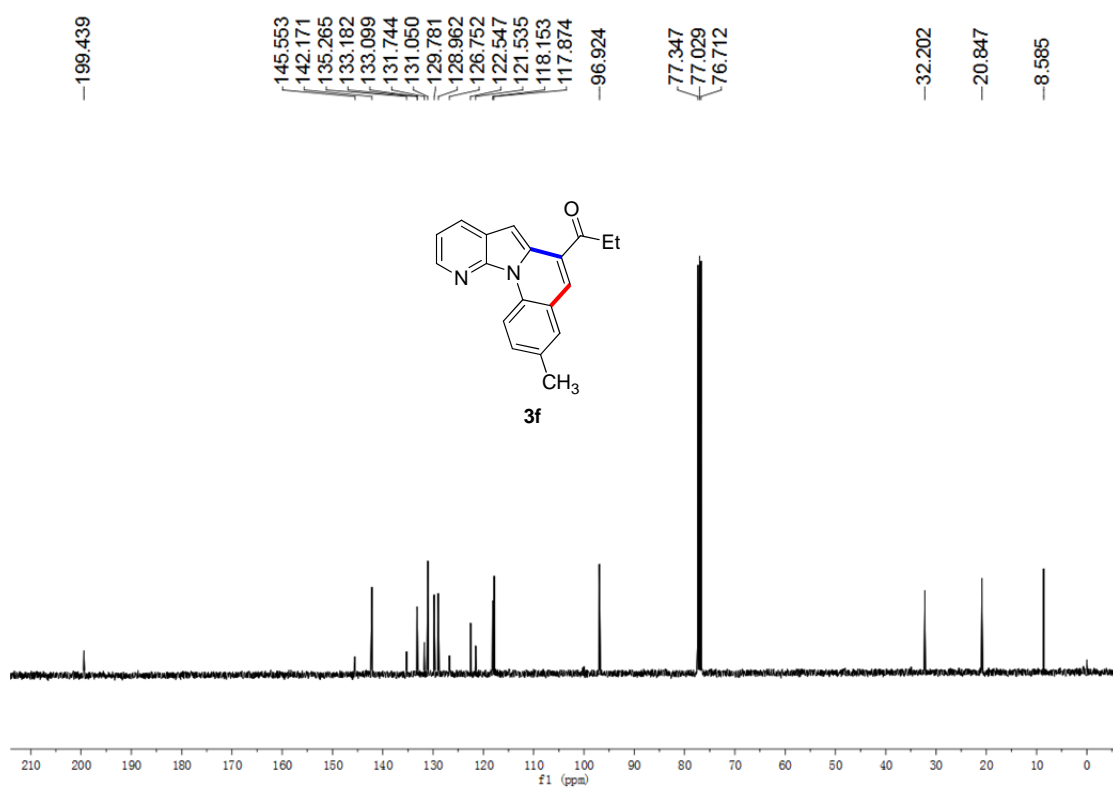
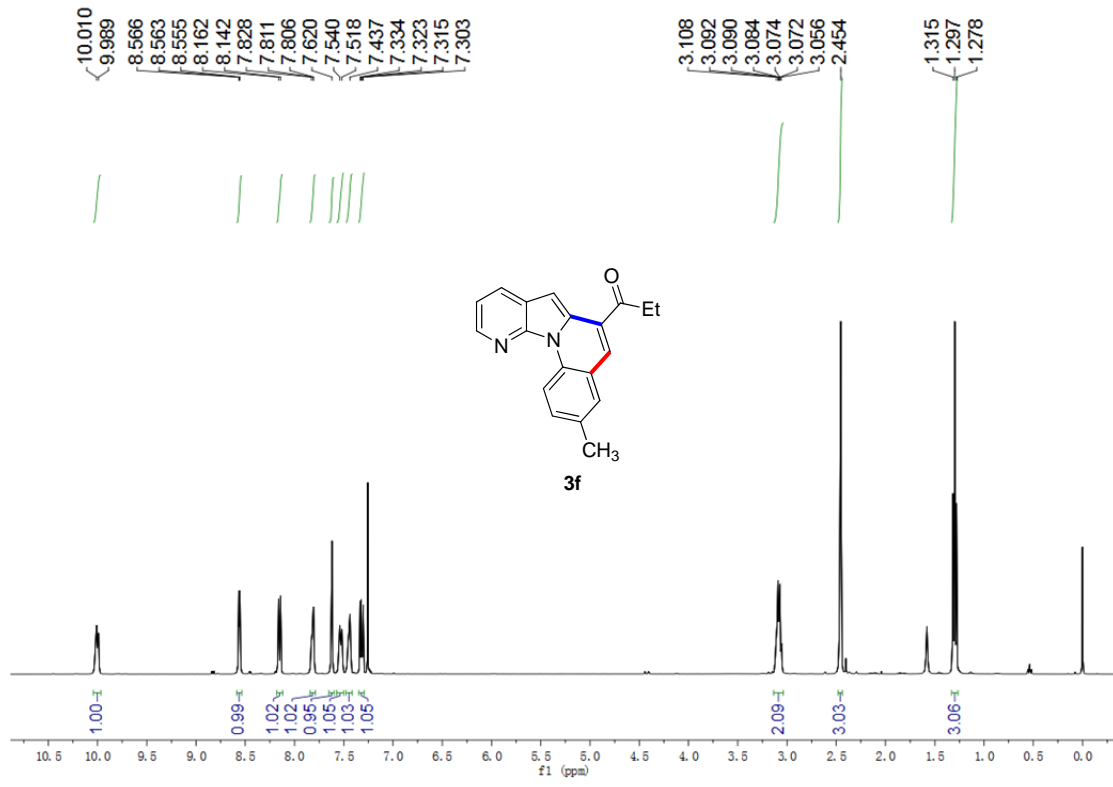


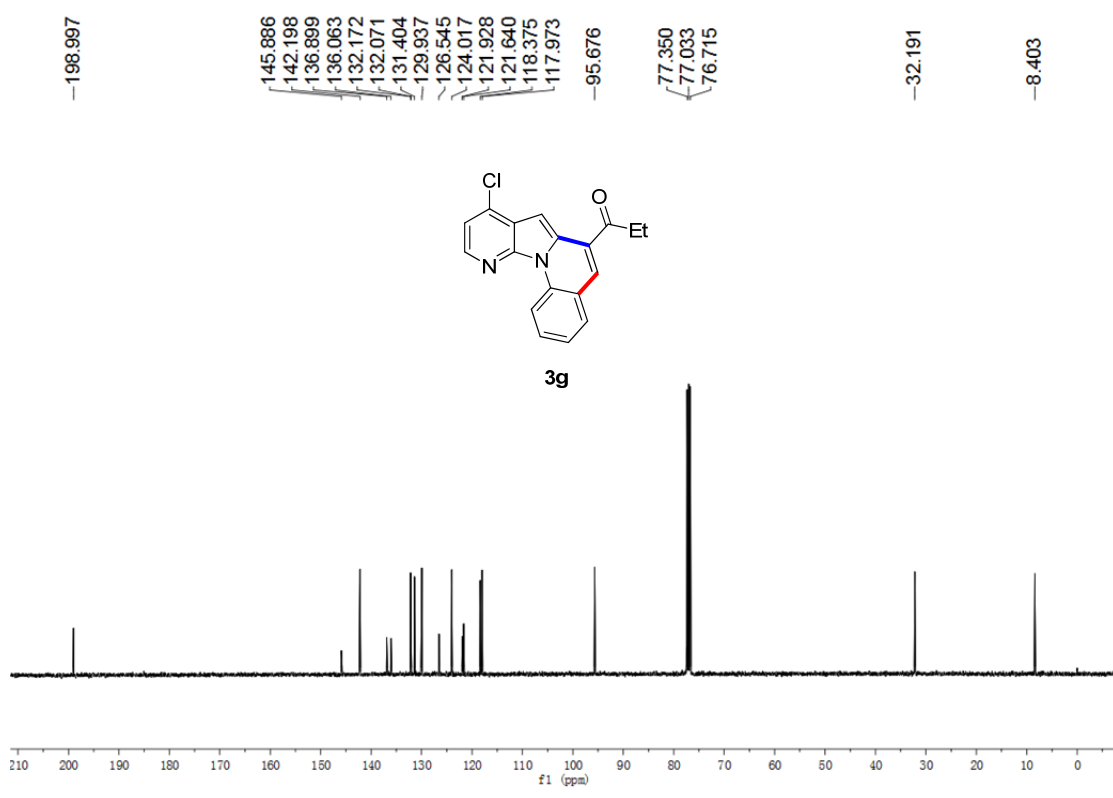
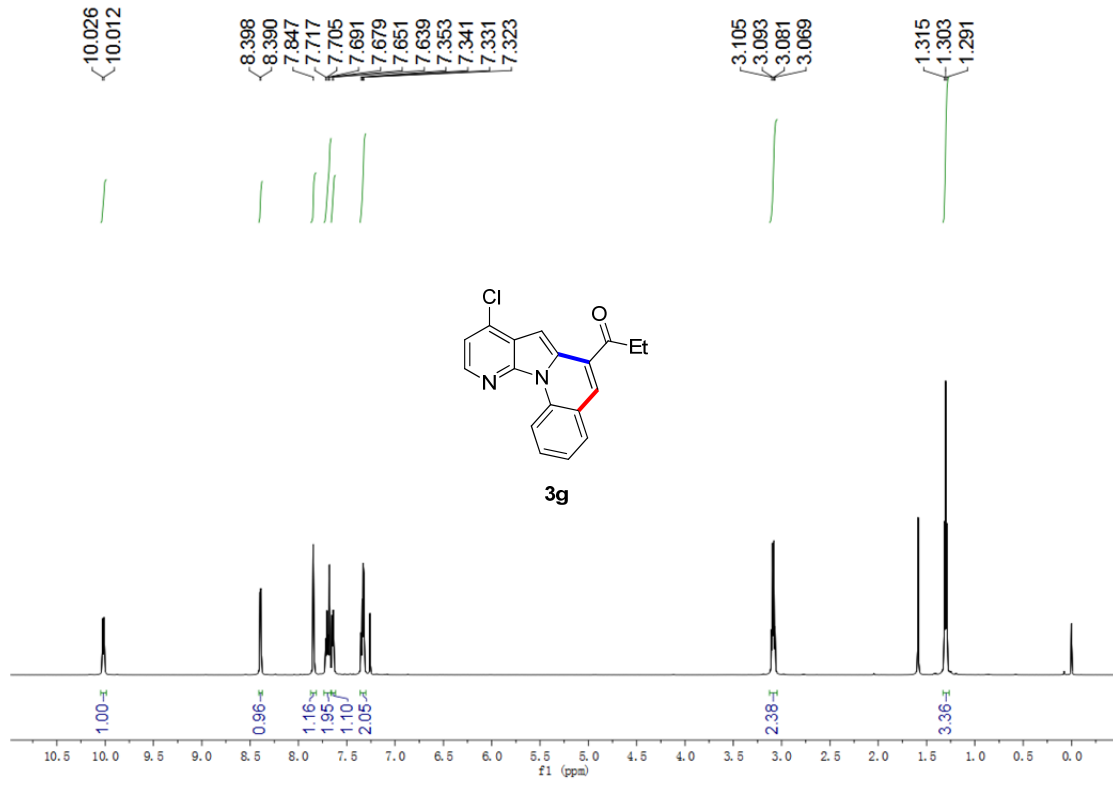
3c

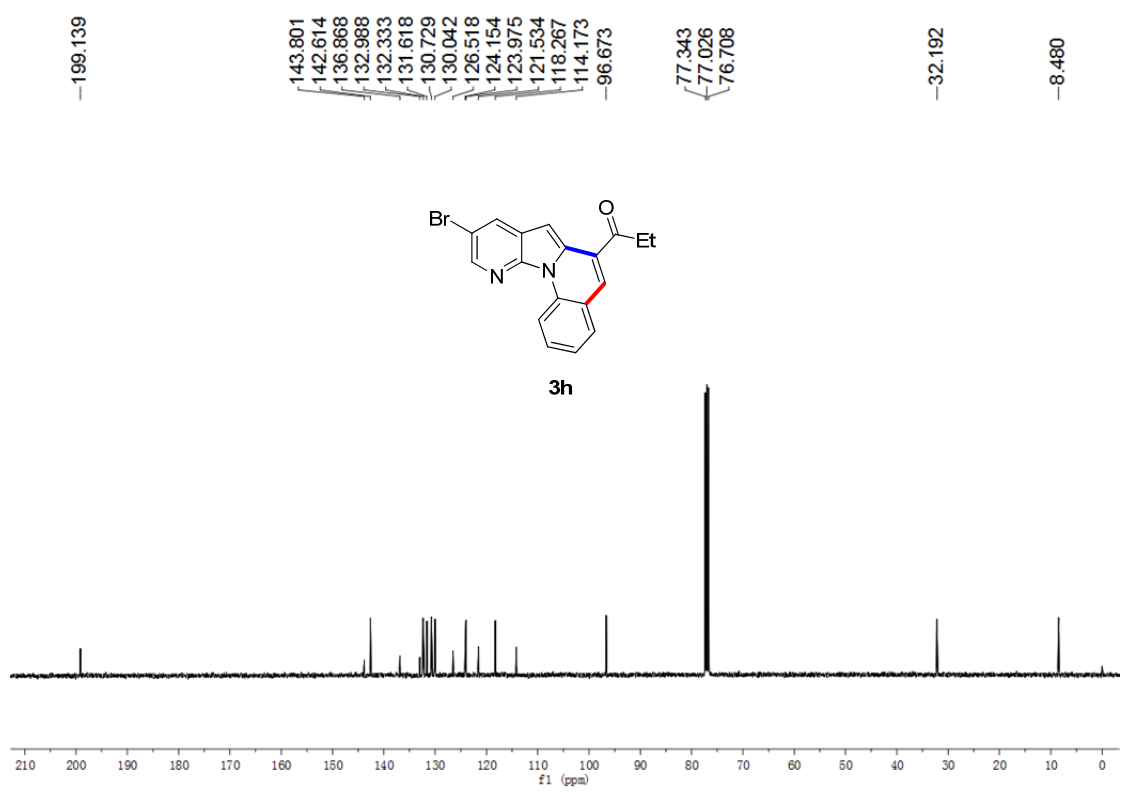
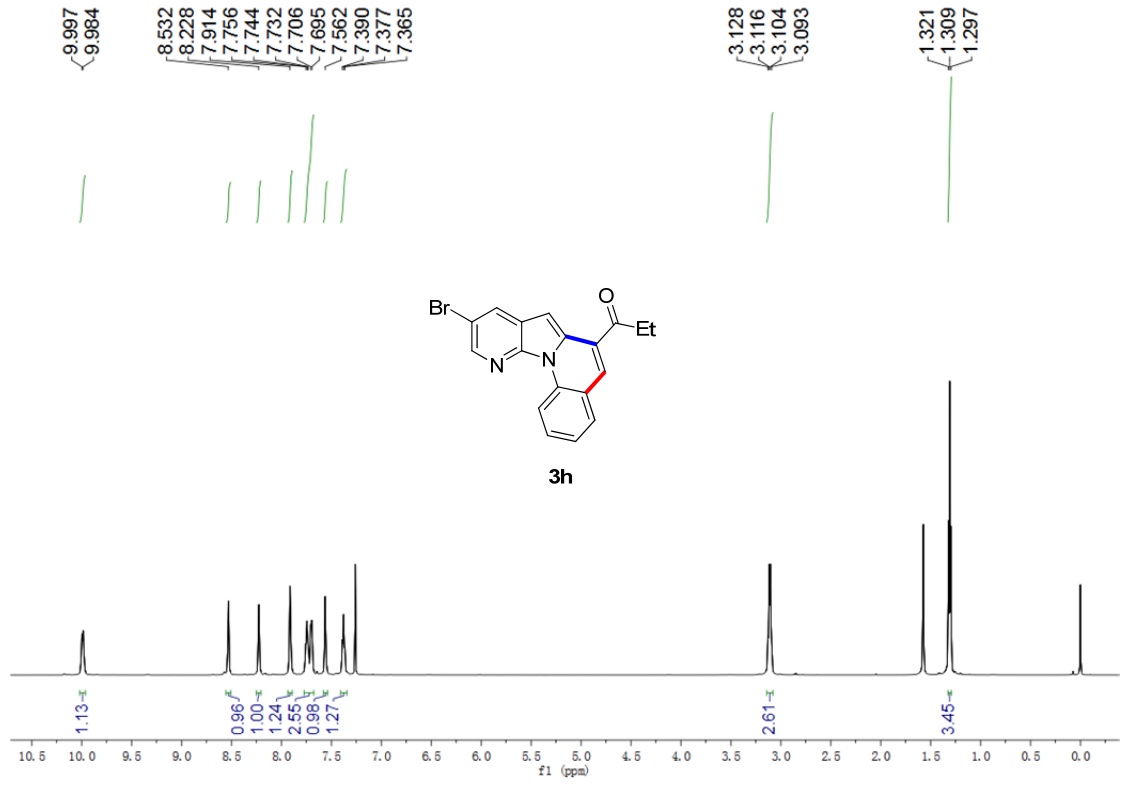


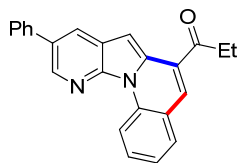
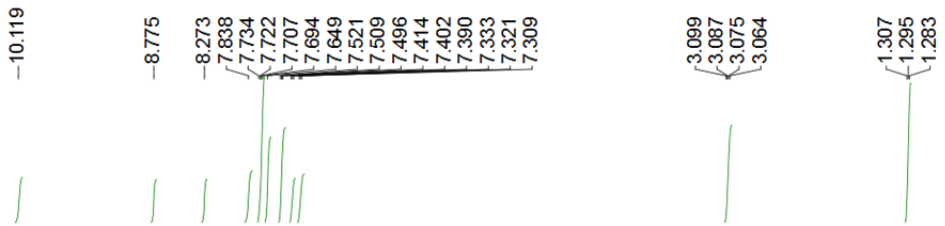




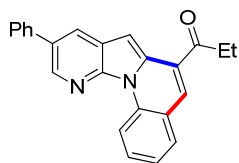
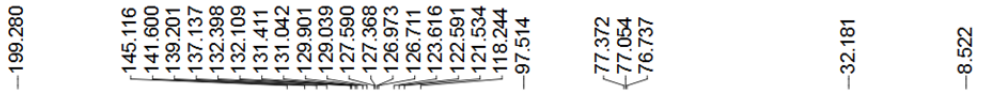
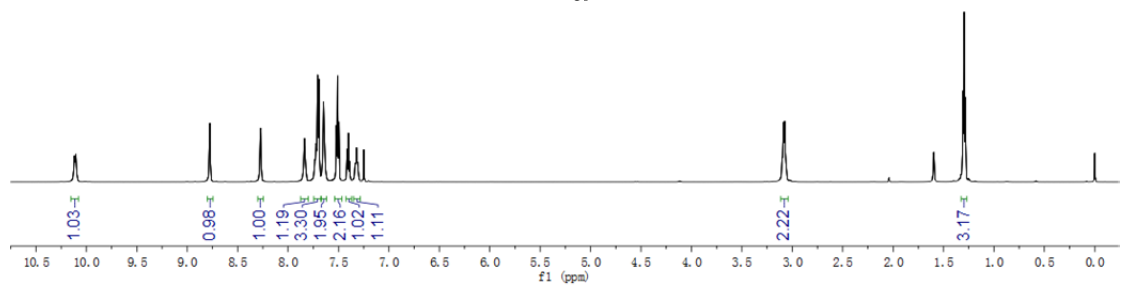








3i



3i

