Metal-Free Assembly of Diverse Polysubstituted Pyridines via Cascade Approach of Tertiary Enaminones and α,β-Unsaturated Sulfonylketimines

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Supplementary Information

1. General Information

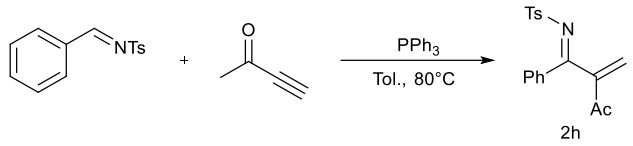
Nuclear magnetic resonance (NMR) spectra were recorded in $CDCl_3$ and DMSO-d_6 on Bruker 600 MHz (at 600 MHz for ^1H, and at 150 MHz for ^{13}C). Proton chemical shifts were reported in parts per million (δ scale). The ^1H NMR chemical shifts are reported in ppm with the internal TMS signal at 0.0 ppm as standard. The ^{13}C NMR chemical shifts were given using $CDCl_3$ as the internal standard ($CDCl_3$: δ = 77.2 ppm and DMSO-d_6: δ = 39.5 ppm). High-resolution mass spectra (HRMS) were obtained using Agilent P/N G1969-90010. High-resolution mass spectra were reported for the molecular ion $[M+H]^+$ or $[M+Na]^+$. Melting points were recorded on BUCHI Melting Point M-565 instrument. X-ray diffraction experiment was carried out on an Agilent D8 QUEST and the data obtained were deposited at the Cambridge Crystallographic Data Centre. UV detection was performed at 254 nm. TLC was performed on glass-backed silica plates; products were visualized using UV light. All reagents and solvents were obtained from commercial sources and used without further purification. *N,N*-dimethyl enaminones **1**[1] and α,β-unsaturated sulfonketimines **2**[2] were prepared according to the literature procedures.

Reference

[1] F. Ma, J. Liu, T. Zhou, M. Lei, J. Chen, X. Wang, Y. Zhang, X. Shen, L. Hu, Discovery and structure-activity relationships study of thieno[2,3-b]pyridine analogues as hepatic gluconeogenesis inhibitors, *Eur. J. Med. Chem*., 2018, 152, 307-317.

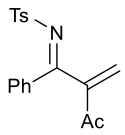
[2] (a) B. Cheng, Y. Wang, T. Li, L. Lu and W. Xiao, Synthesis of polysubstituted pyrroles through a formal [4 + 1] cycloaddition/E1cb elimination/aromatization sequence of sulfur ylides and α,β-unsaturated imines, *J. Org. Chem*., 2017, 82, 12134-12140; (b) P. Zheng, Q. Ouyang, S. Niu, L. Shuai, Y. Yuan, K. Jiang, T. Liu and Y. Chen, Enantioselective [4 + 1] annulation reactions of alpha-substituted ammonium ylides to construct spirocyclic oxindoles, *J. Am. Chem. Soc.*, 2015, 137, 9390-9399.

2. Synthesis and Characterization Data of 2h and 2l

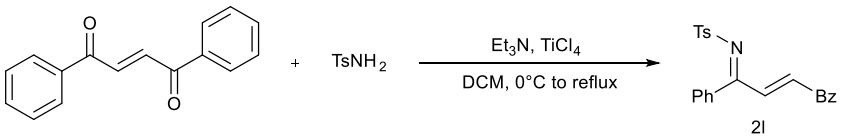


Imine (1.0 mmol) and PPh_3 (0.2 equiv.) were dissolved in toluene (5.0 mL), and added to the mixture alkyne (1.2 equiv.), then stirred at 80 ℃ until complete consumption of the starting material (monitored by TLC). Then, directly purified by flash column chromatography on silica gel using petroleum ether (PE) and ethyl acetate (EA) (30/1 to 15/1 v/v) as eluents to afford the pure products **2h**.

(*E*)-4-methyl-N-(2-methylene-3-oxo-1-phenylbutylidene)benzenesulfonamide (2h)

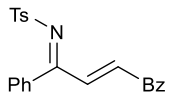


The residue was purified by a silica gel flash chromatography (PE/EA = 30/1 to 15/1 v/v) giving the product **2h** as a colorless oil in 34% yield (110 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.81 – 7.77 (m, 2H), 7.74 (d, *J* = 7.8 Hz, 2H), 7.48 – 7.45 (m, 1H), 7.33 – 7.30 (m,2H), 7.25 (d, *J* = 8.4 Hz, 2H), 6.46 (s, 1H), 5.95 (s, 1H), 2.43 (s, 3H), 2.36 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 195.8, 175.8, 146.0, 144.0, 137.4, 135.7, 134.0, 129.8, 129.6, 128.7, 127.7, 127.5, 26.2, 21.6. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{18}H_{17}NNaO_3S^+$ 350.0821, found 350.0811.



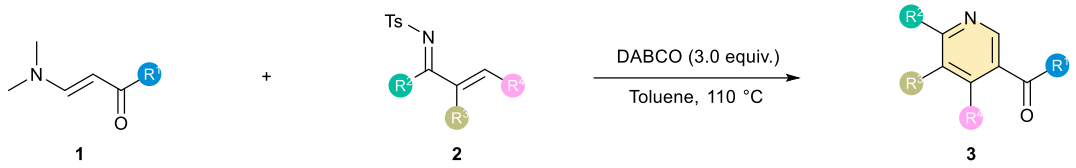
At 0 ℃, enkenone (0.5 g), amine (1.0 equiv.), triethylamine (2.0 equiv.) and titanium tetrachloride (1.0 equiv.) were added to DCM, and the mixture was refluxed until complete consumption of the starting material (monitored by TLC). Then, directly purified by flash column chromatography on silica gel using petroleum ether (PE) and ethyl acetate (EA) (20/1 to 10/1 v/v) as eluents to afford the pure products **2l**.

4-methyl-N-((1*Z*,2*E*)-4-oxo-1,4-diphenylbut-2-en-1-ylidene)benzenesulfonamide (2l)



The residue was purified by a silica gel flash chromatography (PE/EA = 20/1 to 10/1 v/v) giving the product **2l** as a yellow oil in 56% yield (452 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.04 – 7.99 (m, 1H), 7.92 – 7.91 (m, 2H), 7.87 – 7.82 (m, 2H), 7.78 – 7.67 (m, 2H), 7.43 (t, *J* = 7.8 Hz, 2H), 7.38 (t, *J* = 7.8 Hz, 3H), 7.26 (d, *J* = 8.4 Hz, 2H), 7.16 (d, *J* = 16.2 Hz, 1H), 2.36 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 189.6, 144.0, 137.8, 136.5, 133.8, 129.6, 129.1, 128.9, 128.8, 127.5, 21.6. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{23}H_{19}NNaO_3S^+$ 412.0978, found 412.0977.

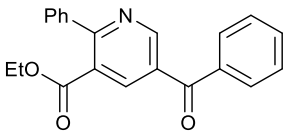
3. General Procedure for the Synthesis of 3 and Characterization Data



1 2 3

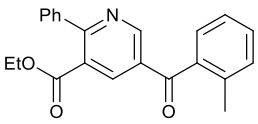
1 (0.12 mmol), **2** (0.1 mmol) and DABCO (3.0 equiv.) were dissolved in toluene (1.0 mL), and the mixture was stirred at 110 ℃ until complete consumption of the starting material (monitored by TLC). Saturated brine was added to terminate the reaction, and the reaction liquid was extracted with DCM (3 × 10 mL). Separated and combined with organic phase, washed with saturated brine, dried and filtered on sodium sulfate, and concentrated filtrate under reduced pressure. Then, directly purified by flash column chromatography on silica gel using petroleum ether (PE) and ethyl acetate (EA) (30/1 to 15/1 v/v) as eluents to afford the pure products **3**.

ethyl 5-benzoyl-2-phenylnicotinate (3a)



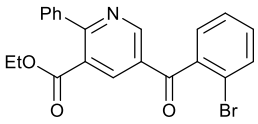
The residue was purified by a silica gel flash chromatography (PE/EA = 30/1 to 15/1 v/v) giving the product **3a** as a white solid in 96% yield (31.8 mg), m.p. 123.7-127.5 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.13 (d, *J* = 2.4 Hz, 1H), 8.50 (d, *J* = 2.4 Hz, 1H), 7.88 – 7.84 (m, 2H), 7.69 – 7.64 (m, 1H), 7.64 – 7.60 (m, 2H), 7.55 (t, *J* = 7.8 Hz, 2H), 7.49 – 7.45 (m, 3H), 4.20 (q, *J* = 7.2 Hz, 2H), 1.09 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 191.8, 165.5, 159.4, 149.9, 137.2, 137.1, 134.6, 131.4, 128.9, 128.0, 127.5, 126.8, 126.8, 126.3, 125.3, 59.9, 11.7. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{21}H_{17}NO_3^+$ 332.1281, found 332.1285.

ethyl 5-(2-methylbenzoyl)-2-phenylnicotinate (3b)



The residue was purified by a silica gel flash chromatography (PE/EA = 30/1 to 15/1 v/v) giving the product **3b** as a white solid in 89% yield (30.8 mg), m.p. 125.1-128.5 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.00 (d, *J* = 2.4 Hz, 1H), 8.41 (d, *J* = 2.4 Hz, 1H), 7.54 – 7.51 (m, 2H), 7.41 – 7.37 (m, 4H), 7.29 (dd, *J* = 18.6, 7.2 Hz, 2H), 7.22 (t, *J* = 7.8 Hz, 1H), 4.11 (q, *J* = 7.2 Hz, 2H), 2.35 (s, 3H), 1.00 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 195.8, 167.6, 161.8, 152.3, 139.1, 139.0, 137.6, 136.9, 131.6, 131.4, 131.1, 129.6, 129.1, 128.7, 128.3, 127.5, 125.6, 61.9, 20.3, 13.7. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{22}H_{19}NNaO_3^+$ 368.1257, found 368.1267.

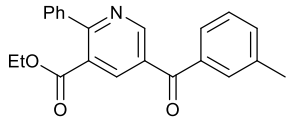
ethyl 5-(2-bromobenzoyl)-2-phenylnicotinate (3c)



The residue was purified by a silica gel flash chromatography (PE/EA = 30/1 to 15/1 v/v) giving the product **3c** as a white solid in 78% yield (32.1 mg), m.p. 102.0-106.1 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.06 (d, *J* = 1.8 Hz, 1H), 8.49 (d, *J* = 2.4 Hz, 1H), 7.71 – 7.69 (m, 1H), 7.63 – 7.59 (m, 2H), 7.50 – 7.44 (m, 4H), 7.43 – 7.41 (m, 2H),

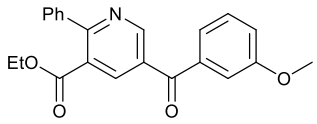
4.19 (q, J = 7.2 Hz, 2H), 1.08 (t, J = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 192.7, 166.6, 161.4, 151.6, 138.3, 138.2, 138.0, 132.7, 131.2, 128.8, 128.6, 128.4, 127.9, 127.4, 126.8, 126.7, 118.7, 61.1, 12.8. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{21}H_{16}BrNNaO_3^+$ 432.0206, found 432.0216.

ethyl 5-(3-methylbenzoyl)-2-phenylnicotinate (3d)



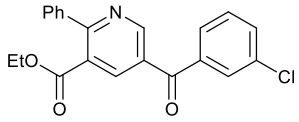
The residue was purified by a silica gel flash chromatography (PE/EA = 30/1 to 15/1) giving the product **3d** as a white solid in 76% yield (26.3 mg), m.p. 125.3-128.8 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.11 (d, J = 2.4 Hz, 1H), 8.50 (d, J = 1.8 Hz, 1H), 7.68 (s, 1H), 7.64 – 7.60 (m, 3H), 7.48 – 7.46 (m, 4H), 7.42 (t, J = 7.2 Hz, 1H), 4.20 (q, J = 7.2 Hz, 2H), 2.45 (s, 3H), 1.09 (t, J = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 194.0, 167.5, 161.4, 151.9, 139.3, 139.1, 138.8, 136.6, 134.2, 131.1, 130.4, 129.4, 128.7, 128.6, 128.3, 127.3, 127.3, 61.9, 21.4, 13.7. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{22}H_{19}NNaO_3^+$ 368.1257, found 368.1267.

ethyl 5-(3-methoxybenzoyl)-2-phenylnicotinate (3e)



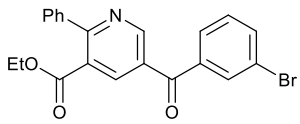
The residue was purified by a silica gel flash chromatography (PE/EA = 30/1 to 15/1) giving the product **3e** as a white solid in 96% yield (34.7 mg), m.p. 106.0-109.0°C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.13 (d, J = 2.4 Hz, 1H), 8.50 (d, J = 1.8 Hz, 1H), 7.64 – 7.60 (m, 2H), 7.49 – 7.46 (m, 3H), 7.44 (t, J = 7.8 Hz, 1H), 7.41 (dd, J = 2.4, 1.2 Hz, 1H), 7.38 (dt, J = 7.8, 1.2 Hz, 1H), 7.20 (ddd, J = 8.4, 3.0, 1.2 Hz, 1H), 4.20 (q, J = 7.2 Hz, 2H), 3.89 (s, 3H), 1.09 (t, J = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 192.2, 166.2, 160.1, 158.6, 150.5, 137.9, 137.8, 136.5, 129.6, 128.3, 128.1, 127.4, 127.0, 125.9, 121.5, 118.6, 112.7, 60.6, 54.2, 12.3. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{22}H_{20}NO_4^+$ 362.1387, found 362.1397.

ethyl 5-(3-chlorobenzoyl)-2-phenylnicotinate (3f)



The residue was purified by a silica gel flash chromatography (PE/EA = 30/1 to 15/1) giving the product **3f** as a white solid in 71% yield (26.0 mg), m.p. 122.7-126.7 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.11 (d, J = 2.4 Hz, 1H), 8.49 (d, J = 2.4 Hz, 1H), 7.85 (t, J = 1.8 Hz, 1H), 7.71 (dt, J = 7.8, 1.8 Hz, 1H), 7.66 – 7.60 (m, 3H), 7.52 – 7.44 (m, 4H), 4.21 (q, J = 7.2 Hz, 2H), 1.09 (t, J = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 192.4, 167.4, 161.8, 151.8, 139.1, 139.1, 138.1, 135.2, 133.4, 130.4, 130.1, 129.8, 129.6, 128.8, 128.4, 128.1, 127.4, 62.0, 13.7. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{21}H_{16}ClNNaO_3^+$ 388.0711, found 388.0717.

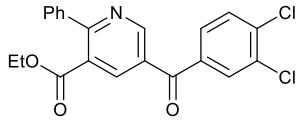
ethyl 5-(3-bromobenzoyl)-2-phenylnicotinate (3g)



The residue was purified by a silica gel flash chromatography (PE/EA = 30/1 to 15/1) giving the product **3g** as a white solid in 67% yield (27.5 mg), m.p. 133.4-136.0 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.11 (d, J = 2.4 Hz, 1H), 8.50 (d, J = 1.8 Hz, 1H), 8.01 (t, J = 1.8 Hz, 1H), 7.79 (ddd, J = 7.8, 2.4, 1.2 Hz, 1H), 7.76 (dt, J = 7.8, 1.2 Hz, 1H), 7.64 – 7.61 (m, 2H), 7.50 – 7.46 (m, 3H), 7.43 (t, J = 7.8 Hz, 1H), 4.21 (q, J

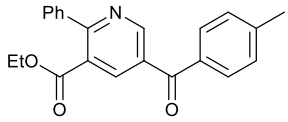
= 7.2 Hz, 2H), 1.10 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 192.3, 167.4, 161.8, 151.7, 139.1, 139.1, 138.3, 136.3, 132.7, 130.3, 130.3, 129.6, 128.8, 128.5, 128.4, 127.4, 123.1, 62.0, 13.7. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{21}H_{16}BrNNaO_3^+$ 432.0206, found 432.0213.

ethyl 5-(3,4-dichlorobenzoyl)-2-phenylnicotinate (3h)



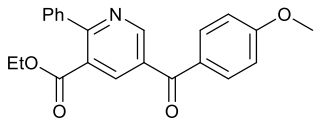
The residue was purified by a silica gel flash chromatography (PE/EA = 30/1 to 15/1) giving the product **3h** as a white solid in 80% yield (32.0 mg), m.p. 123.7-125.9 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.01 (d, *J* = 1.8 Hz, 1H), 8.40 (d, *J* = 2.4 Hz, 1H), 7.88 (d, *J* = 2.4 Hz, 1H), 7.59 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.56 – 7.52 (m, 3H), 7.42 – 7.36 (m, 3H), 4.13 (q, *J* = 7.2 Hz, 2H), 1.01 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 191.4, 167.3, 161.9, 151.5, 139.1, 138.9, 138.2, 136.1, 133.7, 131.7, 130.9, 130.1, 129.7, 128.9, 128.8, 128.4, 127.5, 62.0, 13.7. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{21}H_{15}Cl_2NNaO_3^+$ 422.0321, found 422.0325.

ethyl 5-(4-methylbenzoyl)-2-phenylnicotinate (3i)



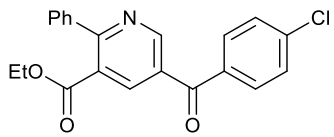
The residue was purified by a silica gel flash chromatography (PE/EA = 30/1 to 15/1) giving the product **3i** as a white solid in 78% yield (26.9 mg), m.p. 128.7-134.6 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.11 (d, *J* = 2.4 Hz, 1H), 8.48 (d, *J* = 1.8 Hz, 1H), 7.80 – 7.77 (m, 2H), 7.63 – 7.60 (m, 2H), 7.49 – 7.45 (m, 3H), 7.34 (d, *J* = 7.8 Hz, 2H), 4.20 (q, *J* = 7.2 Hz, 2H), 2.47 (s, 3H), 1.09 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 191.1, 165.3, 159.0, 149.5, 142.2, 137.0, 136.8, 131.6, 129.0, 128.0, 127.2, 127.1, 126.4, 126.0, 124.9, 59.6, 19.5, 11.4. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{22}H_{19}NNaO_3^+$ 368.1257, found 368.1265.

ethyl 5-(4-methoxybenzoyl)-2-phenylnicotinate (3j)



The residue was purified by a silica gel flash chromatography (PE/EA = 30/1 to 15/1) giving the product **3j** as a white solid in 89% yield (32.3 mg), m.p. 117.5-120.6 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.09 (d, *J* = 1.8 Hz, 1H), 8.46 (d, *J* = 1.8 Hz, 1H), 7.89 – 7.87 (m, 2H), 7.63 – 7.60 (m, 2H), 7.49 – 7.45 (m, 3H), 7.02 (dt, *J* = 9.0, 3.0 Hz, 2H), 4.20 (q, *J* = 7.2 Hz, 2H), 3.92 (s, 3H), 1.09 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 192.3, 167.6, 164.0, 161.0, 151.5, 139.3, 138.9, 132.6, 131.7, 129.4, 129.2, 128.7, 128.3, 127.2, 114.1, 61.9, 55.6, 13.7. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{22}H_{20}NO_4^+$ 362.1387, found 362.1396.

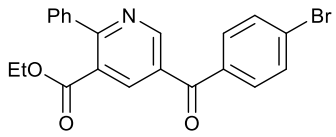
ethyl 5-(4-chlorobenzoyl)-2-phenylnicotinate (3k)



The residue was purified by a silica gel flash chromatography (PE/EA = 30/1 to 15/1) giving the product **3k** as a white solid in 90% yield (32.9 mg), m.p. 104.8-108.5 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.10 (d, *J* = 1.8 Hz, 1H), 8.47 (d, *J* = 2.4 Hz, 1H), 7.74 – 7.69 (m, 4H), 7.63 – 7.60 (m, 2H), 7.49 – 7.45 (m, 3H), 4.20 (q, *J* = 7.2 Hz, 2H), 1.09 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 191.8, 166.5, 160.7, 150.7, 138.2, 138.1, 134.3, 131.2, 130.5, 129.6, 128.6, 127.8,

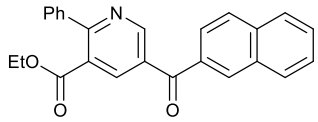
127.8, 127.4, 126.4, 61.0, 12.7. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{21}H_{17}ClNO_3^+$ 366.0891, found 366.0898.

ethyl 5-(4-bromobenzoyl)-2-phenylnicotinate (3l)



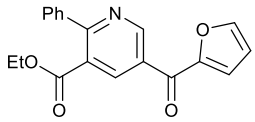
The residue was purified by a silica gel flash chromatography (PE/EA = 30/1 to 15/1) giving the product **3l** as a white solid in 82% yield (33.7 mg), m.p. 106.0-110.3 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.10 (d, *J* = 1.8 Hz, 1H), 8.46 (d, *J* = 1.8 Hz, 1H), 7.74 – 7.68 (m, 4H), 7.63 – 7.60 (m, 2H), 7.49 – 7.45 (m, 3H), 4.20 (q, *J* = 7.2 Hz, 2H), 1.09 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 192.7, 167.4, 161.7, 151.7, 139.1, 139.0, 135.3, 132.2, 131.4, 130.5, 129.6, 128.7, 128.7, 128.3, 127.4, 62.0, 13.7. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{21}H_{17}BrNO_3^+$ 410.0386, found 410.0392.

ethyl 5-(2-naphthoyl)-2-phenylnicotinate (3m)



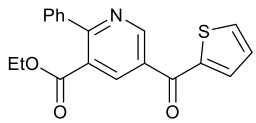
The residue was purified by a silica gel flash chromatography (PE/EA = 30/1 to 15/1) giving the product **3m** as a white solid in 87% yield (33.2 mg), m.p. 105.0-108.5 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.19 (d, *J* = 1.8 Hz, 1H), 8.57 (d, *J* = 1.8 Hz, 1H), 8.33 (s, 1H), 8.01 – 7.98 (m, 2H), 7.95 (t, *J* = 9.0 Hz, 2H), 7.67 – 7.64 (m, 3H), 7.61 – 7.58 (m, 1H), 7.50 – 7.47 (m, 3H), 4.21 (q, *J* = 7.2 Hz, 2H), 1.10 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 192.9, 166.7, 160.6, 151.0, 138.4, 138.4, 134.9, 133.0, 131.5, 131.5, 130.5, 128.8, 128.7, 128.1, 128.1, 128.0, 127.6, 127.1, 126.6, 126.4, 124.4, 61.1, 12.9. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{25}H_{19}NNaO_3^+$ 404.1257, found 404.1265.

ethyl 5-(furan-2-carbonyl)-2-phenylnicotinate (3n)



The residue was purified by a silica gel flash chromatography (PE/EA = 30/1 to 15/1) giving the product **3n** as a light brown solid in 84% yield (27.0 mg), m.p. 84.3-91.3 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.36 (d, *J* = 1.8 Hz, 1H), 8.70 (d, *J* = 2.4 Hz, 1H), 7.77 (d, *J* = 1.8 Hz, 1H), 7.64 – 7.60 (m, 2H), 7.50 – 7.45 (m, 3H), 7.41 (d, *J* = 3.6 Hz, 1H), 6.68 (dd, *J* = 3.6, 1.8 Hz, 1H), 4.21 (q, *J* = 7.2 Hz, 2H), 1.10 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 177.1, 165.4, 159.5, 150.0, 149.2, 145.6, 137.1, 136.6, 128.3, 127.3, 126.6, 126.2, 125.2, 118.8, 110.7, 59.8, 11.5. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{19}H_{16}NO_4^+$ 322.1074, found 322.1083.

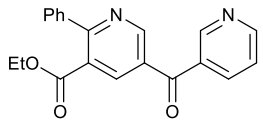
ethyl 2-phenyl-5-(thiophene-2-carbonyl)nicotinate (3o)



The residue was purified by a silica gel flash chromatography (PE/EA = 30/1 to 15/1) giving the product **3o** as a white solid in 84% yield (28.4 mg), m.p. 124.0-128.8 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.21 (t, *J* = 1.8 Hz, 1H), 8.55 (t, *J* = 1.8 Hz, 1H), 7.82 (d, *J* = 4.8 Hz, 1H), 7.72 (d, *J* = 3.6 Hz, 1H), 7.63 – 7.60 (m, 2H), 7.48 – 7.47 (m, 3H), 7.24 – 7.22 (m, 1H), 4.21 (qd, *J* = 7.2, 1.2 Hz, 2H), 1.09 (td, *J* = 7.2, 1.8 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 183.0, 165.4, 159.5, 148.9, 140.8, 137.2, 136.5, 133.5, 133.2, 129.5, 127.5, 126.7, 126.5, 126.3, 125.3, 59.9, 11.7. HRMS (ESI-TOF) m/z: $[M+Na]^+$

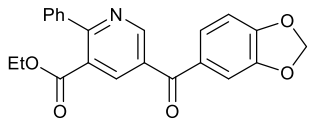
Calcd for $C_{19}H_{15}NNaO_3S^+$ 360.0665, found 360.0674.

ethyl 5-nicotinoyl-2-phenylnicotinate (3p)



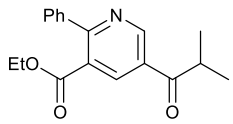
The residue was purified by a silica gel flash chromatography (PE/EA = 30/1 to 15/1) giving the product **3p** as a white solid in 91% yield (30.3 mg), m.p. 125.3-129.6 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.15 (d, *J* = 2.4 Hz, 1H), 9.08 (s, 1H), 8.89 (d, *J* = 3.0 Hz, 1H), 8.51 (d, *J* = 1.8 Hz, 1H), 8.18 (dt, *J* = 7.8, 1.8 Hz, 1H), 7.65 – 7.61 (m, 2H), 7.52 (dd, *J* = 7.8, 4.8 Hz, 1H), 7.50 – 7.46 (m, 3H), 4.21 (q, *J* = 7.2 Hz, 2H), 1.09 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 192.2, 167.3, 162.1, 153.7, 151.7, 150.8, 139.0, 139.0, 137.1, 132.2, 130.1, 129.7, 128.8, 128.4, 127.5, 123.7, 62.0, 13.7. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{20}H_{16}N_2NaO_3^+$ 355.1053, found 355.1058.

ethyl 5-(benzo[d][1,3]dioxole-5-carbonyl)-2-phenylnicotinate (3q)



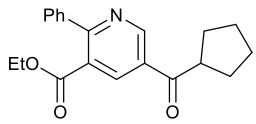
The residue was purified by a silica gel flash chromatography (PE/EA = 30/1 to 15/1) giving the product **3q** as a brown solid in 92% yield (34.6 mg), m.p. 97.0-98.3 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.99 (d, *J* = 2.4 Hz, 1H), 8.37 (d, *J* = 2.4 Hz, 1H), 7.56 – 7.50 (m, 2H), 7.43 – 7.37 (m, 3H), 7.35 – 7.31 (m, 2H), 6.85 – 6.81 (m, 1H), 6.02 (s, 2H), 4.12 (q, *J* = 7.2 Hz, 2H), 1.01 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 192.0, 167.5, 161.1, 152.4, 151.4, 148.5, 139.3, 138.9, 131.6, 131.0, 129.4, 128.7, 128.3, 127.2, 127.2, 109.5, 108.0, 102.2, 61.9, 13.7. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{22}H_{18}NO_5^+$ 376.1179, found 376.1187.

ethyl 5-isobutyryl-2-phenylnicotinate (3r)



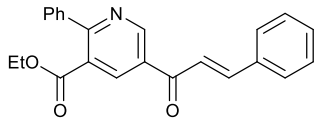
The residue was purified by a silica gel flash chromatography (PE/EA = 30/1 to 15/1) giving the product **3r** as a white solid in 78% yield (23.2 mg), m.p. 68.1-71.7 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.27 (d, *J* = 1.8 Hz, 1H), 8.59 (d, *J* = 2.4 Hz, 1H), 7.62 – 7.56 (m, 2H), 7.50 – 7.43 (m, 3H), 4.20 (q, *J* = 7.2 Hz, 2H), 3.56 (hept, *J* = 7.2 Hz, 1H), 1.29 (s, 3H), 1.27 (s, 3H), 1.09 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 202.2, 167.6, 161.8, 150.7, 139.2, 137.7, 129.4, 129.1, 128.7, 128.3, 127.5, 61.9, 36.2, 18.8, 13.7. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{18}H_{20}NO_3^+$ 298.1438, found 298.1436.

ethyl 5-(cyclopentanecarbonyl)-2-phenylnicotinate (3s)



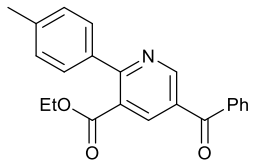
The residue was purified by a silica gel flash chromatography (PE/EA = 30/1 to 15/1) giving the product **3s** as a white solid in 63% yield (20.4 mg), m.p. 87.7-91.8 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.29 (d, *J* = 1.8 Hz, 1H), 8.60 (d, *J* = 1.8 Hz, 1H), 7.61 – 7.57 (m, 2H), 7.48 – 7.44 (m, 3H), 4.20 (q, *J* = 7.2 Hz, 2H), 3.73 (tt, *J* = 8.4, 7.2 Hz, 1H), 2.02 – 1.93 (m, 4H), 1.79 – 1.67 (m, 4H), 1.09 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 200.5, 167.7, 161.7, 150.9, 139.3, 137.8, 129.8, 129.4, 128.7, 128.3, 127.4, 61.9, 46.9, 29.7, 26.3, 13.7. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{20}H_{22}NO_3^+$ 324.1594, found 324.1604.

ethyl 5-cinnamoyl-2-phenylnicotinate (3t)



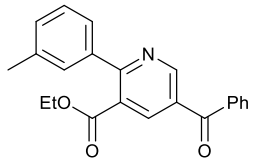
The residue was purified by a silica gel flash chromatography (PE/EA = 30/1 to 15/1) giving the product **3t** as a white solid in 84% yield (30.0 mg), m.p. 149.1-151.1 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.28 (d, *J* = 1.8 Hz, 1H), 8.59 (d, *J* = 2.4 Hz, 1H), 7.83 (d, *J* = 15.6 Hz, 1H), 7.63 – 7.59 (m, 2H), 7.56 – 7.52 (m, 2H), 7.46 (d, *J* = 21 Hz, 1H), 7.42 – 7.35 (m, 6H), 4.14 (q, *J* = 7.2 Hz, 2H), 1.02 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 186.5, 166.2, 160.3, 149.4, 145.0, 137.8, 136.4, 132.9, 129.8, 129.8, 128.0, 127.7, 127.3, 127.3, 126.9, 126.1, 119.6, 60.5, 12.3. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{23}H_{19}NNaO_3^+$ 380.1257, found 380.1258.

ethyl 5-benzoyl-2-(*p*-tolyl)nicotinate (3u)



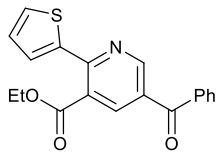
The residue was purified by a silica gel flash chromatography (PE/EA = 30/1 to 15/1) giving the product **3u** as a white solid in 82% yield (28.3 mg), m.p. 134.9-137.6 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.11 (d, *J* = 1.8 Hz, 1H), 8.47 (d, *J* = 2.4 Hz, 1H), 7.88 – 7.84 (m, 2H), 7.66 (t, *J* = 7.2 Hz, 1H), 7.57 – 7.51 (m, 4H), 7.28 (d, *J* = 7.8 Hz, 2H), 4.23 (q, *J* = 7.2 Hz, 2H), 2.43 (s, 3H), 1.14 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 192.3, 166.2, 159.9, 150.3, 138.2, 137.5, 135.1, 134.7, 131.8, 129.1, 128.5, 127.5, 127.2, 125.6, 60.4, 19.9, 12.2. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{22}H_{20}NO_3^+$ 346.1438, found 346.1446.

ethyl 5-benzoyl-2-(*m*-tolyl)nicotinate (3v)



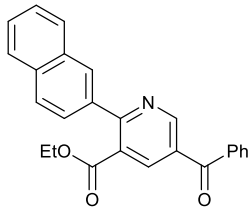
The residue was purified by a silica gel flash chromatography (PE/EA = 30/1 to 15/1) giving the product **3v** as a white solid in 77% yield (26.6 mg), m.p. 101.6-104.8 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.12 (d, *J* = 1.8 Hz, 1H), 8.48 (d, *J* = 1.8 Hz, 1H), 7.88 – 7.84 (m, 2H), 7.69 – 7.63 (m, 1H), 7.58 – 7.52 (m, 2H), 7.47 (t, *J* = 1.8 Hz, 1H), 7.40 – 7.38 (m, 1H), 7.35 (t, *J* = 7.2 Hz, 1H), 7.31 – 7.27 (m, 1H), 4.21 (q, *J* = 7.2 Hz, 2H), 2.43 (s, 3H), 1.11 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 192.2, 166.1, 160.0, 150.3, 137.5, 137.5, 136.5, 135.0, 131.8, 129.3, 128.7, 128.4, 127.8, 127.2, 126.6, 125.8, 124.3, 60.3, 19.9, 12.1. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{22}H_{20}NO_3^+$ 346.1438, found 346.1448.

ethyl 5-benzoyl-2-(thiophen-2-yl)nicotinate (3w)



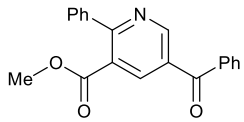
The residue was purified by a silica gel flash chromatography (PE/EA = 30/1 to 15/1) giving the product **3w** as a white solid in 96% yield (32.4 mg), m.p. 112.4-117.6 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.00 (d, *J* = 2.4 Hz, 1H), 8.35 (d, *J* = 2.4 Hz, 1H), 7.86 – 7.81 (m, 2H), 7.68 – 7.63 (m, 1H), 7.57 – 7.51 (m, 4H), 7.13 (dd, *J* = 4.8, 3.6 Hz, 1H), 4.40 (q, *J* = 7.2 Hz, 2H), 1.33 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 193.4, 167.8, 152.9, 151.7, 141.9, 138.8, 136.6, 133.3, 130.5, 130.1, 129.9, 129.2, 128.8, 128.2, 125.6, 62.3, 14.0. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{19}H_{16}NO_3S^+$ 338.0845, found 338.0836.

ethyl 5-benzoyl-2-(naphthalen-2-yl)nicotinate (3x)



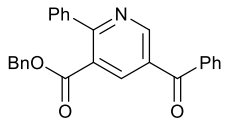
The residue was purified by a silica gel flash chromatography (PE/EA = 30/1 to 15/1) giving the product **3x** as a brown solid in 80% yield (30.4 mg), m.p. 119.7-120.7 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.18 (d, *J* = 1.8 Hz, 1H), 8.55 (d, *J* = 1.8 Hz, 1H), 8.16 (d, *J* = 1.8 Hz, 1H), 7.95 – 7.86 (m, 5H), 7.73 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.67 (td, *J* = 7.2, 1.8 Hz, 1H), 7.59 – 7.50 (m, 4H), 4.19 (q, *J* = 7.2 Hz, 2H), 1.02 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 193.8, 167.7, 161.2, 152.0, 139.3, 136.6, 136.5, 133.7, 133.4, 133.0, 130.9, 130.0, 128.8, 128.8, 128.7, 128.0, 127.8, 127.5, 127.1, 126.5, 126.1, 62.0, 13.7. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{25}H_{19}NNaO_3^+$ 404.1257, found 404.1266.

methyl 5-benzoyl-2-phenylnicotinate (3y)



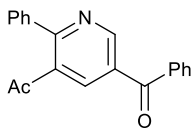
The residue was purified by a silica gel flash chromatography (PE/EA = 30/1 to 15/1) giving the product **3y** as a white solid in 73% yield (23.1 mg), m.p. 126.7-131.8 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.14 (d, *J* = 2.4 Hz, 1H), 8.50 (d, *J* = 2.4 Hz, 1H), 7.88 – 7.83 (m, 2H), 7.69 – 7.65 (m, 1H), 7.65 – 7.60 (m, 2H), 7.55 (t, *J* = 7.8 Hz, 2H), 7.50 – 7.46 (m, 3H), 3.74 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 193.7, 167.9, 161.4, 152.0, 139.2, 139.0, 136.5, 133.4, 130.9, 130.0, 129.6, 128.8, 128.7, 128.4, 126.8, 52.7. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{20}H_{16}NO_3^+$ 318.1125, found 318.1133.

benzyl 5-benzoyl-2-phenylnicotinate (3z)



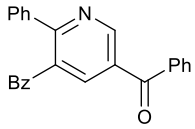
The residue was purified by a silica gel flash chromatography (PE/EA = 30/1 to 15/1) giving the product **3z** as a white solid in 61% yield (24.1 mg), m.p. 107.1-108.5 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.12 (d, *J* = 2.4 Hz, 1H), 8.51 (d, *J* = 1.8 Hz, 1H), 7.87 – 7.83 (m, 2H), 7.68 – 7.63 (m, 1H), 7.61 – 7.57 (m, 2H), 7.54 (t, *J* = 7.8 Hz, 2H), 7.47 – 7.43 (m, 1H), 7.43 – 7.38 (m, 2H), 7.32 – 7.25 (m, 3H), 7.11 – 7.03 (m, 2H), 5.17 (s, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 191.5, 165.3, 159.2, 149.8, 137.0, 136.9, 134.4, 132.4, 131.3, 128.7, 127.8, 127.4, 126.7, 126.6, 126.6, 126.4, 126.4, 126.3, 126.3, 124.8, 65.6. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{26}H_{20}NO_3^+$ 394.1438, found 394.1435.

1-(5-benzoyl-2-phenylpyridin-3-yl)ethan-1-one (3aa)



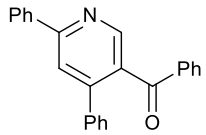
The residue was purified by a silica gel flash chromatography (PE/EA = 30/1 to 15/1 v/v) giving the product **3aa** as a white oil in 68% yield (20.5 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.06 (d, *J* = 2.4 Hz, 1H), 8.19 (d, *J* = 2.4 Hz, 1H), 7.78 (d, *J* = 7.2 Hz, 2H), 7.58 (t, *J* = 1.8 Hz, 3H), 7.49 – 7.42 (m, 5H), 2.06 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 201.3, 192.4, 158.2, 150.1, 137.2, 136.1, 135.0, 134.4, 132.0, 129.8, 128.8, 128.5, 127.8, 127.5, 127.3, 28.8. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{20}H_{16}NO_2^+$ 302.1176, found 302.1171.

(2-phenylpyridine-3,5-diyl)bis(phenylmethanone) (3bb)



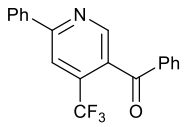
The residue was purified by a silica gel flash chromatography (PE/EA = 30/1 to 15/1 v/v) giving the product **3bb** as a yellow oil in 89% yield (34.7 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.14 (d, J = 2.4 Hz, 1H), 8.19 (d, J = 2.4 Hz, 1H), 7.81 (d, J = 6.6 Hz, 2H), 7.61 – 7.54 (m, 3H), 7.53 – 7.52 (m, 2H), 7.47 (t, J = 7.8 Hz, 2H), 7.40 (t, J = 7.8 Hz, 1H), 7.25 (t, J = 8.4 Hz, 2H), 7.23 – 7.20 (m, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 196.3, 193.9, 160.1, 151.6, 138.4, 138.2, 136.5, 136.1, 134.1, 133.8, 133.4, 130.9, 130.1, 130.0, 129.9, 129.7, 129.4, 128.8, 128.7, 128.6, 128.6. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{25}H_{18}NO_2^+$ 364.1332, found 364.1335.

(4,6-diphenylpyridin-3-yl)(phenyl)methanone (3cc)



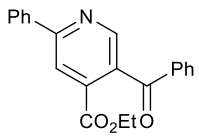
The residue was purified by a silica gel flash chromatography (PE/EA = 30/1 to 15/1 v/v) giving the product **3cc** as a white solid in 76% yield (25.6 mg), m.p. 129.1-130.3 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.82 (s, 1H), 8.14 – 8.09 (m, 2H), 7.85 (s, 1H), 7.73 – 7.68 (m, 2H), 7.55 – 7.50 (m, 2H), 7.50 – 7.43 (m, 2H), 7.36 – 7.33 (m, 2H), 7.32 (t, J = 7.8 Hz, 2H), 7.29 – 7.25 (m, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 196.6, 159.0, 149.8, 149.7, 138.5, 137.9, 137.1, 133.3, 132.6, 129.9, 129.7, 129.1, 129.0, 129.0, 128.9, 128.7, 128.7, 128.6, 128.3, 127.2, 121.0. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{24}H_{18}NO^+$ 336.1383, found 336.1383.

phenyl(6-phenyl-4-(trifluoromethyl)pyridin-3-yl)methanone (3dd)



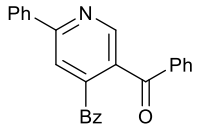
The residue was purified by a silica gel flash chromatography (PE/EA = 30/1 to 15/1 v/v) giving the product **3dd** as a white solid in 66% yield (21.7 mg), m.p. 91.2-95.7 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.78 (s, 1H), 8.12 – 8.07 (m, 3H), 7.87 – 7.83 (m, 2H), 7.69 – 7.63 (m, 1H), 7.56 – 7.54 (m, 1H), 7.54 – 7.52 (m, 2H), 7.49 – 7.52 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 193.4, 159.7, 149.4, 137.3 (q, $J_{C,F}$ = 34.5 Hz)137.2, 136.3, 134.4, 130.5, 130.2, 129.1, 128.8, 127.2, 122.5(q, $J_{C,F}$ = 273 Hz) 116.8(q, $J_{C,F}$ = 4.5 Hz). HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{19}H_{13}F_3NO^+$ 328.0944, found 328.0953.

ethyl 5-benzoyl-2-phenylisonicotinate (3ee)



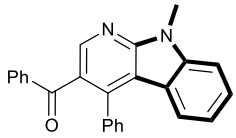
The residue was purified by a silica gel flash chromatography (PE/EA = 30/1 to 15/1 v/v) giving the product **3ee** as a white solid in 74% yield (24.5 mg), m.p. 97.5-98.7 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.73 (s, 1H), 8.20 (s, 1H), 8.07 – 8.02 (m, 2H), 7.77 – 7.73 (m, 2H), 7.57 – 7.51 (m, 1H), 7.50 – 7.37 (m, 5H), 4.06 (q, J = 7.2 Hz, 2H), 1.01 (t, J = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 194.8, 165.1, 159.6, 149.2, 138.4, 137.7, 137.1, 133.6, 132.9, 130.1, 129.4, 129.0, 128.8, 127.2, 119.6, 62.4, 13.5. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{21}H_{18}NO_3^+$ 332.1281, found 332.1280.

(6-phenylpyridine-3,4-diyl)bis(phenylmethanone) (3ff)



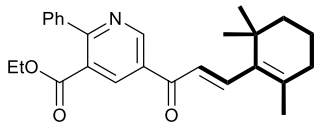
The residue was purified by a silica gel flash chromatography (PE/EA = 30/1 to 15/1 v/v) giving the product **3ff** as a white solid in 70% yield (25.3 mg), m.p. 397.5-400.2 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.93 (s, 1H), 8.04 – 8.02 (m, 2H), 7.82 (s, 1H), 7.69 (d, *J* = 6.6 Hz, 3H), 7.54 – 7.48 (m, 2H), 7.53 – 7.49 m, 3H), 7.38 – 7.34 (m, 4H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 195.3, 194.1, 159.9, 151.0, 149.3, 137.6, 136.8, 136.0, 133.8, 133.5, 131.3, 130.4, 130.0, 129.7, 129.1, 128.7, 128.6, 127.4, 119.1. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{25}H_{18}NO_2^+$ 364.1332, found 364.1336.

(9-methyl-4-phenyl-9*H*-pyrido[2,3-*b*]indol-3-yl)(phenyl)methanone (3gg)



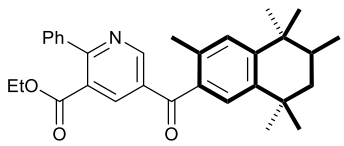
The residue was purified by a silica gel flash chromatography (PE/EA = 30/1 to 15/1 v/v) giving the product **3gg** as a yellow solid in 73% yield (26.4 mg), m.p. 184.0-189.2 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.67 (s, 1H), 7.70 – 7.66 (m, 2H), 7.52 – 7.47 (m, 2H), 7.47 – 7.43 (m, 1H), 7.42 – 7.39 (m, 2H), 7.39 – 7.35 (m, 3H), 7.32 (t, *J* = 7.8 Hz, 2H), 7.26 – 7.23 (m, 1H), 7.07 – 7.02 (m, 1H), 4.05 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 195.2, 150.9, 145.4, 143.2, 139.3, 137.1, 134.9, 131.0, 128.3, 127.3, 126.8, 126.8, 126.5, 125.6, 125.3, 121.3, 118.8, 118.7, 112.4, 107.6, 26.3. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{25}H_{19}N_2O^+$ 363.1492, found 363.1494.

ethyl (*E*)-2-phenyl-5-(3-(2,6,6-trimethylcyclohex-1-en-1-yl)acryloyl)nicotinate (3hh)



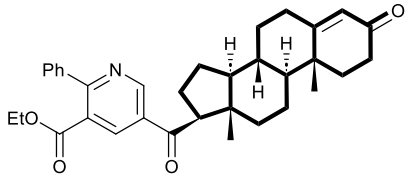
The residue was purified by a silica gel flash chromatography (PE/EA = 30/1 to 15/1 v/v) giving the product **3hh** as a white solid in 66% yield (26.6 mg), m.p. 191.1-193.3 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.20 (d, *J* = 2.4 Hz, 1H), 8.52 (d, *J* = 1.8 Hz, 1H), 7.61 (d, *J* = 16.2 Hz, 1H), 7.54 – 7.51 (m, 2H), 7.40 – 7.36 (m, 3H), 6.87 (d, *J* = 16.2 Hz, 1H), 4.13 (q, *J* = 7.2 Hz, 2H), 2.07 (t, *J* = 6.6 Hz, 2H), 1.81 (s, 3H), 1.61 – 1.56 (m, 2H), 1.47 – 1.41 (m, 2H), 1.23 – 1.11 (m, 1H), 1.08 (s, 5H), 1.02 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 188.2, 167.7, 161.4, 150.7, 146.1, 139.3, 139.0, 137.8, 136.7, 131.5, 129.4, 128.7, 128.3, 127.4, 125.1, 61.9, 39.9, 34.2, 34.0, 28.9, 22.1, 18.8, 13.7. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{26}H_{30}NO_3^+$ 404.2220, found 404.2227.

ethyl (*S*)-5-(3,5,5,6,8,8-hexamethyl-5,6,7,8-tetrahydronaphthalene-2-carbonyl)-2-phenylnicotinate (3ii)



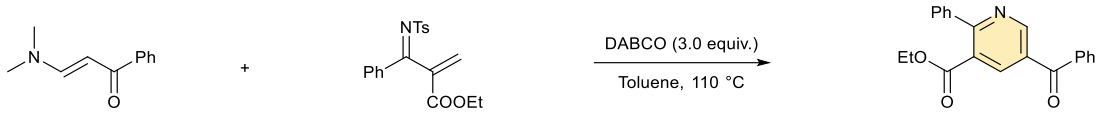
The residue was purified by a silica gel flash chromatography (PE/EA = 30/1 to 15/1 v/v) giving the product **3ii** as a yellow solid in 94% yield (44.1 mg), m.p. 105.1-108.3 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.11 (d, *J* = 2.4 Hz, 1H), 8.51 (d, *J* = 1.8 Hz, 1H), 7.59 – 7.64 (m, 2H), 7.49 – 7.43 (m, 3H), 7.34 (s, 1H), 7.31 (s, 1H), 4.19 (q, *J* = 7.2 Hz, 2H), 2.42 (s, 3H), 1.93 – 1.87 (m, 1H), 1.69 – 1.61 (m, 1H), 1.42 – 1.38 (m, 1H), 1.37 (s, 3H), 1.25 (s, 3H), 1.23 (s, 3H), 1.11 (s, 3H), 1.09 (t, *J* = 7.2 Hz, 3H), 1.01 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 193.8, 166.0, 159.9, 150.9, 148.5, 140.5, 137.7, 137.6, 133.3, 132.2, 129.9, 128.8, 127.8, 127.1, 127.0, 126.7, 125.7, 60.2, 41.8, 36.4, 32.8, 32.5, 30.7, 30.3, 26.8, 23.2, 18.6, 15.2, 12.1. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{31}H_{36}NO_3^+$ 470.2690, found 470.2699.

ethyl 5-((9S,14S,17S)-10,13-dimethyl-3-oxo-2,3,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthrene-17-carbonyl)-2-phenylnicotinate (3jj)



The residue was purified by a silica gel flash chromatography (PE/EA = 30/1 to 15/1 v/v) giving the product **3jj** as a white solid in 84% yield (44.2 mg), m.p. 187.1-189.2 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.21 (d, *J* = 1.8 Hz, 1H), 8.54 (d, *J* = 1.8 Hz, 1H), 7.60 – 7.55 (m, 2H), 7.47 – 7.43 (m, 3H), 5.73 (d, *J* = 1.8 Hz, 1H), 4.20 (q, *J* = 7.2 Hz, 2H), 3.50 (t, *J* = 8.4 Hz, 1H), 2.52 – 2.46 (m, 1H), 2.44 – 2.36 (m, 2H), 2.35 – 2.27 (m, 2H), 1.98 (ddd, *J* = 13.2, 4.8, 3.0 Hz, 1H), 1.93 – 1.87 (m, 1H), 1.87 – 1.81 (m, 2H), 1.72 – 1.65 (m, 2H), 1.61 (qd, *J* = 10.2, 3.0 Hz, 1H), 1.57 – 1.52 (m, 2H), 1.48 – 1.42 (m, 1H), 1.41 – 1.36 (m, 2H), 1.36 – 1.31 (m, 1H), 1.15 (s, 3H), 1.08 (t, *J* = 7.2 Hz, 3H), 1.00 (ddd, *J* = 12.6, 10.2, 3.6 Hz, 1H), 0.69 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 198.4, 198.4, 169.7, 166.7, 160.7, 149.7, 138.2, 136.7, 130.8, 128.5, 127.7, 127.3, 126.3, 123.0, 60.9, 56.9, 55.5, 52.6, 44.4, 38.2, 37.6, 34.8, 34.7, 32.9, 31.8, 31.0, 23.7, 22.7, 20.0, 16.4, 12.8, 12.7. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{34}H_{40}NO_4^+$ 526.2952, found 526.2949.

4. Mmol-Scale Synthesis of Compound 3a



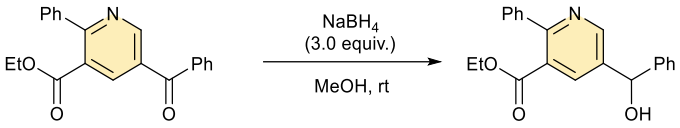
1a
526 mg, 3 mmol

2a
894 mg, 2.5 mmol

3a
305 mg, 92% yield

(*E*)-3-(dimethylamino)-1-phenylprop-2-en-1-one **1a** (3.0 mmol, 526 mg) and ethyl (*Z*)-2-(phenyl(tosylimino)methyl)acrylate **2a** (2.5 mmol, 894 mg), DABCO (3.0 equiv.) were dissolved in toluene (10.0 mL), and the mixture was stirred at 110 ℃ until complete consumption of the starting material (monitored by TLC). Saturated brine was added to terminate the reaction, and the reaction liquid was extracted with DCM (3 × 100 mL). Separated and combined with organic phase, washed with saturated brine, dried and filtered on sodium sulfate, and concentrated filtrate under reduced pressure. Then, directly purified by flash column chromatography on silica gel using petroleum ether (PE) and ethyl acetate (EA) (30/1 to 15/1 v/v) as eluents to afford the pure products **3a** as a white solid in 92% yield (305.0 mg).

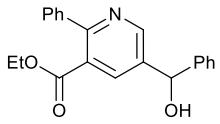
5. Synthesis of 4 and Characterization Data



3a **4**, 94% yield

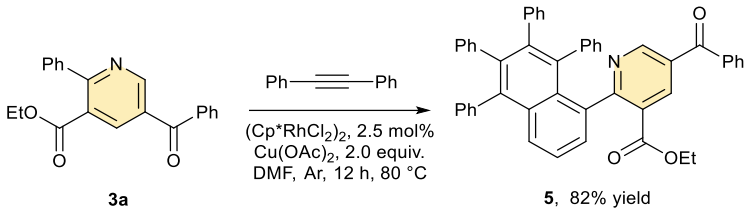
Dissolved compound **3a** (33.1 mg, 0.10 mmol, 1.0 equiv.) in anhydrous methanol (4.0 mL), a solution of sodium borohydride in methanol (11.3 mg, 3.0 equiv.) was added. The solution was stirred at room temperature. When TLC indicated complete consumption of the starting material, saturated brine was added to terminate the reaction, and the reaction liquid was extracted with DCM (3 × 10 mL). Separated and combined with organic phase, washed with saturated brine, dried and filtered on sodium sulfate, and concentrated filtrate under reduced pressure. Then, directly purified by flash column chromatography on silica gel using petroleum ether (PE) and ethyl acetate (EA) (30/1 to 15/1 v/v) as eluents to give compound **4** (31.3 mg, 94% yield) as a yellow solid.

ethyl 5-(hydroxy(phenyl)methyl)-2-phenylnicotinate (4)



The residue was purified by a silica gel flash chromatography (PE/EA = 30/1 to 15/1 v/v) giving the product **4** as a yellow solid in 94% yield (31.4 mg), m.p. 97.1-98.3 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.69 (d, *J* = 2.4 Hz, 1H), 8.06 (d, *J* = 2.4 Hz, 1H), 7.50 – 7.45 (m, 2H), 7.43 – 7.38 (m, 3H), 7.38 – 7.33 (m, 4H), 7.32 – 7.27 (m, 1H), 5.84 (s, 1H), 4.11 (q, *J* = 7.2 Hz, 2H), 1.00 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 167.5, 157.0, 148.8, 141.9, 139.1, 136.9, 135.2, 128.2, 127.9, 127.8, 127.5, 127.4, 126.4, 125.9, 72.9, 60.9, 12.9. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{21}H_{20}NO_3^+$ 334.1438, found 334.1445.

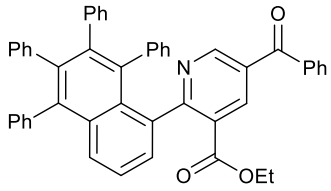
6. Synthesis of 5 and Characterization Data



3a **5**, 82% yield

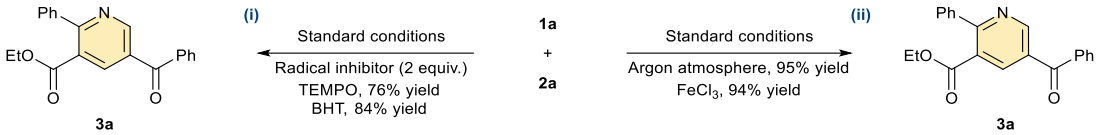
Dissolved compound **3a** (33.1 mg, 0.10 mmol, 1.0 equiv.) and diphenylacetylene (21.4 mg, 0.12mmol, 1.2 equiv.) in anhydrous *N*,*N*-dimethylformamide (4.0 mL). Bis[(pentamethylcyclopentadienyl)dichloro-rhodium] (2.5 mol%) and copper(II) acetate (2.0 equiv.) was added too. The whole reaction system is in argon atmosphere, and the solution was stirred at 80 ℃ for 12 h. When TLC indicated complete consumption of the starting material, saturated brine was added to terminate the reaction, and the reaction liquid was extracted with DCM (3 × 10 mL). Separated and combined with organic phase, washed with saturated brine, dried and filtered on sodium sulfate, and concentrated filtrate under reduced pressure. Then, directly purified by flash column chromatography on silica gel using petroleum ether (PE) and ethyl acetate (EA) (30/1 to 15/1 v/v) as eluents to give compound **5** (56.2 mg, 82% yield) as a light green solid.

ethyl 5-benzoyl-2-(5,6,7,8-tetraphenylnaphthalen-1-yl)nicotinate (5)



The residue was purified by a silica gel flash chromatography (PE/EA = 30/1 to 15/1 v/v) giving the product **5** as a light green solid in 82% yield (56.2 mg), m.p. 110.4-116.4 °C. ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.73 (d, J = 1.8 Hz, 1H), 8.05 (d, J = 1.8 Hz, 1H), 7.78 – 7.73 (m, 3H), 7.67 (t, J = 7.8 Hz, 2H), 7.57 (d, J = 8.4 Hz, 1H), 7.50 (t, J = 7.8 Hz, 1H), 7.35 – 7.26 (m, 3H), 7.26 – 7.21 (m, 3H), 6.92 – 6.83 (m, 4H), 6.82 – 6.78 (m, 2H), 6.77 – 6.68 (m, 7H), 6.67 – 6.63 (m, 2H), 4.06 (qt, J = 7.2, 3.6 Hz, 2H), 0.98 (t, J = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 193.5, 165.3, 164.6, 151.4, 141.2, 140.6, 140.6, 140.4, 140.0, 139.9, 139.2, 138.9, 138.7, 137.7, 136.5, 134.0, 133.2, 132.9, 131.6, 131.4, 131.2, 131.2, 130.4, 130.1, 129.9, 129.8, 129.4, 128.2, 128.1, 127.7, 127.1, 127.0, 126.9, 126.7, 126.6, 126.6, 126.0, 125.9, 125.6, 125.4, 125.3, 61.4, 13.9. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{49}H_{36}NO_3^+$ 686.2690, found 686.2693.

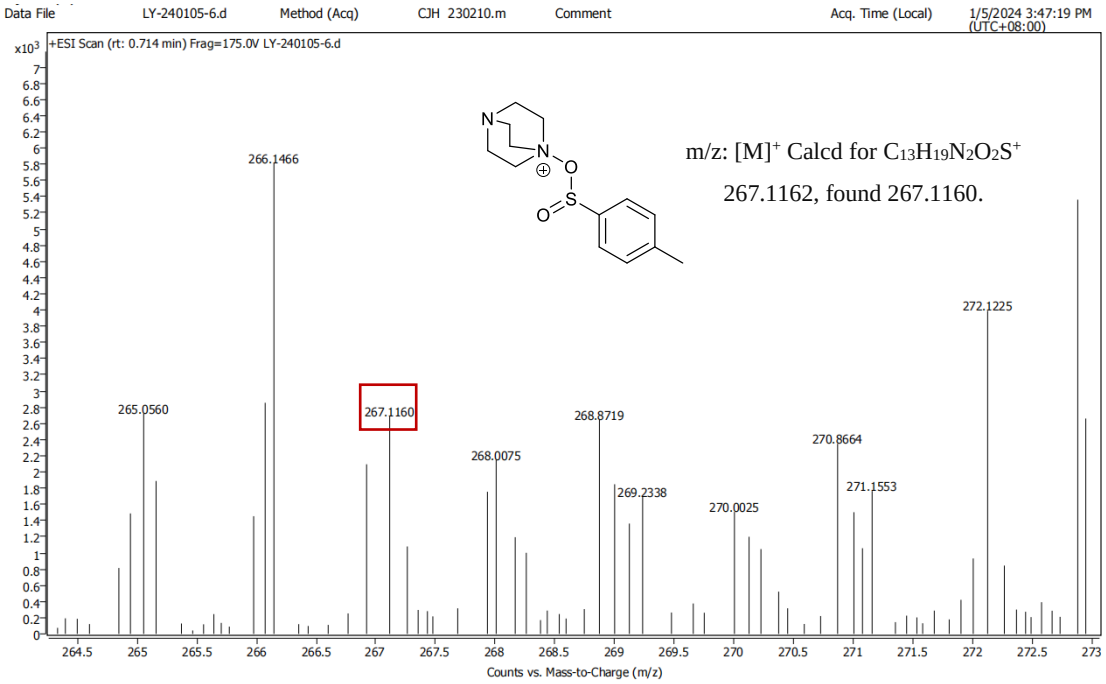
7. Control experiments

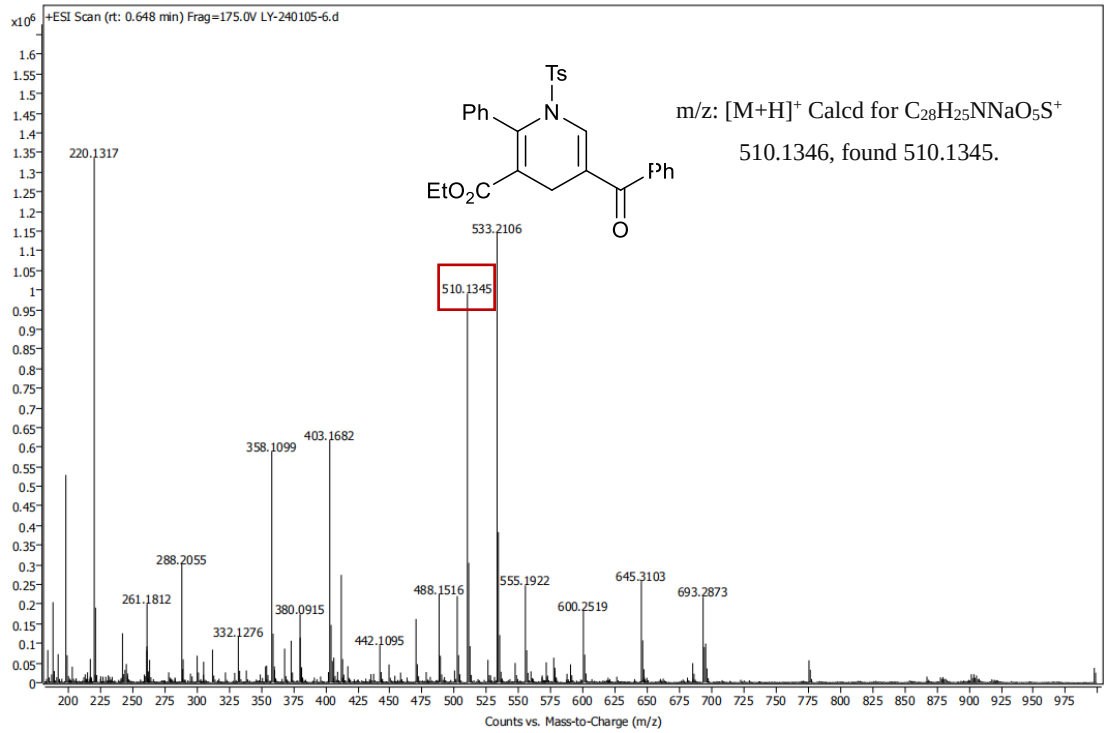


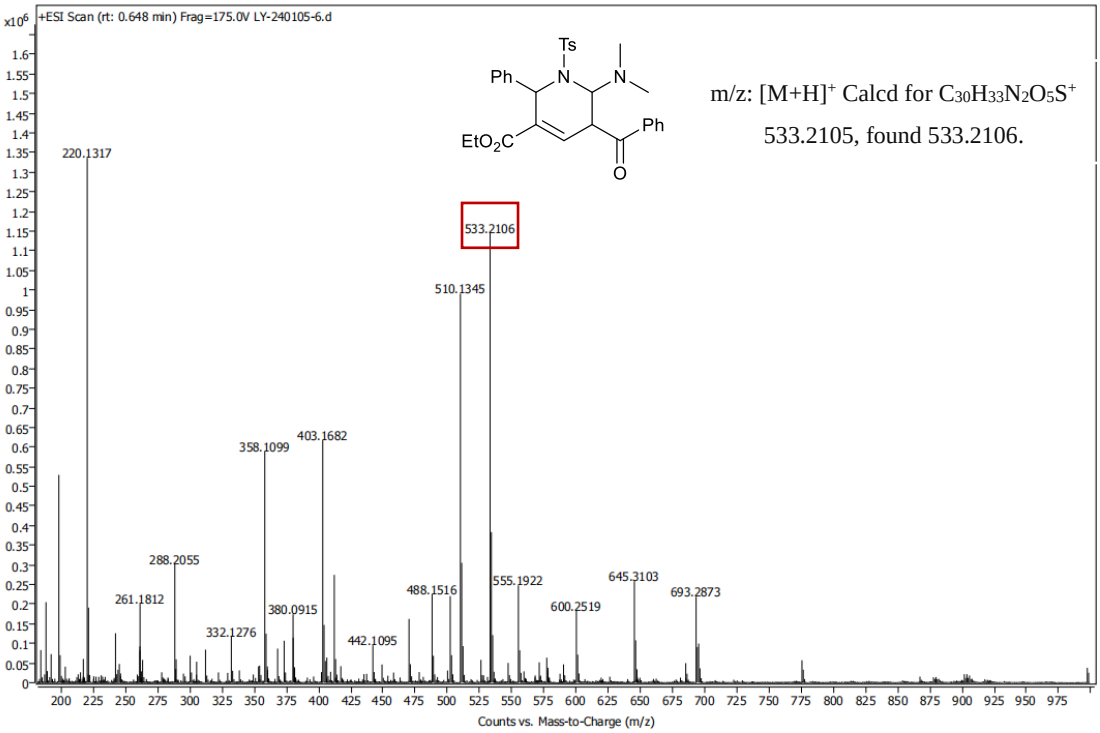
(i) (*E*)-3-(dimethylamino)-1-phenylprop-2-en-1-one **1a** (0.12 mmol, 21.0 mg) and ethyl (*Z*)-2-(phenyl(tosylimino)methyl)acrylate **2a** (0.1 mmol, 35.7mg), DABCO (3.0 equiv.) were dissolved in toluene (1.0 mL), then added TEMPO (2.0 equiv.) or BHT (2.0 equiv.), and the mixture was stirred at 110 ℃ until complete consumption of the starting material. Saturated brine was added to terminate the reaction, and the reaction liquid was extracted with DCM (3 × 10 mL). Separated and combined with organic phase, washed with saturated brine, dried and filtered on sodium sulfate, and concentrated filtrate under reduced pressure. Then, directly purified by flash column chromatography on silica gel using petroleum ether (PE) and ethyl acetate (EA) (30/1 to 15/1 v/v) as eluents to afford the pure products **3a** as a white solid in 76 % yield (25.3 mg, TEMPO) and 84% yield (27.8 mg, BHT).

(ii) (*E*)-3-(dimethylamino)-1-phenylprop-2-en-1-one **1a** (0.12 mmol, 21.0 mg) and ethyl (*Z*)-2-(phenyl(tosylimino)methyl)acrylate **2a** (0.1 mmol, 35.7mg), DABCO (3.0 equiv.) were dissolved in toluene (1.0 mL). The whole reaction system was in argon atmosphereand or in the presence of $FeCl_3$, and the mixture was stirred at 110 ℃ until complete consumption of the starting material. Saturated brine was added to terminate the reaction, and the reaction liquid ws extracted with DCM (3 × 10 mL). Separated and combined with organic phase, washed with saturated brine, dried and filtered on sodium sulfate, and concentrated filtrate under reduced pressure. Then, directly purified by flash column chromatography on silica gel using petroleum ether (PE) and ethyl acetate (EA) (30/1 to 15/1 v/v) as eluents to afford the pure products **3a** as a white solid in 95% yield (31.6 mg, in argon atmosphereand) and 94% yield 31.1 mg, in the presence of $FeCl_3$).

Mass spectrometry of intermediates.



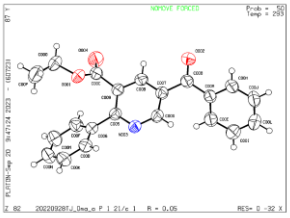




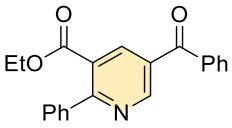
m/z: $[M+H]^+$ Calcd for $C_{30}H_{33}N_2O_5S^+$ 533.2105, found 533.2106.

8. X-ray Crystal Data of 3a

To a 10 mL tube containing **3a** (15.0 mg) was added a mixture of solvent (MeOH/DCM=10:1) (2.2 mL). A clear solution was obtained through ultrasound treatment and was kept at room temperature and the crystals were obtained after the solvent evaporated, which were characterized by X-ray single crystal diffraction. X-ray diffraction experiment was carried out on an Agilent Gemini and the data obtained were deposited at the Cambridge Crystallographic Data Centre.



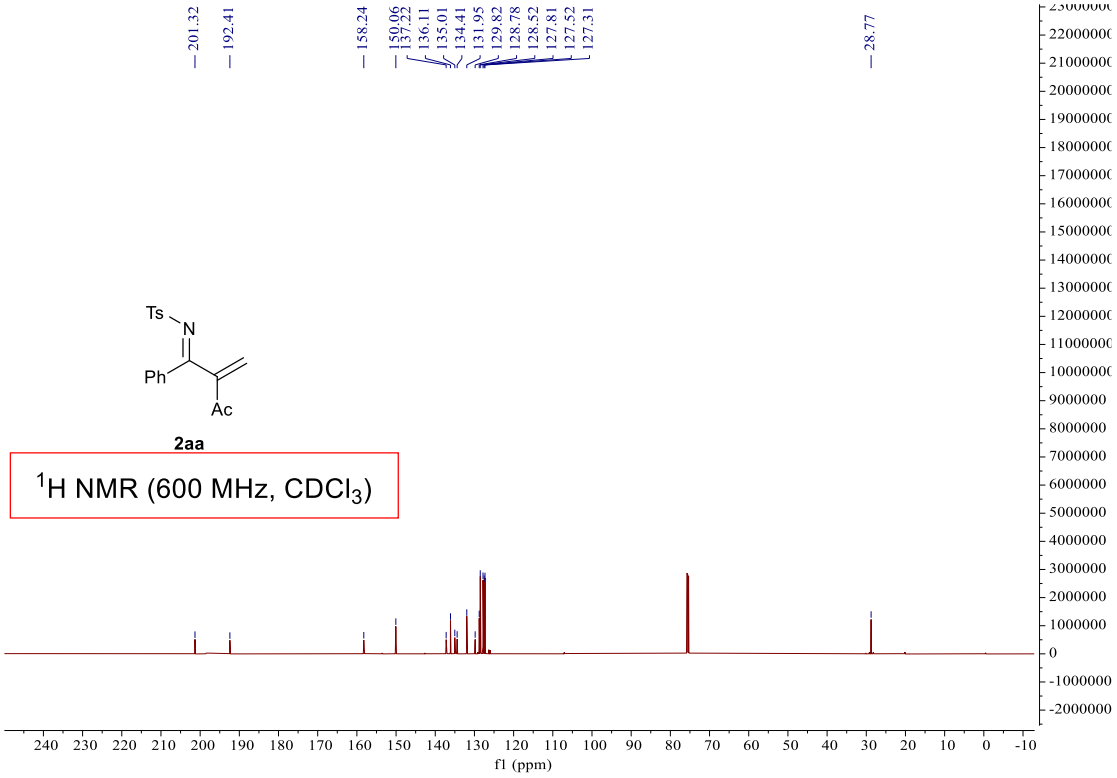
(ellipsoid contour probability 50%)

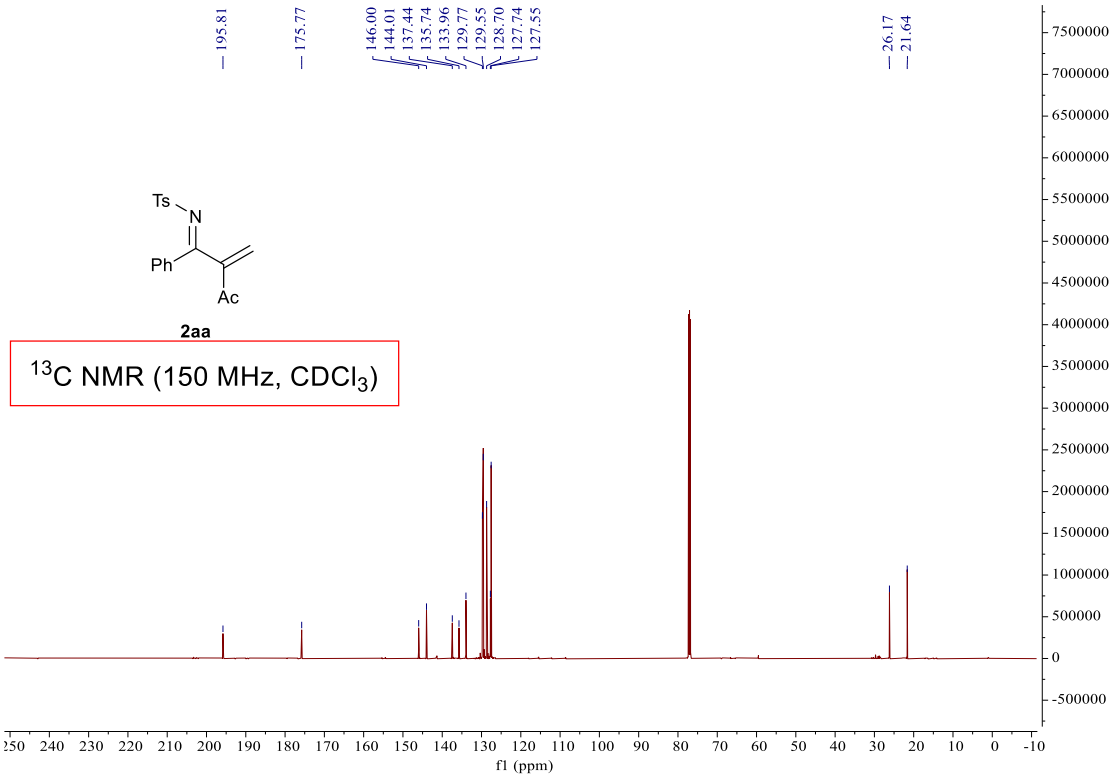


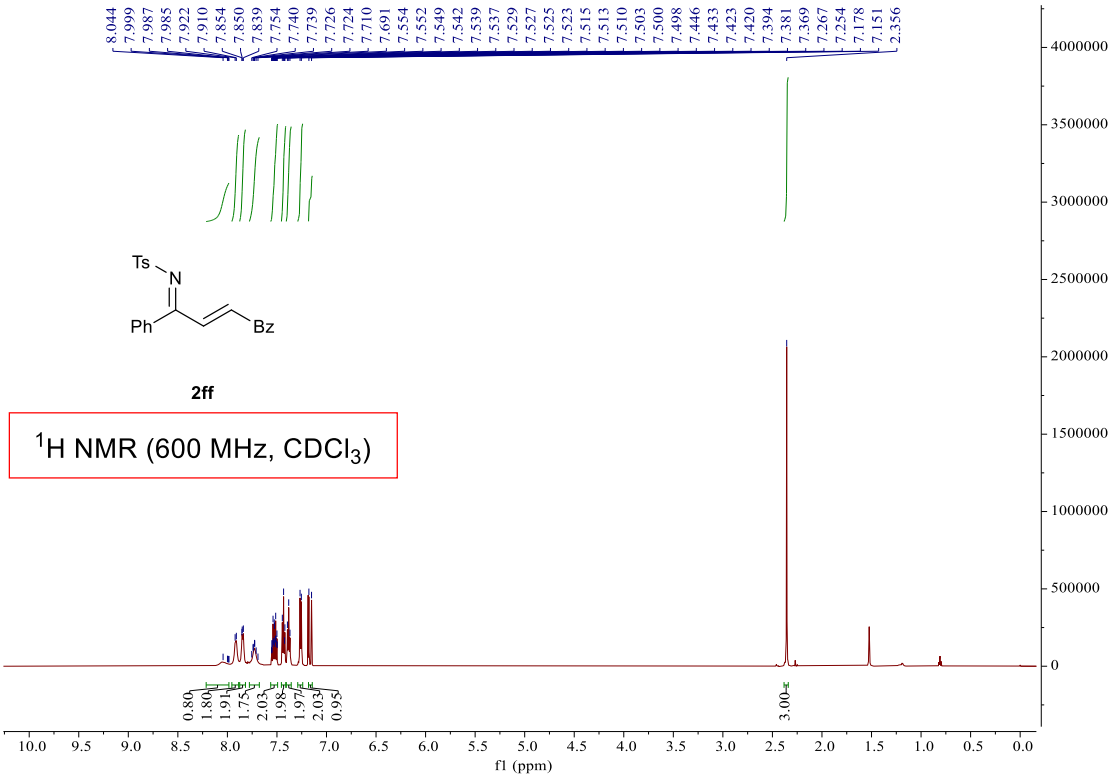
3a, CCDC **2296784**

Identification code	20220928TJ
Empirical formula	$C_{21}H_{17}NO_3$
Formula weight	331.36
Temperature/K	293(2)
Crystal system	monoclinic
Space group	P1 21/c 1
a/Å	8.8129(2)
b/Å	24.2864(6)
c/Å	8.4619(2)
α/°	90
β/°	108.0690(10)
γ/°	90
Volume/Å^3	1721.81(7)
Z	4
ρ_{calc}g/cm^3	1.278
μ/mm^{-1}	0.693
F(000)	696
2Θ range for data collection/°	3.64 to 68.34
Index ranges	$-10 \le h \le 10$, $-28 \le k \le 29$, $-10 \le l \le 10$
Reflections collected	30807
Independent reflections	3157 [R_{int} = 0.0567]
Data/restraints/parameters	3157/0/227
Goodness-of-fit on F^2	1.075
Final R indexes [I>=2σ (I)]	R_1 = 0.0532, wR_2 = 0.1454
Final R indexes [all data]	R_1 = 0.0616, wR_2 = 0.1555
Largest diff. peak/hole / e Å^{-3}	0.334/-0.298

9. NMR Spectra

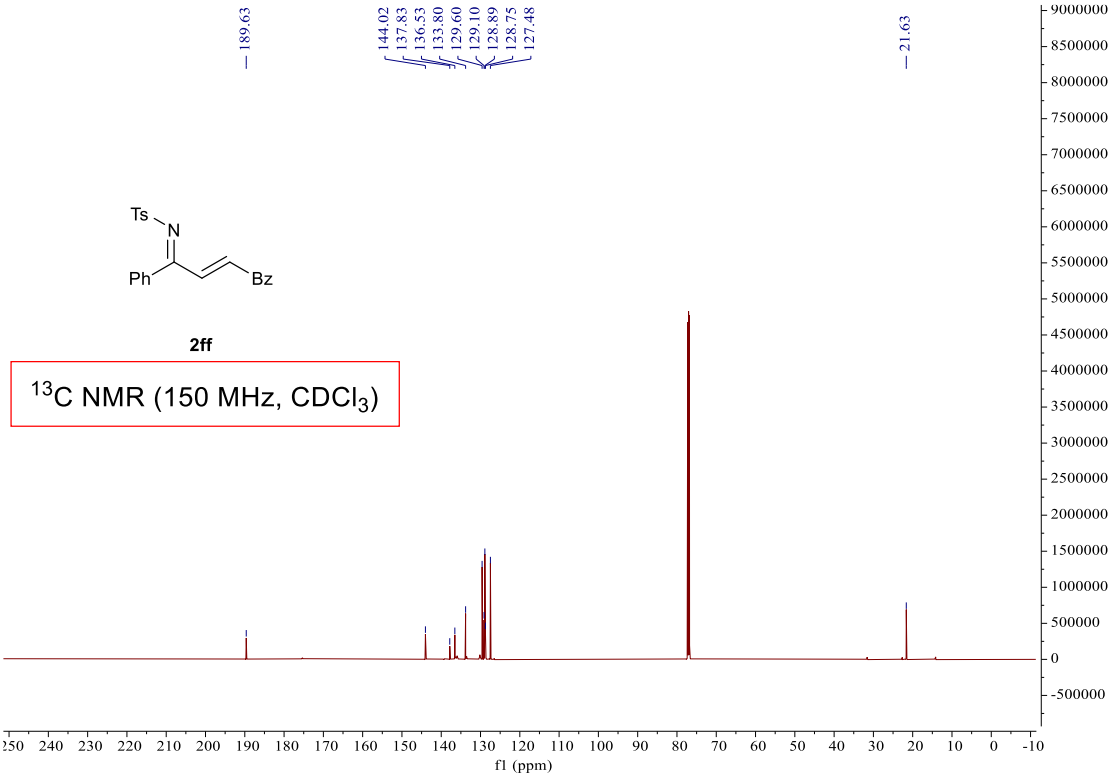






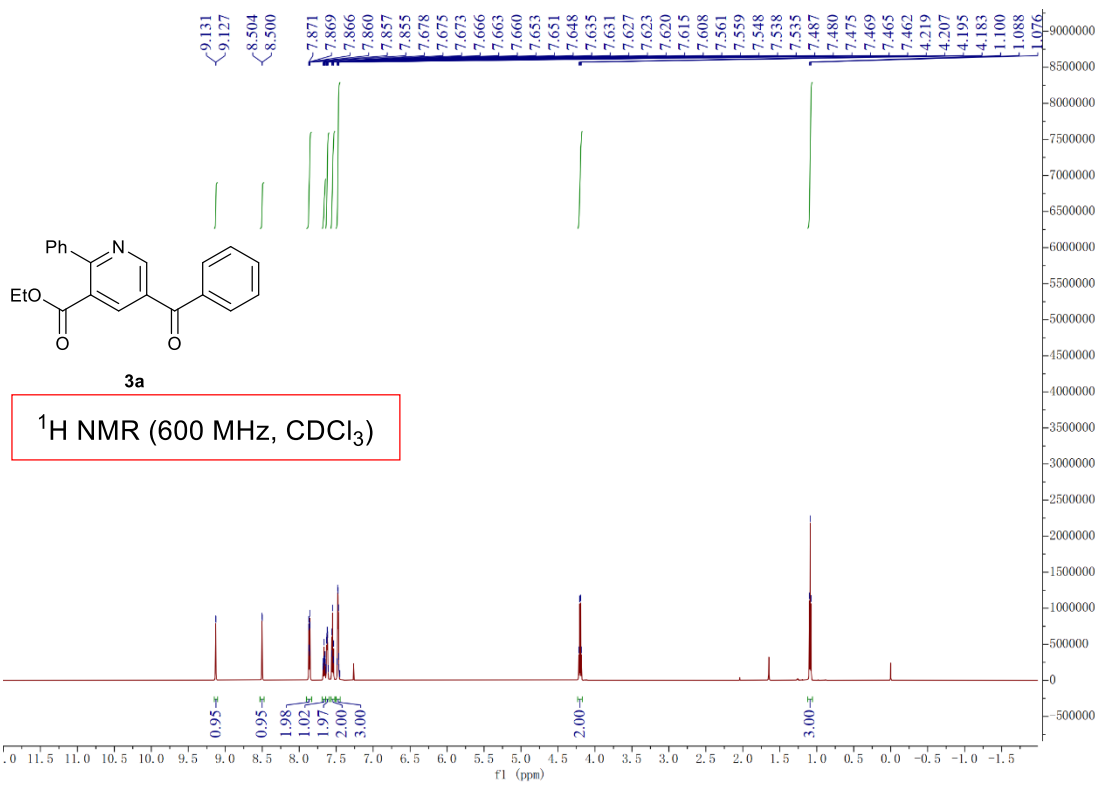
2ff

^{1}H NMR (600 MHz, $CDCl_3$)



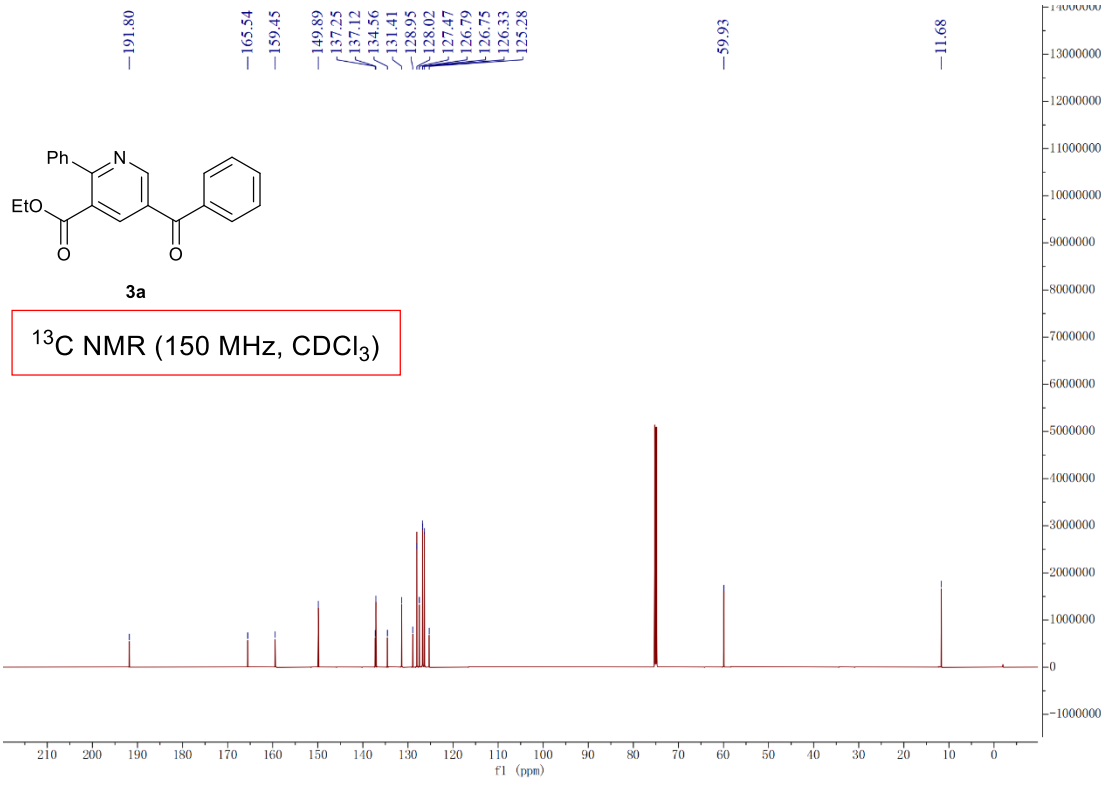
2ff

^{13}C NMR (150 MHz, $CDCl_3$)



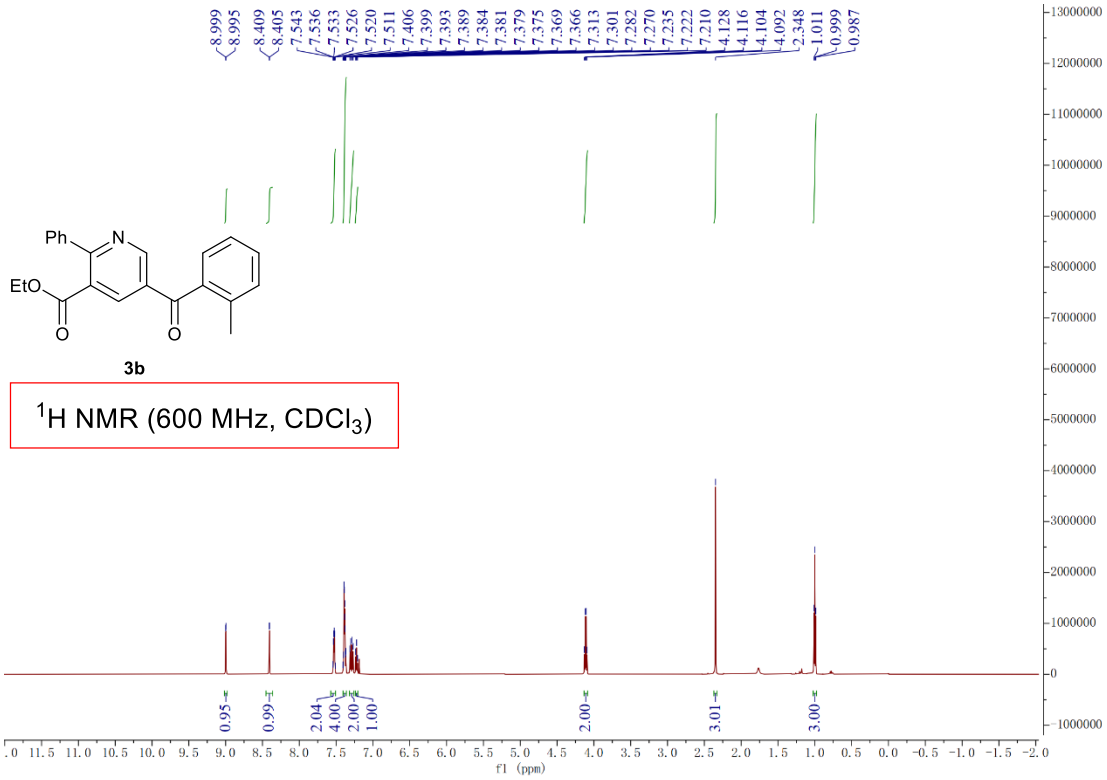
3a

^{1}H NMR (600 MHz, $CDCl_3$)



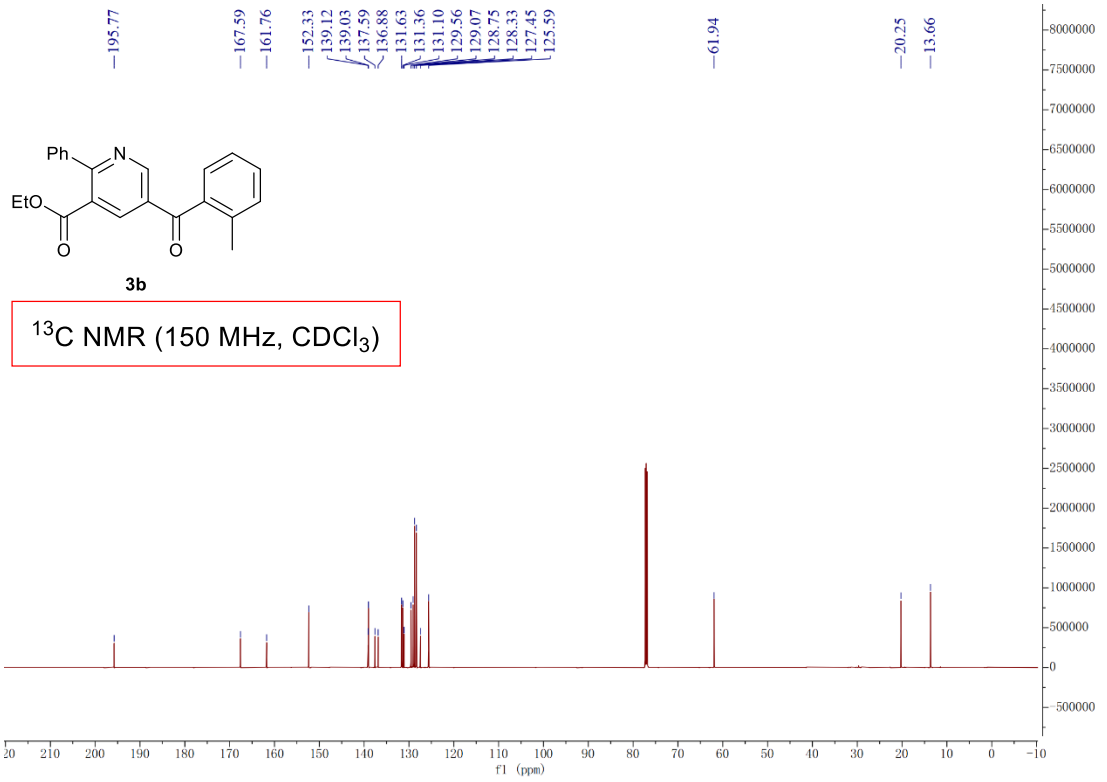
3a

^{13}C NMR (150 MHz, $CDCl_3$)



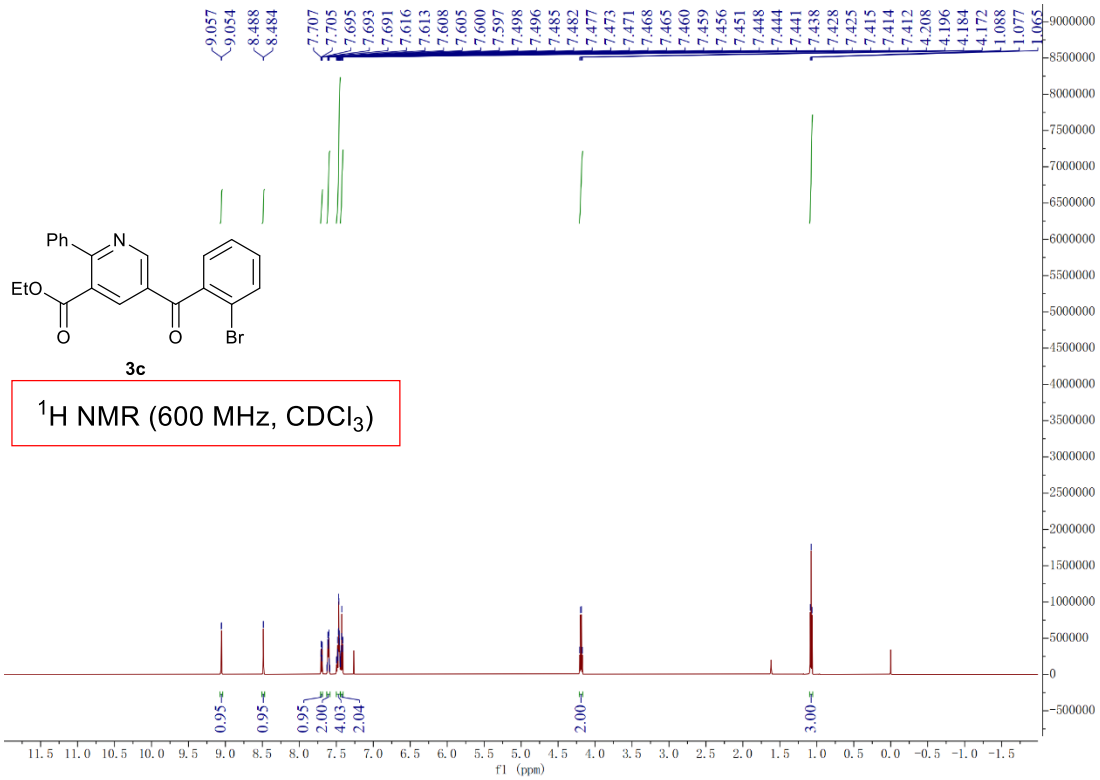
3b

^{1}H NMR (600 MHz, $CDCl_3$)



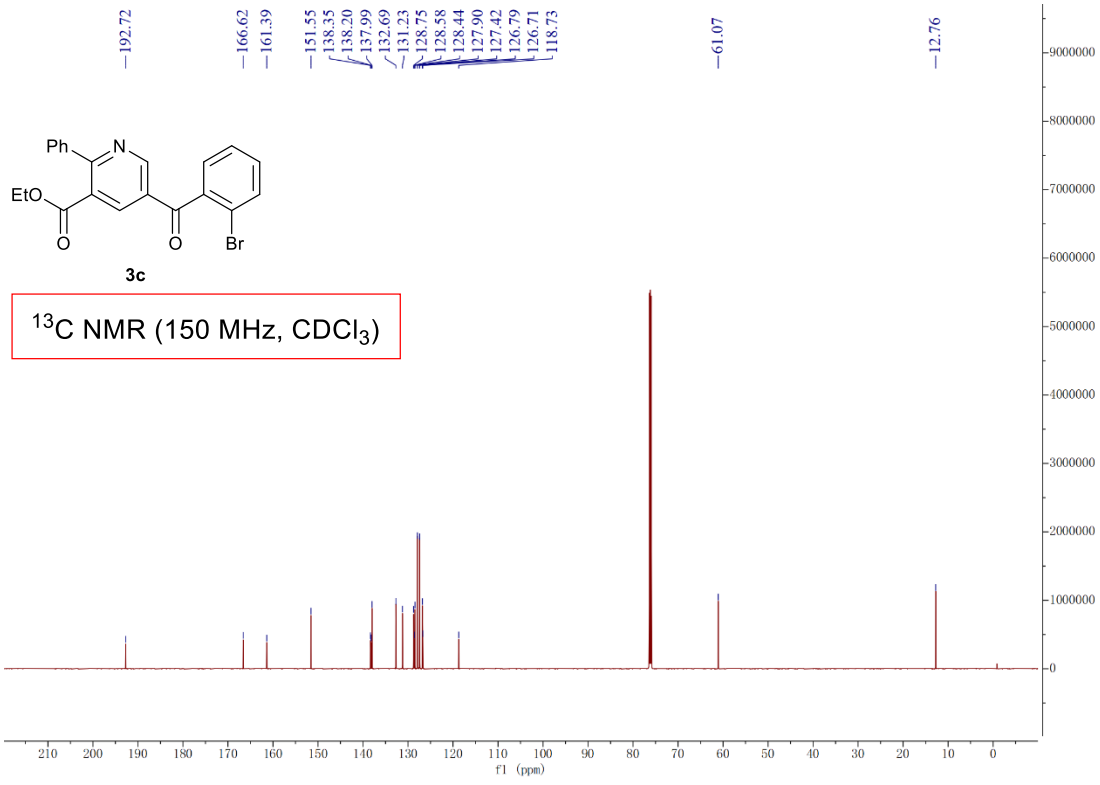
3b

^{13}C NMR (150 MHz, $CDCl_3$)



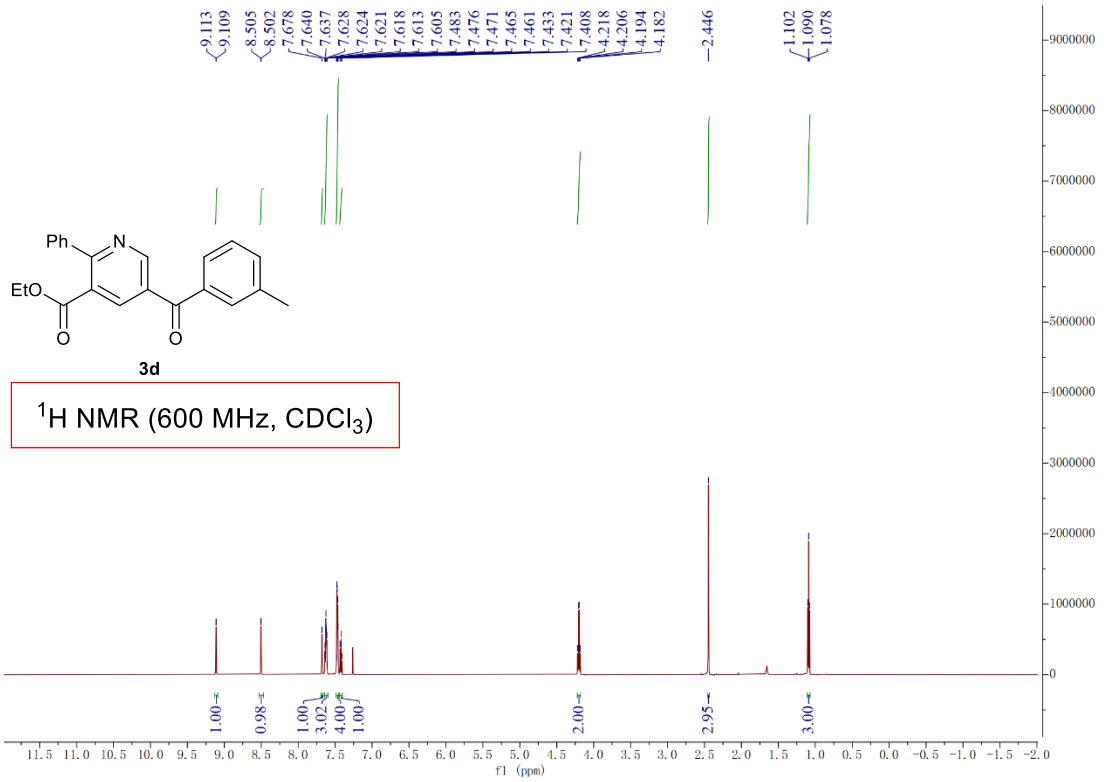
3c

^{1}H NMR (600 MHz, $CDCl_3$)



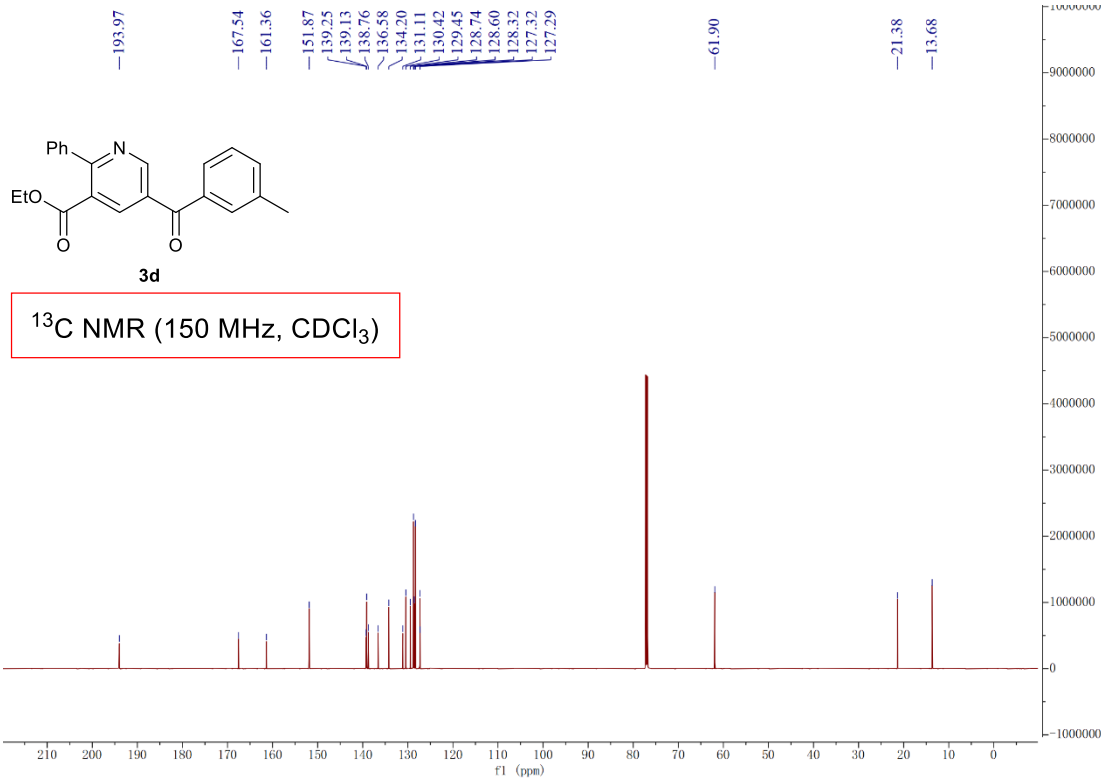
3c

^{13}C NMR (150 MHz, $CDCl_3$)



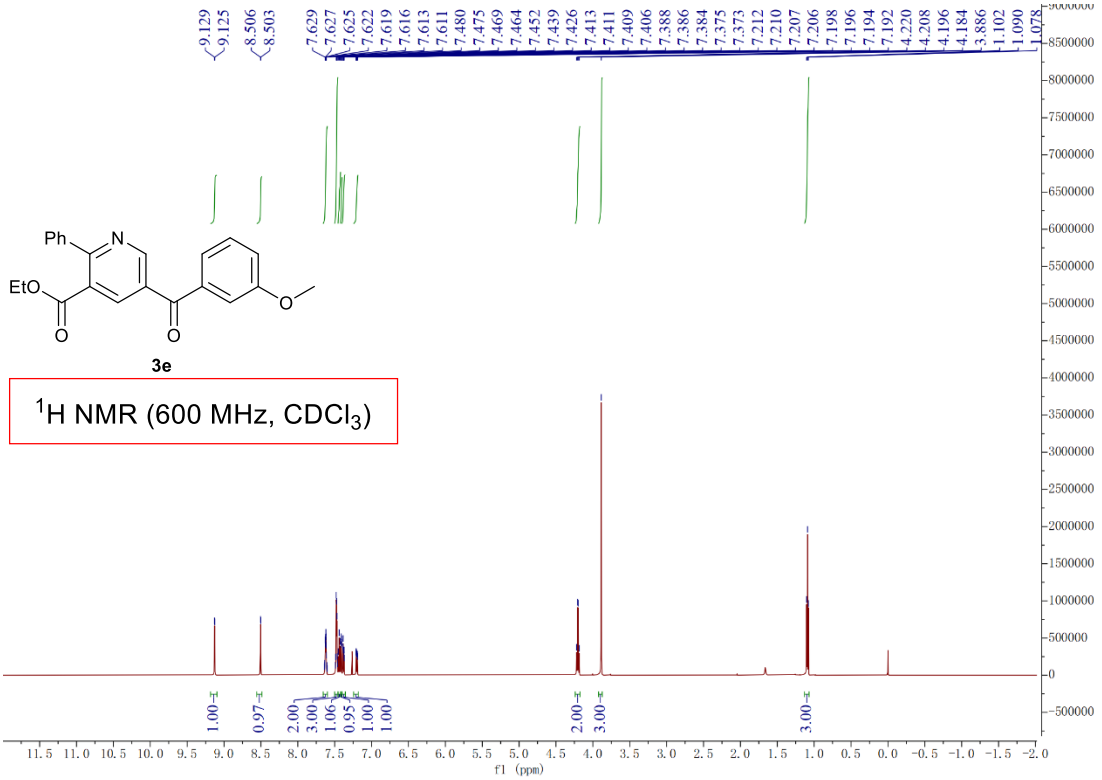
3d

^{1}H NMR (600 MHz, $CDCl_3$)



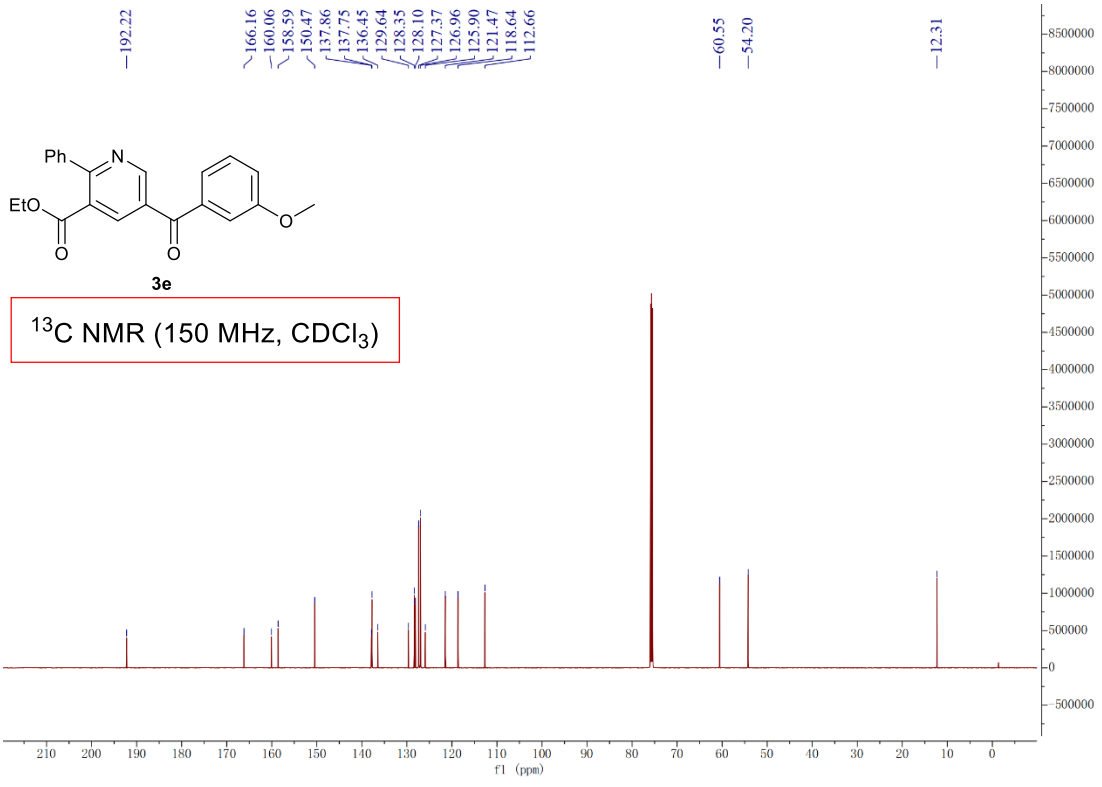
3d

^{13}C NMR (150 MHz, $CDCl_3$)



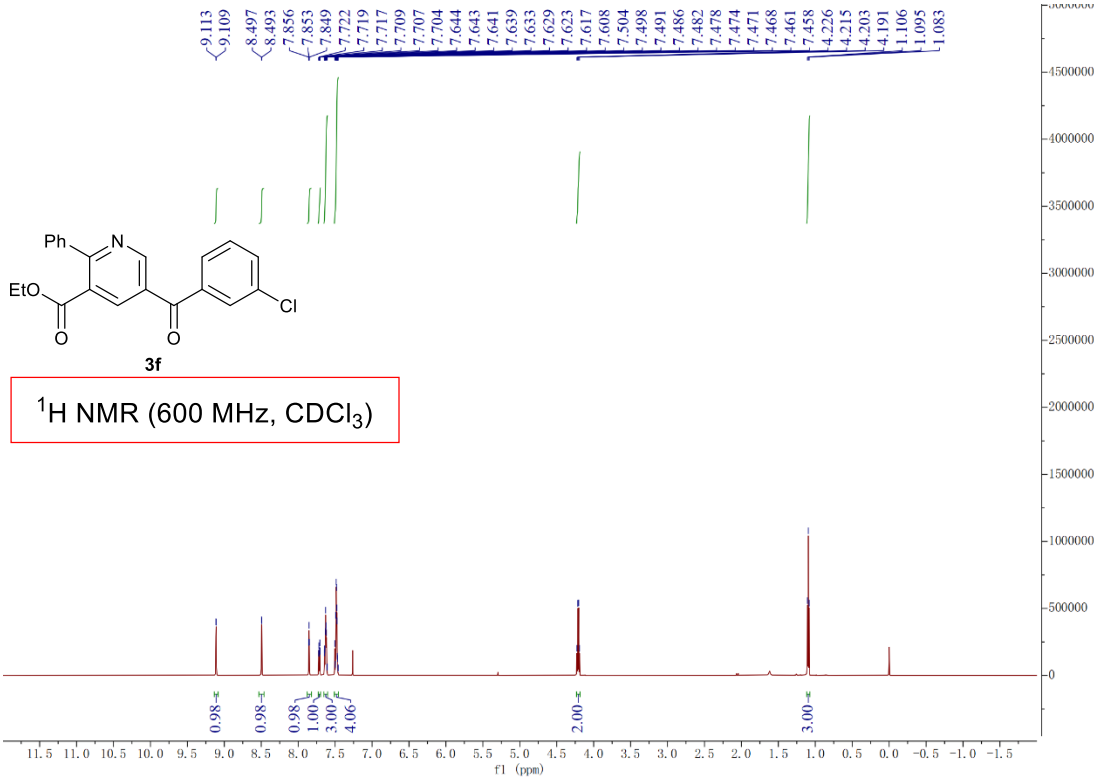
3e

^{1}H NMR (600 MHz, $CDCl_3$)

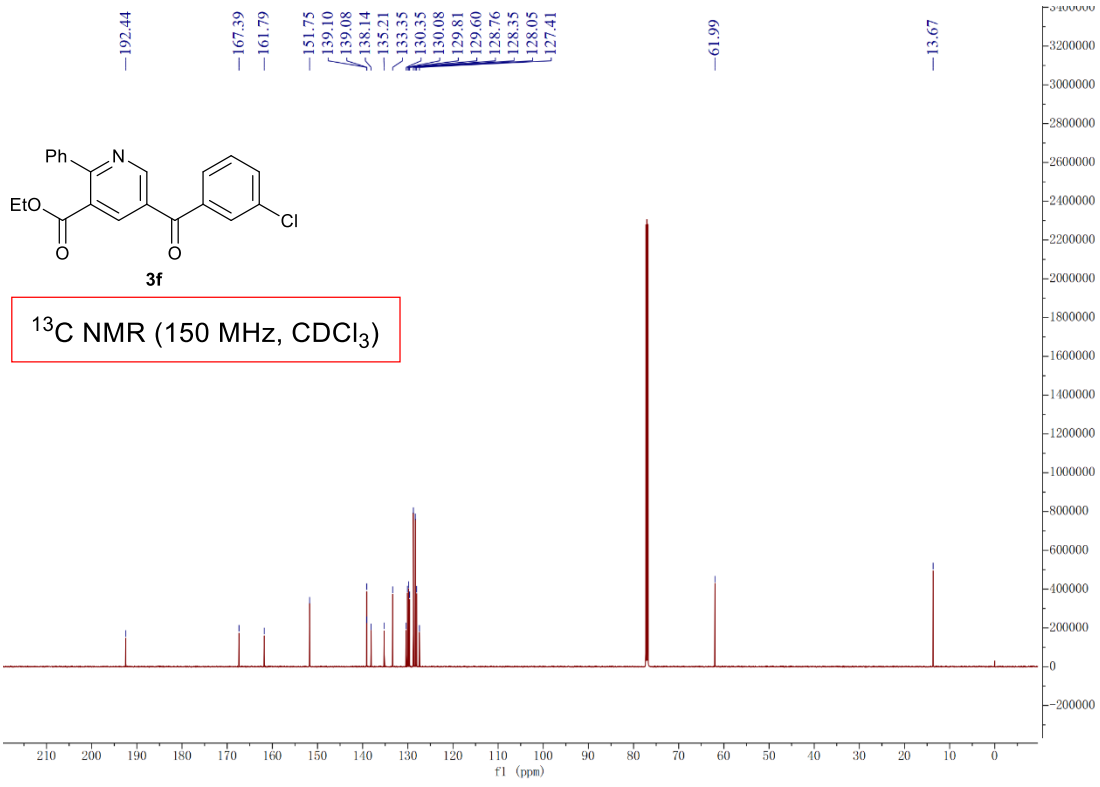


3e

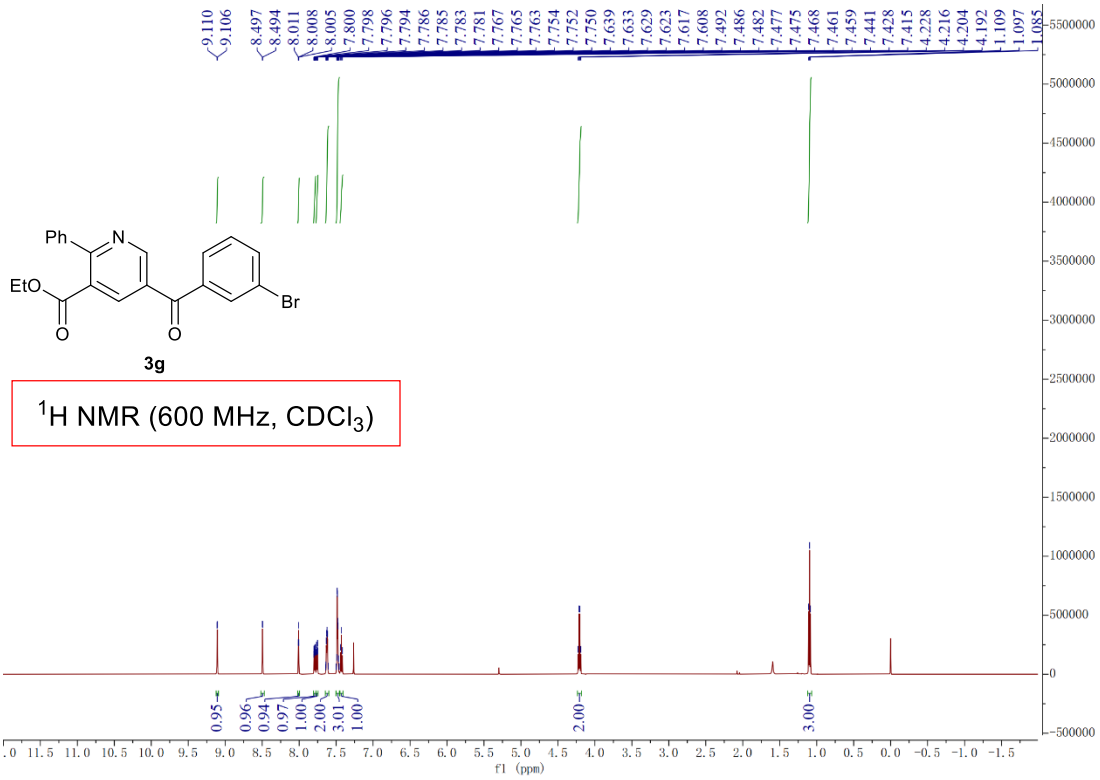
^{13}C NMR (150 MHz, $CDCl_3$)



^{1}H NMR (600 MHz, $CDCl_3$)

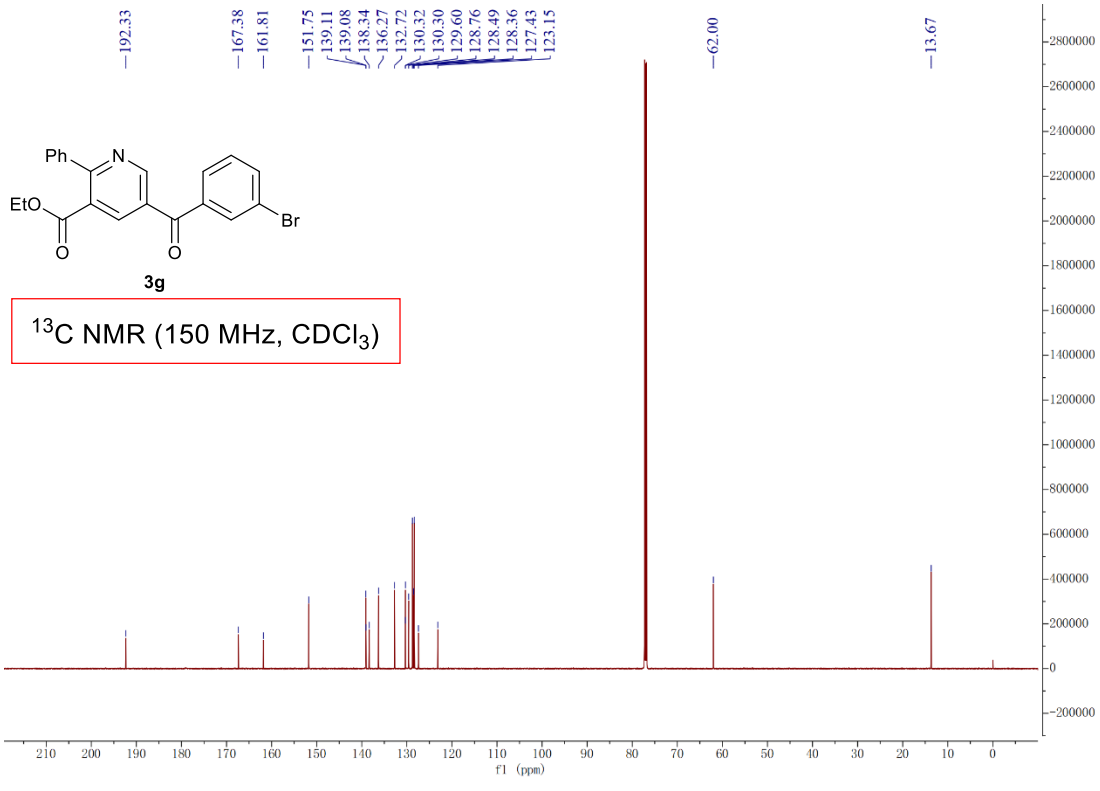


^{13}C NMR (150 MHz, $CDCl_3$)



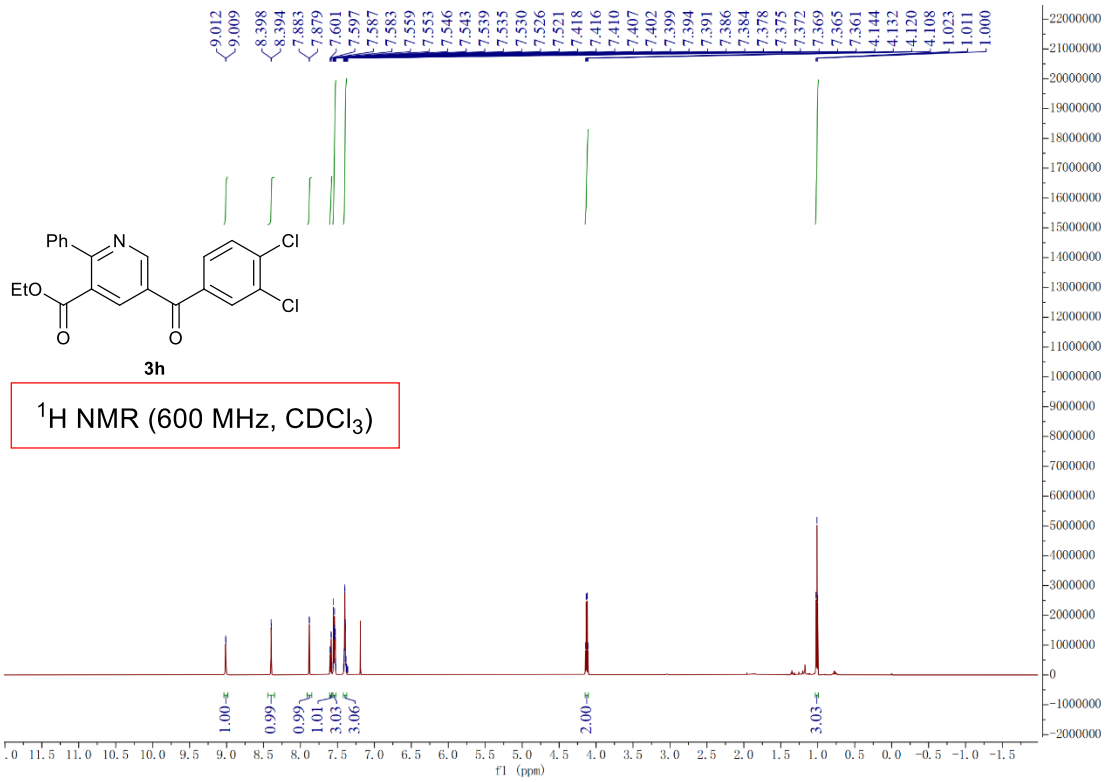
3g

^{1}H NMR (600 MHz, $CDCl_3$)



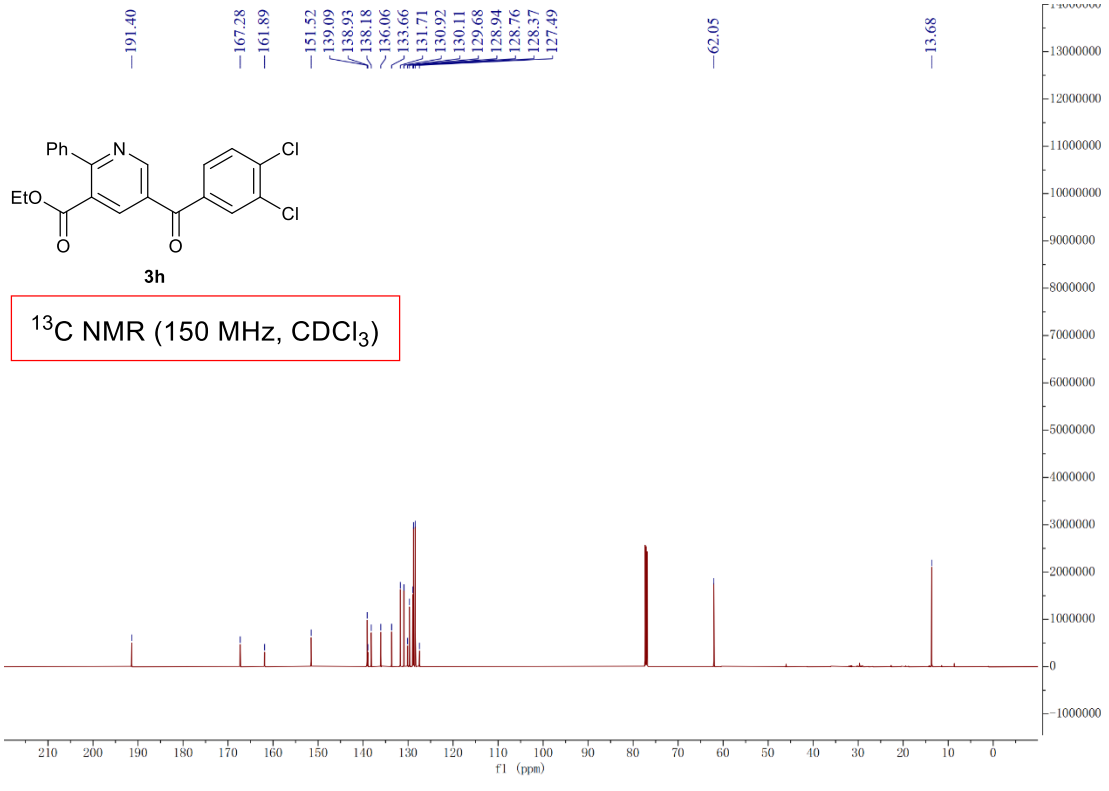
3g

^{13}C NMR (150 MHz, $CDCl_3$)



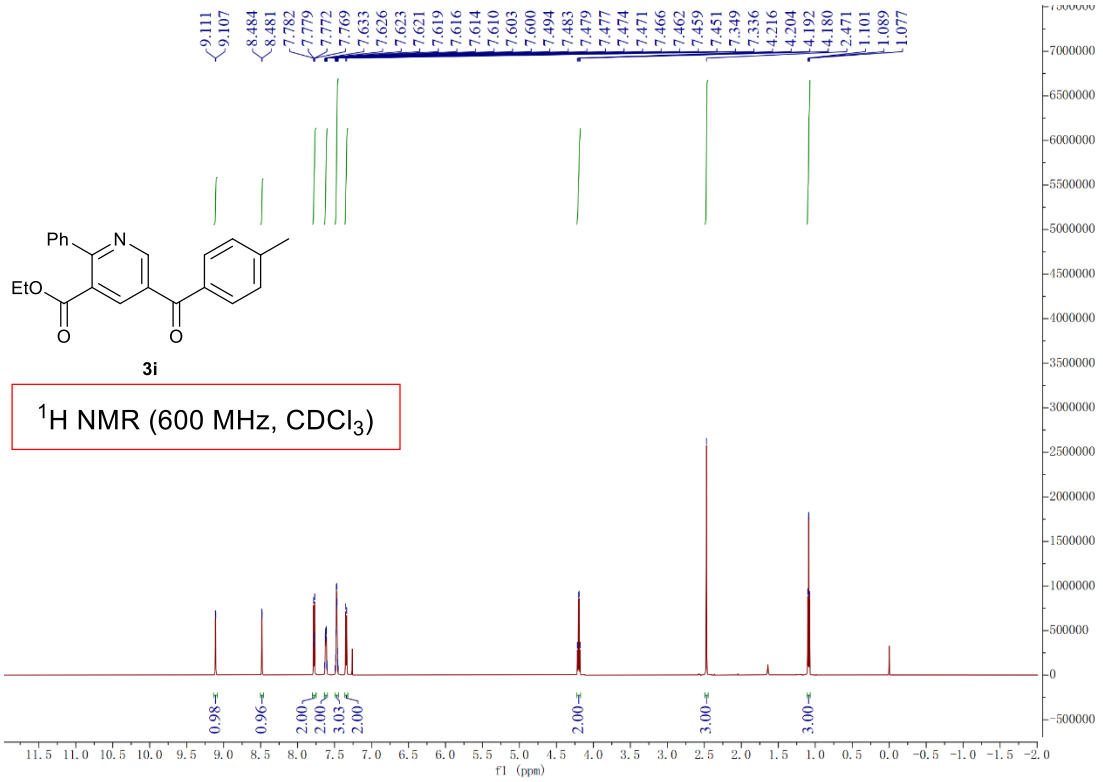
3h

^{1}H NMR (600 MHz, $CDCl_3$)



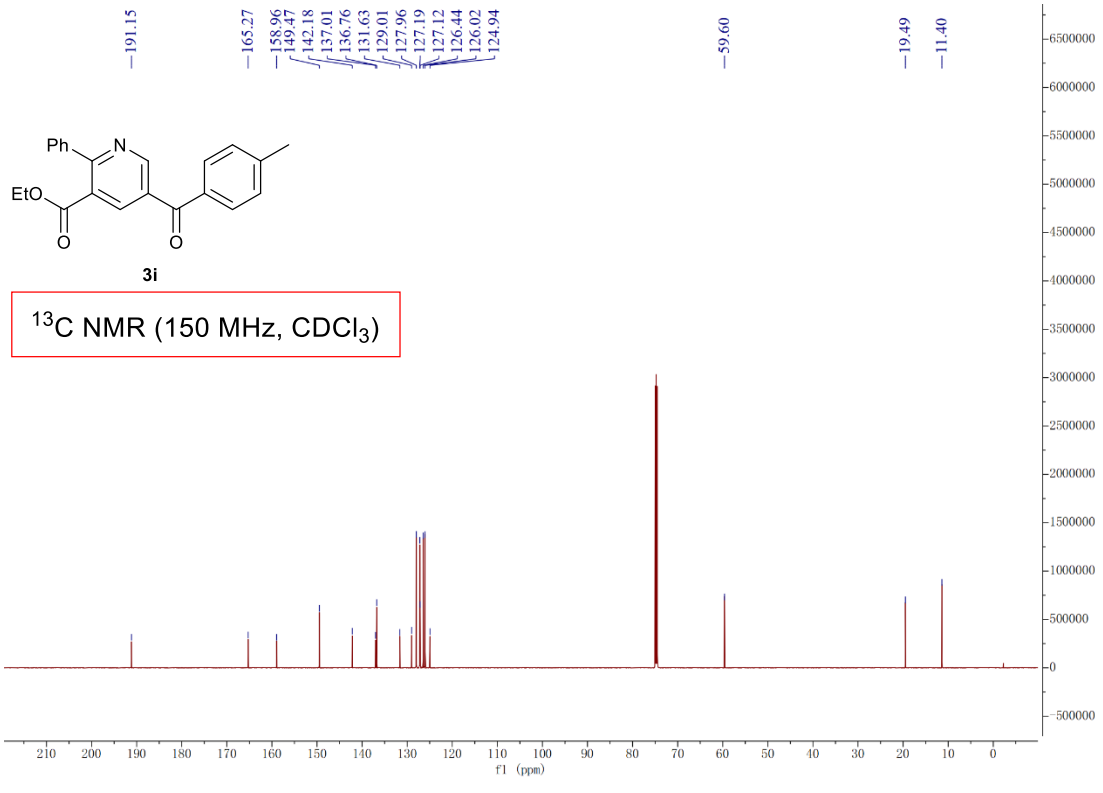
3h

^{13}C NMR (150 MHz, $CDCl_3$)



3i

^{1}H NMR (600 MHz, $CDCl_3$)



3i

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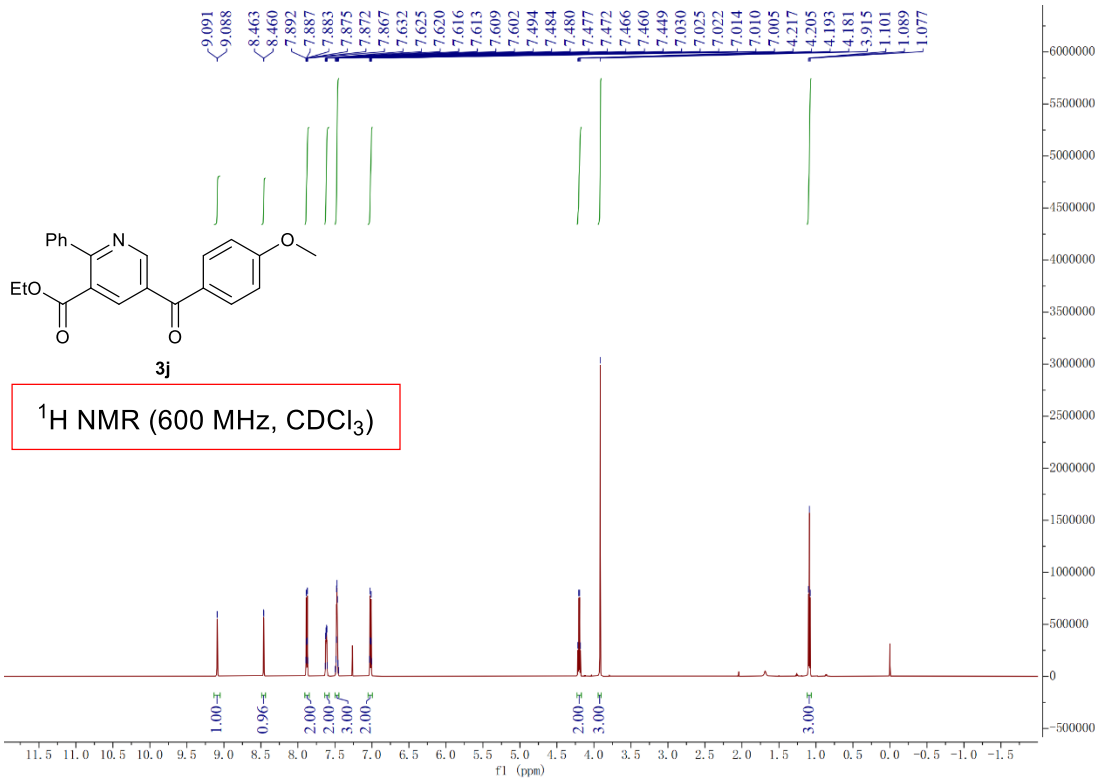

3j

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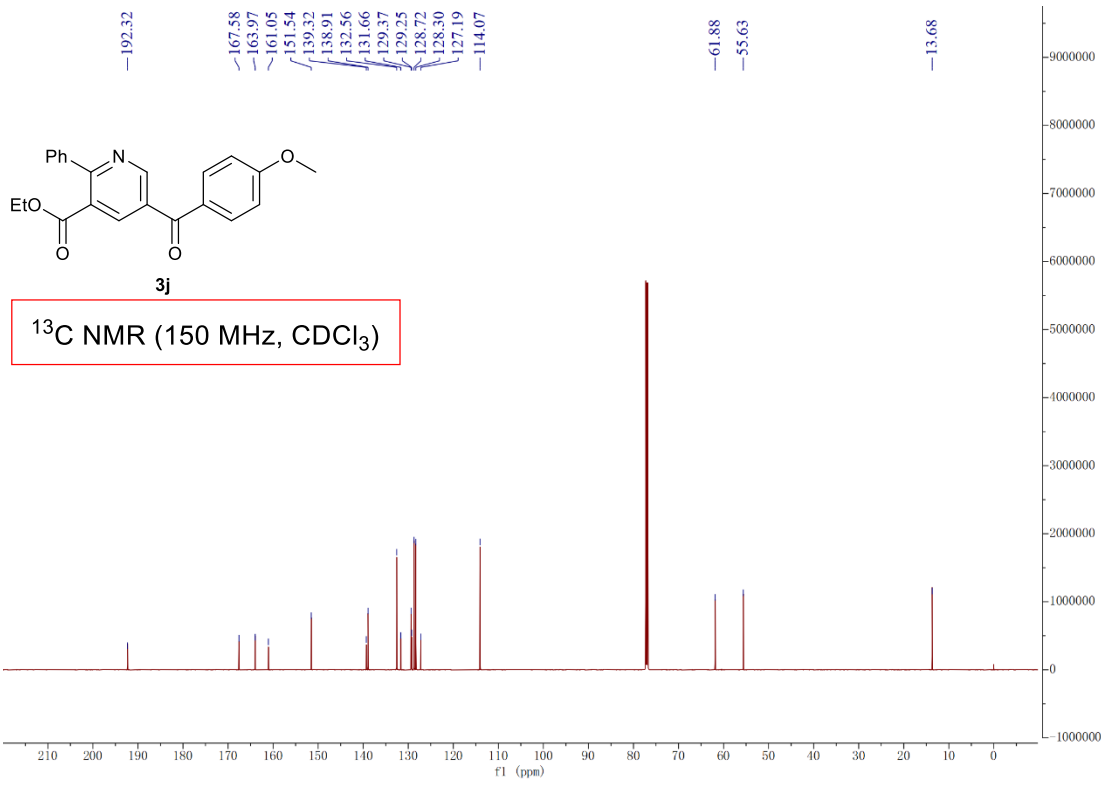
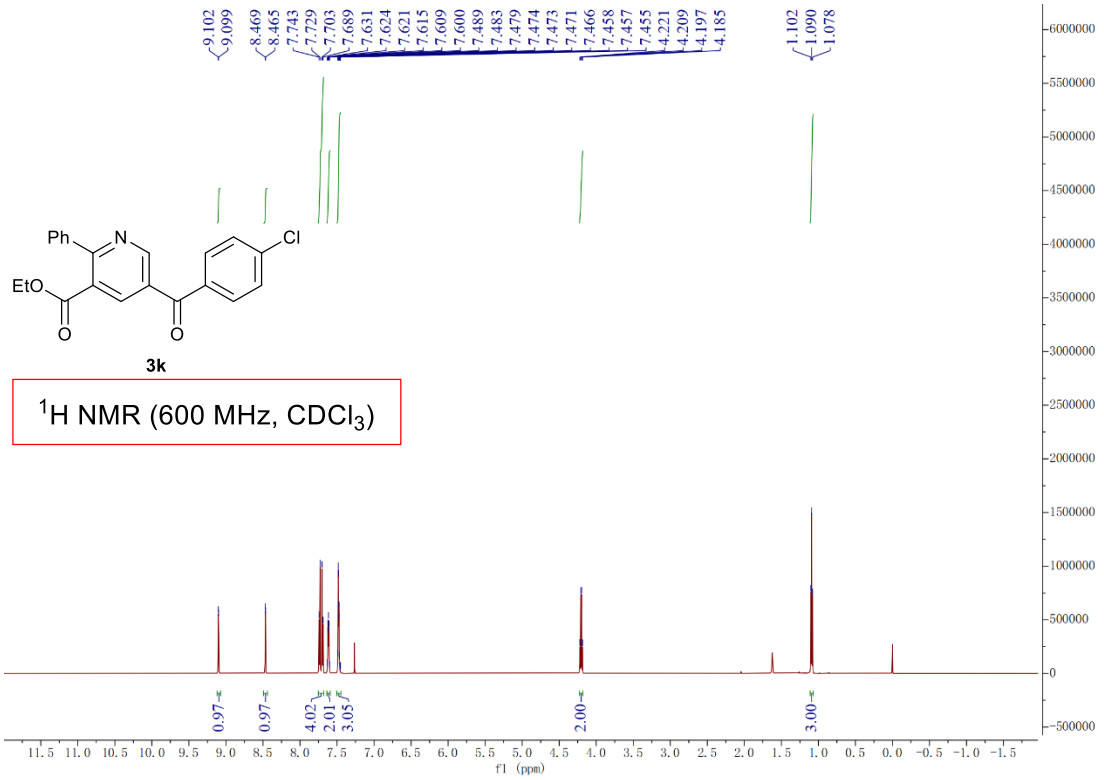


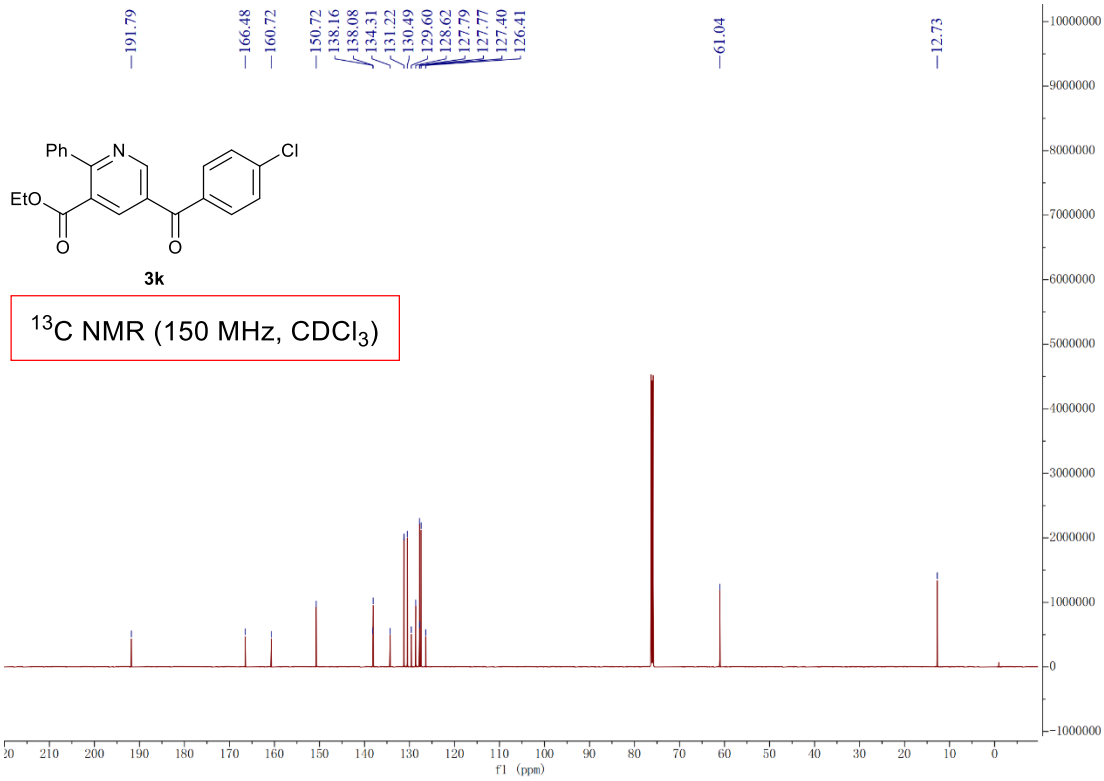
3j

^{13}C NMR (150 MHz, $CDCl_3$)



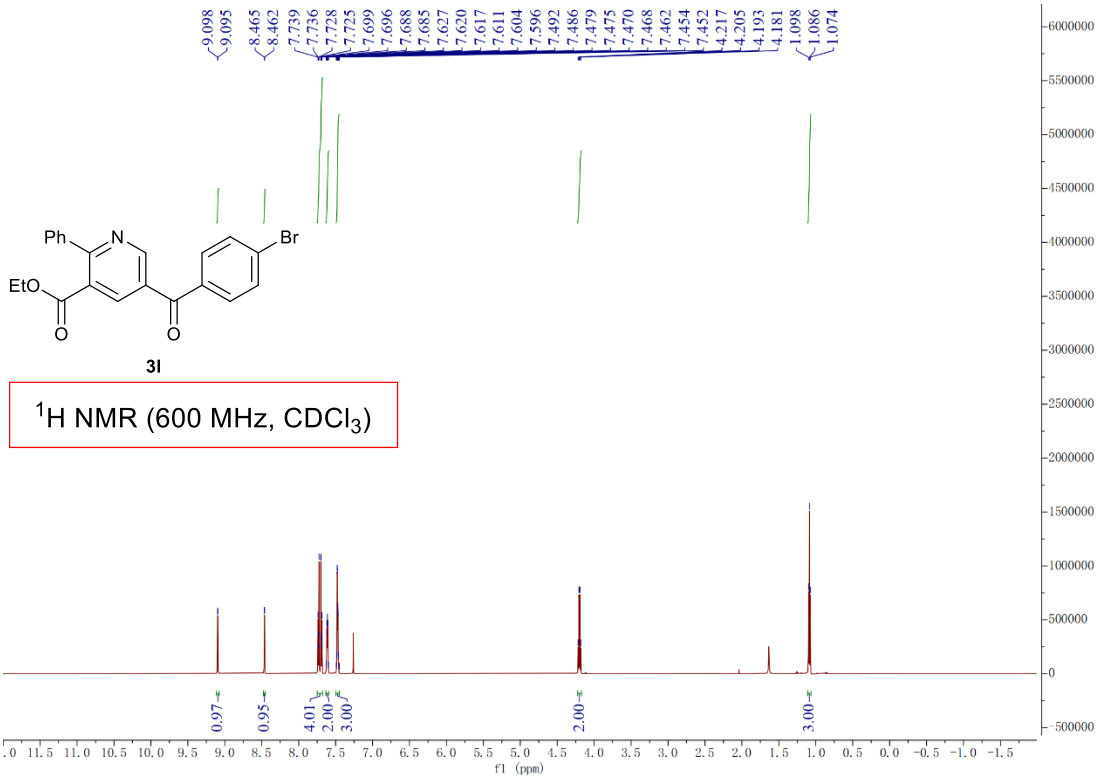
3k

^{1}H NMR (600 MHz, $CDCl_3$)



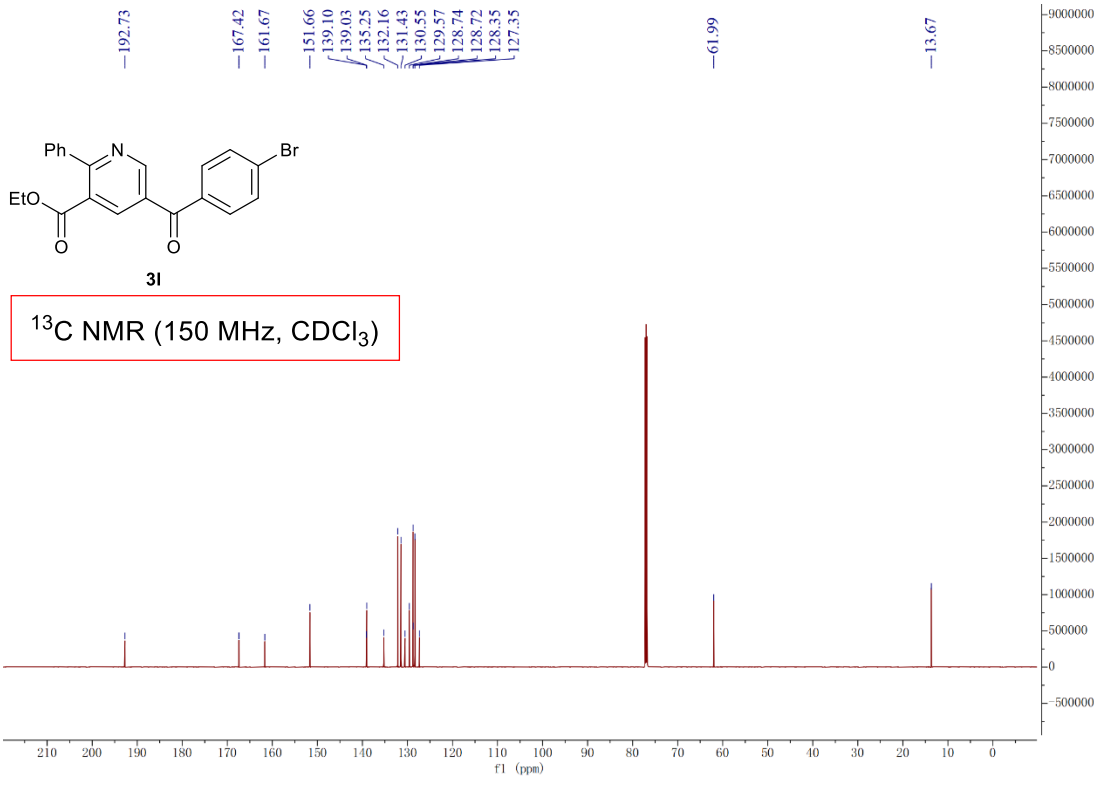
3k

^{13}C NMR (150 MHz, $CDCl_3$)



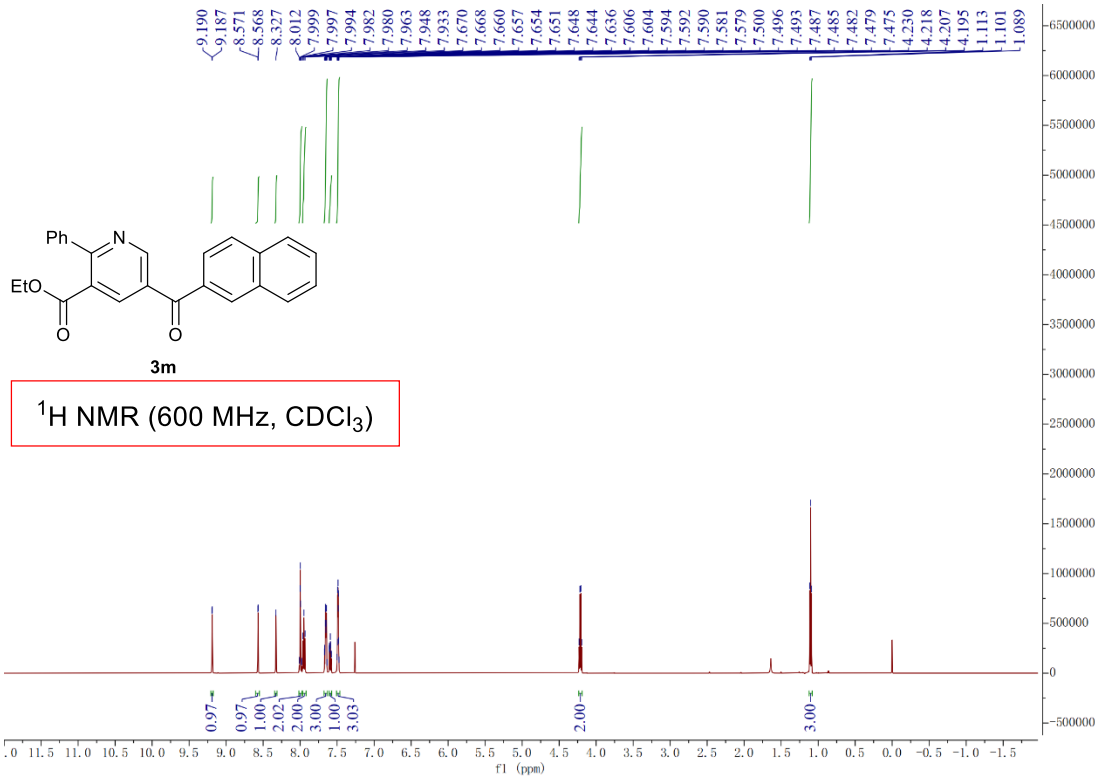
3l

^{1}H NMR (600 MHz, $CDCl_3$)



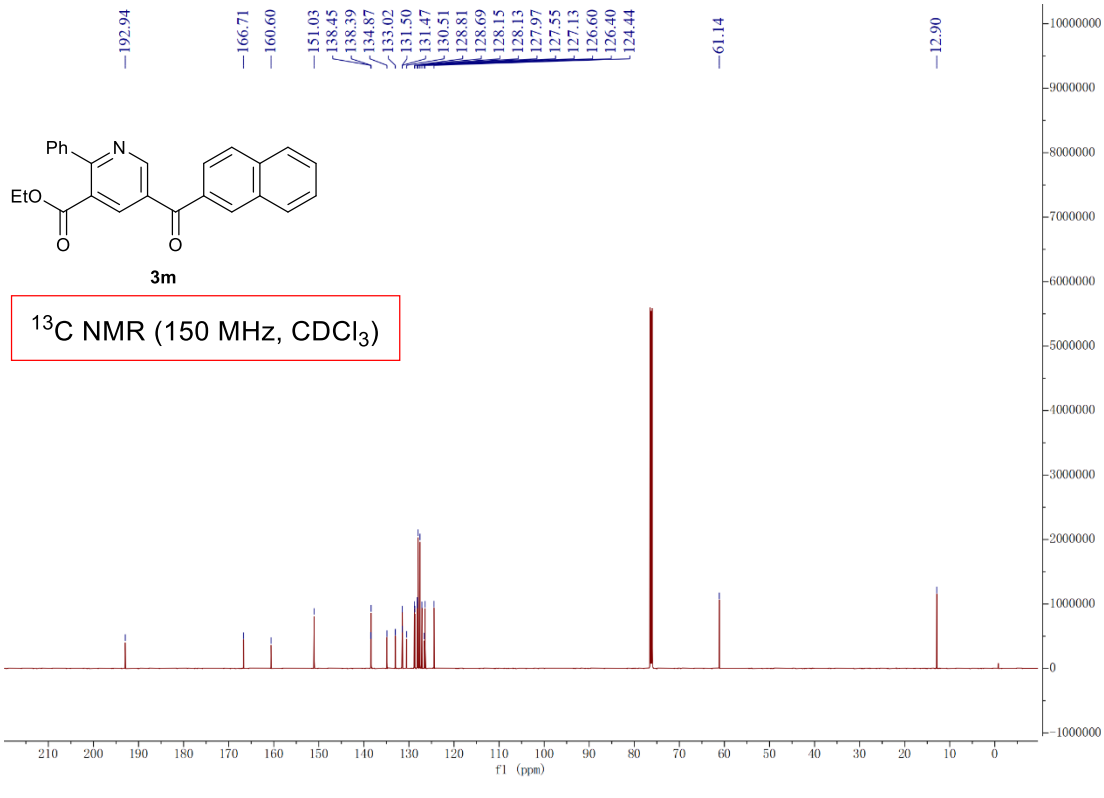
3l

^{13}C NMR (150 MHz, $CDCl_3$)



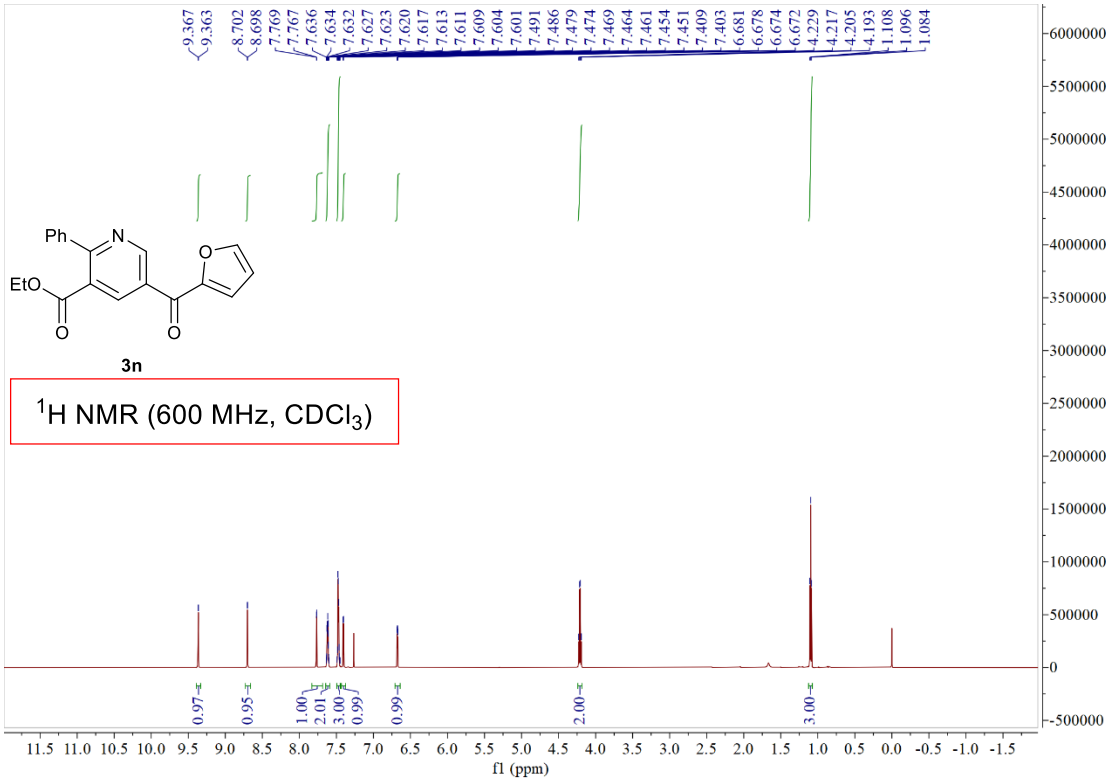
3m

^{1}H NMR (600 MHz, $CDCl_3$)



3m

^{13}C NMR (150 MHz, $CDCl_3$)


9.367
9.363
8.702
8.698
7.769
7.767
7.636
7.634
7.632
7.627
7.623
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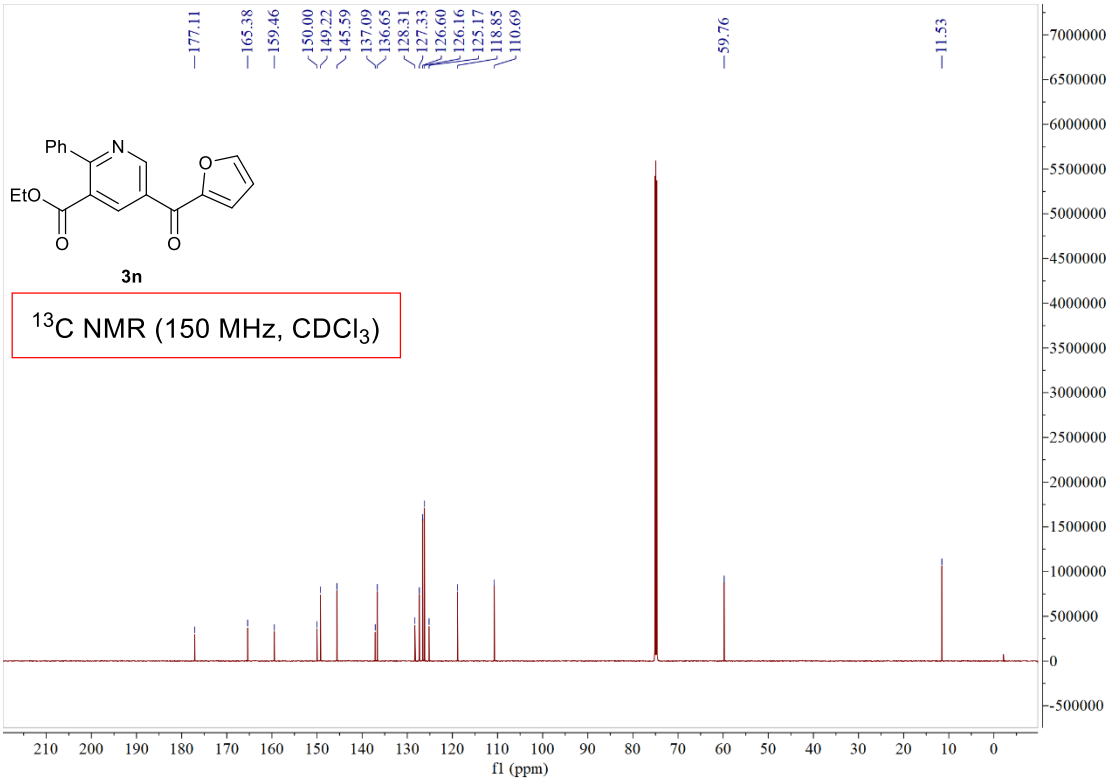
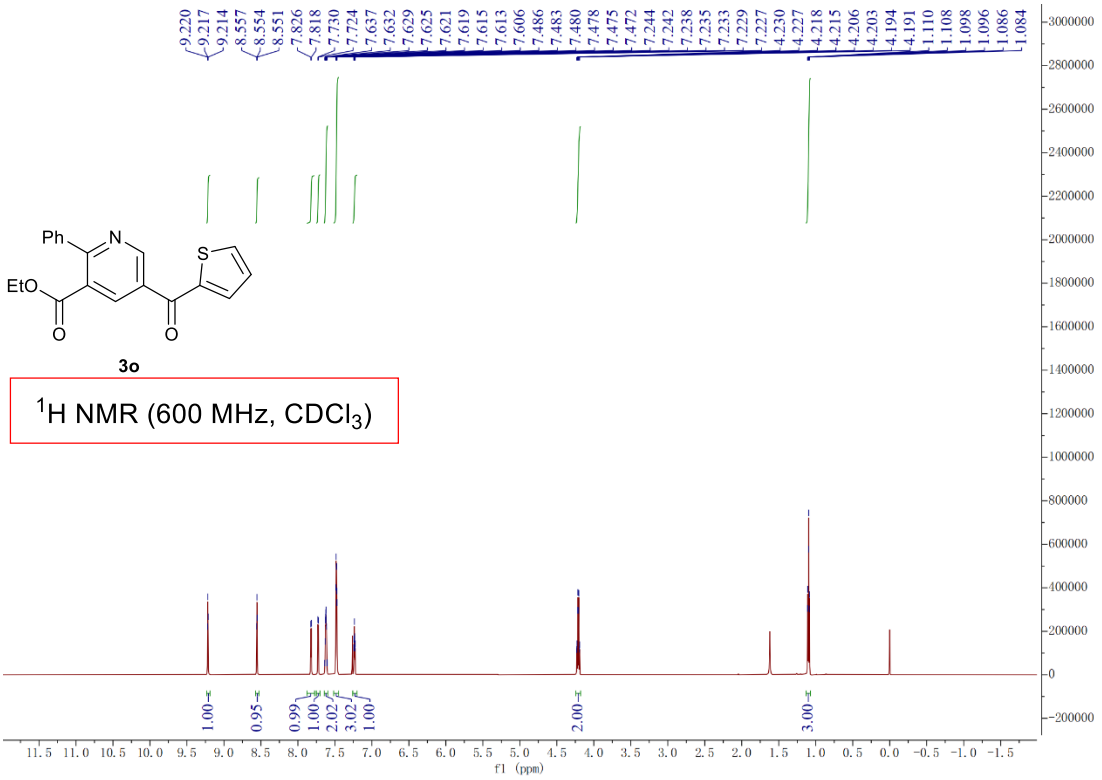
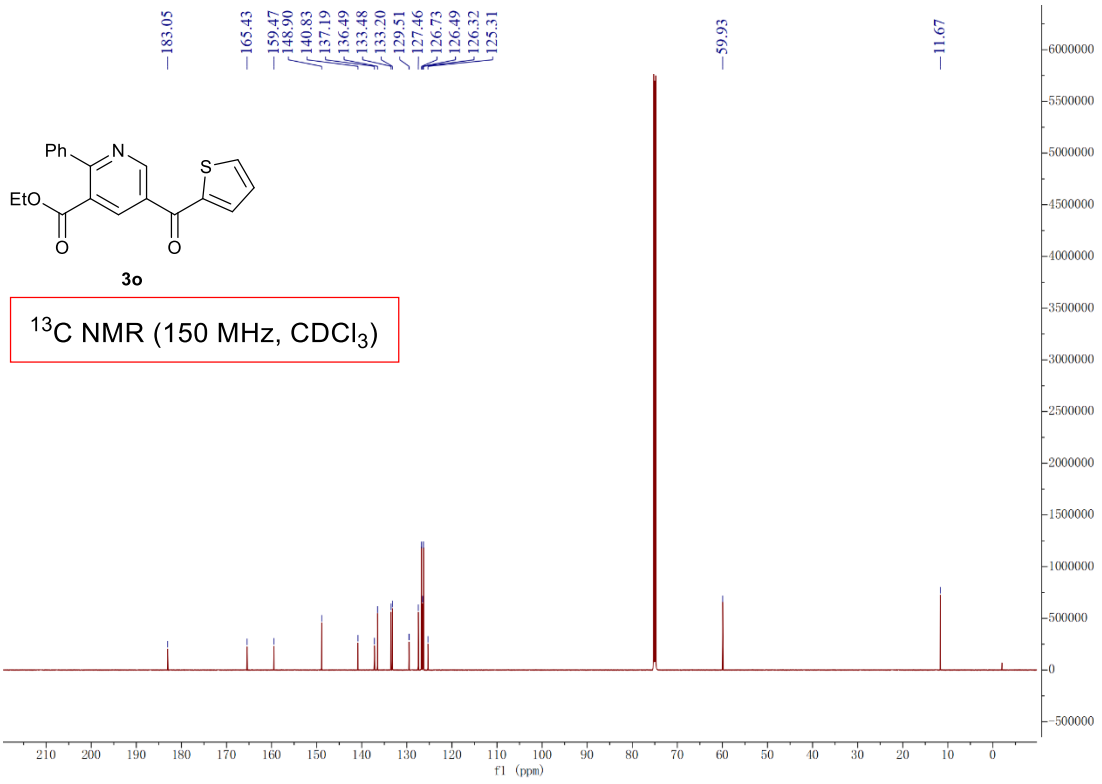
7.617
7.613
7.611
7.609
7.604
7.601
7.491
7.486
7.479
7.474
7.469
7.464
7.461
7.454
7.451
7.409
7.403
6.681
6.678
6.674
6.672
4.229
4.217
4.205
4.193
1.108
1.096
1.084
Ph
N
O
EtO
O
O
3n
^{1}H NMR (600 MHz, CDCl$_3$)
0.97
0.95
1.00
2.01
3.00
0.99
0.99
2.00
3.00
fl (ppm)


177.11
165.38
159.46
150.00
149.22
145.59
137.09
136.65
128.31
127.33
126.60
126.16
125.17
118.85
110.69
59.76
11.53
Ph
N
O
EtO
O
O
3n
^{13}C NMR (150 MHz, CDCl$_3$)
fl (ppm)



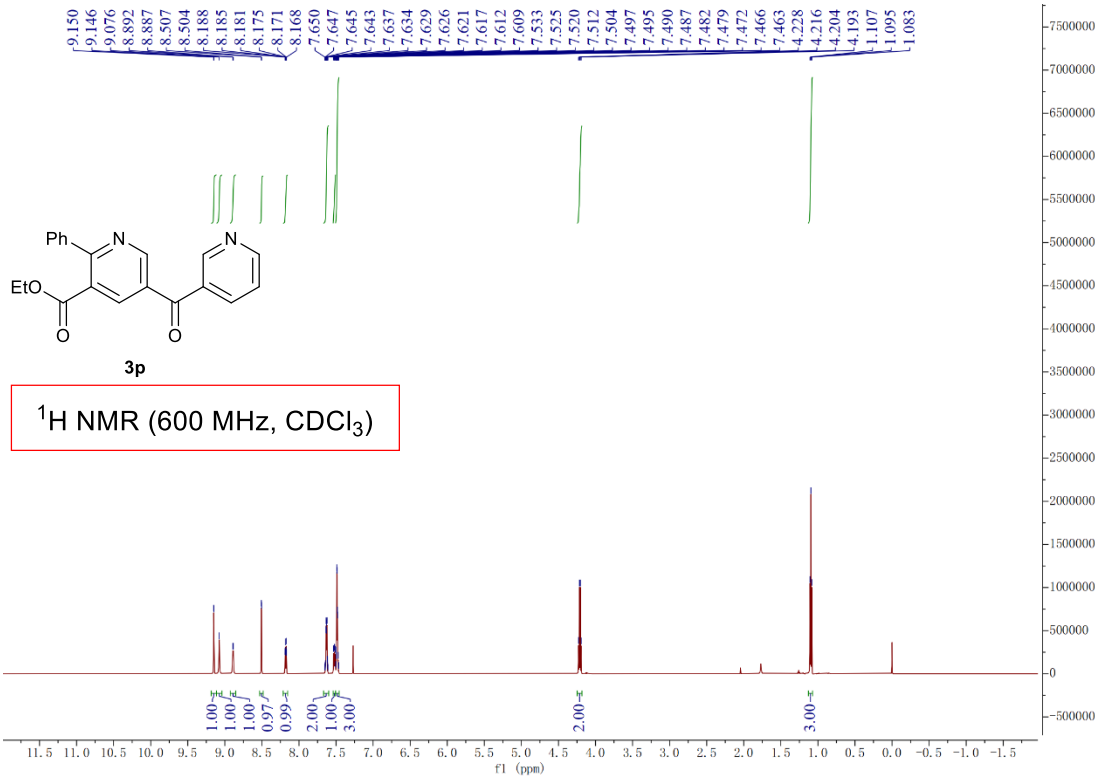
3o

^{1}H NMR (600 MHz, $CDCl_3$)



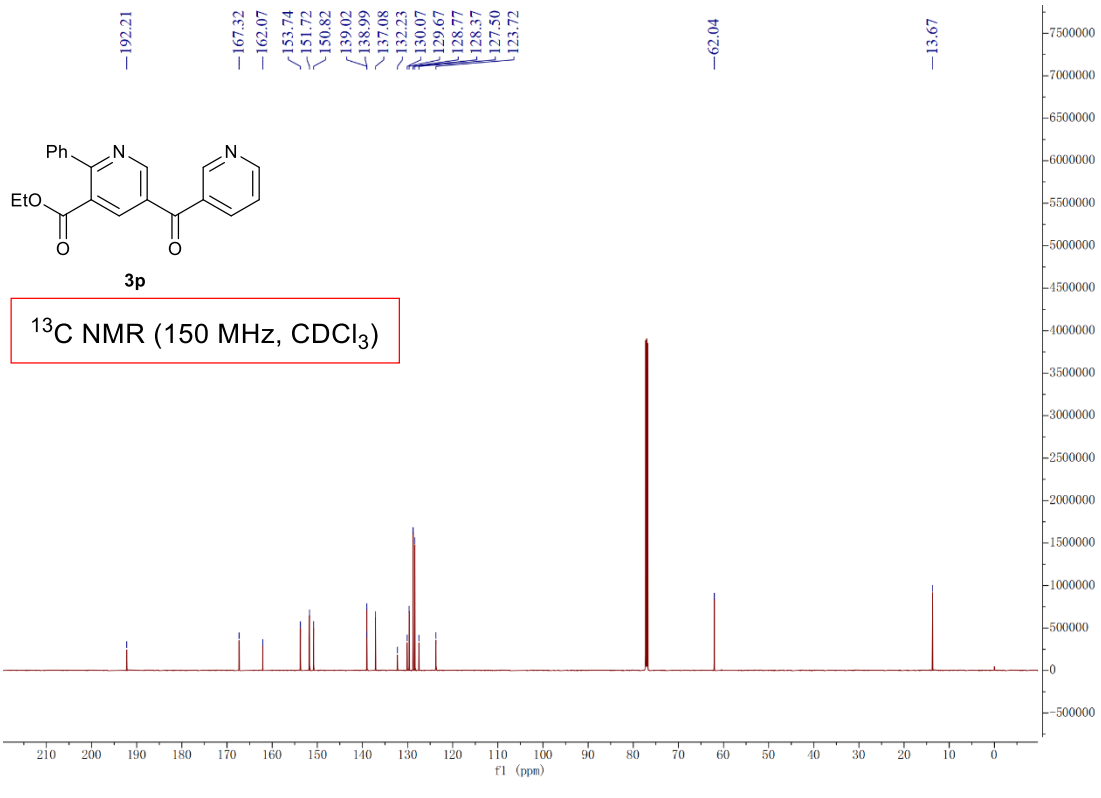
3o

^{13}C NMR (150 MHz, $CDCl_3$)



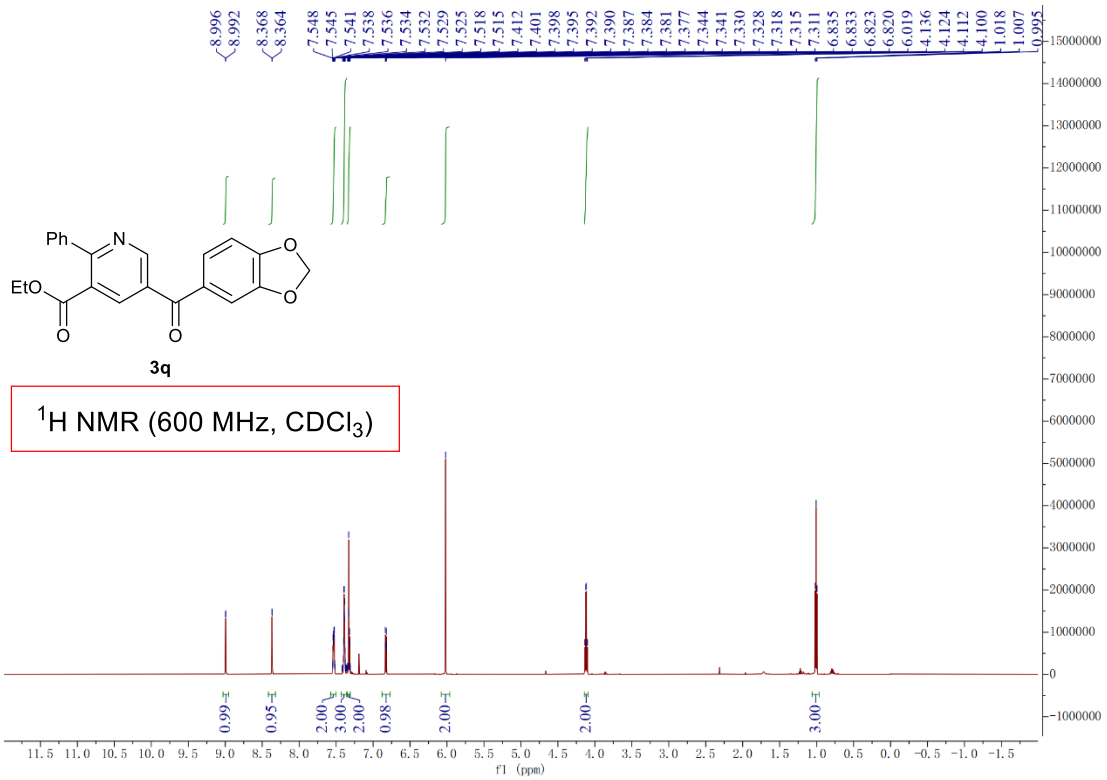
3p

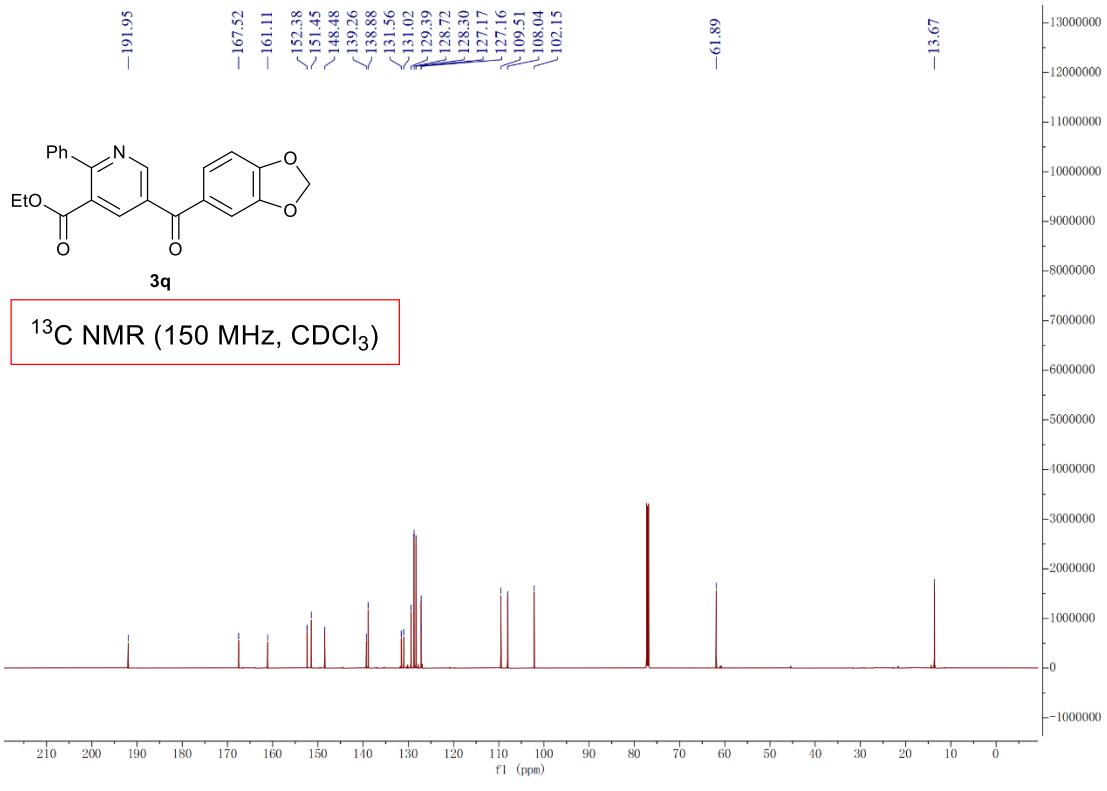
^{1}H NMR (600 MHz, $CDCl_3$)

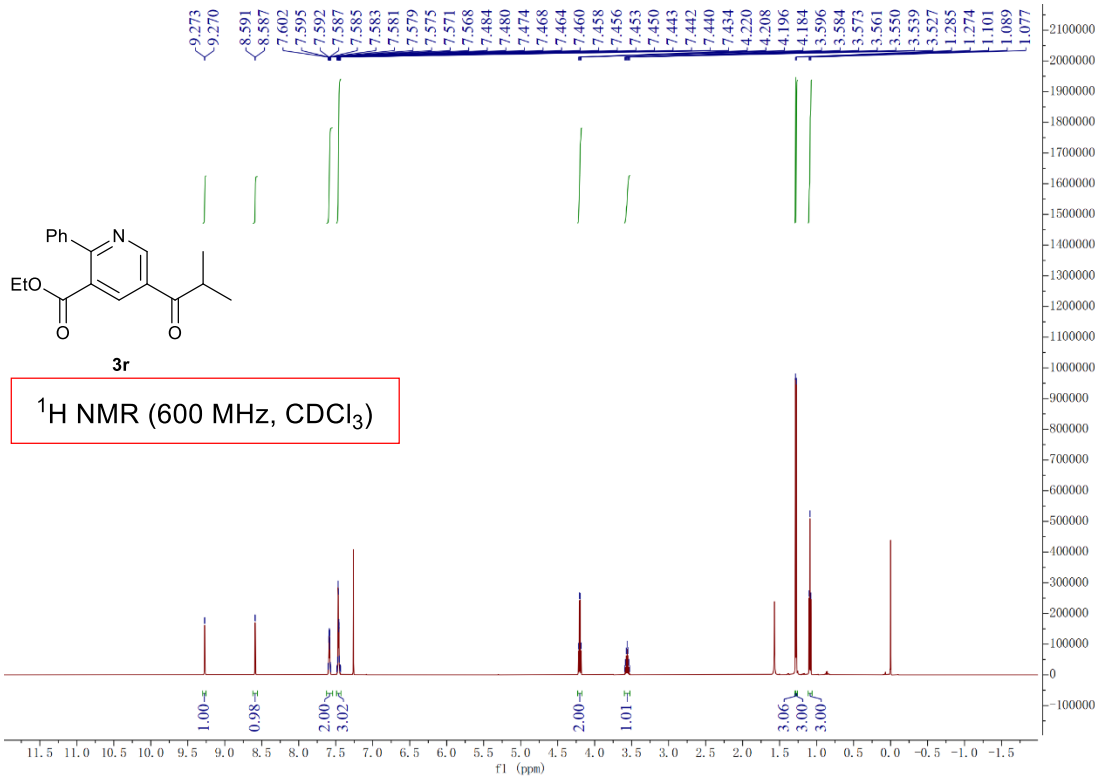


3p

^{13}C NMR (150 MHz, $CDCl_3$)

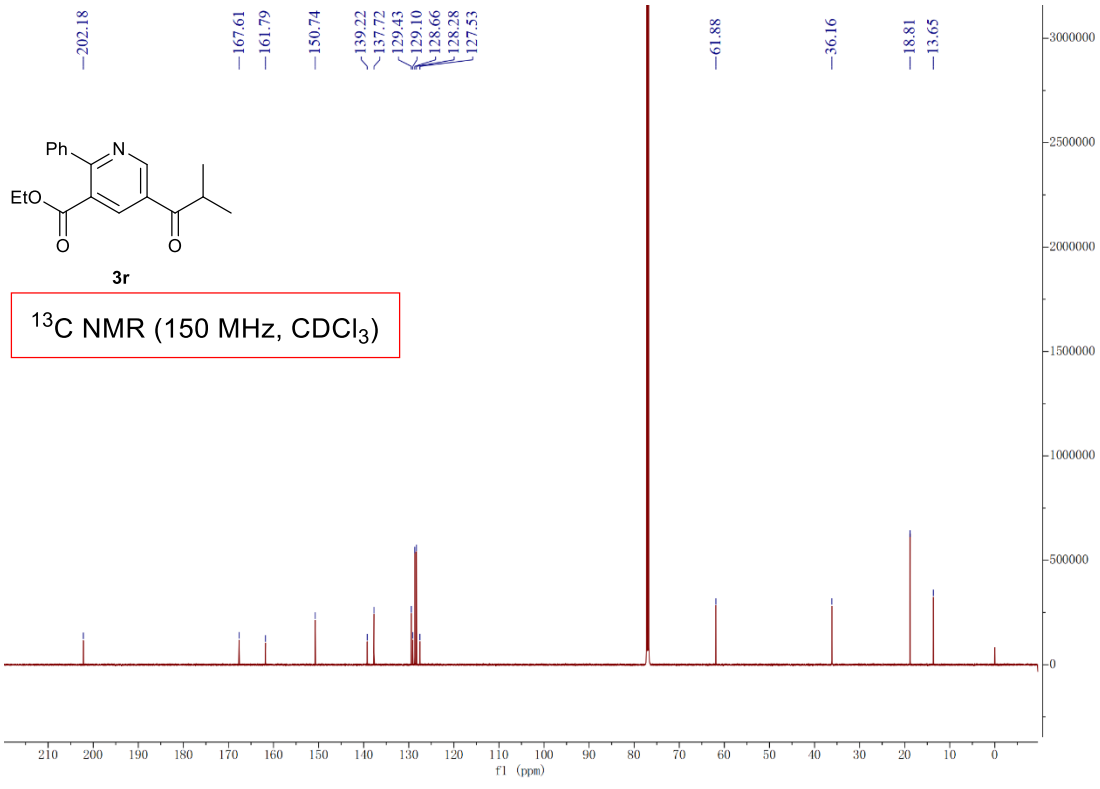

Ph
N
EtO
O
O
O
O
3q
1H NMR (600 MHz, CDCl3)
8.996
8.992
8.368
8.364
7.548
7.545
7.541
7.538
7.536
7.534
7.532
7.529
7.525
7.518
7.515
7.412
7.401
7.398
7.395
7.392
7.390
7.387
7.384
7.381
7.377
7.344
7.341
7.330
7.328
7.318
7.315
7.311
6.835
6.833
6.823
6.820
6.019
4.136
4.124
4.112
4.100
1.018
1.007
0.995
0.99
0.95
2.00
3.00
2.00
0.98
2.00
2.00
3.00
f1 (ppm)


Ph
N
EtO
O
O
O
O
3q
13C NMR (150 MHz, CDCl3)
191.95
167.52
161.11
152.38
151.45
148.48
139.26
138.88
131.56
131.02
129.39
128.72
128.30
127.17
127.16
109.51
108.04
102.15
61.89
13.67
f1 (ppm)



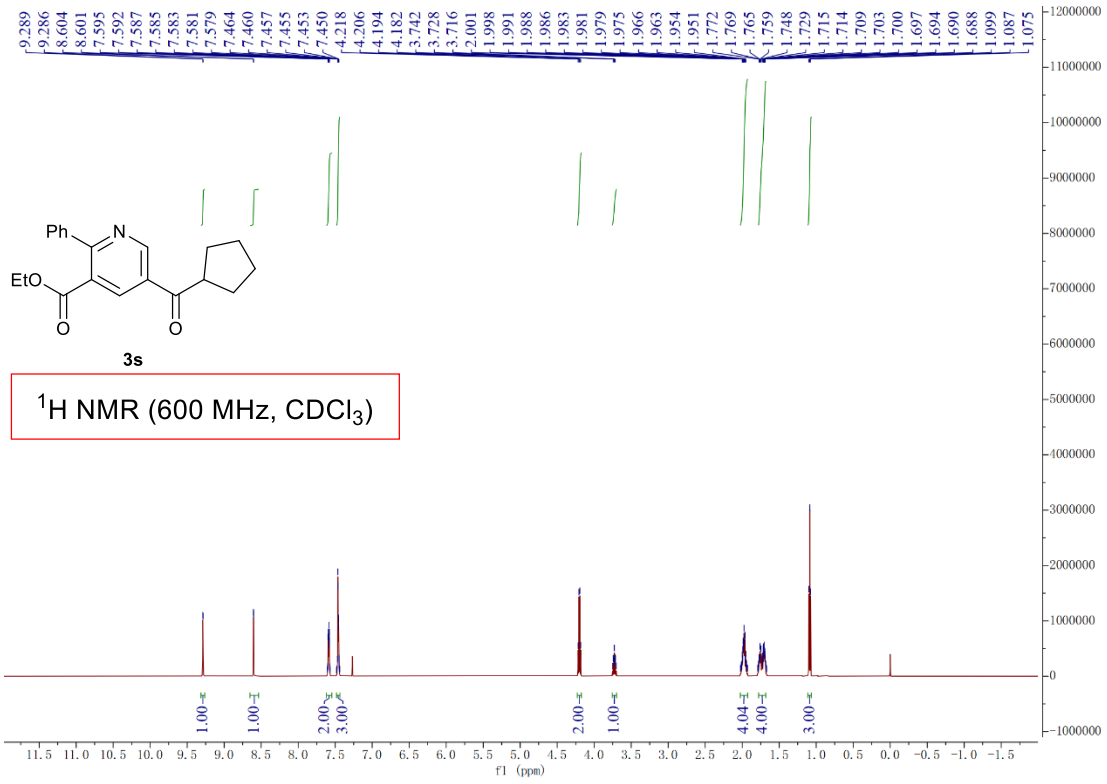
3r

^{1}H NMR (600 MHz, $CDCl_3$)



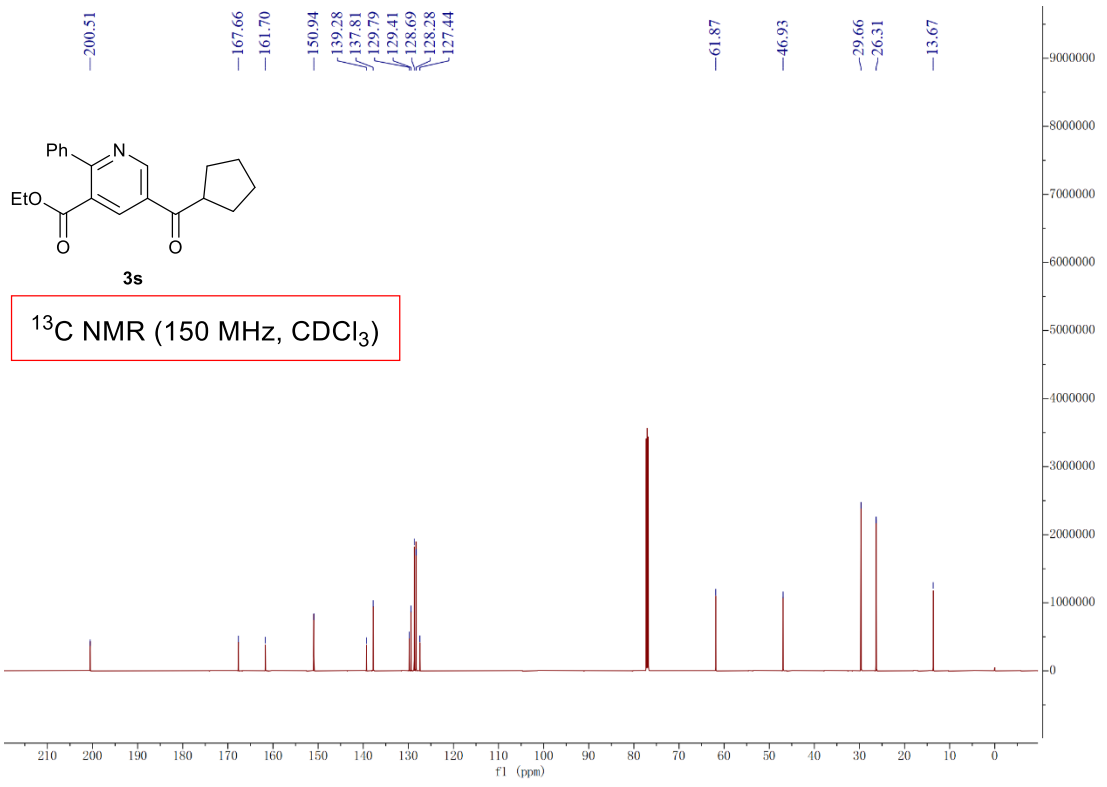
3r

^{13}C NMR (150 MHz, $CDCl_3$)



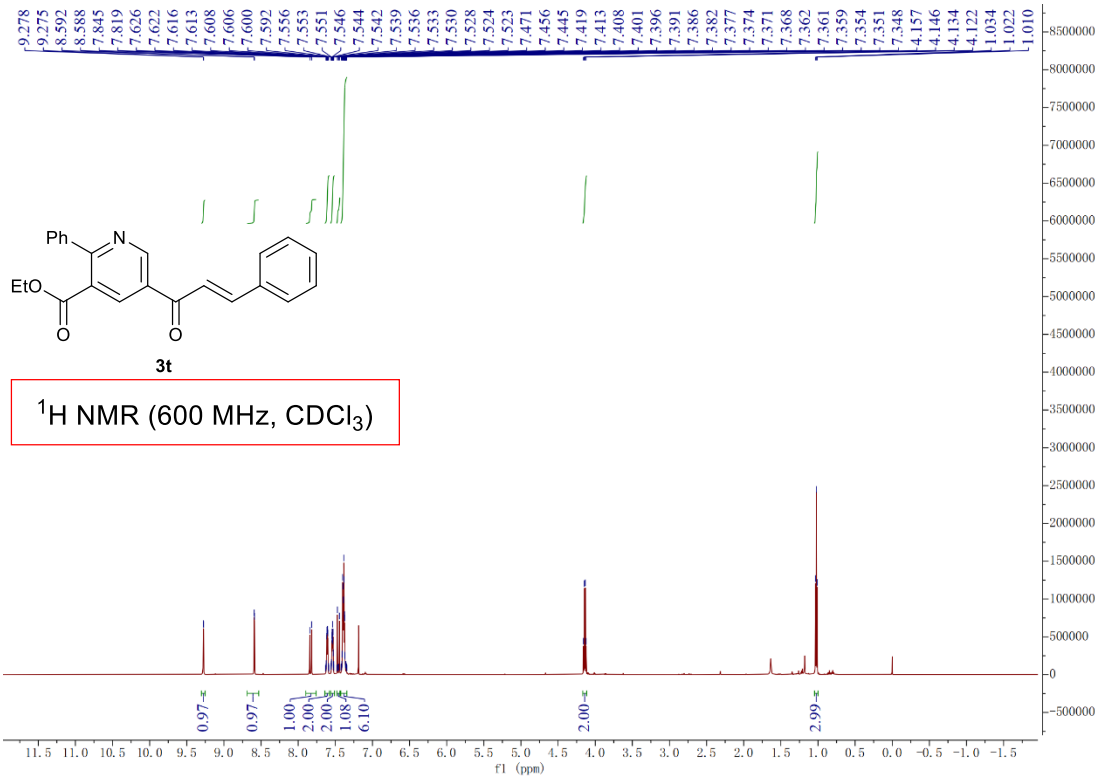
3s

^{1}H NMR (600 MHz, $CDCl_3$)



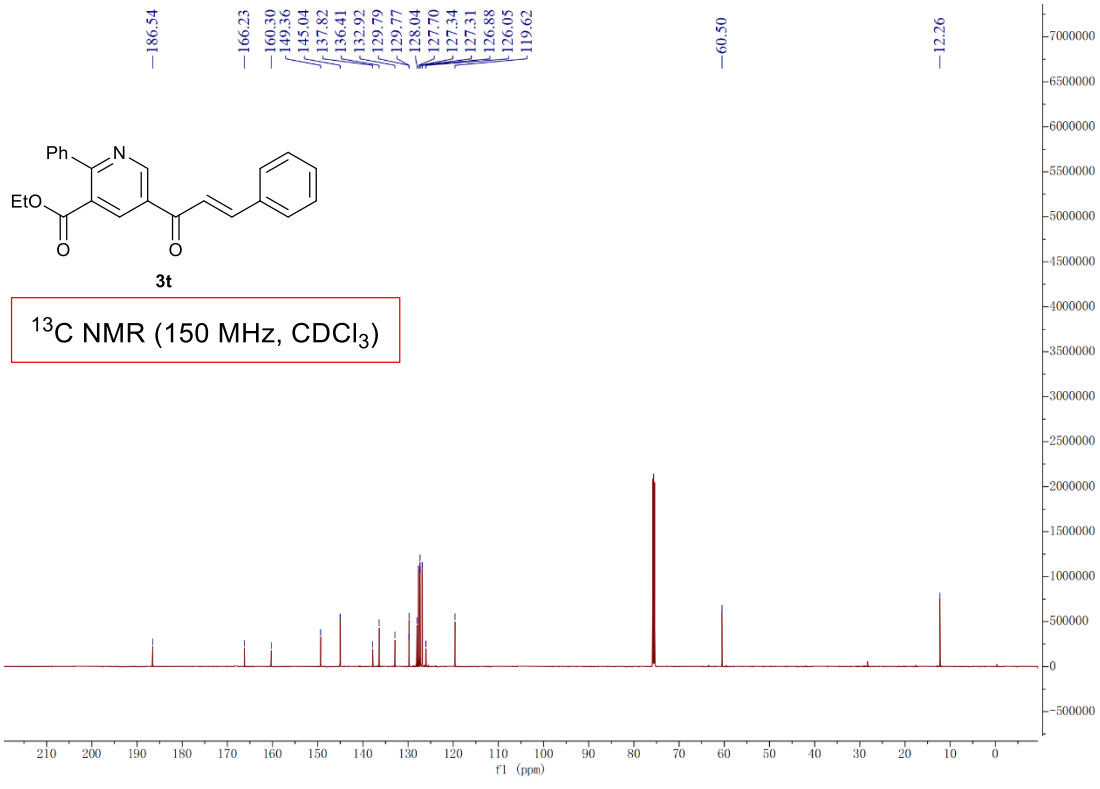
3s

^{13}C NMR (150 MHz, $CDCl_3$)



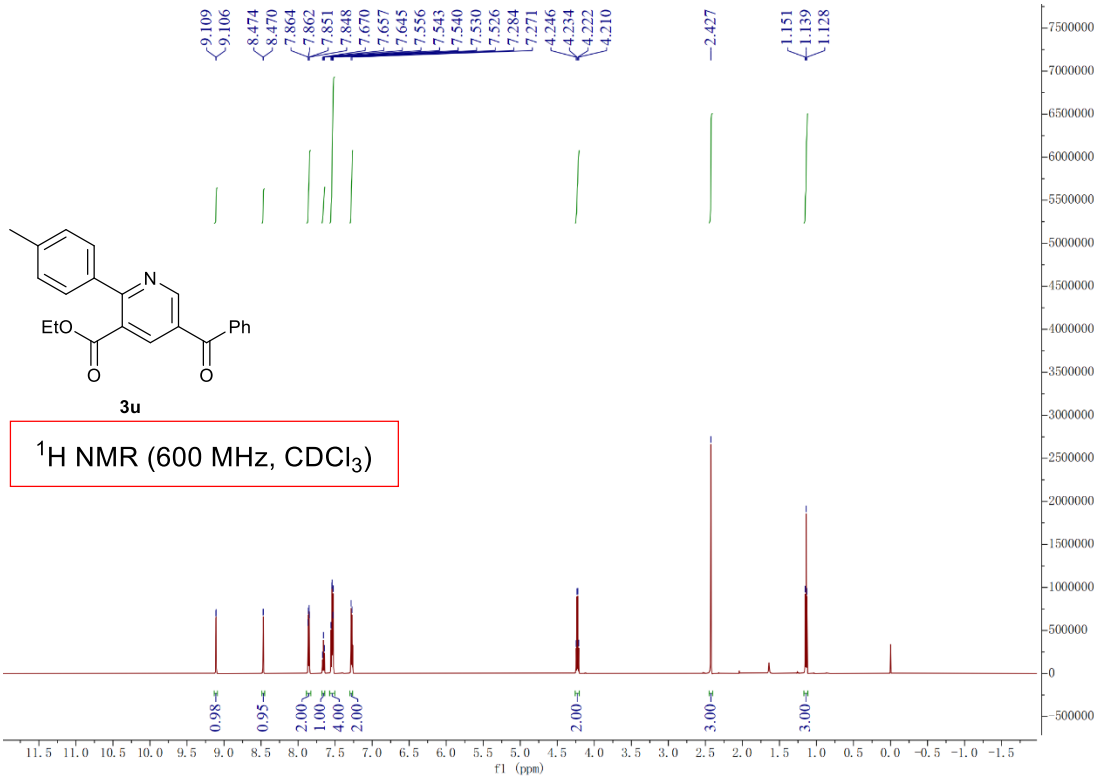
3t

^{1}H NMR (600 MHz, $CDCl_3$)



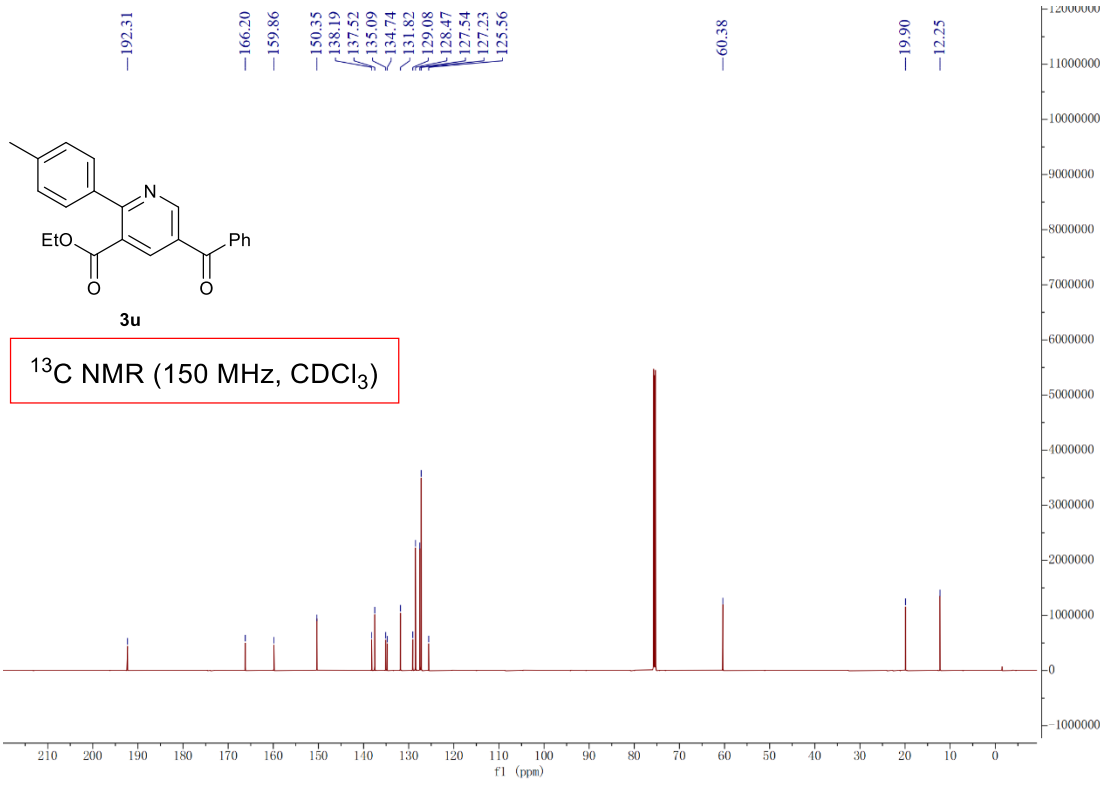
3t

^{13}C NMR (150 MHz, $CDCl_3$)



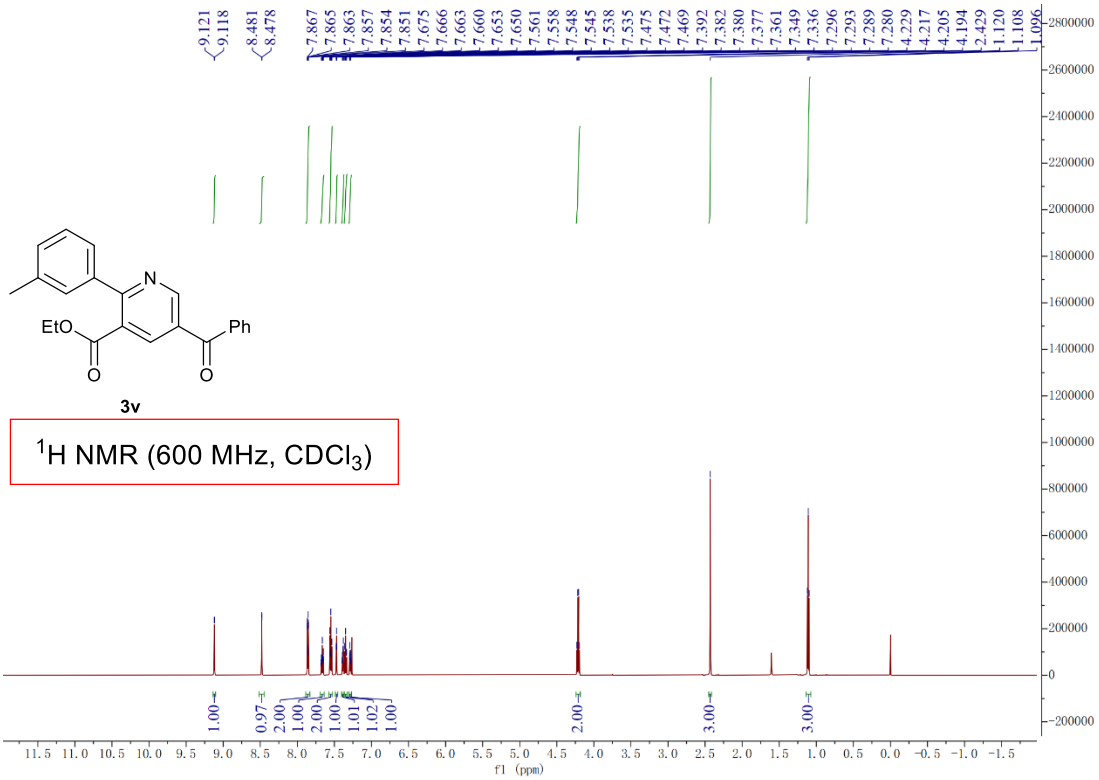
3u

^{1}H NMR (600 MHz, $CDCl_3$)



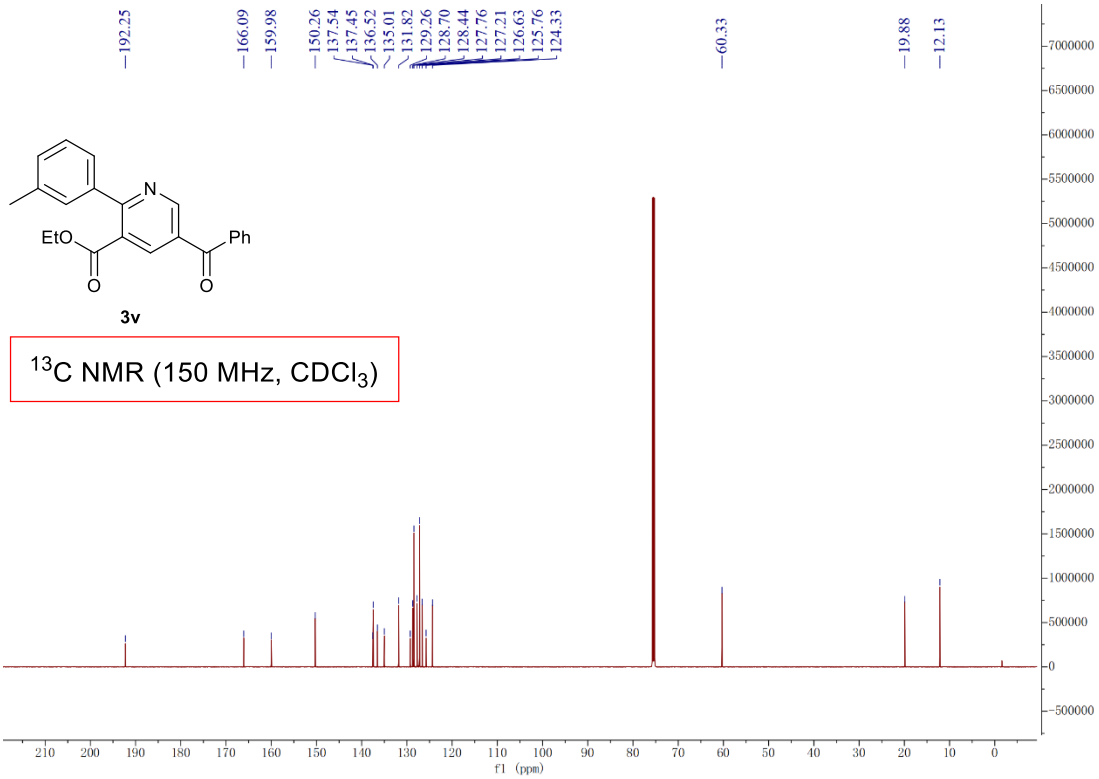
3u

^{13}C NMR (150 MHz, $CDCl_3$)



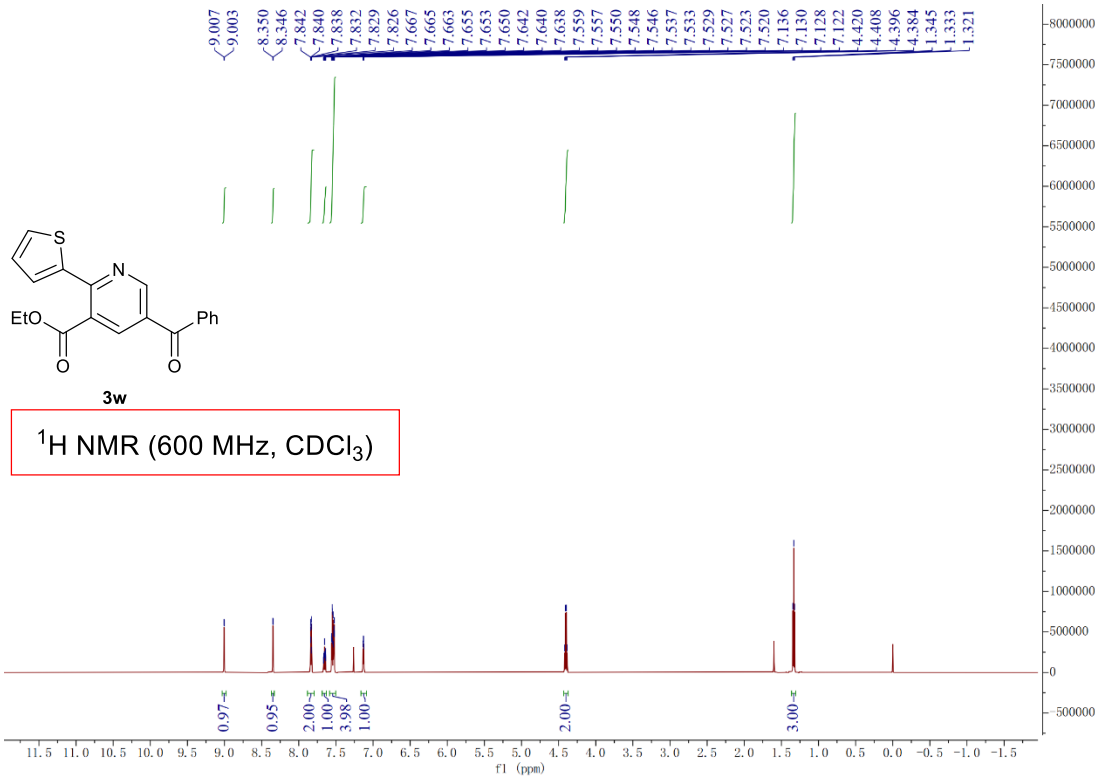
3v

^{1}H NMR (600 MHz, $CDCl_3$)



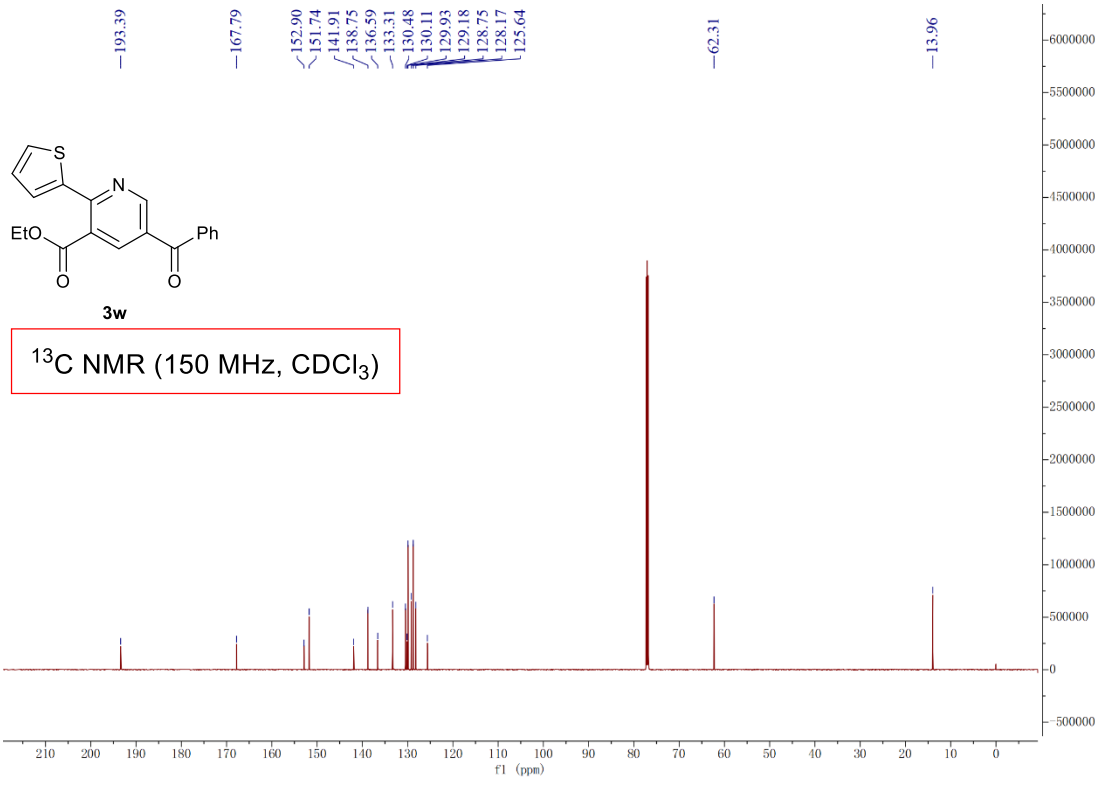
3v

^{13}C NMR (150 MHz, $CDCl_3$)



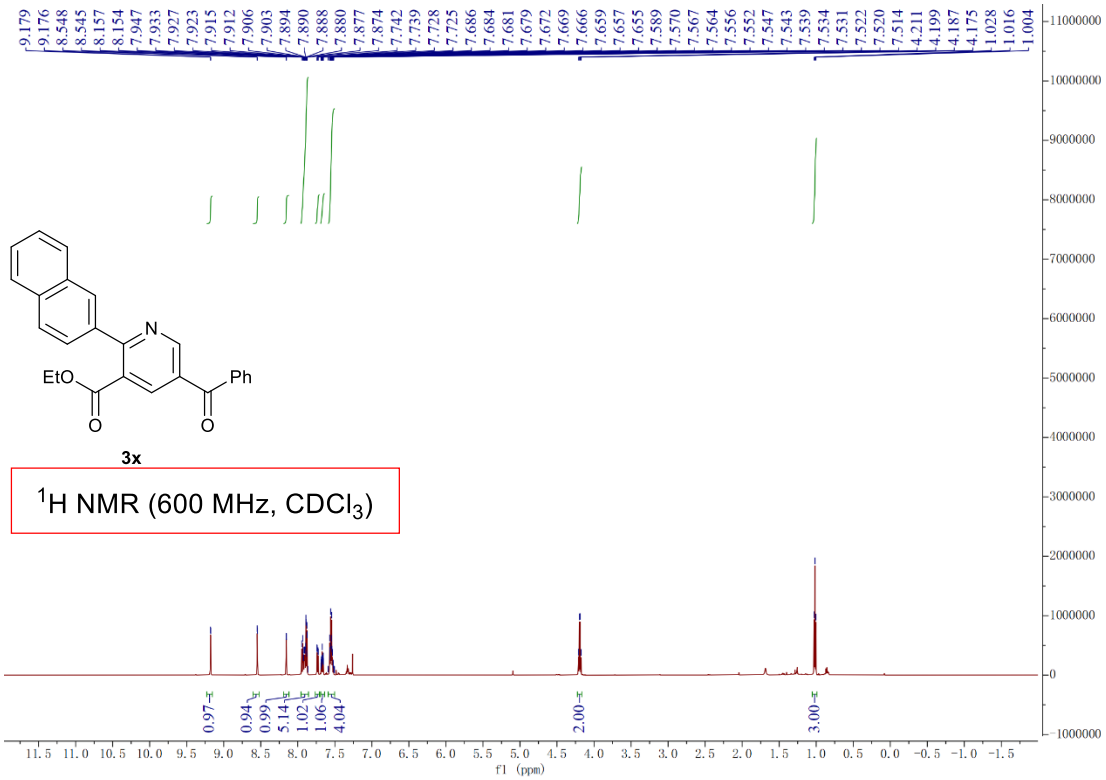
3w

^{1}H NMR (600 MHz, $CDCl_3$)



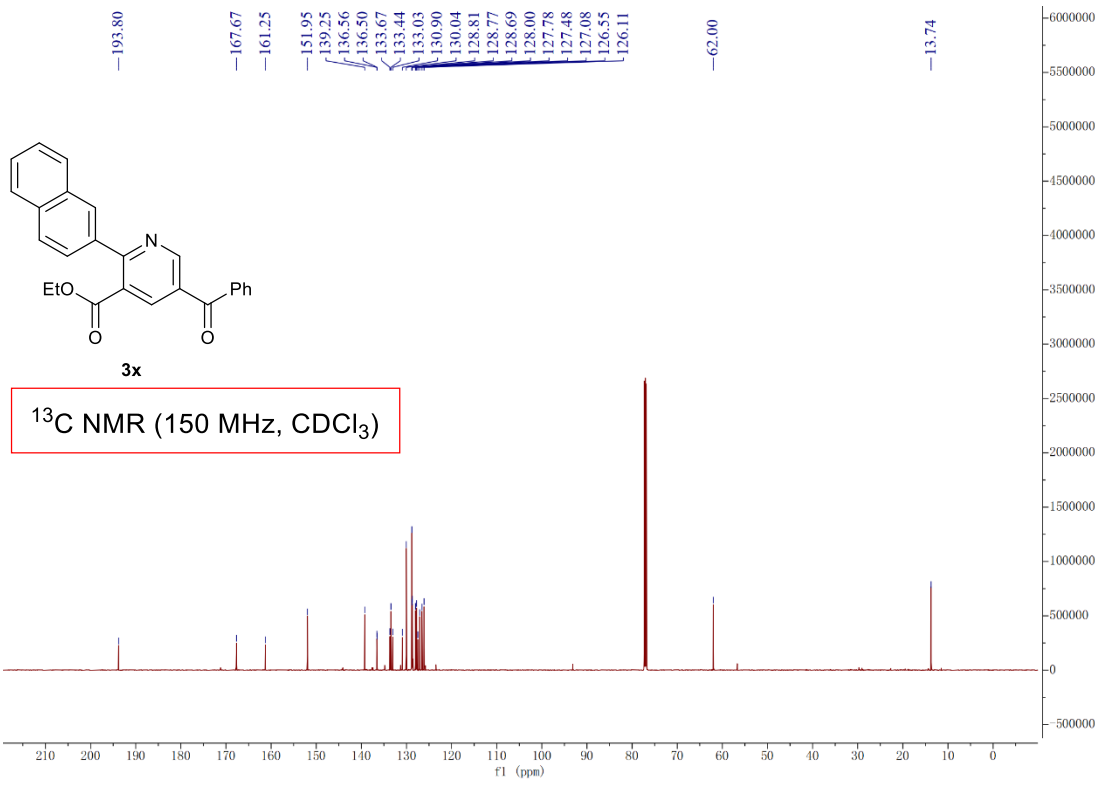
3w

^{13}C NMR (150 MHz, $CDCl_3$)



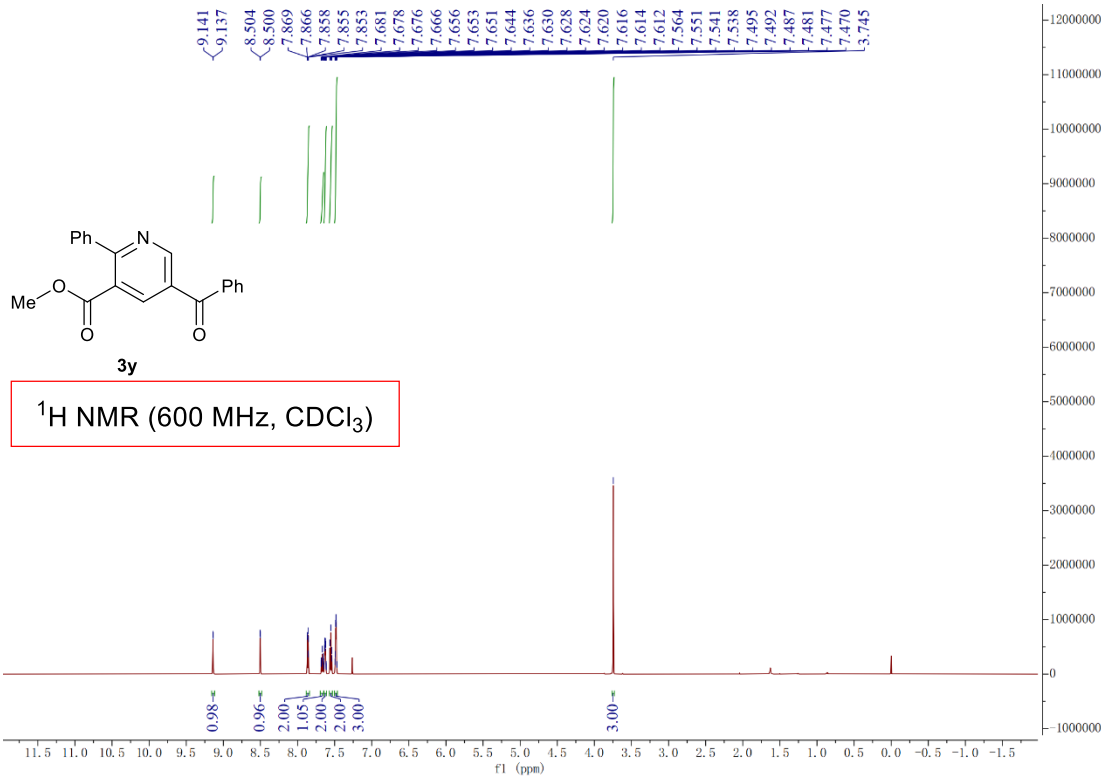
3x

^{1}H NMR (600 MHz, $CDCl_3$)



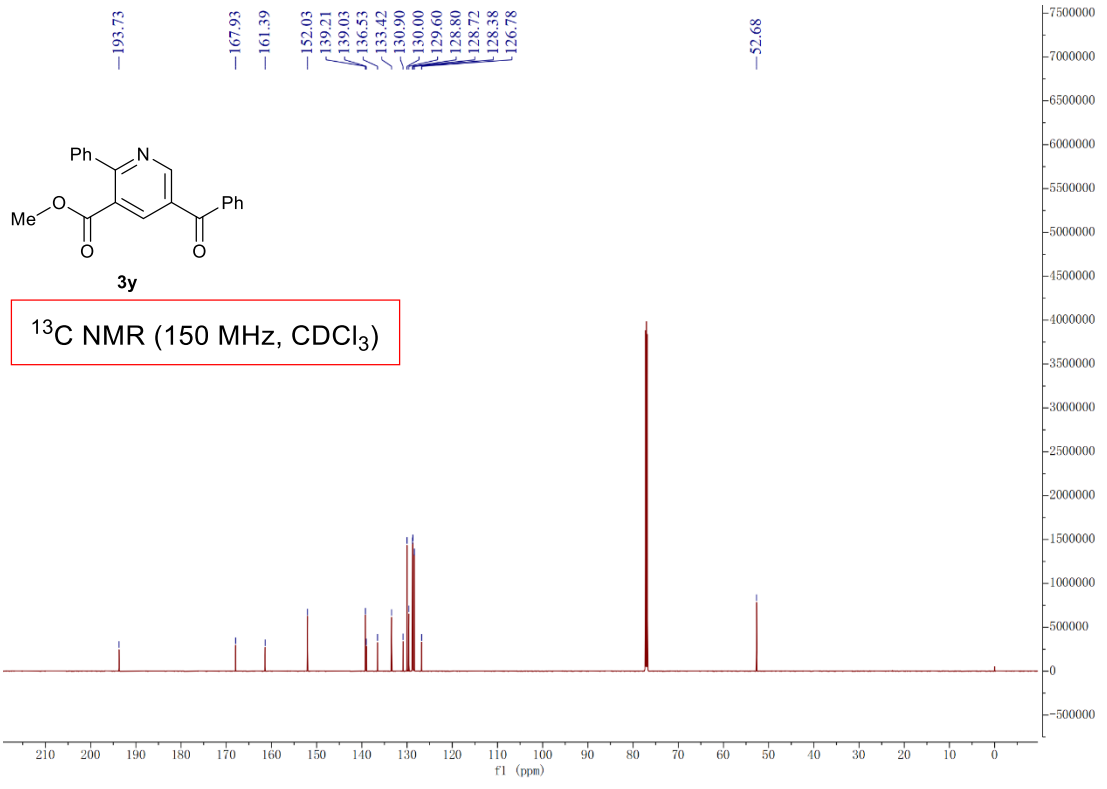
3x

^{13}C NMR (150 MHz, $CDCl_3$)



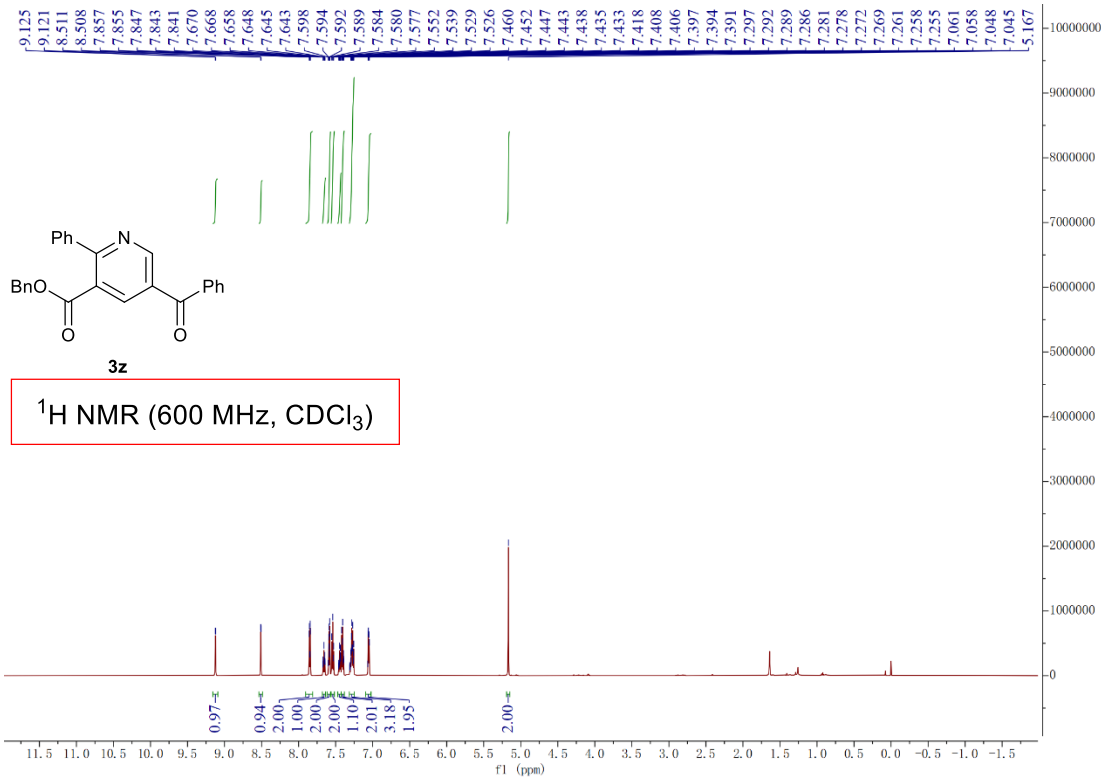
3y

^{1}H NMR (600 MHz, $CDCl_3$)



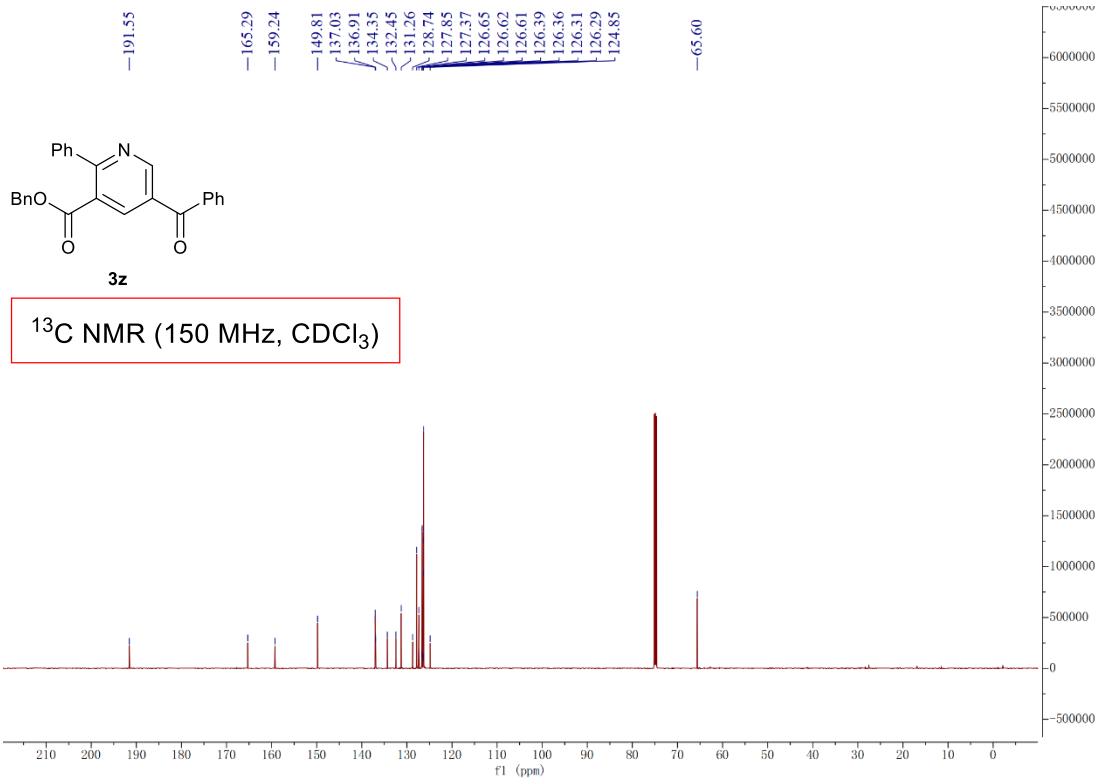
3y

^{13}C NMR (150 MHz, $CDCl_3$)



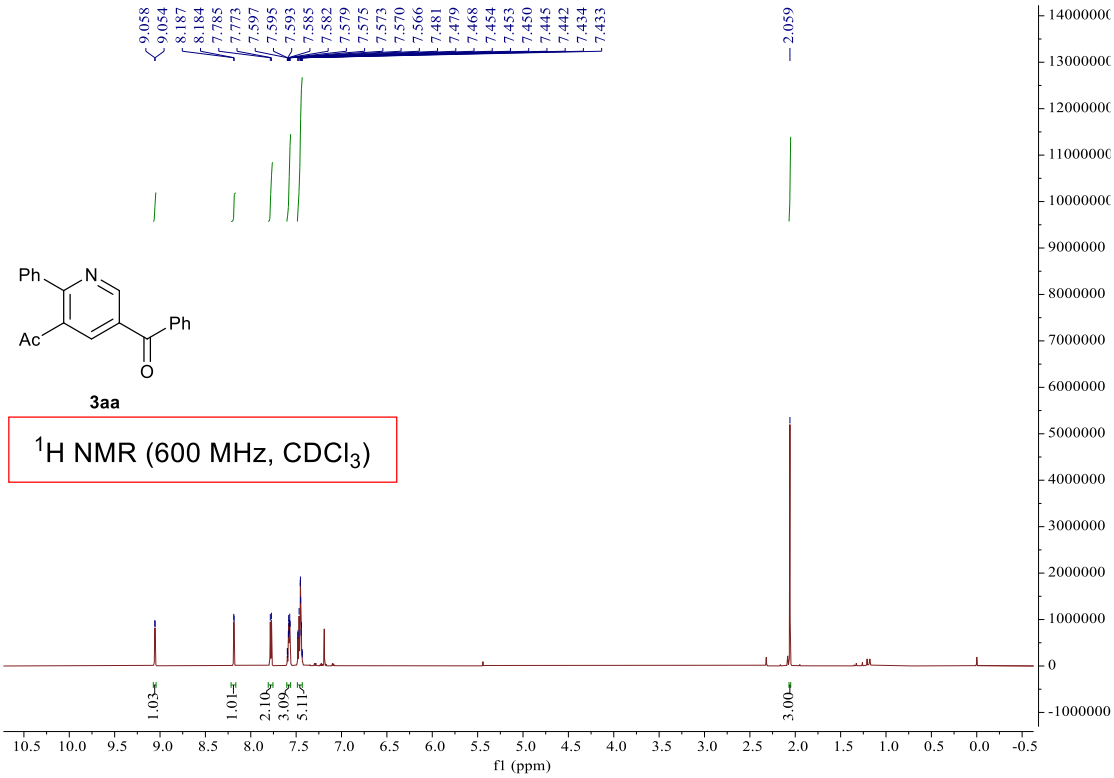
3z

^{1}H NMR (600 MHz, $CDCl_3$)



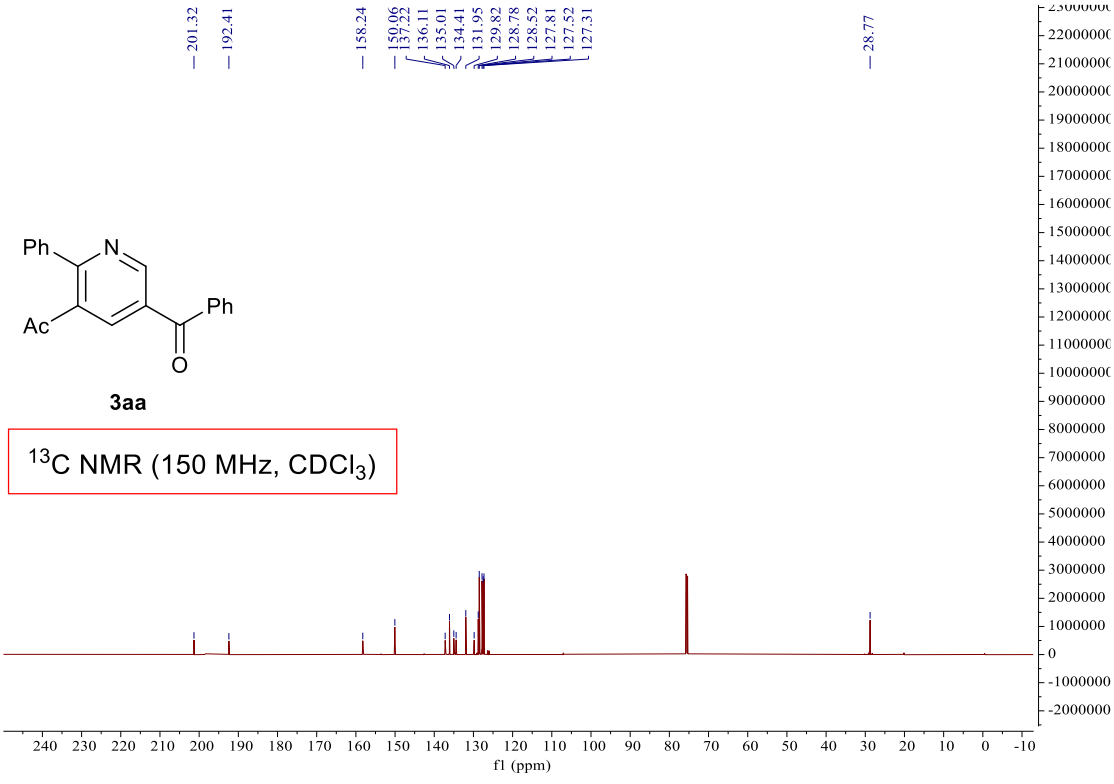
3z

^{13}C NMR (150 MHz, $CDCl_3$)



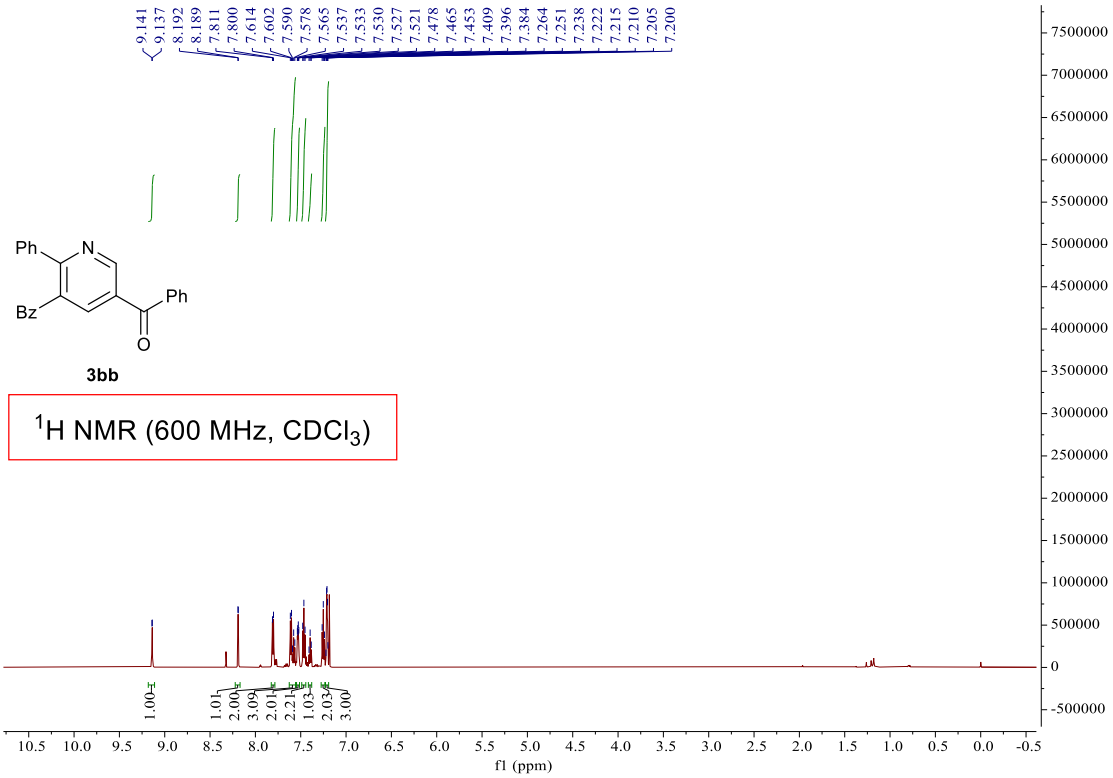
3aa

^{1}H NMR (600 MHz, $CDCl_3$)



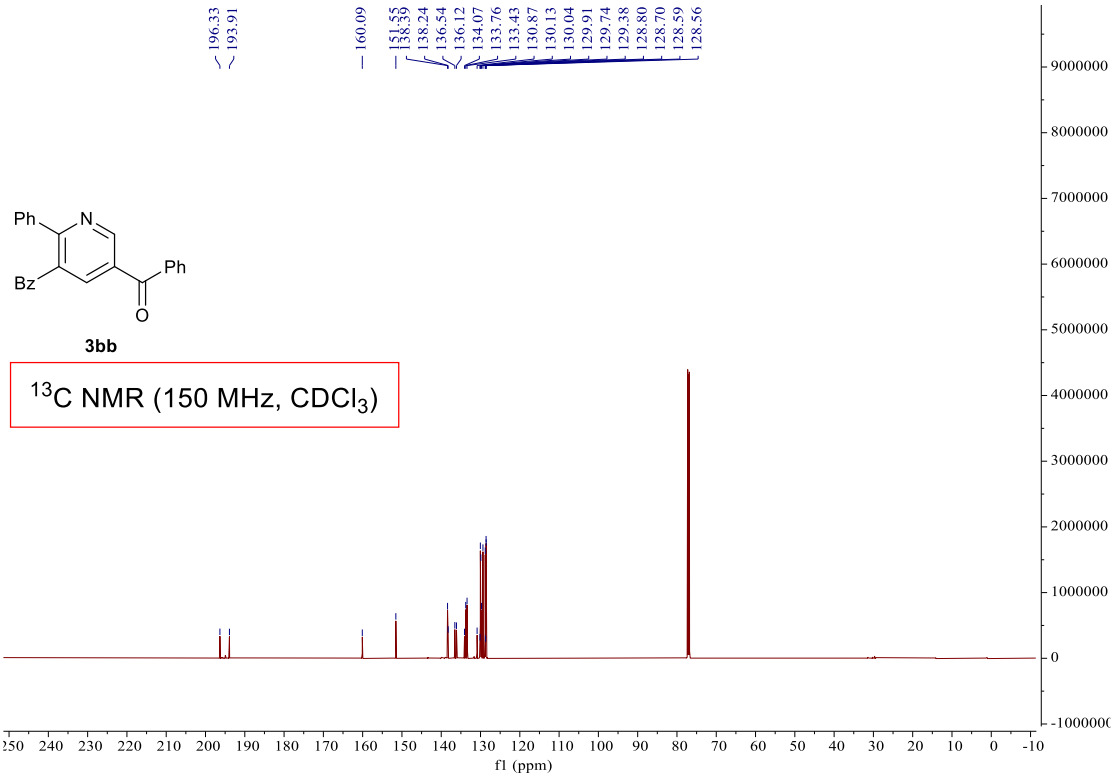
3aa

^{13}C NMR (150 MHz, $CDCl_3$)



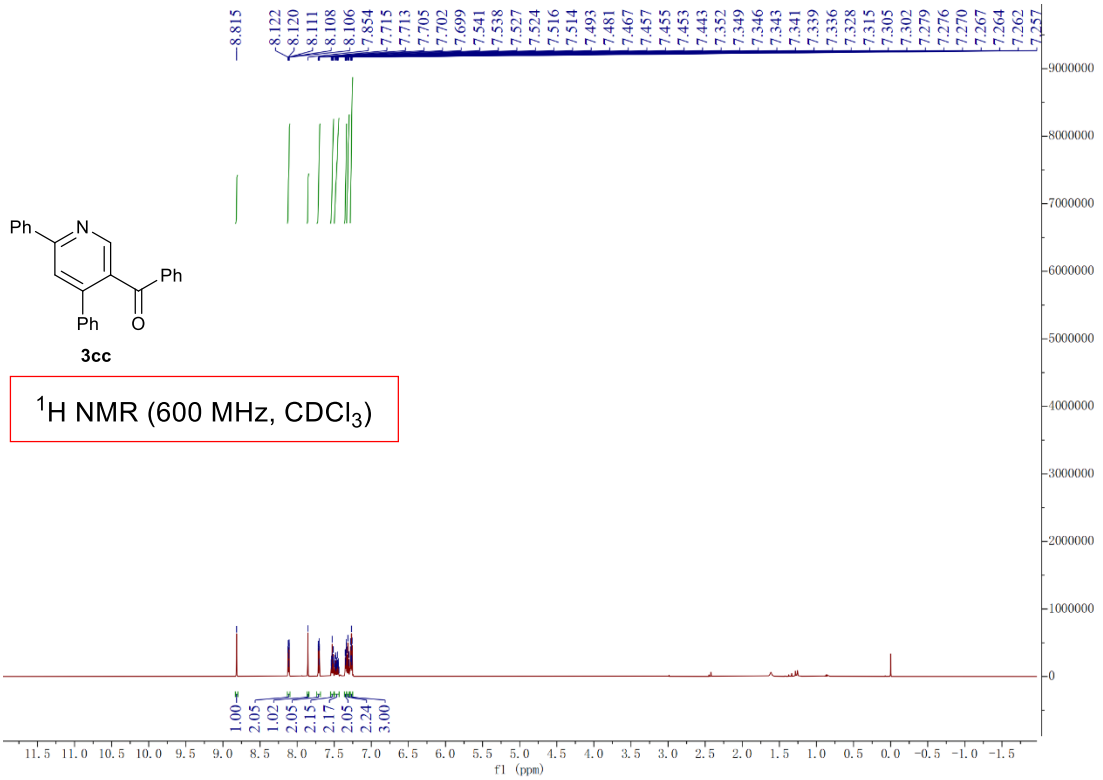
3bb

^{1}H NMR (600 MHz, $CDCl_3$)



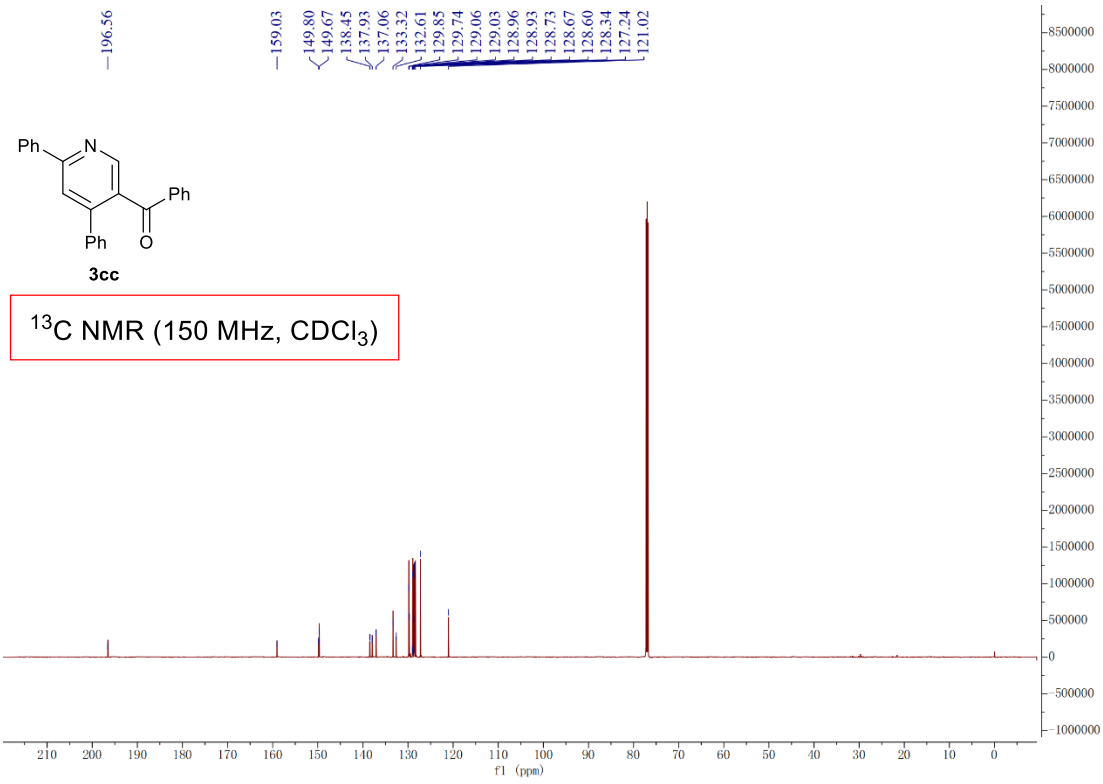
3bb

^{13}C NMR (150 MHz, $CDCl_3$)



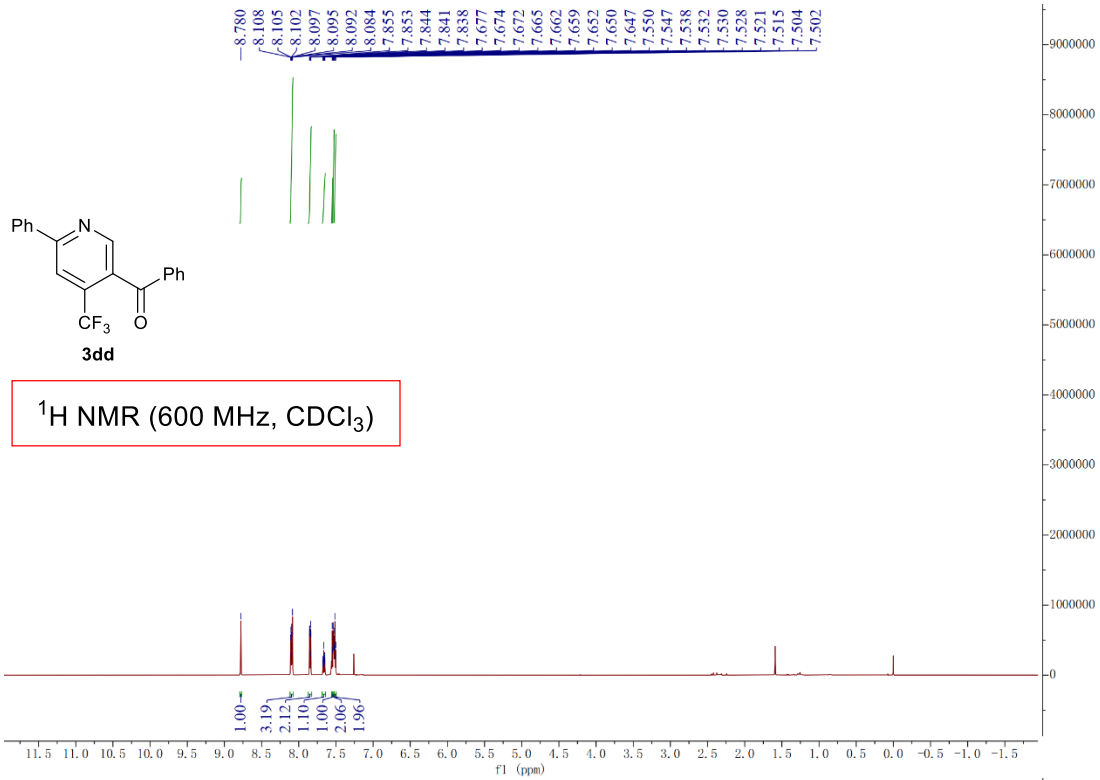
3cc

^{1}H NMR (600 MHz, $CDCl_3$)

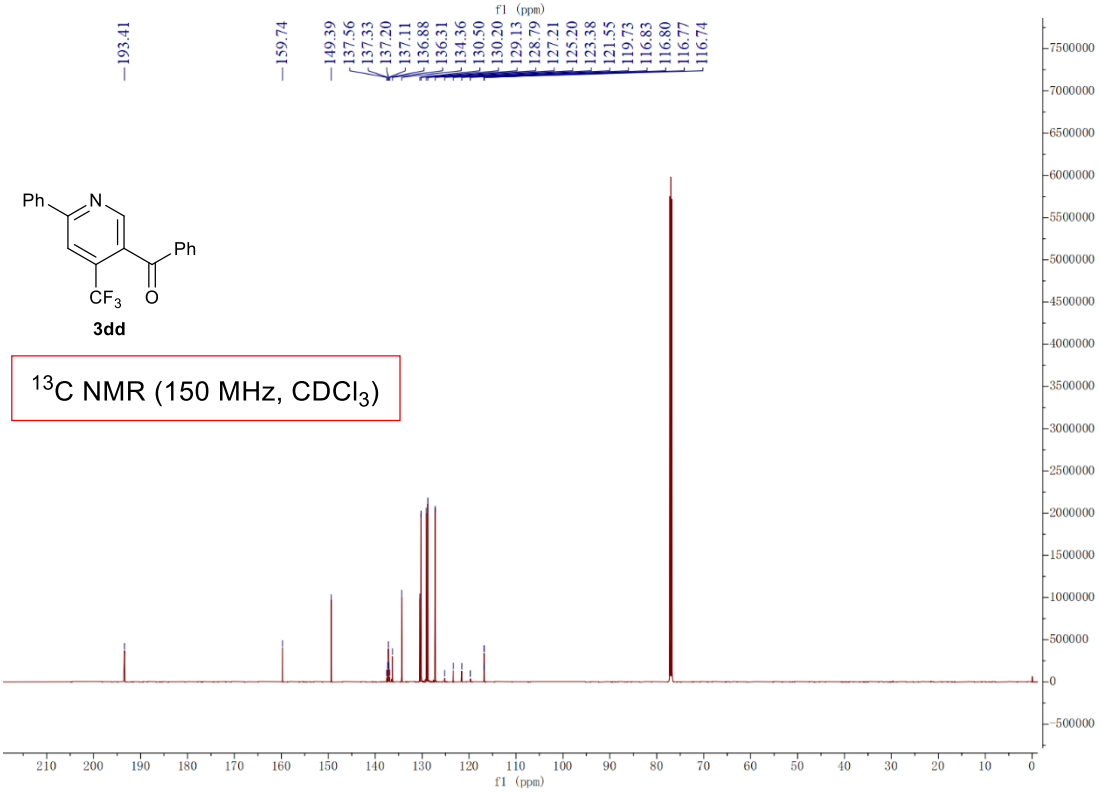


3cc

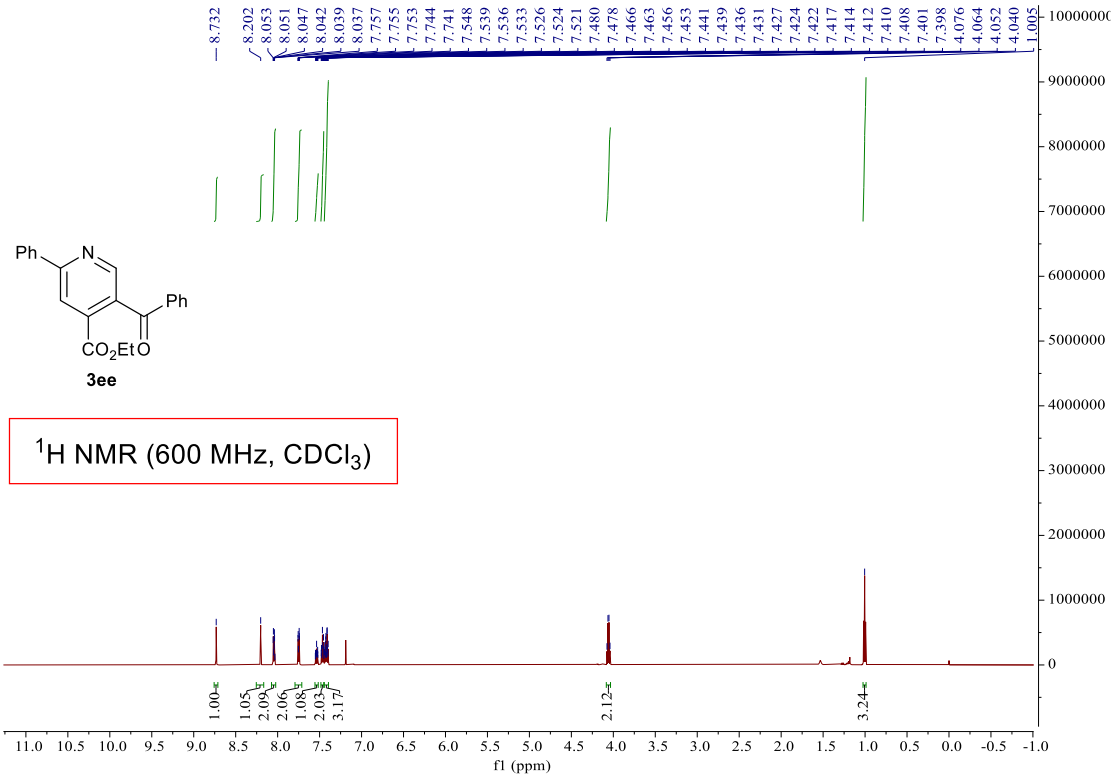
^{13}C NMR (150 MHz, $CDCl_3$)

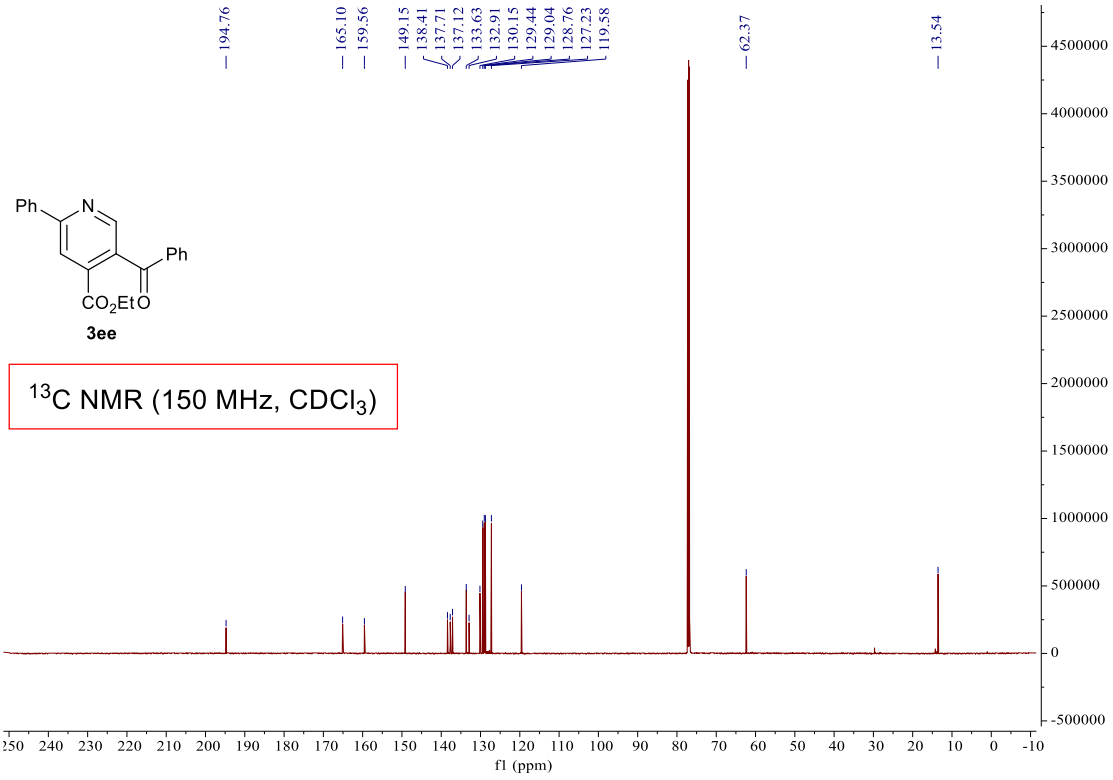


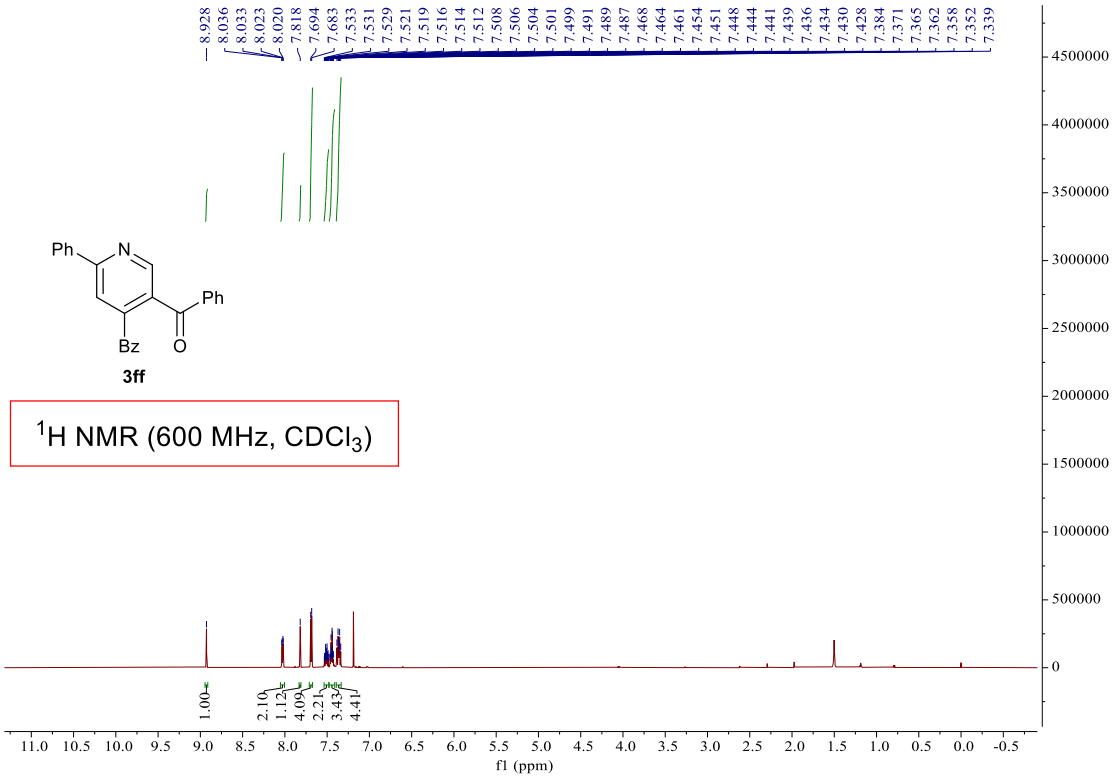
^{1}H NMR (600 MHz, $CDCl_3$)



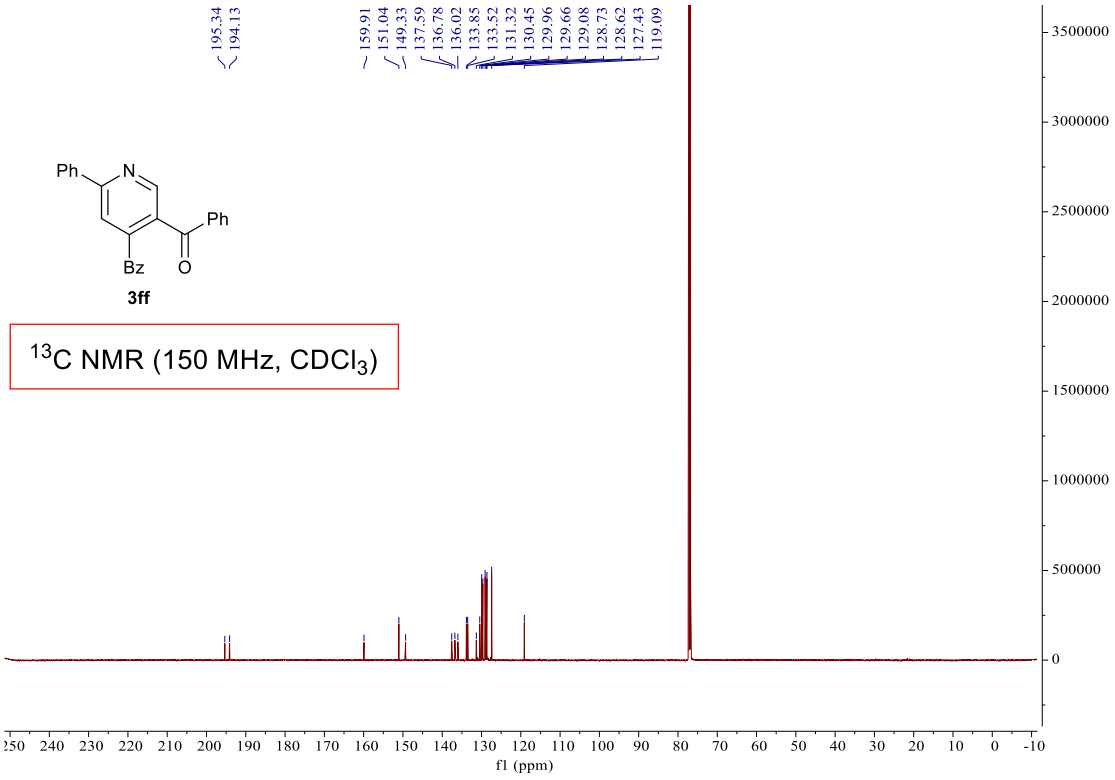
^{13}C NMR (150 MHz, $CDCl_3$)


Ph
N
Ph
CO2Et
O
3ee
1H NMR (600 MHz, CDCl3)
f1 (ppm)

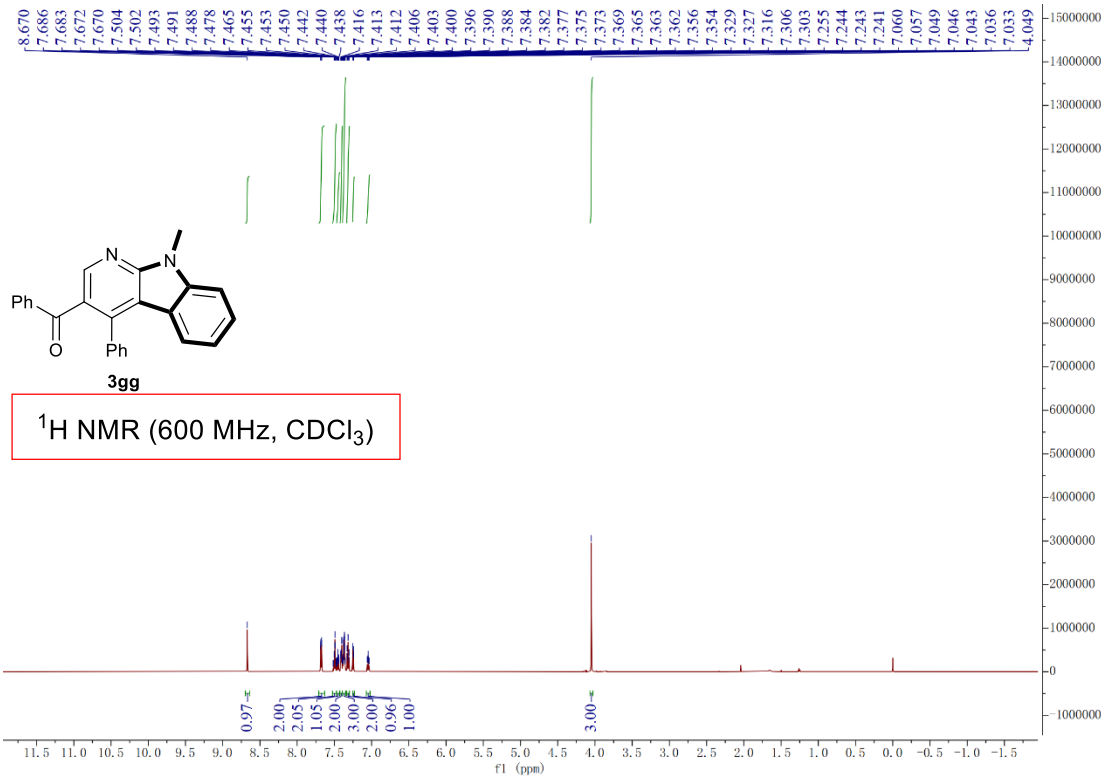

Ph
N
Ph
CO2Et
O
3ee
13C NMR (150 MHz, CDCl3)
f1 (ppm)



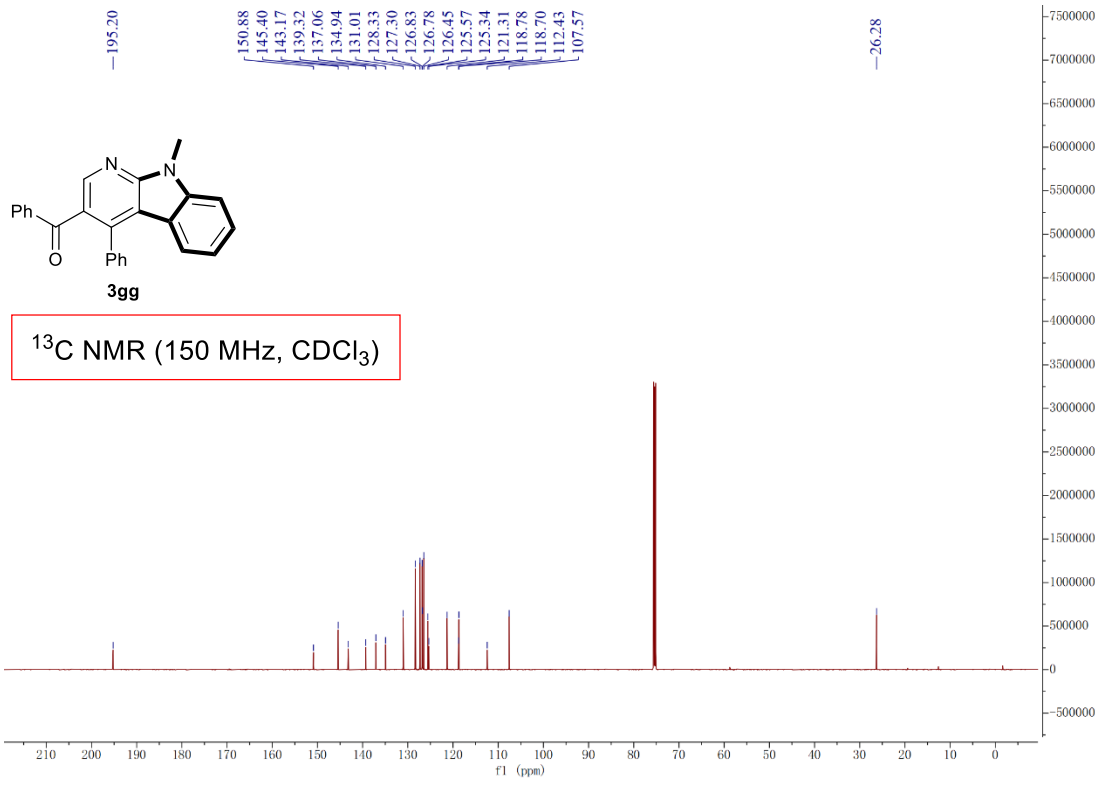
^{1}H NMR (600 MHz, $CDCl_3$)



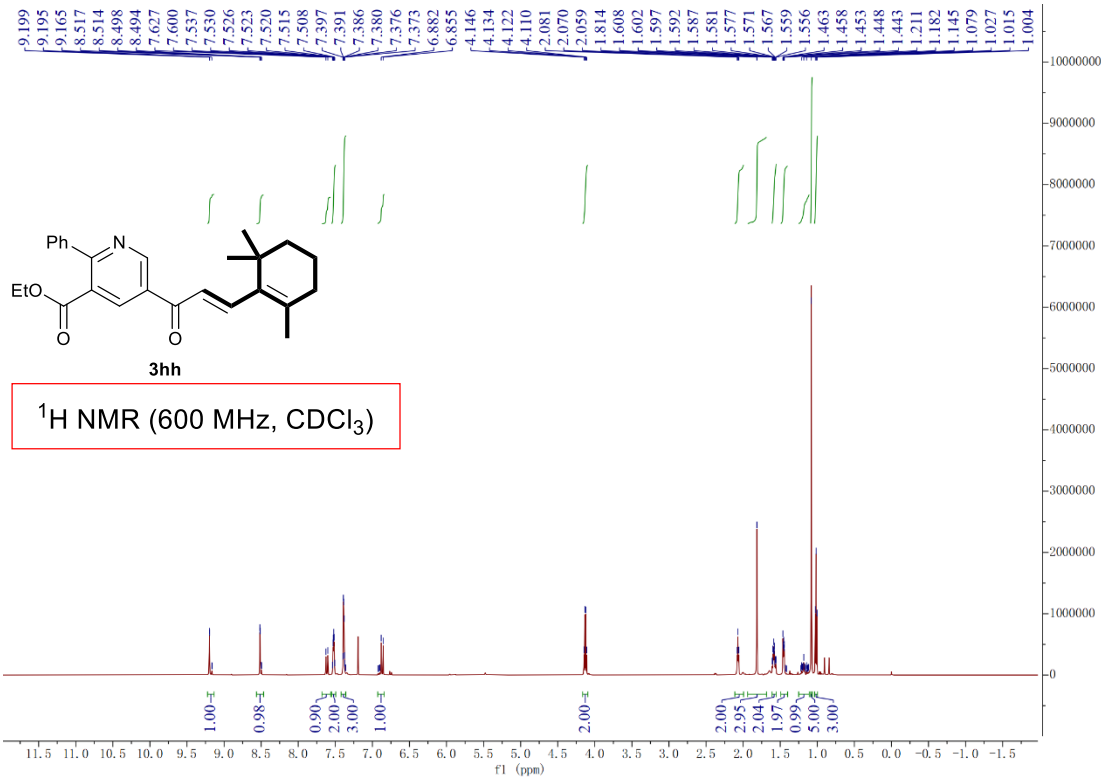
^{13}C NMR (150 MHz, $CDCl_3$)



^{1}H NMR (600 MHz, $CDCl_3$)

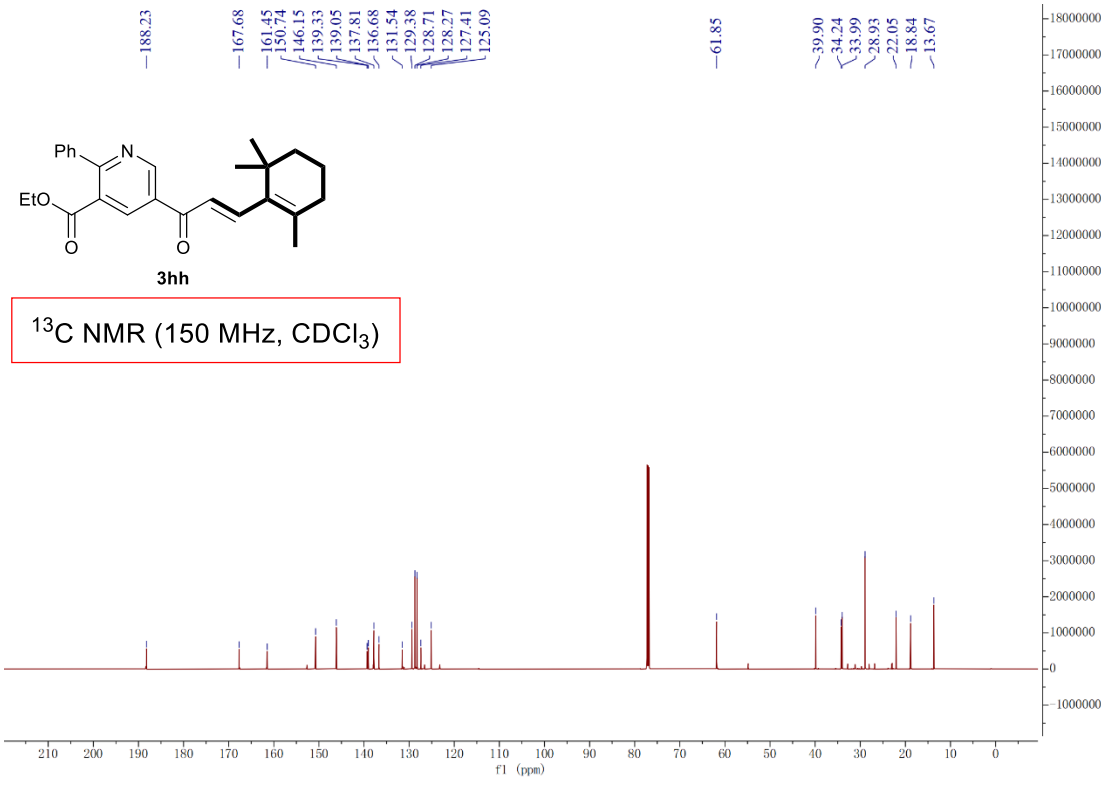


^{13}C NMR (150 MHz, $CDCl_3$)



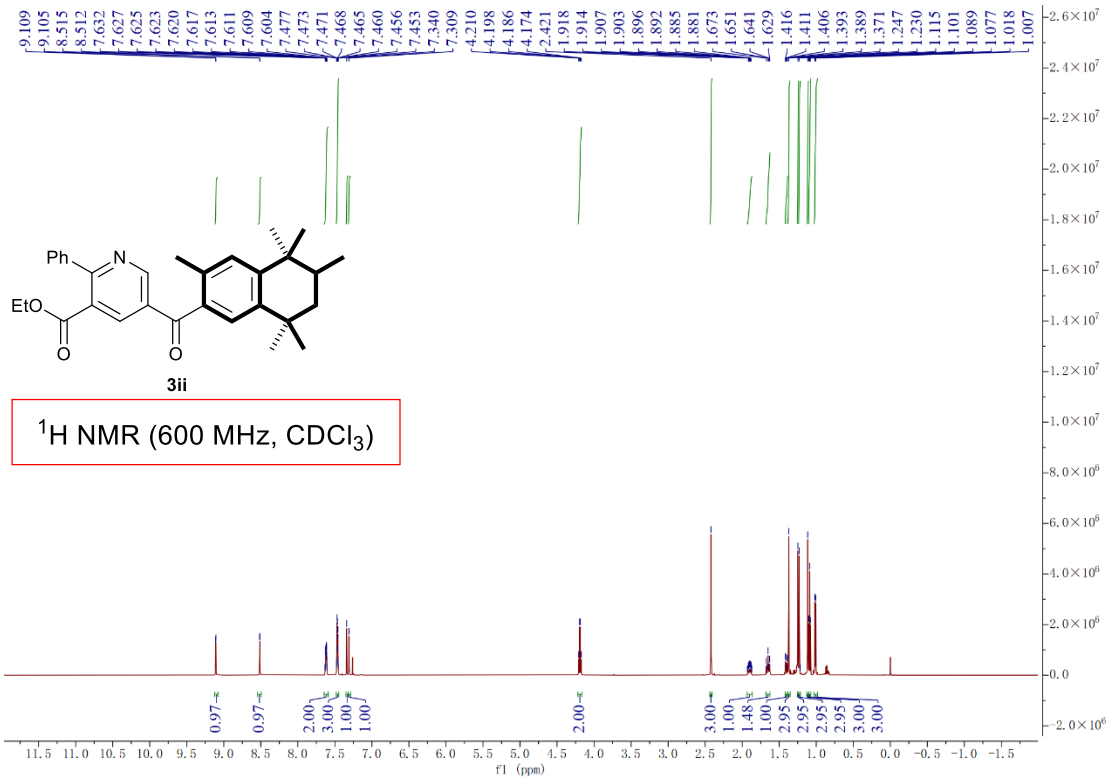
3hh

^{1}H NMR (600 MHz, $CDCl_3$)



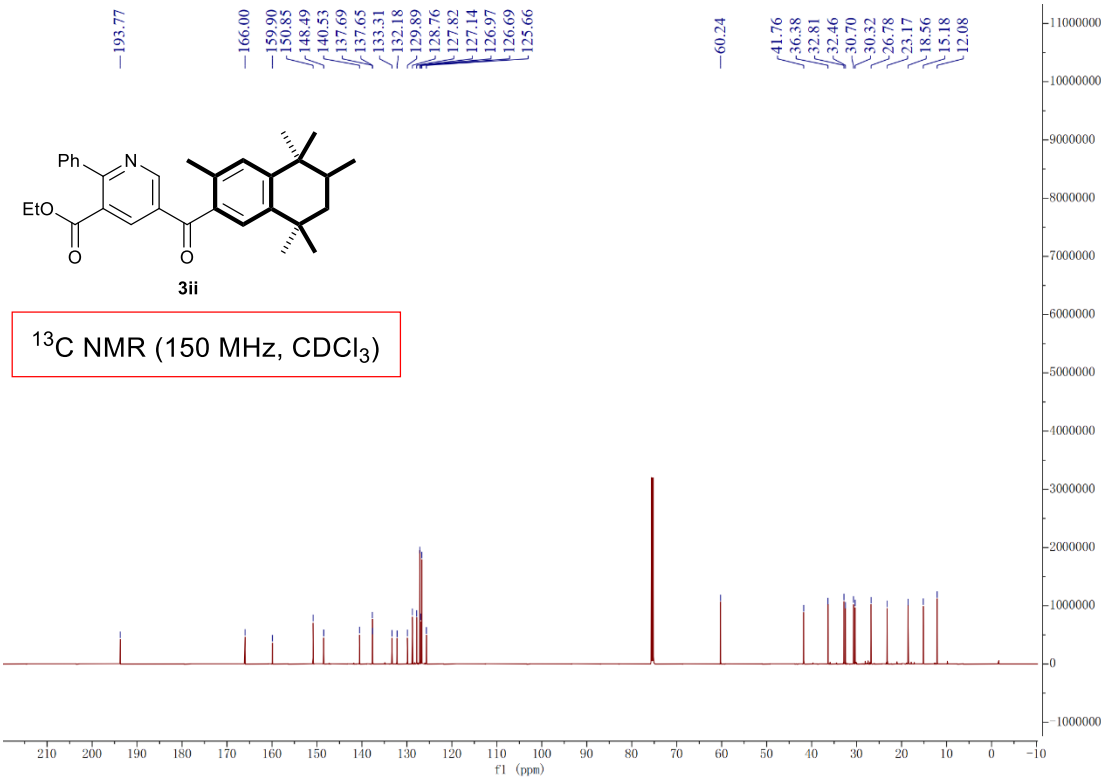
3hh

^{13}C NMR (150 MHz, $CDCl_3$)



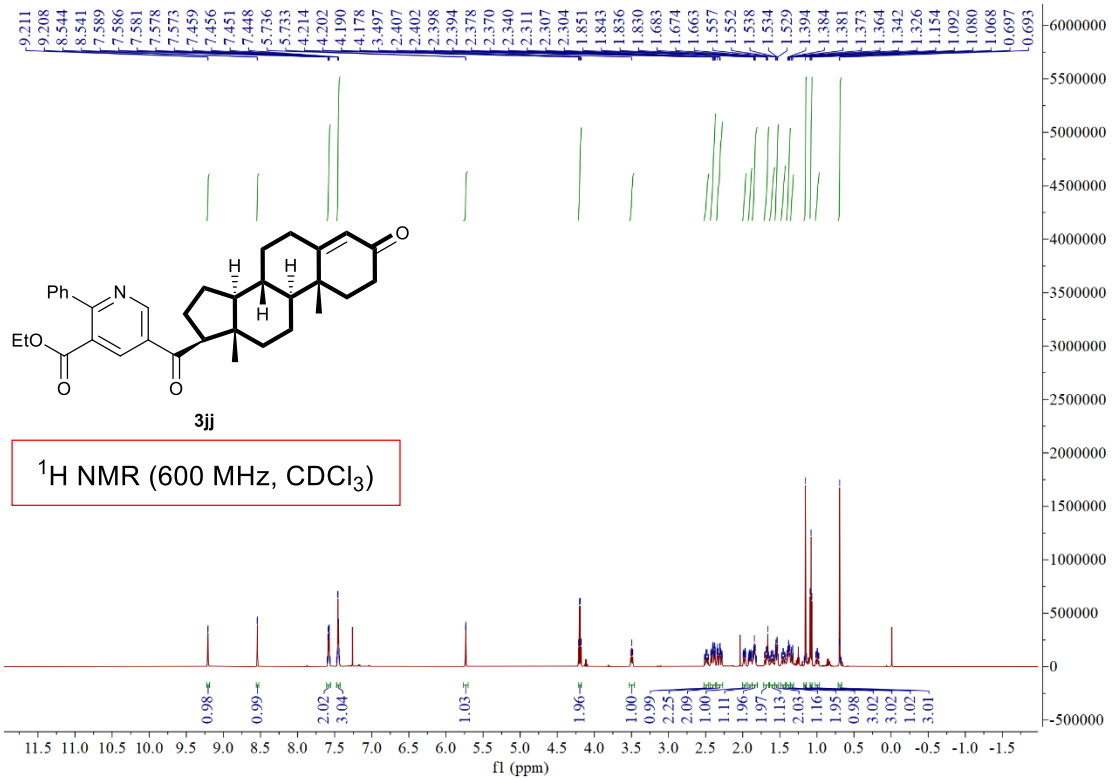
3ii

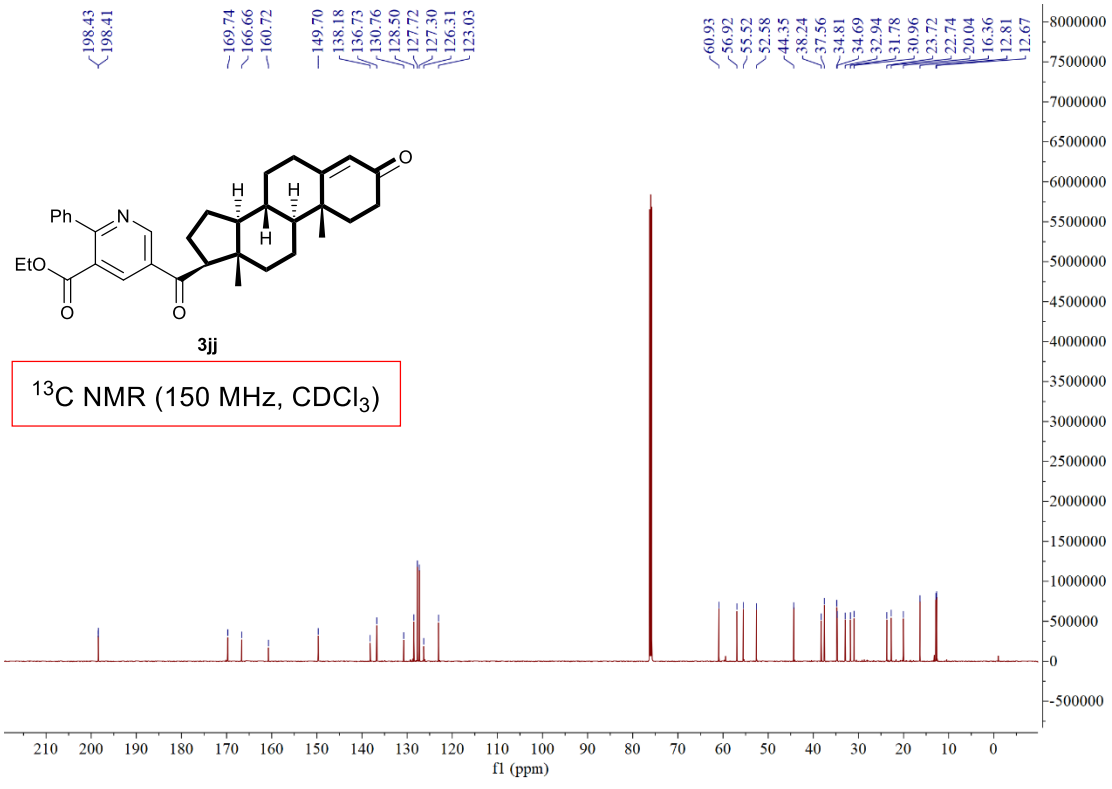
^{1}H NMR (600 MHz, $CDCl_3$)

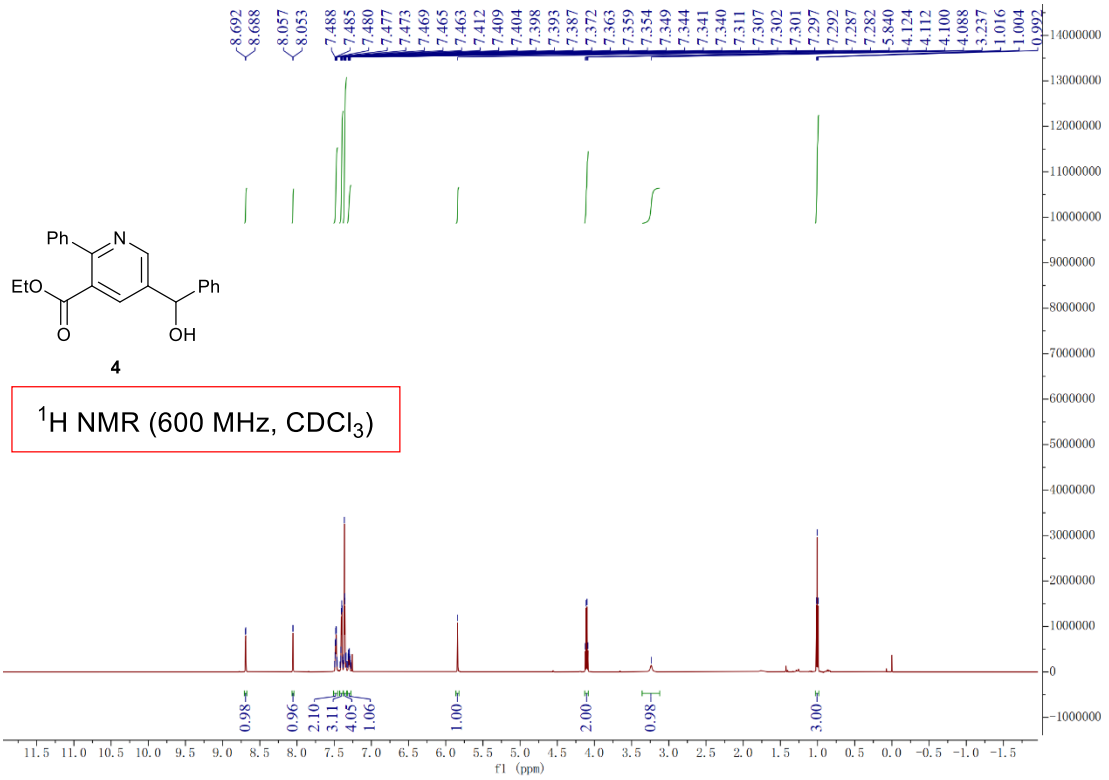


3ii

^{13}C NMR (150 MHz, $CDCl_3$)

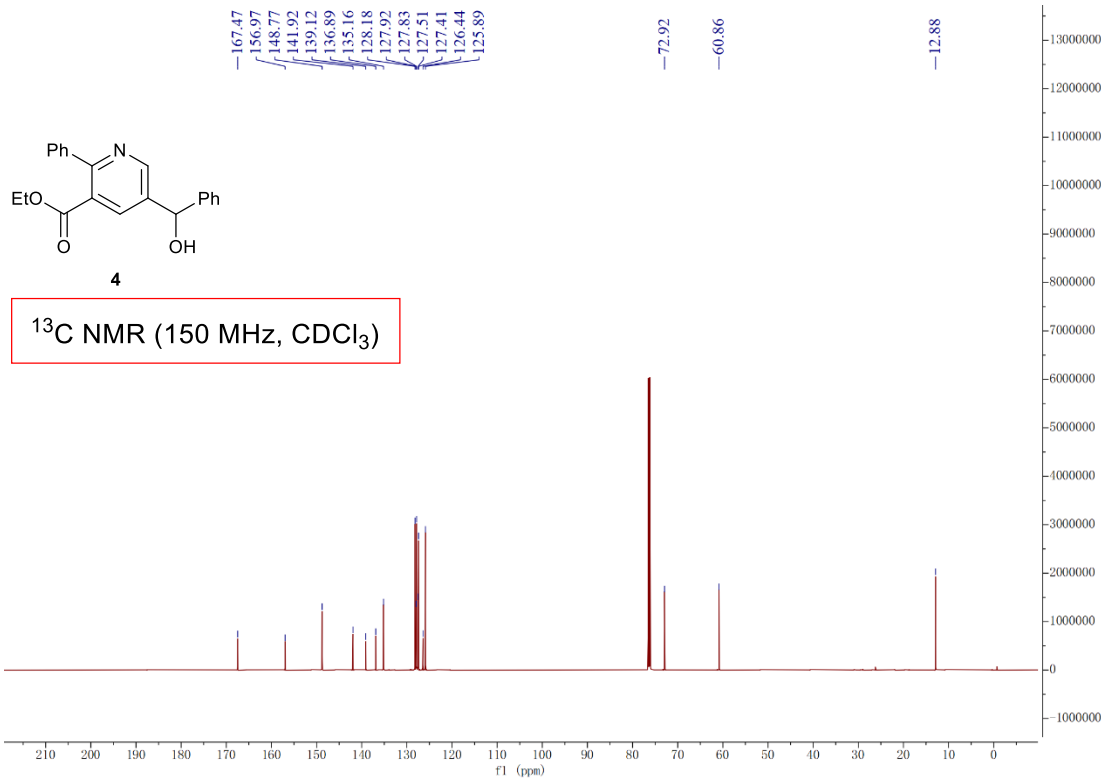

9.211
9.208
8.544
8.541
7.589
7.586
7.581
7.578
7.573
7.459
7.456
7.451
7.448
5.736
5.733
4.214
4.202
4.190
4.178
3.497
2.407
2.402
2.398
2.394
2.378
2.370
2.340
2.311
2.307
2.304
1.851
1.843
1.836
1.830
1.683
1.674
1.663
1.557
1.552
1.538
1.534
1.529
1.394
1.384
1.381
1.373
1.364
1.342
1.326
1.154
1.092
1.080
1.068
0.697
0.693
Ph
N
EtO
O
O
O
H
H
H
3jj
^{1}H NMR (600 MHz, CDCl$_3$)
0.98
0.99
2.02
3.04
1.03
1.96
1.00
0.99
2.25
2.09
1.00
1.11
1.96
1.97
1.13
2.03
1.16
1.95
0.98
3.02
3.02
1.02
3.01
f1 (ppm)


198.43
198.41
169.74
166.66
160.72
149.70
138.18
136.73
130.76
128.50
127.72
127.30
126.31
123.03
60.93
56.92
55.52
52.58
44.35
38.24
37.56
34.81
34.69
32.94
31.78
30.96
23.72
22.74
20.04
16.36
12.81
12.67
Ph
N
EtO
O
O
O
H
H
H
3jj
^{13}C NMR (150 MHz, CDCl$_3$)
f1 (ppm)



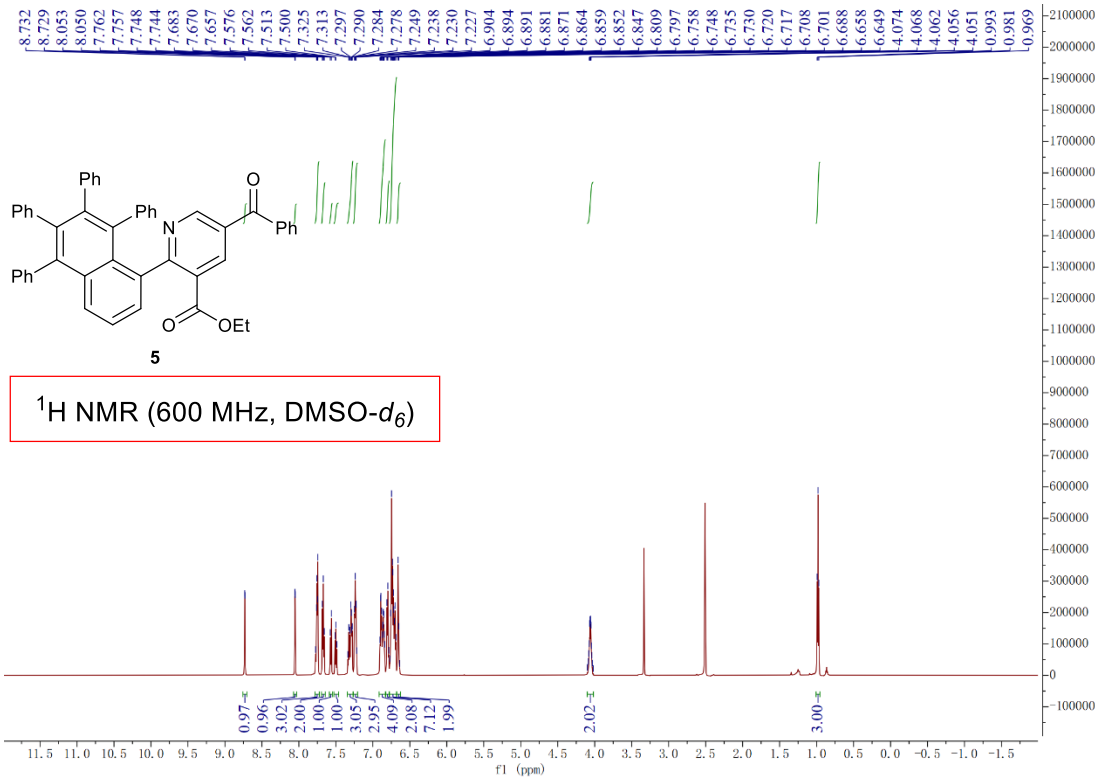
4

^{1}H NMR (600 MHz, $CDCl_3$)



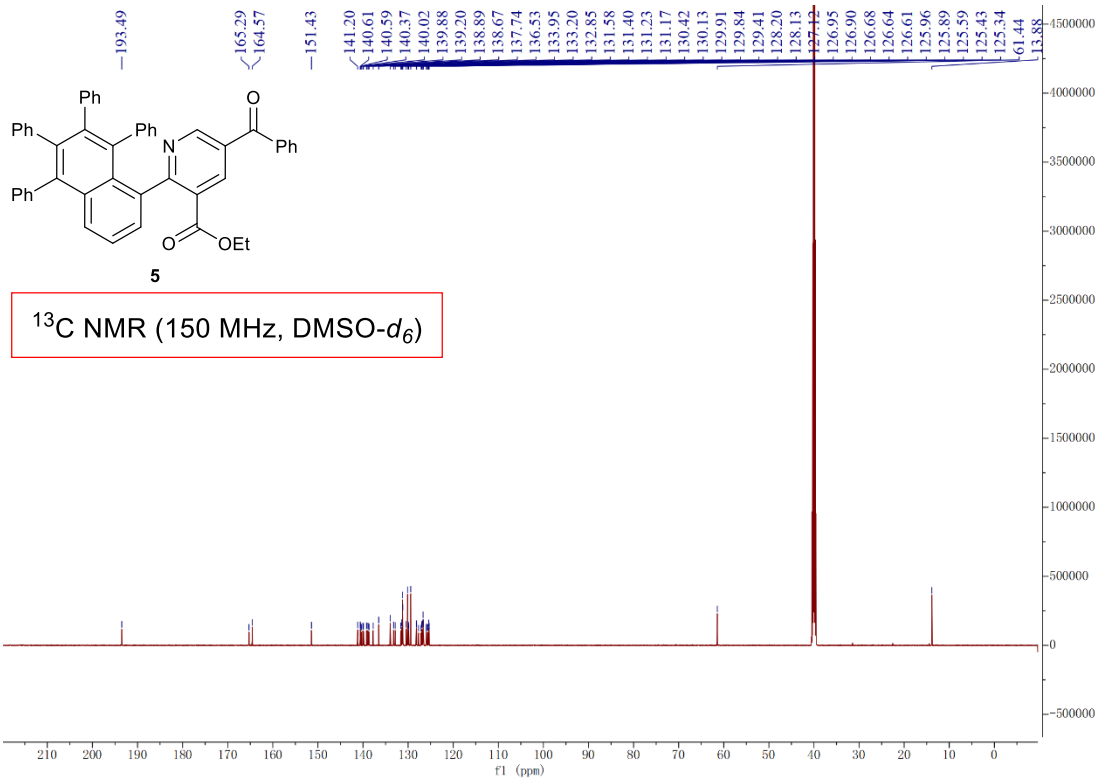
4

^{13}C NMR (150 MHz, $CDCl_3$)



5

^{1}H NMR (600 MHz, DMSO-d_6)



5

^{13}C NMR (150 MHz, DMSO-d_6)