

Supporting Information

Photocatalyzed alkoxy-carbonylmethylation of pyridines with α -diazooesters

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I. General Methods

All reactions were carried out in flame-dried sealed borosilicate glass tubes with magnetic stirring. If a reaction requires heating, an oil bath heating method was employed. PR160L Tuna Blue LED Lights (Kessil PR160L, 30 W, $\lambda_{\text{max}} = 456$ nm, spectrum 10,000K to Actinic.) were used to irradiate the reaction mixtures, which were bought from Kessil (<https://kessil.com/>). Unless otherwise noted, all the photocatalysts and chemical reagents were purchased from Accela, Acros, Aladdin, Adamas, Energy Chemical or TCI. Solvents were treated with 4 Å molecular sieves or sodium and distilled prior to use. Reactions were performed in 10 mL vials with two LEDs in Ar (approximately 5 cm away from the light sources). Purifications of reaction products were carried out by flash chromatography using Qingdao Haiyang Chemical Co. Ltd silica gel (400 – 630 mesh). Infrared spectra (IR) were recorded on a Bruker TENSOR 27 FTIR spectrophotometer and are reported as wavenumbers (cm^{-1}). Infrared spectra were recorded by preparing a KBr pellet containing the title compounds. ^1H NMR and ^{13}C NMR spectra were recorded with tetramethylsilane (TMS) as internal standard at ambient temperature on a Bruker Avance III 400 MHz or 500 MHz for ^1H NMR and 101 MHz or 126 MHz for ^{13}C NMR. Chemical shifts are reported in parts per million (ppm) and coupling constants are reported as Hertz (Hz). The following abbreviations are used to describe multiplicities s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets. High resolution mass spectra (HR-MS, m/z) were recorded on an IF-TOF spectrometer (Micromass).



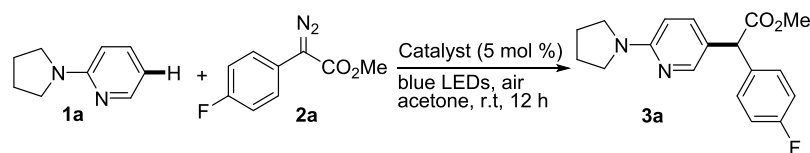
Light source: Kessil PR160L, $\lambda_{\text{max}} = 456$ nm



Photoreaction-setup used in this research

II. Experimental procedure for the optimization studies

Table S-1 . Photocatalyst screening^a



entry	catalyst	yield (%) ^b
1	Ru(bpy) ₃ Cl ₂ · 6H ₂ O	31
2	Eosin Y	35
3	<i>fac</i> -Ir(ppy) ₃	38
4	MesAcr ⁺ ClO ₄ ⁻	40
5	TPT ^c	46
6	DPM ^d	54
7	CeCl ₃	43

^aAll the reactions were carried out using 2-(pyrrolidin-1-yl)pyridine (**1a**) (0.10 mmol) and diazo compound (**2a**) (0.20 mmol) with different photocatalysts (5 mol %) in acetone (2.0 mL) at room temperature for 12 h under blue LEDs radiation (30W, approximately 5 cm away from the reaction mixture, no filter) and air atmosphere in a sealed tube, followed by flash chromatography on SiO₂; ^bIsolated yield. ^cTPT refers to 2,4,6-triphenylpyrylium tetrafluoroborate. ^dDPM refers to diphenylmethanone.

Table S-2. Base screening^a



entry	bases	yield (%) ^b
1	Cs ₂ CO ₃	37
2	Na ₂ CO ₃	32
3	K ₃ PO ₄	42
4	NaOAc	40
5	K ₂ CO ₃	26
6	KH ₂ PO ₄	42
7	NaBF ₄	12
6	DIPEA	47
7	Et ₃ N	72
8	DBU	52

^aAll the reactions were carried out using 2-(pyrrolidin-1-yl)pyridine (**1a**) (0.10 mmol) and α -diazo compound (**2a**) (0.20 mmol) with DPM (5 mol %) in the presence of base (1.0 eq.) in acetone (2.0 mL) at room temperature for 12 h under blue LEDs radiation (30W, approximately 5 cm away from the reaction mixture, no filter) and air atmosphere in a sealed tube, followed by flash chromatography on SiO₂; ^bIsolated yield.

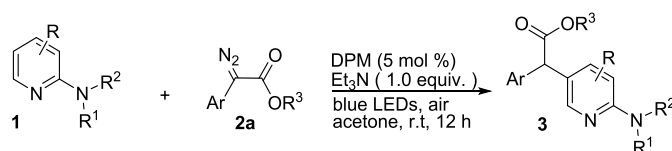
Table S-3. Solvent screening ^a

entry	solvent	yield (%) ^b
1	CHCl ₃	27
2	DMF	19
3	DCE	35
4	1,4-dioxane	30
5	<i>i</i> -PrOH	10
6	DMAc	16
7	acetone	72
8	TFE	8
9	DCM	24

^aAll the reactions were carried out using 2-(pyrrolidin-1-yl)pyridine (**1a**) (0.10 mmol) and diazo compound (**2a**) (0.20 mmol) with DPM (5 mol %) in the presence of Et₃N (1.0 eq.) in solvents (2.0 mL) at room temperature for 12 h under blue LEDs radiation (30W, approximately 5 cm away from the reaction mixture, no filter) and Air atmosphere in a sealed tube, followed by flash chromatography on SiO₂; ^b Isolated yield.

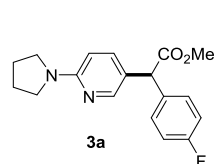
III. Experimental procedure

1. Procedure for the photocatalyzed alkoxy carbonylmethylation of pyridines with α -diazo esters.



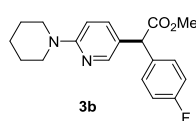
To a 10 mL vial equipped with a magnetic stir bar, was added pyridines **1** (0.2 mmol), diazo compounds **2** (0.6 mmol, 3.0 equiv.), Et₃N (20 mg, 0.2 mmol, 1.0 equiv.), DPM (2.2 mg, 0.01 mmol, 5 mol %) and acetone (2.0 mL) under air atmosphere conditions. The vial was equipped with a Teflon septum and stirred under blue LED irradiation with Kessil LEDs (30 W, approximately 5 cm away from the reaction mixture) for 12 hours. Organic solvents were removed under reduced pressure and the residue was purified by chromatography on silica gel with acetone/petroleum as the eluent to give the corresponding products.

2. Spectroscopic data of carbenoid products

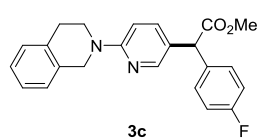


Methyl-2-(4-fluorophenyl)-2-(6-(pyrrolidin-1-yl)pyridin-3-yl)acetate:
Light yellow liquid. ¹H NMR (400 MHz, CDCl₃) δ 8.04 (s, 1H), 7.40 (d, *J* = 8.7 Hz, 1H), 7.31 – 7.21 (m, 2H), 7.04 – 6.95 (m, 2H), 6.33 (d, *J* = 8.7 Hz, 1H), 4.86 (s, 1H), 3.72 (s, 3H), 3.49 – 3.38 (m, 4H), 2.04 – 1.92 (m, 4H); ¹³C

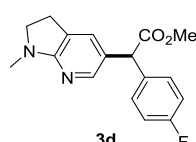
NMR (101 MHz, CDCl₃) δ 173.0, 163.2, 160.7, 156.6, 147.8, 137.1, 134.7(d, *J* = 12.8 Hz), 129.9 (d, *J* = 32 Hz), 121.0, 115.5, 115.3, 106.5, 53.0, 52.3, 46.7, 25.5. **HR-MS (ESI)** calcd for [M+1]⁺: C₁₈H₁₉FN₂O₂: 315.1503, found: 315.1499.



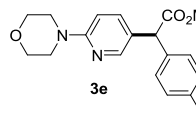
Methyl-2-(4-fluorophenyl)-2-(6-(piperidin-1-yl)pyridin-3-yl)acetate: Light yellow liquid. **¹H NMR** (400 MHz, CDCl₃) δ 8.06 (s, 1H), 7.41 (d, *J* = 8.8 Hz, 1H), 7.31 – 7.21 (m, 2H), 7.04 – 6.95 (m, 2H), 6.61 (d, *J* = 8.9 Hz, 1H), 4.86 (s, 1H), 3.73 (s, 3H), 3.55 – 3.48 (m, 4H), 1.66 – 1.58 (m, 6H); **¹³C NMR** (101 MHz, CDCl₃) δ 172.9, 163.2, 160.8, 158.9, 147.6, 137.5, 134.5(d, *J* = 13.2 Hz), 129.9 (d, *J* = 32 Hz), 122.2, 115.6, 115.4, 106.9, 52.9, 52.4, 46.2, 25.5, 24.7. **HR-MS (ESI)** calcd for [M+1]⁺: C₁₉H₂₁FN₂O₂: 329.1660, found: 329.1649.



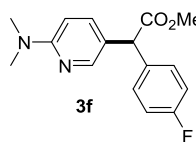
Methyl-2-(6-(3,4-dihydroisoquinolin-2(1H)-yl)pyridin-3-yl)-2-(4-fluorophenyl)acetate: Light yellow liquid. **¹H NMR** (400 MHz, CDCl₃) δ 8.14 (s, 1H), 7.51 (dd, *J* = 8.8, 1.9 Hz, 1H), 7.30 (dd, *J* = 7.4, 4.6 Hz, 2H), 7.25 – 7.17 (m, 4H), 7.04 (t, *J* = 8.6 Hz, 2H), 6.68 (d, *J* = 8.8 Hz, 1H), 4.92 (s, 1H), 4.72 (s, 2H), 3.86 (t, *J* = 5.8 Hz, 2H), 3.77 (s, 3H), 2.98 (t, *J* = 5.6 Hz, 2H); **¹³C NMR** (101 MHz, CDCl₃) δ 172.9, 163.3, 160.8, 158.0, 147.6, 137.6, 135.3, 134.5(d, *J* = 12.4 Hz), 134.2, 129.9(d, *J* = 32 Hz), 128.4, 126.6, 126.5, 126.2, 122.4, 115.6, 115.4, 106.6, 53.0, 52.4, 47.2, 42.6, 29.0. **HR-MS (ESI)** calcd for [M+1]⁺: C₂₃H₂₂FN₂O₂: 377.1621, found: 377.1678.



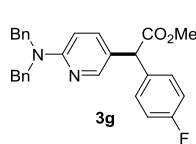
Methyl-2-(4-fluorophenyl)-2-(1-methyl-2,3-dihydro-1H-pyrrolo[2,3-b]pyridin-5-yl)acetate: Light yellow liquid. **¹H NMR** (400 MHz, CDCl₃) δ 7.77 – 7.74 (m, 1H), 7.29 – 7.24 (m, 2H), 7.18 (d, *J* = 1.3 Hz, 1H), 7.05 – 6.99 (m, 2H), 4.83 (s, 1H), 3.75 (s, 3H), 3.49 (t, *J* = 8.4 Hz, 2H), 2.99 – 2.93 (m, 5H); **¹³C NMR** (101 MHz, CDCl₃) δ 173.1, 163.1, 145.0, 130.9, 129.9, 129.8, 124.0, 122.3, 115.6, 115.4, 53.1, 52.4, 52.3, 32.6, 25.8. **HR-MS(ESI)** calcd for [M+1]⁺: C₁₇H₁₇FN₂O₂: 301.1347, found: 301.1343.



Methyl-2-(4-fluorophenyl)-2-(6-morpholinopyridin-3-yl)acetate: Light yellow liquid. **¹H NMR** (400 MHz, CDCl₃) δ 8.09 (s, 1H), 7.48 (dd, *J* = 8.8, 1.9 Hz, 1H), 7.29 – 7.22 (m, 2H), 7.00 (t, *J* = 8.5 Hz, 2H), 6.61 (d, *J* = 8.8 Hz, 1H), 4.89 (s, 1H), 3.82 – 3.78 (m, 4H), 3.74 (s, 3H), 3.52 – 3.45 (m, 4H); **¹³C NMR** (101 MHz, CDCl₃) δ 172.8, 163.3, 160.8, 158.8, 147.6, 137.7, 134.3(d, *J* = 13.2 Hz), 129.9 (d, *J* = 32 Hz), 123.8, 115.7, 115.5, 106.8, 66.7, 52.9, 52.5, 45.5. **HR-MS (ESI)** calcd for [M+1]⁺: C₁₈H₁₉FN₂O₃: 331.1452, found: 331.1444.

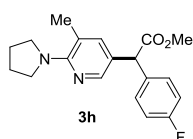


Methyl-2-(6-(dimethylamino)pyridin-3-yl)-2-(4-fluorophenyl)acetate: Light yellow liquid. **¹H NMR** (400 MHz, CDCl₃) δ 8.06 (s, 1H), 7.41 (d, *J* = 8.8 Hz, 1H), 7.29 – 7.22 (m, 2H), 7.03 – 6.96 (m, 2H), 6.49 (d, *J* = 8.9 Hz, 1H), 4.86 (s, 1H), 3.73 (s, 3H), 3.06 (s, 6H); **¹³C NMR** (101 MHz, CDCl₃) δ 173.0, 163.2, 160.8, 158.7, 147.5, 137.3, 134.6 (d, *J* = 12.8 Hz), 129.9(d, *J* = 32 Hz), 121.4, 115.6, 115.4, 105.4, 52.9, 52.4, 38.1. **HR-MS (ESI)** calcd for [M+1]⁺: C₁₆H₁₇FN₂O₂: 289.1347, found: 289.1336.

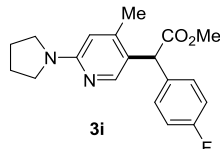


Methyl-2-(6-(dibenzylamino)pyridin-3-yl)-2-(4-fluorophenyl)acetate: Light yellow liquid. **¹H NMR** (400 MHz, CDCl₃) δ 8.09 (s, 1H), 7.38 – 7.32 (m, 1H), 7.31 – 7.24 (m, 6H), 7.24 – 7.17 (m, 6H), 6.98 (t, *J* = 8.6 Hz, 2H), 6.43 (d, *J* = 8.9 Hz, 1H), 4.85 (s, 1H), 4.75 (s, 4H), 3.70 (s, 3H); **¹³C NMR** (101 MHz, CDCl₃) δ 173.0, 163.3, 160.9, 158.1, 147.7, 138.3, 137.6, 134.5 (d, *J* = 12.8 Hz), 130.0 (d, *J* = 32

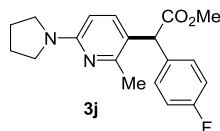
Hz), 128.7, 127.2, 127.1, 122.4, 115.7, 115.5, 105.9, 53.1, 52.4, 51.1. **HR-MS (ESI)** calcd for $[M+1]^+$: $C_{28}H_{25}FN_2O_2$: 441.1973, found: 441.1963.



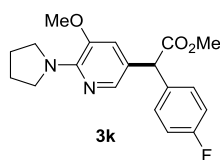
Methyl-2-(4-fluorophenyl)-2-(5-methyl-6-(pyrrolidin-1-yl)pyridin-3-yl)acetate: Light yellow liquid. 1H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.28 (m, 1H), 7.24 – 7.17 (m, 2H), 7.01 (t, $J = 8.6$ Hz, 2H), 6.22 (d, $J = 8.6$ Hz, 1H), 5.09 (s, 1H), 3.75 (s, 3H), 3.49 – 3.42 (m, 4H), 2.40 (s, 3H), 2.04 – 1.96 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.4, 156.1, 154.9, 136.9, 134.3 (d, $J = 12.8$ Hz), 130.2 (d, $J = 32$ Hz), 118.8, 115.5, 115.3, 103.9, 52.3, 51.6, 46.6, 25.6, 22.7. **HR-MS (ESI)** calcd for $[M+1]^+$: $C_{19}H_{22}FN_2O_2$: 329.1621, found: 329.1663.



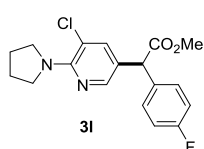
Methyl-2-(4-fluorophenyl)-2-(4-methyl-6-(pyrrolidin-1-yl)pyridin-3-yl)acetate: Light yellow liquid. 1H NMR (400 MHz, $CDCl_3$) δ 7.94 (s, 1H), 7.26 – 7.20 (m, 2H), 7.05 – 6.97 (m, 2H), 6.20 (s, 1H), 5.02 (s, 1H), 3.75 (s, 3H), 3.49 – 3.41 (m, 4H), 2.16 (s, 3H), 2.00 (t, $J = 6.3$ Hz, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.1, 156.7, 147.4, 146.4, 133.8 (d, $J = 12.8$ Hz), 130.4 (d, $J = 32$ Hz), 120.6, 115.5, 115.3, 107.8, 52.4, 50.8, 46.6, 25.6, 19.8. **HR-MS (ESI)** calcd for $[M+1]^+$: $C_{19}H_{22}FN_2O_2$: 329.1621, found: 329.1670.



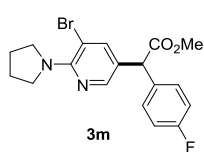
Methyl-2-(4-fluorophenyl)-2-(2-methyl-6-(pyrrolidin-1-yl)pyridin-3-yl)acetate: Light yellow liquid. 1H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, $J = 1.7$ Hz, 1H), 7.32 – 7.26 (m, 2H), 7.23 (s, 1H), 7.02 (t, $J = 8.6$ Hz, 2H), 4.87 (s, 1H), 3.76 (s, 3H), 3.53 (t, $J = 6.5$ Hz, 4H), 2.31 (s, 3H), 1.96 – 1.89 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.0, 158.8, 144.2, 139.3, 130.0 (d, $J = 31.6$ Hz), 123.7, 119.6, 115.6, 115.4, 52.9, 52.4, 49.7, 25.6, 20.7. **HR-MS (ESI)** calcd for $[M+1]^+$: $C_{19}H_{22}FN_2O_2$: 329.1621, found: 329.1666.



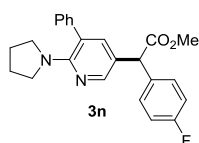
Methyl-2-(4-fluorophenyl)-2-(5-methoxy-6-(pyrrolidin-1-yl)pyridin-3-yl)acetate: Light yellow liquid. 1H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, $J = 1.7$ Hz, 1H), 7.32 – 7.26 (m, 2H), 7.06 – 6.99 (m, 2H), 6.90 (d, $J = 1.7$ Hz, 1H), 4.89 (s, 1H), 3.76 (s, 3H), 3.74 (s, 3H), 3.66 – 3.59 (m, 4H), 1.95 – 1.87 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.0, 163.2, 160.8, 150.3, 144.6, 138.4, 134.5 (d, $J = 13.6$ Hz), 129.9 (d, $J = 32$ Hz), 122.5, 116.9, 115.5, 115.3, 55.6, 52.9, 52.4, 49.1, 25.4. **HR-MS (ESI)** calcd for $[M+1]^+$: $C_{19}H_{21}FN_2O_3$: 345.1609, found: 345.1611.



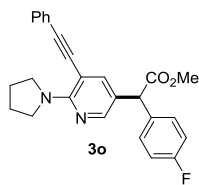
Methyl-2-(5-chloro-6-(pyrrolidin-1-yl)pyridin-3-yl)-2-(4-fluorophenyl)acetate: Light yellow liquid. 1H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, $J = 2.1$ Hz, 1H), 7.46 (d, $J = 2.1$ Hz, 1H), 7.30 – 7.25 (m, 2H), 7.07 – 7.01 (m, 2H), 4.87 (s, 1H), 3.76 (s, 3H), 3.67 (t, $J = 6.7$ Hz, 4H), 1.96 – 1.88 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.5, 163.3, 160.9, 154.6, 145.0, 138.8, 133.91 (d, $J = 13.2$ Hz), 130.0 (d, $J = 32.4$ Hz), 123.9, 116.4, 115.8, 115.6, 52.5, 52.4, 49.8, 25.7. **HR-MS (ESI)** calcd for $[M+1]^+$: $C_{18}H_{18}ClFN_2O_2$: 349.1114, found: 349.1118.



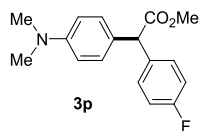
Methyl-2-(5-bromo-6-(pyrrolidin-1-yl)pyridin-3-yl)-2-(4-fluorophenyl)acetate: Light yellow liquid. 1H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, $J = 2.0$ Hz, 1H), 7.67 (d, $J = 2.0$ Hz, 1H), 7.31 – 7.26 (m, 2H), 7.07 – 7.01 (m, 2H), 4.86 (s, 1H), 3.77 (s, 3H), 3.70 – 3.65 (m, 4H), 1.95 – 1.90 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.5, 155.6, 145.4, 142.4, 133.9 (d, $J = 13.2$ Hz), 130.0 (d, $J = 32$ Hz), 124.6, 115.8, 115.6, 104.9, 52.6, 52.4, 50.3, 25.8. **HR-MS (ESI)** calcd for $[M+1]^+$: $C_{18}H_{18}BrFN_2O_2$: 393.0608, found: 393.0610.



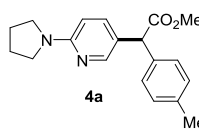
Methyl-2-(4-fluorophenyl)-2-(5-phenyl-6-(pyrrolidin-1-yl)pyridin-3-yl)acetate: Light yellow liquid. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.06 (s, 1H), 7.37 – 7.25 (m, 9H), 7.00 (t, $J = 8.1$ Hz, 2H), 4.90 (s, 1H), 3.73 (s, 3H), 3.11 (t, $J = 5.8$ Hz, 4H), 1.78 – 1.70 (m, 4H); $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 172.9, 163.0, 161.1, 156.1, 145.8, 140.8, 139.6, 134.4 (d, $J = 10.4$ Hz), 130.0 (d, $J = 26$ Hz), 128.9, 127.99, 126.7, 122.7, 122.6, 115.6, 115.4, 53.0, 52.4, 50.0, 25.6. **HR-MS (ESI)** calcd for $[\text{M}+1]^+$: $\text{C}_{24}\text{H}_{23}\text{FN}_2\text{O}_2$: 391.1816, found: 391.1812.



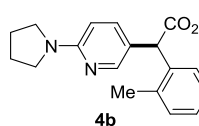
Methyl-2-(4-fluorophenyl)-2-(5-(phenylethynyl)-6-(pyrrolidin-1-yl)pyridin-3-yl)acetate: Light yellow liquid. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.02 (d, $J = 2.4$ Hz, 1H), 7.61 (d, $J = 2.4$ Hz, 1H), 7.50 – 7.45 (m, 2H), 7.38 – 7.26 (m, 5H), 7.10 – 7.01 (m, 2H), 4.88 (s, 1H), 3.88 – 3.82 (m, 4H), 3.78 (s, 3H), 2.00 – 1.94 (m, 4H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 172.7, 160.8, 157.0, 147.5, 142.6, 130.8, 130.0 (d, $J = 32.4$ Hz), 128.4, 128.2, 123.6, 121.6, 115.6 (d, $J = 85.6$ Hz), 103.0, 100.0, 93.3, 88.6, 52.7, 52.5, 49.3, 25.8. **HR-MS (ESI)** calcd for $[\text{M}+1]^+$: $\text{C}_{26}\text{H}_{23}\text{FN}_2\text{O}_2$: 415.1816, found: 415.1821.



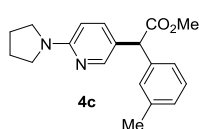
Methyl-2-(4-(dimethylamino)phenyl)-2-(4-fluorophenyl)acetate: Light yellow liquid. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.29 – 7.24 (m, 2H), 7.14 (d, $J = 8.4$ Hz, 2H), 6.97 (t, $J = 8.4$ Hz, 2H), 6.68 (d, $J = 8.3$ Hz, 2H), 4.91 (s, 1H), 3.72 (s, 3H), 2.91 (s, 6H); $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 173.5, 162.9, 161.0, 150.0, 135.3, 135.2, 130.2 (d, $J = 31.5$ Hz), 130.1, 129.1, 126.2, 115.4, 115.2 (d, $J = 84.5$ Hz), 112.6, 55.3, 52.3, 40.5. **HR-MS (ESI)** calcd for $[\text{M}+1]^+$: $\text{C}_{17}\text{H}_{19}\text{FNO}_2$: 288.1394, found: 288.1399.



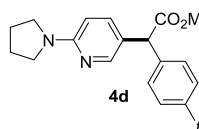
Methyl-2-(6-(pyrrolidin-1-yl)pyridin-3-yl)-2-(p-tolyl)acetate¹: Light yellow liquid. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.11 – 8.07 (m, 1H), 7.46 (d, $J = 8.7$ Hz, 1H), 7.20 (d, $J = 7.5$ Hz, 2H), 7.14 (d, $J = 7.7$ Hz, 2H), 6.35 (d, $J = 8.7$ Hz, 1H), 4.88 (s, 1H), 3.75 (s, 3H), 3.49 – 3.42 (m, 4H), 2.34 (s, 3H), 2.05 – 1.98 (m, 4H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 173.4, 156.6, 147.9, 137.3, 136.8, 135.9, 129.3, 128.1, 121.4, 106.5, 53.4, 52.3, 46.7, 25.6, 21.0.



Methyl-2-(6-(pyrrolidin-1-yl)pyridin-3-yl)-2-(o-tolyl)acetate: Light yellow liquid. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.03 (d, $J = 2.2$ Hz, 1H), 7.36 (dd, $J = 8.8, 2.4$ Hz, 1H), 7.30 – 7.25 (m, 1H), 7.22 – 7.15 (m, 3H), 6.35 (d, $J = 8.8$ Hz, 1H), 5.07 (s, 1H), 3.75 (s, 3H), 3.45 (t, $J = 6.5$ Hz, 4H), 2.31 (s, 3H), 2.04 – 1.98 (m, 4H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 173.3, 156.6, 147.9, 138.8, 138.3, 137.4, 128.9, 128.5, 128.0, 125.2, 121.3, 106.5, 53.8, 52.3, 46.7, 25.6, 21.5. **HR-MS (ESI)** calcd for $[\text{M}+1]^+$: $\text{C}_{19}\text{H}_{22}\text{N}_2\text{O}_2$: 311.1754, found: 311.1761.

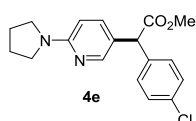


Methyl-2-(6-(pyrrolidin-1-yl)pyridin-3-yl)-2-(m-tolyl)acetate: Light yellow liquid. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.09 (d, $J = 2.3$ Hz, 1H), 7.46 (dd, $J = 8.8, 2.4$ Hz, 1H), 7.25 – 7.16 (m, 1H), 7.13 – 7.04 (m, 3H), 6.35 (d, $J = 8.8$ Hz, 1H), 4.87 (s, 1H), 3.75 (s, 3H), 3.45 (t, $J = 6.6$ Hz, 4H), 2.33 (s, 3H), 2.04 – 1.95 (m, 4H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 173.3, 156.6, 147.9, 138.8, 138.3, 137.3, 128.9, 128.5, 127.9, 125.2, 121.3, 106.5, 53.8, 52.3, 46.7, 25.6, 21.5. **HR-MS (ESI)** calcd for $[\text{M}+1]^+$: $\text{C}_{19}\text{H}_{22}\text{N}_2\text{O}_2$: 311.1754, found: 311.1759.



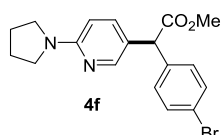
Methyl-2-(4-(tert-butyl)phenyl)-2-(6-(pyrrolidin-1-yl)pyridin-3-yl)acetate¹: Light yellow liquid. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.05 (d, $J = 2.1$ Hz,

1H), 7.46 (dd, $J = 8.8, 2.3$ Hz, 1H), 7.32 (d, $J = 8.3$ Hz, 2H), 7.21 (d, $J = 8.3$ Hz, 2H), 6.33 (d, $J = 8.8$ Hz, 1H), 4.85 (s, 1H), 3.72 (s, 3H), 3.46 – 3.39 (m, 4H), 2.01 – 1.95 (m, 4H), 1.29 (s, 9H); ^{13}C NMR (126 MHz, CDCl_3) δ 173.4, 156.6, 150.0, 147.9, 137.3, 135.8, 127.8, 125.6, 121.4, 106.5, 53.4, 52.3, 46.7, 34.4, 31.3, 25.6.



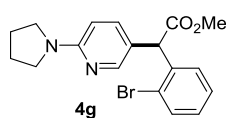
Methyl-2-(4-chlorophenyl)-2-(6-(pyrrolidin-1-yl)pyridin-3-yl)acetate¹:

Light yellow liquid. ^1H NMR (400 MHz, CDCl_3) δ 8.04 (d, $J = 2.3$ Hz, 1H), 7.39 (dd, $J = 8.8, 2.4$ Hz, 1H), 7.30 – 7.25 (m, 2H), 7.24 – 7.19 (m, 2H), 6.33 (d, $J = 8.8$ Hz, 1H), 4.84 (s, 1H), 3.73 (s, 3H), 3.46 – 3.39 (m, 4H), 2.01 – 1.96 (m, 4H); ^{13}C NMR (101 MHz, CDCl_3) δ 172.8, 156.6, 147.8, 137.4, 137.1, 133.1, 129.7, 128.7, 120.7, 106.6, 53.1, 46.7, 29.7, 25.5.



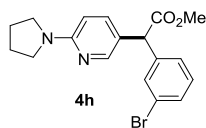
Methyl-2-(4-bromophenyl)-2-(6-(pyrrolidin-1-yl)pyridin-3-yl)acetate¹:

Light yellow liquid. ^1H NMR (500 MHz, CDCl_3) δ 8.06 (d, $J = 2.4$ Hz, 1H), 7.41 (dd, $J = 8.8, 2.5$ Hz, 1H), 7.29 (d, $J = 8.6$ Hz, 2H), 7.24 (d, $J = 8.5$ Hz, 2H), 6.35 (d, $J = 8.8$ Hz, 1H), 4.86 (s, 1H), 3.75 (s, 3H), 3.48 – 3.42 (m, 4H), 2.03 – 1.99 (m, 4H); ^{13}C NMR (101 MHz, CDCl_3) δ 172.7, 156.6, 147.8, 138.0, 137.1, 131.7, 130.0, 121.2, 120.6, 106.6, 53.2, 52.4, 46.7, 25.5.



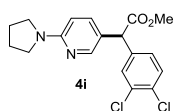
Methyl-2-(3-bromophenyl)-2-(6-(pyrrolidin-1-yl)pyridin-3-yl)acetate¹:

Light yellow liquid. ^1H NMR (500 MHz, CDCl_3) δ 8.07 (d, $J = 2.1$ Hz, 1H), 7.55 (d, $J = 8.0$ Hz, 1H), 7.37 (dd, $J = 8.8, 2.3$ Hz, 1H), 7.31 (d, $J = 7.7$ Hz, 1H), 7.26 (dd, $J = 9.1, 5.9$ Hz, 1H), 7.11 (t, $J = 7.5$ Hz, 1H), 6.34 (d, $J = 8.8$ Hz, 1H), 5.31 (s, 1H), 3.73 (s, 3H), 3.48 – 3.40 (m, 4H), 2.00 – 1.95 (m, 4H); ^{13}C NMR (126 MHz, CDCl_3) δ 172.6, 156.6, 148.5, 138.3, 137.4, 133.1, 129.8, 128.8, 127.6, 124.9, 119.6, 106.5, 53.3, 52.5, 46.7, 25.6.



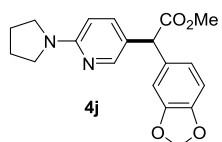
Methyl-2-(2-bromophenyl)-2-(6-(pyrrolidin-1-yl)pyridin-3-yl)acetate¹:

Light yellow liquid. ^1H NMR (400 MHz, CDCl_3) δ 8.07 (d, $J = 2.4$ Hz, 1H), 7.48 – 7.37 (m, 3H), 7.27 – 7.15 (m, 2H), 6.36 (d, $J = 8.8$ Hz, 1H), 4.85 (s, 1H), 3.76 (s, 3H), 3.45 (t, $J = 6.6$ Hz, 4H), 2.04 – 1.98 (m, 4H); ^{13}C NMR (101 MHz, CDCl_3) δ 172.6, 156.7, 147.9, 141.2, 137.1, 131.3, 130.4, 130.1, 127.0, 122.7, 120.4, 106.7, 53.3, 52.5, 46.7, 25.6.



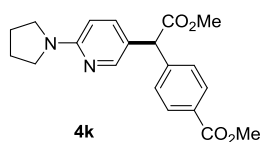
Methyl-2-(3,4-dichlorophenyl)-2-(6-(pyrrolidin-1-yl)pyridin-3-yl)acetate¹:

Light yellow liquid. ^1H NMR (400 MHz, CDCl_3) δ 8.10 (s, 1H), 7.49 – 7.44 (m, 1H), 7.31 – 7.27 (m, 1H), 7.19 – 7.15 (m, 1H), 7.02 (d, $J = 4.9$ Hz, 1H), 6.35 (d, $J = 8.8$ Hz, 1H), 4.93 (s, 1H), 3.75 (s, 3H), 3.50 – 3.39 (m, 4H), 2.05 – 1.95 (m, 4H); ^{13}C NMR (101 MHz, CDCl_3) δ 172.9, 156.7, 147.8, 139.1, 137.1, 127.8, 125.9, 122.4, 120.9, 106.5, 77.4, 77.1, 76.7, 52.4, 49.4, 46.7, 25.6.



Methyl(S)-2-(benzo[d][1,3]dioxol-5-yl)-2-(6-(pyrrolidin-1-yl)pyridin-3-yl)acetate¹:

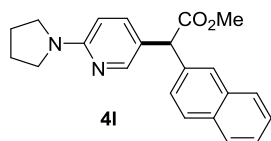
Light yellow liquid. ^1H NMR (500 MHz, CDCl_3) δ 8.06 (d, $J = 2.3$ Hz, 1H), 7.44 (dd, $J = 8.8, 2.5$ Hz, 1H), 6.81 (s, 1H), 6.76 – 6.74 (m, 2H), 6.35 (d, $J = 8.8$ Hz, 1H), 5.93 (s, 2H), 4.81 (s, 1H), 3.74 (s, 4H), 3.48 – 3.42 (m, 4H), 2.03 – 1.97 (m, 4H); ^{13}C NMR (101 MHz, CDCl_3) δ 173.2, 156.6, 147.9, 147.8, 146.7, 137.1, 132.7, 121.5, 121.2, 108.9, 108.2, 106.5, 101.1, 53.4, 52.3, 46.7, 25.6.



Methyl-4-(2-methoxy-2-oxo-1-(6-(pyrrolidin-1-yl)pyridin-3-yl)ethyl)benzoate¹:

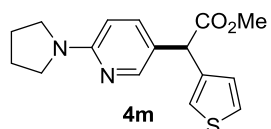
Light yellow liquid. ^1H NMR (500 MHz, CDCl_3) δ 8.06 (d, $J = 2.2$ Hz, 1H), 7.98 (d, $J = 8.3$ Hz, 2H), 7.40 (dd, $J = 8.8, 2.4$ Hz, 1H),

7.36 (d, $J = 8.2$ Hz, 2H), 6.33 (d, $J = 8.8$ Hz, 1H), 4.92 (s, 1H), 3.89 (s, 3H), 3.74 (s, 3H), 3.47 – 3.40 (m, 4H), 2.02 – 1.96 (m, 4H); ^{13}C NMR (126 MHz, CDCl_3) δ 172.6, 166.8, 156.7, 147.9, 144.0, 137.1, 129.9, 129.1, 128.3, 120.4, 106.6, 53.7, 52.4, 52.1, 46.7, 25.5.



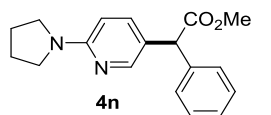
4l

Methyl-2-(naphthalen-1-yl)-2-(6-(pyrrolidin-1-yl)pyridin-3-yl)acetate¹: Light yellow liquid. ^1H NMR (500 MHz, CDCl_3) δ 8.17 (d, $J = 2.4$ Hz, 1H), 7.84 – 7.79 (m, 3H), 7.76 (s, 1H), 7.51 – 7.46 (m, 3H), 7.43 (dd, $J = 8.6, 1.7$ Hz, 1H), 6.36 (d, $J = 8.8$ Hz, 1H), 5.08 (s, 1H), 3.79 (s, 3H), 3.49 – 3.41 (m, 4H), 2.05 – 1.97 (m, 4H); ^{13}C NMR (126 MHz, CDCl_3) δ 173.2, 156.6, 148.0, 137.5, 136.4, 133.4, 132.5, 128.4, 128.0, 127.6, 126.8, 126.6, 126.2, 126.0, 121.1, 106.6, 53.9, 52.4, 46.7, 25.6.



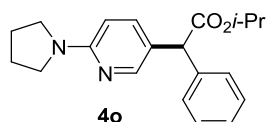
4m

Methyl-2-(6-(pyrrolidin-1-yl)pyridin-3-yl)-2-(thiophen-3-yl)acetate¹: Light yellow liquid. ^1H NMR (400 MHz, CDCl_3) δ 8.09 (d, $J = 2.3$ Hz, 1H), 7.45 (dd, $J = 8.8, 2.5$ Hz, 1H), 7.27 (dd, $J = 5.0, 3.0$ Hz, 1H), 7.17 – 7.12 (m, 1H), 7.01 (dd, $J = 5.0, 1.1$ Hz, 1H), 6.34 (d, $J = 8.8$ Hz, 1H), 4.92 (s, 1H), 3.73 (s, 3H), 3.44 (t, $J = 6.6$ Hz, 4H), 2.04 – 1.94 (m, 4H); ^{13}C NMR (101 MHz, CDCl_3) δ 172.9, 147.74, 139.1, 137.1, 127.8, 125.9, 122.4, 121.0, 106.5, 52.3, 49.4, 46.7, 25.6.



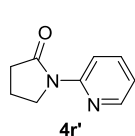
4n

Methyl-2-phenyl-2-(6-(pyrrolidin-1-yl)pyridin-3-yl)acetate¹: Light yellow liquid. ^1H NMR (400 MHz, CDCl_3) δ 8.06 (d, $J = 2.3$ Hz, 1H), 7.43 (dd, $J = 8.8, 2.4$ Hz, 1H), 7.33 – 7.26 (m, 4H), 7.26 – 7.19 (m, 1H), 6.32 (d, $J = 8.8$ Hz, 1H), 4.88 (s, 1H), 3.72 (s, 3H), 3.46 – 3.37 (m, 4H), 2.02 – 1.93 (m, 4H); ^{13}C NMR (101 MHz, CDCl_3) δ 173.2, 156.6, 147.9, 138.9, 137.3, 128.6, 128.3, 127.2, 121.2, 106.5, 53.8, 52.3, 46.7, 25.6.



4o

Isopropyl-2-phenyl-2-(6-(pyrrolidin-1-yl)pyridin-3-yl)acetate¹: Light yellow liquid. ^1H NMR (500 MHz, CDCl_3) δ 8.06 (s, 1H), 7.46 – 7.40 (m, 1H), 7.31 – 7.27 (m, 4H), 7.25 – 7.19 (m, 1H), 6.32 (d, $J = 8.8$ Hz, 1H), 5.09 – 5.01 (m, 1H), 4.82 (s, 1H), 3.42 (n, $J = 6.0$ Hz, 4H), 2.01 – 1.94 (m, 4H), 1.22 (d, $J = 6.3$ Hz, 6H); ^{13}C NMR (126 MHz, CDCl_3) δ 172.2, 156.6, 147.9, 139.2, 137.4, 128.5, 128.5, 128.2, 127.0, 126.5, 121.5, 106.5, 68.6, 54.1, 46.7, 25.5, 21.7.

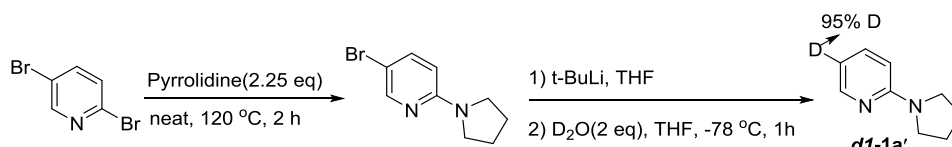


4r'

1-(pyridin-2-yl)pyrrolidin-2-one⁵: Light yellow liquid. ^1H NMR (400 MHz, CDCl_3) δ 8.41 (d, $J = 8.5$ Hz, 1H), 8.37 (dd, $J = 4.9, 1.1$ Hz, 1H), 7.75 – 7.65 (m, 1H), 7.07 – 7.02 (m, 1H), 4.13 (t, 2H), 2.68 (t, $J = 8.1$ Hz, 2H), 2.21 – 2.09 (m, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ 175.0, 151.9, 147.5, 137.5, 119.4, 114.7, 47.4, 33.7, 17.7.

V. Control experiments for mechanism studies

1. The procedure for the preparation of *d1-1a'* (95% D)^{2,4}



A mixture of 2,5-dibromopyridine (236 mg, 1.0 mmol), pyrrolidine (251 mg, 2.25 mmol) was heated at 120 °C for 2 h in sealed tube. After cooling, the reaction mixture was poured into water and extracted with EtOAc. The organic layer was washed with brine and concentrated in *vacuo*. The residue was purified by preparative TLC (silica gel, hexanes/EtOAc) to give

5-bromo-2-(pyrrolidin-1-yl)pyridine.

A solution of 5-bromo-2-(pyrrolidin-1-yl)pyridine (227 mg, 1 mmol) in THF (extra dry, 6 mL) was cooled to $-78\text{ }^{\circ}\text{C}$ and *t*-BuLi (1.17 mL, 2 mmol) was added dropwise under nitrogen. After 5 min at $-78\text{ }^{\circ}\text{C}$, D_2O (1.17 mL, 2 mmol) was added dropwise. The reaction medium was then allowed to warm to r.t. The aqueous layer was then extracted with EtOAc. The organic layer was dried (Na_2SO_4) and the solvent was evaporated under reduced pressure. The residue was purified by silica gel flash chromatography to give the desired product *d1-1a'*.

2-(Pyrrolidin-1-yl)pyridine (*d1-1a'*)^{1,3}: $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.16 (d, $J = 1.9\text{ Hz}$, 1H), 7.43 (dd, $J = 8.5, 2.0\text{ Hz}$, 1H), 6.51 (dd, $J = 7.1, 5.0\text{ Hz}$, 0.05H), 6.36 (dd, $J = 8.5, 0.8\text{ Hz}$, 1H), 3.49 – 3.42 (m, 4H), 2.05 – 1.96 (m, 4H).

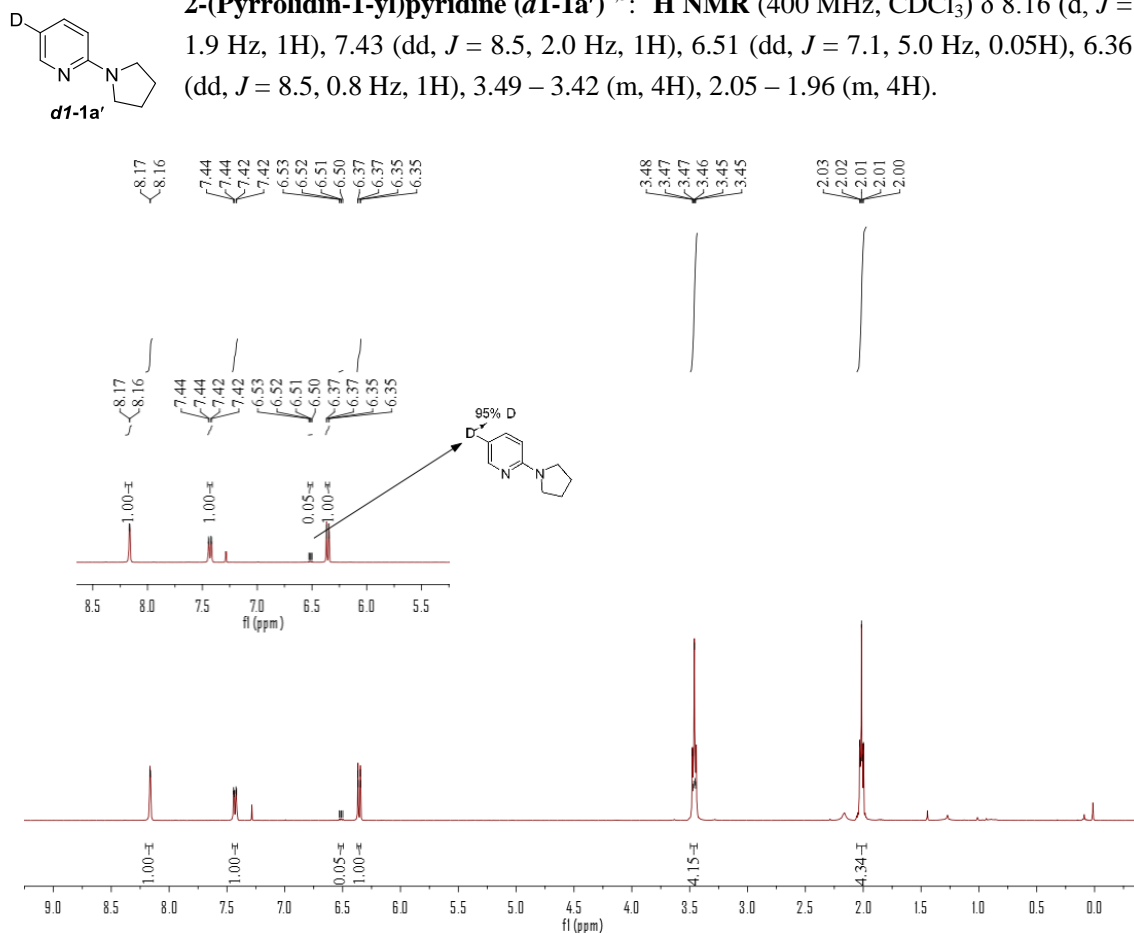
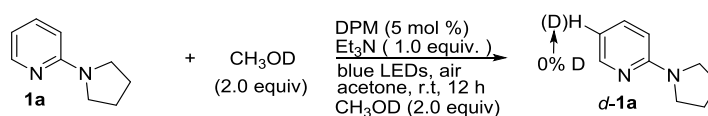


Figure S-1. $^1\text{H NMR}$ spectrum for *d1-1a'*

2. H/D Exchange of 2-(pyrrolidin-1-yl)pyridine (**1a**)



To a screw capped vial with a spinnable triangular-shaped Teflon stir bar were added 2-(pyrrolidin-1-yl)pyridine (29.6 mg, 0.2 mmol), CH_3OD (6.6 mg, 0.2 mmol), DPM (2.2 mg, 0.01 mmol, 5 mol %), Et_3N (20 mg, 0.2 mmol, 1.0 equiv.) and acetone (2.0 mL) under air atmosphere conditions. The vial was equipped with a Teflon septum and stirred under blue LED irradiation with Kessil LEDs (30 W) for 12 hours. Organic solvents were removed under reduced pressure and the residue was purified by chromatography on silica gel with acetone/petroleum as the eluent to give the *d-1a*.

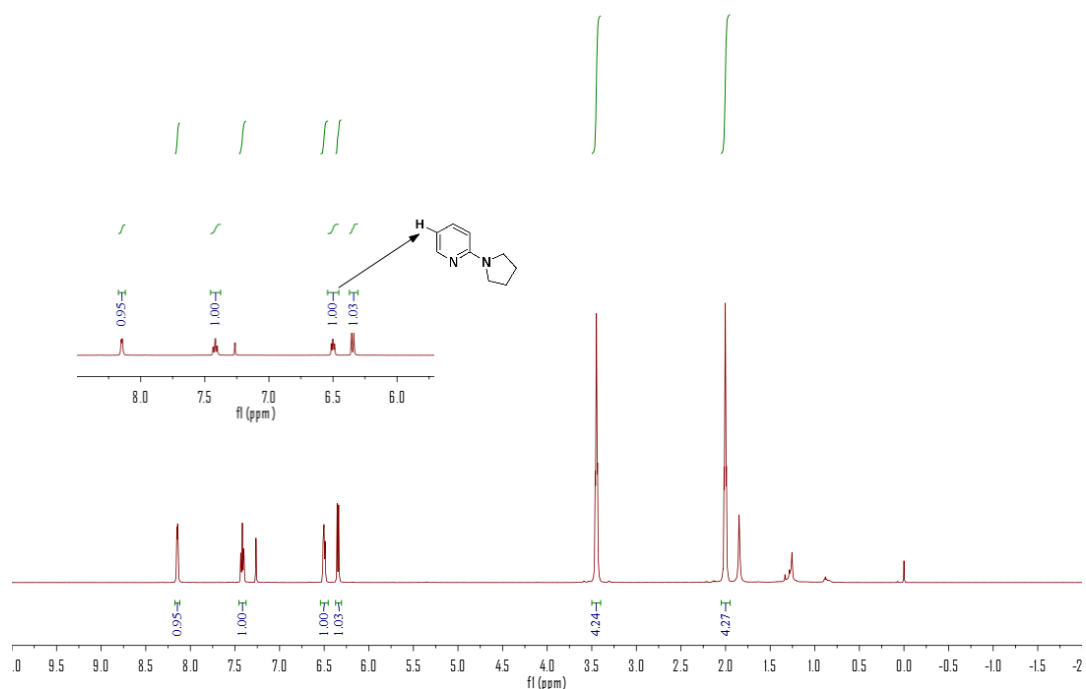
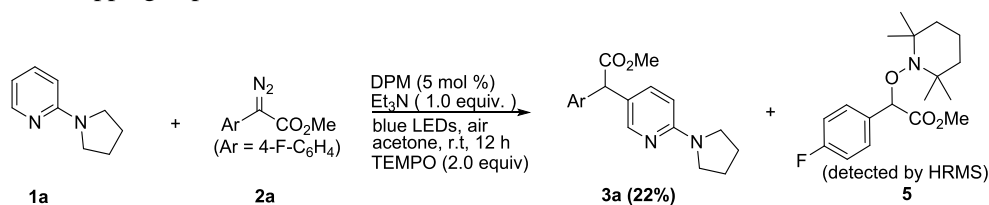


Figure S-2. ^1H NMR spectrum for *d-1a*

3. Radical-trapping experiment with TEMPO



To a screw capped vial with a spinnable triangular-shaped Teflon stir bar were added 2-(pyrrolidin-1-yl)pyridine (29.6 mg, 0.2 mmol), methyl 2-diazo-2-phenylacetate (105.6 mg, 0.2 mmol), TEMPO (62.5 mg, 0.4 mmol), DPM (2.2 mg, 0.01 mmol, 5 mol %), Et_3N (20 mg, 0.2 mmol, 1.0 equiv.) and acetone (2.0 mL) under air atmosphere. The vial was equipped with a Teflon septum and stirred under blue LED irradiation with Kessil LEDs (30 W) for 12 hours. The reaction solution was concentrated under reduced pressure. Then, the residue was analyzed by HRMS, and the radical intermediates trapped by TEMPO were detected (the data of $[\text{M}+\text{H}]^+$ is showed in **Figure S-3**). In addition, **3a** was obtained in 22% yield by column chromatography isolation on silica gel.

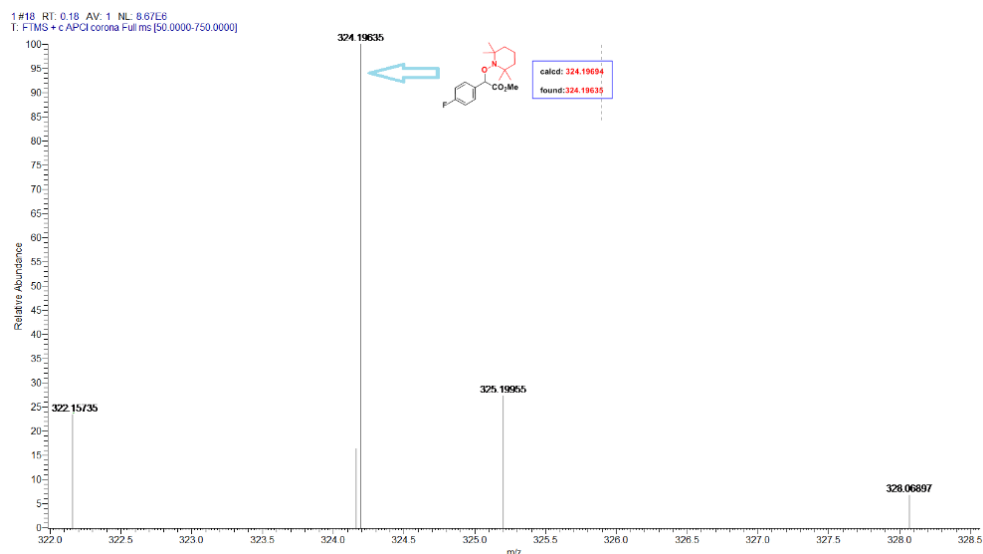
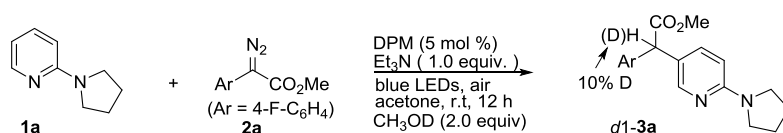


Figure S-3. HR-MS spectrum of the by-product **5**

4. Photocatalyzed regioselective pyridine C-H coupling of **1a** with **2a** in deuterated solvent system



To a screw capped vial with a spinnable triangular-shaped Teflon stir bar were added 2-(pyrrolidin-1-yl)pyridine (29.6 mg, 0.2 mmol), methyl 2-diazo-2-phenylacetate (105.6 mg, 0.2 mmol), CH₃OD (13.2 mg, 0.4 mmol), DPM (2.2 mg, 0.01 mmol, 5 mol %), Et₃N (20 mg, 0.2 mmol, 5 mol %) and acetone (2.0 mL) under air atmosphere. The reaction mixture was stirred at room temperature for 12 h. Organic solvents were removed under reduced pressure and the residue was purified by chromatography on silica gel with acetone/petroleum as the eluent to give the **d1-3a**.

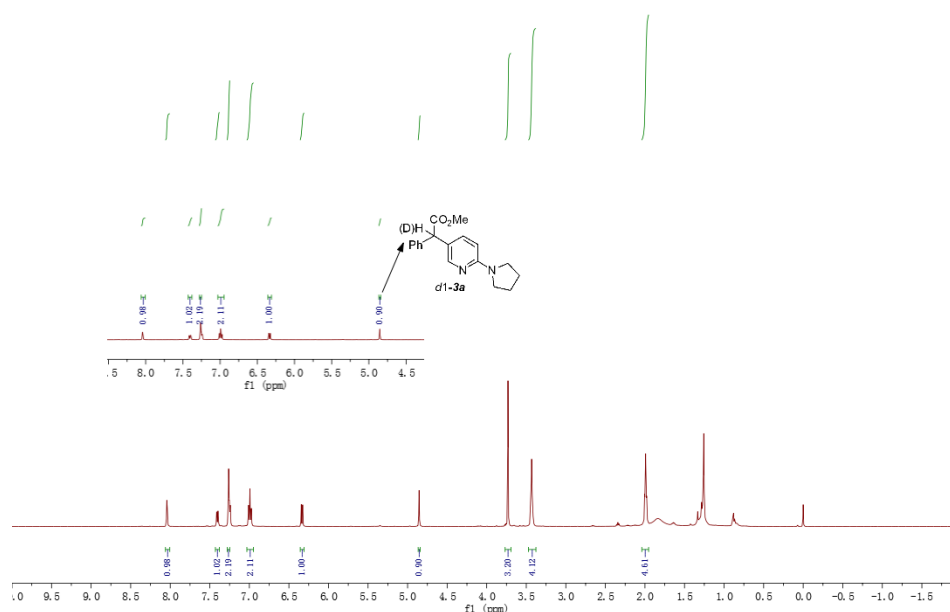


Figure S-4. ¹H NMR spectrum for **d1-3a**

5. Photocatalyzed regioselective pyridine C-H coupling of *d1-1a'* with **2a**



To a screw capped vial with a spinvane triangular-shaped Teflon stir bar were added 2-phenyl-2-(6-(pyrrolidin-1-yl)pyridin-3-yl)acetate (*d1-1a'*, 95% D, 29.6 mg, 0.2 mmol), CH₃OD (2.0 equiv.), DPM (2.2 mg, 0.01 mmol, 5 mol %), Et₃N (20 mg, 0.2 mmol, 1.0 equiv.) and acetone (2.0 mL) under air atmosphere conditions. The vial was equipped with a Teflon septum and stirred under blue LED irradiation with Kessil LEDs (30 W) for 12 h, filtered through a pad of celite and then washed with ethyl acetate (3 × 10 mL). The combined organic layers were removed under reduced pressure and the residue was purified by chromatography on silica gel. The product *d1-3a'* deuterium was observed by ¹H NMR method.

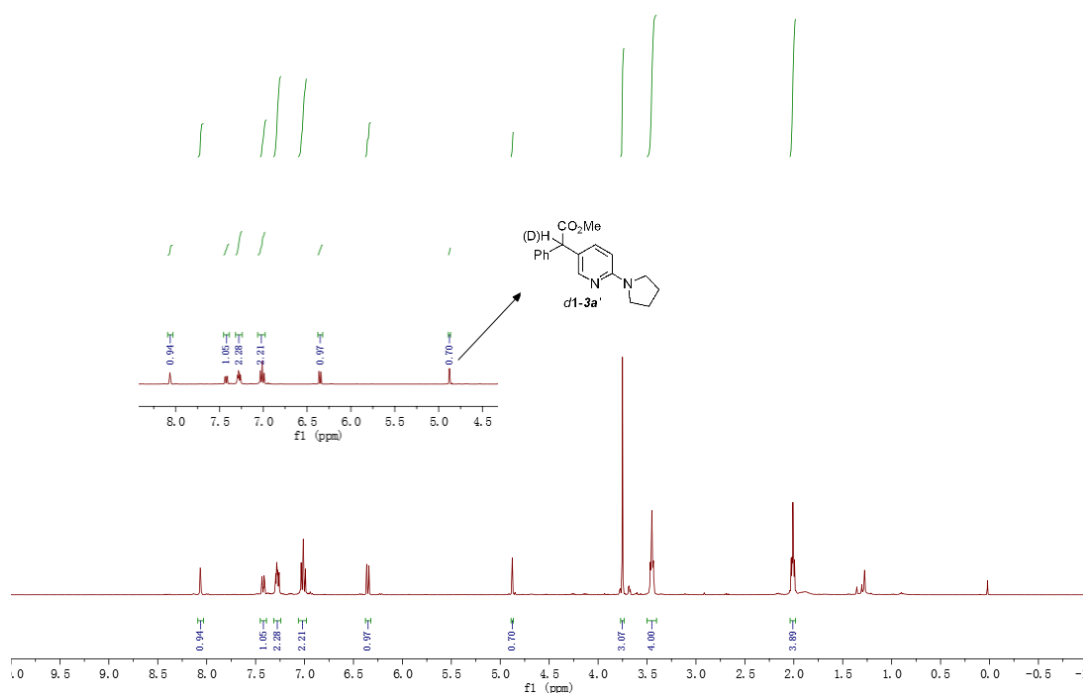


Figure S-5. ¹H NMR spectrum for *d1-3a'*

6. Light sources emission spectra

The following spectrum of light source was recorded by OHSP660 spectrum reflectance spectrometer produced by WATTCAS (<https://www.hopoocolor.com/product/detail/reflectance.html>).

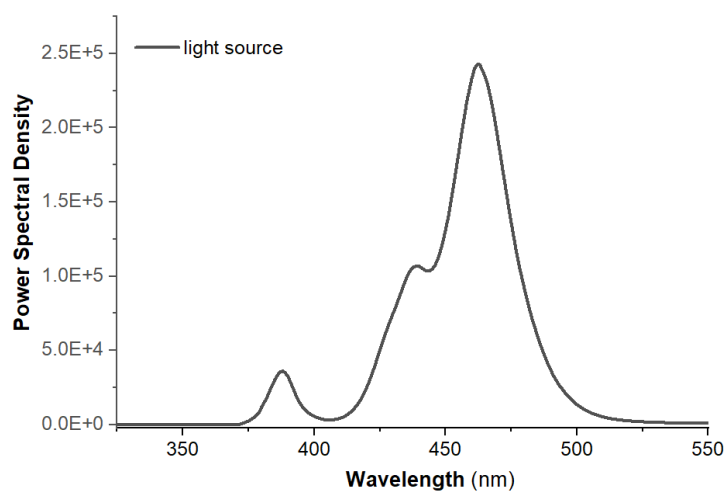


Figure S-6. Emission spectra of the light source used in this work

7. Absorption spectrum of benzophenone

UV-vis absorption spectra of benzophenone **DPM** was collected on Shimadzu UV-vis spectrophotometer UV-2600 and measured in diluted acetone solution (10^{-3} M).

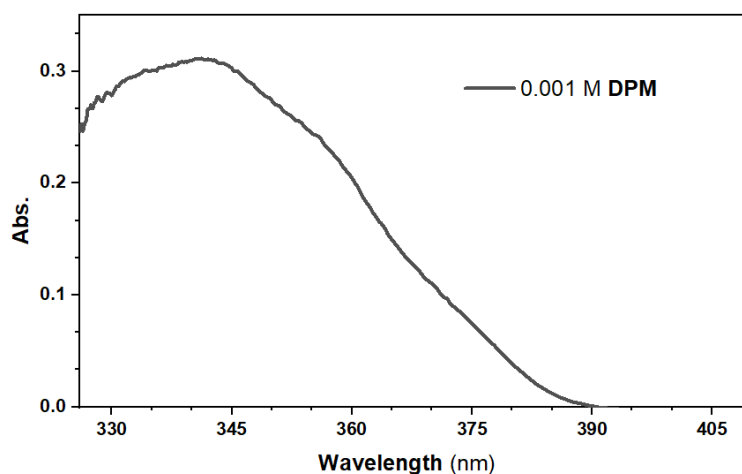


Figure S-7. Absorption spectra of the **DPM** in 0.001 M acetone

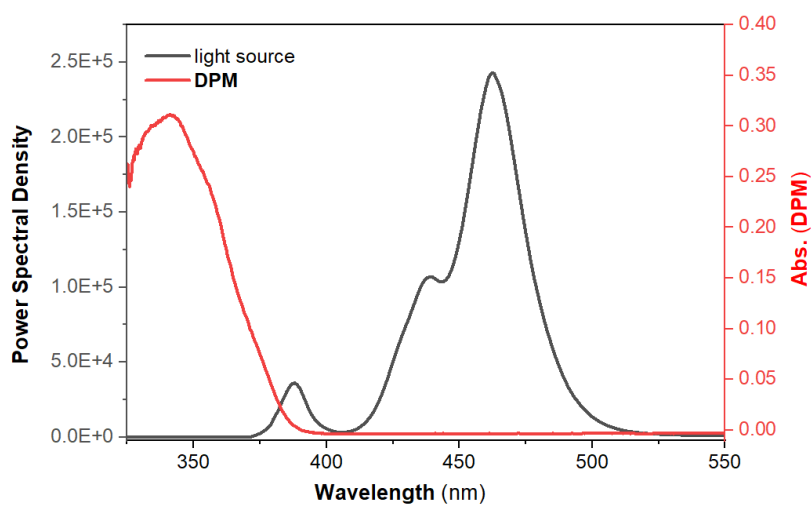


Figure S-8. Absorption spectra of **DPM** and emission of the light source used in this work.

8. The ^1H NMR spectrum of the **1a**- and benzophenone-containing mixture in d_6 -acetone

The ^1H NMR of 2-(pyrrolidin-1-yl)pyridine **1a**, benzophenone, and the mixture of 2-(pyrrolidin-1-yl)pyridine **1a** and benzophenone using d_6 -acetone as solvent were shown in **Figure S-9**. Compared with the ^1H NMR spectrum from **1a** and benzophenone, it was not found that their chemical shift (δ) derived from aryl $\text{Csp}^2\text{-H}$ of the **1a**- and benzophenone-containing mixture were apparently changed. Based on these facts, the possibility involved the formation of donor-acceptor complex from pyridine substrate and benzophenone did not occur.

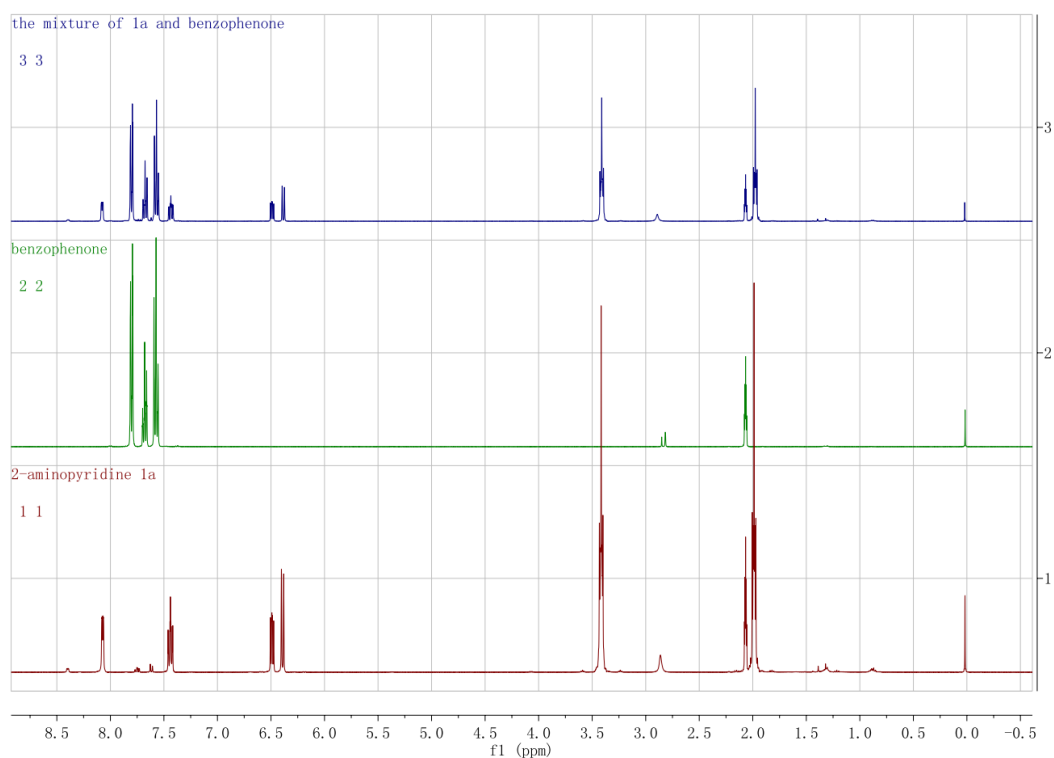


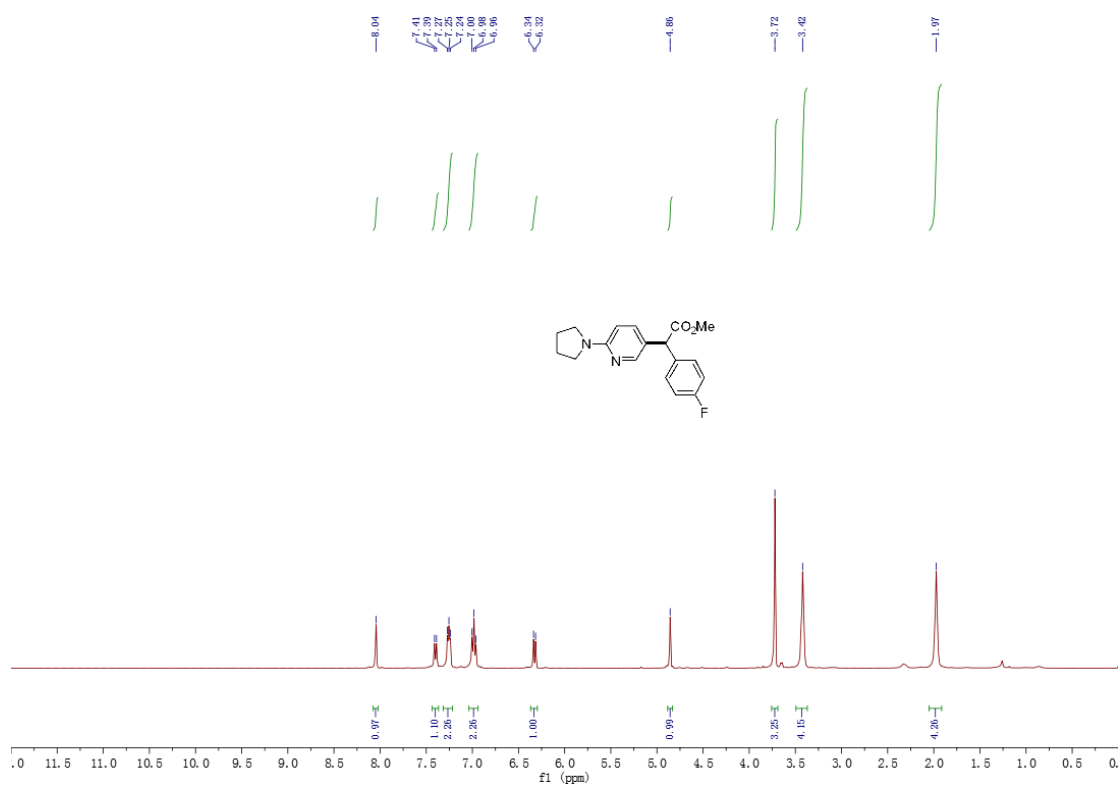
Figure S-9. ^1H NMR spectrum of **1a**, benzophenone and the mixture of **1a** and benzophenone

IX. Reference

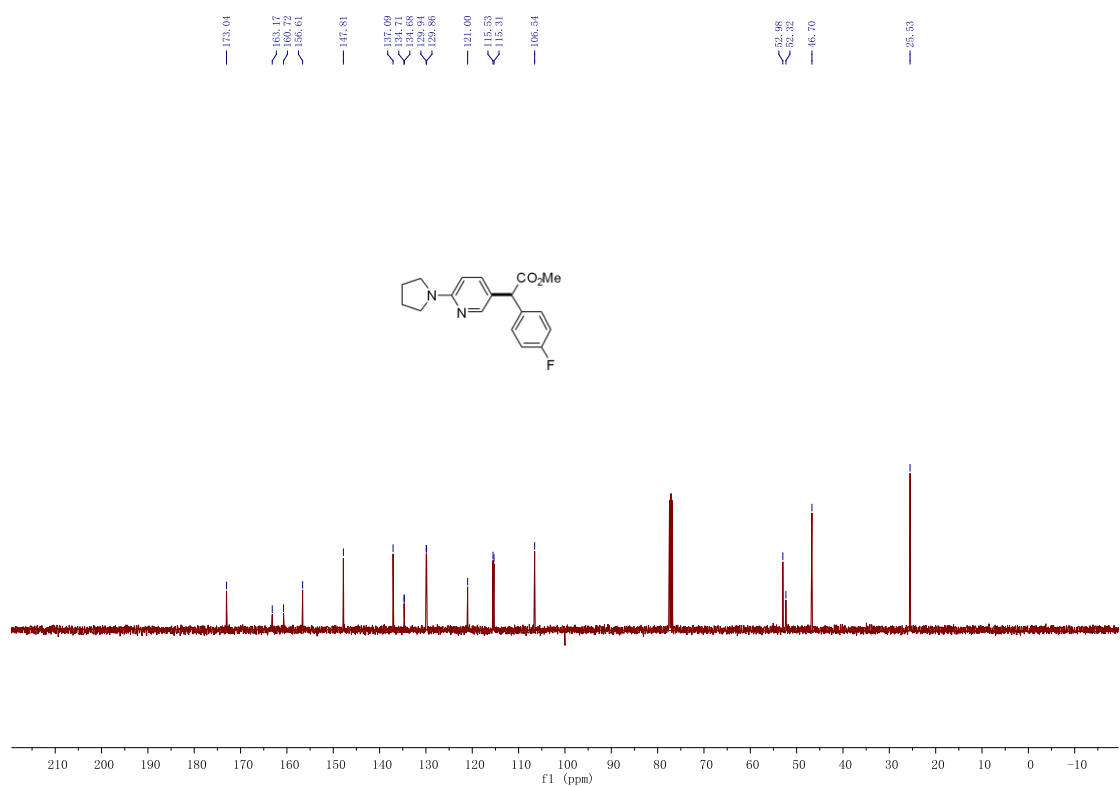
1. Xie, H. S; Shao, Y. X; Gui, J.; Lan, J. Y.; Liu, Z. P.; Ke, Z. F.; Deng, Y. F.; Jiang, H. F.; Zeng, W. *Org. Lett.* **2019**, *21*, 3427.
2. Pichowicz, M.; Crumpler, S.; McDonald, E.; Blagg, J. *Tetrahedron* **2010**, *66*, 2389.
3. Cui, X.; Li, J.; Liu, L.; Guo, Q. X. *Chin. Chem. Lett.* **2007**, *18*, 625.
4. Pierrat, P.; Gros, P.; Fort, Y. *Synlett* **2004**, *13*, 2319.
5. Lv, X.; Bao, W. L. *J. Org. Chem.* **2007**, *72*, 3863.

Appendix II: Spectral Copies of ^1H and ^{13}C NMR of Compounds

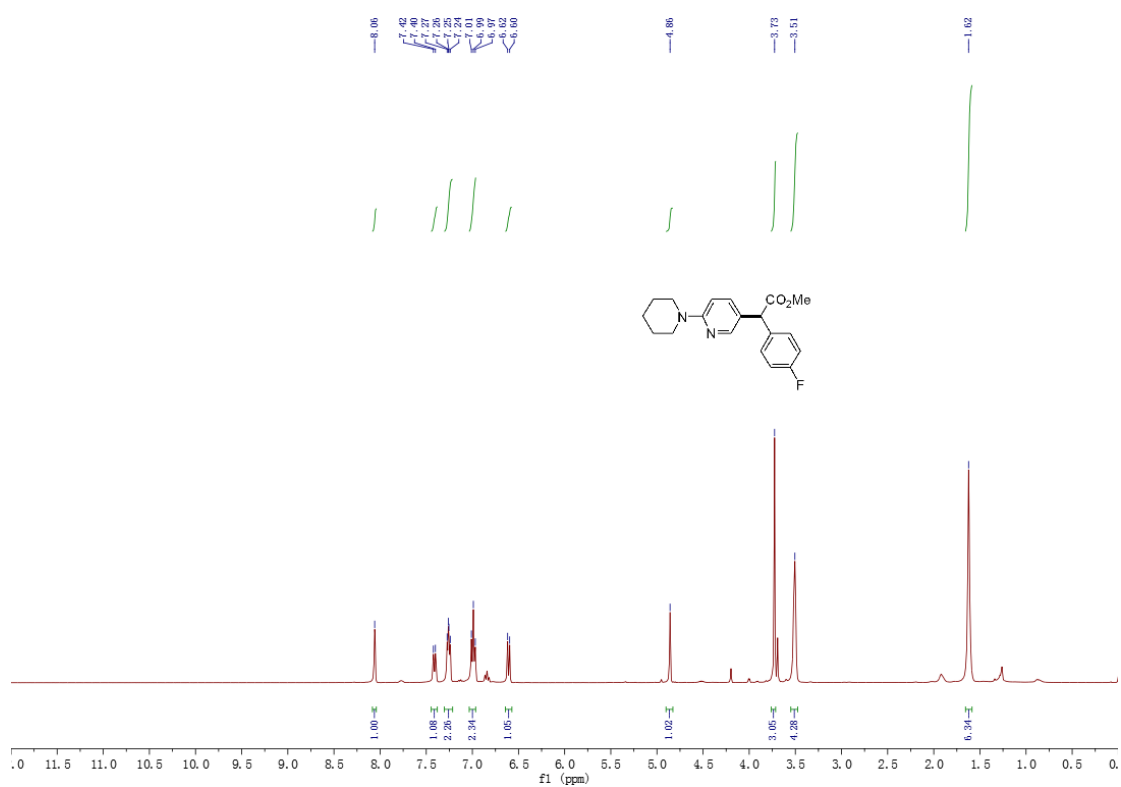
^1H NMR spectrum (400 MHz, CDCl_3) of **3a**



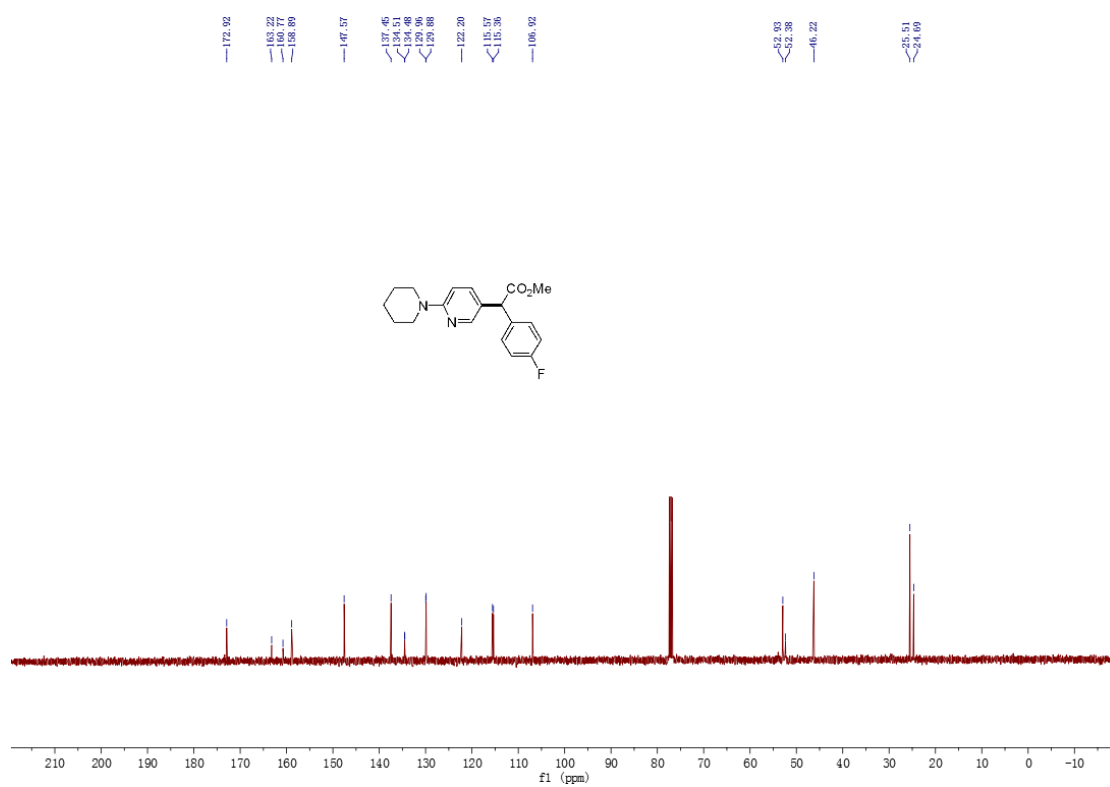
^{13}C NMR spectrum (400 MHz, CDCl_3) of **3a**



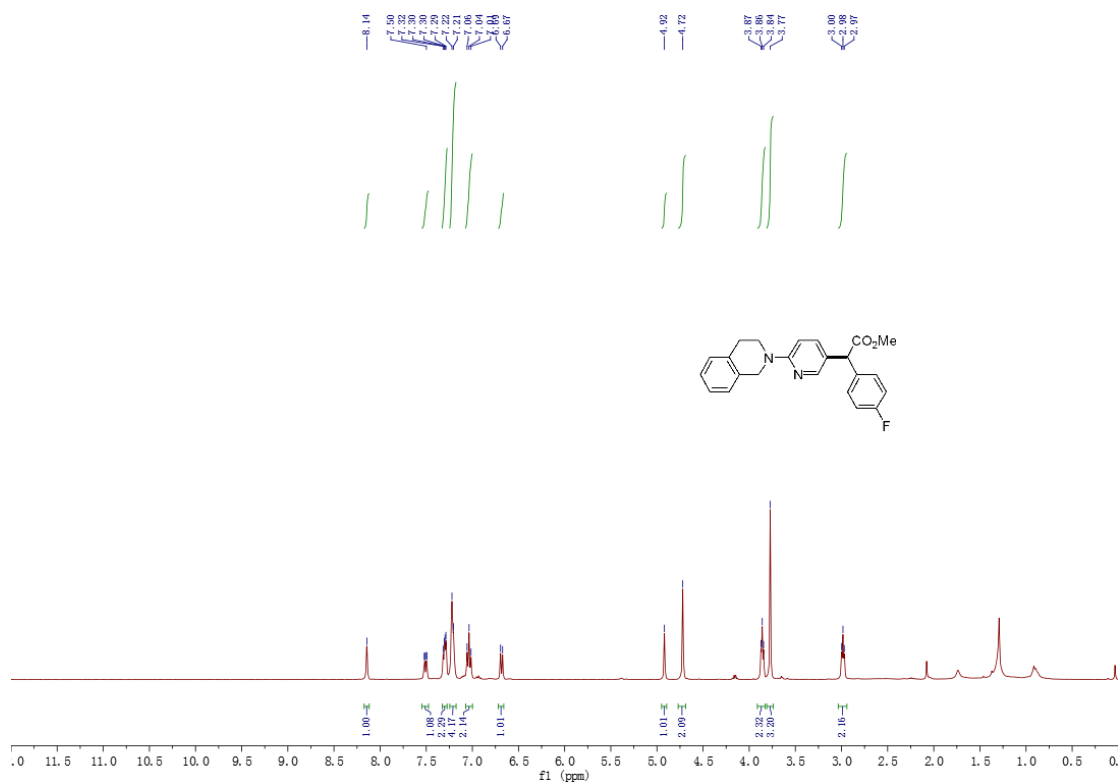
^1H NMR spectrum (400 MHz, CDCl_3) of **3b**



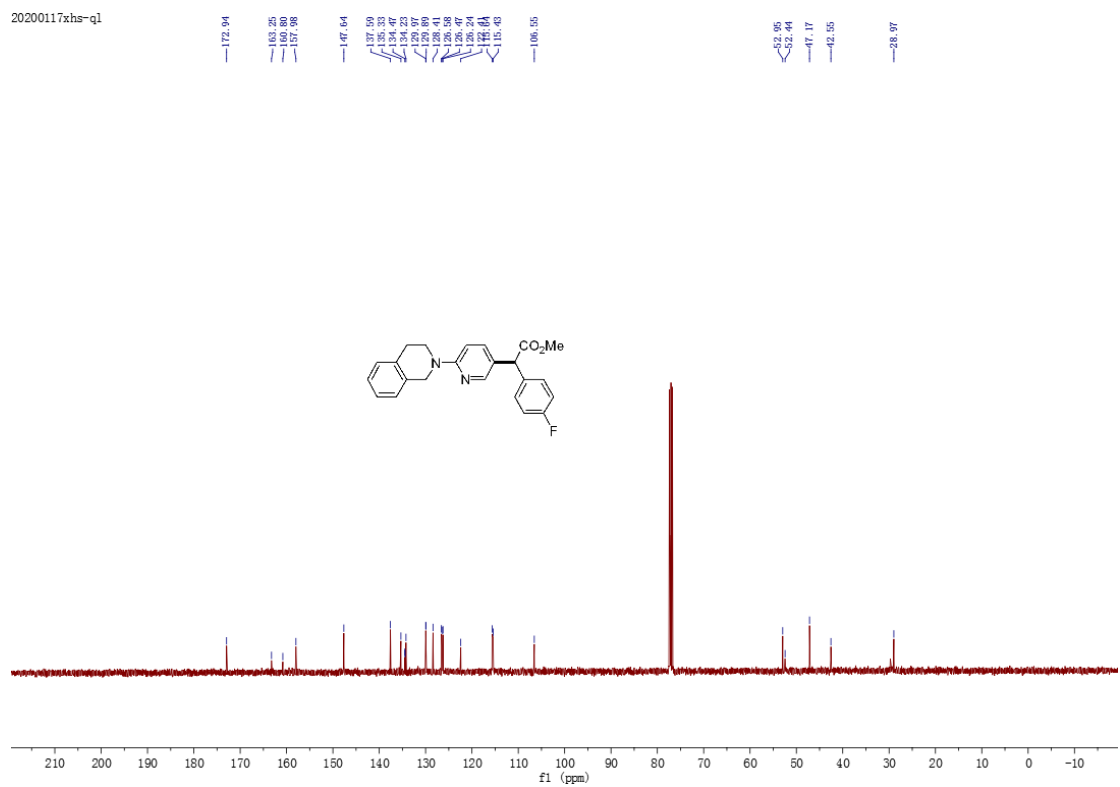
^{13}C NMR spectrum (100 MHz, CDCl_3) of **3b**



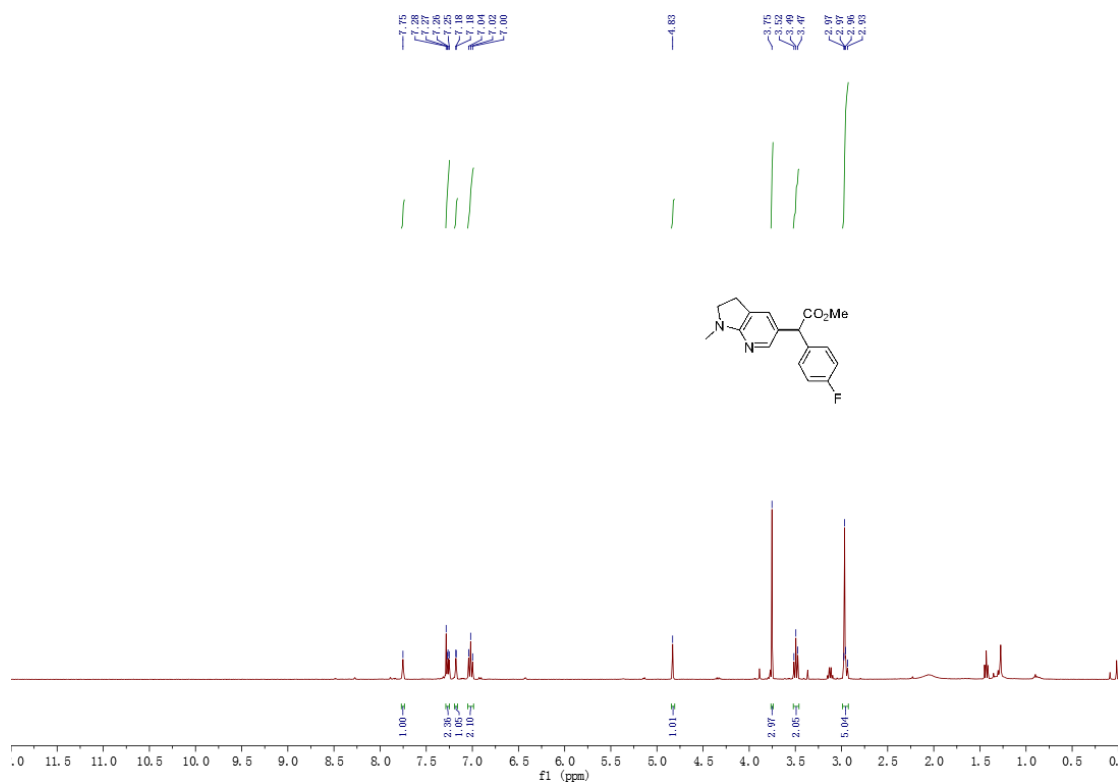
¹H NMR spectrum (400 MHz, CDCl₃) of **3c**



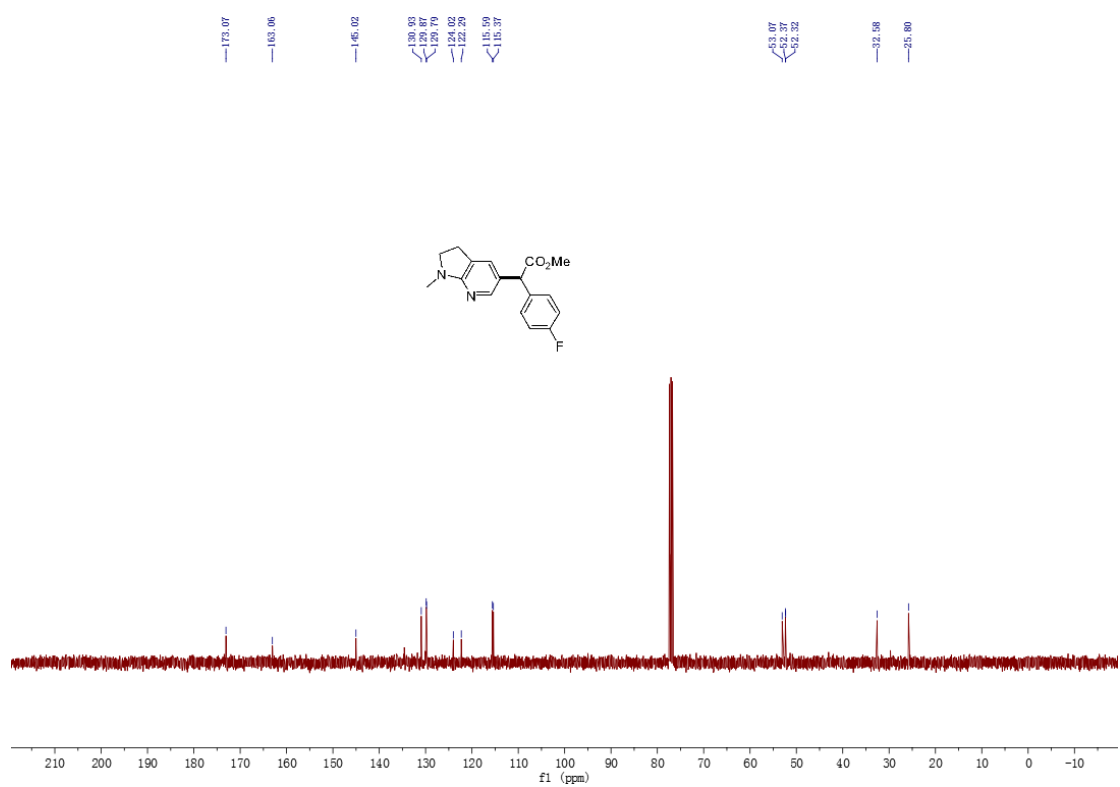
¹³C NMR spectrum (100 MHz, CDCl₃) of **3c**



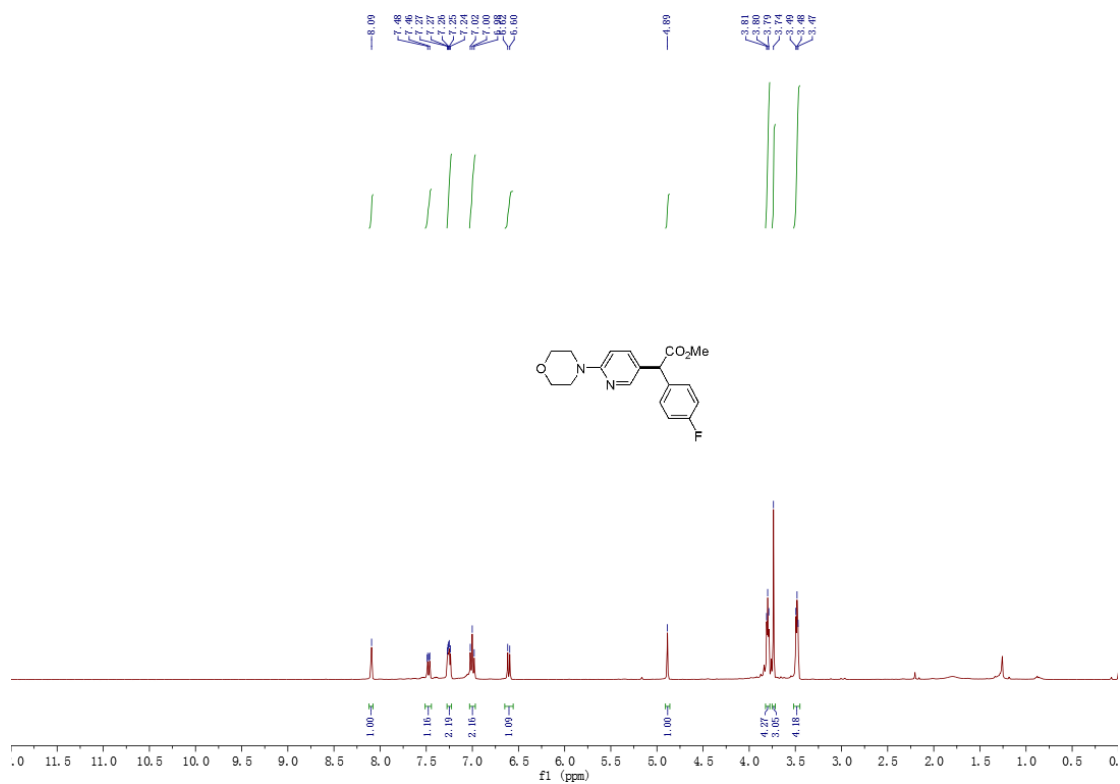
^1H NMR spectrum (400 MHz, CDCl_3) of **3d**



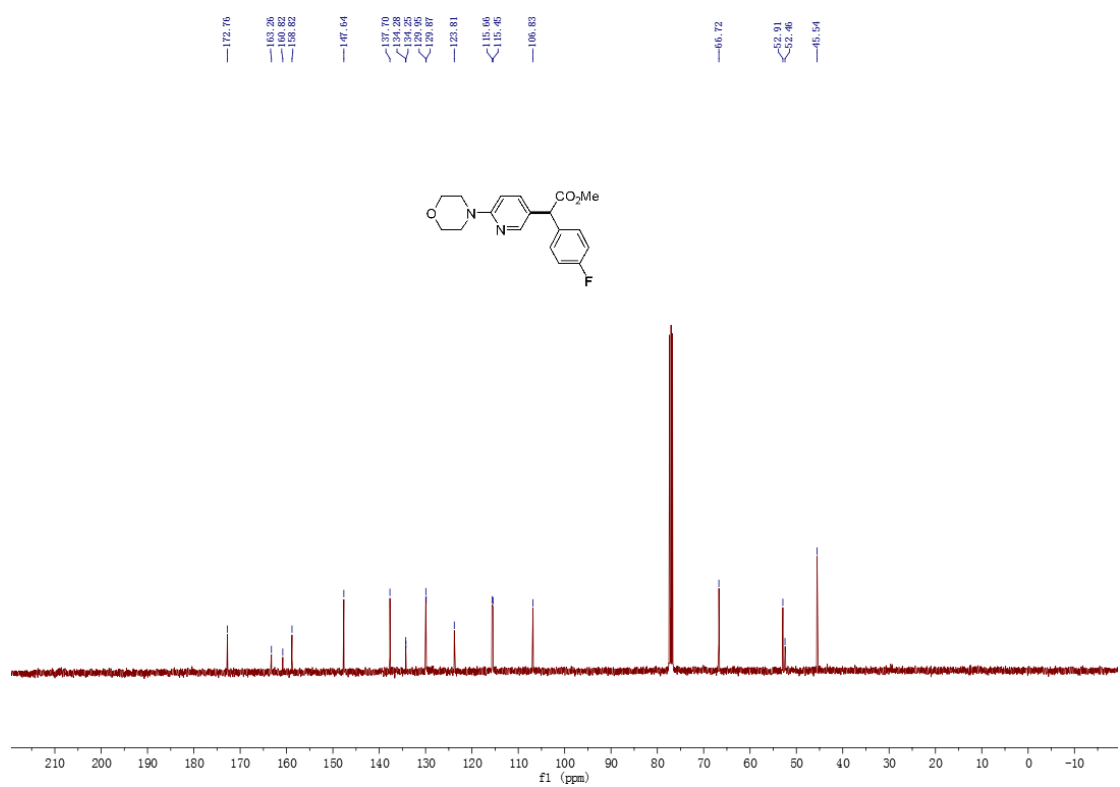
^{13}C NMR spectrum (100 MHz, CDCl_3) of **3d**



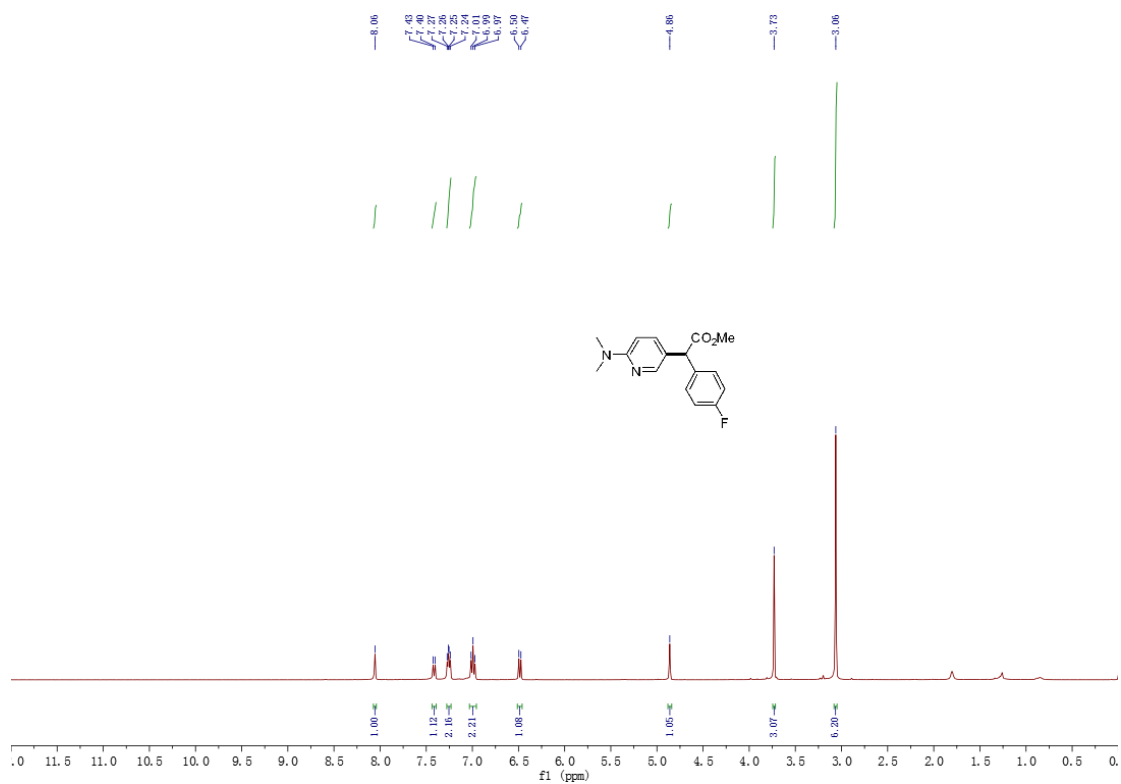
^1H NMR spectrum (400 MHz, CDCl_3) of **3e**



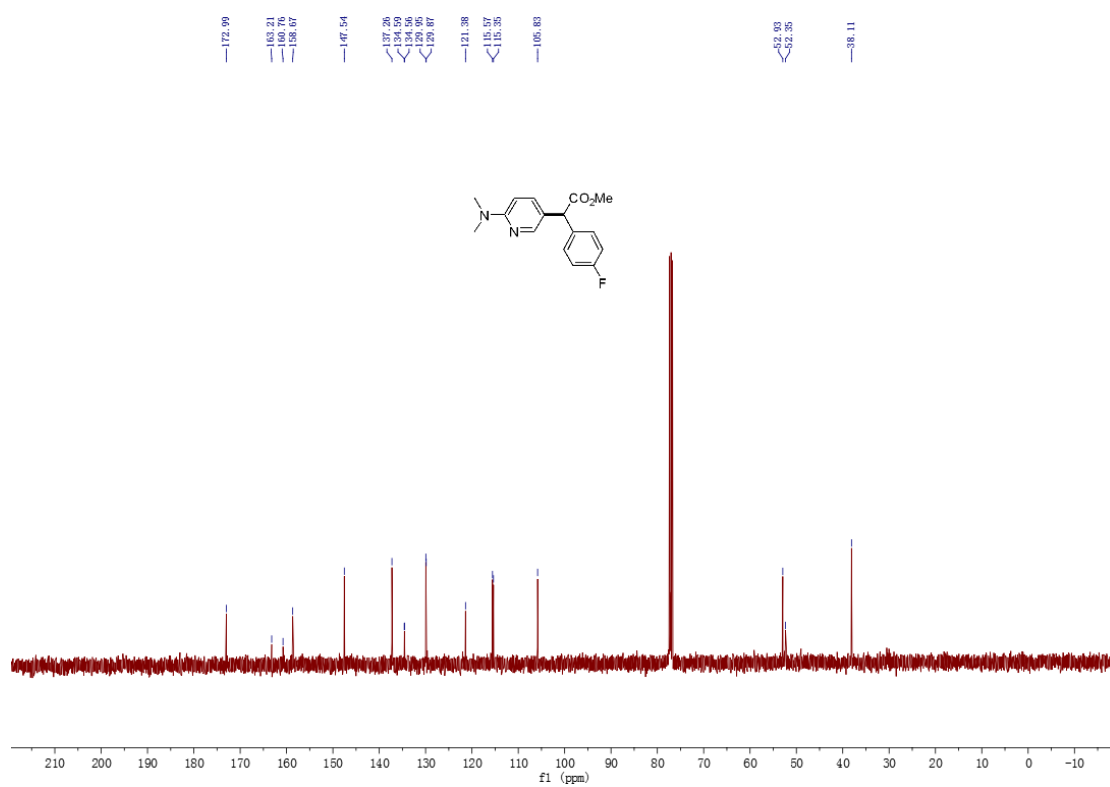
^{13}C NMR spectrum (100 MHz, CDCl_3) of **3e**



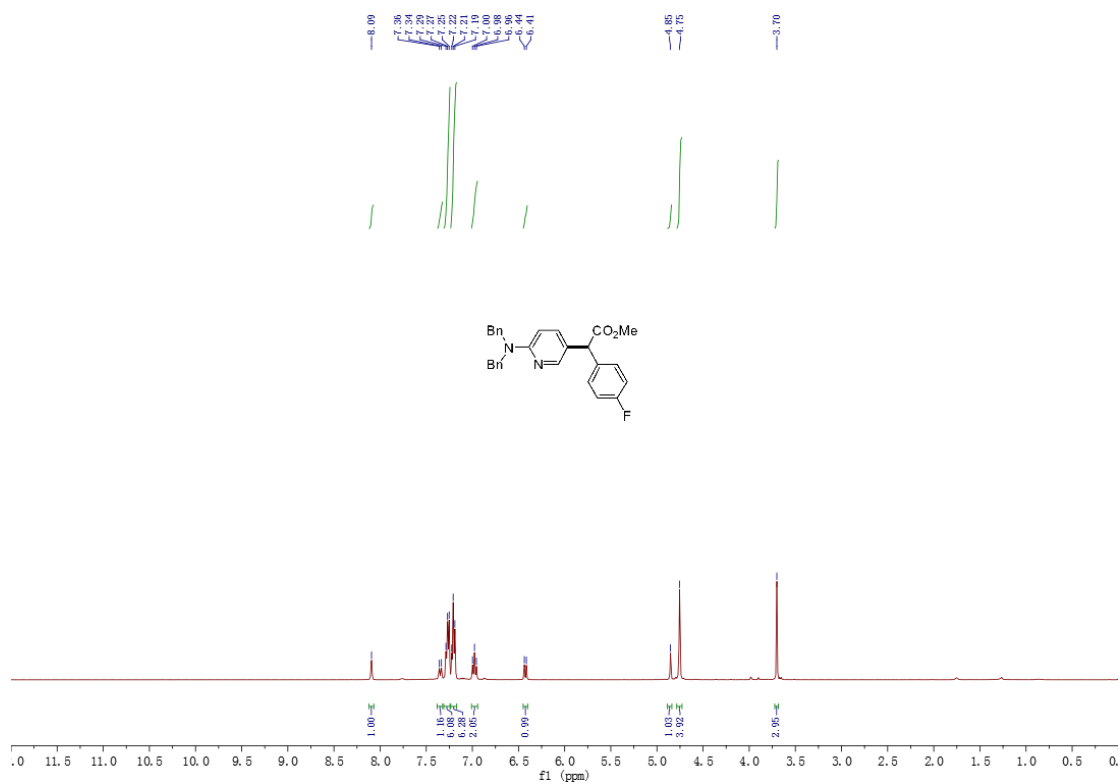
^1H NMR spectrum (400 MHz, CDCl_3) of **3f**



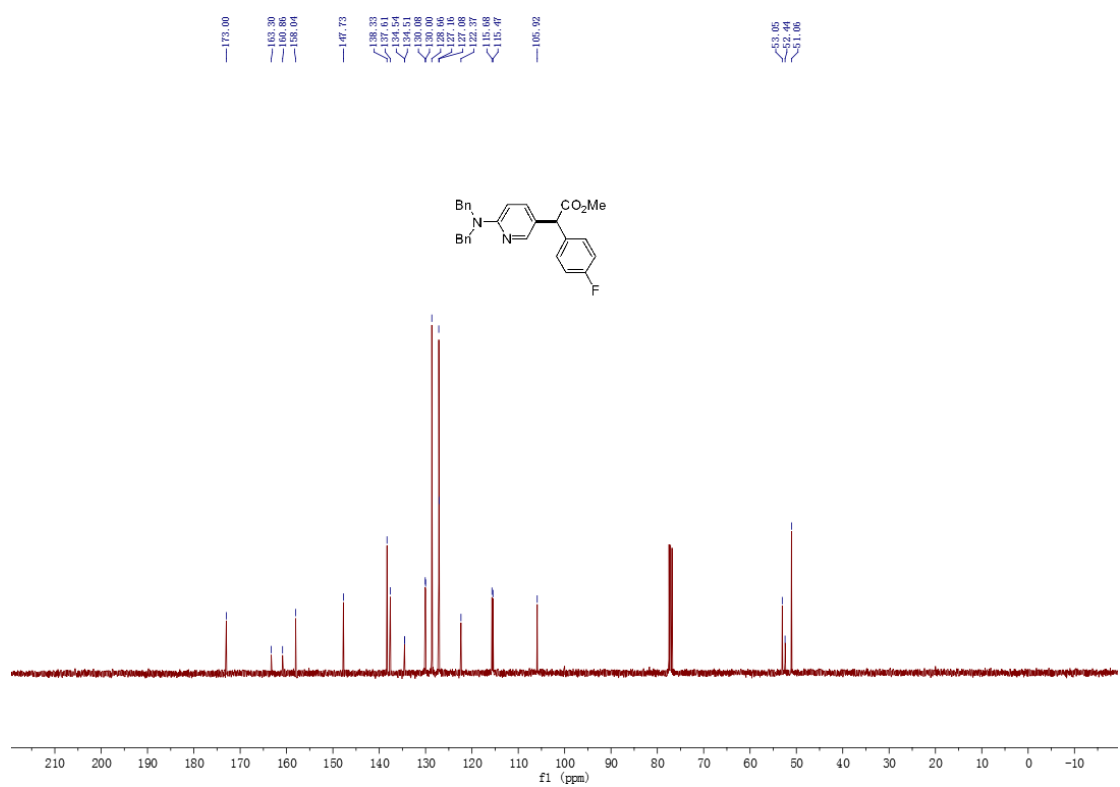
^{13}C NMR spectrum (100 MHz, CDCl_3) of **3f**



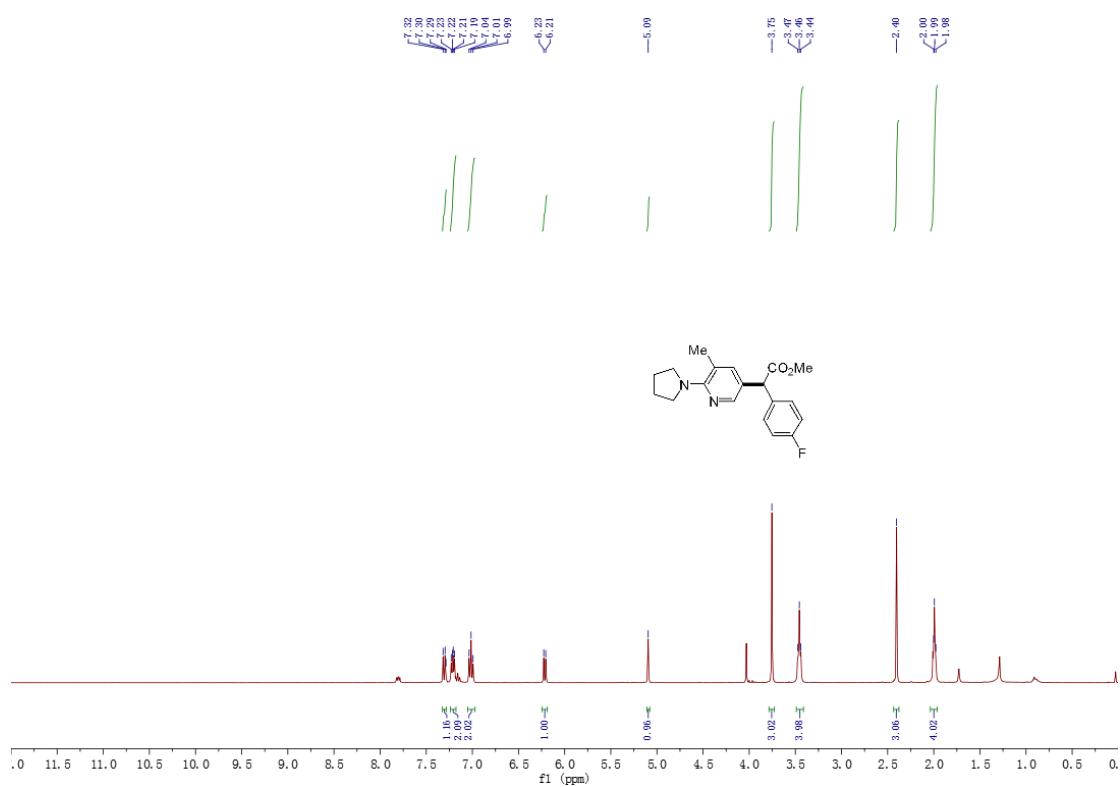
^1H NMR spectrum (400 MHz, CDCl_3) of **3g**



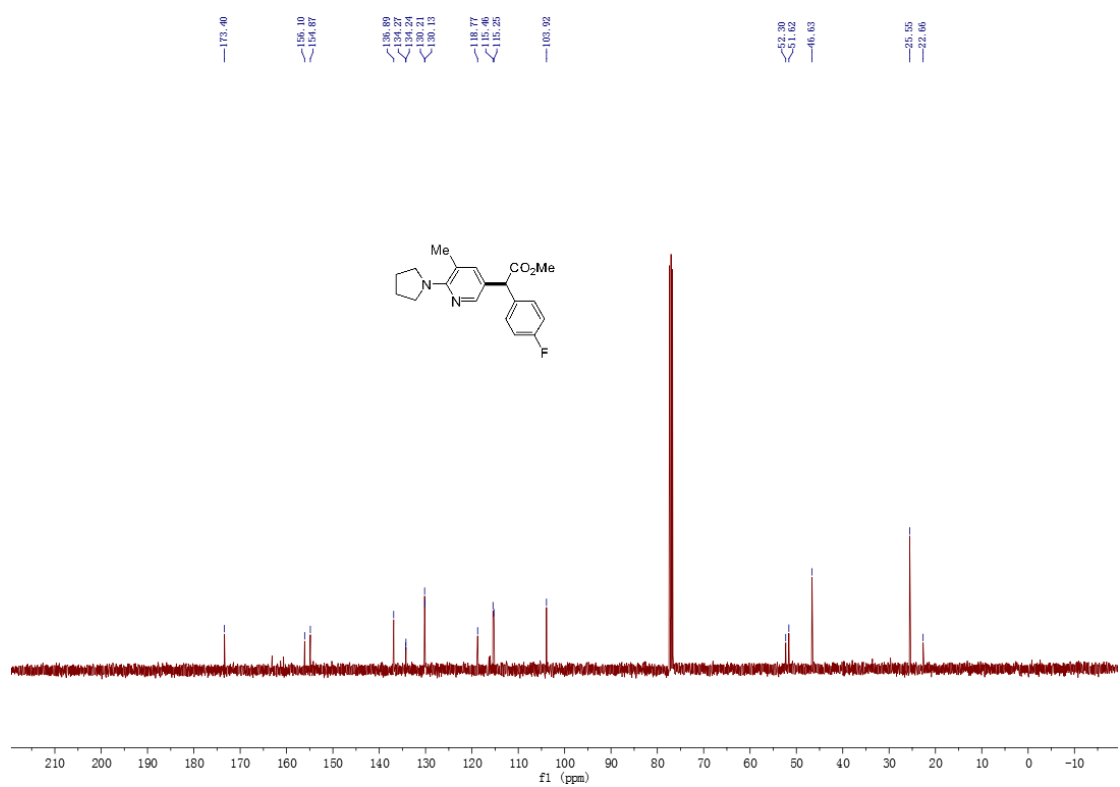
^{13}C NMR spectrum (100 MHz, CDCl_3) of **3g**



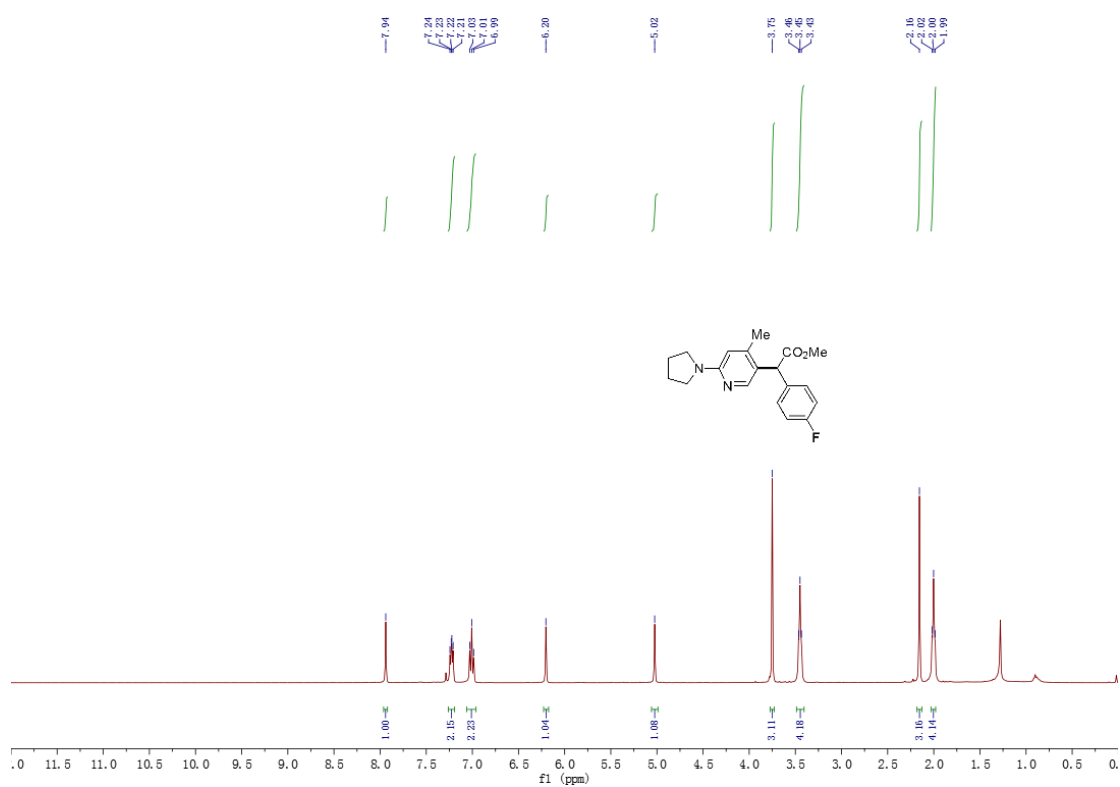
^1H NMR spectrum (400 MHz, CDCl_3) of **3h**



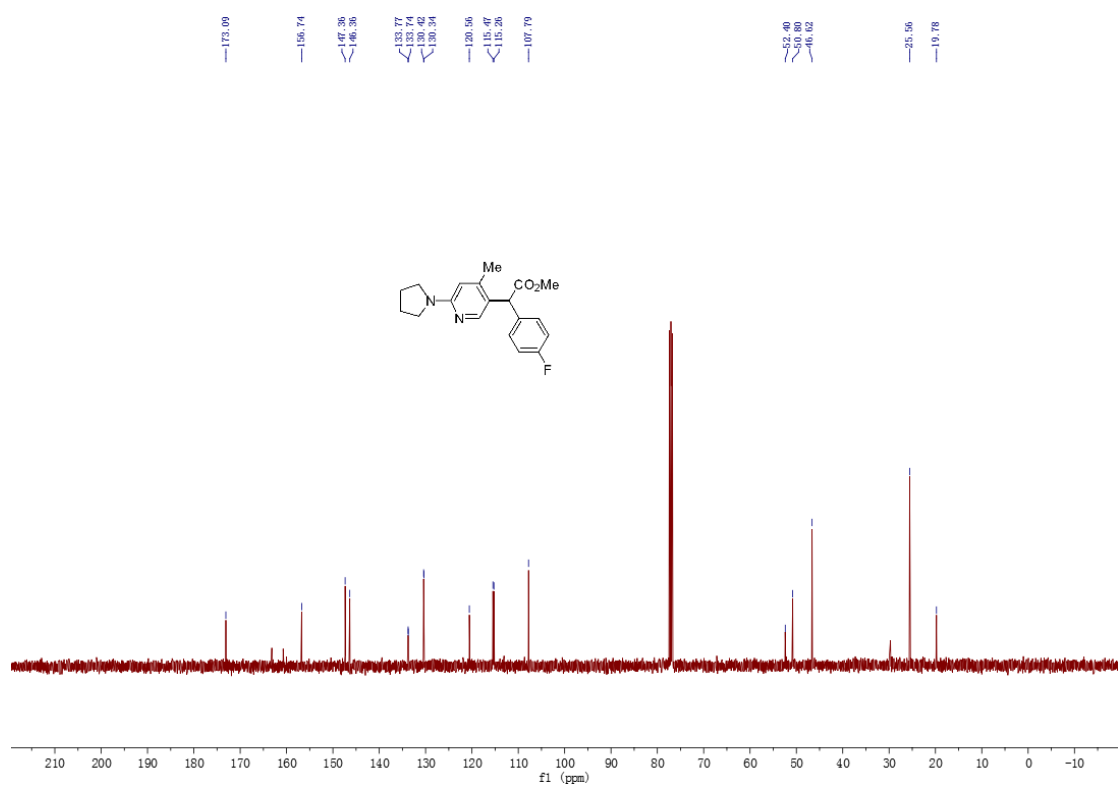
^{13}C NMR spectrum (100 MHz, CDCl_3) of **3h**



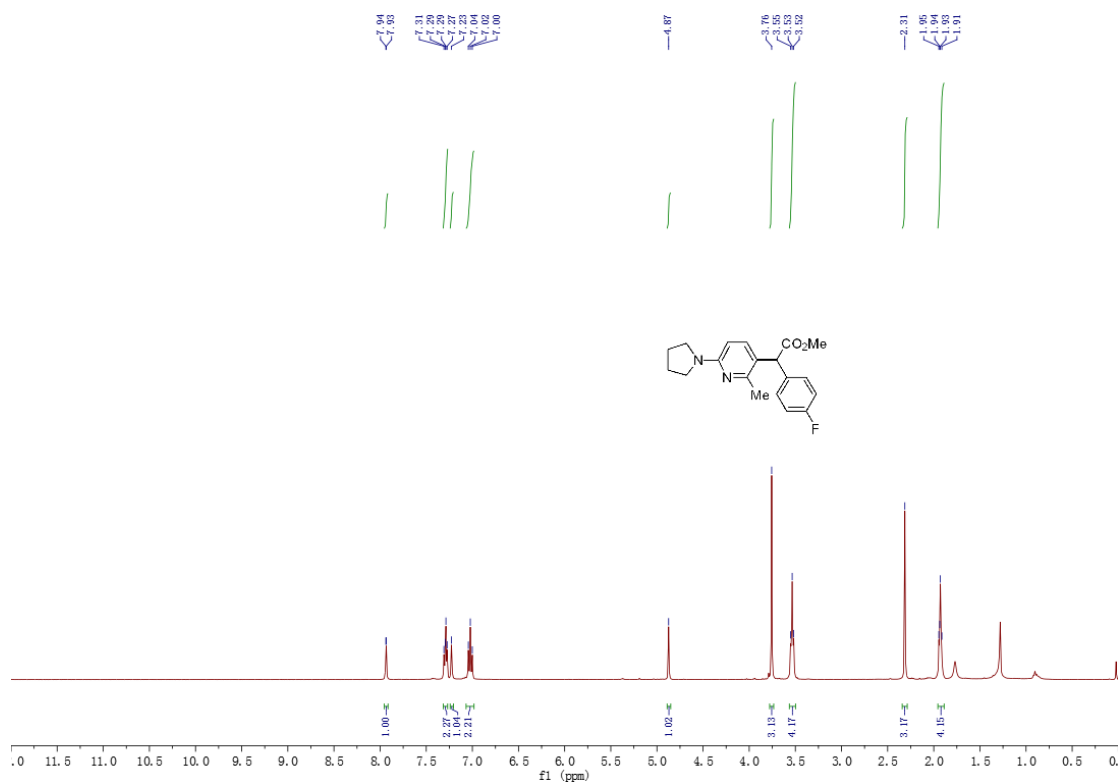
^1H NMR spectrum (400 MHz, CDCl_3) of **3i**



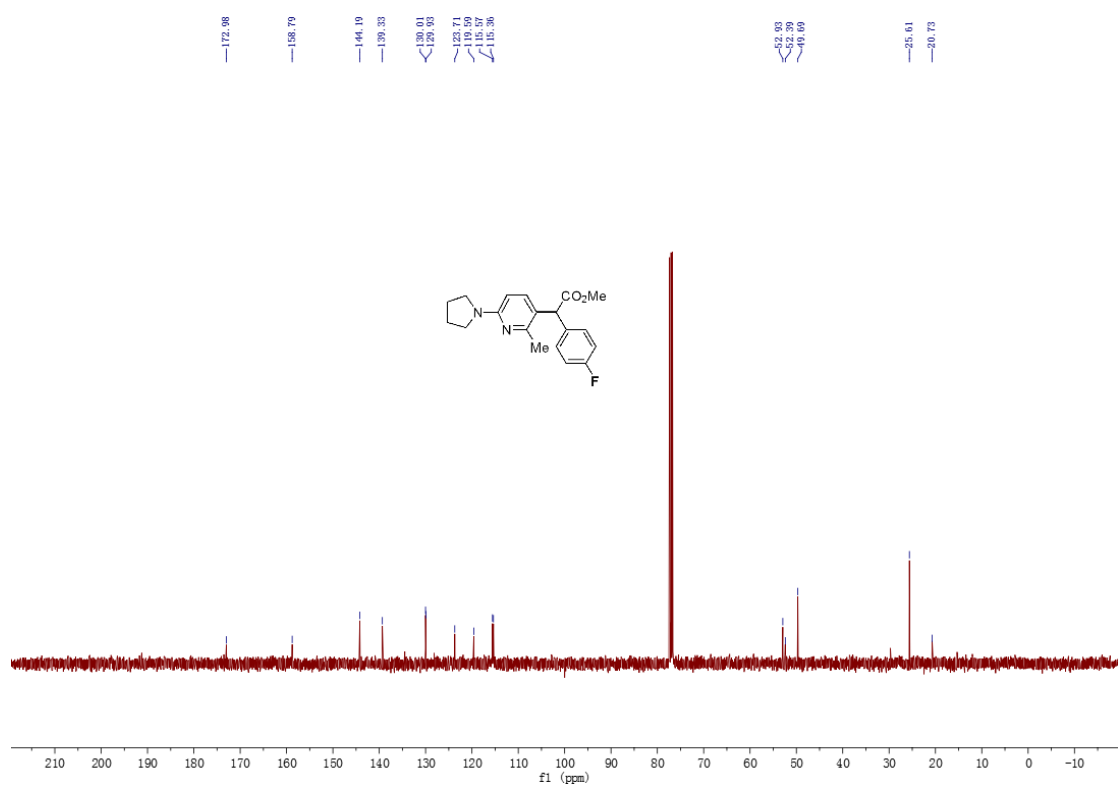
^{13}C NMR spectrum (100 MHz, CDCl_3) of **3i**



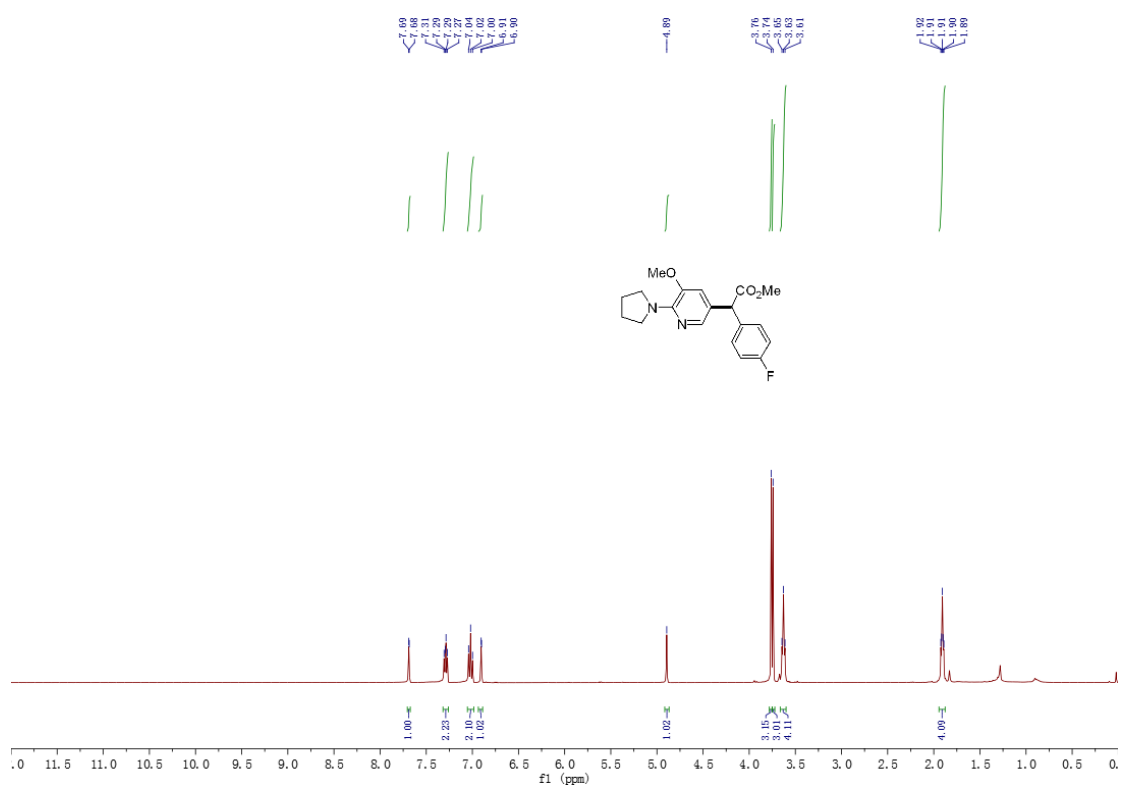
^1H NMR spectrum (400 MHz, CDCl_3) of **3j**



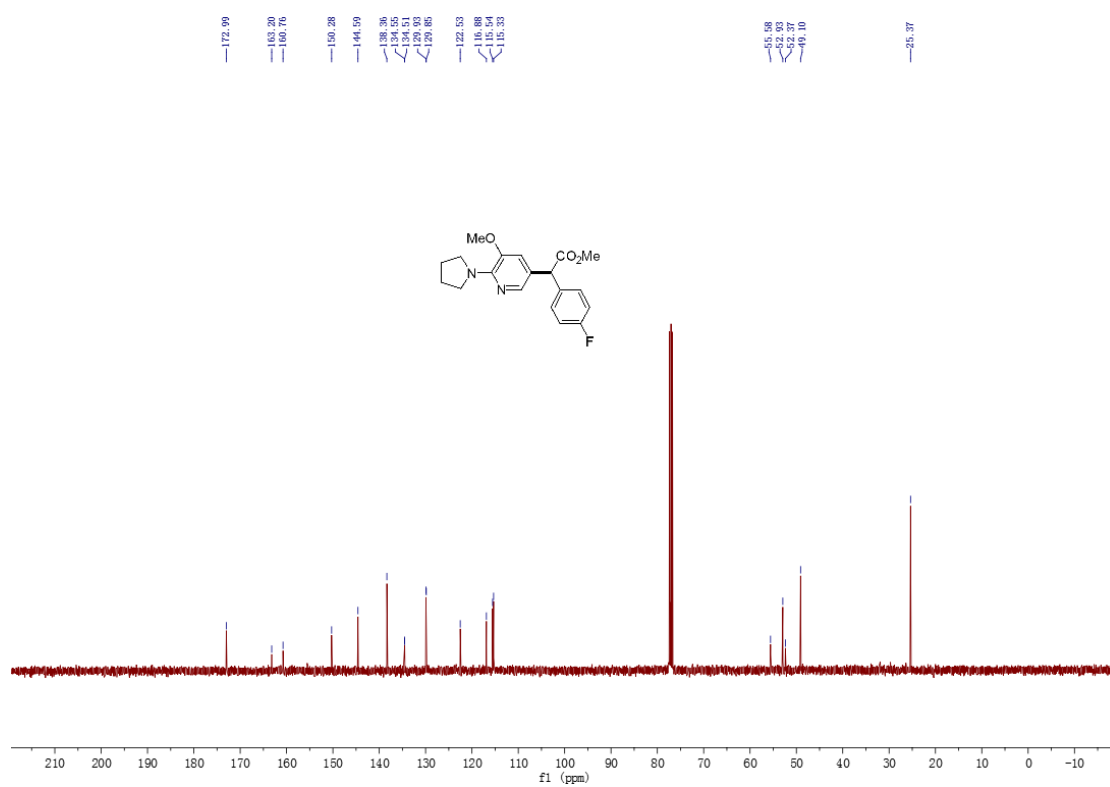
^{13}C NMR spectrum (100 MHz, CDCl_3) of **3j**



^1H NMR spectrum (400 MHz, CDCl_3) of **3k**

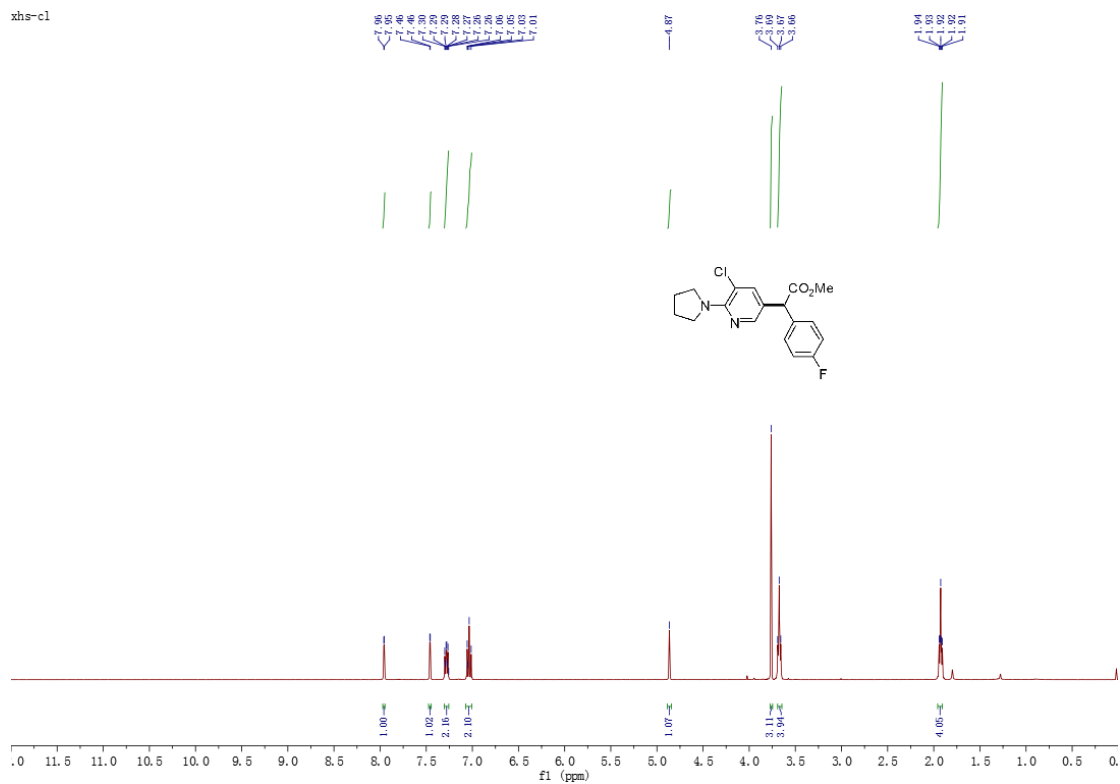


^{13}C NMR spectrum (100 MHz, CDCl_3) of **3k**

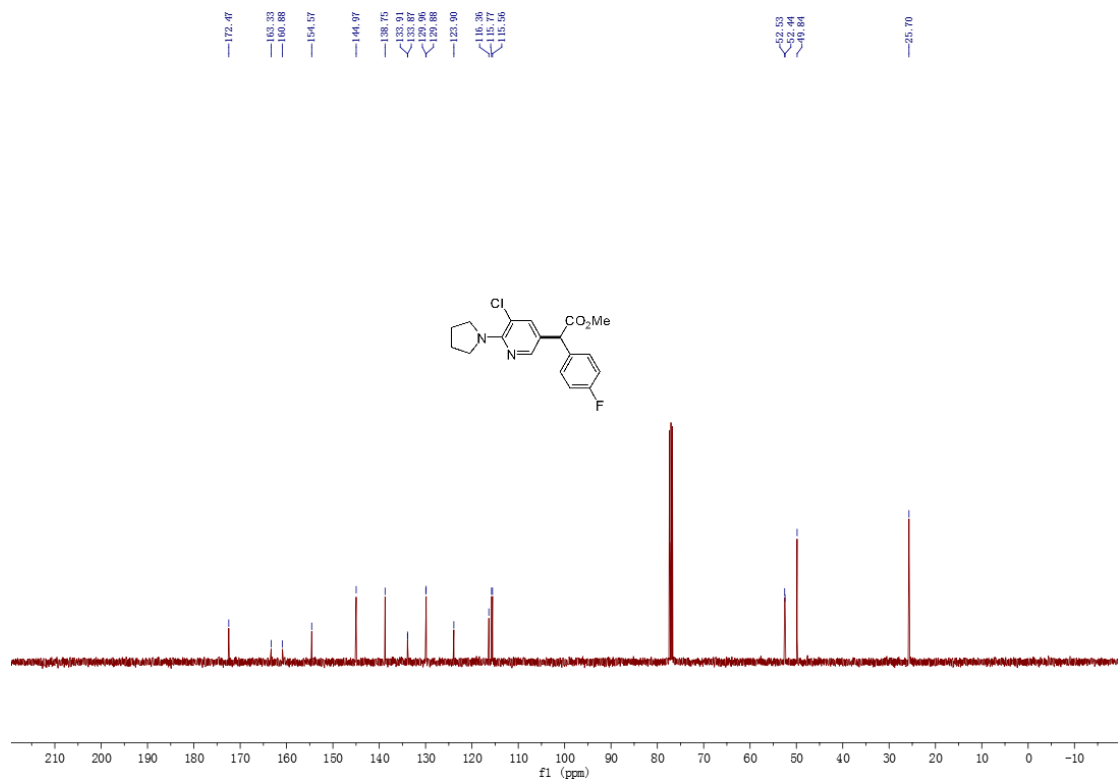


¹H NMR spectrum (400 MHz, CDCl₃) of **31**

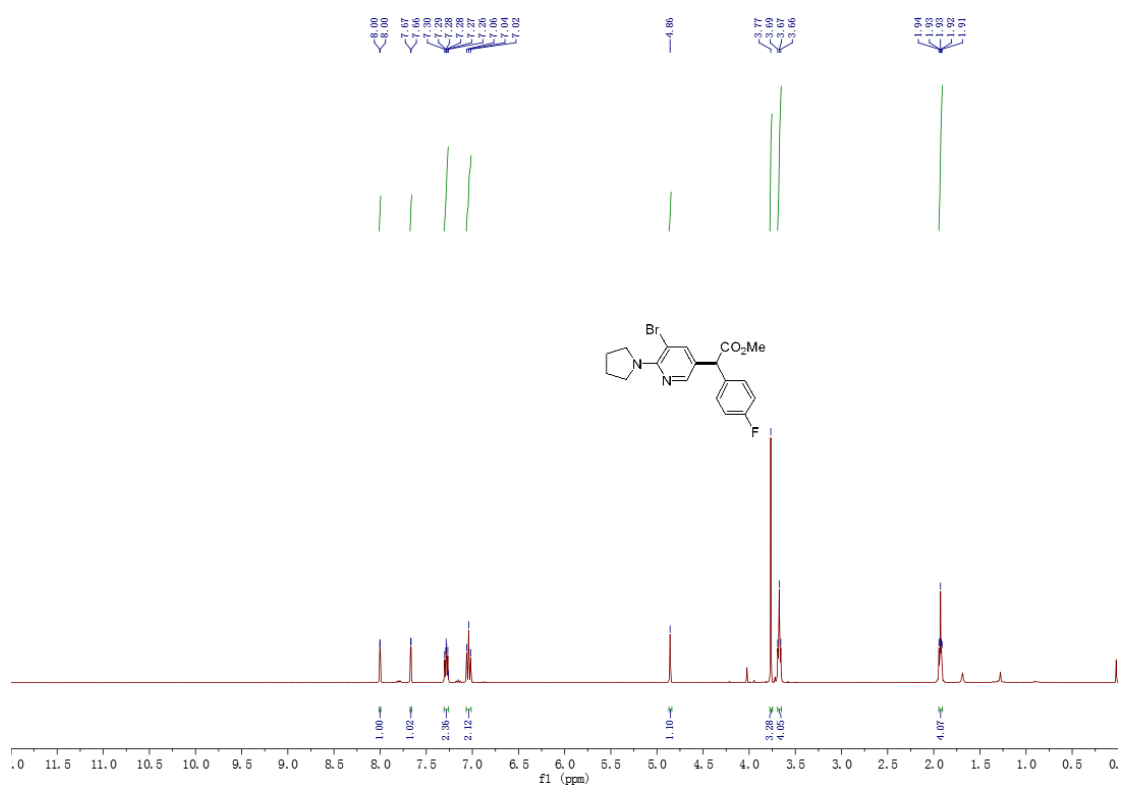
xhs-c1



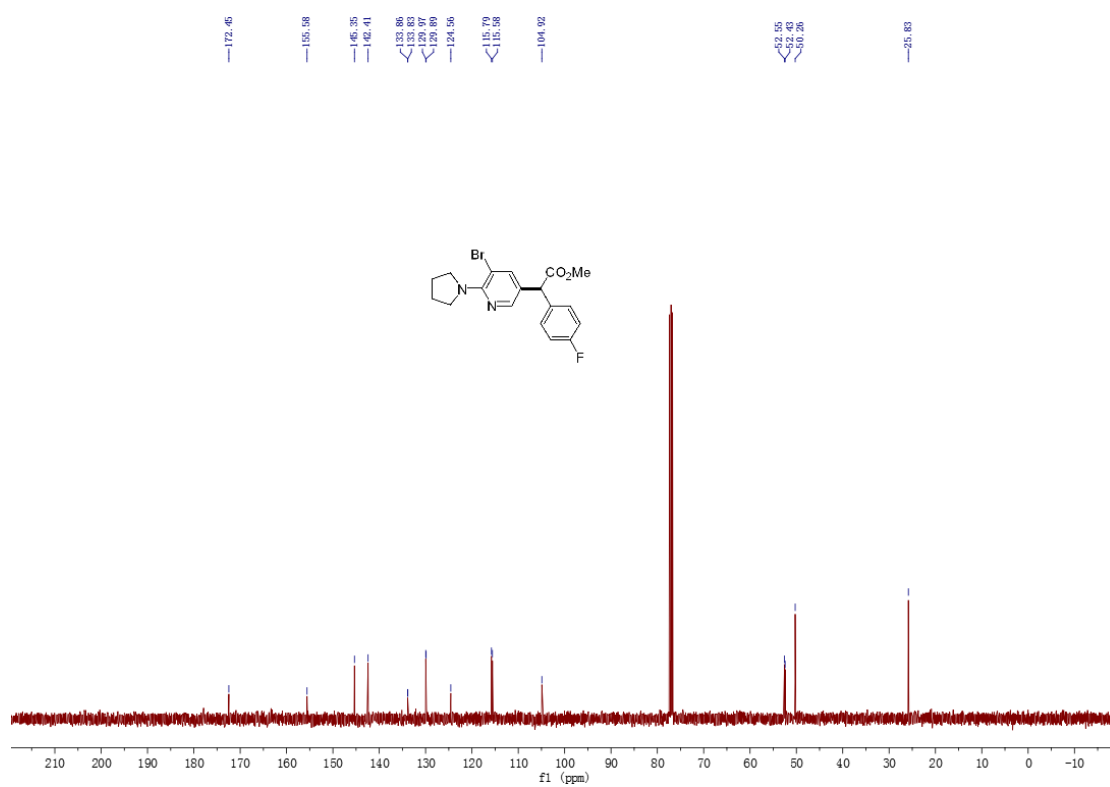
¹³C NMR spectrum (100 MHz, CDCl₃) of **31**



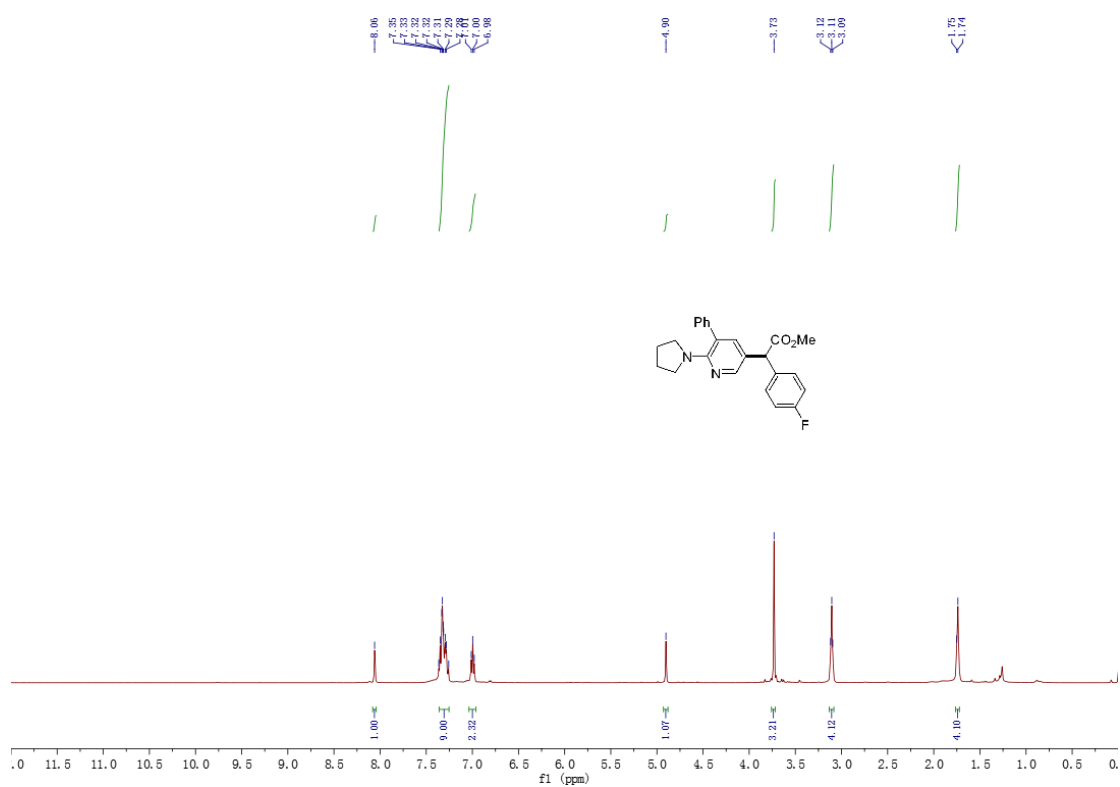
^1H NMR spectrum (400 MHz, CDCl_3) of **3m**



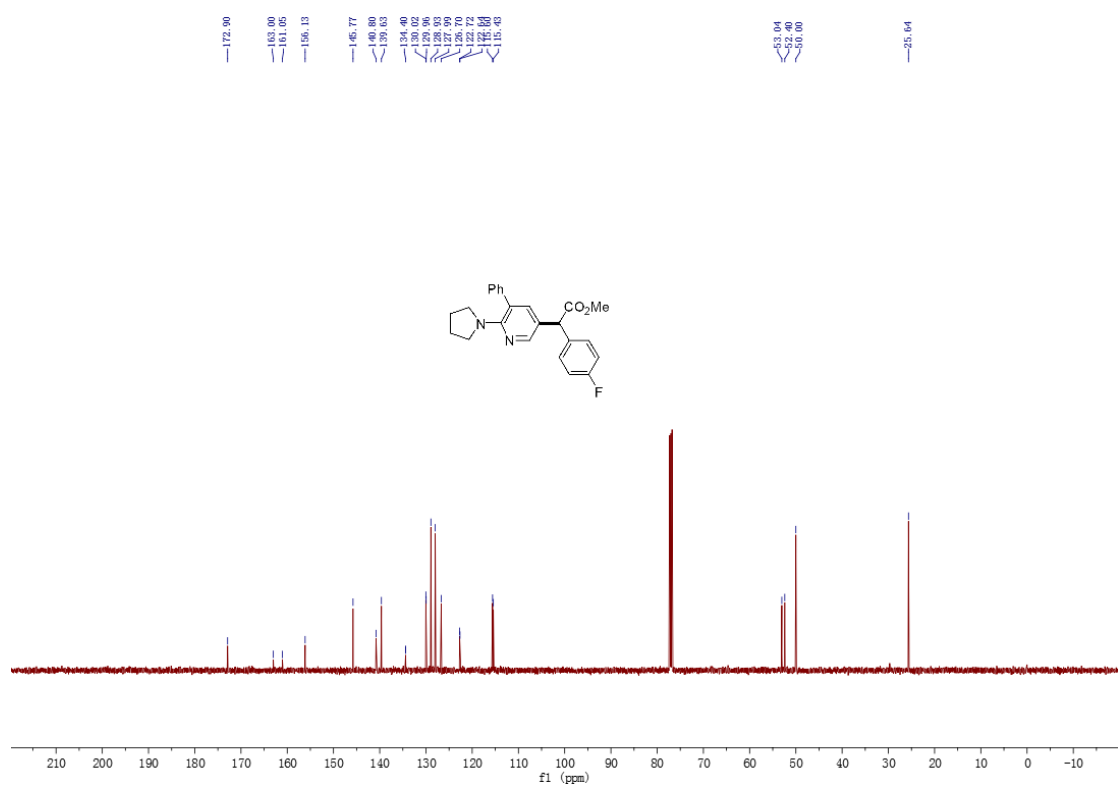
^{13}C NMR spectrum (100 MHz, CDCl_3) of **3m**



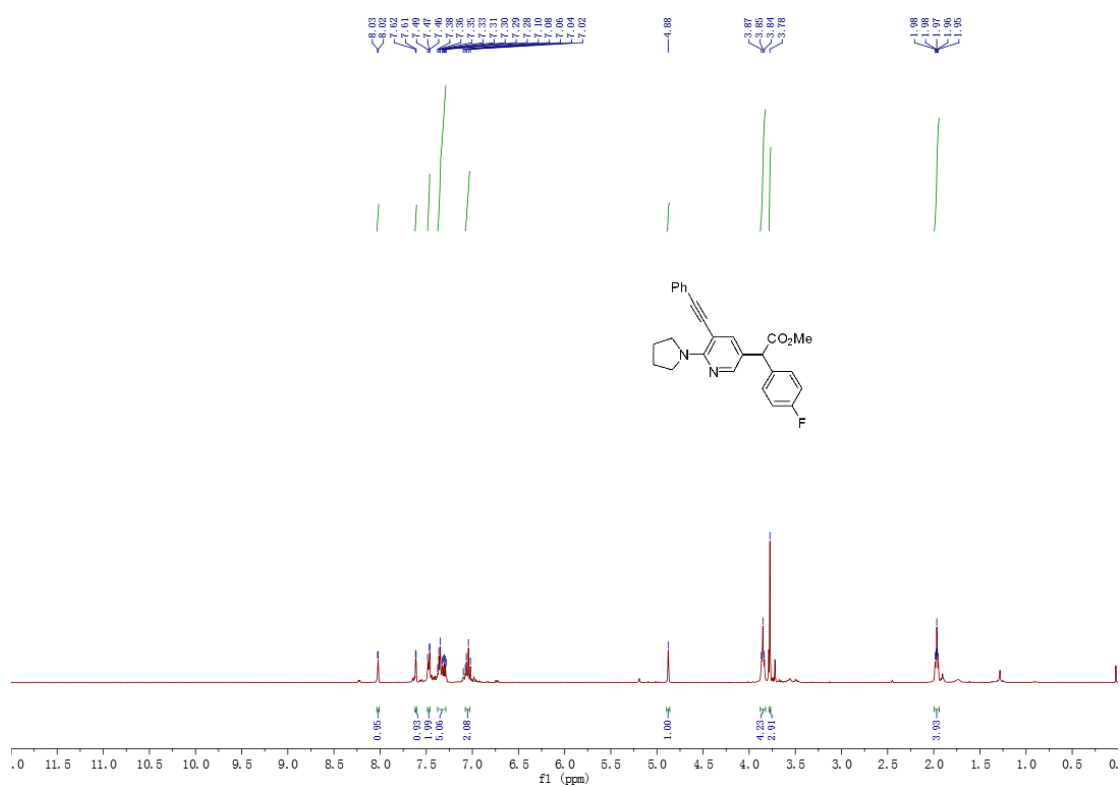
^1H NMR spectrum (400 MHz, CDCl_3) of **3n**



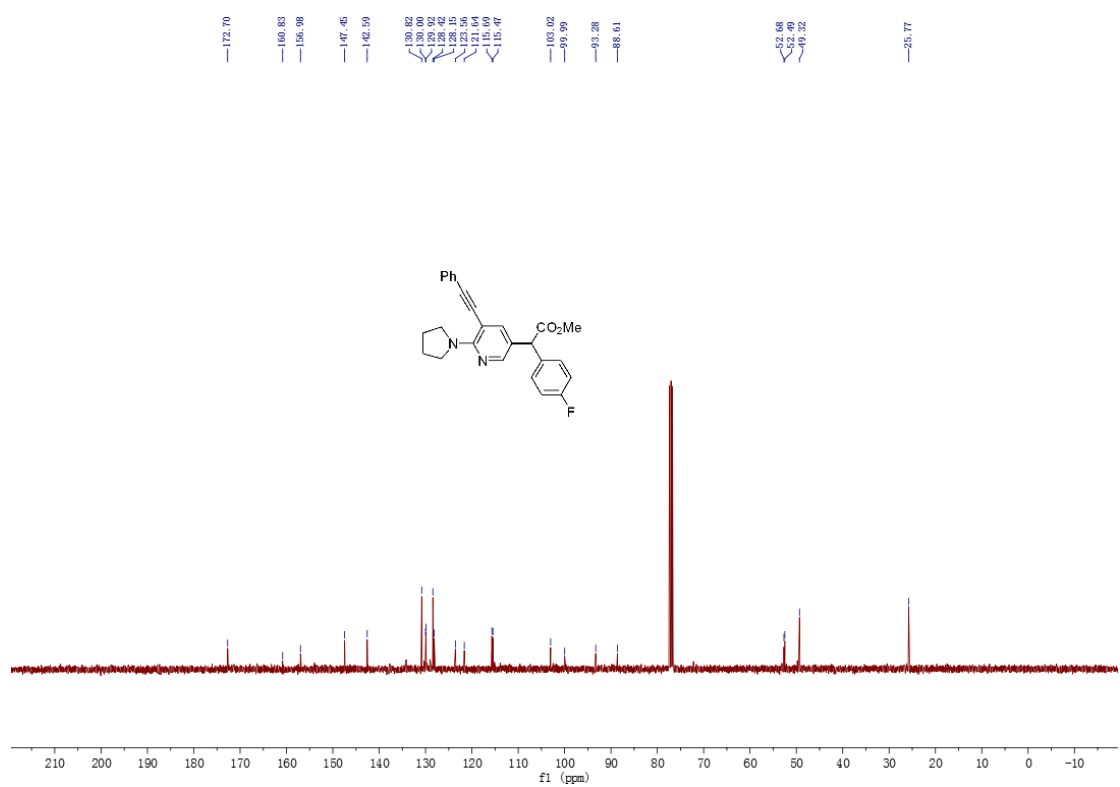
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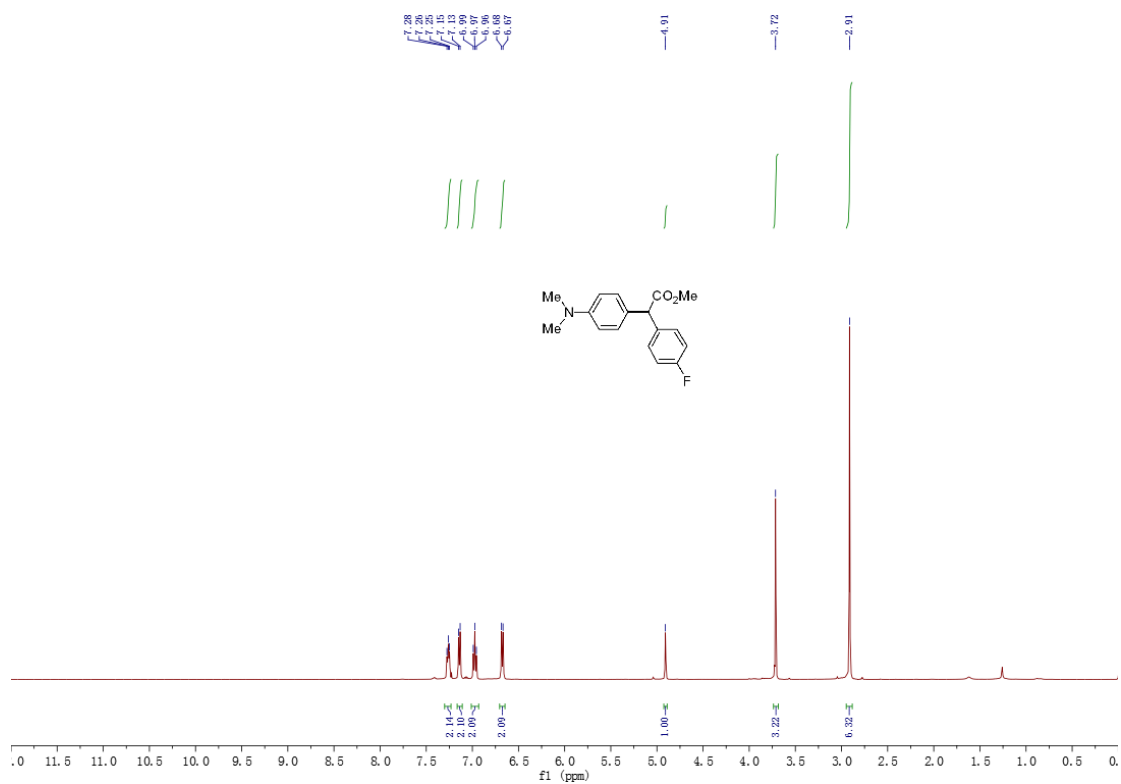
¹H NMR spectrum (401 MHz, CDCl₃) of **3o**



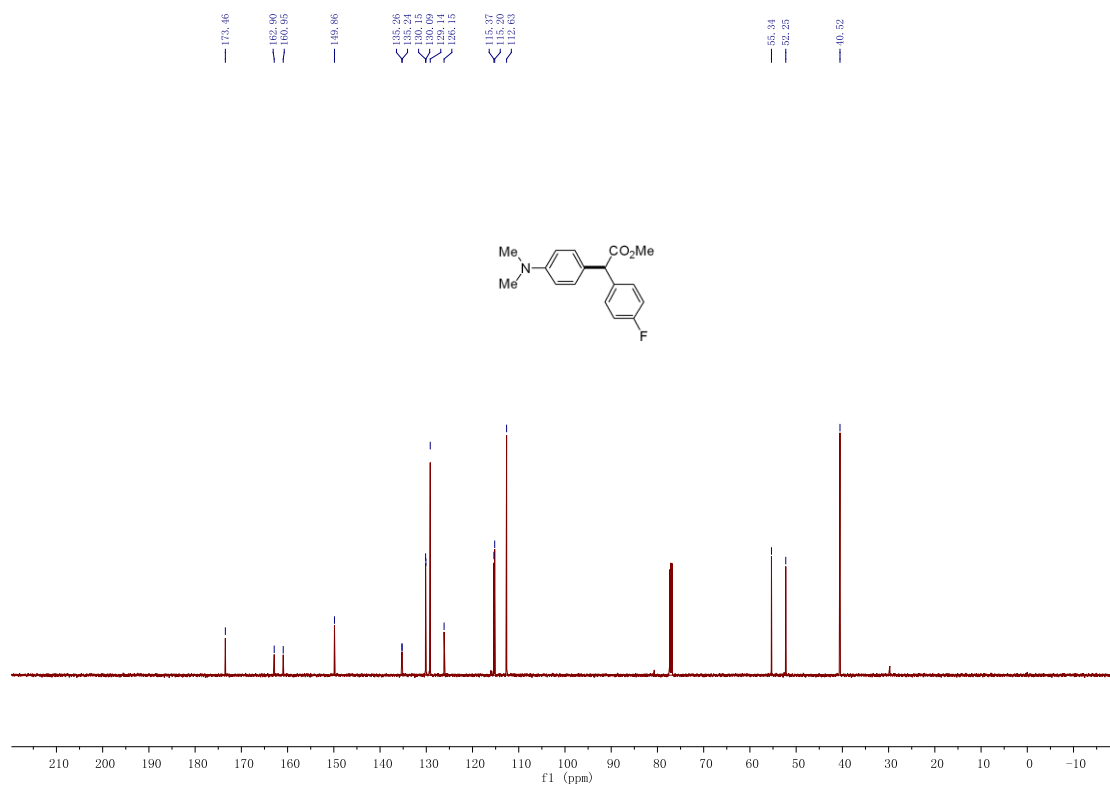
¹³C NMR spectrum (100 MHz, CDCl₃) of **3o**



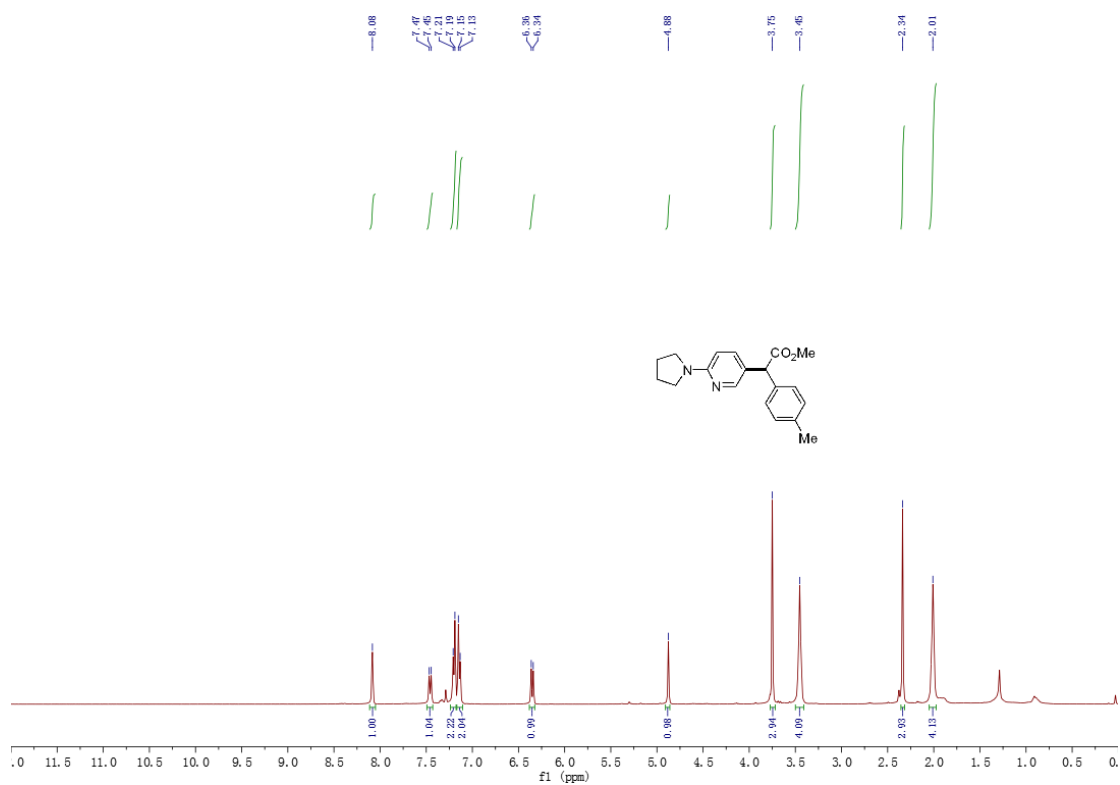
^1H NMR spectrum (500 MHz, CDCl_3) of **3p**



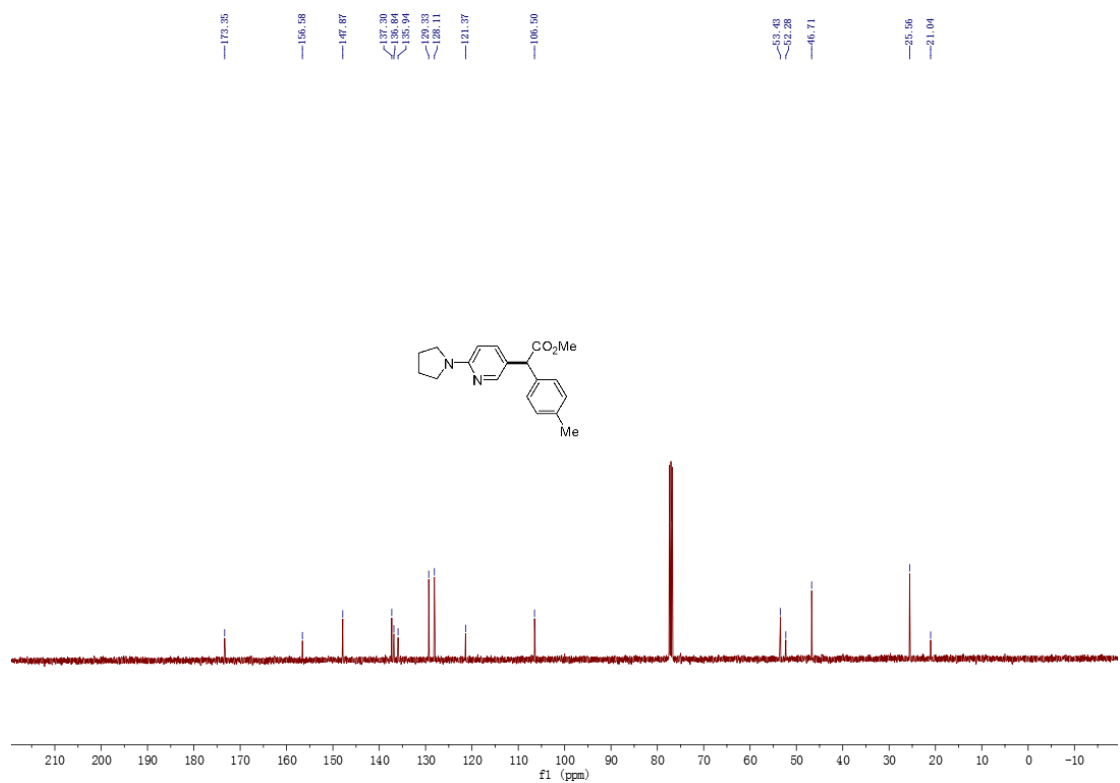
^{13}C NMR spectrum (100 MHz, CDCl_3) of **3p**



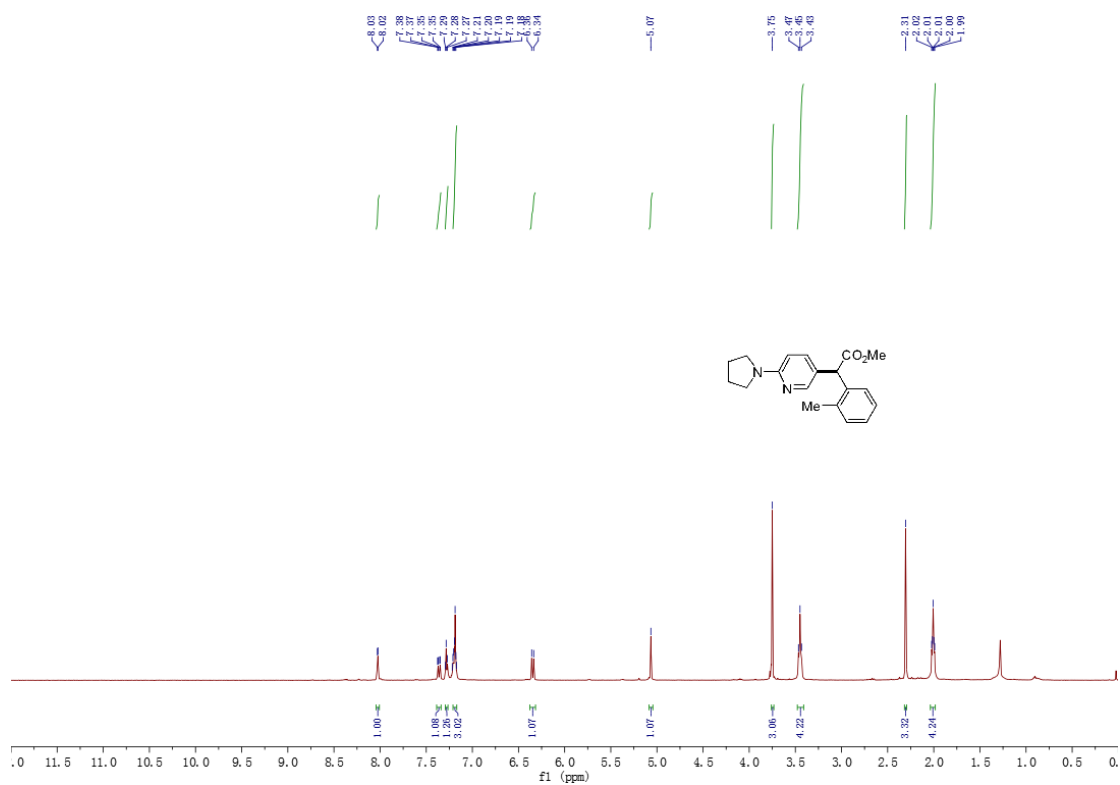
^1H NMR spectrum (400 MHz, CDCl_3) of **4a**



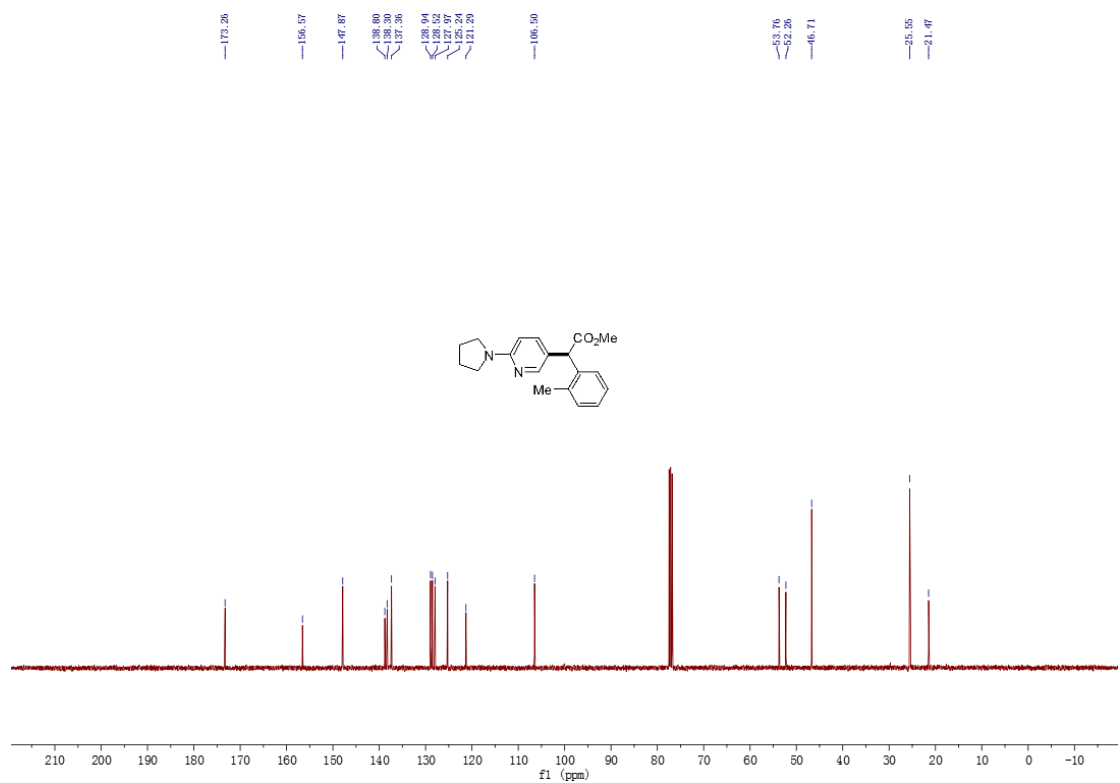
^{13}C NMR spectrum (100 MHz, CDCl_3) of **4a**



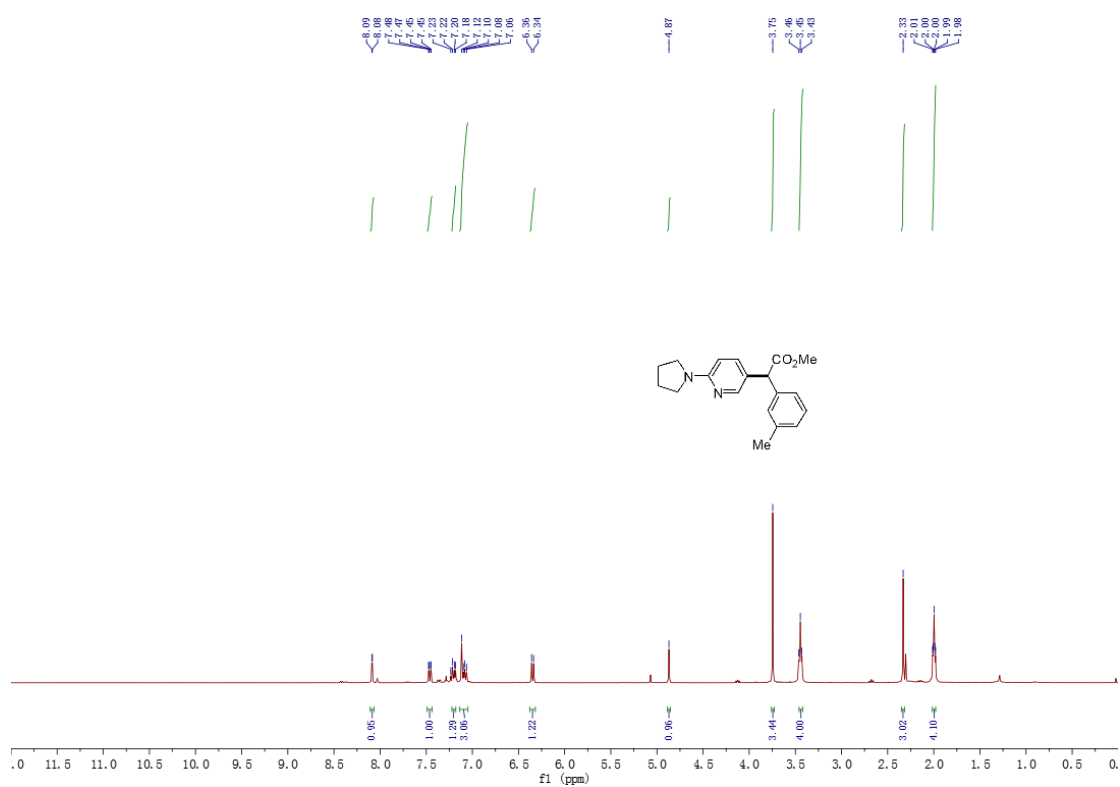
^1H NMR spectrum (400 MHz, CDCl_3) of **4b**



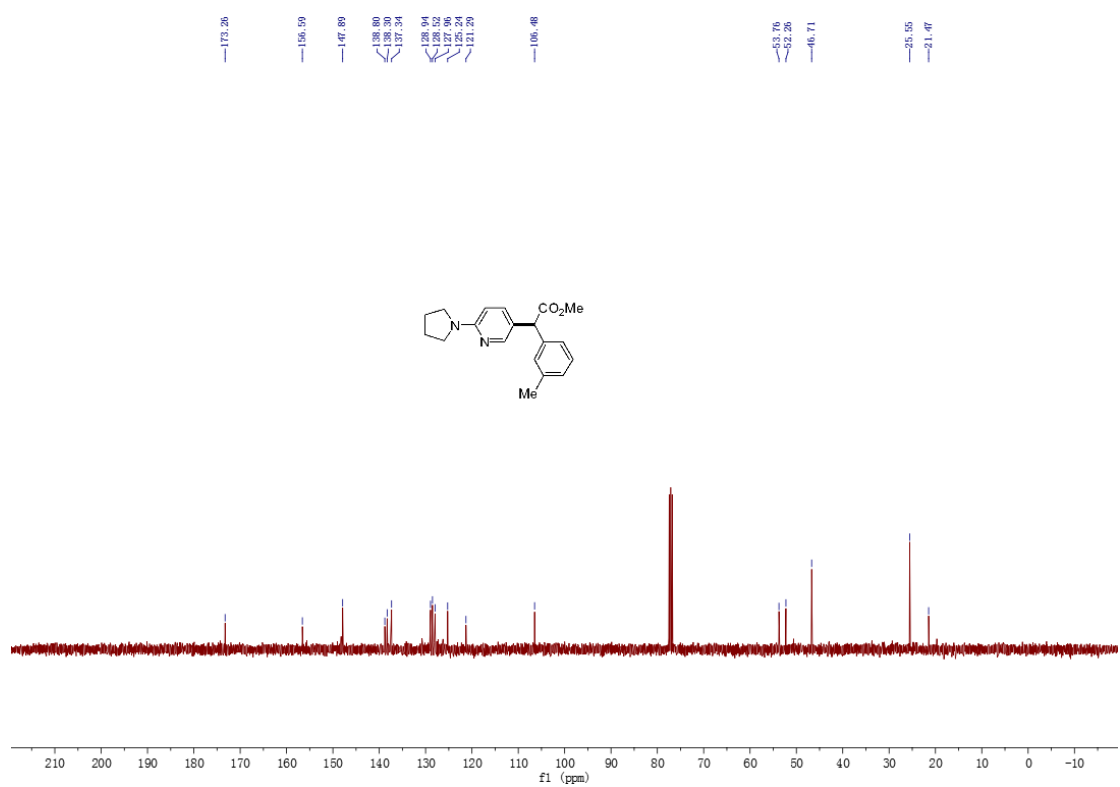
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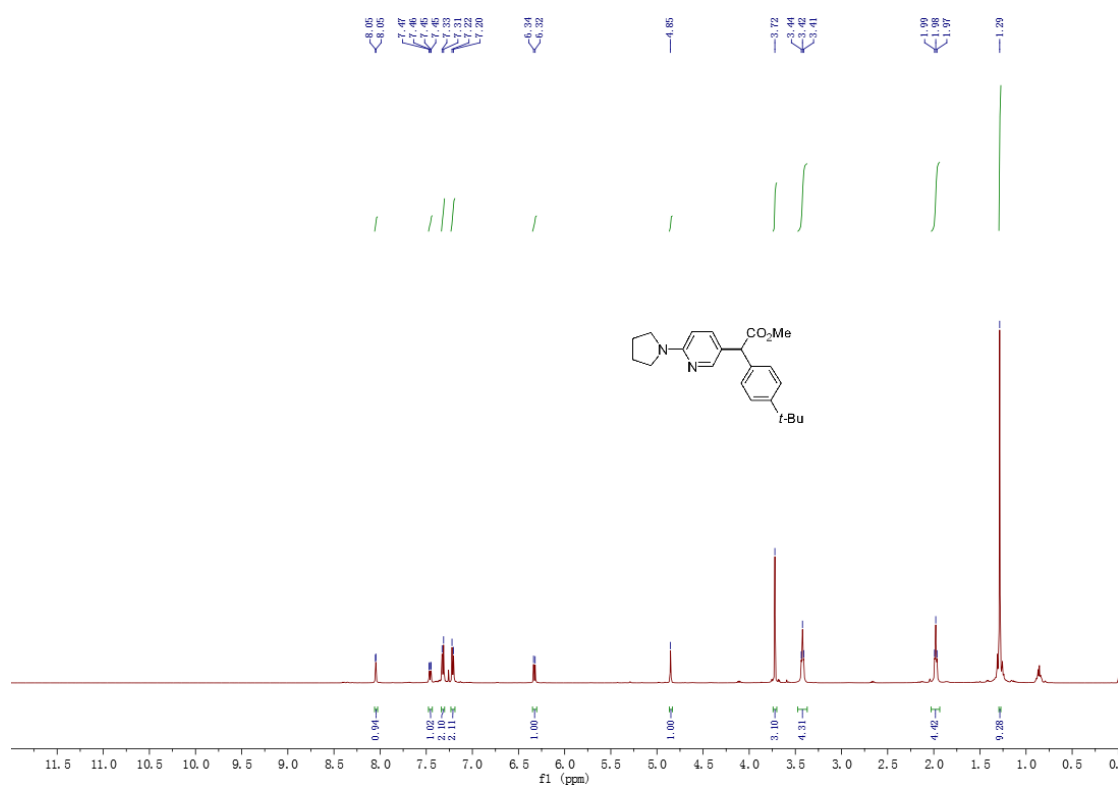
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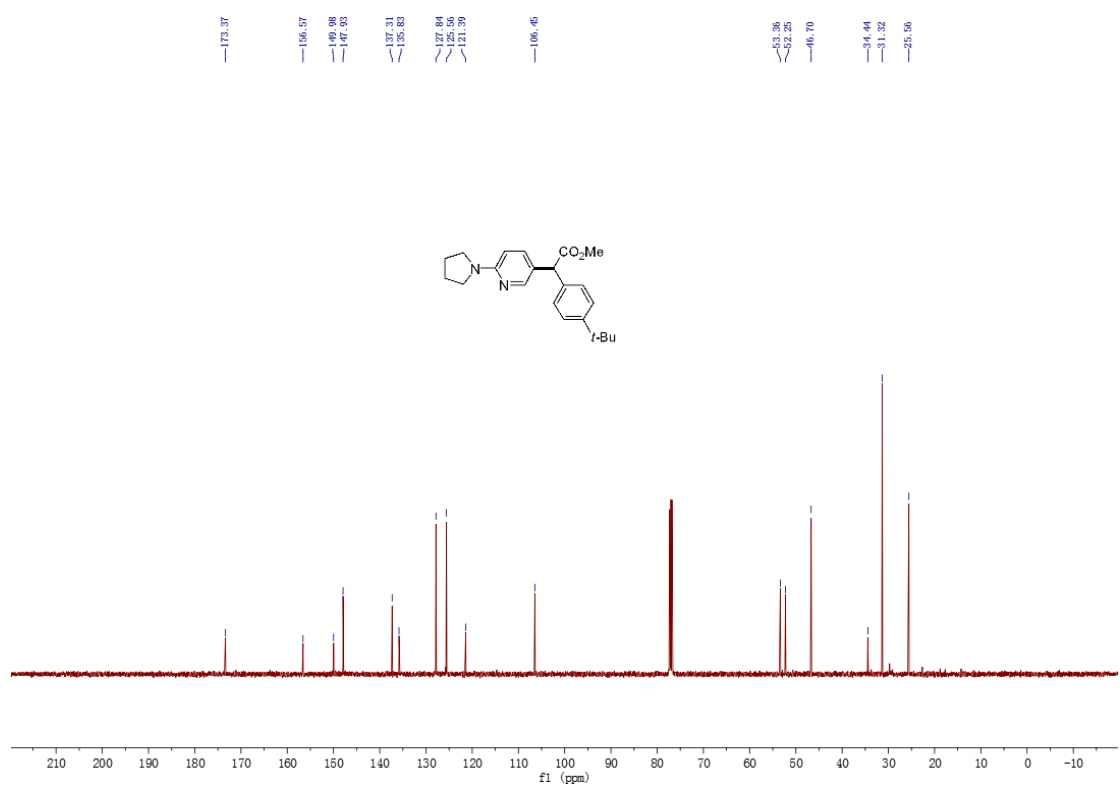
¹³C NMR spectrum (100 MHz, CDCl₃) of **4c**



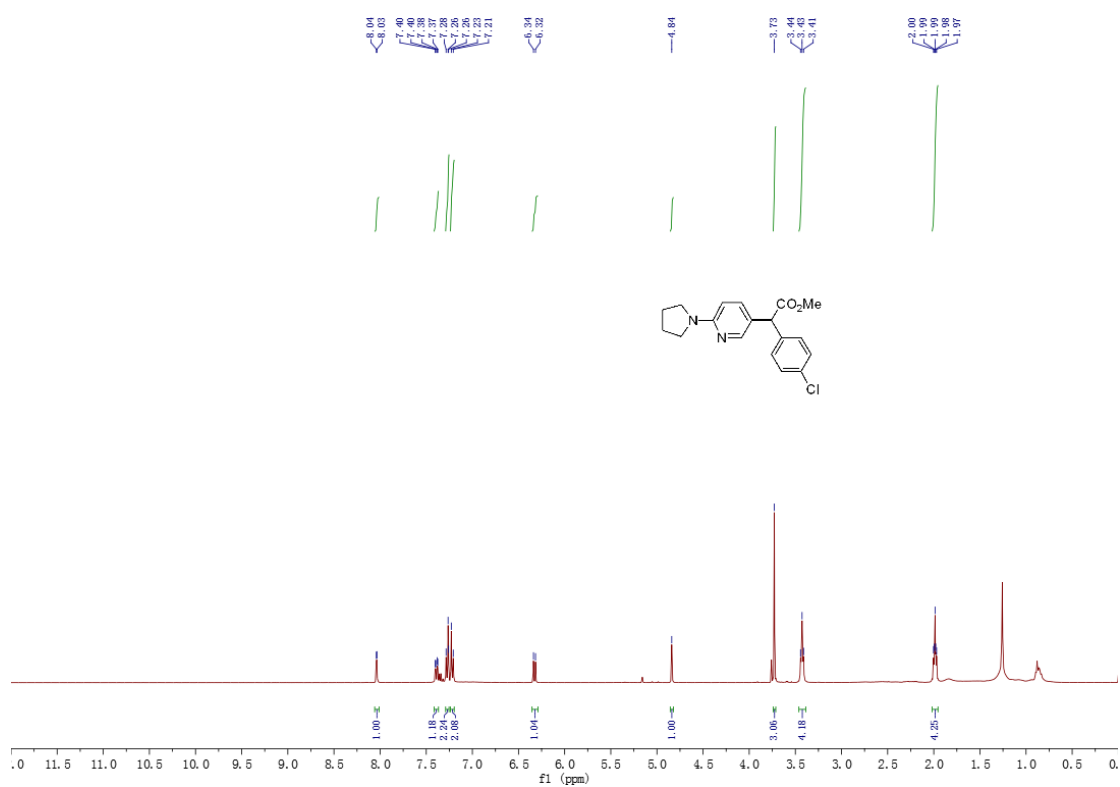
¹H NMR spectrum (400 MHz, CDCl₃) of **4d**



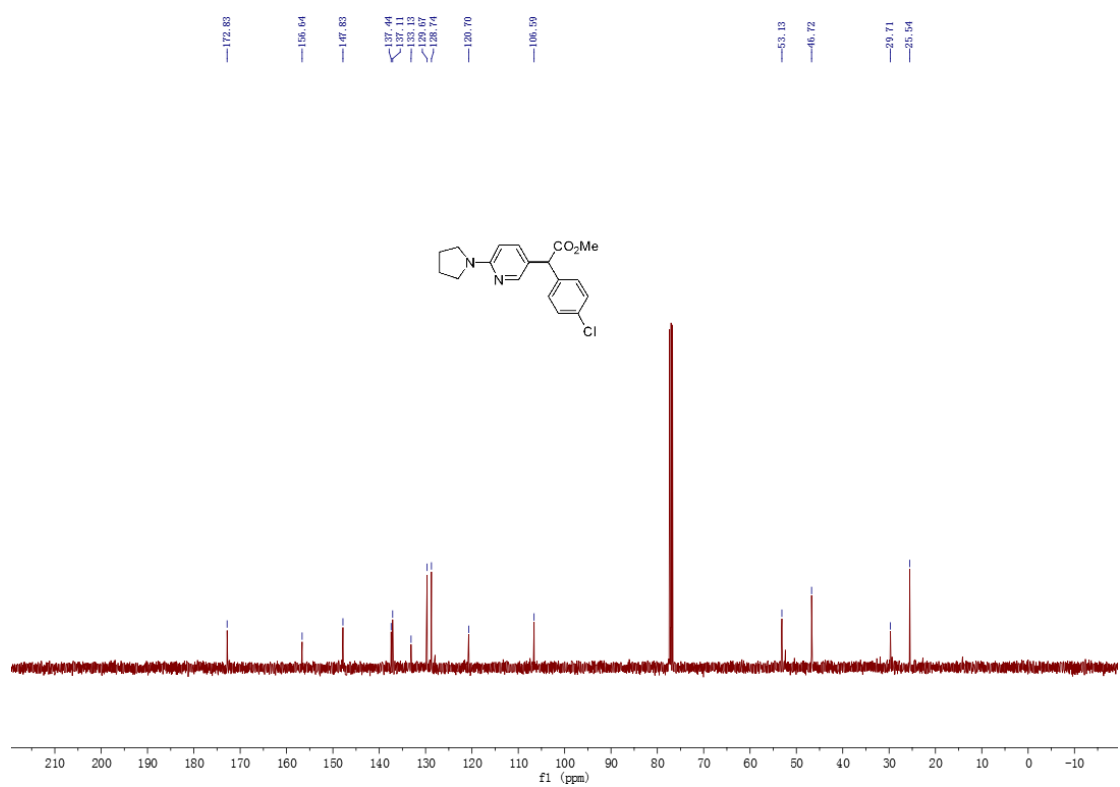
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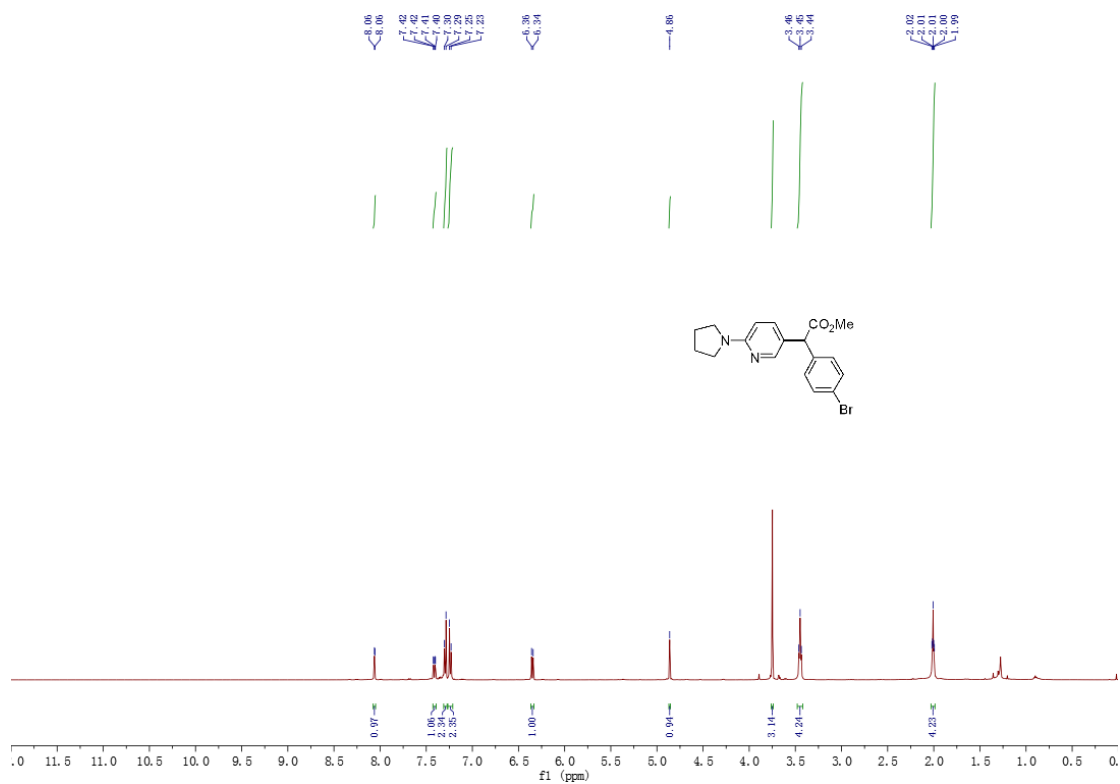
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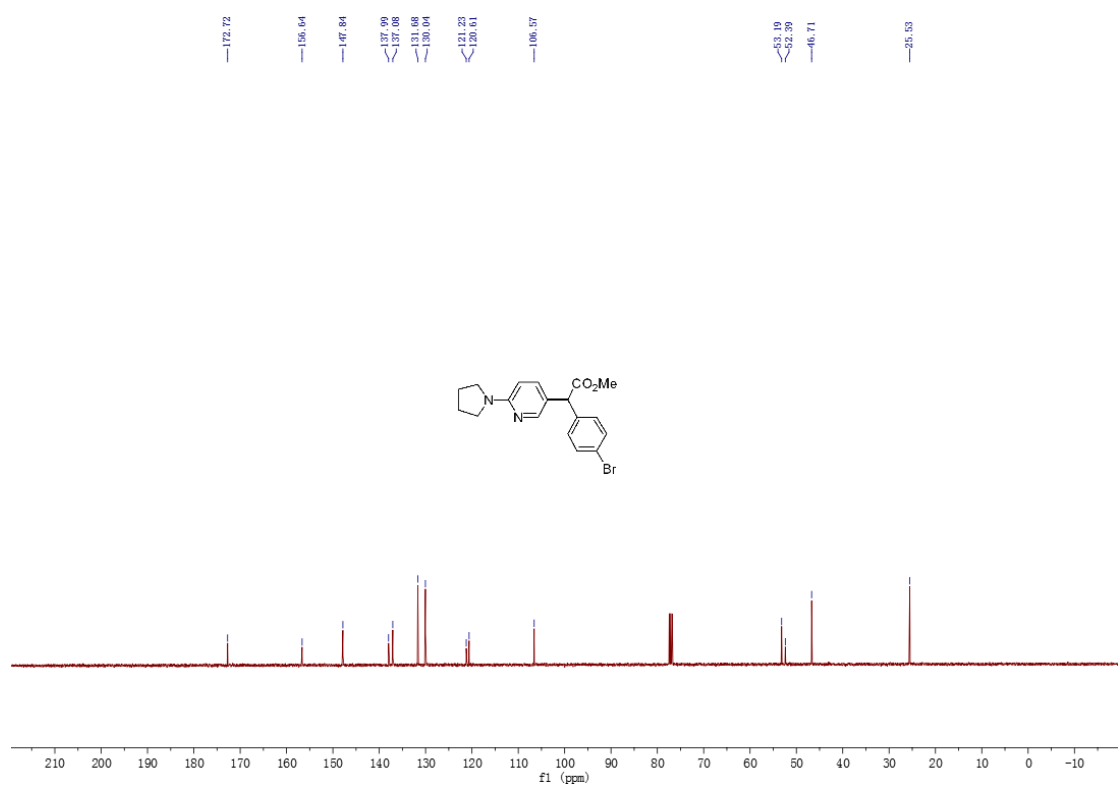
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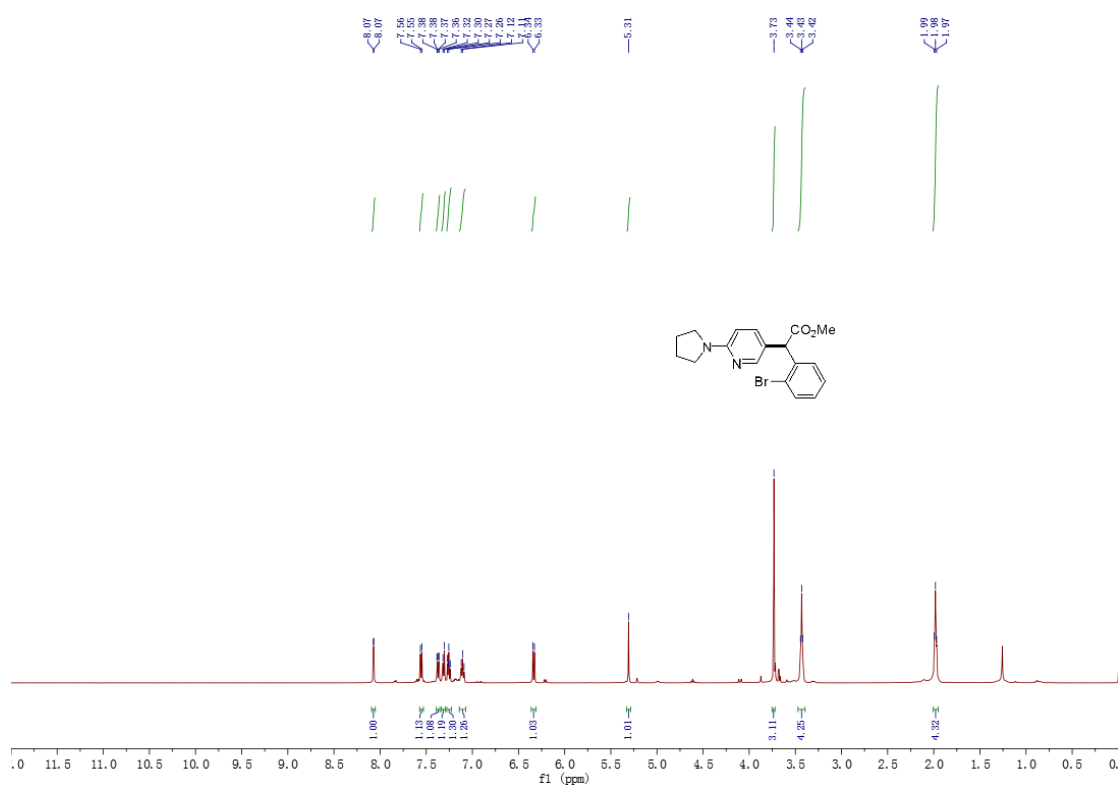
^1H NMR spectrum (400 MHz, CDCl_3) of **4f**



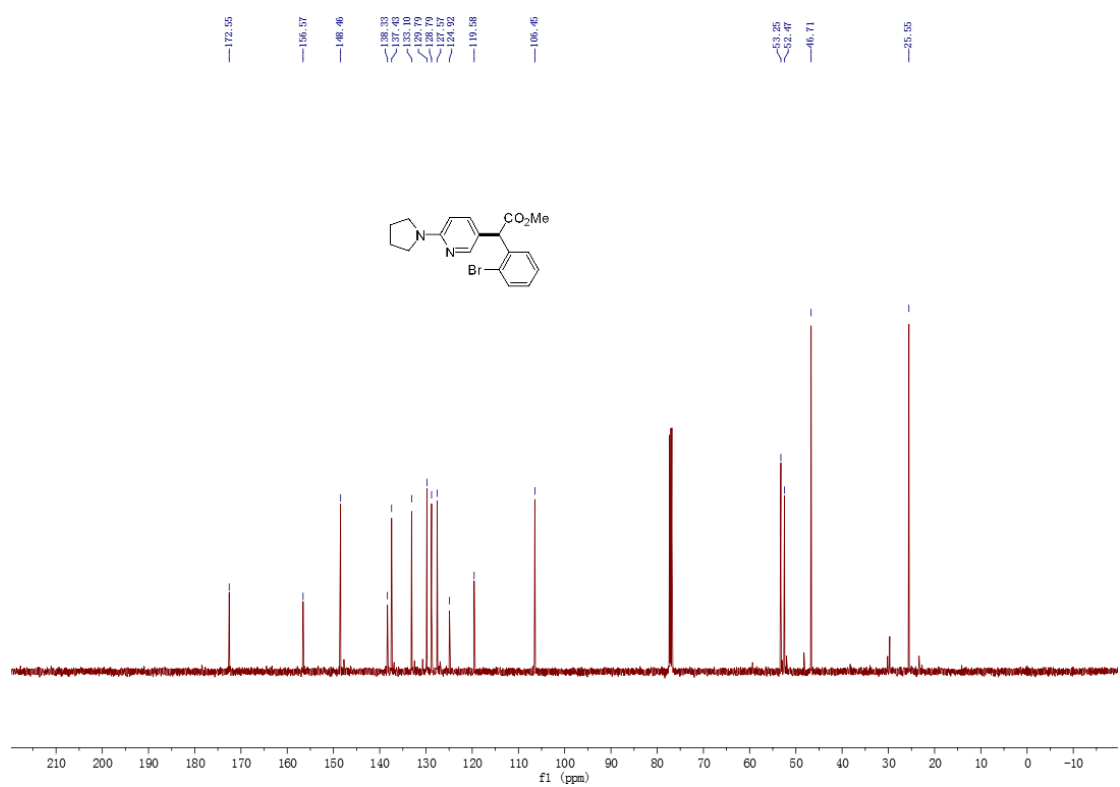
^{13}C NMR spectrum (100 MHz, CDCl_3) of **4f**



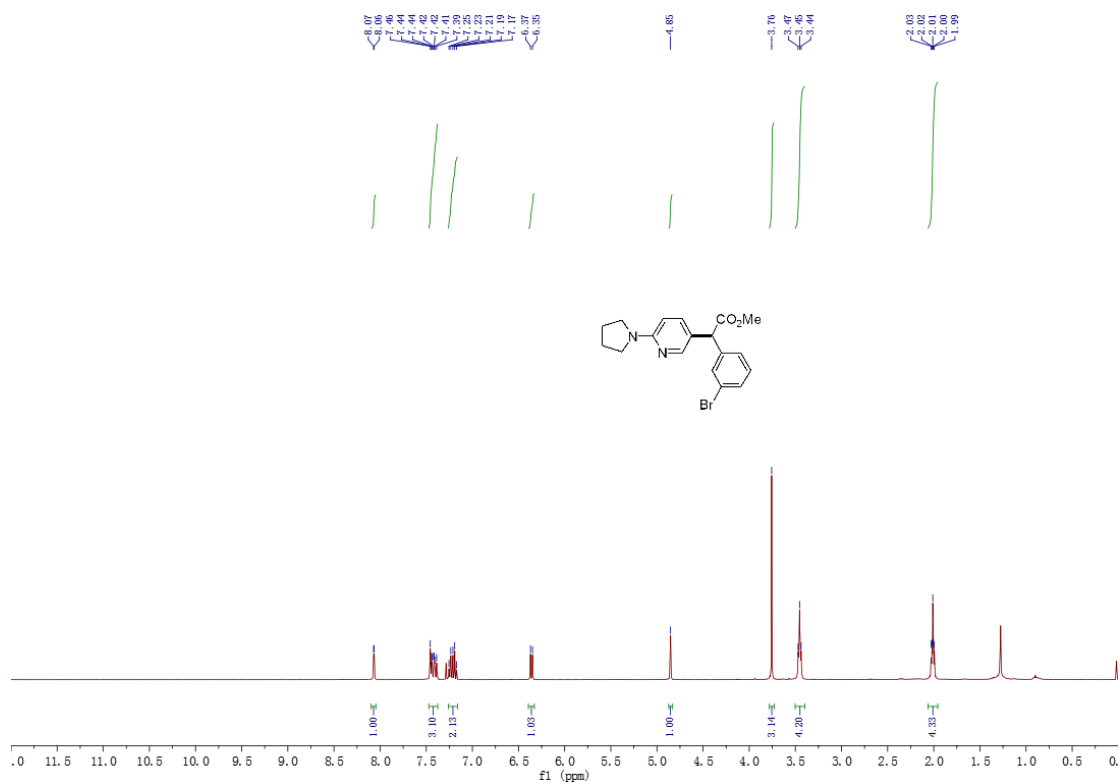
¹H NMR spectrum (400 MHz, CDCl₃) of **4g**



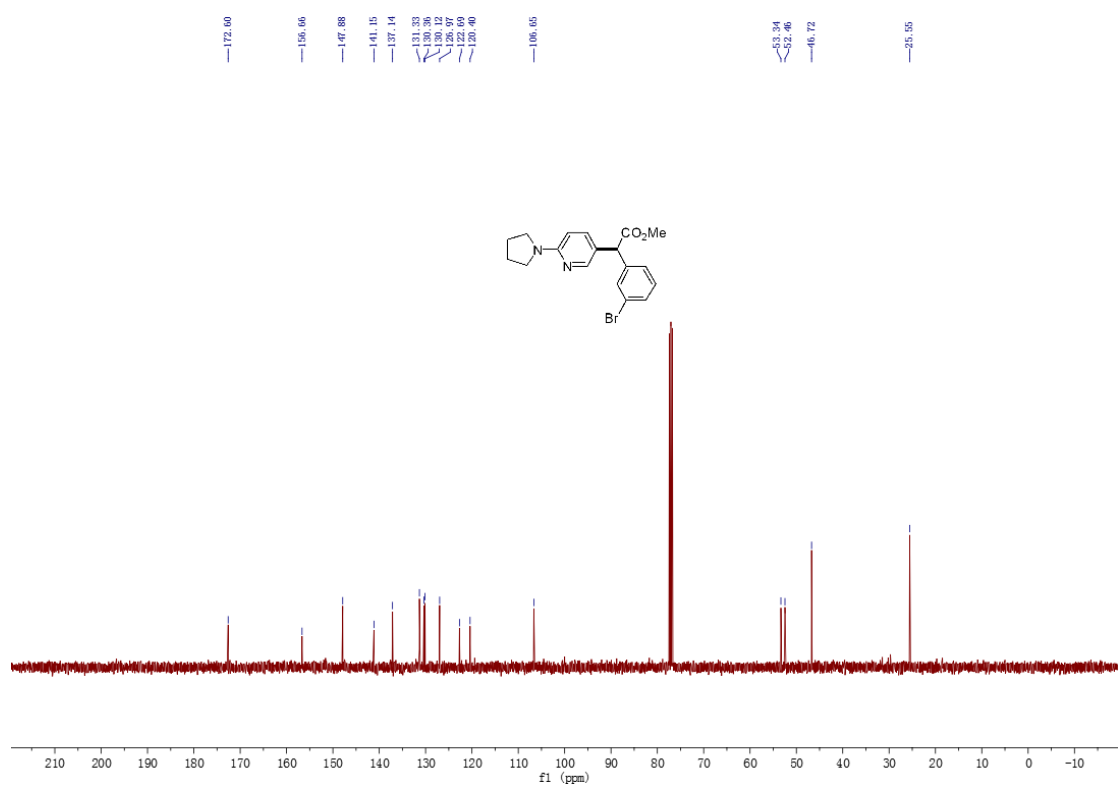
¹³C NMR spectrum (100 MHz, CDCl₃) of **4g**



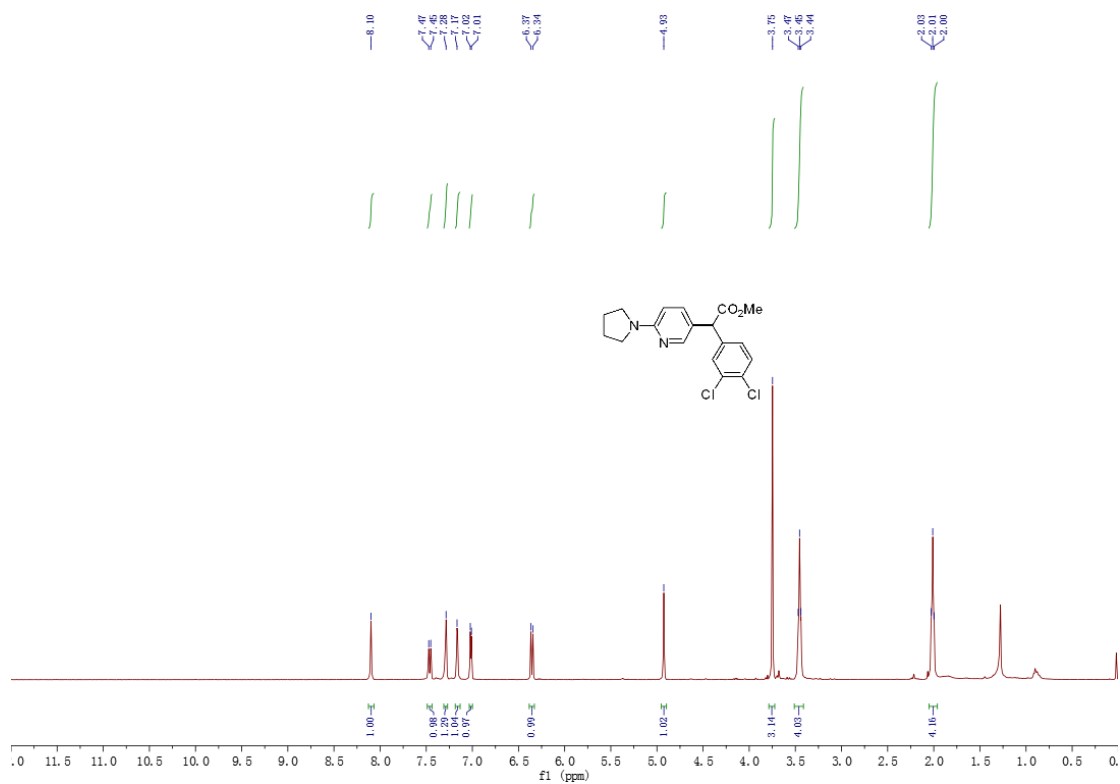
^1H NMR spectrum (400 MHz, CDCl_3) of **4h**



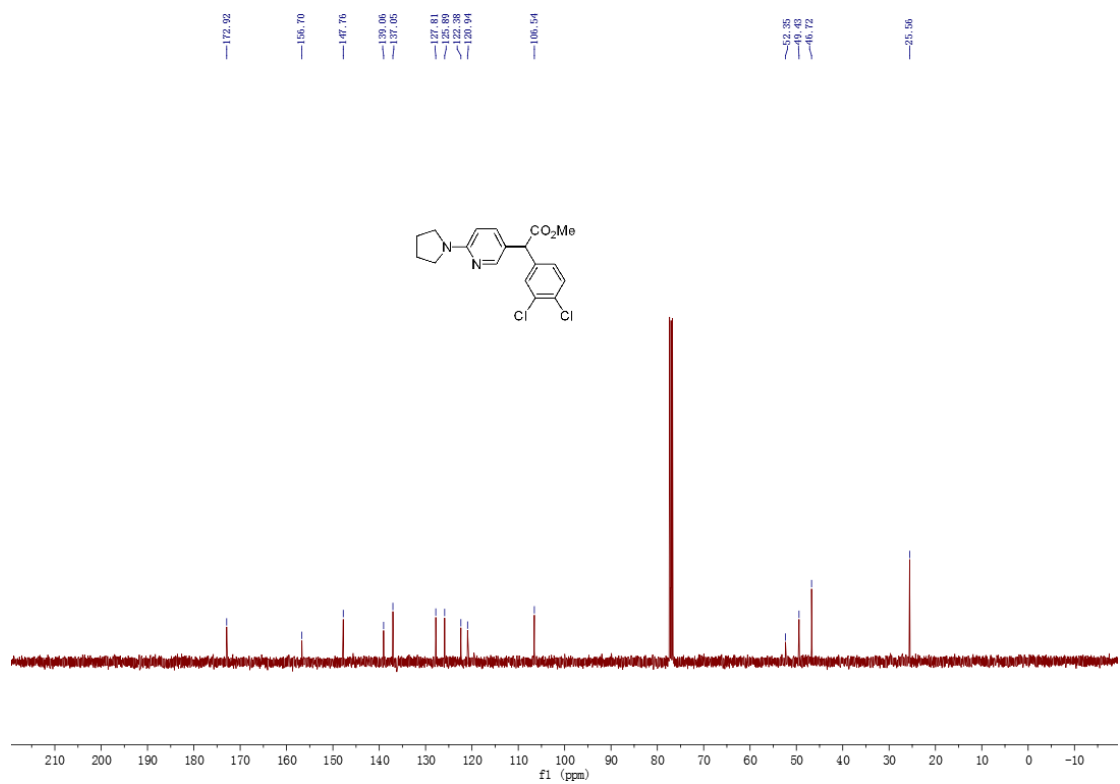
^{13}C NMR spectrum (100 MHz, CDCl_3) of **4h**



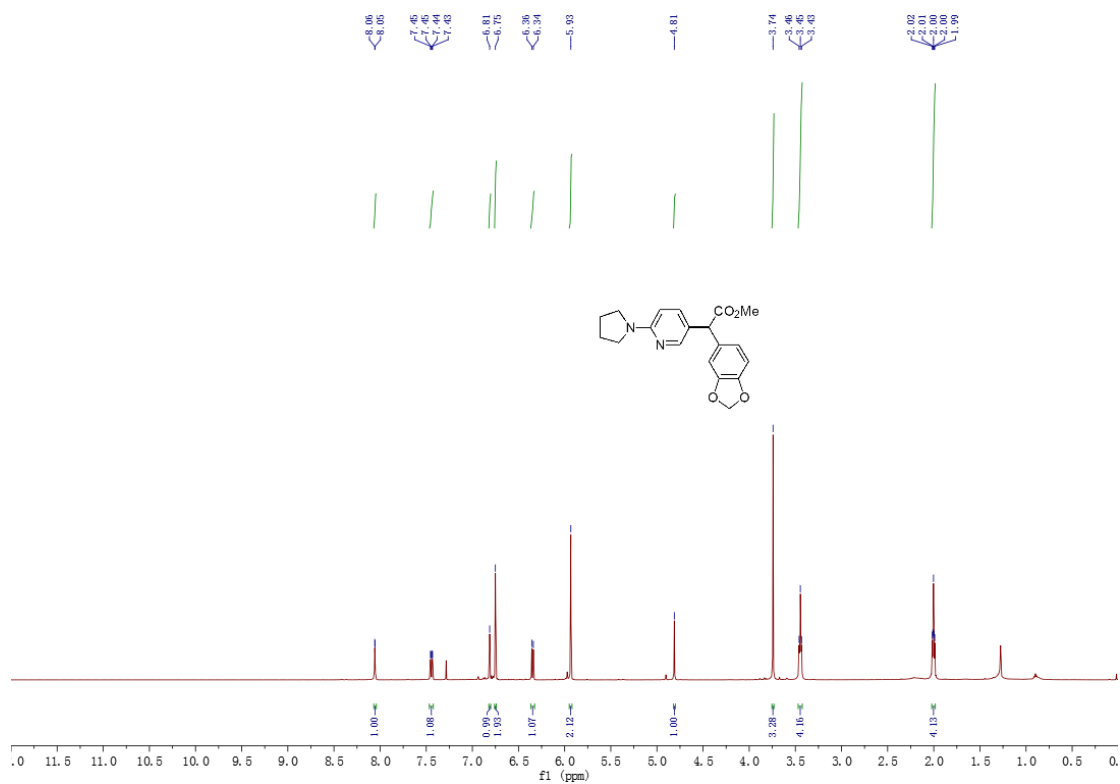
^1H NMR spectrum (400 MHz, CDCl_3) of **4i**



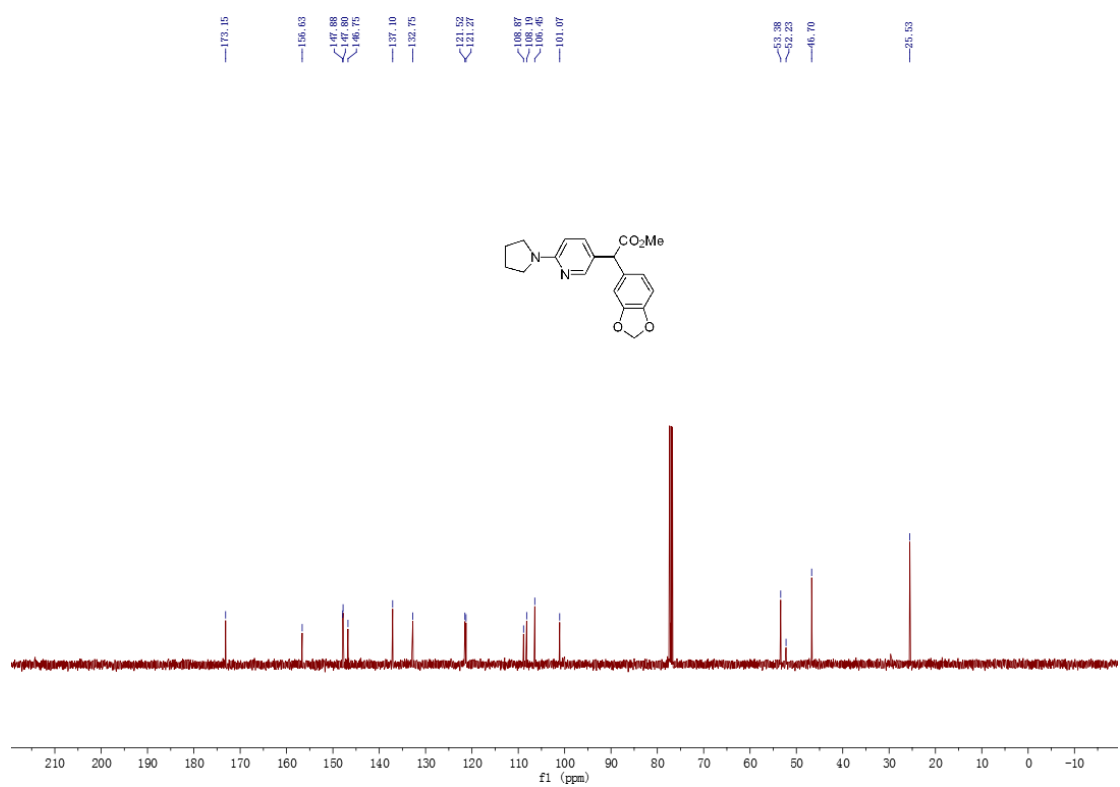
^{13}C NMR spectrum (100 MHz, CDCl_3) of **4i**



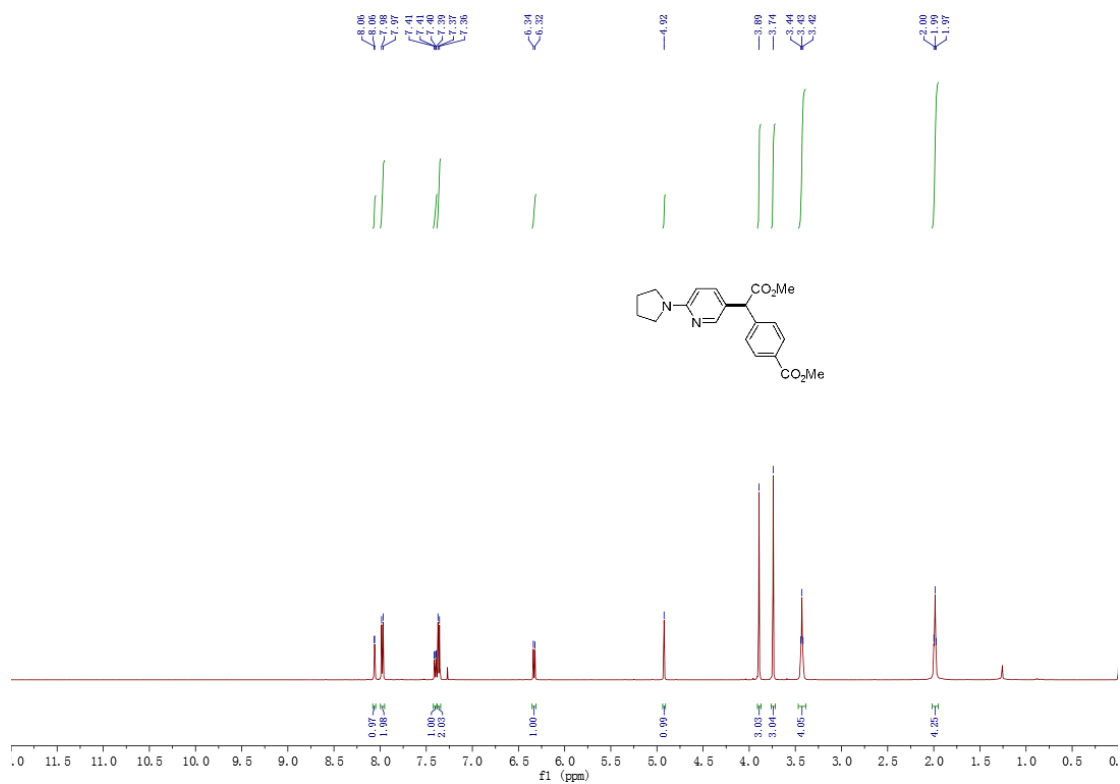
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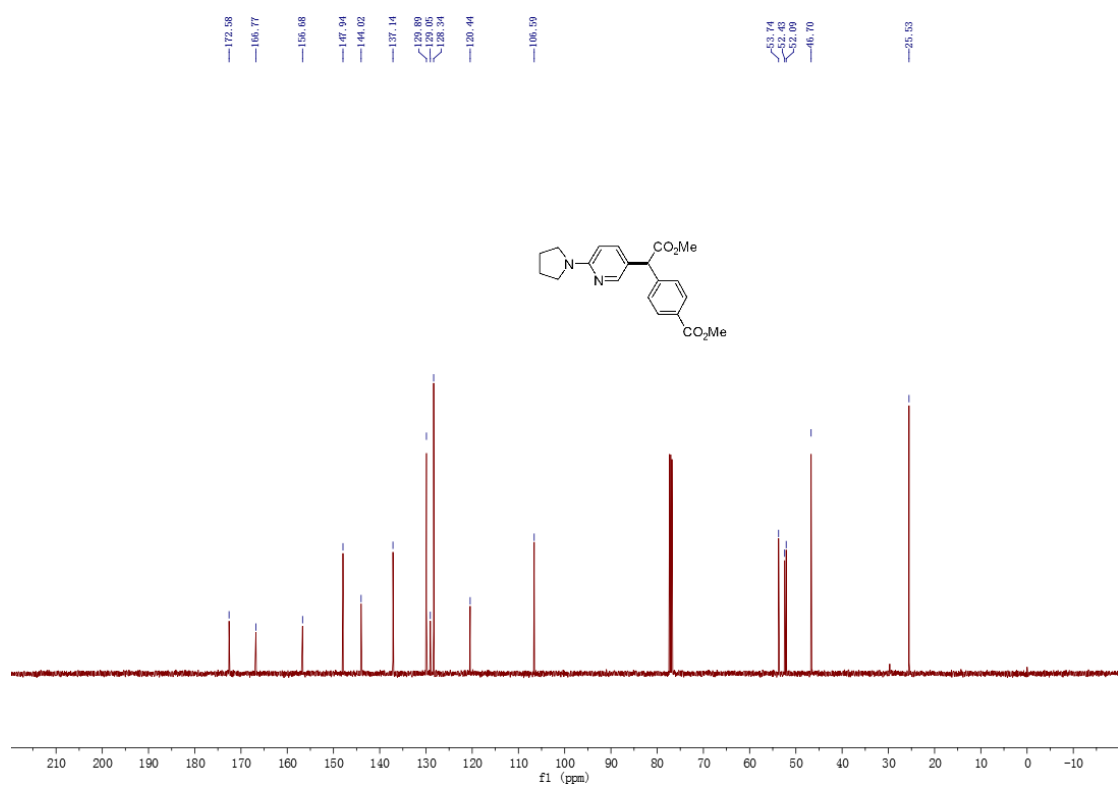
^{13}C NMR spectrum (100 MHz, CDCl_3) of **4j**



^1H NMR spectrum (400 MHz, CDCl_3) of **4k**

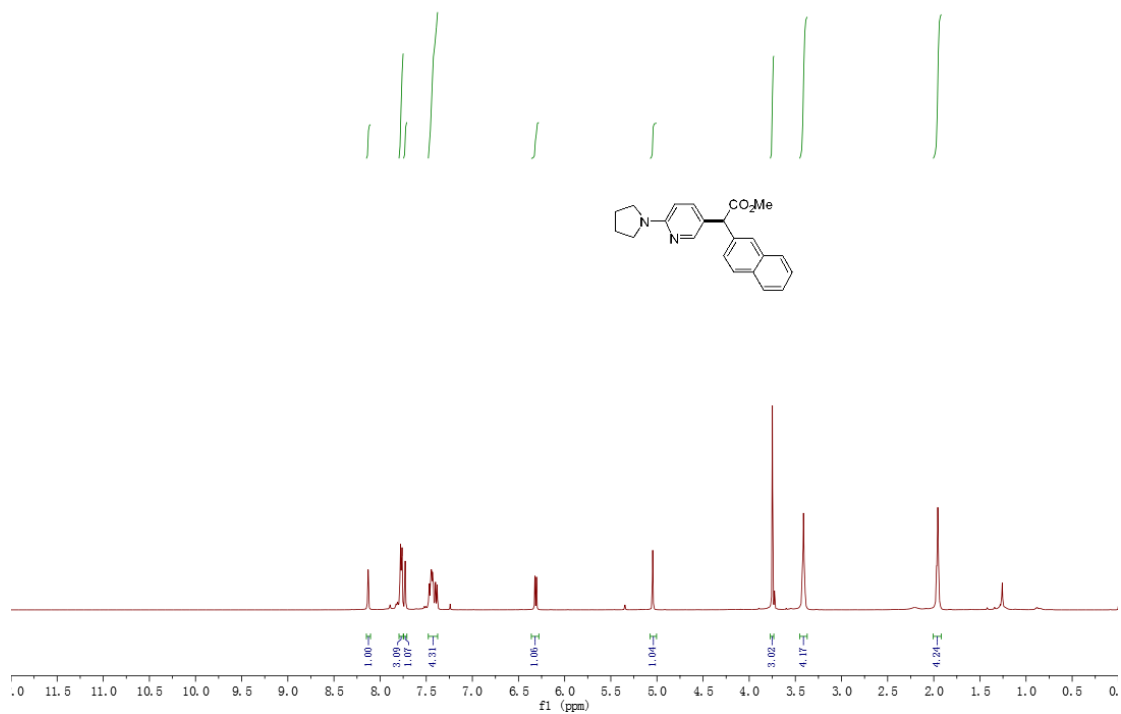


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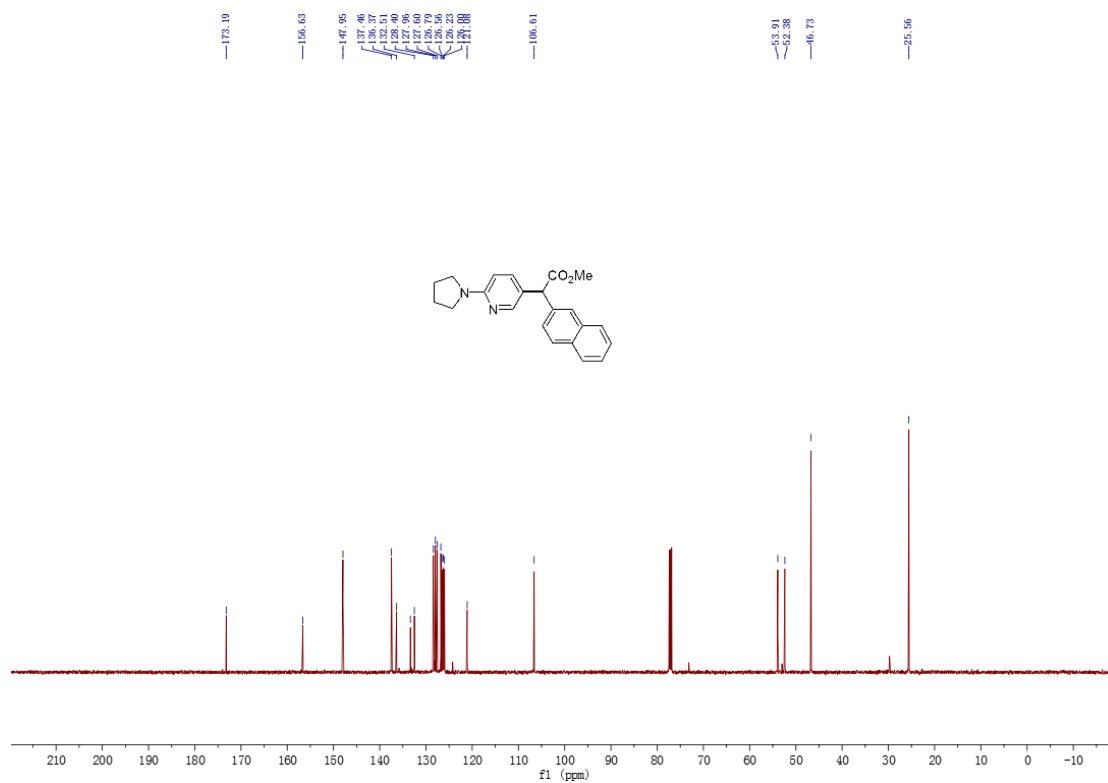


^1H NMR spectrum (400 MHz, CDCl_3) of **41**

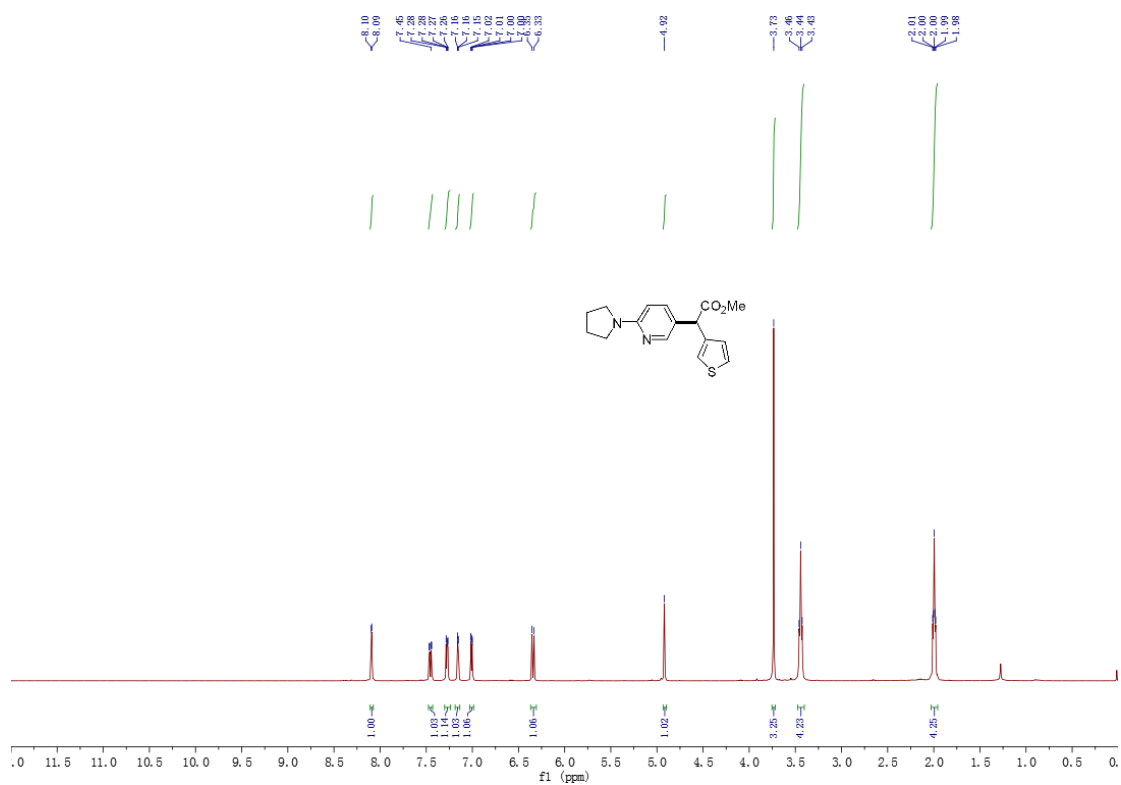
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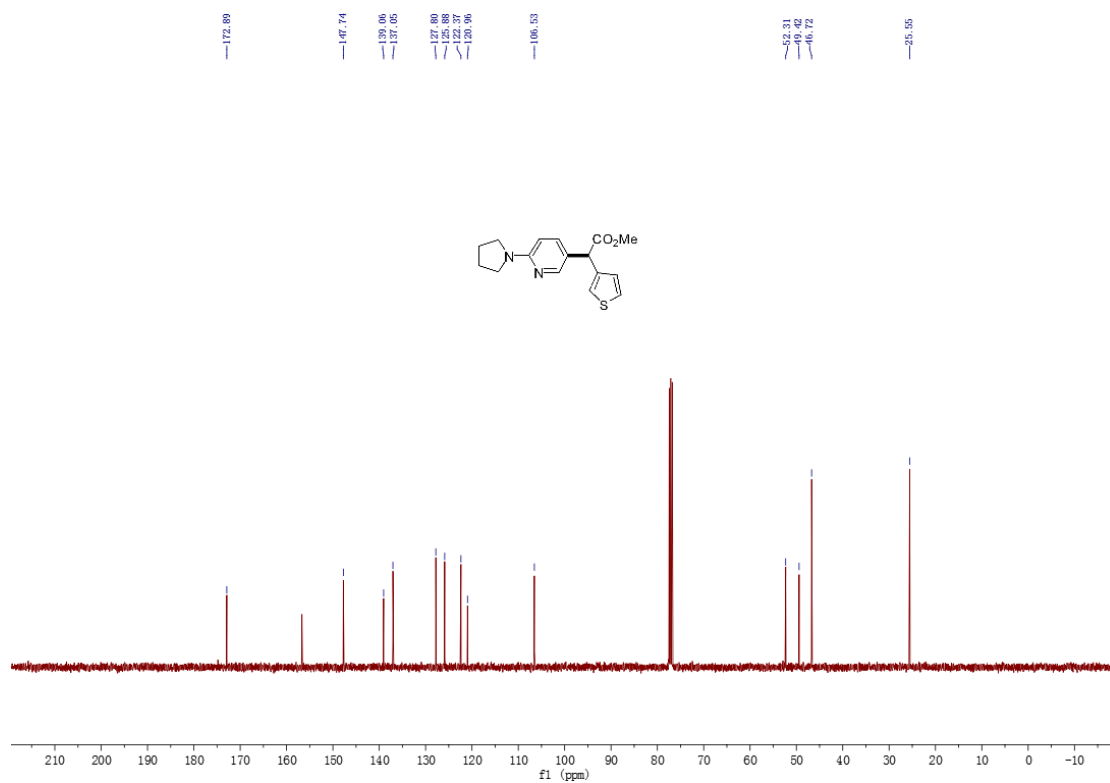
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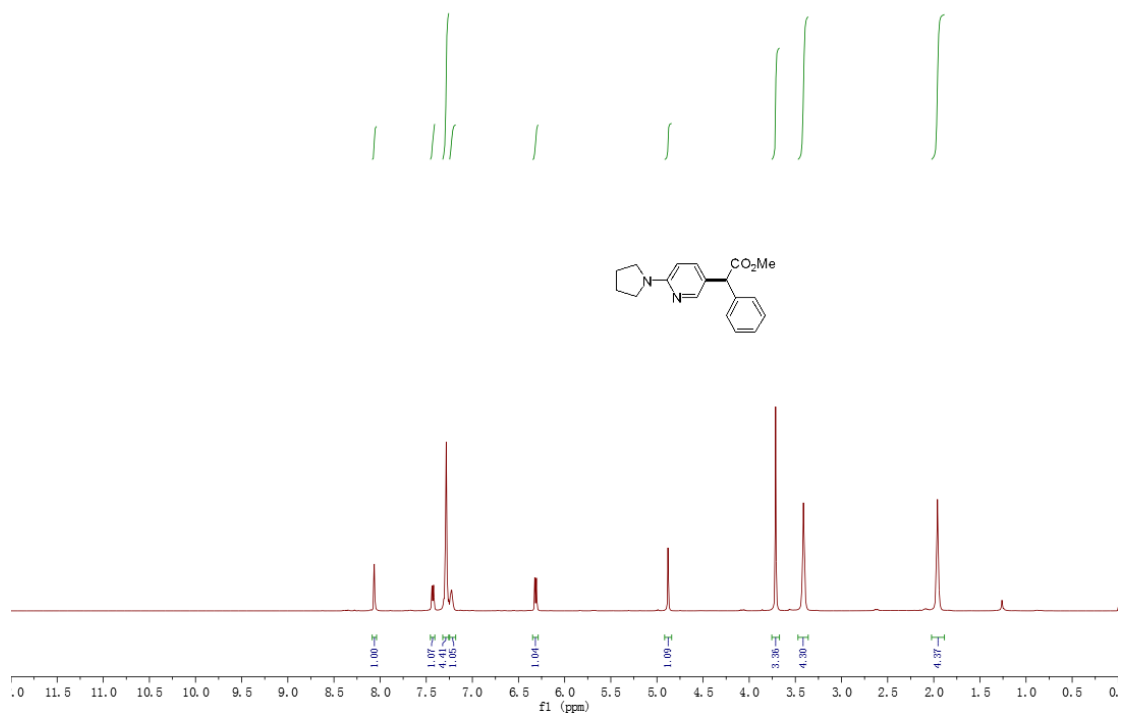
^1H NMR spectrum (400 MHz, CDCl_3) of **4m**



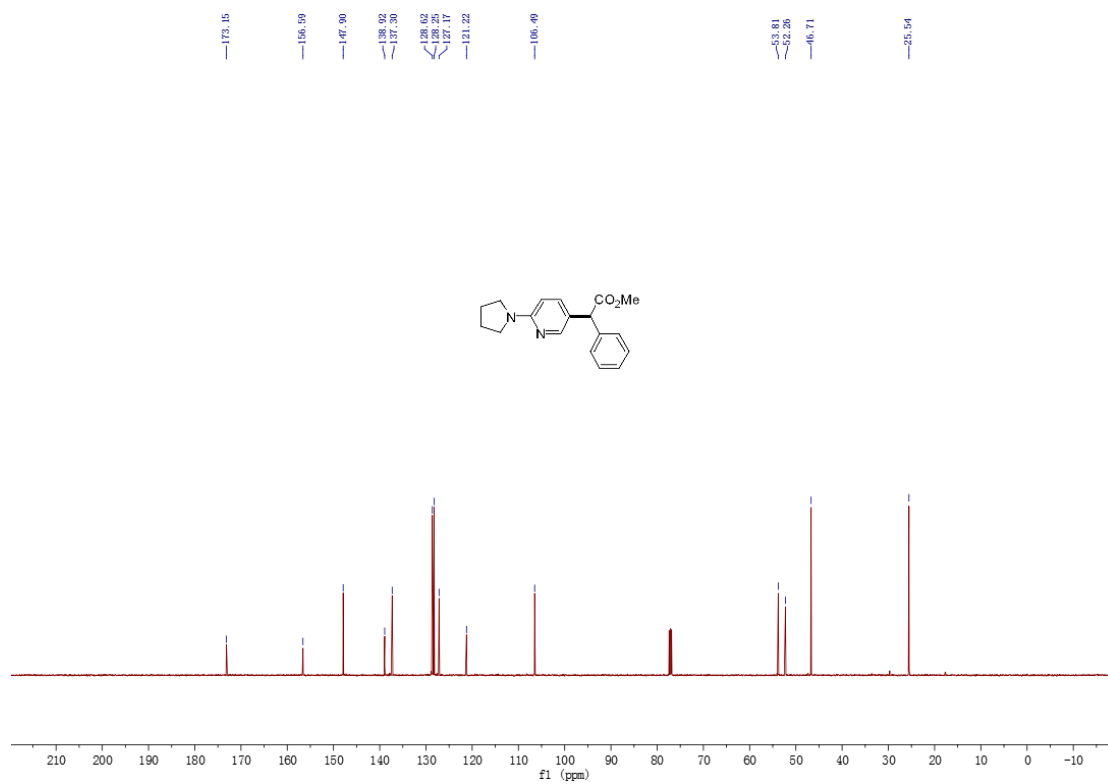
^{13}C NMR spectrum (100 MHz, CDCl_3) of **4m**



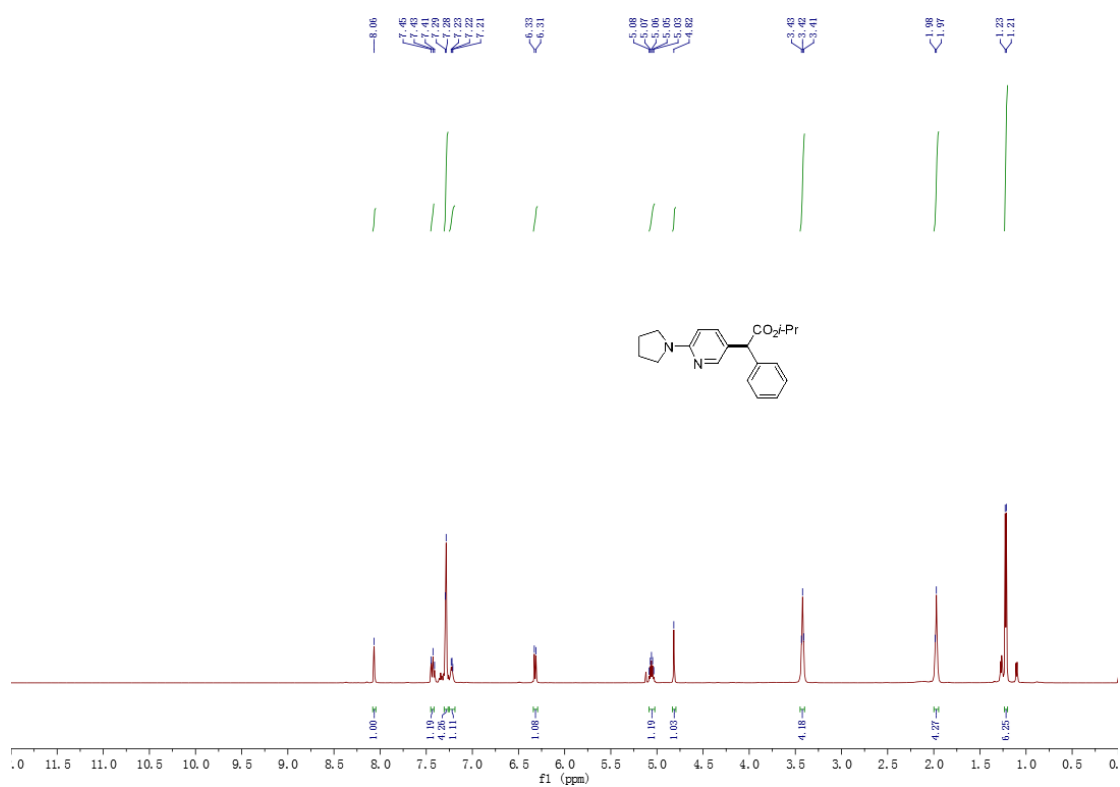
^1H NMR spectrum (400 MHz, CDCl_3) of **4n**



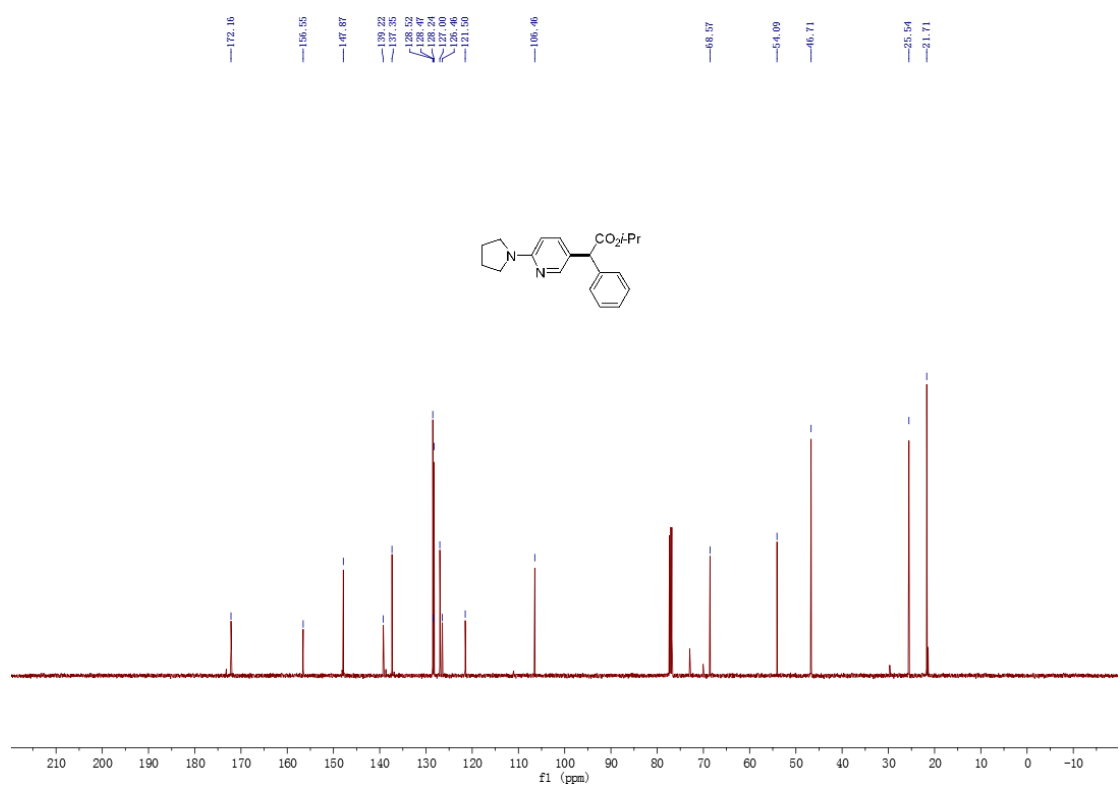
^{13}C NMR spectrum (100 MHz, CDCl_3) of **4n**



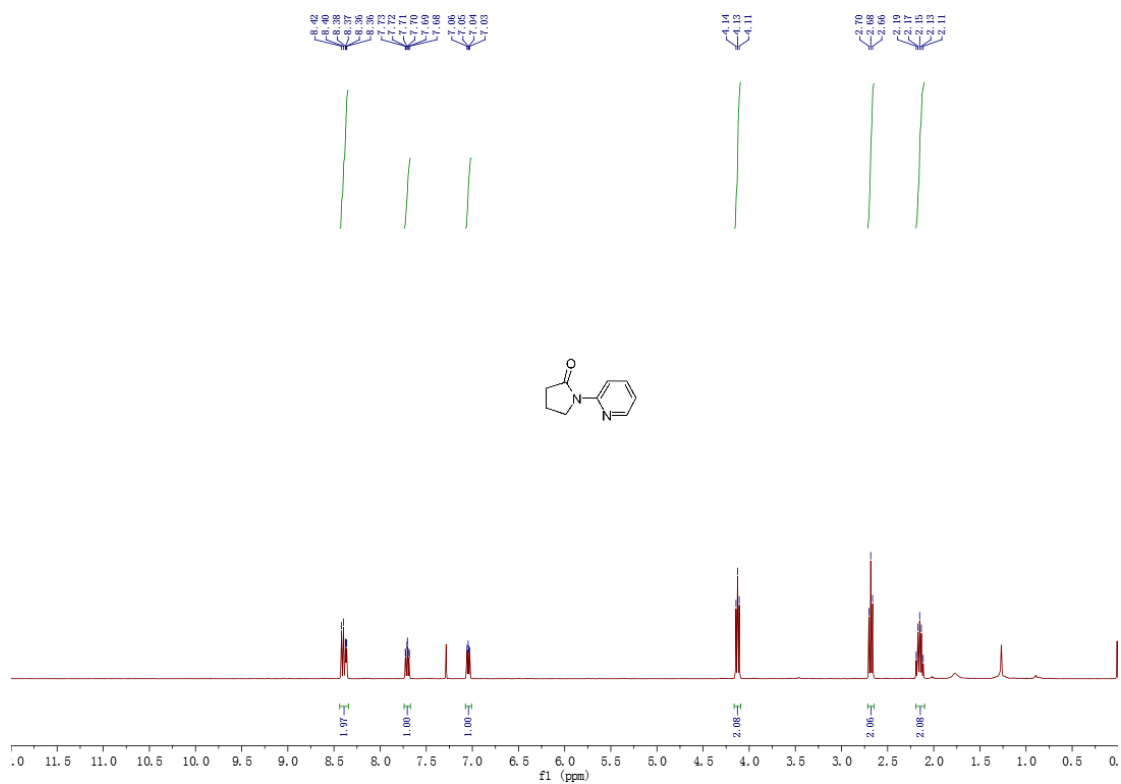
^1H NMR spectrum (400 MHz, CDCl_3) of **4o**



^{13}C NMR spectrum (100 MHz, CDCl_3) of **4o**



^1H NMR spectrum (400 MHz, CDCl_3) of **4r'**



^{13}C NMR spectrum (100 MHz, CDCl_3) of **4r'**

