Supporting information:

Photoinduced Direct Hydration of Dipyridylacetylenes in Acidic Aqueous Solution

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Table of Contents

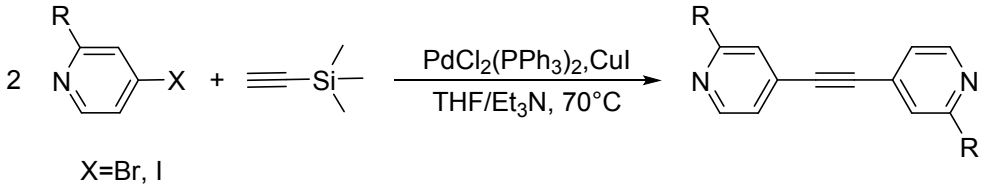
Ⅰ. General information

All the pyridyl halides and solvents were commercially available and used without further purification. Internal alkynes were synthesized according to the literature. [1] ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Ascend Ⅲ400 (400 MHz) spectrometer. High resolution mass spectra were recorded using Agilent G6500 Series Q-TOF instrument. Flash column chromatography was performed on silica gel (200~300 mesh). Melting points were determined using Guoming RY-2 apparatus and the thermometer was uncorrected. The photochemical reaction was conducted with a 250W high-pressure mercury lamp equipped with a water-cooled double-layer glass chiller.

1. A. Elangovan, S.-W. Yang, J.-H. Lin, K.-M. Kao and T.-I. Ho, *Organic & Biomolecular Chemistry*, 2004, **2**, 1597-1602.

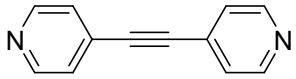
Ⅱ. Synthesis of internal alkynes **1a - 1o**.

Synthesis of symmetrical internal alkynes **1a - 1i**:



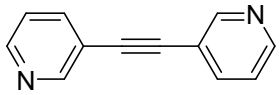
To an oven-dried 100 mL round-bottom flask were added $Pd(PPh_3)_2Cl_2$ (140.38 mg, 2.5 mol %), CuI (76.18 mg, 5 mol %), and either 4-iodo or 4-bromopyridine with different substituents (8 mmol, 1.0 equiv), and the flask was purged with nitrogen. THF-Et_3N (4:1 v/v, 60 mL) was added to dissolve these reactants. Trimethylsilylethyne (392.88 mg, 0.5 equiv) was then added by syringe. The mixture was stirred at 70 °C for 4 hours. After the reaction mixture was cooled to room temperature, 10 ml of 1 M TBAF solution in THF was added and stirred at room temperature for 2 hours. The reaction mixture was then partitioned in 100 ml of ethyl acetate (EA) and 100 ml of distilled water. The organic layer was washed with distilled water three times and then dried over $MgSO_4$. The crude product was purified by silica gel column chromatography (EA/petroleum ether).

1,2-Di(pyridin-4-yl)acetylene (**1a**).



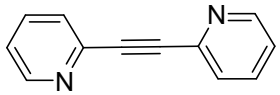
Yellow solid, 0.60 g, 83%, MP: 198 - 200 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.67 (d, J = 5.6 Hz, 4H), 7.42 (d, J = 5.9 Hz, 4H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 148.79, 129.22, 124.58, 89.62 ppm.

1,2-Di(pyridin-3-yl)acetylene (**1b**).



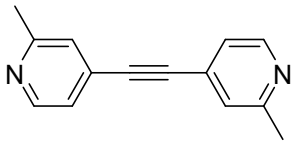
Brown solid, 0.36 g, 35%, MP: 57 - 58 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.80 (s, 2H), 8.60 (d, J = 4.9 Hz, 2H), 7.85 (dt, J = 7.9, 1.9 Hz, 2H), 7.33 (dd, J = 7.8, 5.0 Hz, 2H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 152.17, 148.97, 138.67, 123.17, 119.81, 89.19 ppm.

1,2-Di(pyridin-2-yl)acetylene (**1c**)



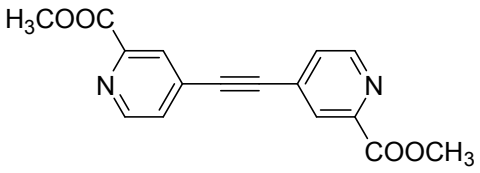
Brown solid, 0.60 g, 42%, MP: 48 - 50 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.65 (d, J = 4.2 Hz, 2H), 7.71 (t, J = 7.7 Hz, 2H), 7.63 (d, J = 7.8 Hz, 2H), 7.29 (t, J = 6.1 Hz, 2H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 1150.11, 142.63, 136.29, 127.79, 123.37, 87.88 ppm.

1,2-Bis(2-methylpyridin-4-yl)acetylene (**1d**).



Brown solid, 0.44 g, 54%, MP:112 - 114 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.53 (d, J = 5.1 Hz, 2H), 7.29 (s, 2H), 7.21 (d, J = 5.1 Hz, 2H), 2.59 (s, 6H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 158.82, 149.30, 129.57, 125.55, 123.08, 80.30, 24.35 ppm. HRMS(ESI): m/z calcd for $C_{14}H_{12}N_2$ $[M+H]^+$ 209.1058, found 209.1073.

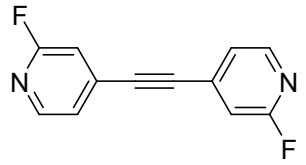
1,2-Bis(2-methoxycarbonylpyridin-4-yl)acetylene (**1e**).



Grayish white solid, 0.39 g, 33%, MP: 160 - 162 °C. ^{1}H NMR (400 MHz,

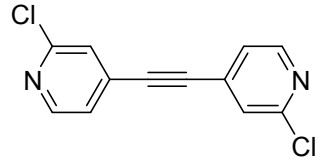
$CDCl_3$): δ 8.80 – 8.77 (m, 2H), 8.24 (s, 2H), 7.60 – 7.57 (m, 2H), 4.04 (d, J = 3.1 Hz, 6H) ppm.^{13}C NMR (101 MHz, $CDCl_3$): δ 164.84, 150.04, 148.35, 130.70, 129.03, 127.58, 79.89, 53.18 ppm. HRMS(ESI): m/z calcd for $C_{16}H_{12}N_2O_2$ $[M+H]^+$ 297.0866, found 297.0870.

1,2-Bis(2-fluoropyridin-4-yl)acetylene (**1f**).



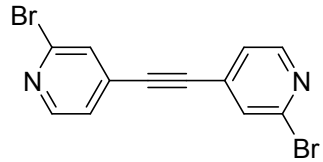
Yellow solid, 0.35 g, 41%, MP: 141 - 142 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.30 (d, J = 5.1 Hz, 2H), 7.32 (d, J = 5.1 Hz, 2H), 7.09 (s, 2H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.68 (d, J = 239.7 Hz), 148.14 (d, J = 15.6 Hz), 134.57 (d, J = 9.3 Hz), 123.45 (d, J = 4.5 Hz), 111.94 (d, J = 39.5 Hz), 90.34 (d, J = 5.0 Hz) ppm. HRMS(ESI): m/z calcd for $C_{12}H_6N_2F_2$ $[M+H]^+$ 217.0555, found 217.0572.

1,2-Bis(2-chloropyridin-4-yl)acetylene (**1g**).



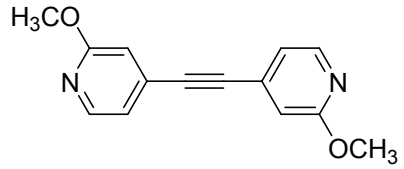
Yellow solid, 0.43 g, 44%, MP: 170 - 171 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.46 (d, J = 5.1 Hz, 2H), 7.48 (s, 2H), 7.35 (dd, J = 5.1, 1.3 Hz, 2H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 151.99, 149.92, 132.49, 126.21, 124.18, 90.38, 77.34 ppm. HRMS(ESI): m/z calcd for $C_{12}H_6N_2Cl_2$ $[M+H]^+$ 248.9936, found 248.9981.

1,2-Bis(2-bromopyridin-4-yl)acetylene (**1h**).



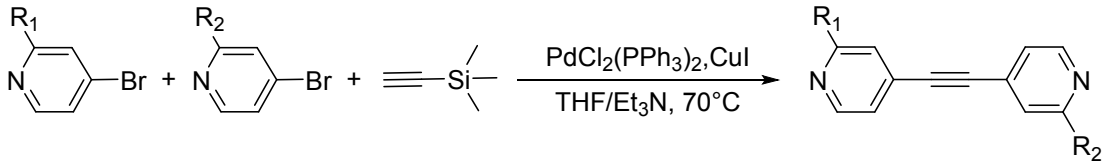
Yellow solid, 0.79 g, 59%, MP: 174 - 175 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.42 (d, J = 5.0 Hz, 2H), 7.62 (s, 2H), 7.36 (dd, J = 5.1, 1.4 Hz, 2H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 150.22, 142.43, 132.16, 129.85, 124.48, 90.27 ppm. HRMS(ESI): m/z calcd for $C_{12}H_6N_2Br_2$ $[M+H]^+$ 338.8946, found 338.8970.

1,2-Bis(2-methoxypyridin-4-yl)acetylene (**1i**).



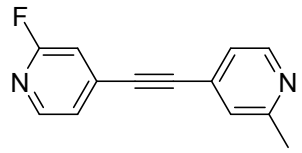
Yellow solid, 0.49 g, 51%, MP: 108 - 110 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.18 (t, J = 5.3 Hz, 2H), 6.97 (dd, J = 10.2, 5.3 Hz, 2H), 6.88 (d, J = 6.4 Hz, 2H), 3.96 (d, J = 5.1 Hz, 6H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 164.25, 164.17, 147.19, 147.07, 132.48, 131.51, 119.00, 118.71, 113.96, 113.27, 89.96, 80.04, 53.65, 53.62 ppm. HRMS(ESI): m/z calcd for $C_{14}H_{12}N_2O_2$ $[M+H]^+$ 241.0952, found 241.0972.

Synthesis of asymmetrical internal alkynes **1j-1o**:



To an oven-dried 100 mL round-bottom flask were added $Pd(PPh_3)_2Cl_2$ (70.19 mg, 2.5 mol%), CuI (38.09 mg, 5 mol%), and either pyridyl iodide or bromine (4 mmol, 1.0 equiv), and the flask was purged with nitrogen. THF-Et_3N (4:1 v/v, 60 mL) was added to dissolve the reagents. Trimethylsilylethyne (392.88 mg, 1.0 equiv) was then added by syringe. The mixture was stirred at 70 °C for 4 hours. After the reaction mixture was cooled at room temperature, 10 ml of 1 M TBAF solution in THF was added and then added another either pyridyl iodide or bromine (4 mmol, 1 equiv), and stirred at room temperature for 2 hours. Then the reaction mixture was partitioned in 100 ml of EA and 100 ml of distilled water. The organic layer was washed with distilled water three times and then dried over $MgSO_4$. The crude product was purified by silica gel column chromatography (EA/petroleum ether).

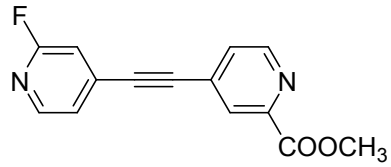
1-(2-Fluoropyridin-4-yl)-2-(2-methylpyridin-4-yl)acetylene (**1j**).



Yellow solid, 0.34 g, 40%, MP: 110 - 112 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.55 (dd, J = 5.2, 2.2 Hz, 1H), 8.25 (dd, J = 5.2, 2.3 Hz, 1H), 7.29 (dt, J = 5.4, 1.6 Hz, 2H), 7.22 (dd, J = 4.9, 1.9 Hz, 1H), 7.06 (d, J = 1.8 Hz, 1H), 2.59 (s, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 163.70 (d, J = 239.3 Hz), 158.91, 149.38, 147.99 (d, J = 15.7 Hz), 135.24 (d, J = 9.3 Hz), 129.84, 125.12, 123.44 (d, J = 4.3 Hz), 122.60,

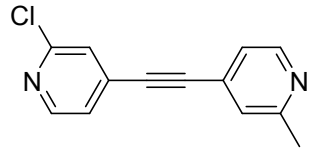
111.80 (d, J = 39.3 Hz), 92.07, 88.81 (d, J = 4.9 Hz), 24.38 ppm. HRMS(ESI): *m/z* calcd for $C_{13}H_9FN_2$ $[M+H]^+$ 213.0827, found 213.0823.

1-(2-Fluoropyridin-4-yl)-2-(2-methoxycarbonylpyridin-4-yl)acetylene (**1k**).



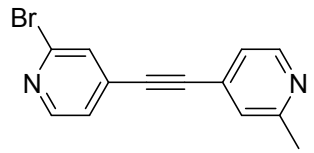
Yellow solid, 0.41 g, 41%, MP: 132 - 134 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.80 (d, J = 4.9 Hz, 1H), 8.28 (d, J = 5.2 Hz, 1H), 8.26 (s, 1H), 7.60 (d, J = 5.0 Hz, 1H), 7.32 (d, J = 5.1 Hz, 1H), 7.09 (s, 0H), 4.05 (s, 3H) ppm.^{13}C NMR (101 MHz, $CDCl_3$): δ 164.96, 163.78 (d, J = 239.1 Hz), 150.07, 148.36, 148.16 (d, J = 15.7 Hz), 134.63 (d, J = 9.3 Hz), 131.22, 128.53, 127.16, 123.46 (d, J = 4.6 Hz), 111.92 (d, J = 39.3 Hz), 90.66, 90.58 (d, J = 4.8 Hz), 53.19 ppm. HRMS(ESI): *m/z* calcd for $C_{14}H_9FN_2O_2$ $[M+H]^+$ 257.0709, found 257.0721.

1-(2-Chloropyridin-4-yl)-2-(2-methylpyridin-4-yl)acetylene (**1l**).



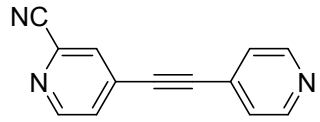
Yellow solid, 0.33 g, 36%, MP: 120 - 122 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.56 (d, J = 5.0 Hz, 1H), 8.43 (d, J = 4.9 Hz, 1H), 7.46 (s, 1H), 7.33 (d, J = 5.1 Hz, 1H), 7.30 (s, 1H), 7.22 (d, J = 5.0 Hz, 1H), 2.60 (s, 2H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 158.91, 151.88, 149.78, 149.35, 133.16, 129.85, 126.15, 125.12, 124.20, 122.61, 92.26, 88.67, 24.37 ppm. HRMS(ESI): *m/z* calcd for $C_{13}H_9ClN_2$ $[M+H]^+$ 229.0517, found 229.0527.

1-(2-Bromopyridin-4-yl)-2-(2-methylpyridin-4-yl)acetylene (**1m**).



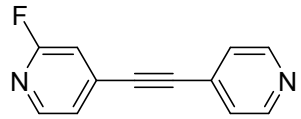
Yellow solid, 0.36 g, 35%, MP: 98 - 100 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.55 (d, J = 5.1 Hz, 1H), 8.39 (d, J = 5.1 Hz, 1H), 7.61 (s, 1H), 7.35 (dd, J = 5.1, 1.4 Hz, 1H), 7.28 (s, 1H), 7.21 (d, J = 3.6 Hz, 1H), 2.59 (s, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 158.92, 150.10, 149.39, 142.36, 132.87, 129.82, 125.12, 124.51, 122.60, 92.36, 88.48, 24.39 ppm. HRMS(ESI): *m/z* calcd for $C_{13}H_9BrN_2$ $[M+H]^+$ 273.0014, found 273.0022.

1-(2-Cyanopyridin-4-yl)-2-(pyridin-4-yl)acetylene (**1n**).



Yellow solid, 0.43 g, 70%, MP: 98-100 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.75 (d, J = 5.0 Hz, 1H), 8.70 (d, J = 5.0 Hz, 2H), 7.81 (s, 1H), 7.62 (dd, J = 5.1, 1.6 Hz, 1H), 7.43 (d, J = 6.0, 2H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 151.31, 150.09, 134.45, 131.94, 130.15, 129.29, 128.59, 125.59, 116.54, 93.30, 88.34 ppm. HRMS(ESI): *m/z* calcd for $C_{13}H_7N_3$ $[M+H]^+$ 206.0708, found 206.0713.

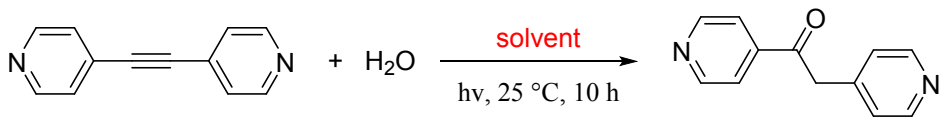
1-(2-Fluoropyridin-4-yl)-2-(pyridin-4-yl)acetylene (**1o**).



Yellow solid, 0.43 g, 72%, MP:169-171 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.69 (s, 2H), 8.28 (d, J = 5.1 Hz, 1H), 7.43 (d, J = 4.2 Hz, 2H), 7.31 (d, J = 3.6 Hz, 1H), 7.08 (s, 1H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 163.71 (d, J = 239.4 Hz), 149.99, 148.04 (d, J = 15.6 Hz), 135.08 (d, J = 9.4 Hz), 129.73, 125.60, 123.44 (d, J = 4.4 Hz), 111.84 (d, J = 39.5 Hz), 91.67, 89.38 (d, J = 5.0 Hz) ppm. HRMS(ESI): *m/z* calcd for $C_{12}H_7FN_2$ $[M+H]^+$ 199.0671, found 199.0666.

Ⅲ. Reaction optimization

Table S1. Solvent investigation. [a]



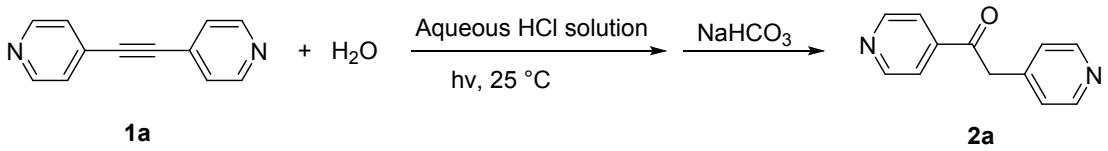
1a **2a**

Entry	Solvent	Yield [b]
1	MeOH	0
2	DMF	0
3	Acetone	0
4	CH_3CN	0
5	1 M HCl aqueous solution	84
6	THF	0

[a] Reaction were carried out with **1a** (0.1 mmol) dissolving in 2.0 mL solvent at room

temperature upon UV irradiation with a 250-W high-pressure mercury lamp for 10 hours. [b] Yields were determined by the ^{1}H NMR spectra using pyrazine as an internal standard.

Table S2. The acidity of solution investigation [a].



1a **2a**

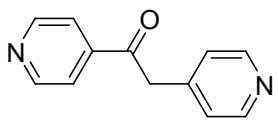
Entry	pH	Yield [b]
1	-1	26%
2	0	75%
3	1	82%

[a] Reaction were carried out with 1a (0.1 mmol) dissolving in 2.0 mL different acidity of solvent at room temperature upon irradiation with a 250-W high-pressure mercury lamp for 1 hours. [b] Yields were determined by the ^{1}H NMR spectra using pyrazine as an internal standard.

Ⅳ. General procedure for the hydration of internal alkynes **1**.

Internal alkyne (1 mmol) was dissolved in 40 ml of 1M aqueous HCl or CH_3SO_3H solution and irradiated with a 250-W high-pressure mercury lamp, and the reaction was monitored by TLC. The reaction solution was neutralized with solid $NaHCO_3$ and extracted three times with EA. The organic phase was taken, dried over anhydrous sodium sulfate, filtered, and the solvent was removed under reduced pressure. Flash column chromatography was performed using MeOH/EA/PE=1:30:150.

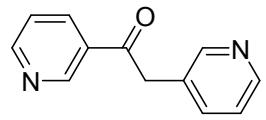
1,2-Di(pyridin-4-yl)ethan-1-one (**2a**).



Yellow solid, 155 mg, 78%, MP: 238 – 240 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.87 (d, J = 6.0 Hz, 1H), 8.62 (d, J = 6.0 Hz, 1H), 7.78 (d, J = 6.1 Hz, 1H), 7.23 (d, J = 6.1 Hz, 1H), 4.32 (s, 2H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 195.27, 151.20,

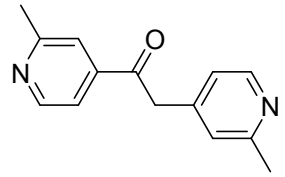
149.87, 142.45, 141.94, 124.91, 121.20, 44.75. HRMS(ESI): *m/z* calcd for $C_{12}H_{10}N_2O$ $[M+H]^+$ 199.0871, found 199.0866.

1,2-Di(pyridin-3-yl)ethan-1-one (**2b**).



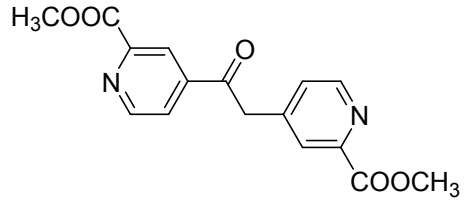
Yellow solid, 159 mg, 80%, MP: 79 - 81 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.27 (s, 1H), 8.84 (d, *J* = 5.1 Hz, 1H), 8.57 (d, J = 7.4 Hz, 1H), 8.30 (dt, J = 8.1, 2.0 Hz, 1H), 7.66 (dd, J = 7.9, 2.1 Hz, 1H), 7.48 (dd, J = 8.0, 4.8 Hz, 1H), 7.33 (dt, J = 7.9, 4.0 Hz, 1H), 4.36 (s,2H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 195.20, 153.97, 150.36, 150.32, 149.86, 148.43, 148.38, 137.52, 137.47, 135.73, 131.53, 129.40, 123.83, 42.58 ppm. HRMS(ESI): *m/z* calcd for $C_{12}H_{10}N_2O$ $[M+H]^+$ 199.0853, found 199.0866.

1,2-Bis(2-methylpyridin-4-yl)ethan-1-one (**2d**).



Yellow solid, 163 mg, 72%, MP:186 - 188 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 (d, *J* = 5.1 Hz, 1H), 8.50 (d, *J* = 5.2 Hz, 1H), 7.64 (s, 1H), 7.57 (dd, *J* = 5.1, 1.6 Hz, 1H), 7.12 (s, 1H), 7.08 (d, *J* = 5.2 Hz, 1H), 4.28 (s, 2H), 2.68 (s, 3H), 2.62 (s, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.63, 160.28, 158.30, 150.50, 148.40, 143.71, 142.42, 124.82, 122.26, 120.79, 118.37, 44.81, 24.62, 23.84 ppm. HRMS m/z (ESI) calcd for $C_{14}H_{14}N_2O$ $[M+H]^+$ 227.1148, found:227.1179.

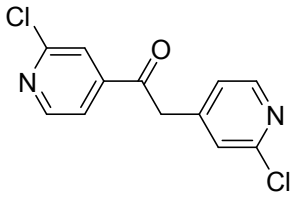
1,2-Bis(2-methoxycarbonylpyridin-4-yl)ethan-1-one (**2e**).



Yellow solid, 232 mg, 74%, MP: 119 - 121 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.99 (d, *J* = 4.9 Hz, 1H), 8.76 (d, *J* = 4.9 Hz, 1H), 8.61 (s, 1H), 8.07 (s, 1H), 7.42 (dd, J = 4.9, 1.7 Hz, 1H), 4.46 (s, 2H), 4.07 (s, 3H), 4.02 (s, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.87, 165.45, 164.89, 151.32, 150.10, 149.59, 148.35, 143.20, 143.13, 128.17, 126.41, 124.26, 122.63, 53.31, 53.01, 44.60 ppm. HRMS m/z (ESI) calcd for

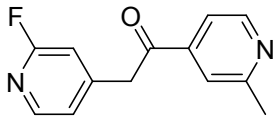
$C_{16}H_{14}N_2O_5$ $[M+H]^+$ 315.0968, found:315.0975.

1,2-Bis(2-chloropyridin-4-yl)ethan-1-one (**2g**).



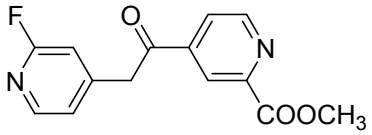
Yellow solid, 110 mg, 41% , MP: 95 - 97 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (d, J = 5.1 Hz, 1H), 8.39 (d, J = 5.1 Hz, 1H), 7.80 (s, 1H), 7.69 (dd, J = 5.1, 1.6 Hz, 1H), 7.25 (s, 1H), 7.12 (d, J = 5.1 Hz, 1H), 4.28 (s, 2H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.20, 153.24, 152.02, 151.22, 149.91, 144.76, 144.59, 125.39, 123.64, 122.46, 119.87, 77.36, 44.31 ppm. HRMS m/z (ESI) calcd for $C_{12}H_8Cl_2N_2O$ $[M+H]^+$ 267.0075, found:267.0086.

2-(2-Fluoropyridin-4-yl)-1-(2-methylpyridin-4-yl)ethan-1-one (**2j**).



Yellow solid, 87 mg, 38%, MP: 50-52 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 (d, J = 4.6 Hz, 1H), 8.21 (dd, J = 5.2, 3.2 Hz, 1H), 7.63 (s, 1H), 7.57 (d, J = 3.0 Hz, 1H), 7.07 (d, J = 5.0 Hz, 1H), 6.84 (s, 1H), 4.32 (s, 2H), 2.68 (d, J = 3.1 Hz, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.94, 164.02 (d, J=238.9 Hz), 160.29, 150.40, 147.86 (d, J = 14.6 Hz), 142.37, 122.62 (d, J = 4.1 Hz), 120.82, 118.34, 110.70 (d, J = 37.8 Hz), 44.43 (d, J = 3.0 Hz), 24.54 ppm. HRMS m/z (ESI) calcd for $C_{13}H_{11}FN_2O$ $[M+H]^+$ 231.0914, found:231.0928.

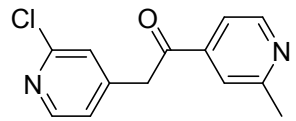
2-(2-Fluoropyridin-4-yl)-1-(2-methoxycarbonylpyridin-4-yl)ethan-1-one (**2k**).



Yellow solid, 99 mg, 36%, MP: 92 - 93 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 (d, J = 5.1 Hz, 1H), 8.20 (d, J = 5.1 Hz, 1H), 7.63 (s, 1H), 7.57 (dd, J = 5.2, 1.6 Hz, 1H), 7.08 (dt, J = 5.3, 1.7 Hz, 1H), 6.85 (s, 1H), 4.33 (s, 2H), 2.68 (s, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.99, 164.00 (d, J = 239.0 Hz), 160.34, 150.51, 147.95, 147.81 (d, J = 15.3 Hz), 142.29, 122.63 (d, J = 4.1 Hz), 120.72, 118.27, 110.69 (d, J = 37.8 Hz), 44.40 (d, J = 3.0 Hz), 24.59 ppm. HRMS m/z (ESI) calcd for $C_{14}H_{11}FN_2O_3$

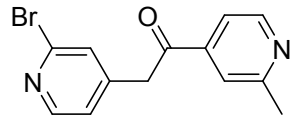
$[M+H]^+$ 275.0813, found:275.0826.

2-(2-Chloropyridin-4-yl)-1-(2-methylpyridin-4-yl)ethan-1-one (**2l**).



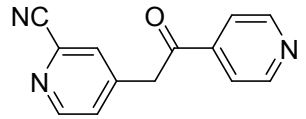
Yellow solid, 86 mg, 35%, MP: 48 - 50 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 (d, J = 5.1 Hz, 1H), 8.36 (d, J = 5.1 Hz, 1H), 7.62 (s, 1H), 7.56 (d, J = 3.6 Hz, 1H), 7.24 (s, 1H), 7.12 (d, J = 5.1 Hz, 1H), 4.28 (s, 2H), 2.67 (s, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.96, 160.35, 151.89, 150.54, 149.78, 145.48, 142.23, 132.09, 131.99, 128.56, 128.44, 125.40, 123.71, 120.69, 118.25, 44.22, 24.62 ppm. HRMS m/z (ESI) calcd for $C_{13}H_{11}ClN_2O$ $[M+H]^+$ 247.0618, found:247.0633.

2-(2-Bromopyridin-4-yl)-1-(2-methylpyridin-4-yl)ethan-1-one (**2m**).



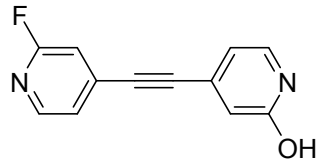
Yellow solid, 108 mg, 37%, MP: 68 - 70 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 (d, J = 5.1 Hz, 1H), 8.37 (d, J = 5.0 Hz, 1H), 7.64 (s, 1H), 7.57 (d, J = 3.7 Hz, 1H), 7.42 (s, 1H), 7.17 (dd, J = 5.1, 1.4 Hz, 1H), 4.27 (s, 2H), 2.69 (s, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.84, 159.30, 149.44, 149.18, 144.13, 141.57, 141.28, 128.14, 123.04, 119.76, 117.29, 43.10, 23.52 ppm. HRMS m/z (ESI) calcd for $C_{13}H_{11}BrN_2O$ $[M+H]^+$ 291.0130, found:291.0128.

2-(2-Bromopyridin-4-yl)-1-(pyridin-4-yl)ethan-1-one (**2n**).



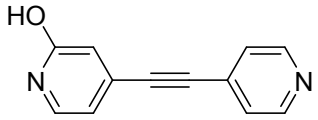
White solid, 90 mg, 50%, MP: 116-118 °C. ^{1}H NMR (400 MHz, CDCl3): δ 8.91 (d, J = 4.3 Hz, 2H), 8.72 (d, J = 5.0 Hz, 1H), 7.80 (d, J = 4.8 Hz, 2H), 7.64 (s, 1H), 7.45 (d, J = 5.0 Hz, 1H), 4.41 (s, 2H) ppm. ^{13}C NMR (101 MHz, CDCl3): δ 194.13, 151.35, 151.21, 143.83, 141.57, 134.25, 129.82, 128.34, 121.01, 117.05, 44.02 ppm. HRMS m/z (ESI) calcd for $C_{13}H_9N_3O$ $[M+H]^+$ 224.0820, found:224.0818.

4-((2-fluoropyridin-4-yl)ethynyl)pyridin-2-ol (**3f**).



White solid, 64 mg, 30%, MP: 184-186 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 13.37 (s, 1H), 8.27 (d, J = 5.1 Hz, 1H), 7.41 (d, J = 6.7 Hz, 1H), 7.29 (d, J = 5.2 Hz, 1H), 7.06 (s, 1H), 6.77 (s, 1H), 6.39 (d, J = 6.7 Hz, 1H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.87, 163.59 (d, J = 221.6 Hz), 148.09 (d, J = 15.6 Hz), 135.41, 134.89, 134.75 (d, J = 9.4 Hz), 123.47 (d, J = 4.3 Hz), 111.92 (d, J = 39.4 Hz), 108.94, 91.09, 90.59 (d, J = 4.9 Hz) ppm. HRMS m/z (ESI) calcd for $C_{12}H_7FN_2O$ $[M+H]^+$ 215.0622, found: 215.0615.

4-(pyridin-4-ylethynyl)pyridin-2-ol (**3o**).



White solid, 0.100 g, 51%, MP: 224-226 °C. ^{1}H NMR (400 MHz, CDCl3): δ 13.38 (s, 1H), 8.66 (d, J = 6.0 Hz, 1H), 7.44 – 7.35 (m, 3H), 6.77 (s, 1H), 6.39 (dd, J = 6.7, 1.6 Hz, 1H) ppm. ^{13}C NMR (101 MHz, CDCl3): δ 164.77, 149.98, 135.84, 134.73, 129.91, 125.61, 123.28, 109.01, 91.89, 90.13 ppm. HRMS m/z (ESI) calcd for $C_{12}H_8N_2O$ $[M+H]^+$ 197.0709, found:197.0709.

V. UV spectra of **1a** in methanol and ethyl acetate

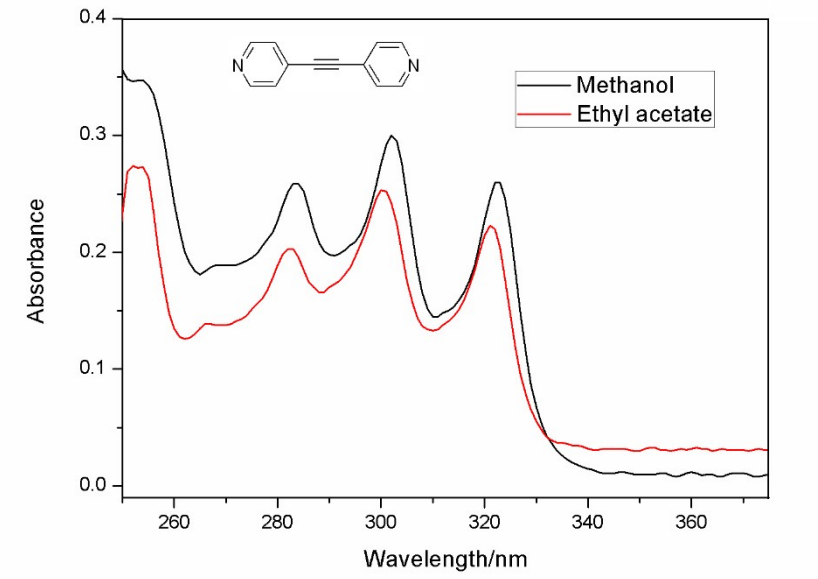


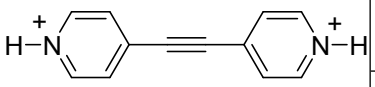
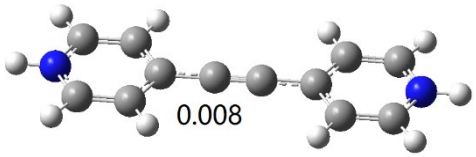
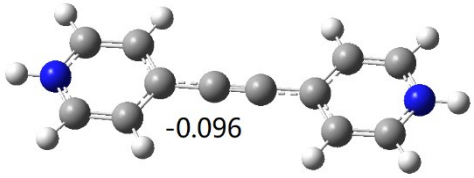
Fig. S1 The UV spectra of **1a** in methanol and ethyl acetate.

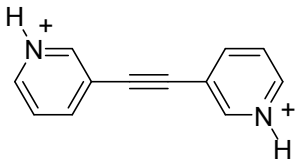
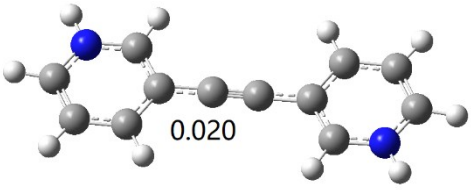
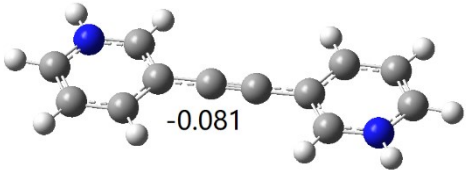
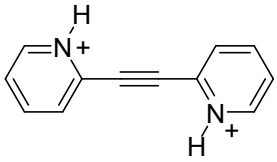
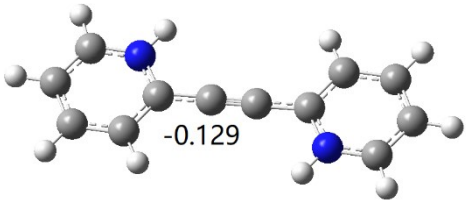
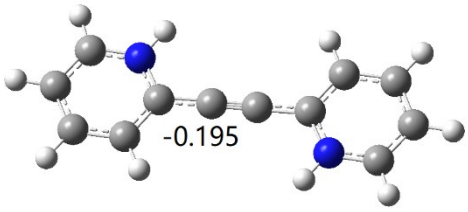
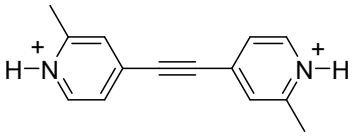
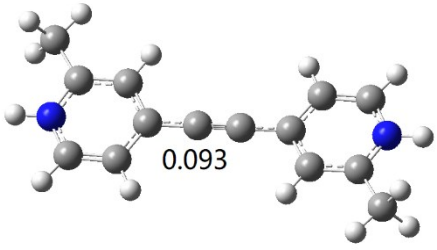
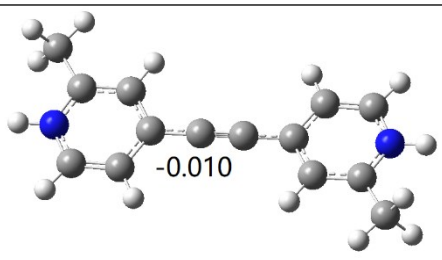
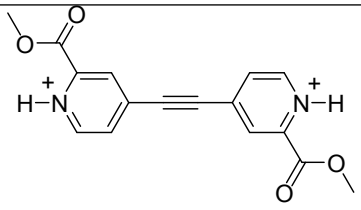
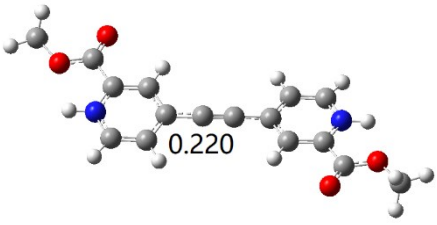
Ⅵ. Theoretical calculation of the Mulliken charge values of protonated DPAs

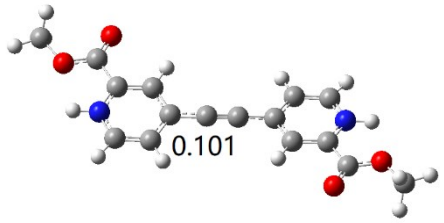
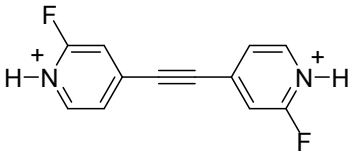
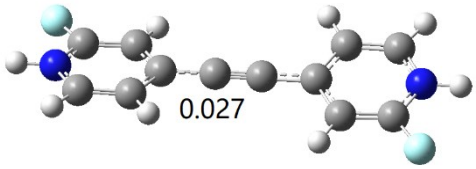
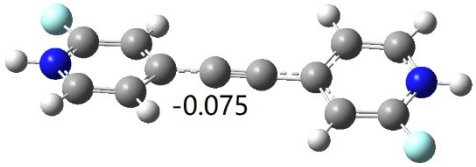
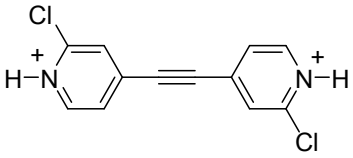
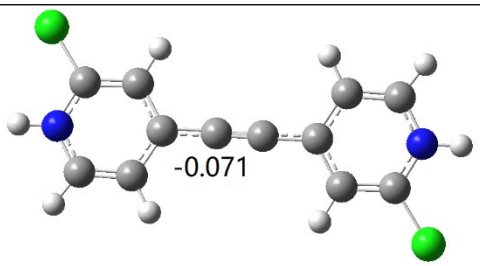
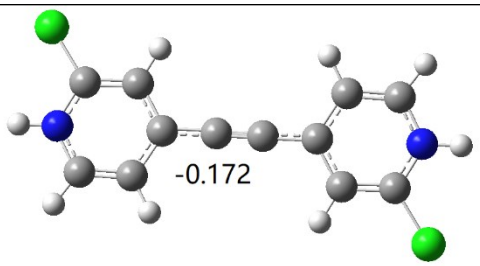
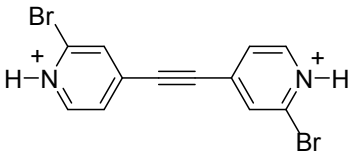
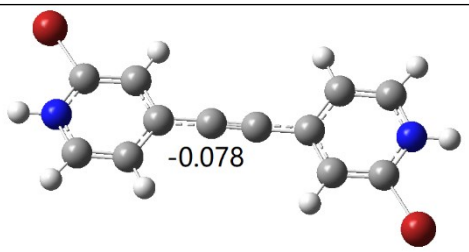
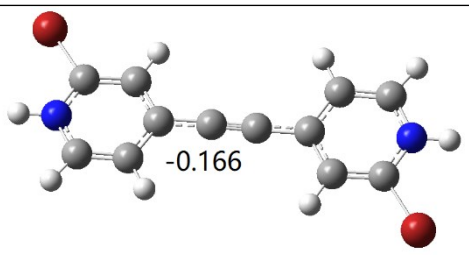
All the DFT calculations were performed using Gaussian 09 program package. [2] The optimization and frequency calculation of the protonated DPAs in water were calculated at B3LYP/6-31+g(d,p) level of theory, and the excited singlet states of the protonated DPAs were calculated using TD DFT method. [3~4]

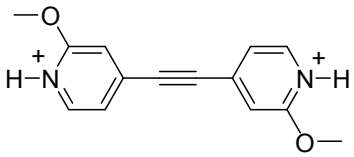
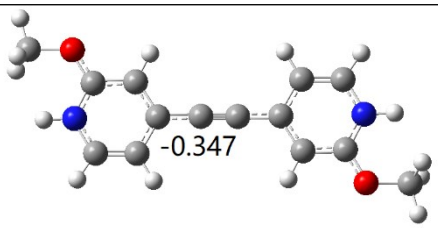
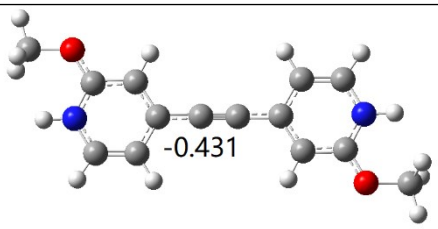
2. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, *Gaussian 09*, Revision D.01, (Gaussian, Inc., Wallingford CT, 2009).
3. A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648-5652.
4. C. Lee, W. Yang and R. G. Parr, *Physical Review B*, 1988, **37**, 785-789.

Table S1 Calculated Mulliken charge values of carbon-carbon triple bonds of protonated DPAs in ground and excited states at B3LYP/6-31+G(d,p) level of theory.

DPAs	Protonated DPAs	Ground state Excited state
1a		S_1  0.008
		S_0  -0.096

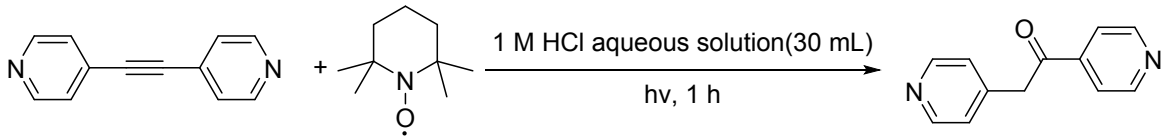
1b		S_1  S_0 
1c		S_1  S_0 
1d		S_1  S_0 
1e		S_1 

		S_0 
1f		S_1  S_0 
1g		S_1  S_0 
1h		S_1  S_0 

1i		S_1  S_0 

VII. Additional experiment to elucidate the mechanistic pathway

a. Radical blocking experiment

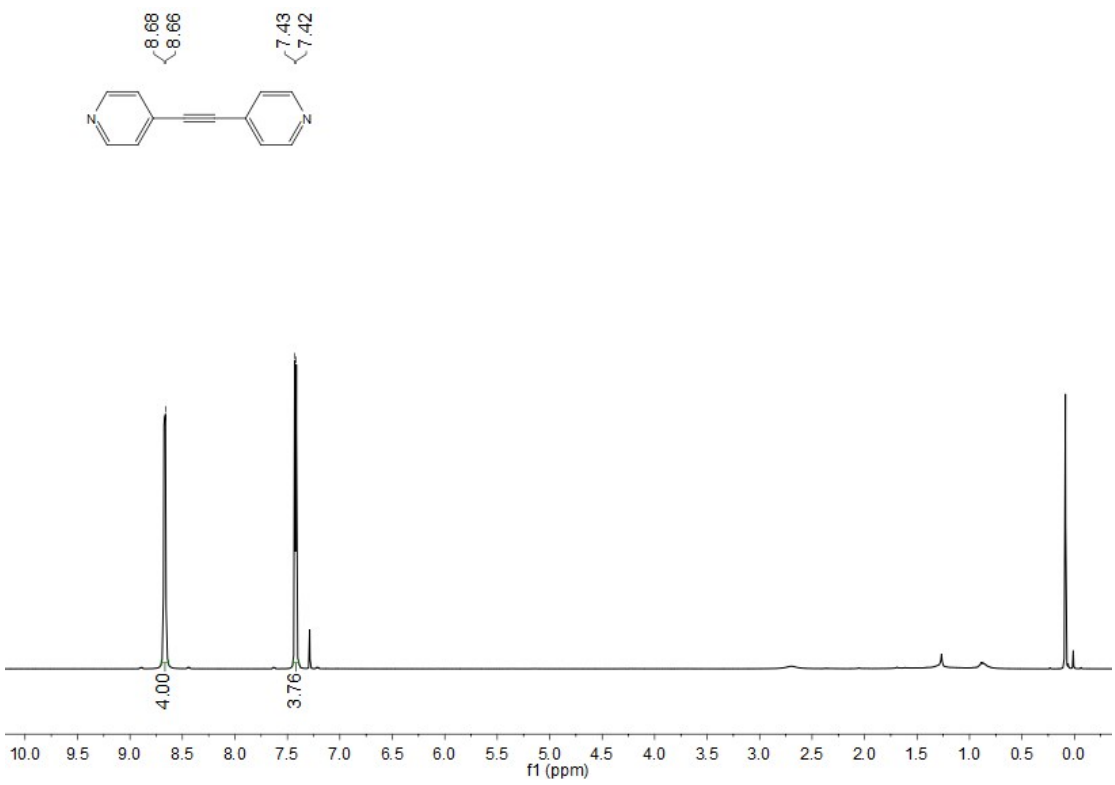


1 mmol(1 eq) 3 mmol(3 eq) 143 mg(Yield:72%)

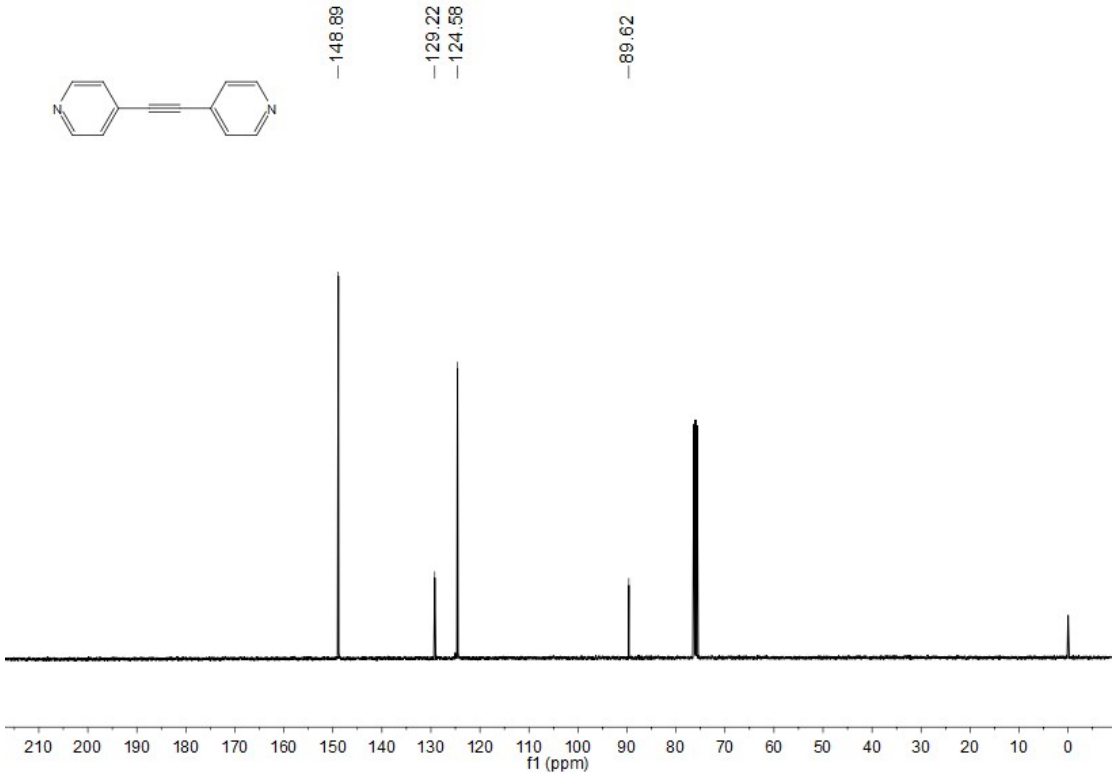
The experimental results show that this hydration reaction does not proceed via a free-radical pathway.

Ⅷ. ^{1}H NMR and ^{13}C NMR spectra of alkynes and ketones.

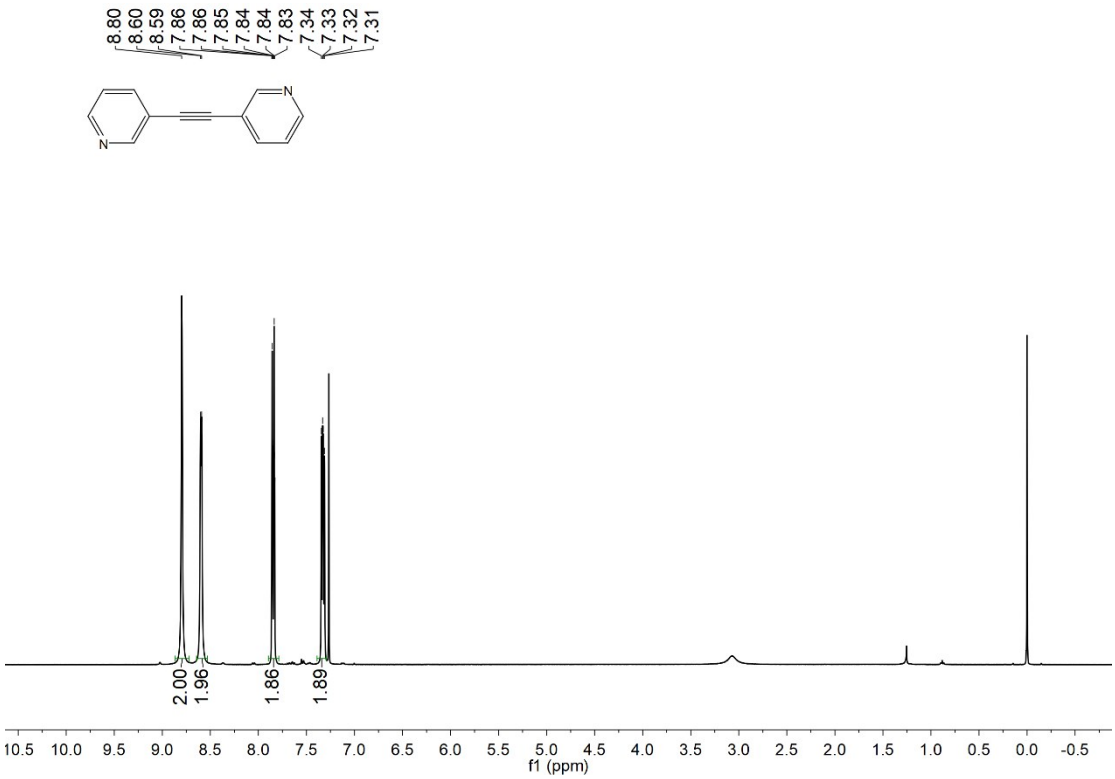
^{1}H NMR of Compound **1a** in $CDCl_3$



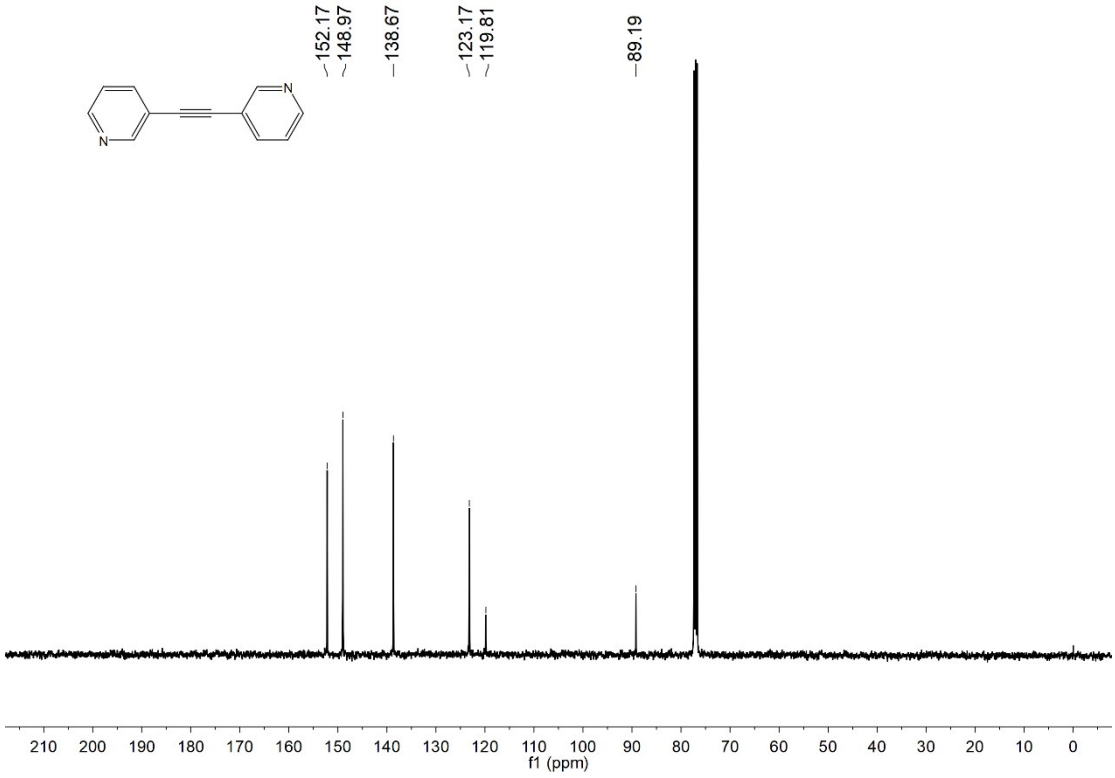
^{13}C NMR of Compound **1a** in $CDCl_3$



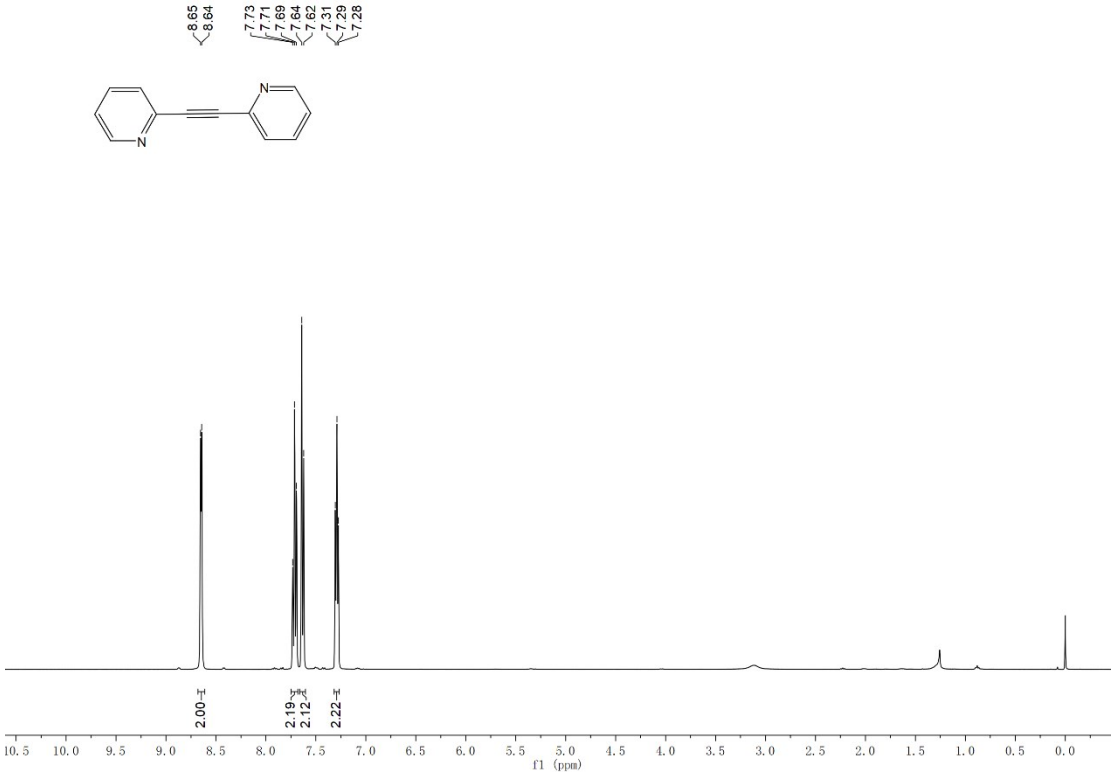
^{1}H NMR of Compound **1b** in $CDCl_3$



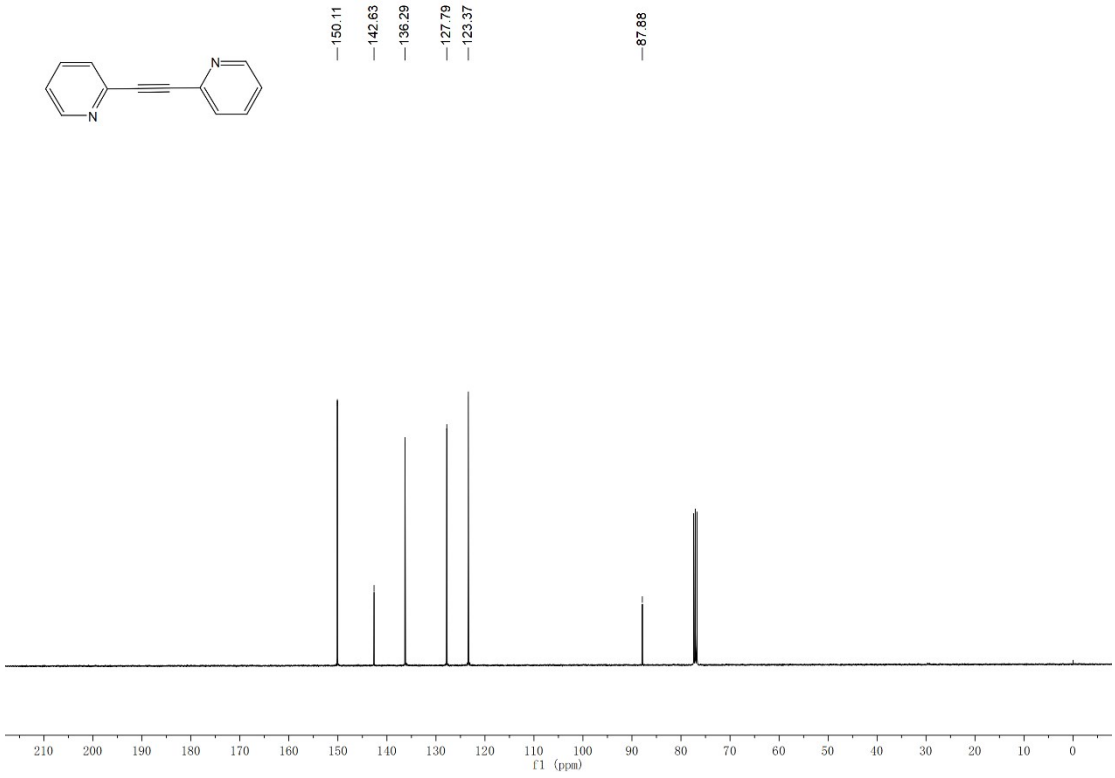
^{13}C NMR of Compound **1b** in $CDCl_3$



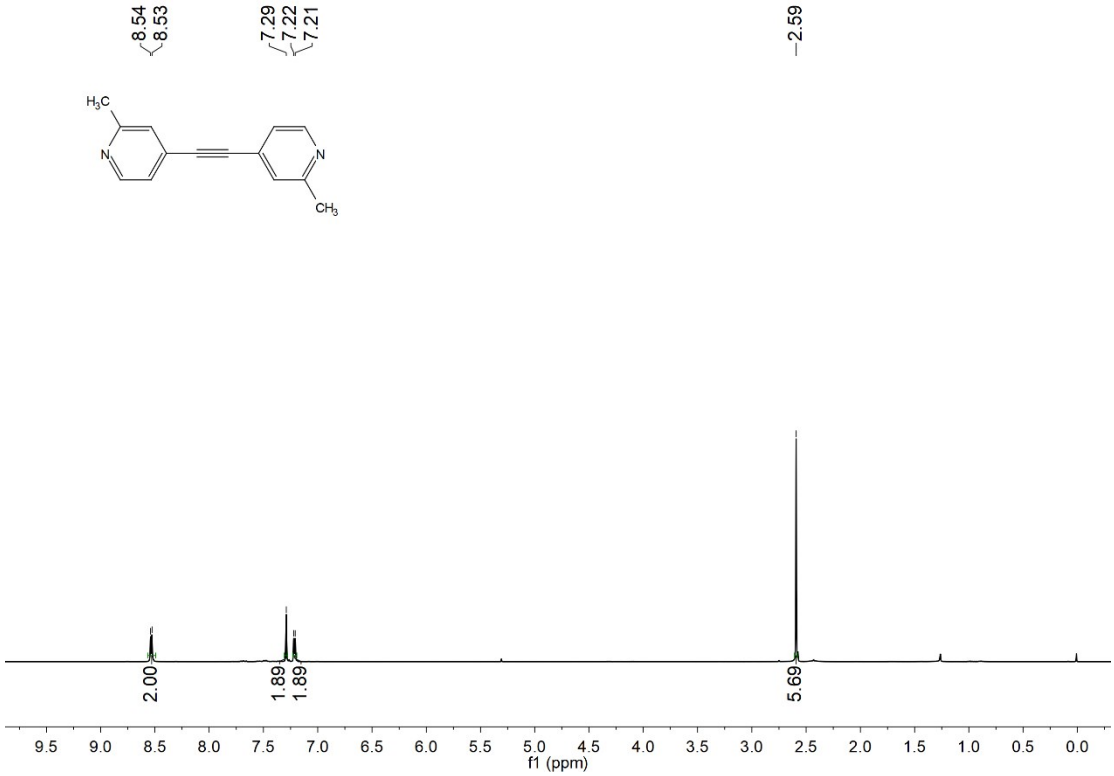
^{1}H NMR of Compound **1c** in $CDCl_3$



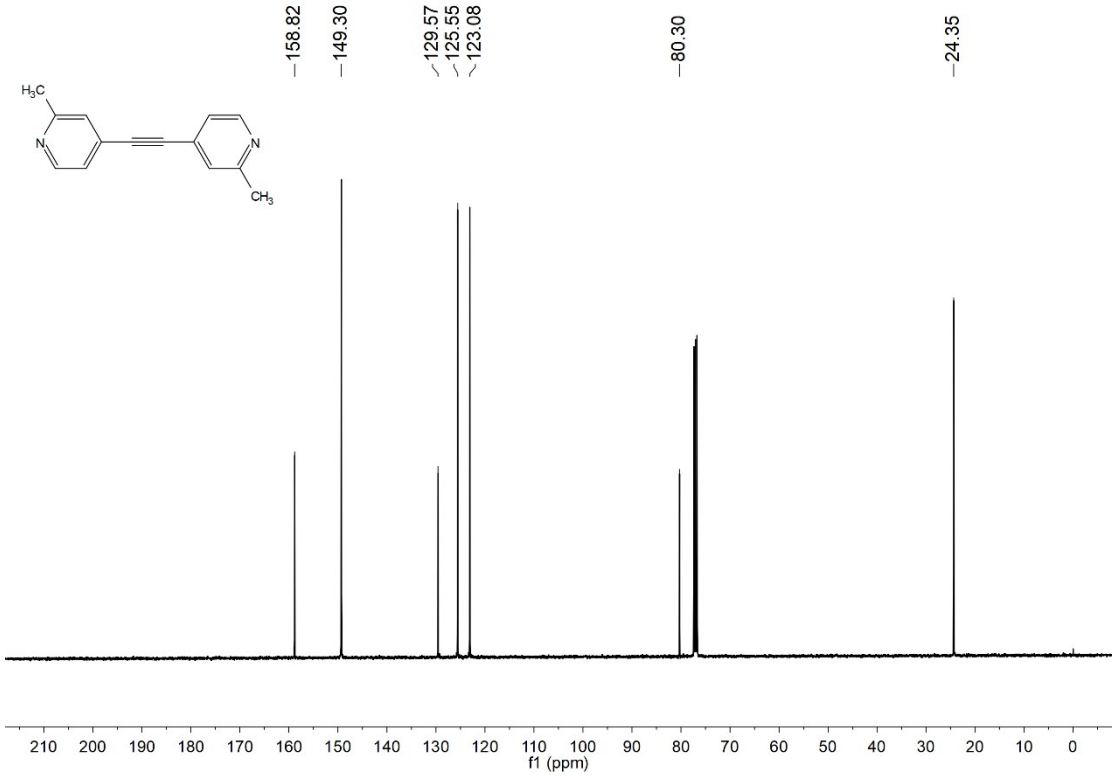
^{13}C NMR of Compound **1c** in $CDCl_3$



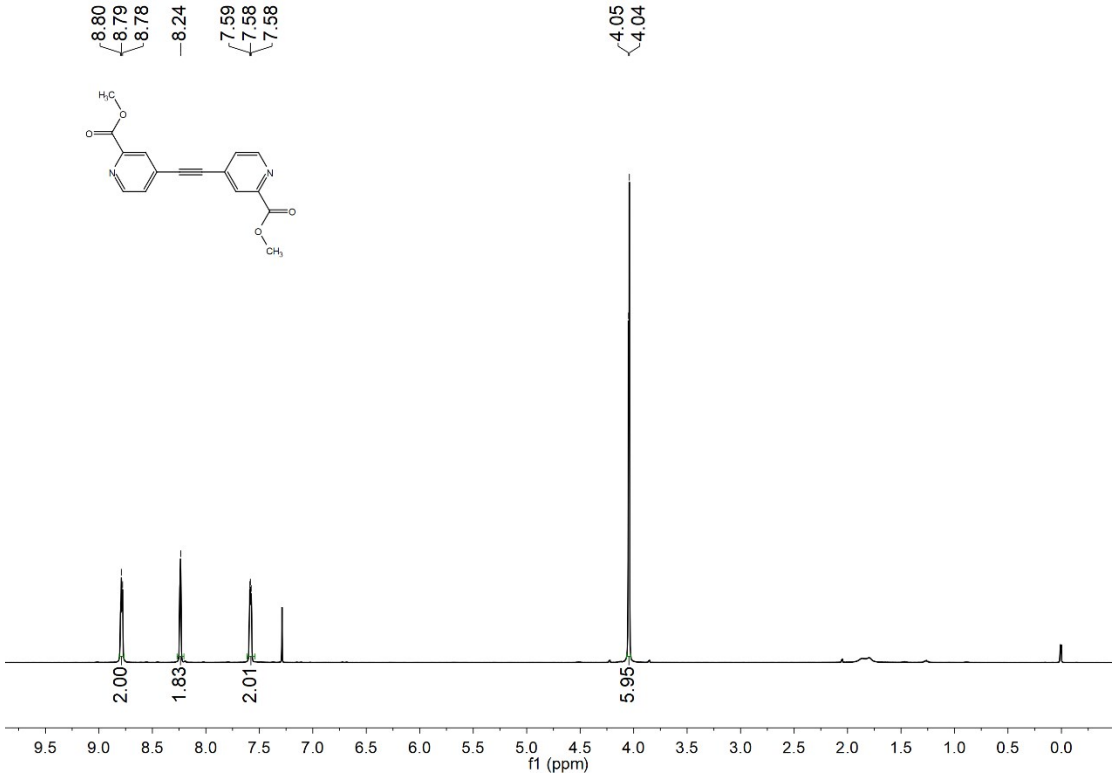
^{1}H NMR of Compound **1d** in $CDCl_3$



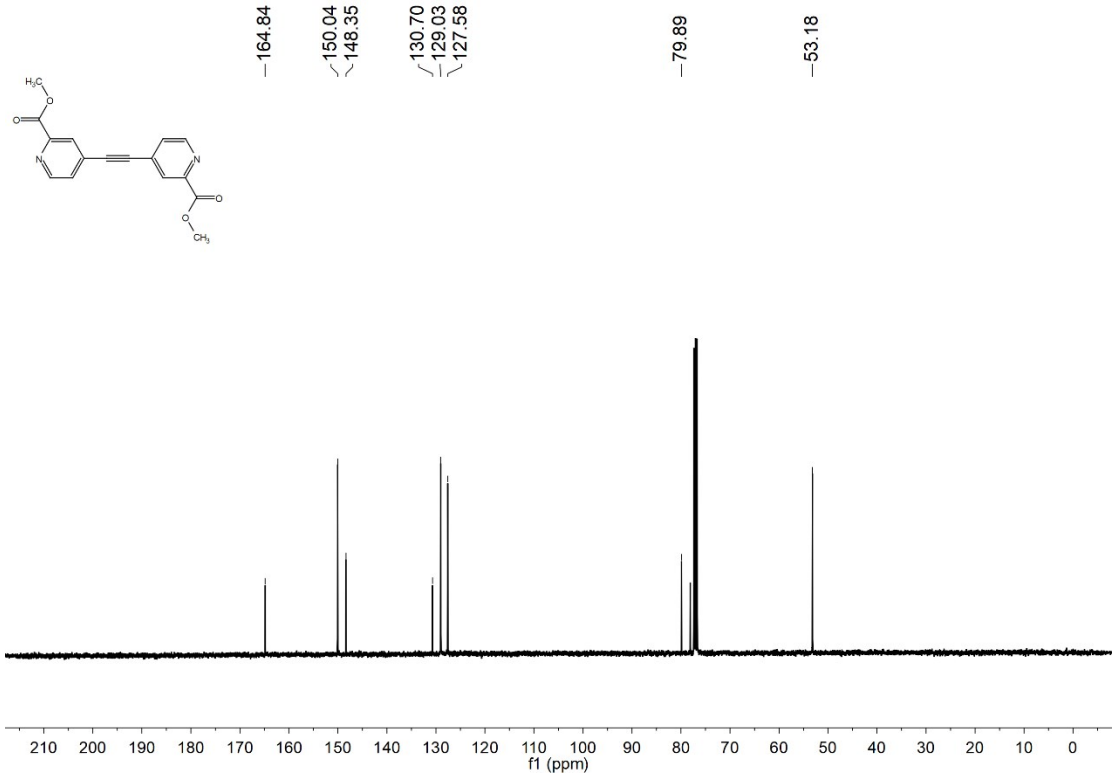
^{13}C NMR of Compound **1d** in $CDCl_3$



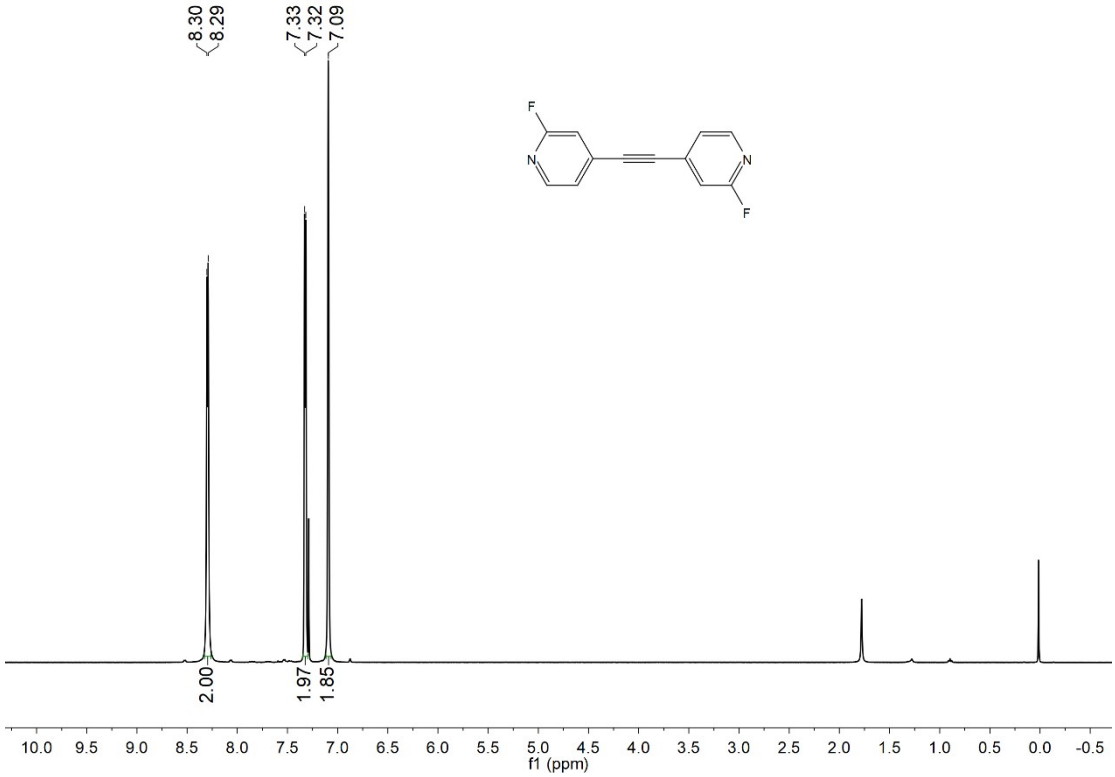
^{1}H NMR of Compound **1e** in $CDCl_3$



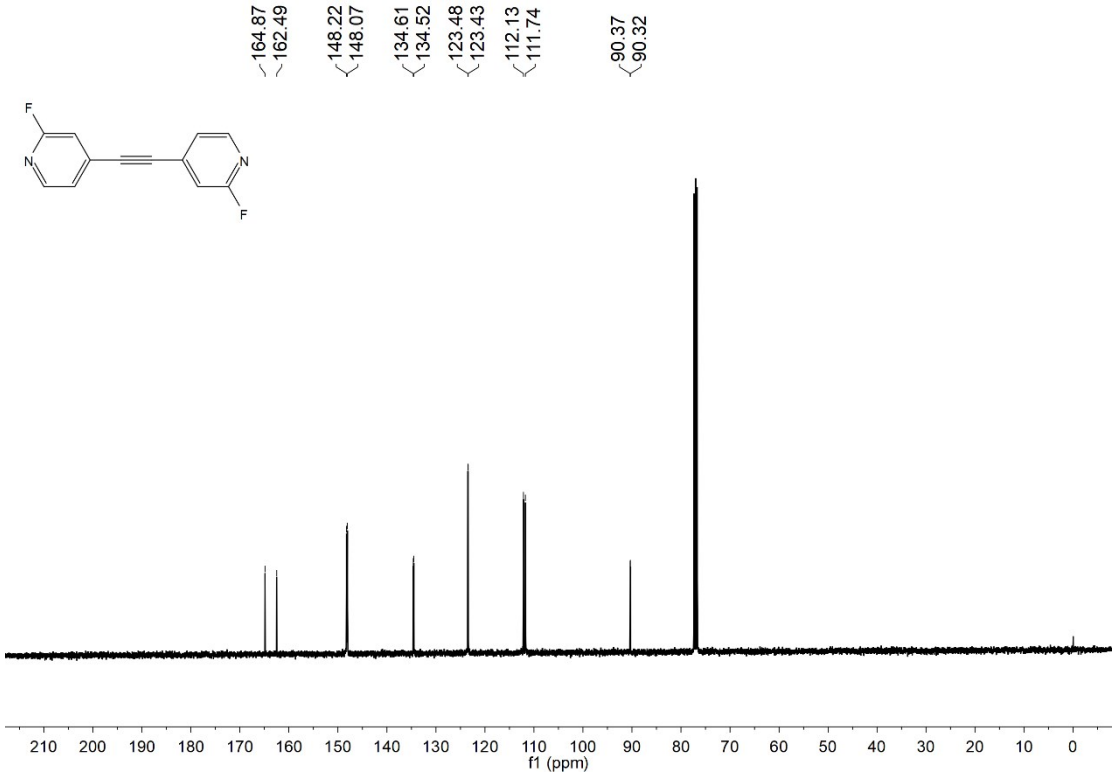
^{13}C NMR of Compound **1e** in $CDCl_3$



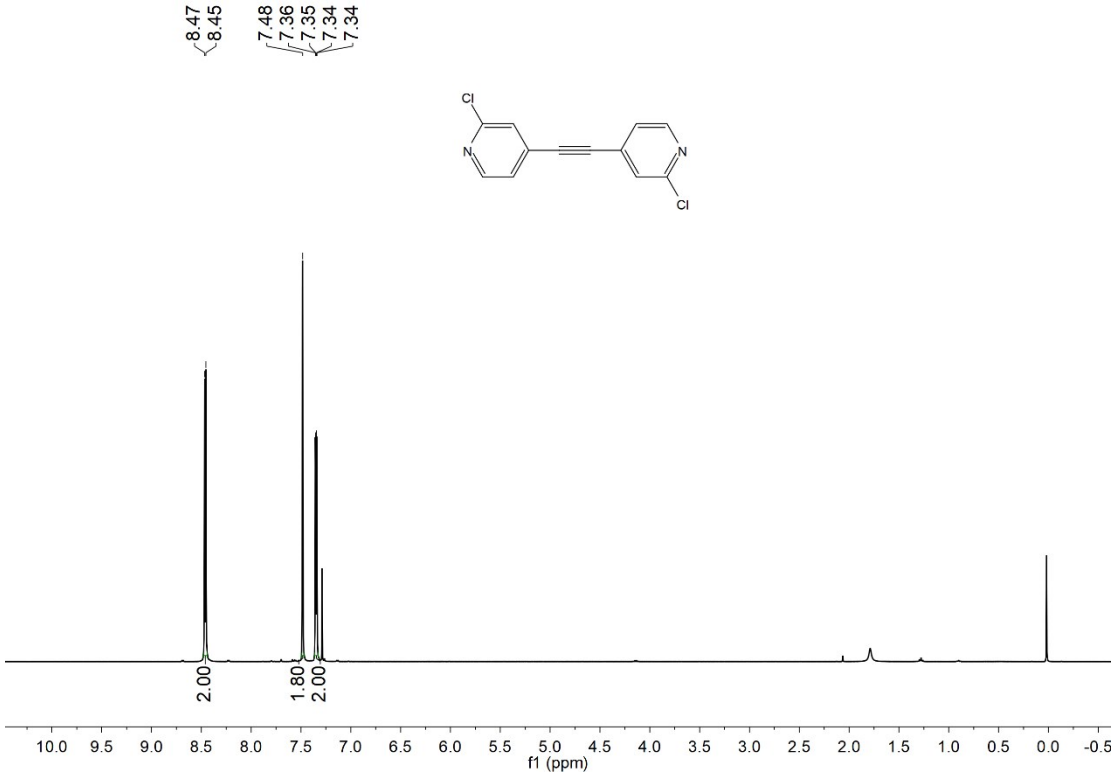
^{1}H NMR of Compound **1f** in $CDCl_3$



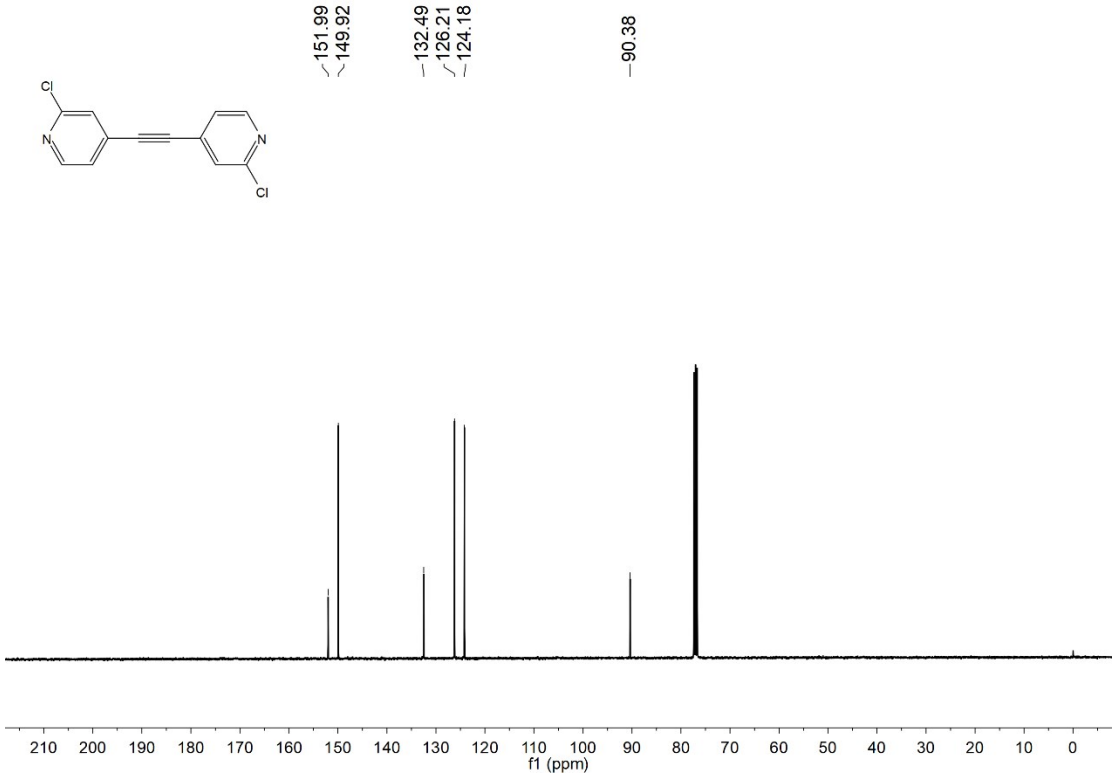
^{13}C NMR of Compound **1f** in $CDCl_3$



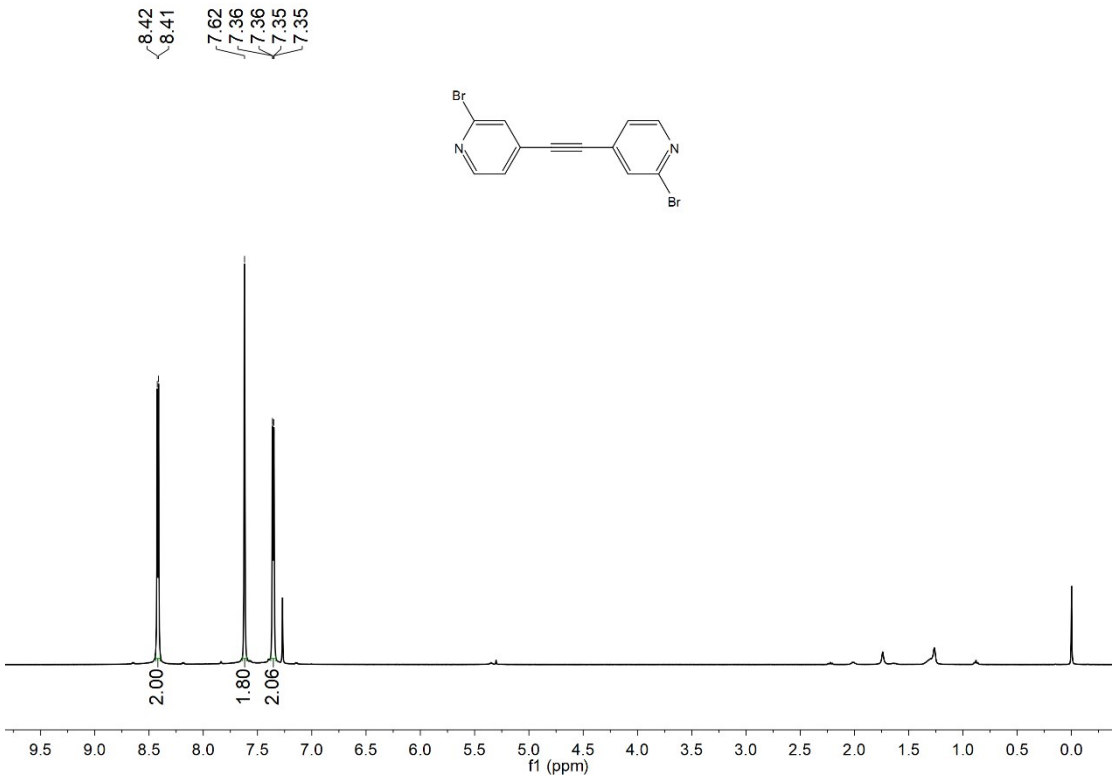
^{1}H NMR of Compound **1g** in $CDCl_3$



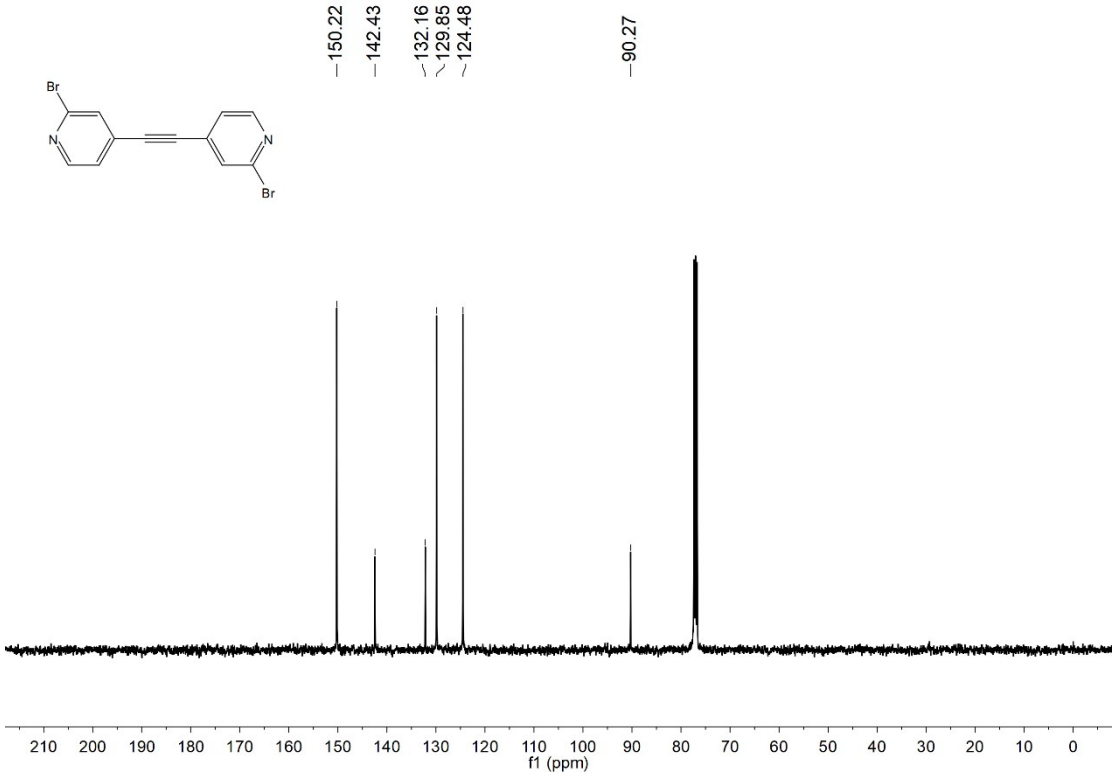
^{13}C NMR of Compound **1g** in $CDCl_3$



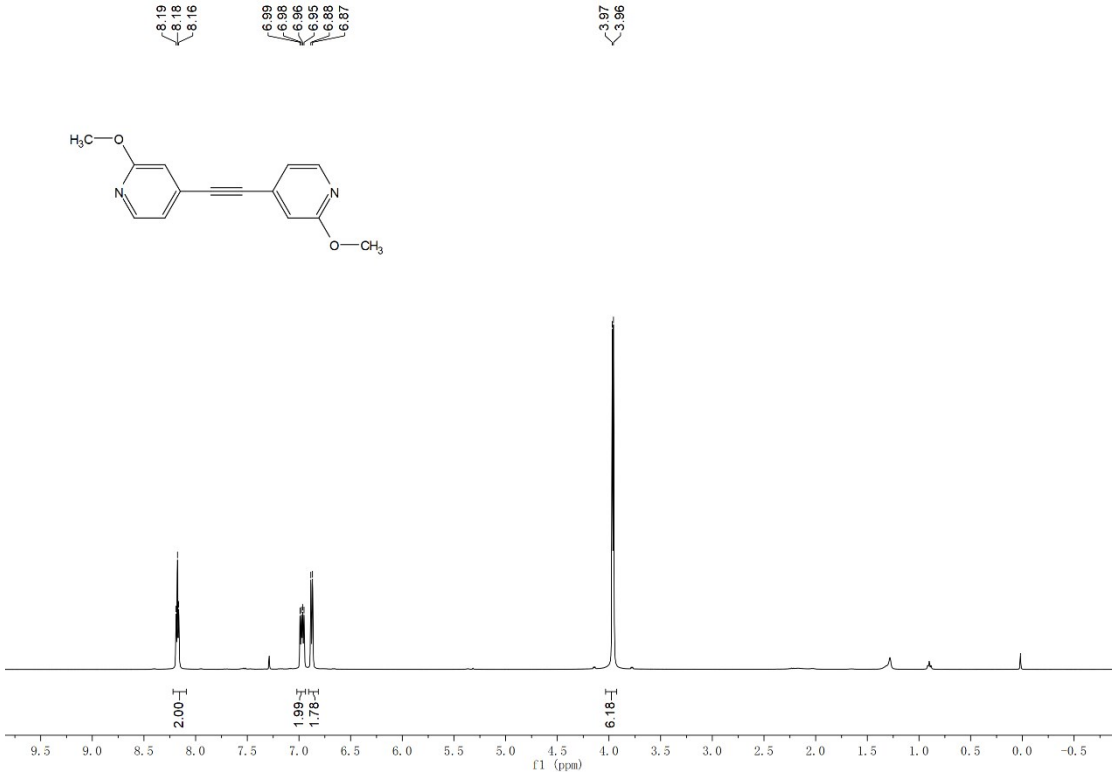
^{1}H NMR of Compound **1h** in $CDCl_3$



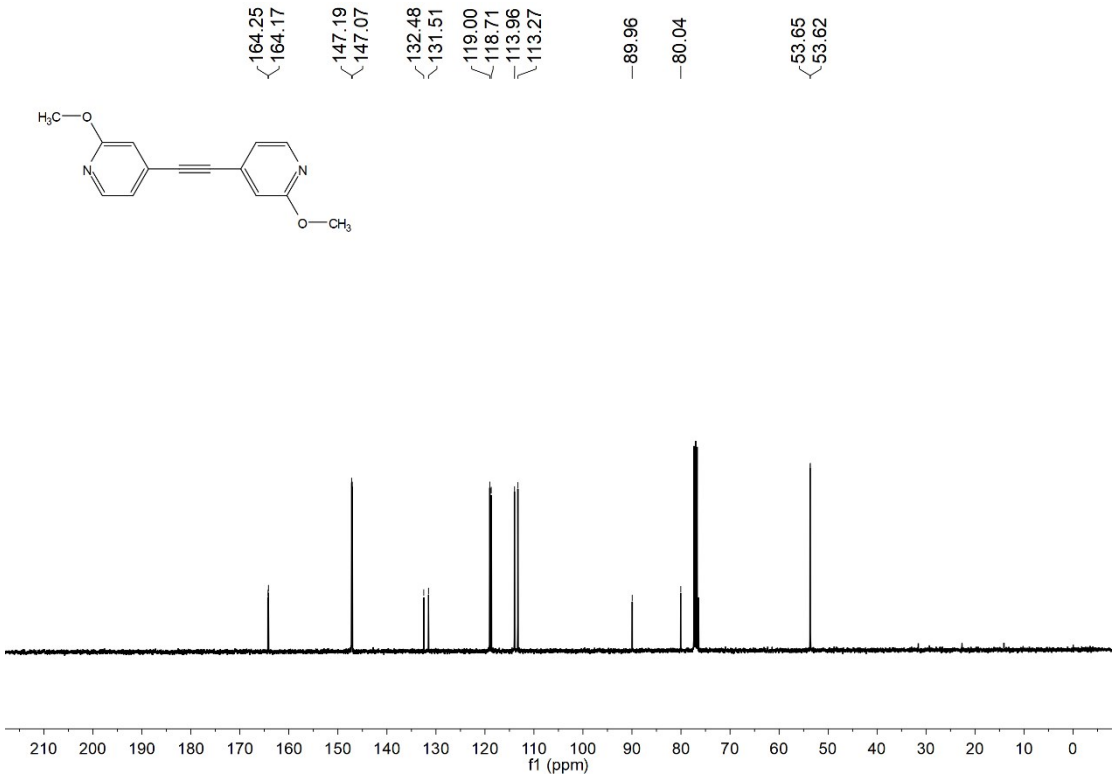
^{13}C NMR of Compound **1h** in $CDCl_3$



^{1}H NMR of Compound **1i** in $CDCl_3$



^{13}C NMR of Compound **1i** in $CDCl_3$



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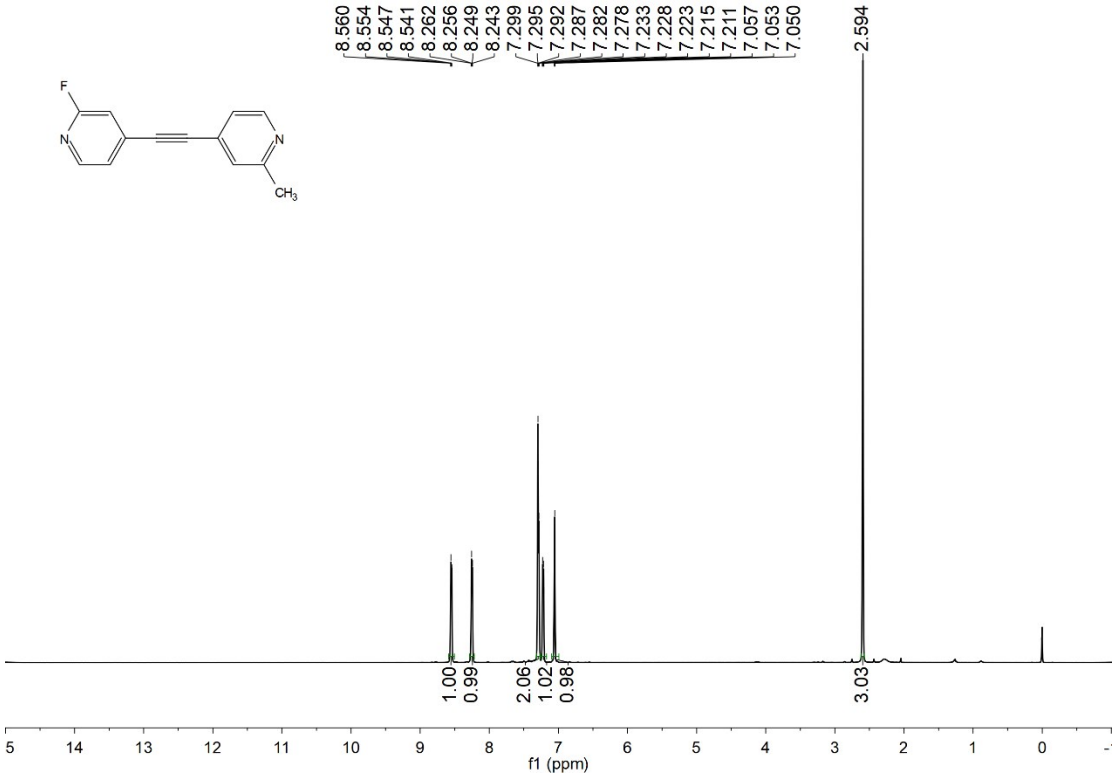

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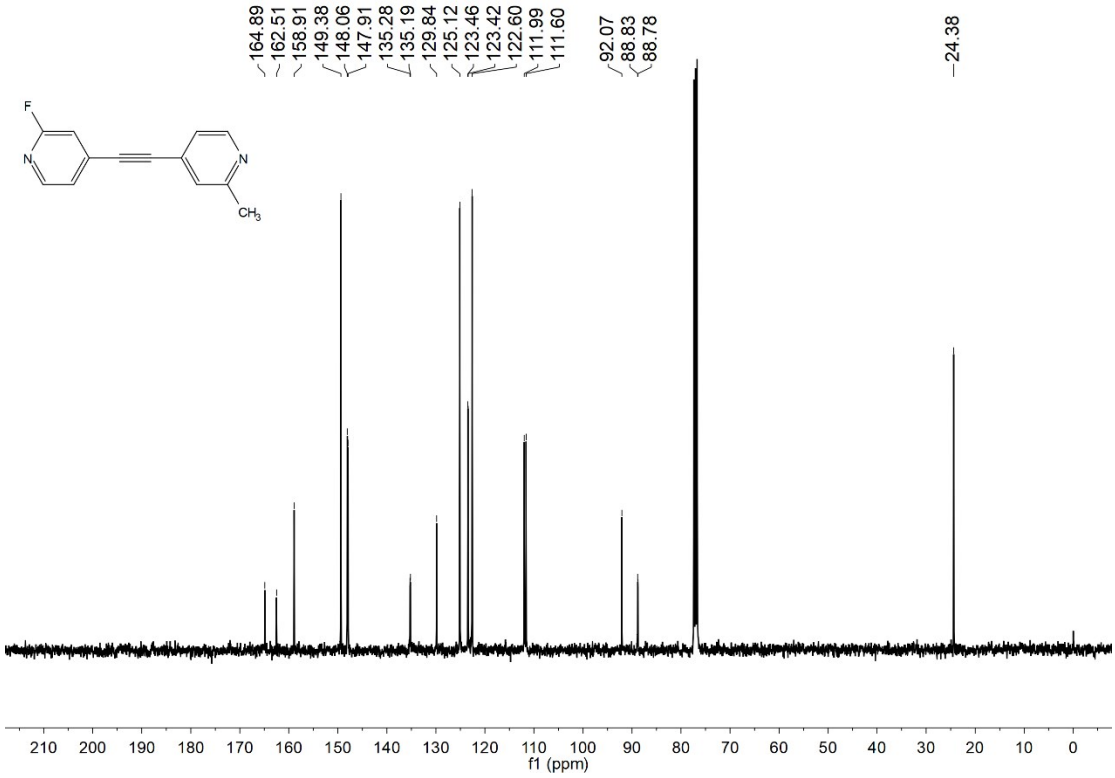
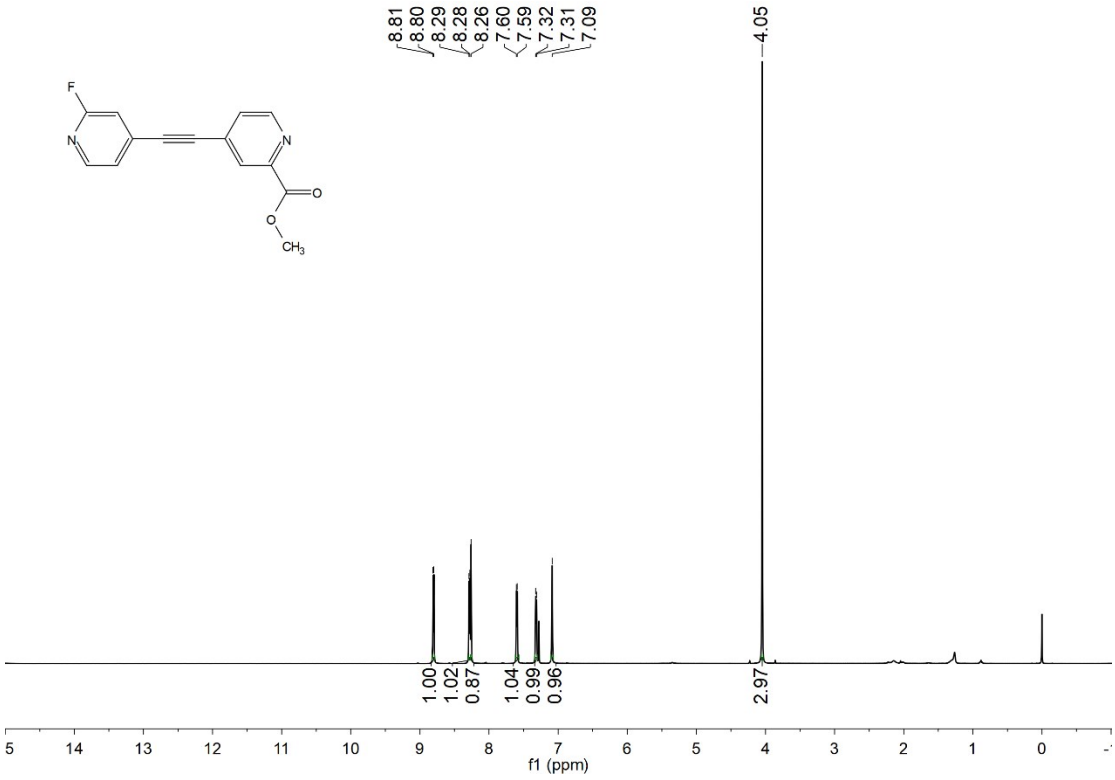
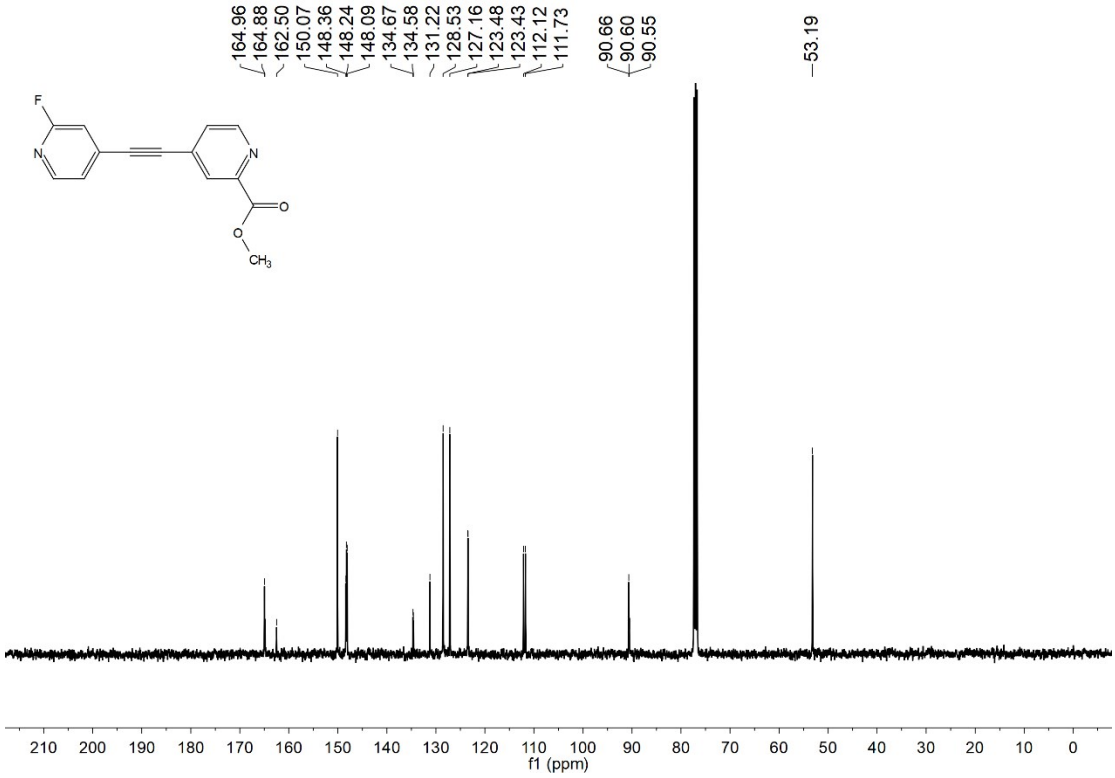


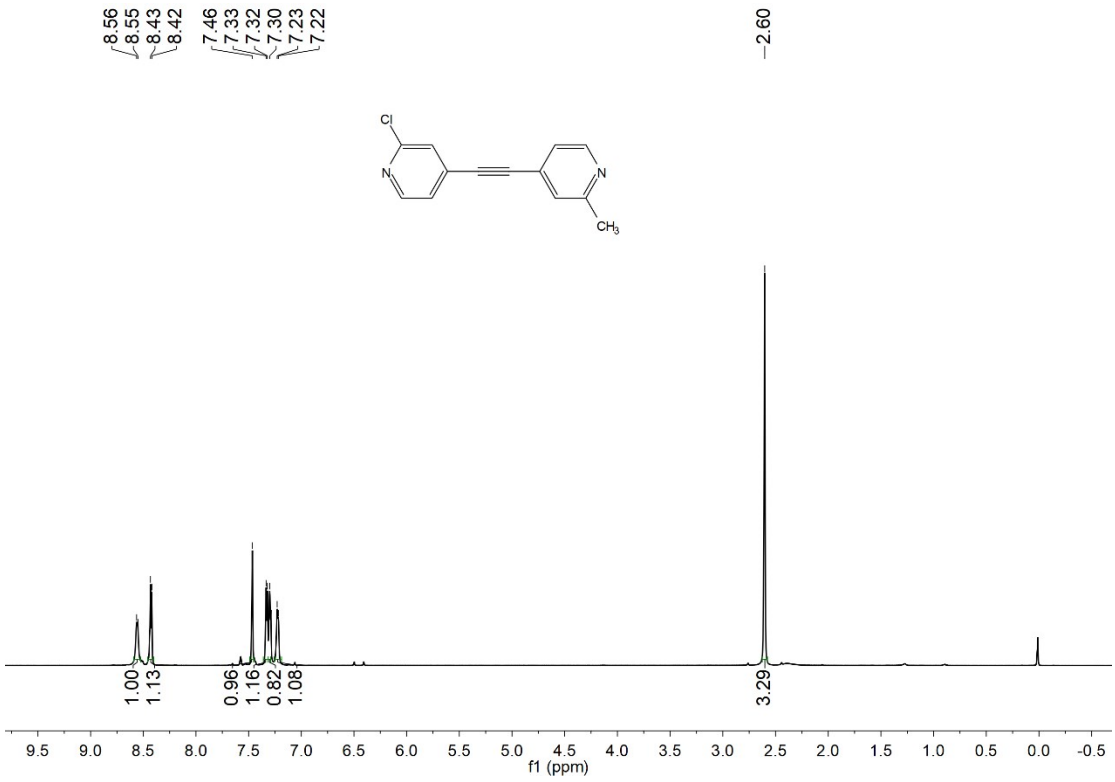
^{1}H NMR of Compound **1k** in $CDCl_3$



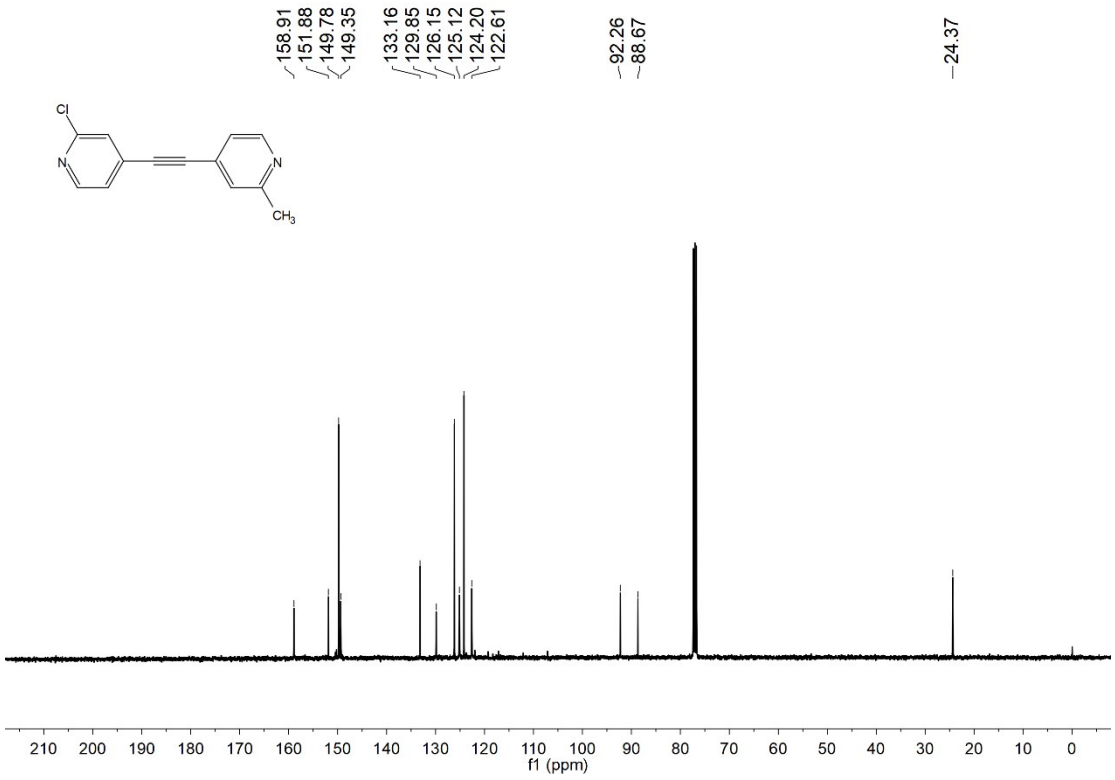
^{13}C NMR of Compound **1k** in $CDCl_3$



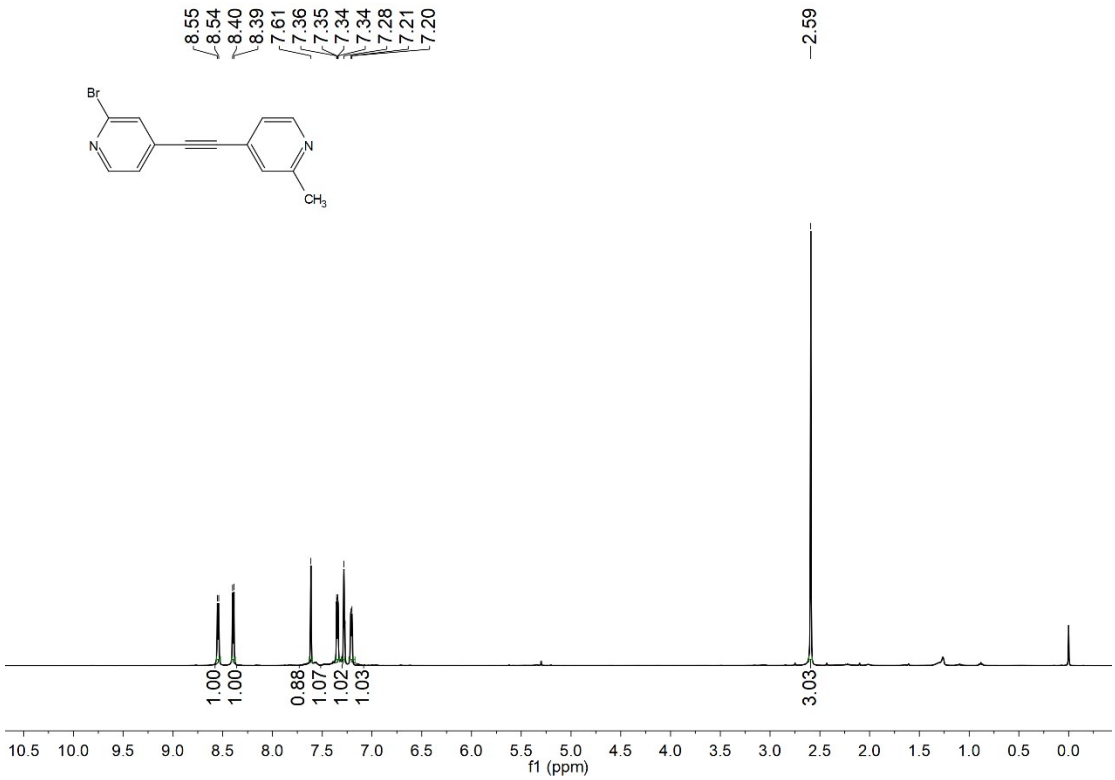
^{1}H NMR of Compound **1l** in $CDCl_3$



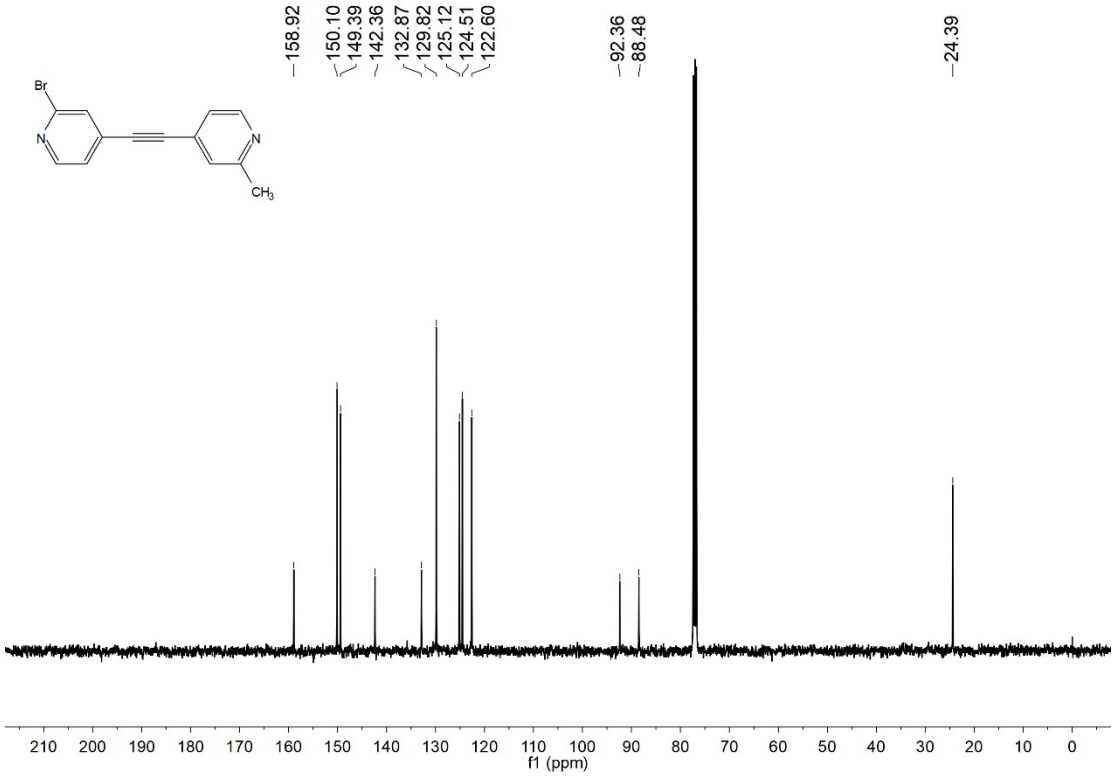
^{13}C NMR of Compound **1l** in $CDCl_3$



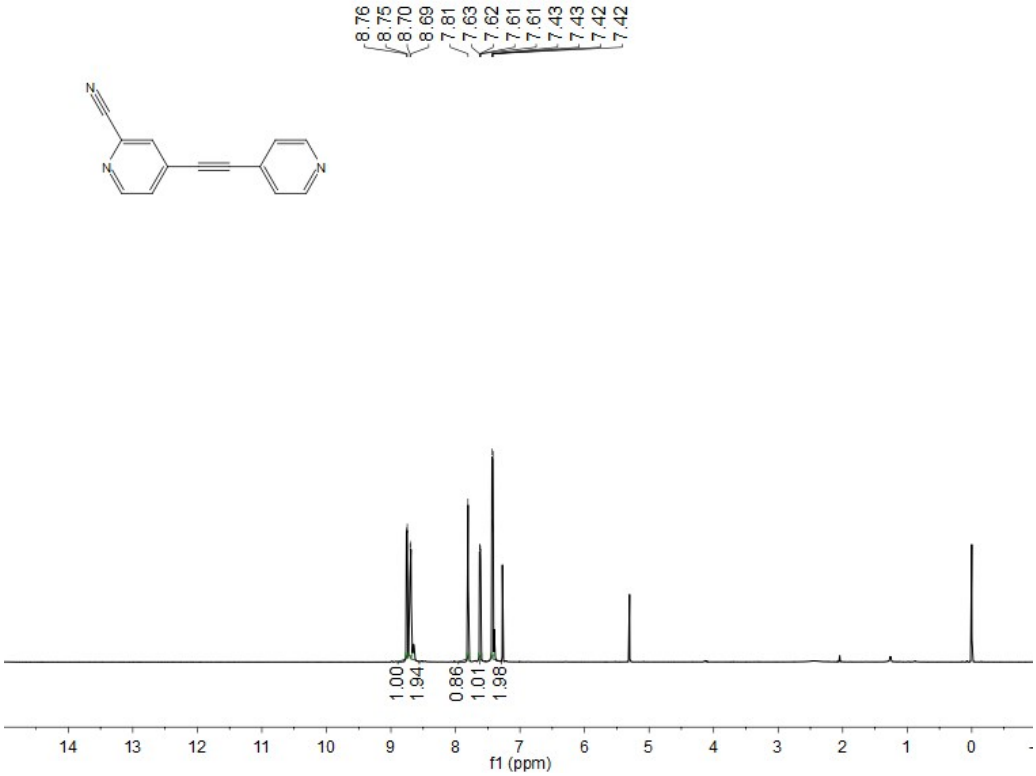
^{1}H NMR of Compound **1m** in $CDCl_3$



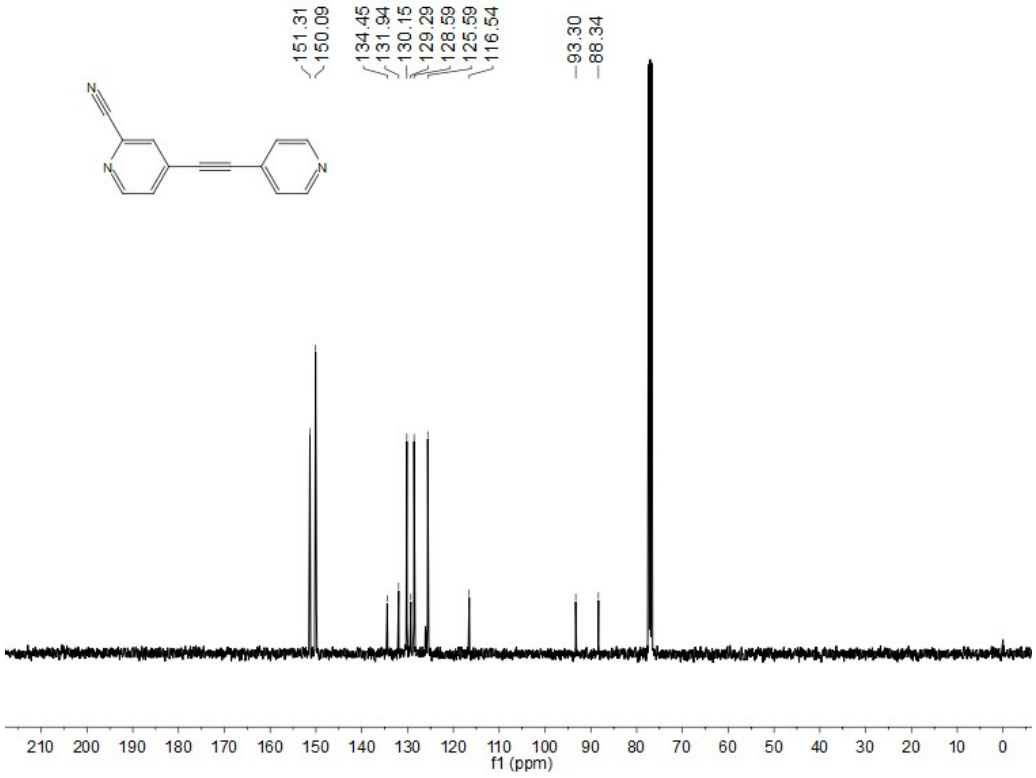
^{13}C NMR of Compound **1m** in $CDCl_3$



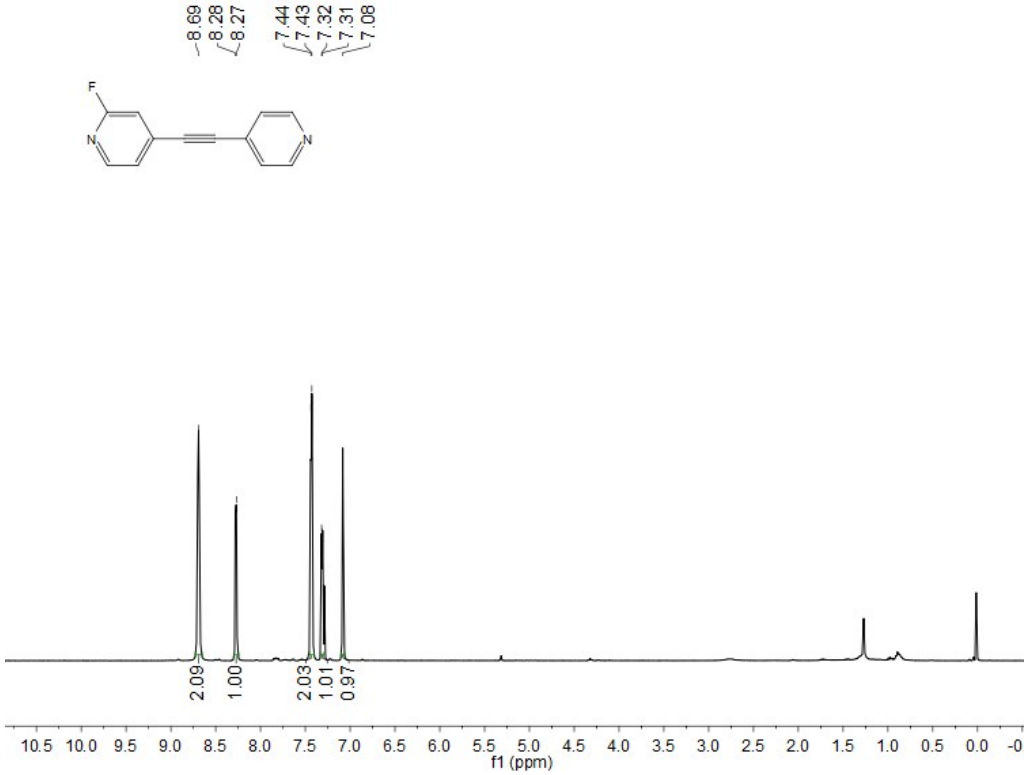
^{1}H NMR of Compound **1n** in $CDCl_3$



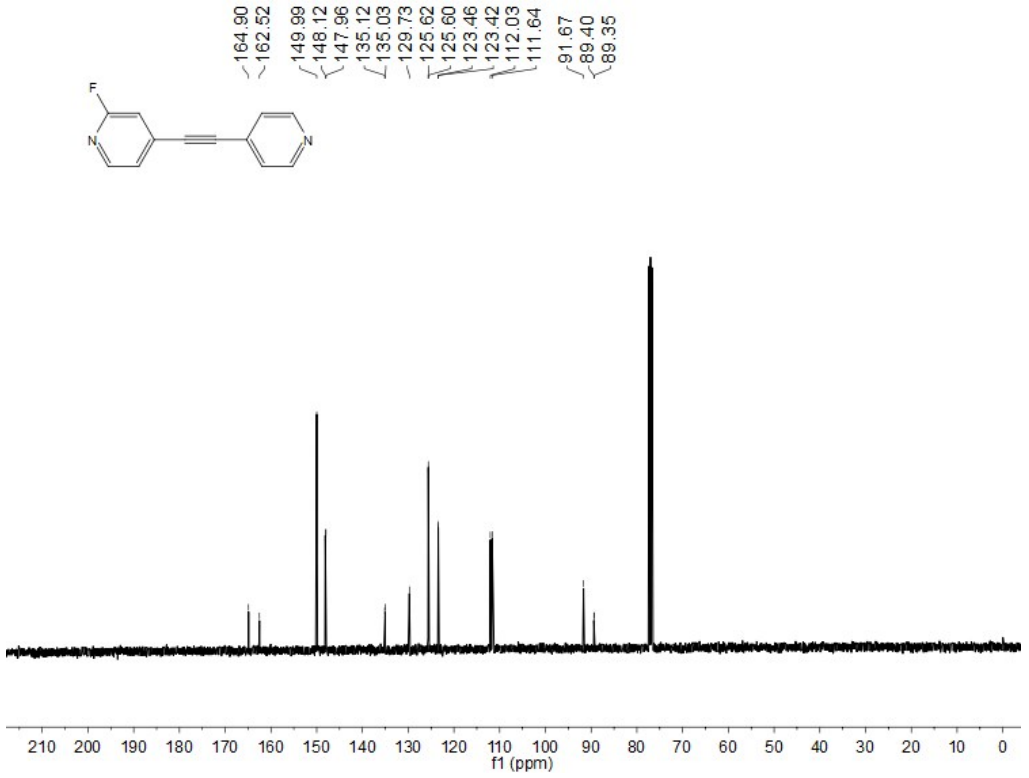
^{13}C NMR of Compound **1n** in $CDCl_3$



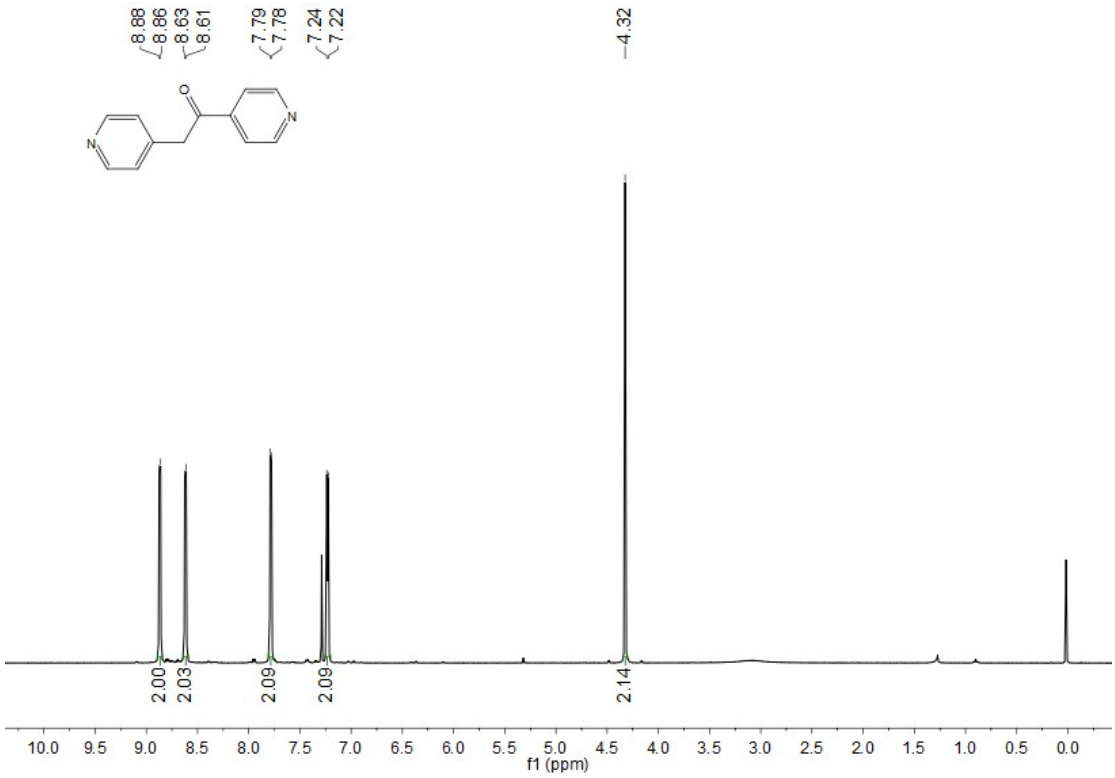
^{1}H NMR of Compound **1o** in $CDCl_3$



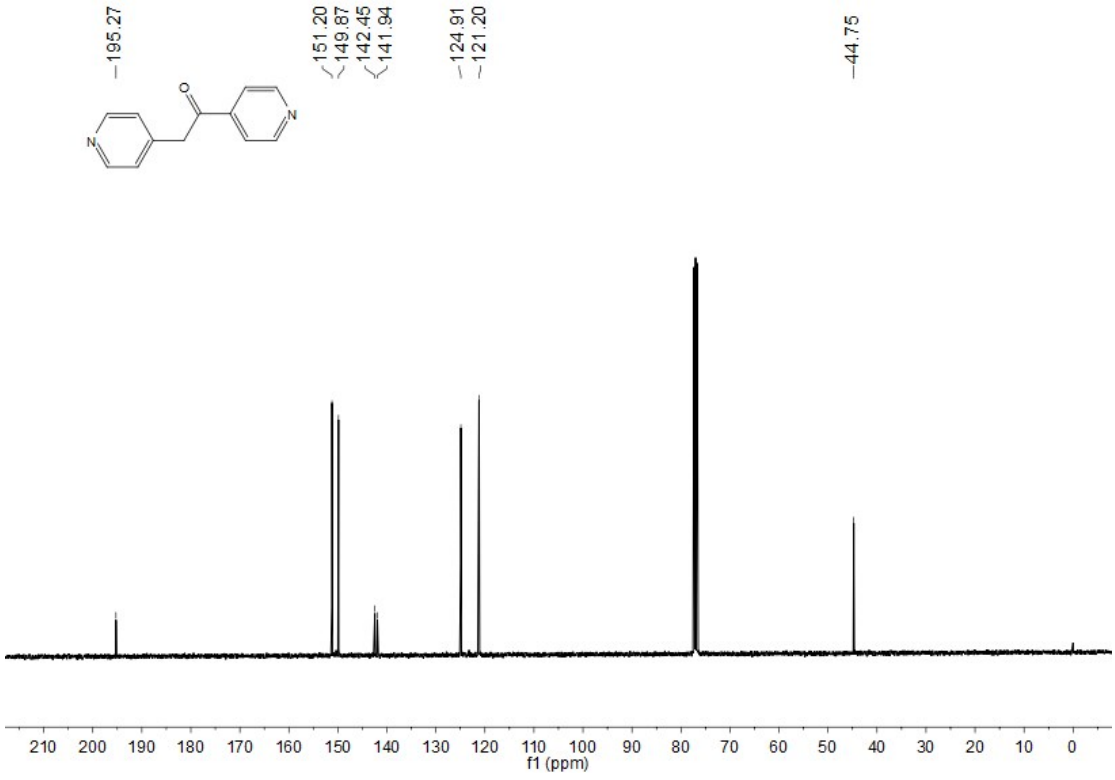
^{13}C NMR of Compound **1o** in $CDCl_3$



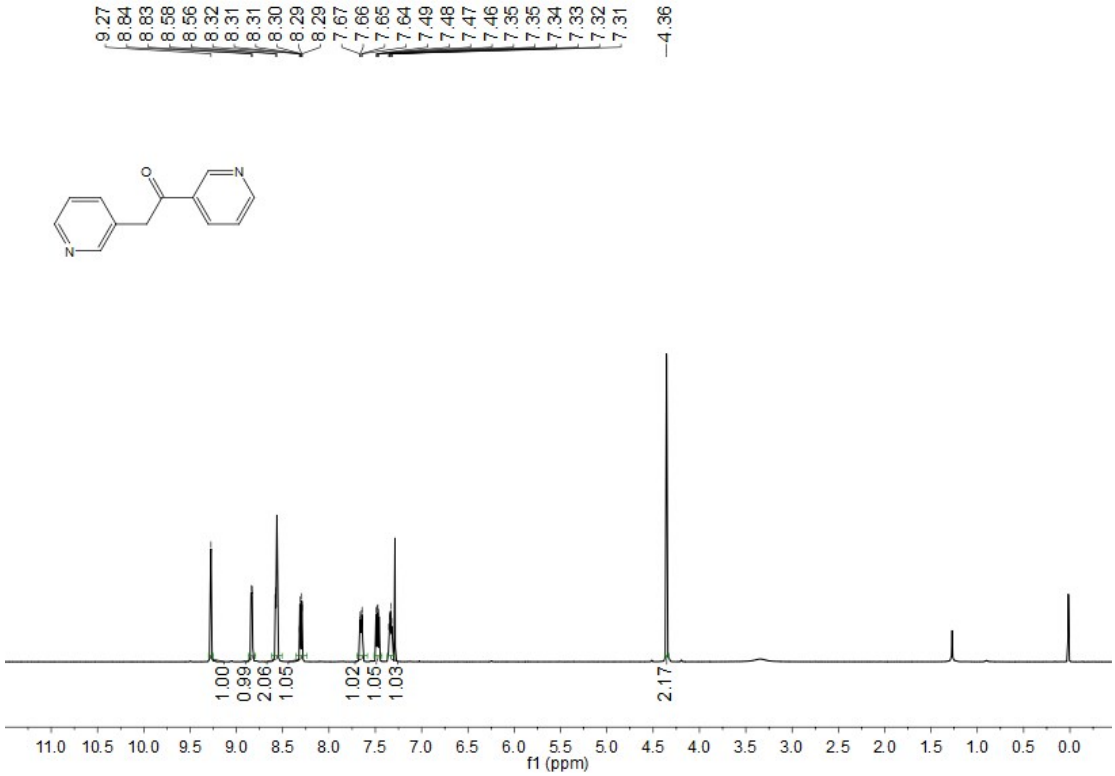
^{1}H NMR of Compound **2a** in $CDCl_3$



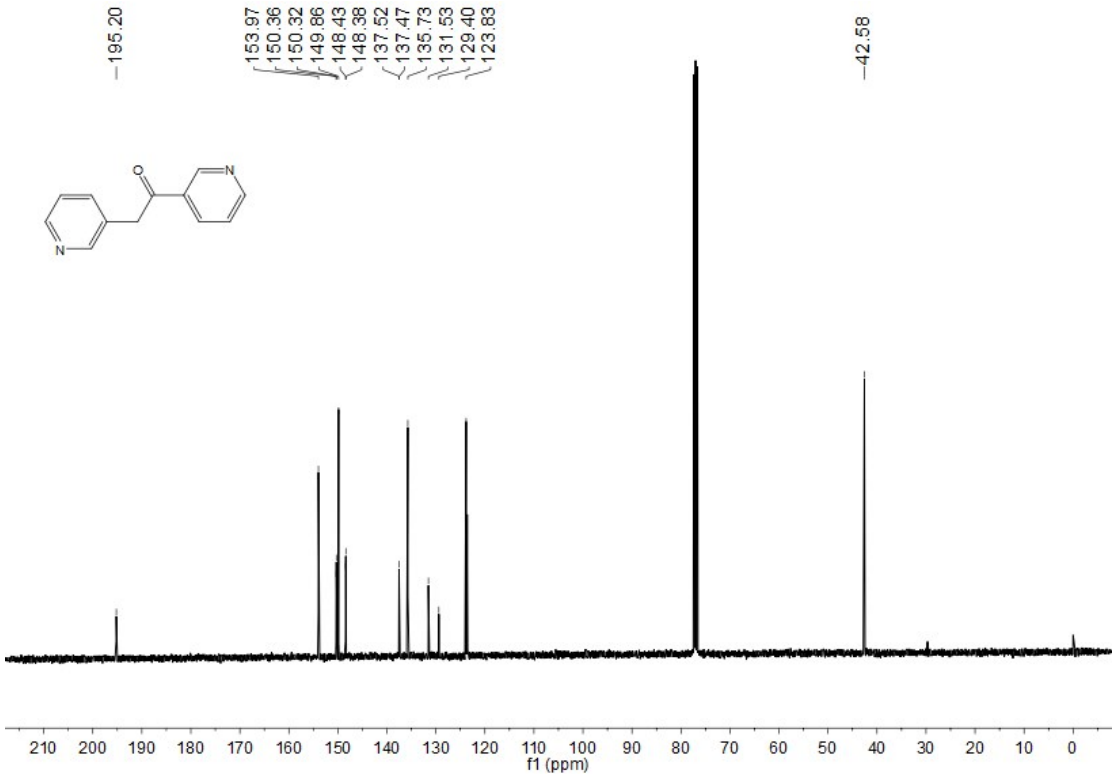
^{13}C NMR of Compound **2a** in $CDCl_3$



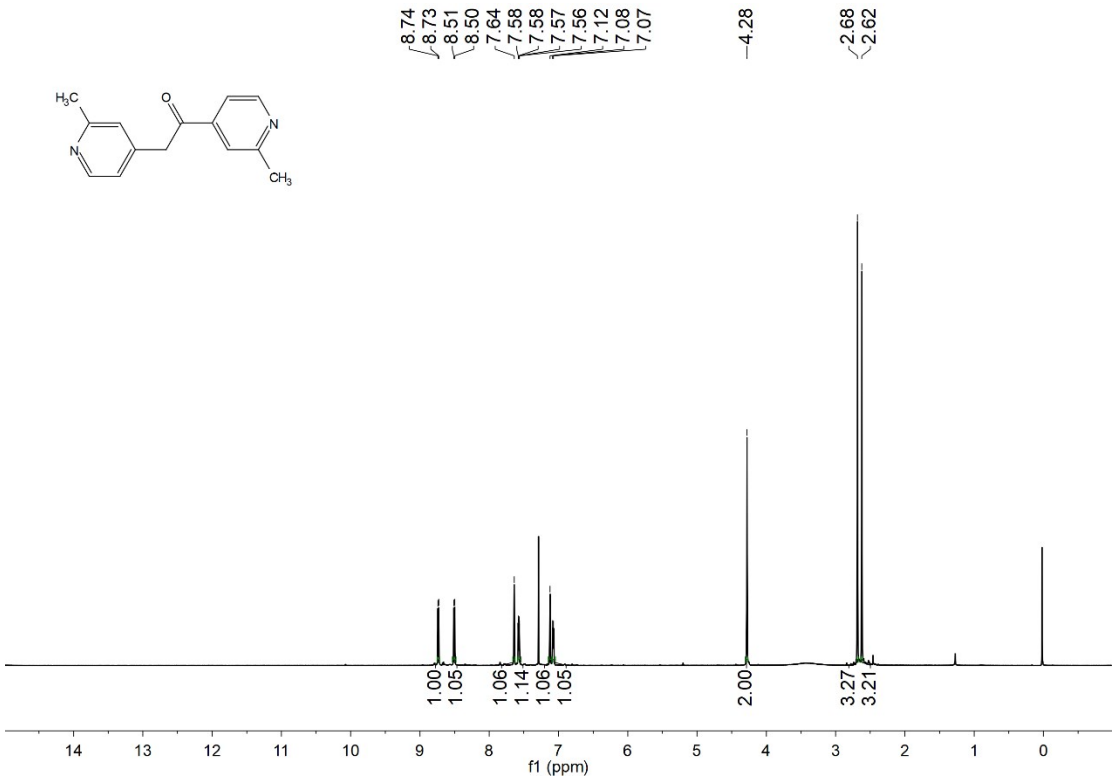
^{1}H NMR of Compound **2b** in $CDCl_3$



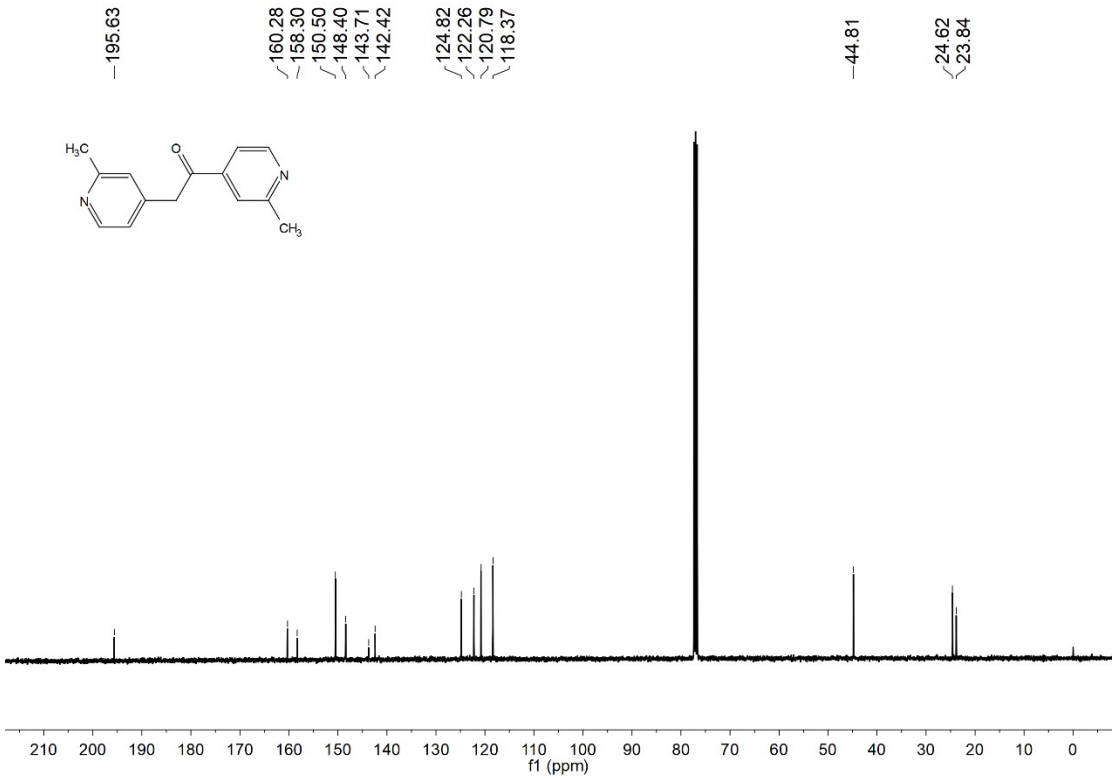
^{13}C NMR of Compound **2b** in $CDCl_3$



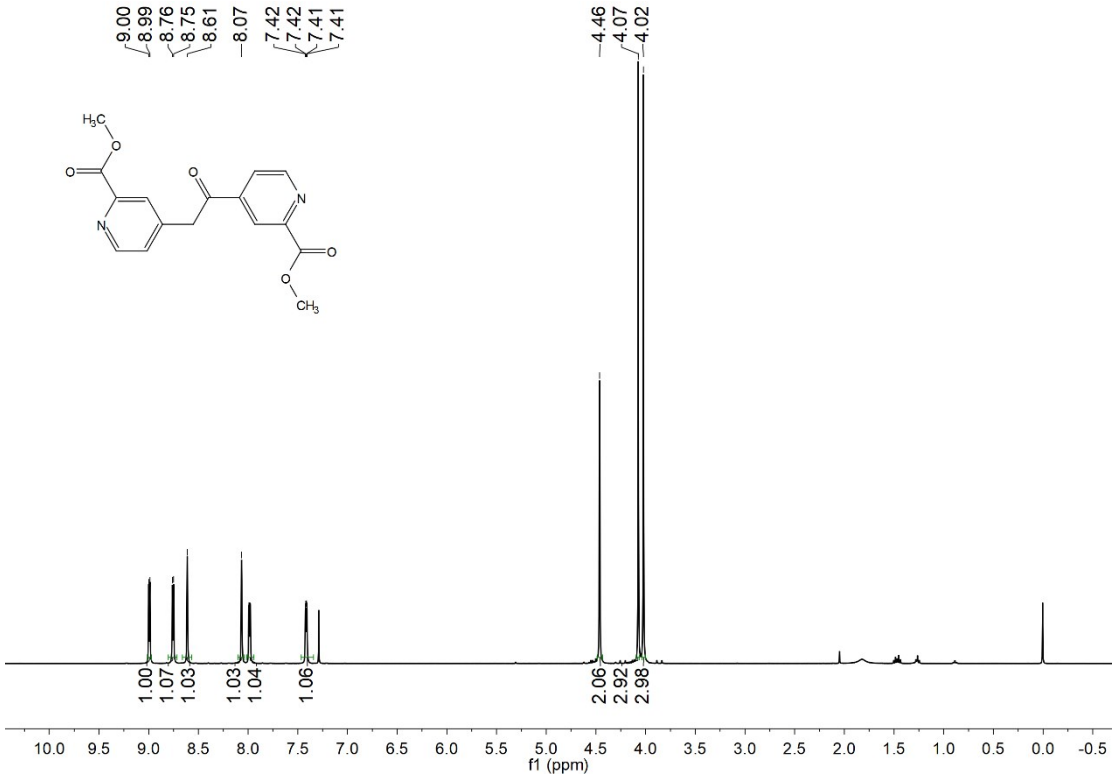
^{1}H NMR of Compound **2d** in $CDCl_3$



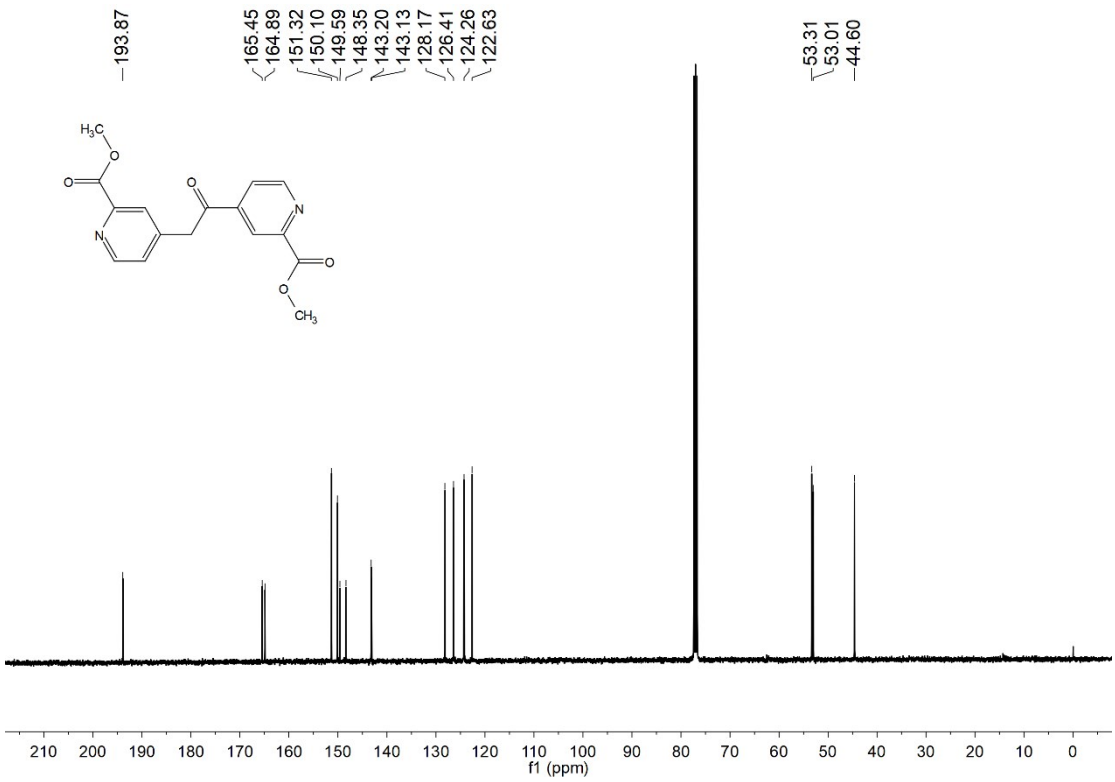
^{13}C NMR of Compound **2d** in $CDCl_3$



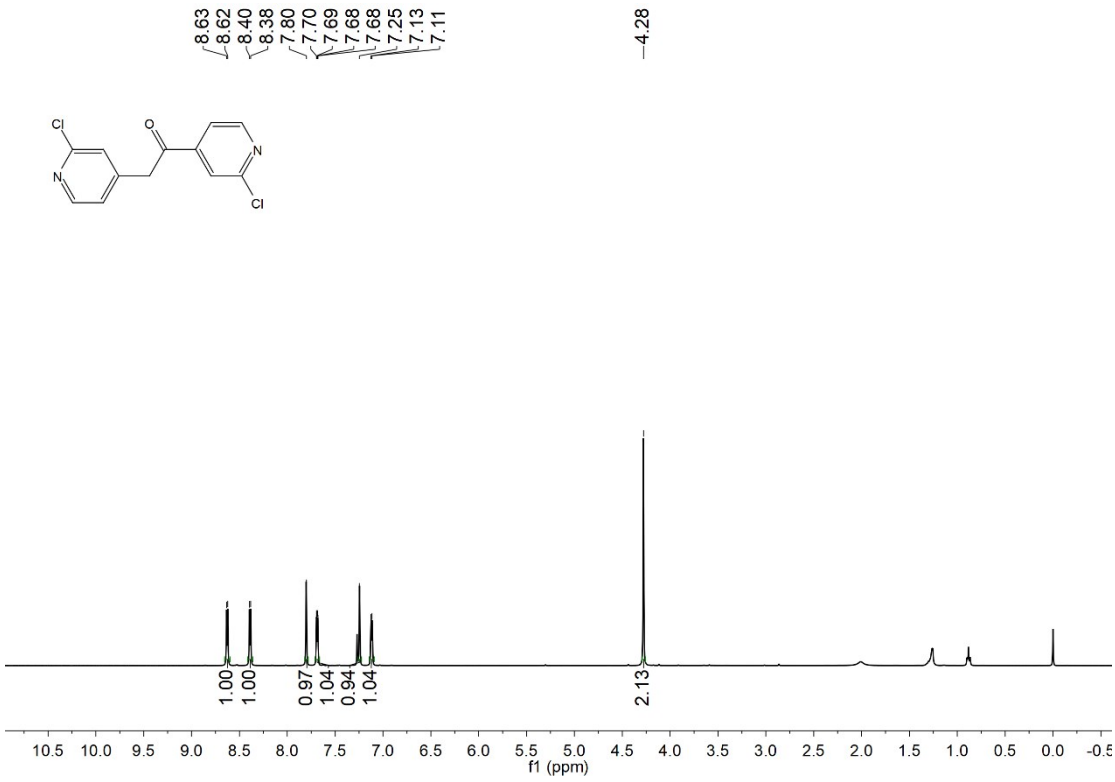
^{1}H NMR of Compound **2e** in $CDCl_3$



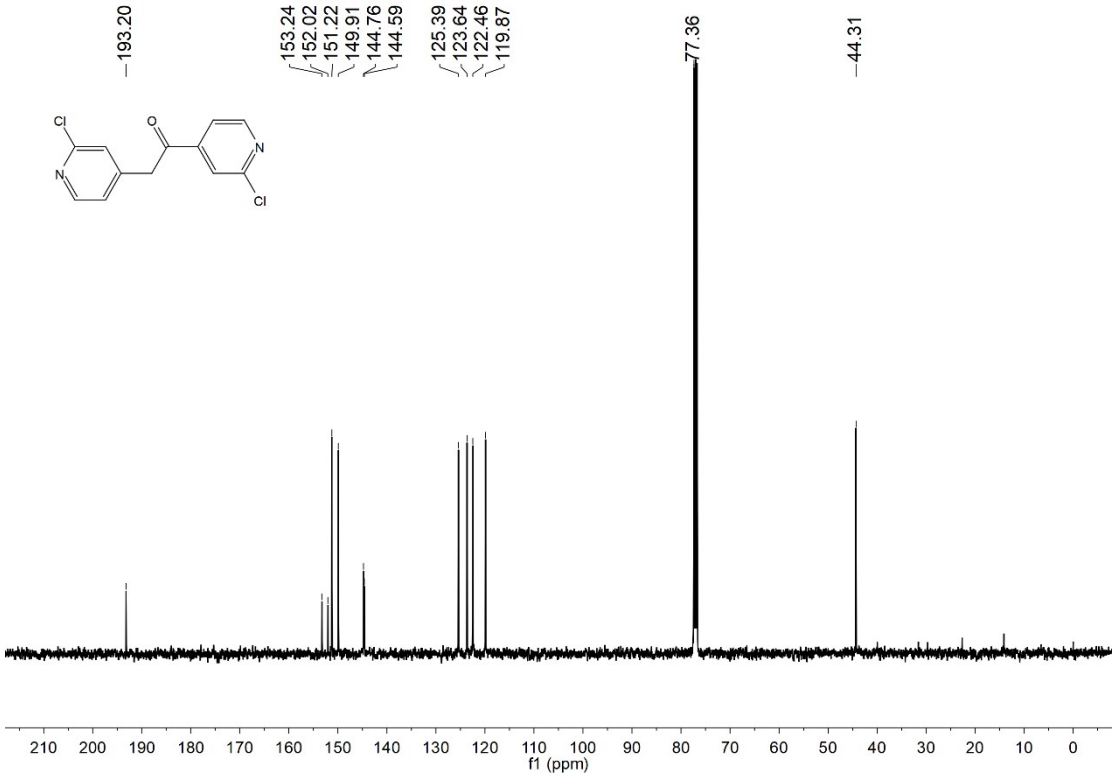
^{13}C NMR of Compound **2e** in $CDCl_3$



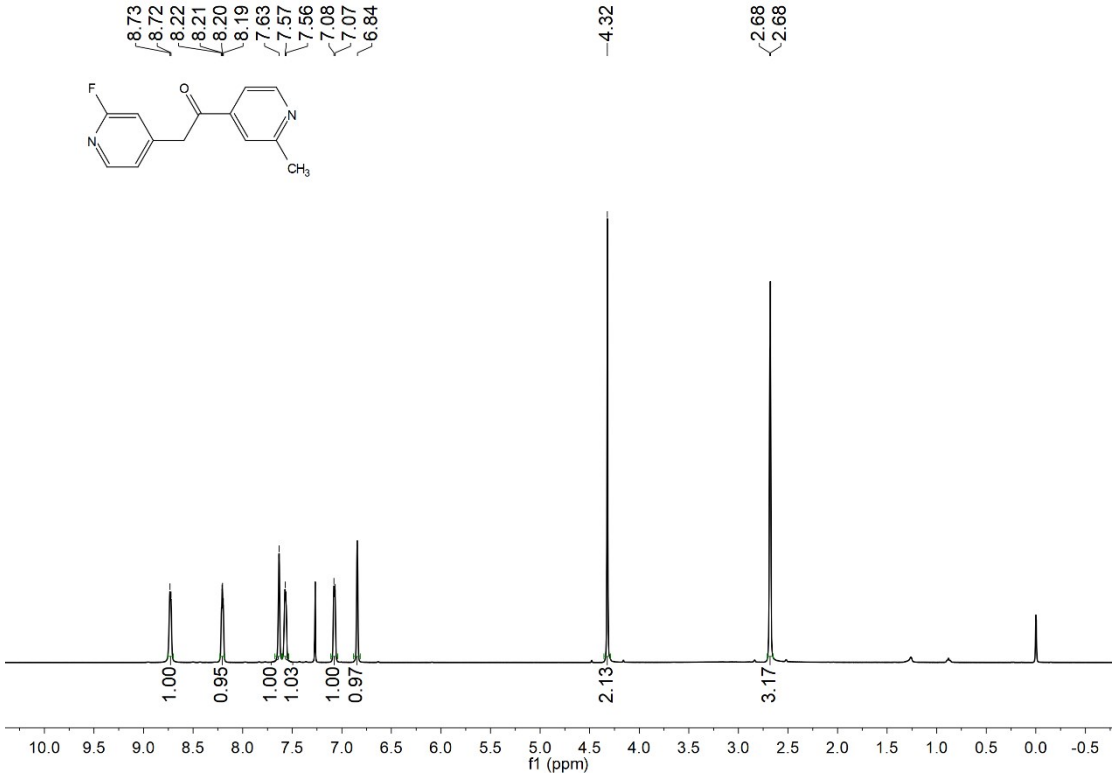
^{1}H NMR of Compound **2g** in $CDCl_3$



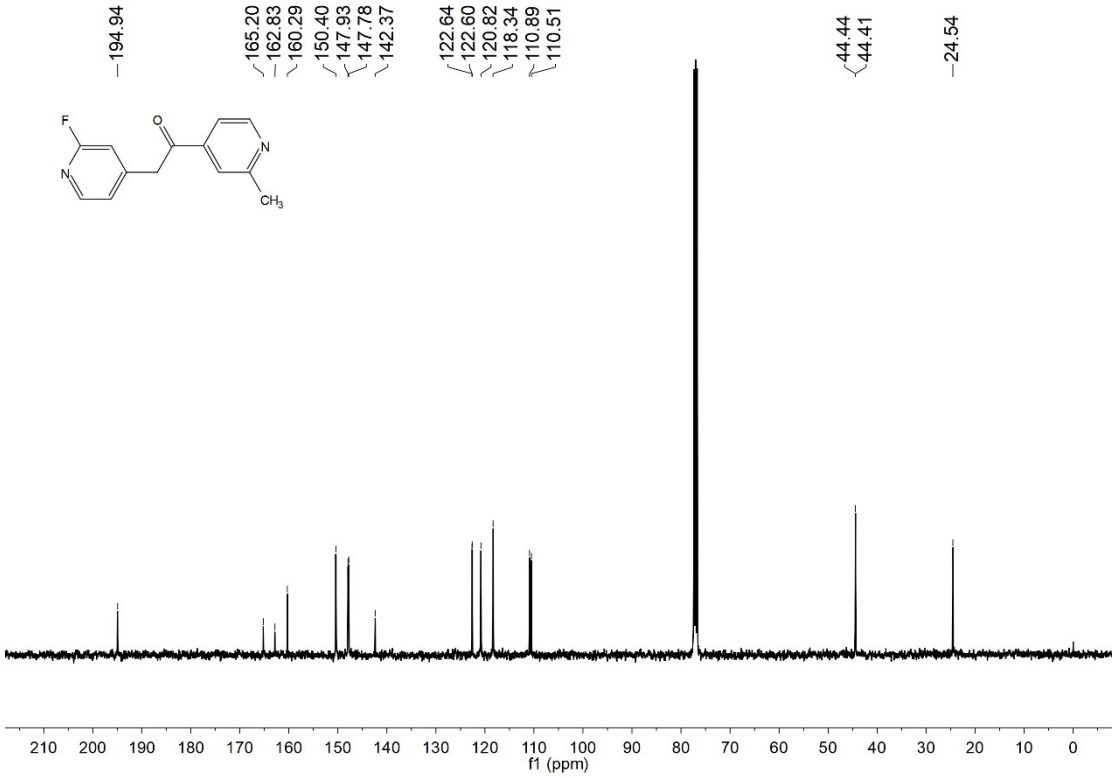
^{13}C NMR of Compound **2g** in $CDCl_3$



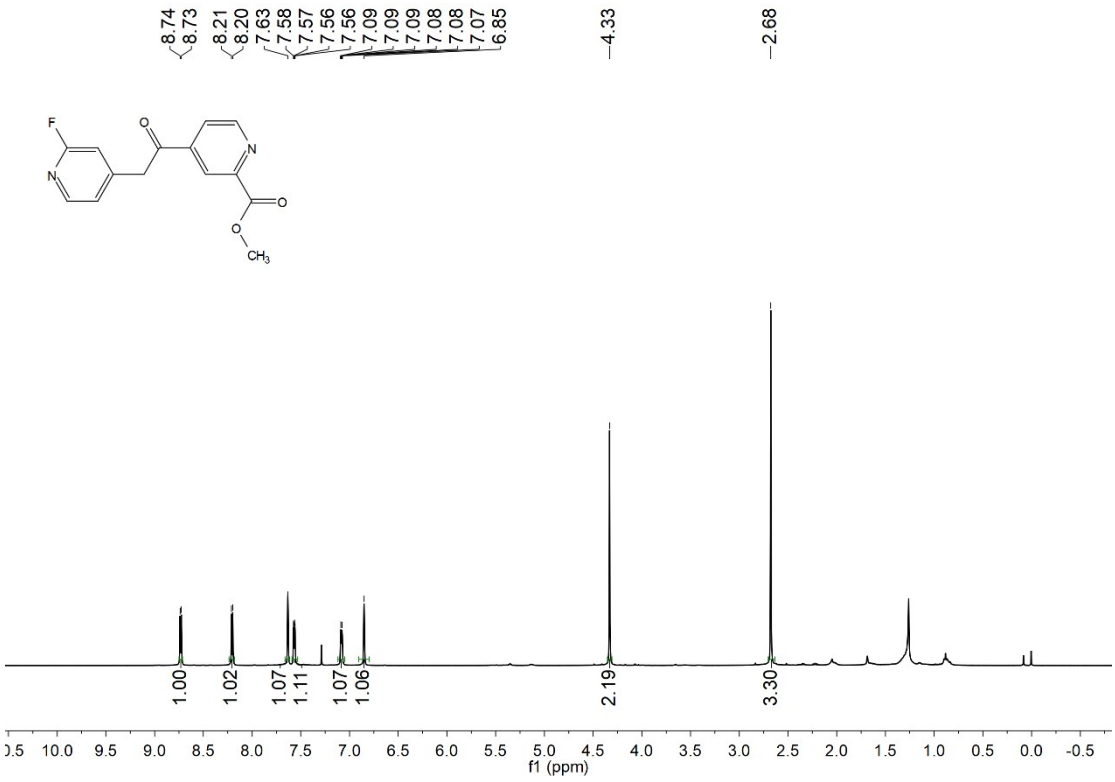
^{1}H NMR of Compound **2j** in $CDCl_3$



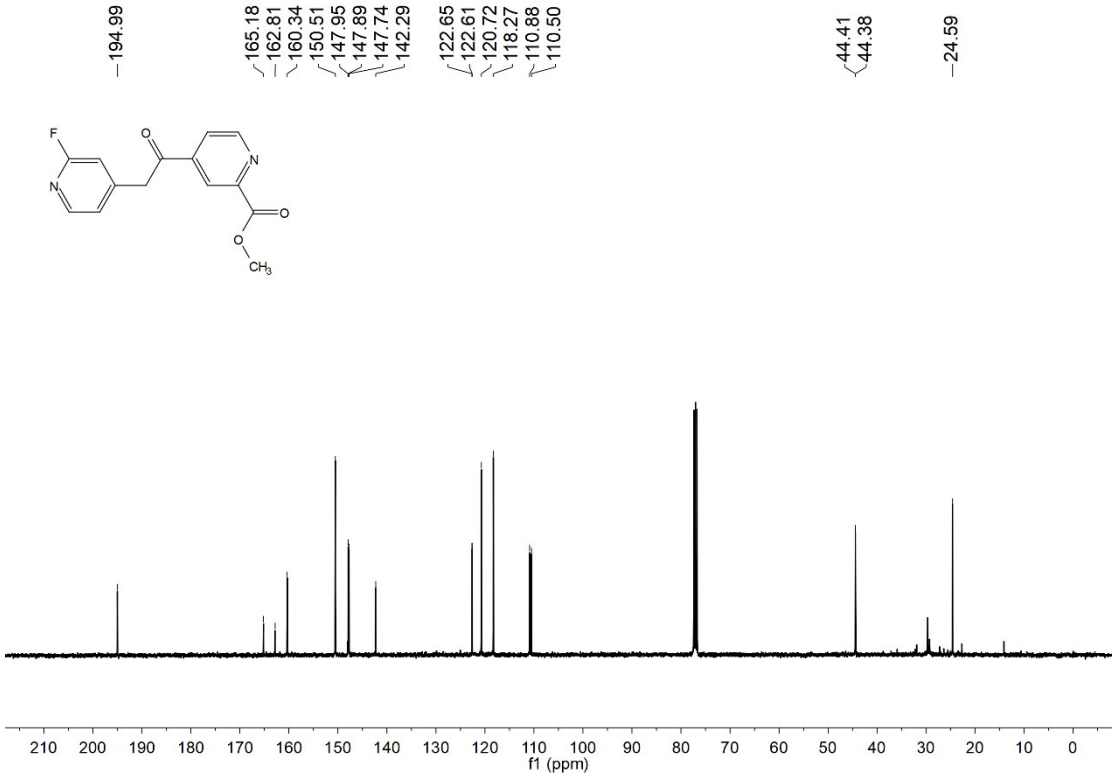
^{13}C NMR of Compound **2j** in $CDCl_3$



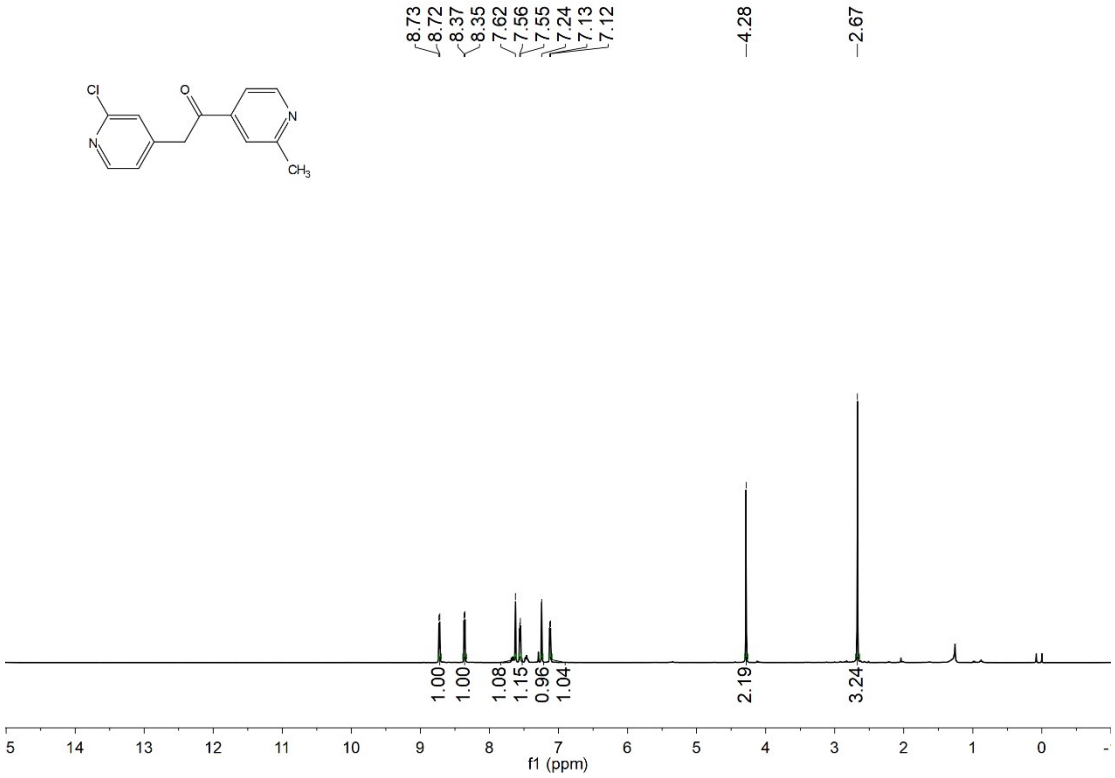
^{1}H NMR of Compound **2k** in $CDCl_3$



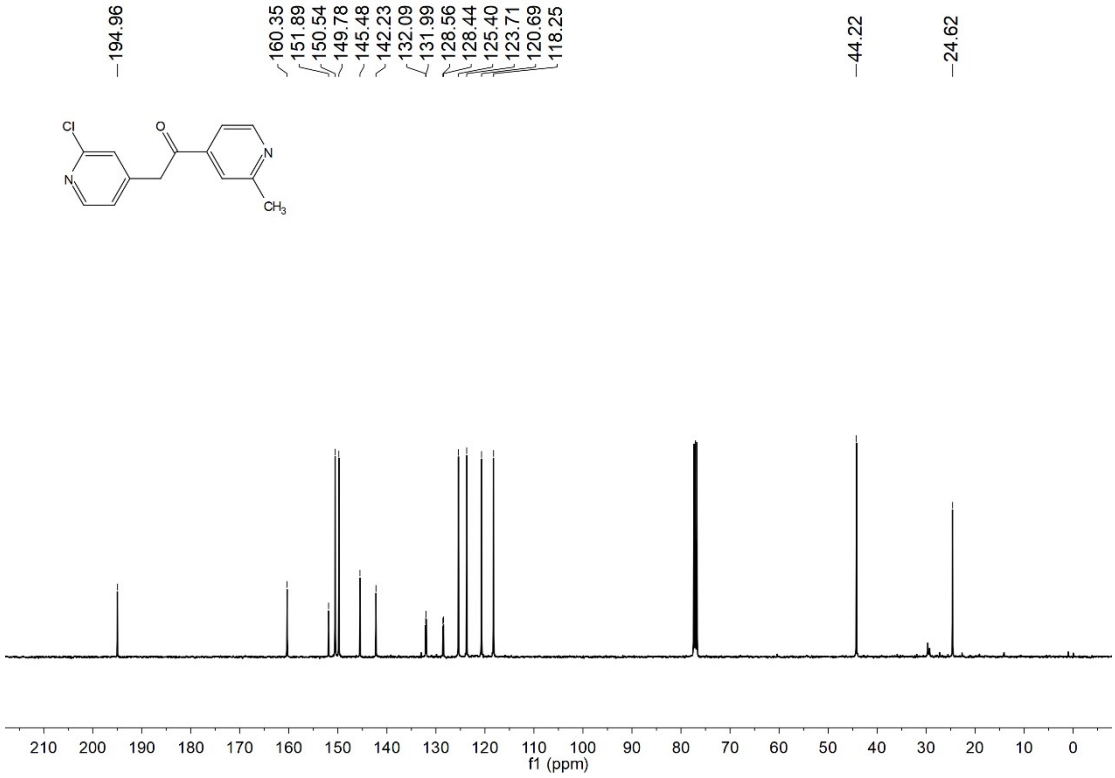
^{13}C NMR of Compound **2k** in $CDCl_3$



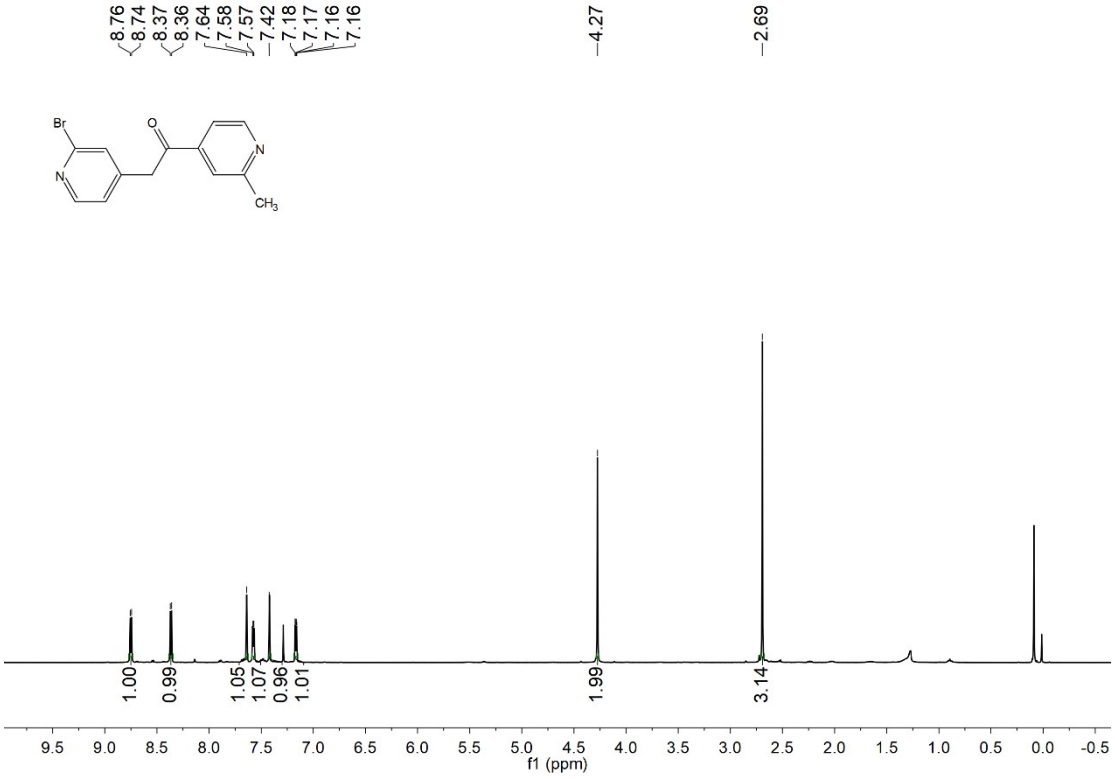
^{1}H NMR of Compound **2l** in $CDCl_3$



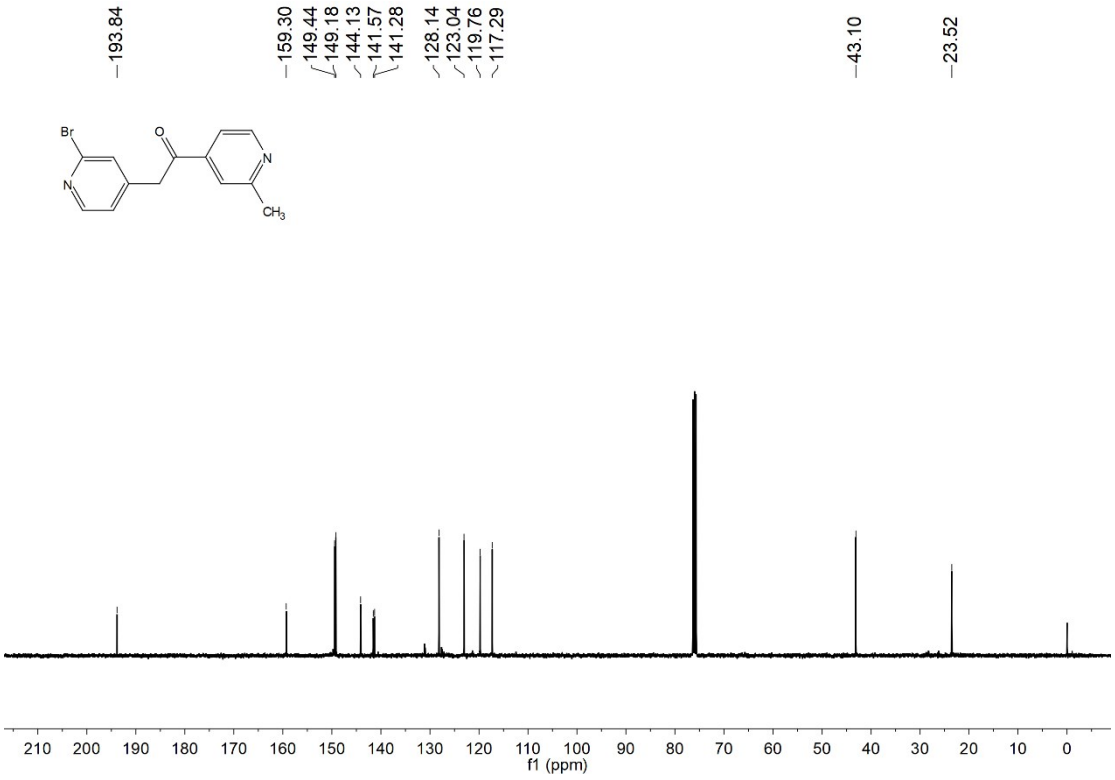
^{13}C NMR of Compound **2l** in $CDCl_3$



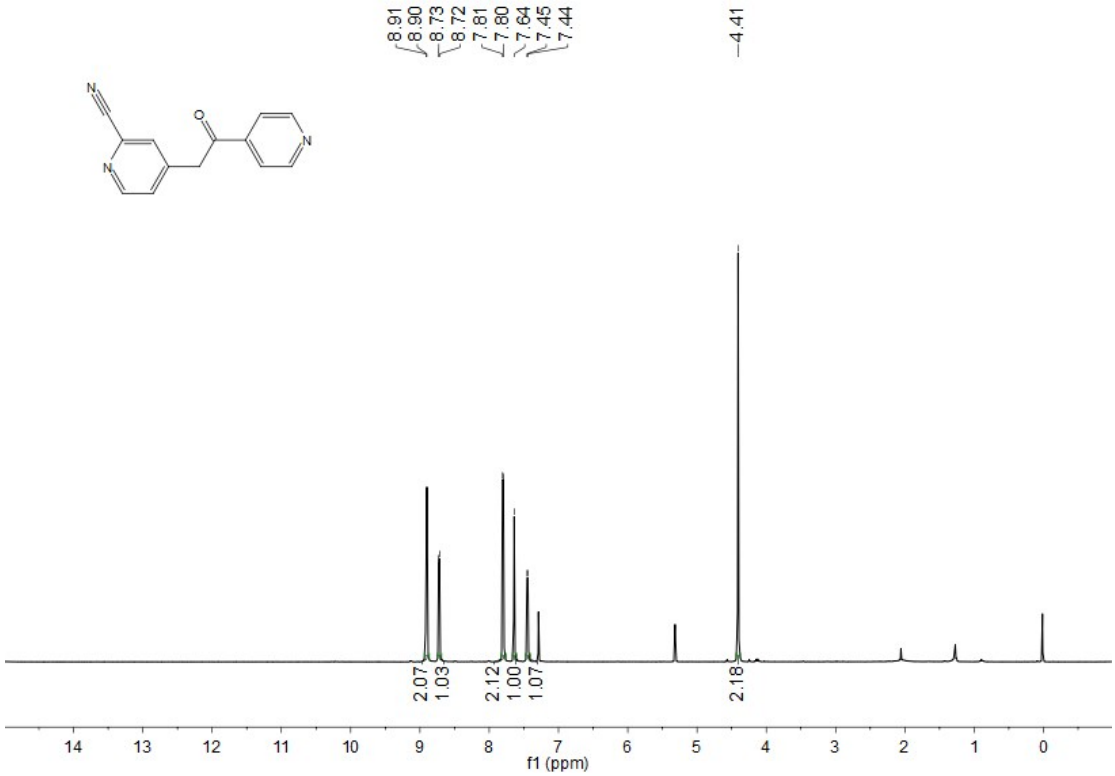
^{1}H NMR of Compound **2m** in $CDCl_3$



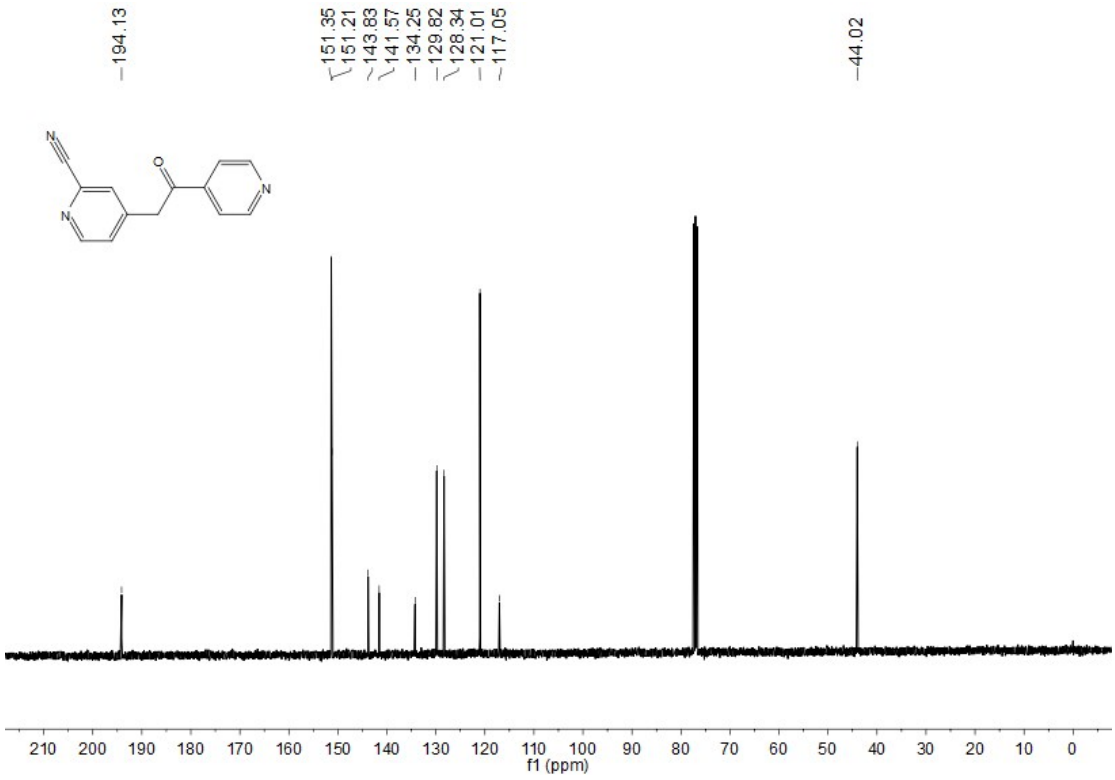
^{13}C NMR of Compound **2m** in $CDCl_3$



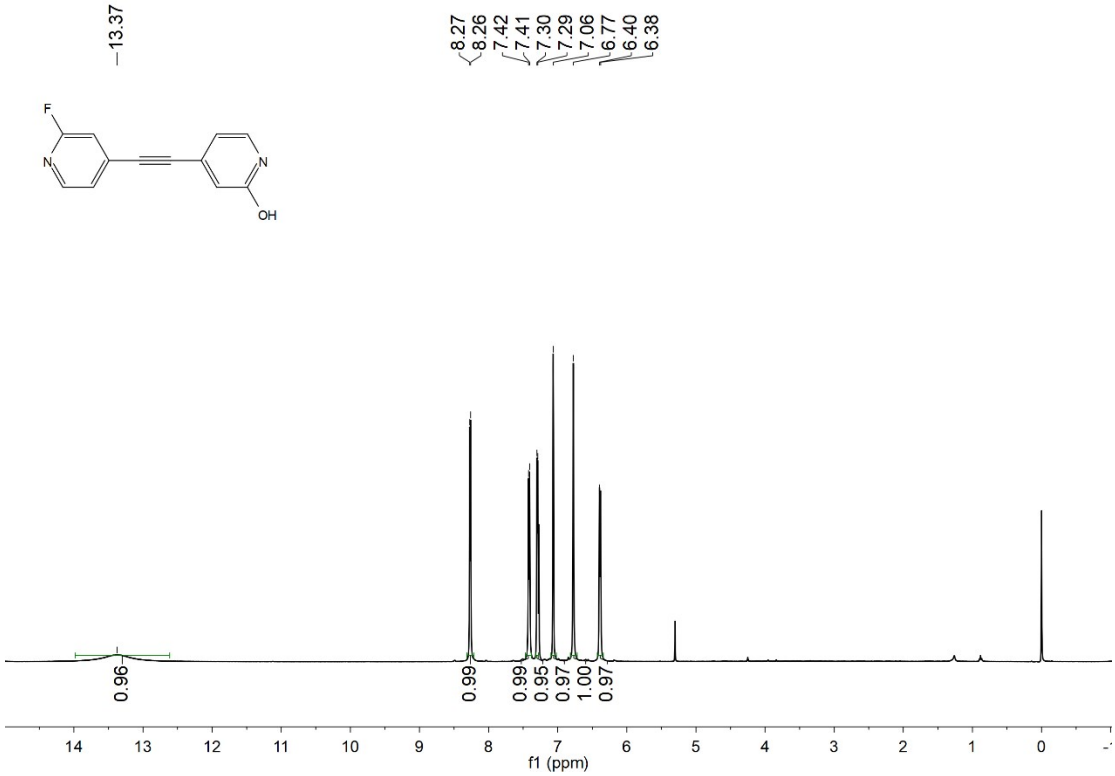
^{1}H NMR of Compound **2n** in $CDCl_3$



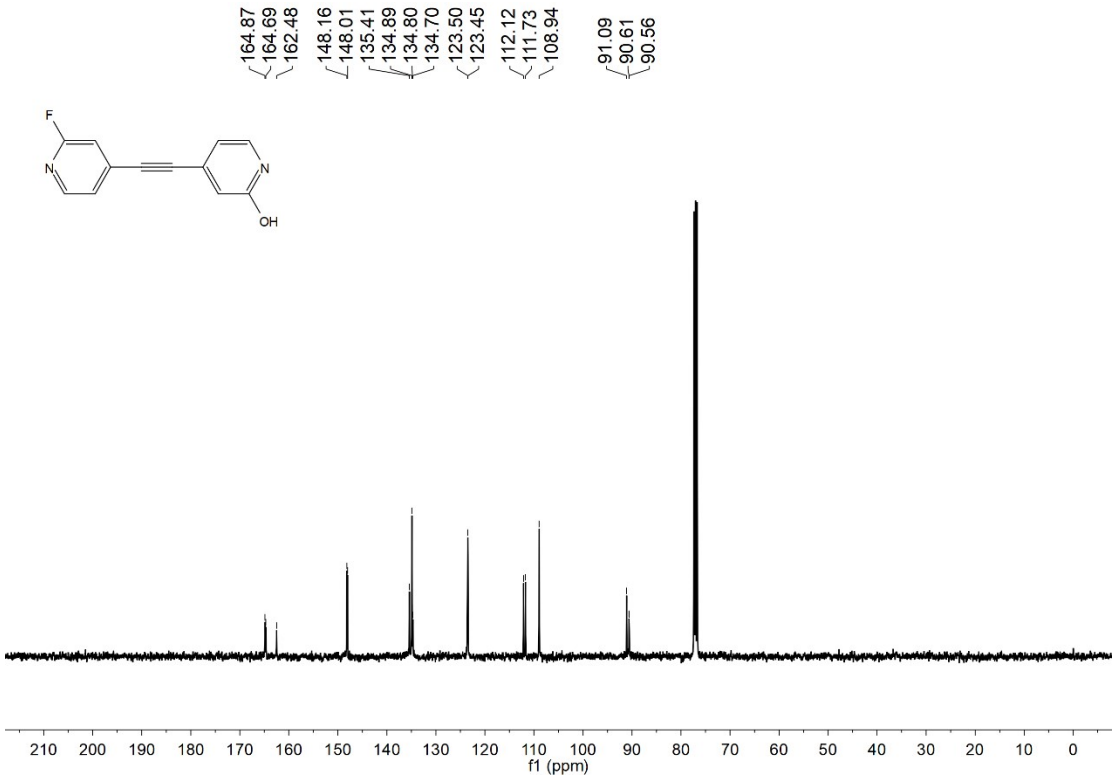
^{13}C NMR of Compound **2n** in $CDCl_3$



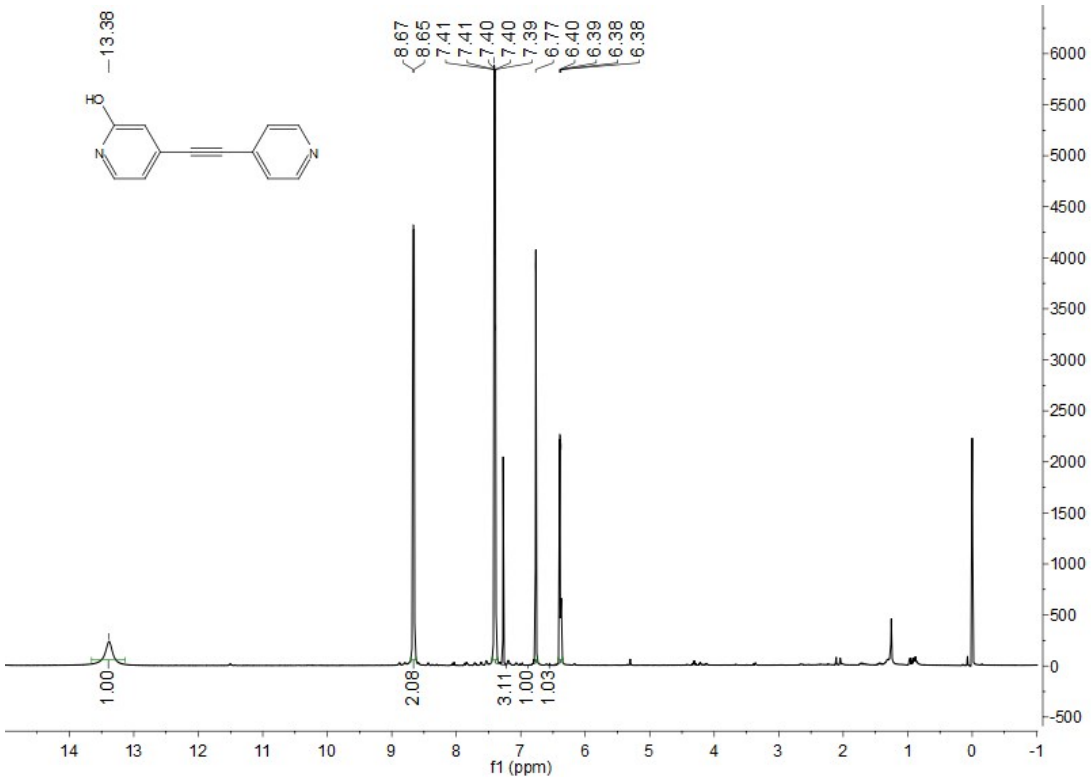
^{1}H NMR of Compound **3f** in $CDCl_3$



^{13}C NMR of Compound **3f** in $CDCl_3$



^{1}H NMR of Compound **3o** in $CDCl_3$



^{13}C NMR of Compound **3o** in $CDCl_3$