Electronic Supplementary Material (ESI) for ChemComm.

Cobalt(Ⅲ)-Catalyzed Alkenylation of Arenes and 6-Arylpurines with Terminal Alkynes: Efficient Access to Functional Dyes

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SUPPORTING INFORMATION

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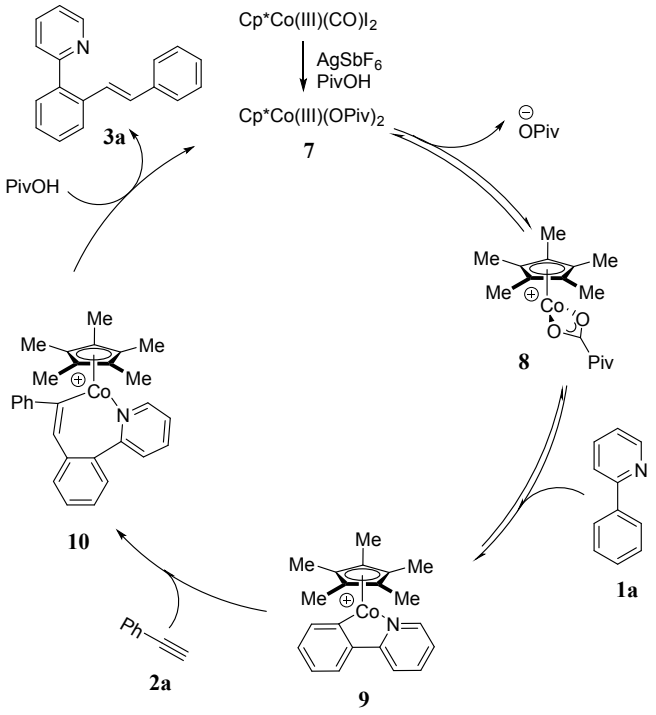
General Considerations. Reactions were performed without special precautions in 1-dram screw-cap vials equipped with a stir bar. For chromatography, 200-300 mesh silica gel (Qingdao, China) was employed. Preparative thin layer chromatography was performed on Analtech TLC plates (20 cm × 20 cm, 20 microns). ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded on an Bruker Avance 400 MHz instrument in deuterated chloroform $CDCl_3$ using TMS or residual solvent peak as a standard. Mass spectroscopy (ESI-MS) and High Resolution Mass spectroscopy (HRMS) data were recorded on a Finnigan LCQ^{DECA} and a Bruker Daltonics Bio TOF mass spectroscopy respectively. Fluorescence emission spectra were obtained using FluoroMax-4 Spectrofluorophotometer (HORIBA Jobin Yvon) at 298 K. All solvents were dried according to the standard methods prior to use. All of the solvents were either HPLC or spectroscopic grade in the optical spectroscopic studies.

General Procedure For Co(Ⅲ)-Catalyzed Addition of Arene C-H Bonds. A suspension of 2-phenylpyridine **1a** (0.20 mmol), phenylacetylene **2a** (0.2 mmol), $Cp^*CoI_2(CO)$ (4.8 mg, 5.0 mol %), $AgSbF_6$ (7.2 mg, 10.0 mol %) and PivOH (12μL, 0.5 eq) in DCE (1.0 mL) was stirred at 60 °C for 5 h. At ambient temperature, the solvent was evaporated in vacuo and the remaining residue was purified by column chromatography on silica gel (n-hexane /EtOAc) to yield product **3a**.

General Procedure For Co(Ⅲ)-Catalyzed Addition of 6-arylpurines. A suspension of 6-arylpurine **5a** (0.20 mmol), phenylacetylene **2a** (0.2 mmol), $Cp^*CoI_2(CO)$ (4.8 mg, 5.0 mol %), $AgSbF_6$ (7.2 mg, 10.0 mol %) and PivOH (12μL, 0.5 eq) in DCE (1.0 mL) was stirred at 60 °C for 5 h. At ambient temperature, the solvent was evaporated in vacuo and the remaining residue was purified by column chromatography on silica gel (n-hexane /EtOAc) to yield product **6a**.

Proposed catalytic cycle.



Scheme S1. Proposed catalytic cycle.

A plausible reaction mechanism is described in Scheme 3. We propose that the initial step is a ligand exchange between $Cp^*Co(CO)I_2$ and PivOH,[1] reversibly generating the catalytically active species **8**. The species **9** was formed via the coordination of 2-phenylpyridine **1a** and regioselective C-H metalation. 1-(Pyrinidin-2-yl)-1H-indole and 6-arylpurines afforded mono-additive products only, implying the progress through the five-membered metallo-cycle **9**. Thereafter, phenylacetylene **2a** was inserted into the coordinated species **9** to produce the key intermediate **10**. Ultimately, the protodemetalation of **10** gave the desired product **3a** and regenerated the initial complex **7**.

Preparations of InD. InD was prepared by 1-(pyrimidin-2-yl)-1H-indole-5-carbaldehyde and 4-ethynylbenzaldehyde in present of Cp*CoI_2(CO) (4.8 mg, 5.0 mol %), $AgSbF_6$ (7.2 mg, 10.0 mol %) and PivOH (12 μL, 10.0 mol %) in DCE (1.0 mL) was stirred at 60 °C for ten minutes.

Fluorescence analysis. Probe **InD** was prepared in DMSO at a concentration of 5 mM. All UV/Vis and fluorescence titration experiments were performed using 5 μM **InD** in PBS buffer solution (pH 7.4, 20 mM) with variety of analytes (100 μM) at room temperature. Fluorescence emission spectra were obtained with a Xenon lamp and 1.0 cm quartz cells.

Confocal imaging of living cells. All cells were cultured in Dulbecco's modified Eagle medium (DMEM) containing 10% fetal bovine serum and 1% Antibiotic-Antimycotic at 37 ºC in a 5% CO_2/95% air incubator. For fluorescence imaging, cells (4×10^3/well) were passed on a 6-well plate and incubated for 24h. After the treatment of cells, the imaging was carried out on Leica TCS SP8.

Table S1: The optical properties of **InD** in different solvents.

Solvent	λ_{abs}/nm[a]	λ_{max}/nm[b]	$\Delta\lambda$/nm	Φ[c]
PhMe	337	459	122	0.68
$CHCl_3$	343	464	121	0.88
MeCN	350	480	130	0.69
DMSO	356	488	132	0.95
EtOH	348	507	159	0.69
PBS	348	558	210	0.031

[a]The maximal absorption of the dye in different solvents.

[b]The maximal emission of the dye in different solvents.

[c]Φ is the relative fluorescence quantum yield estimated by using fluorescein (Φ = 0.85 in 0.1 N NaOH).[2]

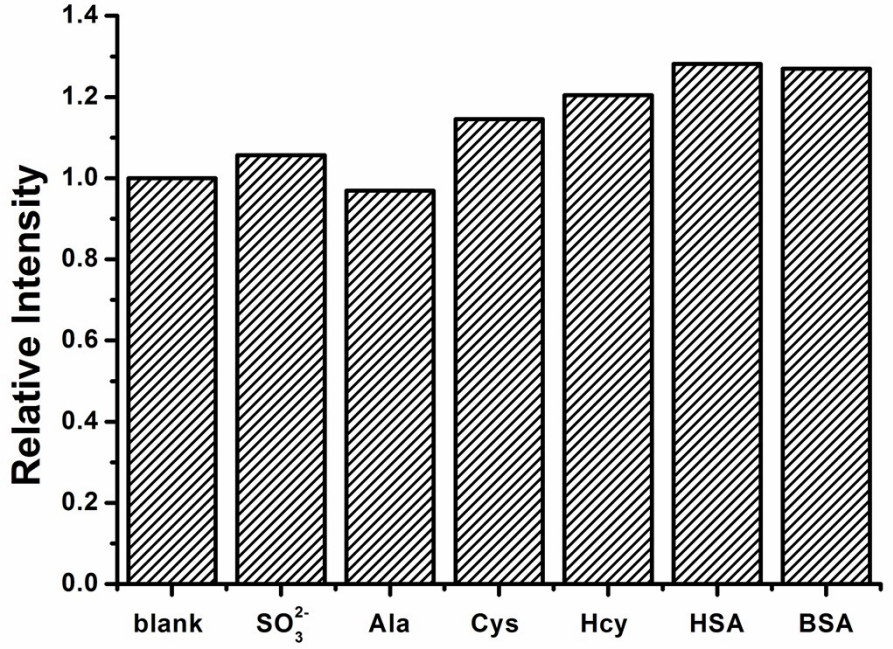


Figure S1: The reactivity of **InD** towards some nucleophilic species and biological species.

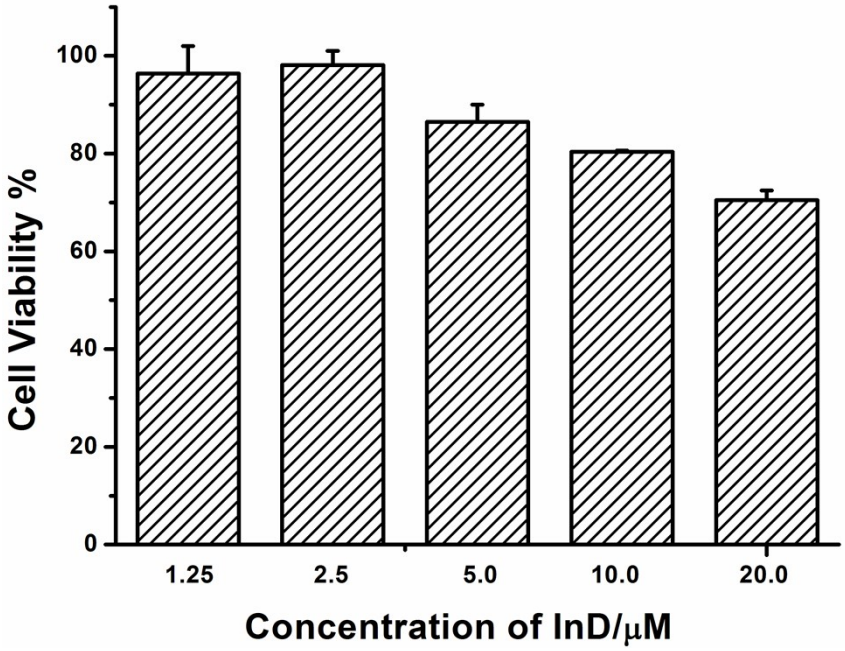


Figure S2: Effects of **InD** at varied concentrations on the viability of HepG2 cells. The results are the mean standard deviation of three separate measurements.

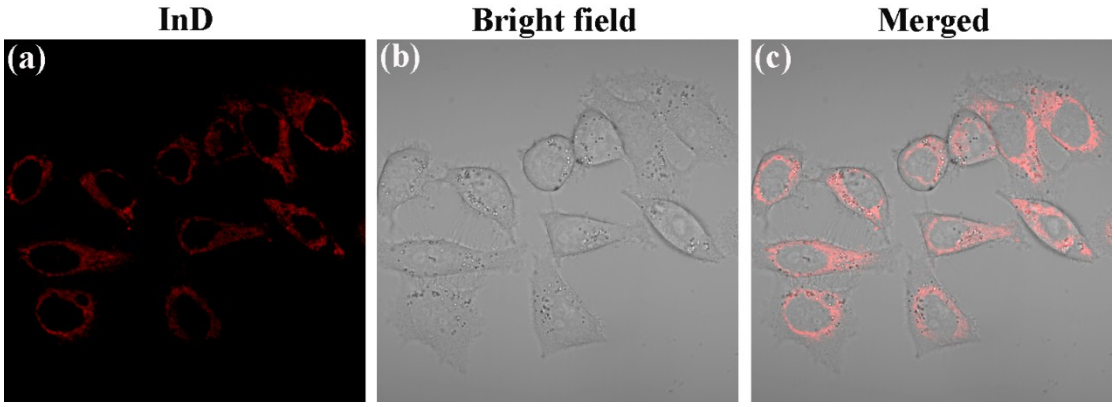
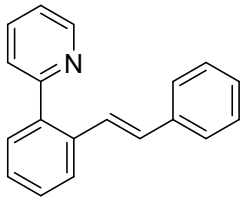


Figure S3. Confocal imaging of HepG2 cells with **InD**. HepG2 cells were loaded with 10 μM **InD** for 30 min. (a): fluorescence image of **InD** excited at 405 nm; (b): bright field image of **InD**; (c): merged images.

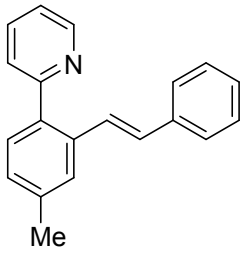
Characterization Data for Products

(*E*)-2-(2-styrylphenyl)pyridine. (3a)[3]



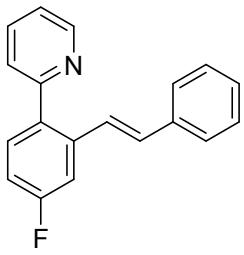
R_f = 0.22 (petroleum ether/EtOAc, 10:1). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 (d, *J* = 4.5 Hz, 1H), 7.77-7.72 （m, 2H), 7.55 (d, *J* = 7.4 Hz, 1H), 7.48 – 7.35 (m, 5H), 7.32-7.26 (m, 3H), 7.25-7.19 (m, 2H), 7.06 (d, *J* = 16.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.79, 149.53, 139.54, 137.53, 136.03, 135.66, 130.22, 130.24, 128.67, 128.62, 127.69, 127.55, 127.50, 126.59, 126.24, 125.08, 121.88. MS (EI) m/z (%) 257 (M+, 20), 180 (100), 152 (18).

(*E*)-2-(4-methyl-2-styrylphenyl)pyridine. (3b)[3]



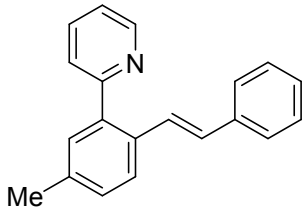
R_f = 0.24 (petroleum ether/EtOAc, 10:1). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 (d, *J* = 4.7 Hz, 1H), 7.71 (t, *J* = 7.6 Hz, 1H), 7.57 (s, 1H), 7.44 (dd, *J* = 13.3, 7.8 Hz, 2H), 7.39 (d, *J* = 7.6 Hz, 2H), 7.30 (t, *J* = 7.5 Hz, 2H), 7.26-7.23 (m, 2H), 7.20 (d, *J* = 9.8 Hz, 2H), 7.05 (d, *J* = 16.2 Hz, 1H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.86, 149.45, 138.35, 137.64, 136.96, 135.90, 135.45, 130.17, 129.76, 128.58, 127.69, 127.44, 126.76, 126.54, 125.01, 121.61, 21.35. MS (EI) m/z (%) 271 (M+, 20), 194 (100).

(*E*)-2-(4-fluoro-2-styrylphenyl)pyridine. (3c)[4]



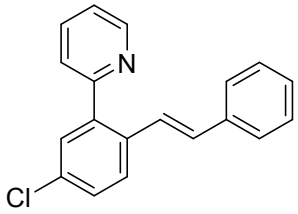
R_f = 0.22 (petroleum ether/EtOAc, 10:1). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 (d, *J* = 4.8 Hz, 1H), 7.75 (td, *J* = 7.7, 1.8 Hz, 1H), 7.54 (dd, *J* = 8.5, 6.0 Hz, 1H), 7.48 – 7.36 (m, 4H), 7.35 – 7.27 (m, 3H), 7.26 – 7.23 (m, 1H), 7.19 (d, *J* = 16.2, 1.4 Hz, 1H), 7.07 (m, 2H). ^{13}C NMR (101 MHz, $CDCll_3$) δ 162.95 (d, *J*=245.6 Hz), 157.90, 149.58, 137.87 (d, *J* = 8.0 Hz), 137.02, 136.16, 135.69 (d, *J* = 3.0 Hz), 132.13 (d, *J* = 8.6 Hz), 131.11, 128.68, 127.92, 126.72, 126.46 (d, *J* = 2.4 Hz), 125.03, 121.98 (s), 114.66 (d, *J*=21.6 Hz), 112.48 (d, *J*=22.2 Hz). MS m/z (%) 275 (M+, 20), 198 (100).

(*E*)-2-(5-methyl-2-styrylphenyl)pyridine. (3d)[5]



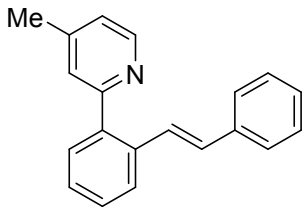
R_f = 0.24 (petroleum ether/EtOAc, 10:1). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 (d, *J* = 4.7 Hz, 1H), 7.73 – 7.69 (m, 1H), 7.65 (d, *J* = 8.0 Hz, 1H), 7.43 (d, *J* = 7.8 Hz, 1H), 7.36 (d, *J* = 7.5 Hz, 3H), 7.30-7.16 (m, 6H), 7.01 (d, *J* = 16.2 Hz, 1H), 2.40 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 158.81, 149.53, 139.38, 137.66, 137.60, 135.93, 132.82, 130.76, 129.50, 129.20, 128.58, 127.36, 126.48, 126.17, 125.15, 121.83, 21.20. MS m/z (%) 271 (M+, 20), 194 (100).

(*E*)-2-(5-chloro-2-styrylphenyl)pyridine. (3e)[3]



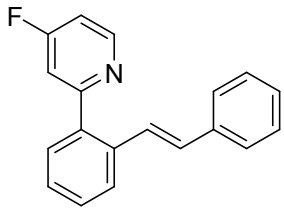
R_f = 0.39 (petroleum ether/EtOAc, 1:1). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 (d, *J* = 4.8 Hz, 1H), 7.74 (t, 1.3 Hz, 1H), 7.67 (d, *J* = 8.4 Hz, 1H), 7.54 (d, *J* = 1.9 Hz, 1H), 7.43 (d, *J* = 7.8 Hz, 1H), 7.44-7.35 (m, 4.5 Hz, 3H), 7.29 (t, *J* = 7.1 Hz, 3H), 7.23 (d, *J* = 7.8 Hz, 1H), 7.14 (d, *J* = 16.2 Hz, 1H), 7.02 (d, *J* = 16.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.46, 149.66, 140.79, 137.20, 136.20, 134.22, 133.27, 130.58, 130.08, 128.70, 128.64, 127.75, 127.58, 126.60, 126.30, 124.94, 122.33. MS (EI) m/z (%) 291 (M +, 30), 214 (100), 178 (12), 127 (15).

(*E*)-4-methyl-2-(2-styrylphenyl)pyridine. (3f)



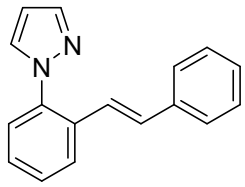
R_f = 0.23 (petroleum ether/EtOAc, 10:1). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (d, *J* = 5.0 Hz, 1H), 7.76 (d, *J* = 7.6 Hz, 1H), 7.51 (d, *J* = 7.4 Hz, 1H), 7.45 – 7.14 (m, 9H), 7.10 – 7.03 (m, 2H), 2.38 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.78, 149.14, 147.15, 139.72, 137.64, 135.65, 130.12, 129.76, 128.57, 128.49, 127.56, 127.55, 127.43, 126.54, 126.05, 125.85, 122.87, 21.14. HRMS (ESI+): Calculated for $C_{20}H_{17}N$ $[M+H]^+$ 272.1439, Found 272.1441.

(*E*)-4-fluoro-2-(2-styrylphenyl)pyridine. (3g)



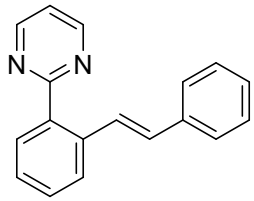
R_f = 0.30 (petroleum ether/EtOAc, 10:1). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (dd, *J* = 8.7, 5.7 Hz, 1H), 7.78 (d, *J* = 7.5 Hz, 1H), 7.53 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.46 (td, *J* = 7.5, 1.4 Hz, 1H), 7.42 – 7.37 (m, 3H), 7.35-7.33 (m, 2H), 7.27-7.20 (m, 3H), 7.10-7.03 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.87 (s), 167.26 (s), 162.05 (d, *J* = 7.0 Hz), 151.75 (d, *J* = 7.2 Hz), 138.45 (s), 137.34 (s), 135.75 (s), 130.56 (s), 130.07 (s), 129.15 (s), 128.64 (s), 127.71 (d, *J* = 3.1 Hz), 126.95 (s), 126.63 (s), 126.42 (s), 112.67 (d, *J* = 16.9 Hz), 109.88 (d, *J* = 16.3 Hz).HRMS (ESI+): Calculated for $C_{19}H_{14}FN$ $[M+H]^+$ 276.1189, Found 276.1184.

(*E*)-1-(2-styrylphenyl)-1H-pyrazole. (3h)[4]



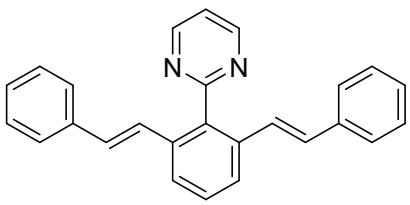
R_f = 0.37 (petroleum ether/EtOAc, 10:1). Yellow oil. ^{1}H NMR (400 MHz, $CDCll_3$) δ 7.76 (d, *J* = 7.3 Hz, 2H), 7.65 (d, *J* = 2.0 Hz, 1H), 7.45 – 7.36 (m, 4H), 7.36 – 7.27 (m, 3H), 7.25 – 7.21 (m, 1H), 7.04 (d, *J* = 16.3 Hz, 1H), 6.93 (d, *J* = 16.3 Hz, 1H), 6.46 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.73, 138.74， 137.00, 133.00, 131.52, 131.23, 128.64, 128.59, 128.39, 128.10, 127.93, 126.68, 126.56, 126.3, 123.89, 106.57. MS (EI) m/z (%) 245 (M+, 60), 217 (25), 169 (100), 115 (10).

(*E*)-2-(2-styrylphenyl)pyrimidine. (3i)[3]



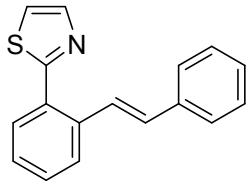
R_f = 0.22 (toluene). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.88 (d, *J* = 4.8 Hz, 2H), 7.89 (d, *J* = 7.6 Hz, 1H), 7.80 (d, *J* = 7.8 Hz, 1H), 7.68 (d, *J* = 16.2 Hz, 1H), 7.49-7.38 (m, 4H), 7.32 (t, *J* = 7.5 Hz, 2H), 7.25 – 7.21 (m, 2H), 7.06 (d, *J* = 16.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.12, 157.00, 137.77, 137.25, 136.74, 130.93, 130.00, 129.81, 128.53, 128.00, 127.56, 127.44, 126.67, 118.64. MS m/z (%) 258 (M+, 20), 181 (100), 128 (12).

2-(2,6-di((*E*)-styryl)phenyl)pyrimidine. (3i')



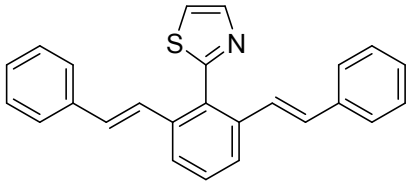
R_f=0.33 (toluene). White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.94 (d, *J* = 4.9 Hz, 2H), 7.70 (d, *J* = 7.8 Hz, 2H), 7.47 (t, *J* = 7.8 Hz, 1H), 7.36 (t, *J* = 4.9 Hz, 1H), 7.31 – 7.24 (m, 8H), 7.24 – 7.17 (m, 2H), 6.99 (d, *J* = 16.1 Hz, 2H), 6.74 (d, *J* = 16.1 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.46, 157.16, 137.34, 137.16, 136.35, 130.78, 129.06, 128.52, 127.61, 126.58, 126.52, 125.13, 119.19. HRMS (ESI+): Calculated for $C_{26}H_{20}N_2$ $[M+H]^+$ 361.1705, Found 361.1700.

(*E*)-2-(2-styrylphenyl)thiazole. (3j)[6]



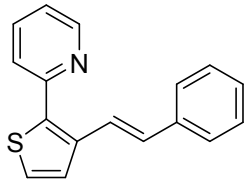
R_f = 0.44 (petroleum ether/EtOAc, 20:1). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 2.9 Hz, 1H), 7.81 – 7.65 (m, 3H), 7.47 (t, *J* = 7.3 Hz, 2H), 7.44 – 7.39 (m, 2H), 7.37-7.32 (m, 3H), 7.24 (s, 1H), 7.05 (d, *J* = 16.1 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.11, 143.28, 137.39, 136.50, 132.04, 131.42, 130.24, 129.64, 128.63, 127.74, 127.63, 127.28, 126.99, 126.79, 120.19. MS m/z (%) 263 (M+, 18), 186 (100).

2-(2,6-di((*E*)-styryl)phenyl)thiazole. (3j')



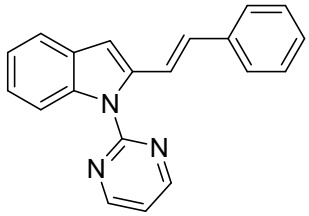
R_f = 0.31 (petroleum ether/EtOAc, 20:1). White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 3.3 Hz, 1H), 7.70 (d, *J* = 7.8 Hz, 2H), 7.58 (d, *J* = 3.3 Hz, 1H), 7.49 (t, *J* = 7.8 Hz, 1H), 7.35 – 7.27 (m, 8H), 7.25 – 7.20 (m, 2H), 7.02 (d, *J* = 16.2 Hz, 2H), 6.87 (d, *J* = 16.2 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.19, 142.98, 138.13, 137.14, 131.20, 130.93, 129.79, 128.59, 127.78, 126.68, 126.24, 124.71, 121.40. HRMS (ESI+): Calculated for $C_{25}H_{19}NS$ $[M+H]^+$ 366.1316, Found 366.1311.

(*E*)-2-(3-styrylthiophen-2-yl)pyridine. (3k)



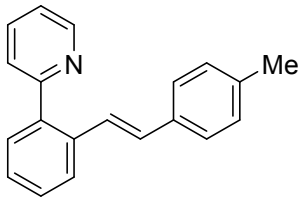
R_f = 0.44 (petroleum ether/EtOAc, 10:1). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 2.9 Hz, 1H), 7.73 – 7.58 (m, 3H), 7.40 (t, *J* = 7.3 Hz, 2H), 7.37 – 7.32 (m, 2H), 7.27 (dd, *J* = 13.8, 7.0 Hz, 3H), 7.17 (s, 1H), 6.98 (d, *J* = 16.1 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.07, 149.85, 139.44, 137.44, 136.90, 136.54, 130.79, 128.66, 127.62, 126.88, 126.50, 126.31, 123.05, 122.58, 121.78. HRMS (ESI+): Calculated for $C_{17}H_{13}NS$ $[M+H]^+$ 264.0847, Found 264.0814.

(*E*)-1-(pyrimidin-2-yl)-2-styryl-1H-indole. (3l)[7]



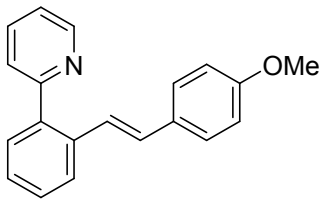
R_f = 0.44 (petroleum ether/EtOAc, 5:1). White solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.96 (d, *J* = 4.8 Hz, 2H), 8.10 (d, *J* = 7.8 Hz, 1H), 7.64 (d, *J* = 16.3 Hz, 1H), 7.58 (d, *J* = 7.3 Hz, 1H), 7.51 (d, *J* = 7.4 Hz, 2H), 7.47-7.45 (m, 1H), 7.33 (t, *J* = 7.5 Hz, 2H), 7.29 – 7.07 (m, 6H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 159.49, 157.38, 138.78, 137.47, 137.12, 129.80, 129.17, 129.09, 128.14, 126.89, 123.62, 122.52, 120.65, 120.48, 118.91, 113.98, 104.48. HRMS (ESI+): Calculated for $C_{20}H_{15}N_3$ $[M+H]^+$ 298.1344, Found 298.1349.

(*E*)-2-(2-(4-methylstyryl)phenyl)pyridine. (4a)[3]



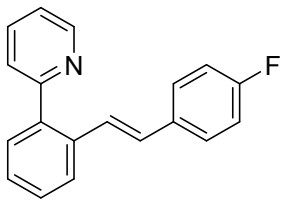
R_f = 0.30 (petroleum ether/EtOAc, 10:1). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 (d, *J* = 4.4 Hz, 1H), 7.76 – 7.68 (m, 2H), 7.54 (d, *J* = 7.4 Hz, 1H), 7.49 – 7.33 (m, 3H), 7.29 – 7.24 (m, 3H), 7.17 (d, *J* = 16.2 Hz, 1H), 7.11 (d, *J* = 7.8 Hz, 2H), 7.02 (d, *J* = 16.2 Hz, 1H), 2.32 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.88, 149.49, 139.43, 137.43, 135.93, 135.84, 134.78, 130.17, 130.00, 129.30, 128.60, 127.46, 126.53, 126.49, 126.14, 125.06, 121.79, 21.21. MS m/z (%) 271 (M+, 25), 180 (100).

(*E*)-2-(2-(4-methoxystyryl)phenyl)pyridine. (4b)[3]



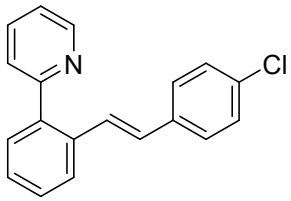
R_f = 0.15 (petroleum ether/EtOAc, 10:1). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 (d, *J* = 4.6 Hz, 1H), 7.75 – 7.70 (m, 2H), 7.53 (d, *J* = 7.4 Hz, 1H), 7.46 – 7.24 (m, 6H), 7.08 (d, *J* = 16.2 Hz, 1H), 6.99 (d, *J* = 16.2 Hz, 1H), 6.84 (d, *J* = 8.6 Hz, 2H), 3.79 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.20, 158.95, 149.46, 139.28, 139.95, 135.93, 130.39, 130.17, 129.56, 128.59, 127.77, 127.28, 125.98, 125.36, 125.06, 121.78, 114.03, 55.28. MS (EI) m/z (%) 287 (M +, 30), 180 (100).

(*E*)-2-(2-(4-fluorostyryl)phenyl)pyridine. (4c)[3]



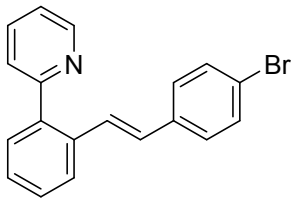
R_f = 0.19 (petroleum ether/EtOAc, 10:1). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 (dd, *J* = 4.1, 0.8 Hz, 1H), 7.79 – 7.73 (m, 2H), 7.55 (dd, *J* = 7.4, 1.6 Hz, 1H), 7.48 – 7.41 (m, 2H), 7.40 (dd, *J* = 7.4, 1.3 Hz, 1H), 7.38 – 7.33 (m, 2H), 7.30 (dd, *J* = 7.1, 5.3 Hz, 1H), 7.15 (d, *J* = 16.2 Hz, 1H), 7.06 – 6.97 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.46, 161.00, 158.83, 149.46, 139.48, 136.10, 135.50, 133.74, 130.23, 128.72 (d, *J* = 10.5 Hz), 128.04 (d, *J* = 7.9 Hz), 127.69, 127.26 (d, *J* = 2.2 Hz), 126.11, 124.98, 121.90, 115.52 (d, *J*=21.5 Hz). MS m/z (%) 274 (M+,22), 180 (100).

(*E*)-2-(2-(4-chlorostyryl)phenyl)pyridine. (4d)[8]



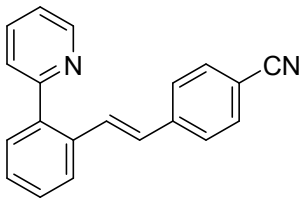
R_f = 0.28 (petroleum ether/EtOAc, 10:1). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 (d, *J* = 4.6 Hz, 1H), 7.77 – 7.72 (m, 2H), 7.53 (d, *J* = 7.2 Hz, 1H), 7.47 – 7.34 (m, 3H), 7.32 – 7.16 (m, 6H), 6.98 (d, *J* = 16.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.77, 149.50, 139.61, 136.12, 136.04, 135.33, 133.05, 130.25, 128.75, 128.69, 128.64, 128.12, 127.88, 127.72, 126.19, 124.95, 121.93. MS m/z (%) 291 (M+, 20), 180 (100).

(*E*)-2-(2-(4-bromostyryl)phenyl)pyridine. (4e)[8]



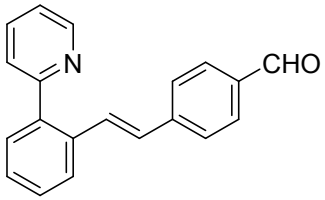
R_f = 0.23 (petroleum ether/EtOAc, 10:1). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 (d, *J* = 4.8 Hz, 1H), 7.75-7.72 (m, 2H), 7.53 (d, *J* = 7.7 Hz, 1H), 7.46 – 7.32 (m, 5H), 7.32 – 7.25 (m, 1H), 7.24-7.19 (m, 3H), 6.97 (d, *J* = 16.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.77, 149.45, 139.60, 136.50, 136.11, 135.32, 131.67, 130.24, 128.70, 128.68, 128.27, 128.02, 127.88, 126.18, 124.93, 121.92, 121.21. HRMS (ESI+): Calculated for $C_{19}H_{14}BrN$ $[M+H]^+$ 336.0388, Found 336.0373.

(*E*)-4-(2-(pyridin-2-yl)styryl)benzonitrile. (4f)



R_f = 0.43 (petroleum ether/EtOAc, 3:1). Light yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 (d, *J* = 4.5 Hz, 1H), 7.82 – 7.70 (m, 2H), 7.57 – 7.53 (m, 3H), 7.48 – 7.21 (m, 7H), 7.02 (d, *J* = 16.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.56, 149.35, 142.04, 139.89, 136.43, 134.75, 132.39, 131.30, 130.34, 128.81, 128.52, 127.96, 126.91, 126.36, 124.89, 122.11, 119.01, 110.43. HRMS (ESI+): Calculated for $C_{20}H_{14}N_2$ $[M+H]^+$ 283.1235, Found 283.1228.

(*E*)-4-(2-(pyridin-2-yl)styryl)benzaldehyde. (4g)



R_f = 0.40 (petroleum ether/EtOAc, 3:1). Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.95 (s, 1H), 8.74 (d, *J* = 4.4 Hz, 1H), 7.81 – 7.74 (m, 4H), 7.59 – 7.38 (m, 7H), 7.30 (dd, *J* = 7.0, 5.4 Hz, 1H), 7.08 (d, *J* = 16.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.58, 158.65, 149.47, 143.64, 139.96, 136.24, 135.19, 134.97, 131.11, 130.32, 130.15, 128.74, 128.56, 128.39, 126.95, 126.35, 124.89, 122.03. HRMS (ESI+): Calculated for $C_{20}H_{15}NO$ $[M+H]^+$ 286.1232, Found 286.1203

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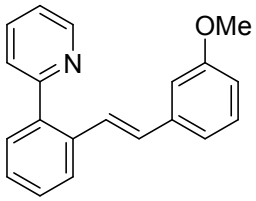
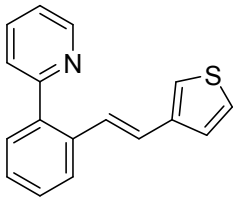
(*E*)-2-(2-(3-methoxystyryl)phenyl)pyridine. (4h)



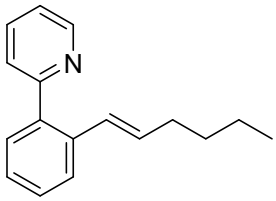
R_f = 0.16 (petroleum ether/EtOAc, 10:1). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 (d, *J* = 4.6 Hz, 1H), 7.75-7.71 (m, 7.9 Hz, 2H), 7.54 (d, *J* = 7.4 Hz, 1H), 7.47 – 7.32 (m, 3H), 7.30 – 7.17 (m, 3H), 7.03 – 6.91 (m, 3H), 6.78 (dd, *J* = 8.2, 1.8 Hz, 1H), 3.78 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.76, 158.79, 149.48, 139.57, 139.03, 135.99, 135.58, 130.19, 129.92, 129.54, 128.63, 127.91, 127.70, 126.26, 125.03, 121.86, 119.26, 112.97, 112.05, 55.19. HRMS (ESI+): Calculated for $C_{20}H_{17}NO$ $[M+H]^+$ 288.1388, Found 288.1383.

(*E*)-2-(2-(2-(thiophen-3-yl)vinyl)phenyl)pyridine. (4i)



R_f = 0.19 (petroleum ether/EtOAc, 10:1). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 (ddd, *J* = 4.8, 1.7, 0.9 Hz, 1H), 7.79 – 7.70 (m, 2H), 7.55 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.49 – 7.34 (m, 3H), 7.31 – 7.27 (m, 1H), 7.27 – 7.25 (m, 1H), 7.21 (dd, *J* = 2.9, 1.3 Hz, 1H), 7.16 (dd, *J* = 5.0, 1.2 Hz, 1H), 7.08 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.83, 149.50, 140.35, 139.36, 135.99, 135.63, 130.21, 128.64, 127.54, 127.43, 126.06, 125.96, 125.05, 125.02, 124.19, 122.38, 121.86. HRMS (ESI+): Calculated for $C_{17}H_{13}NS$ $[M+H]^+$ 268.0847, Found 264.0838.

(*E*)-2-(2-(hex-1-en-1-yl)phenyl)pyridine. (4j)



R_f = 0.40 (petroleum ether/EtOAc, 10:1). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (d, *J* = 4.7 Hz, 1H), 7.74 – 7.67 (m, 1H), 7.57 (d, *J* = 7.7 Hz, 1H), 7.46 (d, *J* = 7.3 Hz, 1H), 7.41 (d, *J* = 7.8 Hz, 1H), 7.36-7.25 (m, 2H), 7.25 – 7.19 (m, 1H), 6.43 (d, *J* = 15.7 Hz, 1H), 6.19 – 6.11 (m, 1H), 2.13 (q, *J* = 6.9 Hz, 2H), 1.44 – 1.29 (m, 4H), 0.88 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.12, 149.37, 138.72, 136.22, 135.74, 132.69, 129.94, 128.41, 128.36, 126.84, 126.23, 124.94, 121.61, 32.79, 31.35, 22.18, 13.92. HRMS (ESI+): Calculated for $C_{17}H_{19}N$ $[M+H]^+$ 238.1596, Found 238.1594

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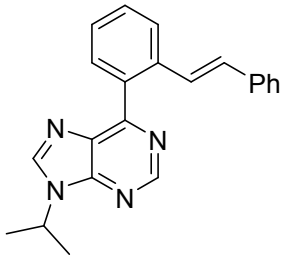
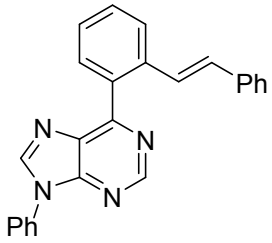
(*E*)-9-isopropyl-6-(2-styrylphenyl)-9H-purine. (6a)



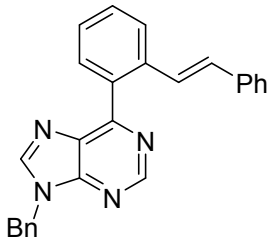
R_f = 0.19 (petroleum ether/EtOAc, 3:1). White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.99 (s, 1H), 8.07 (s, 1H), 7.78 (dd, *J* = 16.6, 7.7 Hz, 2H), 7.42 (t, *J* = 7.5 Hz, 1H), 7.38-7.34 (m, 2H), 7.27 (d, *J* = 7.6 Hz, 2H), 7.19 (t, *J* = 6.8 Hz, 2H), 7.12-7.09 (m, 1H), 7.01 (d, *J* = 16.2 Hz, 1H), 4.95-4.88 (m, 1H), 1.61 (d, *J* = 6.8 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.91, 151.78, 151.70, 142.43, 137.65, 136.62, 134.09, 132.83, 131.47, 130.07, 129.90, 128.46, 127.43, 127.39, 127.36, 126.64, 126.39, 47.45, 22.55. HRMS (ESI+): Calculated for $C_{22}H_{20}N_4$ $[M+H]^+$ 341.1766, Found 341.1769.

(*E*)-9-phenyl-6-(2-styrylphenyl)-9H-purine. (6b)



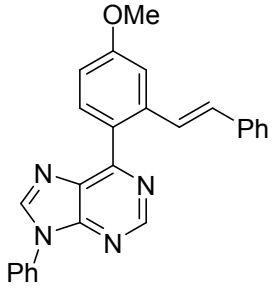
R_f = 0.29 (petroleum ether/EtOAc, 3:1). Light yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.16 (s, 1H), 8.39 (s, 1H), 7.94 – 7.87 (m, 2H), 7.79 (d, *J* = 7.7 Hz, 2H), 7.64 (t, *J* = 7.8 Hz, 2H), 7.58 – 7.51 (m, 2H), 7.47 (dd, *J* = 15.5, 7.4 Hz, 2H), 7.38 (d, *J* = 7.5 Hz, 2H), 7.30 (d, *J* = 7.4 Hz, 2H), 7.21 (t, *J* = 7.2 Hz, 1H), 7.14 (d, *J* = 16.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.66, 152.84, 151.81, 143.67, 137.57, 136.75, 134.31, 133.85, 132.91, 131.52, 130.32, 130.14, 130.00, 128.58, 128.50, 127.52, 127.45, 127.21, 126.66, 126.48, 123.63. HRMS (ESI+): Calculated for $C_{25}H_{18}N_4$ $[M+H]^+$ 375.1610, Found 375.1605.

(*E*)-9-benzyl-6-(2-styrylphenyl)-9H-purine. (6c)



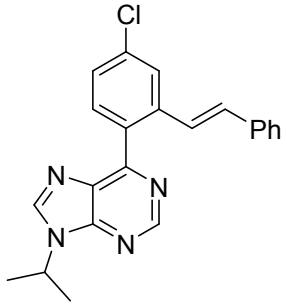
R_f = 0.19 (petroleum ether/EtOAc, 3:1). Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.05 (s, 1H), 8.00 (s, 1H), 7.79 (t, *J* = 8.8 Hz, 2H), 7.44 (t, *J* = 7.5 Hz, 1H), 7.39 – 7.33 (m, 2H), 7.33 – 7.16 (m, 9H), 7.12 (t, *J* = 7.1 Hz, 1H), 7.02 (d, *J* = 16.2 Hz, 1H), 5.43 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.07, 152.39, 144.55, 137.62, 136.68, 135.09, 133.94, 132.30, 131.49, 130.12, 130.00, 129.17, 128.62, 128.46, 127.84, 127.45, 127.42, 127.34, 126.62, 126.42, 109.99, 47.51. HRMS (ESI+): Calculated for $C_{26}H_{20}N_4$ $[M+H]^+$ 389.1766, Found 389.1764.

(*E*)-6-(4-methoxy-2-styrylphenyl)-9-phenyl-9H-purine. (6d)



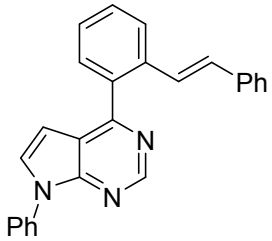
R_f = 0.35 (petroleum ether/EtOAc, 1:1). White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.11 (s, 1H), 8.35 (s, 1H), 7.96 (d, *J* = 8.6 Hz, 1H), 7.76 (d, *J* = 7.8 Hz, 2H), 7.64 – 7.46 (m, 4H), 7.44 – 7.34 (m, 3H), 7.28 (t, *J* = 7.5 Hz, 2H), 7.20 (t, *J* = 7.2 Hz, 1H), 7.11 (d, *J* = 16.1 Hz, 1H), 7.02 (dd, *J* = 8.6, 2.2 Hz, 1H), 3.94 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.01, 158.36, 152.79, 151.71, 143.30, 138.68, 137.51, 134.37, 133.50, 132.73, 130.30, 130.00, 128.54, 127.59, 127.56, 126.73, 123.64, 113.35, 111.72, 55.49. HRMS (ESI+): Calculated for $C_{26}H_{20}N_4O$ $[M+H]^+$ 405.1715, Found 405.1711.

(*E*)-6-(4-chloro-2-styrylphenyl)-9-isopropyl-9H-purine. (6e)



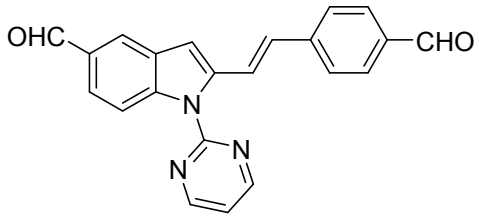
R_f = 0.40 (petroleum ether/EtOAc, 3:1). White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.06 (s, 1H), 8.15 (s, 1H), 7.83 (dd, *J* = 11.5, 4.8 Hz, 2H), 7.44-7.38 (m, 2H), 7.35 (d, *J* = 7.5 Hz, 2H), 7.28 (t, *J* = 7.4 Hz, 2H), 7.21 (t, *J* = 7.2 Hz, 1H), 7.09 (d, *J* = 16.2 Hz, 1H), 5.03-4.96 (m, 1H), 1.69 (d, *J* = 6.8 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.73, 151.80, 142.58, 138.53, 137.16, 136.09, 132.98, 132.77, 132.36, 131.26, 128.55, 127.85, 127.36, 126.80, 126.35, 126.13, 47.53, 22.57. HRMS (ESI+): Calculated for $C_{22}H_{19}ClN_4$ $[M+H]^+$ 375.1376, Found 375.1375.

(*E*)-7-phenyl-4-(2-styrylphenyl)-7H-pyrrolo[2,3-d]pyrimidine. (6f)



R_f = 0.63 (petroleum ether/EtOAc, 3:1). White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.08 (s, 1H), 7.91 (d, *J* = 7.9 Hz, 1H), 7.78 (d, *J* = 7.7 Hz, 2H), 7.65 (d, *J* = 7.3 Hz, 1H), 7.58 (t, *J* = 7.9 Hz, 2H), 7.54 – 7.48 (m, 2H), 7.43 (dd, *J* = 17.2, 7.9 Hz, 2H), 7.34 (d, *J* = 7.4 Hz, 2H), 7.30 (d, *J* = 5.2 Hz, 1H), 7.26 (m, 2H), 7.20 (t, *J* = 7.2 Hz, 1H), 7.15 (d, *J* = 16.2 Hz, 1H), 6.63 (d, *J* = 3.7 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.40, 152.07, 150.92, 137.39, 137.61, 136.04, 130.52, 130.10, 129.56, 128.71, 128.54, 127.62, 127.52, 127.17, 126.97, 126.63, 126.05, 124.04, 118.91, 110.10, 102.32. HRMS (ESI+): Calculated for $C_{26}H_{19}N_3$ $[M+H]^+$ 374.1657, Found 374.1655.

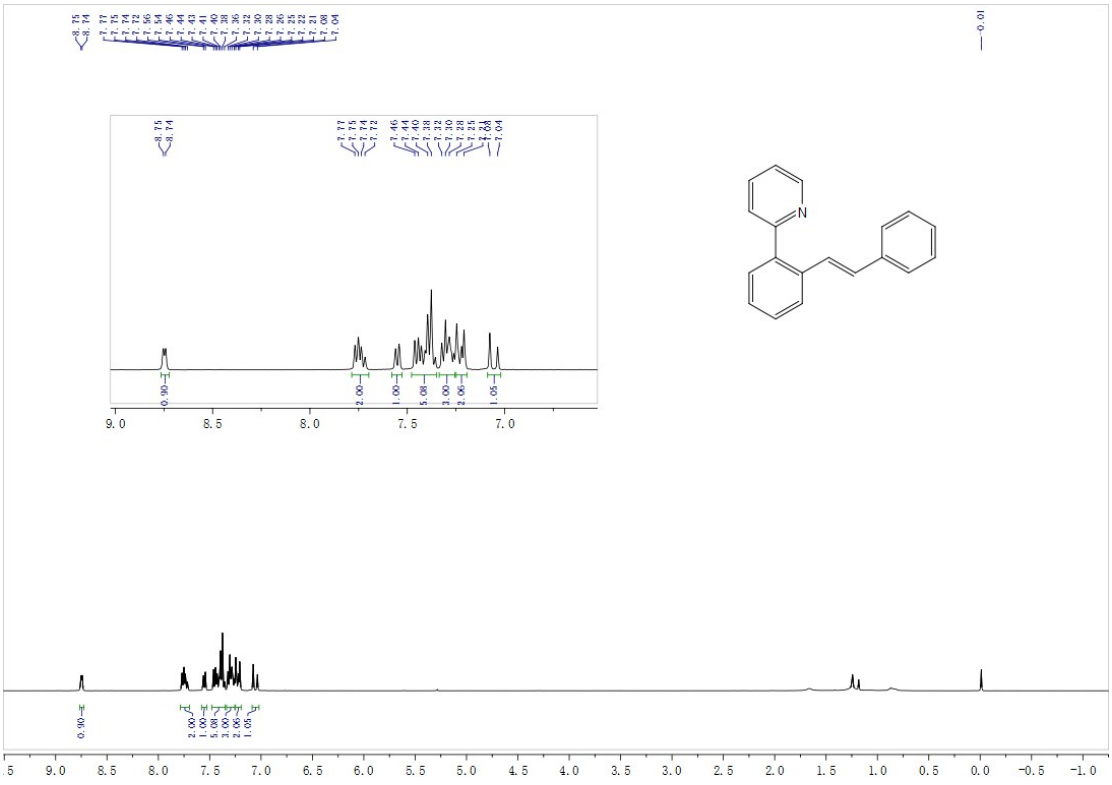
(*E*)-2-(4-formylstyryl)-1-(pyrimidin-2-yl)-1H-indole-5-carbaldehyde. (InD)

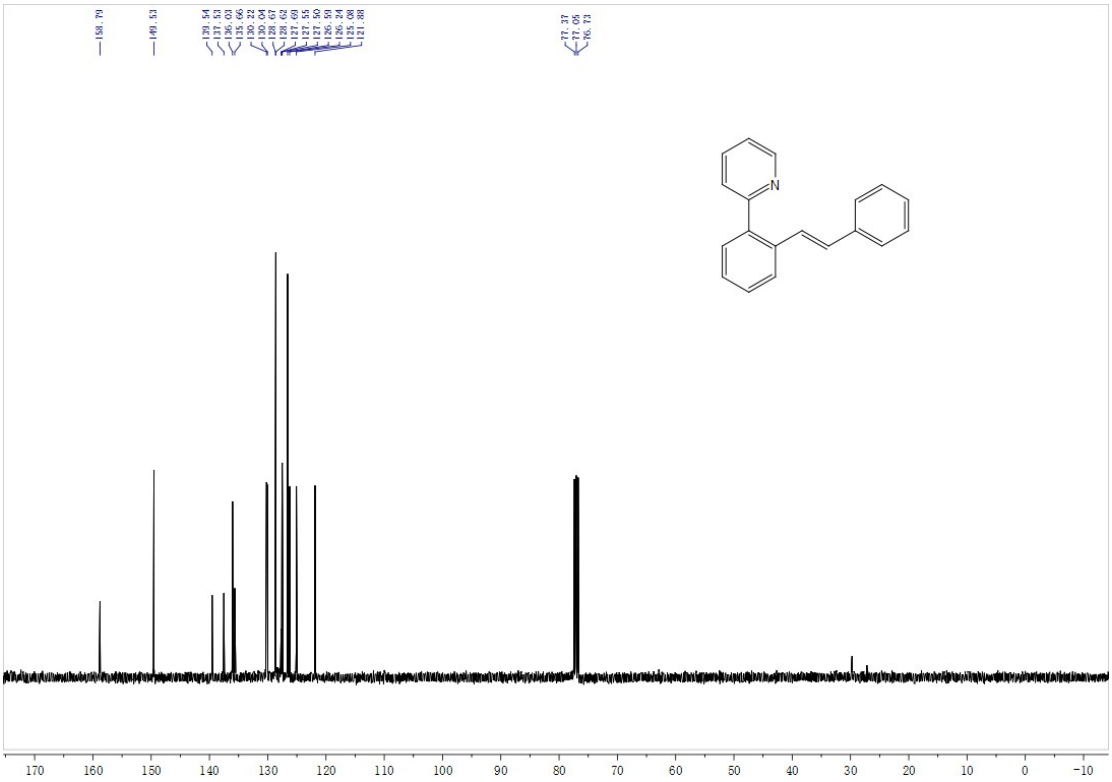


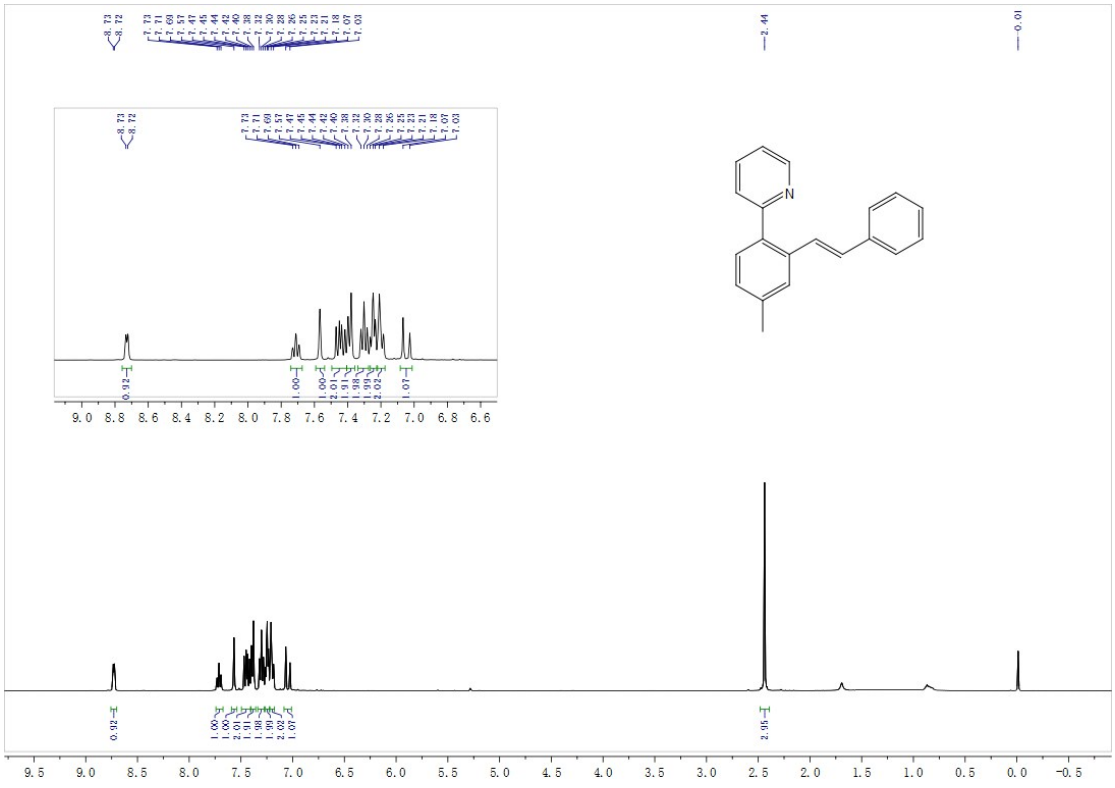
R_f = 0.28 (petroleum ether/EtOAc, 3:1). White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.08 (s, 1H), 10.01 (s, 1H), 8.93 (d, *J* = 4.8 Hz, 2H), 8.39 (d, *J* = 8.8 Hz, 1H), 8.16 (s, 1H), 7.90 – 7.79 (m, 4H), 7.64 (d, *J* = 8.0 Hz, 2H), 7.34 (t, *J* = 4.8 Hz, 1H), 7.25 – 7.20 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.24, 191.60, 158.63, 157.46, 143.04, 140.74, 139.86, 135.44, 131.58, 130.24, 129.30, 129.06, 127.09, 124.54, 124.47, 123.03, 118.32, 114.55, 106.53. HRMS (ESI+): Calculated for $C_{22}H_{15}N_3O_2$ $[M+Na]^+$ 376.1062, Found 376.1046.

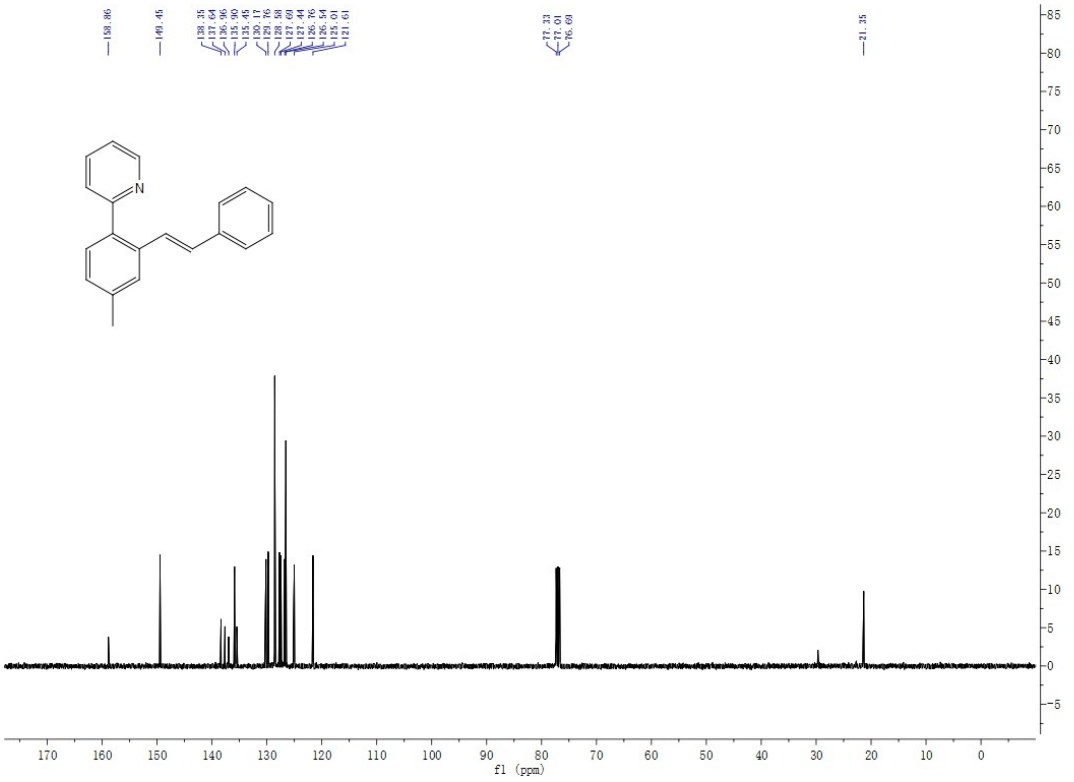
References

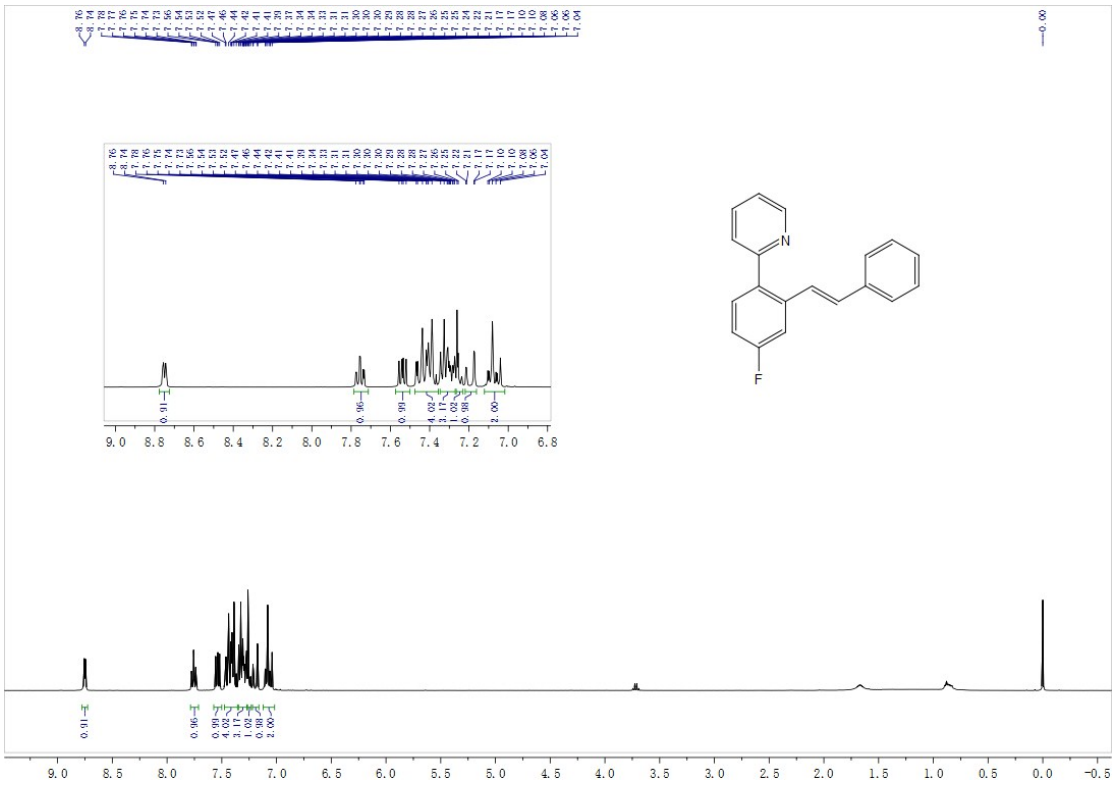
1. L. Li, W. W. Brennessel and W. D. Jones, *J. Am. Chem. Soc.* 2008, **130**, 12414 - 12419.
2. T. Miura, Y. Urano, K. Tanaka, T. Nagano, K. Ohkubo and S. Fukuzumi, *J. Am. Chem. Soc.* 2003, **125**, 8666.
3. K. Cheng, B. Yao, J. Zhao and Y. Zhang, *Org. Lett.* 2008, **10**, 5309.
4. R. Qiu, L. Zhang, C. Xu, Y. Pan, H. Pang, L. Xu and H. Li, *Adv.Synth. Catal.* 2015, **357**, 1229.
5. Y. Matsuura, M. Tamura, T. Kochi, M. Sato, N. Chatani and F. Kakiuchi, *J. Am. Chem. Soc*. 2007, **129**, 9858.
6. K. Hiraki, Y. Fuchita, S. Takakura, *J. Organomet. Chem.* 1981, **210**, 273.
7. H. Ikemoto, T. Yoshino, K. Sakata, S. Matsunaga and M. Kanai, *J. Am. Chem. Soc.* 2014, **136**, 5424.
8. B. Zhou, H. Chen, C. Wang, *J. Am. Chem. Soc.* 2013, **135**, 1264.







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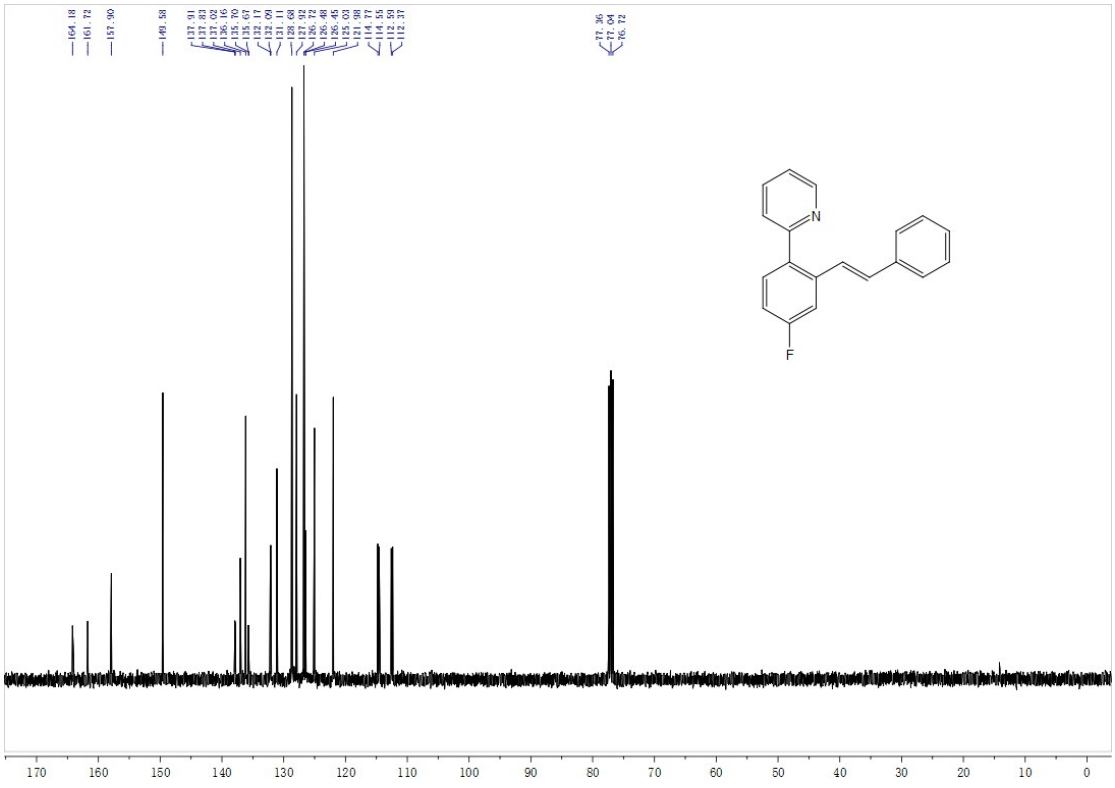
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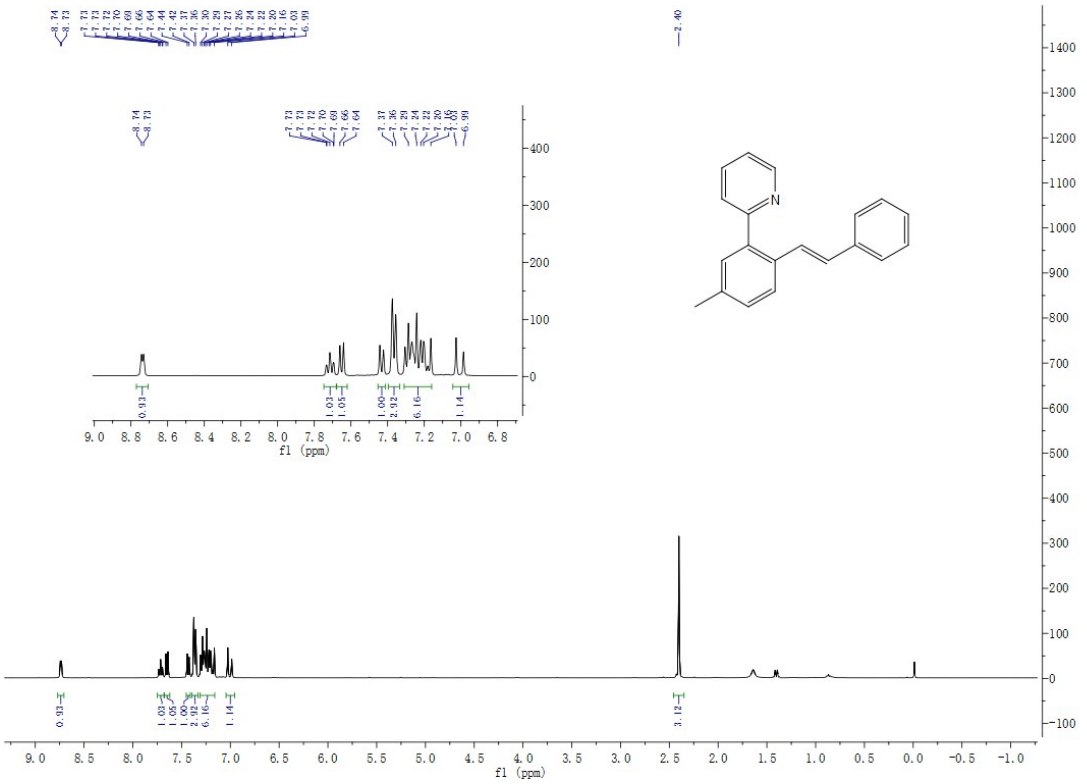
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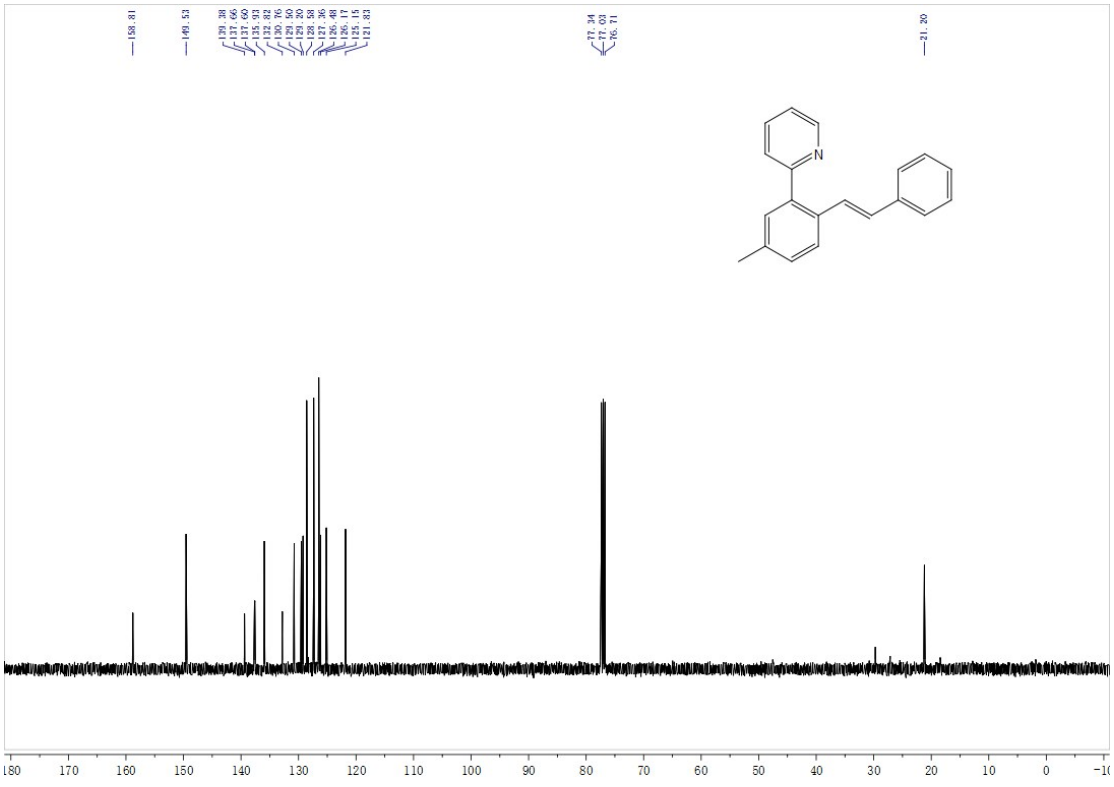
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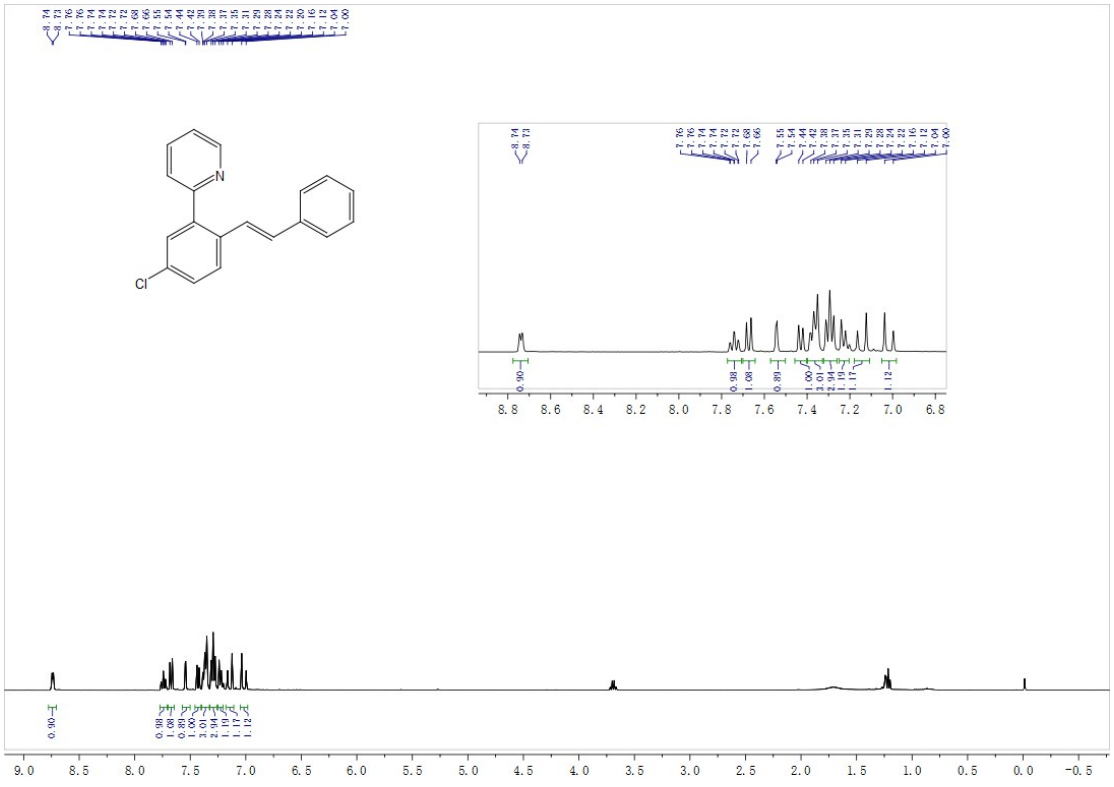
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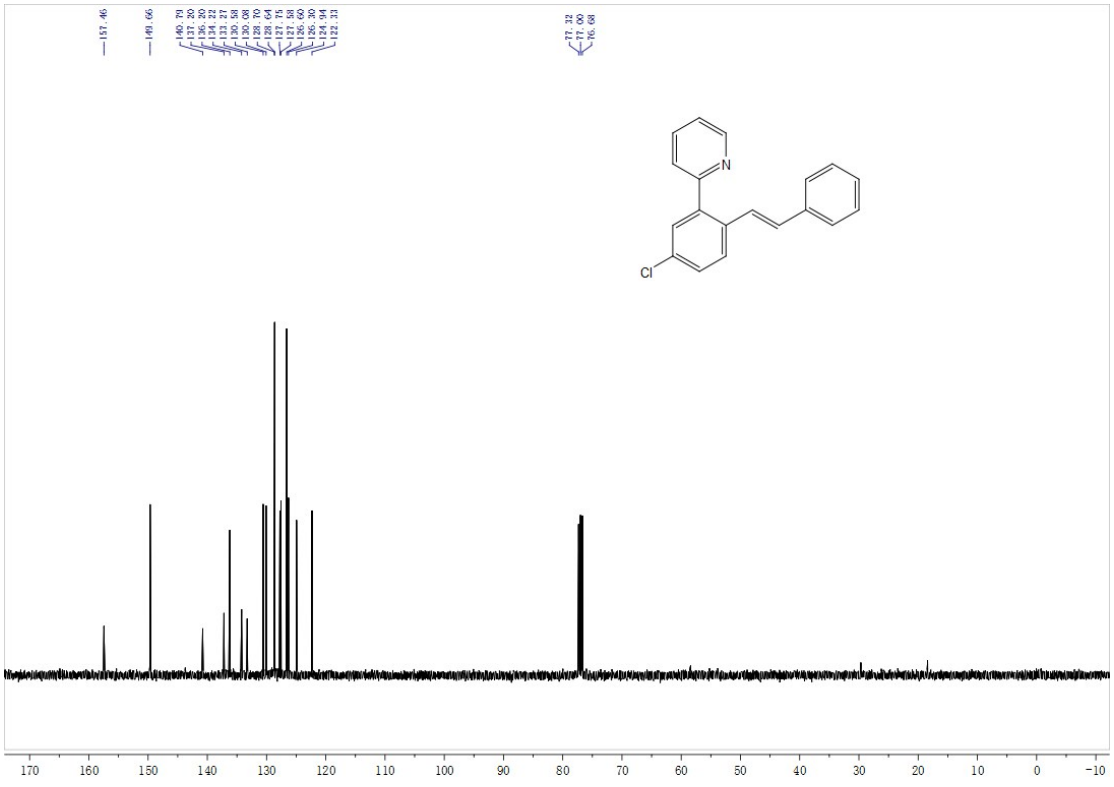
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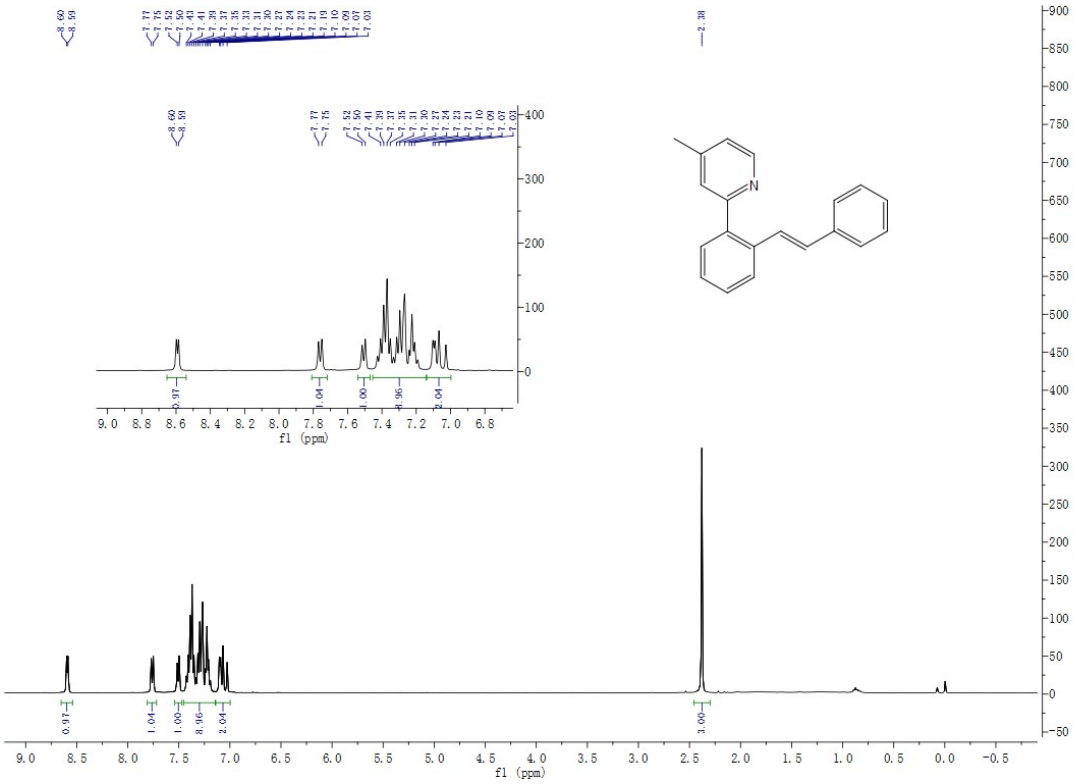
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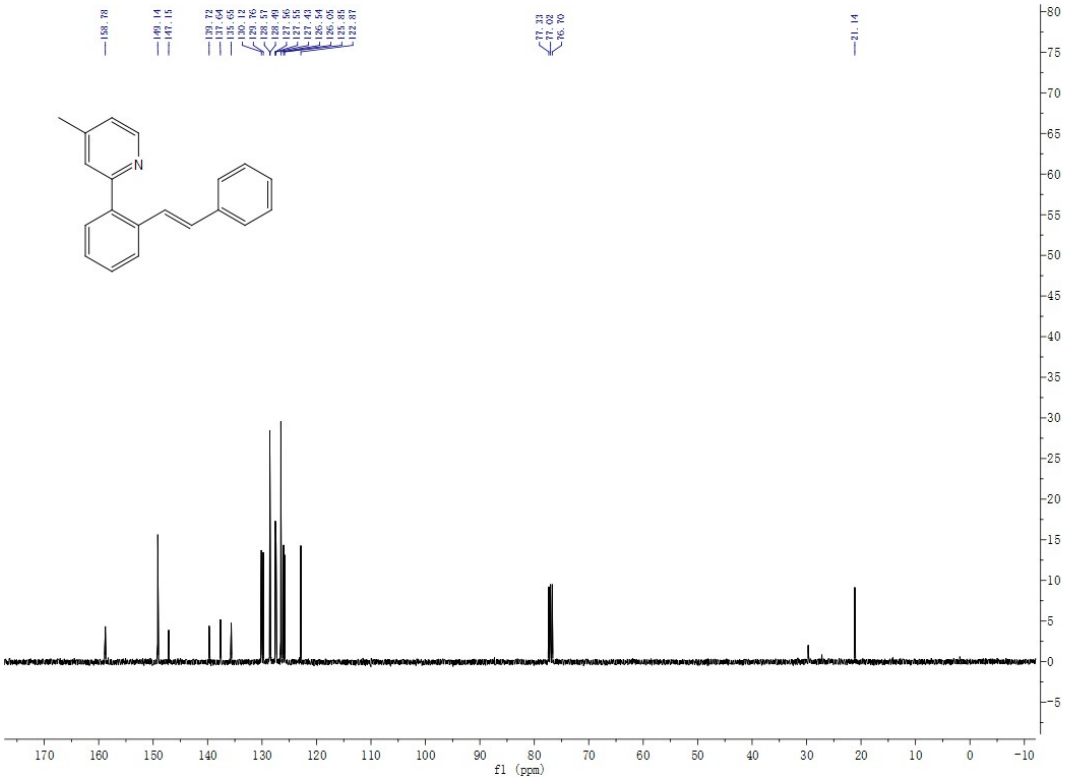
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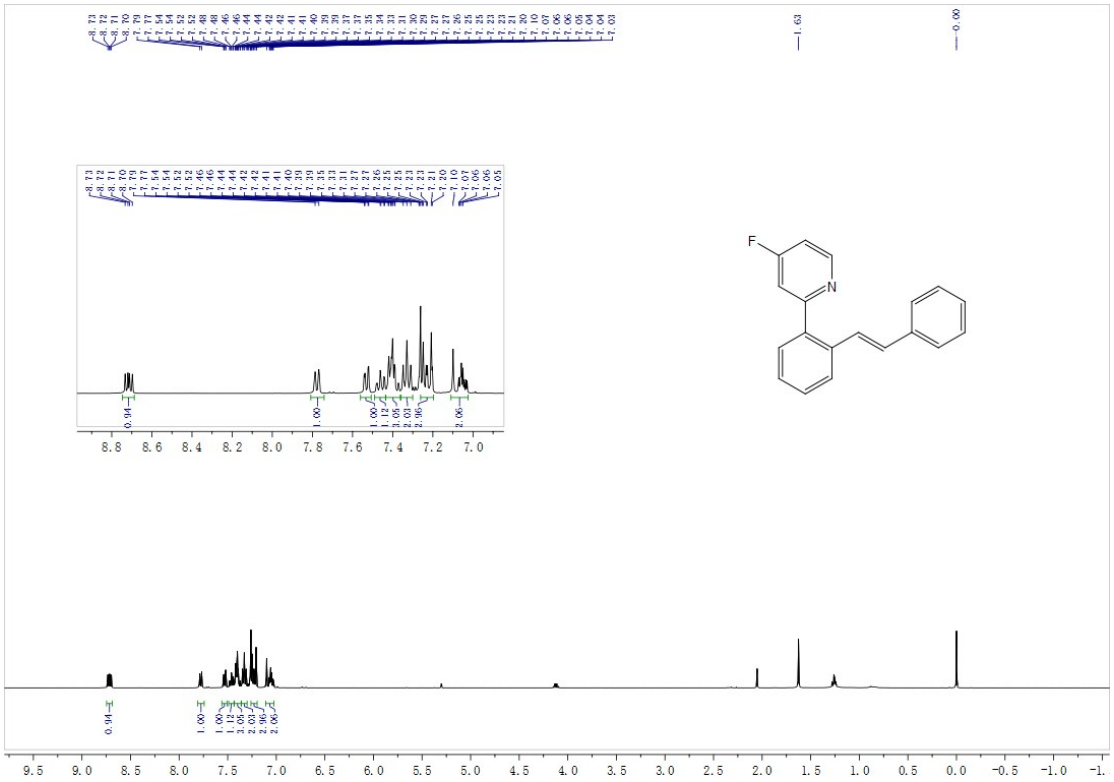
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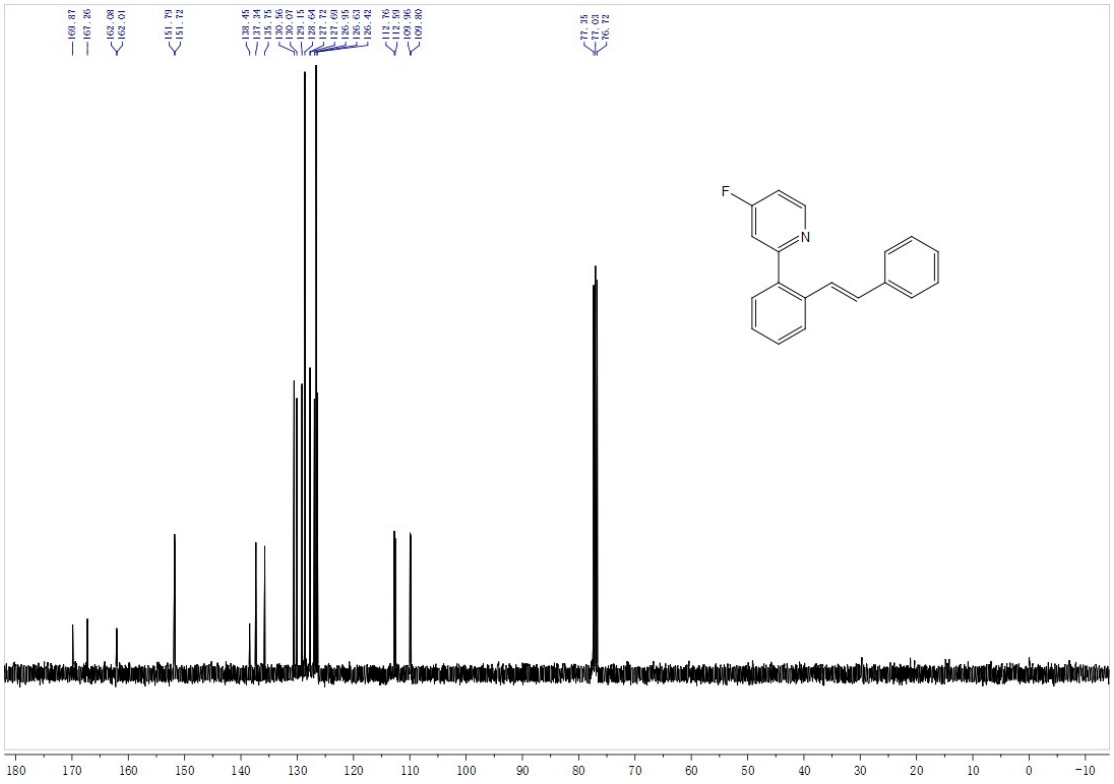
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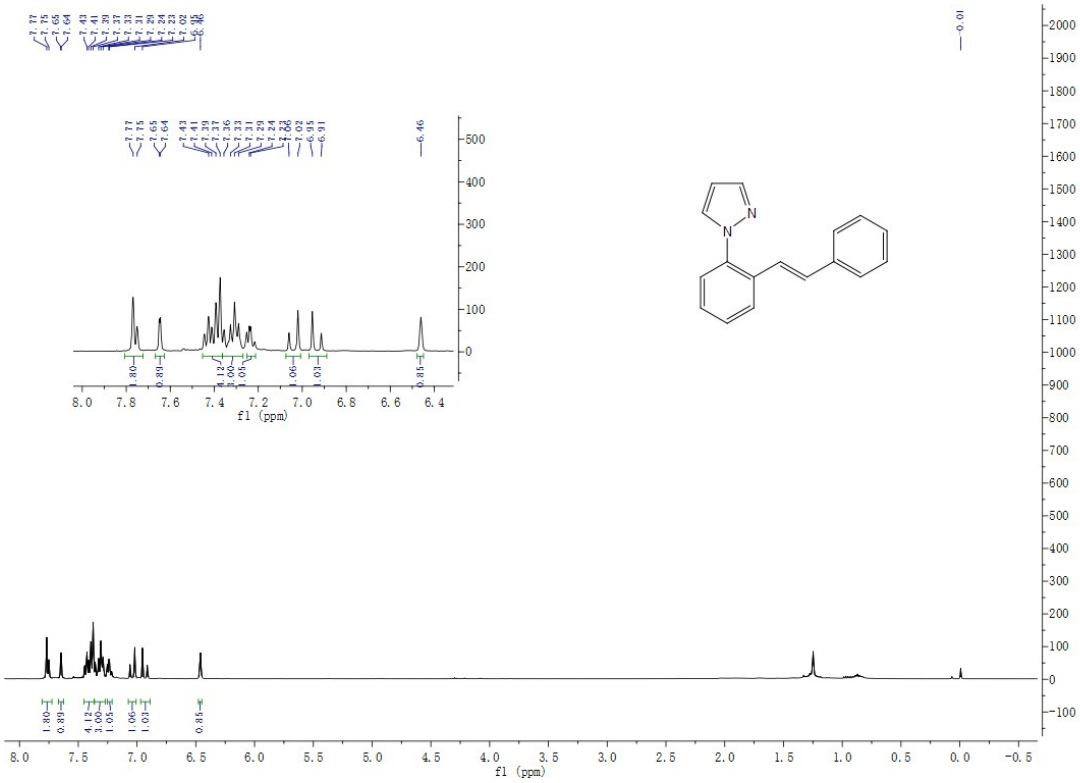

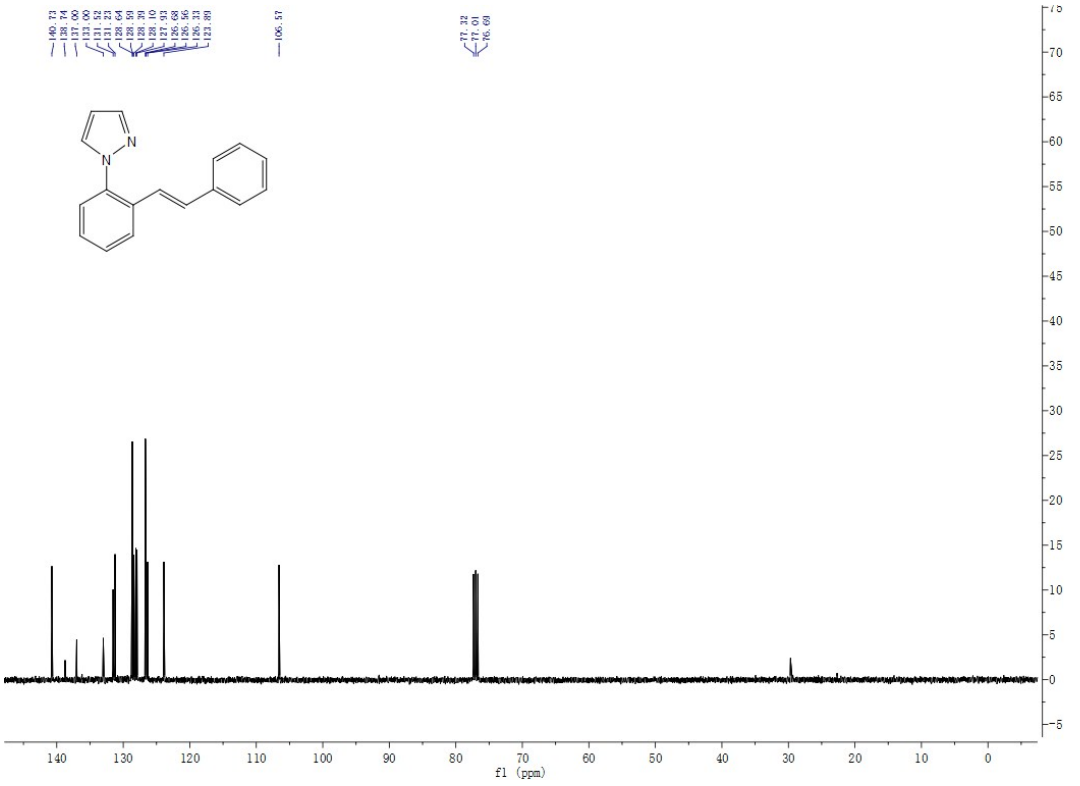

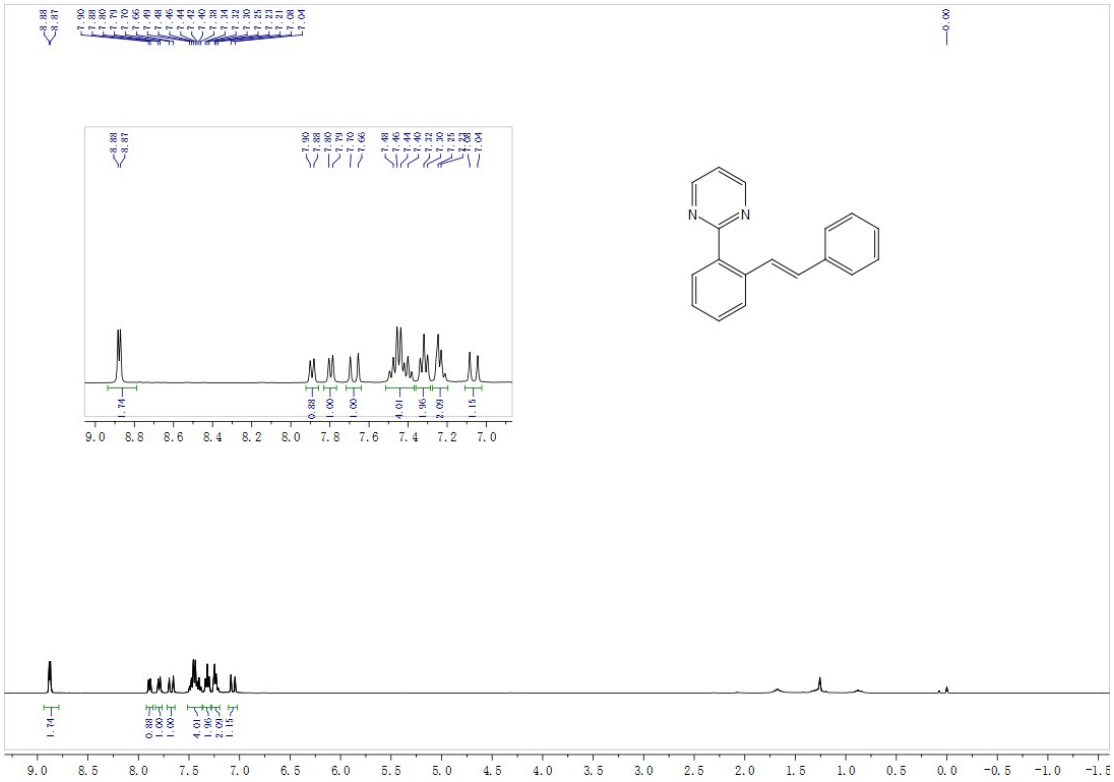

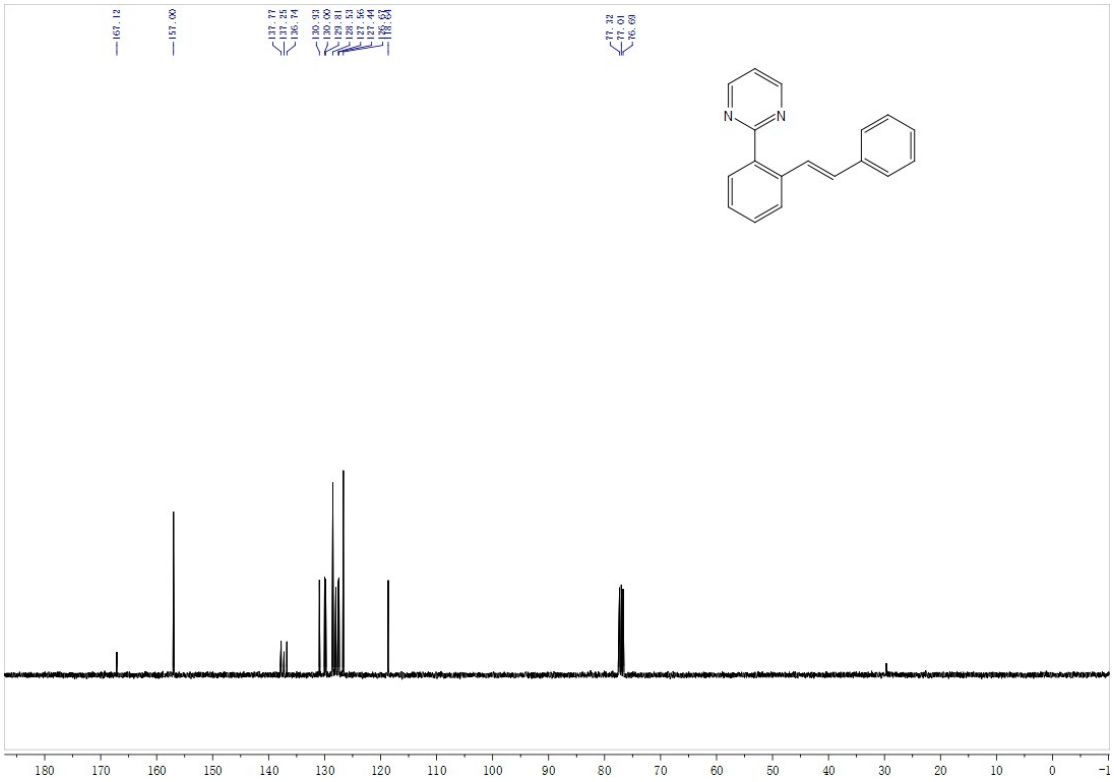

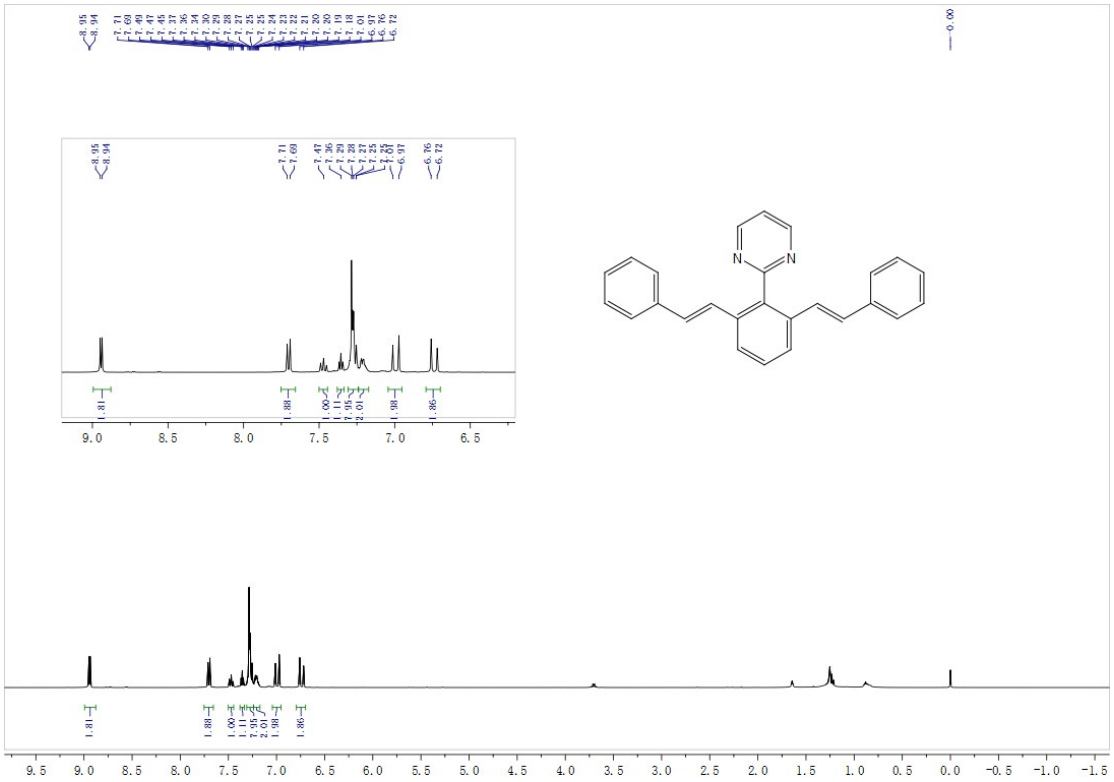

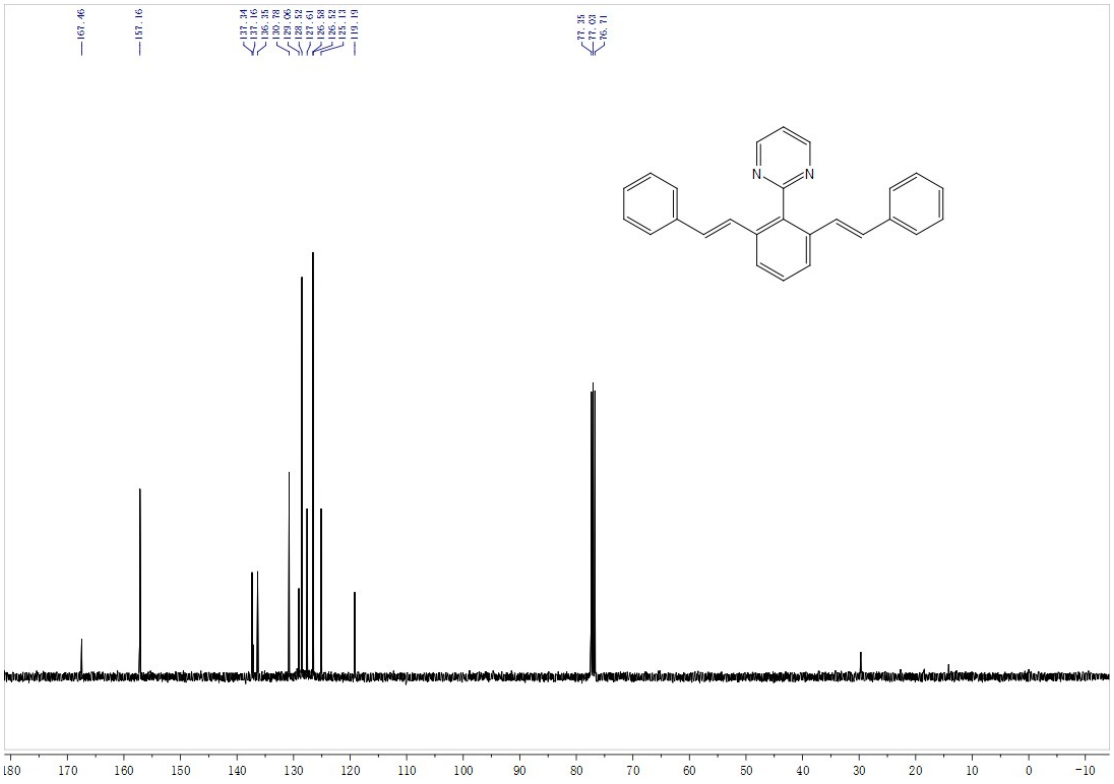

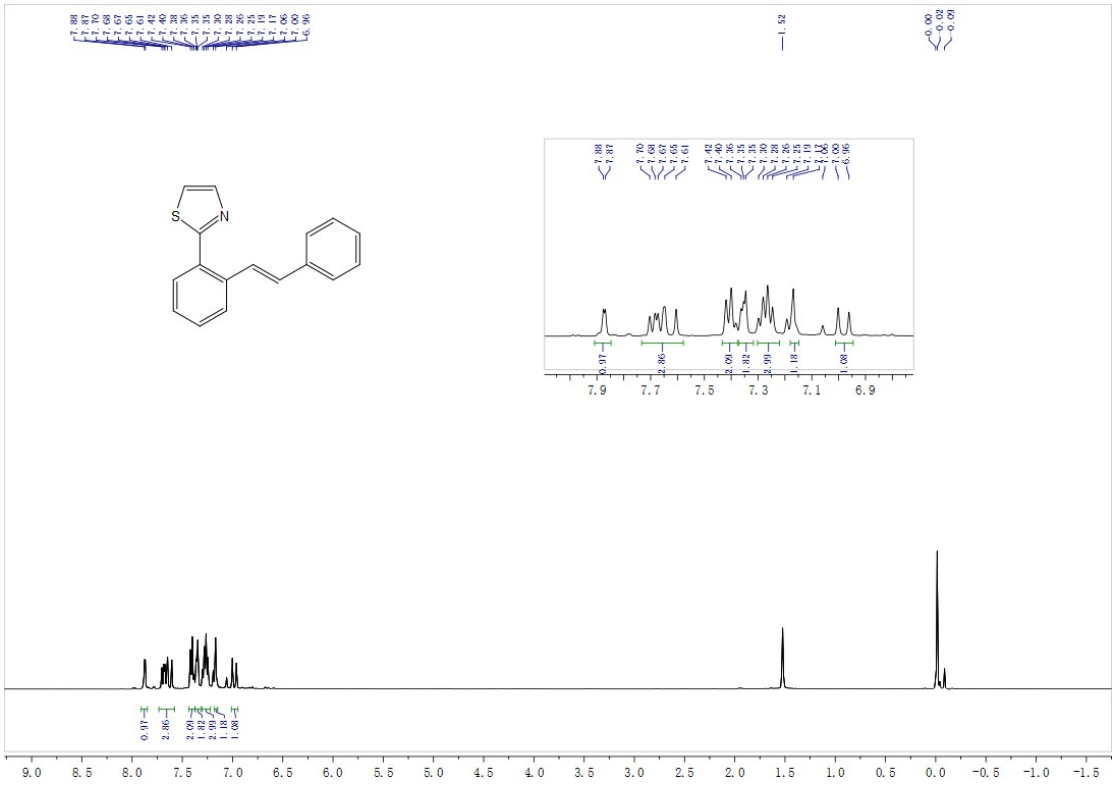

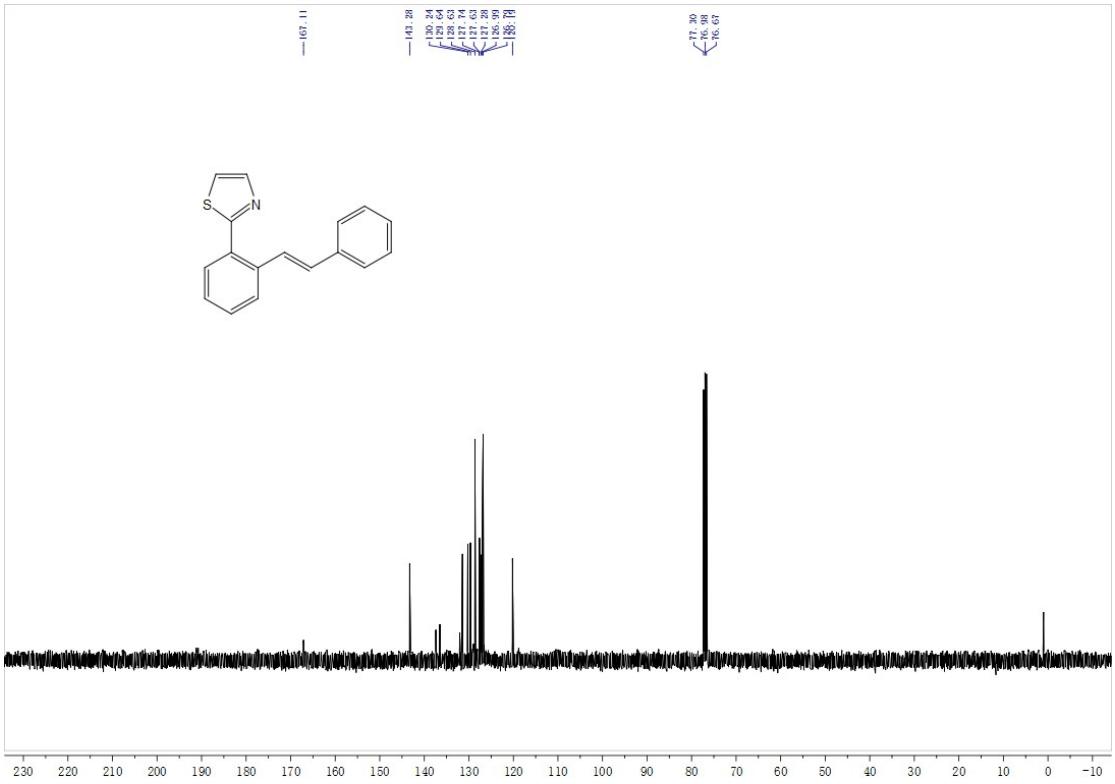

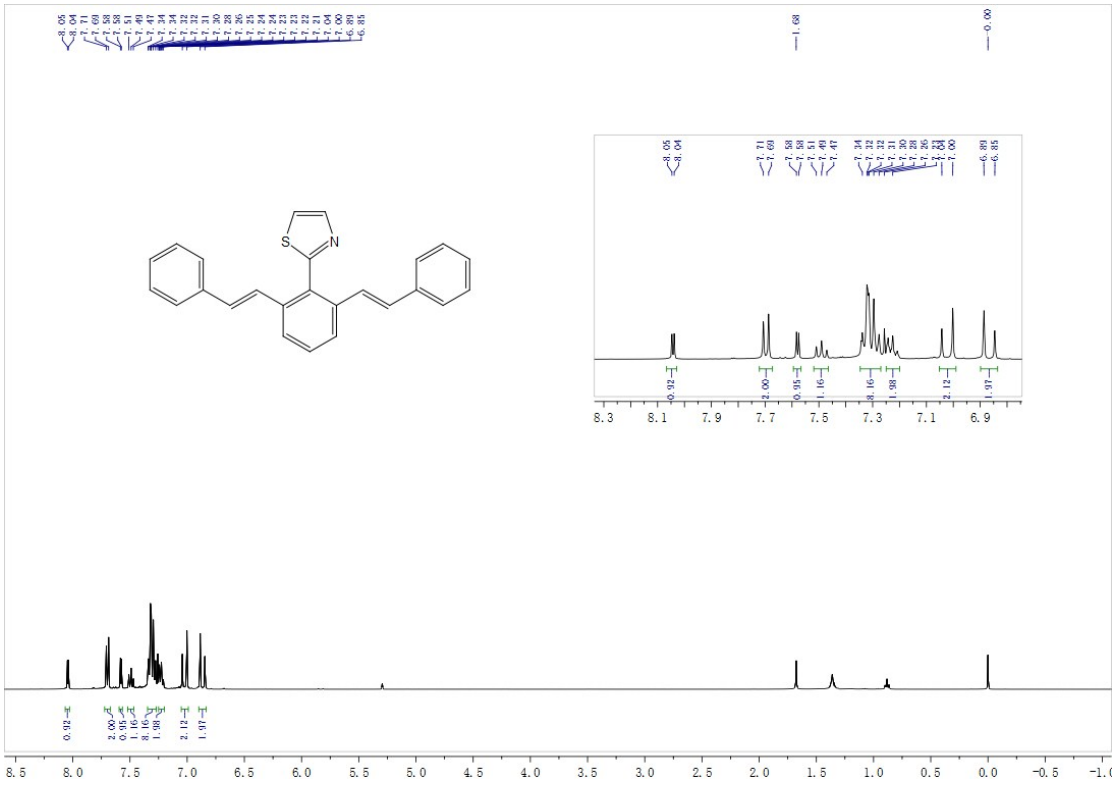

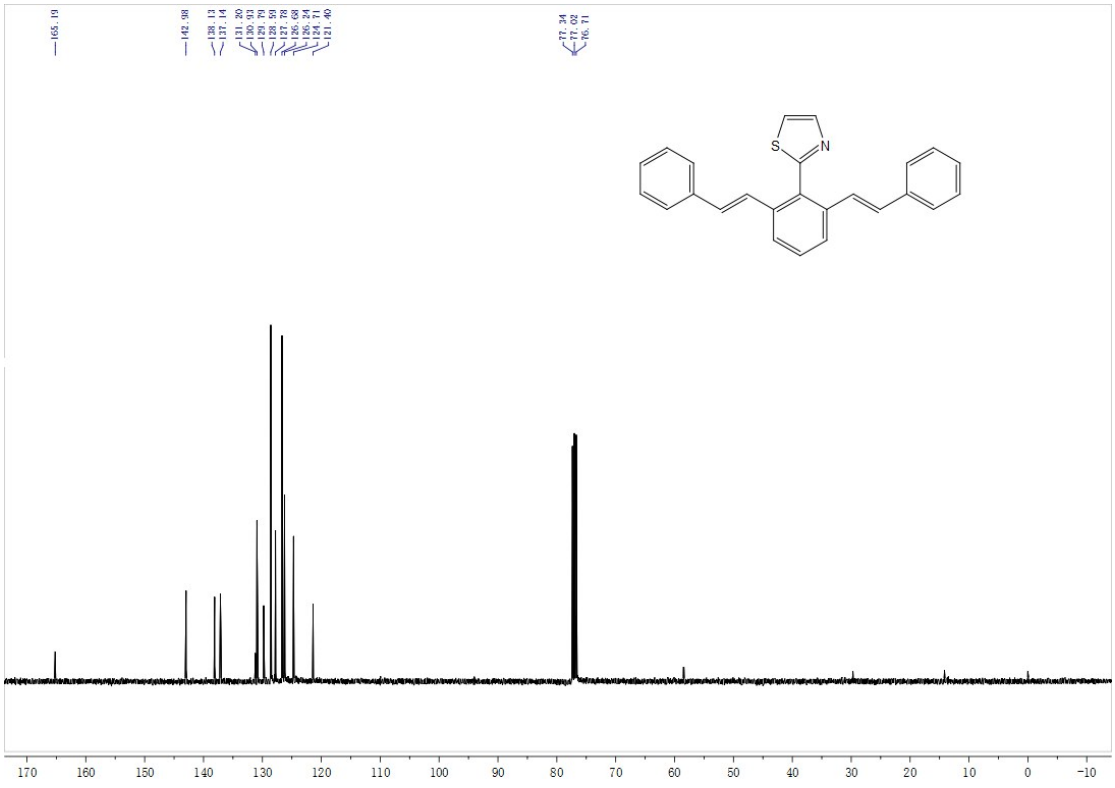

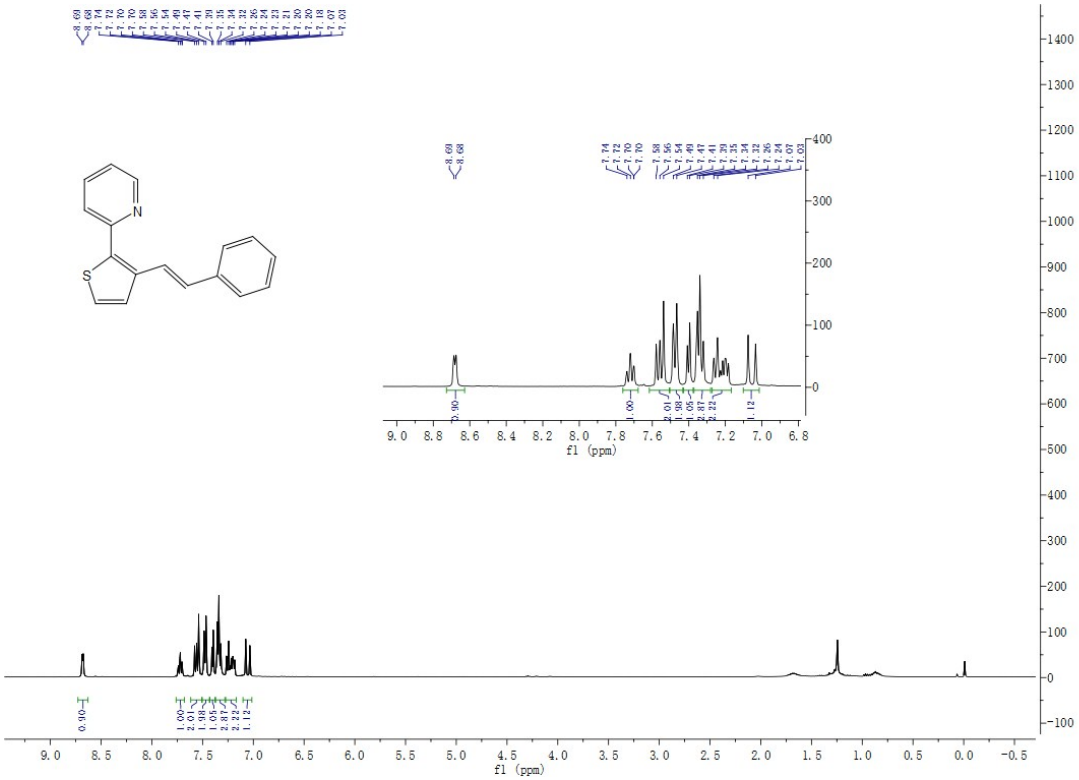
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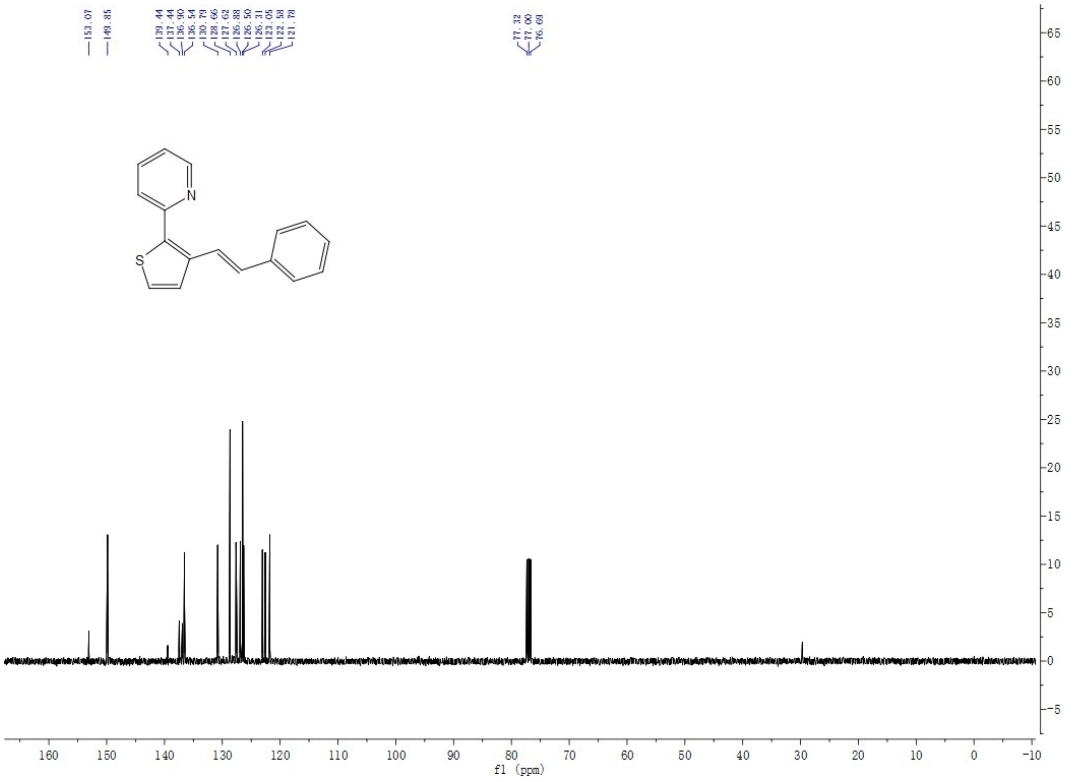
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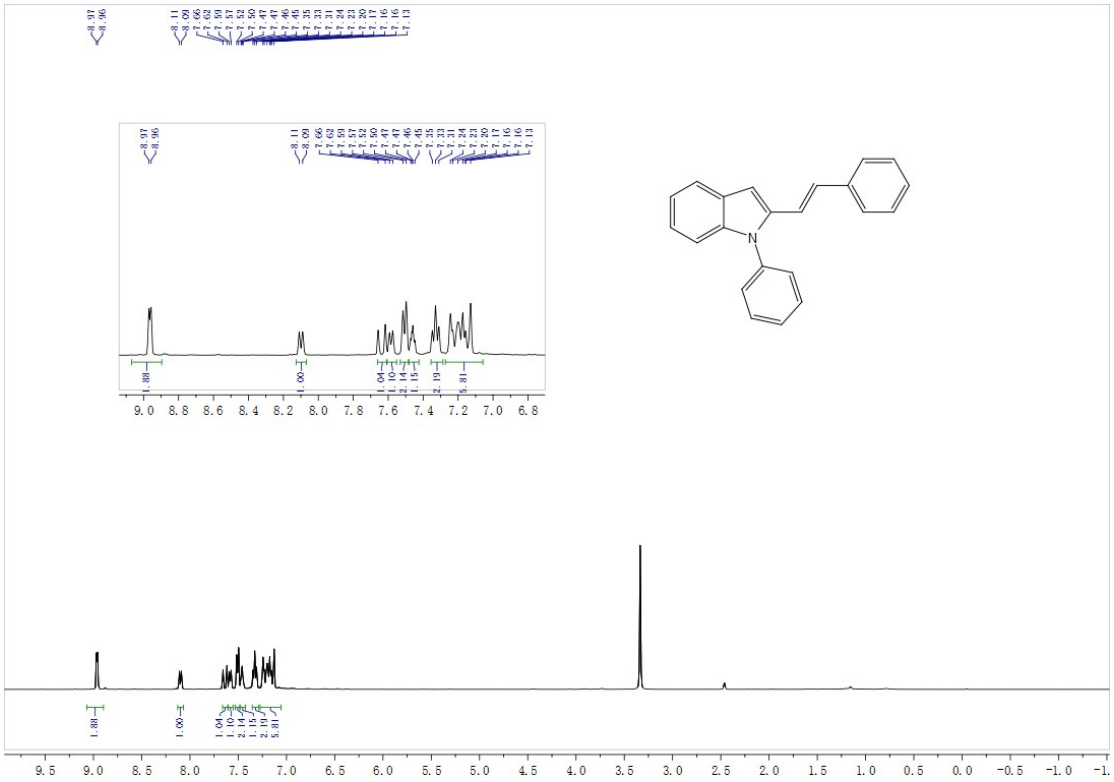
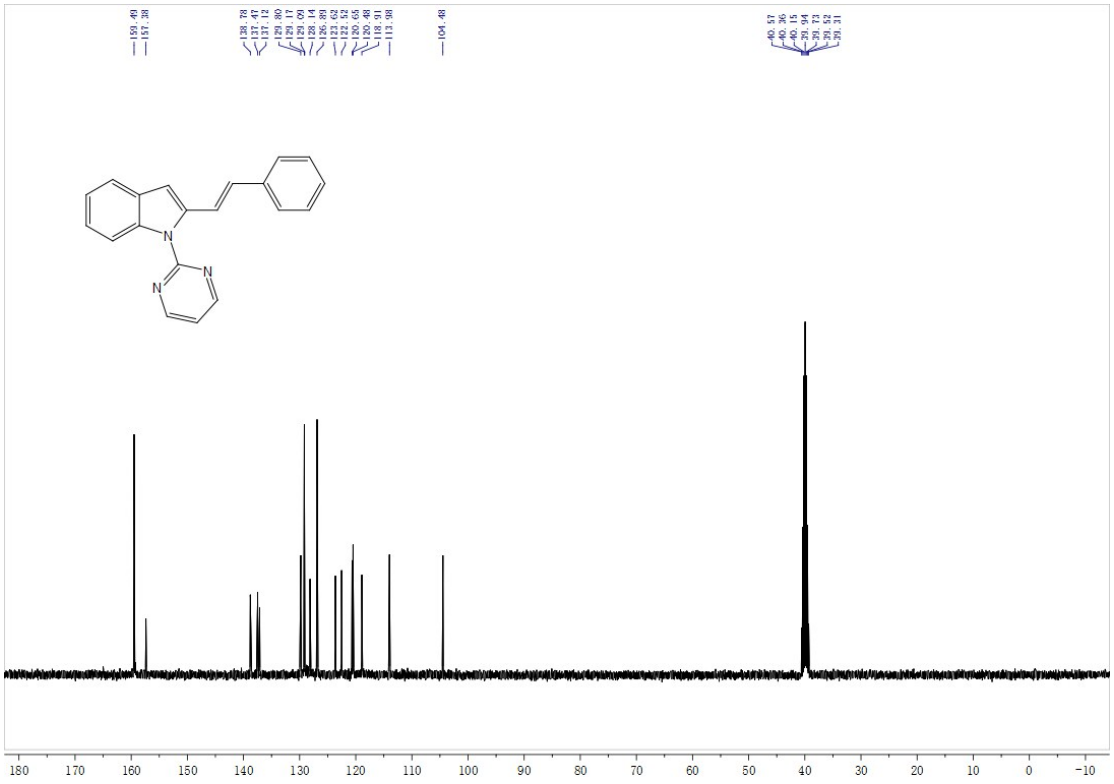
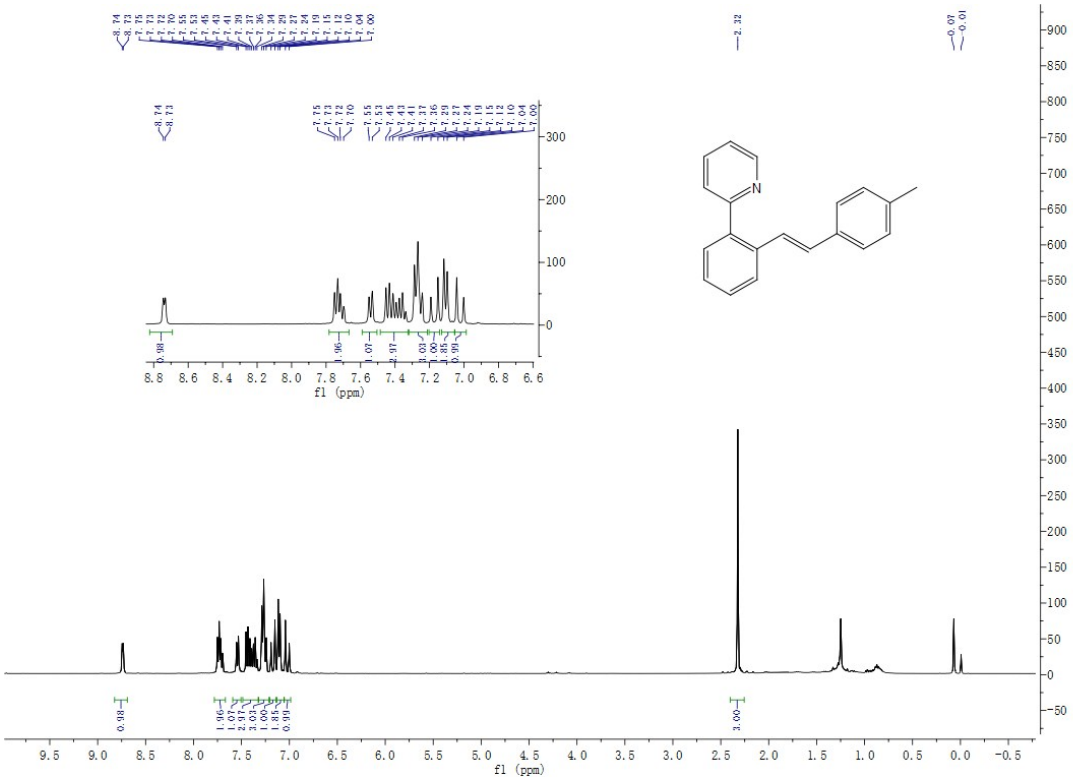
S
f1 (ppm)



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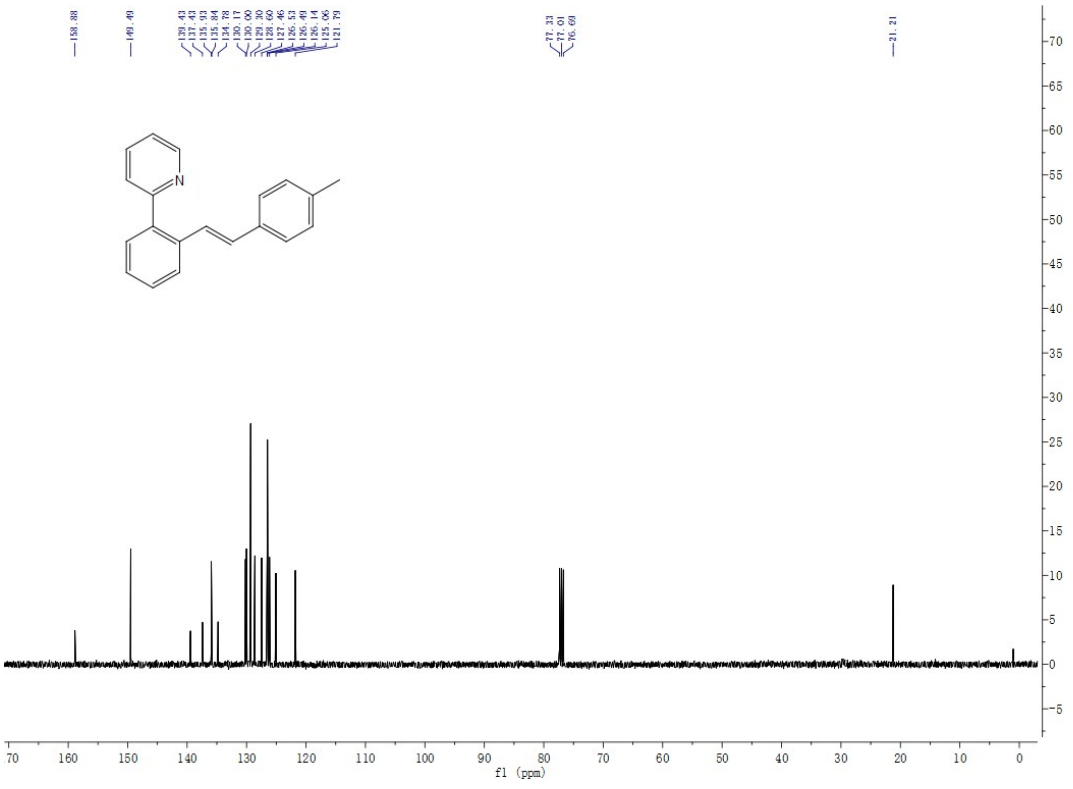
N
f1 (ppm)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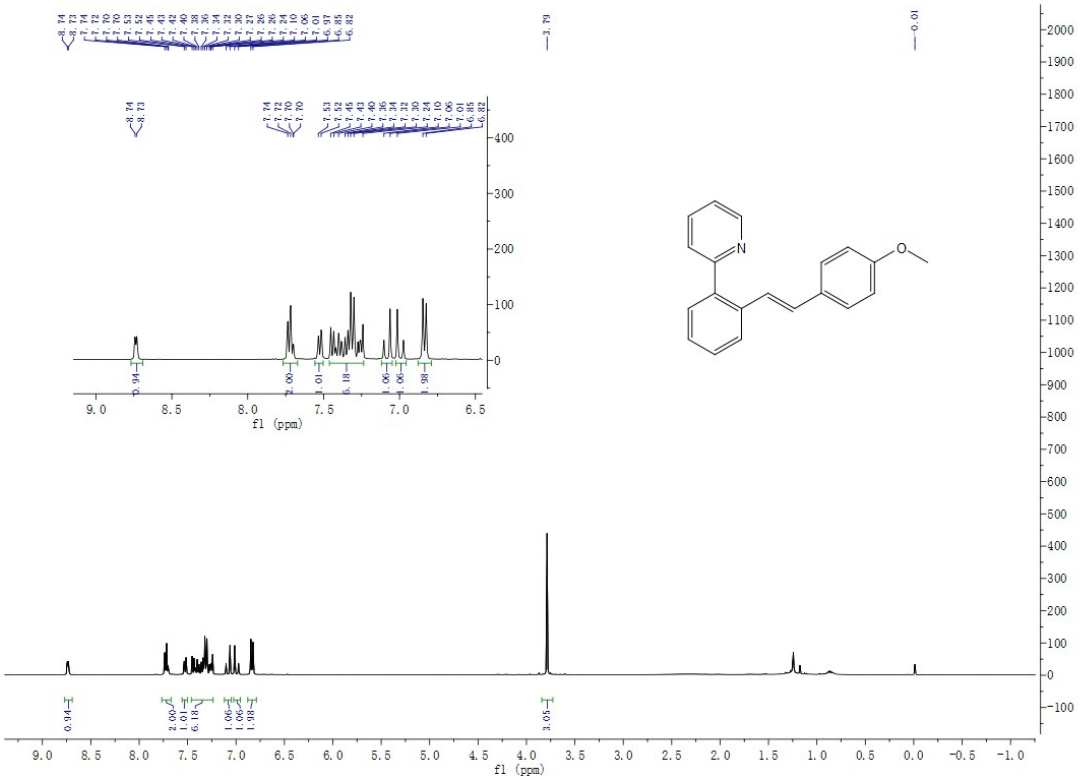
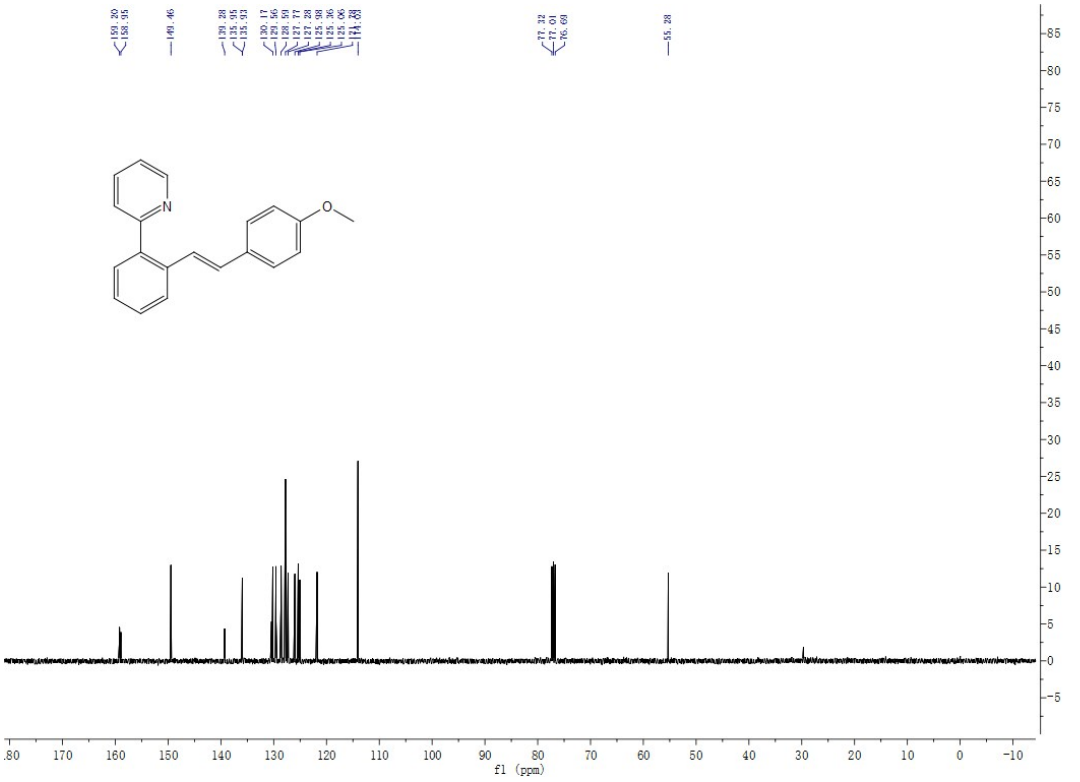
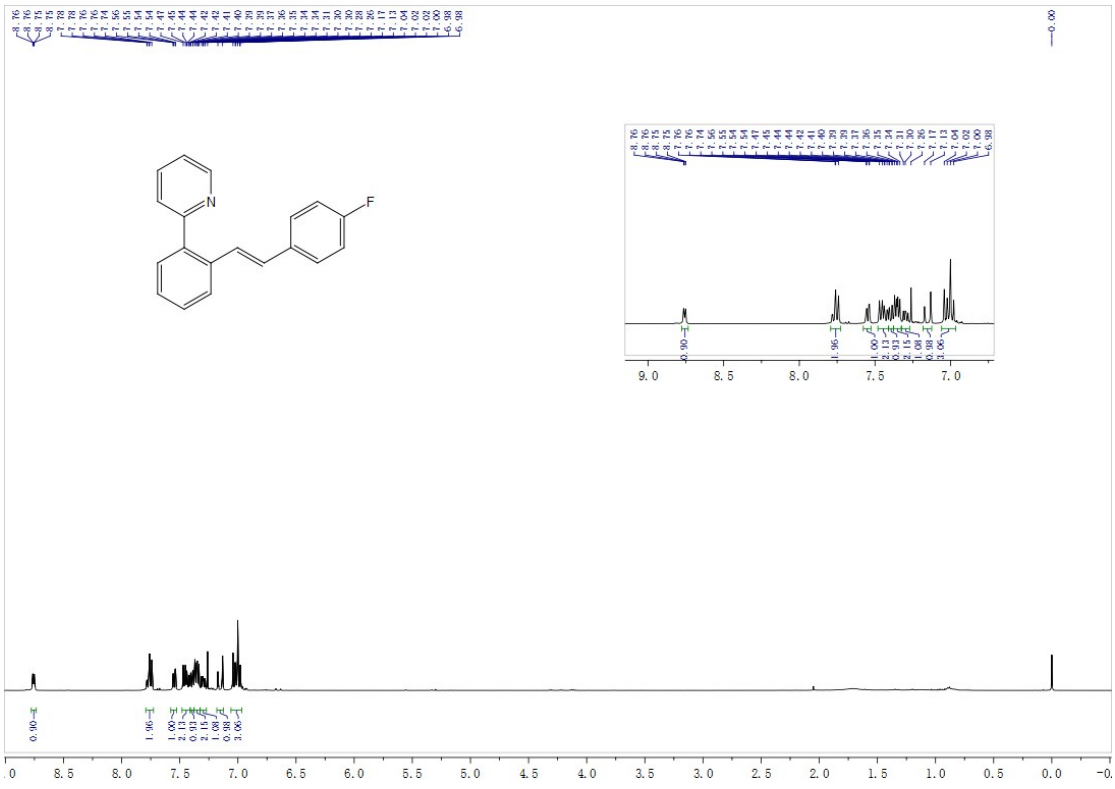
f1 (ppm)



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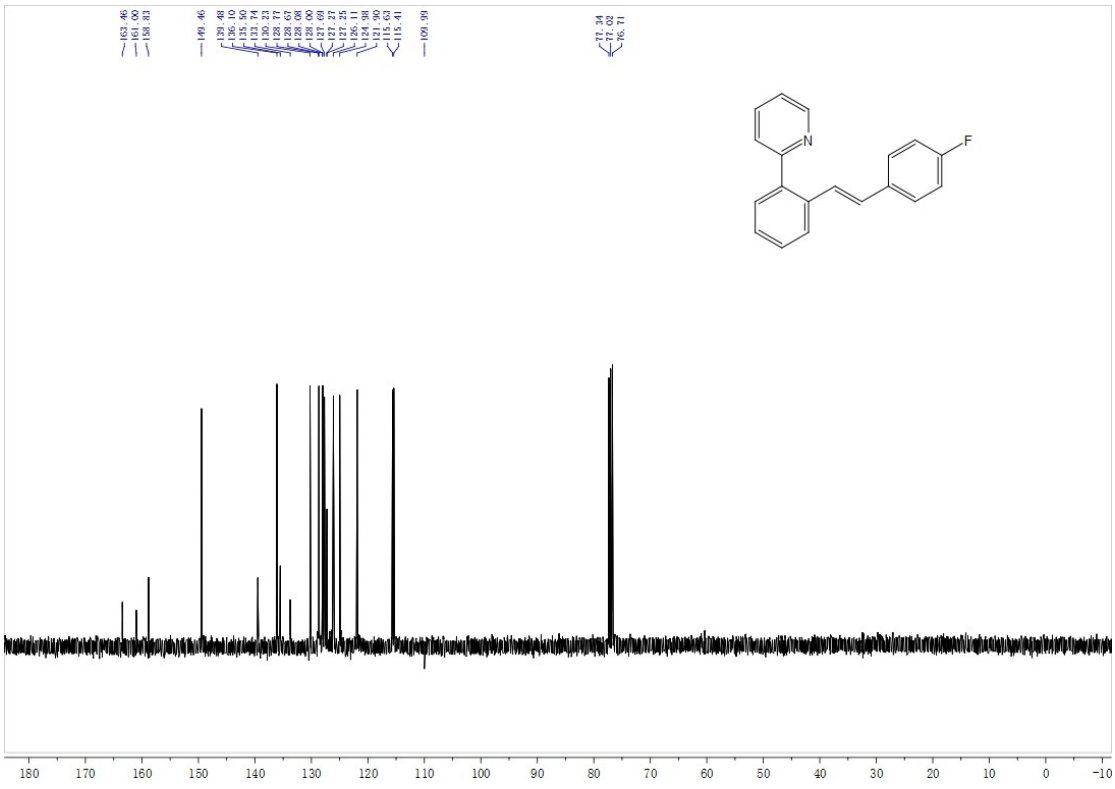
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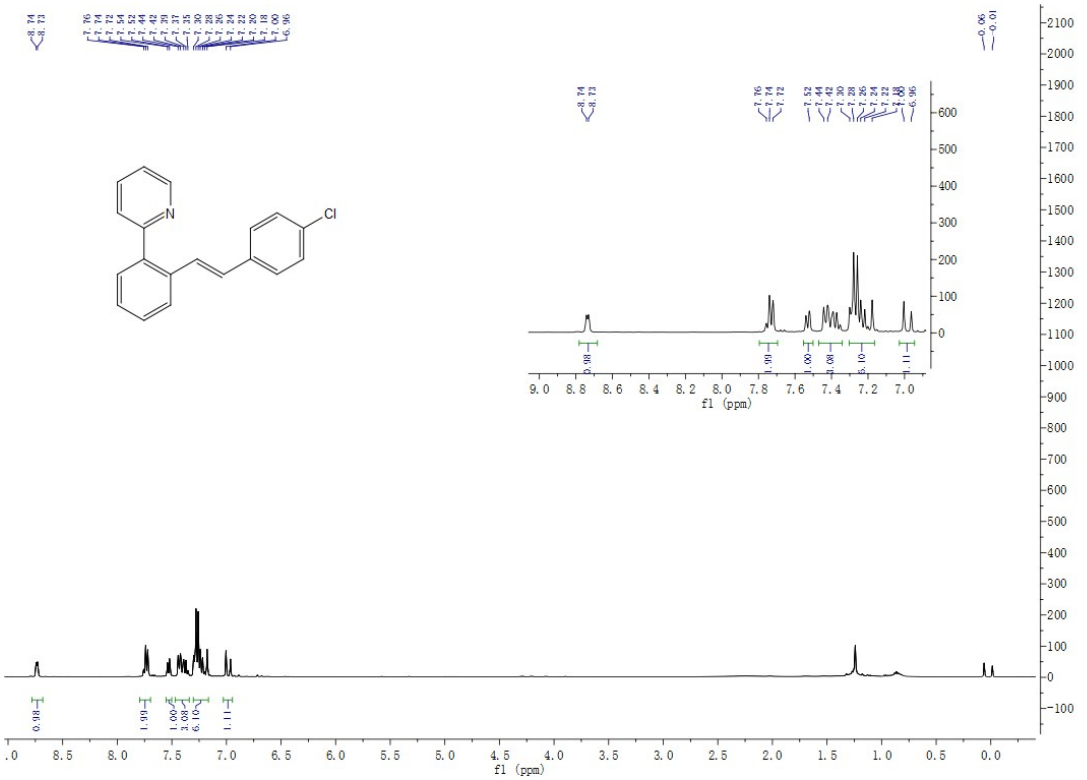
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Cl
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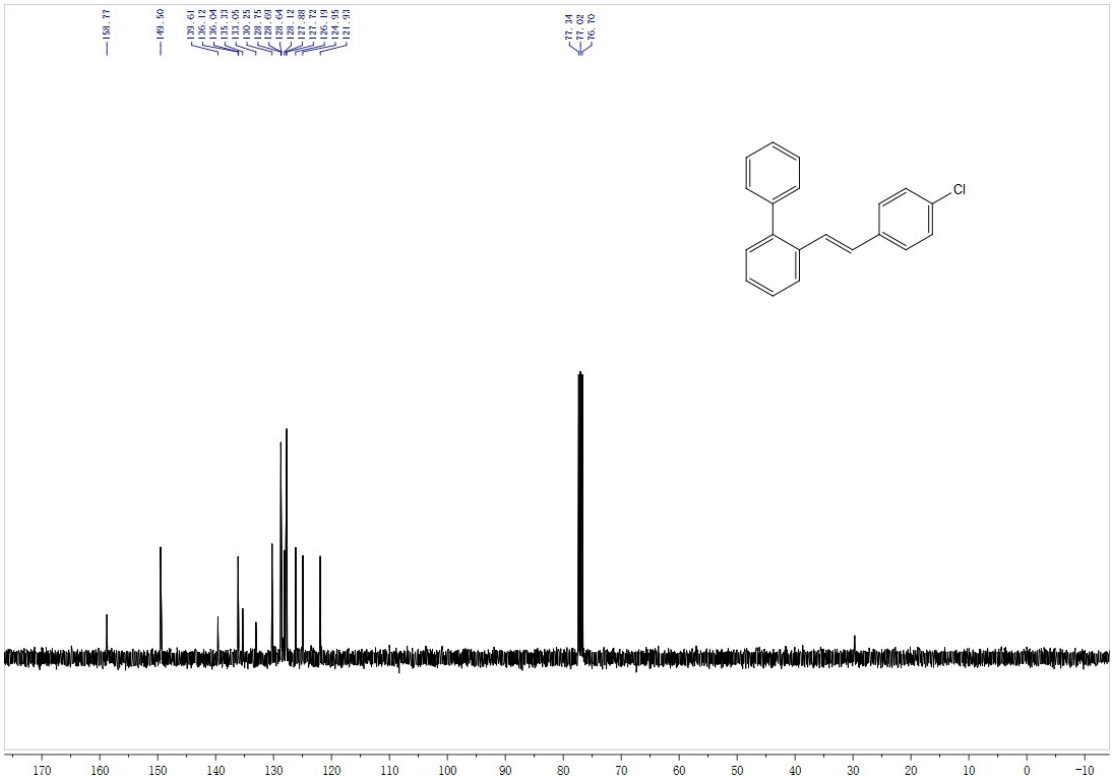
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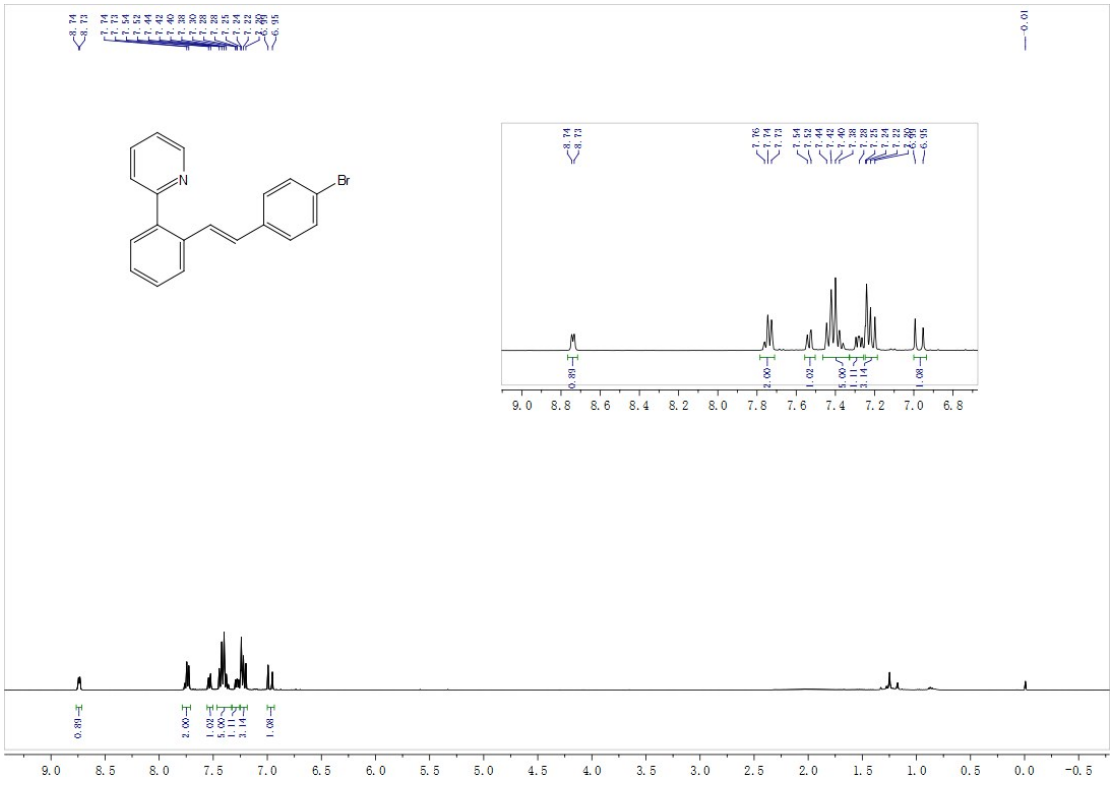
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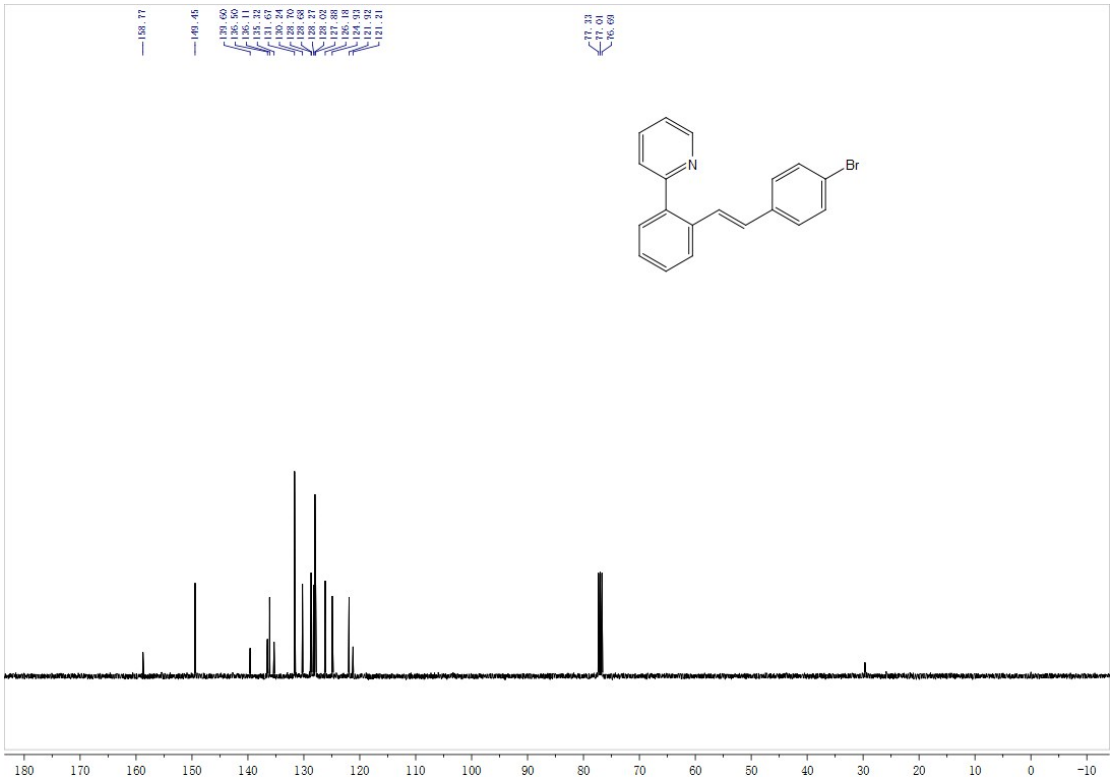
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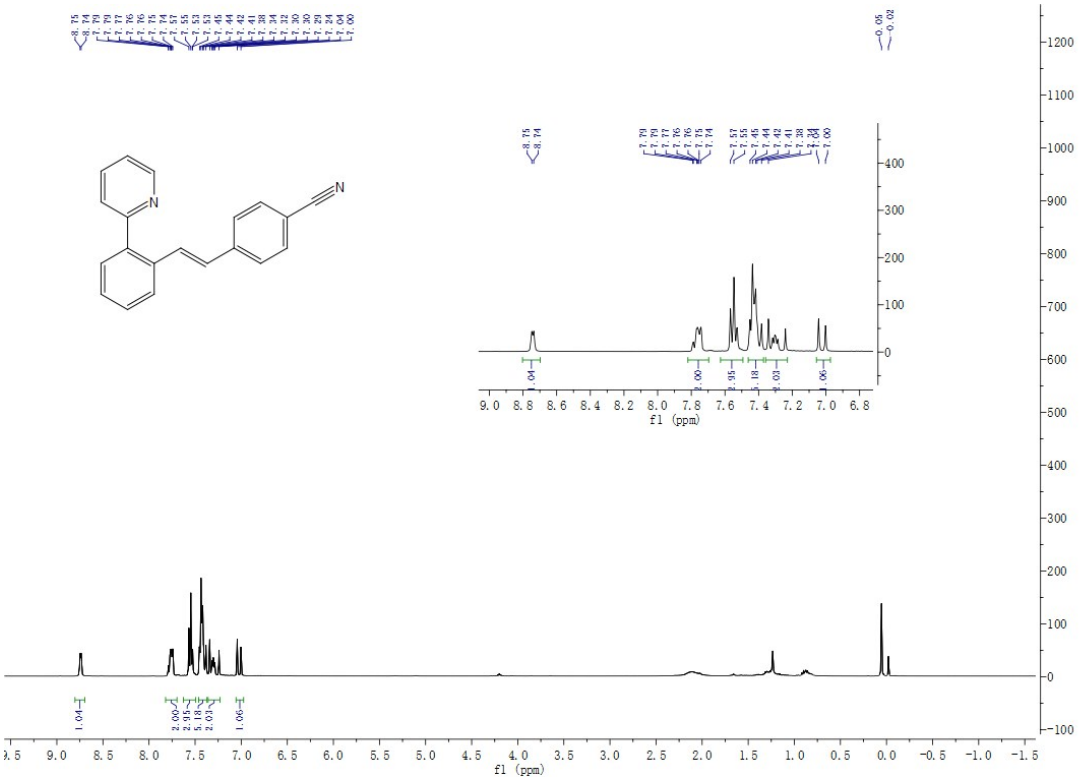
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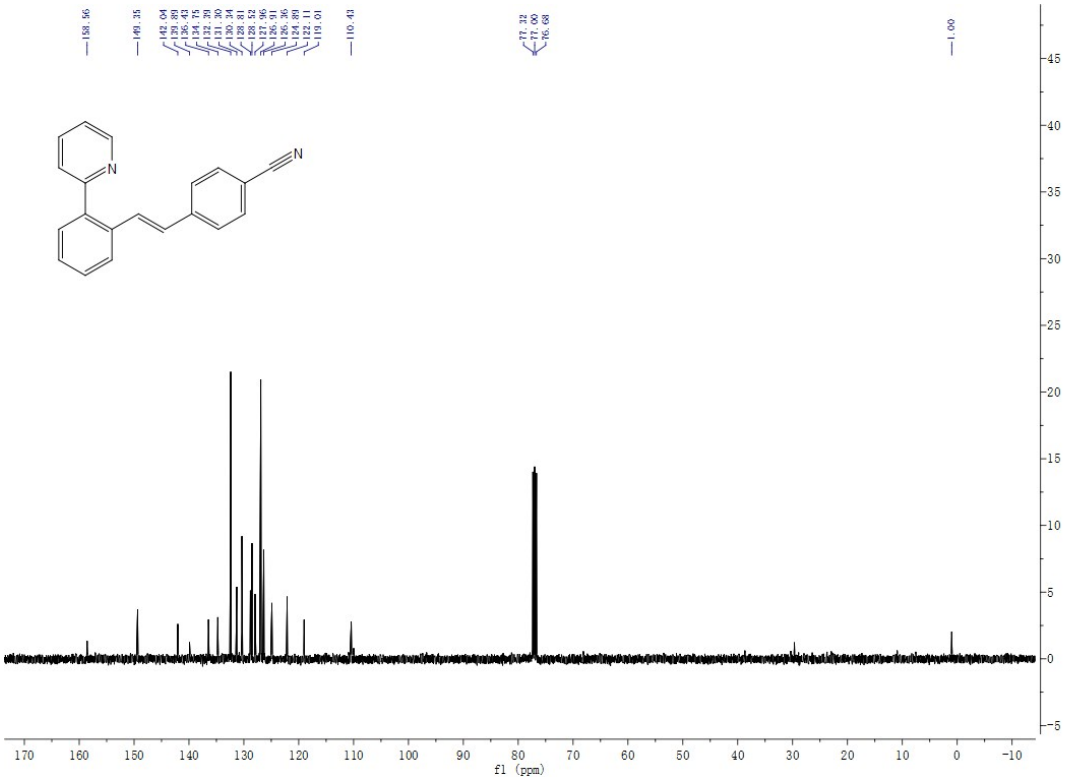
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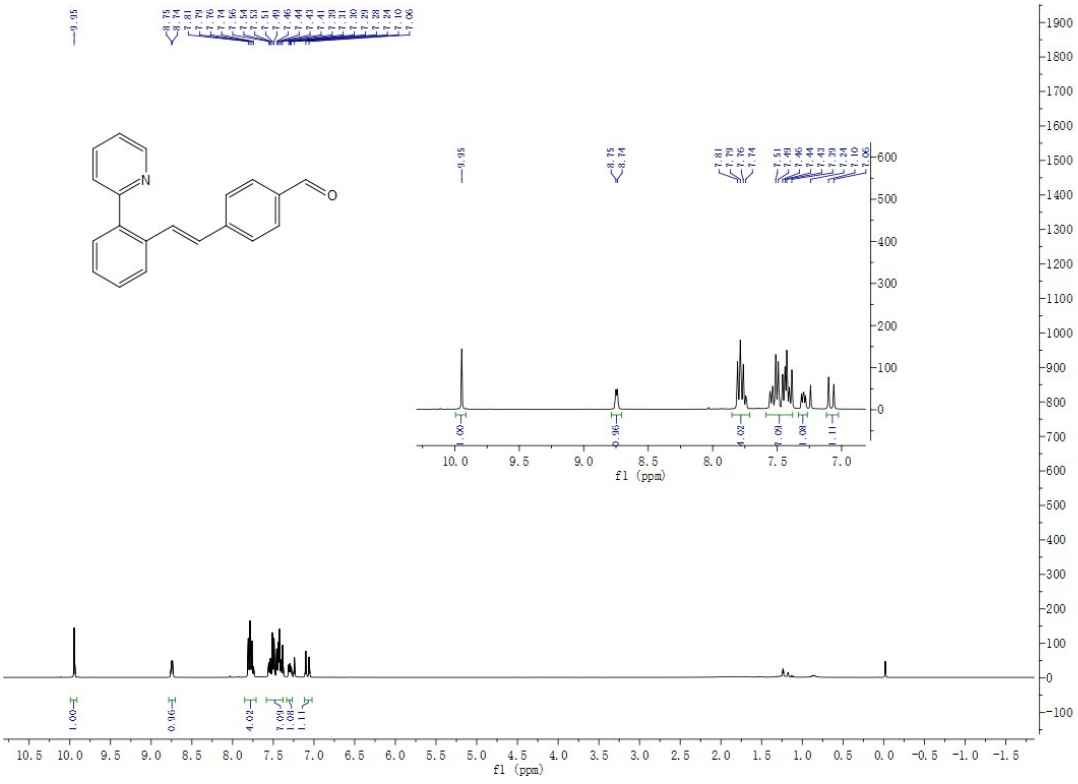
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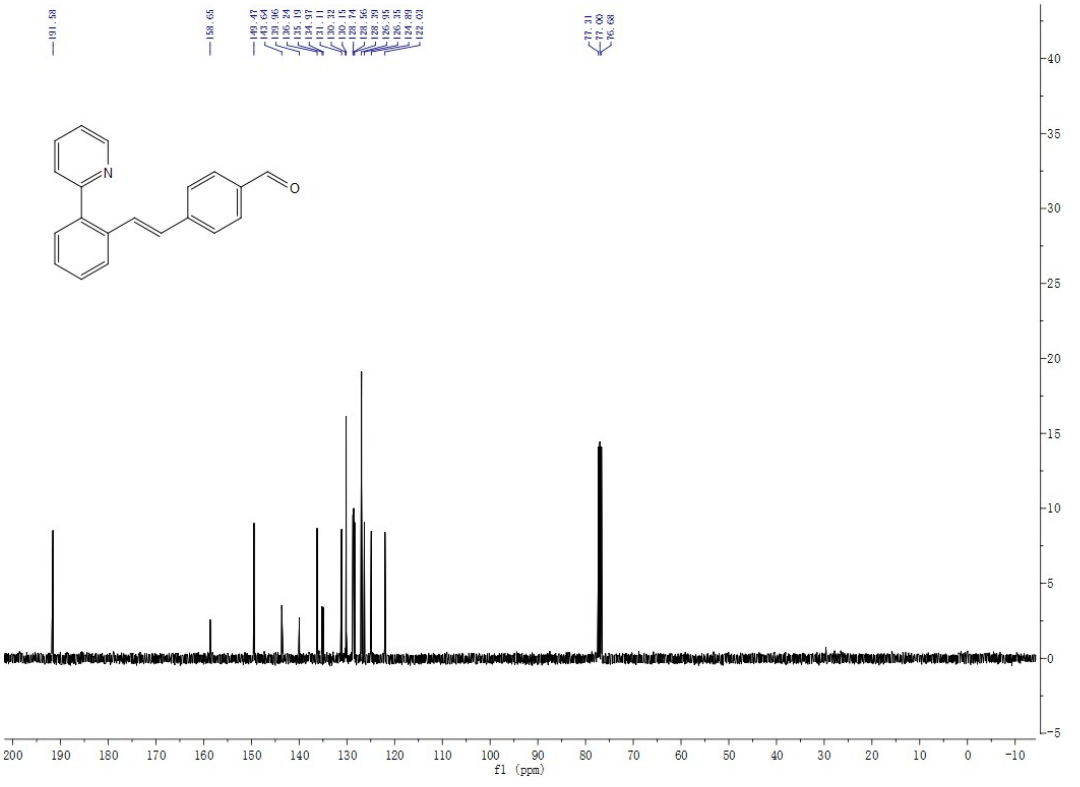
f1 (ppm)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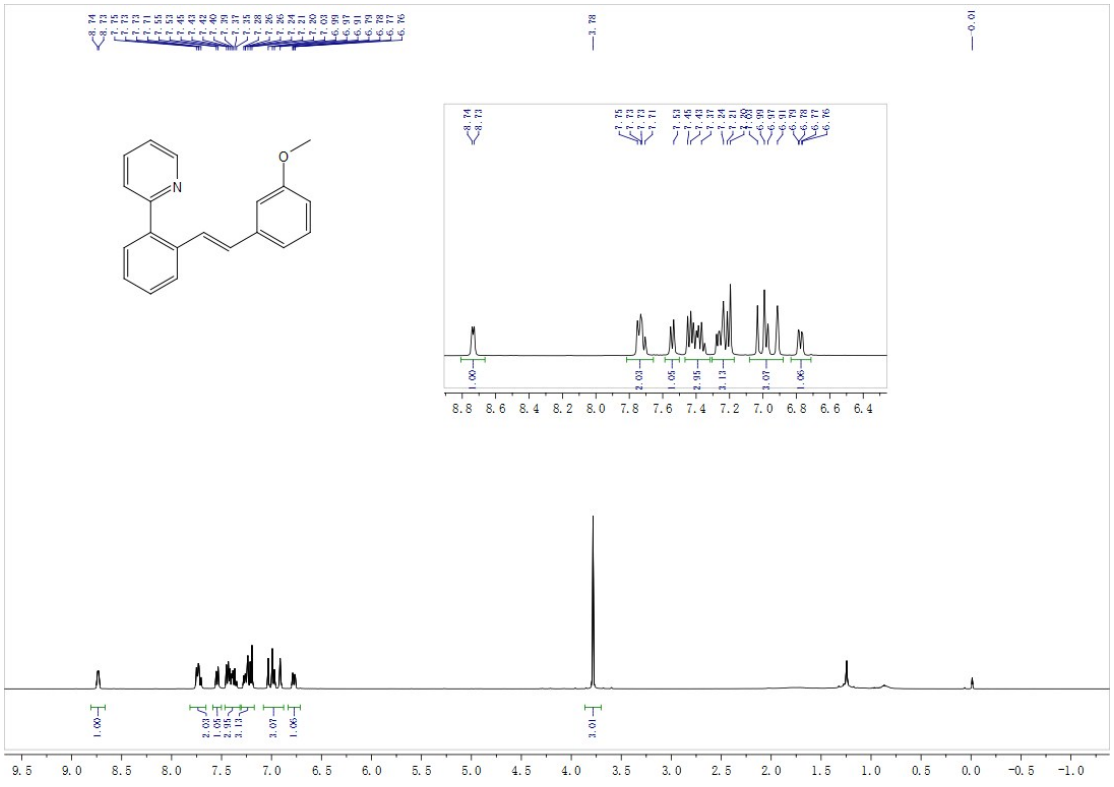
O
f1 (ppm)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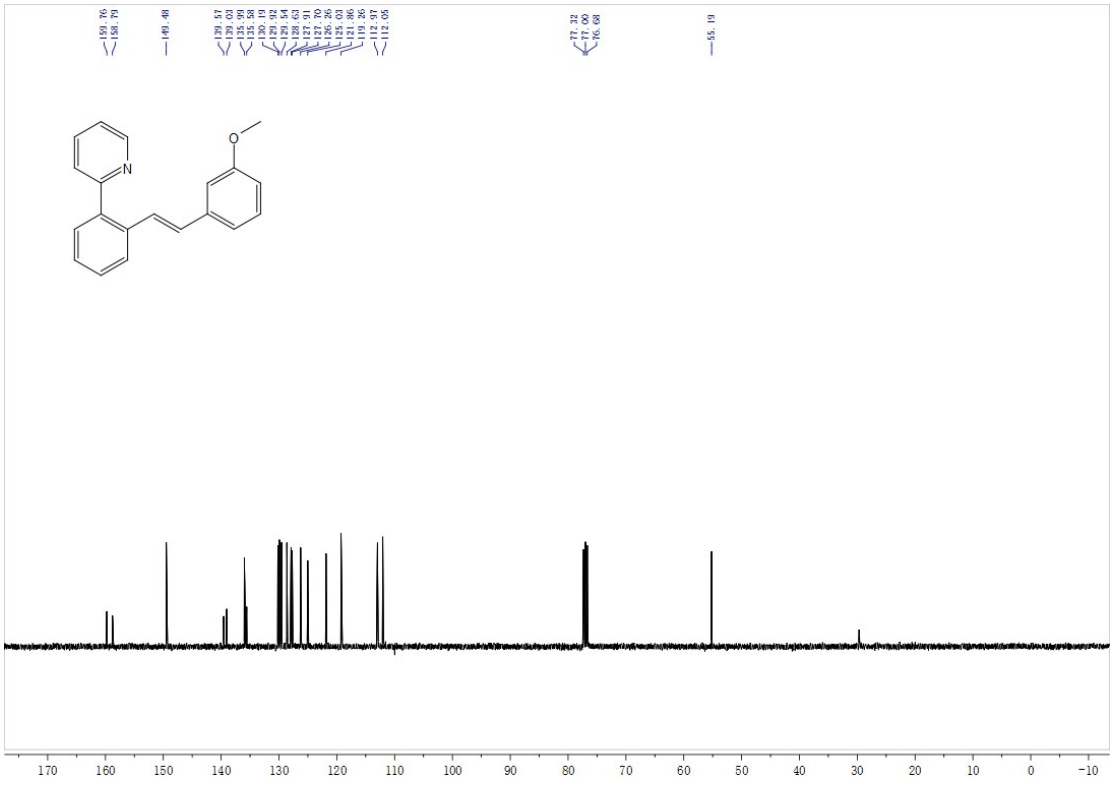
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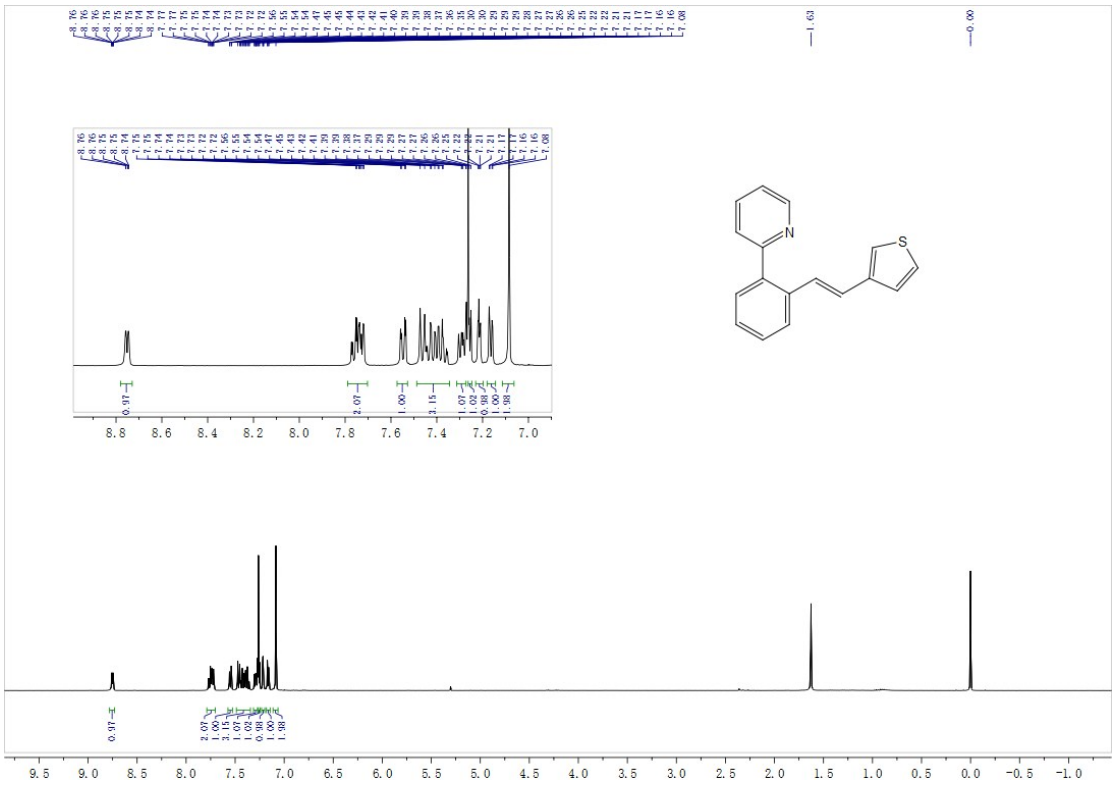
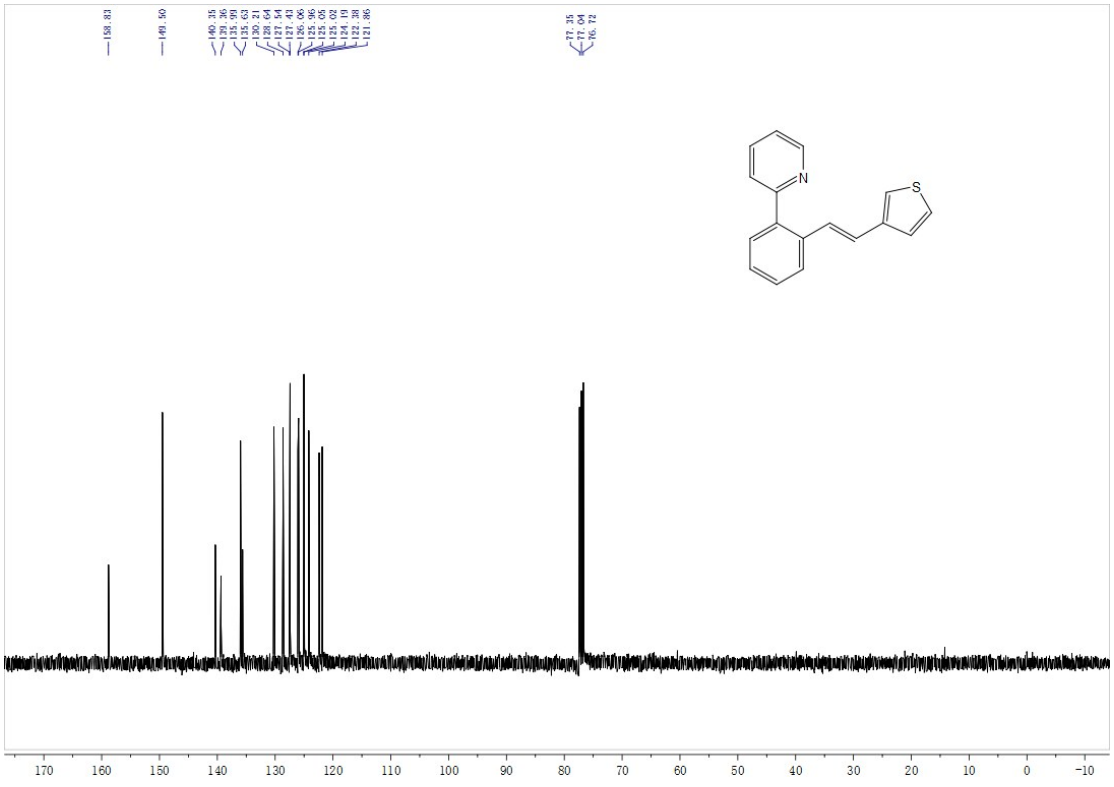
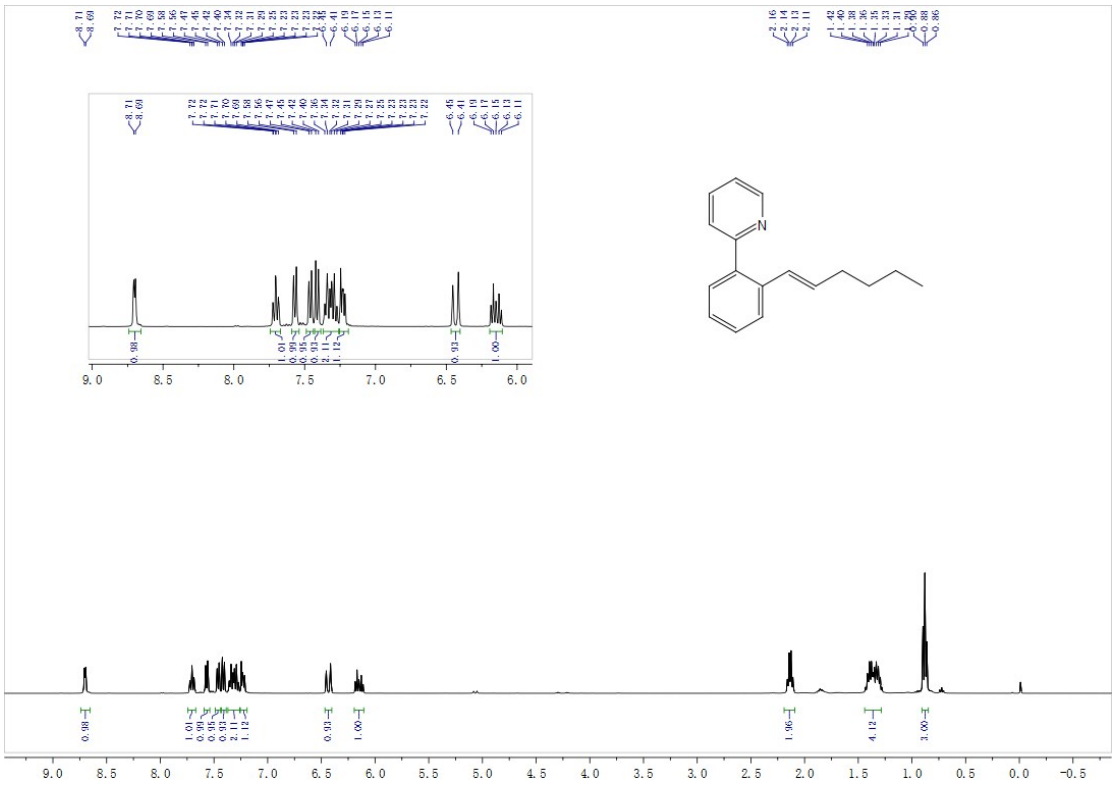
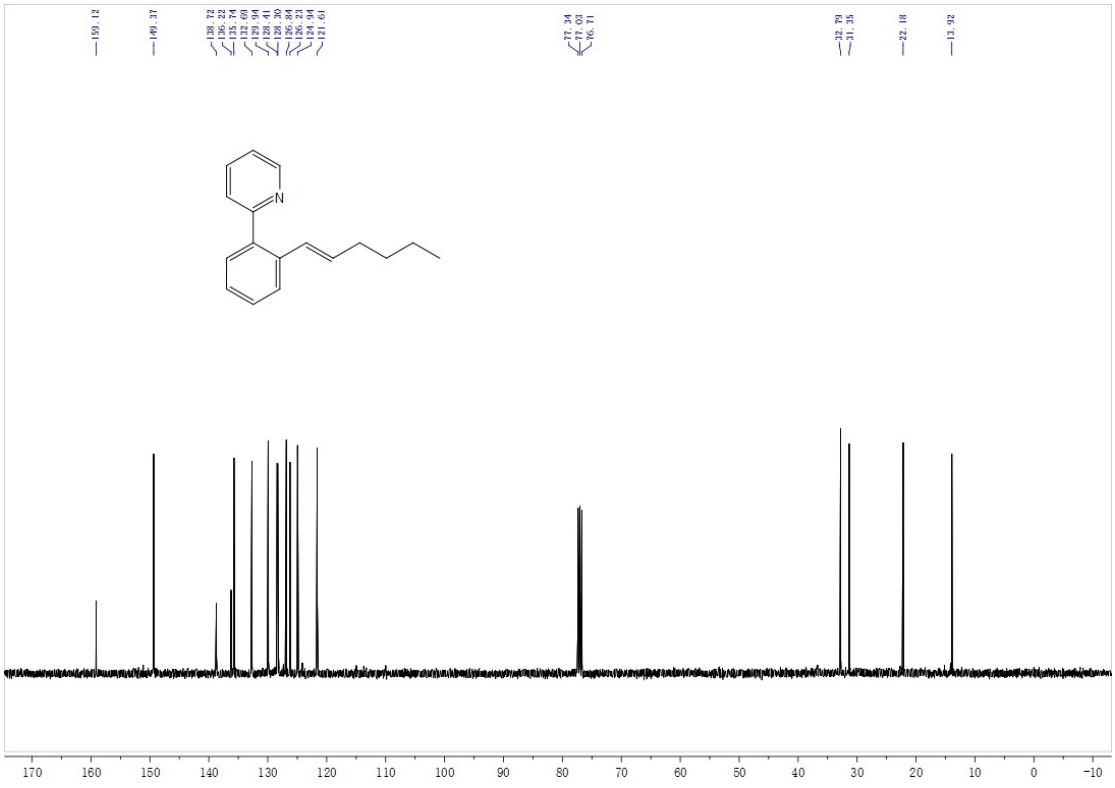
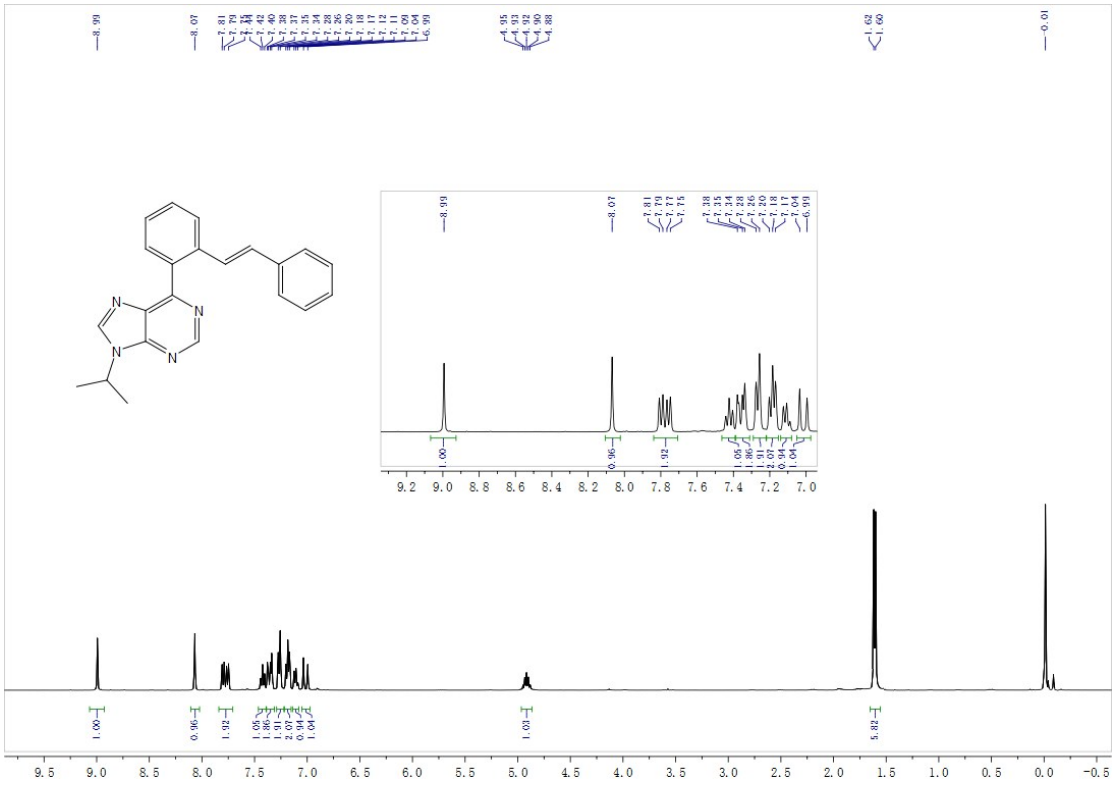
N
O

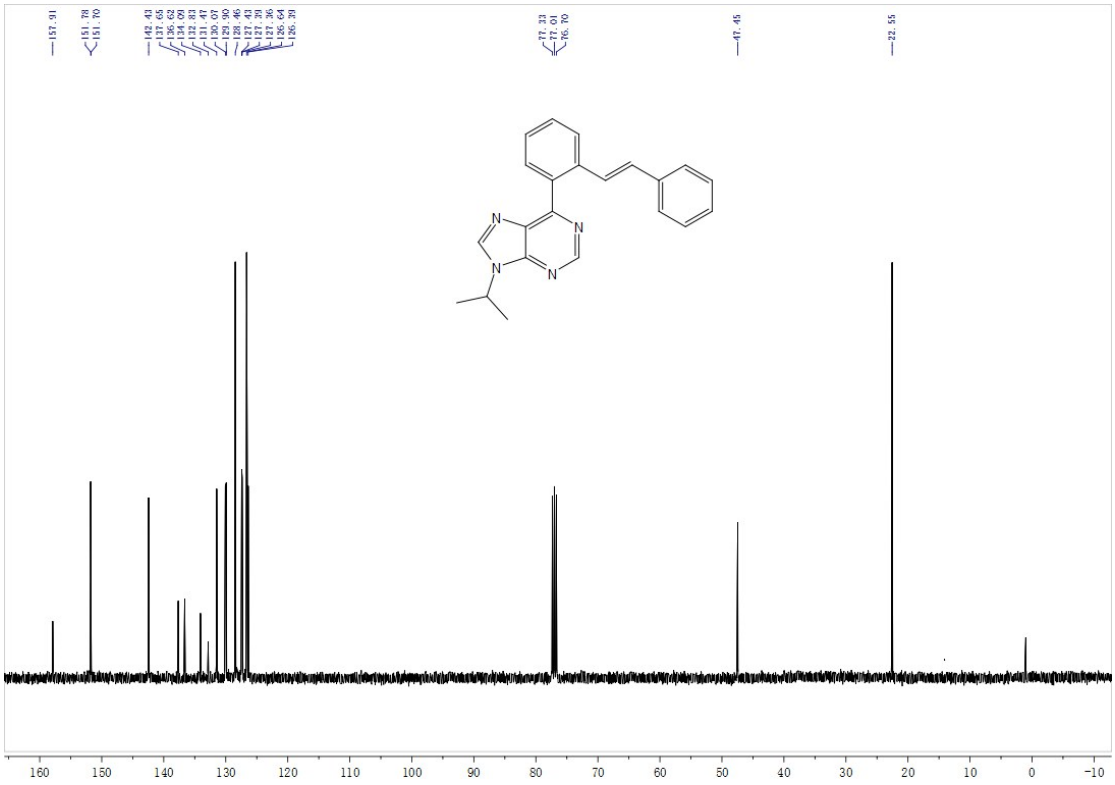


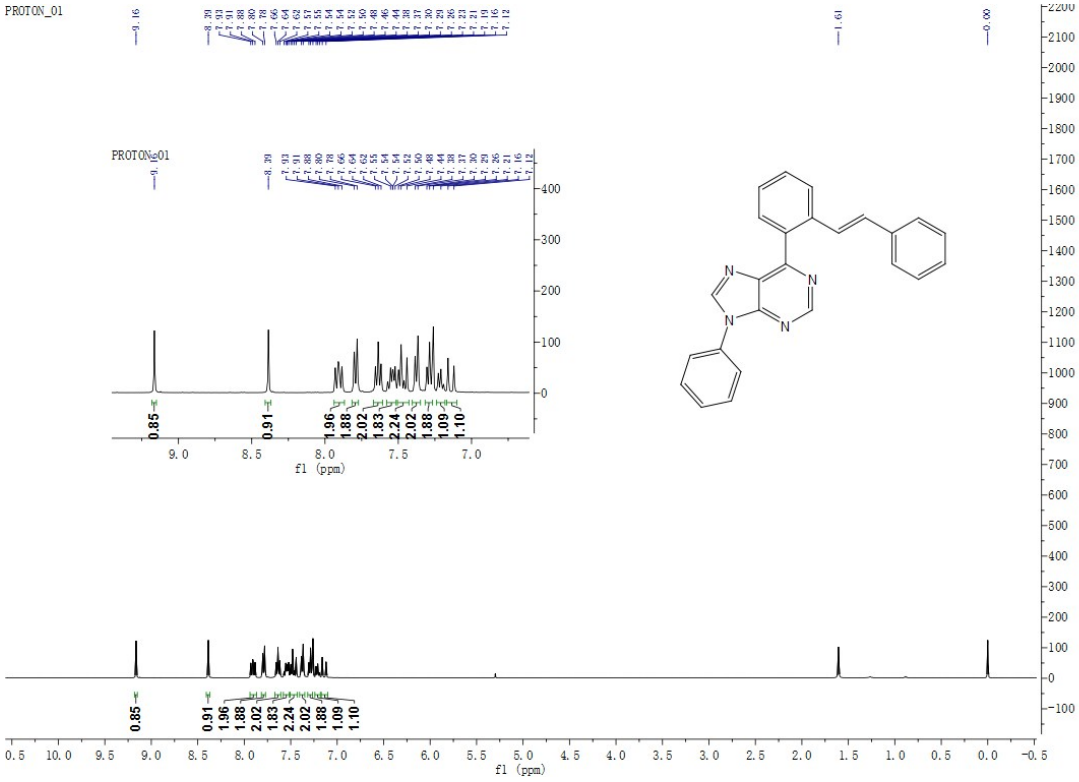








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PROTON_01
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1.88
2.02
1.83
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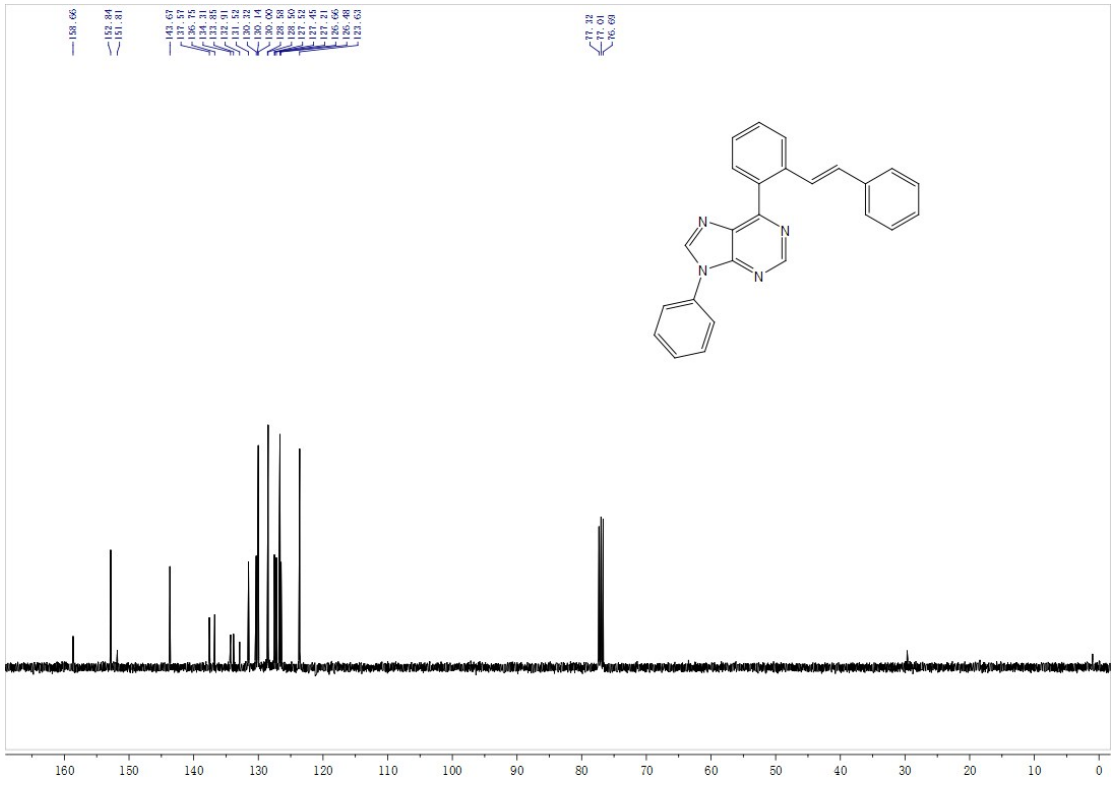
1.88
1.09
1.10
f1 (ppm)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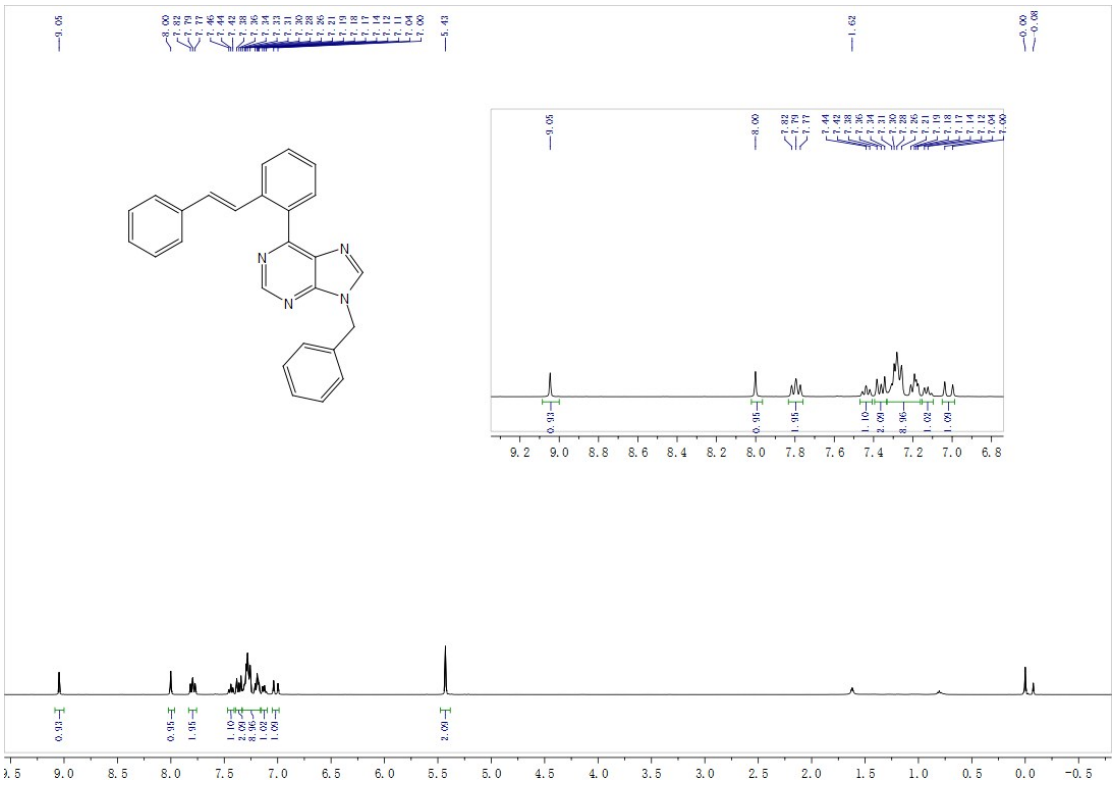

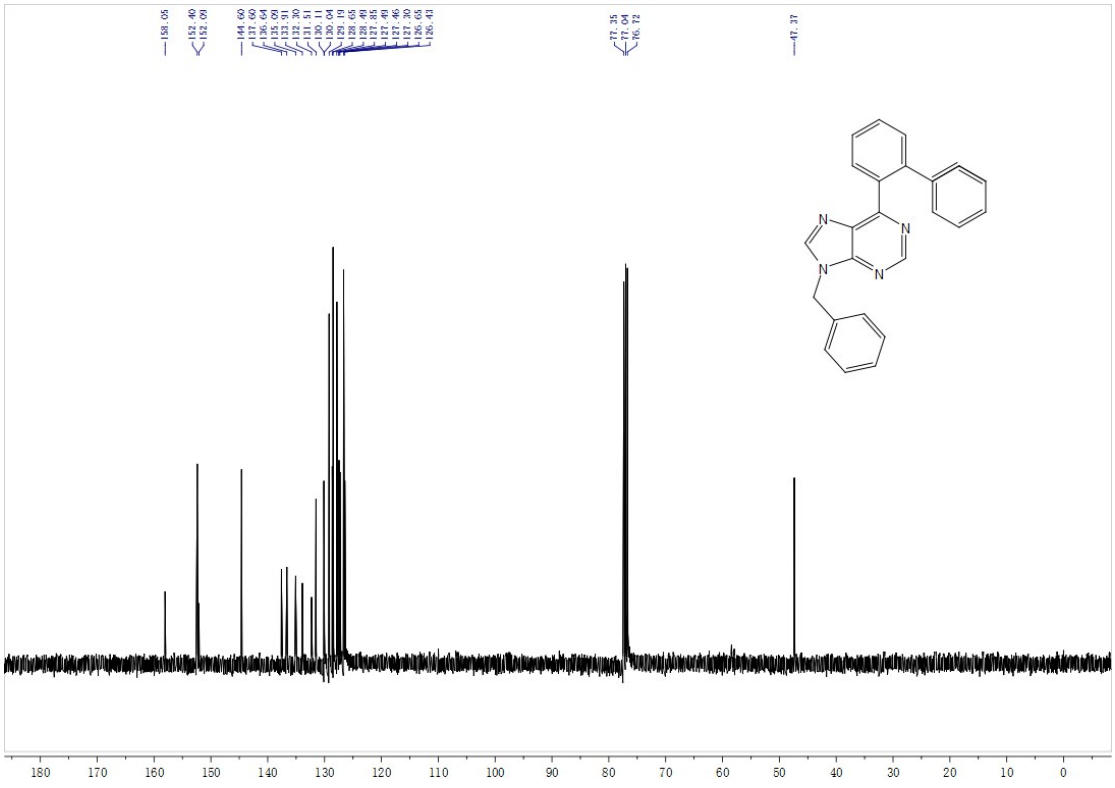

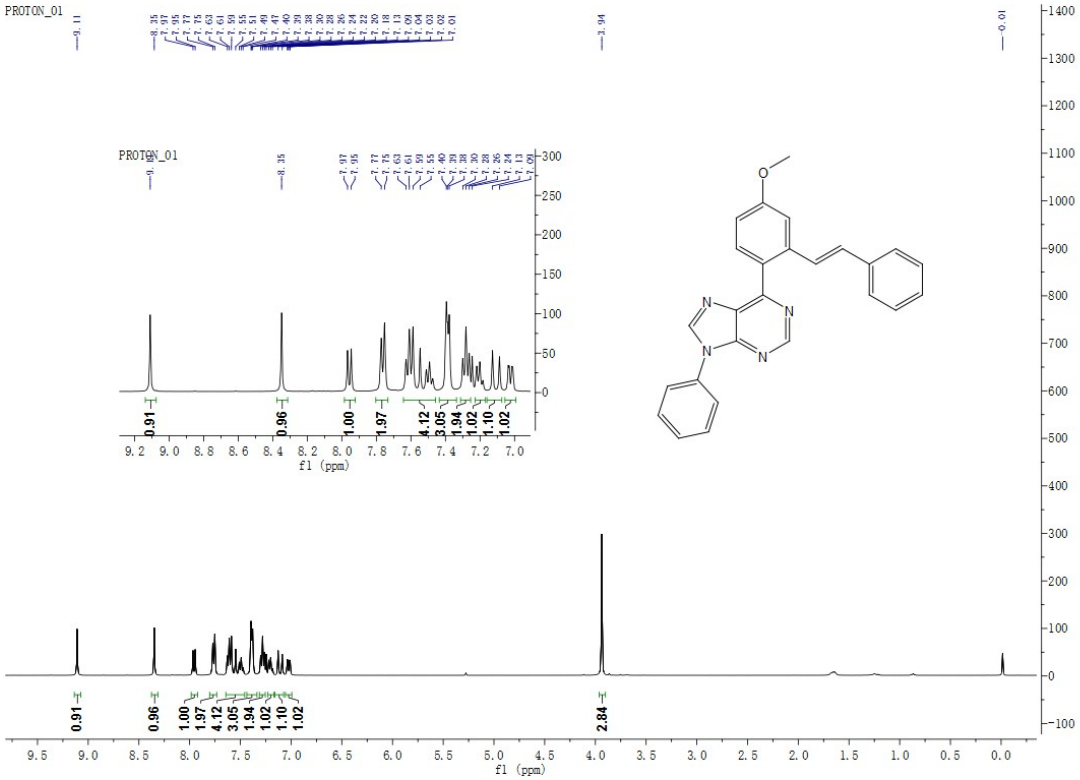
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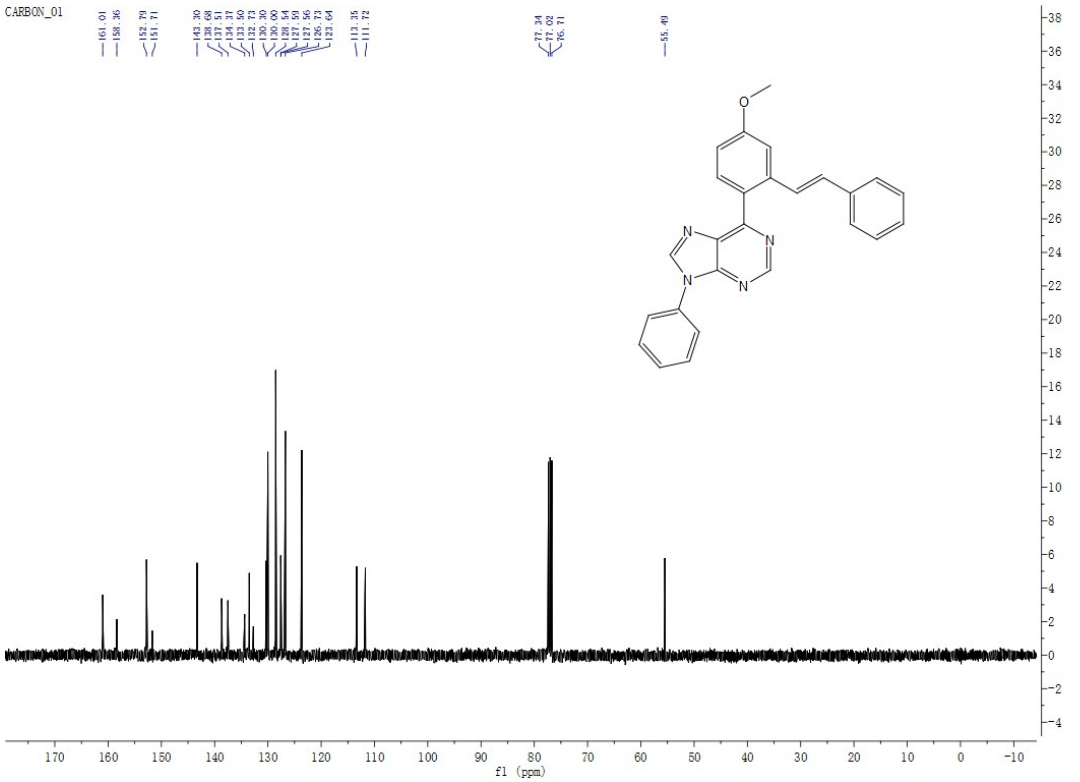
f1 (ppm)
f1 (ppm)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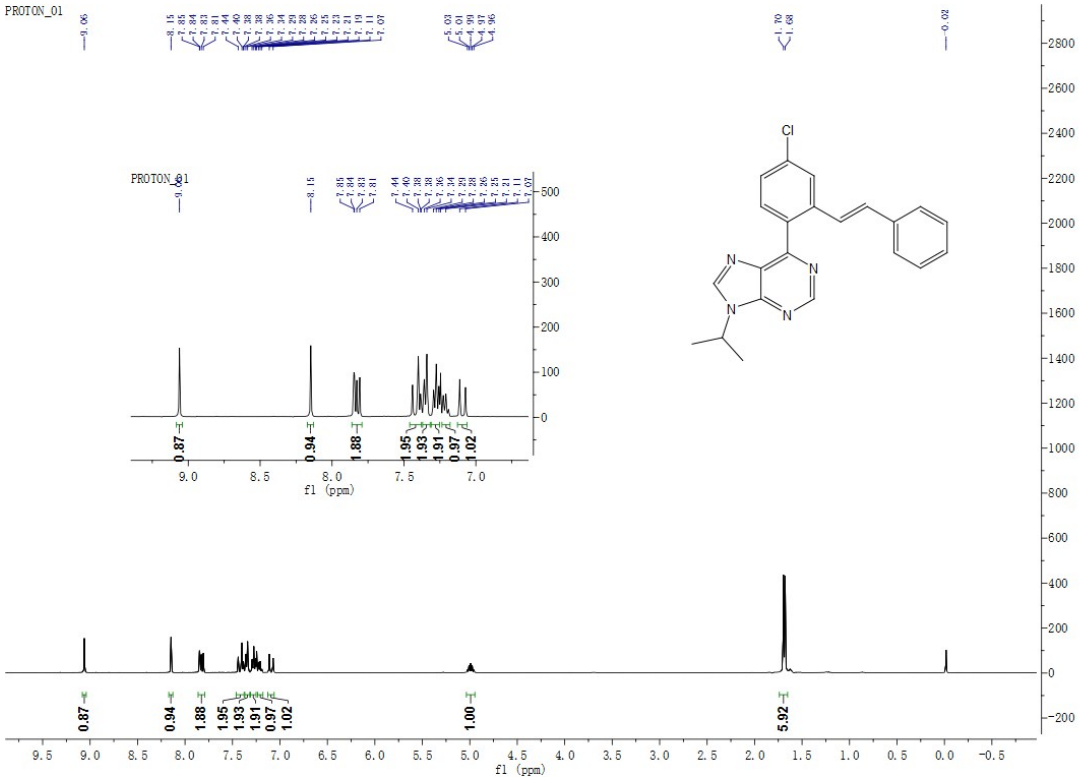
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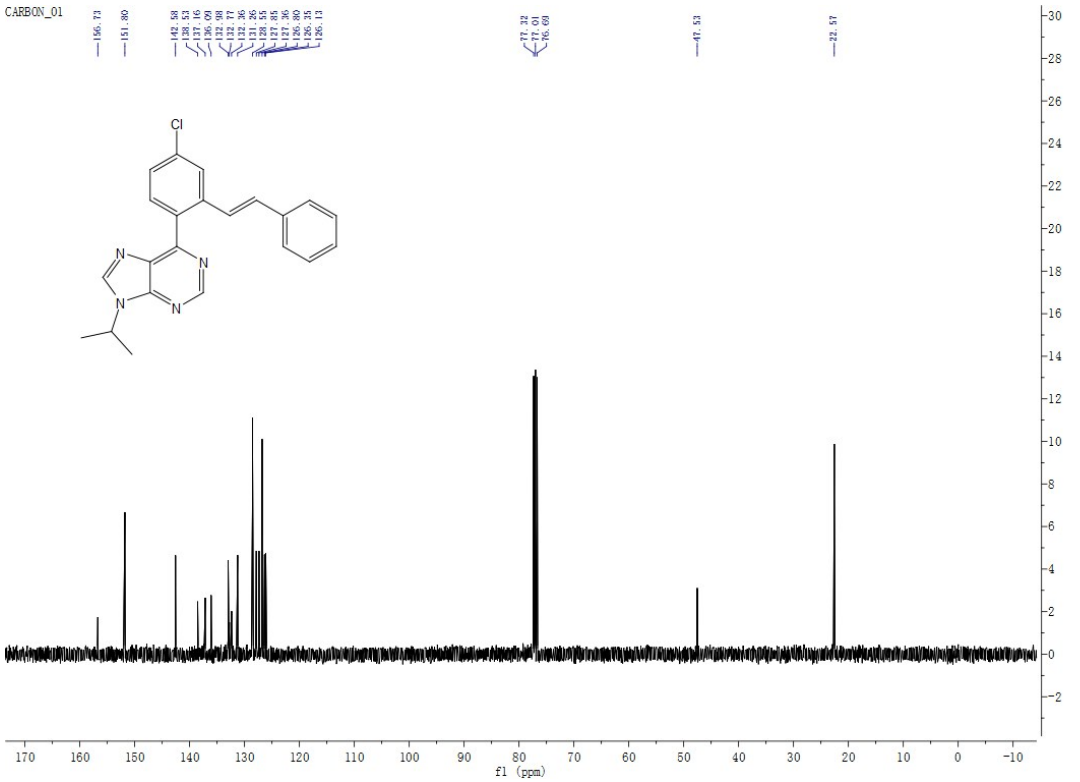
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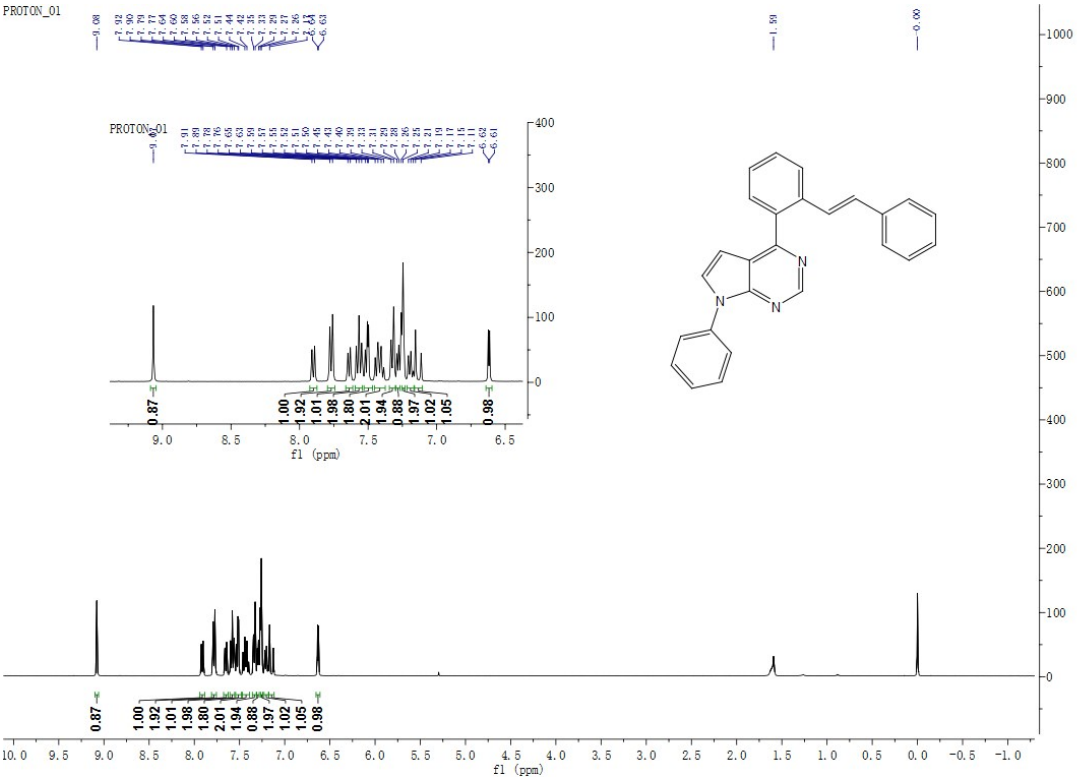
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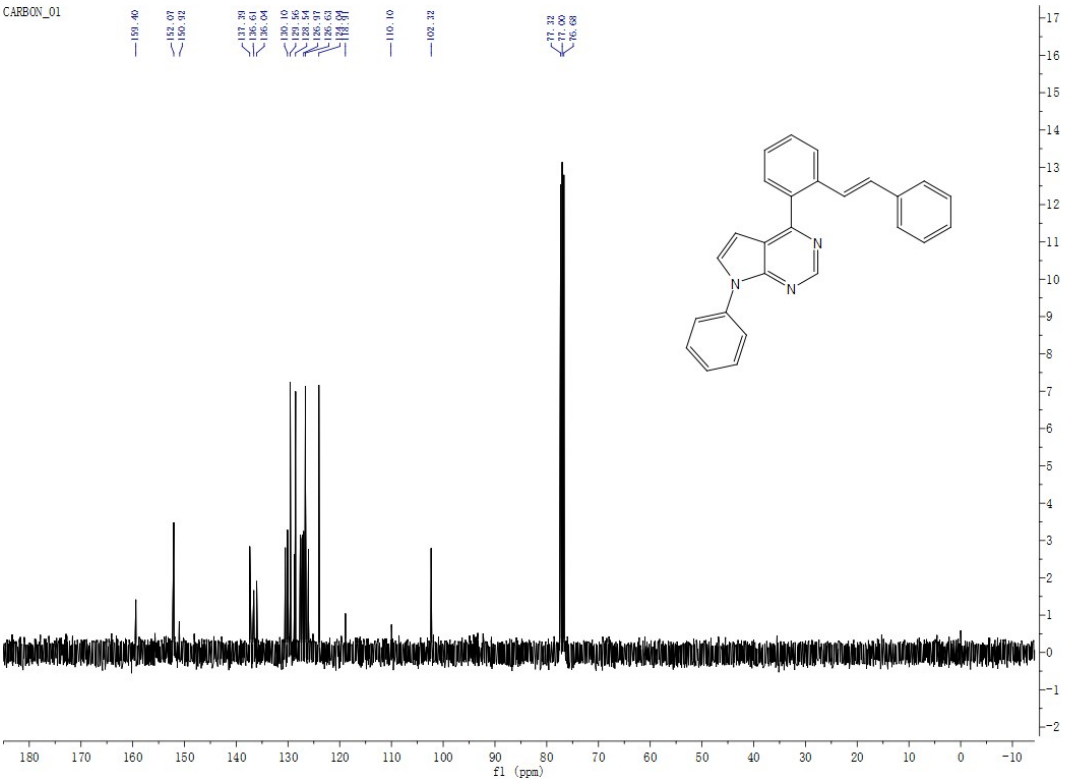
f1 (ppm)
f1 (ppm)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f1 (ppm)