Supporting information

Photocatalyzed *E*→*Z* contra-Thermodynamic isomerization of Enamides

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1. General Information

Photocatalysts were purchased from Acros, Alfa Aesar, Aldrich, Ark Pharm, and Strem. Other chemicals were purchased from TCI, Adamas, and Energy chemicals, and were directly used without further purifications. Yields for optimization were determined by HPLC with 1,3,5-trimethoxybenzene as an internal standard. Yields for scope of substrates were determined by the column chromatography which was generally performed on silica gel (200-300 mesh) using petroleum ether PE/EtOAc as eluent, and reactions were monitored by thin layer chromatography (TLC) on a glass pate coated with silica gel with fluorescent indicator (GF254) using UV light and iodine chromogenic method.

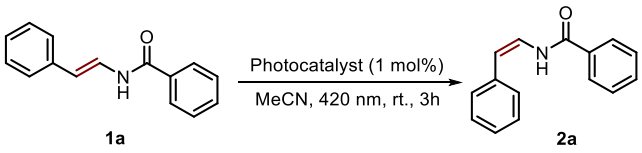
^{1}H and ^{13}C NMR spectra were collected on a Bruker AVANCE III 400MHz spectrometer at room temperature. ^{1}H NMR spectra were reported in parts per million (ppm) downfield of tetramethylsilane (TMS) and were referenced to the signal of DMSO (2.50 ppm). ^{13}C NMR spectra were reported in ppm relative to residual DMSO (39.52 ppm). Coupling constants, *J*, are reported in hertz (Hz). HPLC analysis was performed on Agilent 1260. *E*-enamides are synthesized according the literature procedure[1].

2. Optimization of Reaction Parameters

General Procedure

To a 10 mL reaction tube with a stir bar was charged with photocatalyst (1 mol %, 0.002 mmol) and substrates **1a** (44.6 mg, 0.2 mmol), The tube was sealed with rubber septum, then evacuated and backfilled with nitrogen for three cycles, MeCN (2.0 mL) was added. The reaction mixture was stirred at appreciate temperature for 3 h under 420 nm irrorations. 1,3,5-trimethoxybenzene (20 mg) was added into mixture, diluted with ethyl acetate (2 mL), and analyzed by HPLC. The yield was determined versus the internal standard (1,3,5-trimethoxybenzene).

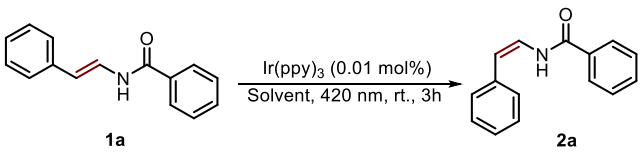
Table S1. Effect of photocatalyst[a]



entry	Photocatalyst	yield (%)	Z/E
1	Riboflavine	NR.	--
2	$Ru(bpy)_3Cl_2·6H_2O$	NR.	--
3	Anthracene	NR.	--
4	Thioxanthone	52	1/1
5	Xanthone	54	1/1
6	2-acetonaphthone	49	1/1
7	**$Ir(ppy)_3$**	**98**	**> 20/1**
8	Benzophenone	NR.	--
9	Fluorenone	NR.	--

[a]Reaction conditions: **1a** (0.2 mmol) and Photocatalyst (0.002 mmol) were used, the yields were determined by HPLC with 1,3,5-trimethoxybenzene as an internal standard.

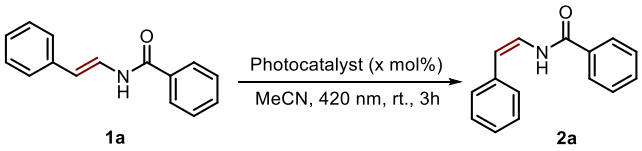
Table S2. Effect of solvent[a]



entry	Solvent	yield (%)	Z/E
1	DMF	81	4/1
2	DMSO	75	3/1
3	THF	25	1/3
4	**MeCN**	**98**	**> 20/1**
5	DME	20	1/4
6	EtOH	NR.	--
7	Dioxane	35	1/2

[a]Reaction conditions: **1a** (0.2 mmol) and $Ir(ppy)_3$ (0.002 mmol) were used, the yields were determined by HPLC with 1,3,5-trimethoxybenzene as an internal standard.

Table S3. Effect of photocatalyst loading[a]



entry	x	yield (%)	Z/E
1	1	98	> 20/1
2	0.5	98	> 20/1
3	0.1	99	> 20/1
4	**0.01**	**98 (96)[b]**	**> 20/1**
5	0.001	90	9/1

[a]Reaction conditions: **1a** (0.2 mmol) and Photocatalyst (0.002 mmol) were used, the yields were determined by HPLC with 1,3,5-trimethoxybenzene as an internal standard; [b] isolated yield.

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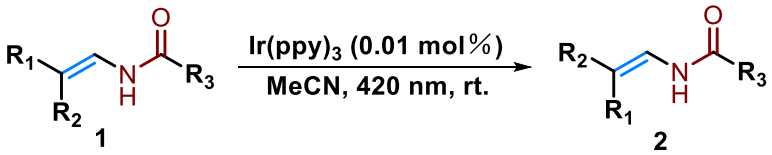
3. Photoredox-Catalyzed Contra-Thermodynamic Isomerization of Enamides

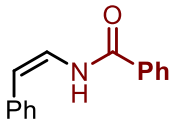
3.1. General Procedure



To a 10 mL reaction tube with a stir bar was charged substrates **1** (0.2 mmol), The tube was sealed with rubber septum, then evacuated and backfilled with nitrogen for three cycles, the solution of MeCN contains $Ir(ppy)_3$ (2.0 mL, 13 mg/L) was added. The mixture was stirred at room temperature for 3 h under 420 nm irrorations. The reaction was quenched with water (20.0 mL), and extracted with ethyl acetate (3 × 15.0 mL). The combined organic layers were washed with water, brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to afford the desired product **2**.

3.2. Characterization Data of Products

(*Z*)-N-styrylbenzamide (2a)



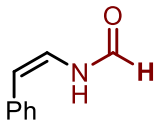
This compound was prepared according to the General procedure from the reaction of **1a** (44.6 mg, 0.2 mmol).

42.8 mg, 96% yield, Z/E > 20/1, white solid.

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 10.05 (d, *J* = 9.3 Hz, 1H), 8.04 – 7.91 (m, 2H), 7.67 – 7.51 (m, 5H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.29 (t, *J* = 7.3 Hz, 1H), 7.00 (t, *J* = 9.5 Hz, 1H), 5.91 (d, *J* = 9.7 Hz, 1H).**^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ** 163.46, 137.23, 136.93, 132.53, 130.02, 129.21, 129.07, 126.84, 125.78, 124.46, 113.78.

Spectroscopic data are in accordance with that reported in the literature.[2]

(*Z*)-N-styrylformamide (2b)



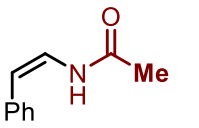
This compound was prepared according to the General procedure from the reaction of **1b** (29.4 mg, 0.2 mmol).

26.5 mg, 90% yield, Z/E = 9/1, white solid.

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 10.03 (d, 1H), 8.19 (s, 1H), 7.47 – 7.40 (m, 4H), 7.34 – 7.25 (m, 1H), 6.92 – 6.80 (m, 1H), 5.77 (d, *J* = 10.8 Hz, 1H). **^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ** 160.61, 135.74, 129.13, 128.94, 128.68, 127.15, 120.43, 110.83.

Spectroscopic data are in accordance with that reported in the literature.[3]

(*Z*)-N-styrylacetamide (2c)



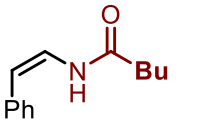
This compound was prepared according to the General procedure from the reaction of **1c** (32.2 mg, 0.2 mmol).

29.0 mg, 90% yield, Z/E = 9/1, white solid.

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 9.61 (d, *J* = 10.5 Hz, 1H), 7.40 – 7.36 (m, 3H), 7.34 (d, *J* = 8.2 Hz, 1H), 7.25 – 7.18 (m, 1H), 6.75 (t, *J* = 10.2 Hz, 1H), 5.60 (d, *J* = 10.0 Hz, 1H), 2.03 (s, 3H). **^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ** 169.20, 136.12, 128.96, 128.69, 126.79, 122.75, 109.68, 23.16.

Spectroscopic data are in accordance with that reported in the literature.[4]

(*Z*)-N-styrylpentanamide (2d)



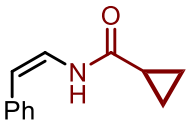
This compound was prepared according to the General procedure from the reaction of **1d** (40.6 mg, 0.2 mmol).

30.0 mg, 74% yield, Z/E = 3/1, white solid.

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 9.55 (d, *J* = 10.5 Hz, 1H), 7.41 – 7.31 (m, 4H), 7.26 – 7.17 (m, 1H), 6.76 (t, *J* = 10.2 Hz, 1H), 5.60 (d, *J* = 9.9 Hz, 1H), 2.33 (t, *J* = 7.5 Hz, 2H), 1.57 – 1.46 (m, 2H), 1.35 – 1.22 (m, 2H), 0.88 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ** 172.16, 136.17, 128.95, 128.68, 126.76, 122.79, 109.76, 35.15, 27.60, 22.28, 14.17.

Spectroscopic data are in accordance with that reported in the literature.[5]

(*Z*)-N-styrylcyclopropanecarboxamide (2e)



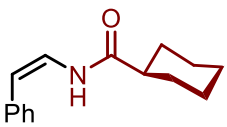
This compound was prepared according to the General procedure from the reaction of **1e** (37.4 mg, 0.2 mmol).

31.0 mg, 83% yield, Z/E = 5/1, white solid.

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 9.89 (d, *J* = 10.5 Hz, 1H), 7.44 – 7.34 (m, 4H), 7.25 – 7.19 (m, 1H), 6.76 (t, *J* = 10.2 Hz, 1H), 5.59 (d, *J* = 10.0 Hz, 1H), 2.07 – 1.98 (m, 1H), 0.82 – 0.75 (m, 4H). **^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ** 172.78, 136.16, 128.98, 128.71, 126.78, 122.81, 109.49, 13.79, 8.09.

Spectroscopic data are in accordance with that reported in the literature.[5]

(*Z*)-N-styrylcyclohexanecarboxamide (2f)



This compound was prepared according to the General procedure from the reaction of **1f** (45.8 mg, 0.2 mmol).

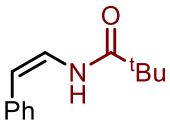
40.8 mg, 89% yield, Z/E = 8/1, white solid.

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 9.54 (d, *J* = 10.4 Hz, 1H), 7.44 – 7.38 (m, 4H), 7.30 – 7.24 (m, 1H), 6.79 (t, *J* = 10.1 Hz, 1H), 5.66 (d, *J* = 9.9 Hz, 1H), 2.55 – 2.48 (m, 1H), 1.83 – 1.74 (m, 4H), 1.71 – 1.64 (m, 1H), 1.47 – 1.34 (m, 2H), 1.33 – 1.19 (m, 3H). **^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ** 175.08,

136.20, 128.94, 128.69, 126.73, 122.89, 109.91, 43.61, 29.49, 25.87, 25.64.

Spectroscopic data are in accordance with that reported in the literature.[5]

(*Z*)-N-styrylpivalamide (2g)



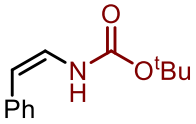
This compound was prepared according to the General procedure from the reaction of **1g** (40.6 mg, 0.2 mmol).

34.9 mg, 86% yield, Z/E = 6/1, white solid.

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 8.89 (d, *J* = 9.5 Hz, 1H), 7.37 (d, *J* = 4.4 Hz, 4H), 7.25 – 7.19 (m, 1H), 6.73 (t, *J* = 9.6 Hz, 1H), 5.72 (d, *J* = 9.6 Hz, 1H), 1.19 (s, 9H). **^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ** 176.56, 136.37, 129.12, 128.51, 126.95, 123.45, 111.59, 38.95, 27.25.

Spectroscopic data are in accordance with that reported in the literature.[4]

tert-butyl (*Z*)-styrylcarbamate (2h)



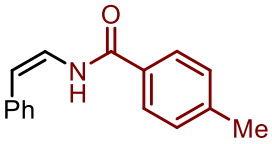
This compound was prepared according to the General procedure from the reaction of **1h** (43.8 mg, 0.2 mmol).

32.8 mg, 75% yield, Z/E = 3/1, white solid.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.32 – 7.27 (m, 2H), 7.20 – 7.17 (m, 2H), 7.14 (t, *J* = 7.4 Hz, 1H), 6.78 (s, 1H), 6.61 (t, *J* = 10.5 Hz, 1H), 5.51 (d, *J* = 9.5 Hz, 1H), 1.41 (s, 9H). **^{13}C NMR (101 MHz, CDCl$_3$) δ** 152.90, 136.06, 128.97, 127.81, 126.51, 123.53, 107.03, 80.94, 28.25.

Spectroscopic data are in accordance with that reported in the literature.[6]

(*Z*)-4-methyl-N-styrylbenzamide (2i)



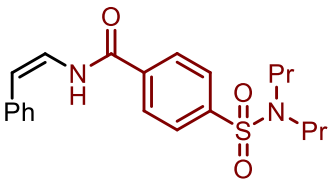
This compound was prepared according to the General procedure from the reaction of **1i** (47.4 mg, 0.2 mmol).

44.1 mg, 93% yield, Z/E = 13/1, white solid.

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 9.90 (d, *J* = 8.7 Hz, 1H), 7.88 – 7.81 (m, 2H), 7.51 – 7.45 (m, 2H), 7.39 (t, *J* = 7.7 Hz, 2H), 7z.31 (d, *J* = 7.9 Hz, 2H), 7.27 – 7.21 (m, 1H), 6.94 (t, *J* = 9.3 Hz, 1H), 5.84 (d, *J* = 9.7 Hz, 1H), 2.37 (s, 3H). **^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ** 164.36, 142.46, 137.15, 130.96, 129.49, 129.20, 128.12, 126.67, 125.68, 124.70, 113.11, 21.50.

Spectroscopic data are in accordance with that reported in the literature.[5]

(*Z*)-4-(N,N-dipropylsulfamoyl)-N-styrylbenzamide (2j)



This compound was prepared according to the General procedure from the reaction of **1j** (77.2 mg, 0.2 mmol).

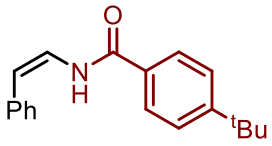
72.6 mg, 94% yield, Z/E = 16/1, white solid.

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 10.28 (d, *J* = 9.2 Hz, 1H), 8.10 (d, *J* = 8.3 Hz, 2H), 7.93 – 7.88 (m,

2H), 7.49 (d, J = 7.4 Hz, 2H), 7.40 (d, J = 7.6 Hz, 2H), 7.25 (t, J = 7.4 Hz, 1H), 6.93 (t, J = 9.4 Hz, 1H), 5.91 (d, J = 9.8 Hz, 1H), 3.14 – 3.01 (m, 4H), 1.53 – 1.44 (m, 4H), 0.82 (t, J = 7.4 Hz, 6H). **^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ** 163.33, 142.67, 137.26, 136.75, 129.18, 129.07, 127.37, 126.90, 125.80, 124.25, 114.24, 50.03, 22.02, 11.39.

Spectroscopic data are in accordance with that reported in the literature.[7]

(*Z*)-4-(tert-butyl)-N-styrylbenzamide (2k)



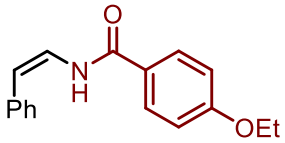
This compound was prepared according to the General procedure from the reaction of **1k** (55.8 mg, 0.2 mmol).

48.5 mg, 87% yield, Z/E = 7/1, white solid.

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 9.89 (d, J = 9.3 Hz, 1H), 7.89 – 7.85 (m, 2H), 7.54 – 7.46 (m, 4H), 7.40 – 7.35 (m, 2H), 7.26 – 7.21 (m, 1H), 6.94 (t, J = 9.5 Hz, 1H), 5.84 (d, J = 9.7 Hz, 1H), 1.31 (s, 9H). **^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ** 165.60, 155.22, 136.31, 131.16, 129.04, 128.83, 128.19, 127.01, 125.67, 123.39, 112.87, 35.17, 31.37.

Spectroscopic data are in accordance with that reported in the literature.[8]

(*Z*)-4-ethoxy-N-styrylbenzamide (2l)



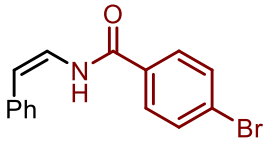
This compound was prepared according to the General procedure from the reaction of **1l** (53.4 mg, 0.2 mmol).

43.8 mg, 82% yield, Z/E = 5/1, white solid.

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 9.82 (d, J = 9.0 Hz, 1H), 7.93 – 7.87 (m, 2H), 7.50 – 7.44 (m, 2H), 7.42 – 7.36 (m, 2H), 7.26 – 7.20 (m, 1H), 7.05 – 6.99 (m, 2H), 6.94 (t, J = 9.4 Hz, 1H), 5.81 (d, J = 9.7 Hz, 1H), 4.10 (q, J = 7.0 Hz, 2H), 1.35 (t, J = 7.0 Hz, 3H).**^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ** 165.12, 161.91, 136.41, 130.31, 129.04, 128.79, 126.94, 125.78, 123.55, 114.50, 112.48, 63.88, 14.99.

Spectroscopic data are in accordance with that reported in the literature.[2]

(*Z*)-4-bromo-N-styrylbenzamide (2m)



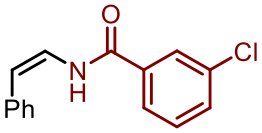
This compound was prepared according to the General procedure from the reaction of **1m** (60.4 mg, 0.2 mmol).

56.8 mg, 94% yield, Z/E = 16/1, white solid.

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 10.64 (d, J = 9.8 Hz, 1H), 8.10 – 8.01 (m, 2H), 7.64 (dd, J = 10.7, 9.8 Hz, 1H), 7.43 – 7.35 (m, 5H), 7.36 – 7.27 (m, 3H), 7.18 (t, J = 7.3 Hz, 1H), 6.46 (d, J = 10.7 Hz, 1H). **^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ** 163.46, 137.00, 130.89, 130.79, 130.31, 130.28, 129.21, 126.78, 125.74, 124.56, 116.06, 115.84, 113.52.

Spectroscopic data are in accordance with that reported in the literature.[9]

(*Z*)-3-chloro-N-styrylbenzamide (2n)



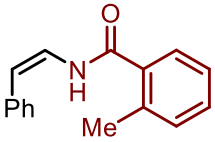
This compound was prepared according to the General procedure from the reaction of **1n** (51.5 mg, 0.2 mmol).

43.3 mg, 88% yield, Z/E = 7/1, white solid.

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 10.17 (d, *J* = 9.1 Hz, 1H), 7.98 (t, *J* = 1.9 Hz, 1H), 7.89 (dt, *J* = 7.8 Hz, 1.4 Hz, 1H), 7.68 – 7.61 (m, 1H), 7.54 (t, *J* = 7.9 Hz, 1H), 7.51 – 7.44 (m, 2H), 7.43 – 7.34 (m, 2H), 7.29 – 7.20 (m, 1H), 6.90 (t, *J* = 9.4 Hz, 1H), 5.89 (d, *J* = 9.7 Hz, 1H). **^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ** 164.68, 136.14, 136.00, 133.60, 132.05, 130.79, 129.00, 128.97, 128.16, 127.16, 123.18, 113.93.

Spectroscopic data are in accordance with that reported in the literature.[2]

(*Z*)-2-methyl-N-styrylbenzamide (2o)



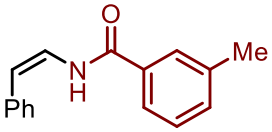
This compound was prepared according to the General procedure from the reaction of **1o** (47.4 mg, 0.2 mmol).

35.1 mg, 74% yield, Z/E = 3/1, white solid.

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 9.97 (d, *J* = 9.9 Hz, 1H), 7.46 – 7.41 (m, 3H), 7.37 – 7.31 (m, 3H), 7.27 (d, *J* = 7.7 Hz, 2H), 7.23 – 7.18 (m, 1H), 6.93 (t, *J* = 9.9 Hz, 1H), 5.80 (d, *J* = 9.9 Hz, 1H), 2.37 (s, 3H). **^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ** 168.43, 136.39, 136.12, 136.05, 130.90, 130.23, 128.86, 127.92, 126.94, 125.97, 122.86, 112.26, 20.02.

Spectroscopic data are in accordance with that reported in the literature.[2]

(*Z*)-3-methyl-N-styrylbenzamide (2p)



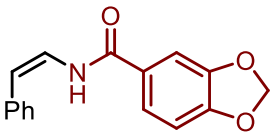
This compound was prepared according to the General procedure from the reaction of **1p** (47.4 mg, 0.2 mmol).

44.1 mg, 93% yield, Z/E = 13/1, white solid.

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 10.09 (d, *J* = 8.5 Hz, 1H), 7.75 – 7.73 (m, 1H), 7.73 – 7.67 (m, 1H), 7.51 (t, *J* = 1.9 Hz, 1H), 7.46 – 7.34 (m, 5H), 7.29 (dt, *J* = 7.2 Hz, 1.9 Hz, 1H), 6.97 (t, *J* = 9.2 Hz, 1H), 5.83 (d, *J* = 9.7 Hz, 1H), 2.38 (s, 3H). **^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ** 164.63, 138.29, 137.10, 133.80, 132.95, 129.20, 128.84, 128.57, 126.71, 125.71, 125.25, 124.66, 113.29, 21.41.

Spectroscopic data are in accordance with that reported in the literature.[5]

(*Z*)-N-styrylbenzo[d][1,3]dioxole-5-carboxamide (2q)



This compound was prepared according to the General procedure from the reaction of **1q** (53.4 mg, 0.2 mmol).

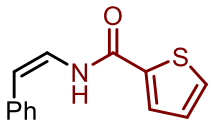
49.7 mg, 93% yield, Z/E = 13/1, white solid.

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 9.87 (s, 1H), 7.58 (d, *J* = 8.6 Hz, 1H), 7.55 – 7.45 (m, 3H), 7.45 –

7.35 (m, 2H), 7.31 – 7.20 (m, 1H), 7.04 (t, J = 8.9 Hz, 1H), 6.98 – 6.87 (m, 1H), 6.14 (s, 2H), 5.84 (d, J = 9.8 Hz, 1H). **^{13}C NMR (101 MHz, DMSO-d_6) δ** 164.89, 150.81, 147.86, 136.38, 129.07, 128.88, 127.77, 127.04, 123.76, 123.56, 112.96, 108.48, 108.37, 102.34.

Spectroscopic data are in accordance with that reported in the literature.[7]

(*Z*)-N-styrylthiophene-2-carboxamide (2r)



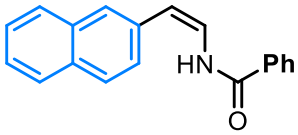
This compound was prepared according to the General procedure from the reaction of **1r** (45.8 mg, 0.2 mmol).

44.0 mg, 96% yield, Z/E > 20/1, white solid.

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.05 (d, J = 9.0 Hz, 1H), 8.01 (dd, J = 3.8 Hz, 1.2 Hz, 1H), 7.86 (dd, J = 4.9 Hz, 1.1 Hz, 1H), 7.49 – 7.44 (m, 2H), 7.40 – 7.36 (m, 2H), 7.24 (t, J = 7.4 Hz, 1H), 7.19 (dd, J = 5.0 Hz, 3.8 Hz, 1H), 6.85 (t, J = 9.3 Hz, 1H), 5.85 (d, J = 9.7 Hz, 1H). **^{13}C NMR (101 MHz, DMSO-d_6) δ** 160.45, 138.92, 136.19, 132.73, 130.49, 129.03, 128.92, 128.66, 127.12, 122.97, 113.34.

Spectroscopic data are in accordance with that reported in the literature.[2]

(*Z*)-N-(2-(naphthalen-2-yl)vinyl)benzamide (2s)



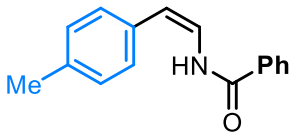
This compound was prepared according to the General procedure from the reaction of **1s** (54.6 mg, 0.2 mmol).

46.4 mg, 85% yield, Z/E = 6/1, white solid.

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.16 (d, J = 9.3 Hz, 1H), 8.01 – 7.95 (m, 3H), 7.94 – 7.87 (m, 3H), 7.65 – 7.57 (m, 2H), 7.54 – 7.46 (m, 4H), 7.04 (t, J = 9.5 Hz, 1H), 6.02 (d, J = 9.7 Hz, 1H). **^{13}C NMR (101 MHz, DMSO-d_6) δ** 165.94, 133.99, 133.95, 133.67, 132.32, 132.26, 128.85, 128.40, 128.35, 128.29, 127.89, 127.48, 127.27, 126.69, 126.31, 123.85, 113.04.

Spectroscopic data are in accordance with that reported in the literature.[5]

(*Z*)-N-(4-methylstyryl)benzamide (2t)



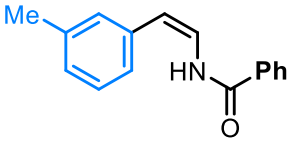
This compound was prepared according to the General procedure from the reaction of **1t** (47.4 mg, 0.2 mmol).

42.7 mg, 90% yield, Z/E = 9/1, white solid.

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.90 (d, J = 8.7 Hz, 1H), 7.87 – 7.81 (m, 2H), 7.51 – 7.44 (m, 2H), 7.43 – 7.34 (m, 2H), 7.31 (d, J = 7.9 Hz, 2H), 7.23 (t, J = 7.4 Hz, 1H), 6.94 (t, J = 9.3 Hz, 1H), 5.84 (d, J = 9.7 Hz, 1H), 2.37 (s, 3H). **^{13}C NMR (101 MHz, DMSO-d_6) δ** 165.62, 142.40, 136.34, 131.07, 129.40, 129.05, 128.83, 128.35, 127.01, 123.42, 112.88, 21.50.

Spectroscopic data are in accordance with that reported in the literature.[5]

(*Z*)-N-(3-methylstyryl)benzamide (2u)



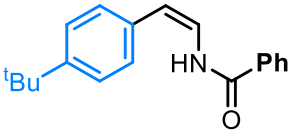
This compound was prepared according to the General procedure from the reaction of **1u** (47.4 mg, 0.2 mmol).

44.1 mg, 93% yield, Z/E = 13/1, white solid.

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 9.97 (d, *J* = 9.0 Hz, 1H), 7.81 – 7.70 (m, 2H), 7.54 – 7.47 (m, 2H), 7.44 – 7.37 (m, 4H), 7.30 – 7.22 (m, 1H), 7.02 – 6.87 (m, 1H), 5.86 (d, *J* = 5.8 Hz, 1H), 2.39 (s, 3H). **^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ** 165.97, 138.21, 136.34, 133.95, 132.93, 129.08, 128.89, 128.78, 127.08, 125.48, 123.44, 113.13, 21.44.

Spectroscopic data are in accordance with that reported in the literature.[2]

(*Z*)-N-(4-(tert-butyl)styryl)benzamide (2v)



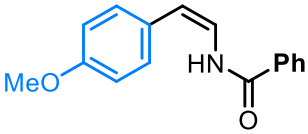
This compound was prepared according to the General procedure from the reaction of **1v** (55.8 mg, 0.2 mmol).

53.0 mg, 95% yield, Z/E = 19/1, white solid.

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 9.99 (d, *J* = 8.6 Hz, 1H), 7.96 – 7.93 (m, 2H), 7.61 – 7.56 (m, 1H), 7.53 – 7.48 (m, 2H), 7.41 (s, 4H), 6.90 (t, *J* = 9.3 Hz, 1H), 5.82 (d, *J* = 9.7 Hz, 1H), 1.29 (s, 9H). **^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ** 165.77, 149.50, 133.96, 133.47, 132.25, 128.82, 128.61, 128.32, 125.79, 122.84, 113.09, 34.75, 31.56.

Spectroscopic data are in accordance with that reported in the literature.[5]

(*Z*)-N-(4-methoxystyryl)benzamide (2w)



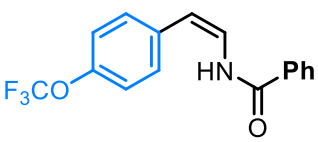
This compound was prepared according to the General procedure from the reaction of **1w** (30.6 mg, 0.2 mmol).

25.1 mg, 82% yield, Z/E = 5/1, white solid.

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 9.90 (d, *J* = 8.8 Hz, 1H), 7.99 – 7.91 (m, 2H), 7.60 – 7.55 (m, 1H), 7.53 – 7.47 (m, 2H), 7.45 – 7.39 (m, 2H), 6.99 – 6.93 (m, 2H), 6.83 (t, *J* = 9.3 Hz, 1H), 5.81 (d, *J* = 9.7 Hz, 1H), 3.77 (s, 3H). **^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ** 165.70, 158.44, 134.02, 132.22, 130.17, 128.83, 128.73, 128.28, 121.74, 114.49, 113.23, 55.59.

Spectroscopic data are in accordance with that reported in the literature.[4]

(*Z*)-N-(4-(trifluoromethoxy)styryl)benzamide (2x)



This compound was prepared according to the General procedure from the reaction of **1x** (61.4 mg, 0.2 mmol).

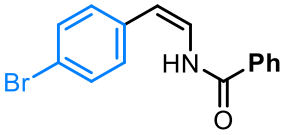
50.3 mg, 82% yield, Z/E = 5/1, white solid.

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 10.12 (d, *J* = 9.0 Hz, 1H), 7.96 – 7.91 (m, 2H), 7.62 – 7.56 (m, 3H), 7.53 – 7.48 (m, 2H), 7.36 (d, *J* = 8.3 Hz, 2H), 6.99 (t, *J* = 9.4 Hz, 1H), 5.87 (d, *J* = 9.8 Hz, 1H).

^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ 166.06, 147.06 (q, $J_{C\text{-}F}$ = 2.0 Hz), 135.75, 133.87, 132.34, 130.66, 128.97, 128.80, 128.43, 124.29, 121.53, 120.6 (q, $J_{C\text{-}F}$ = 257.5 Hz), 111.58.

Spectroscopic data are in accordance with that reported in the literature.[5]

(*Z*)-N-(4-bromostyryl)benzamide (2y)



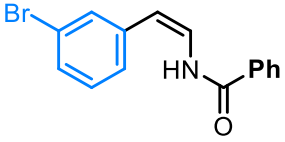
This compound was prepared according to the General procedure from the reaction of **1y** (60.4 mg, 0.2 mmol).

53.7 mg, 89% yield, Z/E = 8/1, white solid.

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 10.05 (d, *J* = 9.2 Hz, 1H), 7.95 – 7.89 (m, 2H), 7.62 – 7.53 (m, 3H), 7.53 – 7.47 (m, 2H), 7.45 – 7.39 (m, 2H), 6.97 (t, *J* = 9.5 Hz, 1H), 5.82 (d, *J* = 9.7 Hz, 1H). **^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ** 165.94, 135.58, 133.85, 132.35, 131.83, 130.97, 128.82, 128.41, 124.15, 119.80, 111.88.

Spectroscopic data are in accordance with that reported in the literature.[2]

(*Z*)-N-(3-bromostyryl)benzamide (2z)



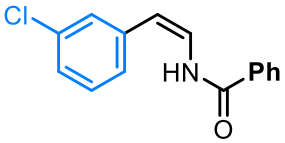
This compound was prepared according to the General procedure from the reaction of **1z** (60.4 mg, 0.2 mmol).

55.6 mg, 92% yield, Z/E = 12/1, white solid.

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 10.17 (d, *J* = 8.8 Hz, 1H), 7.98 – 7.91 (m, 2H), 7.70 – 7.64 (m, 1H), 7.64 – 7.58 (m, 1H), 7.54 (d, *J* = 8.2 Hz, 4H), 7.49 – 7.41 (m, 1H), 7.42 – 7.33 (m, 1H), 7.05 – 6.95 (m, 1H), 5.86 (d, *J* = 10.4 Hz, 1H). **^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ** 165.76, 136.94, 133.94, 132.34, 128.91, 128.74, 128.38, 126.53, 123.76, 122.25, 108.39.

Spectroscopic data are in accordance with that reported in the literature.[5]

(*Z*)-N-(3-chlorostyryl)benzamide (2aa)



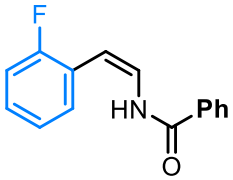
This compound was prepared according to the General procedure from the reaction of **1aa** (51.4 mg, 0.2 mmol).

51.4 mg, 88% yield, Z/E = 7/1, white solid.

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 10.14 (d, *J* = 9.2 Hz, 1H), 7.95 – 7.90 (m, 2H), 7.62 – 7.57 (m, 1H), 7.55 – 7.49 (m, 3H), 7.47 – 7.38 (m, 2H), 7.29 (dt, *J* = 7.8 Hz, 1.7 Hz, 1H), 6.99 (t, *J* = 9.5 Hz, 1H), 5.84 (d, *J* = 9.8 Hz, 1H). **^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ** 166.03, 138.51, 133.88, 133.63, 132.38, 130.76, 128.84, 128.54, 128.38, 127.47, 126.76, 124.70, 111.65.

Spectroscopic data are in accordance with that reported in the literature.[5]

(*Z*)-N-(2-fluorostyryl)benzamide (2ab)



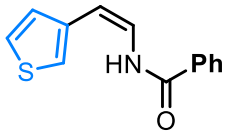
This compound was prepared according to the General procedure from the reaction of **1ab** (48.2 mg, 0.2 mmol).

38.1 mg, 79% yield, Z/E = 4/1, white solid.

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 9.99 (d, *J* = 9.8 Hz, 1H), 7.94 – 7.88 (m, 2H), 7.61 – 7.56 (m, 2H), 7.53 – 7.47 (m, 2H), 7.34 – 7.27 (m, 1H), 7.25 – 7.19 (m, 2H), 7.09 (t, *J* = 9.8 Hz, 1H), 5.82 (d, *J* = 9.8 Hz, 1H). **^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ** 165.63, 159.77 (d, $J_{C\text{-}F}$ = 246.4 Hz), 133.85, 132.37, 130.75 (d, $J_{C\text{-}F}$ = 4.0 Hz), 129.05 (d, $J_{C\text{-}F}$ = 8.0 Hz), 128.82, 128.33, 125.10, 124.89 (d, $J_{C\text{-}F}$ = 3.0 Hz), 123.82 (d, $J_{C\text{-}F}$ = 14.1 Hz), 116.53 (d, $J_{C\text{-}F}$ = 22.2 Hz), 104.59.

Spectroscopic data are in accordance with that reported in the literature.[2]

(*Z*)-N-(2-(thiophen-2-yl)vinyl)benzamide (2ac)



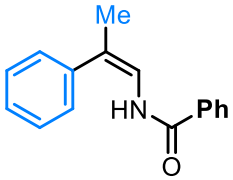
This compound was prepared according to the General procedure from the reaction of **1ac** (45.8 mg, 0.2 mmol).

31.6 mg, 69% yield, Z/E = 2/1, white solid.

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 9.87 (d, *J* = 9.1 Hz, 1H), 8.03 – 7.97 (m, 2H), 7.71 – 7.67 (m, 1H), 7.67 – 7.60 (m, 2H), 7.60 – 7.54 (m, 2H), 7.40 – 7.31 (m, 1H), 6.91 (t, *J* = 9.3 Hz, 1H), 5.98 (d, *J* = 9.5 Hz, 1H). **^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ** 165.76, 136.94, 133.94, 132.34, 128.91, 128.74, 128.38, 126.53, 123.76, 122.25, 108.39.

Spectroscopic data are in accordance with that reported in the literature.[5]

(*Z*)-N-(2-phenylprop-1-en-1-yl)benzamide (2ad)



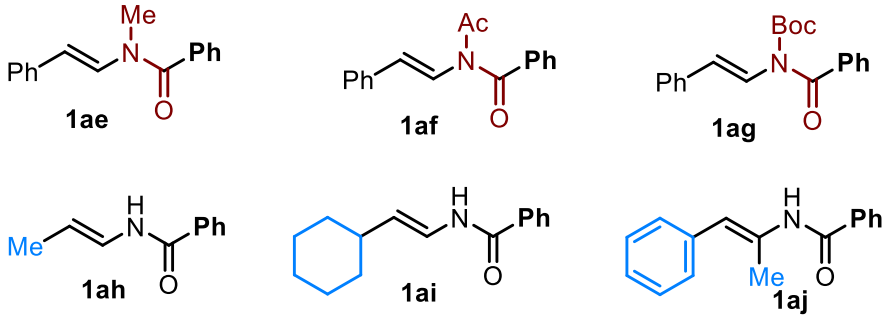
This compound was prepared according to the General procedure from the reaction of **1ad** (47.4 mg, 0.2 mmol).

40.8 mg, 86% yield, Z/E = 6/1, white solid.

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 9.39 (d, *J* = 9.1 Hz, 1H), 7.84 – 7.80 (m, 2H), 7.60 – 7.56 (m, 1H), 7.51 – 7.45 (m, 6H), 7.34 – 7.31 (m, 1H), 6.93 (d, *J* = 9.3 Hz, 1H), 2.12 (s, 3H). **^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ** 170.94, 166.88, 164.99, 159.68, 152.87, 136.88, 132.65, 128.33, 122.56, 116.85, 110.75, 24.05.

Spectroscopic data are in accordance with that reported in the literature.[4]

3.3 Unsuccessful Substrates



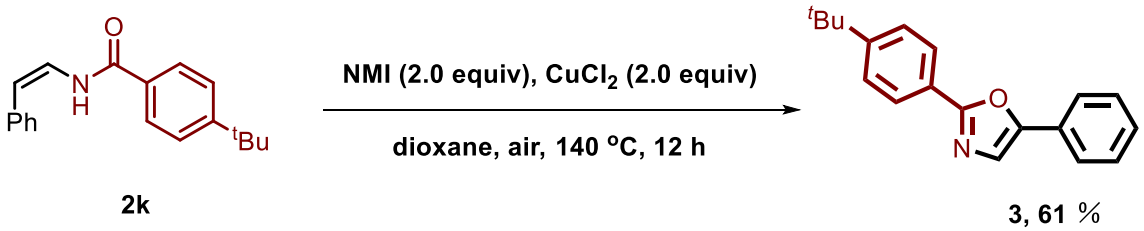
Scheme S1 Unsuccessful Substrates

4. Gram-scale reaction and Further Applications

4.1 Gram-scale reaction

To a 50 mL bottom with a stir bar was charged substrates **1k** (1.4 g, 5.0 mmol) and $Ir(ppy)_3$ (), The tube was sealed with rubber septum, then evacuated, and backfilled with nitrogen for three cycles, the solution of MeCN contains $Ir(ppy)_3$ (20 mL, 16.4 mg/L) was added. The mixture was stirred at room temperature for 62 h under 420 nm irrorations. The reaction was quenched with water (30.0 mL), and extracted with ethyl acetate (3 × 25.0 mL). The combined organic layers were washed with water, brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to afford the desired product **2k** for 1.19g (81% yield).

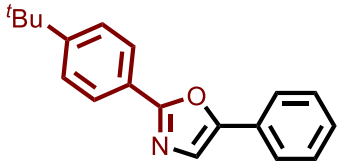
4.2 Further Applications[8]



2k **3, 61 %**

In a 20 mL seal tube equipped with a stir bar were added **2k** (139.5 mg, 0.5 mmol) and $CuCl_2$ (134 mg, 1mmol), 1,4-Dioxane (5 mL, 0.1 M) was added, followed by NMI (82 μL, 1 mmol) under air atmosphere. After sealing, the sealed tube was allowed to stir at 140 °C for 12 h. The reaction was quenched with water (30.0 mL) after cool to room temperature, and extracted with ethyl acetate (3 × 15.0 mL). The combined organic layers were washed with water, brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to afford the desired product **3**.

2-(4-(tert-butyl)phenyl)-5-phenyloxazole (3)



84.5 mg, 61% yield, white solid.

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 8.11 – 8.07 (m, 2H), 7.79 – 7.76 (m, 2H), 7.76 – 7.74 (m, 1H), 7.60 – 7.54 (m, 3H), 7.54 – 7.51 (m, 2H), 1.32 (s, 9H). **^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ** 160.44, 151.78, 151.39, 131.01, 129.64, 127.36, 126.34, 125.19, 124.38, 124.08, 34.96, 31.42.

5. Mechanistic Investigation

5.1 Photocontrolled switching experiment

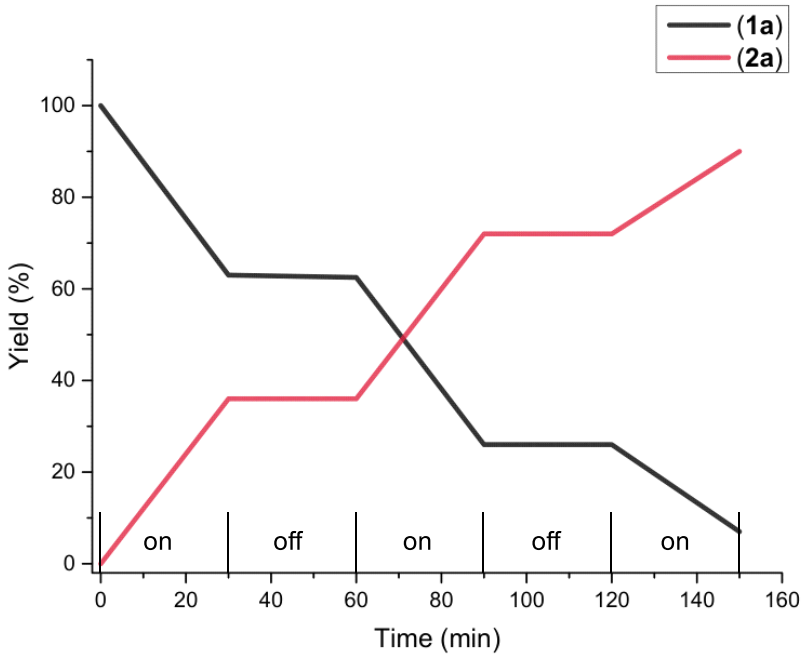
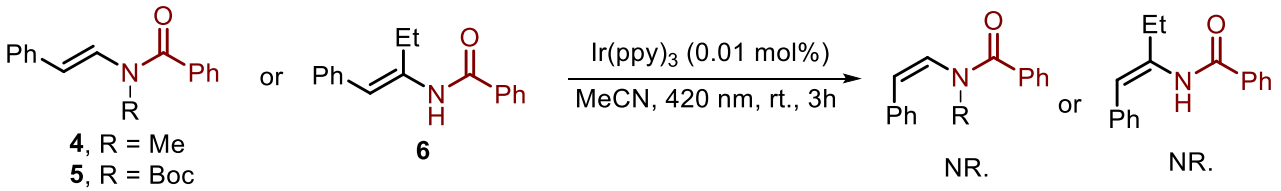


Figure S1 Photocontrolled switching experiment

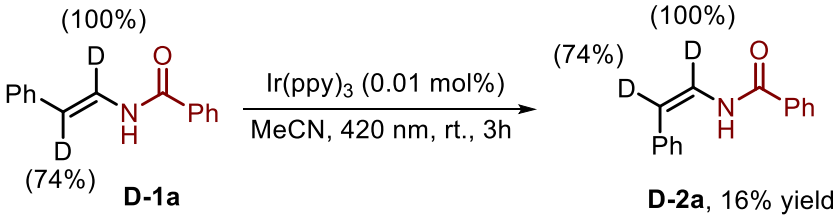
5.2 Control experiment



To a 10 mL reaction tube with a stir bar was charged protected enamides **4, 5** or **6** (0.2 mmol), The tube was sealed with rubber septum, then evacuated, and backfilled with nitrogen for three cycles, the solution of MeCN contains $Ir(ppy)_3$ (2.0 mL, 13 mg/L) was added. The mixture was stirred at room temperature for 3 h under 420 nm irrorations. The reaction mixture was diluted with ethyl acetate (10 mL), washed with water, brine, and dried over anhydrous Na_2SO_4. A 0.2 mL of solution was collected, diluted with ethyl acetate (2 mL), and analyzed by HPLC.

No isomerized products was observed, and substrate **4, 5** and **6** remained intact.

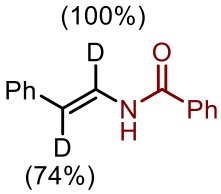
5.3 Deuterium experiment



D-1a **D-2a**, 16% yield

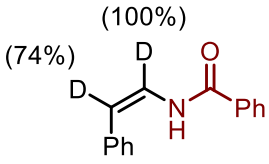
To a 10 mL reaction tube with a stir bar was charged substrates **D-1a** (45 mg, 0.2 mmol), The tube was sealed with rubber septum, then evacuated and backfilled with nitrogen for three cycles, the solution of MeCN contains $Ir(ppy)_3$ (2.0 mL, 13 mg/L) was added. The mixture was stirred at room temperature for 3 h under 420 nm irrorations. The reaction was quenched with water (20.0 mL), and extracted with ethyl acetate (3 × 15.0 mL). The combined organic layers were washed with water, brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to afford the desired product **D-2a** for 16% yield, and 83% of **D-1a** was recovered.

(*E*)-N-(2-phenylvinyl-1,2-*d*$_2$)benzamide (D-1a)



^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 10.63 (s, 1H), 8.02 – 7.93 (m, 2H), 7.63 – 7.58 (m, 1H), 7.57 – 7.50 (m, 2H), 7.42 – 7.38 (m, 2H), 7.35 – 7.28 (m, 2H), 7.21 – 7.15 (m, 1H), 6.47 (s, 0.26H).

(*Z*)-N-(2-phenylvinyl-1,2-*d*$_2$)benzamide (D-2a)



7.2 mg, 16% yield, white solid.

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 10.00 (s, 1H), 7.96 – 7.91 (m, 2H), 7.61 – 7.56 (m, 1H), 7.54 – 7.48 (m, 3H), 7.48 – 7.47 (m, 1H), 7.41 – 7.36 (m, 2H), 7.26 – 7.21 (m, 1H), 5.85 (s, 0.26H).

5.4 UV-Vis Absorption Spectra

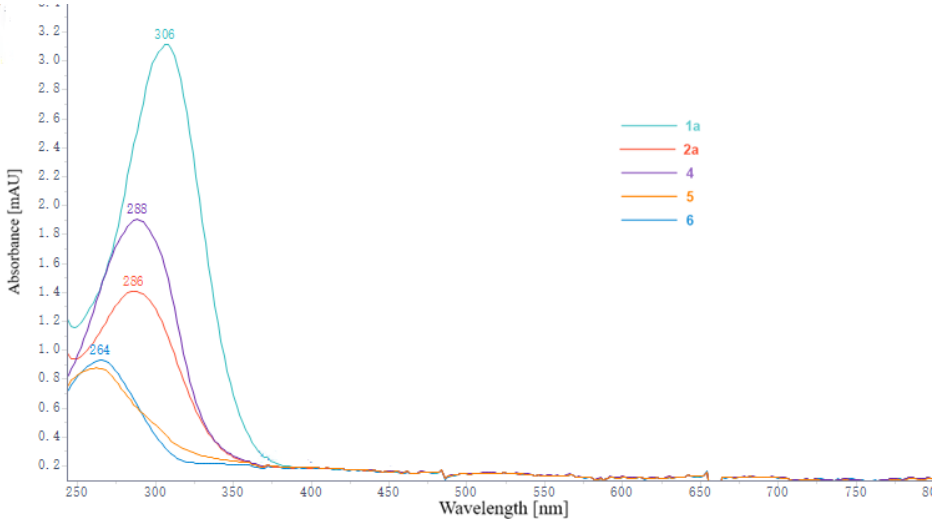


Figure S2 UV Vis Absorption Spectra

6. References

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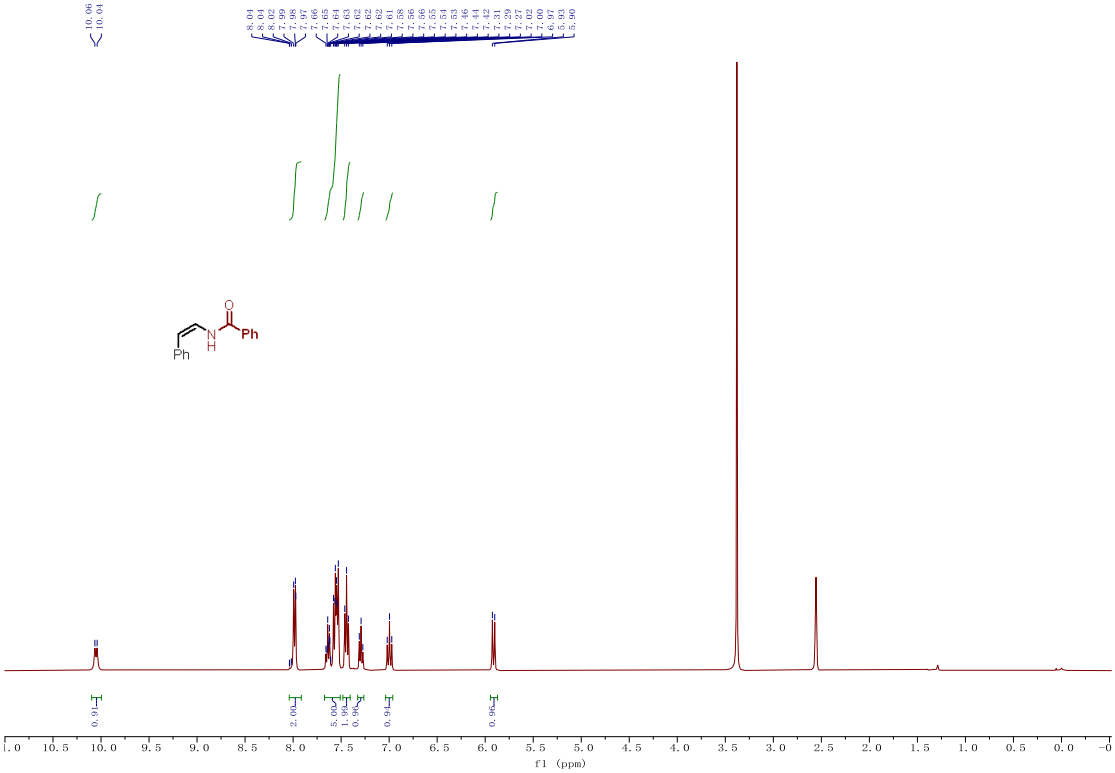
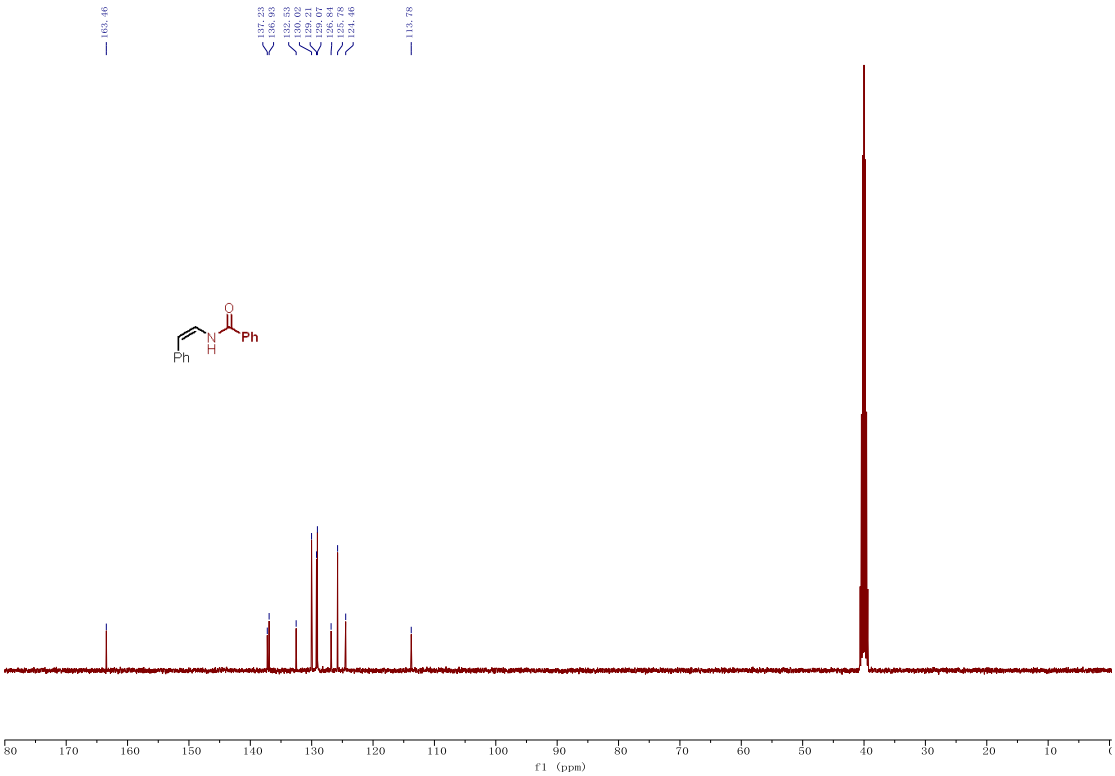
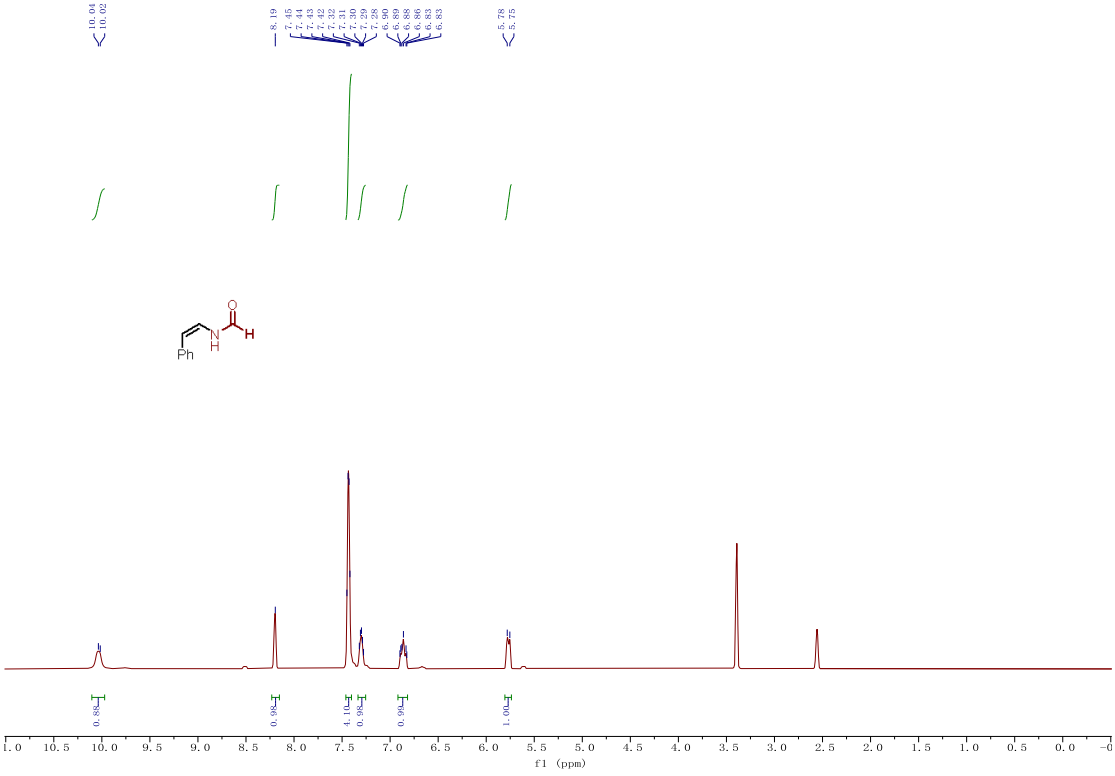
7. Copies of NMR Spectra

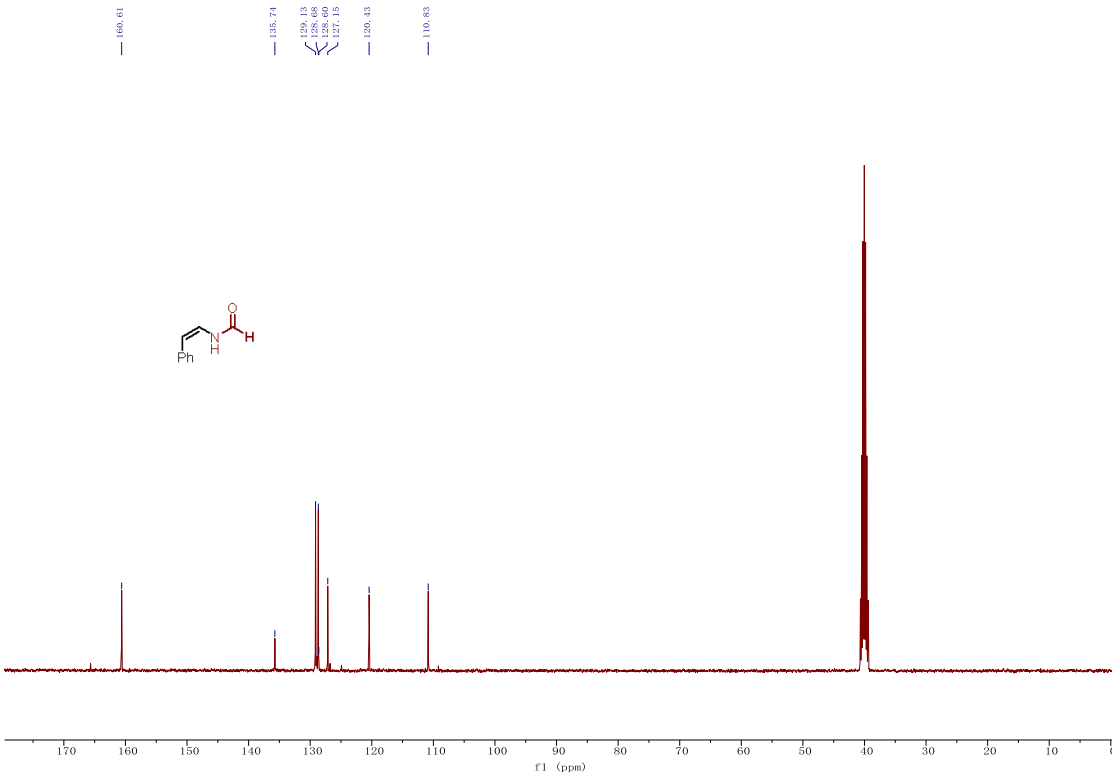
2a, ^{1}H NMR (400 MHz, DMSO-d_6); ^{13}C NMR (101 MHz, DMSO-d_6)



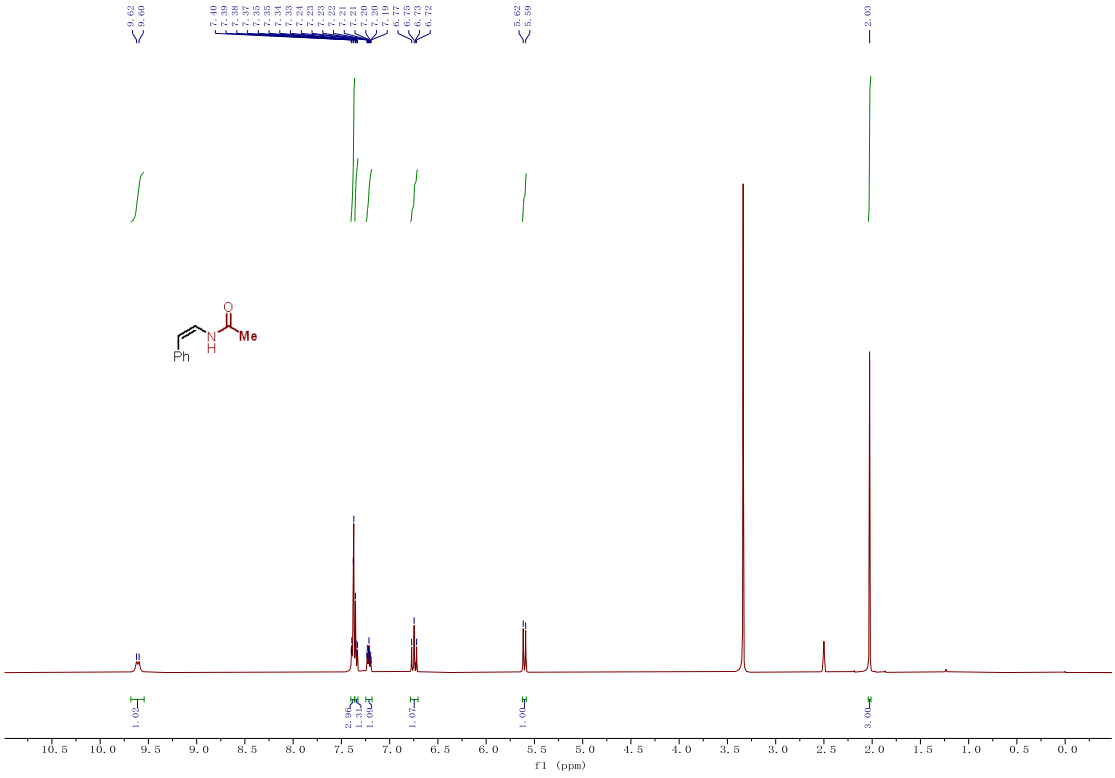


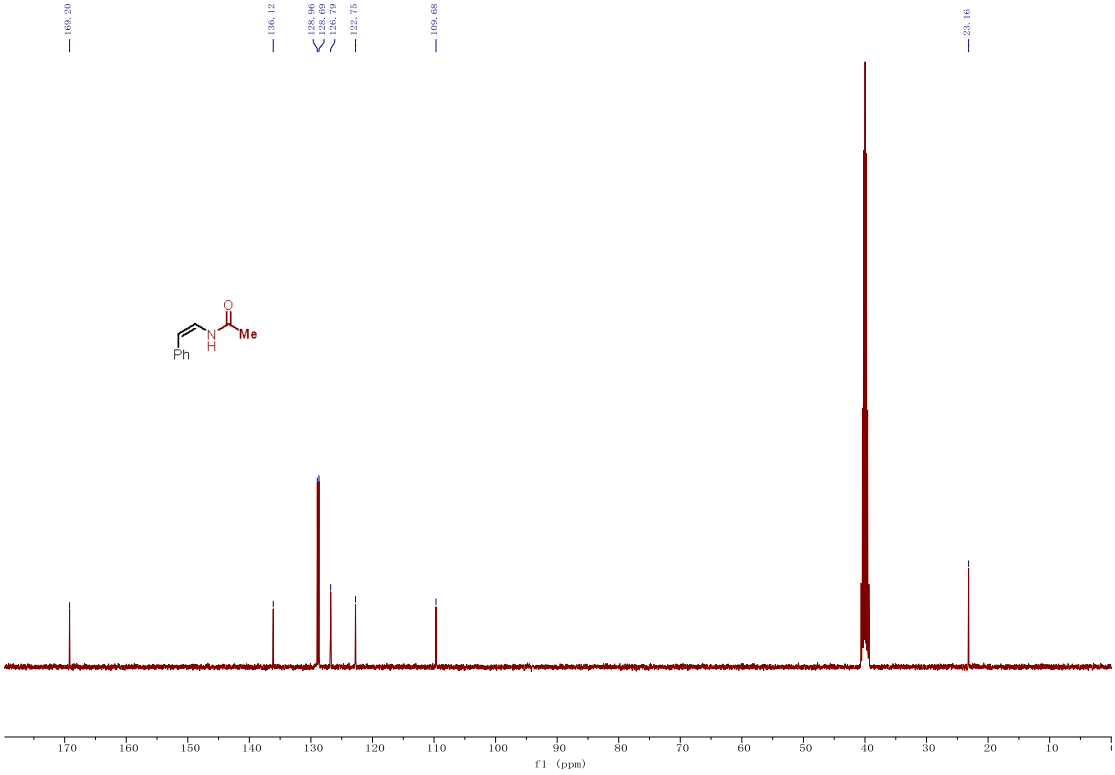
2b, ^{1}H NMR (400 MHz, DMSO-d_6); ^{13}C NMR (101 MHz, DMSO-d_6)



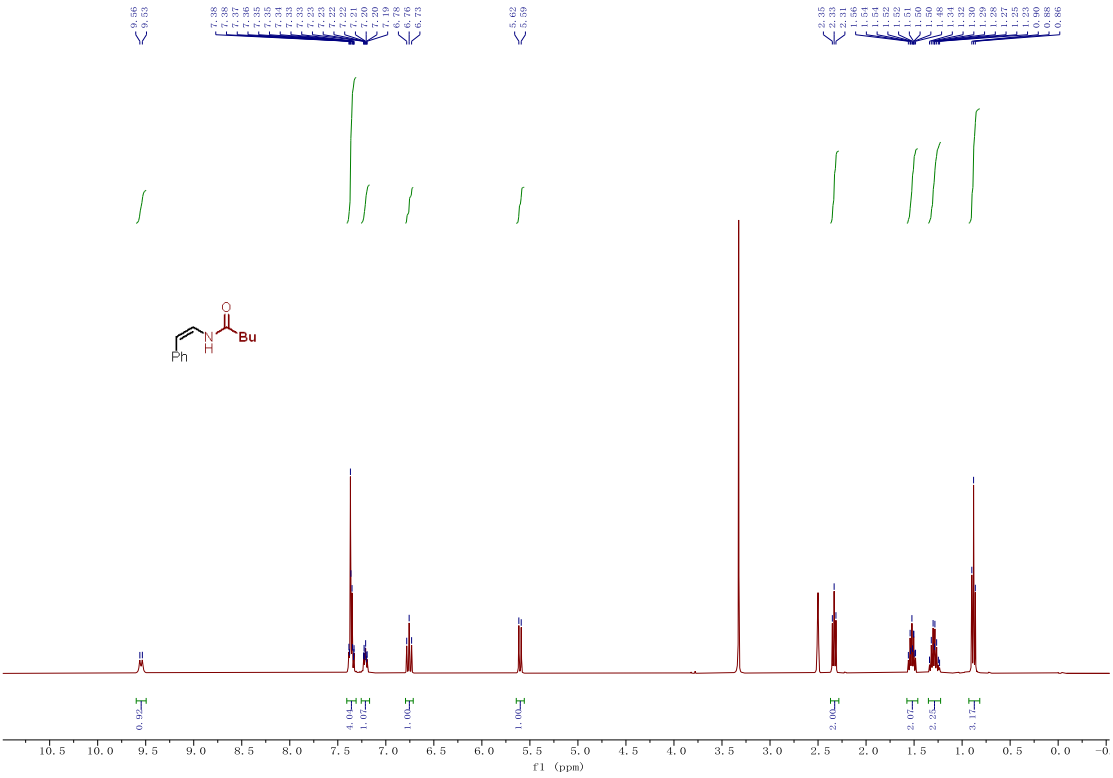


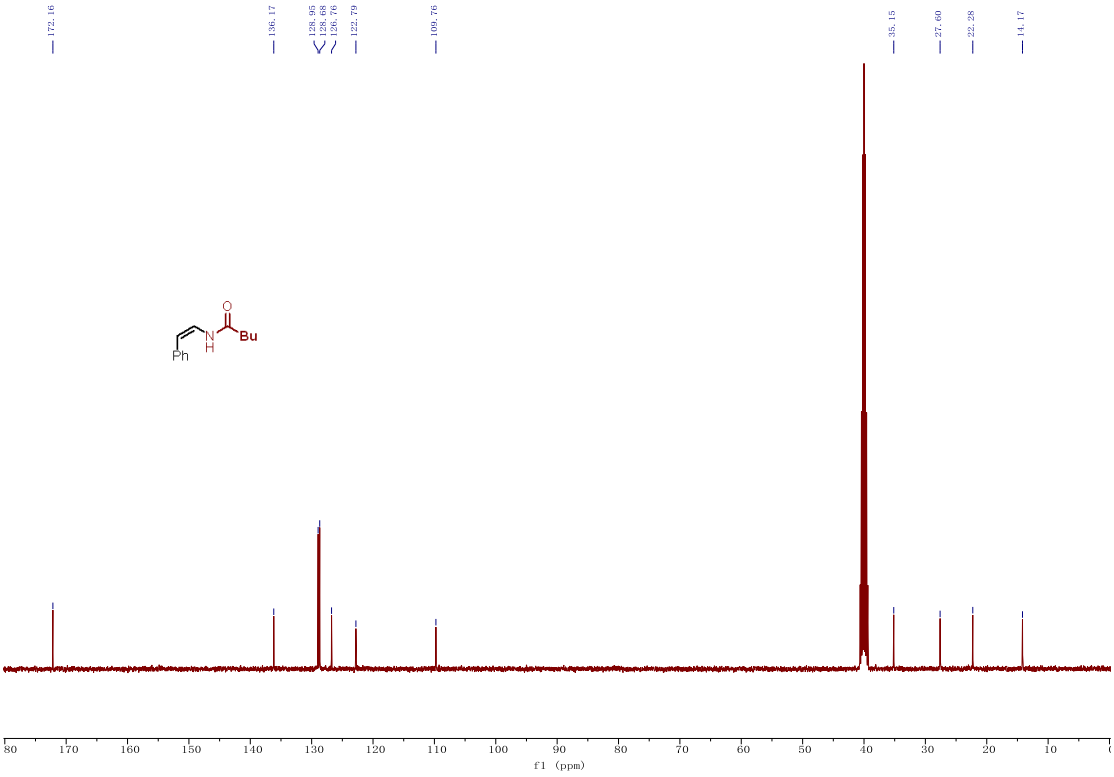
2c, ^{1}H NMR (400 MHz, DMSO-d_6); ^{13}C NMR (101 MHz, DMSO-d_6)



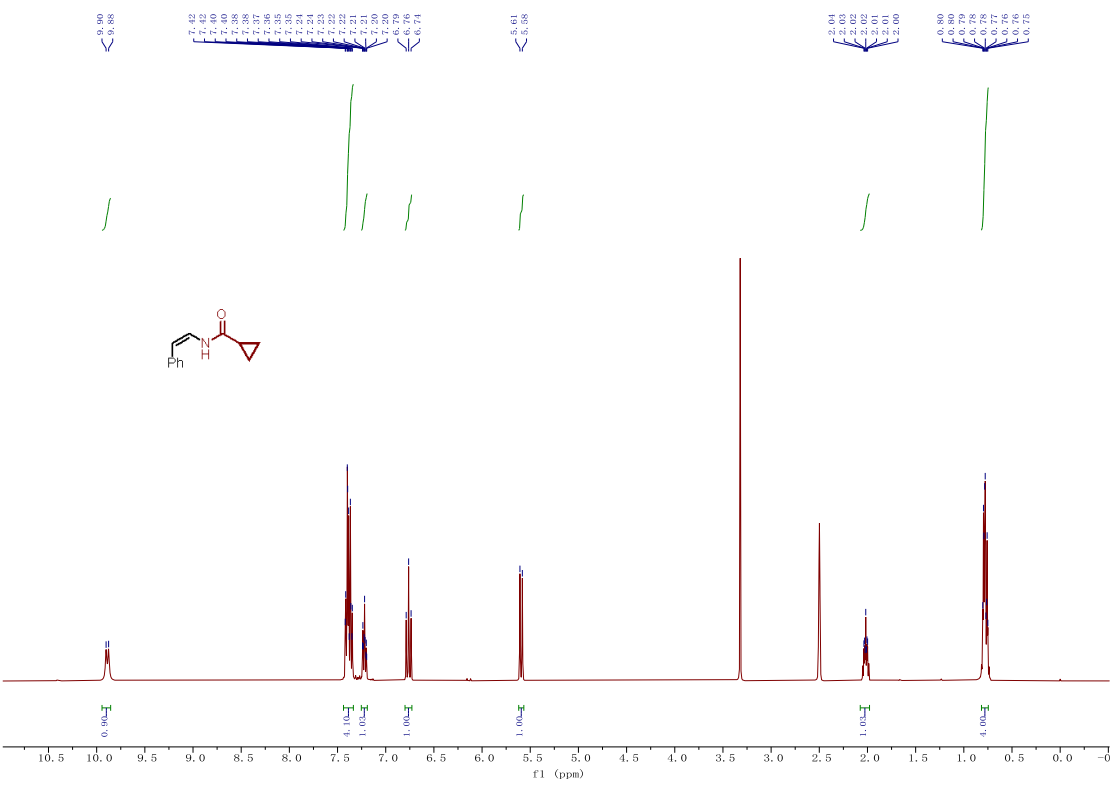


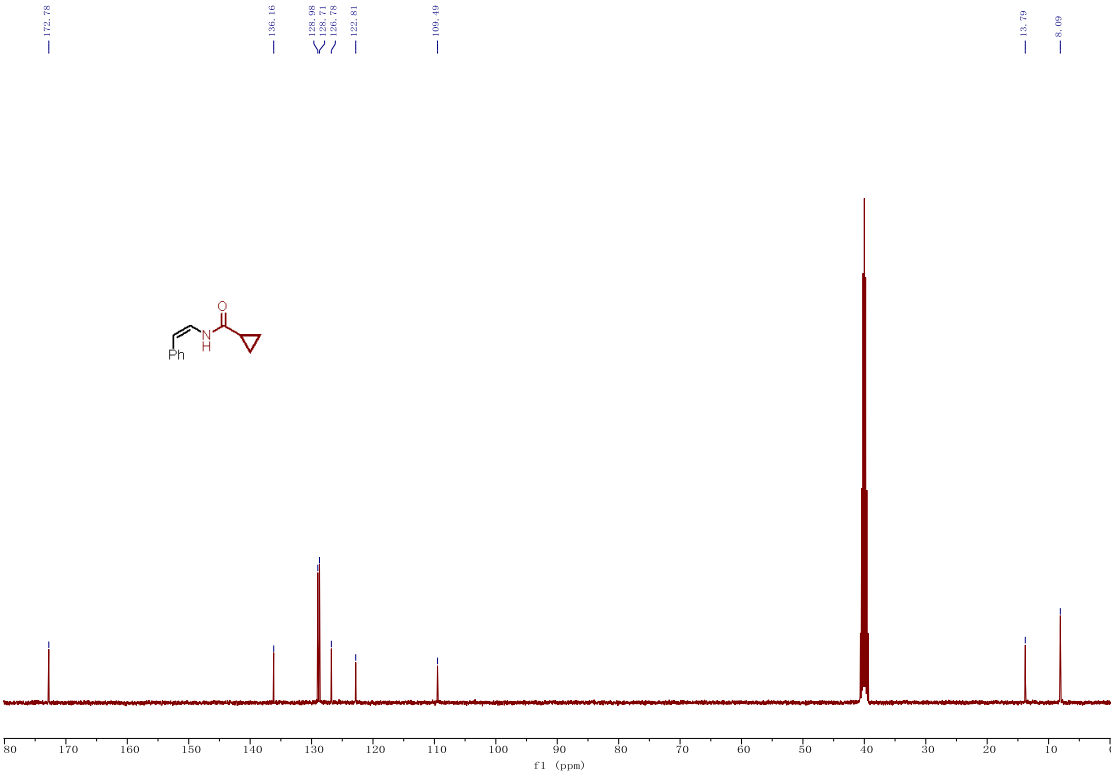
2d, ^{1}H NMR (400 MHz, DMSO-*d*$_6$); ^{13}C NMR (101 MHz, DMSO-*d*$_6$)



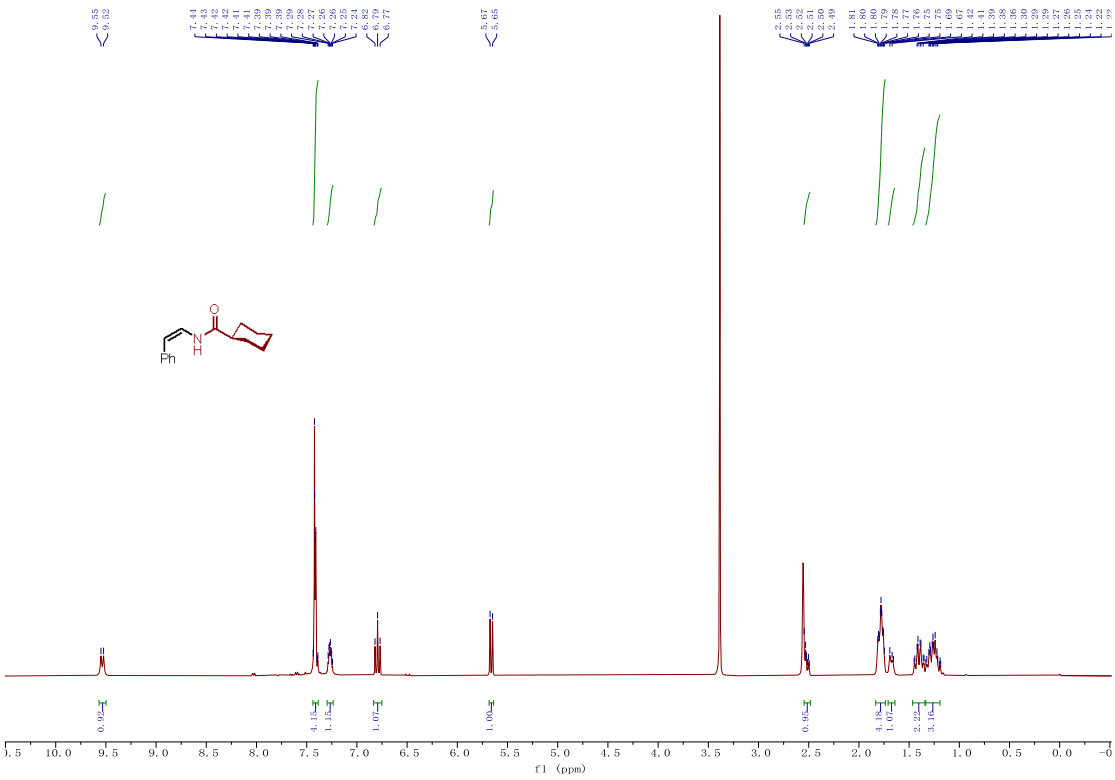


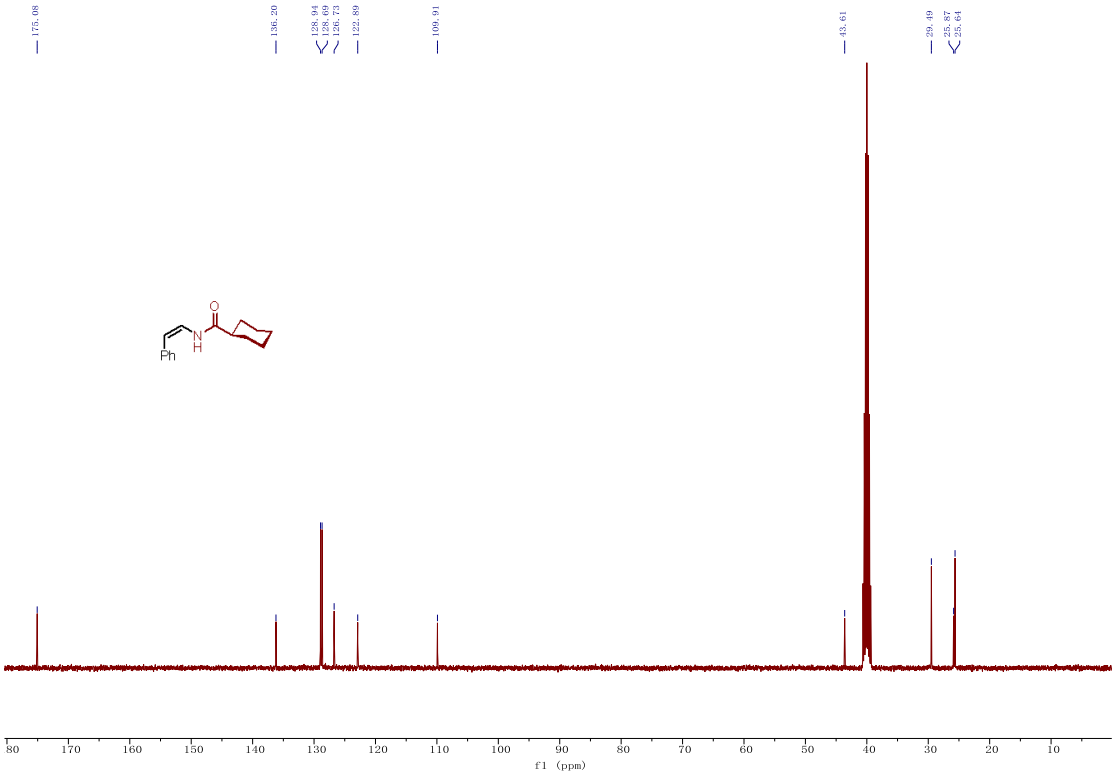
2e, ^{1}H NMR (400 MHz, DMSO-d_6); ^{13}C NMR (101 MHz, DMSO-d_6)



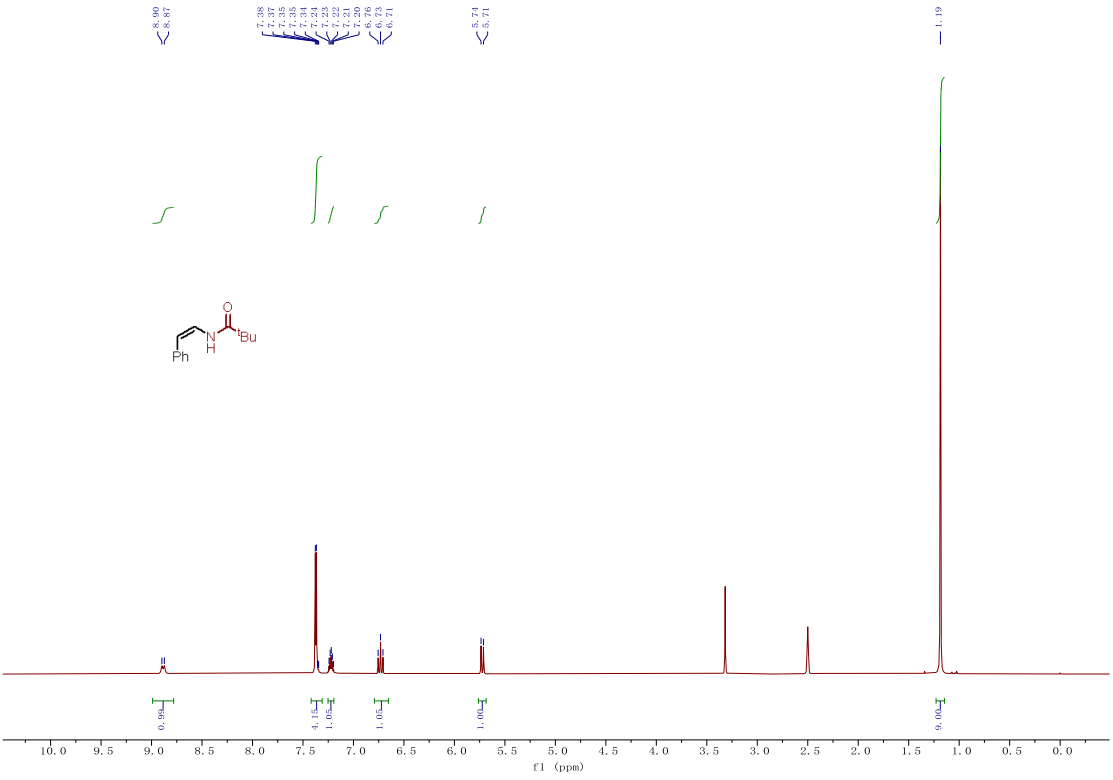


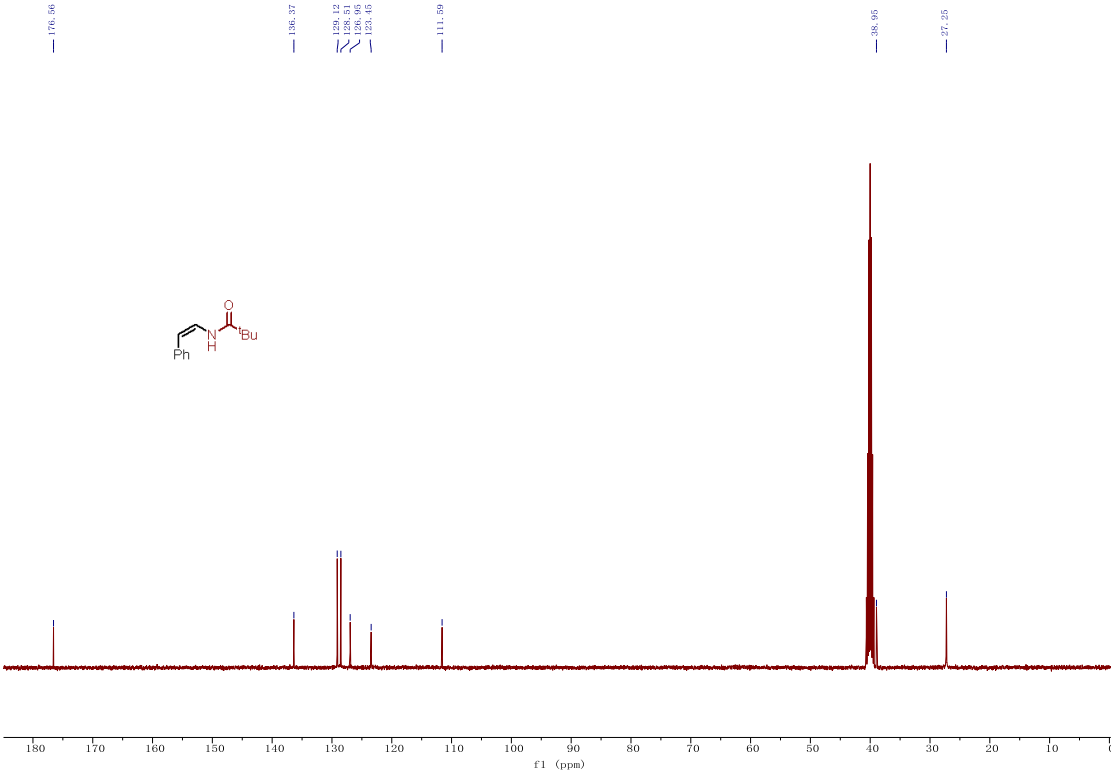
2f, ^{1}H NMR (400 MHz, DMSO-*d*$_6$); ^{13}C NMR (101 MHz, DMSO-*d*$_6$)



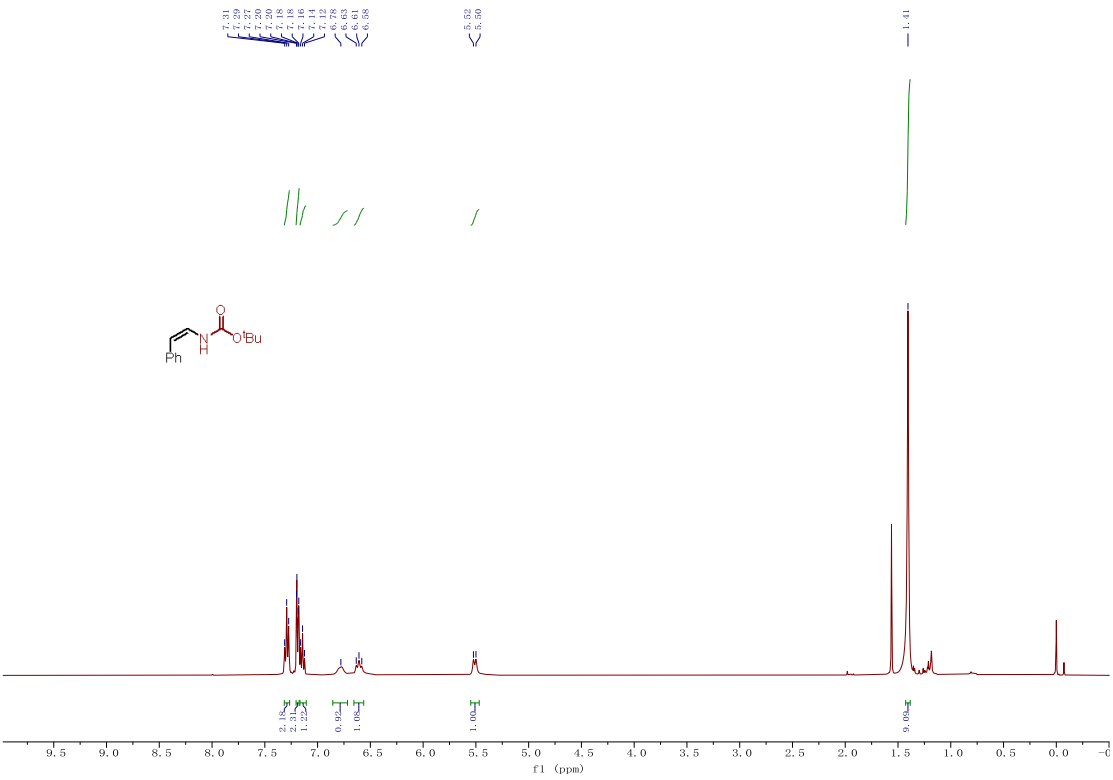


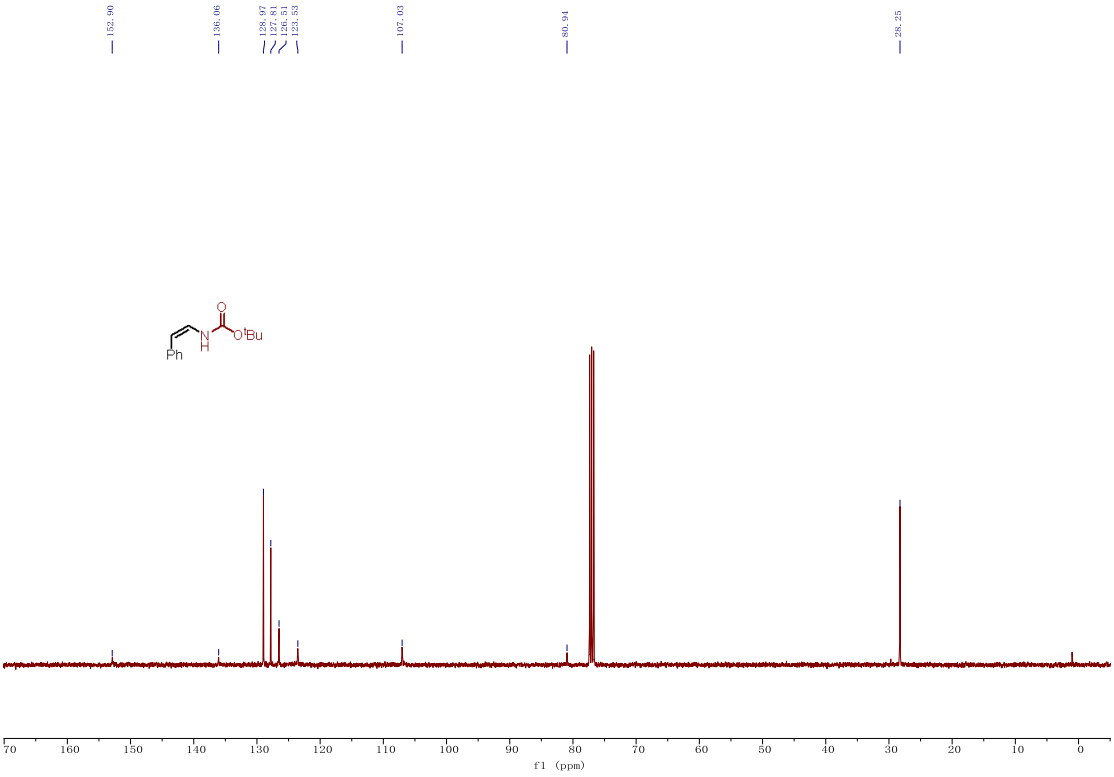
2g, ^{1}H NMR (400 MHz, DMSO-d_6); ^{13}C NMR (101 MHz, DMSO-d_6)



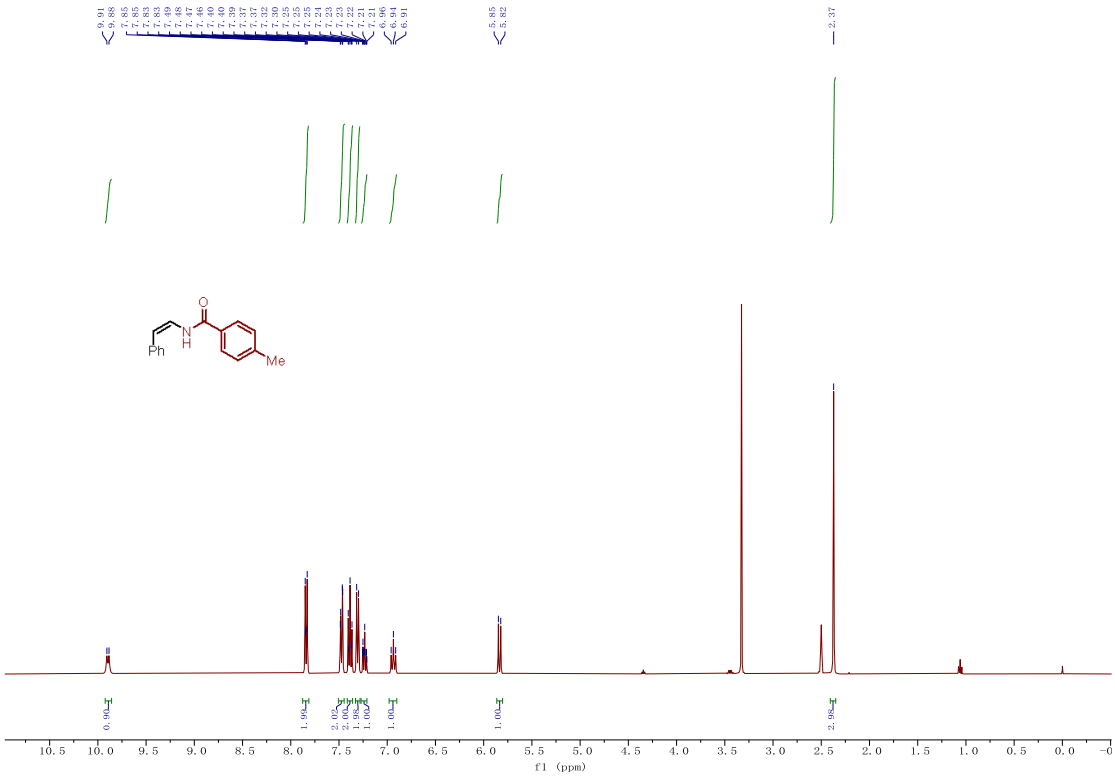


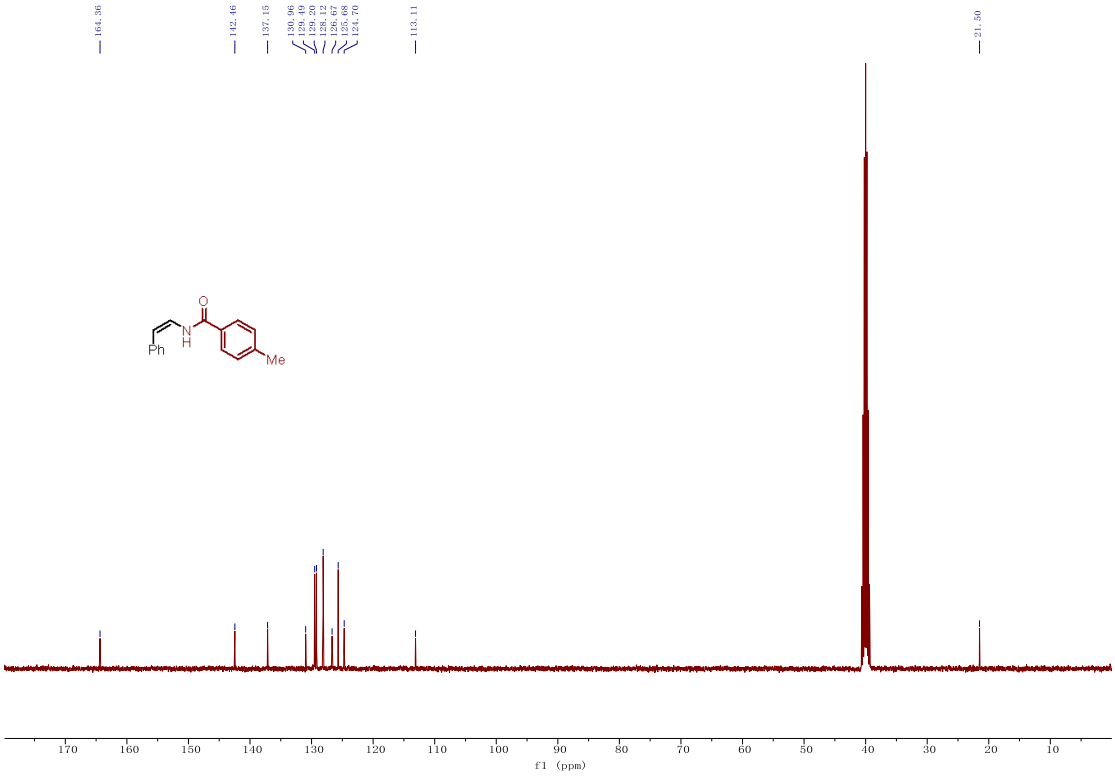
2h, ^{1}H NMR (400 MHz, $CDCl_3$); ^{13}C NMR (101 MHz, $CDCl_3$)



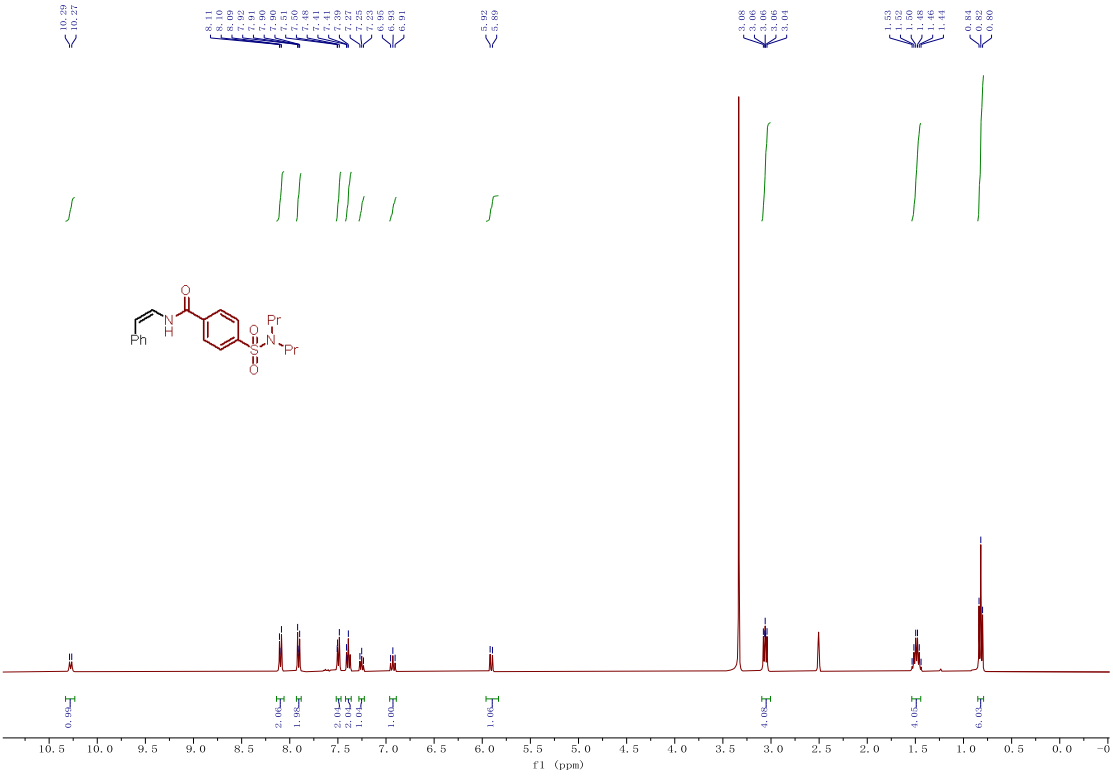


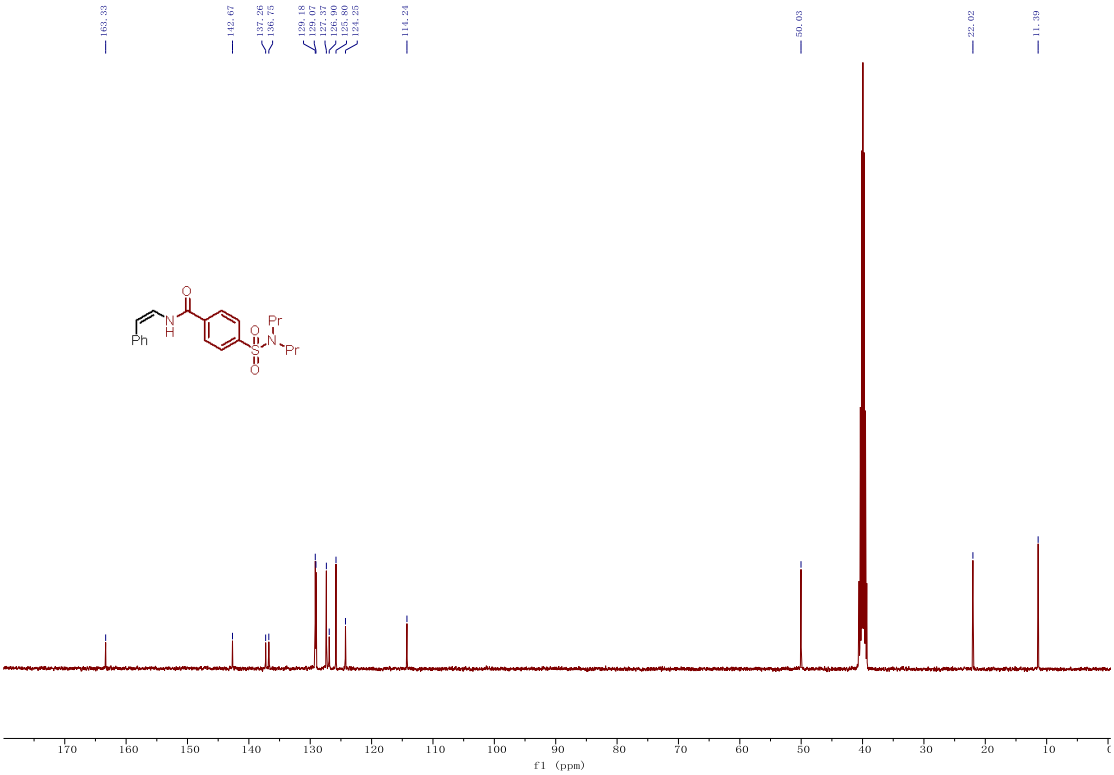
2i, ^{1}H NMR (400 MHz, DMSO-d_6); ^{13}C NMR (101 MHz, DMSO-d_6)



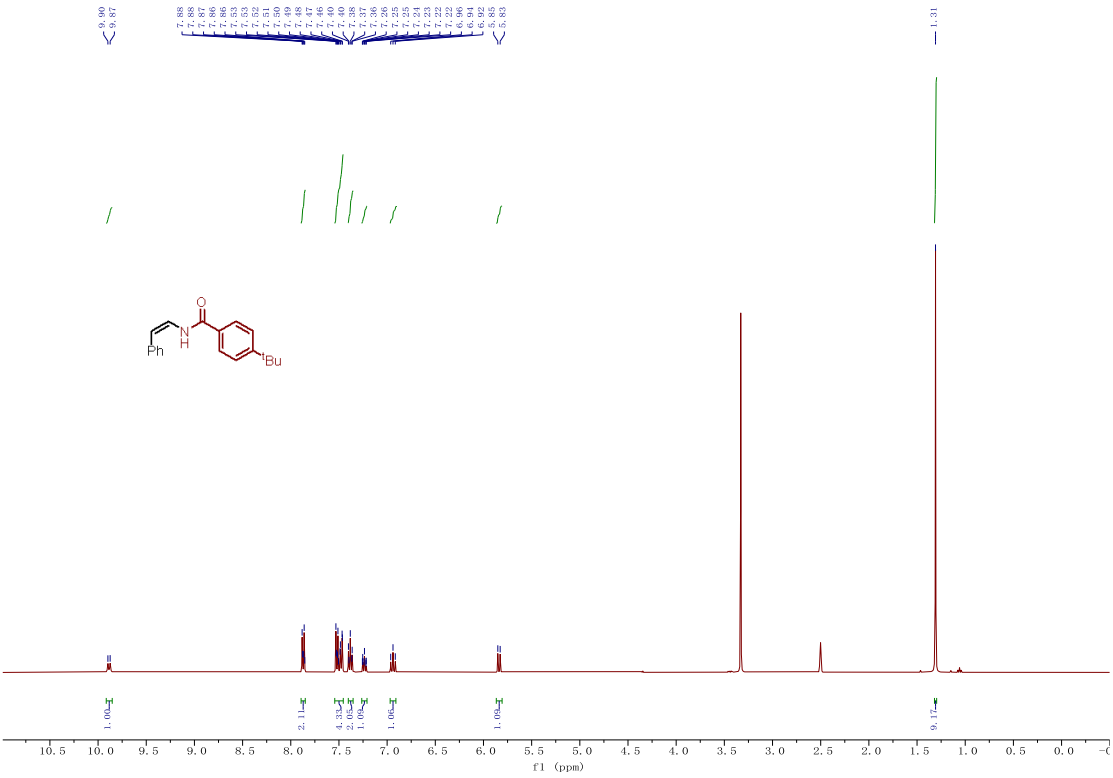


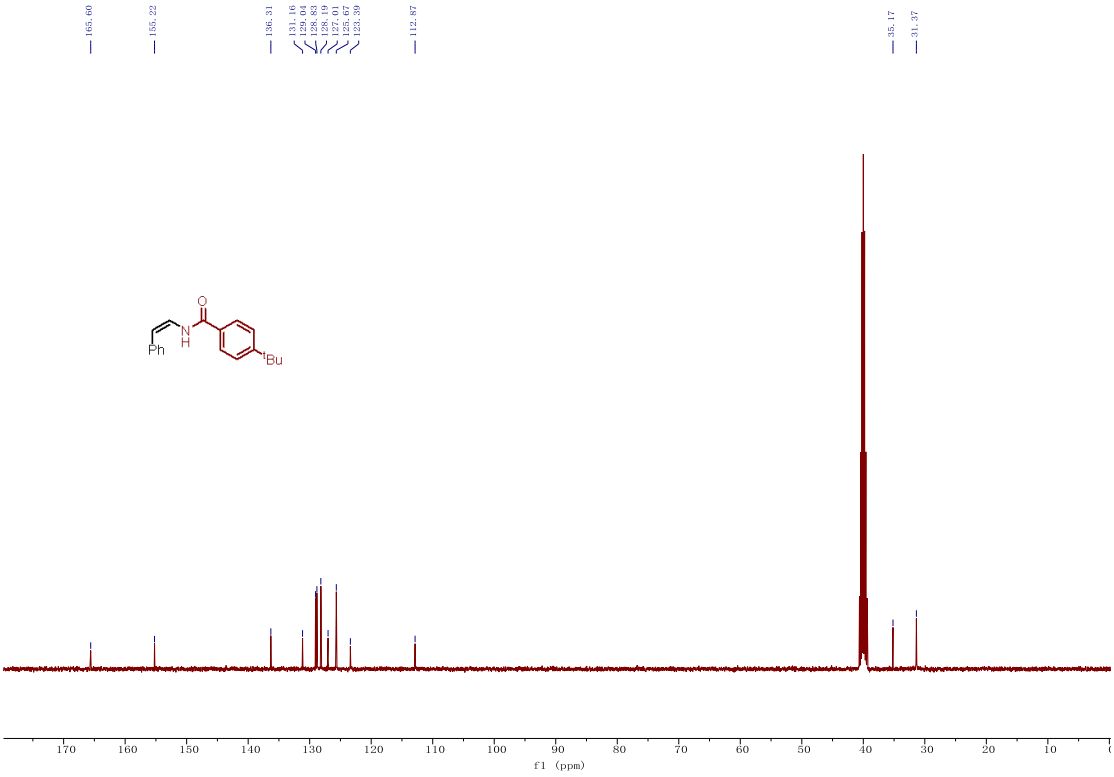
2j, ^{1}H NMR (400 MHz, DMSO-d_6); ^{13}C NMR (101 MHz, DMSO-d_6)



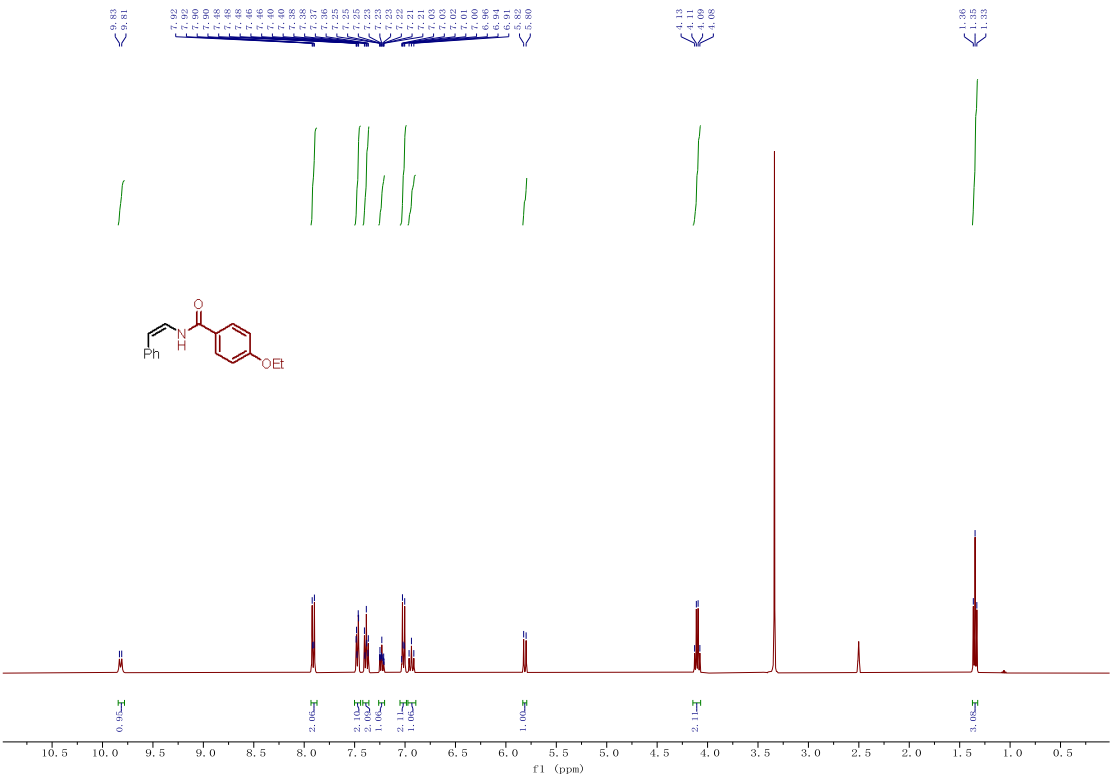


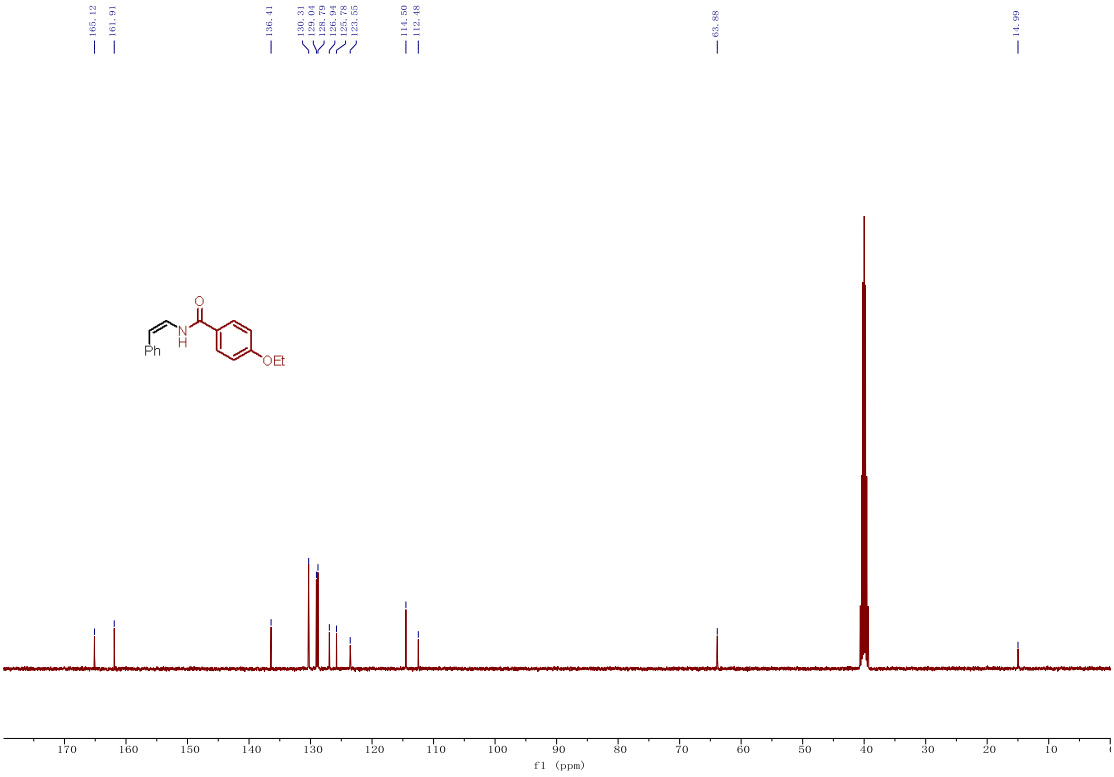
2k, ^{1}H NMR (400 MHz, DMSO-d_6); ^{13}C NMR (101 MHz, DMSO-d_6)



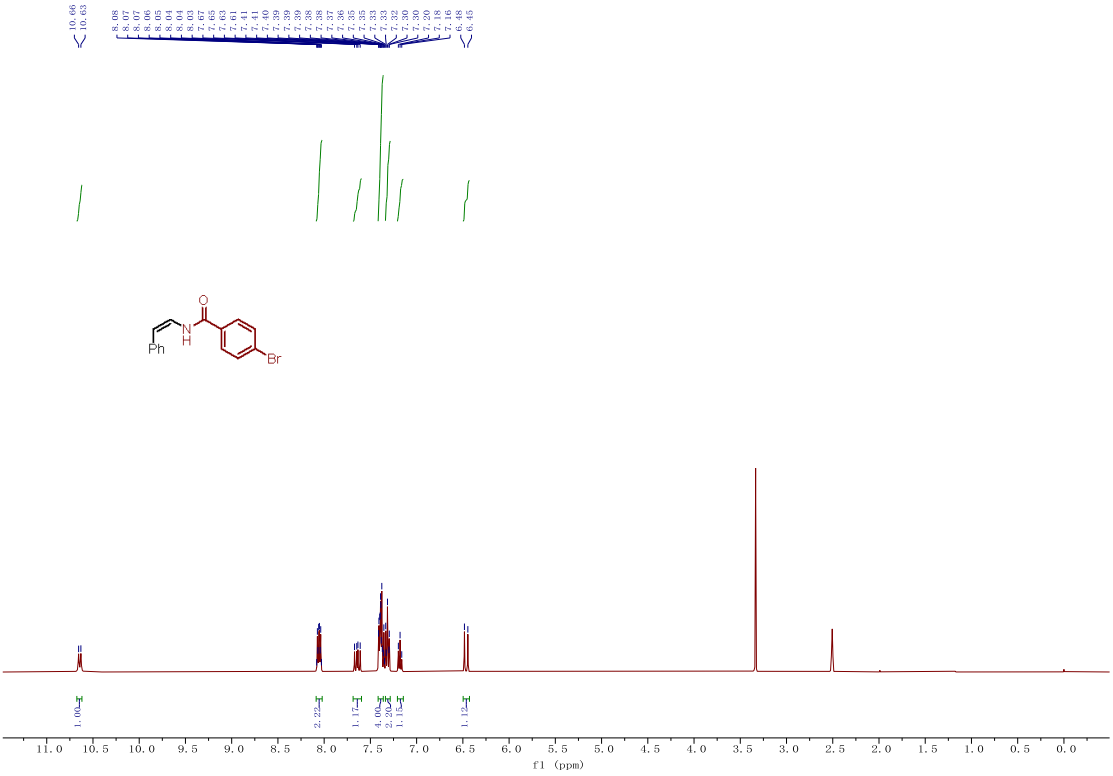


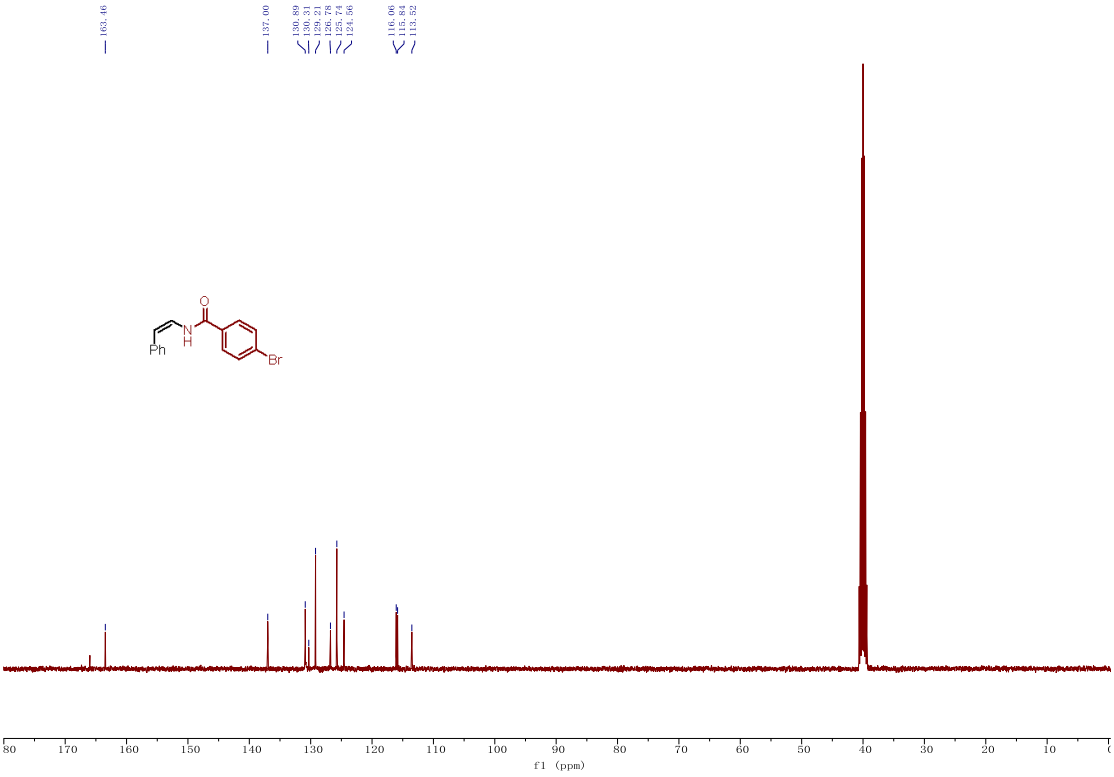
2l, ^{1}H NMR (400 MHz, DMSO-d_6); ^{13}C NMR (101 MHz, DMSO-d_6)



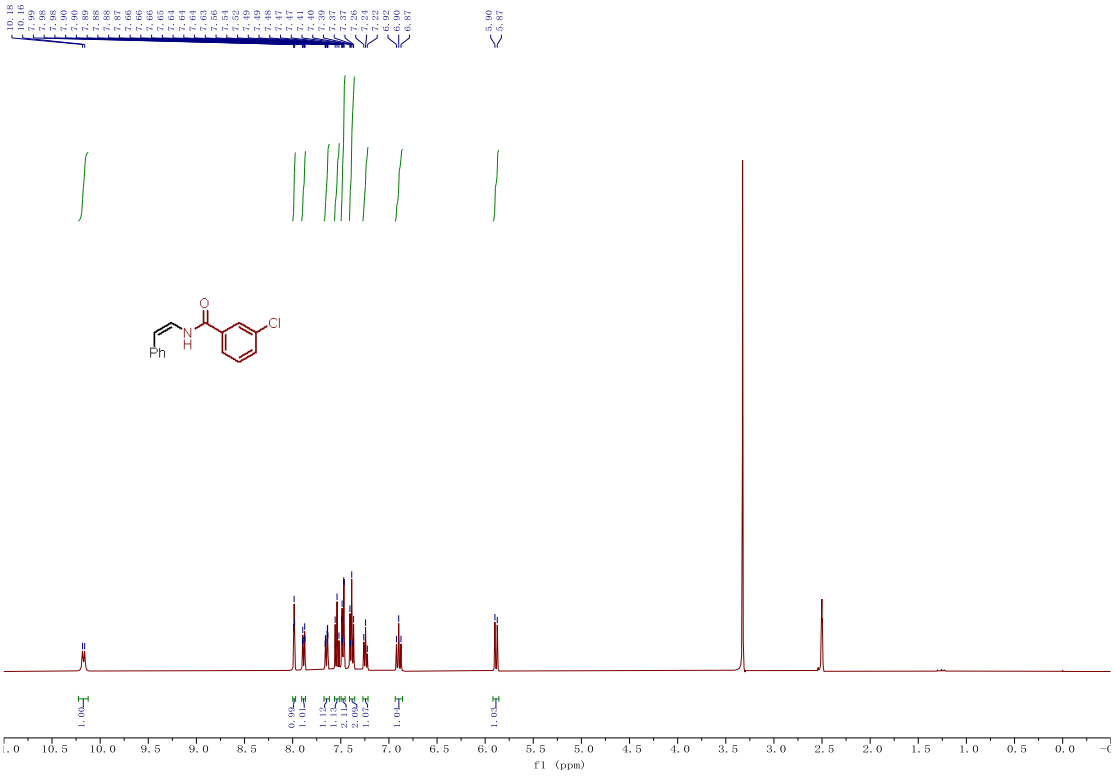


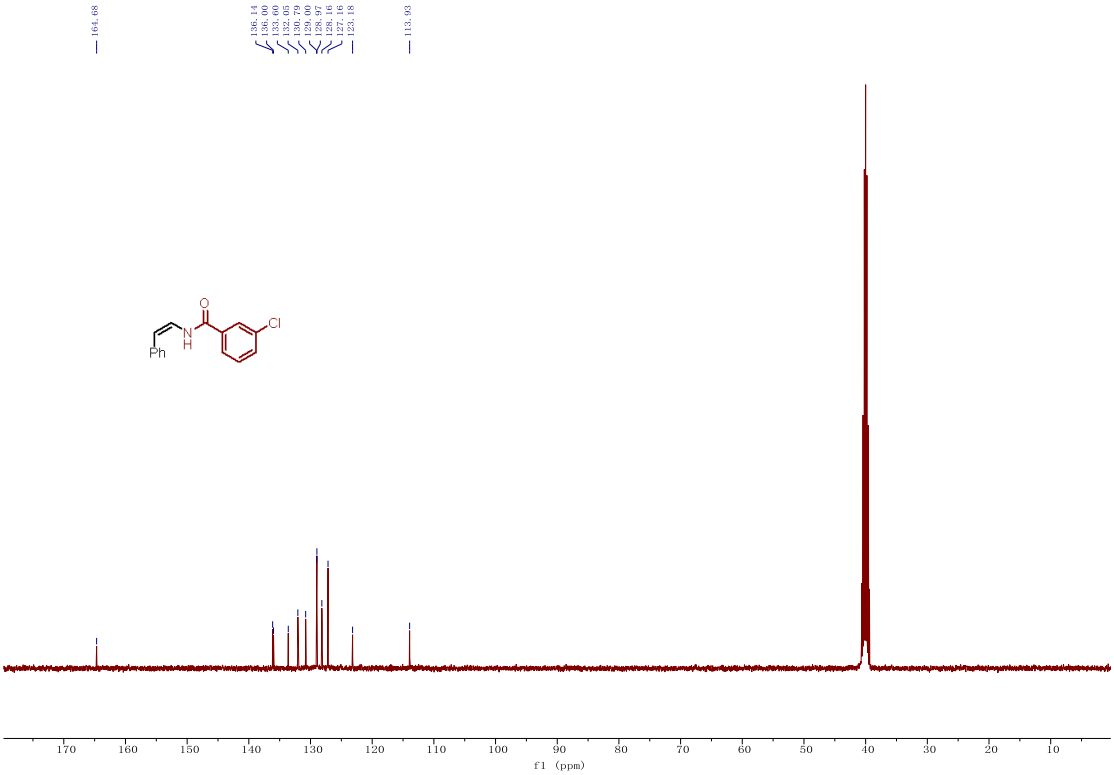
2m, ^{1}H NMR (400 MHz, DMSO-d_6); ^{13}C NMR (101 MHz, DMSO-d_6)



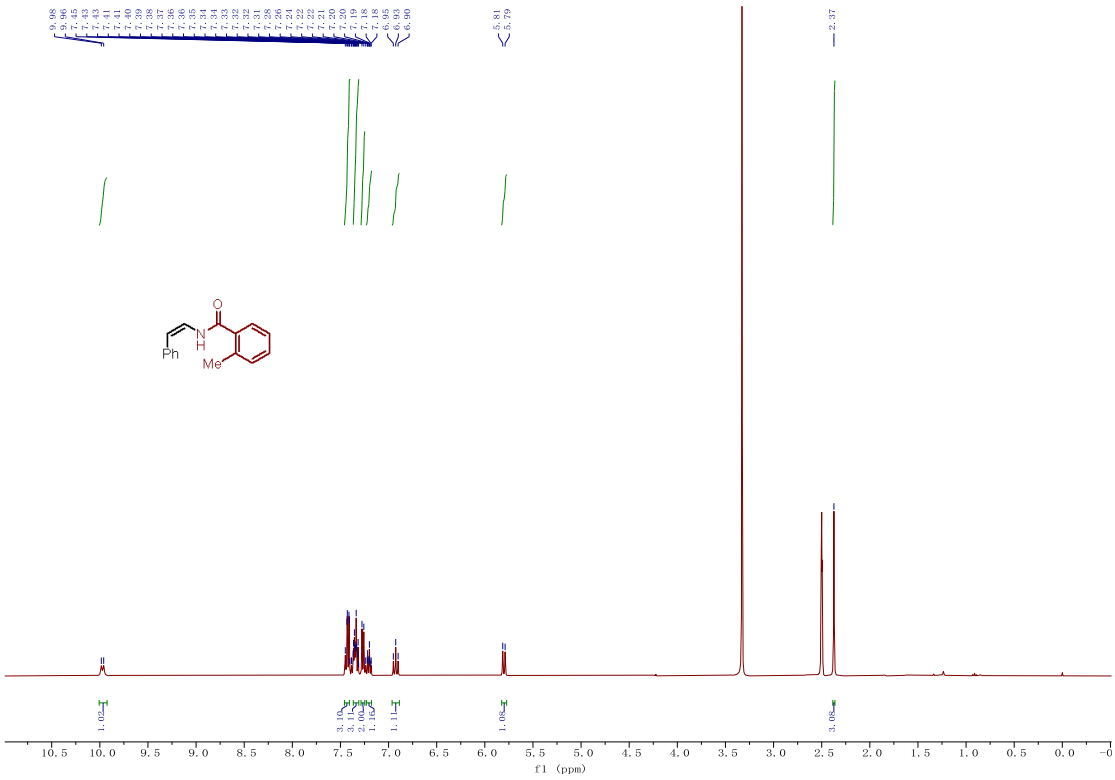


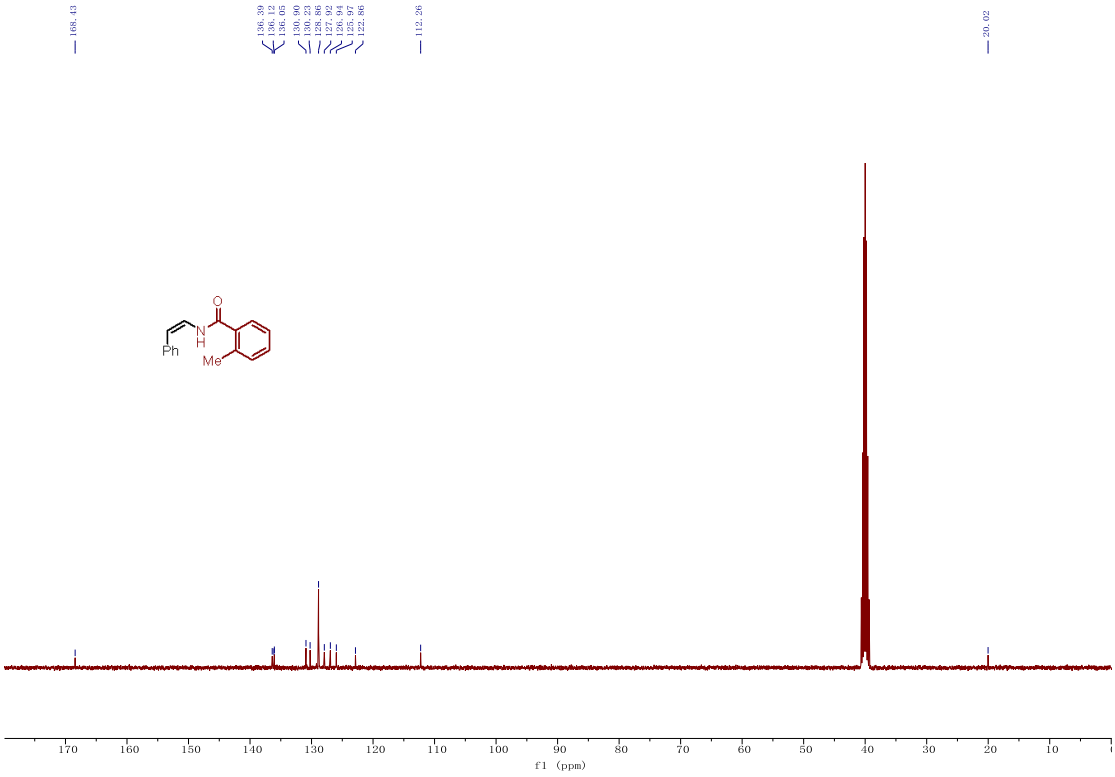
2n, ^{1}H NMR (400 MHz, DMSO-d_6); ^{13}C NMR (101 MHz, DMSO-d_6)



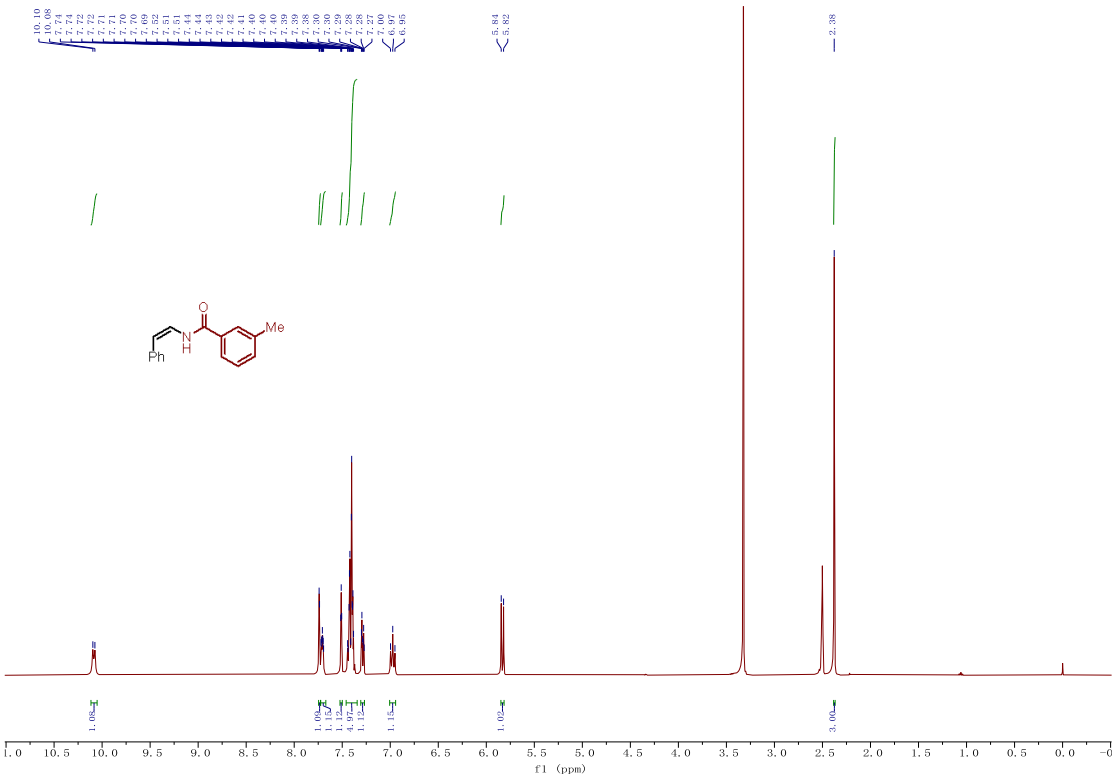


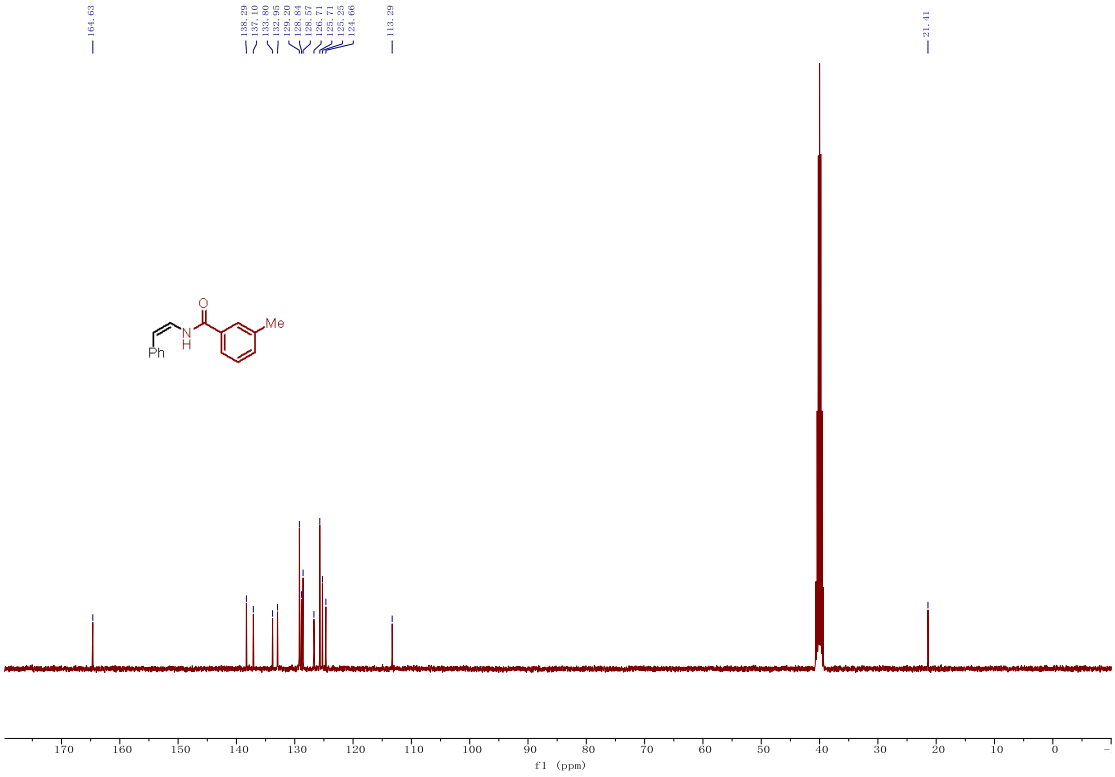
2o, ^{1}H NMR (400 MHz, DMSO-d_6); ^{13}C NMR (101 MHz, DMSO-d_6)



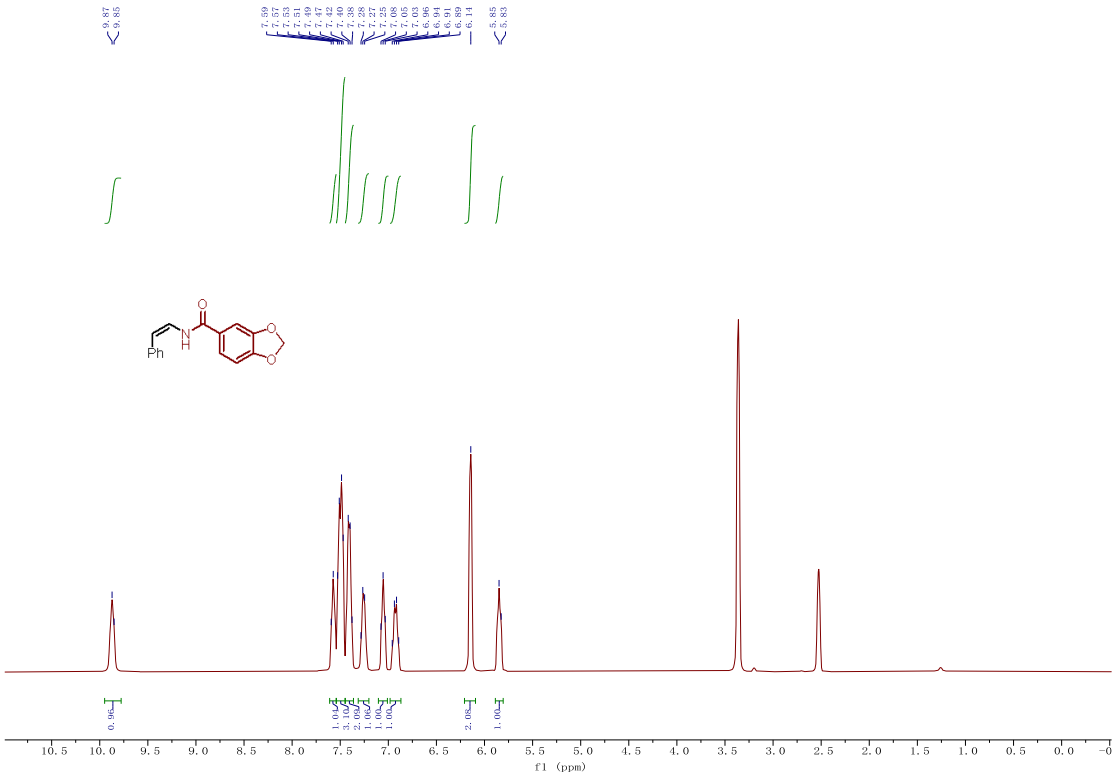


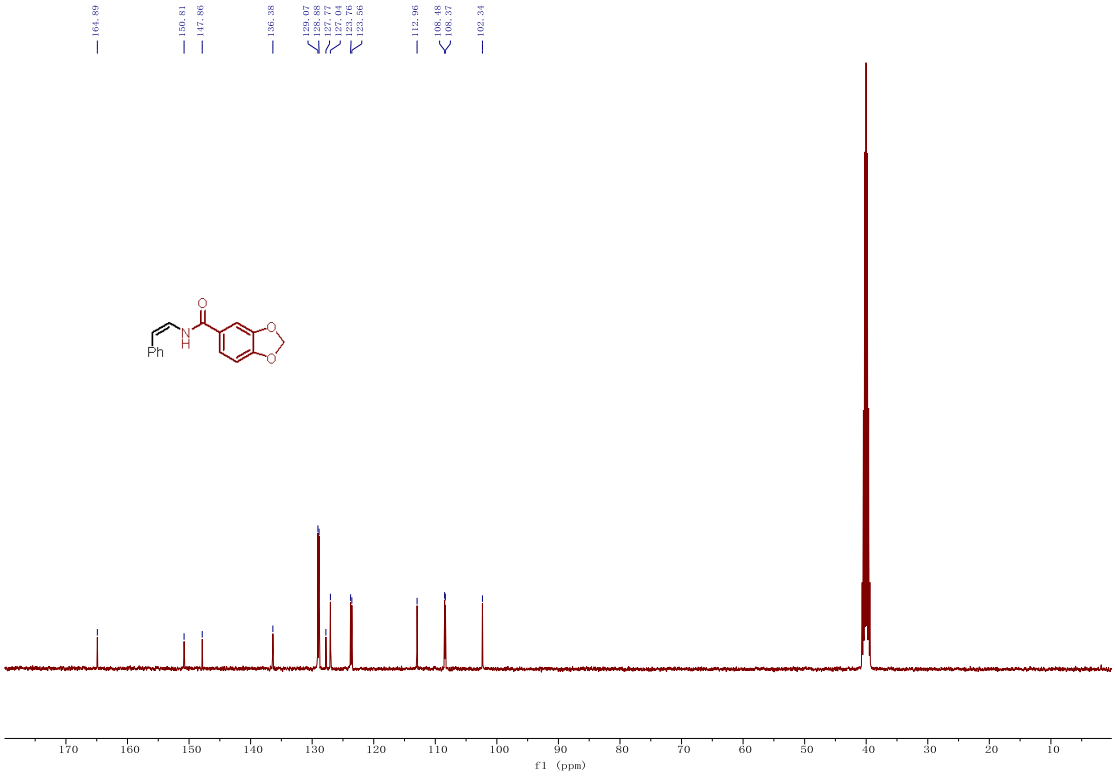
2p, ^{1}H NMR (400 MHz, DMSO-d_6); ^{13}C NMR (101 MHz, DMSO-d_6)



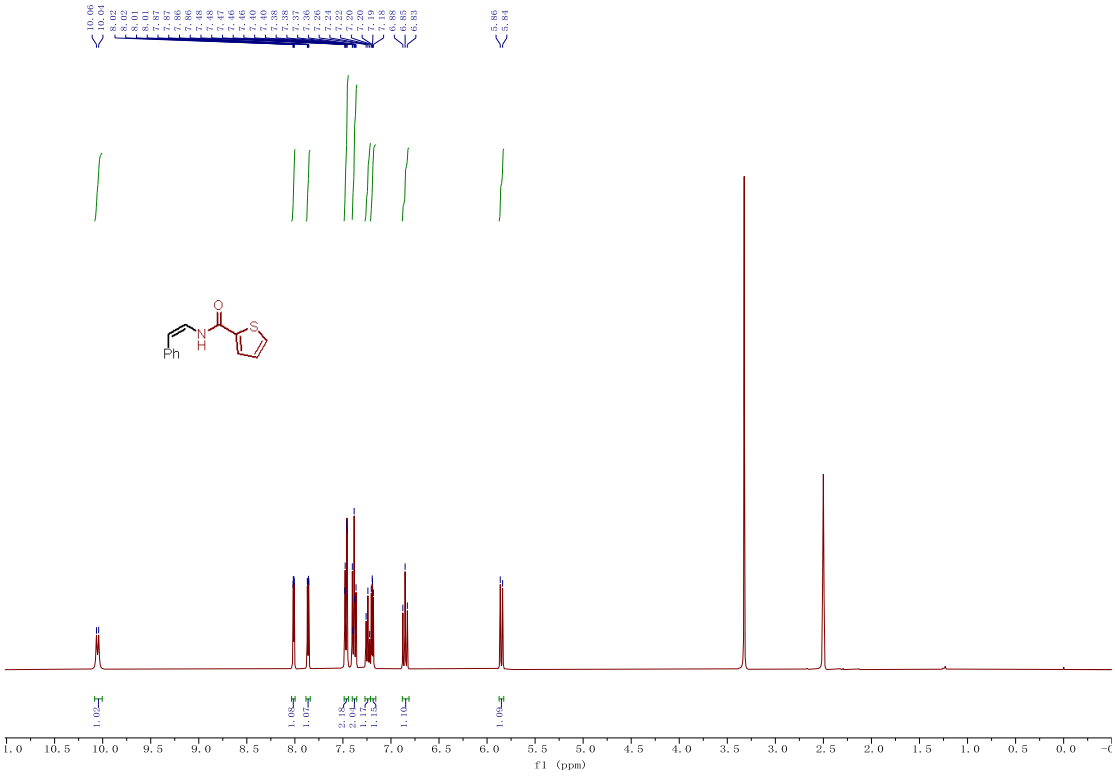


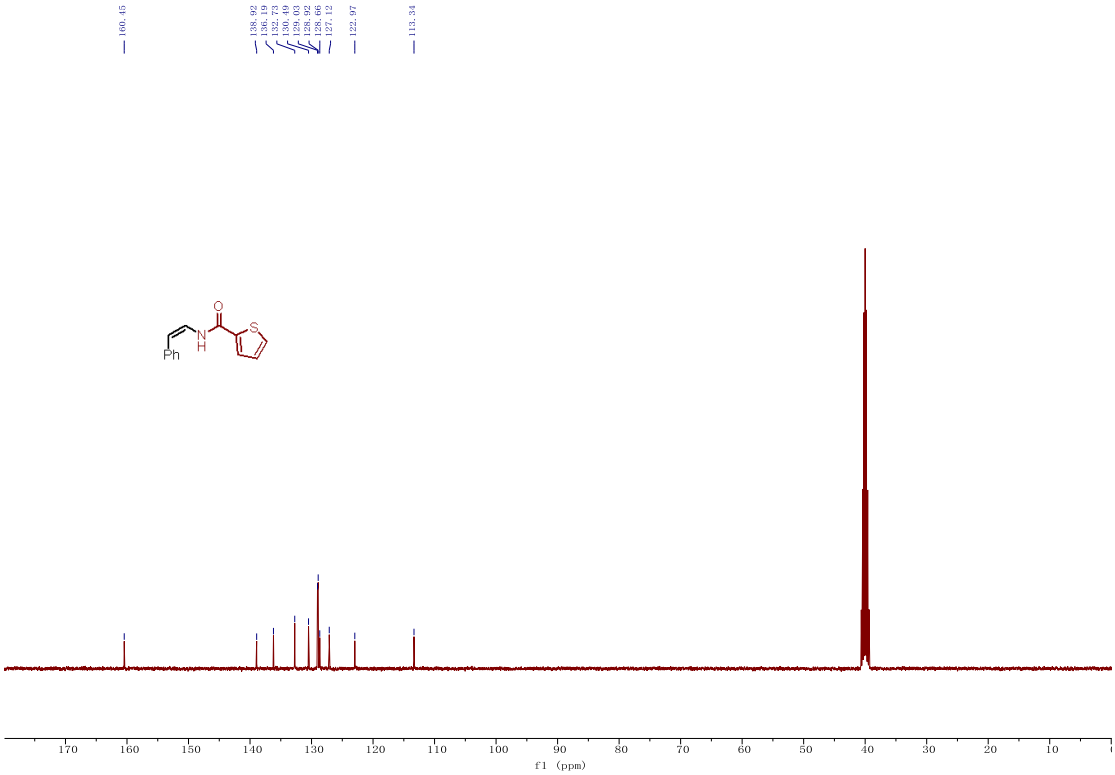
2q, ^{1}H NMR (400 MHz, DMSO-d_6); ^{13}C NMR (101 MHz, DMSO-d_6)





2r, ^{1}H NMR (400 MHz, DMSO-d_6); ^{13}C NMR (101 MHz, DMSO-d_6)





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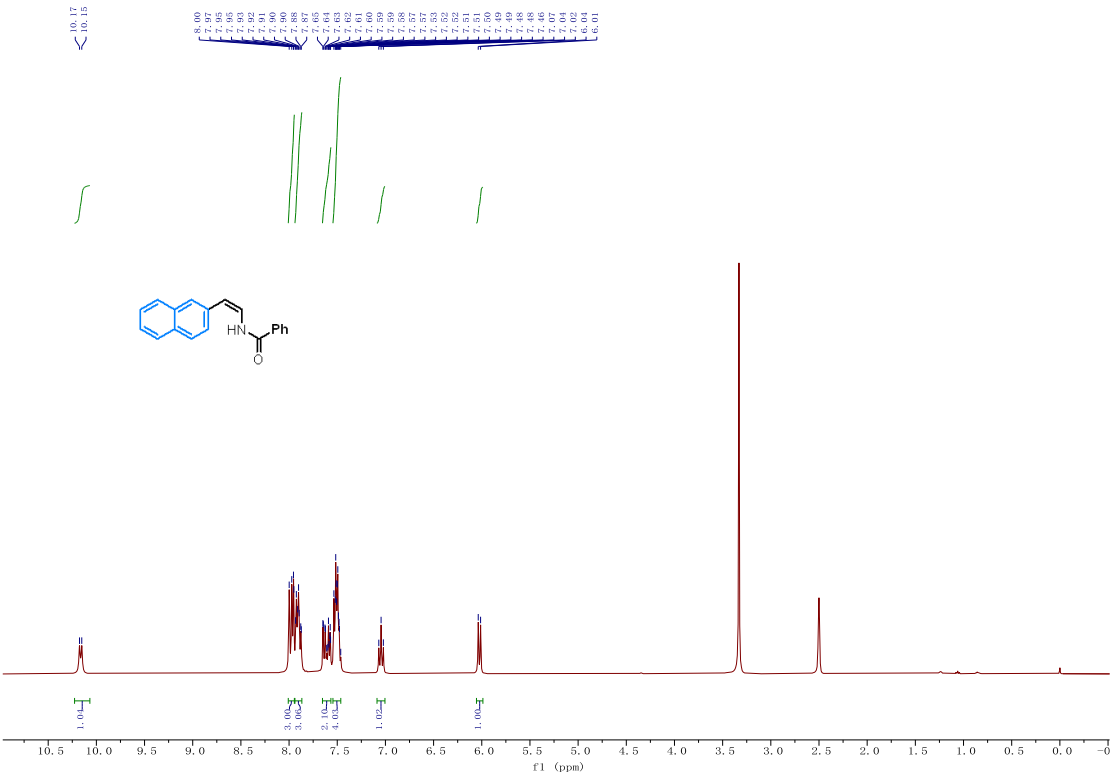

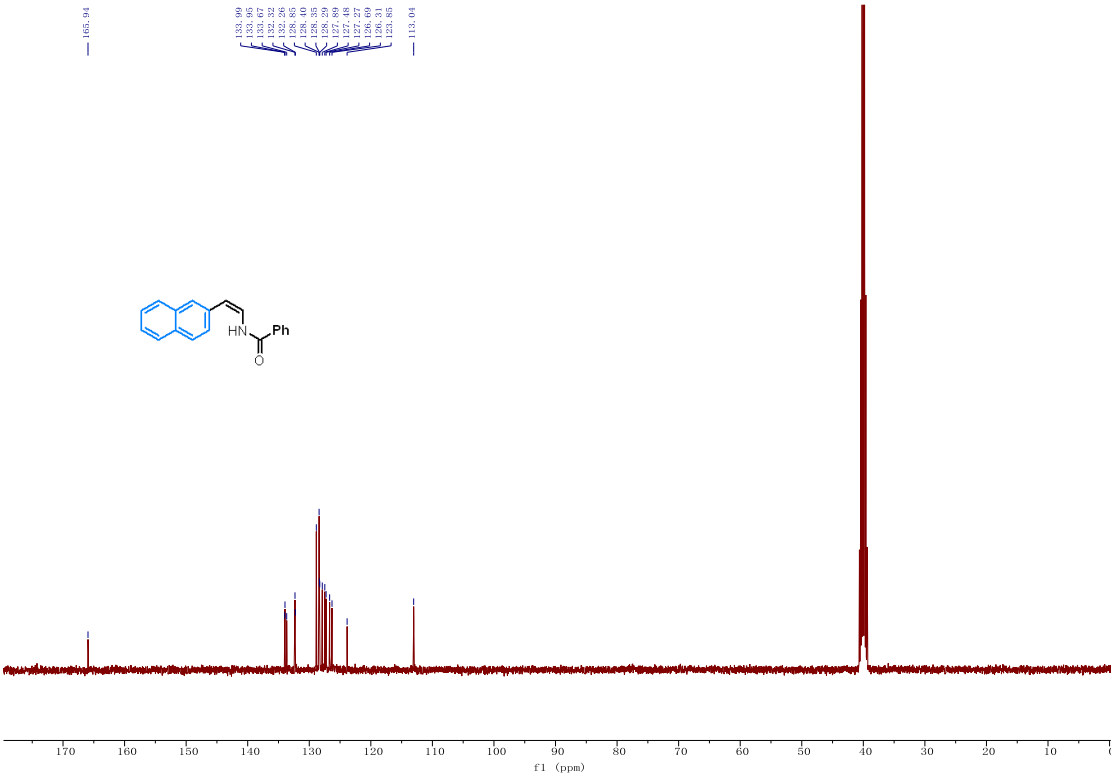

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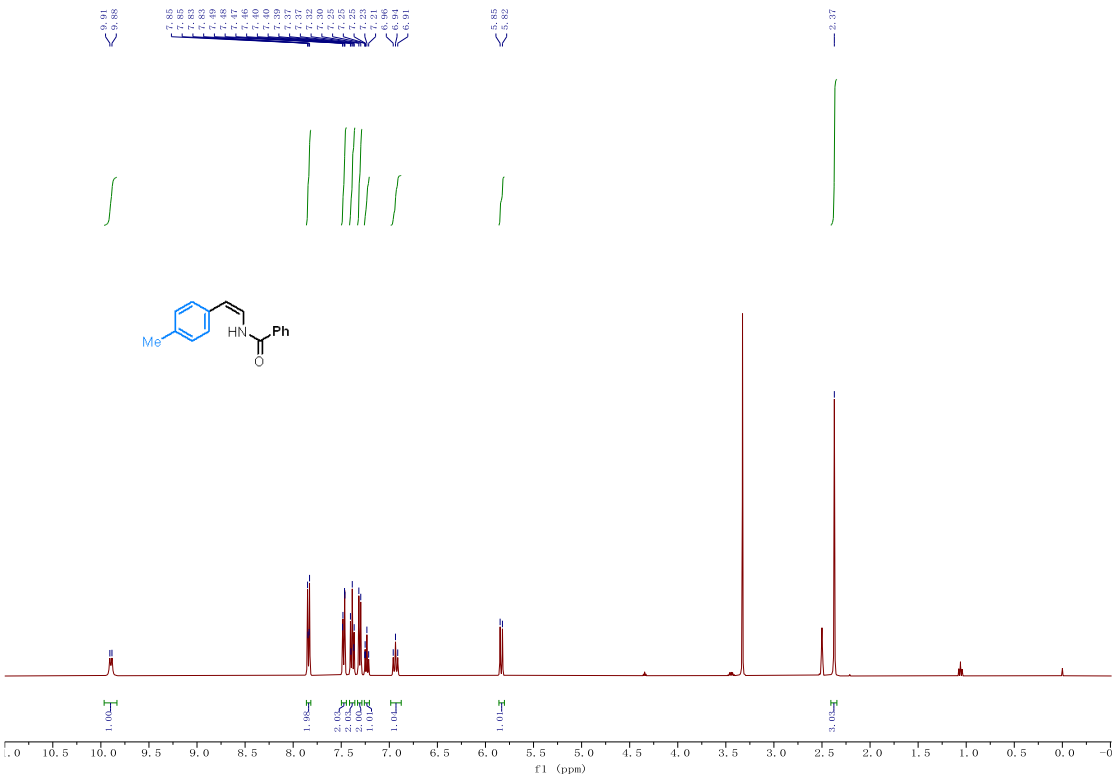

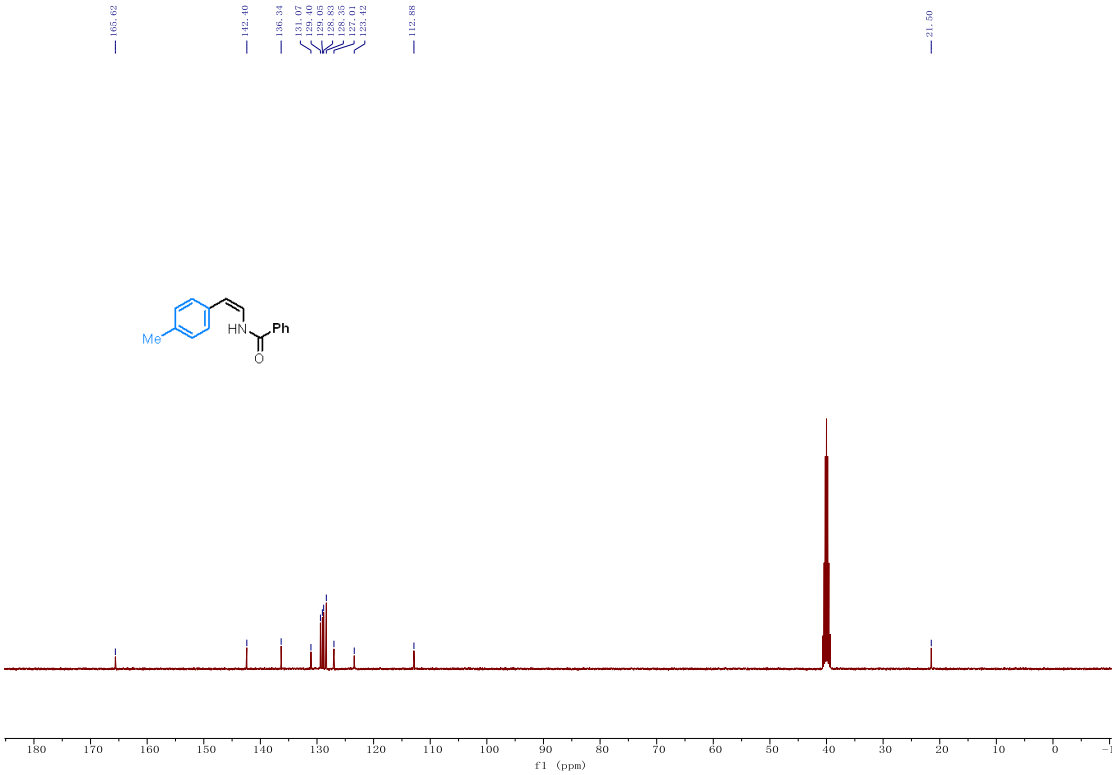

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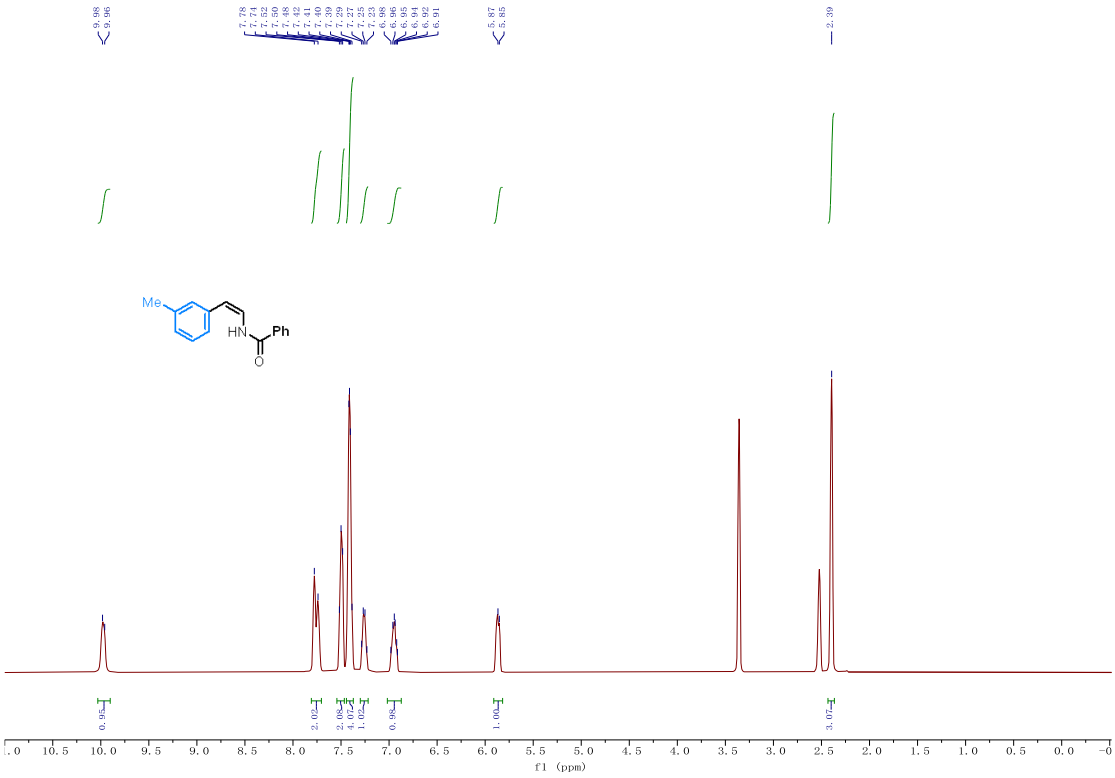
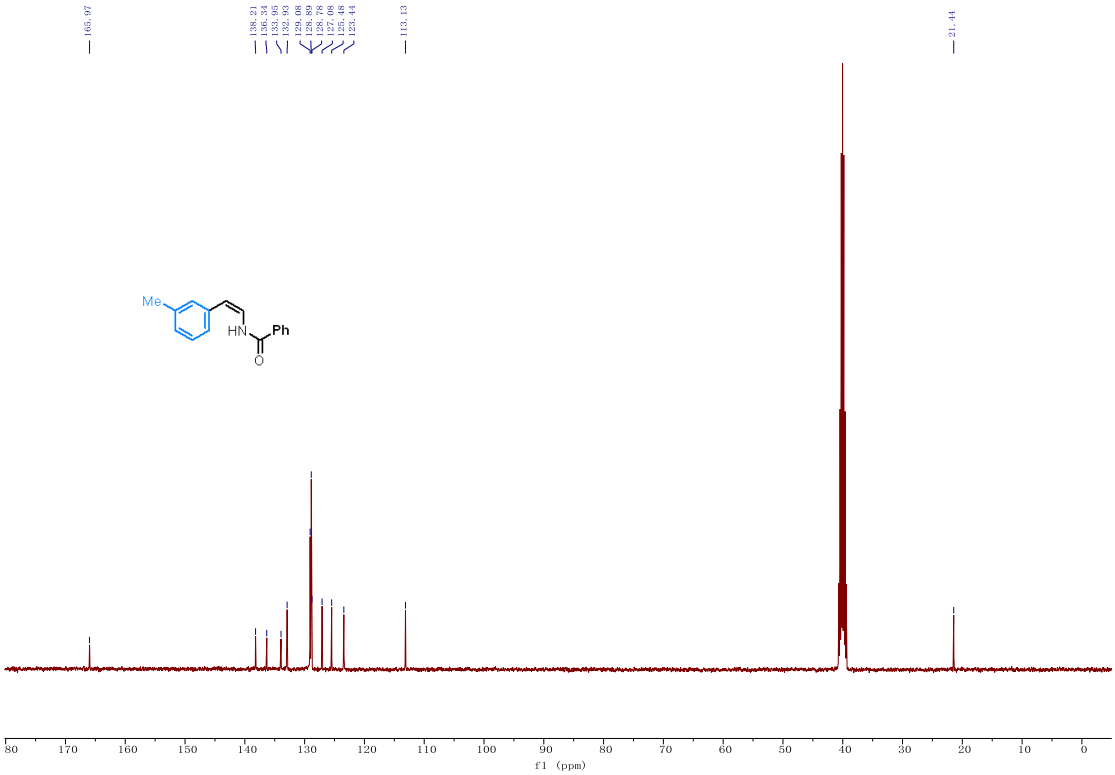
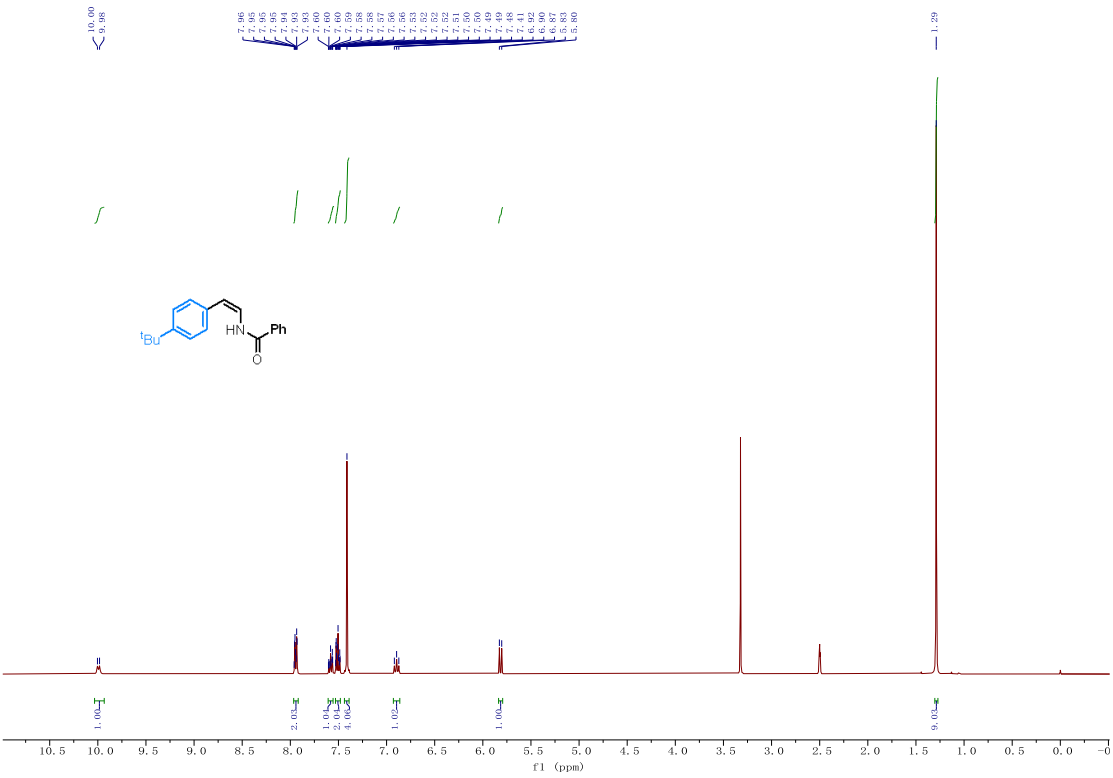
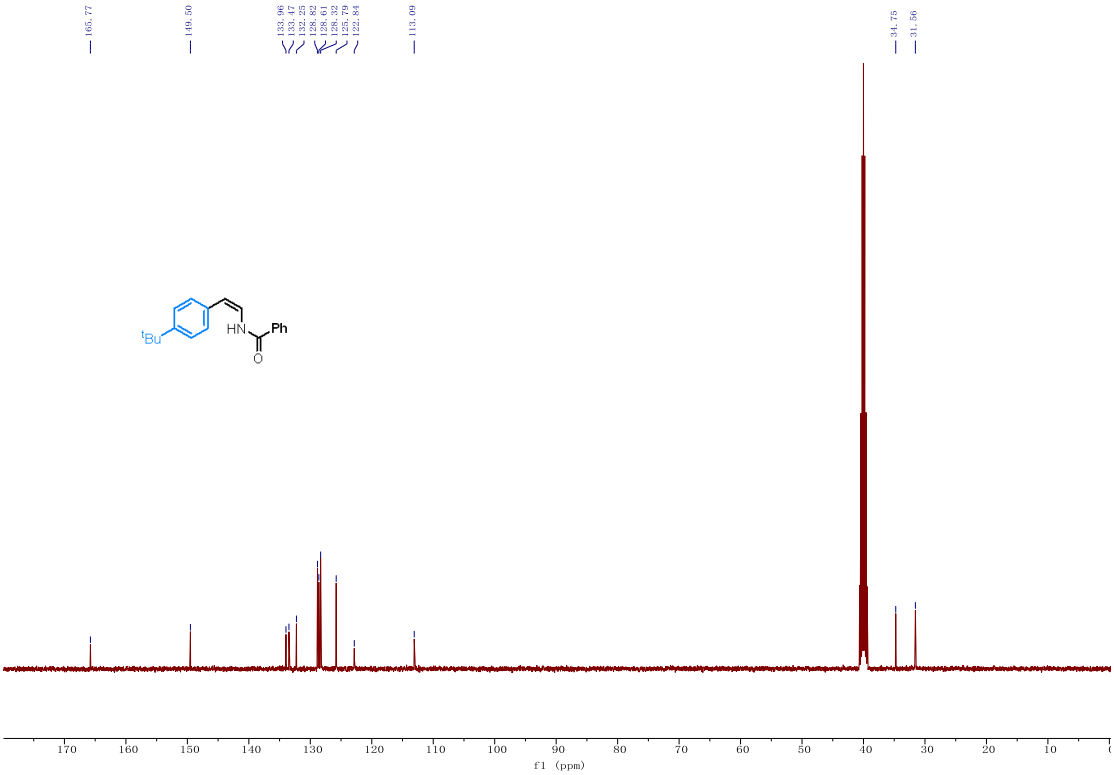


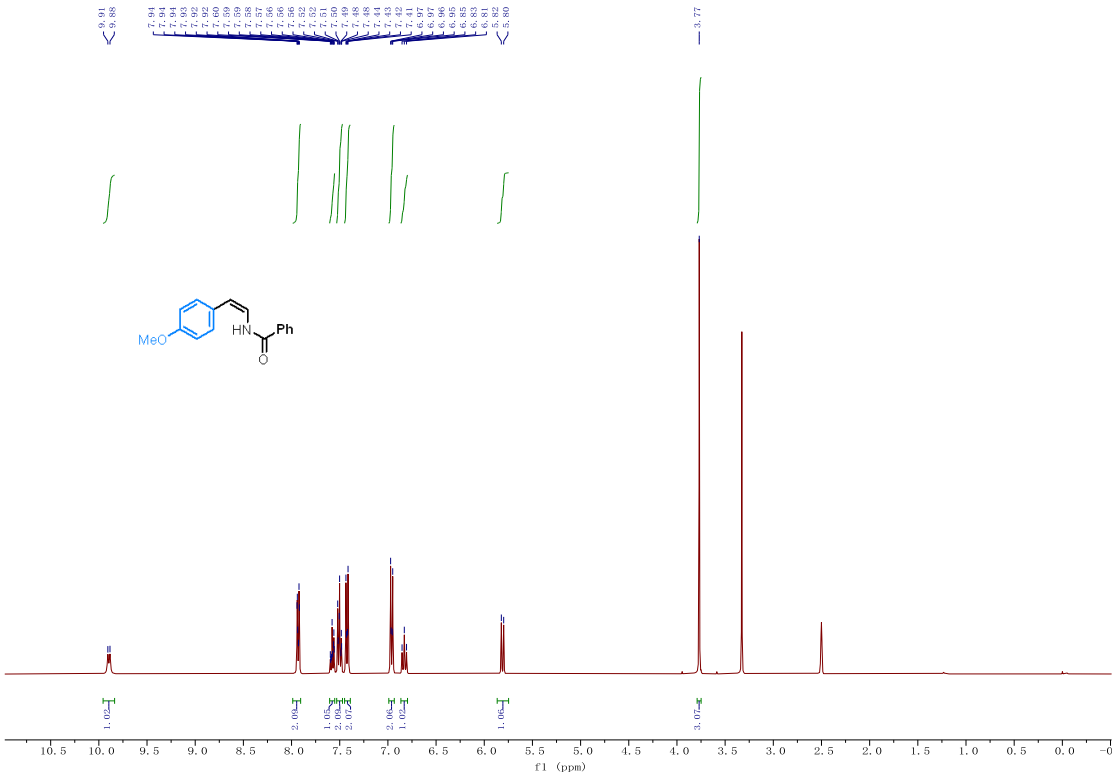


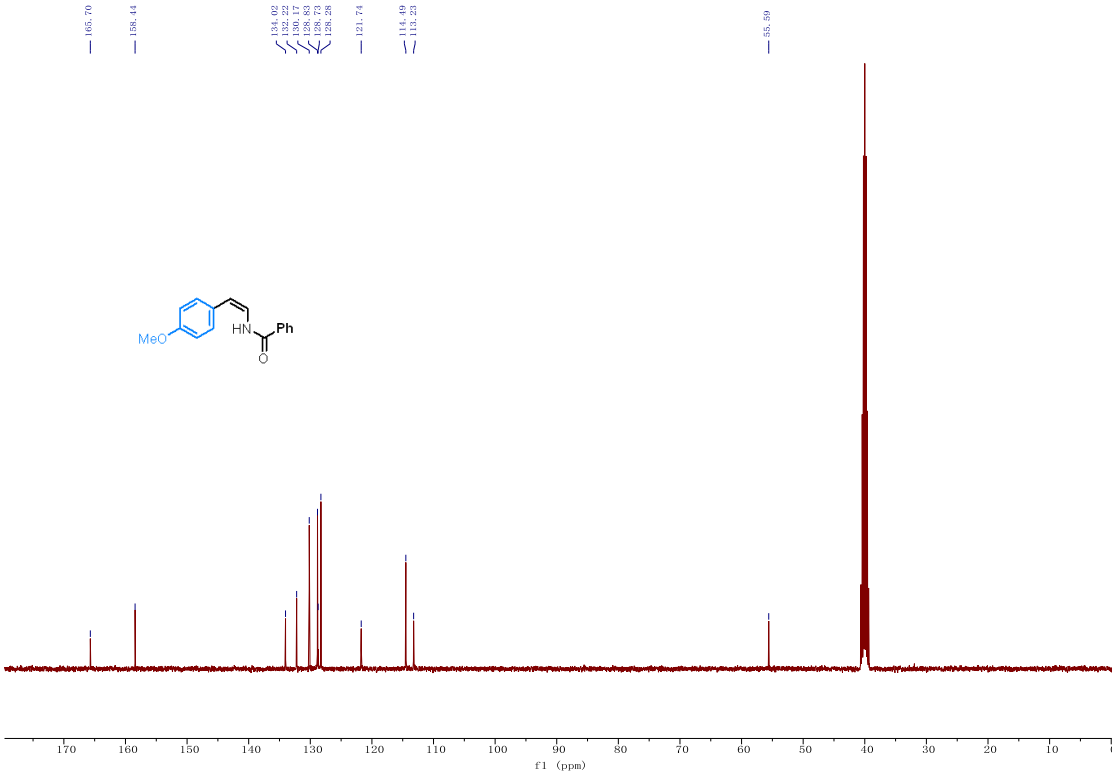
2v, ^{1}H NMR (400 MHz, DMSO-d_6); ^{13}C NMR (101 MHz, DMSO-d_6)



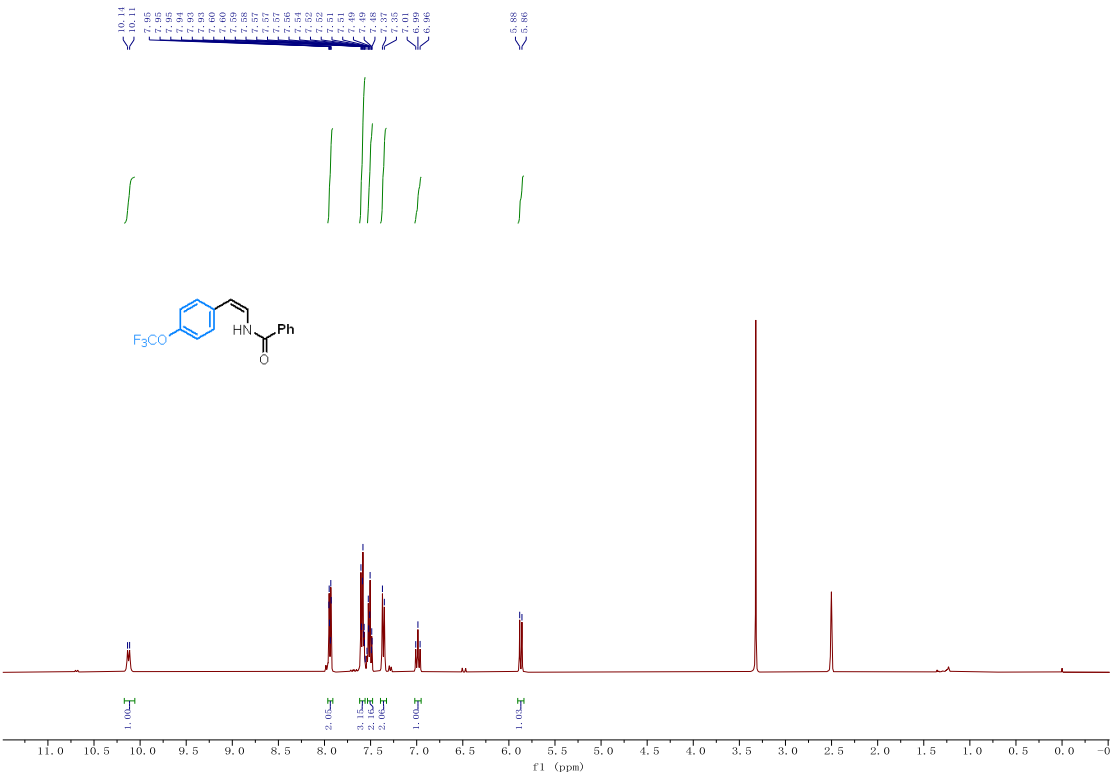


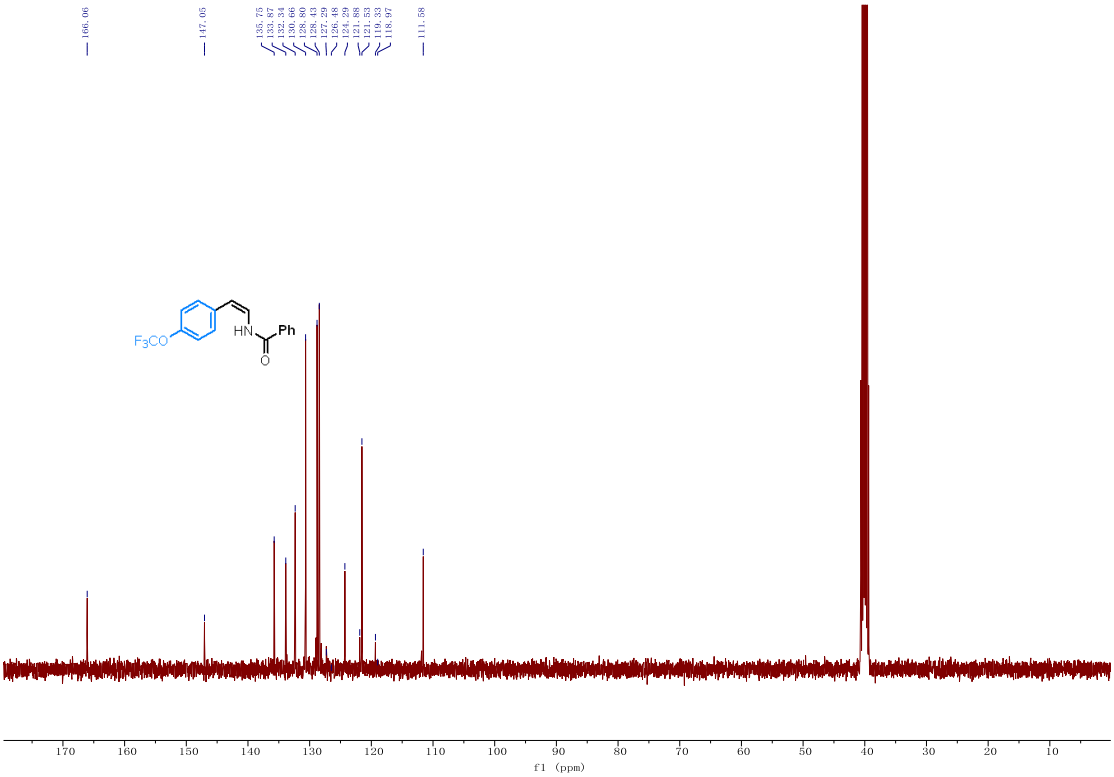
2w, ^{1}H NMR (400 MHz, DMSO-d_6); ^{13}C NMR (101 MHz, DMSO-d_6)



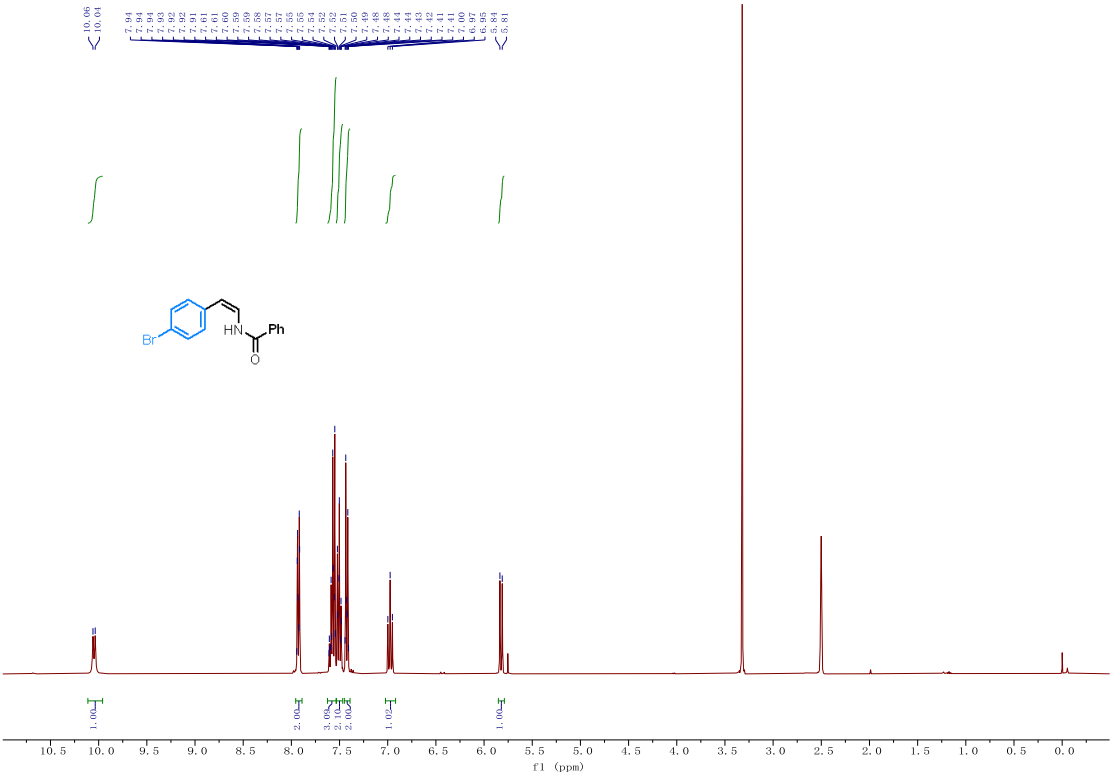


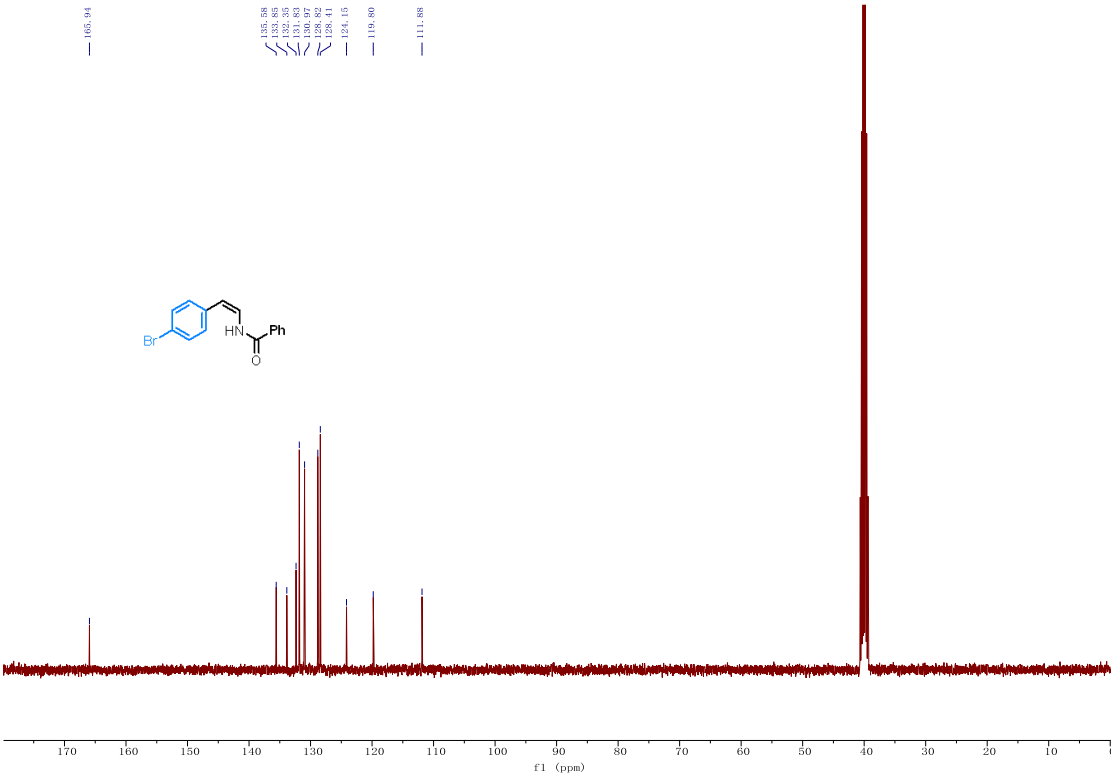
2x, ^{1}H NMR (400 MHz, DMSO-d_6); ^{13}C NMR (101 MHz, DMSO-d_6)



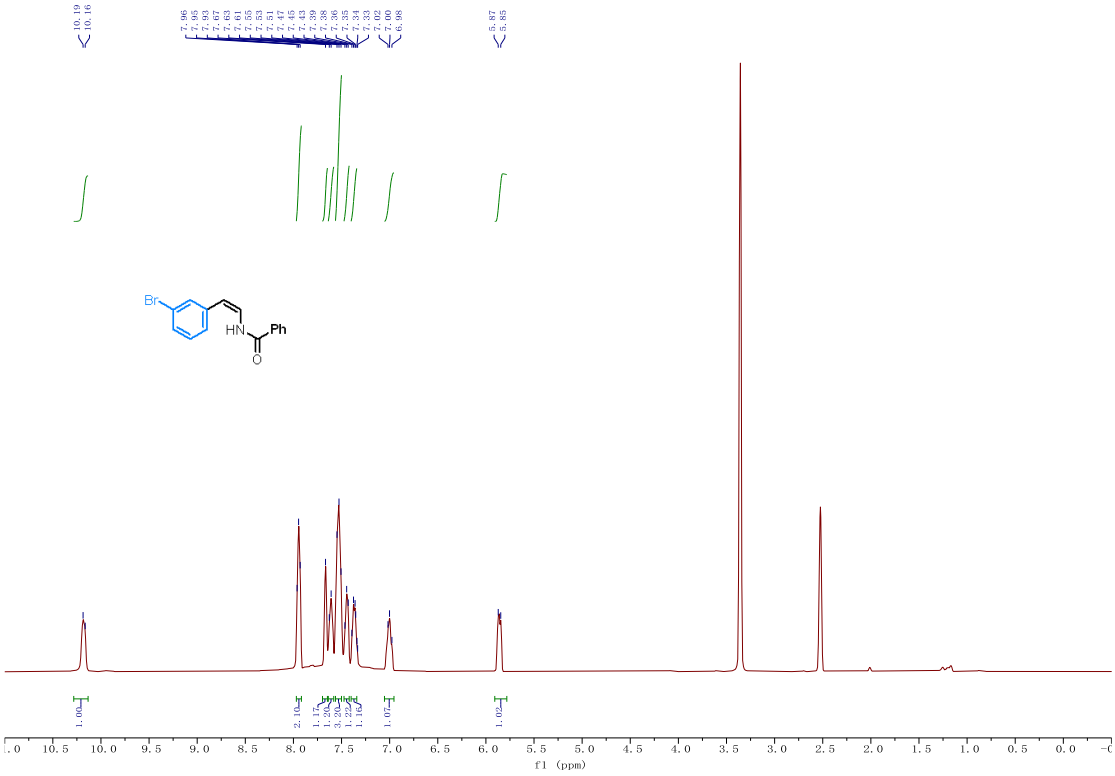


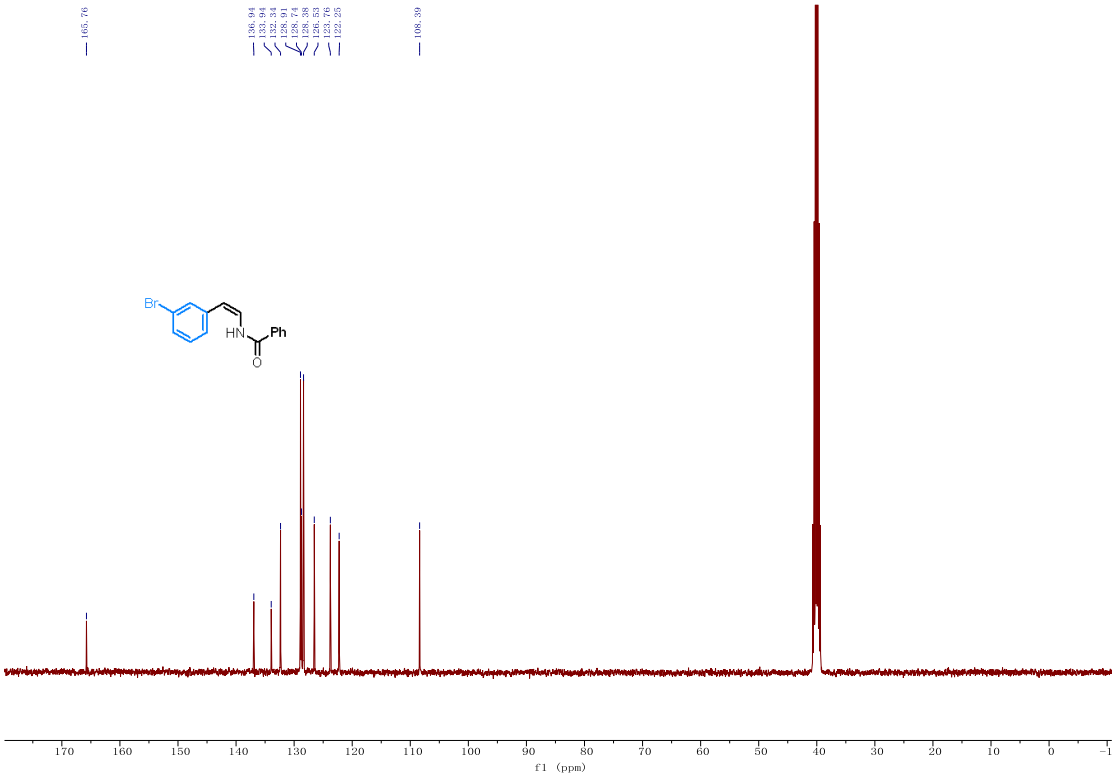
2y, ^{1}H NMR (400 MHz, DMSO-d_6); ^{13}C NMR (101 MHz, DMSO-d_6)



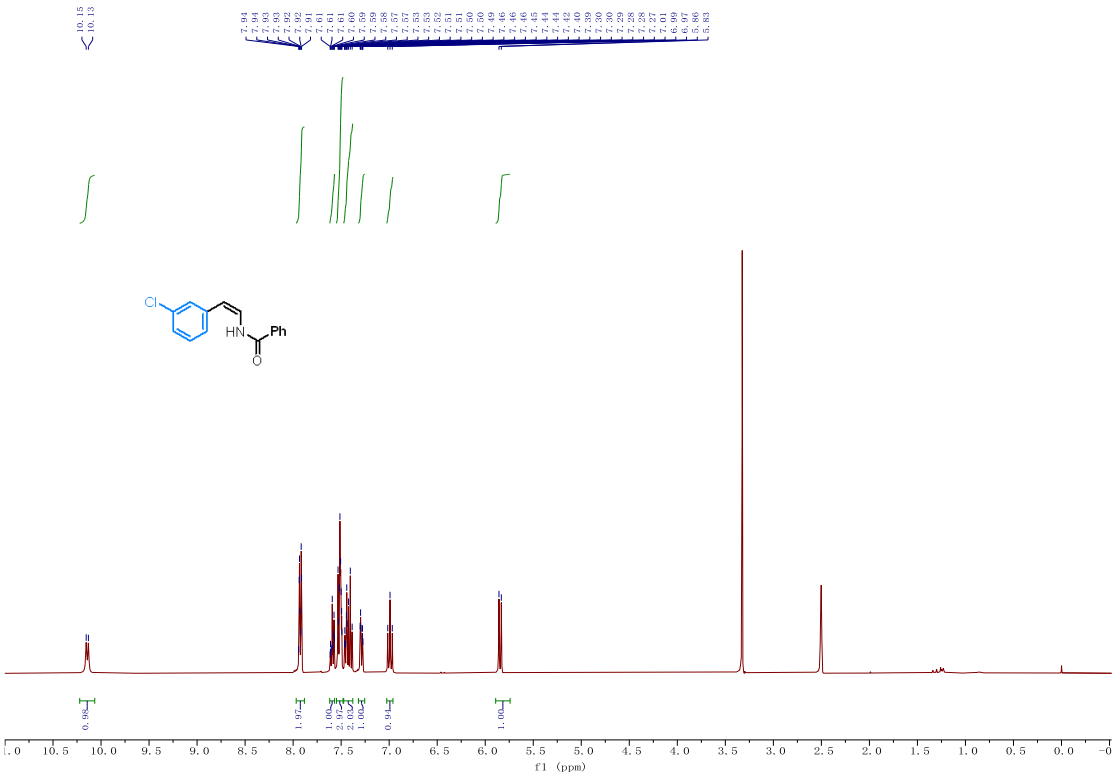


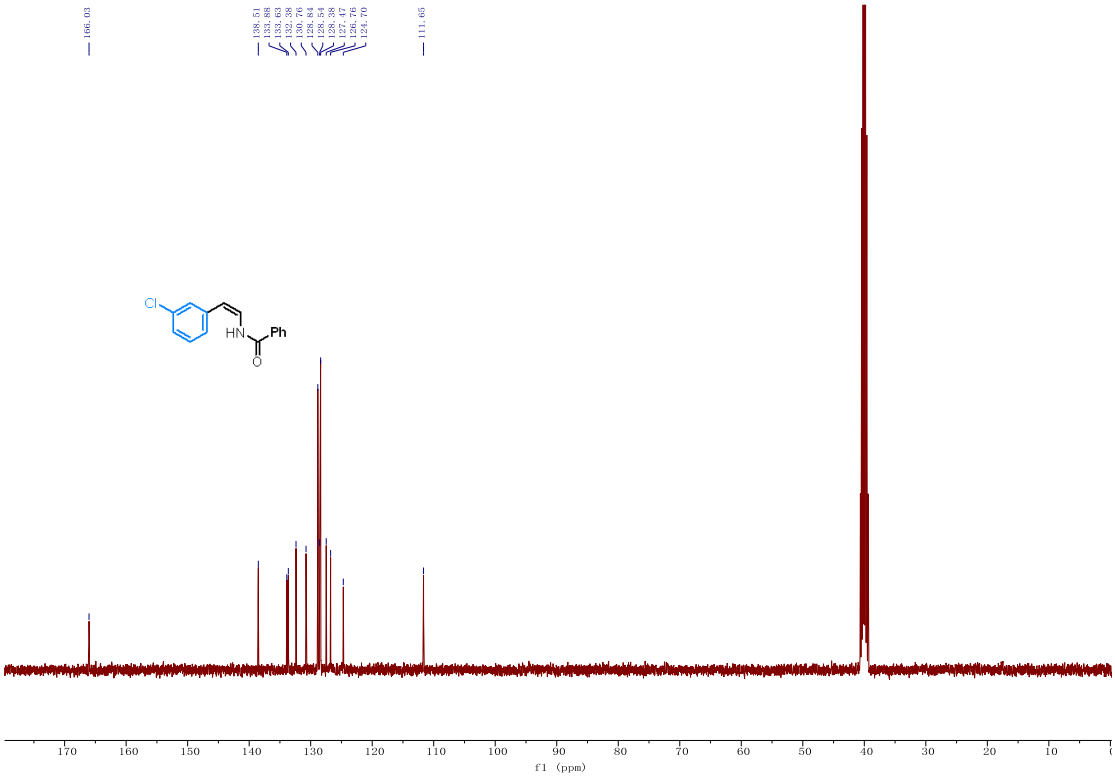
2z, ^{1}H NMR (400 MHz, DMSO-d_6); ^{13}C NMR (101 MHz, DMSO-d_6)



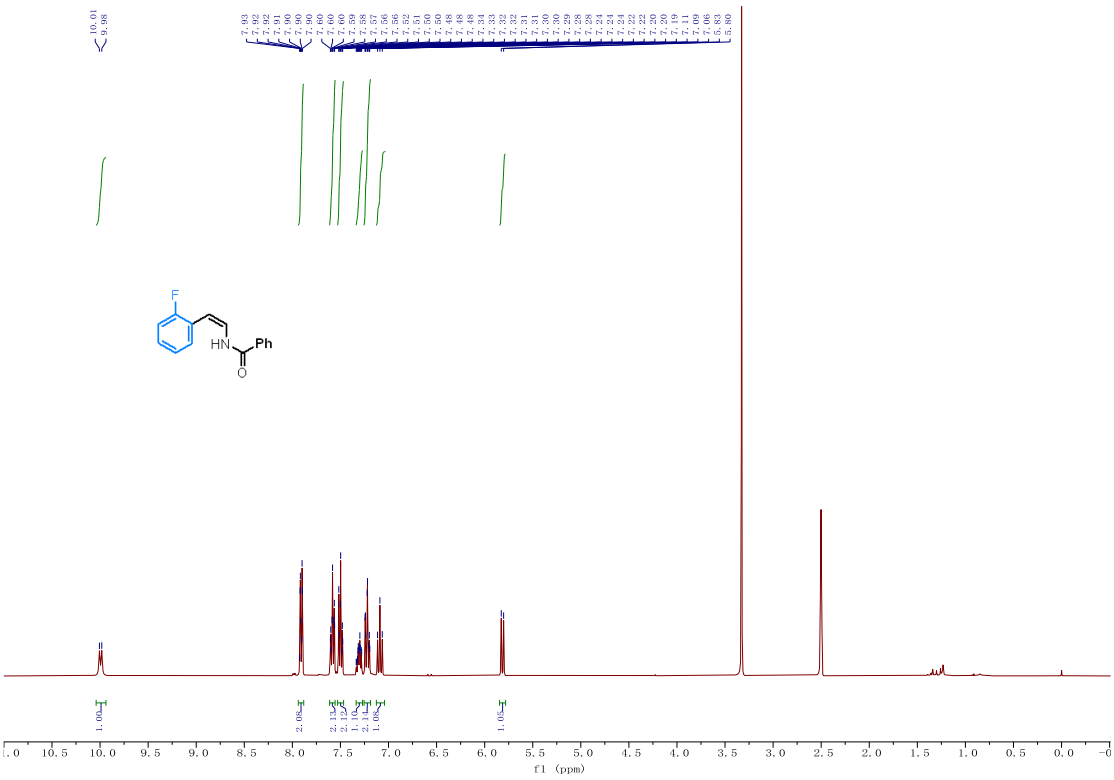


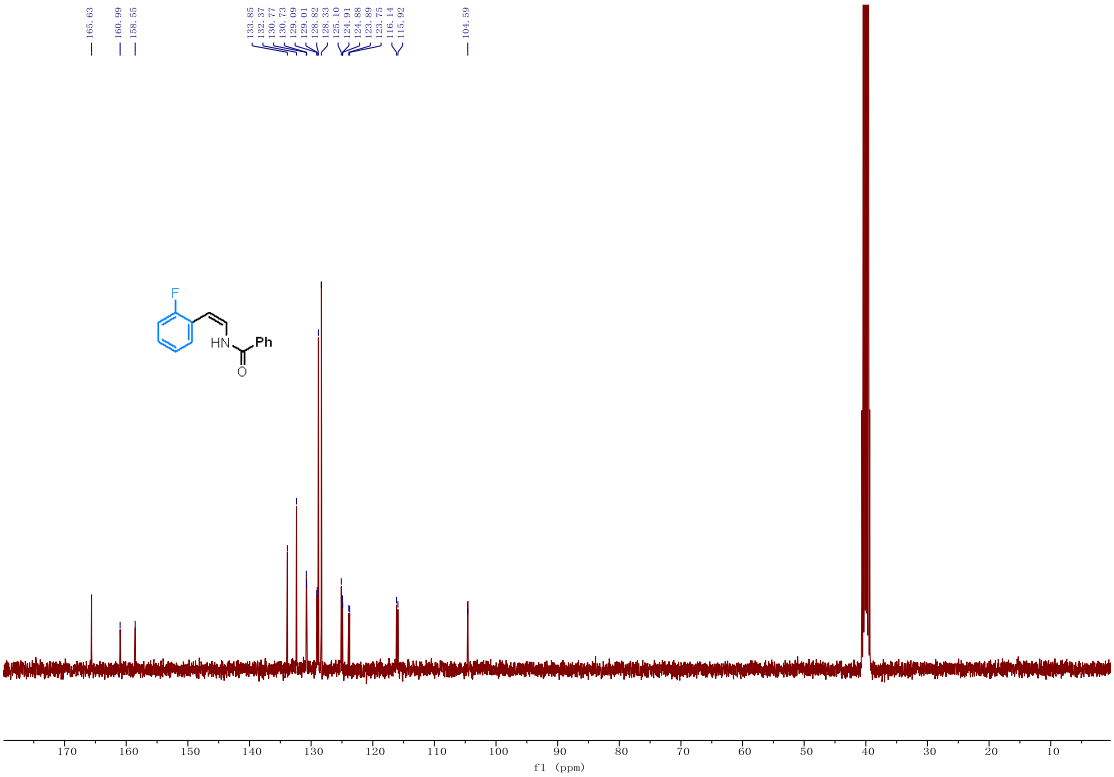
2aa, ^{1}H NMR (400 MHz, DMSO-d_6); ^{13}C NMR (101 MHz, DMSO-d_6)



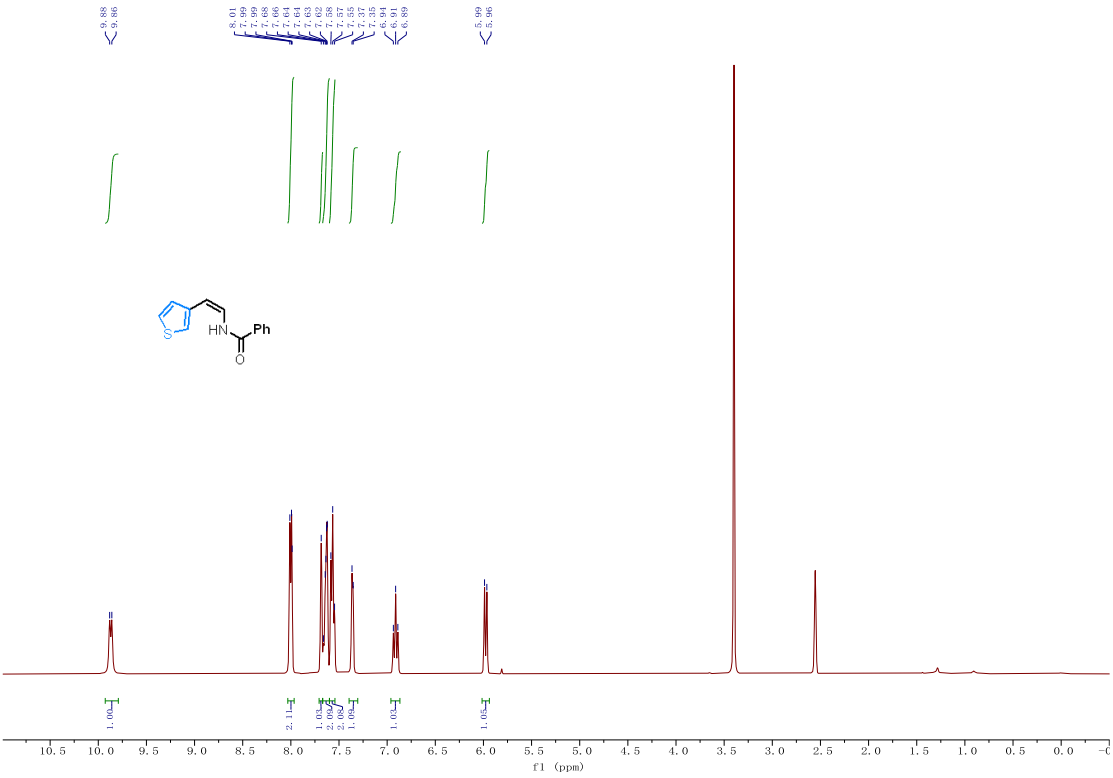


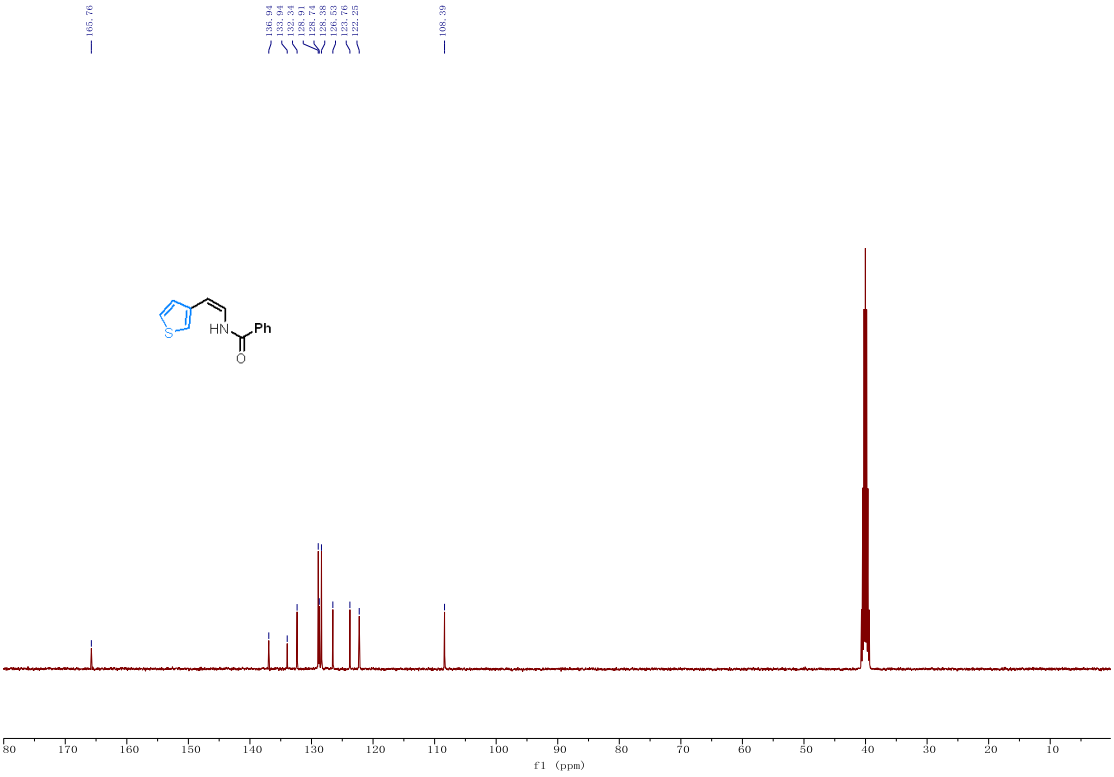
2ab, ^{1}H NMR (400 MHz, DMSO-d_6); ^{13}C NMR (101 MHz, DMSO-d_6)



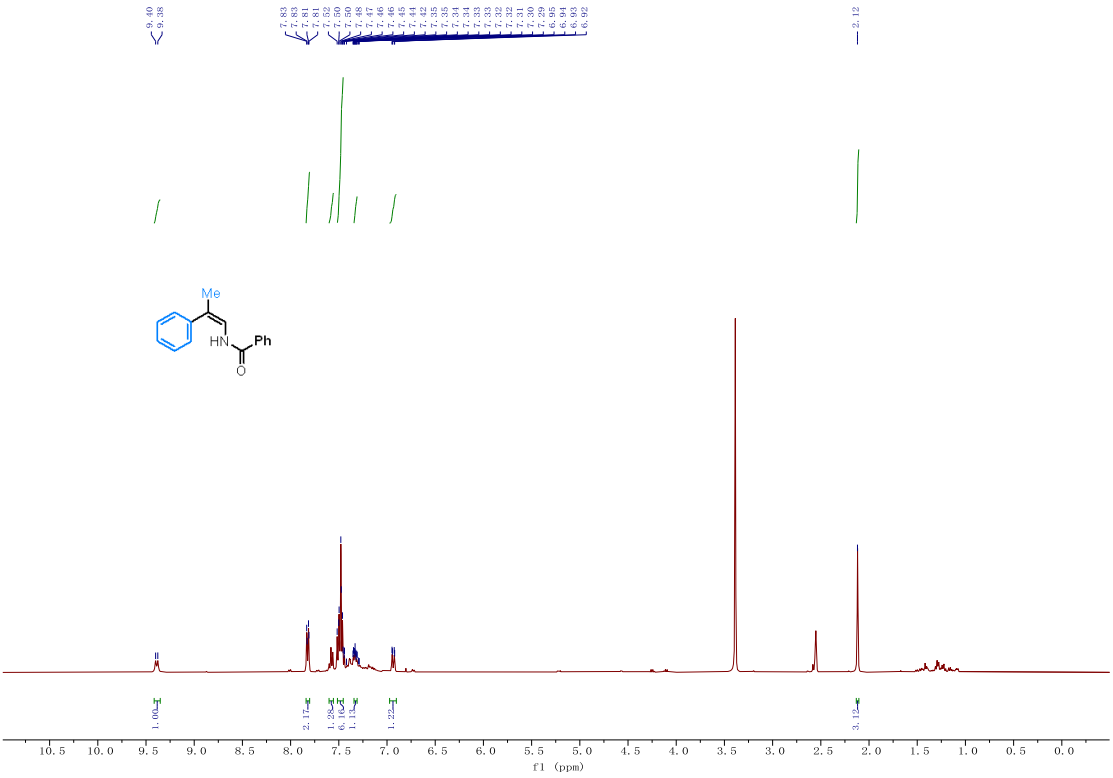


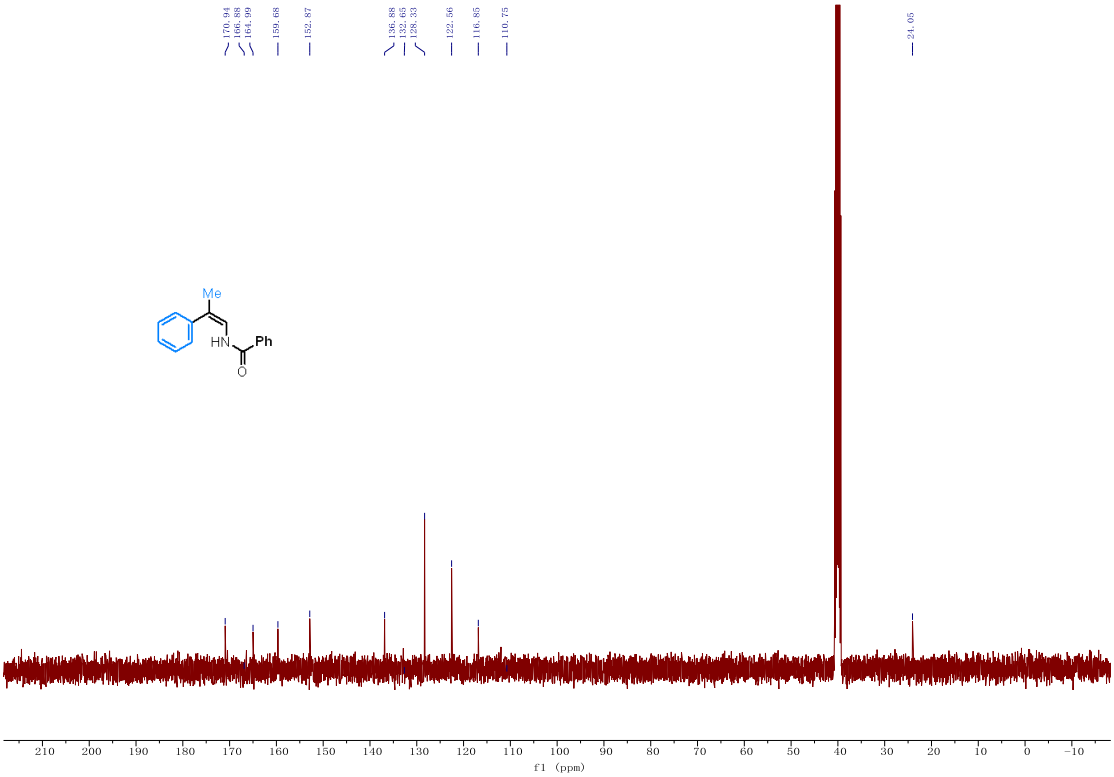
2ac, ^{1}H NMR (400 MHz, DMSO-d_6); ^{13}C NMR (101 MHz, DMSO-d_6)



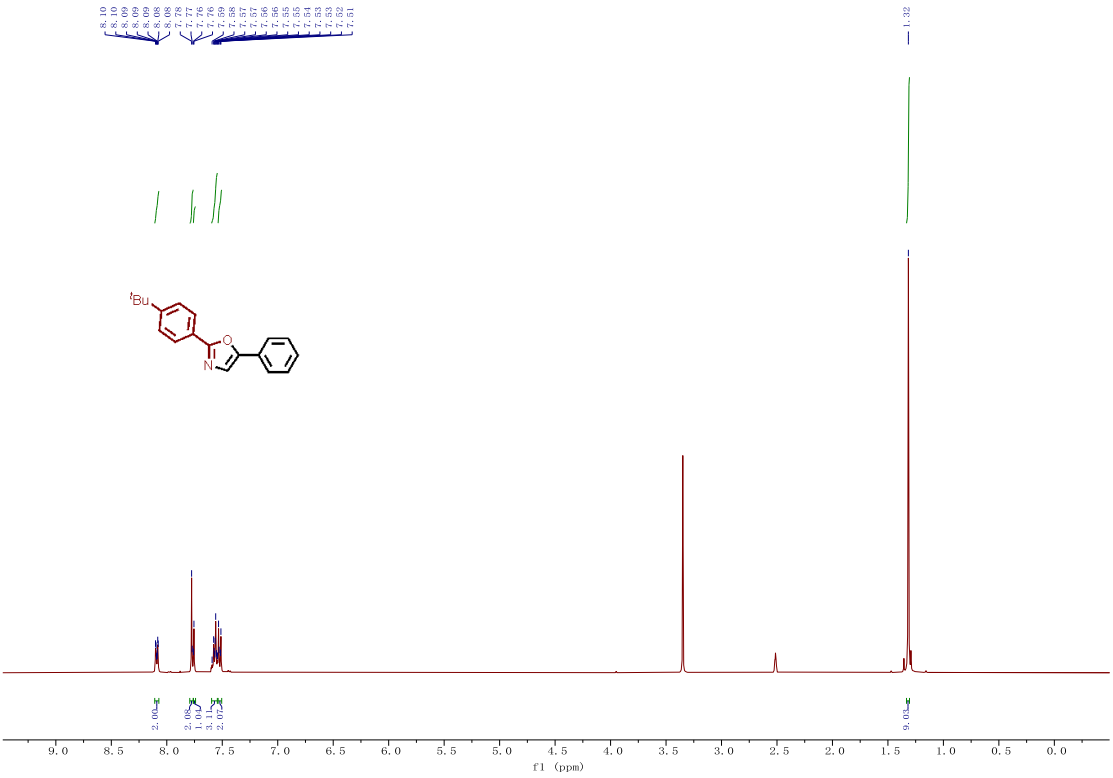


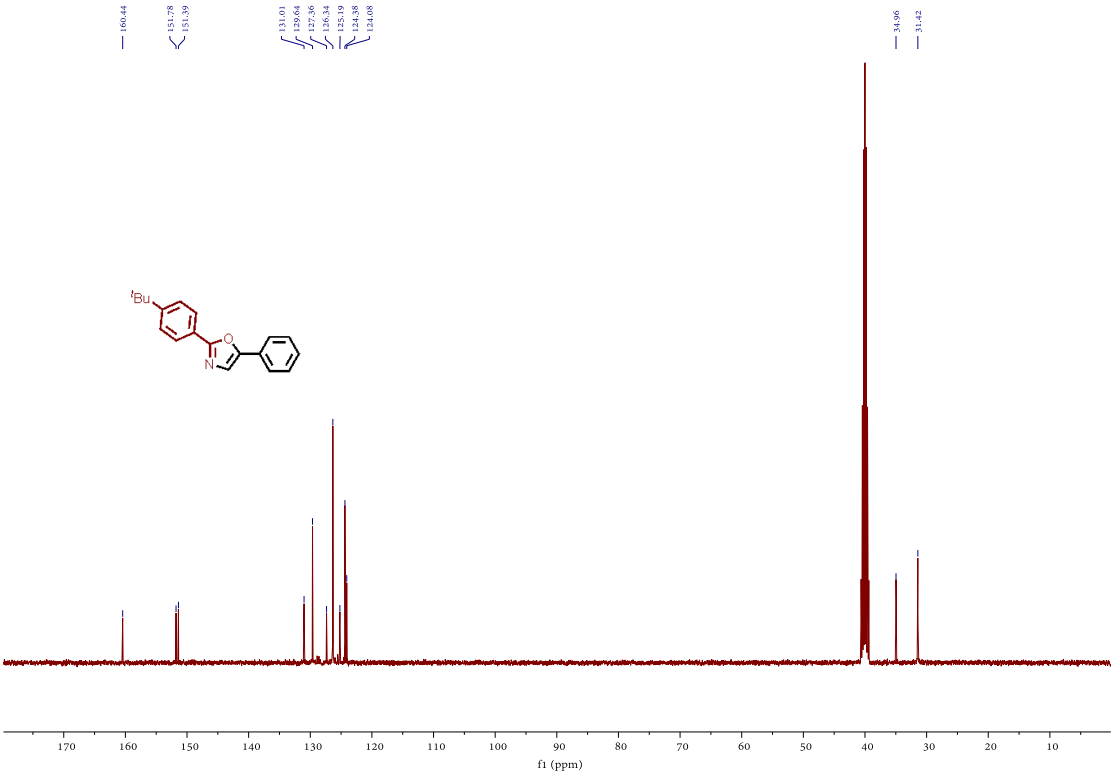
2ad, ^{1}H NMR (400 MHz, DMSO-d_6); ^{13}C NMR (101 MHz, DMSO-d_6)



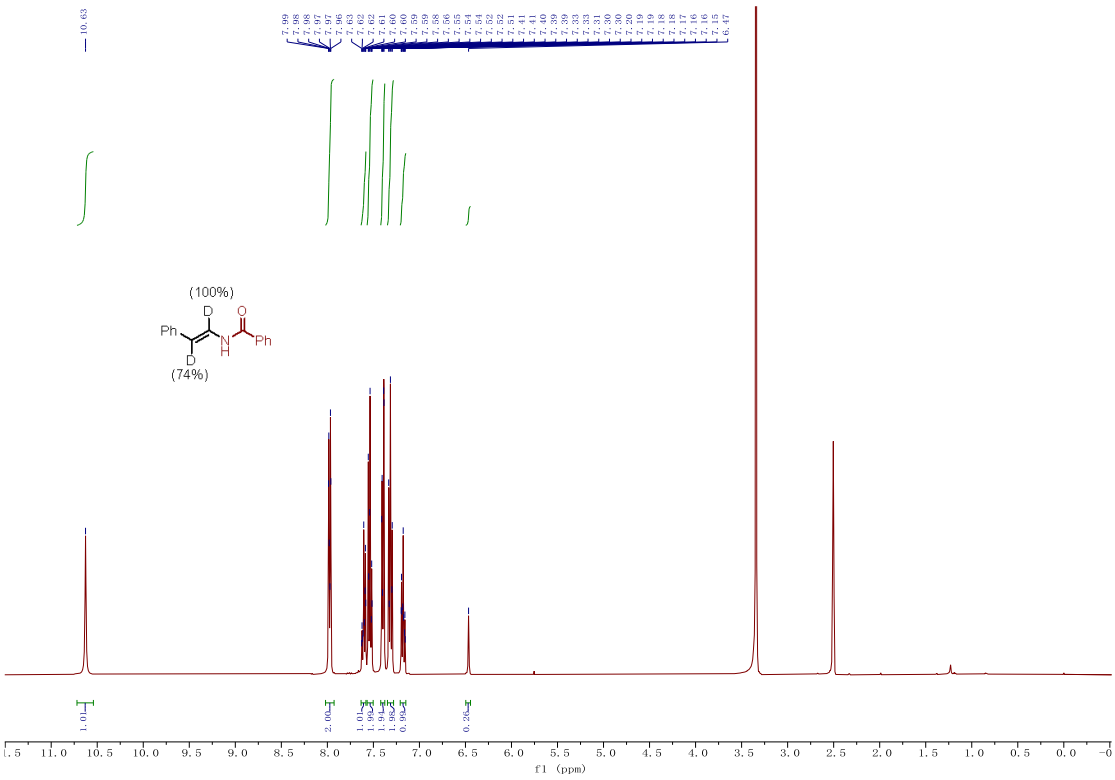


3, ^{1}H NMR (400 MHz, DMSO-d_6); ^{13}C NMR (101 MHz, DMSO-d_6)





D-1a, ^{1}H NMR (400 MHz, DMSO-d_6)



D-2a, ^{1}H NMR (400 MHz, DMSO-d_6)