Supporting Information

Convergent synthesis of triarylamines via Ni-catalyzed dual C(sp^2)-H amination from benzamides with benzohydroxamic acids

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Supporting Information Placeholder

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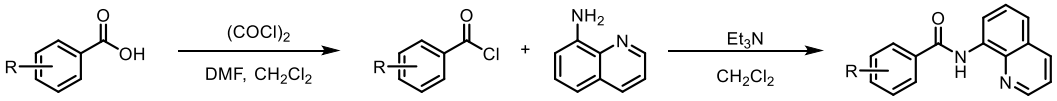
1. General Information

All chemicals were obtained from commercial sources and were used as received without any purification. *N*-(quinolin-8-yl)benzamides and *N*-hydroxybenzamides were synthesized according to the relevant references.[1-9] ^{1}H NMR and ^{13}C NMR spectra were measured on a 500 MHz or 400 MHz Bruker spectrometer, using $CDCl_3$ as the solvent with tetramethylsilane (TMS) as the internal standard at room temperature. Chemical shifts are given δ relative to tetramethylsilane, and the coupling constants J are given in hertz. The multiplicities are reported as follows: singlet (s), doublet (d), triplet (t), doublet of doublets (dd), and multiplet (m). High-resolution mass spectra (HRMS) were recorded on an electrospray ionization (ESI-TOF) quadrupole time-of-flight mass spectrometer. Analytical thin-layer chromatography (TLC) was performed on pre-coated, and glass-backed silica gel plates flash column chromatography was performed over silica gel (300-400 mesh) using ethyl acetate (EA)/petroleum ether (PE) as eluent.

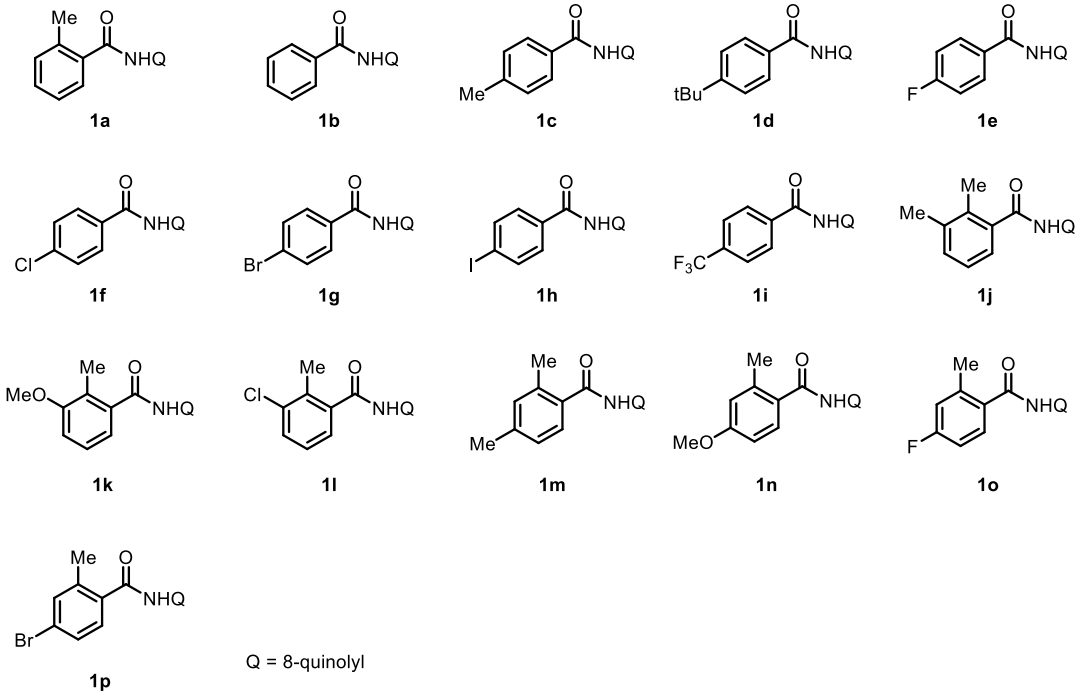
2. Experimental Section

2.1. General procedure for the preparation of benzamide derivatives (1).

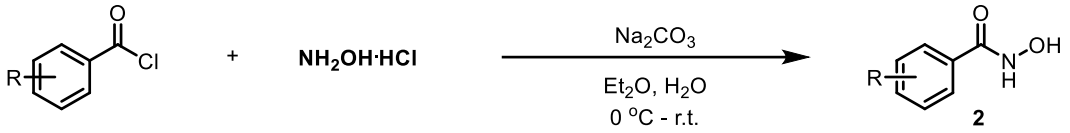


N-(quinolin-8-yl)benzamides were prepared according to the reported methods[1-7]: To a stirred solution of a carboxylic acid (15 mmol) and DMF (5 drops) in CH_2Cl_2 (10 mL), and $(COCl)_2$ (1.5 mL, 18 mmol) was added dropwise. The solution was stirred at room temperature for 2 h. The solvent was then removed by evaporation under reduced pressure, and the resulting residue was dissolved in CH_2Cl_2 (15 mL). After cooling the reaction mixture to 0 °C, a solution of 8-aminoquinoline (17 mmol) and triethylamine (30 mmol) in 10 mL of the same solvent was added dropwise. The resulting mixture was allowed to warm to room temperature and stirred overnight. The solution containing the crude product was washed with saturated aqueous $NaHCO_3$ (20 mL), and CH_2Cl_2 (3×20 mL) separately. The combined organic phase was washed with 1 M HCl aq. (20 mL). The organic phase was dried over anhydrous Na_2SO_4 and the solvent

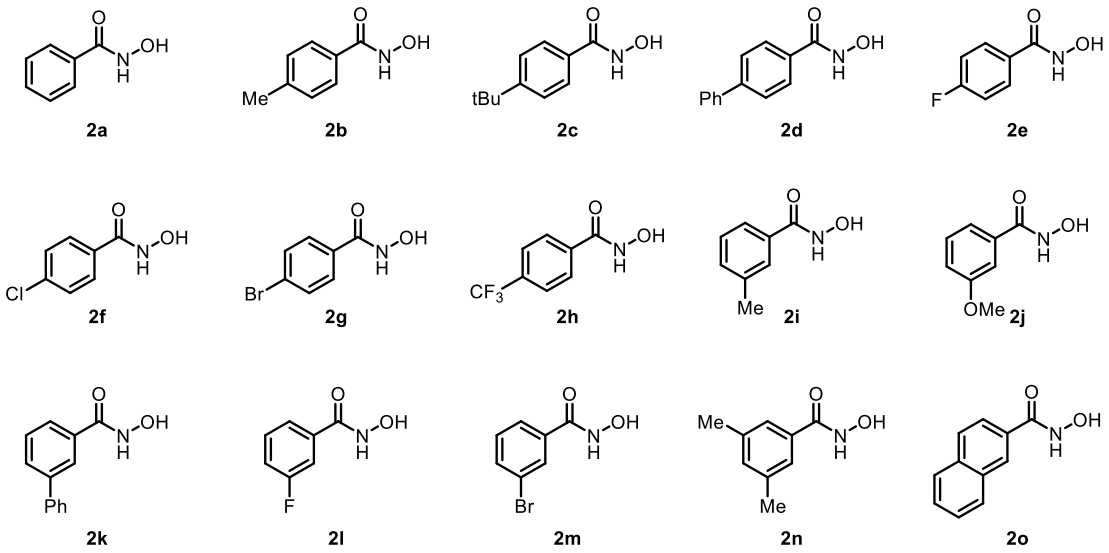
was removed by evaporation. The resulting crude amide was purified by flash chromatography on silica gel (eluent: PE/EtOAc = 5/1) to give the corresponding *N*-(quinolin-8-yl)benzamides (**1a-1p**).



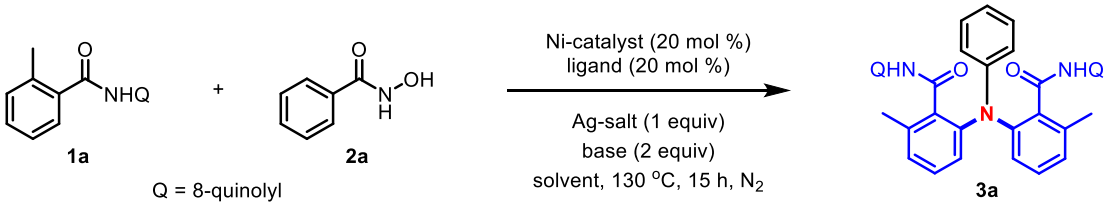
2.2. General procedure for the preparation of benzohydroxamic acids (2).



Benzohydroxamic acids were prepared according to a modified literature method[8]: A solution of Na_2CO_3 (2.12 g, 20 mmol) in H_2O (3 mL) was added to a stirred solution of $NH_2OH{\cdot}HCl$ (1.39 g, 20 mol) in Et_2O (20 mL). After stirring for additional 30 minutes at room temperature, benzoyl chloride (2.32 mL, 20 mol) in Et_2O (10 mL) was added dropwise at 0 ℃ and stirring was continued at the same temperature for another 1.0 h. After slowly warming to room temperature, the precipitated white solid was isolated through filtration and poured into EtOAc (100 mL). The resulting suspension was then heated to reflux for an additional 10 min. The undissolved base was removed through hot filtration at 70 ℃ and the filtrate was cooled and concentrated under reduced pressure to give the crude product as a white solid (**2a**-**2o**).



2.3. Table S1. Optimization of reaction conditions[a,b]

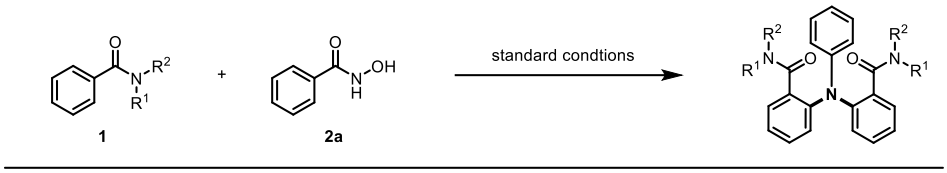


entry	catalyst	ligand	base	additive	solvent	yield(%)[b]
1	$Ni(acac)_2$	PPh_3	AdCOOK	Ag_3PO_4	DMAc	30
2	$Ni(OTf)_2$	PPh_3	AdCOOK	Ag_3PO_4	DMAc	48
3	$Ni(OAc)_2{\cdot}4H_2O$	PPh_3	AdCOOK	Ag_3PO_4	DMAc	57
4	$Ni(OAc)_2{\cdot}4H_2O$	PPh_3	AdCOOK	Ag_3PO_4	DMSO	42
5	$Ni(OAc)_2{\cdot}4H_2O$	PPh_3	AdCOOK	Ag_3PO_4	DMF	35
6	$Ni(OAc)_2{\cdot}4H_2O$	PPh_3	AdCOOK	Ag_3PO_4	NMP	33
7	$Ni(OAc)_2{\cdot}4H_2O$	PPh_3	AdCOOK	Ag_2CO_3	DMAc	trace
8	$Ni(OAc)_2{\cdot}4H_2O$	PPh_3	AdCOOK	Ag_2SO_4	DMAc	44
9	$Ni(OAc)_2{\cdot}4H_2O$	PPh_3	AdCOOK	AgOAc	DMAc	13
10	$Ni(OAc)_2{\cdot}4H_2O$	PPh_3	KOPiv	Ag_3PO_4	DMAc	54
11	$Ni(OAc)_2{\cdot}4H_2O$	PPh_3	CsOPiv	Ag_3PO_4	DMAc	trace
12	$Ni(OAc)_2{\cdot}4H_2O$	PPh_3	NaOPiv	Ag_3PO_4	DMAc	38
13	$Ni(OAc)_2{\cdot}4H_2O$	PPh_3	*t*BuOK	Ag_3PO_4	DMAc	trace
14	$Ni(OAc)_2{\cdot}4H_2O$	dppb	AdCOOK	Ag_3PO_4	DMAc	28
15	$Ni(OAc)_2{\cdot}4H_2O$	dppe	AdCOOK	Ag_3PO_4	DMAc	55
16	$Ni(OAc)_2{\cdot}4H_2O$	Cy_3P	AdCOOK	Ag_3PO_4	DMAc	46
17	$Ni(OAc)_2{\cdot}4H_2O$	Ph_2MeP	AdCOOK	Ag_3PO_4	DMAc	35
18	**$Ni(OAc)_2{\cdot}4H_2O$**	**dppm**	**AdCOOK**	**Ag_3PO_4**	**DMAc**	**70**
19	$Ni(OAc)_2{\cdot}4H_2O$	--	AdCOOK	Ag_3PO_4	DMAc	48
20	--	dppm	AdCOOK	Ag_3PO_4	DMAc	nd

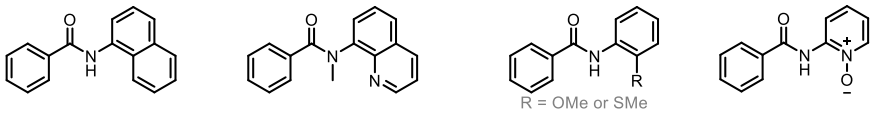
21	$Ni(OAc)_2{\cdot}4H_2O$	dppm	--	Ag_3PO_4	DMAc	trace
22	$Ni(OAc)_2{\cdot}4H_2O$	dppm	AdCOOK	--	DMAc	trace
23	$Pd(TFA)_2$	dppm	AdCOOK	Ag_3PO_4	DMAc	nd
24	$Cu(OAc)_2$	dppm	AdCOOK	Ag_3PO_4	DMAc	nd
25	$Co(OAc)_2$	dppm	AdCOOK	Ag_3PO_4	DMAc	trace

[a]Reaction conditions: **1a** (0.3 mmol), **2a** (0.1 mmol), Ni-catalyst (20 mol %), ligand (20 mol %), additive (1 equiv), base (2 equiv), solvent (1 mL), 130 °C, 15 h, N_2. [b]Isolated yields. AdCOOK = potassium amantadate. nd = not detected.

2.4. Table S2. Optimization of benzamide directing groups[a,b]



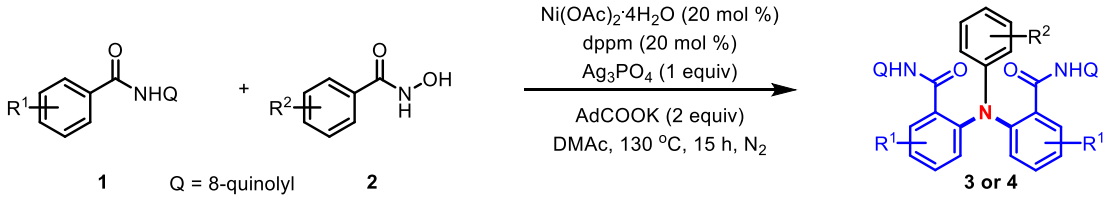
Unsuccessful benzamide derivatives examples:



nr nr nr nr

[a]Reaction conditions: **1** (0.3 mmol), **2a** (0.1 mmol), $Ni(OAc){\cdot}4H_2O$ (20 mol %), dppm (20 mol %), Ag_3PO_4 (1 equiv), AdCOOK (2 equiv), DMAc (1 mL), 130 °C, 15 h, N_2. nr = no reaction.

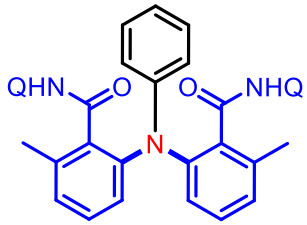
2.5. General procedure for the synthesis of triarylamines 3 or 4.



In a 10 mL Schlenk reaction tube with a stir bar, *N*-(quinolin-8-yl)benzamide (**1**, 0.3 mmol), *N*-hydroxybenzamide (**2**, 0.1 mmol), $Ni(OAc)_2{\cdot}4H_2O$ (0.04 mmol, 10 mg), dppm (0.04 mmol, 15.6 mg), Ag_3PO_4 (0.2 mmol, 84 mg), AdCOOK (0.4 mmol, 87.2 mg) were dissolved in DMAc (1 mL). The reaction mixture was charged with nitrogen three times, then heated at 130 °C (oil bath) with vigorous stirring for 15 h under an N_2 atmosphere. After the reaction equilibrium, the mixture was extracted with ethyl acetate, and the combined organic layers were dried over anhydrous Na_2SO_4. The filtrate was concentrated in vacuo and purified by a silica gel packed flash chromatography with petroleum ether/ethyl acetate (5:1) as eluent to afford the targeted product **3** or **4**.

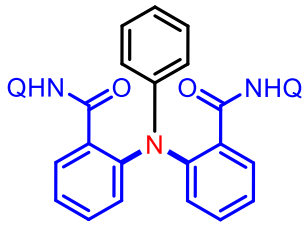
3. Analytical Data for All Products

6,6'-(phenylazanediyl)bis(2-methyl-*N*-(quinolin-8-yl)benzamide) (3a):



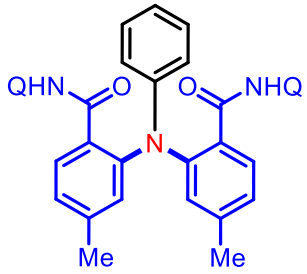
White solid (43.0 mg, 70%); mp: 213-214 °C. Column chromatography on silica gel (Eluent: petroleum ether/ethyl acetate, 5/1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.95 (s, 2H), 8.71 (s, 2H), 8.53 (d, *J* = 6.5 Hz, 2H), 8.10 (d, *J* = 8.0 Hz, 2H), 7.44 (d, *J* = 6.5 Hz, 4H), 7.39-7.36 (m, 2H), 7.03-6.98 (m, 4H), 6.91 (d, *J* = 8.0 Hz, 2H), 6.76 (t, *J* = 8.0 Hz, 2H), 6.69 (t, *J* = 6.5 Hz, 1H), 6.50 (d, *J* = 7.0 Hz, 2H), 2.21 (s, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 166.8, 148.6, 148.0, 144.4, 138.5, 136.6, 136.1, 134.6, 134.6, 129.5, 128.7, 127.7, 127.1, 126.1, 125.7, 123.4, 121.9, 121.4, 116.7, 19.6. **HRMS (ESI-TOF)** m/z: $[M + H]^+$ Calcd for $C_{40}H_{32}N_5O_2$ 614.2551; Found 614.2562.

2,2'-(phenylazanediyl)bis(*N*-(quinolin-8-yl)benzamide) (3b):



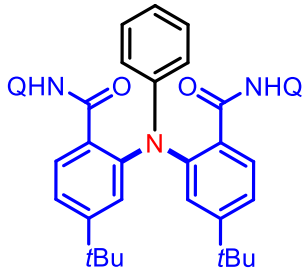
White solid (28.1 mg, 48%); mp: 239-240 °C. Column chromatography on silica gel (Eluent: petroleum ether/ethyl acetate, 5/1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 10.56 (s, 2H), 8.61 (s, 2H), 8.38 (d, *J* = 7.0 Hz, 2H), 8.08 (d, *J* = 8.0 Hz, 2H), 7.65 (d, *J* = 7.0 Hz, 2H), 7.42-7.36 (m, 8H), 7.28 (d, *J* = 7.0 Hz, 2H), 7.06 (t, *J* = 7.0 Hz, 2H), 6.85 (d, *J* = 7.5 Hz, 2H), 6.76 (t, *J* = 7.5 Hz, 2H), 6.58 (t, *J* = 7.0 Hz, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 166.2, 147.9, 147.6, 145.3, 138.6, 136.1, 134.5, 132.5, 131.2, 130.0, 128.6, 128.0, 127.7, 127.2, 124.2, 123.0, 122.6, 121.4, 121.4, 116.6. **HRMS (ESI-TOF)** m/z: $[M + H]^+$ Calcd for $C_{38}H_{28}N_5O_2$ 586.2238; Found 586.2234.

2,2'-(phenylazanediyl)bis(4-methyl-*N*-(quinolin-8-yl)benzamide) (3c):



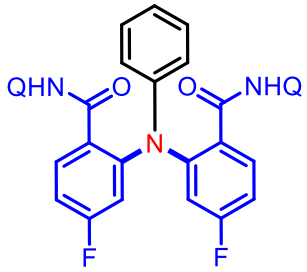
White solid (27.5 mg, 45%); mp: 179-180 °C. Column chromatography on silica gel (Eluent: petroleum ether/ ethyl acetate, 5/1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 10.44 (s, 2H), 8.60 (s, 2H), 8.43 (d, *J* = 7.0 Hz, 2H), 8.09 (d, *J* = 8.0 Hz, 2H), 7.50 (d, *J* = 7.5 Hz, 2H), 7.42-7.37 (m, 6H), 7.05 (s, 2H), 6.94 (d, *J* = 8.0 Hz, 2H), 6.87 (t, *J* = 7.5 Hz, 2H), 6.79 (d, *J* = 7.5 Hz, 2H), 6.67 (t, *J* = 7.0 Hz, 1H), 1.99 (s, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 166.4, 147.8, 147.8, 145.1, 141.5, 138.5, 136.0, 134.6, 130.1, 129.9, 128.6, 127.7, 127.2, 125.0, 122.8, 122.3, 122.2, 121.4, 121.2, 116.4, 21.1. **HRMS (ESI-TOF)** m/z: $[M + H]^+$ Calcd for $C_{40}H_{32}N_5O_2$ 614.2551; Found 614.2556.

2,2'-(phenylazanediyl)bis(4-(*tert*-butyl)-*N*-(quinolin-8-yl)benzamide) (3d):



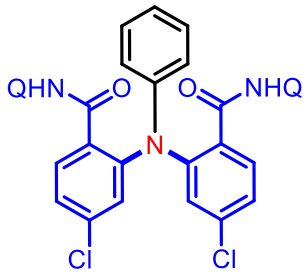
White solid (37.6 mg, 54%); mp: 252-253 °C. Column chromatography on silica gel (Eluent: petroleum ether/ ethyl acetate, 5/1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 10.50 (s, 2H), 8.57 (s, 2H), 8.45 (d, *J* = 7.0 Hz, 2H), 8.07 (d, *J* = 8.0 Hz, 2H), 7.54 (d, *J* = 8.0 Hz, 2H), 7.41-7.33 (m, 6H), 7.23 (s, 2H), 7.08 (d, *J* = 7.5 Hz, 2H), 7.00 (d, *J* = 8.0 Hz, 2H), 6.95 (t, *J* = 7.0 Hz, 2H), 6.75 (t, *J* = 7.0 Hz, 1H), 0.93 (s, 18H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 166.4, 154.4, 148.0, 147.9, 145.0, 138.5, 136.0, 134.6, 129.9, 129.5, 128.6, 127.8, 127.3, 124.8, 123.1, 122.4, 121.4, 121.3, 121.1, 116.5, 34.6, 30.7. **HRMS (ESI-TOF)** m/z: $[M + H]^+$ Calcd for $C_{46}H_{44}N_5O_2$ 698.3490; Found 698.3493.

2,2'-(phenylazanediyl)bis(4-fluoro-*N*-(quinolin-8-yl)benzamide) (3e):



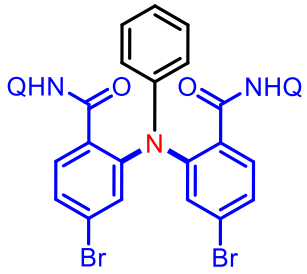
White solid (24.3 mg, 39%); mp: 251-252 °C. Column chromatography on silica gel (Eluent: petroleum ether/ ethyl acetate, 5/1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 10.44 (s, 2H), 8.59 (s, 2H), 8.31 (d, *J* = 7.5 Hz, 2H), 8.04 (d, *J* = 8.5 Hz, 2H), 7.53 (t, *J* = 7.0 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.34-7.31 (m, 4H), 6.91 (d, *J* = 10.5 Hz, 2H), 6.86-6.80 (m, 4H), 6.66 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 165.2, 164.2 (d, $J_{C\text{-}F}$ = 250.0 Hz), 148.0, 146.8, 146.8, 146.6, 138.6, 136.2, 134.2, 131.7 (d, $J_{C\text{-}F}$ = 10.0 Hz), 129.0, 128.6, 127.8, 127.2, 124.0, 121.6 (d, $J_{C\text{-}F}$ = 15.0 Hz), 116.7, 114.4 (d, $J_{C\text{-}F}$ = 23.8 Hz), 111.6, 111.4. **HRMS (ESI-TOF)** m/z: $[M + H]^+$ Calcd for $C_{38}H_{26}F_2N_5O_2$ 622.2049; Found 622.2039.

6,6'-(phenylazanediyl)bis(3-methoxy-2-methyl-*N*-(quinolin-8-yl)benzamide) (3f):



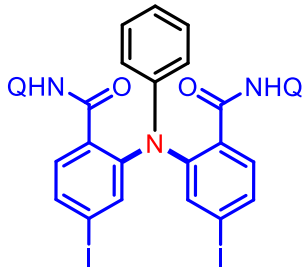
White solid (29.3 mg, 45%); mp: 254-255 °C. Column chromatography on silica gel (Eluent: petroleum ether/ ethyl acetate, 5/1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 10.47 (s, 2H), 8.69 (s, 2H), 8.39 (d, *J* = 7.5 Hz, 2H), 8.12 (d, *J* = 8.0 Hz, 2H), 7.55-7.35 (m, 8H), 7.26 (s, 2H), 6.99-6.92 (m, 6H), 6.76 (s, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 165.1, 148.1, 146.6, 145.7, 138.4, 136.9, 136.2, 134.0, 131.0, 130.9, 129.0, 127.8, 127.6, 127.2, 124.6, 123.9, 123.8, 121.8, 121.6, 116.6. **HRMS (ESI-TOF)** m/z: $[M + H]^+$ Calcd for $C_{38}H_{26}Cl_2N_5O_2$ 654.1458; Found 654.1456.

2,2'-(phenylazanediyl)bis(4-bromo-*N*-(quinolin-8-yl)benzamide) (3g):



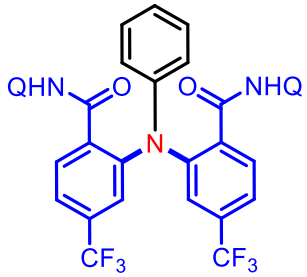
White solid (37.1 mg, 50%); mp: 242-243 °C. Column chromatography on silica gel (Eluent: petroleum ether/ ethyl acetate, 5/1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 10.45 (s, 2H), 8.70 (d, *J* = 3.0 Hz, 2H), 8.40 (d, *J* = 7.5 Hz, 2H), 8.12 (d, *J* = 8.0 Hz, 2H), 7.47-7.37 (m, 10H), 7.11 (d, *J* = 8.0 Hz, 2H), 6.94 (d, *J* = 6.5 Hz, 4H), 6.78 (t, *J* = 6.5 Hz, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 165.2, 148.1, 146.6, 145.7, 138.4, 136.2, 134.0, 131.3, 131.1, 130.6, 129.1, 127.8, 127.5, 127.3, 125.0, 123.9, 123.9, 121.8, 121.6, 116.6. **HRMS (ESI-TOF)** m/z: $[M + H]^+$ Calcd for $C_{38}H_{26}Br_2N_5O_2$ 742.0448 and 744.0431; Found 742.0447 and 744.0433.

2,2'-(phenylazanediyl)bis(4-bromo-*N*-(quinolin-8-yl)benzamide) (3h):



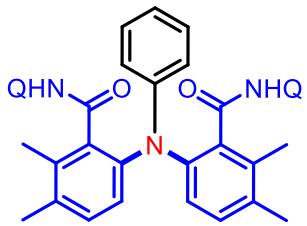
White solid (55.2 mg, 66%); mp: 158-159 °C. Column chromatography on silica gel (Eluent: petroleum ether/ ethyl acetate, 5/1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 10.42 (s, 2H), 8.70 (s, 2H), 8.43 (d, *J* = 7.0 Hz, 2H), 8.12 (d, *J* = 8.0 Hz, 2H), 7.52 (s, 2H), 7.49-7.39 (m, 6H), 7.29-7.24 (m, 4H), 7.00 (s, 4H), 6.83 (s, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 165.3, 148.2, 146.6, 145.4, 138.4, 136.5, 136.2, 134.0, 133.4, 132.0, 131.1, 129.1, 127.9, 127.4, 123.9, 121.8, 121.7, 121.6, 116.6, 96.8. **HRMS (ESI-TOF)** m/z: $[M + H]^+$ Calcd for $C_{38}H_{26}I_2N_5O_2$ 838.0170; Found 838.0176.

2,2'-(phenylazanediyl)bis(*N*-(quinolin-8-yl)-4-(trifluoromethyl)benzamide) (3i):



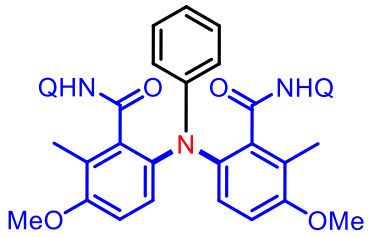
White solid (33.3 mg, 46%); mp: 197-198 °C. Column chromatography on silica gel (Eluent: petroleum ether/ ethyl acetate, 5/1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 10.47 (s, 2H), 8.68 (d, *J* = 3.5 Hz, 2H), 8.39 (d, *J* = 7.5 Hz, 2H), 8.14 (d, *J* = 8.5 Hz, 2H), 7.58 (d, *J* = 8.0 Hz, 2H), 7.49 (d, *J* = 8.0 Hz, 2H), 7.43-7.40 (m, 4H), 7.35 (s, 2H), 7.18-7.13 (m, 4H), 7.09 (d, *J* = 8.0 Hz, 2H), 6.98 (t, *J* = 6.5 Hz, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 165.0, 148.2, 146.6, 145.0 138.4, 136.2, 135.2, 133.7, 132.9 (q, $J_{C\text{-}F}$ = 32.5 Hz), 130.4, 129.5, 127.8, 127.2, 124.6 (q, $J_{C\text{-}F}$ = 5.0 Hz), 124.5, 124.4, 123.0 (q, $J_{C\text{-}F}$ = 272.5 Hz), 122.1, 121.9, 120.7 (q, $J_{C\text{-}F}$ = 3.8 Hz), 116.8. **HRMS (ESI-TOF)** m/z: $[M + H]^+$ Calcd for $C_{40}H_{26}F_6N_5O_2$ 722.1985; Found 722.1995.

6,6'-(phenylazanediyl)bis(2,3-dimethyl-*N*-(quinolin-8-yl)benzamide) (3j):



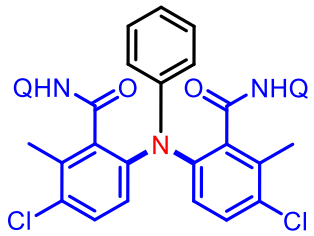
White solid (18.6 mg, 29%); mp: 214-215 °C. Column chromatography on silica gel (Eluent: petroleum ether/ ethyl acetate, 5/1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.90 (s, 2H), 8.72 (d, *J* = 3.0 Hz, 2H), 8.61 (d, *J* = 6.0 Hz, 2H), 8.12 (d, *J* = 8.0 Hz, 2H), 7.47 (d, *J* = 6.5 Hz, 4H), 7.40-7.38 (m, 2H), 7.06-6.97 (m, 4H), 6.82 (d, *J* = 8.0 Hz, 2H), 6.71 (t, *J* = 6.5 Hz, 1H), 6.51 (d, *J* = 8.0 Hz, 2H), 2.02 (s, 6H), 1.57 (s, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 167.4, 149.2, 147.9, 141.9, 138.4, 136.0, 135.2, 134.8, 134.2, 132.8, 130.9, 128.6, 127.7, 127.2, 126.2, 122.4, 121.3, 121.2, 121.0, 116.6, 19.2, 16.4. **HRMS (ESI-TOF)** m/z: $[M + H]^+$ Calcd for $C_{42}H_{36}N_5O_2$ 642.2864; Found 642.2879.

6,6'-(phenylazanediyl)bis(3-methoxy-2-methyl-*N*-(quinolin-8-yl)benzamide) (3k):



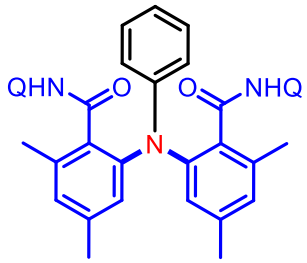
White solid (20.8 mg, 31%); mp: 244-245 °C. Column chromatography on silica gel (Eluent: petroleum ether/ ethyl acetate, 5/1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.87 (s, 2H), 8.67 (d, *J* = 8.0 Hz, 4H), 8.11 (d, *J* = 8.0 Hz, 2H), 7.47 (s, 4H), 7.40-7.37 (m, 2H), 7.02 (t, *J* = 7.5 Hz, 2H), 6.96-6.90 (m, 4H), 6.66 (t, *J* = 7.0 Hz, 1H), 6.11 (d, *J* = 9.0 Hz, 2H), 3.20 (s, 6H), 2.00 (s, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 166.7, 154.0, 149.8, 148.0, 138.3, 136.5, 136.5, 135.8, 134.9, 128.5, 127.6, 127.5, 127.1, 124.4, 121.5, 121.1, 120.9, 120.1, 116.5, 111.0, 55.0, 12.8. **HRMS (ESI-TOF)** m/z: $[M + H]^+$ Calcd for $C_{42}H_{36}N_5O_4$ 674.2762; Found 674.2754.

6,6'-(phenylazanediyl)bis(4-bromo-2-methyl-*N*-(quinolin-8-yl)benzamide) (3l):



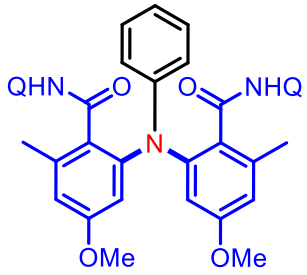
White solid (33.3 mg, 49%); mp: 161-162 °C. Column chromatography on silica gel (Eluent: petroleum ether/ ethyl acetate, 5/1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 10.01 (s, 2H), 8.74 (d, *J* = 3.5 Hz, 2H), 8.59 (d, *J* = 7.0 Hz, 2H), 8.15 (d, *J* = 8.0 Hz, 2H), 7.51 (t, *J* = 9.0 Hz, 4H), 7.43-7.40 (m, 2H), 7.09 (t, *J* = 7.5 Hz, 2H), 7.03 (d, *J* = 7.5 Hz, 2H), 6.83-6.78 (m, 3H), 6.69 (d, *J* = 8.5 Hz, 2H), 2.15 (s, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 165.8, 148.4, 148.1, 142.3, 138.3, 136.3, 134.2, 134.0, 130.3, 130.2, 130.2, 128.9, 127.9, 127.4, 127.1, 123.2, 122.4, 122.0, 121.5, 116.7, 17.2. **HRMS (ESI-TOF)** m/z: $[M + H]^+$ Calcd for $C_{40}H_{30}Cl_2N_5O_2$ 682.1771; Found 682.1773.

6,6'-(phenylazanediyl)bis(2,4-dimethyl-*N*-(quinolin-8-yl)benzamide) (3m):



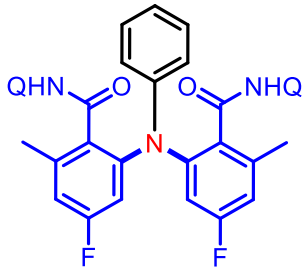
White solid (30.8 mg, 48%); mp: 161-162 °C. Column chromatography on silica gel (Eluent: petroleum ether/ ethyl acetate, 5/1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.91 (s, 2H), 8.71 (d, *J* = 3.5 Hz, 2H), 8.58 (t, *J* = 4.0 Hz, 2H), 8.11 (d, *J* = 8.0 Hz, 2H), 7.45 (d, *J* = 4.0 Hz, 4H), 7.40-7.37 (m, 2H), 7.10 (d, *J* = 4.0 Hz, 4H), 6.84-6.76 (m, 1H), 6.60 (s, 2H), 6.21 (s, 2H), 2.15 (s, 6H), 1.65 (s, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 167.0, 149.0, 148.0, 144.2, 139.4, 138.4, 136.3, 136.0, 134.8, 132.2, 128.7, 127.6, 127.2, 126.7, 126.6, 123.0, 121.5, 121.4, 121.2, 116.4, 20.6, 19.5. **HRMS (ESI-TOF)** m/z: $[M + H]^+$ Calcd for $C_{42}H_{36}N_5O_2$ 642.2864; Found 642.2861.

6,6'-(phenylazanediyl)bis(4-methoxy-2-methyl-*N*-(quinolin-8-yl)benzamide) (3n):



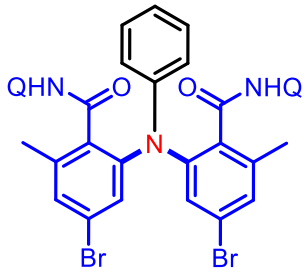
White solid (36.3 mg, 54%); mp: 237-238 °C. Column chromatography on silica gel (Eluent: petroleum ether/ ethyl acetate, 5/1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.96 (s, 2H), 8.72 (s, 2H), 8.58 (s, 2H), 8.11 (d, *J* = 8.0 Hz, 2H), 7.46 (s, 4H), 7.40-7.38 (m, 2H), 7.08 (d, *J* = 8.0 Hz, 4H), 6.80 (s, 1H), 6.36 (s, 2H), 5.98 (s, 2H), 3.17 (s, 6H), 2.17 (s, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 166.8, 159.9, 148.3, 148.0, 145.7, 138.4, 137.9, 136.0, 134.8, 128.7, 128.0, 127.7, 127.2, 123.3, 122.0, 121.4, 121.2, 116.4, 112.2, 110.7, 54.7, 19.9. **HRMS (ESI-TOF)** m/z: $[M + H]^+$ Calcd for $C_{42}H_{36}N_5O_4$ 674.2762; Found 674.2799.

6,6'-(phenylazanediyl)bis(4-fluoro-2-methyl-*N*-(quinolin-8-yl)benzamide) (3o):



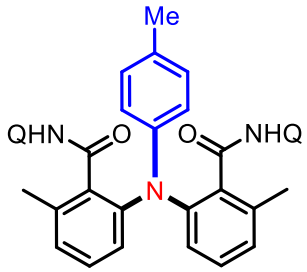
White solid (35.1 mg, 54%); mp: 272-273 °C. Column chromatography on silica gel (Eluent: petroleum ether/ ethyl acetate, 5/1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 10.00 (s, 2H), 8.76 (d, *J* = 3.5 Hz, 2H), 8.53 (d, *J* = 7.0 Hz, 2H), 8.13 (d, *J* = 8.0 Hz, 2H), 7.50-7.44 (m, 4H), 7.42-7.40 (m, 2H), 7.05 (s, 4H), 6.82 (s, 1H), 6.56 (d, *J* = 10.0 Hz, 2H), 6.21 (d, *J* = 8.5 Hz, 2H), 2.17 (s, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 165.9, 162.7 (d, $J_{C\text{-}F}$ = 247.5 Hz), 148.1, 147.5, 145.8 (d, $J_{C\text{-}F}$ = 10.0 Hz), 139.0, 138.9, 138.4, 136.2, 134.2, 130.7 (d, $J_{C\text{-}F}$ = 2.5 Hz), 129.0, 127.7, 127.2, 124.3, 123.3, 121.6 (d, $J_{C\text{-}F}$ = 25.0 Hz), 116.6, 113.0, 112.7, 19.7. **HRMS (ESI-TOF)** m/z: $[M + H]^+$ Calcd for $C_{40}H_{30}F_2N_5O_2$ 650.2362; Found 650.2357.

6,6'-(phenylazanediyl)bis(4-bromo-2-methyl-*N*-(quinolin-8-yl)benzamide) (3p):



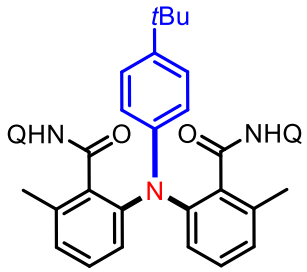
White solid (47.7 mg, 62%); mp: 218-219 °C. Column chromatography on silica gel (Eluent: petroleum ether/ ethyl acetate, 5/1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 10.00 (s, 2H), 8.76 (d, *J* = 4.0 Hz, 2H), 8.55 (t, *J* = 4.0 Hz, 2H), 8.14 (d, *J* = 8.0 Hz, 2H), 7.50 (d, *J* = 4.0 Hz, 4H), 7.42-7.40 (m, 2H), 7.14-7.08 (m, 4H), 6.94 (s, 2H), 6.88 (t, *J* = 7.0 Hz, 1H), 6.62 (s, 2H), 2.15 (s, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 165.6, 148.1, 147.6, 145.0, 138.4, 138.3, 136.2, 134.0, 133.4, 129.1, 128.8, 128.7, 127.8, 127.5, 124.1, 123.3, 123.2, 121.8, 121.5, 116.8, 19.4. **HRMS (ESI-TOF)** m/z: $[M + H]^+$ Calcd for $C_{40}H_{30}Br_2N_5O_2$ 770.0761 and 772.0744; Found 770.0754 and 772.0739.

6,6'-(*p*-tolylazanediyl)bis(2-methyl-*N*-(quinolin-8-yl)benzamide) (4a):



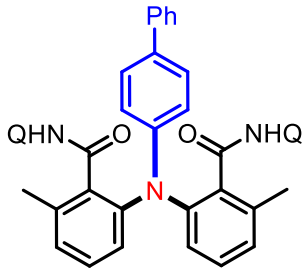
White solid (28.8 mg, 46%); mp: 216-217 °C. Column chromatography on silica gel (Eluent: petroleum ether/ ethyl acetate, 5/1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.90 (s, 2H), 8.71 (s, 2H), 8.52 (d, *J* = 6.0 Hz, 2H), 8.09 (d, *J* = 8.0 Hz, 2H), 7.43 (d, *J* = 6.0 Hz, 4H), 7.39-7.36 (m, 2H), 6.91 (d, *J* = 7.0 Hz, 4H), 6.79 (t, *J* = 8.0 Hz, 2H), 6.73 (d, *J* = 8.0 Hz, 2H), 6.52 (d, *J* = 7.5 Hz, 2H), 2.21 (s, 6H), 1.91 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 166.9, 147.9, 146.1, 144.9, 138.5, 136.5, 136.0, 134.6, 134.4, 131.7, 129.4, 129.3, 127.7, 127.1, 125.8, 125.4, 124.0, 121.3, 121.3, 116.6, 20.4, 19.6. **HRMS (ESI-TOF)** m/z: $[M + H]^+$ Calcd for $C_{41}H_{34}N_5O_2$ 628.2707; Found 628.2723.

6,6'-((4-bromophenyl)azanediyl)bis(2-methyl-*N*-(quinolin-8-yl)benzamide) (4b):



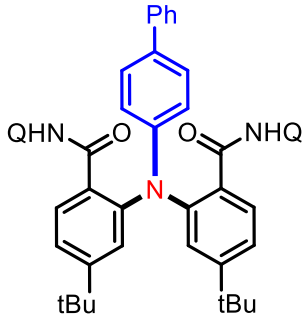
White solid (36.1 mg, 54%); mp: 196-197 °C. Column chromatography on silica gel (Eluent: petroleum ether/ ethyl acetate, 5/1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.85 (s, 2H), 8.70 (s, 2H), 8.49 (d, *J* = 7.0 Hz, 2H), 8.08 (d, *J* = 8.0 Hz, 2H), 7.41 (d, *J* = 8.0 Hz, 4H), 7.39-7.35 (m, 2H), 7.01 (d, *J* = 8.0 Hz, 2H), 6.89-6.84 (m, 6H), 6.58 (d, *J* = 7.5 Hz, 2H), 2.23 (s, 6H), 0.92 (s, 9H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 166.8, 148.0, 145.6, 145.0, 144.6, 138.5, 136.5, 136.0, 134.5, 134.4, 129.6, 127.7, 127.7, 127.1, 126.0, 125.5, 125.4, 123.1, 121.3, 116.6, 33.8, 31.0, 19.6. **HRMS (ESI-TOF)** m/z: $[M + H]^+$ Calcd for $C_{44}H_{40}N_5O_2$ 670.3177; Found 670.3190.

6,6'-((4-bromophenyl)azanediyl)bis(2-methyl-*N*-(quinolin-8-yl)benzamide) (4c):



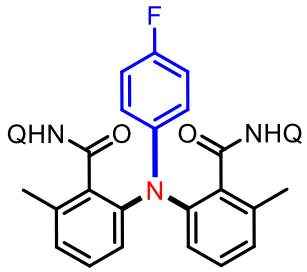
White solid (41.3 mg, 60%); mp: 205-206 °C. Column chromatography on silica gel (Eluent: petroleum ether/ ethyl acetate, 5/1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.87 (s, 2H), 8.63 (s, 2H), 8.52 (s, 2H), 8.01 (d, *J* = 8.0 Hz, 2H), 7.38 (d, *J* = 4.0 Hz, 4H), 7.31-7.07 (m, 9H), 7.03-6.99 (m, 4H), 6.90-6.78 (m, 2H), 6.56 (d, *J* = 7.0 Hz, 2H), 2.22 (s, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 166.7, 147.9, 144.4, 140.7, 138.4, 136.7, 136.0, 134.8, 134.6, 134.4, 129.7, 128.4, 127.7, 127.3, 127.1, 126.5, 126.4, 126.3, 126.0, 123.3, 121.4, 121.4, 116.5, 19.6. **HRMS (ESI-TOF)** m/z: $[M + H]^+$ Calcd for $C_{46}H_{36}N_5O_2$ 690.2864; Found 690.2880.

2,2'-([1,1'-biphenyl]-4-ylazanediyl)bis(4-(*tert*-butyl)-*N*-(quinolin-8-yl)benzamide) (4d):



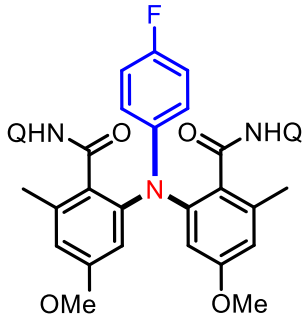
White solid (38.6 mg, 50%); mp: 237-238 °C. Column chromatography on silica gel (Eluent: petroleum ether/ ethyl acetate, 5/1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 10.46 (s, 2H), 8.56 (d, *J* = 2.5 Hz, 2H), 8.45 (d, *J* = 7.0 Hz, 2H), 8.06 (d, *J* = 8.0 Hz, 2H), 7.57 (d, *J* = 8.0 Hz, 2H), 7.40-7.25 (m, 13H), 7.14 (d, *J* = 8.5 Hz, 2H), 7.09 (d, *J* = 8.5 Hz, 2H), 7.04 (d, *J* = 8.0 Hz, 2H), 0.97 (s, 18H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 166.4, 154.6, 147.9, 147.4, 144.9, 140.8, 138.5, 136.0, 134.7, 134.6, 129.9, 129.8, 128.5, 127.8, 127.3, 127.2, 127.1, 126.5, 125.1, 122.8, 121.5, 121.4, 121.2, 116.5, 34.6, 30.8. **HRMS (ESI-TOF)** m/z: $[M + H]^+$ Calcd for $C_{52}H_{48}N_5O_2$ 774.3803; Found 774.3805.

6,6'-((4-fluorophenyl)azanediyl)bis(2-methyl-*N*-(quinolin-8-yl)benzamide) (4e):



White solid (32.8 mg, 52%); mp: 218-219 °C. Column chromatography on silica gel (Eluent: petroleum ether/ ethyl acetate, 5/1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.92 (s, 2H), 8.71 (d, J = 3.0 Hz, 2H), 8.53 (d, J = 6.0 Hz, 2H), 8.11 (d, J = 8.0 Hz, 2H), 7.44 (d, J = 7.0 Hz, 4H), 7.40-7.38 (m, 2H), 6.95-6.91 (m, 4H), 6.84 (t, J = 8.0 Hz, 2H), 6.58 (dd, J_1 = 20.0 Hz, J_2 = 8.0 Hz, 4H), 2.22 (s, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 166.7, 159.3 (d, $J_{C\text{-}F}$ = 240.0 Hz), 148.0, 144.7, 144.6, 144.6, 138.4, 136.7, 136.1, 134.5, 134.3, 129.6, 127.7, 127.2, 125.7, 125.4 (d, $J_{C\text{-}F}$ = 7.5 Hz), 121.5, 121.4, 116.6, 115.3 (d, $J_{C\text{-}F}$ = 22.5 Hz), 19.6. **HRMS (ESI-TOF)** m/z: $[M + H]^+$ Calcd for $C_{40}H_{31}FN_5O_2$ 632.2456; Found 632.2451.

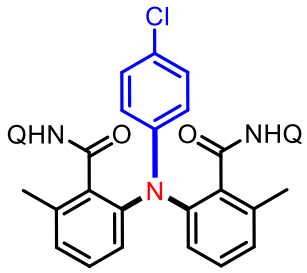
6,6'-((3-fluorophenyl)azanediyl)bis(2-methyl-*N*-(quinolin-8-yl)benzamide) (4f):



White solid (31.8 mg, 46%); mp: 245-246 °C. Column chromatography on silica gel (Eluent: petroleum ether/ ethyl acetate, 5/1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.95 (s, 2H), 8.73 (d, J = 3.5 Hz, 2H), 8.57 (d, J = 6.0 Hz, 2H), 8.12 (d, J = 8.5 Hz, 2H), 7.46 (s, 4H), 7.42-7.39 (m, 2H), 7.02 (s, 2H), 6.71 (t, J = 8.0 Hz, 2H), 6.37 (s, 2H), 6.02 (s, 2H), 3.25 (s, 6H), 2.17 (s, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 166.7, 160.0, 158.4 (d, $J_{C\text{-}F}$ = 240.0 Hz), 148.0, 145.9, 144.4, 138.4, 138.0, 136.1, 134.7, 127.7, 127.6, 127.2, 125.3 (d, $J_{C\text{-}F}$ = 7.5 Hz), 121.4, 121.2, 116.3, 115.4 (d, $J_{C\text{-}F}$ = 22.5 Hz), 112.0, 110.6, 54.7, 19.9. **HRMS (ESI-TOF)** m/z: $[M + H]^+$ Calcd for $C_{42}H_{35}FN_5O_4$ 692.2668; Found

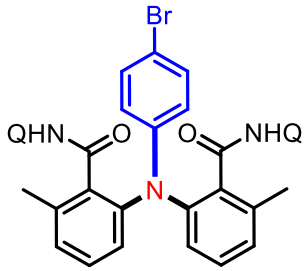
692.2696.

6,6'-((4-chlorophenyl)azanediyl)bis(2-methyl-*N*-(quinolin-8-yl)benzamide) (4g):



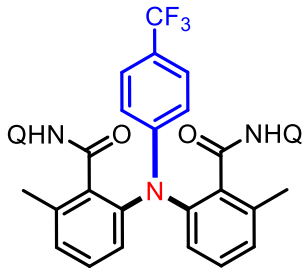
White solid (29.1 mg, 45%) mp: 244-245 °C. Column chromatography on silica gel (Eluent: petroleum ether/ ethyl acetate, 5/1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.86 (s, 2H), 8.69 (d, *J* = 2.5 Hz, 2H), 8.53 (d, *J* = 4.5 Hz, 2H), 8.11 (d, *J* = 7.0 Hz, 2H), 7.45 (d, *J* = 6.5 Hz, 4H), 7.40-7.38 (m, 2H), 6.99 (d, *J* = 8.0 Hz, 2H), 6.87-6.80 (m, 6H), 6.58 (d, *J* = 7.5 Hz, 2H), 2.24 (s, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 166.6, 148.0, 147.1, 144.1, 138.3, 136.7, 136.1, 134.7, 134.4, 129.7, 128.6, 127.7, 127.1, 126.8, 126.2, 126.1, 124.3, 121.5, 121.4, 116.5, 19.5. **HRMS (ESI-TOF)** m/z: $[M + H]^+$ Calcd for $C_{40}H_{31}ClN_5O_2$ 648.2161; Found 648.2188.

6,6'-((4-bromophenyl)azanediyl)bis(2-methyl-*N*-(quinolin-8-yl)benzamide) (4h):



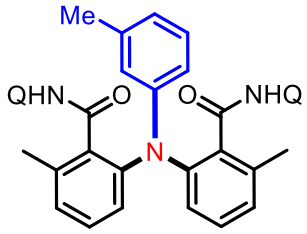
White solid (26.3 mg, 38%); mp: 265-266 °C. Column chromatography on silica gel (Eluent: petroleum ether/ ethyl acetate, 5/1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.84 (s, 2H), 8.69 (s, 2H), 8.53 (d, *J* = 5.5 Hz, 2H), 8.11 (d, *J* = 8.0 Hz, 2H), 7.45 (d, *J* = 6.5 Hz, 4H), 7.40-7.38 (m, 2H), 7.00 (d, *J* = 8.0 Hz, 2H), 6.93 (d, *J* = 8.5 Hz, 2H), 6.85 (t, *J* = 8.0 Hz, 2H), 6.80 (d, *J* = 8.5 Hz, 2H), 6.59 (d, *J* = 7.5 Hz, 2H), 2.24 (s, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 166.6, 148.0, 147.6, 144.1, 138.4, 136.8, 136.2, 134.8, 134.4, 131.6, 129.7, 127.7, 127.1, 126.2, 126.1, 124.6, 121.5, 121.4, 116.5, 114.3, 19.6. **HRMS (ESI-TOF)** m/z: $[M + H]^+$ Calcd for $C_{40}H_{31}BrN_5O_2$ 692.1656 and 694.1638; Found 692.1643 and 694.1624.

6,6'-((4-(trifluoromethyl)phenyl)azanediyl)bis(2-methyl-*N*-(quinolin-8-yl)benzamide) (4i):



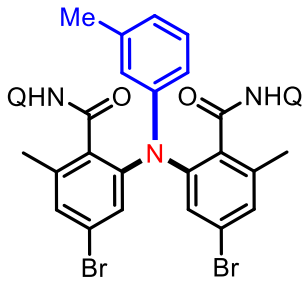
White solid (23.8 mg, 35%) mp: 200-201 °C. Column chromatography on silica gel (Eluent: petroleum ether/ ethyl acetate, 5/1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.80 (s, 2H), 8.65 (d, *J* = 3.5 Hz, 2H), 8.52 (d, *J* = 7.0 Hz, 2H), 8.10 (d, *J* = 8.5 Hz, 2H), 7.46-7.41 (m, 4H), 7.39-7.36 (m, 2H), 7.09 (d, *J* = 8.0 Hz, 2H), 7.05 (d, *J* = 8.0 Hz, 2H), 6.93 (d, *J* = 8.0 Hz, 2H), 6.88 (t, *J* = 8.0 Hz, 2H), 6.65 (d, *J* = 7.0 Hz, 2H), 2.27 (s, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 166.4, 151.2, 147.9, 143.4, 138.2, 136.8, 136.1, 135.2, 134.3, 129.8, 127.7, 127.0 (d, $J_{C\text{-}F}$ = 18.8 Hz), 126.6, 125.8 (d, $J_{C\text{-}F}$ = 3.8 Hz), 124.2 (d, $J_{C\text{-}F}$ = 270 Hz), 122.5, 122.2, 121.6, 121.4, 121.2, 116.4, 19.6. **HRMS (ESI-TOF)** m/z: $[M + H]^+$ Calcd for $C_{41}H_{31}F_3N_5O_2$ 682.2424; Found 682.2417.

6,6'-(*m*-tolylazanediyl)bis(2-methyl-*N*-(quinolin-8-yl)benzamide) (4j):



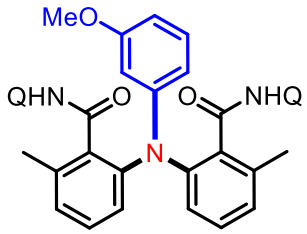
White solid (39.5 mg, 63%); mp: 223-224 °C. Column chromatography on silica gel (Eluent: petroleum ether/ ethyl acetate, 5/1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.90 (s, 2H), 8.70 (s, 2H), 8.53 (d, *J* = 3.5 Hz, 2H), 8.09 (d, *J* = 8.0 Hz, 2H), 7.43 (d, *J* = 6.0 Hz, 4H), 7.38-7.36 (m, 2H), 6.93 (d, *J* = 8.0 Hz, 2H), 6.83-6.78 (m, 5H), 6.54 (d, *J* = 7.5 Hz, 2H), 6.42 (s, 1H), 2.22 (s, 6H), 1.95 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 166.8, 148.5, 147.9, 144.7, 138.5, 138.4, 136.6, 136.0, 134.6, 134.6, 129.4, 128.5, 127.7, 127.1, 126.1, 125.6, 124.4, 122.9, 121.4, 121.3, 121.0, 116.6, 21.2, 19.6. **HRMS (ESI-TOF)** m/z: $[M + H]^+$ Calcd for $C_{41}H_{34}N_5O_2$ 628.2707; Found 628.2726.

6,6'-(*m*-tolylazanediyl)bis(4-bromo-2-methyl-*N*-(quinolin-8-yl)benzamide) (4k):



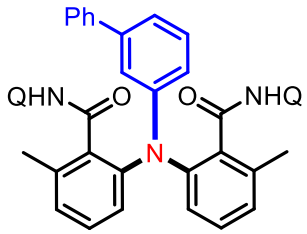
White solid (44.6 mg, 57%); mp: 257-258 °C. Column chromatography on silica gel (Eluent: petroleum ether/ ethyl acetate, 5/1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.97 (s, 2H), 8.77 (d, *J* = 2.5 Hz, 2H), 8.58-8.49 (m, 2H), 8.15 (d, *J* = 8.0 Hz, 2H), 7.50 (d, *J* = 4.0 Hz, 4H), 7.43-7.41 (m, 2H), 7.00-6.85 (m, 5H), 6.64 (s, 3H), 2.15 (s, 6H), 2.09 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 165.6, 148.1, 147.5, 145.2, 139.0, 138.3, 136.2, 134.1, 134.0, 133.3, 128.9, 128.6, 127.7, 127.5, 125.1, 124.4, 123.2, 123.2, 121.7, 121.5, 116.8, 21.3, 19.4. **HRMS (ESI-TOF)** m/z: $[M + H]^+$ Calcd for $C_{41}H_{32}Br_2N_5O_2$ 784.0917 and 786.0901; Found 784.0928 and 786.0899.

6,6'-((3-methoxyphenyl)azanediyl)bis(2-methyl-*N*-(quinolin-8-yl)benzamide) (4l):



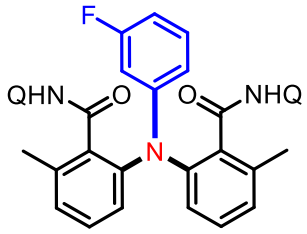
White solid (36.0 mg, 56%); mp: 224-225 °C. Column chromatography on silica gel (Eluent: petroleum ether/ ethyl acetate, 5/1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.89 (s, 2H), 8.69 (d, *J* = 3.0 Hz, 2H), 8.55 (s, 2H), 8.10 (d, *J* = 8.0 Hz, 2H), 7.44 (d, *J* = 5.5 Hz, 4H), 7.38-7.36 (m, 2H), 6.96 (d, *J* = 8.0 Hz, 2H), 6.85-6.78 (m, 3H), 6.59 (d, *J* = 8.0 Hz, 1H), 6.56-6.50 (m, 3H), 6.15 (d, *J* = 8.0 Hz, 1H), 3.44 (s, 3H), 2.22 (s, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 166.7, 160.0, 149.8, 147.9, 144.3, 138.4, 136.6, 136.0, 134.7, 134.6, 129.5, 129.2, 127.6, 127.1, 126.2, 125.8, 121.4, 121.3, 116.6, 116.0, 109.0, 107.9, 55.0, 19.6. **HRMS (ESI-TOF)** m/z: $[M + H]^+$ Calcd for $C_{41}H_{34}N_5O_3$ 644.2656; Found 644.2685.

6,6'-([1,1'-biphenyl]-3-ylazanediyl)bis(2-methyl-*N*-(quinolin-8-yl)benzamide) (4m):



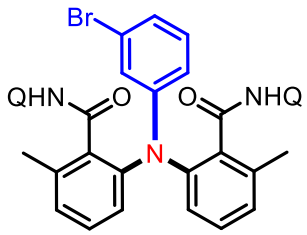
White solid (35.1 mg, 51%); mp: 148-149 °C. Column chromatography on silica gel (Eluent: petroleum ether/ ethyl acetate, 5/1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.92 (s, 2H), 8.53 (d, *J* = 6.0 Hz, 4H), 8.07 (d, *J* = 8.0 Hz, 2H), 7.40 (d, *J* = 9.5 Hz, 4H), 7.34 (s, 2H), 7.21 (s, 3H), 7.16 (s, 1H), 7.05-6.98 (m, 6H), 6.86 (t, *J* = 7.5 Hz, 2H), 6.79 (s, 1H), 6.60 (s, 2H), 2.25 (s, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 166.7, 148.8, 148.0, 144.6, 141.6, 140.9, 138.4, 136.7, 136.0, 134.6, 134.5, 129.6, 129.0, 128.3, 127.6, 127.2, 127.0, 126.9, 126.2, 126.0, 122.4, 122.0, 121.4, 121.3, 120.7, 116.5, 19.7. **HRMS (ESI-TOF)** m/z: $[M + H]^+$ Calcd for $C_{46}H_{36}N_5O_2$ 690.2864; Found 690.2882.

6,6'-((3-fluorophenyl)azanediyl)bis(2-methyl-*N*-(quinolin-8-yl)benzamide) (4n):



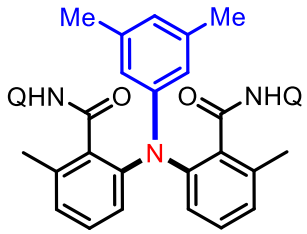
White solid (29.0 mg, 46%); mp: 213-214 °C. Column chromatography on silica gel (Eluent: petroleum ether/ ethyl acetate, 5/1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.87 (s, 2H), 8.69 (d, *J* = 3.0 Hz, 2H), 8.59-53 (m, 2H), 8.11 (d, *J* = 8.0 Hz, 2H), 7.45 (d, *J* = 6.0 Hz, 4H), 7.40-7.37 (m, 2H), 6.98 (d, *J* = 8.0 Hz, 2H), 6.88-6.82 (m, 1H), 6.79 (t, *J* = 8.0 Hz, 2H), 6.73 (d, *J* = 8.0 Hz, 1H), 6.67 (d, *J* = 11.0 Hz, 1H), 6.55 (d, *J* = 7.5 Hz, 2H), 6.26 (t, *J* = 7.5 Hz, 1H), 2.23 (s, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 166.5, 163.2 (d, $J_{C\text{-}F}$ = 242.5 Hz), 150.2 (d, $J_{C\text{-}F}$ = 10 Hz), 147.9, 143.7, 138.4, 136.7, 136.1, 134.5, 134.5, 129.5 (d, $J_{C\text{-}F}$ = 10.0 Hz), 127.6, 127.1, 126.4, 121.4, 118.1, 116.5, 109.7, 109.6, 109.5, 108.2, 108.1, 19.5. **HRMS (ESI-TOF)** m/z: $[M + H]^+$ Calcd for $C_{40}H_{31}FN_5O_2$ 632.2456; Found 632.2470.

6,6'-((3-bromophenyl)azanediyl)bis(2-methyl-*N*-(quinolin-8-yl)benzamide) (4o):



White solid (29.7 mg, 43%); mp: 216-217 °C. Column chromatography on silica gel (Eluent: petroleum ether/ ethyl acetate, 5/1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.86 (s, 2H), 8.72 (s, 2H), 8.55 (d, *J* = 3.0 Hz, 2H), 8.11 (d, *J* = 8.0 Hz, 2H), 7.46 (d, *J* = 5.5 Hz, 4H), 7.40-7.38 (m, 2H), 7.11 (s, 1H), 6.95 (d, *J* = 7.5 Hz, 2H), 6.90 (d, *J* = 8.0 Hz, 1H), 6.81 (t, *J* = 8.0 Hz, 2H), 6.75 (t, *J* = 8.0 Hz, 1H), 6.67 (d, *J* = 7.5 Hz, 1H), 6.58 (d, *J* = 7.0 Hz, 2H), 2.24 (s, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 166.5, 149.9, 148.3, 148.0, 143.7, 138.4, 136.8, 136.1, 134.9, 134.4, 129.8, 129.7, 127.7, 127.2, 126.5, 126.3, 125.7, 124.5, 122.4, 121.6, 121.5, 116.5, 19.6. **HRMS (ESI-TOF)** m/z: $[M + H]^+$ Calcd for $C_{40}H_{31}BrN_5O_2$ 692.1656 and 694.1638; Found 692.1676 and 694.1659.

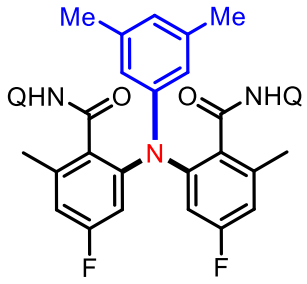
6,6'-((3,5-dimethylphenyl)azanediyl)bis(2-methyl-*N*-(quinolin-8-yl)benzamide) (4p):



White solid (34.0 mg, 53%); mp: 236-237 °C. Column chromatography on silica gel (Eluent: petroleum ether/ ethyl acetate, 5/1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.83 (s, 2H), 8.70 (s, 2H), 8.54 (s, 2H), 8.09 (d, *J* = 8.0 Hz, 2H), 7.43 (s, 4H), 7.37 (t, *J* = 5.0 Hz, 2H), 6.96 (d, *J* = 7.5 Hz, 2H), 6.85 (t, *J* = 7.0 Hz, 2H), 6.58 (d, *J* = 8.5 Hz, 4H), 6.09 (s, 1H), 2.23 (s, 6H), 1.86 (s, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 166.8, 148.3, 147.8, 145.0, 138.4, 138.2, 136.4, 136.0, 134.7, 134.6, 129.5, 127.7, 127.1, 126.2, 125.4, 124.0, 122.0, 121.3, 121.2, 116.4, 21.0, 19.6. **HRMS (ESI-TOF)** m/z: $[M + H]^+$ Calcd for $C_{42}H_{36}N_5O_2$ 642.2864; Found 642.2888.

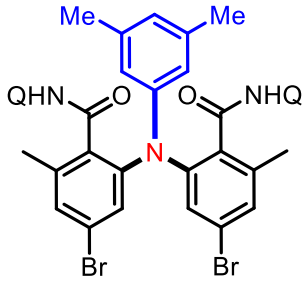
6,6'-((3,5-dimethylphenyl)azanediyl)bis(4-fluoro-2-methyl-*N*-(quinolin-8-

yl)benzamide) (4q):



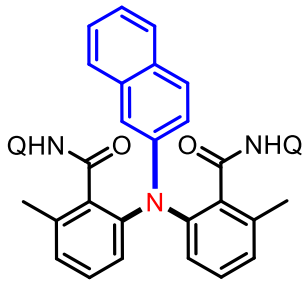
White solid (37.9 mg, 56%) mp: 281-282 °C. Column chromatography on silica gel (Eluent: petroleum ether/ ethyl acetate, 5/1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.91 (s, 2H), 8.74 (d, *J* = 2.5 Hz, 2H), 8.55 (d, *J* = 3.5 Hz, 2H), 8.12 (d, *J* = 8.5 Hz, 2H), 7.46 (d, *J* = 5.5 Hz, 4H), 7.41-7.39 (m, 2H), 6.64 (s, 2H), 6.58 (d, *J* = 10.0 Hz, 2H), 6.27 (d, *J* = 10.0 Hz, 3H), 2.19 (s, 6H), 1.94 (s, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 166.0, 162.7 (d, $J_{C\text{-}F}$ = 246.2 Hz), 148.0, 147.3, 146.3, 146.2, 138.8 (d, $J_{C\text{-}F}$ = 10.0 Hz), 138.6, 138.4, 136.2, 134.3, 130.6, 127.7, 127.2, 125.3, 122.7, 121.5 (d, $J_{C\text{-}F}$ = 11.2 Hz), 116.4, 112.8, 112.6 (d, $J_{C\text{-}F}$ = 15.0 Hz), 21.0, 19.8. **HRMS (ESI-TOF)** m/z: $[M + H]^+$ Calcd for $C_{42}H_{34}F_2N_5O_2$ 678.2675; Found 678.2680.

6,6'-((3,5-dimethylphenyl)azanediyl)bis(4-bromo-2-methyl-*N*-(quinolin-8-yl)benzamide) (4r):



White solid (39.9 mg, 50%); mp: 288-289 °C. Column chromatography on silica gel (Eluent: petroleum ether/ ethyl acetate, 5/1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.92 (s, 2H), 8.76 (d, *J* = 3.0 Hz, 2H), 8.55 (d, *J* = 8.5 Hz, 2H), 8.13 (d, *J* = 8.0 Hz, 2H), 7.49 (d, *J* = 6.5 Hz, 4H), 7.42-7.39 (m, 2H), 6.96 (s, 2H), 6.67 (s, 4H), 6.39 (s, 1H), 2.16 (s, 6H), 2.02 (s, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 165.6, 148.0, 147.4, 145.4, 138.7, 138.3, 138.3, 136.2, 134.1, 133.3, 128.7, 128.5, 127.7, 127.5, 125.5, 123.2, 122.6, 121.6, 121.5, 116.7, 21.1, 19.4. **HRMS (ESI-TOF)** m/z: $[M + H]^+$ Calcd for $C_{42}H_{34}Br_2N_5O_2$ 798.1074 and 800.1058; Found 798.1076 and 800.1053.

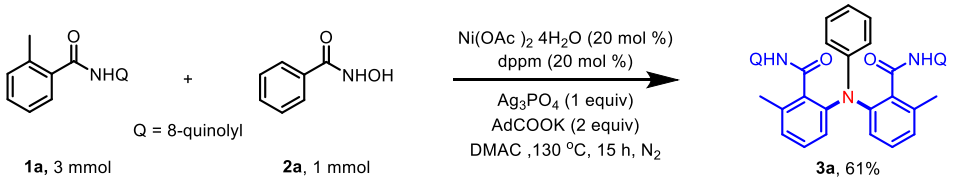
6,6'-(naphthalen-2-ylazanediyl)bis(2-methyl-*N*-(quinolin-8-yl)benzamide) (4s):



White solid (26.5 mg, 40%); mp: 245-246 °C. Column chromatography on silica gel (Eluent: petroleum ether/ ethyl acetate, 5/1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.89 (s, 2H), 8.57 (s, 1H), 8.47 (d, *J* = 7.0 Hz, 2H), 8.04 (d, *J* = 8.5 Hz, 2H), 7.45-7.33 (m, 9H), 7.30 (d, *J* = 3.5 Hz, 2H), 7.23-7.18 (m, 2H), 7.10 (t, *J* = 7.5 Hz, 1H), 6.97 (d, *J* = 7.5 Hz, 2H), 6.80 (t, *J* = 8.0 Hz, 2H), 6.57 (d, *J* = 7.5 Hz, 2H), 2.24 (s, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 166.7, 147.8, 146.2, 144.4, 138.3, 136.6, 135.9, 134.8, 134.4, 134.2, 129.6, 129.6, 128.4, 127.6, 127.1, 127.0, 126.8, 126.3, 126.2, 126.0, 125.7, 123.8, 123.7, 121.3, 119.8, 116.5, 19.6. **HRMS (ESI-TOF)** m/z: $[M + H]^+$ Calcd for $C_{44}H_{34}N_5O_2$ 664.2707; Found 664.2703.

4. Synthetic Applications

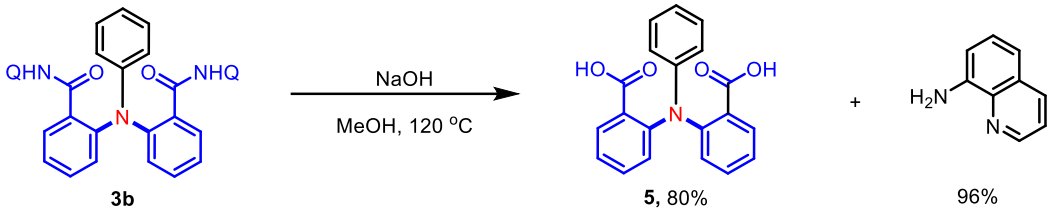
4.1. Scale-up reaction for the synthesis of triarylamine (3a).



In a 100 mL Schlenk reaction tube, 2-methyl-*N*-(quinolin-8-yl)benzamide (**1a**, 3 mmol, 780 mg), *N*-hydroxybenzamide (**2a**, 1 mmol, 137 mg), $Ni(OAc)_2$•$4H_2O$ (0.4 mmol, 100 mg), dppm (0. 4 mmol, 156 mg), Ag_3PO_4 (2 mmol, 840 mg), AdCOOK (4 mmol, 872 mg) were dissolved in DMAc (10 mL). The reaction mixture was charge with N_2 for several times, and then heated at 130 °C (oil bath) with vigorous stirring for 15 h under N_2 atmosphere. After the reaction equilibrium, the mixture was extracted with ethyl acetate, the combined organic layers were dried over anhydrous Na_2SO_4. The filtrate was concentrated in vacuo and purified by a silica gel packed flash chromatography with petroleum ether/ ethyl acetate (5:1) as eluent to afford the targeted product **3a**

(61%, 0.374g).

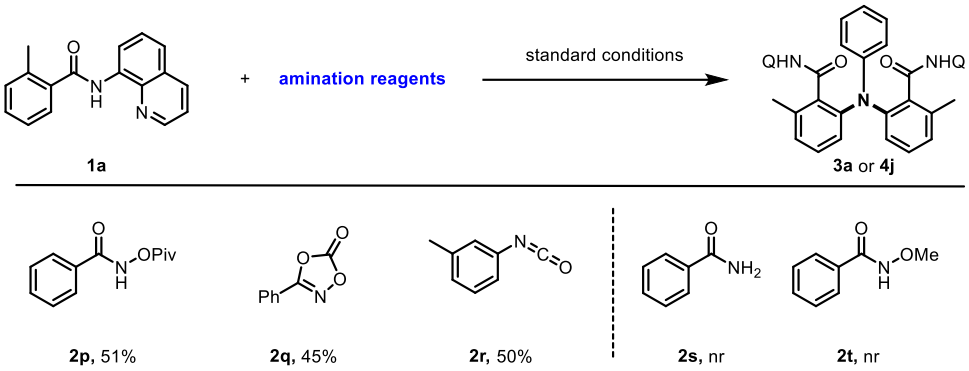
4.2. The removal of 8-aminoquinoline auxiliary group.



The procedure for the removal of the directing group on the targeted product (**3b**) was according to the previous literature[9]: A 15 mL dry screw cap vial was equipped with a magnetic stir bar and charged with prodcut **3b** (58.6 mg, 0.1 mmol) and 6 mol/L NaOH in MeOH (3 mL). This vessel was stirred at 120 °C (oil bath) for 36 h. After completion, the resulting mixture was cooled to room temperature and 10 mL MeOH was added. The mixture was concentrated in vacuum and extracted with ethyl acetate (2 x 20 mL) and H_2O (20 mL). The organic phase was dried over Na_2SO_4 and was concentrated in vacuo, affording 8-aminoquinoline in 96% yield. Then 2.0 mol/L HCl was added to the aqueous layer until pH = 4. Next, the aqueous layer was extracted with ethyl acetate (2 x 20 mL). The organic layer was collected and dried over Na_2SO_4. After concentration in vacuum, the residue was purified by preparative TLC on silica gel (Hexane/Ethyl acetate/HOAc = 50:50:1), the targeted compound **5** was obtained in 80% yield concomitant with 96% recovery of aminoquinoline.

2,2'-((phenylazanediyl)bis(2,1-phenylene))bis(2-oxoacetic acid) (5). White solid (26.6 mg, 80%); mp: 234-235 °C. Cloumn chromatography on silica gel (Eluent: Hexane/Ethyl acetate/HOAc = 50:50:1; R_f = 0.50) **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.52 (br, 2H), 7.79 (d, *J* = 7.5 Hz, 2H), 7.38 (t, *J* = 7.5 Hz, 2H), 7.19-7.12 (m, 4H), 7.01 (t, *J* = 7.0 Hz, 1H), 6.90 (d, *J* = 8.0 Hz, 2H), 6.83 (d, *J* = 7.5 Hz, 2H) **^{13}C NMR** (125 MHz, $CDCl_3$) δ 170.1, 148.1, 147.3, 133.3, 132.4, 129.3, 126.3, 125.5, 124.4, 123.9, 123.7.

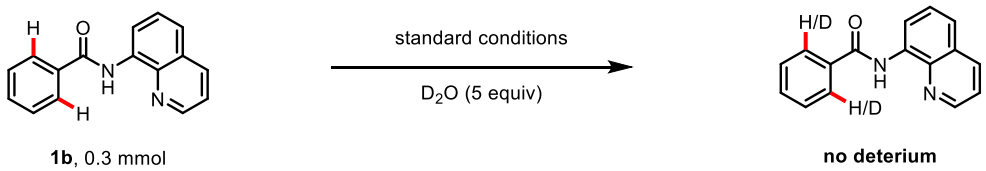
4.3. Scope of other aminated reagents.



In a 10 mL Schlenk reaction tube with a stir bar, 2-methyl-*N*-(quinolin-8-yl)benzamide (**1a**, 0.3 mmol, 78.6 mg), other amination reagent (**2p-2t**, 0.1 mmol), $Ni(OAc)_2 \cdot 4H_2O$ (0.04 mmol, 10 mg), dppm (0.04 mmol, 15.6 mg), Ag_3PO_4 (0.2 mmol, 84 mg), AdCOOK (0.4 mmol, 87.2 mg), were dissolved in DMAc (1 mL), the mixture was charged with nitrogen three times. The reaction mixture was then heated at 130 °C (oil bath) with vigorous stirring for 15 h under N_2 atmosphere. After the reaction equilibrium, the mixture was extracted with ethyl acetate, the combined organic layers were dried over anhydrous Na_2SO_4. The filtrate was concentrated in vacuo and purified by a silica gel packed flash chromatography with petroleum ether/ethyl acetate (5:1) as eluent to afford the targeted product **3a** or **4j**. It was found that the targeted product **3a** could be obtained in 51% and 45%, respectively, when using *N*-(pivaloyloxy)benzamide (**2p**), 3-phenyl-1,4,2-dioxazol-5-one (**2q**) as the amination reagent. Moreover, the triarylamine product (**4j**) was isolated in 50% yield using 1-isocyanato-3-methylbenzene (**2r**) as a substrate. However, bare benzamide (**2s**) and *N*-methoxy benzamide (**2t**) were both ineffective substrates for this conversion, no desired triarylamine were observed during the reaction course.

5. The Mechanistic Investigations

5.1. H/D exchange experiment.



In a 10 mL Schlenk reaction tube with a stir bar, *N*-(quinolin-8-yl)benzamide (**1b**, 0.3

mmol, 73.8 mg), D_2O (10 mmol, 30 mg), $Ni(OAc)_2 \cdot 4H_2O$ (20 mol %, 10 mg), dppm (0.04 mmol, 15.6 mg), Ag_3PO_4 (0.2 mmol, 84 mg), AdCOOK (0.4 mmol, 87.2 mg) were dissolved in DMAc (1 mL). Then, the solution was charged with nitrogen three times. The reaction mixture was then heated at 130 °C (oil bath) with vigorous stirring for 15 h under N_2 atmosphere. After the reaction equilibrium, the mixture was extracted with ethyl acetate, the combined organic layers were dried over anhydrous Na_2SO_4. The filtrate was concentrated in vacuo and purified by a silica gel packed flash chromatography with petroleum ether/ethyl acetate (5:1) as eluent to afford benzamide **1b**. It was found that no deuterium was detected on the *ortho* C-H bond of the benzamide **1b**.

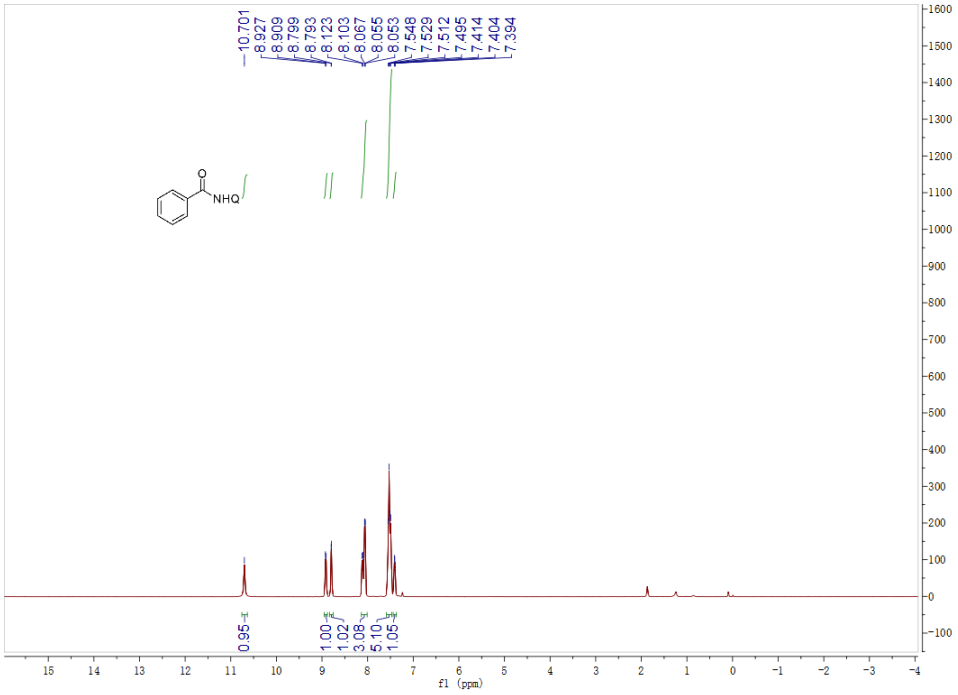
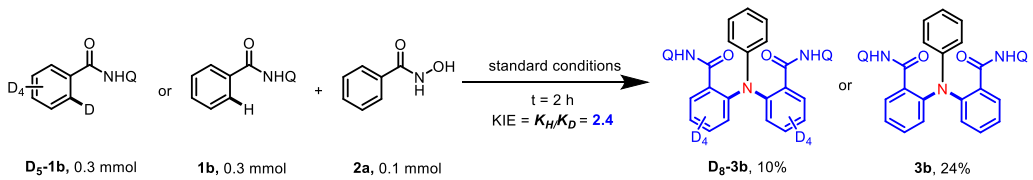


Figure S1: ^{1}H NMR spectrum of substrate 1b after the H/D exchange experiment

5.2. Parallel Kinetic isotopic effect experiments.



In a 10 mL Schlenk reaction tube with a stir bar, deuterated *N*-(quinolin-8-yl)benzamide (**D_5-1b**, 0.3 mmol, 75.9 mg), *N*-hydroxybenzamide (**2a**, 0.1 mmol, 13.7 mg), $Ni(OAc)_2 \cdot 4H_2O$ (0.04 mmol, 10 mg), dppm (0.04 mmol, 15.6 mg), Ag_3PO_4 (0.2 mmol,

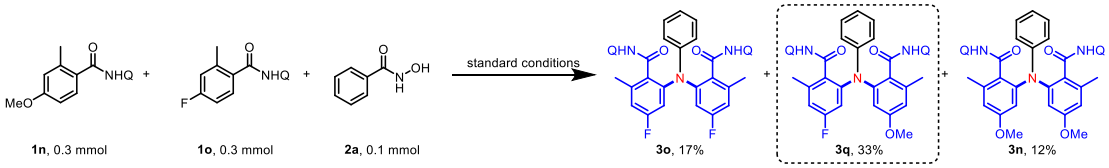
84 mg), AdCOOK (0.4 mmol, 87.2 mg) were dissolved in DMAc (1 mL), the mixture was charged with N_2 three times. The reaction mixture was then heated at 130 °C (oil bath) with vigorous stirring for 2 h under N_2 atmosphere. After the reaction equilibrium, the mixture was extracted with ethyl acetate, the combined organic layers were dried over anhydrous Na_2SO_4. The filtrate was concentrated in vacuo and purified by a silica gel packed flash chromatography with petroleum ether/ ethyl acetate (5:1) as eluent to afford the desired product **D_8-3b** in 10% yield.

In a 10 mL Schlenk reaction tube, *N*-(quinolin-8-yl)benzamide (**1b**, 0.3 mmol, 74.4 mg), *N*-hydroxybenzamide (**2a**, 0.1 mmol, 13.7 mg), $Ni(OAc)_2$•$4H_2O$ (0.04 mmol, 10 mg), dppm (0.04 mmol, 15.6 mg), Ag_3PO_4 (0.2 mmol, 84 mg), AdCOOK (0.4 mmol, 87.2 mg) were dissolved in DMAc (1 mL), the mixture was charged with N_2 three times. The reaction mixture was then heated at 130 °C (oil bath) with vigorous stirring for 2 h under N_2 atmosphere. After the reaction equilibrium, the mixture was extracted with ethyl acetate, the combined organic layers were dried over anhydrous Na_2SO_4. The filtrate was concentrated in vacuo and purified by a silica gel packed flash chromatography with petroleum ether/ ethyl acetate (5:1) as eluent to afford the desired product **3b** in 24% yield.

Consequently, the parallel kinetic isotopic effect value equals 2.4. KIE = 24%/10%

5.3. Competitive experiments.

5.3.1 Competitive experiments between benzamides 1n and 1o.

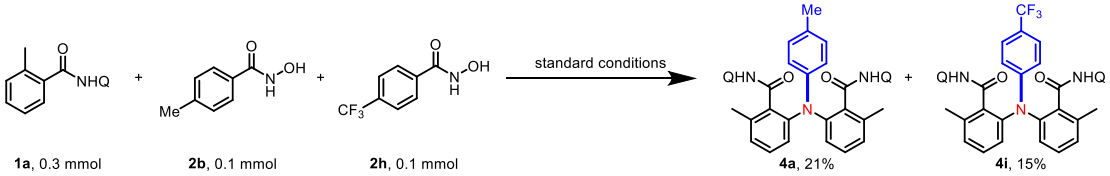


In a 10 mL Schlenk reaction tube , 4-methoxy-2-methyl-*N*-(quinolin-8-yl)benzamide (**1n**, 0.3 mmol, 87.6 mg), 4-fluoro-2-methyl-*N*-(quinolin-8-yl)benzamide (**1o**, 0.3 mmol, 84 mg), *N*-hydroxybenzamide (**2a**, 0.1 mmol, 13.7 mg), $Ni(OAc)_2$•$4H_2O$ (0.04 mmol, 10 mg), dppm (0.04 mmol, 15.6 mg), Ag_3PO_4 (0.2 mmol, 84 mg), AdCOOK (0.4 mmol, 87.2 mg) were dissolved in DMAc (1 mL), which was charged with N_2 three times. The reaction mixture was then heated at 130 °C (oil bath) with vigorous stirring for 15 h under N_2 atmosphere. After the reaction equilibrium, the mixture was extracted with

ethyl acetate, the combined organic layers were dried over anhydrous Na_2SO_4. The filtrate was concentrated in vacuo and purified by a silica gel packed flash chromatography with petroleum ether/ethyl acetate (5:1) as eluent to afford the mixed product. The obtained product **3n**, **3o** and **3q** were isolated in 12%, 17% and 33% yield, respectively.

4-fluoro-2-((5-methoxy-3-methyl-2-(quinolin-7-ylcarbamoyl)phenyl)(phenyl)amino)-6-methyl-*N*-(quinolin-7-yl)benzamide (3q): White solid (26.5 mg, 33%); mp: 95-96 °C. Column chromatography on silica gel (Eluent: petroleum ether/ ethyl acetate, 5/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.03 (d, *J* = 12.0 Hz, 2H), 8.78 (dd, J_1 = 11.6, J_2 = 2.8 Hz, 2H), 8.63-8.59 (m, 2H), 8.16 (d, *J* = 8.0 Hz, 2H), 7.54-7.48 (m, 4H), 7.46-7.41 (m, 2H), 7.12 (d, *J* = 5.2 Hz, 4H), 6.87-6.84 (m, 1H), 6.60 (d, *J* = 10.4 Hz, 1H), 6.41 (s, 1H), 6.23 (d, *J* = 6.8 Hz, 1H), 6.06 (s, 1H), 3.25 (s, 3H), 2.22 (d, *J* = 4.0 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.7, 166.1, 162.6 (d, $J_{C\text{-}F}$ = 246.0 Hz), 160.1, 148.1, 148.0, 147.9, 146.3, 146.2, 145.4, 138.9, 138.8, 138.5, 138.4, 138.1, 136.2, 134.5 (d, $J_{C\text{-}F}$ = 6.0 Hz), 130.6, 128.8, 128.0, 127.7, 127.2 (d, $J_{C\text{-}F}$ = 13.0 Hz), 123.8, 122.7, 121.5, 116.5 (d, $J_{C\text{-}F}$ = 5.0 Hz), 112.5, 111.1, 54.7, 19.9, 19.8. **HRMS (ESI-TOF)** m/z: $[M + H]^+$ Calcd for $C_{41}H_{33}FN_5O_3$ 662.2562; Found 662.2580.

5.3.2 Competitive experiments between *N*-hydroxybenzamides 2b and 2h.

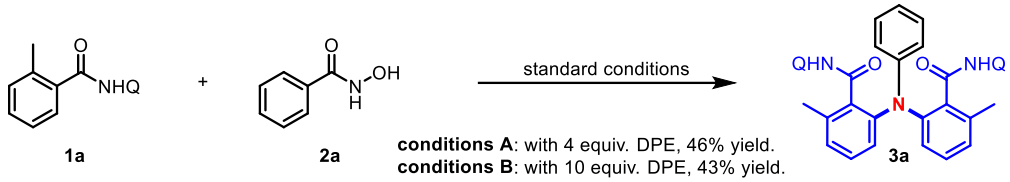


In a 10 mL Schlenk reaction tube, 2-methyl-*N*-(quinolin-8-yl)benzamide (**1a**, 0.3 mmol, 78 mg), *N*-hydroxy-4-methylbenzamide (**2b**, 0.1 mmol, 15.1 mg), *N*-hydroxy-4-(trifluoromethyl)benzamide (**2h**, 0.1 mmol, 20.5 mg), $Ni(OAc)_2{\cdot}4H_2O$ (0.04 mmol, 10 mg), dppm (0.04 mmol, 15.6 mg), Ag_3PO_4 (0.2 mmol, 84 mg), AdCOOK (0.4 mmol, 87.2 mg) were dissolved in DMAc (1 mL), then the mixture was charged with N_2 three times. The reaction mixture was then heated at 130 °C (oil bath) with vigorous stirring for 15 h under N_2 atmosphere. After the reaction equilibrium, the mixture was extracted

with ethyl acetate, the combined organic layers were dried over anhydrous Na_2SO_4. The filtrate was concentrated in vacuo and purified by a silica gel packed flash chromatography with petroleum ether/ethyl acetate (5:1) as eluent to afford the mixed products. The obtained products **4a** and **4i** were isolated in 21% and 15% yield, respectively.

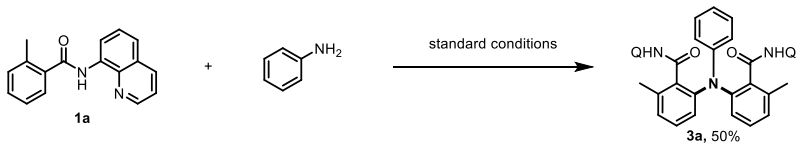
5.4. Control experiments.

5.4.1. Radical-trapping experiments.



Conditions A: In a 10 mL Schlenk reaction tube with a stir bar, 2-methyl-*N*-(quinolin-8-yl)benzamide (**1a**, 0.3 mmol, 78.6 mg), *N*-hydroxybenzamide (**2a**, 0.1 mmol, 13.7 mg), $Ni(OAc)_2$•$4H_2O$ (0.04 mmol, 10 mg), dppm (0.04 mmol, 15.6 mg), Ag_3PO_4 (0.2 mmol, 84 mg), AdCOOK (0.4 mmol, 87.2 mg), DPE (0.8 mmol, 144.2 mg) or DPE (2.0 mmol, 360.5 mg) , were dissolved in DMAc (1 mL), the mixture was charged with nitrogen three times. The reaction mixture was then heated at 130 °C (oil bath) with vigorous stirring for 15 h under N_2 atmosphere. After the reaction equilibrium, the mixture was extracted with ethyl acetate, the combined organic layers were dried over anhydrous Na_2SO_4. The filtrate was concentrated in vacuo and purified by a silica gel packed flash chromatography with petroleum ether/ethyl acetate (5:1) as eluent to afford the targeted product **3a** in 46% and 43% yield, respectively.

5.4.2. Using aniline as amination reagent for this reaction



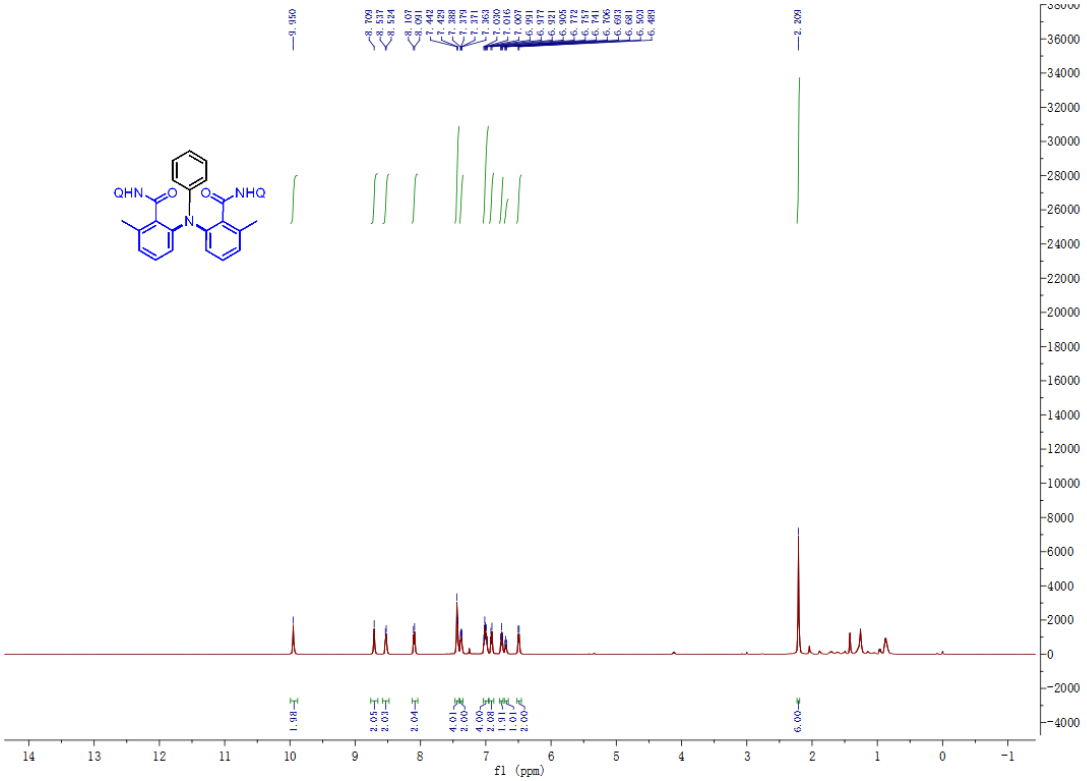
In a 10 mL Schlenk reaction tube with a stir bar, 2-methyl-*N*-(quinolin-8-yl)benzamide (**1a**, 0.3 mmol, 78 mg), aniline (0.1 mmol, 9.3 mg), $Ni(OAc)_2$•$4H_2O$ (0.04 mmol, 10 mg), dppm (0.04 mmol, 15.6 mg), Ag_3PO_4 (0.2 mmol, 84 mg), AdCOOK (0.4 mmol, 87.2 mg) were dissolved in DMAc (1 mL), then the mixture was charged with N_2 three

times. The reaction mixture was then heated at 130 °C (oil bath) with vigorous stirring for 15 h under N_2 atmosphere. After the reaction equilibrium, the mixture was extracted with ethyl acetate, the combined organic layers were dried over anhydrous Na_2SO_4. The filtrate was concentrated in vacuo and purified by a silica gel packed flash chromatography with petroleum ether/ethyl acetate (5:1) as eluent to afford the mixed products. The obtained products **3a** was isolated in 50% yield.

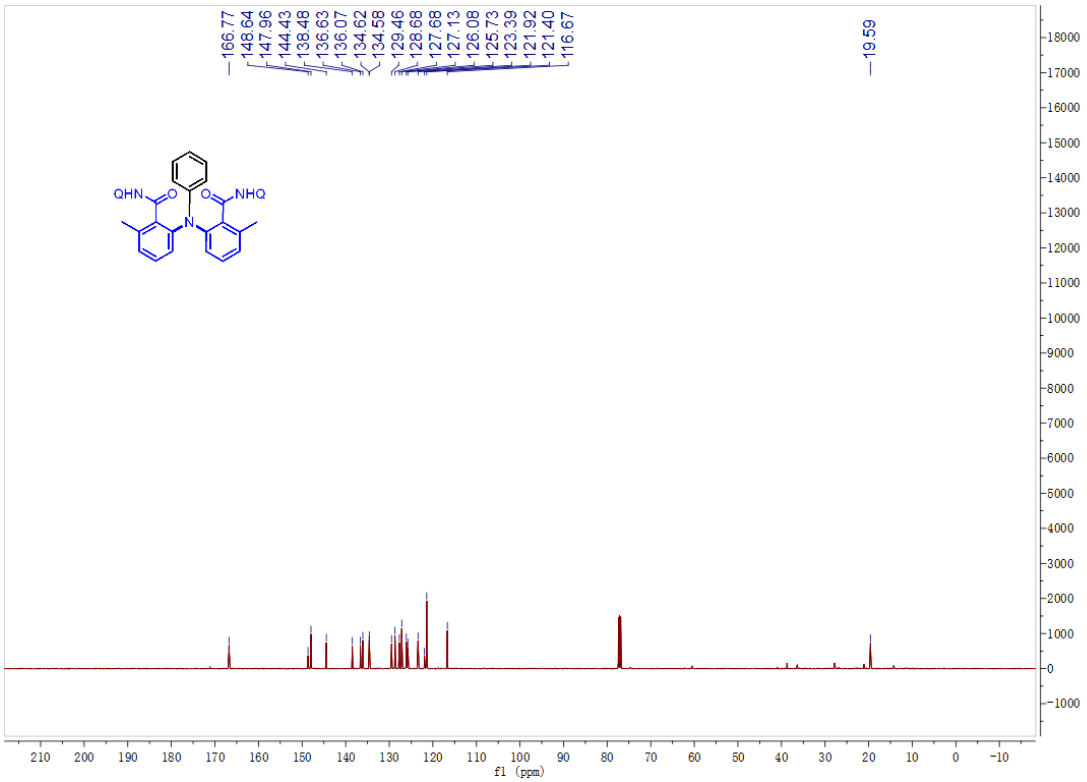
6.Reference

[1] L. D. Tran, I. Popov and O. Daugulis, *J. Am. Chem. Soc.*, 2012, **134,** 18237−12840.
[2] Y. Ano, M. Tobisu and N. Chatani, *Org. Lett.*, 2012, **14**, 354−357.
[3] L. D. Tran, J. Roane and O. Daugulis, *Angew. Chem. Int. Ed.*, 2013, **52,** 6043−6046.
[4] L. Grigorjeva and O. Daugulis, *Angew. Chem. Int. Ed.*, 2014, **53,** 10209−10212.
[5] F.-R. Gou, X.-C. Wang, P.-F. Huo, H.-P. Bi, Z.-H. Guan and Y.-M. Liang, *Org. Lett.*, 2009, **11,** 5726−5729.
[6] K. Shibata and N. Chatani, *Org. Lett.*, 2014, **16,** 5148−5151.
[7] N. Lv, Z. Chen, S. Yu, Z. Liu and Y. Zhang, *Org. Chem. Front*., 2020, **7,** 2224−2229.
[8] H. Jiang and A. Studer, *Angew. Chem. Int. Ed.*, 2017, **56,** 12273−12276.
[9] C. Du, P.-X. Li, X. Zhu, J.-N. Han, J.-L. Niu and M.-P. Song, *ACS Catal.*, 2017, **7,** 2810−2814.

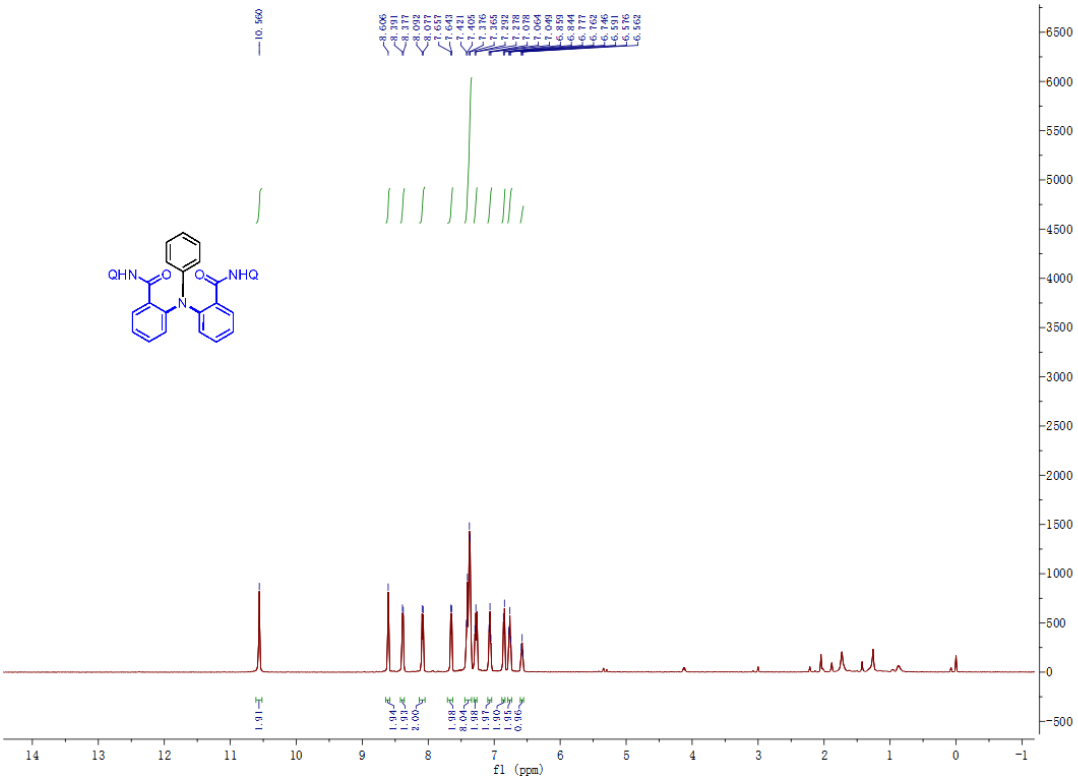
7. NMR Spectra for All Products.



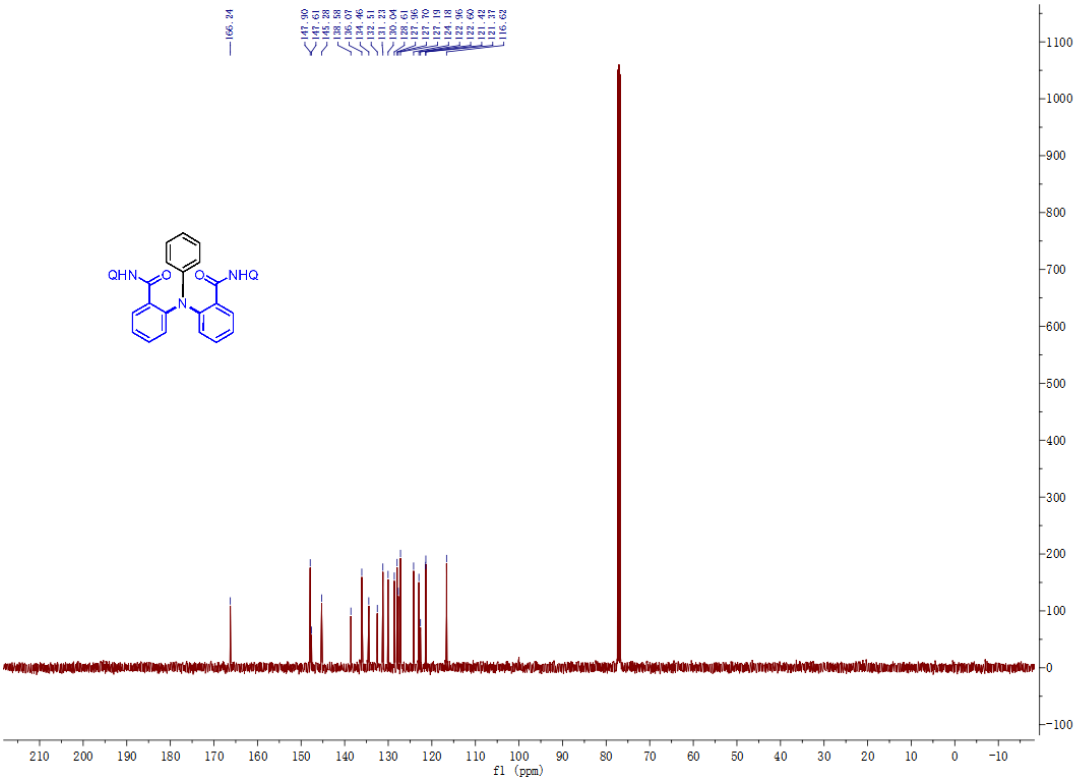
^{1}H NMR (500 MHz, $CDCl_3$) of product **3a**



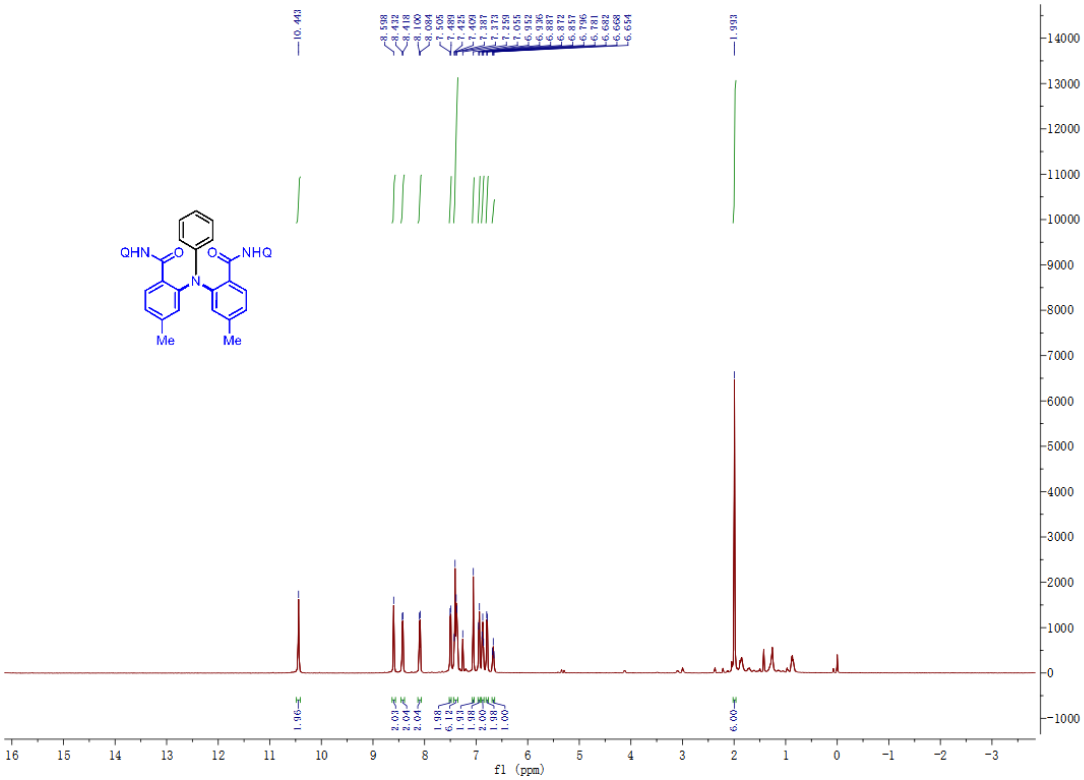
^{13}C NMR (125 MHz, $CDCl_3$) of product **3a**



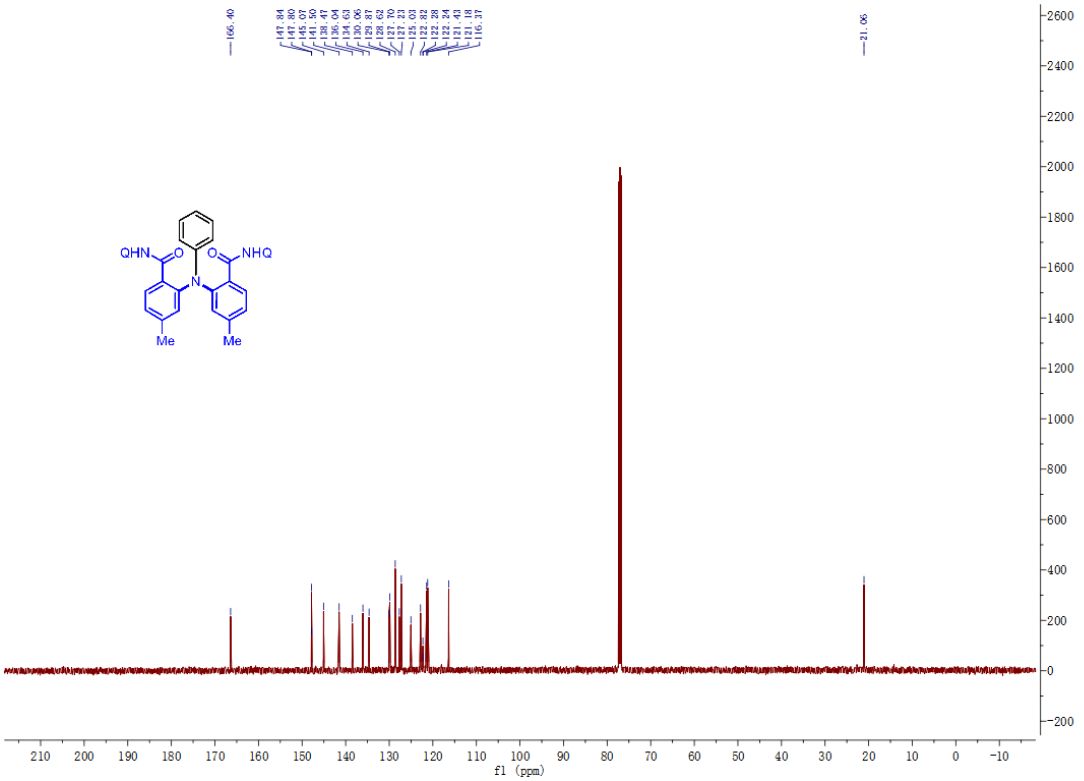
^{1}H NMR (500 MHz, $CDCl_3$) of product **3b**



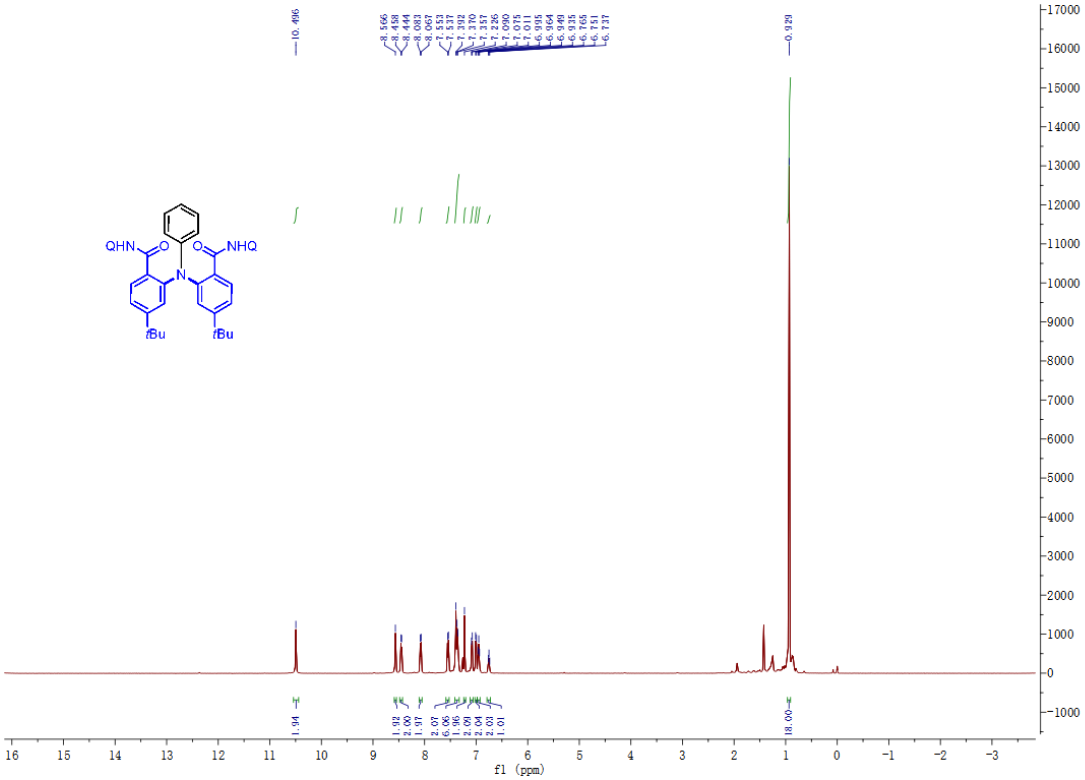
^{13}C NMR (125 MHz, $CDCl_3$) of product **3b**



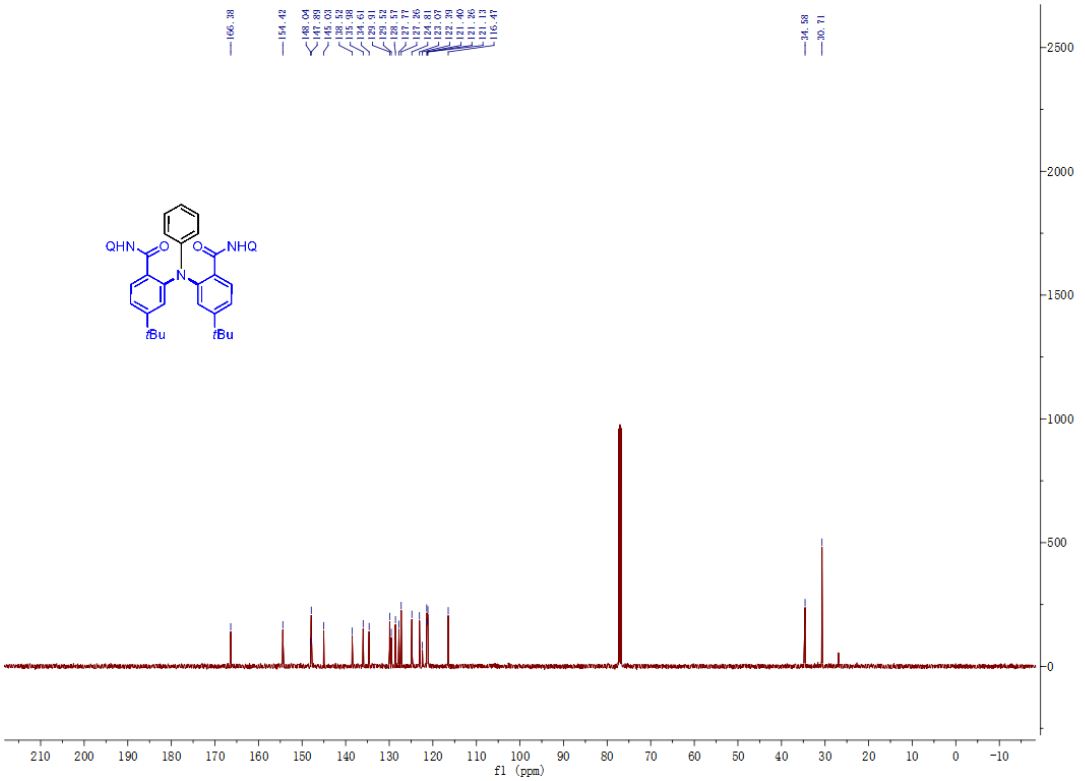
^{1}H NMR (500 MHz, $CDCl_3$) of product **3c**



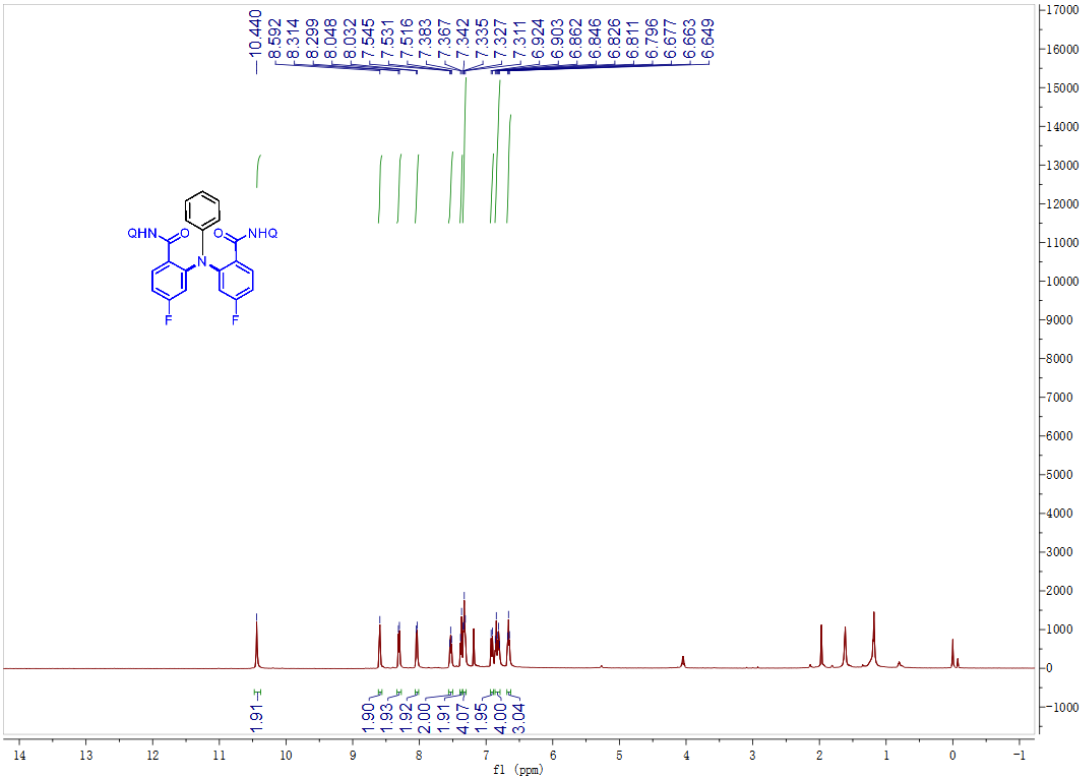
^{13}C NMR (125 MHz, $CDCl_3$) of product **3c**



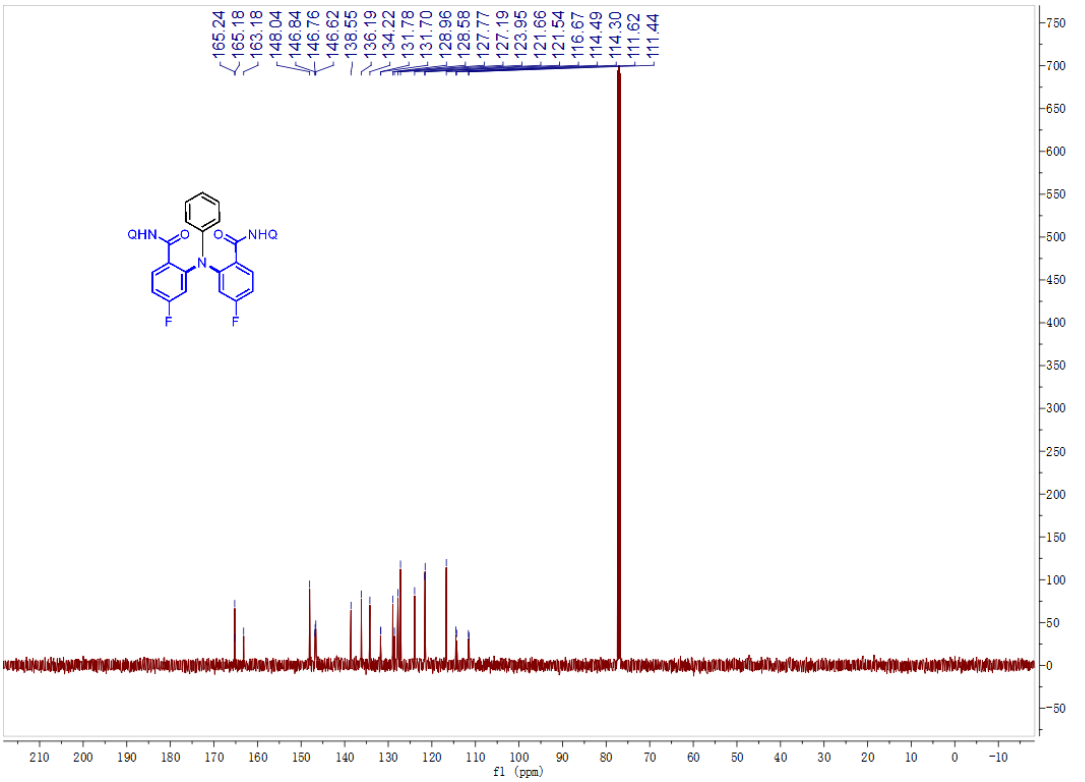
^{1}H NMR (500 MHz, $CDCl_3$) of product **3d**



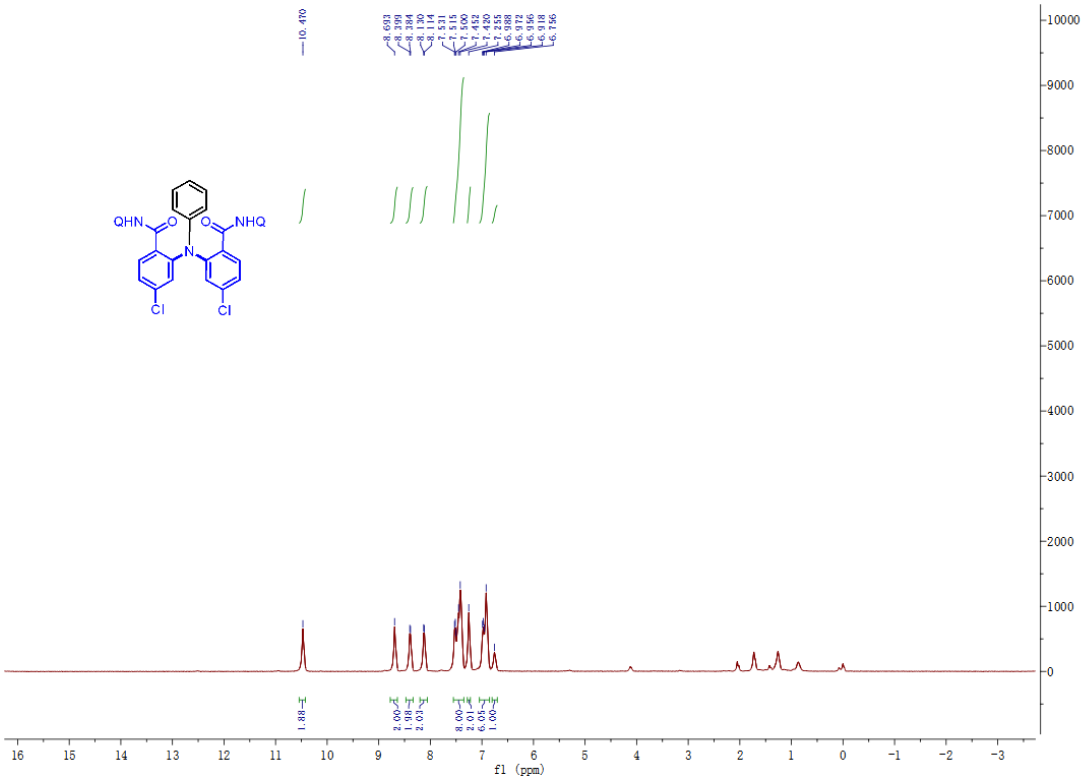
^{13}C NMR (125 MHz, $CDCl_3$) of product **3d**



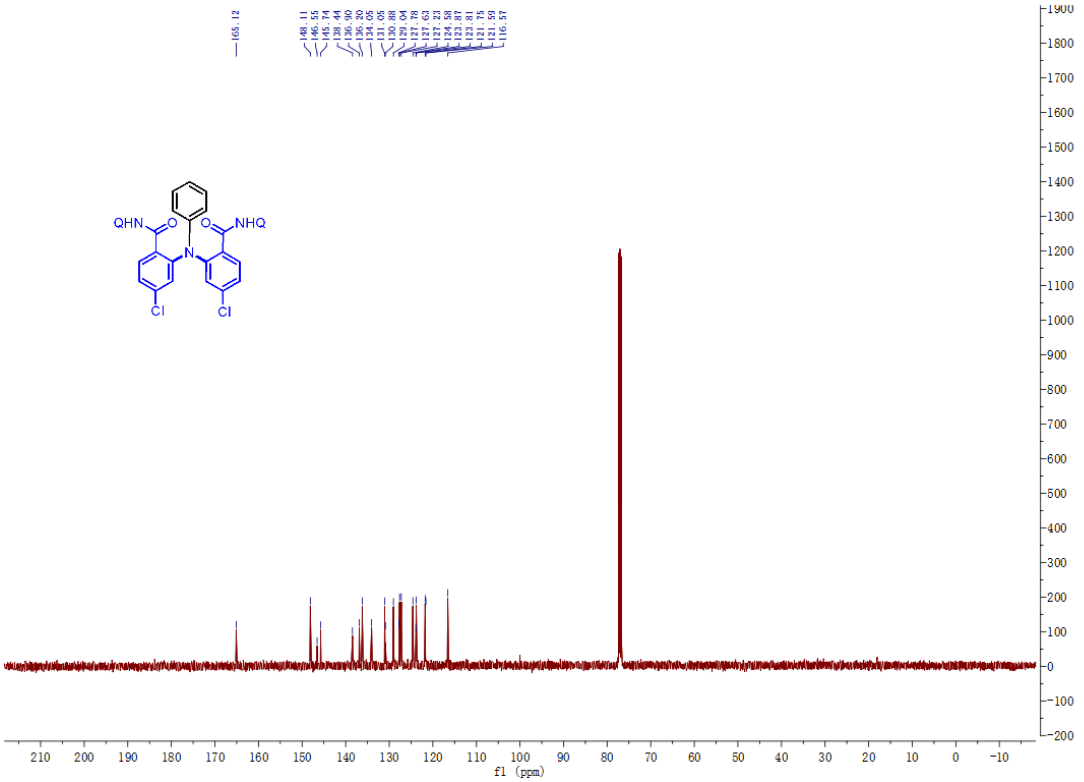
^{1}H NMR (500 MHz, $CDCl_3$) of product **3e**



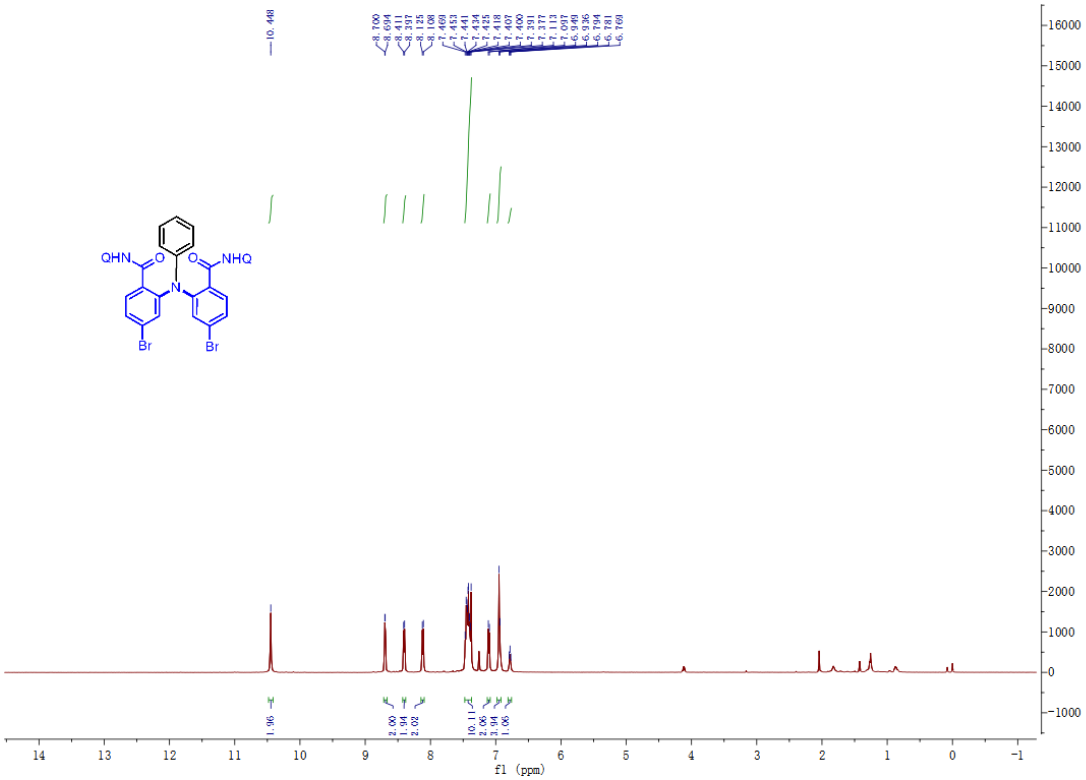
^{13}C NMR (125 MHz, $CDCl_3$) of product **3e**



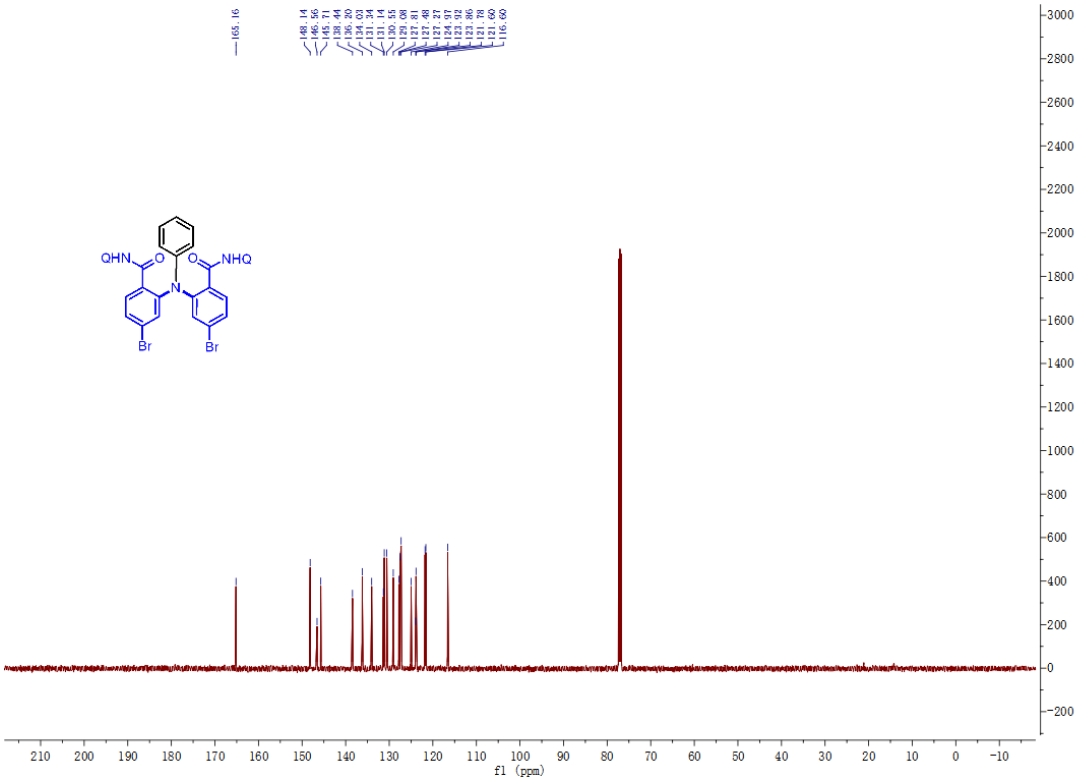
^{1}H NMR (500 MHz, $CDCl_3$) of product **3f**



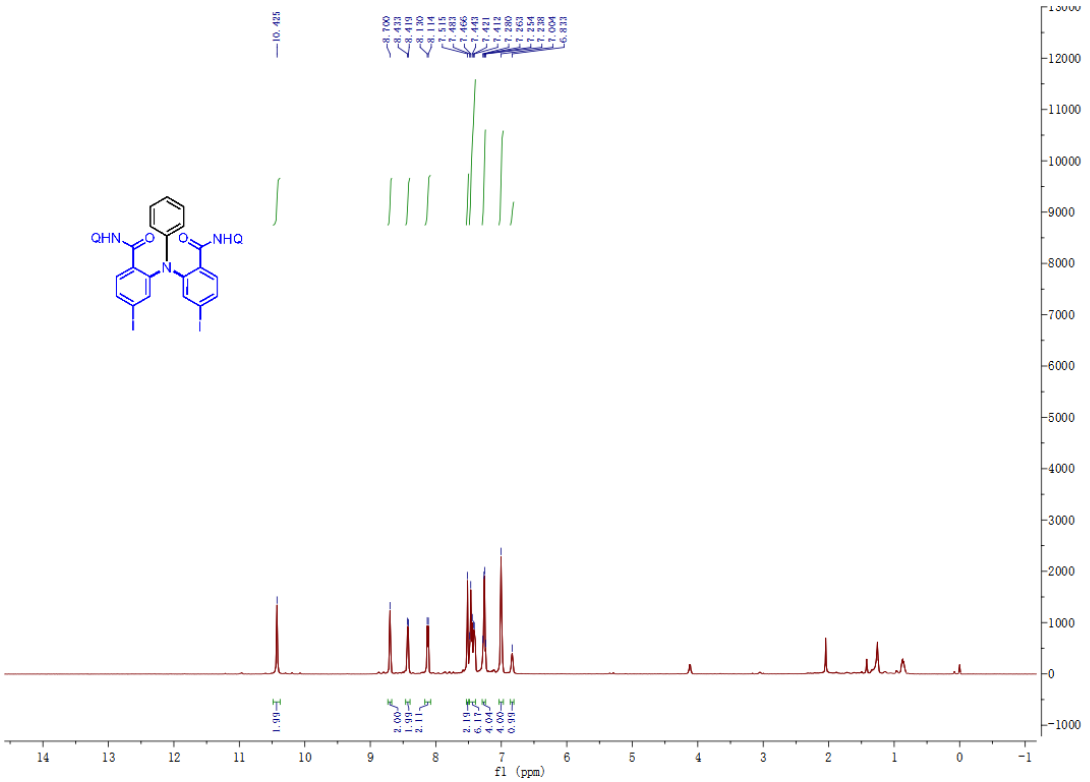
^{13}C NMR (125 MHz, $CDCl_3$) of product **3f**



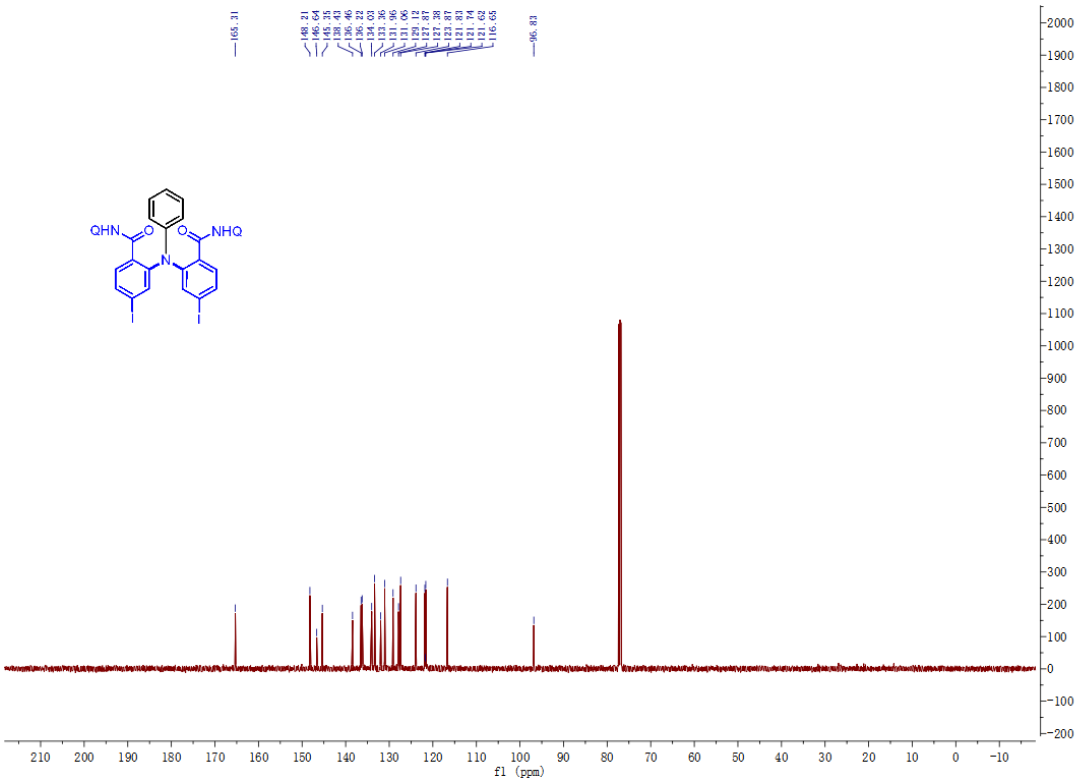
^{1}H NMR (500 MHz, $CDCl_3$) of product **3g**



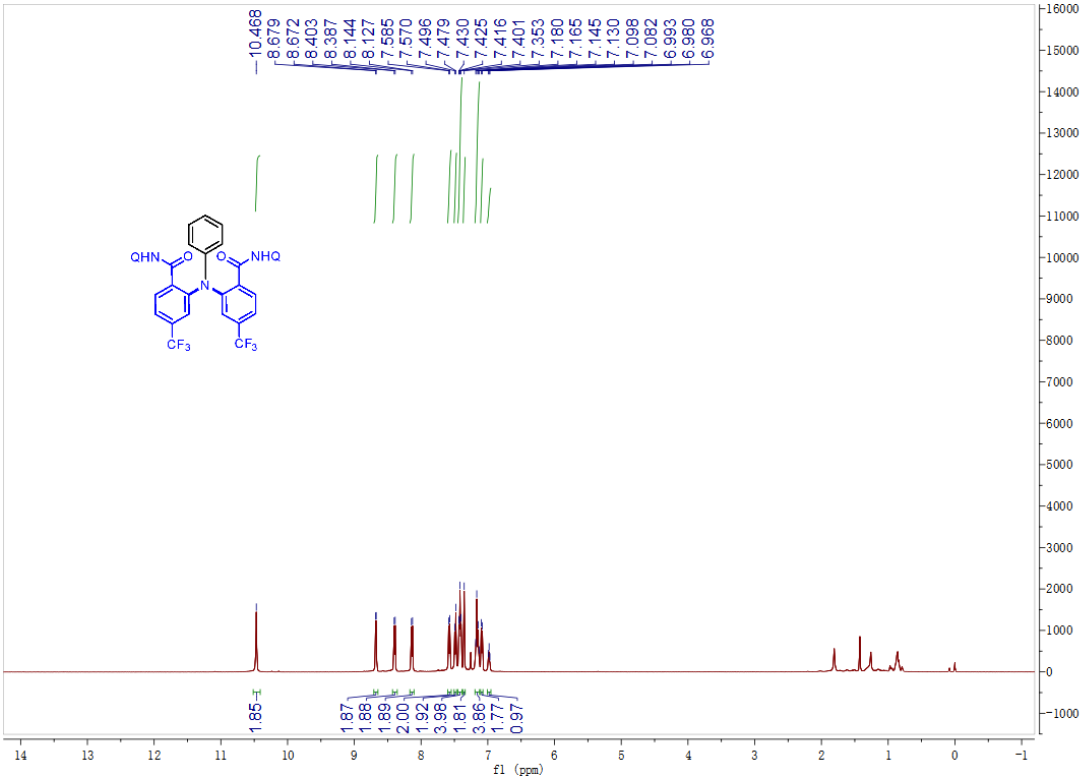
^{13}C NMR (125 MHz, $CDCl_3$) of product **3g**



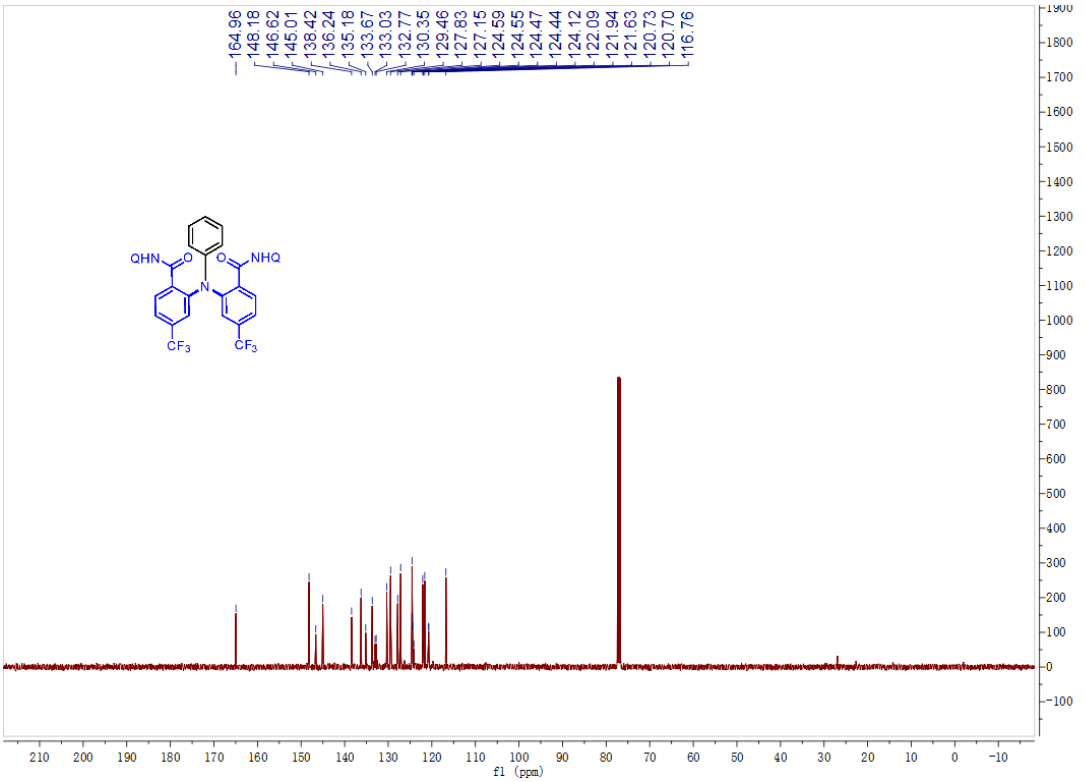
^{1}H NMR (500 MHz, $CDCl_3$) of product **3h**



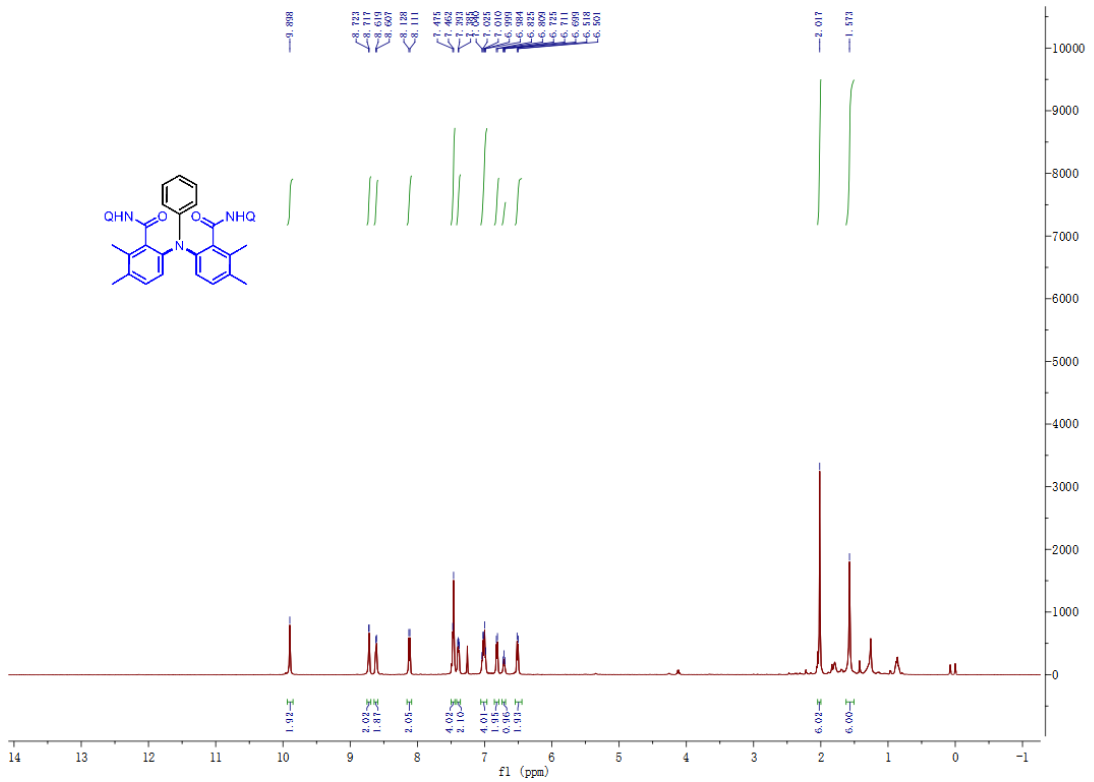
^{13}C NMR (125 MHz, $CDCl_3$) of product **3h**



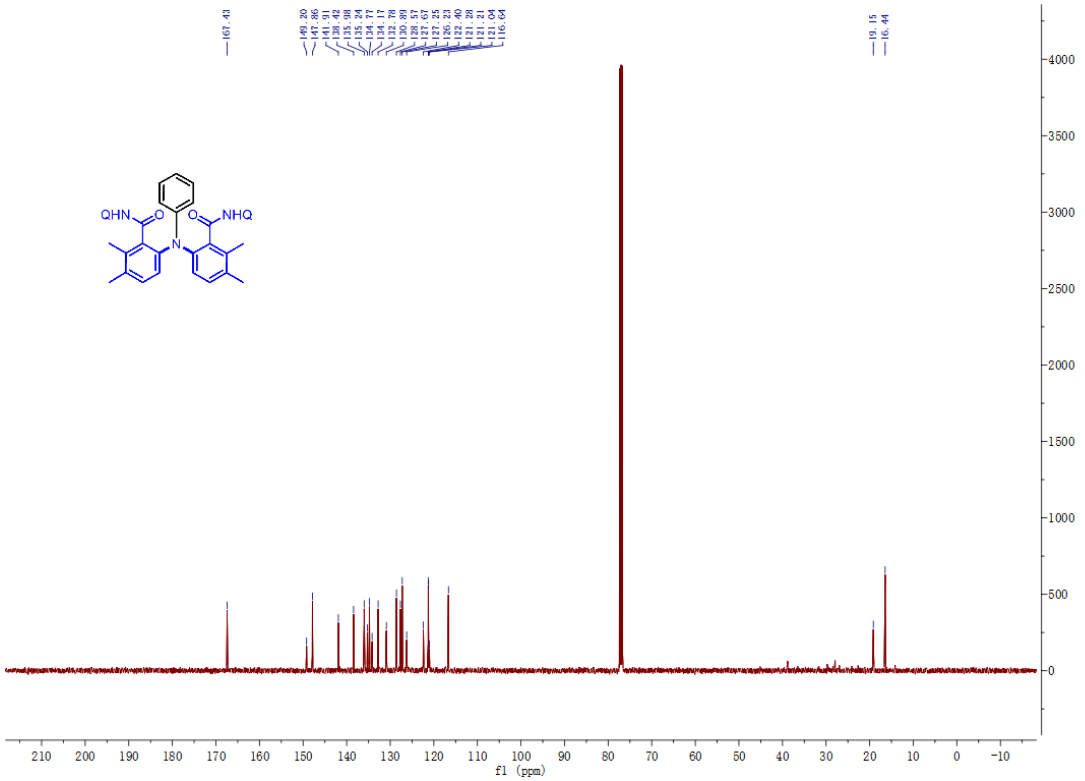
^{1}H NMR (500 MHz, $CDCl_3$) of product **3i**



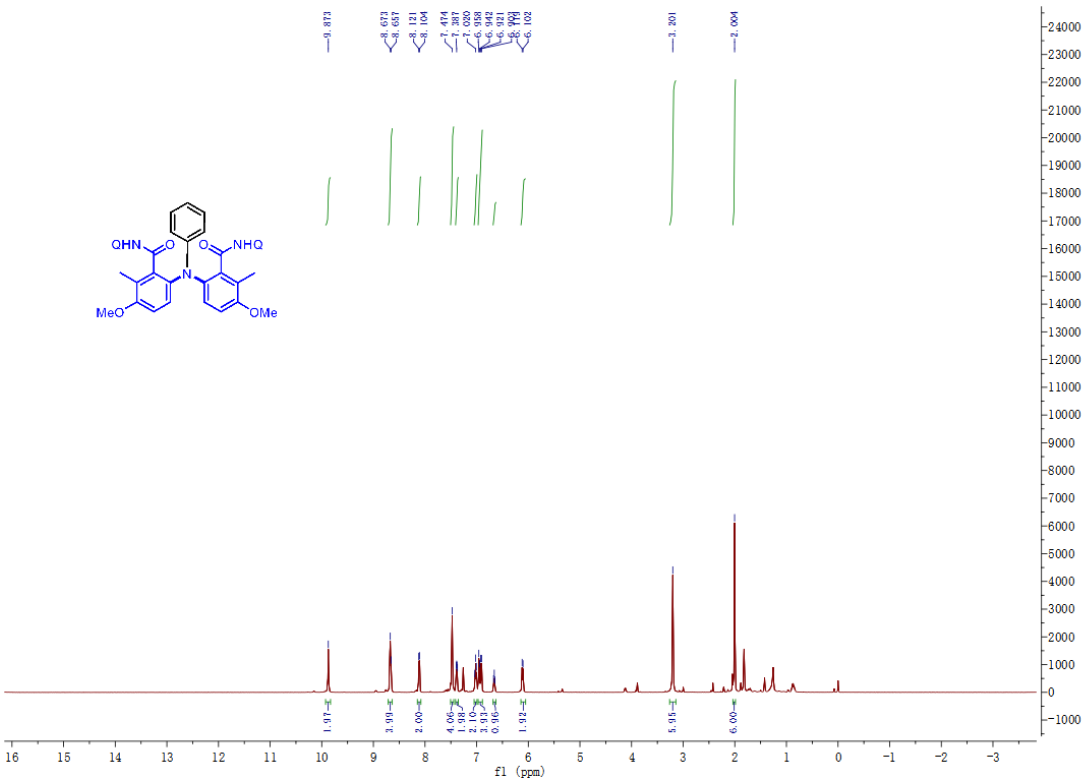
^{13}C NMR (125 MHz, $CDCl_3$) of product **3i**



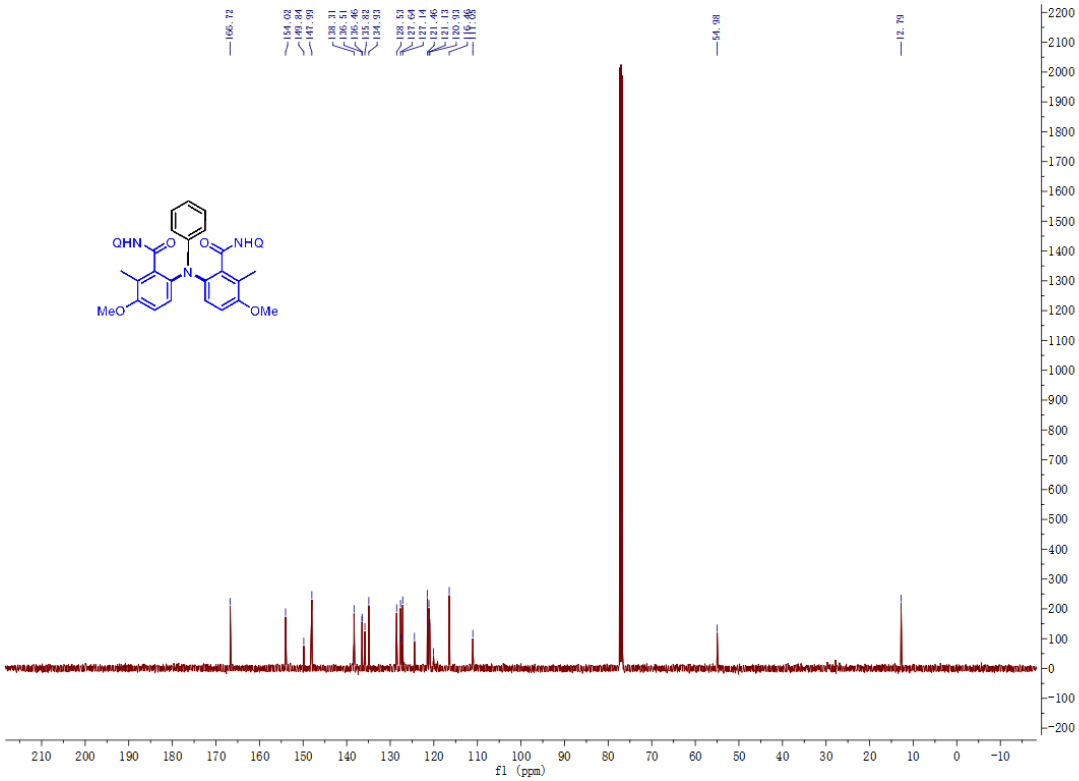
^{1}H NMR (500 MHz, $CDCl_3$) of product **3j**



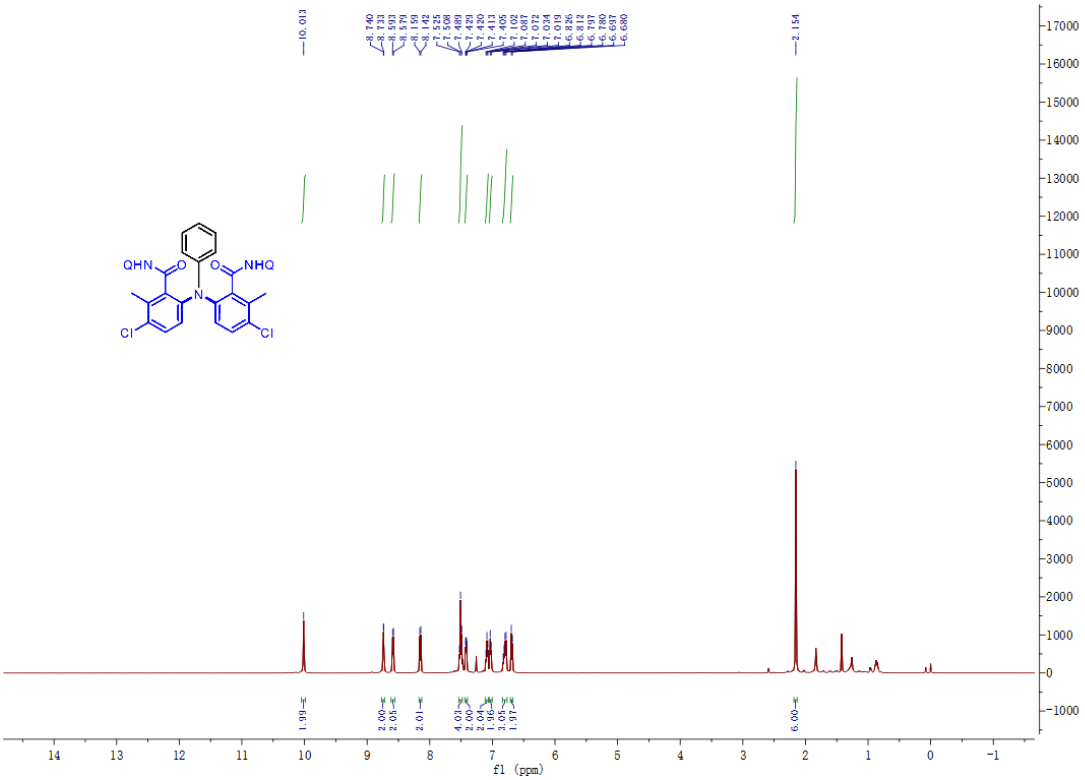
^{13}C NMR (125 MHz, $CDCl_3$) of product **3j**



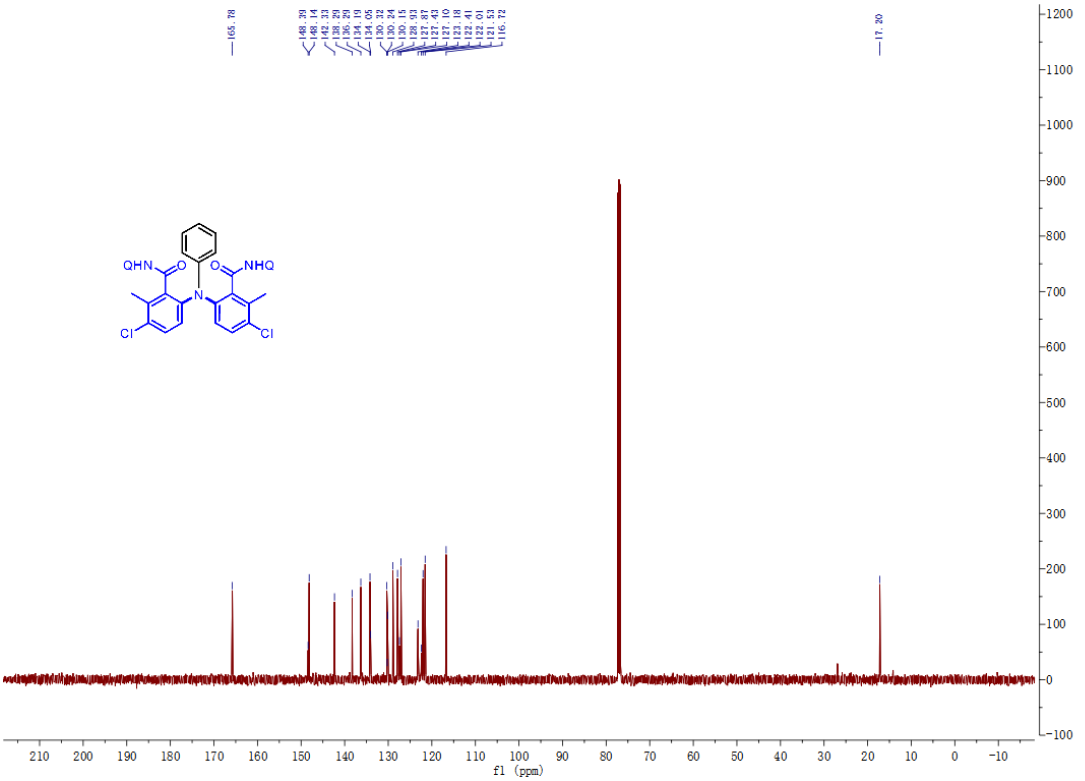
^{1}H NMR (500 MHz, $CDCl_3$) of product **3k**



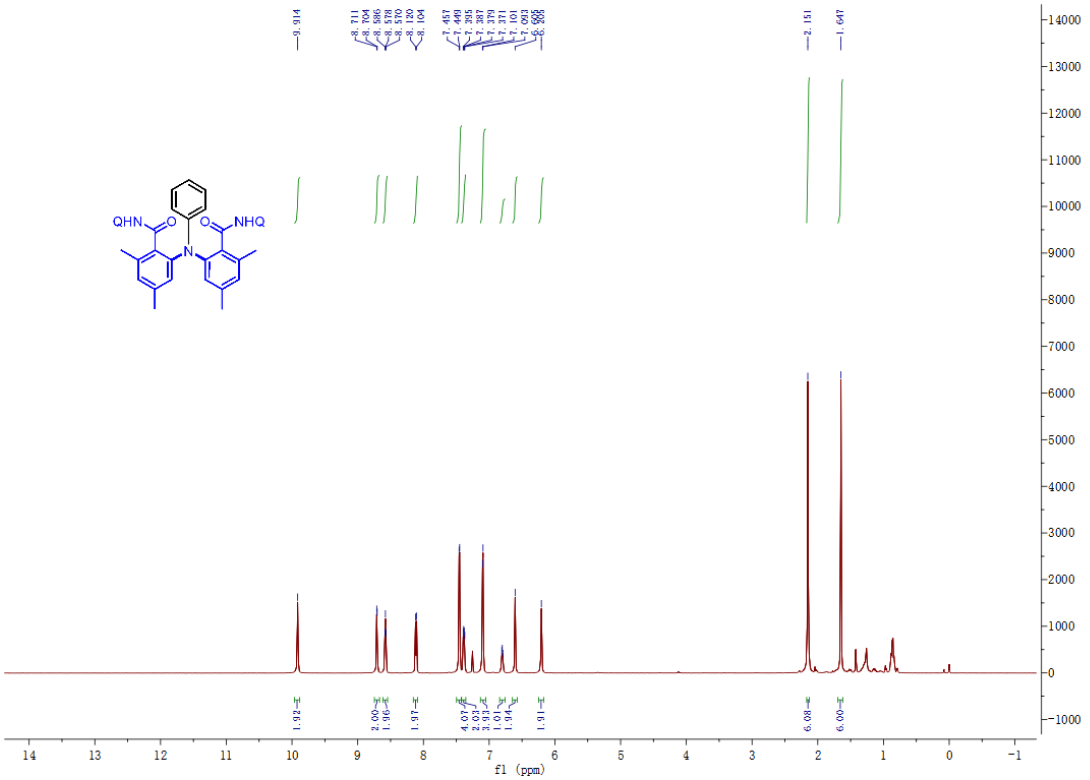
^{13}C NMR (125 MHz, $CDCl_3$) of product **3k**



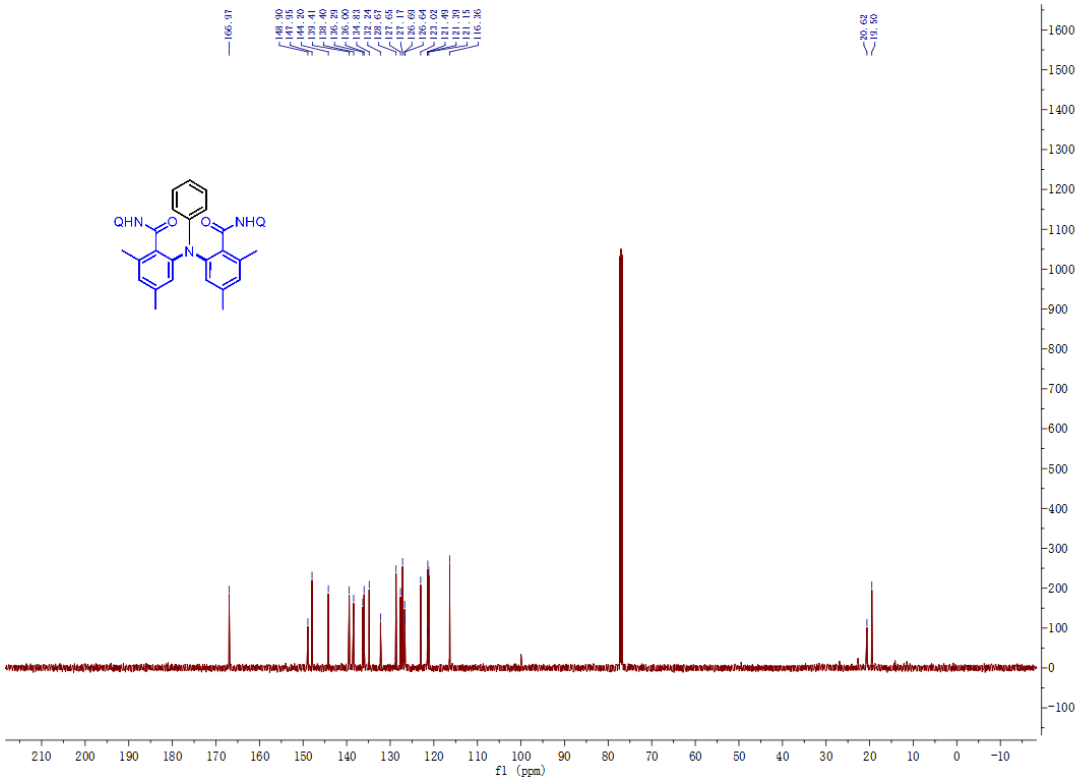
^{1}H NMR (500 MHz, $CDCl_3$) of product **3l**



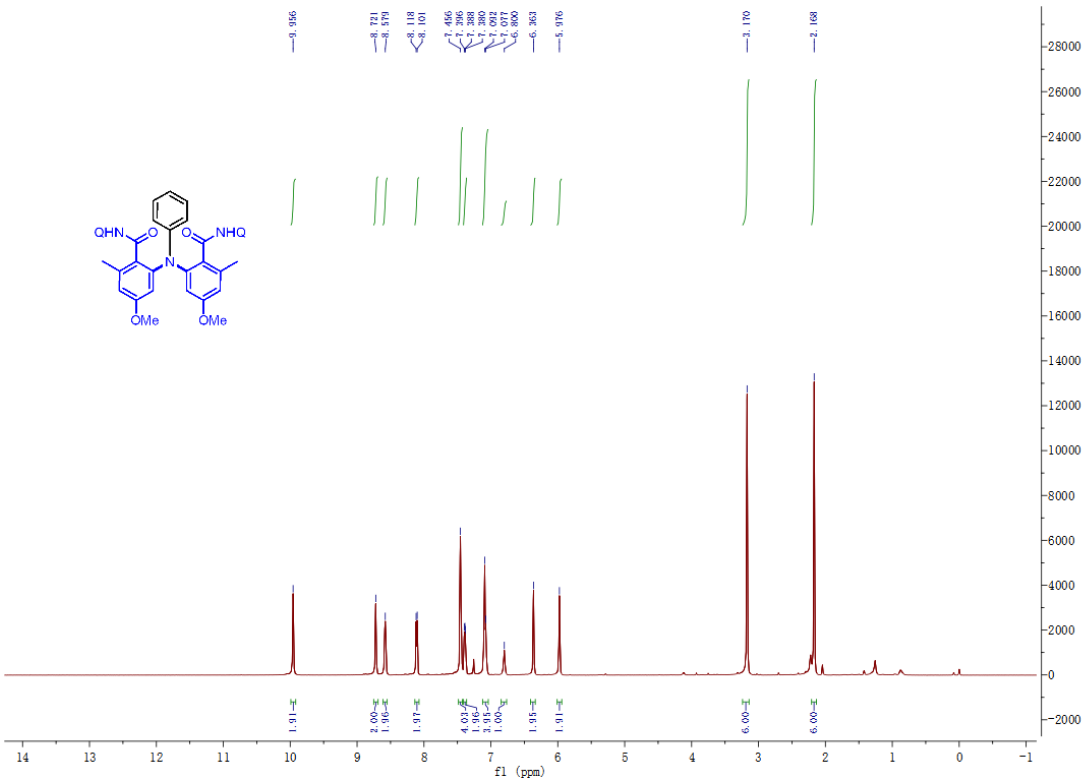
^{13}C NMR (125 MHz, $CDCl_3$) of product **3l**



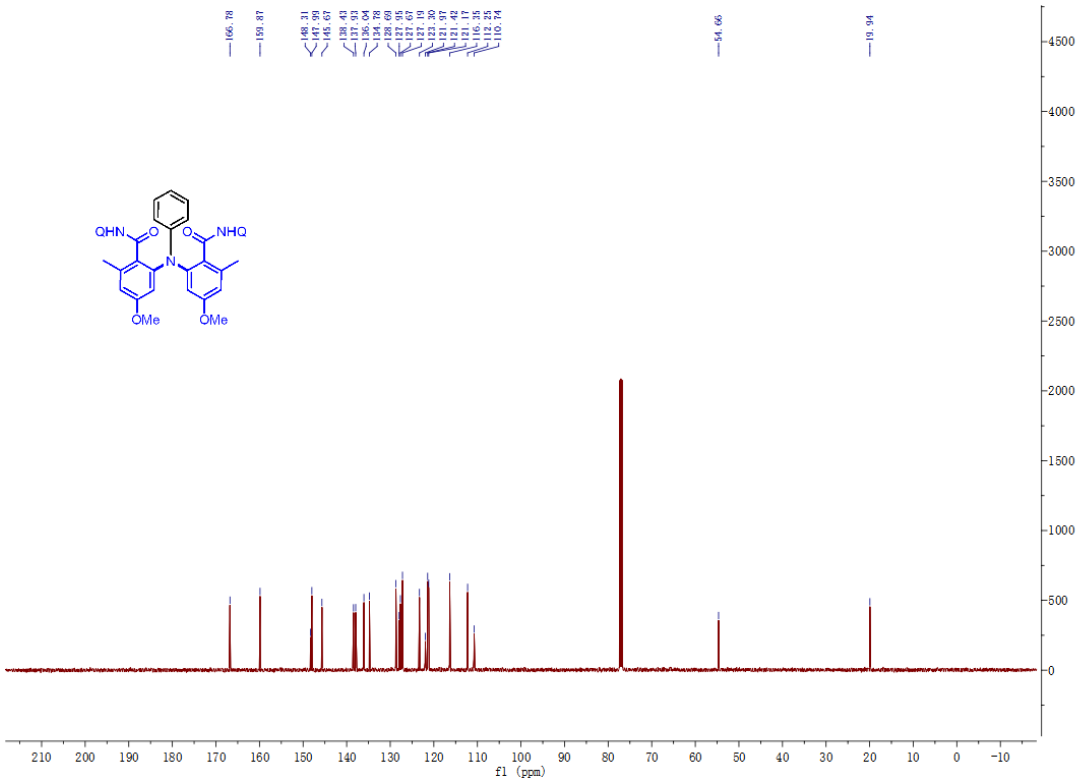
^{1}H NMR (500 MHz, $CDCl_3$) of product **3m**



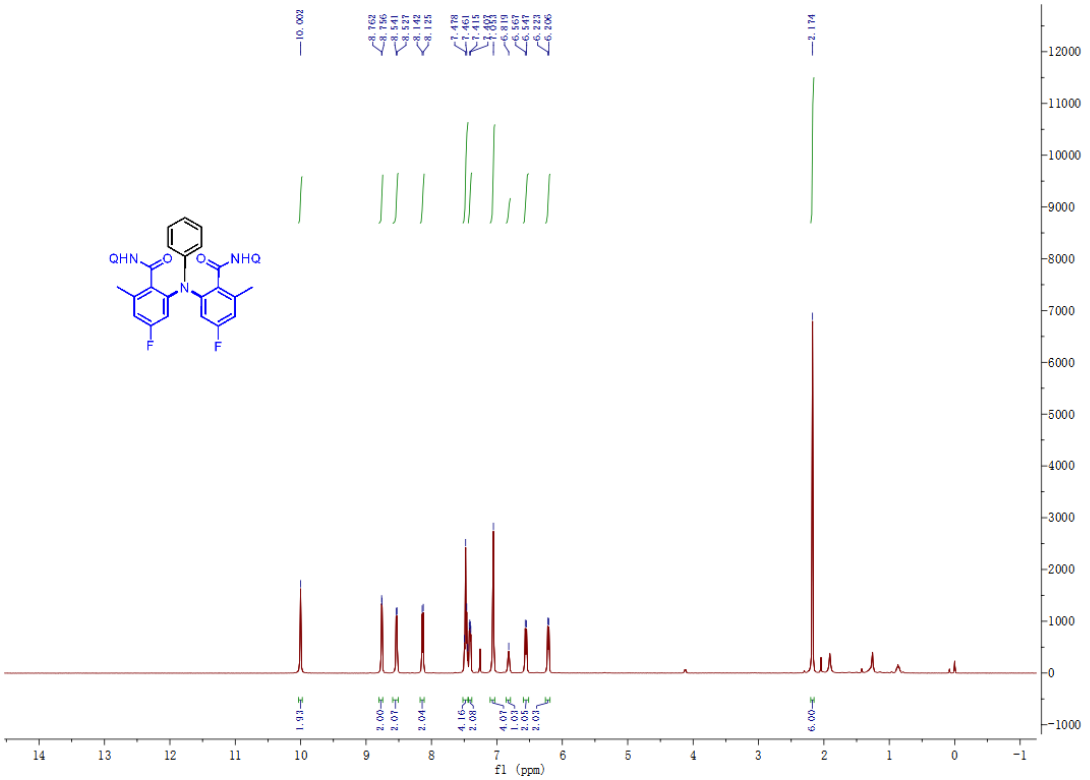
^{13}C NMR (125 MHz, $CDCl_3$) of product **3m**



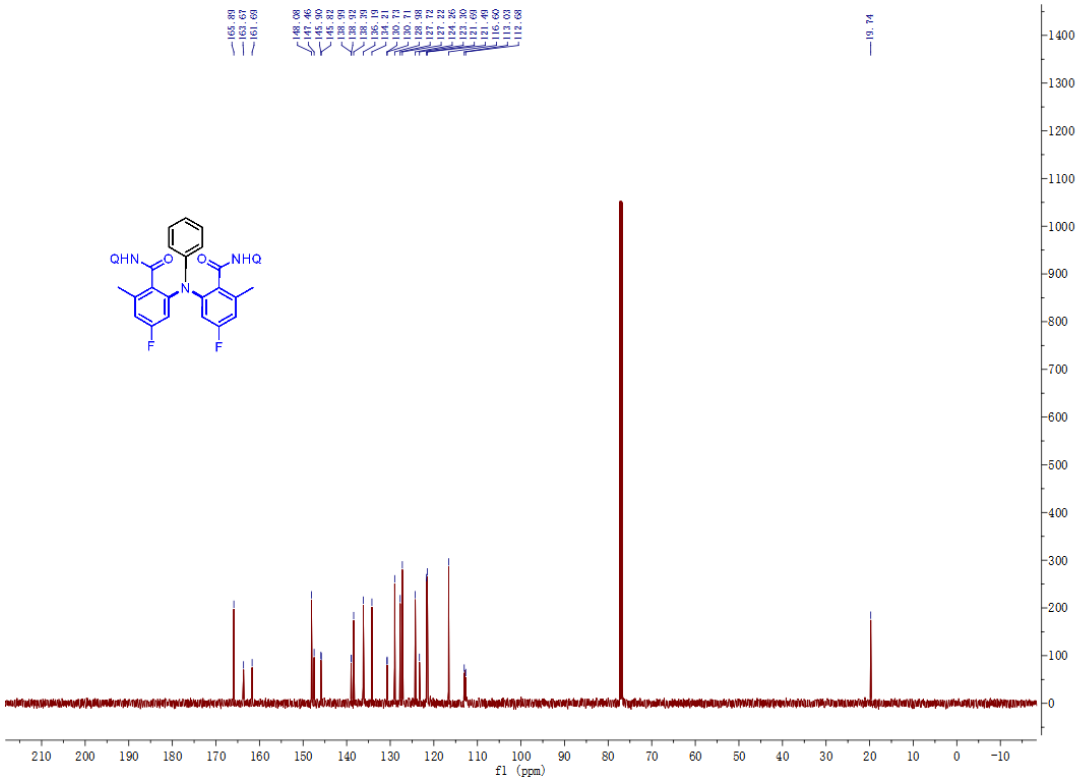
^{1}H NMR (500 MHz, $CDCl_3$) of product **3n**



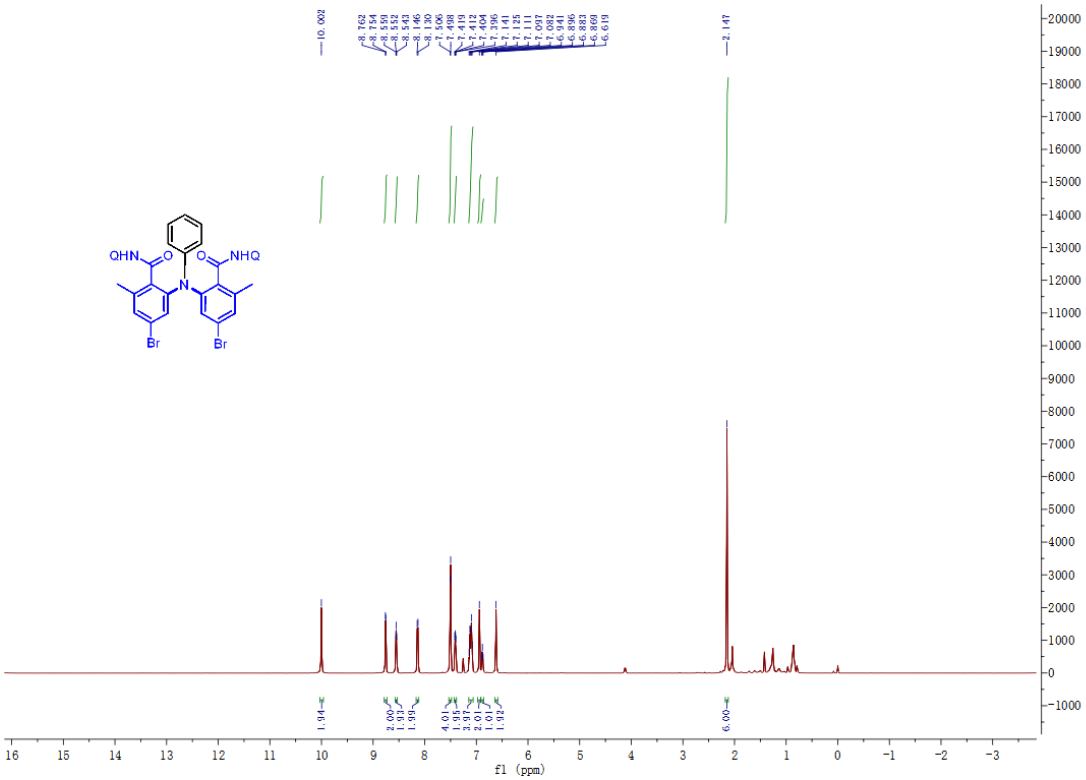
^{13}C NMR (125 MHz, $CDCl_3$) of product **3n**



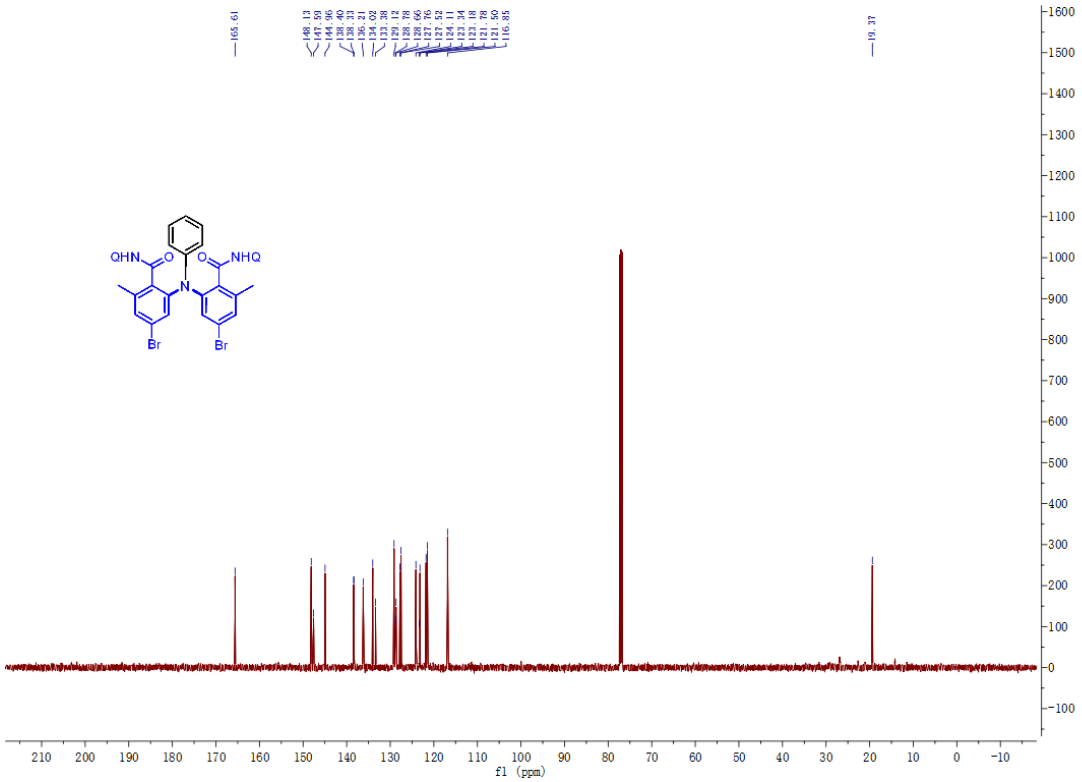
^{1}H NMR (500 MHz, $CDCl_3$) of product **3o**



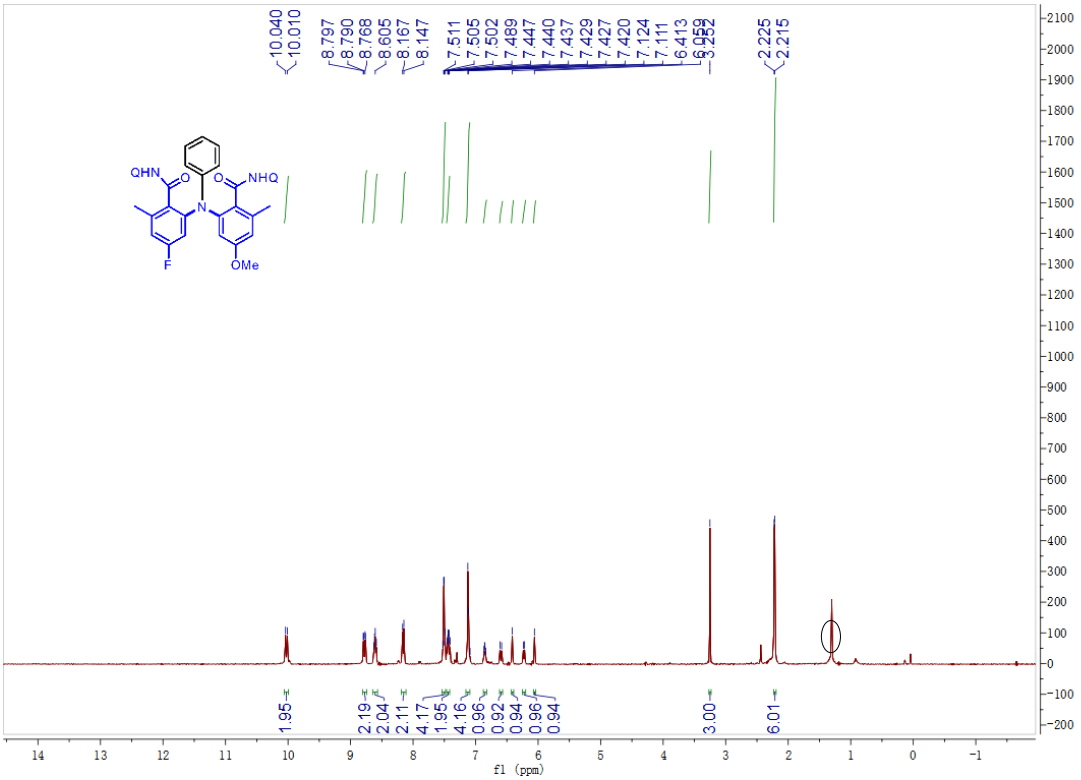
^{13}C NMR (125 MHz, $CDCl_3$) of product **3o**



^{1}H NMR (500 MHz, $CDCl_3$) of product **3p**

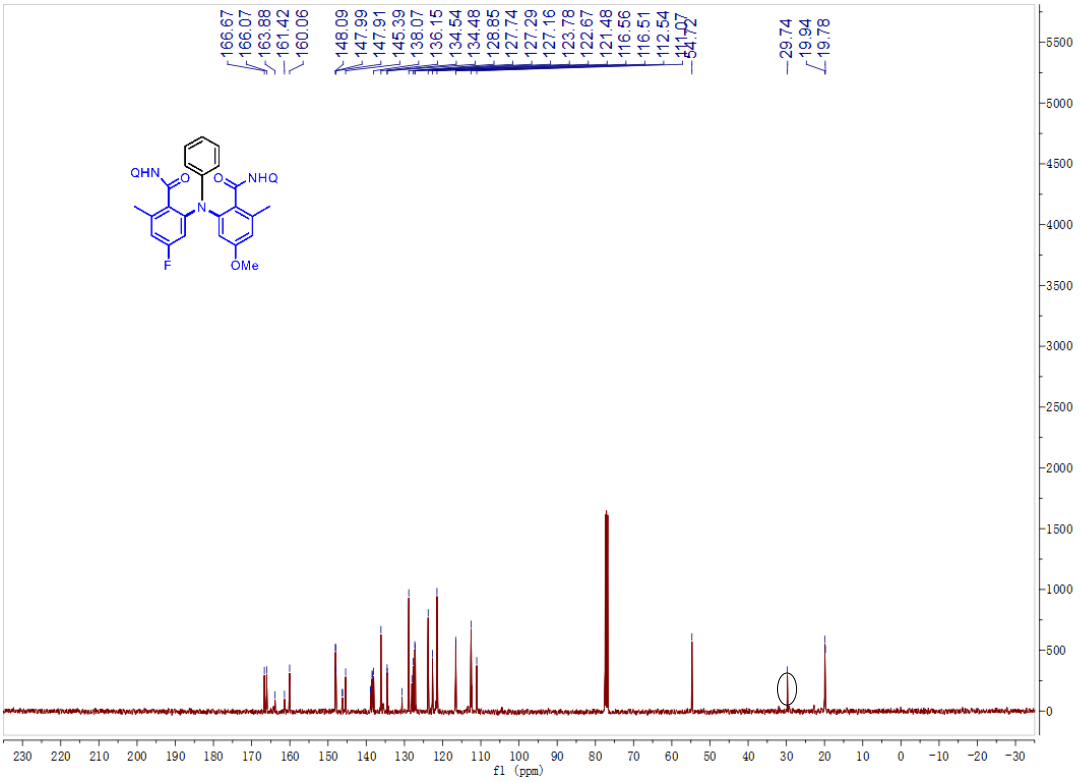


^{13}C NMR (125 MHz, $CDCl_3$) of product **3p**

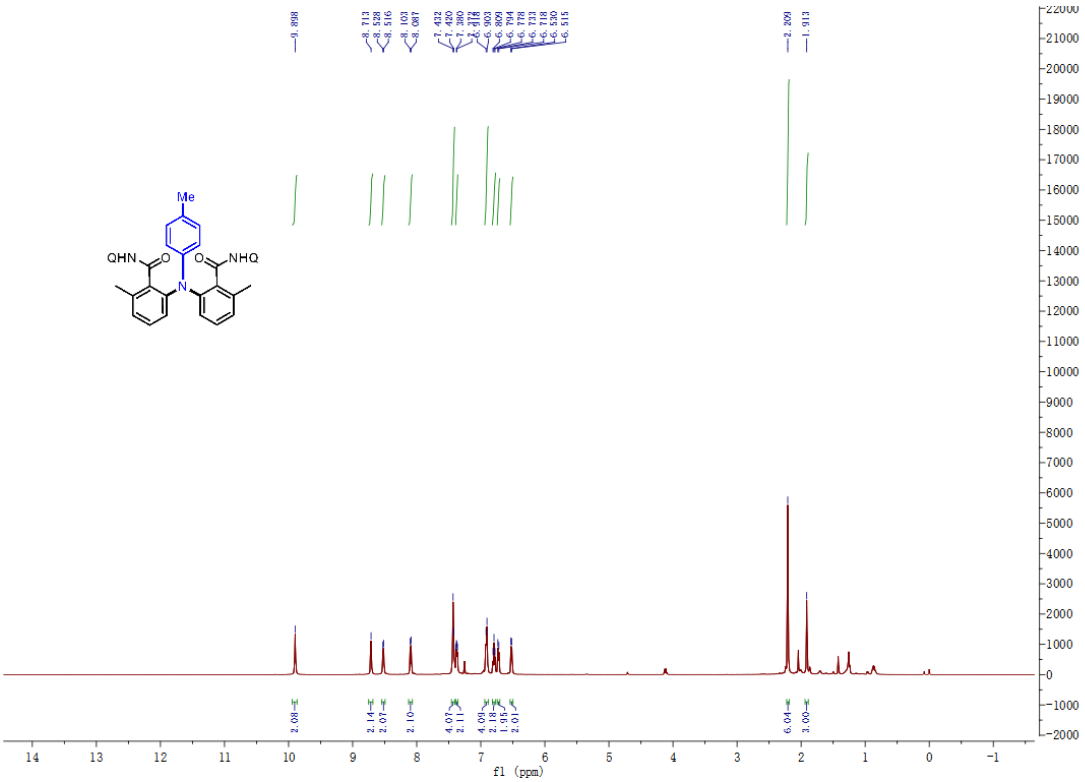


^{1}H NMR (400 MHz, $CDCl_3$) of compound **3q**

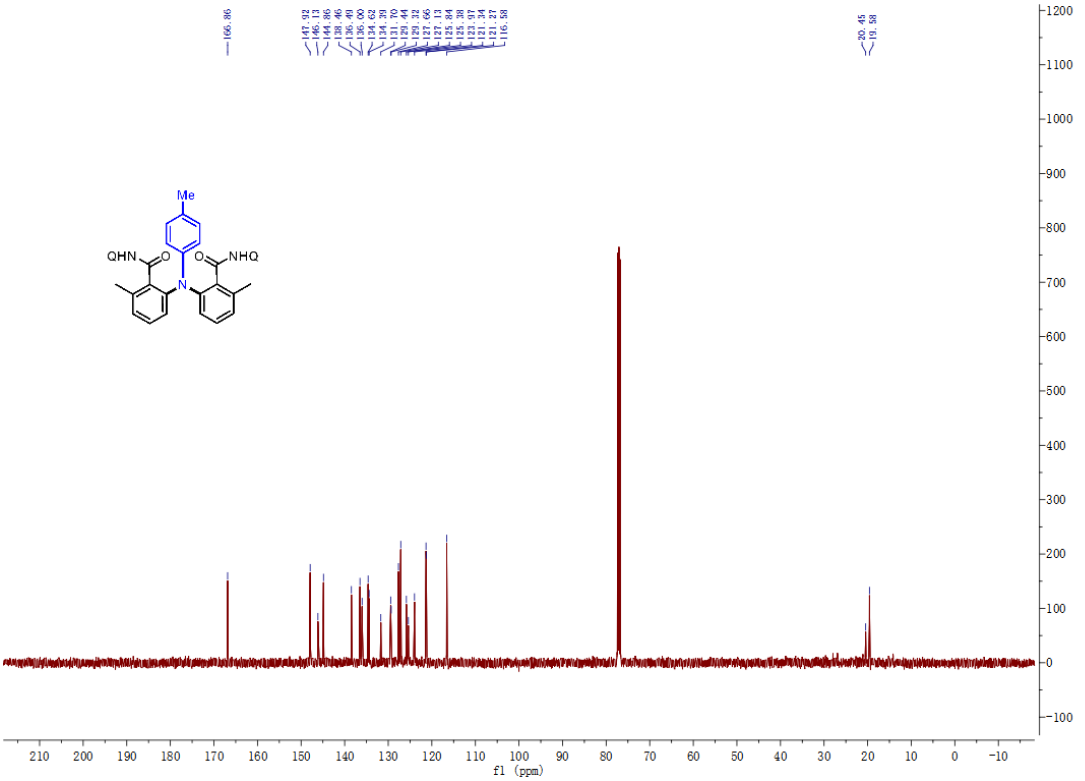
The peak in black oval is the signal of Apiezon grease.



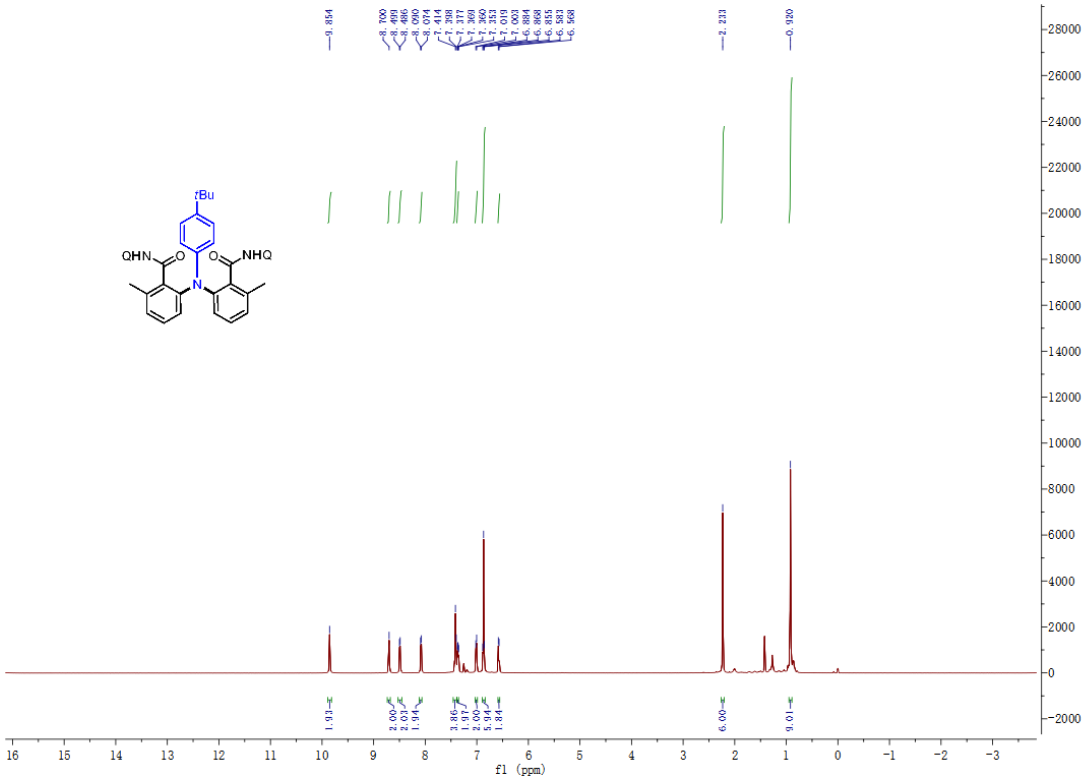
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3q**



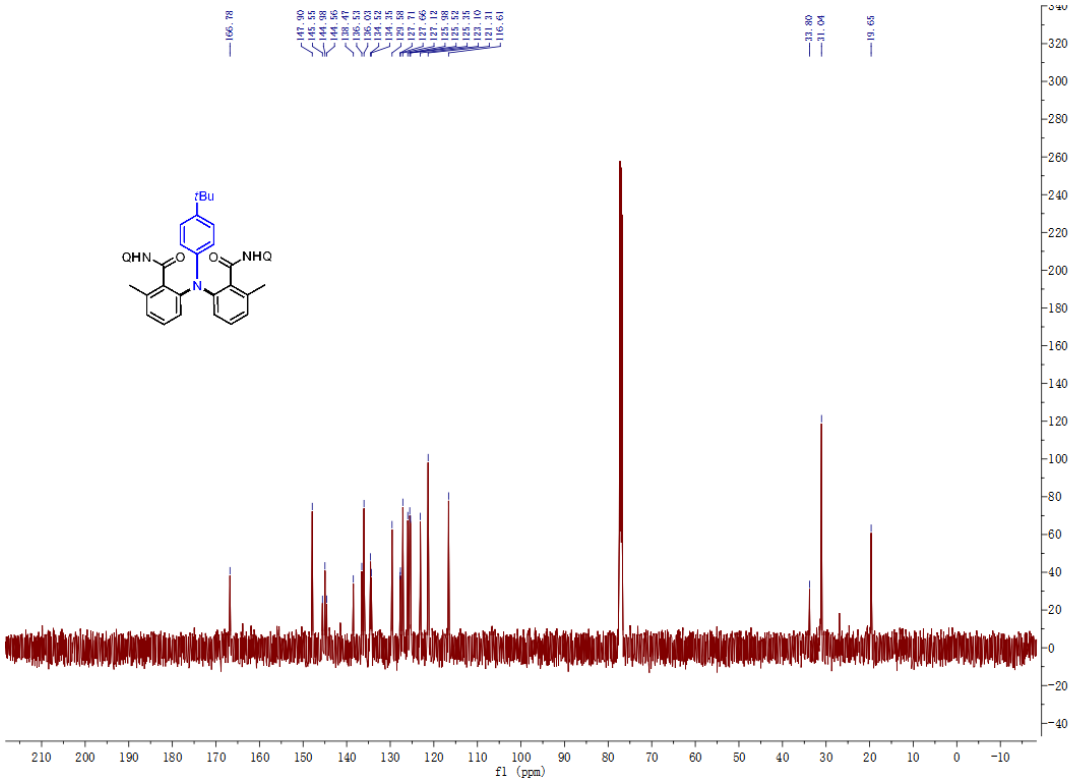
^{1}H NMR (500 MHz, $CDCl_3$) of product **4a**



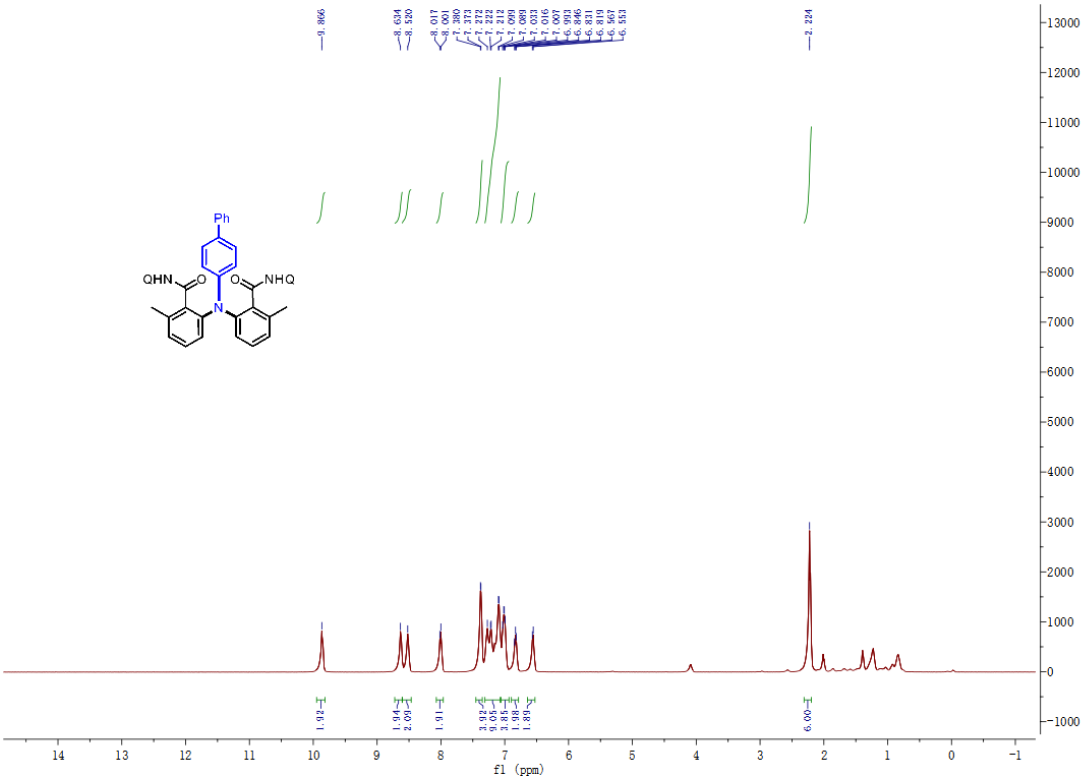
^{13}C NMR (125 MHz, $CDCl_3$) of product **4a**



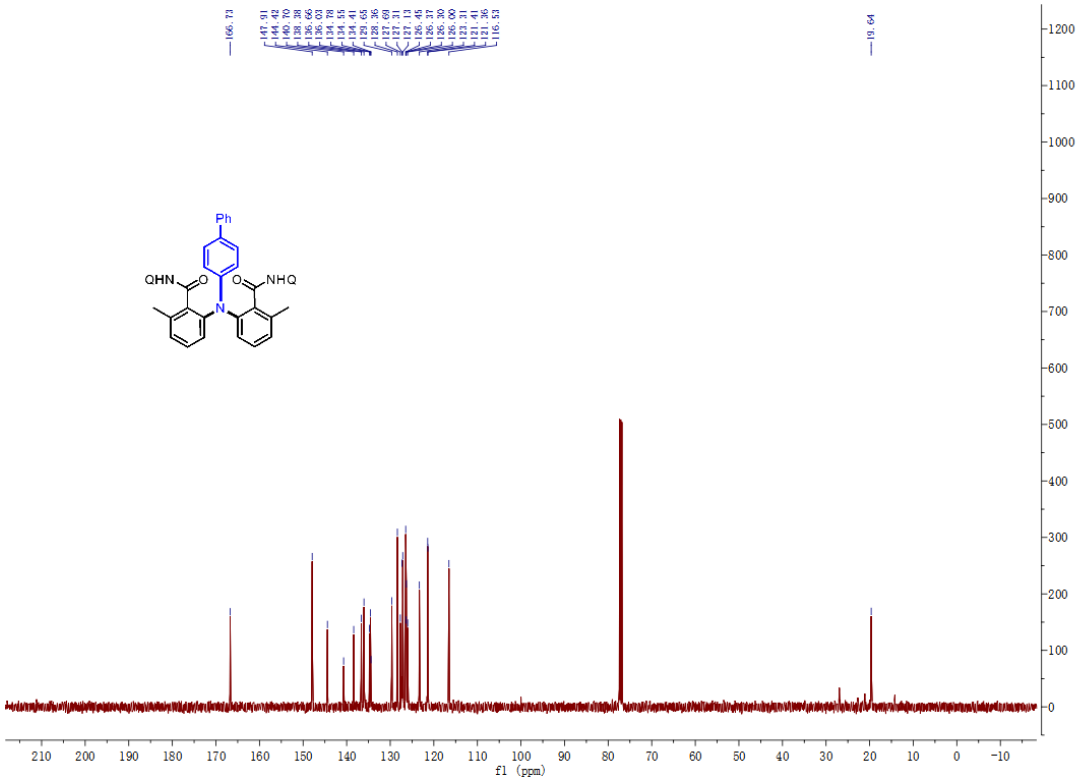
^{1}H NMR (500 MHz, $CDCl_3$) of product **4b**



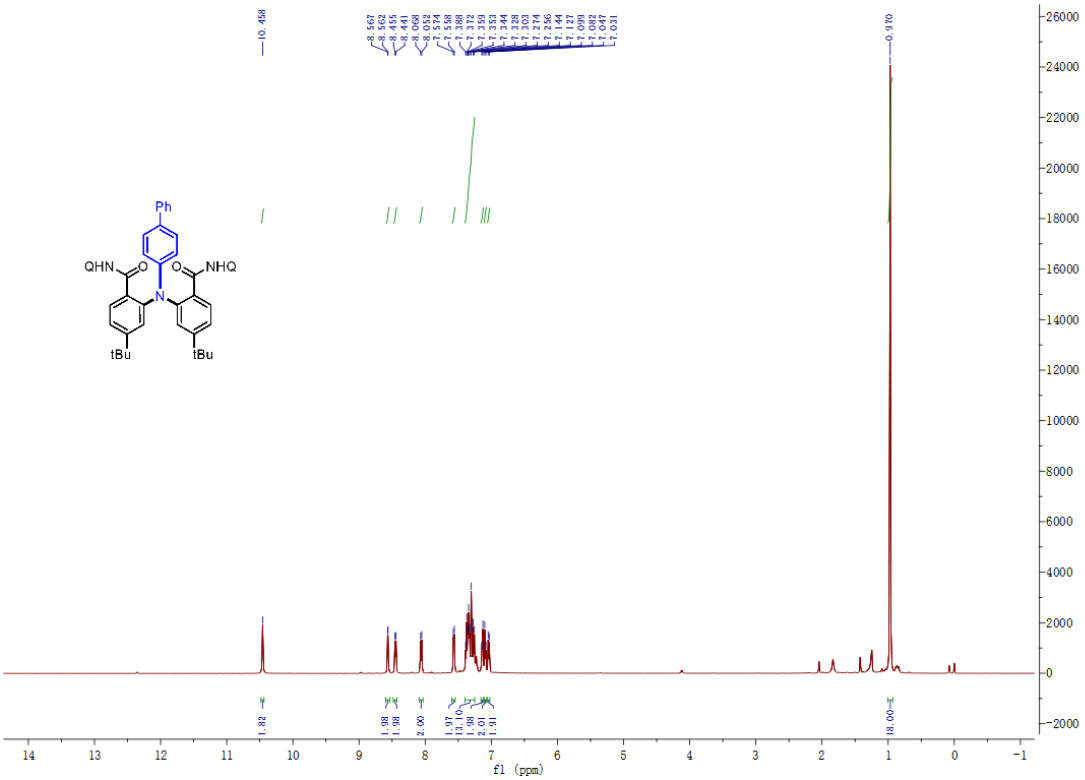
^{13}C NMR (125 MHz, $CDCl_3$) of product **4b**



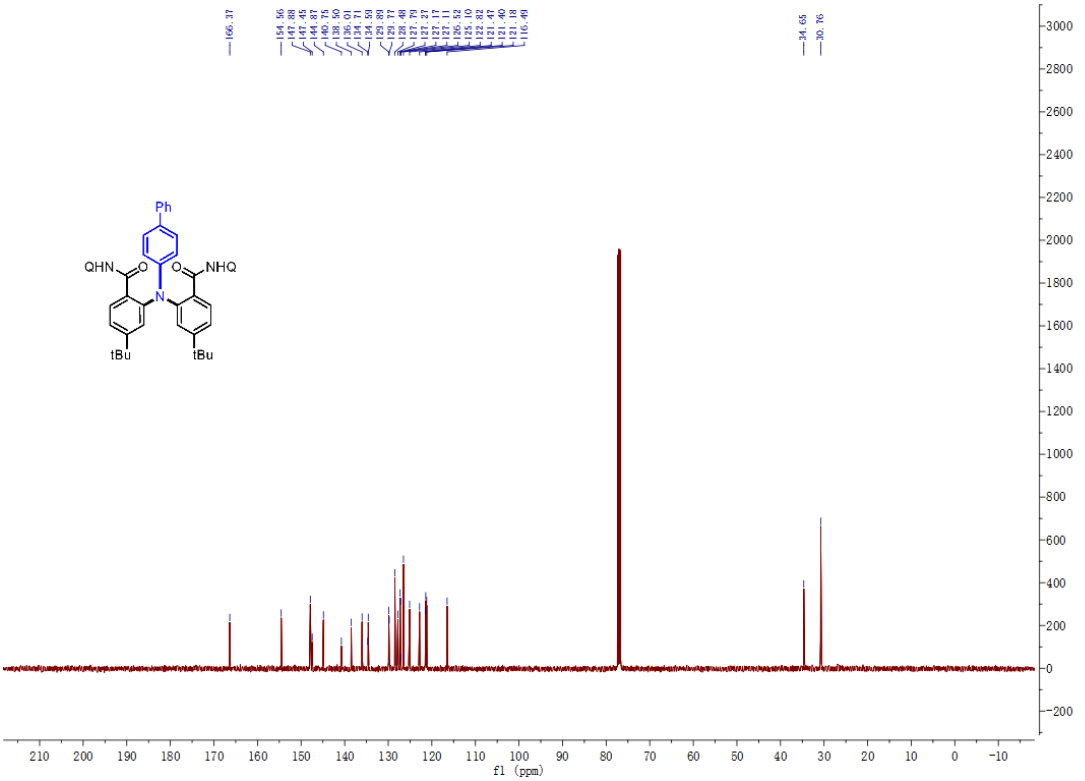
^{1}H NMR (500 MHz, $CDCl_3$) of product **4c**



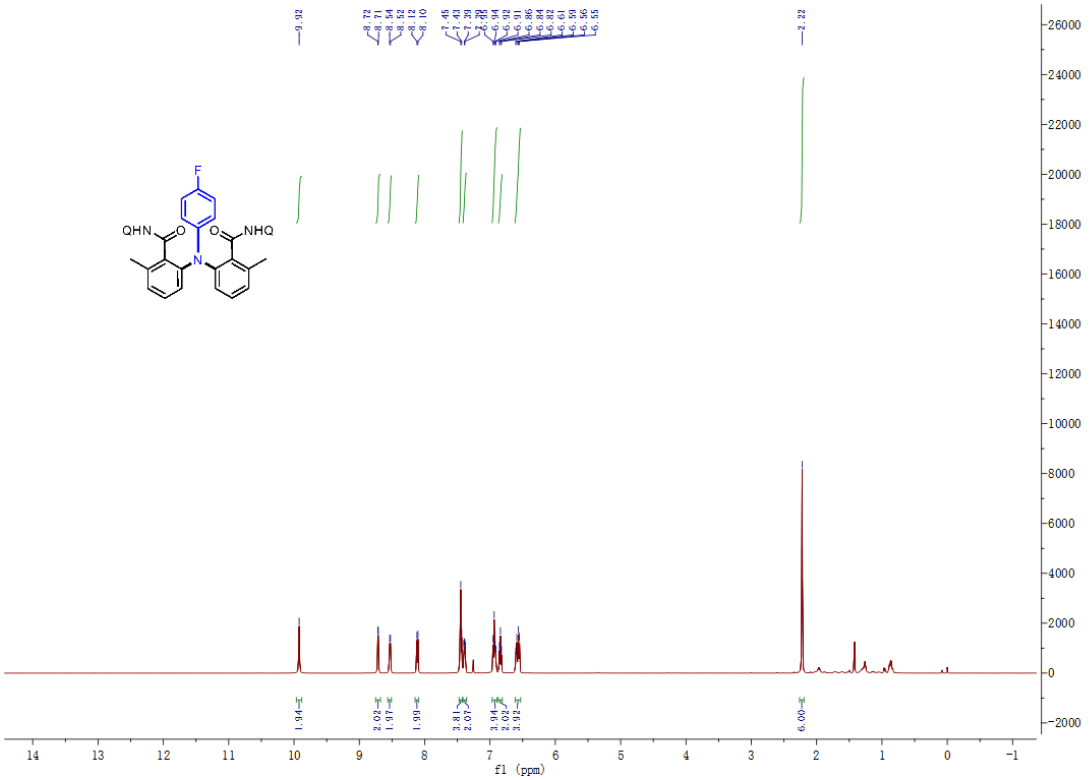
^{13}C NMR (125 MHz, $CDCl_3$) of product **4c**



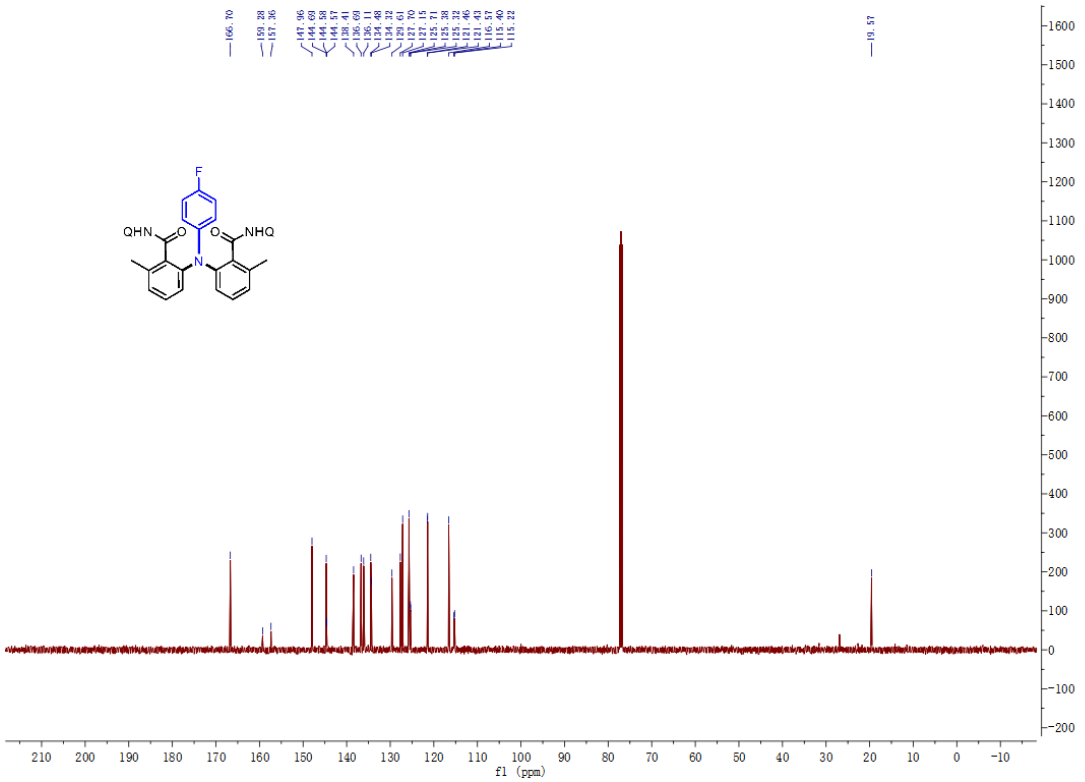
^{1}H NMR (500 MHz, $CDCl_3$) of product **4d**



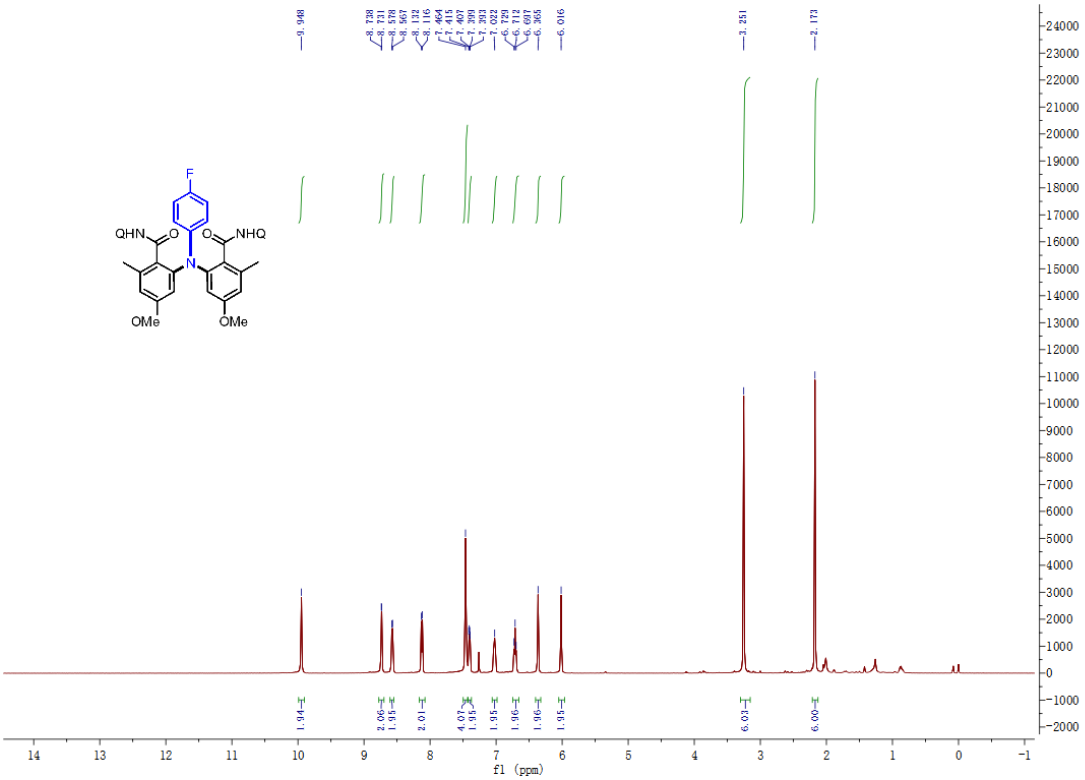
^{13}C NMR (125 MHz, $CDCl_3$) of product **4d**



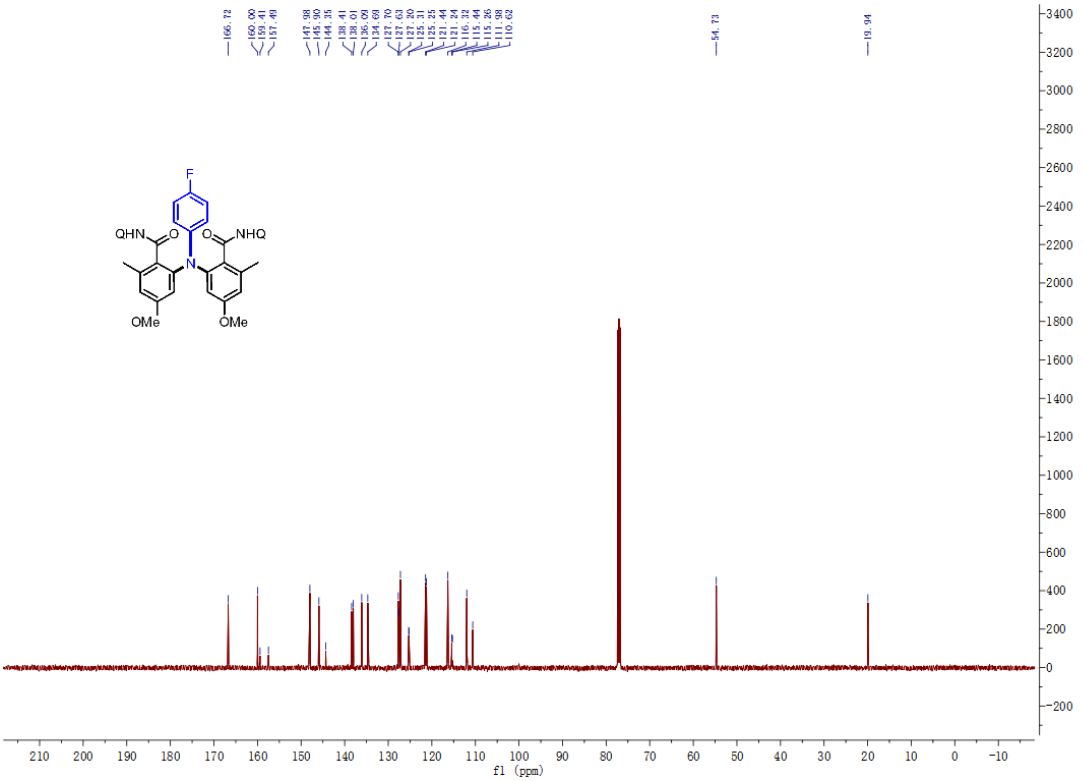
^{1}H NMR (500 MHz, $CDCl_3$) of product **4e**



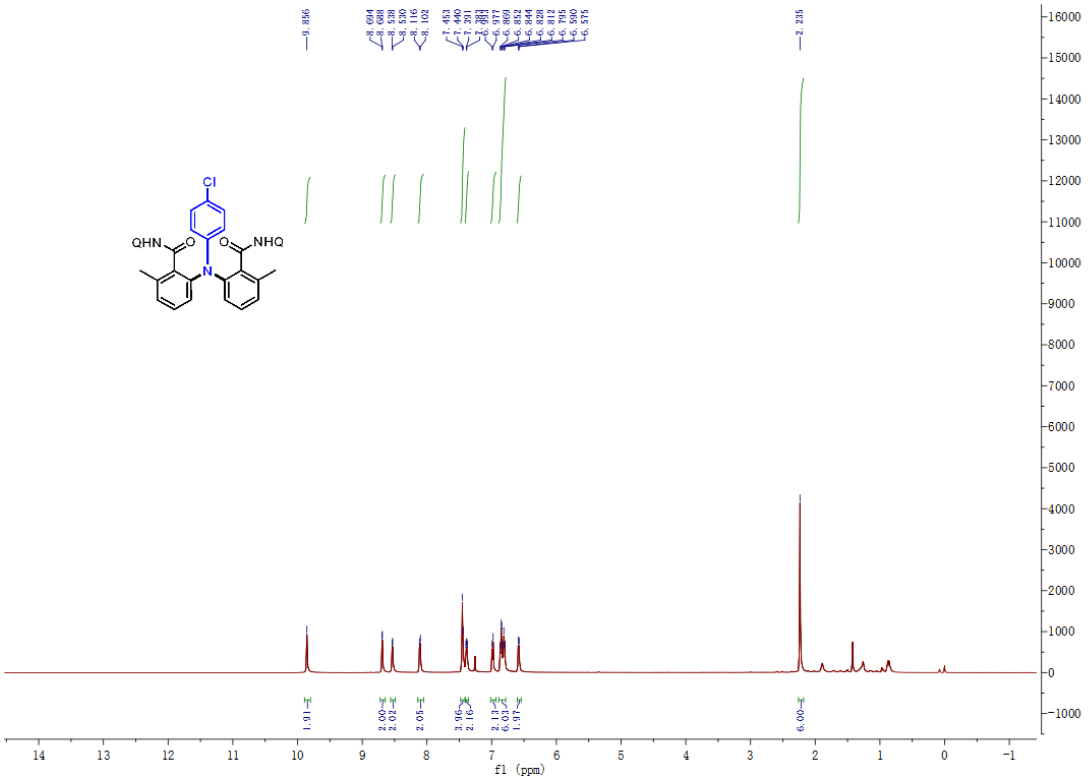
^{13}C NMR (125 MHz, $CDCl_3$) of product **4e**



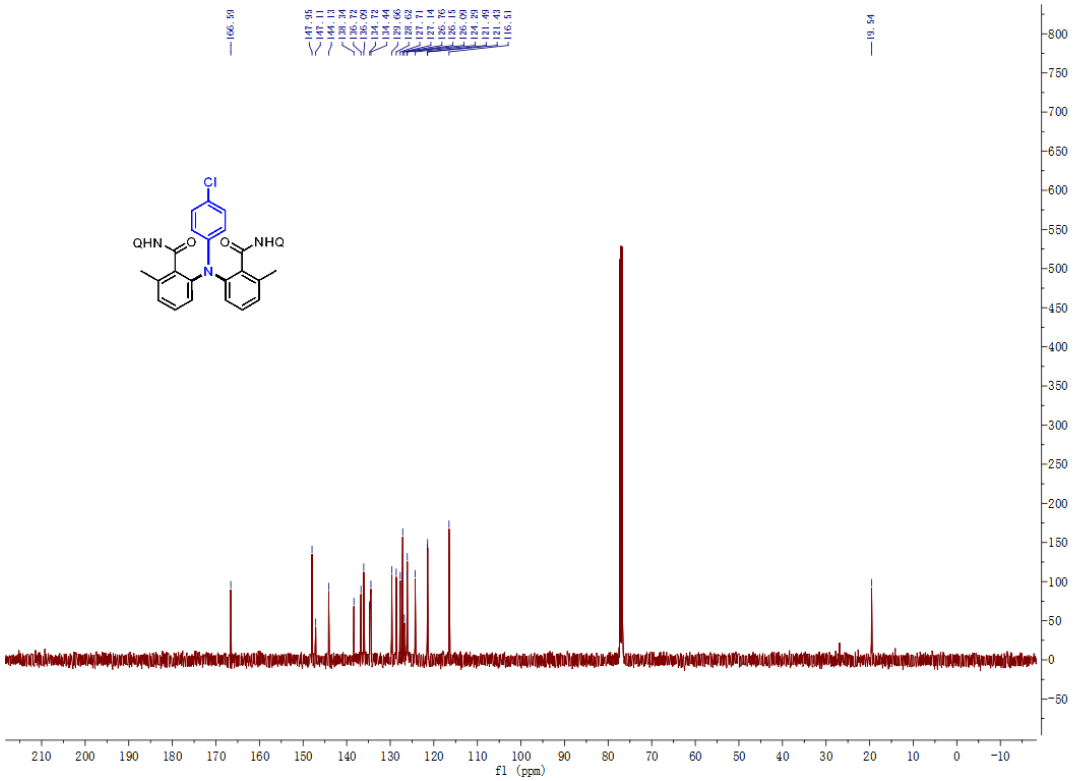
^{1}H NMR (500 MHz, $CDCl_3$) of product **4f**



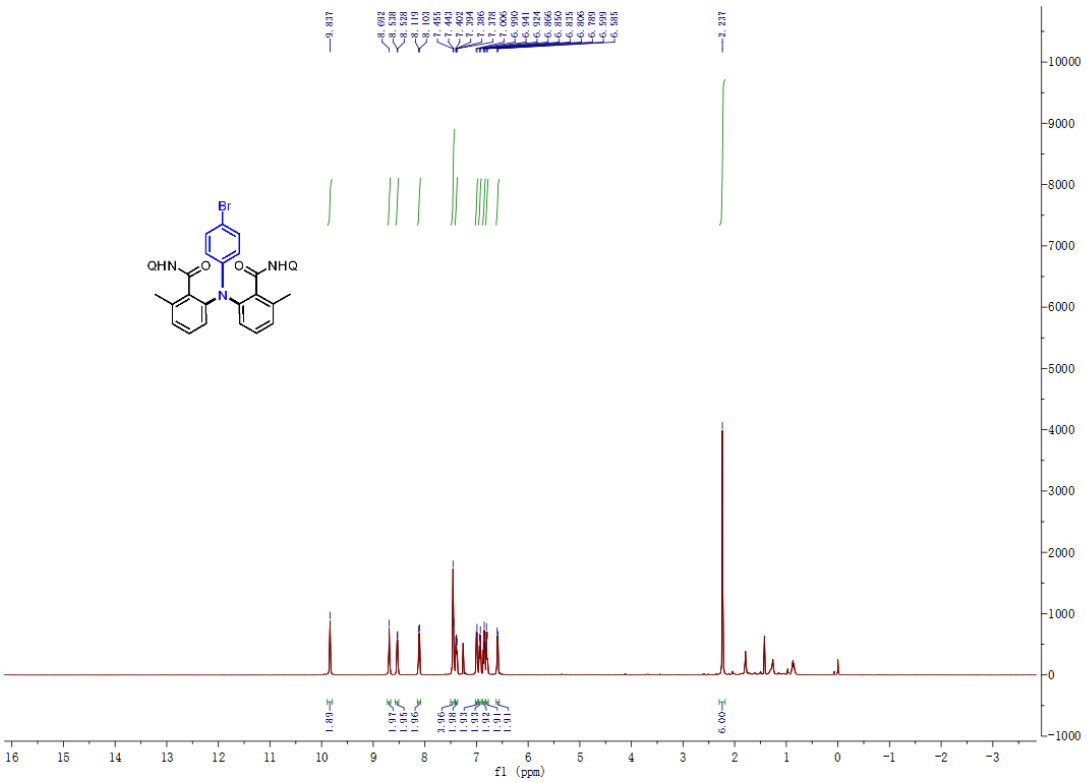
^{13}C NMR (125 MHz, $CDCl_3$) of product **4f**



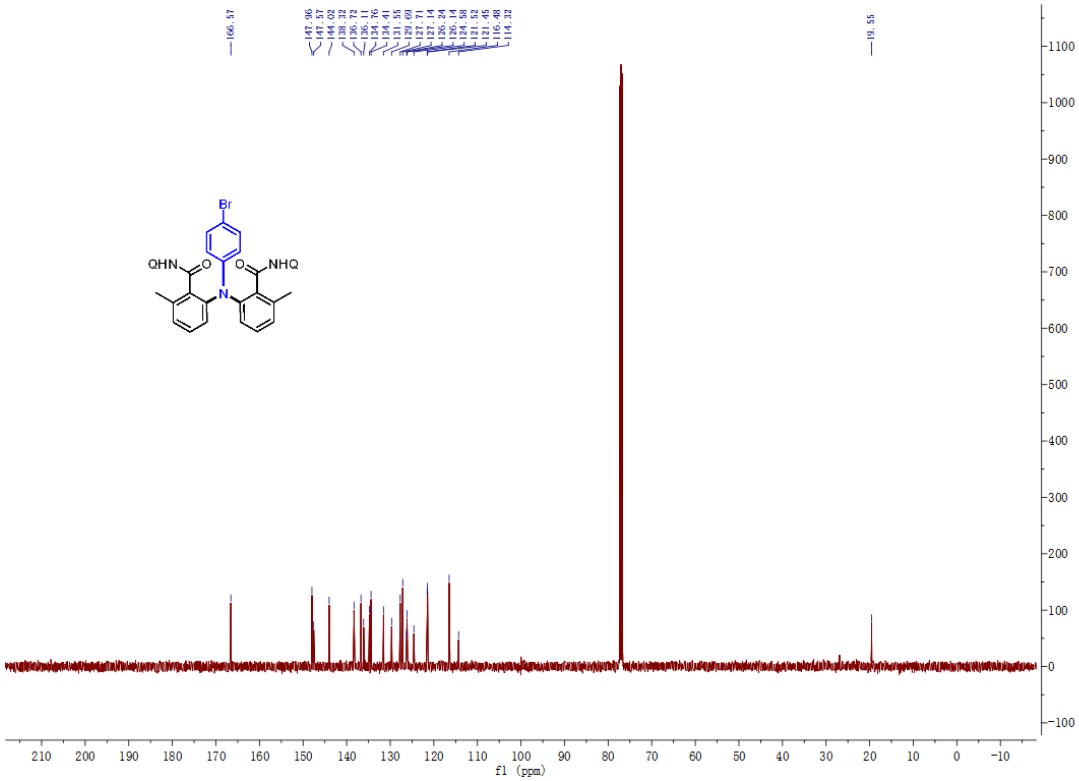
^{1}H NMR (500 MHz, $CDCl_3$) of product **4g**



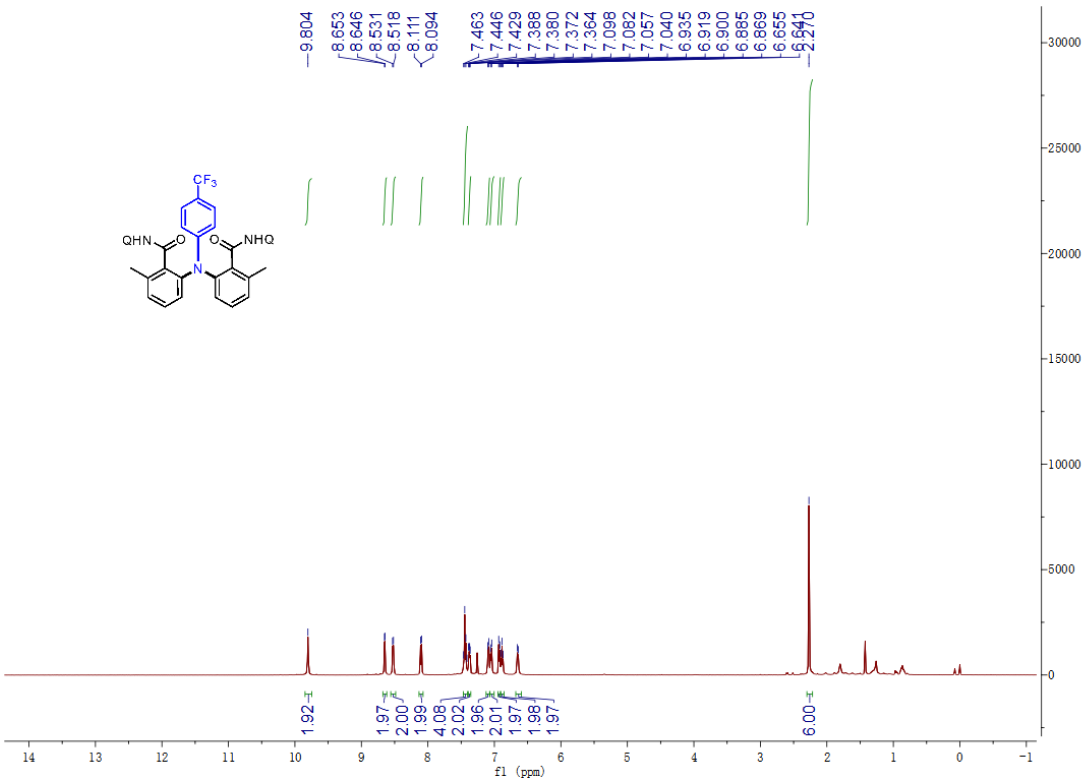
^{13}C NMR (125 MHz, $CDCl_3$) of product **4g**



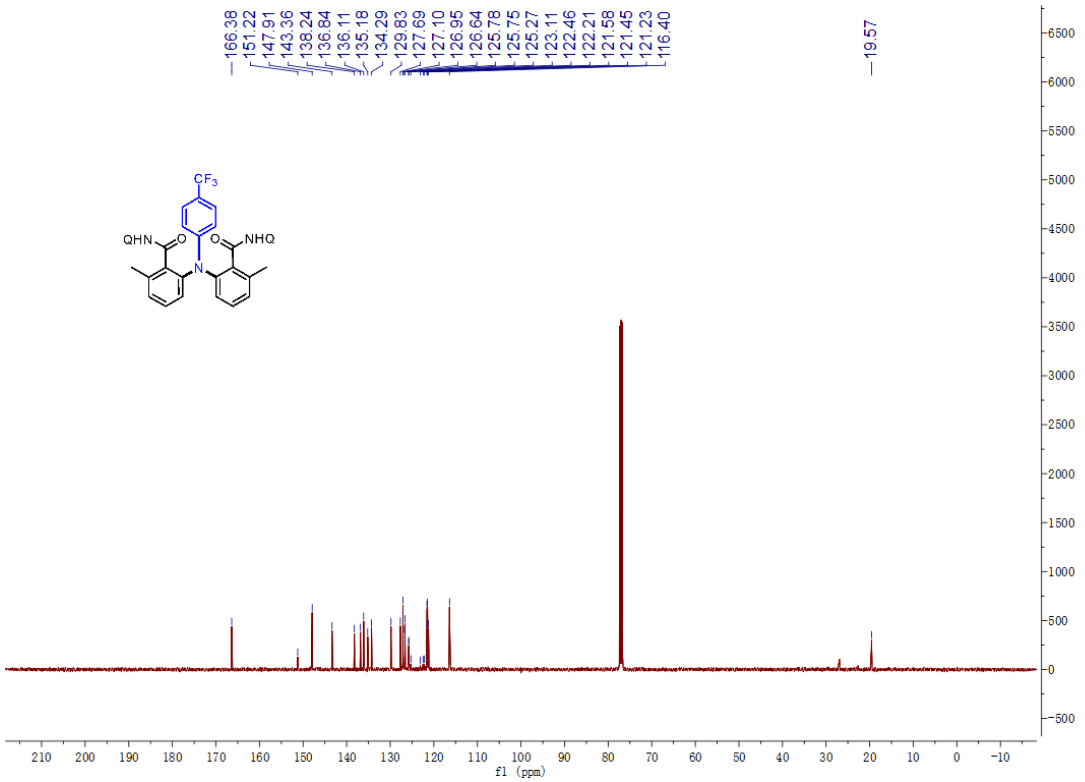
^{1}H NMR (500 MHz, $CDCl_3$) of product **4h**



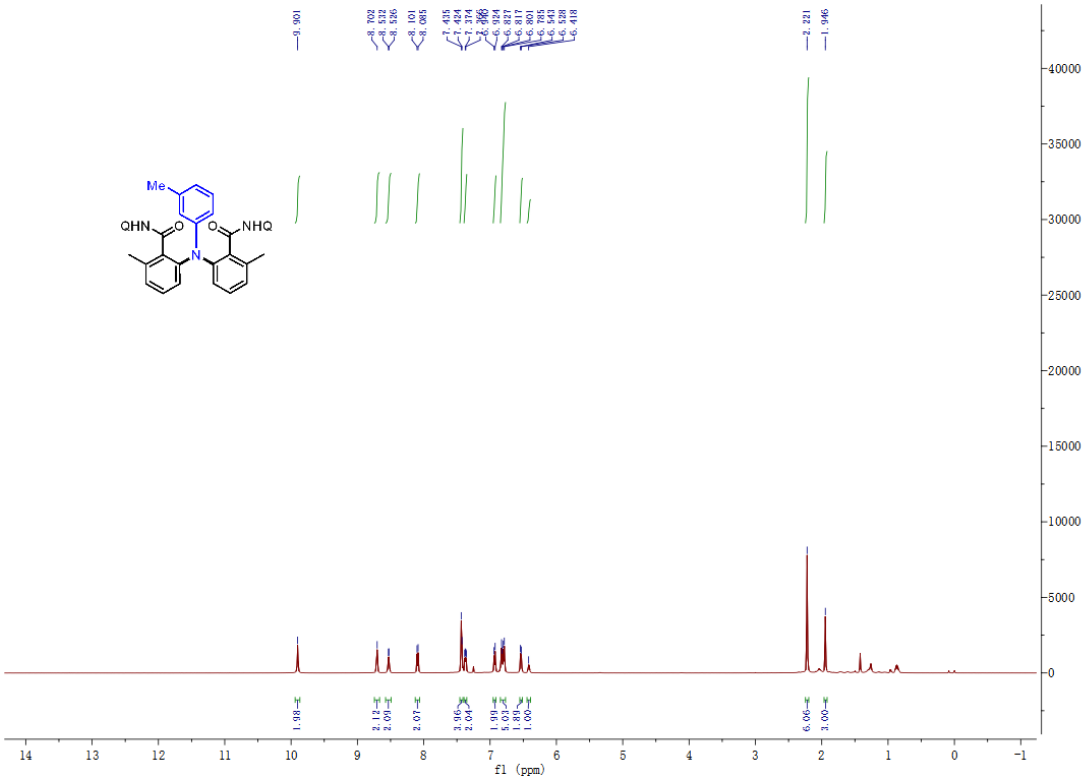
^{13}C NMR (125 MHz, $CDCl_3$) of product **4h**



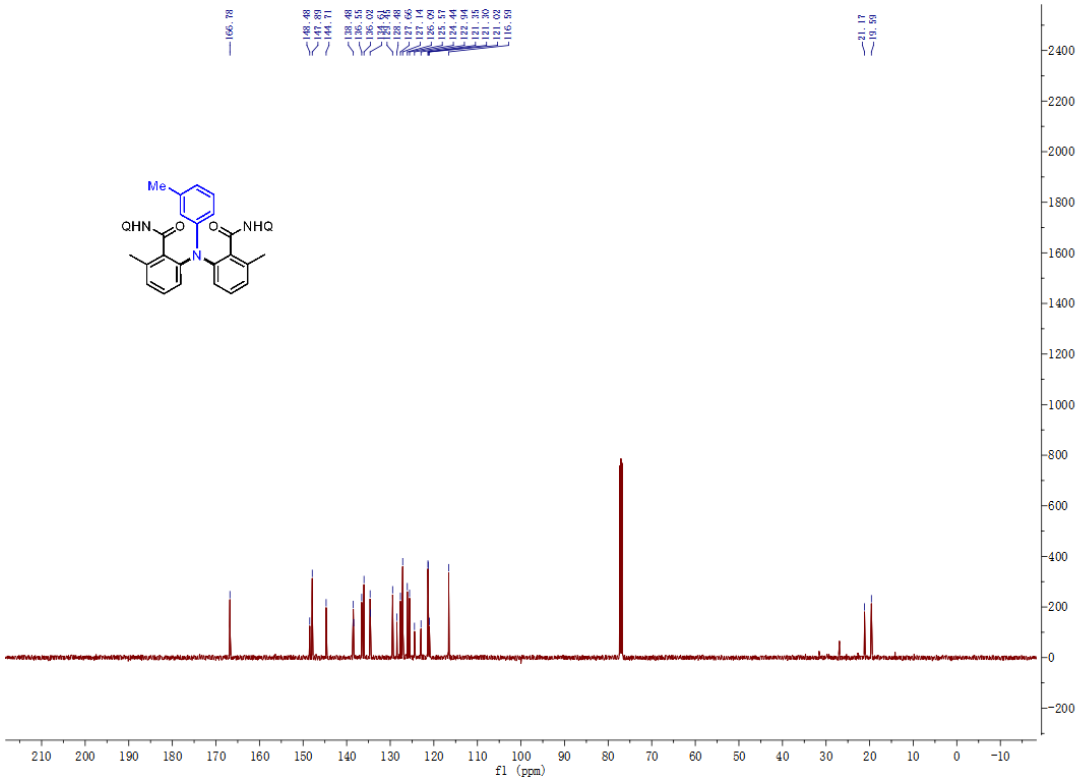
^{1}H NMR (500 MHz, $CDCl_3$) of product **4i**



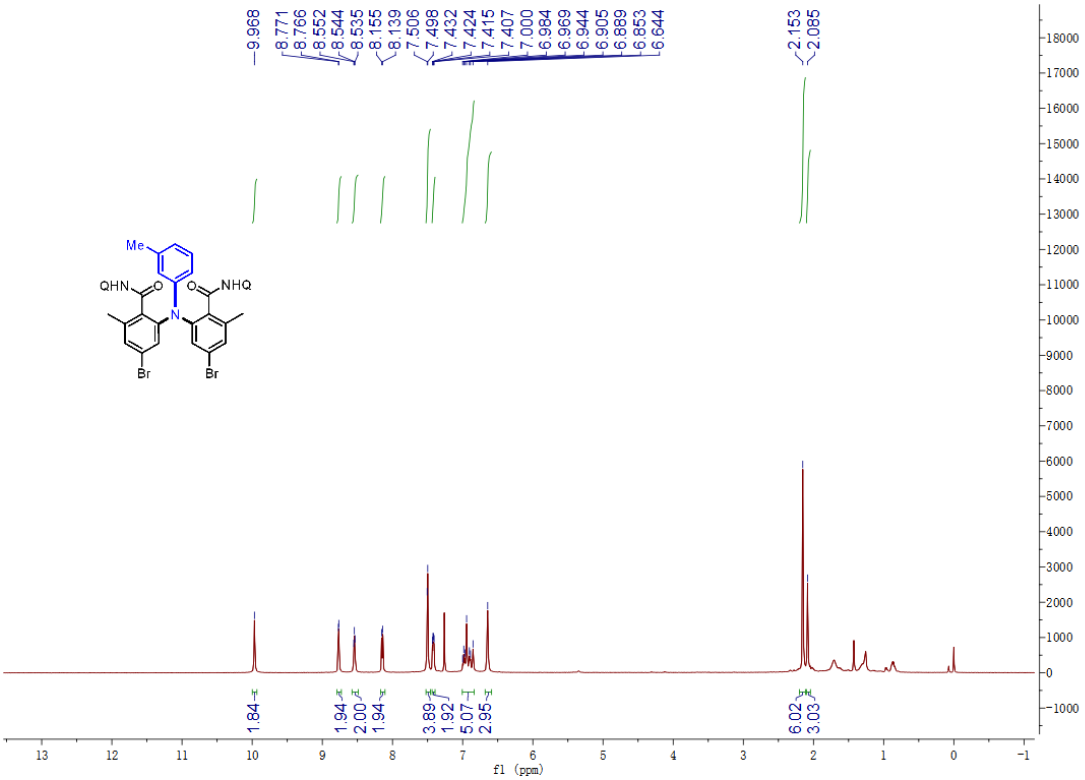
^{13}C NMR (125 MHz, $CDCl_3$) of product **4i**



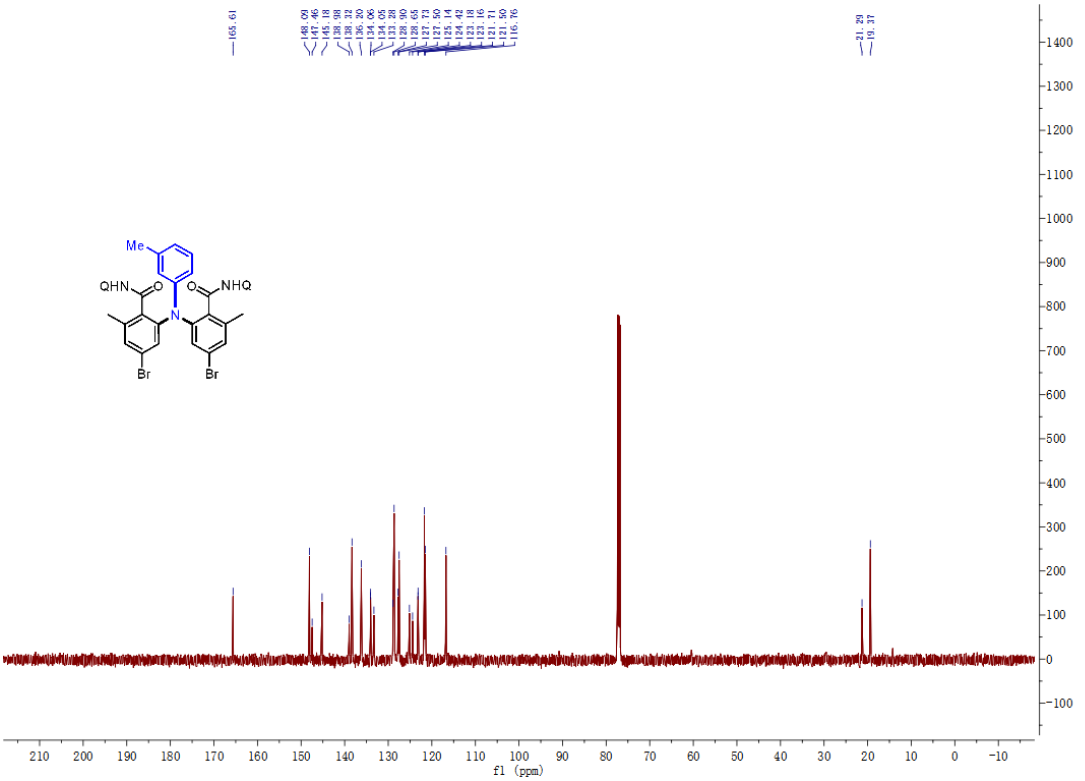
^{1}H NMR (500 MHz, $CDCl_3$) of product **4j**



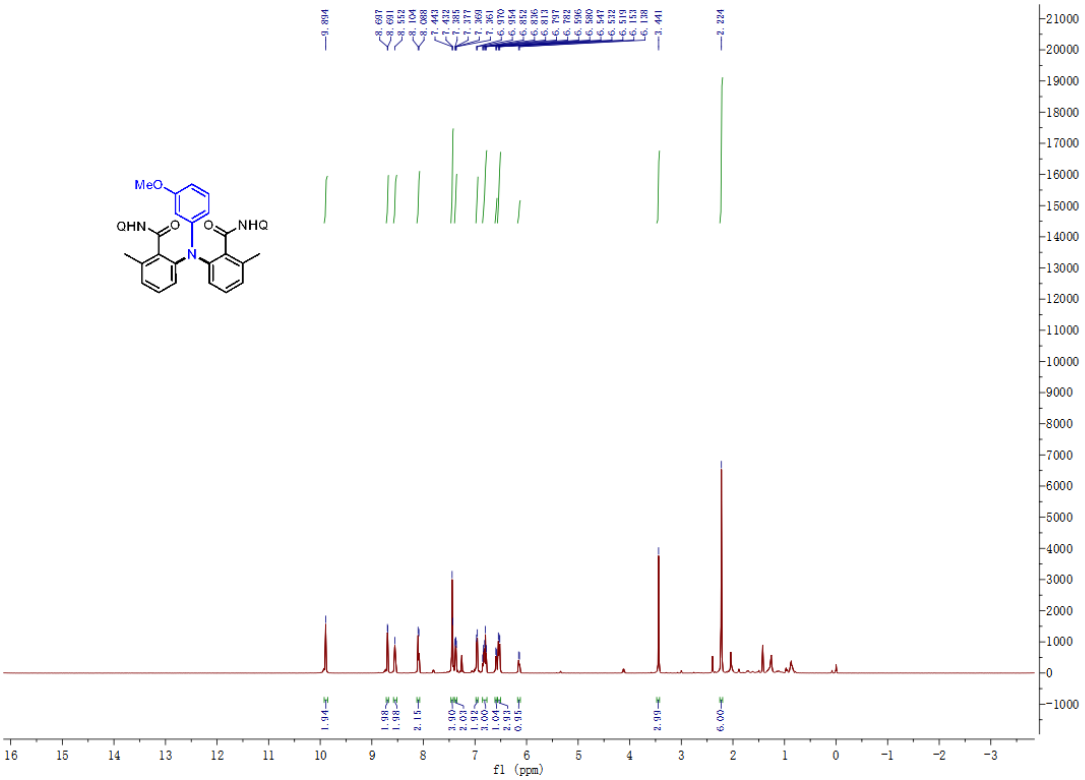
^{13}C NMR (125 MHz, $CDCl_3$) of product **4j**



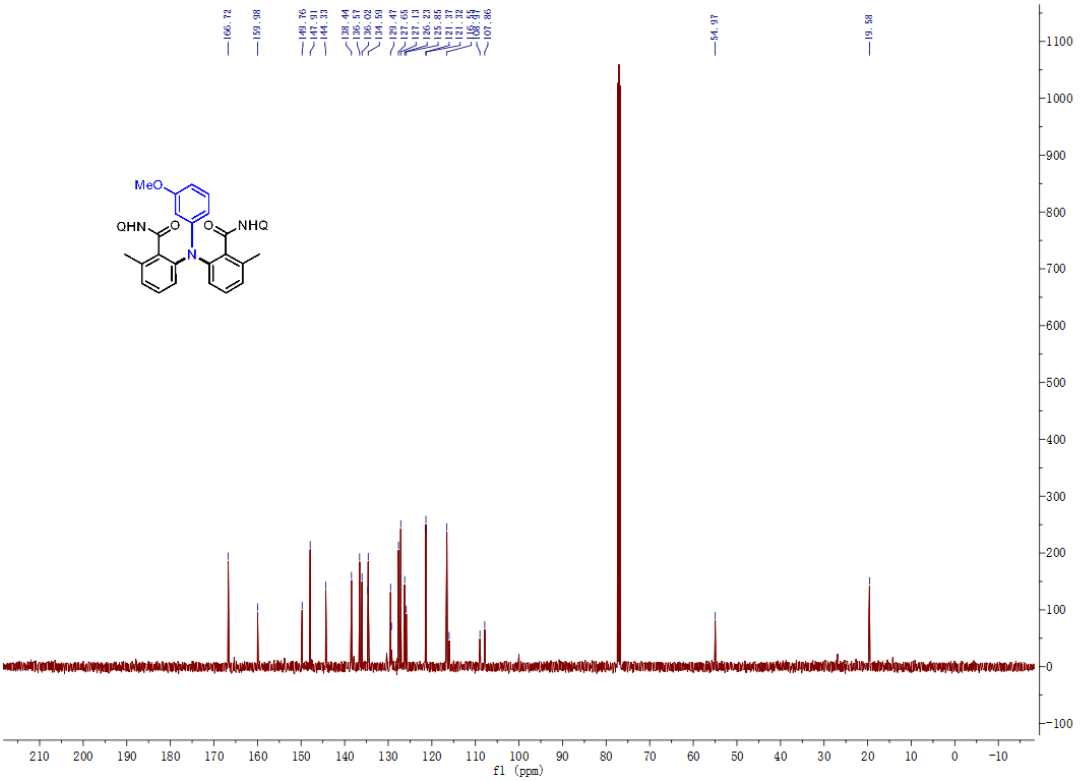
^{1}H NMR (500 MHz, $CDCl_3$) of product **4k**



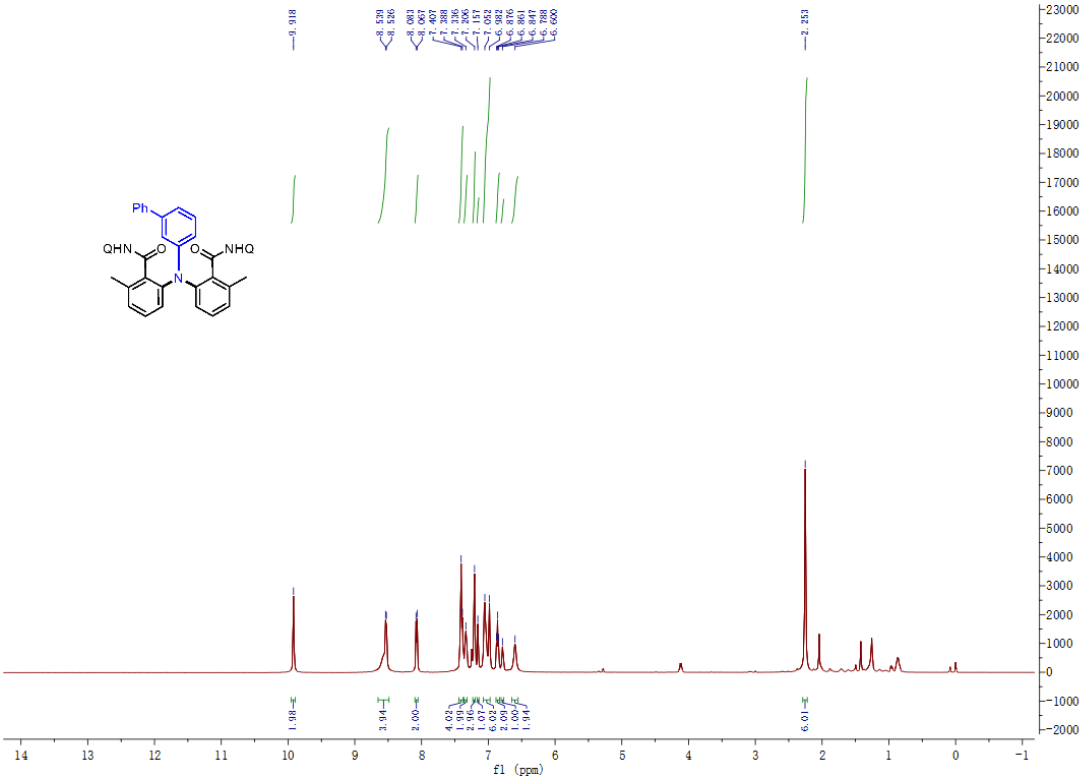
^{13}C NMR (125 MHz, $CDCl_3$) of product **4k**



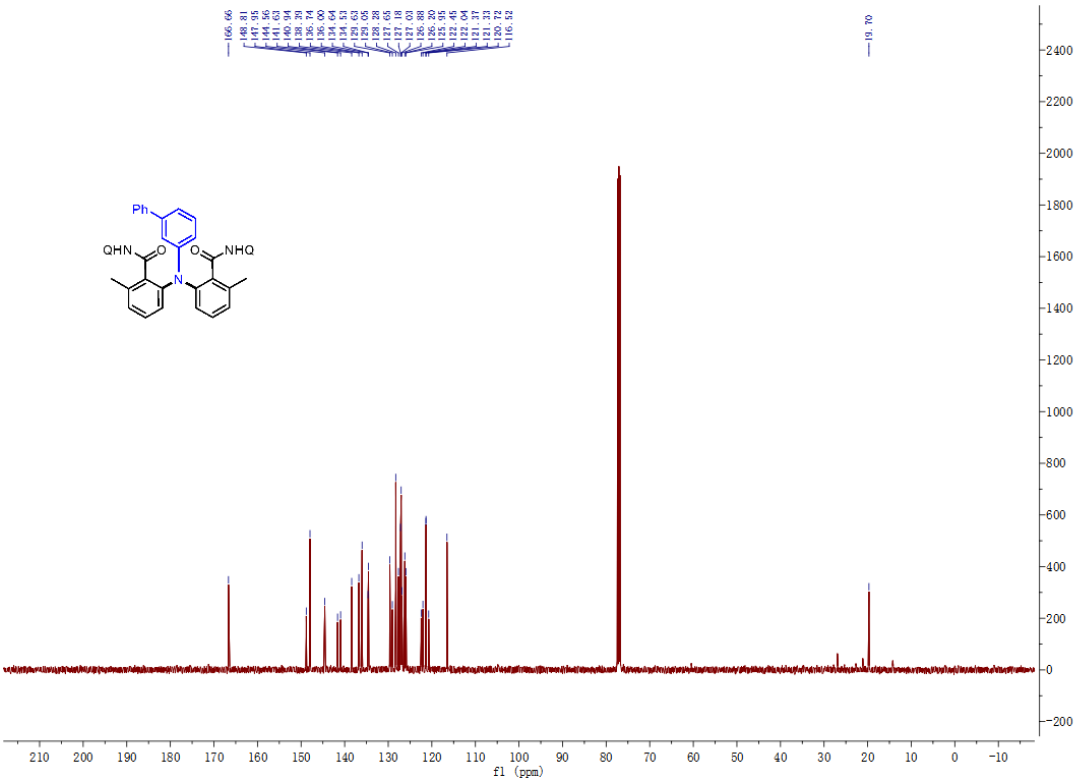
^{1}H NMR (500 MHz, $CDCl_3$) of product **4l**



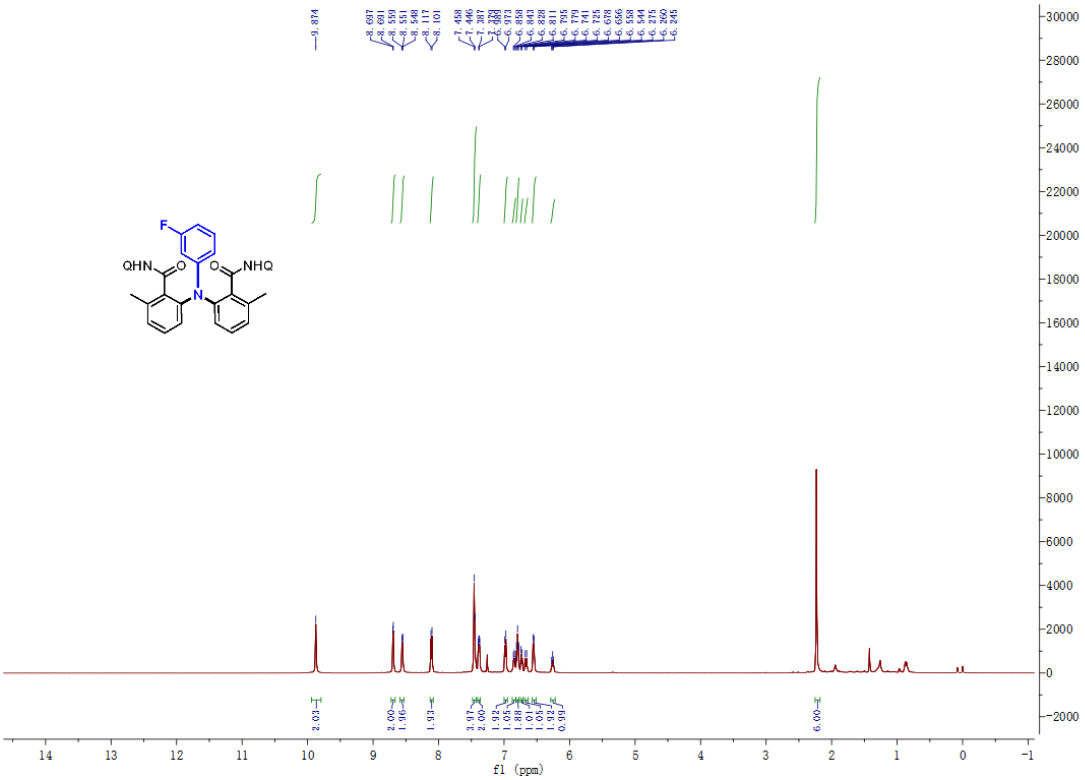
^{13}C NMR (125 MHz, $CDCl_3$) of product **4l**



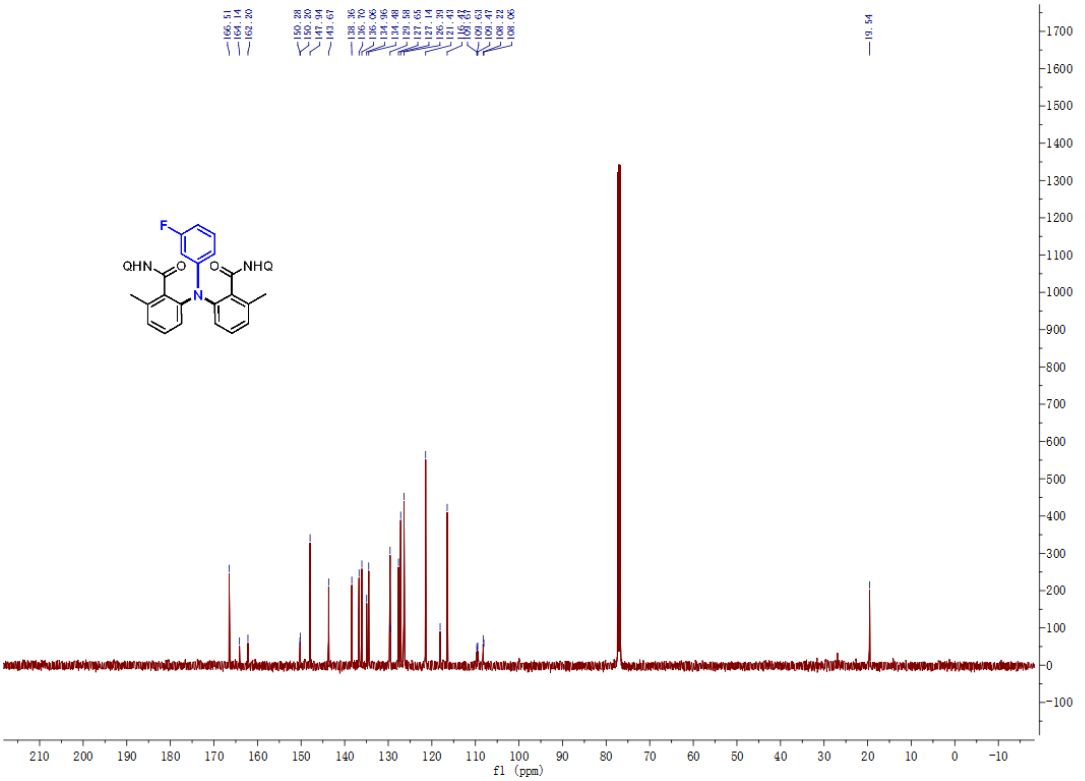
^{1}H NMR (500 MHz, $CDCl_3$) of product **4m**



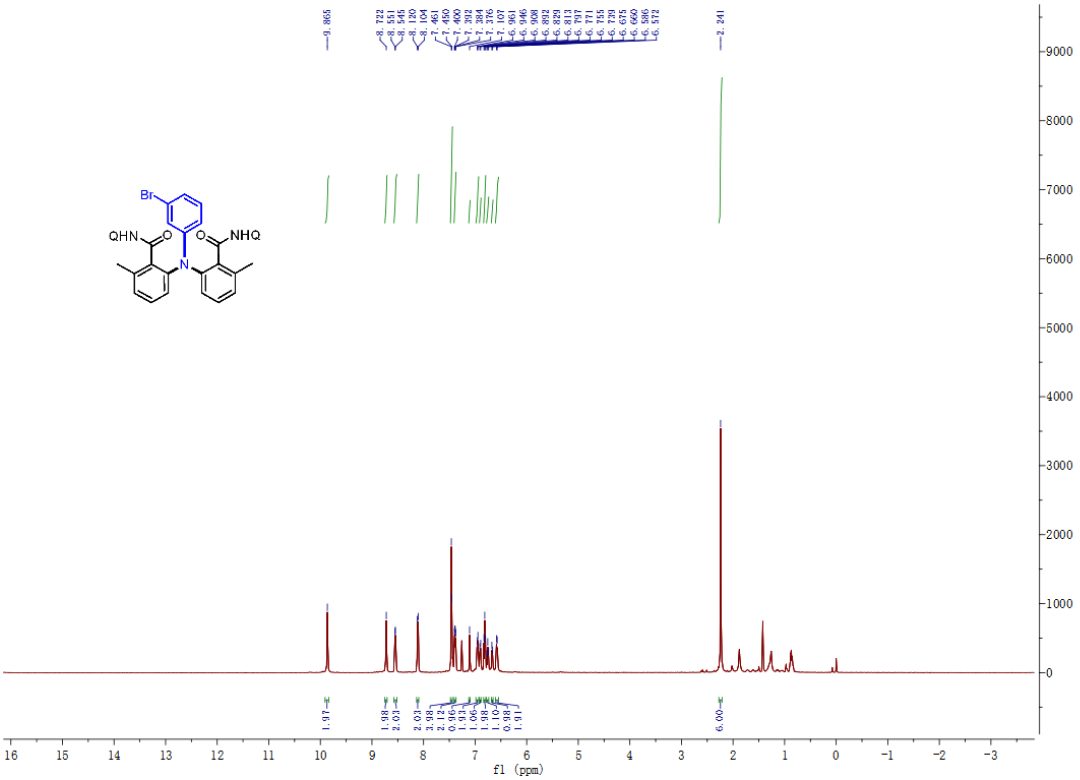
^{13}C NMR (125 MHz, $CDCl_3$) of product **4m**



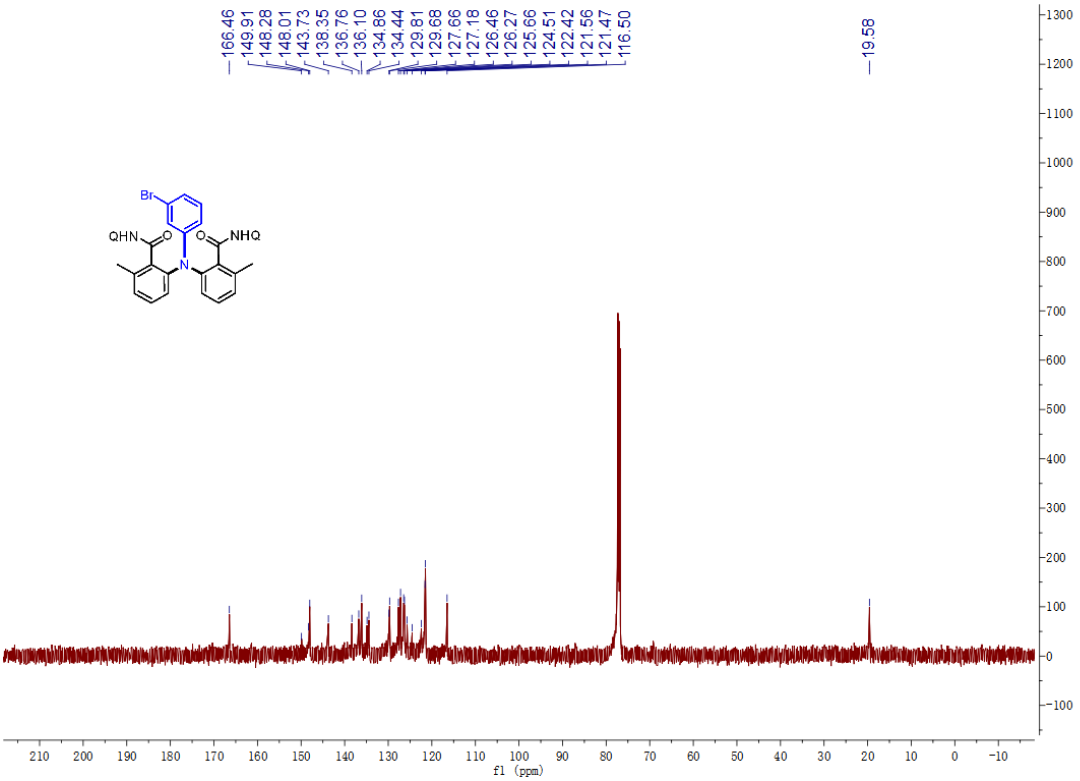
^{1}H NMR (500 MHz, $CDCl_3$) of product **4n**



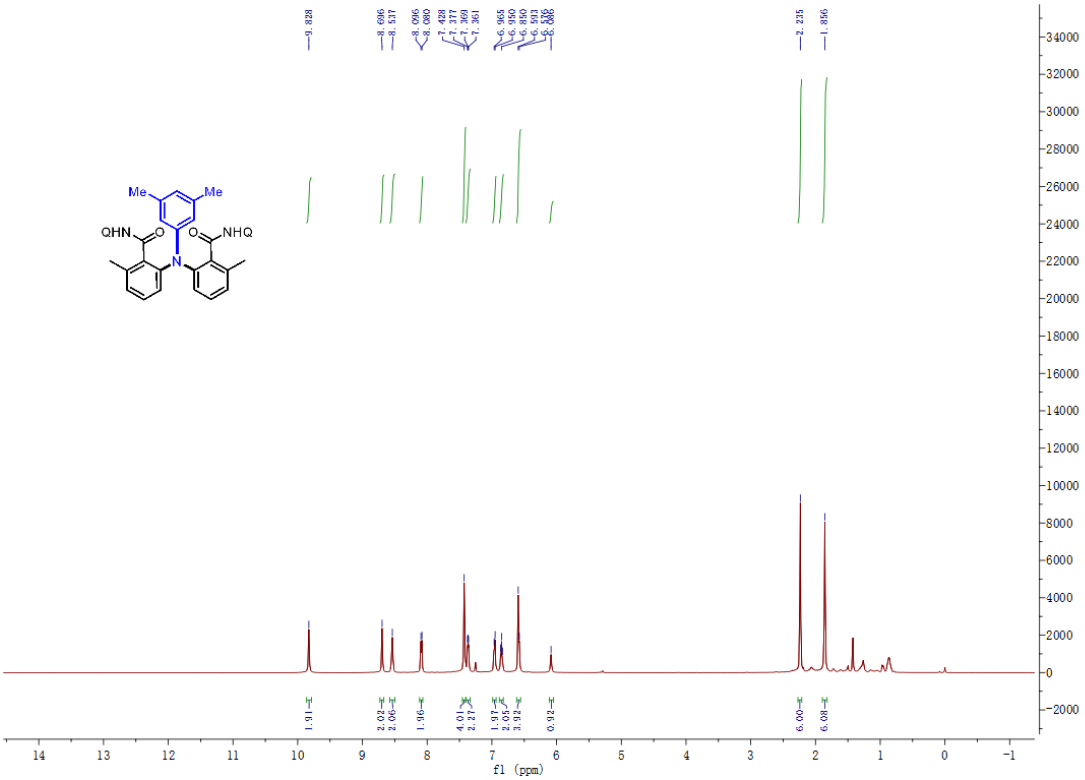
^{13}C NMR (125 MHz, $CDCl_3$) of product **4n**



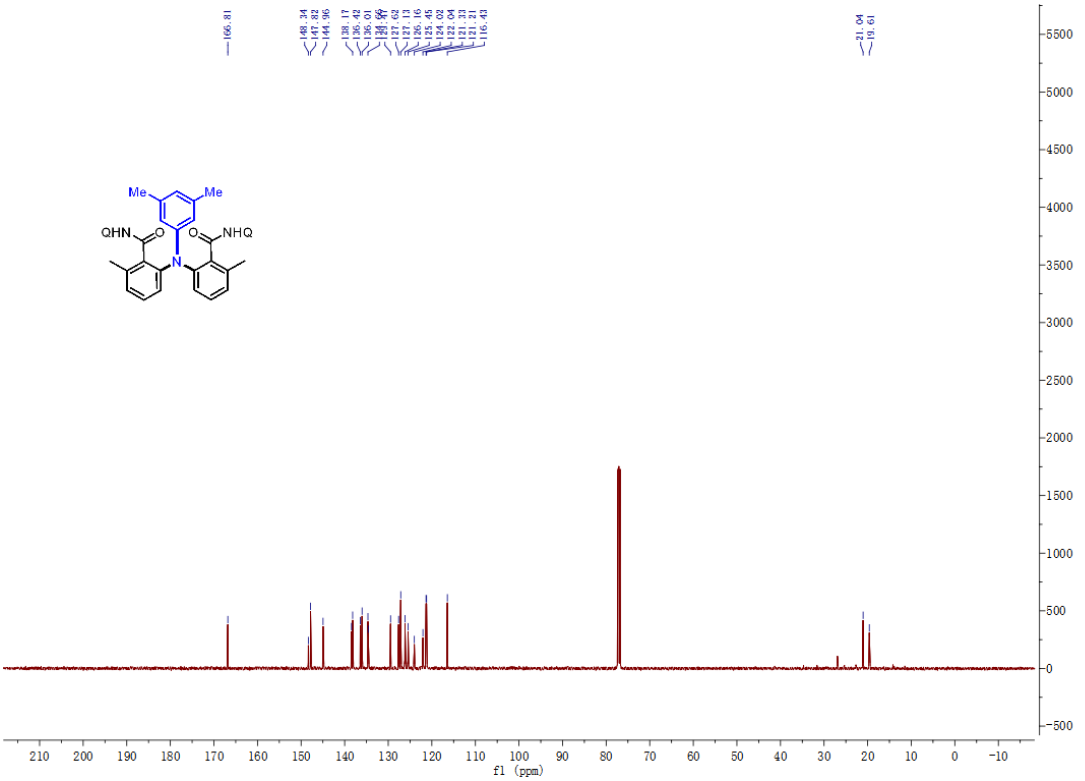
^{1}H NMR (500 MHz, $CDCl_3$) of product **4o**



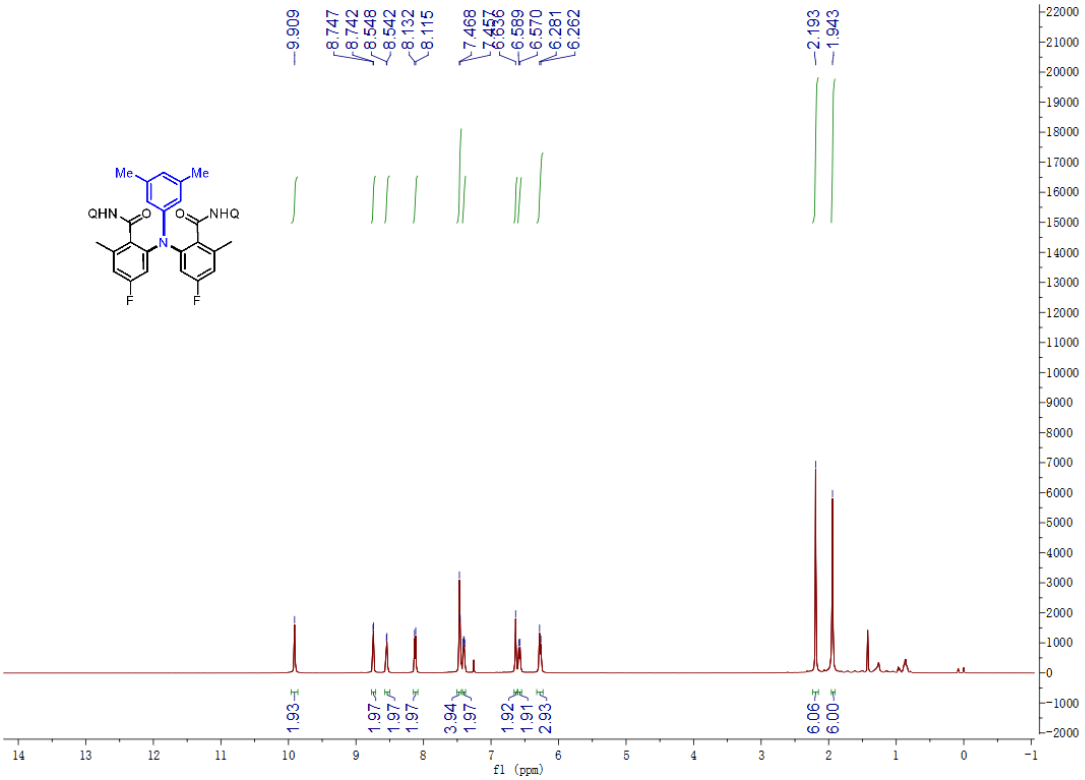
^{13}C NMR (125 MHz, $CDCl_3$) of product **4o**



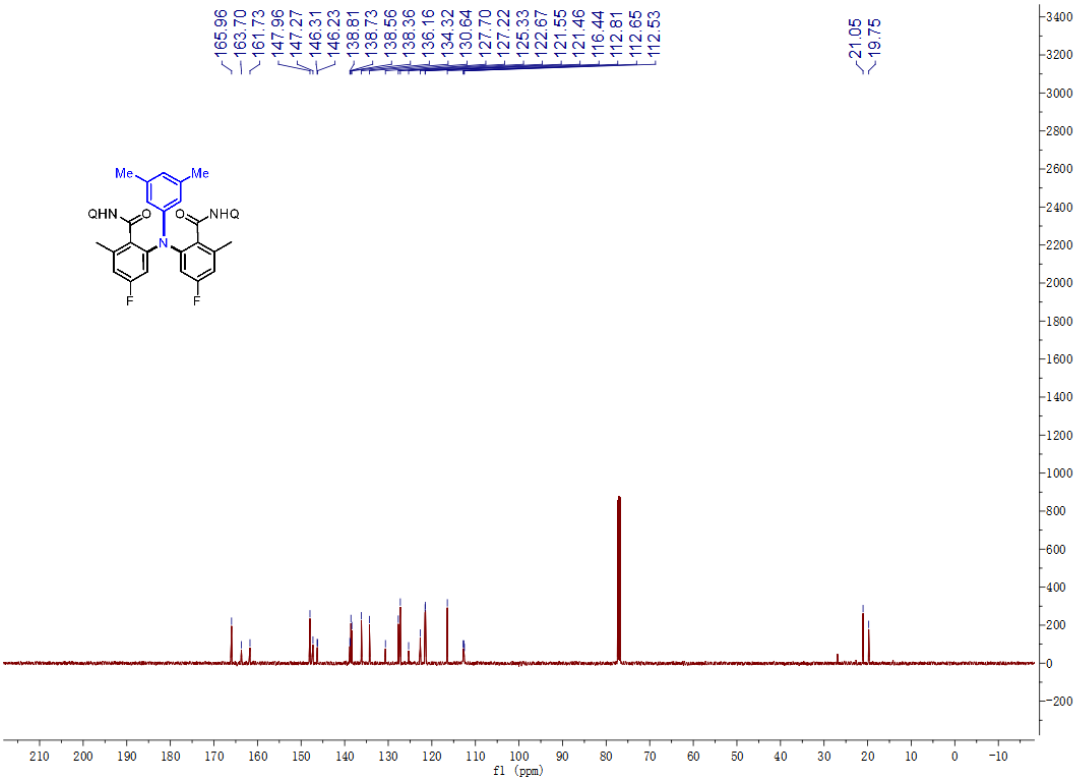
^{1}H NMR (500 MHz, $CDCl_3$) of product **4p**



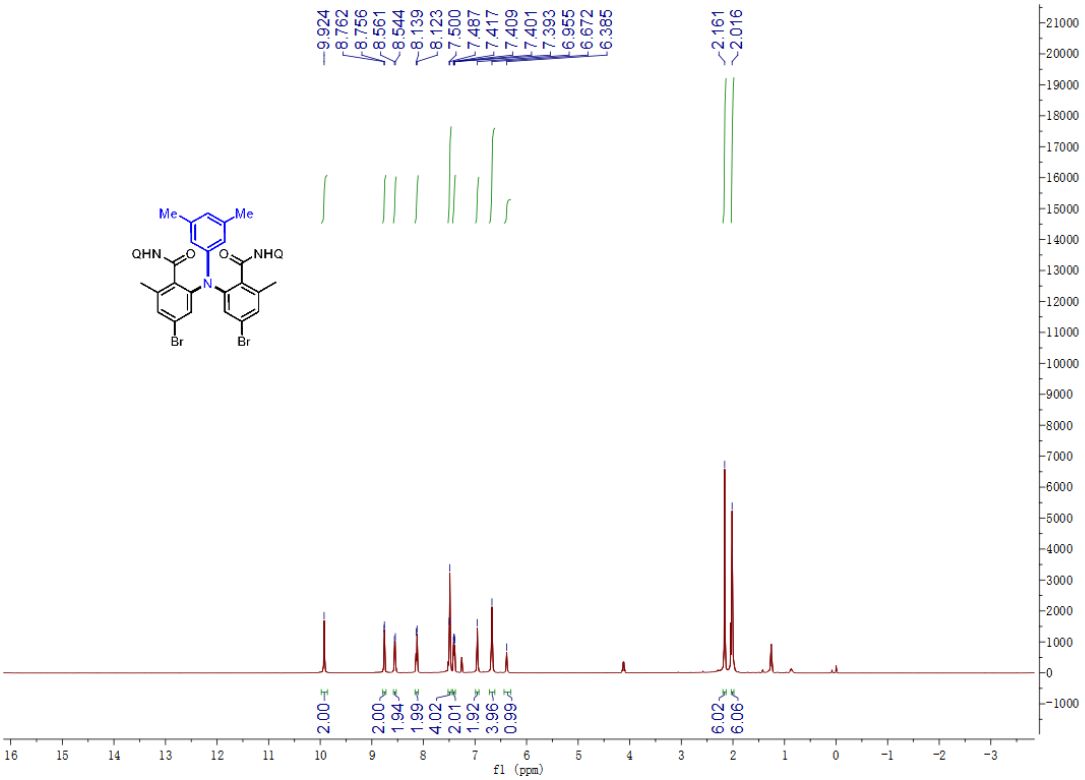
^{13}C NMR (125 MHz, $CDCl_3$) of product **4p**



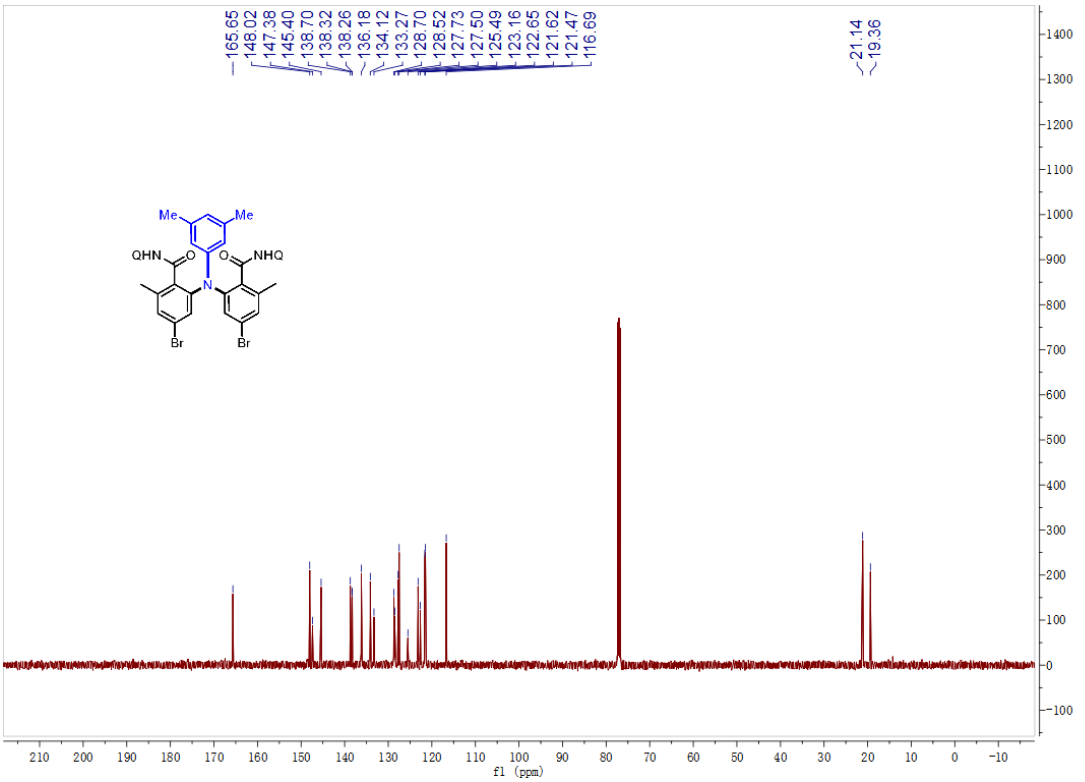
^{1}H NMR (500 MHz, $CDCl_3$) of product **4q**



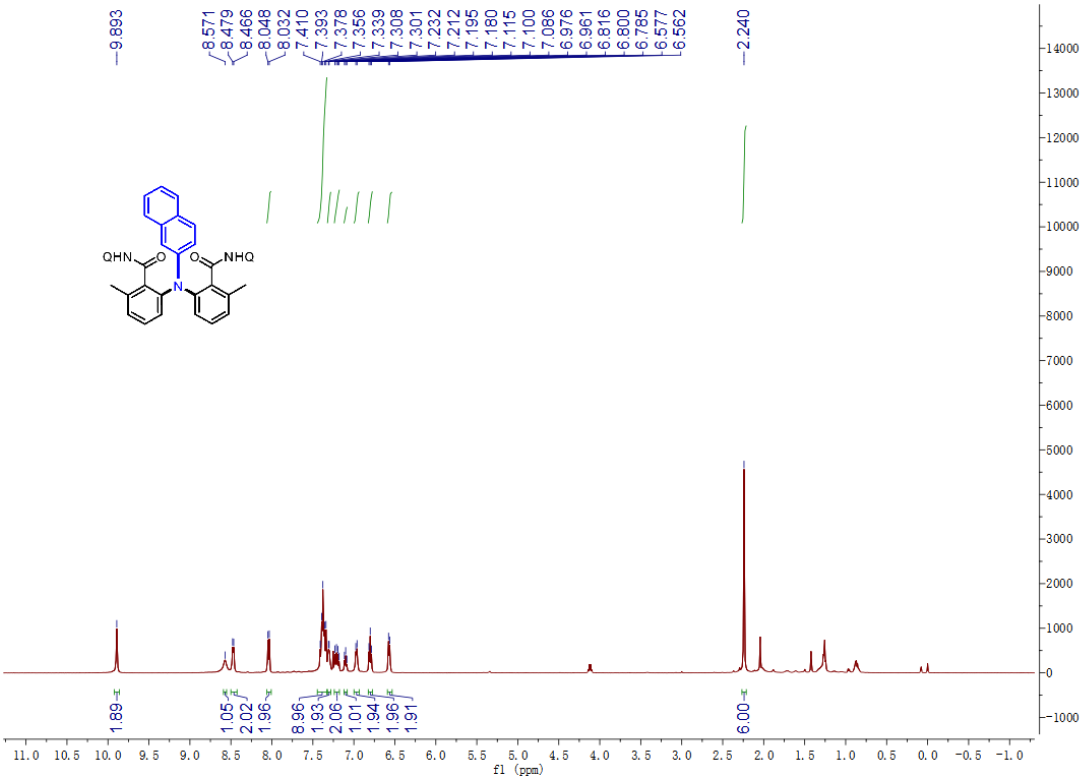
^{13}C NMR (125 MHz, $CDCl_3$) of product **4q**



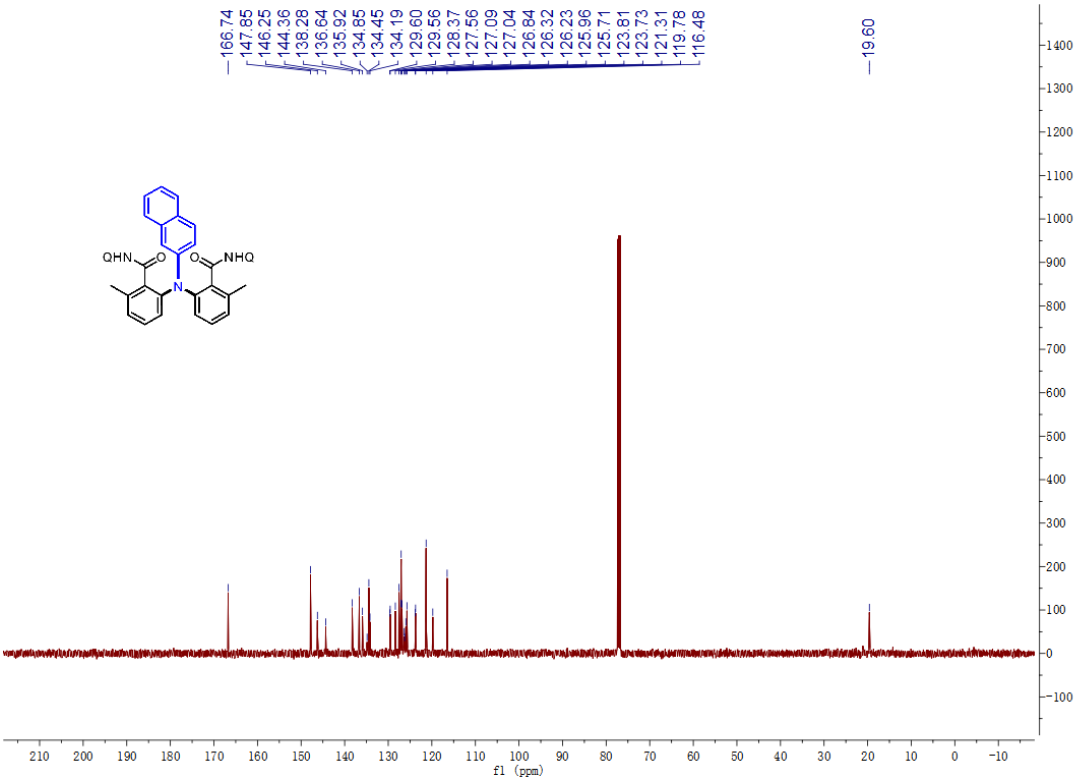
^{1}H NMR (500 MHz, $CDCl_3$) of product **4r**



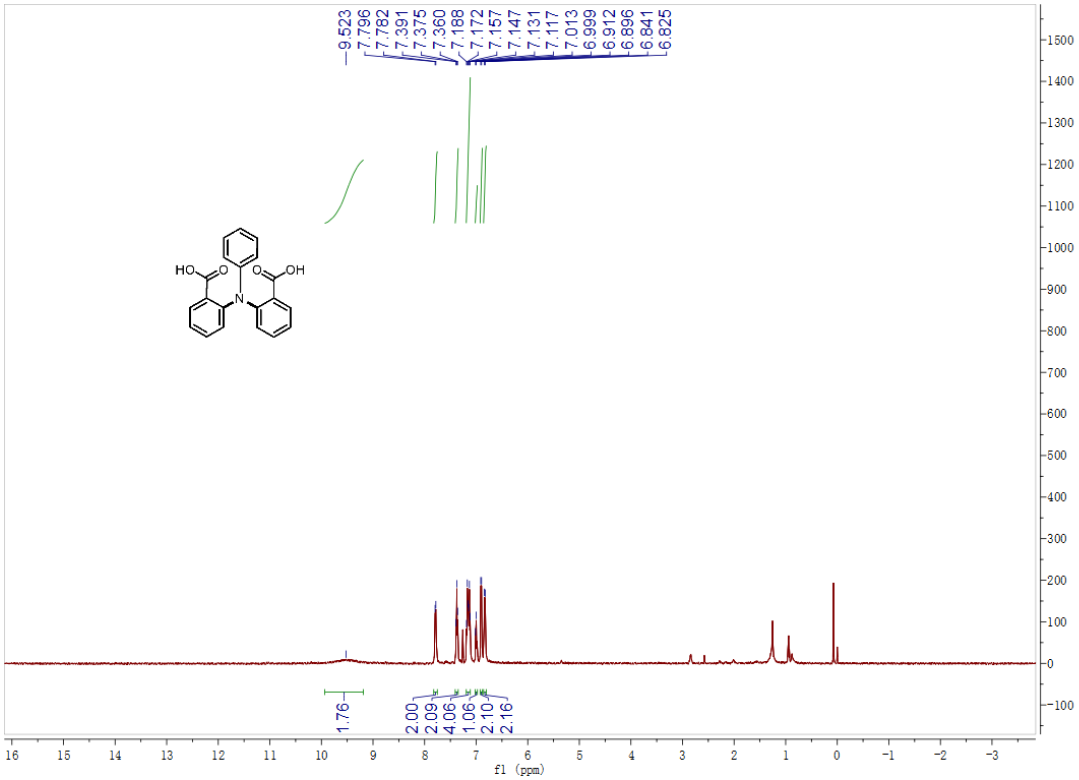
^{13}C NMR (125 MHz, $CDCl_3$) of product **4r**



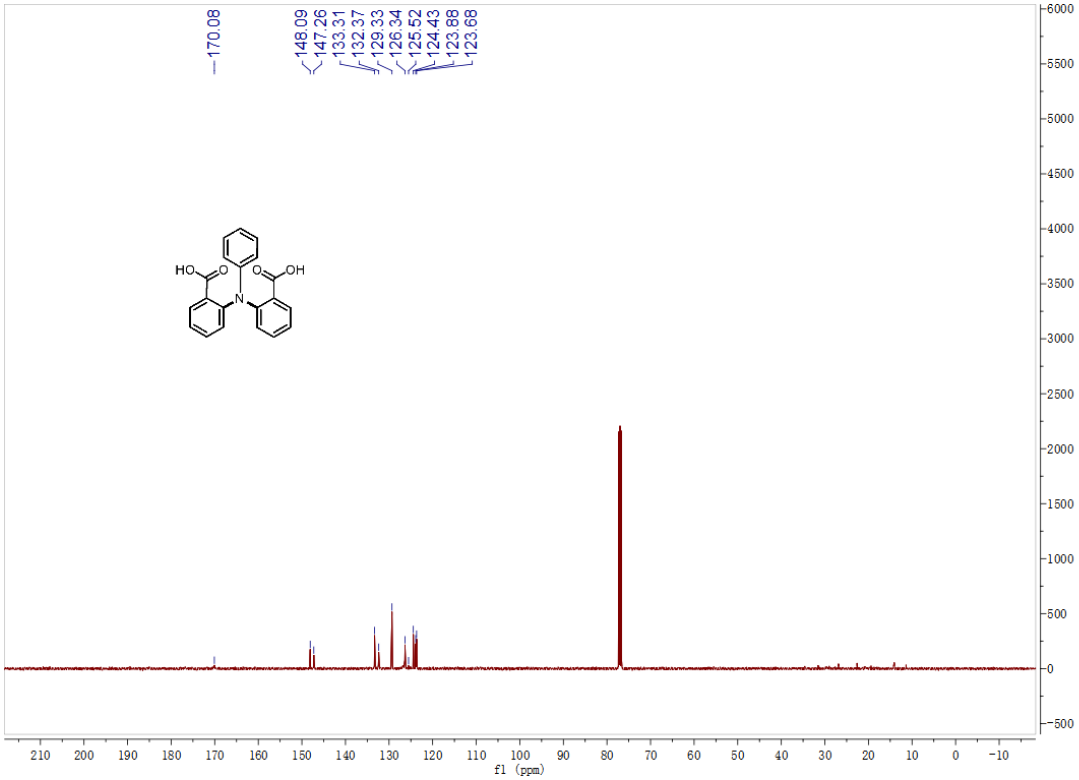
^{1}H NMR (500 MHz, $CDCl_3$) of product **4s**



^{13}C NMR (125 MHz, $CDCl_3$) of product **4s**



^{1}H NMR (500 MHz, $CDCl_3$) of product **5**



^{13}C NMR (125 MHz, $CDCl_3$) of product **5**