Supporting Information

Aminoquinoline-Assisted Vinylic C−H Arylation of Unsubstituted Acrylamide for the Selective Synthesis of *Z* Olefins

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Table of Contents:

1. General Information

All reagents and metal catalysts were obtained from commercial sources without further purification. Analytical thin layer chromatography (TLC) was performed on precoated silica plates. Yields of the products refer to purification by silica-gel column chromatography. Silica gel 60H (200-300 mesh) manufactured by Qingdao Haiyang Chemical Group Co. (China) was used for general chromatography. IR spectra were recorded on a Nicolet IS-10 Fourier transform infrared spectrometer. High resolution mass spectra (HRMS) were obtained on a TOF MS instrument with an EI source. ^{1}H and ^{13}C NMR spectra were recorded with a Bruker AV-300 spectrometer operating at 300 MHz/500 MHz and 75 MHz/125 MHz respectively, with chemical shift values being reported in ppm relative to chloroform (δ=7.26 ppm) for ^{1}H NMR, and chloroform (δ=77.16 ppm) for ^{13}C NMR.

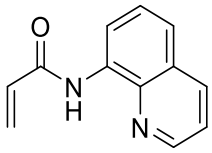
2. Preparation of Starting Materials

All amides bearing 8-aminoquinoline moiety were prepared by the reaction of the corresponding acid chlorides with 8-aminoquinoline. *N*-(quinolin-8-yl)acrylamide, *N*-(quinolin-8-yl)methacrylamide was prepared by reported procedure.[1] (*E*)-2-methyl-*N*-(quinolin-8-yl)but-2-enamide, (*E*)-2-methyl-*N*-(quinolin-8-yl)pent-2-enamide was prepared by previously reported procedure.[2] *N*-(quinolin-8-yl)cyclohex-1-ene-1-carboxamide, *N*-(quinolin-8-yl)cyclopent-1-ene-1-carboxamide was prepared by previously reported procedure.[3]

General procedure for preparing **1a** and **1b**.[1]

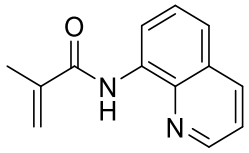
8-Aminoquinoline (1.44 g, 10 mmol) and triethylamine (1.6 mL, 12 mmol) were dissolved in DCM (40 mL) in a 100 ml round-bottom flask followed by dropwise addition of acryloyl chloride (0.98 mL, 12 mmol) through syringe at 0 ^{o}C with ice bath. The reaction mixture was stirred for 6 h. After reaction, the solution was diluted with DCM (10 mL), washed by aqueous H_2O (20 mL), sat. $NaHCO_3$ (20 mL) and brine (20 mL), combine the organic phase then dried over Na_2SO_4. To remove the solvent by evaporation after filtration. Further purification by column chromatography in petroleum ether(PE) /EtOAc (10:1) afforded corresponding product.

_N_-(quinolin-8-yl)acrylamide(1a)



The title compound was prepared from acryloyl chloride and 8-aminoquinoline.
The compound was obtained as a colorless solid. This compound is known. ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.99 (s, 1H), 8.87 (dd, *J* = 6.9, 2.0 Hz, 1H), 8.82 (dd, *J* = 4.3, 1.7 Hz, 1H), 8.18 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.66-7.40 (m, 3H), 6.54-6.49 (m, 2H), 5.84 (dd, *J* = 6.8, 4.7 Hz, 1H).

_N_-(quinolin-8-yl)methacrylamide(1b)



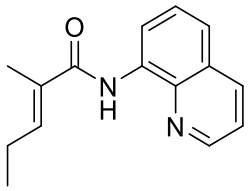
The title compound was prepared from methacryloyl chloride and 8-aminoquinoline. The compound was obtained as a brown solid.
^{1}H NMR (500 MHz, $CDCl_3$) δ 10.35 (s, 1H), 8.81 (dd, *J* = 14.8, 5.8 Hz, 2H), 8.13 (d, *J* = 8.2 Hz, 1H), 7.53 (t, *J* = 7.9 Hz, 2H), 7.43 (s, 1H), 6.04 (s, 1H), 5.55 (s, 1H), 2.18 (s, 3H).

General procedure for preparing **1c** and **1d**.[2]

(*E*)-2-methylbut-2-enoic acid (501 mg 5 mmol) was placed in 100 mL round bottom

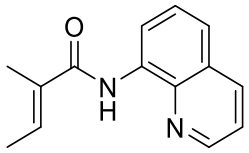
flask and thionyl chloride (3 mL) was added. The reaction mixture was stirred at 80 ℃ for 90 min, and then the excess thionyl chloride was removed *in vacuo*. After the reaction mixture was diluted with dichloromethane (10 mL) at 0 ℃, triethylamine (5 eq.) and 8-aminoquinoline (1.2 eq.) were added and the reaction mixture was stirred for 10 h at room temperature, followed by the addition of a saturated aqueous NH_4Cl solution. The organic layer was separated, and the aqueous layer was extracted with dichloromethane for 3 times. The obtained crude amide was purified by silica gel column chromatography (PE/EtOAc = 10/1) to afford the product.

(*E*)-2-methyl-*N*-(quinolin-8-yl)pent-2-enamide(1c)



The compound was obtained as a pale yellow liquid.
^{1}H NMR (500 MHz, $CDCl_3$) δ 10.33 (s, 1H), 8.93-8.83 (m, 2H), 8.25- 8.18 (m, 1H), 7.60 (t, *J* = 7.9 Hz, 1H), 7.56 -7.53 (m, 1H), 7.50 (dd, *J* = 8.2, 4.2 Hz, 1H), 6.71 (td, *J* = 7.2, 1.3 Hz, 1H), 2.37-2.30 (m, 2H), 2.12 (d, *J* = 0.7 Hz, 3H), 1.17 (t, *J* = 7.6 Hz, 3H).

(*E*)-2-methyl-*N*-(quinolin-8-yl)but-2-enamide(1d)



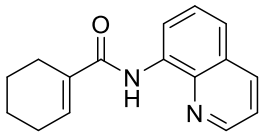
The compound was obtained as a pale yellow liquid.
^{1}H NMR (500 MHz, $CDCl_3$) δ 10.32 (s, 1H), 8.92-8.85 (m, 2H), 8.20 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.59 (t, *J* = 7.9 Hz, 1H), 7.57-7.53 (m, 1H), 7.49 (dd, *J* = 8.2, 4.2 Hz, 1H), 6.80 (qd, *J* = 6.9, 1.3 Hz, 1H), 2.12 (d, *J* = 1.0 Hz, 3H), 1.93 (dd, *J* = 6.9, 1.0 Hz, 3H).

General procedure for preparing **1e** and **1f**.[3]

To an oven-dried 50 mL flask, cyclohex-1-ene-1-carboxylic acid (252 mg, 2 mmol), DMF (1 drops) and DCM (3 mL) were added. Oxalyl chloride (0.2 mL, 2.4 mmol, 1.2 equiv.) was added dropwise at 0 ℃ resulting in vigorous stirring. The mixture was stirred for 5 h at room temperature, and the solvent was then condensed in vacuo. The resulting acid chloride was used immediately without further purification.
To another oven-dried 50 mL flask, 8-aminoquinoline (346 mg, 2.4 mmol, 1.2 equiv.), Et_3N (0.6mL, 4 mmol, 2 equiv.) and DCM (5 mL) were added. A solution of the acid chloride in DCM (5 mL) was added dropwise to the solution at 0 ℃, and the solution was then warmed to room temperature. After stirring overnight, the reaction system was quenched with sat. aq. $NaHCO_3$ (5 mL) and the organic layer was separated. The aqueous layer was extracted with DCM (2 x 3 mL). The combined organic layers and brine (5 mL), dried over $MgSO_4$, filtered and evaporated in vacuo. The obtained crude amide was purified by column chromatography on silica gel (PE/EtOAc = 10/1) to

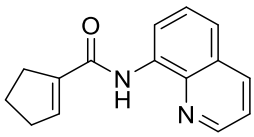
afford the desired product.

***N*-(quinolin-8-yl)cyclohex-1-ene-1-carboxamide(1e)**



The compound was obtained as a white solid.
^{1}H NMR (300 MHz, $CDCl_3$) δ 10.24 (s, 1H), 8.82 (dd, *J* = 9.5, 5.2 Hz, 2H), 8.16 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.65-7.34 (m, 3H), 7.04-6.86 (m, 1H), 2.61-2.37 (m, 2H), 2.29 (dd, *J* = 6.1, 2.6 Hz, 2H), 1.86-1.74 (m, 2H), 1.73-1.63 (m, 2H).

***N*-(quinolin-8-yl)cyclopent-1-ene-1-carboxamide(1f)**

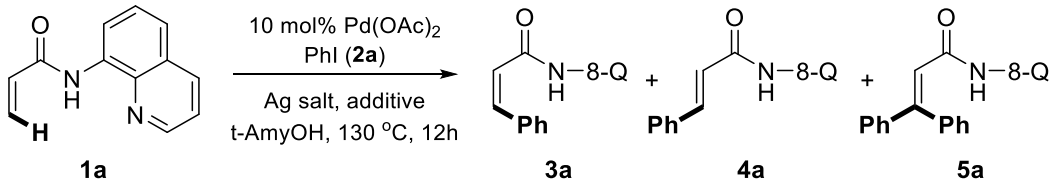


The compound was obtained as an orange solid.
^{1}H NMR (300 MHz, $CDCl_3$) δ10.20 (s, 1H), 8.84 (d, *J* = 7.0 Hz, 2H), 8.19 (d, *J* = 8.3 Hz, 1H), 7.51 (m, 3H), 6.85 (s, 1H), 2.83 (d, *J* = 6.0 Hz, 2H), 2.61 (d, *J* = 7.4 Hz, 2H), 2.19-1.98 (m, 2H).

3. Optimization of Reaction Conditions for Stereoselective Arylation

To a 15 mL Schlenk tube**,** substrate **1a** (0.2 mmol), catalyst (10% mol), iodide, silver salts, additives and solvent were combine added under air. After sealing the tube with a Teflon cap, the mixture was stirred at the required temperature. After the reaction, the reaction was cooled to room temperature, filtered through a pad of silica gel and washed with 100 mL 50% EtOAc/ petroleum ether. The solvents were removed under reduced pressure and the crude yield was measured by NMR.

Table 1S. Optimization studies for Stereoselective Arylation[a]



1a **3a** **4a** **5a**

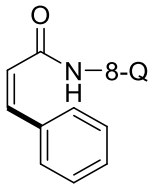
entry	Cat.	Solvent	Ag source	additive	Conv.	*cis/trans/di*	Yield[b] of *cis*-isomer	T/t
1	$Pd(OAc)_2$	t-AmyOH	Ag_2CO_3	-	65	100:110:9	30	130 °C /12h
2	$Pd(OAc)_2$	t-AmyOH	Ag_2CO_3	CH_3COOH	100	100:50:26	57	130 °C /12h
3	$Pd(OAc)_2$	t-AmyOH	AgOAc	CH_3COOH	100	100:24:13	73	130 °C /12h
4	$Pd(OAc)_2$	t-AmyOH	AgF	CH_3COOH	100	100:21:4	80	130 °C /12h
5	$Pd(OAc)_2$	t-AmyOH	AgF	PivOH	70	100:30:2	54	130 °C /12h
6	$Pd(OAc)_2$	t-AmyOH	AgF	$(BnO)_2PO_2H$	100	100:17:0	84	130 °C /12h
7	PdCl2	t-AmyOH	AgOAc	$(BnO)_2PO_2H$	100	100:16:19	74	130 °C /12h
8	$Cu(OAc)_2$	t-AmyOH	AgOAc	$(BnO)_2PO_2H$	0	-	-	130 °C /12h
9	$Pd(TFA)_2$	t-AmyOH	AgOAc	$(BnO)_2PO_2H$	100	100:17:0.8	82	130 °C /12h
10	$Pd(TFA)_2$	t-AmyOH	AgF	$(BnO)_2PO_2H$	65	100:33:0	49	130 °C /12h
11	$Pd(OAc)_2$	t-AmyOH	AgOAc	$(BnO)_2PO_2H$	100	100:30:3	75	130 °C /12h
12	$Pd(OAc)_2$	t-AmyOH	AgF	$(BnO)_2PO_2H$(1)	97	100:21:0	80	130 °C /12h
13	$Pd(OAc)_2$	t-AmyOH	AgF	$(BnO)_2PO_2H$(0.3)	97	100:20:0	80	130 °C /12h
14	$Pd(OAc)_2$	t-AmyOH	AgF(0.8)	$(BnO)_2PO_2H$	87	100:14:0	76	130 °C /12h
15	$Pd(OAc)_2$	t-AmyOH	AgF(3)	$(BnO)_2PO_2H$	44	100:76:0	25	130 °C /12h
16	$Pd(OAc)_2$	t-AmyOH	AgF	$(BnO)_2PO_2H$	trace	-	-	80 °C /12h
17	$Pd(OAc)_2$	t-AmyOH	AgF	$(BnO)_2PO_2H$	95	100:15:0-	78	110 °C /12h
18	$Pd(OAc)_2$	t-AmyOH	AgF	$(BnO)_2PO_2H$	99	100:19:1	82	150 °C /12h
19	$Pd(OAc)_2$	t-AmyOH	AgF	$(BnO)_2PO_2H$ BQ(1)	95	100:5:0	90	130 °C /12h
20	$Pd(OAc)_2$	t-AmyOH	AgF	$(BnO)_2PO_2H$ BQ(1)	98	100:12:0	88	130 °C /24h
21	$Pd(OAc)_2$	t-AmyOH	AgOAc	$(BnO)_2PO_2H$ BQ(1)	100	100:18:6	81	130 °C /12h
22	$Pd(OAc)_2$	t-AmyOH	AgF	$(BnO)_2PO_2H$	97	100:9:0	89	130 °C /12h

23	$Pd(OAc)_2$	t-AmyOH	AgOAc	BQ(2) $(BnO)_2PO_2H$ BQ(1)	100	100:11:3	88	110 °C /12h
24	**$Pd(OAc)_2$**	**t-AmyOH**	**AgF**	**$(BnO)_2PO_2H$ $K_2S_2O_8$(1)**	**100**	**100:7:0**	**93**	**130 °C /12h**
25	**$Pd(OAc)_2$**	**t-AmyOH**	**AgF**	**$(BnO)_2PO_2H$ oxone(1)**	**95**	**100:2:0**	**93(80)**	**130 °C /12h**

4. General Procedure for Stereoselective Arylation

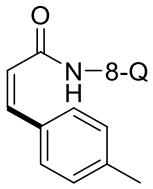
To a 15 mL Schlenk tube, substrate **1a** (39.6 mg, 0.2 mmol), aryl iodide (0.6 mmol), $Pd(OAc)_2$ (4.4 mg, 0.02 mmol), AgF (38.0 mg, 0.3 mmol), $(BnO)_2PO_2H$ (27.8 mg, 0.1 mmol), oxone(122.0 mg, 0.2 mmol) and *t*-AmyOH (1 mL) were combine added under air, sealed with a Teflon cap. The tube was heated at 130 ^oC in an oil bath and stirring for 12-24 hours. After cooling to room temperature, the reaction mixture was diluted with dichloromethane (15 mL) and washed with H_2O (10 mL), aqueous layer was extracted by DCM (3 x 5 mL). Combined organic layers were dried over Na_2SO_4. To remove the solvent by evaporation after filtration, the residue was purified by flash chromatography to give the target products. Furthermore, some were purified by preparative thin-layer chromatography.

(*Z*)-3-phenyl-*N*-(quinolin-8-yl)acrylamide(3a)



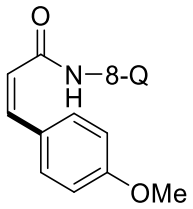
This amide was obtained as a colorless oil liquid. Purified by column chromatography (DCM) (43.9 mg, 80%); ^1H NMR (300 MHz, $CDCl_3$) δ 9.91 (s, 1H), 8.84 (d, *J* = 7.1 Hz, 1H), 8.62 (d, *J* = 5.7 Hz, 1H), 8.13 (dd, *J* = 8.3, 1.5 Hz, 1H), 7.55 (m, 4H), 7.40 (dd, *J* = 8.3, 4.2 Hz, 1H), 7.30 (d, *J* = 7.4 Hz, 3H), 6.99 (d, *J* = 12.5 Hz, 1H), 6.29 (d, *J* = 12.5 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.55, 147.57, 138.61, 137.96, 135.83, 134.56, 134.05, 129.04, 128.33, 127.95, 127.48, 126.99, 124.31, 121.25, 121.14, 116.22. IR (neat) 3345, 2926, 1676, 1524, 1485, 1424, 1383, 1325, 1162, 825, 791, 694. HRMS (EI) calcd. for $C_{18}H_{14}N_2O$: 274.1106. Found: 274.1103.

(*Z*)-*N*-(quinolin-8-yl)-3-(p-tolyl)acrylamide(3b):



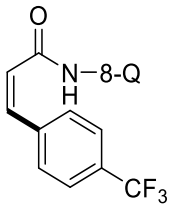
This amide was obtained as a white oil liquid. Purified by column chromatography (DCM) as a white solid (44.8 mg, 78%); ^1H NMR (300 MHz, $CDCl_3$) δ 9.91 (s, 1H), 8.85 (d, *J* = 7.0 Hz, 1H), 8.73-8.47 (m, 1H), 8.11 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.63-7.46 (m, 4H), 7.39 (dd, *J* = 8.2, 4.2 Hz, 1H), 7.12 (d, *J* = 7.6 Hz, 2H), 6.94 (d, *J* = 12.4 Hz, 1H), 6.22 (d, *J* = 12.4 Hz, 1H), 2.31 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.75, 147.53, 138.85, 138.46, 138.01, 135.81, 134.14, 131.73, 129.15, 128.64, 127.50, 126.99, 123.33, 121.19, 116.23, 20.97. IR (neat) 3342, 2911, 1669, 1518, 1481, 1422, 1381, 1322，1182，1160，823，789，755. HRMS (EI) calcd. for $C_{19}H_{16}N_2O$: 288.1263. Found: 288.1255.

(Z)-3-(4-methoxyphenyl)-*N*-(quinolin-8-yl)acrylamide(3c):



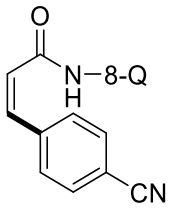
This amide was obtained as a white solid. Purified by column chromatography (DCM) and prepare TLC (46.5 mg, 75%, *Z/E*=2.8/1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.92 (s, 1H), 8.86 (dd, *J* = 7.3, 1.4 Hz, 1H), 8.66 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.13 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.72-7.63 (m, 2H), 7.60-7.45 (m, 2H), 7.40 (dd, *J* = 8.3, 4.2 Hz, 1H), 6.99-6.75 (m, 3H), 6.16 (d, *J* = 12.5 Hz, 1H), 3.77 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.79, 159.80, 147.56, 138.88, 138.00, 135.88, 134.21, 131.16, 127.54, 127.18, 127.02, 121.92, 121.13, 116.24, 112.96, 54.85. IR (neat) 3345, 2923, 1665, 1602, 1524, 1507, 1484, 1423, 1383, 1323, 1251, 1174, 1159, 1028, 824, 790. HRMS (EI) calcd. for $C_{19}H_{16}N_2O_2$: 304.1212. Found: 304.1219.

(*Z*)-*N*-(quinolin-8-yl)-3-(4-(trifluoromethyl)phenyl)acrylamide(3d):



This amide was obtained as a pale yellow oil liquid. Purified by column chromatography (DCM) (46.9 mg, 69%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.89 (s, 1H), 8.80 (dd, *J* = 6.6, 2.3 Hz, 1H), 8.61 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.12 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.70 (d, *J* = 8.1 Hz, 2H), 7.63-7.48 (m, 4H), 7.40 (dd, *J* = 8.3, 4.2 Hz, 1H), 6.99 (d, *J* = 12.4 Hz, 1H), 6.38 (d, *J* = 12.5 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.68, 147.68, 138.17, 137.93, 137.27, 135.89, 133.76, 130.00, 129.23, 127.78, 127.51, 126.93, 126.15, 125.44, 124.83, 121.83, 121.57, 121.24, 116.33. IR (neat) 3336, 2928, 1668, 1520, 1484, 1318, 1161, 1110, 1065, 1017, 824, 789. HRMS (EI) calcd. for $C_{19}H_{13}F_3N_2O$: 342.0980. Found: 342.0988.

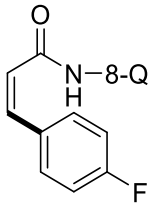
(*Z*)-3-(4-cyanophenyl)-*N*-(quinolin-8-yl)acrylamide(3e):



This amide was obtained as a yellow solid. Purified by column chromatography (DCM) (28.8 mg, 48%, *Z/E*=7/1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.90 (s, 1H), 8.81-8.74 (m, 1H), 8.67 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.15 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.70 (d, *J* = 8.7 Hz,

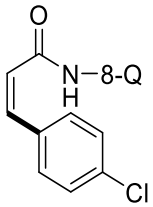
2H), 7.59 (d, *J* = 8.3 Hz, 2H), 7.55-7.52 (m, 2H), 7.44 (dd, *J* = 8.2, 4.2 Hz, 1H), 6.96 (d, *J* = 12.4 Hz, 1H), 6.42 (d, *J* = 12.5 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.32, 147.74, 139.26, 137.89, 137.05, 136.04, 133.64, 132.24, 131.57, 129.60, 127.99, 127.55, 126.96, 126.69, 121.74, 121.36, 116.43. IR (neat) 3336, 2920, 2225, 1674, 1522, 1484, 1424, 1383, 1324, 1164, 825, 791. HRMS (EI) calcd. for $C_{19}H_{13}N_3O$: 299.1059. Found: 299.1063.

(*Z*)-3-(4-fluorophenyl)-*N*-(quinolin-8-yl)acrylamide(3f):



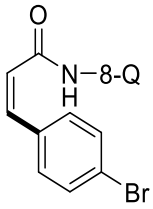
This amide was obtained as a white solid. Purified by column chromatography (DCM) (40.4 mg, 69%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.91 (s, 1H), 8.83 (dd, *J* = 6.9, 1.6 Hz, 1H), 8.72-8.55 (m, 1H), 8.14 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.65 (dd, *J* = 8.4, 5.6 Hz, 2H), 7.52 (q, *J* = 6.7 Hz, 2H), 7.42 (dd, *J* = 8.3, 4.2 Hz, 1H), 7.10-6.84 (m, 3H), 6.26 (d, *J* = 12.5 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.25, 158.91(d, *J* = 304.1 Hz), 147.64, 137.95, 135.97, 133.95, 131.32, 131.21, 130.66, 127.53, 127.01, 123.89, 121.40, 121.26, 116.29, 115.07, 114.78. IR (neat) 3339, 2923, 1671, 1520, 1507, 1483, 1423, 1381, 1323, 1228, 1158, 824, 789. HRMS (EI) calcd. for $C_{18}H_{13}FN_2O$: 292.1012. Found: 292.1020.

(*Z*)-3-(4-chlorophenyl)-*N*-(quinolin-8-yl)acrylamide(3g):



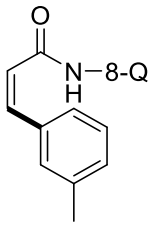
This amide was obtained as a white solid. Purified by column chromatography (DCM) (43.0 mg, 70%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.90 (s, 1H), 8.82 (dd, *J* = 6.9, 1.9 Hz, 1H), 8.65 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.13 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.63-7.46 (m, 4H), 7.41 (dd, *J* = 8.3, 4.2 Hz, 1H), 7.28 (d, *J* = 8.5 Hz, 2H), 6.91 (d, *J* = 12.5 Hz, 1H), 6.29 (d, *J* = 12.5 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.05, 147.67, 137.93, 137.66, 135.89, 134.29, 133.90, 133.02, 130.51, 128.13, 127.51, 126.96, 124.68, 121.43, 121.24, 116.28. IR (neat) 3339, 2923, 1674, 1519, 1482, 1422, 1381, 1323, 1161, 1089, 1014, 822, 788, 756. HRMS (EI) calcd. for $C_{18}H_{13}ClN_2O$: 308.0716. Found: 308.0712.

(*Z*)-3-(4-bromophenyl)-*N*-(quinolin-8-yl)acrylamide(3h):



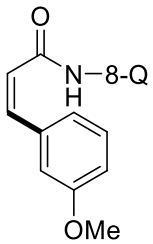
This amide was obtained as a pale yellow solid. Purified by column chromatography (DCM) (52.1 mg, 74%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.90 (s, 1H), 8.81 (dd, *J* = 6.6, 2.0 Hz, 1H), 8.66 (dd, *J* = 4.1, 1.4 Hz, 1H), 8.14 (dd, *J* = 8.3, 1.4 Hz, 1H), 7.64-7.32 (m, 7H), 6.90 (d, *J* = 12.5 Hz, 1H), 6.30 (d, *J* = 12.5 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.05, 147.71, 137.93, 137.71, 135.91, 133.88, 133.46, 131.72, 131.10, 130.74, 127.51, 126.97, 124.81, 122.63, 121.46, 121.27, 116.28. IR (neat) 3339，2928，1667，1518，1482，1422，1381，1323，1161，1070，1009，823，788，755. HRMS (EI) calcd. for $C_{18}H_{13}BrN_2O$: 352.0211. Found: 352.0215.

(*Z*)-*N*-(quinolin-8-yl)-3-(m-tolyl)acrylamide(3i):



This amide was obtained as a white oil liquid. Purified by column chromatography (DCM) (36.9 mg, 64%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.89 (s, 1H), 8.85 (d, *J* = 7.2 Hz, 1H), 8.58 (dd, *J* = 4.0, 1.1 Hz, 1H), 8.11 (dd, *J* = 8.3, 1.2 Hz, 1H), 7.60-7.46 (m, 2H), 7.40 (m, 3H), 7.20 (t, *J* = 7.6 Hz, 1H), 7.09 (d, *J* = 7.6 Hz, 1H), 6.96 (d, *J* = 12.5 Hz, 1H), 6.25 (d, *J* = 12.5 Hz, 1H), 2.25 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.69, 147.52, 138.62, 137.96, 137.52, 135.79, 134.49, 134.09, 129.64, 129.08, 127.90, 127.47, 126.98, 126.01, 124.29, 121.21, 121.12, 116.19, 20.95. IR (neat) 3342, 2917, 1668, 1517, 1482, 1423, 1381, 1323, 1162, 824, 789, 689. HRMS (EI) calcd. for $C_{19}H_{16}N_2O$: 288.1263. Found: 288.1259.

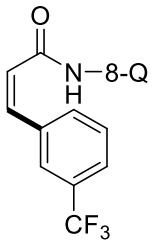
(*Z*)-3-(3-methoxyphenyl)-*N*-(quinolin-8-yl)acrylamide(3j):



This amide was obtained as an oil liquid. Purified by column chromatography (DCM) (40.9 mg, 67%).This amide was obtained as a pale yellow oil liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.91 (s, 1H), 8.84 (dd, *J* = 7.1, 1.4 Hz, 1H), 8.60 (dd, *J* = 4.1, 1.5 Hz, 1H), 8.11 (dd, *J* = 8.2, 1.5 Hz, 1H), 7.62-7.45 (m, 2H), 7.39 (dd, *J* = 8.3, 4.2 Hz, 1H), 7.26-7.08 (m, 3H), 6.96 (d, *J* = 12.5 Hz, 1H), 6.83 (dd, *J* = 7.6, 1.7 Hz, 1H), 6.28 (d, *J*

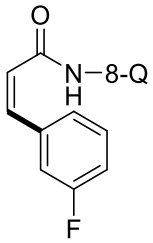
= 12.5 Hz, 1H), 3.69 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.63, 159.08, 147.59, 138.12, 137.94, 135.83, 134.03, 129.03, 127.47, 126.97, 124.74, 121.52, 121.29, 121.17, 116.19, 114.68, 113.56, 54.78. IR (neat) 3339, 2921, 1670, 1518, 1482, 1423, 1381, 1323, 1258, 1239, 1161, 1041, 824, 788, 685. HRMS (EI) calcd. for $C_{19}H_{16}N_2O_2$: 304.1212. Found: 304.1216.

(*Z*)-3-(pyridin-3-yl)-*N*-(quinolin-8-yl)acrylamide(3k):



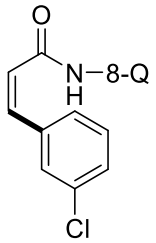
This amide was obtained as white solid. Purified by column chromatography (DCM) as (28.8 mg, 42%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.92 (s, 1H), 8.82 (dd, *J* = 6.8, 1.9 Hz, 1H), 8.70-8.56 (m, 1H), 8.16 (d, *J* = 7.1 Hz, 1H), 7.84 (d, *J* = 8.0 Hz, 2H), 7.59-7.49 (m, 3H), 7.42 (m, 2H), 7.00 (d, *J* = 12.5 Hz, 1H), 6.40 (d, *J* = 12.5 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.73, 147.53, 140.17, 140.03, 137.77, 137.30, 136.42, 136.08, 135.34, 133.69, 132.26, 128.34, 127.52, 127.02, 125.84, 124.86, 123.96, 121.52, 121.19, 116.50. IR (neat) 3342, 2923, 1678, 1524, 1486, 1383, 1328, 1162, 1124, 1075, 825, 791, 688. HRMS (EI) calcd. for $C_{19}H_{13}F_3N_2O$: 342.0980. Found: 342.0983.

(*Z*)-3-(3-fluorophenyl)-*N*-(quinolin-8-yl)acrylamide(3l):



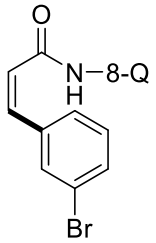
This amide was obtained as a white solid. Purified by column chromatography (DCM) (38.6 mg, 66%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.90 (s, 1H), 8.83 (dd, *J* = 7.0, 1.8 Hz, 1H), 8.65 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.12 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.53 (dd, *J* = 12.5, 5.2 Hz, 2H), 7.46-7.32 (m, 3H), 7.27 (dd, *J* = 8.1, 5.7 Hz, 1H), 7.09-6.88 (m, 2H), 6.32 (d, *J* = 12.5 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.95, 163.24, 160.62, 147.64, 137.97, 137.31, 136.76, 136.65, 135.88, 133.90, 129.47, 129.36, 127.50, 126.98, 125.36, 124.90, 121.42, 121.20, 116.32, 115.84, 115.20. IR (neat) 3336, 2920, 1672, 1578, 1519, 1483, 1423, 1381, 1324, 1163, 1131, 824, 788, 680. HRMS (EI) calcd. for $C_{18}H_{13}FN_2O$: 292.1012. Found: 292.1017.

(*Z*)-3-(3-chlorophenyl)-*N*-(quinolin-8-yl)acrylamide(3m):



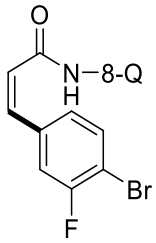
This amide was obtained as an oil liquid. Purified by column chromatography (DCM) (38.2 mg, 62%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.88 (s, 1H), 8.82 (dd, *J* = 7.0, 1.8 Hz, 1H), 8.65 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.13 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.60 (s, 1H), 7.58-7.45 (m, 3H), 7.41 (dd, *J* = 8.3, 4.2 Hz, 1H), 7.28-7.17 (m, 2H), 6.91 (d, *J* = 12.5 Hz, 1H), 6.32 (d, *J* = 12.5 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.86, 147.66, 137.93, 137.20, 136.38, 135.88, 133.84, 129.18, 128.98, 128.27, 127.49, 127.14, 126.97, 125.57, 121.43, 121.20, 116.31. IR (neat) 3345, 2923, 1674, 1522, 1484, 1424, 1382, 1325, 1163, 825, 790, 680. HRMS (EI) calcd. for $C_{18}H_{13}ClN_2O$: 308.0716. Found: 308.0719.

(*Z*)-3-(3-bromophenyl)-*N*-(quinolin-8-yl)acrylamide(3n):



This amide was obtained as an oil liquid. Purified by column chromatography (DCM) (40.9 mg, 58%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.88 (s, 1H), 8.81 (dd, *J* = 7.0, 1.8 Hz, 1H), 8.65 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.12 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.74 (s, 1H), 7.61-7.47 (m, 3H), 7.41 (dd, *J* = 8.3, 4.2 Hz, 2H), 7.15 (t, *J* = 7.9 Hz, 1H), 6.90 (d, *J* = 12.5 Hz, 1H), 6.31 (d, *J* = 12.5 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.84, 147.68, 137.94, 137.09, 136.68, 135.88, 133.85, 131.86, 131.18, 129.45, 127.57, 126.97, 125.63, 121.94, 121.44, 121.21, 116.31. IR (neat) 3336, 2917, 1673, 1520, 1483, 1423, 1382, 1324, 1162, 824, 789, 681. HRMS (EI) calcd. for $C_{18}H_{13}BrN_2O$: 352.0211. Found: 352.0217.

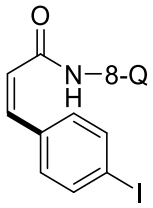
(*Z*)-3-(4-bromo-3-fluorophenyl)-*N*-(quinolin-8-yl)acrylamide(3o):



This amide was obtained as a white solid. Purified by column chromatography (DCM) (44.7 mg, 60%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.91 (s, 1H), 8.81 (dd, *J* = 6.4, 2.4 Hz, 1H), 8.68 (dd, *J* = 4.2, 1.5 Hz, 1H), 8.15 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.61-7.34 (m, 5H), 7.31-7.22 (m, 1H), 6.85 (d, *J* = 12.5 Hz, 1H), 6.34 (d, *J* = 12.5 Hz, 1H). ^{13}C NMR (75

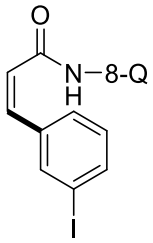
MHz, $CDCl_3$) δ 163.55, 147.74, 137.92, 136.72, 135.98, 133.75, 132.88, 127.54, 126.98, 126.14, 125.67, 121.60, 121.28, 117.19, 116.87, 116.41, 109.22, 108.94. IR (neat) 3336, 2917, 1674, 1521, 1483, 1422, 1382, 1324, 1164, 1039, 824, 789. HRMS (EI) calcd. for $C_{18}H_{12}BrFN_2O$: 370.0117. Found: 370.0121.

(*Z*)-3-(4-iodophenyl)-*N*-(quinolin-8-yl)acrylamide(3p)



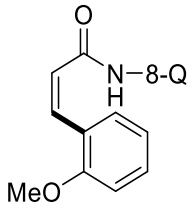
This amide was obtained as a white solid. Purified by column chromatography (DCM) (48.8 mg, 61%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.88 (s, 1H), 8.82 (d, *J* = 7.0 Hz, 1H), 8.65 (dd, *J* = 4.2, 1.3 Hz, 1H), 8.14 (d, *J* = 8.2 Hz, 1H), 7.91 (s, 1H), 7.60 (d, *J* = 8.1 Hz, 2H), 7.52 (dd, *J* = 8.9, 6.9 Hz, 2H), 7.42 (dd, *J* = 8.3, 4.2 Hz, 1H), 7.01 (t, *J* = 7.8 Hz, 1H), 6.89 (d, *J* = 12.5 Hz, 1H), 6.31 (d, *J* = 12.5 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.20, 147.90, 144.84, 138.54, 138.02, 137.38, 137.06, 136.40, 134.05, 129.87, 128.45, 127.83, 127.35, 125.83, 122.73, 121.77, 121.49, 116.84, 109.80, 93.93. IR (neat) 3334, 2923, 2845, 1674, 1521, 1482, 1423, 1382, 1323, 1161, 1005, 823, 789. HRMS (EI) calcd. for $C_{18}H_{13}IN_2O$: 400.0073. Found: 400.0070.

(*Z*)-3-(3-iodophenyl)-*N*-(quinolin-8-yl)acrylamide(3q)



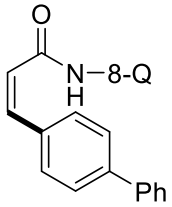
This amide was obtained as a white solid. Purified by column chromatography (DCM) (51.2 mg, 64%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.83 (s, 1H), 8.73 (d, *J* = 7.2 Hz, 1H), 8.63-8.55 (m, 1H), 8.07 (d, *J* = 8.2 Hz, 1H), 7.56 (d, *J* = 8.3 Hz, 2H), 7.45 (dt, *J* = 8.2, 7.6 Hz, 2H), 7.35 (dd, *J* = 8.2, 4.2 Hz, 1H), 7.27 (d, *J* = 8.2 Hz, 2H), 6.80 (d, *J* = 12.5 Hz, 1H), 6.22 (d, *J* = 12.5 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.34, 147.86, 138.20, 137.97, 137.34, 136.50, 134.21, 131.14, 129.49, 127.87, 127.36, 125.16, 121.80, 121.53, 116.89, 94.84. IR (neat) 3336, 2914, 2842, 1672, 1519, 1482, 1422, 1381, 1324, 1160, 824, 787, 755, 683, 656. HRMS (EI) calcd. for $C_{18}H_{13}IN_2O$: 400.0073. Found: 400.0071.

(*Z*)-3-(2-methoxyphenyl)-*N*-(quinolin-8-yl)acrylamide(3r):



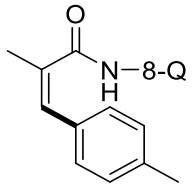
This amide was obtained as an oil liquid. Purified by column chromatography (DCM) (19.5 mg, 32%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.90 (s, 1H), 8.81 (dd, *J* = 7.2, 1.4 Hz, 1H), 8.56 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.11 (dd, *J* = 8.3, 1.5 Hz, 1H), 7.62-7.43 (m, 3H), 7.38 (dd, *J* = 8.3, 4.2 Hz, 1H), 7.31-7.22 (m, 1H), 7.16 (d, *J* = 12.4 Hz, 1H), 6.86 (dd, *J* = 16.3, 8.2 Hz, 2H), 6.29 (d, *J* = 12.4 Hz, 1H), 3.84 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.71, 156.83, 147.44, 137.98, 135.72, 134.51, 134.18, 130.25, 129.79, 127.43, 126.98, 124.74, 123.59, 121.03, 120.08, 116.06, 110.11, 55.13. IR (neat) 3339, 2917, 1667, 1519, 1483, 1461, 1424, 1381, 1323, 1248, 1159, 1109, 1025, 825, 790, 751. HRMS (EI) calcd. for $C_{19}H_{16}N_2O_2$: 304.1212. Found: 304.1221.

(*Z*)-3-([1,1'-biphenyl]-4-yl)-*N*-(quinolin-8-yl)acrylamide(3s):



This amide was obtained as a white solid. Purified by column chromatography (DCM) (46.0 mg, 66%, *Z/E*=5/1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.97 (s, 1H), 8.88 (d, *J* = 7.3 Hz, 1H), 8.59 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.12 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.72 (d, *J* = 8.2 Hz, 2H), 7.45 (m, 12H), 7.01 (d, *J* = 12.5 Hz, 1H), 6.30 (d, *J* = 12.5 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.81, 147.78, 142.30, 141.28, 139.89, 138.08, 136.11, 134.27, 133.40, 129.69, 129.01, 128.51, 128.18, 127.62, 127.39, 127.15, 126.67, 121.30, 121.01, 118.62, 116.53. IR (neat) 3350, 3187, 2919, 1646, 1624, 1523, 1485, 1423, 1385, 1260, 1161, 1076, 826, 791, 767, 679. HRMS (EI) calcd. for $C_{24}H_{18}N_2O$: 350.1419. Found: 350.1426.

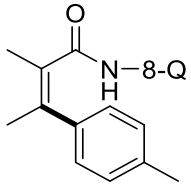
(*Z*)-2-methyl-*N*-(quinolin-8-yl)-3-(p-tolyl)acrylamide(3bb)



This amide was obtained as a colorless solid. Purified by column chromatography (DCM/PE=50/50) (36.3 mg, 60%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.74 (s, 1H), 8.82 (d, *J* = 7.3 Hz, 1H), 8.51 (dd, *J* = 4.1, 1.3 Hz, 1H), 8.08 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.51 (dt, *J* = 8.2, 7.5 Hz, 3H), 7.34 (dd, *J* = 8.2, 4.2 Hz, 1H), 7.25 (d, *J* = 7.9 Hz, 3H), 6.96 (d, *J* = 7.9 Hz, 2H), 6.71 (s, 1H), 2.25 (d, *J* = 1.2 Hz, 3H), 2.17 (s, 3H). ^{13}C NMR (75 MHz,

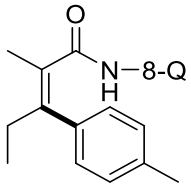
$CDCl_3$) δ 168.77, 147.39, 137.01, 135.68, 134.11, 133.68, 132.50, 130.55, 129.19, 128.60, 127.84, 127.42, 126.92, 121.17, 120.96, 116.17, 21.56, 20.69. HRMS (EI) calcd. for $C_{20}H_{18}N_2O$: 302.1419. Found: 302.1421.

(*Z*)-2-methyl-*N*-(quinolin-8-yl)-3-(p-tolyl)but-2-enamide(3bc)



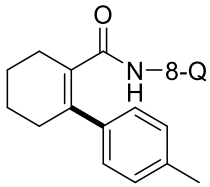
This amide was obtained as a colorless solid. Purified by column chromatography (DCM/PE=50/50) as a white solid (21.5 mg, 34%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.35 (s, 1H), 8.68 (d, *J* = 7.4 Hz, 1H), 8.53 (d, *J* = 2.9 Hz, 1H), 8.04 (d, *J* = 8.1 Hz, 1H), 7.46 (t, *J* = 7.9 Hz, 1H), 7.39 (d, *J* = 7.8 Hz, 1H), 7.32 (dd, *J* = 8.3, 4.2 Hz, 1H), 7.22 (d, *J* = 8.0 Hz, 2H), 6.92 (d, *J* = 7.8 Hz, 2H), 2.18 (s, 6H), 2.05 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.38, 147.20, 139.55, 138.49, 137.99, 136.82, 136.26, 134.42, 130.43, 128.74, 127.63, 127.48, 127.31, 121.07, 116.97, 116.43, 29.61, 21.25, 20.85, 17.08. IR (neat)3339, 2922, 2851, 1666, 1520, 1483, 1424, 1384, 1326, 823, 791. HRMS (EI) calcd. for $C_{21}H_{20}N_2O$: 316.1576. Found: 316.1580.

(*Z*)-2-methyl-*N*-(quinolin-8-yl)-3-(p-tolyl)pent-2-enamide(3bd)



This amide was obtained as an oil liquid. Purified by column chromatography (DCM) (26.4 mg, 40%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.33 (s, 1H), 8.66 (d, *J* = 7.4 Hz, 1H), 8.56 (d, *J* = 3.9 Hz, 1H), 8.03 (d, *J* = 8.2 Hz, 1H), 7.44 (t, *J* = 7.9 Hz, 1H), 7.40-7.29 (m, 2H), 7.20 (d, *J* = 7.7 Hz, 2H), 6.93 (d, *J* = 7.6 Hz, 2H), 2.58 (q, *J* = 7.4 Hz, 2H), 2.19 (s, 3H), 2.04 (s, 4H), 1.00 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (75 MHz, Acetone) δ 170.36, 147.32, 144.46, 138.10, 136.73, 135.94, 134.53, 129.95, 128.73, 127.97, 127.57, 127.20, 121.08, 120.94, 27.93, 20.85, 16.25, 11.93. IR (neat) 3337, 2969, 2926, 1633, 1519, 1483, 1459, 1423, 1384, 1326, 824, 791. HRMS (EI) calcd. for $C_{22}H_{22}N_2O$: 330.1732. Found: 330.1735.

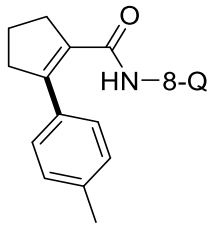
4'-methyl-*N*-(quinolin-8-yl)-3,4,5,6-tetrahydro-[1,1'-biphenyl]-2-carboxamide(3be)



This amide was obtained as a white solid. Purified by column chromatography (DCM)

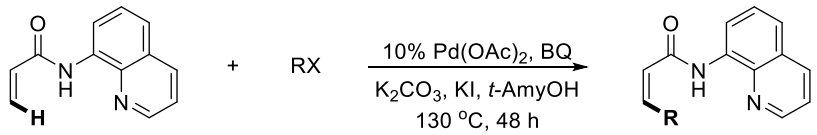
(41.0 mg, 60%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.39 (s, 1H), 8.69 (d, *J* = 7.4 Hz, 1H), 8.53 (s, 1H), 8.05 (d, *J* = 8.2 Hz, 1H), 7.40 (ddd, *J* = 16.1, 11.9, 6.3 Hz, 3H), 7.23 (d, *J* = 7.7 Hz, 2H), 6.95 (d, *J* = 7.6 Hz, 2H), 2.61 (s, 2H), 2.49 (s, 2H), 2.08 (s, 3H), 1.82 (s, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.79, 147.24, 140.58, 138.82, 136.95, 136.05, 134.54, 132.56, 128.83, 127.61, 127.43, 127.25, 121.07, 120.98, 116.30, 31.91, 27.13, 22.70, 22.11, 20.90. IR (neat) 3342, 2927, 2854, 1662, 1521, 1483, 1423, 1384, 1325, 825, 791. HRMS (EI) calcd. for $C_{23}H_{22}N_2O$: 342.1732. Found: 342.1736.

_N_-(quinolin-8-yl)-2-(p-tolyl)cyclopent-1-ene-1-carboxamide(3bf)



This amide was obtained as a white solid. Purified by column chromatography (DCM) (19.7 mg, 30%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.38 (s, 1H), 8.70 (d, *J* = 7.5 Hz, 1H), 8.52 (dd, *J* = 4.2, 1.5 Hz, 1H), 8.03 (d, *J* = 8.2 Hz, 1H), 7.45 (t, *J* = 7.9 Hz, 1H), 7.38 (d, *J* = 8.2 Hz, 1H), 7.32 (dd, *J* = 8.2, 4.2 Hz, 1H), 7.23 (d, *J* = 8.0 Hz, 2H), 6.95 (d, *J* = 7.8 Hz, 2H), 2.61 (s, 2H), 2.48 (s, 2H), 2.07 (s, 3H), 1.87-1.79 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.79, 147.24, 140.58, 138.82, 136.95, 136.05, 134.54, 132.56, 128.83, 127.61, 127.43, 127.25, 121.07, 120.98, 116.30, 31.91, 27.13, 22.70, 22.11, 20.90. IR (neat) 3310, 2917, 2845, 1660, 1521, 1484, 1423, 1384, 1324, 824, 790. HRMS (EI) calcd. for $C_{22}H_{20}N_2O$: 328.1576. Found: 328.1573.

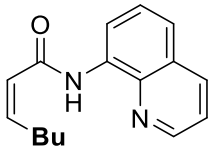
5. General Procedures for Stereoselective Alkylation



1a **6** **7**

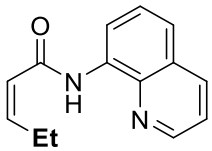
To a 15 mL Schlenk tube, substrate **1a** (39.6 mg, 0.2 mmol), alkyl iodide or bromide (1.0 mmol), $Pd(OAc)_2$ (4.4 mg, 0.02 mmol), K_2CO_3(55.3 mg, 0.4 mmol), KI (66.4 mg, 0.4 mmol), BQ(43.2 mg, 0.2mmol) and *t*-AmyOH (1 mL) were added, sealed with a Teflon cap. The tube was heated at 130 °C in an oil bath and stirring for 48 hours. After cooling to room temperature, the reaction mixture was diluted with dichloromethane (15 mL) and washed with H_2O (10 mL), aqueous layer was extracted by DCM (3 x 5 mL). Combined organic layers were dried over Na_2SO_4. To remove the solvent by evaporation after filtration, the residue was purified by flash chromatography to give the target products.

(*Z*)-*N*-(quinolin-8-yl)hept-2-enamide(7a)



This amide was obtained as a yellow oil liquid. Purified by column chromatography (5% PE/EtOAc) (10.7 mg, 21%).^{1}H NMR (300 MHz, $CDCl_3$) δ 9.85 (s, 1H), 8.85 (dd, *J* = 7.1, 1.7 Hz, 1H), 8.84-8.70 (m, 1H), 8.16 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.63-7.36 (m, 3H), 6.20 (dt, *J* = 11.5, 7.2 Hz, 1H), 6.14-6.01 (m, 1H), 2.81 (dt, *J* = 8.3, 4.1 Hz, 2H), 1.55-1.34 (m, 4H), 0.94 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, CDCl3) δ 164.63, 147.68, 147.29, 138.03, 136.00, 135.48, 134.30, 127.59, 127.07, 122.58, 121.19, 121.03, 116.01, 31.14, 28.30, 22.07, 13.57. IR (neat) 3351, 2955, 2923, 2860, 1679, 1522, 1485, 1426, 1382, 1325, 1164, 825, 791. HRMS (EI) calcd. for $C_{16}H_{18}N_2O$: 254.1419. Found: 254.1422.

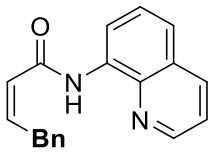
(*Z*)-*N*-(quinolin-8-yl)pent-2-enamide(7b)



This amide was obtained as a yellow oil liquid. Purified by column chromatography (5% PE/EtOAc) (16.7 mg, 37%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.84 (s, 1H), 8.93 -8.71 (m, 2H), 8.15 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.65-7.36 (m, 3H), 6.19 (dt, *J* = 11.4, 7.3 Hz, 1H), 6.07 (t, *J* = 6.3 Hz, 1H), 2.82 (pd, *J* = 7.5, 1.3 Hz, 2H), 1.13 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.58, 148.60, 147.69, 138.03, 136.00, 134.28, 127.57, 127.05, 122.14, 121.19, 121.05, 115.99, 21.96, 13.40. IR (neat) 3345, 2969, 2929, 2857, 1679, 1523, 1486, 1425, 1382, 1325, 1162, 825, 791, 670. HRMS (EI) calcd. for

$C_{14}H_{14}N_2O$: 226.1106. Found: 226.1103.

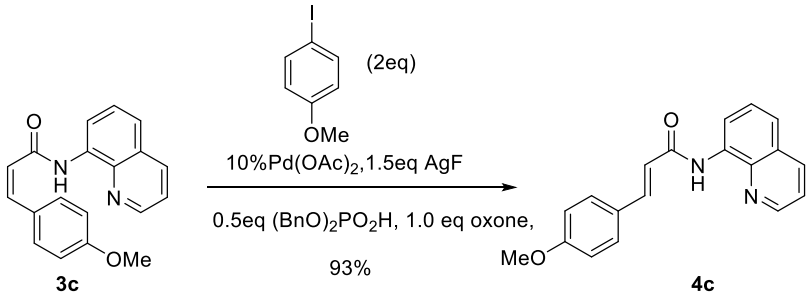
(*Z*)-4-phenyl-*N*-(quinolin-8-yl)but-2-enamide(7c)



This amide was obtained as a yellow oil liquid. Purified by column chromatography (5% PE/EtOAc) (12.7 mg, 22%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.94 (s, 1H), 8.90 (dd, *J* = 7.1, 1.5 Hz, 1H), 8.81 (dd, *J* = 4.2, 1.5 Hz, 1H), 8.19 (dd, *J* = 8.3, 1.4 Hz, 1H), 7.62-7.51 (m, 2H), 7.47 (dd, *J* = 8.3, 4.2 Hz, 1H), 7.32 (d, *J* = 4.3 Hz, 3H), 7.26-7.10 (m, 2H), 6.36 (dt, *J* = 11.3, 7.4 Hz, 1H), 6.20 (d, *J* = 11.3 Hz, 1H), 4.22 (dd, *J* = 7.4, 1.2 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.34, 147.74, 145.17, 139.57, 138.02, 136.08, 134.18, 128.34, 128.22, 127.61, 127.08, 125.86, 122.68, 121.25, 116.19, 34.63. IR (neat) 3342, 2969, 2923, 2871, 1678, 1636, 1522, 1483, 1459, 1426, 1383, 1325, 1186, 1165, 825, 790,757. HRMS (EI) calcd. for $C_{19}H_{16}N_2O$: 288.1263. Found: 288.1267.

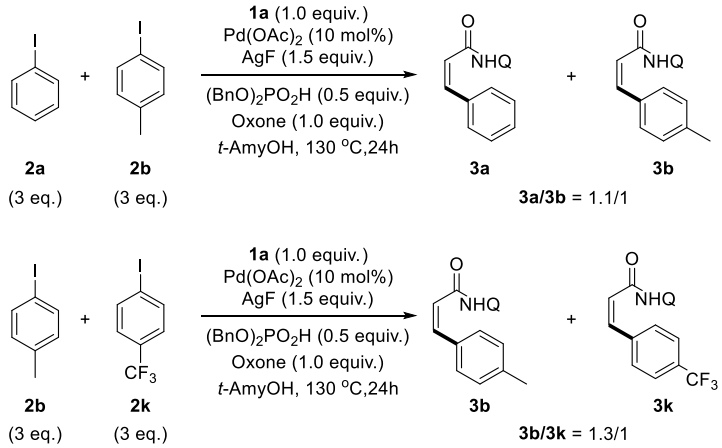
6. Control Experiment

*Control experiment of Z-isomer **3c** under reaction conditions:*



To a 15 mL Schlenk tube**, 3c** (0.05 mmol), $Pd(OAc)_2$ (10% mmol), iodide(2 eq.), AgF(1.5 eq.), $(BnO)_2PO_2H$(0.5 eq.) and t-AmyOH(0.5 mL) were combine added under air. After sealing the tube with a Teflon cap, the mixture was stirred at the 130 ^oC for 24 h. After the reaction, the reaction was cooled to room temperature, filtered through a pad of silica gel and washed with 100 mL 50% EtOAc/ petroleum ether. The solvents were removed under reduced pressure and the crude yield was measured by NMR.

Intermolecular Competition Experiments



7. Scale up Experiment on Gram Scale

To a 100 mL round bottom flask, substrate **1** (0.99 g, 5 mmol), 1-bromo-4-iodobenzene (4.2 g, 15 mmol), $Pd(OAc)_2$ (0.11 g, 0.5 mmol), AgF (0.95 g, 4.5 mmol), $(BnO)_2PO_2H$ (0.70 g, 2.5 mmol), oxone(3.05 g, 5 mmol) and *t*-AmyOH (25 mL) were added, reflux at 130 ^oC in oil bath for 24 h. After cooling to room temperature, the reaction mixture was diluted with dichloromethane (30 mL) and washed with H_2O (20 mL), aqueous layer was extracted by DCM (3 x 20 mL). Combined organic layers were dried over Na_2SO_4. To remove the solvent by evaporation after filtration, the residue was purified by flash chromatography to give 1.0 g product **3g** as a white solid.

8. Removal of Directing Group

The procedure was followed by a literature procedure.[4]

To a 35 mL Schlenk tube equipped with a stir bar was added (*Z*)-3-(4-bromophenyl)-*N*-(quinolin-8-yl) acrylamide (**3h**) (0.2 mmol, 70.6 mg). Dry methanol (3 mL) was added to the tube. $BF_3{\cdot}Et_2O$ (0.17 mL, 1.32 mmol) was added dropwise to the stirred solution. The resulting mixture was stirred at 110 ℃ for 30 h. After cooling to r.t., Et_3N (0.28 mL, 2 mmol) was added dropwise to the reaction mixture with stirring. Evaporation to remove the organic solvents gave the crude product. The crude NMR showed a *Z/E* product ratio of 100:3 (*See following crude NMR spectrum for reference, page S48*). Purification by flash chromatography (PE/EtOAc=97/3) gave 44.9 mg of yellow liquid (**8h**) (93%). This compound is known.[5] ^1H NMR (300 MHz, $CDCl_3$) δ 7.54-7.42 (m, 4H), 6.88 (d, *J* = 12.6 Hz, 1H), 5.98 (d, *J* = 12.6 Hz, 1H), 3.72 (s, 3H).

(*Z*)-Methyl 4-Bromocinnamate:

(Jacobsen, E. N.; Deng, L.; Furukawa, Y.; Martinez, L. E. *Tetrahedron* 1994, **50**, 4323–4334.)

^1H NMR ($CDC1_3$) 3.72 (s, 3 H), 5.98 (d, J = 12.6 Hz, 1 H), 6.88 (d, J= 12.6 Hz, 1 H), 7.48 (br, 4 H).

(*E*)-Methyl 4-Bromocinnamate:

(Oger, N.; Grognec, E. L.; Felpin, F-X. *J. Org. Chem.* 2014, **79**, 8255−8262.)

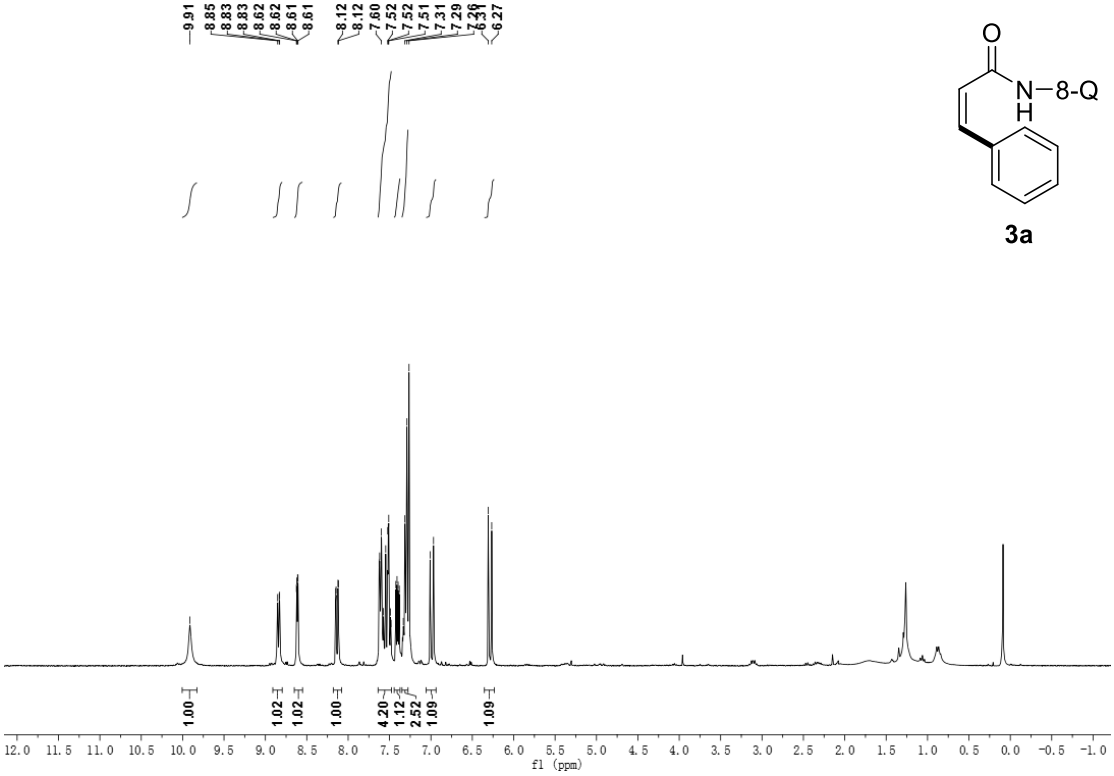
^1H NMR ($CDCl_3$, 300 MHz): δ 3.81 (s, 3H), 6.43 (d, 1H, J = 16.0 Hz), 7.39 (d, 2H, J = 8.4 Hz), 7.52 (d, 2H, J = 8.5 Hz), 7.62 (d, 1H, J = 16.0 Hz).

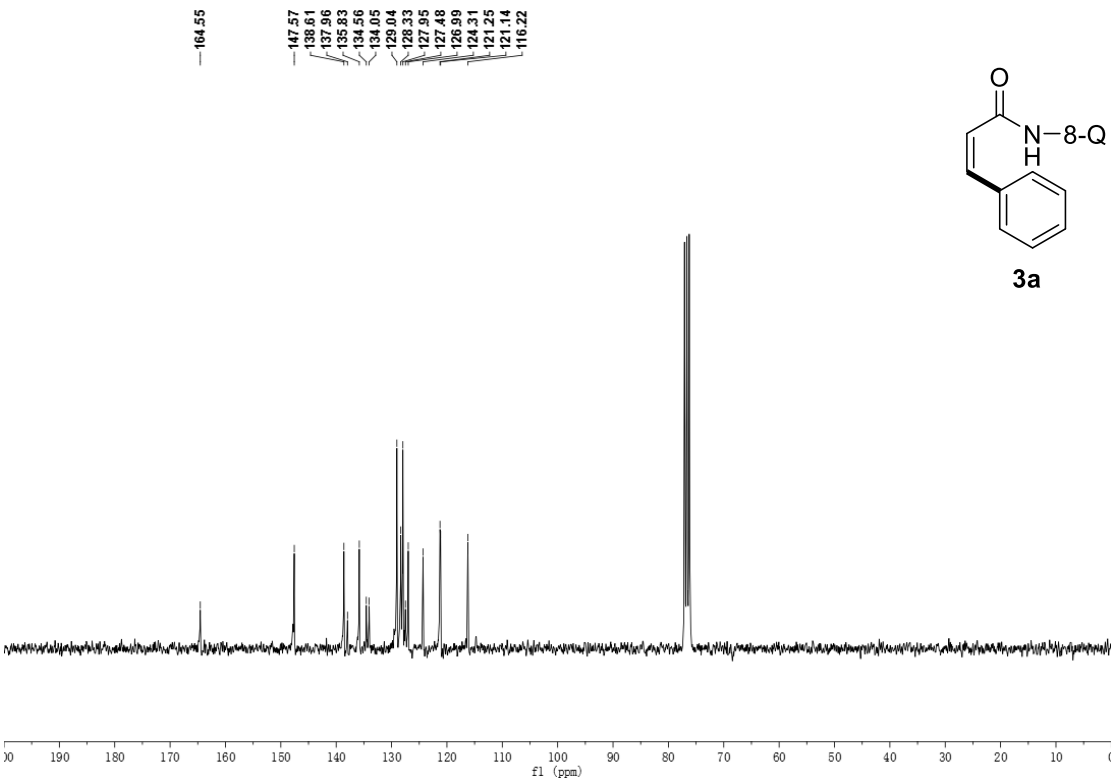
9. References

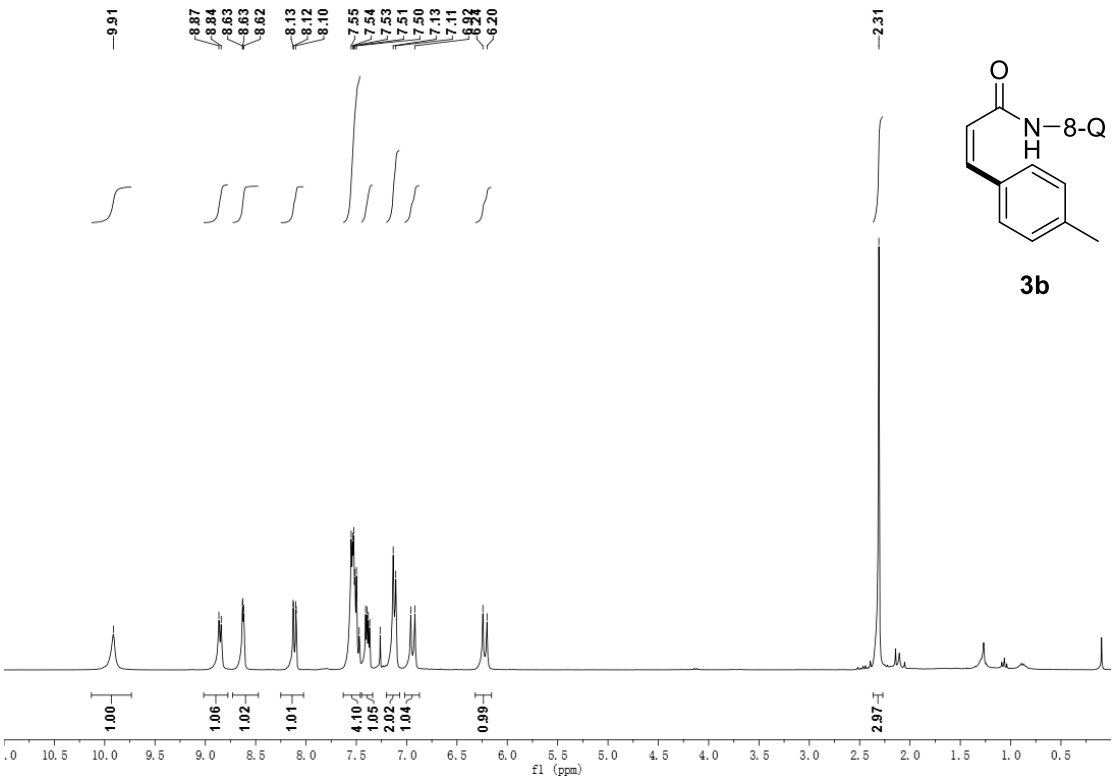
1. B. M. Monks, E. R. Fruchey, S. P. Cook, *Angew. Chem. Int. Ed.*, 2014, **53**, 11065.
2. L. Ilies, T. Matsubara, S. Ichikawa, S. Asako, E. Nakamura, *J. Am. Chem. Soc.*, 2014, **136**, 13126.
3. Y. Aihara, N. Chatani, *J. Am. Chem. Soc.*, 2013, **135**, 5308.
4. L. D. Tran, O. Daugulis, *Angew. Chem., Int. Ed.*, 2012, **51**, 5188.
5. (a) G. R. Pettit, P. D. Quistorf, J. A. Fry, D. L. Herald, E. Hamel, J. C. Chapuis, *J. Nat. Prod.*, 2009, **72**, 876; (b) Jacobsen, E. N.; Deng, L.; Furukawa, Y.; Martinez, L. E. *Tetrahedron* 1994, **50**, 4323–4334.

10.[1]H and [13]C NMR spectra of products

Note: A mixture spectrum of **3e** and **3s** were given due to separation challenge.



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8.87
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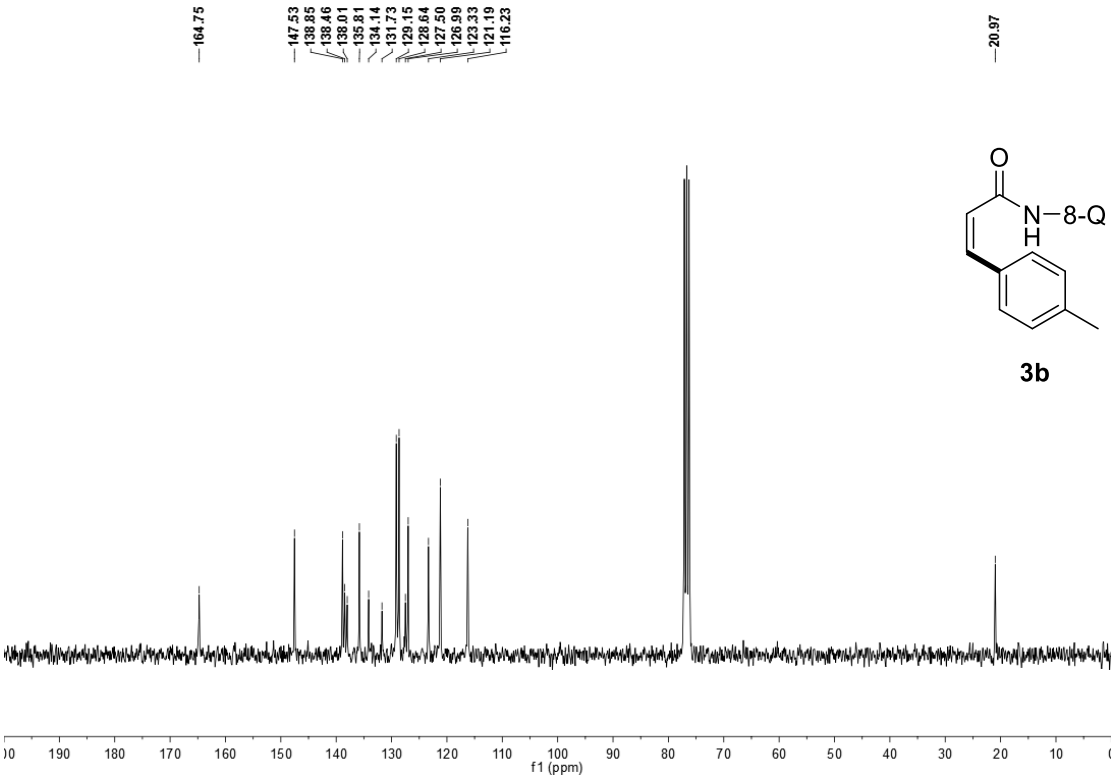
8.63
8.63
8.62
8.13
8.12
8.10
7.55
7.54
7.53
7.51
7.50
7.13
7.11
6.20
2.31
1.00
1.06
1.02
1.01
4.10
1.05
2.02
1.04
0.99
2.97
f1 (ppm)
O
N
H
8-Q

3b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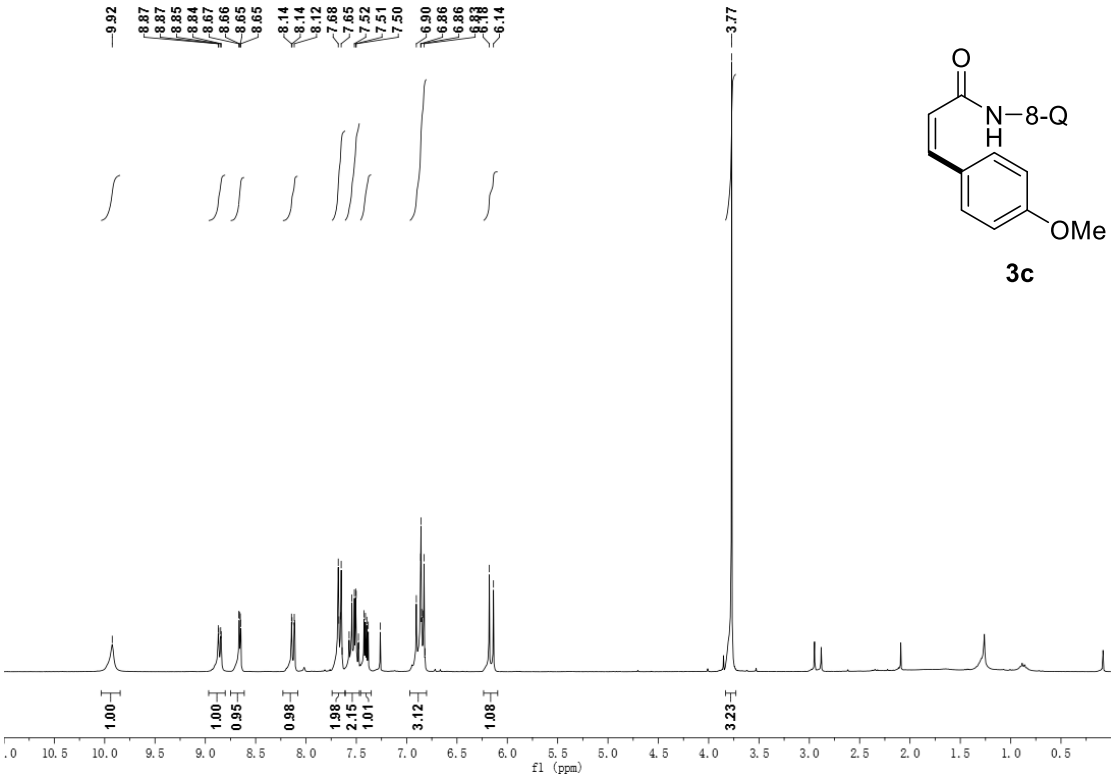
20.97
f1 (ppm)
O
N
H
8-Q

3b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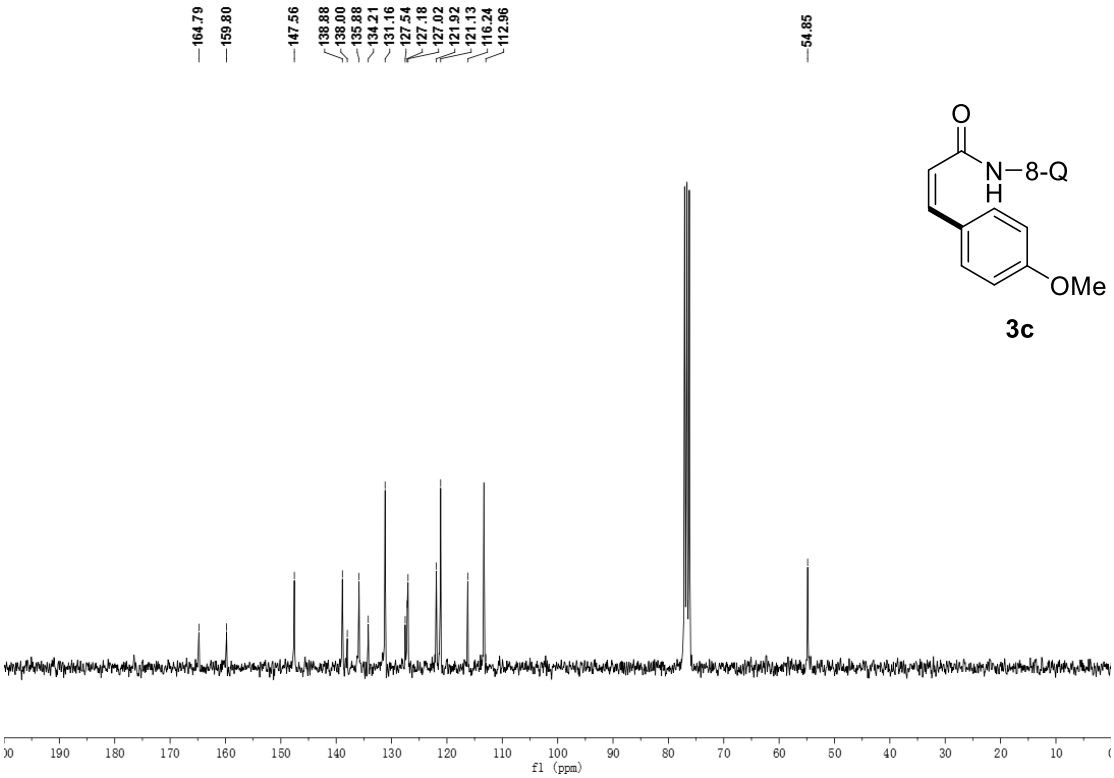
7.52
7.51
7.50
6.90
6.86
6.86
6.83
6.18
6.14
3.77
1.00
1.00
0.95
0.98
1.98
2.15
1.01
3.12
1.08
3.23
f1 (ppm)
O
N–8-Q
H
OMe
3c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134.21
131.16
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127.18
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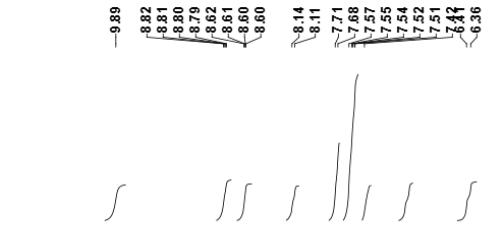
f1 (ppm)
O
N–8-Q
H
OMe
3c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8.60
8.60
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8.11
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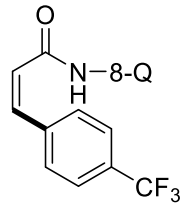
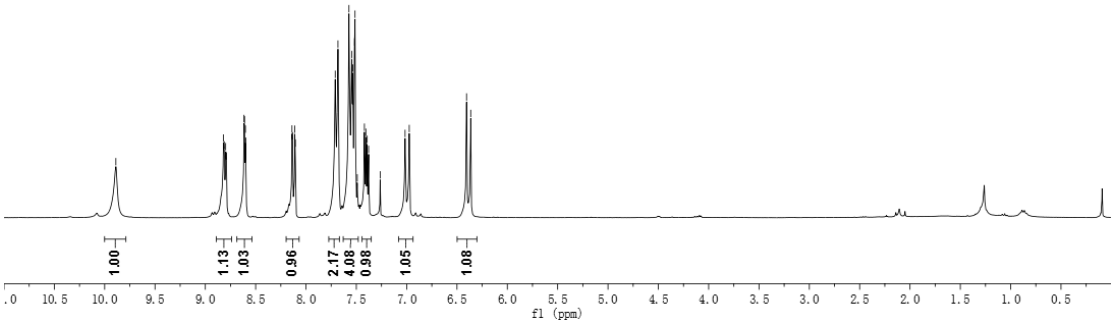
7.54
7.52
7.51
6.44
6.36


O
N
H
8-Q
CF3

3d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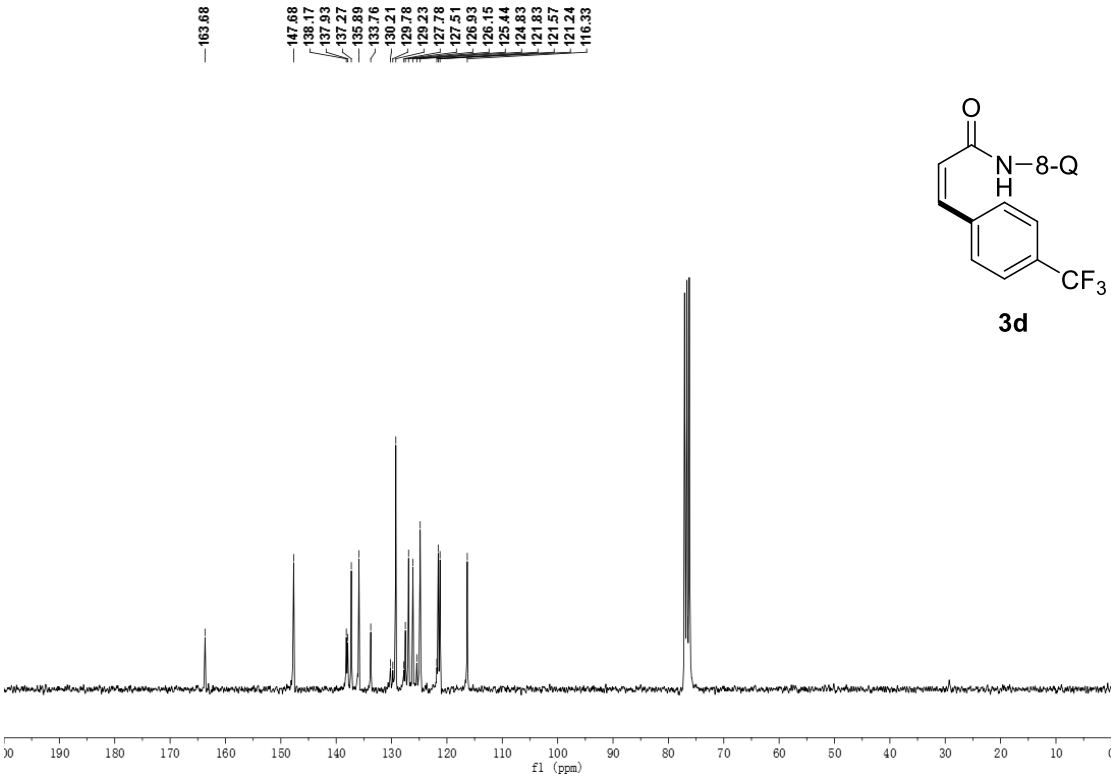
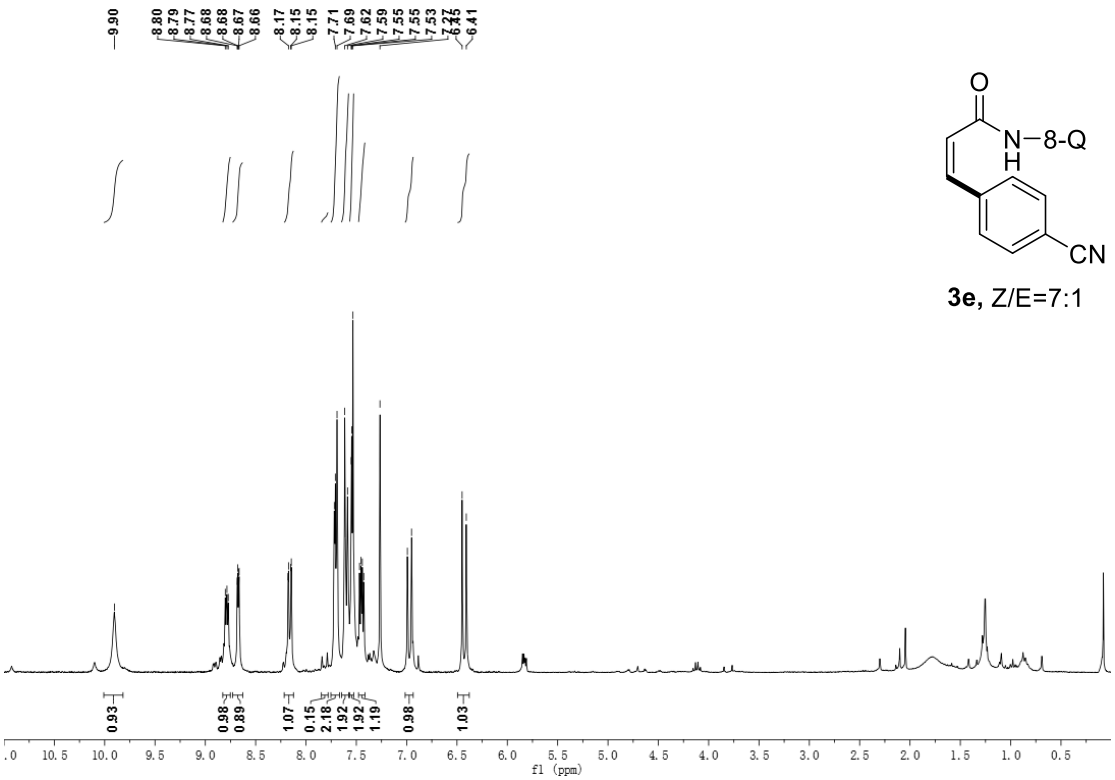
4.08
0.98
1.05
1.08
f1 (ppm)

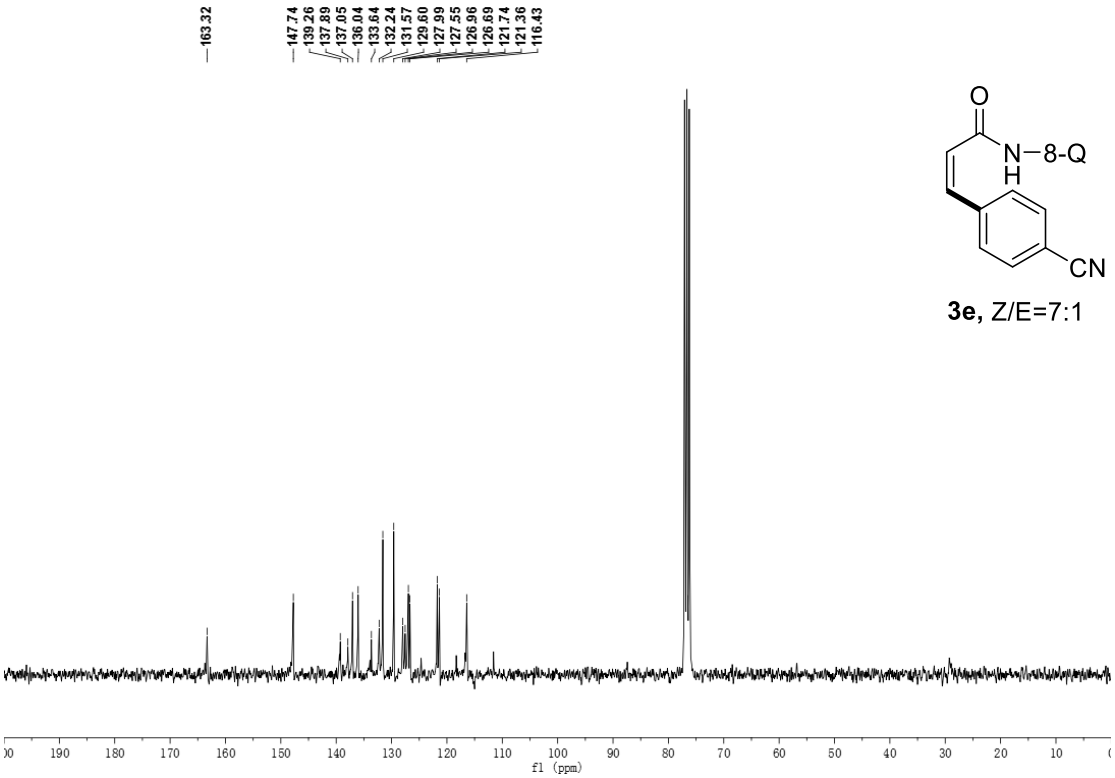

163.68
147.68
138.17
137.93
137.27
135.89
133.76
130.21
129.78
129.23
127.78
127.51
126.93
126.15
125.44
124.83
121.83
121.57
121.24
116.33
f1 (ppm)

O
N
H
8-Q
CF3

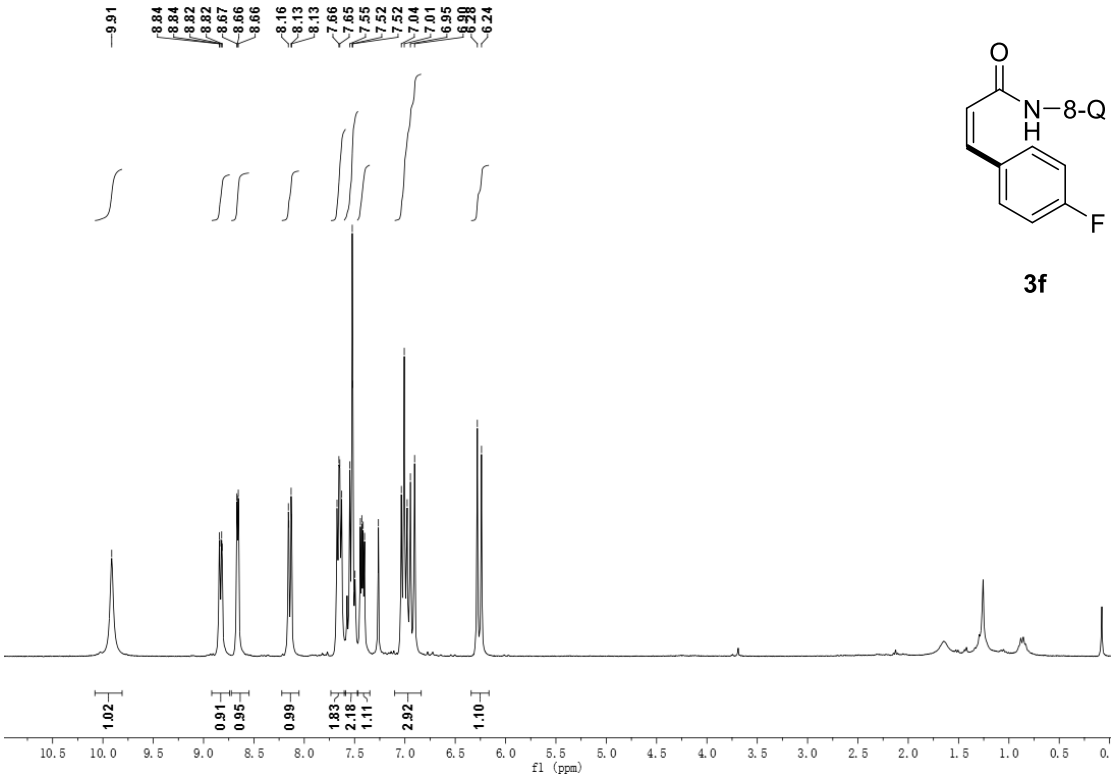
3d



3e, Z/E=7:1

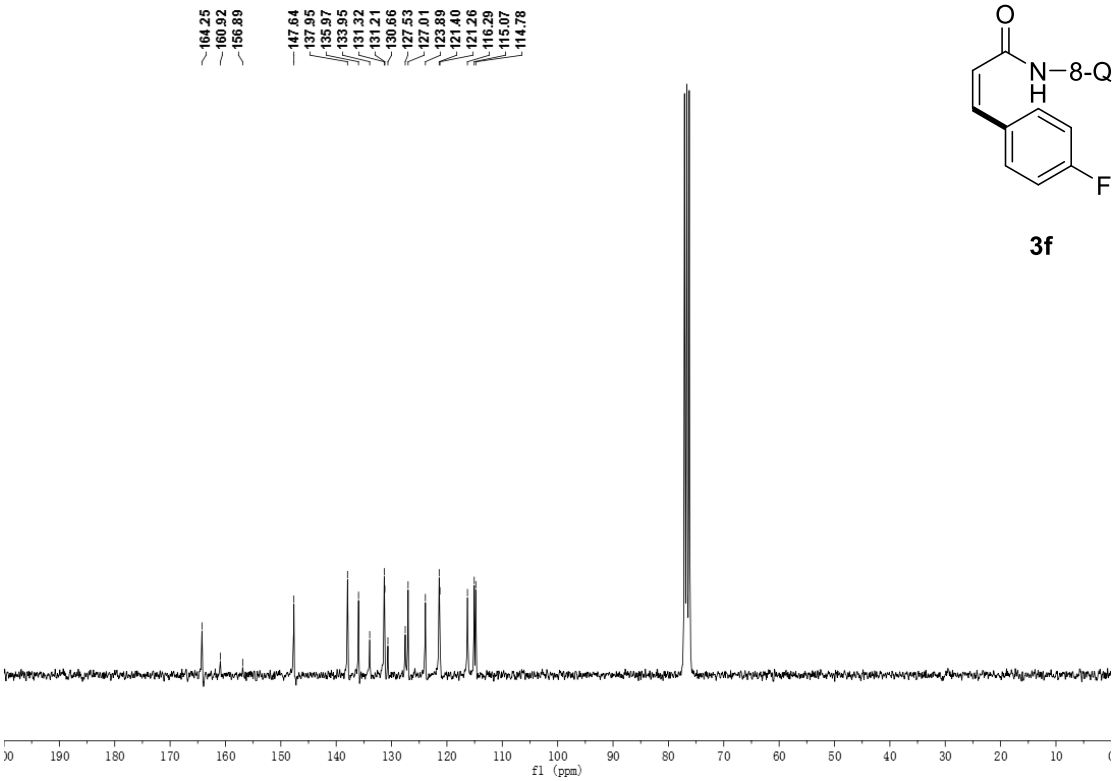


3e, Z/E=7:1


9.91
8.84
8.84
8.82
8.82
8.67
8.66
8.66
8.16
8.13
8.13
7.66
7.65
7.55
7.52
7.52
7.04
7.01
6.95
6.24
1.02
0.91
0.95
0.99
1.83
2.18
1.11
2.92
1.10
f1 (ppm)

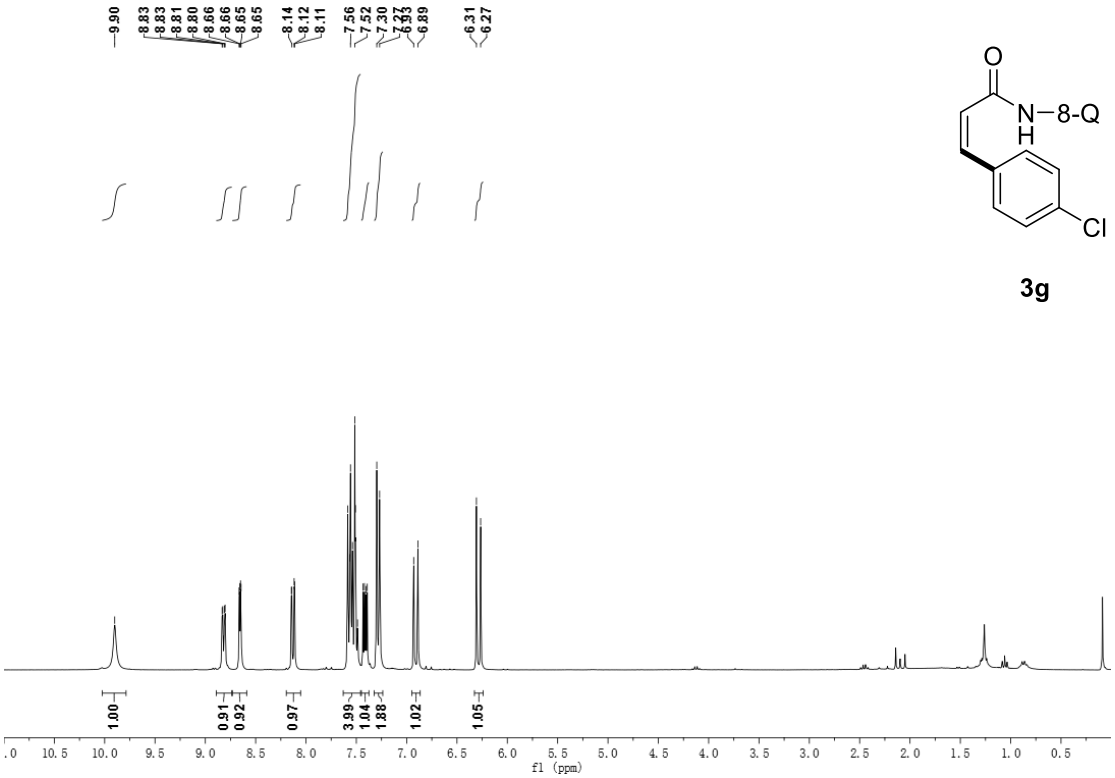
O
N
H
8-Q
F

3f

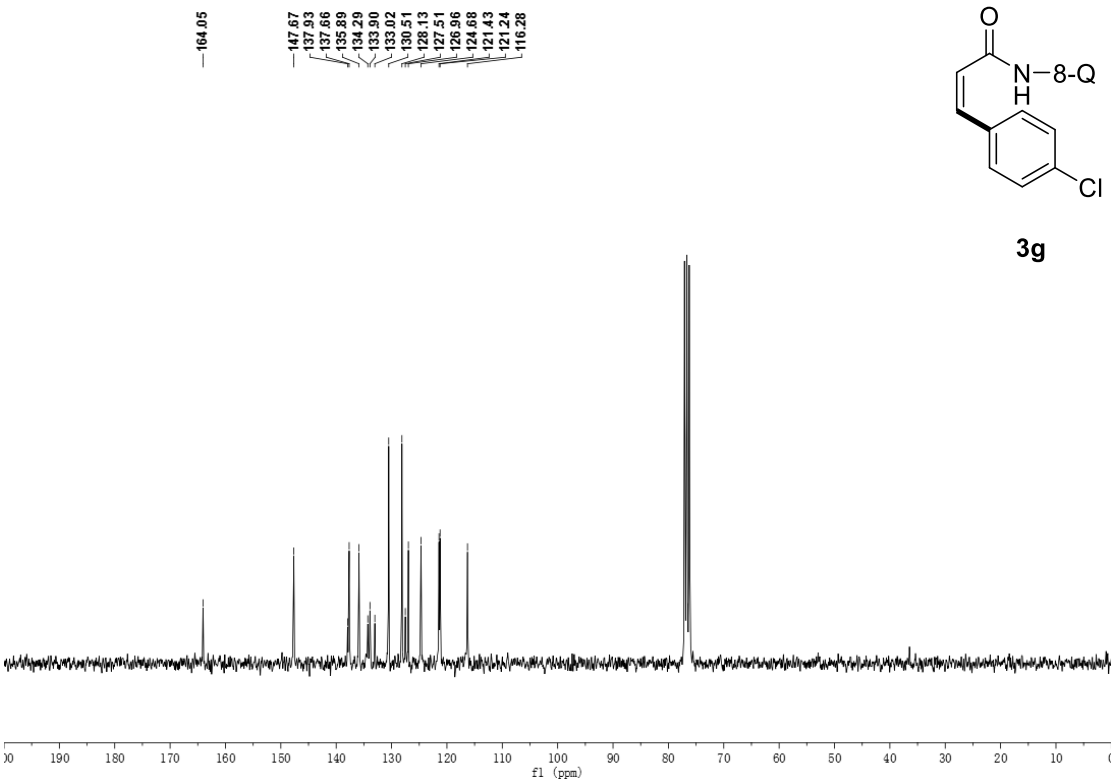

164.25
160.92
156.89
147.64
137.95
135.97
133.95
131.32
131.21
130.66
127.53
127.01
123.89
121.40
121.26
116.29
115.07
114.78
f1 (ppm)

O
N
H
8-Q
F

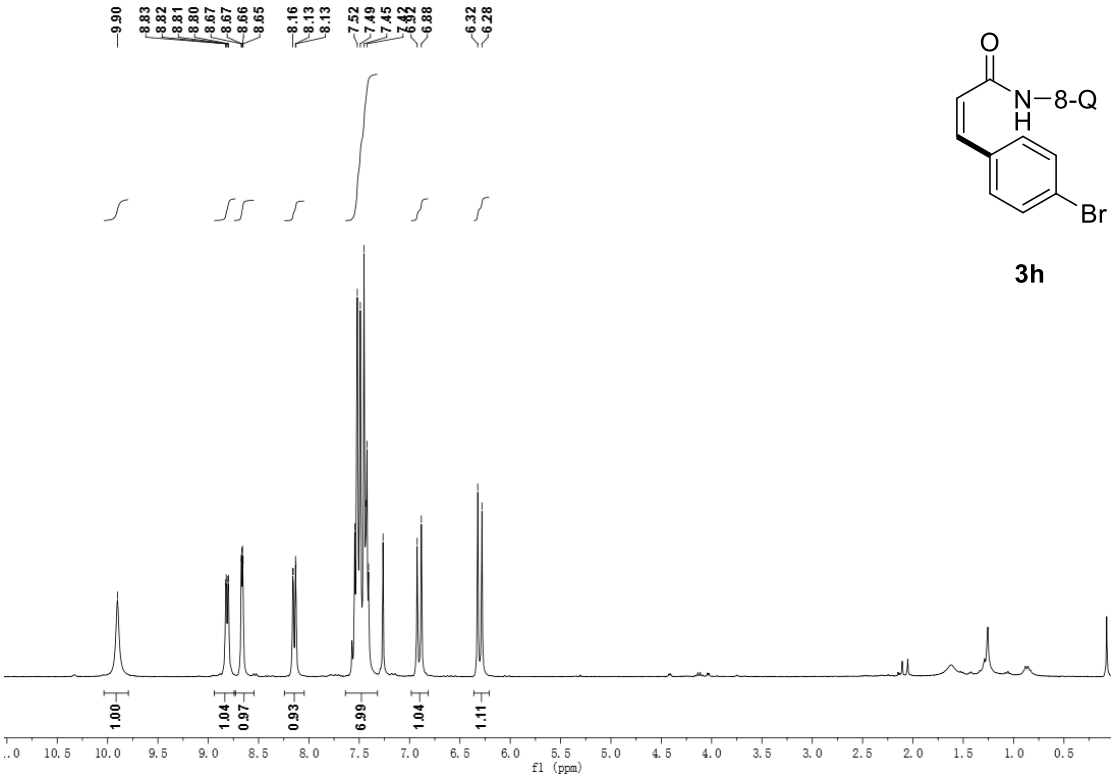
3f


9.90
8.83
8.83
8.81
8.80
8.66
8.66
8.65
8.65
8.14
8.12
8.11
7.56
7.52
7.30
6.89
6.31
6.27
O
N
H
8-Q
Cl
1.00
0.91
0.92
0.97
3.99
1.04
1.88
1.02
1.05
f1 (ppm)

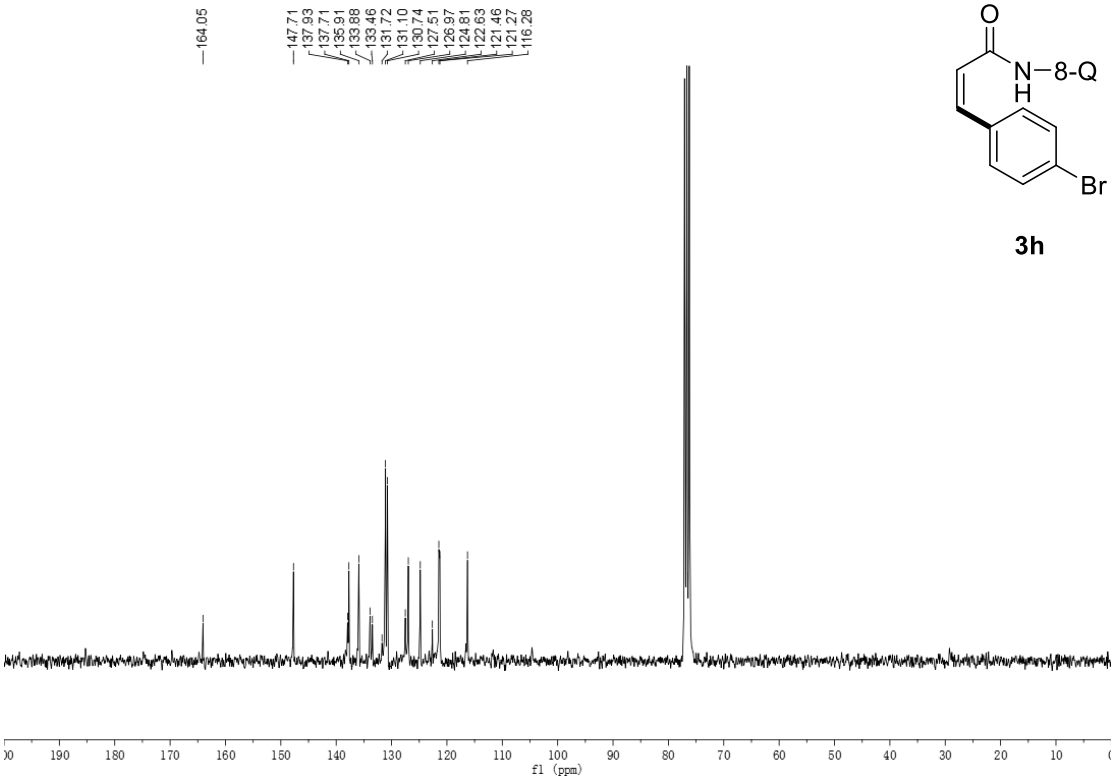
3g


164.05
147.67
137.93
137.66
135.89
134.29
133.90
133.02
130.51
128.13
127.51
126.96
124.68
121.43
121.24
116.28
O
N
H
8-Q
Cl
f1 (ppm)

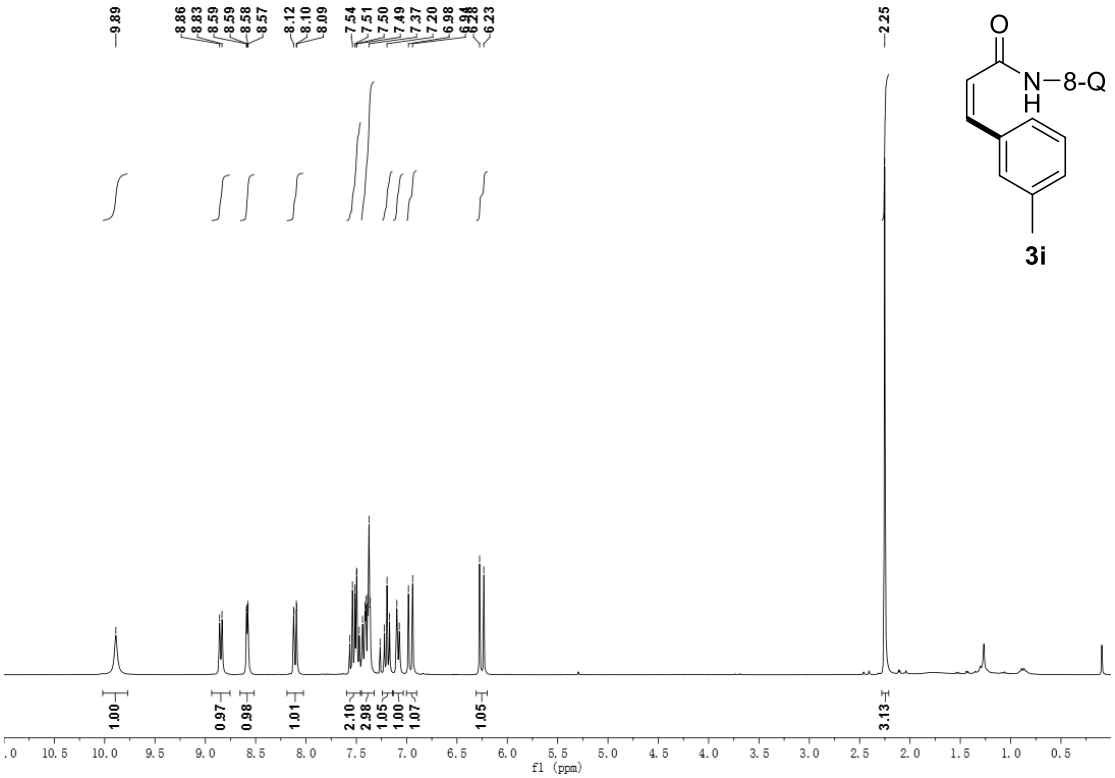
3g

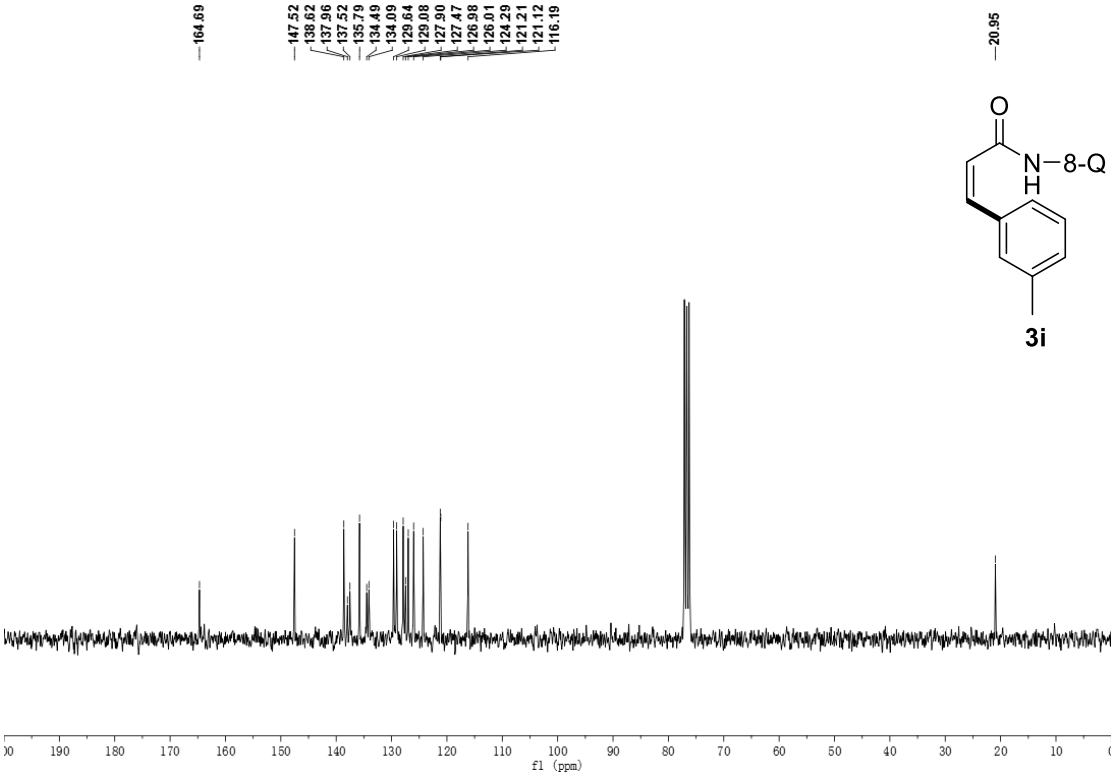

9.90
8.83
8.82
8.81
8.80
8.67
8.67
8.66
8.65
8.16
8.13
8.13
7.52
7.49
7.45
7.42
6.92
6.88
6.32
6.28
1.00
1.04
0.97
0.93
6.99
1.04
1.11
f1 (ppm)
O
N
H
8-Q
Br

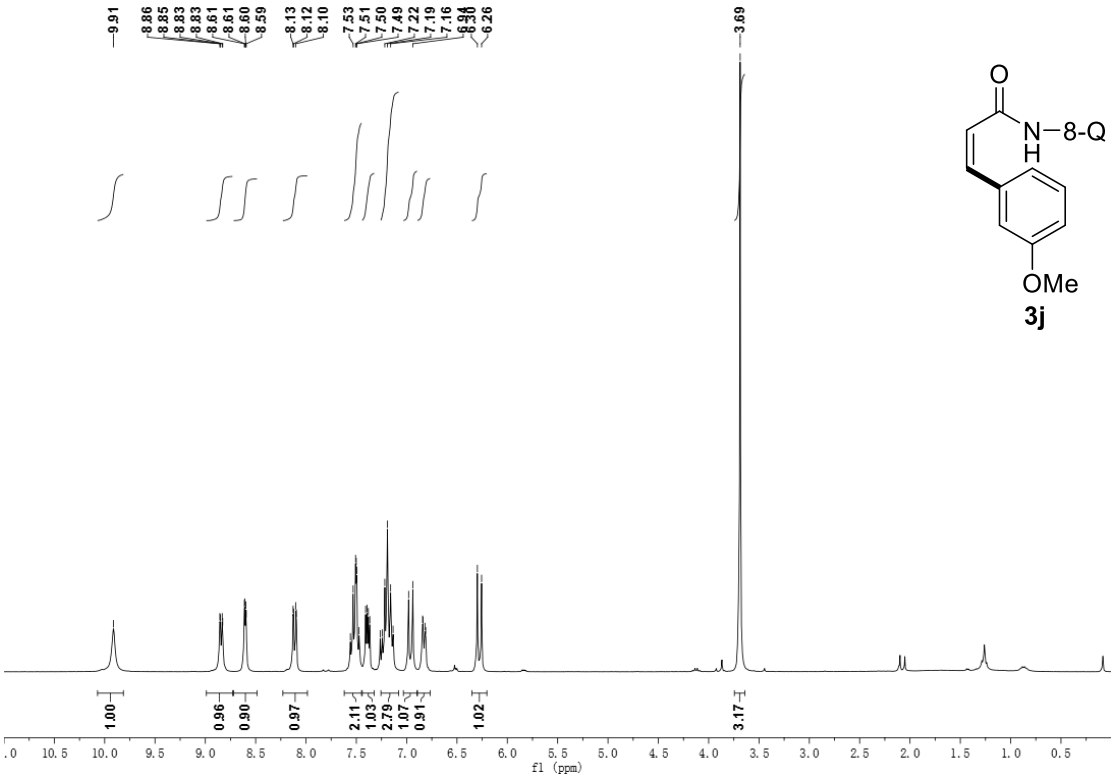
3h

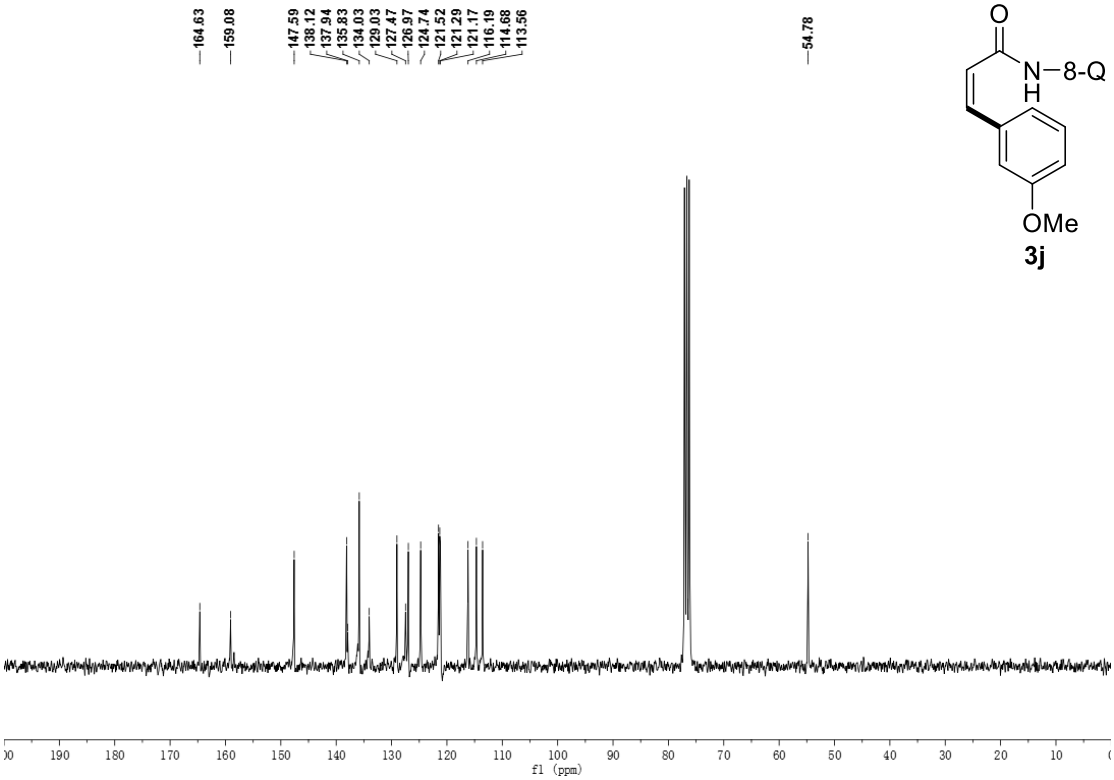

164.05
147.71
137.93
137.71
135.91
133.88
133.46
131.72
131.10
130.74
127.51
126.97
124.81
122.63
121.46
121.27
116.28
f1 (ppm)
O
N
H
8-Q
Br

3h


9.89
8.86
8.83
8.59
8.59
8.58
8.57
8.12
8.10
8.09
7.54
7.51
7.50
7.49
7.37
7.20
6.98
6.23
2.25
1.00
0.97
0.98
1.01
2.10
2.98
1.05
1.00
1.07
1.05
3.13
f1 (ppm)
O
N
H
8-Q
3i


164.69
147.52
138.62
137.96
137.52
135.79
134.49
134.09
129.64
129.08
127.90
127.47
126.98
126.01
124.29
121.21
121.12
116.19
20.95
f1 (ppm)
O
N
H
8-Q
3i


9.91
8.86
8.85
8.83
8.61
8.60
8.59
8.13
8.12
8.10
7.53
7.51
7.50
7.49
7.22
7.19
7.16
6.94
6.93
6.26
3.69
1.00
0.96
0.90
0.97
2.11
1.03
2.79
1.07
0.91
1.02
3.17
f1 (ppm)
O
N
H
8-Q
OMe
3j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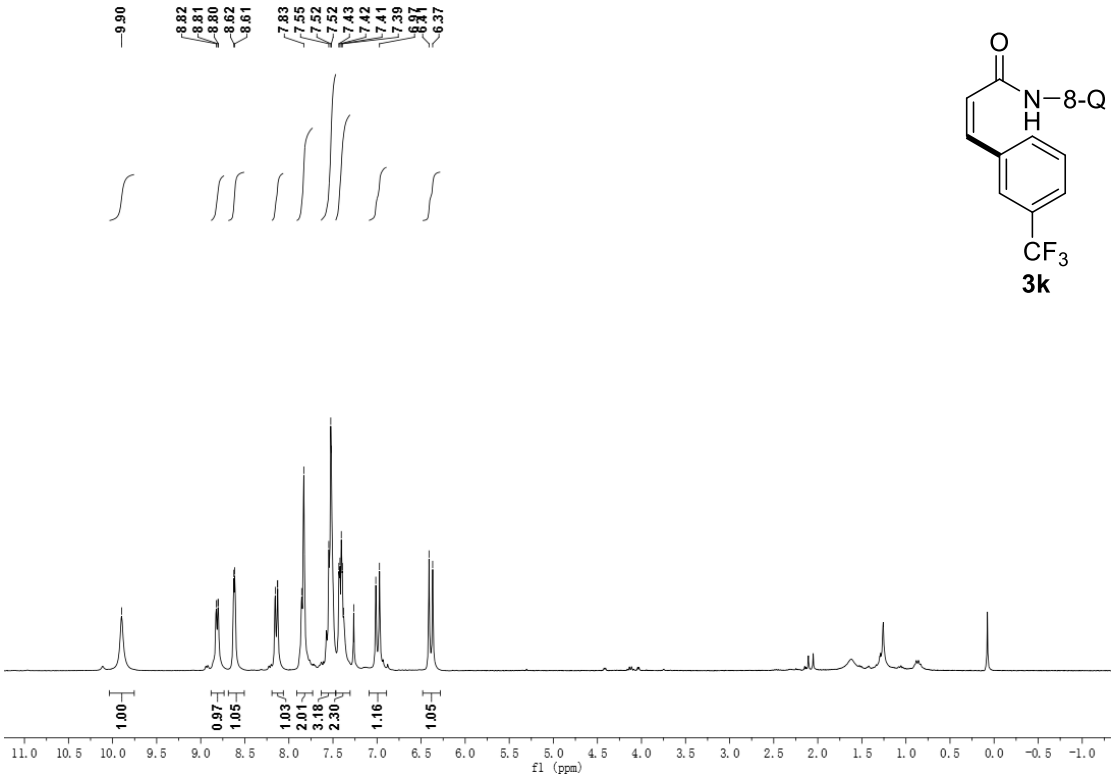
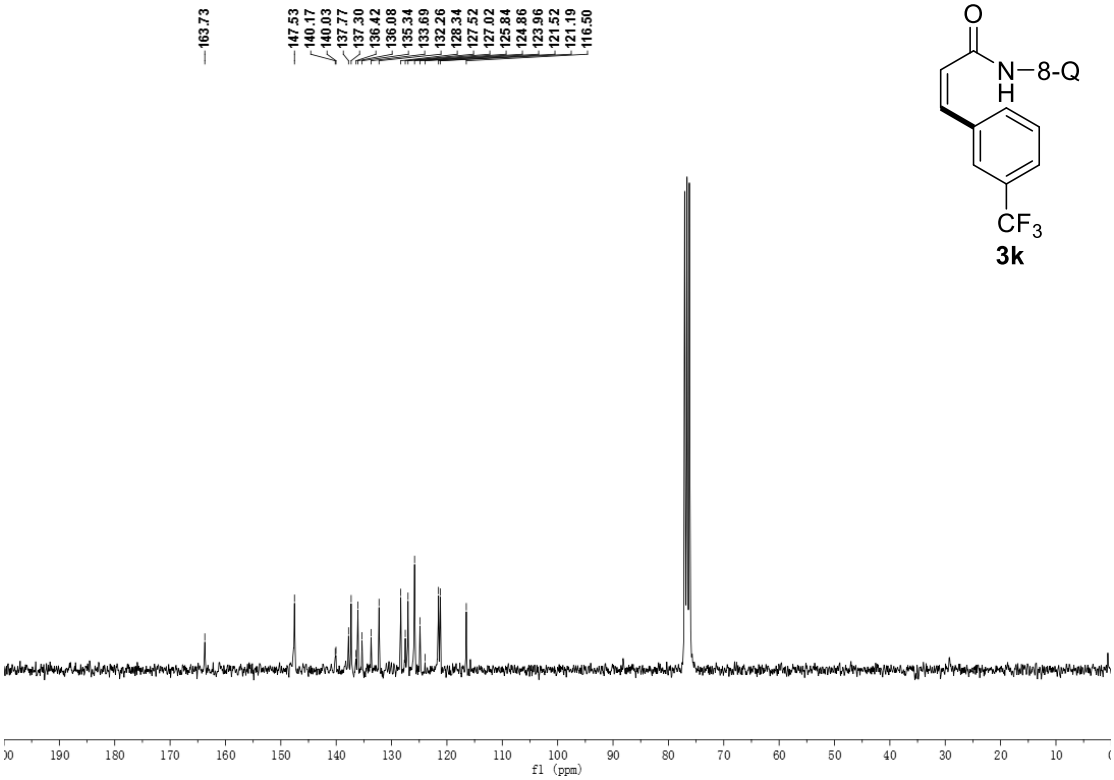
159.08
147.59
138.12
137.94
135.83
134.03
129.03
127.47
126.97
124.74
121.52
121.29
121.17
116.19
114.68
113.56
54.78
f1 (ppm)
O
N
H
8-Q
OMe
3j


9.90
8.82
8.81
8.80
8.62
8.61
7.83
7.55
7.52
7.52
7.43
7.42
7.41
7.39
6.41
6.37
O
N−8-Q
H
CF3
3k
1.00
0.97
1.05
1.03
2.01
3.18
2.30
1.16
1.05
f1 (ppm)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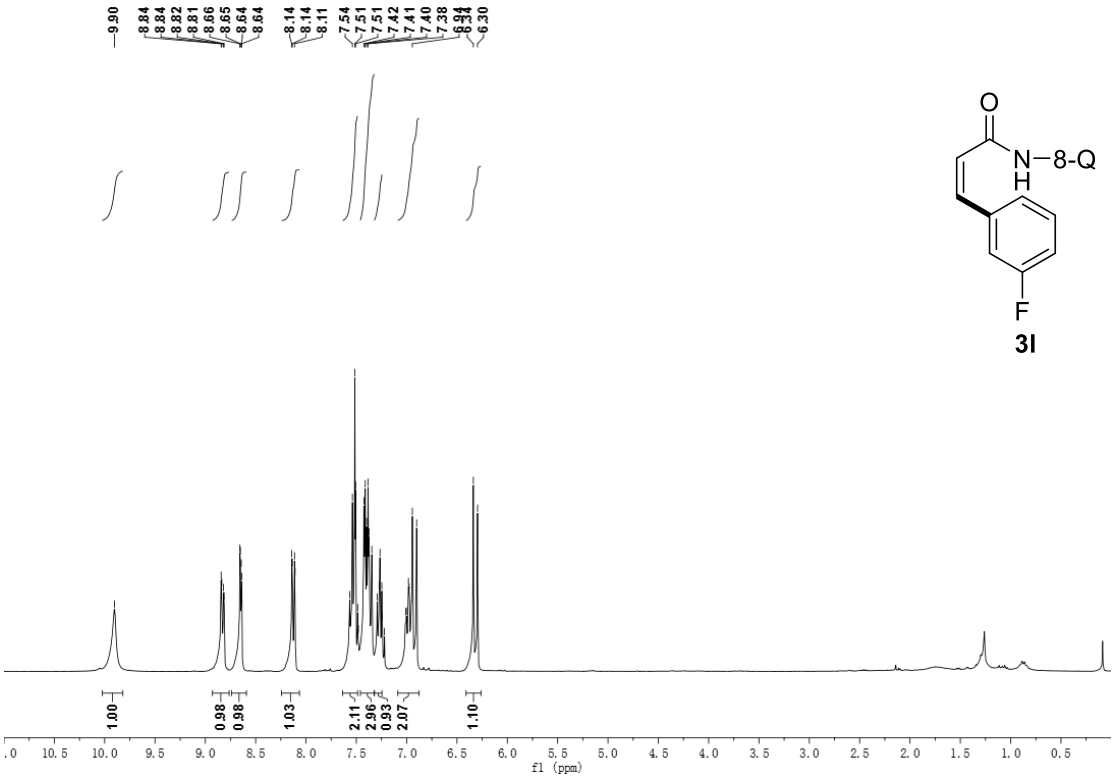
140.03
137.77
137.30
136.42
136.08
135.34
133.69
132.26
128.34
127.52
127.02
125.84
124.86
123.96
121.52
121.19
116.50
O
N−8-Q
H
CF3
3k
f1 (ppm)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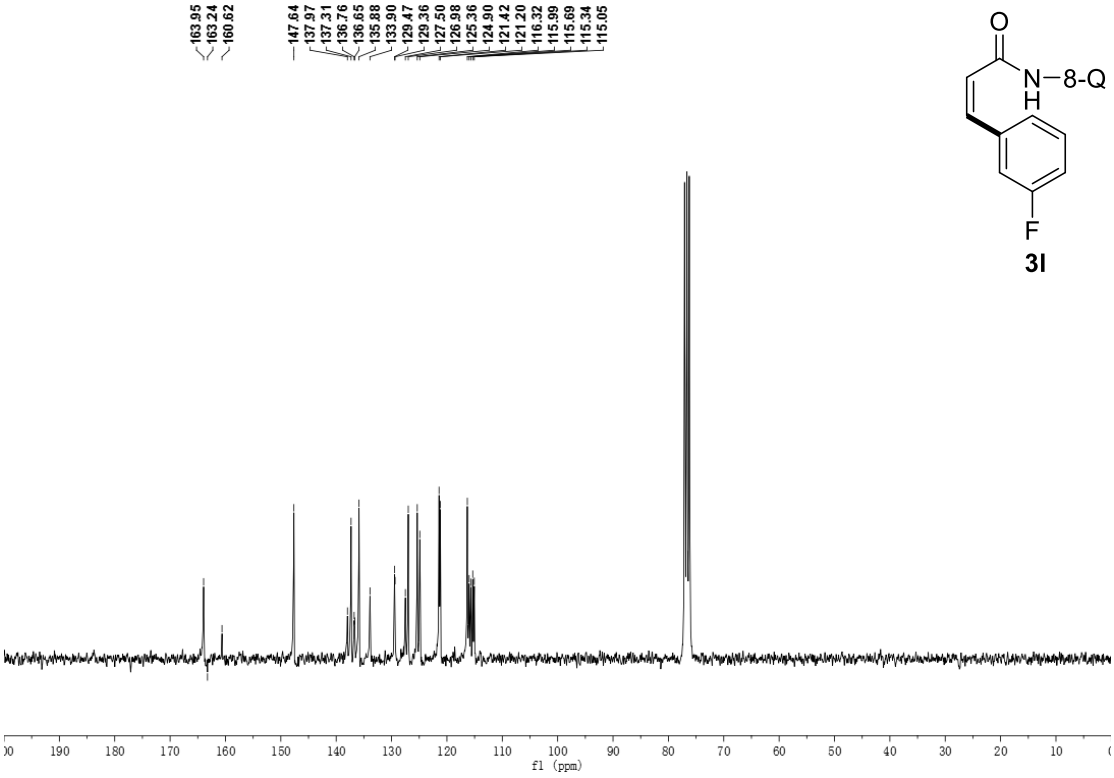
8.84
8.84
8.82
8.81
8.66
8.65
8.64
8.64
8.14
8.14
8.11
7.54
7.51
7.51
7.42
7.41
7.40
7.38
6.34
6.30
O
N
H
8-Q
F
3l
1.00
0.98
0.98
1.03
2.11
2.96
0.93
2.07
1.10
f1 (ppm)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136.76
136.65
135.88
133.90
129.47
129.36
127.50
126.98
125.36
124.90
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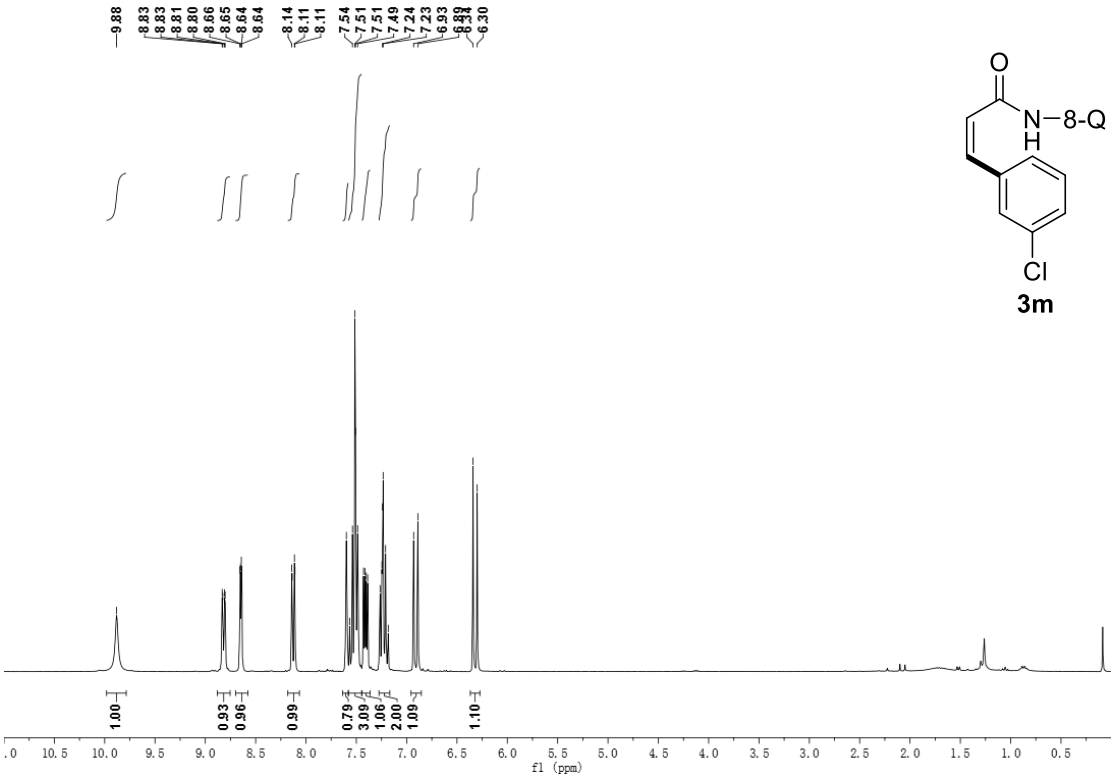
O
N
H
8-Q
F
3l
f1 (ppm)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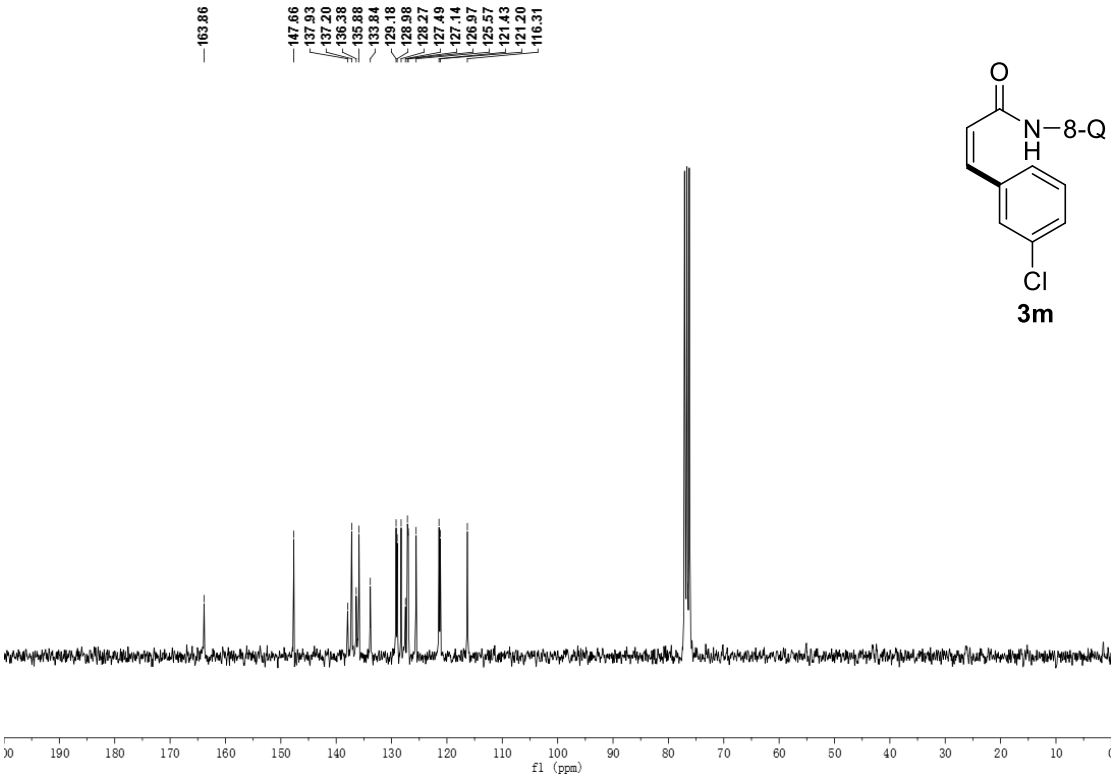
8.83
8.83
8.81
8.80
8.66
8.65
8.64
8.64
8.14
8.11
8.11
7.54
7.51
7.51
7.49
7.24
7.23
6.93
6.89
6.34
6.30
O
N
H
8-Q
Cl
3m
1.00
0.93
0.96
0.99
0.79
3.09
1.06
2.00
1.09
1.10
f1 (ppm)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137.20
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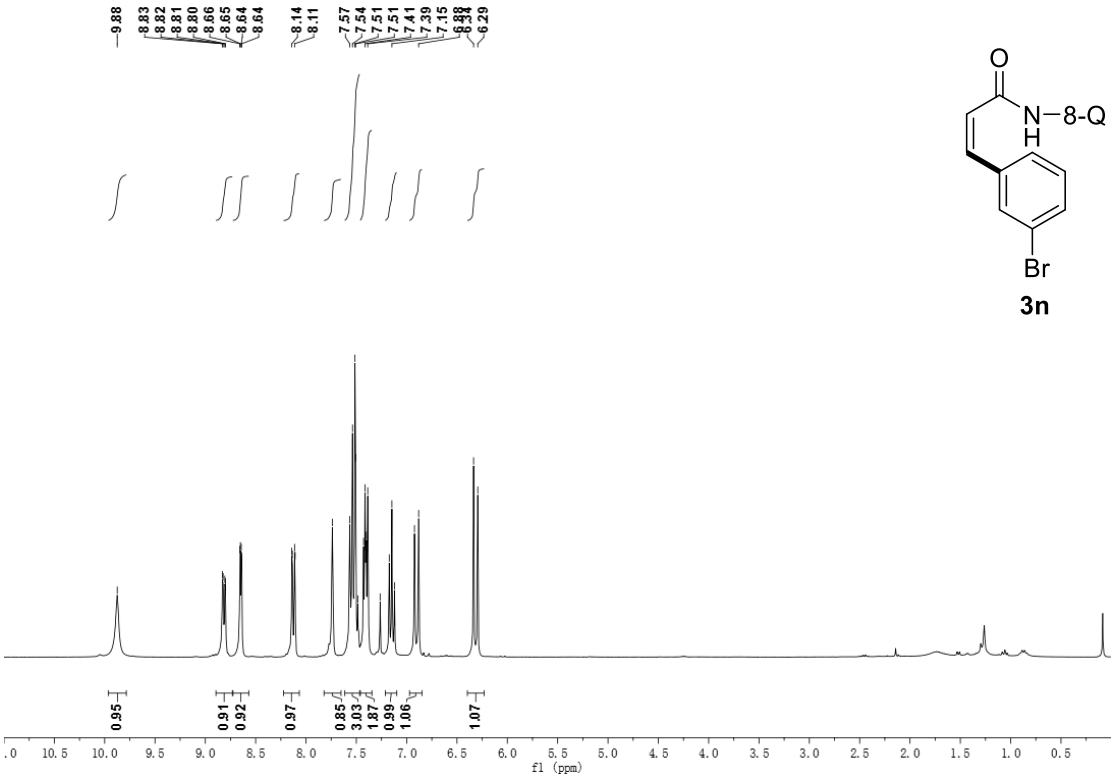
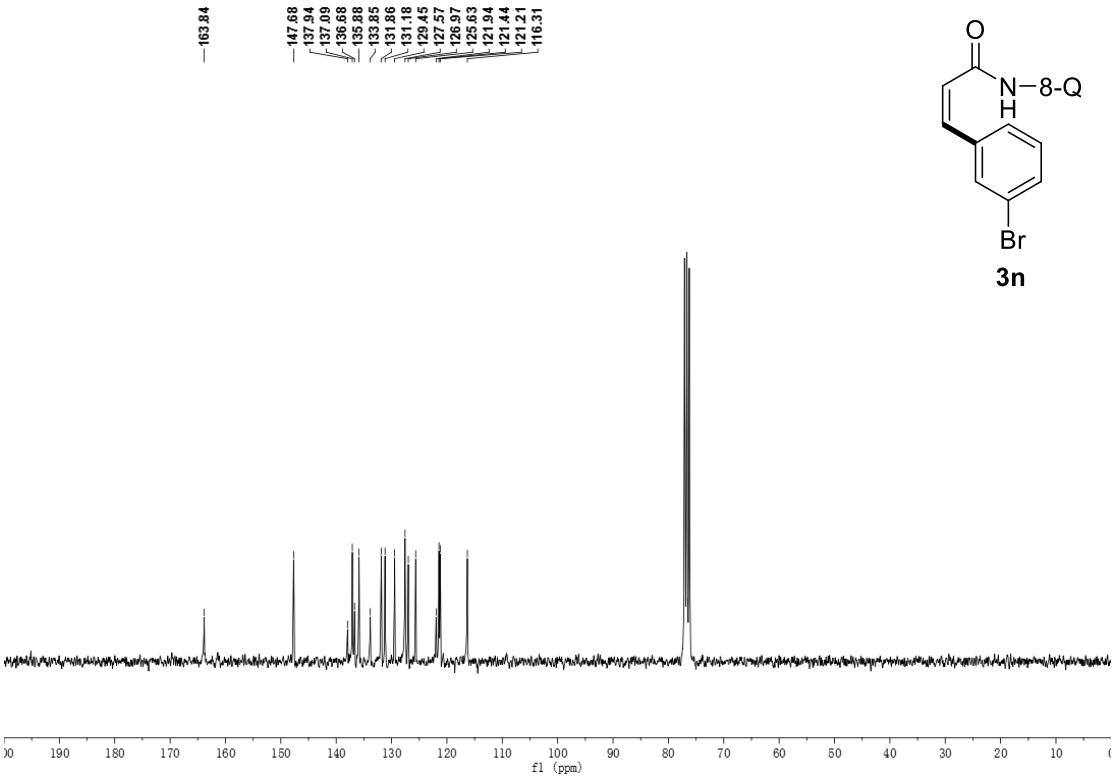
135.88
133.84
129.18
128.98
128.27
127.49
127.14
126.97
125.57
121.43
121.20
116.31
O
N
H
8-Q
Cl
3m
f1 (ppm)


9.88
8.83
8.82
8.81
8.80
8.66
8.65
8.64
8.64
8.14
8.11
7.57
7.54
7.51
7.51
7.41
7.39
7.15
6.88
6.34
6.29
0.95
0.91
0.92
0.97
0.85
3.03
1.87
0.99
1.06
1.07
f1 (ppm)
O
N
H
8-Q
Br

3n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136.68
135.88
133.85
131.86
131.18
129.45
127.57
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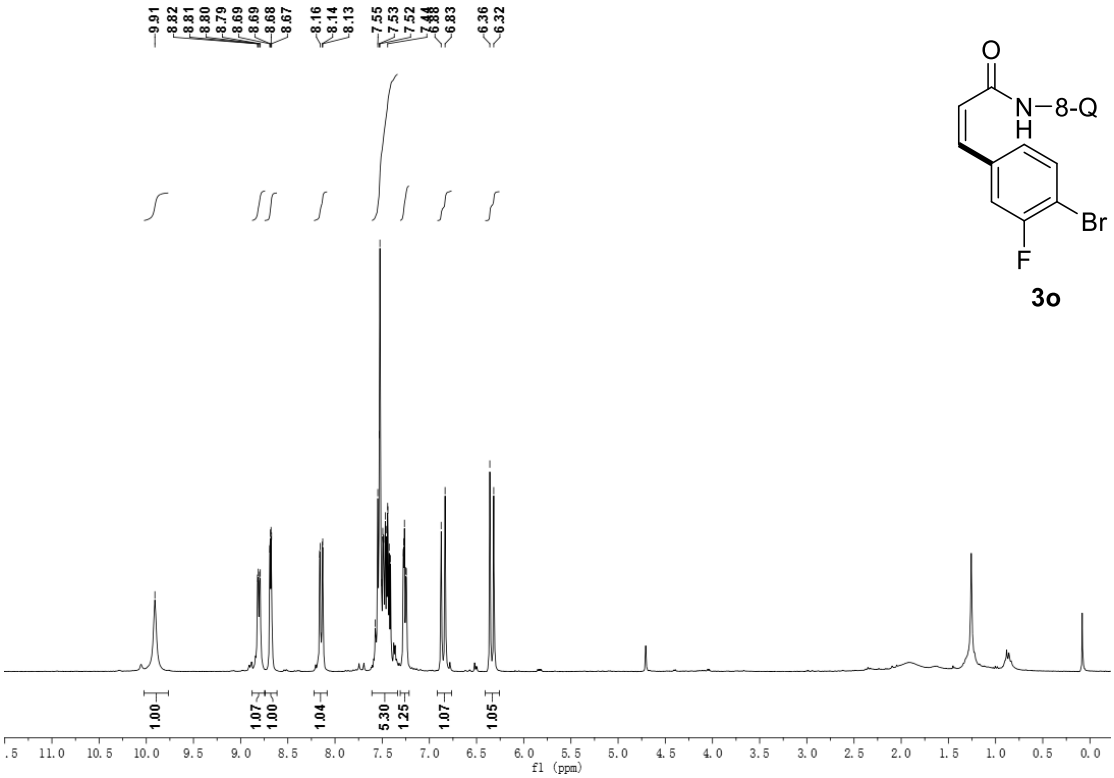
125.63
121.94
121.44
121.21
116.31
f1 (ppm)
O
N
H
8-Q
Br

3n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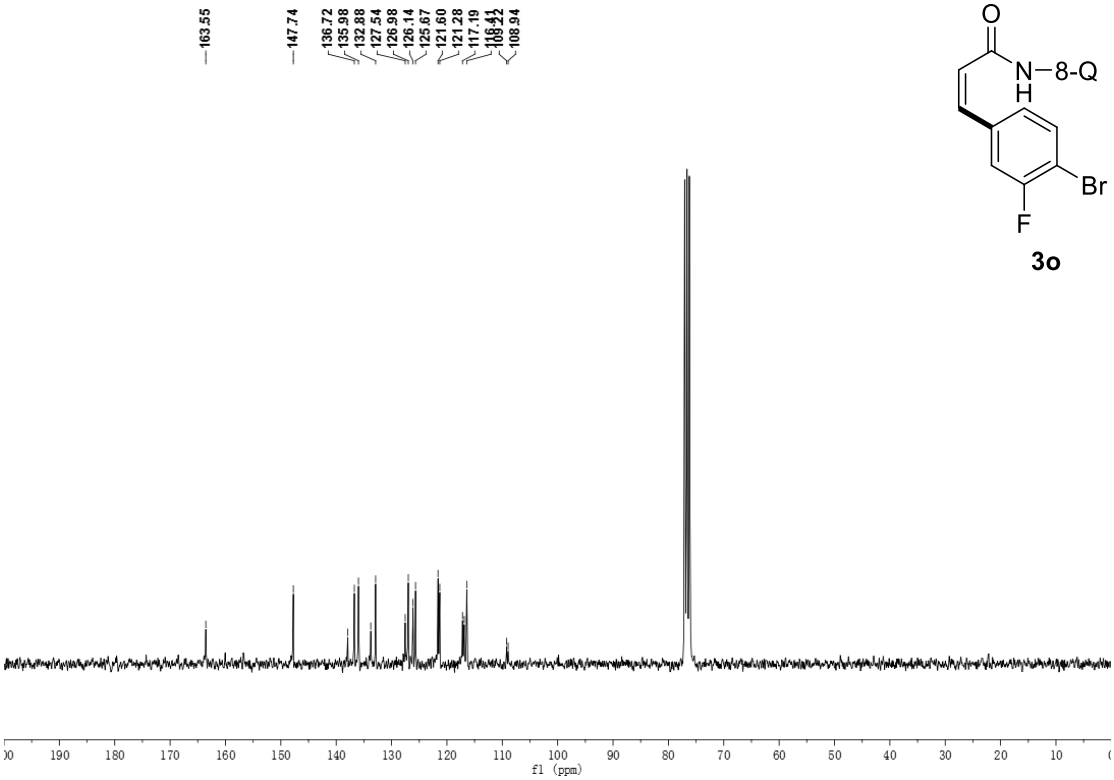
8.82
8.81
8.80
8.79
8.69
8.69
8.68
8.67
8.16
8.14
8.13
7.55
7.53
7.52
6.83
6.36
6.32
1.00
1.07
1.00
1.04
5.30
1.25
1.07
1.05
f1 (ppm)
O
N
H
8-Q
Br
F
3o


163.55
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136.72
135.98
132.88
127.54
126.98
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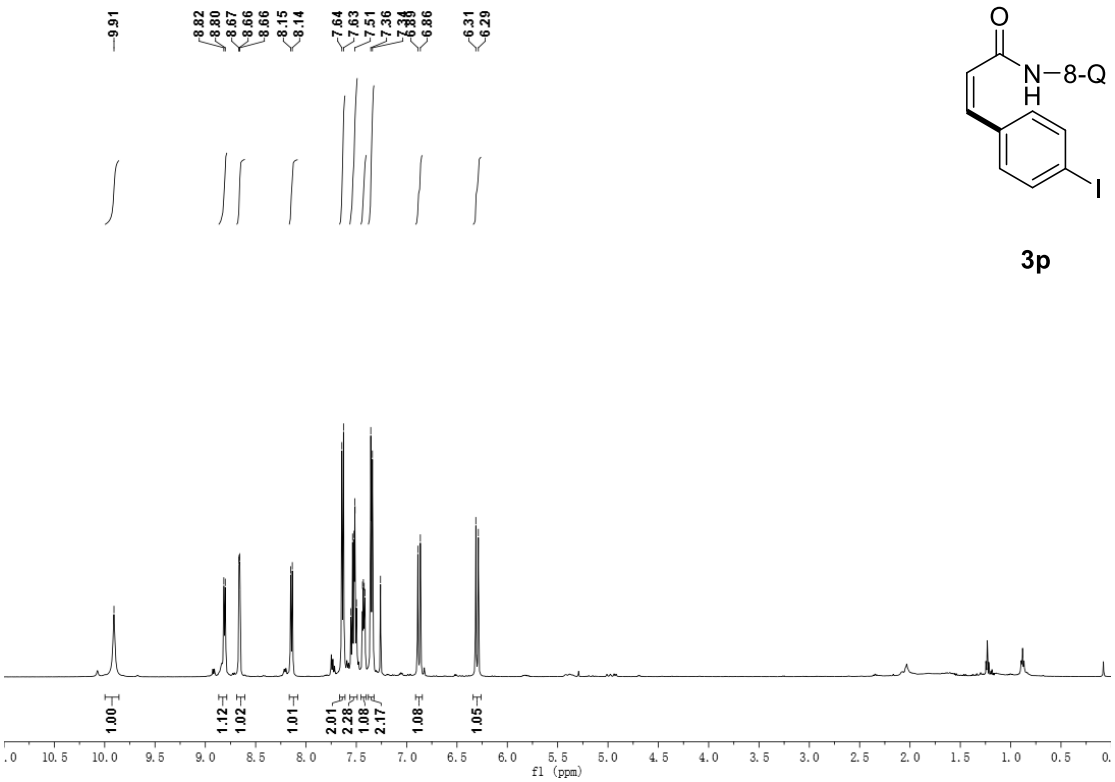
125.67
121.60
121.28
117.19
108.94
f1 (ppm)
O
N
H
8-Q
Br
F
3o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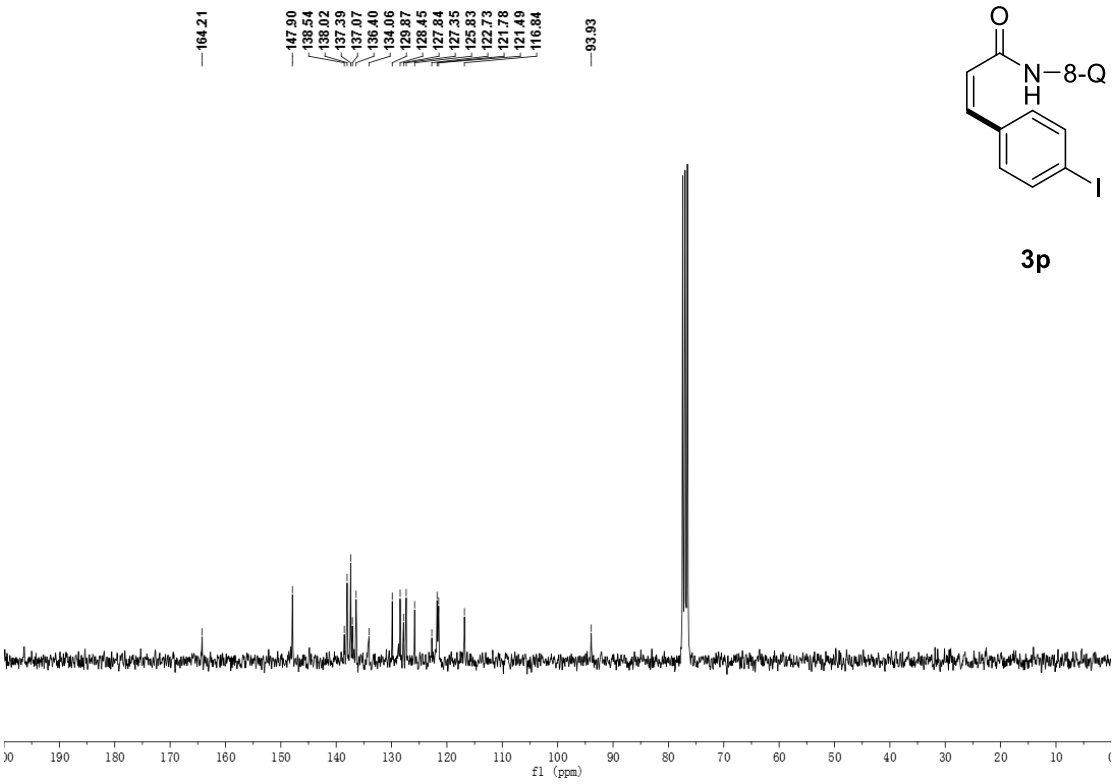
8.82
8.80
8.67
8.66
8.66
8.15
8.14
7.64
7.63
7.51
7.36
6.86
6.31
6.29
O
N
H
8-Q
I
1.00
1.12
1.02
1.01
2.01
2.28
1.08
2.17
1.08
1.05
f1 (ppm)

3p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138.02
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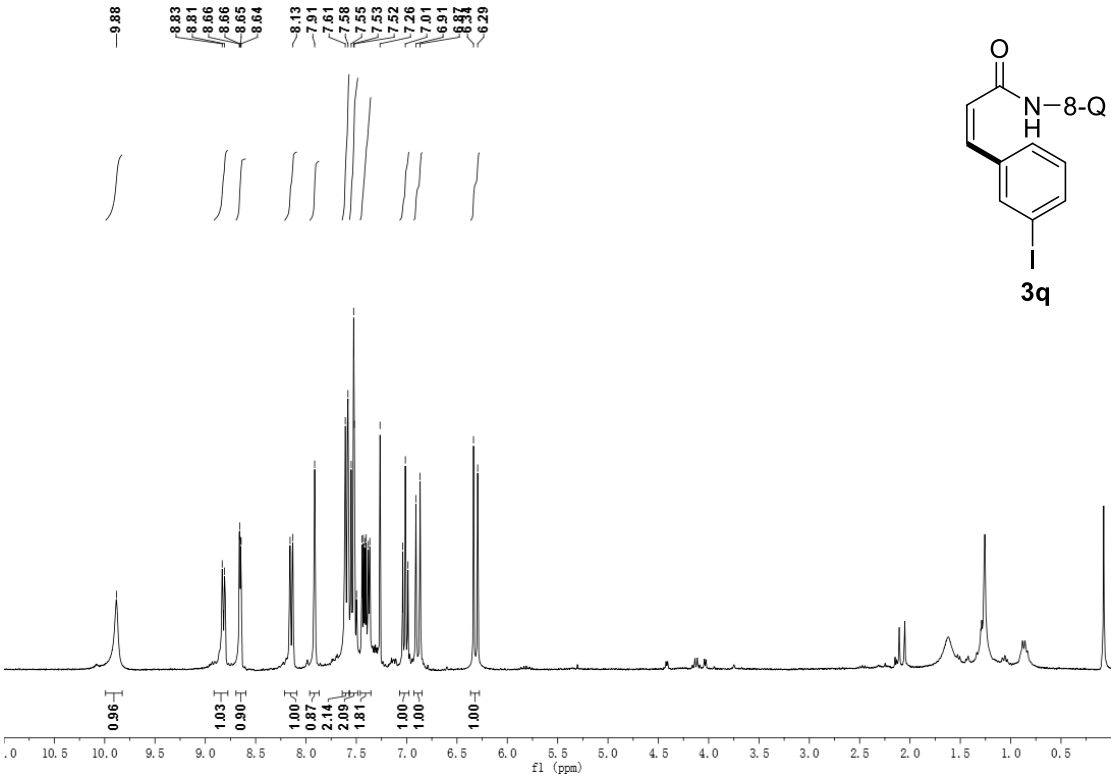
137.07
136.40
134.06
129.87
128.45
127.84
127.35
125.83
122.73
121.78
121.49
116.84
93.93
O
N
H
8-Q
I
f1 (ppm)

3p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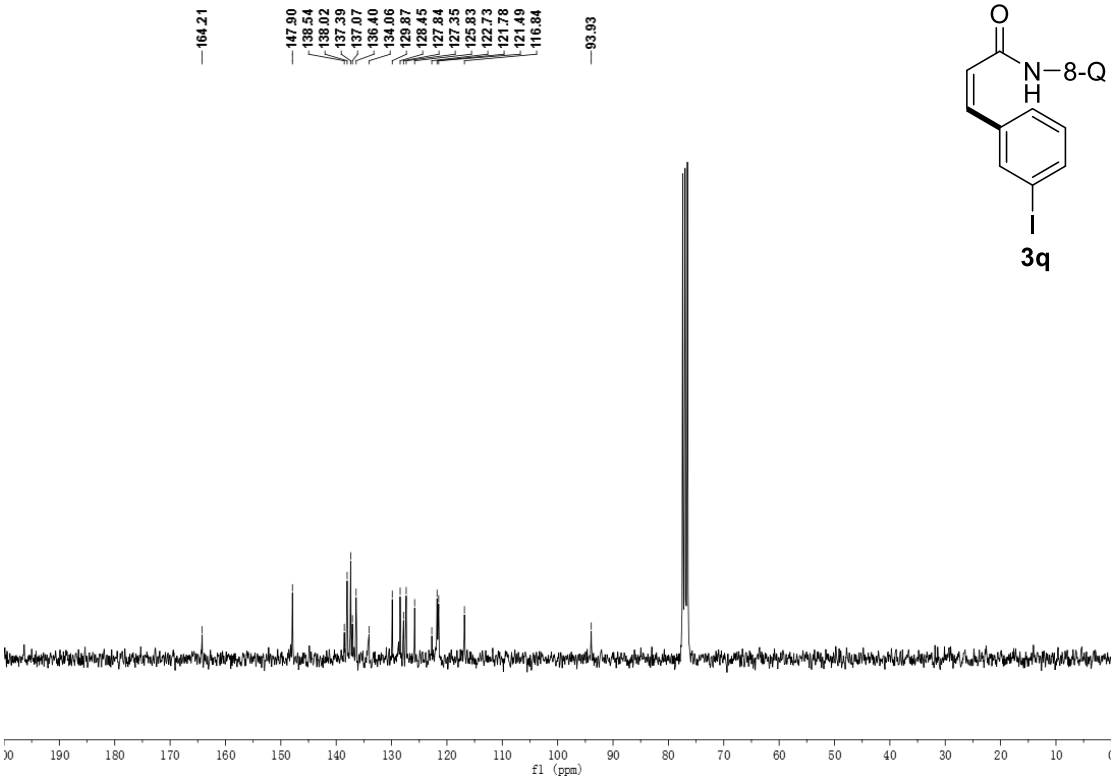
8.83
8.81
8.66
8.66
8.65
8.64
8.13
7.91
7.61
7.58
7.55
7.53
7.52
7.26
7.01
6.91
6.87
6.34
6.29
O
N—8-Q
H
I
3q
0.96
1.03
0.90
1.00
0.87
2.14
2.09
1.81
1.00
1.00
1.00
f1 (ppm)


164.21
147.90
138.54
138.02
137.39
137.07
136.40
134.06
129.87
128.45
127.84
127.35
125.83
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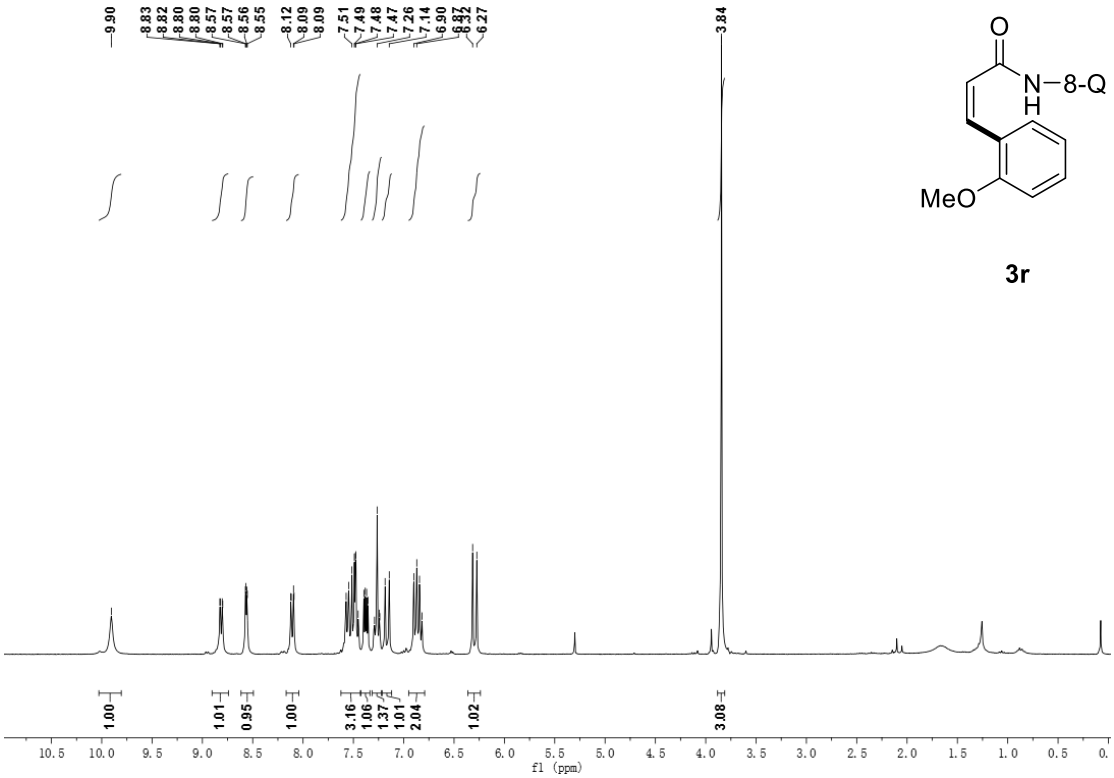
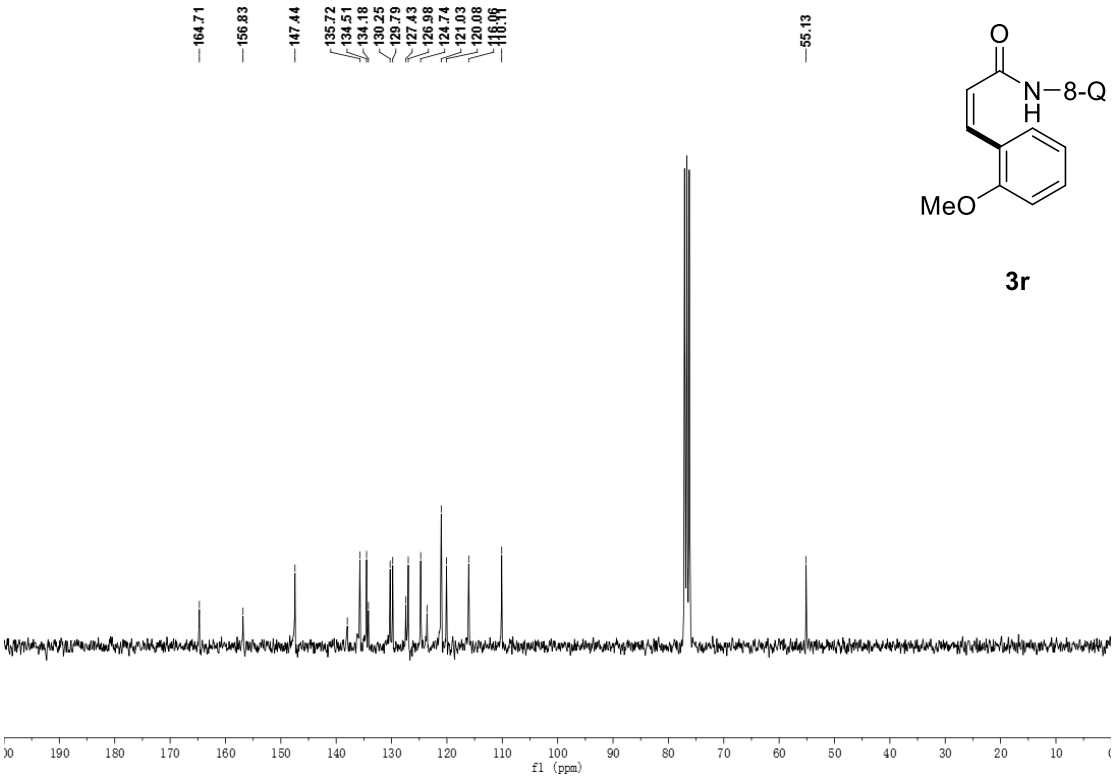
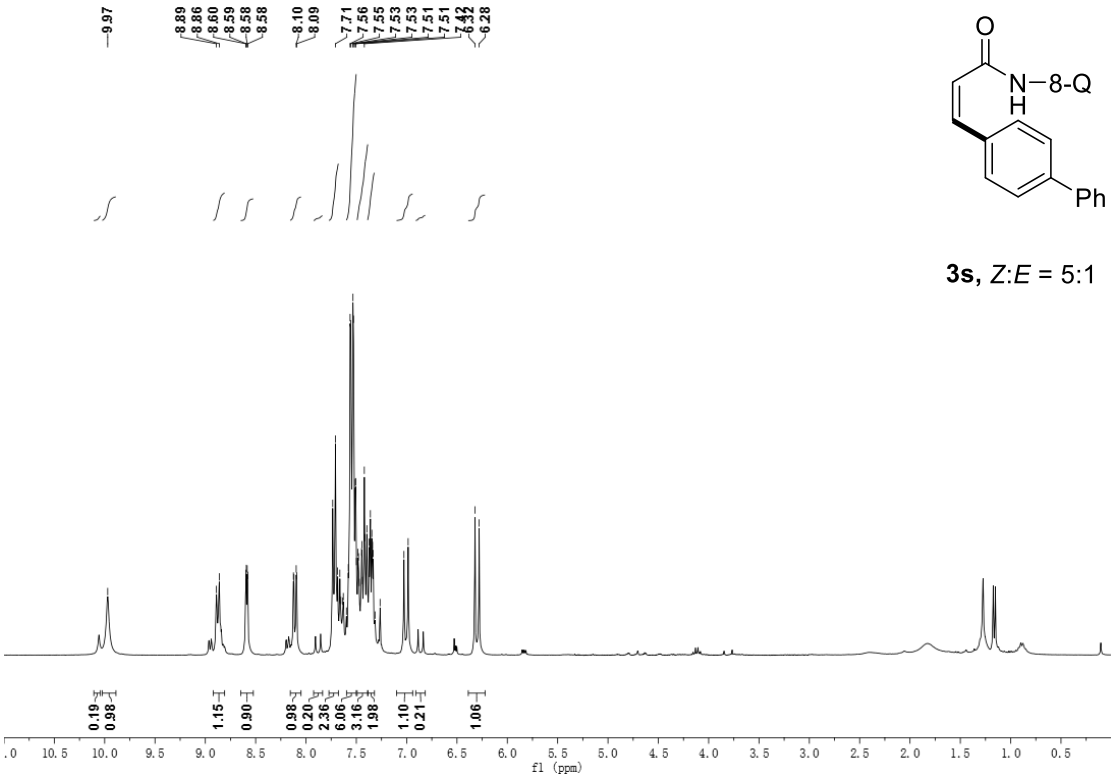
121.78
121.49
116.84
93.93
O
N—8-Q
H
I
3q
f1 (ppm)


9.90
8.83
8.82
8.80
8.80
8.57
8.57
8.56
8.55
8.12
8.09
8.09
7.51
7.49
7.48
7.47
7.26
7.14
6.90
6.27
3.84
1.00
1.01
0.95
1.00
3.16
1.06
1.37
1.01
2.04
1.02
3.08
f1 (ppm)
O
N
H
8-Q
MeO

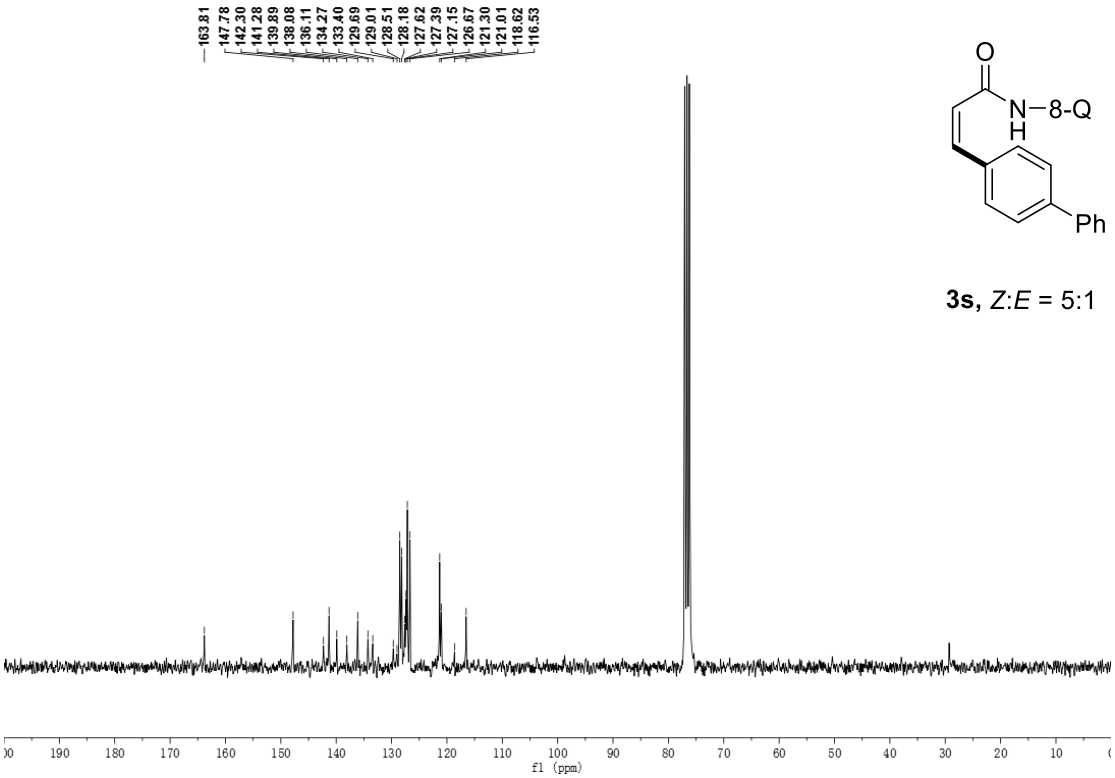
3r


164.71
156.83
147.44
135.72
134.51
134.18
130.25
129.79
127.43
126.98
124.74
121.03
120.08
55.13
f1 (ppm)
O
N
H
8-Q
MeO

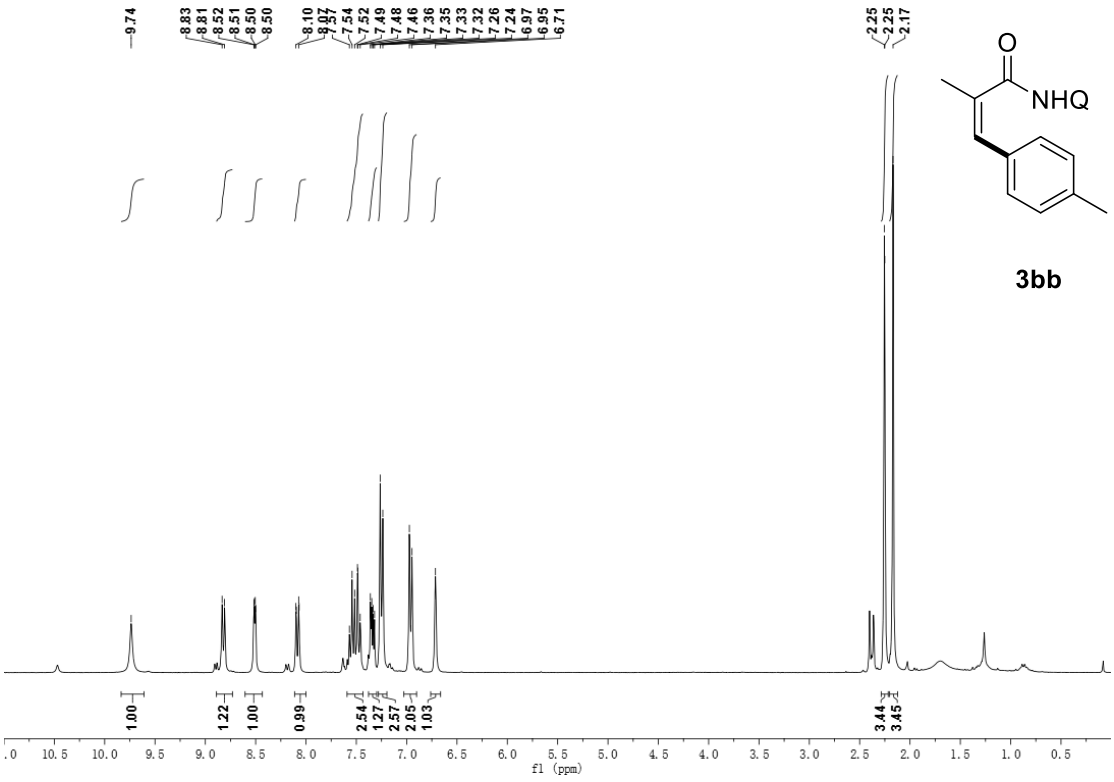
3r

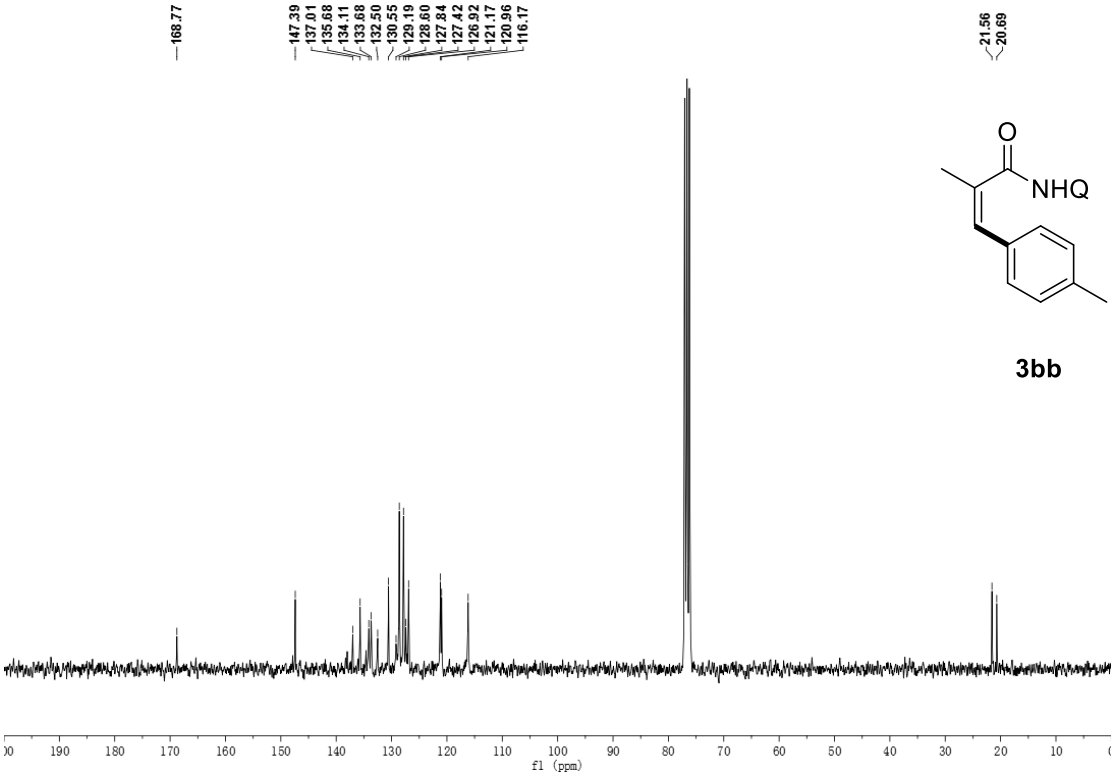


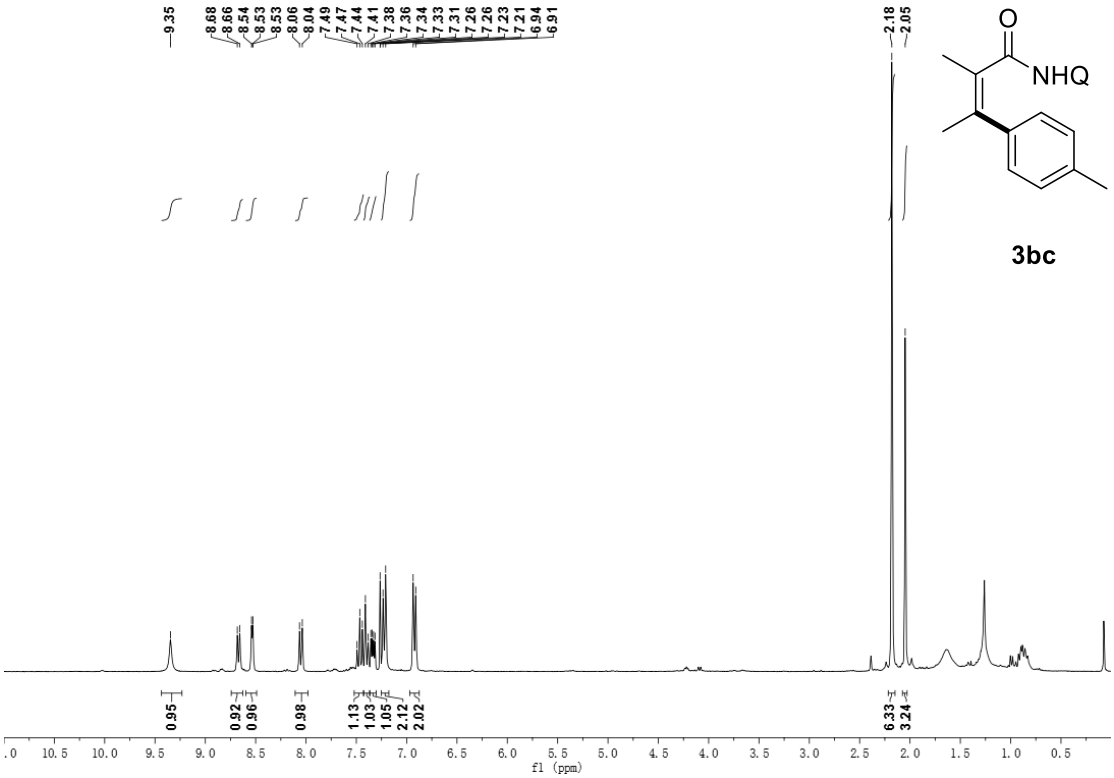
3s, *Z*:*E* = 5:1

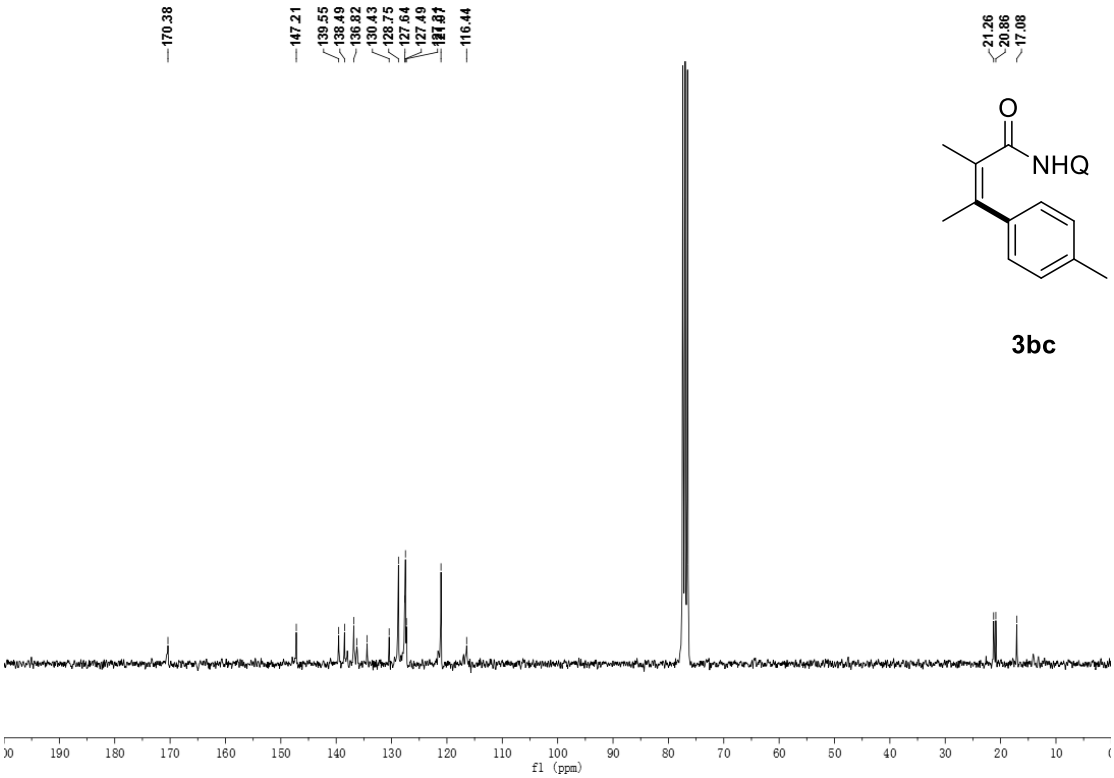


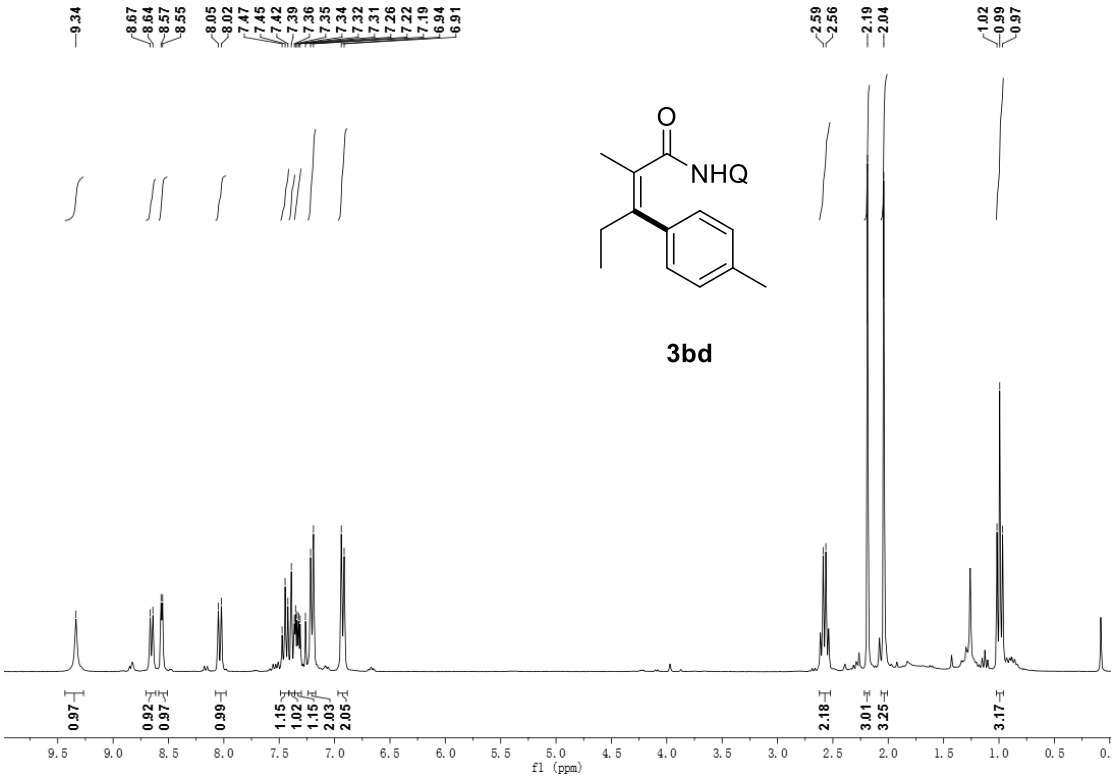
3s, *Z*:*E* = 5:1


9.74
8.83
8.81
8.52
8.51
8.50
8.50
8.10
8.07
7.54
7.52
7.49
7.48
7.46
7.36
7.35
7.33
7.32
7.26
7.24
6.97
6.95
6.71
2.25
2.25
2.17
O
NHQ
3bb
1.00
1.22
1.00
0.99
2.54
1.27
2.57
2.05
1.03
3.44
3.45
f1 (ppm)


168.77
147.39
137.01
135.68
134.11
133.68
132.50
130.55
129.19
128.80
127.84
127.42
126.92
121.17
120.96
116.17
21.56
20.69
O
NHQ
3bb
f1 (ppm)


9.35
8.68
8.66
8.54
8.53
8.06
8.04
7.49
7.47
7.44
7.41
7.38
7.36
7.34
7.33
7.31
7.26
7.26
7.23
7.21
6.94
6.91
2.18
2.05
0.95
0.92
0.96
0.98
1.13
1.03
1.05
2.12
2.02
6.33
3.24
f1 (ppm)
O
NHQ
3bc


170.38
147.21
139.55
138.49
136.82
130.43
128.75
127.64
127.49
116.44
21.26
20.86
17.08
f1 (ppm)
O
NHQ
3bc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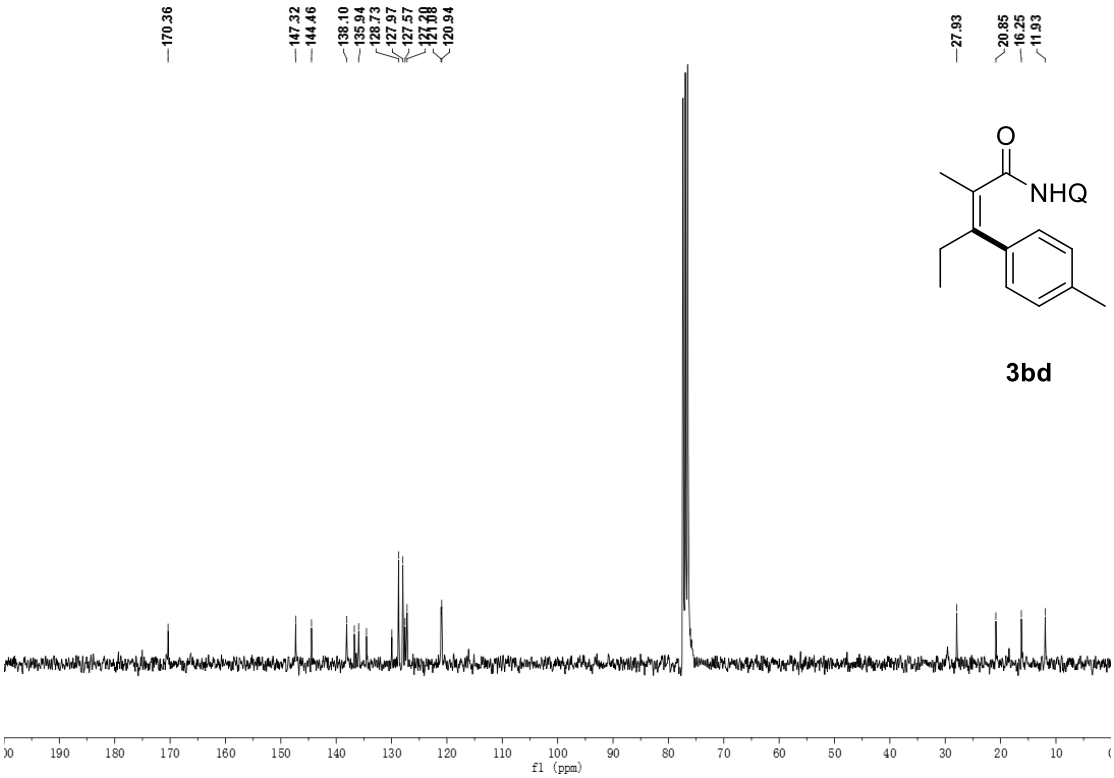
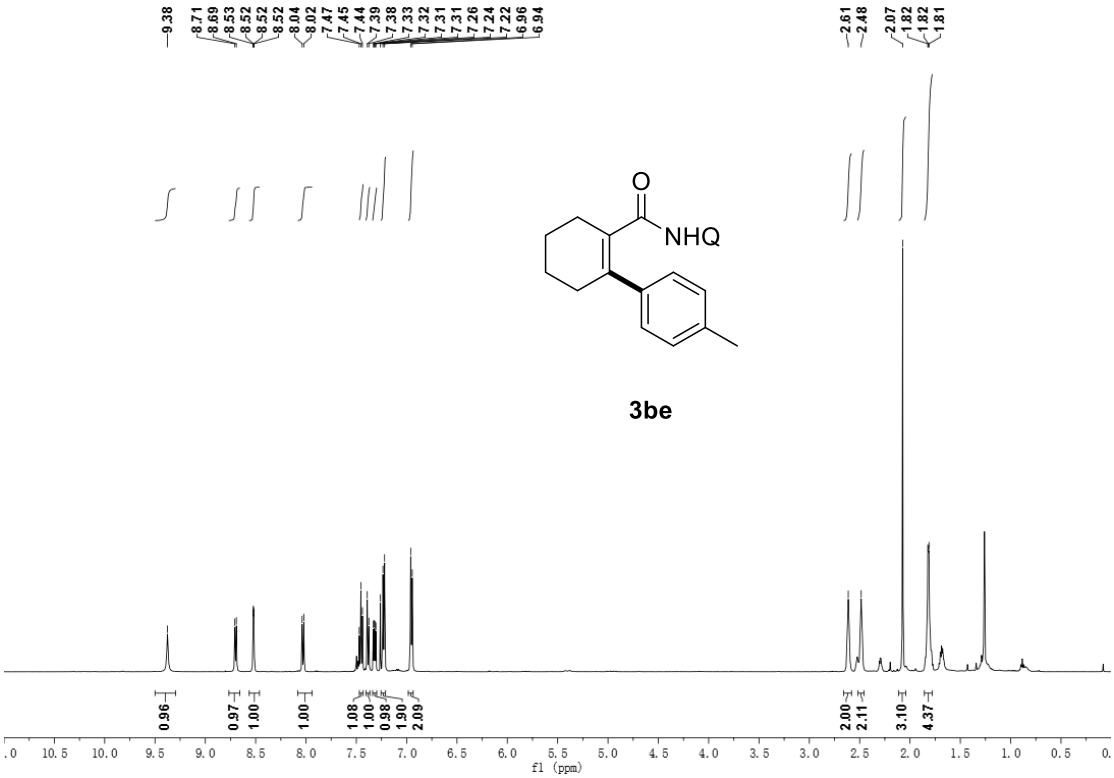
8.67
8.64
8.57
8.55
8.05
8.02
7.47
7.45
7.42
7.39
7.36
7.35
7.34
7.32
7.31
7.26
7.22
7.19
6.94
6.91
2.59
2.56
2.19
2.04
1.02
0.99
0.97
O
NHQ
0.97
0.92
0.97
0.99
1.15
1.02
1.15
2.03
2.05
2.18
3.01
3.25
3.17
f1 (ppm)

3bd


170.36
147.32
144.46
138.10
135.94
128.73
127.97
127.57
120.94
27.93
20.85
16.25
11.93
O
NHQ
f1 (ppm)

3bd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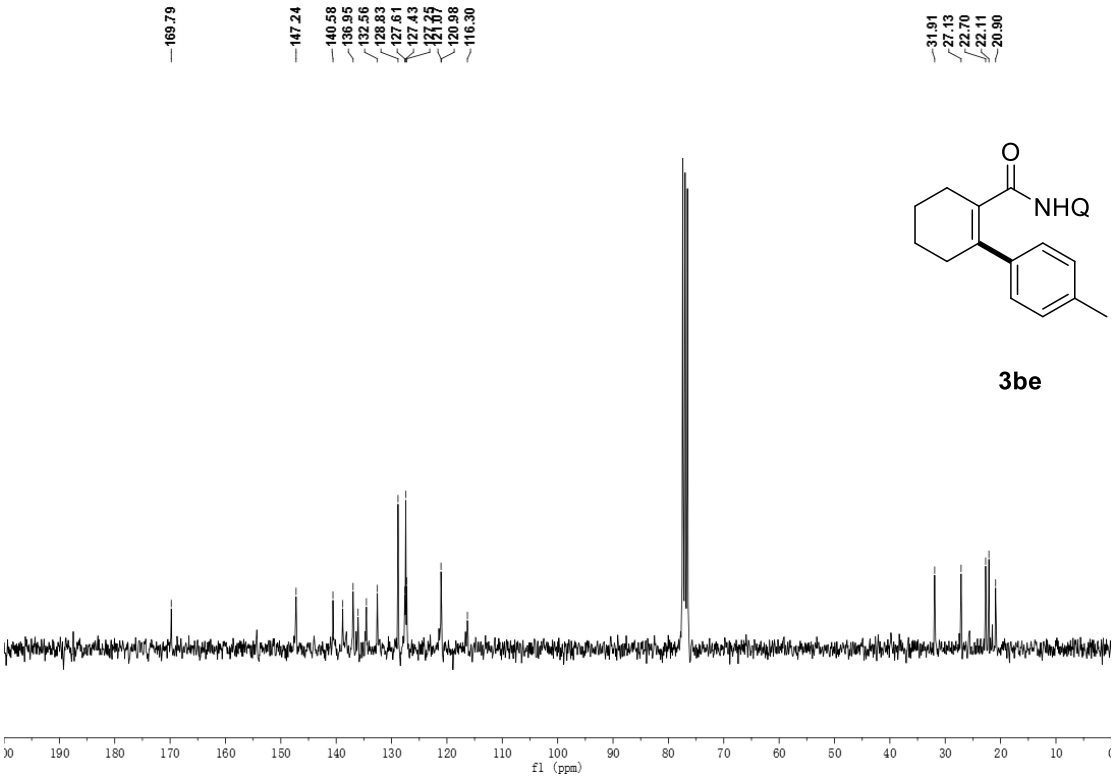
8.71
8.69
8.53
8.52
8.52
8.52
8.04
8.02
7.47
7.45
7.44
7.39
7.38
7.33
7.32
7.31
7.31
7.26
7.24
7.22
6.96
6.94
2.61
2.48
2.07
1.82
1.82
1.81
O
NHQ
0.96
0.97
1.00
1.00
1.08
1.00
0.98
1.90
2.09
2.00
2.11
3.10
4.37
f1 (ppm)

3be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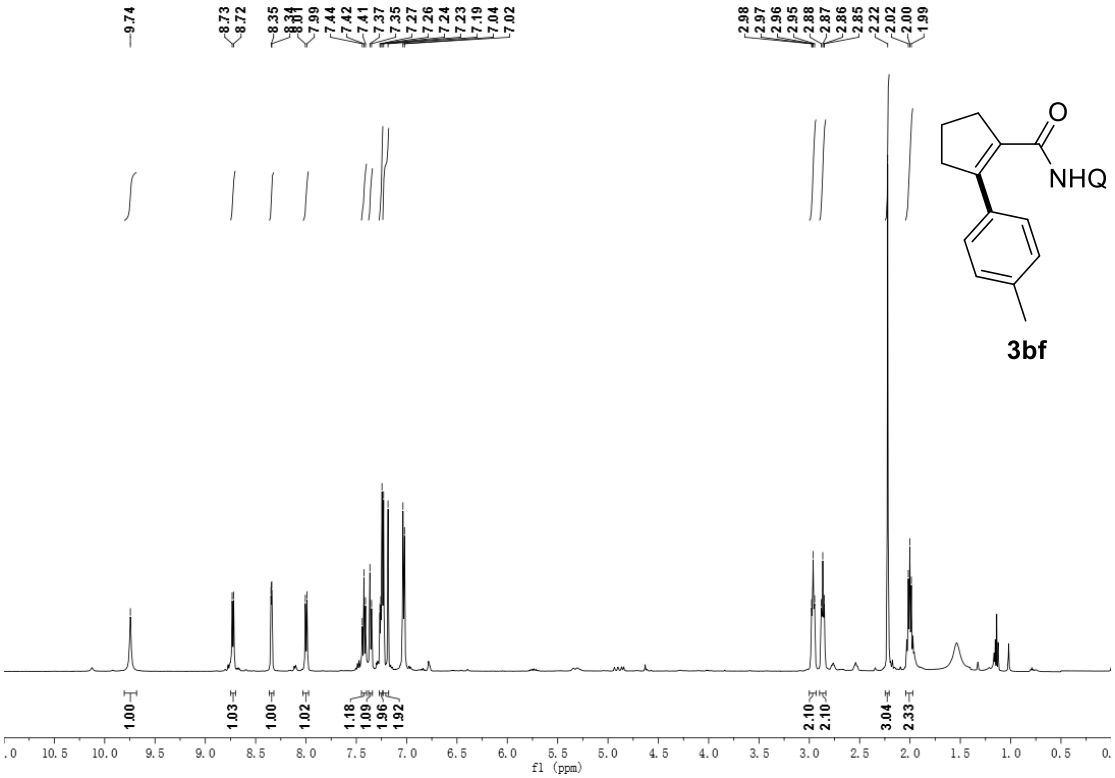
147.24
140.58
136.95
132.56
128.83
127.61
127.43
120.98
116.30
31.91
27.13
22.70
22.11
20.90
O
NHQ
f1 (ppm)

3be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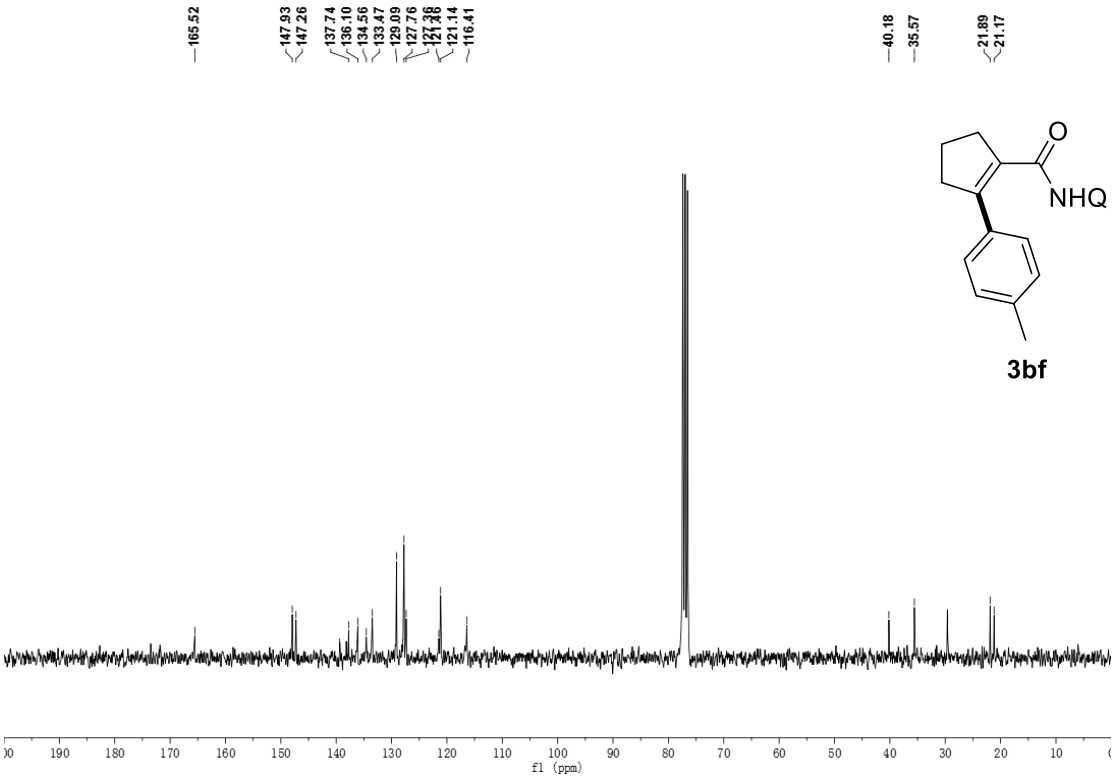
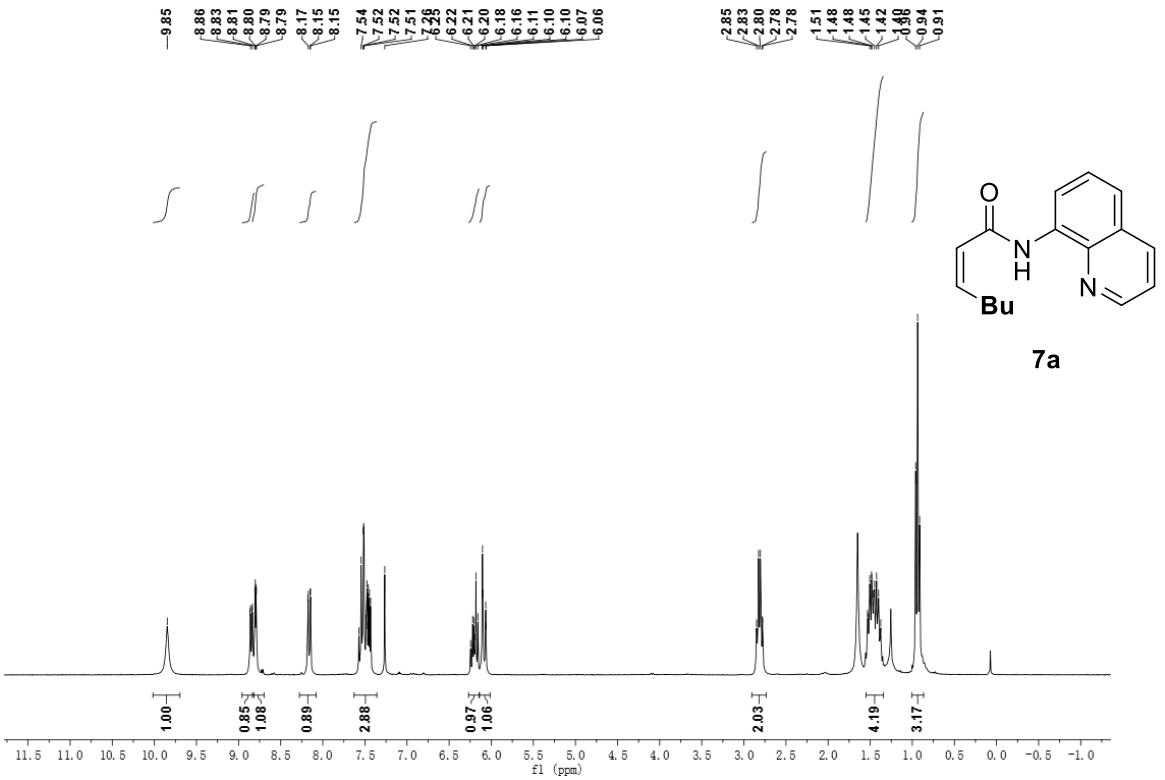
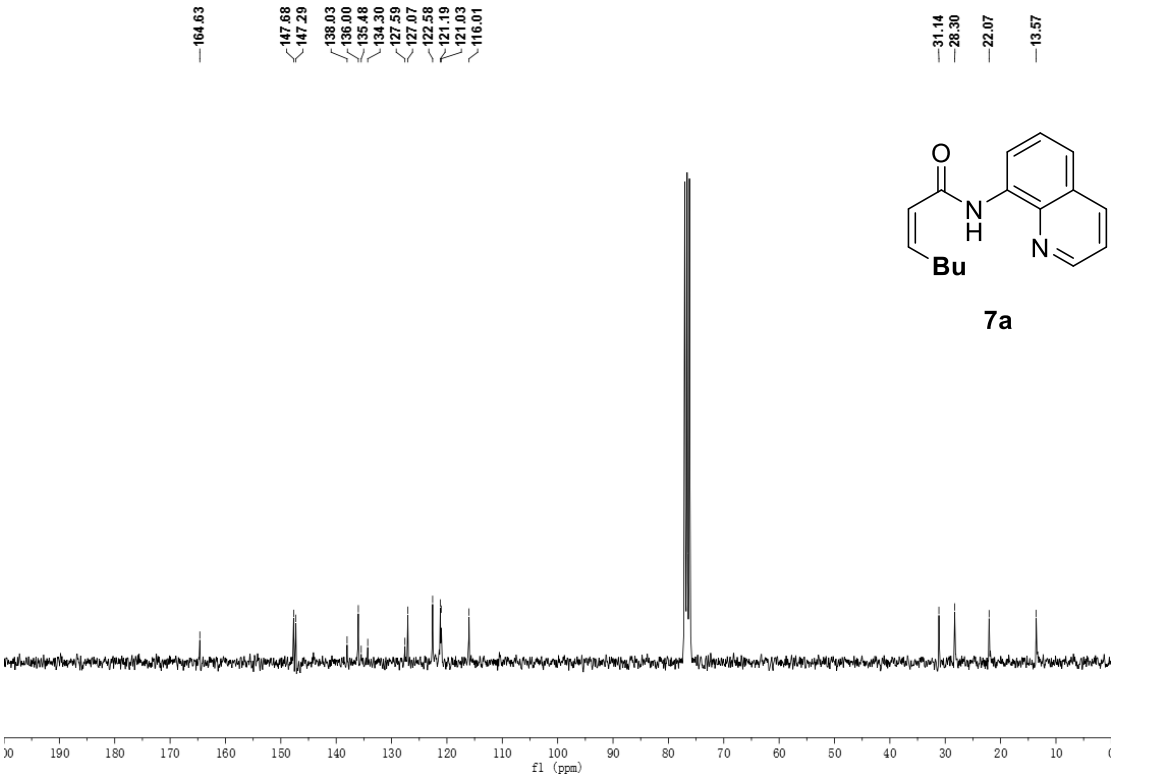
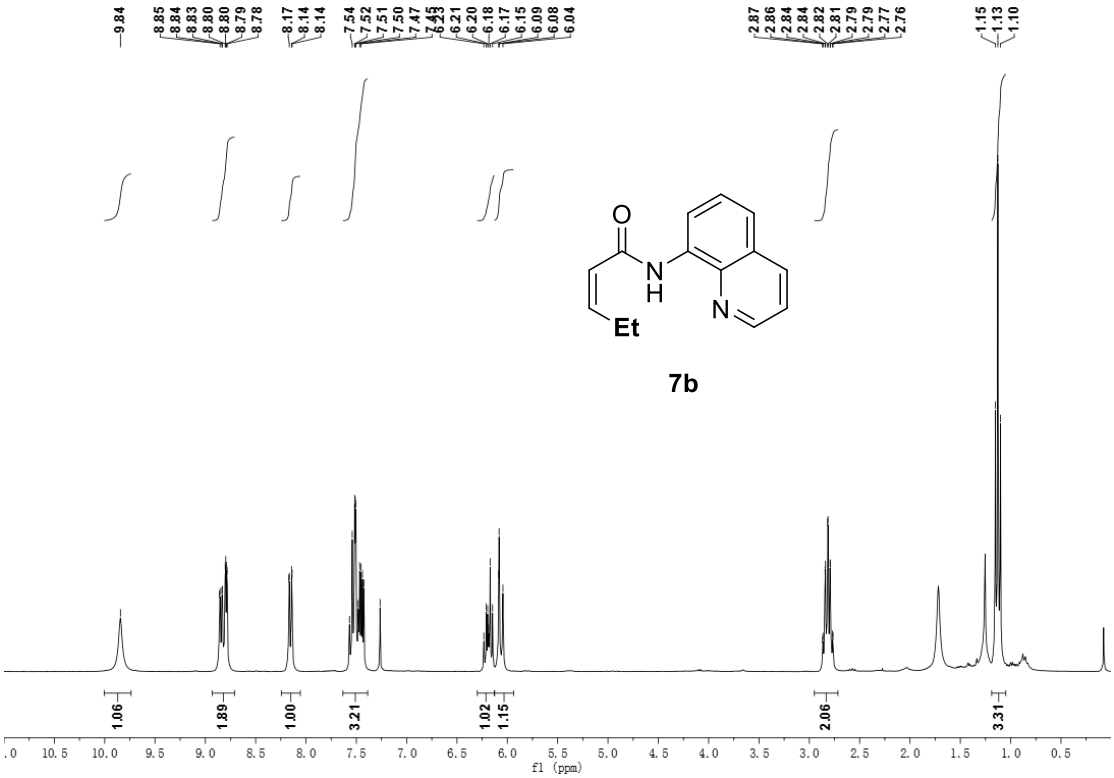
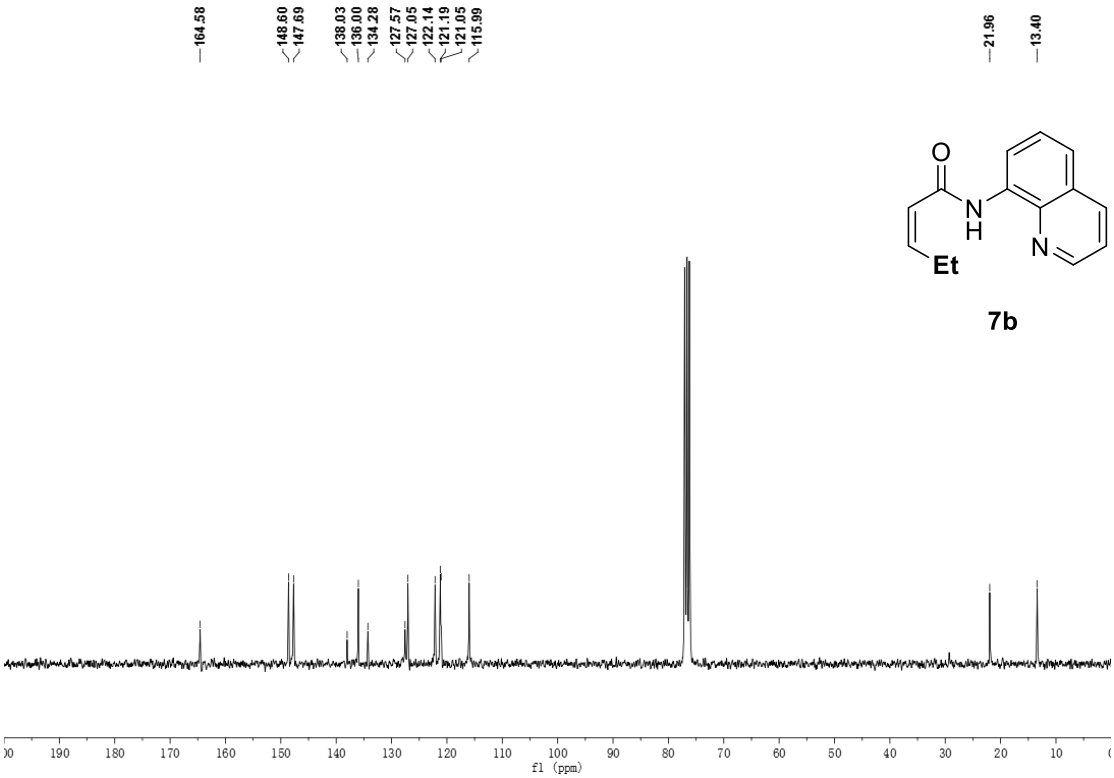
8.73
8.72
8.35
8.34
8.31
8.01
7.99
7.44
7.42
7.41
7.37
7.35
7.27
7.26
7.24
7.23
7.19
7.04
7.02
2.98
2.97
2.96
2.95
2.88
2.87
2.86
2.85
2.22
2.02
2.00
1.99
O
NHQ
3bf
1.00
1.03
1.00
1.02
1.18
1.09
1.96
1.92
2.10
2.10
3.04
2.33
f1 (ppm)

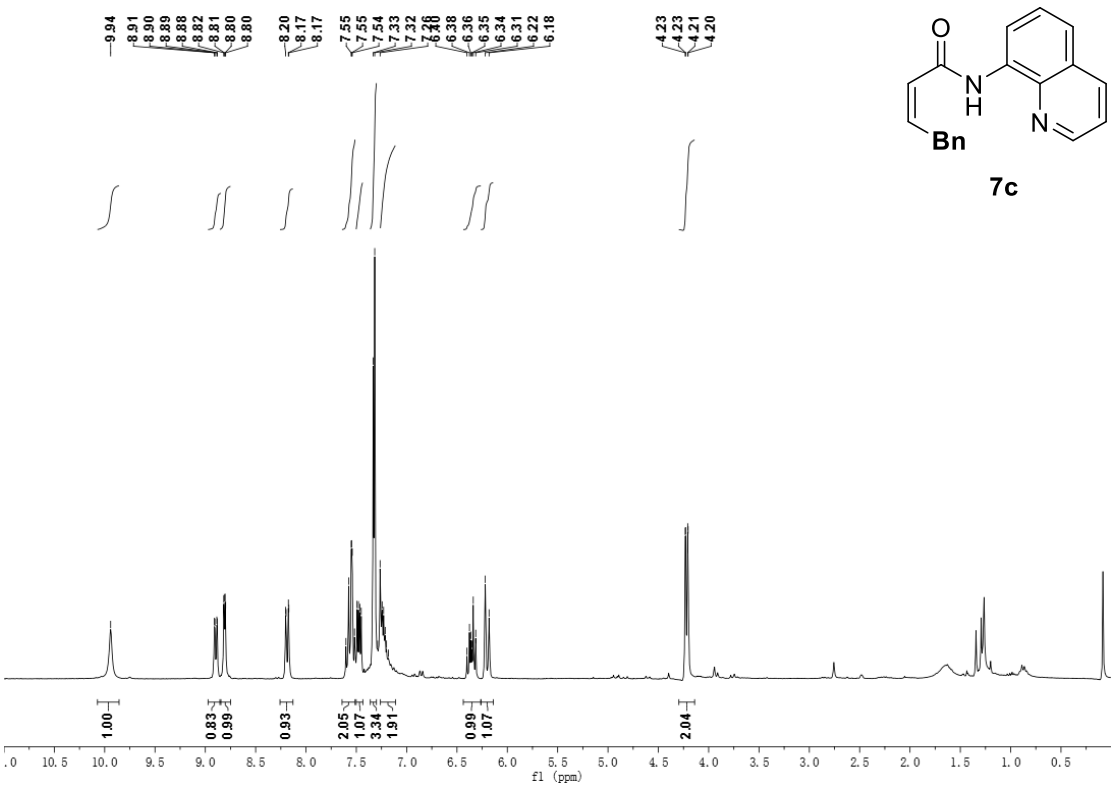

165.52
147.93
147.26
137.74
136.10
134.56
133.47
129.09
127.76
121.38
121.14
116.41
40.18
35.57
21.89
21.17
O
NHQ
3bf
f1 (ppm)


9.85
8.86
8.83
8.81
8.80
8.79
8.79
8.17
8.15
8.15
7.54
7.52
7.52
7.51
6.22
6.21
6.20
6.18
6.16
6.11
6.10
6.10
6.07
6.06
2.85
2.83
2.80
2.78
2.78
1.51
1.48
1.48
1.45
1.42
0.94
0.91
1.00
0.85
1.08
0.89
2.88
0.97
1.06
2.03
4.19
3.17
f1 (ppm)
O
N
H
N
Bu
7a


164.63
147.68
147.29
138.03
136.00
135.48
134.30
127.59
127.07
122.58
121.19
121.03
116.01
31.14
28.30
22.07
13.57
f1 (ppm)
O
N
H
N
Bu
7a

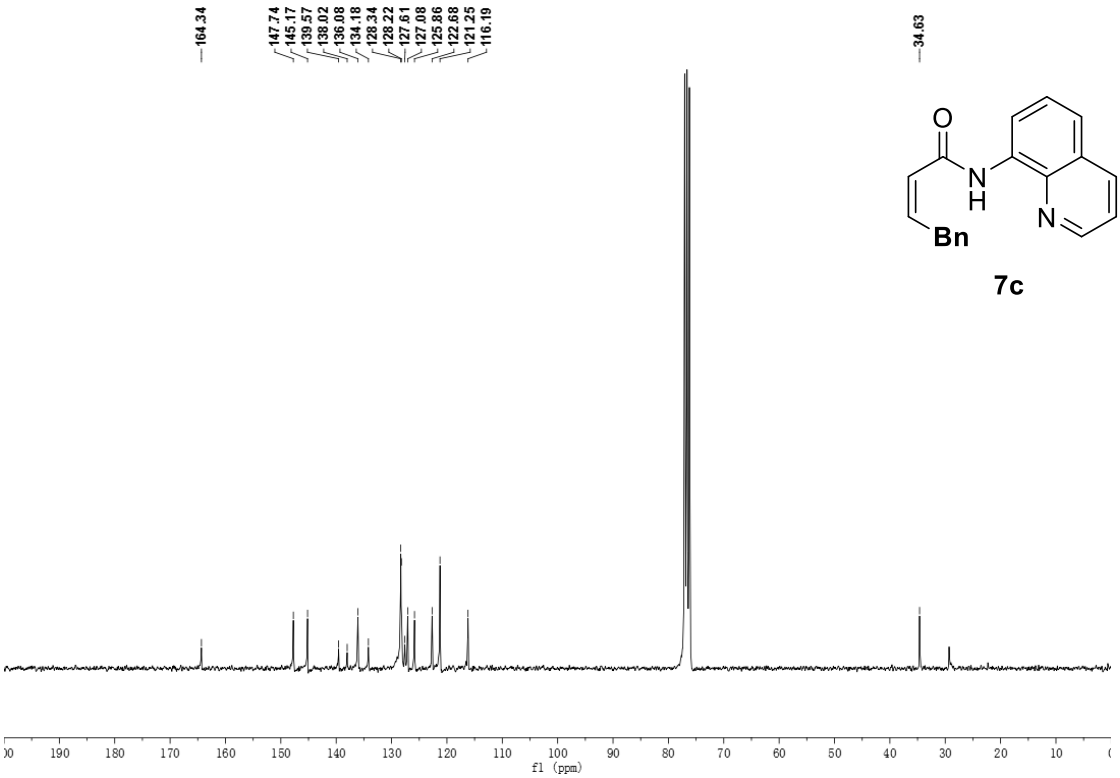

9.84
8.85
8.84
8.83
8.80
8.80
8.79
8.78
8.17
8.14
8.14
7.54
7.52
7.51
7.50
7.47
6.21
6.20
6.18
6.17
6.15
6.09
6.08
6.04
2.87
2.86
2.84
2.84
2.82
2.81
2.79
2.79
2.77
2.76
1.15
1.13
1.10
O
N
H
Et
N
7b
1.06
1.89
1.00
3.21
1.02
1.15
2.06
3.31
f1 (ppm)


164.58
148.60
147.69
138.03
136.00
134.28
127.57
127.05
122.14
121.19
121.05
115.99
21.96
13.40
O
N
H
Et
N
7b
f1 (ppm)


9.94
8.91
8.90
8.89
8.88
8.82
8.81
8.80
8.80
8.20
8.17
8.17
7.55
7.55
7.54
7.33
7.32
6.38
6.36
6.35
6.34
6.31
6.22
6.18
4.23
4.23
4.21
4.20
1.00
0.83
0.99
0.93
2.05
1.07
3.34
1.91
0.99
1.07
2.04
f1 (ppm)

O
N
H
N
Bn

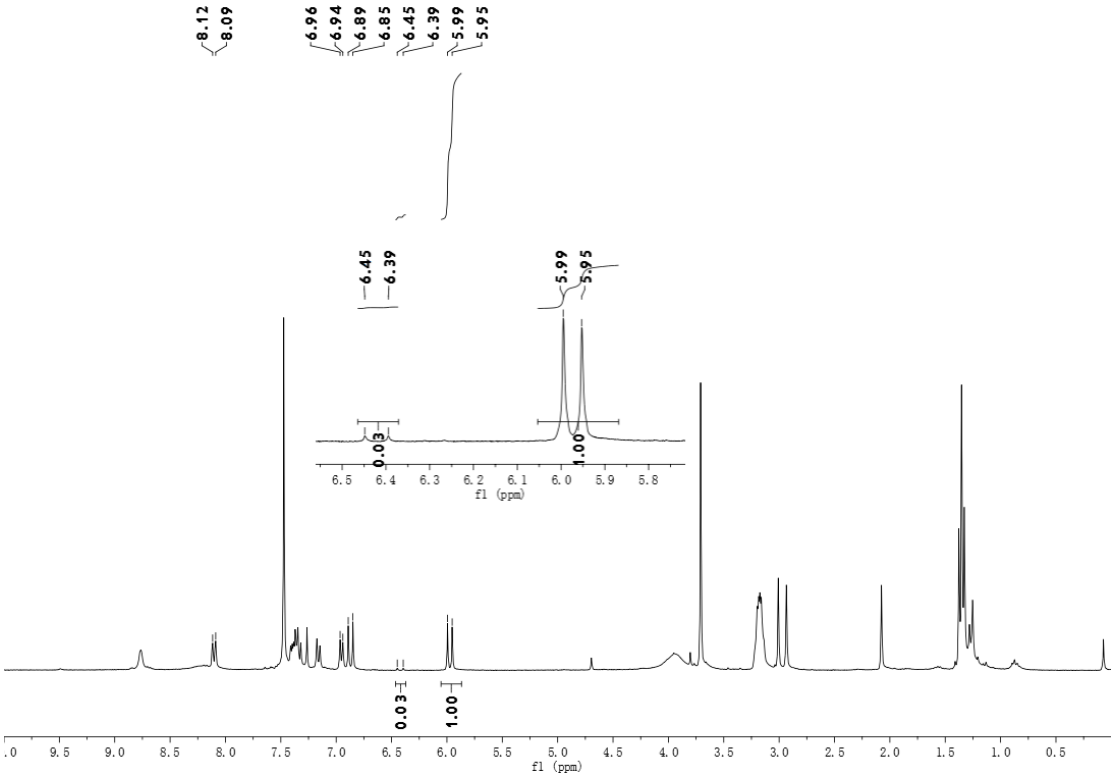
7c


164.34
147.74
145.17
139.57
138.02
136.08
134.18
128.34
128.22
127.61
127.08
125.86
122.68
121.25
116.19
34.63
f1 (ppm)

O
N
H
N
Bn

7c

Crude NMR (300M) for directing group removal of 3h



8h