Ammonia as an Ultimate Amino Source in the Synthesis of Primary Amines via Nickel-Promoted C-H Bond Amination

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Supporting Information

Table of contents

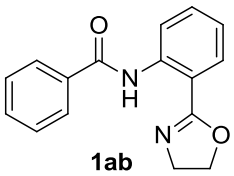
1. General information

^{1}H NMR and ^{13}C NMR were recorded in $CDCl_3$ or DMSO-d_6 at room temperature on the Varian INOVA-400 spectrometer (400 MHz ^{1}H) or Bruker spectrometer (400 MHz ^{1}H). The chemical-shifts scale is based on internal TMS. The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; qui, quin tet; sxt, sextet. The coupling constants, *J* are reported in Hertz (Hz). Mass spectros -copy data were collected on an HRMS-ESI instrument.

Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification. Anhydrous $NiCl_2$ was purchased from Alfa Aesar. All solvents were purified and dried according to standard methods prior to use. Products were purified by flash column chromatography on 100-160 mesh silica gel, SiO_2.

2. Typical procedure for the preparation of aryl amides

All amides **1** were synthesized from the corresponding benzoic acids or benzoyl chlorides and aromatic amine. The deuterated amides were synthesized according to a literature method, spectral properties are consistent with literature values.[1] The amides **1ab-1v** were synthesized according to literature procedures.[2]



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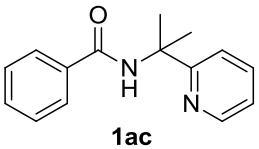

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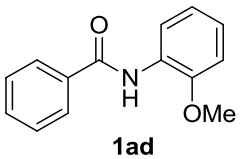

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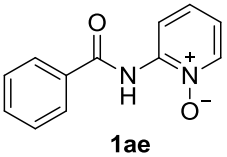

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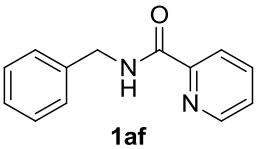

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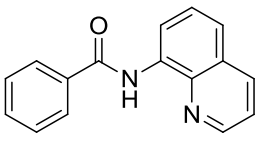

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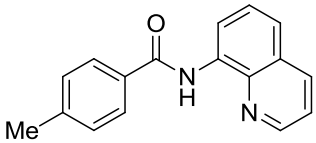

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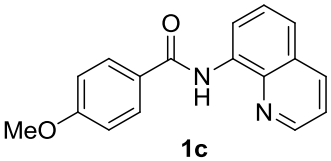

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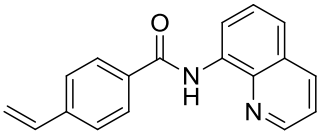

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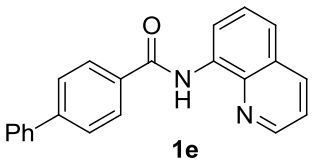

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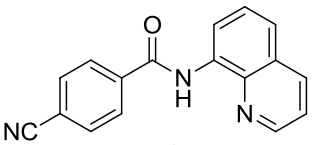

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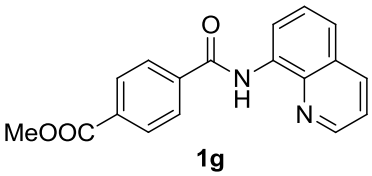

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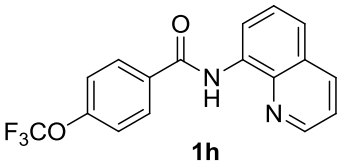

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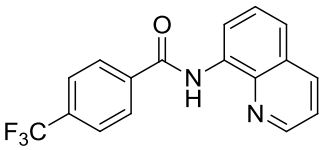

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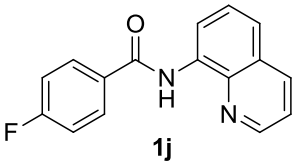

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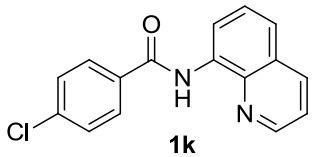

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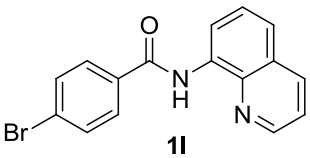

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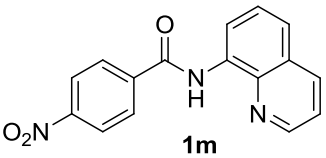

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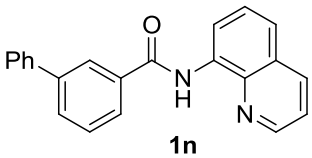

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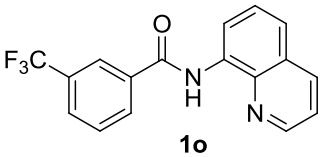

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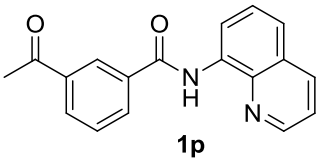

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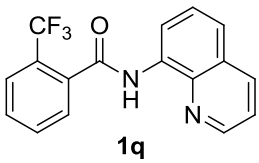

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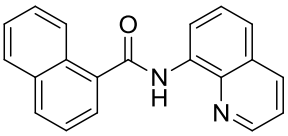

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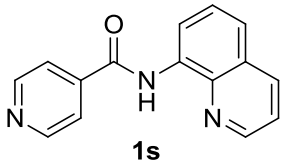

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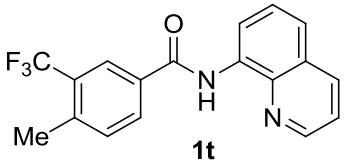

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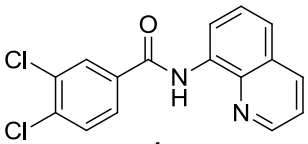

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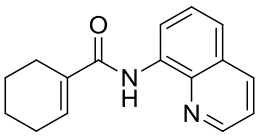

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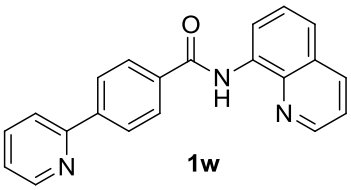
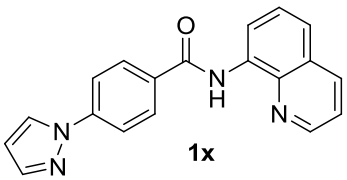
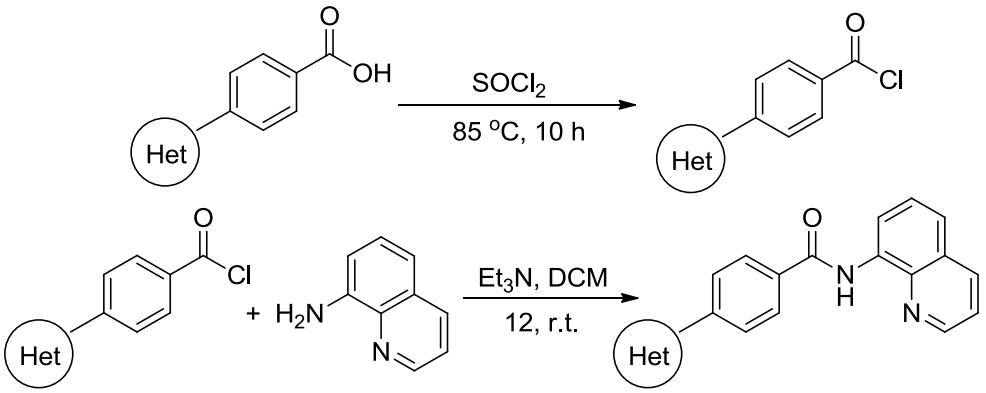


1w



1x

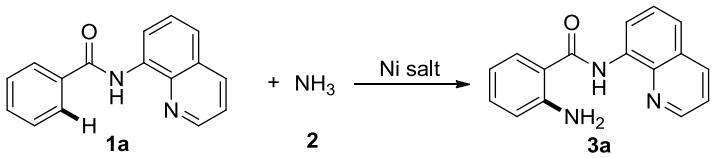
Procedure for the synthesis of substrates **1w** and **1x**[3].



An acid chloride (5 mmol), prepared from the corresponding carboxylic acid and thionyl chloride and quinolin-8-amine (5 mmol) were added to a 50 mL flask and then dissolved with DCM (20 mL). Et_3N (10 mmol) was taken to the vigorously stirred solution via a syringe. The reaction mixture was stirred at room temperature for 12 h and quenched with saturated $NaHCO_3$. H_2O was added to the mixture and extracted with DCM. Combined organic phase was washed with saturated brine and dried over Na_2SO_4, and then filtered, the solvent was removed in a rotary evaporator. The crude product was purified by silica gel column with petroleum ether/ethyl acetate eluent gave the desired product **1w** or **1x**.

3. Nickel-promoted C-H amination to form primary anilines

3.1 Further optimization of the reaction conditions



Entry	$NiCl_2$ (equiv)	AgTFA (equiv)	TBAA (equiv)	Solvent	Temp (°C)	Yield (%)[a,b]
1	2	2	2	DMSO	140	68
2	1	2	2	DMSO	140	38
3	0	2	2	DMSO	140	0
4	2	1	2	DMSO	140	65
5	2	0	2	DMSO	140	63

6	2	0	1	DMSO	140	50
7	2	0	0	DMSO	140	26
7	2	0	2	NMP	140	65
8	2	0	2	NMP	130	63
9[c]	**2**	**0**	**2**	**NMP**	**120**	**66**
10[d]	2	0	2	NMP	110	47
11[e]	0.5	0	2	NMP	120	21
12[f]	0.5	0	2	NMP	120	<10
13[g]	0.5	0	2	NMP	120	<10
14[h]	0.5	0	2	NMP	120	trace
15[i]	0.1	2	2	NMP	120	<10
16[j]	0.1	2	2	NMP	120	<10
17[k]	0.1	2	2	NMP	120	<10
18[l]	2	0	2	NMP	120	18

[a]Reaction conditions: amide **1a** (0.15 mmol), $NiCl_2$ (x mmol), K_2CO_3 (0.3 mmol), TBAA (x mmol), Solvent (5.0 mL), reaction run in a sealed tube under NH_3 (1 atm, closed) for 2 h. [b]Isolated yield. [c]12 hours. [d]24 hours. [e]Add 0.3 mmol NMO as oxidant. [f]Add 0.3 mmol Ag_2O as oxidant. [g]Add 0.3 mmol MnO_2 as oxidant. [h]Add 0.3 mmol $K_2S_2O_8$ as oxidant. [i]Add 0.03 mmol PPh_3 as ligand. [j]Add 0.015 mmol dppe as ligand. [k]Add 0.015 mmol 1,10-phen as ligand. [l]using aqueous ammonia instead of gaseous ammonia and under N_2 atmosphere.

3.2 General procedure for nickel-promoted C-H amination to form primary anilines

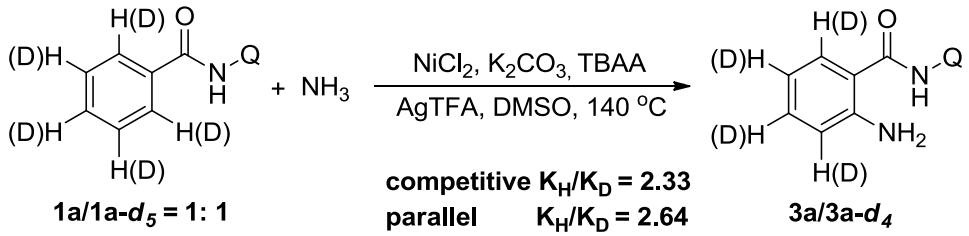
Aromatic amide **1** (0.15 mmol), $NiCl_2$ (39 mg, 0.3 mmol), K_2CO_3 (42 mg, 0.3 mmol), TBAA (90 mg, 0.3 mmol) and NMP (5.0 mL) were added to a 35 mL Schlenk flask equipped with a high-vacuum PTFE valve-to-glass seal. After air-evacuation and being refilled with NH_3 (1 atm) three times, ammonia gas was injected for 10 minutes via a balloon. Then the flask was sealed under NH_3 (1 atm) and stirred at 120 ℃ for 12 h. After the reaction was quenched by addition of brine, the mixture was extracted with dichloromethane, and the combined organic layer was dried over sodium sulfate. Concentration in vacuo followed by silica gel column purification with petroleum ether /ethyl acetate/triethylamine eluent gave the desired product **3.** (The procedure of

reaction condition B are similar to those of reaction condition A).

3.3 Procedure for 1 mmol scale reaction with 1a

A dried round bottom flask charged with benzamide **1a** (248 mg, 1.0 mmol), $NiCl_2$ (259.2 mg, 2.0 mmol), K_2CO_3 (276.4 mg, 2.0 mmol), TBAA (603 mg, 2.0 mmol), AgTFA (441.8 mg, 2.0 mmol), was evacuated and purged with argon. DMSO (30 mL) was added by syringe under argon. After air-evacuation and being refilled with NH_3 (1 atm) three times, ammonia gas was injected for 10 minutes via a balloon. Then the flask was sealed under NH_3 and stirred at 140 ℃ for 2 h. After the reaction was quenched by addition of brine, the mixture was extracted with dichloromethane, and the combined organic layer was dried over sodium sulfate. Concentration in vacuo followed by silica gel column purification with petroleum ether /ethyl acetate/triethylamine eluent (80:10:1) gave the desired product **3a** in 65% yield (171 mg).

3.4 Deuterium-labeling experiments.



Intermolecular competition KIE Following general procedure: **1a** (37 mg, 0.15 mmol), **1a-*d*$_5$** (38 mg, 0.15 mmol), $NiCl_2$ (78 mg, 0.6 mmol), K_2CO_3 (83 mg, 0.6 mmol), tetrabutylammonium acetate (181 mg, 0.6 mmol), AgTFA (133 mg, 0.6 mmol) and DMSO (10.0 mL) were added to a 75 mL Schlenk flask equipped with a high-vacuum PTFE valve-to-glass seal. The flask was injected with ammonia gas for 10 minutes. Then the flask was sealed under NH_3 and stirred at 140 ℃ for 8 min. The product was separated by column chromatography to give the desired product in 15 % yield.

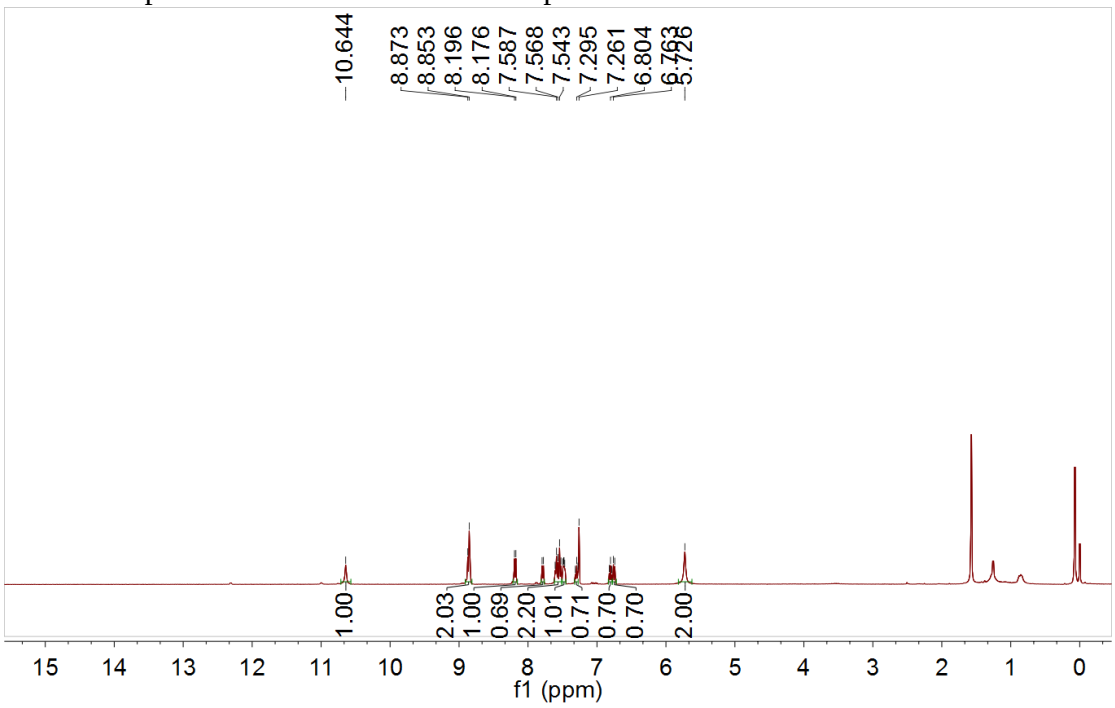
^{1}H NMR (400 MHz, $CDCl_3$): δ 10.64 (s, 1.00H), 8.89-8.83 (m, 2.00H), 8.19 (d, J = 8.2 Hz, 1.00H), 7.79 (d, J = 7.9 Hz, 0.69H), 7.62-7.51 (m, 2.00H), 7.48 (dd, J = 6.1,

3.9 Hz, 1.00H), 7.29 (t, *J* = 7.6 Hz, 0.71H), 6.80 (t, *J* = 7.5 Hz, 0.70H), 6.75 (d, *J* = 8.2 Hz, 0.70H), 5.73 (s, 2.00H). The KIE value was calculated as k_H/k_D = 2.33.

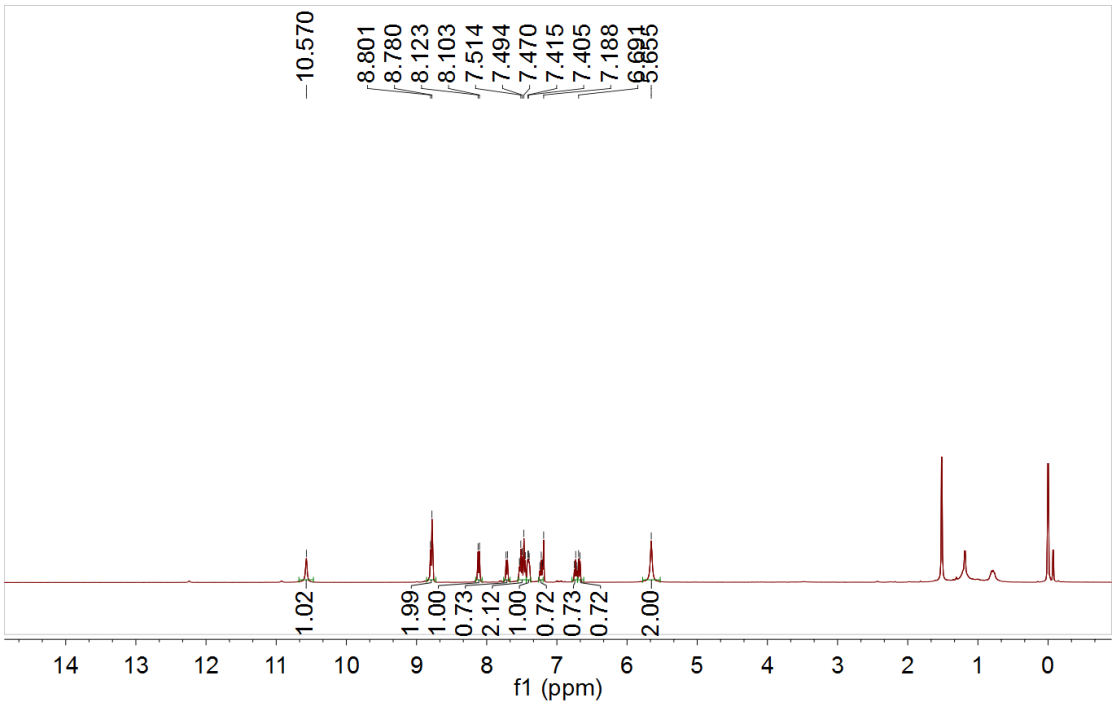
Intermolecular parallel KIE Following general procedure: **1a** (37 mg, 0.15 mmol) or **1a-*d*$_5$** (38 mg, 0.15 mmol), $NiCl_2$ (39 mg, 0.3 mmol), K_2CO_3 (42 mg, 0.15 mmol), tetrabutylammonium acetate (90 mg, 0.3 mmol), AgTFA (66 mg, 0.3 mmol) and DMSO (5.0 mL) were added to a 75 mL Schlenk flask equipped with a high-vacuum PTFE valve-to-glass seal. Then the flask was sealed under NH_3 and stirred at 140 ℃ for 8 min. The product was separated by column chromatography to give the desired product in 12 % yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 10.57 (s, 1.00H), 8.85-8.75 (m, 2.00H), 8.11 (d, *J* = 8.3 Hz, 1.00H), 7.71 (d, *J* = 7.8 Hz, 0.73H), 7.55-7.44 (m, 2.00H), 7.48 (dd, *J* = 8.2, 4.2 Hz, 1.00H), 7.22 (t, *J* = 7.7 Hz, 0.72H), 6.73 (t, *J* = 7.4 Hz, 0.73H), 6.68 (d, *J* = 8.1 Hz, 0.72H), 5.66 (s, 2.00H). The KIE value was calculated as k_H/k_D = 2.64.

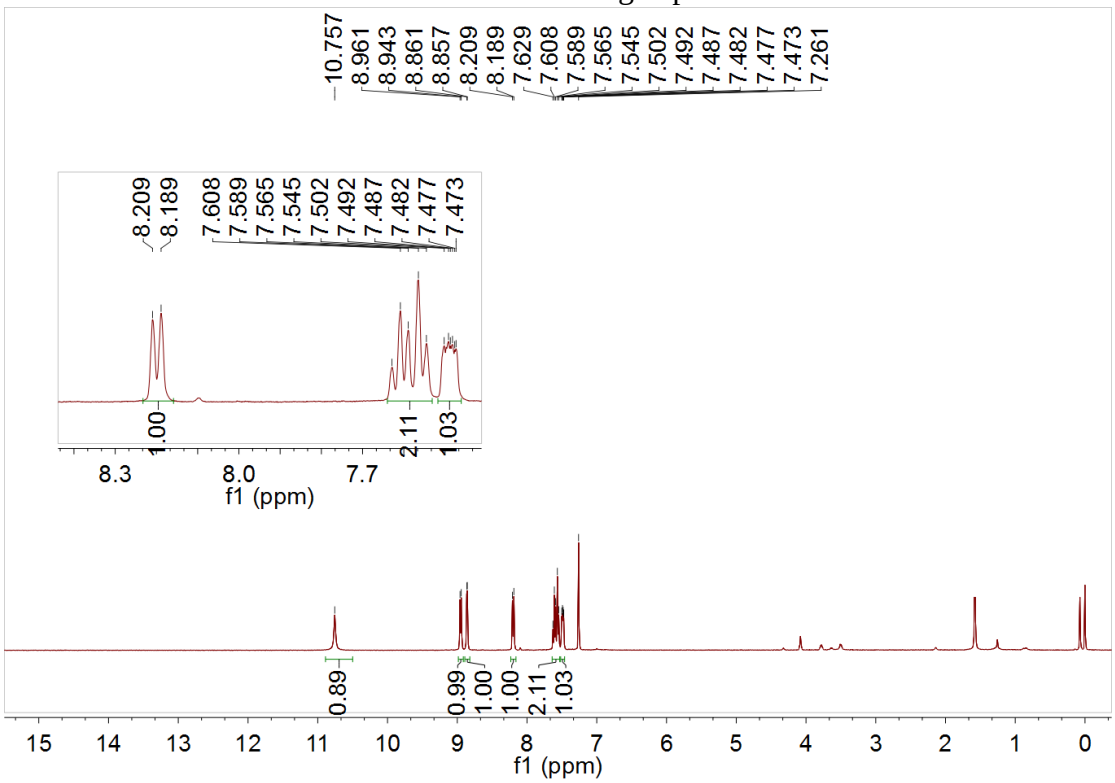
^{1}H NMR Spectrum of Intermolecular competition



^{1}H NMR Spectrum of Intermolecular parallel

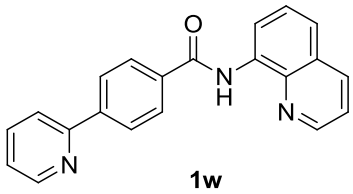


^{1}H NMR Spectrum of recovered amide (**1a-*d*$_5$**): We didn't observed the H/D exchange in the recovered amide in the deuterium labelling experiments.



4. Characterization data of products.

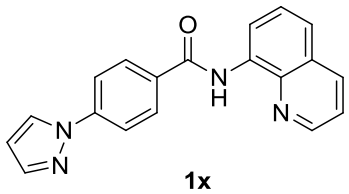
4-(pyridin-2-yl)-*N*-(quinolin-8-yl)benzamide (1w):



1w

Following the general procedure the title compound was isolated by flash chromatography (eluent: petrol ether/ethyl acetate = 2/1) as a white solid in 83 % yield (1.349 g), mp 152-153 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.79 (s, 1H), 8.95 (d, J = 7.4 Hz, 1H), 8.84 (d, J = 1.9 Hz, 1H), 8.72 (d, J = 3.1 Hz, 1H), 8.25-8.12 (m, 5H), 7.83-7.74 (m, 2H), 7.61-7.50 (m, 2H), 748-7.42 (m, 1H), 7.29-7.23 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.0, 156.1, 149.8, 148.3, 142.5, 138.7, 136.8, 136.3, 135.2, 134.5, 127.9, 127.7, 127.4, 127.2, 122.7, 121.7, 121.6, 120.8, 116.5; HRMS (ESI, m/z): calcd for $C_{21}H_{15}N_3O$ $[M+H]^+$: 326.1288; Found: 326.1302.

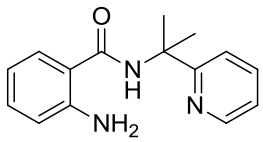
4-(1H-pyrazol-1-yl)-*N*-(quinolin-8-yl)benzamide (1x):



1x

Following the general procedure the title compound was isolated by flash chromatography (eluent: petrol ether/ethyl acetate = 2/1) as a white solid in 62 % yield (0.973 g), mp 183-184 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.74 (s, 1H), 8.92 (d, J = 6.9 Hz, 1H), 8.84 (d, J = 2.6 Hz, 1H), 8.24-8.10 (m, 3H), 8.01 (d, J = 1.9 Hz, 1H), 7.87 (d, J = 8.6, 2H), 7.77 (s, 1H), 7.62-7.50 (m, 2H), 7.46 (dd, J = 8.2, 4.2 Hz, 1H), 6.51 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.3, 148.3, 142.5, 141.8, 138.7, 136.3, 134.4, 132.6, 128.7, 127.9, 127.4, 126.8, 121.7, 121.7, 118.7, 116.5, 108.3; HRMS (ESI, m/z): calcd for $C_{19}H_{14}N_4O$ $[M+H]^+$: 315.1240; Found: 315.1255.

2-amino-*N*-(2-(pyridin-2-yl)propan-2-yl)benzamide (3ac):

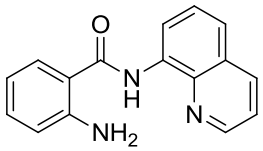


3ac

Following the general procedure the title compound was isolated by flash chromatography (eluent: petrol ether/ethyl acetate/triethylamine = 80/10/1) as a semisolid in 9 % yield (3.4 mg), ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.54 (d, J = 3.9 Hz,, 1H), 8.46 (s, 1H), 7.71 (t, J = 7.6 Hz, 1H), 7.53 (d, J = 7.8 Hz, 1H), 7.44 (d, J = 8.0 Hz, 1H), 7.19 (t, J = 6.8, 2H), 6.73-6.64 (m, 2H), 5.55 (s, 2H), 1.85 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.6, 164.7, 148.6, 147.6, 137.0, 131.7, 127.6, 121.8, 119.4,

117.6, 117.1, 116.5, 56.6, 27.6; HRMS (ESI, m/z): calcd for $C_{15}H_{17}N_3O$ $[M+H]^+$: 256.1444; Found: 256.1450.

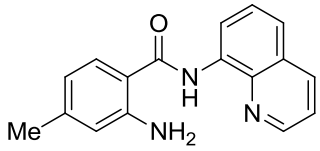
2-amino-*N*-(quinolin-8-yl)benzamide (3a):



3a

Following the general procedure the title compound was isolated by flash chromatography (eluent: petrol ether/ethyl acetate/triethylamine = 80/10/1) as a white solid in 66% (68%) yield (26.7 mg). This compound is known[4]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.53 (s, 1H), 8.78-8.72 (m, 2H), 8.05 (d, J = 8.2 Hz, 1H), 7.68 (d, J = 7.9 Hz, 1H), 7.51-7.38 (m, 2H), 7.34 (dd, J = 8.1, 4.2 Hz, 1H), 7.19 (t, J = 7.6, 1H), 6.69 (t, J = 7.5 Hz, 1H), 6.65 (d, J = 8.2 Hz, 1H), 5.65 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.6, 149.4, 148.2, 138.8, 136.3, 134.7, 132.7, 128.0, 127.6, 127.3, 121.6, 121.4, 117.5, 116.7, 116.2.

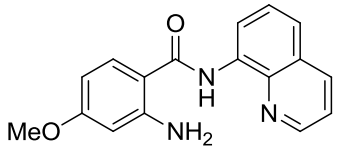
2-amino-4-methyl-*N*-(quinolin-8-yl)benzamide (3b):



3b

Following the general procedure the title compound was isolated by flash chromatography (eluent: petrol ether/ethyl acetate/triethylamine = 80/10/1) as a white solid in 45% (51%) yield (21.2 mg). This compound is known[4]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.61 (s, 1H), 8.89-8.80 (m, 2H), 8.15 (d, J = 8.2 Hz, 1H), 7.68 (d, J = 8.1 Hz, 1H), 7.57 (t, J = 7.9 Hz, 1H), 7.50 (d, J = 8.2 Hz, 1H), 7.44 (dd, J = 8.2, 4.2 Hz, 1H), 6.61 (d, J = 8.1 Hz, 1H), 6.55 (s, 1H), 5.75 (s, 2H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.6, 149.6, 148.1, 143.3, 138.8, 136.2, 134.8, 128.0, 127.6, 127.3, 121.5, 121.2, 118.0, 117.7, 116.1, 113.5, 21.4.

2-amino-4-methoxy-*N*-(quinolin-8-yl)benzamide (3c):

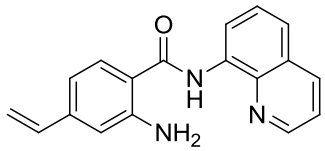


3c

Following the general procedure the title compound was isolated by flash chromatography (eluent: petrol ether/ethyl acetate/triethylamine = 80/10/1) as a white solid in 51% (62%) yield (27.3 mg). This compound is known[4]. ^{1}H NMR (400 MHz,

$CDCl_3$): δ 10.55 (s, 1H), 8.83 (d, J = 5.5 Hz, 2H), 8.16 (d, J = 8.2 Hz, 1H), 7.73 (d, J = 8.7 Hz, 1H), 7.60-7.41 (m, 3H), 6.37 (d, J = 8.7 Hz, 1H), 6.20 (s, 1H), 5.93 (s, 2H), 3.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.4, 163.2, 151.7, 148.1, 138.8, 136.3, 135.0, 129.4, 128.0, 127.4, 121.6, 121.0, 116.0, 109.3, 104.4, 100.6, 55.2.

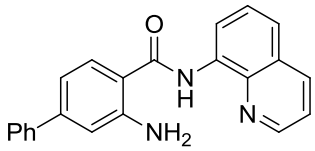
2-amino-*N*-(quinolin-8-yl)-4-vinylbenzamide (3d):



3d

Following the general procedure the title compound was isolated by flash chromatography (eluent: petrol ether/ethyl acetate/triethylamine = 80/10/1) as a white solid in 50% (53%) yield (23.0 mg). This compound is known[4]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.64 (s, 1H), 8.85 (d, J = 7.2 Hz, 2H), 8.19 (d, J = 8.2 Hz, 1H), 7.76 (d, J = 8.0 Hz, 1H), 7.62-7.50 (m, 2H), 7.47 (dd, J = 6.4, 3.9 Hz, 1H), 6.89 (d, J = 8.1 Hz, 1H), 6.74 (s, 1H), 6.66 (dd, J = 17.5, 10.8 Hz, 1H), 5.82 (d, J = 17.6 Hz, 1H), 5.34 (d, J = 10.8 Hz, 1H); Due to H/D exchange of NH_2 with $CDCl_3$, NH_2 disappear. ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.4, 149.7, 148.2, 141.7, 138.8, 136.3, 136.2, 134.8, 128.0, 128.0, 127.4, 121.6, 121.3, 116.2, 115.9, 115.4, 115.3, 114.6.

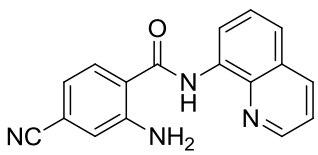
2-amino-4-phenyl-*N*-(quinolin-8-yl)benzamide (3e):



3e

Following the general procedure the title compound was isolated by flash chromatography (eluent: petrol ether/ethyl acetate/triethylamine = 80/10/1) as a white solid in 46% (66%) yield (33.6 mg). This compound is known[4]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.70 (s, 1H), 8.93-8.84 (m, 2H), 8.18 (d, J = 8.2 Hz, 1H), 7.86 (d, J = 8.2 Hz, 1H), 7.66-7.36 (m, 8H), 7.04 (d, J = 8.1 Hz, 1H), 6.96 (s, 1H), 5.87 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.5, 149.8, 148.2, 145.5, 140.3, 138.8, 136.3, 134.8, 128.8, 128.2, 128.0, 127.9, 127.4, 127.1, 121.6, 121.4, 116.2, 115.9, 115.8, 115.0.

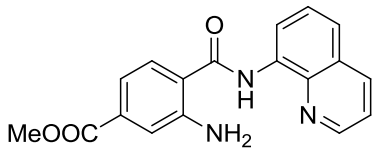
2-amino-4-cyano-*N*-(quinolin-8-yl)benzamide (3f):



3f

Following the general procedure the title compound was isolated by flash chromatography (eluent: petrol ether/ethyl acetate/triethylamine = 80/10/1) as a yellow solid in 63% (75%) yield (34.9 mg), mp 165-166 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.64 (s, 1H), 8.90-8.75 (m, 2H), 8.19 (d, J = 8.2 Hz, 1H), 7.80 (d, J = 8.0 Hz, 1H), 7.62-7.50 (m, 2H), 7.49 (dd, J = 7.2, 3.5 Hz, 1H), 7.04-6.96 (m, 2H), 5.91 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.1, 149.2, 148.4, 138.7, 136.4, 134.1, 128.4, 128.0, 127.3, 122.1, 121.8, 120.4, 119.5, 119.3, 118.3, 116.5, 115.7; HRMS (ESI, m/z): calcd for $C_{17}H_{12}N_4O$ [M+Na]$^+$: 311.0903; Found: 311.0917.

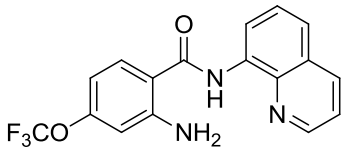
methyl 3-amino-4-(quinolin-8-ylcarbamoyl)benzoate (3g):



3g

Following the general procedure the title compound was isolated by flash chromatography (eluent: petrol ether/ethyl acetate/triethylamine = 80/10/1) as a yellow solid in 68% (73%) yield (35.2 mg). This compound is known[4]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.65 (s, 1H), 8.84 (d, J = 3.7 Hz, 2H), 8.17 (d, J = 8.1 Hz, 1H), 7.80 (d, J = 8.0 Hz, 1H), 7.60-7.44 (m, 3H), 7.41 (d, J = 8.5 Hz, 2H), 5.81 (s, 2H), 3.92 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.8, 166.5, 149.1, 148.3, 138.7, 136.4, 134.4, 133.6, 128.0, 127.8, 127.3, 121.8, 121.7, 119.5, 118.5, 117.3, 116.4, 52.3.

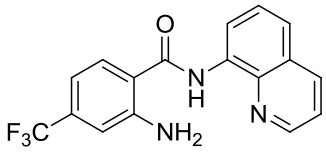
2-amino-*N*-(quinolin-8-yl)-4-(trifluoromethoxy)benzamide (3h):



3h

Following the general procedure the title compound was isolated by flash chromatography (eluent: petrol ether/ethyl acetate/triethylamine = 80/10/1) as a white solid in 40 (54%) yield (28.1 mg). This compound is known[4]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.59 (s, 1H), 8.83 (d, J = 7.4 Hz, 2H), 8.19 (d, J = 8.1 Hz, 1H), 7.79 (d, J = 8.7 Hz, 1H), 7.63-7.51 (m, 2H), 7.48 (dd, J = 8.2, 4.2 Hz, 1H), 6.63 (d, J = 8.6 Hz, 1H), 6.56 (s, 1H), 5.93 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.7, 152.4 (q, $J_{C\text{-}F}$ = 2.0 Hz), 151.0, 148.3, 138.8, 136.4, 134.5, 129.5, 128.0, 127.4, 121.7, 121.6, 116.3, 114.5, 108.5, 108.2; ^{19}F NMR (377 MHz, $CDCl_3$) δ -57.3.

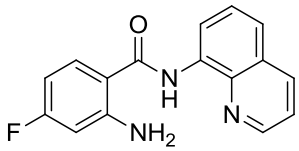
2-amino-*N*-(quinolin-8-yl)-4-(trifluoromethoxy)benzamide (3i):



3i

Following the general procedure the title compound was isolated by flash chromatography (eluent: petrol ether/ethyl acetate/triethylamine = 80/10/1) as a white solid in 74% (81%) yield (40.2 mg), mp 122-123 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.65 (s, 1H), 8.83 (d, J = 4.3 Hz, 2H), 8.18 (d, J = 8.2 Hz, 1H), 7.85 (d, J = 8.0 Hz, 1H), 7.61-7.53 (m, 2H), 7.51-7.44 (m, 1H), 7.07-6.93 (m, 2H), 5.90 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.6, 149.2, 148.4, 138.7, 136.4, 134.3, 134.2 (q, $J_{C\text{-}F}$ = 32.1 Hz), 128.4, 128.0, 127.3, 123.6 (q, $J_{C\text{-}F}$ = 271.0 Hz), 121.9, 121.8, 118.7, 116.4, 114.0 (q, $J_{C\text{-}F}$ = 3.8 Hz), 112.9 (q, $J_{C\text{-}F}$ = 3.6 Hz); ^{19}F NMR (377 MHz, $CDCl_3$) δ -63.6; HRMS (ESI, m/z): calcd for $C_{17}H_{12}F_3N_3O$ $[M+H]^+$: 332.1005; Found: 332.1016.

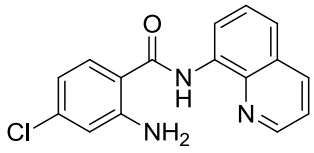
2-amino-4-fluoro-*N*-(quinolin-8-yl)benzamide (3j):



3j

Following the general procedure the title compound was isolated by flash chromatography (eluent: petrol ether/ethyl acetate/triethylamine = 80/10/1) as a white solid in 49% (58%) yield (24.5 mg). This compound is known[4]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.54 (s, 1H), 8.84-8.75 (m, 2H), 8.16 (d, J = 8.2 Hz, 1H), 7.75 (t, J = 7.3 Hz, 1H), 7.60-7.49 (m, 2H), 7.45 (dd, J = 7.4, 3.8 Hz, 1H), 6.48 (t, J = 8.4 Hz, 1H), 6.41 (d, J = 10.8 Hz, 1H), 5.95 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.9, 165.6 (d, $J_{C\text{-}F}$ = 248.4 Hz), 151.7 (d, $J_{C\text{-}F}$ = 12.1 Hz), 148.2, 138.7, 136.3, 134.6, 129.9 (d, $J_{C\text{-}F}$ = 11.2 Hz), 128.0, 127.3, 121.6, 121.4, 116.2, 112.6, 104.3 (d, $J_{C\text{-}F}$ = 22.6 Hz), 103.1 (d, $J_{C\text{-}F}$ = 24.1 Hz); ^{19}F NMR (377 MHz, $CDCl_3$): δ -107.4.

2-amino-4-chloro-*N*-(quinolin-8-yl)benzamide (3k):

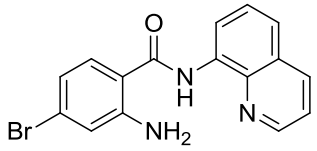


3k

Following the general procedure the title compound was isolated by flash chromatography (eluent: petrol ether/ethyl acetate/triethylamine = 80/10/1) as a white solid in 54% (62%) yield (27.6 mg). This compound is known[4]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.58 (s, 1H), 8.84-8.78 (m, 2H), 8.17 (d, J = 8.2 Hz, 1H), 7.68 (d, J = 8.2

Hz, 1H), 7.60-744 (m, 3H), 6.74 (d, J = 8.3 Hz, 2H), 5.86 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.9, 150.4, 148.3, 138.7, 138.5, 136.3, 134.5, 128.9, 128.0, 127.3, 121.7, 121.6, 116.9, 116.7, 116.3, 114.5.

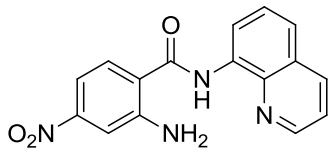
2-amino-4-bromo-*N*-(quinolin-8-yl)benzamide (3l):



3l

Following the general procedure the title compound was isolated by flash chromatography (eluent: petrol ether/ethyl acetate/triethylamine = 80/10/1) as a white solid in 47% (69%) yield (35.3 mg). This compound is known[4]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.57 (s, 1H), 8.84-8.78 (m, 2H), 8.16 (d, J = 8.2 Hz, 1H), 7.62-7.45 (m, 4H), 6.94-6.84 (m, 2H), 5.84 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.9, 150.4, 148.2, 138.7, 136.3, 134.4, 128.9, 127.9, 127.3, 127.0, 121.7, 121.6, 119.7, 116.3, 114.9.

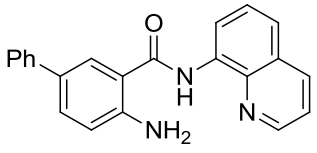
2-amino-4-nitro-*N*-(quinolin-8-yl)benzamide (3m):



3m

Following the general procedure the title compound was isolated by flash chromatography (eluent: petrol ether/ethyl acetate/triethylamine = 20/10/1) as a yellow solid in 58% (71%) yield (32.8 mg), mp 218-219 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.59 (s, 1H), 8.93 (s, 1H), 8.64 (d, J = 7.5 Hz, 1H), 8.43 (d, J = 8.2 Hz, 1H), 7.89 (d, J = 8.6, 1H), 7.77-7.58 (m, 4H), 7.41 (d, J = 8.5 Hz, 1H), 6.91 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.6, 150.3, 150.0, 149.4, 138.6, 136.9, 134.0, 129.7, 128.0, 127.1 122.8, 122.5, 120.2, 117.3, 111.1, 109.3; HRMS (ESI, m/z): calcd for $C_{16}H_{12}N_4O_3$ $[M+H]^+$: 309.0982; Found: 309.0982.

4-amino-*N*-(quinolin-8-yl)-[1,1'-biphenyl]-3-carboxamide (3n):

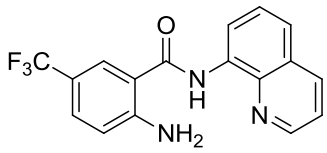


3n

Following the general procedure the title compound was isolated by flash chromatography (eluent: petrol ether/ethyl acetate/triethylamine = 40/10/1) as a yellow solid in 56% (63%) yield (32.0 mg). This compound is known[4]. ^{1}H NMR (400

MHz, $CDCl_3$): δ 10.68 (s, 1H), 8.88 (d, J = 7.5 Hz, 1H), 8.83 (d, J = 3.7 Hz, 1H), 8.18 (d, J = 8.2 Hz, 1H), 7.99 (s, 1H), 7.66-7.50 (m, 5H), 7.47 (t, J = 6.9 Hz, 3H), 7.34 (t, J = 7.2 Hz, 1H), 6.84 (d, J = 8.4 Hz, 1H), 5.74 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.7, 148.6, 148.3, 140.6, 138.8, 136.3, 134.7, 131.5, 129.9, 128.8, 128.0, 127.3, 126.5, 126.4, 126.1, 121.6, 121.5, 117.9, 116.8, 116.4.

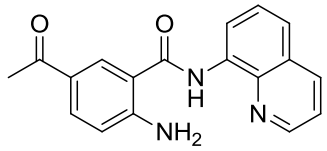
2-amino-*N*-(quinolin-8-yl)-5-(trifluoromethyl)benzamide (3o):



3o

Following the general procedure the title compound was isolated by flash chromatography (eluent: petrol ether/ethyl acetate/triethylamine = 80/10/1) as a white solid in 76% (82%) yield (40.7 mg). This compound is known[4]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.61 (s, 1H), 8.85 (d, J = 3.9 Hz, 1H), 8.80 (d, J = 7.1 Hz, 1H), 8.17 (d, J = 8.2 Hz, 1H), 7.98 (s, 1H), 7.60-7.52 (m, 2H), 7.47 (dd, J = 7.4, 5.6 Hz, 2H), 6.77 (d, J = 8.6 Hz, 1H), 6.09 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.6, 151.8, 148.5, 138.7, 136.3, 134.3, 129.3 (q, $J_{C\text{-}F}$ = 3.2 Hz), 128.0, 127.2, 125.2 (q, $J_{C\text{-}F}$ = 3.9 Hz), 124.4 (q, $J_{C\text{-}F}$ = 269.0 Hz), 121.9, 121.7, 118.3 (q, $J_{C\text{-}F}$ = 32.8 Hz), 117.2, 116.5, 115.3; ^{19}F NMR (377 MHz, $CDCl_3$): δ -61.3.

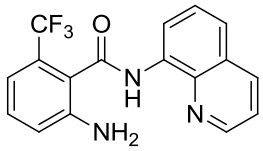
5-acetyl-2-amino-*N*-(quinolin-8-yl)benzamide (3p):



3p

Following the general procedure the title compound was isolated by flash chromatography (eluent: petrol ether/ethyl acetate/triethylamine = 80/10/1) as a white solid in 52% (60%) yield (27.5 mg), mp 212-213 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.71 (s, 1H), 8.86 (s, 1H), 8.80 (d, J = 6.9 Hz, 1H), 8.47 (s, 1H), 8.19 (d, J = 8.2 Hz, 1H), 7.89 (d, J = 8.6, 1H), 7.62-7.46 (m, 3H), 6.72 (d, J = 8.3 Hz, 1H), 6.31 (s, 2H), 2.60 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.6, 167.0, 153.2, 148.5, 138.8, 136.3, 134.4, 133.0, 129.4, 128.0, 127.3, 126.2, 121.8, 121.8, 116.6, 116.4, 115.0, 26.0; HRMS (ESI, m/z): calcd for $C_{18}H_{15}N_3O_2$ $[M+H]^+$: 306.1237; Found: 306.1252.

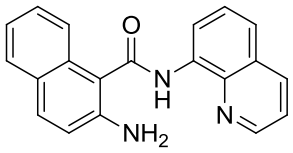
2-amino-*N*-(quinolin-8-yl)-6-(trifluoromethyl)benzamide (3q)



3q

Following the general procedure the title compound was isolated by flash chromatography (eluent: petrol ether/ethyl acetate/triethylamine = 80/10/1) as a white solid in 40% (53%) yield (26.3 mg), mp 140-141 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.19 (s, 1H), 8.93 (d, J = 3.6 Hz, 1H), 8.75 (s, 1H), 8.16 (d, J = 8.1 Hz, 1H), 7.65-7.52 (m, 2H), 7.44 (dd, J = 8.0 Hz, 4.0 Hz, 1H), 7.31 (t, J = 7.6 Hz, 1H), 7.11 (d, J = 7.6 Hz, 1H), 6.93 (d, J = 8.0 Hz, 1H), 4.45 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.4, 148.4, 145.7, 138.5, 136.3, 134.2, 130.3, 130.0, 127.2, 122.5, 121.7, 120.1 (q, $J_{C\text{-}F}$ = 2.2 Hz), 119.8, 117.0, 115.6 (q, $J_{C\text{-}F}$ = 5.2 Hz); ^{19}F NMR (377 MHz, $CDCl_3$): δ -58.3; HRMS (ESI, m/z): calcd for $C_{17}H_{12}F_3N_3O$ $[M+H]^+$: 332.1005; Found: 332.1017.

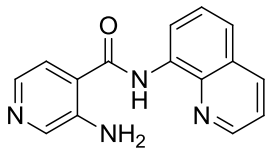
2-amino-*N*-(quinolin-8-yl)-1-naphthamide (3r)



3r

Following the general procedure the title compound was isolated by flash chromatography (eluent: petrol ether/ethyl acetate/triethylamine = 80/10/1) as a white solid in 78% (80%) yield (37.6 mg), mp 207-208 ℃. ^{1}H NMR (400 MHz, DMSO-d_6): 10.24 (s, 1H), 8.86 (d, J = 6.5 Hz, 1H), 8.79 (d, J = 2.4 Hz, 1H), 8.43 (d, J = 8.1 Hz, 1H), 7.86 (d, J = 8.4 Hz, 1H), 7.81-7.66 (m, 4H), 7.60 (dd, J = 8.0, 4.0 Hz, 1H), 7.38 (t, J = 7.4 Hz, 1H), 7.21 (t, J = 7.2 Hz, 1H), 7.14 (d, J = 8.9 Hz, 1H), 6.03 (s, 2H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 166.9, 149.1, 145.1, 138.3, 136.8, 134.5, 131.6, 131.2, 128.4, 128.0, 127.4, 127.2, 126.5, 122.4, 122.4, 122.3, 121.7, 119.2, 117.1, 111.1; HRMS (ESI, m/z): calcd for $C_{20}H_{15}N_3O$ $[M+H]^+$: 314.1288; Found: 314.1301.

3-amino-*N*-(quinolin-8-yl)isonicotinamide (3s)

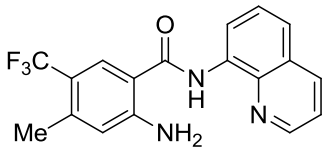


3s

Following the general procedure the title compound was isolated by flash chromatography (eluent: petrol ether/ethyl acetate/triethylamine = 40/10/1) as a yellow solid in 33% (48%) yield (19.0 mg). This compound is known[4]. ^{1}H NMR (400

MHz, $CDCl_3$): δ 10.73 (s, 1H), 8.90-8.72 (m, 2H), 8.23 (s, 1H), 8.17 (d, J = 8.2 Hz, 1H), 8.05 (d, J = 4.0 Hz, 1H), 7.60-7.45 (m, 4H), 5.74 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.7, 148.4, 144.0, 141.1, 138.6, 137.7, 136.4, 134.0, 127.9, 127.3, 122.1, 121.8, 120.6, 119.8, 116.5.

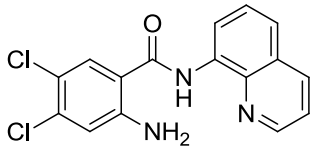
2-amino-4-methyl-*N*-(quinolin-8-yl)-5-(trifluoromethyl)benzamide (3t)



3t

Following the general procedure the title compound was isolated by flash chromatography (eluent: petrol ether/ethyl acetate/triethylamine = 80/10/1) as a white solid in 66% (73%) yield (37.8 mg), mp 146-147 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.60 (s, 1H), 8.86 (d, J = 1.6 Hz, 1H), 8.79 (d, J = 7.0 Hz, 1H), 8.18 (d, J = 8.1 Hz, 1H), 7.98 (s, 1H), 7.61-7.51 (m, 2H), 7.48 (dd, J = 4.9, 3.2 Hz, 1H), 6.59 (s, 1H), 6.05 (s, 2H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.7, 151.7, 148.4, 141.4, 138.8, 136.3, 134.4, 128.0, 127.3, 126.0 (q, $J_{C\text{-}F}$ = 5.7 Hz), 124.8 (q, $J_{C\text{-}F}$ = 270.1 Hz), 121.7, 121.7, 119.8, 117.1 (q, $J_{C\text{-}F}$ = 30.1 Hz), 116.3, 112.5, 19.4; ^{19}F NMR (377 MHz, $CDCl_3$): δ -60.0; HRMS (ESI, m/z): calcd for $C_{18}H_{14}F_3N_3O$ $[M+H]^+$: 346.1162; Found: 346.1175.

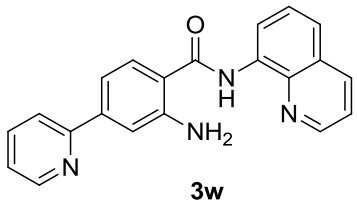
2-amino-4,5-dichloro-*N*-(quinolin-8-yl)benzamide (3u)



3u

Following the general procedure the title compound was isolated by flash chromatography (eluent: petrol ether/ethyl acetate/triethylamine = 40/10/1) as a white solid in 53% (61%) yield (30.3 mg). This compound is known[4]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.52 (s, 1H), 8.87 (s, 1H), 8.79 (d, J = 6.4 Hz, 1H), 8.19 (d, J = 8.1 Hz, 1H), 7.80 (s, 1H), 7.64-7.54 (m, 2H), 7.50 (dd, J = 7.6, 3.8 Hz, 1H), 6.85 (s, 1H), 5.77 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.8, 148.5, 148.5, 138.7, 136.5, 136.4, 134.2, 128.9, 128.0, 127.3, 121.9, 121.8, 119.3,118.3, 116.5, 116.0.

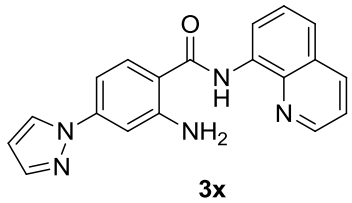
2-amino-4-(pyridin-2-yl)-*N*-(quinolin-8-yl)benzamide (3w)



3w

Following the general procedure the title compound was isolated by flash chromatography (eluent: petrol ether/ethyl acetate/triethylamine = 20/10/1) as a white solid in 51% (65%) yield (41.3 mg), mp 184-185 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.68 (s, 1H), 8.90-8.80 (m, 2H), 8.69 (d, J = 3.8 Hz, 1H), 8.16 (d, J = 8.3, 1H), 7.86 (d, J = 8.2, 1H), 7.78-7.70 (m, 2H), 7.60-7.48 (m, 2H), 7.49-7.41 (m, 2H), 7.35 (d, J = 8.2, 1H), 7.25 (d, J = 6.8, 1H), 5.86 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.4, 156.4, 149.8, 149.7, 148.2, 143.2, 138.8, 136.8, 136.3, 134.7, 128.2, 128.0, 127.4, 122.7, 121.6, 121.4, 120.8, 116.4, 116.3, 115.7, 115.2; HRMS (ESI, m/z): calcd for $C_{21}H_{16}N_4O$ $[M+H]^+$: 341.1397; Found: 341.1406.

2-amino-4-(2H-pyrrol-2-yl)-*N*-(quinolin-8-yl)benzamide (3x)



3x

Following the general procedure the title compound was isolated by flash chromatography (eluent: petrol ether/ethyl acetate/triethylamine = 20/10/1) as a white solid in 59% (68%) yield (42.0 mg), mp 195-196 ℃. ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.56 (s, 1H), 9.00-8.95 (m, 1H), 8.69 (d, J = 7.4 Hz, 1H), 8.50-8.43 (m, 2H), 7.83 (d, J = 8.7 Hz, 1H), 7.79 (s, 1H), 7.75-7.61 (m, 3H), 7.37 (s, 1H), 7.16 (d, J = 8.5 Hz, 1H), 6.83 (s, 2H), 6.58 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 166.4, 151.4, 149.2, 142.8, 141.5, 138.4, 136.9, 134.4, 129.4, 128.0, 128.0, 127.2, 122.4, 122.0, 116.5, 112.4, 108.3, 105.8, 105.6; HRMS (ESI, m/z): calcd for $C_{19}H_{15}N_5O$ $[M+H]^+$: 330.1349; Found: 330.1364.

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Ed. **2013**, *52*, 6043-6046; (h) M. Nishino, K. Hirano, T. Satoh, M. Miura, *Angew. Chem. Int. Ed.* **2013**, *52*, 4457-4461; (i) J. Roane, O. Daugulis, *J. Am. Chem. Soc.* **2016**, *138*, 4601-4607; (j) K. Shibata, N. Chatani, *Org. Lett.* **2014**, *16*, 5148-5151.

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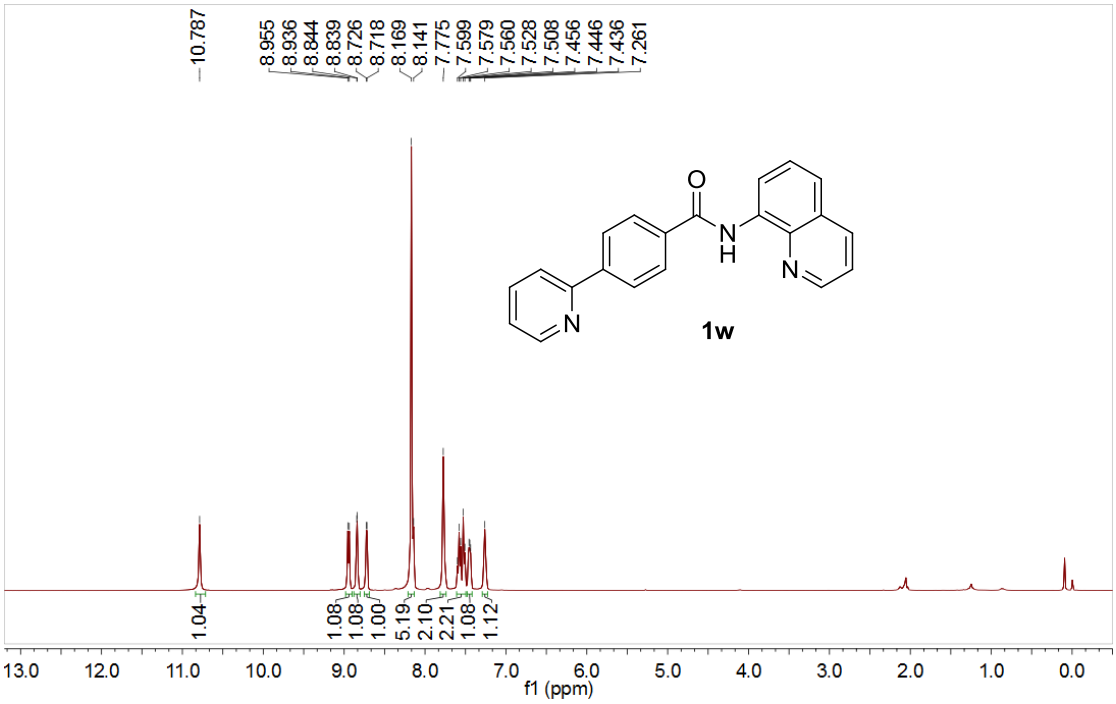
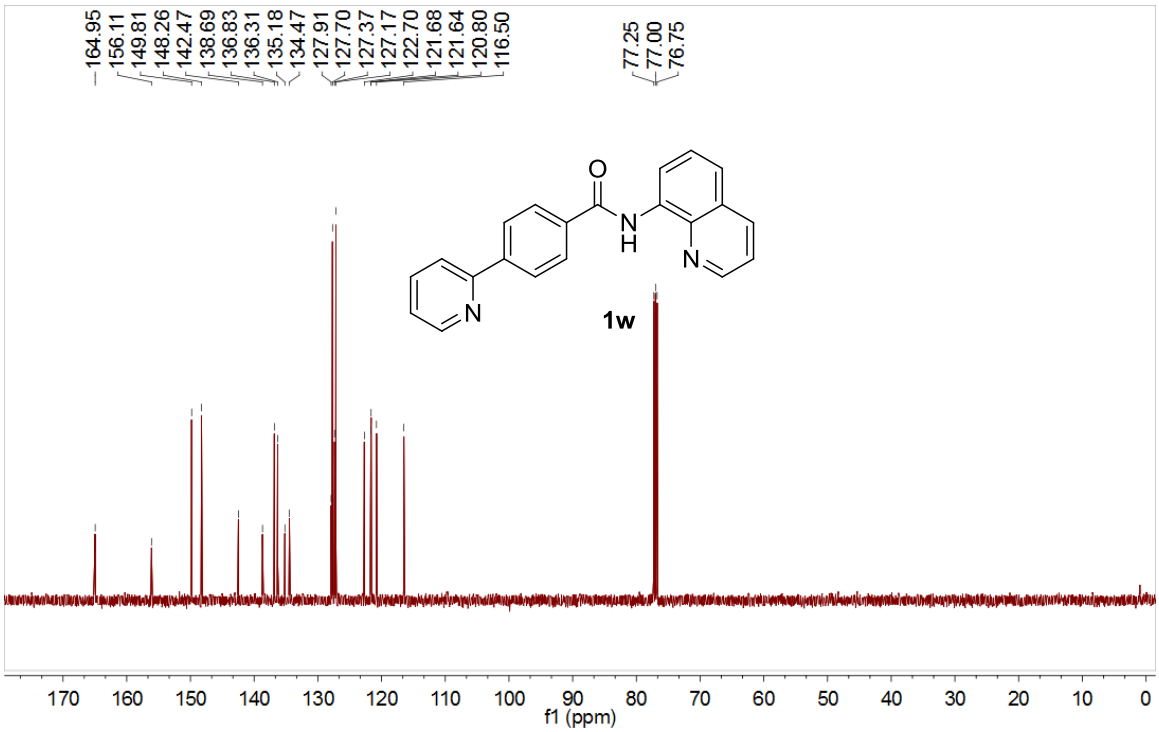
4. (a) L. Yu, X. Chen, D. Liu, L. Hu, Y. Yu, H. Huang, Z. Tan, Q. Gui, *Adv. Synth. Catal.* **2018**, *360*, 1346-1351; (b) Z. Li, H. Yu, C. Bolm, *Angew. Chem. Int. Ed.* **2017**, *56*, 9532-9535.

5. NMR spectra

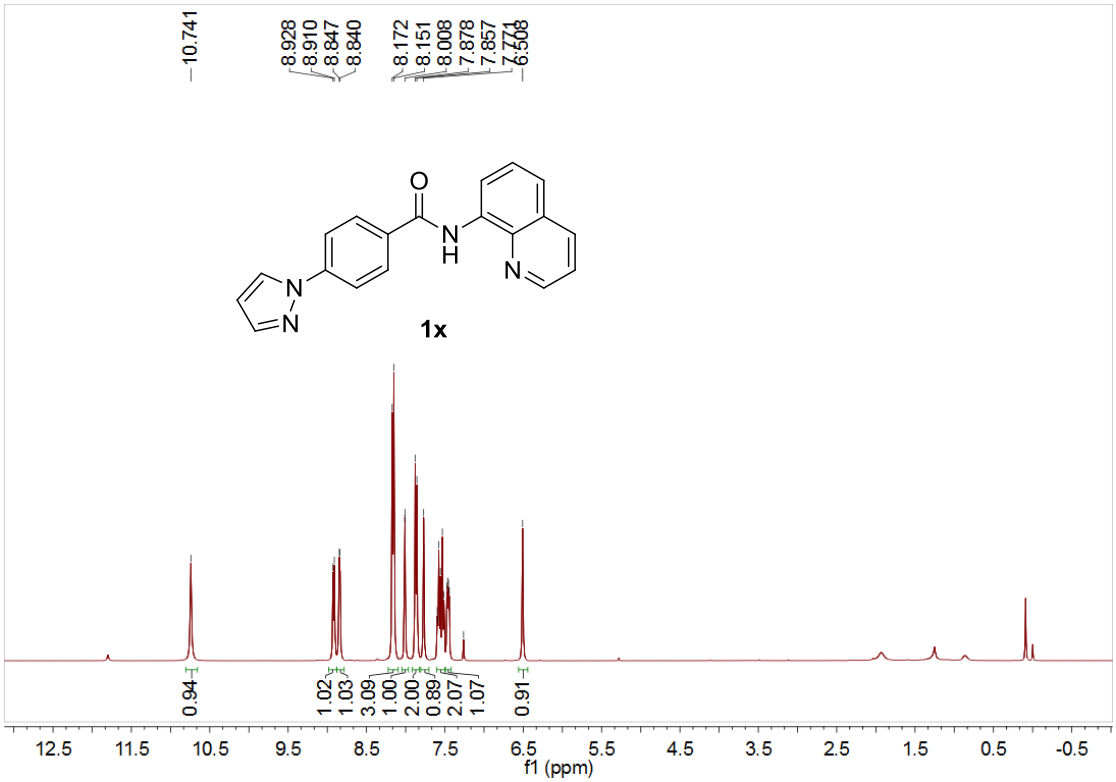
^{1}H NMR Spectrum of **1w**



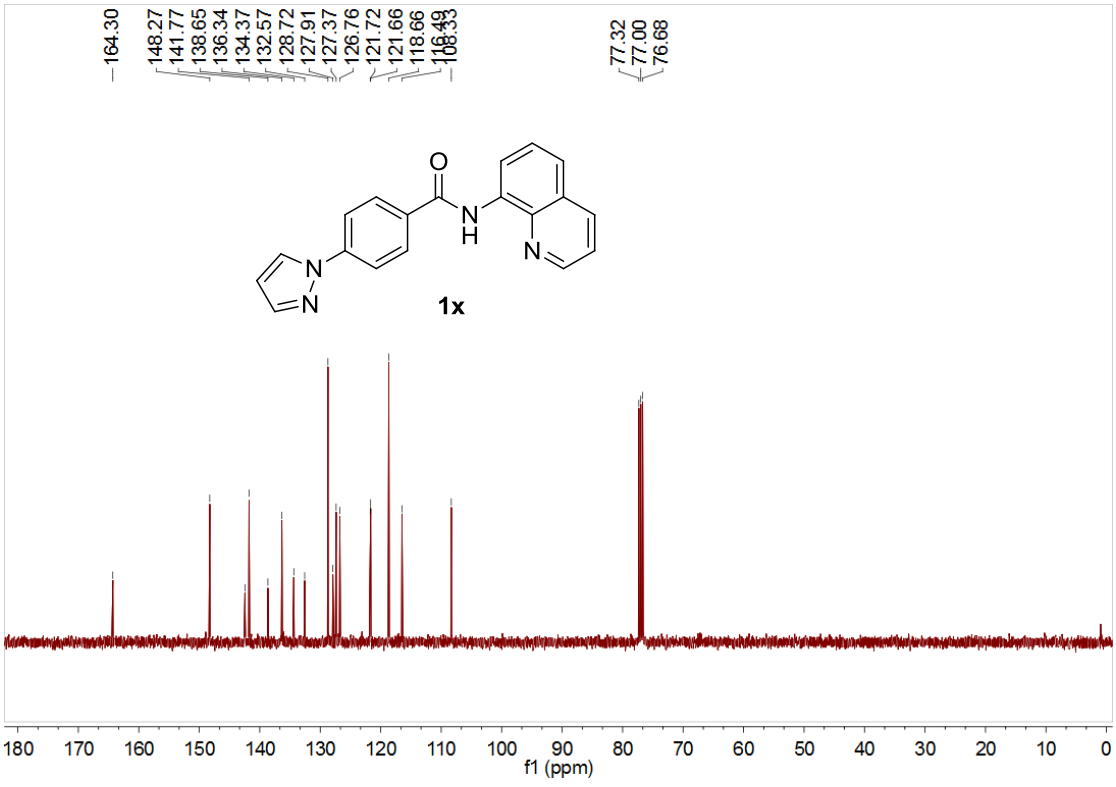
^{13}C NMR Spectrum of **1w**



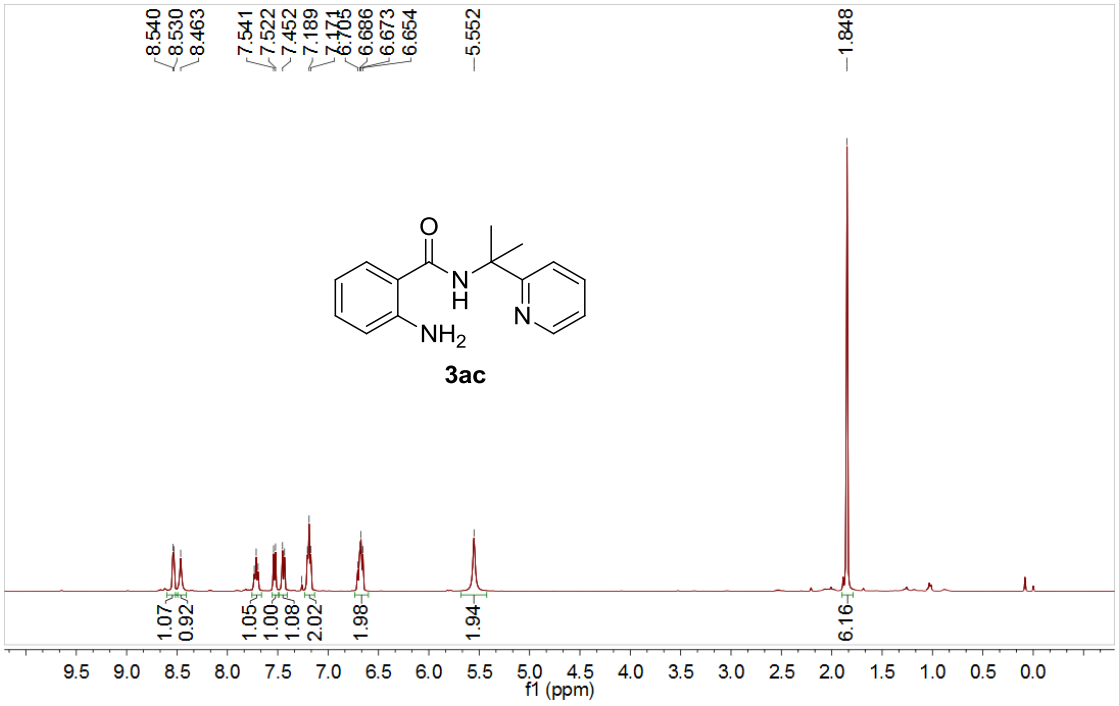
^{1}H NMR Spectrum of **1x**



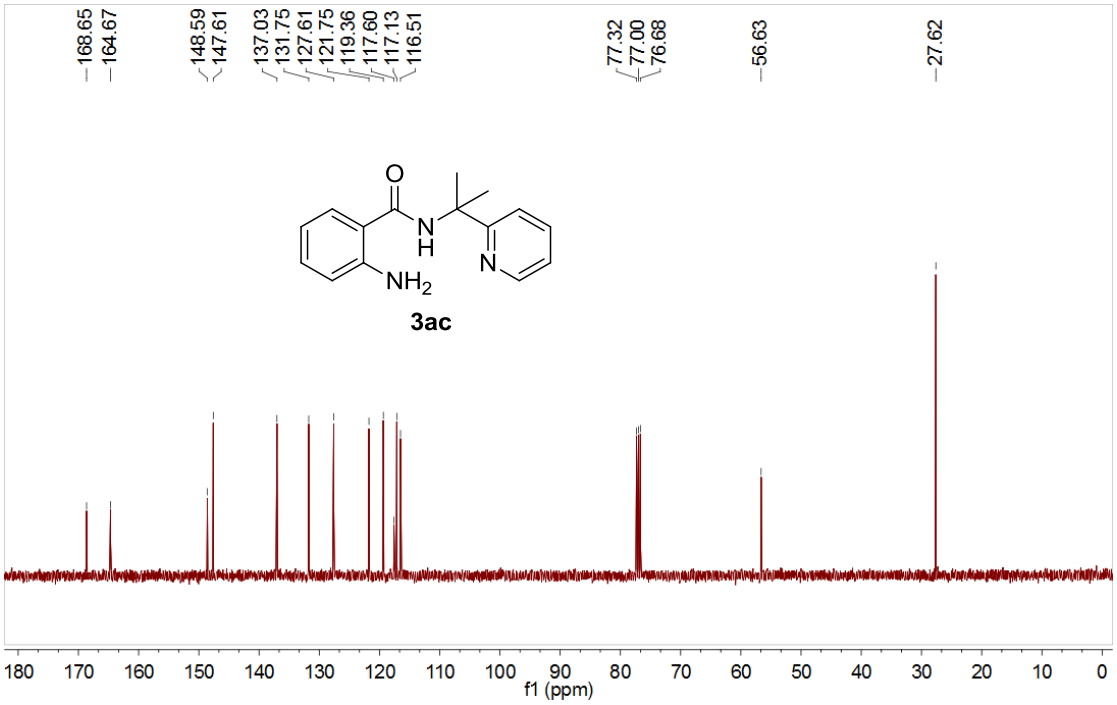
^{13}C NMR Spectrum of **1x**



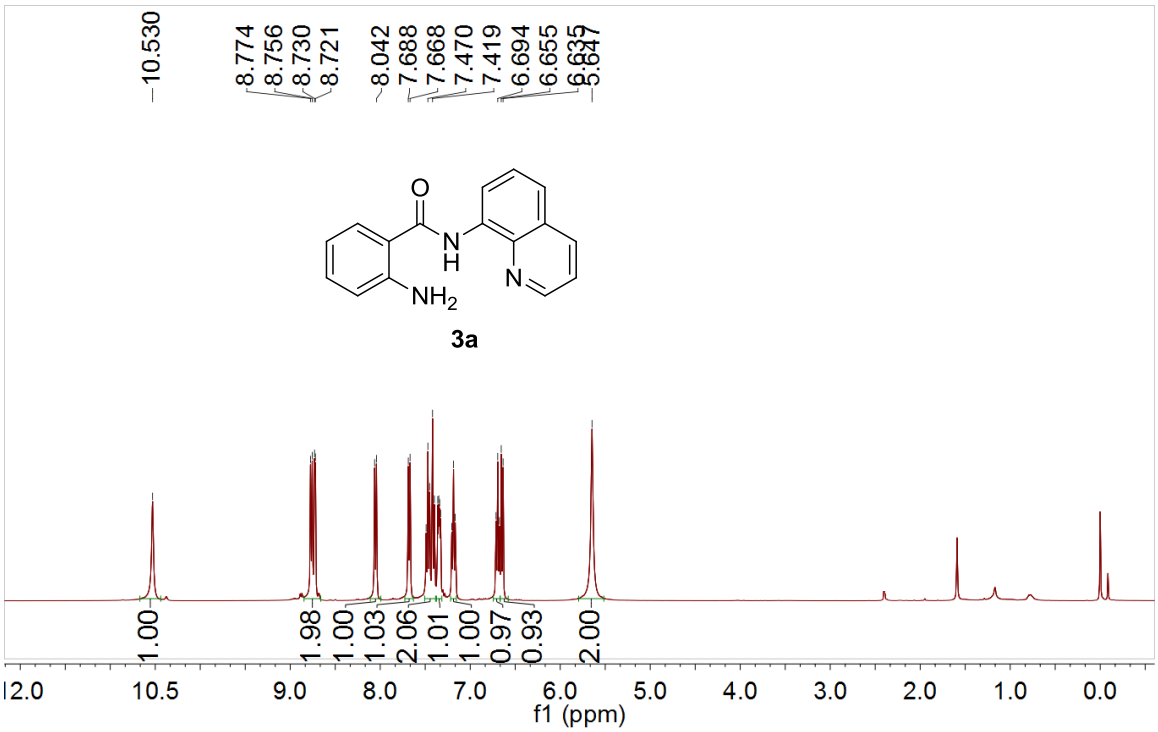
^{1}H NMR Spectrum of **3ac**



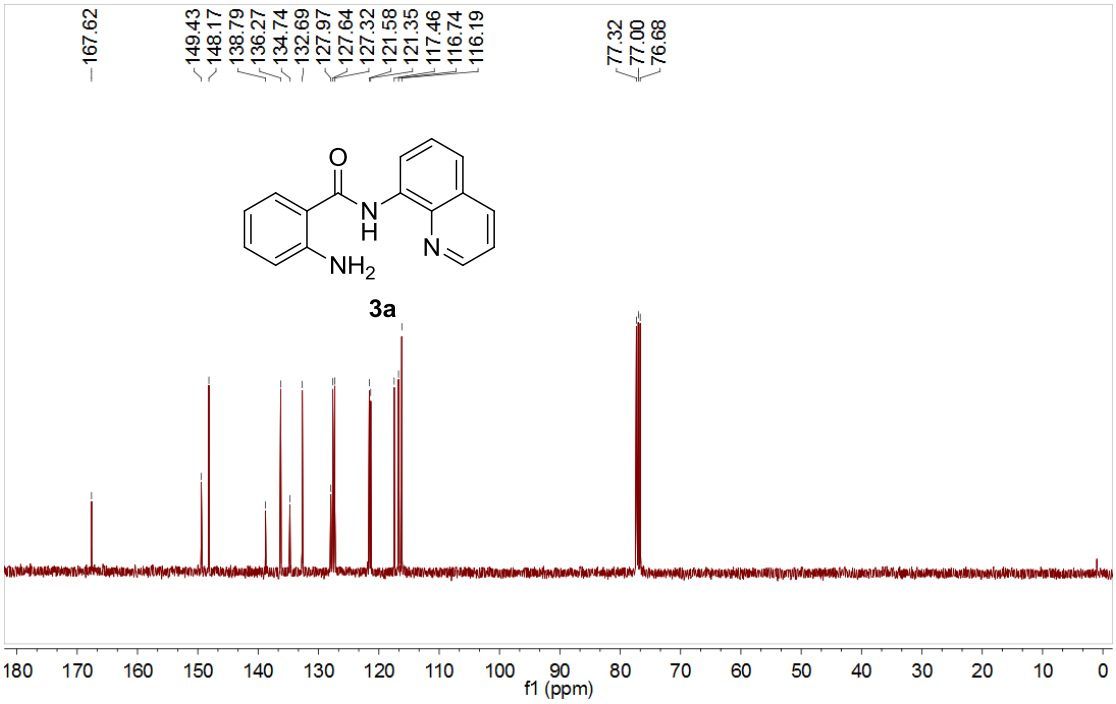
^{13}C NMR Spectrum of **3ac**



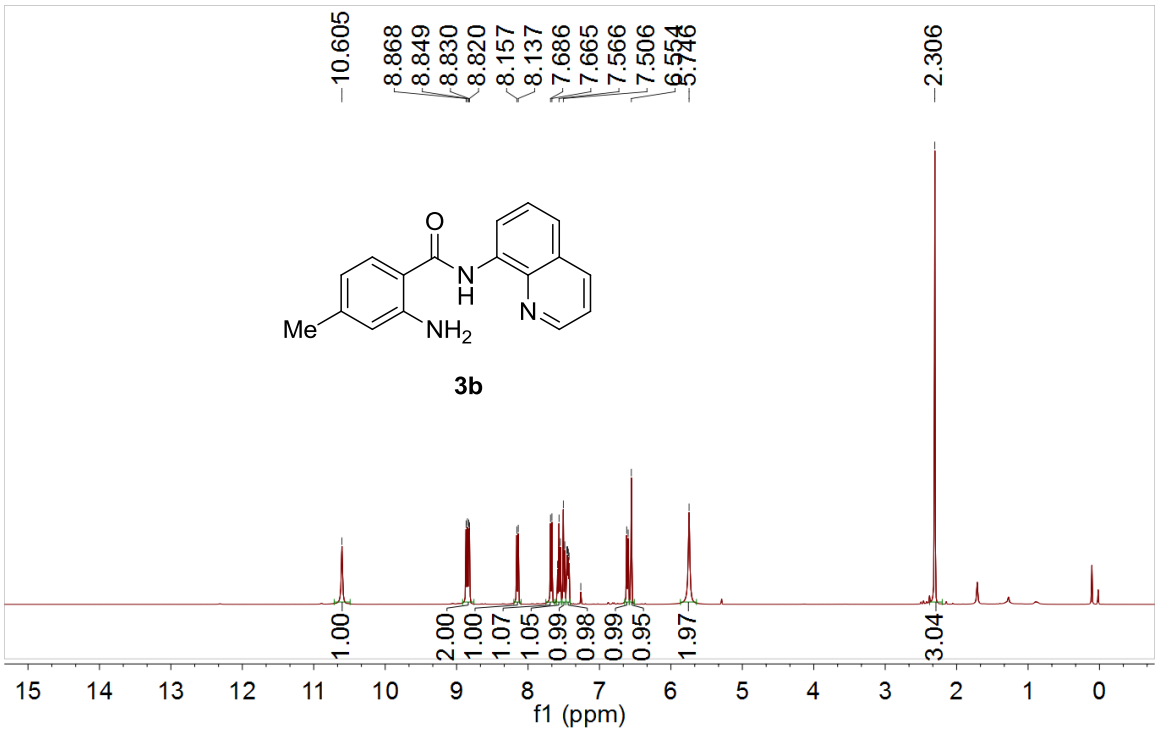
^{1}H NMR Spectrum of **3a**



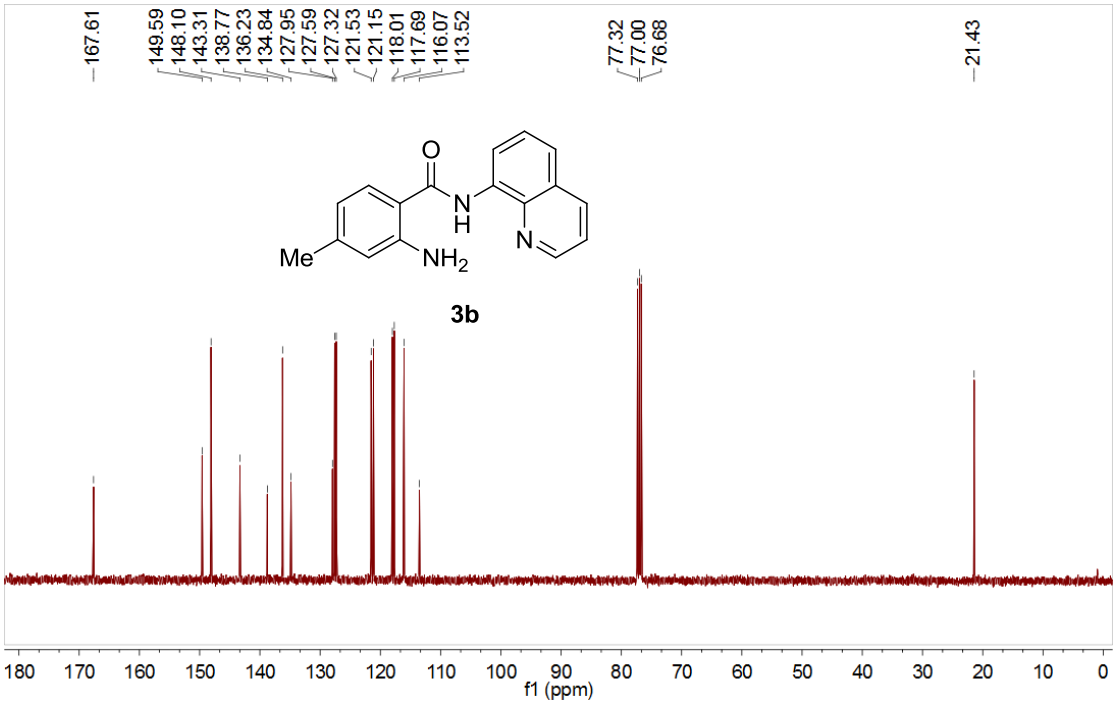
^{13}C NMR Spectrum of **3a**



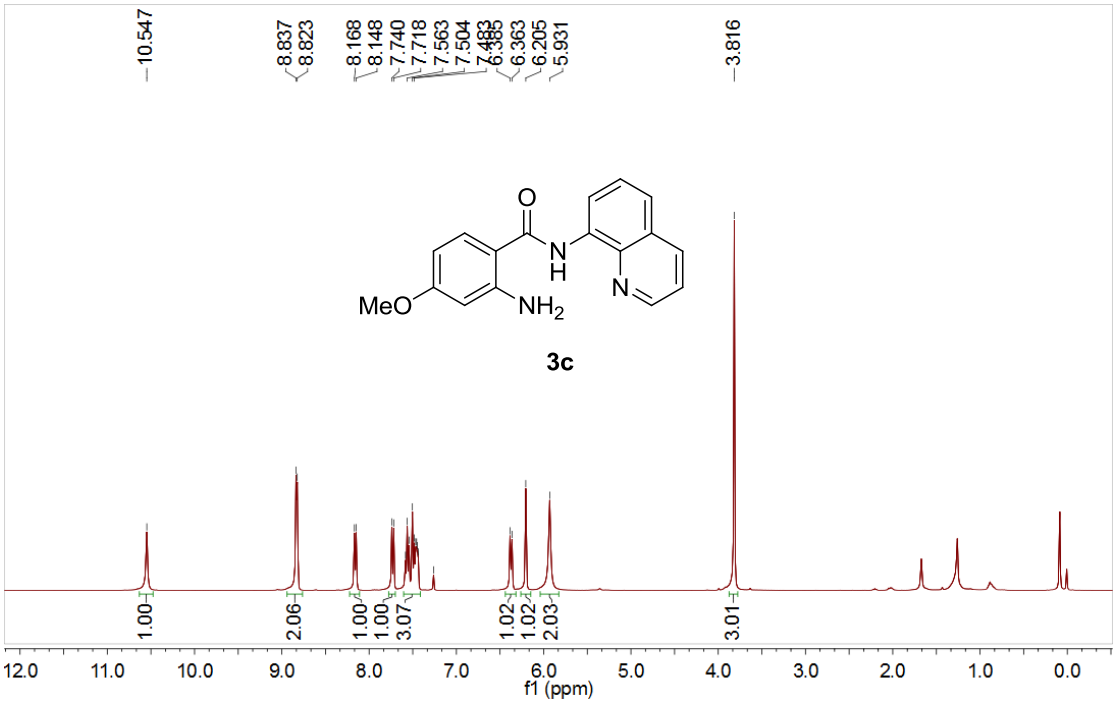
^{1}H NMR Spectrum of **3b**



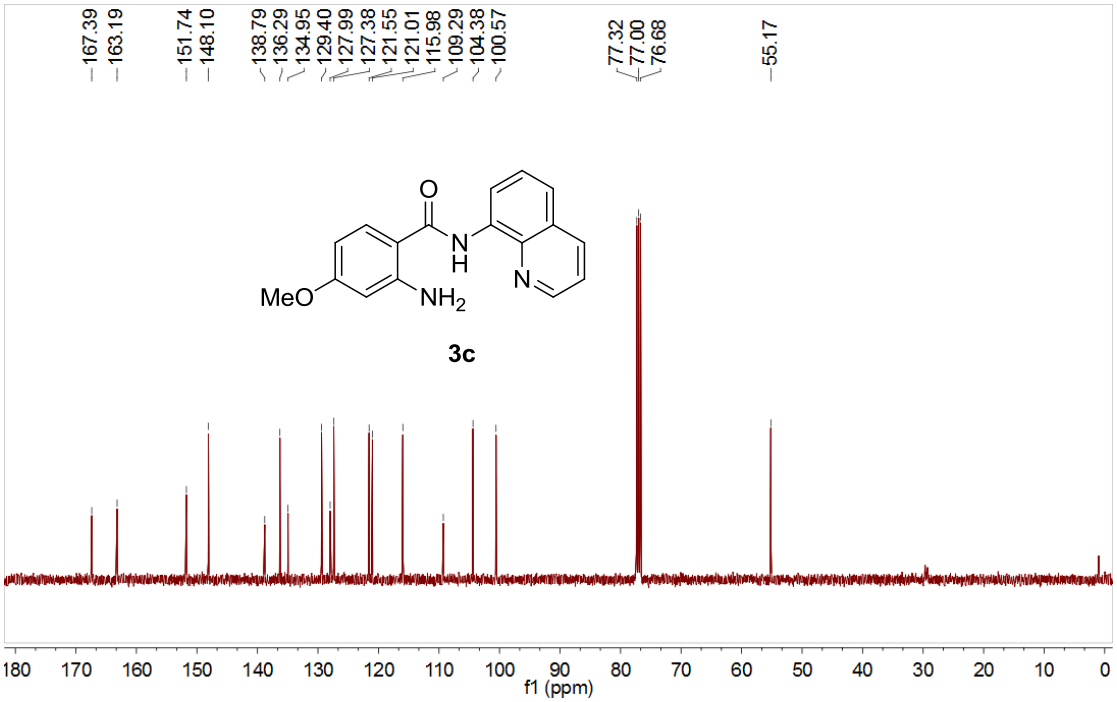
^{13}C NMR Spectrum of **3b**



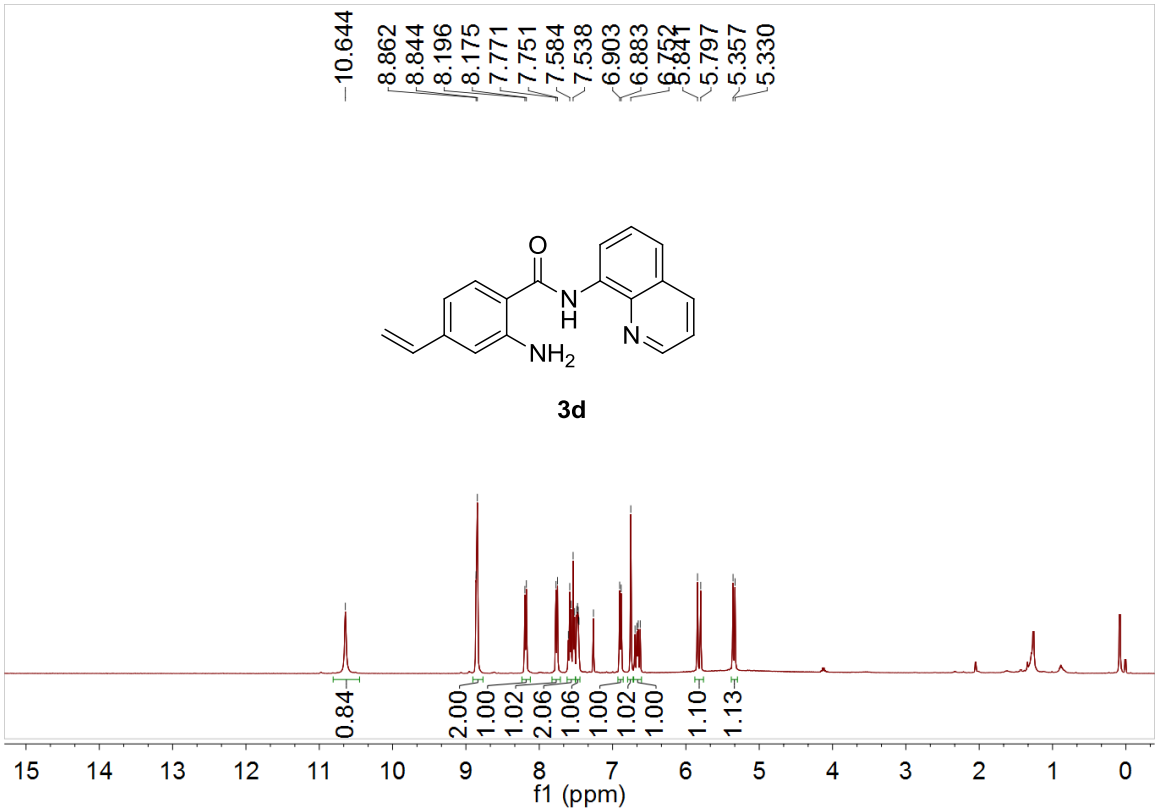
^{1}H NMR Spectrum of **3c**



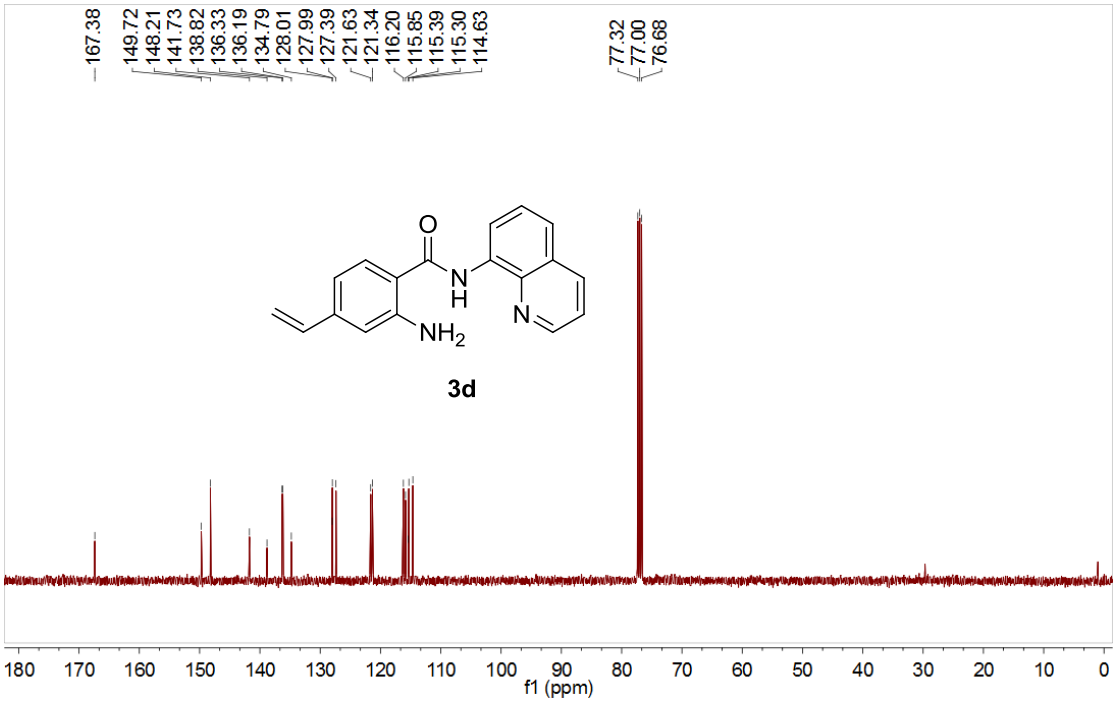
^{13}C NMR Spectrum of **3c**



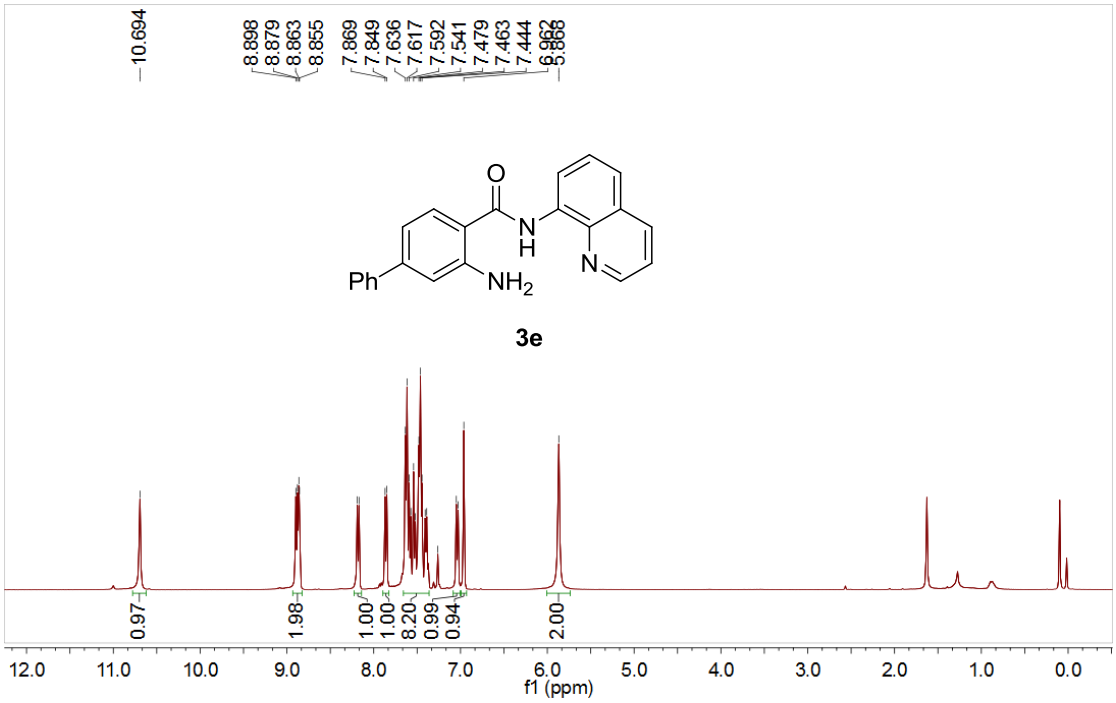
^{1}H NMR Spectrum of **3d**



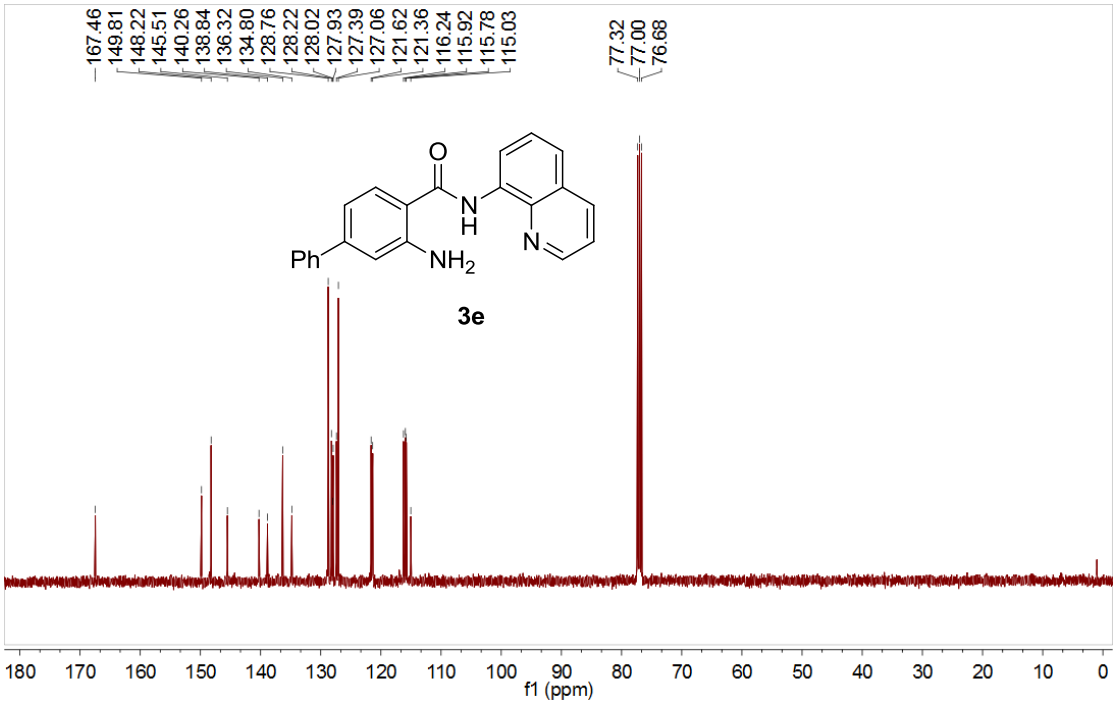
^{13}C NMR Spectrum of **3d**



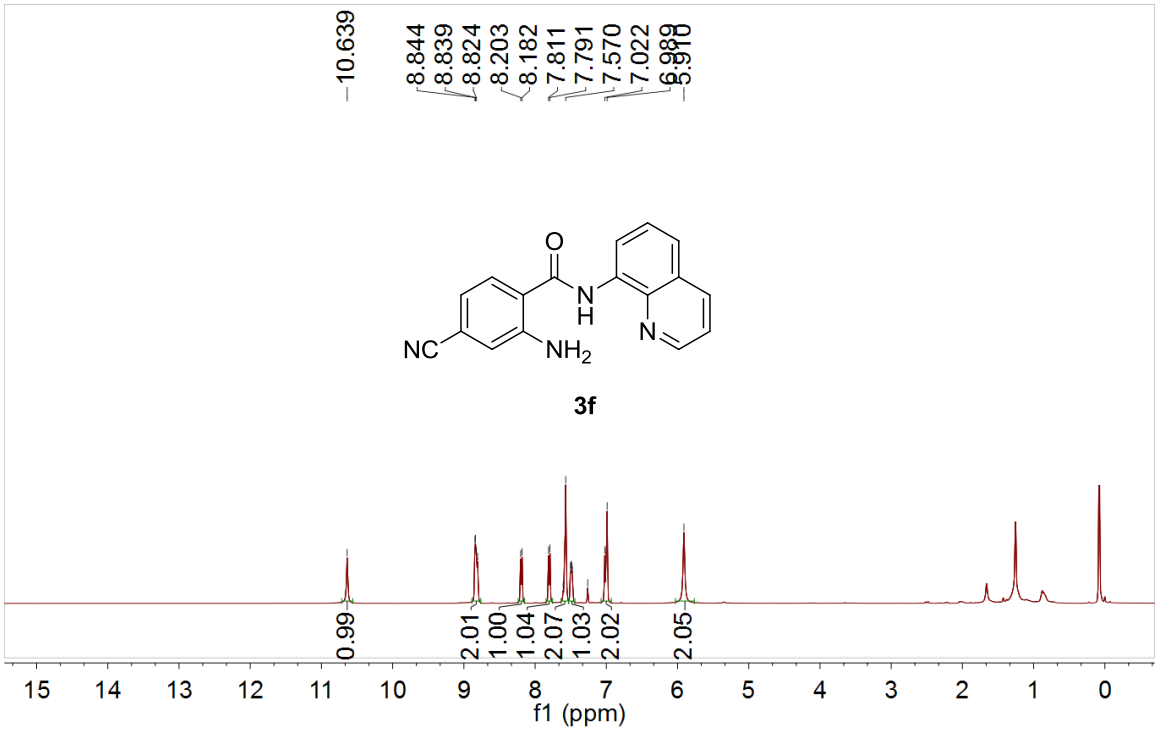
^{1}H NMR Spectrum of **3e**



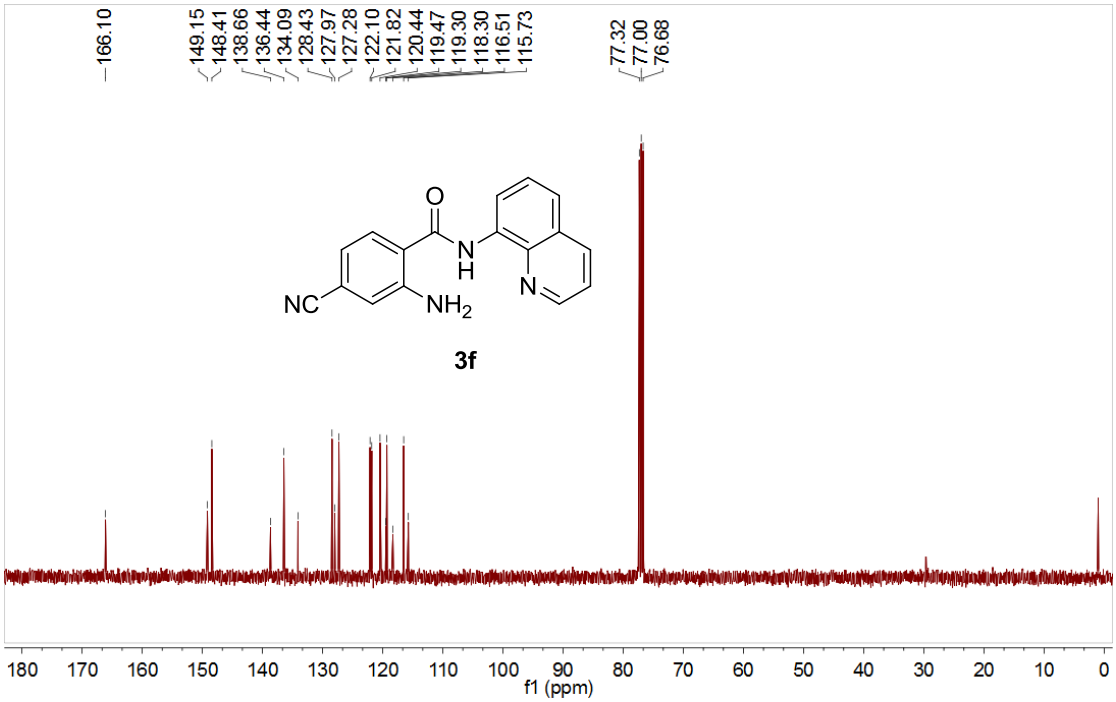
^{13}C NMR Spectrum of **3e**



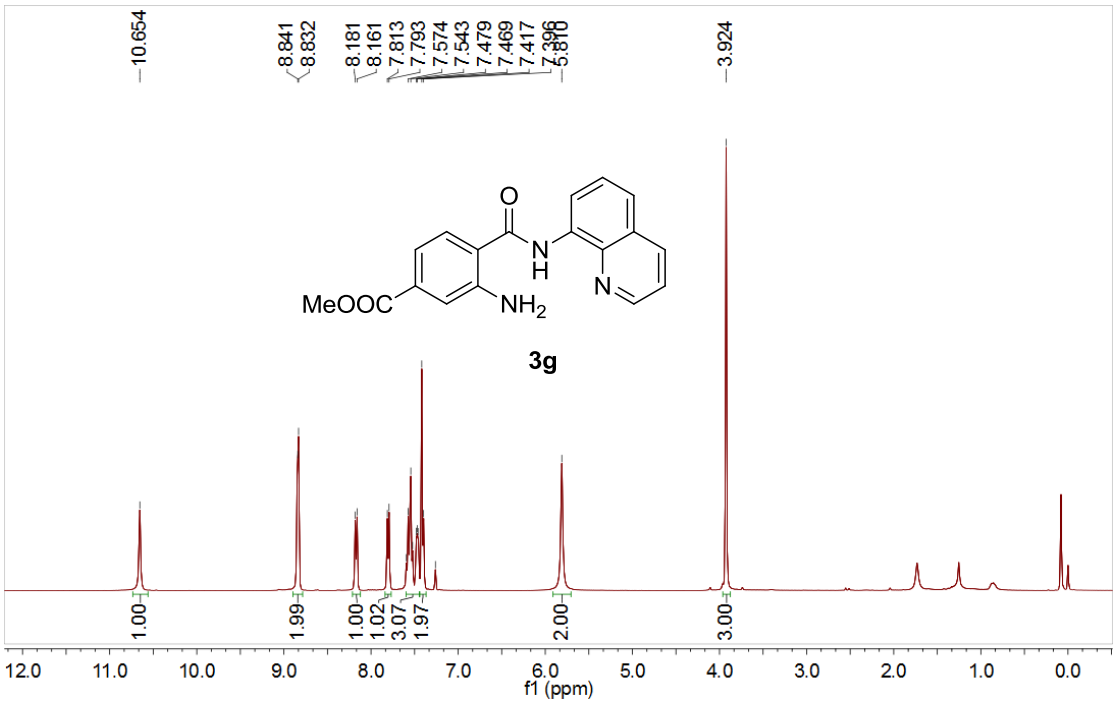
^{1}H NMR Spectrum of **3f**



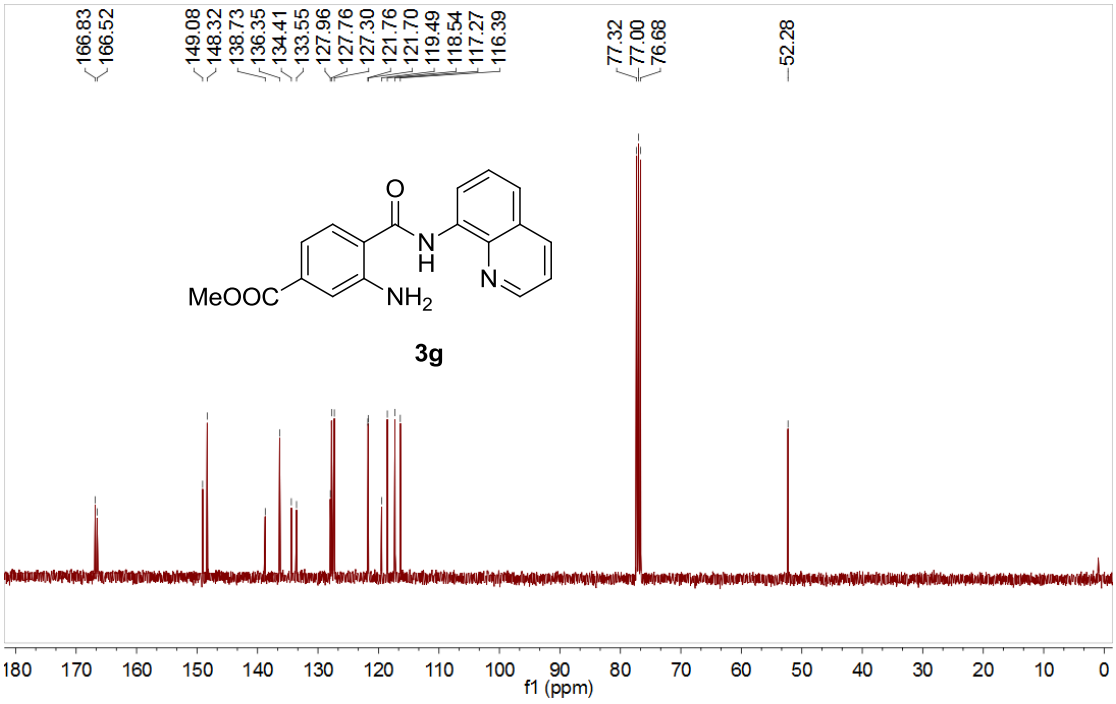
^{13}C NMR Spectrum of **3f**



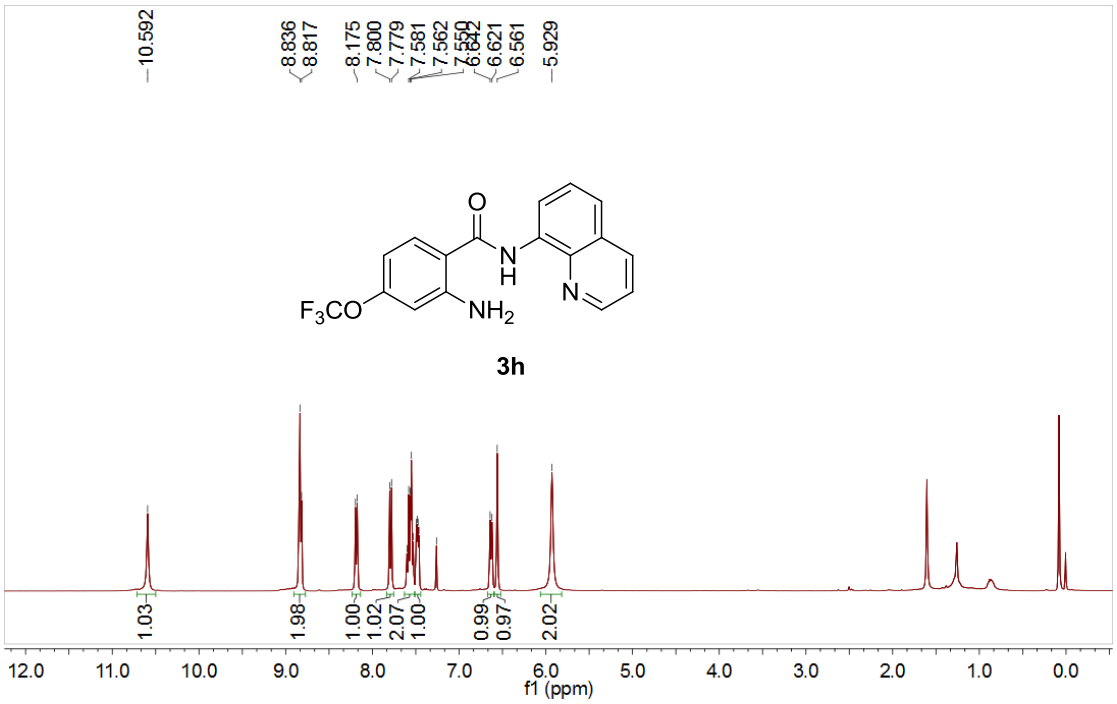
^{1}H NMR Spectrum of **3g**



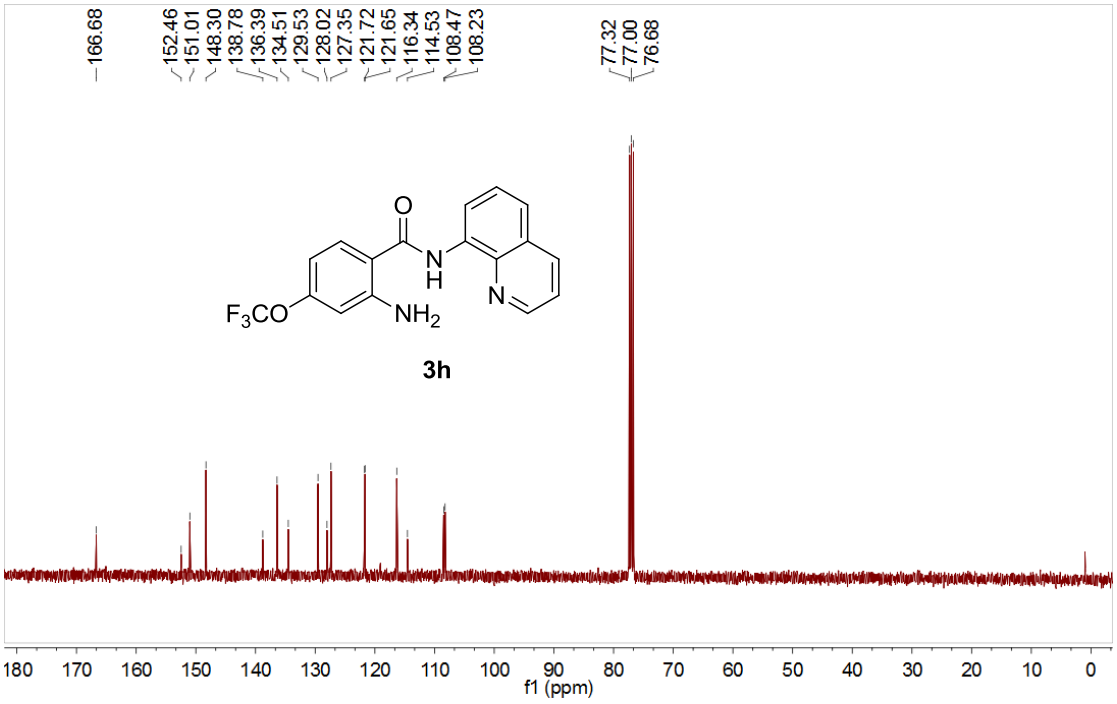
^{13}C NMR Spectrum of **3g**



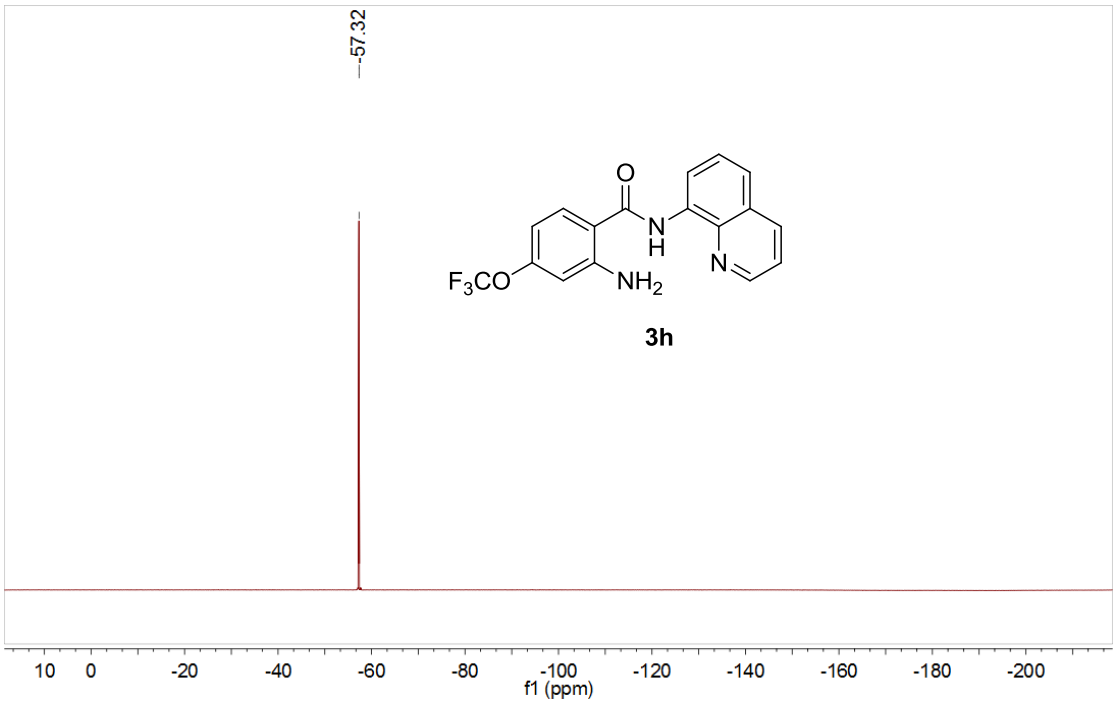
^{1}H NMR Spectrum of **3h**



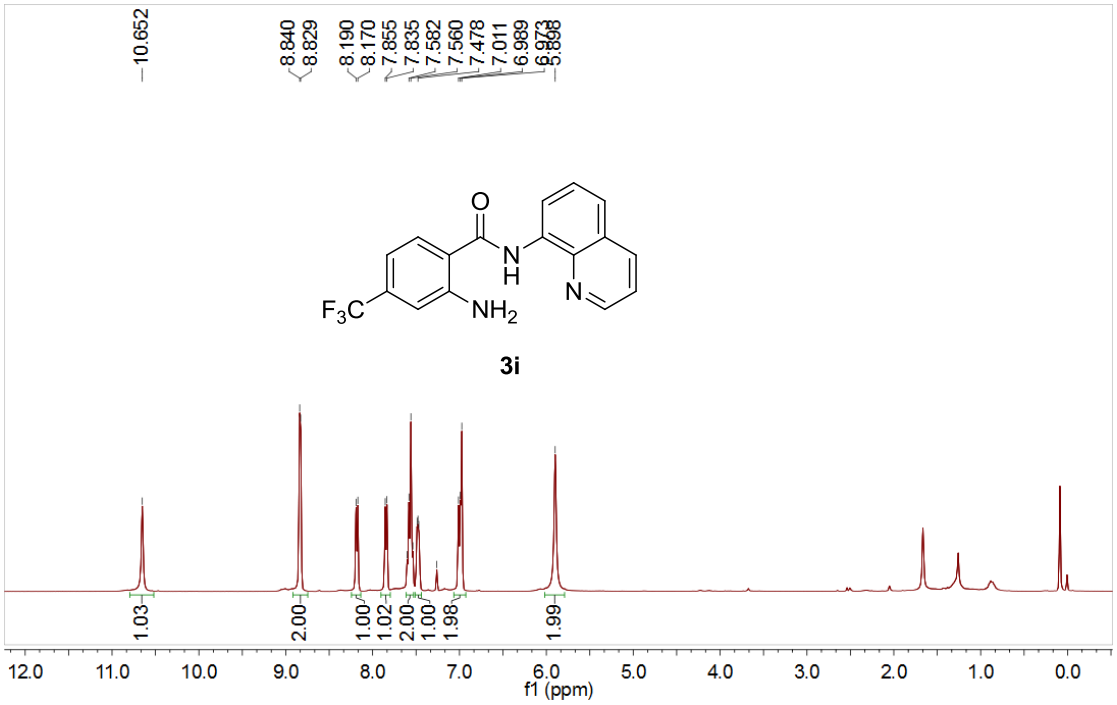
^{13}C NMR Spectrum of **3h**



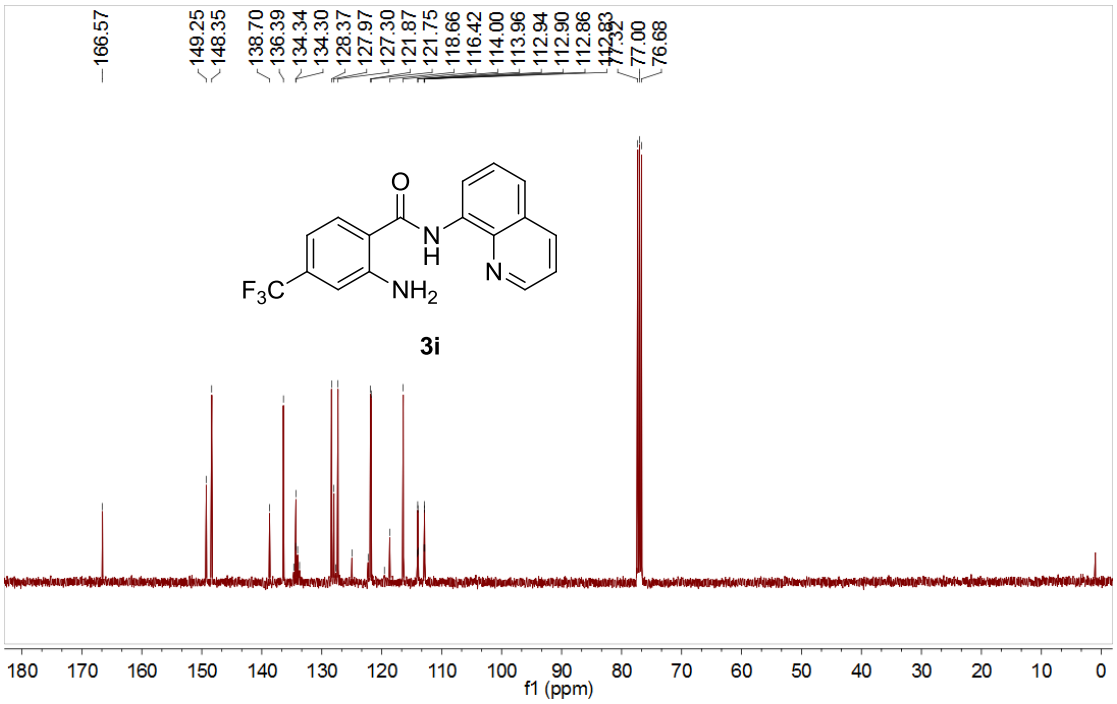
^{19}F NMR Spectrum of **3h**



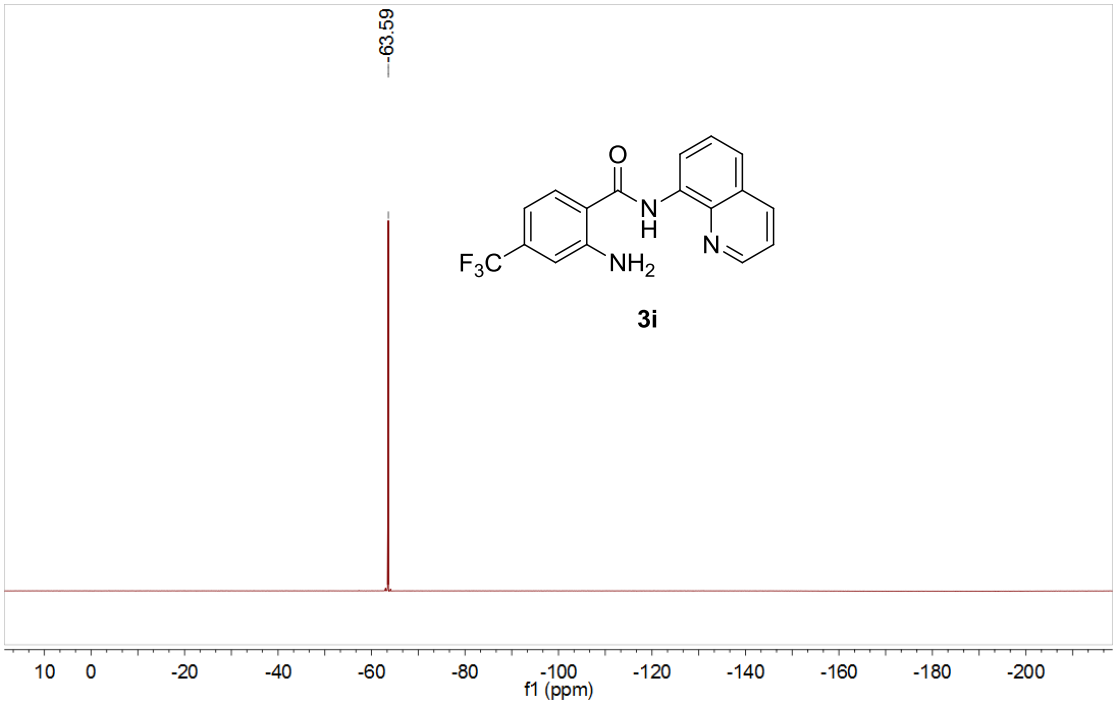
^{1}H NMR Spectrum of **3i**



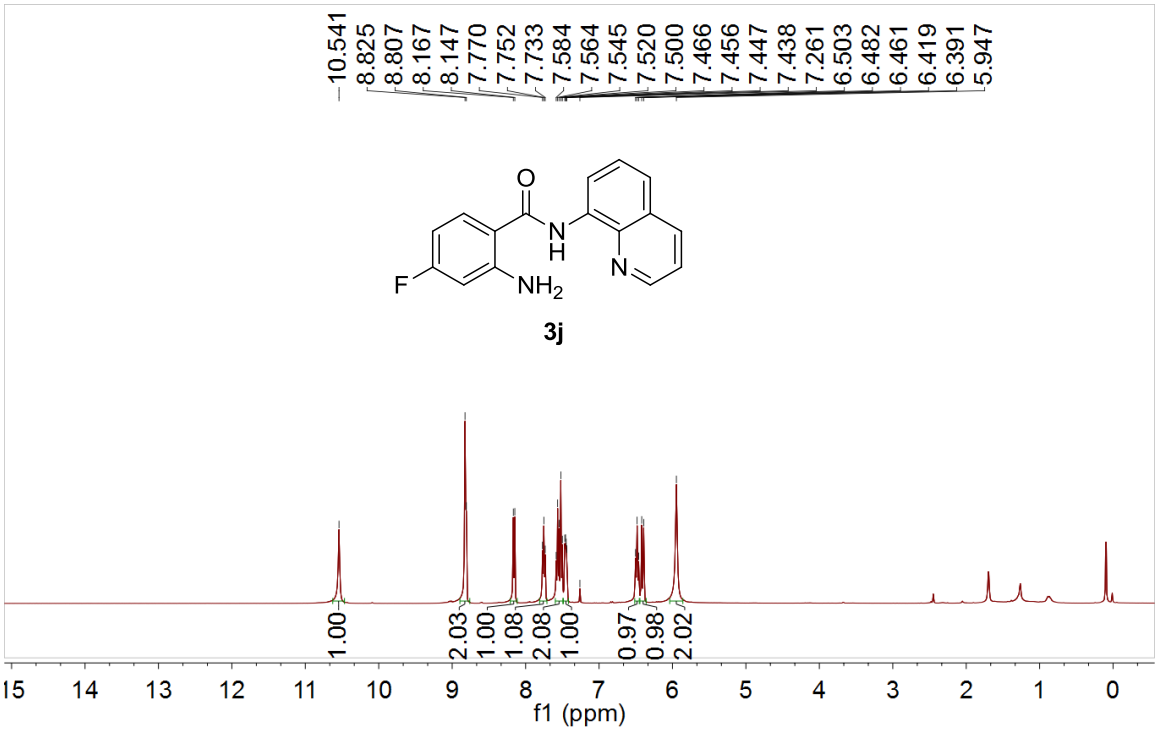
^{13}C NMR Spectrum of **3i**



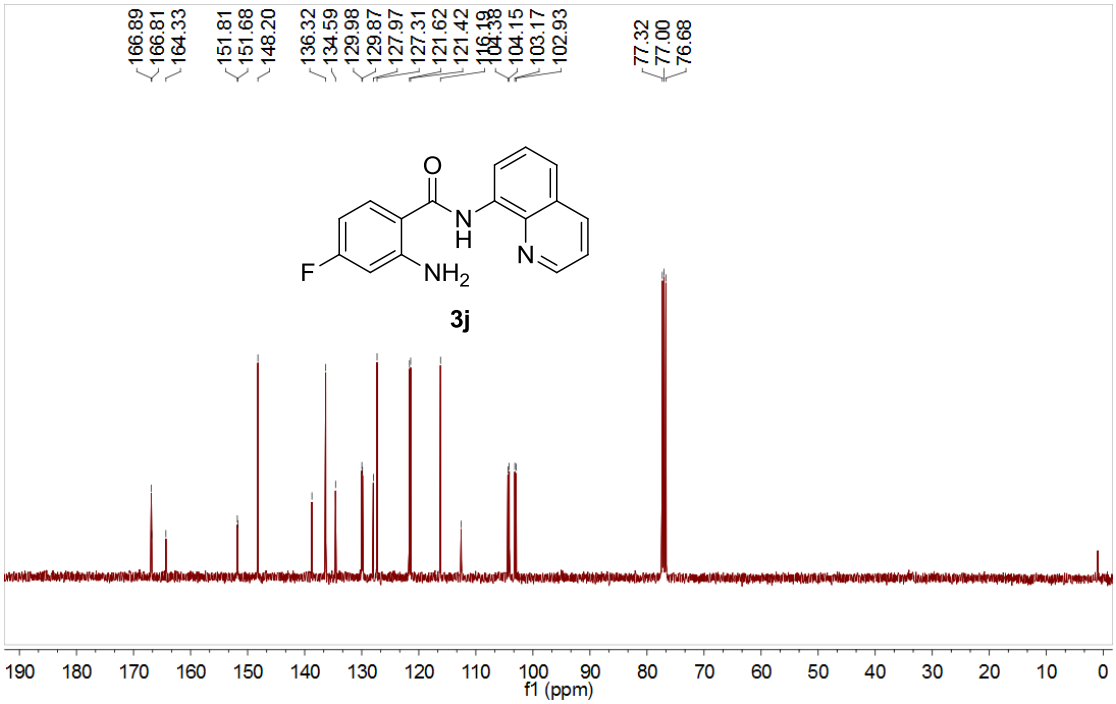
^{19}F NMR Spectrum of **3i**



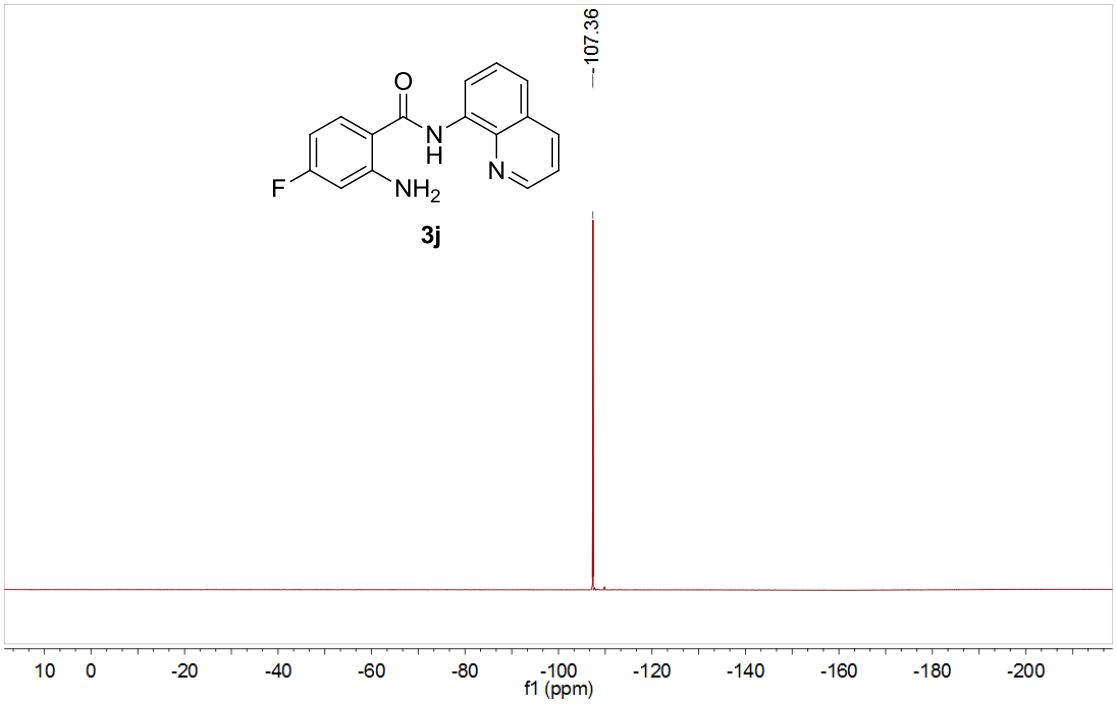
^{1}H NMR Spectrum of **3j**



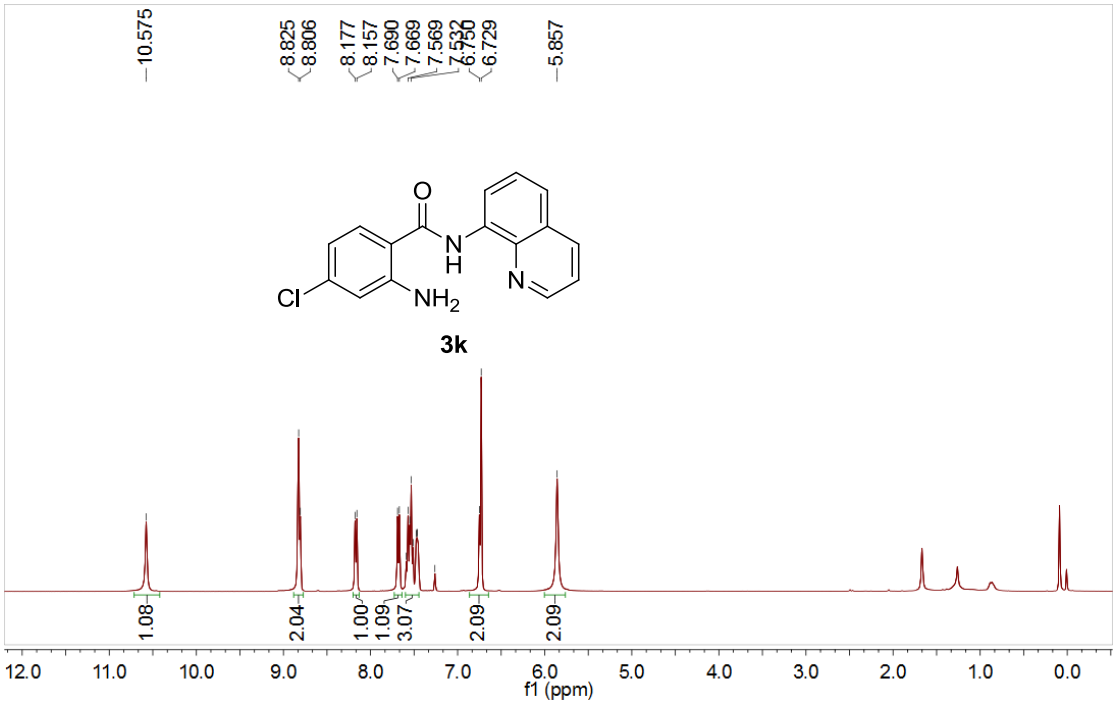
^{13}C NMR Spectrum of **3j**



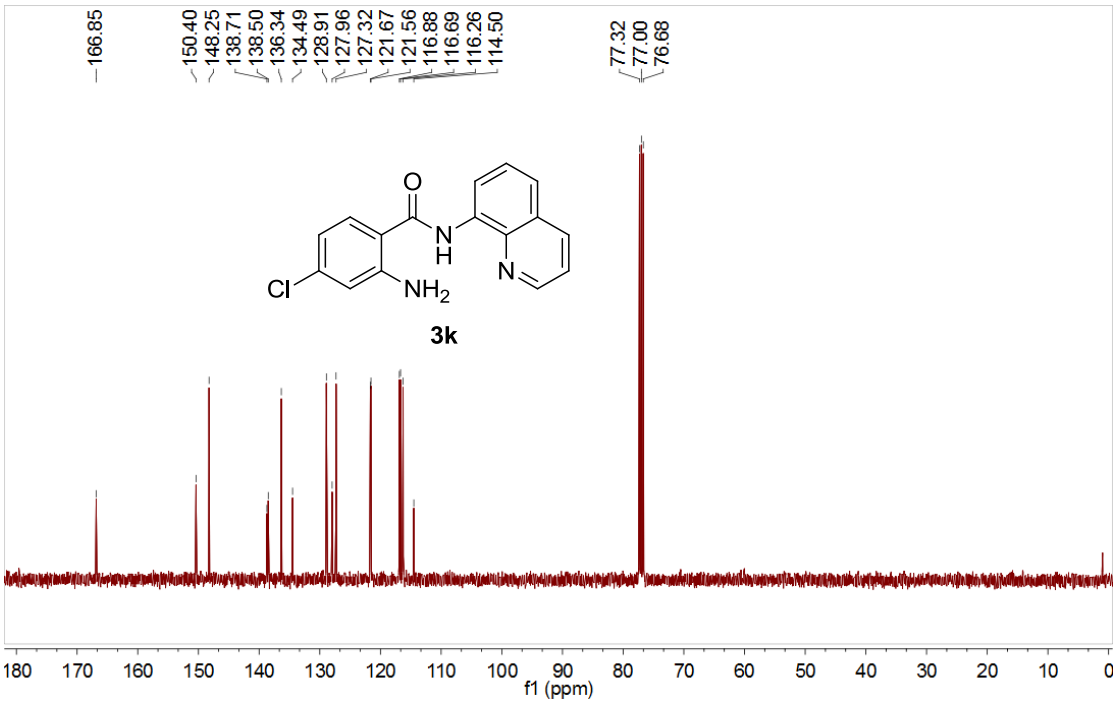
^{19}F NMR Spectrum of **3j**



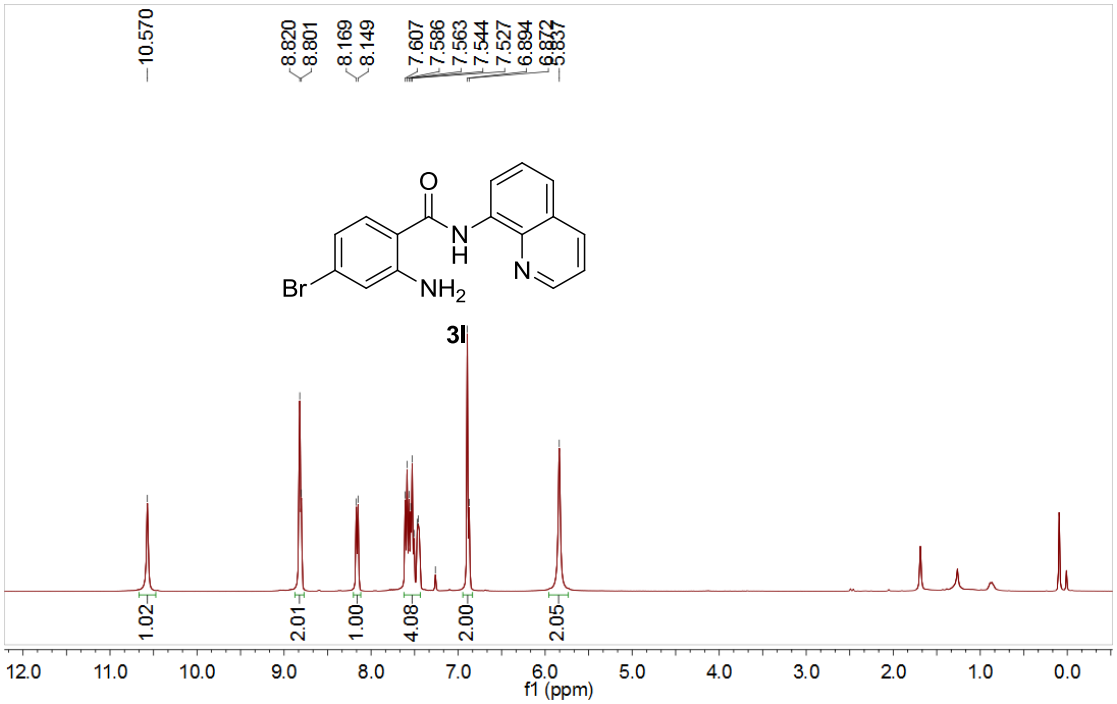
^{1}H NMR Spectrum of **3k**



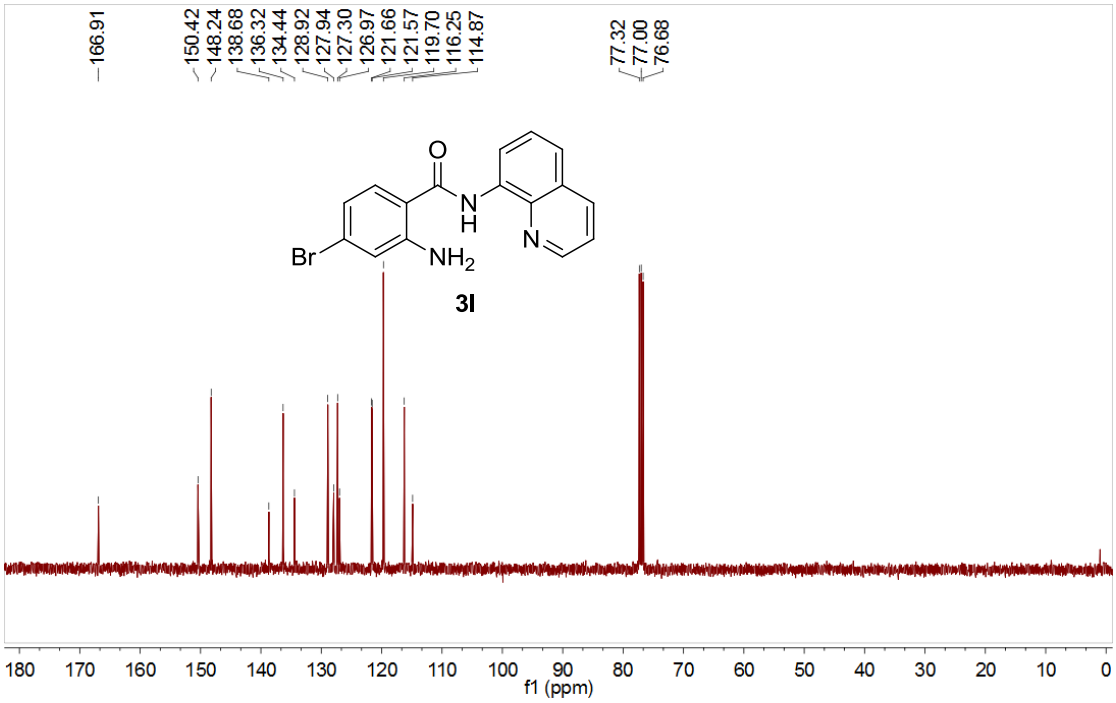
^{13}C NMR Spectrum of **3k**



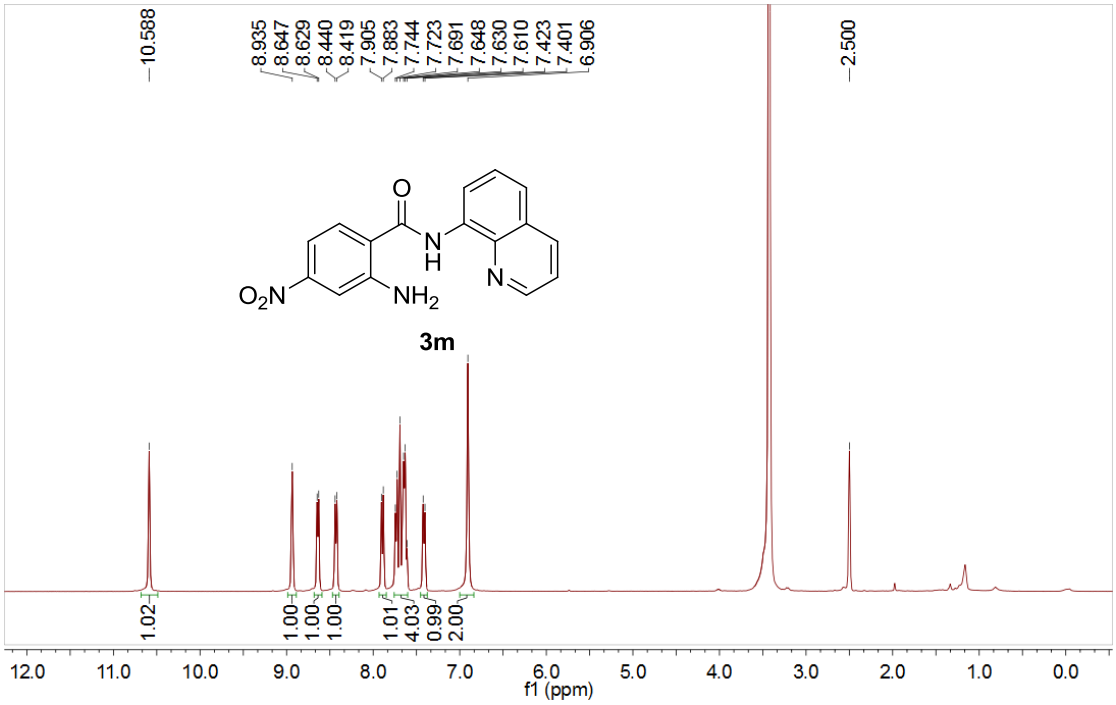
^{1}H NMR Spectrum of **3l**



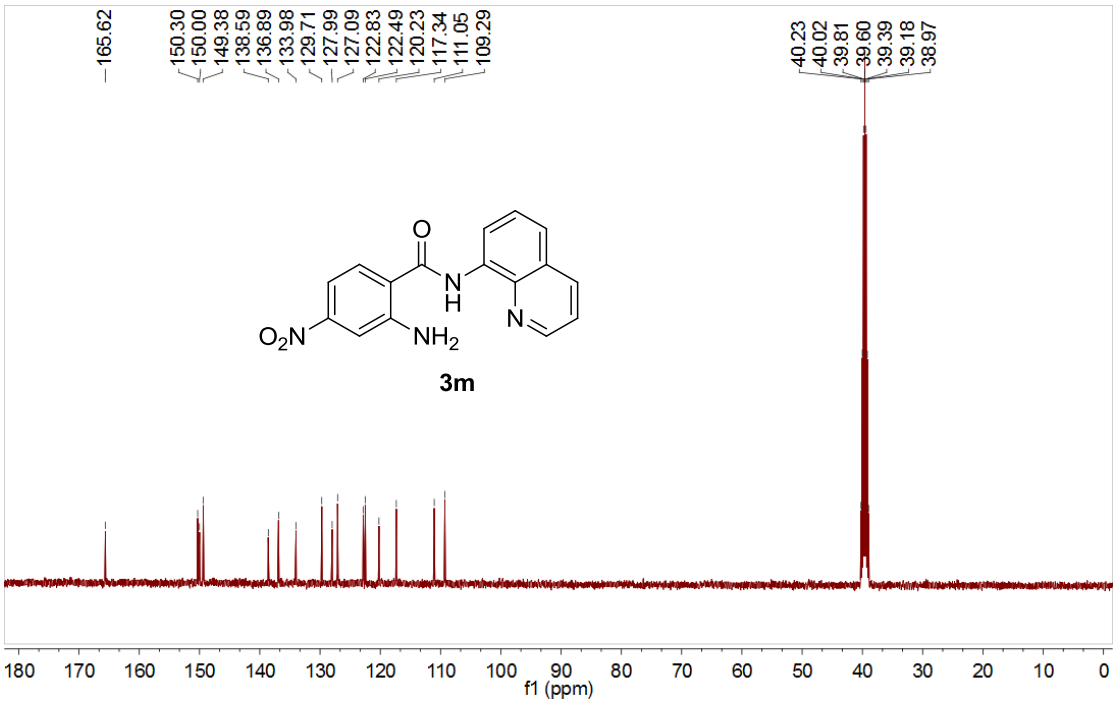
^{13}C NMR Spectrum of **3l**



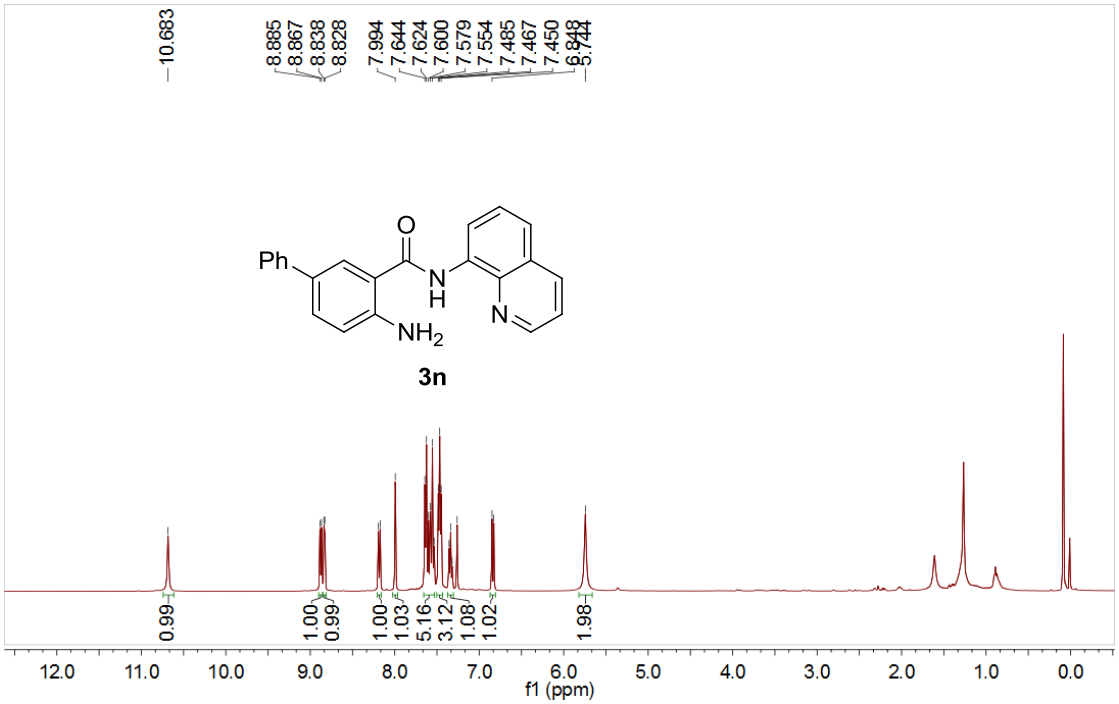
^{1}H NMR Spectrum of **3m**



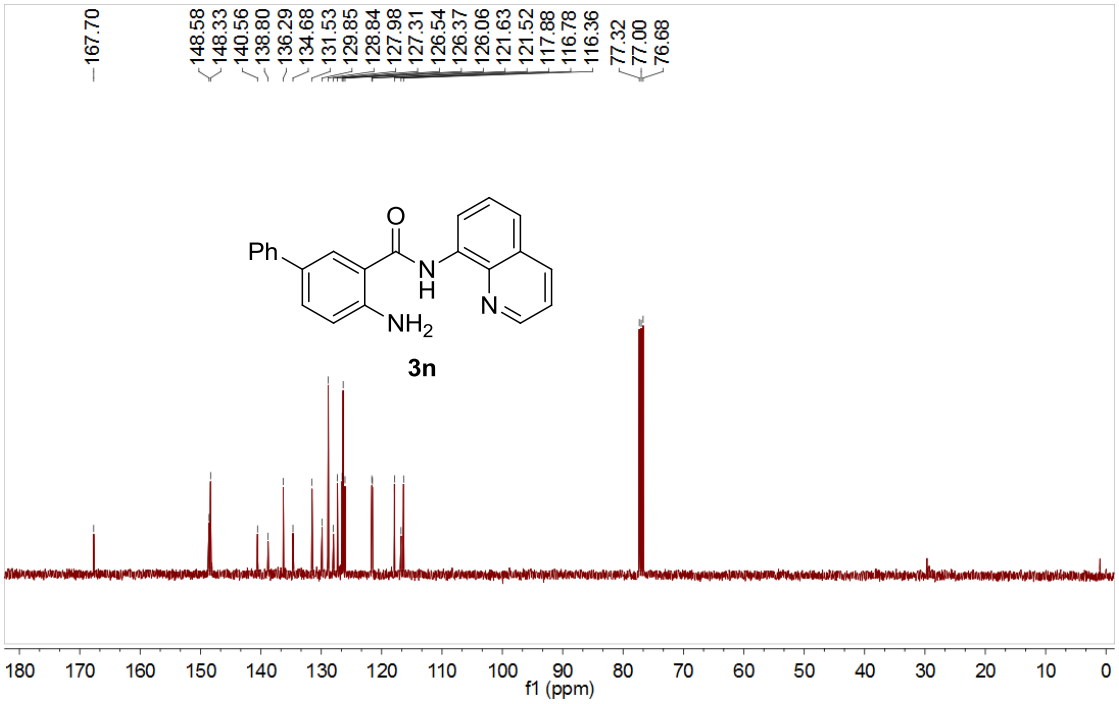
^{13}C NMR Spectrum of **3m**



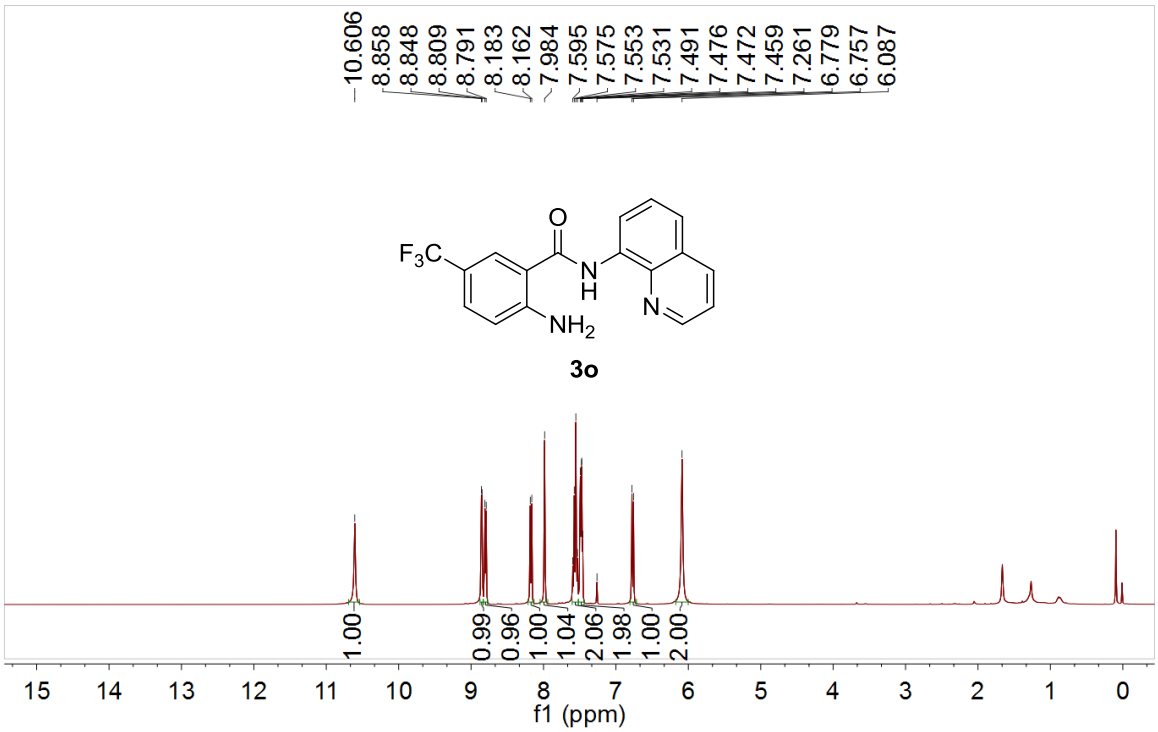
^{1}H NMR Spectrum of **3n**



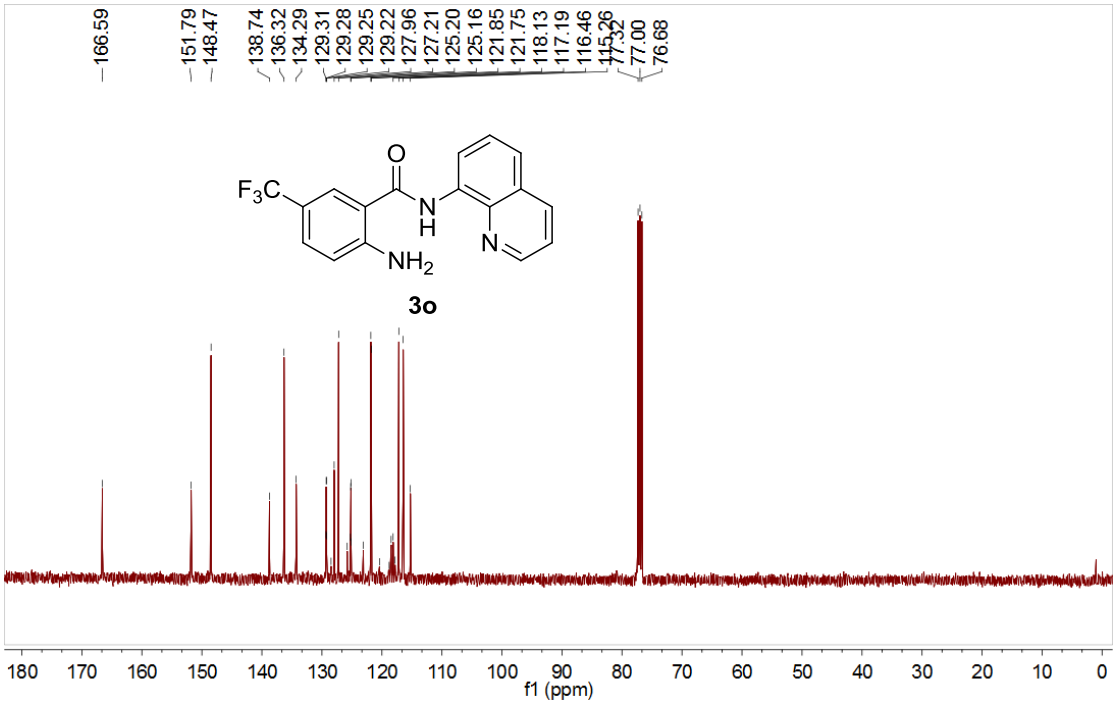
^{13}C NMR Spectrum of **3n**



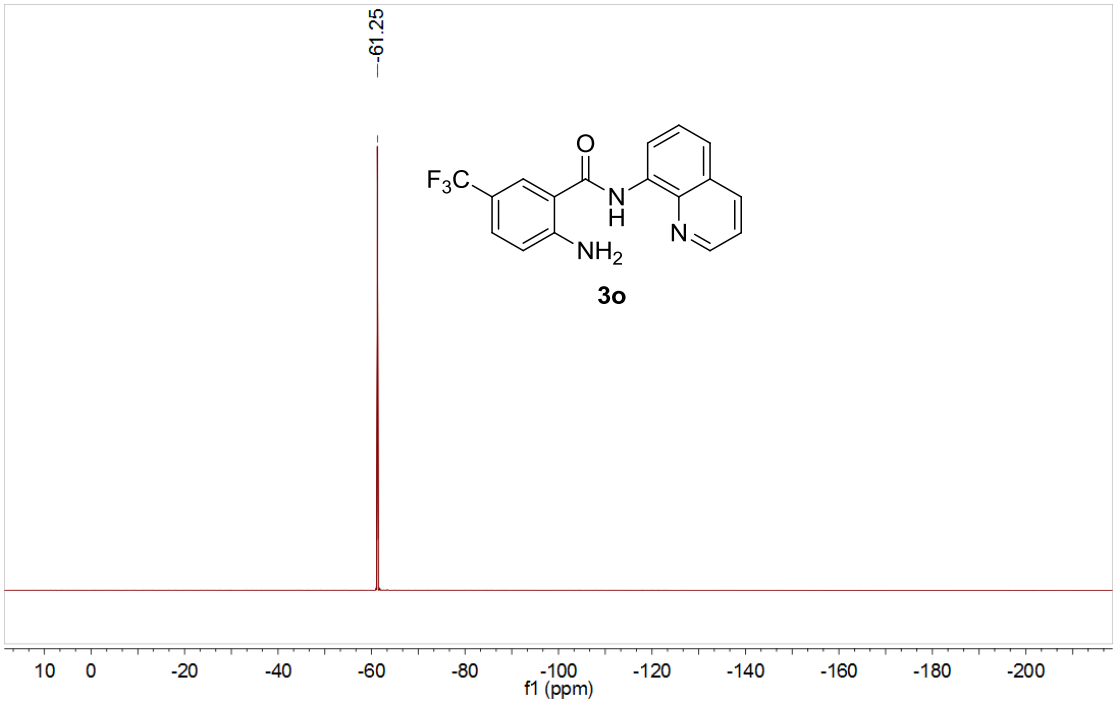
^{1}H NMR Spectrum of **3o**



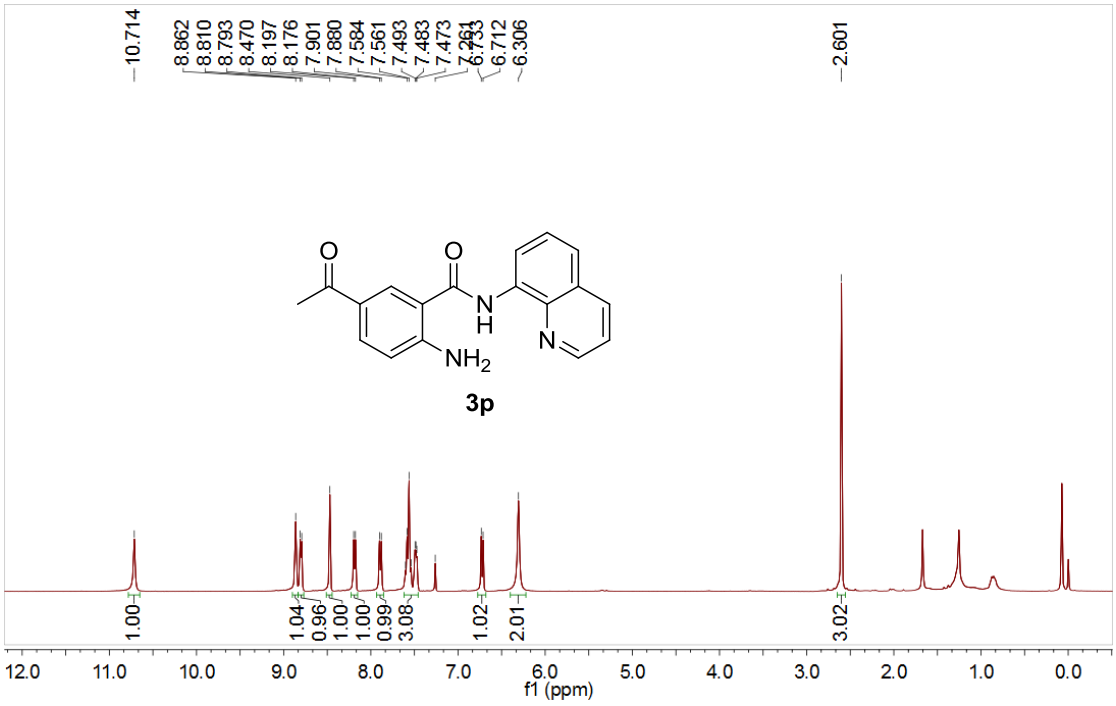
^{13}C NMR Spectrum of **3o**



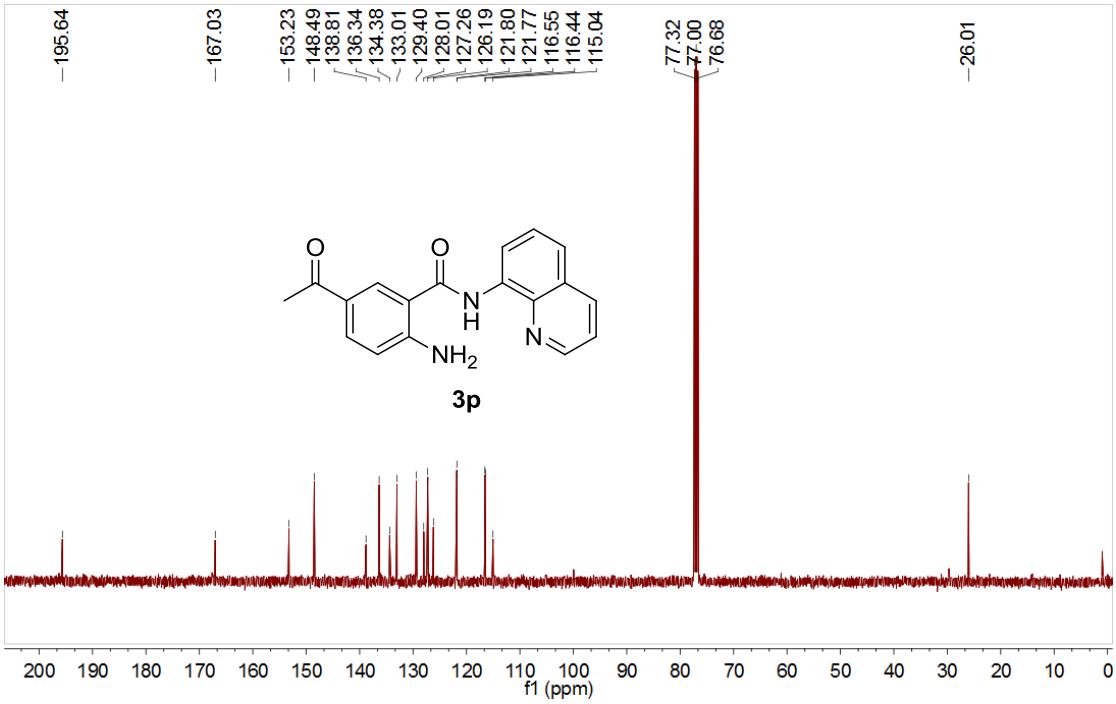
^{19}F NMR Spectrum of **3o**



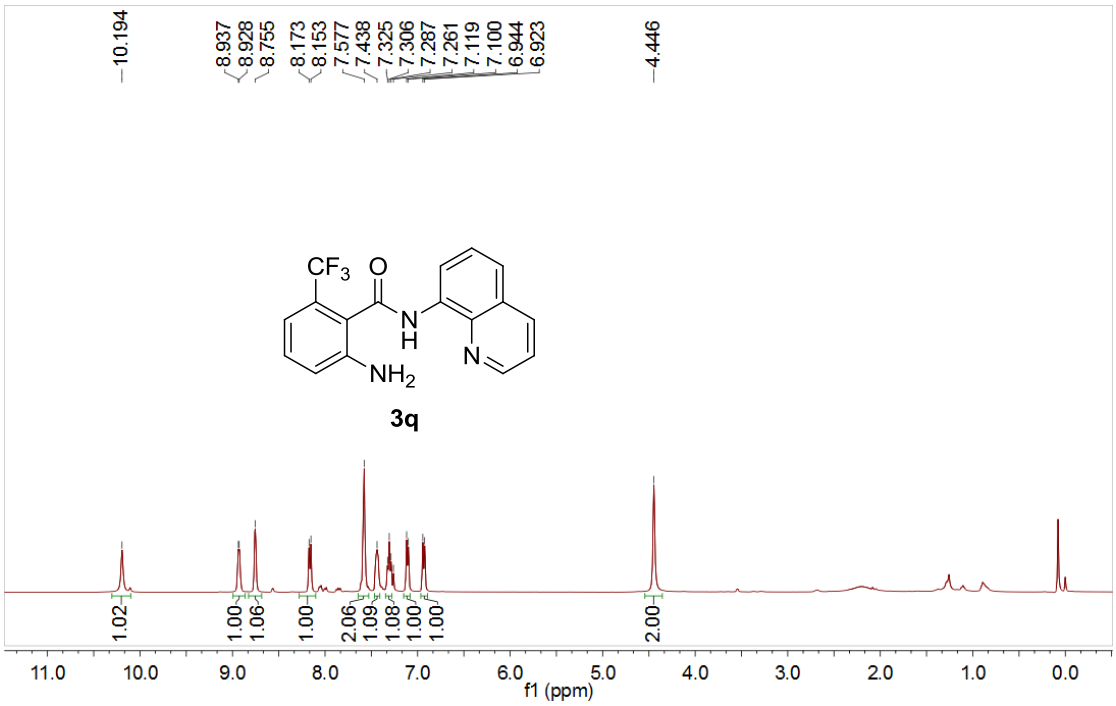
^{1}H NMR Spectrum of **3p**



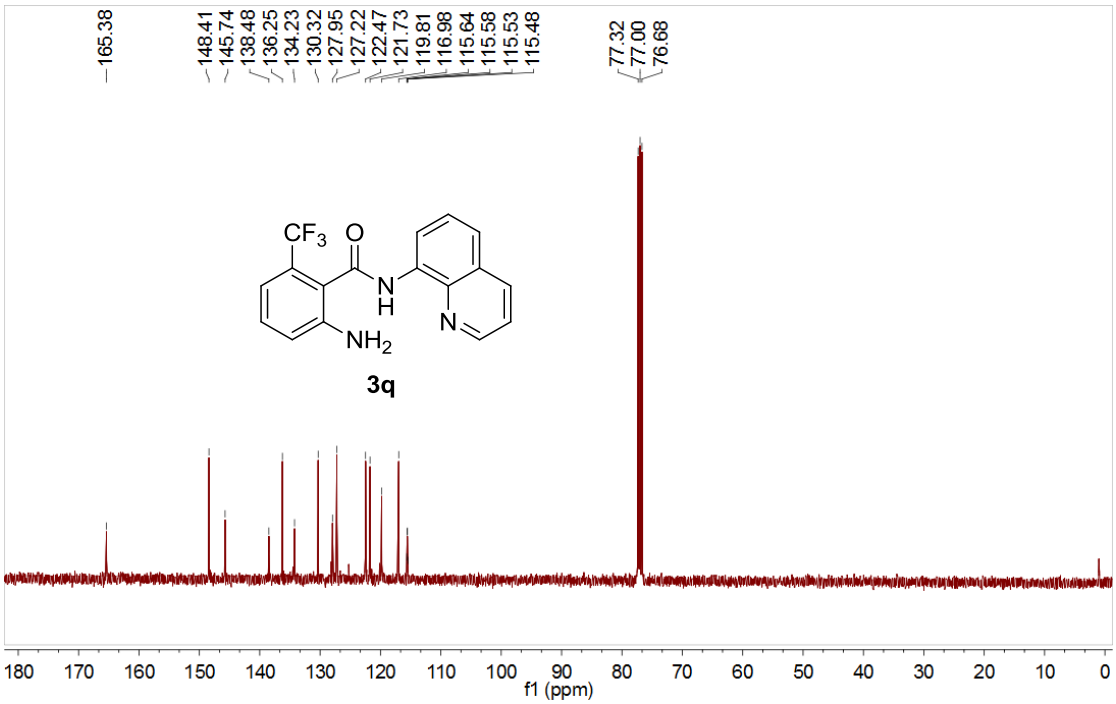
^{13}C NMR Spectrum of **3p**



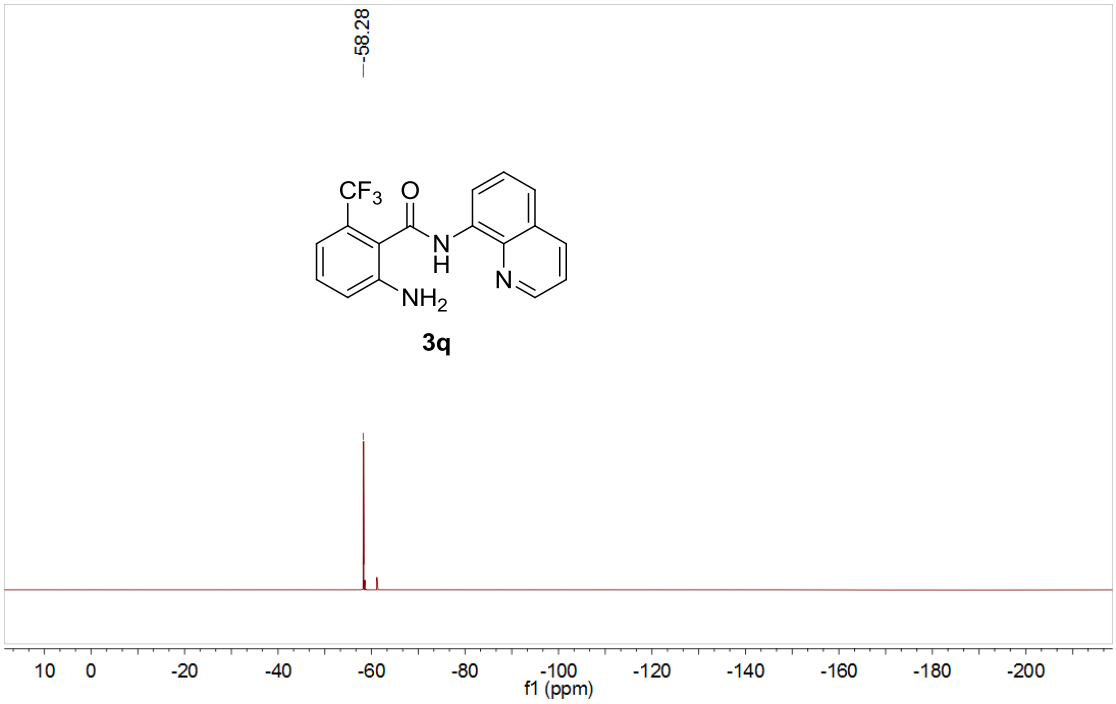
^{1}H NMR Spectrum of **3q**



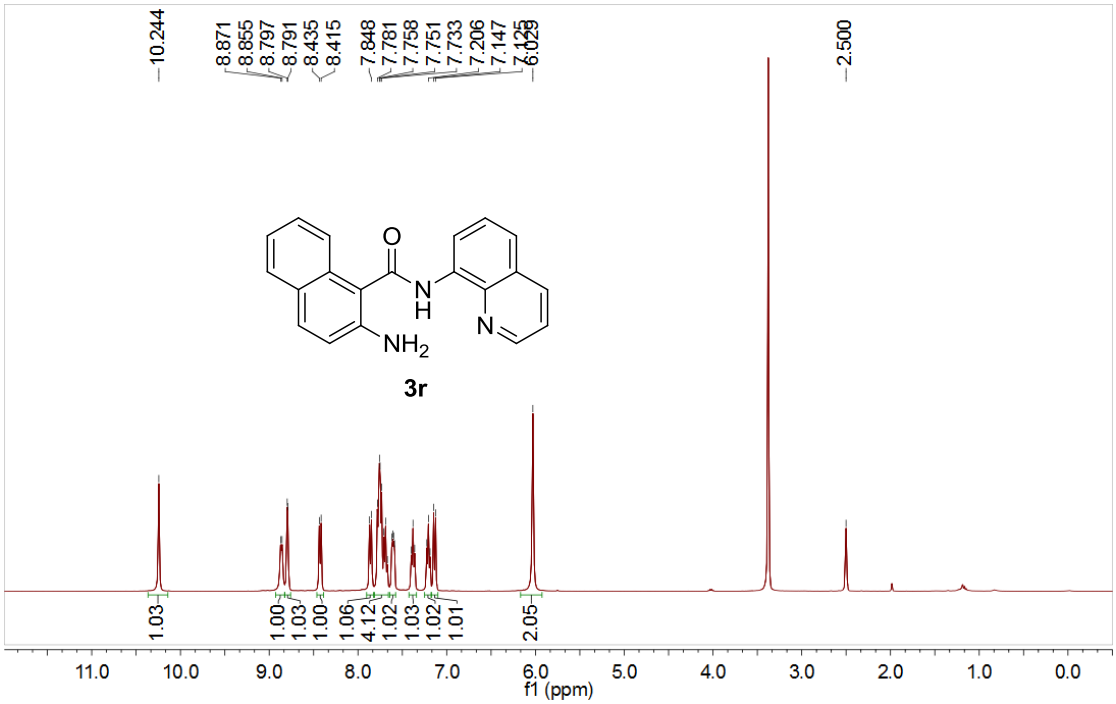
^{13}C NMR Spectrum of **3q**



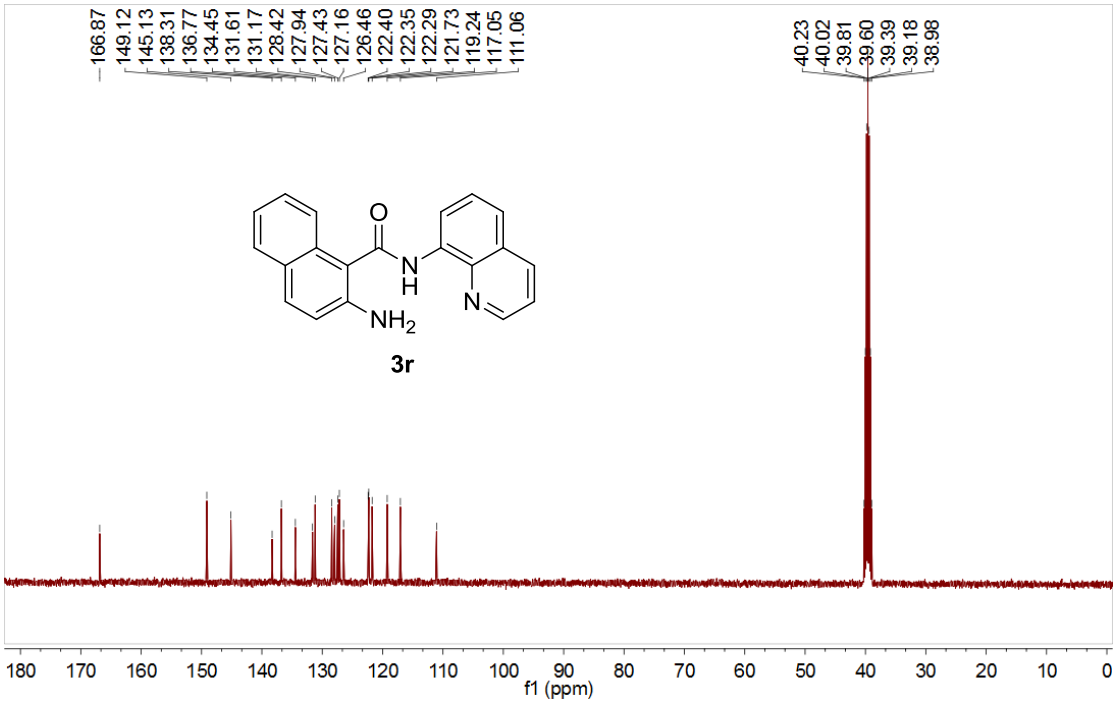
^{19}F NMR Spectrum of **3q**



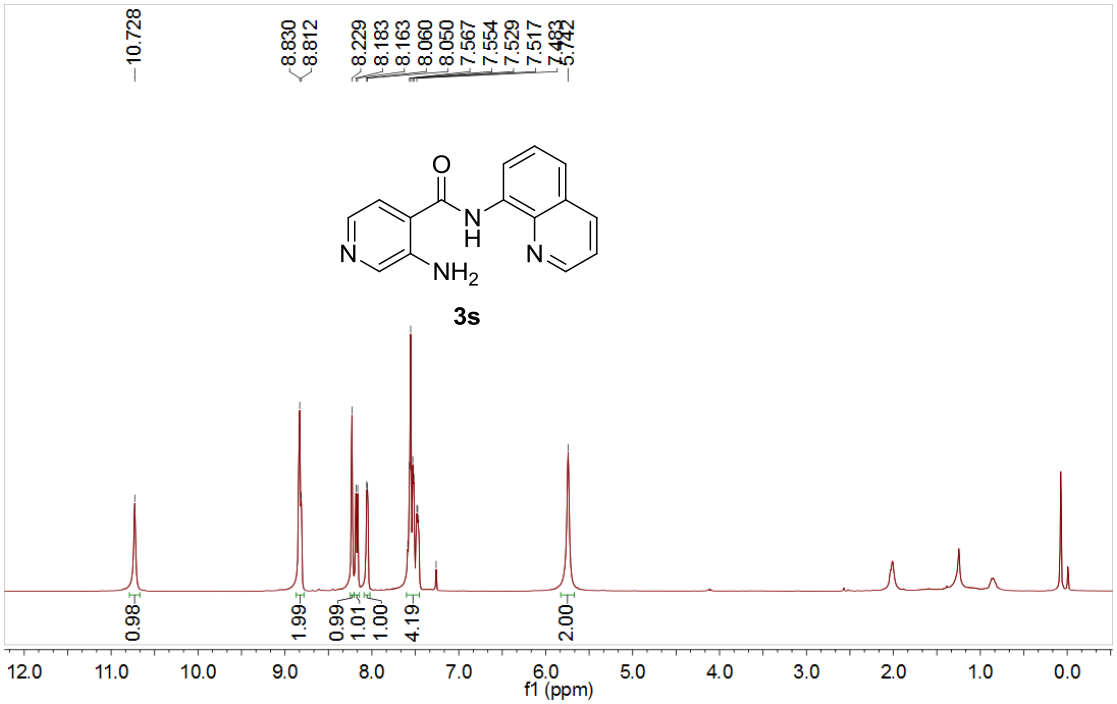
^{1}H NMR Spectrum of **3r**



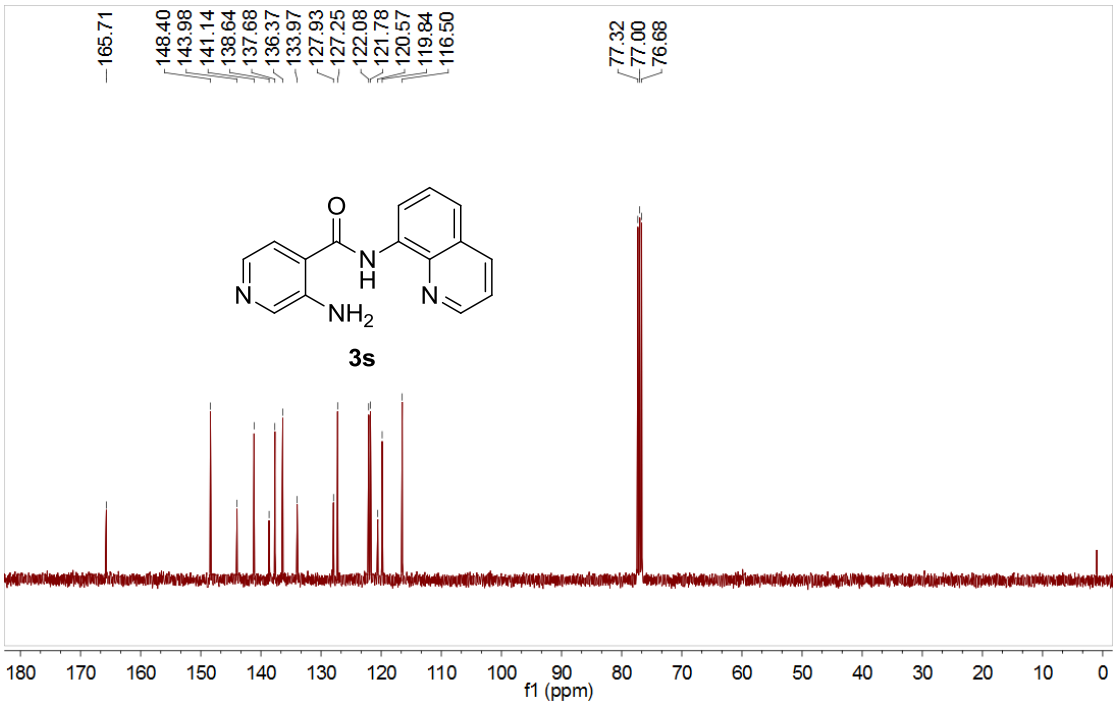
^{13}C NMR Spectrum of **3r**



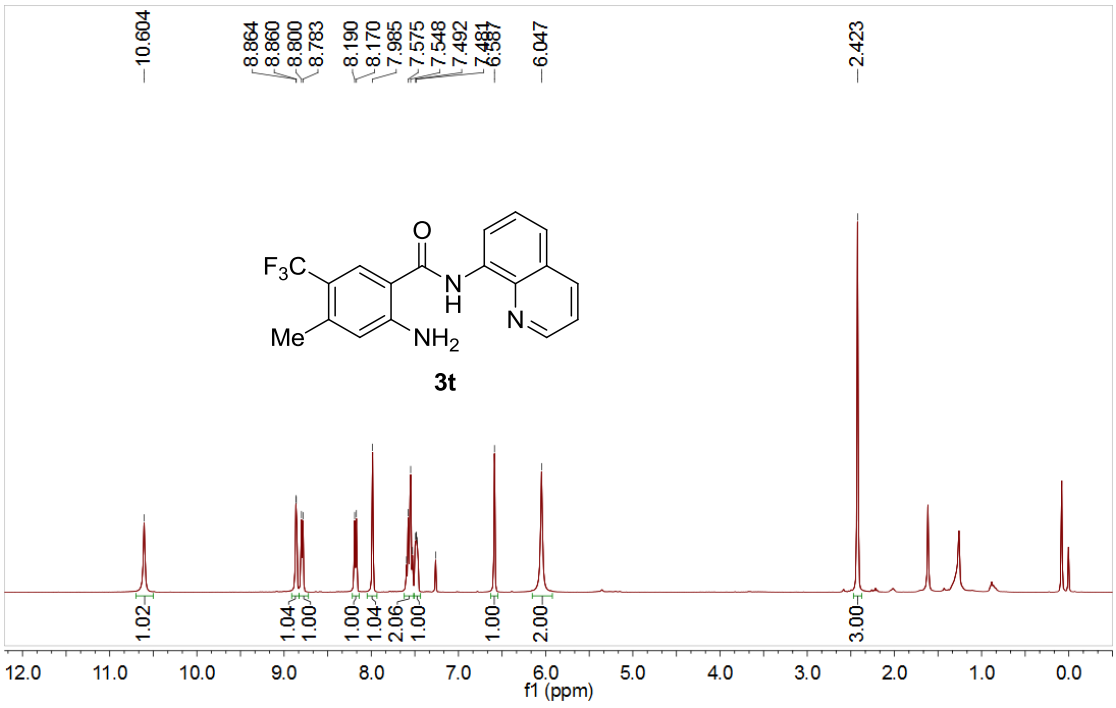
^{1}H NMR Spectrum of **3s**



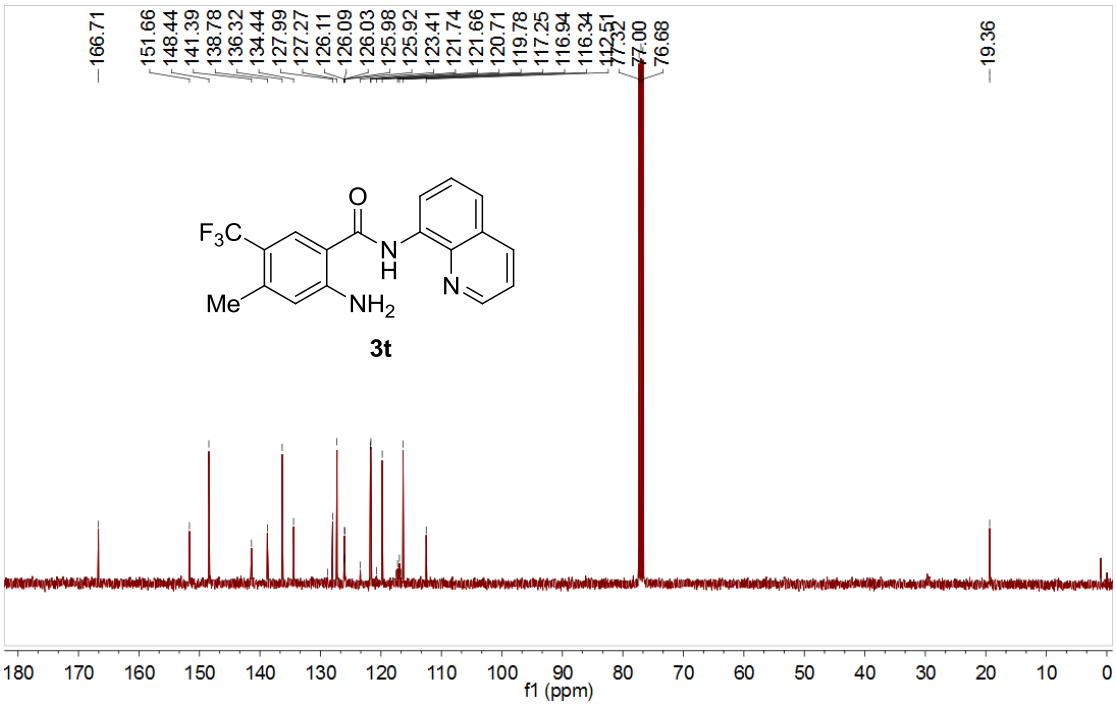
^{13}C NMR Spectrum of **3s**



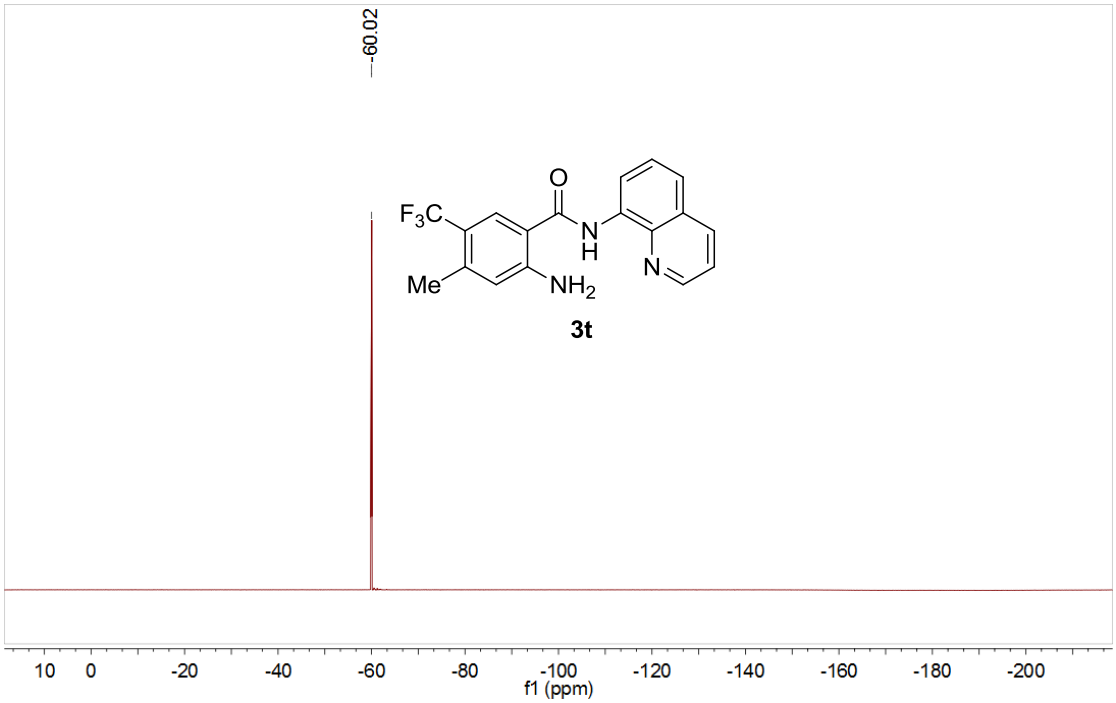
^{1}H NMR Spectrum of **3t**



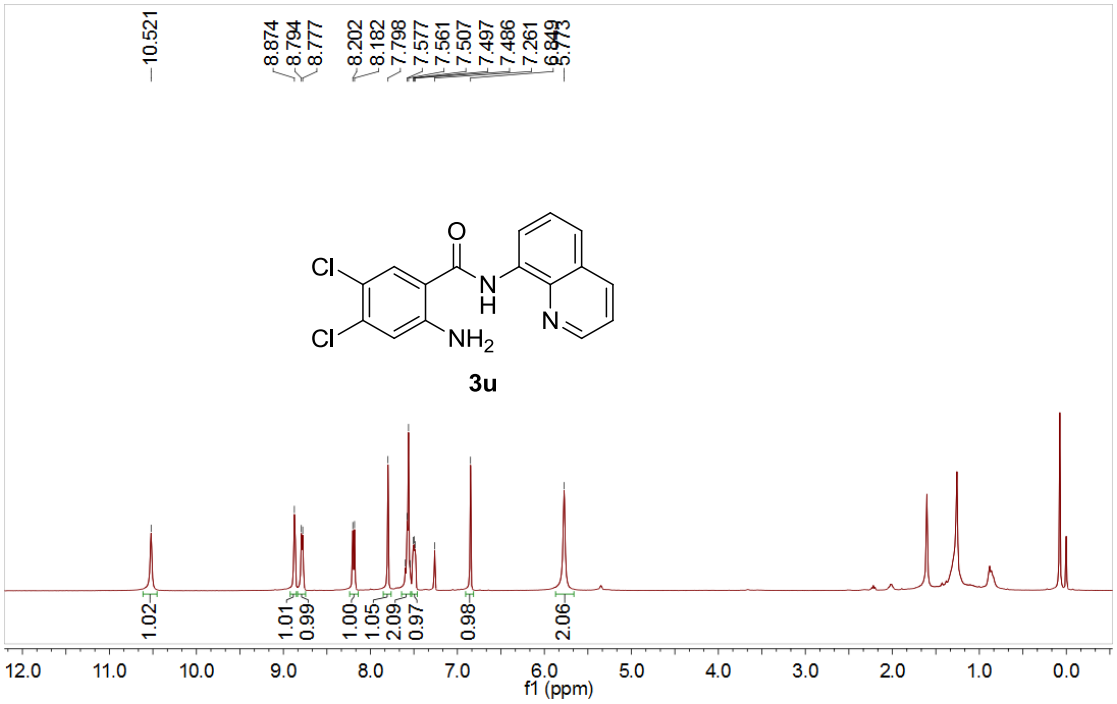
^{13}C NMR Spectrum of **3t**



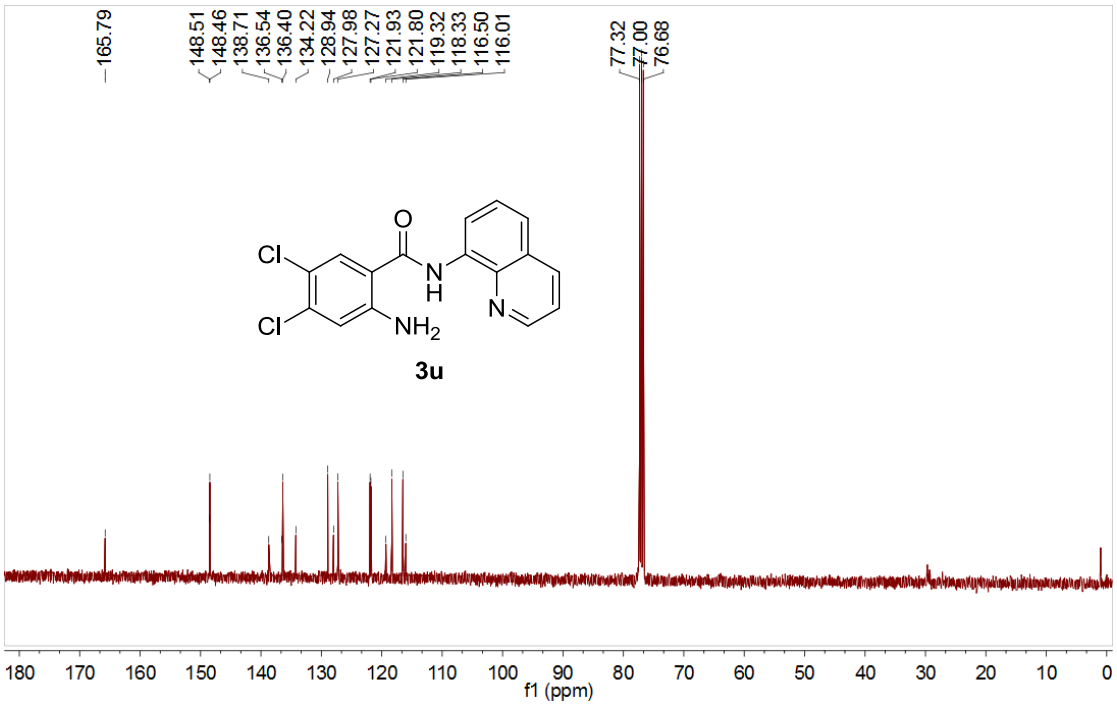
^{19}F NMR Spectrum of **3t**



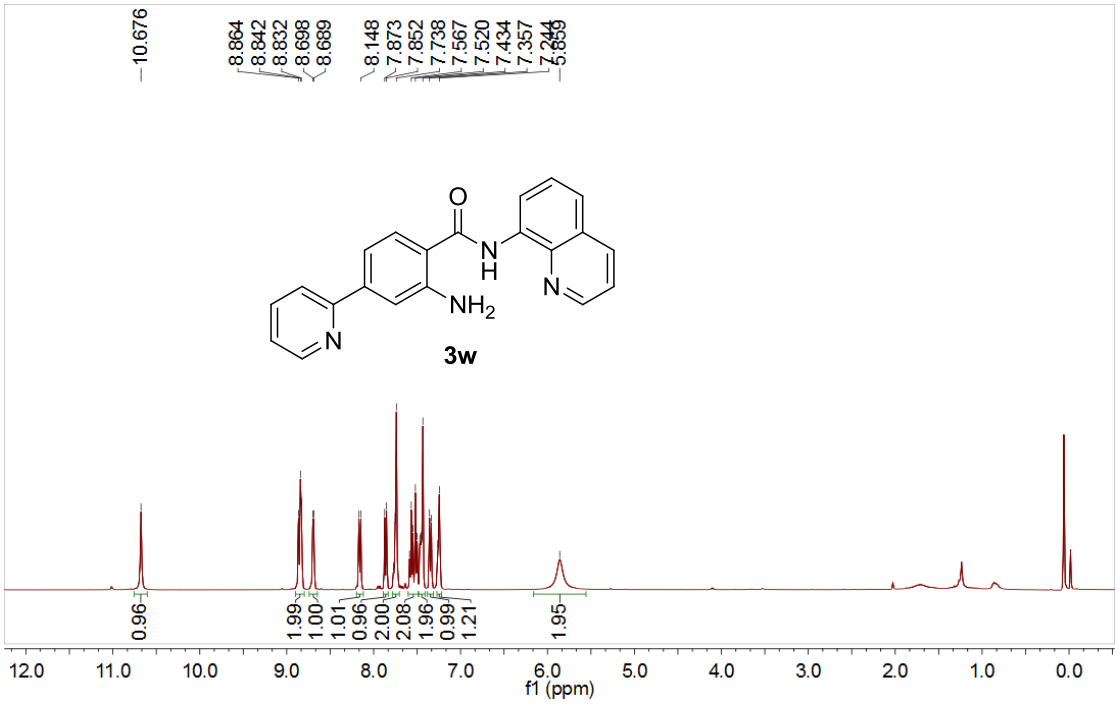
^{1}H NMR Spectrum of **3u**



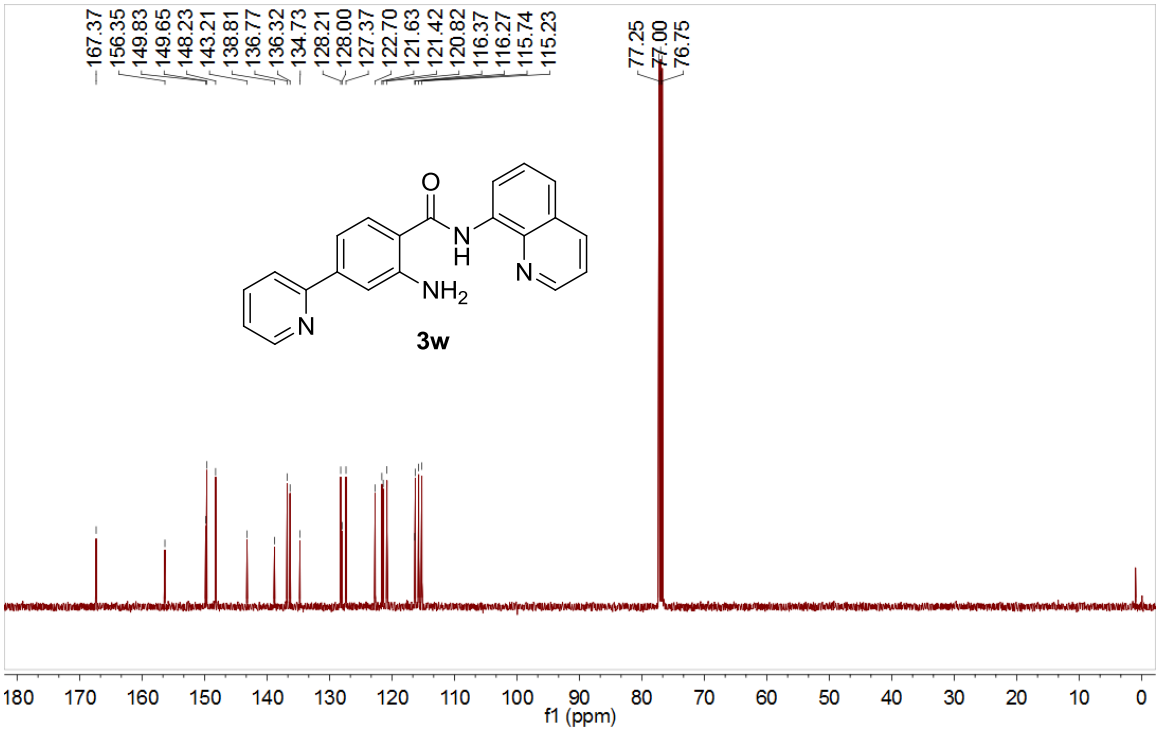
^{13}C NMR Spectrum of **3u**



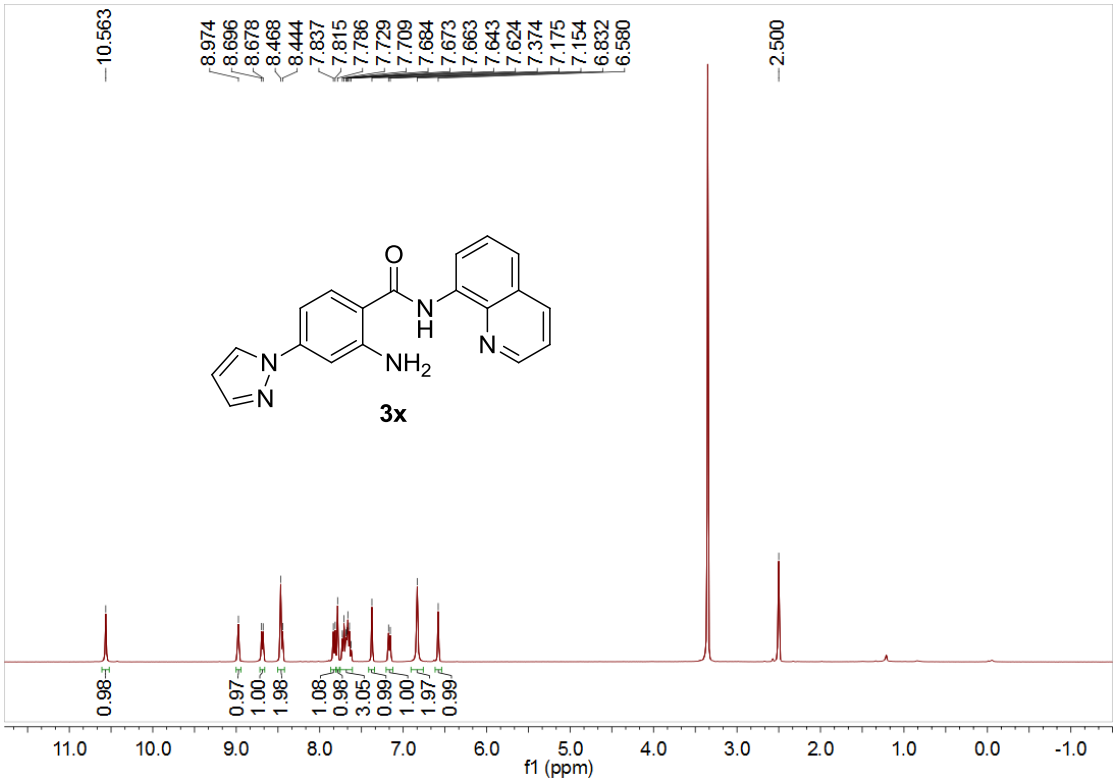
^{1}H NMR Spectrum of **3w**



^{13}C NMR Spectrum of **3w**



^{1}H NMR Spectrum of **3x**



^{13}C NMR Spectrum of **3x**