

## Electronic Supplementary Information (ESI)

# Nickel-Catalyzed Dual C(sp<sup>2</sup>)-H Activation of Arenes: A New Route to Diaryl Ether

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## Content

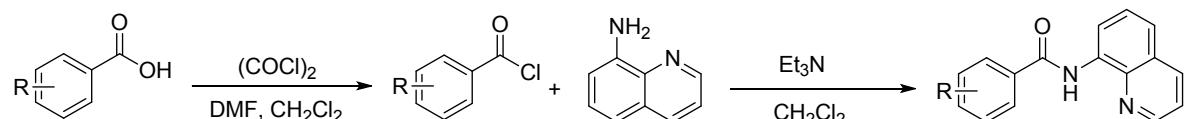
### 1. General Information

All chemicals were obtained from commercial sources and were used as received without any purification. Analytical thin-layer chromatography (TLC) was performed on pre-coated, glass-backed silica gel plates. Starting materials benzamides were synthesized according to corresponding acid or acid chloride reacting with 8-aminoquinoline.<sup>1-6</sup> Visualization of the developed chromatogram was performed by UV absorbance (254 nm). <sup>1</sup>H NMR spectra were recorded at 400 MHz and 500 MHz NMR spectrometers using TMS as an internal standard, <sup>13</sup>C NMR spectra were recorded at 100 MHz spectrometers using TMS as an internal standard, and were fully decoupled by broad band proton decoupling. The multiplicities are reported as follows: singlet (s), doublet (d), triplet (t), doublet of doublets

(dd), triplet of doublets multiplet (td), quarter (q), and broad (br). High-resolution mass spectra (HRMS) were recorded on Waters TOFMS GCT Premier using ESI ionization. GC-MS spectra were recorded using a HP6890 gas chromatograph with a HP5973 mass spectrometric detector equipped with an electron ionization source and a single-stage quadrupole. Melting points were measured with WRR digital point apparatus. Column chromatography was performed on silica gel column using ethyl acetate (EA)/petroleum ether(PE).

## 2. Experimental Section

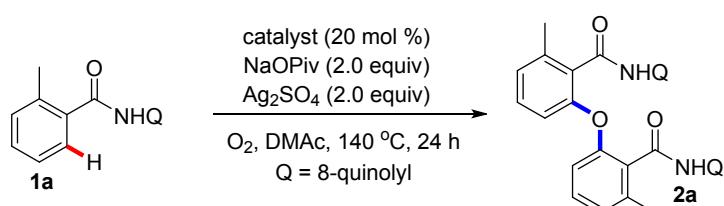
### 2.1. General procedure for the preparation of benzamides from carboxylic acids.<sup>1-6</sup>



To a stirred solution of a carboxylic acid (15 mmol) and DMF (5 drops) in  $\text{CH}_2\text{Cl}_2$  (10 mL),  $(\text{COCl})_2$  (1.5 mL, 18 mmol) was added dropwise. The solution was stirred at room temperature for 2 h. The solvent was then removed by evaporation under reduced pressure, and the resulting residue was dissolved in  $\text{CH}_2\text{Cl}_2$  (15 mL). After cooling the reaction mixture to 0 °C, a solution of 8-aminoquinoline (17 mmol) and triethylamine (30 mmol) in 10 mL of the same solvent was added dropwise. The resulting mixture was allowed to warm to r.t. and stirred overnight. The solution containing the crude product was washed with saturated aqueous  $\text{NaHCO}_3$  (20 mL), and  $\text{CH}_2\text{Cl}_2$  ( $3 \times 20$  mL). The combined organic phase was washed with 1 M HCl aq. (20 mL). The organic phase was dried over anhydrous  $\text{Na}_2\text{SO}_4$  and the solvent removed by evaporation. The resulting crude amide was purified by flash chromatography on silica gel (eluent: hexane/EtOAc = 5/1) to give the corresponding benzamides.

### 2.2. Optimization of reaction conditions.

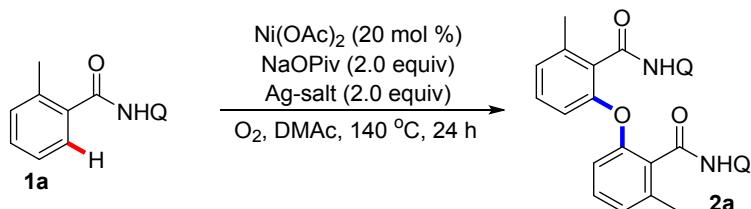
**Table S1.** Optimization of catalysts.<sup>a</sup>



entry	catalyst	oxidant	additive	solvent	yield(%) <sup>b</sup>
1	Ni(OAc) <sub>2</sub>	Ag <sub>2</sub> SO <sub>4</sub>	NaOPiv	DMAc	36
2	Ni(OAc) <sub>2</sub>	Ag <sub>2</sub> SO <sub>4</sub>	-	DMAc	trace
3	Ni(OTf) <sub>2</sub>	Ag <sub>2</sub> SO <sub>4</sub>	NaOPiv	DMAc	28
4	Ni(acac) <sub>2</sub>	Ag <sub>2</sub> SO <sub>4</sub>	NaOPiv	DMAc	nr
5	NiBr <sub>2</sub>	Ag <sub>2</sub> SO <sub>4</sub>	NaOPiv	DMAc	22
6	Ni(OH) <sub>2</sub>	Ag <sub>2</sub> SO <sub>4</sub>	NaOPiv	DMAc	nr
7	Ni <sub>2</sub> CO <sub>3</sub>	Ag <sub>2</sub> SO <sub>4</sub>	NaOPiv	DMAc	nr
8	Ni <sub>2</sub> Cl <sub>2</sub> (PPh <sub>3</sub> ) <sub>3</sub>	Ag <sub>2</sub> SO <sub>4</sub>	NaOPiv	DMAc	20
9	Ni <sub>2</sub> Cl <sub>2</sub> (PCy <sub>3</sub> ) <sub>3</sub>	Ag <sub>2</sub> SO <sub>4</sub>	NaOPiv	DMAc	21

<sup>a</sup>Reactions were carried out by using **1a** (0.20 mmol), catalyst (20 mol %), Ag<sub>2</sub>SO<sub>4</sub> (2.0 equiv), NaOPiv (2.0 equiv), in solvent DMAc (2.0 mL), under O<sub>2</sub> atmosphere at 140 °C for 24 h. DMAc = *N,N*-dimethyl acetamide. <sup>b</sup>Isolated yield. nr = no reaction.

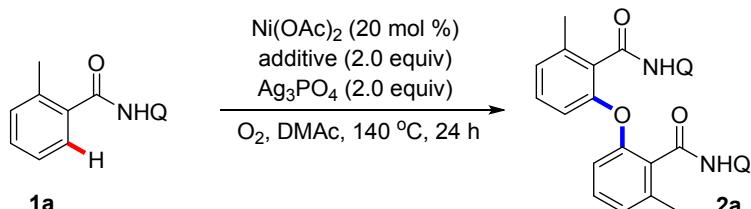
**Table S2.** Optimization of oxidants.<sup>a</sup>



entry	catalyst	oxidant	additive	solvent	yield(%) <sup>b</sup>
1	Ni(OAc) <sub>2</sub>	Ag <sub>2</sub> SO <sub>4</sub>	NaOPiv	DMAc	36
2	Ni(OAc) <sub>2</sub>	Ag <sub>3</sub> PO <sub>4</sub>	NaOPiv	DMAc	45
3	Ni(OAc) <sub>2</sub>	Ag <sub>2</sub> CO <sub>3</sub>	NaOPiv	DMAc	25
4	Ni(OAc) <sub>2</sub>	AgOAc	NaOPiv	DMAc	21
5	Ni(OAc) <sub>2</sub>	AgNO <sub>3</sub>	NaOPiv	DMAc	trace
6	Ni(OAc) <sub>2</sub>	AgNO <sub>2</sub>	NaOPiv	DMAc	trace
7	Ni(OAc) <sub>2</sub>	AgI	NaOPiv	DMAc	18
8	Ni(OAc) <sub>2</sub>	AgOPiv	NaOPiv	DMAc	18
9	Ni(OAc) <sub>2</sub>	PhCOOAg H <sub>2</sub> O	NaOPiv	DMAc	trace
10	Ni(OAc) <sub>2</sub>	AgO	NaOPiv	DMAc	16
11	Ni(OAc) <sub>2</sub>	AdCOOAg	NaOPiv	DMAc	23
12 <sup>c</sup>	Ni(OAc) <sub>2</sub>	Ag <sub>3</sub> PO <sub>4</sub>	NaOPiv	DMAc	trace

<sup>a</sup>Reactions were carried out by using **1a** (0.20 mmol), Ni(OAc)<sub>2</sub> (20 mol %), Ag salt (2.0 equiv), NaOPiv (2.0 equiv), in solvent DMAc (2.0 mL), under O<sub>2</sub> atmosphere at 140 °C for 24 h. <sup>b</sup>Isolated yield. <sup>c</sup>0.2 equiv Ag<sub>3</sub>PO<sub>4</sub> was used.

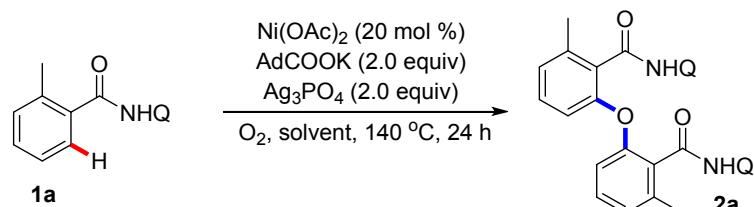
**Table S3.** Optimization of additives.<sup>a</sup>



entry	catalyst	oxidant	additive	solvent	yield(%) <sup>b</sup>
1	Ni(OAc) <sub>2</sub>	Ag <sub>3</sub> PO <sub>4</sub>	NaOPiv	DMAc	45
2	Ni(OAc) <sub>2</sub>	Ag <sub>3</sub> PO <sub>4</sub>	NaOAc	DMAc	38
3	Ni(OAc) <sub>2</sub>	Ag <sub>3</sub> PO <sub>4</sub>	HCOONa	DMAc	nr
4	Ni(OAc) <sub>2</sub>	Ag <sub>3</sub> PO <sub>4</sub>	PhCOONa	DMAc	25
5	Ni(OAc) <sub>2</sub>	Ag <sub>3</sub> PO <sub>4</sub>	Na <sub>2</sub> CO <sub>3</sub>	DMAc	nr
6	Ni(OAc) <sub>2</sub>	Ag <sub>3</sub> PO <sub>4</sub>	NaHCO <sub>3</sub>	DMAc	nr
7	Ni(OAc) <sub>2</sub>	Ag <sub>3</sub> PO <sub>4</sub>	Na <sub>3</sub> PO <sub>4</sub>	DMAc	nr
8	Ni(OAc) <sub>2</sub>	Ag <sub>3</sub> PO <sub>4</sub>	Na <sub>2</sub> HPO <sub>4</sub>	DMAc	nr
9	Ni(OAc) <sub>2</sub>	Ag <sub>3</sub> PO <sub>4</sub>	KOtBu	DMAc	nr
10	Ni(OAc) <sub>2</sub>	Ag <sub>3</sub> PO <sub>4</sub>	LiOAc	DMAc	29
11	Ni(OAc) <sub>2</sub>	Ag <sub>3</sub> PO <sub>4</sub>	CF <sub>3</sub> COOK	DMAc	nr
12	Ni(OAc) <sub>2</sub>	Ag <sub>3</sub> PO <sub>4</sub>	PhOK	DMAc	36
13	Ni(OAc) <sub>2</sub>	Ag <sub>3</sub> PO <sub>4</sub>	KOPiv	DMAc	50
14	Ni(OAc) <sub>2</sub>	Ag <sub>3</sub> PO <sub>4</sub>	CsOPiv	DMAc	45
15	Ni(OAc) <sub>2</sub>	Ag <sub>3</sub> PO <sub>4</sub>	AdCOONa	DMAc	62
16	Ni(OAc) <sub>2</sub>	Ag <sub>3</sub> PO <sub>4</sub>	AdCOOK	DMAc	72
17	Ni(OAc) <sub>2</sub>	Ag <sub>3</sub> PO <sub>4</sub>	AdCOOCs	DMAc	60
18	Ni(OAc) <sub>2</sub>	Ag <sub>3</sub> PO <sub>4</sub>	AdCOOH	DMAc	trace

<sup>a</sup>Reactions were carried out by using **1a** (0.20 mmol), Ni(OAc)<sub>2</sub> (20 mol %), Ag<sub>3</sub>PO<sub>4</sub> (2.0 equiv), additive (2.0 equiv), in solvent DMAc (2.0 mL), under O<sub>2</sub> atmosphere at 140 °C for 24 h. <sup>b</sup>Isolated yield. AdCOOK = Potassium amantadate. nr = no reaction.

**Table S4.** Optimization of solvents.<sup>a</sup>

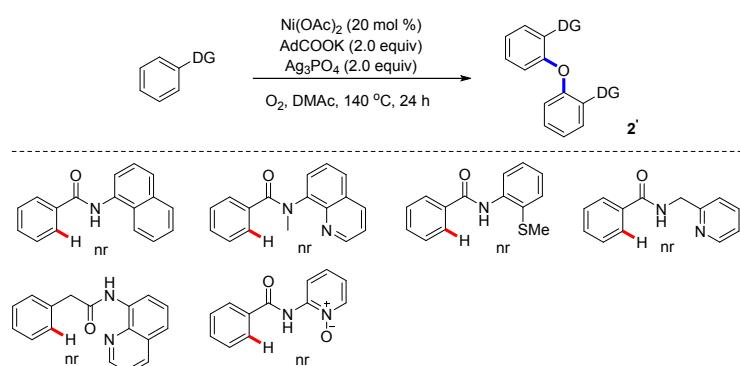


entry	catalyst	oxidant	additive	solvent	yield(%) <sup>b</sup>
1	Ni(OAc) <sub>2</sub>	Ag <sub>3</sub> PO <sub>4</sub>	AdCOOK	DMAc	72
2	Ni(OAc) <sub>2</sub>	Ag <sub>3</sub> PO <sub>4</sub>	AdCOOK	DMF	50
3	Ni(OAc) <sub>2</sub>	Ag <sub>3</sub> PO <sub>4</sub>	AdCOOK	toluene	nr
4	Ni(OAc) <sub>2</sub>	Ag <sub>3</sub> PO <sub>4</sub>	AdCOOK	NMP	48
5	Ni(OAc) <sub>2</sub>	Ag <sub>3</sub> PO <sub>4</sub>	AdCOOK	THF	nr
6	Ni(OAc) <sub>2</sub>	Ag <sub>3</sub> PO <sub>4</sub>	AdCOOK	1,4-dioxane	nr
7	Ni(OAc) <sub>2</sub>	Ag <sub>3</sub> PO <sub>4</sub>	AdCOOK	GDE	nr
8	-	Ag <sub>3</sub> PO <sub>4</sub>	AdCOOK	DMAc	nr
9	Ni(OAc) <sub>2</sub>	-	AdCOOK	DMAc	nr
10 <sup>c</sup>	Ni(OAc) <sub>2</sub>	Ag <sub>3</sub> PO <sub>4</sub>	AdCOOK	DMAc	55
11 <sup>d</sup>	Ni(OAc) <sub>2</sub>	Ag <sub>3</sub> PO <sub>4</sub>	AdCOOK	DMAc	51
12 <sup>e</sup>	Ni(OAc) <sub>2</sub>	Ag <sub>3</sub> PO <sub>4</sub>	AdCOOK	DMAc	53
13 <sup>f</sup>	Ni(OAc) <sub>2</sub>	Ag <sub>3</sub> PO <sub>4</sub>	AdCOOK	DMAc	50

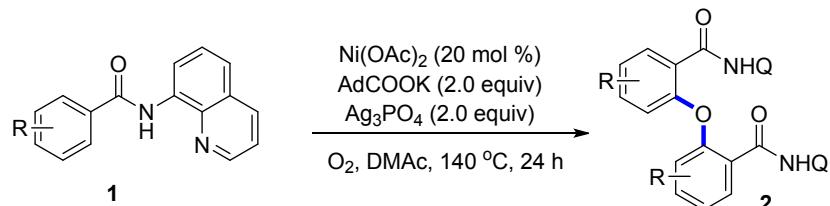
14 <sup>g</sup>	Ni(OAc) <sub>2</sub>	Ag <sub>3</sub> PO <sub>4</sub>	AdCOOK	DMAc	33(20)
15 <sup>h</sup>	Ni(OAc) <sub>2</sub>	Ag <sub>3</sub> PO <sub>4</sub>	AdCOOK	DMAc	70
16 <sup>i</sup>	Ni(OAc) <sub>2</sub>	Ag <sub>3</sub> PO <sub>4</sub>	AdCOOK	DMAc	62
17	Co(OAc) <sub>2</sub> ·4H <sub>2</sub> O	Ag <sub>3</sub> PO <sub>4</sub>	AdCOOK	DMAc	nr

<sup>a</sup>Reactions were carried out by using **1a** (0.20 mmol), Ni(OAc)<sub>2</sub> (20 mol %), Ag<sub>3</sub>PO<sub>4</sub> (2.0 equiv), AdCOOK (2.0 equiv), in solvent (2.0 mL), under O<sub>2</sub> atmosphere at 140 °C for 24 h. <sup>b</sup>Isolated yield. DMF = *N,N*-dimethyl formamide. NMP = *N*-methylpyrrolidone. THF = tetrahydrofuran. GDE = 1,2-Dimethoxyethane. nr = no reaction. <sup>c</sup>10 mol % Ni(OAc)<sub>2</sub> was used. <sup>d</sup>1.0 equiv. Ag<sub>3</sub>PO<sub>4</sub> was used. <sup>e</sup>1.0 equiv. AdCOOK was used. <sup>f</sup>under air atmosphere. <sup>g</sup>under N<sub>2</sub> atmosphere, the alkylated product was obtained in 20% yield. <sup>h</sup>T = 150 °C. <sup>i</sup>T = 130 °C.

**Table S5.** The effect of diverse Bidentate directing groups.<sup>a</sup>

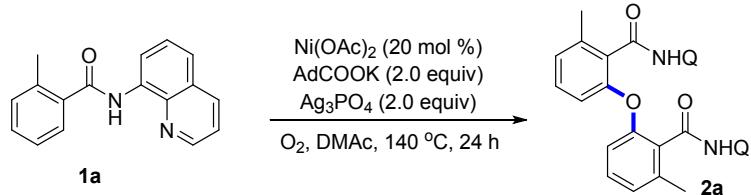


### 2.3. General procedure for the synthesis of symmetrical diaryl ether.



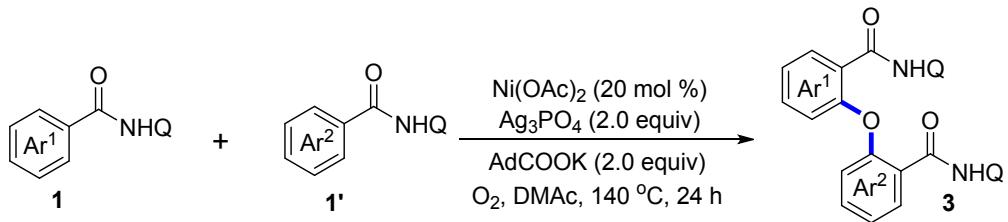
To a 25 mL seal tube with a stir bar was added benzamide (**1**, 0.20 mmol), Ni(OAc)<sub>2</sub> (0.04 mmol, 7.0 mg), Ag<sub>3</sub>PO<sub>4</sub> (0.40 mmol, 166 mg) and AdCOOK (0.40 mmol, 90 mg) in DMAc (2.0 mL), the vial was evacuated and filled with O<sub>2</sub> atmosphere and stirred by oil bath at 140 °C for 24 h, then cooled to room temperature, filtered through a pad of celite, and then washed with EtOAc (10 mL×3), washed by 1 mol/L NaOH solution (20 mL) three times and saturated NaCl (20 mL), then dried with sodium sulfate. Organic solvents were removed under reduced pressure and the crude reaction mixture was purified by column chromatography on silica gel column with EtOAc/petroleum ether (1:10~1:5, v/v) as an eluent to afford the desired product **2**.

### 2.4. Scale-up experiment for the synthesis of symmetrical diaryl ether.



To a 50 mL seal tube with a stir bar was added benzamide (**1a**, 1.0 mmol), Ni(OAc)<sub>2</sub> (0.20 mmol, 35.0 mg), Ag<sub>3</sub>PO<sub>4</sub> (2.0 mmol, 830 mg) and AdCOOK (2.0 mmol, 450 mg) in DMAc (10.0 mL), the vial was evacuated and filled with O<sub>2</sub> atmosphere and stirred by oil bath at 140 °C for 24 h, then cooled to room temperature, filtered through a pad of celite, and then washed with EtOAc (20 mL×3), washed by 1 mol/L NaOH solution (30 mL) three times and saturated NaCl (30 mL), then dried with sodium sulfate. Organic solvents were removed under reduced pressure and the crude reaction mixture was purified by column chromatography on silica gel column with EtOAc/petroleum ether (1:10~1:5, v/v) as an eluent to afford the desired product **2a** (yield 82%, 441.2 mg).

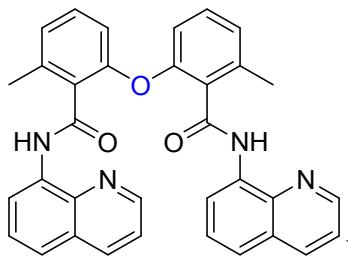
### **2.5. General procedure for the synthesis of unsymmetrical diaryl ether.**



To a 25 mL seal tube with a stir bar was added benzamide (**1**, 0.20 mmol), and another benzamide (**1'**, 0.24 mmol), Ni(OAc)<sub>2</sub> (0.04 mmol, 7.0 mg), Ag<sub>3</sub>PO<sub>4</sub> (0.40 mmol, 166 mg) and AdCOOK (0.40 mmol, 90 mg) in DMAc (2.0 mL), the vial was evacuated and filled with O<sub>2</sub> atmosphere and stirred by oil bath at 140 °C for 24 h, then cooled to room temperature, filtered through a pad of celite, and then washed with EtOAc (10 mL×3), washed by 1 mol/L NaOH solution (20 mL) three times and saturated NaCl (20 mL), then dried with sodium sulfate. Organic solvents were removed under reduced pressure and the crude reaction mixture was purified by column chromatography on silica gel column with EtOAc/petroleum ether (1:10~1:5, v/v) and recrystallization to afford the desired product **3**.

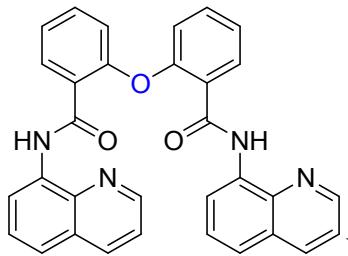
## **3. Characterization of the Products**

### **6,6'-oxybis(2-methyl-N-(quinolin-8-yl)benzamide) (2a)**



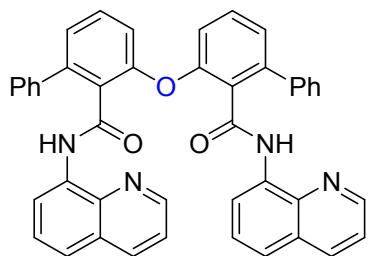
Yield: (38.8 mg, 72%); White solid; mp: >230 °C. **<sup>1</sup>H NMR** ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  9.94 (s, 2H), 8.74 (d,  $J = 7.6$  Hz, 2H), 8.10 (dd,  $J_1 = 4.0$  Hz,  $J_2 = 1.2$  Hz, 2H), 7.79 (dd,  $J_1 = 8.0$  Hz,  $J_2 = 1.2$  Hz, 2H), 7.35 (t,  $J = 8.0$  Hz, 2H), 7.28-7.23 (m, 4H), 7.05 (dd,  $J_1 = 8.4$  Hz,  $J_2 = 4.4$  Hz, 2H), 6.99 (d,  $J = 7.6$  Hz, 2H), 6.93 (d,  $J = 8.0$  Hz, 2H), 2.40 (s, 6H). **<sup>13</sup>C NMR** ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  165.4, 153.8, 147.7, 137.9, 137.8, 135.4, 134.3, 130.4, 129.6, 127.4, 126.9, 125.8, 121.5, 121.1, 116.5, 116.4, 19.5. **HRMS** (ESI-TOF) calcd for  $\text{C}_{34}\text{H}_{27}\text{N}_4\text{O}_3^+ [\text{M}+\text{H}]^+$ : 539.2078, found: 539.2083.

### 2,2'-oxybis(*N*-(quinolin-8-yl)benzamide) (2b)



Yield: (33.2 mg, 65%); White solid; mp: 214.4-214.9 °C. **<sup>1</sup>H NMR** ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  12.37 (s, 2H), 8.96 (dd,  $J_1 = 7.6$  Hz,  $J_2 = 1.2$  Hz, 2H), 8.52 (dd,  $J_1 = 8.0$  Hz,  $J_2 = 1.6$  Hz, 2H), 8.16 (dd,  $J_1 = 4.4$  Hz,  $J_2 = 1.6$  Hz, 2H), 7.92 (d,  $J = 8.4$  Hz, 2H), 7.53-7.48 (m, 4H), 7.40-7.37 (m, 4H), 7.17-7.13 (m, 4H). **<sup>13</sup>C NMR** ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  162.8, 154.7, 148.1, 138.9, 135.7, 135.3, 133.4, 132.4, 127.8, 127.2, 126.1, 124.8, 121.7, 121.5, 119.8, 116.9. **HRMS** (ESI-TOF) calcd for  $\text{C}_{32}\text{H}_{23}\text{N}_4\text{O}_3^+ [\text{M}+\text{H}]^+$ : 511.1765, found: 511.1770.

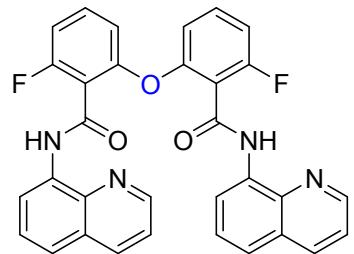
### 3,3''-oxybis(*N*-(quinolin-8-yl)-[1,1'-biphenyl]-2-carboxamide) (2c)



Yield: (40.4 mg, 61%); White solid; mp: >230 °C. **<sup>1</sup>H NMR** ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  9.81 (s, 2H), 8.56 (d,  $J = 7.2$  Hz, 2H), 8.11 (s, 2H), 7.77 (d,  $J = 8.0$  Hz, 2H), 7.48-7.43 (m, 6H), 7.24-7.12 (m, 14H), 7.01 (dd,  $J_1 = 7.6$  Hz,  $J_2 = 4.0$  Hz, 2H). **<sup>13</sup>C NMR**

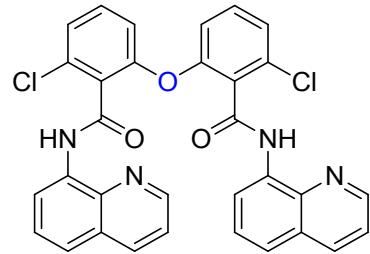
**NMR** ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  164.9, 154.4, 147.5, 141.9, 139.6, 137.9, 135.3, 134.3, 130.6, 129.2, 128.5, 128.3, 127.5, 127.3, 126.9, 125.7, 121.3, 120.9, 118.4, 116.5. **HRMS** (ESI-TOF) calcd for  $\text{C}_{44}\text{H}_{31}\text{N}_4\text{O}_3^+ [\text{M}+\text{H}]^+$ : 663.2391, found: 663.2396.

**6,6'-oxybis(2-fluoro-N-(quinolin-8-yl)benzamide) (2d)**



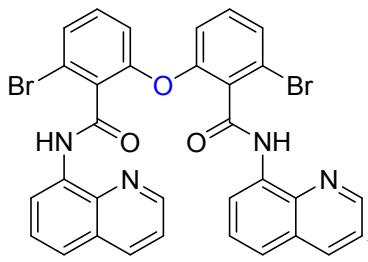
Yield: (30.6 mg, 56%); White solid; mp: 202.5-203.2 °C.  **$^1\text{H}$  NMR** ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  10.29 (s, 2H), 8.76 (dd,  $J_1 = 7.6$  Hz,  $J_2 = 1.2$  Hz, 2H), 8.26 (dd,  $J_1 = 4.4$  Hz,  $J_2 = 1.6$  Hz, 2H), 7.91 (dd,  $J_1 = 8.4$  Hz,  $J_2 = 1.6$  Hz, 2H), 7.44-7.35 (m, 6H), 7.13 (dd,  $J_1 = 8.4$  Hz,  $J_2 = 4.4$  Hz, 2H), 6.98 (d,  $J = 8.4$  Hz, 2H), 6.93 (d,  $J = 8.4$  Hz, 2H).  **$^{13}\text{C}$  NMR** ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  160.1 (d,  $J_{\text{C}-\text{F}} = 251.0$  Hz), 159.5, 154.4 (d,  $J_{\text{C}-\text{F}} = 6.3$  Hz), 147.5, 137.7, 135.2, 133.7, 131.3 (d,  $J_{\text{C}-\text{F}} = 9.9$  Hz), 127.1, 126.6, 121.5, 120.8, 117.8 (d,  $J_{\text{C}-\text{F}} = 19.0$  Hz), 116.5, 114.7 (d,  $J_{\text{C}-\text{F}} = 3.6$  Hz), 111.5 (d,  $J_{\text{C}-\text{F}} = 21.6$  Hz). **HRMS** (ESI-TOF) calcd for  $\text{C}_{32}\text{H}_{21}\text{F}_2\text{N}_4\text{O}_3^+ [\text{M}+\text{H}]^+$ : 547.1576, found: 547.1578.

**6,6'-oxybis(2-chloro-N-(quinolin-8-yl)benzamide) (2e)**



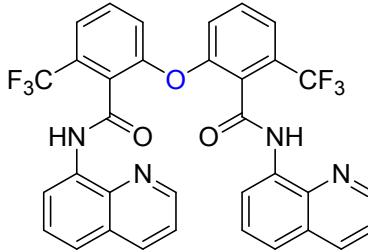
Yield: (26.0 mg, 45%); White solid; mp: 203.4-204.5 °C.  **$^1\text{H}$  NMR** ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  9.92 (s, 2H), 8.72 (dd,  $J_1 = 7.6$  Hz,  $J_2 = 1.2$  Hz, 2H), 8.19 (dd,  $J_1 = 4.4$  Hz,  $J_2 = 1.6$  Hz, 2H), 7.84 (dd,  $J_1 = 8.4$  Hz,  $J_2 = 1.6$  Hz, 2H), 7.36 (d,  $J = 7.6$  Hz, 2H), 7.31 (d,  $J = 8.4$  Hz, 2H), 7.27 (dd,  $J_1 = 8.0$  Hz,  $J_2 = 1.2$  Hz, 2H), 7.22 (dd,  $J_1 = 8.4$  Hz,  $J_2 = 0.8$  Hz, 2H), 7.10 (dd,  $J_1 = 8.0$  Hz,  $J_2 = 4.0$  Hz, 2H), 7.04 (dd,  $J_1 = 8.0$  Hz,  $J_2 = 0.8$  Hz, 2H).  **$^{13}\text{C}$  NMR** ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  162.1, 154.4, 147.8, 137.9, 135.5, 133.9, 132.6, 131.2, 129.4, 127.4, 126.9, 125.5, 121.9, 121.2, 117.6, 116.8. **HRMS** (ESI-TOF) calcd for  $\text{C}_{32}\text{H}_{21}\text{Cl}_2\text{N}_4\text{O}_3^+ [\text{M}+\text{H}]^+$ : 579.0985, found: 579.0988.

**6,6'-oxybis(2-bromo-N-(quinolin-8-yl)benzamide) (2f)**



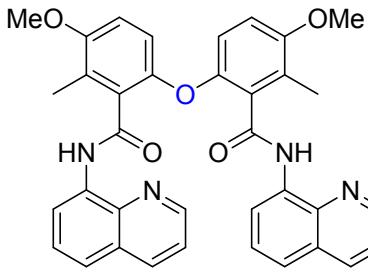
Yield: (28.0 mg, 42%); White solid; mp: 205.0-206.7 °C. **<sup>1</sup>H NMR** ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  9.88 (s, 2H), 8.71 (dd,  $J_1 = 7.6$  Hz,  $J_2 = 1.2$  Hz, 2H), 8.19 (dd,  $J_1 = 4.4$  Hz,  $J_2 = 1.6$  Hz, 2H), 7.83 (dd,  $J_1 = 8.4$  Hz,  $J_2 = 1.6$  Hz, 2H), 7.39 (dd,  $J_1 = 8.0$  Hz,  $J_2 = 0.8$  Hz, 2H), 7.34 (t,  $J = 8.0$  Hz, 2H), 7.28-7.24 (m, 4H), 7.11-7.08 (m, 4H). **<sup>13</sup>C NMR** ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  163.1, 154.3, 147.8, 137.9, 135.5, 133.9, 131.5, 128.6, 127.4, 126.9, 121.9, 121.2, 120.9, 118.2, 116.8. **HRMS** (ESI-TOF) calcd for  $\text{C}_{32}\text{H}_{21}\text{Br}_2\text{N}_4\text{O}_3^+$   $[\text{M}+\text{H}]^+$ : 666.9975, found: 666.9978.

#### 6,6'-oxybis(*N*-(quinolin-8-yl)-2-(trifluoromethyl)benzamide) (2g)



Yield: (29.1 mg, 45%); White solid; mp: 169.9-171.0 °C. **<sup>1</sup>H NMR** ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  9.91 (s, 2H), 8.69 (dd,  $J_1 = 7.6$  Hz,  $J_2 = 1.2$  Hz, 2H), 8.11 (dd,  $J_1 = 4.4$  Hz,  $J_2 = 1.6$  Hz, 2H), 7.83 (dd,  $J_1 = 8.0$  Hz,  $J_2 = 1.6$  Hz, 2H), 7.54-7.51 (m, 4H), 7.36-7.32 (m, 4H), 7.26 (dd,  $J_1 = 8.4$  Hz,  $J_2 = 1.2$  Hz, 2H), 7.06 (dd,  $J_1 = 8.0$  Hz,  $J_2 = 4.0$  Hz, 2H). **<sup>13</sup>C NMR** ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  162.2, 154.2, 147.7, 137.8, 135.5, 133.9, 131.1, 129.3 (q,  $J_{C-F} = 32.5$  Hz), 128.3 (q,  $J_{C-F} = 2.7$  Hz), 127.3, 126.9, 122.9, 122.8 (q,  $J_{C-F} = 330.4$  Hz), 122.1 (q,  $J_{C-F} = 4.5$  Hz), 122.0, 121.2, 116.8. **HRMS** (ESI-TOF) calcd for  $\text{C}_{34}\text{H}_{21}\text{F}_6\text{N}_4\text{O}_3^+$   $[\text{M}+\text{H}]^+$ : 647.1512, found: 647.1516.

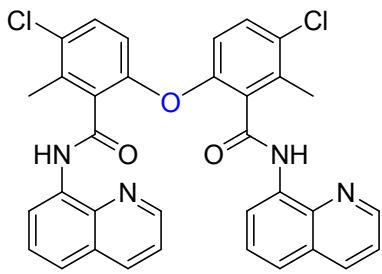
#### 6,6'-oxybis(3-methoxy-2-methyl-*N*-(quinolin-8-yl)benzamide) (2h)



Yield: (28.8 mg, 48%); White solid; mp: 197.8-198.1 °C. **<sup>1</sup>H NMR** ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  9.85 (s, 2H), 8.74 (dd,  $J_1 = 7.6$  Hz,  $J_2 = 0.8$  Hz, 2H), 8.13 (dd,

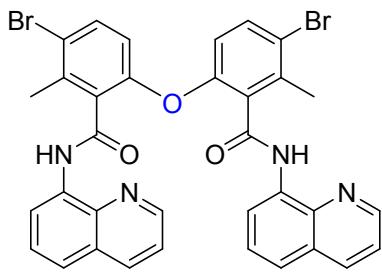
$J_1 = 4.0$  Hz,  $J_2 = 1.6$  Hz, 2H), 7.81 (dd,  $J_1 = 8.0$  Hz,  $J_2 = 1.2$  Hz, 2H), 7.33 (t,  $J = 8.0$  Hz, 2H), 7.23 (dd,  $J_1 = 8.4$  Hz,  $J_2 = 1.2$  Hz, 2H), 7.06 (dd,  $J_1 = 8.0$  Hz,  $J_2 = 4.4$  Hz, 2H), 6.89 (d,  $J = 9.2$  Hz, 2H), 6.82 (d,  $J = 8.0$  Hz, 2H), 3.80 (s, 6H), 2.22 (s, 6H).  **$^{13}\text{C}$  NMR** ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  165.4, 153.8, 147.7, 147.6, 137.9, 135.4, 134.3, 130.9, 127.3, 126.9, 125.8, 121.4, 121.1, 116.7, 116.5, 111.9, 56.0, 12.9. **HRMS** (ESI-TOF) calcd for  $\text{C}_{36}\text{H}_{31}\text{N}_4\text{O}_5^+$  [M+H]<sup>+</sup>:599.2289, found:599.2292.

**6,6'-oxybis(3-chloro-2-methyl-N-(quinolin-8-yl)benzamide) (2i)**



Yield: (33.9 mg, 56%); White solid; mp: >230 °C.  **$^1\text{H}$  NMR** ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  9.83 (s, 2H), 8.69 (dd,  $J_1 = 7.6$  Hz,  $J_2 = 1.2$  Hz, 2H), 8.17 (dd,  $J_1 = 4.0$  Hz,  $J_2 = 1.6$  Hz, 2H), 7.84 (dd,  $J_1 = 8.0$  Hz,  $J_2 = 1.2$  Hz, 2H), 7.37 (d,  $J = 8.8$  Hz, 2H), 7.33 (t,  $J = 8.0$  Hz, 2H), 7.25 (dd,  $J_1 = 8.0$  Hz,  $J_2 = 1.2$  Hz, 2H), 7.11 (dd,  $J_1 = 8.0$  Hz,  $J_2 = 4.0$  Hz, 2H), 6.89 (d,  $J = 8.8$  Hz, 2H), 2.38 (s, 6H).  **$^{13}\text{C}$  NMR** ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  164.3, 151.9, 147.8, 137.8, 135.5, 135.4, 133.9, 131.4, 130.9, 130.2, 127.4, 126.9, 121.8, 121.2, 117.6, 116.6, 17.3. **HRMS** (ESI-TOF) calcd for  $\text{C}_{34}\text{H}_{25}\text{Cl}_2\text{N}_4\text{O}_3^+$  [M+H]<sup>+</sup>:607.1298, found:607.1301.

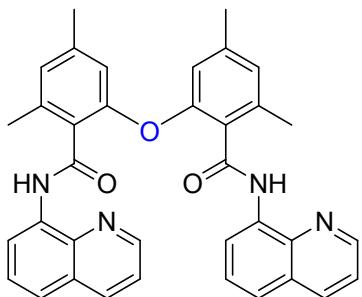
**6,6'-oxybis(3-bromo-2-methyl-N-(quinolin-8-yl)benzamide) (2j)**



Yield: (36.1 mg, 52%); White solid; mp: >230 °C.  **$^1\text{H}$  NMR** ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  9.82 (s, 2H), 8.68 (d,  $J = 7.6$  Hz, 2H), 8.17 (d,  $J = 2.8$  Hz, 2H), 7.83 (d,  $J = 8.0$  Hz, 2H), 7.55 (d,  $J = 8.4$  Hz, 2H), 7.31 (d,  $J = 8.0$  Hz, 2H), 7.25 (t,  $J = 8.4$  Hz, 2H), 7.11 (dd,  $J_1 = 8.0$  Hz,  $J_2 = 4.0$  Hz, 2H), 6.83 (d,  $J = 8.8$  Hz, 2H), 2.40 (s, 6H).  **$^{13}\text{C}$  NMR** ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  164.4, 152.5, 147.8, 137.8, 137.0, 135.5, 134.2, 133.9, 131.4, 127.3, 126.9, 121.9, 121.2, 120.3, 117.9, 116.6, 20.3. **HRMS** (ESI-TOF) calcd for

$C_{34}H_{25}Br_2N_4O_3^+ [M+H]^+$ :695.0288, found:695.0289.

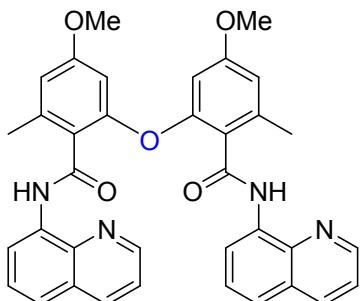
**6,6'-oxybis(2,4-dimethyl-N-(quinolin-8-yl)benzamide) (2k)**



Yield: (31.2 mg, 55%); White solid; mp: >230 °C.  **$^1H$  NMR**

( $CDCl_3$ , 400 MHz)  $\delta$  9.99 (s, 2H), 8.78 (d,  $J$  = 7.2 Hz, 2H), 8.08 (dd,  $J_1$  = 4.4 Hz,  $J_2$  = 1.6 Hz, 2H), 7.83 (dd,  $J_1$  = 8.4 Hz,  $J_2$  = 1.6 Hz, 2H), 7.40 (t,  $J$  = 8.0 Hz, 2H), 7.28 (dd,  $J_1$  = 8.0 Hz,  $J_2$  = 0.8 Hz, 2H), 7.05 (dd,  $J_1$  = 8.4 Hz,  $J_2$  = 4.4 Hz, 2H), 6.82 (s, 2H), 6.74 (s, 2H), 2.38 (s, 6H), 2.29 (s, 6H).  **$^{13}C$  NMR** ( $CDCl_3$ , 100 MHz)  $\delta$  165.6, 154.1, 147.6, 140.8, 138.0, 137.6, 135.4, 134.5, 127.4, 127.0, 126.8, 126.7, 121.4, 121.1, 117.2, 116.5, 21.4, 19.6. **HRMS** (ESI-TOF) calcd for  $C_{36}H_{31}N_4O_3^+ [M+H]^+$ :567.2391, found:567.2390.

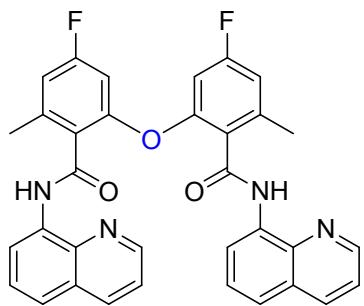
**6,6'-oxybis(4-methoxy-2-methyl-N-(quinolin-8-yl)benzamide) (2l)**



Yield: (36.5 mg, 61%); White solid; mp: 185.5-186.4 °C.  **$^1H$  NMR**

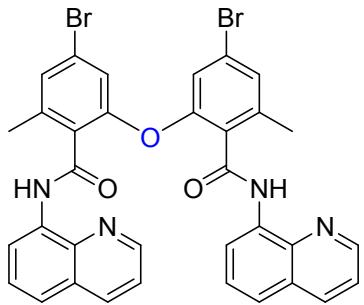
( $CDCl_3$ , 400 MHz)  $\delta$  10.04 (s, 2H), 8.76 (d,  $J$  = 7.6 Hz, 2H), 8.11 (d,  $J$  = 2.8 Hz, 2H), 7.83 (dd,  $J_1$  = 8.4 Hz,  $J_2$  = 1.6 Hz, 2H), 7.40 (t,  $J$  = 7.6 Hz, 2H), 7.28 (d,  $J$  = 7.2 Hz, 2H), 7.07 (dd,  $J_1$  = 8.4 Hz,  $J_2$  = 4.4 Hz, 2H), 6.55 (d,  $J$  = 2.0 Hz, 2H), 6.47 (d,  $J$  = 2.4 Hz, 2H), 3.80 (s, 6H), 2.40 (s, 6H).  **$^{13}C$  NMR** ( $CDCl_3$ , 100 MHz)  $\delta$  165.2, 161.0, 155.1, 147.7, 139.6, 138.1, 135.4, 134.6, 127.5, 127.0, 122.3, 121.4, 121.1, 116.5, 112.0, 102.3, 55.5, 20.2. **HRMS** (ESI-TOF) calcd for  $C_{36}H_{31}N_4O_5^+ [M+H]^+$ : 599.2289, found:599.2291.

**6,6'-oxybis(4-fluoro-2-methyl-N-(quinolin-8-yl)benzamide) (2m)**



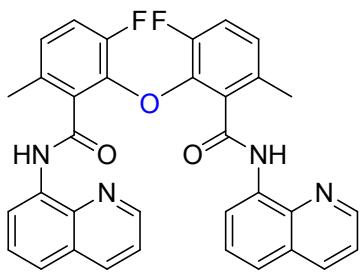
Yield: (30.0 mg, 52%); White solid; mp: 144.4-144.7 °C. **<sup>1</sup>H NMR** ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  9.92 (s, 2H), 8.71 (dd,  $J_1 = 7.6$  Hz,  $J_2 = 0.8$  Hz, 2H), 8.19 (dd,  $J_1 = 4.4$  Hz,  $J_2 = 1.6$  Hz, 2H), 7.86 (dd,  $J_1 = 8.0$  Hz,  $J_2 = 1.6$  Hz, 2H), 7.37 (t,  $J = 8.0$  Hz, 2H), 7.29 (dd,  $J_1 = 8.4$  Hz,  $J_2 = 1.2$  Hz, 2H), 7.12 (dd,  $J_1 = 8.0$  Hz,  $J_2 = 4.0$  Hz, 2H), 6.76 (dd,  $J_1 = 9.2$  Hz,  $J_2 = 2.4$  Hz, 2H), 6.69 (dd,  $J_1 = 9.6$  Hz,  $J_2 = 2.0$  Hz, 2H), 2.39 (s, 6H). **<sup>13</sup>C NMR** ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  164.3, 163.2 (d,  $J_{C-F} = 248.3$  Hz), 154.5 (d,  $J_{C-F} = 10.8$  Hz), 147.8, 140.3 (d,  $J_{C-F} = 9.0$  Hz), 137.9, 135.5, 134.1, 127.4, 127.0, 125.9 (d,  $J_{C-F} = 3.6$  Hz), 121.7, 121.2, 116.6, 113.3 (d,  $J_{C-F} = 21.6$  Hz), 104.4 (d,  $J_{C-F} = 25.2$  Hz), 19.7. **HRMS** (ESI-TOF) calcd for  $\text{C}_{34}\text{H}_{25}\text{F}_2\text{N}_4\text{O}_3^+ [\text{M}+\text{H}]^+$ : 575.1889, found: 575.1894.

#### 6,6'-oxybis(4-bromo-2-methyl-N-(quinolin-8-yl)benzamide) (2n)



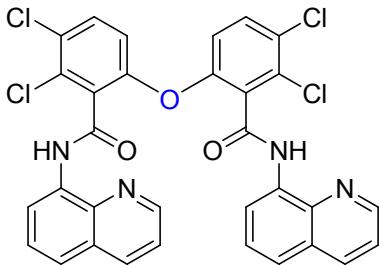
Yield: (41.7 mg, 60%); White solid; mp: 162.6-164.2 °C. **<sup>1</sup>H NMR** ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  9.94 (s, 2H), 8.73 (d,  $J = 7.2$  Hz, 2H), 8.21 (s, 2H), 7.88 (d,  $J = 8.0$  Hz, 2H), 7.39 (t,  $J = 8.0$  Hz, 2H), 7.31 (d,  $J = 8.0$  Hz, 2H), 7.18 (s, 2H), 7.14-7.09 (m, 4H), 2.37 (s, 6H). **<sup>13</sup>C NMR** ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  164.1, 153.8, 147.9, 139.7, 137.9, 135.6, 134.1, 129.3, 128.6, 127.4, 127.0, 123.7, 121.8, 121.3, 119.8, 116.6, 19.4. **HRMS** (ESI-TOF) calcd for  $\text{C}_{34}\text{H}_{25}\text{Br}_2\text{N}_4\text{O}_3^+ [\text{M}+\text{H}]^+$ : 695.0288, found: 695.0293.

#### 6,6'-oxybis(5-fluoro-2-methyl-N-(quinolin-8-yl)benzamide) (2o)



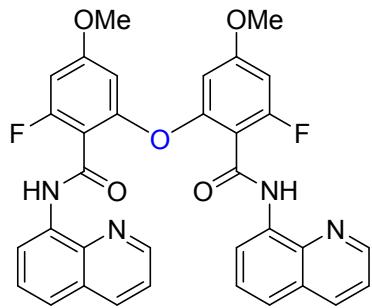
Yield: (23.0 mg, 40%); White solid; mp: 171.2-172.8 °C. **<sup>1</sup>H NMR** ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  10.17 (s, 2H), 8.81 (dd,  $J_1 = 7.6$  Hz,  $J_2 = 0.8$  Hz, 2H), 8.32 (dd,  $J_1 = 4.0$  Hz,  $J_2 = 1.6$  Hz, 2H), 7.98 (dd,  $J_1 = 8.0$  Hz,  $J_2 = 1.6$  Hz, 2H), 7.46 (t,  $J = 7.6$  Hz, 2H), 7.42 (dd,  $J_1 = 8.0$  Hz,  $J_2 = 1.2$  Hz, 2H), 7.22 (dd,  $J_1 = 8.0$  Hz,  $J_2 = 4.0$  Hz, 2H), 7.01 (dd,  $J_1 = 11.2$  Hz,  $J_2 = 8.8$  Hz, 2H), 6.91 (d,  $J = 4.4$  Hz, 2H), 2.36 (s, 6H). **<sup>13</sup>C NMR** ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  163.9 (d,  $J_{C-F} = 2.7$  Hz), 151.8 (d,  $J_{C-F} = 247.4$  Hz), 147.9, 141.6 (d,  $J_{C-F} = 9.0$  Hz), 138.3, 135.8, 134.4, 132.9 (d,  $J_{C-F} = 3.6$  Hz), 130.4, 127.7, 127.1, 126.3 (d,  $J_{C-F} = 7.2$  Hz), 121.9, 121.4, 117.3 (d,  $J_{C-F} = 18.1$  Hz), 116.9, 19.1. **HRMS** (ESI-TOF) calcd for  $\text{C}_{34}\text{H}_{25}\text{F}_2\text{N}_4\text{O}_3^+ [\text{M}+\text{H}]^+$ : 575.1889, found: 575.1888.

#### 6,6'-oxybis(2,3-dichloro-N-(quinolin-8-yl)benzamide) (2p)



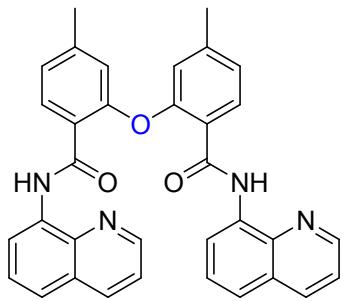
Yield: (29.1 mg, 45%); White solid; mp: 170.5-171.2 °C. **<sup>1</sup>H NMR** ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  9.93 (s, 2H), 8.69 (dd,  $J_1 = 7.6$  Hz,  $J_2 = 1.2$  Hz, 2H), 8.25 (dd,  $J_1 = 4.4$  Hz,  $J_2 = 1.6$  Hz, 2H), 7.88 (dd,  $J_1 = 8.4$  Hz,  $J_2 = 1.6$  Hz, 2H), 7.47 (d,  $J = 8.8$  Hz, 2H), 7.36 (t,  $J = 8.0$  Hz, 2H), 7.30 (dd,  $J_1 = 8.4$  Hz,  $J_2 = 1.6$  Hz, 2H), 7.15 (dd,  $J_1 = 8.4$  Hz,  $J_2 = 4.0$  Hz, 2H), 7.02 (d,  $J = 8.8$  Hz, 2H). **<sup>13</sup>C NMR** ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  161.2, 152.3, 147.9, 137.9, 135.7, 133.6, 131.7, 131.0, 131.0, 129.2, 127.4, 126.9, 122.2, 121.3, 118.7, 116.9. **HRMS** (ESI-TOF) calcd for  $\text{C}_{32}\text{H}_{19}\text{Cl}_4\text{N}_4\text{O}_3^+ [\text{M}+\text{H}]^+$ : 647.0206, found: 647.0215.

#### 6,6'-oxybis(2-fluoro-4-methoxy-N-(quinolin-8-yl)benzamide) (2q)



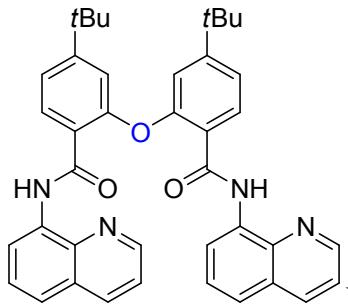
Yield: (23.1 mg, 38%); White solid; mp: >230 °C. **<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 400 MHz) δ 10.48 (s, 2H), 8.80 (d, J = 7.6 Hz, 2H), 8.30 (dd, J<sub>1</sub> = 4.4 Hz, J<sub>2</sub> = 1.6 Hz, 2H), 7.93 (dd, J<sub>1</sub> = 8.4 Hz, J<sub>2</sub> = 1.6 Hz, 2H), 7.46 (t, J = 8.0 Hz, 2H), 7.38 (dd, J<sub>1</sub> = 8.4 Hz, J<sub>2</sub> = 1.2 Hz, 2H), 7.14 (dd, J<sub>1</sub> = 8.4 Hz, J<sub>2</sub> = 4.4 Hz, 2H), 6.53 (dd, J<sub>1</sub> = 11.6 Hz, J<sub>2</sub> = 2.4 Hz, 2H), 6.46 (d, J = 1.6 Hz, 2H), 3.77 (s, 6H). **<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 100 MHz) δ 162.4 (d, J<sub>C-F</sub> = 13.5 Hz), 162.1 (d, J<sub>C-F</sub> = 250.1 Hz), 155.8 (d, J<sub>C-F</sub> = 9.0 Hz), 147.9, 138.4, 135.7, 134.5, 127.7, 127.1, 121.8, 121.3, 117.0, 110.8 (d, J<sub>C-F</sub> = 17.1 Hz), 101.7 (d, J<sub>C-F</sub> = 3.6 Hz), 98.6 (d, J<sub>C-F</sub> = 26.2 Hz), 55.9. **HRMS** (ESI-TOF) calcd for C<sub>34</sub>H<sub>25</sub>F<sub>2</sub>N<sub>4</sub>O<sub>5</sub><sup>+</sup> [M+H]<sup>+</sup>: 607.1788, found: 607.1793.

### 2,2'-oxybis(4-methyl-N-(quinolin-8-yl)benzamide) (2r)



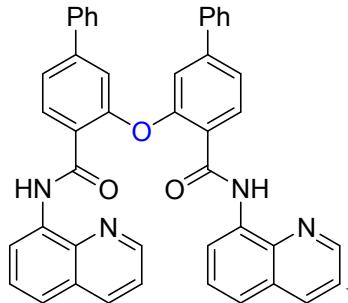
Yield: (24.3 mg, 45%); White solid; mp: >230 °C. **<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 400 MHz) δ 12.42 (s, 2H), 8.98 (d, J = 7.6 Hz, 2H), 8.42 (d, J = 8.0 Hz, 2H), 8.18 (d, J = 3.2 Hz, 2H), 7.89 (t, J = 8.0 Hz, 2H), 7.50 (t, J = 8.0 Hz, 2H), 7.36 (d, J = 8.4 Hz, 2H), 7.18 (d, J = 8.0 Hz, 2H), 7.13 (dd, J<sub>1</sub> = 8.0 Hz, J<sub>2</sub> = 4.0 Hz, 2H), 6.91 (s, 2H), 2.33 (s, 6H). **<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 100 MHz) δ 162.9, 154.7, 148.0, 144.6, 138.9, 135.7, 135.4, 132.2, 127.8, 127.2, 125.8, 123.3, 121.5, 120.2, 116.8, 21.5. **HRMS** (ESI-TOF) calcd for C<sub>34</sub>H<sub>27</sub>N<sub>4</sub>O<sub>3</sub><sup>+</sup> [M+H]<sup>+</sup>: 539.2078, found: 539.2079.

### 2,2'-oxybis(4-(*tert*-butyl)-N-(quinolin-8-yl)benzamide) (2s)



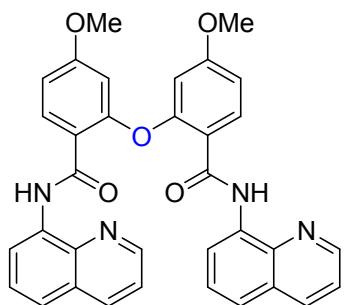
Yield: (32.4 mg, 52%); White solid; mp: >230 °C. **<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 400 MHz) δ 12.35 (s, 2H), 8.97 (dd, *J*<sub>1</sub> = 7.6 Hz, *J*<sub>2</sub> = 0.8 Hz, 2H), 8.46 (d, *J* = 8.4 Hz, 2H), 8.19 (dd, *J*<sub>1</sub> = 4.0 Hz, *J*<sub>2</sub> = 1.6 Hz, 2H), 7.88 (dd, *J*<sub>1</sub> = 8.0 Hz, *J*<sub>2</sub> = 1.6 Hz, 2H), 7.48 (t, *J* = 8.0 Hz, 2H), 7.39 (dd, *J*<sub>1</sub> = 8.0 Hz, *J*<sub>2</sub> = 1.6 Hz, 2H), 7.34 (dd, *J*<sub>1</sub> = 8.0 Hz, *J*<sub>2</sub> = 0.8 Hz, 2H), 7.13 (t, *J* = 4.0 Hz, 2H), 7.11 (d, *J* = 1.6 Hz, 2H), 1.25 (s, 18H). **<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 100 MHz) δ 163.0, 157.5, 154.6, 148.0, 138.9, 135.6, 135.5, 132.2, 127.7, 127.1, 123.1, 121.6, 121.5, 116.7, 116.6, 35.2, 31.0. **HRMS** (ESI-TOF) calcd for C<sub>40</sub>H<sub>39</sub>N<sub>4</sub>O<sub>3</sub><sup>+</sup> [M+H]<sup>+</sup>: 623.3017, found: 623.3018.

### 3,3''-oxybis(N-(quinolin-8-yl)-[1,1'-biphenyl]-4-carboxamide) (2t)



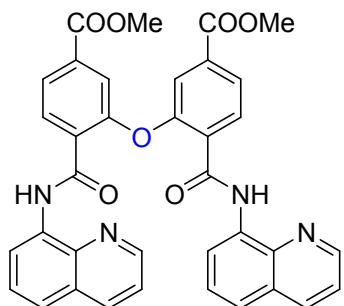
Yield: (27.9 mg, 42%); White solid; mp: 204.0-205.0 °C. **<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 400 MHz) δ 12.45 (s, 2H), 9.00 (dd, *J*<sub>1</sub> = 7.6 Hz, *J*<sub>2</sub> = 1.2 Hz, 2H), 8.59 (d, *J* = 8.0 Hz, 2H), 8.22 (dd, *J*<sub>1</sub> = 4.0 Hz, *J*<sub>2</sub> = 1.6 Hz, 2H), 7.93 (dd, *J*<sub>1</sub> = 8.4 Hz, *J*<sub>2</sub> = 1.6 Hz, 2H), 7.64 (dd, *J*<sub>1</sub> = 8.0 Hz, *J*<sub>2</sub> = 1.6 Hz, 2H), 7.54-7.50 (m, 6H), 7.41-7.33 (m, 10H), 7.16 (dd, *J*<sub>1</sub> = 8.4 Hz, *J*<sub>2</sub> = 4.4 Hz, 2H). **<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 100 MHz) δ 162.7, 155.0, 148.1, 146.6, 138.9, 138.8, 135.7, 135.3, 133.0, 128.9, 128.5, 127.8, 127.2, 124.7, 123.5, 121.7, 121.6, 118.1, 116.9. **HRMS** (ESI-TOF) calcd for C<sub>44</sub>H<sub>31</sub>N<sub>4</sub>O<sub>3</sub><sup>+</sup> [M+H]<sup>+</sup>: 663.2391, found: 663.2394.

### (2,2'-oxybis(4-methoxy-N-(quinolin-8-yl)benzamide) (2u)



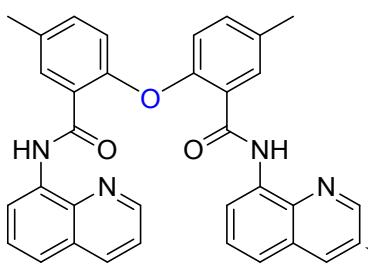
Yield: (28.0 mg, 49%); White solid; mp: 205.2-205.4 °C. **<sup>1</sup>H NMR** ( $\text{CDCl}_3$ , 400 MHz) δ 12.32 (s, 2H), 8.96 (dd,  $J_1 = 7.6$  Hz,  $J_2 = 0.8$  Hz, 2H), 8.48 (d,  $J = 9.2$  Hz, 2H), 8.21 (dd,  $J_1 = 4.4$  Hz,  $J_2 = 1.6$  Hz, 2H), 7.91 (dd,  $J_1 = 8.4$  Hz,  $J_2 = 1.6$  Hz, 2H), 7.50 (t,  $J = 8.0$  Hz, 2H), 7.36 (dd,  $J_1 = 8.4$  Hz,  $J_2 = 1.2$  Hz, 2H), 7.14 (dd,  $J_1 = 8.0$  Hz,  $J_2 = 4.0$  Hz, 2H), 6.91 (dd,  $J_1 = 8.8$  Hz,  $J_2 = 2.4$  Hz, 2H), 6.61 (d,  $J = 2.4$  Hz, 2H), 3.77 (s, 6H). **<sup>13</sup>C NMR** ( $\text{CDCl}_3$ , 100 MHz) δ 163.6, 162.7, 155.8, 148.0, 138.9, 135.7, 135.5, 133.8, 127.8, 127.2, 121.5, 121.4, 118.7, 116.7, 110.7, 105.3, 55.8. **HRMS** (ESI-TOF) calcd for  $\text{C}_{34}\text{H}_{27}\text{N}_4\text{O}_5^+$  [M+H]<sup>+</sup>: 571.1976, found: 571.1980.

#### dimethyl 3,3'-oxybis(4-(quinolin-8-ylcarbamoyl)benzoate) (2v)



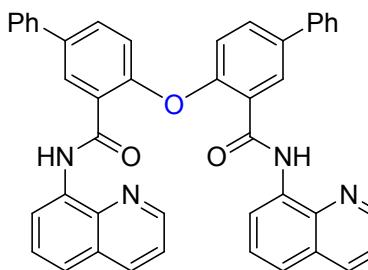
Yield: (21.6 mg, 35%); White solid; mp: 208.9-209.8 °C. **<sup>1</sup>H NMR** ( $\text{CDCl}_3$ , 400 MHz) δ 12.31 (s, 2H), 8.95 (dd,  $J_1 = 7.6$  Hz,  $J_2 = 1.2$  Hz, 2H), 8.61 (d,  $J = 8.4$  Hz, 2H), 8.14 (dd,  $J_1 = 4.4$  Hz,  $J_2 = 1.6$  Hz, 2H), 8.08 (dd,  $J_1 = 8.4$  Hz,  $J_2 = 1.2$  Hz, 2H), 7.95 (dd,  $J_1 = 8.4$  Hz,  $J_2 = 1.6$  Hz, 2H), 7.76 (d,  $J = 1.2$  Hz, 2H), 7.52 (t,  $J = 8.0$  Hz, 2H), 7.42 (dd,  $J_1 = 8.0$  Hz,  $J_2 = 0.8$  Hz, 2H), 7.17 (dd,  $J_1 = 8.4$  Hz,  $J_2 = 4.4$  Hz, 2H), 3.87 (s, 6H). **<sup>13</sup>C NMR** ( $\text{CDCl}_3$ , 100 MHz) δ 165.4, 161.6, 154.2, 148.2, 138.8, 135.9, 134.9, 134.8, 132.9, 129.9, 127.8, 127.2, 125.9, 122.2, 121.6, 120.7, 117.1, 52.6. **HRMS** (ESI-TOF) calcd for  $\text{C}_{36}\text{H}_{27}\text{N}_4\text{O}_7^+$  [M+H]<sup>+</sup>: 627.1874, found: 627.1883.

#### 6,6'-oxybis(3-methyl-N-(quinolin-8-yl)benzamide) (2w)



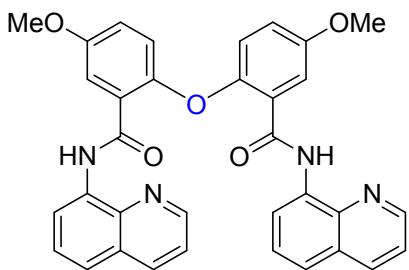
Yield: (34.0 mg, 63%); White solid; mp: 201.1-202.7 °C. **<sup>1</sup>H NMR** ( $\text{CDCl}_3$ , 400 MHz) δ 12.41 (s, 2H), 8.96 (d,  $J = 7.6$  Hz, 2H), 8.30 (s, 2H), 8.19 (d,  $J = 2.4$  Hz, 2H), 7.92 (d,  $J = 8.0$  Hz, 2H), 7.51 (t,  $J = 8.0$  Hz, 2H), 7.38 (d,  $J = 8.0$  Hz, 2H), 7.28 (d,  $J = 8.0$  Hz, 2H), 7.14 (dd,  $J_1 = 8.0$  Hz,  $J_2 = 4.0$  Hz, 2H), 7.01 (d,  $J = 8.0$  Hz, 2H), 2.45 (s, 6H). **<sup>13</sup>C NMR** ( $\text{CDCl}_3$ , 100 MHz) δ 163.1, 152.8, 148.1, 139.0, 135.7, 135.4, 134.3, 133.9, 132.5, 127.8, 127.2, 125.5, 121.6, 121.5, 119.6, 116.9, 20.8. **HRMS** (ESI-TOF) calcd for  $\text{C}_{34}\text{H}_{27}\text{N}_4\text{O}_3^+$  [M+H]<sup>+</sup>:539.2078, found: 539.2080.

#### 4,4''-oxybis(N-(quinolin-8-yl)-[1,1'-biphenyl]-3-carboxamide) (2x)



Yield: (29.8 mg, 45%); White solid; mp: >230 °C. **<sup>1</sup>H NMR** ( $\text{CDCl}_3$ , 400 MHz) δ 12.43 (s, 2H), 8.99 (dd,  $J_1 = 7.6$  Hz,  $J_2 = 0.8$  Hz, 2H), 8.79 (d,  $J = 2.4$  Hz, 2H), 8.22 (dd,  $J_1 = 4.0$  Hz,  $J_2 = 1.6$  Hz, 2H), 7.93 (dd,  $J_1 = 8.4$  Hz,  $J_2 = 1.6$  Hz, 2H), 7.76 (dd,  $J_1 = 8.4$  Hz,  $J_2 = 2.4$  Hz, 2H), 7.71 (d,  $J = 7.6$  Hz, 4H), 7.54-7.47 (m, 6H), 7.41-7.37 (m, 4H), 7.27 (d,  $J = 8.8$  Hz, 2H), 7.16 (dd,  $J_1 = 8.4$  Hz,  $J_2 = 4.0$  Hz, 2H). **<sup>13</sup>C NMR** ( $\text{CDCl}_3$ , 100 MHz) δ 162.7, 154.0, 148.2, 139.4, 138.9, 137.9, 135.8, 135.3, 131.7, 130.9, 129.0, 127.8, 127.7, 127.2, 127.1, 126.3, 121.8, 121.6, 120.2, 116.9. **HRMS** (ESI-TOF) calcd for  $\text{C}_{44}\text{H}_{31}\text{N}_4\text{O}_3^+$  [M+H]<sup>+</sup>:663.2391, found: 663.2394.

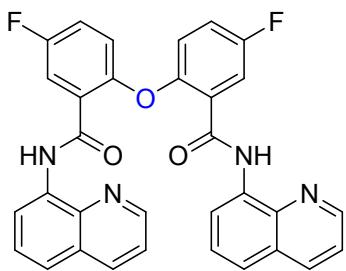
#### 6,6''-oxybis(3-methoxy-N-(quinolin-8-yl)benzamide) (2y)



Yield: (24.0 mg, 42%); White solid; mp: 228.0-229.2 °C. **<sup>1</sup>H NMR** ( $\text{CDCl}_3$ , 400 MHz) δ 12.50 (s, 2H), 8.97 (dd,  $J_1 = 7.6$  Hz,  $J_2 = 1.2$  Hz, 2H), 8.21

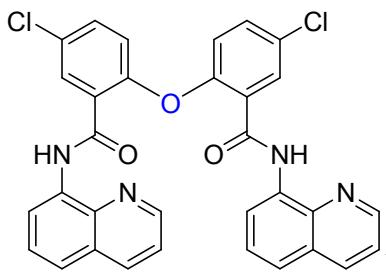
(dd,  $J_1$  = 4.4 Hz,  $J_2$  = 2.0 Hz, 2H), 8.01 (t,  $J$  = 1.6 Hz, 2H), 7.93 (dd,  $J_1$  = 8.0 Hz,  $J_2$  = 1.6 Hz, 2H), 7.51 (t,  $J$  = 8.0 Hz, 2H), 7.39 (dd,  $J_1$  = 8.4 Hz,  $J_2$  = 1.2 Hz, 2H), 7.16 (dd,  $J_1$  = 8.0 Hz,  $J_2$  = 4.0 Hz, 2H), 7.04 (d,  $J$  = 1.2 Hz, 4H), 3.92 (s, 6H).  $^{13}\text{C}$  NMR (CDCl<sub>3</sub>, 100 MHz) δ 162.7, 156.2, 148.8, 148.1, 138.9, 135.7, 135.3, 127.8, 127.2, 126.4, 121.7, 121.5, 120.9, 120.3, 116.9, 115.0, 55.9. HRMS (ESI-TOF) calcd for C<sub>34</sub>H<sub>27</sub>N<sub>4</sub>O<sub>5</sub><sup>+</sup> [M+H]<sup>+</sup>: 571.1976, found: 571.1981.

#### 6,6'-oxybis(3-fluoro-N-(quinolin-8-yl)benzamide) (2z)



Yield: (25.2 mg, 46%); White solid; mp: 207.6-208.9 °C.  $^1\text{H}$  NMR (CDCl<sub>3</sub>, 400 MHz) δ 12.35 (s, 2H), 8.93 (dd,  $J_1$  = 8.0 Hz,  $J_2$  = 1.2 Hz, 2H), 8.22-8.19 (m, 4H), 7.95 (dd,  $J_1$  = 8.0 Hz,  $J_2$  = 1.6 Hz, 2H), 7.51 (t,  $J$  = 8.0 Hz, 2H), 7.42 (dd,  $J_1$  = 8.0 Hz,  $J_2$  = 1.2 Hz, 2H), 7.24-7.17 (m, 4H), 7.10 (dd,  $J_1$  = 9.2 Hz,  $J_2$  = 4.4 Hz, 2H).  $^{13}\text{C}$  NMR (CDCl<sub>3</sub>, 100 MHz) δ 161.3 (d,  $J_{C-F}$  = 1.8 Hz), 159.3 (d,  $J_{C-F}$  = 243.8 Hz), 150.6 (d,  $J_{C-F}$  = 2.8 Hz), 148.1, 138.8, 135.9, 134.8, 127.8, 127.7 (d,  $J_{C-F}$  = 6.4 Hz), 122.1, 121.7, 121.1 (d,  $J_{C-F}$  = 8.1 Hz), 120.3 (d,  $J_{C-F}$  = 24.4 Hz), 118.7 (d,  $J_{C-F}$  = 24.3 Hz), 117.1. HRMS (ESI-TOF) calcd for C<sub>32</sub>H<sub>21</sub>F<sub>2</sub>N<sub>4</sub>O<sub>3</sub><sup>+</sup> [M+H]<sup>+</sup>: 547.1576, found: 547.1571.

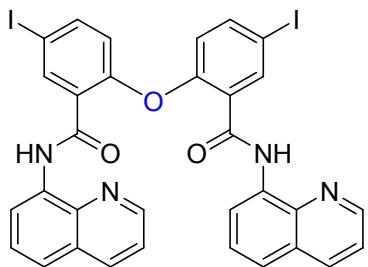
#### 6,6'-oxybis(3-chloro-N-(quinolin-8-yl)benzamide) (2aa)



Yield: (24.3 mg, 42%); White solid; mp: 213.5-214.6 °C.  $^1\text{H}$  NMR (CDCl<sub>3</sub>, 400 MHz) δ 12.21 (s, 2H), 8.92 (dd,  $J_1$  = 7.6 Hz,  $J_2$  = 1.2 Hz, 2H), 8.63 (d,  $J$  = 2.8 Hz, 2H), 8.19 (dd,  $J_1$  = 4.0 Hz,  $J_2$  = 1.2 Hz, 2H), 7.96 (dd,  $J_1$  = 8.4 Hz,  $J_2$  = 1.6 Hz, 2H), 7.62 (dd,  $J_1$  = 8.8 Hz,  $J_2$  = 2.4 Hz, 2H), 7.52 (t,  $J$  = 8.0 Hz, 2H), 7.43 (dd,  $J_1$  = 8.4 Hz,  $J_2$  = 1.2 Hz, 2H), 7.20 (dd,  $J_1$  = 8.0 Hz,  $J_2$  = 4.4 Hz, 2H), 7.02 (d,  $J$  = 8.8 Hz, 2H).  $^{13}\text{C}$  NMR (CDCl<sub>3</sub>, 100 MHz) δ 161.0, 153.3, 148.2, 138.8, 136.2, 135.9, 135.3, 134.8, 127.8,

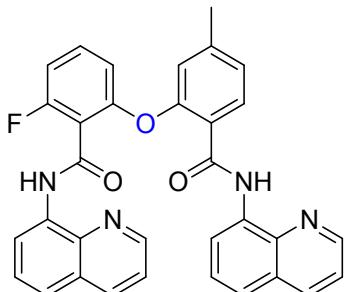
127.2, 122.1, 121.7, 121.3, 118.2, 117.1. **HRMS** (ESI-TOF) calcd for  $C_{32}H_{21}Cl_2N_4O_3^+$  [M]<sup>+</sup>: 579.0985, found: 579.0992.

**6,6'-oxybis(3-iodo-N-(quinolin-8-yl)benzamide) (2ab)**



Yield: (26.7 mg, 35%); White solid; mp: 228.6-229.6 °C. **<sup>1</sup>H NMR** ( $CDCl_3$ , 400 MHz) δ 12.18 (s, 2H), 8.91 (dd,  $J_1 = 7.6$  Hz,  $J_2 = 1.2$  Hz, 2H), 8.80 (d,  $J = 2.0$  Hz, 2H), 8.19 (dd,  $J_1 = 4.0$  Hz,  $J_2 = 1.6$  Hz, 2H), 7.96 (dd,  $J_1 = 8.4$  Hz,  $J_2 = 1.6$  Hz, 2H), 7.80 (dd,  $J_1 = 8.8$  Hz,  $J_2 = 2.4$  Hz, 2H), 7.52 (t,  $J = 8.0$  Hz, 2H), 7.43 (dd,  $J_1 = 8.4$  Hz,  $J_2 = 1.2$  Hz, 2H), 7.20 (dd,  $J_1 = 8.4$  Hz,  $J_2 = 4.4$  Hz, 2H), 6.88 (d,  $J = 8.8$  Hz, 2H). **<sup>13</sup>C NMR** ( $CDCl_3$ , 100 MHz) δ 160.9, 154.1, 148.2, 142.1, 141.2, 138.8, 135.9, 134.8, 128.0, 127.8, 127.2, 122.1, 121.7, 121.5, 117.1, 88.6. **HRMS** (ESI-TOF) calcd for  $C_{32}H_{21}I_2N_4O_3^+$  [M+H]<sup>+</sup>: 762.9698, found: 762.9705.

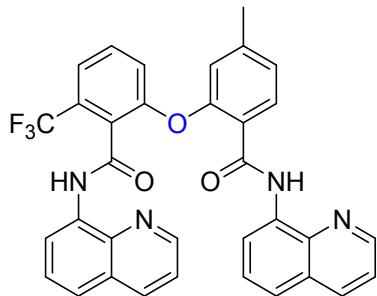
**2-(3-fluoro-2-(quinolin-8-ylcarbamoyl)phenoxy)-4-methyl-N-(quinolin-8-yl)benzamide (3a)**



Yield: (30.4 mg, 28%); White solid; mp: 180.5-181.2 °C. **<sup>1</sup>H NMR** ( $CDCl_3$ , 400 MHz) δ 12.04 (s, 1H), 10.85 (s, 1H), 8.93-8.87 (m, 2H), 8.38 (dd,  $J_1 = 4.0$  Hz,  $J_2 = 1.6$  Hz, 1H), 8.23 (d,  $J = 8.0$  Hz, 1H), 8.01-7.95 (m, 2H), 7.77 (dd,  $J_1 = 4.0$  Hz,  $J_2 = 1.6$  Hz, 1H), 7.56-7.38 (m, 5H), 7.20 (dd,  $J_1 = 8.0$  Hz,  $J_2 = 4.0$  Hz, 1H), 7.13 (dd,  $J_1 = 8.4$  Hz,  $J_2 = 4.0$  Hz, 2H), 7.08 (t,  $J = 8.8$  Hz, 1H), 6.98 (s, 1H), 6.85 (d,  $J = 8.4$  Hz, 1H), 2.36 (s, 3H). **<sup>13</sup>C NMR** ( $CDCl_3$ , 100 MHz) δ 162.6, 162.5, 160.1, 159.9, 155.3, 155.2, 154.5, 148.3, 147.7, 144.7, 139.1, 138.5, 135.9, 135.8, 135.4, 134.4, 132.1, 132.0, 131.9, 127.9, 127.7, 127.3, 127.1, 126.0, 123.1, 122.1, 121.6, 121.5, 121.4, 120.8, 118.3, 117.2, 117.2, 114.9, 114.8, 112.1, 111.9, 21.4. **HRMS** (ESI-TOF) calcd for  $C_{33}H_{24}FN_4O_3^+$

$[M+H]^+$ : 543.1827, found: 543.1823.

**4-methyl-N-(quinolin-8-yl)-2-(quinolin-8-ylcarbamoyl)-3-(trifluoromethyl)phenoxybenzamide (3b)**

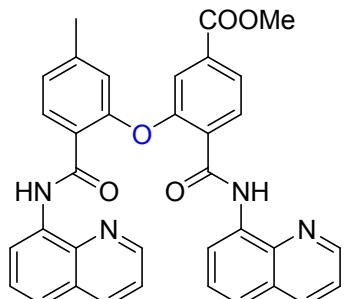


Yield: (39.1 mg, 33%); White solid; mp: 185.2-187.8 °C.  $^1\text{H}$

**NMR** ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  11.93 (s, 1H), 10.60 (s, 1H), 8.89-8.84 (m, 2H), 8.27 (dd,  $J_1 = 4.4$  Hz,  $J_2 = 2.0$  Hz, 1H), 8.22 (d,  $J = 8.0$  Hz, 1H), 8.04 (dd,  $J_1 = 8.0$  Hz,  $J_2 = 1.2$  Hz, 1H), 7.93 (dd,  $J_1 = 8.0$  Hz,  $J_2 = 1.6$  Hz, 1H), 7.61 (d,  $J = 7.6$  Hz, 1H), 7.56-7.46 (m, 5H), 7.42 (dd,  $J_1 = 8.4$  Hz,  $J_2 = 1.2$  Hz, 1H), 7.25-7.21 (m, 2H), 7.13 (d,  $J = 8.0$  Hz, 1H), 7.08 (dd,  $J_1 = 8.4$  Hz,  $J_2 = 4.4$  Hz, 1H), 6.98 (s, 1H), 2.35 (s, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  162.5, 162.4, 154.9, 154.3, 148.1, 147.5, 144.9, 139.2, 138.5, 136.0, 135.8, 135.3, 134.3, 132.1, 131.1, 130.0, 129.7, 128.1, 128.1, 127.9, 127.7, 127.3, 127.1, 126.3, 123.3, 122.5, 122.3, 122.1, 121.9, 121.8, 121.8, 121.7, 121.6, 121.3, 121.2, 117.5, 117.4, 27.0, 26.9, 21.3.

**HRMS** (ESI-TOF) calcd for  $\text{C}_{34}\text{H}_{24}\text{F}_3\text{N}_4\text{O}_3^+$   $[M+H]^+$ : 593.1795, found: 593.1792.

**methyl3-(5-methyl-2-(quinolin-8-ylcarbamoyl)phenoxy)-4-(quinolin-8-ylcarbamoyl)benzoate (3c)**

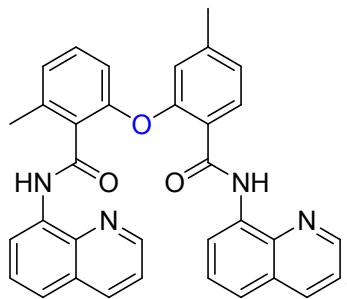


Yield: (30.3 mg, 26%); White solid; mp: 216.6-219.6 °C.  $^1\text{H}$

**NMR** ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  12.43 (s, 1H), 12.29 (s, 1H), 8.98-8.94 (t,  $J = 6.8$  Hz, 2H), 8.60 (d,  $J = 8.0$  Hz, 1H), 8.42 (d,  $J = 8.4$  Hz, 1H), 8.18 (dd,  $J_1 = 4.4$  Hz,  $J_2 = 1.6$  Hz, 1H), 8.14 (dd,  $J_1 = 4.4$  Hz,  $J_2 = 1.6$  Hz, 1H), 8.03 (dd,  $J_1 = 8.0$  Hz,  $J_2 = 1.6$  Hz, 1H), 7.95 (dd,  $J_1 = 3.6$  Hz,  $J_2 = 1.6$  Hz, 1H), 7.93 (dd,  $J_1 = 4.0$  Hz,  $J_2 = 2.0$  Hz, 1H), 7.78 (d,  $J = 1.6$  Hz, 1H), 7.51 (td,  $J_1 = 8.0$  Hz,  $J_2 = 1.2$  Hz, 2H), 7.43-7.38 (m, 2H), 7.22 (d,  $J = 8.0$  Hz, 1H), 7.18-7.13 (m, 2H), 6.88 (s, 1H), 3.87 (s, 3H), 2.35 (s, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  165.6, 162.7,

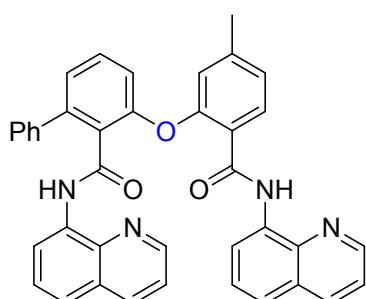
161.9, 154.6, 154.3, 148.2, 147.9, 144.8, 138.9, 135.8, 135.7, 135.3, 134.9, 134.7, 132.6, 132.5, 130.3, 129.8, 129.2, 127.8, 127.7, 127.2, 127.1, 126.2, 125.4, 123.4, 122.1, 121.6, 121.6, 121.5, 120.9, 120.0, 117.1, 116.9, 52.6, 21.5. **HRMS** (ESI-TOF) calcd for C<sub>35</sub>H<sub>27</sub>N<sub>4</sub>O<sub>5</sub><sup>+</sup> [M+H]<sup>+</sup>:583.1976, found:583.1975.

**4-methyl-2-(3-methyl-2-(quinolin-8-ylcarbamoyl)phenoxy)-N-(quinolin-8-yl)benzamide (3d)**



Yield: (32.2 mg, 30%); White solid; mp: 140.4-143.6 °C. **<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 400 MHz) δ 12.20 (s, 1H), 10.52 (s, 1H), 8.85-8.82 (m, 2H), 8.32 (dd, J<sub>1</sub> = 4.4 Hz, J<sub>2</sub> = 1.6 Hz, 1H), 8.18 (d, J = 8.4 Hz, 1H), 8.03 (dd, J<sub>1</sub> = 8.4 Hz, J<sub>2</sub> = 1.6 Hz, 1H), 7.93 (dd, J<sub>1</sub> = 8.0 Hz, J<sub>2</sub> = 1.6 Hz, 1H), 7.56 (dd, J<sub>1</sub> = 4.4 Hz, J<sub>2</sub> = 1.6 Hz, 1H), 7.51-7.39 (m, 4H), 7.32 (t, J = 8.0 Hz, 1H), 7.25 (dd, J<sub>1</sub> = 8.0 Hz, J<sub>2</sub> = 4.4 Hz, 1H), 7.17 (d, J = 7.2 Hz, 1H), 7.09-7.05 (m, 2H), 6.95 (s, 1H), 6.93 (d, J = 8.4 Hz, 1H), 2.66 (s, 3H), 2.34 (s, 3H). **<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 100 MHz) δ 165.0, 162.8, 155.4, 153.7, 148.2, 147.4, 144.5, 139.3, 138.8, 138.5, 135.8, 135.7, 135.6, 134.5, 131.9, 130.7, 129.7, 127.8, 127.7, 127.3, 127.1, 126.5, 125.3, 122.5, 121.9, 121.5, 121.4, 121.2, 120.3, 117.1, 117.0, 21.4, 19.9. **HRMS** (ESI-TOF) calcd for C<sub>34</sub>H<sub>27</sub>N<sub>4</sub>O<sub>3</sub><sup>+</sup> [M+H]<sup>+</sup>:539.2078, found:539.2074.

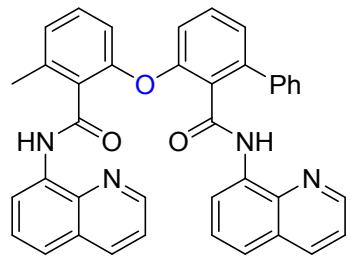
**3-(5-methyl-2-(quinolin-8-ylcarbamoyl)phenoxy)-N-(quinolin-8-yl)-[1,1'-biphenyl]-2-carboxamide (3e)**



Yield: (36.0 mg, 30%); White solid; mp: 193.2-195.0 °C. **<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 400 MHz) δ 12.22 (s, 1H), 10.47 (s, 1H), 8.89 (dd, J<sub>1</sub> = 7.6 Hz, J<sub>2</sub> = 0.8 Hz, 1H), 8.63 (dd, J<sub>1</sub> = 7.2 Hz, J<sub>2</sub> = 1.6 Hz, 1H), 8.35 (dd, J<sub>1</sub> = 4.4 Hz, J<sub>2</sub> = 1.6 Hz, 1H), 8.21 (d, J = 8.0 Hz, 1H), 8.01 (dd, J<sub>1</sub> = 8.0 Hz, J<sub>2</sub> = 1.6 Hz, 1H), 7.92 (dd, J<sub>1</sub> = 8.0 Hz, J<sub>2</sub> = 1.6 Hz,

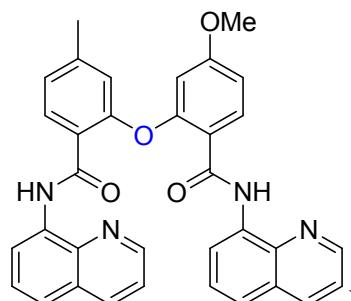
1H), 7.67 (d,  $J$  = 7.2 Hz, 2H), 7.58 (dd,  $J_1$  = 4.0 Hz,  $J_2$  = 1.6 Hz, 1H), 7.55 (t,  $J$  = 8.0 Hz, 1H), 7.50-7.45 (m, 2H), 7.41-7.35 (m, 5H), 7.31 (d,  $J$  = 7.2 Hz, 1H), 7.19 (dd,  $J_1$  = 8.0 Hz,  $J_2$  = 4.4 Hz, 1H), 7.08 (d,  $J$  = 8.4 Hz, 2H), 7.07 (d,  $J$  = 8.4 Hz, 1H), 7.03(s, 1H), 2.35 (s, 3H).  $^{13}\text{C}$  NMR (CDCl<sub>3</sub>, 100 MHz) δ 164.7, 162.9, 155.3, 154.2, 148.2, 147.4, 144.6, 142.6, 139.9, 139.3, 138.4, 135.8, 135.7, 135.6, 134.4, 131.9, 130.9, 129.2, 128.6, 127.9, 127.8, 127.7, 127.3, 127.1, 126.2, 125.5, 122.8, 121.8, 121.4, 121.2, 120.7, 118.4, 117.2, 117.0, 21.4. HRMS (ESI-TOF) calcd for C<sub>39</sub>H<sub>29</sub>N<sub>4</sub>O<sub>3</sub><sup>+</sup> [M+H]<sup>+</sup>:601.2234, found:601.2230.

**3-(3-methyl-2-(quinolin-8-ylcarbamoyl)phenoxy)-N-(quinolin-8-yl)-[1,1'-biphenyl]-4-carboxamide (3f)**



Yield: (33.6 mg, 28%); White solid; mp: 215.2-217.7 °C.  $^1\text{H}$  NMR (CDCl<sub>3</sub>, 400 MHz) δ 9.99 (s, 1H), 9.72 (s, 1H), 8.76 (dd,  $J_1$  = 7.6 Hz,  $J_2$  = 0.8 Hz, 1H), 8.53 (dd,  $J_1$  = 7.2 Hz,  $J_2$  = 1.2 Hz, 1H), 8.14 (dd,  $J_1$  = 4.4 Hz,  $J_2$  = 1.6 Hz, 1H), 8.08 (dd,  $J_1$  = 4.0 Hz,  $J_2$  = 1.6 Hz, 1H), 7.79 (td,  $J_1$  = 8.8 Hz,  $J_2$  = 1.6 Hz, 2H), 7.46-7.40 (m, 3H), 7.36-7.26 (m, 3H), 7.23-7.16 (m, 5H), 7.13-7.01 (m, 6H), 2.42 (s, 3H).  $^{13}\text{C}$  NMR (CDCl<sub>3</sub>, 100 MHz) δ 165.4, 164.9, 154.6, 153.6, 147.7, 147.5, 141.9, 139.6, 138.0, 137.9, 137.8, 135.4, 135.3, 134.3, 134.2, 130.5, 130.4, 129.9, 129.4, 128.8, 128.5, 128.2, 127.5, 127.4, 127.3, 126.9, 126.1, 125.3, 121.5, 121.2, 121.1, 120.9, 117.5, 117.2, 116.6, 116.4, 19.5. HRMS (ESI-TOF) calcd for C<sub>39</sub>H<sub>29</sub>N<sub>4</sub>O<sub>3</sub><sup>+</sup> [M+H]<sup>+</sup>:601.2234, found:601.2232.

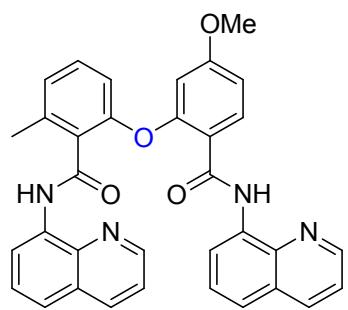
**4-methoxy-2-(5-methyl-2-(quinolin-8-ylcarbamoyl)phenoxy)-N-(quinolin-8-yl)benzamide (3g)**



Yield: (44.4 mg, 40%); White solid; mp: 210.7-211.2 °C.  $^1\text{H}$  NMR (CDCl<sub>3</sub>, 400 MHz) δ 12.38 (s, 1H), 12.35 (s, 1H), 8.97 (d,  $J$  = 7.6 Hz, 2H), 8.48 (d,  $J$  = 8.8 Hz, 1H), 8.41 (d,  $J$  = 8.0 Hz, 1H), 8.21-8.19 (m, 2H), 7.91 (d,  $J$  = 8.4 Hz, 2H), 7.50 (t,

$J = 8.0$  Hz, 2H), 7.38 (dd,  $J_1 = 3.2$  Hz,  $J_2 = 1.2$  Hz, 1H), 7.36 (dd,  $J_1 = 3.2$  Hz,  $J_2 = 1.2$  Hz, 1H), 7.19 (d,  $J = 8.4$  Hz, 1H), 7.16-7.12 (m, 2H), 6.94 (s, 1H), 6.91 (dd,  $J_1 = 8.8$  Hz,  $J_2 = 2.4$  Hz, 1H), 6.59 (d,  $J = 6.4$  Hz, 1H), 3.77 (s, 3H), 2.34 (s, 3H).  $^{13}\text{C}$  NMR (CDCl<sub>3</sub>, 100 MHz) δ 163.6, 162.9, 162.8, 156.2, 154.4, 148.0, 148.0, 144.6, 138.9, 135.7, 135.6, 135.4, 133.8, 132.3, 127.8, 127.2, 127.1, 125.9, 123.3, 121.5, 121.4, 121.3, 120.2, 118.7, 116.8, 116.7, 110.5, 105.3, 55.8, 21.5. HRMS (ESI-TOF) calcd for C<sub>34</sub>H<sub>27</sub>N<sub>4</sub>O<sub>4</sub><sup>+</sup> [M+H]<sup>+</sup>:555.2027, found:555.2029.

**4-methoxy-2-(3-methyl-2-(quinolin-8-ylcarbamoyl)phenoxy)-N-(quinolin-8-yl)benzamide (3h)**



Yield: (35.5 mg, 32%); White solid; mp: 146.8-148.1 °C.  $^1\text{H}$  NMR (CDCl<sub>3</sub>, 400 MHz) δ 12.14 (s, 1H), 10.51 (s, 1H), 8.97 (d,  $J = 7.6$  Hz, 2H), 8.84-8.80 (m, 2H), 8.34 (dd,  $J_1 = 4.0$  Hz,  $J_2 = 1.6$  Hz, 1H), 8.24 (d,  $J = 8.8$  Hz, 1H), 8.03 (dd,  $J_1 = 8.4$  Hz,  $J_2 = 1.6$  Hz, 1H), 7.93 (dd,  $J_1 = 8.4$  Hz,  $J_2 = 1.6$  Hz, 1H), 7.55 (dd,  $J_1 = 4.0$  Hz,  $J_2 = 1.6$  Hz, 1H), 7.52-7.39 (m, 4H), 7.34 (t,  $J = 8.0$  Hz, 1H), 7.26 (dd,  $J_1 = 8.4$  Hz,  $J_2 = 4.0$  Hz, 1H), 7.18 (d,  $J = 7.6$  Hz, 1H), 7.07 (dd,  $J_1 = 8.0$  Hz,  $J_2 = 4.0$  Hz, 1H), 6.97 (d,  $J = 8.0$  Hz, 1H), 3.79 (s, 3H), 2.65 (s, 3H).  $^{13}\text{C}$  NMR (CDCl<sub>3</sub>, 100 MHz) δ 164.9, 163.7, 162.6, 156.9, 153.4, 148.2, 147.4, 139.3, 138.8, 138.5, 135.8, 135.7, 135.6, 134.5, 133.4, 130.7, 129.8, 127.8, 127.7, 127.3, 127.1, 126.8, 121.9, 121.4, 121.2, 121.2, 117.8, 117.2, 117.0, 110.4, 104.9, 55.7, 19.9. HRMS (ESI-TOF) calcd for C<sub>34</sub>H<sub>27</sub>N<sub>4</sub>O<sub>4</sub><sup>+</sup> [M+H]<sup>+</sup>:555.2027, found:555.2026.

#### 4. Crystal Structure of Product 2a and 2b

The ORTEP diagram and Crystal Parameters of **2a** and **2b** wherein thermal ellipsoids are drawn at 30% probability level. The crystals of suitable quality were obtained from EA/PE within 2 days under aerobic conditions, and were analyzed by single crystal diffractometer (Varian, Gemini A Ultra). Atomic coordinates, bond lengths, bond angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. CCDC deposit number of **2a** and **2b** is 1952681 and 1907742 respectively.

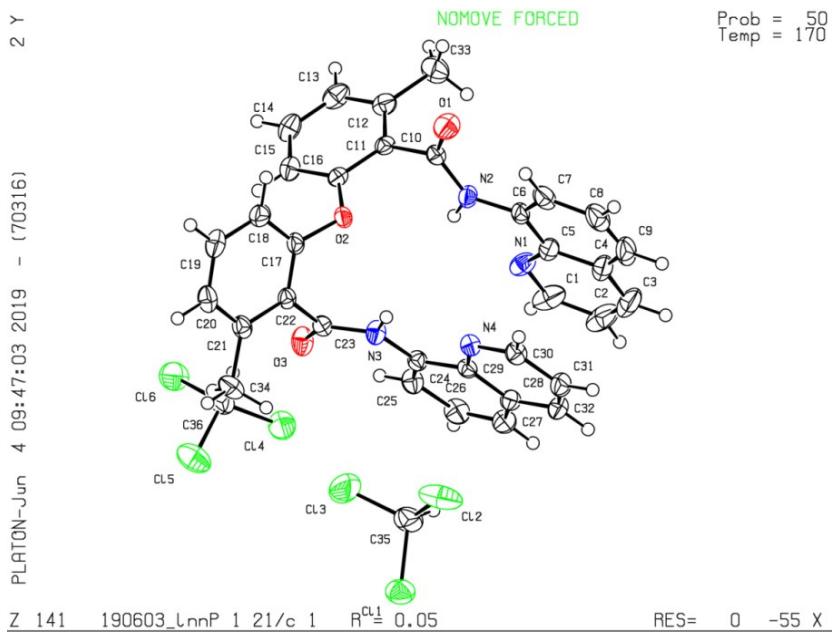


Figure S1: Crystal XRD image of **2a**

### Datablock: 190603\_Lnn\_4\_17\_4\_0m

Bond precision:	C-C = 0.0035 Å	Wavelength=0.71073	
Cell:	a=12.1345 (3) alpha=90	b=14.3083 (3) beta=104.081(1)	c=20.8054 (6) gamma=90
Temperature:	170 K		
	Calculated	Reported	
Volume	3503.78(15)	3503.78(15)	
Space group	P 21/c	P 1 21/c 1	
Hall group	-P 2ybc	-P 2ybc	
Moiety formula	C34 H26 N4 O3, 2(C H Cl3)	2(C H Cl3), C34 H26 N4 O3	
Sum formula	C36 H28 Cl6 N4 O3	C36 H28 Cl6 N4 O3	
Mr	777.32	777.32	
Dx, g cm <sup>-3</sup>	1.474	1.474	
Z	4	4	
Mu (mm <sup>-1</sup> )	0.534	0.534	
F000	1592.0	1592.0	
F000'	1596.07		
h, k, lmax	15,17,26	15,17,25	
Nref	7163	7156	
Tmin, Tmax	0.784, 0.843	0.683, 0.745	
Tmin'	0.782		

Correction method= # Reported T Limits: Tmin=0.683 Tmax=0.745  
AbsCorr = MULTI-SCAN

Data completeness= 0.999	Theta (max)= 26.386
R(reflections)= 0.0509( 6398)	wR2(reflections)= 0.1308( 7156)
S = 1.035	Npar= 444

Figure S2: Crystal data of **2a**

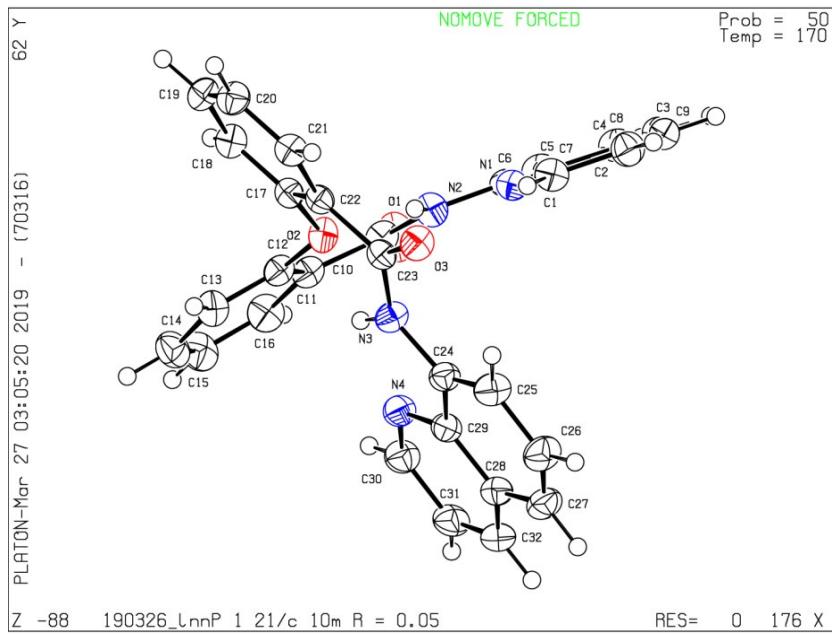


Figure S3: Crystal XRD image of **2b**

### Datablock: 190326\_Lnn\_3\_160\_13\_0m

Bond precision: C-C = 0.0026 Å Wavelength=0.71073

Cell:  $a=11.0659(3)$   $b=20.0575(6)$   $c=11.9398(3)$   
 $\alpha=90^\circ$   $\beta=110.868(1)$   $\gamma=90^\circ$   
 Temperature: 170 K

	Calculated	Reported
Volume	2476.25(12)	2476.25(12)
Space group	P 21/c	P 1 21/c 1
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C32 H22 N4 O3	C32 H22 N4 O3
Sum formula	C32 H22 N4 O3	C32 H22 N4 O3
Mr	510.54	510.53
Dx, g cm <sup>-3</sup>	1.369	1.369
Z	4	4
μ (mm <sup>-1</sup> )	0.090	0.090
F000	1064.0	1064.0
F000'	1064.45	
h, k, lmax	14, 25, 15	14, 25, 15
Nref	5463	5446
Tmin, Tmax	0.963, 0.969	0.698, 0.746
Tmin'	0.963	

Correction method= # Reported T Limits: Tmin=0.698 Tmax=0.746  
 AbsCorr = MULTI-SCAN

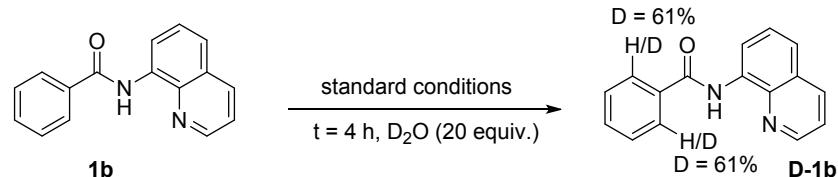
Data completeness= 0.997 Theta (max)= 27.107  
 R(reflections)= 0.0463( 4689) wR2(reflections)= 0.1237( 5446)  
 S = 1.059 Npar= 352

Figure S4: Crystal data of **2b**

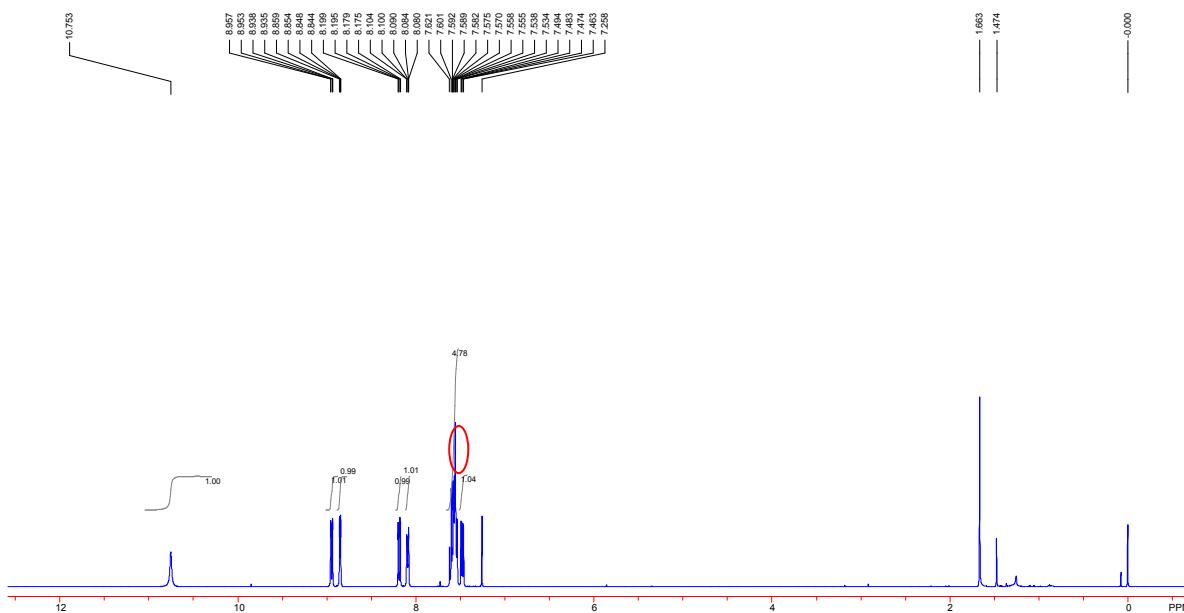
## 5. The Mechanistic Investigations

### 5.1. H/D exchange and kinetic isotopic effect experiments of synthesis of diaryl ether

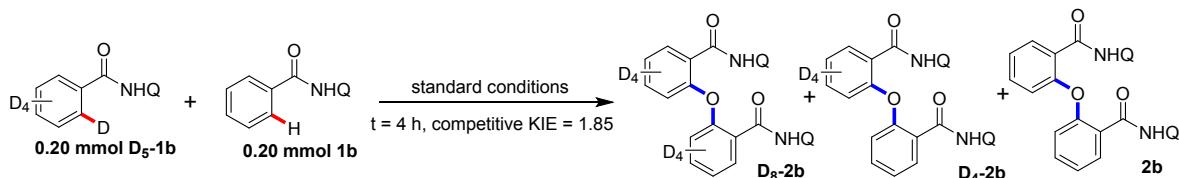
#### 5.1.1. H/D exchange of synthesis of diaryl ether



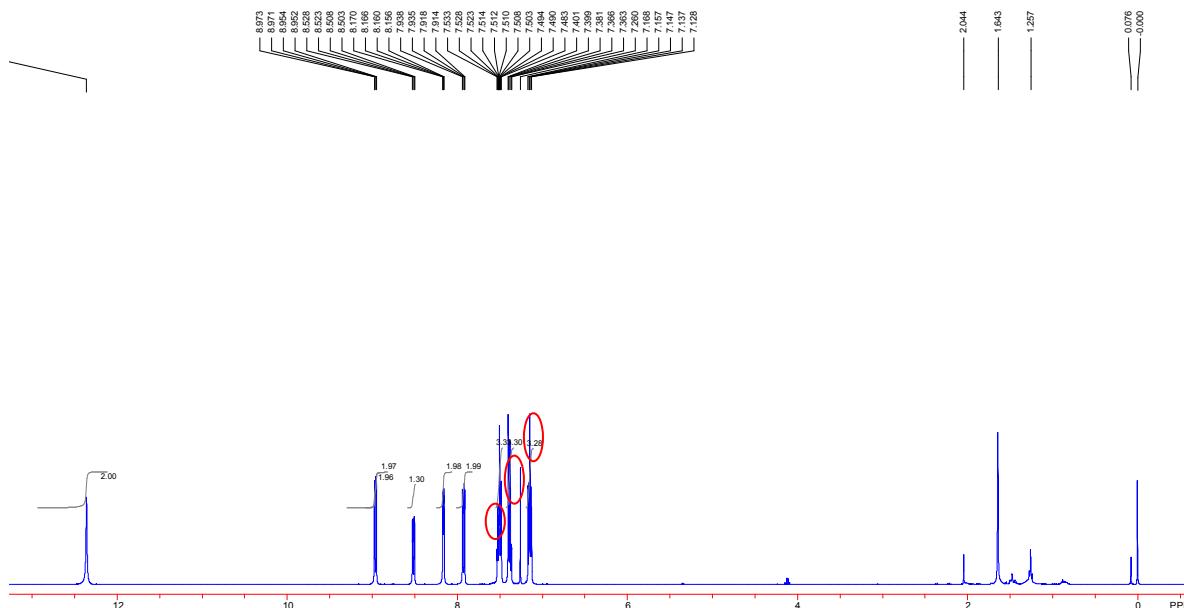
To a 25 mL seal tube with a stir bar was added benzamide (**1b**, 0.20 mmol), Ni(OAc)<sub>2</sub> (0.04 mmol, 7.0 mg), Ag<sub>3</sub>PO<sub>4</sub> (0.40 mmol, 166 mg), AdCOOK (0.40 mmol, 90 mg) and D<sub>2</sub>O (4.0 mmol, 80 mg) in DMAc (2.0 mL), the vial was evacuated and filled with O<sub>2</sub> atmosphere and stirred by oil bath at 140 °C for 4 h, then cooled to room temperature, filtered through a pad of celite, and then washed with EtOAc (10 mL×3), washed by 1 mol/L NaOH solution (20 mL) three times and saturated NaCl (20 mL), then dried with sodium sulfate. Organic solvents were removed under reduced pressure and the crude reaction mixture was purified by column chromatography on silica gel column with EtOAc/petroleum ether (1:10 v/v) as an eluent to afford the desired product **D-1b** (H/D D = 61%).



### 5.1.2. Competitive kinetic isotopic effect of synthesis of diaryl ether

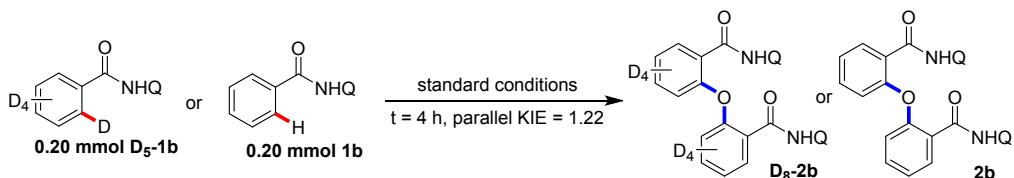


To a 25 mL seal tube with a stir bar was added benzamide (**D<sub>5</sub>-1b**, 0.20 mmol), benzamide (**1b**, 0.20 mmol), Ni(OAc)<sub>2</sub> (0.04 mmol, 7.0 mg), Ag<sub>3</sub>PO<sub>4</sub> (0.40 mmol, 166 mg) and AdCOOK (0.40 mmol, 90 mg) in DMAc (2.0 mL), the vial was evacuated and filled with O<sub>2</sub> atmosphere and stirred by oil bath at 140 °C for 4 h, then cooled to room temperature, filtered through a pad of celite, and then washed with EtOAc (10 mL×3), washed by 1 mol/L NaOH solution (20 mL) three times and saturated NaCl (20 mL), then dried with sodium sulfate. Organic solvents were removed under reduced pressure and the crude reaction mixture was purified by column chromatography on silica gel column with EtOAc/petroleum ether (1:10~1:5~1:2 v/v) as an eluent to afford the desired product **D<sub>8</sub>-2b**, **D<sub>4</sub>-2b** and **2b**, the value of competitive KIE is **1.85**.



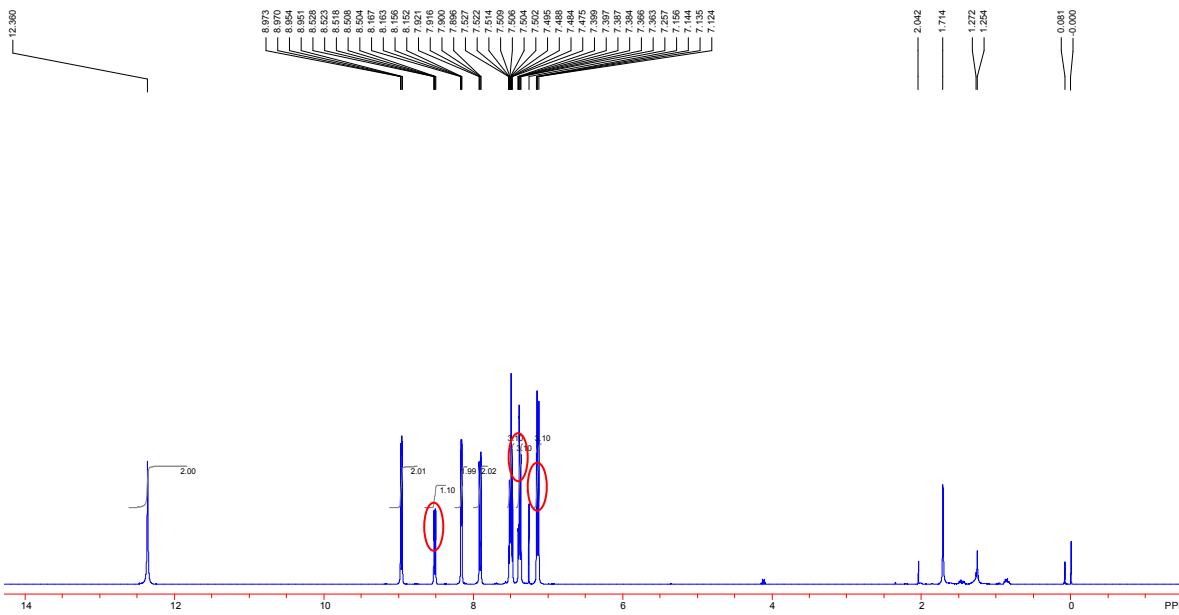
$$\text{KIE} = \text{K}_H/\text{K}_D = 1.3/0.7 = 1.85$$

### 5.1.3. Parallel kinetic isotopic effect of synthesis of diaryl ether



To a 25 mL seal tube with a stir bar was added benzamide (**D<sub>5</sub>-1b**, 0.20 mmol), Ni(OAc)<sub>2</sub> (0.04 mmol, 7.0 mg), Ag<sub>3</sub>PO<sub>4</sub> (0.40 mmol, 166 mg) and AdCOOK (0.40 mmol, 90 mg) in DMAc (2.0 mL), the vial was evacuated and filled with O<sub>2</sub> atmosphere and stirred by oil bath at 140 °C for 4 h, then cooled to room temperature, filtered through a pad of celite, and then washed with EtOAc (10 mL×3), washed by 1 mol/L NaOH solution (20 mL) three times and saturated NaCl (20 mL), then dried with sodium sulfate. Organic solvents were removed under reduced pressure and the crude reaction mixture was purified by column chromatography on silica gel column with EtOAc/petroleum ether (1:10~1:5~1:2 v/v) as an eluent to afford the desired product **D<sub>8</sub>-2b**.

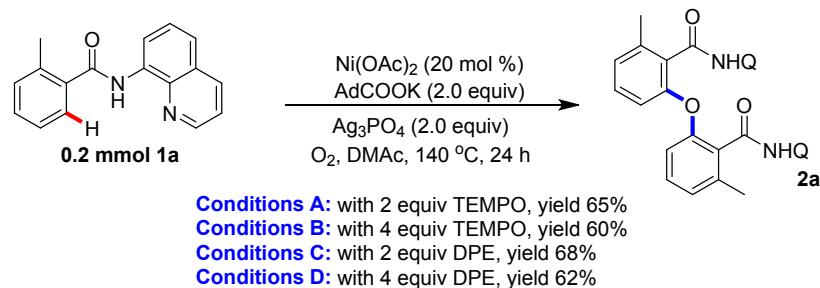
To a 25 mL seal tube with a stir bar was added benzamide (**1b**, 0.20 mmol), Ni(OAc)<sub>2</sub> (0.04 mmol, 7.0 mg), Ag<sub>3</sub>PO<sub>4</sub> (0.40 mmol, 166 mg) and AdCOOK (0.40 mmol, 90 mg) in DMAc (2.0 mL), the vial was evacuated and filled with O<sub>2</sub> atmosphere and stirred by oil bath at 140 °C for 4 h, then cooled to room temperature, filtered through a pad of celite, and then washed with EtOAc (10 mL×3), washed by 1 mol/L NaOH solution (20 mL) three times and saturated NaCl (20 mL), then dried with sodium sulfate. Organic solvents were removed under reduced pressure and the crude reaction mixture was purified by column chromatography on silica gel column with EtOAc/petroleum ether (1:10~1:5~1:2 v/v) as an eluent to afford the desired product **2b**, the value of parallel KIE is **1.22**.



$$KIE = K_H/K_D = 1.1/0.9 = 1.22$$

## 5.2. Mechanistic control experiments of synthesis of diaryl ether

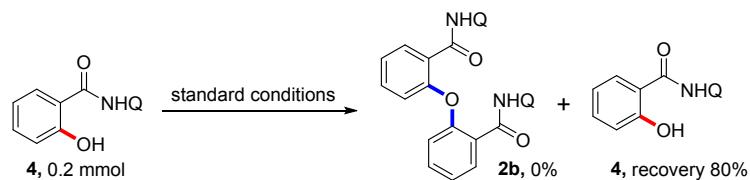
### 5.2.1. Radical-trapping experiment of synthesis of diaryl ether



To a 25 mL seal tube with a stir bar was added benzamide (**1a**, 0.20 mmol),  $\text{Ni}(\text{OAc})_2$  (0.04 mmol, 7.0 mg),  $\text{Ag}_3\text{PO}_4$  (0.40 mmol, 166 mg), AdCOOK (0.40 mmol, 90 mg) and with different equivalents TEMPO or DPE in DMAc (2.0 mL), the vial was evacuated and filled with  $\text{O}_2$  atmosphere and stirred by oil bath at 140 °C for 24 h, then cooled to room temperature, filtered through a pad of celite, and then washed with EtOAc (10 mL×3), washed by 1 mol/L NaOH solution (20 mL) three times and saturated NaCl (20 mL), then dried with sodium sulfate. Organic solvents were removed under reduced pressure and the crude reaction mixture was purified by column chromatography on silica gel column with

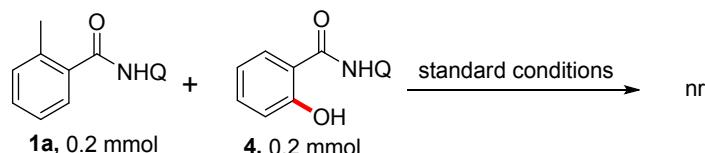
EtOAc/petroleum ether (1:10~1:5~1:2 v/v) as an eluent to afford the desired product **2a**, the yield of the **2a** hasn't decreased.

### 5.2.2. Control experiments of synthesis of diaryl ether

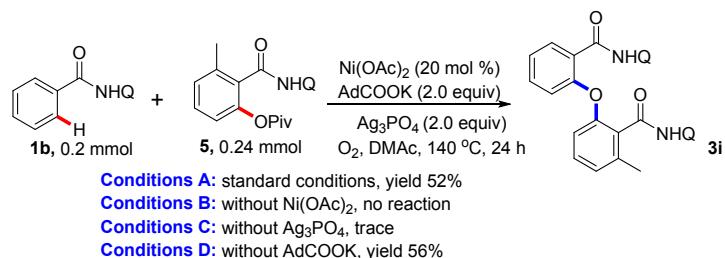


To a 25 mL seal tube with a stir bar was added benzamide **4**<sup>7</sup> (0.20 mmol), Ni(OAc)<sub>2</sub> (0.04 mmol, 7.0 mg), Ag<sub>3</sub>PO<sub>4</sub> (0.40 mmol, 166 mg), AdCOOK (0.40 mmol, 90 mg) in DMAc (2.0 mL), the vial was evacuated and filled with O<sub>2</sub> atmosphere and stirred by oil bath at 140 °C for 24 h, then cooled to room temperature and analyzed by TLC, only **4** was observed in this system, indicating that **2b** is not formed through dehydration of **4**.

**4;** <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 12.33 (s, 1H), 10.93 (s, 1H), 8.85 (dd, *J*<sub>1</sub> = 4.0 Hz, *J*<sub>2</sub> = 1.6 Hz, 1H), 8.79 (dd, *J*<sub>1</sub> = 6.4 Hz, *J*<sub>2</sub> = 2.8 Hz, 1H), 8.16 (dd, *J*<sub>1</sub> = 8.0 Hz, *J*<sub>2</sub> = 1.2 Hz, 1H), 7.83 (dd, *J*<sub>1</sub> = 8.0 Hz, *J*<sub>2</sub> = 0.8 Hz, 1H), 7.58-7.53 (m, 2H), 7.49-7.44 (m, 2H), 7.05 (d, *J* = 8.0 Hz, 1H), 6.99 (t, *J* = 8.0 Hz, 1H).



To a 25 mL seal tube with a stir bar was added benzamide (**1a**, 0.20 mmol) and benzamides (**4**, 0.20 mmol), Ni(OAc)<sub>2</sub> (0.04 mmol, 7.0 mg), Ag<sub>3</sub>PO<sub>4</sub> (0.40 mmol, 166 mg), AdCOOK (0.40 mmol, 90 mg) in DMAc (2.0 mL), the vial was evacuated and filled with O<sub>2</sub> atmosphere and stirred by oil bath at 140 °C for 24 h, only substrate **1a** and **4** was detected in this system, the corresponding diaryl ether product hasn't been observed.

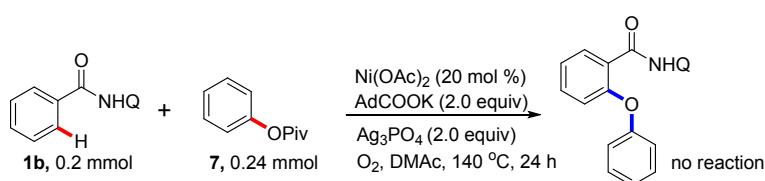


To a 25 mL seal tube with a stir bar was added substrate benzamide (**1b**, 0.20 mmol) and acyloxylated benzamides (**5**,<sup>8</sup> 0.24 mmol), in DMAc (2.0 mL) under O<sub>2</sub> atmosphere

according to the condition **A** to **D**. The reaction mixture was stirred at 140 °C for 24 h, cooled to room temperature, filtered through a pad of celite, and then washed with EtOAc (10 mL×3), washed by 1 mol/L NaOH solution (20 mL) three times and saturated NaCl (20 mL), then dried with sodium sulfate. Organic solvents were removed under reduced pressure and the crude reaction mixture was purified by column chromatography on silica gel column with EtOAc/petroleum ether (1:10~1:5~1:2 v/v) as an eluent to afford the diaryl ether product of **3i**. As for condition **B** and **C**, no or trace of product **3i** was observed. As for condition **A** and **D** the desired product **3i** was isolated in 52%, 56% respectively.

**5**; **1H NMR** ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  10.00 (s, 1H), 8.94 (dd,  $J_1 = 7.2$  Hz,  $J_2 = 1.6$  Hz, 1H), 8.77 (dd,  $J_1 = 4.0$  Hz,  $J_2 = 1.6$  Hz, 1H), 8.15 (dd,  $J_1 = 8.4$  Hz,  $J_2 = 1.6$  Hz, 1H), 7.60-7.53 (m, 2H), 7.43 (dd,  $J_1 = 8.0$  Hz,  $J_2 = 4.0$  Hz, 1H), 7.35 (t,  $J = 7.6$  Hz, 1H), 7.16 (d,  $J = 7.6$  Hz, 1H), 7.01 (d,  $J = 8.0$  Hz, 1H), 2.47 (s, 3H), 1.08 (s, 9H).

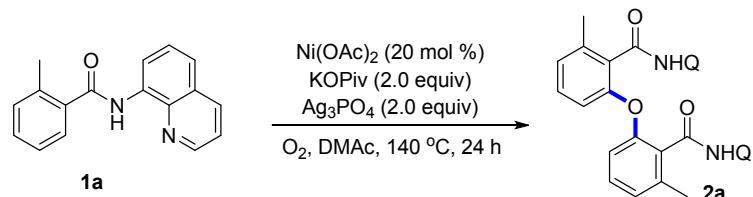
**3i**; White solid; mp: 189.8-192.1°C. **1H NMR** ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  12.19 (s, 1H), 10.45 (s, 1H), 8.89 (d,  $J = 7.6$  Hz, 2H), 8.34 (dd,  $J_1 = 4.4$  Hz,  $J_2 = 1.6$  Hz, 1H), 8.27 (dd,  $J_1 = 8.0$  Hz,  $J_2 = 1.2$  Hz, 1H), 8.01 (d,  $J = 8.0$  Hz, 1H), 7.90 (d,  $J = 8.0$  Hz, 1H), 7.56 (dd,  $J_1 = 4.0$  Hz,  $J_2 = 1.2$  Hz, 1H), 7.51-7.43 (m, 4H), 7.40-7.32 (m, 2H), 7.27-7.22 (m, 2H), 7.18-7.13 (dd,  $J_1 = 13.2$  Hz,  $J_2 = 7.6$  Hz, 2H), 7.05 (dd,  $J_1 = 8.4$  Hz,  $J_2 = 4.4$  Hz, 1H), 6.97 (d,  $J = 8.4$  Hz, 1H), 2.63 (s, 3H). **13C NMR** ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  164.4, 162.2, 155.1, 153.0, 147.8, 147.0, 138.7, 138.4, 137.9, 135.3, 135.2, 135.0, 133.9, 132.8, 131.5, 130.2, 129.4, 127.3, 127.2, 126.8, 126.6, 126.3, 124.6, 123.6, 121.4, 121.0, 120.7, 119.1, 116.9, 116.7, 116.5, 19.9. **HRMS** (ESI-TOF) calcd for  $\text{C}_{33}\text{H}_{25}\text{N}_4\text{O}_3^+$  [M+H]<sup>+</sup>:525.1921, found:525.1920.



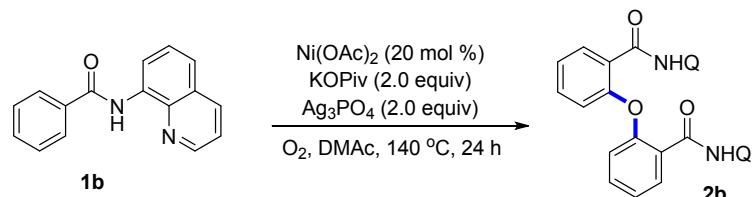
To a 25 mL seal tube with a stir bar was added substrate benzamide (**1b**, 0.20 mmol) and phenyl pivalate (**7**, 0.24 mmol),  $\text{Ni}(\text{OAc})_2$  (0.04 mmol, 7.0 mg),  $\text{Ag}_3\text{PO}_4$  (0.40 mmol, 166 mg), AdCOOK (0.40 mmol, 90 mg) in DMAc (2.0 mL), the vial was evacuated and filled with  $\text{O}_2$  atmosphere and stirred by oil bath at 140 °C for 24 h, only substrate **1b** and **7** was detected in this system, the corresponding diaryl ether product hasn't been observed.

**7;  $^1\text{H NMR}$**  ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  7.39-7.35 (m, 2H), 7.25-7.19 (m, 1H), 7.06 (dd,  $J = 8.8$  Hz,  $J = 1.2$  Hz, 1H), 1.36 (s, 9H).

### **5.3. The substances detected by GC-MS**



To a 25 mL seal tube with a stir bar was added benzamide (**1a**, 0.2 mmol), Ni(OAc)<sub>2</sub> (0.04 mmol, 7 mg), Ag<sub>3</sub>PO<sub>4</sub> (0.4 mmol, 166 mg) and KOPiv (2.0 mmol, 56 mg) in DMAc (2.00 mL), the vial was evacuated and filled with O<sub>2</sub> atmosphere and stirred by oil bath at 140 °C for different time, then cooled to room temperature, filtered through a pad of celite, and then washed with EtOAc (20 mL×3). The samples were detected by GC-MS respectively.



To a 50 mL seal tube with a stir bar was added benzamide (**1b**, 0.2 mmol), Ni(OAc)<sub>2</sub> (0.04 mmol, 7 mg), Ag<sub>3</sub>PO<sub>4</sub> (0.4 mmol, 166 mg) and KOPiv (2.0 mmol, 56 mg) in DMAc (2.00 mL), the vial was evacuated and filled with O<sub>2</sub> atmosphere and stirred by oil bath at 140 °C for different time, then cooled to room temperature, filtered through a pad of celite, and then washed with EtOAc (20 mL×3). The sample was detected by GC-MS respectively.

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2	3.092	115	118	120	VV 3	15397195	410156962	6.25%	2.995%	
3	3.131	120	122	125	VV 3	15345477	380583633	5.80%	2.779%	
4	3.173	125	127	135	VV 3	15262220	485785710	7.40%	3.548%	
5	7.783	658	663	673	PV	314449	10965824	0.17%	0.080%	
6	8.107	673	701	767	VV	19956146	1809580089	27.58%	13.215%	
7	8.695	767	769	796	VV 3	665196	64416876	0.98%	0.470%	
8	8.969	796	801	843	VV 7	314764	40500647	0.62%	0.296%	
9	9.533	843	867	871	VV 5	166340	7121860	0.11%	0.052%	
10	9.666	871	882	893	VV 2	244628	13261735	0.20%	0.097%	
11	10.480	970	977	1000	PV	719136	54672340	0.83%	0.399%	
12	10.708	1000	1003	1017	VV 4	174820	9094901	0.14%	0.066%	
13	12.213	1172	1178	1193	VV	293223	21630937	0.33%	0.158%	
14	12.463	1193	1207	1213	VV 9	279090	23679977	0.36%	0.173%	
15	12.589	1213	1222	1229	VV 4	370638	25416826	0.39%	0.186%	
16	12.724	1229	1238	1325	VV 3	28607299	2429026277	37.02%	17.739%	
17	13.503	1325	1328	1339	VV 4	593826	38614230	0.59%	0.282%	
18	14.095	1385	1397	1476	VV	17856664	760955848	11.60%	5.557%	
19	14.936	1485	1495	1556	VV	2264432	112751823	1.72%	0.823%	
20	26.314	2787	2817	2950	BBA	1995622	432993341	6.60%	3.162%	

修正后的面积和: 13692966782

lan.M Fri Aug 30 12:51:36 2019

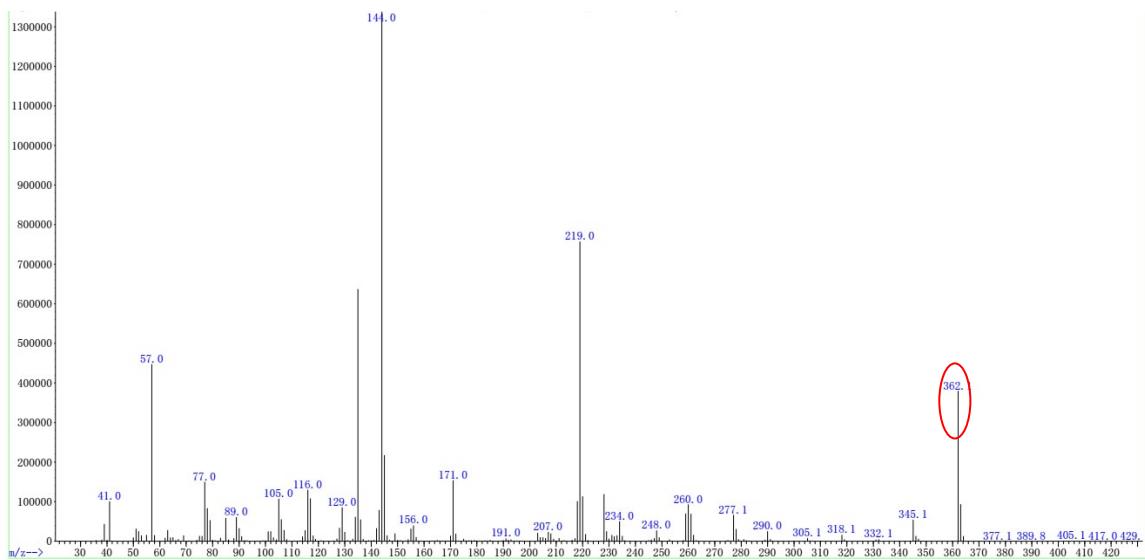
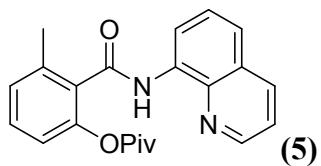
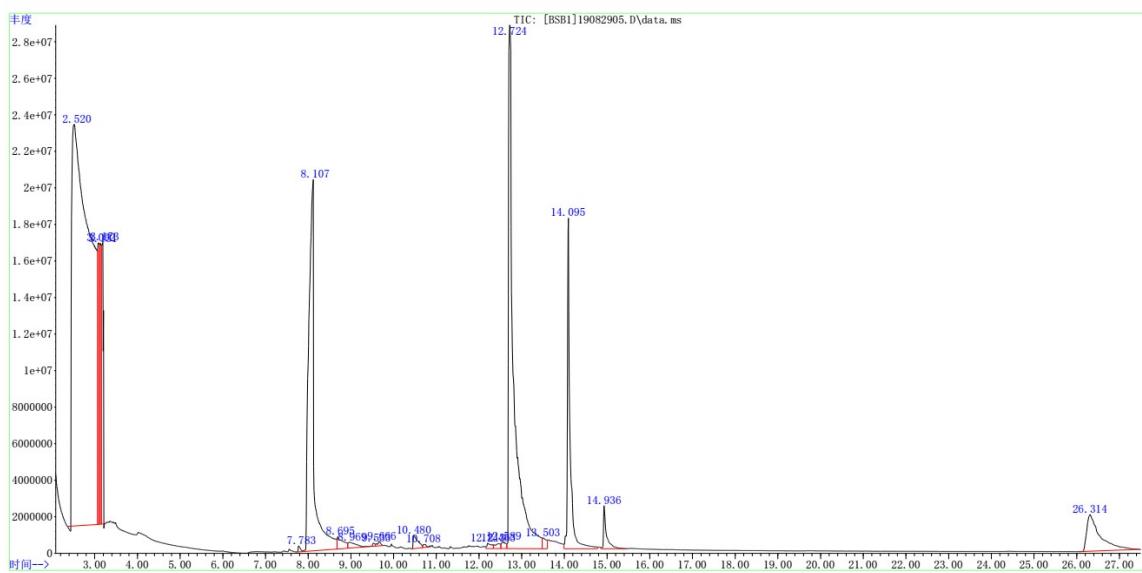


Figure S5: GC-MS information of compound 5

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1	2.567	41	55	132	BV 5	19457351	7803892809	100.00%	44.386%
2	3.259	132	133	138	VV 3	15204653	522900166	6.70%	2.974%
3	3.318	138	140	145	VV 4	15151259	534816878	6.85%	3.042%
4	3.380	145	147	154	VV 6	15120011	753074618	9.65%	4.283%
5	3.513	154	162	167	VV 7	15132504	1009464199	12.94%	5.742%
6	3.576	167	169	173	VV 5	15141194	457585668	5.86%	2.603%
7	3.623	173	174	176	VV 2	15136345	267816073	3.43%	1.523%
8	3.812	176	196	199	VV 4	16193760	1711027661	21.93%	9.732%
9	3.875	199	203	206	PV	535829	12131558	0.16%	0.069%
10	3.947	206	211	228	VB	2947904	61186563	0.78%	0.348%
11	4.530	267	276	308	BB	11744395	280980572	3.60%	1.598%
12	11.190	1018	1028	1082	BV 2	23731387	1280845342	16.41%	7.285%
13	12.453	1157	1170	1177	BB	737224	10640552	0.14%	0.061%
14	12.770	1194	1206	1287	BV 3	24297797	2875500113	36.85%	16.355%

修正后的面积和: 17581862771

lan.M Mon Apr 15 20:00:48 2019

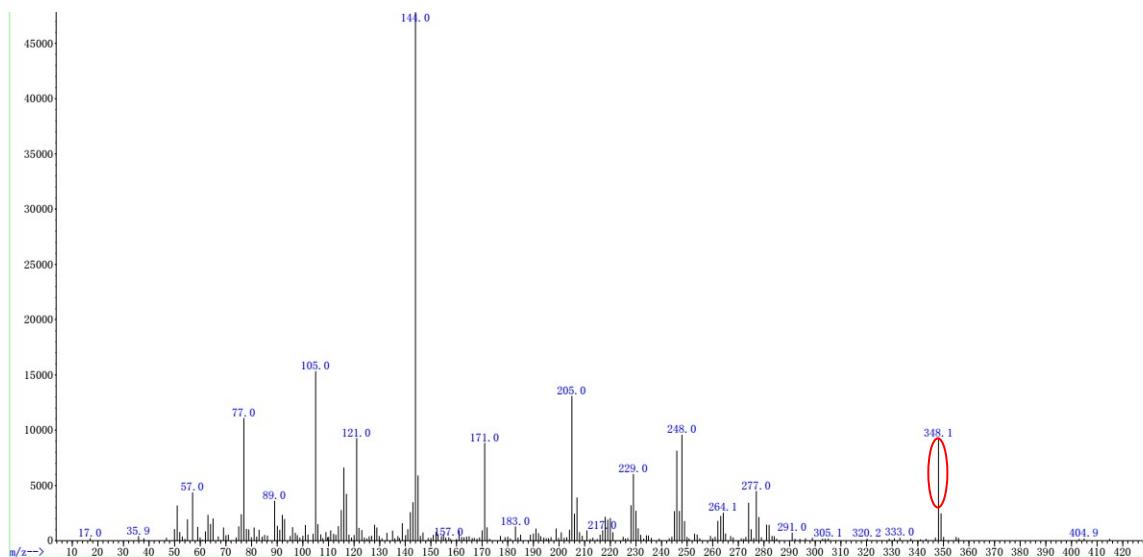
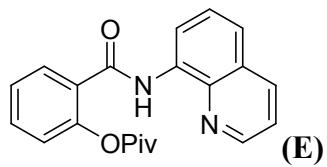
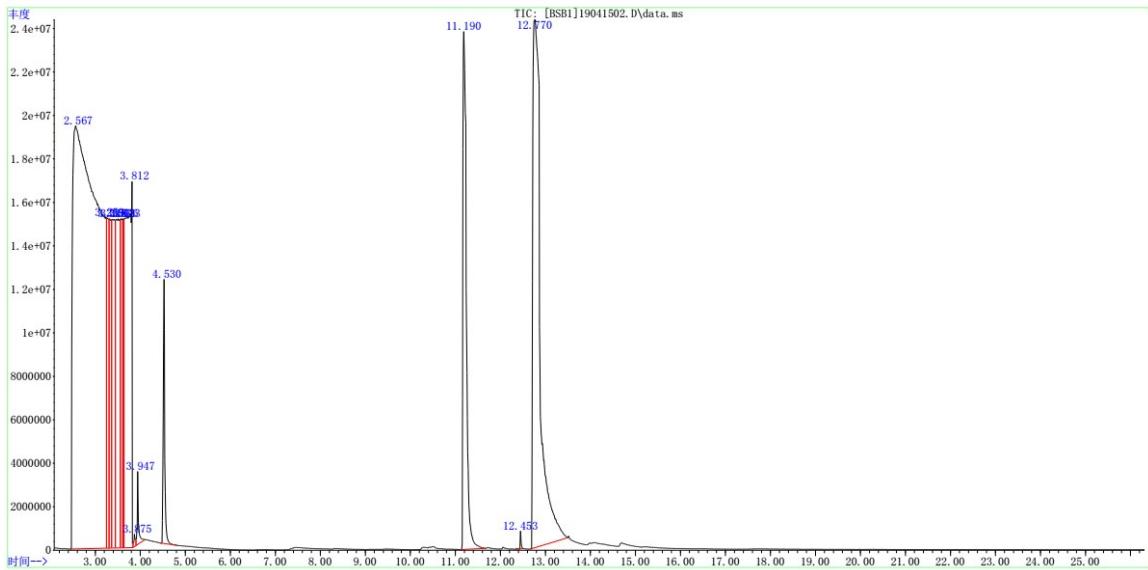
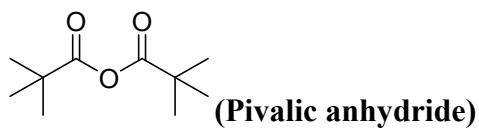


Figure S6: GC-MS information of intermediate **E**



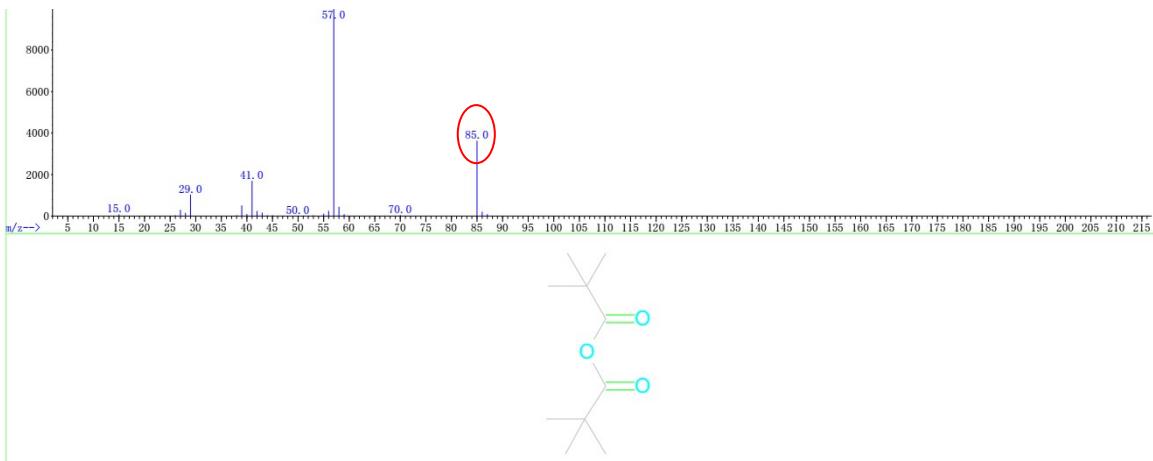
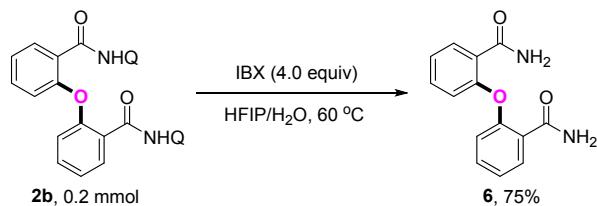


Figure S7: GC-MS information of Pivalic anhydride

## 6. Removal of 8-quinolyl Auxiliary



To a 25 mL round-bottom flask with a stir bar was added diaryl ether (**2b**, 0.20 mmol), IBX (0.80 mmol, 224 mg), in the mixed solvent of HFIP/H<sub>2</sub>O (3.0 mL, V<sub>HFIP</sub>/V<sub>H2O</sub> = 1:1) and stirred by oil bath at 60 °C for 6 h.<sup>9</sup> Then cooled to room temperature, the reaction was quenched by the addition of NaHCO<sub>3</sub> (aq 10 mL); the resulting mixture was extracted with dichloromethane (3×5 mL). Organic solvents were removed under reduced pressure and the crude reaction mixture was purified by column chromatography on silica gel column with EtOAc/petroleum ether (1:1, v/v) as an eluent to afford the primary benzamide product **6** in 75% yield.

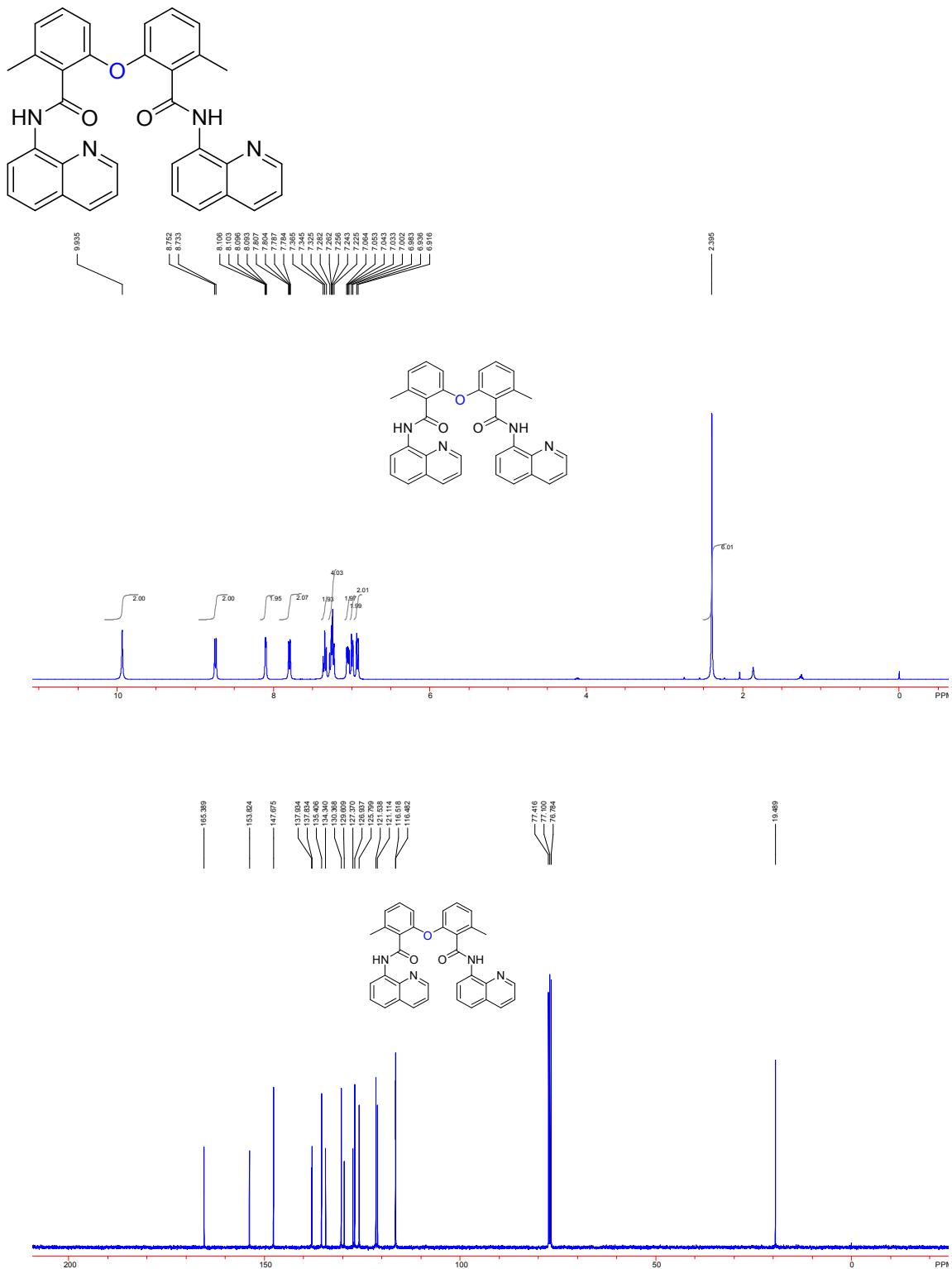
**6**; (75%, 38.4 mg); White solid; mp: >220 °C. <sup>1</sup>H NMR ((CD<sub>3</sub>)<sub>2</sub>SO, 500 MHz) δ 8.05 (s, 2H), 7.76 (d, *J* = 7.0 Hz, 2H), 7.56 (s, 2H), 7.47 (t, *J* = 8.0 Hz, 2H), 7.24 (t, *J* = 7.0 Hz, 2H), 6.87 (d, *J* = 8.0 Hz, 2H). <sup>13</sup>C NMR ((CD<sub>3</sub>)<sub>2</sub>SO, 100 MHz) δ 166.8, 153.3, 132.2, 130.5, 126.6, 123.8, 118.5. HRMS (ESI-TOF) calcd for C<sub>14</sub>H<sub>12</sub>N<sub>2</sub>O<sub>3</sub>Na<sup>+</sup> [M+Na]<sup>+</sup>:279.0740, found: 279.0743.

## 7. Reference

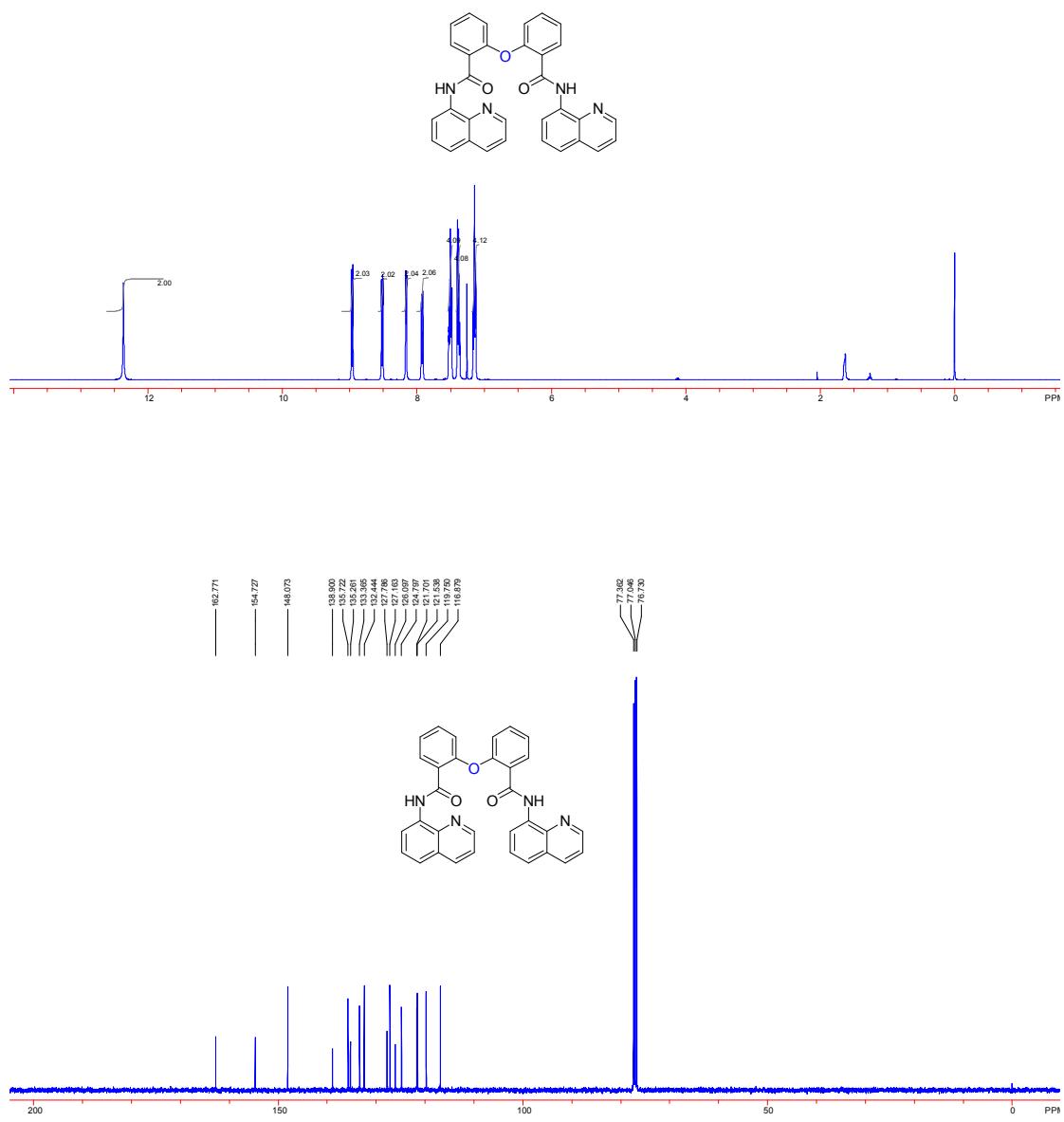
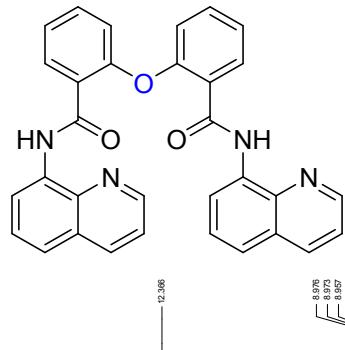
- [1] L. D. Tran, I. Popov and O. Daugulis. Copper-Promoted Sulfenylation of sp<sup>2</sup> C–H Bonds *J. Am. Chem. Soc.*, 2012, **134**, 18237–12840.
- [2] Y. Ano, M. Tobisu and N. Chatani. Palladium-Catalyzed Direct *ortho*-Alkynylation of Aromatic Carboxylic Acid Derivatives *Org. Lett.*, 2012, **14**, 354–357.
- [3] L. D. Tran, J. Roane and O. Daugulis. Directed Amination of Non-Acidic Arene C–H Bonds by a Copper–Silver Catalytic System. *Angew. Chem. Int. Ed.*, 2013, **52**, 6043–6046.
- [4] L. Grigorjeva and O. Daugulis. Cobalt-Catalyzed, Aminoquinoline-Directed C(sp<sup>2</sup>)–H Bond Alkenylation by Alkynes. *Angew. Chem. Int. Ed.*, 2014, **53**, 10209–10212.
- [5] F.-R. Gou, X.-C. Wang, P.-F. Huo, H.-P. Bi, Z.-H. Guan and Y.-M. Liang. Palladium-Catalyzed Aryl C–H Bonds Activation/Acetoxylation Utilizing a Bidentate System. *Org. Lett.*, 2009, **11**, 5726–5729.
- [6] K. Shibata, and N. Chatani. Rhodium-Catalyzed Alkylation of C-H Bonds in Aromatic Amides with  $\alpha,\beta$ -Unsaturated Esters. *Org. Lett.*, 2014, **16**, 5148–5151.
- [7] B. K. Singh and R. Jana. Ligand-Enabled, Copper-Promoted Regio- and Chemoselective Hydroxylation of Arenes, Aryl Halides, and Aryl Methyl Ethers *J. Org. Chem.*, 2016, **81**, 831–841.
- [8] C. Lin, Z. Chen, Z. Liu and Y. Zhang. Direct *ortho*-Acyloxylation of Arenes and Alkenes by Cobalt Catalysis. *Adv. Synth. Catal.*, 2018, **360**, 519–532.
- [9] Z. Zhang, X. Li, M. Song, Y. Wan, D. Zheng, G. Zhang, and G. Chen. Selective Removal of Aminoquinoline Auxiliary by IBX Oxidation. *J. Org. Chem.*, 2019, **84**, 12792–12799.

## 8. Copies of $^1\text{H}$ and $^{13}\text{C}$ NMR Spectra

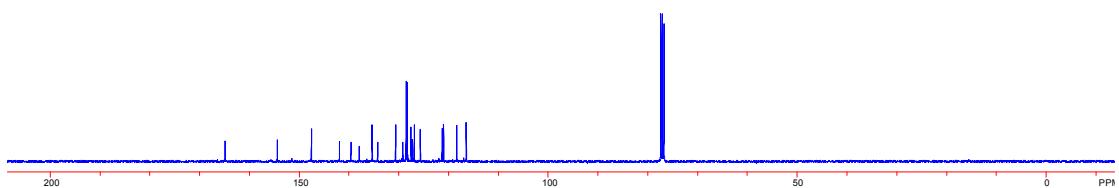
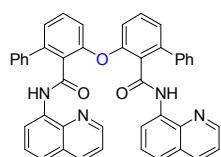
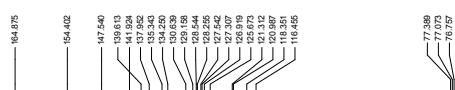
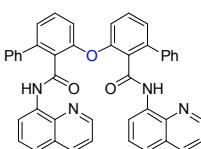
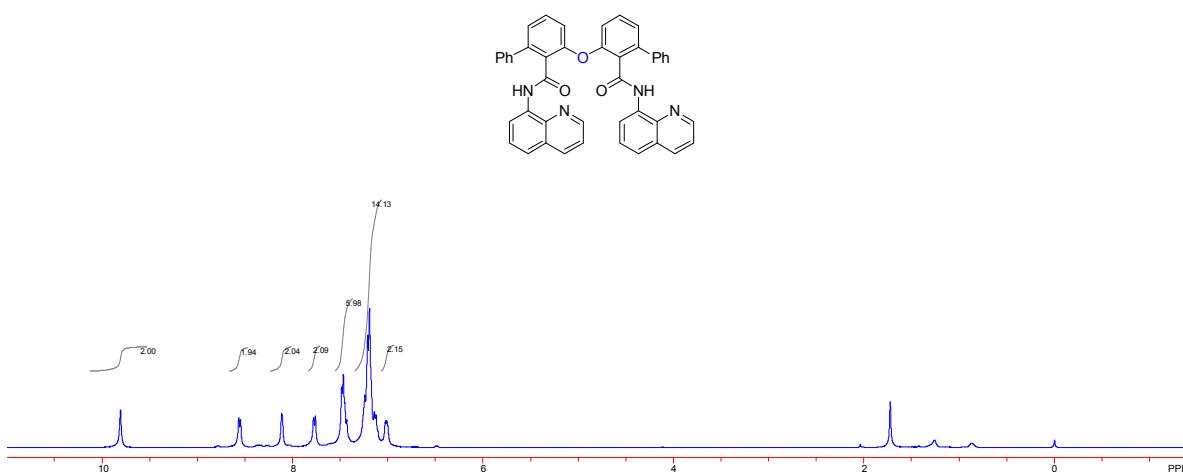
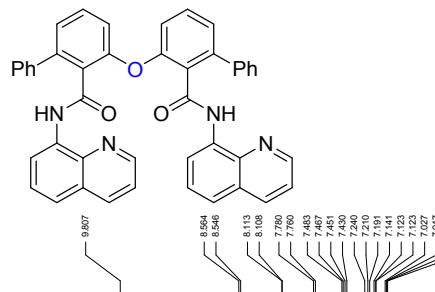
### **6,6'-oxybis(2-methyl-N-(quinolin-8-yl)benzamide) (2a)**



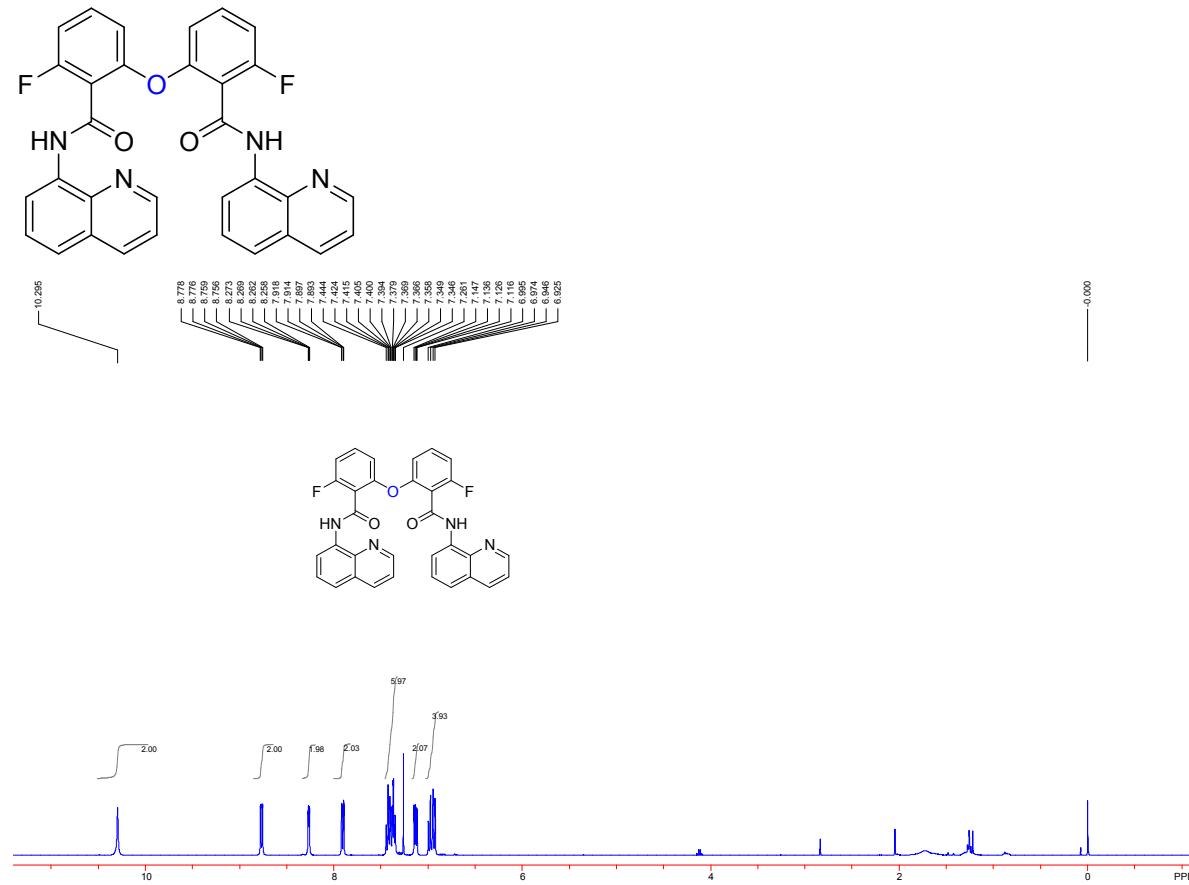
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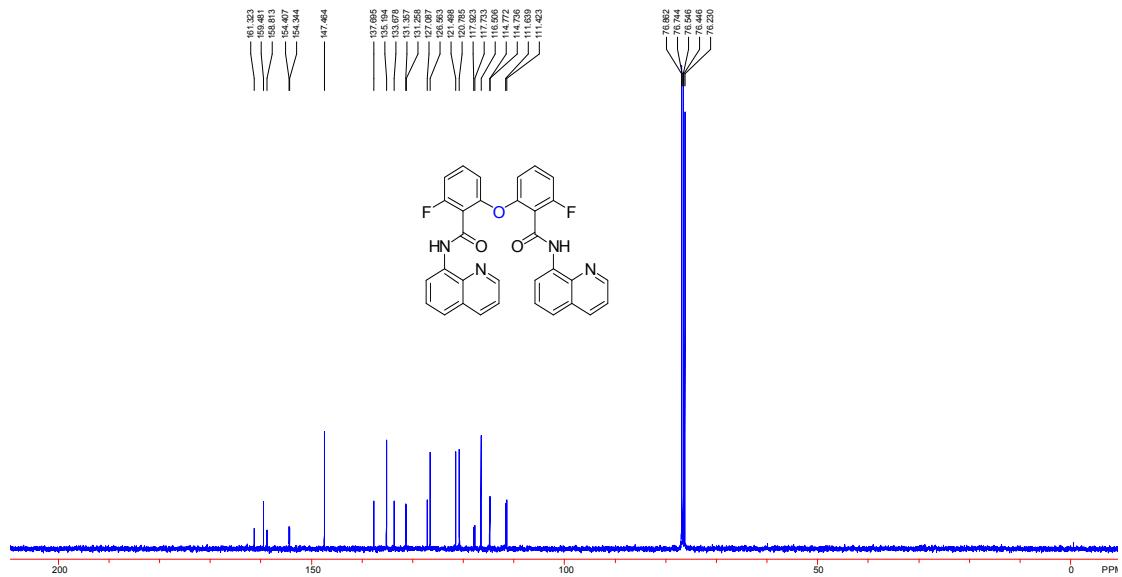


**3,3''-oxybis(*N*-(quinolin-8-yl)-[1,1'-biphenyl]-2-carboxamide) (2c)**

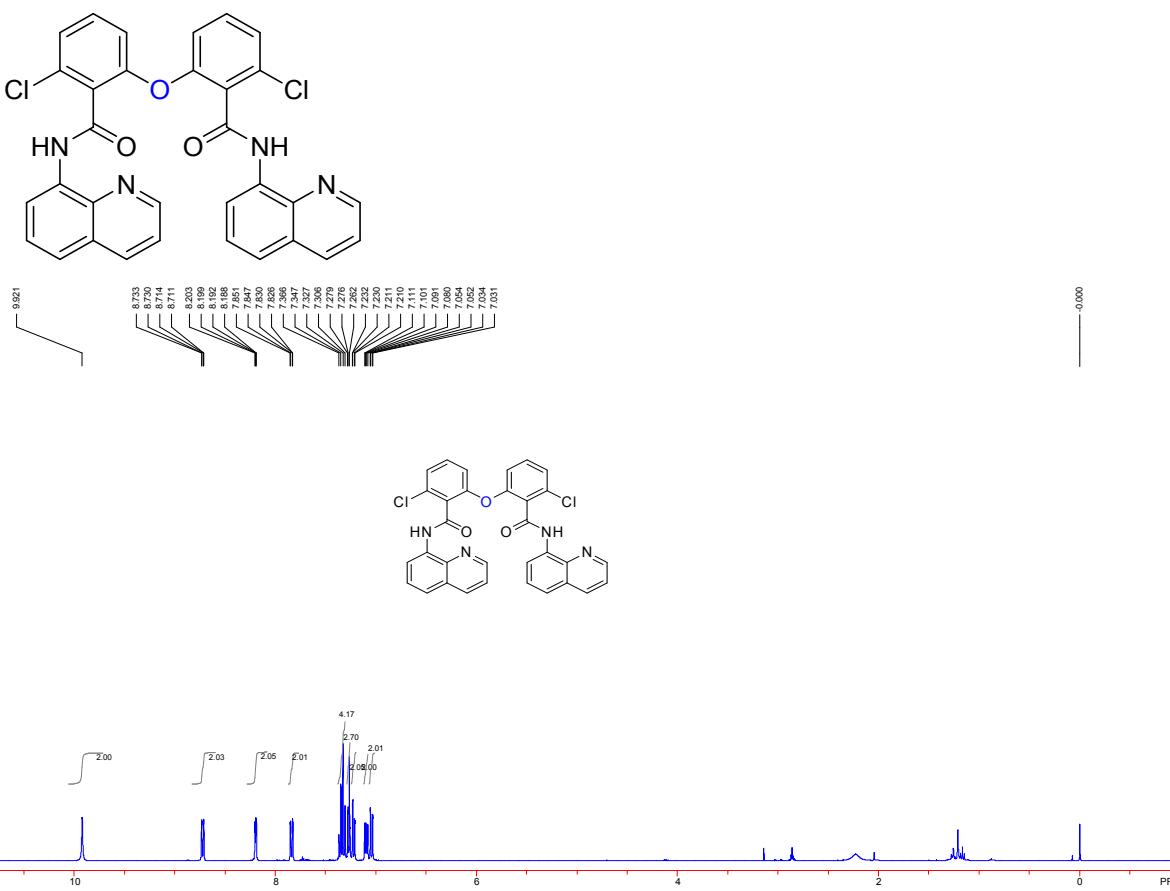


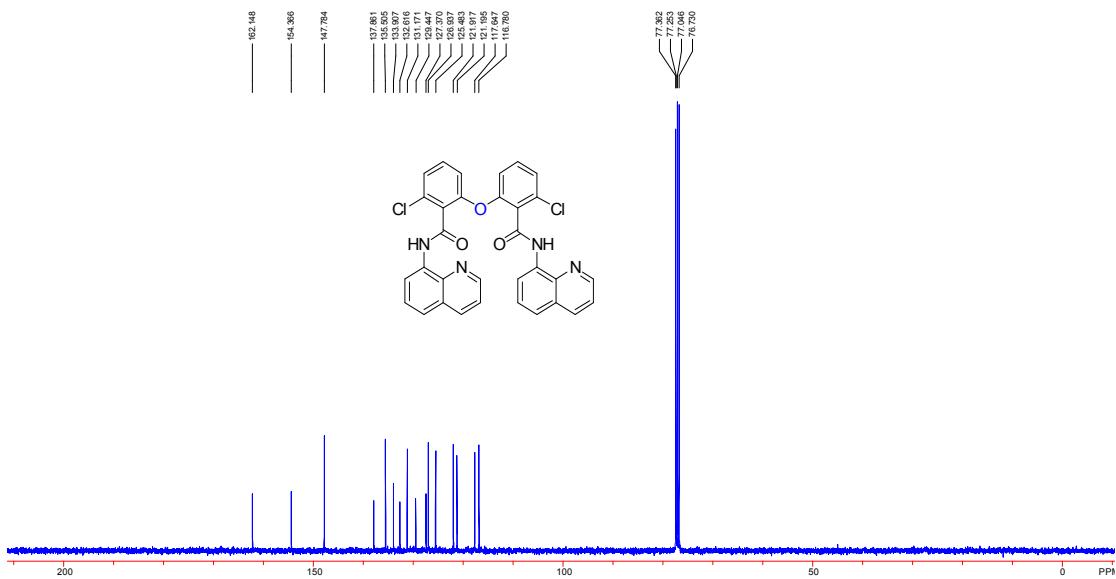
**6,6'-oxybis(2-fluoro-N-(quinolin-8-yl)benzamide) (2d)**



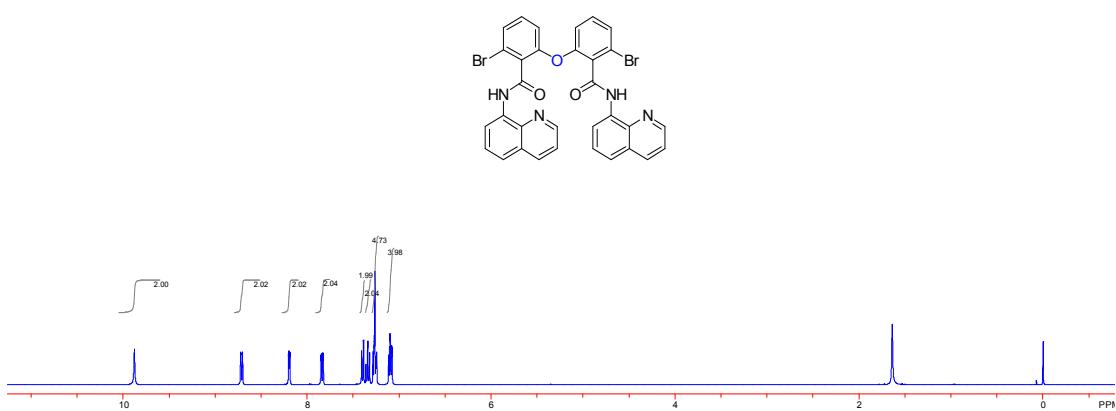
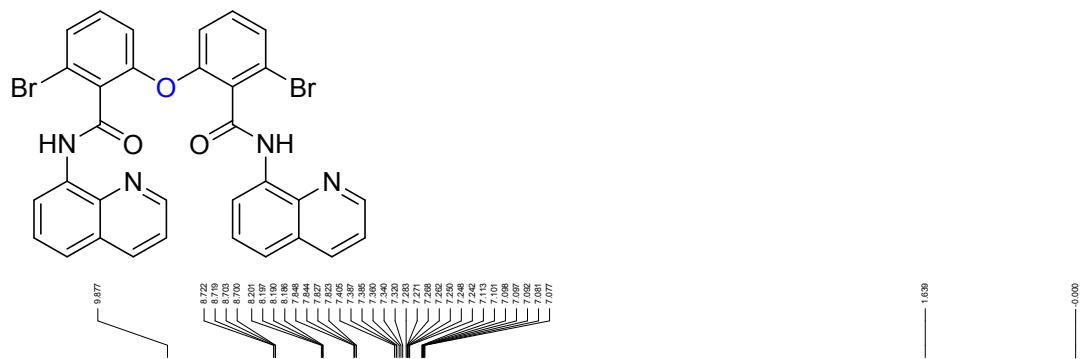


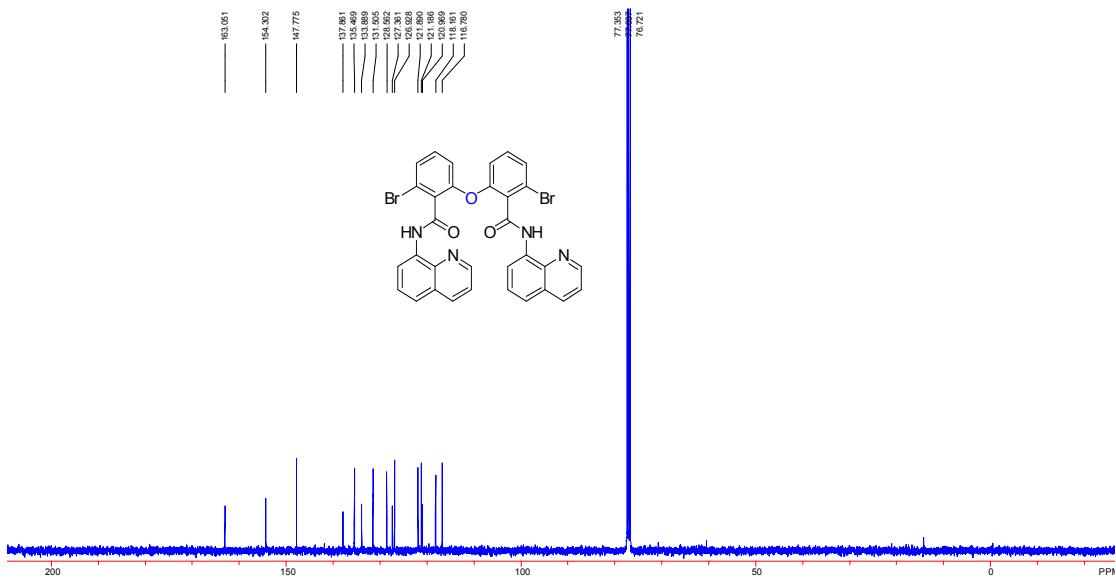
#### 6,6'-oxybis(2-chloro-N-(quinolin-8-yl)benzamide) (2e)



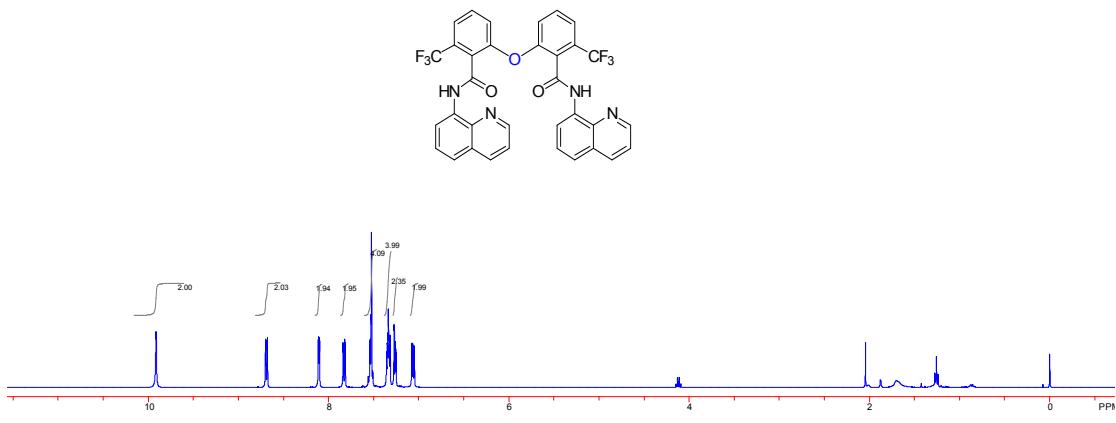
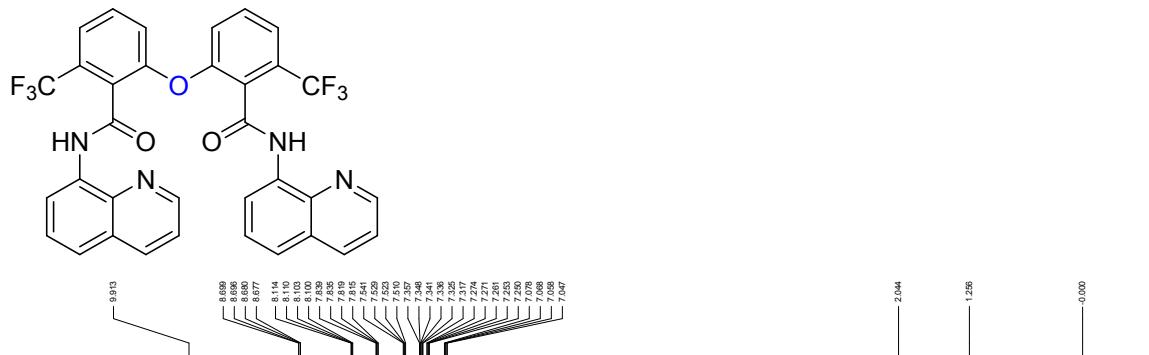


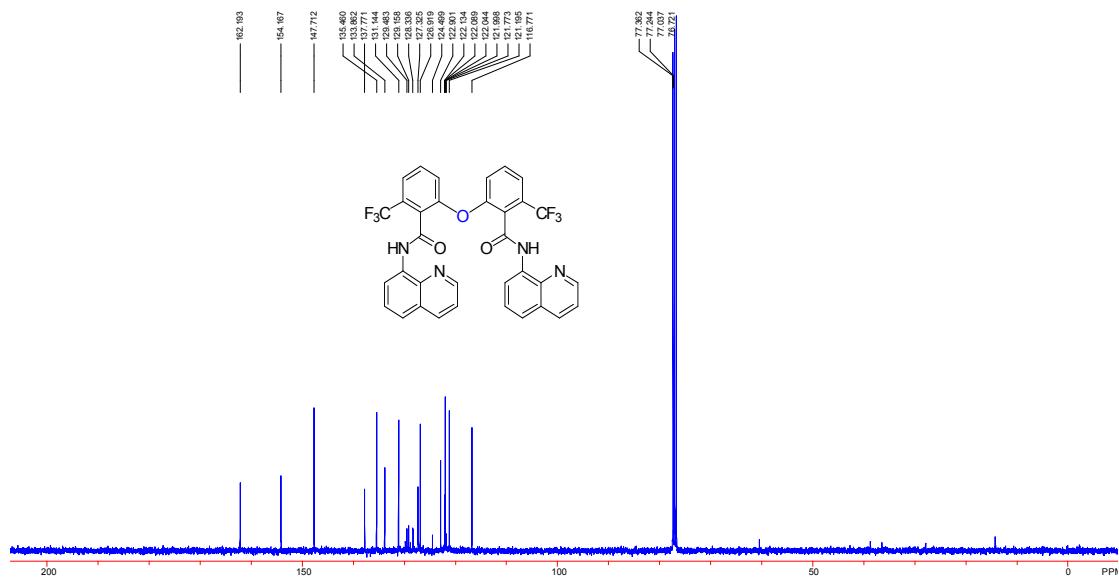
### 6,6'-oxybis(2-bromo-N-(quinolin-8-yl)benzamide) (2f)



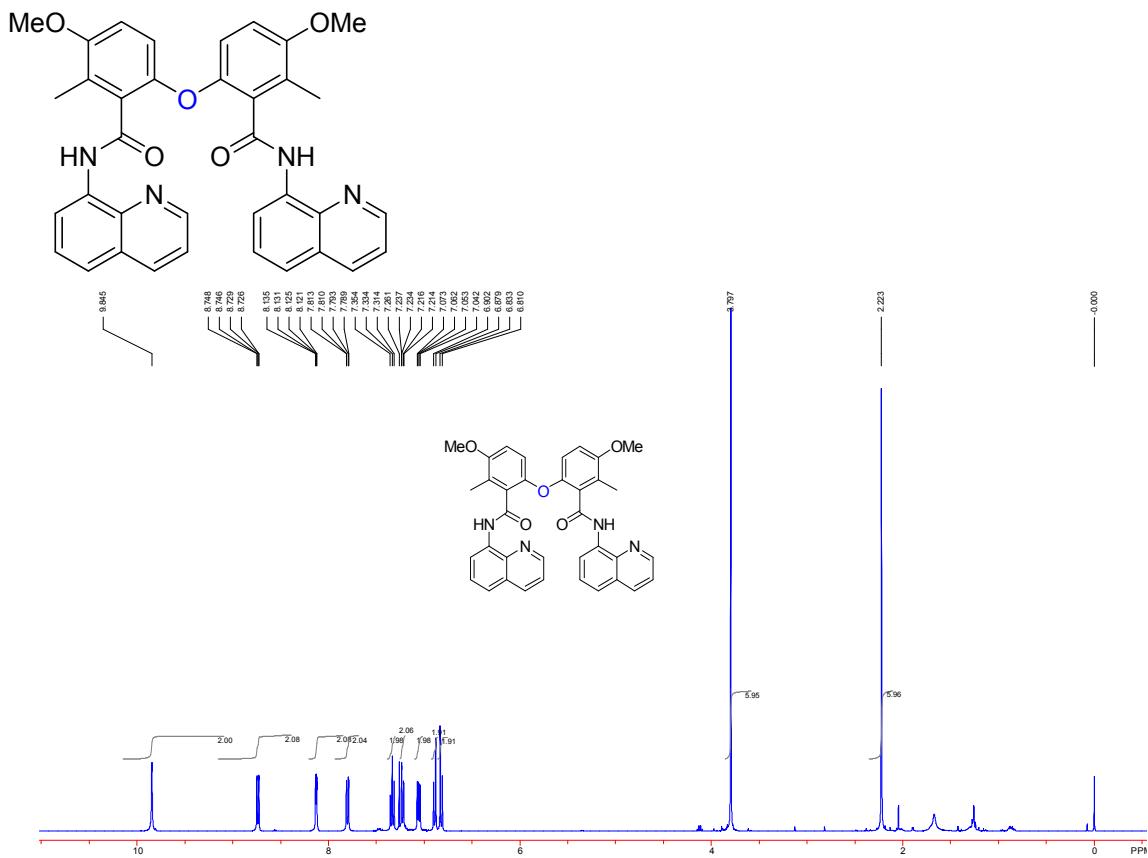


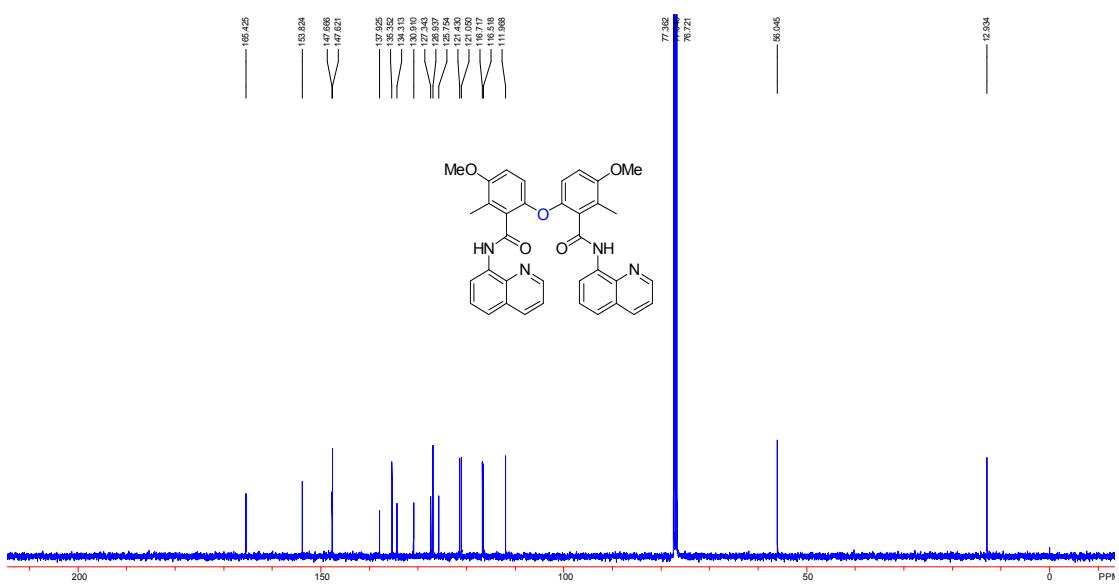
### **6,6'-oxybis(*N*-(quinolin-8-yl)-2-(trifluoromethyl)benzamide) (2g)**



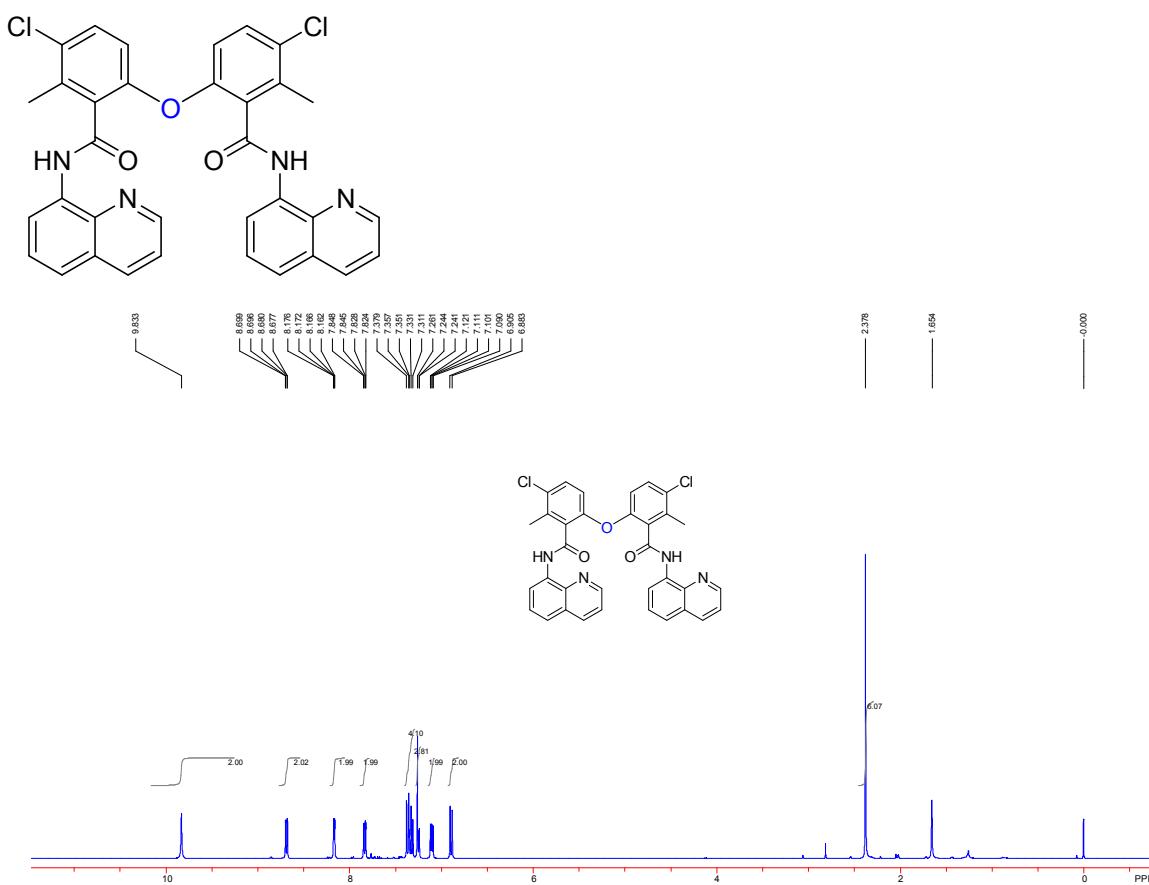


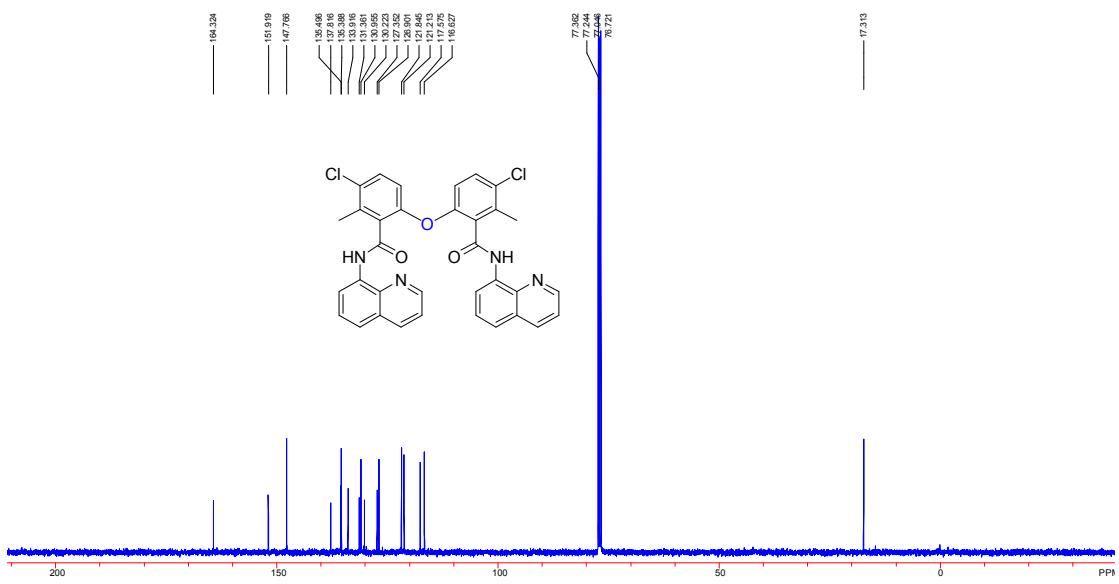
### 6,6'-oxybis(3-methoxy-2-methyl-N-(quinolin-8-yl)benzamide) (2h)



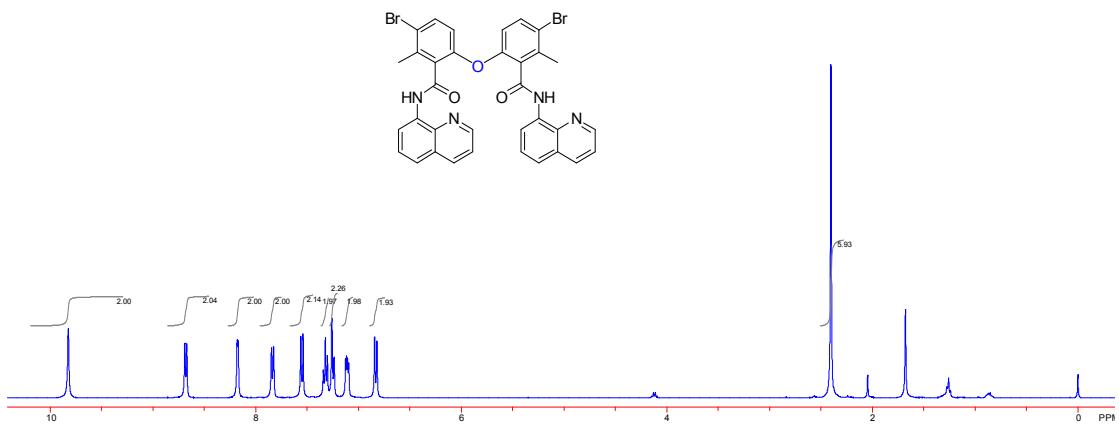
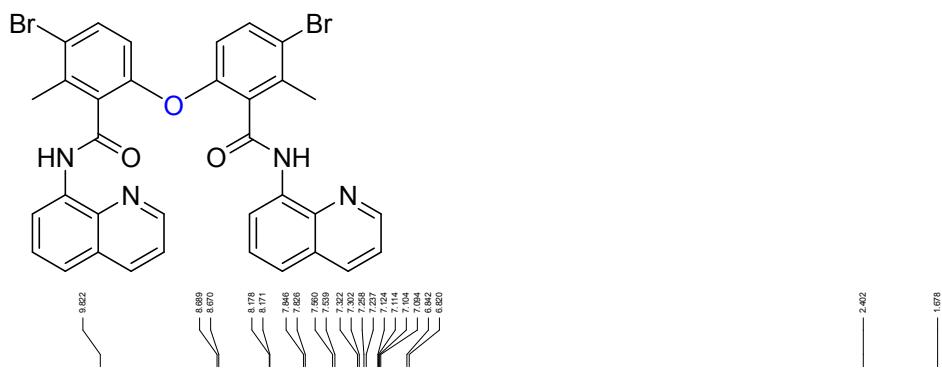


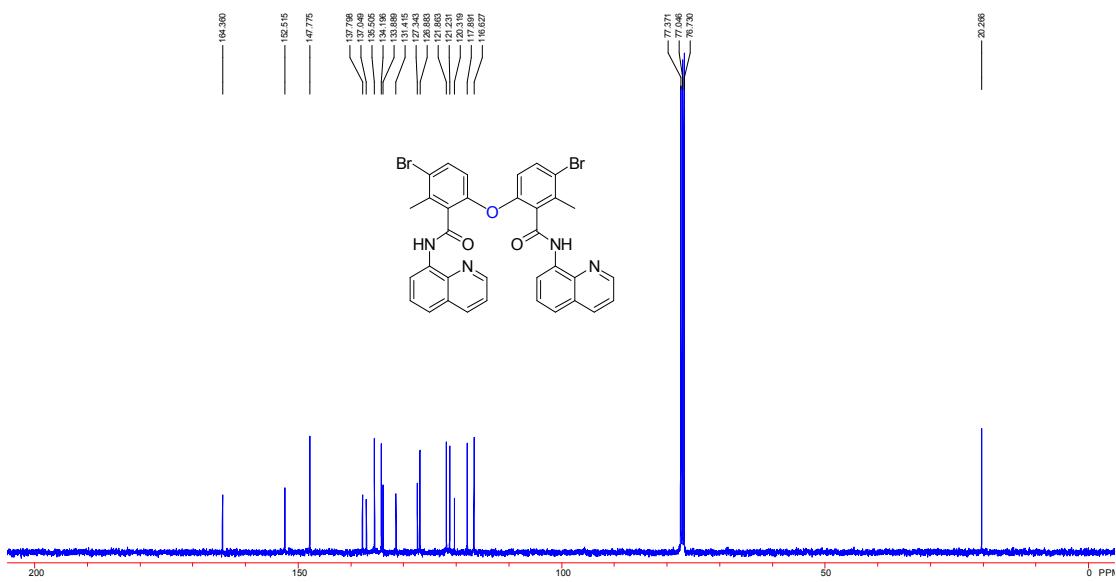
**6,6'-oxybis(3-chloro-2-methyl-N-(quinolin-8-yl)benzamide) (2i)**



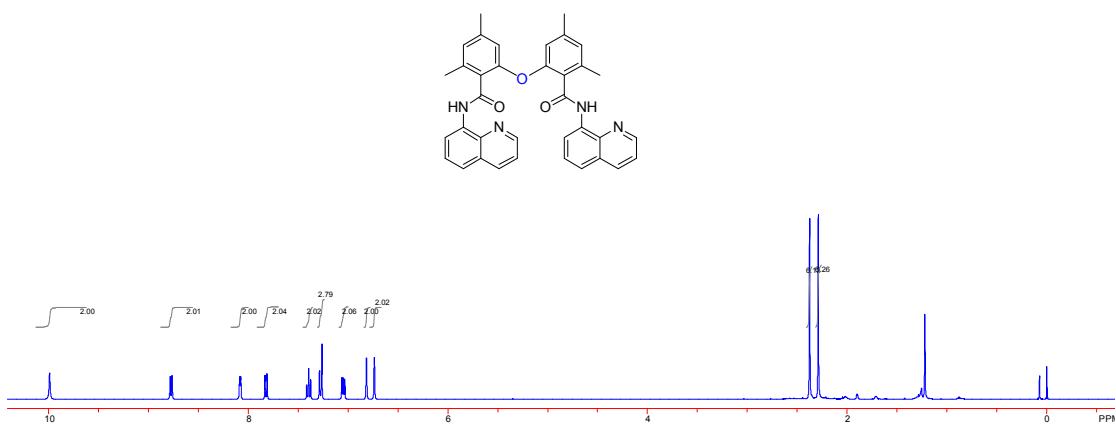
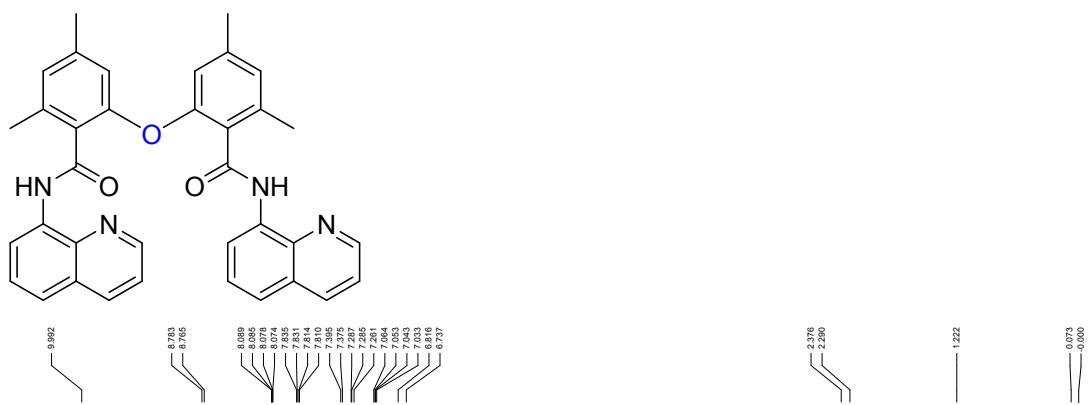


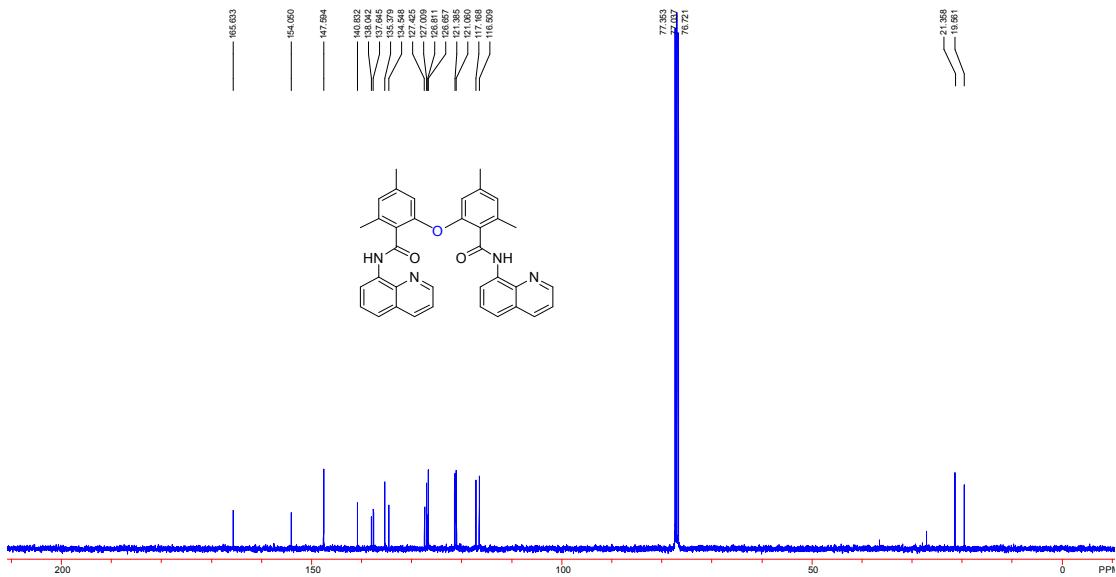
### 6,6'-oxybis(3-bromo-2-methyl-N-(quinolin-8-yl)benzamide) (2j)



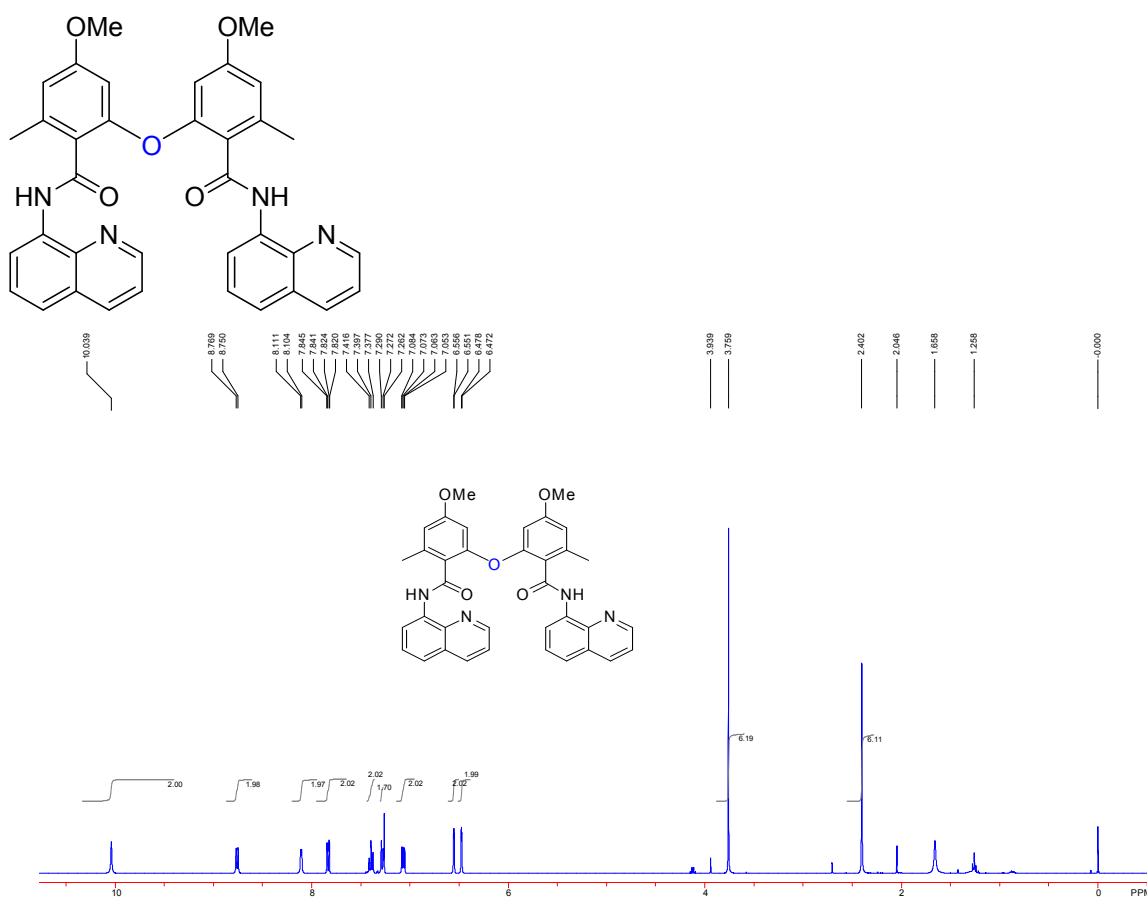


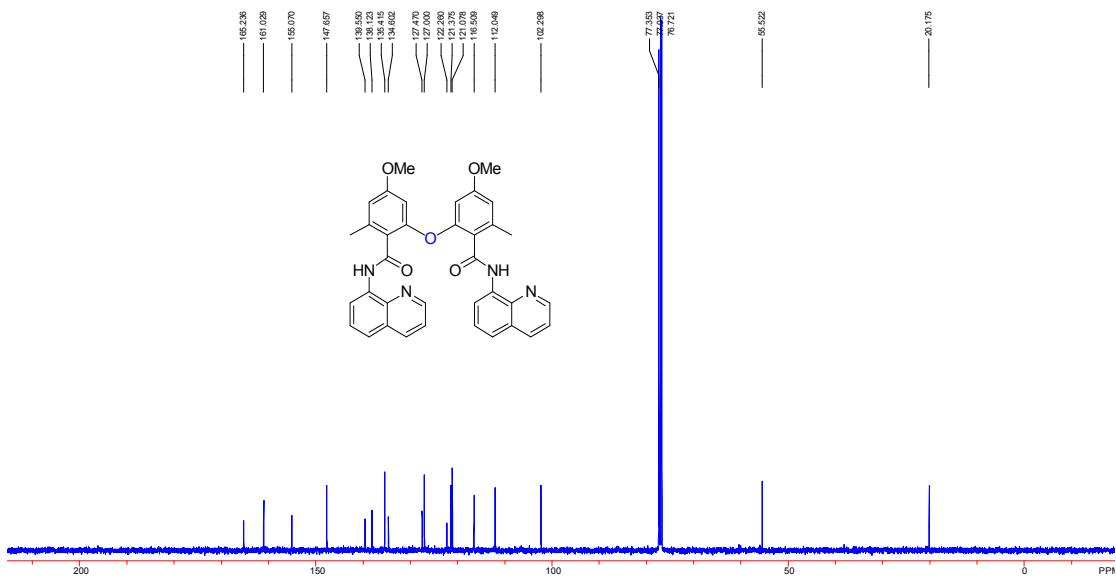
### 6,6'-oxybis(2,4-dimethyl-N-(quinolin-8-yl)benzamide) (2k)



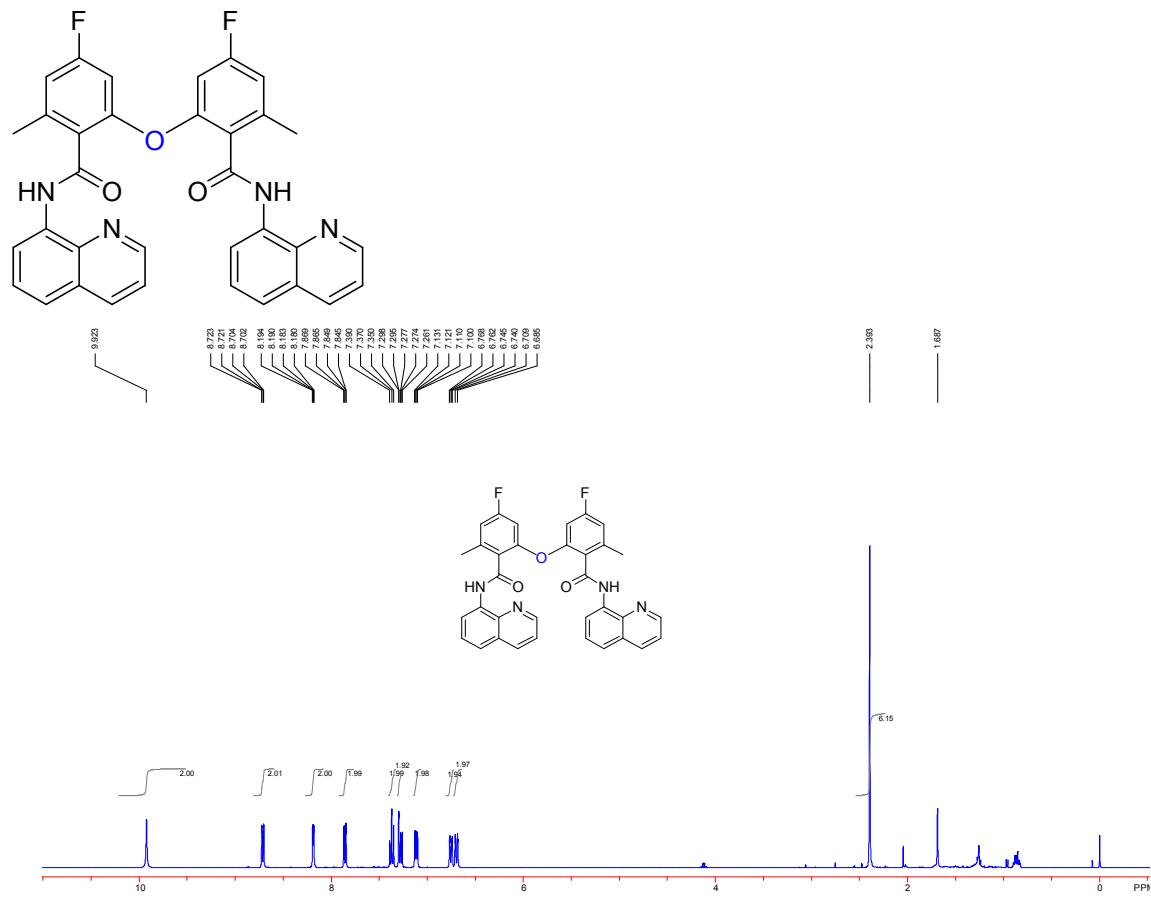


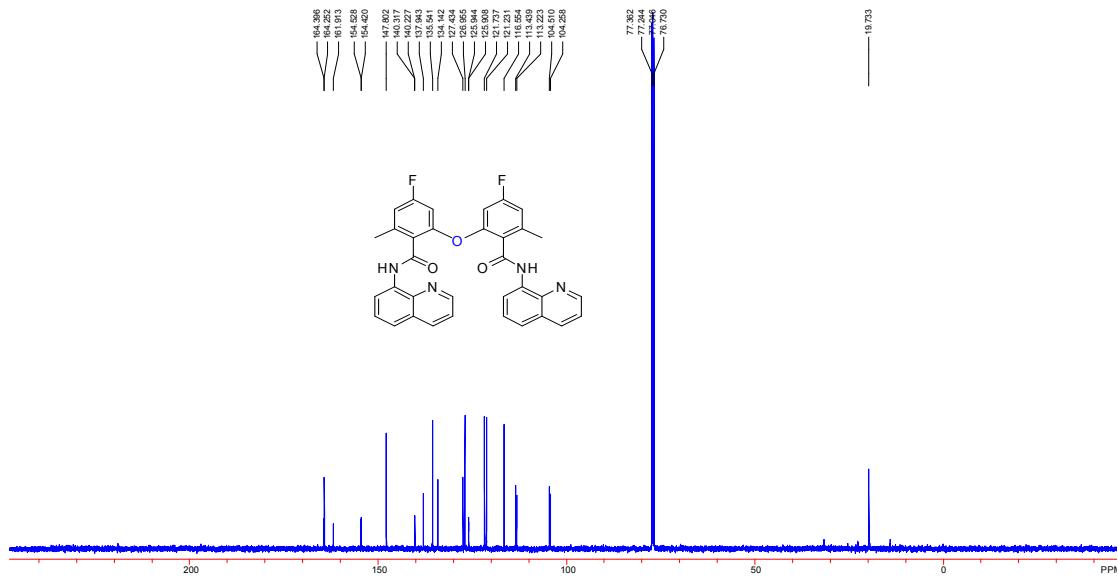
### 6,6'-oxybis(4-methoxy-2-methyl-N-(quinolin-8-yl)benzamide) (2l)



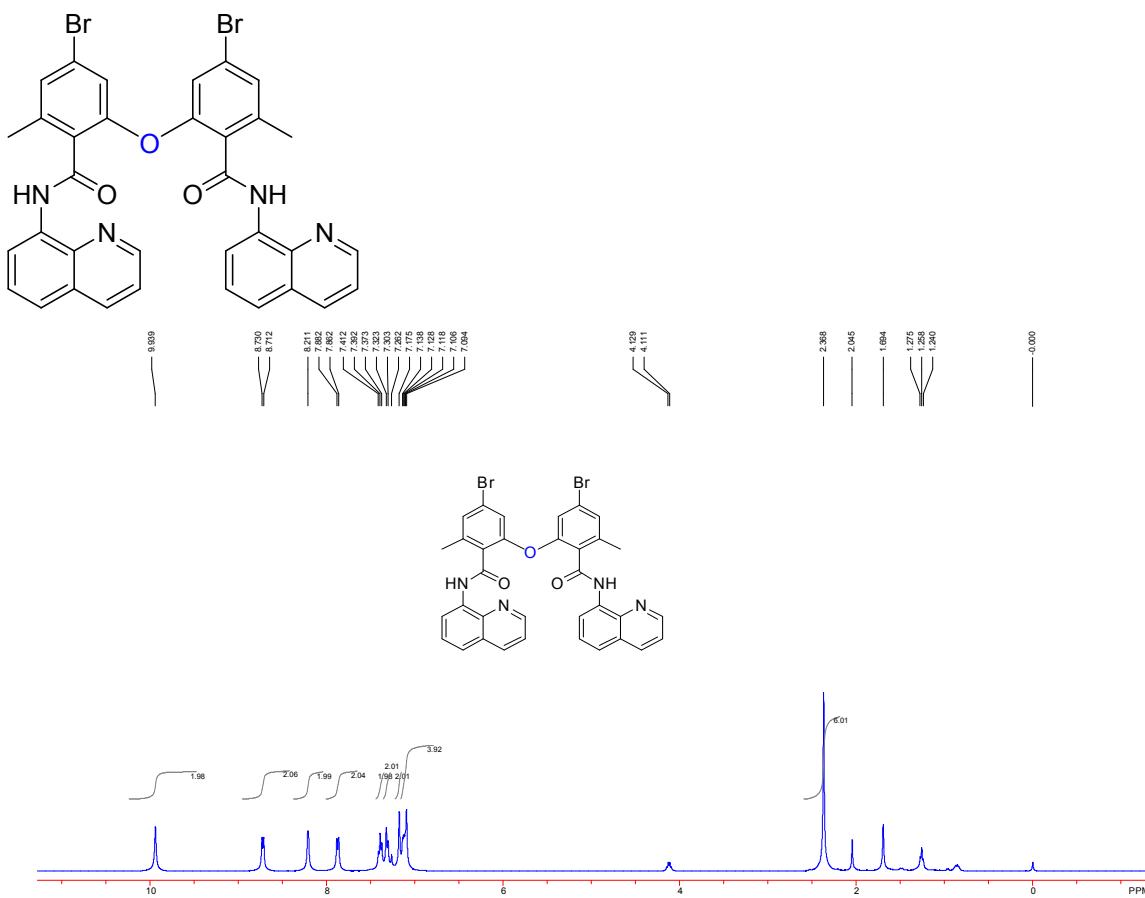


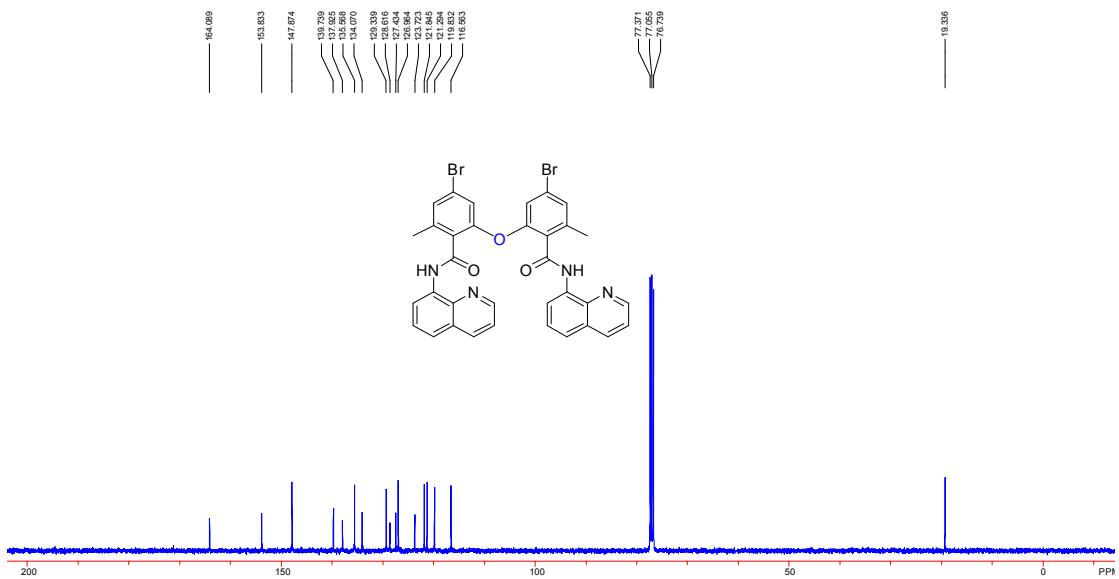
### 6,6'-oxybis(4-fluoro-2-methyl-N-(quinolin-8-yl)benzamide) (2m)



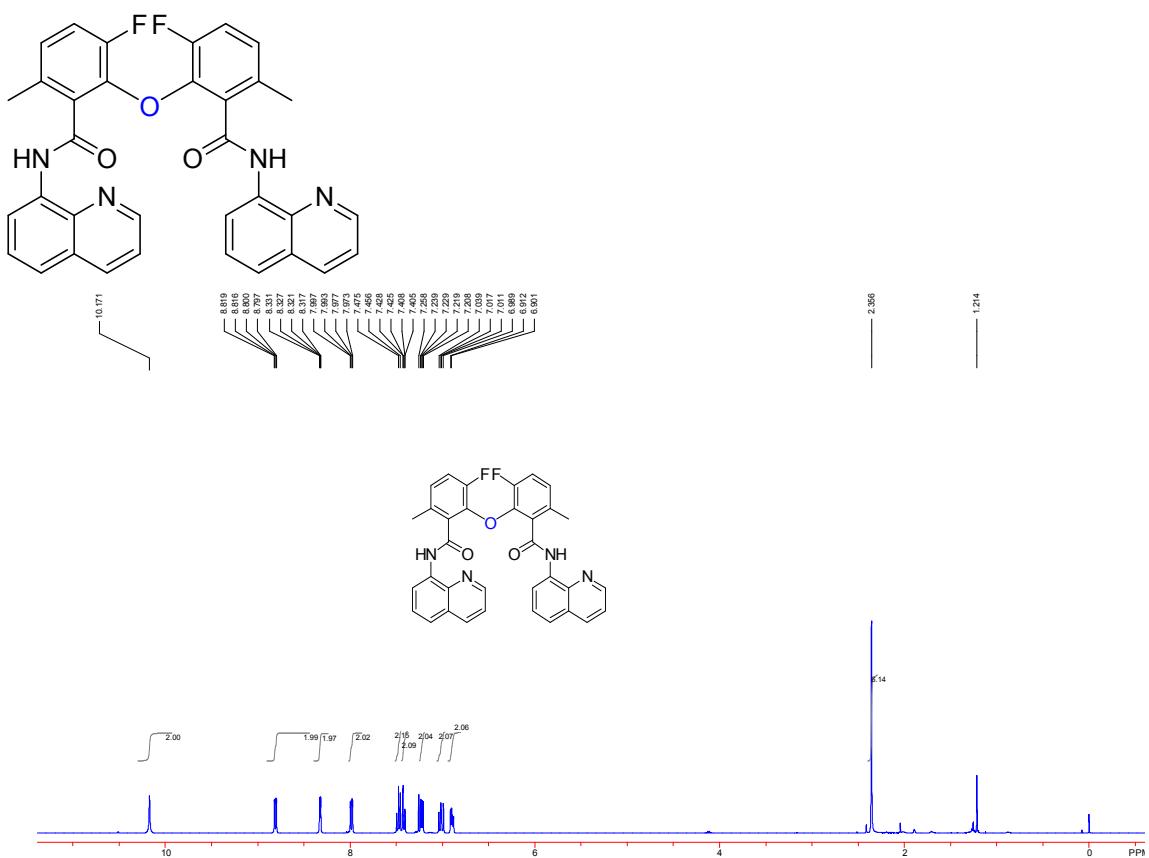


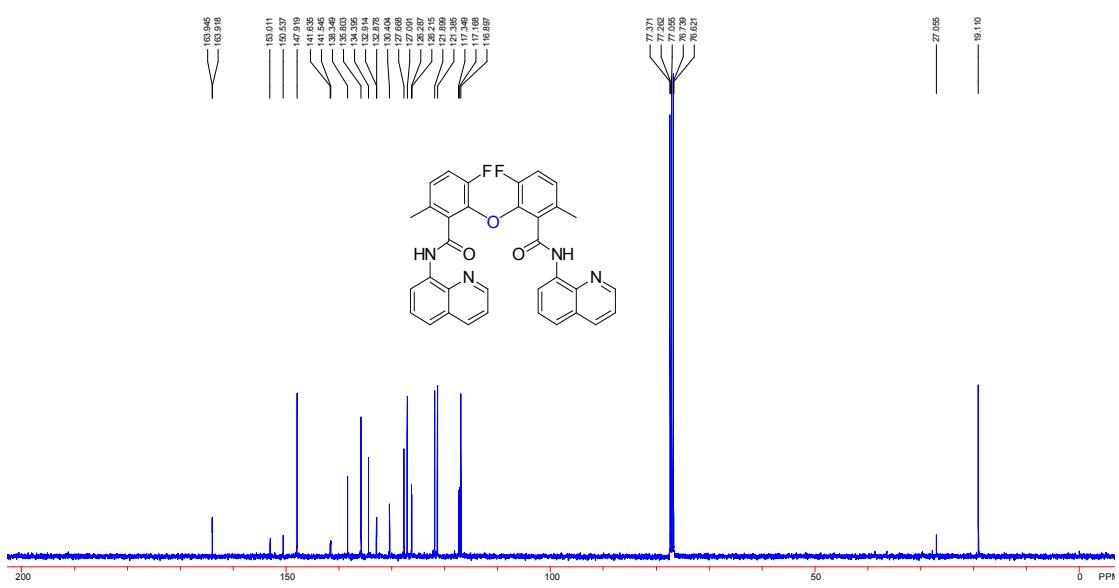
**6,6'-oxybis(4-bromo-2-methyl-N-(quinolin-8-yl)benzamide) (2n)**



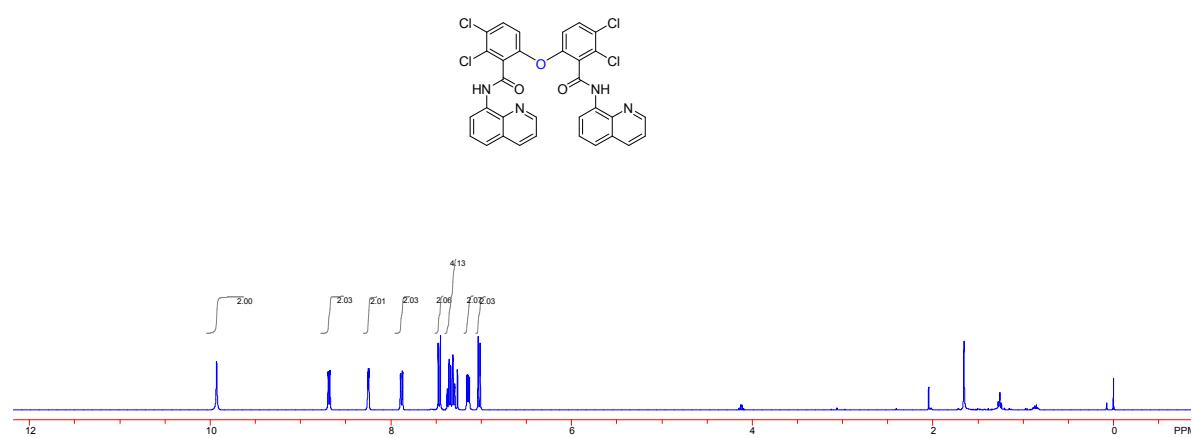
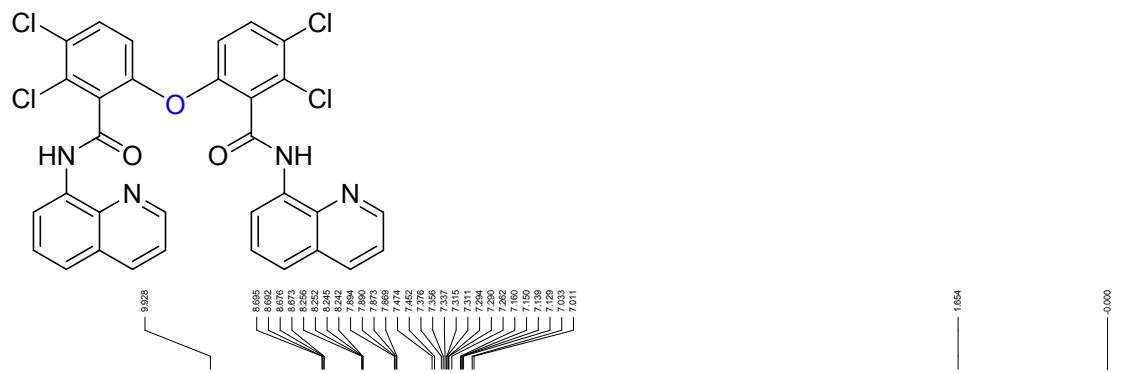


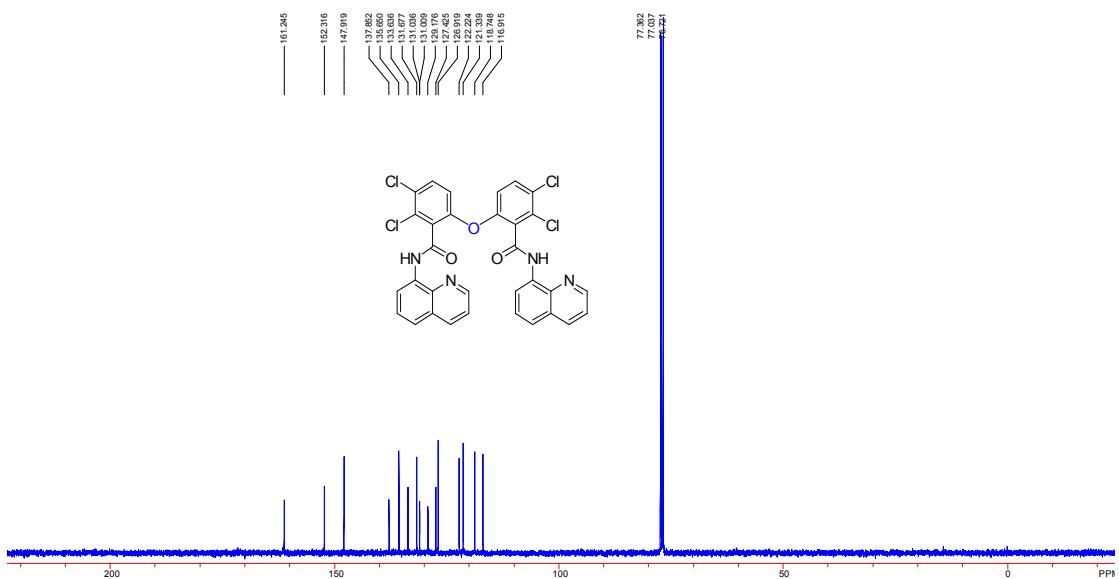
### **6,6'-oxybis(5-fluoro-2-methyl-N-(quinolin-8-yl)benzamide) (2o)**



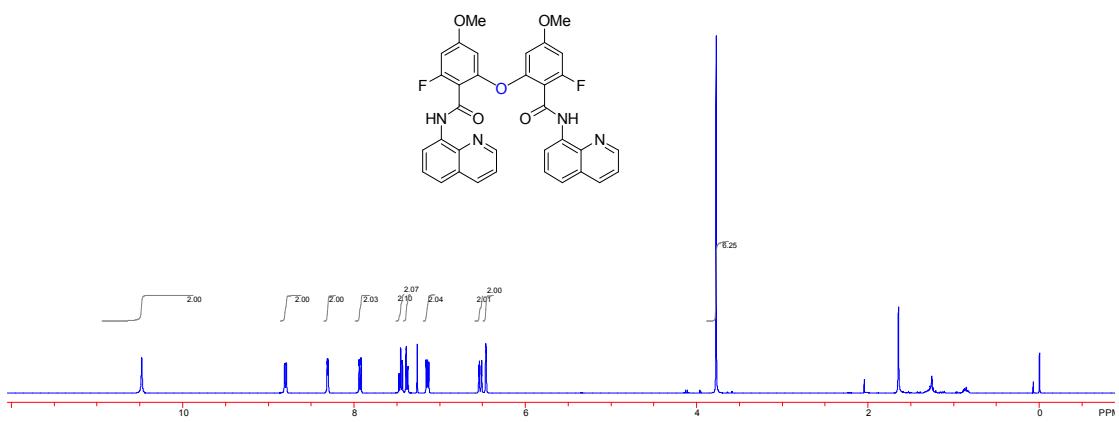
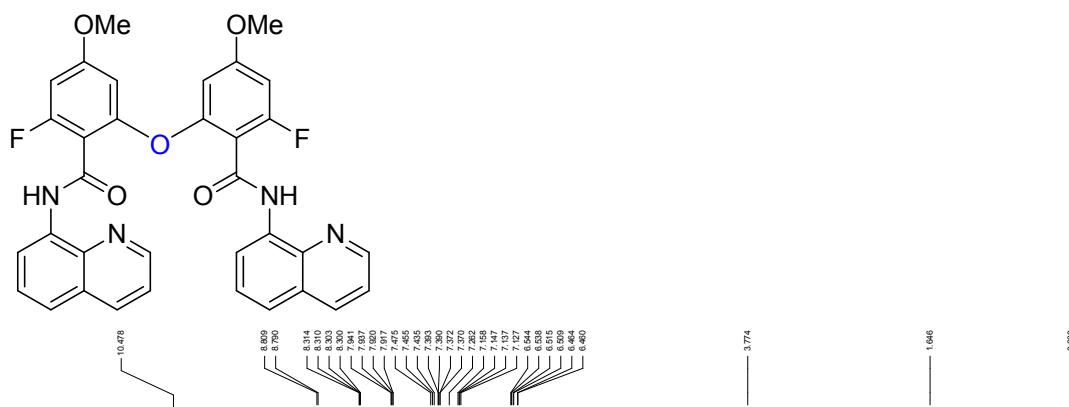


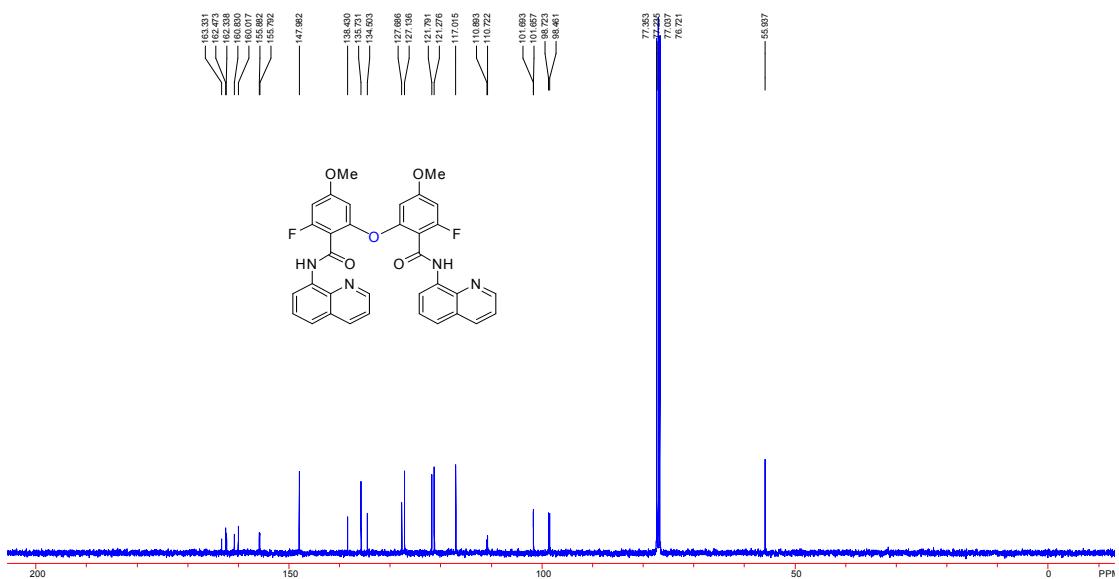
### 6,6'-oxybis(2,3-dichloro-N-(quinolin-8-yl)benzamide) (2p)



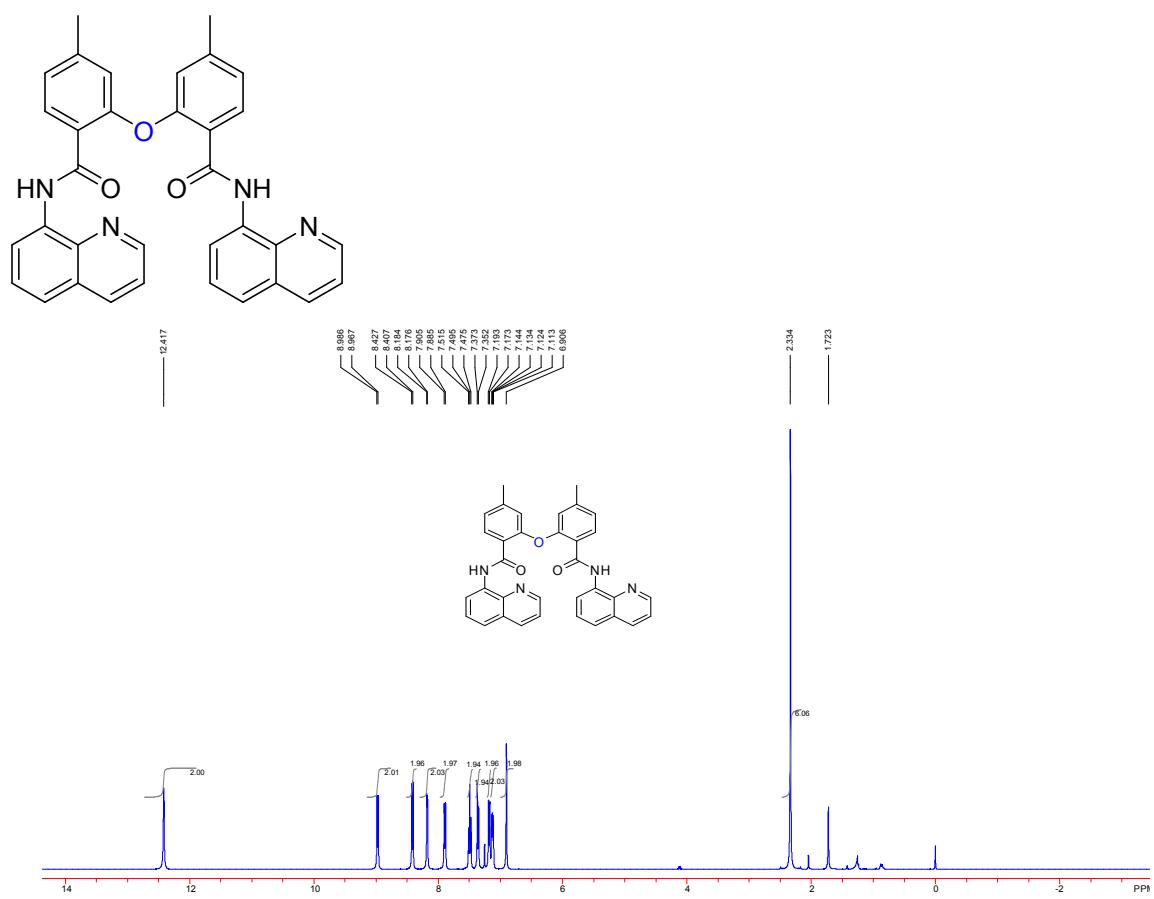


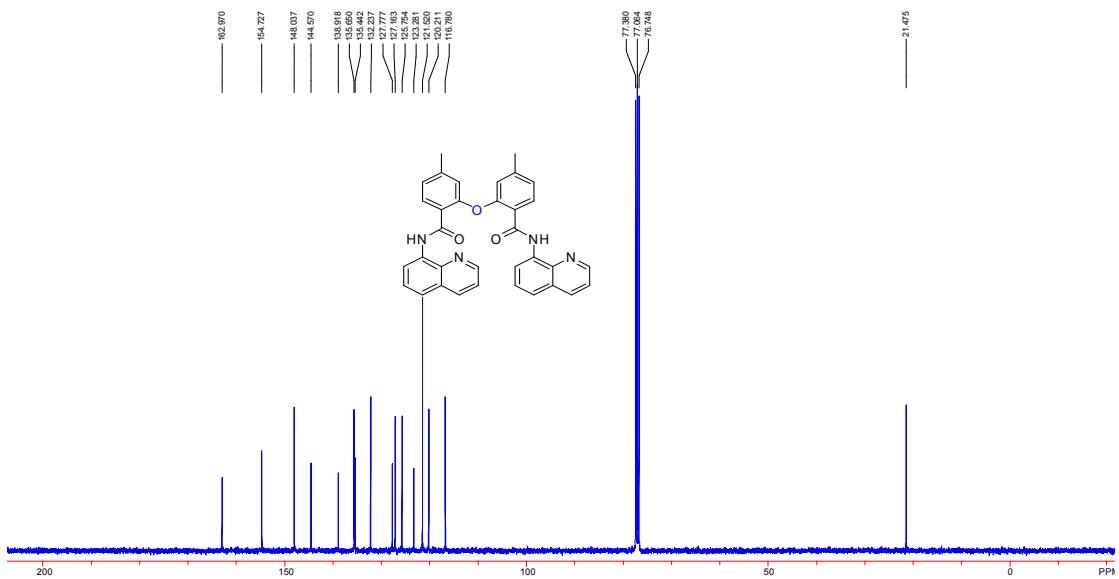
**6,6'-oxybis(2-fluoro-4-methoxy-N-(quinolin-8-yl)benzamide) (2q)**



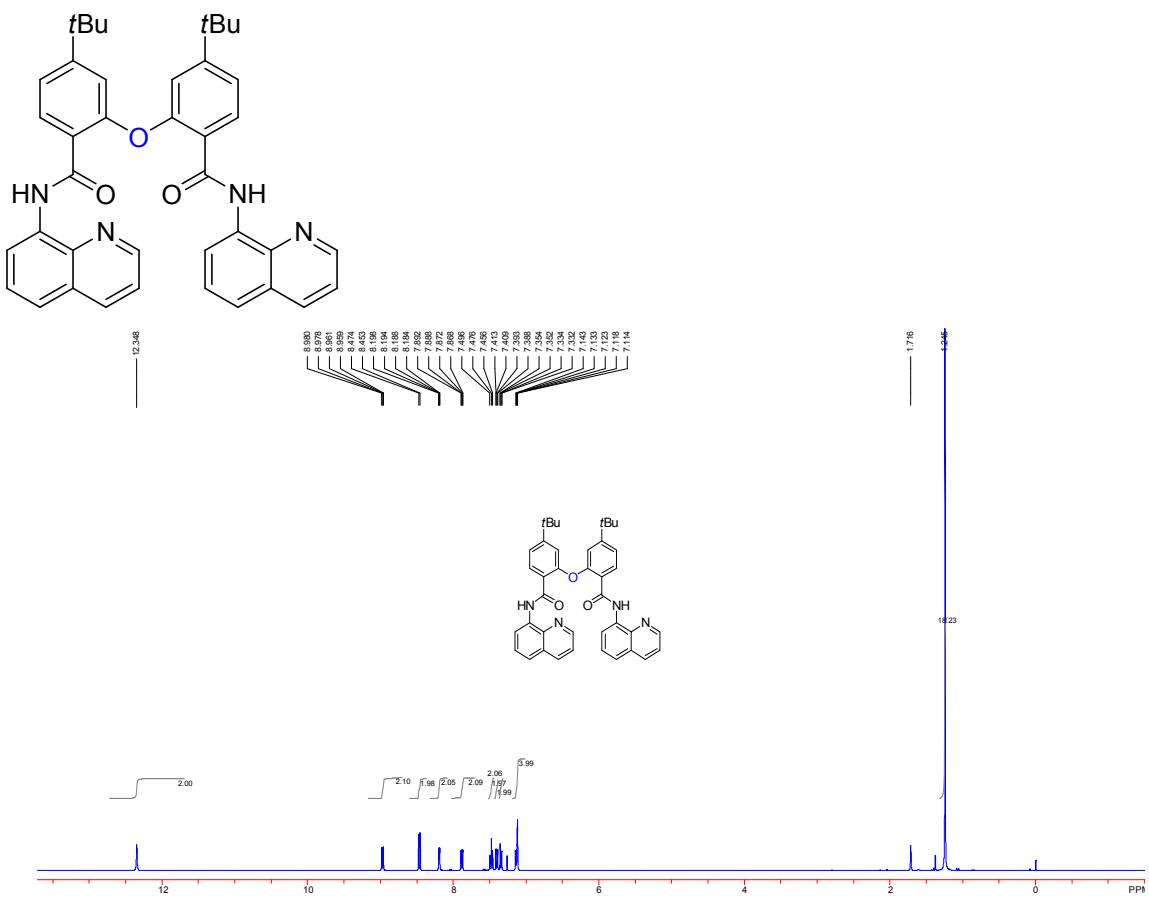


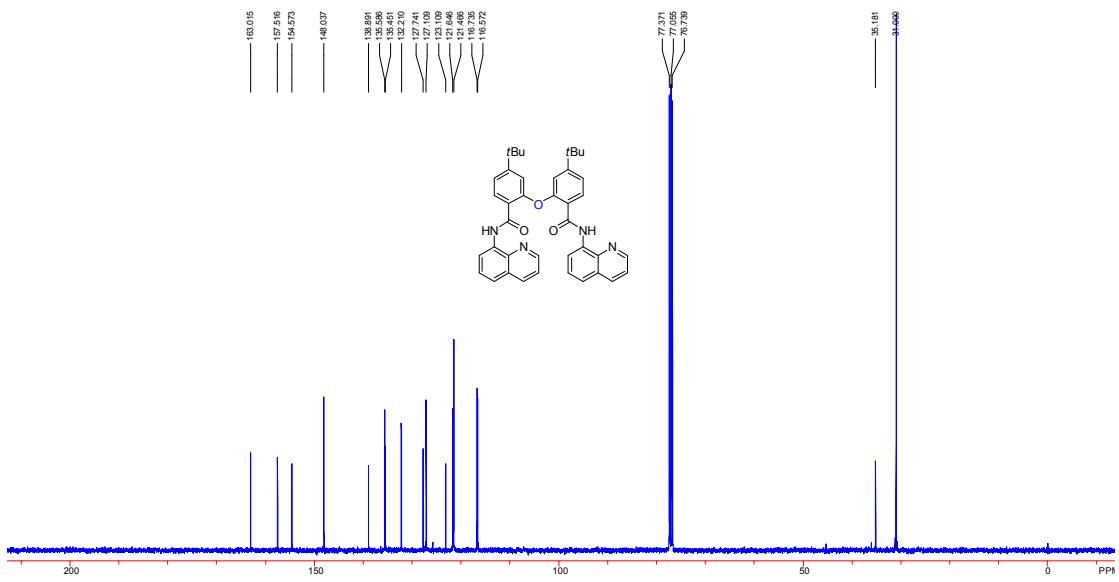
### 2,2'-oxybis(4-methyl-N-(quinolin-8-yl)benzamide) (2r)



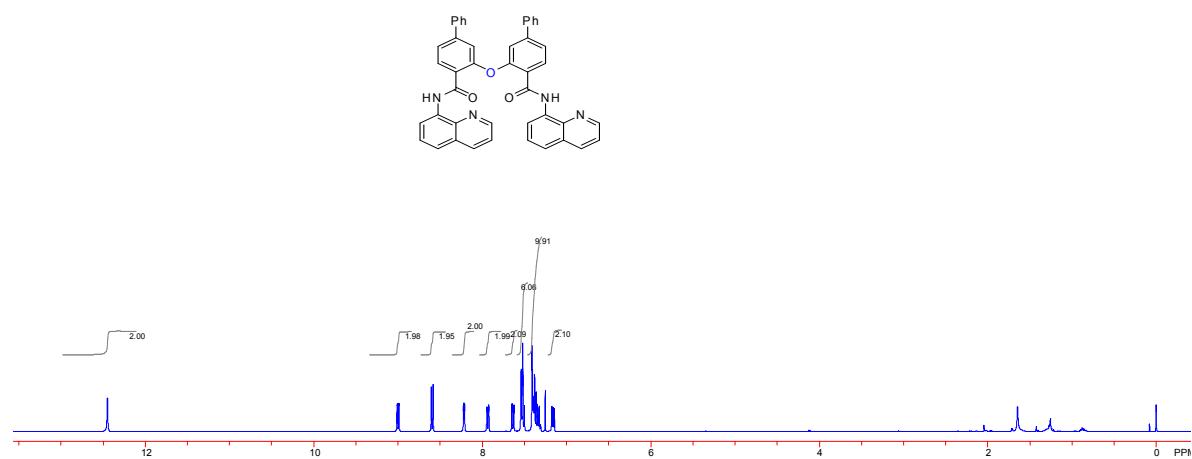
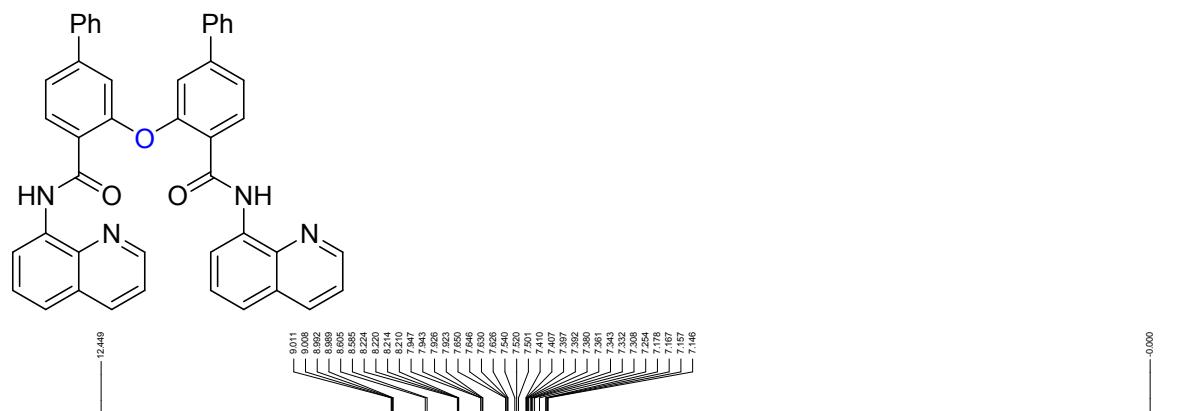


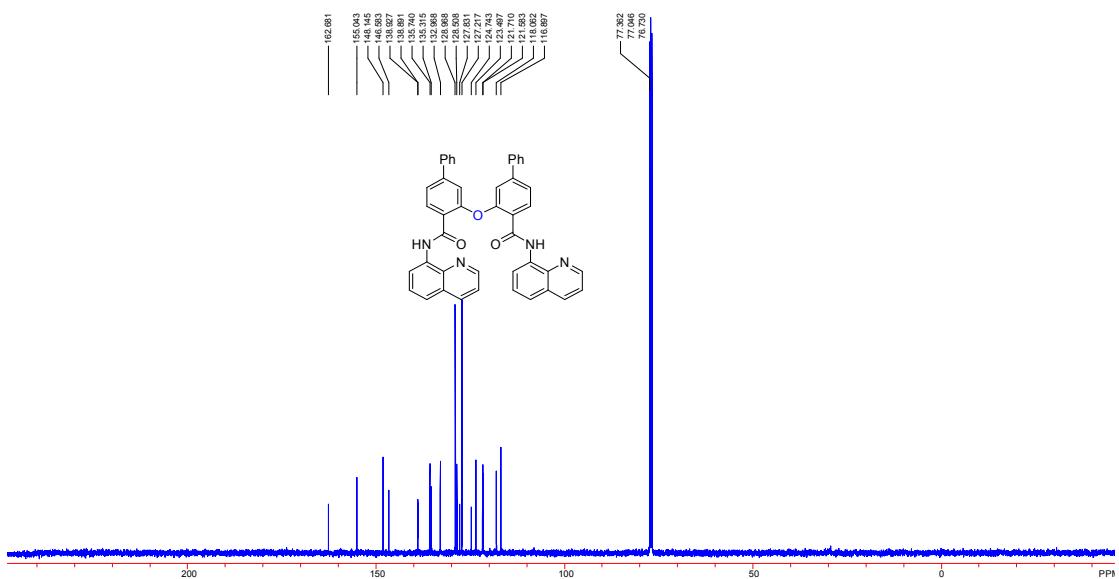
**2,2'-oxybis(4-(*tert*-butyl)-*N*-(quinolin-8-yl)benzamide) (2s)**



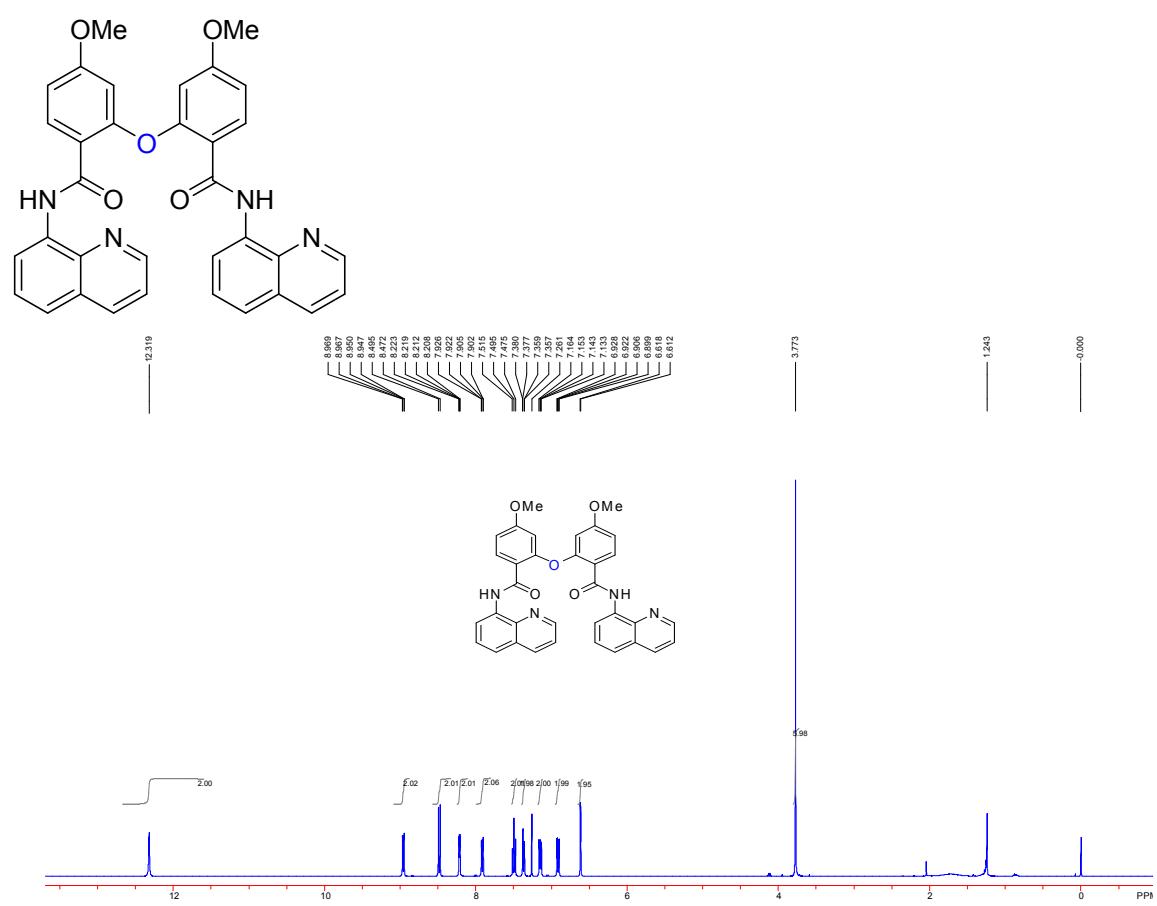


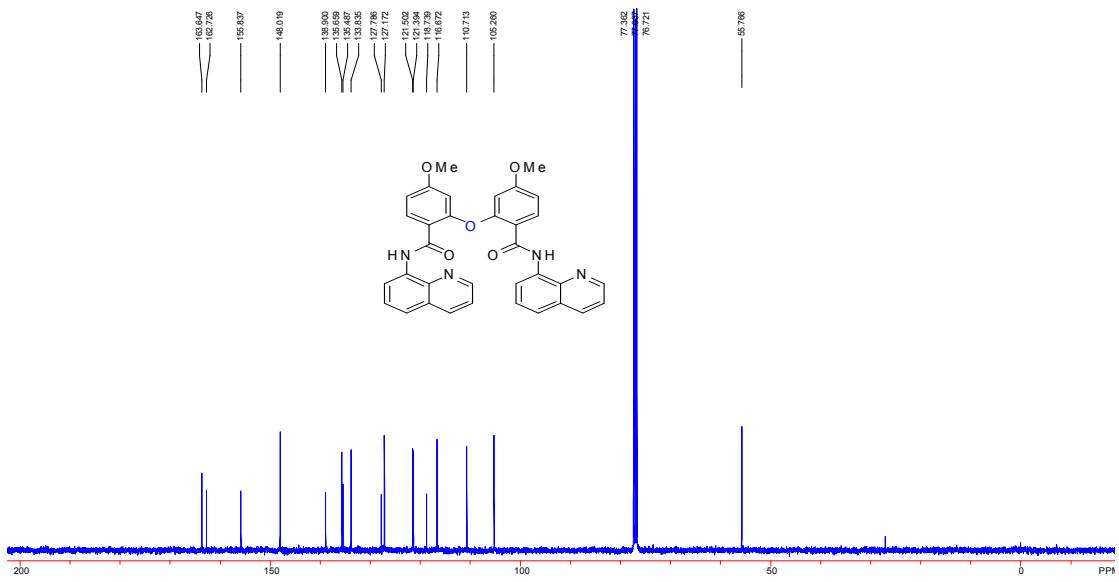
**3,3''-oxybis(*N*-(quinolin-8-yl)-[1,1'-biphenyl]-4-carboxamide) (2t)**



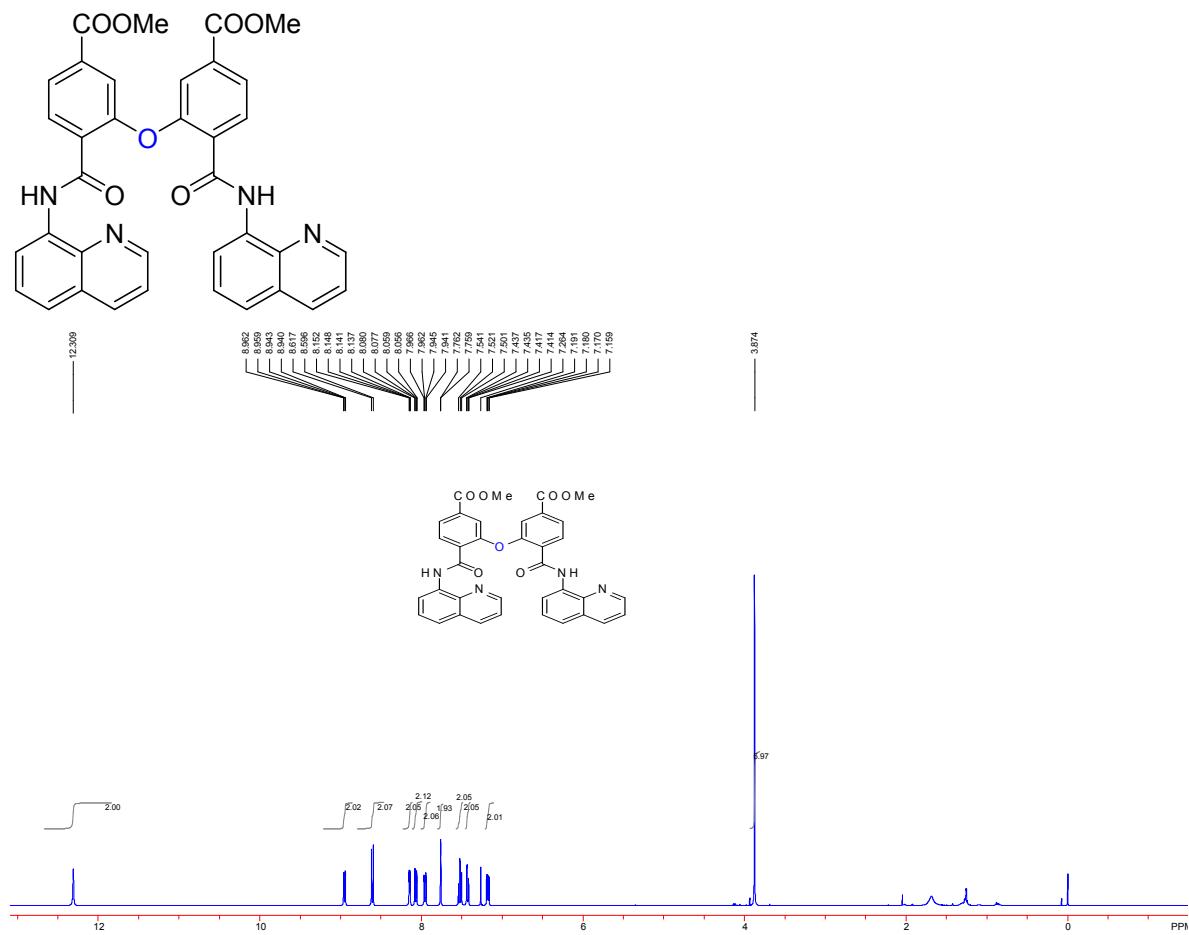


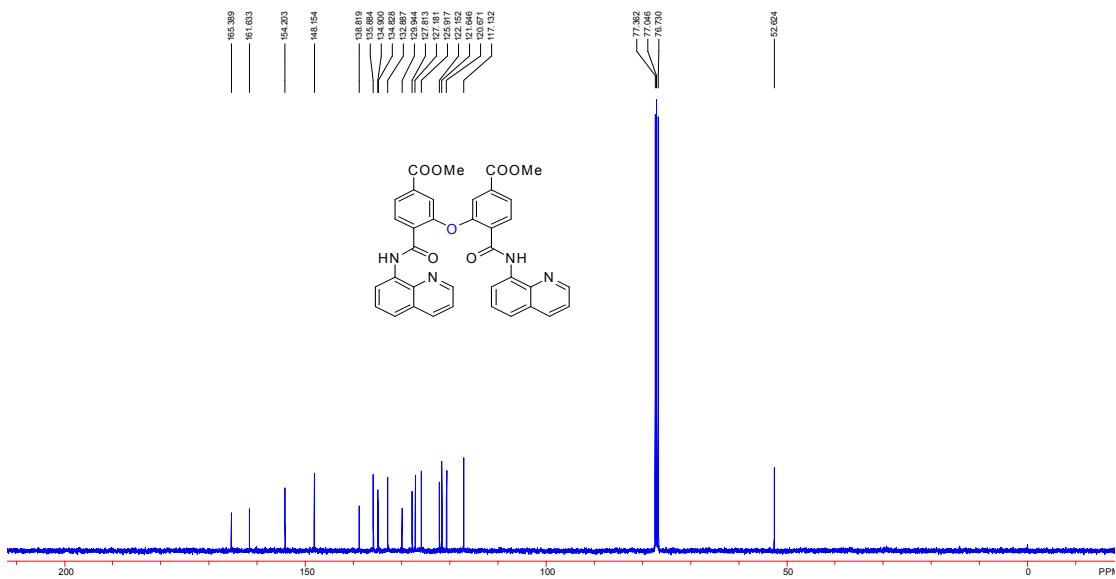
**(2,2'-oxybis(4-methoxy-N-(quinolin-8-yl)benzamide) (2u)**



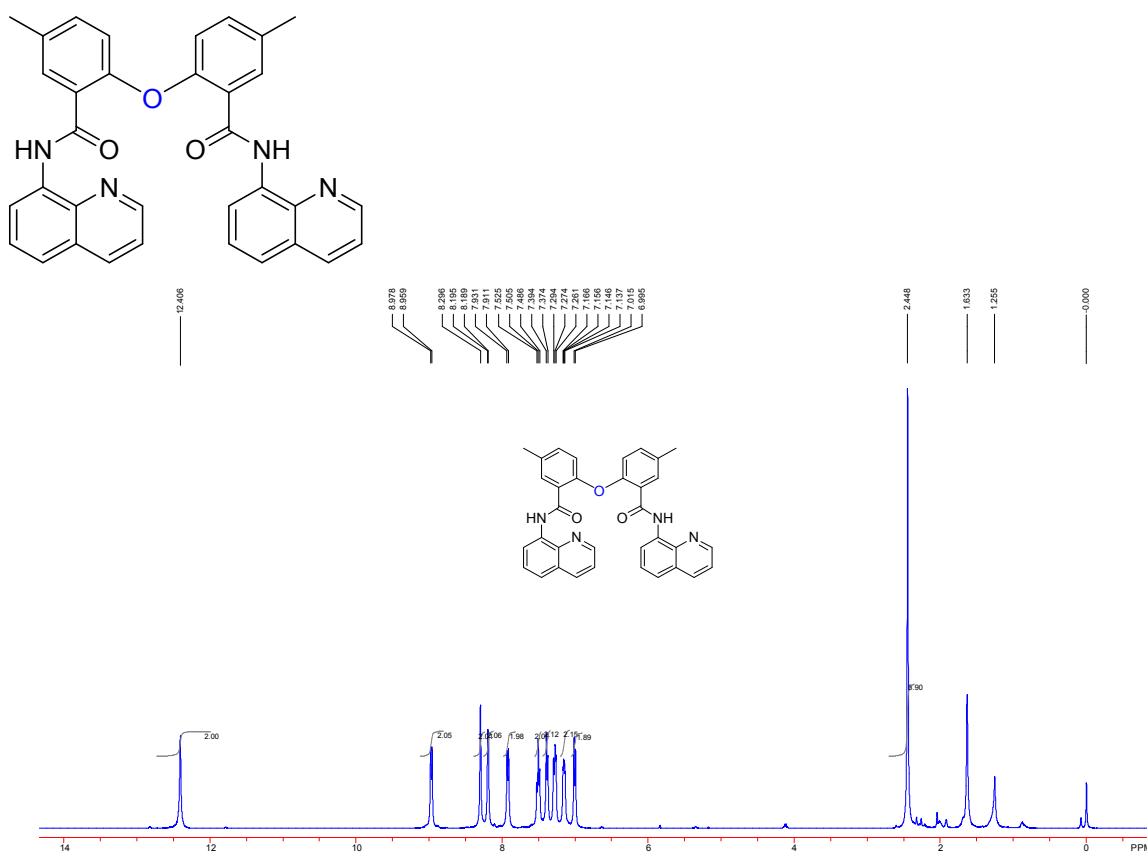


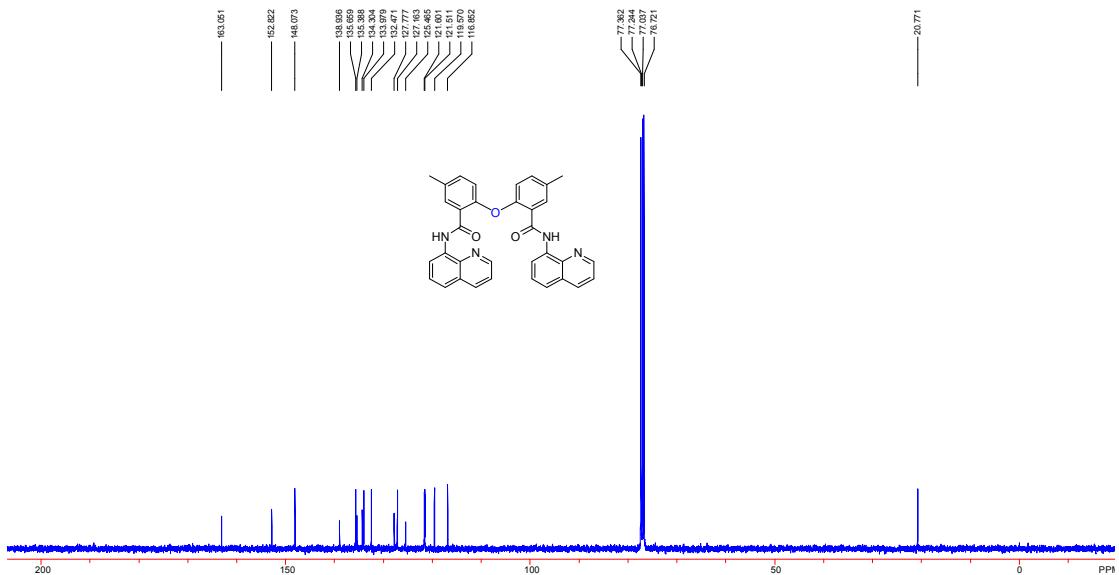
**dimethyl 3,3'-oxybis(4-(quinolin-8-ylcarbamoyl)benzoate) (2v)**



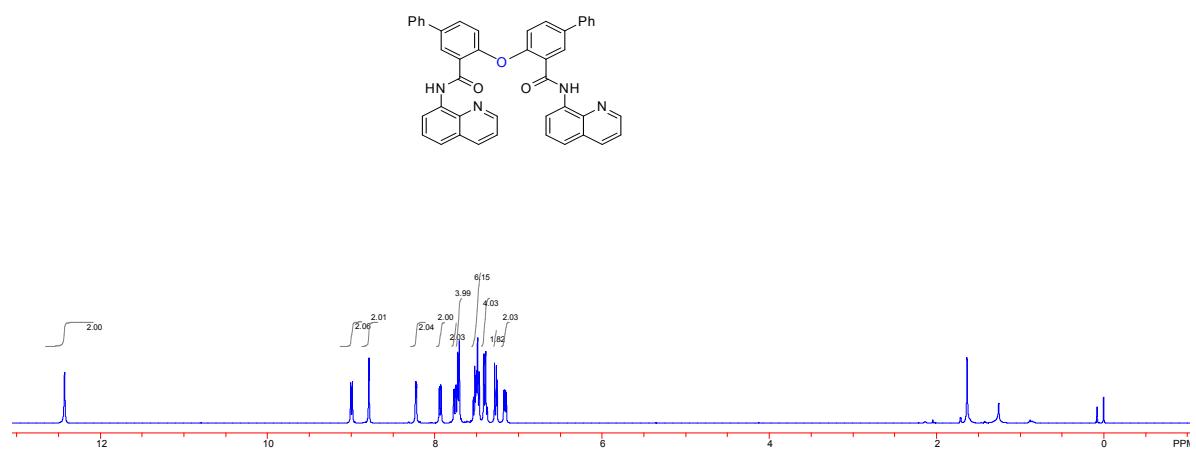
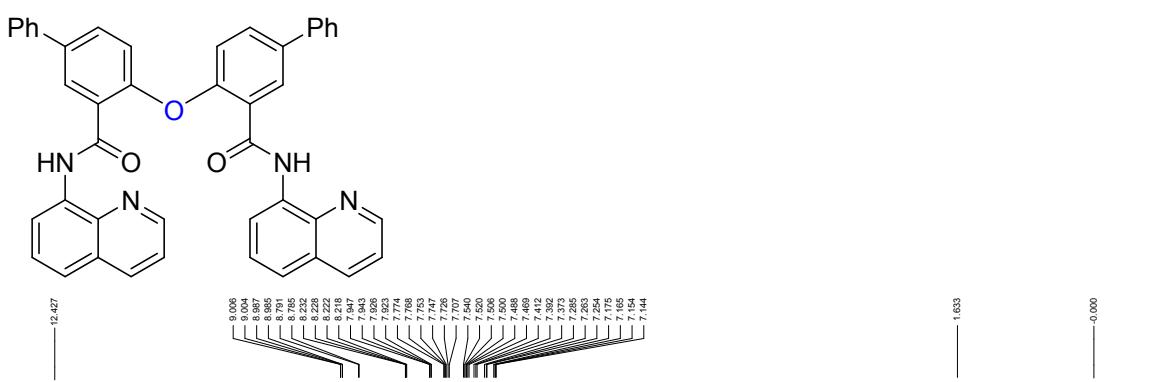


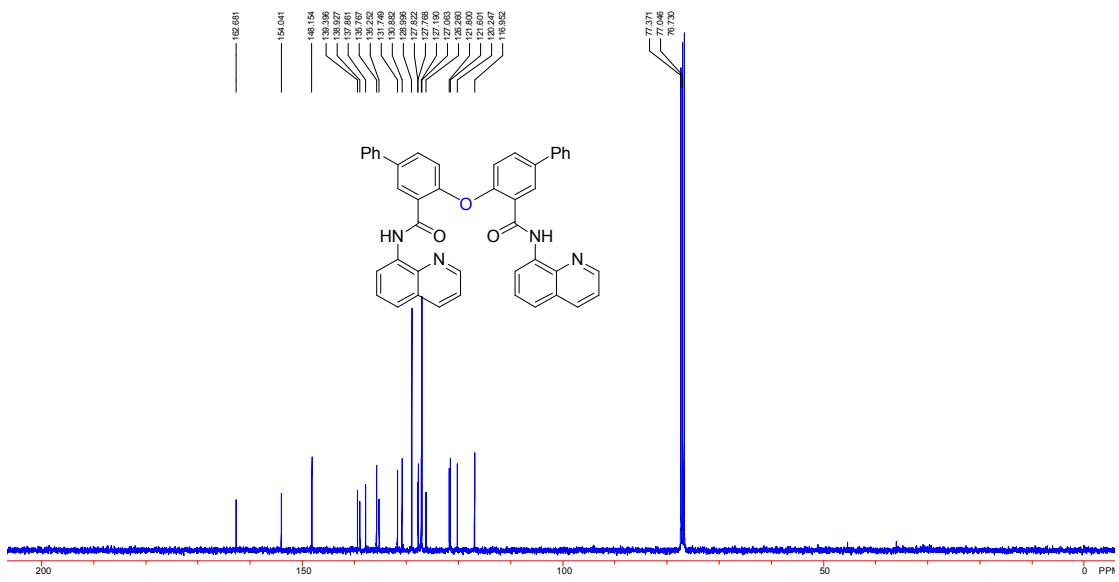
### 6,6'-oxybis(3-methyl-N-(quinolin-8-yl)benzamide) (2w)



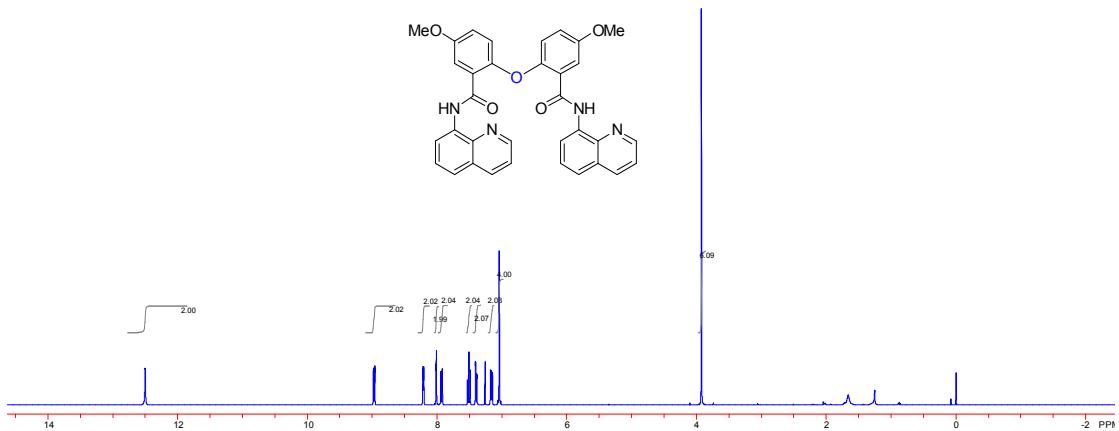
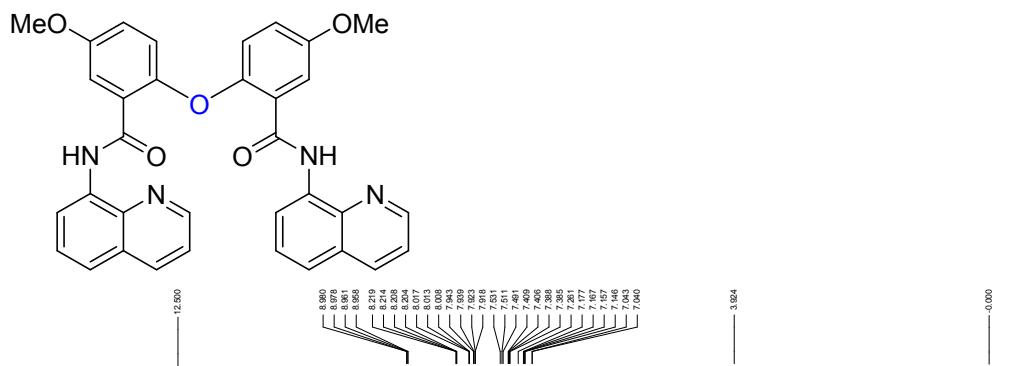


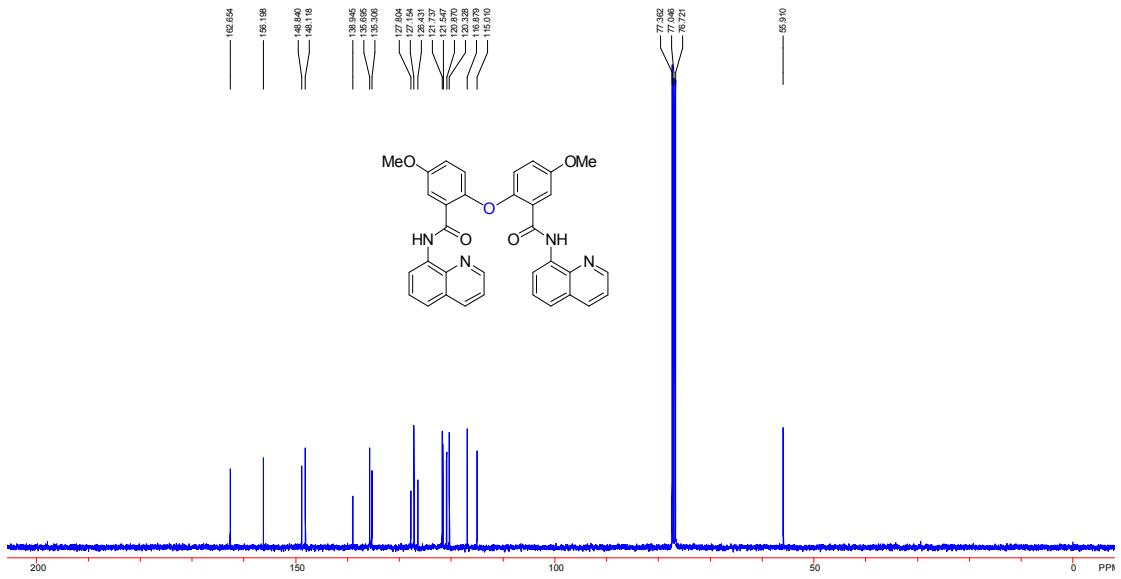
### 4,4''-oxybis(N-(quinolin-8-yl)-[1,1'-biphenyl]-3-carboxamide) (2x)



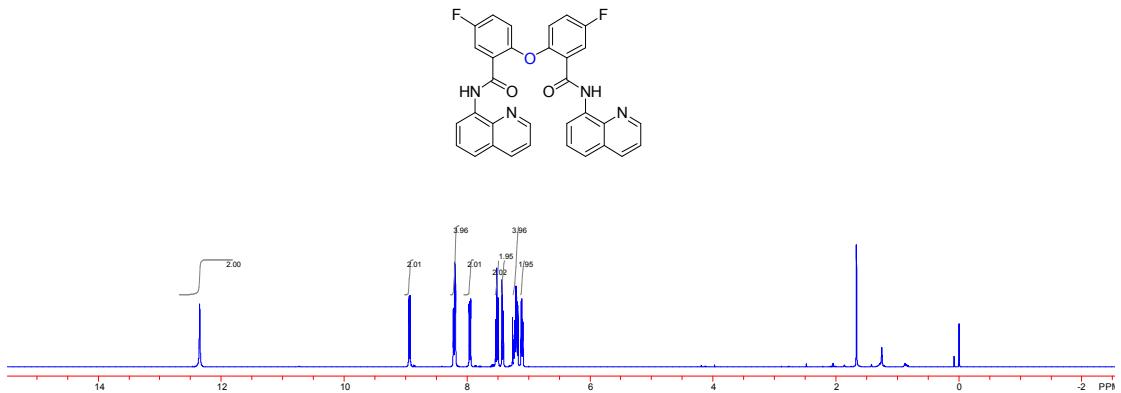
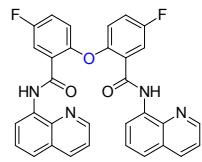
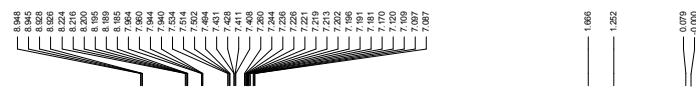
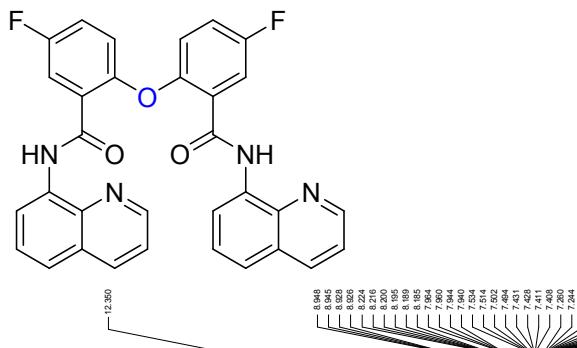


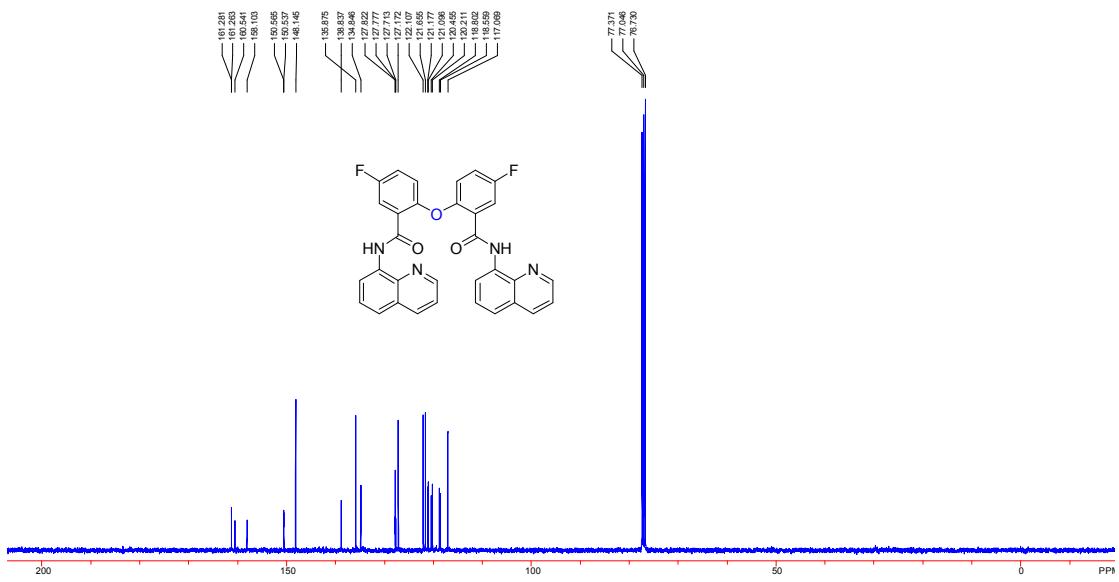
### 6,6'-oxybis(3-methoxy-N-(quinolin-8-yl)benzamide) (2y)



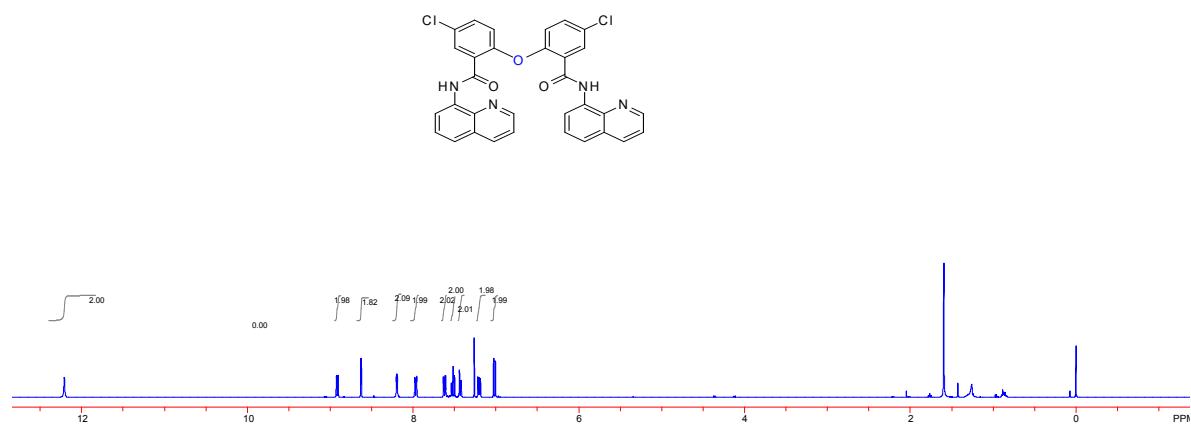
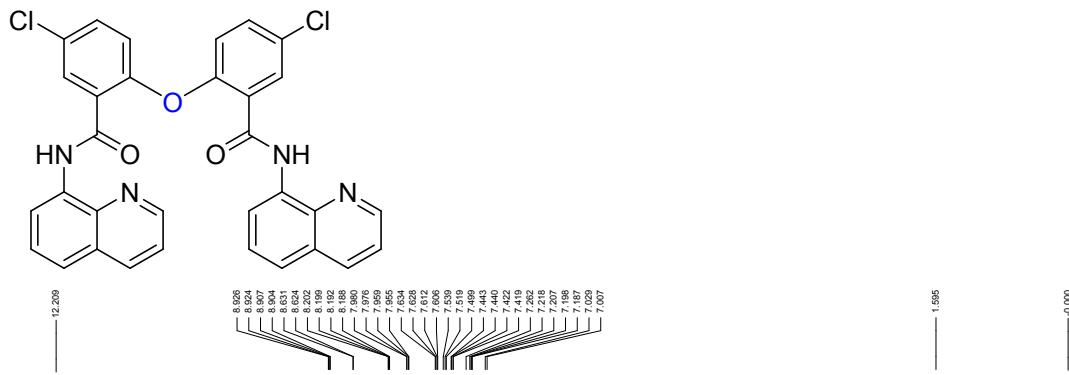


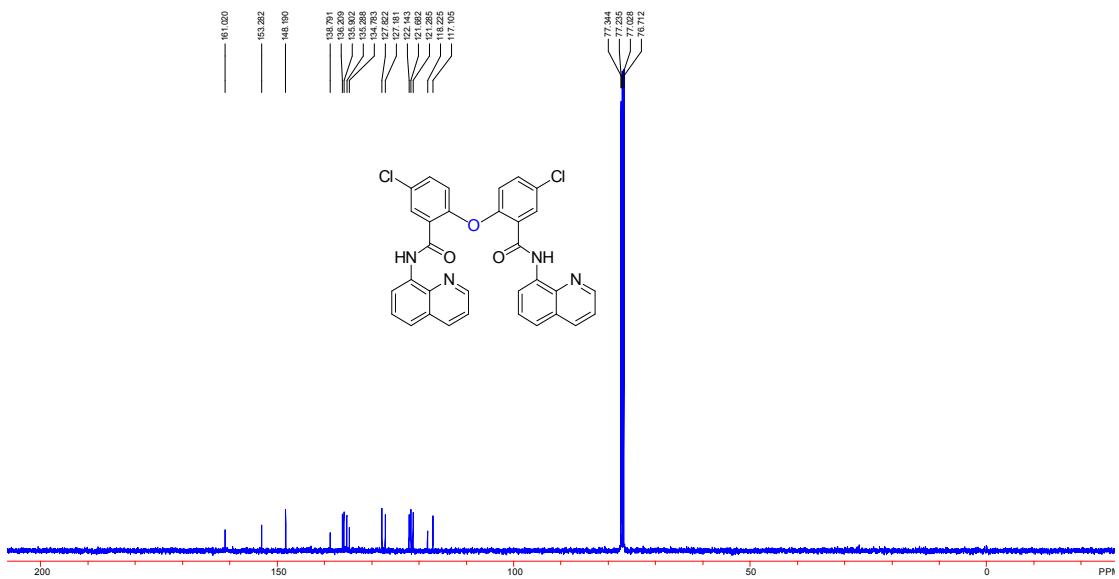
### 6,6'-oxybis(3-fluoro-N-(quinolin-8-yl)benzamide) (2z)



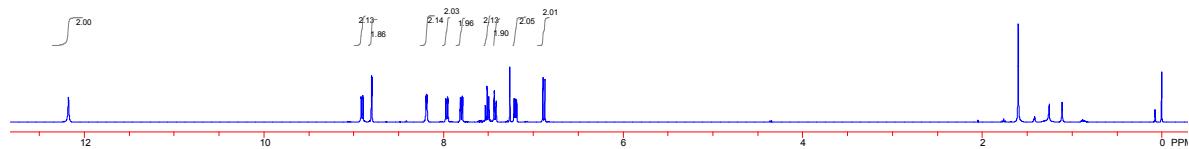
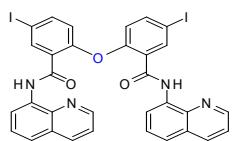
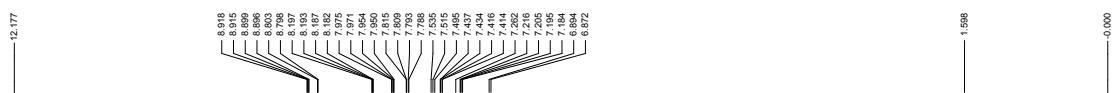
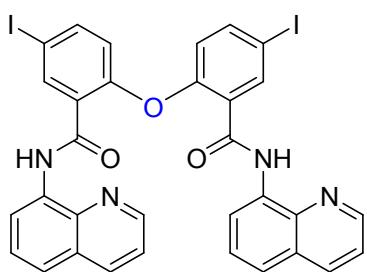


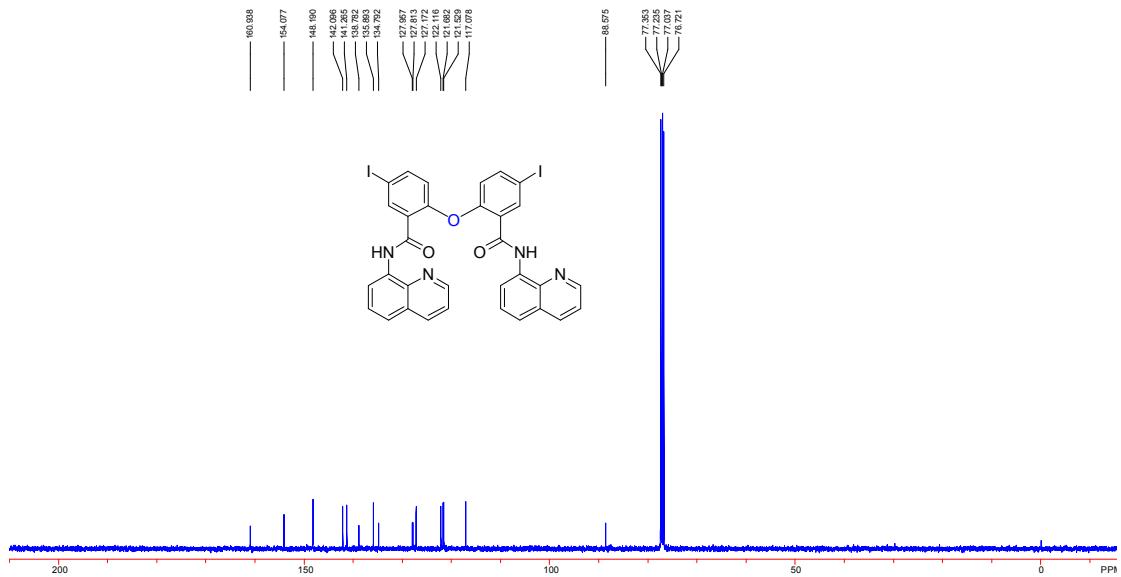
### 6,6'-oxybis(3-chloro-N-(quinolin-8-yl)benzamide) (2aa)



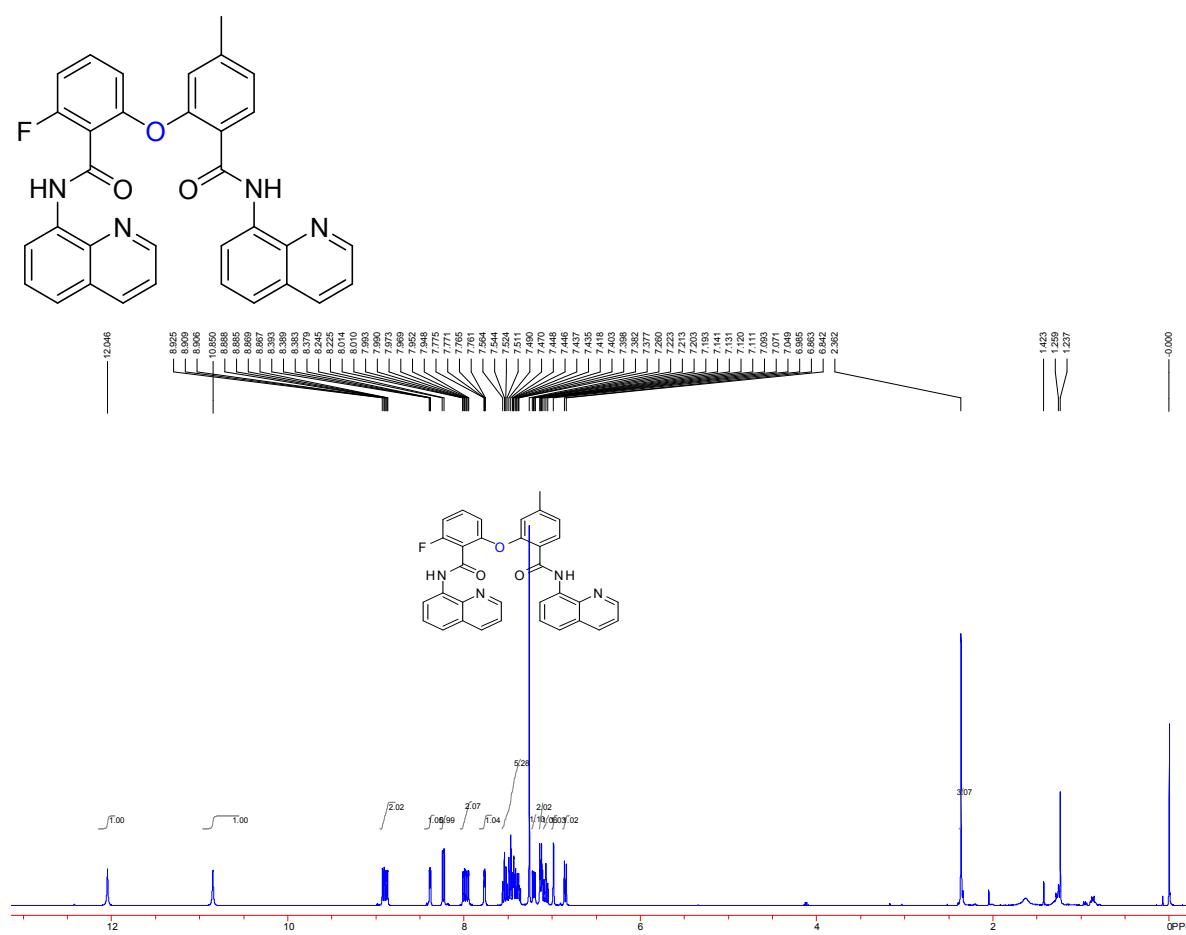


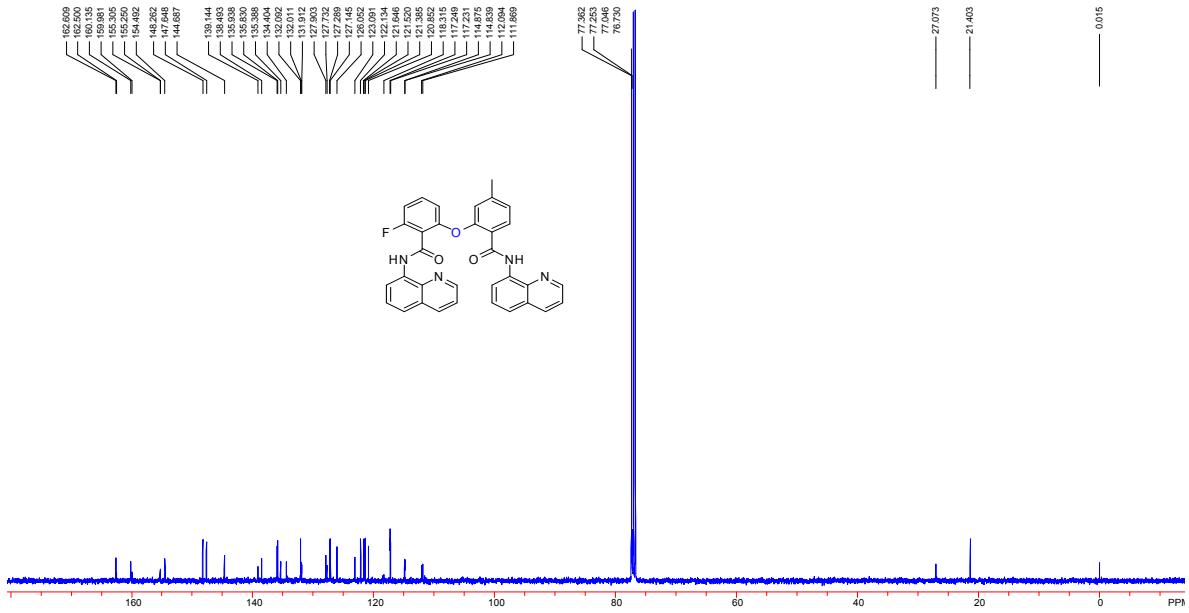
### 6,6'-oxybis(3-iodo-N-(quinolin-8-yl)benzamide) (2ab)



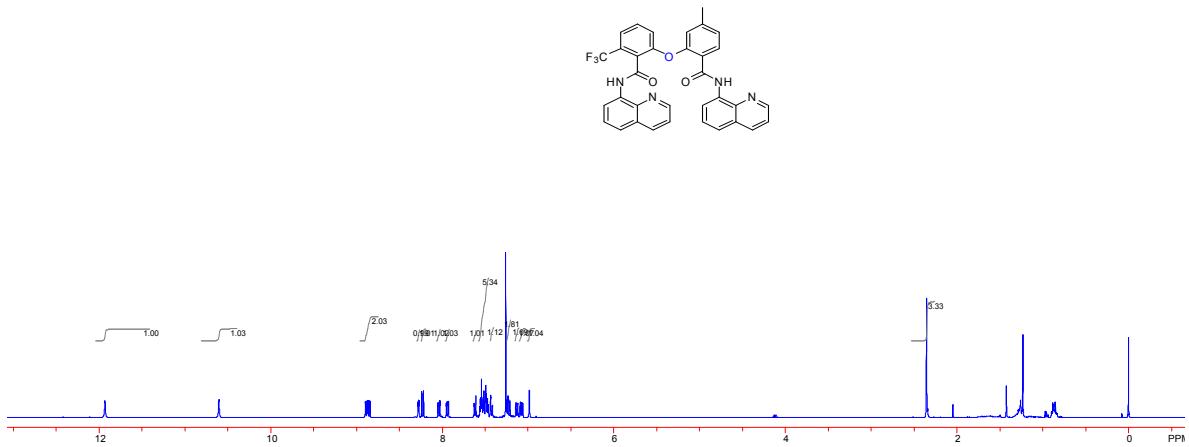
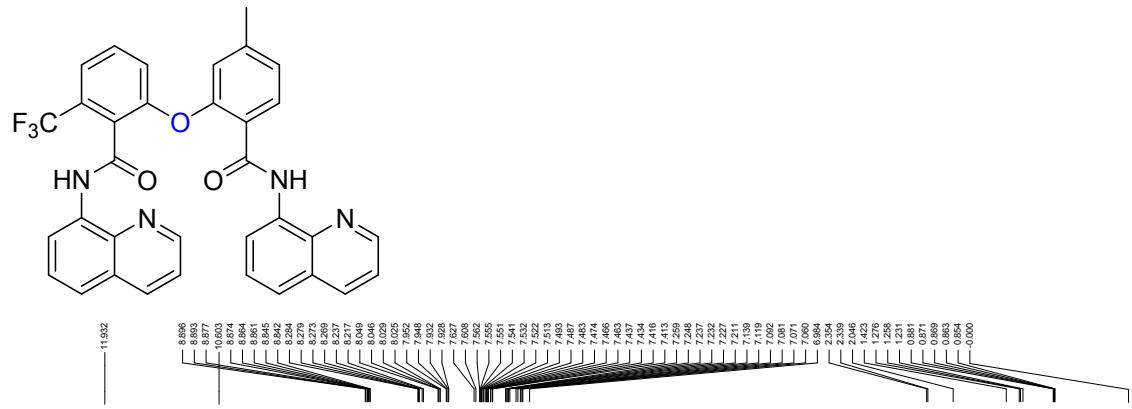


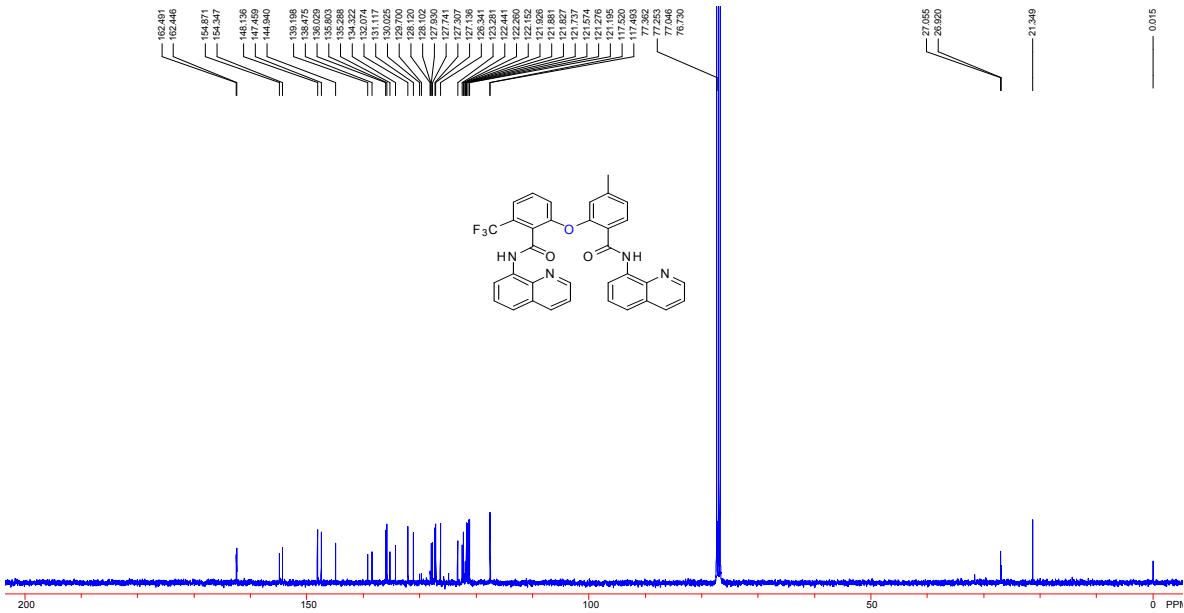
**2-(3-fluoro-2-(quinolin-8-ylcarbamoyl)phenoxy)-4-methyl-N-(quinolin-8-yl)benzamide  
(3a)**



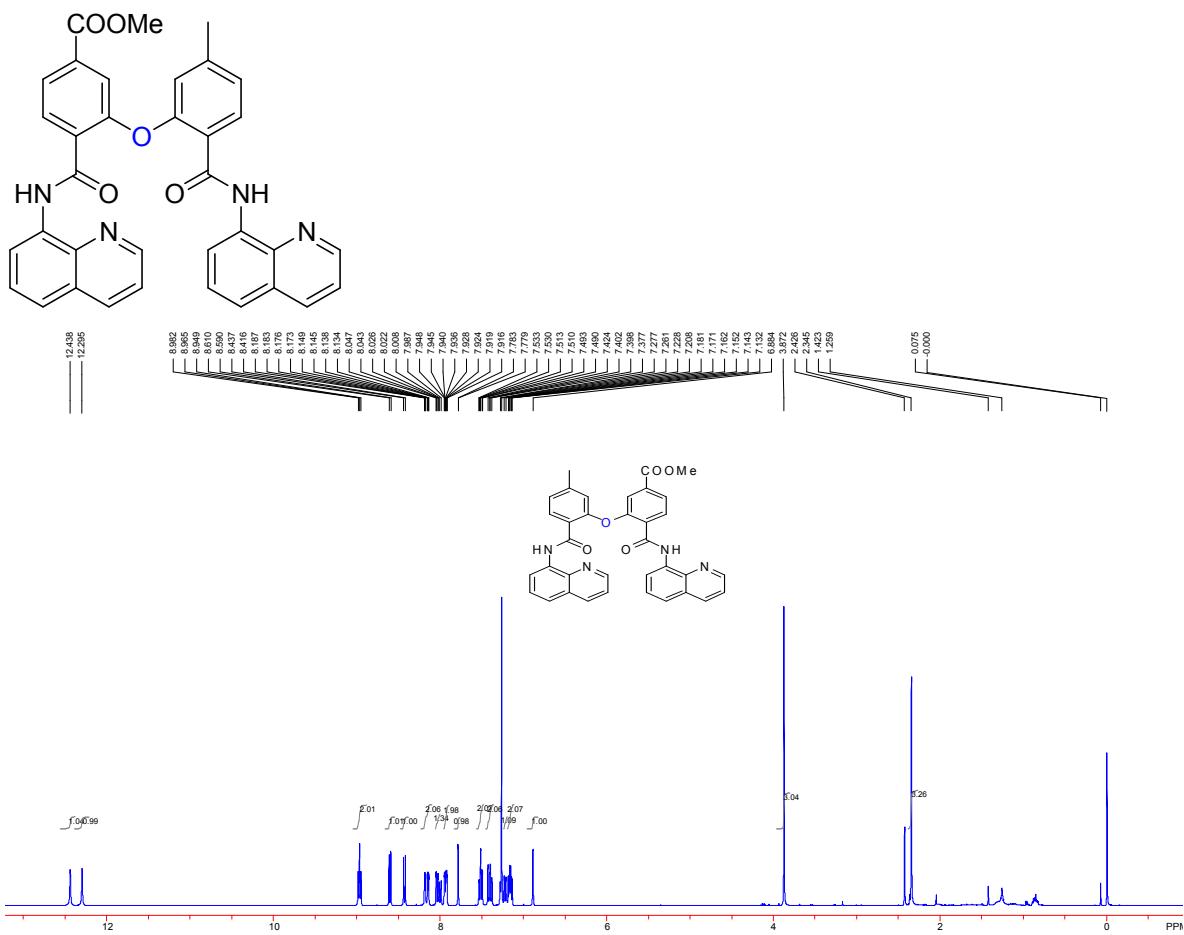


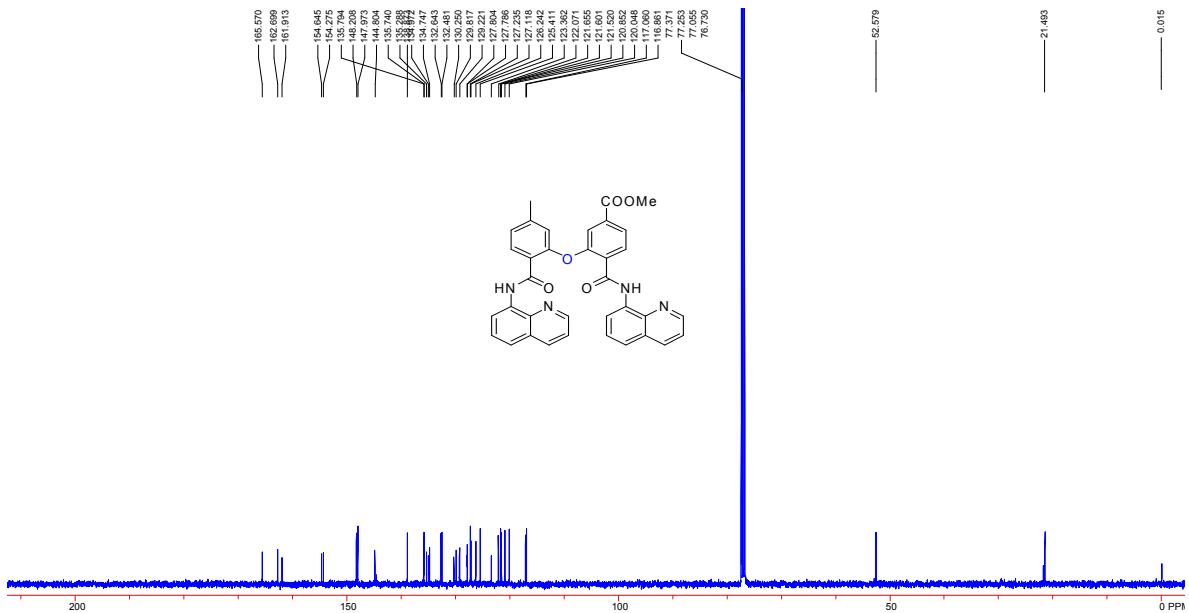
### **4-methyl-N-(quinolin-8-yl)-2-(2-(quinolin-8-ylcarbamoyl)-3-(trifluoromethyl)phenoxy)benzamide (3b)**



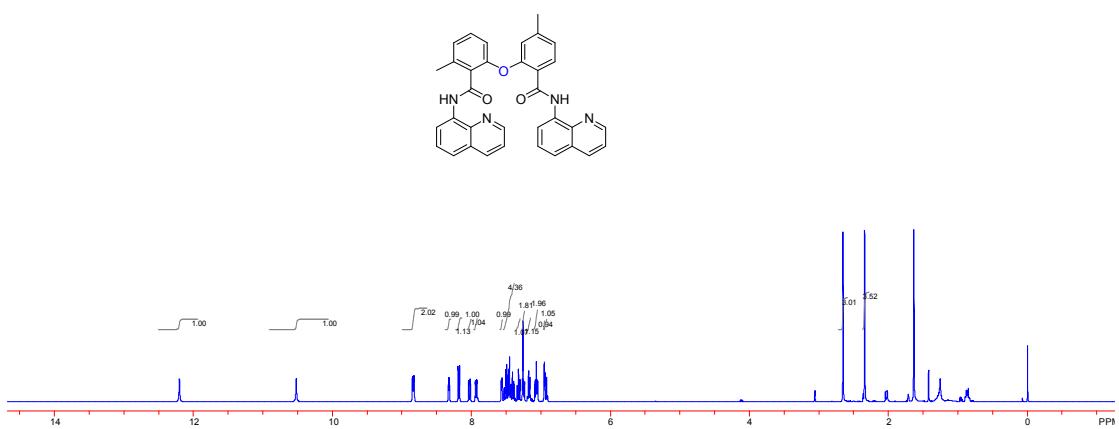
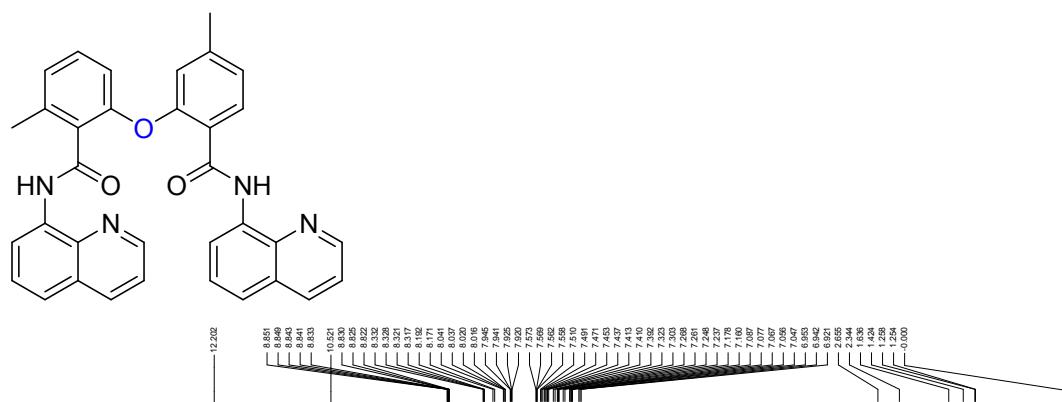


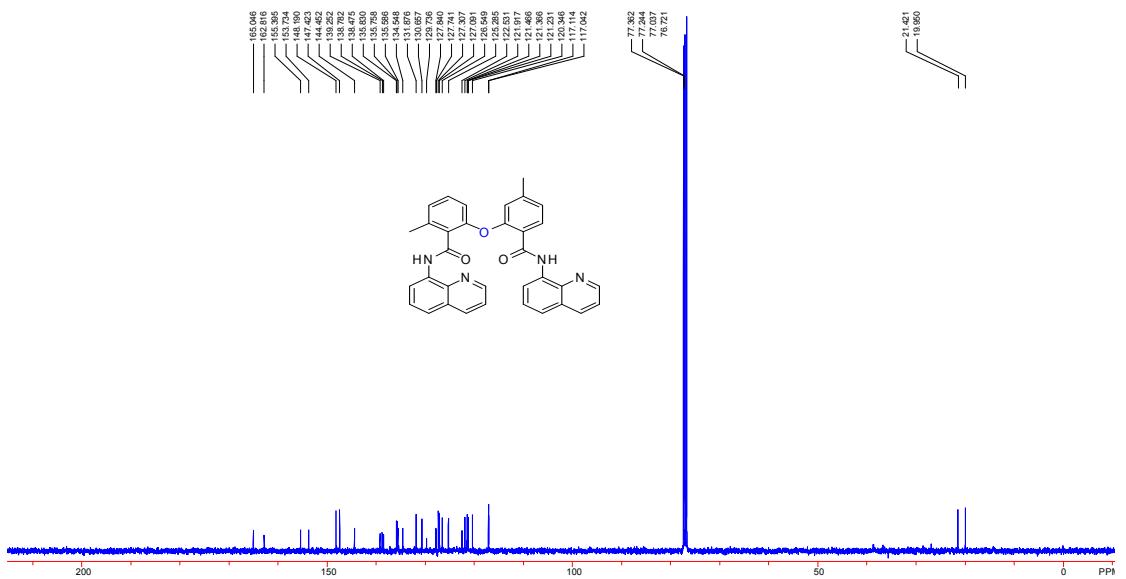
**methyl 3-(5-methyl-2-(quinolin-8-ylcarbamoyl)phenoxy)-4-(quinolin-8-ylcarbamoyl)benzoate (3c)**



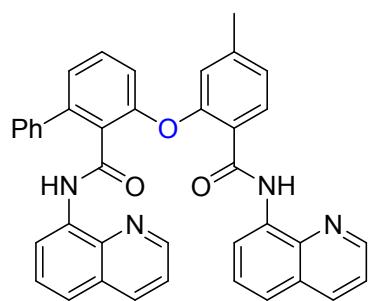


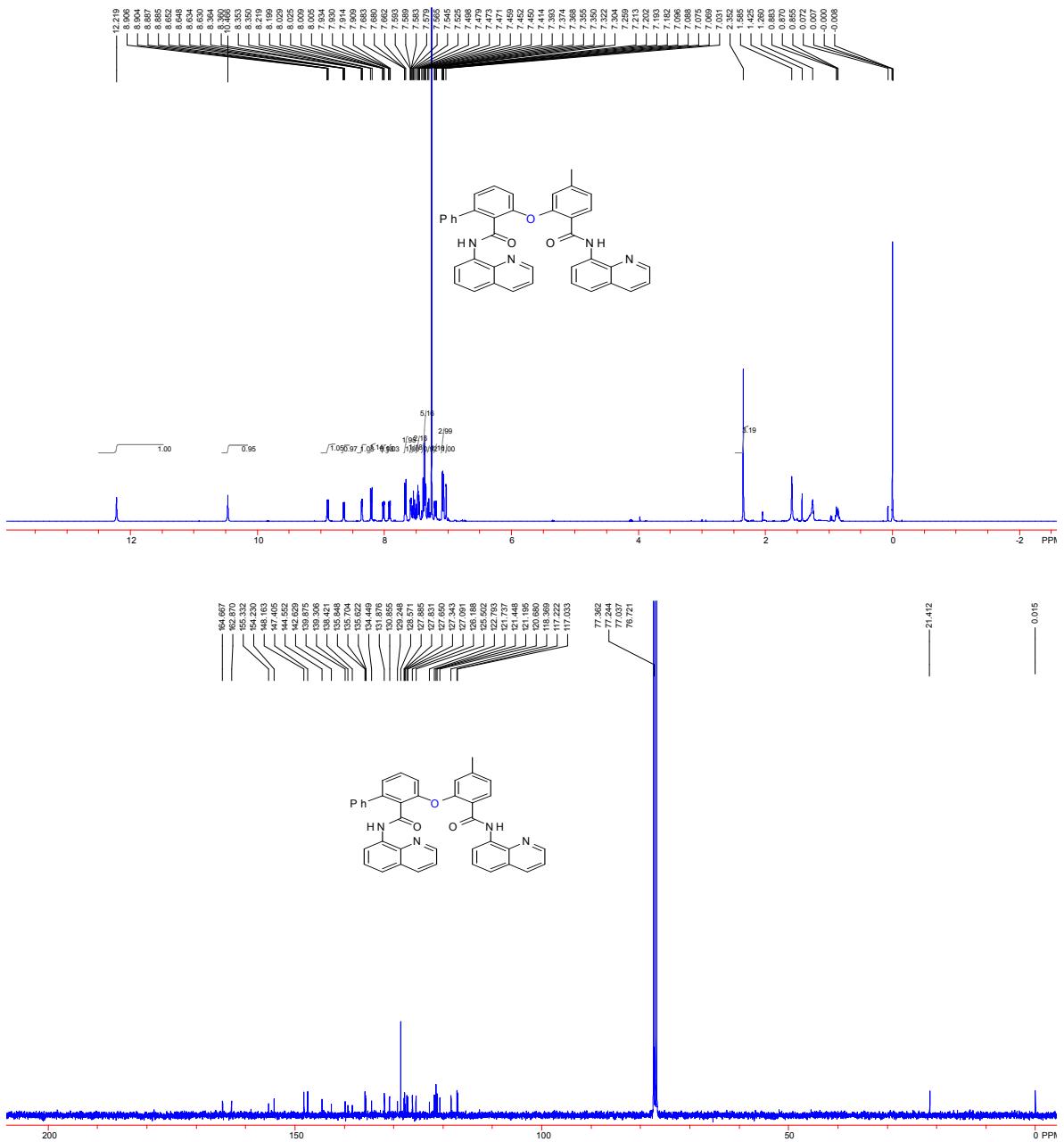
### **4-methyl-2-(3-methyl-2-(quinolin-8-ylcarbamoyl)phenoxy)-N-(quinolin-8-yl)benzamide (3d)**



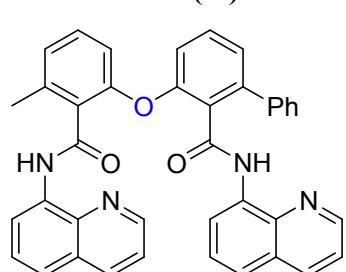


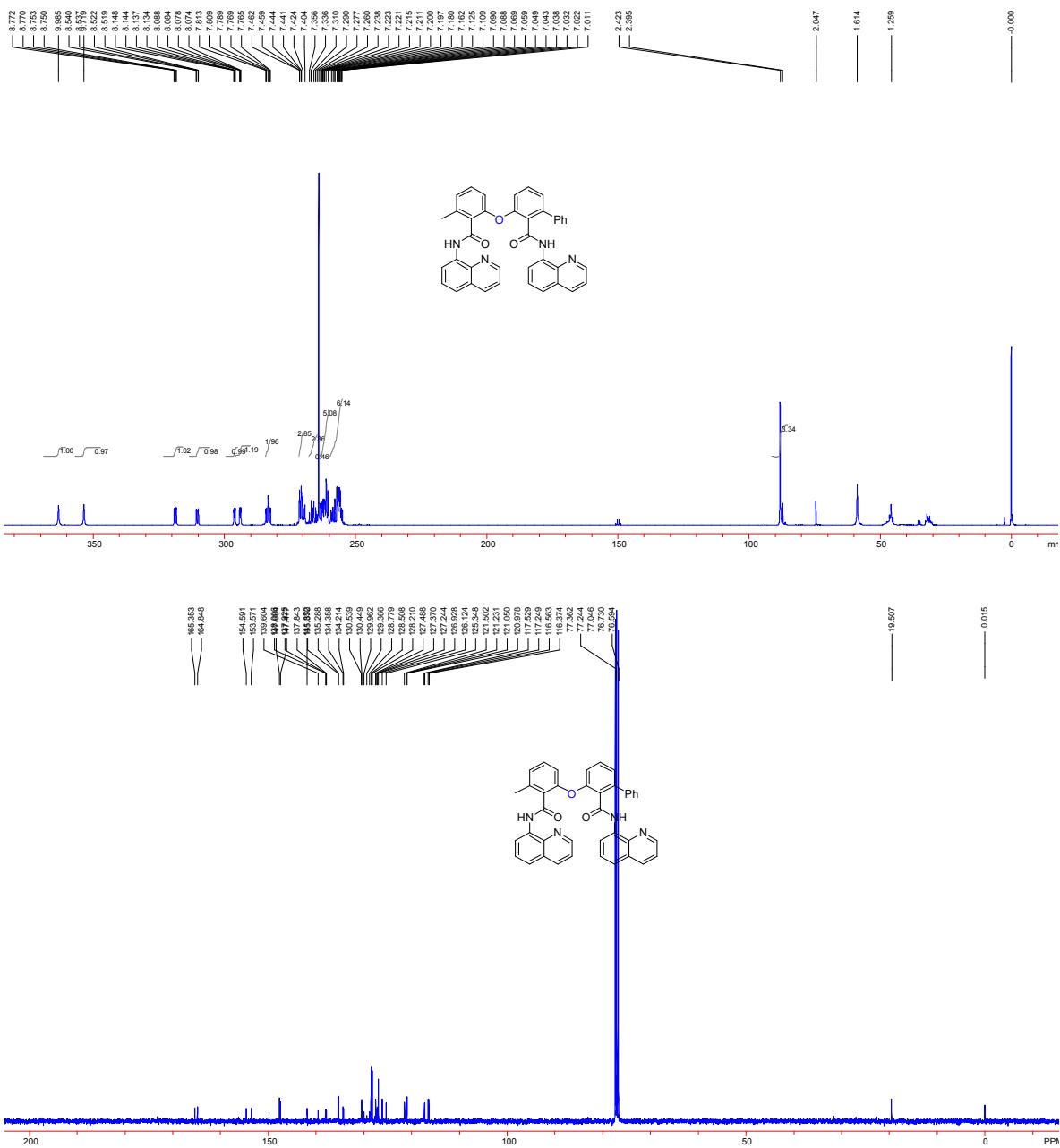
**3-(5-methyl-2-(quinolin-8-ylcarbamoyl)phenoxy)-N-(quinolin-8-yl)-[1,1'-biphenyl]-2-carboxamide (3e)**



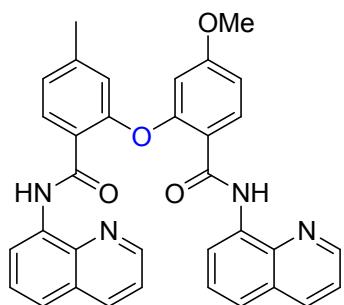


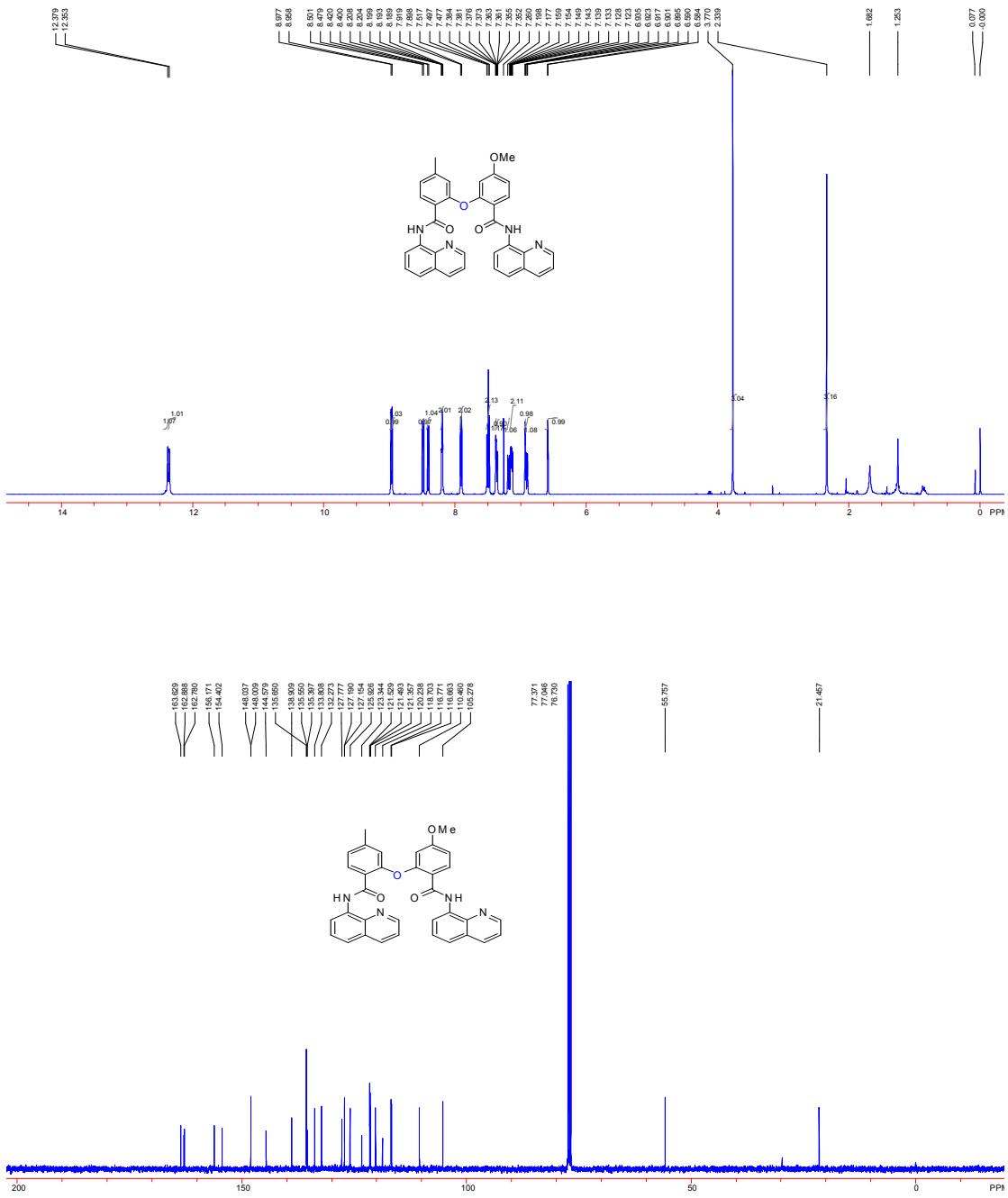
**3-(3-methyl-2-(quinolin-8-ylcarbamoyl)phenoxy)-N-(quinolin-8-yl)-[1,1'-biphenyl]-4-carboxamide (3f)**



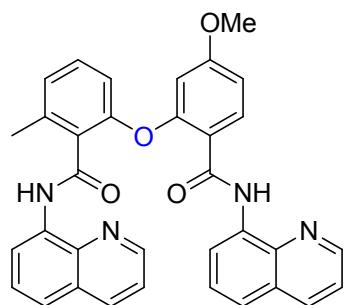


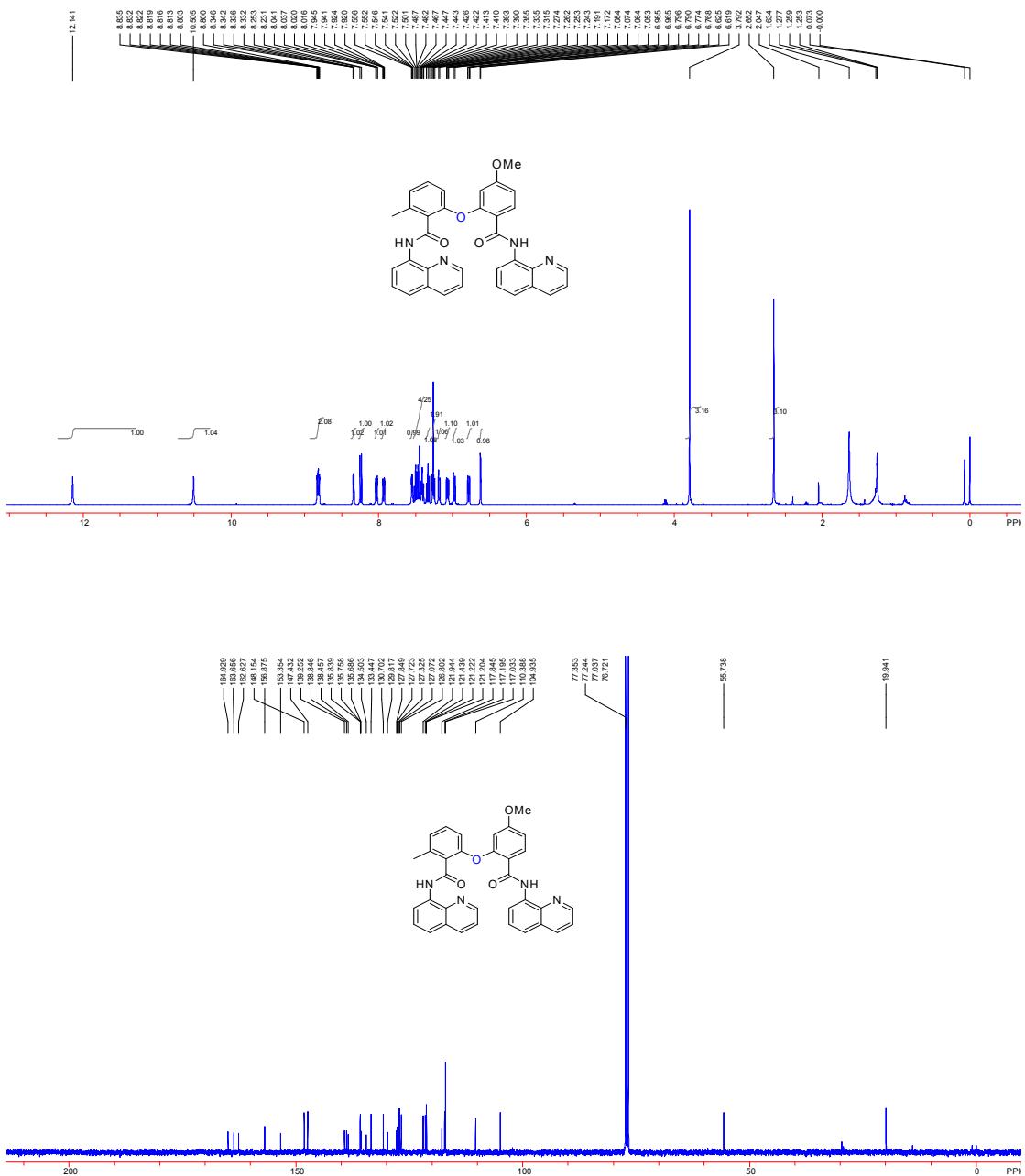
**4-methoxy-2-(5-methyl-2-(quinolin-8-ylcarbamoyl)phenoxy)-N-(quinolin-8-yl)benzamide (3g)**



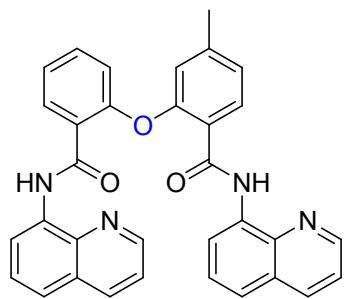


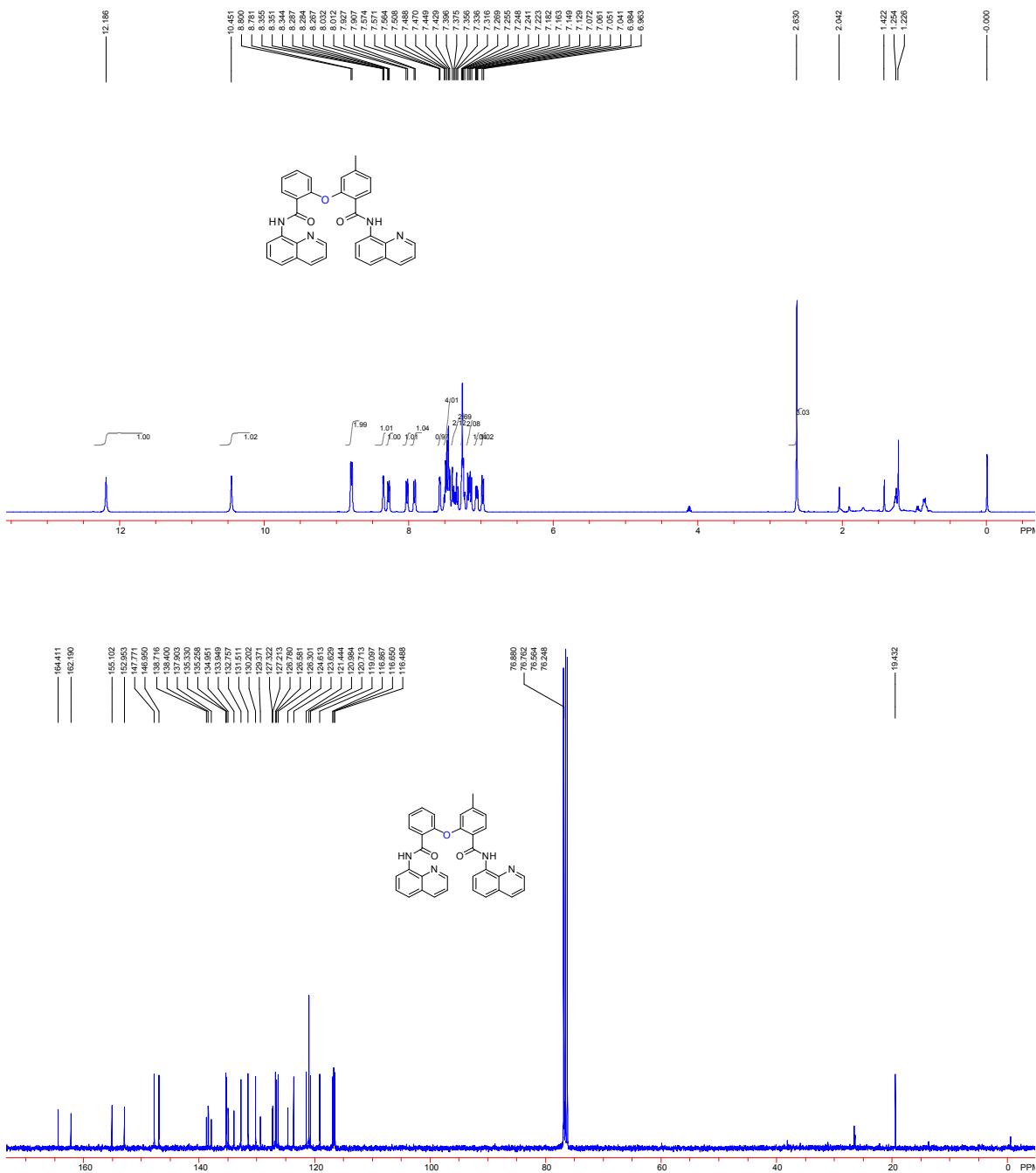
### **4-methoxy-2-(3-methyl-2-(quinolin-8-ylcarbamoyl)phenoxy)-N-(quinolin-8-yl)benzamide (3h)**



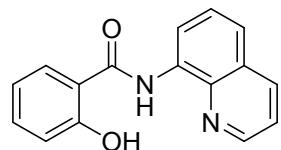


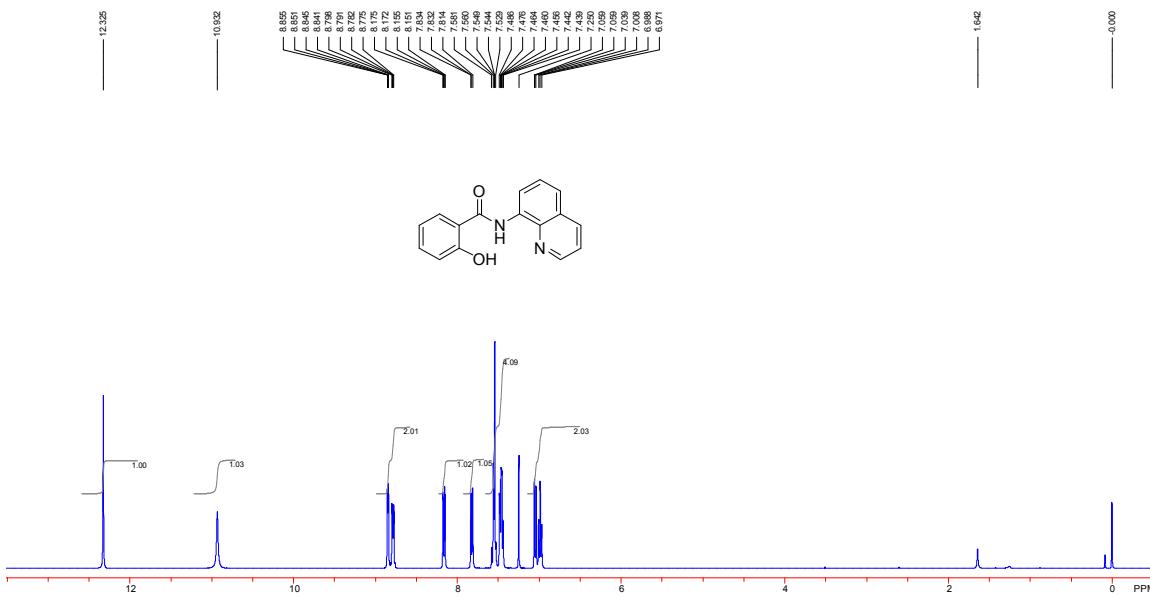
**4-methyl-N-(quinolin-8-yl)-2-(quinolin-8-ylcarbamoyl)phenoxy)benzamide (3i)**



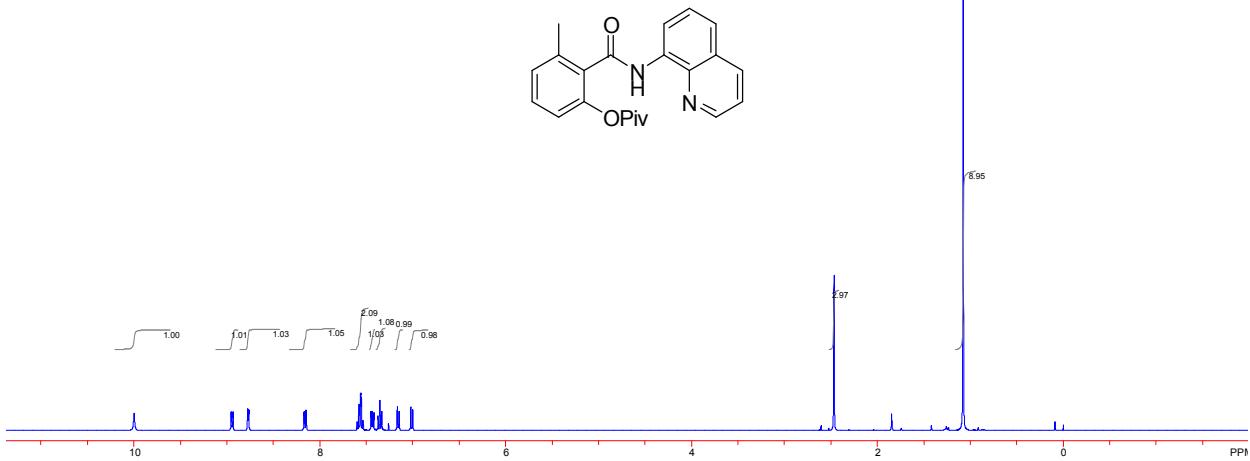
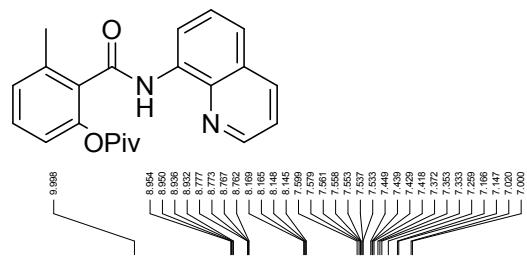


**2-hydroxy-*N*-(quinolin-8-yl)benzamide (4)**

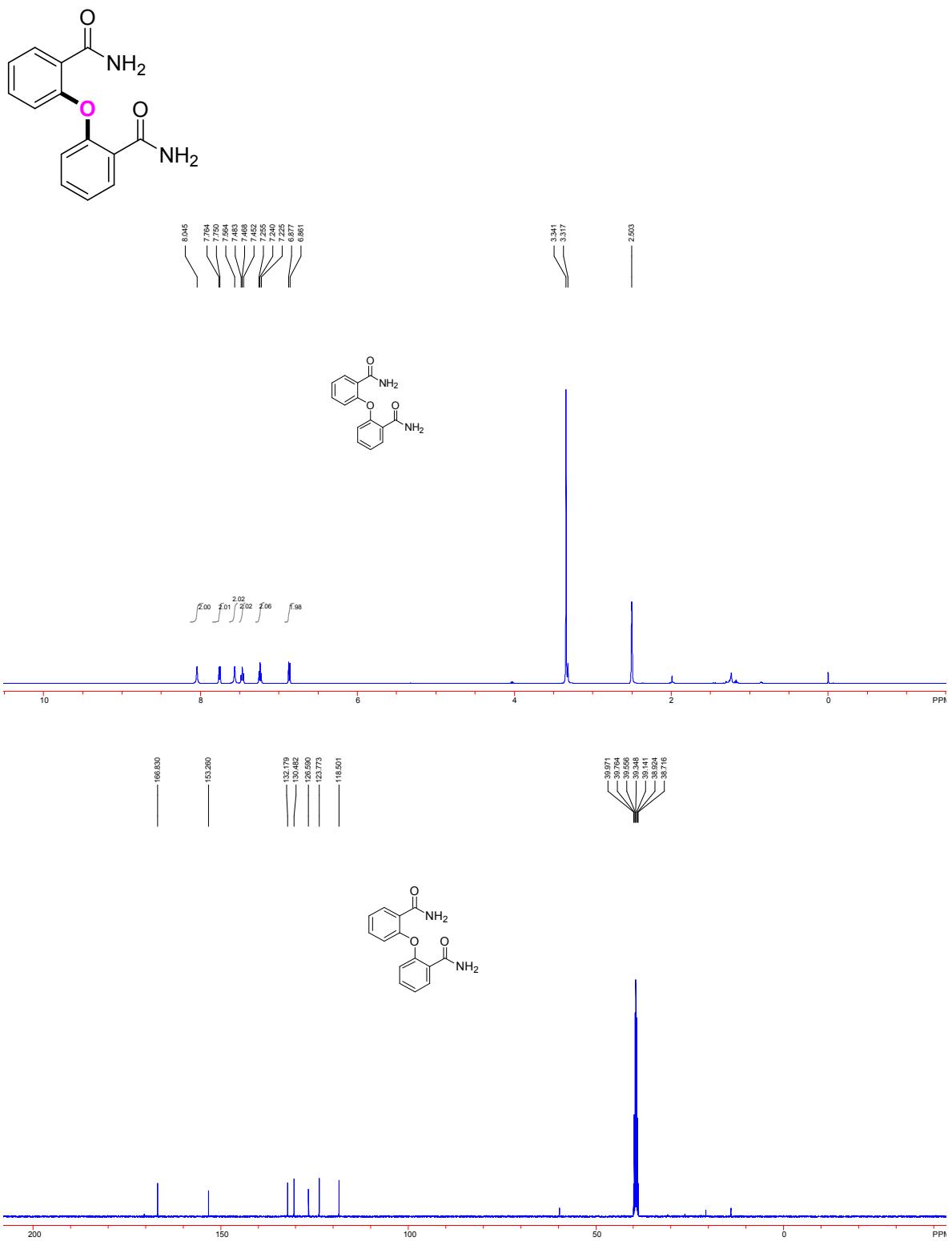




### **3-methyl-2-(quinolin-8-ylcarbamoyl)phenyl pivalate (5)**



### 2,2'-oxydibenzamide (6)



**phenyl pivalate (7)**

