

## **Supporting Information**

### **Copper-Catalyzed Direct $sp^2$ C–H Silylation of Arylamides using Disilanes**

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## **General Information:**

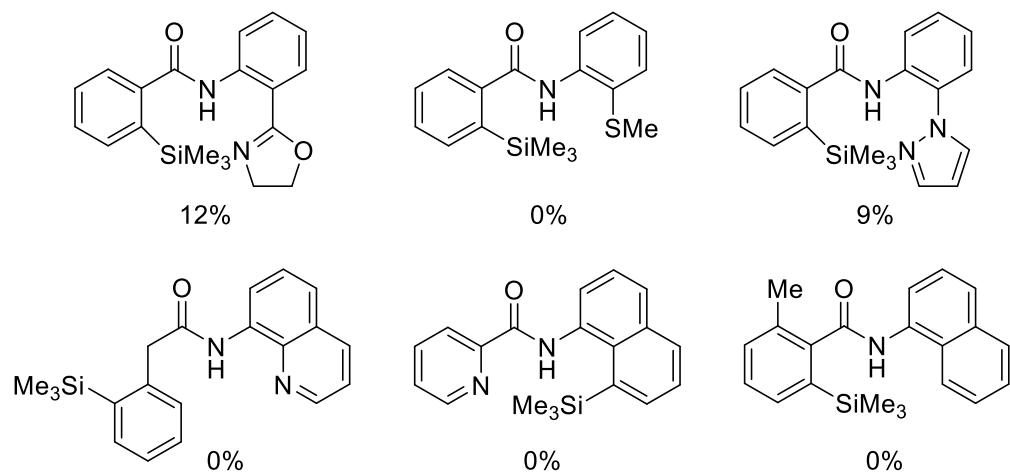
All reactions were carried out in oven-dried reaction vessels under air atmosphere unless otherwise mentioned. TLC analysis was performed on silica gel TLC plates. Column chromatography was done using 230–400 mesh silica gel by applying pressure through an air pump. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on 400 and 600 MHz spectrometers and are reported as chemical shifts ( $\delta$ ) in parts per million (ppm), and multiplicities are abbreviated as s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, comp = complex. Internal standards or residual solvent signals were used as reference. HRMS (m/z) was recorded using ESI (Q-Tof, positive ion) mode. Melting points were determined in a capillary melting point apparatus and are uncorrected. Single-crystal X-ray diffraction data were collected on either Bruker APEX II diffractometer with a graphite monochromator using Mo K $\alpha$  radiation or Bruker D8 Venture with a microfocus optics using Cu K $\alpha$  radiation. The CIF files were submitted to CCDC ([2054613-2054622](#)) and can be obtained at <https://summary.ccdc.cam.ac.uk/structure-summary-form>. The arylamides were prepared following literature method.<sup>1</sup> Benzamide **1a-d<sub>1</sub>** was prepared according to literature procedure.<sup>2</sup> Single crystals of the silylated compounds were obtained taking 5-10 mg of the sample in 5 mL vials using either a mono-solvent system by solvent evaporation method or using a bi-solvent system applying solvent diffusion technique. The choice of solvent systems and methods for crystal growth for each compound (**3a-3e**, **3q**, **3s**, **3t**, **3ac**, **3ag**) are provided in the characterization data section.

**Table S1: Additional optimization of reaction conditions:<sup>a</sup>**

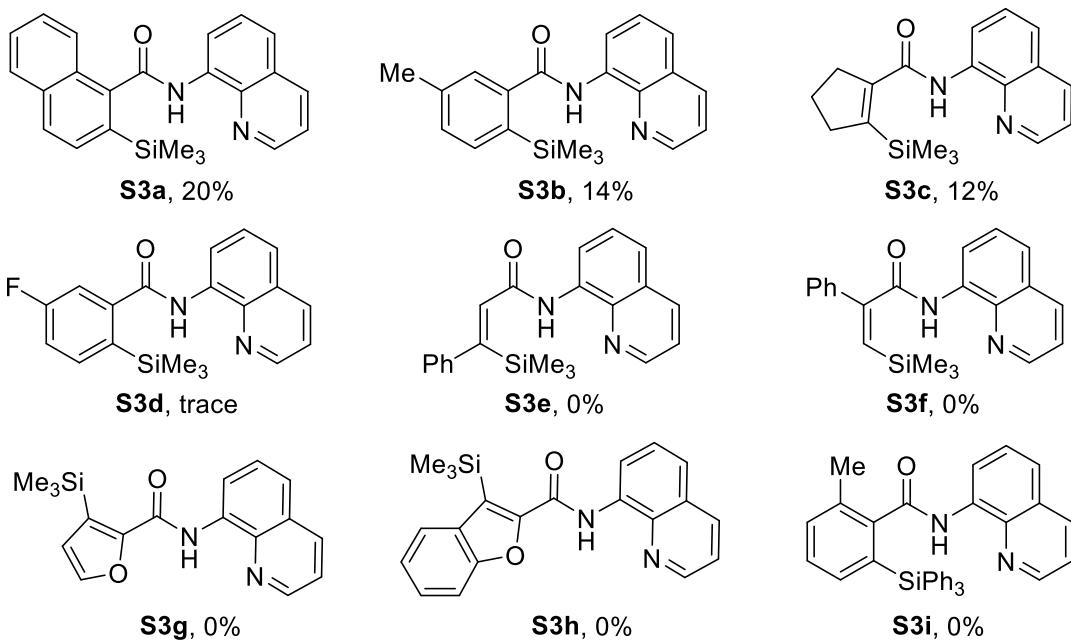
entry	Cu(OAc) <sub>2</sub> (x mol %)	additive (x equiv)	oxidant (x equiv)	solvent (0.1 M)	Yield of <b>3a</b> <sup>b</sup> (%)
1	Cu(OAc) <sub>2</sub> (20)	-	Ag <sub>2</sub> CO <sub>3</sub> (2.0)	DMF	20
2	Cu(OAc) <sub>2</sub> (20)	-	AgOAc (2.0)	DMF	7
3	Cu(OAc) <sub>2</sub> (20)	-	p-BQ (2.0)	DMF	nr
4	Cu(OAc) <sub>2</sub> (20)	-	Ag <sub>2</sub> CO <sub>3</sub> (1.5)	DMSO	nr
5	Cu(OAc) <sub>2</sub> (20)	-	Ag <sub>2</sub> CO <sub>3</sub> (1.5)	MeCN	nr
6	Cu(OAc) <sub>2</sub> (20)	-	Ag <sub>2</sub> CO <sub>3</sub> (1.5)	DMA	16
7	Cu(OAc) <sub>2</sub> (20)	-	Ag <sub>2</sub> CO <sub>3</sub> (1.5)	1,4-Dioxane	7
8	Cu(OAc) <sub>2</sub> (20)	-	Ag <sub>2</sub> CO <sub>3</sub> (1.5)	DCE	nr
9	Cu(OAc) <sub>2</sub> (20)	KF (2.0)	Ag <sub>2</sub> CO <sub>3</sub> (1.5)	DMF	nr
10 <sup>c</sup>	Cu(OAc) <sub>2</sub> (20)	MgSO <sub>4</sub> (2.0)	Ag <sub>2</sub> CO <sub>3</sub> (1.5)	DMF	41
11 <sup>d</sup>	Cu(OAc) <sub>2</sub> (20)	MgSO <sub>4</sub> (2.0)	Ag <sub>2</sub> CO <sub>3</sub> (1.5)	DMF	nr
12	Cu(OAc) <sub>2</sub> (20)	MgSO <sub>4</sub> (3.0)	Ag <sub>2</sub> CO <sub>3</sub> (1.5)	DMF	49
13 <sup>e</sup>	Cu(OAc) <sub>2</sub> (20)	MgSO <sub>4</sub> (2.0)	Ag <sub>2</sub> CO <sub>3</sub> (1.5)	DMF	56
14 <sup>f,g</sup>	Cu(OAc) <sub>2</sub> (20)	MgSO <sub>4</sub> (2.0)	Ag <sub>2</sub> CO <sub>3</sub> (1.5)	DMF	51
15 <sup>f,h</sup>	Cu(OAc) <sub>2</sub> (20)	MgSO <sub>4</sub> (2.0)	Ag <sub>2</sub> CO <sub>3</sub> (1.5)	DMF	20
16 <sup>f,i</sup>	Cu(OAc) <sub>2</sub> (20)	MgSO <sub>4</sub> (2.0)	Ag <sub>2</sub> CO <sub>3</sub> (1.5)	DMF	20
17 <sup>f,j</sup>	Cu(OAc) <sub>2</sub> (10)	MgSO <sub>4</sub> (2.0)	Ag <sub>2</sub> CO <sub>3</sub> (1.5)	DMF	68
18 <sup>f,k,l</sup>	Cu(OAc) <sub>2</sub> (10)	MgSO <sub>4</sub> (2.0)	Ag <sub>2</sub> CO <sub>3</sub> (1.5)	DMF	80
19 <sup>f,k,m</sup>	Cu(OAc) <sub>2</sub> (10)	MgSO <sub>4</sub> (2.0)	Ag <sub>2</sub> CO <sub>3</sub> (1.5)	DMF	74

<sup>a</sup>Reaction conditions: Unless otherwise mentioned, substrate **1a** (0.1 mmol), **2a** (2.0 equiv), Cu(OAc)<sub>2</sub> (20 mol %), additive (2.0 equiv), oxidant (1.5 equiv), solvent (1.0 mL) at 120 °C under N<sub>2</sub> atmosphere for 21 h. <sup>b</sup>Isolated yield. <sup>c</sup>PivOH (1.0 equiv). <sup>d</sup>TBAB (2.0 equiv). <sup>e</sup>**2a** (5.0 equiv). <sup>f</sup>**2a** (10.0 equiv). <sup>g</sup>PPPh<sub>3</sub> (40 mol %). <sup>h</sup>1,10-phen (20 mol %). <sup>i</sup>DMEDA (20 mol %). <sup>j</sup>100 °C. <sup>k</sup>under air atmosphere. <sup>l</sup>reaction run for 30 h. <sup>m</sup>reaction run for 48 h.

**Table S2: Scope of other bidentate directing groups:**

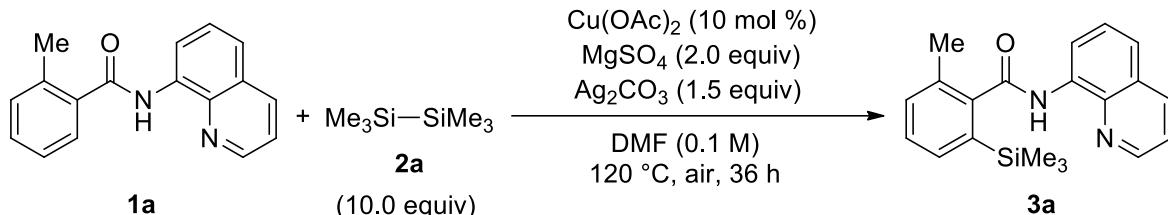


**Table S3: Scope of other substrates:**



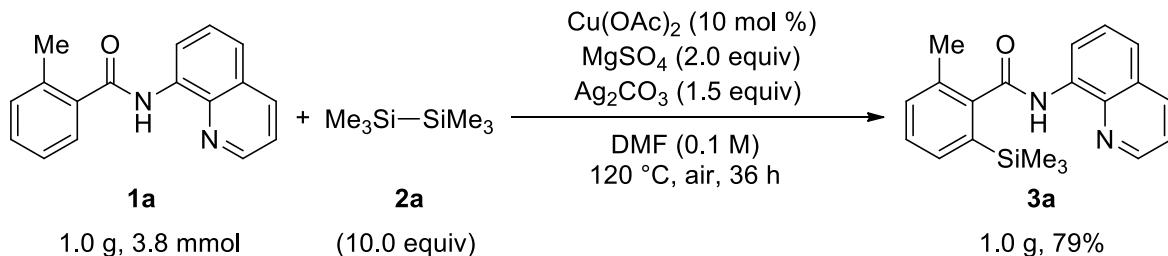
### **General procedure for silylation:**

(0.2 mmol scale);



In an oven dried 10 mL Schlenk tube, 2-methyl-*N*-(quinolin-8-yl)benzamide (**1a**) (52.5 mg, 0.2 mmol, 1.0 equiv), Cu(OAc)<sub>2</sub> (3.6 mg, 0.02 mmol, 0.1 equiv), MgSO<sub>4</sub> (48.2 mg, 0.4 mmol, 2.0 equiv), and Ag<sub>2</sub>CO<sub>3</sub> (82.8 mg, 0.3 mmol, 1.5 equiv) were taken. Then hexamethyldisilane (0.41 mL, 2.0 mmol, 10.0 equiv) and 2.0 mL (0.1 M) of anhydrous DMF was added. The tube was closed with a teflon-lined cap and kept on stirring in an oil bath. The bath temperature was slowly increased to 120 °C. After 36 h, the reaction was stopped and cooled to room temperature. The reaction mixture was filtered through a short pad of celite, poured to water (20 mL) and extracted with ethyl acetate (3 x 5 mL). The combined organic layers were washed with brine solution (2 x 5 mL). The organic phase was separated, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under vacuo. The crude reaction mixture was directly purified by column chromatography on silica gel using pet ether/ethyl acetate as eluent to obtain 2-methyl-*N*-(quinolin-8-yl)-6-(trimethylsilyl)benzamide (**3a**) (57.4 mg, 86% yield).

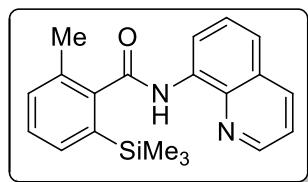
**(Gram scale):**



To an oven dried 100 mL round bottom flask equipped with a reflux condenser, 2-methyl-*N*-(quinolin-8-yl)benzamide (**1a**) (1.0 g, 3.8 mmol, 1.0 equiv), Cu(OAc)<sub>2</sub> (69.2 mg, 0.38 mmol, 0.1 equiv), MgSO<sub>4</sub> (0.92 g, 7.6 mmol, 2.0 equiv), and Ag<sub>2</sub>CO<sub>3</sub> (1.58 g, 5.7 mmol, 1.5 equiv) were taken. Then hexamethyldisilane (7.8 mL, 38.1 mmol, 10.0 equiv) and 38.0 mL (0.1 M) of anhydrous DMF was added. The tube was closed with a teflon-lined cap and kept on stirring in an oil bath. The bath temperature was slowly increased to 120 °C. After 36 h, the reaction was stopped and cooled to room temperature. The reaction mixture was filtered through a short pad of celite, poured to water (400 mL) and extracted with ethyl acetate (3 x 80 mL). The combined organic layers were washed with brine solution (2 x 25 mL). The organic phase was separated, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under vacuo. The crude reaction mixture was directly purified by column chromatography on silica gel using pet ether/ethyl acetate as eluent to obtain 2-methyl-*N*-(quinolin-8-yl)-6-(trimethylsilyl)benzamide (**3a**) (1.0 g, 79% yield).

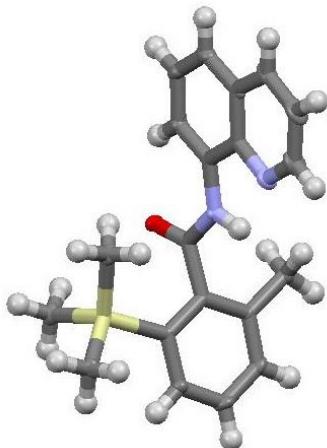
### Characterization of silylated products:

#### 2-methyl-N-(quinolin-8-yl)-6-(trimethylsilyl)benzamide (3a):<sup>3</sup>



**Yield** 86% (57.4 mg); colorless solid; **R<sub>f</sub>** 0.30 (pet ether/ethyl acetate = 9:1); **eluent composition** petroleum ether/ethyl acetate = 19:1; **mp** 106-108 °C (crystallization from DCM and hexane using solvent diffusion method); **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 9.96 (br s, 1H), 9.00 (app d, *J* = 7.2 Hz, 1H), 8.73 (app d, *J* = 4.0 Hz, 1H), 8.18 (app d, *J* = 8.4 Hz, 1H), 7.62 (app t, *J* = 8.0 Hz, 1H), 7.57 (app d, *J* = 8.4 Hz, 1H), 7.50 (app d, *J* = 7.2 Hz, 1H), 7.44 (dd, *J* = 8.0 Hz, 4.0 Hz, 1H), 7.35 (app t, *J* = 7.2 Hz, 1H), 7.29 (app d, *J* = 7.2 Hz, 1H), 2.46 (s, 3H), 0.28 (s, 9H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 170.0, 148.4, 143.4, 138.6, 137.4, 136.5, 134.6, 134.2, 132.4, 131.3, 128.7, 128.2, 127.6, 122.0, 121.8, 116.9, 19.8, 0.1; **HRMS** (ESI, m/z) calcd for C<sub>20</sub>H<sub>22</sub>N<sub>2</sub>OSi [M + Na]<sup>+</sup> 357.1399, found 357.1400.

**Figure S1.** X-ray crystal structure of **3a** (ellipsoid contour at 50% probability level)

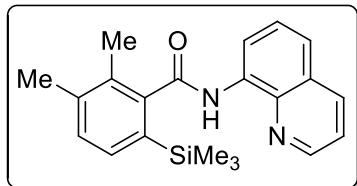


#### Crystal data and structure refinement for **3a**, CCDC No. 2054613

Empirical formula	C <sub>20</sub> H <sub>22</sub> N <sub>2</sub> OSi
Formula weight	334.48
Temperature/K	100.0
Crystal system	monoclinic
Space group	P2 <sub>1</sub> /n
a/Å	10.1808(4)
b/Å	13.5406(5)
c/Å	13.5834(5)
α/°	90
β/°	95.202(2)

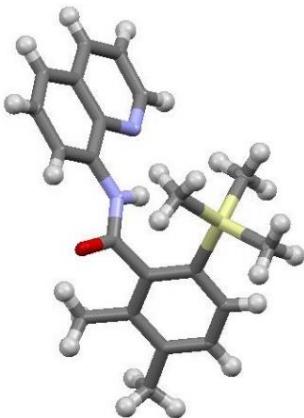
$\gamma/^\circ$	90
Volume/ $\text{\AA}^3$	1864.82(12)
Z	4
$\rho_{\text{calcd}}/\text{cm}^3$	1.191
$\mu/\text{mm}^{-1}$	1.165
F(000)	712.0
Crystal size/mm <sup>3</sup>	0.35 $\times$ 0.275 $\times$ 0.2
Radiation	Cu K $\alpha$ ( $\lambda = 1.54178$ )
2 $\Theta$ range for data collection/°	9.24 to 144.214
Index ranges	-12 $\leq$ h $\leq$ 12, -16 $\leq$ k $\leq$ 16, -16 $\leq$ l $\leq$ 16
Reflections collected	26183
Independent reflections	3614 [ $R_{\text{int}} = 0.0627$ , $R_{\text{sigma}} = 0.0384$ ]
Data/restraints/parameters	3614/0/221
Goodness-of-fit on $F^2$	1.142
Final R indexes [ $I \geq 2\sigma(I)$ ]	$R_1 = 0.0528$ , $wR_2 = 0.1204$
Final R indexes [all data]	$R_1 = 0.0548$ , $wR_2 = 0.1214$
Largest diff. peak/hole / e $\text{\AA}^{-3}$	0.28/-0.37

**2,3-dimethyl-N-(quinolin-8-yl)-6-(trimethylsilyl)benzamide (3b):**



**Yield** 73% (51.0 mg); colorless solid; **R<sub>f</sub>** 0.40 (pet ether/ethyl acetate = 9:1); **eluent composition** petroleum ether/ethyl acetate = 19:1; **mp** 150–152 °C (crystallization from CDCl<sub>3</sub> using solvent evaporation method); **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 9.97 (br s, 1H), 9.01 (dd, *J* = 7.2 Hz, 1.6 Hz, 1H), 8.73 (dd, *J* = 4.0 Hz, 1.6 Hz, 1H), 8.19 (dd, *J* = 8.4 Hz, 1.6 Hz, 1H), 7.63 (app t, *J* = 8.0 Hz, 1H), 7.57 (dd, *J* = 8.4 Hz, 1.2 Hz, 1H), 7.44 (dd, *J* = 8.4 Hz, 4.0 Hz, 1H), 7.40 (d, *J* = 7.6 Hz, 1H), 7.25 (d, *J* = 7.6 Hz, 1H), 2.35 (s, 3H), 2.34 (s, 3H), 0.25 (s, 9H); **<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>) δ 170.5, 148.3, 143.7, 138.5 (x 2), 136.6, 134.6, 134.4, 132.8, 132.3, 130.1, 128.2, 127.7, 122.0, 121.8, 117.0, 20.5, 16.5, 0.1; **HRMS** (ESI, m/z) calcd for C<sub>21</sub>H<sub>24</sub>N<sub>2</sub>OSi [M + H]<sup>+</sup> 349.1736, found 349.1739.

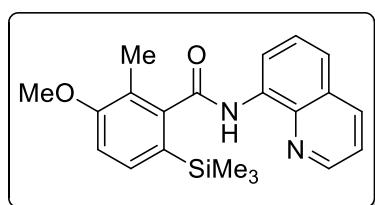
**Figure S2.** X-ray crystal structure of **3b** (ellipsoid contour at 50% probability level)



**Crystal data and structure refinement for **3b**, CCDC No. 2054616**

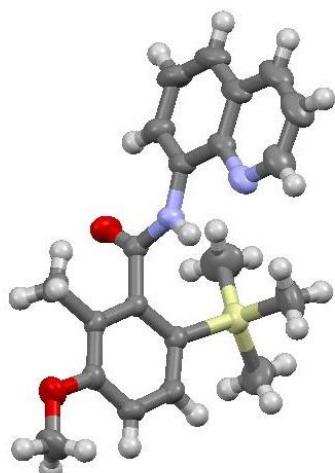
Empirical formula	C <sub>21</sub> H <sub>24</sub> N <sub>2</sub> OSi
Formula weight	348.51
Temperature/K	100.0
Crystal system	monoclinic
Space group	P2 <sub>1</sub> /n
a/Å	12.3232(8)
b/Å	10.8891(8)
c/Å	14.1794(9)
α/°	90
β/°	97.493(3)
γ/°	90
Volume/Å <sup>3</sup>	1886.5(2)
Z	4
ρ <sub>calc</sub> g/cm <sup>3</sup>	1.227
μ/mm <sup>-1</sup>	1.171
F(000)	744.0
Crystal size/mm <sup>3</sup>	0.5 × 0.315 × 0.275
Radiation	Cu Kα ( $\lambda = 1.54178$ )
2Θ range for data collection/°	10.192 to 127.54
Index ranges	-14 ≤ h ≤ 14, -12 ≤ k ≤ 12, -16 ≤ l ≤ 16
Reflections collected	43942
Independent reflections	2998 [ $R_{\text{int}} = 0.0566$ , $R_{\text{sigma}} = 0.0236$ ]
Data/restraints/parameters	2998/0/231
Goodness-of-fit on F <sup>2</sup>	1.079
Final R indexes [I>=2σ (I)]	$R_1 = 0.0432$ , $wR_2 = 0.1126$
Final R indexes [all data]	$R_1 = 0.0434$ , $wR_2 = 0.1128$
Largest diff. peak/hole / e Å <sup>-3</sup>	0.21/-0.30

**3-methoxy-2-methyl-N-(quinolin-8-yl)-6-(trimethylsilyl)benzamide (3c):**



**Yield** 78% (56.9 mg); colorless solid; **R<sub>f</sub>** 0.30 (pet ether/ethyl acetate = 9:1); **eluent composition** petroleum ether/ethyl acetate = 19:1; **mp** 122-124 °C (crystallization from CHCl<sub>3</sub> and hexane using solvent diffusion method); **<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ 9.97 (br s, 1H), 8.99 (dd, *J* = 7.8 Hz, 1.2 Hz, 1H), 8.72 (dd, *J* = 4.2 Hz, 1.8 Hz, 1H), 8.18 (dd, *J* = 7.8 Hz, 1.8 Hz, 1H), 7.62 (app t, *J* = 7.8 Hz, 1H), 7.57 (dd, *J* = 8.4 Hz, 1.2 Hz, 1H), 7.47 (d, *J* = 7.8 Hz, 1H), 7.44 (dd, *J* = 8.4 Hz, 4.2 Hz, 1H), 6.93 (d, *J* = 8.4 Hz, 1H), 3.88 (s, 3H), 2.31 (s, 3H), 0.25 (s, 9H); **<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>) δ 169.7, 158.6, 148.3, 144.7, 138.5, 136.5, 134.6, 133.8, 128.2, 127.8, 127.7, 123.4, 122.0, 121.8, 117.0, 110.3, 55.6, 12.9, 0.2; **HRMS** (ESI, m/z) calcd for C<sub>21</sub>H<sub>24</sub>N<sub>2</sub>O<sub>2</sub>Si [M + H]<sup>+</sup> 365.1685, found 365.1691.

**Figure S3.** X-ray crystal structure of **3c** (ellipsoid contour at 50% probability level)

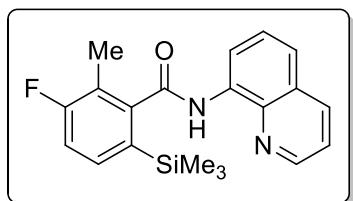


**Crystal data and structure refinement for 3c, CCDC No. 2054617**

Empirical formula	C <sub>21</sub> H <sub>24</sub> N <sub>2</sub> O <sub>2</sub> Si
Formula weight	364.51
Temperature/K	296.15
Crystal system	monoclinic
Space group	P2 <sub>1</sub> /n
a/Å	12.6160(10)
b/Å	11.1461(10)
c/Å	14.1882(12)
α/°	90
β/°	96.307(2)

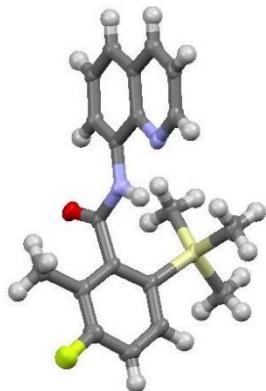
$\gamma/^\circ$	90
Volume/ $\text{\AA}^3$	1983.1(3)
Z	4
$\rho_{\text{calcd}}/\text{cm}^3$	1.221
$\mu/\text{mm}^{-1}$	0.135
F(000)	776.0
Crystal size/mm <sup>3</sup>	0.2 × 0.2 × 0.2
Radiation	MoK $\alpha$ ( $\lambda = 0.71073$ )
2 $\Theta$ range for data collection/°	4.578 to 60.012
Index ranges	-17 ≤ h ≤ 17, -15 ≤ k ≤ 15, -19 ≤ l ≤ 19
Reflections collected	33353
Independent reflections	5588 [R <sub>int</sub> = 0.0493, R <sub>sigma</sub> = 0.0332]
Data/restraints/parameters	5588/0/240
Goodness-of-fit on F <sup>2</sup>	1.023
Final R indexes [I >= 2σ (I)]	R <sub>1</sub> = 0.0475, wR <sub>2</sub> = 0.1234
Final R indexes [all data]	R <sub>1</sub> = 0.0767, wR <sub>2</sub> = 0.1423
Largest diff. peak/hole / e $\text{\AA}^{-3}$	0.24/-0.22

**3-fluoro-2-methyl-N-(quinolin-8-yl)-6-(trimethylsilyl)benzamide (3d):**



**Yield** 75% (53.1 mg); colorless solid; **R<sub>f</sub>** 0.40 (pet ether/ethyl acetate = 9:1); **eluent composition** petroleum ether/ethyl acetate = 19:1; **mp** 108-110 °C (crystallization from CHCl<sub>3</sub> using solvent evaporation method); **<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ 9.98 (br s, 1H), 8.98 (dd, *J* = 7.2 Hz, 1.2 Hz, 1H), 8.75 (dd, *J* = 4.2 Hz, 1.8 Hz, 1H), 8.20 (dd, *J* = 8.4 Hz, 1.2 Hz, 1H), 7.63 (app t, *J* = 7.8 Hz, 1H), 7.59 (dd, *J* = 8.4 Hz, 1.2 Hz, 1H), 7.47-7.45 (comp, 2H), 7.13-7.10 (m, 1H), 2.36 (app d, *J* = 2.4 Hz, 3H), 0.26 (s, 9H); **<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>) δ 168.6 (d, *J* = 3.0 Hz), 162.0 (d, <sup>1</sup>J<sub>F-C</sub> = 246.0 Hz), 148.4, 145.6 (d, <sup>4</sup>J<sub>F-C</sub> = 3.0 Hz), 138.5, 136.6, 134.3, 134.1 (d, <sup>3</sup>J<sub>F-C</sub> = 7.5 Hz), 132.8 (d, <sup>3</sup>J<sub>F-C</sub> = 4.5 Hz), 128.2, 127.6, 122.3, 122.0 (d, <sup>2</sup>J<sub>F-C</sub> = 16.5 Hz), 121.9, 117.1, 115.4 (d, <sup>2</sup>J<sub>F-C</sub> = 21.0 Hz), 11.7 (d, *J* = 4.5 Hz), 0.0; **HRMS** (ESI, m/z) calcd for C<sub>20</sub>H<sub>21</sub>FN<sub>2</sub>OSi [M + H]<sup>+</sup> 353.1485, found 353.1488.

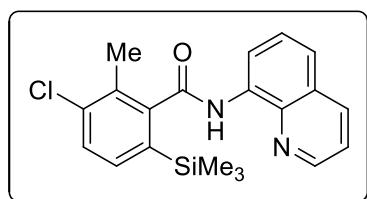
**Figure S4.** X-ray crystal structure of **3d** (ellipsoid contour at 50% probability level)



**Crystal data and structure refinement for 3d, CCDC No. 2054618**

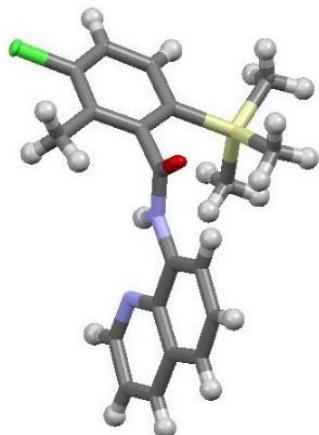
Empirical formula	C <sub>20</sub> H <sub>21</sub> FN <sub>2</sub> OSi
Formula weight	352.48
Temperature/K	100.0
Crystal system	monoclinic
Space group	P2 <sub>1</sub> /c
a/Å	8.5937(9)
b/Å	12.5787(12)
c/Å	16.9182(16)
α/°	90
β/°	93.235(4)
γ/°	90
Volume/Å <sup>3</sup>	1825.9(3)
Z	4
ρ <sub>calcd</sub> /cm <sup>3</sup>	1.282
μ/mm <sup>-1</sup>	1.299
F(000)	744.0
Crystal size/mm <sup>3</sup>	0.402 × 0.25 × 0.12
Radiation	Cu Kα ( $\lambda = 1.54178$ )
2Θ range for data collection/°	8.764 to 125.102
Index ranges	-9 ≤ h ≤ 9, -14 ≤ k ≤ 14, -17 ≤ l ≤ 19
Reflections collected	19963
Independent reflections	2905 [ $R_{\text{int}} = 0.2155$ , $R_{\text{sigma}} = 0.1175$ ]
Data/restraints/parameters	2905/0/230
Goodness-of-fit on $F^2$	1.327
Final R indexes [I>=2σ (I)]	$R_1 = 0.1575$ , $wR_2 = 0.3389$
Final R indexes [all data]	$R_1 = 0.1659$ , $wR_2 = 0.3511$
Largest diff. peak/hole / e Å <sup>-3</sup>	0.94/-1.30

**3-chloro-2-methyl-N-(quinolin-8-yl)-6-(trimethylsilyl)benzamide (3e):**



**Yield** 54% (39.8 mg); colorless solid; **R<sub>f</sub>** 0.40 (pet ether/ethyl acetate = 9:1); **eluent composition** petroleum ether/ethyl acetate = 19:1; **mp** 146-148 °C (crystallization from DCM and hexane using solvent diffusion method); **<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ 9.96 (br s, 1H), 8.97 (dd, *J* = 7.2 Hz, 1.2 Hz, 1H), 8.75 (dd, *J* = 4.2 Hz, 1.8 Hz, 1H), 8.20 (dd, *J* = 8.4 Hz, 1.8 Hz, 1H), 7.63 (app t, *J* = 7.8 Hz, 1H), 7.59 (dd, *J* = 8.4 Hz, 1.2 Hz, 1H), 7.46 (dd, *J* = 8.4 Hz, 4.2 Hz, 1H), 7.44 (dd, *J* = 7.8 Hz, 4.2 Hz, 1H), 7.41 (d, *J* = 7.8 Hz, 1H), 2.48 (s, 3H), 0.26 (s, 9H); **<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>) δ 168.9, 148.5, 145.1, 138.5, 136.6, 136.5, 136.0, 134.3, 133.5, 132.4, 129.4, 128.2, 127.6, 122.3, 121.9, 117.0, 17.2, -0.1; **HRMS** (ESI, m/z) calcd for C<sub>20</sub>H<sub>21</sub>ClN<sub>2</sub>OSi [M + H]<sup>+</sup> 369.1190, found 369.1195.

**Figure S5.** X-ray crystal structure of **3e** (ellipsoid contour at 50% probability level)

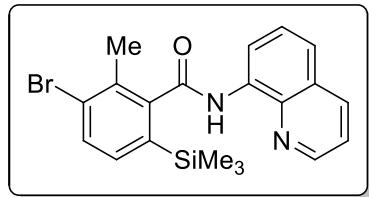


**Crystal data and structure refinement for 3e, CCDC No. 2054619**

Empirical formula	C <sub>20</sub> H <sub>21</sub> ClN <sub>2</sub> OSi
Formula weight	368.93
Temperature/K	100.0
Crystal system	monoclinic
Space group	P2 <sub>1</sub> /c
a/Å	8.4502(2)
b/Å	12.8498(2)
c/Å	17.2023(3)
α/°	90
β/°	93.0220(10)
γ/°	90
Volume/Å <sup>3</sup>	1865.29(6)

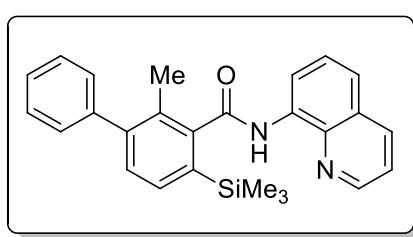
Z	4
$\rho_{\text{calcg}}/\text{cm}^3$	1.314
$\mu/\text{mm}^{-1}$	2.503
F(000)	776.0
Crystal size/mm <sup>3</sup>	0.54 × 0.45 × 0.4
Radiation	Cu K $\alpha$ ( $\lambda = 1.54178$ )
2 $\Theta$ range for data collection/°	8.594 to 133.266
Index ranges	-10 ≤ h ≤ 9, -15 ≤ k ≤ 15, -20 ≤ l ≤ 20
Reflections collected	30755
Independent reflections	3277 [ $R_{\text{int}} = 0.0642$ , $R_{\text{sigma}} = 0.0312$ ]
Data/restraints/parameters	3277/0/230
Goodness-of-fit on $F^2$	1.093
Final R indexes [ $I \geq 2\sigma(I)$ ]	$R_1 = 0.0426$ , $wR_2 = 0.1006$
Final R indexes [all data]	$R_1 = 0.0431$ , $wR_2 = 0.1010$
Largest diff. peak/hole / e Å <sup>-3</sup>	0.27/-0.37

**3-bromo-2-methyl-N-(quinolin-8-yl)-6-(trimethylsilyl)benzamide (3f):**



**Yield** 37% (30.3 mg); colorless solid; **R<sub>f</sub>** 0.40 (pet ether/ethyl acetate = 9:1); **eluent composition** petroleum ether/ethyl acetate = 19:1; **mp** 134-136 °C; **<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ 9.97 (br s, 1H), 8.97 (dd, *J* = 7.2 Hz, 1.2 Hz, 1H), 8.75 (dd, *J* = 4.8 Hz, 1.2 Hz, 1H), 8.20 (dd, *J* = 8.4 Hz, 1.2 Hz, 1H), 7.63 (app t, *J* = 7.2 Hz, 2H), 7.59 (dd, *J* = 8.4 Hz, 1.2 Hz, 1H), 7.46 (dd, *J* = 8.4 Hz, 4.2 Hz, 1H), 7.32 (d, *J* = 7.8 Hz, 1H), 2.51 (s, 3H), 0.26 (s, 9H); **<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>) δ 168.9, 148.4, 144.9, 138.5, 136.7, 136.6, 134.3, 134.0, 133.7, 132.8, 128.2, 127.6, 127.5, 122.4, 121.9, 117.1, 20.3, -0.1; **HRMS** (ESI, m/z) calcd for C<sub>20</sub>H<sub>21</sub>BrN<sub>2</sub>OSi [M + H]<sup>+</sup> 413.0685, found 413.0694.

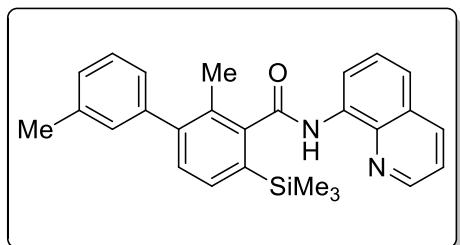
**2-methyl-N-(quinolin-8-yl)-4-(trimethylsilyl)-[1,1'-biphenyl]-3-carboxamide (3g):**



**Yield** 50% (41.1 mg); colorless oil; **R<sub>f</sub>** 0.40 (pet ether/ethyl acetate = 9:1); **eluent composition** petroleum ether/ethyl acetate = 19:1; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 10.00 (br s, 1H), 9.02 (dd, *J* = 7.2 Hz, 1.6 Hz, 1H), 8.76 (dd, *J* = 4.4 Hz, 1.6 Hz, 1H), 8.20 (dd, *J* = 8.4 Hz, 1.6 Hz, 1H), 7.63 (app t, *J* = 8.0 Hz, 1H), 7.58 (dd, *J* = 8.0 Hz, 1.6 Hz, 1H), 7.54 (d, *J* = 7.6 Hz, 1H), 7.48-7.42 (comp, 3H), 7.38-7.34 (comp, 3H), 7.32 (d, *J* = 7.6 Hz, 1H), 2.34 (s, 3H), 0.30 (s, 9H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 170.1, 148.3, 144.3, 143.7, 141.7, 138.5, 136.6, 136.3, 134.6, 132.3, 131.6, 130.1,

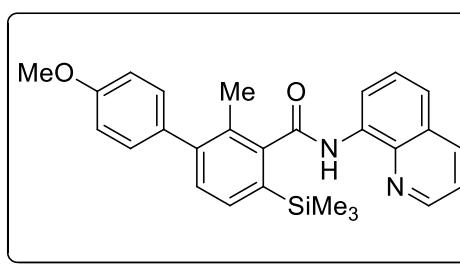
129.4 (x 2), 128.3 (x 2), 128.2, 127.7, 127.2, 122.1, 121.8, 117.2, 17.6, 0.1; **HRMS** (ESI, m/z) calcd for C<sub>26</sub>H<sub>26</sub>N<sub>2</sub>OSi [M + H]<sup>+</sup> 411.1893, found 411.1897.

**2,3'-dimethyl-N-(quinolin-8-yl)-4-(trimethylsilyl)-[1,1'-biphenyl]-3-carboxamide (3h):**



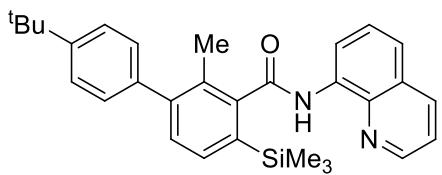
**Yield** 49% (41.2 mg); colorless solid; **R<sub>f</sub>** 0.40 (pet ether/ethyl acetate = 9:1); **eluent composition** petroleum ether/ethyl acetate = 19:1; **mp** 58-60 °C; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 10.05 (br s, 1H), 9.03 (dd, *J* = 7.2 Hz, 1.6 Hz, 1H), 8.77 (dd, *J* = 4.0 Hz, 1.6 Hz, 1H), 8.19 (dd, *J* = 8.4 Hz, 1.6 Hz, 1H), 7.64 (app t, *J* = 8.0 Hz, 1H), 7.58 (dd, *J* = 8.0 Hz, 1.2 Hz, 1H), 7.54 (d, *J* = 7.6 Hz, 1H), 7.46 (dd, *J* = 8.0 Hz, 4.0 Hz, 1H), 7.35-7.31 (comp, 2H), 7.19-7.16 (comp, 3H), 2.42 (s, 3H), 2.35 (s, 3H), 0.31 (s, 9H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 170.3, 148.4, 144.3, 143.8, 141.6, 138.6, 137.9, 136.5, 136.1, 134.6, 132.2, 131.6, 130.1 (x 2), 128.2, 128.2, 127.9, 127.7, 126.4, 122.1, 121.8, 117.0, 21.6, 17.6, 0.1; **HRMS** (ESI, m/z) calcd for C<sub>27</sub>H<sub>28</sub>N<sub>2</sub>OSi [M + H]<sup>+</sup> 425.2049, found 425.2050.

**4'-methoxy-2-methyl-N-(quinolin-8-yl)-4-(trimethylsilyl)-[1,1'-biphenyl]-3-carboxamide (3i):**



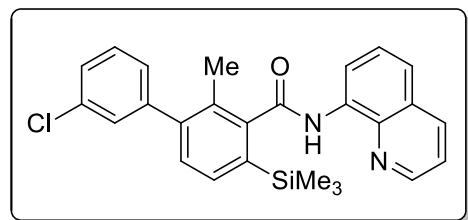
**Yield** 37% (32.5 mg); colorless solid; **R<sub>f</sub>** 0.30 (pet ether/ethyl acetate = 9:1); **eluent composition** petroleum ether/ethyl acetate = 19:1; **mp** 126-128 °C; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 10.04 (br s, 1H), 9.02 (dd, *J* = 7.6 Hz, 1.2 Hz, 1H), 8.76 (dd, *J* = 4.4 Hz, 1.6 Hz, 1H), 8.19 (dd, *J* = 8.0 Hz, 1.6 Hz, 1H), 7.63 (app t, *J* = 8.0 Hz, 1H), 7.58 (dd, *J* = 8.0 Hz, 0.8 Hz, 1H), 7.53 (d, *J* = 7.6 Hz, 1H), 7.46 (dd, *J* = 8.4 Hz, 4.4 Hz, 1H), 7.31 (d, *J* = 7.6 Hz, 1H), 7.30-7.27 (comp, 2H), 6.99-6.96 (comp, 2H), 3.86 (s, 3H), 2.35 (s, 3H), 0.30 (s, 9H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 170.3, 158.9, 148.4, 144.3, 143.3, 138.6, 136.6, 135.9, 134.6, 134.0, 132.3, 131.8, 130.5 (x 2), 130.3, 128.2, 127.7, 122.1, 121.8, 117.1, 113.8 (x 2), 55.4, 17.6, 0.1; **HRMS** (ESI, m/z) calcd for C<sub>27</sub>H<sub>28</sub>N<sub>2</sub>O<sub>2</sub>Si [M + H]<sup>+</sup> 441.1998, found 441.2001.

**4'-(tert-butyl)-2-methyl-N-(quinolin-8-yl)-4-(trimethylsilyl)-[1,1'-biphenyl]-3-carboxamide (3j):**



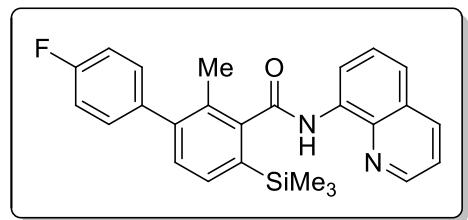
**Yield** 41% (38.6 mg); colorless oil; **R<sub>f</sub>** 0.40 (pet ether/ethyl acetate = 9:1); **eluent composition** petroleum ether/ethyl acetate = 19:1; **<sup>1</sup>H NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta$  10.04 (br s, 1H), 9.02 (dd,  $J$  = 7.2 Hz, 1.6 Hz, 1H), 8.76 (dd,  $J$  = 4.4 Hz, 1.6 Hz, 1H), 8.19 (dd,  $J$  = 8.0 Hz, 1.6 Hz, 1H), 7.63 (app t,  $J$  = 8.0 Hz, 1H), 7.58 (dd,  $J$  = 8.4 Hz, 1.2 Hz, 1H), 7.53 (d,  $J$  = 8.0 Hz, 1H), 7.48-7.44 (comp, 3H), 7.33 (d,  $J$  = 7.6 Hz, 1H), 7.31-7.28 (comp, 2H), 2.36 (s, 3H), 1.37 (s, 9H), 0.30 (s, 9H); **<sup>13</sup>C NMR** (100 MHz,  $\text{CDCl}_3$ )  $\delta$  170.4, 150.1, 148.3, 144.3, 143.6, 138.6, 138.5, 136.6, 136.0, 134.6, 132.3, 131.7, 130.2, 129.0 (x 2), 128.2, 127.7, 125.2 (x 2), 122.1, 121.8, 117.1, 34.7, 31.5, 17.6, 0.1; **HRMS** (ESI, m/z) calcd for  $\text{C}_{30}\text{H}_{34}\text{N}_2\text{OSi}$  [M + H]<sup>+</sup> 467.2519, found 467.2516.

**3'-chloro-2-methyl-N-(quinolin-8-yl)-4-(trimethylsilyl)-[1,1'-biphenyl]-3-carboxamide (3k):**



**Yield** 36% (32.0 mg); colorless solid; **R<sub>f</sub>** 0.30 (pet ether/ethyl acetate = 9:1); **eluent composition** petroleum ether/ethyl acetate = 19:1; **mp** 112-114 °C; **<sup>1</sup>H NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta$  10.04 (br s, 1H), 9.02 (dd,  $J$  = 7.2 Hz, 1.6 Hz, 1H), 8.77 (dd,  $J$  = 4.4 Hz, 1.6 Hz, 1H), 8.20 (dd,  $J$  = 8.4 Hz, 1.6 Hz, 1H), 7.63 (app t,  $J$  = 8.0 Hz, 1H), 7.58 (dd,  $J$  = 4.0 Hz, 1.6 Hz, 1H), 7.54 (d,  $J$  = 7.6 Hz, 1H), 7.47 (dd,  $J$  = 8.0 Hz, 4.0 Hz, 1H), 7.38-7.33 (comp, 3H), 7.28 (d,  $J$  = 7.6 Hz, 1H), 7.24-7.22 (m, 1H), 2.32 (s, 3H), 0.30 (s, 9H); **<sup>13</sup>C NMR** (100 MHz,  $\text{CDCl}_3$ )  $\delta$  170.0, 148.4, 144.4, 143.5, 142.2, 138.5, 136.7, 134.5, 134.2, 132.4, 131.6, 129.9, 129.6, 129.4, 128.2, 127.7, 127.6, 127.4, 125.2, 122.2, 121.9, 117.2, 17.5, 0.0; **HRMS** (ESI, m/z) calcd for  $\text{C}_{26}\text{H}_{25}\text{ClN}_2\text{OSi}$  [M + H]<sup>+</sup> 445.1503, found 445.1505.

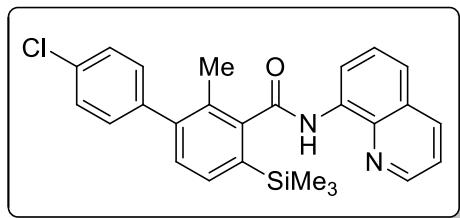
**4'-fluoro-2-methyl-N-(quinolin-8-yl)-4-(trimethylsilyl)-[1,1'-biphenyl]-3-carboxamide (3l):**



**Yield** 36% (31.0 mg); colorless solid; **R<sub>f</sub>** 0.40 (pet ether/ethyl acetate = 9:1); **eluent composition** petroleum ether/ethyl acetate = 19:1; **mp** 160-162 °C; **<sup>1</sup>H NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta$  10.03 (br s, 1H), 9.01 (dd,  $J$  = 7.2 Hz, 1.6 Hz, 1H), 8.76 (dd,  $J$  = 4.4 Hz, 1.6 Hz, 1H), 8.20 (dd,  $J$  = 8.0 Hz, 1.6 Hz, 1H), 7.63 (app t,  $J$  = 8.0 Hz, 1H), 7.58 (dd,  $J$  = 4.4 Hz, 1.6 Hz, 1H), 7.54 (d,  $J$  = 8.0 Hz, 1H), 7.46 (dd,  $J$  = 8.0 Hz, 4.0 Hz, 1H), 7.34-7.28 (comp, 3H), 7.15-7.09 (comp, 2H),

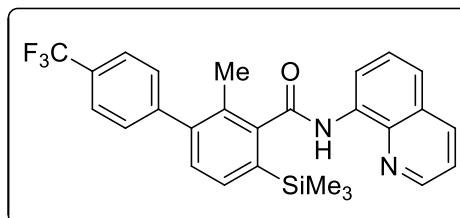
2.32 (s, 3H), 0.30 (s, 9H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 170.2, 162.2 (d, <sup>1</sup>J<sub>F-C</sub> = 245.0 Hz), 148.4, 144.4, 142.6, 138.6, 137.6 (d, <sup>4</sup>J<sub>F-C</sub> = 3.0 Hz), 136.6, 136.6 (d, <sup>3</sup>J<sub>F-C</sub> = 5.0 Hz), 134.5, 132.4, 131.7, 130.9 (d, <sup>3</sup>J<sub>F-C</sub> = 7.0 Hz), 130.1, 128.2, 127.7, 122.2, 121.9, 117.1, 115.3 (d, <sup>2</sup>J<sub>F-C</sub> = 21.0 Hz), 17.6, 0.0; **HRMS** (ESI, m/z) calcd for C<sub>26</sub>H<sub>25</sub>FN<sub>2</sub>OSi [M + H]<sup>+</sup> 429.1798, found 429.1806.

**4'-chloro-2-methyl-N-(quinolin-8-yl)-4-(trimethylsilyl)-[1,1'-biphenyl]-3-carboxamide (3m):**



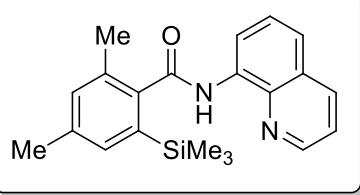
**Yield** 42% (37.7 mg); colorless solid; **R<sub>f</sub>** 0.40 (pet ether/ethyl acetate = 9:1); **eluent composition** petroleum ether/ethyl acetate = 19:1; **mp** 152-154 °C; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 10.03 (br s, 1H), 9.01 (dd, *J* = 7.6 Hz, 1.6 Hz, 1H), 8.76 (dd, *J* = 4.4 Hz, 1.6 Hz, 1H), 8.20 (dd, *J* = 8.4 Hz, 1.6 Hz, 1H), 7.63 (app t, *J* = 8.0 Hz, 1H), 7.58 (dd, *J* = 8.0 Hz, 1.2 Hz, 1H), 7.54 (d, *J* = 7.6 Hz, 1H), 7.47 (dd, *J* = 8.0 Hz, 4.0 Hz, 1H), 7.42-7.39 (comp, 2H), 7.30-7.28 (comp, 3H), 2.32 (s, 3H), 0.30 (s, 9H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 170.1, 148.4, 144.4, 142.4, 140.1, 138.5, 136.8, 136.6, 134.5, 133.3, 132.4, 131.6, 130.7 (x 2), 130.0, 128.6 (x 2), 128.2, 127.7, 122.2, 121.9, 117.1, 17.5, 0.0; **HRMS** (ESI, m/z) calcd for C<sub>26</sub>H<sub>25</sub>ClN<sub>2</sub>OSi [M + H]<sup>+</sup> 445.1503, found 445.1504.

**2-methyl-N-(quinolin-8-yl)-4'-(trifluoromethyl)-4-(trimethylsilyl)-[1,1'-biphenyl]-3-carboxamide (3n):**



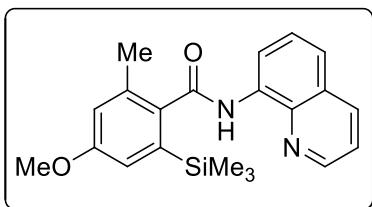
**Yield** 45% (42.6 mg); colorless solid; **R<sub>f</sub>** 0.30 (pet ether/ethyl acetate = 9:1); **eluent composition** petroleum ether/ethyl acetate = 19:1; **mp** 136-138 °C; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 10.05 (br s, 1H), 9.02 (dd, *J* = 7.2 Hz, 1.6 Hz, 1H), 8.77 (dd, *J* = 4.0 Hz, 1.6 Hz, 1H), 8.20 (dd, *J* = 8.4 Hz, 1.6 Hz, 1H), 7.72-7.70 (comp, 2H), 7.64 (app t, *J* = 8.0 Hz, 1H), 7.60-7.57 (comp, 2H), 7.49-7.45 (comp, 3H), 7.30 (d, *J* = 7.6 Hz, 1H), 2.33 (s, 3H), 0.32 (s, 9H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 170.0, 148.4, 145.4, 144.5, 142.2, 138.6, 137.3, 136.6, 134.5, 132.5, 131.5, 129.8, 129.7 (x 2), 129.1 (q, *J* = 41.0 Hz), 128.2, 127.7, 127.1 (q, *J* = 282.0 Hz), 125.3 (q, *J* = 4.0 Hz), 122.3, 121.9, 117.1, 17.5, 0.0; **HRMS** (ESI, m/z) calcd for C<sub>27</sub>H<sub>25</sub>F<sub>3</sub>N<sub>2</sub>OSi [M + H]<sup>+</sup> 479.1766, found 479.1768.

**2,4-dimethyl-N-(quinolin-8-yl)-6-(trimethylsilyl)benzamide (3o):**



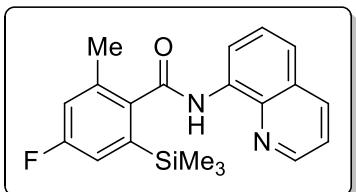
**Yield** 82% (57.0 mg); colorless solid; **R<sub>f</sub>** 0.40 (pet ether/ethyl acetate = 9:1); **eluent composition** petroleum ether/ethyl acetate = 19:1; **mp** 82–84 °C; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 9.96 (br s, 1H), 8.99 (dd, *J* = 7.6 Hz, 1.2 Hz, 1H), 8.72 (dd, *J* = 4.4 Hz, 1.6 Hz, 1H), 8.17 (dd, *J* = 8.0 Hz, 1.6 Hz, 1H), 7.62 (app t, *J* = 8.0 Hz, 1H), 7.56 (dd, *J* = 8.0 Hz, 1.6 Hz, 1H), 7.44 (dd, *J* = 8.0 Hz, 4.0 Hz, 1H), 7.29 (app s, 1H), 7.11 (app s, 1H), 2.44 (s, 3H), 2.39 (s, 3H), 0.28 (s, 9H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 170.2, 148.3, 140.8, 138.6, 138.2, 137.4, 136.4, 134.7, 134.2, 133.0, 132.0, 128.2, 127.6, 121.9, 121.8, 116.8, 21.5, 19.7, 0.1; **HRMS** (ESI, m/z) calcd for C<sub>21</sub>H<sub>24</sub>N<sub>2</sub>OSi [M + H]<sup>+</sup> 349.1736, found 349.1746.

#### 4-methoxy-2-methyl-N-(quinolin-8-yl)-6-(trimethylsilyl)benzamide (3p):



**Yield** 61% (44.2 mg); colorless solid; **R<sub>f</sub>** 0.20 (pet ether/ethyl acetate = 9:1); **eluent composition** petroleum ether/ethyl acetate = 19:1; **mp** 116–118 °C; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 9.95 (br s, 1H), 8.98 (dd, *J* = 7.6 Hz, 1.2 Hz, 1H), 8.73 (dd, *J* = 4.0 Hz, 1.6 Hz, 1H), 8.17 (dd, *J* = 8.4 Hz, 1.6 Hz, 1H), 7.61 (app t, *J* = 8.0 Hz, 1H), 7.55 (dd, *J* = 8.0 Hz, 1.6 Hz, 1H), 7.44 (dd, *J* = 8.4 Hz, 4.0 Hz, 1H), 7.02 (d, *J* = 2.8 Hz, 1H), 6.80 (d, *J* = 2.4 Hz, 1H), 3.86 (s, 3H), 2.46 (s, 3H), 0.28 (s, 9H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 170.1, 159.3, 148.3, 139.7, 138.6, 136.4 (x 2), 136.3, 134.7, 128.2, 127.6, 121.9, 121.8, 118.3, 116.8, 115.7, 55.3, 20.2, 0.0; **HRMS** (ESI, m/z) calcd for C<sub>21</sub>H<sub>24</sub>N<sub>2</sub>O<sub>2</sub>Si [M + Na]<sup>+</sup> 387.1505, found 387.1514.

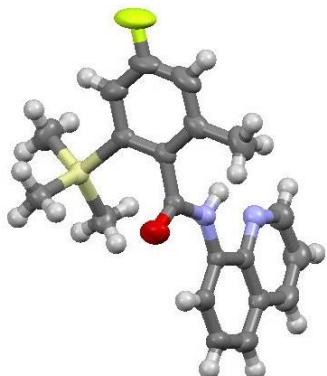
#### 4-fluoro-2-methyl-N-(quinolin-8-yl)-6-(trimethylsilyl)benzamide (3q):<sup>3</sup>



**Yield** 61% (43.2 mg); colorless solid; **R<sub>f</sub>** 0.40 (pet ether/ethyl acetate = 9:1); **eluent composition** petroleum ether/ethyl acetate = 19:1; **mp** 110–112 °C (crystallization from CHCl<sub>3</sub> and hexane using solvent diffusion method); **<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ 9.96 (br s, 1H), 8.97 (dd, *J* = 7.2 Hz, 1.2 Hz, 1H), 8.75 (dd, *J* = 4.2 Hz, 1.8 Hz, 1H), 8.20 (dd, *J* = 8.4 Hz, 1.8 Hz, 1H), 7.62 (app t, *J* = 8.4 Hz, 1H), 7.58 (dd, *J* = 8.4 Hz, 1.2 Hz, 1H), 7.46 (dd, *J* = 8.4 Hz, 4.2 Hz, 1H), 7.15 (dd, *J* = 9.6 Hz, 2.4 Hz, 1H), 6.97 (dd, *J* = 8.4 Hz, 2.4 Hz, 1H), 2.46 (s, 3H), 0.27 (s, 9H); **<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>) δ 169.4, 162.5 (d, <sup>1</sup>J<sub>F-C</sub> = 249.0 Hz), 148.4, 141.1 (d, <sup>3</sup>J<sub>F-C</sub> = 4.5 Hz), 139.5 (d, <sup>4</sup>J<sub>F-C</sub> = 3.0 Hz), 138.4, 137.5 (d, <sup>3</sup>J<sub>F-C</sub> = 7.5 Hz), 136.6, 134.4,

128.2, 127.7, 122.2, 121.9, 118.7 (d,  $^2J_{F-C} = 18.0$  Hz), 117.8 (d,  $^2J_{F-C} = 21.0$  Hz), 117.0, 19.9, 0.1;  
**HRMS** (ESI, m/z) calcd for  $C_{20}H_{21}FN_2OSi$  [M + H]<sup>+</sup> 353.1485, found 353.1487.

**Figure S6.** X-ray crystal structure of **3q** (ellipsoid contour at 50% probability level)



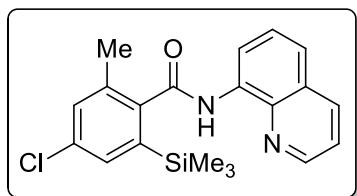
**Crystal data and structure refinement for 3q, CCDC No. 2054620**

Empirical formula	$C_{20}H_{21}FN_2OSi$
Formula weight	352.48
Temperature/K	296.15
Crystal system	orthorhombic
Space group	Pbca
a/Å	8.859(4)
b/Å	16.866(8)
c/Å	24.048(12)
$\alpha/^\circ$	90
$\beta/^\circ$	90
$\gamma/^\circ$	90
Volume/Å <sup>3</sup>	3593(3)
Z	8
$\rho_{calcd}/\text{cm}^3$	1.303
$\mu/\text{mm}^{-1}$	0.151
F(000)	1488.0
Crystal size/mm <sup>3</sup>	0.48 × 0.32 × 0.18
Radiation	MoKα ( $\lambda = 0.71073$ )
2Θ range for data collection/°	3.388 to 51.314
Index ranges	-10 ≤ h ≤ 10, -20 ≤ k ≤ 20, -29 ≤ l ≤ 29
Reflections collected	35360
Independent reflections	3352 [ $R_{int} = 0.0397$ , $R_{sigma} = 0.0197$ ]
Data/restraints/parameters	3352/0/230
Goodness-of-fit on $F^2$	1.042
Final R indexes [I>=2σ (I)]	$R_1 = 0.0370$ , $wR_2 = 0.1005$

Final R indexes [all data]  
Largest diff. peak/hole / e Å<sup>-3</sup>

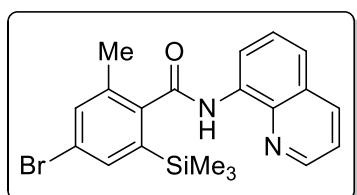
R<sub>1</sub> = 0.0492, wR<sub>2</sub> = 0.1108  
0.18/-0.21

**4-chloro-2-methyl-N-(quinolin-8-yl)-6-(trimethylsilyl)benzamide (3r):**



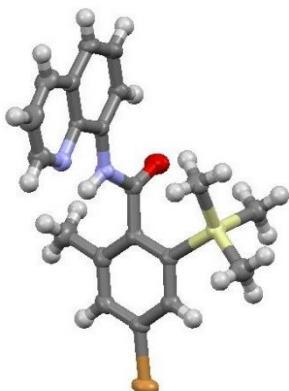
**Yield** 65% (47.6 mg); colorless solid; **R<sub>f</sub>** 0.40 (pet ether/ethyl acetate = 9:1); **eluent composition** petroleum ether/ethyl acetate = 19:1; **mp** 134-136 °C; **<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ 9.95 (br s, 1H), 8.96 (dd, *J* = 7.2 Hz, 1.6 Hz, 1H), 8.74 (dd, *J* = 4.4 Hz, 1.6 Hz, 1H), 8.18 (dd, *J* = 8.4 Hz, 1.6 Hz, 1H), 7.62 (app t, *J* = 8.0 Hz, 1H), 7.56 (dd, *J* = 8.0 Hz, 1.6 Hz, 1H), 7.45 (dd, *J* = 8.0 Hz, 4.0 Hz, 1H), 7.43 (d, *J* = 1.6 Hz, 1H), 7.28 (d, *J* = 1.6 Hz, 1H), 2.44 (s, 3H), 0.28 (s, 9H); **<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>) δ 161.9, 148.5, 141.7, 140.3, 138.5, 136.5 (x 2), 134.8, 134.3, 132.1, 131.0, 128.2, 127.6, 122.3, 121.9, 116.9, 19.6, -0.1; **HRMS** (ESI, m/z) calcd for C<sub>20</sub>H<sub>21</sub>ClN<sub>2</sub>OSi [M + H]<sup>+</sup> 369.1190, found 369.1198.

**4-bromo-2-methyl-N-(quinolin-8-yl)-6-(trimethylsilyl)benzamide (3s):**



**Yield** 43% (35.4 mg); colorless solid; **R<sub>f</sub>** 0.40 (pet ether/ethyl acetate = 9:1); **eluent composition** petroleum ether/ethyl acetate = 19:1; **mp** 132-134 °C (crystallization from DCM and hexane using solvent diffusion method); **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 9.94 (br s, 1H), 8.95 (dd, *J* = 7.2 Hz, 1.6 Hz, 1H), 8.74 (dd, *J* = 4.4 Hz, 1.6 Hz, 1H), 8.19 (dd, *J* = 8.4 Hz, 1.6 Hz, 1H), 7.62 (app t, *J* = 8.0 Hz, 1H), 7.59-7.57 (comp, 2H), 7.48-7.44 (comp, 2H), 2.43 (s, 3H), 0.28 (s, 9H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 169.1, 148.5, 142.1, 140.6, 138.5, 136.7, 136.5, 134.9, 134.3, 133.9, 128.2, 127.6, 123.6, 122.3, 121.9, 116.9, 19.6, -0.1; **HRMS** (ESI, m/z) calcd for C<sub>20</sub>H<sub>21</sub>BrN<sub>2</sub>OSi [M + H]<sup>+</sup> 413.0685, found 413.0691.

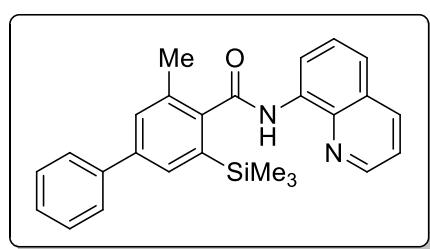
**Figure S7.** X-ray crystal structure of **3s** (ellipsoid contour at 50% probability level)



**Crystal data and structure refinement for 3s, CCDC No. 2054621**

Empirical formula	C <sub>20</sub> H <sub>21</sub> BrN <sub>2</sub> OSi
Formula weight	413.39
Temperature/K	296.15
Crystal system	triclinic
Space group	P-1
a/Å	8.7091(13)
b/Å	9.3209(14)
c/Å	12.996(2)
α/°	87.899(3)
β/°	78.083(3)
γ/°	70.996(3)
Volume/Å <sup>3</sup>	975.4(3)
Z	2
ρ <sub>calcg</sub> /cm <sup>3</sup>	1.407
μ/mm <sup>-1</sup>	2.178
F(000)	424.0
Crystal size/mm <sup>3</sup>	0.75 × 0.375 × 0.235
Radiation	MoKα ( $\lambda = 0.71073$ )
2Θ range for data collection/°	4.624 to 60.12
Index ranges	-11 ≤ h ≤ 12, -13 ≤ k ≤ 12, -18 ≤ l ≤ 18
Reflections collected	54434
Independent reflections	5434 [ $R_{int} = 0.0667$ , $R_{sigma} = 0.0396$ ]
Data/restraints/parameters	5434/0/230
Goodness-of-fit on F <sup>2</sup>	1.138
Final R indexes [I>=2σ (I)]	$R_1 = 0.0567$ , $wR_2 = 0.1026$
Final R indexes [all data]	$R_1 = 0.0930$ , $wR_2 = 0.1211$
Largest diff. peak/hole / e Å <sup>-3</sup>	0.83/-0.66

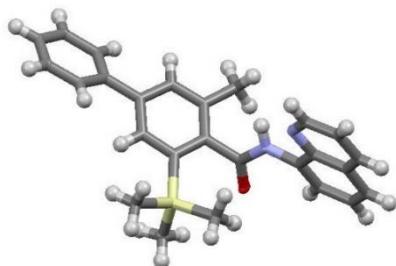
**3-methyl-N-(quinolin-8-yl)-5-(trimethylsilyl)-[1,1'-biphenyl]-4-carboxamide (3t):**



**Yield** 54% (44.0 mg); colorless solid; **R<sub>f</sub>** 0.40 (pet ether/ethyl acetate = 9:1); **eluent composition** petroleum ether/ethyl acetate = 19:1; **mp** 150-152 °C (crystallization from DCM and hexane using solvent diffusion method); **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 10.05 (br s, 1H), 9.03 (dd, *J* = 7.6 Hz, 1.2 Hz, 1H), 8.76 (dd, *J* = 4.4 Hz, 1.6 Hz, 1H), 8.19 (dd, *J* = 8.4 Hz, 1.6 Hz, 1H), 7.71 (d, *J* = 1.6 Hz, 1H), 7.66-7.63 (comp, 3H), 7.59 (dd, *J* = 8.0 Hz, 1.6 Hz, 1H), 7.51-7.48 (comp, 3H), 7.46 (dd, *J* = 8.8 Hz, 4.8 Hz, 1H), 7.42-7.38 (m, 1H), 2.56 (s, 3H), 0.34 (s, 9H); **<sup>13</sup>C NMR** (100

MHz, CDCl<sub>3</sub>) δ 170.0, 148.4, 142.3, 141.5, 141.2, 138.6, 138.2, 136.5, 134.7, 134.6, 131.3, 130.2, 129.0 (x 2), 128.2, 127.7 (x 2), 127.4 (x 2), 122.1, 121.8, 117.0, 20.0, 0.1; **HRMS** (ESI, m/z) calcd for C<sub>26</sub>H<sub>26</sub>N<sub>2</sub>OSi [M + H]<sup>+</sup> 411.1893, found 411.1911.

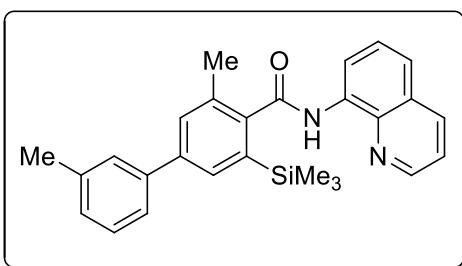
**Figure S8.** X-ray crystal structure of **3t** (ellipsoid contour at 50% probability level)



**Crystal data and structure refinement for 3t, CCDC No. 2054622**

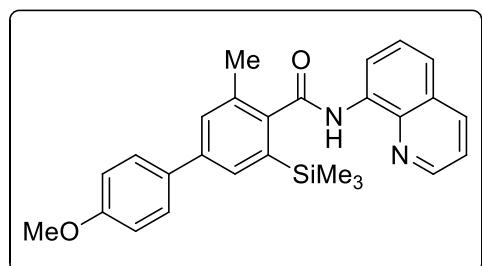
Empirical formula	C <sub>26</sub> H <sub>26</sub> N <sub>2</sub> OSi
Formula weight	410.58
Temperature/K	100.0
Crystal system	triclinic
Space group	P-1
a/Å	8.1234(10)
b/Å	11.3451(14)
c/Å	12.8468(16)
α/°	82.183(4)
β/°	74.803(5)
γ/°	74.099(4)
Volume/Å <sup>3</sup>	1096.2(2)
Z	2
ρ <sub>calcg/cm<sup>3</sup></sub>	1.244
μ/mm <sup>-1</sup>	1.090
F(000)	436.0
Crystal size/mm <sup>3</sup>	0.5 × 0.365 × 0.25
Radiation	Cu Kα (λ = 1.54178)
2Θ range for data collection/°	7.148 to 128.018
Index ranges	-9 ≤ h ≤ 9, -13 ≤ k ≤ 12, -14 ≤ l ≤ 14
Reflections collected	23938
Independent reflections	3578 [R <sub>int</sub> = 0.0734, R <sub>sigma</sub> = 0.0452]
Data/restraints/parameters	3578/0/275
Goodness-of-fit on F <sup>2</sup>	1.071
Final R indexes [I>=2σ (I)]	R <sub>1</sub> = 0.0469, wR <sub>2</sub> = 0.1191
Final R indexes [all data]	R <sub>1</sub> = 0.0496, wR <sub>2</sub> = 0.1212
Largest diff. peak/hole / e Å <sup>-3</sup>	0.29/-0.40

**3,3'-dimethyl-N-(quinolin-8-yl)-5-(trimethylsilyl)-[1,1'-biphenyl]-4-carboxamide (3u):**



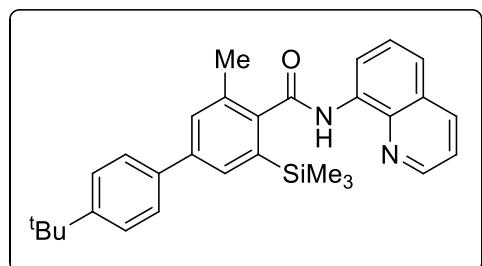
**Yield** 60% (51.3 mg); colorless oil; **R<sub>f</sub>** 0.40 (pet ether/ethyl acetate = 9:1); **eluent composition** petroleum ether/ethyl acetate = 19:1; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 10.05 (br s, 1H), 9.03 (dd, *J* = 7.6 Hz, 0.8 Hz, 1H), 8.76 (dd, *J* = 4.0 Hz, 1.6 Hz, 1H), 8.20 (dd, *J* = 8.4 Hz, 1.2 Hz, 1H), 7.70 (d, *J* = 1.2 Hz, 1H), 7.65 (app t, *J* = 8.0 Hz, 1H), 7.59 (dd, *J* = 8.0 Hz, 0.8 Hz, 1H), 7.50 (d, *J* = 0.8 Hz, 1H), 7.47-7.44 (comp, 3H), 7.39 (app t, *J* = 8.0 Hz, 1H), 7.22 (d, *J* = 7.6 Hz, 1H), 2.55 (s, 3H), 2.48 (s, 3H), 0.34 (s, 9H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 170.0, 148.4, 142.3, 141.6, 141.2, 138.6, 138.1, 136.5, 134.7, 134.6, 131.3, 130.2, 128.9 (x 2), 128.4, 128.2 (x 2), 127.7, 124.6, 122.1, 121.8, 117.0, 21.7, 19.9, 0.1; **HRMS** (ESI, m/z) calcd for C<sub>27</sub>H<sub>28</sub>N<sub>2</sub>OSi [M + H]<sup>+</sup> 425.2049, found 425.2038.

**4'-methoxy-3-methyl-N-(quinolin-8-yl)-5-(trimethylsilyl)-[1,1'-biphenyl]-4-carboxamide (3v):**



**Yield** 54% (47.2 mg); colorless solid; **R<sub>f</sub>** 0.30 (pet ether/ethyl acetate = 9:1); **eluent composition** petroleum ether/ethyl acetate = 19:1; **mp** 142-144 °C; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 10.03 (br s, 1H), 9.02 (dd, *J* = 7.6 Hz, 1.2 Hz, 1H), 8.74 (dd, *J* = 4.4 Hz, 1.6 Hz, 1H), 8.19 (dd, *J* = 8.4 Hz, 1.6 Hz, 1H), 7.66 (d, *J* = 2.0 Hz, 1H), 7.63 (d, *J* = 8.0 Hz, 1H), 7.59-7.56 (comp, 3H), 7.47-7.43 (comp, 2H), 7.04-7.01 (comp, 2H), 3.88 (s, 3H), 2.53 (s, 3H), 0.33 (s, 9H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 170.0, 159.5, 148.4, 141.8, 141.0, 138.6, 138.1, 136.5, 134.7, 134.6, 133.6, 130.9, 129.8, 128.5 (x 2), 128.2, 127.6, 122.0, 121.8, 116.9, 114.4 (x 2), 55.5, 20.0, 0.1; **HRMS** (ESI, m/z) calcd for C<sub>27</sub>H<sub>28</sub>N<sub>2</sub>O<sub>2</sub>Si [M + H]<sup>+</sup> 441.1998, found 441.2014.

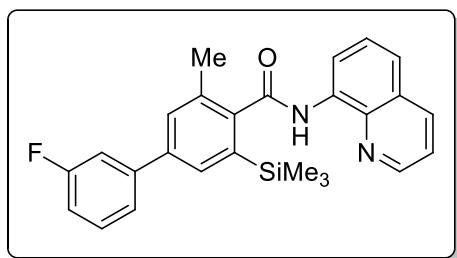
**4'-(tert-butyl)-3-methyl-N-(quinolin-8-yl)-5-(trimethylsilyl)-[1,1'-biphenyl]-4-carboxamide (3w):**



**Yield** 71% (66.1 mg); colorless solid; **R<sub>f</sub>** 0.40 (pet ether/ethyl acetate = 9:1); **eluent composition** petroleum ether/ethyl acetate = 19:1; **mp** 166-168 °C; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 10.05 (br s, 1H), 9.04

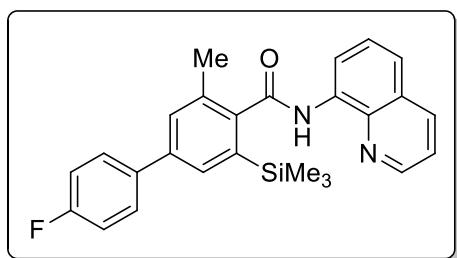
(dd,  $J = 7.2$  Hz, 1.2 Hz, 1H), 8.76 (dd,  $J = 4.0$  Hz, 1.6 Hz, 1H), 8.19 (dd,  $J = 8.0$  Hz, 1.6 Hz, 1H), 7.71 (d,  $J = 0.8$  Hz, 1H), 7.64 (app t,  $J = 8.0$  Hz, 1H), 7.60-7.58 (comp, 3H), 7.54-7.51 (comp, 3H), 7.46 (dd,  $J = 8.4$  Hz, 4.0 Hz, 1H), 2.55 (s, 3H), 1.41 (s, 9H), 0.34 (s, 9H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  170.1, 150.7, 148.4, 142.1, 141.4, 138.6, 138.3, 138.0, 136.5, 134.6, 134.6, 131.3, 130.1, 128.2, 127.7, 127.1 (x 2), 125.9 (x 2), 122.0, 121.8, 117.0, 34.7, 31.5, 20.0, 0.1; HRMS (ESI, m/z) calcd for  $\text{C}_{30}\text{H}_{34}\text{N}_2\text{OSi} [\text{M} + \text{H}]^+$  467.2519, found 467.2510.

**3'-fluoro-3-methyl-N-(quinolin-8-yl)-5-(trimethylsilyl)-[1,1'-biphenyl]-4-carboxamide (3x):**



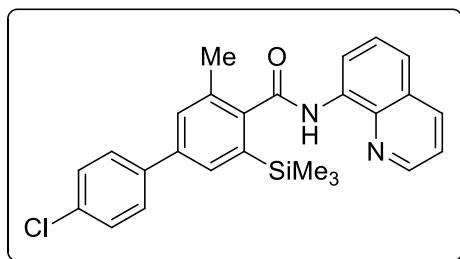
**Yield** 62% (53.5 mg); colorless solid; **R<sub>f</sub>** 0.20 (pet ether/ethyl acetate = 9:1); **eluent composition** petroleum ether/ethyl acetate = 19:1; **mp** 116-118 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  10.04 (br s, 1H), 9.02 (dd,  $J = 7.6$  Hz, 1.2 Hz, 1H), 8.75 (dd,  $J = 4.0$  Hz, 1.6 Hz, 1H), 8.19 (dd,  $J = 8.0$  Hz, 1.6 Hz, 1H), 7.67 (d,  $J = 1.2$  Hz, 1H), 7.64 (app t,  $J = 8.0$  Hz, 1H), 7.59 (dd,  $J = 8.0$  Hz, 0.8 Hz, 1H), 7.49 (app s, 1H), 7.47-7.40 (comp, 3H), 7.33 (dd,  $J = 6.4$  Hz, 1.6 Hz, 1H), 7.11-7.06 (m, 1H), 2.54 (s, 3H), 0.34 (s, 9H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  169.8, 163.3 (d,  $^1J_{\text{F-C}} = 244.0$  Hz), 148.4, 143.4 (d,  $^3J_{\text{F-C}} = 8.0$  Hz), 142.9, 140.2, 138.6, 138.5, 136.5, 134.9, 134.5, 131.2, 130.4 (d,  $^3J_{\text{F-C}} = 9.0$  Hz), 130.1, 128.2, 127.6, 123.1 (d,  $^3J_{\text{F-C}} = 4.5$  Hz), 122.2, 121.9, 117.0, 114.4 (d,  $^2J_{\text{F-C}} = 21.0$  Hz), 114.3 (d,  $^2J_{\text{F-C}} = 22.0$  Hz), 19.9, 0.1; HRMS (ESI, m/z) calcd for  $\text{C}_{26}\text{H}_{25}\text{FN}_2\text{OSi} [\text{M} + \text{H}]^+$  429.1798, found 429.1802.

**4'-fluoro-3-methyl-N-(quinolin-8-yl)-5-(trimethylsilyl)-[1,1'-biphenyl]-4-carboxamide (3y):**



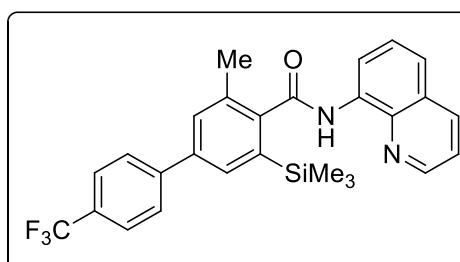
**Yield** 67% (57.3 mg); colorless solid; **R<sub>f</sub>** 0.40 (pet ether/ethyl acetate = 9:1); **eluent composition** petroleum ether/ethyl acetate = 19:1; **mp** 166-168 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  10.04 (br s, 1H), 9.02 (dd,  $J = 7.2$  Hz, 0.8 Hz, 1H), 8.75 (dd,  $J = 4.0$  Hz, 1.6 Hz, 1H), 8.19 (dd,  $J = 8.0$  Hz, 1.6 Hz, 1H), 7.66-7.62 (comp, 2H), 7.60-7.56 (comp, 3H), 7.47-7.44 (comp, 2H), 7.20-7.14 (comp, 2H), 2.54 (s, 3H), 0.34 (s, 9H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  169.9, 162.8 (d,  $^1J_{\text{F-C}} = 245.0$  Hz), 148.4, 142.4, 140.5, 138.6, 138.3, 137.2 (d,  $^4J_{\text{F-C}} = 4.5$  Hz), 136.5, 134.8, 134.5, 131.1, 130.0, 129.0 (d,  $^3J_{\text{F-C}} = 8.0$  Hz), 128.2, 127.7 (x 2), 122.0 (d,  $^2J_{\text{F-C}} = 28.0$  Hz), 117.0, 115.8 (d,  $^2J_{\text{F-C}} = 21.0$  Hz), 19.9, 0.1; HRMS (ESI, m/z) calcd for  $\text{C}_{26}\text{H}_{25}\text{FN}_2\text{OSi} [\text{M} + \text{H}]^+$  429.1798, found 429.1801.

**4'-chloro-3-methyl-N-(quinolin-8-yl)-5-(trimethylsilyl)-[1,1'-biphenyl]-4-carboxamide (3z):**



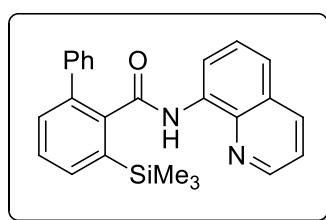
**Yield** 45% (40.2 mg); colorless solid; **R<sub>f</sub>** 0.30 (pet ether/ethyl acetate = 9:1); **eluent composition** petroleum ether/ethyl acetate = 19:1; **mp** 148-150 °C; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 10.03 (br s, 1H), 9.02 (dd, *J* = 7.2 Hz, 1.6 Hz, 1H), 8.75 (dd, *J* = 4.0 Hz, 1.6 Hz, 1H), 8.19 (dd, *J* = 8.0 Hz, 1.6 Hz, 1H), 7.66-7.64 (m, 1H), 7.63 (d, *J* = 7.6 Hz, 1H), 7.59 (dd, *J* = 8.0 Hz, 1.6 Hz, 1H), 7.56-7.54 (comp, 2H), 7.46-7.44 (comp, 4H), 2.54 (s, 3H), 0.33 (s, 9H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 169.8, 148.4, 142.6, 140.2, 139.6, 138.6, 138.4, 136.5, 134.9, 134.5, 133.8, 131.1, 130.0, 129.1 (x 2), 128.7 (x 2), 128.2, 127.7, 122.1, 121.8, 117.0, 19.9, 0.1; **HRMS** (ESI, m/z) calcd for C<sub>26</sub>H<sub>25</sub>ClN<sub>2</sub>OSi [M + H]<sup>+</sup> 445.1503, found 445.1507.

**3-methyl-N-(quinolin-8-yl)-4'-(trifluoromethyl)-5-(trimethylsilyl)-[1,1'-biphenyl]-4-carboxamide (3aa):**



**Yield** 52% (50.0 mg); colorless solid; **R<sub>f</sub>** 0.30 (pet ether/ethyl acetate = 9:1); **eluent composition** petroleum ether/ethyl acetate = 19:1; **mp** 142-144 °C; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 10.05 (br s, 1H), 9.03 (dd, *J* = 7.6 Hz, 1.2 Hz, 1H), 8.76 (dd, *J* = 4.0 Hz, 1.6 Hz, 1H), 8.20 (dd, *J* = 8.4 Hz, 1.6 Hz, 1H), 7.76-7.72 (comp, 4H), 7.70 (d, *J* = 1.6 Hz, 1H), 7.65 (app t, *J* = 8.0 Hz, 1H), 7.60 (dd, *J* = 8.4 Hz, 1.2 Hz, 1H), 7.51 (d, *J* = 0.8 Hz, 1H), 7.46 (dd, *J* = 8.4 Hz, 4.0 Hz, 1H), 2.56 (s, 3H), 0.34 (s, 9H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 169.7, 148.4, 144.7, 143.2, 140.0, 138.6, 138.6, 136.6, 135.1, 134.5, 131.4, 130.3, 129.7 (q, *J* = 32.0 Hz), 128.2, 127.7 (x 2), 127.7, 125.9 (q, *J* = 3.0 Hz), 124.4 (q, *J* = 271.0 Hz), 122.2, 121.9, 117.0, 19.9, 0.1; **HRMS** (ESI, m/z) calcd for C<sub>27</sub>H<sub>25</sub>F<sub>3</sub>N<sub>2</sub>OSi [M + H]<sup>+</sup> 479.1766, found 479.1765.

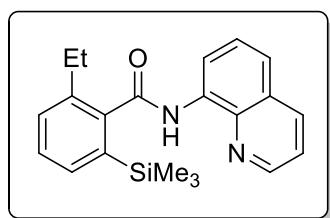
**N-(quinolin-8-yl)-3-(trimethylsilyl)-[1,1'-biphenyl]-2-carboxamide (3ab):**



**Yield** 31% (24.3 mg); colorless solid; **R<sub>f</sub>** 0.40 (pet ether/ethyl acetate = 9:1); **eluent composition** petroleum ether/ethyl acetate = 19:1; **mp** 146-148 °C; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 9.62 (br s, 1H), 8.75 (dd, *J* = 7.2 Hz, 1.6 Hz, 1H), 8.57 (dd, *J* = 8.0 Hz, 1.6 Hz, 1H), 8.07 (dd, *J* = 8.0 Hz, 1.6 Hz, 1H), 7.69 (dd, *J* = 8.0 Hz, 1.6 Hz,

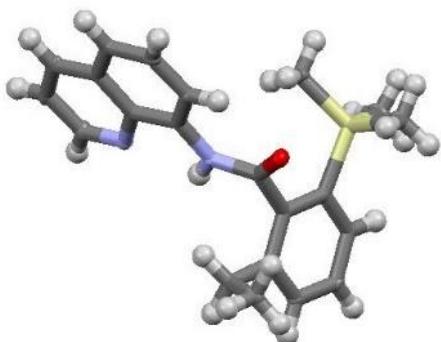
1H), 7.54-7.48 (comp, 4H), 7.47 (dd,  $J = 8.0$  Hz, 1.6 Hz, 1H), 7.44 (dd,  $J = 8.0$  Hz, 1.2 Hz, 1H), 7.34 (dd,  $J = 8.0$  Hz, 4.0 Hz, 1H), 7.20-7.17 (comp, 2H), 7.07-7.03 (m, 1H), 0.35 (s, 9H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  169.5, 147.9, 142.5, 140.7, 139.4, 139.3, 138.4, 136.1, 134.6, 134.1, 131.0, 128.9 (x 2), 128.8, 128.2 (x 2), 127.9, 127.4, 127.3, 121.6, 121.5, 116.4, 0.2; HRMS (ESI, m/z) calcd for  $\text{C}_{25}\text{H}_{24}\text{N}_2\text{OSi} [\text{M} + \text{H}]^+$  397.1736, found 397.1753.

**2-ethyl-N-(quinolin-8-yl)-6-(trimethylsilyl)benzamide (3ac):**



**Yield** 57% (39.8 mg); colorless solid; **R<sub>f</sub>** 0.30 (pet ether/ethyl acetate = 9:1); **eluent composition** petroleum ether/ethyl acetate = 19:1; **mp** 110-112 °C (crystallization from  $\text{CHCl}_3$  using solvent evaporation method);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  9.99 (br s, 1H), 9.01 (dd,  $J = 7.2$  Hz, 0.8 Hz, 1H), 8.73 (dd,  $J = 8.0$  Hz, 1.6 Hz, 1H), 8.18 (dd,  $J = 7.6$  Hz, 1.6 Hz, 1H), 7.63 (app t,  $J = 8.0$  Hz, 1H), 7.57 (dd,  $J = 8.0$  Hz, 0.8 Hz, 1H), 7.51 (dd,  $J = 7.2$  Hz, 0.8 Hz, 1H), 7.44 (dd,  $J = 8.0$  Hz, 4.0 Hz, 1H), 7.40 (app t,  $J = 7.2$  Hz, 1H), 7.35 (d,  $J = 7.2$  Hz, 1H), 2.79 (q,  $J = 7.6$  Hz, 2H), 1.29 (t,  $J = 7.6$  Hz, 3H), 0.28 (s, 9H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  170.0, 148.4, 142.9, 140.3, 138.6, 137.4, 136.4, 134.6, 132.4, 129.7, 128.8, 128.2, 127.6, 122.0, 121.8, 116.9, 26.6, 16.1, 0.1; HRMS (ESI, m/z) calcd for  $\text{C}_{21}\text{H}_{24}\text{N}_2\text{OSi} [\text{M} + \text{H}]^+$  349.1736, found 349.1735.

**Figure S9.** X-ray crystal structure of **3ac** (ellipsoid contour at 50% probability level)

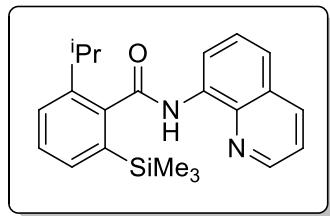


**Crystal data and structure refinement for 3ac, CCDC No. 2054614**

Empirical formula	$\text{C}_{21}\text{H}_{24}\text{N}_2\text{OSi}$
Formula weight	348.51
Temperature/K	100.0
Crystal system	monoclinic
Space group	P2 <sub>1</sub> /n
a/Å	10.3889(6)
b/Å	13.8214(14)

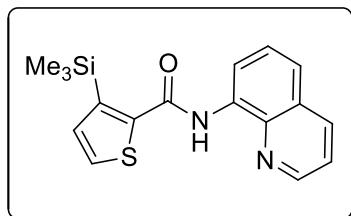
c/Å	13.617(2)
$\alpha/^\circ$	90
$\beta/^\circ$	94.158(7)
$\gamma/^\circ$	90
Volume/Å <sup>3</sup>	1950.1(4)
Z	4
$\rho_{\text{calcd}}/\text{cm}^3$	1.187
$\mu/\text{mm}^{-1}$	1.133
F(000)	744.0
Crystal size/mm <sup>3</sup>	0.35 × 0.25 × 0.2
Radiation	Cu Kα ( $\lambda = 1.54178$ )
2Θ range for data collection/°	9.128 to 133.466
Index ranges	-11 ≤ h ≤ 12, -16 ≤ k ≤ 16, -16 ≤ l ≤ 16
Reflections collected	28695
Independent reflections	3437 [ $R_{\text{int}} = 0.0586$ , $R_{\text{sigma}} = 0.0314$ ]
Data/restraints/parameters	3437/0/230
Goodness-of-fit on $F^2$	1.077
Final R indexes [ $I \geq 2\sigma(I)$ ]	$R_1 = 0.0399$ , $wR_2 = 0.0946$
Final R indexes [all data]	$R_1 = 0.0416$ , $wR_2 = 0.0958$
Largest diff. peak/hole / e Å <sup>-3</sup>	0.20/-0.29

**2-isopropyl-N-(quinolin-8-yl)-6-(trimethylsilyl)benzamide (3ad):**



**Yield** 53% (38.4 mg); colorless solid; **R<sub>f</sub>** 0.40 (pet ether/ethyl acetate = 9:1); **eluent composition** petroleum ether/ethyl acetate = 19:1; **mp** 154-156 °C; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 10.00 (br s, 1H), 9.00 (app d, *J* = 7.2 Hz, 1H), 8.72 (dd, *J* = 8.0 Hz, 1.6 Hz, 1H), 8.18 (dd, *J* = 8.4 Hz, 1.2 Hz, 1H), 7.63 (app t, *J* = 8.0 Hz, 1H), 7.57 (d, *J* = 7.6 Hz, 1H), 7.51-7.49 (m, 1H), 7.46-7.42 (comp, 3H), 3.27-3.17 (m, 1H), 1.29 (d, *J* = 6.8 Hz, 6H), 0.27 (s, 9H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 170.0, 148.3, 145.0, 142.3, 138.5, 137.2, 136.5, 134.6, 132.5, 128.9, 128.2, 127.7, 126.7, 122.0, 121.8, 116.9, 30.8, 24.7, 0.1; **HRMS** (ESI, m/z) calcd for C<sub>22</sub>H<sub>26</sub>N<sub>2</sub>O<sub>2</sub>Si [M + H]<sup>+</sup> 363.1893, found 363.1894.

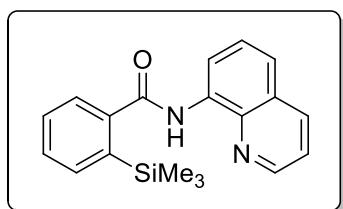
**N-(quinolin-8-yl)-3-(trimethylsilyl)thiophene-2-carboxamide (3ae):<sup>3</sup>**



**Yield** 15% (9.6 mg); colorless solid; **R<sub>f</sub>** 0.40 (pet ether/ethyl acetate = 9:1); **eluent composition** petroleum ether/ethyl acetate = 19:1; **mp** 118-120 °C; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 10.44 (br s, 1H), 8.84-8.86 (comp, 2H), 8.18 (dd, *J* = 8.0 Hz, 1.6 Hz, 1H), 7.58

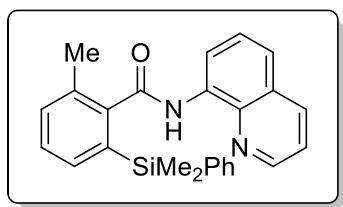
(app t,  $J = 8.0$  Hz, 1H), 7.54 (dd,  $J = 8.0$  Hz, 1.6 Hz, 1H), 7.49-7.46 (comp, 2H), 7.25 (d,  $J = 4.8$  Hz, 1H), 0.41 (s, 9H);  **$^{13}\text{C}$  NMR** (100 MHz,  $\text{CDCl}_3$ )  $\delta$  161.4, 148.4, 147.3, 143.2, 138.7, 136.5, 135.1, 134.9, 128.2, 127.6, 127.3, 121.8, 121.7, 116.8, -0.0; **HRMS** (ESI, m/z) calcd for  $\text{C}_{17}\text{H}_{18}\text{N}_2\text{OSSi} [\text{M} + \text{H}]^+$  327.0987, found 327.0986.

***N*-(quinolin-8-yl)-2-(trimethylsilyl)benzamide (**3af**):<sup>3</sup>**



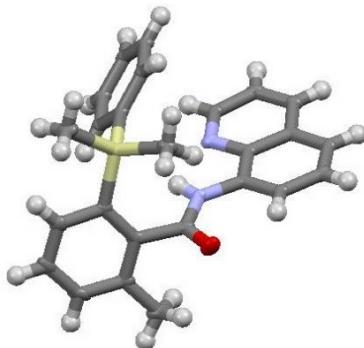
**Yield** 11% (7.2 mg); colorless solid; **R<sub>f</sub>** 0.40 (pet ether/ethyl acetate = 9:1); **eluent composition** petroleum ether/ethyl acetate = 19:1; **mp** 106-108 °C;  **$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta$  10.32 (br s, 1H), 8.94 (dd,  $J = 7.2$  Hz, 1.6 Hz, 1H), 8.79 (dd,  $J = 4.0$  Hz, 1.6 Hz, 1H), 8.19 (dd,  $J = 8.4$  Hz, 1.6 Hz, 1H), 7.80-7.75 (m, 1H), 7.74-7.71 (m, 1H), 7.61 (app t,  $J = 8.0$  Hz, 1H), 7.56 (dd,  $J = 8.4$  Hz, 1.6 Hz, 1H), 7.53-7.49 (comp, 2H), 7.47 (dd,  $J = 8.4$  Hz, 4.4 Hz, 1H), 0.36 (s, 9H);  **$^{13}\text{C}$  NMR** (100 MHz,  $\text{CDCl}_3$ )  $\delta$  169.4, 148.3, 142.9, 140.2, 138.7, 136.6, 135.7, 134.9, 129.9, 129.1, 128.2, 127.7, 126.5, 121.9, 121.8, 116.8, 0.3; **HRMS** (ESI, m/z) calcd for  $\text{C}_{19}\text{H}_{20}\text{N}_2\text{OSi} [\text{M} + \text{H}]^+$  321.1423, found 321.1422.

**2-(dimethyl(phenyl)silyl)-6-methyl-N-(quinolin-8-yl)benzamide (**3ag**):**



**Yield** 67% (53.4 mg); colorless solid; **R<sub>f</sub>** 0.30 (pet ether/ethyl acetate = 9:1); **eluent composition** petroleum ether/ethyl acetate = 19:1; **mp** 132-134 °C (crystallization from  $\text{CHCl}_3$  using solvent evaporation method);  **$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta$  9.71 (br s, 1H), 8.84 (dd,  $J = 7.2$  Hz, 1.6 Hz, 1H), 8.61 (dd,  $J = 4.4$  Hz, 1.6 Hz, 1H), 8.15 (dd,  $J = 8.0$  Hz, 1.6 Hz, 1H), 7.58 (app t,  $J = 8.0$  Hz, 1H), 7.54 (dd,  $J = 8.0$  Hz, 1.6 Hz, 1H), 7.45 (dd,  $J = 6.8$  Hz, 1.6 Hz, 1H), 7.44-7.39 (comp, 3H), 7.36-7.30 (comp, 2H), 7.06-7.02 (comp, 3H), 2.43 (s, 3H), 0.58 (s, 6H);  **$^{13}\text{C}$  NMR** (100 MHz,  $\text{CDCl}_3$ )  $\delta$  169.6, 148.1, 143.8, 138.5, 138.2, 136.3, 135.6, 134.4, 134.4, 134.2 (x 2), 133.5, 131.6, 128.6, 128.6, 128.0, 127.6 (x 2), 127.5, 121.9, 121.6, 116.9, 19.8, -1.3; **HRMS** (ESI, m/z) calcd for  $\text{C}_{25}\text{H}_{24}\text{N}_2\text{OSi} [\text{M} + \text{H}]^+$  397.1736, found 397.1739.

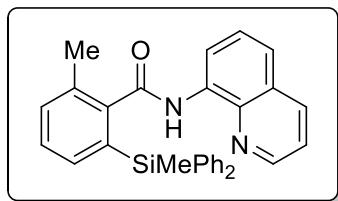
**Figure S10.** X-ray crystal structure of **3ag** (ellipsoid contour at 50% probability level)



**Crystal data and structure refinement for 3ag, CCDC No. 2054615**

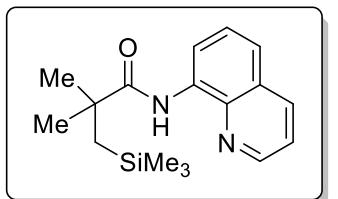
Empirical formula	C <sub>25</sub> H <sub>24</sub> N <sub>2</sub> OSi
Formula weight	396.55
Temperature/K	100.0
Crystal system	monoclinic
Space group	P2 <sub>1</sub> /c
a/Å	12.9104(3)
b/Å	11.5100(3)
c/Å	15.1097(4)
α/°	90
β/°	114.9740(10)
γ/°	90
Volume/Å <sup>3</sup>	2035.35(9)
Z	4
ρ <sub>calcg/cm<sup>3</sup></sub>	1.294
μ/mm <sup>-1</sup>	1.156
F(000)	840.0
Crystal size/mm <sup>3</sup>	0.25 × 0.18 × 0.12
Radiation	Cu Kα (λ = 1.54178)
2Θ range for data collection/°	7.554 to 127.608
Index ranges	-15 ≤ h ≤ 14, -13 ≤ k ≤ 13, -13 ≤ l ≤ 17
Reflections collected	15965
Independent reflections	3297 [R <sub>int</sub> = 0.0730, R <sub>sigma</sub> = 0.0568]
Data/restraints/parameters	3297/0/265
Goodness-of-fit on F <sup>2</sup>	1.061
Final R indexes [I>=2σ (I)]	R <sub>1</sub> = 0.0603, wR <sub>2</sub> = 0.1655
Final R indexes [all data]	R <sub>1</sub> = 0.0652, wR <sub>2</sub> = 0.1707
Largest diff. peak/hole / e Å <sup>-3</sup>	0.37/-0.62

**2-methyl-6-(methyldiphenylsilyl)-N-(quinolin-8-yl)benzamide (3ah):**



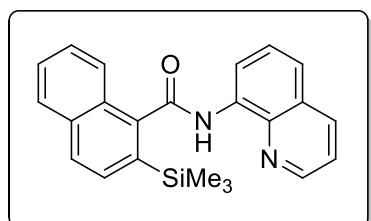
**Yield** 47% (42.9 mg); colorless solid; **R<sub>f</sub>** 0.30 (pet ether/ethyl acetate = 9:1); **eluent composition** petroleum ether/ethyl acetate = 19:1; **mp** 160-162 °C; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 9.58 (br s, 1H), 8.66-8.61 (m, 1H), 8.49 (dd, *J* = 4.0 Hz, 1.6 Hz, 1H), 8.11 (dd, *J* = 8.0 Hz, 1.6 Hz, 1H), 7.50-7.48 (comp, 2H), 7.43-7.41 (comp, 4H), 7.38-7.27 (comp, 4H), 7.15-7.08 (comp, 6H), 2.47 (s, 3H), 0.85 (s, 3H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 169.2, 147.8, 144.3, 138.2, 136.4, 136.3, 135.2 (x 4), 135.0, 134.7, 134.2, 133.6, 132.0, 129.0 (x 2), 128.5, 127.8, 127.7 (x 4), 127.4, 121.8, 121.3, 117.0, 19.9, -2.6; **HRMS** (ESI, m/z) calcd for C<sub>30</sub>H<sub>26</sub>N<sub>2</sub>OSi [M + H]<sup>+</sup> 459.1893, found 459.1896.

**2,2-dimethyl-N-(quinolin-8-yl)-3-(trimethylsilyl)propanamide (3ai):**



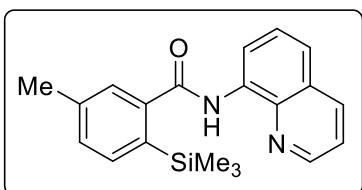
**Yield** 13% (8.0 mg); colorless oil; **R<sub>f</sub>** 0.30 (pet ether/ethyl acetate = 9:1); **eluent composition** petroleum ether/ethyl acetate = 19:1; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 10.27 (br s, 1H), 8.82 (dd, *J* = 4.0 Hz, *J* = 1.6 Hz, 1H), 8.79 (dd, *J* = 7.2 Hz, *J* = 1.6 Hz, 1H), 8.16 (dd, *J* = 8.0 Hz, *J* = 1.6 Hz, 1H), 7.54 (app t, *J* = 8.0 Hz, 1H), 7.48 (dd, *J* = 8.8 Hz, 1.2 Hz, 1H), 7.45 (dd, *J* = 8.0 Hz, 4.0 Hz, 1H), 1.47 (s, 6H), 1.20 (s, 2H), 0.03 (s, 9H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 177.5, 148.3, 138.9, 136.5, 134.9, 128.1, 127.7, 121.6, 121.3, 116.4, 43.0, 31.0, 29.1, 0.3; **HRMS** (ESI, m/z) calcd for C<sub>17</sub>H<sub>24</sub>N<sub>2</sub>OSi [M + H]<sup>+</sup> 301.1736, found 301.1738.

**N-(quinolin-8-yl)-2-(trimethylsilyl)-1-naphthamide (S3a):<sup>3</sup>**



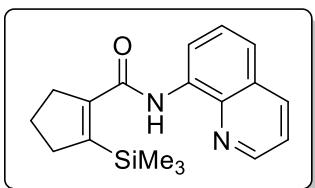
**Yield** 20% (14.9 mg); colorless solid; **R<sub>f</sub>** 0.40 (pet ether/ethyl acetate = 9:1); **eluent composition** petroleum ether/ethyl acetate = 19:1; **mp** 156-158 °C; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 10.20 (br s, 1H), 9.13 (app d, *J* = 7.6 Hz, 1H), 8.66 (app d, *J* = 2.8 Hz, 1H), 8.19 (app d, *J* = 7.6 Hz, 1H), 8.10 (app d, *J* = 8.0 Hz, 1H), 7.93 (app d, *J* = 8.4 Hz, 1H), 7.78 (app d, *J* = 7.6 Hz, 1H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.68 (app t, *J* = 8.0 Hz, 1H), 7.61 (d, *J* = 7.6 Hz, 1H), 7.54-7.46 (comp, 2H), 7.43 (dd, *J* = 8.4 Hz, 4.0 Hz, 1H), 0.36 (s, 9H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 169.6, 148.4, 142.0, 138.5, 136.5, 135.1, 134.7, 133.7, 130.5, 130.0, 128.4, 128.2, 128.1, 127.7, 127.1, 126.8, 125.4, 122.2, 121.8, 117.5, 0.0; **HRMS** (ESI, m/z) calcd for C<sub>23</sub>H<sub>22</sub>N<sub>2</sub>OSi [M + H]<sup>+</sup> 371.1580, found 371.1574.

**N-(quinolin-8-yl)-2-(trimethylsilyl)benzamide (S3b):<sup>3</sup>**



**Yield** 14% (9.3 mg); colorless solid; **R<sub>f</sub>** 0.30 (pet ether/ethyl acetate = 9:1); **eluent composition** petroleum ether/ethyl acetate = 19:1; **mp** 110-112 °C; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 10.26 (br s, 1H), 8.94 (dd, *J* = 7.2 Hz, 1.6 Hz, 1H), 8.80 (dd, *J* = 4.4 Hz, 1.6 Hz, 1H), 8.20 (dd, *J* = 8.4 Hz, 1.6 Hz, 1H), 7.63-7.59 (comp, 2H), 7.57-7.54 (comp, 2H), 7.47 (dd, *J* = 8.0 Hz, 4.0 Hz, 1H), 7.32 (dd, *J* = 7.6 Hz, 0.8 Hz, 1H), 2.45 (s, 3H), 0.33 (s, 9H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 169.7, 148.3, 143.1, 139.1, 138.7, 136.6, 136.4, 135.7, 135.0, 130.6, 128.2, 127.7, 127.3, 121.8, 121.8, 116.8, 21.5, 0.3; **HRMS** (ESI, m/z) calcd for C<sub>20</sub>H<sub>22</sub>N<sub>2</sub>OSi [M + H]<sup>+</sup> 335.1580, found 335.1590.

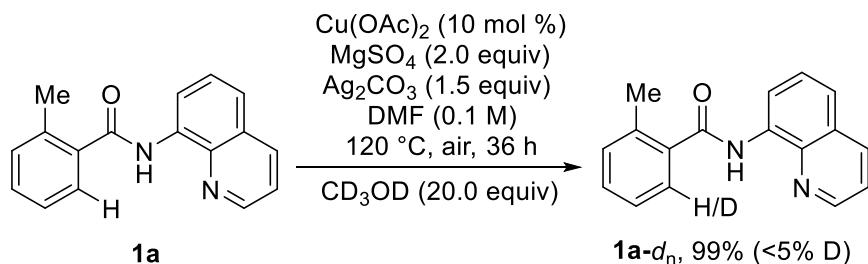
**N-(quinolin-8-yl)-2-(trimethylsilyl)cyclopent-1-ene-1-carboxamide (S3c):<sup>4</sup>**



**Yield** 12% (7.4 mg); colorless solid; **R<sub>f</sub>** 0.40 (pet ether/ethyl acetate = 9:1); **eluent composition** petroleum ether/ethyl acetate = 19:1; **mp** 122-124 °C; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 10.02 (br s, 1H), 8.85 (dd, *J* = 7.6 Hz, *J* = 1.6 Hz, 1H), 8.81 (dd, *J* = 4.4 Hz, *J* = 1.6 Hz, 1H), 8.17 (dd, *J* = 8.4 Hz, *J* = 1.6 Hz, 1H), 7.56 (app t, *J* = 8.0 Hz, 1H), 7.51 (dd, *J* = 8.0 Hz, 1.6 Hz, 1H), 7.46 (dd, *J* = 8.4 Hz, 4.4 Hz, 1H), 2.98-2.92 (m, 2H), 2.69-2.64 (m, 2H), 2.05-1.98 (m, 2H), 0.22 (s, 9H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 165.7, 155.0, 148.2, 147.2, 138.5, 136.7, 134.8, 128.2, 127.7, 121.7, 121.5, 117.0, 39.8, 36.0, 24.1, -0.7; **HRMS** (ESI, m/z) calcd for C<sub>18</sub>H<sub>22</sub>N<sub>2</sub>OSi [M + H]<sup>+</sup> 311.1580, found 311.1589.

**Mechanistic experiments:**

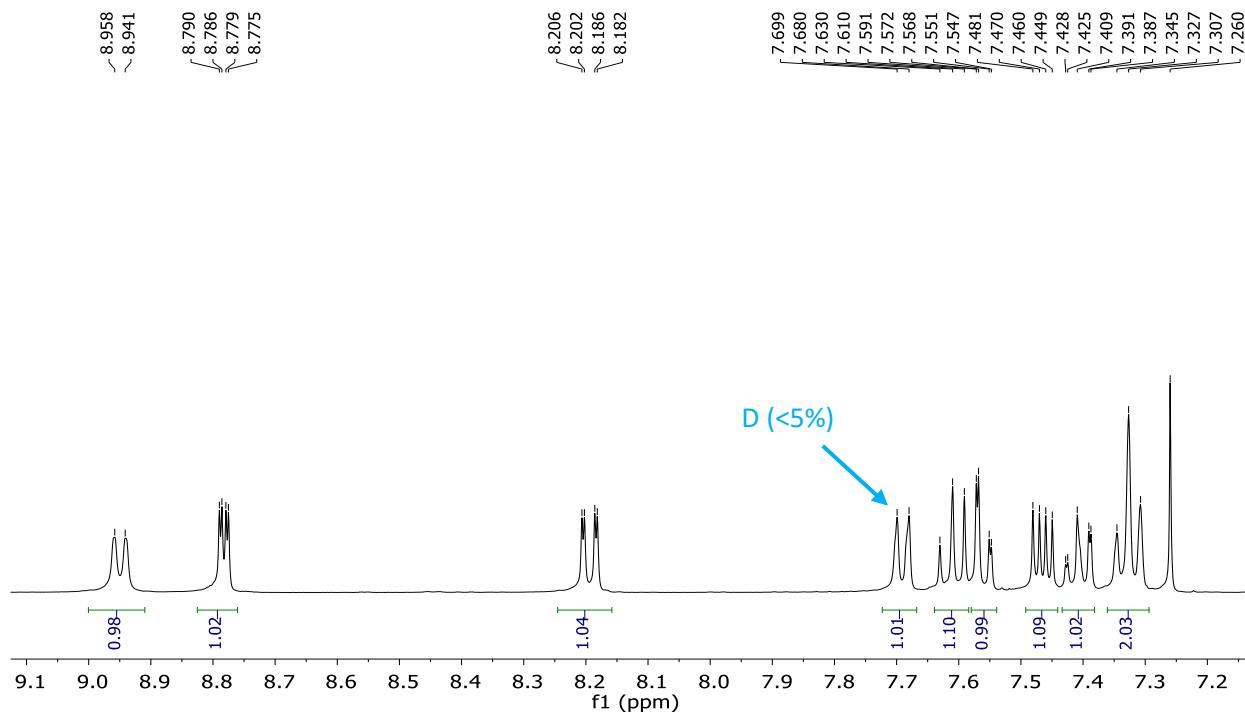
**(a) Procedure for H/D exchange experiment (with 1a):**



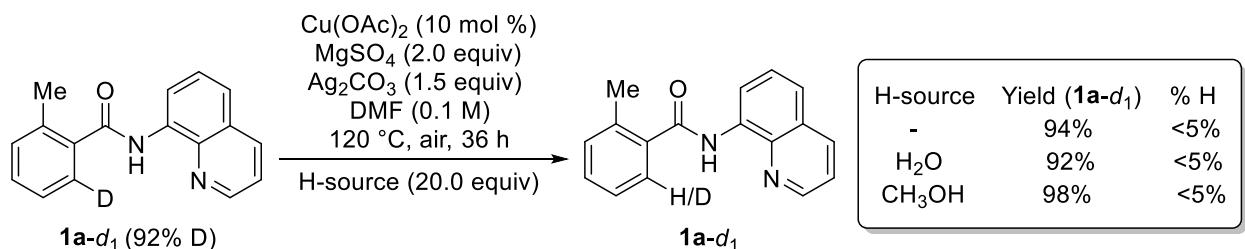
An oven dried 10 mL schlenk tube was charged with 2-methyl-N-(quinolin-8-yl)benzamide (**1a**) (52.5 mg, 0.2 mmol, 1.0 equiv) Cu(OAc)<sub>2</sub> (3.6 mg, 0.02 mmol, 0.1 equiv), MgSO<sub>4</sub> (48.2 mg, 0.4

mmol, 2.0 equiv),  $\text{Ag}_2\text{CO}_3$  (82.8 mg, 0.3 mmol, 1.5 equiv). Then  $\text{CD}_3\text{OD}$  (0.16 mL, 4.0 mmol, 20.0 equiv) and 2.0 mL (0.1 M) of anhydrous DMF was added. The tube was closed with a teflon-lined cap and kept on stirring in an oil bath. The bath temperature was slowly increased to 120 °C. After 36 h, the reaction was stopped and cooled to room temperature. The reaction mixture was filtered through a short pad of celite, poured to water (20 mL) and extracted with ethyl acetate ( $3 \times 5$  mL). The combined organic layers were washed with brine solution ( $2 \times 5$  mL). The organic phase was separated, dried over anhydrous  $\text{Na}_2\text{SO}_4$ , filtered and concentrated under vacuo. The starting material (**1a-d<sub>n</sub>**) was recovered (51.7 mg, 99%) by purifying through column chromatography on silica gel using ethyl acetate/pet ether as eluent. The deuterium incorporation (<5%) was determined by  $^1\text{H}$  NMR spectroscopy.

**$^1\text{H}$  NMR of **1a-d<sub>n</sub>** (400 MHz,  $\text{CDCl}_3$ ):**

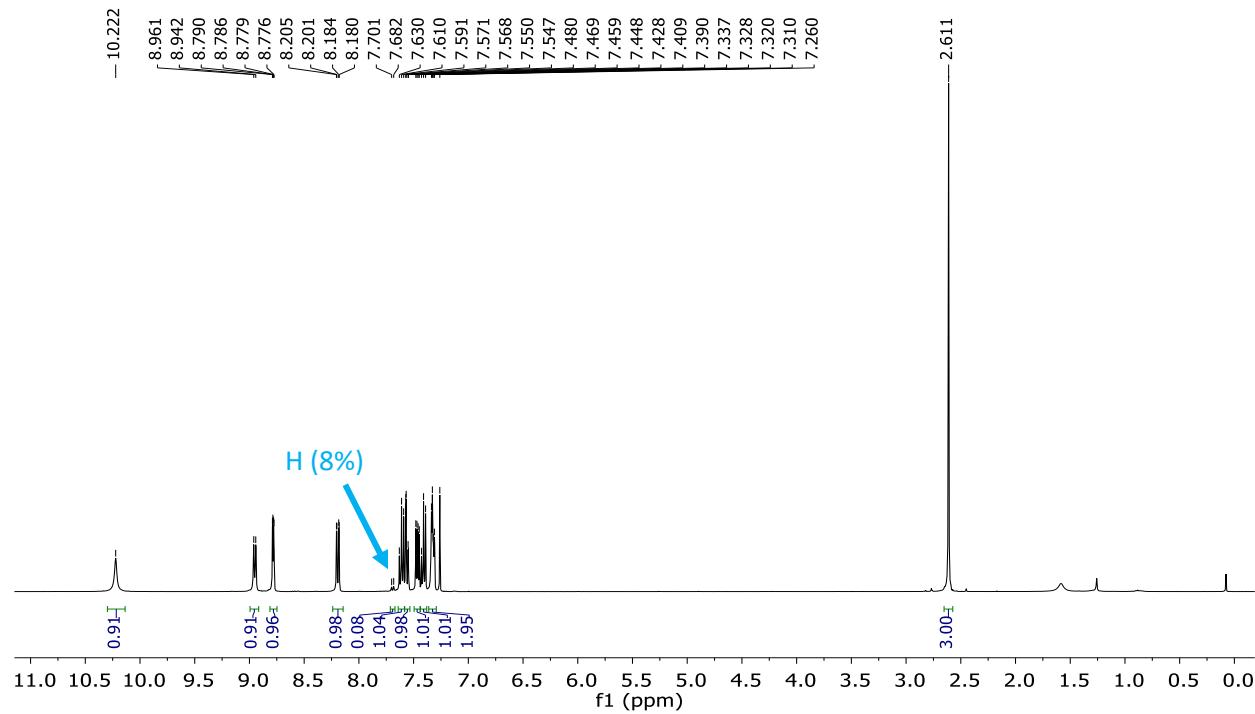


**Procedure for H/D exchange experiment (with **1a-d<sub>1</sub>**):**

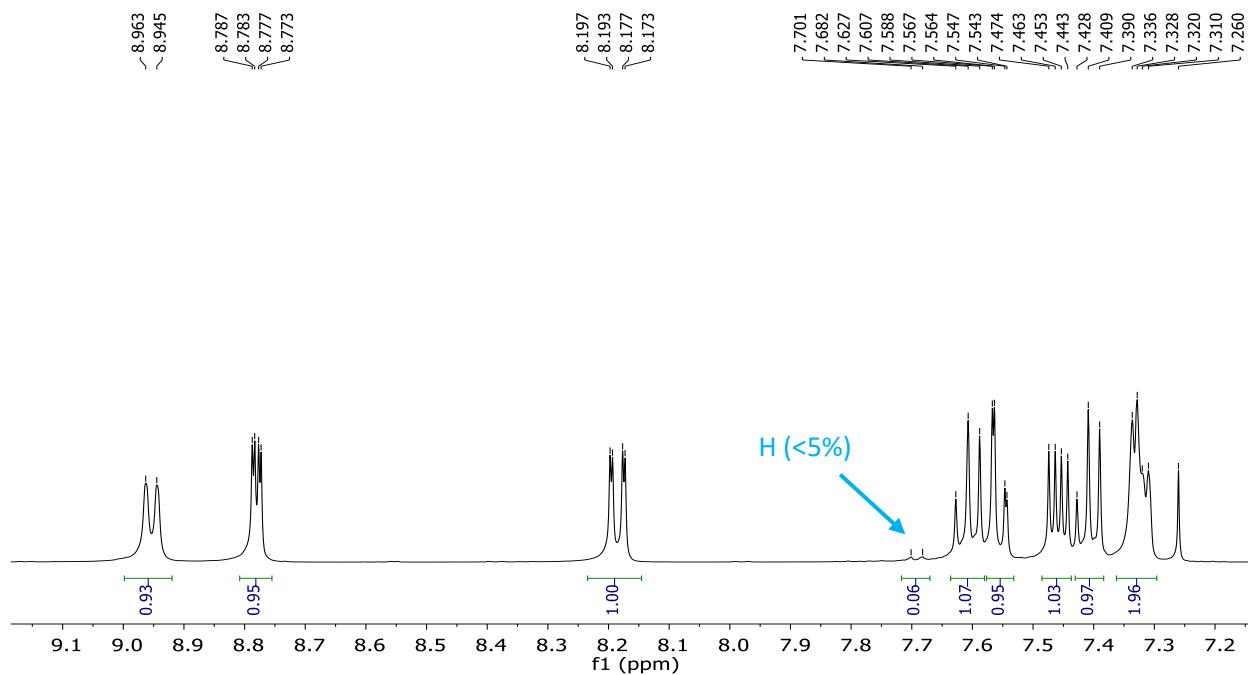


An oven dried 10 mL schlenk tube was charged with 2-methyl-*N*-(quinolin-8-yl)benzamide-6-*d* (**1a-d<sub>1</sub>**, 92% D) (52.5 mg, 0.2 mmol, 1.0 equiv) Cu(OAc)<sub>2</sub> (3.6 mg, 0.02 mmol, 0.1 equiv), MgSO<sub>4</sub> (48.2 mg, 0.4 mmol, 2.0 equiv), Ag<sub>2</sub>CO<sub>3</sub> (82.8 mg, 0.3 mmol, 1.5 equiv). Then a H-source (4.0 mmol, 20.0 equiv) and 2.0 mL (0.1 M) of anhydrous DMF was added. The tube was closed with a teflon-lined cap and kept on stirring in an oil bath. The bath temperature was slowly increased to 120 °C. After 36 h, the reaction was stopped and cooled to room temperature. The reaction mixture was filtered through a short pad of celite, poured to water (20 mL) and extracted with ethyl acetate (3 x 5 mL). The combined organic layers were washed with brine solution (2 x 5 mL). The organic phase was separated, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under vacuo. The starting material (**1a-d<sub>1</sub>**) was recovered by purifying through column chromatography on silica gel using ethyl acetate/pet ether as eluent. The hydrogen incorporation was determined by <sup>1</sup>H NMR spectroscopy.

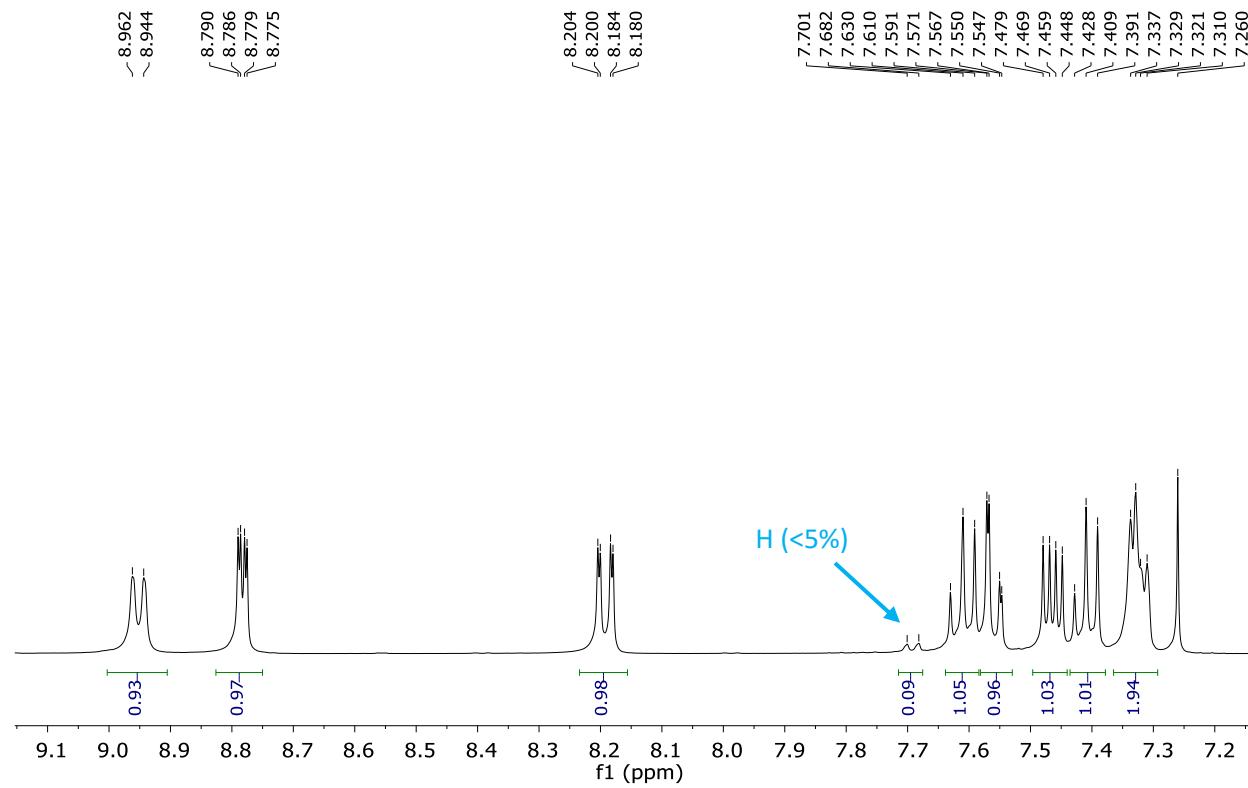
**<sup>1</sup>H NMR of **1a-d<sub>1</sub>** (92% D) (400 MHz, CDCl<sub>3</sub>): (deuterated starting material)**



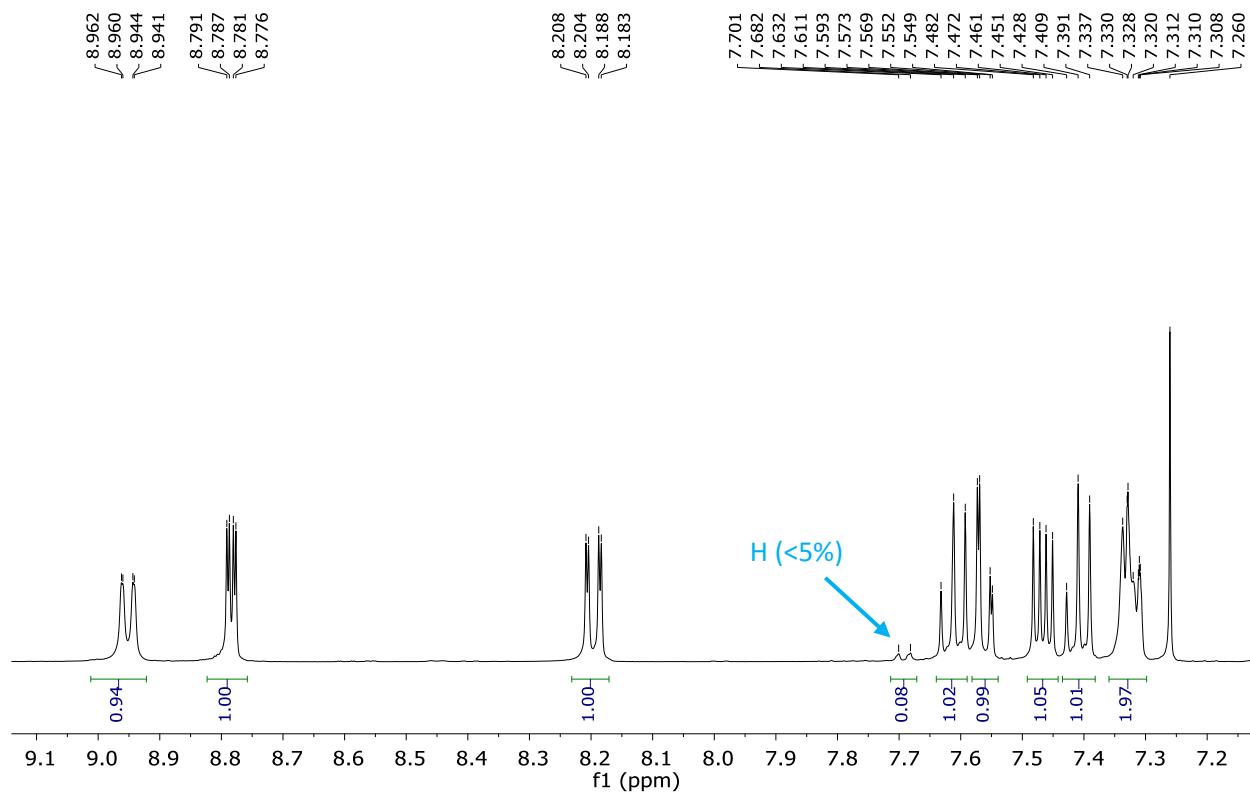
**<sup>1</sup>H NMR of 1a-d<sub>1</sub> (400 MHz, CDCl<sub>3</sub>): (without any external H-source)**



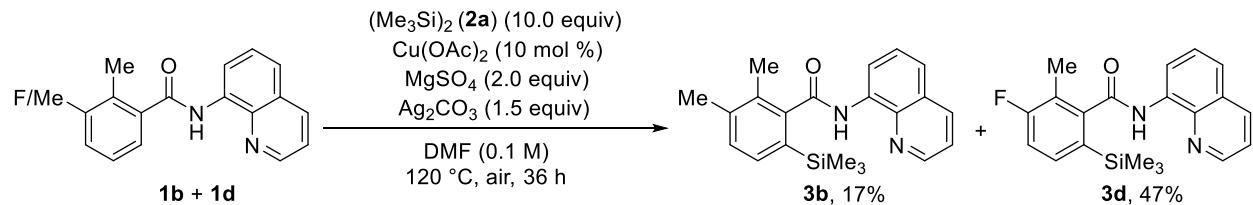
**<sup>1</sup>H NMR of 1a-d<sub>1</sub> (400 MHz, CDCl<sub>3</sub>): (H<sub>2</sub>O as H-source)**



**<sup>1</sup>H NMR** of **1a-d<sub>1</sub>** (400 MHz, CDCl<sub>3</sub>): (CH<sub>3</sub>OH as H-source)

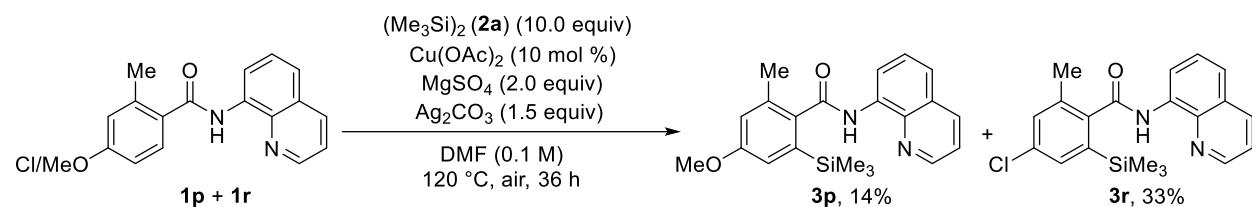


**(b) Procedure for competitive experiment between **1b** and **1d**:**



To an oven dried 10 mL schlenk tube a mixture of **1b** and **1d** (0.1 mmol each) were subjected under standard condition. After 36 h, the reaction was stopped and cooled to room temperature. The reaction mixture was filtered through a short pad of celite and concentrated under vacuo. The crude reaction mixture was directly purified by column chromatography on silica gel using pet ether/ethyl acetate as eluent to obtain pure **3b** and **3d** in 17% and 47% yields respectively.

**(c) Procedure for competitive experiment between **1p** and **1r**:**



To an oven dried 10 mL schlenk tube a mixture of **1p** and **1r** (0.1 mmol each) were subjected under standard condition. After 36 h, the reaction was stopped and cooled to room temperature. The reaction mixture was filtered through a short pad of celite and concentrated under vacuo. The crude reaction mixture was directly purified by column chromatography on silica gel using pet ether/ethyl acetate as eluent to obtain pure **3p** and **3r** in 14% and 33% yields respectively.

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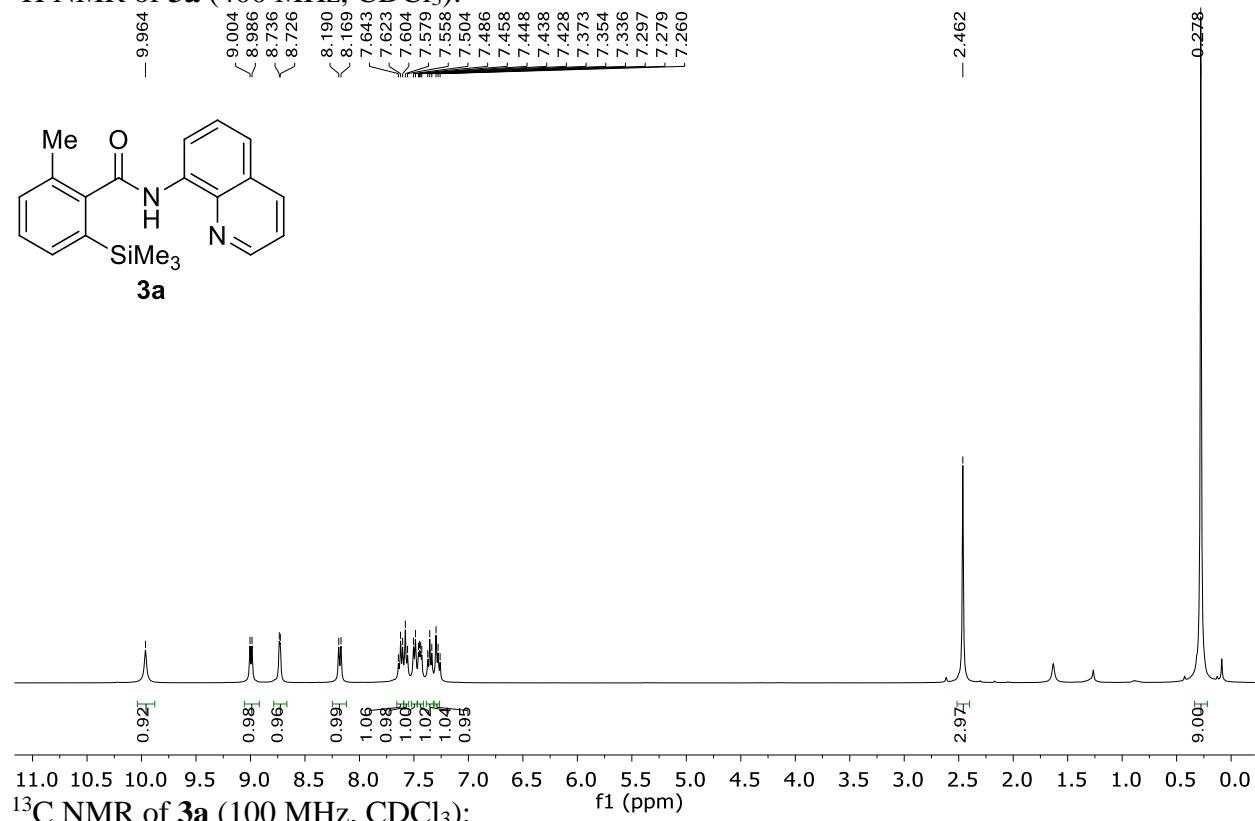
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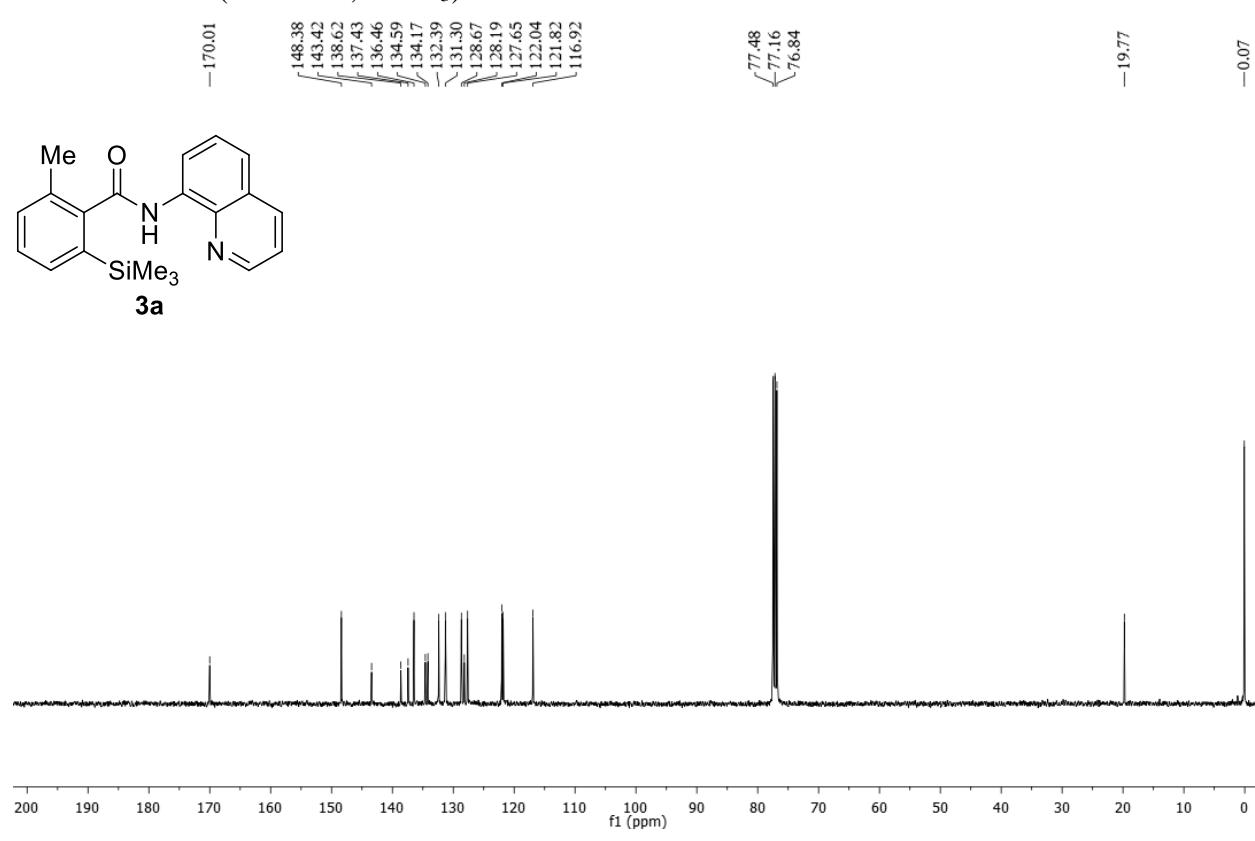
7. (a) Mishra, A.; Vats, T. K.; Nair, M. P.; Das, A.; Deb, I. Rhodium-Catalyzed sp<sup>2</sup> C-H Acetoxylation of *N*-Aryl Azaindoles/*N*-Heteroaryl Indolines. *J. Org. Chem.* **2017**, *82*, 12406-12415. (b) Mishra, A.; Mukherjee, U.; Vats, T. K.; Deb, I. Ir(III)/MPAA-Catalyzed Mild and Selective C-H Amidation of *N*-Sulfonyl Ketimines: Access To Benzosultam-Fused Quinazolines/Quinazolinones. *J. Org. Chem.* **2018**, *83*, 3756-3767. (c) Mishra, A.; Mukherjee, U.; Sarkar, W.; Meduri, S. L.; Bhowmik, A.; Deb, I. Diastereoselective Spirocyclization of Cyclic *N*-Sulfonyl Ketimines with Nitroalkenes via Iridium-Catalyzed Redox-Neutral Cascade Reaction. *Org. Lett.* **2019**, *21*, 2056-2059. (d) Mishra, A.; Bhowmik, A.; Samanta, S.; Sarkar, W.; Das, S.; Deb, I. Diastereoselective Spirocyclization of Benzoxazines with Nitroalkenes via Rhodium-Catalyzed C-H Functionalization/Annulation Cascade under Mild Conditions. *Org. Lett.* **2020**, *22*, 1340-1344.

**<sup>1</sup>H and <sup>13</sup>C NMR spectra of compounds:**

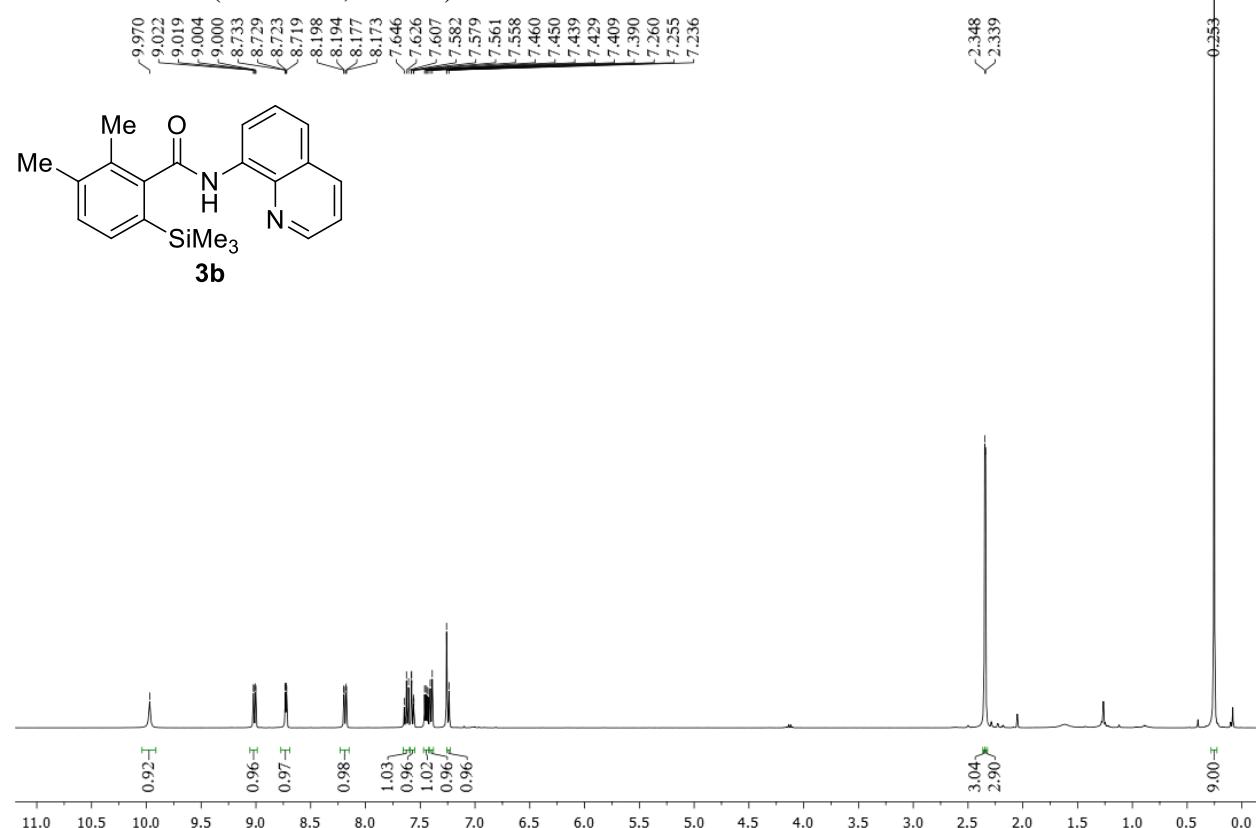
<sup>1</sup>H NMR of **3a** (400 MHz, CDCl<sub>3</sub>):



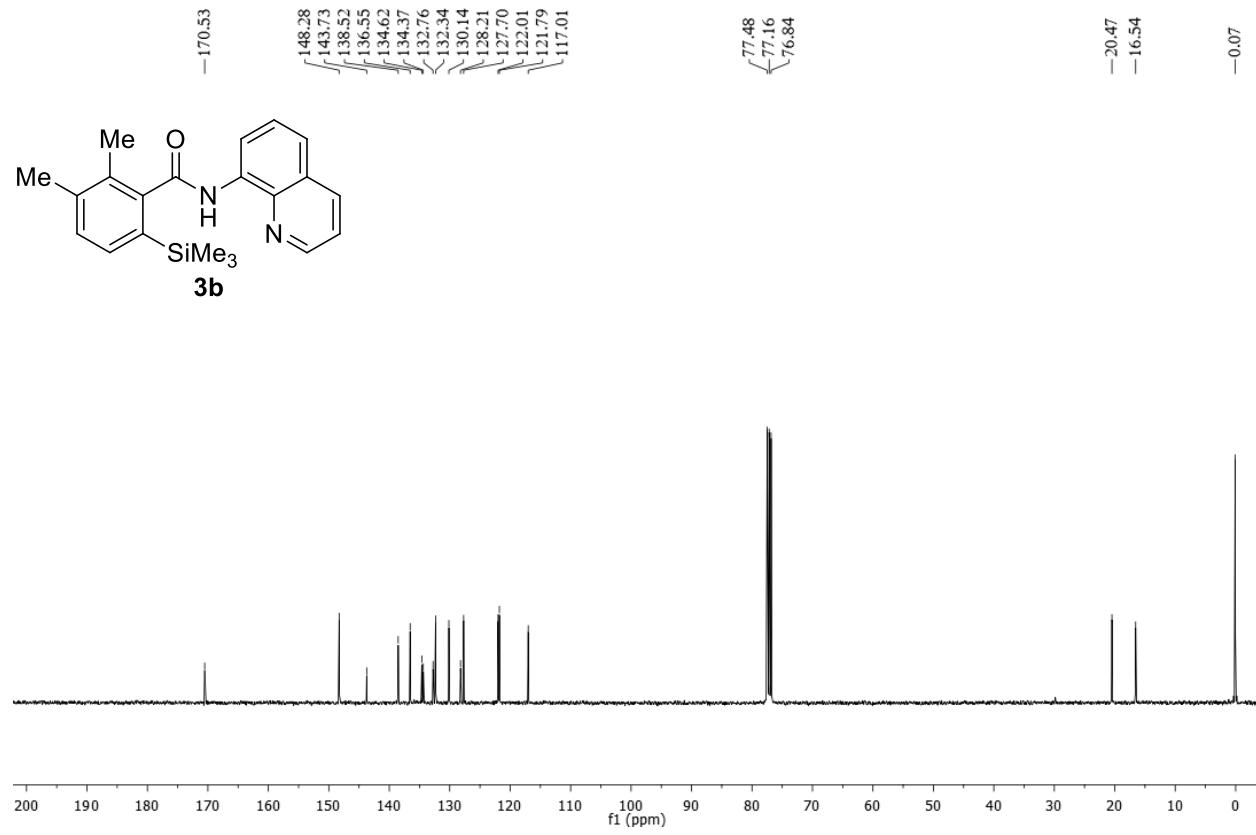
<sup>13</sup>C NMR of **3a** (100 MHz, CDCl<sub>3</sub>):



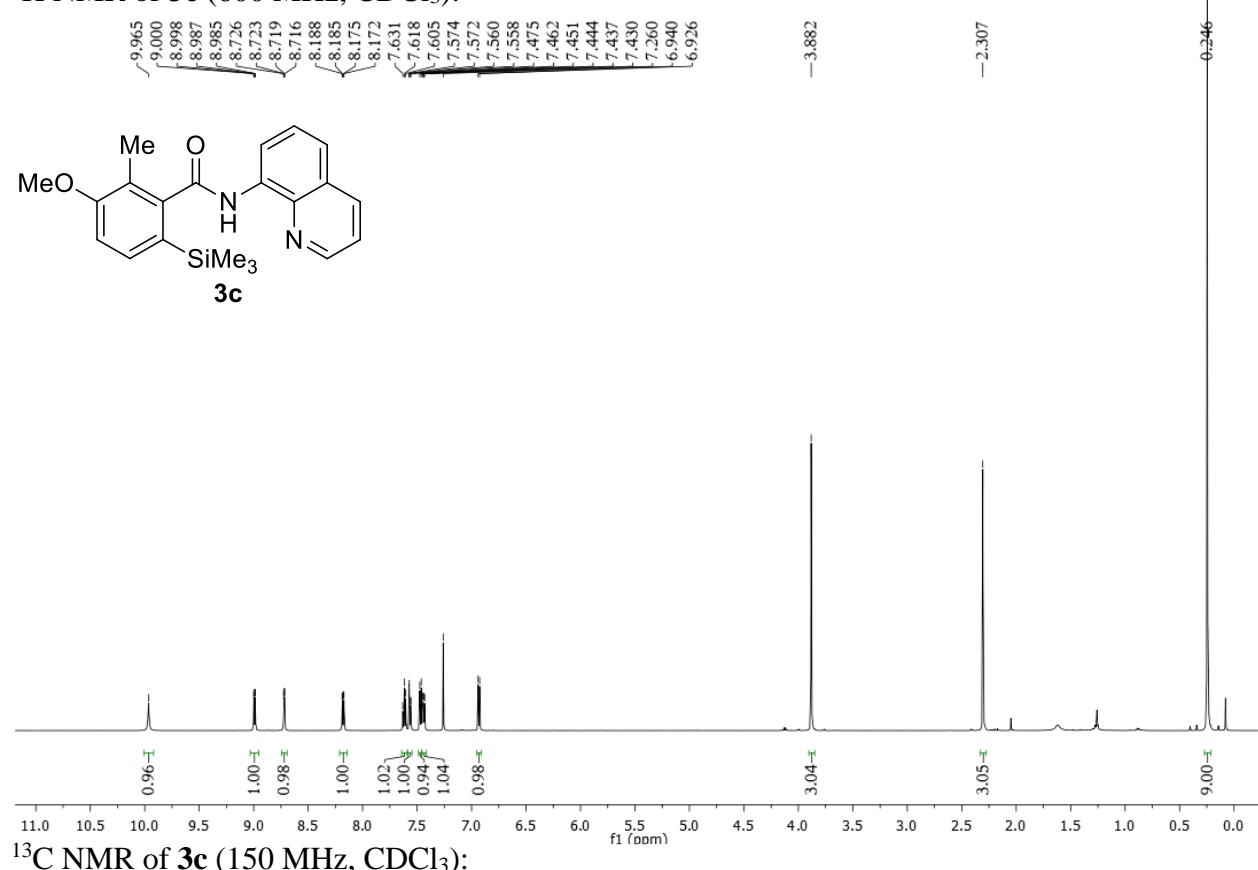
<sup>1</sup>H NMR of **3b** (400 MHz, CDCl<sub>3</sub>):



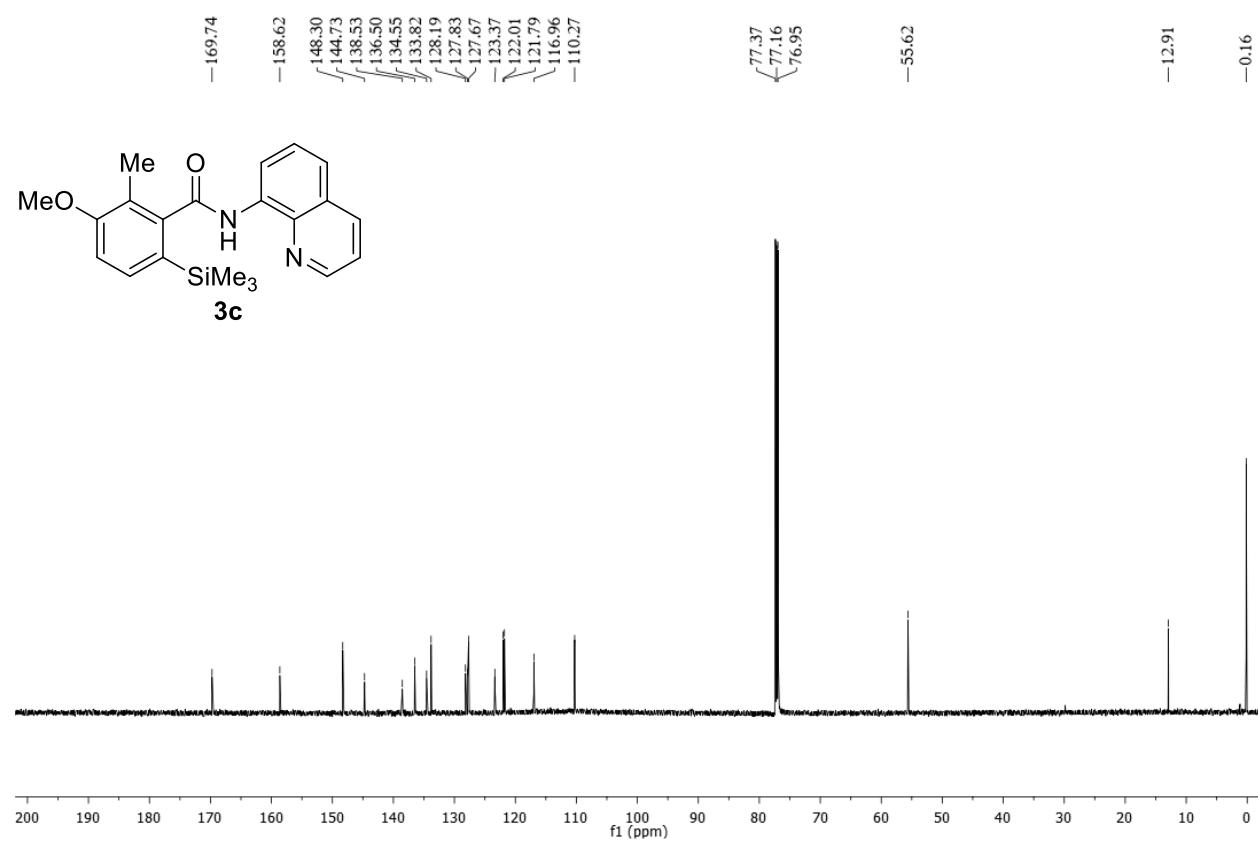
<sup>13</sup>C NMR of **3b** (100 MHz, CDCl<sub>3</sub>):



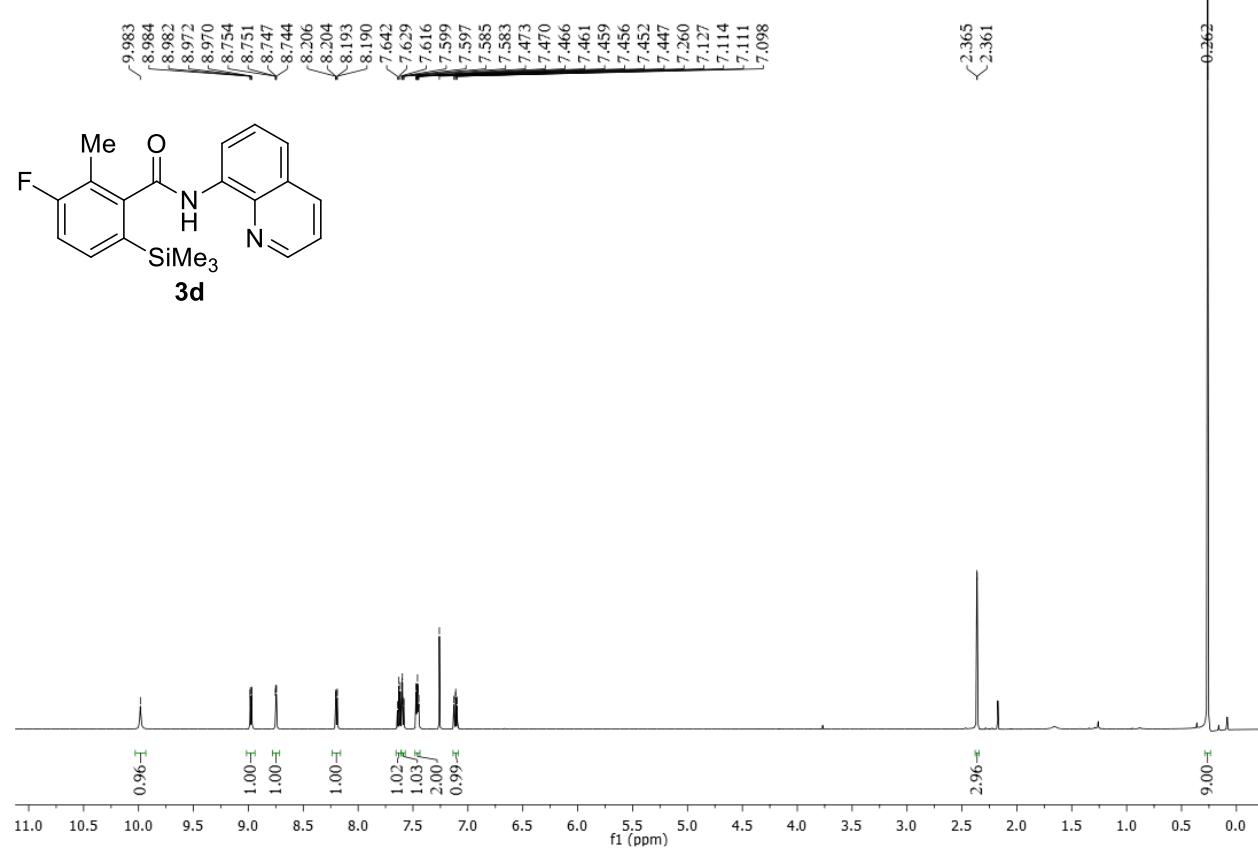
<sup>1</sup>H NMR of **3c** (600 MHz, CDCl<sub>3</sub>):



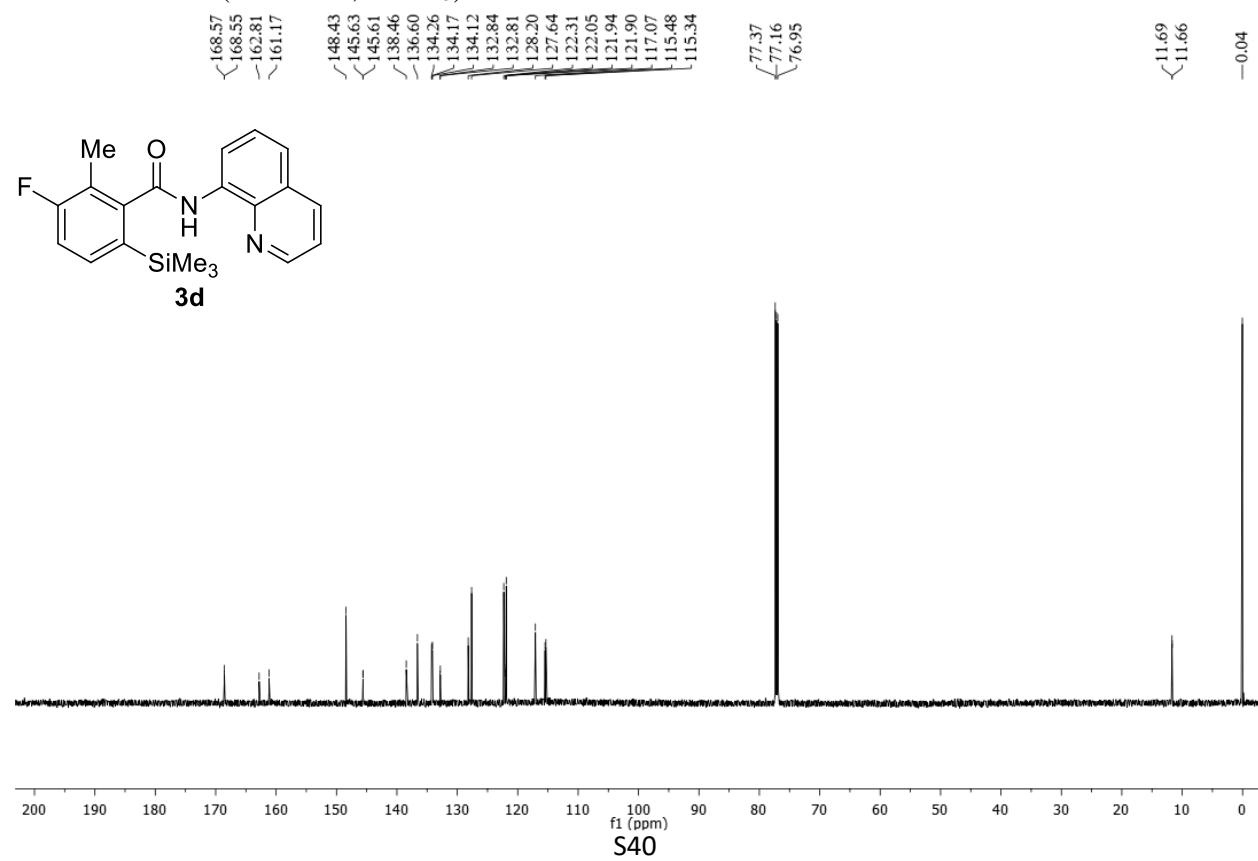
<sup>13</sup>C NMR of **3c** (150 MHz, CDCl<sub>3</sub>):



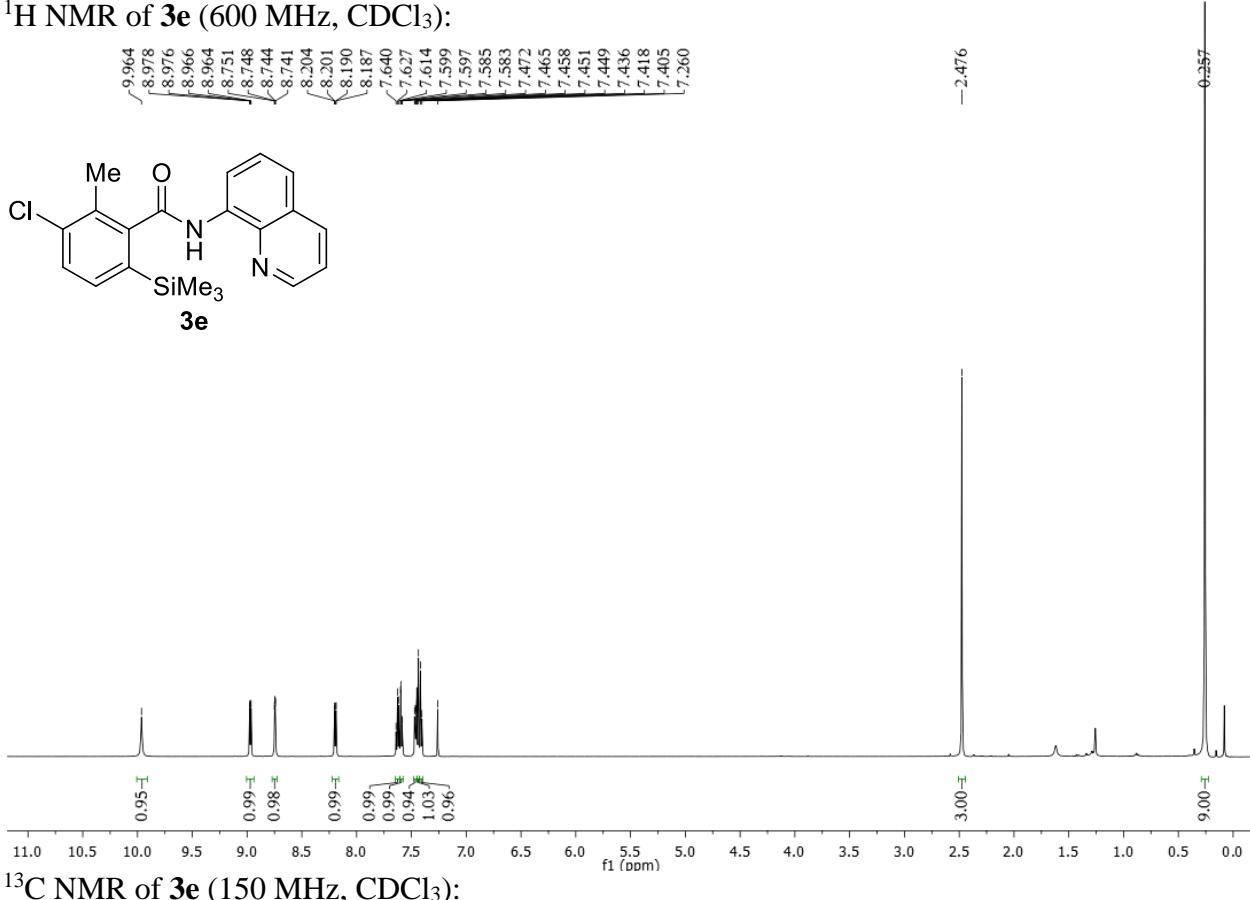
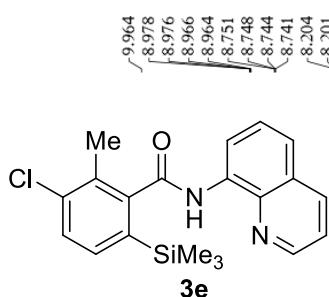
<sup>1</sup>H NMR of **3d** (600 MHz, CDCl<sub>3</sub>):



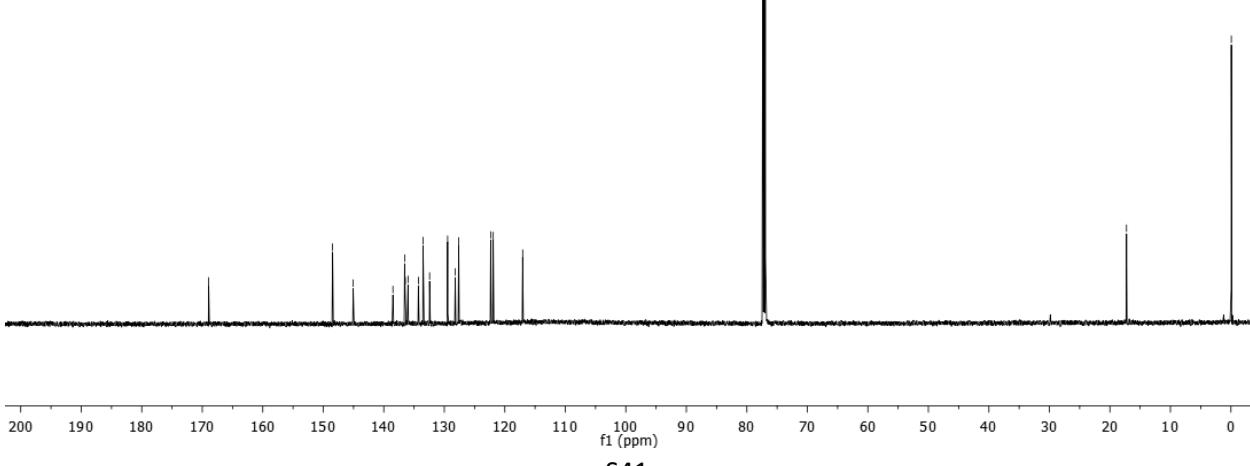
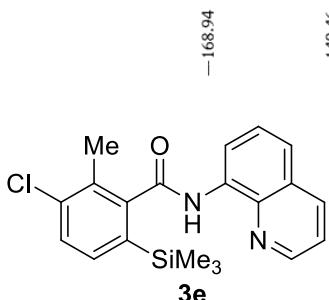
<sup>13</sup>C NMR of **3d** (150 MHz, CDCl<sub>3</sub>):



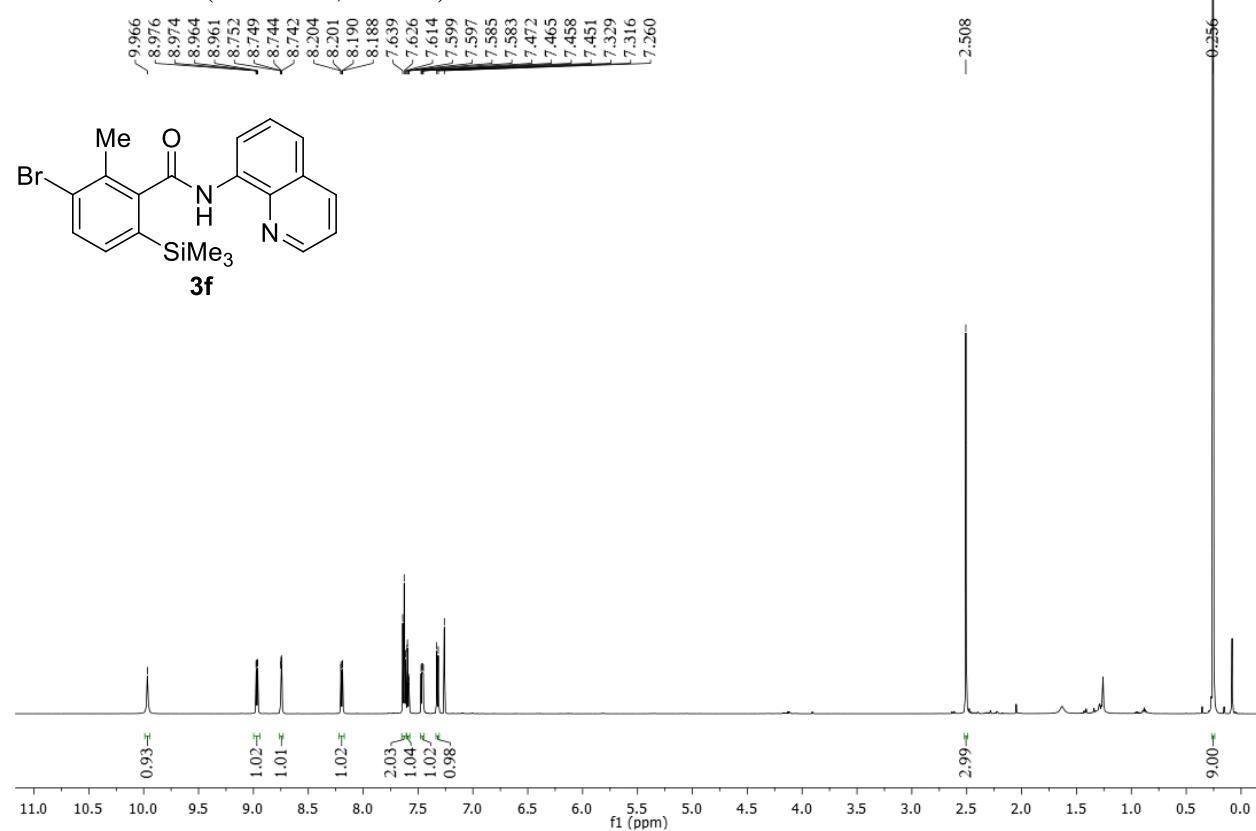
<sup>1</sup>H NMR of **3e** (600 MHz, CDCl<sub>3</sub>):



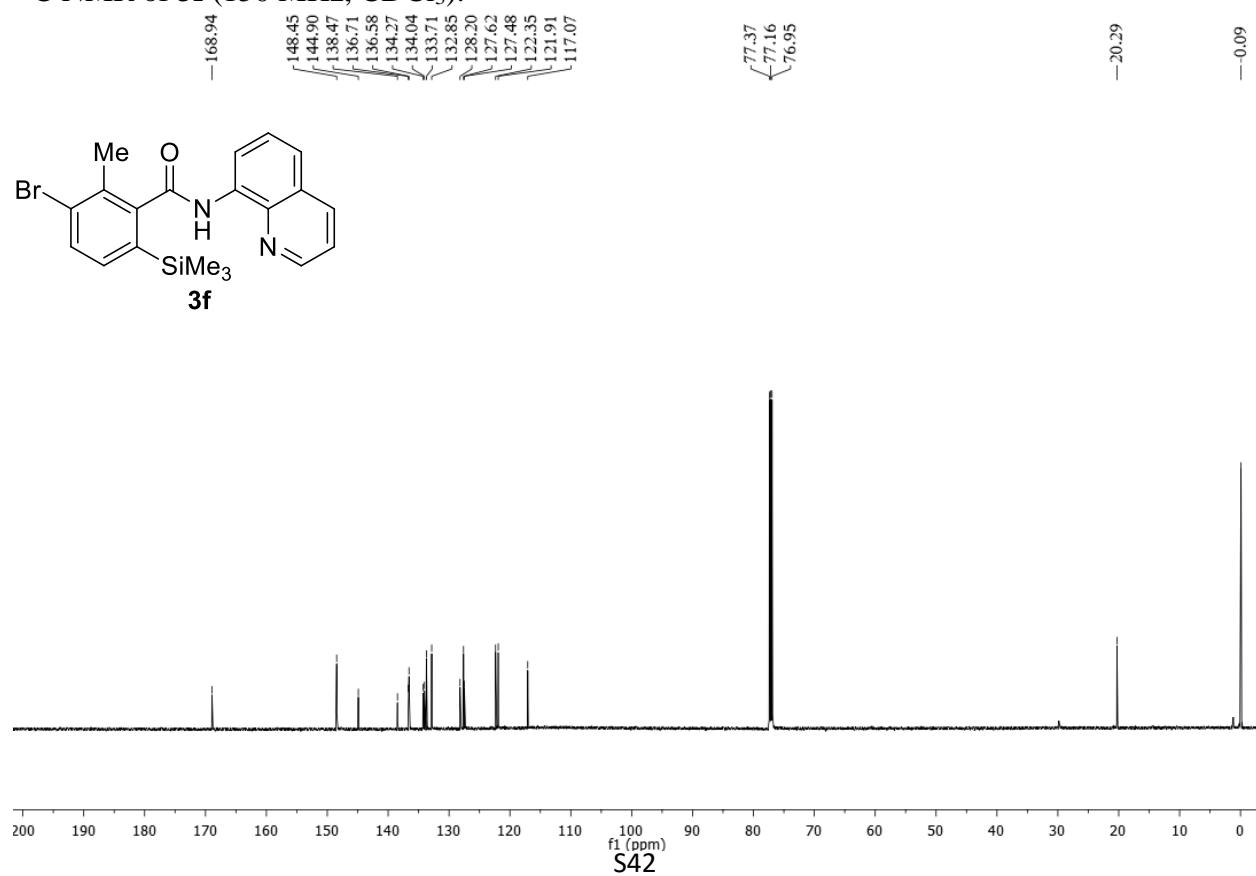
<sup>13</sup>C NMR of **3e** (150 MHz, CDCl<sub>3</sub>):



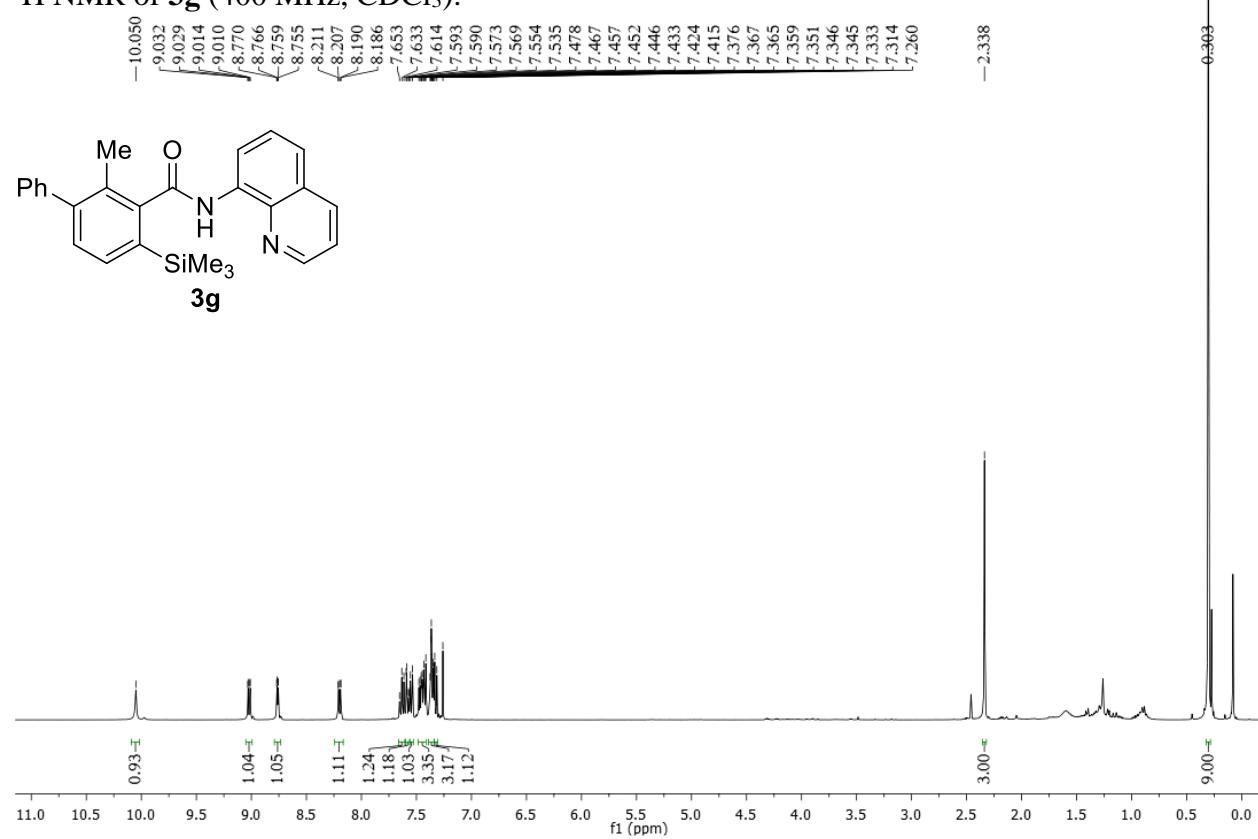
<sup>1</sup>H NMR of **3f** (600 MHz, CDCl<sub>3</sub>):



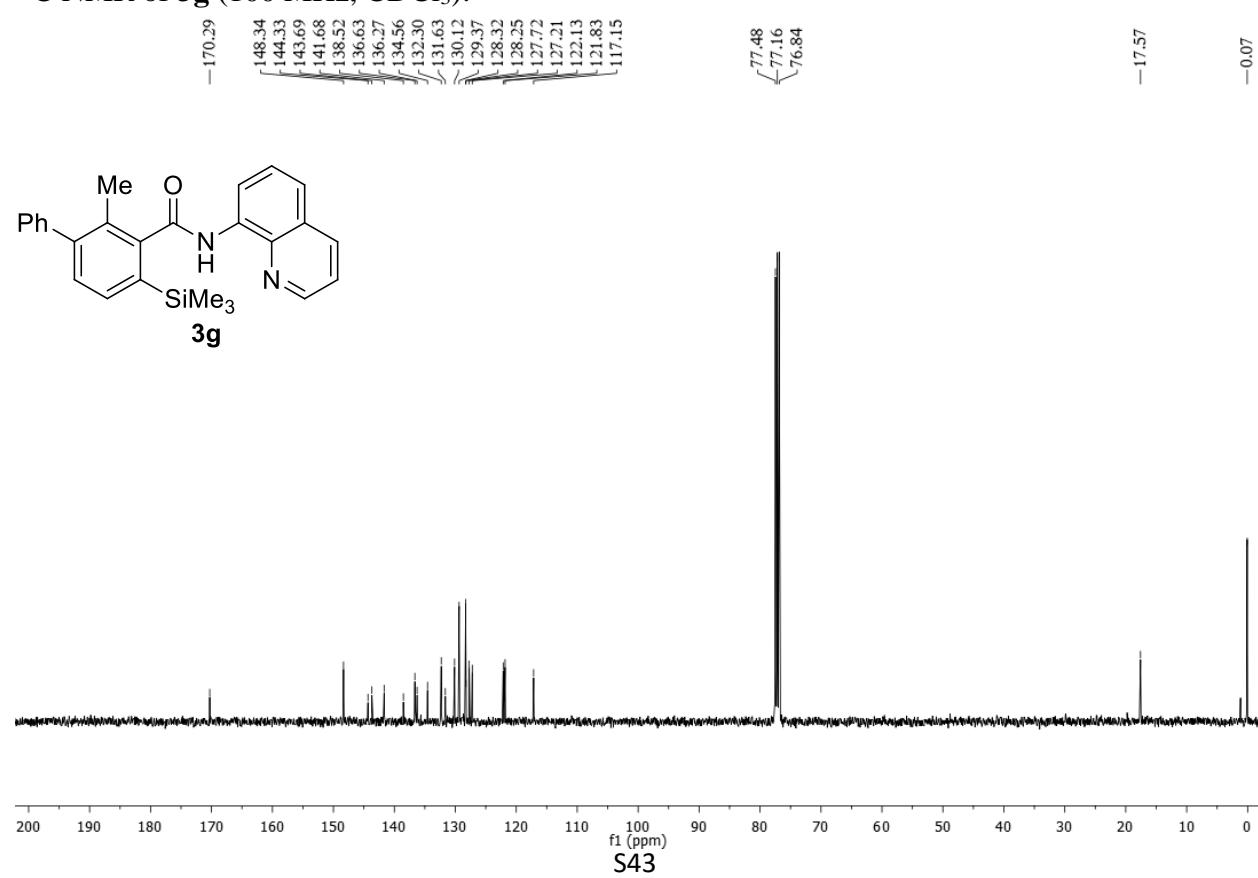
<sup>13</sup>C NMR of **3f** (150 MHz, CDCl<sub>3</sub>):



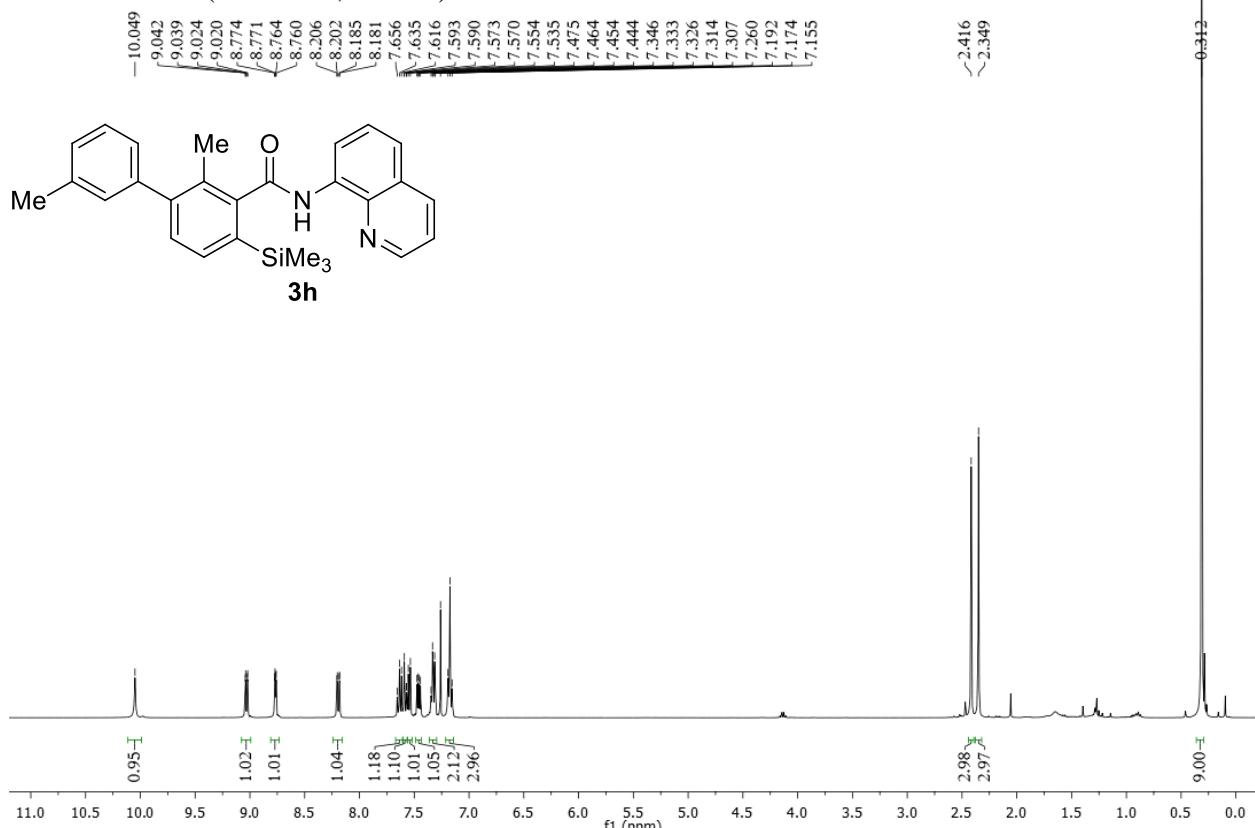
<sup>1</sup>H NMR of **3g** (400 MHz, CDCl<sub>3</sub>):



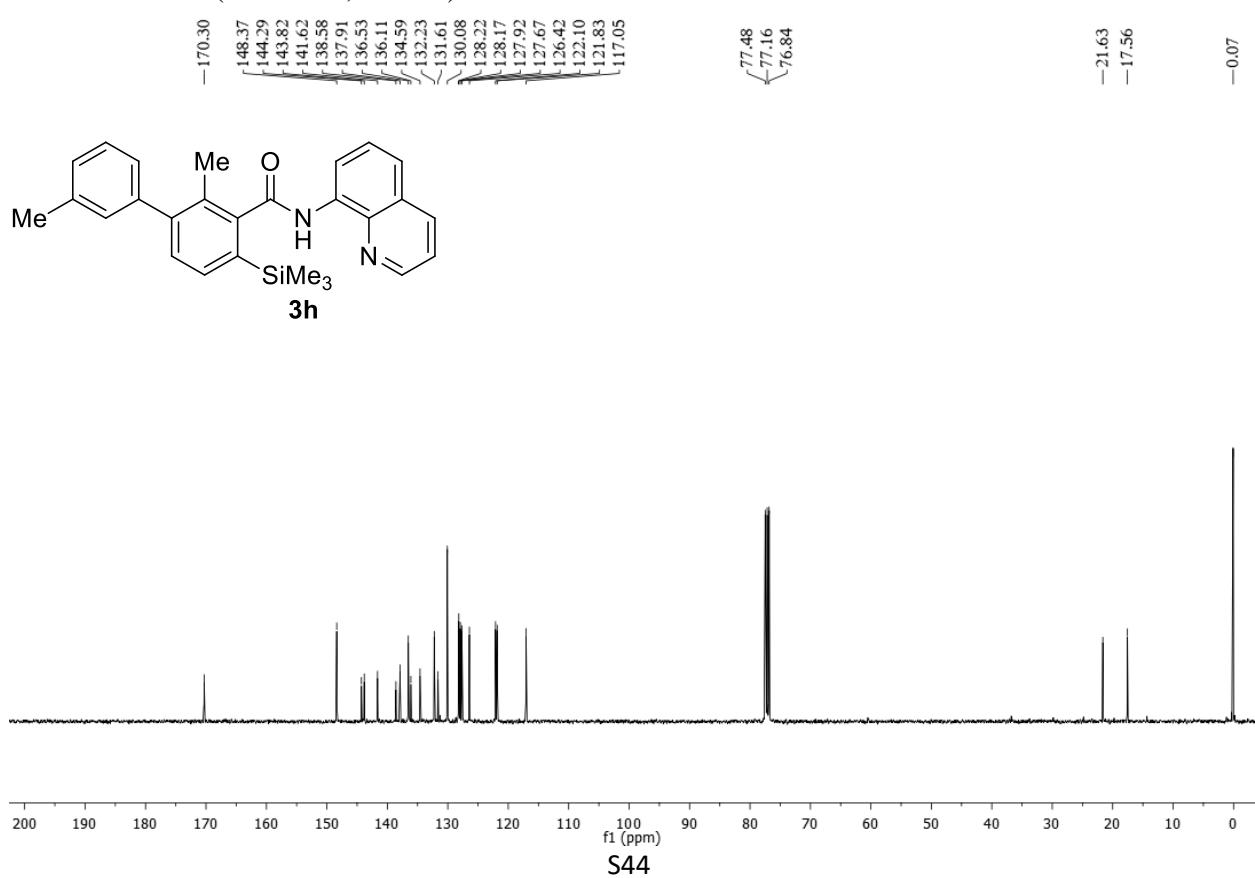
<sup>13</sup>C NMR of **3g** (100 MHz, CDCl<sub>3</sub>):



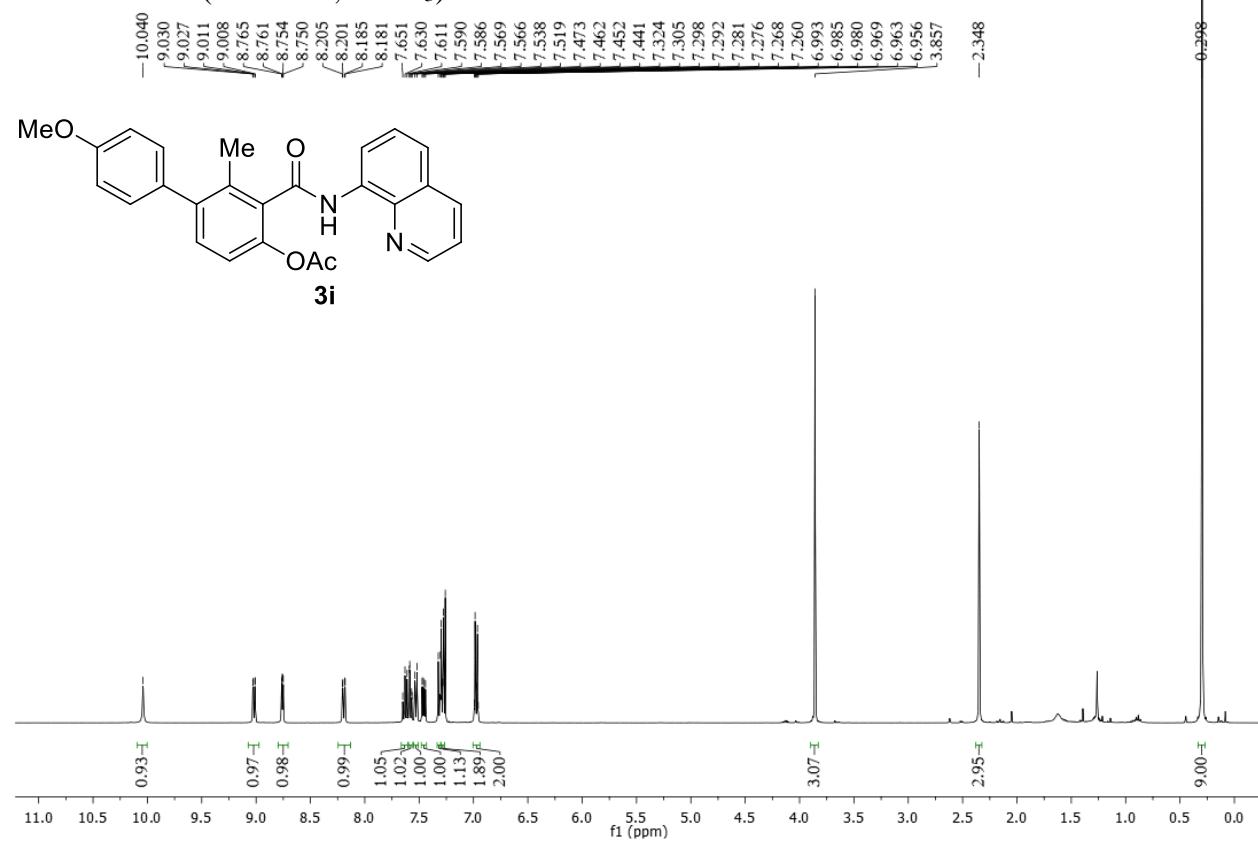
<sup>1</sup>H NMR of **3h** (400 MHz, CDCl<sub>3</sub>):



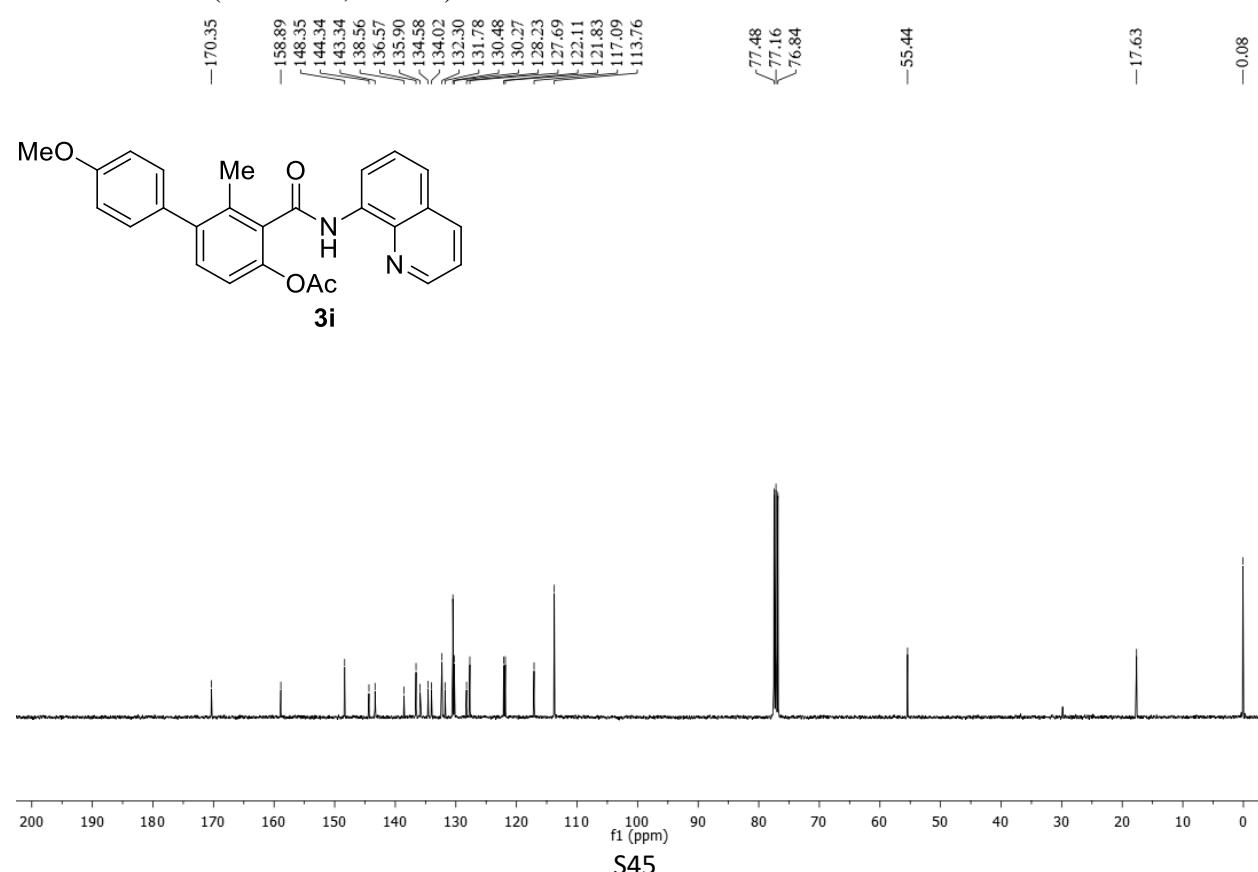
<sup>13</sup>C NMR of **3h** (100 MHz, CDCl<sub>3</sub>):



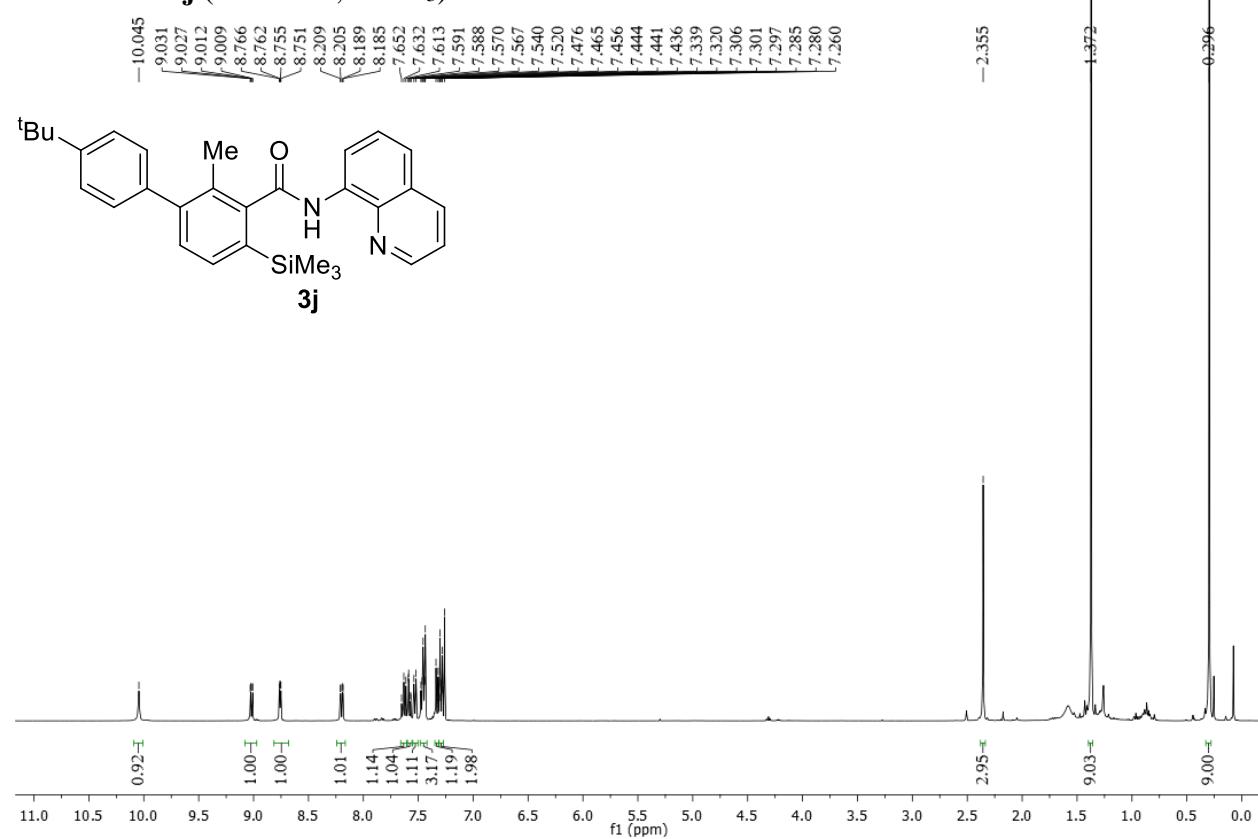
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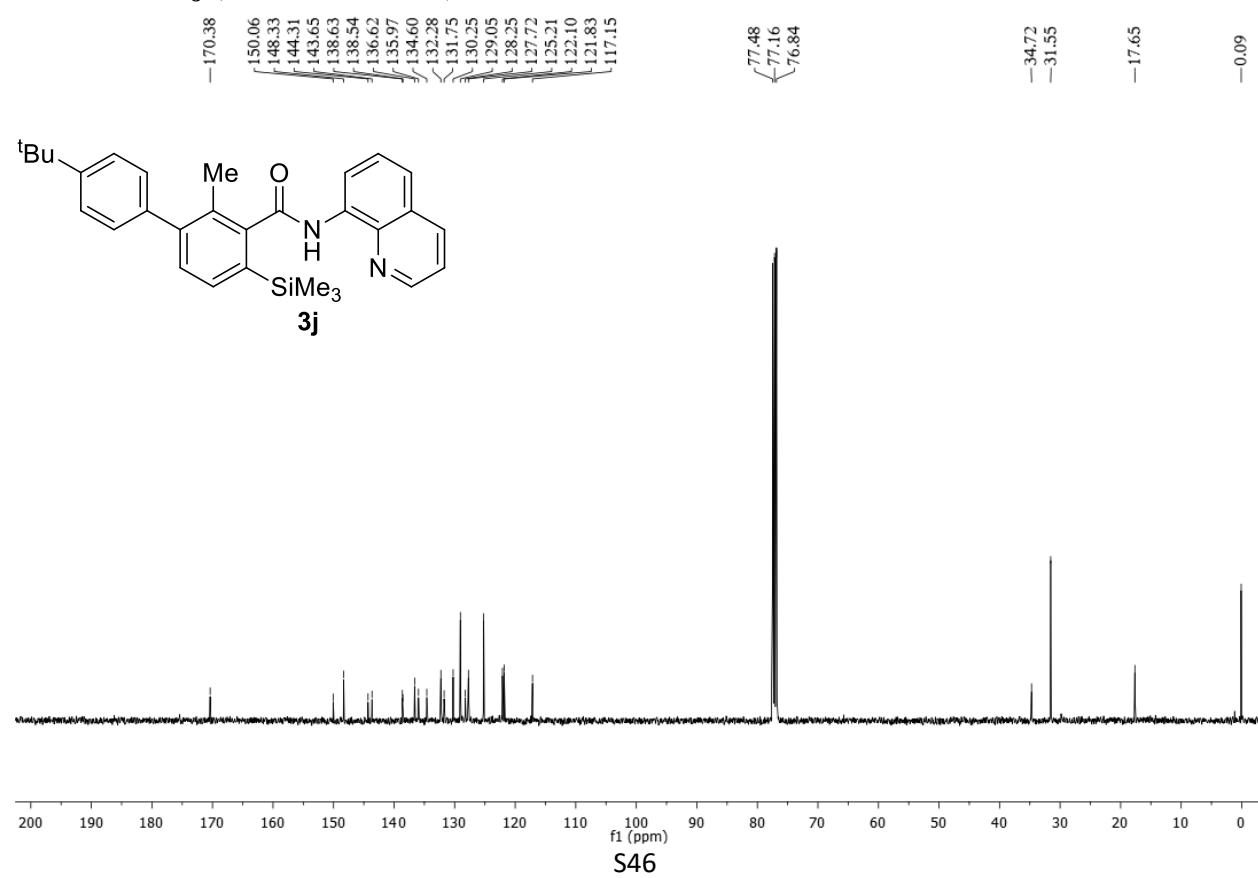
<sup>13</sup>C NMR of **3i** (100 MHz, CDCl<sub>3</sub>):



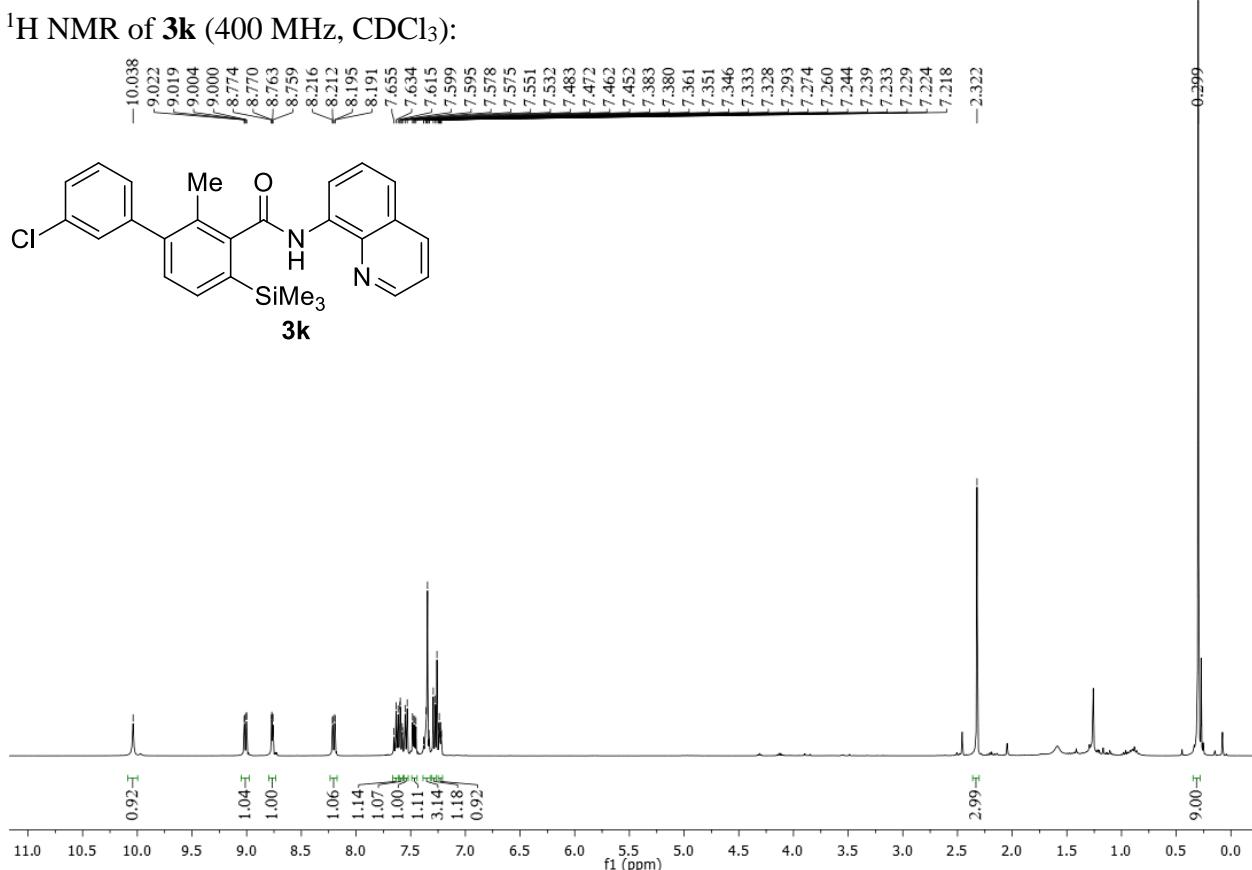
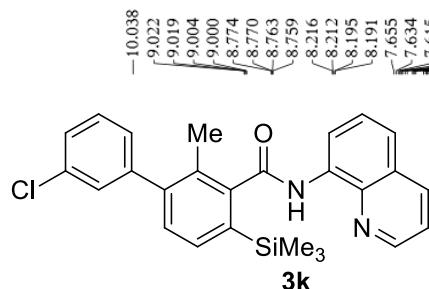
<sup>1</sup>H NMR of **3j** (400 MHz, CDCl<sub>3</sub>):



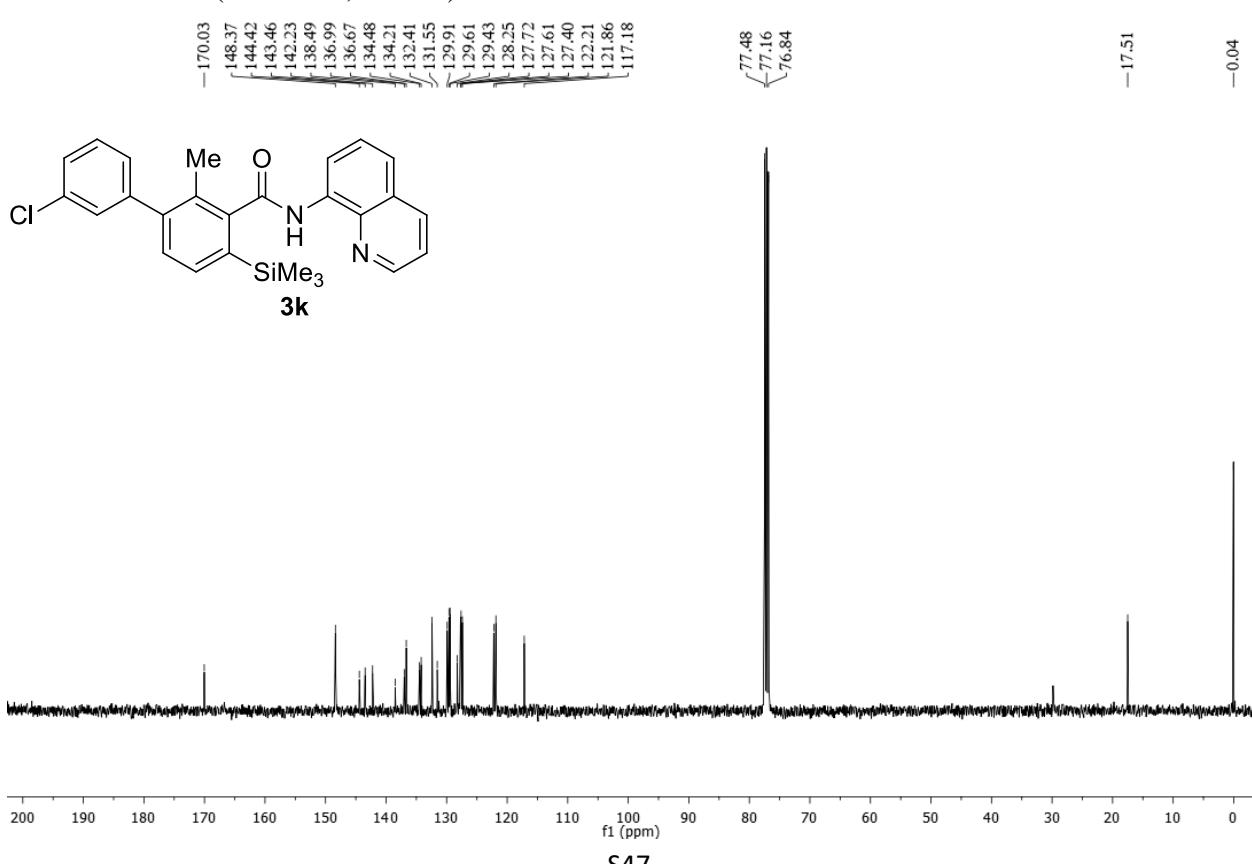
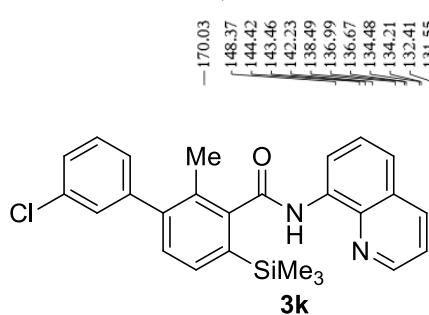
<sup>13</sup>C NMR of **3j** (100 MHz, CDCl<sub>3</sub>):



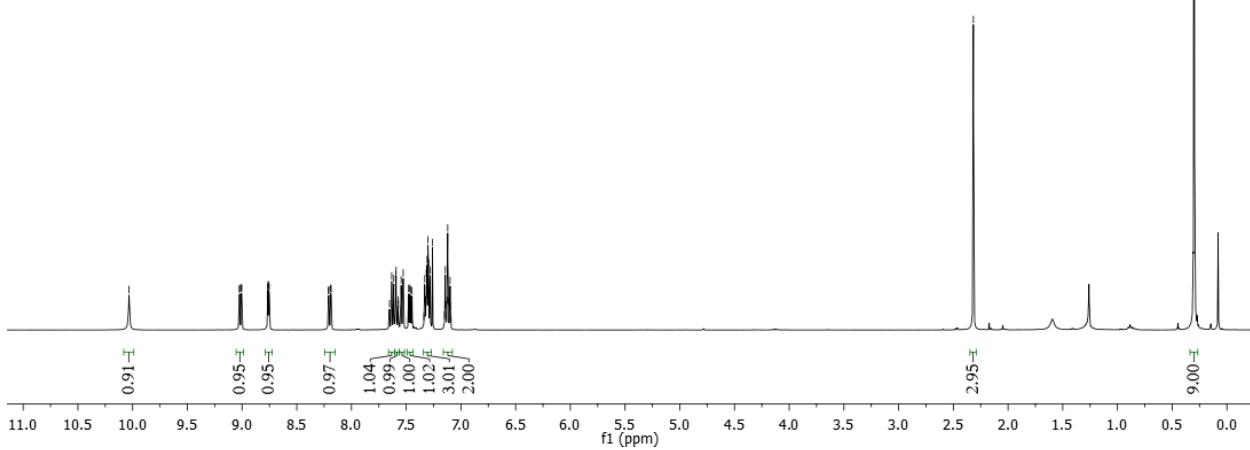
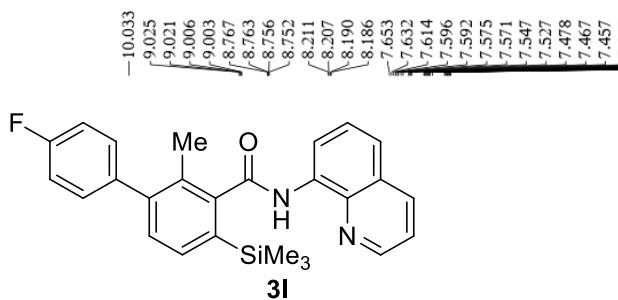
<sup>1</sup>H NMR of **3k** (400 MHz, CDCl<sub>3</sub>):



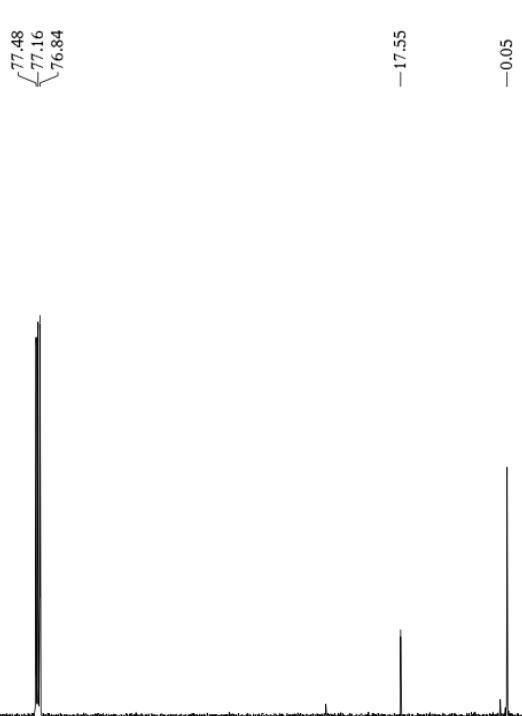
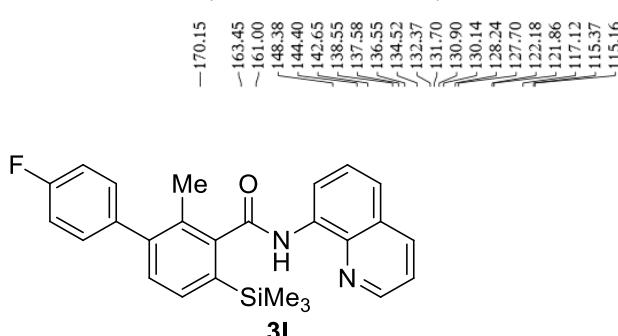
<sup>13</sup>C NMR of **3k** (100 MHz, CDCl<sub>3</sub>):



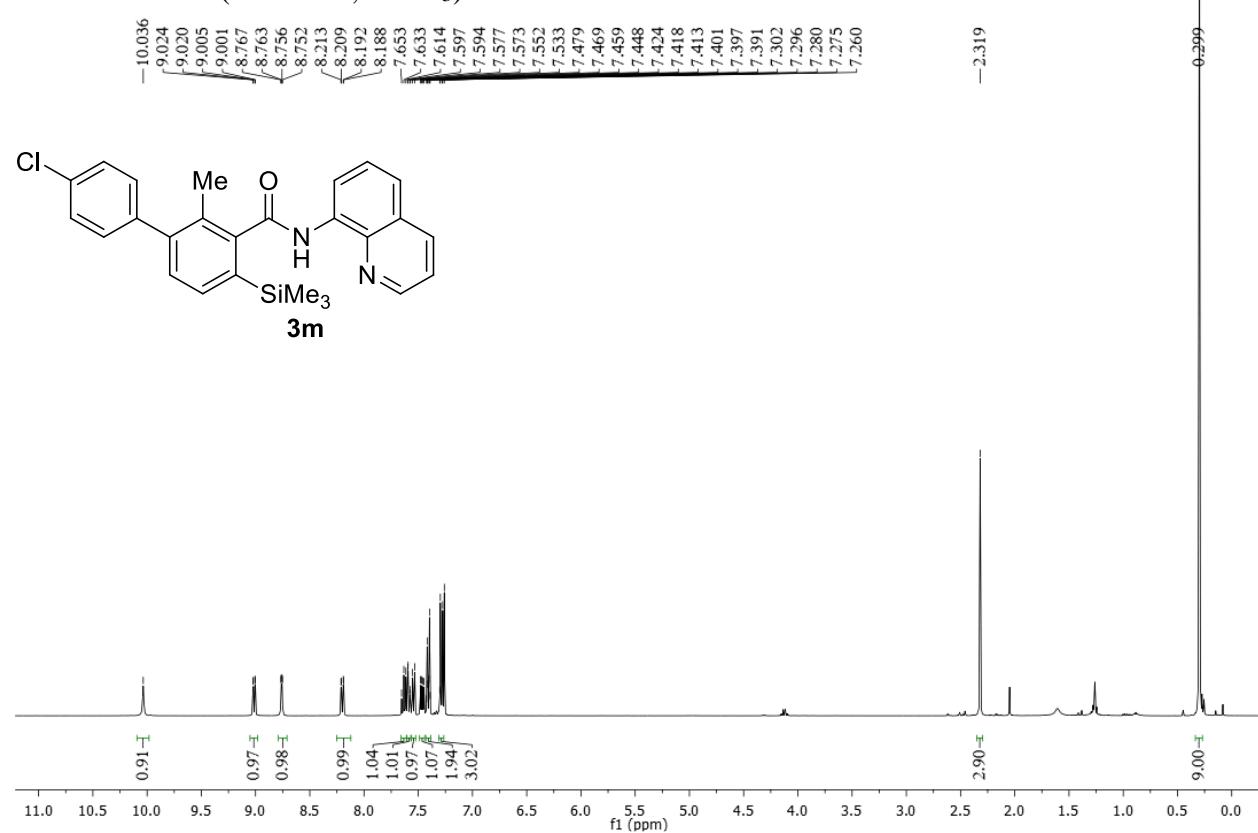
<sup>1</sup>H NMR of **3l** (400 MHz, CDCl<sub>3</sub>):



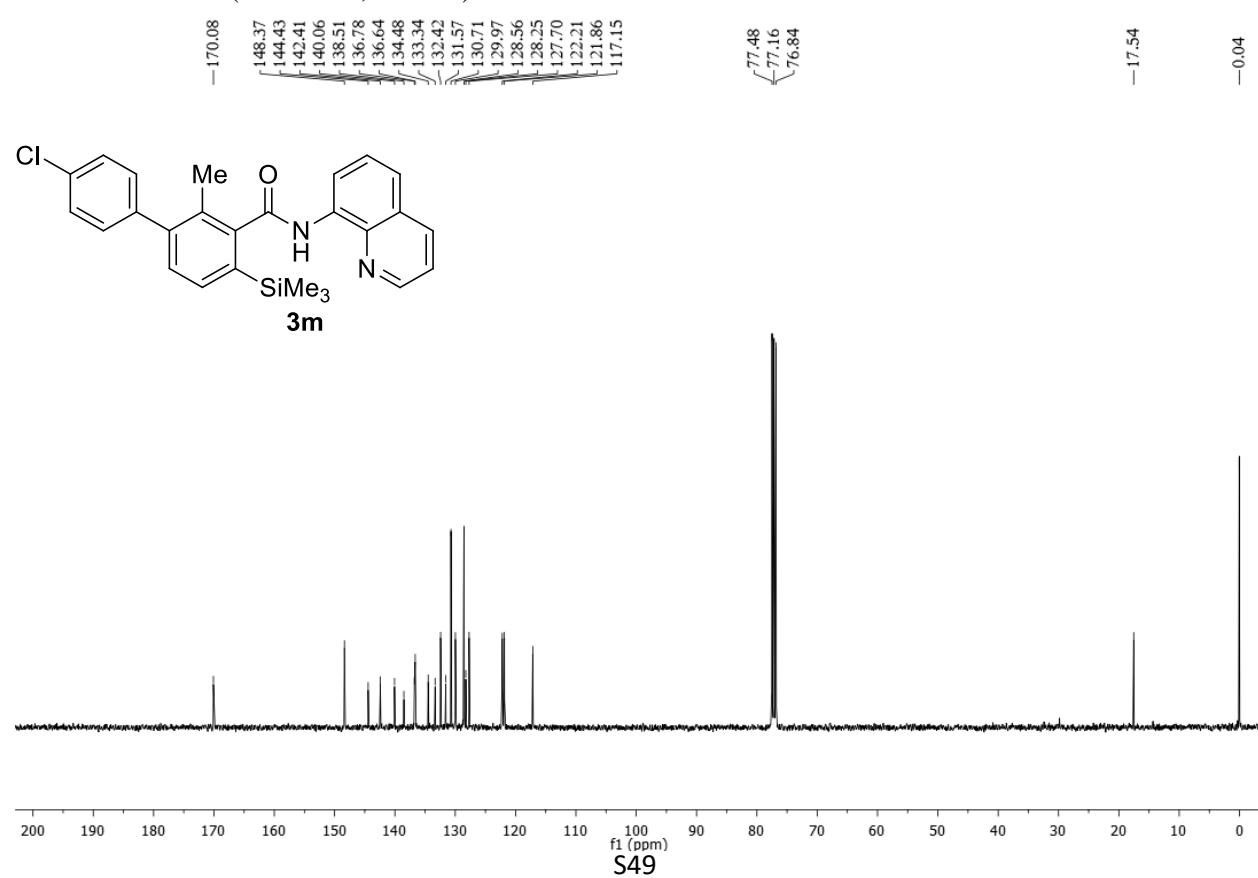
<sup>13</sup>C NMR of **3l** (100 MHz, CDCl<sub>3</sub>):



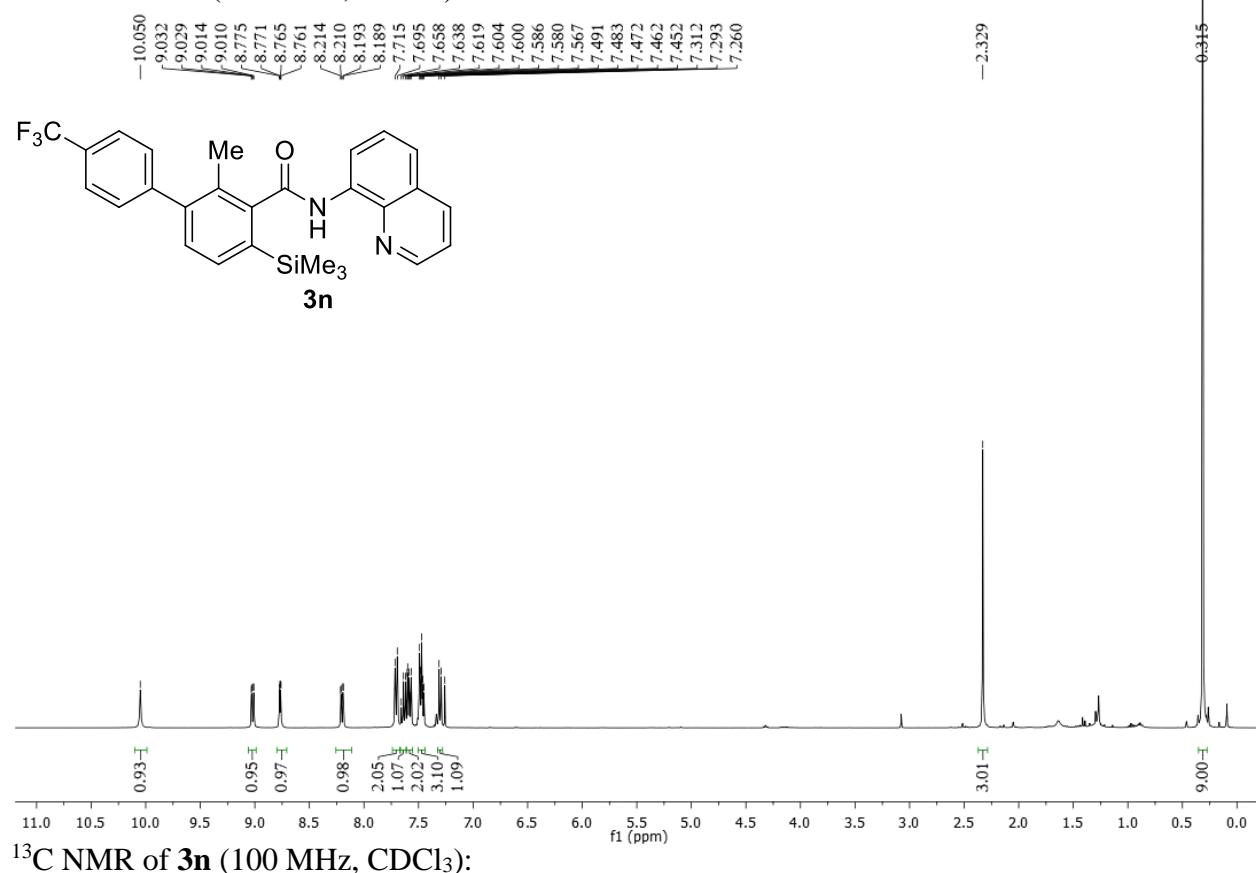
<sup>1</sup>H NMR of **3m** (400 MHz, CDCl<sub>3</sub>):



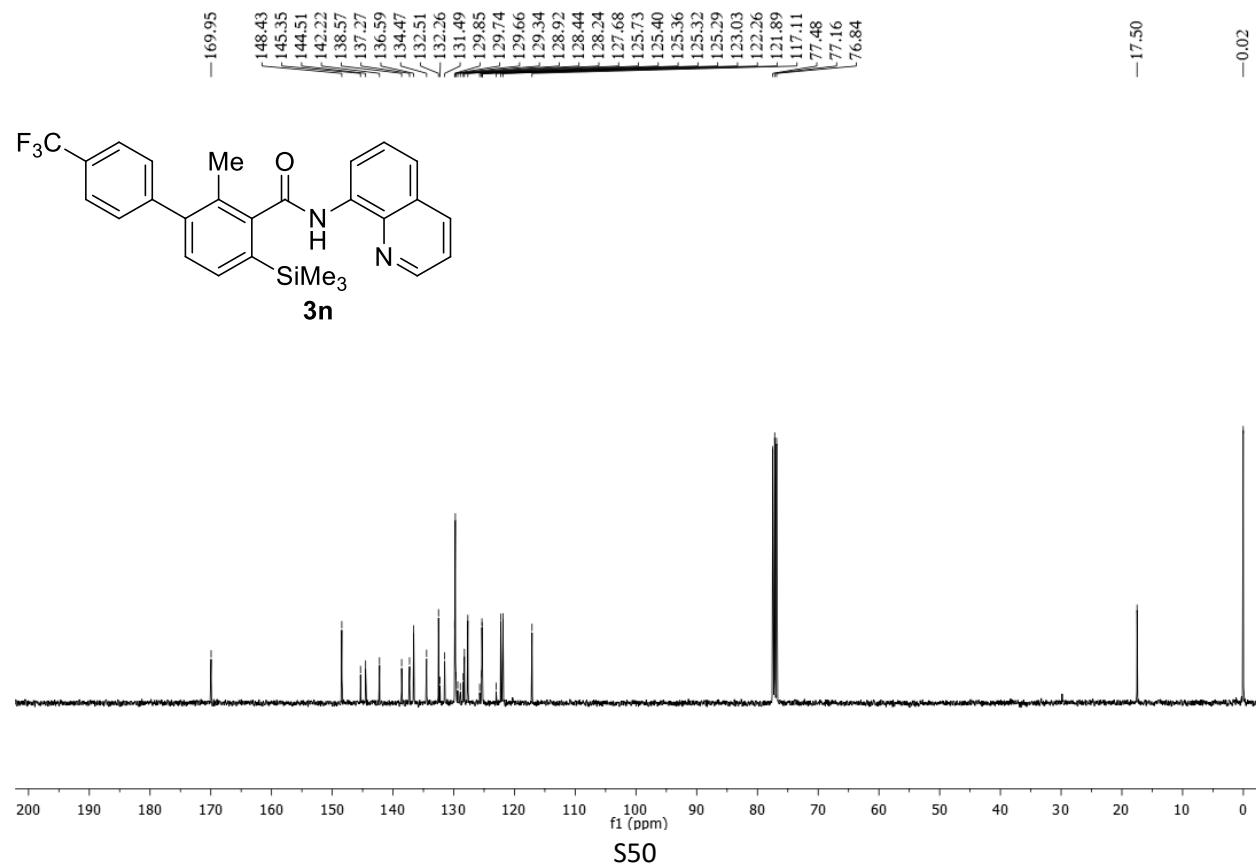
<sup>13</sup>C NMR of **3m** (100 MHz, CDCl<sub>3</sub>):



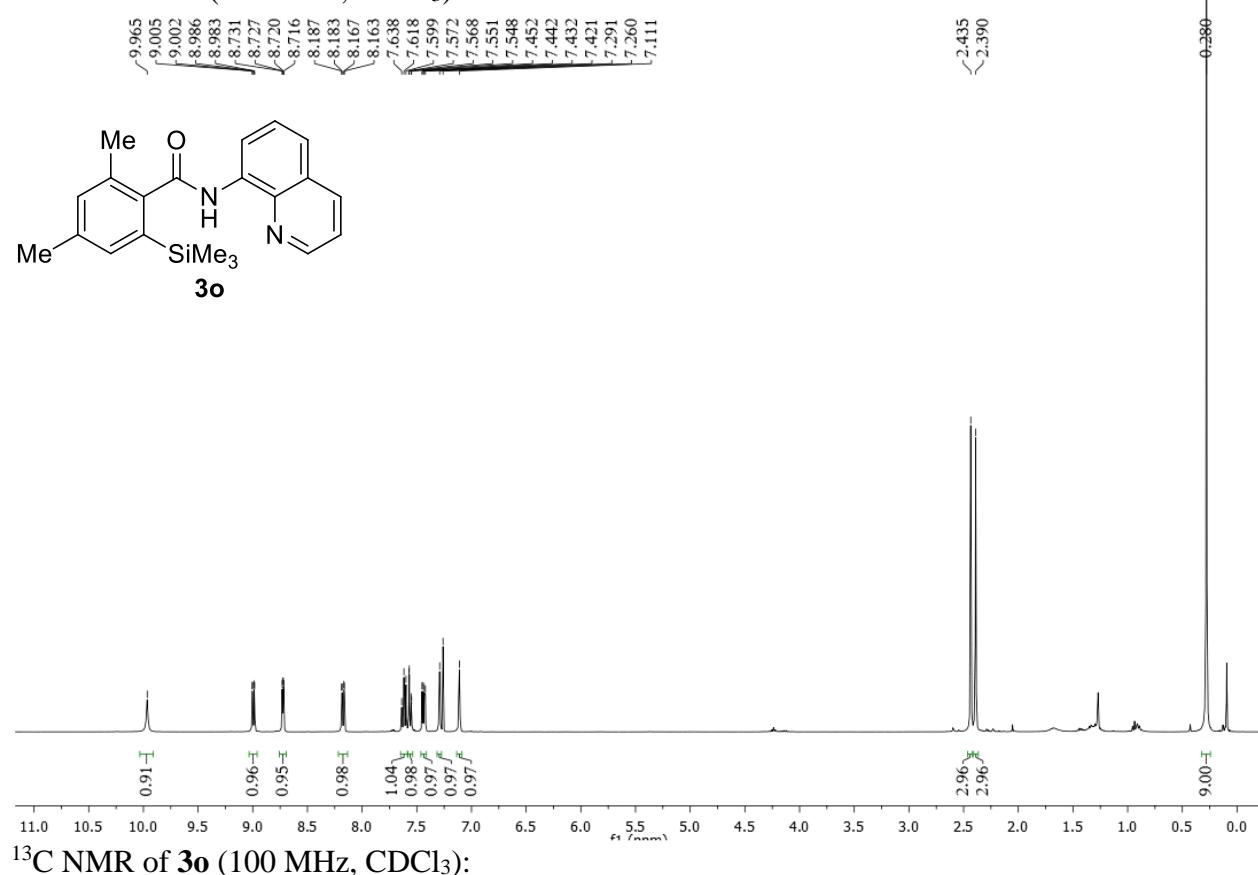
<sup>1</sup>H NMR of **3n** (400 MHz, CDCl<sub>3</sub>):



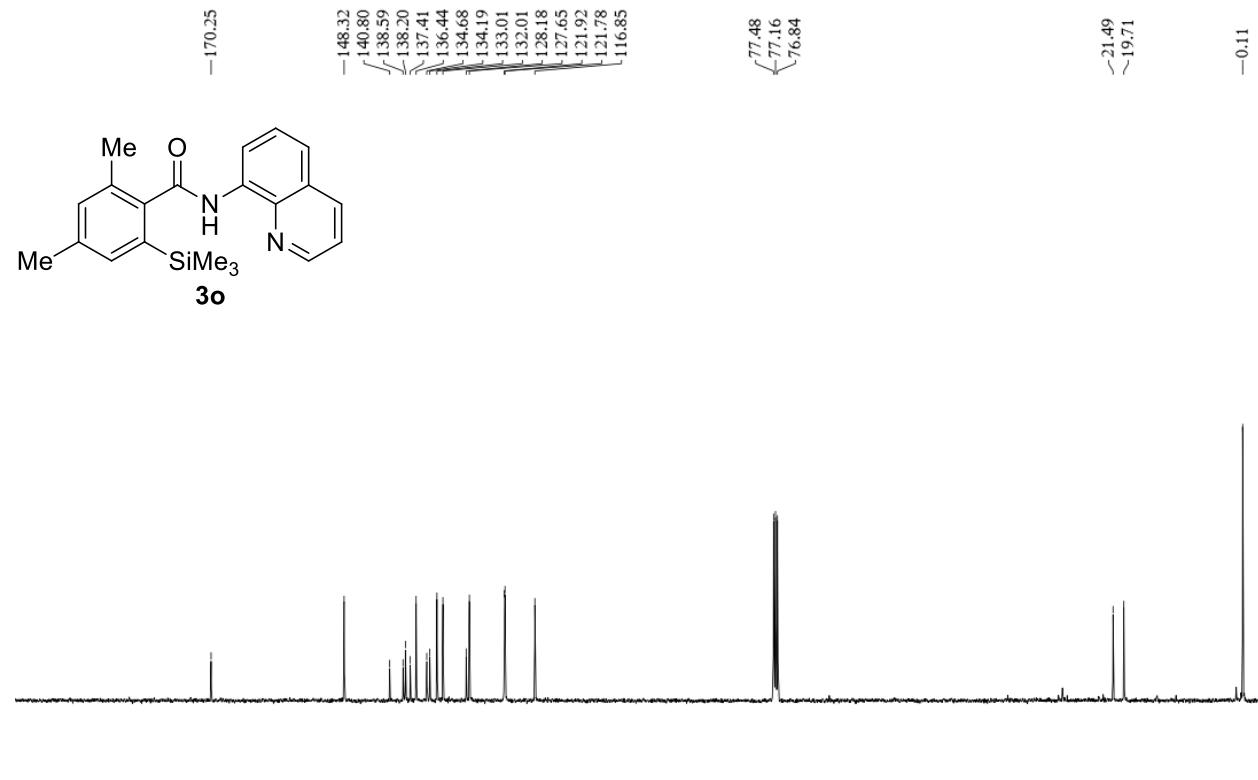
<sup>13</sup>C NMR of **3n** (100 MHz, CDCl<sub>3</sub>):



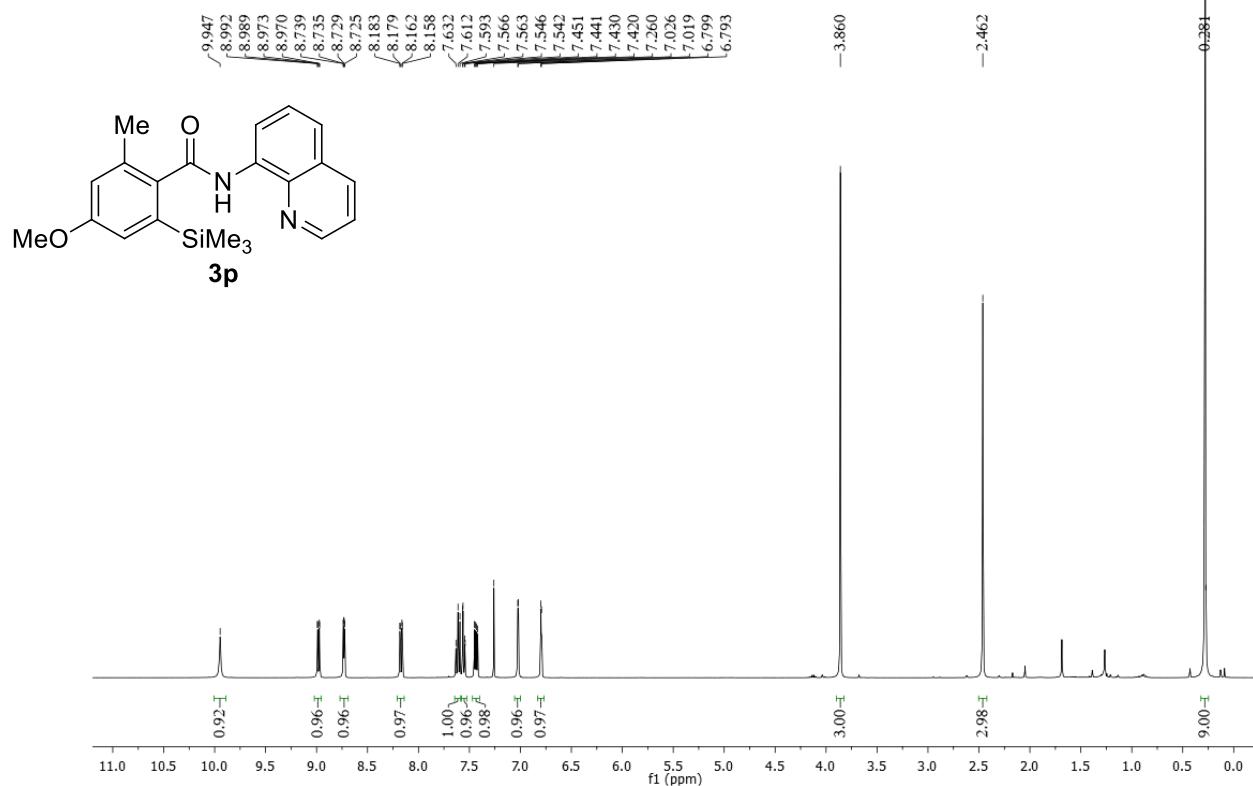
<sup>1</sup>H NMR of **3o** (400 MHz, CDCl<sub>3</sub>):



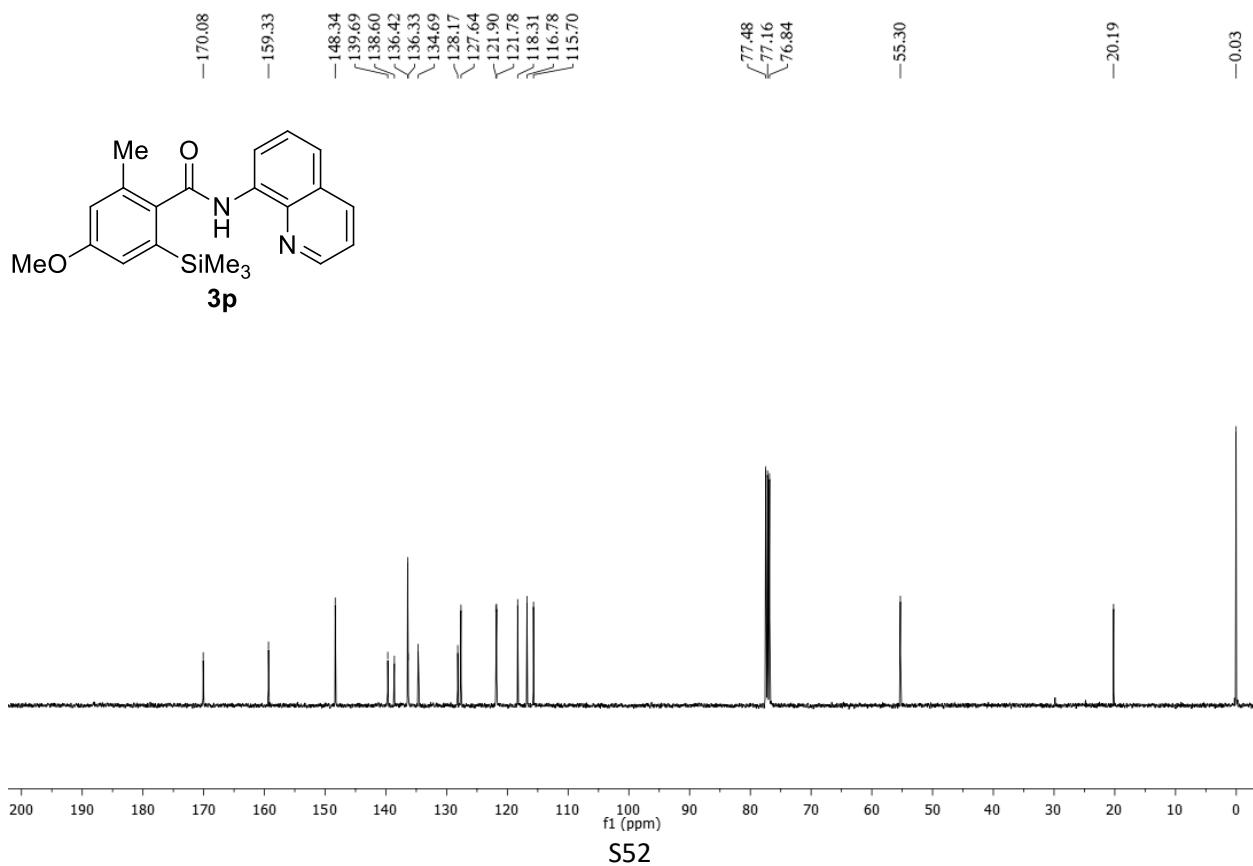
<sup>13</sup>C NMR of **3o** (100 MHz, CDCl<sub>3</sub>):



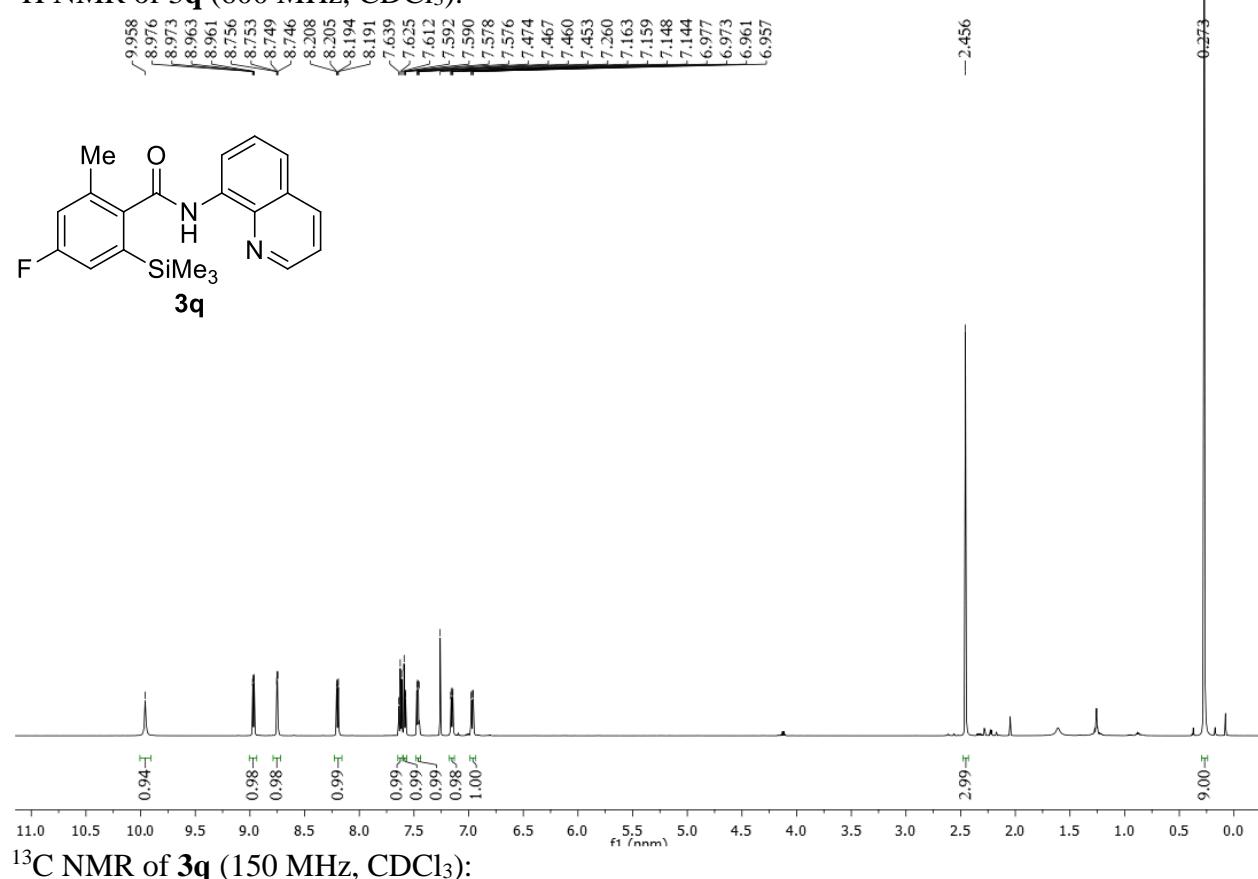
<sup>1</sup>H NMR of **3p** (400 MHz, CDCl<sub>3</sub>):



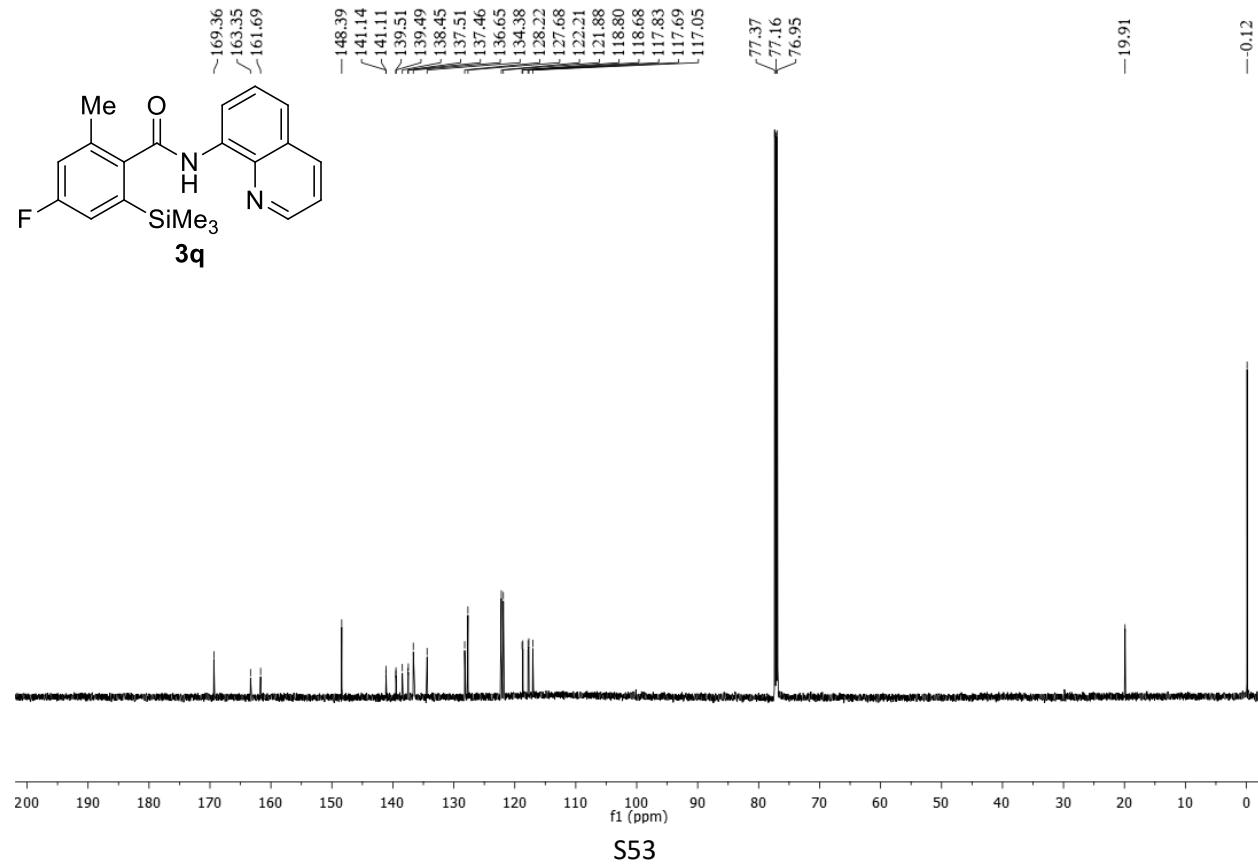
<sup>13</sup>C NMR of **3p** (100 MHz, CDCl<sub>3</sub>):



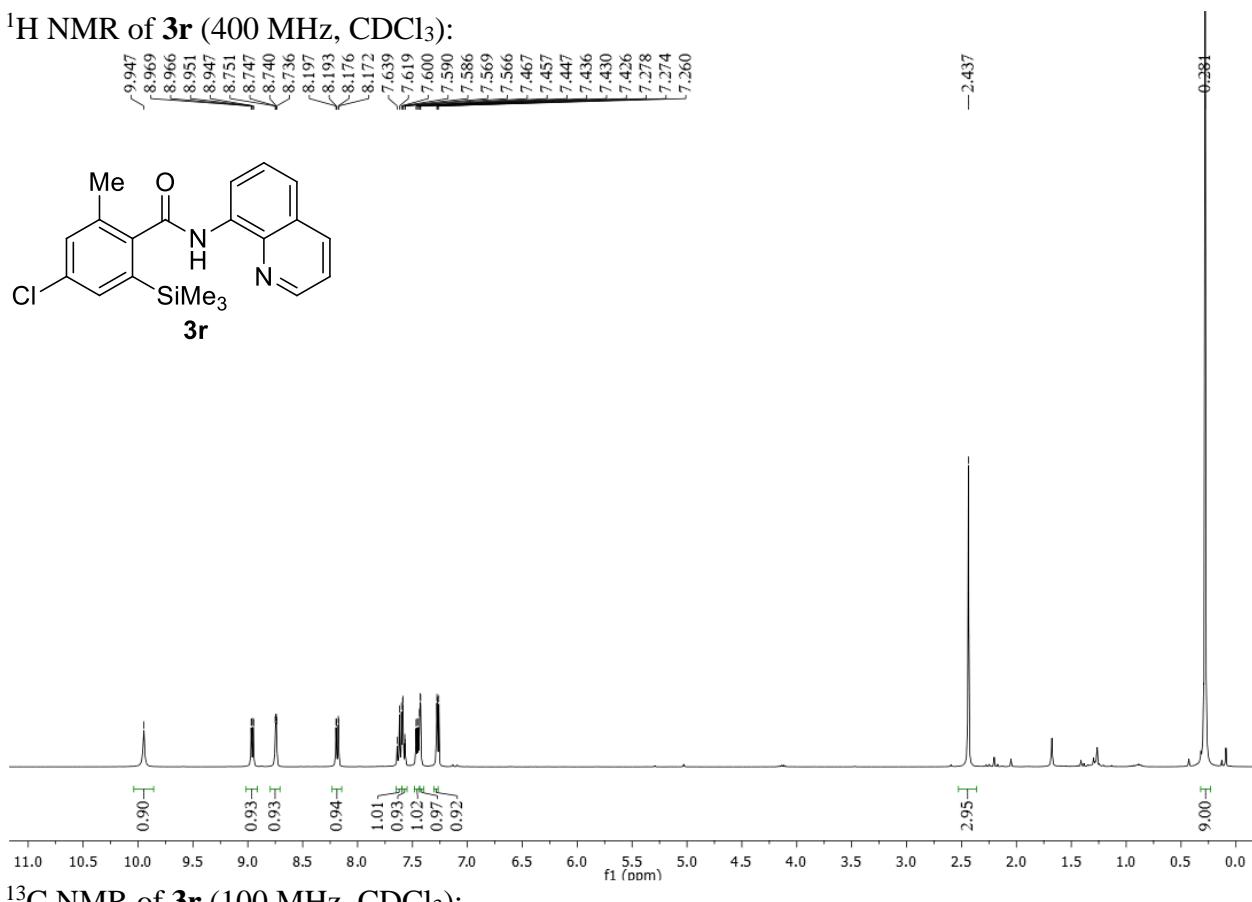
<sup>1</sup>H NMR of 3q (600 MHz, CDCl<sub>3</sub>):



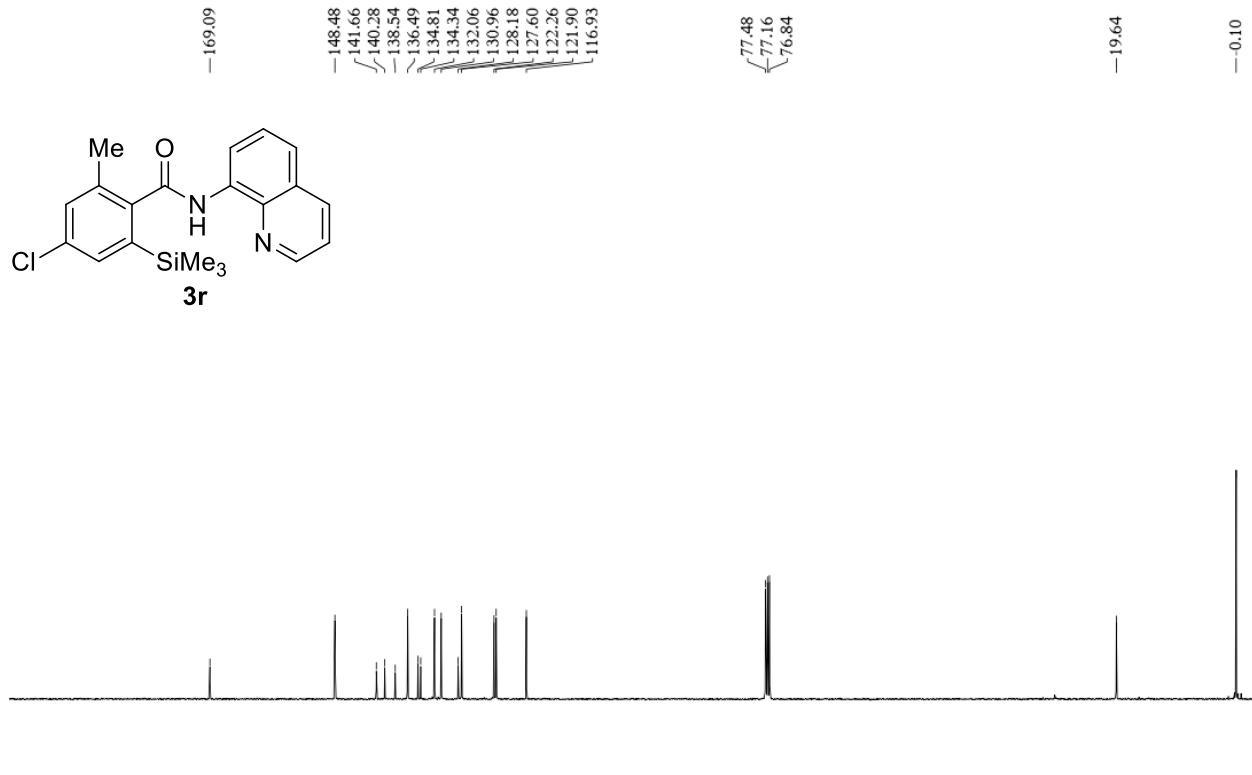
<sup>13</sup>C NMR of 3q (150 MHz, CDCl<sub>3</sub>):



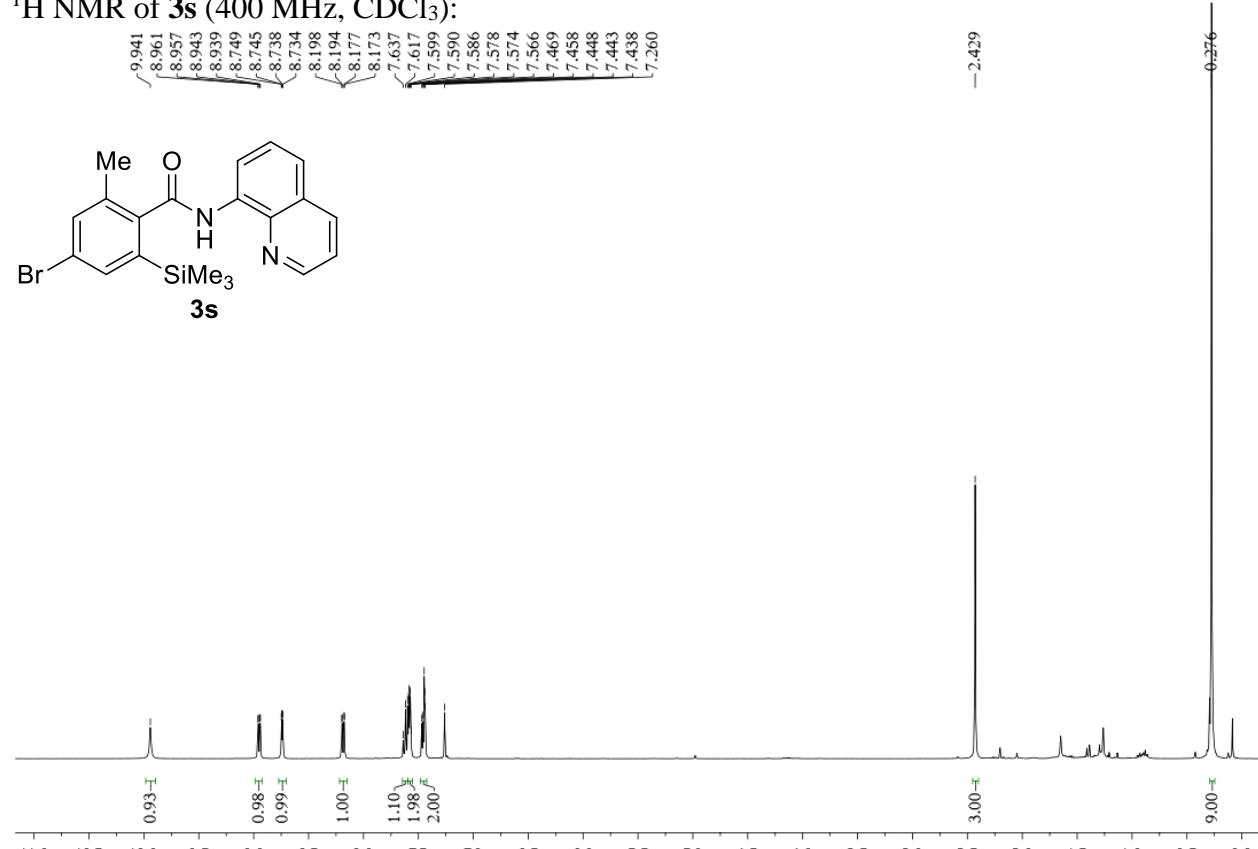
<sup>1</sup>H NMR of **3r** (400 MHz, CDCl<sub>3</sub>):



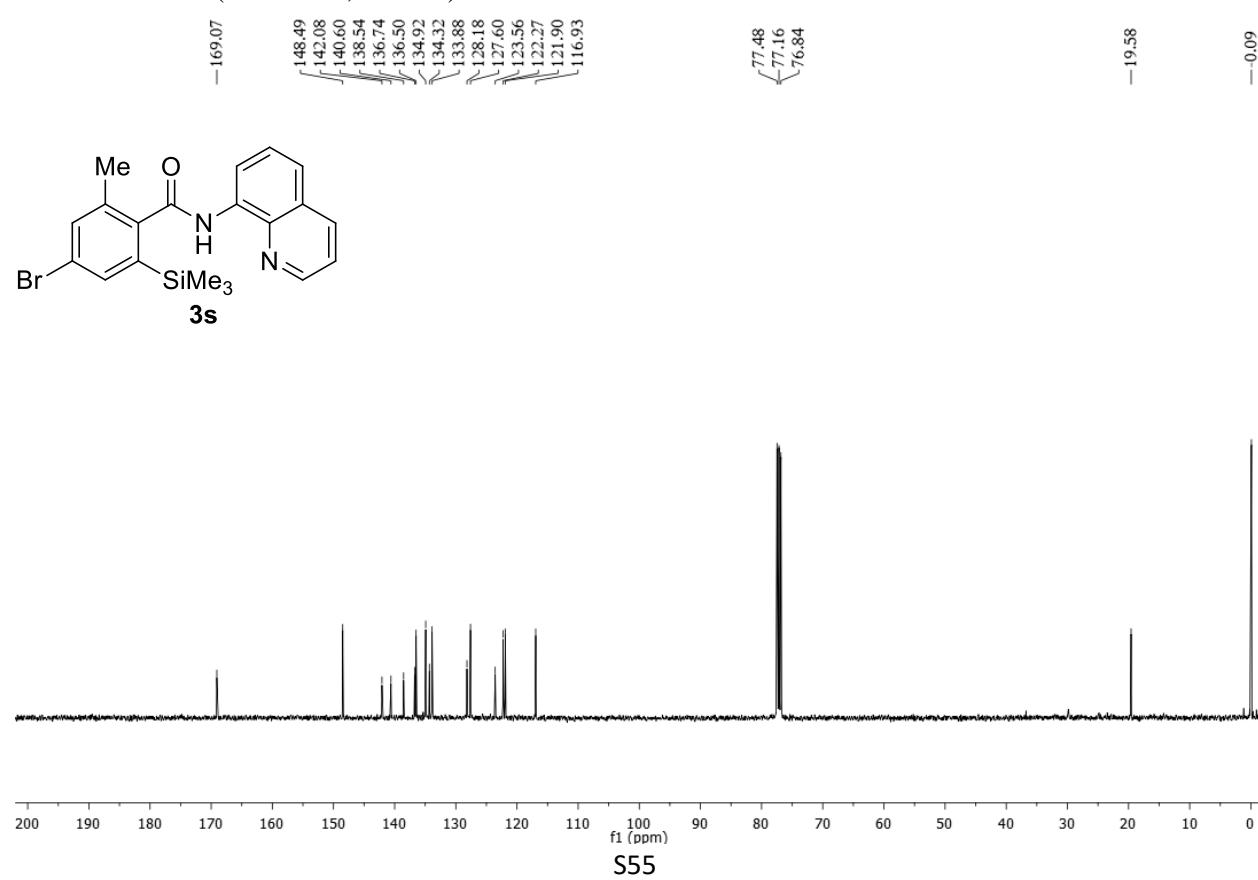
<sup>13</sup>C NMR of **3r** (100 MHz, CDCl<sub>3</sub>):



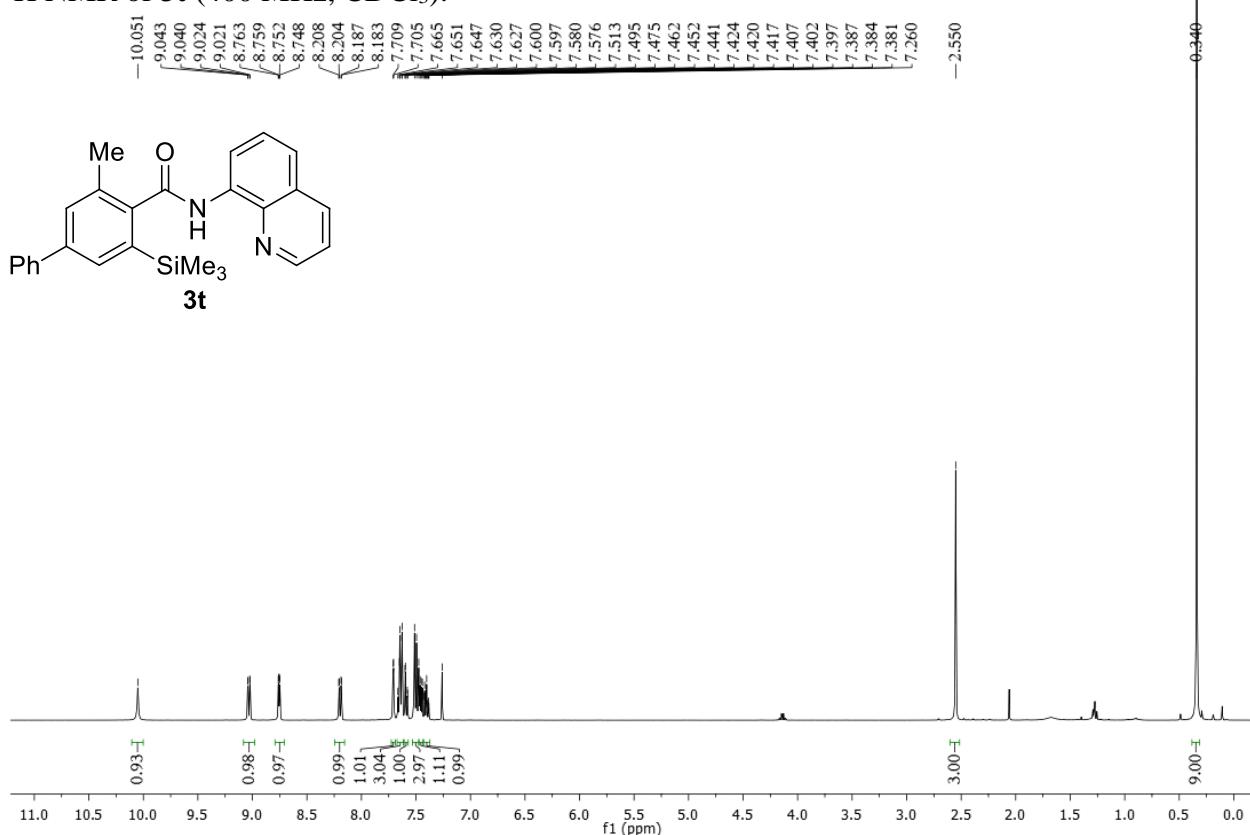
<sup>1</sup>H NMR of **3s** (400 MHz, CDCl<sub>3</sub>):



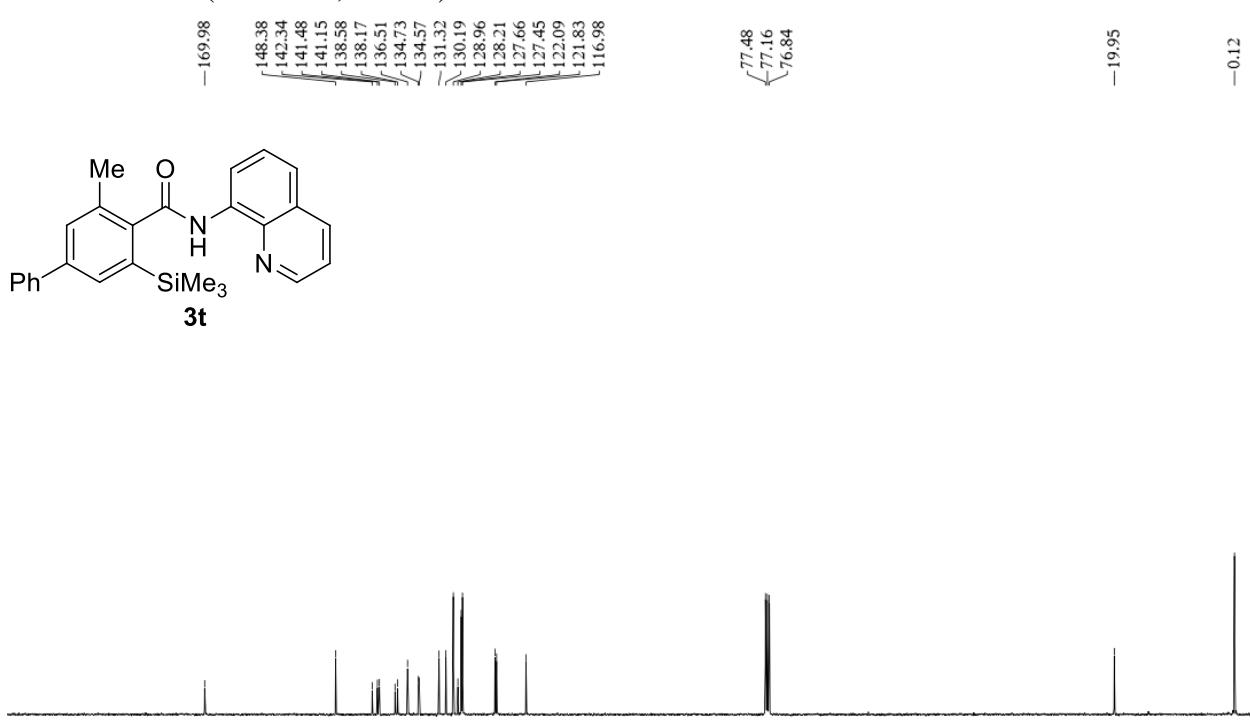
<sup>13</sup>C NMR of **3s** (100 MHz, CDCl<sub>3</sub>):



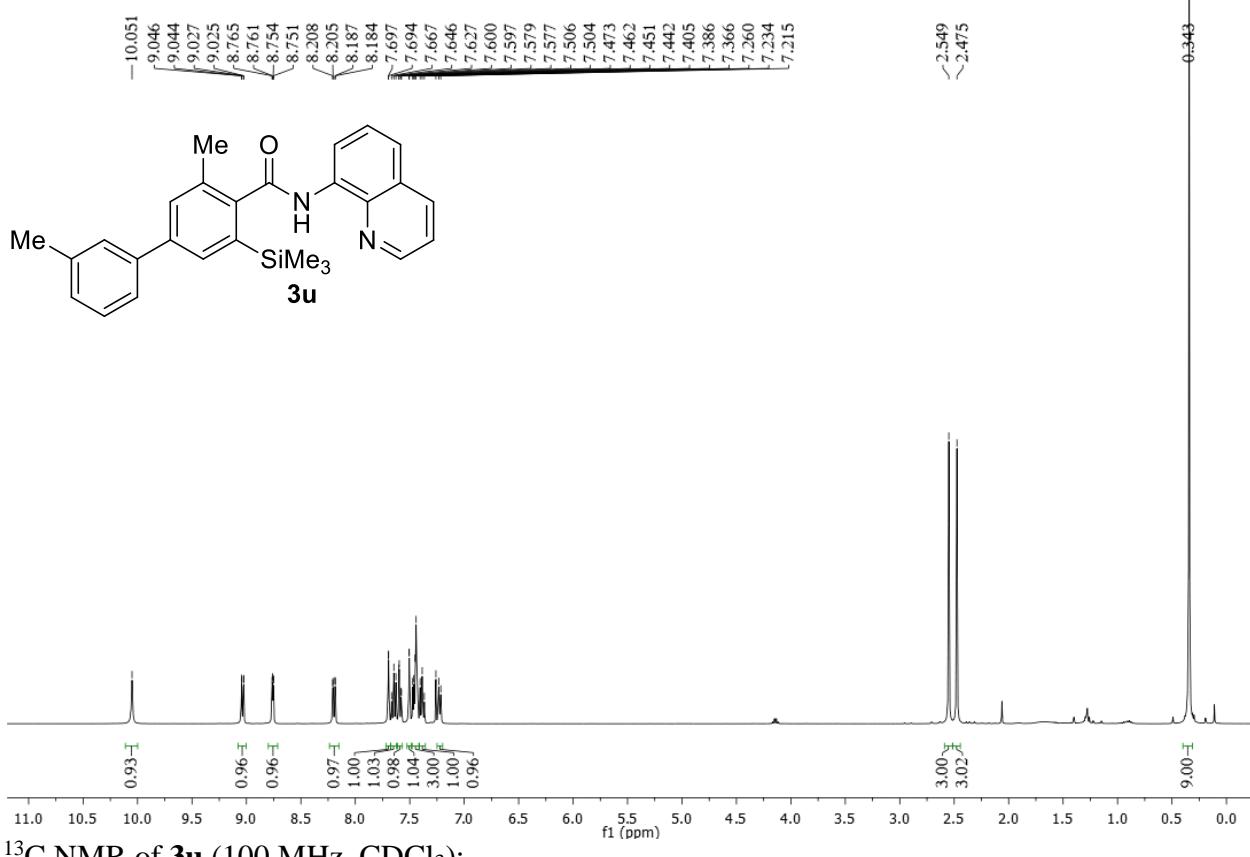
<sup>1</sup>H NMR of **3t** (400 MHz, CDCl<sub>3</sub>):



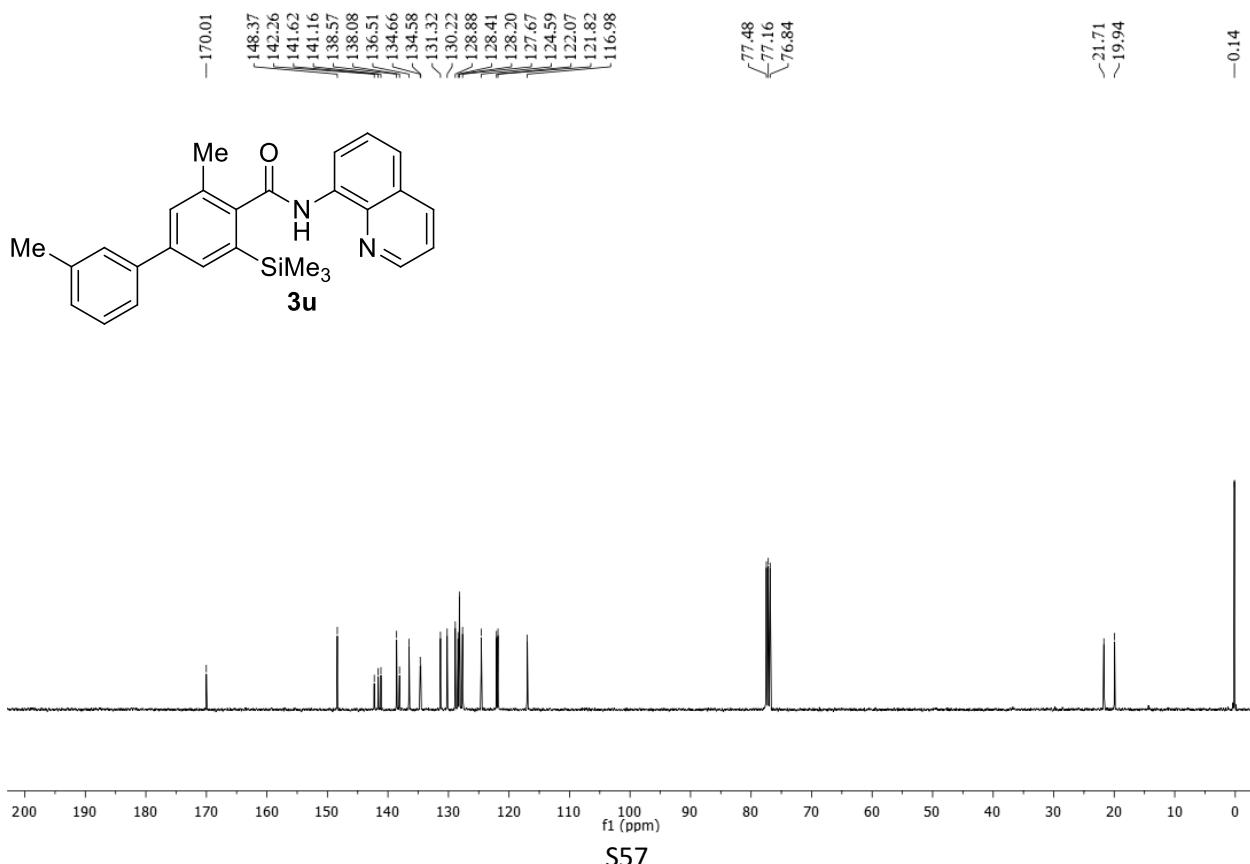
<sup>13</sup>C NMR of **3t** (100 MHz, CDCl<sub>3</sub>):



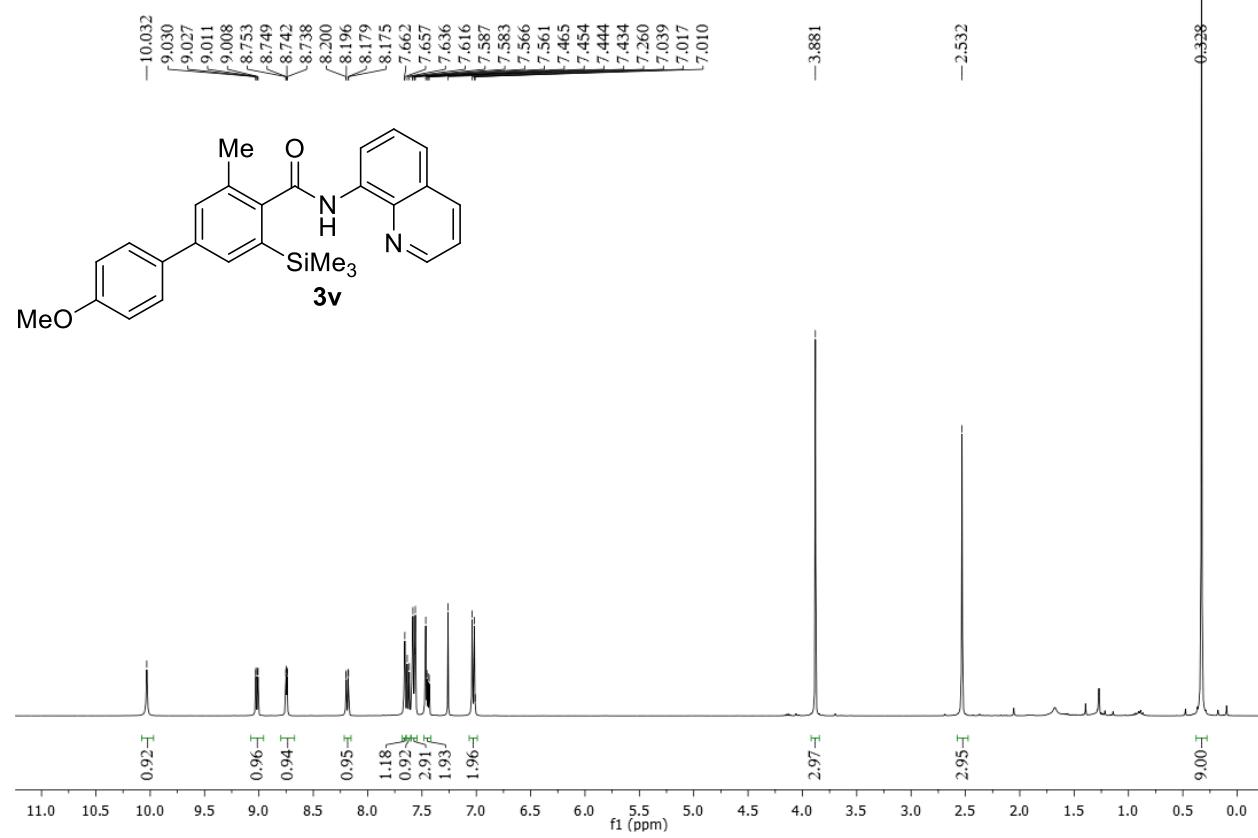
<sup>1</sup>H NMR of **3u** (400 MHz, CDCl<sub>3</sub>):



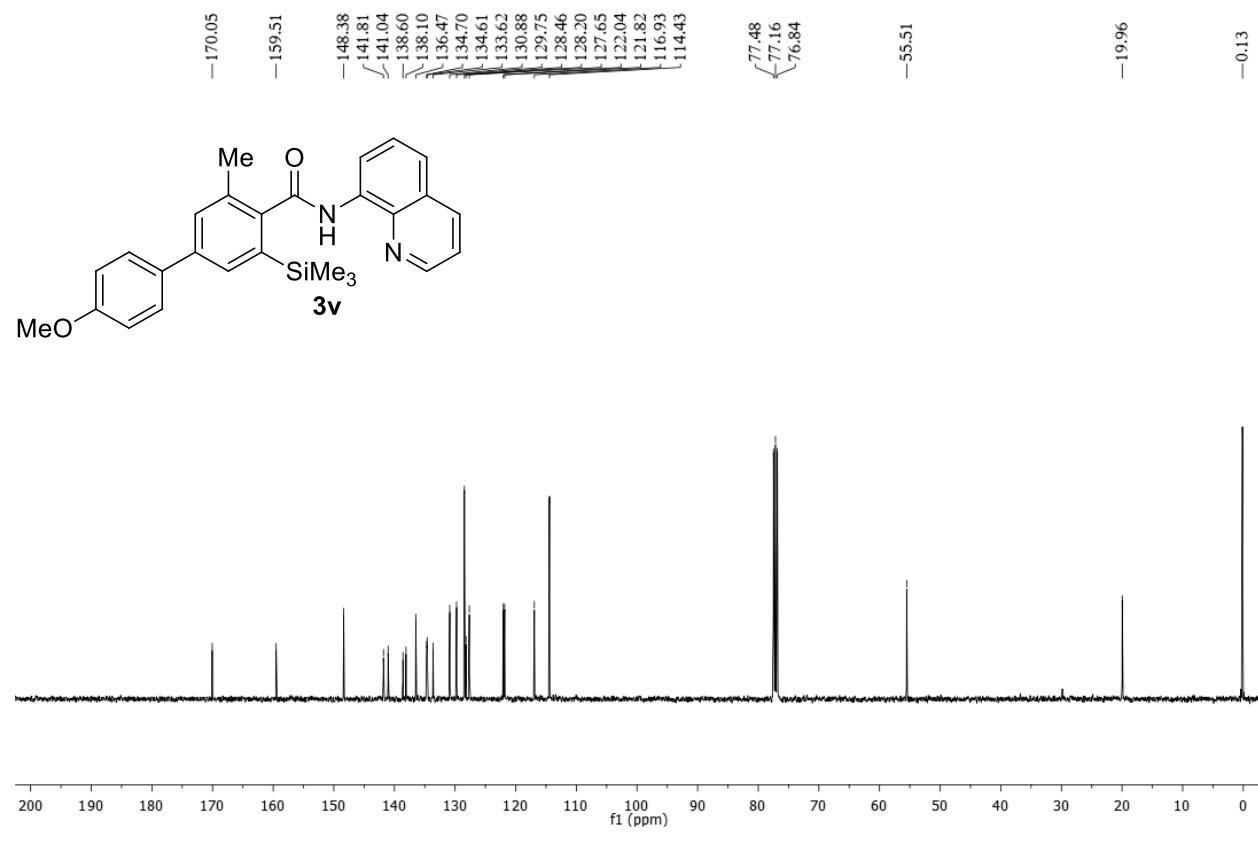
<sup>13</sup>C NMR of **3u** (100 MHz, CDCl<sub>3</sub>):



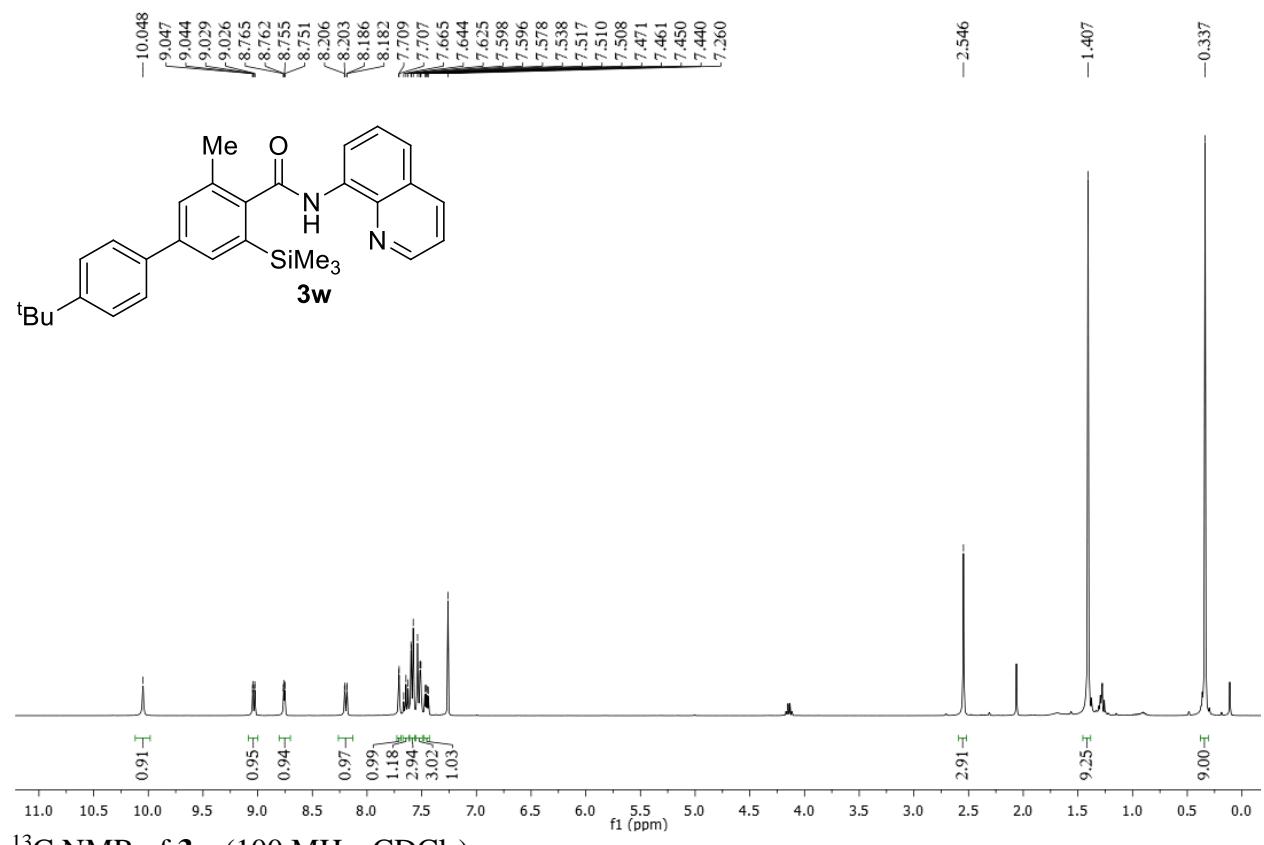
<sup>1</sup>H NMR of **3v** (400 MHz, CDCl<sub>3</sub>):



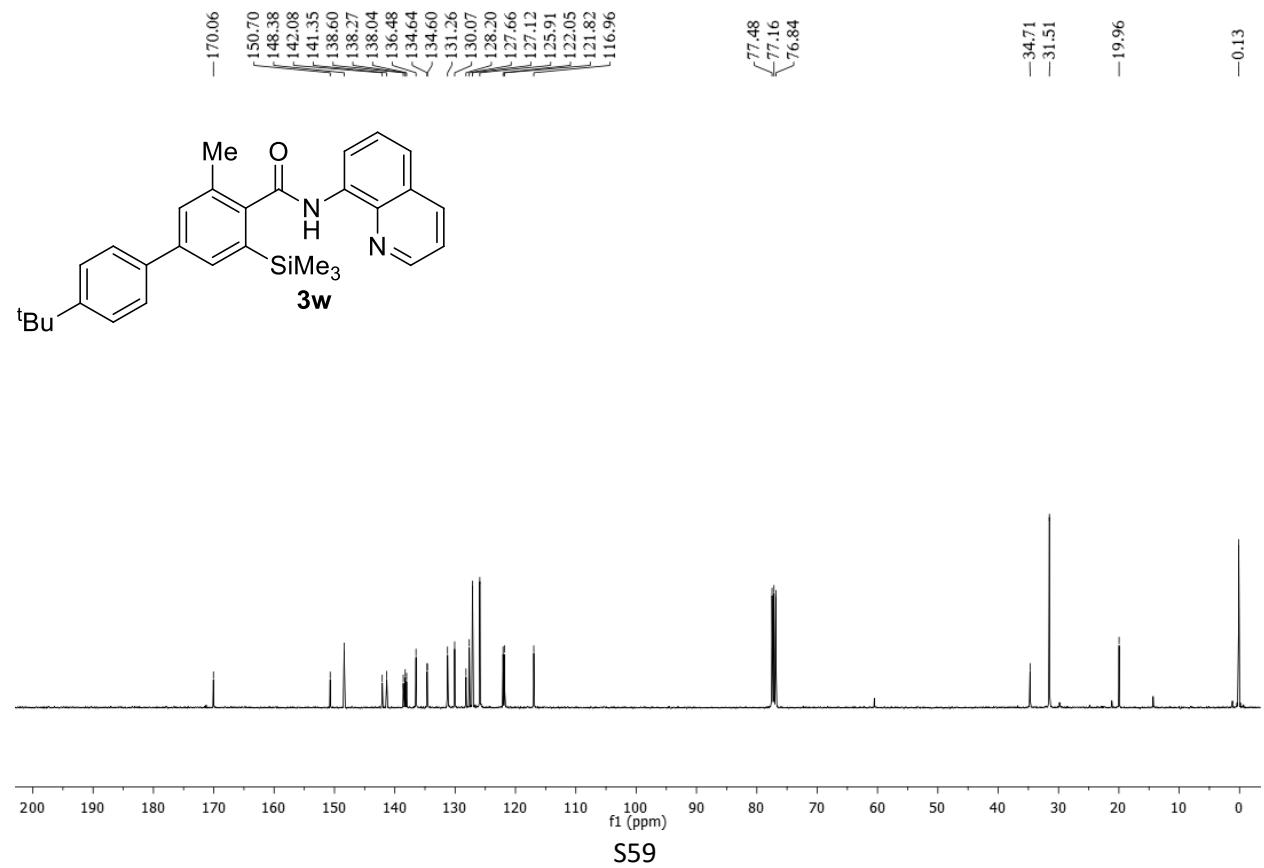
<sup>13</sup>C NMR of **3v** (100 MHz, CDCl<sub>3</sub>):



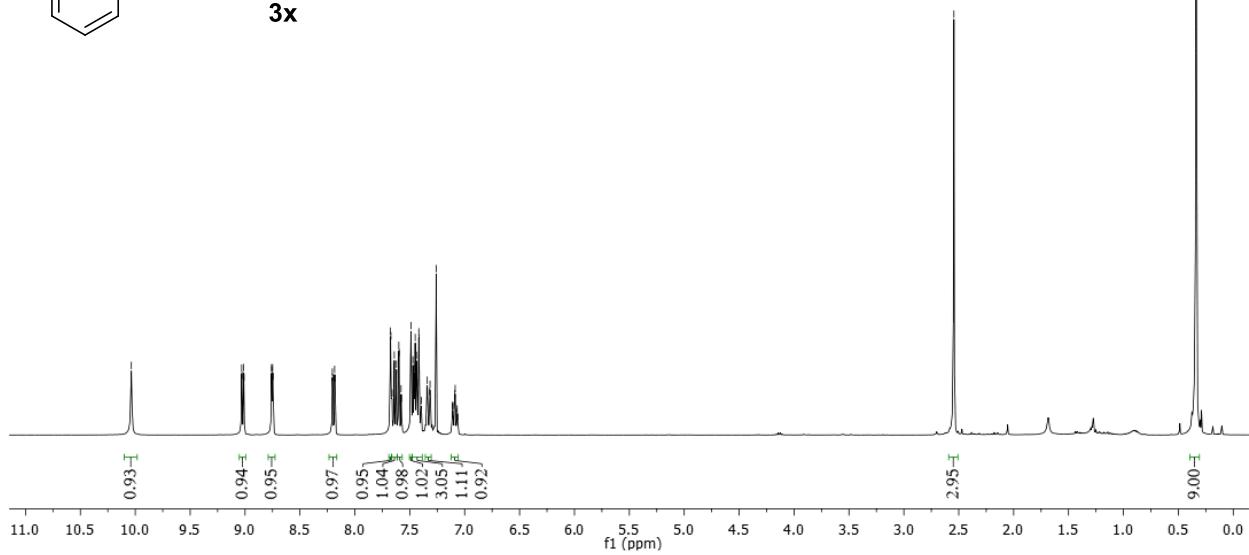
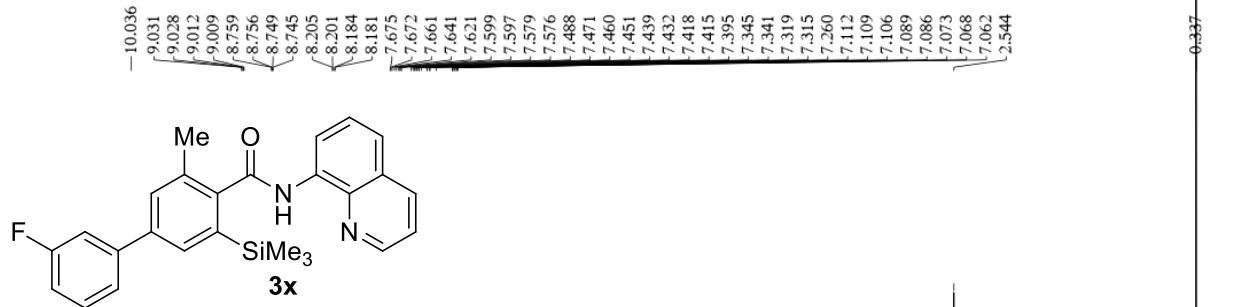
<sup>1</sup>H NMR of **3w** (400 MHz, CDCl<sub>3</sub>):



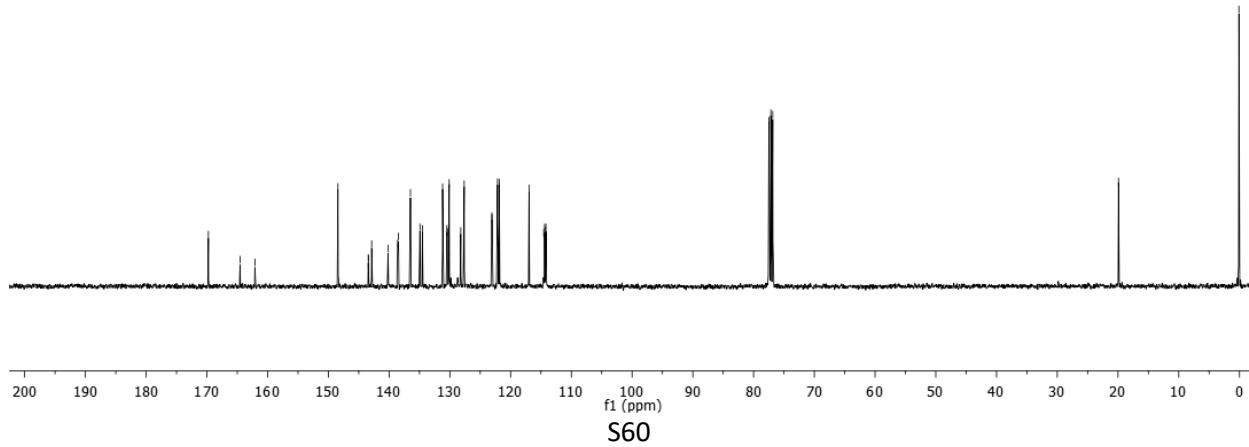
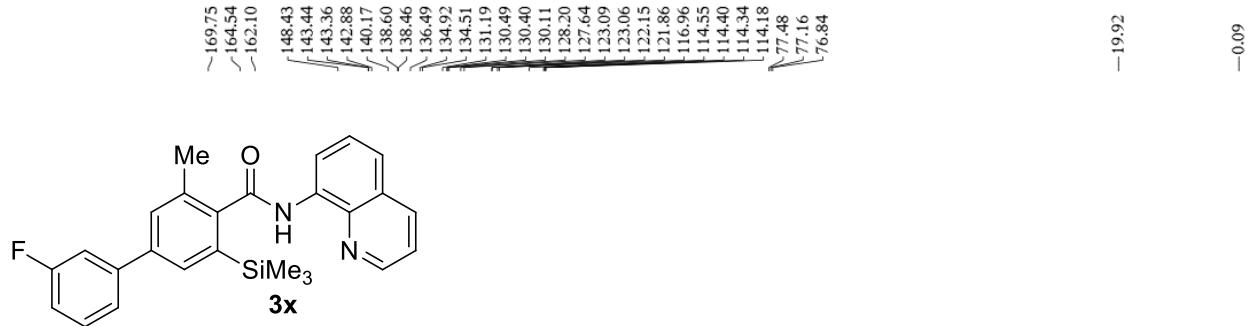
<sup>13</sup>C NMR of **3w** (100 MHz, CDCl<sub>3</sub>):



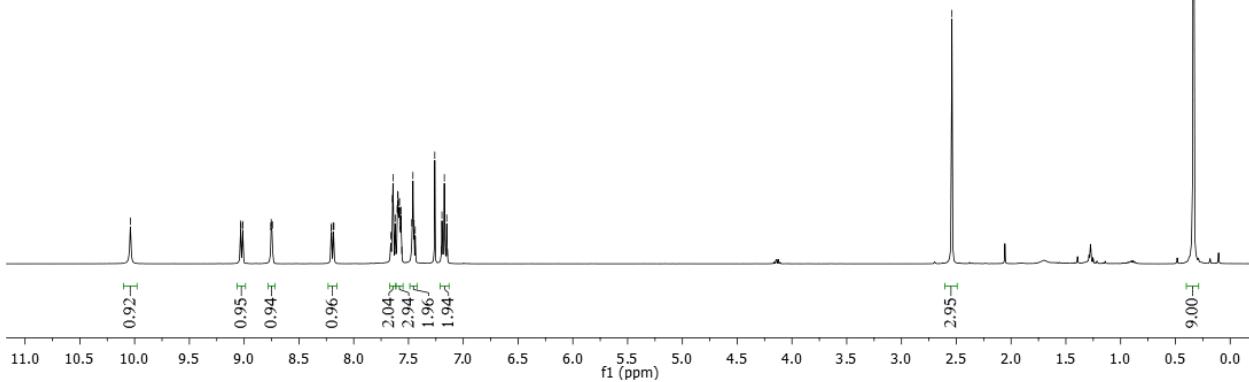
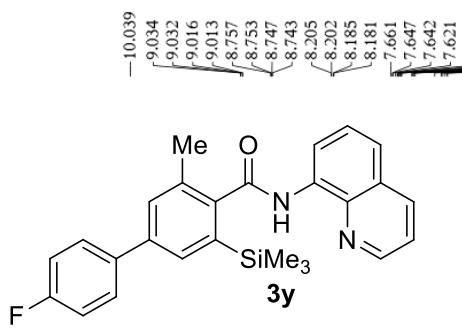
<sup>1</sup>H NMR of **3x** (400 MHz, CDCl<sub>3</sub>):



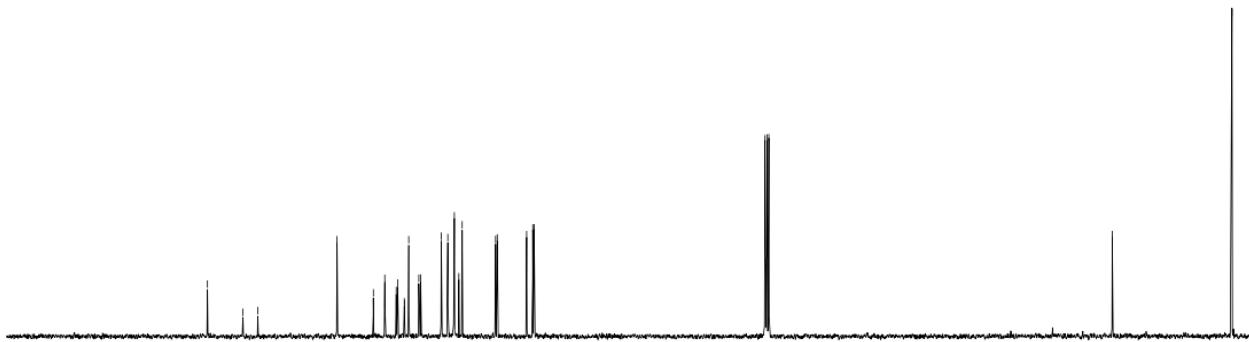
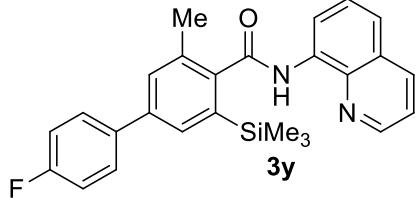
<sup>13</sup>C NMR of **3x** (100 MHz, CDCl<sub>3</sub>):



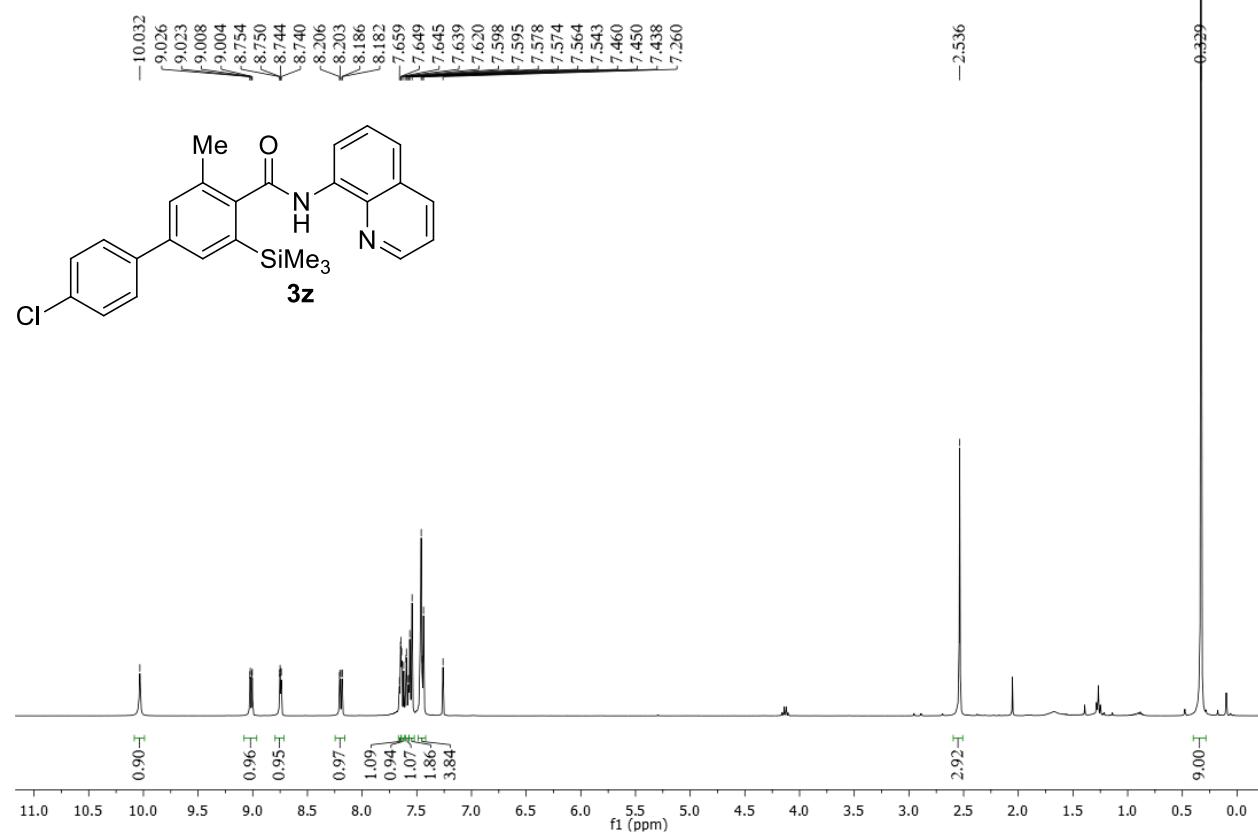
<sup>1</sup>H NMR of **3y** (400 MHz, CDCl<sub>3</sub>):



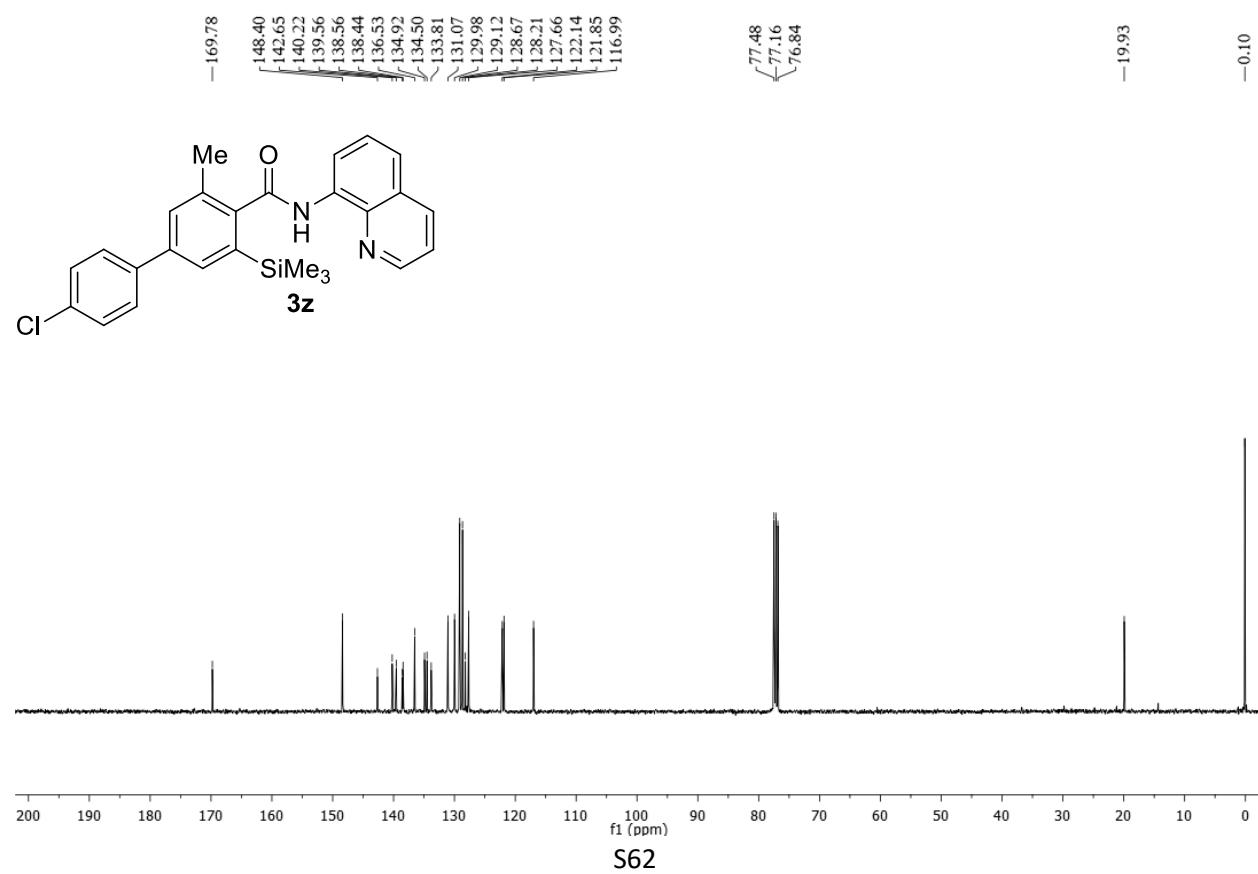
<sup>13</sup>C NMR of **3y** (100 MHz, CDCl<sub>3</sub>):



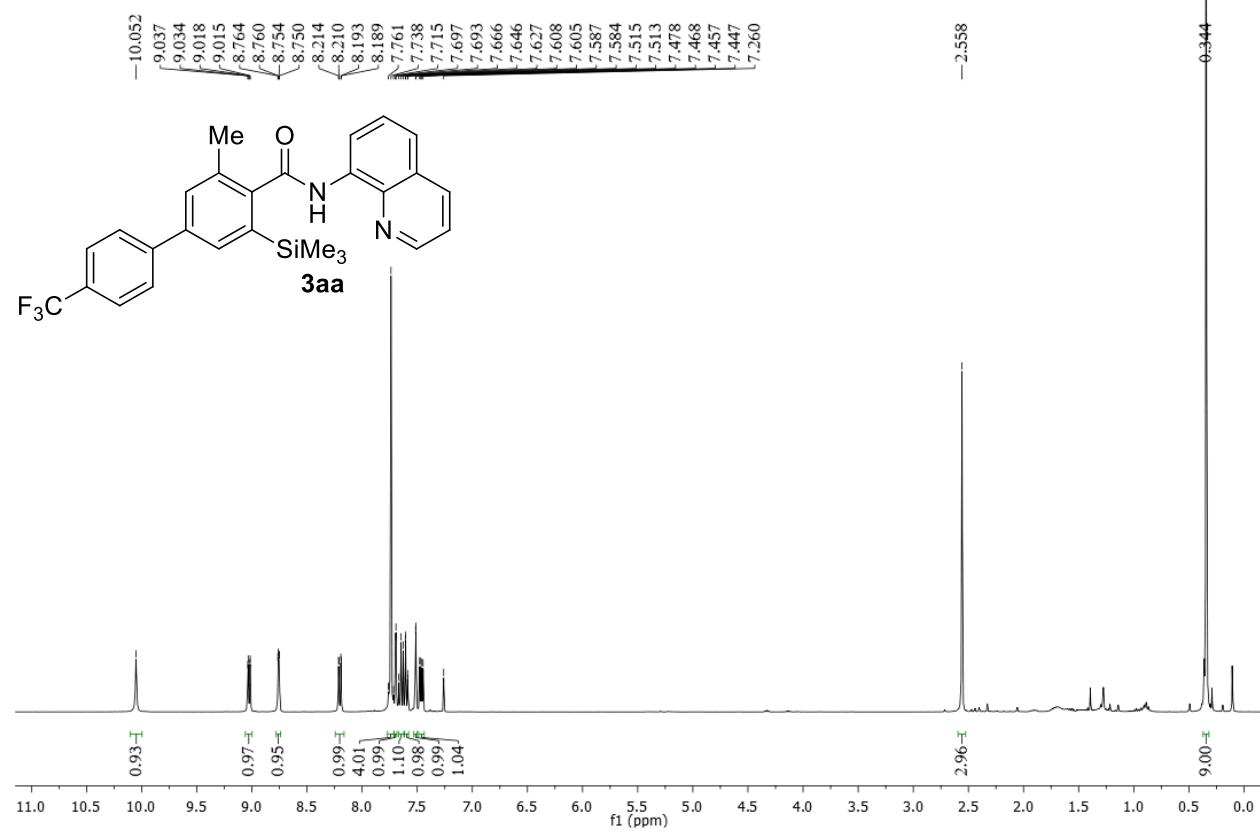
<sup>1</sup>H NMR of **3z** (400 MHz, CDCl<sub>3</sub>):



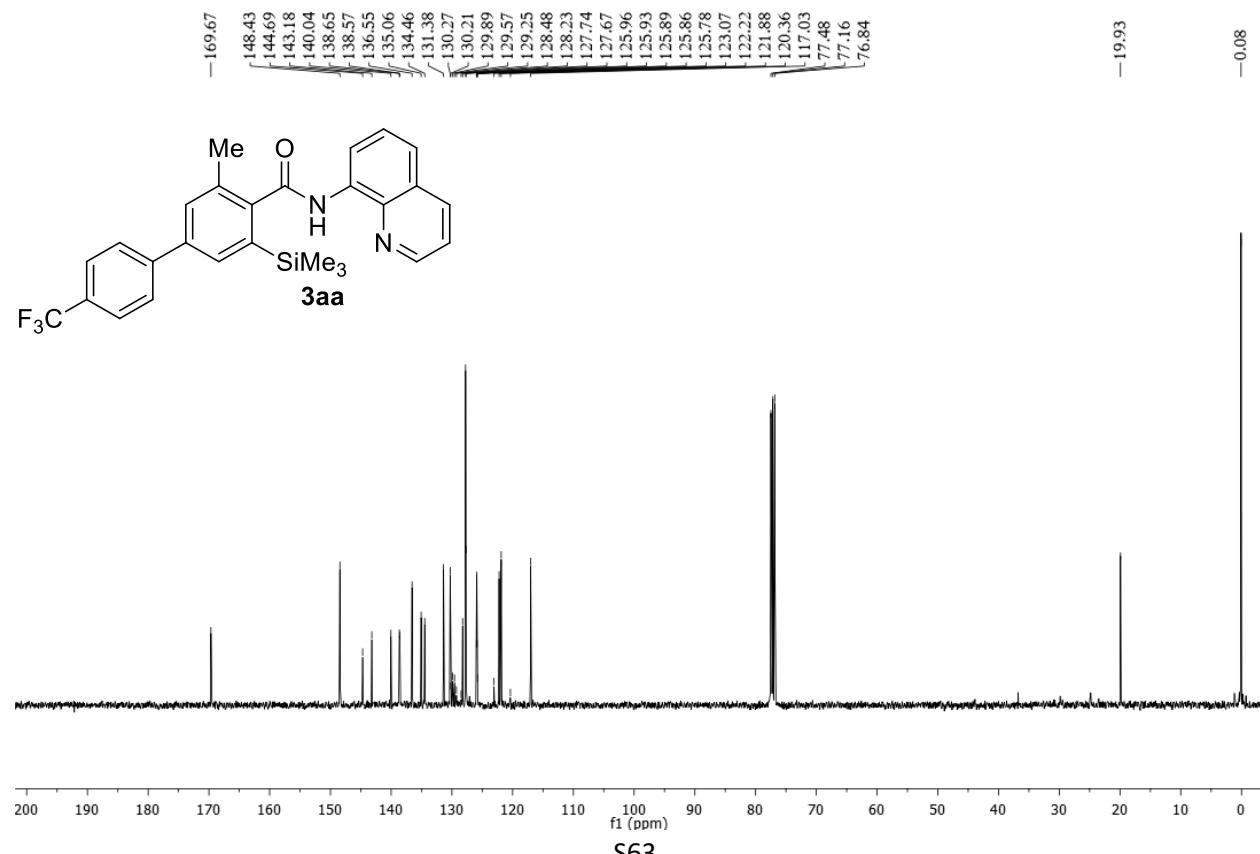
<sup>13</sup>C NMR of **3z** (100 MHz, CDCl<sub>3</sub>):



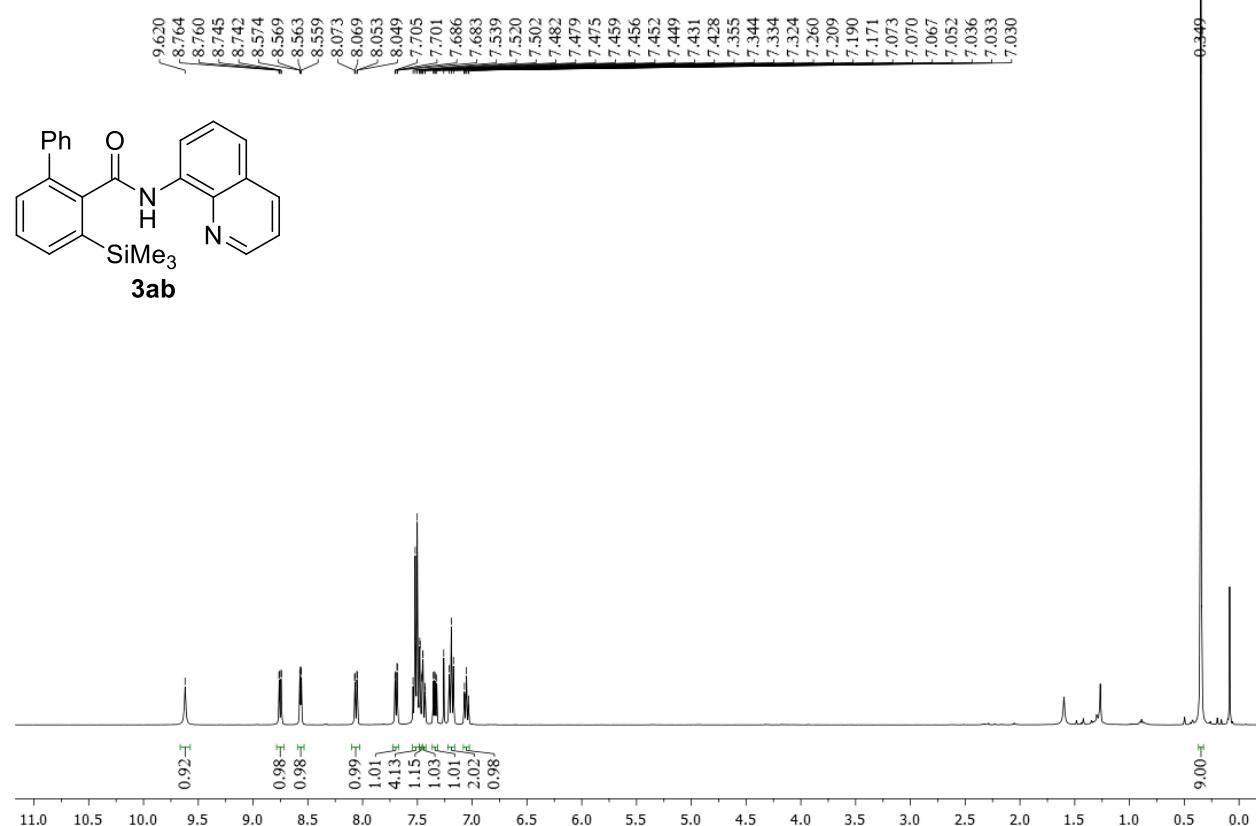
<sup>1</sup>H NMR of **3aa** (400 MHz, CDCl<sub>3</sub>):



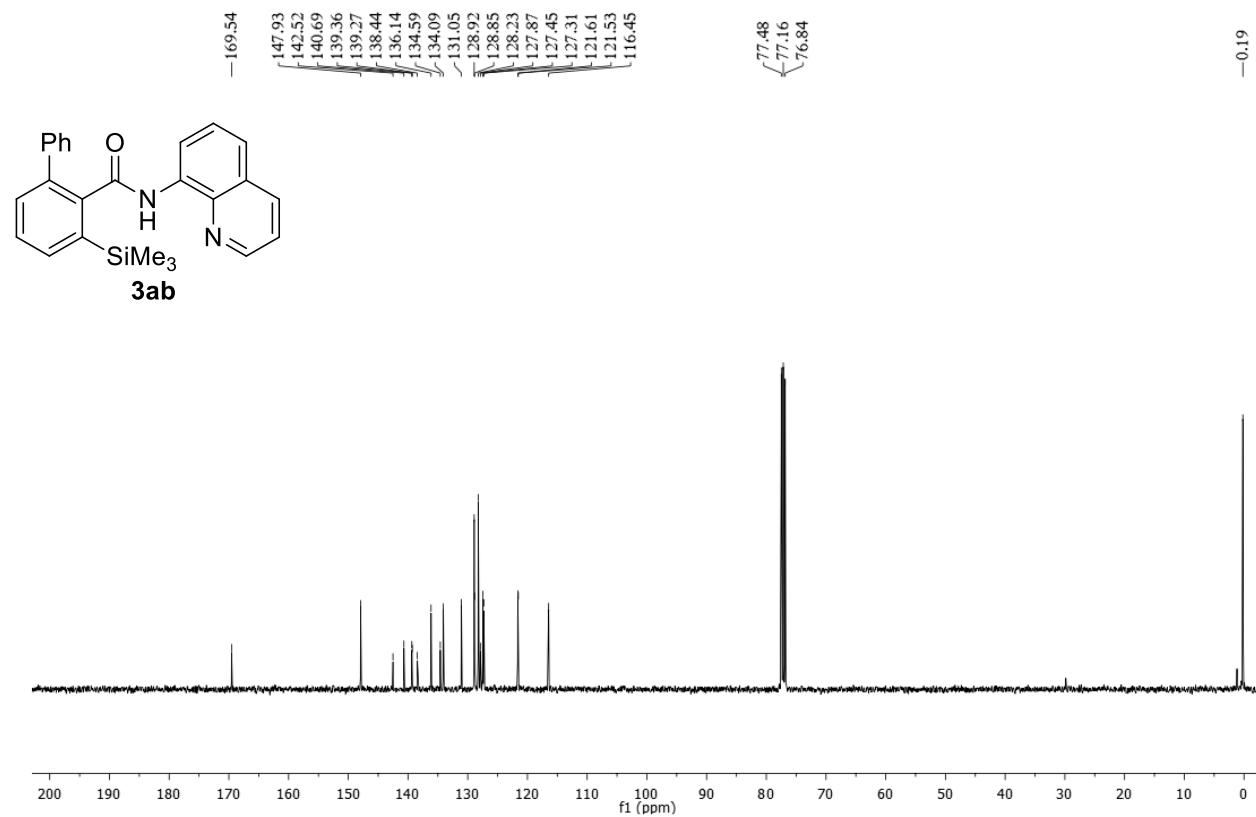
<sup>13</sup>C NMR of **3aa** (100 MHz, CDCl<sub>3</sub>):



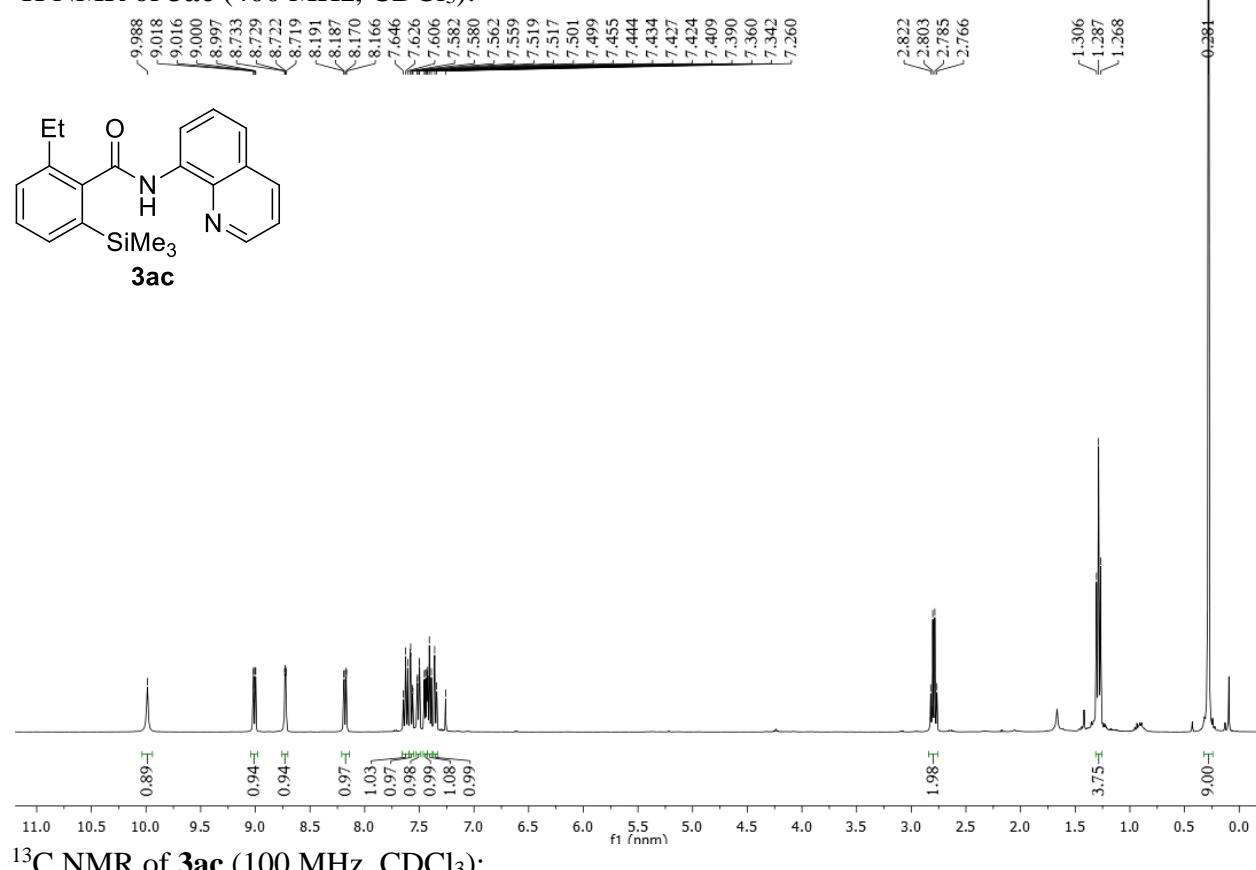
<sup>1</sup>H NMR of **3ab** (400 MHz, CDCl<sub>3</sub>):



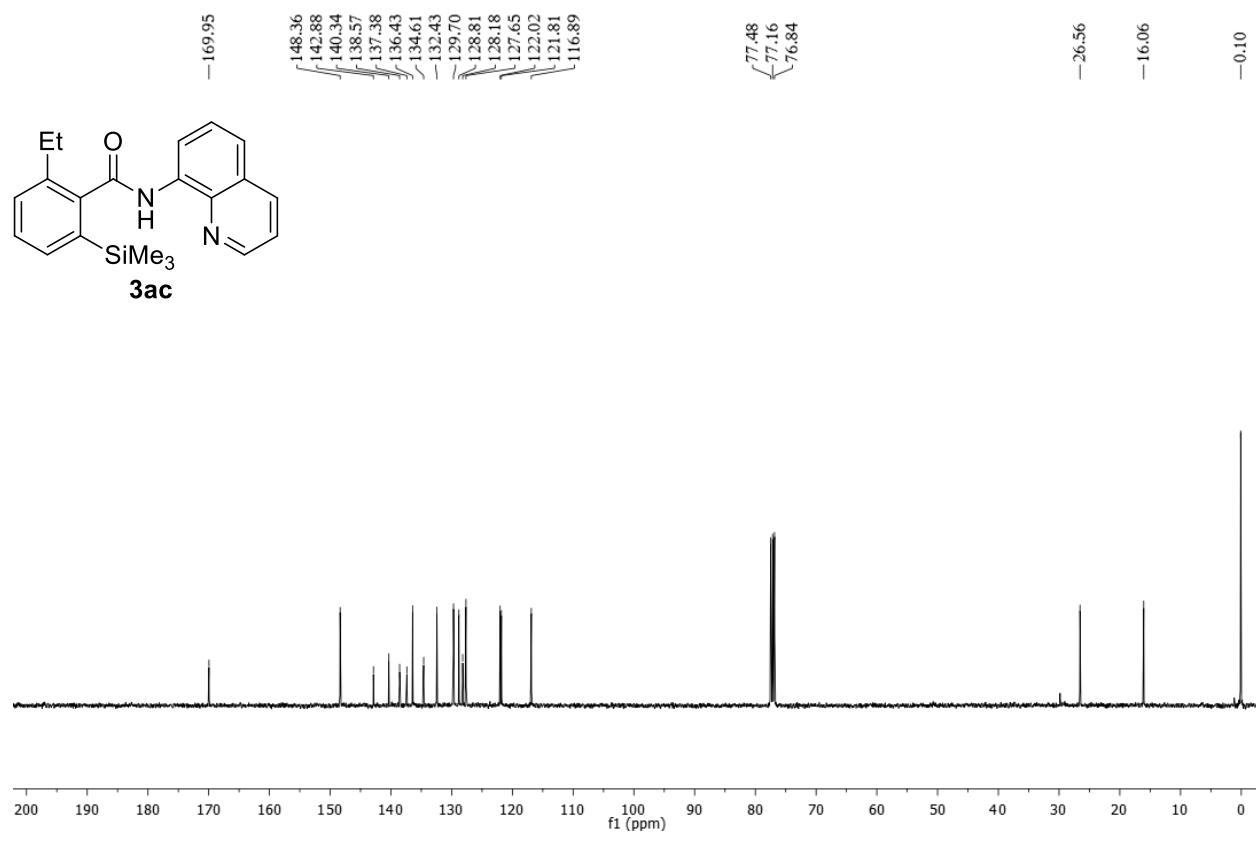
<sup>13</sup>C NMR of **3ab** (100 MHz, CDCl<sub>3</sub>):



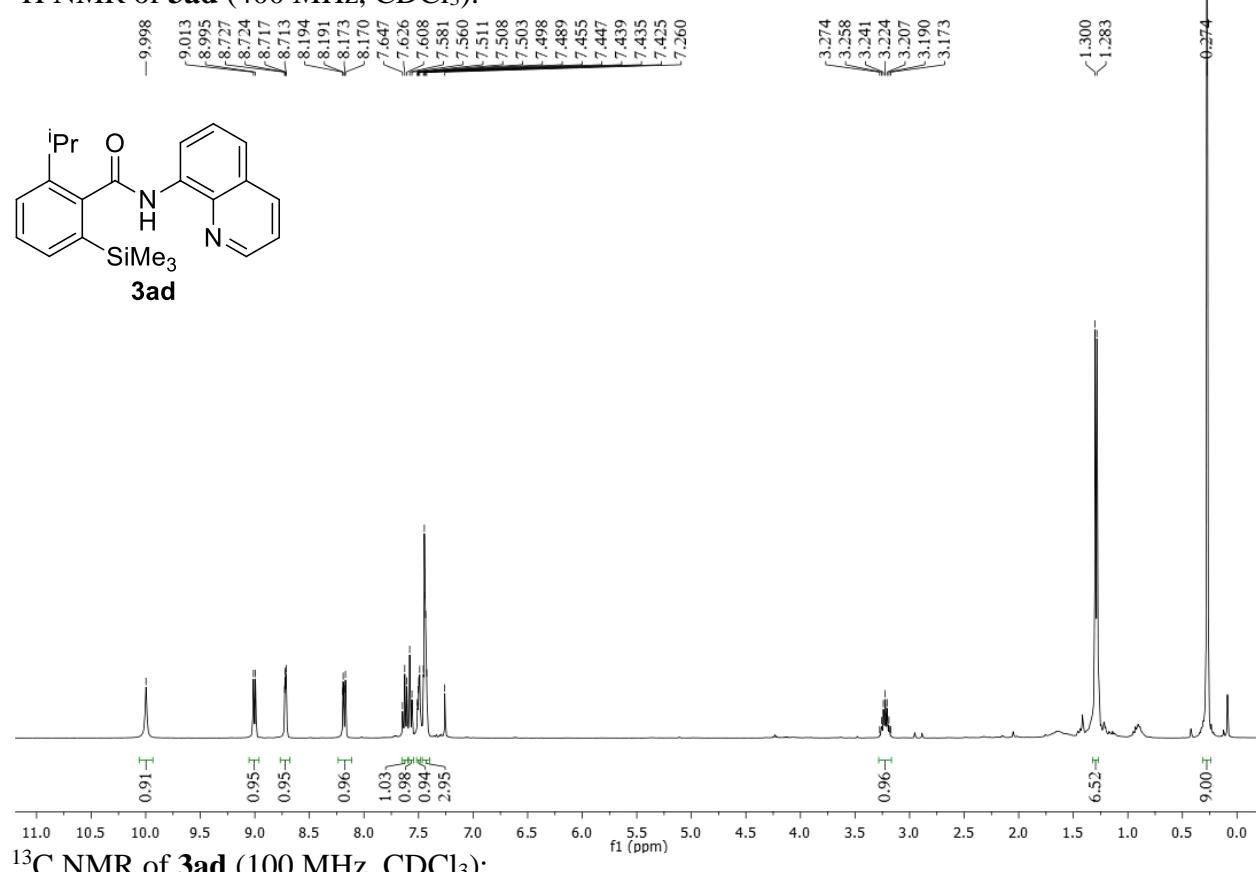
<sup>1</sup>H NMR of **3ac** (400 MHz, CDCl<sub>3</sub>):



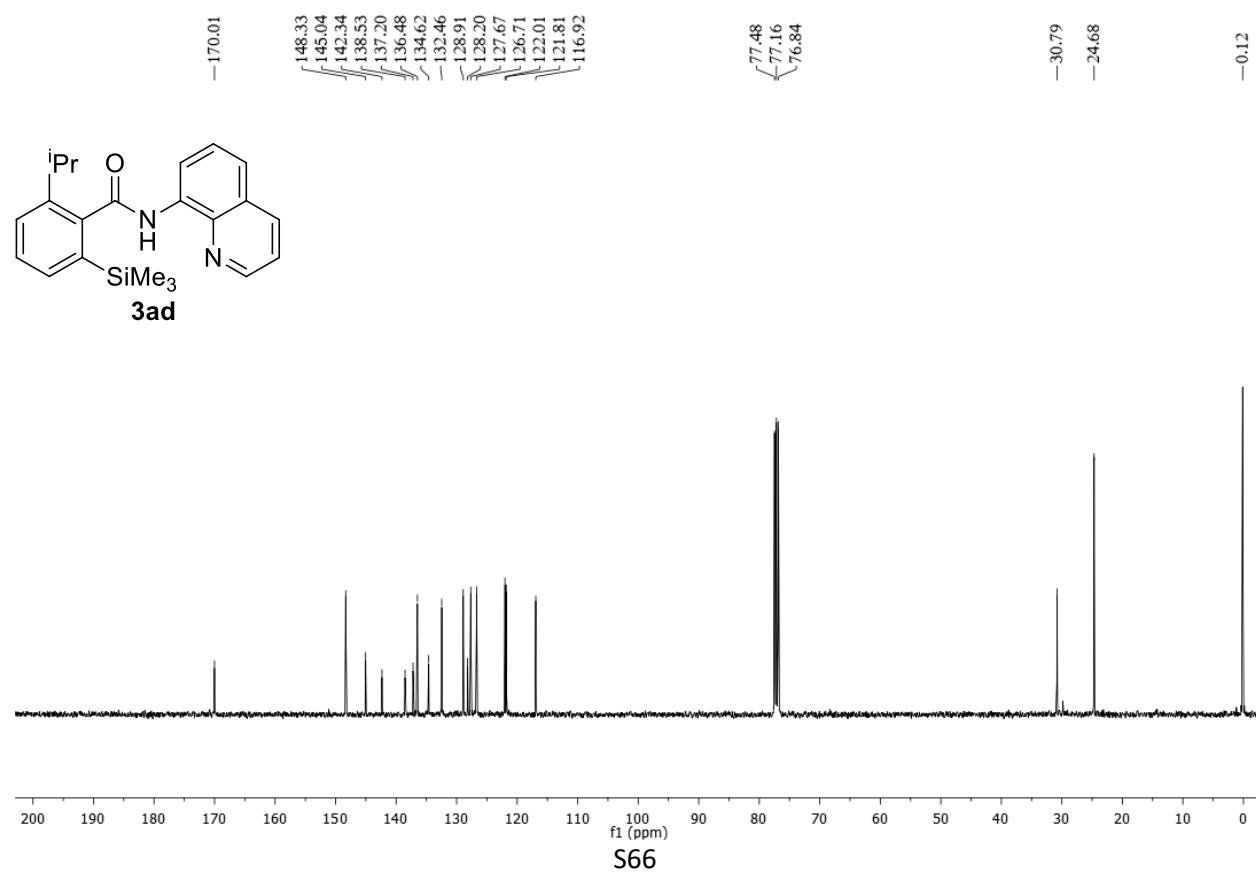
<sup>13</sup>C NMR of **3ac** (100 MHz, CDCl<sub>3</sub>):



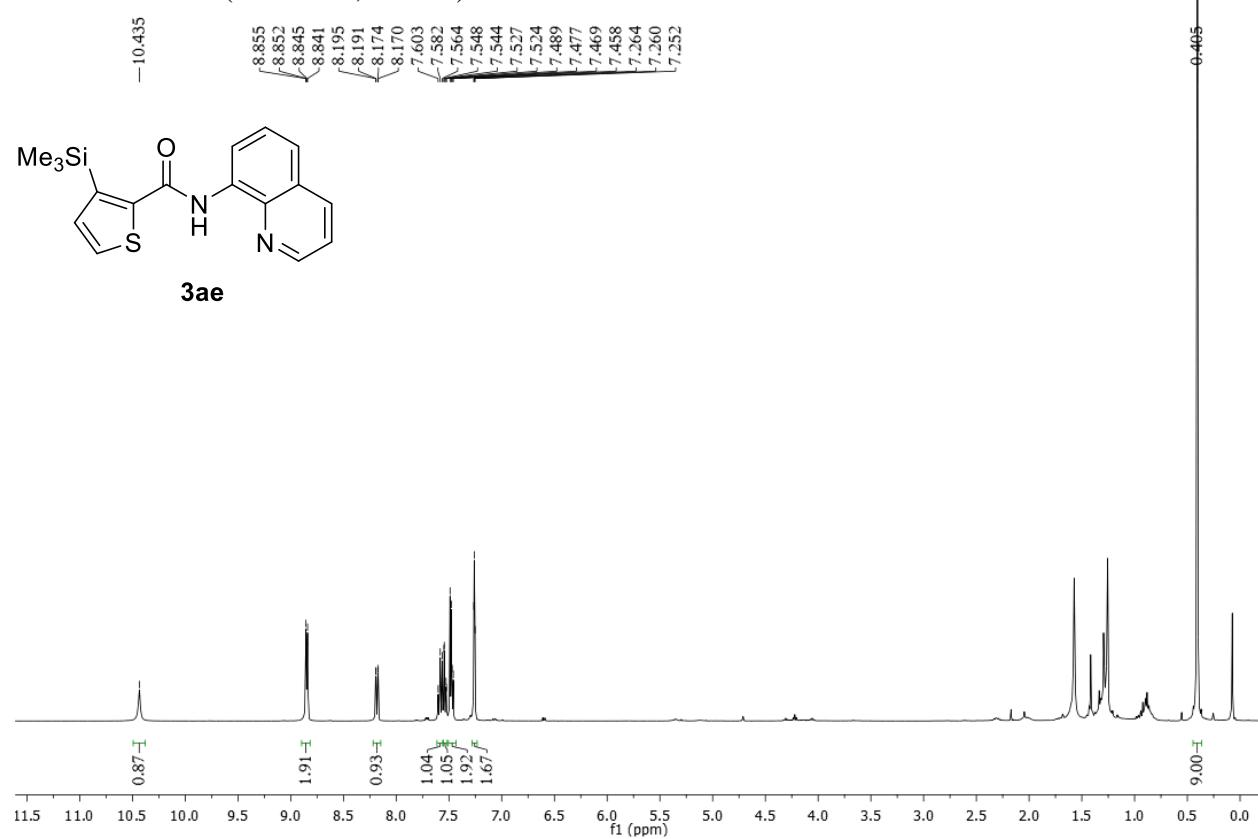
<sup>1</sup>H NMR of **3ad** (400 MHz, CDCl<sub>3</sub>):



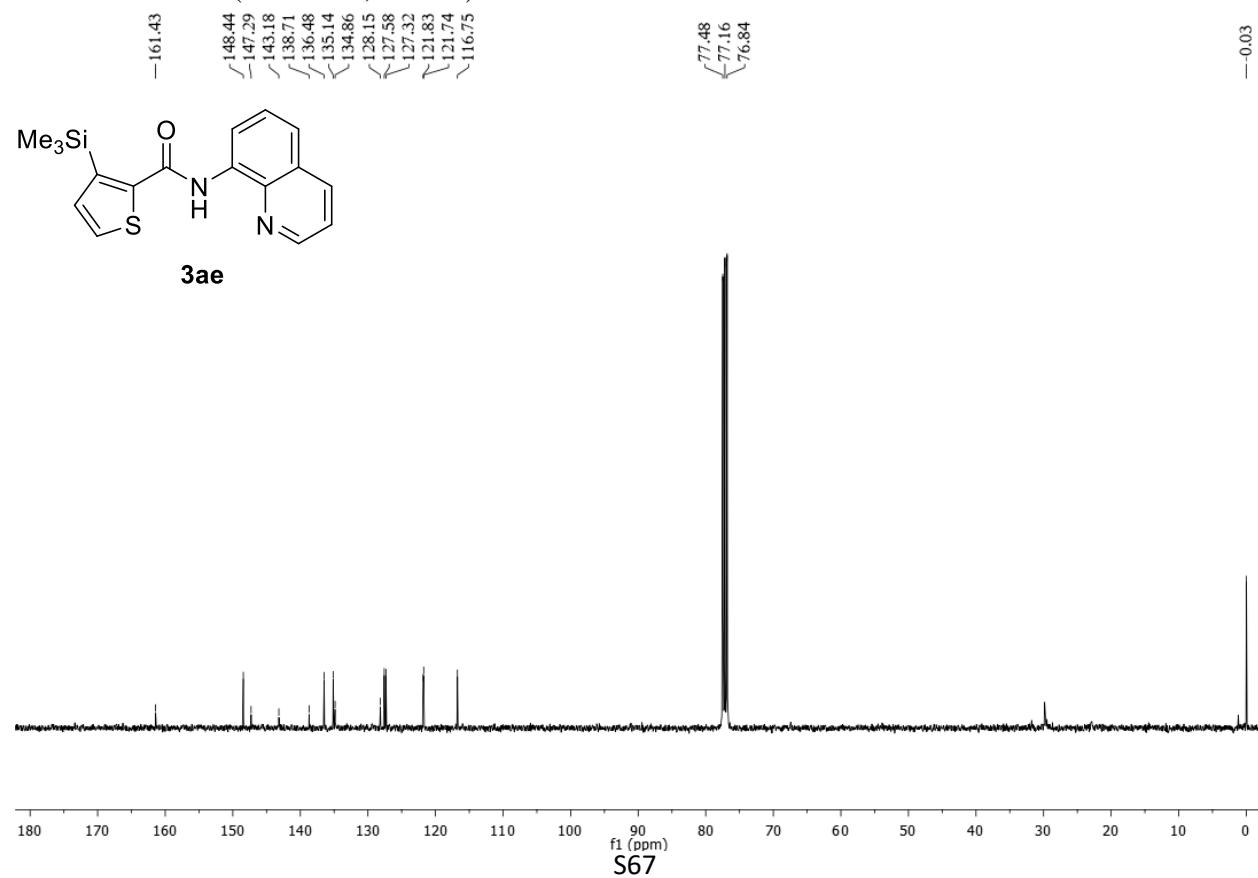
<sup>13</sup>C NMR of **3ad** (100 MHz, CDCl<sub>3</sub>):



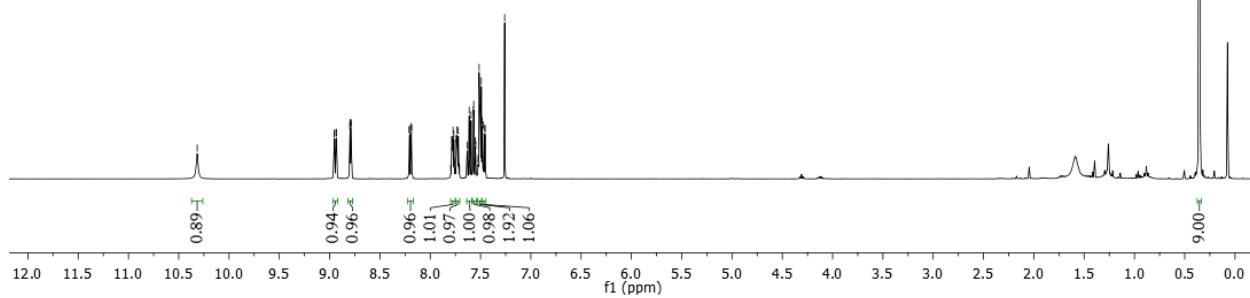
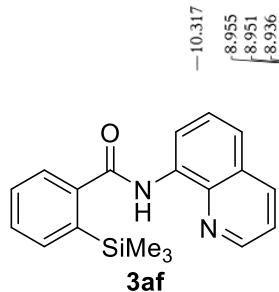
<sup>1</sup>H NMR of **3ae** (400 MHz, CDCl<sub>3</sub>):



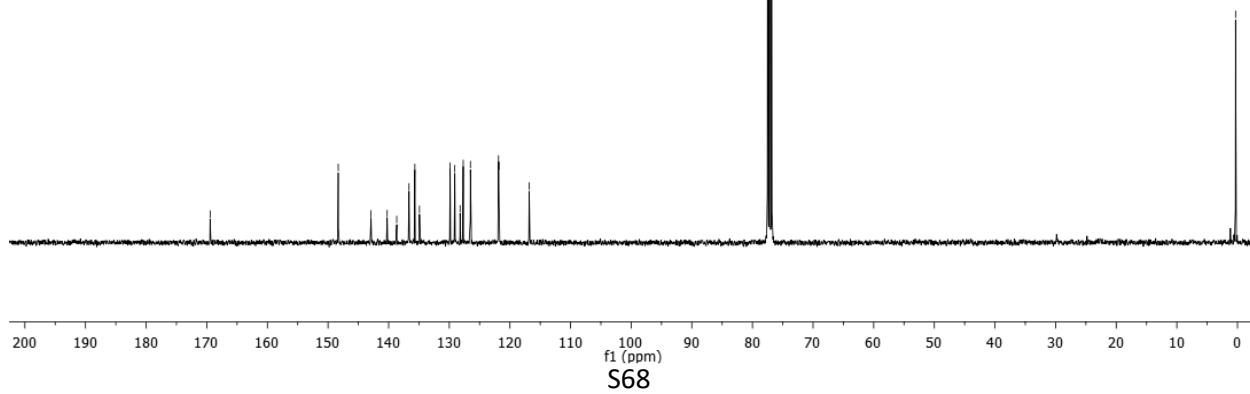
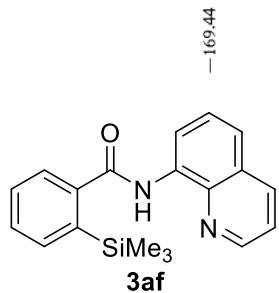
<sup>13</sup>C NMR of **3ae** (100 MHz, CDCl<sub>3</sub>):



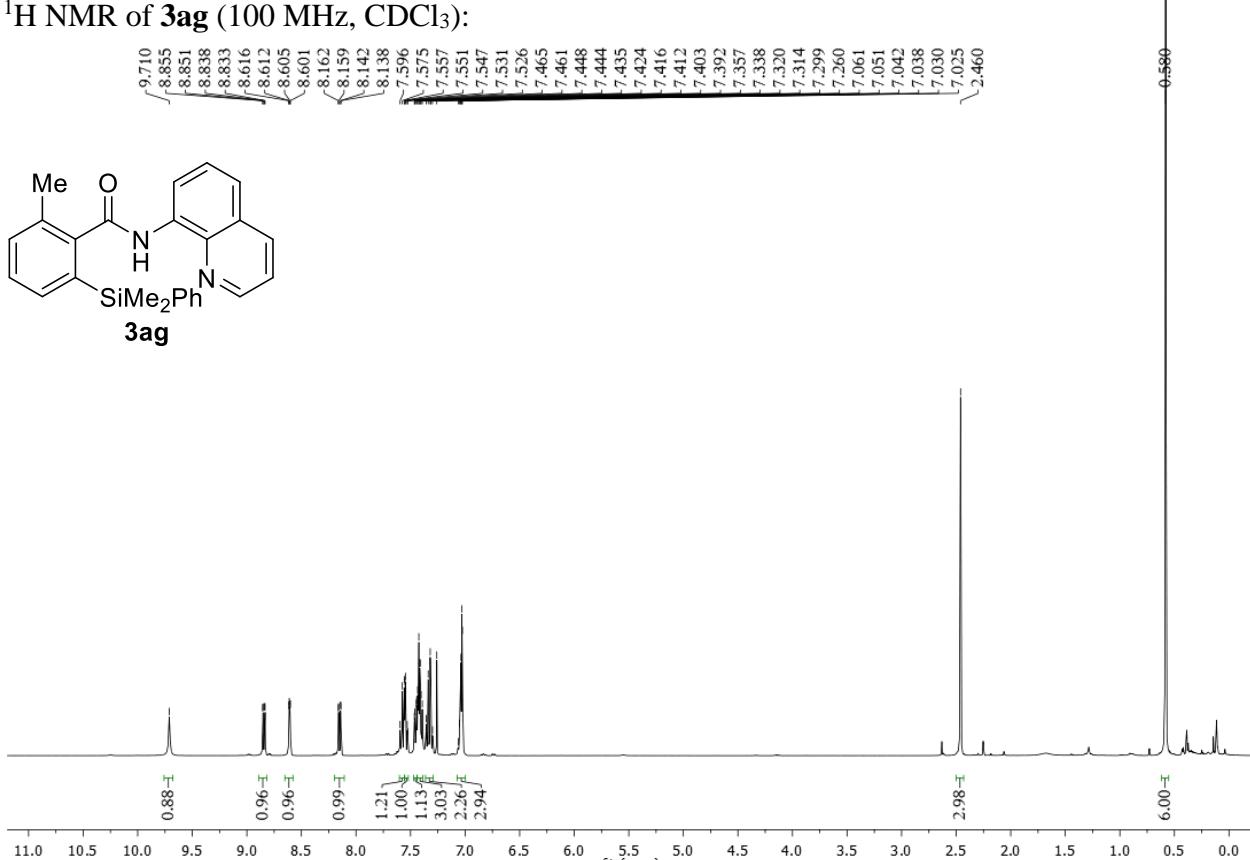
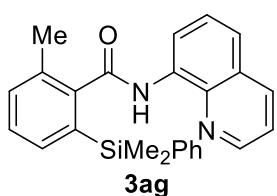
<sup>1</sup>H NMR of **3af** (400 MHz, CDCl<sub>3</sub>):



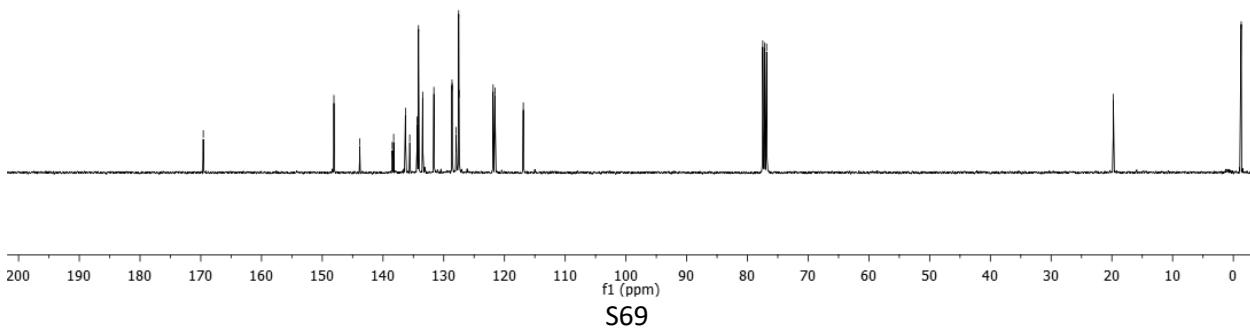
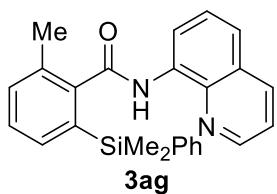
<sup>13</sup>C NMR of **3af** (100 MHz, CDCl<sub>3</sub>):



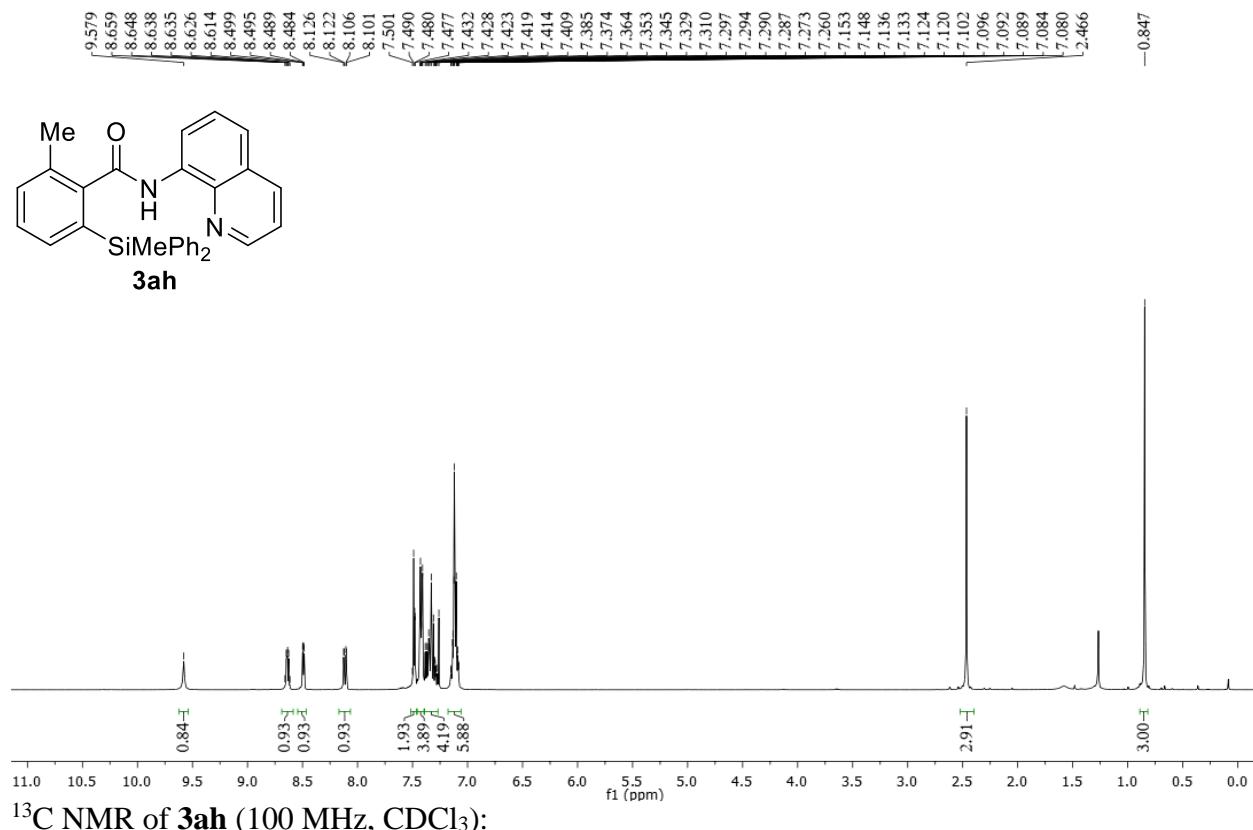
<sup>1</sup>H NMR of **3ag** (100 MHz, CDCl<sub>3</sub>):



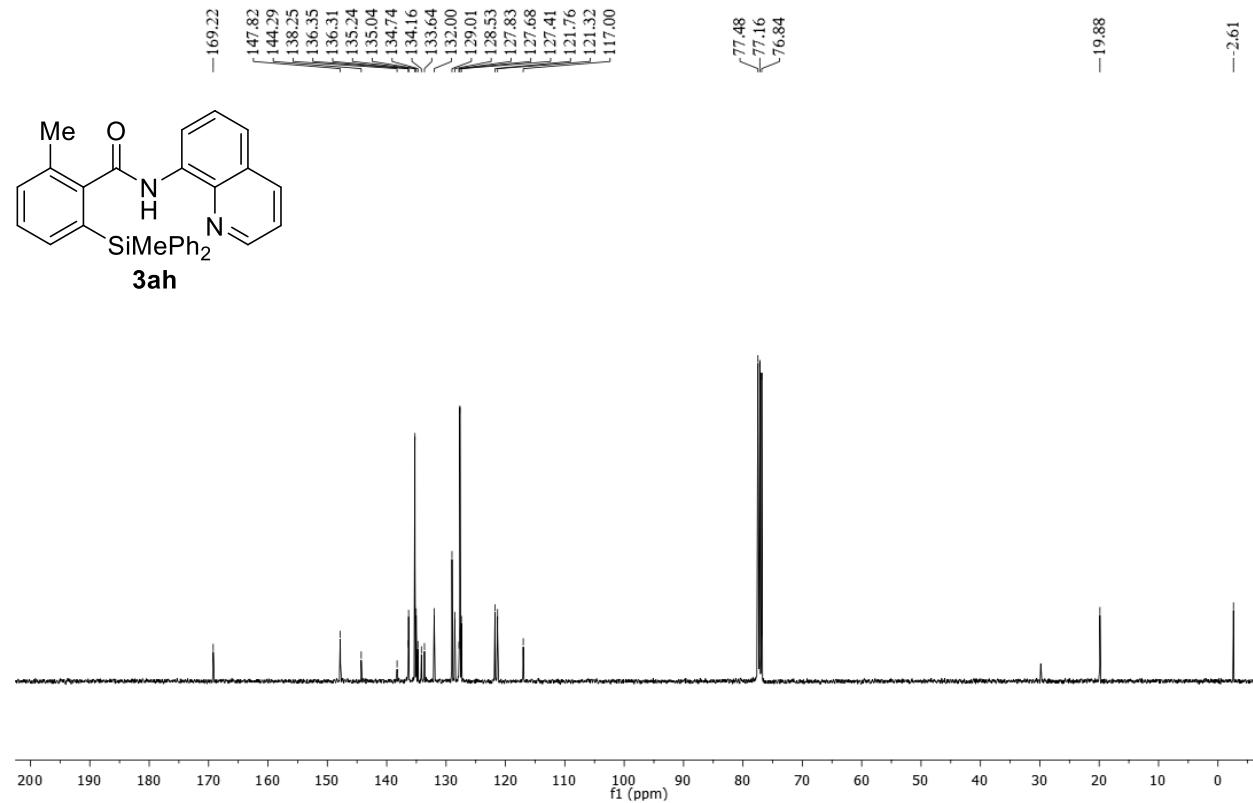
<sup>13</sup>C NMR of **3ag** (100 MHz, CDCl<sub>3</sub>):



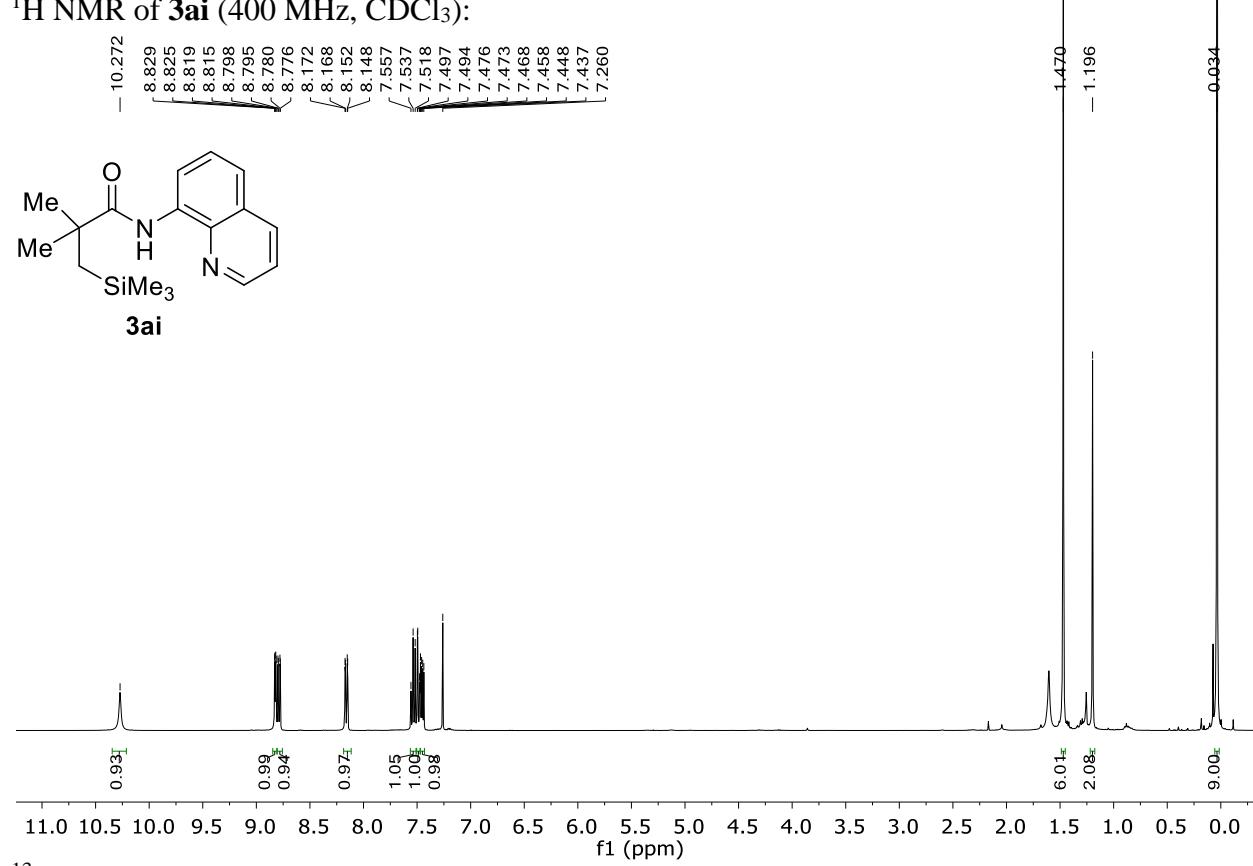
<sup>1</sup>H NMR of **3ah** (400 MHz, CDCl<sub>3</sub>):



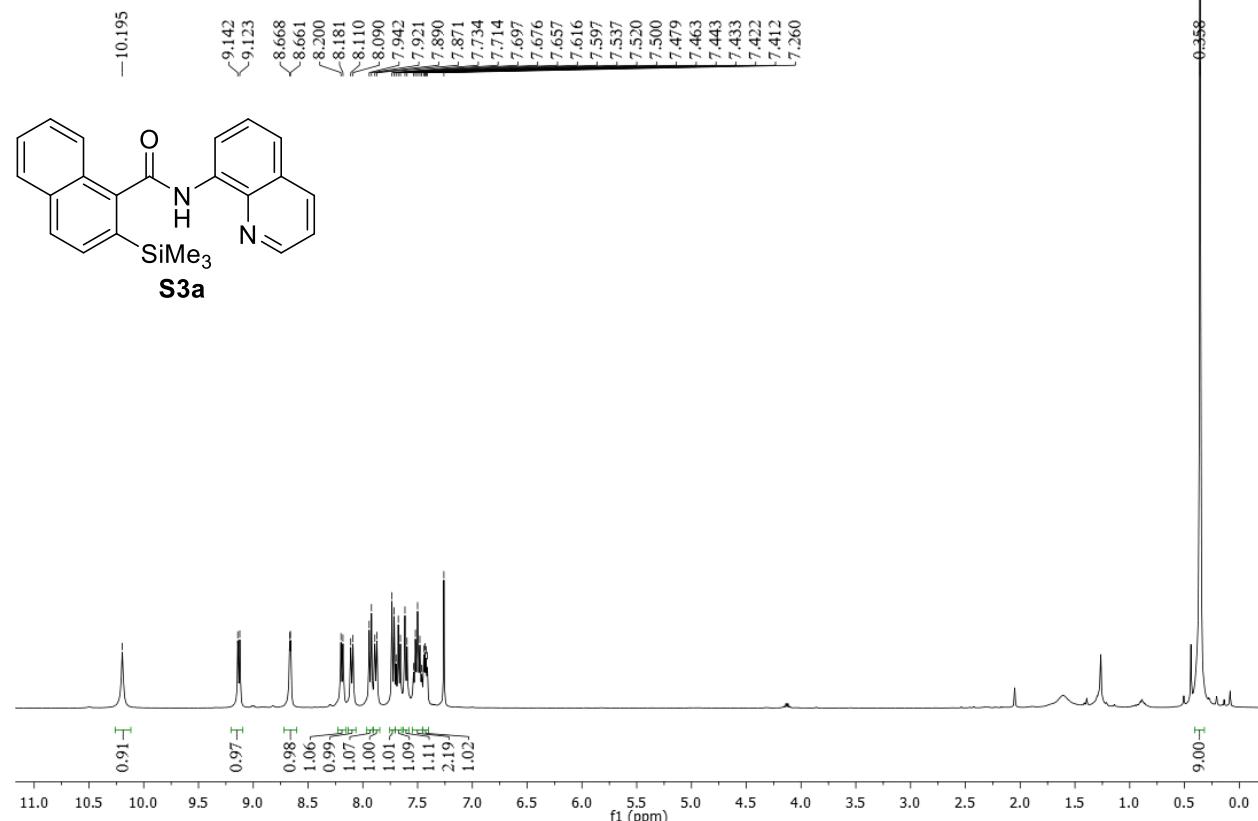
<sup>13</sup>C NMR of **3ah** (100 MHz, CDCl<sub>3</sub>):



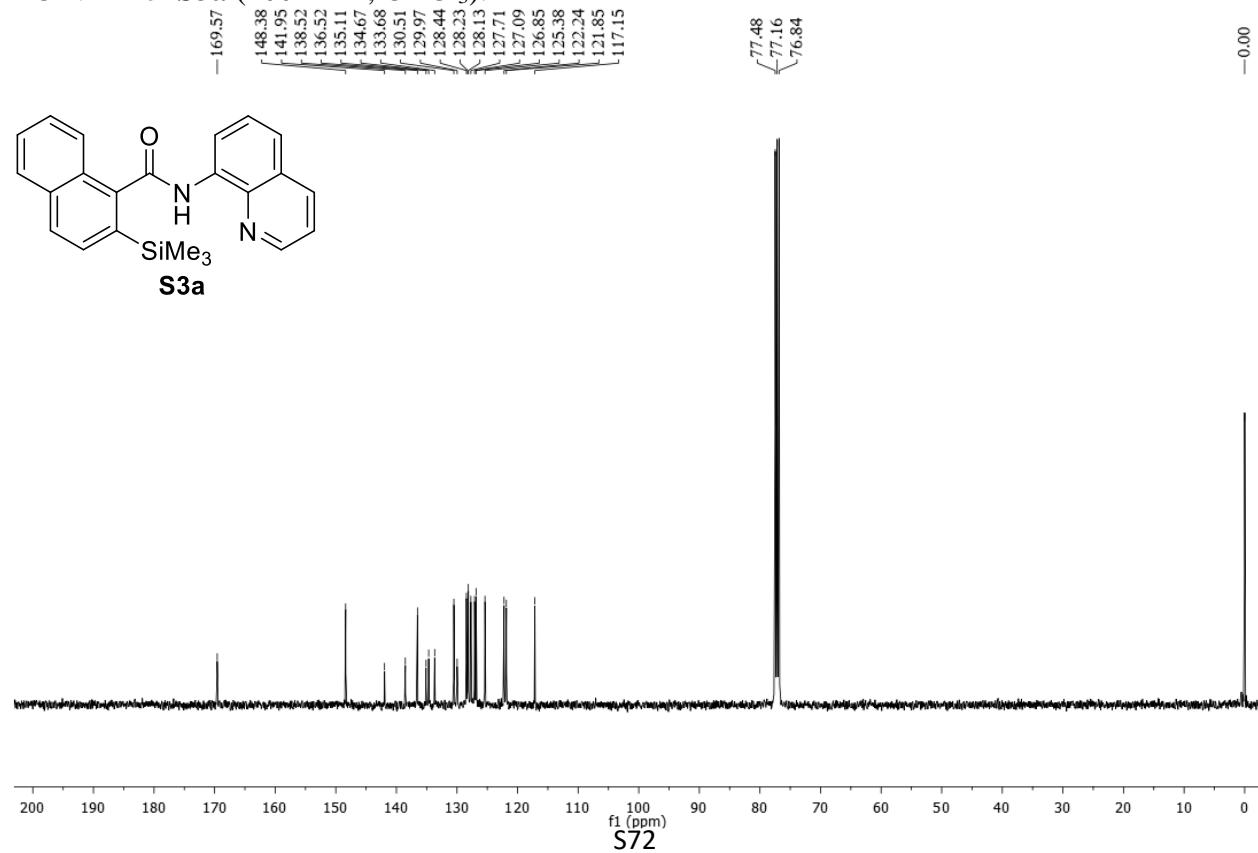
<sup>1</sup>H NMR of **3ai** (400 MHz, CDCl<sub>3</sub>):



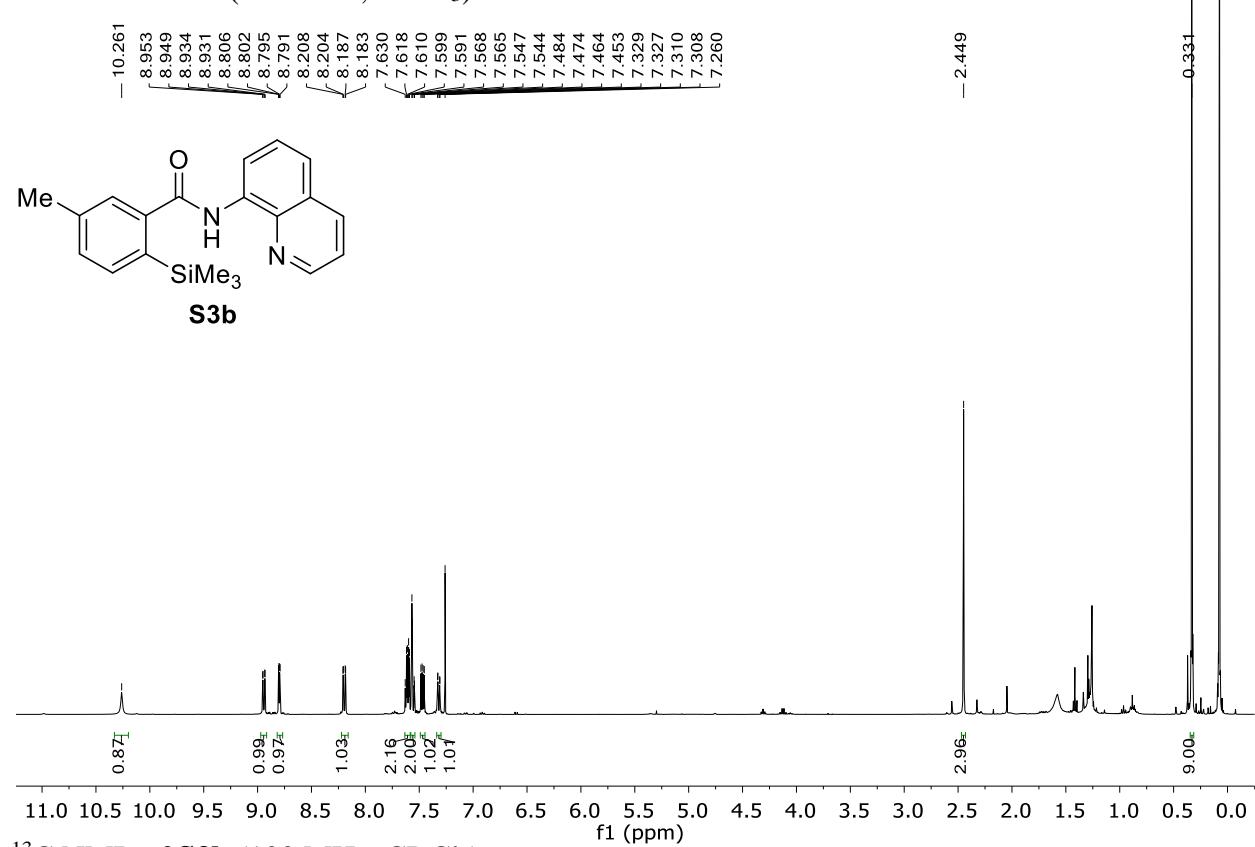
<sup>1</sup>H NMR of **S3a** (400 MHz, CDCl<sub>3</sub>):



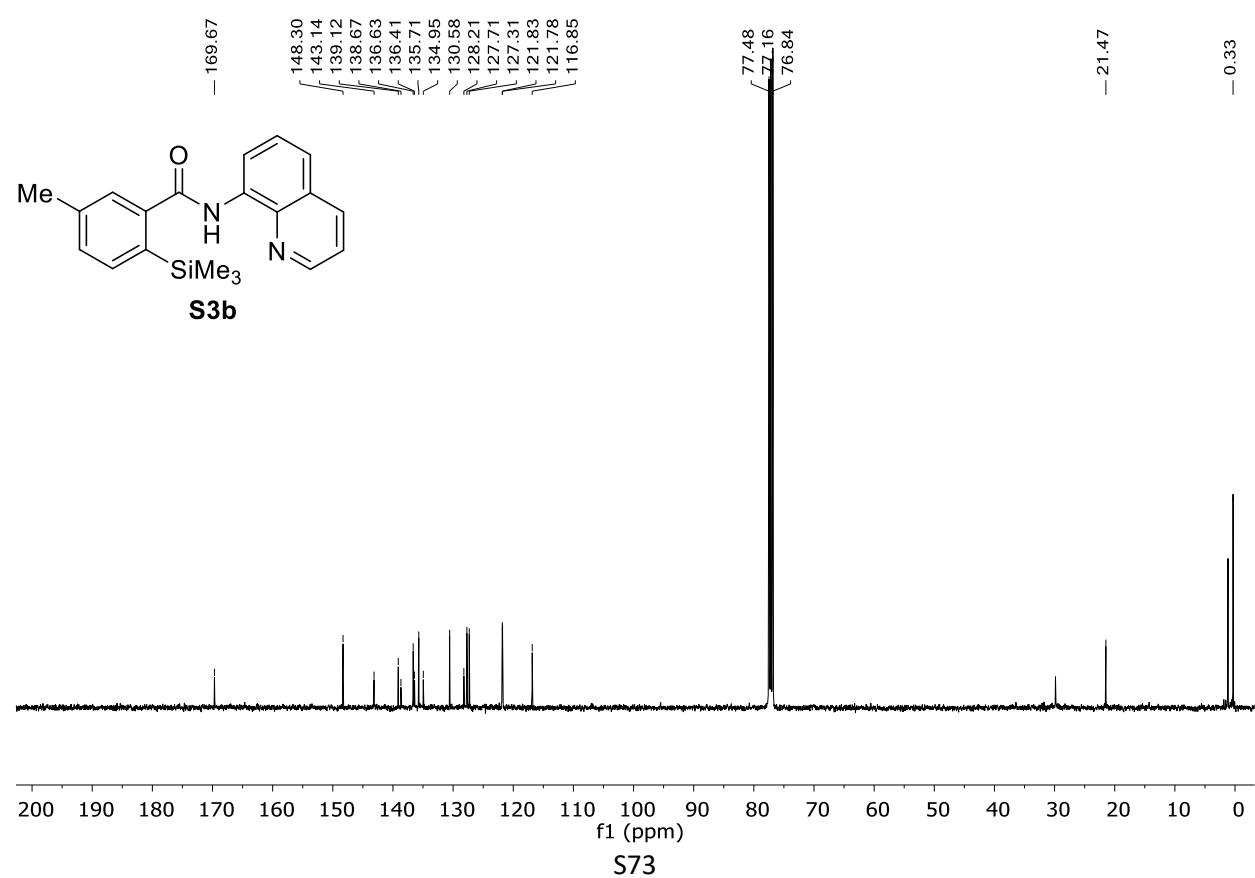
<sup>13</sup>C NMR of **S3a** (100 MHz, CDCl<sub>3</sub>):



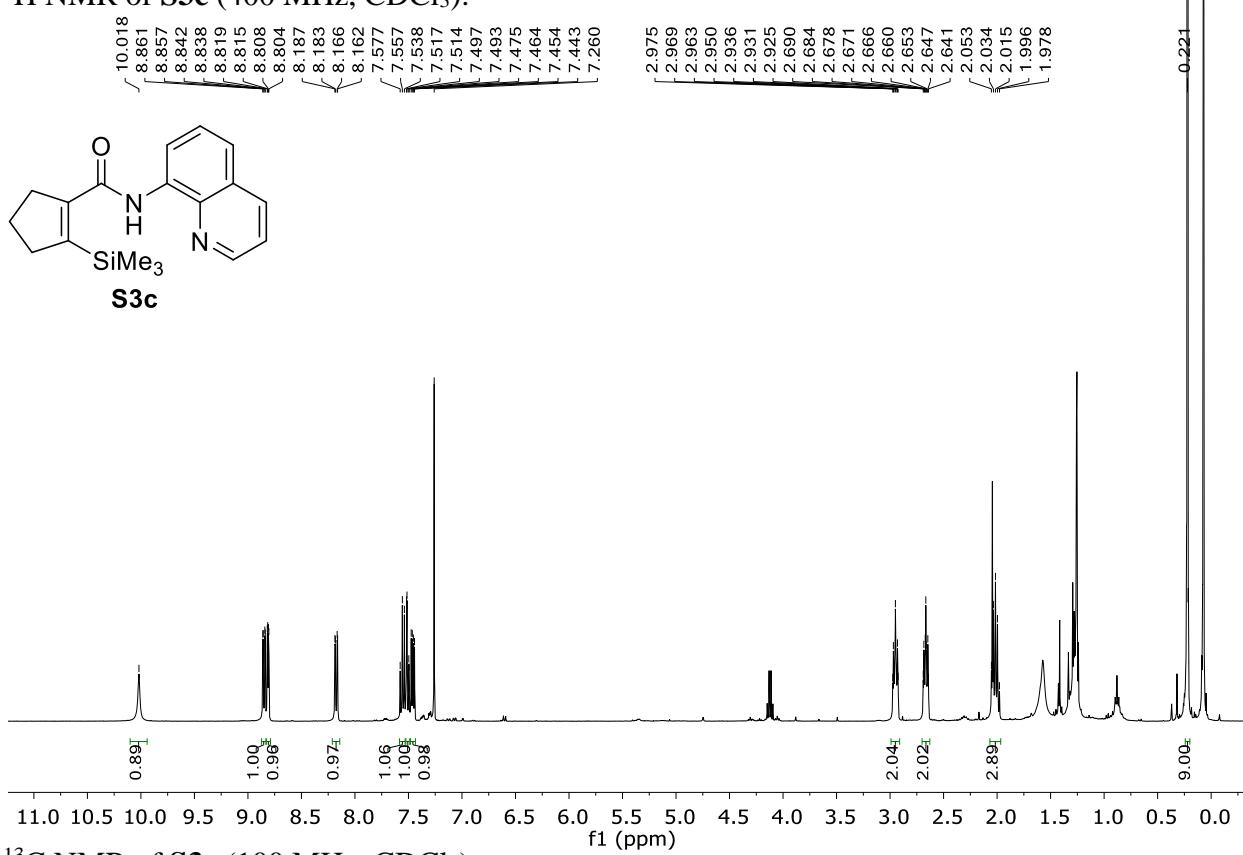
<sup>1</sup>H NMR of **S3b** (400 MHz, CDCl<sub>3</sub>):



<sup>13</sup>C NMR of **S3b** (100 MHz, CDCl<sub>3</sub>):



<sup>1</sup>H NMR of **S3c** (400 MHz, CDCl<sub>3</sub>):



<sup>13</sup>C NMR of **S3c** (100 MHz, CDCl<sub>3</sub>):

