Supporting Information

Ruthenium-Catalyzed Remote C5-Sulfonation of *N*-Alkyl-8-Aminoquinolines

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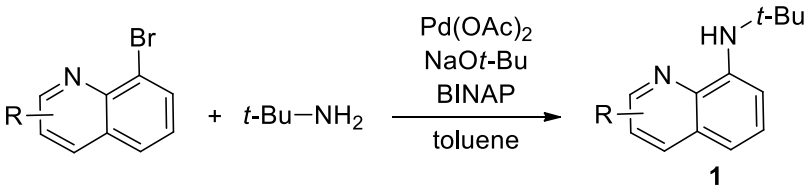
Contents

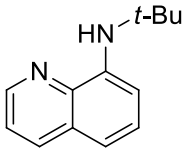
General Remarks

All catalytic reactions were carried out in pre-dried glassware under an argon atmosphere. All solvents were purchased from *Energy Chemical*, *J&K* Scientific and used directly without further purification. Substrates **1a** and **1d-h** were synthesized according to previously described procedures.[1] Other chemicals were obtained from commercial sources and were used without further purification, unless otherwise noted. TLC: Merck TLC Silica gel 60 F_{254}, TLC Aluminum plates. Detection under UV light at 254 nm. Chromatography: Separations were carried out on Qingdao silica gel (60, 0.040-0.063 mm). ^{1}H-NMR spectra were recorded on a 400 MHz Brucker NMR spectrometer in $CDCl_3$ (all signals are reported in ppm with the internal chloroform signal at 7.26 ppm). ^{13}C-NMR spectra were recorded with ^{1}H-decoupling on a 101 or 176 MHz Brucker spectrometer in $CDCl_3$ (all signals are reported in ppm with the internal chloroform signal at 77.16 ppm). Infrared Spectroscopy (IR) were measured on a Bruker FT-IR Alpha device. High-resolution mass spectra (HRMS) were measured on a mass spectrometer (ESI-oa-TOF). Melting points (M. p.) were measured on a melting point with a thermometer and the reported values were uncorrected.

Preparation and Characterization Data for Compounds 1

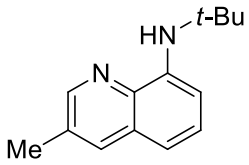


General Procedure A: Literature procedure was used for the synthesis of **1**.[1] $Pd(OAc)_2$ (12.8 mg, 1.9 mol %) and BINAP (35.5 mg, 1.9 mol %) were preheated at 85 °C for 30 min in 5 mL of toluene. The mixture was added to a 50 mL reaction bomb flask containing bromoquinoline (3.0 mmol), *tert*-butylamine (329.1 mg, 4.5 mmol), and sodium *tert*-butoxide (403.6 mg, 4.2 mmol) in 10 mL of toluene. The resulting reaction mixture was dark purple and heated at 110 °C for 24 h. The solution was then cooled to room temperature in air, diluted with EA, and washed with H_2O and brine. The organic layer was collected, dried over Na_2SO_4. Removal of solvent in vacuo yielded a dark brown oil, which was purified by flashing through a column of silica with (PE/EA: 20/1) as the eluent to yield the corresponding products.



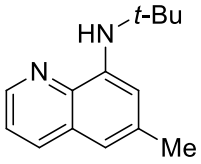
***N*-(*tert*-butyl)-quinolin-8-amine (1a):**

The general procedure A was followed using 8-bromoquinoline (624 mg, 3.0 mmol). Purification by column chromatography on silica gel (PE/EA: 20/1) yielded **1a** (388 mg, 70%) as a yellow liquid. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 8.70 (d, J = 1.6 Hz, 1H), 8.03 (d, J = 8.2 Hz, 1H), 7.34 (d, J = 8.0 Hz, 2H), 7.02 (d, J = 8.1 Hz, 1H), 6.95 (d, J = 7.6 Hz, 1H), 6.47 (s, 1H), 1.54 (s, 9H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ 146.6, 143.4, 139.0, 136.2, 129.0, 127.6, 121.3, 113.3, 107.2, 50.7, 29.6. **IR** (neat): 3373, 2974, 1574, 1526, 1381, 1230, 791 cm^{-1}. **HR-MS** (ESI) m/z calcd. for $C_{13}H_{16}N_2$ ($[M+H]^+$) 201.1392, found: 201.1381.



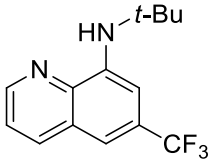
***N*-(*tert*-butyl)-3-methylquinolin-8-amine (1d):**

The general procedure A was followed using 8-bromo-3-methylquinoline (666 mg, 3.0 mmol). Purification by column chromatography on silica gel (PE/EA: 20/1) yielded **1d** (328 mg, 55%) as a yellow liquid. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 8.54 (d, *J* = 2.1 Hz, 1H), 7.80 (s, 1H), 7.32 (dd, *J* = 7.9, 7.9 Hz, 1H), 7.01 – 6.86 (m, 2H), 2.48 (s, 3H), 1.53 (s, 9H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ 148.5, 143.3, 137.4, 135.0, 130.5, 128.8, 127.6, 112.9, 106.6, 50.7, 29.6, 18.7. **IR** (neat): 3373, 2974, 1576, 1521, 1391, 1228, 748 cm^{-1}. **HR-MS** (ESI) m/z calcd. for $C_{14}H_{19}N_2$ ($[M+H]^+$) 215.1548, found: 215.1537.



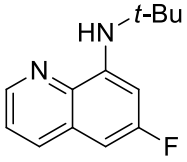
***N*-(*tert*-butyl)-6-methylquinolin-8-amine (1e):**

The general procedure A was followed using 8-bromo-6-methylquinoline (666 mg, 3.0 mmol). Purification by column chromatography on silica gel (PE/EA: 20/1) yielded **1e** (358 mg, 60%) as a yellow liquid. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 8.62 (dd, *J* = 4.2, 1.5 Hz, 1H), 7.94 (dd, *J* = 8.2, 1.1 Hz, 1H), 7.31 (dd, *J* = 8.2, 4.2 Hz, 1H), 6.84 (s, 2H), 2.47 (s, 3H), 1.53 (s, 9H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ 145.8, 143.0, 137.9, 137.4, 135.5, 129.0, 121.4, 112.6, 109.3, 50.6, 29.6, 22.8. **IR** (neat): 3371, 2925, 2855, 1574, 1528, 1383, 1232, 830 cm^{-1}. **HR-MS** (ESI) m/z calcd. for $C_{14}H_{19}N_2$ ($[M+H]^+$) 215.1548, found: 215.1541.



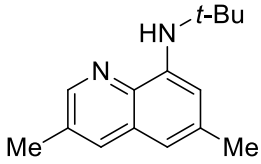
***N*-(*tert*-butyl)-6-(trifluoromethyl)-quinolin-8-amine (1f):**

The general procedure A was followed using 8-bromo-6-(trifluoromethyl)-quinoline (828 mg, 3.0 mmol). Purification by column chromatography on silica gel (PE/EA: 10/1) yielded **1f** (455 mg, 60%) as a yellow solid. **M. p.**: 71-73 °C. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 8.76 (s, 1H), 8.09 (s, 1H), 7.42 (s, 1H), 6.96 (s, 1H), 6.62 (s, 1H), 1.53 (s, 9H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ 148.4, 143.9, 139.8, 137.2, 129.4 (q, J_{C-F}= 31.5 Hz), 127.8, 124.6 (d, J_{C-F} = 272.5 Hz), 122.4, 110.4 (q, J_{C-F} = 4.7 Hz), 101.6 (d, J_{C-F} = 3.2 Hz), 50.9, 29.3. **^{19}F-NMR** (377 MHz, $CDCl_3$) δ -63.0 (s). **IR** (neat): 3383, 2965, 2929, 1579, 1523, 1395, 855 cm^{-1}. **HR-MS** (ESI) m/z calcd. for $C_{14}H_{16}F_3N_2$ ($[M+H]^+$) 269.1266, found:269.1260.



***N*-(*tert*-butyl)-6-fluoroquinolin-8-amine (1g):**

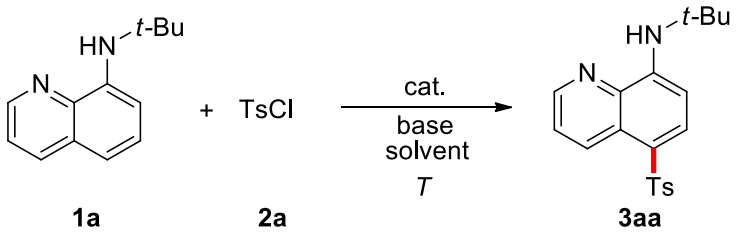
The general procedure A was followed using 8-bromo-6-fluoroquinoline (678 mg, 3.0 mmol). Purification by column chromatography on silica gel (PE/EA: 20/1) yielded **1g** (243 mg, 40%) as a yellow solid. **M. p.**: 60-62 °C. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 8.60 (dd, *J* = 4.2, 1.5 Hz, 1H), 7.94 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.34 (dd, *J* = 8.1, 4.1 Hz, 1H), 6.68 – 6.55 (m, 3H), 1.53 (s, 9H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ 162.2 (d, J_{C-F}= 242.5 Hz), 145.5 (d, J_{C-F}= 2.6 Hz), 145.1 (d, J_{C-F} = 13.9 Hz), 136.4, 135.7 (d, J_{C-F} = 6.0 Hz), 129.5 (d, J_{C-F} = 13.1 Hz), 122.2, 96.7 (d, J_{C-F} = 3-0.9 Hz), 95.7 (d, J_{C-F} = 22.8 Hz), 50.8, 29.3. **^{19}F -NMR** (377 MHz, $CDCl_3$) δ -110.6 (s). **IR** (neat): 3369, 2971, 2931, 1576, 1521, 1391, 1224, 834 cm^{-1}. **HR-MS** (ESI) m/z calcd. for $C_{13}H_{16}FN_2$ ($[M+H]^+$) 219.1298, found: 219.1288.



***N*-(*tert*-butyl)-3, 6-dimethylquinolin-8-amine (1h):**

The general procedure A was followed using 8-bromo-3,6-dimethylquinoline (708 mg, 3.0 mmol). Purification by column chromatography on silica gel (PE/EA: 10/1) yielded **1h** (377 mg, 59%) as a yellow solid. **M. p.**: 49-51 °C. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 8.46 (d, *J* = 1.9 Hz, 1H), 7.69 (s, 1H), 6.72 (d, *J* = 3.6 Hz, 2H), 6.31 (s, 1H), 2.45 (s, 3H), 2.45 (s, 3H), 1.53 (s, 9H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ 147.6, 142.9, 137.4, 136.3, 134.4, 130.6, 128.8, 112.2, 108.7, 50.7, 29.6, 22.8, 18.7. **IR** (neat): 3381, 2965, 1574, 1515, 1383, 1230, 789 cm^{-1}. **HR-MS** (ESI) m/z calcd. for $C_{15}H_{21}N_2$ ($[M+H]^+$) 229.1705, found: 229.1692.

Table S1: Optimization of Catalytic Reaction Conditions.[a]



1a **2a** **3aa**

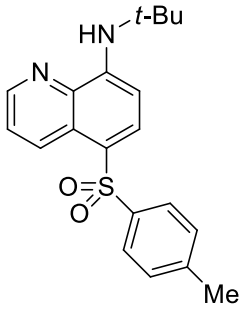
Entry	Catalyst	Base	Solvent	Yield (%)[b]
1	$[RuCl_2(p\text{-cymene})]_2$	K_2CO_3	1,4-dioxane	73
2	$[RuCl_2(p\text{-cymene})]_2$	K_2CO_3	THF	65
3	**$[RuCl_2(p\text{-cymene})]_2$**	**K_2CO_3**	**DME**	**85(82)[c]**
4	$[RuCl_2(p\text{-cymene})]_2$	K_2CO_3	toluene	61
5	$[RuCl_2(p\text{-cymene})]_2$	K_2CO_3	DCE	37
6	$[RuCl_2(p\text{-cymene})]_2$	K_2CO_3	CH_3CN	0
7	$[RuCl_2(p\text{-cymene})]_2$	Na_2CO_3	DME	79
8	$[RuCl_2(p\text{-cymene})]_2$	Cs_2CO_3	DME	10
9	$[RuCl_2(p\text{-cymene})]_2$	K_3PO_4	DME	69
10	$[RuCl_2(p\text{-cymene})]_2$	NaOAc	DME	42
11	$[RuCl_2(p\text{-cymene})]_2$	DBU	DME	0
12	$[RuCl_2(p\text{-cymene})]_2$	Et_3N	DME	0
13[d]	$[RuCl_2(p\text{-cymene})]_2$	K_2CO_3	DME	68
14[e]	$[RuCl_2(p\text{-cymene})]_2$	K_2CO_3	DME	70
15[f]	$[RuCl_2(p\text{-cymene})]_2$	K_2CO_3	DME	60
16	—	K_2CO_3	DME	0
17[g]	$RuCl_2(PPh_3)_3$	K_2CO_3	DME	78
18[g]	$RuCl_3 \cdot 3H_2O$	K_2CO_3	DME	47
19[g]	CuI	K_2CO_3	DME	32
20[g]	$FeCl_3$	K_2CO_3	DME	13
21[g]	$Pd(OAc)_2$	K_2CO_3	DME	trace

[a] Reaction conditions: **1a** (0.25 mmol), **2a** (0.75 mmol), catalyst (5.0 mol%), base (0.50 mmol), solvent (1.0 ml), 120 °C, 16 h, Ar atomsphere. [b] Yield of ^{1}H-NMR with 1,3,5-trimethoxybenzene as the internal standard. [c] Isolated yield in parentheses. [d] **2a** (0.50 mmol). [e] At 110 °C. [f] At 130 °C. [g] Catalyst (10.0 mol %).

Preparation and Characterization Data for Compounds 3

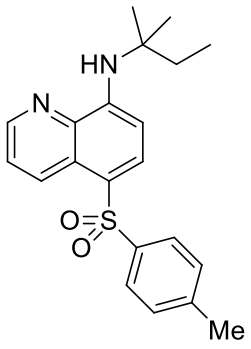
General Procedure B:

A 15 mL pressure sealed tube was equipped with a magnetic stir bar and charged with **1** (0.25 mmol), **2** (0.75 mmol), $[RuCl_2(p\text{-cymene})]_2$ (7.7 mg, 5.0 mol %), and K_2CO_3 (69 mg, 0.50 mmol). The tube was degassed three times with argon, followed by the addition of 1.0 mL anhydrous DME. The mixture was allowed to stir at 120°C for 16 h, and then cooled down to room temperature. The reaction solution was diluted with EtOAc and filtered through a short pad of celite. The filtrate was concentrated *in vacuo* and the resulting residue was purified by column chromatography on silica gel to yield the corresponding products **3**.



***N*-(*tert*-butyl)-5-tosylquinolin-8-amine (3aa):**

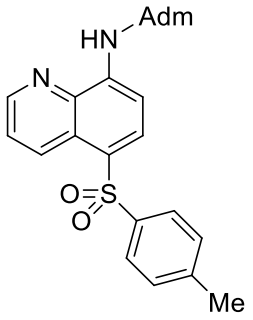
General procedure B was followed using *N*-(*tert*-butyl)-quinolin-8-amine **1a** (50 mg, 0.25 mmol) and 4-methylbenzene-1-sulfonyl chloride **2a** (143 mg, 0.75 mmol). Purification by column chromatography on silica gel (PE/EA: 10/1) yielded **3aa** (73 mg, 82%) as a pale yellow solid. **M. p.**: 162-164 °C. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 8.85 (d, J = 8.6 Hz, 1H), 8.64 (d, J = 1.6 Hz, 1H), 8.30 (d, J = 8.6 Hz, 1H), 7.79 (d, J = 7.7 Hz, 2H), 7.41 (dd, J = 8.0, 3.6 Hz, 1H), 7.22 (d, J = 7.8 Hz, 3H), 6.87 (d, J = 8.6 Hz, 1H), 2.34 (s, 3H), 1.54 (s, 9H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ 148.2, 146.7, 143.2, 140.6, 138.0, 133.2, 133.1, 129.7, 126.9, 125.4, 123.1, 118.5, 103.6, 77.5, 76.8, 51.2, 29.2, 21.6. **IR** (neat): 3357, 3347, 2963, 2927, 2855, 1562, 1379, 1301, 1260, 1195, 814, 683 cm^{-1}. **HR-MS** (ESI) m/z calcd. for $C_{20}H_{23}N_2O_2S$ ($[M+H]^+$) 355.1480, found: 355.1475.



***N*-(*tert*-pentyl)-5-tosylquinolin-8-amine (3ba):**

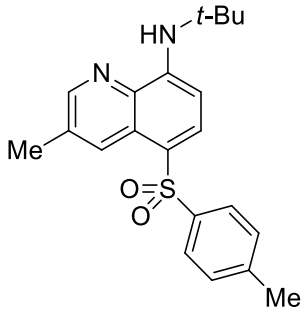
General procedure B was followed using *N*-(*tert*-pentyl)-quinolin-8-amine **1b** (53 mg, 0.25 mmol) and 4-methylbenzene-1-sulfonyl chloride **2a** (143 mg, 0.75 mmol). Purification by column chromatography on silica gel (PE/EA: 10/1) yielded **3ba** (63 mg, 68%) as a pale yellow solid. **M. p.**: 120-122 °C. **^{1}H-NMR**

(400 MHz, $CDCl_3$) δ 8.84 (d, J = 7.8 Hz, 1H), 8.64 (d, J = 2.8 Hz, 1H), 8.28 (d, J = 8.7 Hz, 1H), 7.80 (d, J = 8.2 Hz, 2H), 7.41 (dd, J = 8.7, 4.1 Hz, 1H), 7.22 (d, J = 8.1 Hz, 2H), 7.19 (s, 1H), 6.84 (d, J = 8.7 Hz, 1H), 2.34 (s, 3H), 1.89 (q, J = 7.4 Hz, 2H), 1.48 (s, 6H), 0.92 (t, J = 7.5 Hz, 3H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ 148.3, 146.7, 143.2, 140.6, 138.0, 133.3, 133.1, 129.7, 127.0, 125.4, 123.1, 118.4, 103.4, 54.0, 33.2, 27.0, 21.6, 8.6. **IR** (neat): 3347, 2965, 2920, 2849, 1600, 1562, 1381, 1297, 1132, 814, 681 cm^{-1}. **HR-MS** (ESI) m/z calcd. for $C_{21}H_{25}N_2O_2S$ ($[M+H]^+$) 369.1637, found: 369.1624.



***N*-((3s,5s,7s)-adamantan-1-yl)-5-tosylquinolin-8-amine (3ca):**

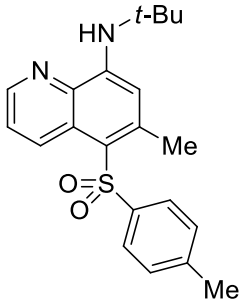
General procedure B was followed using *N*-((3s,5s,7s)-adamantan-1-yl)quinolin-8-amine **1c** (69 mg, 0.25 mmol) and 4-methylbenzene-1-sulfonyl chloride **2a** (143 mg, 0.75 mmol), and $[RuCl_2(p\text{-cymene})]_2$ (15.3 mg, 10.0 mol %). Purification by column chromatography on silica gel (PE/EA: 10/1) yielded **3ca** (84 mg, 78%) as a pale yellow solid. **M. p.**: 215-217 °C. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 8.84 (d, J = 7.8 Hz, 1H), 8.64 (d, J = 2.8 Hz, 1H), 8.28 (d, J = 8.7 Hz, 1H), 7.80 (d, J = 8.2 Hz, 2H), 7.41 (dd, J = 8.7, 4.1 Hz, 1H), 7.22 (d, J = 8.1 Hz, 2H), 7.19 (s, 1H), 6.84 (d, J = 8.7 Hz, 1H), 2.34 (s, 3H), 1.89 (q, J = 7.4 Hz, 2H), 1.48 (s, 6H), 0.92 (t, J = 7.5 Hz, 3H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ 147.9, 146.6, 143.2, 140.6, 138.0, 133.1, 129.7, 126.9, 125.5, 123.0, 118.2, 104.3, 52.0, 41.9, 36.5, 29.7, 21.6. **IR** (neat): 3322, 2916, 2849, 1601, 1532, 1385, 1300, 1138, 810, 679 cm^{-1}. **HR-MS** (ESI) m/z calcd. for $C_{26}H_{29}N_2O_2S$ ($[M+H]^+$) 433.1950, found: 433.1935.



***N*-(*tert*-butyl)-3-methyl-5-tosylquinolin-8-amine (3da):**

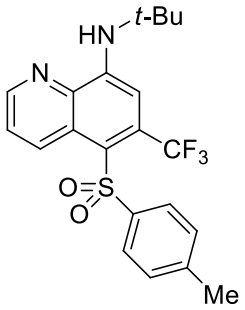
General procedure B was followed using *N*-(*tert*-butyl)-3-methylquinolin-8-amine **1d** (53 mg, 0.25 mmol) and 4-methylbenzene-1-sulfonyl chloride **2a** (143 mg, 0.75 mmol). Purification by column chromatography on silica gel (PE/EA: 10/1) yielded **3da** (56 mg, 61%) as a pale yellow solid. **M. p.**: 205-207 °C. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 8.63 (s, 1H), 8.48 (d, *J* = 1.7 Hz, 1H), 8.26 (d, *J* = 8.7 Hz, 1H), 7.79 (d, *J* = 8.2 Hz, 2H), 7.23 (d, *J* = 8.1 Hz, 2H), 6.82 (d, *J* = 8.7 Hz, 1H), 2.45 (s, 3H), 2.35 (s, 3H), 1.54 (s, 9H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ 148.1, 147.9, 143.3, 140.6, 135.8, 133.3, 132.9, 132.6, 129.7, 126.9, 125.4, 118.1, 103.6, 51.5, 29.2, 21.6(d, *J* = 2.1 Hz), 19.2(d, *J* = 2.2 Hz). **IR** (neat): 3367, 2963, 2920, 2849, 1566, 1379,

1299, 1224, 1138, 816, 687 cm^{-1}. **HR-MS** (ESI) m/z calcd. for $C_{20}H_{23}N_2O_2S$ ($[M+H]^+$) 369.1637, found: 369.1624.



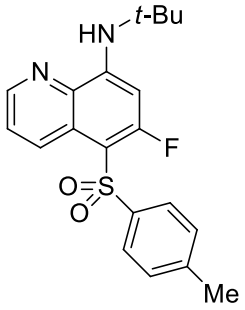
***N*-(*tert*-butyl)-6-methyl-5-tosylquinolin-8-amine (3ea):**

General procedure B was followed using *N*-(*tert*-butyl)-6-methylquinolin-8-amine **1e** (53 mg, 0.25 mmol) and 4-methylbenzene-1-sulfonyl chloride **2a** (143 mg, 0.75 mmol). Purification by column chromatography on silica gel (PE/EA: 10/1) yielded **3ea** (57 mg, 62%) as a pale yellow solid. **M. p.**: 154-156 °C. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 9.34 (dd, *J* = 8.9, 1.3 Hz, 1H), 8.59 (dd, *J* = 4.1, 1.4 Hz, 1H), 7.72 (d, *J* = 8.3 Hz, 2H), 7.41 (dd, *J* = 8.9, 4.1 Hz, 1H), 7.21 (d, *J* = 8.0 Hz, 2H), 6.69 (s, 1H), 2.83 (s, 3H), 2.35 (s, 3H), 1.54 (s, 9H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ 146.9, 145.6, 144.3, 143.1, 141.9, 136.7, 134.3, 129.7, 127.6, 126.0, 122.9, 116.2, 110.2, 51.3, 29.2, 24.8(d, *J* = 1.6 Hz), 21.6(d, *J* = 2.0 Hz). **IR** (neat): 3349, 2976, 2929, 2865, 1532, 1366, 1299, 1222, 1148, 812, 679 cm^{-1}. **HR-MS** (ESI) m/z calcd. for $C_{20}H_{23}N_2O_2S$ ($[M+H]^+$) 369.1637, found: 369.1632.



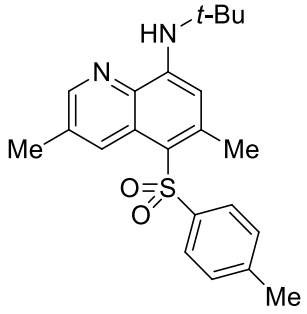
***N*-(*tert*-butyl)-5-tosyl-6-(trifluoromethyl)-quinolin-8-amine (3fa):**

General procedure B was followed using *N*-(*tert*-butyl)-6-(trifluoromethyl)-quinolin-8-amine **1f** (67 mg, 0.25 mmol), 4-methylbenzene-1-sulfonyl chloride **2a** (143 mg, 0.75 mmol), and $[RuCl_2(p\text{-cymene})]_2$ (15.3 mg, 10.0 mol %). Purification by column chromatography on silica gel (PE/EA: 10/1) yielded **3fa** (55 mg, 52%) as a pale yellow solid. **M. p.**: 172-174 °C. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 9.18 (dd, *J* = 9.0, 1.4 Hz, 1H), 8.69 (dd, *J* = 4.0, 1.4 Hz, 1H), 7.78 (d, *J* = 8.3 Hz, 2H), 7.44 (dd, *J* = 9.0, 4.0 Hz, 2H), 7.28 (s, 1H), 7.23 (d, *J* = 8.1 Hz, 2H), 2.36 (s, 3H), 1.58 (s, 9H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ 148.1, 143.4, 141.7, 137.7, 135.9, 133.1 (d, $J_{C\text{-}F}$ = 31.5 Hz), 129.7, 127.5, 126.2, 123.4, 123.4 (d, $J_{C\text{-}F}$ = 275.7 Hz), 117.3, 102.9 (d, $J_{C\text{-}F}$ = 7.9 Hz), 100.1, 51.6, 29.2, 21.6. **^{19}F-NMR** (377 MHz, $CDCl_3$) δ -53.6 (s). **IR** (neat): 3334, 2923, 2851, 1534, 1305, 1220, 1144, 818, 679 cm^{-1}. **HR-MS** (ESI) m/z calcd. for $C_{21}H_{22}F_3N_2O_2S$ ($[M+H]^+$) 423.1354, found: 423.1350.



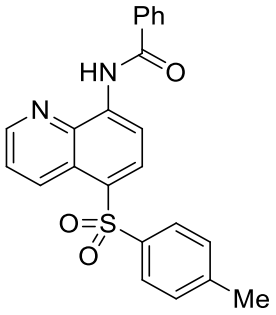
***N*-(*tert*-butyl)-6-fluoro-5-tosylquinolin-8-amine (3ga):**

General procedure B was followed using *N*-(*tert*-butyl)-6-fluoroquinolin-8-amine **1g** (54 mg, 0.25 mmol) and 4-methylbenzene-1-sulfonyl chloride **2a** (143 mg, 0.75 mmol). Purification by column chromatography on silica gel (PE/EA: 10/1) yielded **3ga** (73 mg, 70%) as a pale yellow solid. **M. p.**: 147-149 °C. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 9.56 (dd, *J* = 8.8, 1.5 Hz, 1H), 8.61 (dd, *J* = 4.1, 1.5 Hz, 1H), 7.89 (d, *J* = 8.0 Hz, 2H), 7.52 (dd, *J* = 8.8, 4.1 Hz, 1H), 7.41 (s, 1H), 7.29 – 7.23 (m, 2H), 6.47 (d, *J* = 15.1 Hz, 1H), 2.38 (s, 3H), 1.50 (s, 9H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ 162.6 (d, $J_{C\text{-}F}$ = 255.4 Hz), 149.7 (d, $J_{C\text{-}F}$ = 16.4 Hz), 145.8 (d, $J_{C\text{-}F}$ = 1.8 Hz), 143.6 (s), 141.4 (s), 135.2 (s), 133.4 (d, $J_{C\text{-}F}$ = 6.9 Hz), 129.7 (s), 126.8 (d, $J_{C\text{-}F}$ = 1.7 Hz), 123.9 (s), 105.6 (d, $J_{C\text{-}F}$ = 11.9 Hz), 94.8 (d, $J_{C\text{-}F}$ = 32.3 Hz), 51.4 (s), 29.0 (s), 21.7 (d, *J* = 1.9 Hz). **^{19}F-NMR** (377 MHz, $CDCl_3$) δ -95.8 (s). **IR** (neat): 3332, 2980, 2923, 2872, 1572, 1387, 1303, 1222, 1148, 808, 687 cm^{-1}. **HR-MS** (ESI) m/z calcd. for $C_{20}H_{22}FN_2O_2S$ ($[M+H]^+$) 373.1386, found: 373.1380.



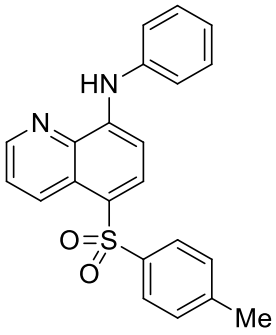
***N*-(*tert*-butyl)-3, 6-dimethyl-5-tosylquinolin-8-amine (3ha):**

General procedure B was followed using *N*-(*tert*-butyl)-3,6-dimethylquinolin-8-amine **1h** (57 mg, 0.25 mmol) and 4-methylbenzene-1-sulfonyl chloride **2a** (143 mg, 0.75 mmol). Purification by column chromatography on silica gel (PE/EA: 10/1) yielded **3ha** (60 mg, 63%) as a pale yellow solid. **M. p.**: 189-191 °C. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 9.10 (s, 1H), 8.42 (d, *J* = 1.7 Hz, 1H), 7.72 (d, *J* = 8.3 Hz, 2H), 7.21 (d, *J* = 8.1 Hz, 2H), 7.12 (s, 1H), 6.62 (s, 1H), 2.80 (s, 3H), 2.44 (s, 3H), 2.35 (s, 3H), 1.53 (s, 9H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ 147.5, 147.2, 144.2, 142.9, 142.2, 135.3, 132.8, 132.5, 129.6, 127.4, 126.0, 115.3, 109.2, 51.0, 29.3, 24.8, 21.6, 19.3. **IR** (neat): 3355, 2982, 2963, 2923, 1552, 1362, 1226, 816, 685 cm^{-1}. **HR-MS** (ESI) m/z calcd. for $C_{22}H_{27}N_2O_2S$ ($[M+H]^+$) 383.1793, found: 383.1794.



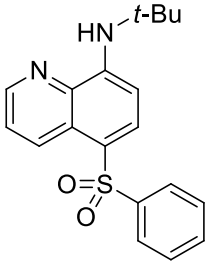
***N*-(5-Tosylquinolin-8-yl)-benzamide (3la):**

General procedure B was followed using *N*-(quinolin-8-yl)-benzamide **1l** (62 mg, 0.25 mmol) and 4-methylbenzene-1-sulfonyl chloride **2a** (143 mg, 0.75 mmol). Purification by column chromatography on silica gel (PE/EA: 10/1) yielded **3la** (24 mg, 24%) as a yellow solid. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 10.97 (s, 1H), 9.06 (dd, *J* = 17.3, 8.6 Hz, 2H), 8.88 (s, 1H), 8.55 (d, *J* = 8.3 Hz, 1H), 8.07 (d, *J* = 7.6 Hz, 2H), 7.84 (d, *J* = 7.7 Hz, 2H), 7.59 (dq, *J* = 15.1, 7.4 Hz, 4H), 7.27 (d, *J* = 7.7 Hz, 2H), 2.36 (s, 3H). The spectra data are in accordance with those reported in the literature.[2]



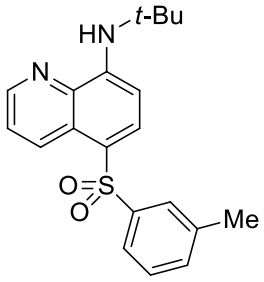
***N*-phenyl-5-tosylquinolin-8-amine (3ma):**

General procedure B was followed using *N*-phenylquinolin-8-amine **1m** (55 mg, 0.25 mmol) and 4-methylbenzene-1-sulfonyl chloride **2a** (143 mg, 0.75 mmol). Purification by column chromatography on silica gel (PE/EA: 10/1) yielded **3ma** (28 mg, 30%) as a pale yellow solid. **M. p.**: 180-182 °C. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 8.96 (dd, *J* = 8.7, 1.2 Hz, 1H), 8.77 (dd, *J* = 4.8, 3.6 Hz, 2H), 8.35 (d, *J* = 8.5 Hz, 1H), 7.81 (d, *J* = 8.2 Hz, 2H), 7.50 (dd, *J* = 8.7, 4.2 Hz, 1H), 7.47 – 7.37 (m, 4H), 7.35 (d, *J* = 8.6 Hz, 1H), 7.24 (d, *J* = 8.1 Hz, 2H), 7.19 (dd, *J* = 7.0 Hz, 7.0 Hz, 1H), 2.35 (s, 3H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ 147.6, 146.3, 143.6, 140.2, 139.7, 137.8, 133.3, 133.0, 129.8, 129.8, 127.1, 125.5, 124.7, 123.5, 122.4, 122.3, 104.2, 21.6. **IR** (neat): 3322, 2923, 2857, 1562, 1517, 1377, 1301, 1146, 820, 683 cm^{-1}. **HR-MS** (ESI) m/z calcd. for $C_{22}H_{19}N_2O_2S$ ($[M+H]^+$) 375.1167, found: 375.1163.



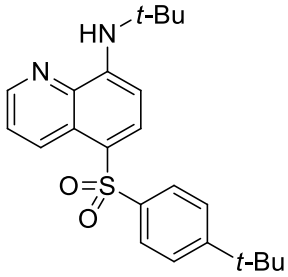
***N*-(*tert*-butyl)-5-(phenylsulfonyl)-quinolin-8-amine (3ab):**

General procedure B was followed using *N*-(*tert*-butyl)quinolin-8-amine **1a** (50 mg, 0.25 mmol) and benzenesulfonyl chloride **2b** (132 mg, 0.75 mmol). Purification by column chromatography on silica gel (PE/EA: 10/1) yielded **3ab** (57 mg, 67%) as a pale yellow solid. **M. p.**: 167-169 °C. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 8.86 (d, *J* = 8.7 Hz, 1H), 8.68 – 8.62 (m, 1H), 8.32 (d, *J* = 8.6 Hz, 1H), 7.91 (d, *J* = 7.4 Hz, 2H), 7.50 – 7.38 (m, 4H), 6.88 (d, *J* = 8.6 Hz, 1H), 1.55 (s, 9H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ 148.2, 146.6, 143.5, 137.9, 133.5, 133.3, 132.5, 129.1, 126.9, 125.5, 123.1, 118.1, 103.8, 51.4, 29.1. **IR** (neat): 3339, 2974, 2965, 2925, 2851, 1562, 1381, 1301, 1218, 1197, 812, 687 cm^{-1}. **HR-MS** (ESI) m/z calcd. for $C_{19}H_{21}N_2O_2S$ ($[M+H]^+$) 341.1324, found: 341.1322.



***N*-(*tert*-butyl)-5-(*m*-tolylsulfonyl)-quinolin-8-amine (3ac):**

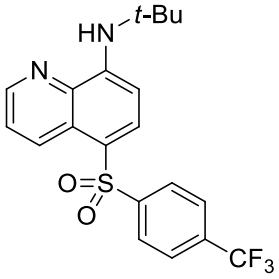
General procedure B was followed using *N*-(*tert*-butyl)quinolin-8-amine **1a** (50 mg, 0.25 mmol) and 3-methylbenzene-1-sulfonyl chloride **2c** (143 mg, 0.75 mmol). Purification by column chromatography on silica gel (PE/EA: 10/1) yielded **3ac** (66 mg, 75%) as a pale yellow solid. **M. p.**: 146-148 °C. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 8.86 (d, *J* = 8.6 Hz, 1H), 8.65 (s, 1H), 8.31 (d, *J* = 8.6 Hz, 1H), 7.70 (s, 2H), 7.46 – 7.39 (m, 1H), 7.35 – 7.27 (m, 2H), 6.89 (d, *J* = 8.6 Hz, 1H), 2.35 (s, 3H), 1.55 (s, 9H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ 148.1, 146.6, 143.4, 139.4, 137.9, 133.4, 129.0, 127.2, 125.6, 124.0, 123.1, 118.4, 103.9, 51.4, 29.2, 21.5. **IR** (neat): 3339, 2974, 2918, 2869, 1562, 1381, 1297, 1220, 1197, 810, 702 cm^{-1}. **HR-MS** (ESI) m/z calcd. for $C_{20}H_{23}N_2O_2S$ ($[M+H]^+$) 355.1480, found: 35501479.



***N*-(*tert*-butyl)-5-{[4-(*tert*-butyl)-phenyl-sulfonyl]-quinolin}-8-amine (3ad):**

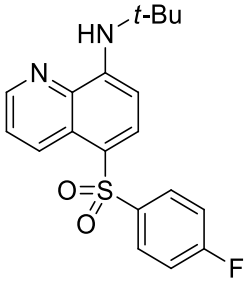
General procedure B was followed using *N*-(*tert*-butyl)quinolin-8-amine **1a** (50 mg, 0.25 mmol) and 4-(*tert*-butyl)-benzene-1-sulfonyl chloride **2d** (175 mg, 0.75 mmol). Purification by column chromatography on silica gel (PE/EA: 20/1) yielded **3ad** (74 mg, 75%) as a yellow solid. **M. p.**: 169-171 °C. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 8.92 (d, *J* = 8.7 Hz, 1H), 8.65 (s, 1H), 8.31 (d, *J* = 8.6 Hz, 1H), 7.83 (d, *J* = 8.0 Hz, 2H), 7.43 (d, *J* = 8.0 Hz, 3H), 6.88 (d, *J* = 8.6 Hz, 1H), 1.55 (s, 9H), 1.27 (s, 9H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ 156.2, 148.0, 146.5, 140.5, 137.8, 133.5, 133.3, 126.8, 126.1, 125.6, 123.1, 118.7, 104.0, 51.4, 35.2, 31.2, 29.1. **IR** (neat): 3357, 3347, 2963, 2929, 2869, 1564, 1383, 1299, 1218, 1193, 814, 673 cm^{-1}. **HR-MS** (ESI)

m/z calcd. for $C_{23}H_{29}N_2O_2S$ ([M+H]$^+$) 397.1950, found: 397.1949.



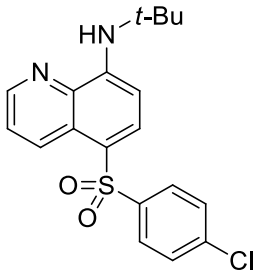
***N*-(*tert*-butyl)-5-{[4-(trifluoromethyl)-phenyl]-sulfonyl}-quinolin-8-amine (3ae):**

General procedure B was followed using *N*-(*tert*-butyl)quinolin-8-amine **1a** (50 mg, 0.25 mmol), 4-(trifluoromethyl)-benzene-1-sulfonyl chloride **2e** (183 mg, 0.75 mmol), and $[RuCl_2(p\text{-cymene})]_2$ (15.3 mg, 10.0 mol %) . Purification by column chromatography on silica gel (PE/EA: 20/1) yielded **3ae** (52 mg, 51%) as a pale yellow solid. **M. p.**: 151-153 °C. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 8.87 (d, J = 8.6 Hz, 1H), 8.67 (s, 1H), 8.33 (d, J = 8.7 Hz, 1H), 8.03 (d, J = 7.9 Hz, 2H), 7.69 (d, J = 7.9 Hz, 2H), 7.50 – 7.43 (m, 1H), 7.40 (s, 1H), 6.92 (d, J = 8.7 Hz, 1H), 1.56 (s, 9H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ 148.8, 147.1, 146.9, 138.0, 134.1 (d, $J_{C\text{-}F}$ = 33.1 Hz), 134.1, 132.7, 127.4, 126.3 (q, $J_{C\text{-}F}$ = 3.7 Hz), 125.5, 123.4, 123.4 (d, $J_{C\text{-}F}$ = 272.8 Hz), 116.6, 103.7, 51.4, 29.1. **^{19}F-NMR** (377 MHz, $CDCl_3$) δ -63.1 (s). **IR** (neat): 3345, 2967, 2923, 1566, 1387, 1299, 1222, 841, 671 cm^{-1}. **HR-MS** (ESI) m/z calcd. for $C_{20}H_{20}F_3N_2O_2S$ ([M+H]$^+$) 409.1198, found: 409.1188.



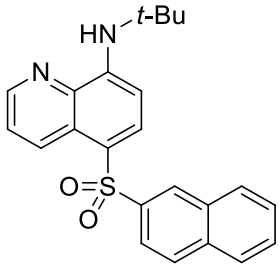
***N*-(*tert*-butyl)-5-[(4-fluorophenyl)-sulfonyl]-quinolin-8-amine (3af):**

General procedure B was followed using *N*-(*tert*-butyl)quinolin-8-amine **1a** (50 mg, 0.25 mmol), 4-fiuorobenzene-1-sulfonyl chloride **2f** (146 mg, 0.75 mmol), and $[RuCl_2(p\text{-cymene})]_2$ (15.3 mg, 10.0 mol %). Purification by column chromatography on silica gel (PE/EA: 15/1) yielded **3af** (47mg, 52%) as a pale yellow solid. **M. p.**: 139-141 °C. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 8.82 (dd, J = 8.7, 1.3 Hz, 1H), 8.65 (dd, J = 4.1, 1.3 Hz, 1H), 8.30 (d, J = 8.7 Hz, 1H), 7.97 – 7.87 (m, 2H), 7.43 (dd, J = 8.7, 4.2 Hz, 1H), 7.29 (s, 1H), 7.10 (dd, J = 8.6, 8.6 Hz, 2H), 6.87 (d, J = 8.7 Hz, 1H), 1.55 (s, 9H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ 164.9 (d, $J_{C\text{-}F}$ = 254.5 Hz), 148.5, 146.8, 139.7 (d, $J_{C\text{-}F}$ = 3.2 Hz), 138.0, 133.5, 132.8, 129.6, 129.5, 125.4, 123.2, 117.6, 116.4, 116.2, 103.6, 51.3, 29.1. **^{19}F-NMR** (377 MHz, $CDCl_3$) δ -105.8 (s). **IR** (neat): 3353, 2974, 2929, 2869, 1566, 1383, 1220, 1146, 818, 687 cm^{-1}. **HR-MS** (ESI) m/z calcd. for $C_{19}H_{20}FN_2O_2S$ ([M+H]$^+$) 359.1230, found: 359.1225.



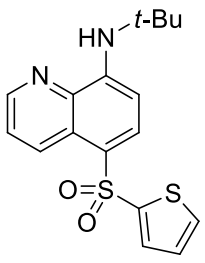
***N*-(*tert*-butyl)-5-[(4-chlorophenyl)-sulfonyl]-quinolin-8-amine (3ag):**

General procedure B was followed using *N*-(*tert*-butyl)quinolin-8-amine **1a** (50 mg, 0.25 mmol), 4-chlorobenzene-1-sulfonyl chloride **2g** (158 mg, 0.75 mmol), and $[RuCl_2(p\text{-cymene})]_2$ (15.3 mg, 10.0 mol %). Purification by column chromatography on silica gel (PE/EA: 15/1) yielded **3ag** (42 mg, 45%) as a pale yellow solid. **M. p.**: 174-176 °C. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 8.82 (d, *J* = 8.6 Hz, 1H), 8.66 (s, 1H), 8.30 (d, *J* = 8.5 Hz, 1H), 7.84 (d, *J* = 7.8 Hz, 2H), 7.42 (dd, *J* = 17.5, 8.2 Hz, 3H), 6.88 (d, *J* = 8.6 Hz, 1H), 1.55 (s, 9H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ 148.5, 146.7, 142.1, 139.0, 137.9, 133.7, 133.1, 129.4, 128.4, 125.5, 123.3, 117.5, 103.8, 51.4, 29.2. **IR** (neat): 3363, 3083, 3059, 2965, 2923, 2853, 1564, 1381, 1309, 1216, 1197, 814, 671 cm^{-1}. **HR-MS** (ESI) m/z calcd. for $C_{19}H_{20}ClN_2O_2S$ ($[M+H]^+$) 375.0934, found: 375.0931.



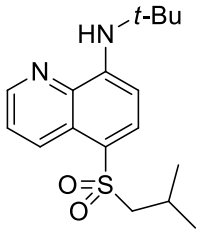
***N*-(*tert*-butyl)-5-(naphthalen-2-ylsulfonyl)-quinolin-8-amine (3ah):**

General procedure B was followed using *N*-(*tert*-butyl)quinolin-8-amine **1a** (50 mg, 0.25 mmol) and naphthalene-2-sulfonyl chloride **2h** (170 mg, 0.75 mmol). Purification by column chromatography on silica gel (PE/EA: 10/1) yielded **3ah** (49 mg, 50%) as a pale yellow solid. **M. p.**: 183-185 °C. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 8.94 (d, *J* = 8.6 Hz, 1H), 8.62 (s, 1H), 8.57 (s, 1H), 8.39 (d, *J* = 8.4 Hz, 1H), 7.96 (d, *J* = 7.1 Hz, 1H), 7.85-7.77 (m, *J* = 8.8 Hz, 3H), 7.58 (d, *J* = 5.0 Hz, 2H), 7.40 (d, *J* = 8.2 Hz, 1H), 6.91 (d, *J* = 8.5 Hz, 1H), 1.55 (s, 9H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ 148.3, 146.6, 140.4, 137.9, 134.8, 133.6, 133.3, 132.3, 129.5, 129.4, 128.8, 128.0, 127.8, 127.5, 125.6, 123.2, 122.5, 118.1, 103.9, 51.4, 29.2. **IR** (neat): 3339, 2967, 2925, 2851, 1562, 1381, 1297, 1218, 1193, 814, 679 cm^{-1}. **HR-MS** (ESI) m/z calcd. for $C_{23}H_{23}N_2O_2S$ ($[M+H]^+$) 391.1480, found:391.1475.



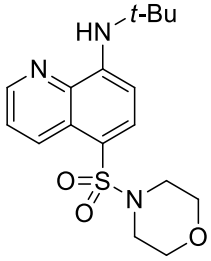
***N*-(*tert*-butyl)-5-(thiophen-2-ylsulfonyl)-quinolin-8-amine (3ai):**

General procedure B was followed using *N*-(*tert*-butyl)quinolin-8-amine **1a** (50 mg, 0.25 mmol) and thiophene-2-sulfonyl chloride **2i** (137 mg, 0.75 mmol). Purification by column chromatography on silica gel (PE/EA: 10/1) yielded **3ai** (26 mg, 30%) as a yellow solid. **M. p.**: 163-165 °C. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 9.03 (d, *J* = 8.5 Hz, 1H), 8.68 (s, 1H), 8.28 (d, *J* = 8.7 Hz, 1H), 7.63 (s, 1H), 7.50 (s, 2H), 6.99 (s, 1H), 6.86 (d, *J* = 8.4 Hz, 1H), 1.55 (s, 9H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ 148.5, 146.8, 145.8, 138.0, 133.2, 132.1, 131.8, 127.4, 125.4, 123.2, 118.9, 103.6, 51.3, 29.2. **IR** (neat): 3349, 3094, 2967, 2925, 2853, 1566, 1383, 1313, 1220, 1195, 816, 683 cm^{-1}. **HR-MS** (ESI) m/z calcd. for $C_{17}H_{19}N_2O_2S_2$ ($[M+H]^+$) 347.0888, found: 347.0880.



***N*-(*tert*-butyl)-5-(isobutylsulfonyl)-quinolin-8-amine (3aj):**

General procedure B was followed using *N*-(*tert*-butyl)quinolin-8-amine **1a** (50 mg, 0.25 mmol), 2-methylpropane-1-sulfonyl chloride **2j** (117 mg, 0.75 mmol), and $[RuCl_2(p\text{-cymene})]_2$ (15.3 mg, 10.0 mol %). Purification by column chromatography on silica gel (PE/EA: 10/1) yiled **3aj** (44 mg, 55%) as a pale yellow solid. **M. p.**: 154-156 °C. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 8.94 (d, *J* = 8.6 Hz, 1H), 8.73 (d, *J* = 3.9 Hz, 1H), 8.09 (d, *J* = 8.6 Hz, 1H), 7.53 (dd, *J* = 8.6, 4.1 Hz, 1H), 7.25 (s, 1H), 6.85 (d, *J* = 8.6 Hz, 1H), 3.05 (d, *J* = 6.3 Hz, 2H), 2.25 (dt, *J* = 13.5, 6.7 Hz, 1H), 1.56 (s, 9H), 1.03 (d, *J* = 6.7 Hz, 6H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ 148.2, 146.8, 138.0, 133.5, 132.9, 125.8, 123.3, 117.8, 103.6, 64.7, 51.2, 29.2, 24.4, 23.0. **IR** (neat): 3396, 3332, 2961, 2874, 1566, 1534, 1389, 1295, 1126, 789 cm^{-1}. **HR-MS** (ESI) m/z calcd. for $C_{17}H_{25}N_2O_2S$ ($[M+H]^+$) 321.1637, found: 321.1635.

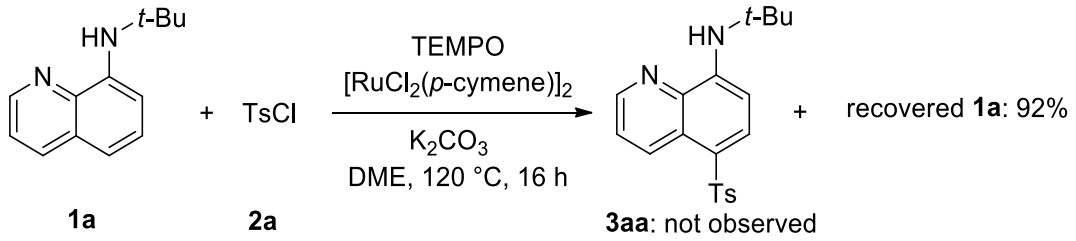


***N*-(*tert*-butyl)-5-(morpholinosulfonyl)-quinolin-8-amine (3ak):**

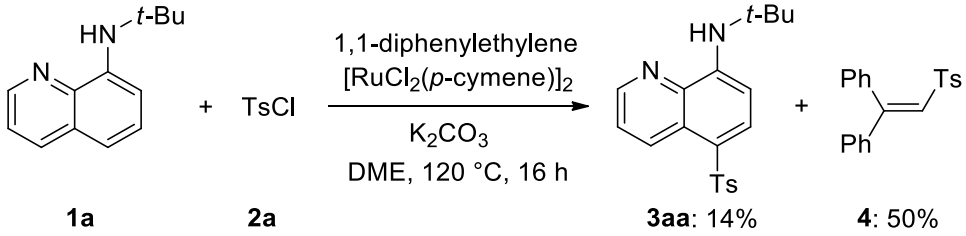
General procedure B was followed using *N*-(*tert*-butyl)quinolin-8-amine **1a** (50 mg, 0.25 mmol), morpholine-4-sulfonyl chloride **2k** (139 mg, 0.75 mmol), and $[RuCl_2(p\text{-cymene})]_2$ (15.3 mg, 10.0 mol %). Purification by column chromatography on silica gel (PE/EA: 10/1) yielded **3ak** (35 mg, 40%) as a pale yellow solid. **M. p.**: 167-169 °C. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 8.96 (dd, *J* = 8.7, 1.5 Hz, 1H), 8.71 (dd, *J* = 4.1, 1.5 Hz, 1H), 8.03 (d, *J* = 8.6 Hz, 1H), 7.49 (dd, *J* = 8.7, 4.1 Hz, 1H), 6.82 (d, *J* = 8.7 Hz, 1H), 3.69 (t, 4H), 3.09 (t, 4H), 1.56 (s, 9H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ 148.1, 146.8, 138.0, 134.4, 133.9, 126.0, 123.0, 113.3, 103.3, 76.8, 66.4, 51.2, 45.6, 29.2. **IR** (neat): 3357, 2971, 2923, 2855, 1568, 1526, 1220, 1150,

816, 720 cm^{-1}. **HR-MS** (ESI) m/z calcd. for $C_{17}H_{24}N_3O_3S$ ($[M+H]^+$) 350.1538, found: 350.1527.

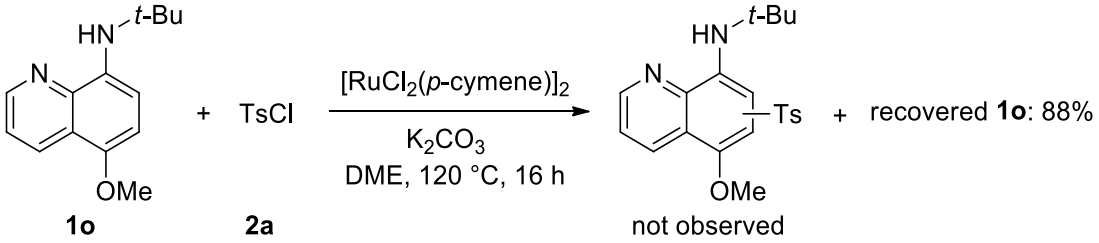
Mechanistic Study



General procedure B was followed using **1a** (50 mg, 0.25 mmol), **2a** (143 mg, 0.75 mmol), $[RuCl_2(p\text{-cymene})]_2$ (7.7 mg, 5.0 mol %), K_2CO_3 (69 mg, 0.50 mmol), TEMPO (117 mg, 0.75 mmol), and 1.0 mL anhydrous DME. Purification by column chromatography on silica gel (PE/EA: 20/1) recovered 46 mg of **1a** (92%), no **3aa** was observed.

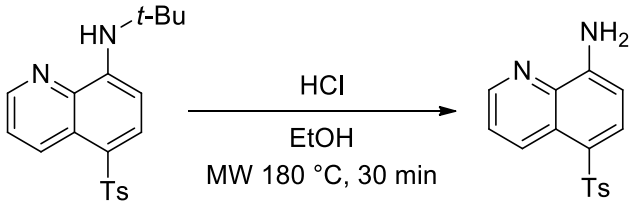


General procedure B was followed using **1a** (50 mg, 0.25 mmol), **2a** (143 mg, 0.75 mmol), $[RuCl_2(p\text{-cymene})]_2$ (7.7 mg, 5.0 mol %), K_2CO_3 (69 mg, 0.50 mmol), 1,1-Diphenylethylene (225 mg, 1.25 mmol), and 1.0 mL anhydrous DME. Purification by column chromatography on silica gel (PE/EA: 20/1) yielded **3aa** (12 mg, 14%) and **4** (125 mg, 50%) as a white solid. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.47 (d, J = 8.3 Hz, 2H), 7.36 (m, 2H), 7.35-7.28 (m, 4H), 7.20 (d, J = 7.2 Hz, 2H), 7.15 (d, J = 8.0 Hz, 2H), 7.10 (d, J = 7.0 Hz, 2H), 6.99 (s, 1H), 2.38 (s, 3H). The spectra data are in accordance with those reported in the literature.[3]



General procedure B was followed using *N*-(*tert*-butyl)-5-methoxyquinolin-8-amine **1o** (57 mg, 0.25 mmol), **2a** (143 mg, 0.75 mmol), $[RuCl_2(p\text{-cymene})]_2$ (7.7 mg, 5.0 mol %), K_2CO_3 (69 mg, 0.50 mmol), and 1.0 mL anhydrous DME. Purification by column chromatography on silica gel (PE/EA: 5/1) recovered 51 mg of **1o** (88%), no addition product of **1o** and **2a** was observed.

Synthesis of Complex 5



3aa 5

Procedure: In a microwave reaction vial equipped with a magnetic stir bar was added 0.4 mmol of **3aa** (dissolved in 2 mL EtOH), followed by 2 mL of 0.2 M HCl. The vial was capped and sealed, then heated in the microwave synthesis apparatus for 30 minutes at 180 °C. After basic aqueous workup (with 2 mL of 3 M NaOH, 1 mL of brine and 2 mL of EA), the organic layers were concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (PE/EA: 3/1) to afford the product **5** (95 mg, 80%) as a pale yellow solid. **M. p.**: 152-154 °C. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 8.88 (dd, *J* = 8.7, 1.5 Hz, 1H), 8.71 (dd, *J* = 4.1, 1.5 Hz, 1H), 8.31 (d, *J* = 8.3 Hz, 1H), 7.78 (d, *J* = 8.3 Hz, 2H), 7.46 – 7.40 (m, 1H), 7.22 (d, *J* = 8.1 Hz, 2H), 6.88 (d, *J* = 8.3 Hz, 1H), 5.66 (s, 2H), 2.34 (s, 3H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ 149.9, 147.7, 143.5, 140.3, 137.5, 132.9, 132.9, 129.8, 127.0, 125.5, 123.3, 121.7, 106.6, 21.6. **IR** (neat): 3436, 3328, 2923, 1617, 1509, 1370, 1281, 1130, 814, 687 cm^{-1}. **HR-MS** (ESI) m/z calcd. for $C_{16}H_{15}N_2O_2S$ ($[M+H]^+$) 299.0854, found: 299.0859. The spectra data are in accordance with those reported in the literature.[2]

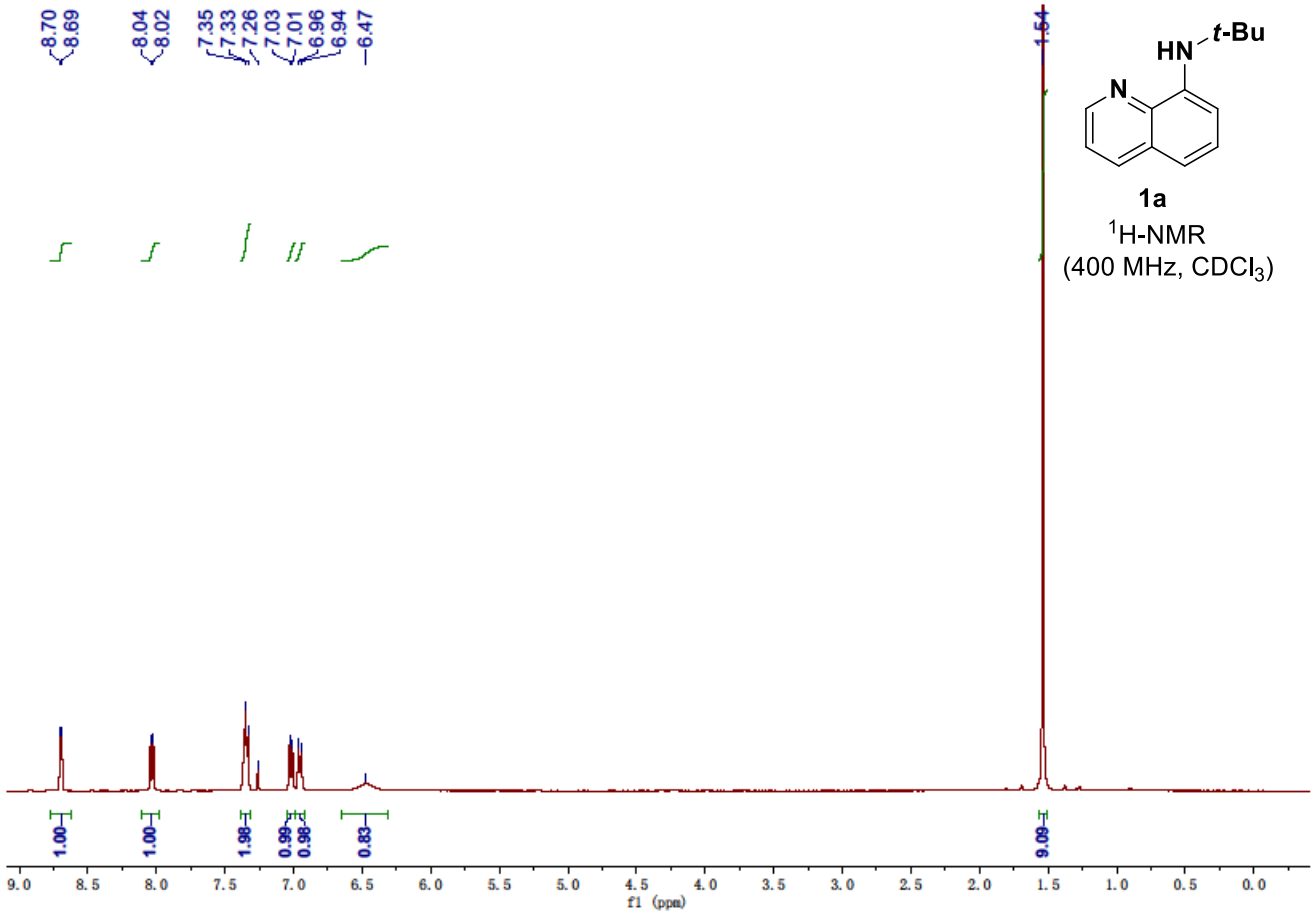
References

[1] N. Muresan, C. C. Lu, M. Ghosh, J. C. Peters, M. Abe, L. M. Henling, T. Weyhermöller, E. Bill and K. Wieghardt, *Inorg. Chem.,* 2008, **47**, 4579.

[2] H.-W. Liang, K. Jiang, W. Ding, Y. Yuan, L. Shuai, Y.-C. Chen and Y. Wei, *Chem. Commun.,* 2015, **51**, 16928.

[3] S. Mao, Y.-R. Gao, X.-Q. Zhu, D.-D. Guo and Y.-Q. Wang, *Org. Lett.,* 2015, **17**, 1692.

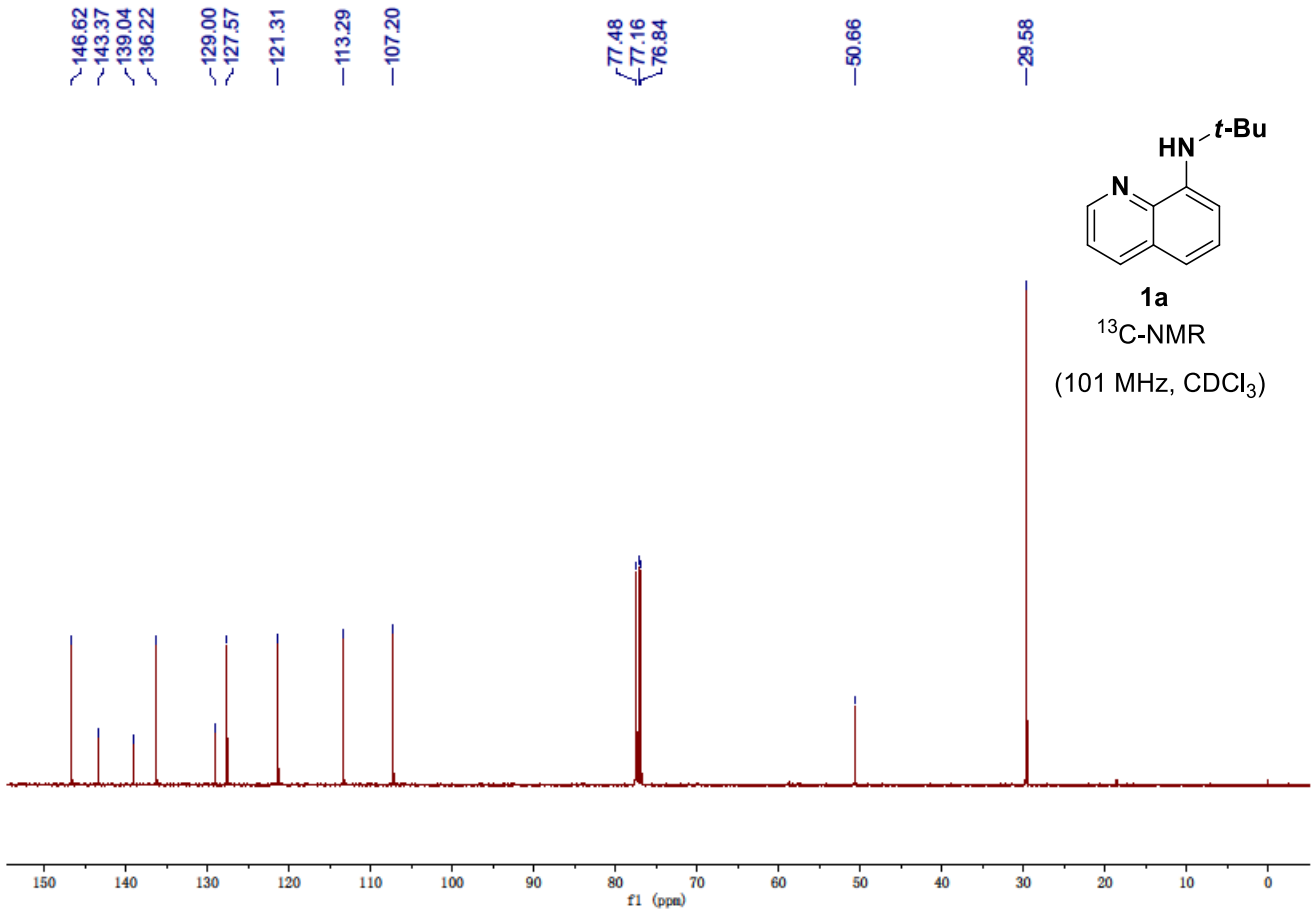
NMR Spectra



1a

^{1}H-NMR

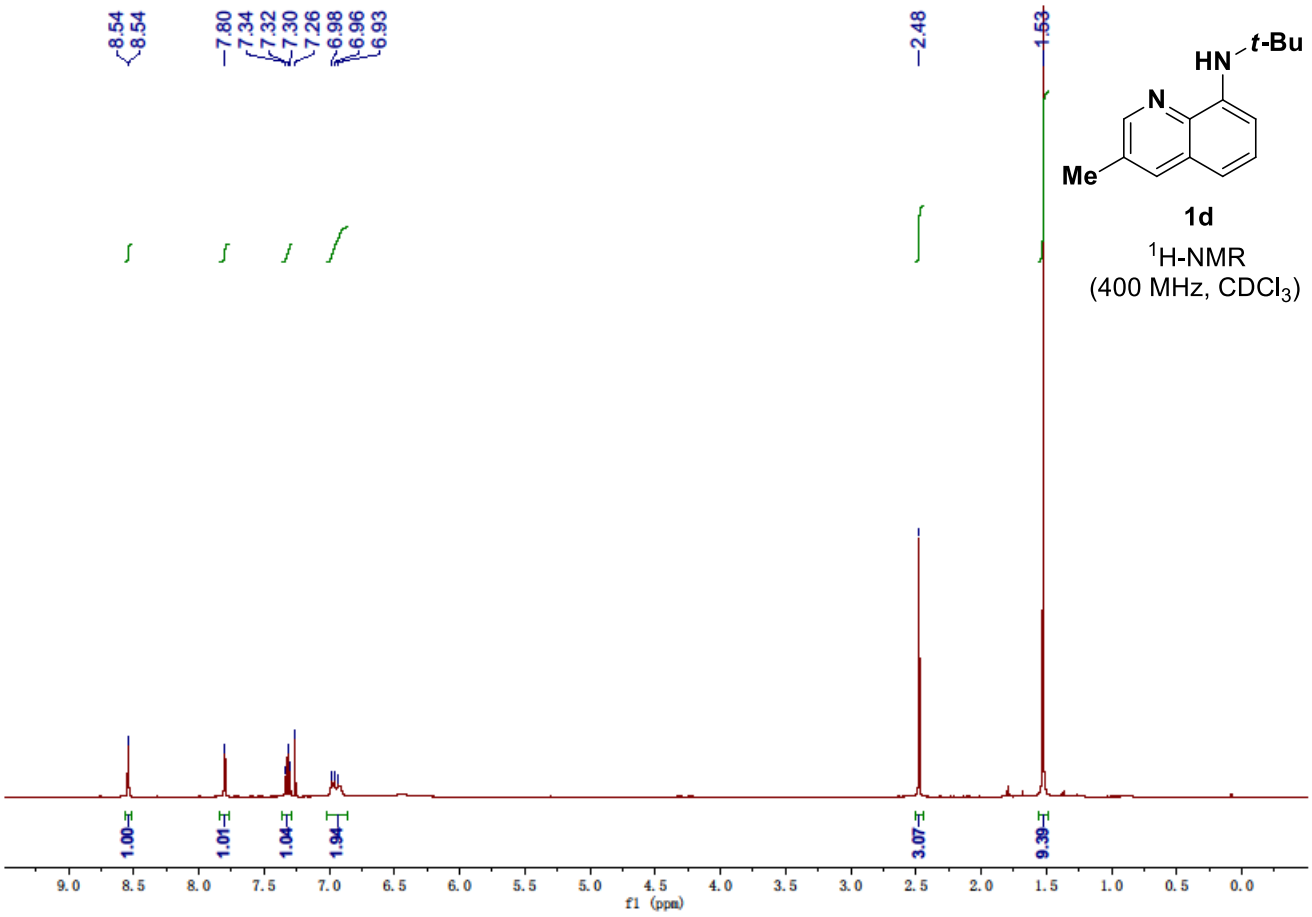
(400 MHz, $CDCl_3$)



1a

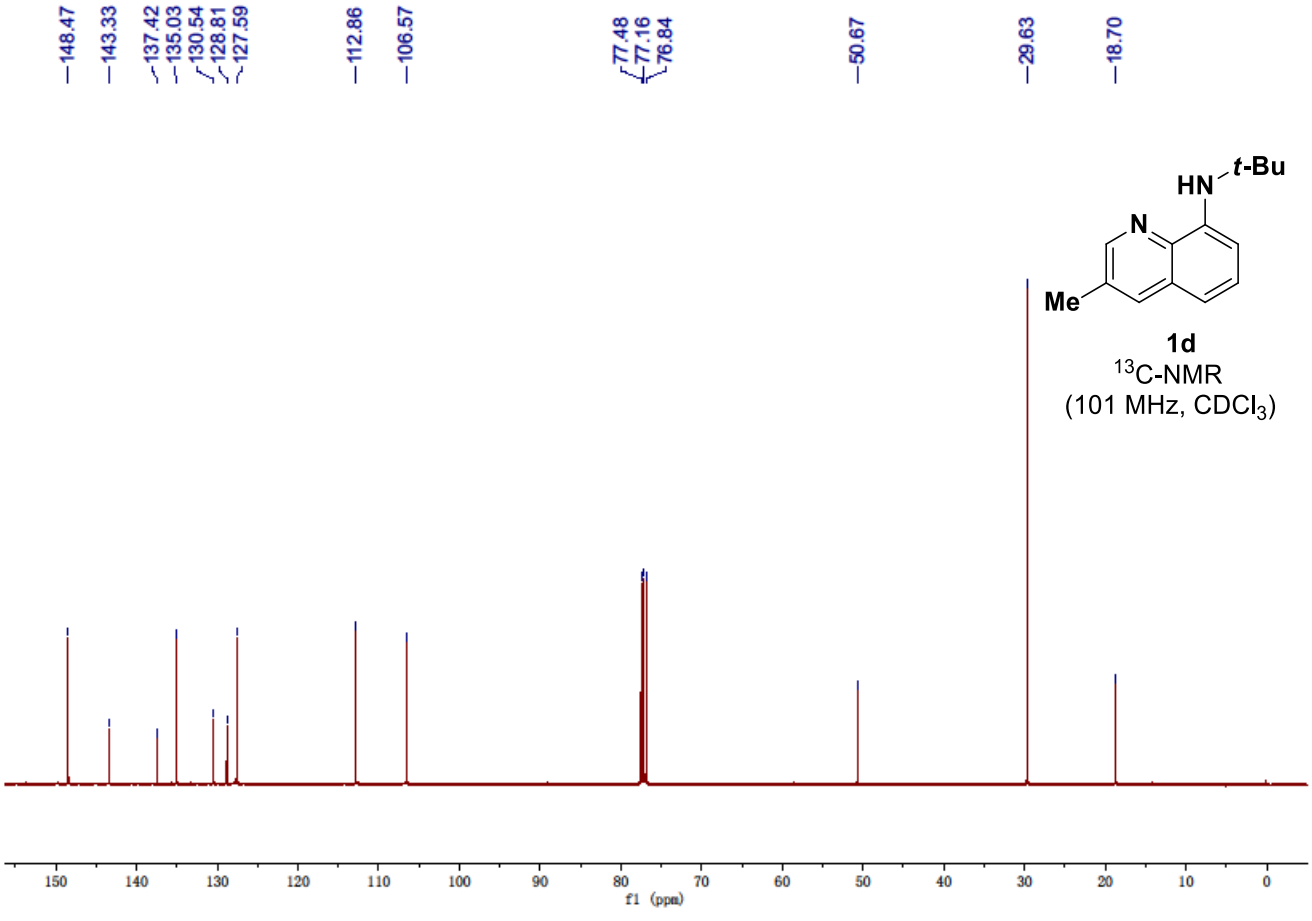
^{13}C-NMR

(101 MHz, $CDCl_3$)



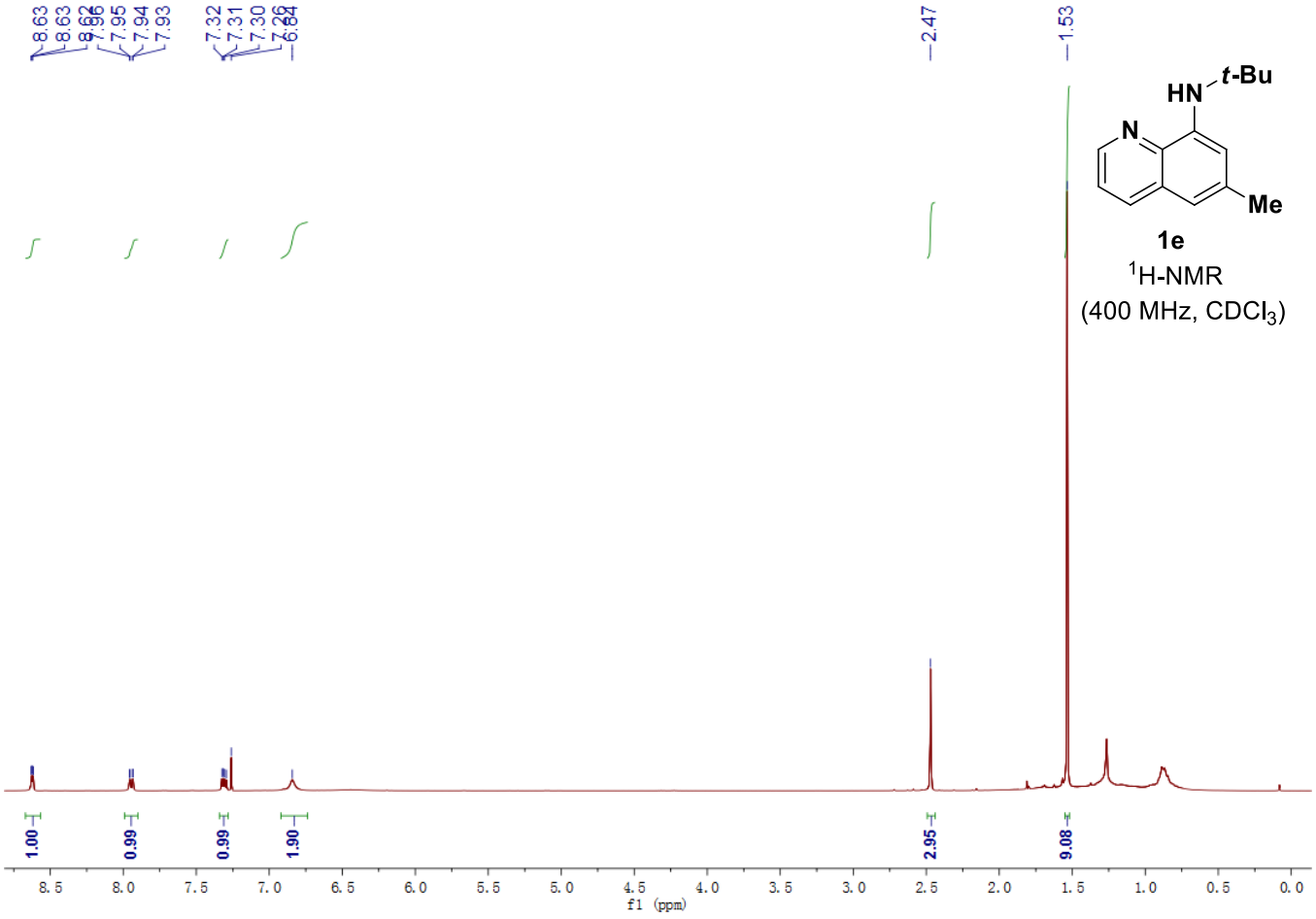
1d

^{1}H-NMR
(400 MHz, $CDCl_3$)



1d

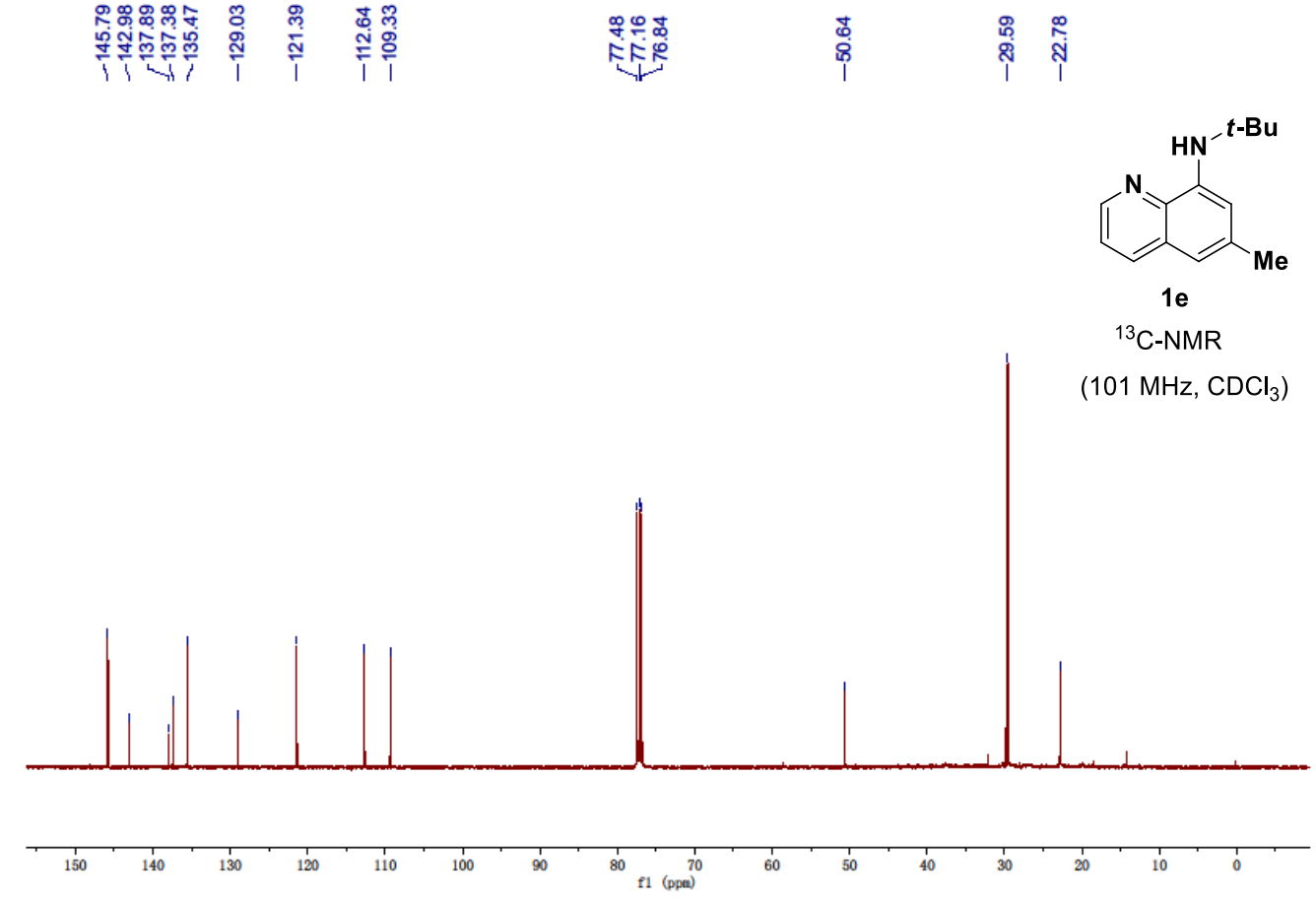
^{13}C-NMR
(101 MHz, $CDCl_3$)



1e

^{1}H-NMR

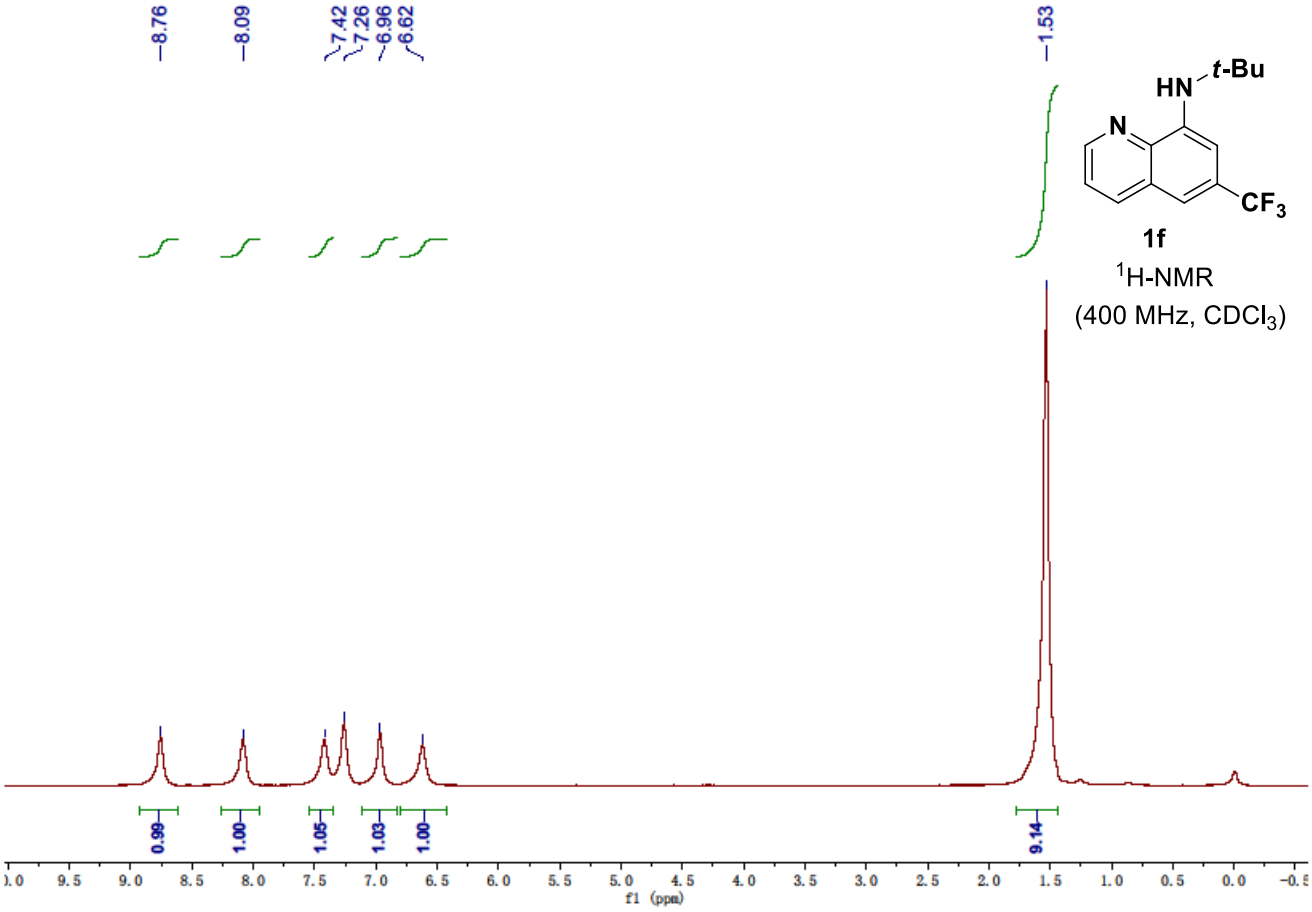
(400 MHz, $CDCl_3$)



1e

^{13}C-NMR

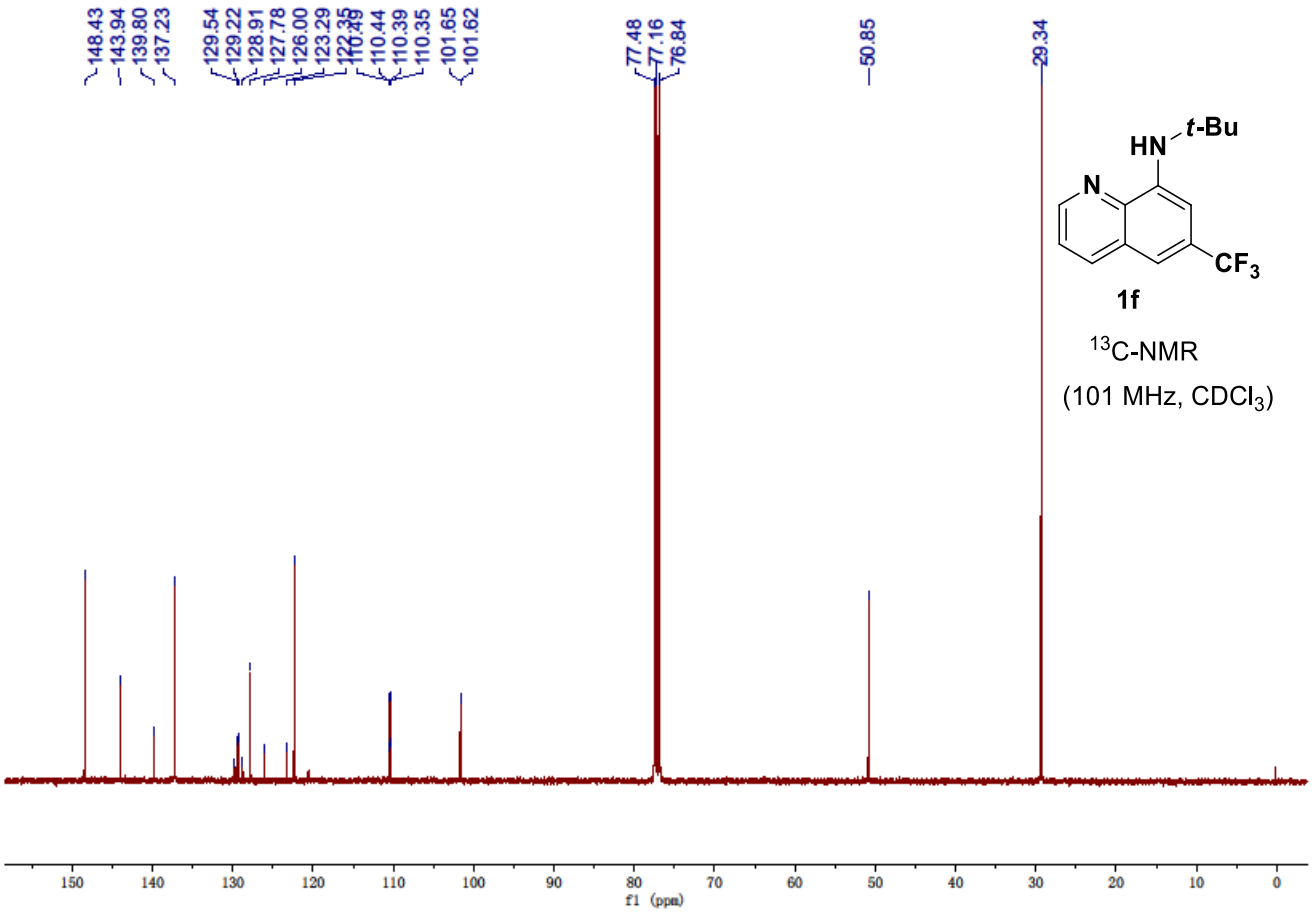
(101 MHz, $CDCl_3$)



1f

^{1}H-NMR

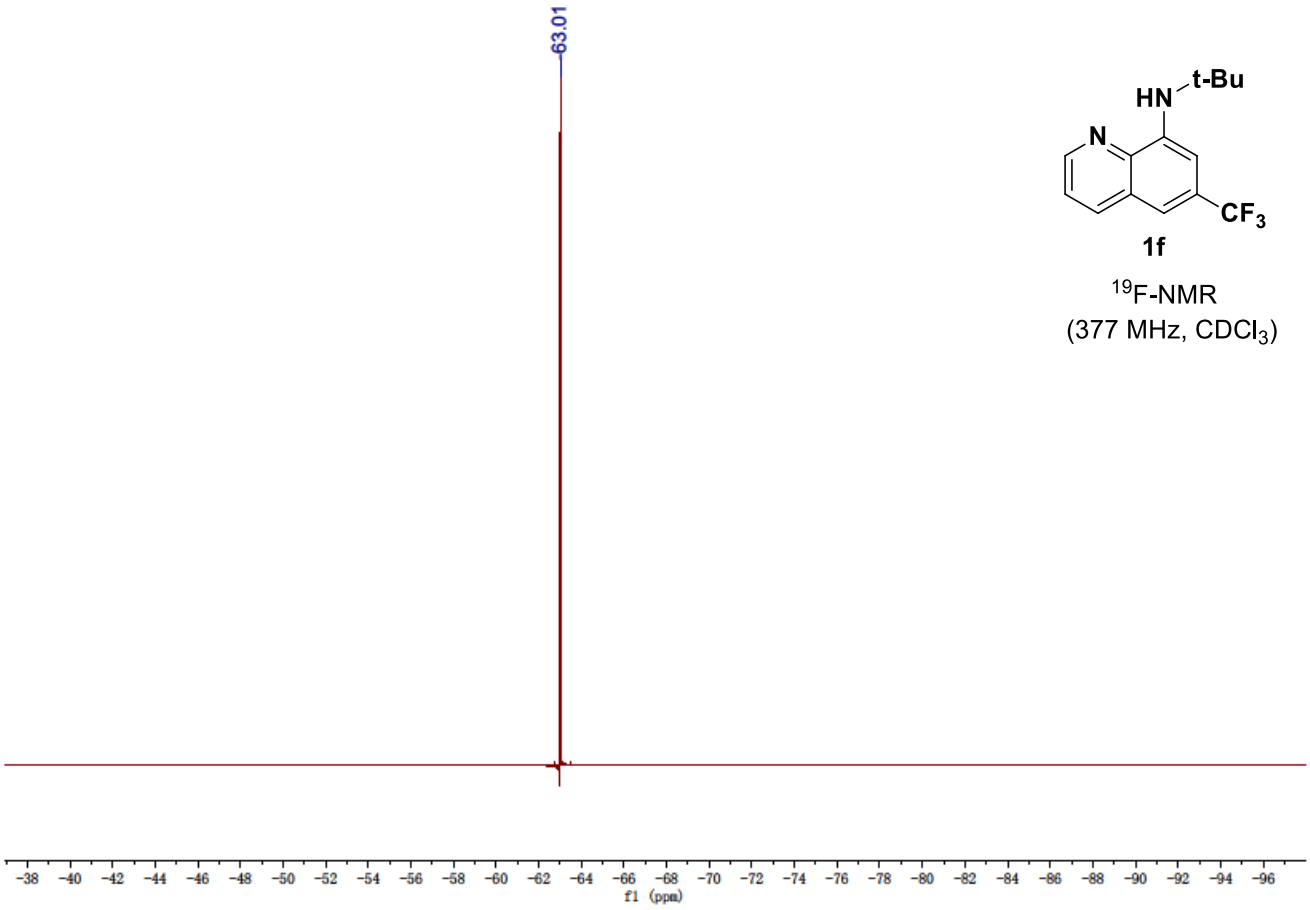
(400 MHz, $CDCl_3$)

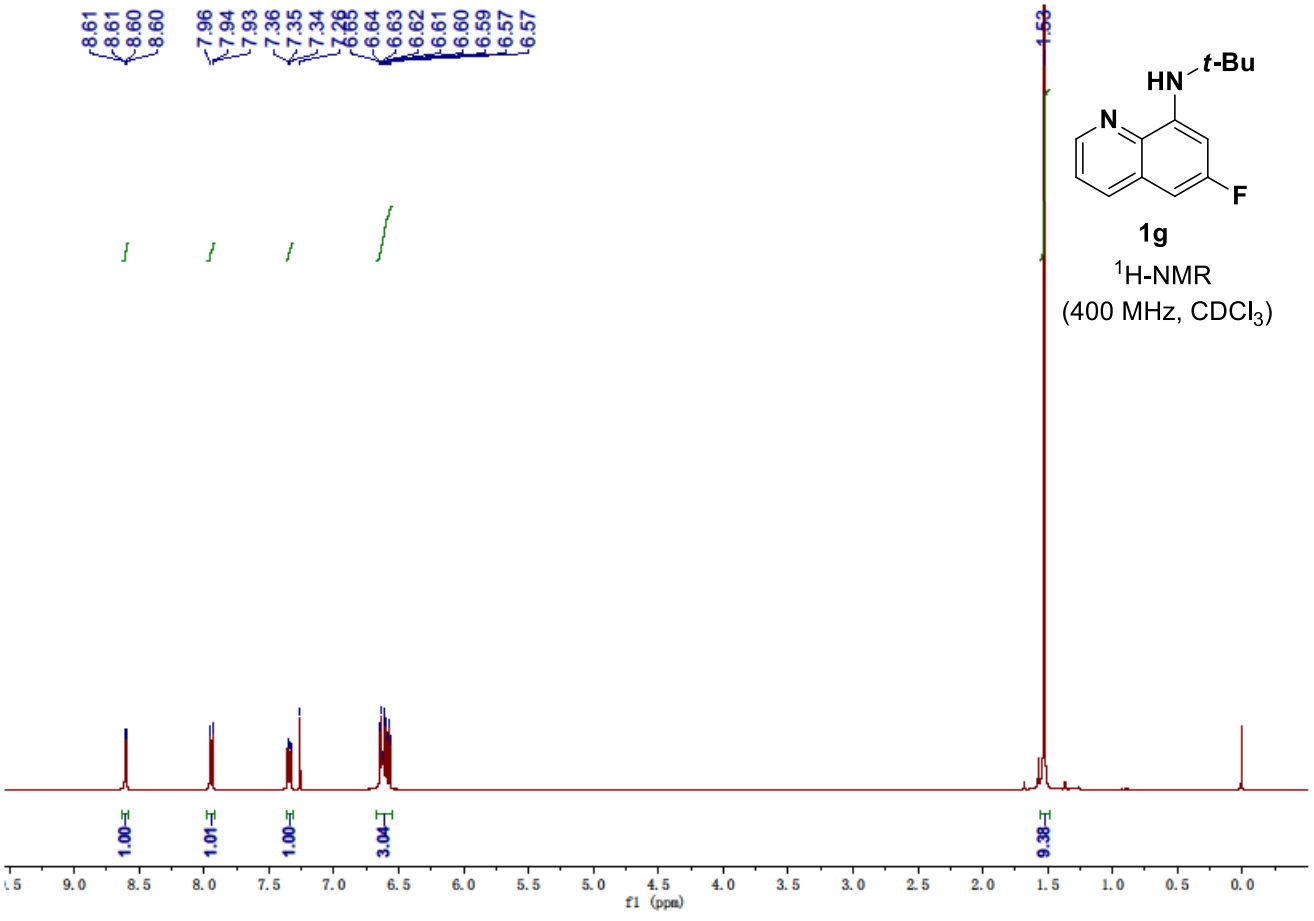


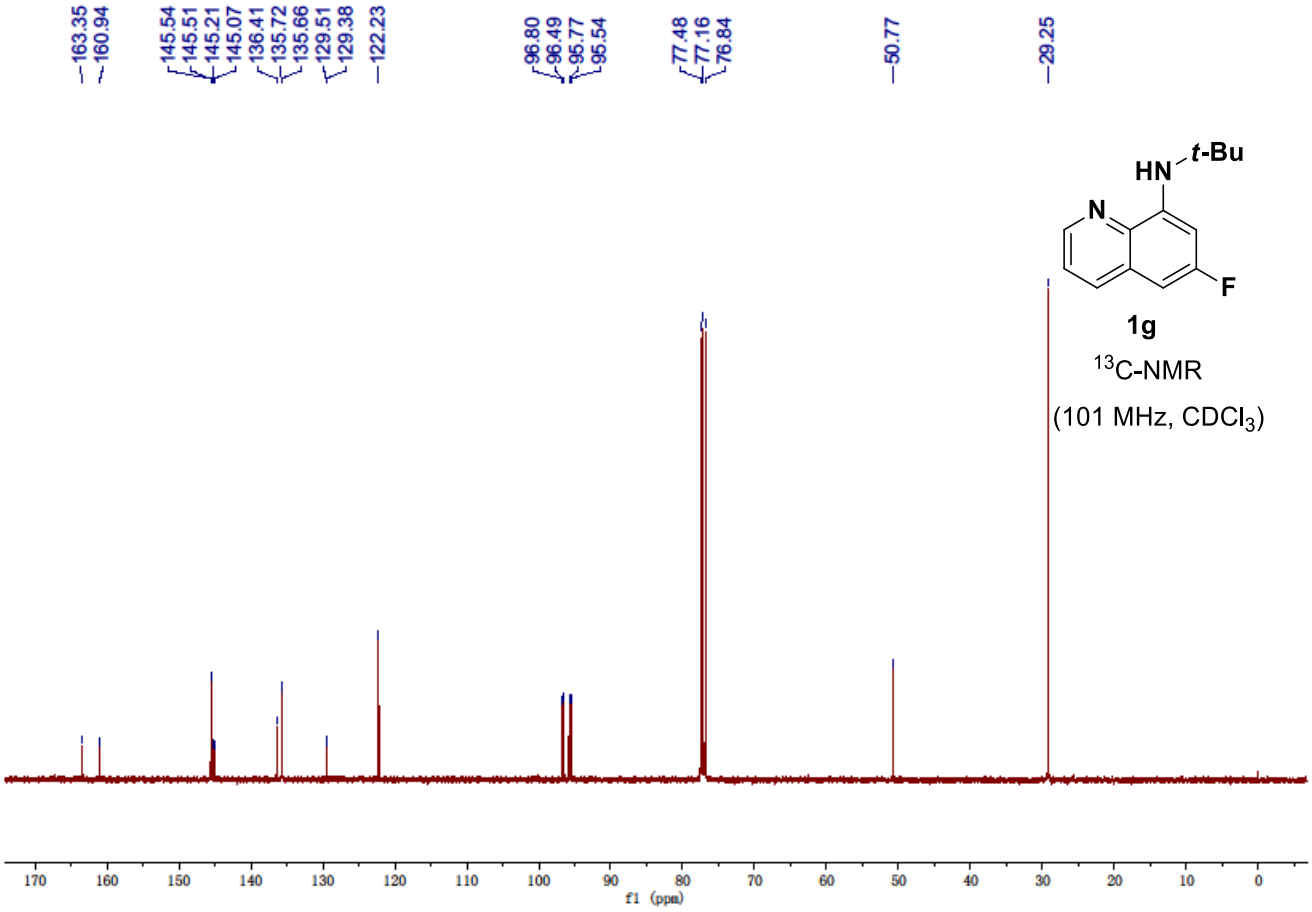
1f

^{13}C-NMR

(101 MHz, $CDCl_3$)


63.01
HN
t-Bu
N
CF3
1f
19F-NMR
(377 MHz, CDCl3)
f1 (ppm)


8.61
8.61
8.60
8.60
7.96
7.94
7.93
7.36
7.35
7.34
6.64
6.63
6.62
6.61
6.60
6.59
6.57
6.57
1.53
HN
t-Bu
N
F
1g
1H-NMR
(400 MHz, CDCl3)
1.00
1.01
1.00
3.04
9.38
f1 (ppm)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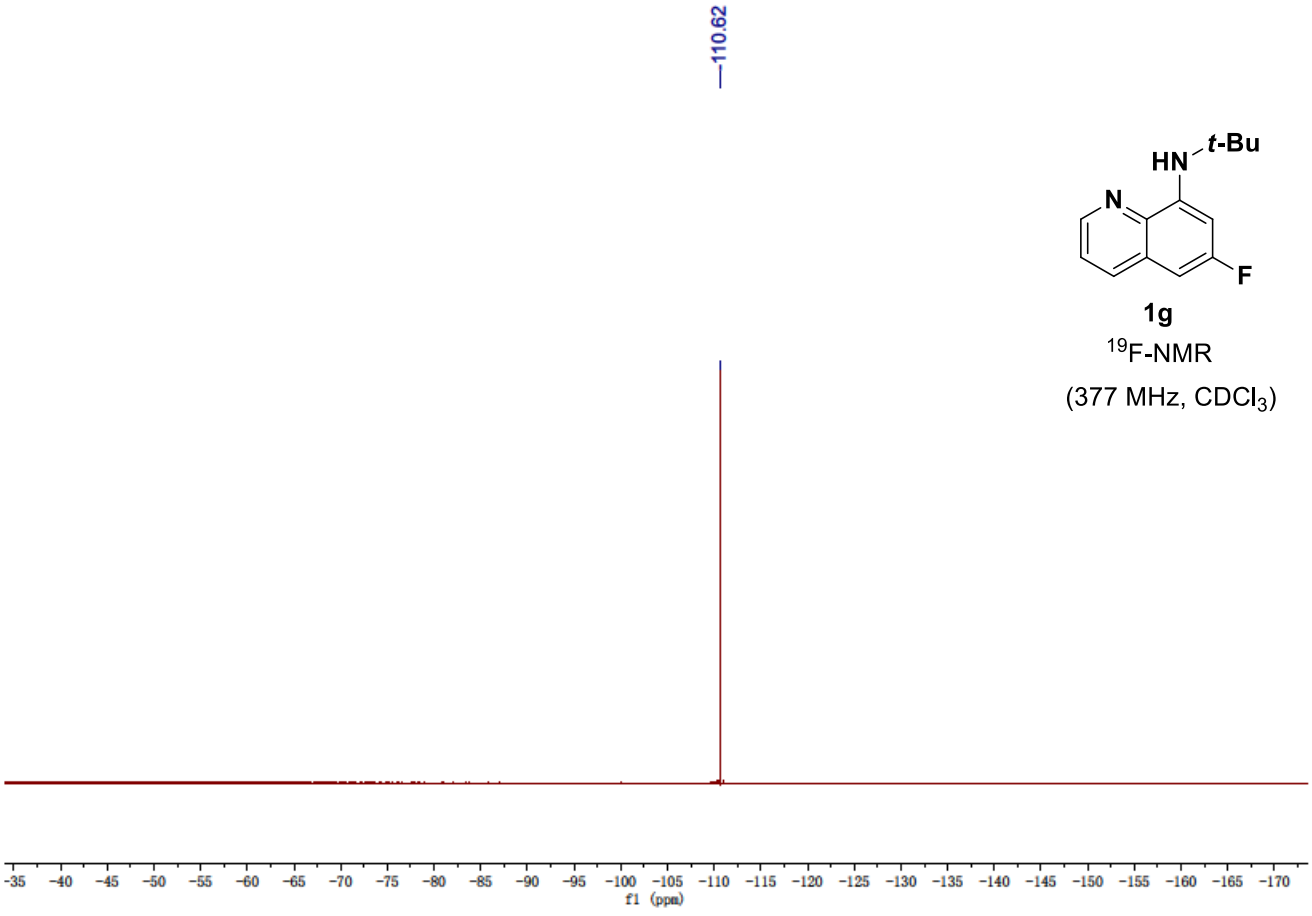
160.94
145.54
145.51
145.21
145.07
136.41
135.72
135.66
129.51
129.38
122.23
96.80
96.49
95.77
95.54
77.48
77.16
76.84
50.77
29.25
HN
t-Bu
N
F
1g
13C-NMR
(101 MHz, CDCl3)
f1 (ppm)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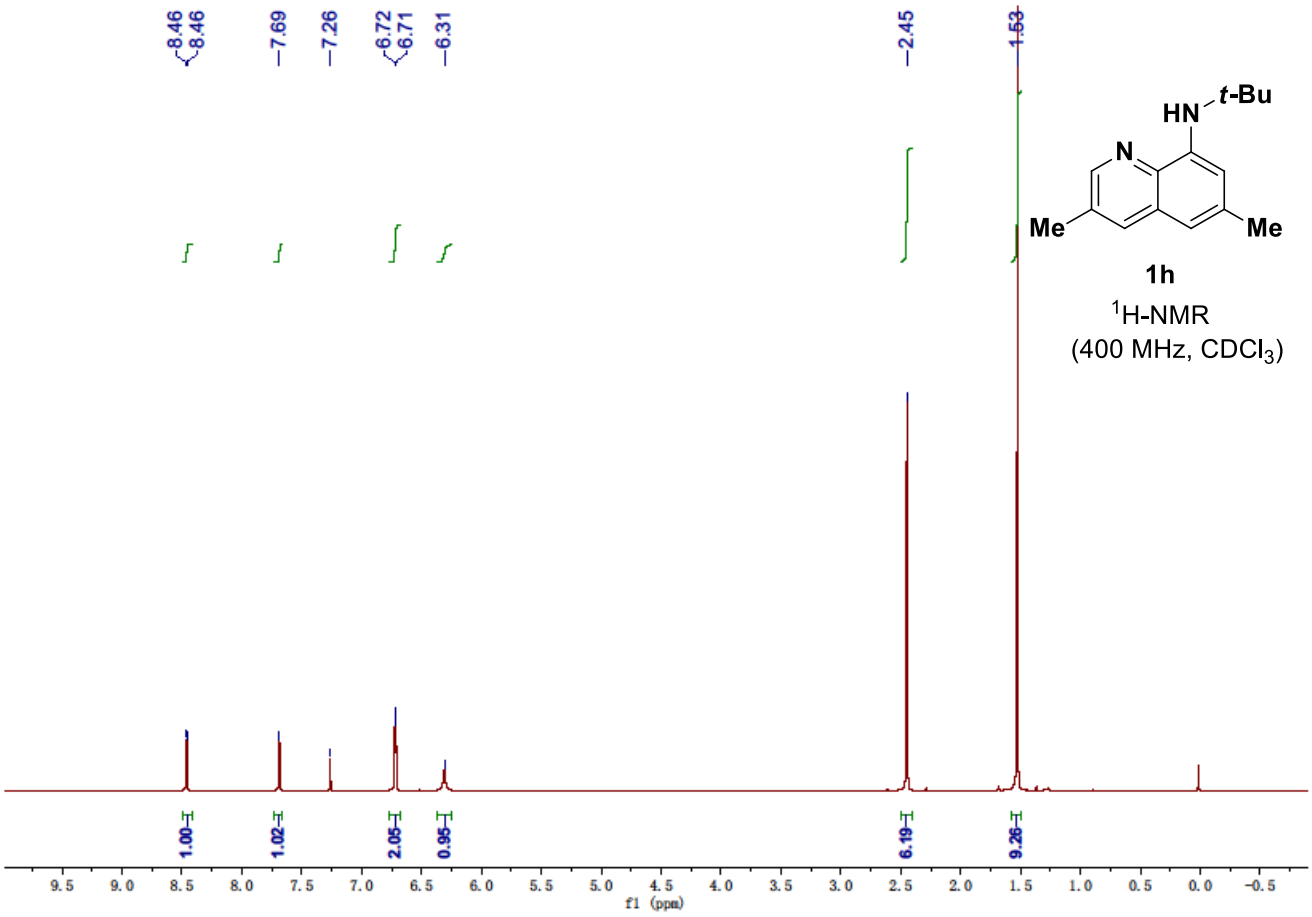
t-Bu
N
F
1g
19F-NMR
(377 MHz, CDCl3)
f1 (ppm)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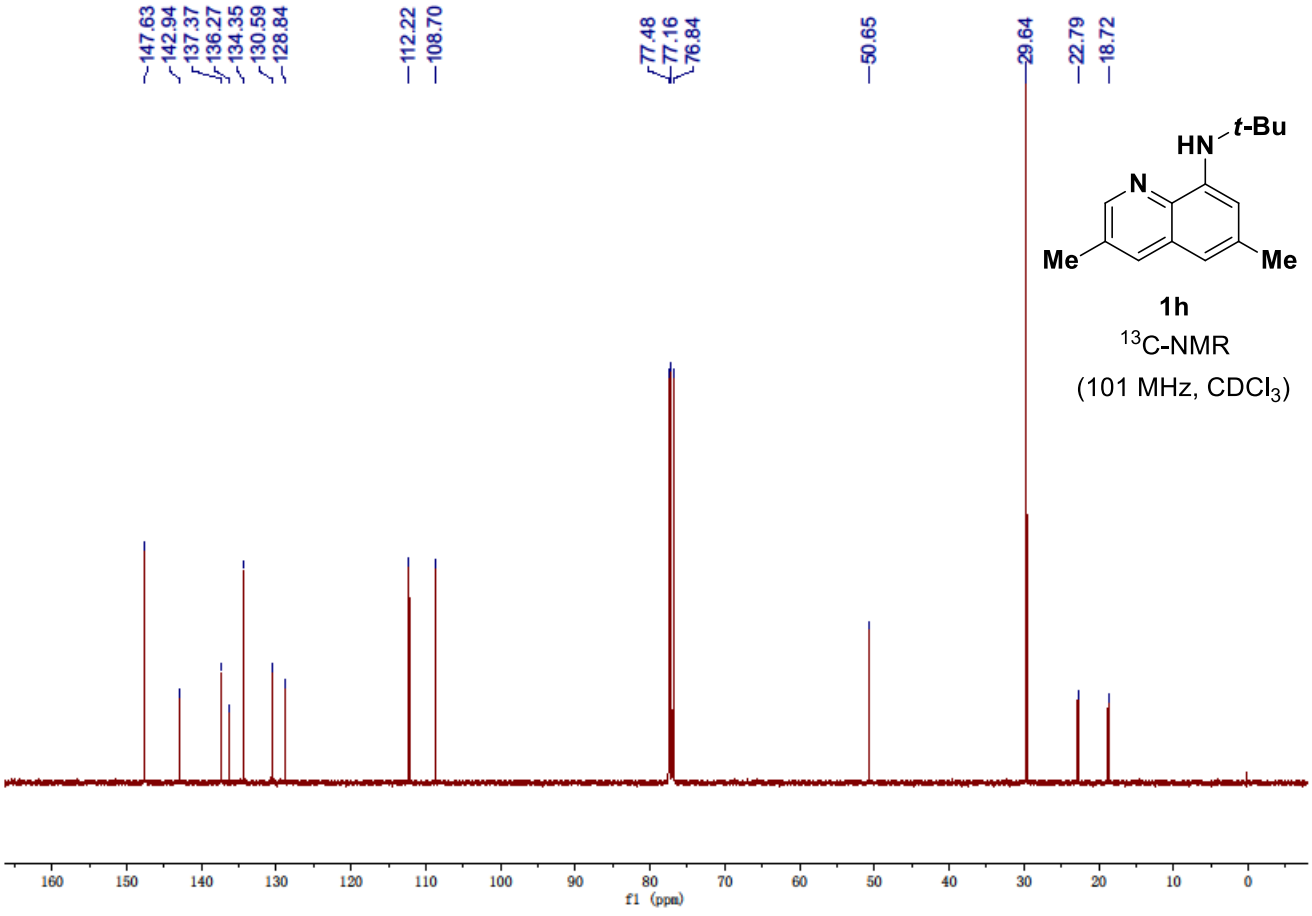
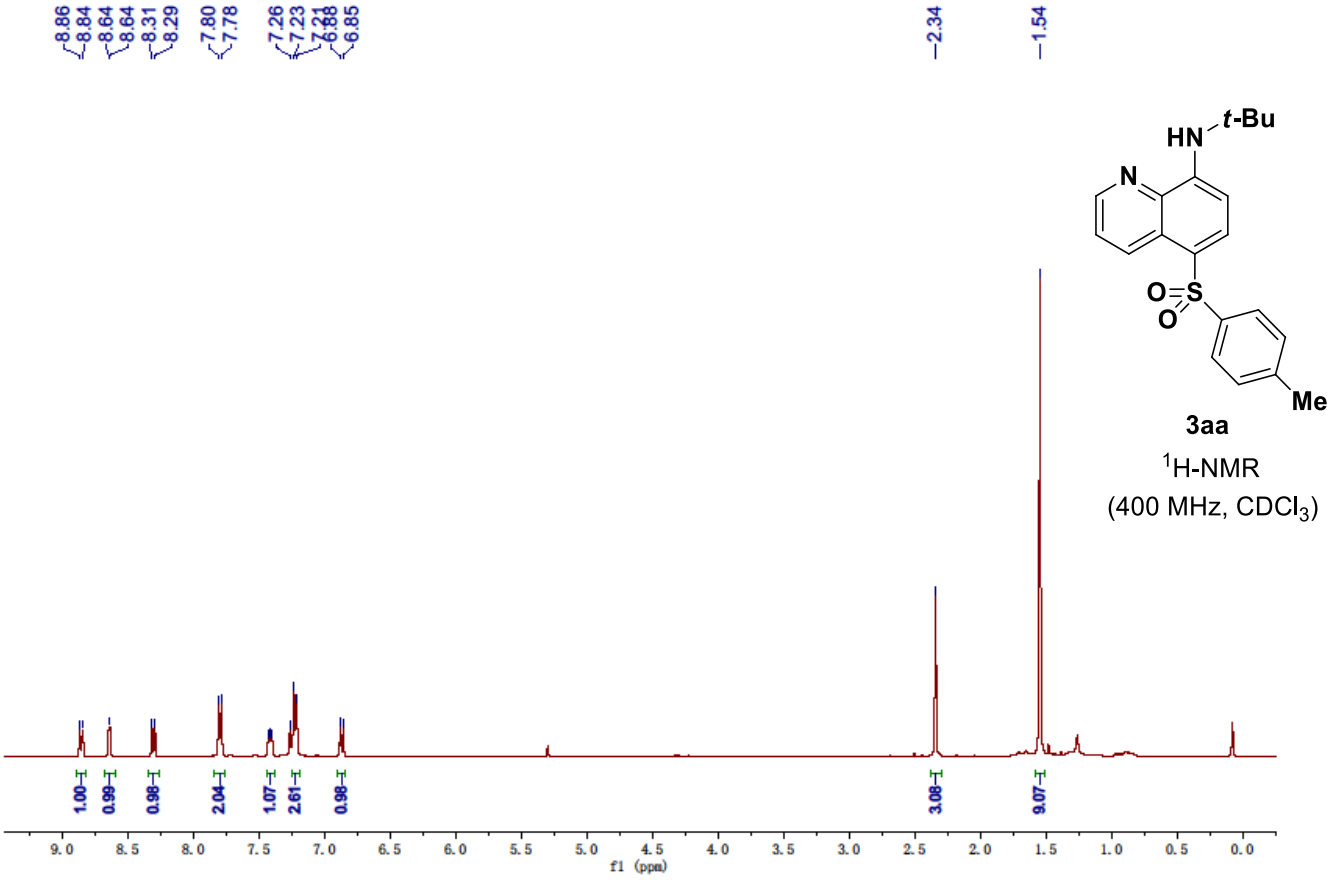
8.46
7.69
7.26
6.72
6.71
6.31
2.45
1.53
HN
t-Bu
N
Me
Me
1h
1H-NMR
(400 MHz, CDCl3)
1.00
1.02
2.05
0.95
6.19
9.26
f1 (ppm)

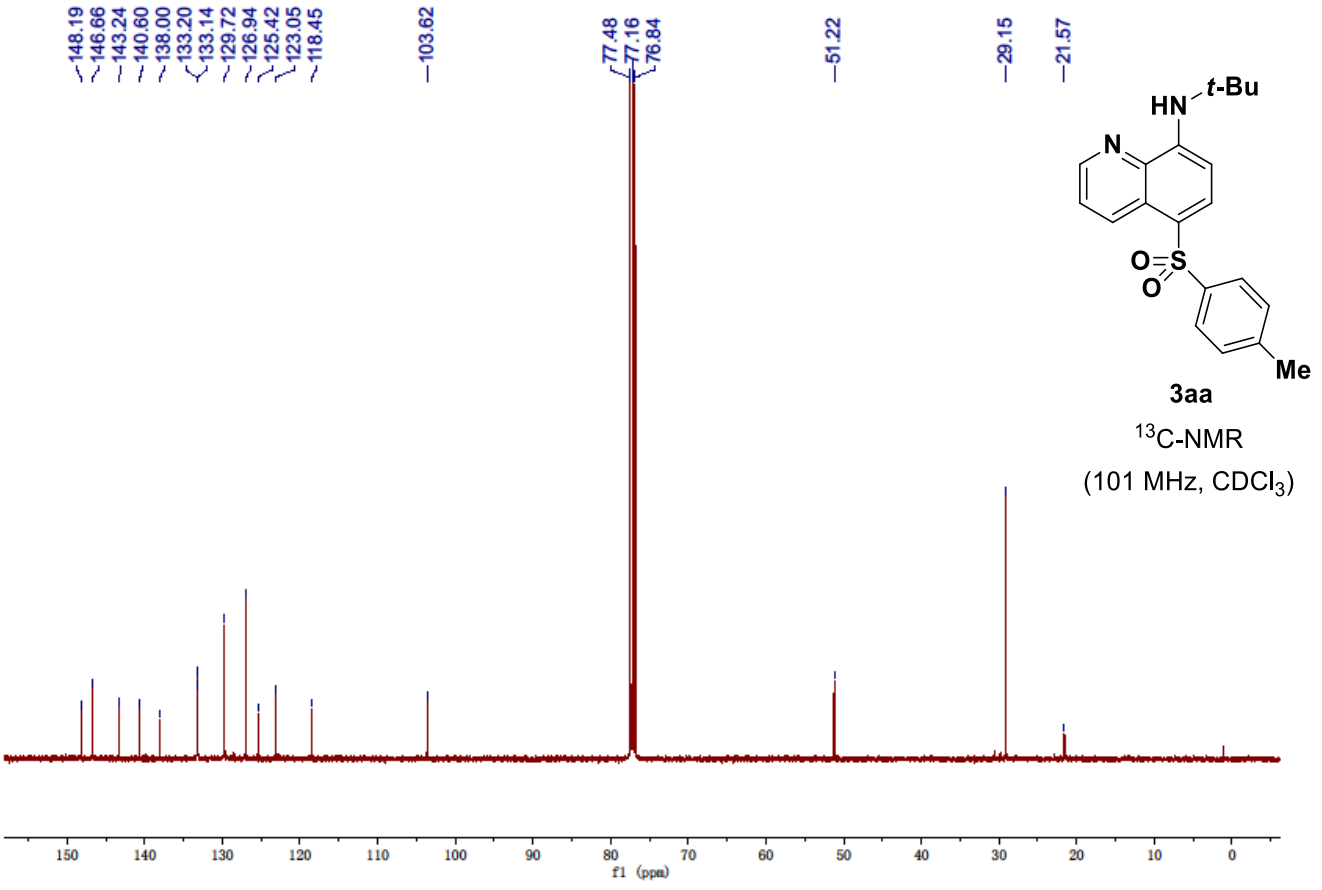

147.63
142.94
137.37
136.27
134.35
130.59
128.84
112.22
108.70
77.48
77.16
76.84
50.65
29.64
22.79
18.72
HN
t-Bu
N
Me
Me
1h
13C-NMR
(101 MHz, CDCl3)
f1 (ppm)



3aa

^{1}H-NMR

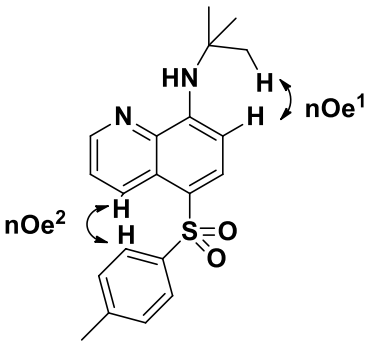
(400 MHz, $CDCl_3$)



3aa

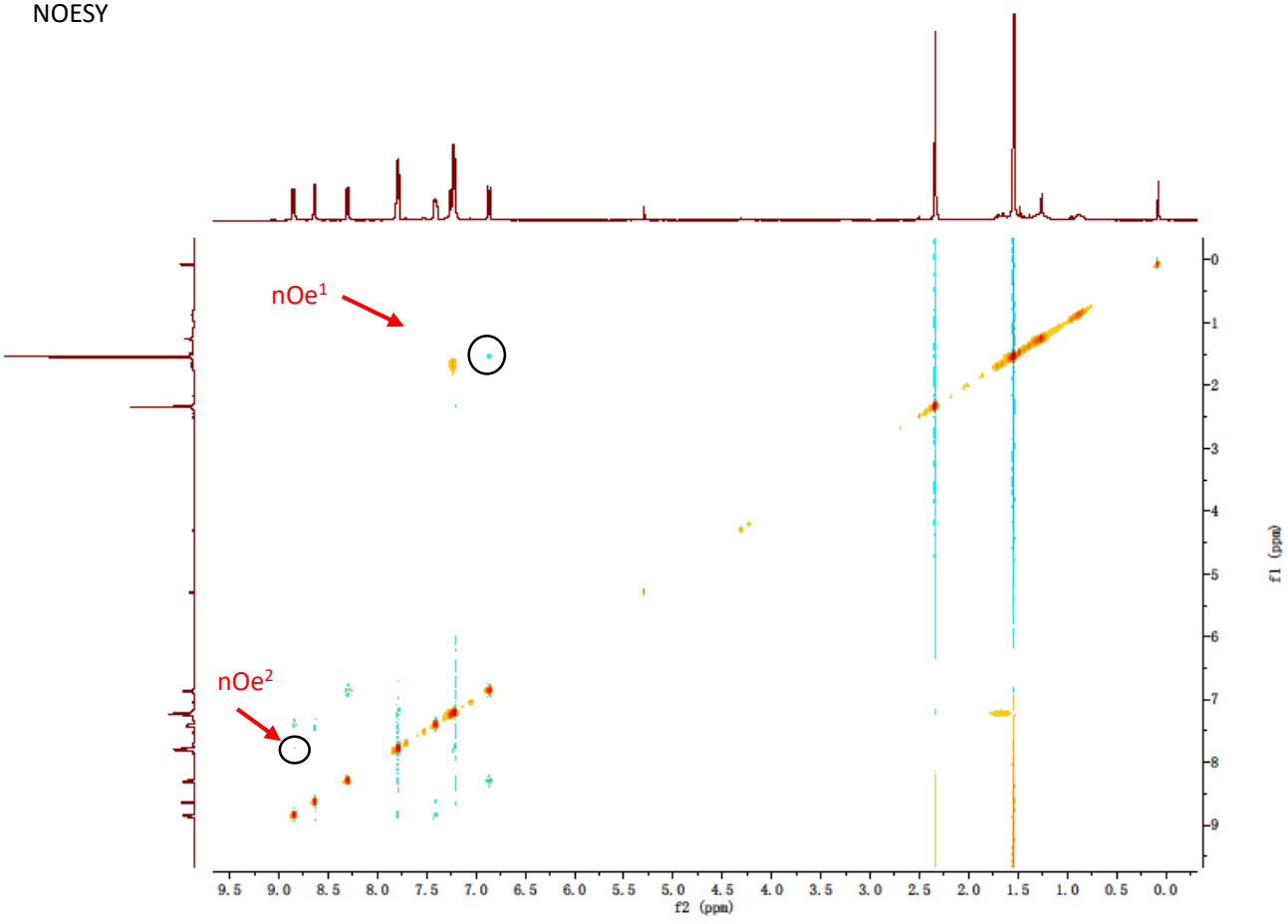
^{13}C-NMR

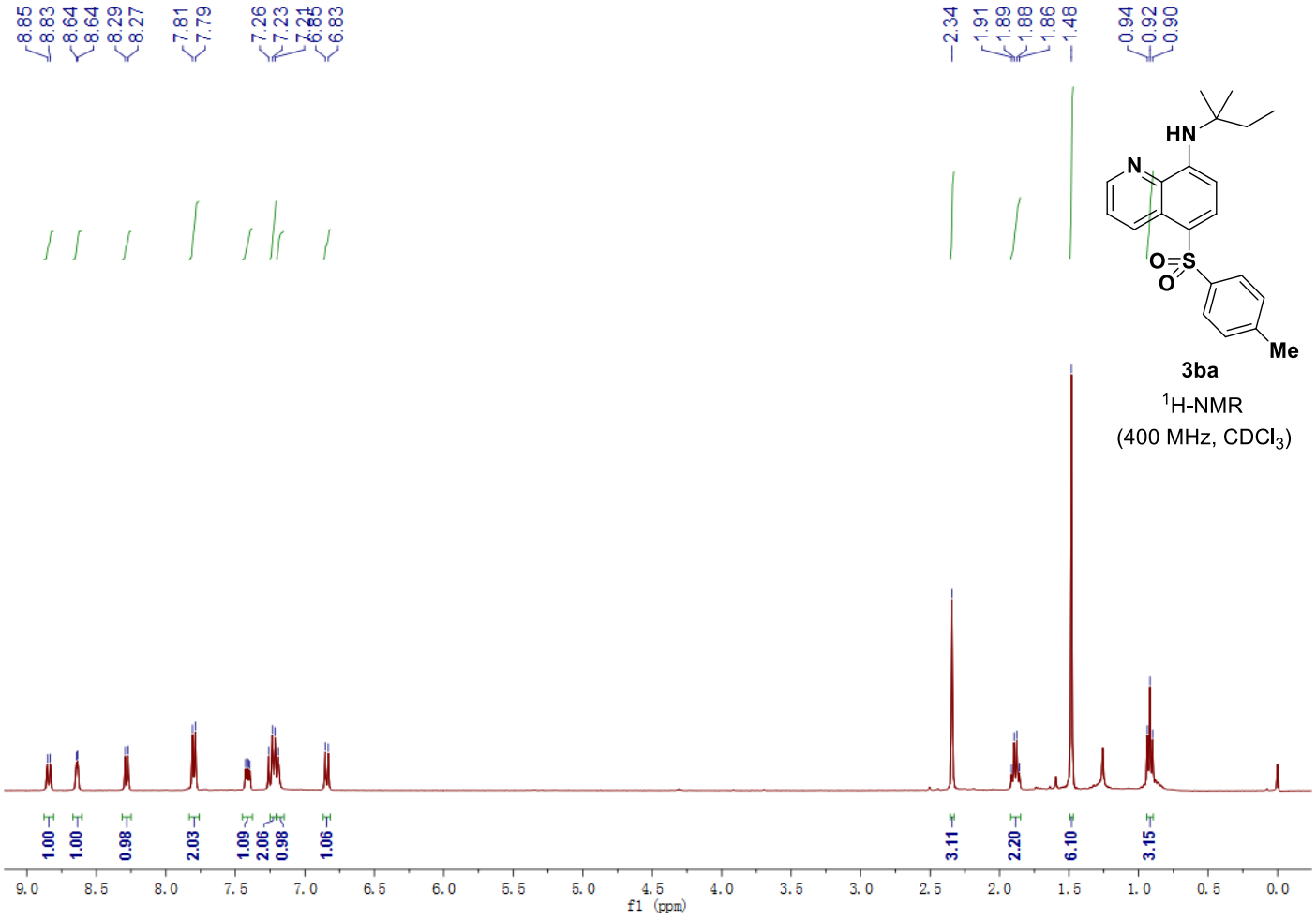
(101 MHz, $CDCl_3$)


HN
H
nOe1
N
H
nOe2
H
H
S
O
O

3aa

NOESY

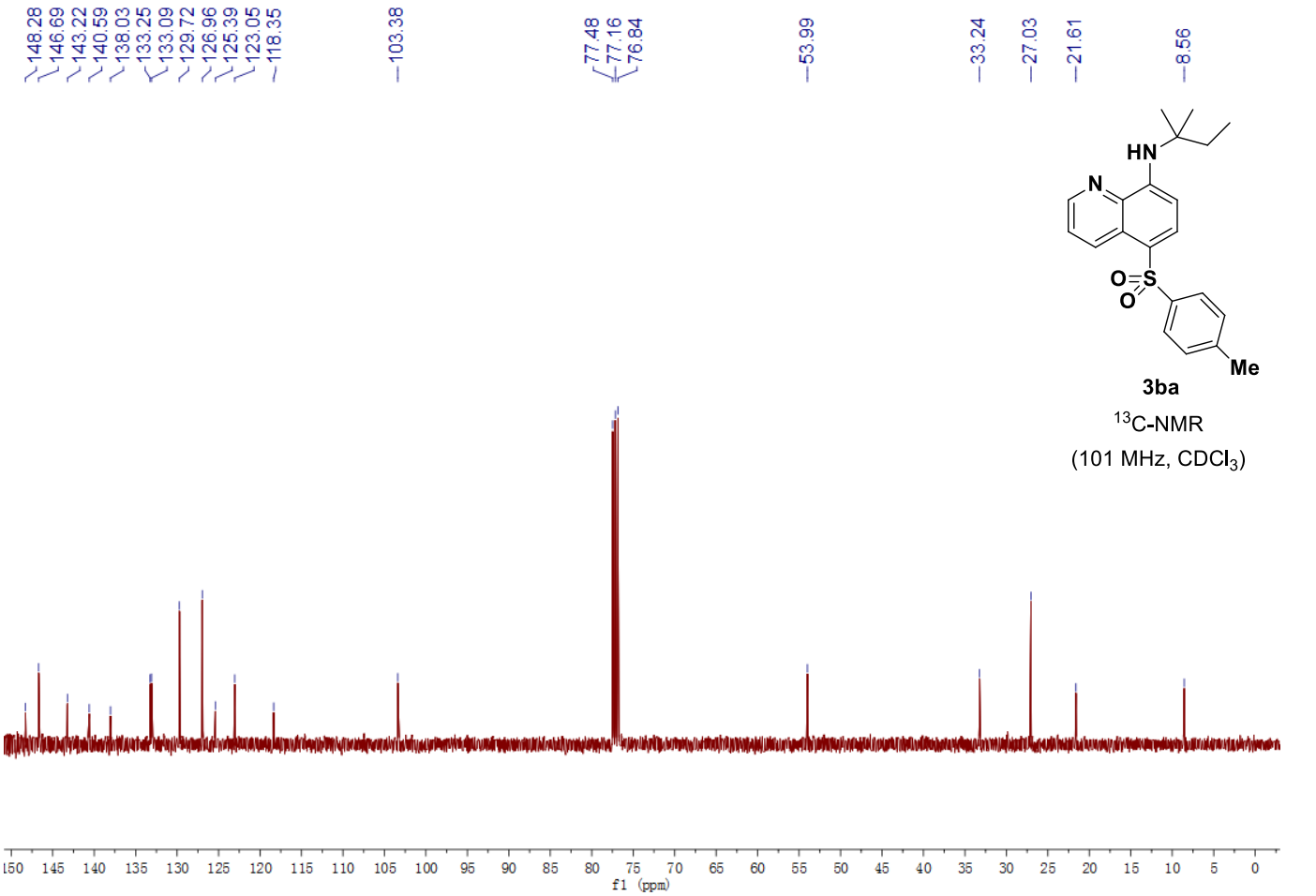

nOe1
nOe2
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f2 (ppm)
0 1 2 3 4 5 6 7 8 9
f1 (ppm)



3ba

^{1}H-NMR

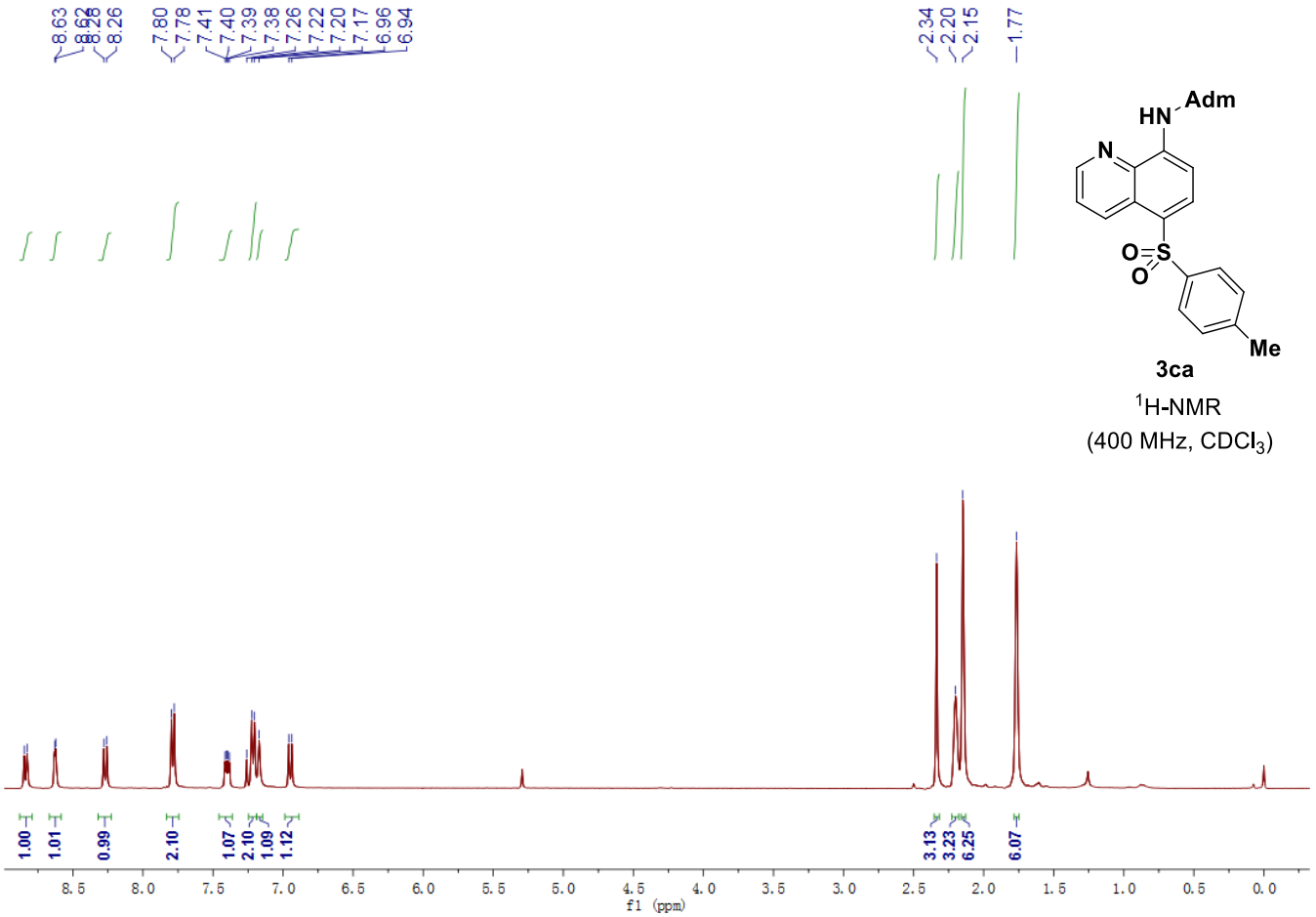
(400 MHz, $CDCl_3$)



3ba

^{13}C-NMR

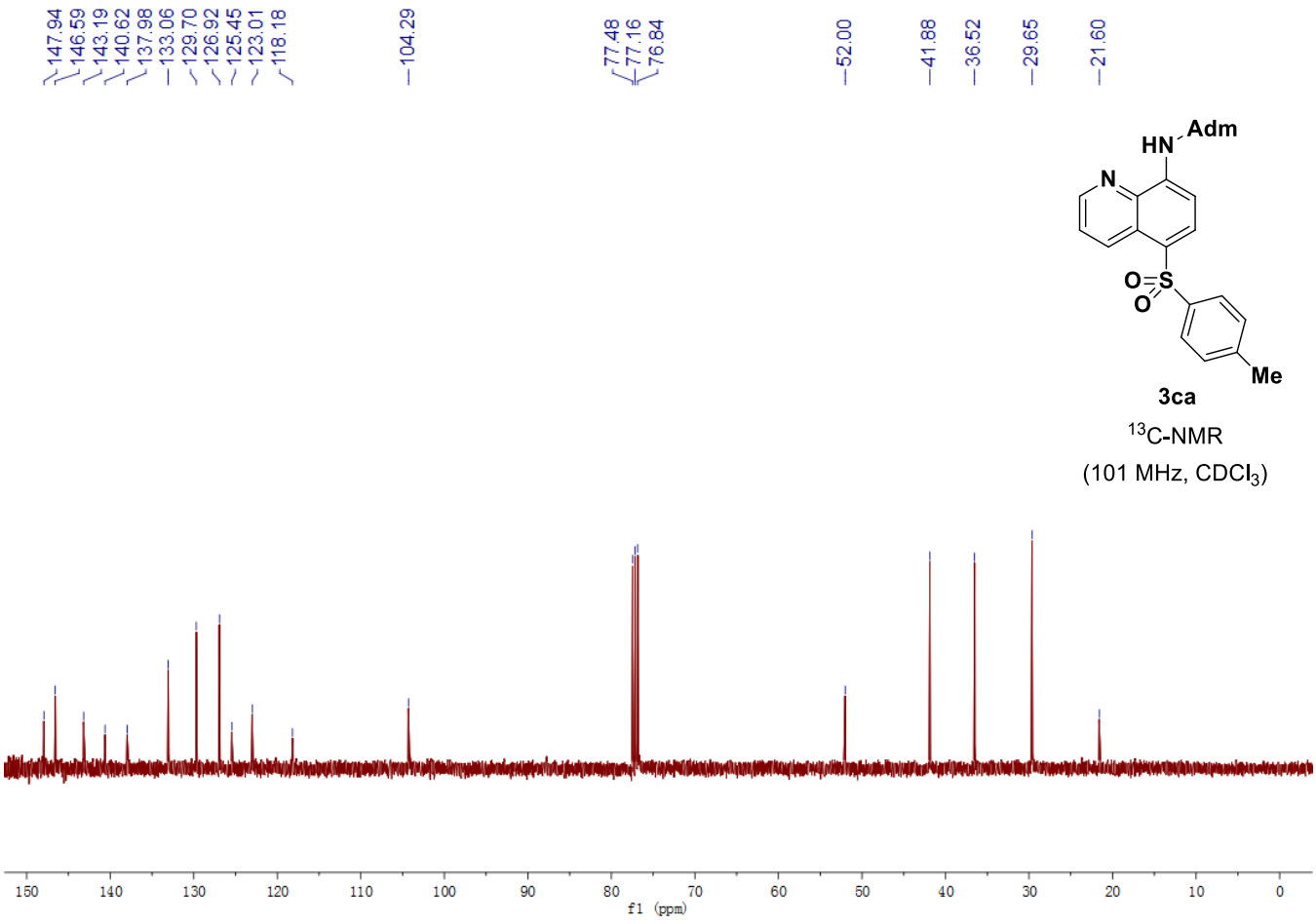
(101 MHz, $CDCl_3$)



3ca

^{1}H-NMR

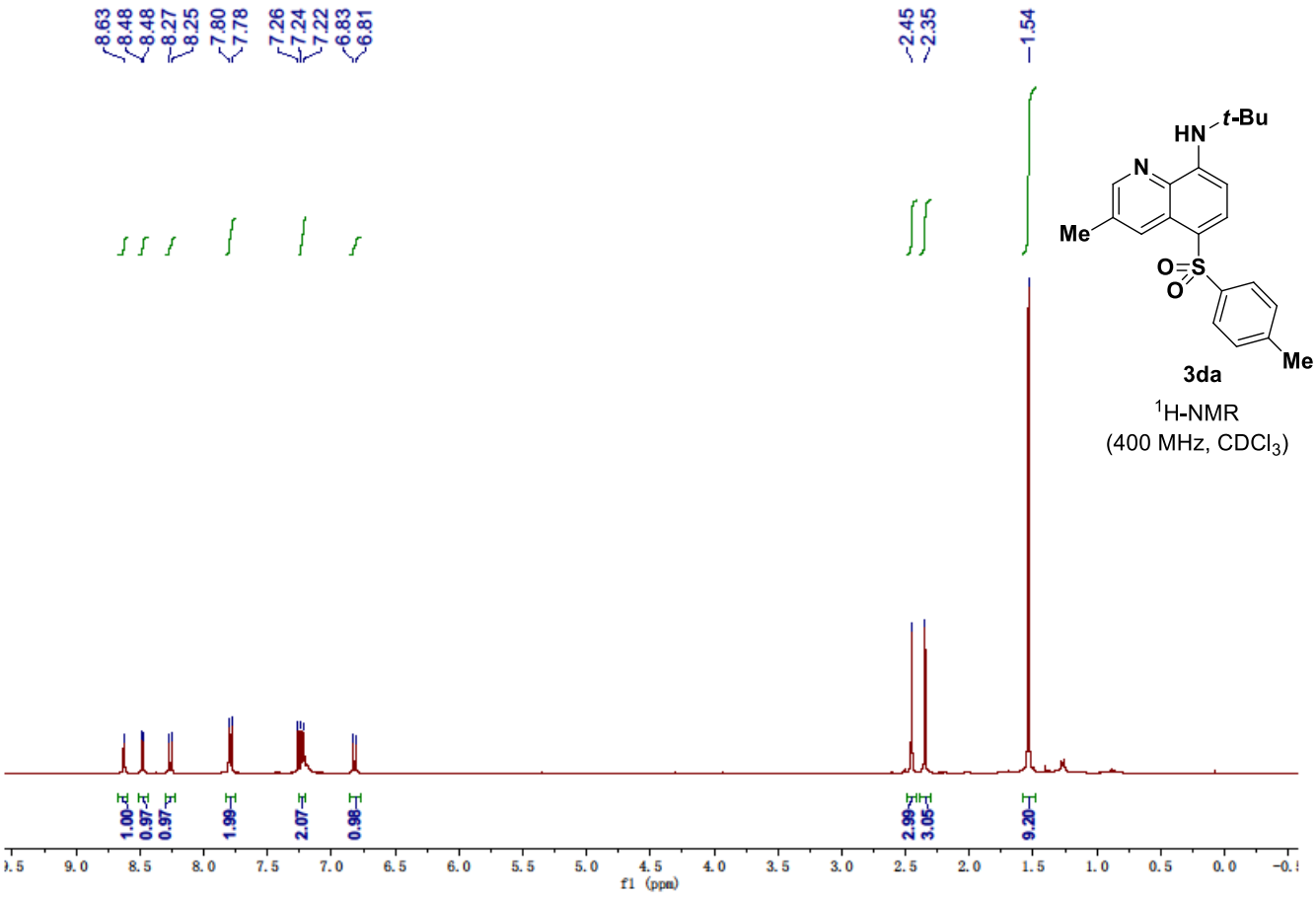
(400 MHz, $CDCl_3$)



3ca

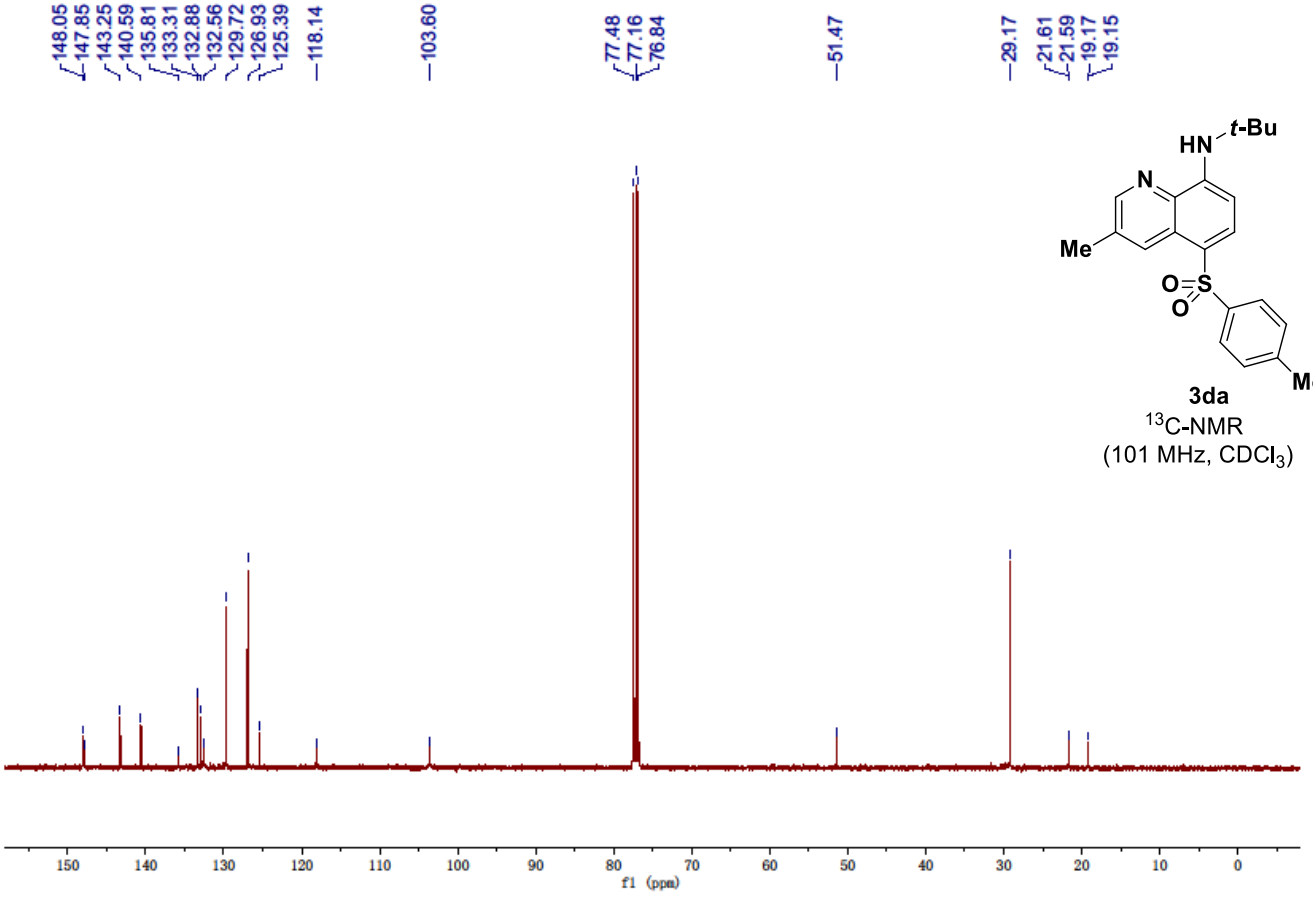
^{13}C-NMR

(101 MHz, $CDCl_3$)



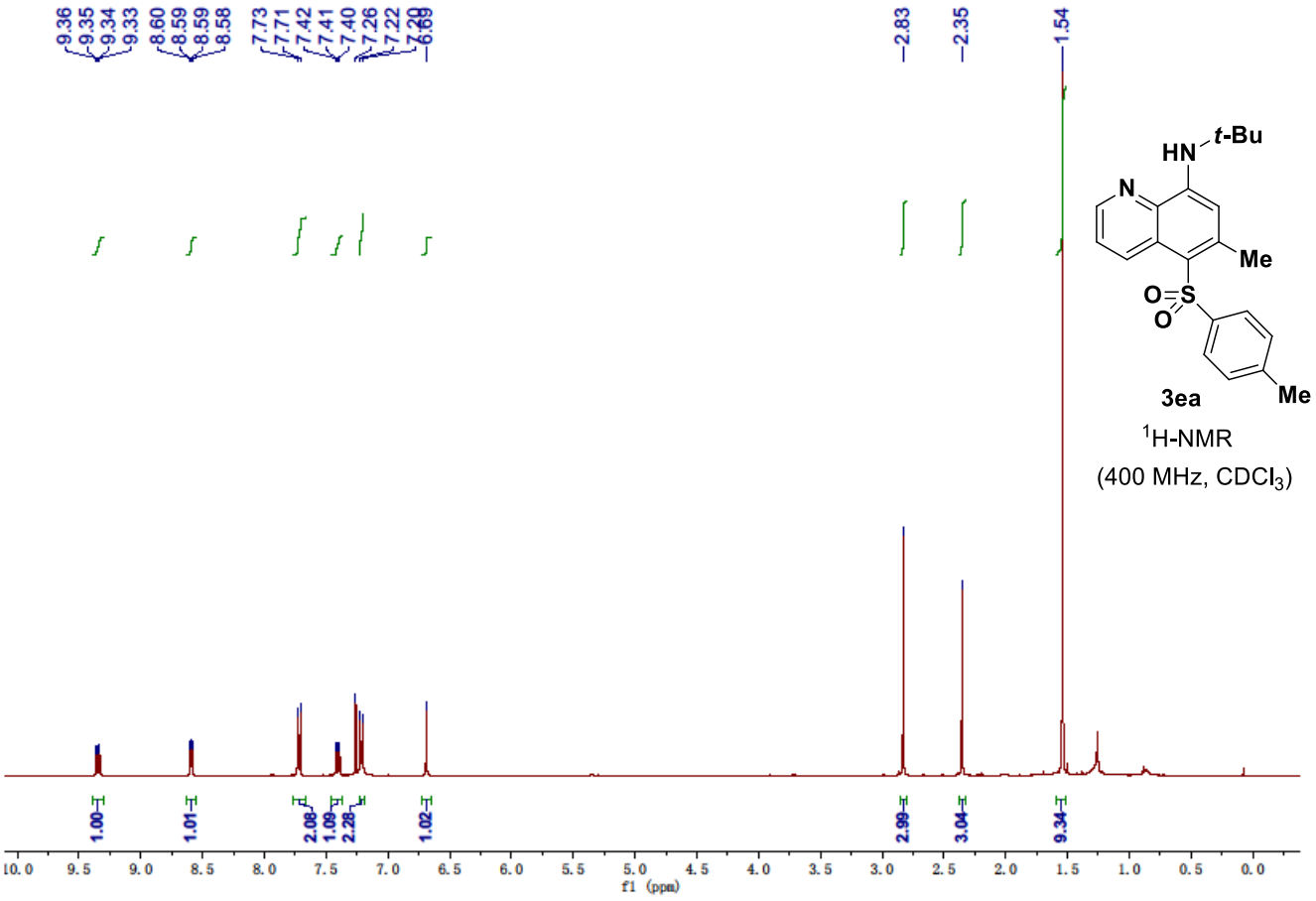
3da

^{1}H-NMR
(400 MHz, $CDCl_3$)

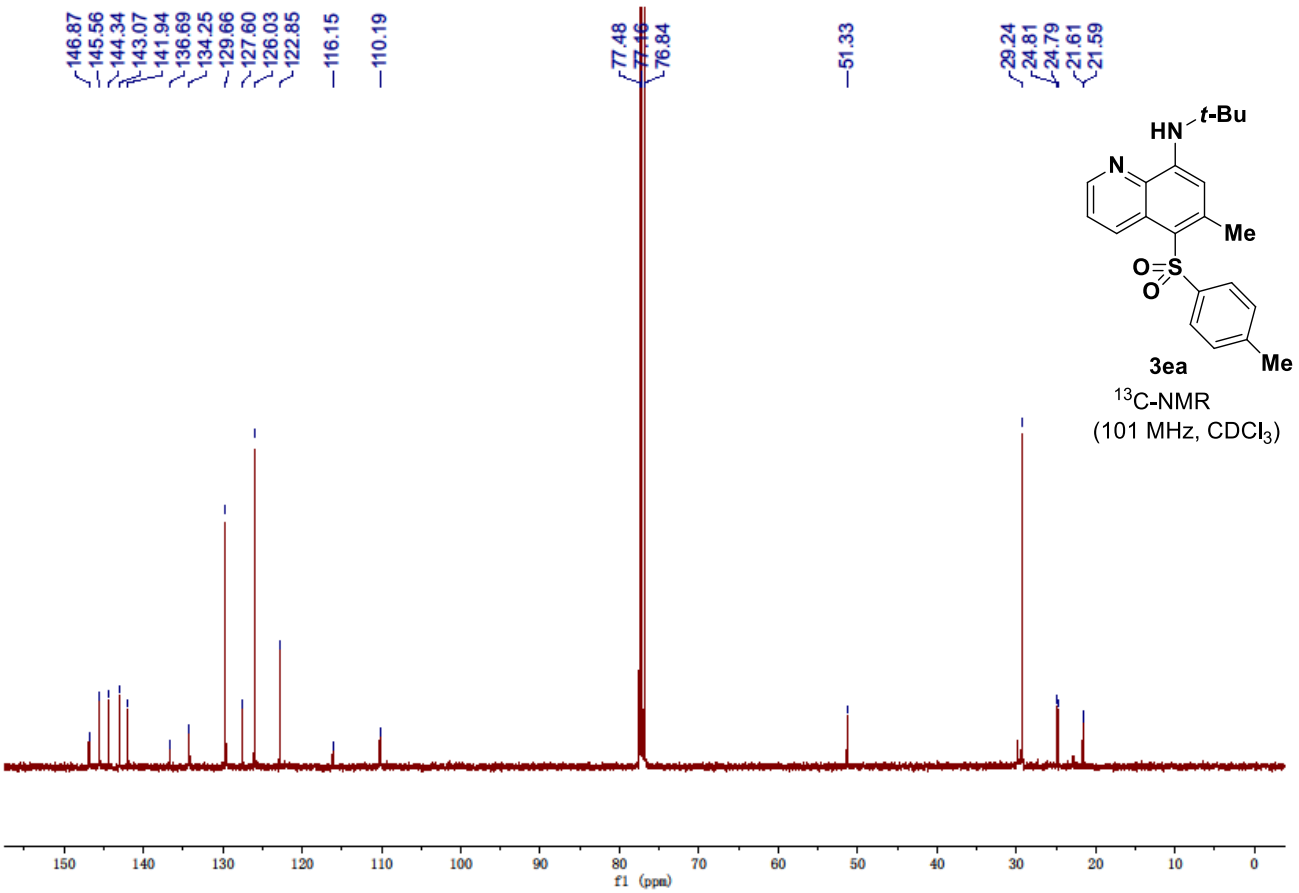


3da

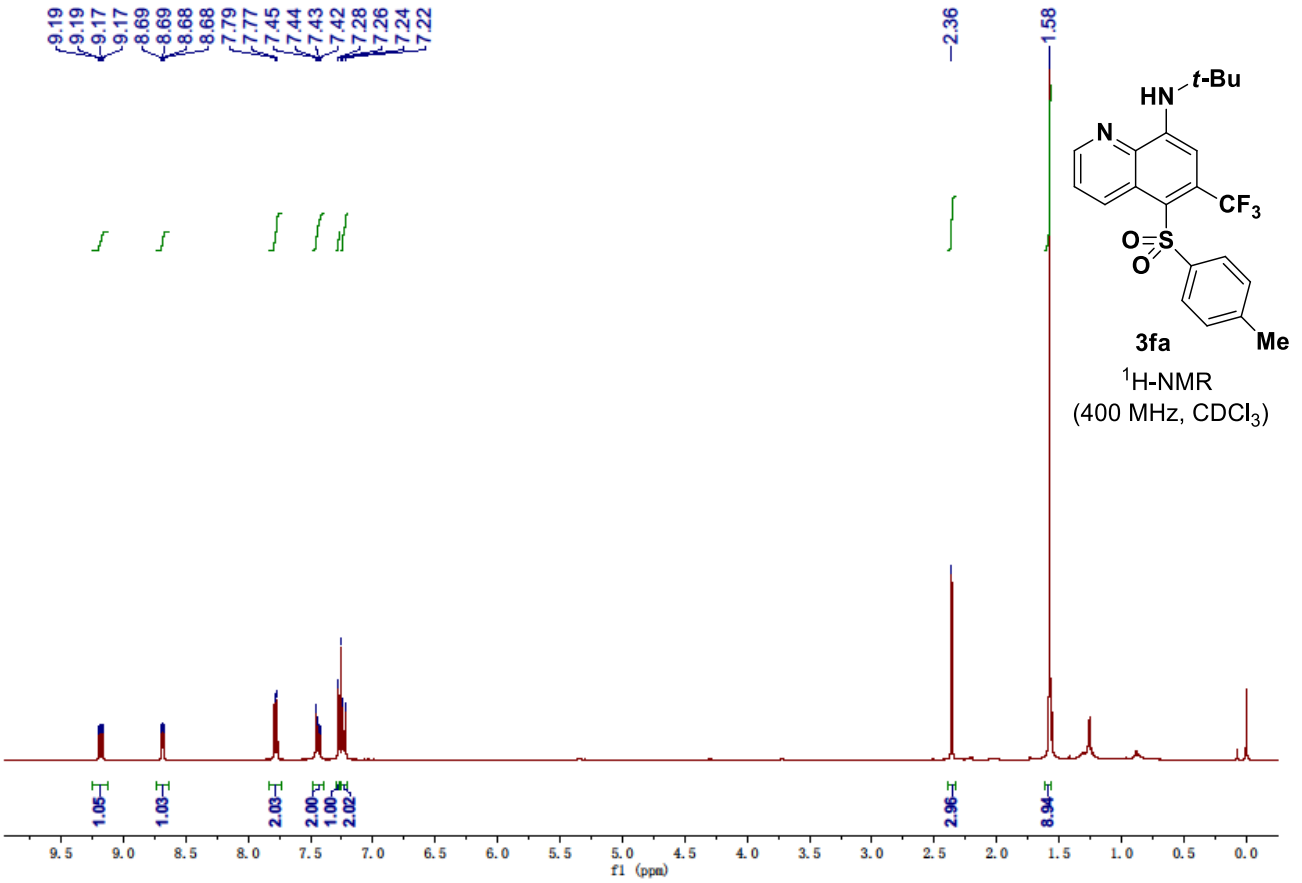
^{13}C-NMR
(101 MHz, $CDCl_3$)



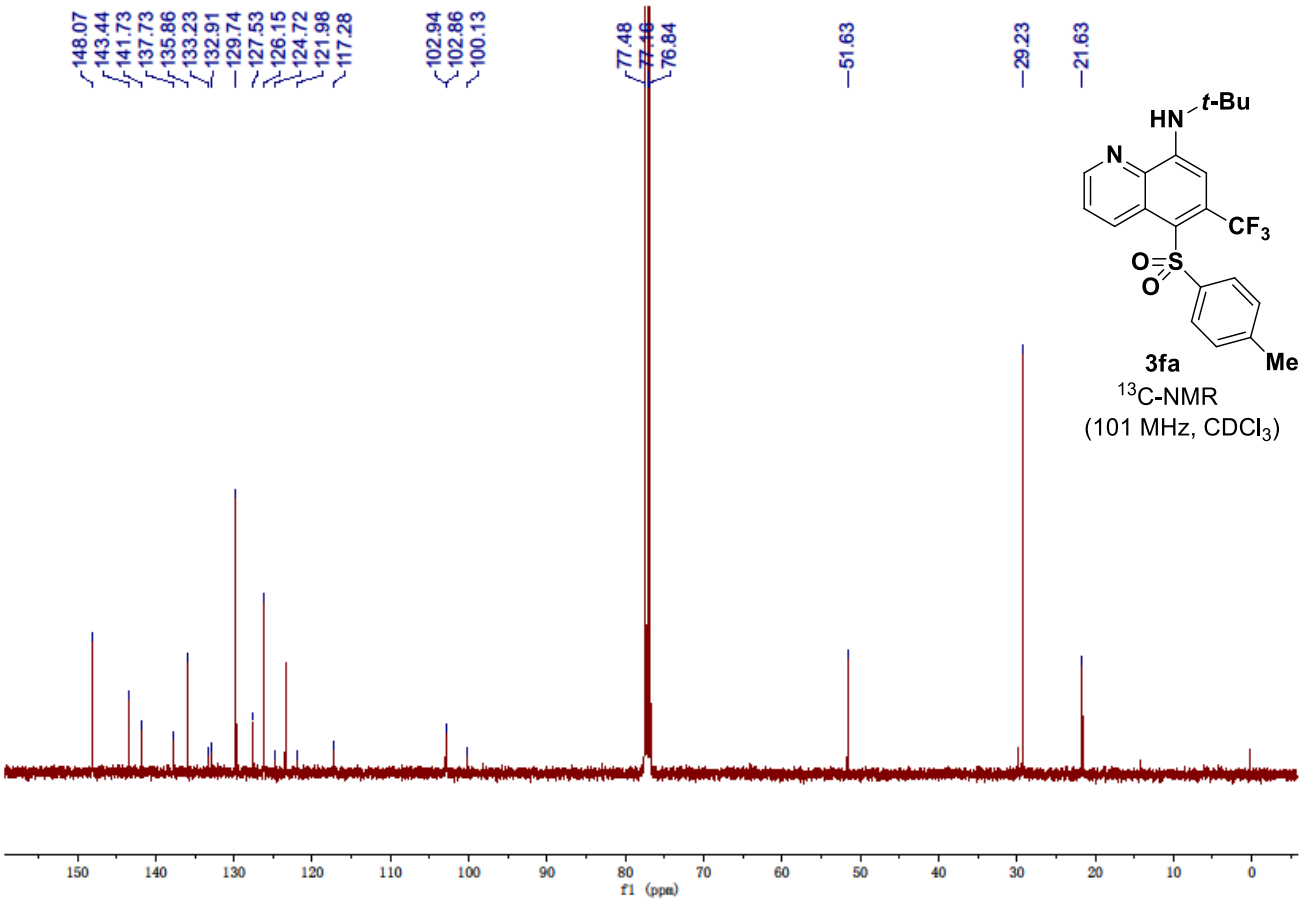
^{1}H-NMR
(400 MHz, $CDCl_3$)



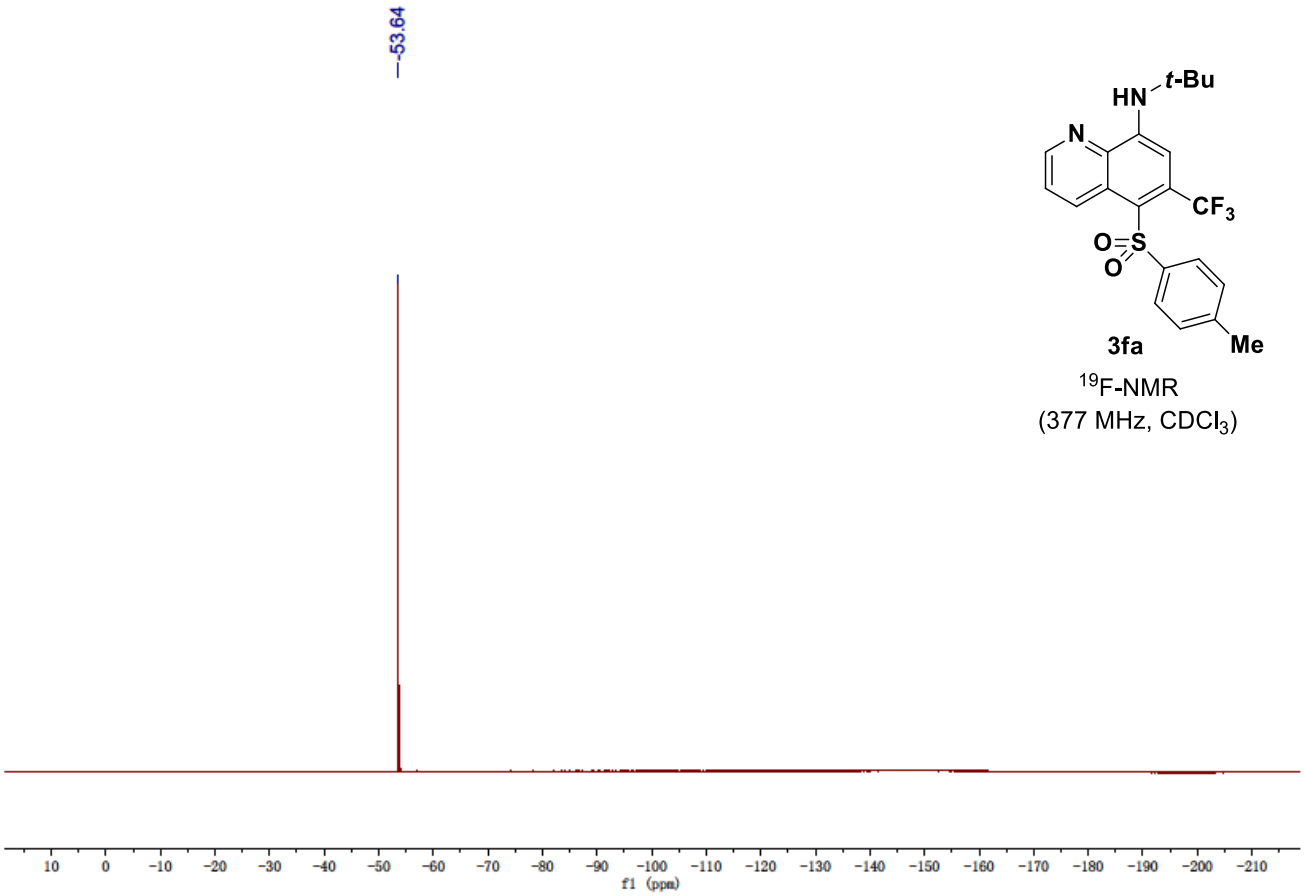
^{13}C-NMR
(101 MHz, $CDCl_3$)

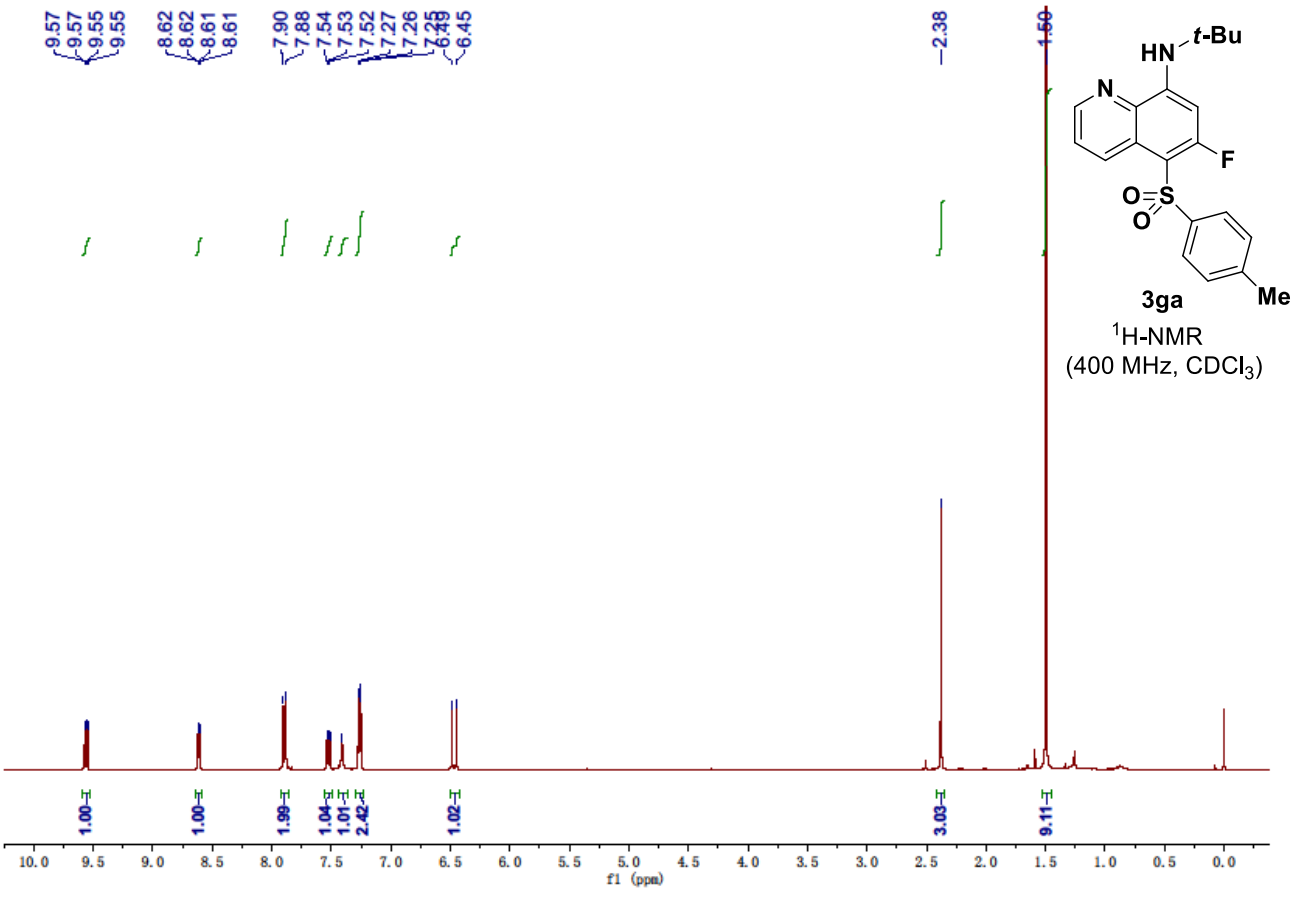


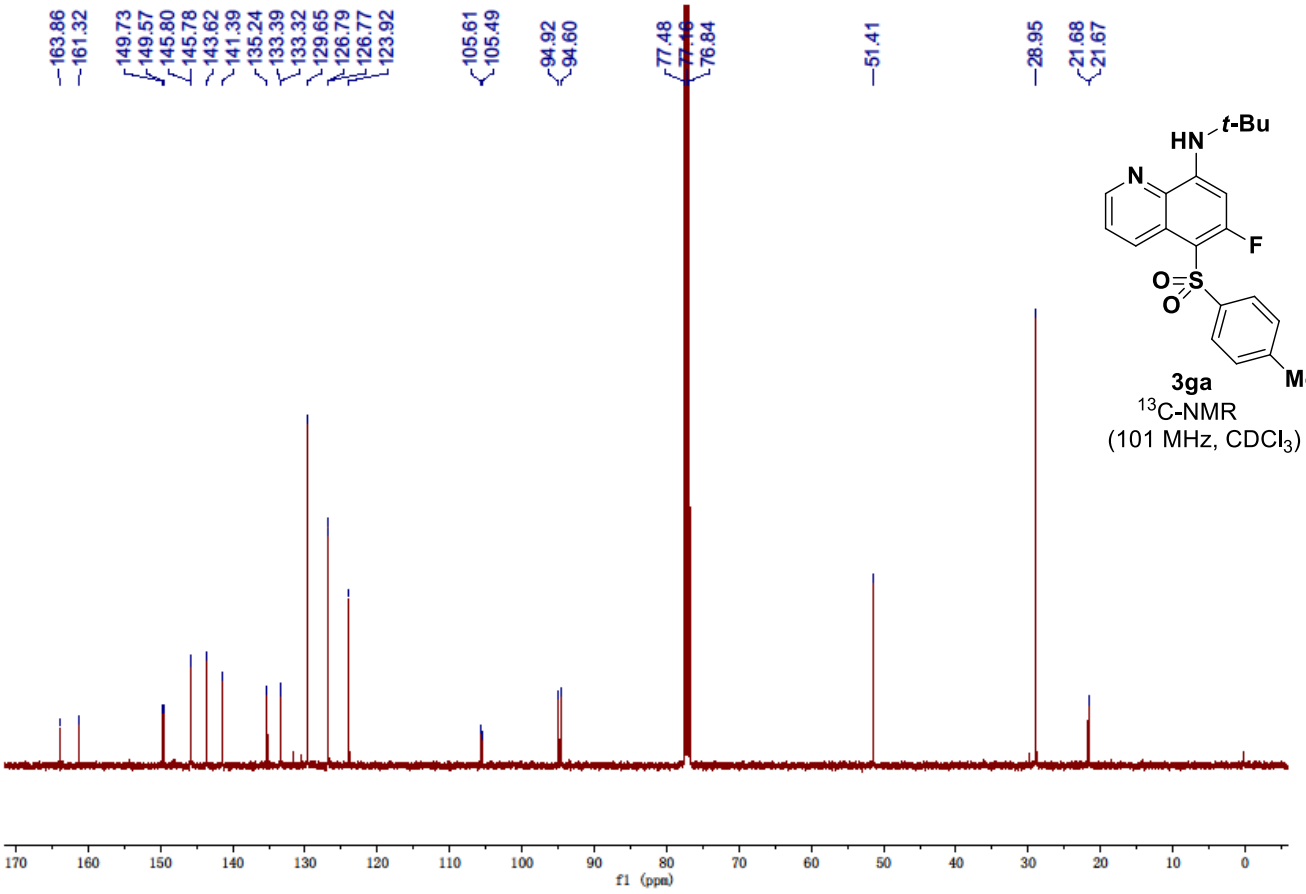
^{1}H-NMR
(400 MHz, $CDCl_3$)

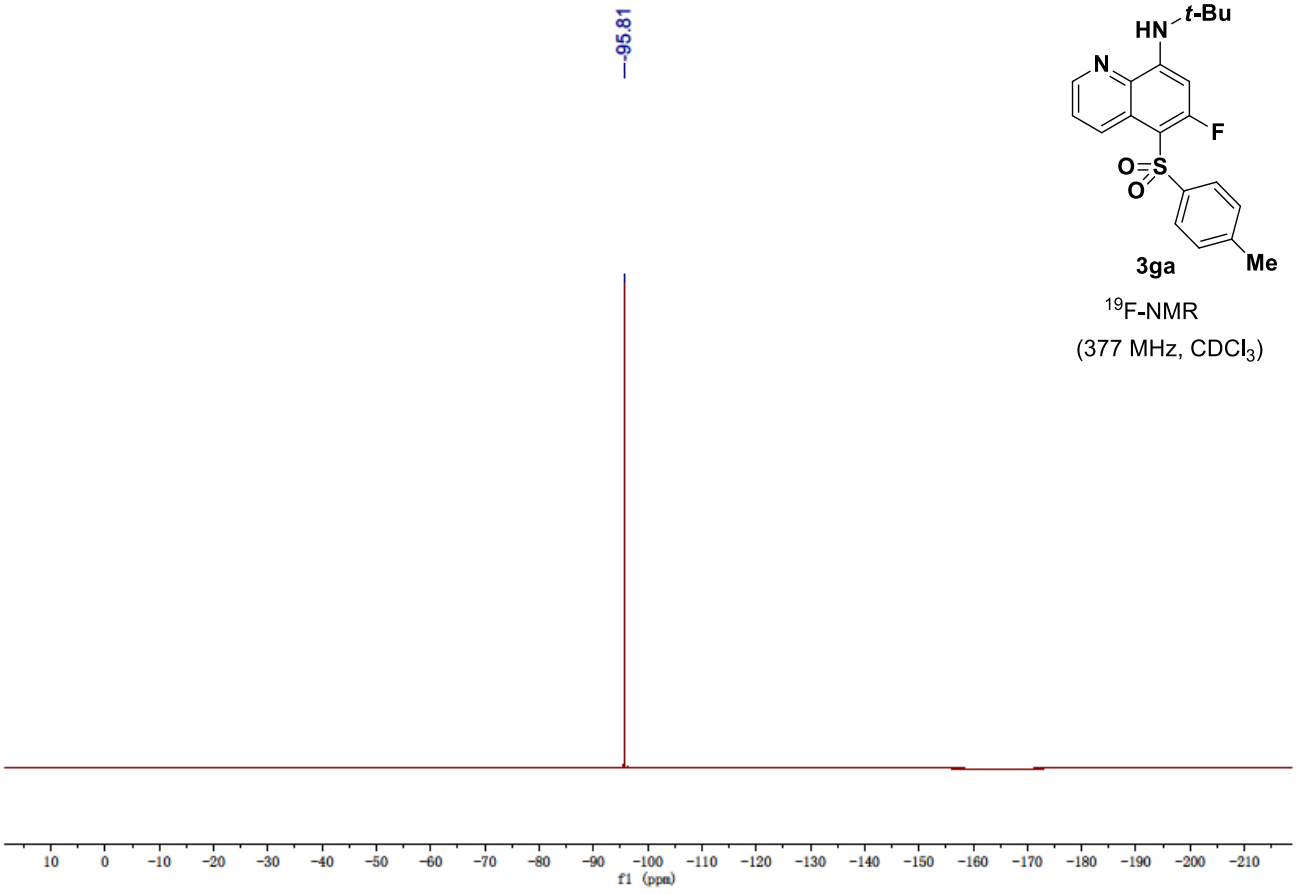


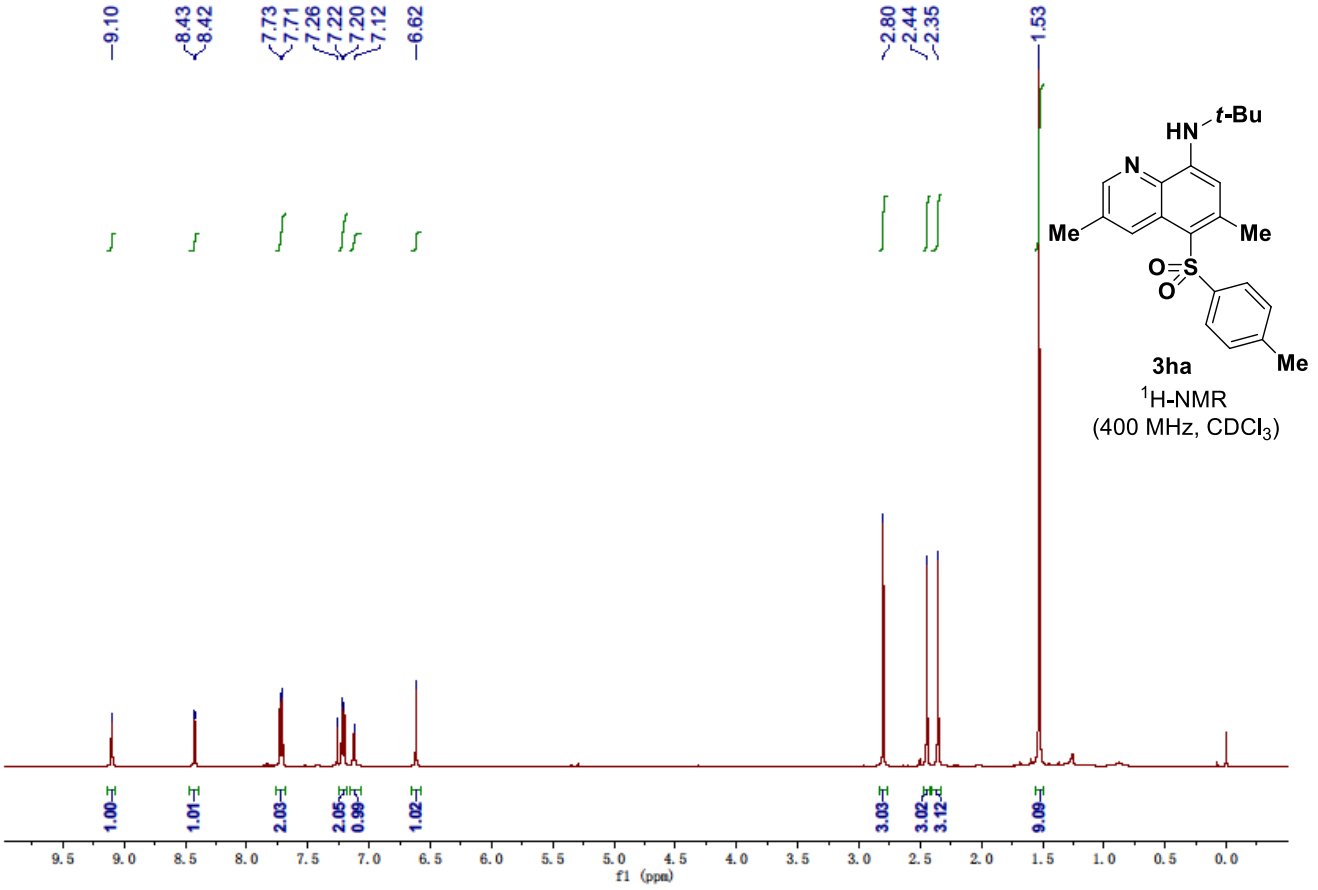
^{13}C-NMR
(101 MHz, $CDCl_3$)

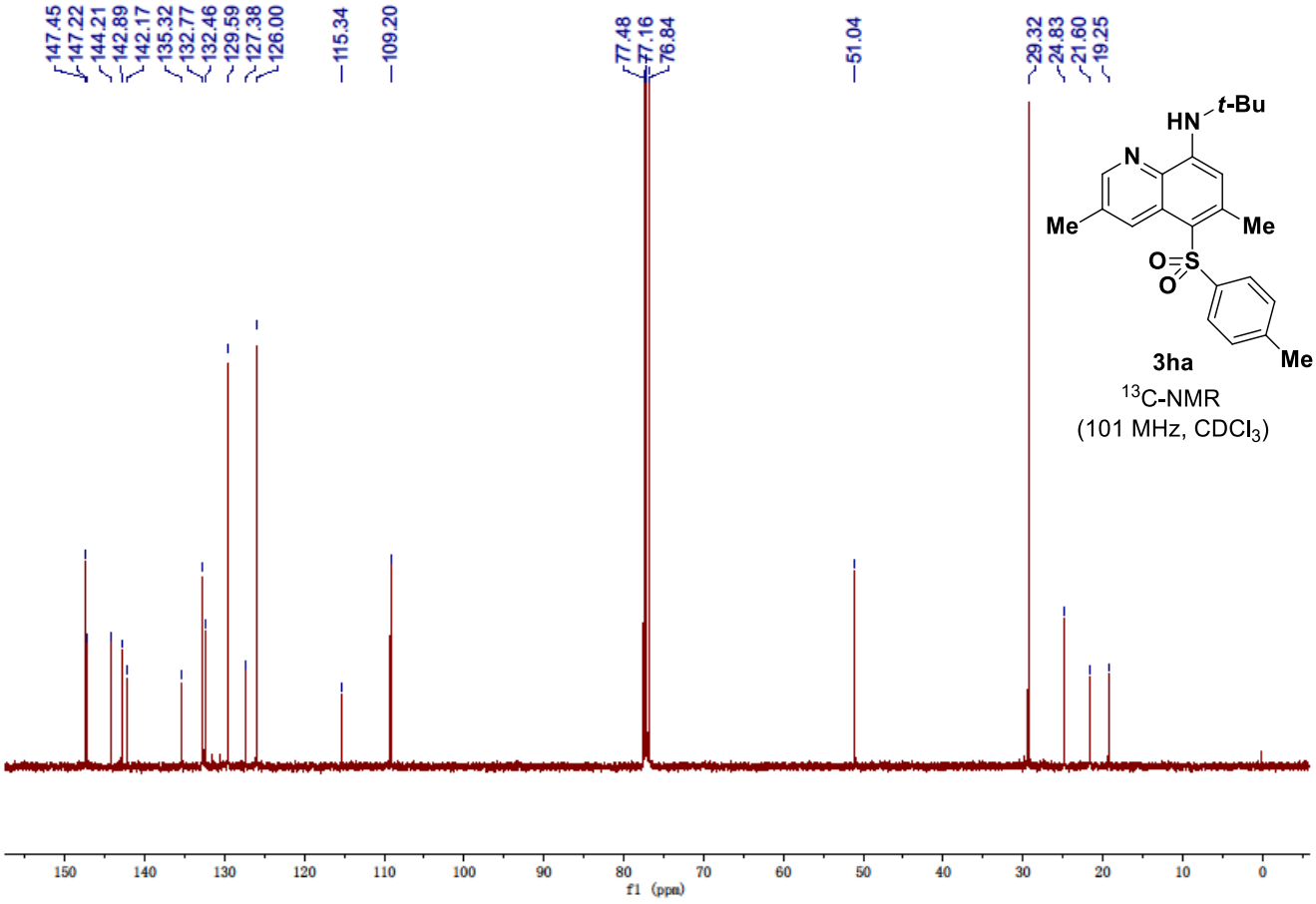

-53.64
HN
t-Bu
N
CF3
O=S
O
Me
3fa
19F-NMR
(377 MHz, CDCl3)
f1 (ppm)

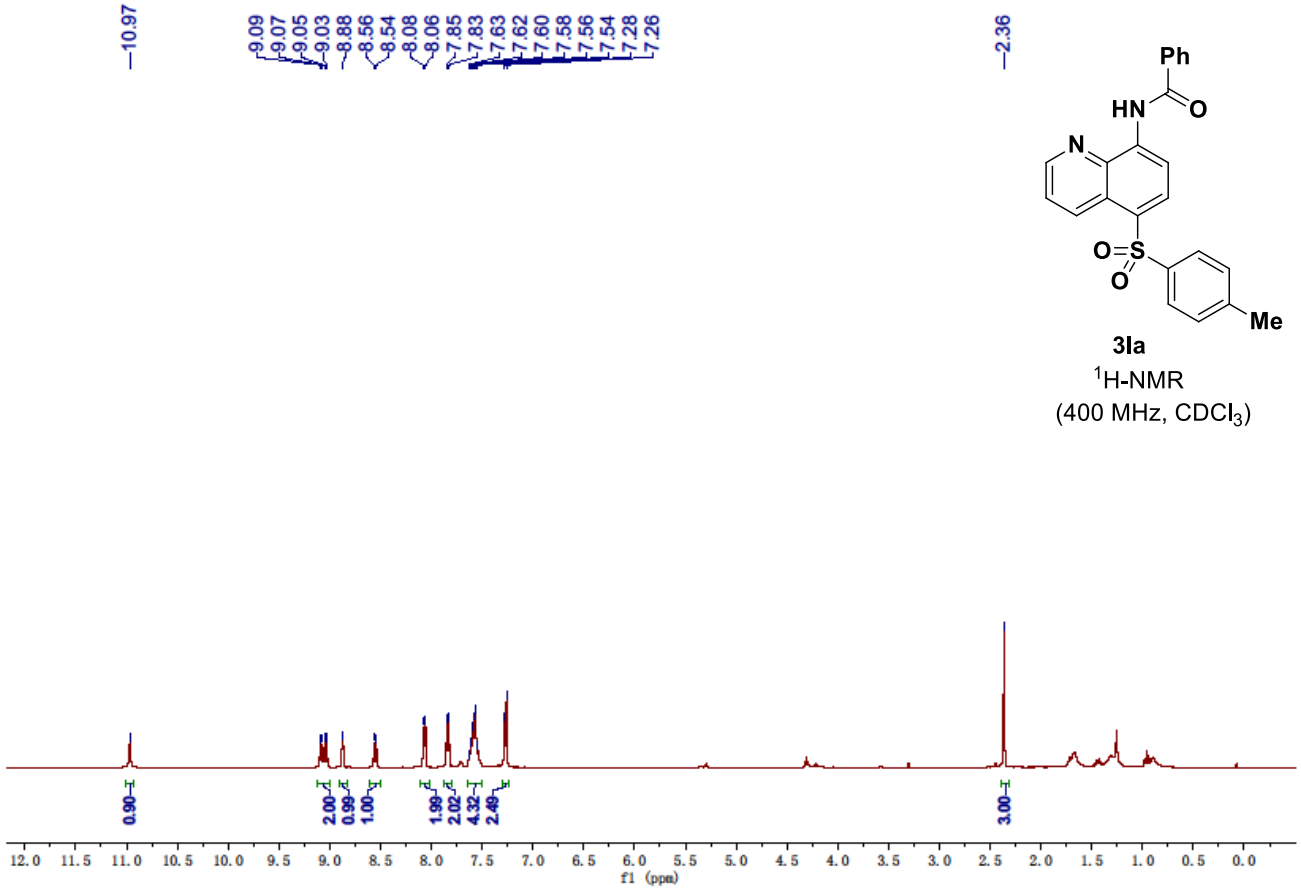

9.57
9.57
9.55
9.55
8.62
8.62
8.61
8.61
7.90
7.88
7.54
7.53
7.52
7.27
7.26
6.45
2.38
1.50
HN
t-Bu
N
F
O=S
O
Me
3ga
1H-NMR
(400 MHz, CDCl3)
1.00
1.00
1.99
1.04
1.01
2.42
1.02
3.03
9.11
f1 (ppm)


163.86
161.32
149.73
149.57
145.80
145.78
143.62
141.39
135.24
133.39
133.32
129.65
126.79
126.77
123.92
105.61
105.49
94.92
94.60
77.48
77.16
76.84
51.41
28.95
21.68
21.67
HN
t-Bu
N
F
O=S
O
Me
3ga
13C-NMR
(101 MHz, CDCl3)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


-95.81
HN
t-Bu
N
F
O=S
O
Me
3ga
19F-NMR
(377 MHz, CDCl3)
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)


9.10
8.43
8.42
7.73
7.71
7.26
7.22
7.20
7.12
6.62
2.80
2.44
2.35
1.53
1.00
1.01
2.03
2.05
0.98
1.02
3.03
3.02
3.12
9.09
f1 (ppm)
HN
t-Bu
N
Me
Me
O=S
O
Me
3ha
1H-NMR
(400 MHz, CDCl3)

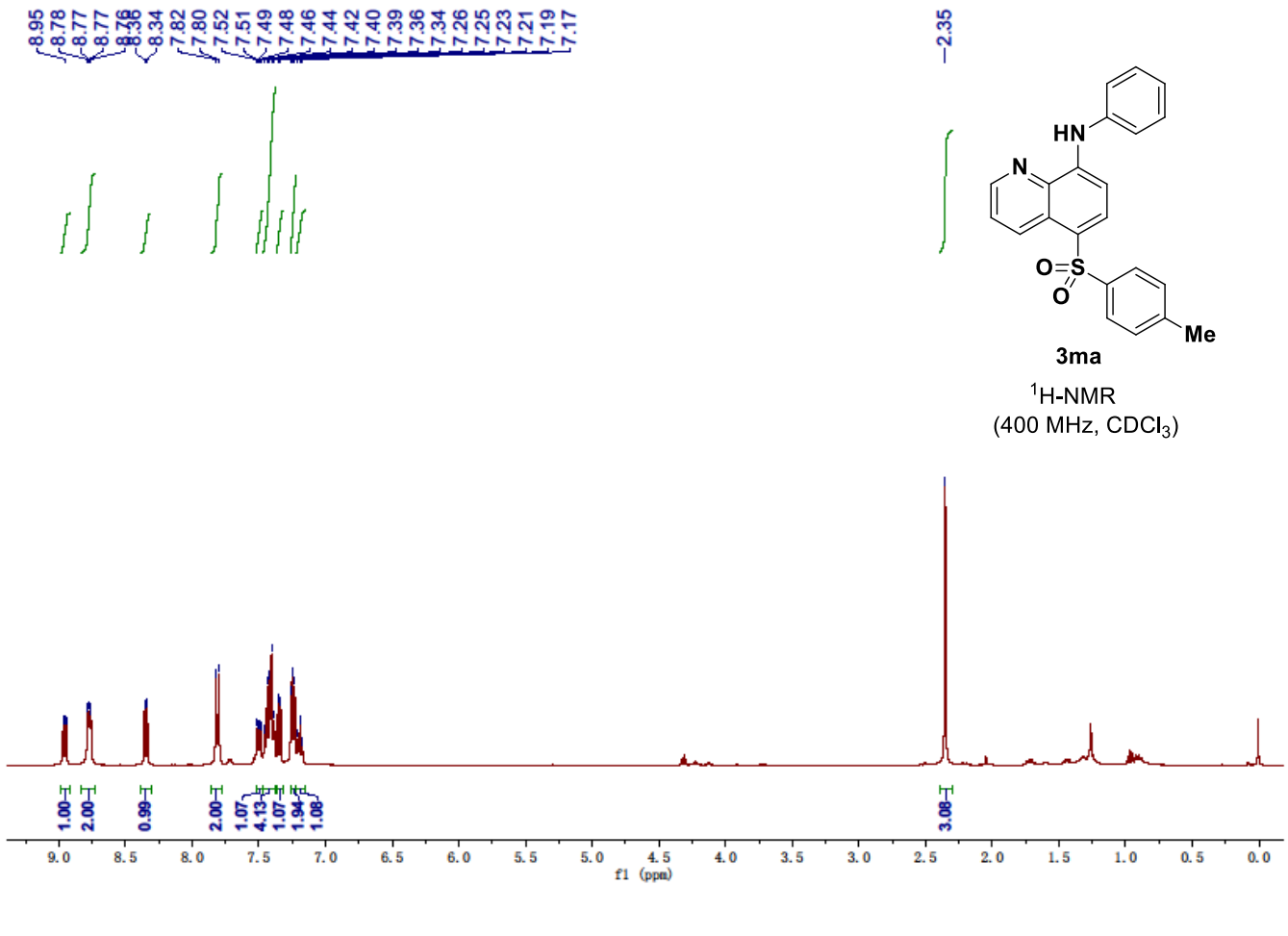

147.45
147.22
144.21
142.89
142.17
135.32
132.77
132.46
129.59
127.38
126.00
115.34
109.20
77.48
77.16
76.84
51.04
29.32
24.83
21.60
19.25
f1 (ppm)
HN
t-Bu
N
Me
Me
O=S
O
Me
3ha
13C-NMR
(101 MHz, CDCl3)



3la

^{1}H-NMR

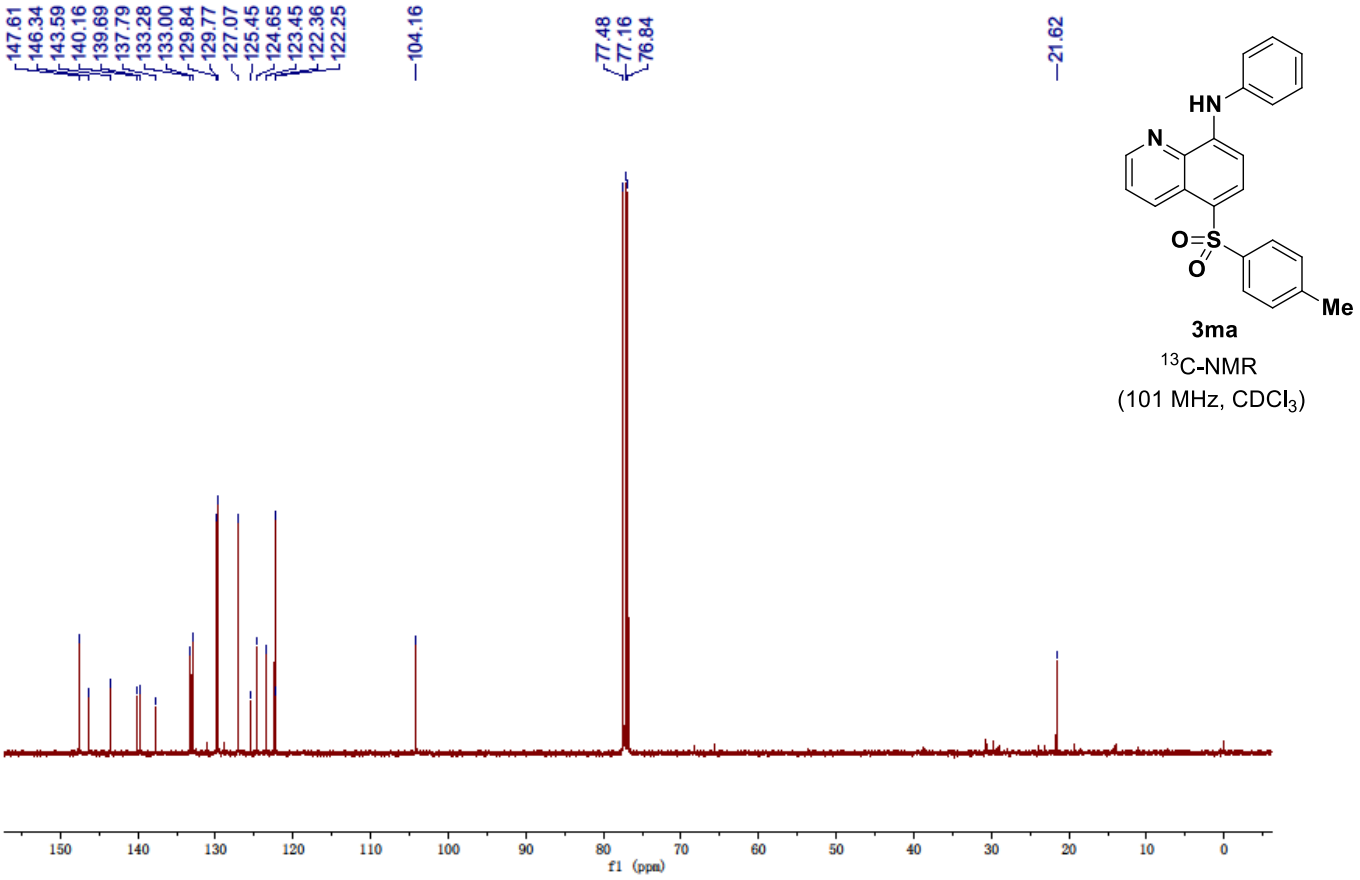
(400 MHz, $CDCl_3$)

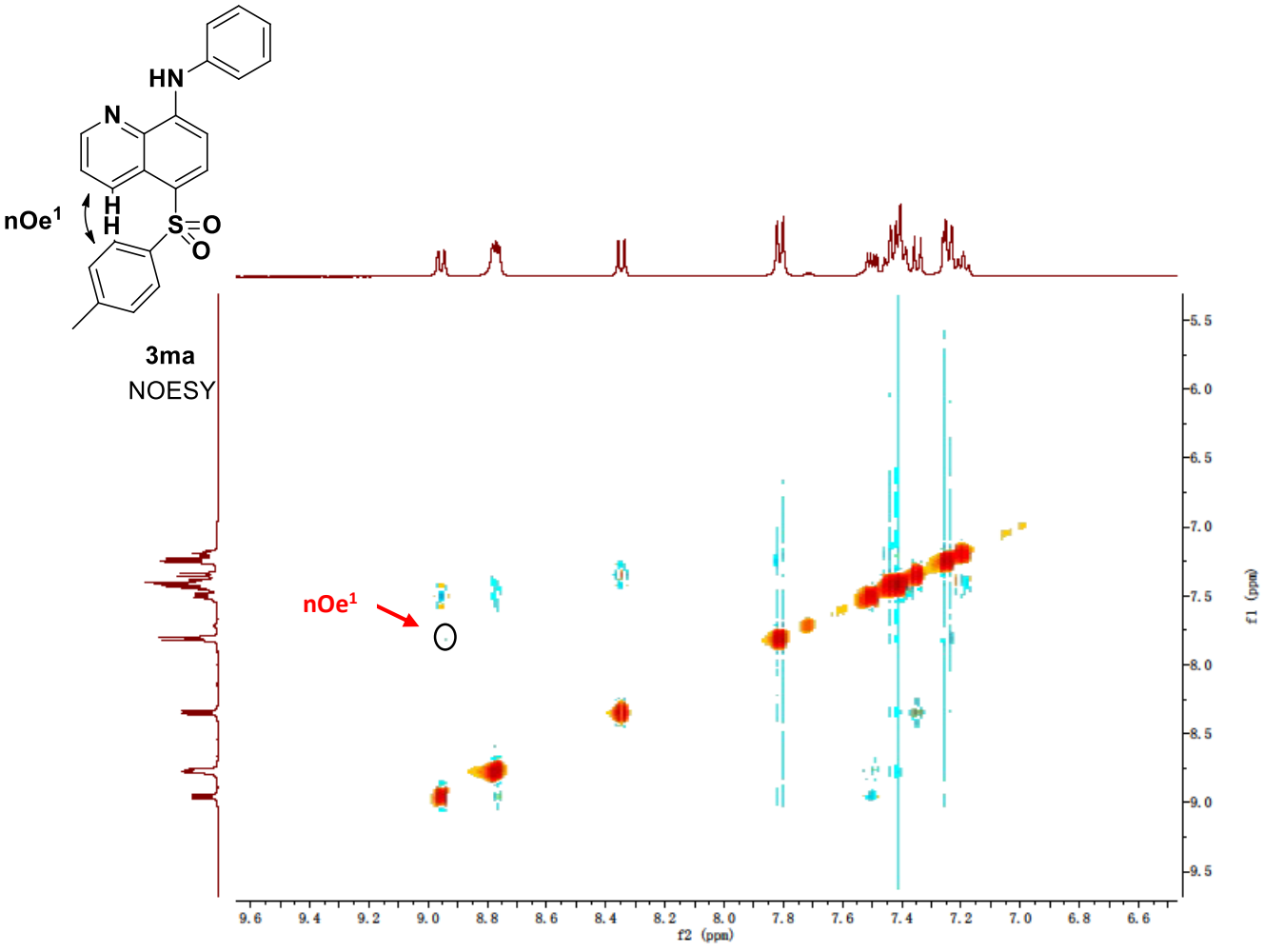


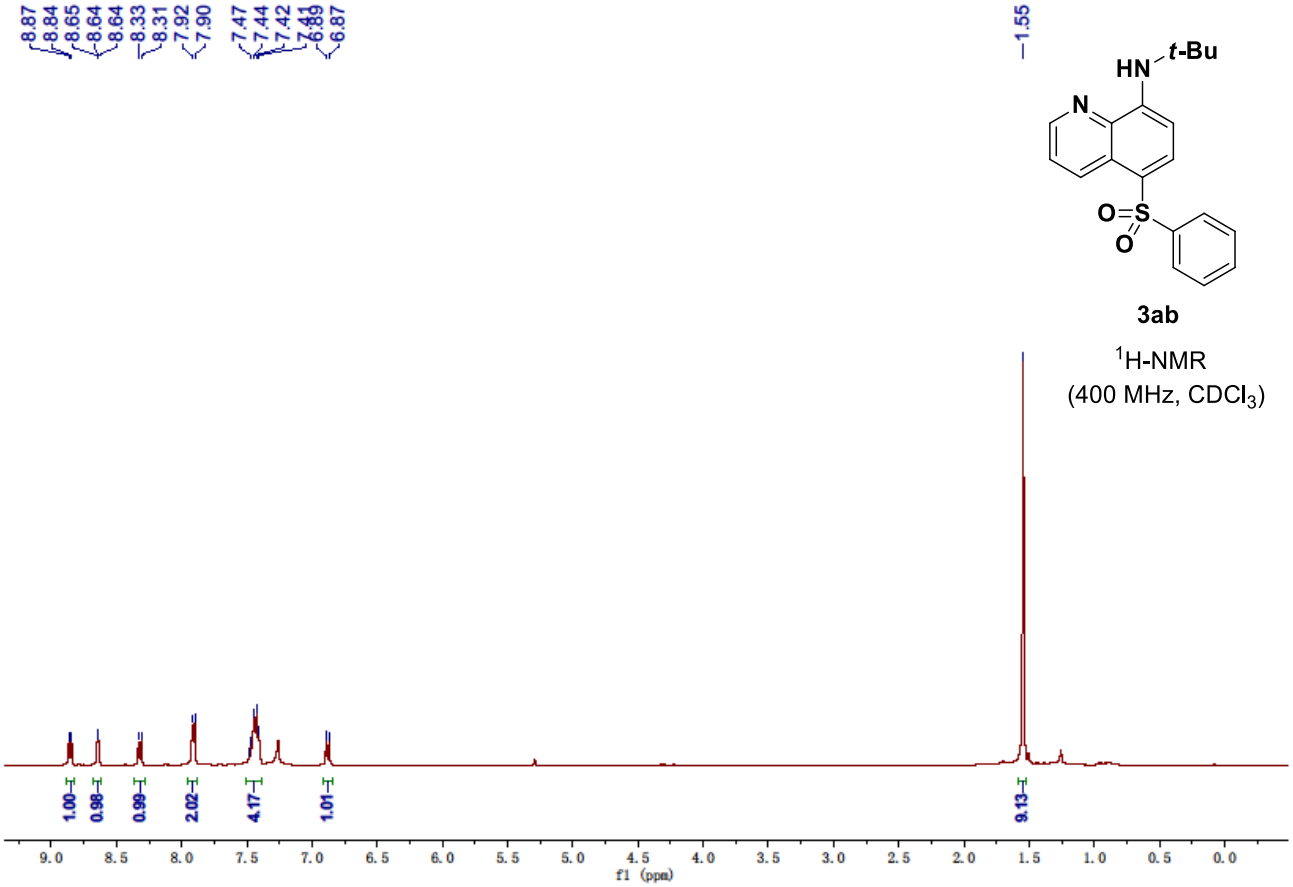
3ma

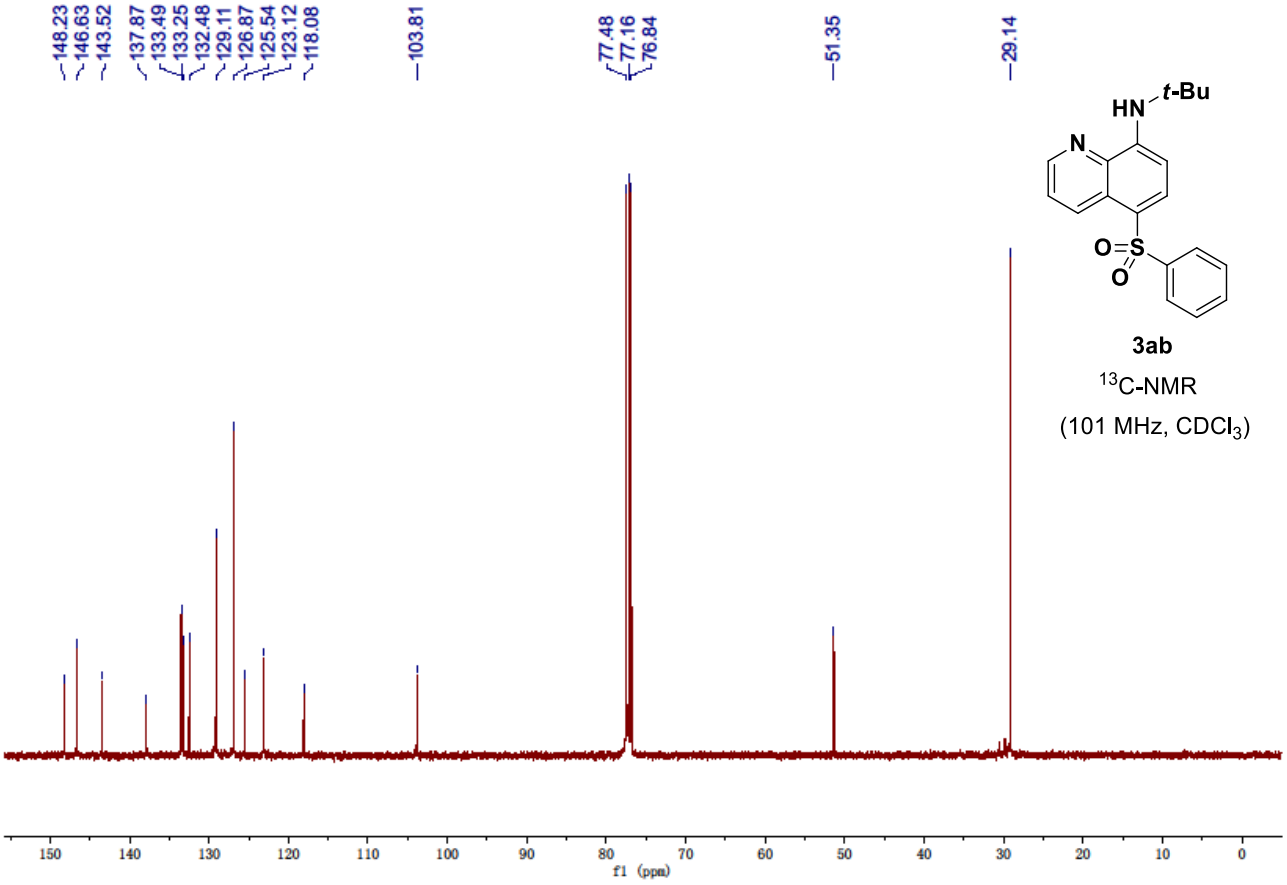
^{1}H-NMR

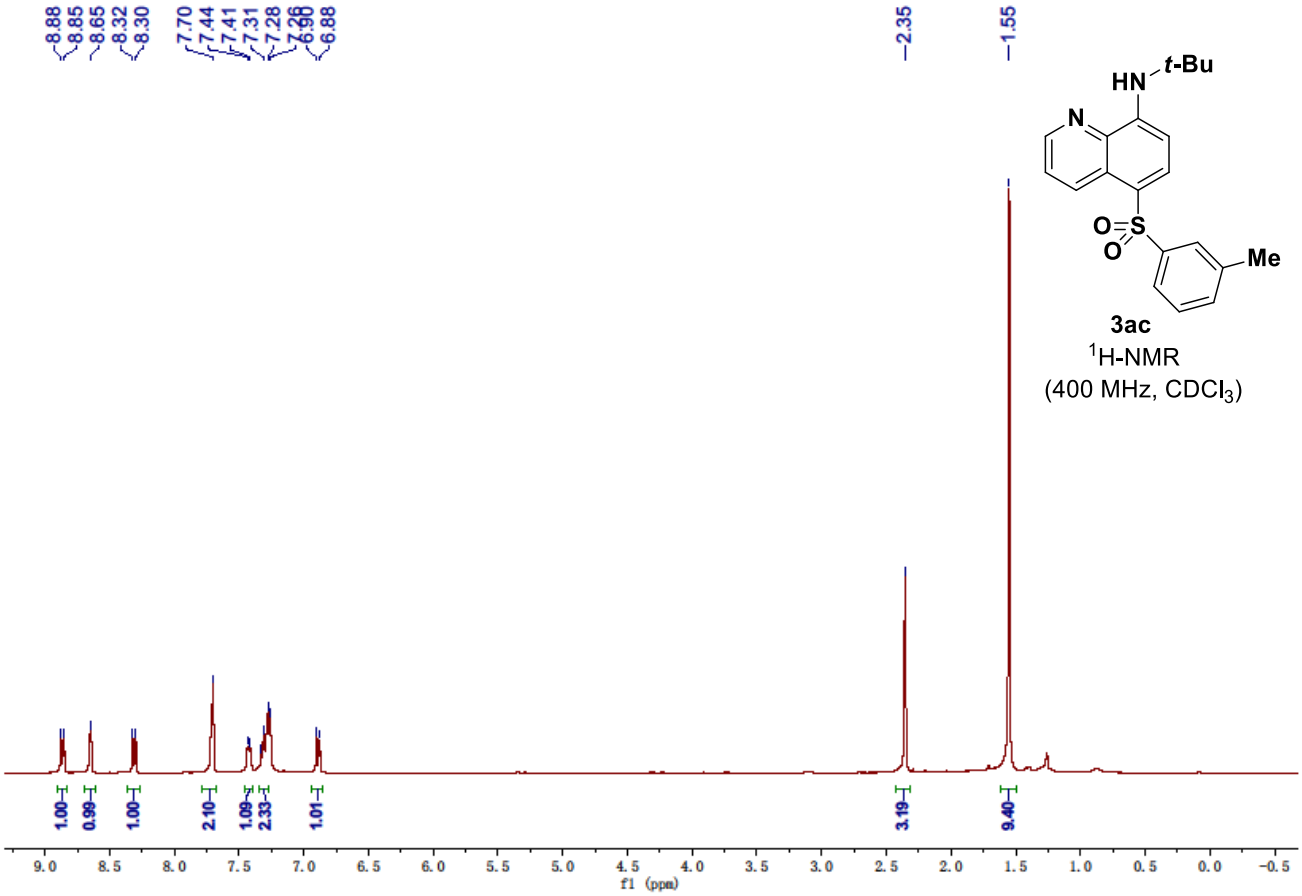
(400 MHz, $CDCl_3$)

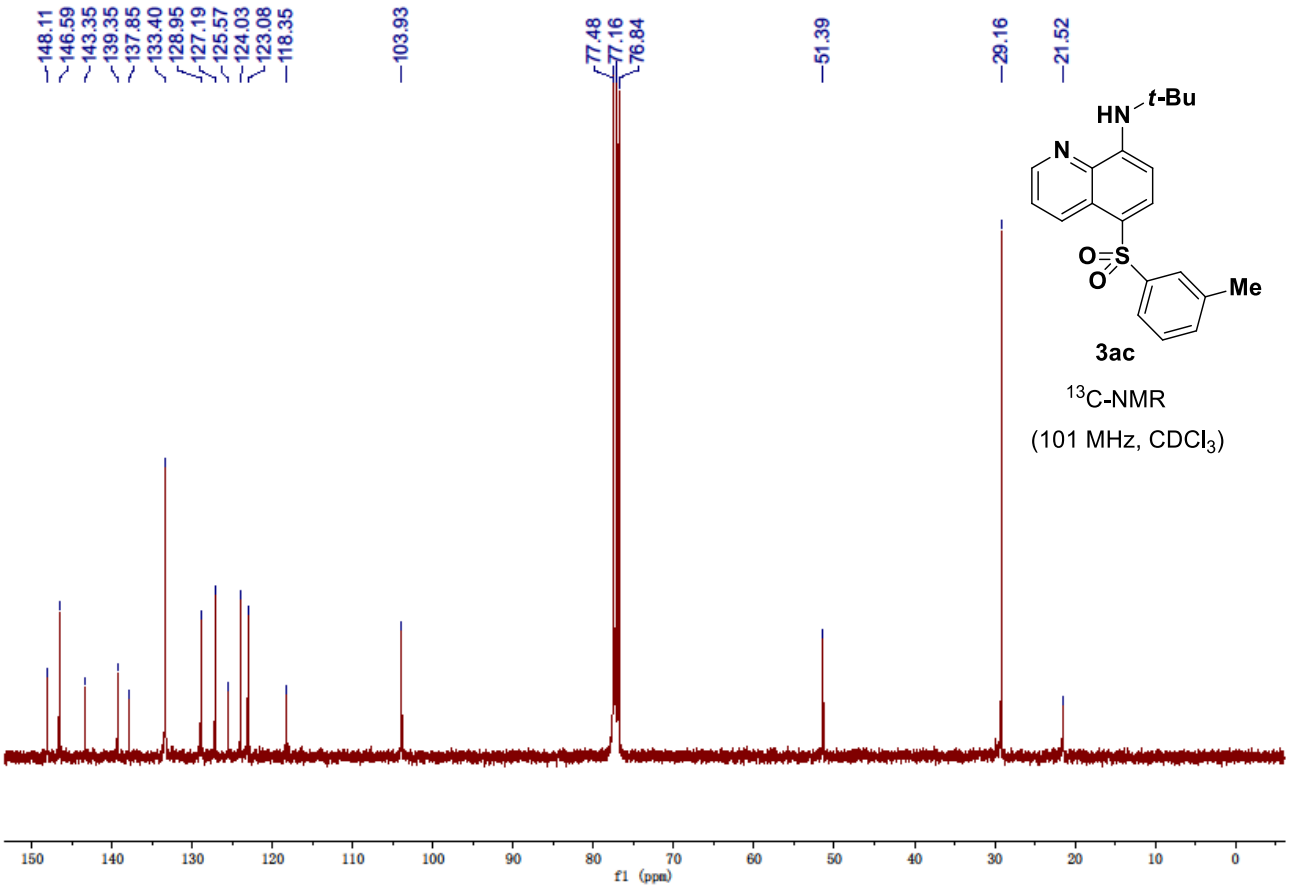

147.61
146.34
143.59
140.16
139.69
137.79
133.28
133.00
129.84
129.77
127.07
125.45
124.65
123.45
122.36
122.25
104.16
77.48
77.16
76.84
21.62
HN
N
O=S
O
Me
3ma
13C-NMR
(101 MHz, CDCl3)
f1 (ppm)

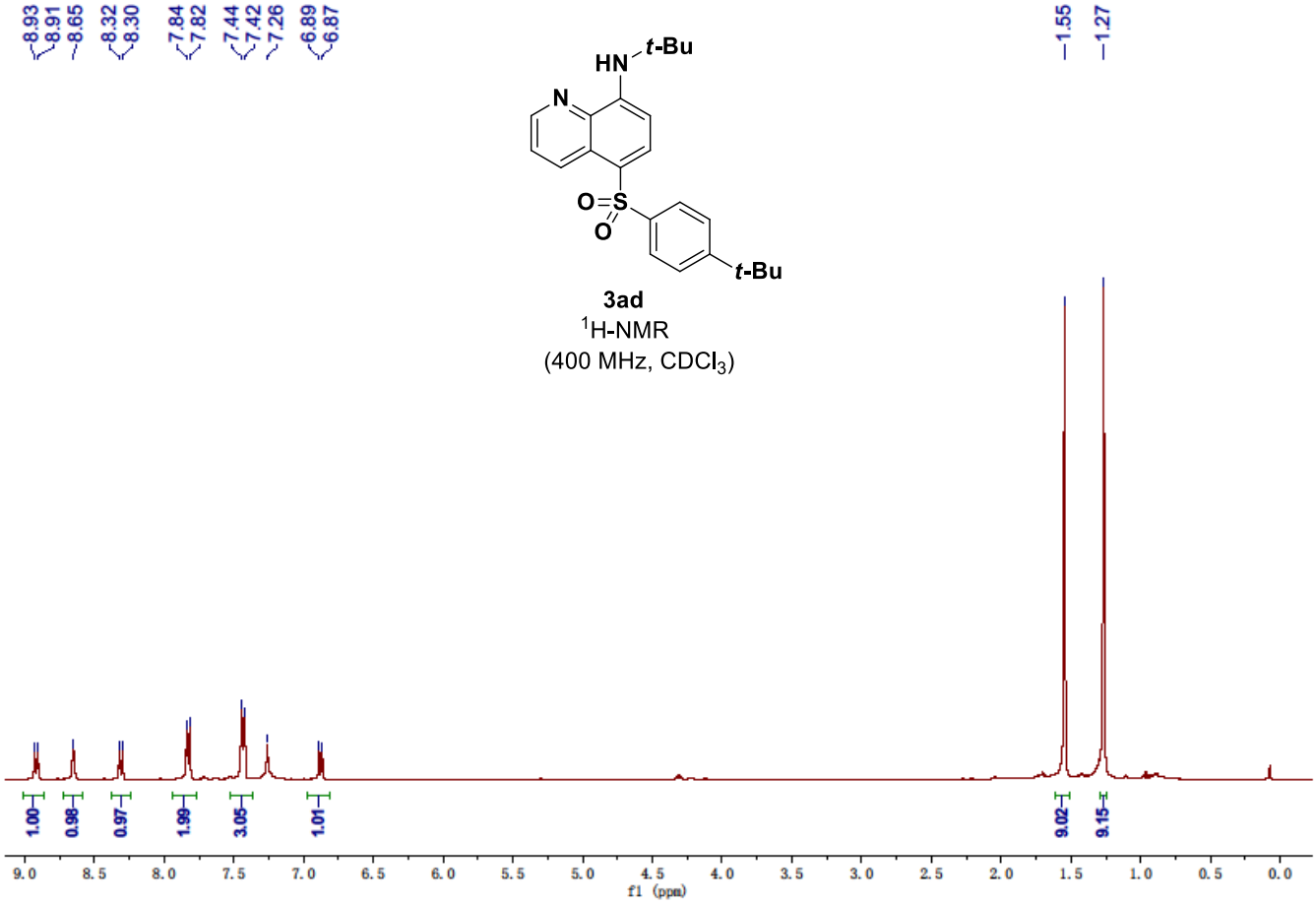

HN
N
H
H
S=O
O
nOe1
3ma
NOESY
nOe1
f2 (ppm)
f1 (ppm)


8.87
8.84
8.65
8.64
8.64
8.33
8.31
7.92
7.90
7.47
7.44
7.42
7.41
6.89
6.87
1.55
HN
t-Bu
N
O=S
O
3ab
1H-NMR
(400 MHz, CDCl3)
1.00
0.98
0.99
2.02
4.17
1.01
9.13
f1 (ppm)


148.23
146.63
143.52
137.87
133.49
133.25
132.48
129.11
126.87
125.54
123.12
118.08
103.81
77.48
77.16
76.84
51.35
29.14
HN
t-Bu
N
O=S
O
3ab
13C-NMR
(101 MHz, CDCl3)
f1 (ppm)


8.88
8.85
8.65
8.32
8.30
7.70
7.44
7.41
7.31
7.28
6.90
6.88
2.35
1.55
HN
t-Bu
N
O=S
O
Me
3ac
1H-NMR
(400 MHz, CDCl3)
1.00
0.99
1.00
2.10
1.09
2.33
1.01
3.19
9.40
f1 (ppm)

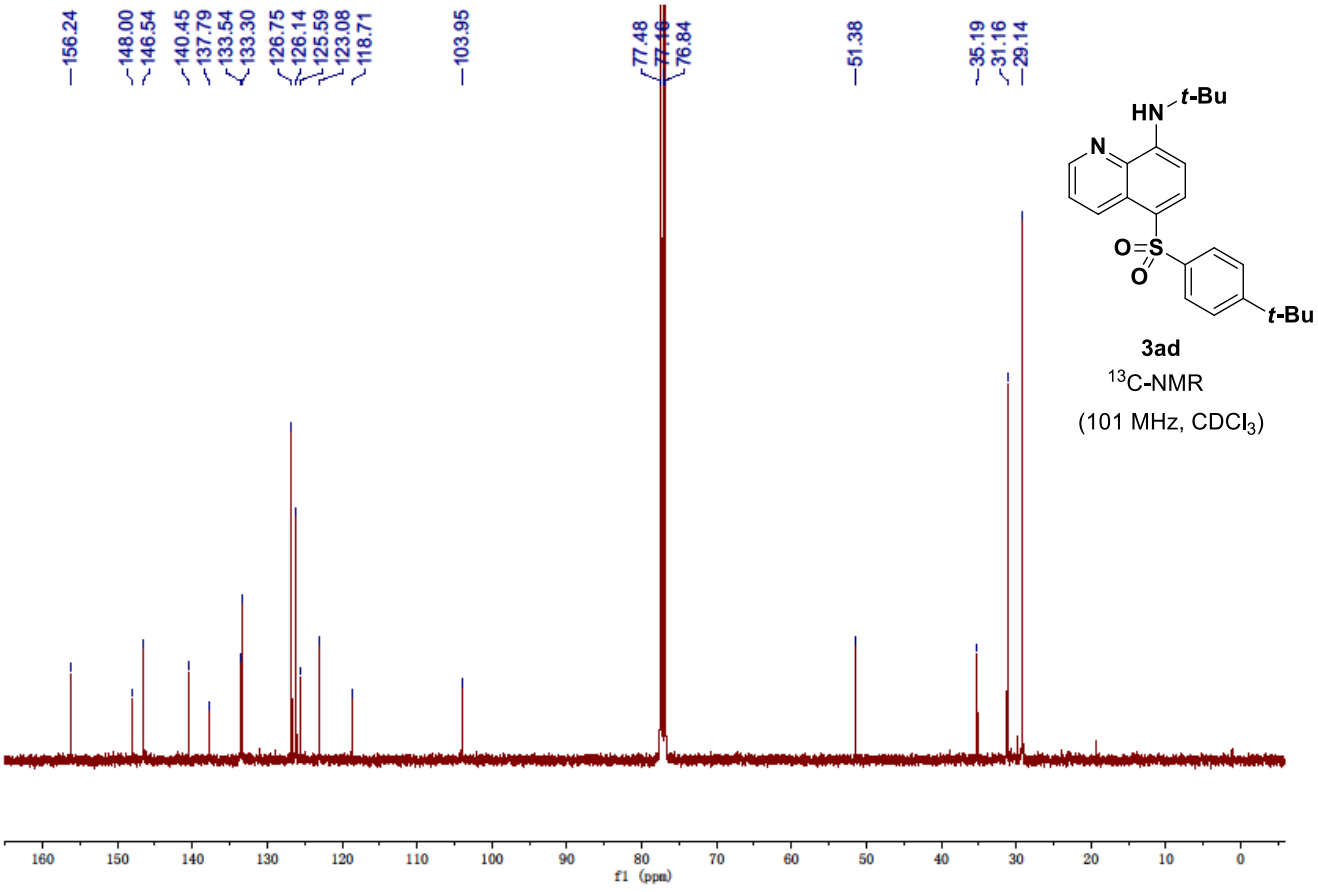

148.11
146.59
143.35
139.35
137.85
133.40
128.95
127.19
125.57
124.03
123.08
118.35
103.93
77.48
77.16
76.84
51.39
29.16
21.52
HN
t-Bu
N
O=S
O
Me
3ac
13C-NMR
(101 MHz, CDCl3)
f1 (ppm)



3ad

^{1}H-NMR

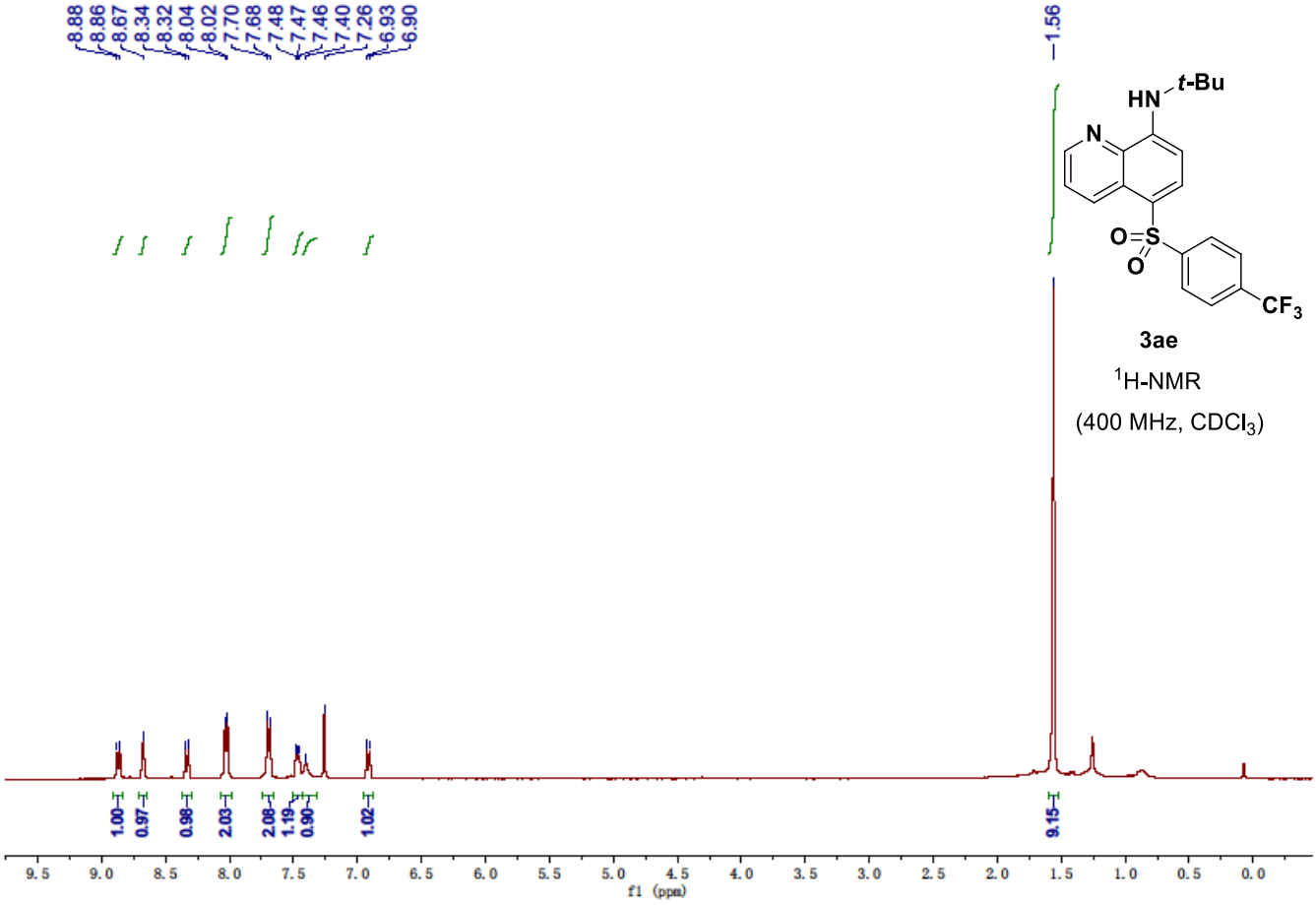
(400 MHz, $CDCl_3$)



3ad

^{13}C-NMR

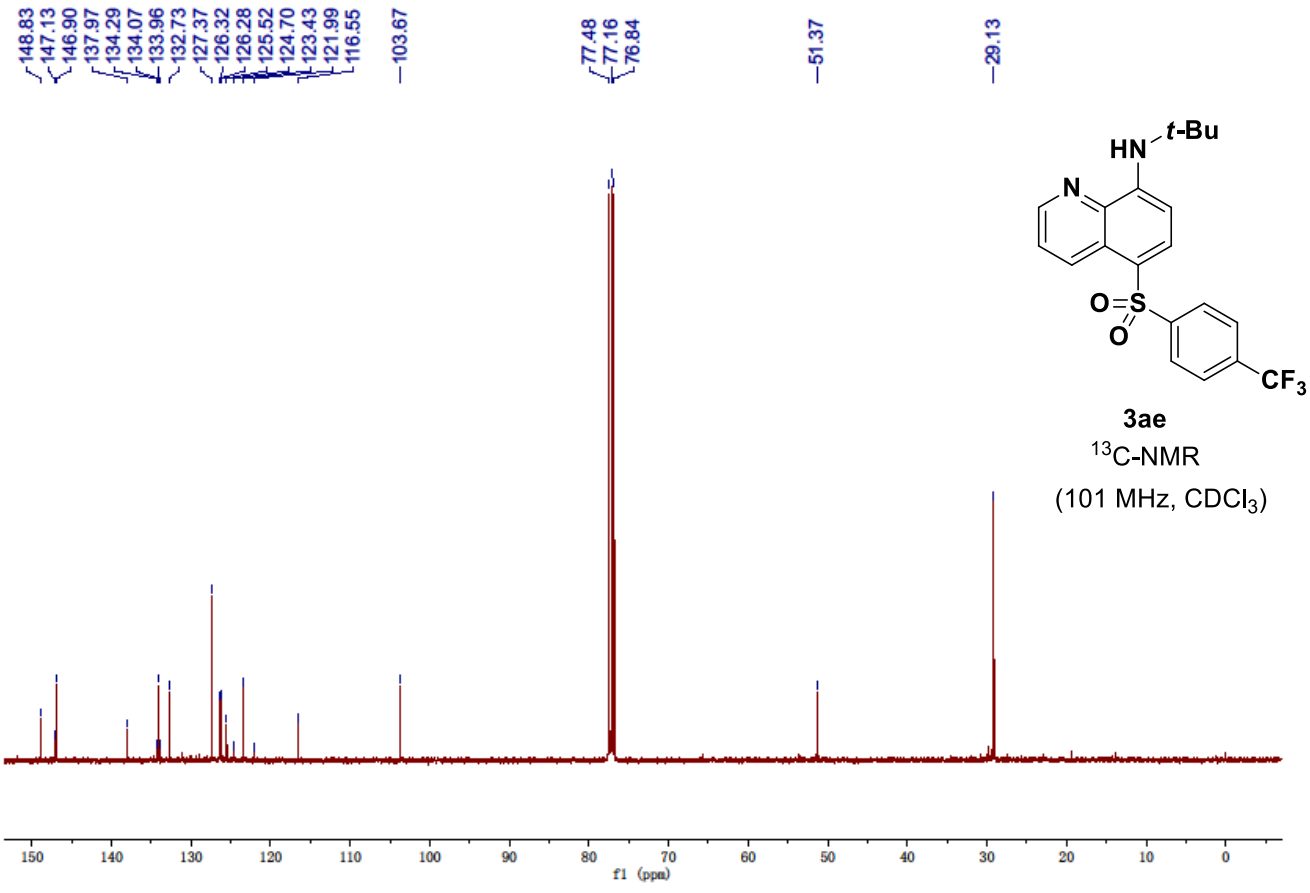
(101 MHz, $CDCl_3$)



3ae

^{1}H-NMR

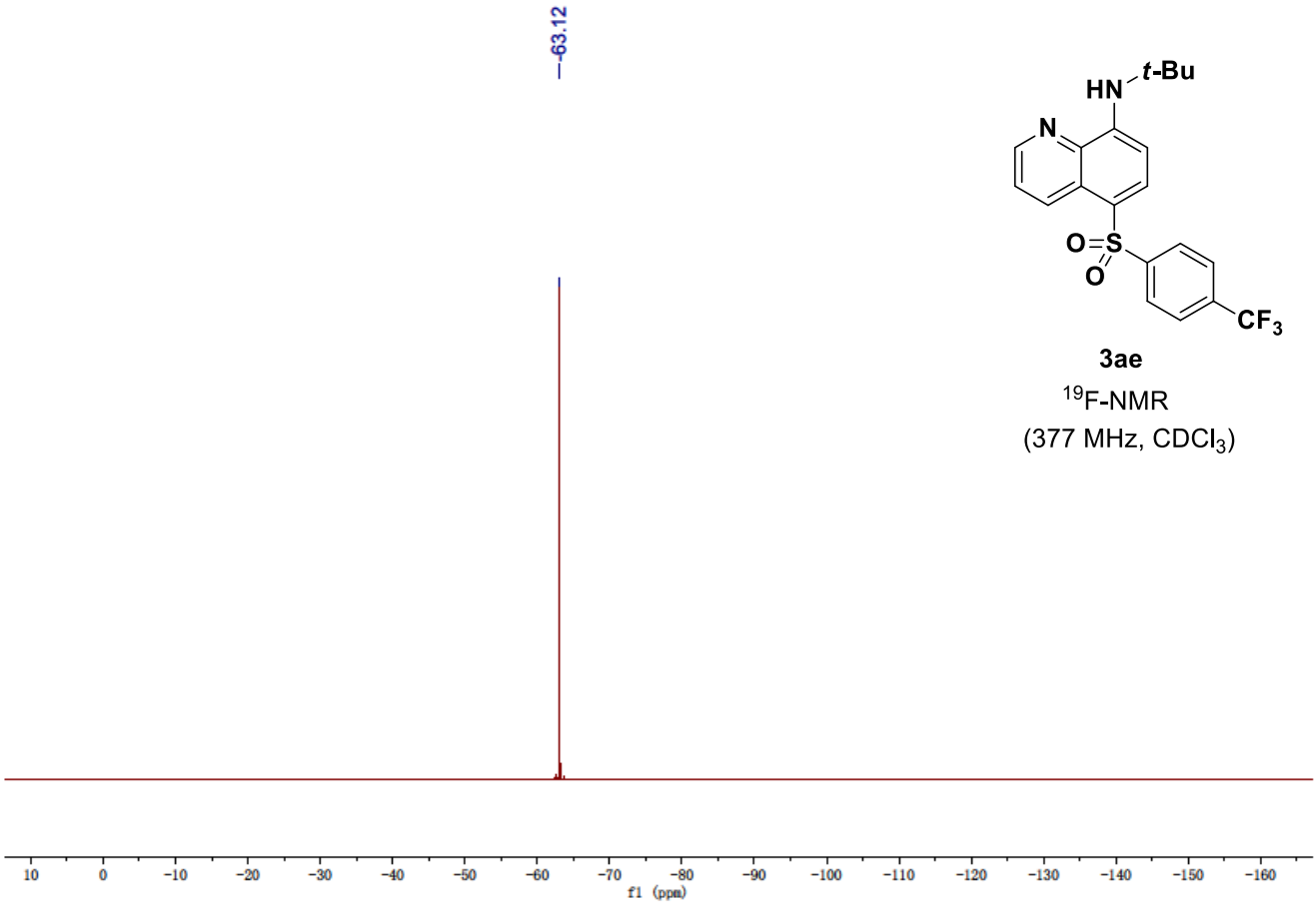
(400 MHz, $CDCl_3$)



3ae

^{13}C-NMR

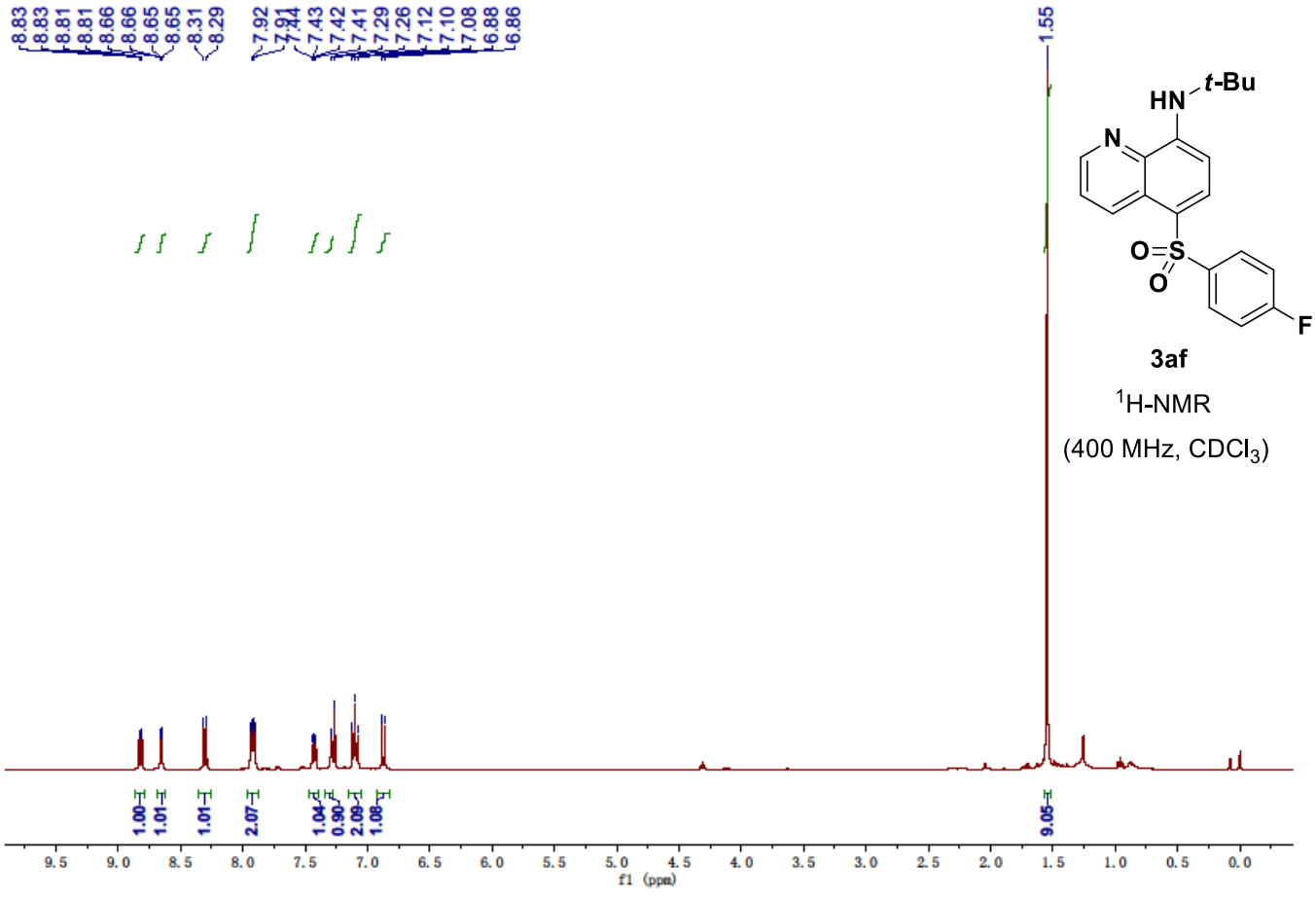
(101 MHz, $CDCl_3$)



3ae

^{19}F-NMR

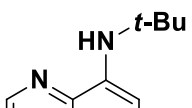
(377 MHz, $CDCl_3$)

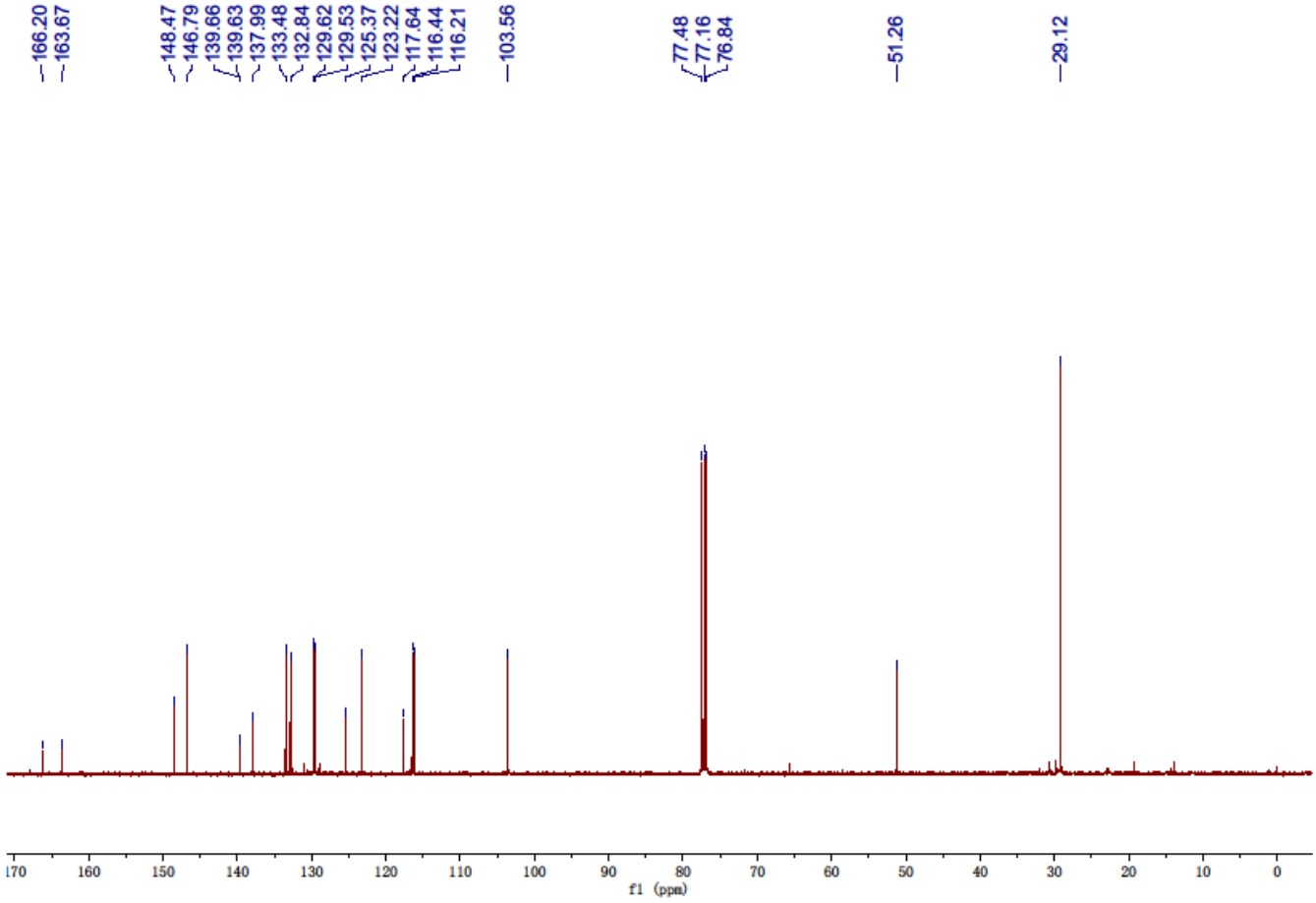


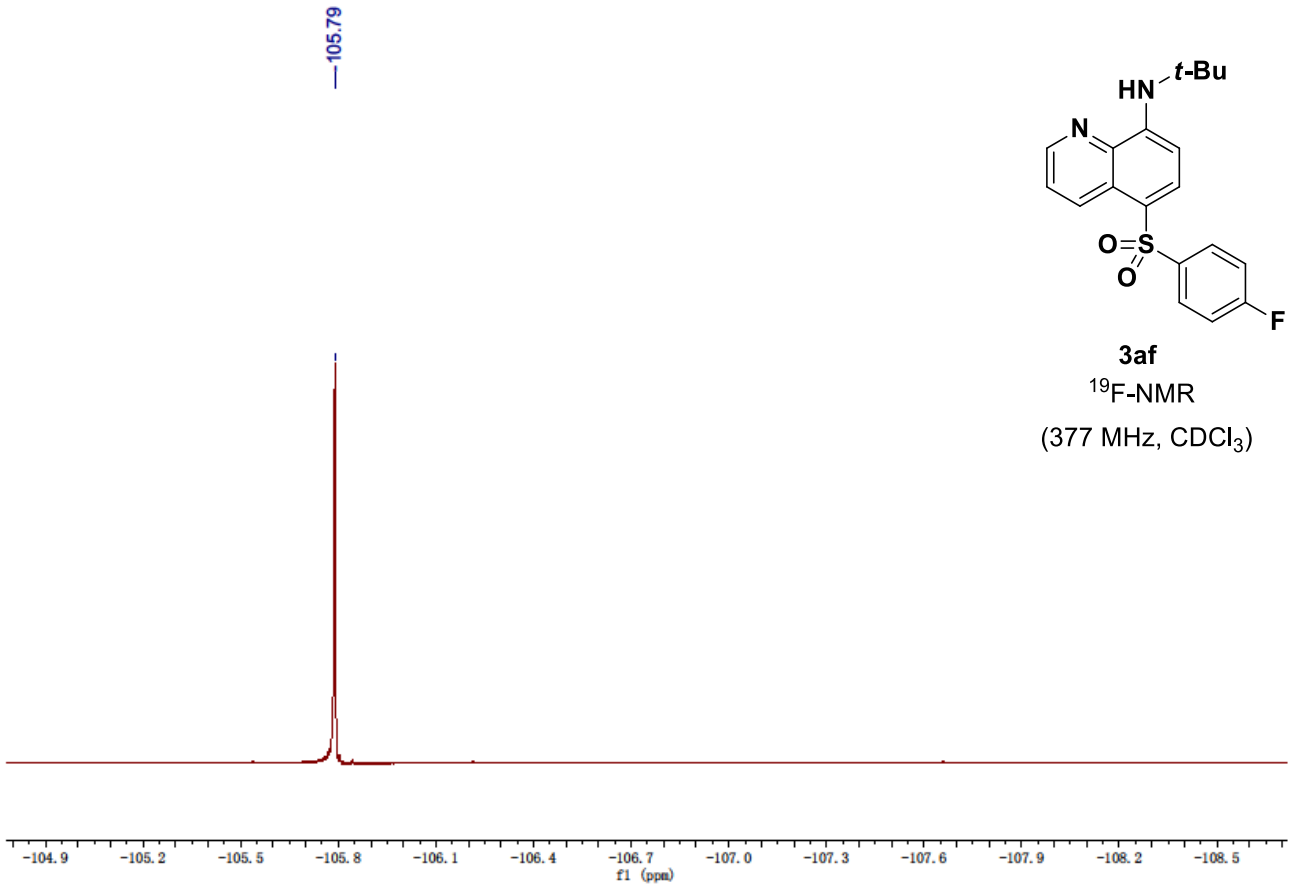
3af

^{1}H-NMR

(400 MHz, $CDCl_3$)



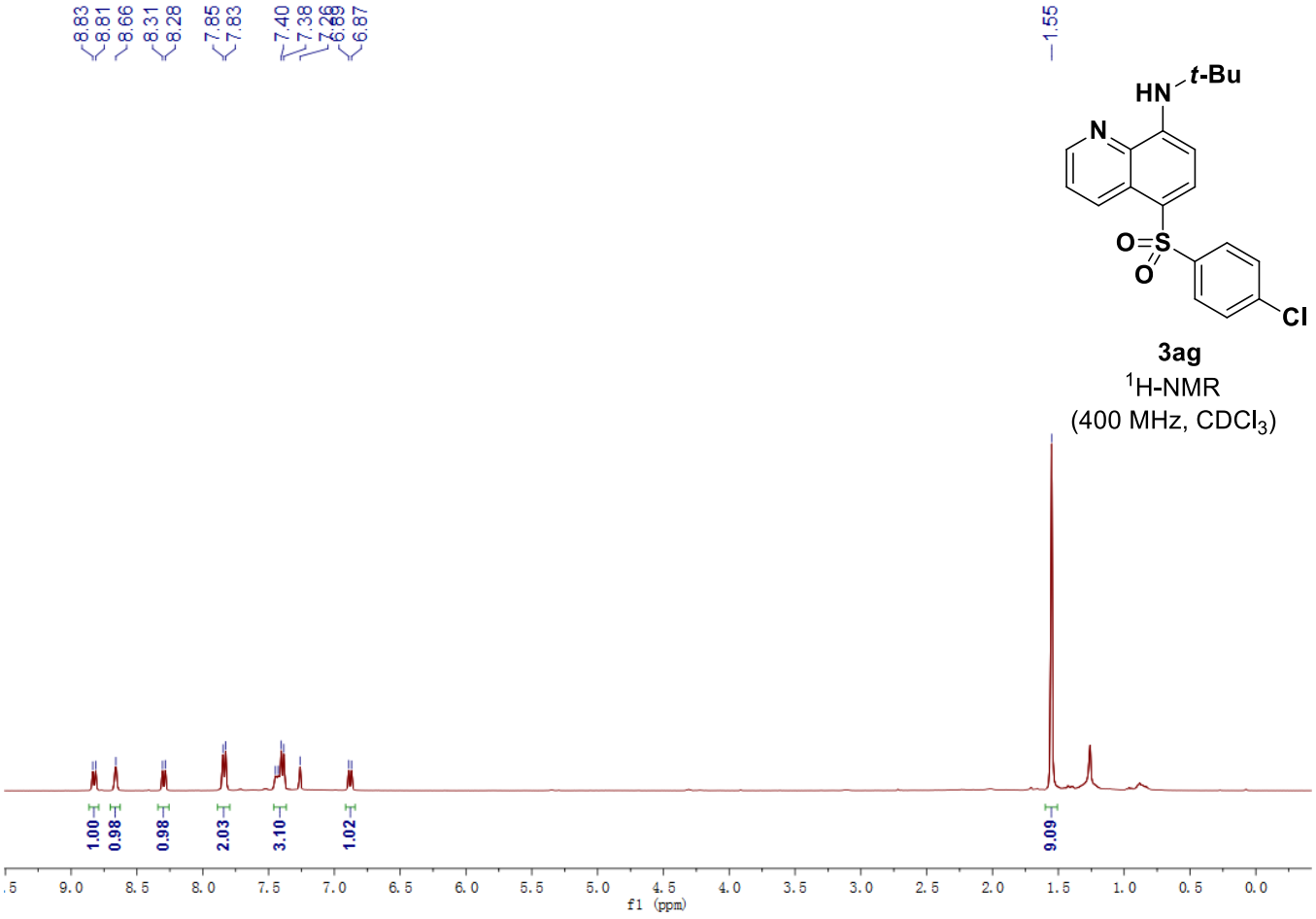




3af

^{19}F-NMR

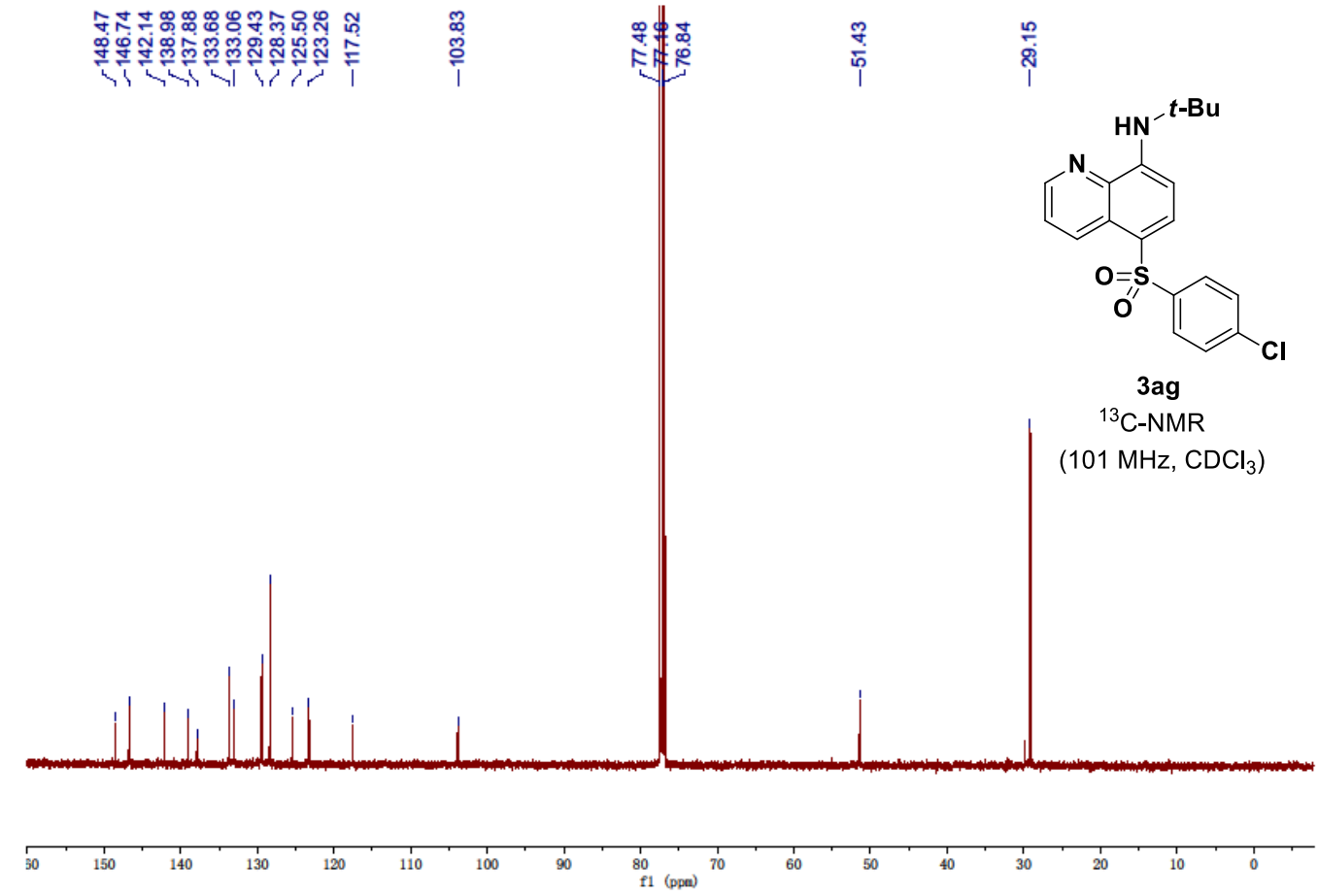
(377 MHz, $CDCl_3$)



3ag

^{1}H-NMR

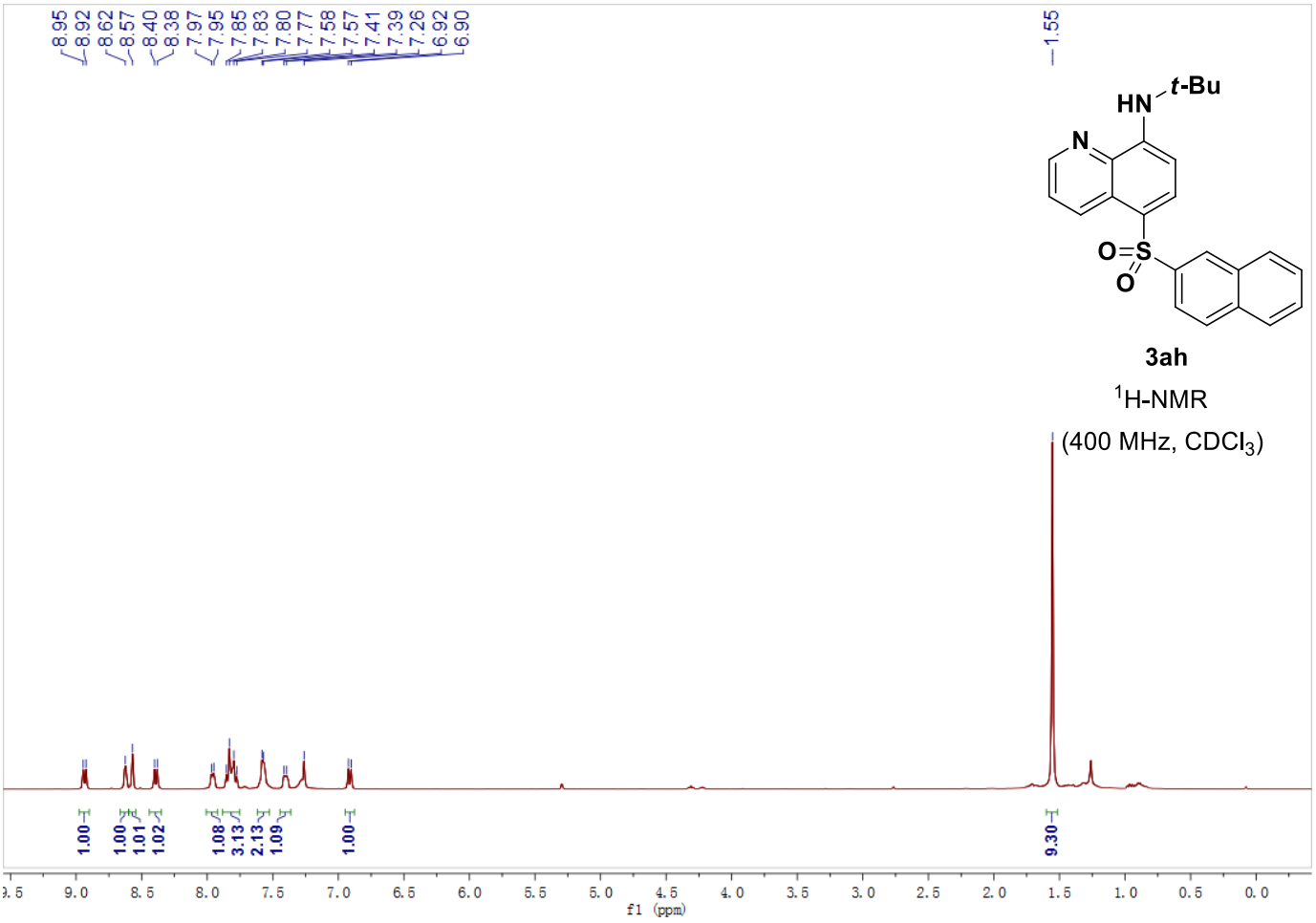
(400 MHz, $CDCl_3$)



3ag

^{13}C-NMR

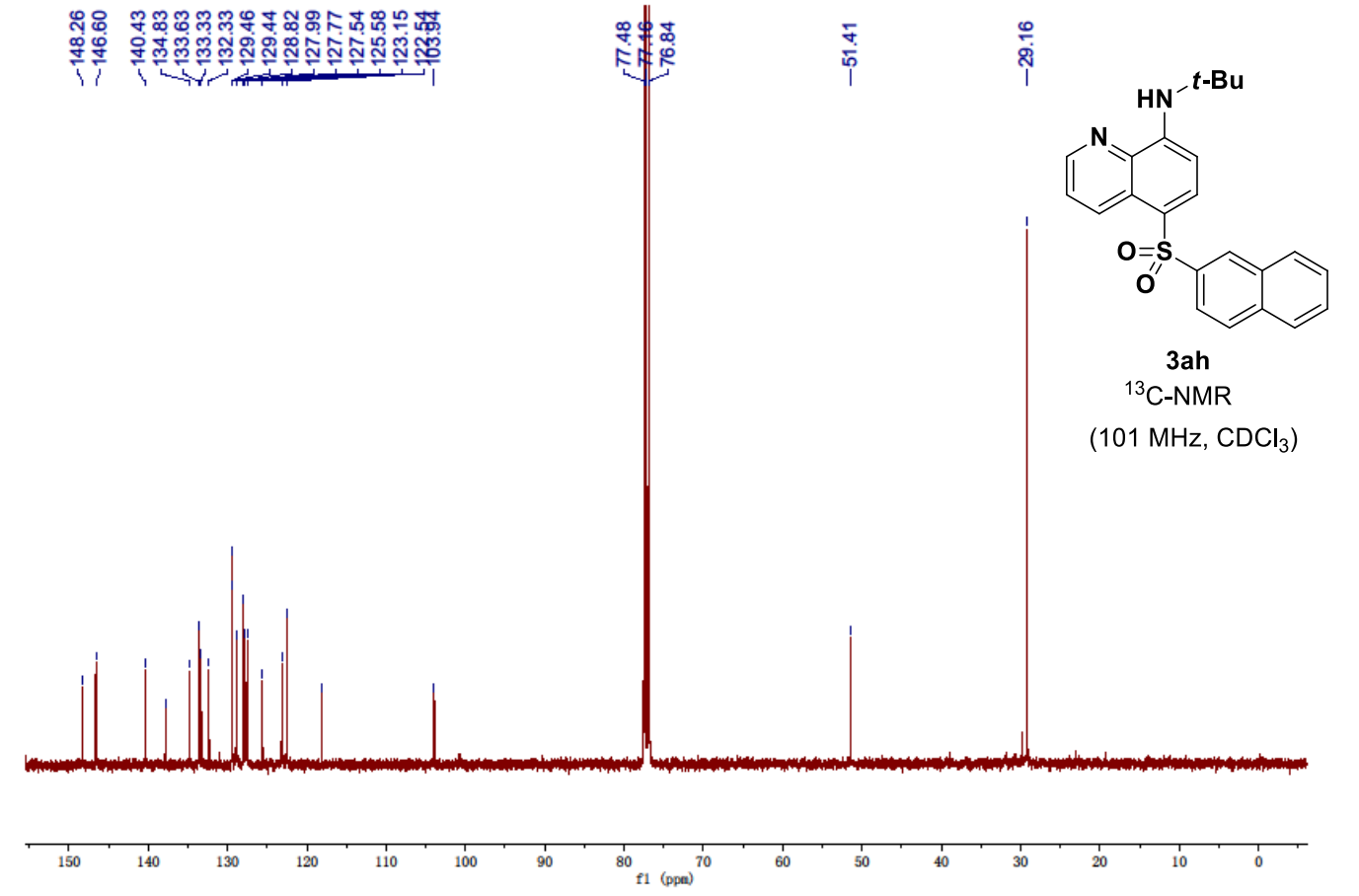
(101 MHz, $CDCl_3$)



3ah

^{1}H-NMR

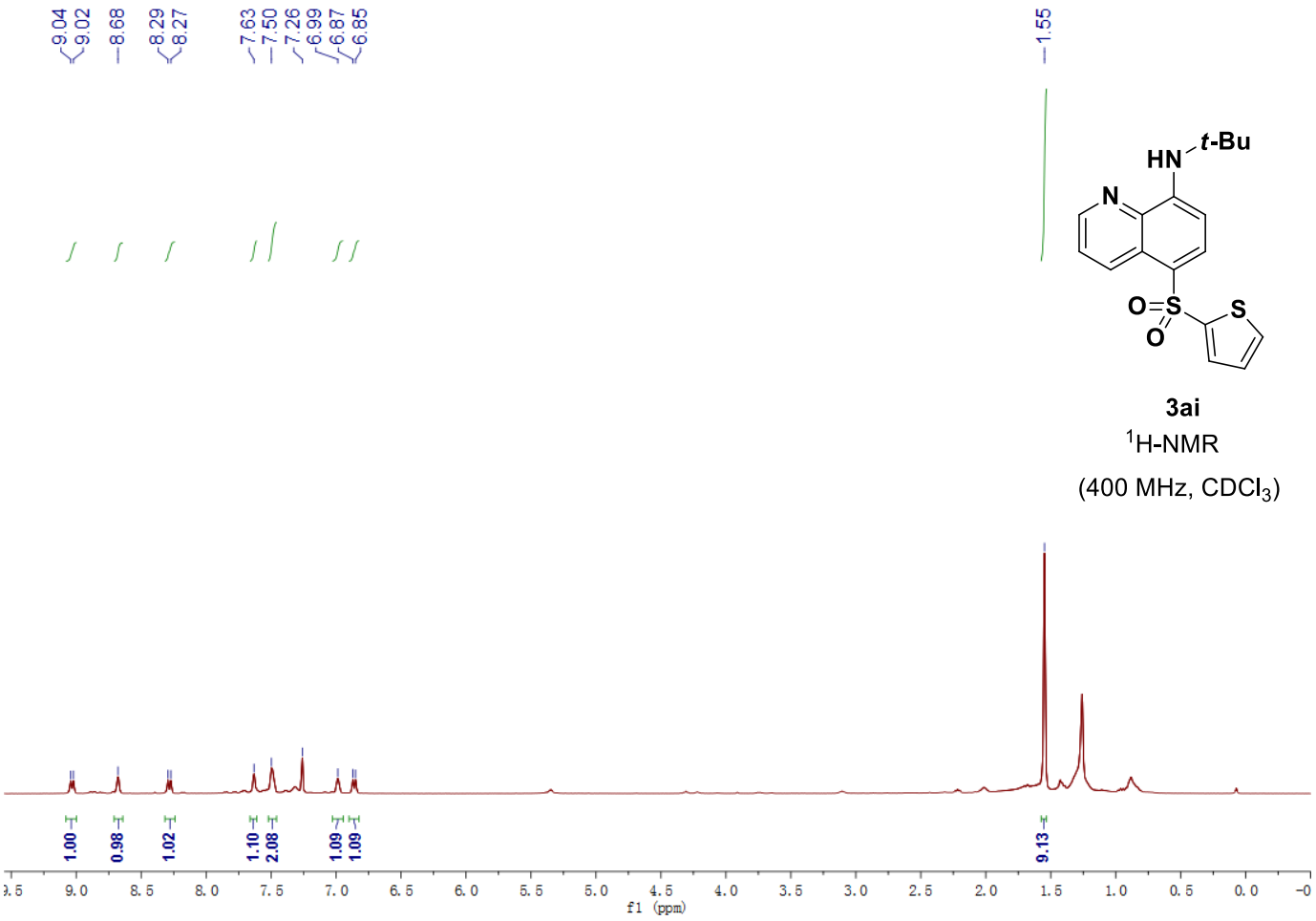
(400 MHz, $CDCl_3$)



3ah

^{13}C-NMR

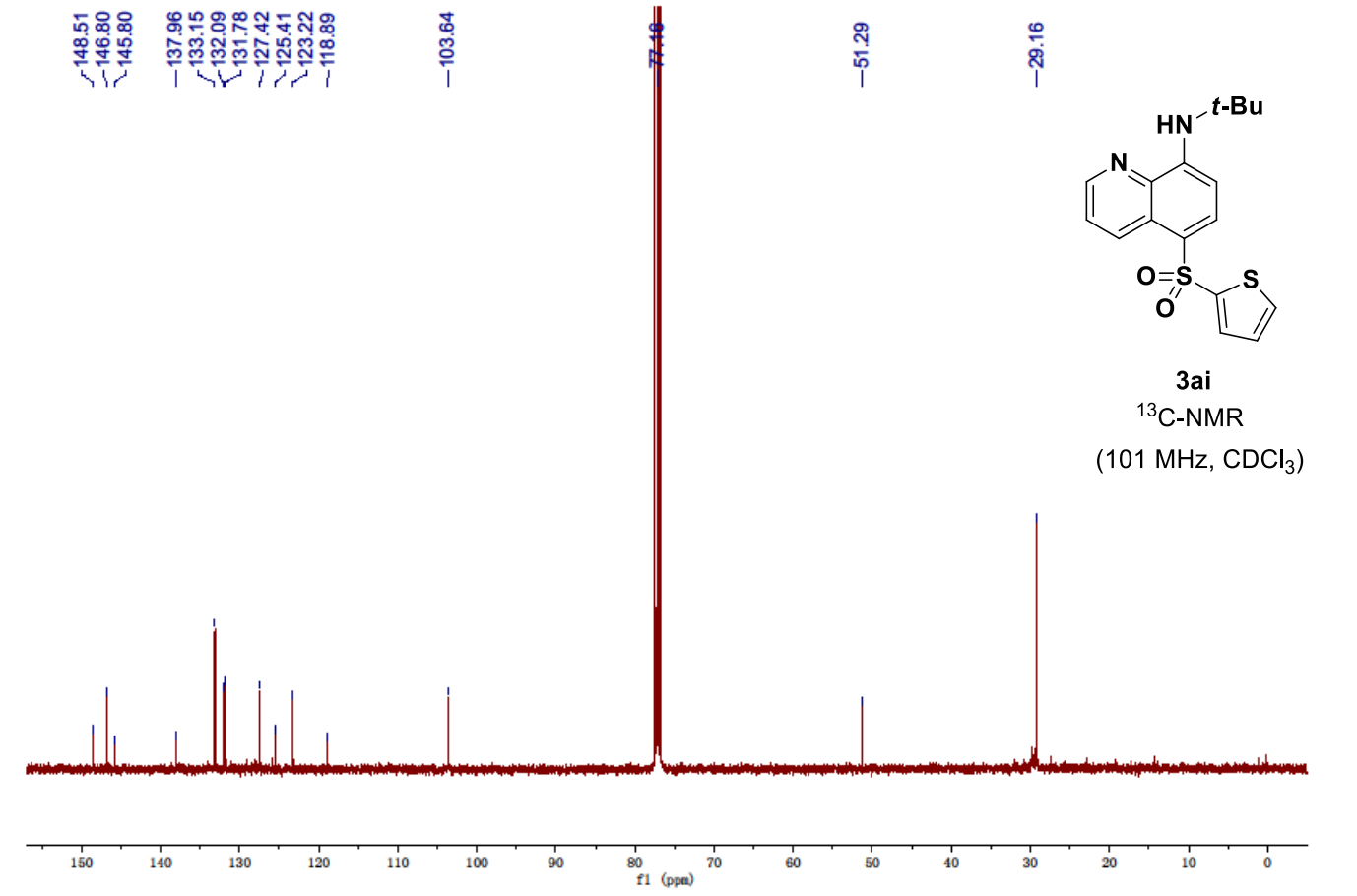
(101 MHz, $CDCl_3$)



3ai

^{1}H-NMR

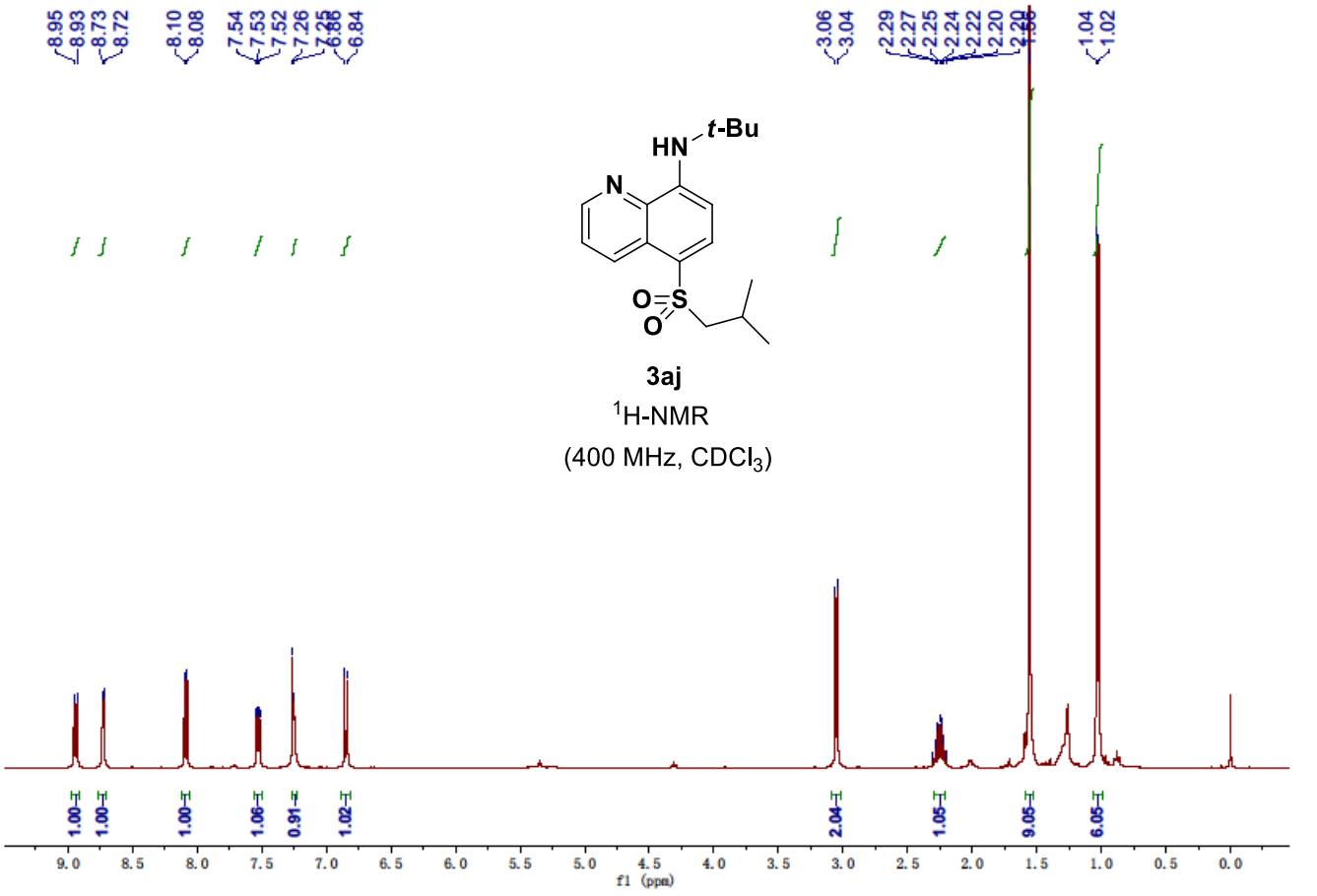
(400 MHz, $CDCl_3$)



3ai

^{13}C-NMR

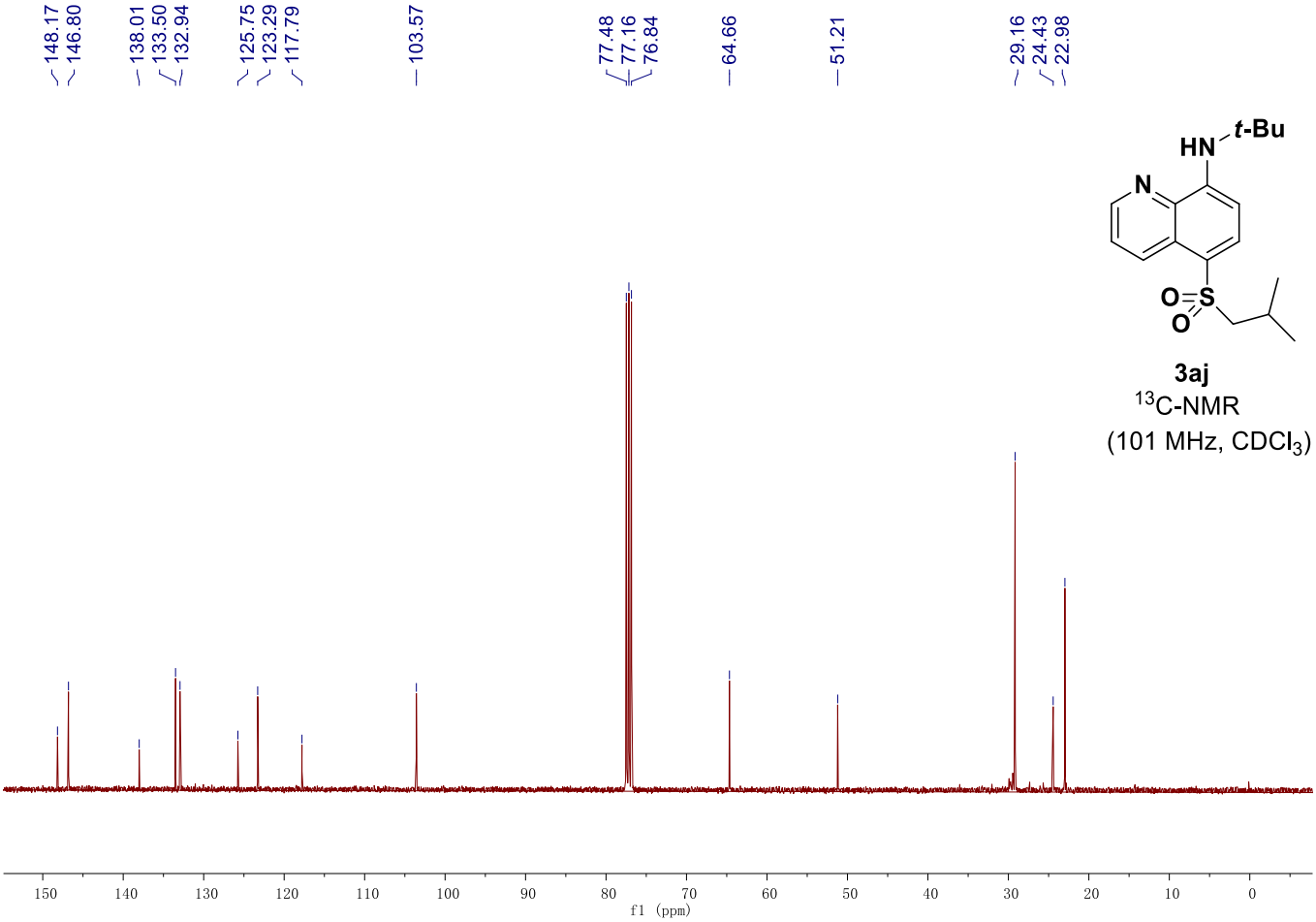
(101 MHz, $CDCl_3$)



3aj

^{1}H-NMR

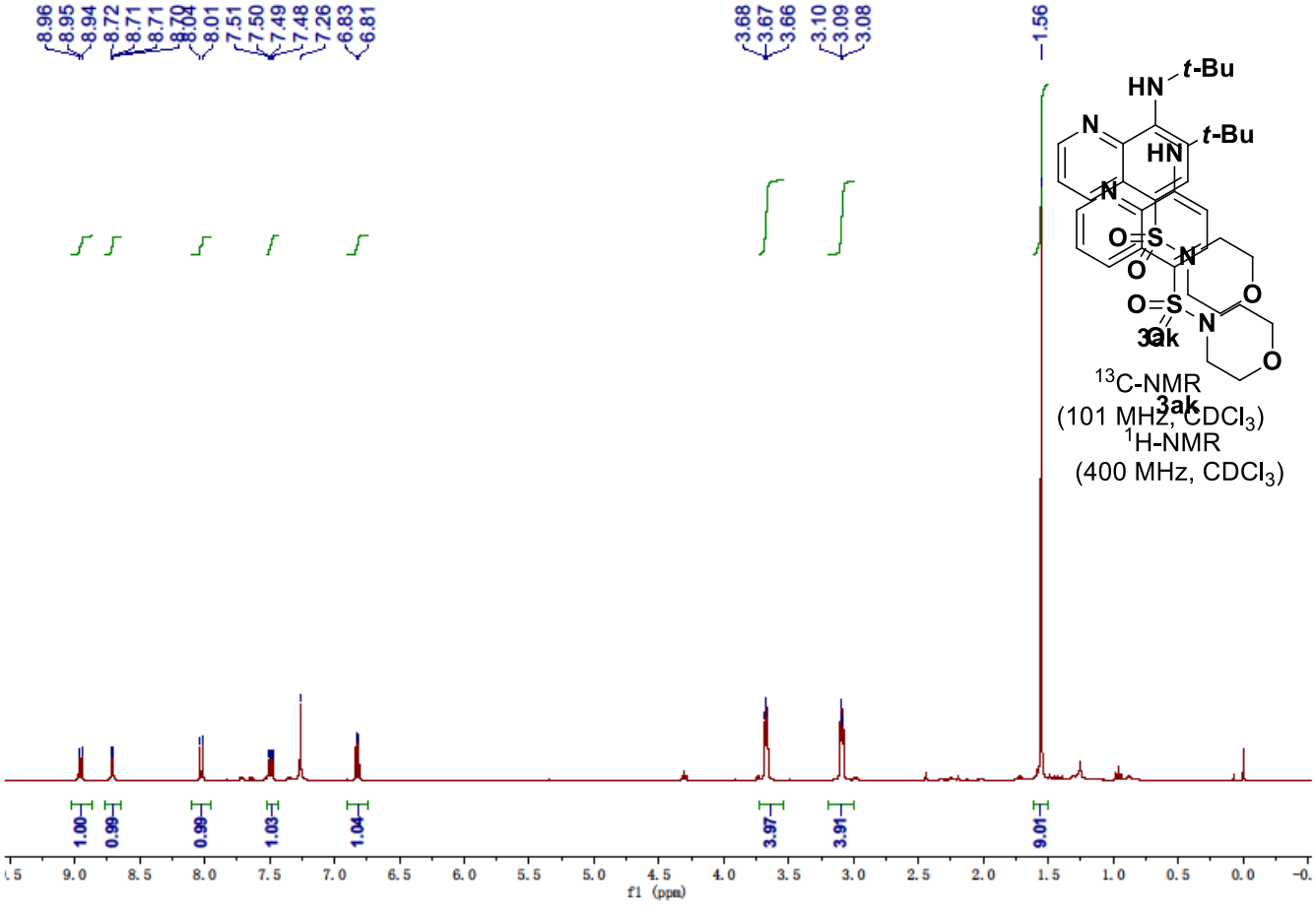
(400 MHz, $CDCl_3$)

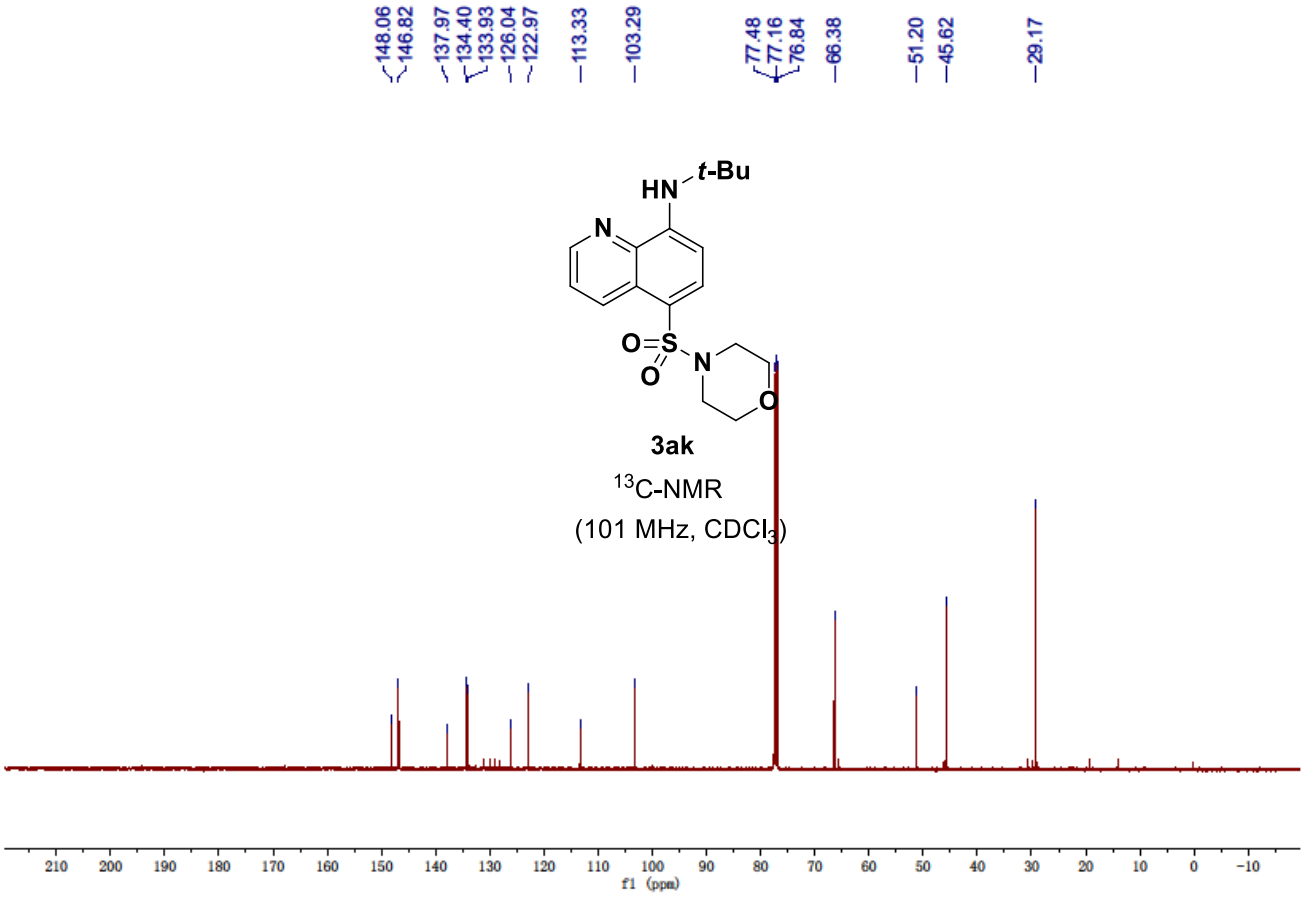


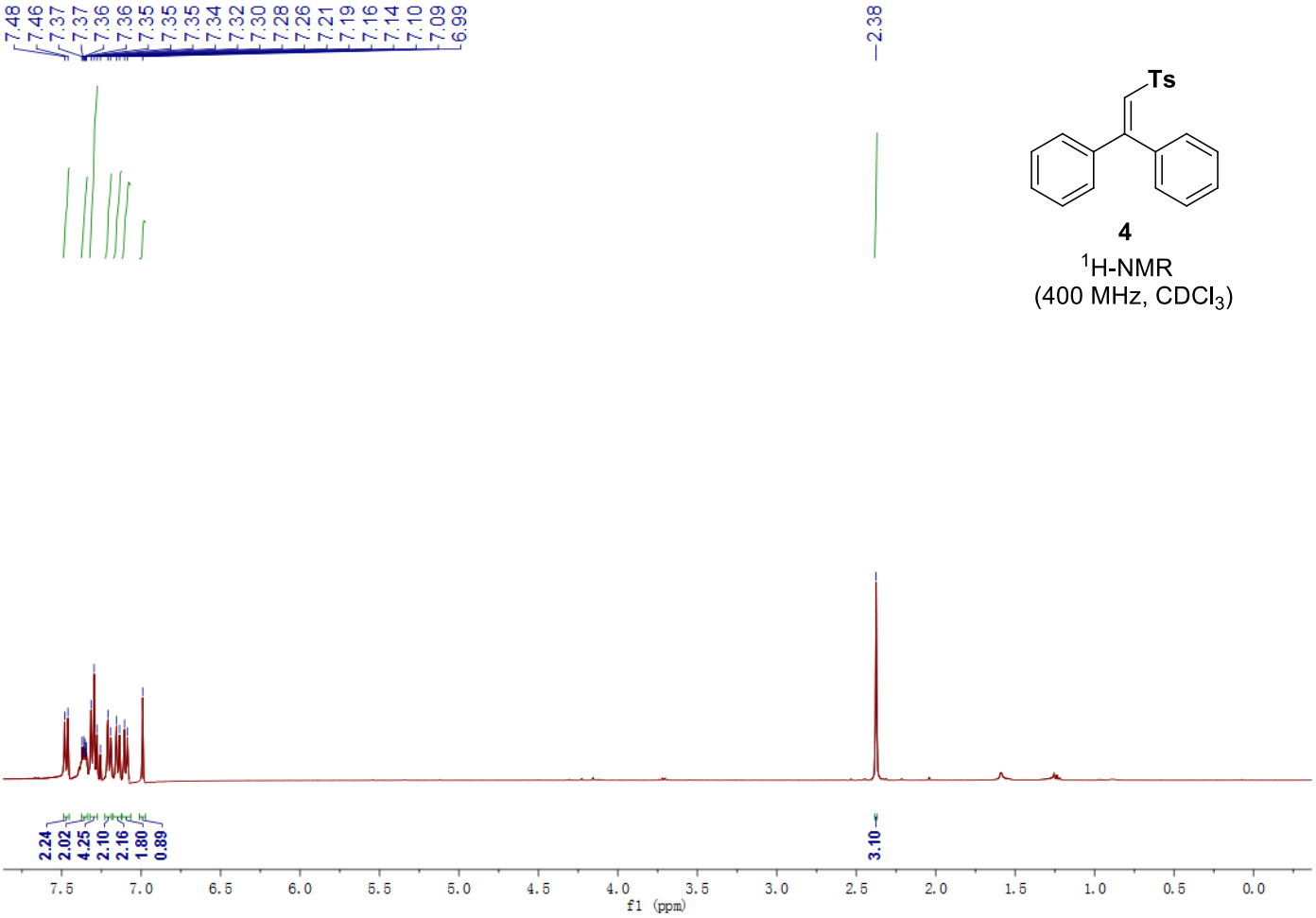
3aj

^{13}C-NMR

(101 MHz, $CDCl_3$)

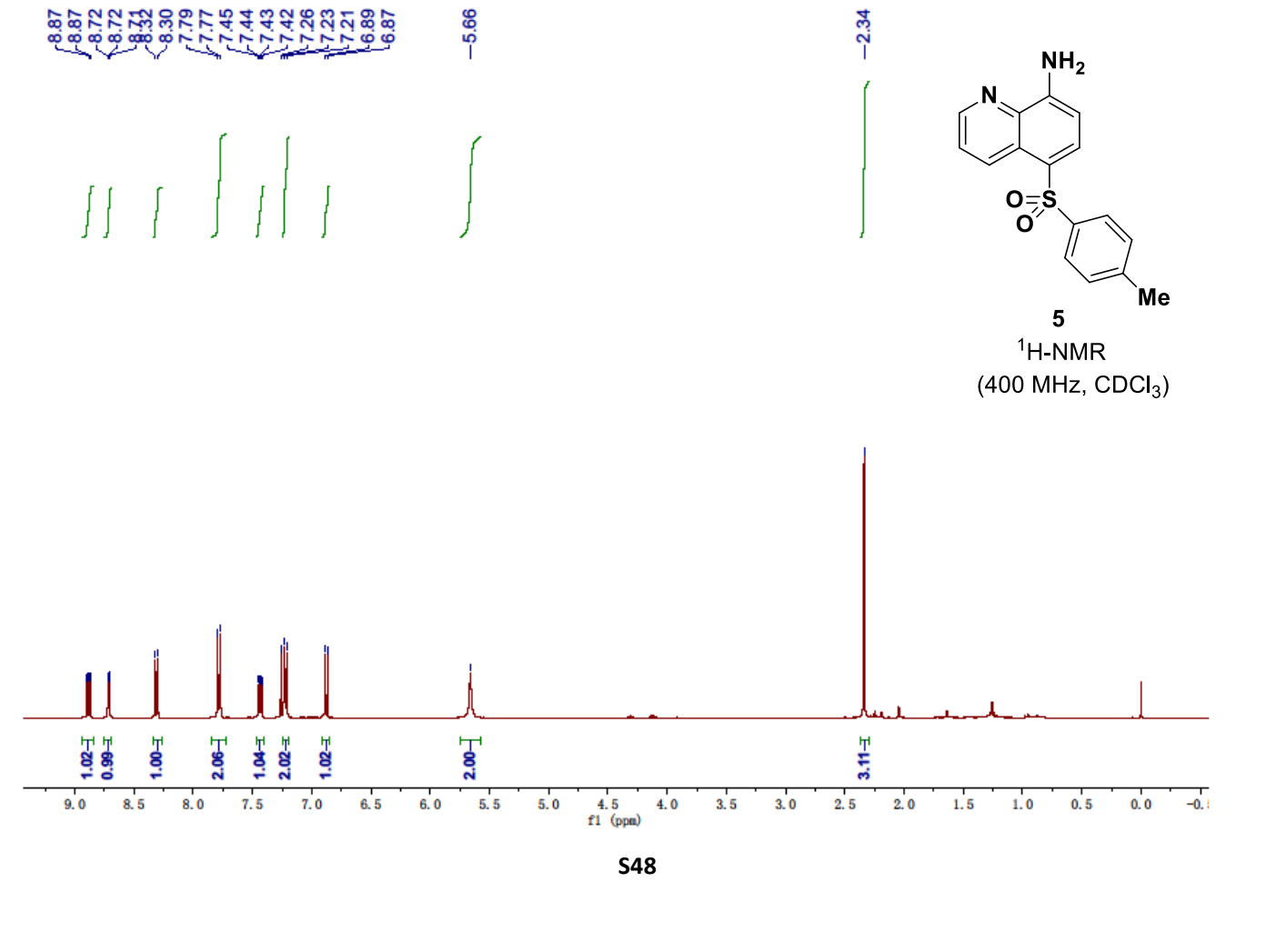

8.96
8.95
8.94
8.72
8.71
8.71
8.70
8.04
8.01
7.51
7.50
7.49
7.48
7.26
6.83
6.81
3.68
3.67
3.66
3.10
3.09
3.08
1.56
1.00
0.99
0.99
1.03
1.04
3.97
3.91
9.01
f1 (ppm)
t-Bu
HN
t-Bu
HN
3ak
13C-NMR
(101 MHz, CDCl3)
1H-NMR
(400 MHz, CDCl3)


148.06
146.82
137.97
134.40
133.93
126.04
122.97
113.33
103.29
77.48
77.16
76.84
66.38
51.20
45.62
29.17
t-Bu
HN
3ak
13C-NMR
(101 MHz, CDCl3)
f1 (ppm)



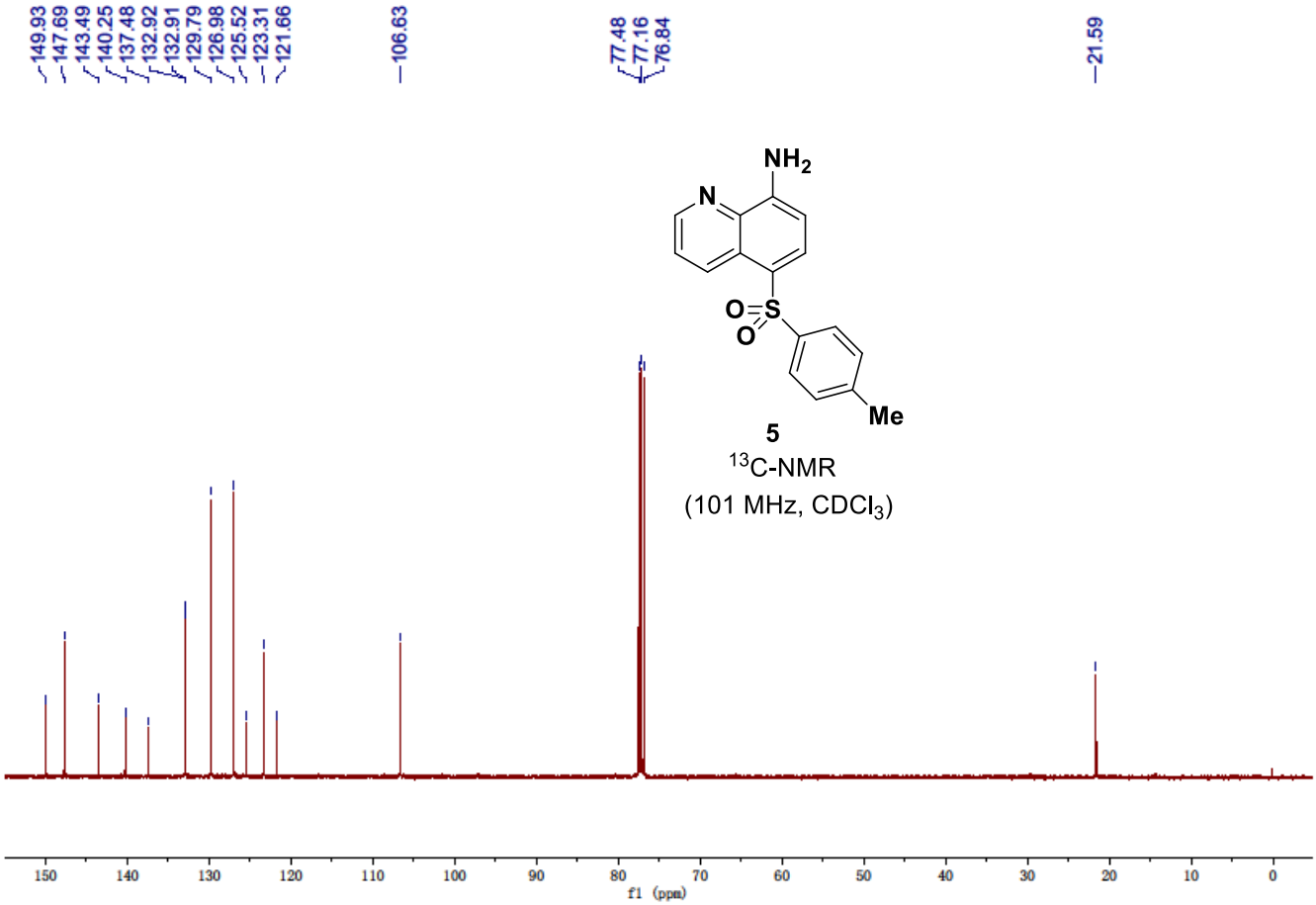
4

^{1}H-NMR
(400 MHz, $CDCl_3$)



5

^{1}H-NMR
(400 MHz, $CDCl_3$)


149.93
147.69
143.49
140.25
137.48
132.92
132.91
129.79
126.98
125.52
123.31
121.66
106.63
77.48
77.16
76.84
21.59
NH2
N
O
S
O
Me
5
13C-NMR
(101 MHz, CDCl3)
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)