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Supporting Information

Synthesis of 3-substituted quinolines by ruthenium-catalyzed aza-Michael addition and intramolecular annulation of enaminones with anthranils

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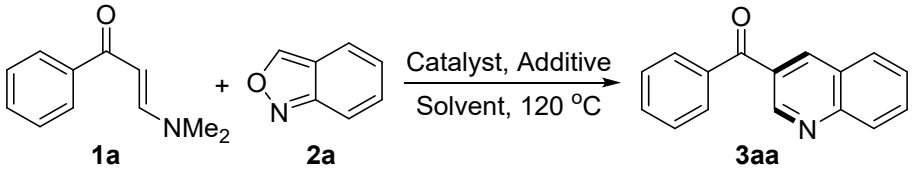
Contents

1. Experimental Section:

General Considerations. All products were prepared under argon atmosphere using standard Schlenk technique. ^{1}H, ^{13}C NMR, and ^{19}F NMR data were recorded with Bruker Advance III (500 MHz) spectrometers with tetramethylsilane as an internal standard. All chemical shifts (δ) are reported in ppm and coupling constants (*J*) in Hz. All chemical shifts are reported relative to tetramethylsilane and d-solvent peaks, respectively. Multiplicities are reported as follows: singlet (s), doublet (d), doublet of doublets (dd), triplet (t), quartet (q), and multiplet (m). Column chromatography was performed on silica gel 200–300 mesh. Analytical thin-layer chromatography (TLC) was performed on pre-coated, glass-backed silica gel plates. Visualization of the developed chromatogram was performed by UV absorbance (254 nm). High-resolution mass spectra (HRMS) were done on Varian 7.0 T FTICR-mass spectrometer. Unless otherwise noted below, all other compounds have been reported in the literature or are commercially available from Aldrich, Acros, Alfa Aesar, and Energy Chemical Company and used as received without any further purification.

2. Table S1. Optimization studies[a]



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

Entry	Catalyst	Additive	Solvent	Yield (%)[b]
1	[(*p*-cymene)$RuCl_2$]$_2$	HOAc	DCE	84
2	[(*p*-cymene)$RuCl_2$]$_2$	NaOAc	DCE	6
3	[(*p*-cymene)$RuCl_2$]$_2$	PivOH	DCE	55
4	[(*p*-cymene)$RuCl_2$]$_2$	1-AdCOOH	DCE	46
5	[(*p*-cymene)$RuCl_2$]$_2$	MesCOOH	DCE	37
6	[(*p*-cymene)$RuCl_2$]$_2$	-	DCE	12
7	[(*p*-cymene)$RuCl_2$]$_2$	HOAc	THF	57
8	[(*p*-cymene)$RuCl_2$]$_2$	HOAc	MeOH	66
9	**[(*p*-cymene)$RuCl_2$]$_2$**	**HOAc**	**MeCN**	**90**
10	[(*p*-cymene)$RuCl_2$]$_2$	HOAc	DMF	63

11	[(*p*-cymene)$RuCl_2$]$_2$	HOAc	Toluene	59
12	-	HOAc	MeCN	0
13	-	HOAc	DMSO	0
14	$RuCl_3$	HOAc	MeCN	38
15	$FeCl_3$	HOAc	MeCN	15
16	$CuCl_2$	HOAc	MeCN	29
17	$BiOTf_3$	HOAc	MeCN	43
18	$InOTf_3$	HOAc	MeCN	31
19	[Cp*$RhCl_2$]$_2$	HOAc	MeCN	22
20	[(*p*-cymene)$RuCl_2$]$_2$	HOAc	MeCN	81[c]

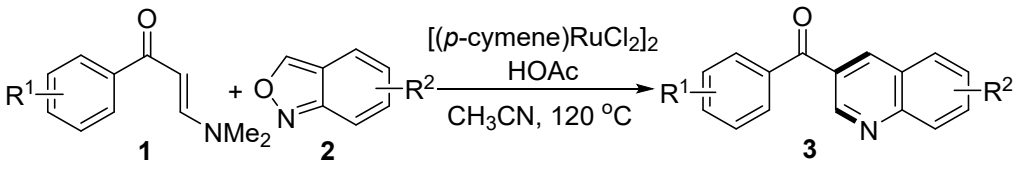
[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.3 mmol), catalyst (5 mol%), additive (1 equiv), solvent (1.5 mL), 120 °C, 12 h, under N_2. [b] Isolated yields. [c] 100 °C.

Initially, (*E*)-3-(dimethylamino)-1-phenylprop-2-en-1-one (**1a**) (0.2 mmol, 1.0 equiv) was introduced to react with benzo[*c*]isoxazole (**2a**) (0.3 mmol, 1.5 equiv) accompanied by [(*p*-cymene)$RuCl_2$]$_2$ (5 mol%) and HOAc (1 equiv) in 1,2-dichloroethane (DCE) at 120 °C under a nitrogen atmosphere for 12 h. The target product phenyl(quinolin-3-yl)methanone (**3aa**) was achieved with a yield of 84% (Table S1, entry 1). The structure of **3aa** was confirmed by its ^{1}H and ^{13}C NMR spectra. Several other additives including NaOAc, PivOH, 1-AdCOOH and MesCOOH were first tested, and generated **3aa** in 6−84% yields (entries 2−5). When no additive was added to the reaction, the product **3aa** could be obtained only in 12% yield (entry 6). Then, several tests on solvents showed that CH_3CN is more suitable for this transformation than tetrahydrofuran (THF), CH_3OH, *N*,*N*-dimethylformamide (DMF) and toluene (entries 7−11). The yields of **3aa** were not higher than 43% when no [(*p*-cymene)$RuCl_2$]$_2$ or other catalysts such as $RuCl_3$, $FeCl_3$, $CuCl_2$, $BiOTf_3$, $InOTf_3$ and [Cp*$RhCl_2$]$_2$ were used in the reactions with CH_3CN or dimethyl sulfoxide (DMSO) as the solvent (entries 12−19). In this reaction, a good catalyst should not only have a good complexation with the carbonyl group of enaminones, but also dissociate at an appropriate time. Other catalysts may be not as good as [(*p*-cymene)$RuCl_2$]$_2$ in meeting these two requirements, and gave lower yields of target

product. In addition, when the reaction temperature reduced to 100 °C, the yield of product **3aa** decreased at the same time (entry 20). Therefore, the factors of entry 9 were selected as the standard conditions.

3. Synthetic Procedures

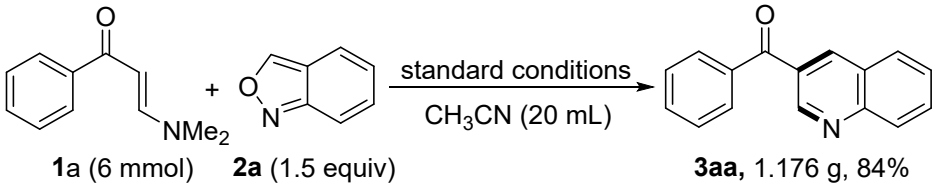
General Procedure for the Ru(II)-Catalyzed Preparation of 3



A mixture of substituted enaminones (**1**) (0.2 mmol, 1.0 equiv), anthranils (**2**) (0.3 mmol, 1.5 equiv) and [Ru(*p*-cymene)Cl_2]$_2$ (6.0 mg, 0.01 mmol, 5 mol%) were weighted in a Schlenk tube equipped with a stir bar. Dry CH_3CN (1.5 mL) and HOAc (0.2 mmol, 1.0 equiv) were added and the mixture was stirred at 120 °C in a pre-heated oil bath for 12 h under N_2 atmosphere. Then, the mixture was cooled to room temperature and concentrated in vacuo and the resulting residue was purified by column chromatography on silica gel with EtOAc/petroleum ether.

4. Gram-Scale Preparation and Derivatization Reactions of 3a

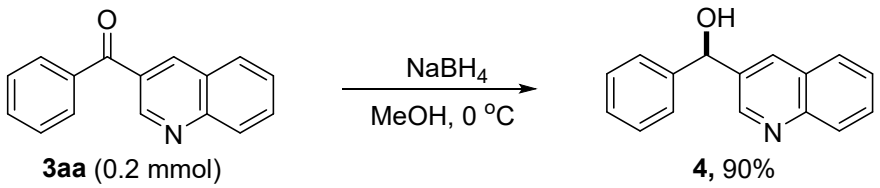
(a) Gram-Scale Preparation of 3a



1a (6 mmol) **2a** (1.5 equiv) **3aa,** 1.176 g, 84%

A mixture of (*E*)-3-(dimethylamino)-1-phenylprop-2-en-1-one (**1a**) (1050.6 mg, 6.0 mmol, 1.0 equiv), benzo[*c*]isoxazole (**2**) (9 mmol, 1.5 equiv) and [Ru(*p*-cymene)Cl_2]$_2$ (0.3 mmol, 5 mol%) were weighted in a Schlenk sealed tube equipped with a stir bar. Dry CH_3CN (20 mL) and HOAc (6 mmol, 1.0 equiv) were added and the mixture was stirred at 120 °C in a pre-heated oil bath for 12 h under N_2 atmosphere. Then, the mixture was cooled to room temperature and concentrated in vacuo and the resulting residue was purified by flash column chromatography on silica gel with EtOAc/petroleum ether, the product **3aa** was affored as a yellow solid in 84% yield (1.176 g, 5.04 mmol).

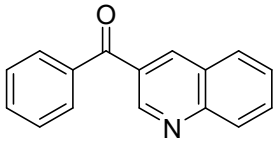
(b) Derivatization Reaction of 3a for the Preparation of 4



3aa (0.2 mmol) **4,** 90%

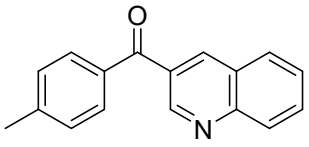
A mixture of phenyl(quinolin-3-yl)methanone (**3aa**) (0.2 mmol, 1.0 equiv) and $NaBH_4$ (0.28 mmol, 1.4 equiv) in MeOH was stirred at 0 °C for 3 hours. Then the residual was extracted with CH_2Cl_2 and concentrated in vacuo and the resulting residue was purified by flash column chromatography on silica gel with EtOAc/petroleum ether to give product **4** in 90% yield (42.3 mg, 0.18 mmol).

5. Characterization of 3–4



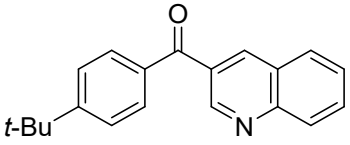
phenyl(quinolin-3-yl)methanone (3aa)[1]

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/5) as a yellow solid in 90% yield (42.0 mg, 0.180 mmol). **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 9.32 (d, *J* = 2.0 Hz, 1H), 8.54 (d, *J* = 1.8 Hz, 1H), 8.18 (d, *J* = 8.5 Hz, 1H), 7.91 (d, *J* = 8.0 Hz, 1H), 7.87 – 7.82 (m, 3H), 7.66 – 7.60 (m, 2H), 7.53 (t, *J* = 7.7 Hz, 2H). **^{13}C NMR ($CDCl_3$, 125 MHz):** δ 194.8, 150.3, 149.4, 138.7, 137.0, 133.0, 131.8, 130.0, 130.0, 129.5, 129.1, 128.6, 127.5, 126.6.



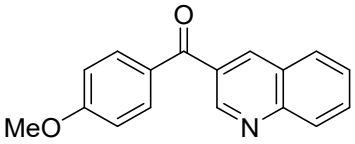
quinolin-3-yl(*p*-tolyl)methanone (3ba)[1]

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/5) as a yellow solid in 93% yield (45.9 mg, 0.186 mmol). **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 9.31 (s, *J* = 1.9 Hz, 1H), 8.55 (s, *J* = 1.9 Hz, 1H), 8.20 (d, *J* = 8.5 Hz, 1H), 7.92 (d, *J* = 8.1 Hz, 1H), 7.87-7.84 (m, 1H), 7.79 (d, *J* = 8.1 Hz, 2H), 7.66 – 7.62 (m, 1H), 7.35 (d, *J* = 7.9 Hz, 2H), 2.48 (s, 3H). **^{13}C NMR ($CDCl_3$, 125 MHz):** δ 194.6, 150.4, 149.4, 144.1, 138.6, 134.4, 131.7, 130.5, 130.3, 129.5, 129.4, 129.1, 127.5, 126.7, 21.72.



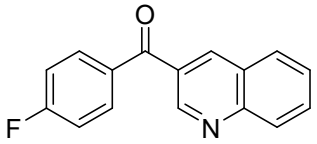
(4-*tert*-butylphenyl)(quinolin-3-yl)methanone (3ca)[2]

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/5) as a yellow solid in 92% yield (53.2 mg, 0.184 mmol). **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 9.32 (d, *J* = 2.0 Hz, 1H), 8.56 (d, *J* = 1.8 Hz, 1H), 8.20 (d, *J* = 8.5 Hz, 1H), 7.92 (d, *J* = 8.0 Hz, 1H), 7.86 – 7.81 (m, 3H), 7.63 (t, *J* = 7.5 Hz, 1H), 7.57 – 7.54 (m, 2H), 1.39 (s, 9H). **^{13}C NMR ($CDCl_3$, 125 MHz):** δ 194.5, 157.0, 150.3, 149.3, 138.6, 134.3, 131.7, 130.47, 130.1, 129.4, 129.1, 127.5, 126.6, 125.6, 35.2, 31.1.



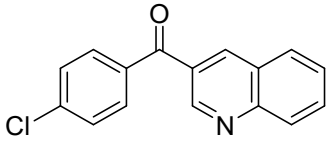
(4-methoxyphenyl)(quinolin-3-yl)methanone (3da)[1]

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/5) as a yellow solid in 89% yield (47.0 mg, 0.178 mmol). **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 9.30 (s, 1H), 8.55 (s, 1H), 8.20 (d, *J* = 8.5 Hz, 1H), 7.92 (d, *J* = 8.1 Hz, 1H), 7.85 (t, *J* = 7.5 Hz, 1H), 7.78 (d, *J* = 8.0 Hz, 2H), 7.64 (t, *J* = 7.5 Hz, 1H), 7.34 (d, *J* = 7.9 Hz, 2H), 2.47 (s, 3H).**^{13}C NMR ($CDCl_3$, 125 MHz):** δ 194.5, 150.3, 149.3, 144.1, 138.6, 134.4, 131.7, 130.4, 130.3, 129.4, 129.3, 129.1, 127.5, 126.7, 21.71.



(4-fluorophenyl)(quinolin-3-yl)methanone (3ea)[1]

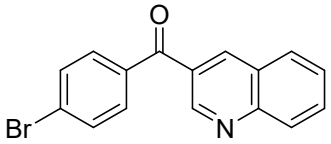
The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/5) as a yellow solid in 90% yield (45.1 mg, 0.180 mmol). **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 9.29 (d, *J* = 1.3 Hz, 1H), 8.53 (d, *J* = 1.9 Hz, 1H), 8.20 (d, *J* = 8.5 Hz, 1H), 7.95 – 7.89 (m, 3H), 7.88 – 7.85(m, 1H), 7.68 – 7.63 (m, 1H), 7.25 – 7.20 (m, 2H). **^{13}C NMR ($CDCl_3$, 125 MHz):** δ 193.4, 166.7 (d, *J* = 255.4 Hz), 150.1, 149.5, 138.6, 133.3 (d, *J* = 2.8 Hz), 132.7 (d, *J* = 9.4 Hz), 131.9, 130.0, 129.5, 129.1, 127.7, 126.6, 115.9 (d, *J* = 21.9 Hz). **^{19}F NMR ($CDCl_3$,471 MHz) :** δ -104.6.



(4-chlorophenyl)(quinolin-3-yl)methanone (3fa)[1]

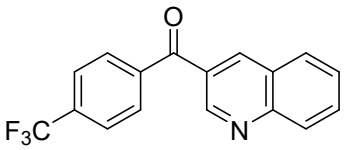
The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/5) as a yellow solid in 88% yield (47.1 mg, 0.176 mmol). **^{1}H NMR (DMSO-d_6, 500 MHz):** δ 9.27 (s, 1H), 8.74 (s, 1H), 8.24 – 8.04 (m, 2H), 7.94 – 7.83 (m, 3H), 7.73 – 7.62 (m, 3H). **^{13}C NMR (DMSO-d_6, 125**

MHz): δ 193.4, 149.5, 148.9, 148.9, 138. 8, 138.1, 135.3, 132.1, 131.7, 129.8, 128.9, 128.8, 127.6, 126.4.



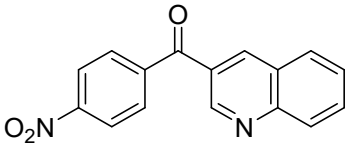
(4-bromophenyl)(quinolin-3-yl)methanone (3ga)[1]

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/5) as a yellow solid in 85% yield (52.9 mg, 0.170 mmol). **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 9.29 (s, 1H), 8.53 (d, *J* = 1.8 Hz, 1H), 8.19 (d, *J* = 8.5 Hz, 1H), 7.92 (d, *J* = 7.9 Hz, 1H), 7.88 – (m, 1H), 7.76 – 7.72 (m, 2H), 7.70 – 7.63 (m, 3H). **^{13}C NMR ($CDCl_3$, 125 MHz):** δ 193.8, 150.0, 149.5, 138.7, 135.7, 132.0, 132.0, 131.5, 129.7, 129.5, 129.1, 128.3, 127.7, 126.5.



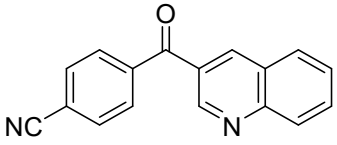
quinolin-3-yl(4-(trifluoromethyl)phenyl)methanone (3ha)[1]

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/5) as a yellow solid in 79% yield (47.5 mg, 0.158 mmol). **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 9.33 (d, *J* = 1.9 Hz, 1H), 8.55 (d, *J* = 1.9 Hz, 1H), 8.21 (d, *J* = 8.5 Hz, 1H), 7.95 (dd, *J* = 18.8, 8.1 Hz, 3H), 7.90 – (m, 1H), 7.82 (d, *J* = 8.2 Hz, 2H), 7.69 – 7.63 (m, 1H). **^{13}C NMR ($CDCl_3$, 125 MHz):** δ 193.8, 150.0, 149.7, 140.0, 139.1, 134.3 (q, *J* = 32.8 Hz), 132.3, 130.2, 129.6, 129.2, 127.8, 126.5, 125.7 (q, *J* = 3.7 Hz), 123.5 (q, *J* = 272.9 Hz). **^{19}F NMR ($CDCl_3$, 471 MHz):** δ -63.1.



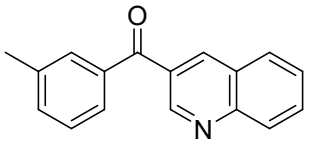
(4-nitrophenyl)(quinolin-3-yl)methanone (3ia)[3]

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/5) as a yellow solid in 65% yield (36.1 mg, 0.130 mmol). **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 9.32 (d, *J* = 1.8 Hz, 1H), 8.55 (d, *J* = 1.9 Hz, 1H), 8.42 – 8.37 (m, 2H), 8.21 (d, *J* = 8.5 Hz, 1H), 8.03 – 7.99 (m, 2H), 7.94 (d, *J* = 8.2 Hz, 1H), 7.92 – (m, 1H), 7.70 – 7.66 (m, 1H). **^{13}C NMR ($CDCl_3$, 125 MHz):** δ 193.1 150.2, 149.8, 142.1, 139.2, 139.2, 132.5, 130.7, 129.6, 129.3, 128.8, 128.0, 126.4, 123.9, 102.8.



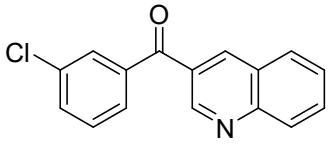
4-(quinoline-3-carbonyl)benzonitrile (3ja)[2]

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/5) as a yellow solid in 51% yield (26.1 mg, 0.101 mmol). **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 9.28 (s, 1H), 8.51 (d, *J* = 1.5 Hz, 1H), 8.18 (d, *J* = 8.5 Hz, 1H), 7.92 (t, *J* = 6.9 Hz, 3H), 7.87 (t, *J* = 7.6 Hz, 1H), 7.82 (d, *J* = 8.3 Hz, 2H), 7.65 (t, *J* = 7.5 Hz, 1H). **^{13}C NMR ($CDCl_3$, 125 MHz):** δ 193.2, 149.7, 149.6, 140.4, 139.0, 132.4, 132.4, 130.1, 129.4, 129.2, 128.8, 127.9, 126.39, 117.79, 116.2.



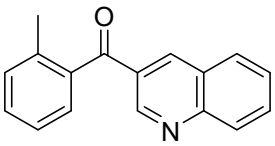
quinolin-3-yl(m-tolyl)methanone (3ka)[4]

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/5) as a yellow solid in 92% yield (45.5 mg, 0.184 mmol). **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 9.32 (s, 1H), 8.59 (s, 1H), 8.23 (d, *J* = 8.5 Hz, 1H), 7.94 (d, *J* = 8.1 Hz, 1H), 7.87 (t, *J* = 7.6 Hz, 1H), 7.70 – 7.62 (m, 3H), 7.47 (d, *J* = 7.5 Hz, 1H), 7.43 (t, *J* = 7.5 Hz, 1H), 2.45 (s, 3H). **^{13}C NMR ($CDCl_3$, 125 MHz):** δ 194.9, 150.2, 139.0, 138.7, 137.0, 133.9, 132.0, 130.4, 129.2, 129.2, 128.5, 127.7, 127.3, 126.7, 21.4.



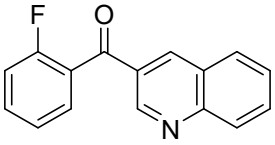
(3-chlorophenyl)(quinolin-3-yl)methanone (3la)[5]

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/5) as a yellow solid in 88% yield (47.0 mg, 0.176 mmol). **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 9.32 (s, 1H), 8.57 (s, 1H), 8.23 (d, *J* = 8.4 Hz, 1H), 7.95 (d, *J* = 8.1 Hz, 1H), 7.91 – 7.87 (m, 1H), 7.85 (t, *J* = 1.8 Hz, 1H), 7.74 – 7.71 (m, 1H), 7.67 (t, *J* = 7.5 Hz, 1H), 7.64 – 7.62(m, 1H), 7.49 (t, *J* = 7.9 Hz, 1H). **^{13}C NMR ($CDCl_3$, 100 MHz):** δ 193.4, 149.9, 149.4, 139.0, 138.6, 135.0, 133.0, 132.2, 130.0, 129.8, 129.4, 129.3, 128.0, 127.8.



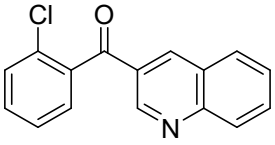
quinolin-3-yl(o-tolyl)methanone (3ma)[5]

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/5) as a yellow solid in 91% yield (45.1 mg, 0.182 mmol). **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 9.36 (s, 1H), 8.48 (d, *J* = 1.9 Hz, 1H), 8.19 (d, *J* = 8.5 Hz, 1H), 7.90 – 7.83 (m, 2H), 7.64 – 7.60 (m, 1H), 7.49 – 7.45 (m, 1H), 7.41 – 7.35 (m, 2H), 7.31 (t, *J* = 7.5 Hz, 1H), 2.41 (s, 3H). **^{13}C NMR ($CDCl_3$, 125 MHz):** δ 197.0, 150.3, 149.7, 139.4, 137.6, 137.3, 132.1, 131.4, 131.0, 129.5, 129.4, 128. 9, 127.6, 125.5, 20.13.



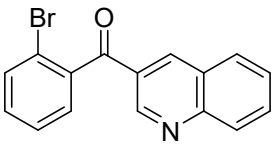
(2-fluorophenyl)(quinolin-3-yl)methanone (3na)[6]

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/5) as a yellow solid in 89% yield (44.7 mg, 0.178 mmol). **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 9.34 (s, 1H), 8.59 (s, 1H), 8.22 (d, *J* = 8.4 Hz, 1H), 7.94 (d, *J* = 8.2 Hz, 1H), 7.89 – 7.86 (m, 1H), 7.70 – 7.61 (m, 3H), 7.37 – 7.33 (m, 1H), 7.23 (t, *J* = 9.4 Hz, 1H). **^{13}C NMR ($CDCl_3$, 125 MHz):** δ 191.7, 160.2 (d, *J* = 253.2 Hz), 149.7, 149.6, 139.1, 134.0 (d, *J* = 8.6 Hz), 132.3, 131.0 (d, *J* = 2.1 Hz), 129.4, 129.3, 127.6, 126.1, 126.0, 124.7 (d, *J* = 3.5 Hz), 116.5 (d, *J* = 21.7 Hz). **^{19}F NMR ($CDCl_3$, 471 MHz):** δ -109.8.



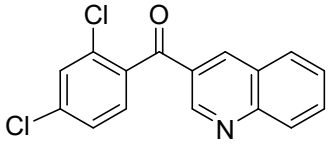
(2-chlorophenyl)(quinolin-3-yl)methanone (3oa)

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/5) as a yellow solid in 87% yield (46.4 mg, 0.174 mmol). Mp: 77 – 78 °C. **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 9.35 (s, 1H), 8.50 (s, 1H), 8.19 (d, *J* = 8.4 Hz, 1H), 7.90 (d, *J* = 8.1 Hz, 1H), 7.86 (t, *J* = 7.7 Hz, 1H), 7.63 (t, *J* = 7.5 Hz, 1H), 7.52 – 7.48 (m, 3H), 7.46 – 7.44 (m, 1H). **^{13}C NMR ($CDCl_3$, 125 MHz):** δ 193.9, 149.9, 149.8, 139.6, 137.6, 132.5, 131.9, 131.5, 130.4, 129.5, 129.5, 129.4, 127.7, 127.1. **HRMS (ESI):** Calcd for $C_{16}H_{11}ClNO$ $[M+H]^+$ 268.0524, found: 268.0523.



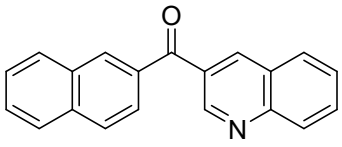
(2-bromophenyl)(quinolin-3-yl)methanone (3pa)[1]

The mixture in the title were obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/5) as a yellow solids in 85% yield (52.6 mg, 0.169 mmol). **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 9.35 (s, 1H), 8.48 (s, 1H), 8.18 (d, *J* = 8.4 Hz, 1H), 7.90 – 7.83 (m, 2H), 7.73 – 7.68 (m, 1H), 7.63 – 7.60 (m, 1H), 7.51 – 7.46 (m, 1H), 7.45 – 7.40 (m, 2H).**^{13}C NMR ($CDCl_3$, 125 MHz):** δ 194. 6, 150.0, 149.9, 139.7, 139.6, 133. 5, 132.4, 131.8, 129.5, 129.3, 128.6, 127.6, 127. 6, 126.8, 123.9, 119.6.



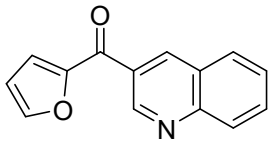
(2,4-dichlorophenyl)(quinolin-3-yl)methanone (3qa)

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/5) as a yellow solid in 80% yield (48.0 mg, 0.159mmol). Mp: 72 – 73 °C. **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 9.33 (s, 1H), 8.49 (s, 1H), 8.21 (d, *J* = 8.3 Hz, 1H), 7.95 – 7.84 (m, 2H), 7.65 (t, *J* = 7.5 Hz, 1H), 7.55 (s, 1H), 7.44 (d, *J* = 0.9 Hz, 2H). **^{13}C NMR ($CDCl_3$, 125 MHz):** δ 192.9, 149.9, 149.7, 139.5, 137.5, 136.0, 132.6, 130.5, 130.3, 129.5, 128.8, 127.8, 127.6, 126.8. **HRMS (ESI):** Calcd for $C_{16}H_{10}Cl_2NO$ $[M+H]^+$ 302.0134, found: 302.0134.



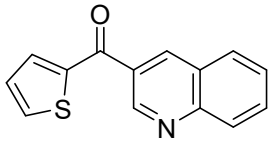
naphthalen-2-yl(quinolin-3-yl)methanone (3ra)[1]

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/5) as a yellow solid in 81% yield (45.8 mg, 0.162 mmol). **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 9.39 (s, 1H), 8.62 (d, *J* = 1.9 Hz, 1H), 8.32 (s, 1H), 8.23 (d, *J* = 8.5 Hz, 1H), 8.00 (d, *J* = 1.0 Hz, 2H), 7.95 – 7.93 (m, 3H), 7.89 – 7.86 (m, 1H), 7.68 – 7.63 (m, 2H), 7.60 – 7.56 (m, 1H). **^{13}C NMR ($CDCl_3$, 125 MHz):** δ 194.9, 150.3, 149.5, 138. 8, 135.5, 134.3, 132.3, 132.1, 131.8, 129.5, 129.2, 128.8, 128.7, 127.9, 127.6, 127.1, 126.7, 125.4.



furan-2-yl(quinolin-3-yl)methanone (3sa)[1]

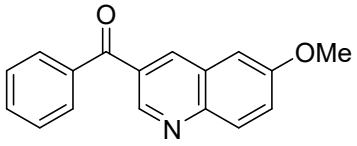
The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/5) as a yellow solid in 90% yield (40.1 mg, 0.180 mmol). **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 9.51 (s, 1H), 8.89 (s, 1H), 8.24 (d, *J* = 8.4 Hz, 1H), 8.00 (d, *J* = 8.0 Hz, 1H), 7.88 (t, *J* = 7.6 Hz, 1H), 7.78 (d, *J* = 1.1 Hz, 1H), 7.67 (t, *J* = 7.5 Hz, 1H), 7.41 (d, *J* = 3.5 Hz, 1H), 6.68 (dd, *J* = 3.6, 1.7 Hz, 1H). **^{13}C NMR ($CDCl_3$, 125 MHz):** δ 180.1, 152.4, 149.5, 147.5, 138. 8, 132.2, 129.3, 129.0, 129.0, 127.8, 120.9, 112.7.



quinolin-3-yl(thiophen-2-yl)methanone (3ta)[1]

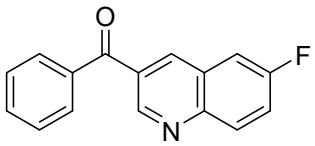
The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/5) as a yellow solid in 91% yield (43.6 mg, 0.182 mmol). **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 9.34 (s, 1H), 8.64 (d, *J* = 1.1 Hz, 1H), 8.18 (d, *J* = 8.4 Hz, 1H), 7.94 (d, *J* = 8.1 Hz, 1H), 7.85 – 7.82 (m, 1H), 7.78 (dd, *J* = 4.9, 0.9 Hz, 1H), 7.70 (dd, *J* = 3.8, 0.9 Hz, 1H), 7.63 (t, *J* = 7.5 Hz, 1H), 7.21 (dd, *J* = 4.8, 3.9 Hz, 1H). **^{13}C**

NMR ($CDCl_3$, 125 MHz): δ 186.1, 149.5, 149.4, 143.1, 137.7, 135.0, 135.0, 131.7, 130.6, 129.4, 129.0, 128.3, 127.6, 126.6.



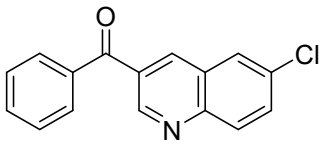
(6-methoxyquinolin-3-yl)(phenyl)methanone (3ab)[3]

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/5) as a yellow solid in 90% yield (47.4 mg, 0.180 mmol). **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 9.14 (s, 1H), 8.45 (d, *J* = 1.6 Hz, 1H), 8.09 (d, *J* = 9.2 Hz, 1H), 7.87 – 7.83 (m, 2H), 7.64 (t, *J* = 7.4 Hz, 1H), 7.53 (t, *J* = 7.7 Hz, 2H), 7.48 (dd, *J* = 9.2, 2.7 Hz, 1H), 7.14 (d, *J* = 2.7 Hz, 1H), 3.93 (s, 3H). **^{13}C NMR ($CDCl_3$, 125 MHz):** δ 195.0, 158.5, 147.7, 145.4, 137.5, 137.1, 133.0, 130.6, 130.4, 130.0, 129.9, 128.7, 128.6, 127.9, 124.8, 106.1, 55.6.



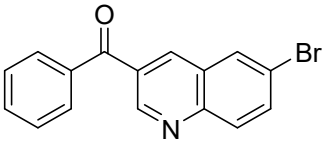
(6-fluoroquinolin-3-yl)(phenyl)methanone (3ac)[7]

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/5) as a yellow solid in 87% yield (43.6 mg, 0.174 mmol). **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 9.28 (s, 1H), 8.51 (d, *J* = 1.3 Hz, 1H), 8.24 – 8.21 (m, 1H), 7.89 – 7.84 (m, 2H), 7.69 – 7.61 (m, 2H), 7.55 (t, *J* = 7.7 Hz, 3H). **^{13}C NMR ($CDCl_3$, 125 MHz):** δ 194.6, 160.9 (d, *J* = 250.4 Hz), 149.5, 146.4, 138.1 (d, *J* = 5.3 Hz), 136.8, 133.3, 131.9 (d, *J* = 8.9 Hz), 130.1, 128.7, 122.1 (d, *J* = 25.8 Hz), 112.0 (d, *J* = 21.8 Hz). **^{19}F NMR ($CDCl_3$, 471 MHz):** δ -111.2.



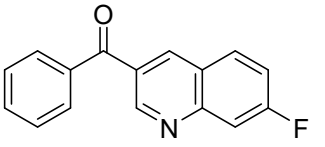
(6-chloroquinolin-3-yl)(phenyl)methanone (3ad)

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/5) as a yellow solid in 85% yield (45.2 mg, 0.169 mmol). Mp: 96 – 97 °C. **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 9.28 (d, *J* = 1.1 Hz, 1H), 8.44 (d, *J* = 1.5 Hz, 1H), 8.12 (d, *J* = 9.0 Hz, 1H), 7.89 (d, *J* = 2.1 Hz, 1H), 7.85 (d, *J* = 7.3 Hz, 2H), 7.76 (dd, *J* = 9.0, 2.2 Hz, 1H), 7.66 (t, *J* = 7.4 Hz, 1H), 7.54 (t, *J* = 7.7 Hz, 2H). **^{13}C NMR ($CDCl_3$, 125 MHz):** δ 194.4, 150.4, 147.7, 137.6, 136.7, 133.4, 133.2, 132.6, 131.0, 130.8, 130.0, 129.7, 128. 7, 128.6, 127.6, 127.2. **HRMS (ESI):** Calcd for $C_{16}H_{11}ClNO$ $[M+H]^+$ 268.0524, found: 268.0524.



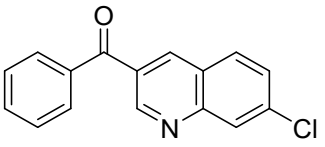
(6-bromoquinolin-3-yl)(phenyl)methanone (3ae)[7]

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/5) as a yellow solid in 84% yield (52.1 mg, 0.168 mmol). **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 9.31 (d, *J* = 1.9 Hz, 1H), 8.46 (d, *J* = 1.8 Hz, 1H), 8.09 – 8.06 (m, 2H), 7.91 (dd, *J* = 9.0, 2.1 Hz, 1H), 7.85 (dd, *J* = 8.2, 1.1 Hz, 2H), 7.67 (t, *J* = 7.5 Hz, 1H), 7.55 (t, *J* = 7.8 Hz, 2H). **^{13}C NMR ($CDCl_3$, 125 MHz):** δ 194.4, 150.6, 147.9, 137.8, 137.6, 137.4, 136.7, 135.2, 133.3, 131.1, 131.0, 130. 8, 130.0, 128.7, 127.8, 121.6.



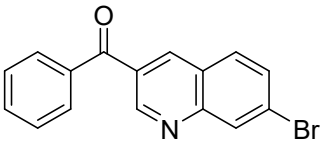
(7-fluoroquinolin-3-yl)(phenyl)methanone (3af)[5]

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/5) as a yellow solid in 86% yield (43.0 mg, 0.171 mmol). **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 9.33 (s, 1H), 8.59 (d, *J* = 1.6 Hz, 1H), 7.95 (dd, *J* = 9.0, 6.0 Hz, 1H), 7.87 – 7.83 (m, 3H), 7.67 (t, *J* = 7.4 Hz, 1H), 7.55 (t, *J* = 7.7 Hz, 2H), 7.47 – 7.43 (m, 1H). **^{13}C NMR ($CDCl_3$, 125 MHz):** δ 194.5, 164.5 (d, *J* = 254.4 Hz), 151.3, 138.8, 136.9, 133.2, 131.4 (d, *J* = 10.4 Hz), 130.0, 129.6, 128.7, 123.7, 118.4 (d, *J* = 25.5 Hz), 113.3 (d, *J* = 20.6 Hz). **^{19}F NMR ($CDCl_3$, 471 MHz):** δ -104.6.



(7-chloroquinolin-3-yl)(phenyl)methanone (3ag)[5]

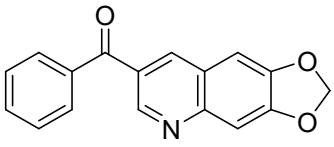
The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/5) as a yellow solid in 85% yield (45.4 mg, 0.170 mmol). **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 9.29 (s, 1H), 8.53 (d, *J* = 1.8 Hz, 1H), 8.19 (d, *J* = 8.5 Hz, 1H), 7.92 (d, *J* = 7.9 Hz, 1H), 7.88 – 7.85 (m, 1H), 7.75 – 7.72 (m, 2H), 7.70 – 7.67 (m, 2H), 7.66 – 7.63 (m, 1H). **^{13}C NMR ($CDCl_3$, 125 MHz):** δ 193.8, 150.0, 149.5, 138.7, 135.7, 132.0, 131.9, 131.5, 130.3, 129.7, 129.5, 129.1, 128.3, 127.7, 127.6, 126.5.



(7-bromoquinolin-3-yl)(phenyl)methanone (3ah)[5]

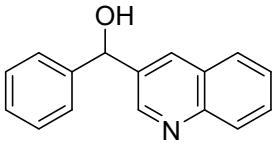
The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/5) as a yellow solid in 83%

yield (51.7 mg, 0.166 mmol). **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 9.30 (d, *J* = 2.1 Hz, 1H), 8.52 (d, *J* = 1.9 Hz, 1H), 8.37 (d, *J* = 1.4 Hz, 1H), 7.87 – 7.83 (m, 2H), 7.78 (d, *J* = 8.7 Hz, 1H), 7.72 (dd, *J* = 8.7, 1.9 Hz, 1H), 7.67 – 7.64 (m, 1H), 7.54 (t, *J* = 7.7 Hz, 2H). **^{13}C NMR ($CDCl_3$, 125 MHz):** δ 194.4, 151.3, 149.8, 138.5, 136.8, 133.2, 131.9, 131.2, 130.3, 130.2, 130.0, 128.7, 126.3, 125.2, 119.7, 118.5.



[1,3]dioxolo[4,5-*g*]quinolin-7-yl(phenyl)methanone (3ai)[1]

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/5) as a yellow solid in 90% yield (50.0 mg, 0.180 mmol). **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 9.09 (d, *J* = 2.1 Hz, 1H), 8.39 (d, *J* = 2.0 Hz, 1H), 7.84 (dd, *J* = 8.2, 1.1 Hz, 2H), 7.65 – 7.62 (m, 1H), 7.52 (t, *J* = 7.7 Hz, 2H), 7.47 (s, 1H), 7.12 (s, 1H), 6.16 (s, 2H).**^{13}C NMR ($CDCl_3$, 125 MHz):** δ 194.8, 152.8, 148.7, 148.4, 148.2, 137.4, 137.2, 132.8, 129.9, 128.7, 128.5, 128.3, 124.0, 105.7, 103.7, 102.3.



phenyl(quinolin-3-yl)methanol (4)[8]

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/5) as a yellow solid in 90% yield (42.3 mg, 0.180 mmol). **^{1}H NMR (DMSO-d_6, 500 MHz):** δ 8.90 (s, 1H), 8.31 (s, 1H), 7.98 (t, *J* = 7.4 Hz, 2H), 7.71 (t, *J* = 7.4 Hz, 1H), 7.58 (t, *J* = 7.5 Hz, 1H), 7.47 (d, *J* = 7.5 Hz, 2H), 7.33 (t, *J* = 7.6 Hz, 2H), 7.23 (t, *J* = 7.3 Hz, 1H), 6.26 (s, 1H), 5.99 (s, 1H). **^{13}C NMR (DMSO-d_6, 125 MHz):** δ 150.0, 146.7, 144.7, 138.5, 132.2, 129.2, 128.6, 128.3, 128.1, 127.5, 127.1, 126.8, 126.4, 72.5.

6. X-ray Crystallography of 3oa

Crystal preparation of compound 3oa.

Compound **3oa** (25 mg) was dissolved in 5 mL of dichloromethane/*n*-hexane (v1/v2 = 1:1), and it was crystallized to give crystal as colorless block after the solvent was slowly volatilized in 4 days at room temperature (~ 25 °C).

All diffraction data were obtained on a Bruker Smart Apex CCD diffractometer equipped

with graphite-monochromated Mo Kα radiation. CCDC-2143900 (**3oa**), contain the supplementary crystallographic data. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre (http://www.ccdc.cam.ac.uk/). Thermal ellipsoids are shown at the 30% level. Hydrogen atoms have been omitted for clarity. X-ray crystallographic data for **3oa** is available as Figure S1.

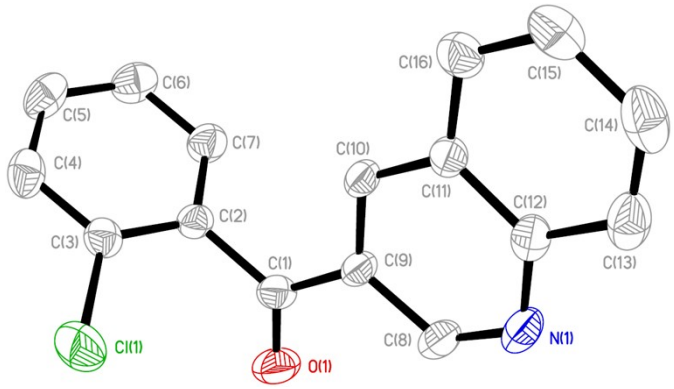


Figure S1. The molecular structure of **3oa**

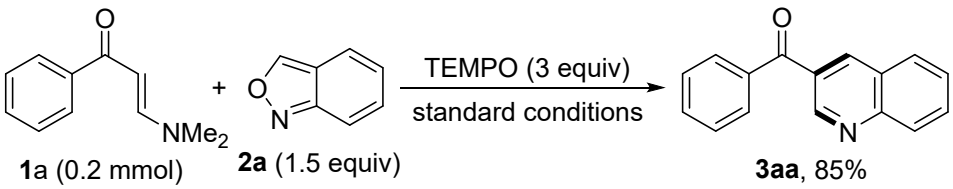
Table S1. Crystal Data and Summary of X-ray Data Collection for 3oa

Empirical formula	$C_{16}H_{10}ClNO$
Formula weight	267.70
Temperature	298(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, C2/c
Unit cell dimensions	a = 24.237(2) A alpha = 90 deg.
	b = 8.5380(7) A beta = 97.588(3) deg.
	c = 12.1562(11) A gamma = 90 deg.
Volume	2493.6(4) A^3
Z, Calculated density	8, 1.426 Mg/m^3
Absorption coefficient	0.295 mm^-1
F(000)	1104
Crystal size	0.30 x 0.20 x 0.15 mm
Theta range for data collection	2.53 to 25.02 deg.
Limiting indices	-28<=h<=19, -10<=k<=9, -12<=l<=14
Reflections collected / unique	6067 / 2201 [R(int) = 0.0468]
Completeness to theta = 25.02	99.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9570 and 0.9166
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2201 / 0 / 172

Goodness-of-fit on F^2	1.040
Final R indices [I>2sigma(I)]	R1 = 0.0449, wR2 = 0.1072
R indices (all data)	R1 = 0.0814, wR2 = 0.1207
Largest diff. peak and hole	0.142 and -0.214 e.A^-3

7. Mechanism Research

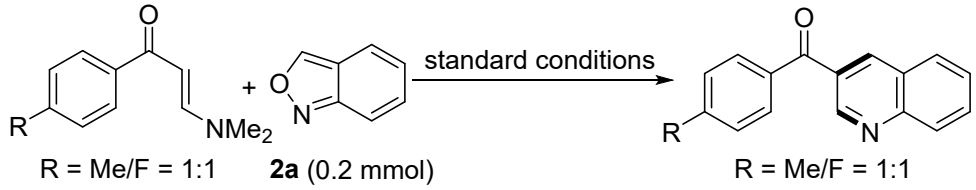
(a) Free Radical Inhibitor Capture Experiment

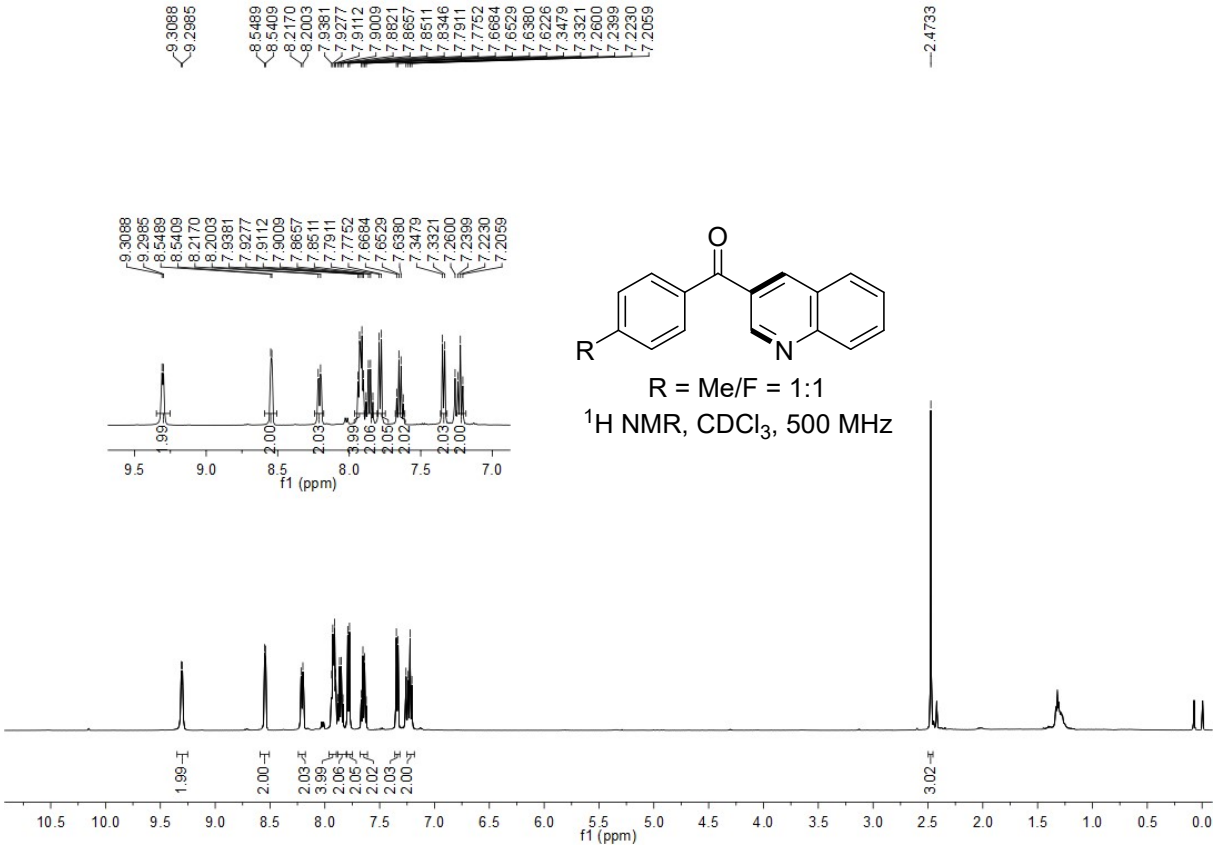


A mixture of (*E*)-3-(dimethylamino)-1-phenylprop-2-en-1-one (**1a**) (0.2 mmol, 1.0 equiv), benzo[*c*]isoxazole (**2**) (0.3 mmol, 1.5 equiv), [Ru(*p*-cymene)Cl_2]$_2$ (0.01 mmol, 5 mol%) and TEMPO (3 equiv) were weighted in a Schlenk sealed tube equipped with a stir bar. Dry CH_3CN (1.5 mL) and HOAc (0.2 mmol, 1.0 equiv) were added and the mixture was stirred at 120 °C in a pre-heated oil bath for 12 h under N_2 atmosphere. Then, the mixture was cooled to room temperature and concentrated in vacuo and the resulting residue was purified by flash column chromatography on silica gel with EtOAc/petroleum ether, the product **3aa** was affored in 85% yield (39.7 mg, 0.170 mmol).

(b) Competition Experiment of 1b and 1e with 2a

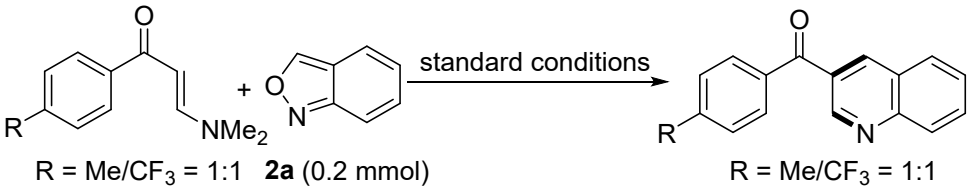
A mixture of (*E*)-3-(dimethylamino)-1-(*p*-tolyl)prop-2-en-1-one (**1b**) (37.8 mg, 0.2 mmol, 1.0 equiv), (*E*)-3-(dimethylamino)-1-(4-fluorophenyl)prop-2-en-1-one (**1e**) (38.6 mg, 0.2 mmol, 1.0 equiv), benzo[*c*]isoxazole (**2a**) (23.8 mg, 0.2 mmol, 1.0 equiv) and [Ru(*p*-cymene)Cl_2]$_2$ (0.01 mmol, 5 mol%) were weighted in a Schlenk sealed tube equipped with a stir bar. Dry CH_3CN (1.5 mL) and HOAc (0.2 mmol, 1.0 equiv) were added and the mixture was stirred at 120 °C in a pre-heated oil bath for 12 h under N_2 atmosphere. Then, the mixture was cooled to room temperature and concentrated in vacuo and the resulting residue was purified by flash column chromatography on silica gel with EtOAc/petroleum ether to give a mixture of products **3ba** and **3ea** at a ratio of 1:1.

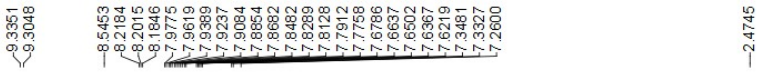


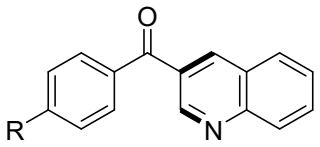


(c) Competition Experiment of 1b and 1h with 2a

A mixture of (*E*)-3-(dimethylamino)-1-(*p*-tolyl)prop-2-en-1-one (**1b**) (37.8 mg, 0.2 mmol, 1.0 equiv), (*E*)-3-(dimethylamino)-1-(4-(trifluoromethyl)phenyl)prop-2-en-1-one (**1h**) (48.6 mg, 0.2 mmol, 1.0 equiv), benzo[*c*]isoxazole (**2a**) (23.8 mg, 0.2 mmol, 1.0 equiv) and [Ru(*p*-cymene)Cl_2]$_2$ (0.01 mmol, 5 mol%) were weighted in a Schlenk sealed tube equipped with a stir bar. Dry CH_3CN (1.5 mL) and HOAc (0.2 mmol, 1.0 equiv) were added and the mixture was stirred at 120 ^oC in a pre-heated oil bath for 12 h under N_2 atmosphere. Then, the mixture was cooled to room temperature and concentrated in vacuo and the resulting residue was purified by flash column chromatography on silica gel with EtOAc/petroleum ether to give a mixture of products **3ba** and **3ha** at a ratio of 1:1.

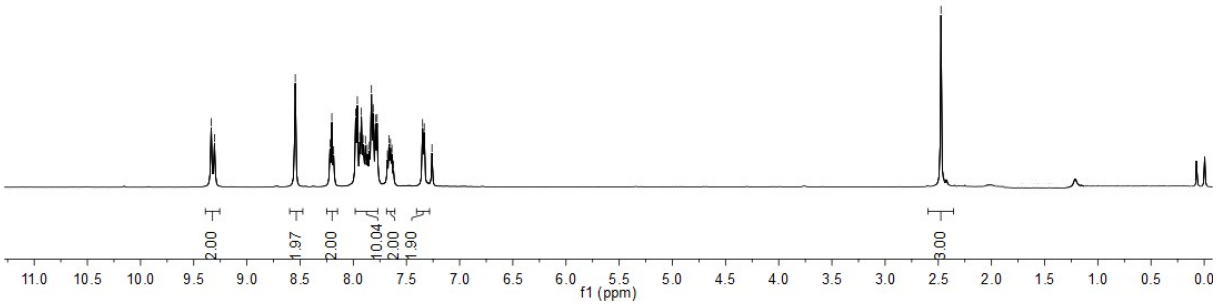






R = Me/CF_3 = 1:1

^{1}H NMR, $CDCl_3$, 500 MHz



8. References:

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7. T.-S. Jiang, Y. Zhou, L. Dai, X. Liu and X. Zhang, *Tetrahedron Lett.*, 2019, **60**, 2078−2083.

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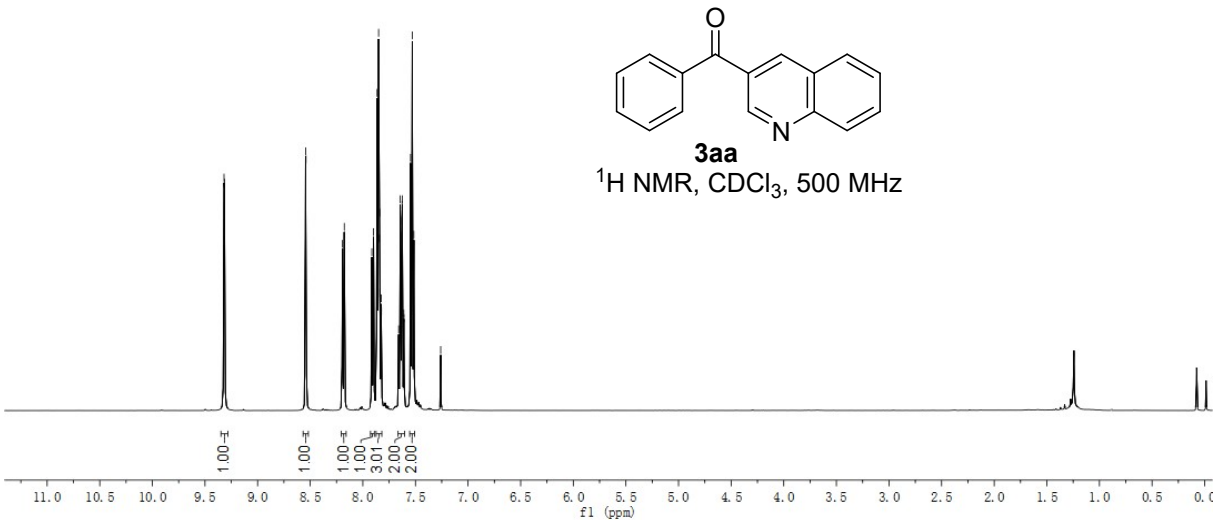
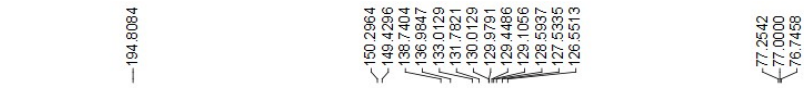
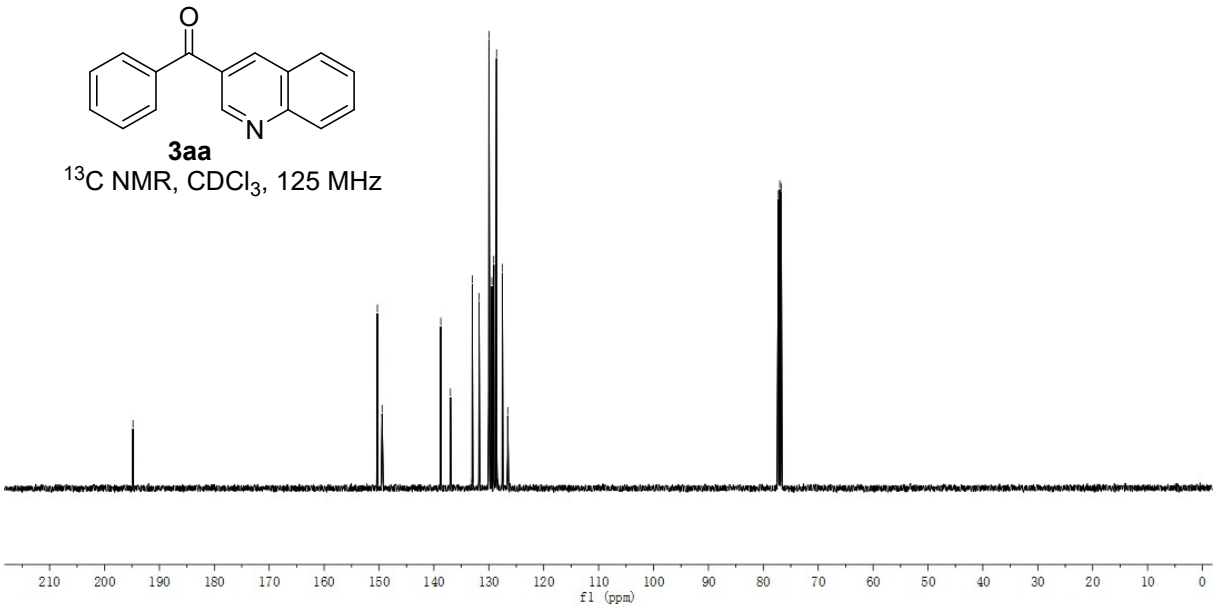
9. NMR Spectra



3aa

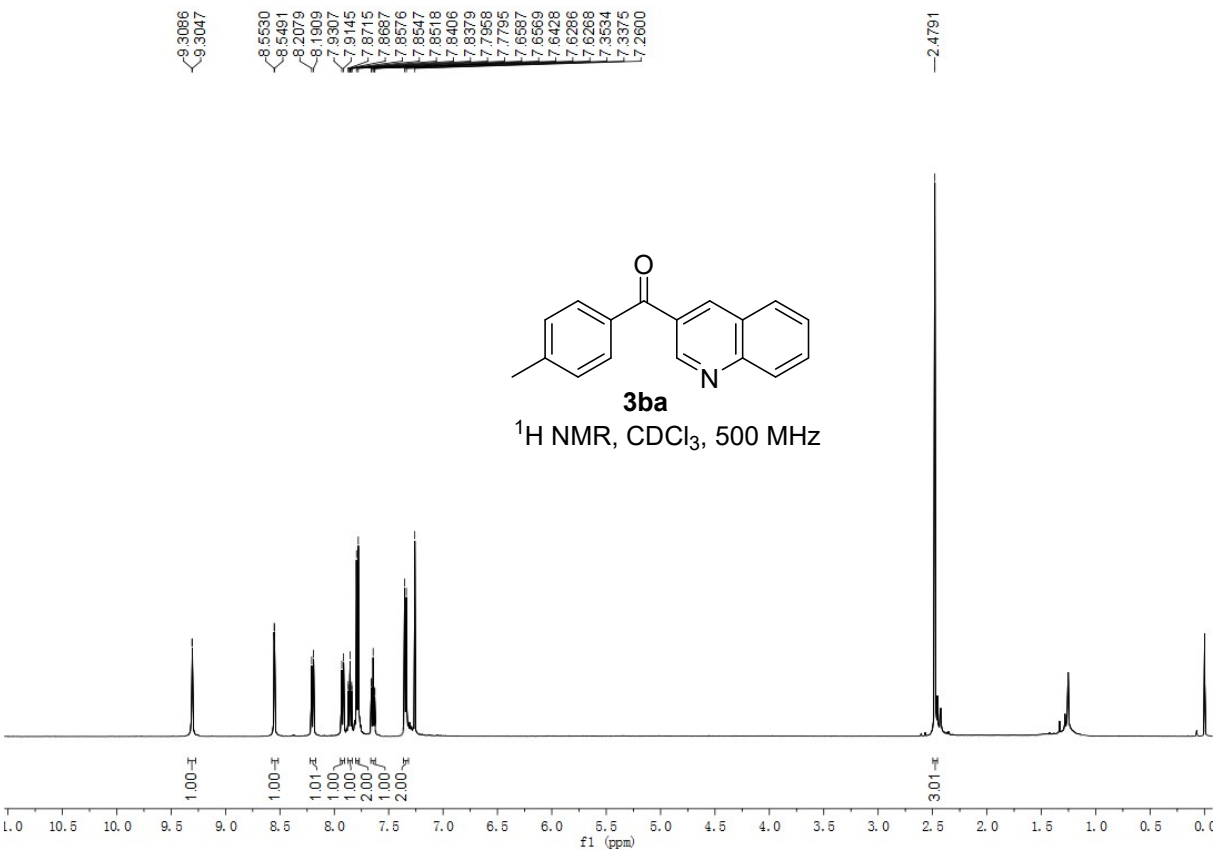
^{1}H NMR, $CDCl_3$, 500 MHz





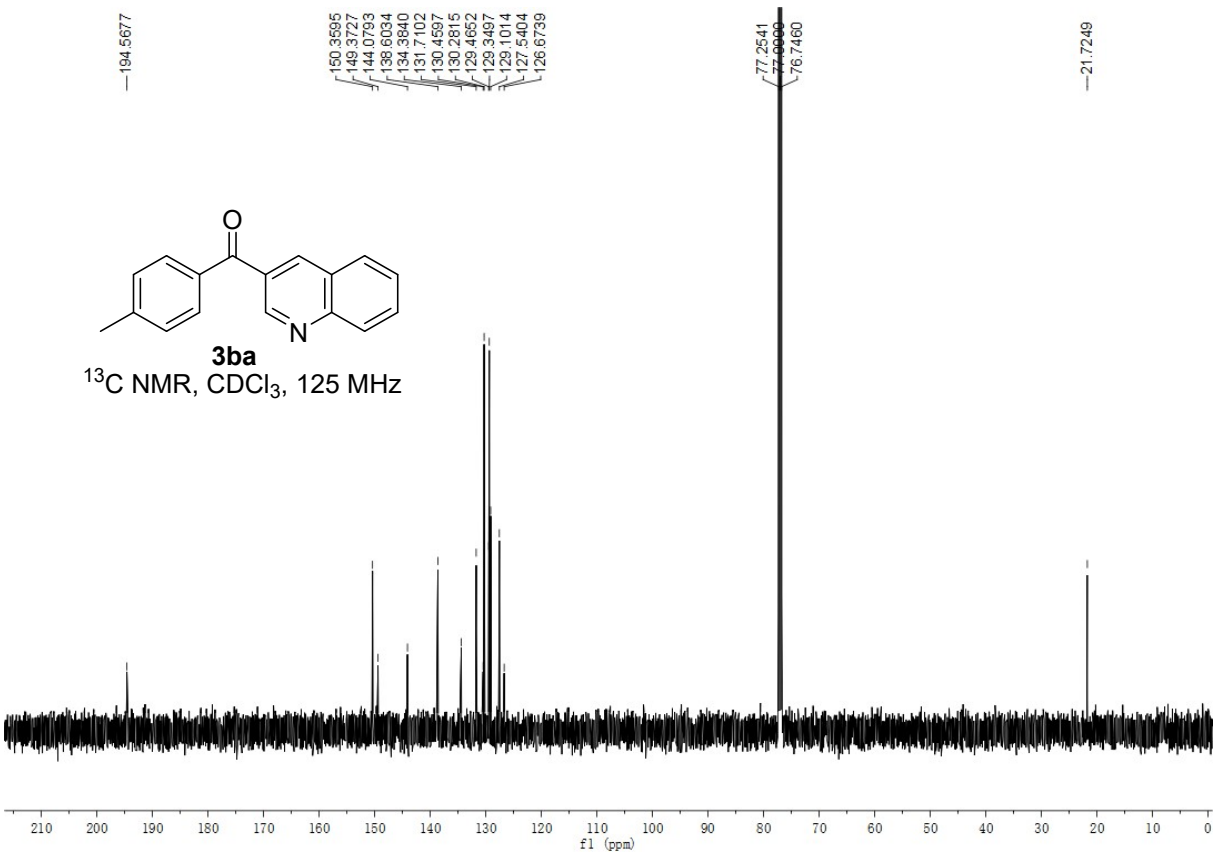
3aa

^{13}C NMR, $CDCl_3$, 125 MHz



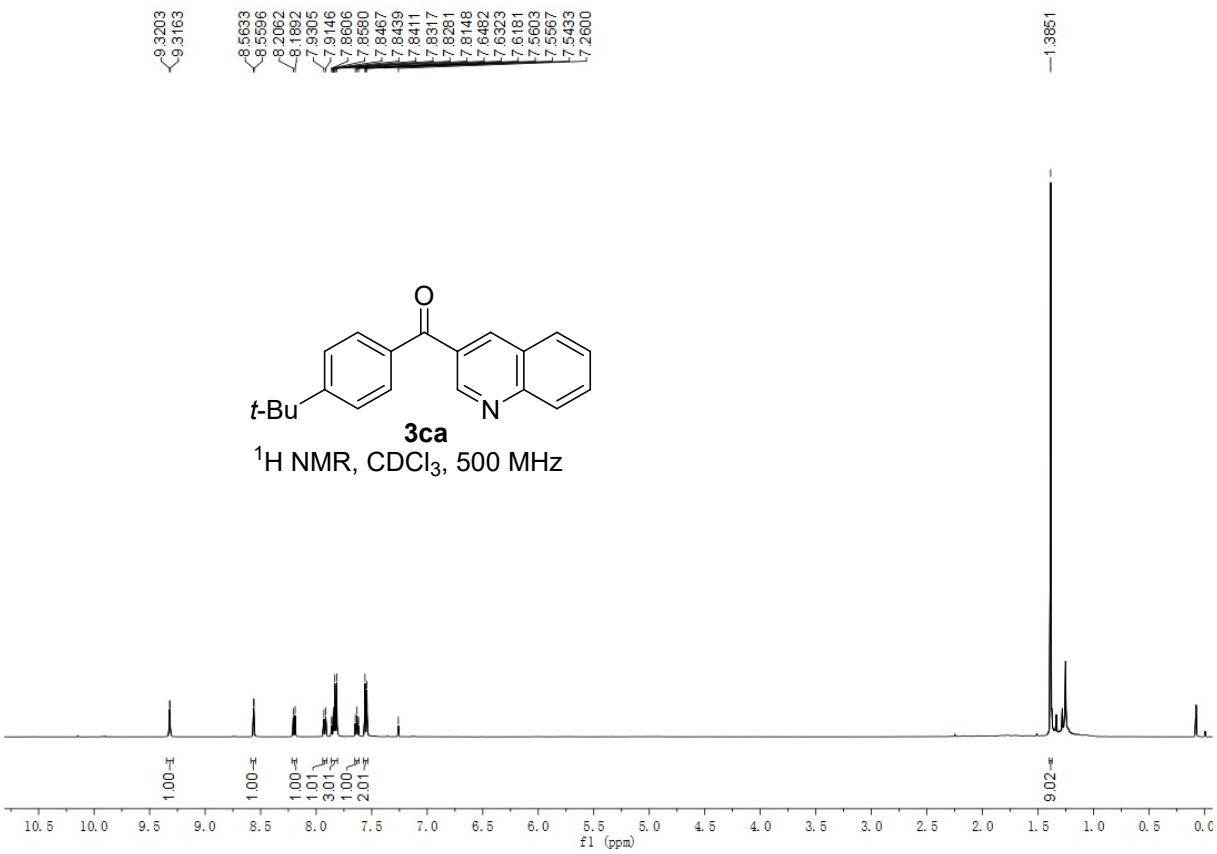
3ba

^{1}H NMR, $CDCl_3$, 500 MHz



3ba

^{13}C NMR, $CDCl_3$, 125 MHz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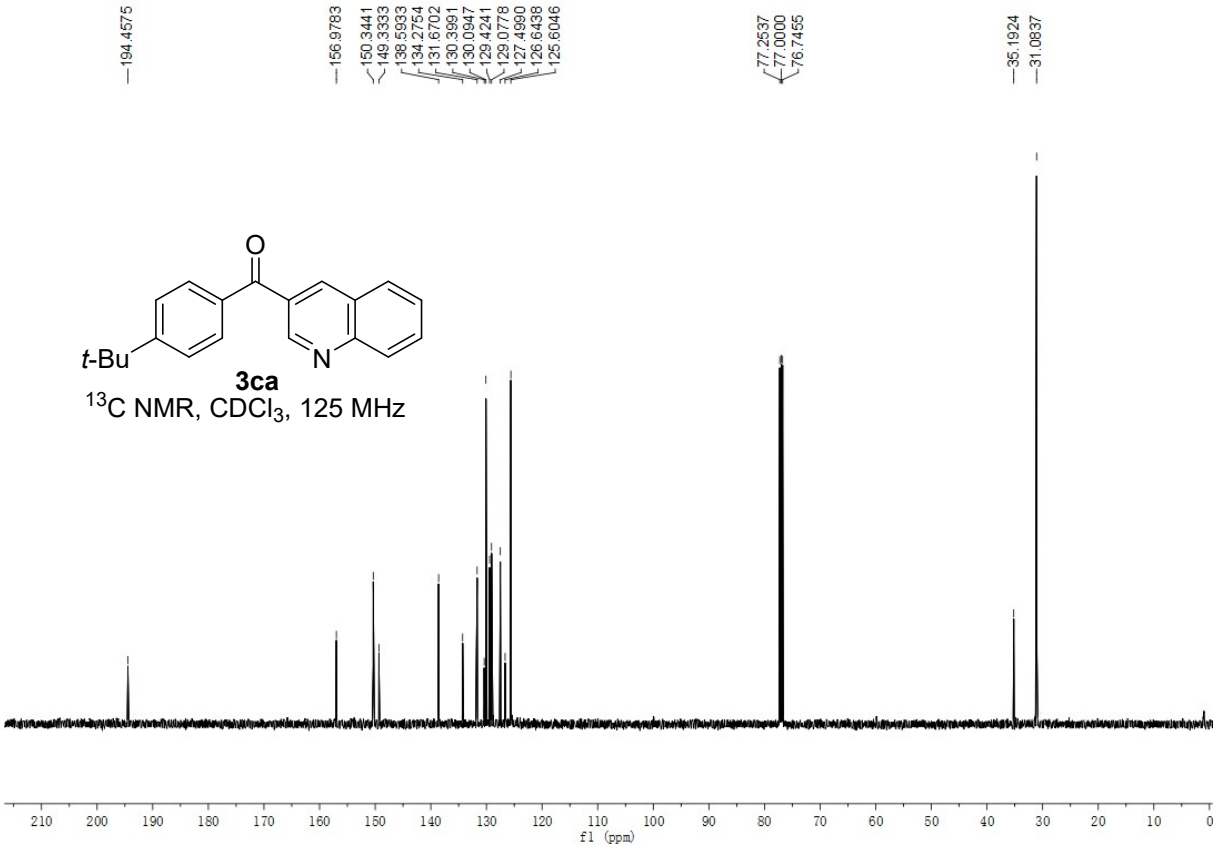
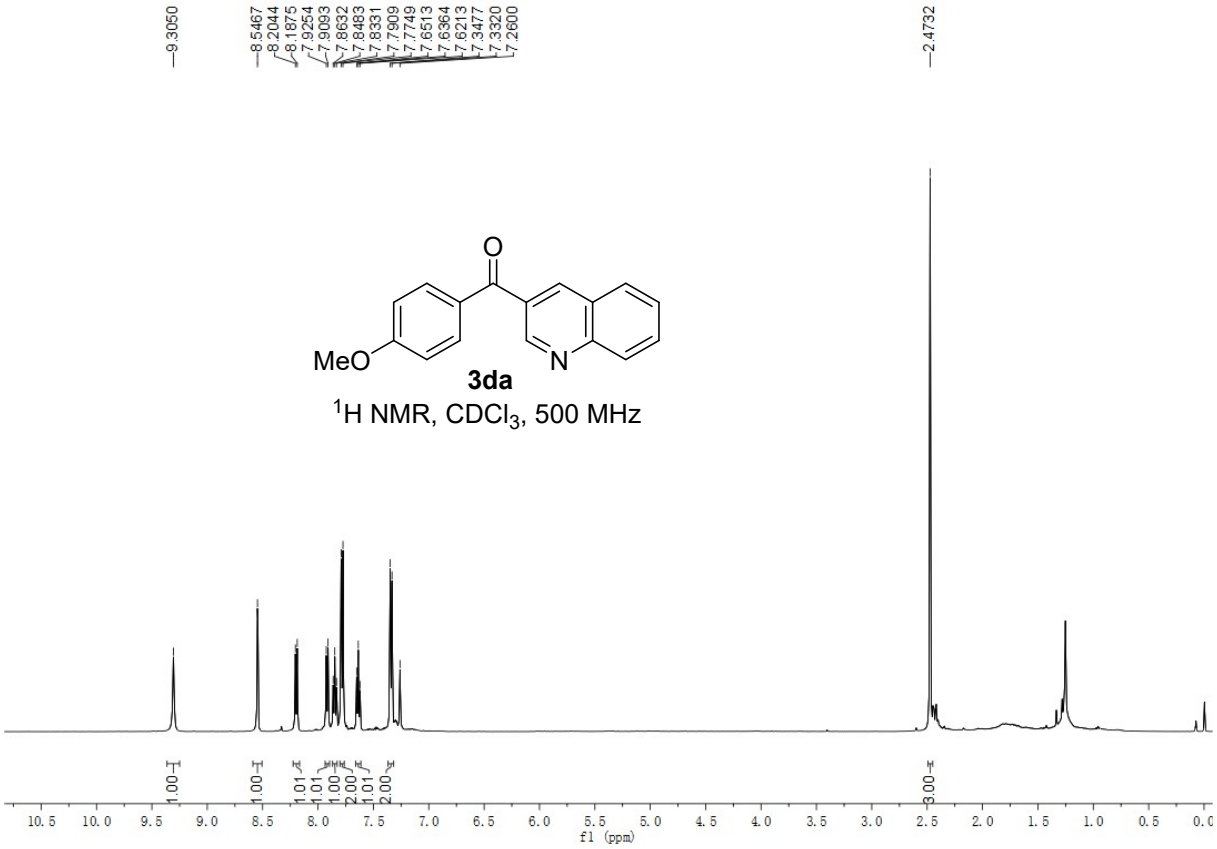
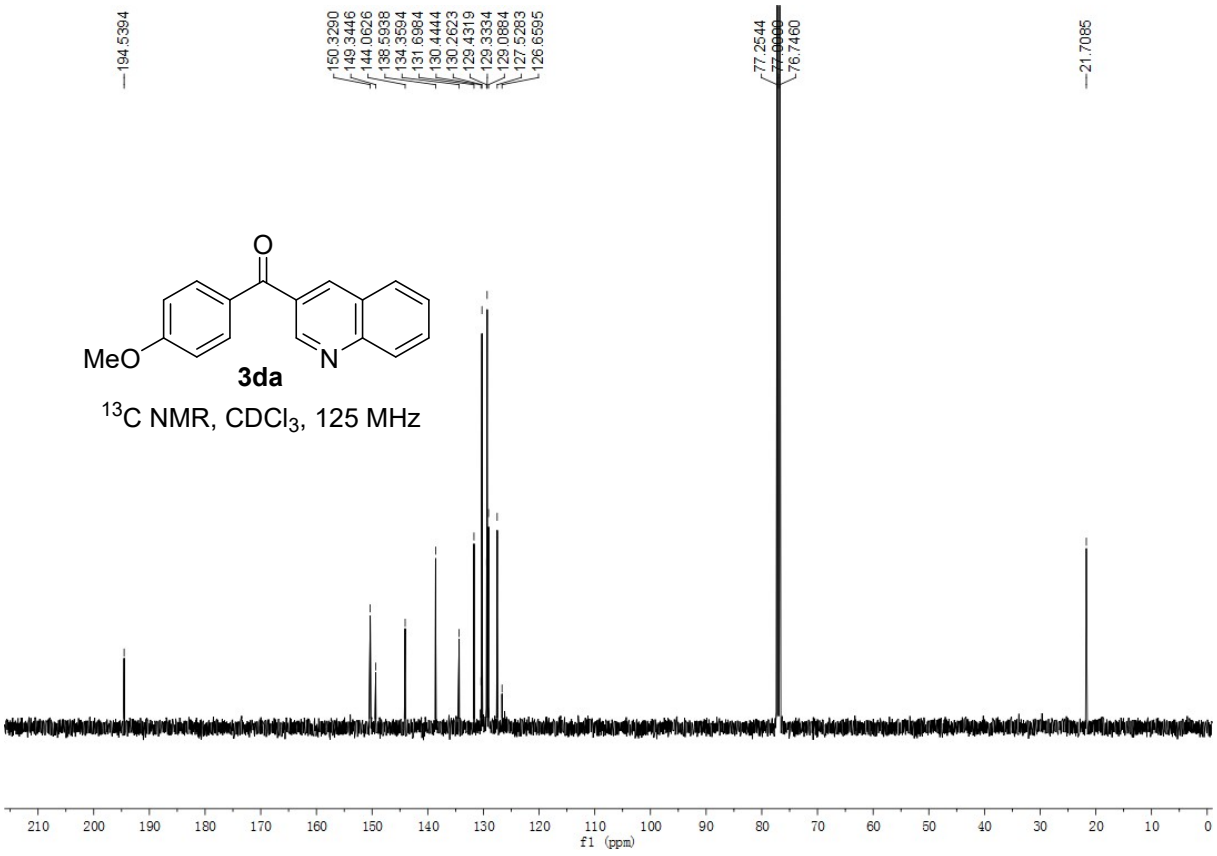
9.3163
8.5633
8.5596
8.2062
8.1892
7.9305
7.9146
7.8606
7.8580
7.8467
7.8439
7.8411
7.8317
7.8281
7.8148
7.6482
7.6323
7.6181
7.5603
7.5567
7.5433
7.2600
1.3851
O
t-Bu
N
3ca
1H NMR, CDCl3, 500 MHz
1.00
1.00
1.00
1.01
3.01
1.00
2.01
9.02
f1 (ppm)


194.4575
156.9783
150.3441
149.3333
138.5933
134.2754
131.6702
130.3991
130.0947
129.4241
129.0778
127.4990
126.6438
125.6046
77.2537
77.0000
76.7455
35.1924
31.0837
O
t-Bu
N
3ca
13C NMR, CDCl3, 125 MHz
f1 (ppm)



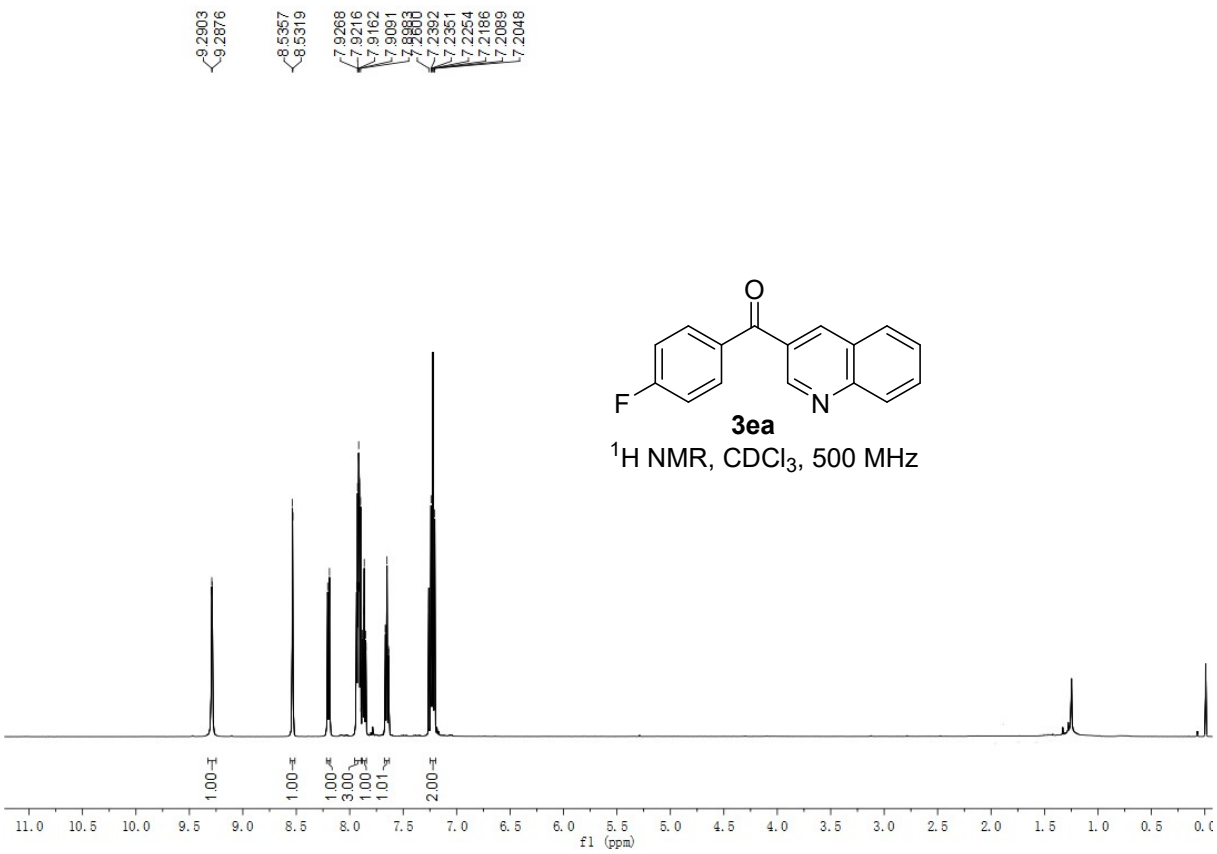
3da

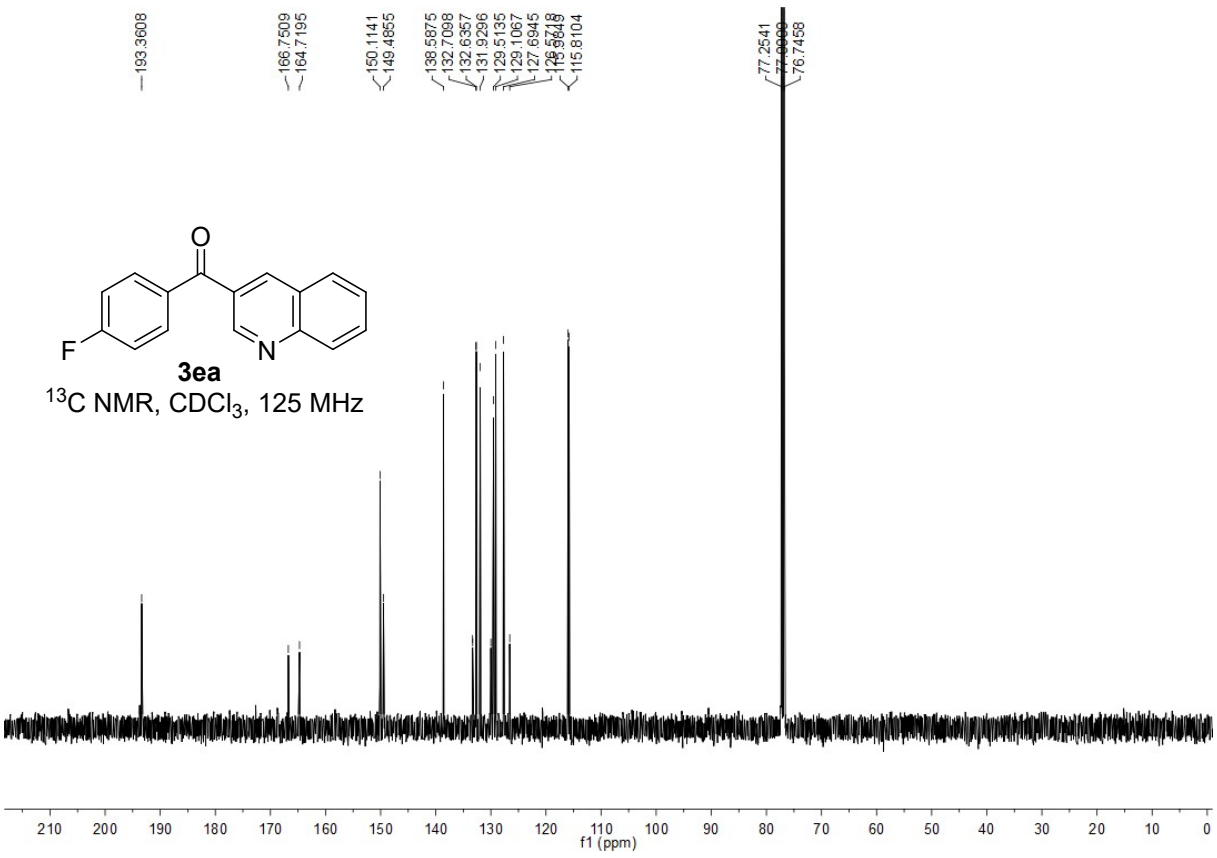
^{1}H NMR, $CDCl_3$, 500 MHz

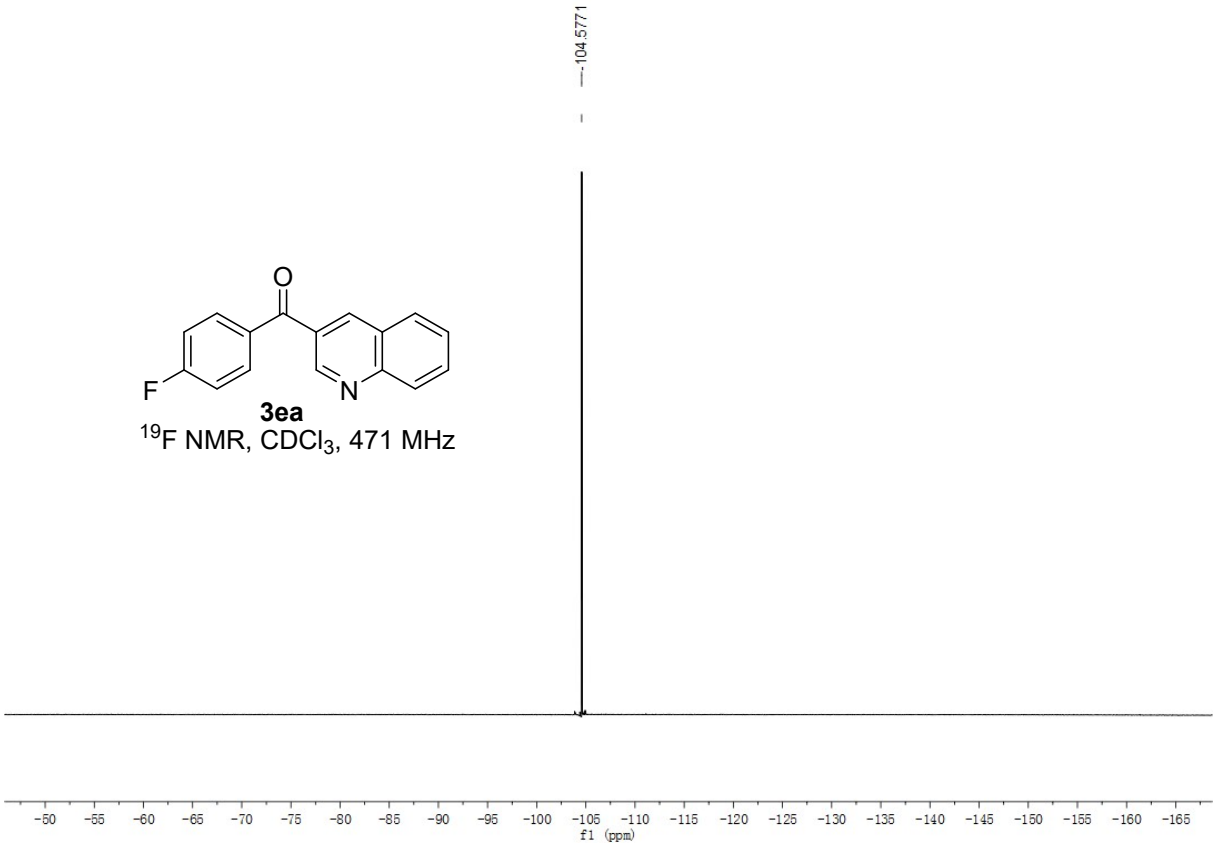


3da

^{13}C NMR, $CDCl_3$, 125 MHz

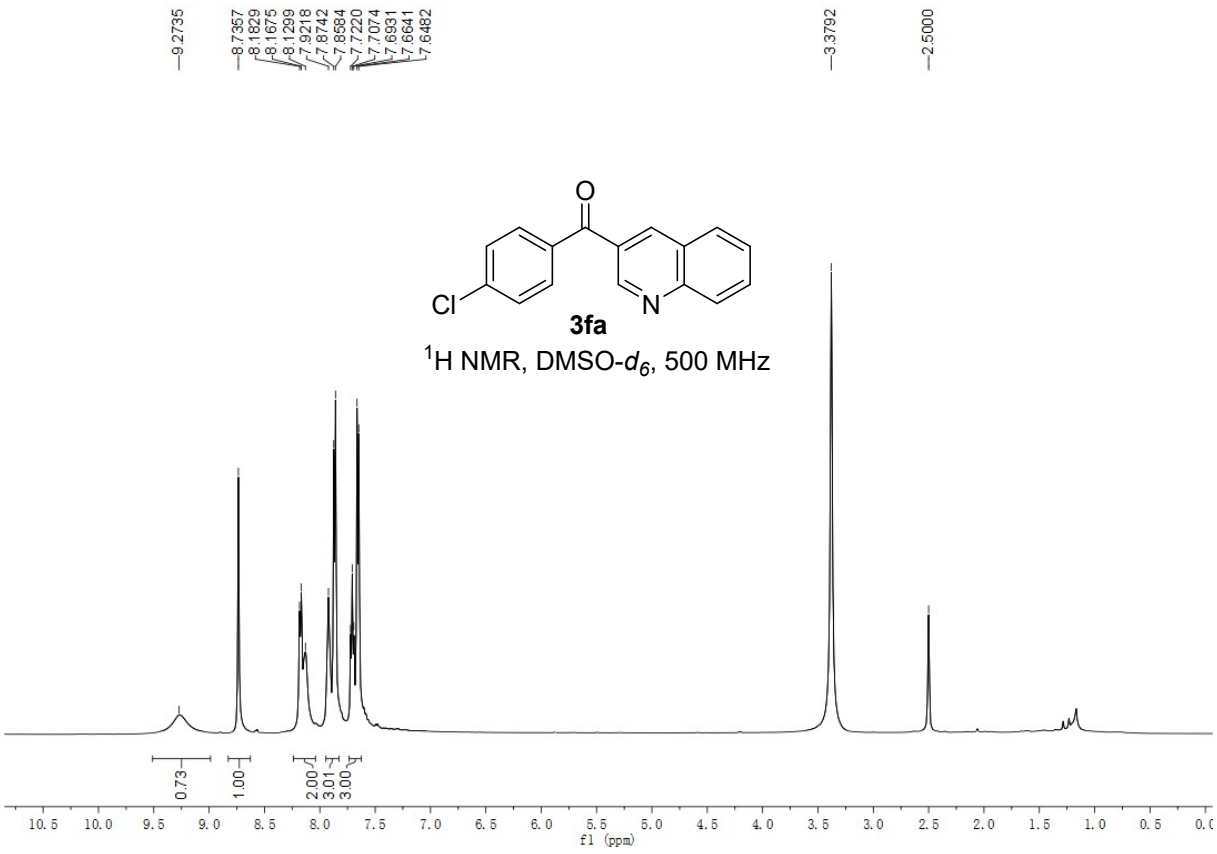

9.2903
9.2876
8.5357
8.5319
7.9268
7.9216
7.9162
7.9091
7.2392
7.2351
7.2254
7.2186
7.2089
7.2048
O
F
N
3ea
1H NMR, CDCl3, 500 MHz
1.00
1.00
1.00
3.00
1.00
1.01
2.00
f1 (ppm)


193.3608
166.7509
164.7195
150.1141
149.4655
138.5875
132.7098
132.6357
131.9296
129.5135
129.1067
127.6945
115.8104
77.2541
76.7458
O
F
N
3ea
13C NMR, CDCl3, 125 MHz
f1 (ppm)



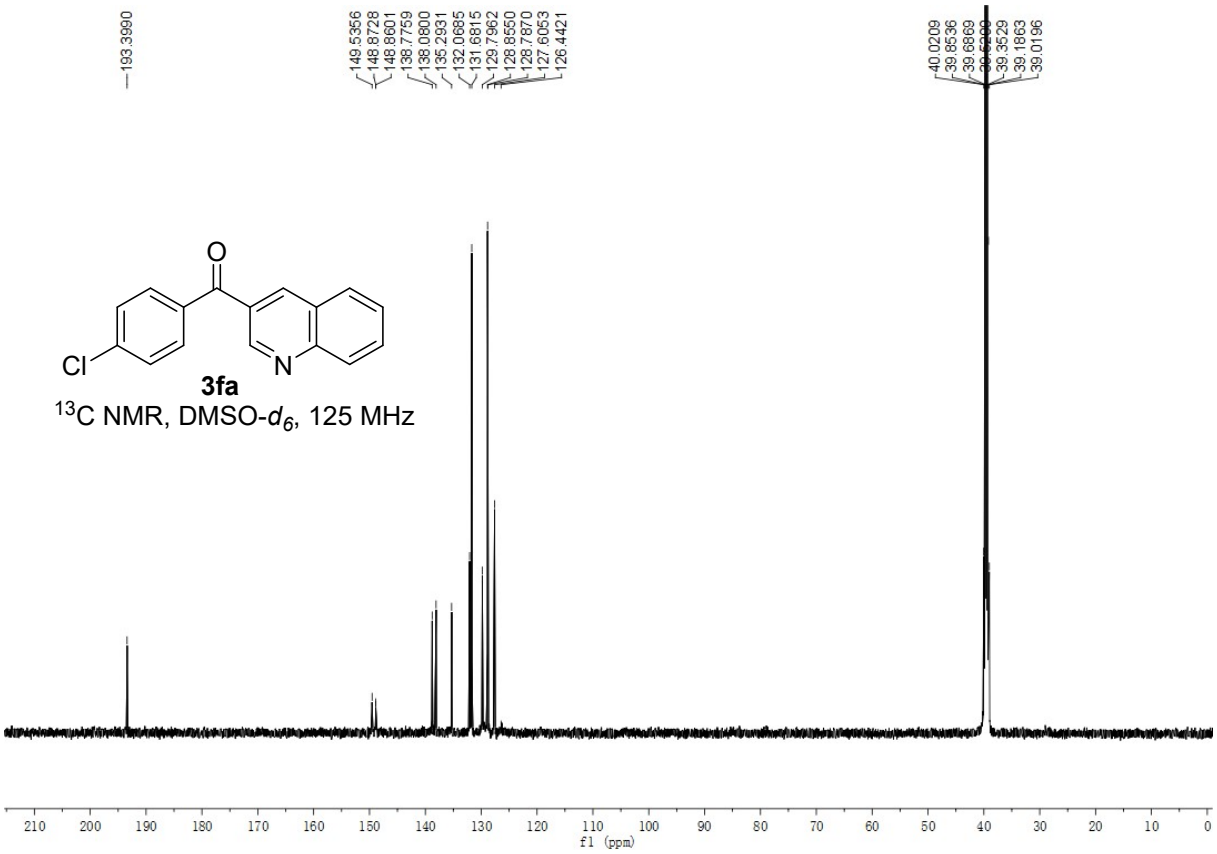
3ea

^{19}F NMR, $CDCl_3$, 471 MHz



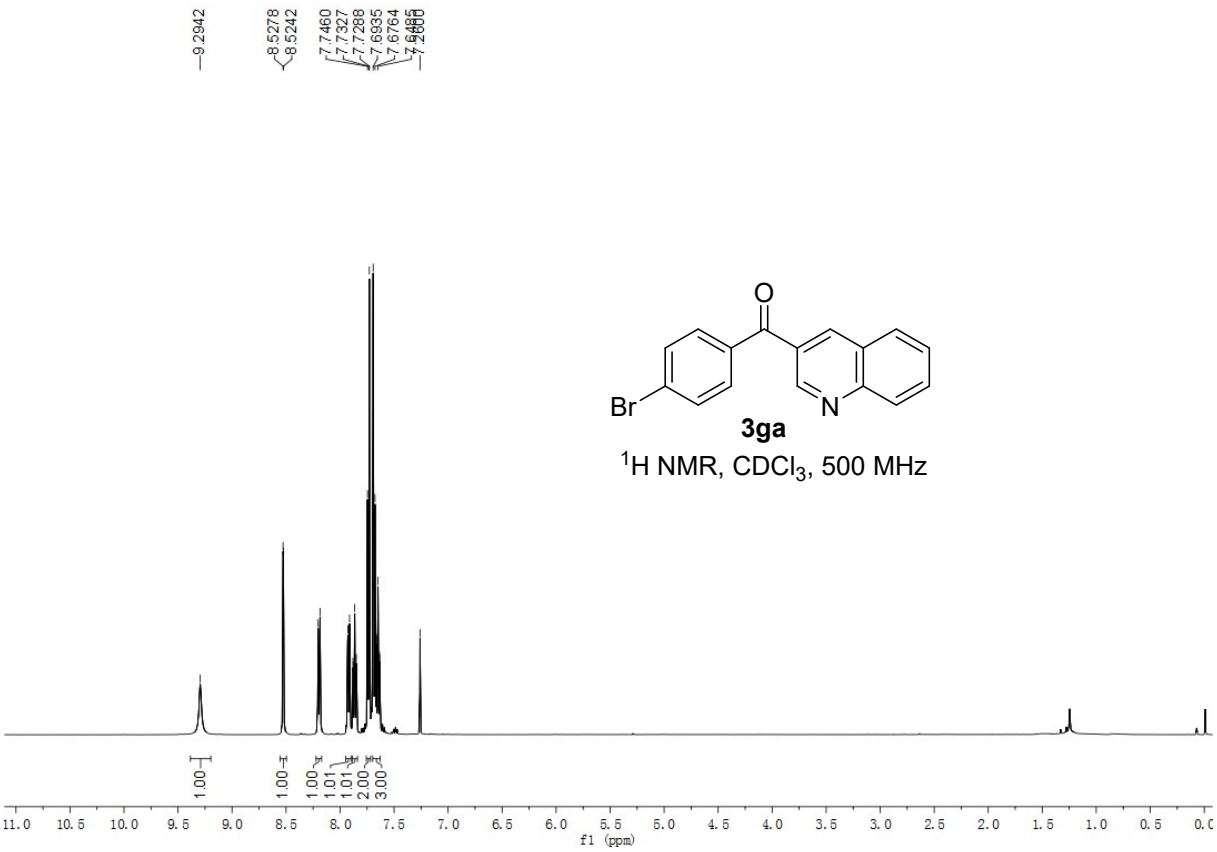
3fa

^{1}H NMR, DMSO-d_6, 500 MHz



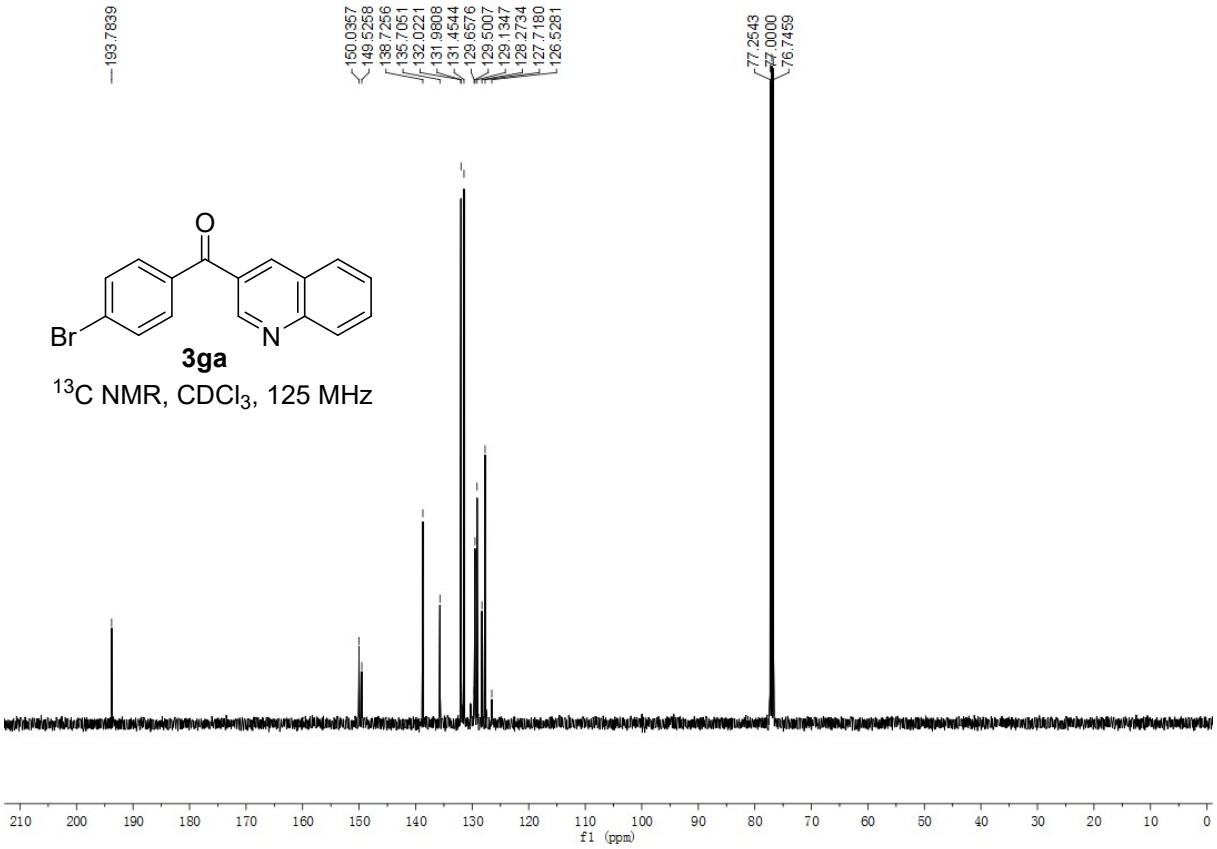
3fa

^{13}C NMR, DMSO-d_6, 125 MHz



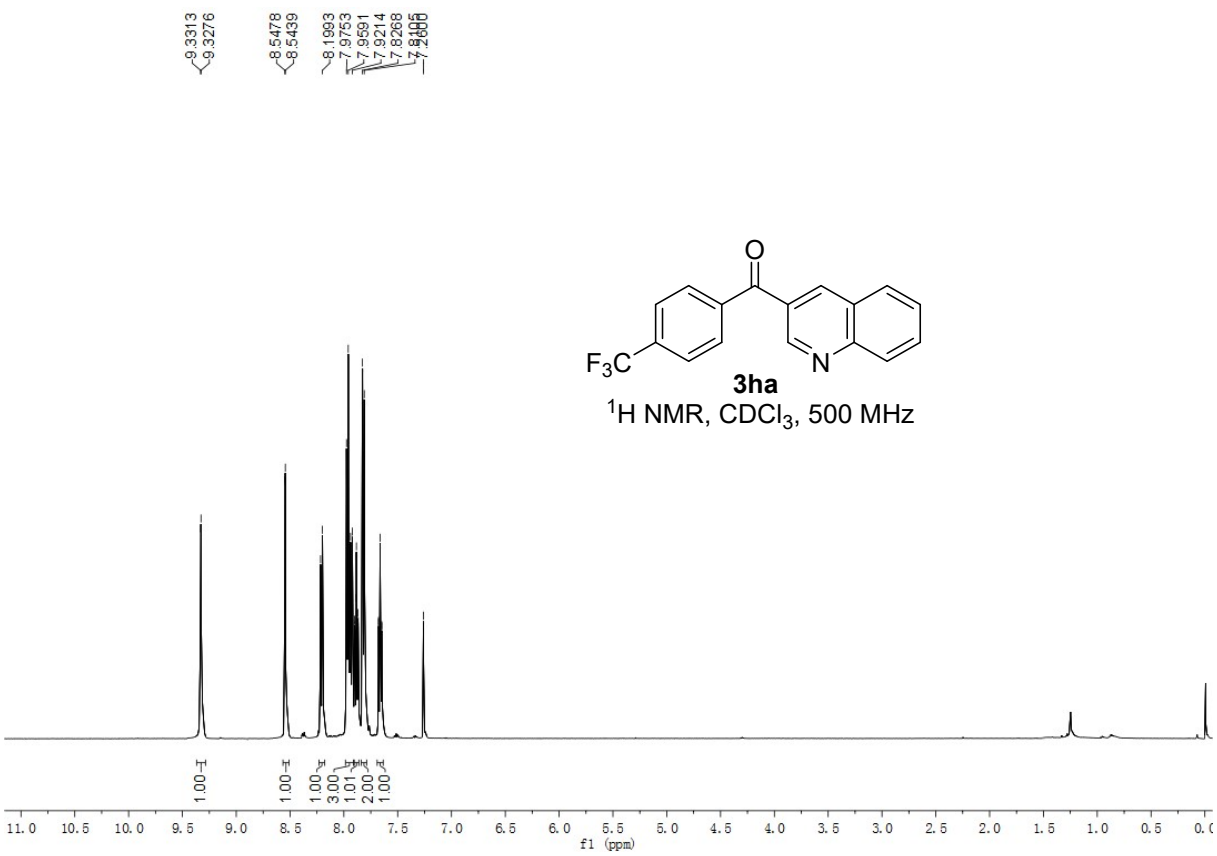
3ga

^{1}H NMR, $CDCl_3$, 500 MHz



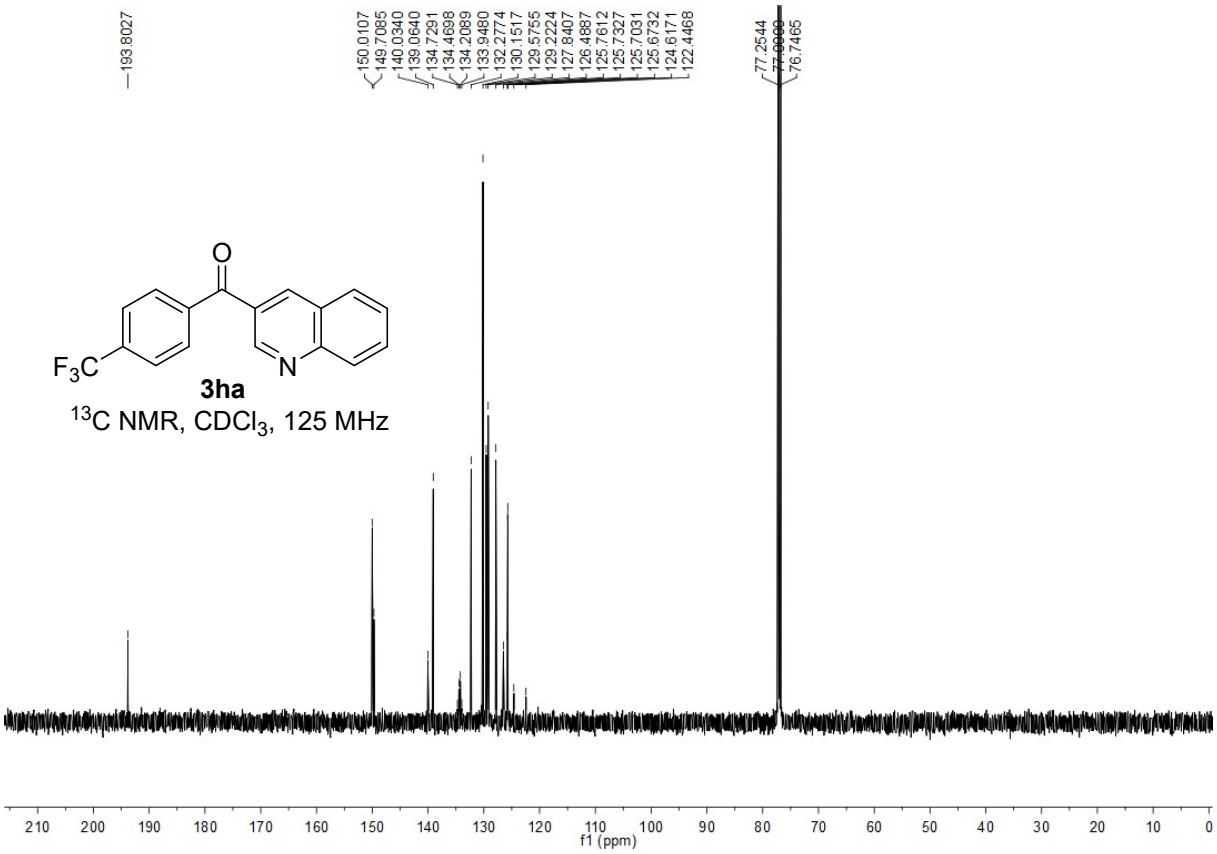
3ga

^{13}C NMR, $CDCl_3$, 125 MHz



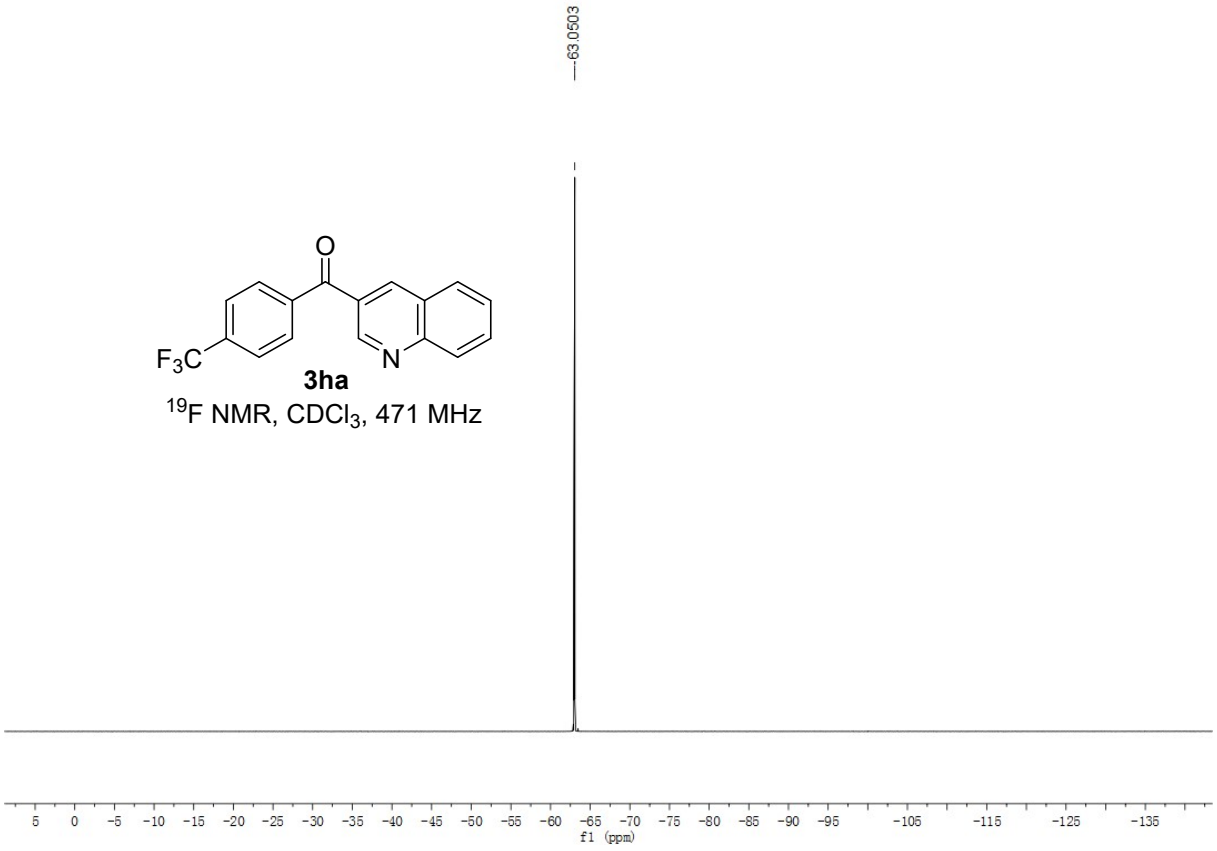
3ha

^{1}H NMR, $CDCl_3$, 500 MHz



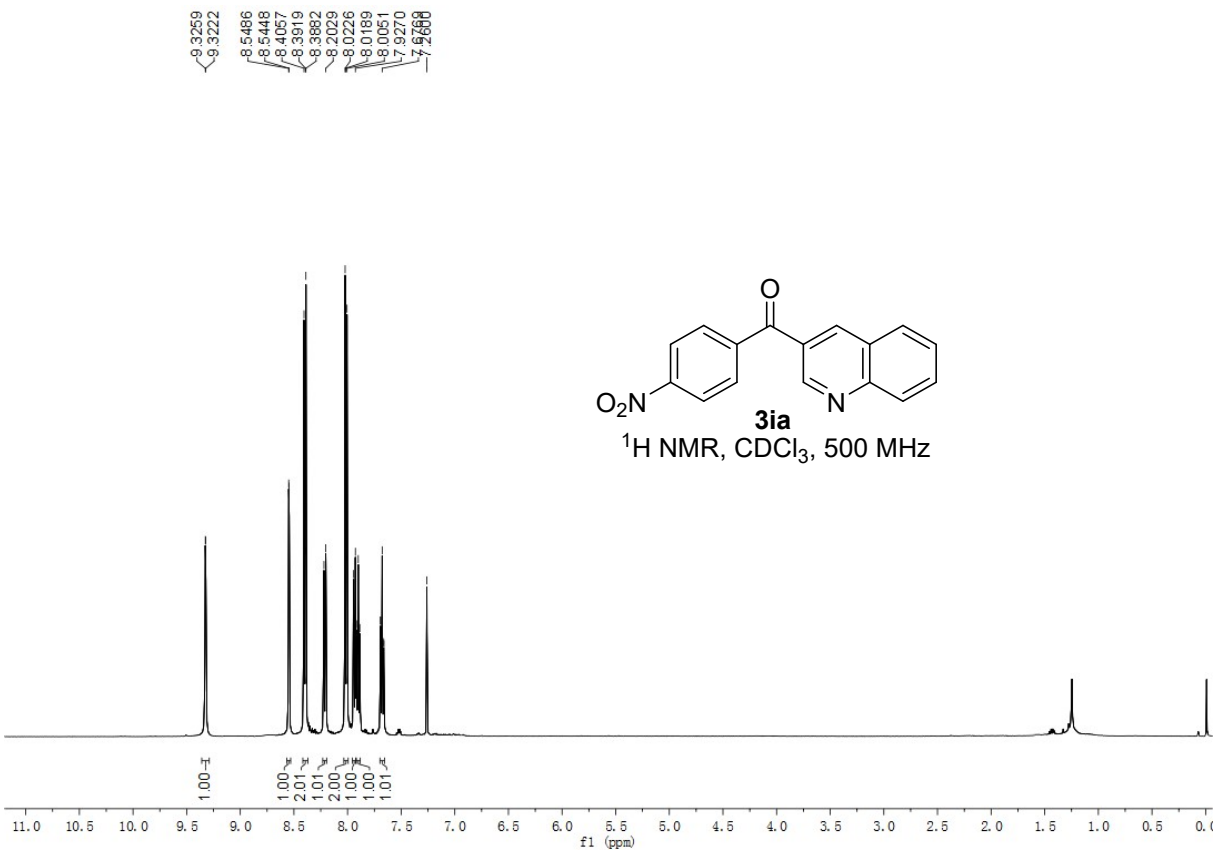
3ha

^{13}C NMR, $CDCl_3$, 125 MHz



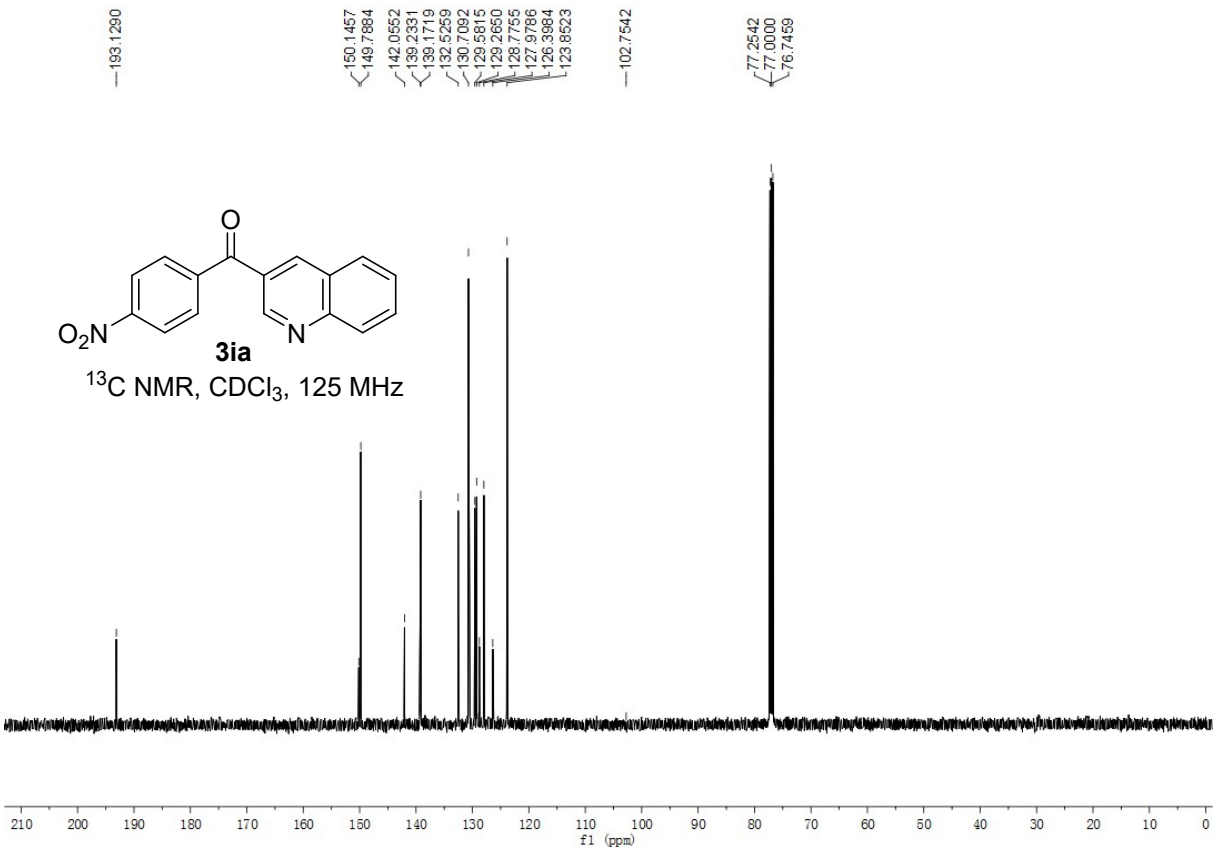
3ha

^{19}F NMR, $CDCl_3$, 471 MHz



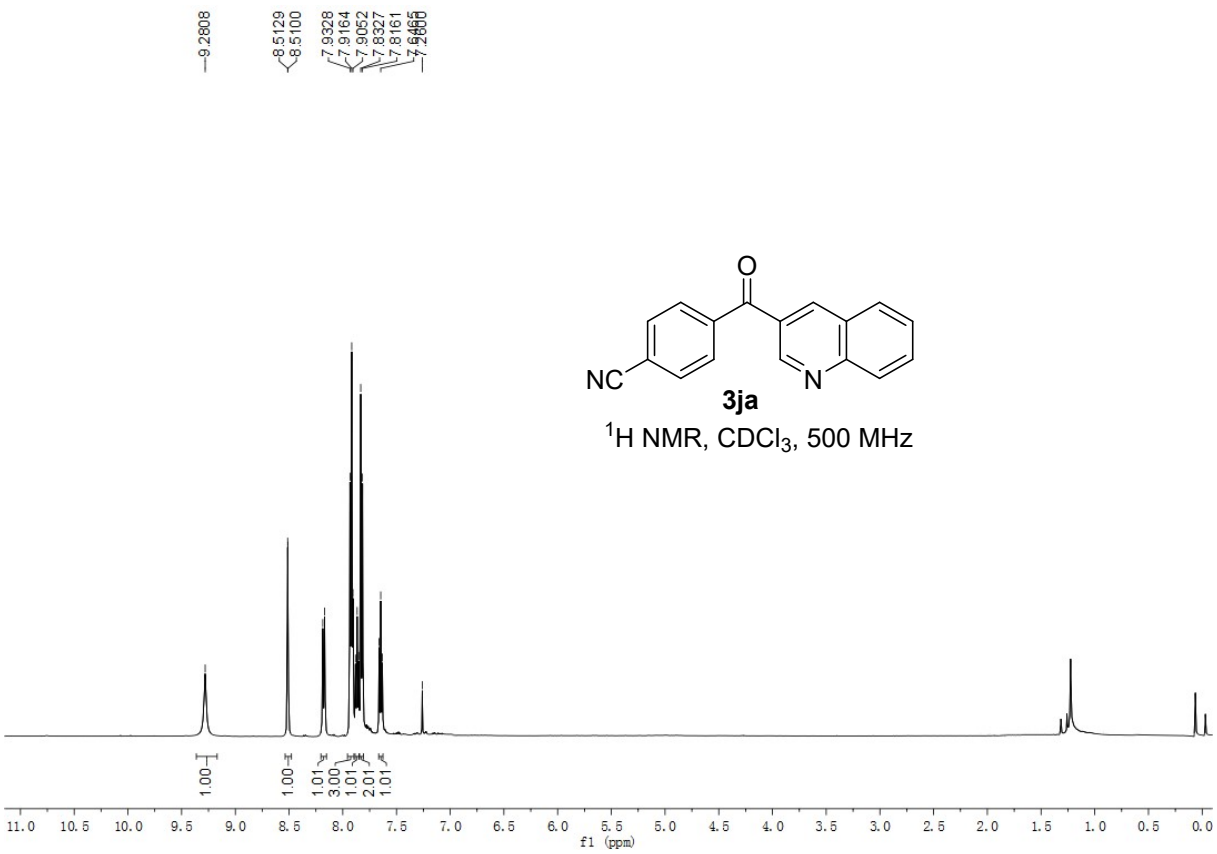
3ia

^{1}H NMR, $CDCl_3$, 500 MHz



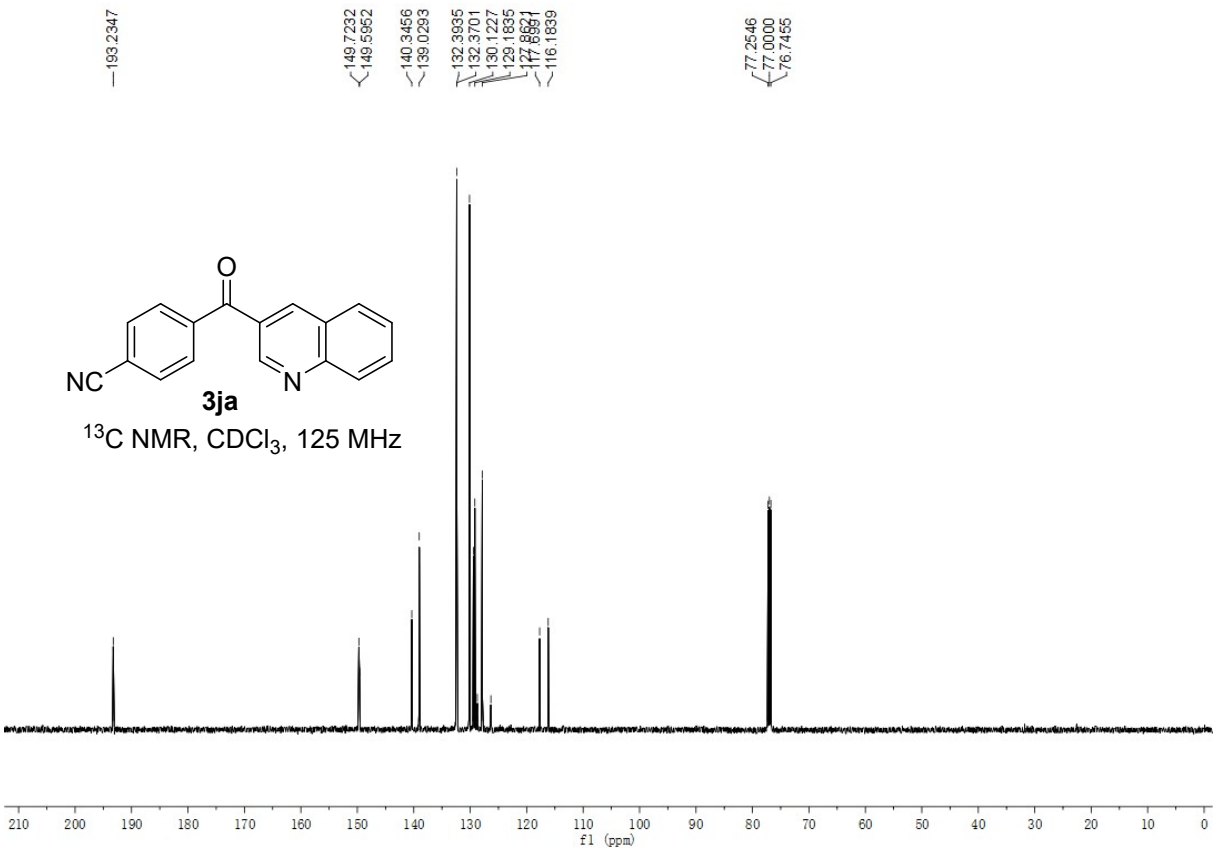
3ia

^{13}C NMR, $CDCl_3$, 125 MHz



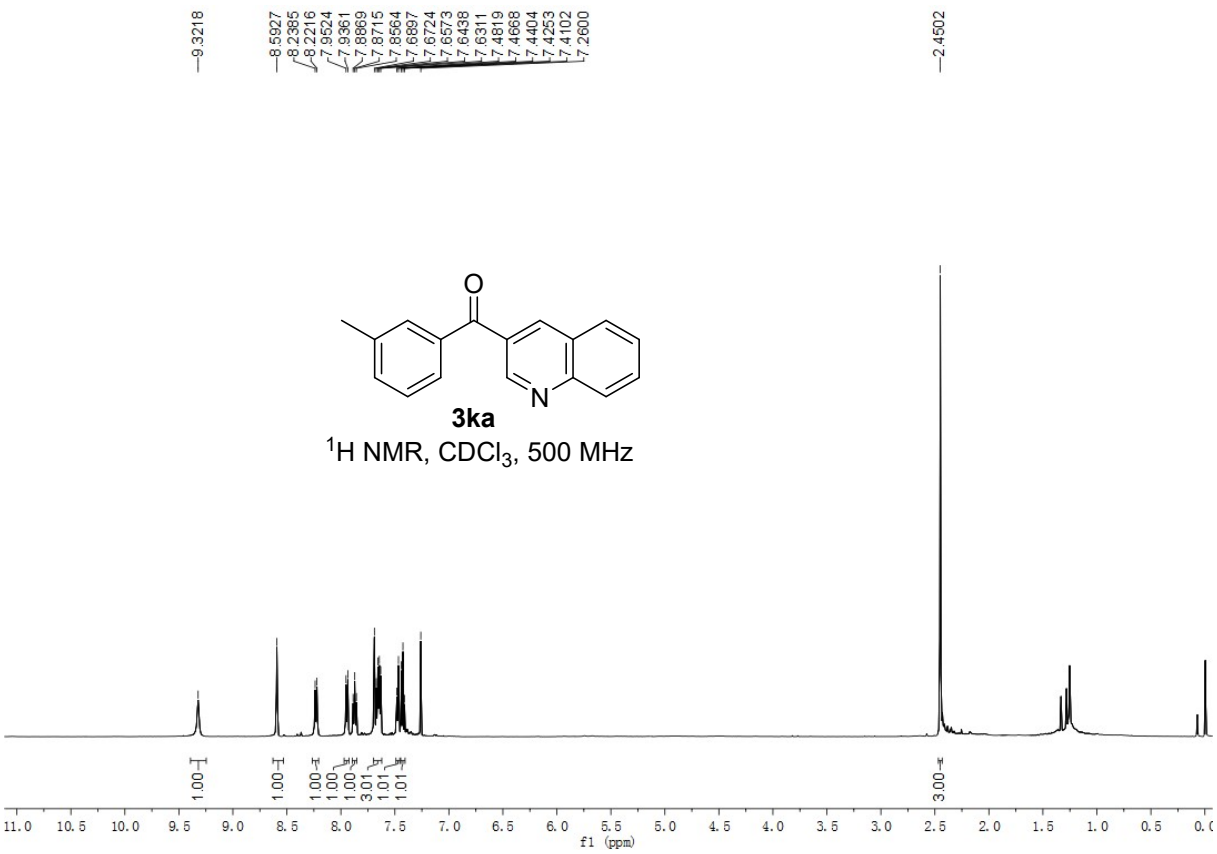
3ja

^{1}H NMR, $CDCl_3$, 500 MHz



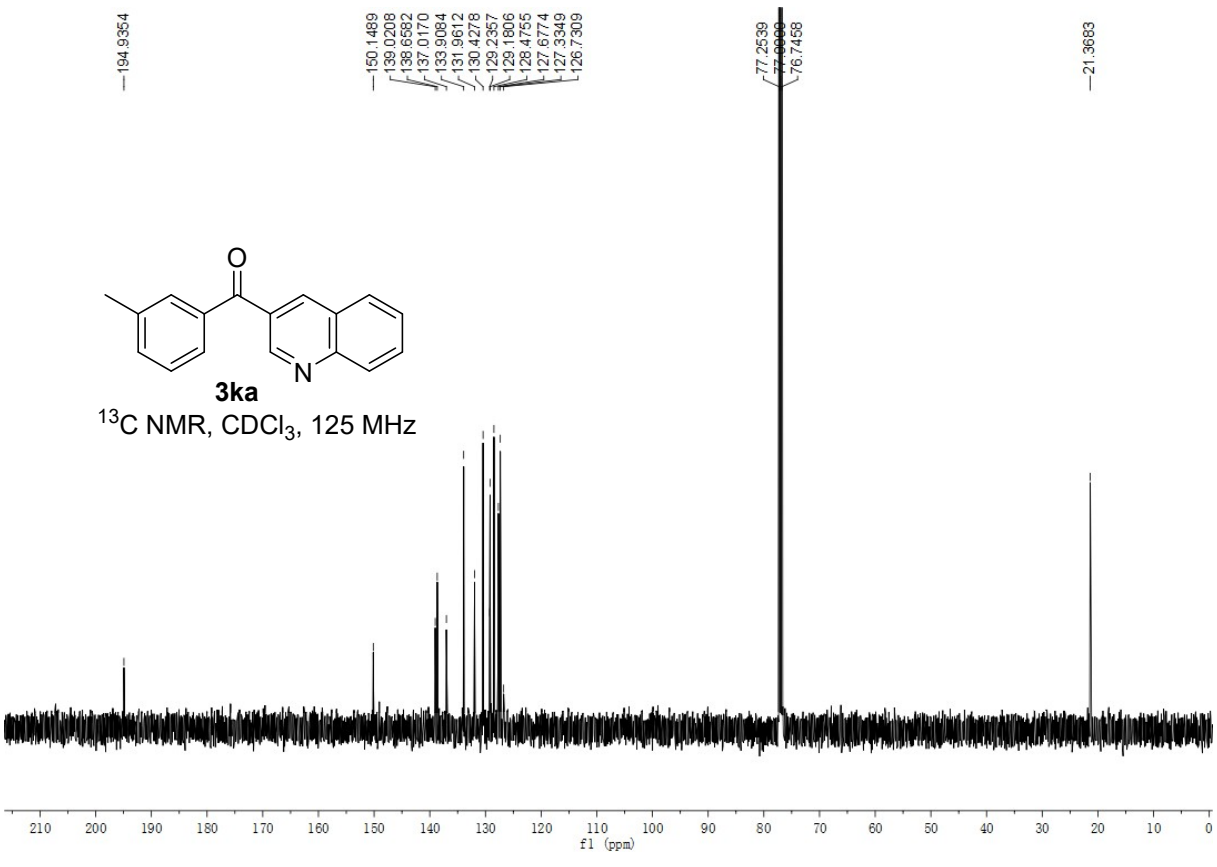
3ja

^{13}C NMR, $CDCl_3$, 125 MHz



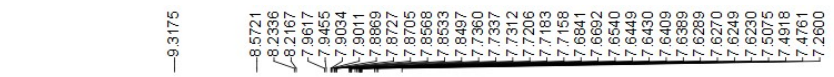
3ka

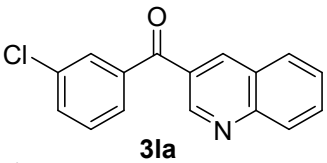
^{1}H NMR, $CDCl_3$, 500 MHz



3ka

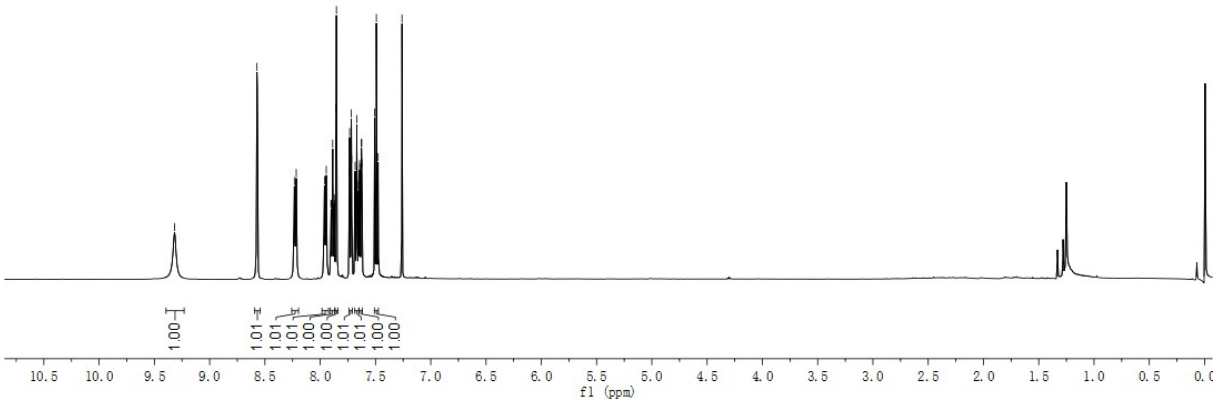
^{13}C NMR, $CDCl_3$, 125 MHz

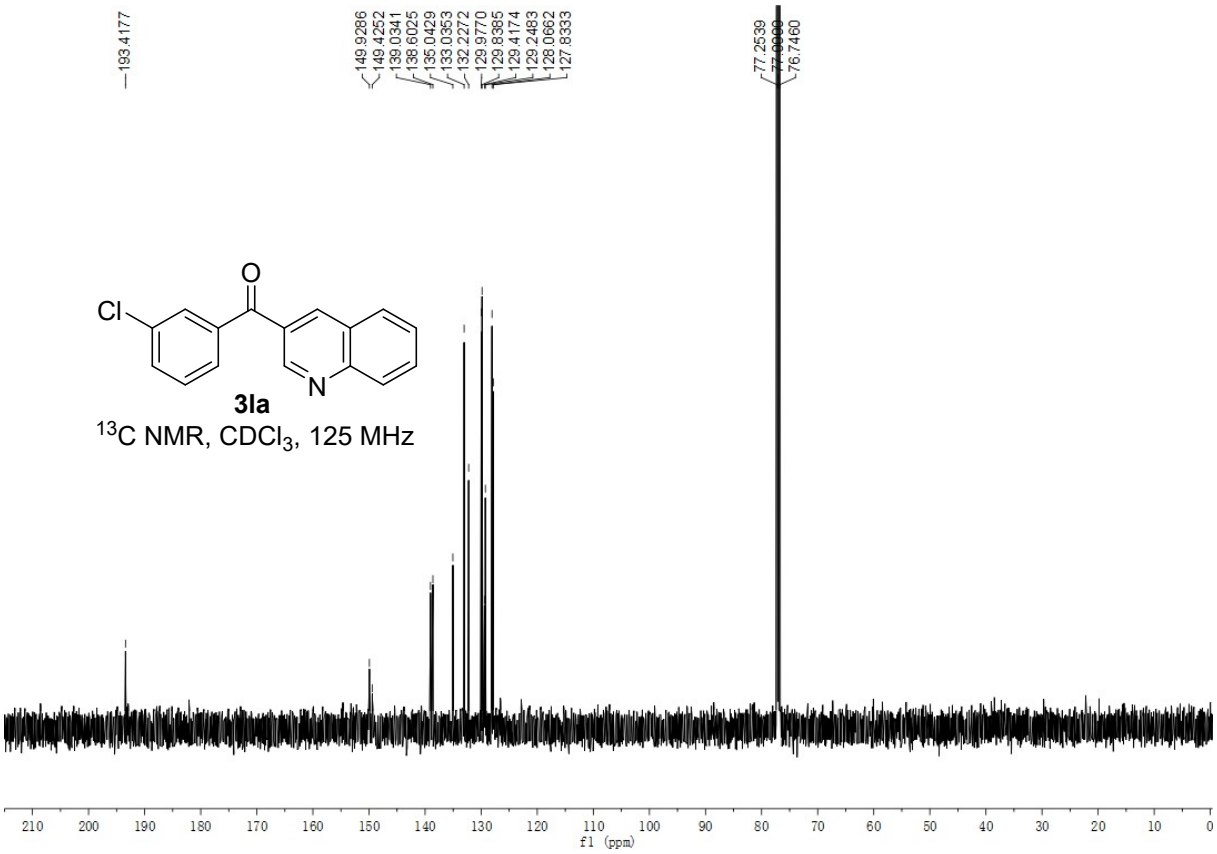




3la

^{1}H NMR, $CDCl_3$, 500 MHz





3la

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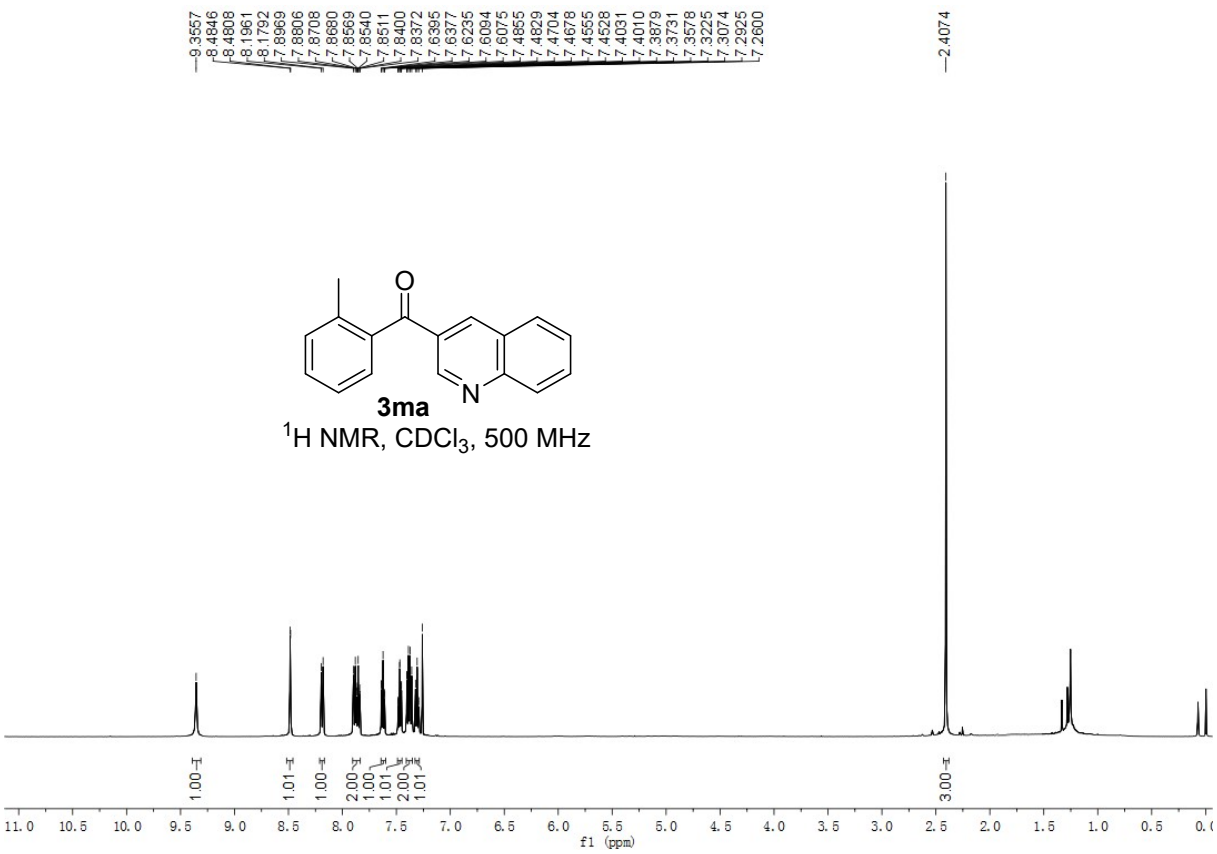
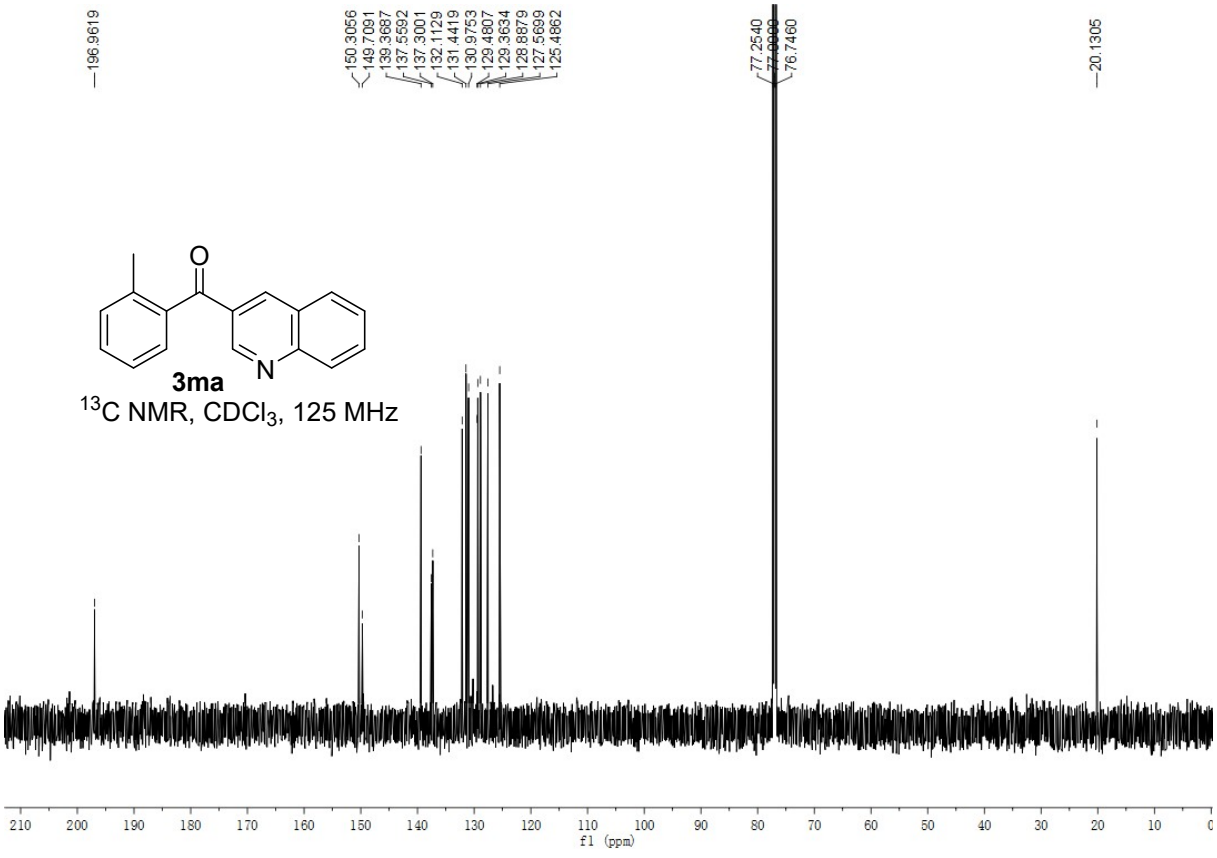


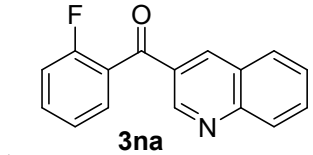
3ma

^{1}H NMR, $CDCl_3$, 500 MHz



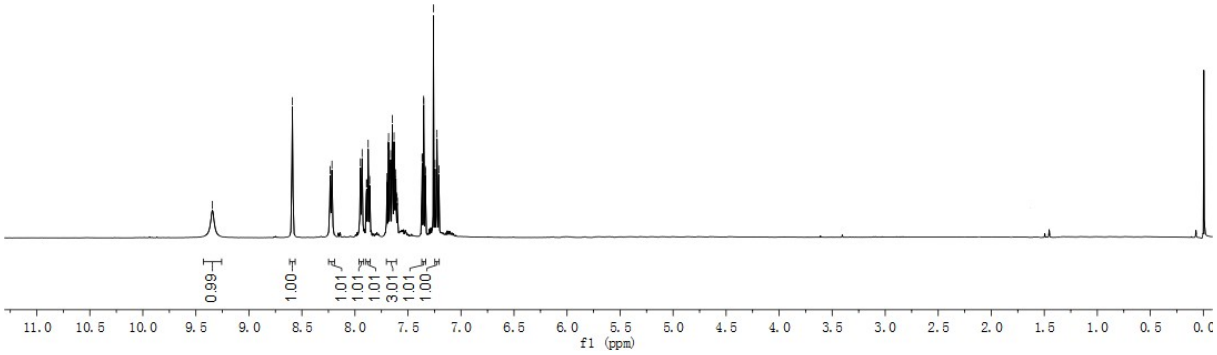
3ma

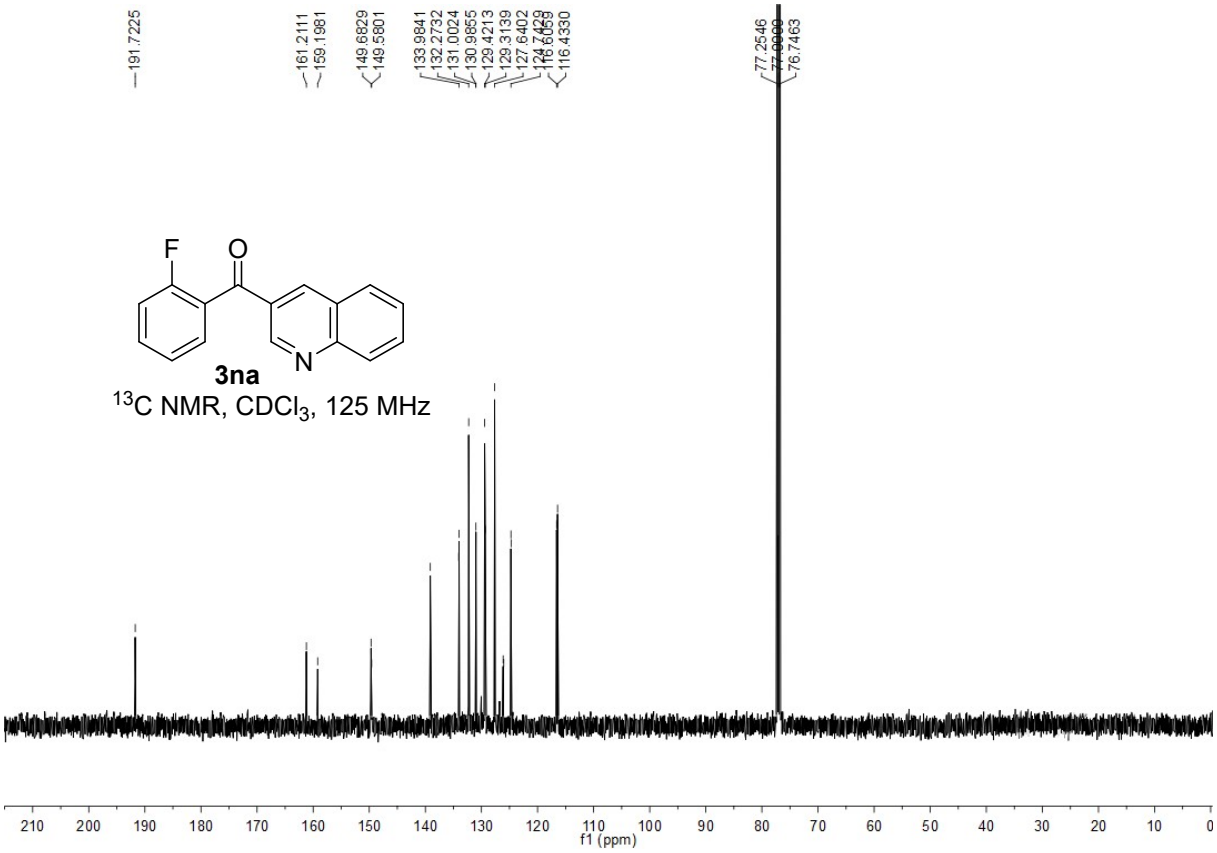
^{13}C NMR, $CDCl_3$, 125 MHz



3na

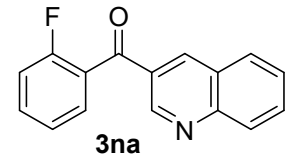
^{1}H NMR, $CDCl_3$, 500 MHz





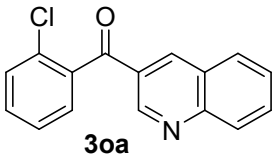
3na

^{13}C NMR, $CDCl_3$, 125 MHz



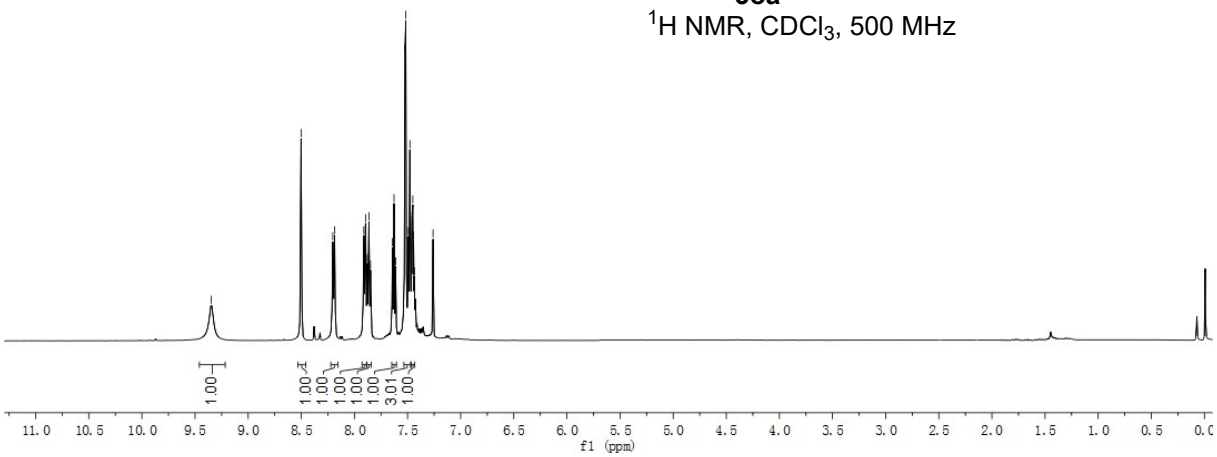
3na

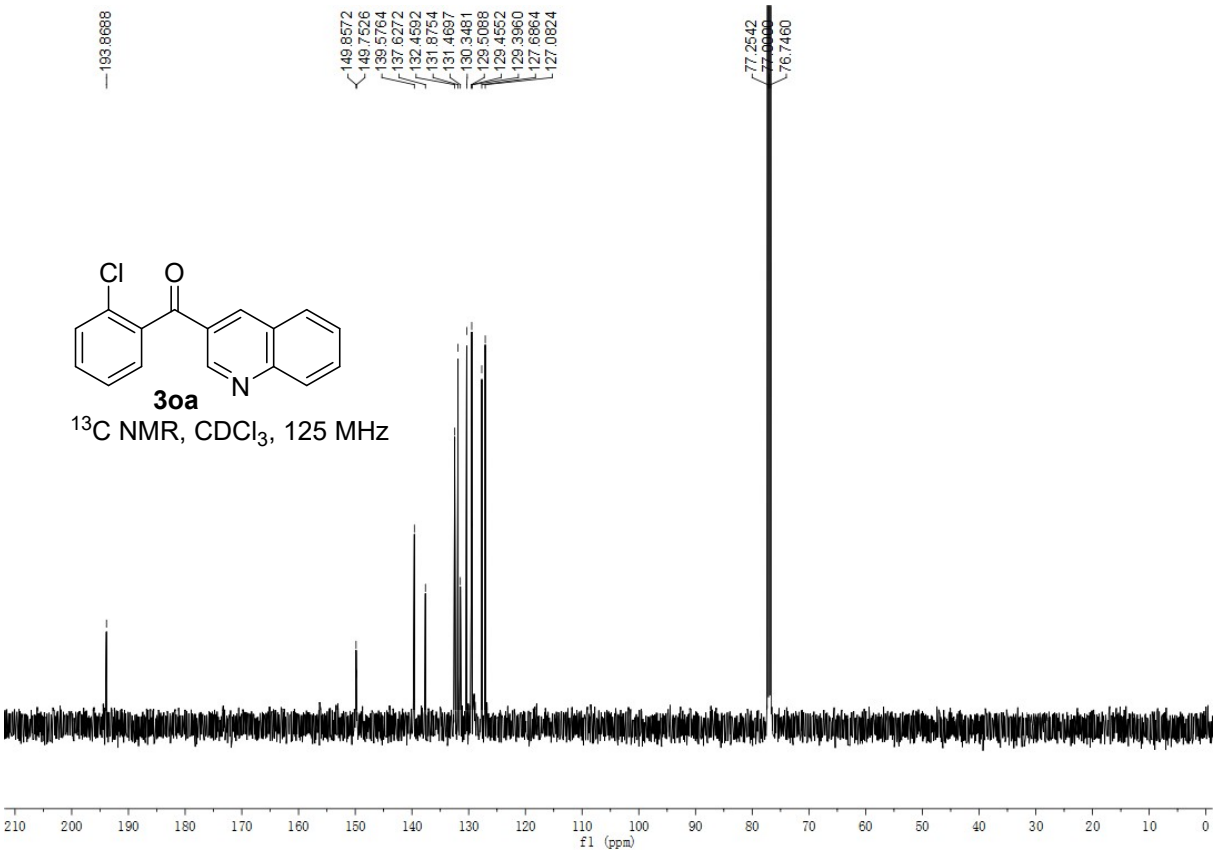
^{19}F NMR, $CDCl_3$, 471 MHz



3oa

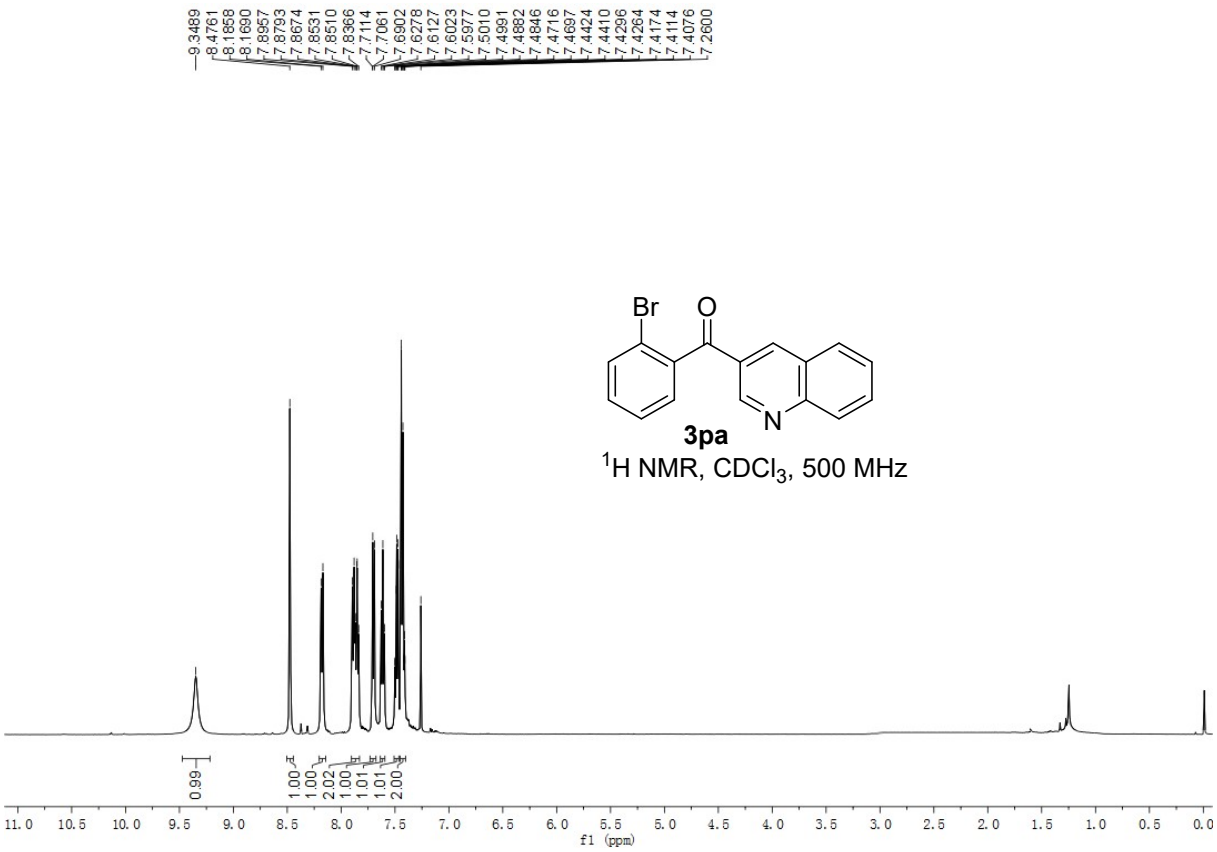
^{1}H NMR, $CDCl_3$, 500 MHz





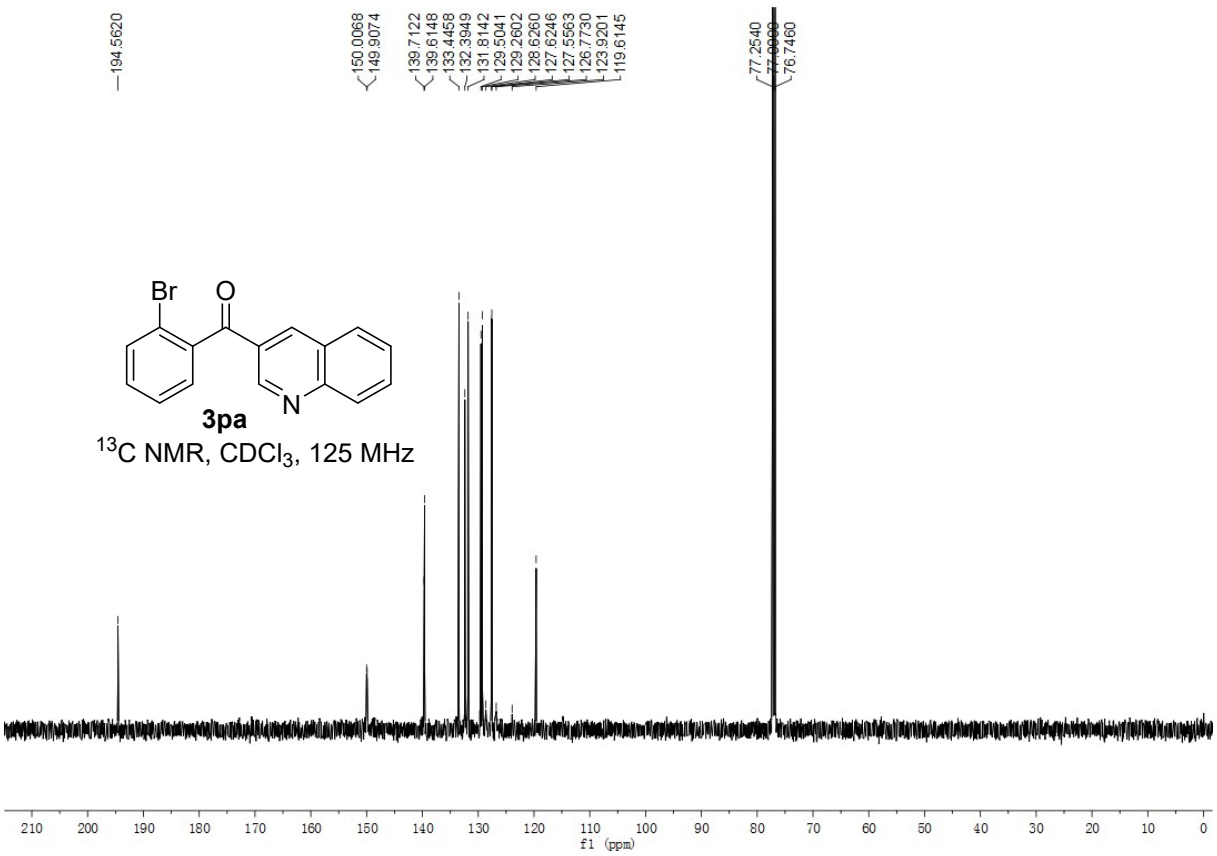
3oa

^{13}C NMR, $CDCl_3$, 125 MHz



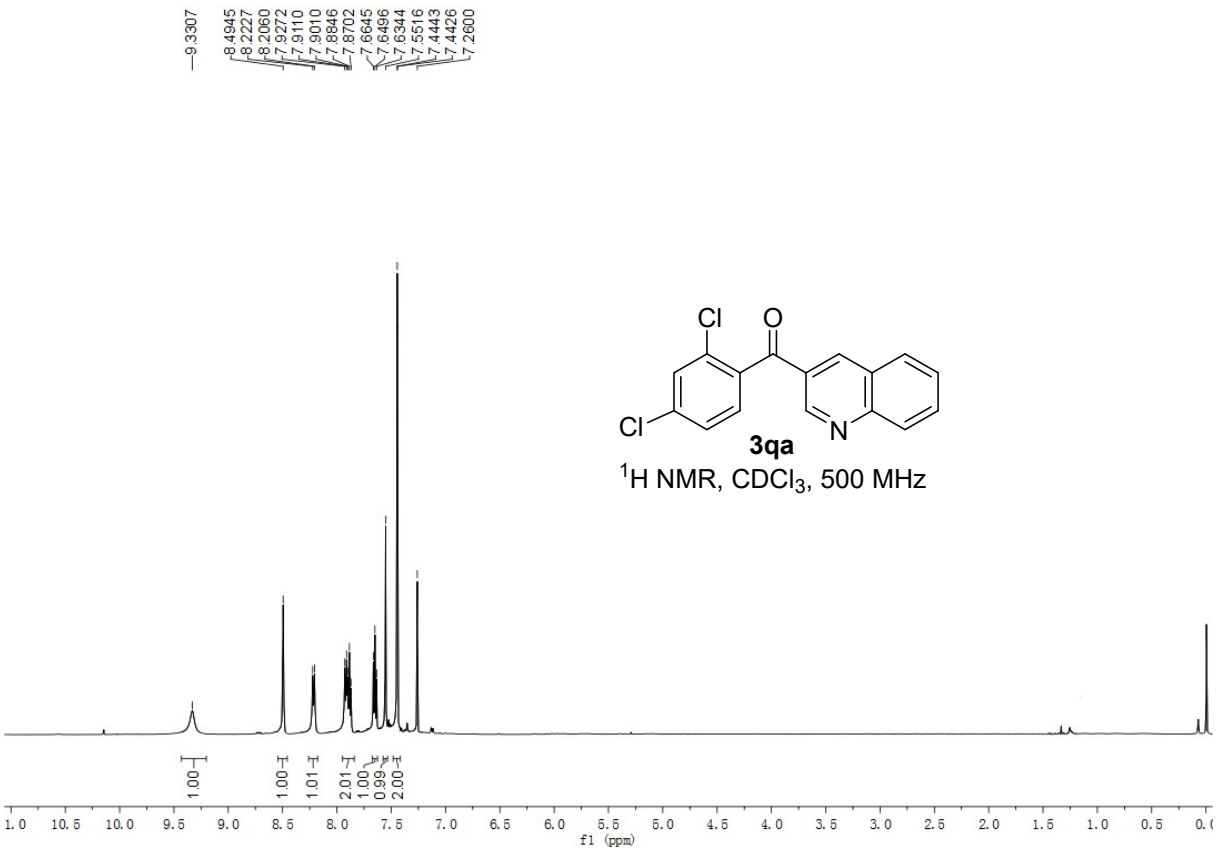
3pa

^{1}H NMR, $CDCl_3$, 500 MHz



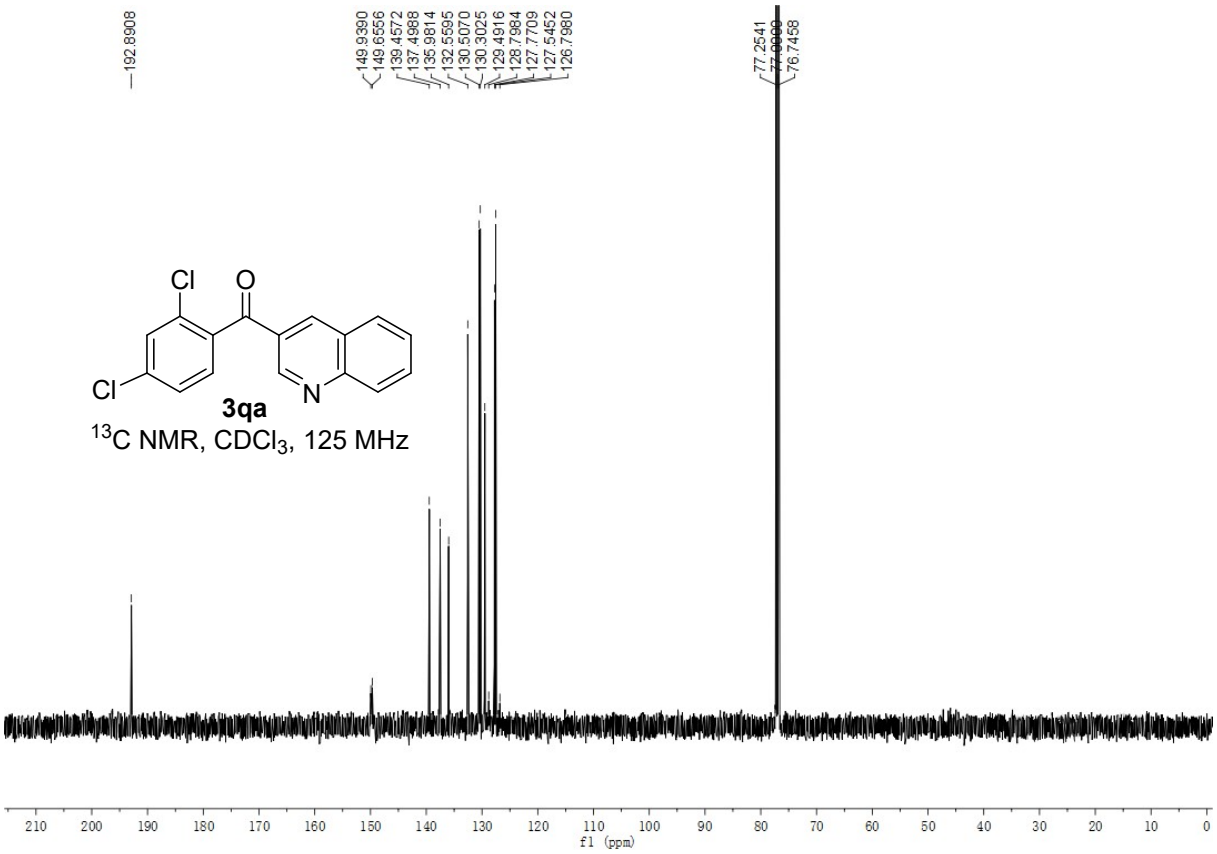
3pa

^{13}C NMR, $CDCl_3$, 125 MHz



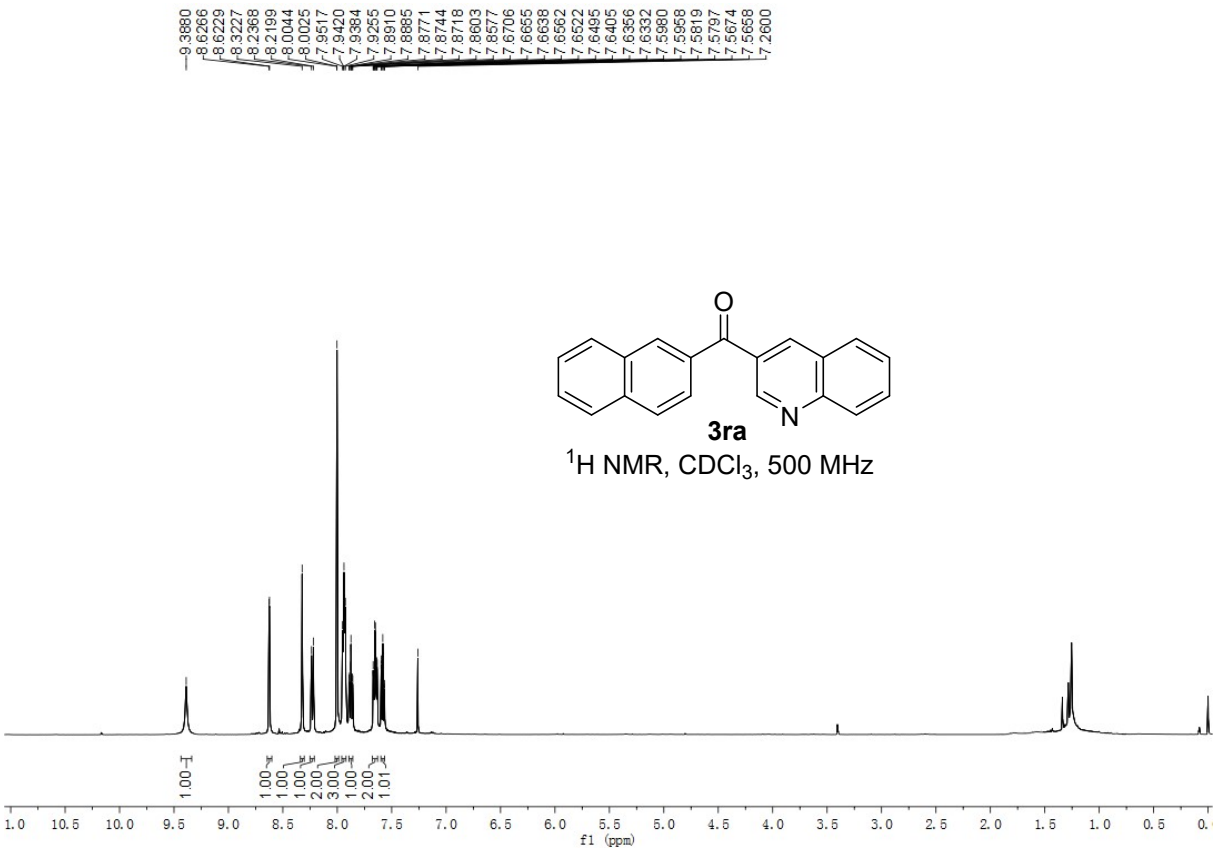
3qa

^{1}H NMR, $CDCl_3$, 500 MHz



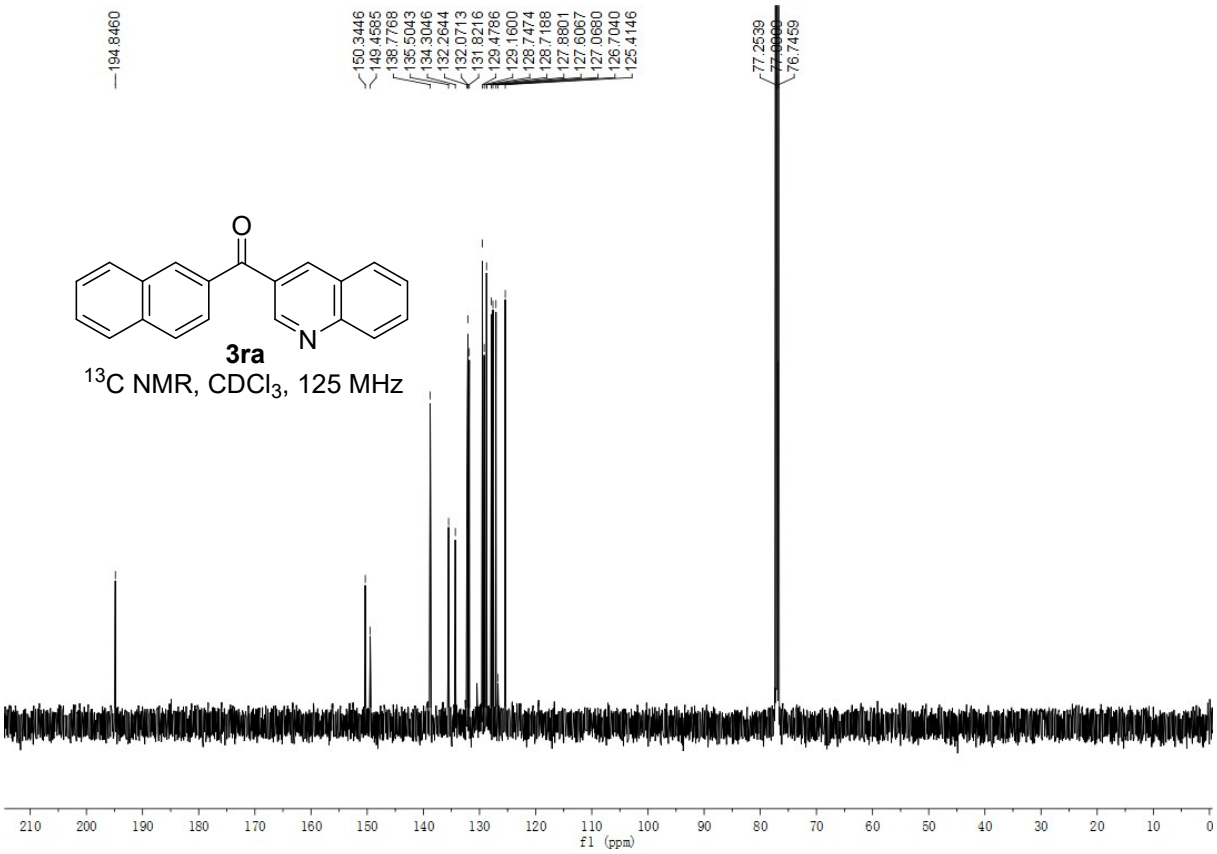
3qa

^{13}C NMR, $CDCl_3$, 125 MHz



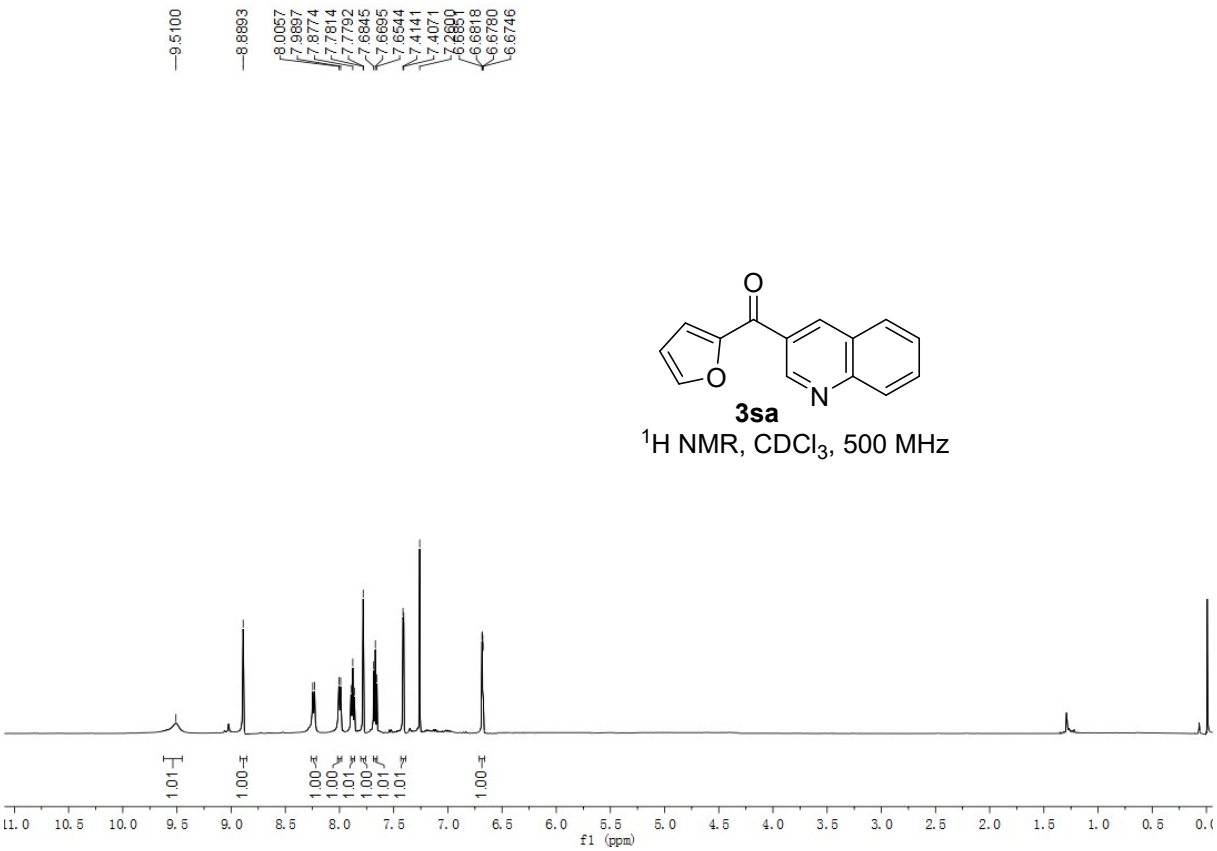
3ra

^{1}H NMR, $CDCl_3$, 500 MHz



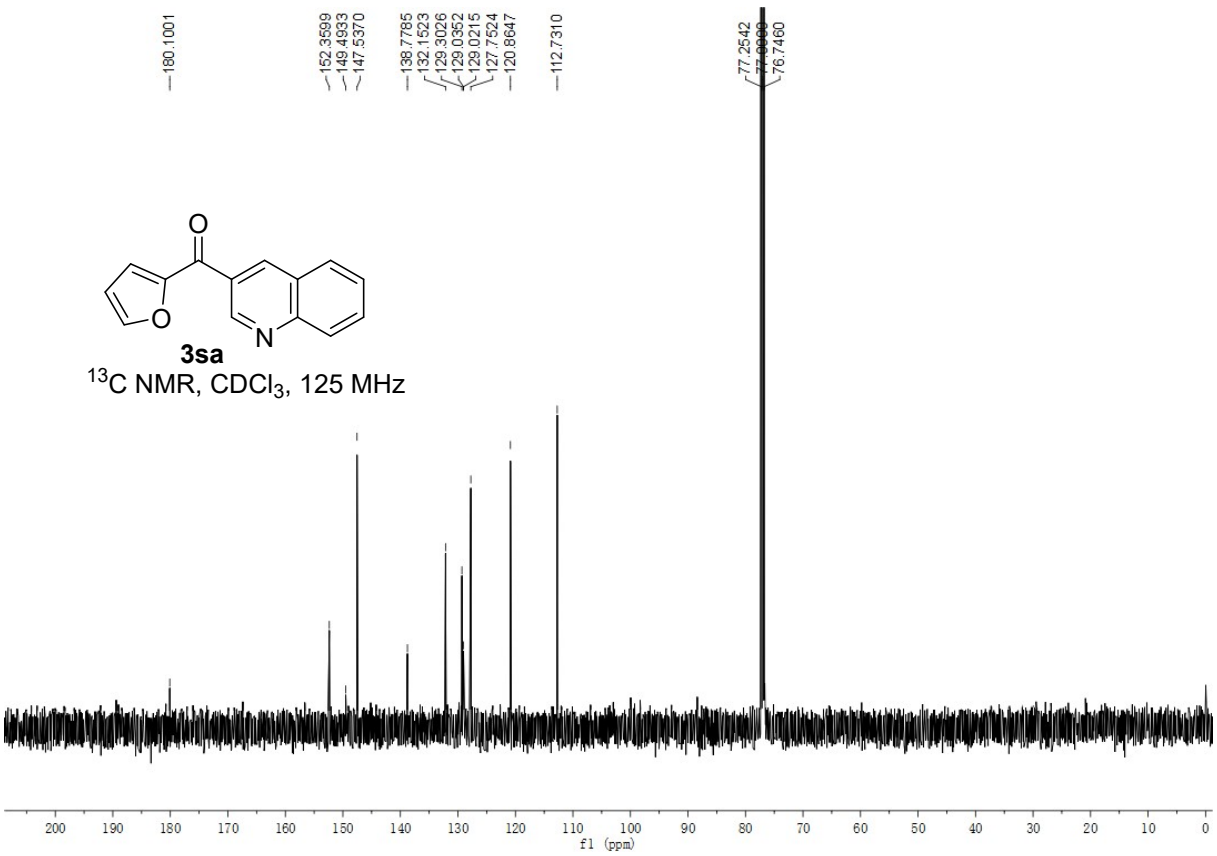
3ra

^{13}C NMR, $CDCl_3$, 125 MHz



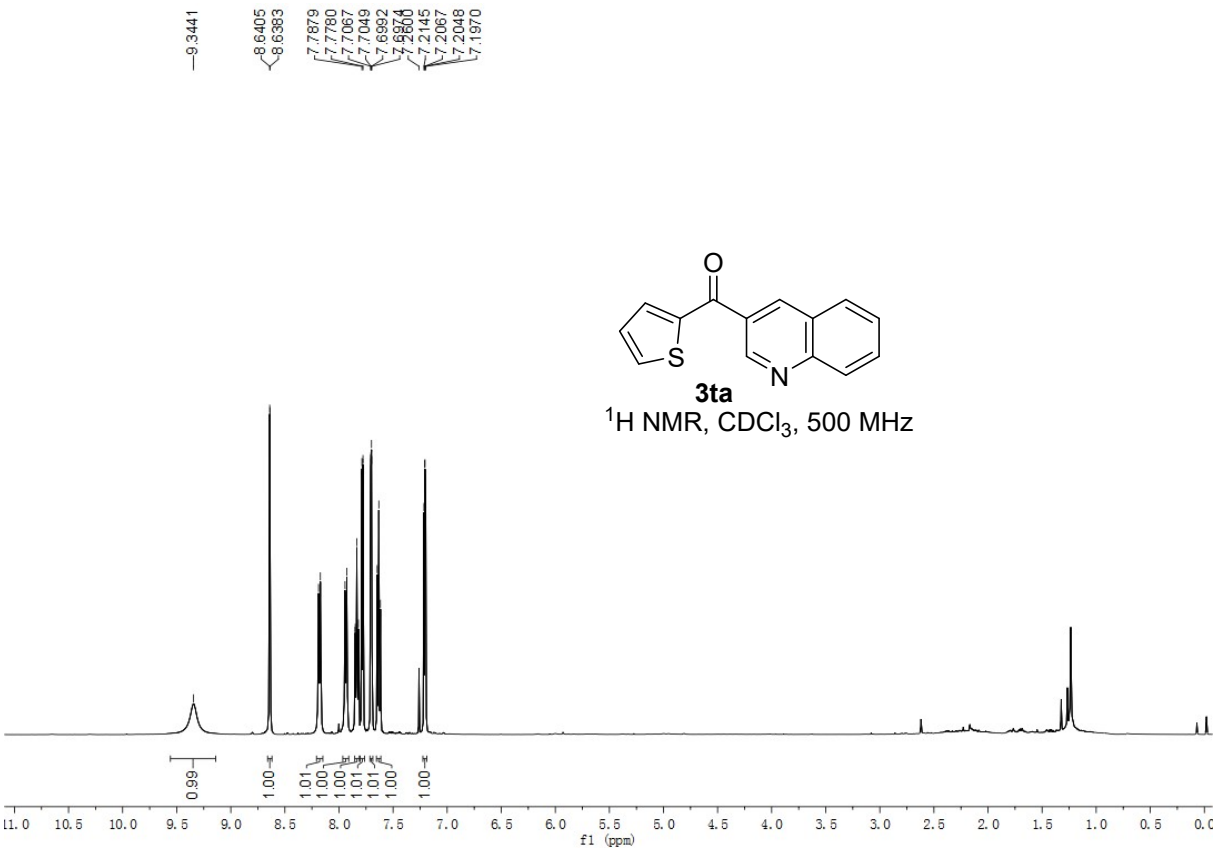
3sa

^{1}H NMR, $CDCl_3$, 500 MHz



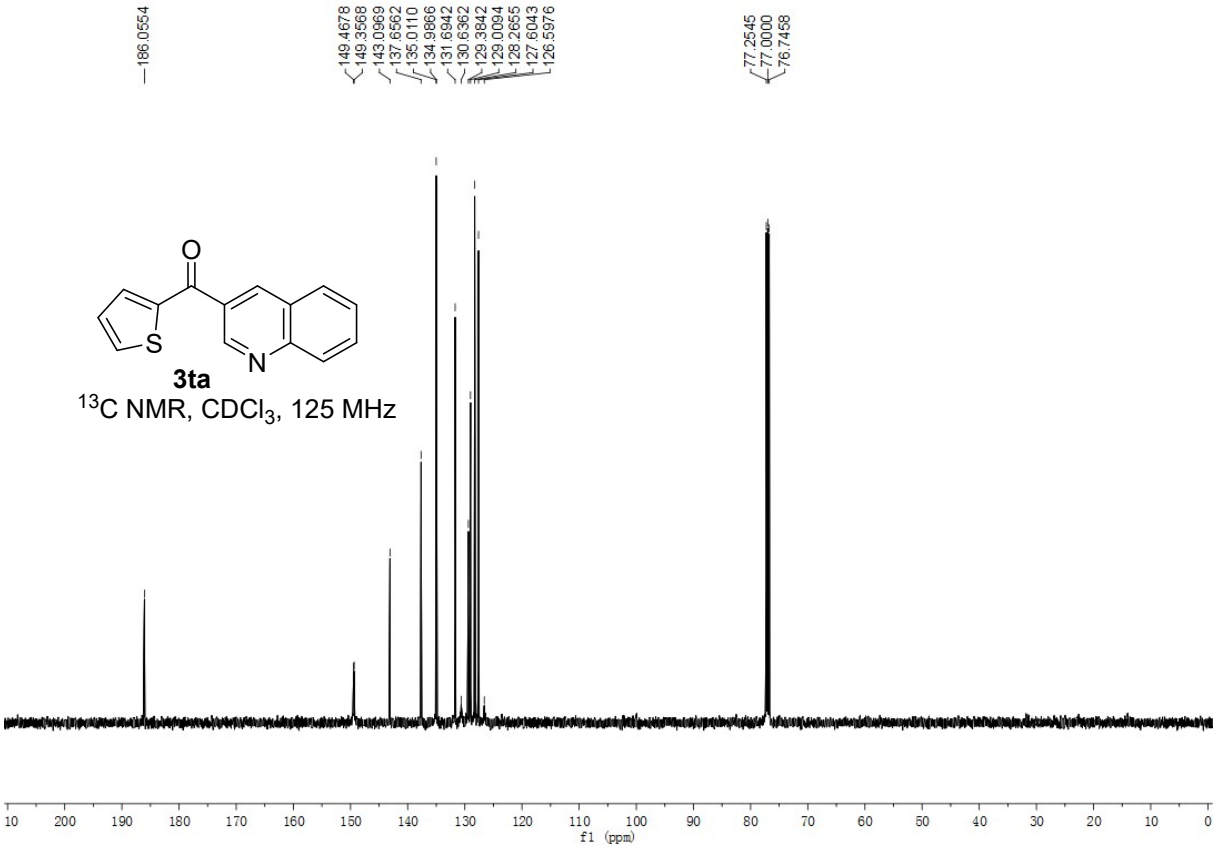
3sa

^{13}C NMR, $CDCl_3$, 125 MHz



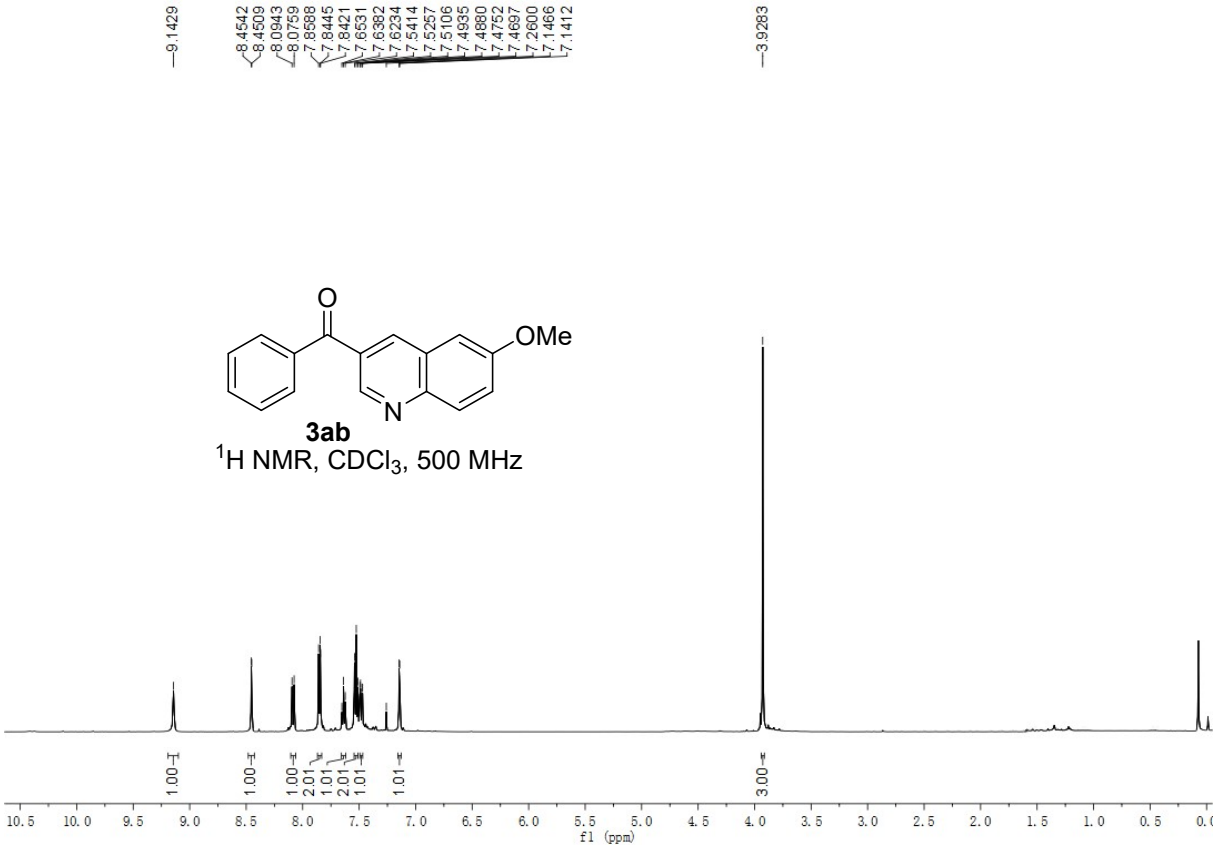
3ta

^{1}H NMR, $CDCl_3$, 500 MHz



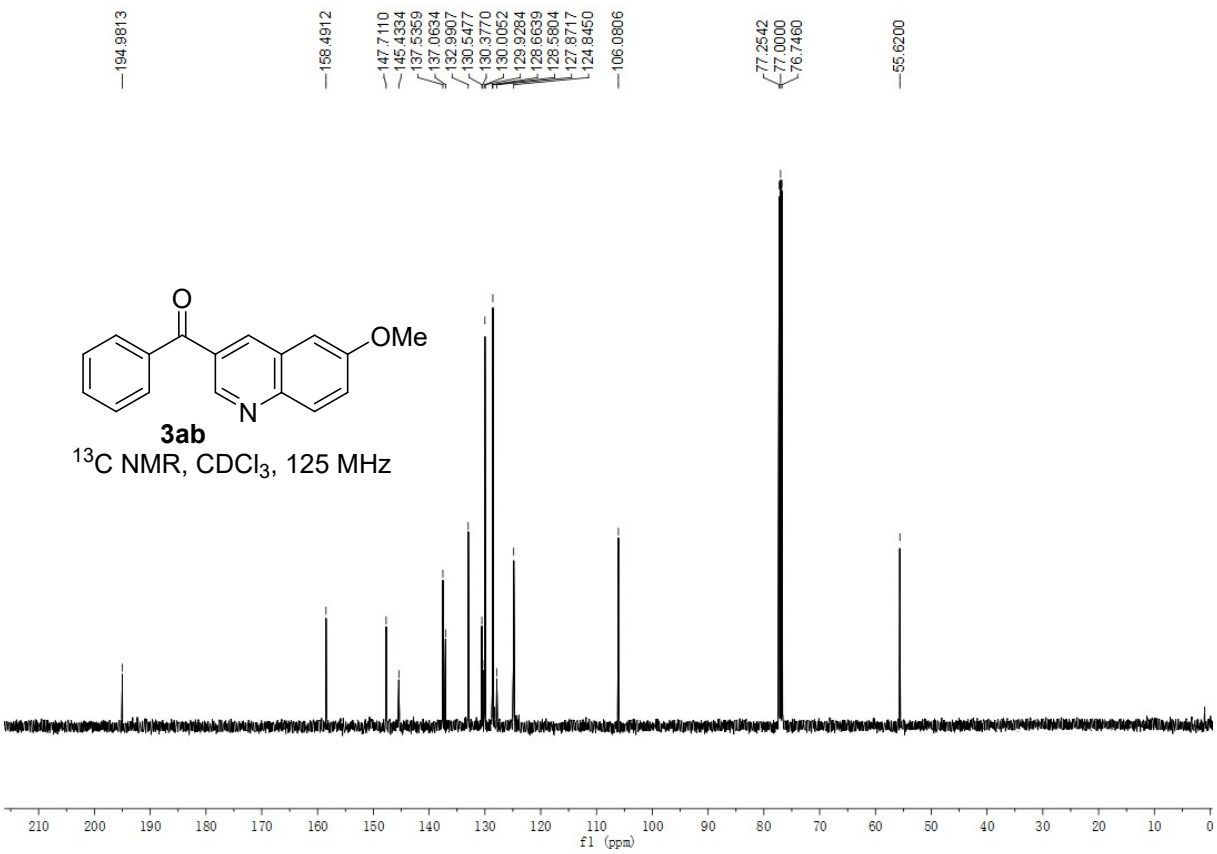
3ta

^{13}C NMR, $CDCl_3$, 125 MHz



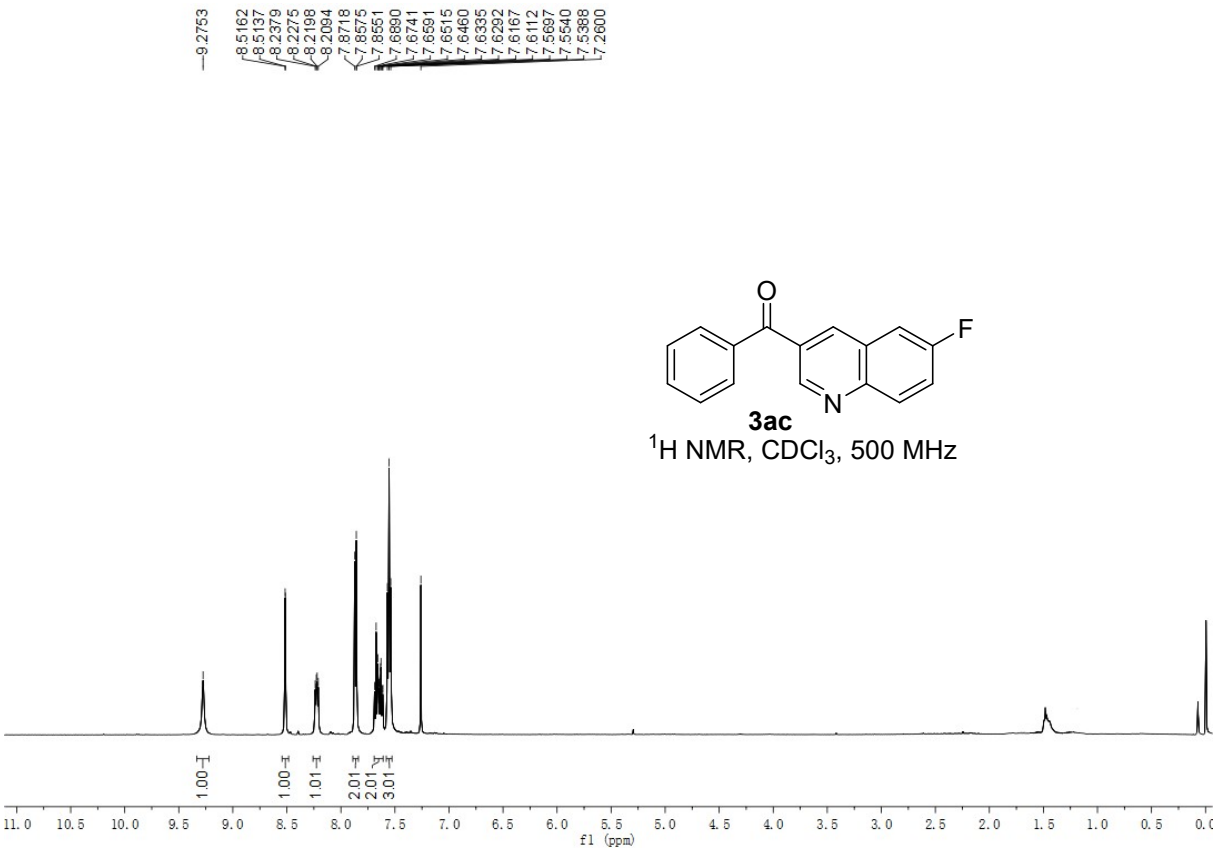
3ab

^{1}H NMR, $CDCl_3$, 500 MHz



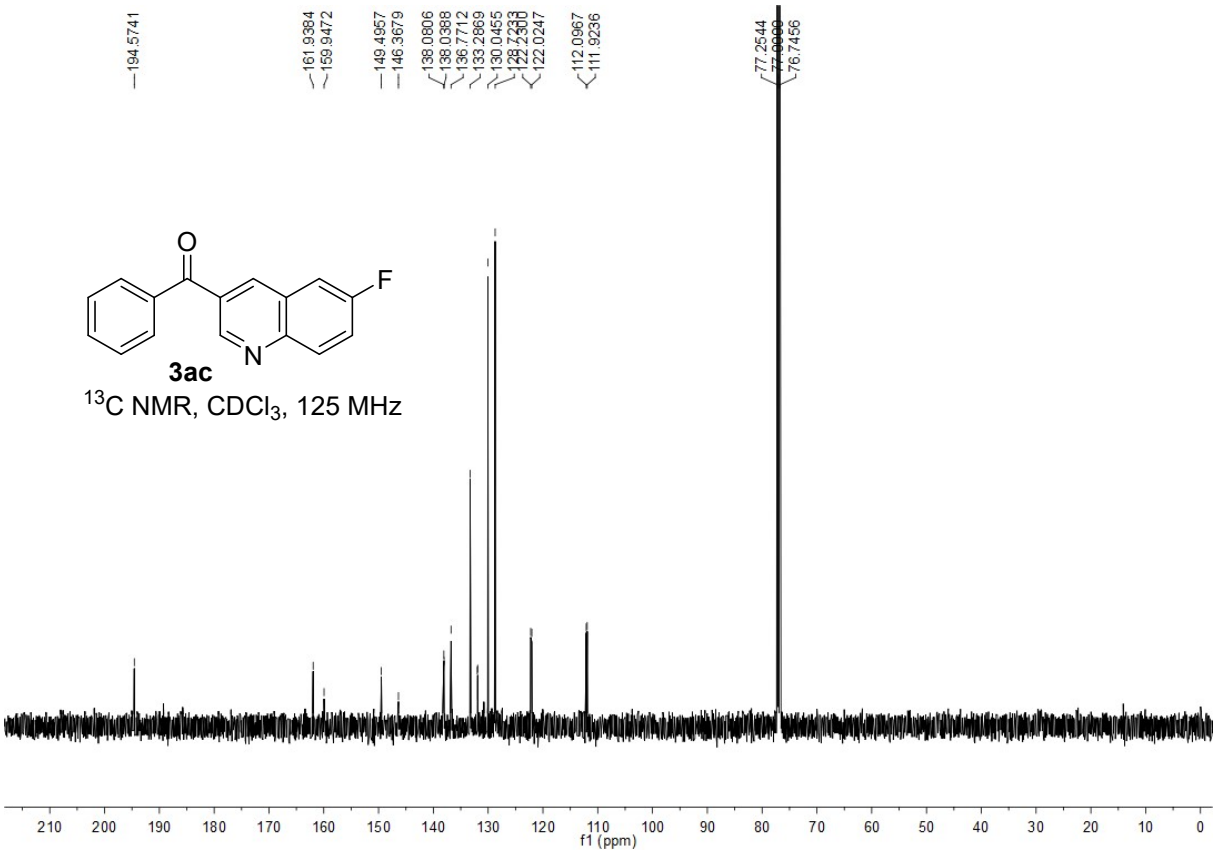
3ab

^{13}C NMR, $CDCl_3$, 125 MHz



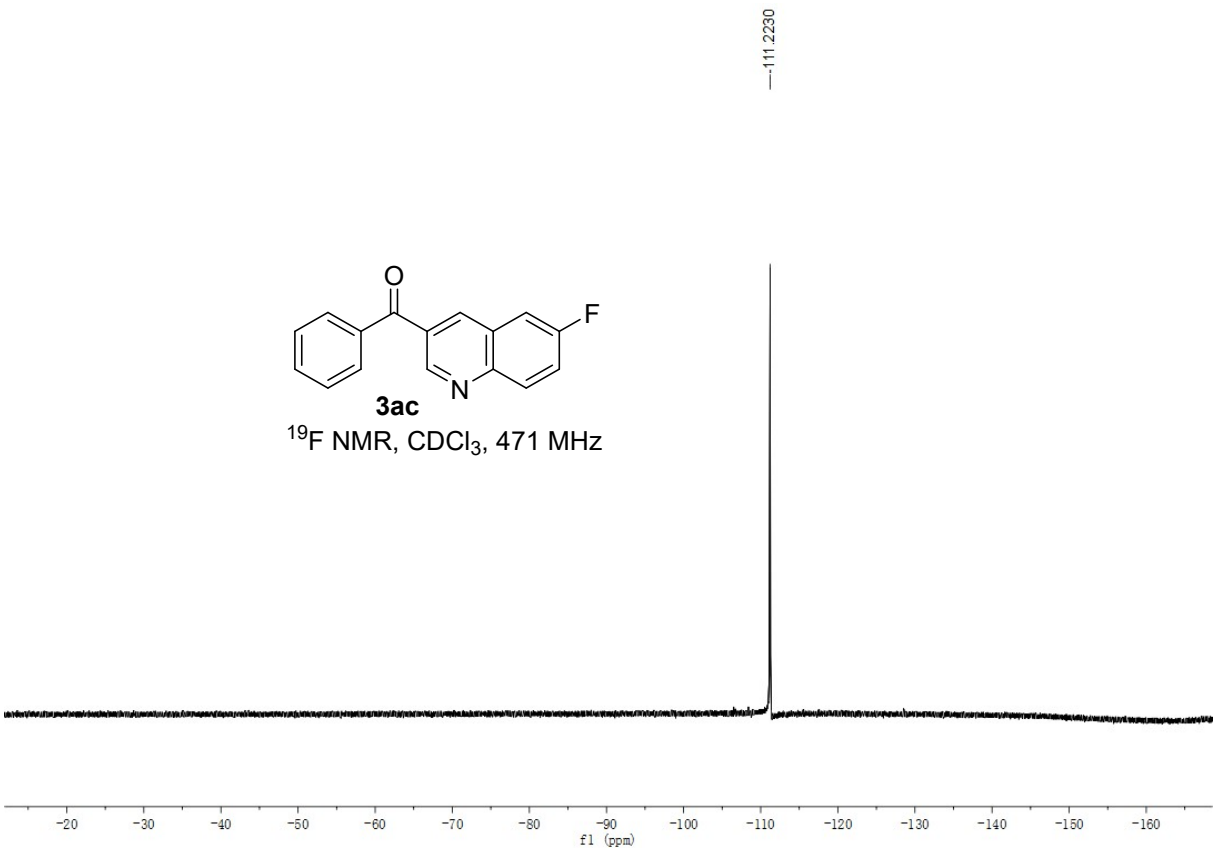
3ac

^{1}H NMR, $CDCl_3$, 500 MHz



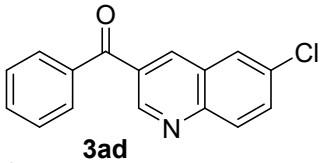
3ac

^{13}C NMR, $CDCl_3$, 125 MHz



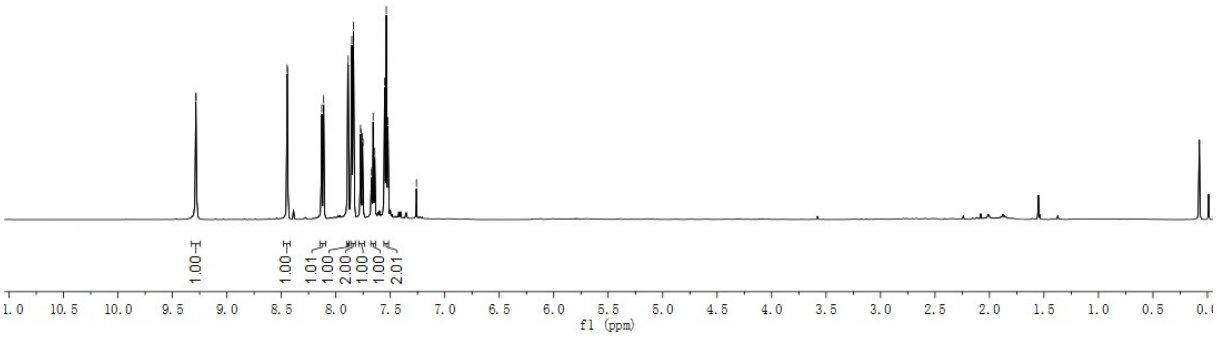
3ac

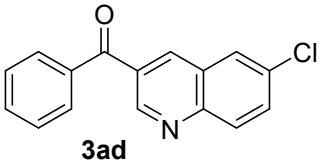
^{19}F NMR, $CDCl_3$, 471 MHz



3ad

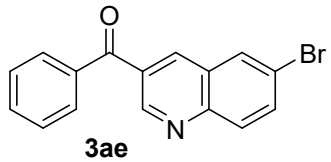
^{1}H NMR, $CDCl_3$, 500 MHz





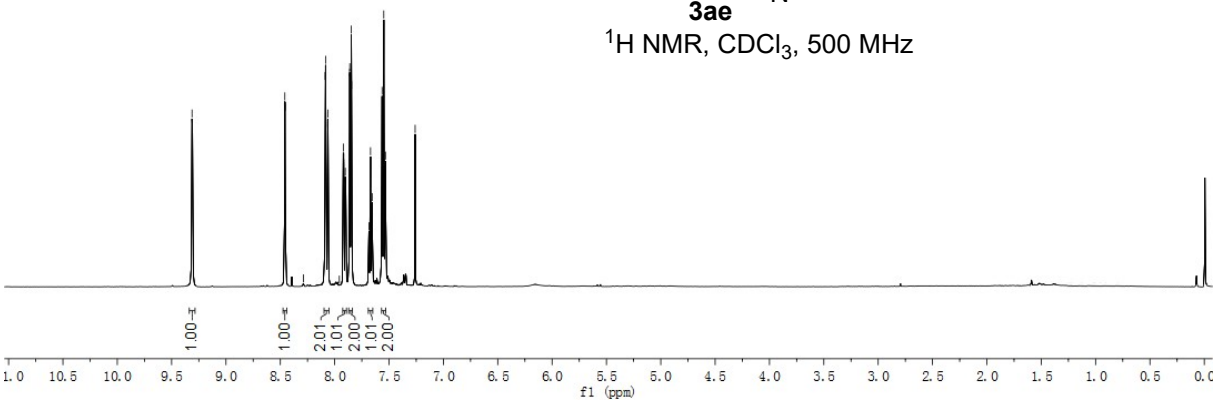
3ad

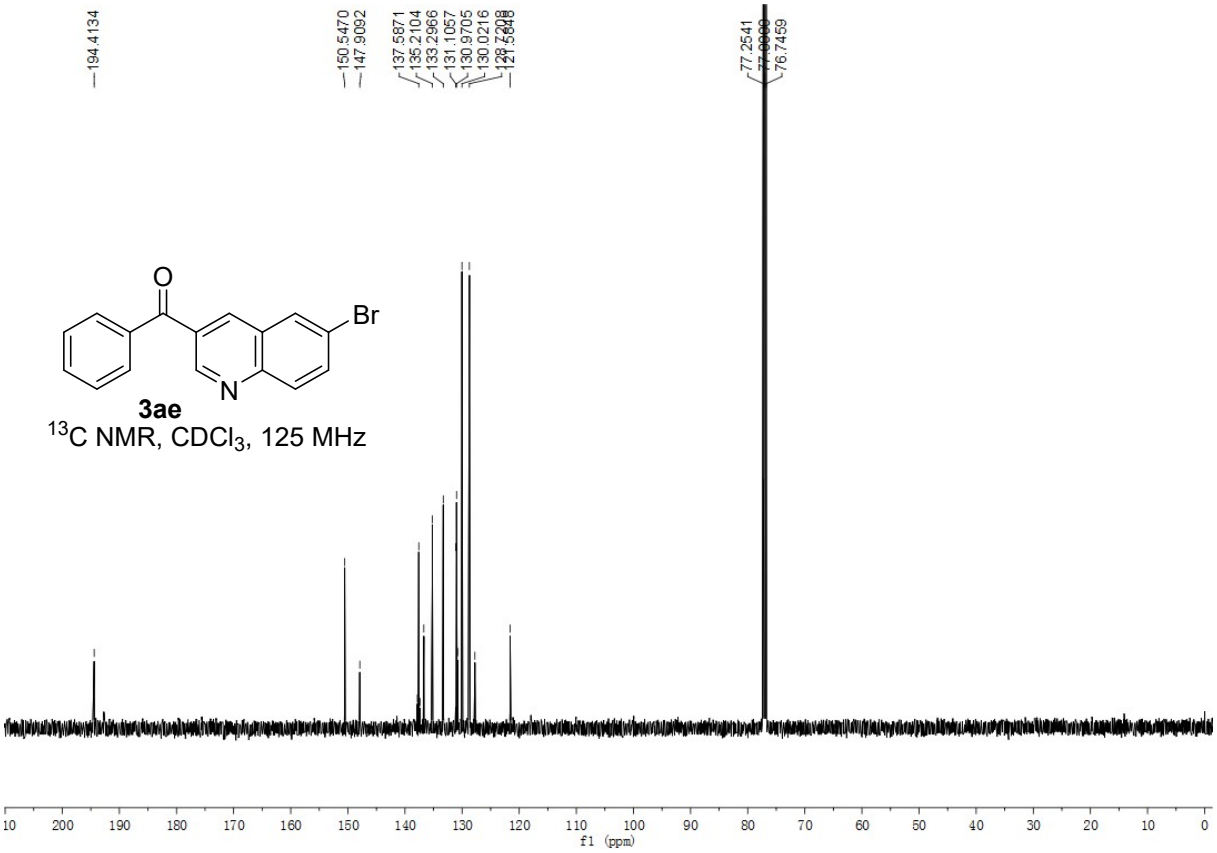
^{13}C NMR, $CDCl_3$, 125 MHz



3ae

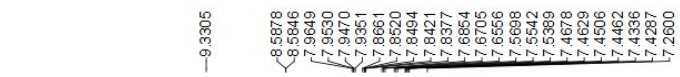
^{1}H NMR, $CDCl_3$, 500 MHz

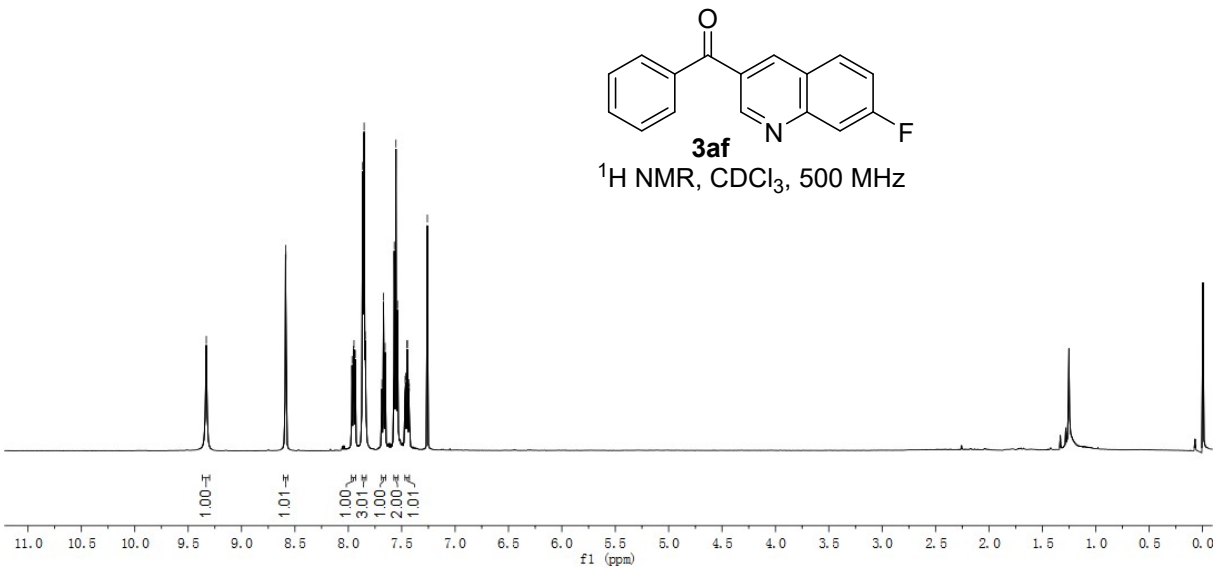




3ae

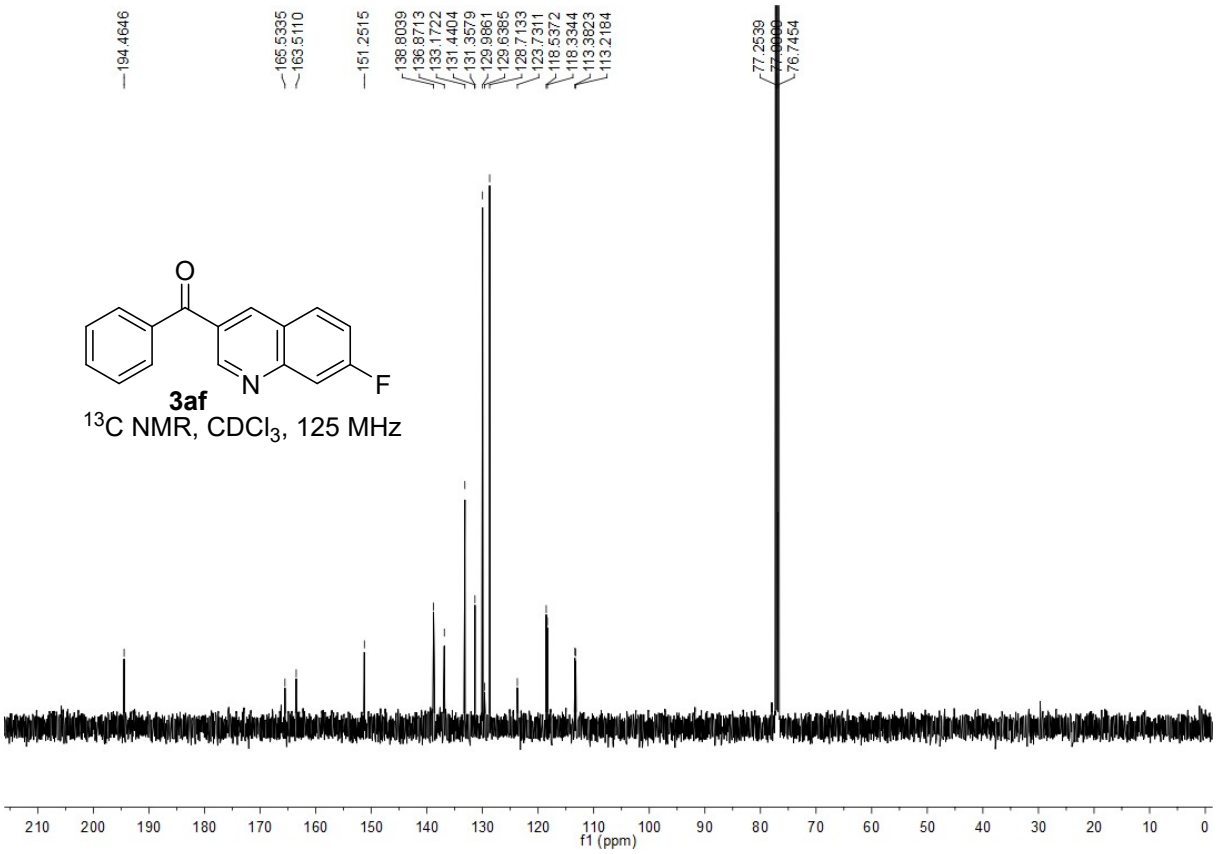
^{13}C NMR, $CDCl_3$, 125 MHz





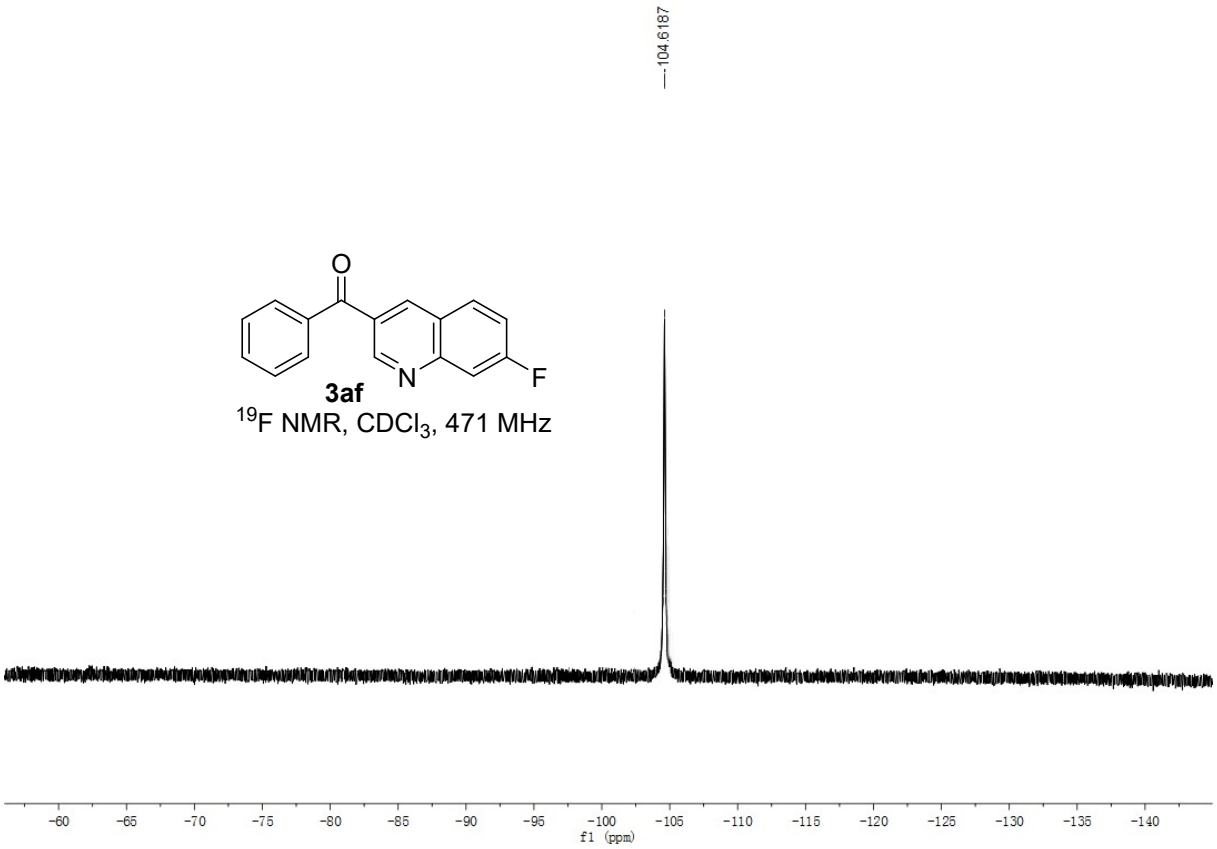
3af

^{1}H NMR, $CDCl_3$, 500 MHz



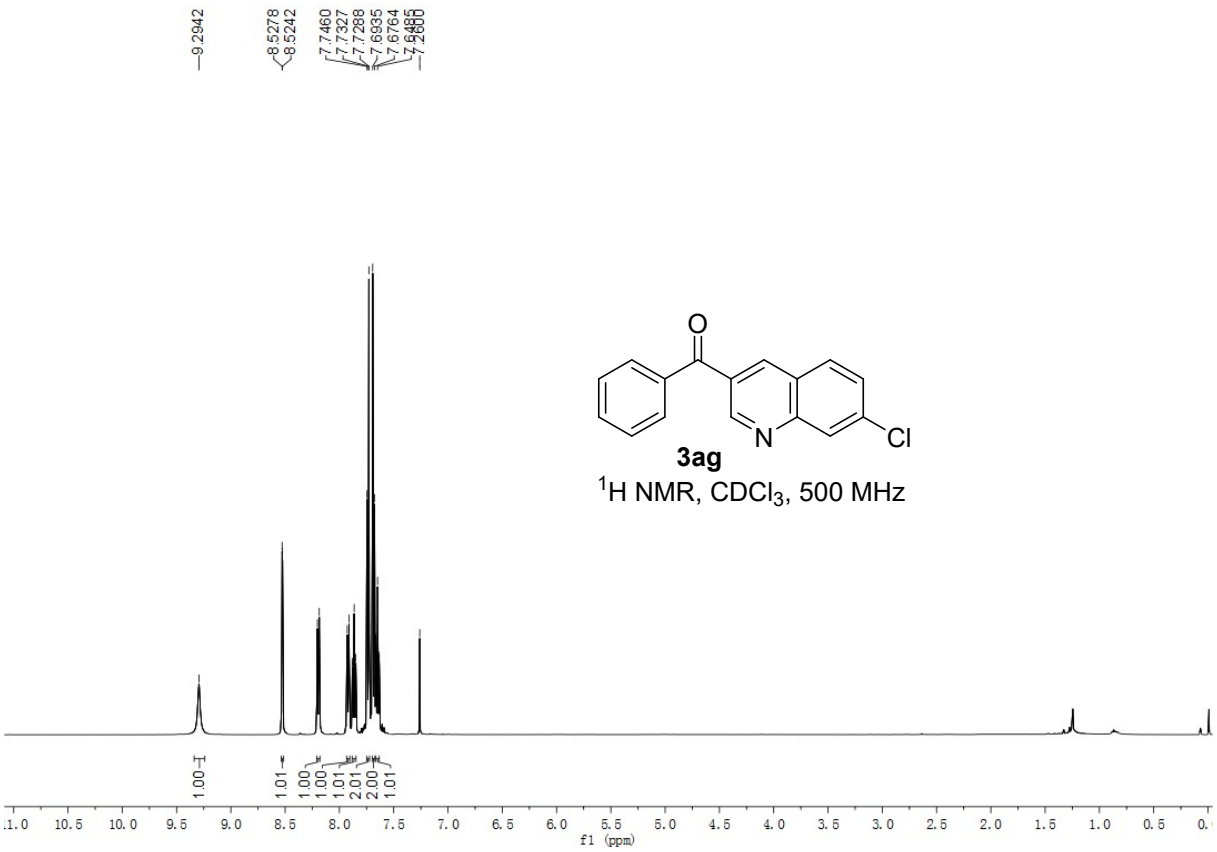
3af

^{13}C NMR, $CDCl_3$, 125 MHz



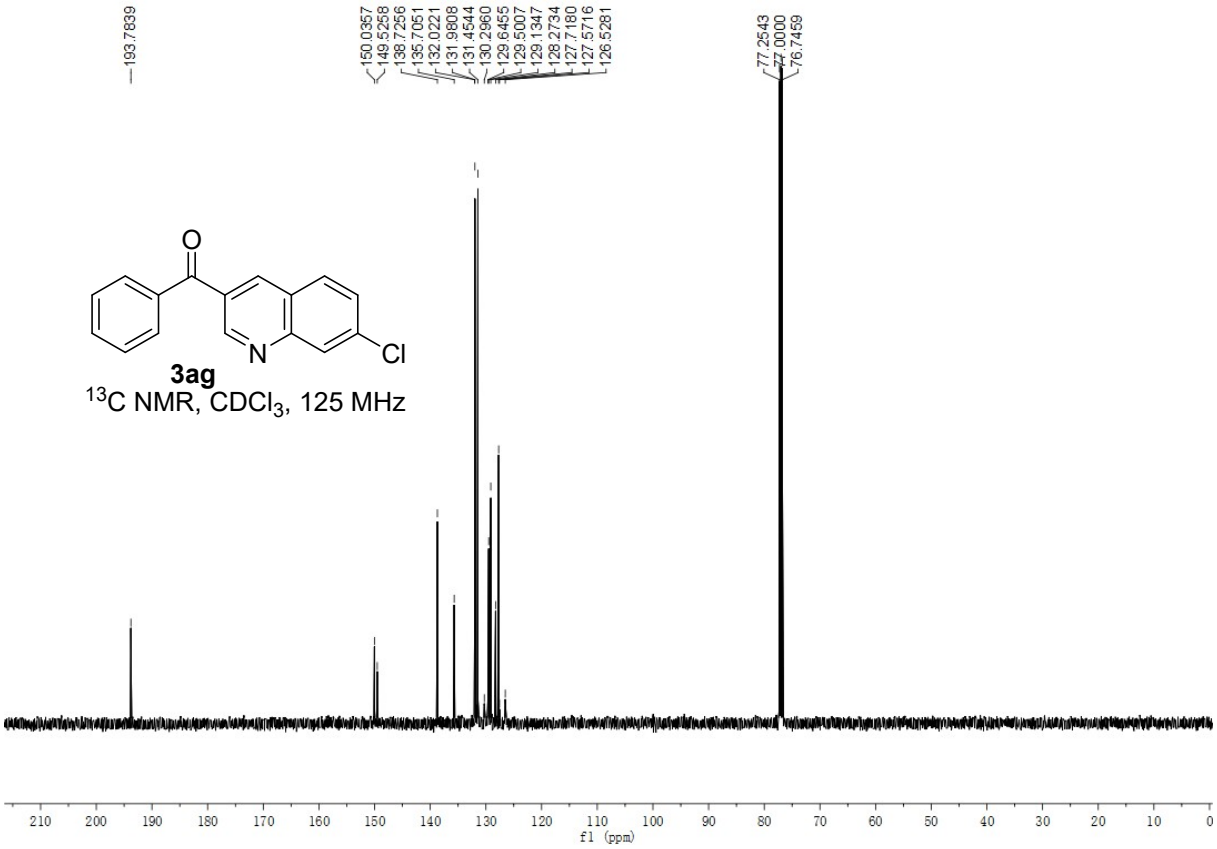
3af

^{19}F NMR, $CDCl_3$, 471 MHz



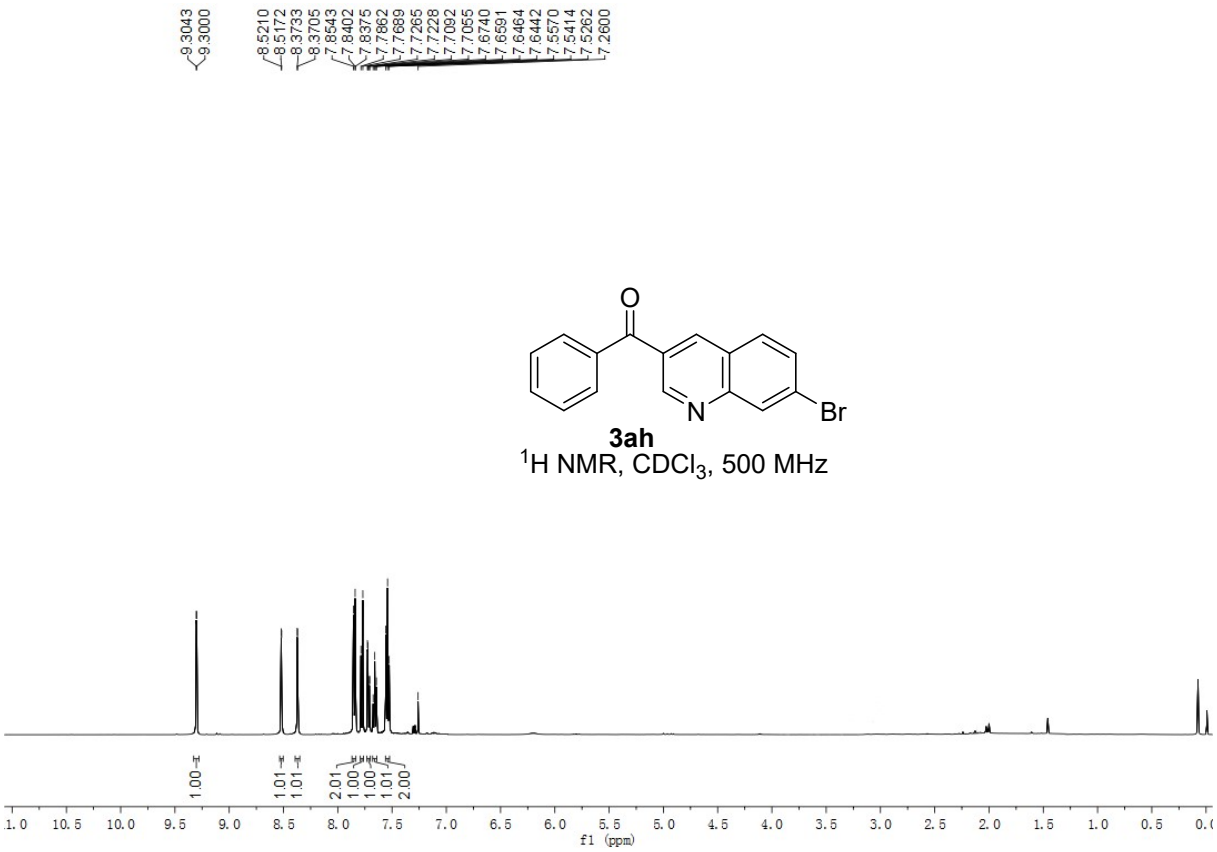
3ag

^{1}H NMR, $CDCl_3$, 500 MHz



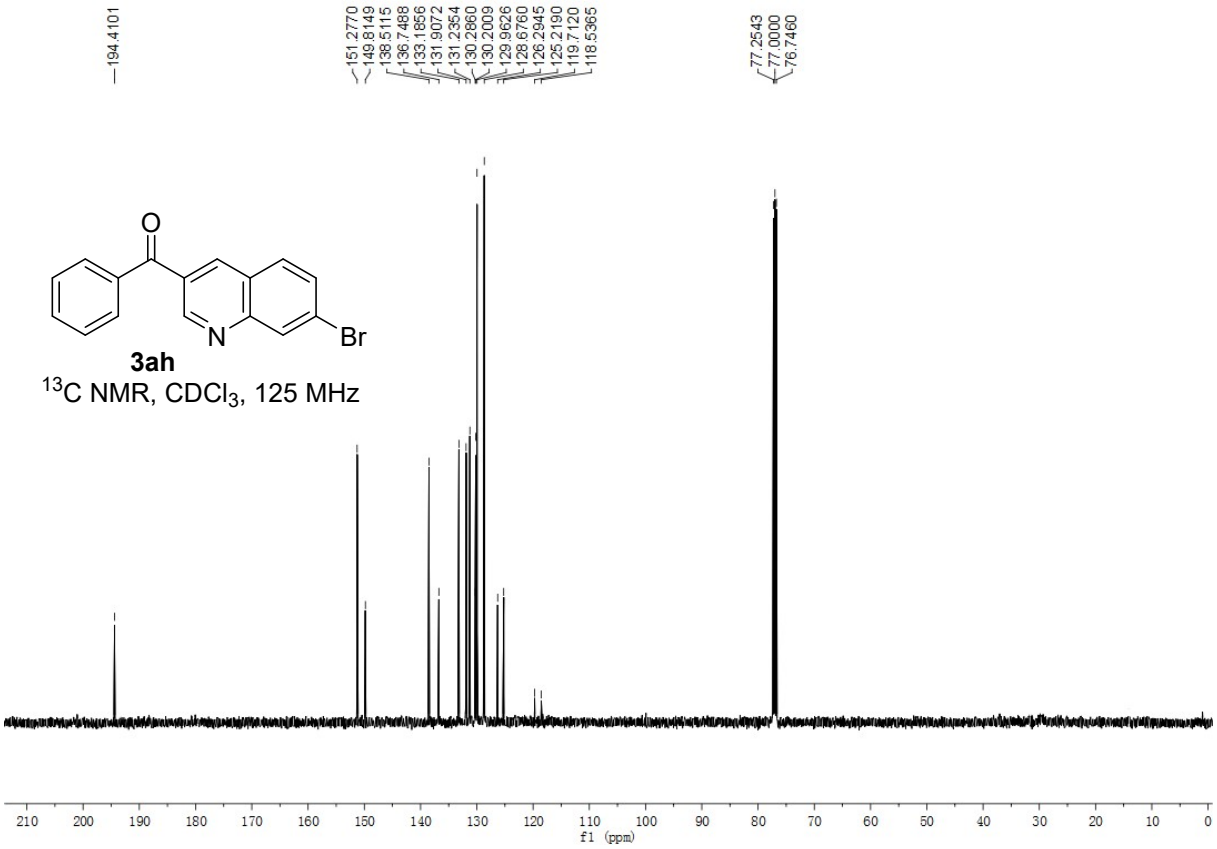
3ag

^{13}C NMR, $CDCl_3$, 125 MHz



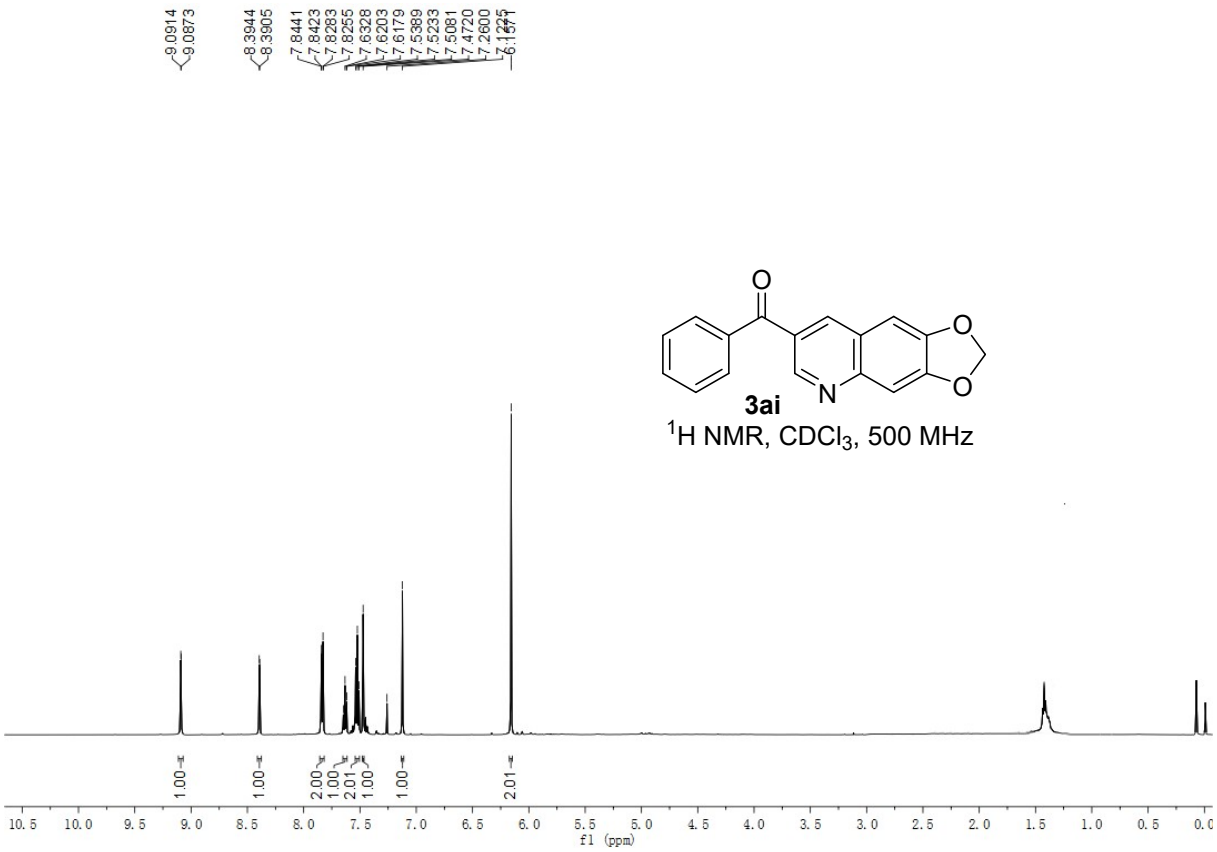
3ah

^{1}H NMR, $CDCl_3$, 500 MHz



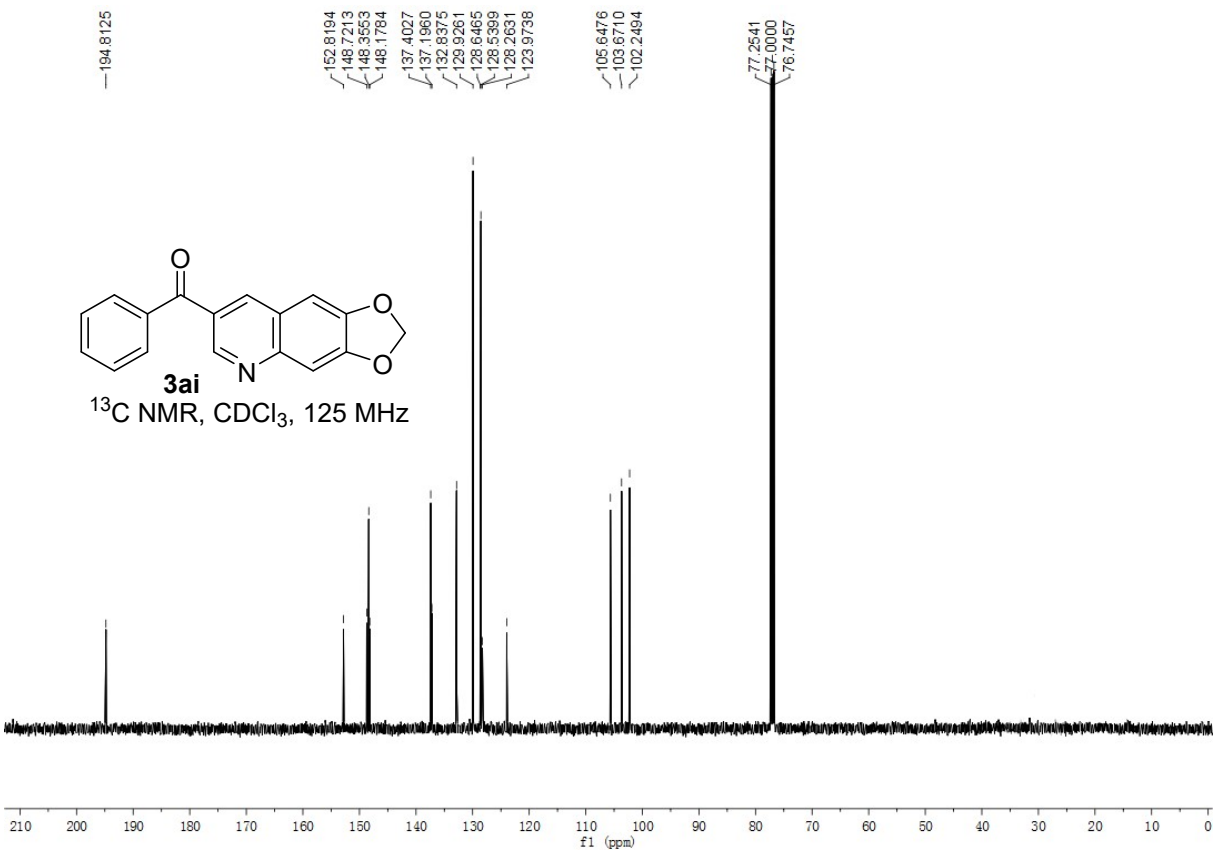
3ah

^{13}C NMR, $CDCl_3$, 125 MHz



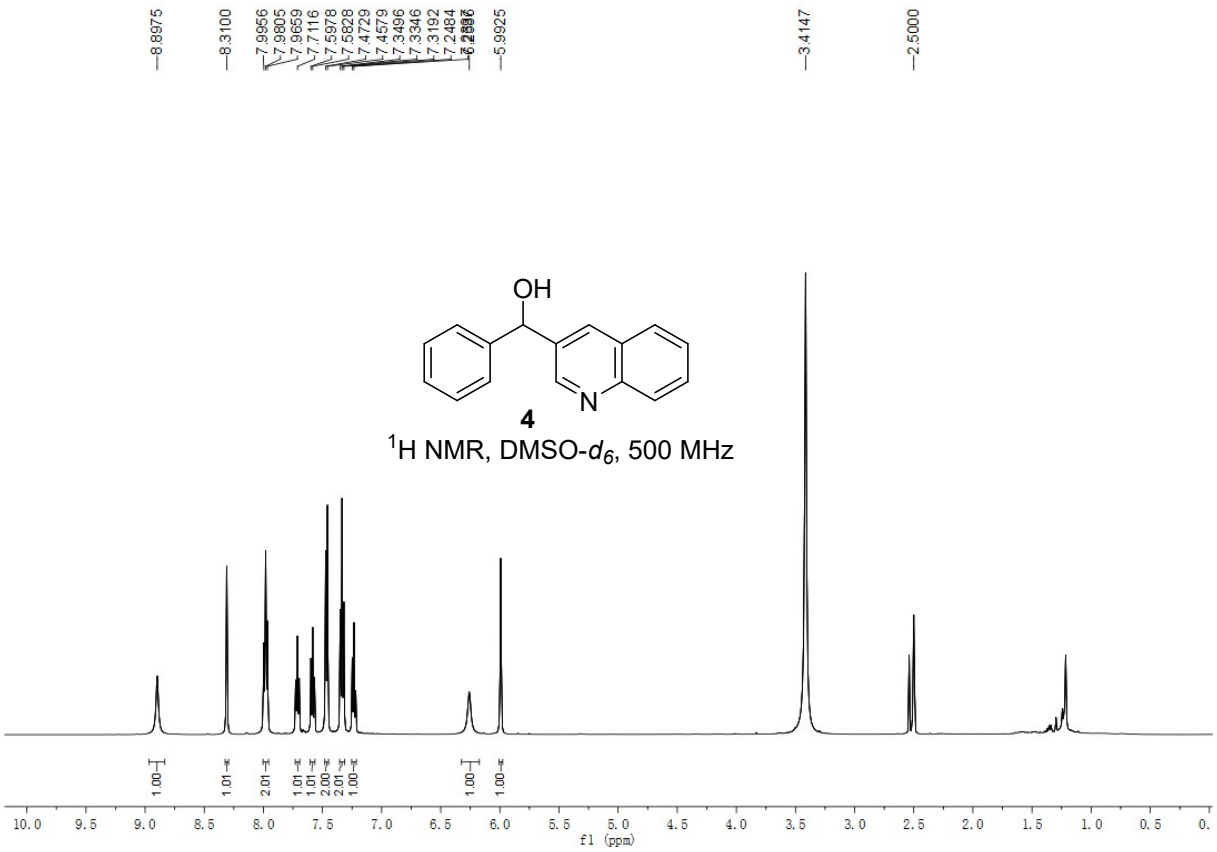
3ai

^{1}H NMR, $CDCl_3$, 500 MHz



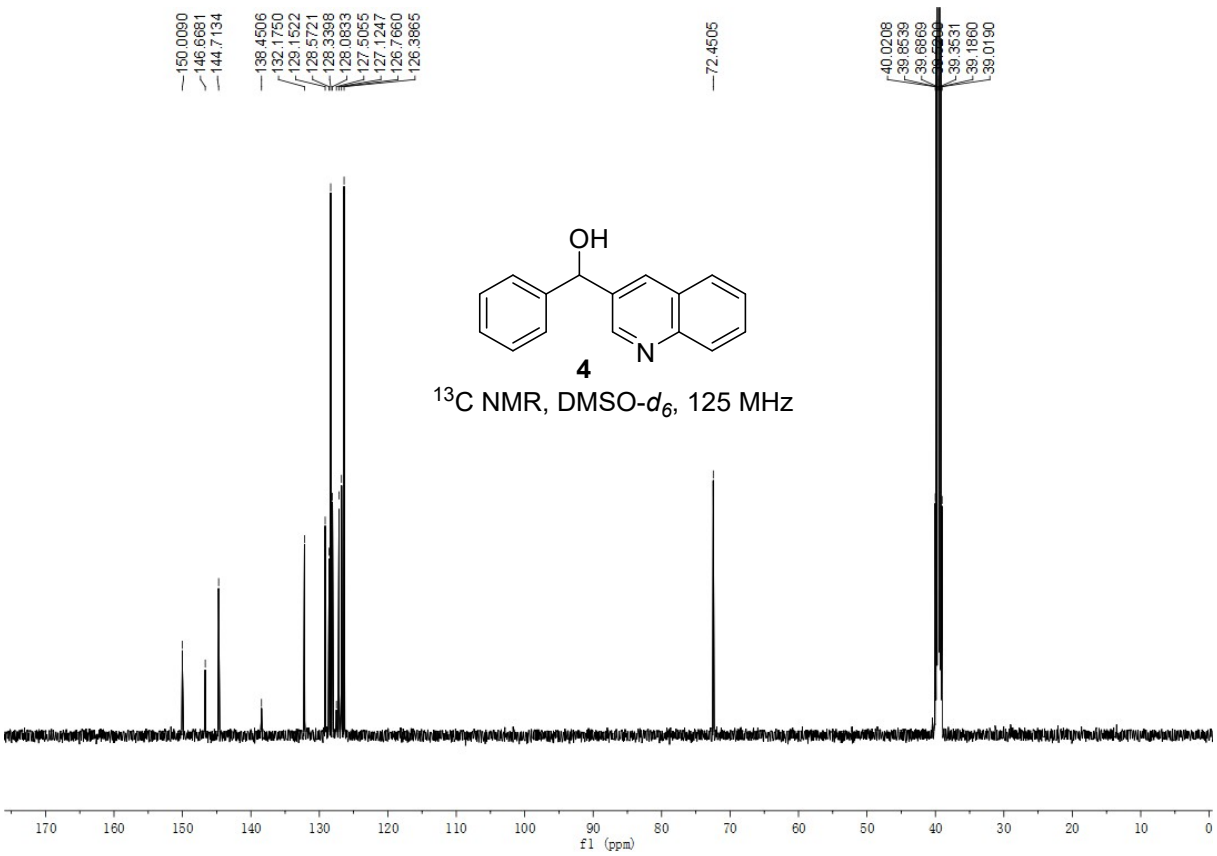
3ai

^{13}C NMR, $CDCl_3$, 125 MHz



4

^{1}H NMR, DMSO-d_6, 500 MHz



4

^{13}C NMR, DMSO-d_6, 125 MHz