Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supplementary Information

for

4CzIPN-Catalyzed Radical-initiated Cascade Cyclizations for the Photosynthesis of Polysubstituted Quinolin-3-amines

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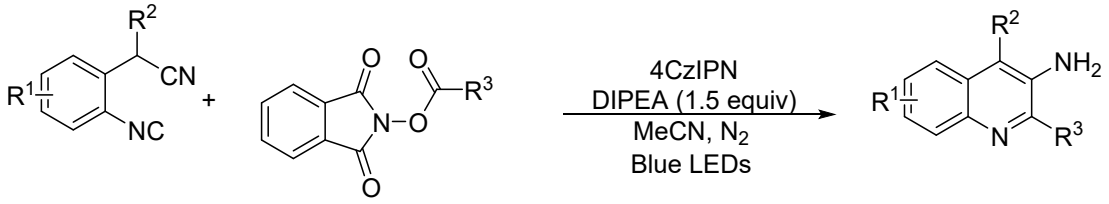
1. General information

All chemicals were purchased from Adamas Reagent, Energy chemical com.p.any, Bide Pharmatech Ltd, J&K SCIENTIFIC LTD and Shang Fluoro Com.p.any. Unless otherwise stated, all experiments were conducted in a sealed tube under N_2 atmosphere. Reactions were monitored by TLC or GC-MS analysis. Flash column chromatography was performed over silica gel (200-300 mesh). N-acyloxyphthalimides and aryl isonitriles were synthesized according to previously described procedures[1,2, 3,4,5].

^{1}H-NMR and ^{13}C-NMR spectra were recorded in $CDCl_3$ and DMSO-d6 on a Bruker Avance 500 spectrometer (500 MHz ^{1}H, 125 MHz ^{13}C (CPD), 470 MHz ^{19}F) at room tem.p.erature. Chemical shifts were reported in ppm on the scale relative to $CDCl_3$ (δ = 7.26 for ^{1}H-NMR, δ = 77.00 for ^{13}C-NMR) as an internal reference. Coupling constants (J) were reported in Hertz (Hz).

2. Experimental procedures:

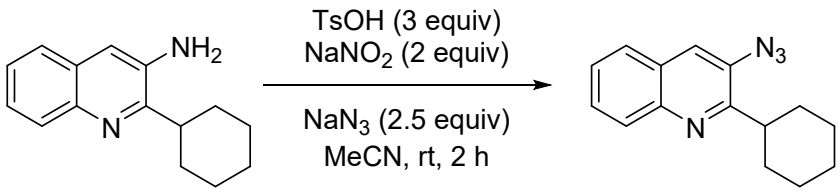
(1). **general procedure 1**



1 **2** **3**

A mixture of **1** (0.4 mmol), **2** (0.6 mmol), 4CzIPN (4 mol%), and DIPEA (1 mmol) were charged into a schleck tube, then the air was removed, N_2 was filled of schleck, CH_3CN (2 mL) was added to the mixture. The mixture was stirred under irradiation of 5 W Blue LEDs at rt for 24h. After the solvent was removed under reduced pressure, the residue was purified by silica gel chromatography to afford the corresponding product.

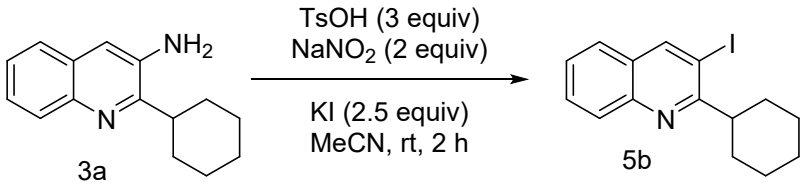
(2). **general procedure 2**



3a **5a**

A mixture of **3a** (0.4 mmol), TsOH (1.2 mmol), $NaNO_2$ (0.6 mmol), NaN_3 (1 mmol), were charged into a schleck tube, then the air was removed, N_2 was filled of schleck, CH_3CN (2 mL) was added to the mixture. The reaction mixture was stirred at room temperature for 2 h. After the solvent was removed under reduced pressure, the residue was purified by silica gel chromatography to afford the corresponding product.

(3). **general procedure 3**

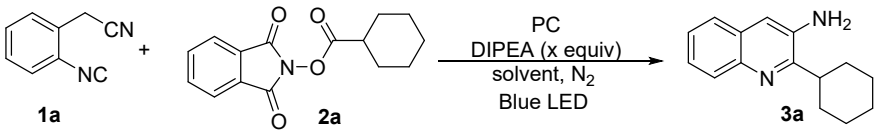


3a 5b

A mixture of **3a** (0.4 mmol), TsOH (1.2 mmol), $NaNO_2$ (0.6 mmol), KI (1 mmol), were charged into a schleck tube, then the air was removed, N_2 was filled of schleck, CH_3CN (2 mL) was added to the mixture. The reaction mixture was stirred at room temperature for 2 h. After the solvent was removed under reduced pressure, the residue was purified by silica gel chromatography to afford the corresponding product.

3. Optimization of Reaction Conditions

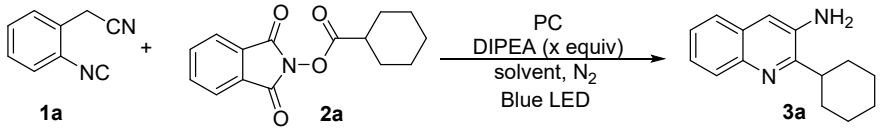
Table S1. Screening of photocatalysts (P.C.) and solvents[a]



Entry	DIPEA (x equiv)	PC	Solvent	Yield(%)
1	1.5	Eosin-Y	MeCN	59
2	1.5	Eosin-B	MeCN	48
3	1.5	fac-Ir(ppy)$_3$	MeCN	38
4	1.5	Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF6	MeCN	40
5	1.5	Ru(bpy)$_3$Cl$_2$	MeCN	26
6	1.5	4CzIPN	MeCN	64
7	1.5	4CzIPN	acetone	60
8	1.5	4CzIPN	DMSO	56
9	1.5	4CzIPN	THF	44
10	1.5	4CzIPN	1,4-dioxane	trace
11	1.5	4CzIPN	toluene	trace
12	1.5	4CzIPN	DCM	25
13	1.5	4CzIPN	DMF	50
14	1.5	4CzIPN	CHCl$_3$	28
15	1.5	4CzIPN	EA	trace

Reaction conditions: [a] The reaction was carried out with **1a** (0.4 mmol), **2a** (0.6 mmol), PC (4 mol%), and DIPEA in the solvent (2 mL), under irradiation of blue LED with N_2 protection at rt for 24h.

Table S2. Further screening of reaction conditions

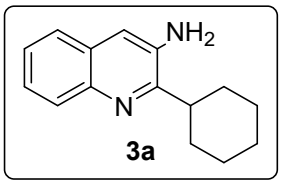


Entry	DIPEA (x equiv)	PC	Additive	Solvent	Yield(%)
1	1.0	4CzIPN	-	MeCN	44
2	1.5	4CzIPN	-	MeCN	64
3	2	4CzIPN	-	MeCN	73
4	2.5	4CzIPN	-	MeCN	76
5	3	4CzIPN	-	MeCN	70
6	2.5	4CzIPN	Cs_2CO_3	MeCN	56
7	2.5	4CzIPN	CsF	MeCN	42
8	2.5	4CzIPN	^{t}BuONa	MeCN	48
9	2.5	4CzIPN	KOMe	MeCN	50
10	2.5	4CzIPN	Na_2HPO_4	MeCN	46
11	2.5	4CzIPN	Na_2CO_3	MeCN	50
12	2.5	4CzIPN	KOAc	MeCN	48
13	2.5	4CzIPN	H_2O	MeCN	trace
14	2.5	4CzIPN	PhSH	MeCN	36
15	2.5	4CzIPN	$MgSO_4$	MeCN	60

Reaction conditions: [a] The reaction was carried out with **1a** (0.4 mmol), **2a** (0.6 mmol), PC (4 mol%), and DIPEA in the solvent (2 mL), under irradiation of blue LED with N_2 protection at rt for 24h.

4. Characterization data for products

2-cyclohexylquinolin-3-amine(3a)



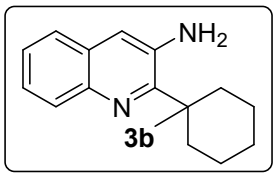
Following the **general procedure 1**, white solid (m.p.: 77 – 79 °C), yield: 76%.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.3 Hz, 1H), 7.57 – 7.53 (m, 1H), 7.45 – 7.41 (m, 1H), 7.40 – 7.35 (m, 1H), 7.16 (s, 1H), 3.88 (s, 2H), 2.87 – 2.78 (m, 1H), 2.04 – 1.76 (m, 8H), 1.46 – 1.41 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 156.2, 142.6, 137.8, 128.7, 128.3, 126.0, 125.4, 125.3, 116.0, 41.3, 31.1, 26.8, 26.2.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{15}H_{19}N_2^+$ 227.1543; Found:227.1538.

2-(1-methylcyclohexyl)quinolin-3-amine(3b)



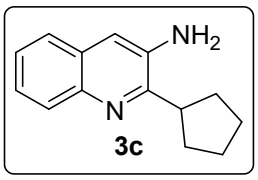
Following the **general procedure 1**, white solid (m.p.: 95 – 98 °C), yield: 88%.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.3 Hz, 1H), 7.57 – 7.53 (m, 1H), 7.45 – 7.41 (m, 1H), 7.40 – 7.35 (m, 1H), 7.16 (s, 1H), 3.88 (s, 2H), 2.87 – 2.78 (m, 2H), 2.04 – 1.76 (m, 8H), 1.46 – 1.41 (m, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 156.5, 141.9, 138.8, 129.2, 128.1, 126.1, 125.2, 124.8, 118.1, 42.0, 36.9, 26.5, 24.9, 23.0.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{16}H_{21}N_2^+$ 241.1699; Found:241.1704.

2-cyclopentylquinolin-3-amine(3c)



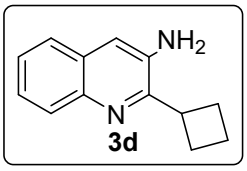
Following the **general procedure 1**, white solid (m.p.: 107 – 108 °C), yield: 47%.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.3 Hz, 1H), 7.57 – 7.53 (m, 1H), 7.45 – 7.41 (m, 1H), 7.40 – 7.35 (m, 1H), 7.16 (s, 1H), 3.88 (s, 2H), 2.87 – 2.78 (m, 1H), 2.04 – 1.76 (m, 8H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 155.2, 142.3, 138.3, 128.8, 128.3, 125.8, 125.2, 125.1, 115.4, 42.4, 30.9, 25.8.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{14}H_{17}N_2^+$ 213.1386; Found:213.1390.

2-cyclobutylquinolin-3-amine(3d)



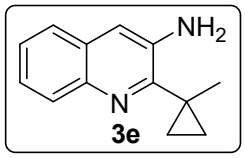
Following the **general procedure 1**, white solid (m.p.: 90 – 92 °C), yield: 48%.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.3 Hz, 1H), 7.57 – 7.53 (m, 1H), 7.45 – 7.41 (m, 1H), 7.40 – 7.35 (m, 1H), 7.16 (s, 1H), 3.88 (s, 2H), 2.87 – 2.78 (m, 1H), 2.04 – 1.76 (m, 4H), 1.46 – 1.41 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 154.1, 142.3, 138.0, 128.8, 128.6, 126.0, 125.3, 125.3, 115.1, 38.4, 26.1, 18.4.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{13}H_{15}N_2^+$ 199.1230; Found: 199.1231.

2-(1-methylcyclopropyl)quinolin-3-amine(3e)



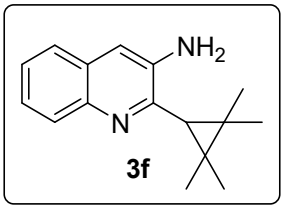
Following the **general procedure 1**, white solid (m.p.: 113 – 116 °C), yield: 71%.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 – 7.97 (m, 1H), 7.60 – 7.56 (m, 1H), 7.46 – 7.37 (m, 2H), 7.24 (s, 1H), 4.25 (s, 2H), 1.52 (s, 3H), 1.14 – 1.09 (m, 2H), 0.94 – 0.91 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 153.9, 142.1, 139.1, 128.9, 128.7, 126.3, 125.3, 125.2, 115.5, 22.1, 20.7, 13.0.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{13}H_{15}N_2^+$ 199.1230; Found: 199.1226.

2-(2,2,3,3-tetramethylcyclopropyl)quinolin-3-amine(3f)



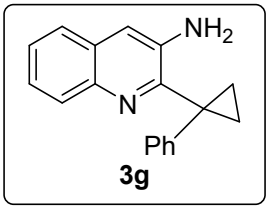
Following the **general procedure 1**, white solid (m.p.: 132 – 134 °C), yield: 52%.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.0 Hz, 1H), 7.57 – 7.52 (m, 1H), 7.43 – 7.33 (m, 2H), 7.19 (s, 1H), 3.96 (s, 2H), 1.39 (s, 6H), 1.26 (d, *J* = 1.9 Hz, 1H), 1.13 (s, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 151.0, 142.1, 140.4, 129.0, 128.3, 126.0, 125.1, 124.9, 114.1, 24.6, 23.7, 18.3.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{16}H_{21}N_2^+$ 241,1699; Found: 241,1704.

2-(1-phenylcyclopropyl)quinolin-3-amine(3g)



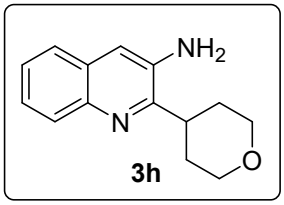
3g

Following the **general procedure 1**, white solid (m.p.: 111 – 113 °C), yield: 65%.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.2 Hz, 1H), 7.64 – 7.60 (m, 1H), 7.51 – 7.42 (m, 2H), 7.26 (d, *J* = 7.1 Hz, 3H), 7.19 (t, *J* = 7.3 Hz, 1H), 7.11 (d, *J* = 7.7 Hz, 2H), 4.00 (s, 2H), 1.69 – 1.64 (m, 2H), 1.56 – 1.51 (m, 2H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 152.1, 142.2, 142.1, 139.7, 129.2, 129.0, 128.7, 126.5, 126.2, 125.5, 125.4, 125.2, 115.9, 28.6, 16.4.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{18}H_{17}N_2^+$ 261.1386; Found: 261.1383.

2-(tetrahydro-2H-pyran-4-yl)quinolin-3-amine(3h)



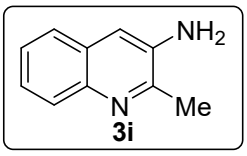
3h

Following the **general procedure 1**, white solid (m.p.: 148 – 150 °C), yield: 78%.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.2 Hz, 1H), 7.59 – 7.55 (m, 1H), 7.46 – 7.36 (m, 2H), 7.23 (s, 1H), 4.21 – 4.13 (m, 2H), 3.87 (s, 2H), 3.62 (td, *J* = 11.9, 2.0 Hz, 2H), 3.13 – 3.03 (m, 1H), 2.28 – 2.16 (m, 2H), 1.92 – 1.85 (m, 2H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 153.9, 142.7, 137.5, 128.9, 128.3, 126.1, 125.5, 125.2, 116.3, 68.1, 38.5, 30.6.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{14}H_{17}N_2O^+$ 229.1335; Found: 229.1338.

2-methylquinolin-3-amine(3i)



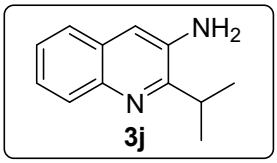
3i

Following the **general procedure 1**, white solid (m.p.: 94 – 96 °C), yield: 62%.

^{1}H NMR (500 MHz, DMSO-d_6) δ 7.74 – 7.70 (m, 1H), 7.59 – 7.55 (m, 1H), 7.34 – 7.28 (m, 2H), 7.17 (s, 1H), 5.40 (s, 2H), 2.49 (s, 3H).
^{13}C NMR (125 MHz, DMSO-d_6) δ 150.1, 141.4, 141.2, 129.4, 128.2, 125.9, 125.5, 124.3, 112.5, 22.0.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{10}H_{11}N_2^+$ 159.0917; Found: 159.0919.

2-isopropylquinolin-3-amine(3j)



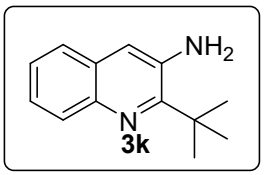
3j

Following the **general procedure 1**, white solid (m.p.: 98 – 100 °C), yield: 68%.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 – 7.93 (m, 1H), 7.58 – 7.54 (m, 1H), 7.45 – 7.35 (m, 2H), 7.20 (s, 1H), 3.88 (d, *J* = 11.4 Hz, 2H), 3.26 – 3.17 (m, 1H), 1.42 (d, *J* = 6.8 Hz, 6H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 156.7, 142.6, 137.6, 128.8, 128.3, 125.9, 125.3, 125.2, 115.8, 30.8, 20.8.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{12}H_{15}N_2^+$ 187.1230; Found: 187.1232.

2-(tert-butyl)quinolin-3-amine(3k)

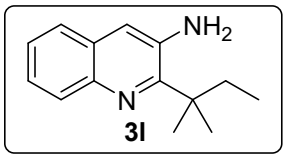


Following the **general procedure 1**, red oil liquid, yield: 78%.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.3 Hz, 1H), 7.66 – 7.61 (m, 1H), 7.54 – 7.44 (m, 2H), 7.26 (s, 1H), 4.09 (s, 2H), 1.65 (s, 9H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 157.3, 141.9, 138.8, 129.3, 128.6, 126.3, 125.5, 125.0, 118.1, 38.6, 29.0.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{13}H_{17}N_2^+$ 201.1386; Found:201.1389.

2-(tert-pentyl)quinolin-3-amine(3l)

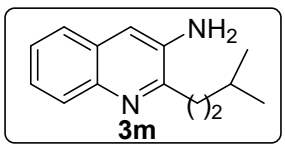


Following the **general procedure 1**, brown oil liquid, yield: 81%.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.2 Hz, 1H), 7.59 (d, *J* = 7.9 Hz, 1H), 7.48 – 7.39 (m, 2H), 7.18 (s, 1H), 4.00 (s, 2H), 2.03 – 1.96 (m, 2H), 1.58 (d, *J* = 1.6 Hz, 6H), 0.85 – 0.79 (m, 3H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 156.3, 141.9, 139.0, 129.3, 128.3, 126.1, 125.2, 124.8, 117.6, 42.3, 33.3, 27.2, 9.5.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{14}H_{19}N_2^+$ 215.1543; Found: 215.1539.

2-(4-methylpentyl)quinolin-3-amine)(3m)

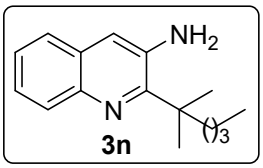


Following the **general procedure 1**, white solid, (m.p.: 116 – 118 °C), yield: 57%.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 – 7.92 (m, 1H), 7.59 – 7.54 (m, 1H), 7.45 – 7.35 (m, 2H), 7.21 (d, *J* = 0.7 Hz, 1H), 3.85 (s, 2H), 2.94 – 2.85 (m, 2H), 1.80 – 1.66 (m, 3H), 1.01 (d, *J* = 6.3 Hz, 6H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 153.0, 142.5, 138.2, 128.6, 128.4, 125.9, 125.5, 125.3, 115.7, 36.3, 32.8, 28.4, 22.5.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{14}H_{19}N_2^+$ 216.1699; Found: 216.1697.

2-(tert-pentyl)quinolin-3-amine (3n)



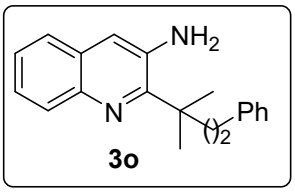
Following the **general procedure 1**, white solid, (m.p.: 118– 119 °C), yield: 63%.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 – 7.92 (m, 1H), 7.57 – 7.53 (m, 1H), 7.49 – 7.38 (m, 2H), 7.15 (d, 1H), 3.99 (s, 2H), 1.93 – 1.87 (m, 2H), 1.55 (d, *J* = 0.9 Hz, 6H), 1.30-1.26 (m, 2H), 1.15 – 1.07 (m, 2H), 0.84 (t, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 156.5, 141.9, 138.9, 129.3, 128.3, 126.1, 125.2, 124.8, 117.5, 42.0, 40.7, 27.7, 27.3, 23.5, 14.0.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{16}H_{23}N_2^+$ 243.1856; Found: 243.1859.

2-(2-methyl-1-phenylpropan-2-yl)quinolin-3-amine(3o)



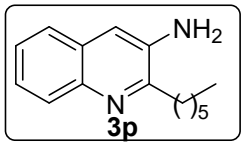
Following the **general procedure 1**, white solid, (m.p.: 110 – 112 °C), yield: 64%.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.3 Hz, 1H), 7.57 – 7.53 (m, 1H), 7.49 – 7.38 (m, 2H), 7.27 – 7.22 (m, 2H), 7.20 (s, 1H), 7.19 – 7.13 (m, 3H), 4.08 – 3.92 (m, 2H), 2.50 – 2.40 (m, 2H), 2.28 – 2.18 (m, 2H), 1.62 (s, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 155.8, 143.2, 138.9, 129.2, 128.4, 128.3, 126.2, 125.6, 125.4, 124.8, 43.4, 42.1, 31.7, 27.6.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{20}H_{23}N_2^+$ 290.1783; Found: 290.1785.

2-hexylquinolin-3-amine(3p)



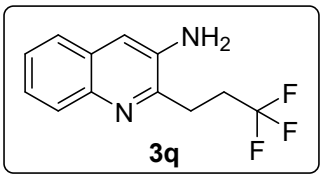
Following the **general procedure 1**, white solid, (m.p.: 119 – 120 °C), yield: 53%.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.3 Hz, 1H), 7.61 – 7.56 (m, 1H), 7.47 – 7.37 (m, 2H), 7.23 (s, 1H), 3.88 (s, 2H), 2.95 – 2.85 (m, 2H), 1.88 – 1.79 (m, 2H), 1.49 (q, *J* = 7.3 Hz, 2H), 1.40 – 1.33 (m, 4H), 0.92 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 152.9, 142.6, 138.3, 128.6, 128.5, 126.0, 125.5, 125.3, 115.7, 34.8, 31.8, 29.5, 27.5, 22.6, 14.1.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{15}H_{21}N_2^+$ 229.1699; Found:229.1701.

2-(3,3,3-trifluoropropyl)quinolin-3-amine(3q)

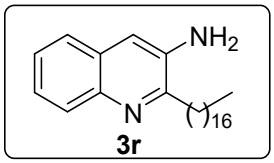


Following the **general procedure 1**, brown oil liquid, yield: 71%.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.2 Hz, 1H), 7.63 – 7.59 (m, 1H), 7.51 – 7.41 (m, 2H), 7.26 (s, 1H), 3.84 (s, 2H), 3.12 – 3.06 (m, 2H), 2.95 – 2.84 (m, 2H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 148.40, 142.41, 138.00, 128.68, 128.65, 126.43, 125.79, 125.45, 115.99, 30.83 (q, *J* = 29.0 Hz), 26.07 (q, *J* = 3.0 Hz).
^{19}F NMR (471 MHz, CDCl3) δ -65.38.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{12}H_{12}F_3N_2^+$ 241.0947; Found: 241.0947.

2-ethylquinolin-3-amine(3r)

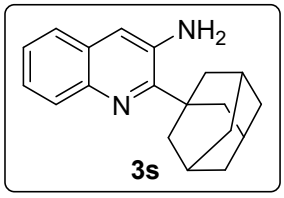


Following the **general procedure 1**, white solid, (m.p.: 104 – 106 °C), yield: 39%.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.3 Hz, 1H), 7.59 (d, *J* = 8.0 Hz, 1H), 7.48 – 7.37 (m, 2H), 7.23 (s, 1H), 3.88 (s, 2H), 2.96 – 2.85 (m, 2H), 1.88 – 1.75 (m, 4H), 1.52 – 1.46 (m, 2H), 1.42 – 1.35 (m, 3H), 1.28 (s, 21H), 0.92 – 0.88 (m, 3H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 152.9, 138.3, 128.6, 128.5, 126.0, 125.5, 125.3, 115.7, 34.8, 31.9, 29.9, 29.7, 29.7, 29.6, 29.6, 29.4, 27.6, 22.7, 14.1.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{26}H_{43}N_2^+$ 383.3421; Found:383.3420.

2-(adamantan-1-yl)quinolin-3-amine(3s)

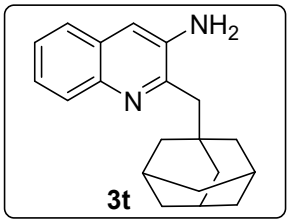


Following the **general procedure 1**, white solid, (m.p.: 165 – 167 °C), yield:52%.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.2 Hz, 1H), 7.57 (s, 1H), 7.47 – 7.37 (m, 2H), 7.18 (s, 1H), 4.08 (s, 2H), 2.32 (d, *J* = 2.9 Hz, 6H), 2.25 – 2.17 (m, 3H), 1.87 (t, *J* = 3.1 Hz, 6H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 156.7, 142.1, 139.0, 129.2, 128.1, 126.1, 125.3, 124.8, 118.2, 41.2, 39.6, 37.1, 28.8.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{19}H_{23}N_2^+$ 279.1856; Found: 279.1858.

2-(adamantan-1-ylmethyl)quinolin-3-amine(3t)

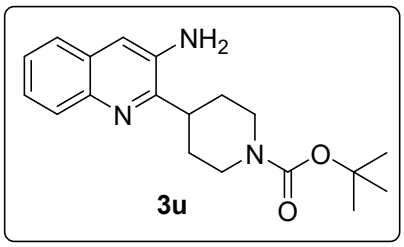


Following the **general procedure 1**, white solid, (m.p.: 140 – 142 °C), yield:55%.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.3 Hz, 1H), 7.59 (d, *J* = 7.9 Hz, 1H), 7.48 – 7.37 (m, 2H), 7.22 (d, *J* = 3.1 Hz, 1H), 3.92 (s, 2H), 2.75 (d, *J* = 3.1 Hz, 2H), 1.98 (t, *J* = 3.3 Hz, 3H), 1.75 – 1.65 (m, 9H), 1.61 (d, *J* = 12.2 Hz, 3H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 150.0, 142.4, 139.6, 128.8, 126.0, 125.4, 125.3, 115.8, 48.0, 43.0, 36.9, 35.7, 28.8.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{20}H_{25}N_2^+$ 293.2012; Found: 293.2008.

tert-butyl 4-(3-aminoquinolin-2-yl)piperidine-1-carboxylate (3u)

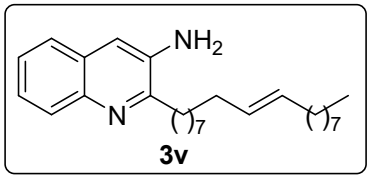


Following the **general procedure 1**, white solid, (m.p.: 104 – 106 °C), yield: 71%.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93-7.90 (m 1H), 7.60-7.56 (m, 1H), 7.42-7.39 (m, 2H), 7.21 (s, 1H), 4.29 (s, 2H), 3.90 (s, 2H), 2.95 – 2.85 (m, 2H), 2.03 (s, 3H), 1.92 (s, 2H), 1.48 (s, 9H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 154.82, 154.06, 142.64, 137.63, 128.83, 128.34, 126.16, 125.52, 125.31, 116.32, 79.44, 39.27, 29.94, 28.53, 22.7

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{19}H_{26}N_3O_2^+$ 328.2020; Found:328.2023.

(E)-2-(octadec-9-en-1-yl)quinolin-3-amine (3v)

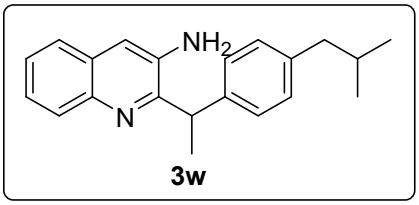


Following the **general procedure 1**, white solid, (m.p.: 122– 124 °C), yield: 34%.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (m, 1H), 7.59 (d, *J* = 1.2 Hz, 1H), 7.45 – 7.43 (m, 2H), 7.21 (s, 1H), 5.36 – 5.32 (m, 2H), 3.90 (s, 3H), 3.86 (s, 2H), 2.91 – 2.86 (m, 2H), 2.00-2.32 (m, 4H), 1.86 – 1.77 (m, 2H), 1.71 (s, 2H), 1.50 – 1.44 (m, 2H), 1.34 – 1.31 (m, 5H), 1.25 (d, *J* = 4.1 Hz, 10H), 0.88 (d, *J* = 6.8 Hz, 3H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 130.2, 129.99, 129.8, 129.5, 129.1, 127.3, 126.8, 126.0, 125.5, 125.3, 115.95, 115.69, 34.8, 31.9, 29.8, 29.79, 29.77, 29.5, 29.5, 29.3, 22.7, 21.0, 14.1.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{27}H_{43}N_2^+$ 395.3421; Found:395.3423

2-(1-(4-isobutylphenyl)ethyl)quinolin-3-amine



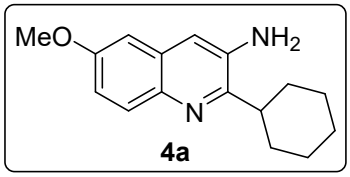
Following the **general procedure 1**, white solid, (m.p.: 112– 114 °C), yield: 42%.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08 (m, 1H), 7.65 – 7.60 (m, 1H), 7.52 – 7.47 (m, 2H), 7.45 – 7.42 (m, 1H), 7.17 (d, *J* = 7.9 Hz, 2H), 7.08 (d, *J* = 8.0 Hz, 2H), 4.38 (m, , 1H), 3.93 (s, 1H), 3.64 (s, 2H), 2.44 (d, *J* = 7.2 Hz, 2H), 1.83 (d, *J* = 7.0 Hz, 3H), 0.90 (d, *J* = 6.7 Hz, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 154.2, 142.4, 141.3, 140.19, 138.6, 130.2, 129.7, 129.2, 128.7, 127.3, 126.1, 125.4, 125.3, 116.6, 45.0, 43.7, 30.2, 22.4, 22.4, 20.9.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{21}H_{25}N_2^+$ 305.2012; Found:305.2011

2-cyclohexyl-6-methoxyquinolin-3-amine(4a)



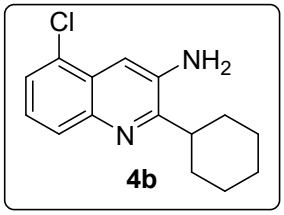
Following the **general procedure 1**, white solid, (m.p.: 115 – 116 °C), yield:45%.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (d, *J* = 9.1 Hz, 1H), 7.14 – 7.06 (m, 2H), 6.86 (d, *J* = 2.7 Hz, 1H), 3.90 (s, 3H), 3.89 – 3.82 (m, 2H), 2.84 – 2.75 (m, 1H), 2.00 – 1.92 (m, 4H), 1.84 – 1.78 (m, 3H), 1.50 – 1.39 (m, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 157.5, 153.5, 138.7, 138.0, 130.3, 129.1, 117.5, 115.2, 103.4, 55.4, 41.1, 31.1, 26.8, 26.2.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{16}H_{21}N_2O^+$ 257.1648; Found: 257.1647.

5-chloro-2-cyclohexylquinolin-3-amine(4b)



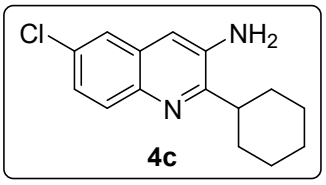
Following the **general procedure 1**, white solid, (m.p.: 118 – 120 °C), yield:61%.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 – 7.87 (m, 1H), 7.58 (d, *J* = 0.9 Hz, 1H), 7.49 – 7.45 (m, 1H), 7.36 – 7.31 (m, 1H), 4.05 (s, 2H), 2.88 – 2.79 (m, 1H), 2.02 – 1.94 (m, 4H), 1.86 – 1.79 (m, 3H), 1.53 – 1.39 (m, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 156.7, 143.1, 138.6, 128.5, 128.0, 126.4, 125.8, 124.7, 112.2, 41.2, 31.0, 26.7, 26.1.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{15}H_{18}ClN_2^+$ 261.1153; Found:261.1156.

6-chloro-2-cyclohexylquinolin-3-amine(4c)



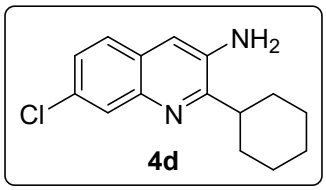
Following the **general procedure 1**, white solid, (m.p.: 113 – 116 °C), yield:81%.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.9 Hz, 1H), 7.53 (d, *J* = 2.3 Hz, 1H), 7.38 – 7.33 (m, 1H), 7.10 (s, 1H), 3.96 (s, 2H), 2.85 – 2.77 (m, 1H), 2.00 – 1.93 (m, 4H), 1.85 – 1.77 (m, 3H), 1.51 – 1.38 (m, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 156.3, 141.0, 138.4, 131.5, 130.4, 129.0, 126.0, 123.8, 114.4, 41.3, 31.0, 26.7, 26.1.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{15}H_{18}ClN_2^+$ 261.1153; Found: 261.1156.

7-chloro-2-cyclohexylquinolin-3-amine(4d)



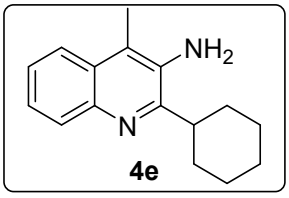
Following the **general procedure 1**, white solid, (m.p.: 103 – 105 °C), yield:78%.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (d, *J* = 2.0 Hz, 1H), 7.49 (d, *J* = 8.6 Hz, 1H), 7.35 – 7.30 (m, 1H), 7.17 (s, 1H), 3.92 (s, 2H), 2.82 (tt, *J* = 11.6, 3.3 Hz, 1H), 1.99 – 1.94 (m, 4H), 1.85 – 1.78 (m, 3H), 1.49 – 1.39 (m, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 157.1, 142.9, 137.8, 130.7, 127.9, 126.7, 126.6, 126.4, 115.4, 41.3, 31.0, 26.7, 26.1.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{15}H_{17}ClN_2Na^+$ 283.0972; Found: 283.0966.

2-cyclohexyl-4-methylquinolin-3-amine(4e)



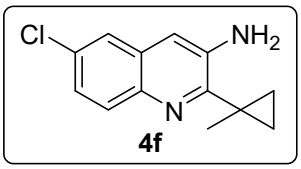
Following the **general procedure 1**, white solid, (m.p.: 119 – 120 °C), yield:61%.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 – 7.96 (m, 1H), 7.86 – 7.82 (m, 1H), 7.47 – 7.42 (m, 2H), 3.89 (s, 2H), 2.91 – 2.81 (m, 1H), 2.48 – 2.43 (m, 3H), 2.03 – 1.94 (m, 4H), 1.90 – 1.81 (m, 3H), 1.53 – 1.40 (m, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 155.1, 142.3, 135.2, 129.7, 127.5, 125.6, 124.8, 122.1, 120.8, 41.7, 31.1, 26.9, 26.2, 11.5.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{16}H_{21}N_2^+$ 241.1699; Found:241.1703.

6-chloro-2-(1-methylcyclopropyl)quinolin-3-amine(4f)



4f

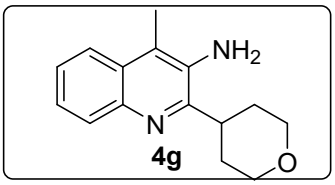
Following the **general procedure 1**, white solid, (m.p.: 112 – 114 °C), yield:57%.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.9 Hz, 1H), 7.54 (d, *J* = 2.4 Hz, 1H), 7.37 – 7.33 (m, 1H), 7.12 (s, 1H), 4.32 (s, 2H), 1.50 (s, 3H), 1.14 – 1.08 (m, 2H), 0.96 – 0.89 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 154.1, 140.3, 139.7, 131.9, 130.3, 129.6, 126.0, 123.7, 114.1, 22.0, 20.6, 12.9.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{13}H_{14}ClN_2^+$ 233.0840; Found:233.0842.

4-methyl-2-(tetrahydro-2H-pyran-4-yl)quinolin-3-amine (4g)



4g

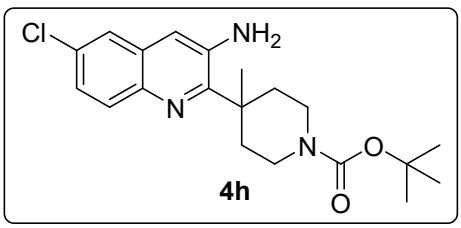
Following the **general procedure 1**, white solid (m.p.: 94 – 96 °C), yield: 40%.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 – 7.96 (m, 1H), 7.87 – 7.82 (m, 1H), 7.50 – 7.42 (m, 2H), 4.23 – 4.13 (m, 2H), 3.90 (s, 2H), 3.69 – 3.59 (m, 2H), 3.15 – 3.08 (m, 1H), 2.44 (s, 3H), 2.28 – 2.20 (m, 2H), 1.93 – 1.85 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 152.9, 142.3, 135.2, 129.7, 127.6, 125.9, 125.1, 122.2, 121.2, 68.2, 38.8, 30.7, 11.5.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C15H19N2O^+$ 243.1492, Found:243.1487.

tert-butyl 4-(3-amino-6-chloroquinolin-2-yl)-4-methylpiperidine-1-carboxylate(4h)



4h

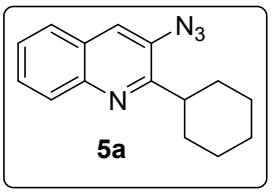
Following the **general procedure 1** , white solid, (m.p.: 127 – 130 °C), yield:55%.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 – 7.90 (m, 1H), 7.60 – 7.56 (m, 1H), 7.42 – 7.39 (m, 1H), 7.24 (s, 1H), 3.94 (s, 2H), 3.76 (s, 2H), 3.28 (d, *J* = 50.4 Hz, 2H), 2.72 (d, *J* = 13.1 Hz, 2H), 1.78 – 1.72 (m, 2H), 1.48 (s, 3H), 1.47 (s, 9H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 155.1, 154.1, 141.8, 138.6, 129.1, 128.2, 126.4, 125.5, 124.9, 118.7, 79.1, 40.3, 31.6, 28.5, 28.5, 25.5, 22.7, 14.1.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{20}H_{26}ClN_3NaO_2^+$ 398.1606; Found:398.1602.

3-azido-2-cyclohexylquinoline(5a)



5a

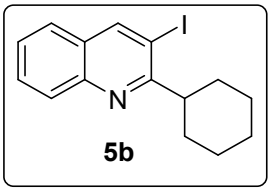
Following the **general procedure 2**, white solid, (m.p.: 127 – 130 °C), yield:82% .

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.61 (s, 1H), 8.04 (d, *J* = 8.5 Hz, 1H), 7.73 – 7.63 (m, 2H), 7.49 (t, *J* = 7.5 Hz, 1H), 3.34 – 3.24 (m, 1H), 2.06 – 1.98 (m, 2H), 1.98 – 1.91 (m, 2H), 1.82 – 1.71 (m, 3H), 1.57 – 1.37 (m, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 160.0, 145.4, 132.6, 129.1, 128.4, 127.2, 126.5, 126.1, 122.2, 41.1, 31.4, 26.6, 26.1.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{15}H_{17}N_4^+$ 253.1448; Found:253.1450.

2-cyclohexyl-3-iodoquinoline(5b)



5b

Following the **general procedure 3**, white solid, (m.p.: 127 – 130 °C), yield: 66%.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.4 Hz, 1H), 7.80 – 7.68 (m, 2H), 7.67 – 7.58 (m, 1H), 7.54 – 7.47 (m, 1H), 3.20 – 3.10 (m, 1H), 1.96 – 1.88 (m, 4H), 1.83 – 1.72 (m, 3H), 1.50 – 1.39 (m, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 164.9, 147.1, 146.2, 129.6, 129.2, 128.3, 126.3, 126.2, 94.4, 48.1, 32.0, 26.5, 26.1.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{15}H_{17}IN^+$ 338.0400; Found:238.0403.

5. References

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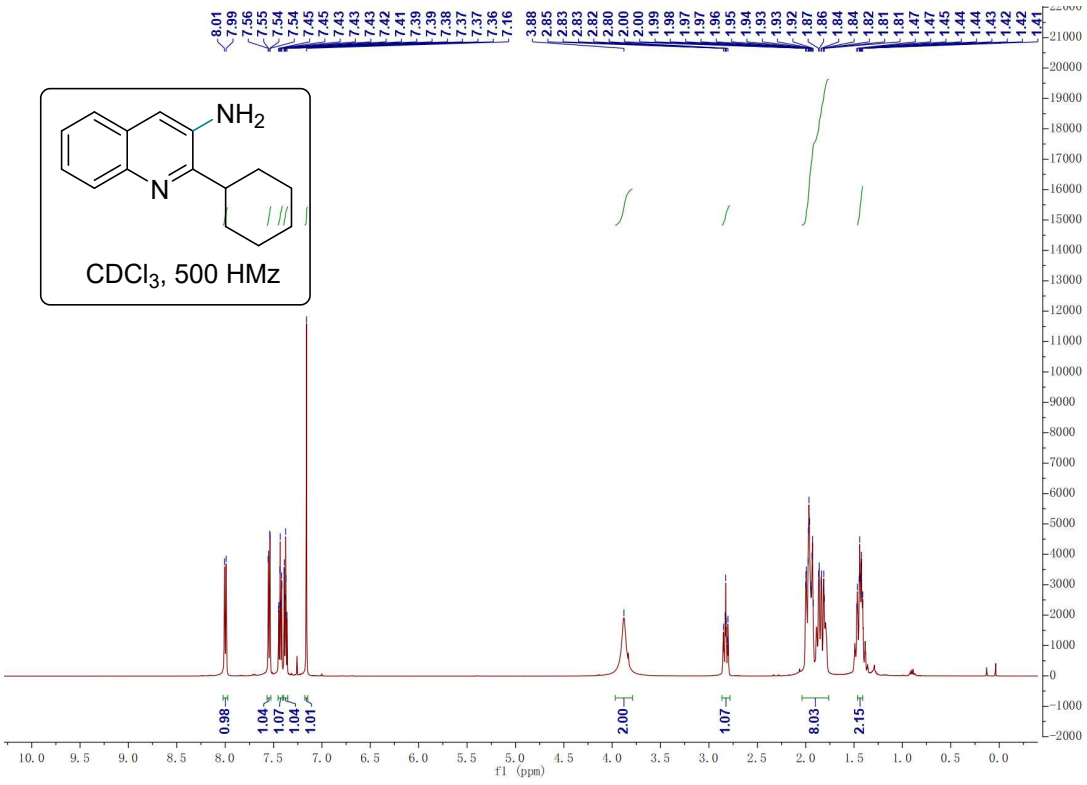
2. S. Ghorai, Y. J.; Lin, Y. Z.; Xia, D. J. Wink, D. Lee, *Org. Lett.* **2020**, *22*, 642.

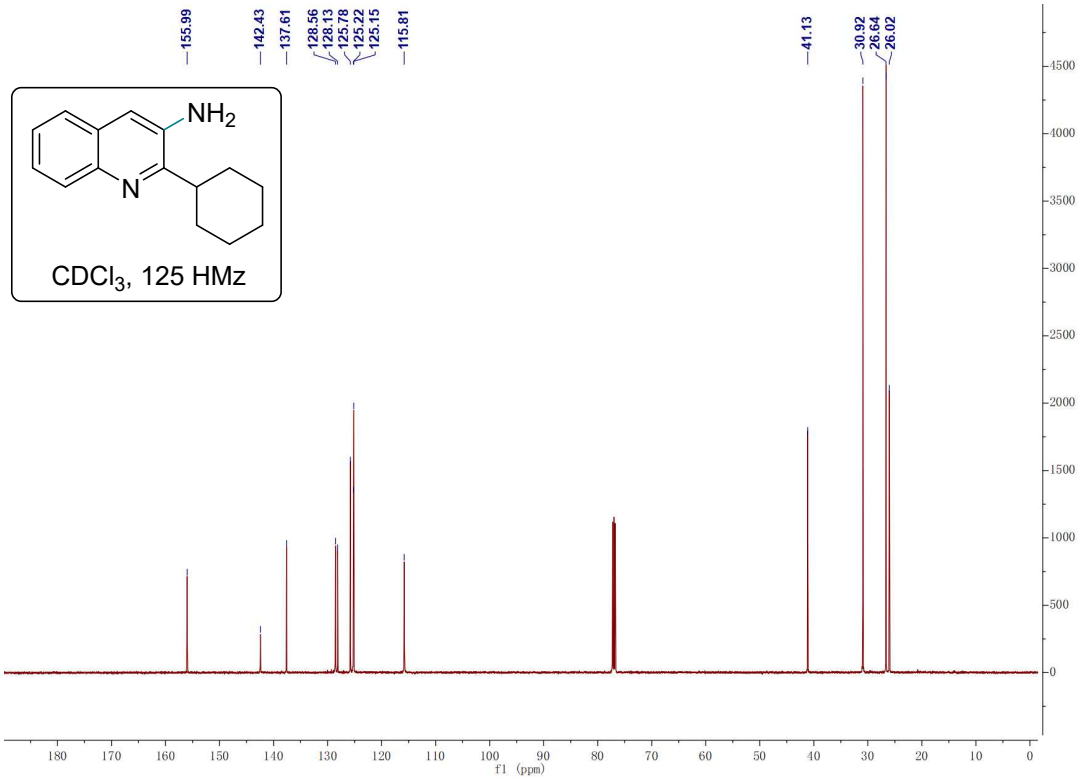
3. I. Choi, H. Chung,; J. W. Park,; Y. K. Chung. *Org. Lett.* **2016**, *18*, 5508.

4. H. G. Cheng, R. M. Zhang, S. W. Yang, M. Wang. X. f. Zeng, L. J. Xie, C. S. Xie, J. Wu, G. F. Zhong, *Adv. Synth. Catal.* **2016**, *358*, 970.

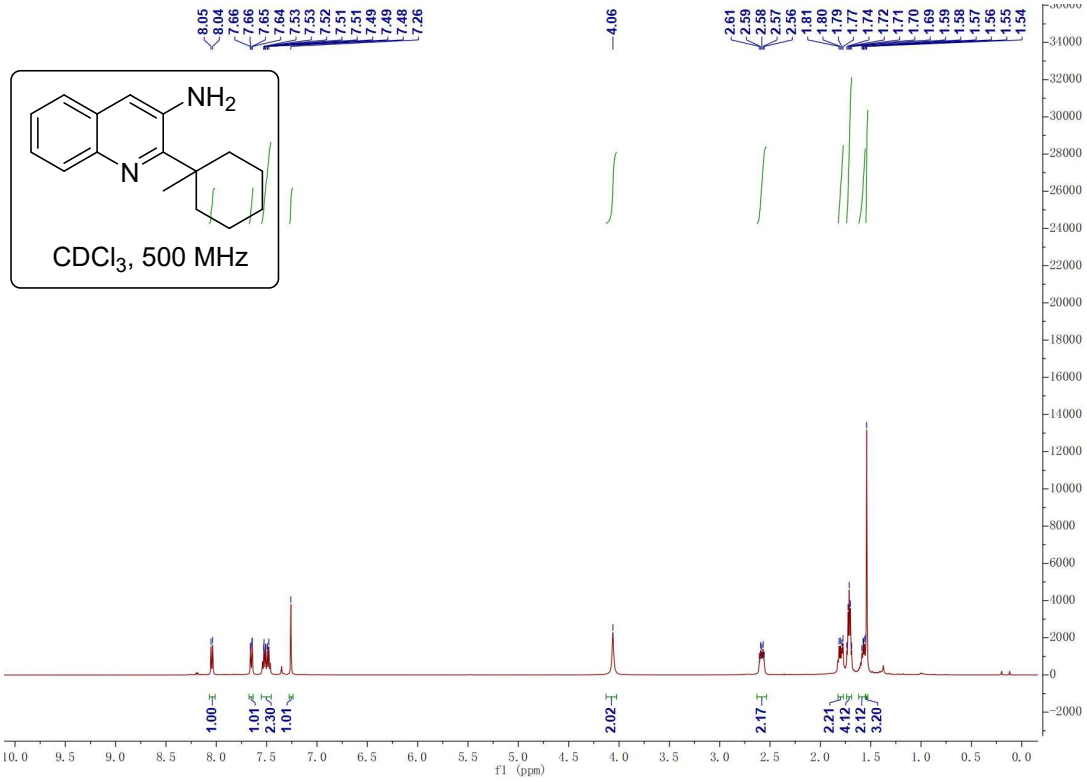
6. NMR spectroscopic data

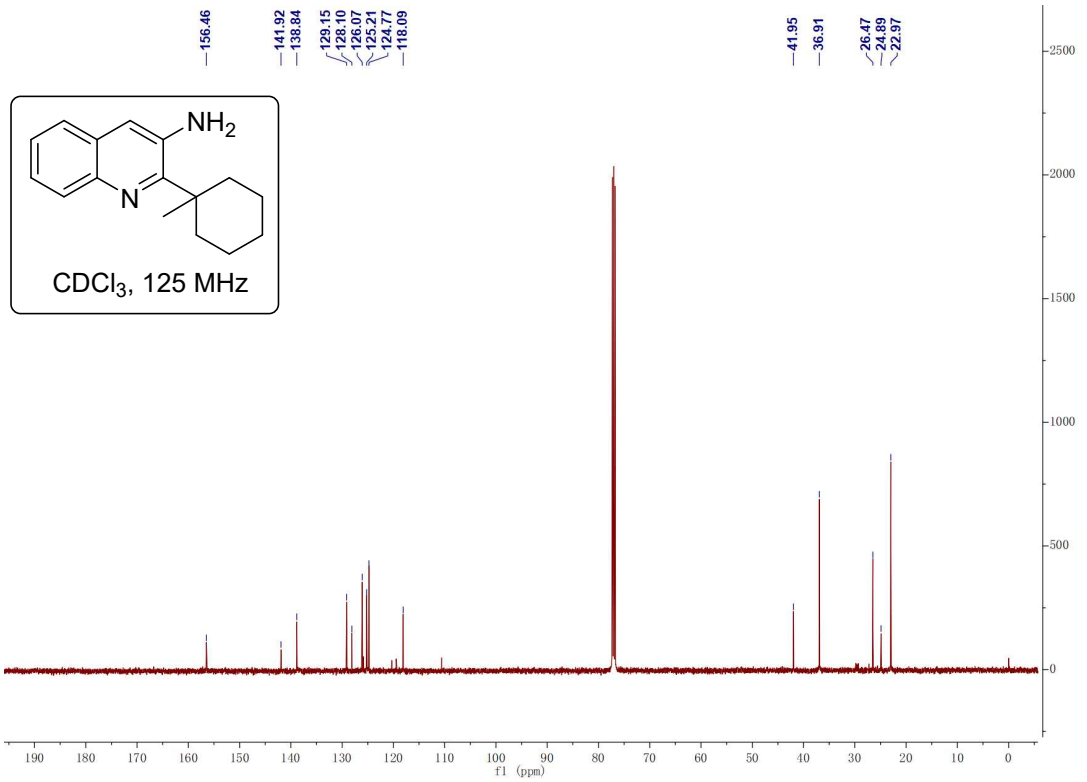
2-cyclohexylquinolin-3-amine(3a)



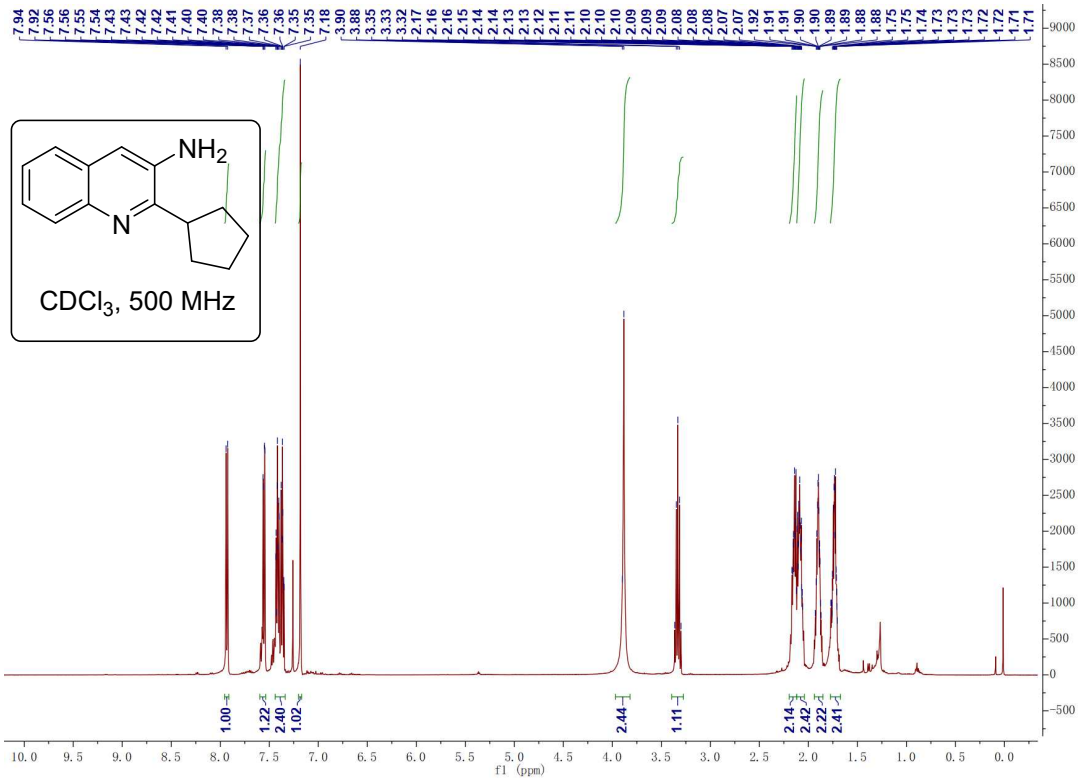


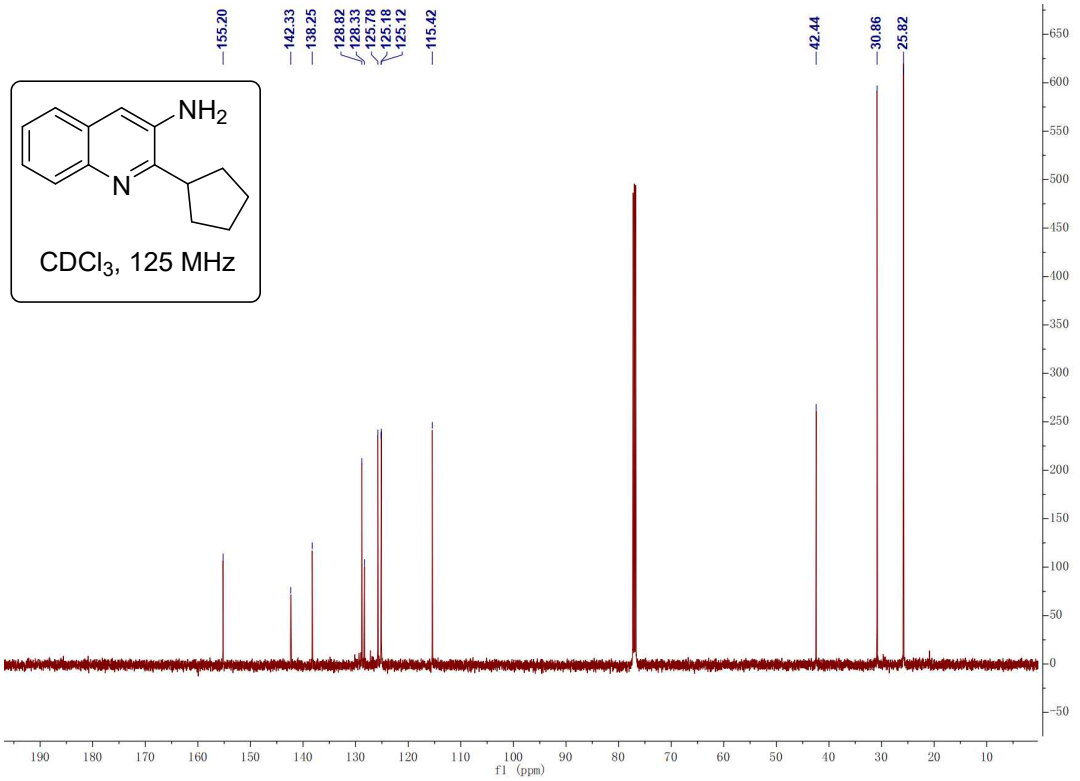
2-(1-methylcyclohexyl)quinolin-3-amine（3b）



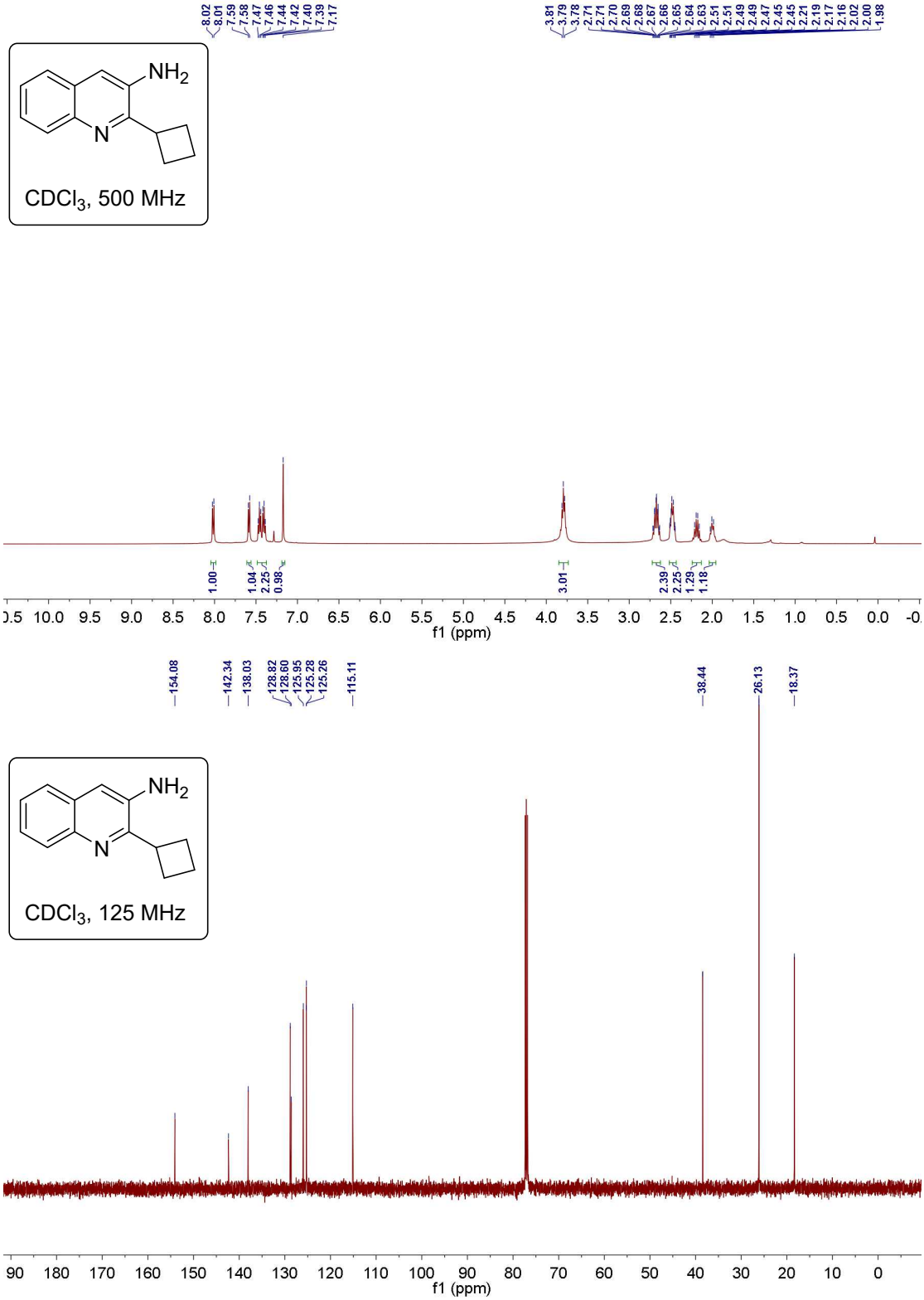


2-cyclopentylquinolin-3-amine（3c）

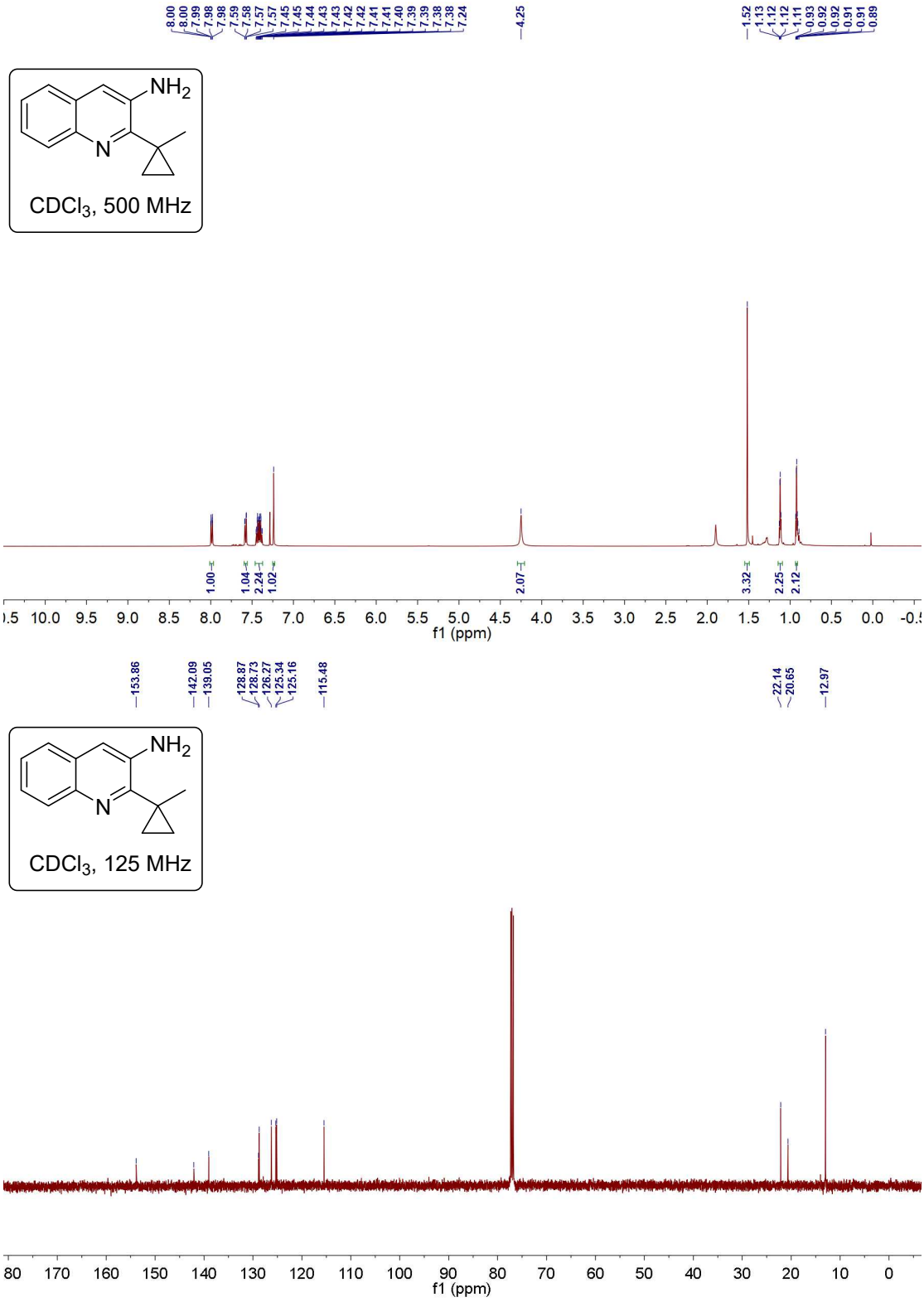




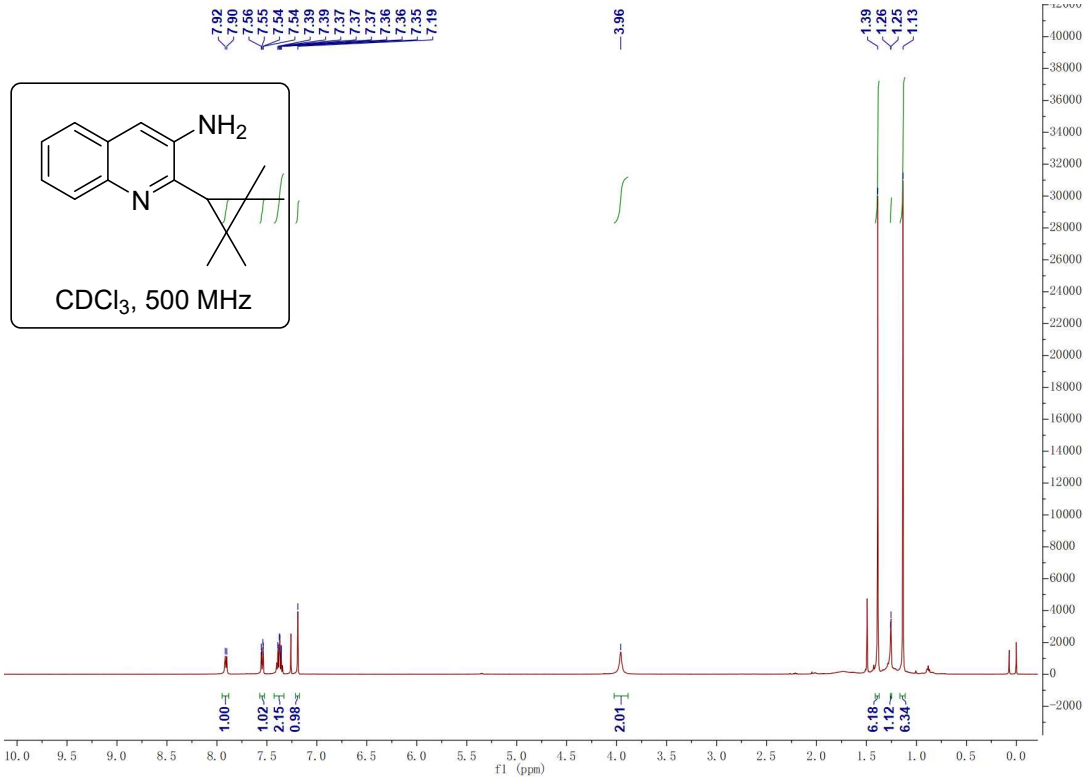
2-cyclobutylquinolin-3-amine(3d)

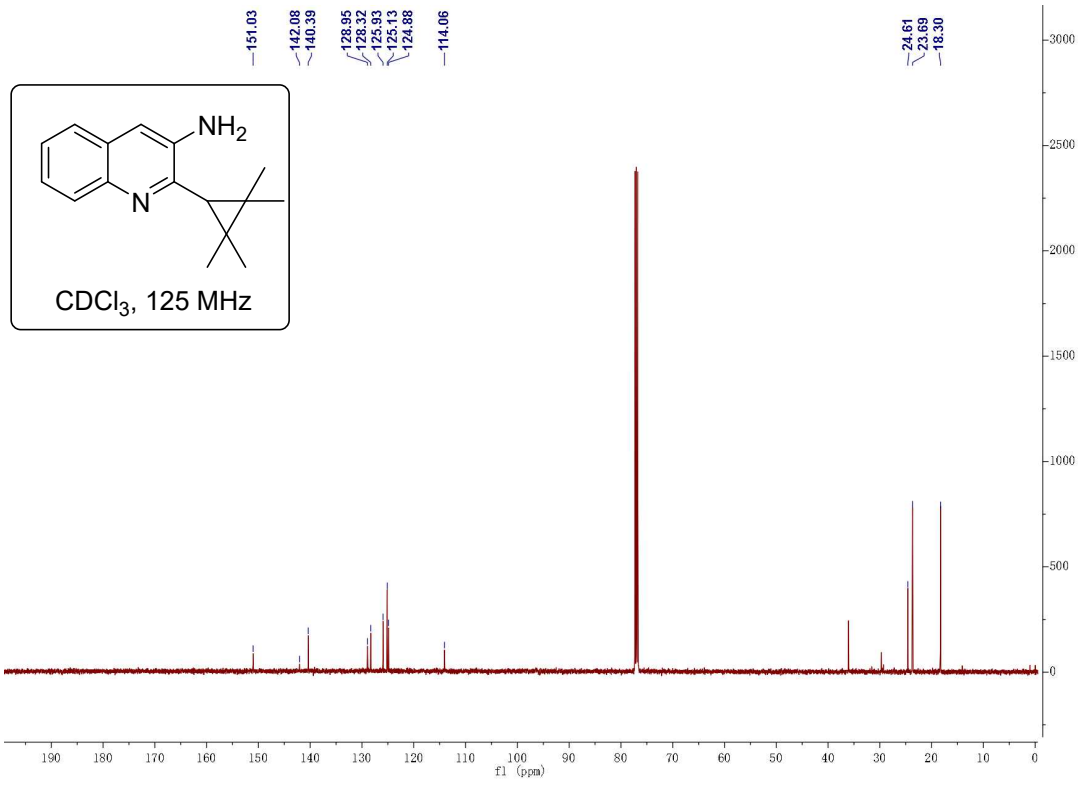


2-(1-methylcyclopropyl)quinolin-3-amine(3e)

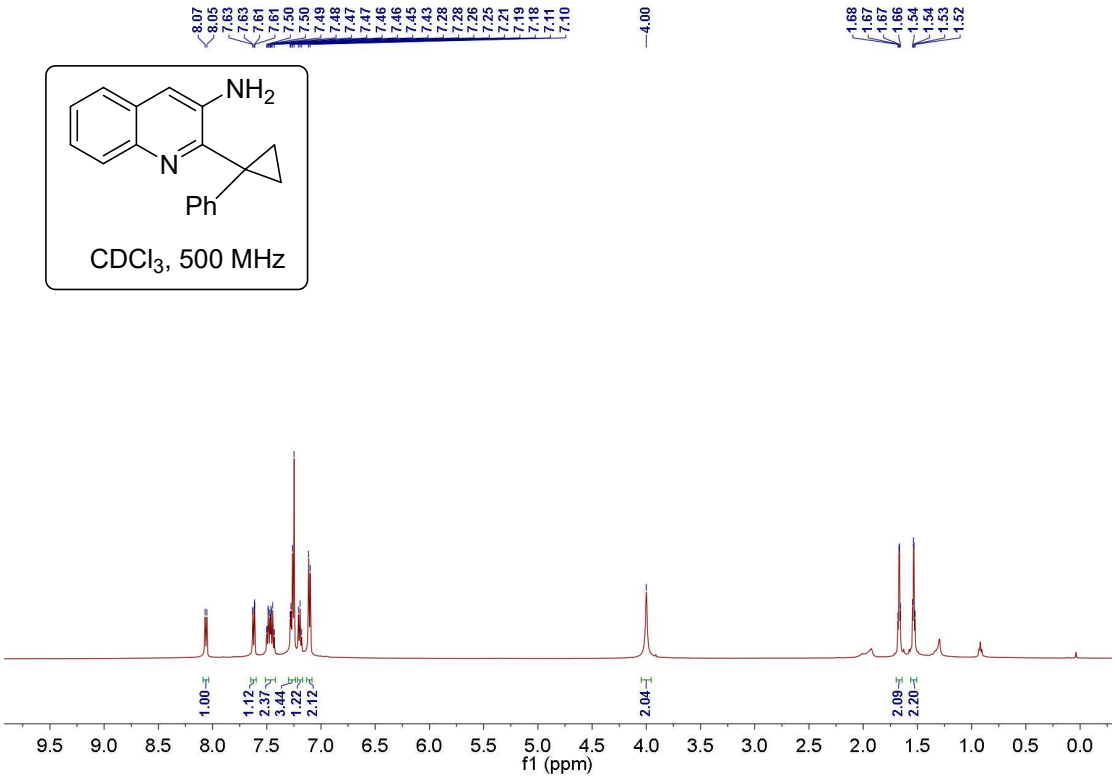


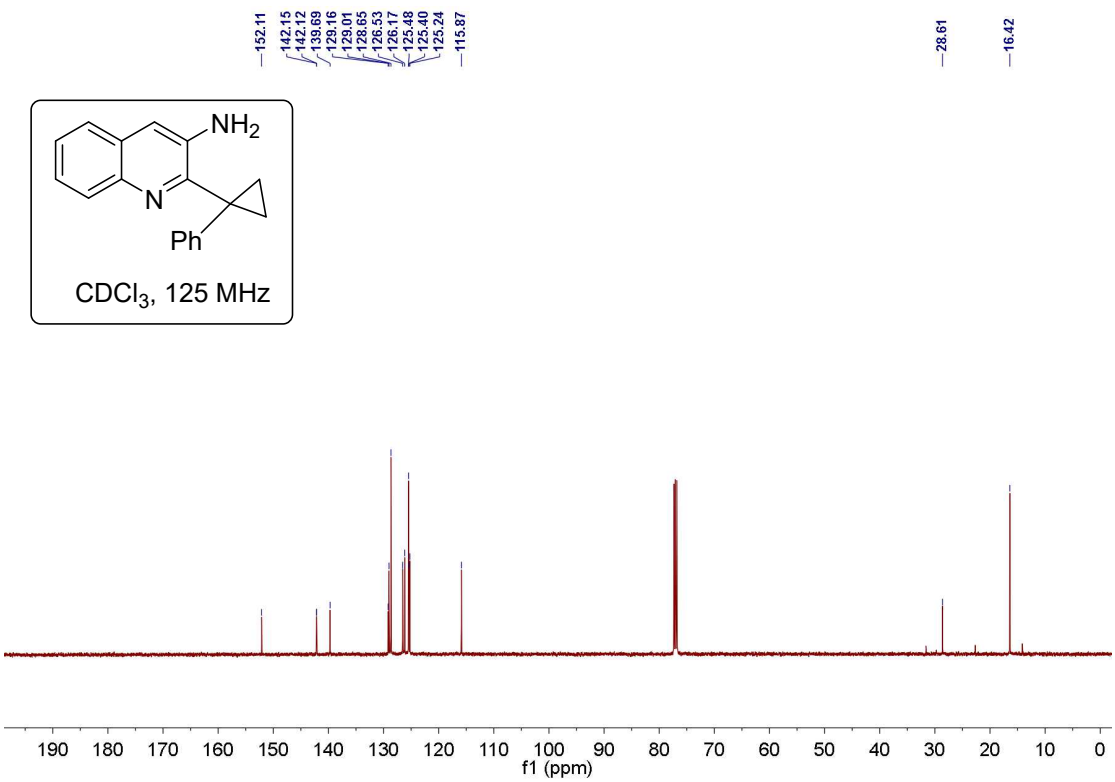
2-(2,2,3,3-tetramethylcyclopropyl)quinolin-3-amine(3f)



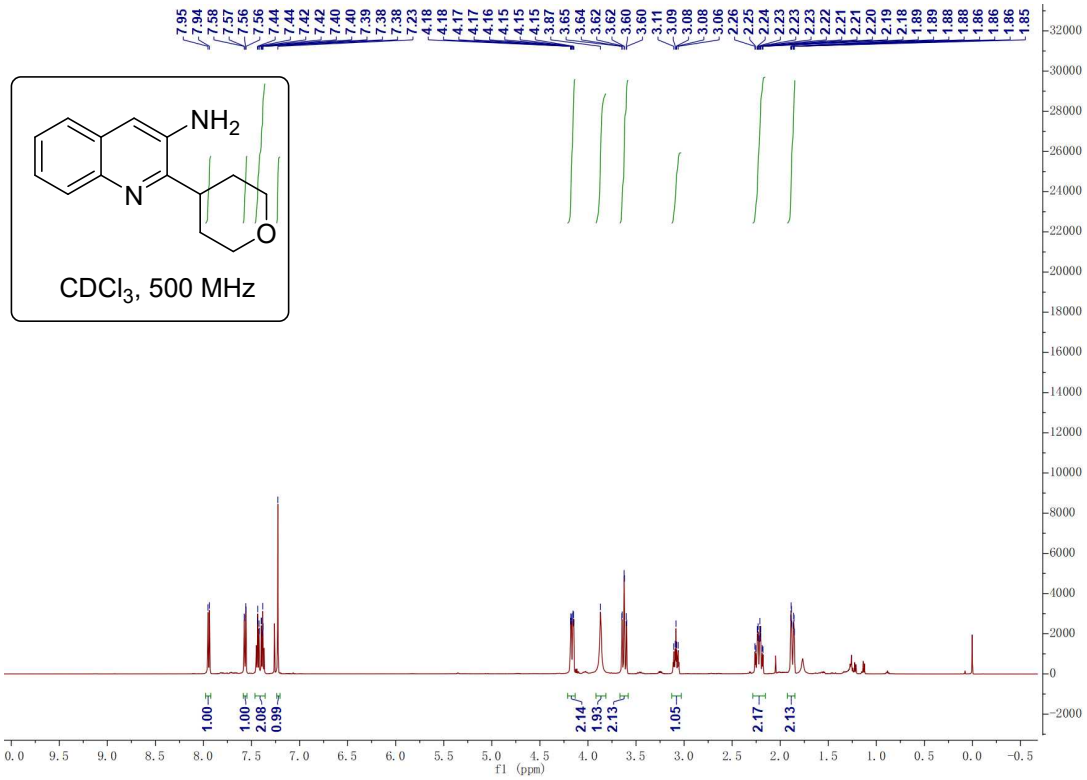


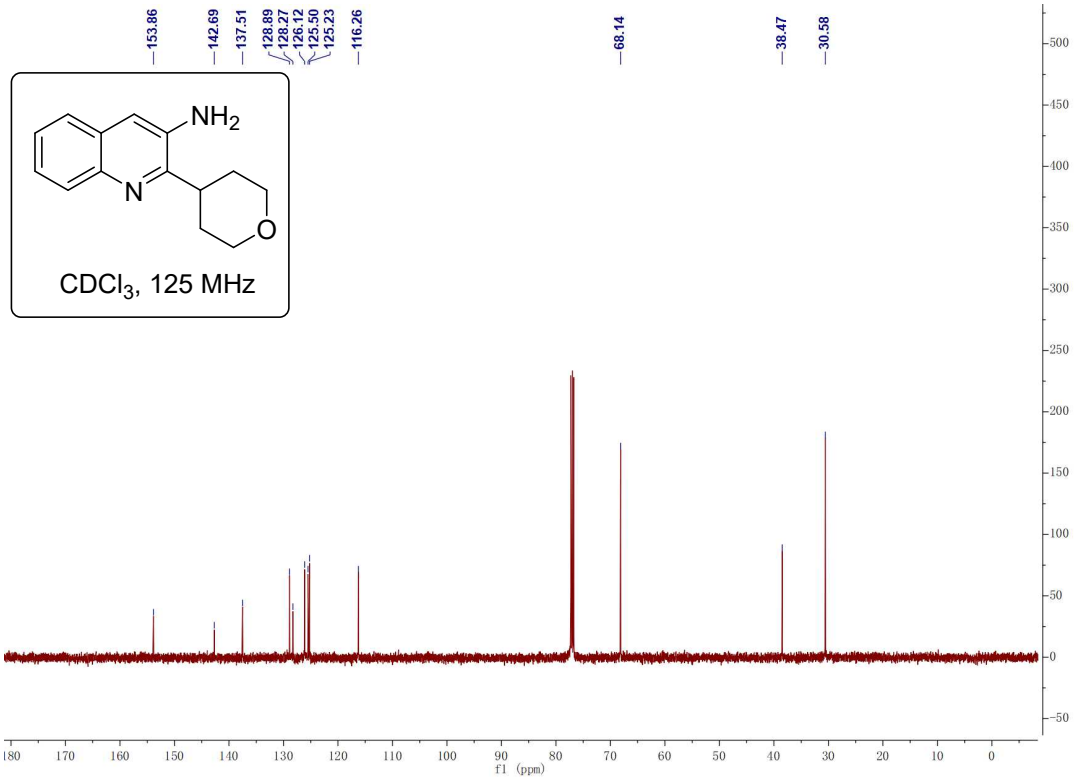
2-(1-phenylcyclopropyl)quinolin-3-amine(3g)



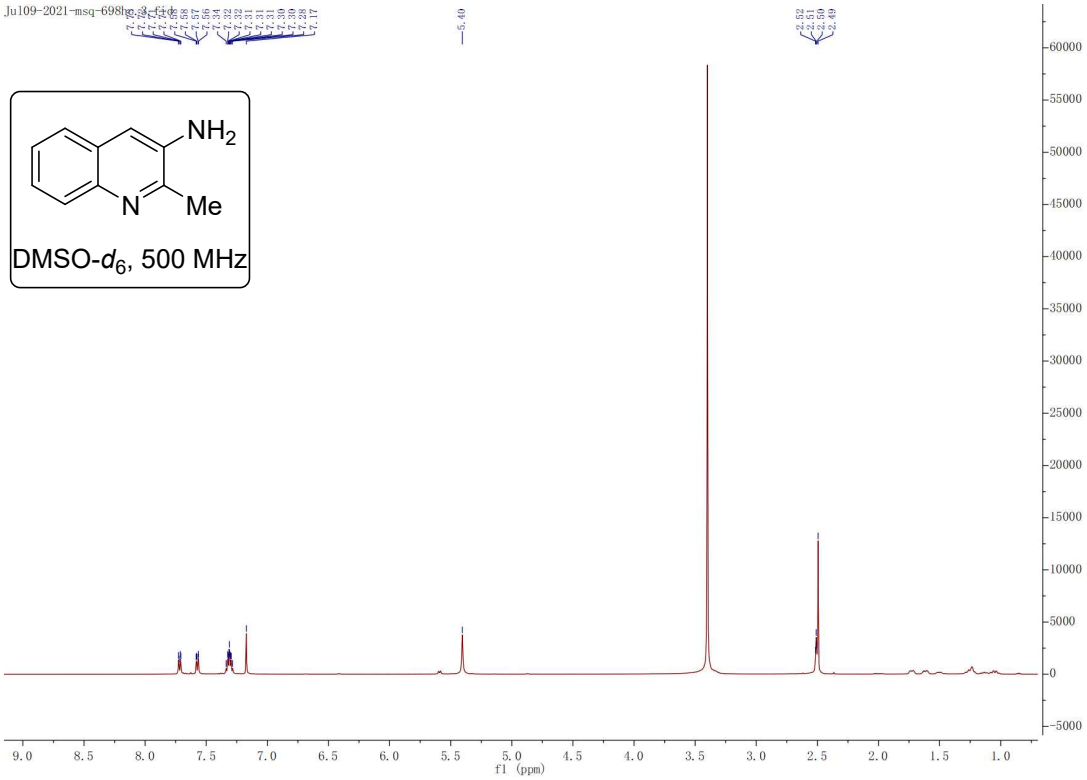


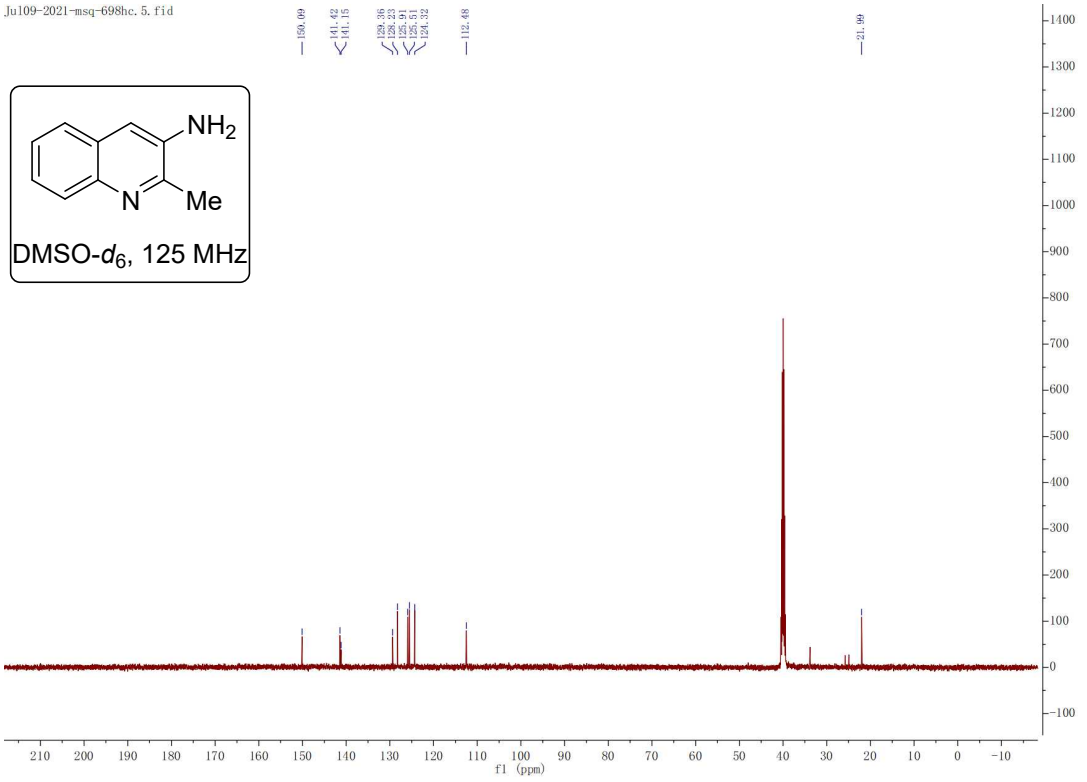
2-(tetrahydro-2H-pyran-4-yl)quinolin-3-amine(3h)



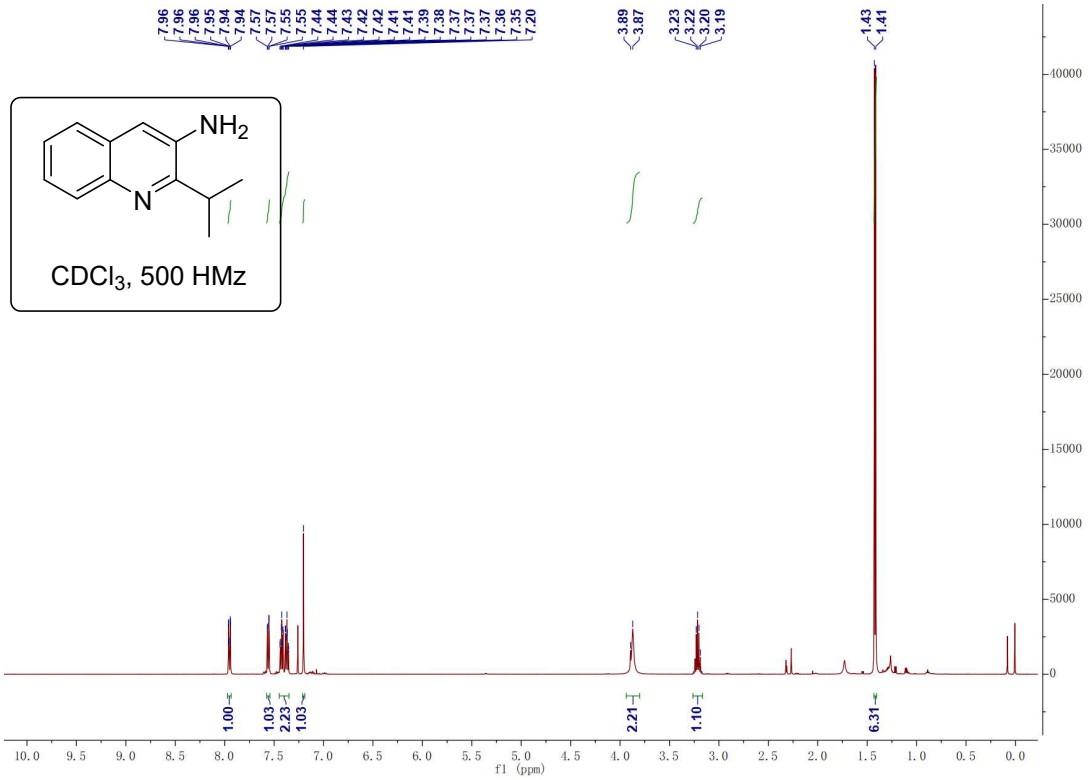


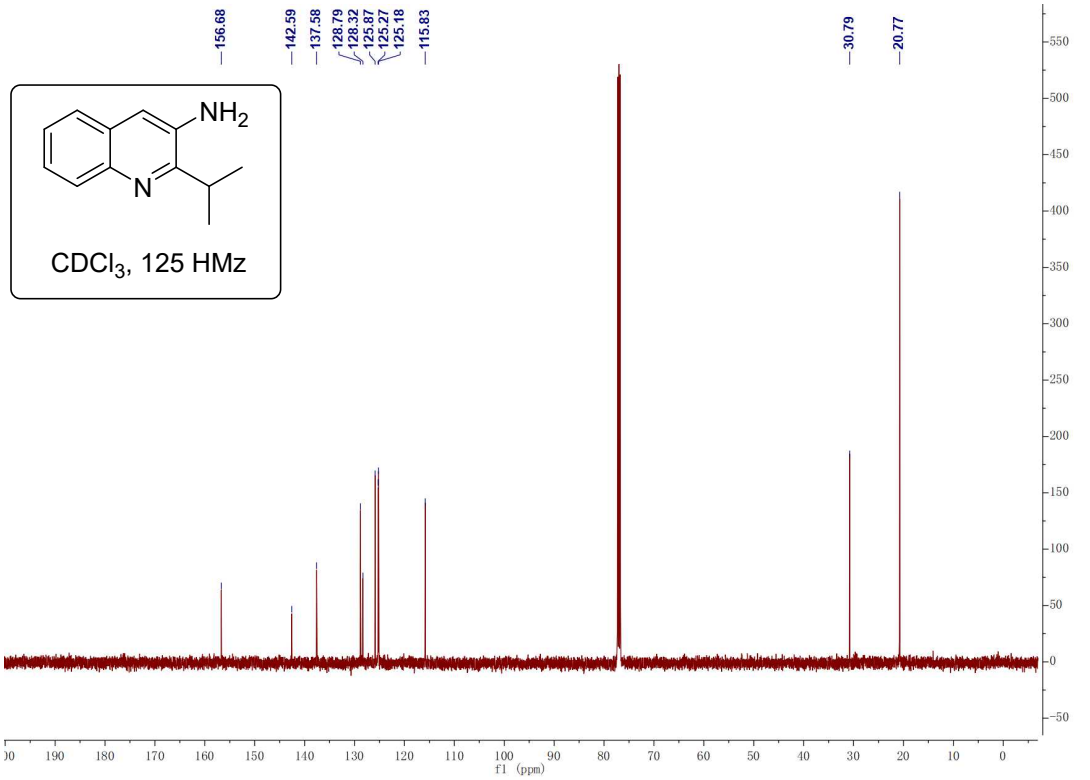
2-methylquinolin-3-amine(3i)



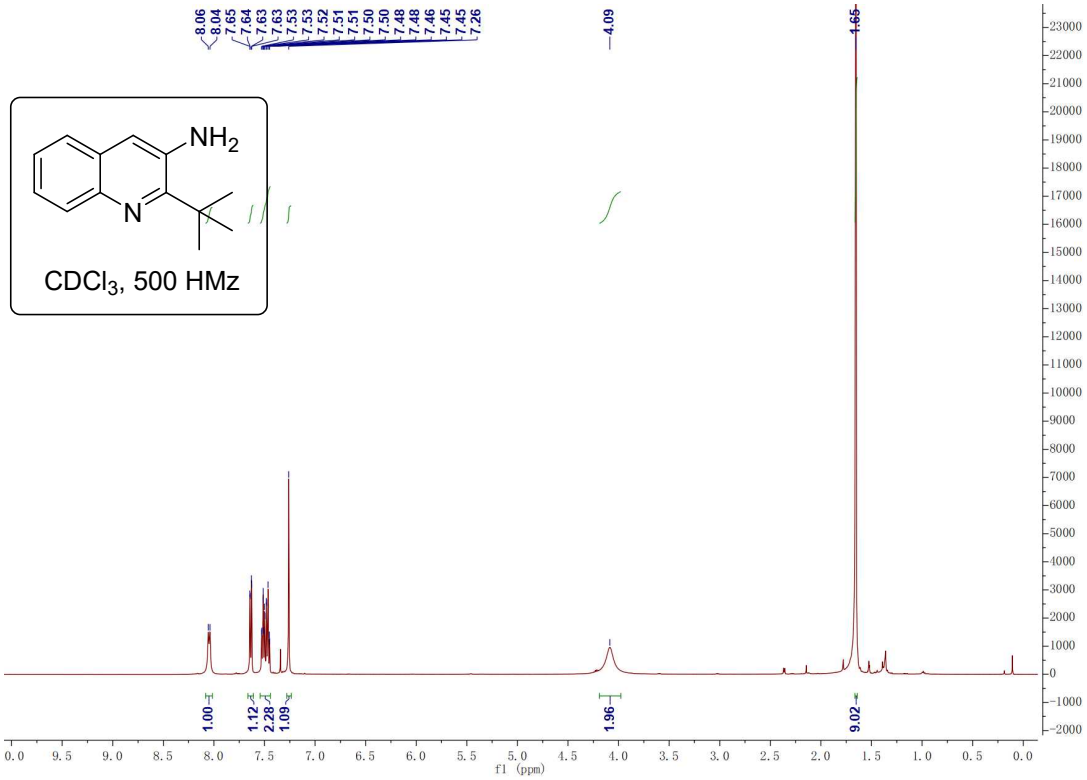


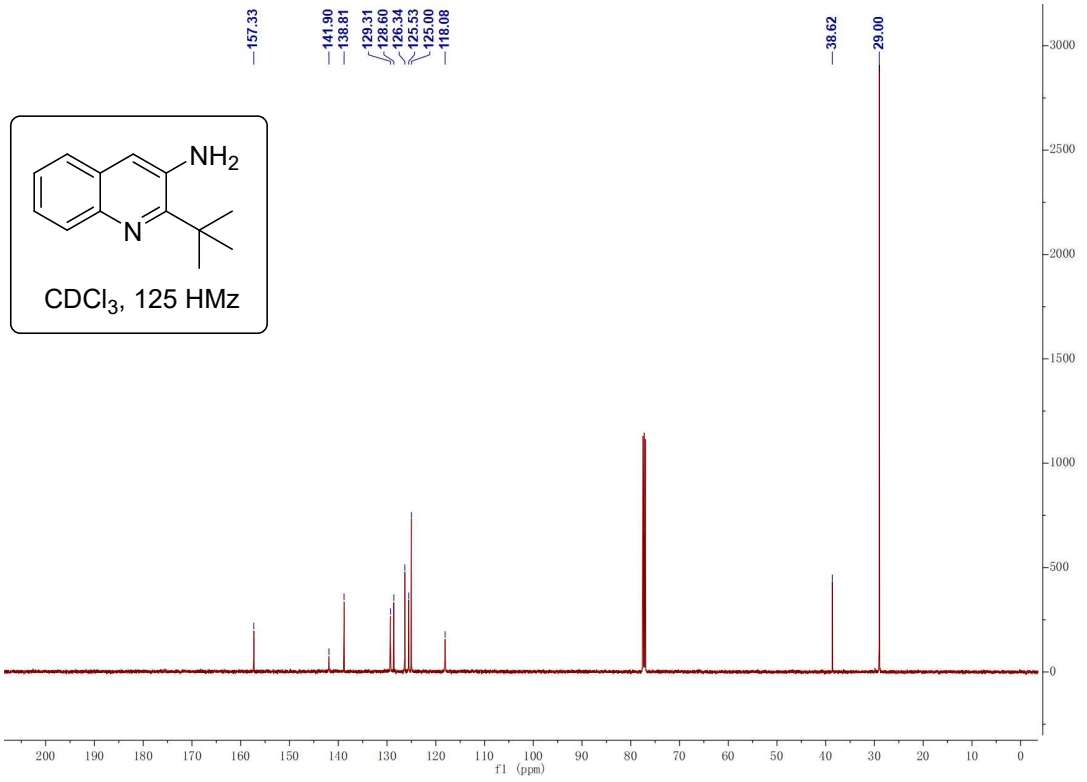
2-isopropylquinolin-3-amine（3j）



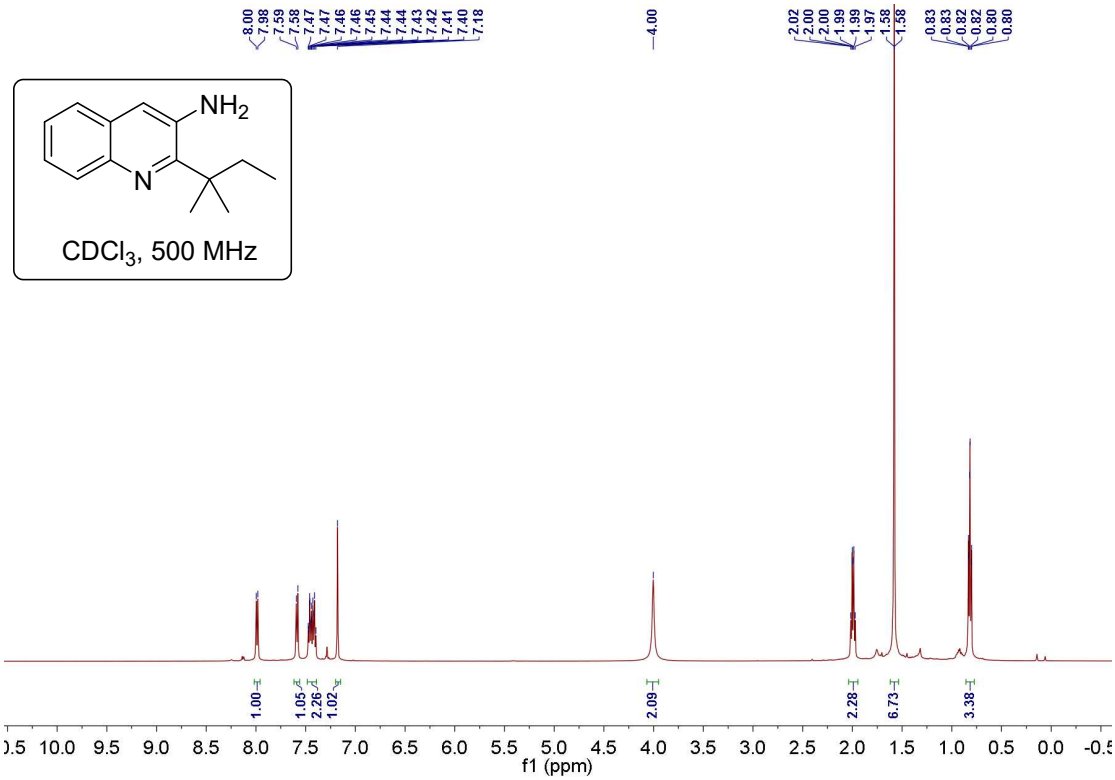


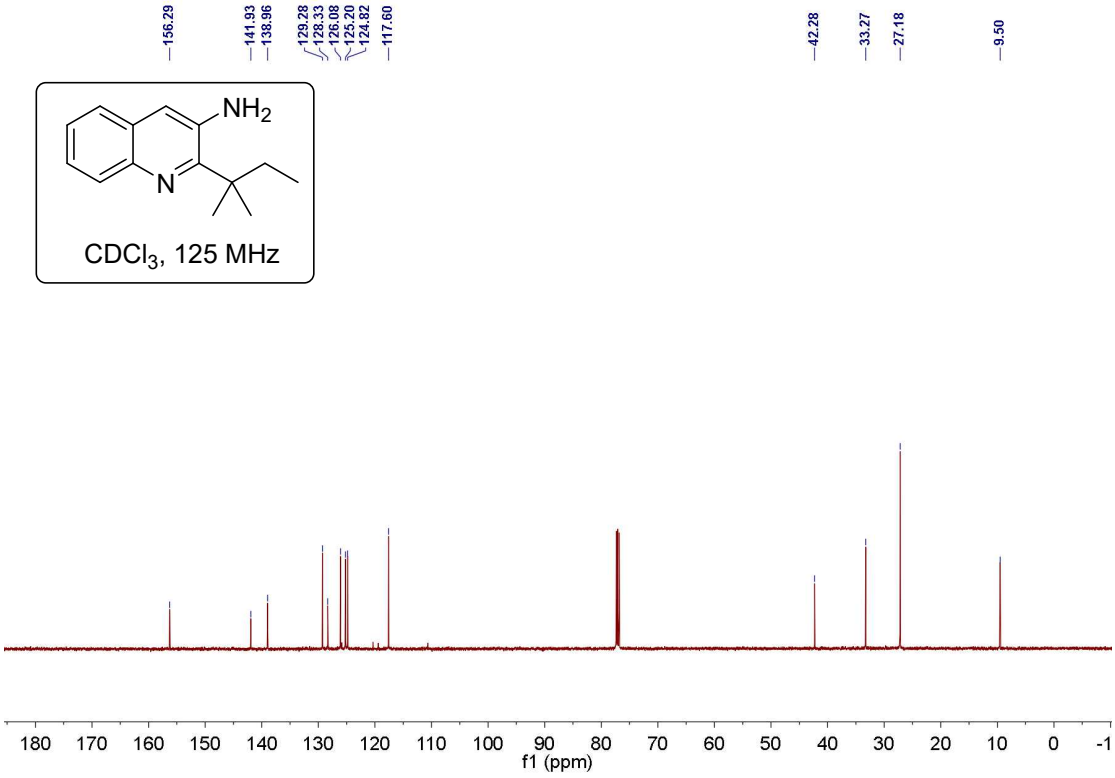
2-(tert-butyl)quinolin-3-amine(3k)



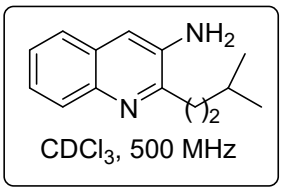


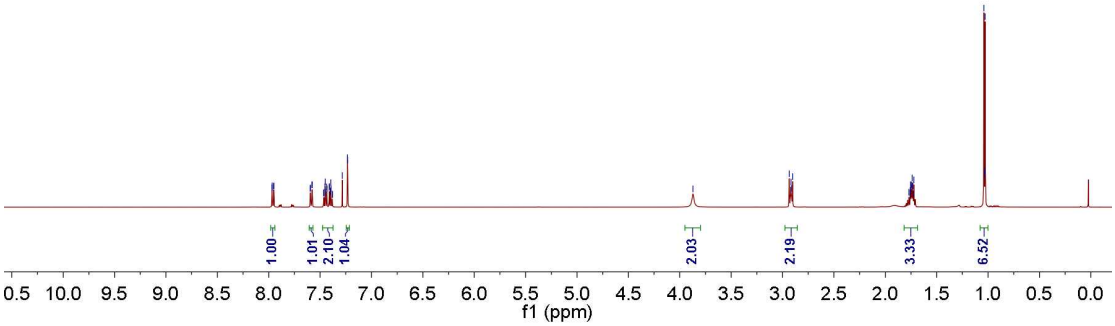
2-(tert-pentyl)quinolin-3-amine(3l)

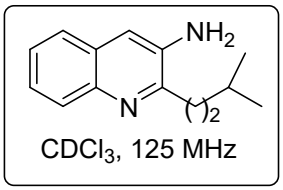




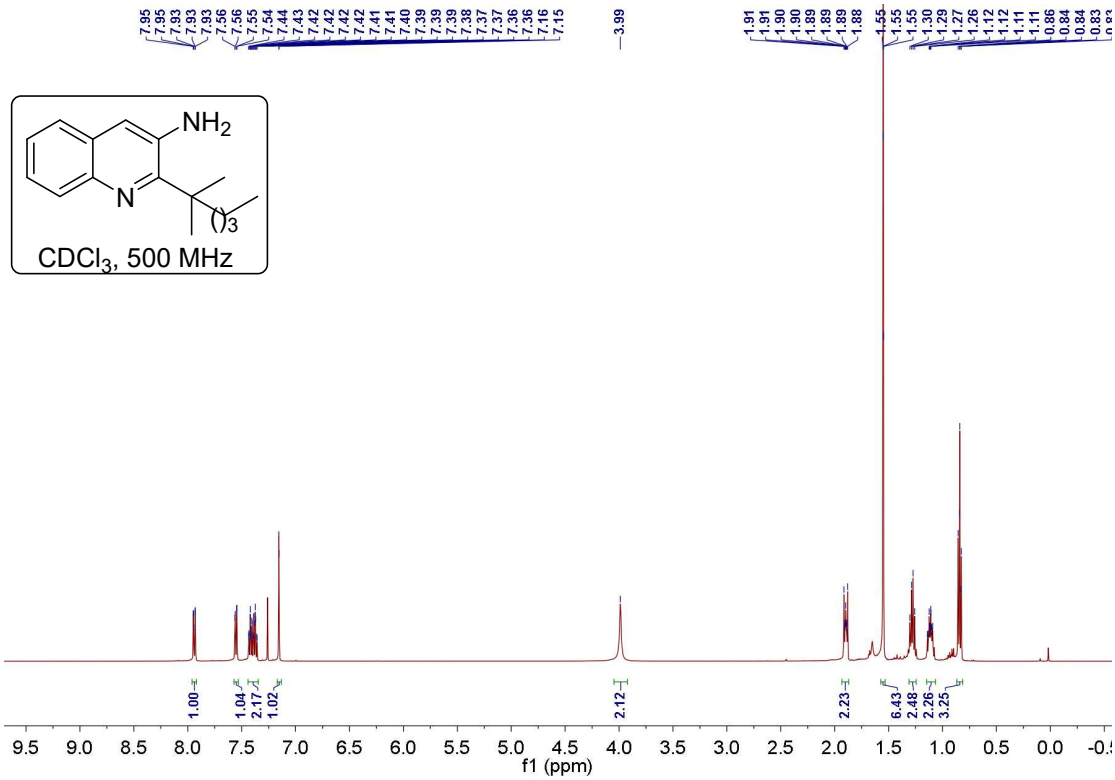
2-(4-methylpentyl)quinolin-3-amine)(3m)

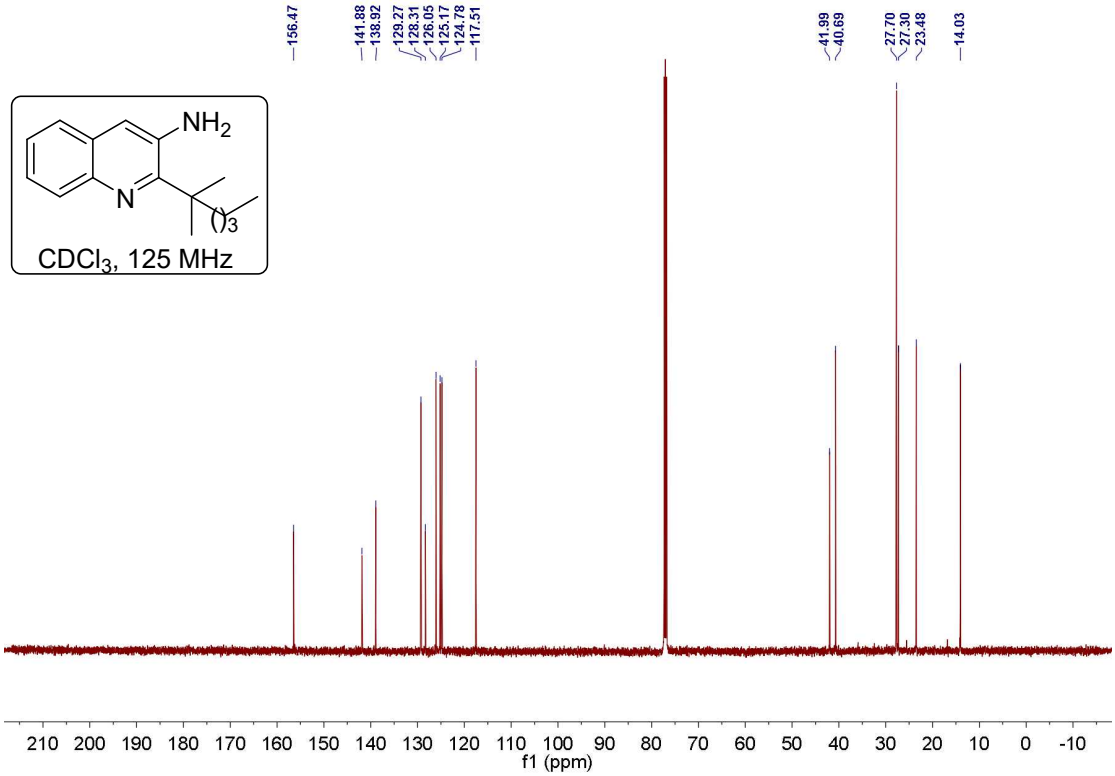




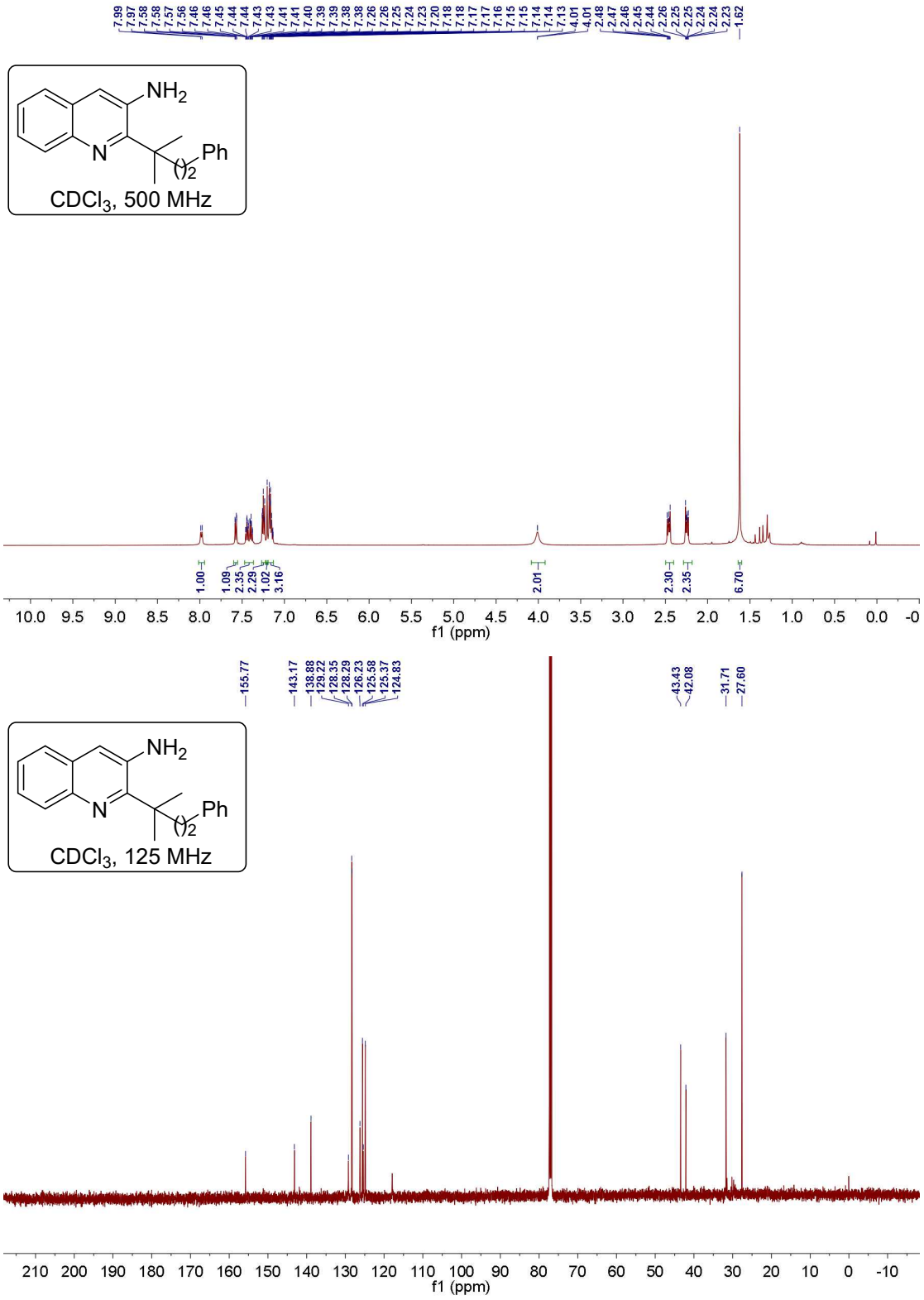


2-(tert-pentyl)quinolin-3-amine (3n)

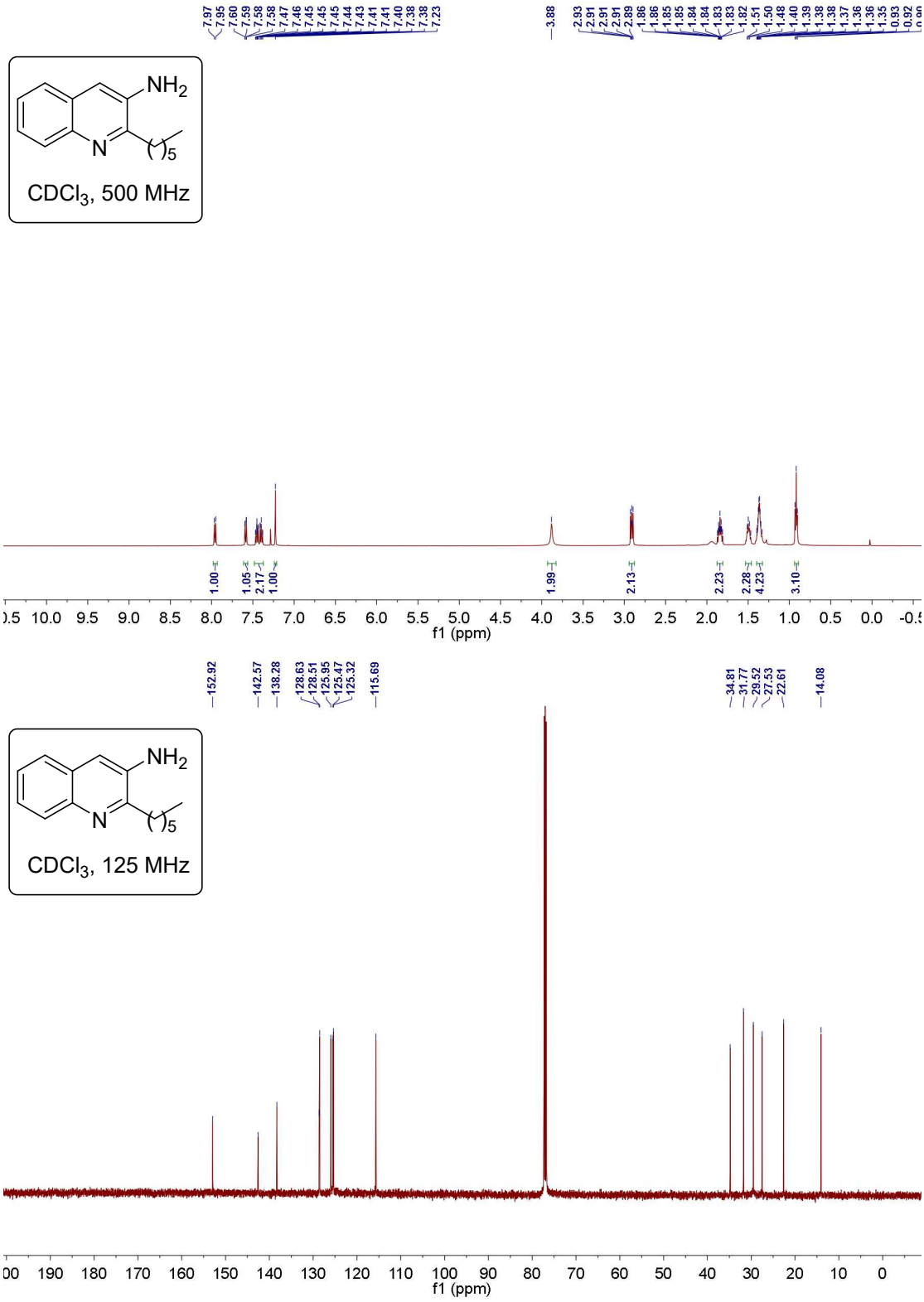




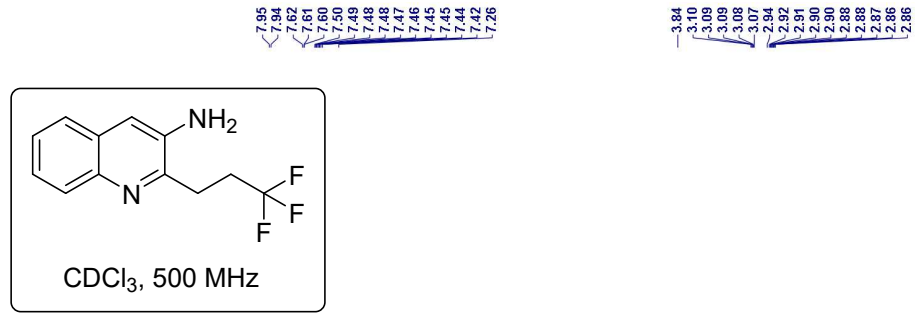
2-(2-methyl-1-phenylpropan-2-yl)quinolin-3-amine(3o)

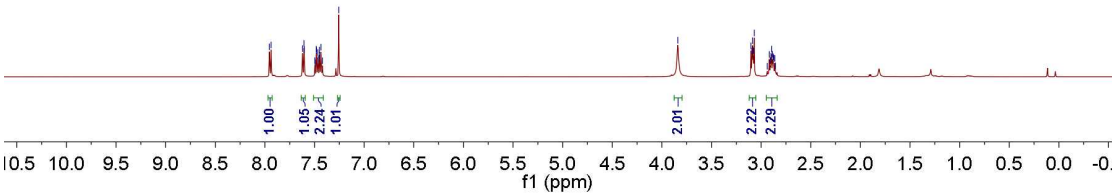


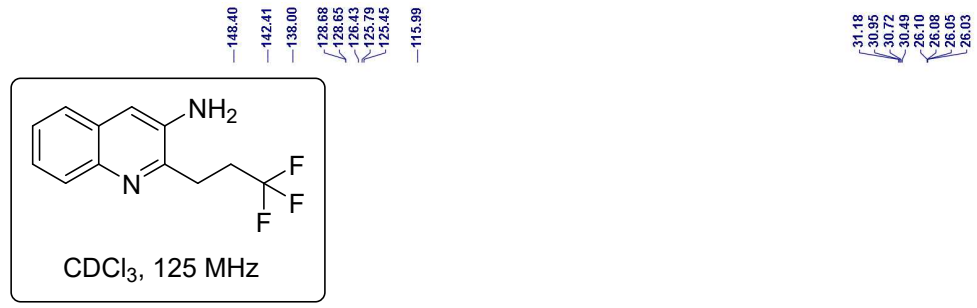
2-hexylquinolin-3-amine(3p)

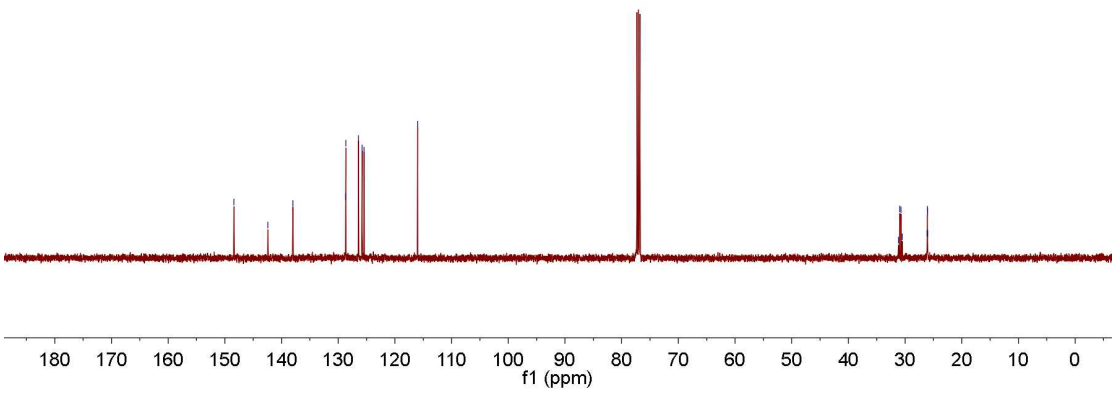


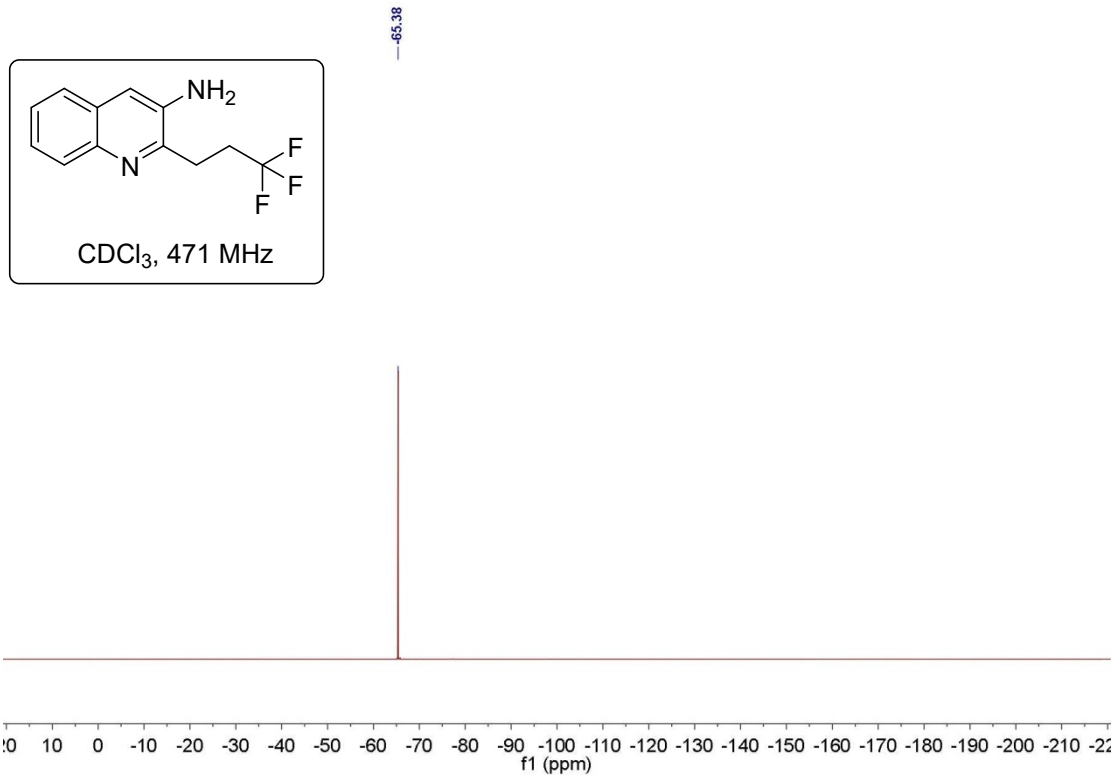
2-(3,3,3-trifluoropropyl)quinolin-3-amine（3q）



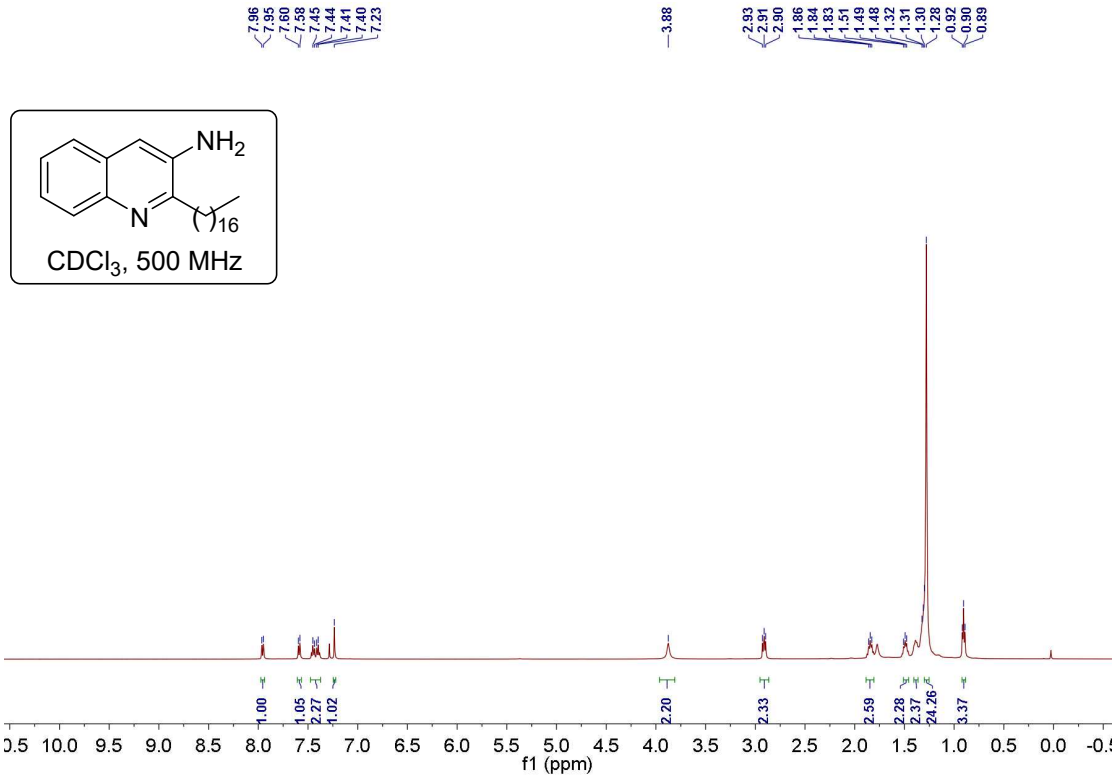


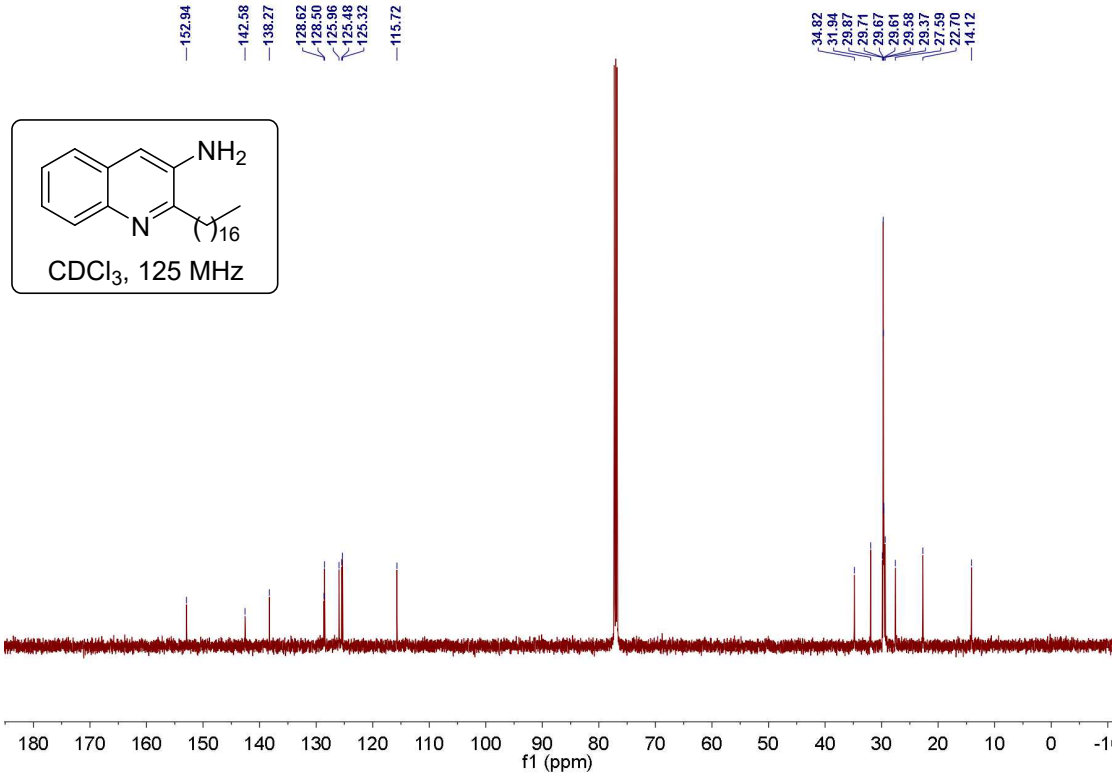




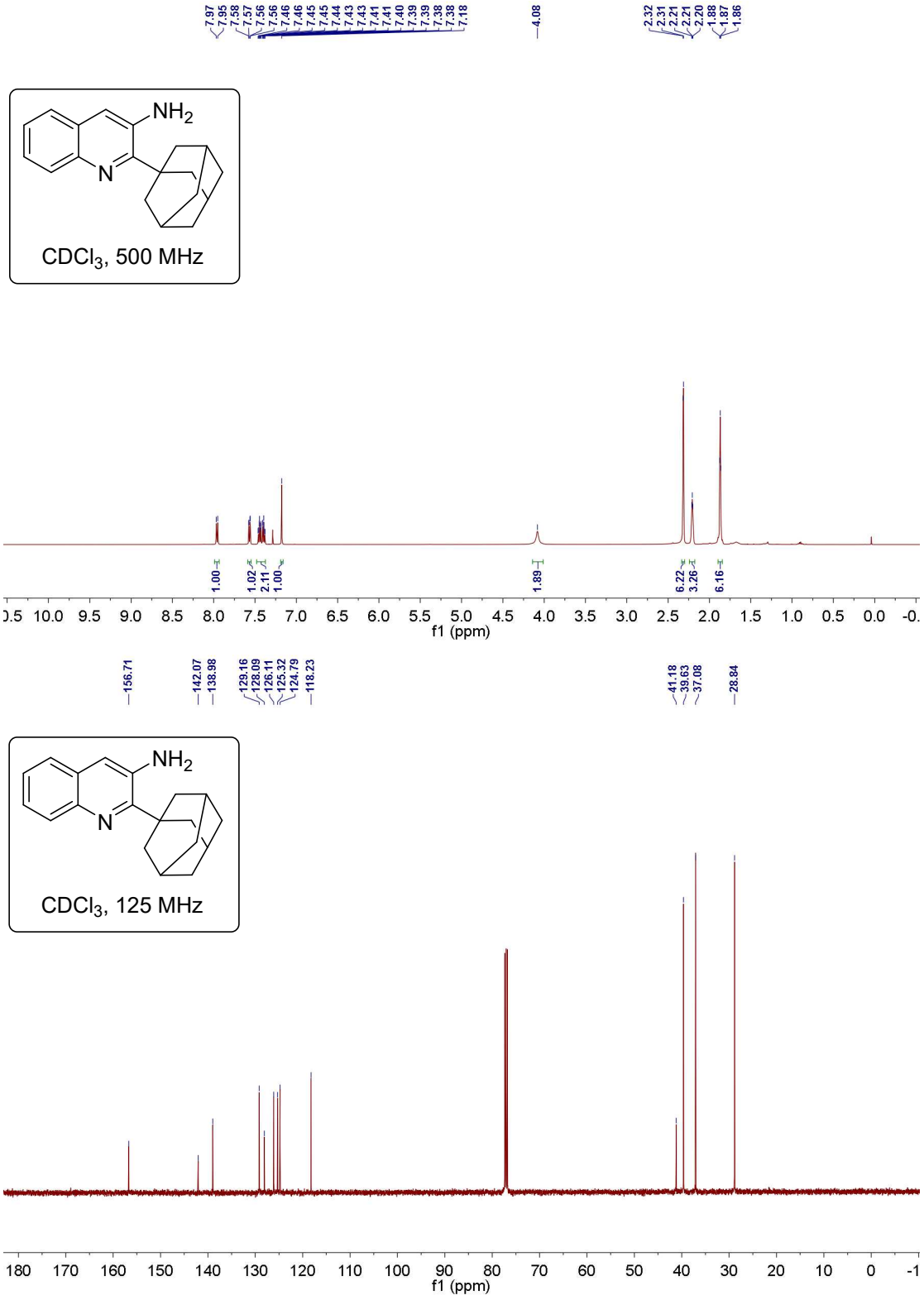

-65.38
NH2
N
F
F
F
CDCl3, 471 MHz
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

2-ethylquinolin-3-amine（3r）

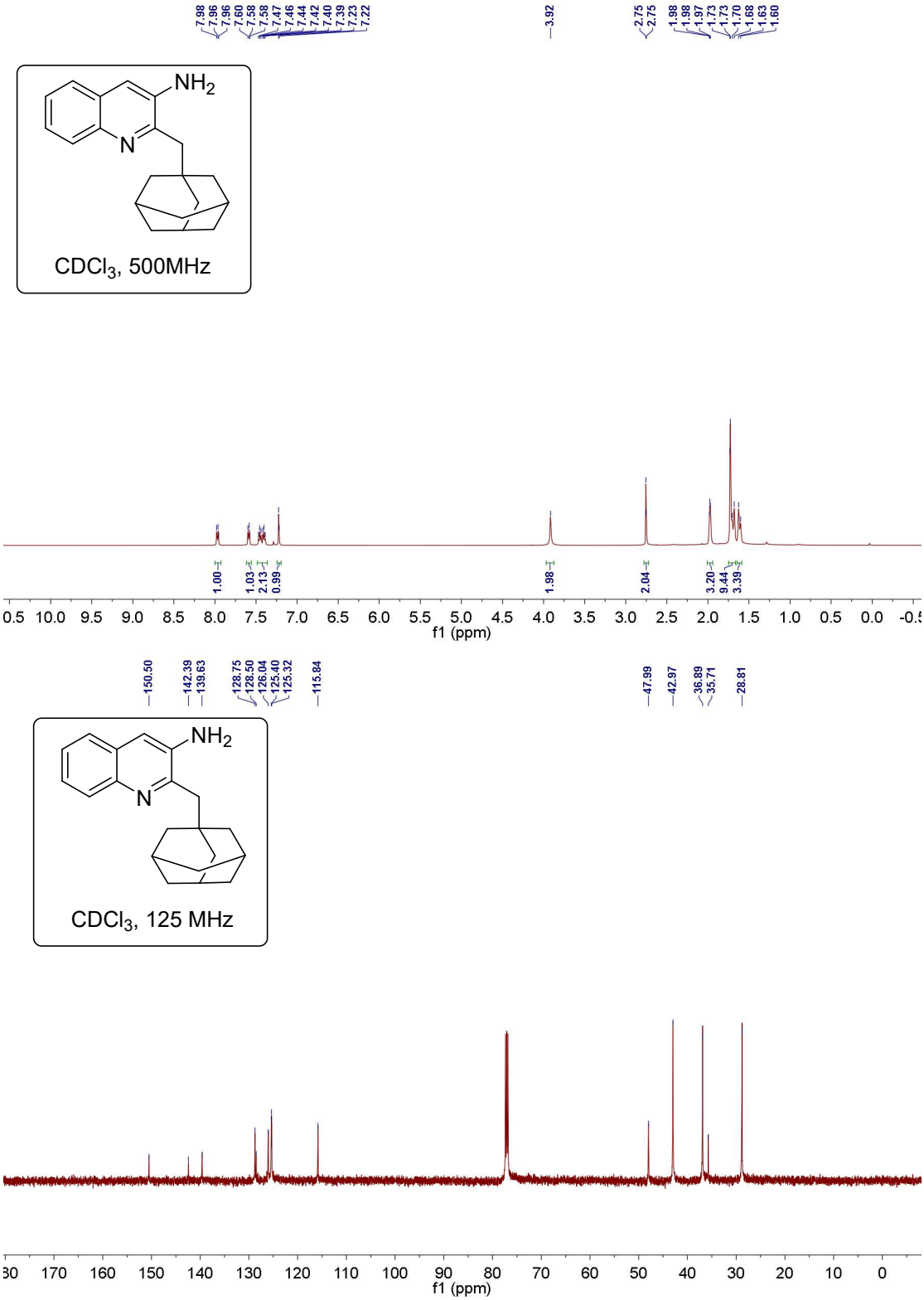




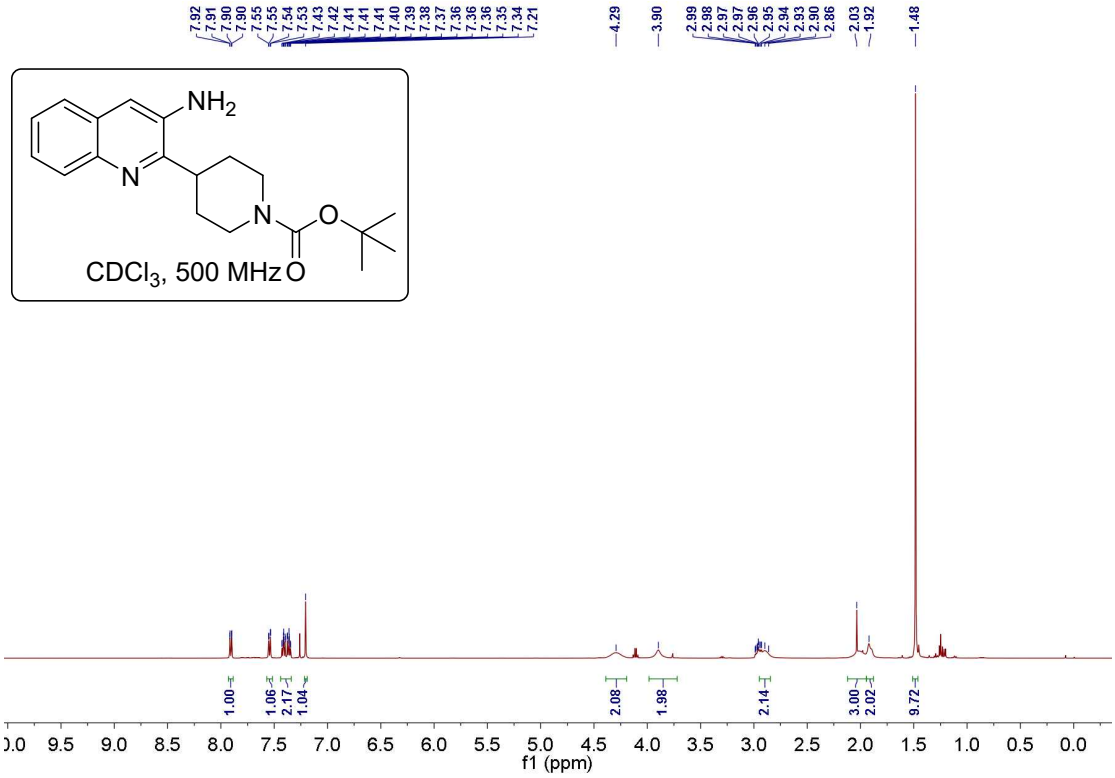
2-(adamantan-1-yl)quinolin-3-amine（3s）

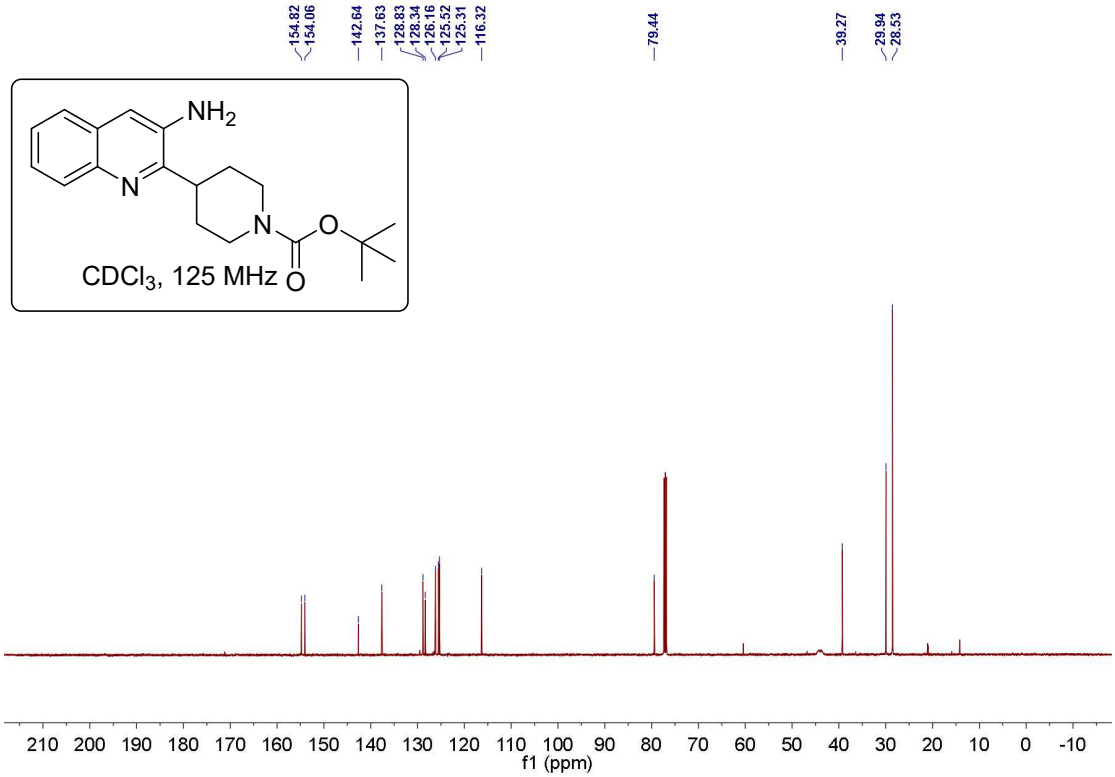


2-(adamantan-1-ylmethyl)quinolin-3-amine(3t)

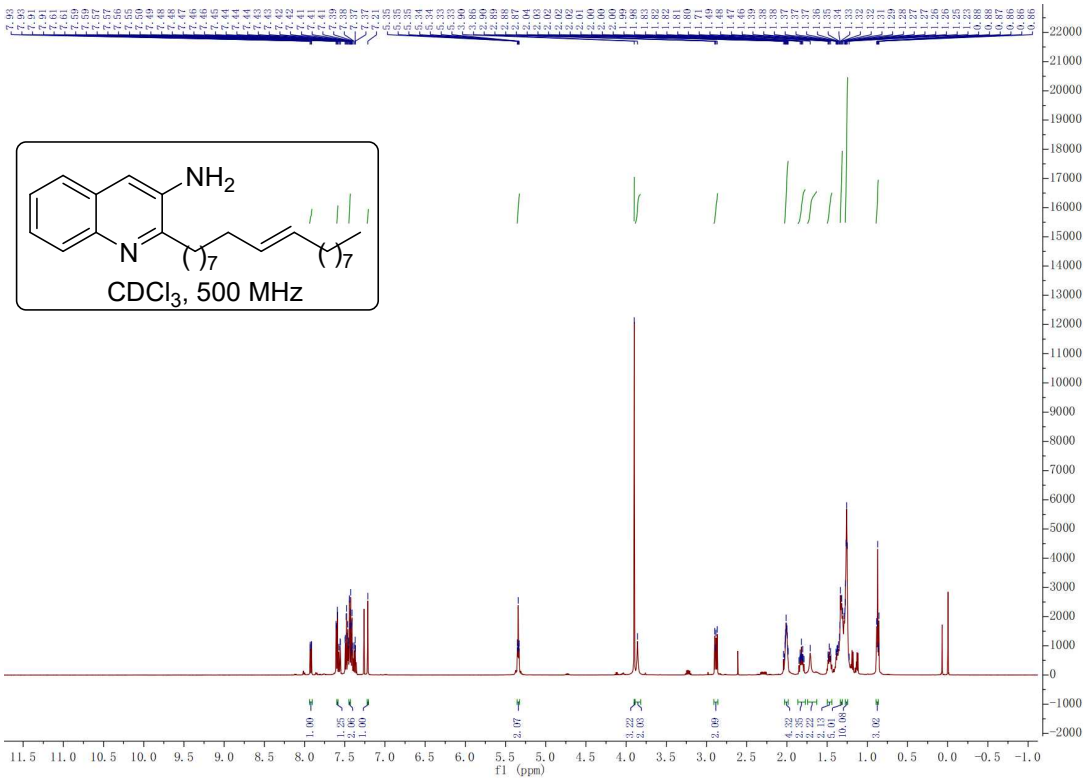


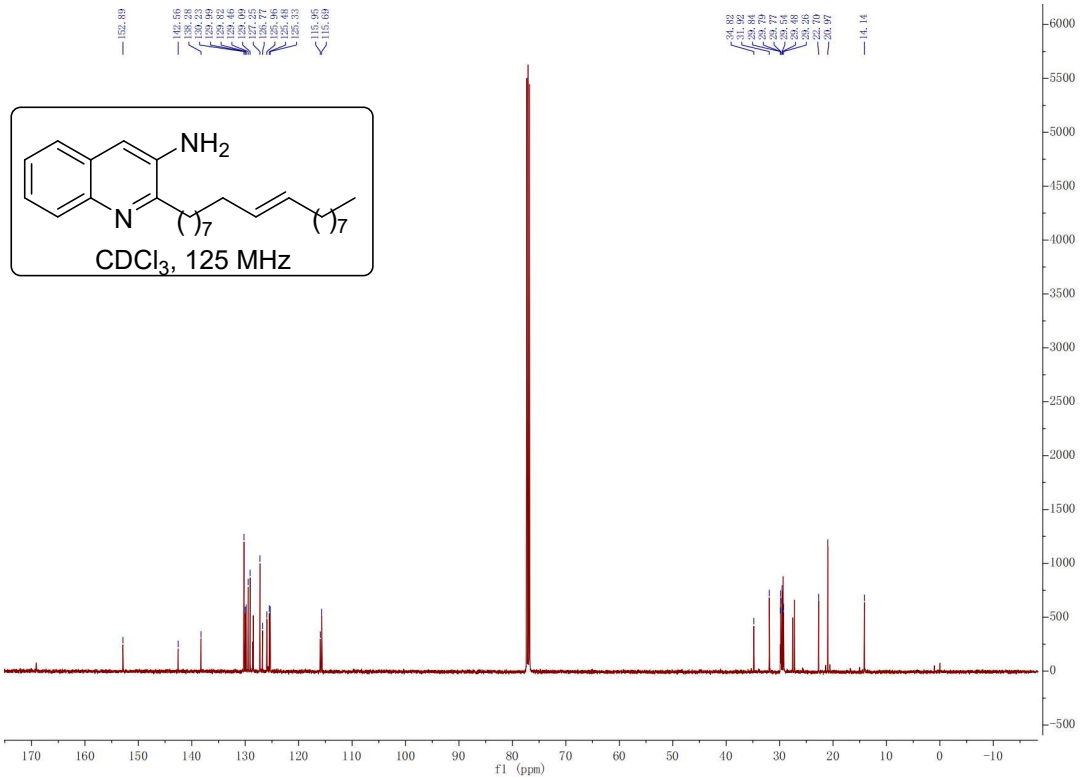
tert-butyl 4-(3-aminoquinolin-2-yl)piperidine-1-carboxylate (3u)



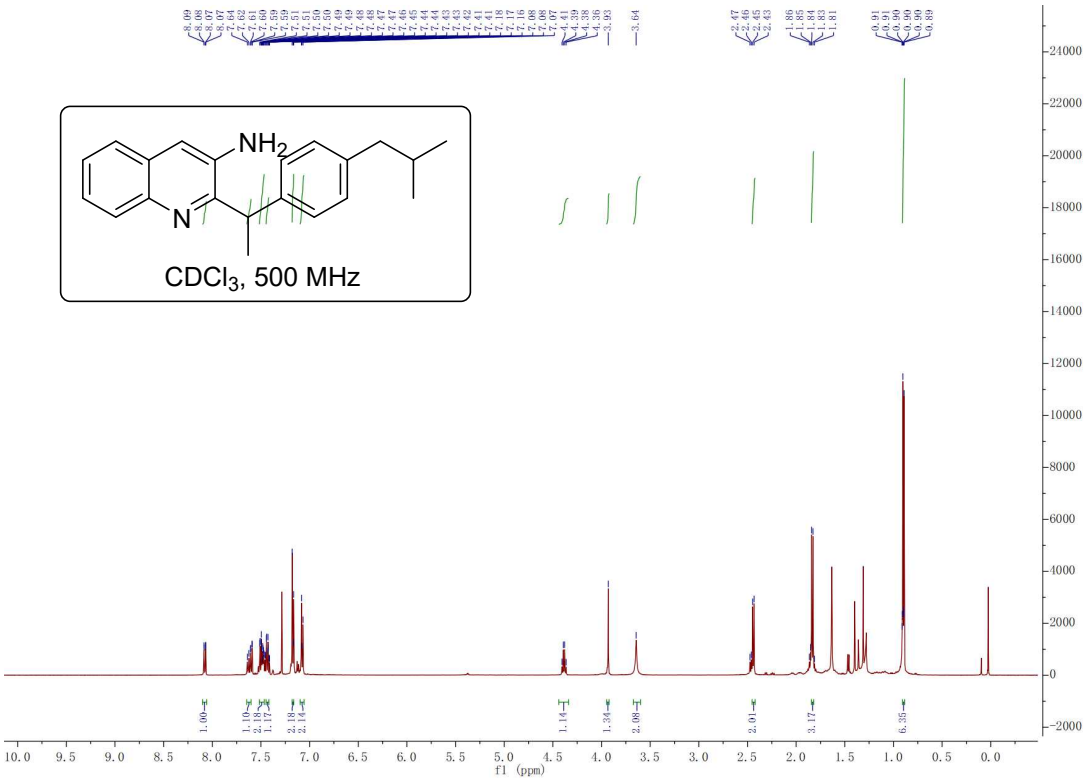


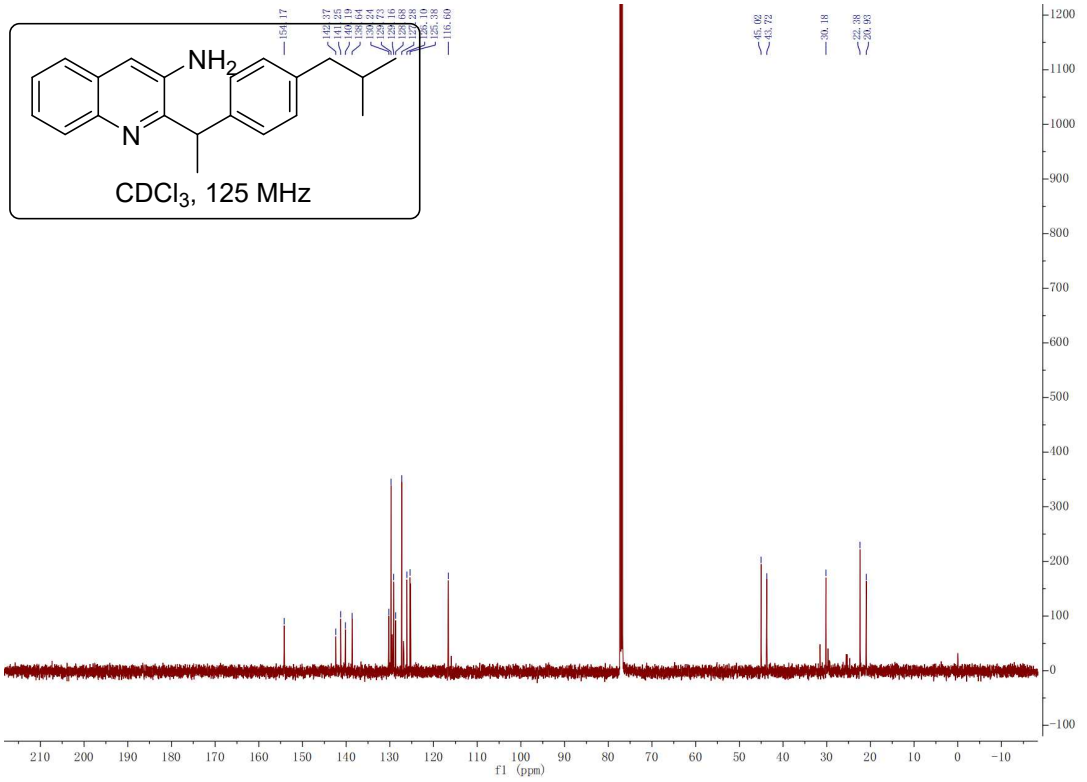
(E)-2-(octadec-9-en-1-yl)quinolin-3-amine (3v)



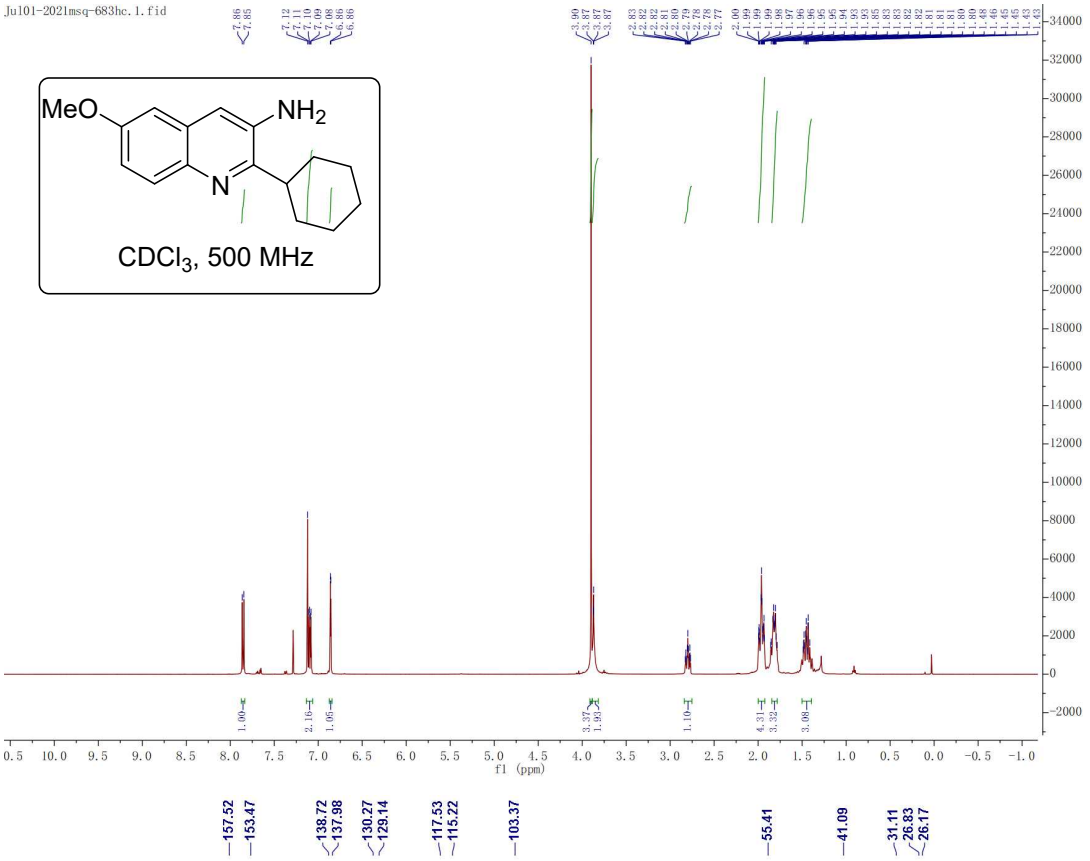


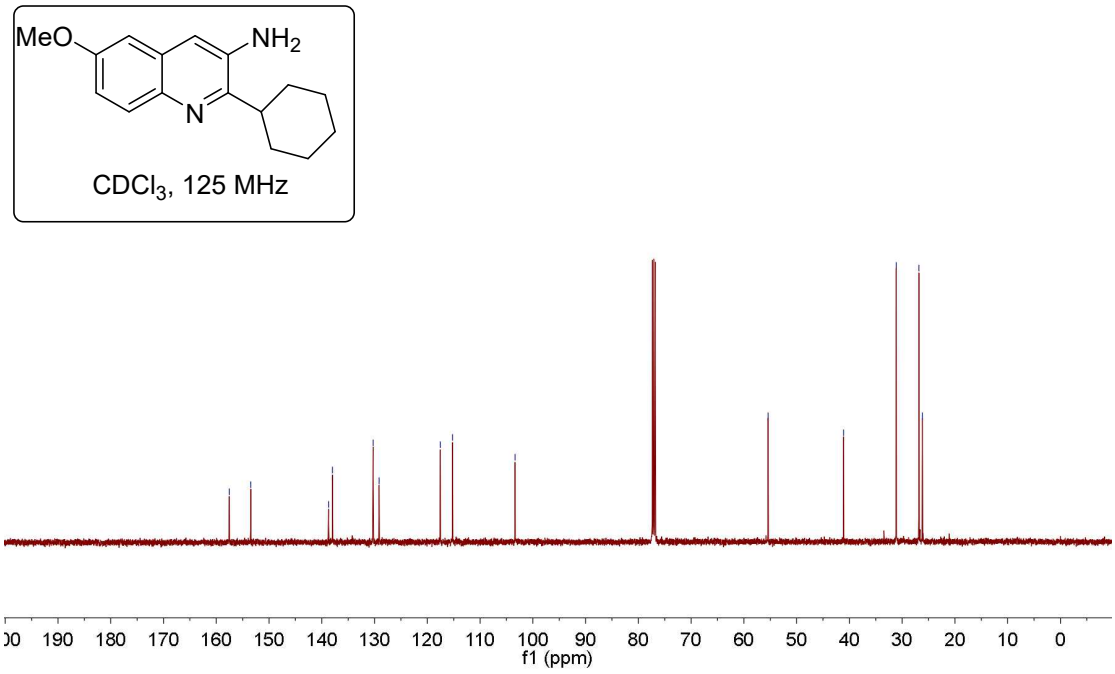
2-(1-(4-isobutylphenyl)ethyl)quinolin-3-amine (3w)



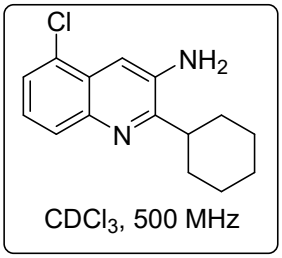


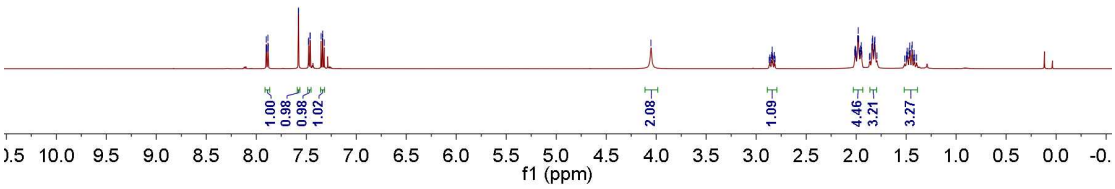
2-cyclohexyl-6-methoxyquinolin-3-amine（4a）

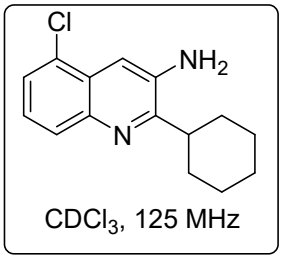


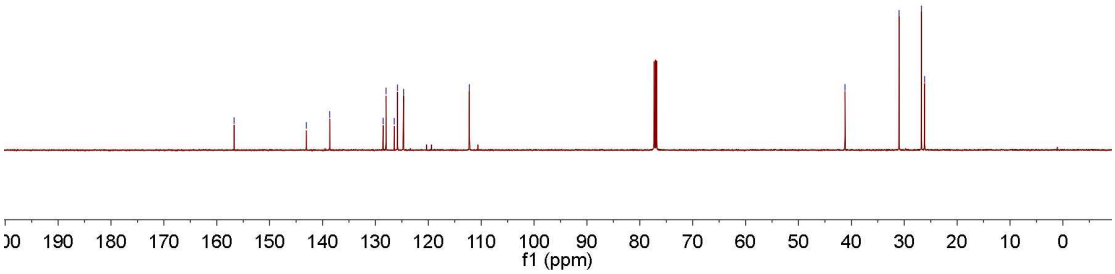


5-chloro-2-cyclohexylquinolin-3-amine(4b)

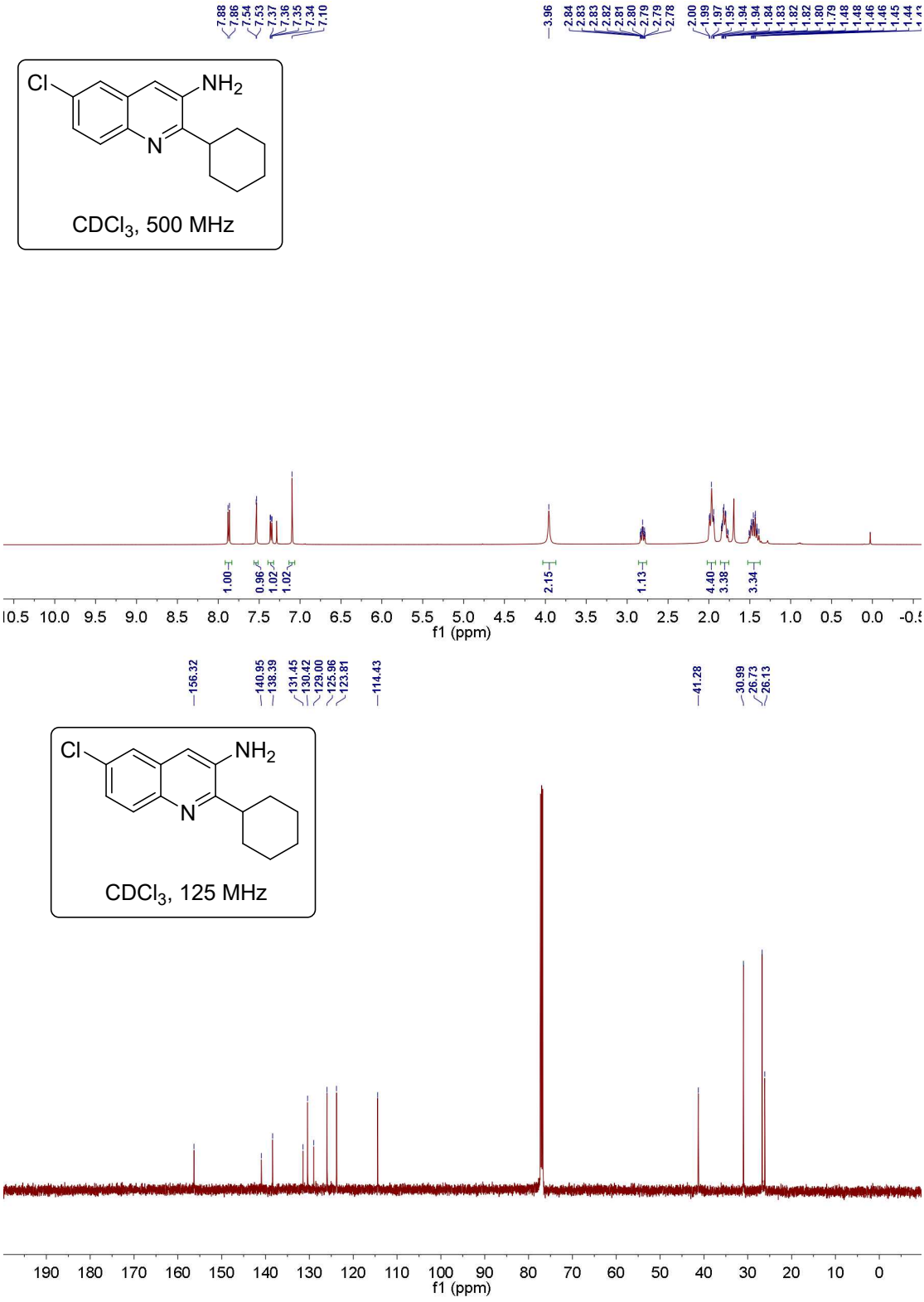




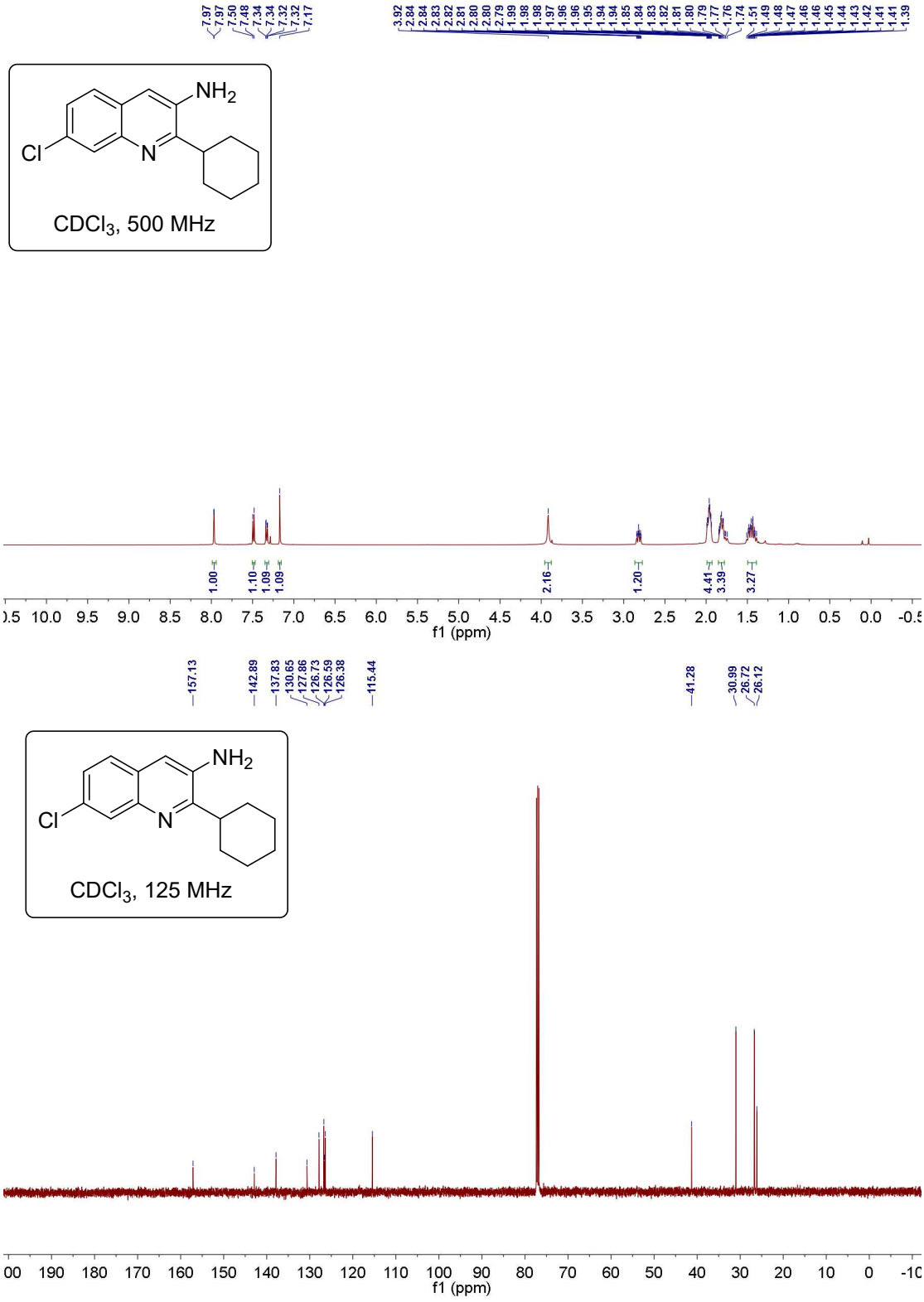




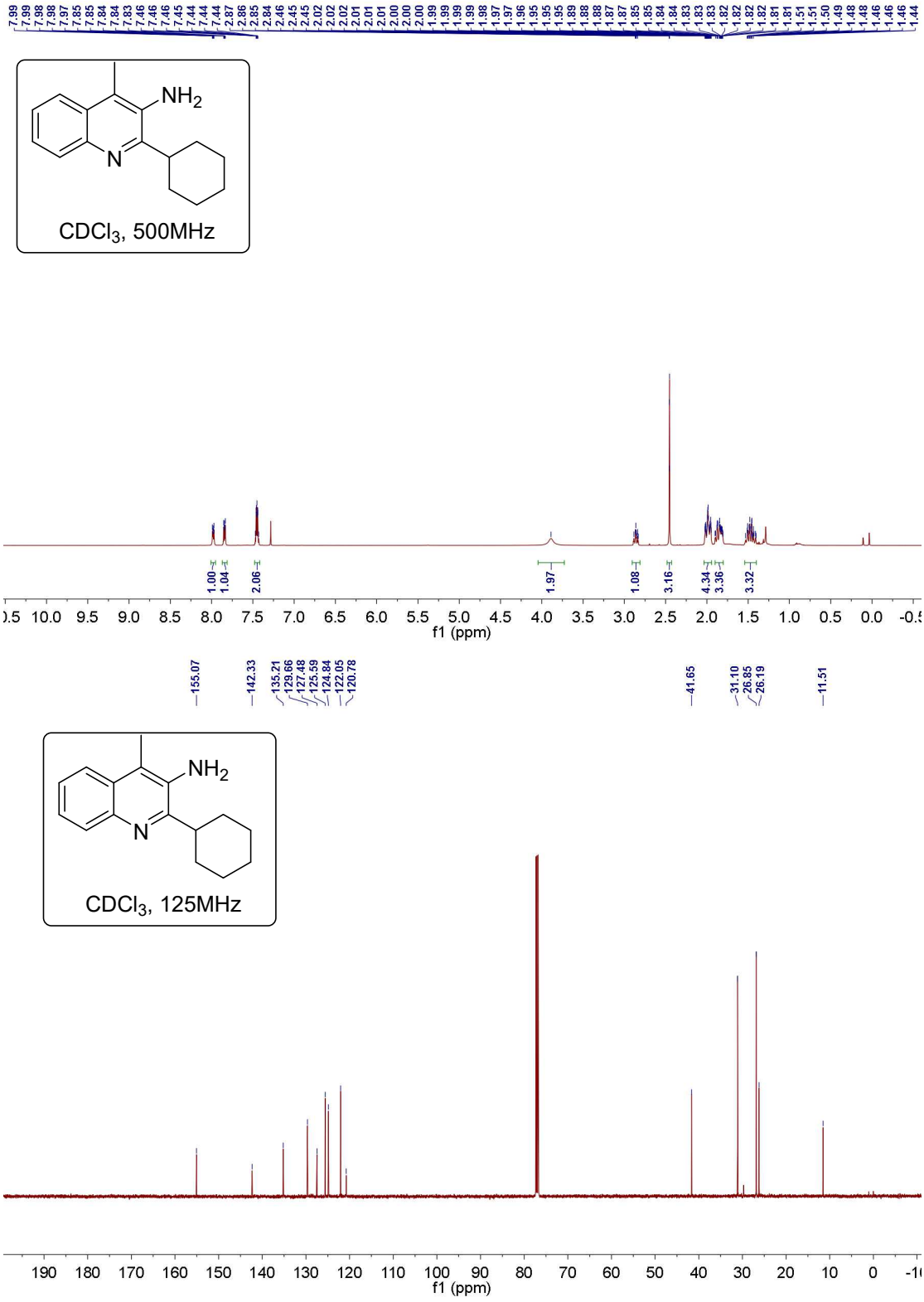
6-chloro-2-cyclohexylquinolin-3-amine(4c)



7-chloro-2-cyclohexylquinolin-3-amine(4d)

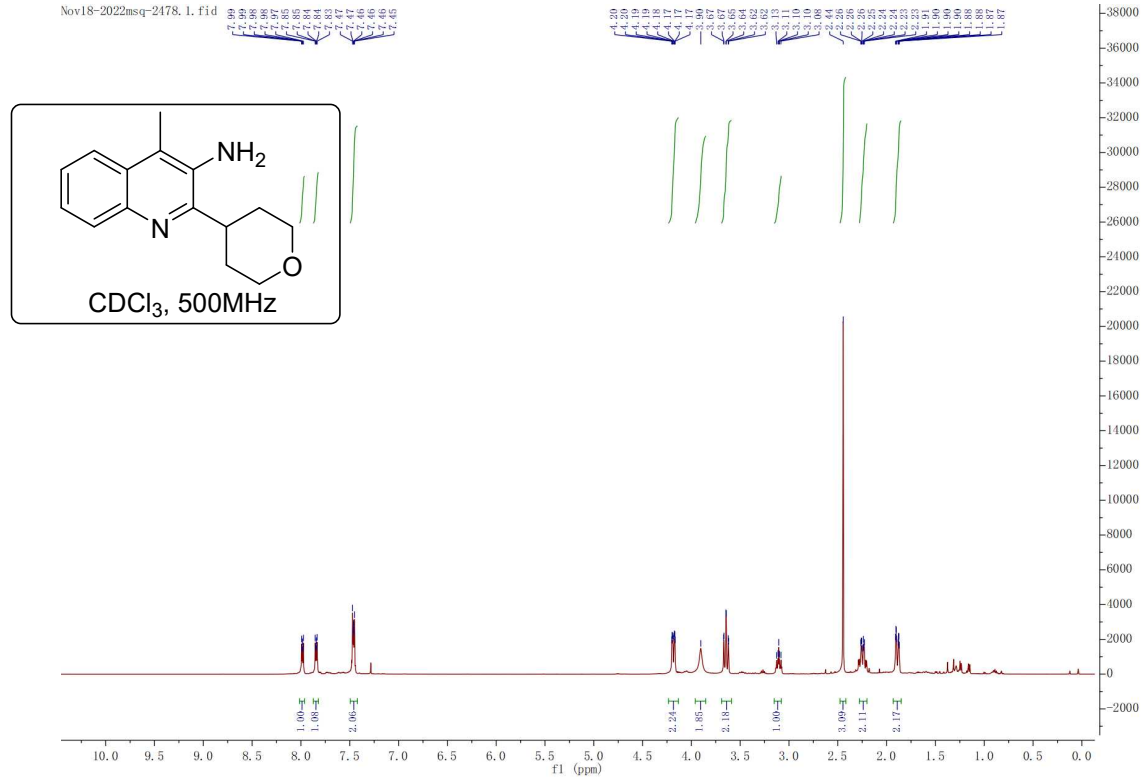


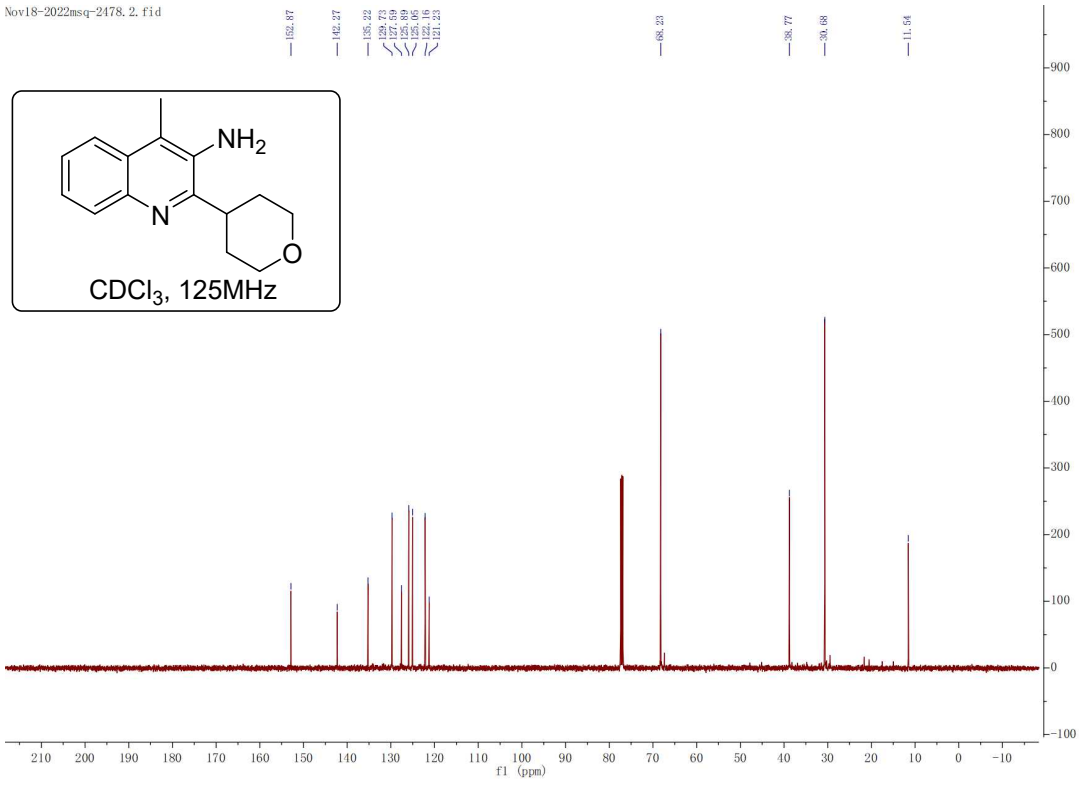
2-cyclohexyl-4-methylquinolin-3-amine(4e)



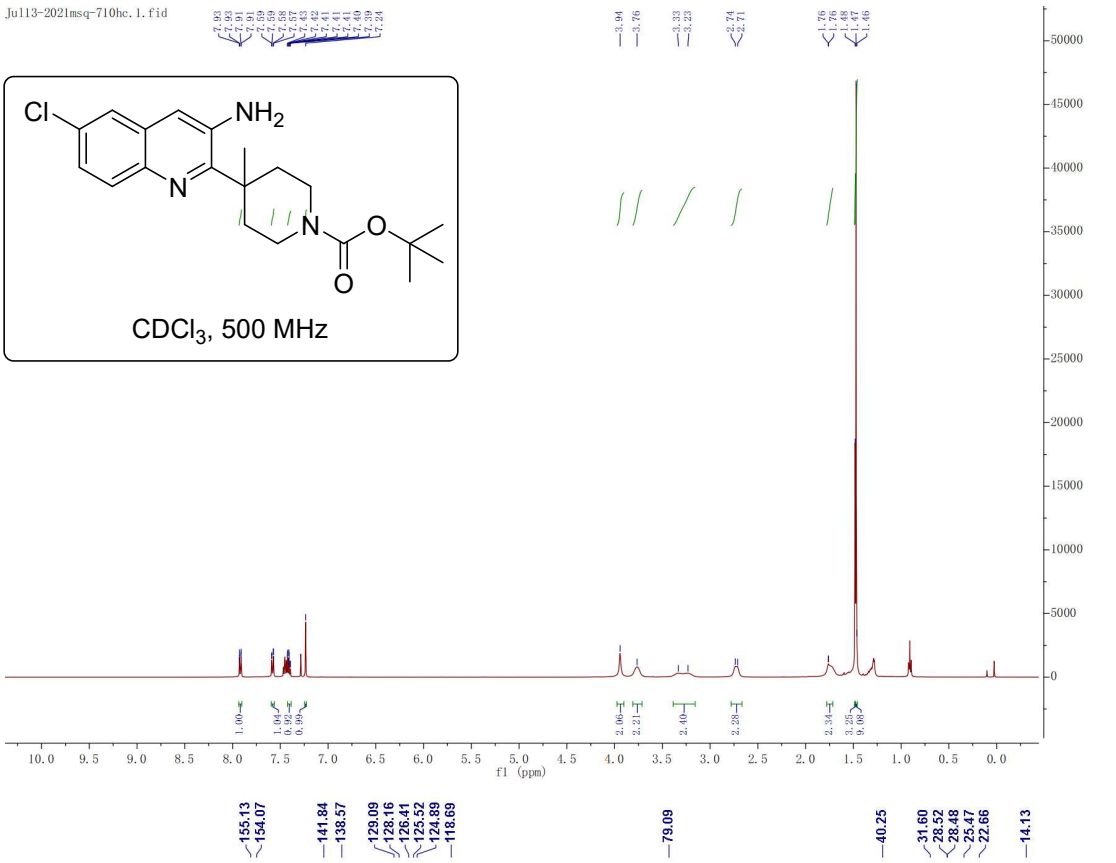
6-chloro-2-(1-methylcyclopropyl)quinolin-3-amine(4f)

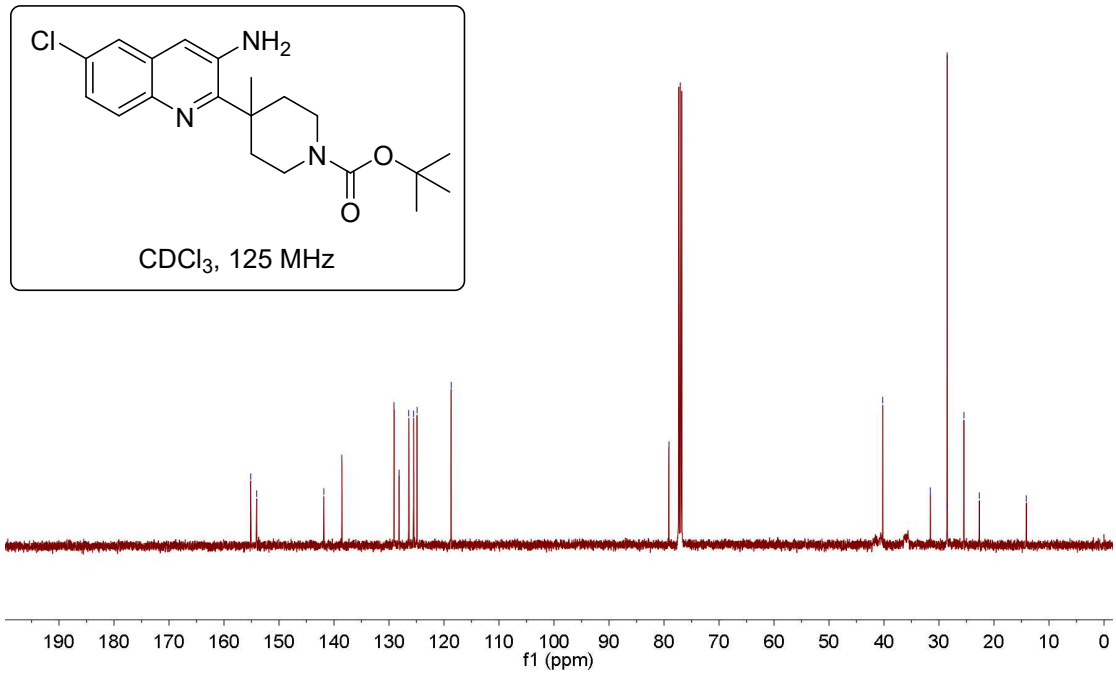
6-chloro-2-(4-methyltetrahydro-2H-pyran-4-yl)quinolin-3-amine（4g）



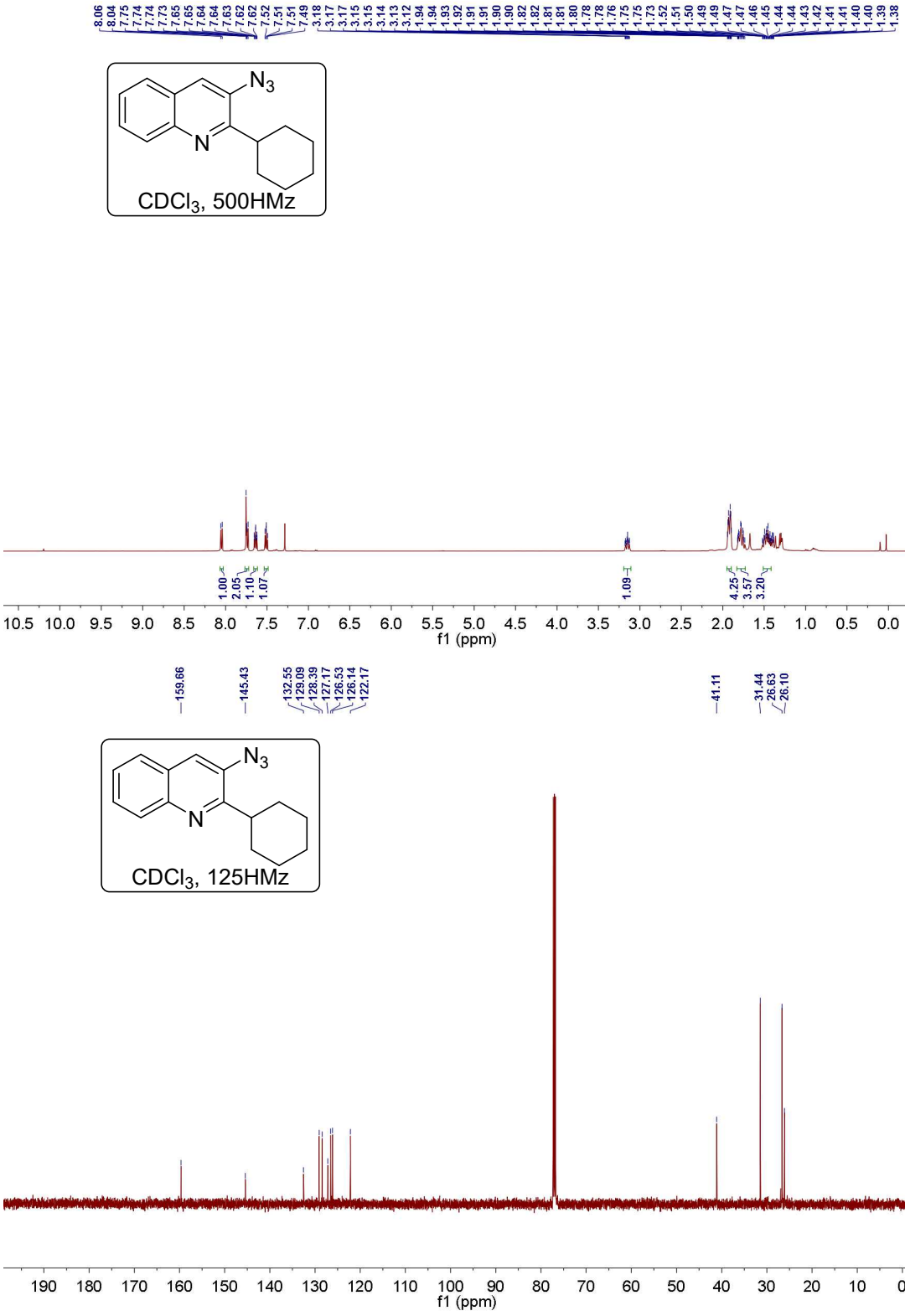


tert-butyl 4-(3-amino-6-chloroquinolin-2-yl)-4-methylpiperidine-1-carboxylate（4h）





3-azido-2-cyclohexylquinoline (5a)



2-cyclohexyl-3-iodoquinoline (5b)