Supplementary Materials for

Metal-Free, Redox-Neutral, Site-Selective Access to Heteroarylamine *via* Direct Radical-Radical Cross-Coupling Powered by Visible Light Photocatalysis

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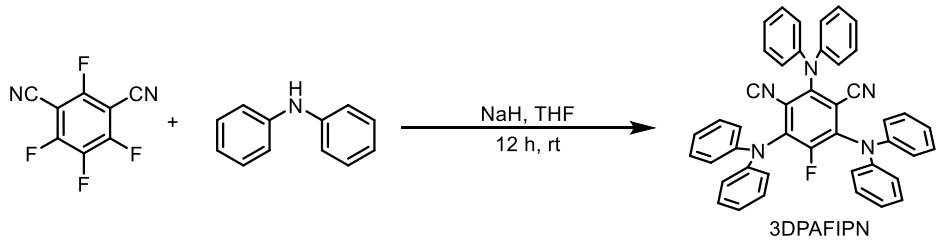
1. Materials and Methods

^{1}H NMR spectra was recorded using a Bruker Avance DPX 400 MHz instrument with tetramethylsilane (TMS) as an internal standard. ^{13}C NMR spectra were obtained at 100 MHz and referenced to the internal solvent signals. Mass spectra were recorded using a Trio-2000 GC-MS spectrometer. The transient absorption spectra were measured using Laser Flash Photolysis Spectrometer, LP980-KS, Edinburgh Instruments, UK. The luminescence spectrum was recorded by steady/transient state Fluorescence Spectrometer, FLS1000, Edinburgh Instruments, UK. UV-vis absorption spectra were obtained from Shimadzu UV-1601 Spectrophotometer. Cyclic voltammograms were obtained on a CHI 660E potentiostat. Commercially available reagents and solvents were used without further purification. Other amines and hydroxylamine derivatives were prepared by using the reported procedure and purified through column chromatography respectively. Blue LEDs (3 W, $\lambda = 450 \pm 10$ nm, 145 lm @700mA) were used as the irradiation light.

2. General procedure for preparation of the photocatalyst and substrates

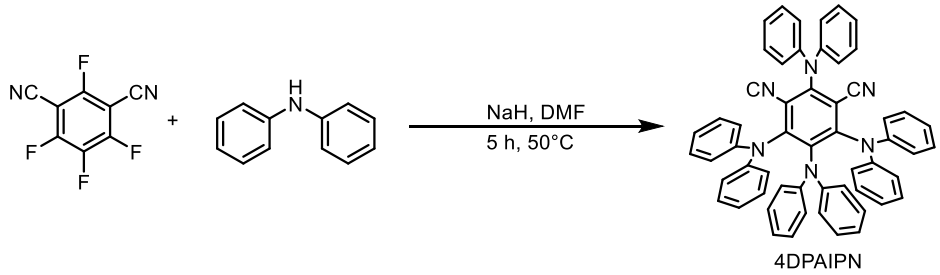
Method A[1]



NaH (60% in oil, 0.60g, 15 mmol) was added slowly to the flask with a stirred solution of diphenylamine (1.69g, 10.0 mmol) in dry THF (40 mL) under the Ar at room temperature. After 30 min, tetrafluoroisophthalonitrile (0.40g, 2.00 mmol) was further added. After stirred at room temperature for 12 h, 2 mL water was added to the reaction mixture to quench the excess NaH. The resulting mixture was then concentrated under reduced pressure and washed by water and EtOH to yield the crude product, which was chromatographed on silica to give the corresponding product 3DPAFIPN. The characterization data of 3DPAFIPN was same as the reported[2] and a crystal structure confirmed the structure (Figure S12).

2,4,6-Tris(diphenylamino)-5-fluoroisophthalonitrile (3DPAFIPN): ^{1}H NMR δ 7.30–7.20 (12 H), 7.11–7.01 (6 H), 7.01–6.93 (12 H). ^{13}CNMR (101 MHz, $CDCl_3$) δ 152.48 (d, *J* = 258.5 Hz), 151.81(d, *J* = 3.2 Hz), 151.19, 145.55, 145.33, 143.07 (d, *J* = 11.1 Hz), 129.45, 129.37, 124.60, 124.02, 122.76, 122.73, 112.61 (d, *J* = 3.2 Hz), 109.05 (d, *J* = 3.0 Hz). ^{19}F NMR (377 MHz, $CDCl_3$) δ -121.30. ESI: Calcd for $C_{44}H_{30}FN_5$ $[M+H]^+$: 648.2558; found: 648.2558.

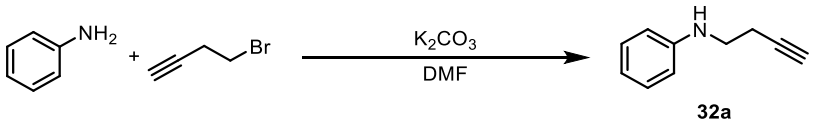
Method B[3]



NaH (60% in oil, 0.32 g, 8 mmol) was added slowly to a stirred solution of diphenylamine (1.01g,6.0 mmol) tetrafluoroisophthalonitrile (0.20 g, 1.00 mmol) in dry DMF (10 mL) under a nitrogen atmosphere at room temperature. The deprotonation was firstly performed at 50°C for 1 h. After stirring at the same temperature for 4 h, water and ice were added to the reaction mixture

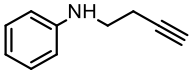
to quench the excess of NaH. The precipitate was filtered and purified by recrystallization from pentane/CH_2Cl_2 then filtered. The brown liquid filtrate was concentrated and purified by column chromatography on silica gel with DCM/Hexane. The characterization data of 4DPAIPN was same as the reported.[3]

Method C[4]



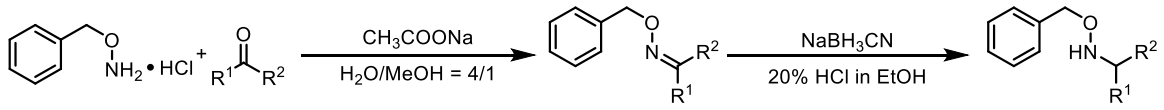
32a

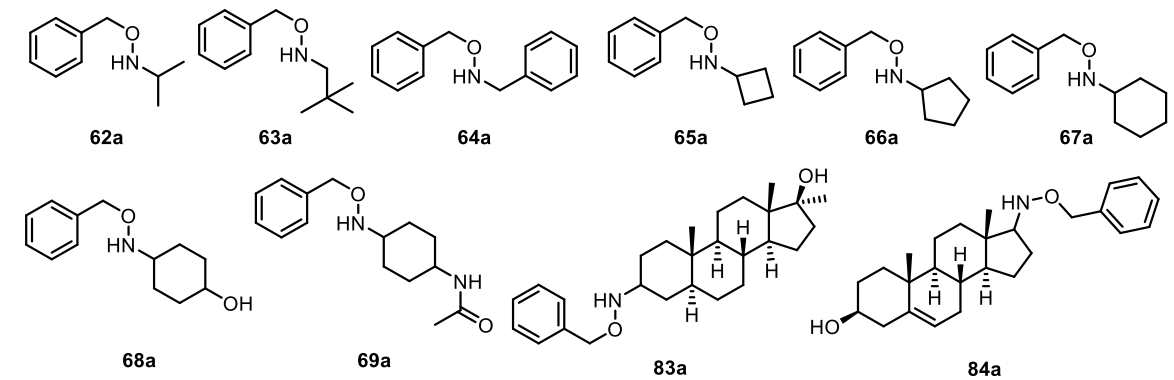
Aniline (10 mmol, 931.3 mg) was added to the flask in DMF (60 ml) under the Ar. Then K_2CO_3 (10.5 mmol, 1451.2 mg) and 4-bromo-1-butyne (10.3 mmol, 1370 mg) were added to the solution. After 12 h at 85 °C, the mixture was quenched by aqueous NH_4Cl solution. The aqueous layer was extracted with diethyl ether. The combined organic layers were dried over anhydrous Na_2SO_4. Finally, the organic solvent was evaporated in vacuo, and the residue was chromatographed on silica to give the corresponding product.



***N*-(but-3-yn-1-yl)aniline (32a)**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (t, *J* = 7.6 Hz, 2 H), 6.74 (t, *J* = 7.3 Hz, 1 H), 6.65 (d, *J* = 8.2 Hz, 2 H), 4.04 (bs, 1 H), 3.33 (t, *J* = 6.6 Hz, 2 H), 2.51 (td, *J* = 6.5, 2.2 Hz, 2 H), 2.11–1.98 (m, 1 H). ^{13}CNMR (101 MHz, $CDCl_3$) δ 147.48, 129.34, 117.99, 113.25, 81.77, 70.05, 42.56, 19.16. ESI: Calcd for $C_{10}H_{11}N$ $[M+H]^+$: 146.0970; found: 146.0962.

Method D[5,6]

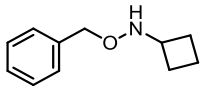




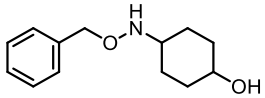
To a stirred solution of sodium acetate (12 mmol, 1.2 equiv.) in 50 mL H_2O/MeOH 4/1 were added *O*-benzylhydroxylamine chlorhydrate (10 mmol, 1 equiv.) and aldehyde or ketone (30 mmol, 3 equiv.). After stirred at room temperature for 12 h, the reaction mixture was extracted

with CH_2Cl_2 (3×50 mL). The combined organic layers were dried over anhydrous Na_2SO_4. Finally, the organic solvent was evaporated in vacuo, and the residue was used without further purification.

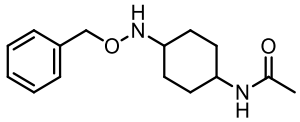
Crude oxime was dissolved in EtOH to a final concentration of 1.5 M. Then, the reaction mixture was cooled to 0 ºC, 5 equivalents of $NaBH_3CN$ were added, and the solution was stirred for 15 min. Next, an equal volume of 20% HCl in EtOH chilled to 0 °C was subsequently added in a drop-wise fashion over 10 min. The reaction was then allowed to warm to room temperature and stirred overnight. Finally, the reaction was neutralized with the addition of Na_2CO_3 aqueous solution until the evolution of gas halted. Then the aqueous layer was extracted with CH_2Cl_2. The combined organic layers were dried over anhydrous Na_2SO_4. Finally, the organic solvent was evaporated in vacuo, and the residue was chromatographed on silica to give the desired oxyamine product (**62a**-**69a** and **83a**-**84a**).



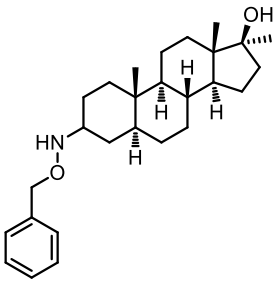
O-benzyl-*N*-cyclobutylhydroxylamine (65a) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41–7.25 (m, 5 H), 4.88 (bs, 1H), 4.71 (s, 2 H), 3.68 (p, *J* = 7.3 Hz, 1 H), 2.13 (dt, *J* = 13.1, 8.2 Hz, 2 H), 1.92–1.64 (m, 4 H). ^{13}CNMR (101 MHz, $CDCl_3$) δ 139.60, 129.70, 129.67, 129.07, 77.83, 57.27, 29.14, 16.69. ESI: Calcd for $C_{11}H_{15}NO$ $[M+H]^+$:178.1232; found: 178.1227.



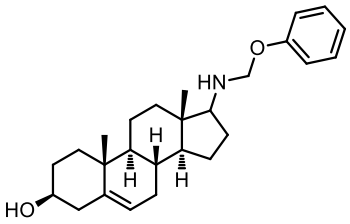
4-((benzyloxy)amino)cyclohexanol (68a) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42–7.26 (m, 5 H), 4.72 (s, 2 H), 3.88 (s, 1 H), 3.06–2.90 (m, 1 H), 1.79–1.49 (m, 8 H). ^{13}CNMR (101 MHz, $CDCl_3$) δ 137.87, 128.43, 128.38, 127.82, 76.85, 67.30, 57.20, 30.90, 25.08. ESI: Calcd for $C_{13}H_{19}NO_2$ $[M+H]^+$: 222.1494; found: 222.1489.



***N*-(4-((benzyloxy)amino)cyclohexyl)acetamide (69a)** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53–7.04 (m, 5 H), 5.53–5.25 (m, 1 H), 4.67 (s, 2 H), 3.84–3.52 (m, 1 H), 2.83 (t, *J* = 10.3 Hz, 1 H), 2.04–1.90 (d, *J* = 22.8 Hz, 7 H), 1.36–0.98 (m, 4 H). ^{13}CNMR (101 MHz, $CDCl_3$) δ 169.31, 137.79, 128.38, 128.37, 127.84, 76.93, 58.82, 48.24, 31.31, 29.14, 23.55. HRMS (MALDI-TOF): Calcd for $C_{15}H_{22}N_2O_2$ $[M+H]^+$: 263.1760; found: 263.1755.



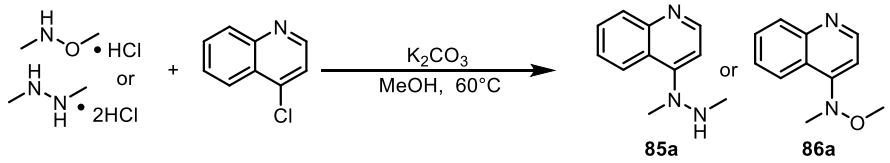
(5S,8R,9S,10S,13S,14S,17S)-3-((benzyloxy)amino)-10,13,17-trimethylhexadecahydro-1H-cyclopenta[a]phenanthren-17-ol (83a): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39–7.27 (m, 5 H), 5.43 (bs, 1 H), 4.71 (s, 2 H), 3.00–2.81 (m, 1 H), 1.85–1.63 (m, 5 H), 1.60–1.40 (m, 5 H), 1.32–1.10 (m, 13 H), 0.98 (dt, *J* = 13.4, 7.0 Hz, 1H), 0.91–0.79 (m, 7 H), 0.70–0.59 (m, 1 H). ^{13}CNMR (101 MHz, $CDCl_3$) δ 137.98, 128.37, 128.29, 127.75, 81.71, 76.90, 60.17, 54.49, 50.74, 45.56, 45.22, 39.03, 37.15, 36.43, 36.19, 33.11, 31.83, 31.70, 28.78, 26.35, 25.82, 23.27, 20.78, 13.99, 12.37. EI: Calcd for $C_{27}H_{41}NO_2$ $[M]^+$: 411.3137; found: 411.3142.



(3S,8R,9S,10R,13S,14S)-10,13-dimethyl-17-((phenoxymethyl)amino)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-ol (84a): ^{1}H NMR (400 MHz, $CDCl_3$) δ7.40–7.27 (m, 5 H), 5.34 (d, *J* = 4.1 Hz, 1 H), 4.70 (s, 2 H), 3.52 (tt, *J* = 9.9, 4.3 Hz, 1 H), 3.08 (t, *J* = 8.4 Hz, 1 H), 2.36–2.17 (m, 2 H), 2.09–1.79 (m, 5 H), 1.70–1.38 (m, 7 H), 1.32–0.88 (m, 9 H), 0.75 (s, 3 H). ^{13}CNMR (101 MHz, $CDCl_3$) δ 140.99, 138.25, 128.33, 127.66, 121.43, 121.42, 75.97, 71.80, 70.47, 53.96, 50.42, 42.63, 42.42, 38.53, 37.38, 36.67, 31.89, 31.78, 26.12, 23.87, 20.96, 19.47, 11.73. EI: Calcd for $C_{26}H_{37}NO_2$ $[M]^+$: 395.2824; found: 395.2830.

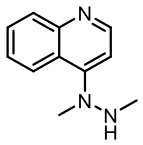
The characterization data of other hydroxylamines (**62a-64a**, **66a-67a**) were same as the reported elsewhere[5-10].

Method E[11]

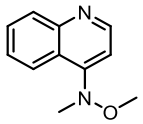


To a stirred mixture of 20g or 10g (142 mmol or 71 mmol) of K_2CO_3 and 19 g (143 mmol) of hydrazine hydrochloride or 13.9 g (143 mmol) of hydroxylamine hydrochloride in 120 mL MeOH, 2 g (12 mmol) of 4-chloroquinoline was added. The mixture was stirred at 60°C for 3 hours. The hot solution was then filtered to remove KCl and was evaporated in vacuo. Next, the residue was neutralized 1 M NaOH aqueous solution (15 mL), and was extracted with CH_2Cl_2

(2×100 mL). The combined organic layers were washed by water (3×100 mL) and dried over anhydrous Na_2SO_4. Finally, the organic solvent was evaporated in vacuo to provide heteroaryl hydrazine **85a** and hydroxylamine **86a** without further purification.

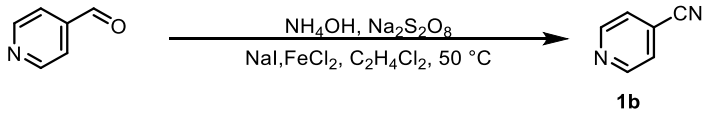


4-(1,2-dimethylhydrazineyl)quinoline (85a) ^{1}H NMR (400 MHz, $CDCl_3$) cδ 8.68 (d, *J* = 4.9 Hz, 1 H), 8.33 (d, *J* = 8.5 Hz, 1 H), 8.02 (d, *J* = 8.4 Hz, 1 H), 7.63 (t, *J* = 7.5 Hz, 1 H), 7.45 (t, *J* = 7.6 Hz, 1 H), 6.86 (d, *J* = 4.9 Hz, 1 H), 3.28 (bs, 1 H), 3.16 (s, 3 H), 2.74 (s, 3 H). ^{13}CNMR (101 MHz, $CDCl_3$) δ 156.87, 151.01, 149.02, 129.71, 129.19, 125.74, 123.10, 121.85, 107.79, 60.15, 46.93. ESI: Calcd for $C_{11}H_{13}N_3$ $[M+H]^+$:188.1183; found: 188.1181.

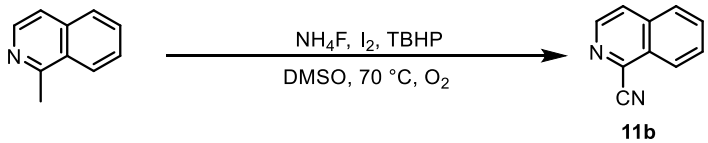


***N*,O-dimethyl-*N*-(quinolin-4-yl)hydroxylamine (86a)** ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.81 (d, *J* = 4.6 Hz, 1 H), 8.08 (d, *J* = 8.4 Hz, 1 H), 7.99 (d, *J* = 8.4 Hz, 1 H), 7.68 (t, *J* = 7.6 Hz, 1 H), 7.51 (t, *J* = 7.5 Hz, 1 H), 7.36 (d, *J* = 4.7 Hz, 1 H), 3.67 (s, 3 H), 3.19 (s, 3 H). ^{13}CNMR (101 MHz, $CDCl_3$) δ 156.83, 151.02, 149.03, 129.72, 129.15, 125.72, 123.08, 121.84, 107.78, 60.13, 46.92. ESI: Calcd for $C_{11}H_{12}N_2O$ $[M+H]^+$:189.1023; found: 189.1024.

Method F[12,13]



To a solution of aldehydes (3 mmol) in 1,2-dichloroethane (10 mL) was added $FeCl_2$ (0.3 mmol), $Na_2S_2O_8$ (4.5 mmol), NaI (0.15 mmol), and $NH_3.H_2O$ (9 mL) at room temperature. After the mixture was stirred at 50°C for 16 hours, it was poured into water (30 mL) and extracted with DCM (3×30 mL). The combined organic extracts were washed with brine and dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica gel to afford the desired product.



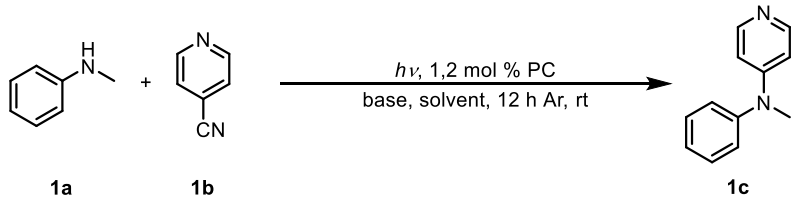
Under O_2, a 20 mL of Schlenk tube equipped with a stir bar was charged with 1-methylisoquinoline (28.6 mg 0.2 mmol), I_2 (10.2 mg, 0.04 mmol), NH_4F (29.6 mg, 0.8 mmol), TBHP (70% in water, 324 μL, 2.4 mmol), DMSO (0.5 mL). The tube was sealed with a Teflon lined cap. The reaction mixture was stirred at 70 °C for 48 h in oil bath. After the completion of

the reaction (monitored by TLC), the solvent was concentrated in vacuum and the residue was purified by flash column chromatography on silica gel to give the desired product.

The characterization of **1b** and **11b** were the same as the reported elsewhere[12-13]. Cyanated heteroarenes are available from the corresponding heteroaryl aldehyde or methyl heteroarenes with oxidant and ammonium salt.

3. Optimization of reaction conditions and general procedures

Table S1. The optimization for the synthesis of heteroarylamines [a]

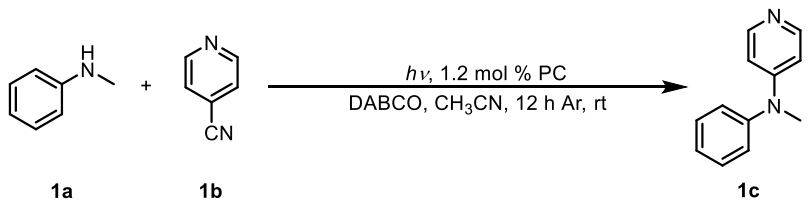


1a **1b** **1c**

Entry	**1a** (mmol)	**1b** (mmol)	photocatalyst	Base	Solvent	Yield (%)[b]
1[c]	0.2	0.2	3DPAFIPN	-	CH_3CN	21
2	0.2	0.2	3DPAFIPN	DABCO	CH_3CN	99
3	0.2	0.2	3DPAFIPN	2,6-lutidine	CH_3CN	99
4	0.2	0.2	3DPAFIPN	Na_2CO_3	CH_3CN	85
5	0.2	0.2	3DPAFIPN	$NaHCO_3$	CH_3CN	82
6	0.2	0.2	3DPAFIPN	DABCO	DCE	63
7	0.2	0.2	3DPAFIPN	DABCO	THF	86
8	0.2	0.2	3DPAFIPN	DABCO	DMSO	92
9[d]	0.2	0.2	-	DABCO	CH_3CN	0
10[e]	0.2	0.2	3DPAFIPN	DABCO	CH_3CN	0
11	0.2	0.2	4DPAIPN	DABCO	CH_3CN	99
12	0.2	0.2	*fac*-Ir(ppy)$_3$	DABCO	CH_3CN	88
13[f]	0.2	0.2	$Ru(bpy)_3(PF_6)_2$	DABCO	CH_3CN	31
14	0.2	0.2	Eosin Y	DABCO	CH_3CN	0
15	0.2	0.2	Rh6G	DABCO	CH_3CN	0
16	0.2	0.2	4CzIPN	DABCO	CH_3CN	0

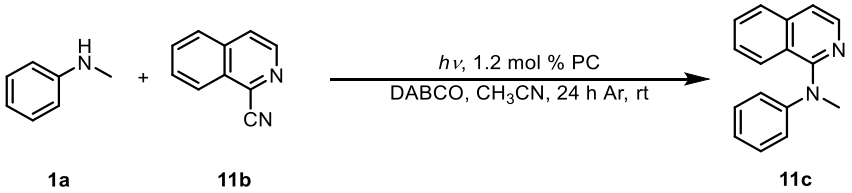
[a]Reaction condition: 0.2 mmol (1 equiv) **1a** (*N*-methylaniline), 0.2 mmol (1 equiv) **1b** (isonicotinonitrile), 1.2 mol % PC, 3 mL solvent, Ar, blue LEDs, room temperature. [b]The yields were determined by ^{1}H NMR using diphenylmethano as the internal standard. [c]no base. [d]No 3DPAFIPN. [e]No light. [f]Green light.

General Procedure A for the scope of arylamines



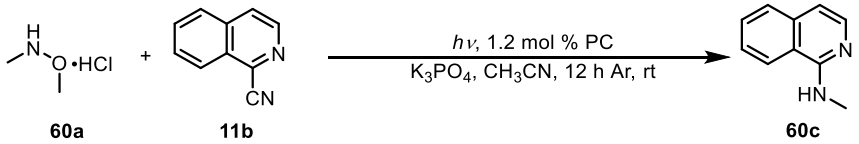
A 10 mL Pyrex tube equipped with a magnetic stir bar was charged with isonicotinonitrile (20.8 mg, 0.2 mmol), DABCO (22.4 mg, 0.2 mmol) and PC (3DPAFIPN) (1.6 mg, 0.0024 mmol) in CH_3CN (3 mL). After the mixture was strictly deaerated, *N*-methylaniline (21.7 ul, 0.2 mmol) was added into the mixture which was further irradiated by blue LEDs (λ = 450 nm) for 12 hours at room temperature. When reaction was finished, the residue was purified by chromatography on silica gel to get isolated product.

General Procedure B for the gram-scale synthesis



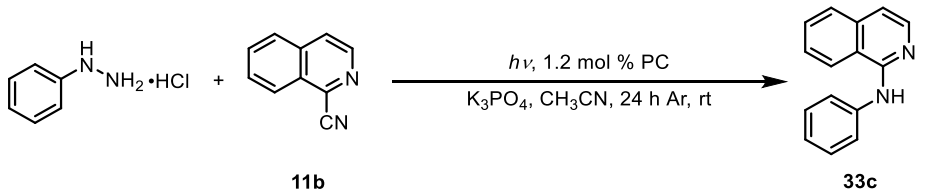
A 100 mL Pyrex tube equipped with a magnetic stir bar was charged with 1-isoquinolinecarbonitrile (770 mg, 5.0 mmol), *N*-methylaniline (542 ul, 5.0 mmol), DABCO (560 mg, 5.0 mmol) and PC (3DPAFIPN) (40 mg, 0.06 mmol) in CH_3CN (50 mL). The mixture was strictly deaerated and irradiated by blue LEDs (λ = 450 nm) for 24 hours at room temperature. When reaction was finished, the system was purified by chromatography on silica gel to get the 1.05g product **11c** with 90% yield.

General Procedure C for the scope of hydroxylamines



A 10 mL Pyrex tube equipped with a magnetic stir bar was charged with N,O-dimethylhydroxylamine hydrochloride (48.8 mg, 0.5 mmol), 1-isoquinolinecarbonitrile (30.8 mg, 0.2 mmol), K_3PO_4 (84.9 mg, 0.4 mmol) and PC (3DPAFIPN) (1.6 mg, 0.0024 mmol) in CH_3CN (3 mL). After the mixture was strictly deaerated, the mixture was further irradiated by blue LEDs (λ = 450 nm) for 12 hours at room temperature. When reaction was finished, the mixture was extracted with EtOAc (6×5 mL). The combined organic layers were dried over anhydrous Na_2SO_4. Finally, the organic solvent was evaporated in vacuo, and the residue was chromatographed on silica to give the desired product.

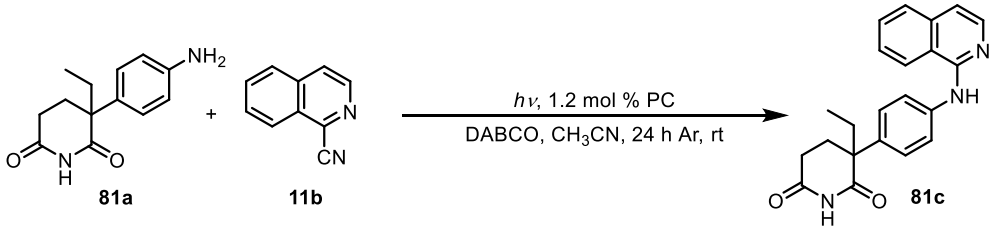
General Procedure D for the scope of hydrazines



11b 33c

A 10 mL Pyrex tube equipped with a magnetic stir bar was charged with phenylhydrazine hydrochloride (57.8 mg, 0.4 mmol), 1-isoquinolinecarbonitrile (30.8 mg, 0.2 mmol), K_3PO_4 (84.9 mg, 0.4 mmol) and PC (3DPAFIPN) (1.6 mg, 0.0024 mmol) in CH_3CN (3 mL). After the mixture was strictly deaerated, the mixture was further irradiated by blue LEDs (λ = 450 nm) for 24 hours at room temperature. When reaction was finished, the mixture was extracted with EtOAc (6×5 mL). The combined organic layers were dried over anhydrous Na_2SO_4. Finally, the organic solvent was evaporated in vacuo, and the residue was chromatographed on silica to give the desired product.

<u>General Procedure E</u> for the facile last-stage decoration of bioactive compounds



81a 11b 81c

A 10 mL Pyrex tube equipped with a magnetic stir bar was charged with aminoglutethimide (46.4 mg, 0.2 mmol), 1-isoquinolinecarbonitrile (30.8 mg, 0.2 mmol), DABCO (22.4 mg, 0.2 mmol) and PC (3DPAFIPN) (1.6 mg, 0.0024 mmol) in CH_3CN (6 mL). After the mixture was strictly deaerated, the mixture was further irradiated by blue LEDs (λ = 450 nm) for 24 hours at room temperature. When reaction was finished, the residue was purified by chromatography on silica gel to get isolated products.

4. Mechanistic Study

4.1 The system with 3DPAFIPN, 1a and 1b

Electrochemical and spectroscopic study

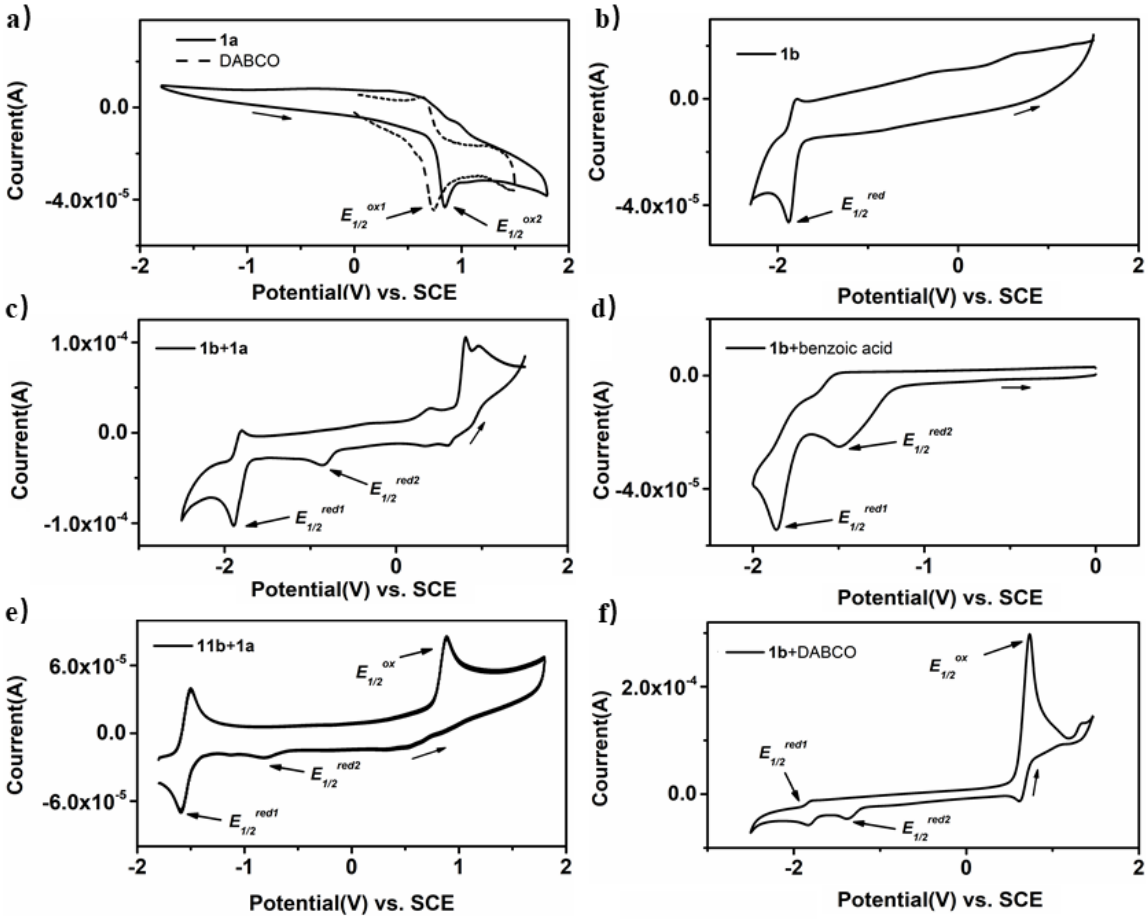


Figure S1. a) The CV experiment of **1a** (1.0×10^{-3} M), DABCO (1.0×10^{-3} M) and NBu_4PF_6 (1.0×10^{-1} M) in degassed CH_3CN, $E_{1/2}^{ox1}$ = 0.68 V SCE for DABCO, $E_{1/2}^{ox2}$ = 0.92 V SCE for **1a**; b) The CV experiment of **1b** (1.0×10^{-3} M) and NBu_4PF_6 (1.0×10^{-1} M) in degassed CH_3CN, $E_{1/2}^{red}$ = -1.84 V SCE; c) The CV experiment of **1b** (1.0×10^{-3} M) with **1a** (1.0×10^{-3} M) and NBu_4PF_6 (1.0×10^{-1} M) in degassed CH_3CN, while **1a** was firstly oxidized and then **1b** was reduced, $E_{1/2}^{red1}$ = -1.84 V SCE, $E_{1/2}^{red2}$ = -0.87 V SCE; d) The CV experiment of **1b** (1.0×10^{-3} M) with benzoic acid (1.0×10^{-3} M) and NBu_4PF_6 (1.0×10^{-1} M) in degassed CH_3CN,, $E_{1/2}^{red1}$ = -1.84 V SCE, $E_{1/2}^{red2}$ = -1.49 V SCE; e) The CV experiment of **11b** (1.0×10^{-3} M) with **1a** (1.0×10^{-3} M) and NBu_4PF_6 (1.0×10^{-1} M) in degassed CH_3CN, while **1a** was firstly oxidized and then **11b** was reduced, $E_{1/2}^{red1}$ = -1.52 V SCE, $E_{1/2}^{red2}$ = -0.81 V SCE; f) The CV experiment of **1b** (1.0×10^{-3} M) with DABCO (1.0×10^{-3} M) and NBu_4PF_6 (1.0×10^{-1} M) in degassed CH_3CN, while DABCO was firstly oxidized and then **1b** was reduced, $E_{1/2}^{red1}$ = -1.84 V SCE, $E_{1/2}^{red2}$ = -1.37 V SCE.

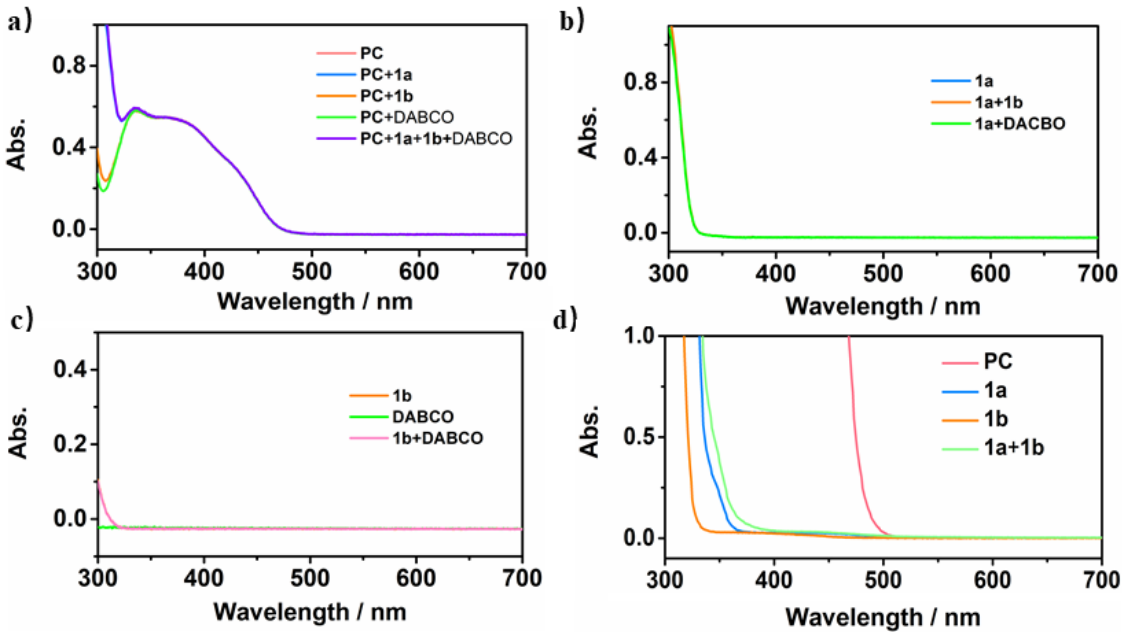


Figure S2. a-c) Absorption spectra of PC (3DPAFIPN) (3.0×10^{-5} M), **1a** (5×10^{-4} M), **1b** (5×10^{-4} M) and DABCO (5×10^{-4} M) and the mixture of **1a** and **1b**; d)Absorption spectra of spectrum of PC (3DPAFIPN) (8.0×10^{-4} M) with **1a** (6.7×10^{-2} M) and **1b** (6.7×10^{-2} M).

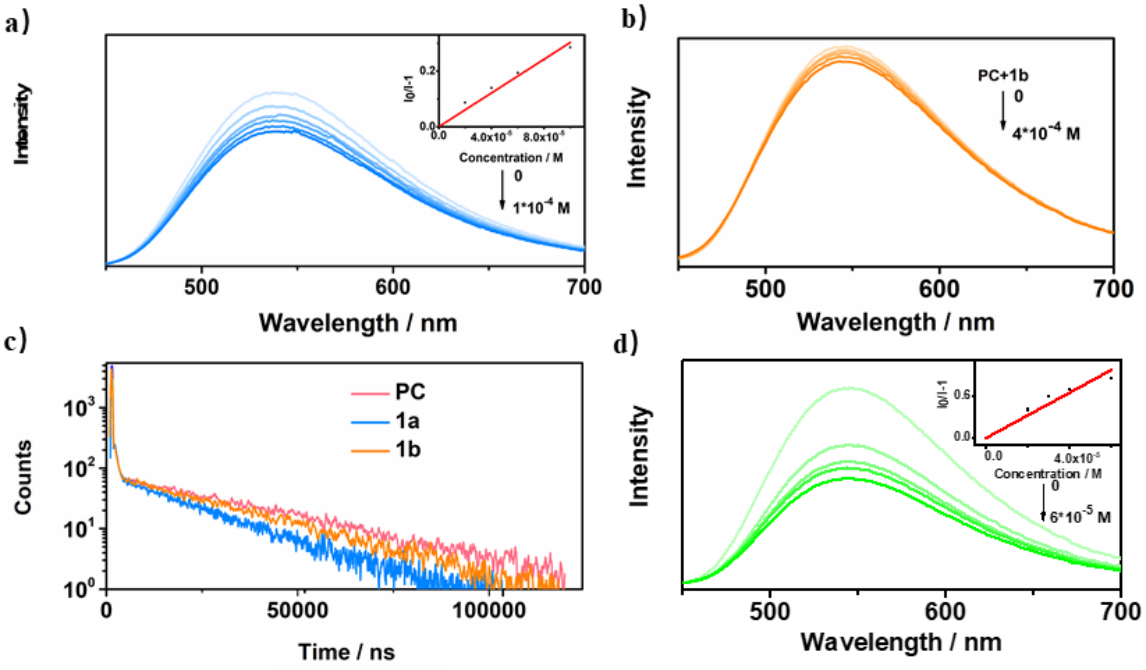


Figure S3. a) The luminescence spectrum of PC (3DPAFIPN) (6.0×10^{-5} M) as a function of concentration of **1a** in degassed CH_3CN with excitation at 430 nm, Quenching constant k_{et} = 9.8×10^{7} s^{-1} M^{-1} for **1a**. b) The luminescence spectrum of PC (3DPAFIPN) (6.0×10^{-5} M) as a function of concentration of **1b** in degassed CH_3CN with excitation at 430 nm; c) The luminescence decay of PC (3DPAFIPN) (6.0×10^{-5} M) with **1a** (5.0×10^{-5} M) and **1b** (5.0×10^{-5} M) in CH_3CN; d) The luminescence spectrum of PC (3DPAFIPN) (6.0×10^{-5} M) as a function of concentration of DABCO in degassed CH_3CN with excitation at 430 nm, Quenching constant k_{et} = 5.3×10^{8} s^{-1} M^{-1} for DABCO.

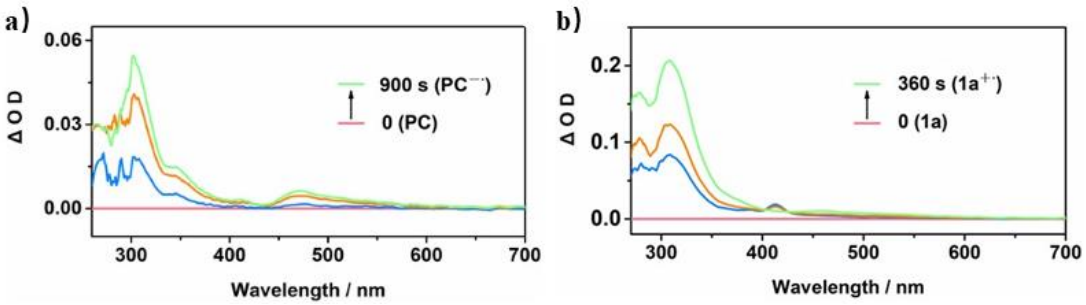


Figure S4. a) The spectroelectrochemical absorption spectrum of $PC^{-\bullet}$ ($[3DPAFIPN]^{-\bullet}$) in CH_3CN by reduction of PC (3DPAFIPN) (3.0×10^{-5} M) at -1.70 V voltage relative to NHE; b) the spectroelectrochemical absorption spectrum of $\mathbf{1a}^{+\bullet}$ in CH_3CN by oxidation of **1a** (2.0×10^{-4} M) at 1.10 V voltage relative to NHE.

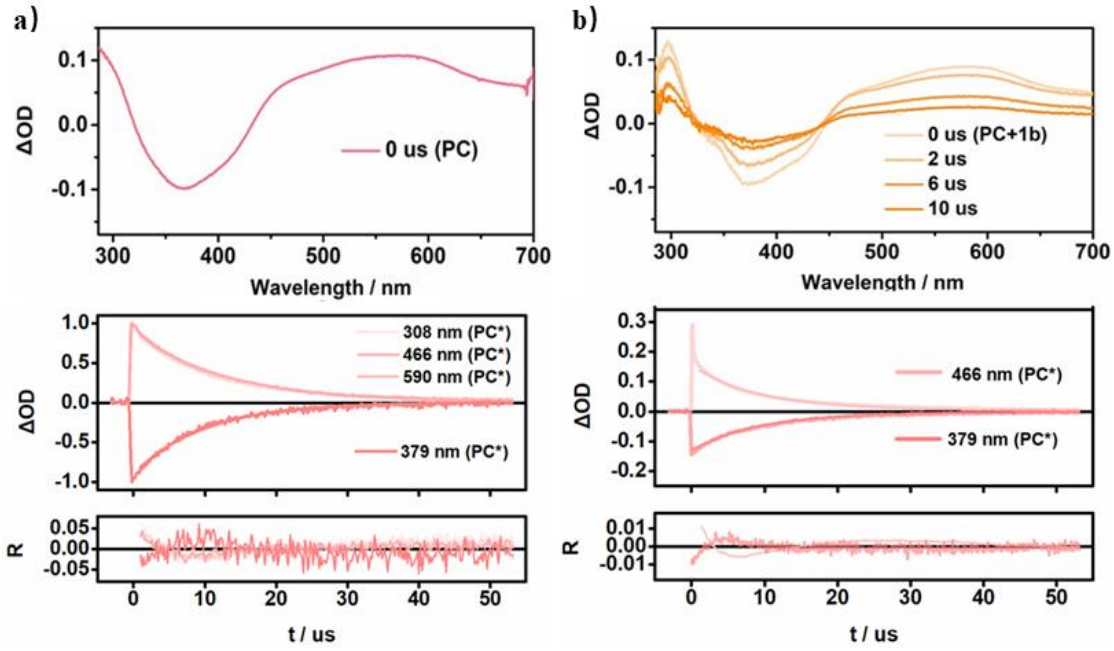


Figure S5. a) The transient absorption spectra of PC (3DPAFIPN) (6×10^{-5} M); b) The transient absorption spectra of PC (3DPAFIPN) (6×10^{-5} M) and PC (3DPAFIPN) (6×10^{-5} M) with **1b** (1×10^{-3} M).

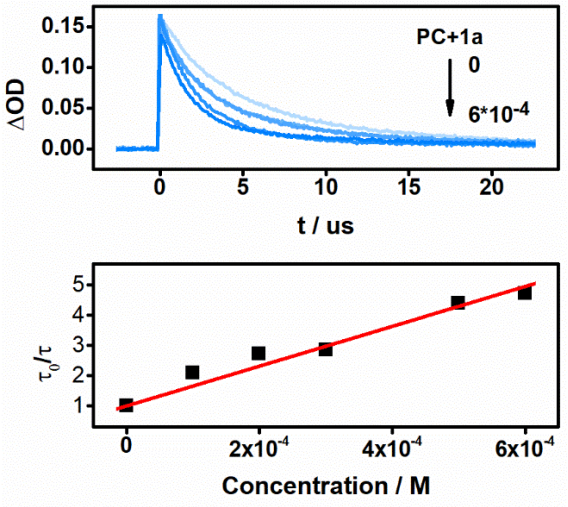


Figure S6. The transient absorption decay of PC (3DPAFIPN) (6×10^{-5} M) with the different concentration of **1a** (from 0 to 6×10^{-4} M) at 590 nm. According to the result, the electron transfer rate constant of **1a** is 5.1×10^{8} M^{-1} s^{-1}.

Transient absorption analysis of the system with 3DPAFIPN, **1a** and **1b**

The photophyscial interaction between these components can be described in the following formulas:

1. PC (3DPAFIPN)+**1a**:

$^3PC^* + \mathbf{1a} \xrightarrow{k_{sq}} PC^{-\cdot} + \mathbf{1a}^{+\cdot}$ Photoinduced single electron transfer

$^3PC^* \xrightarrow{\tau_p} {}^1PC$ Phosphorescence decay of the $^3PC^*$ (^{3}[3DPAFIPN]*)

$PC^{-\cdot} \xrightarrow{\tau_-} {}^1PC$ Decay of PC$^{-\bullet}$ radical anion ([3DPAFIPN]$^{-\bullet}$)

$\mathbf{1a}^{+\cdot} \xrightarrow{\tau_a} \mathbf{1a}$ Decay of **1a**$^{+\bullet}$ radical cation

2. PC (3DPAFIPN)+**1a**+**1b**:

$^3PC^* + \mathbf{1a} \xrightarrow{k_{sq}} PC^{-\cdot} + \mathbf{1a}^{+\cdot}$ Photoinduced single electron transfer

$^3PC^* \xrightarrow{\tau_p} {}^1PC$ Phosphorescence decay of $^3PC^*$ (^{3}[3DPAFIPN]*)

$PC^{-\cdot} \xrightarrow{\tau_-} {}^1PC$ Decay of PC$^{-\bullet}$ radical anion ([3DPAFIPN]$^{-\bullet}$)

$\mathbf{1a}^{+\cdot} \xrightarrow{\tau_a} \mathbf{1a}$ Decay of **1a**$^{+\bullet}$ radical cation

$PC^{-\cdot} + \mathbf{1b} \xrightarrow{k_{et}} {}^1PC + \mathbf{1b}^{-\cdot}$ Electron transfer from PC$^{-\bullet}$ radical anion ([3DPAFIPN]$^{-\bullet}$) to **1b**.

$\mathbf{1a}^{+\cdot} \xrightarrow{\tau_a} \mathbf{1a}$ Decay of **1a**$^{+\bullet}$ radical cation

$\mathbf{1b}^{-\cdot} \xrightarrow{\tau_a} \mathbf{1b}$ Decay of **1b**$^{-\bullet}$ radical anion

The transient absorption spectrum of PC (3DPAFIPN) consists 3 major excited state absorption (ESA) peaks and a ground state bleaching (GSB) peak (Fig. S4). The ESA peaks at 308 nm, 466 nm and 590 nm are the T_1 to T_n transition of 3DPAFIPN, while the GSB peak at 379 nm is due to the excitation of ground state PC. These transient peaks share the similar decay life times (10.0 μs), which is the lifetime of the triplet 3DPAFIPN (^{3}[3DPAFIPN]*).

In the transient absorption spectrum and decay of 3DPAFIPN and **1a** solution (Fig. 1c-2), we found that T_1 to T_n transition decay of PC at 590 nm (4.1 μs) is much faster than pure 3DPAFIPN solution. The acceleration of the triplet decay indicates the photophysical interaction between $^3PC^*$ (^{3}[3DPAFIPN]*) and **1a**. The decay of ESA peak at 308 nm is longer than that in 590 nm, indicating the formation of a new species.

Spectroelectrochemical analysis of 3DPAFIPN and **1a** (Fig. S3) shows that the radical cation of **1a** (**1a**$^{+\bullet}$) has much higher molar absorptivity at 308 nm than the PC$^{-\bullet}$ radical anion ([3DPAFIPN]$^{-\bullet}$). The transient absorption signal at 308 nm after the decay of triplet 3DPAFIPN is then majorly contributed by the **1a**$^{+\bullet}$ cation radical. The decay lifetime **1a**$^{+\bullet}$ cation radical is then calculated to be 13.0 μs from a bi-exponential decay model. The result is in accordance with literature values. The longer lived the species at 466 nm up to 109.1 μs is then assigned to the PC$^{-\bullet}$ radical anion.

λ (nm)	τ_1	B_1	τ_2	B_2	τ_3	B_3	χ^2
308	4.1	1.480×10^{-2}	13.3	8.584×10^{-2}	-	-	1.096
379	4.1	6.259×10^{-3}	11.9	5.891×10^{-2}			0.740
466	4.1	3.796×10^{-3}	13.0	1.406×10^{-2}	109.1	9.972×10^{-3}	1.249
590	4.1	7.084×10^{-2}					1.253

In the transient absorption spectroscopy of 3DPAFIPN and **1b** in solution (Fig. S5), we found the same transient absorption behavior of 3DPAFIPN solution. We can then infer that there is no interaction between the excited states of ^{3}PC* (^{3}[3DPAFIPN]*) and the ground state **1b**.

In the transient absorption spectroscopy of 3DPAFIPN with **1a** and **1b** in solution (Fig. 1c-3), we found that ESA signal at 466 nm has a longer lifetime than the ESA signal at 590 nm. It indicates the formation of PC$^{-\bullet}$ radical anion ([3DPAFIPN]$^{-\bullet}$) due to photo-induced energy transfer from ^{3}PC* to **1a**. However, the ESA lifetime at 466 nm is much shorter than the solution of PC and **1a**. We can then infer an electron transfer from PC$^{-\bullet}$ to **1b**. By a bi-exponential decay fitting, we calculated that the decay lifetime of PC$^{-\bullet}$ was quenched to 12.6 μs.

λ (nm)	τ_1	B_1	τ_2	B_2	χ^2
466	4.1	1.1×10^{-2}	12.6	2.0×10^{-3}	0.704

The electron transfer rate constant can be calculated by the following equations:

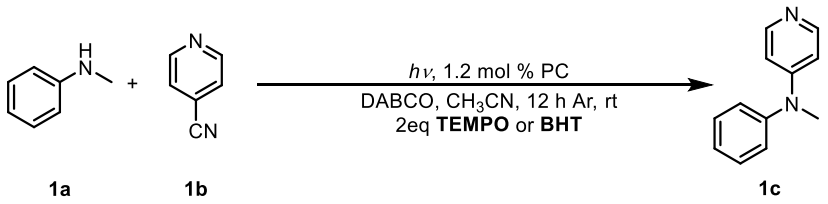
$$\frac{1}{\tau}-\frac{1}{\tau_0}=k_1C \quad \text{(eq. 1)}$$

where τ_0 and τ are the lifetime of ^{3}PC* (^{3}[3DPAFIPN]*) without and with **1a**, k_1 is the electron transfer rate constant from, C is the concentration of **1a**. Therefore, the electron transfer rate constant of **1a** is 1.4×10^8 M^{-1} s^{-1}.

$$\frac{1}{\tau}-\frac{1}{\tau_0}=k_2C \quad \text{(eq. 2)}$$

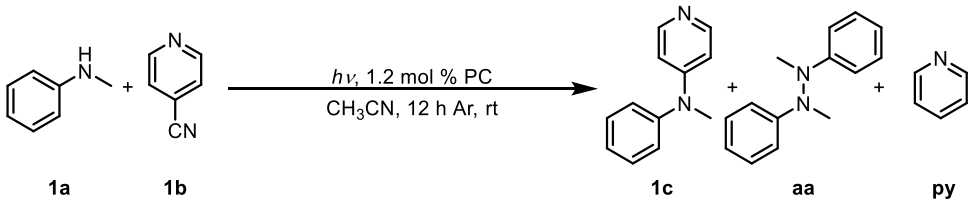
where τ_0 and τ are the lifetime of $PC^{-\bullet}$ radical anion ($[3DPAFIPN]^{-\bullet}$) without and with **1b**, k_2 is the electron transfer rate constant from, C is the concentration of **1b**. Therefore, the electron transfer rate constant of **1b** is 7.0×10^7 M^{-1} s^{-1}.

The radical formation



Scheme S1. The radical-trap experiment.

A 10 mL Pyrex tube equipped with a magnetic stir bar was charged with isonicotinonitrile (20.8 mg, 0.2 mmol), DABCO (22.4 mg, 0.2 mmol), PC (3DPAFIPN) (1.6 mg, 0.0024 mmol), TEMPO (0.4 mmol) or BHT (0.4 mmol) in CH_3CN (3 mL). After the mixture was strictly deaerated, *N*-methylaniline (21.7 ul, 0.2 mmol) was added into the mixture which was further irradiated by blue LEDs (λ = 450 nm) for 12 hours at room temperature. When reaction was finished, the yields were decreased to 0 and 6% respectively, which determined by ^{1}H NMR using diphenylmethano as the internal standard.



Scheme S2. The control experiment.

A 10 mL Pyrex tube equipped with a magnetic stir bar was charged with 1-isoquinolinecarbonitrile (30.8 mg, 0.2 mmol), PC (3DPAFIPN) (1.6 mg, 0.0024 mmol), in CH_3CN (3 mL). After the mixture was strictly deaerated, *N*-methylaniline (21.7 ul, 0.2 mmol) was added into the mixture which was further irradiated by blue LEDs (λ = 450 nm) for 12 hours at room temperature. When reaction was finished, the yield of **1c** was decreased to 21% accompanied with trace **aa** and **py**, which was detected by ESI. All of yields were determined by ^{1}H NMR using diphenylmethano as the internal standard. The characterization data of aa was same as the reported elsewhere.

4.2 The role of DABCO

The transient absorption spectra of the system with DABCO

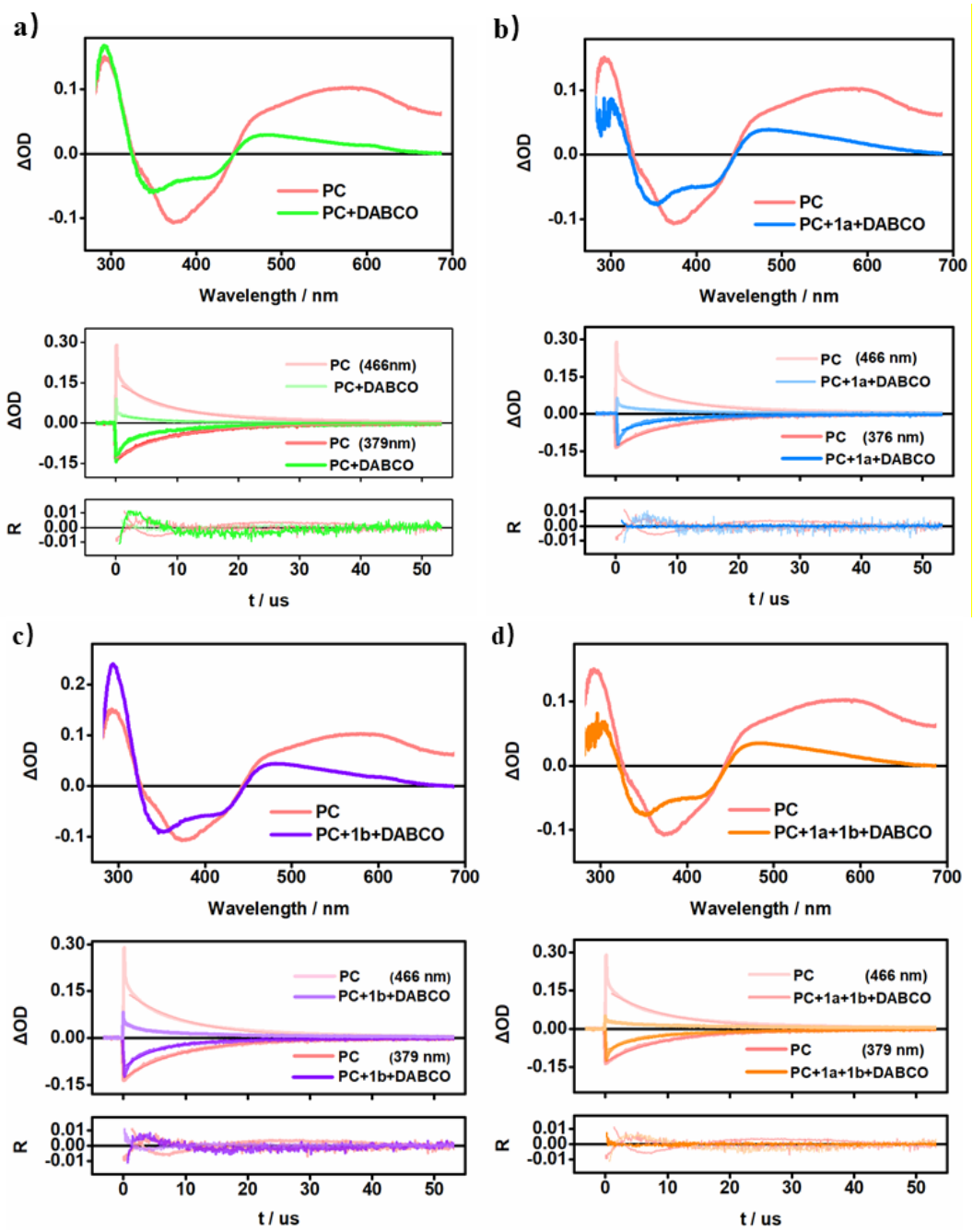


Figure S7. a) The transient absorption spectra of PC (3DPAFIPN) (6×10^{-5} M) with DABCO (1×10^{-3} M); b) The transient absorption spectra of PC (3DPAFIPN) (6×10^{-5} M) with DABCO (1×10^{-3} M) and **1a** (1×10^{-3} M); c) The transient absorption spectra of PC (3DPAFIPN) (6×10^{-5} M) with DABCO (1×10^{-3} M) and **1b** (1×10^{-3} M); d) The transient absorption spectra of PC (3DPAFIPN) (6×10^{-5} M) with DABCO (1×10^{-3} M), **1a** (1×10^{-3} M) and **1b** (1×10^{-3} M).

Transient absorption analysis of the system with DABCO.

After the addition of DABCO into this system, the photophyscial interaction between these components can be described in the following formulas:
1. PC (3DPAFIPN)+DABCO:

$^3PC^* + DABCO \xrightarrow{k_{sq}} PC^{-\cdot} + DABCO^{+\cdot}$ Photoinduced single electron transfer

$^3PC^* \xrightarrow{\tau_p} {}^1PC$ Phosphorescence decay of the ^{3}PC* (^{3}[3DPAFIPN]*)

$PC^{-\cdot} \xrightarrow{\tau_-} {}^1PC$ Decay of PC$^{-\bullet}$ radical anion ([3DPAFIPN]$^{-\bullet}$)

$DABCO^{+\cdot} \xrightarrow{\tau_a} \mathbf{1a}$ Decay of $DABCO^{+\bullet}$ radical cation

2. PC (3DPAFIPN)+$DABCO$+**1b**:

$^3PC^* + DABCO \xrightarrow{k_{sq}} PC^{-\cdot} + DABCO^{+\cdot}$ Photoinduced single electron transfer

$^3PC^* \xrightarrow{\tau_p} {}^1PC$ Phosphorescence decay of ^{3}PC* (^{3}[3DPAFIPN]*)

$PC^{-\cdot} \xrightarrow{\tau_-} {}^1PC$ Decay of PC$^{-\bullet}$ radical anion ([3DPAFIPN]$^{-\bullet}$)

$DABCO^{+\cdot} \xrightarrow{\tau_a} DABCO$ Decay of $DABCO^{+\bullet}$ radical cation

$PC^{-\cdot} + \mathbf{1b} \xrightarrow{k_{et}} {}^1PC + \mathbf{1b}^{-\cdot}$ Electron transfer from PC$^{-\bullet}$ radical anion ([3DPAFIPN]$^{-\bullet}$) to **1b**.

$DABCO^{+\cdot} \xrightarrow{\tau_a} DABCO$ Decay of $DABCO^{+\bullet}$ radical cation

$\mathbf{1b}^{-\cdot} \xrightarrow{\tau_a} \mathbf{1b}$ Decay of **1b**$^{-\bullet}$ radical anion

3. PC (3DPAFIPN)+$DABCO$+**1a**+**1b**:

$^3PC^* + DABCO \xrightarrow{k_{sq}} PC^{-\cdot} + DABCO^{+\cdot}$ Photoinduced single electron transfer

$^3PC^* + \mathbf{1a} \xrightarrow{k_{sq}} PC^{-\cdot} + \mathbf{1a}^{+\cdot}$ Photoinduced single electron transfer

$DABCO^{+\cdot} + \mathbf{1a} \xrightarrow{\tau_r} DABCO + \mathbf{1a}^{+\cdot}$ Relay of $DABCO^{+\bullet}$ radical cation

$^3PC^* \xrightarrow{\tau_p} {}^1PC$ Phosphorescence decay of ^{3}PC* (^{3}[3DPAFIPN]*)

$PC^{-\cdot} \xrightarrow{\tau_-} {}^1PC$ Decay of PC$^{-\bullet}$ radical anion ([3DPAFIPN]$^{-\bullet}$)

$DABCO^{+\cdot} \xrightarrow{\tau_a} DABCO$ Decay of $DABCO^{+\bullet}$ radical cation

$\mathbf{1}\boldsymbol{a}^{+\cdot} \xrightarrow{\tau_a} \mathbf{1}\boldsymbol{a}$ Decay of **1a**$^{+\bullet}$ radical cation

$PC^{-\cdot} + \mathbf{1}\boldsymbol{b} \xrightarrow{k_{et}} {}^1PC + \mathbf{1}\boldsymbol{b}^{-\cdot}$ Electron transfer from PC$^{-\bullet}$ radical anion ([3DPAFIPN]$^{-\bullet}$) to **1b**.

$DABCO^{+\cdot} \xrightarrow{\tau_a} DABCO$ Decay of $DABCO^{+\bullet}$ radical cation

$\mathbf{1}\boldsymbol{b}^{-\cdot} \xrightarrow{\tau_a} \mathbf{1}\boldsymbol{b}$ Decay of **1b**$^{-\bullet}$ radical anion

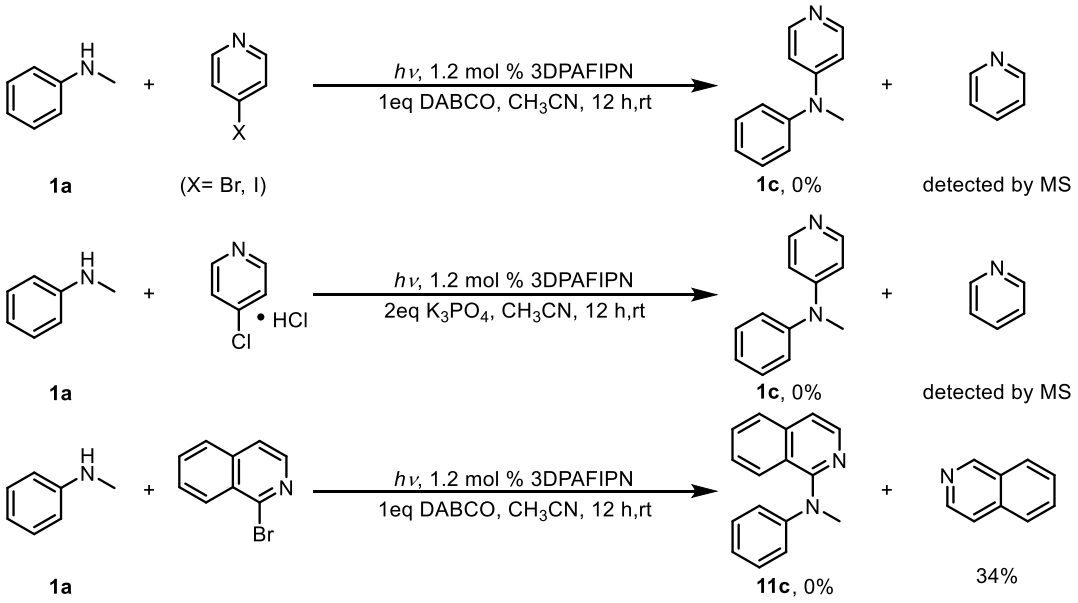
To simplify the system, we used the same method to analyze the transient absorption spectroscopy of DABCO as the above. By a bi-exponential decay fitting at 466 nm, we calculated that the decay lifetime of PC$^{-\bullet}$ was 107μs, 62.1μs, 87.4 μs respectively with the addition of DABCO into the solution containing PC, PC+**1b** or PC+**1a**+**1b**.

Entry	λ (nm)	τ_1	B_1	τ_2	B_2	χ^2
PC+DABCO	466	6.16	2.7×10^{-2}	107	5.0×10^{-3}	0.460
PC+DABCO+**1b**	466	6.13	3.2×10^{-2}	62.1	1.1×10^{-2}	0.417
PC+DABCO+**1a**+**1b**	466	6.82	1.9×10^{-2}	87.4	1.3×10^{-2}	0.624

To figure out the role of DABCO in this radical-radical cross-coupling reaction, the laser flash photolysis measurements of the solutions including PC+DACBCO, PC+**1a**+DACBCO, PC+**1b**+DACBCO and PC+**1a**+**1b**+DACBCO were also carried out. As shown in Figure S7a, the single electron transfer from DABCO to the excited ^{3}PC* provided PC$^{-\bullet}$ with the lifetime 107 μs, similar to that (109.1 μs) in the system of PC+**1a**. With the addition of **1b** into the solution of PC+DACBCO (Figure S7b, S7c), the lifetime of PC$^{-\bullet}$ was decreased to 62.1μs, indicating the singlet electron transfer from PC$^{-\bullet}$ to **1b**. When **1a** was added into the solution including PC+DABCO+**1b**, the lifetime of PC$^{-\bullet}$ was prolonged from 62.1 μs to 87.4 μs. As compared with the lifetime of PC$^{-\bullet}$ (12.6 μs) in the solution with PC+**1a**+**1b** mentioned in Figure S6, the presence of DABCO prolonged the lifetime of PC$^{-\bullet}$ to 87.4 μs (Figure S7d), which was attributed to the relay characteristic of DABCO suppressing charge recombination that is helpful for improving the efficiency of singlet electron transfer C-N formation.

4.3 The reactivity of heteroaryl halide

Given that the abundant source and wide application of aryl halides, a series of heteroaryl halides were examined their compatibility in our system. As shown in Scheme S3, *para*-halogenated pyridine (Cl, Br and I) and 1-bromoisoquinoline failed to couple with **1a**$^{+\bullet}$, but to provide pyridine or isoquinoline as the product instead.



Scheme S3. Photocatalysis for arylamine formation with different heteroaryl halide.

To understand the reason, we selected 4-bromopyridine as a model to investigate the radical formation by flash photolysis (Figure 1). When 4-bromopyridine was added into the system of PC and **1a**, the lifetime of PC$^{-\bullet}$ ([3DPAFIPN]$^{-\bullet}$) at 466 nm was quenched from 109.1 μs to 67.9 μs, indicating the singlet electron transfer (SET) from PC$^{-\bullet}$ to 4-bromopyridine is feasible. However, 4-cyanopyridine **1b** in the manuscript quenched the lifetime of PC$^{-\bullet}$ ([3DPAFIPN]$^{-\bullet}$) at 466 nm from 109.1 μs to 12.6 μs. Obviously, the rate constant of radical formation of 4-bromopyridine (5.5×10^{6} $M^{-1}s^{-1}$) from singlet electron transfer event was much slower than that of **1b** (7.0×10^{7} $M^{-1}s^{-1}$), and even two-order magnitude slower than the singlet electron transfer from ^{3}PC* to **1a** (5.1×10^{8} $M^{-1}s^{-1}$) to produce **1a**$^{+\bullet}$. Therefore, the large rate differences on the radical generation of 4-bromopyridine and **1a** led to no reactivity observed in the following cross-coupling reaction.

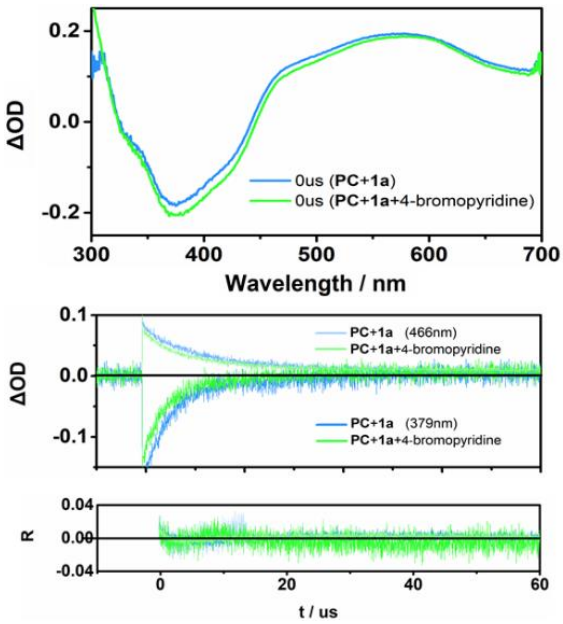


Figure S8. The transient absorption spectra of 3DPAFIPN (6×10^{-5} M) and **1a** (1×10^{-3} M) with or without 4-bromopyridine (1×10^{-3} M).

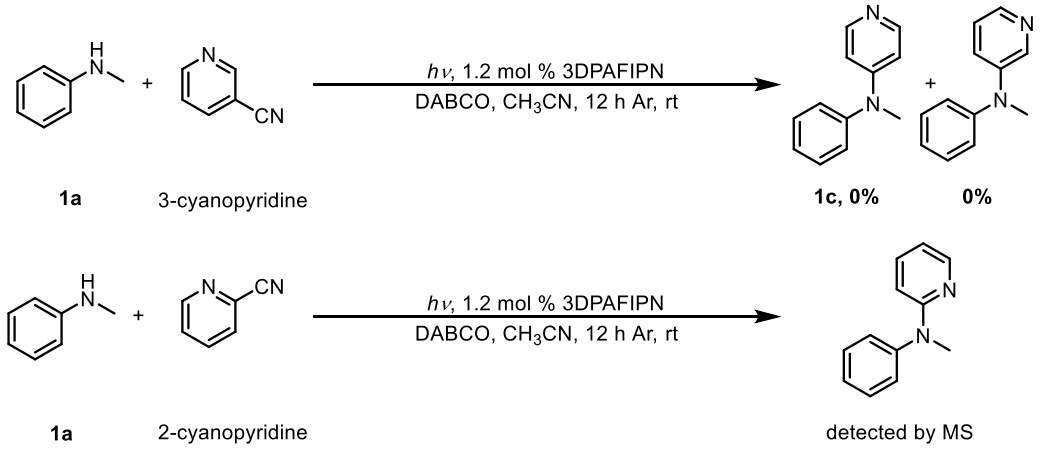
Transient absorption analysis

Replacing **1b** with 4-bromopyridine, we used the same method to analyze the transient absorption spectroscopy as the above. By a bi-exponential decay fitting at 466 nm, we calculated that the decay lifetime of $PC^{-\bullet}$ was 67.9 μs with the addition of 4-bromopyridine into the solution containing PC+**1a**. Furthermore, the electron transfer rate constant of 4-bromopyridine or 2-cyanopyridine with $PC^{-\bullet}$ is 5.5×10^{6} $M^{-1}s^{-1}$.

Entry	λ (nm)	τ_1	B_1	τ_2	B_2	χ^2
PC+**1a**+4-bromopyridine	466	4.5	5.4×10^{-2}	67.9	1.2×10^{-2}	0.706

4.4 The reactivity of 3-cyanopyridine and 2-cyanopyridine

To exclude the possibility of reaction in Minisci-type process, we carried out the control experiment to examine the reactivity of 3-cyanopyridine and 2-cyanopyridine under the standard condition (Scheme S4). It was found that **1a** could not work with 3-cyanopyridine under the standard condition, excluding the Minisci-type reaction process; but poor reactivity of **1a** with 2-cyanopyridine detected by GC-MS.



Scheme S4. The photocatalysis for arylammine formation with different heteroarylnitriles.

To shed more light on the poor reactivity of 2-cyanopyridine, CV experiments were carried out with 3-cyanopyridine as comparison. For 2-cyanopyridine, a new reductive peak was detected after **1a** was added (Figure S9a), indicating that $\mathbf{1a}^{+\bullet}$ could activate 2-cyanopyridine to lower its relative reductive potential from -2.04 V to -1.13 V (vs SCE). The decrease of reductive potential allowed the singlet electron transfer from $PC^{-\bullet}$[$E_{1/2}(PC/PC^{-\bullet})$ = -1.59 V vs SCE] to the activated 2-cyanopyridine. For 3-cyanopyridine, no obvious change in the CV spectra of **1a** and 3-cyanopyridine indicated a weak activation of 3-cyanopyridine ($E_{1/2}^{red}$= -2.11 V SCE) by $\mathbf{1a}^{+\bullet}$ (Figure S9b).

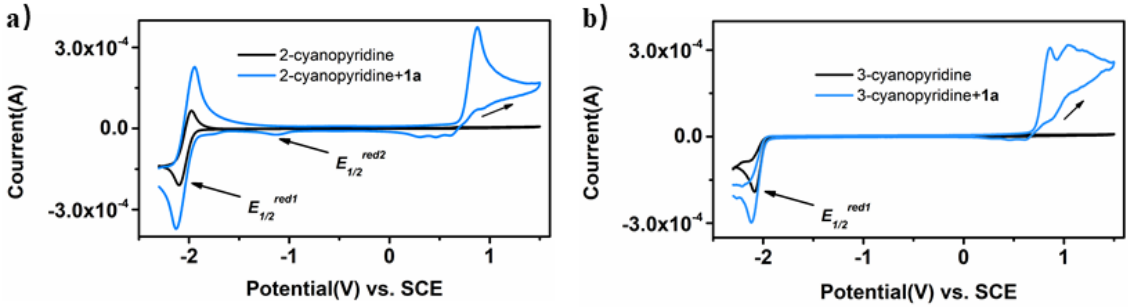


Figure S9. a) The CV spectra of 2-cyanopyridine (5.0×10^{-3} M) and NBu_4PF_6 (1.0×10^{-1} M) in the absence and presence of **1a** (5.0×10^{-3} M) in degassed CH_3CN, $E_{1/2}^{red1}$ = -2.04 V SCE, $E_{1/2}^{red2}$ = -1.13 V SCE; b) The CV spectra of 3-cyanopyridine (5.0×10^{-3} M) and NBu_4PF_6 (1.0×10^{-1} M) in the absence and presence of **1a** (5.0×10^{-3} M) in degassed CH_3CN, $E_{1/2}^{red1}$ = -2.11 V SCE.

Moreover, the flash photolysis showed that 2-cyanopyridine could quench $PC^{-\bullet}$ ($[3DPAFIPN]^{-\bullet}$) at 466 nm from 109.1 μs to 79.7 μs with a rate constant of 3.4×10^6 $M^{-1}s^{-1}$, while 3-cyanopyridine had no any alternation on the lifetime of $PC^{-\bullet}$ ($[3DPAFIPN]^{-\bullet}$) (Figure S10), suggesting the feasibility of the singlet electron transfer from $PC^{-\bullet}$ to 2-cyanopyridine rather than 3-cyanopyridine. However, 4-cyanopyridine **1b** quenched the $PC^{-\bullet}$ ($[3DPAFIPN]^{-\bullet}$) at 466 nm from 109.1 μs to 12.6 μs with a rate constant of 7.0×10^7 $M^{-1}s^{-1}$, which is much faster than the singlet-electron-transfer rate of 2-cyanopyridine (3.4×10^6 $M^{-1}s^{-1}$). More significantly, the two-order magnitude slower of the singlet electron transfer from $PC^{-\bullet}$ ($[3DPAFIPN]^{-\bullet}$) to 2-cyanopyridine (3.4×10^6 $M^{-1}s^{-1}$) than that from $^3PC^*$ to **1a** (5.1×10^8 $M^{-1}s^{-1}$) to produce $\mathbf{1a}^{+\bullet}$ was believed responsible for the poor reactivity of 2-cyanopyridine.

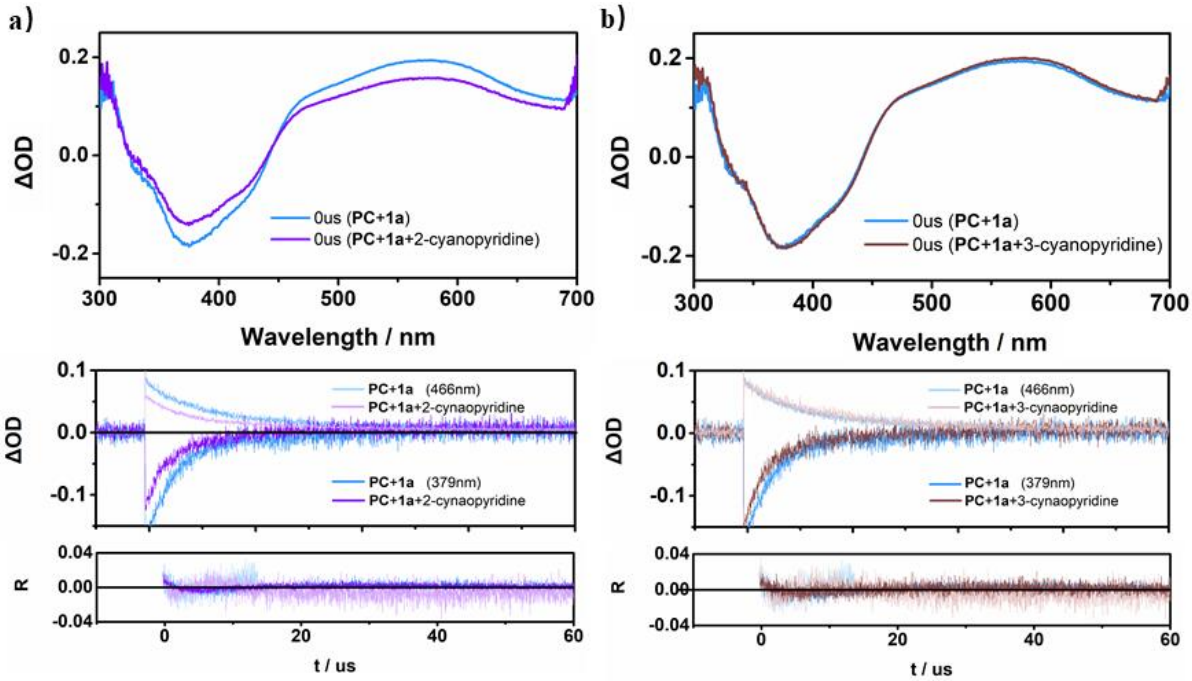


Figure S10. a) The transient absorption spectra of 3DPAFIPN (6×10^{-5} M) and **1a** (1×10^{-3} M) with or without 2-cyanopyridine (1×10^{-3} M); b) The transient absorption spectra of 3DPAFIPN (6×10^{-5} M) and **1a** (1×10^{-3} M) with or without 3-cyanopyridine (1×10^{-3} M).

Transient absorption analysis

Replacing **1b** with 2-cyanopyridine, we used the same method to analyze the transient absorption spectroscopy as the above. By a bi-exponential decay fitting at 466 nm, we calculated that the decay lifetime of $PC^{-\bullet}$ was 79.7 μs with the addition of 2-cyanopyridine into the solution containing PC+**1a**. Furthermore, the electron transfer rate constant of 2-cyanopyridine with $PC^{-\bullet}$ was determined as 3.4×10^6 $M^{-1}s^{-1}$.

Entry	λ (nm)	τ_1	B_1	τ_2	B_2	χ^2
PC+**1a**+2-cyanopyridine	466	4.4	3.7×10^{-2}	79.7	9.1×10^{-3}	0.702

4.5 The scope of photocatalysts

Although their redox potential were matched for this radical-radical cross-coupling reaction, 4CzIPN, Eosin Y and Rh6G showed no product formation as shown in Table S1. To figure out the no reactivities of these photocatalysis, the flash photolysis investigations were also undertaken. The signals of Rh6G in the transient absorption spectra were too weak to obtain any useful information, and only the transient absorption spectra of Eosin Y and 4CzIPN were provided (Figure S11, S12).

Eosin Y displayed strong bleach of the ground state absorption (GSB) at approximately 515 nm and the excited state absorption assigned to the triplet excited state ^{3}Eosin Y* at 570 nm after a laser excitation by 530 nm light (Figure S11a). When **1a** was introduced into the solution of Eosin Y, the new absorption bands at 425 nm appeared at the expense of the ^{3}Eosin Y* absorption at 570 nm, which was assigned to Eosin Y $^{-\bullet}$. However, the introduction of **1b** into the solution with Eosin Y and **1a** resulted in no change of the absorption of Eosin Y $^{-\bullet}$ (Figure S11b). These results indicated the singlet electron transfer from ^{3}Eosin Y* to **1a** is feasible, but not for Eosin Y $^{-\bullet}$ to **1b** in spite of in the suitable potentials (-1.06 V vs SCE for Eosin Y $^{-\bullet}$ and -0.87 V vs SCE for **1b** in the presence of **1a**$^{+\bullet}$).

The situation of 4CzIPN was same as that of Eosin Y. When **1a** was introduced into the solution of 4CzIPN, the new absorption bands at 465 nm appeared (Figure S12a), which was assigned to 4CzIPN $^{-\bullet}$. However, there was no change of the absorption of 4CzIPN $^{-\bullet}$ with the addition of **1b** into the solution of 4CzIPN and **1a** (Figure S12b), which suggested that ^{3}4CzIPN * could efficiently oxidize **1a** to produce **1a**$^{+\bullet}$, while 4CzIPN $^{-\bullet}$ failed to reduce **1b** to provide **1b**$^{-\bullet}$ for subsequent reaction**.**

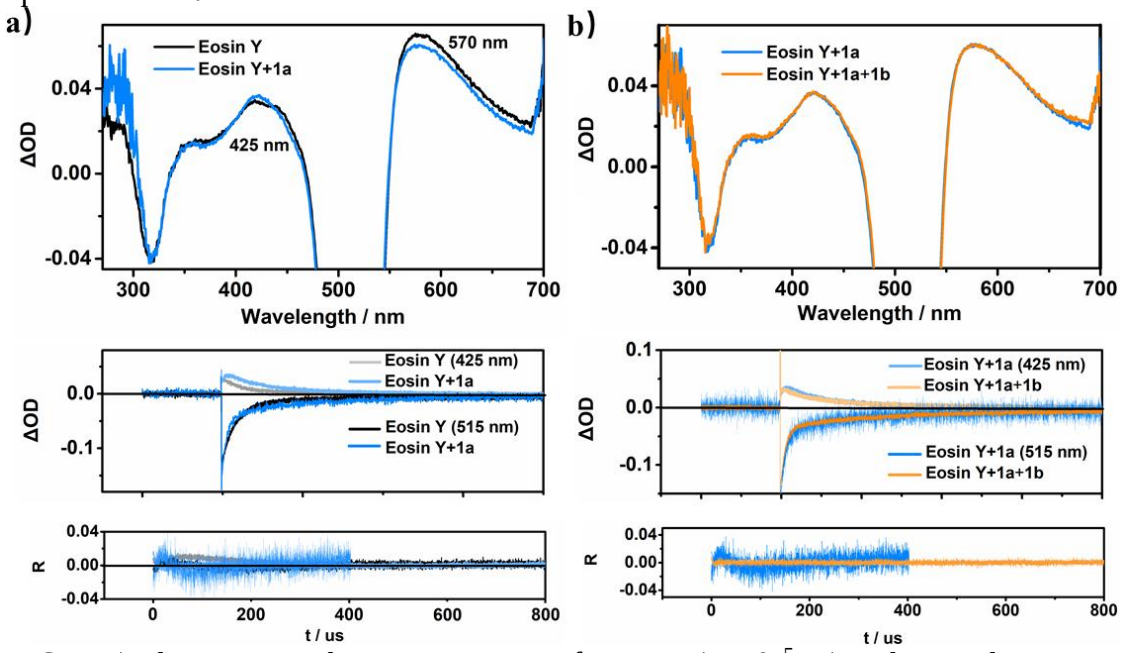


Figure S11. a) The transient absorption spectra of EosinY (5×10^{-5} M) with or without **1a** (1×10^{-3} M); b) The transient absorption spectra of EosinY (5×10^{-5} M) and **1a** (1×10^{-3} M) with or without **1b** (1×10^{-3} M).

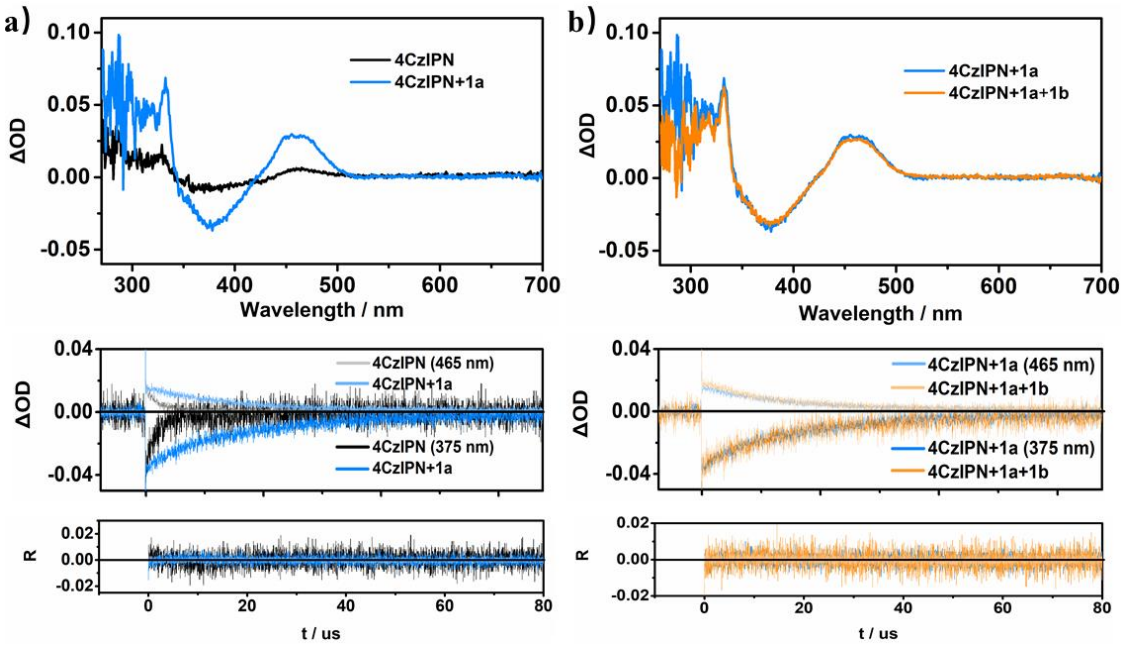


Figure S12. a) The transient absorption spectra of 4CzIPN (5×10^{-5} M) with or without **1a** (1×10^{-3} M); b) The transient absorption spectra of 4CzIPN (5×10^{-5} M) and **1a** (1×10^{-3} M) with or without **1b** (1×10^{-3} M).

Next, CV experiments were further carried out to investigate the reaction. As shown in Figure 4, once reduction of Eosin Y to Eosin Y $^{-\bullet}$, there was no new peak in the CV spectra of the mixture of **1a** and **1b** (Figure S13a), indicating that the association of Eosin Y $^{-\bullet}$ with **1a**$^{+\bullet}$ failed to activate the **1b** from -1.84 V vs SCE for **1b** to -0.87 V SCE for subsequent electron transfer from Eosin Y $^{-\bullet}$ to **1b**, thus showing no catalytic activity. The result was also the case with that of Rh 6G where no new peak appeared in the presence of Rh 6G $^{-\bullet}$ (Figure S13b). For 4CzIPN, a new peak was detected at -0.85 V SCE for **1b** (Figure S13c), indicating that 4CzIPN $^{-\bullet}$ have no much influence on the activation of **1a**$^{+\bullet}$ to **1b**, but the following electron transfer from 4CzIPN $^{-\bullet}$ to **1b** was inefficient.

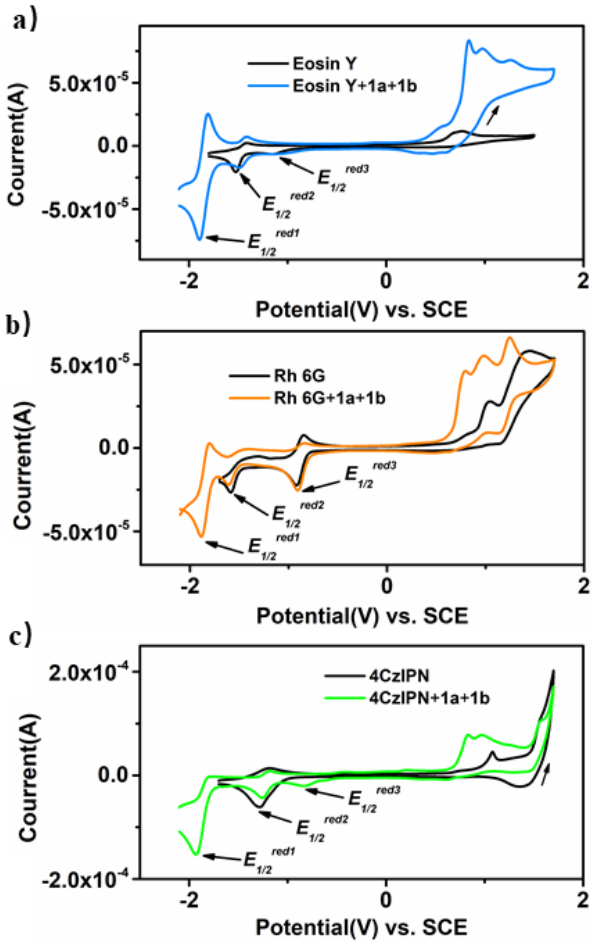
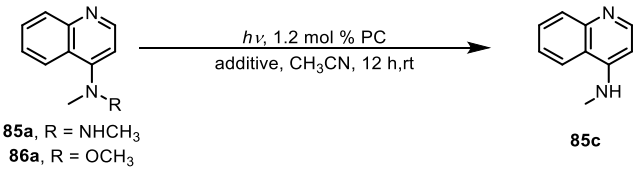


Figure S13. a) The CV spectra of Eosin Y (1.0×10^{-3} M) and NBu_4PF_6 (1.0×10^{-1} M) in the absence and presence of **1a** (1.0×10^{-3} M) and **1b** (1.0×10^{-3} M) in degassed CH_3CN, $E_{1/2}^{red1}$ = -1.84 V SCE for **1b**, $E_{1/2}^{red2}$ = -1.51 V SCE and $E_{1/2}^{red3}$= -1.17 V SCE for Eosin Y; b) The CV spectra of Rh 6G (1.0×10^{-3} M) and NBu_4PF_6 (1.0×10^{-1} M) in the absence and presence of **1a** (1.0×10^{-3} M) and **1b** (1.0×10^{-3} M) in degassed CH_3CN, $E_{1/2}^{red1}$ = -1.84 V SCE for **1b**, $E_{1/2}^{red2}$ = -1.59 V SCE and $E_{1/2}^{red3}$= -0.92 V SCE for Rh 6G; c) The CV spectra of 4CzIPN (1.0×10^{-3} M) and NBu_4PF_6 (1.0×10^{-1} M) in the absence and presence of **1a** (1.0×10^{-3} M) and **1b** (1.0×10^{-3} M) in degassed CH_3CN, $E_{1/2}^{red1}$ = -1.84 V SCE for **1b**, $E_{1/2}^{red2}$ = -1.27 V SCE for 4CzIPN, $E_{1/2}^{red3}$= -0.85 V SCE for **1b** with **1a**$^{+\bullet}$.

4.6 The mechanistic study of hydrazine and hydroxylamine

To make clear the mechanism of hydrazines and hydroxylamines, heteroaryl hydrazine **85a** and hydroxylamine **86a** were synthesized and subjected to an array of reaction systems. As shown in Table S2, both hydrazine **85a** and heteroaryl hydroxylamine **86a** could be converted to their corresponding heteroaryl amine **85c** under direct irradiation (at 450 nm) with 7% and 25% yield (entry 1). With irradiation of 3DPAFIPN and *fac*-Ir(ppy)$_3$ as photocatalysts, the yields of heteroaryl amine **85c** were increased to ~90% (entries 2-3). The reactions couldn't proceed without irradiation (entry 4). The presence of diverse reductants, such as hydrazine, hydroxylamine, and triethylamine, slightly decreased the yield of products (entries 5-7).

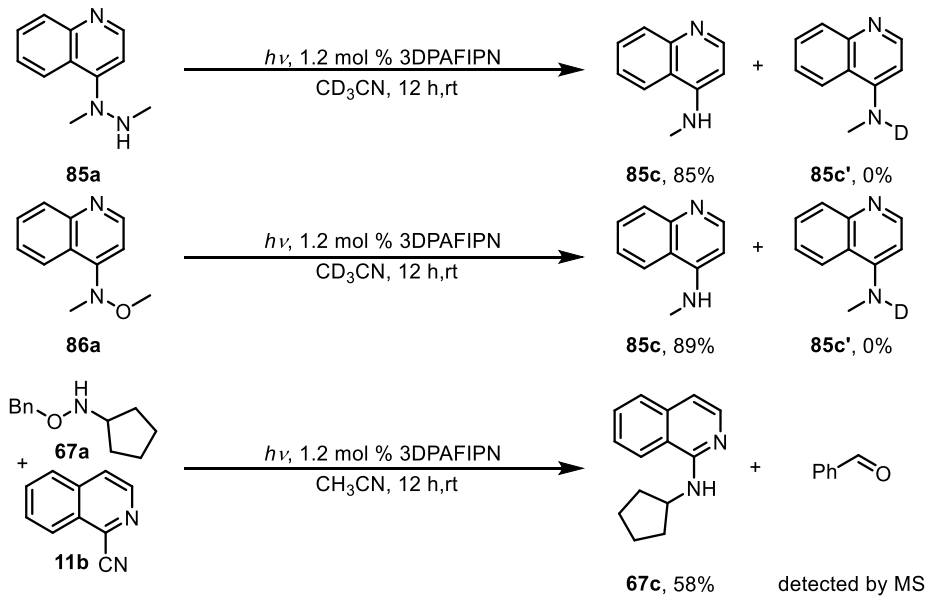
Table S2. The optimization for the synthesis of heteroarylamines [a]



Entry	**85a** or **86a** (mmol)	photocatalyst	additive	Solvent	Yield (**85a**)[b]	Yield (**86a**)[b]
1	0.2	-	-	CH_3CN	7%	25%
2	0.2	3DPAFIPN	-	CH_3CN	87%	90%
3	0.2	*fac*-Ir(ppy)$_3$	-	CH_3CN	92%	93%
4[c]	0.2	3DPAFIPN	-	CH_3CN	0%	0%
5[d]	0.2	3DPAFIPN	*t*-$BuNHNH_2$	CH_3CN	71%	-
6[d]	0.2	3DPAFIPN	CH_3NHOCH_3	CH_3CN	-	74%
7	0.2	3DPAFIPN	Et_3N	CH_3CN	68%	72%

[a]Reaction condition: 0.2 mmol (1 equiv) **85a** or **86a**, 0.2 mmol (1 equiv) additive, 1.2 mol % PC, 3 mL solvent, Ar, blue LEDs, room temperature. [b]The yields were determined by ^{1}H NMR using diphenylmethano as the internal standard. [c]no light. [d] 0.2 mmol (1 equiv) hydrazine or hydroxylamine hydrochloride and 0.2 mmol (1 equiv) K_3PO_4.

To figure out the hydrogen source of N-H in heteroaryl amine **85c**, the deuterium labeling experiments showed no deuterated product **85c** formation with deuterated acetonitrile CD_3CN as the solvent (Scheme S5), implying that the hydrogen source was derived from the substrate itself. The cross-coupling reaction of hydroxylamine **67a** and **11b** produced the target **67c** and benzaldehyde as a byproduct (detected by MS), consistent with the speculation of the substrate itself as the hydrogen source.



Scheme S5. The deuterium labeling experiments.

Next, CV investigation found that the reductive potentials of heteroaryl hydrazine **85a** ($E_{1/2}^{red}$ = -2.31 V SCE) and heteroaryl hydroxylamine **86a** ($E_{1/2}^{red}$ = -1.99 V SCE) were too negative to be reduced by 3DPAFIPN* [$E_{1/2}(PC^{+}/PC^{*})$ = -1.38 V SCE] and *fac*-Ir(ppy)$_3$* [$E_{1/2}(PC^{+}/PC^{*})$ = -1.73 V SCE] (Figure S14), and the oxidative potentials of hydrazine **85a** ($E_{1/2}^{ox1}$ = +0.45 V SCE) and heteroaryl hydroxylamine **86a** ($E_{1/2}^{ox}$ = +1.35 V SCE) were more positive than that of 3DPAFIPN* [$E_{1/2}(PC^{+\bullet}/PC^{*}$ = +1.09 V vs SCE) and *fac*-Ir(ppy)$_3$* [$E_{1/2}(PC^{*}/PC^{-})$ = +0.31 V SCE]. Therefore, the reductive fragmentation of N-X (X = N, O) bond is not thermodynamically feasible.

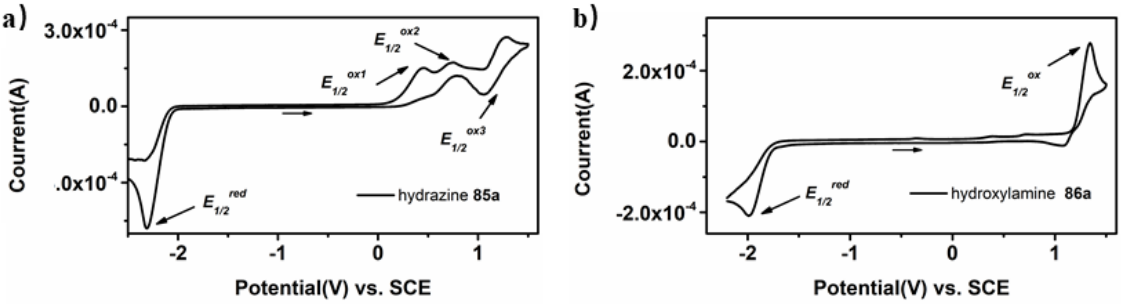


Figure S14. a) The CV spectra of **85a** (5.0×10^{-3} M) and NBu_4PF_6 (1.0×10^{-1} M) in degassed CH_3CN, $E_{1/2}^{red}$ = -2.31 V SCE, $E_{1/2}^{0x1}$ = +0.45 V SCE, $E_{1/2}^{0x2}$ = +0.74 V SCE and $E_{1/2}^{ox3}$ = +1.17 V SCE; b) The CV spectra of **85a** (5.0×10^{-3} M) and NBu_4PF_6 (1.0×10^{-1} M) in degassed CH_3CN, $E_{1/2}^{red}$ = -1.99 V SCE, $E_{1/2}^{0x}$ = +1.35 V SCE.

A series of spectroscopic experiments were then performed. The UV−vis absorption spectra showed that both of heteroaryl hydrazine **85a** and heteroaryl hydroxylamine **86a** at reaction concentration absorbed visible light (Figure S15b). Upon direct excitation, the normalized fluorescence at 298 K and phosphorescence at 77 K (Figure S15b) revealed the possibility of the triplet energy transfer from 3DPAFIPN* (55.8 kcal/mol) or *fac*-Ir(ppy)$_3$* (58.7 kcal/mol) to the substrates **85a** and **86a** with the triplet energy of 55.5 kcal/mol and 56.6 kcal/mol, respectively.

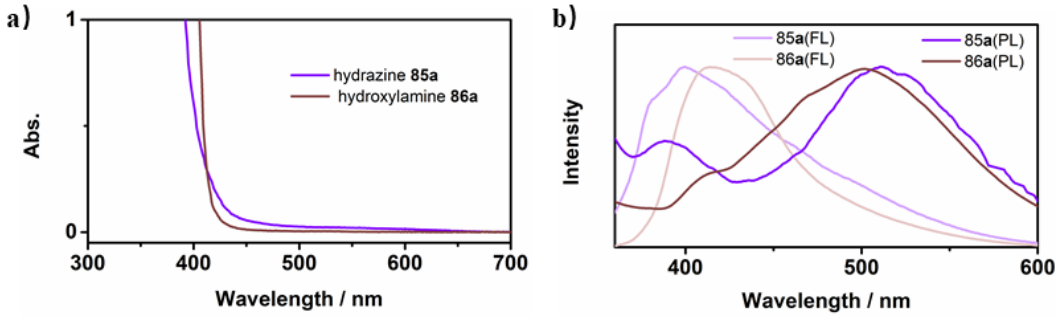
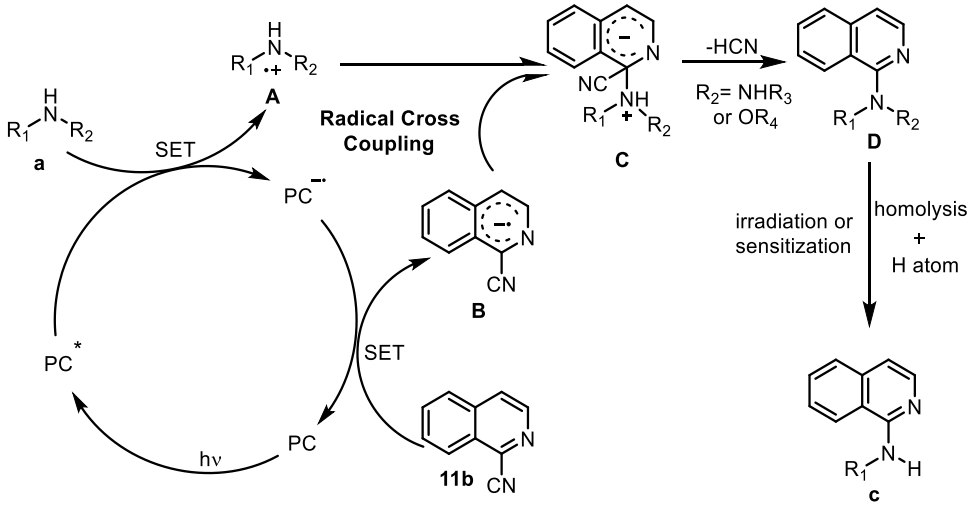


Figure S15. a) Absorption spectra of spectrum of **85a** (6.7×10^{-2} M) and **86a** (6.7×10^{-2} M) at reaction concentration in CH_3CN; b) The normalized fluorescence at 298K and phosphorescence at 77k of **85a** (1.0×10^{-3} M) and **86a** (1.0×10^{-3} M) in degassed 2-methyltetrahydrofuran. The triplet energy of **85a** and **86a** were 55.5 kcal/mol and 56.6 kcal/mol respectively.

Based on the above experimental observations, a revised plausible mechanism was outlined in Scheme S6 for hydrazine and hydroxylamine as substrates. Under visible light irradiation, 3DPAFIPN (PC) was pumped to its excited state (PC*), and subsequently reduced by hydrazine (or hydroxylamine), leading to the formation of the *N*-radical cation **A** along with $PC^{-\bullet}$. SET reduction of **11b** by $PC^{-\bullet}$ provided the radical anion **B**, simultaneously regenerating the ground-state photocatalyst PC thereby closing the photocatalytic cycle. *N*-radical cation **A** coupled with radical anion **B** to produce intermediate **C**, which eliminated HCN to afford heteroaryl hydrazine or heteroaryl hydroxylamine **D**. At last, heteroaryl hydrazine (heteroaryl hydroxylamine **D**) was homolyzed under direct irradiation or sensitization by photocatalysts, which subsequently underwent hydrogen atom abstract or proton-coupled electron transfer to provide the target heteroaryl amines.



Scheme S6. Possible mechanism for hydrazine and hydroxylamine access to heteroarylamine

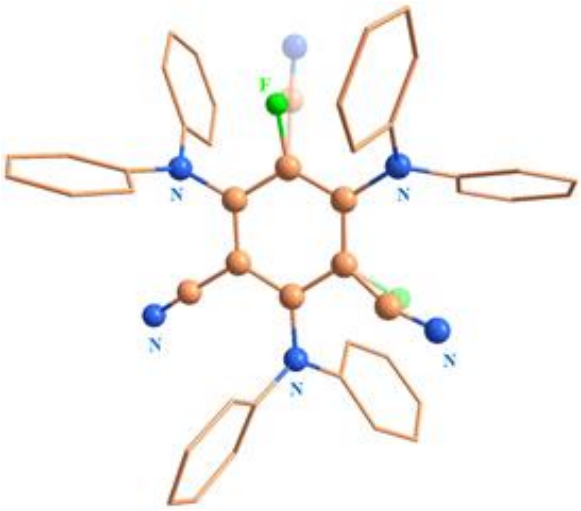


Figure S16. A single crystal was grown by slow diffusion of a solution of 3DPAFIPN in dichloromethane and n-hexane. Supplementary crystallographic data for this compound have been deposited at Cambridge Crystallographic Data Centre (CCDC 2014477) and can be obtained free of charge (DOI: 10.5517/ccdc.csd.cc25m746).

5. References

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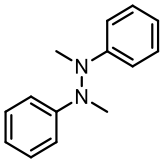
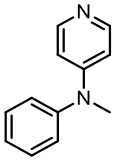
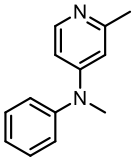
6. Characterization for all products.



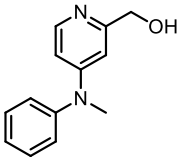
1,2-dimethyl-1,2-diphenylhydrazine (aa) The characterization data of **aa** was same as the reported.



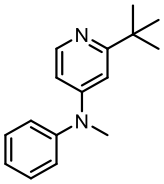
***N*-methyl-*N*-phenylpyridin-4-amine (1c)** The product is obtained as white soild (isolated yield: 98%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 5.5 Hz, 2 H), 7.43 (t, *J* = 7.7 Hz, 2 H), 7.32–7.16 (m, 3 H), 6.54 (d, *J* = 5.7 Hz, 2 H), 3.32 (s, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.79, 149.72, 146.15, 129.96, 126.66, 126.39, 108.28, 39.38. ESI: Calcd.for $C_{12}H_{12}N_2$ $[M+H]^+$: 185.1079; found: 185.1069.



***N*,2-dimethyl-*N*-phenylpyridin-4-amine (2c)** The product is obtained as white soild (isolated yield: 87%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 5.9 Hz, 1 H), 7.42 (t, *J* = 7.8 Hz, 2 H), 7.33–7.12 (m, 3 H), 6.49–6.33 (m, 2 H), 3.30 (s, 3 H), 2.40 (s, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.35, 154.28, 149.17, 146.42, 129.88, 126.66, 126.18, 107.33, 106.04, 39.43, 24.70. ESI: Calcd.for $C_{13}H_{14}N_2$ $[M+H]^+$:199.1235; found:199.1221.

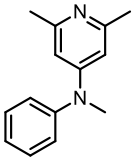


(4-(methyl(phenyl)amino)pyridin-2-yl)methanol (3c) The product is obtained as white soild (isolated yield: 88%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 6.6 Hz, 1 H), 7.45 (t, *J* = 7.5 Hz, 2 H), 7.31 (t, *J* = 7.4 Hz, 1 H), 7.21 (d, *J* = 7.8 Hz, 2 H), 6.48 (s, 2 H), 4.61 (s, 2 H), 3.35 (s, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.98, 155.09, 147.61, 146.05, 130.26, 126.94, 126.81, 107.58, 104.52, 64.17, 39.76. ESI: Calcd. for $C_{13}H_{14}N_2O$ $[M+H]^+$: 215.1184; found: 215.1170.

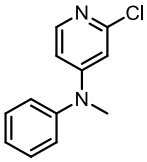


2-(tert-butyl)-*N*-methyl-*N*-phenylpyridin-4-amine (4c) The product is obtained as white soild (isolated yield: 92%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 5.8 Hz, 1 H), 7.42 (t, *J* = 7.7 Hz, 2 H), 7.25 (d, *J* = 5.9 Hz, 1 H), 7.21 (d, *J* = 8.1 Hz, 2 H), 6.65 (d, *J* = 2.0 Hz, 1 H), 6.40 (dd, *J* = 5.8, 2.1 Hz, 1 H), 3.33 (s, 3 H), 1.31 (s, 9 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.38, 154.32,

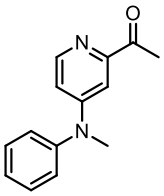
148.61, 146.58, 129.82, 126.42, 125.98, 106.12, 103.68, 39.44, 37.22, 30.15. ESI: Calcd. for $C_{16}H_{20}N_2$ [M+H]$^+$: 241.1705; found: 241.1689.



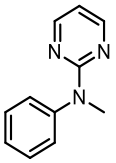
***N*,2,6-trimethyl-*N*-phenylpyridin-4-amine (5c)** The product is obtained as white soild (isolated yield: 88%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (t, *J* = 7.8 Hz, 2 H), 7.26 (d, *J* = 6.6 Hz, 1 H), 7.19 (d, *J* = 7.6 Hz, 2 H), 6.27 (s, 2 H), 3.29 (s, 3 H), 2.38 (s, 6 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.72, 154.77, 146.63, 129.82, 126.65, 126.00, 105.07, 39.49, 24.69. ESI: Calcd. for $C_{14}H_{16}N_2$ [M+H] $^+$: 213.1392; found: 213.1380.



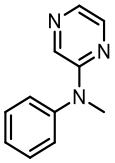
2-chloro-*N*-methyl-*N*-phenylpyridin-4-amine (6c) The product is obtained as white soild (isolated yield: 50%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 5.8 Hz, 1 H), 7.45 (t, *J* = 7.8 Hz, 2 H), 7.32 (t, *J* = 7.4 Hz, 1 H), 7.23–7.15 (m, 2 H), 6.53 (d, *J* = 2.3 Hz, 1 H), 6.43 (dd, *J* = 6.0, 2.3 Hz, 1 H), 3.31 (s, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.83, 152.22, 149.09, 145.53, 130.20, 127.05, 126.76, 107.43, 107.01, 39.69. ESI: Calcd. for $C_{12}H_{11}ClN_2$ [M+H]$^+$: 219.0689; found: 219.0679.



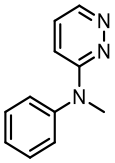
1-(4-(methyl(phenyl)amino)pyridin-2-yl)ethanone (7c) The product is obtained as white soild (isolated yield: 53%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, *J* = 5.8 Hz, 1 H), 7.44 (t, *J* = 7.8 Hz, 2 H), 7.36 (d, *J* = 2.7 Hz, 1 H), 7.33–7.26 (m, 1 H), 7.24–7.16 (m, 2 H), 6.65 (dd, *J* = 5.8, 2.7 Hz, 1 H), 3.37 (s, 3 H), 2.68 (s, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.83, 152.22, 149.09, 145.53, 130.20, 127.05, 126.76, 107.43, 107.01, 39.69. ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.85, 154.55, 154.23, 149.01, 145.83, 130.15, 126.76, 126.61, 111.10, 105.83, 39.67, 26.02. ESI: Calcd. for $C_{14}H_{14}N_2O$ [M+H]$^+$: 227.1184; found: 227.1168.



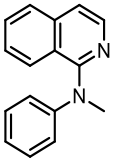
***N*-methyl-*N*-phenylpyrimidin-2-amine (8c)** The product is obtained as white soild (isolated yield: 33%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (d, *J* = 4.7 Hz, 2 H), 7.41 (t, *J* = 7.8 Hz, 2 H), 7.32 (d, *J* = 7.4 Hz, 2 H), 7.25–7.22 (m, 1 H), 6.57 (t, *J* = 4.8 Hz, 1 H), 3.53 (s, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.98, 157.64, 145.55, 129.17, 126.56, 125.85, 110.73, 38.68. ESI: Calcd. for $C_{11}H_{11}N_3$ [M+H] $^+$: 186.1031; found: 186.1023.



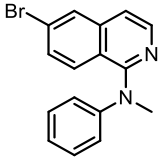
***N*-methyl-*N*-phenylpyrazin-2-amine (9c)** The product is obtained as white soild (isolated yield: 33%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12–8.07 (m, 1 H), 7.94 (d, *J* = 1.2 Hz, 1 H), 7.83 (d, *J* = 2.7 Hz, 1 H), 7.45 (t, *J* = 7.8 Hz, 2 H), 7.33–7.26 (m, 3 H), 3.46 (s, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.00, 144.82, 142.07, 132.37, 131.77, 130.17, 126.77, 126.31, 38.30. ESI: Calcd. for $C_{11}H_{11}N_3$ $[M+H]^+$: 186.1031; found: 186.1023.



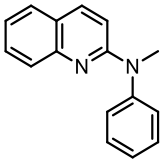
***N*-methyl-*N*-phenylpyridazin-3-amine (10c)** The product is obtained as white soild (isolated yield: 23%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (d, *J* = 4.0 Hz, 1 H), 7.45 (t, *J* = 7.8 Hz, 2 H), 7.35 –7.21 (m, 3 H), 7.07 (dd, *J* = 9.3, 4.5 Hz, 1 H), 6.75 (dd, *J* = 9.3, 1.1 Hz, 1 H), 3.60 (s, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.56, 145.47, 143.54, 130.14, 126.67, 126.56, 126.39, 114.14, 38.86. ESI: Calcd. for $C_{11}H_{11}N_3$ $[M+Na]^+$: 208.0851; found: 208.0841.



***N*-methyl-*N*-phenylisoquinolin-1-amine (11c)** The product is obtained as white soild (isolated yield: 98%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, *J* = 5.7 Hz, 1 H), 7.71 (dd, *J* = 16.5, 8.4 Hz, 2 H), 7.52 (t, *J* = 7.5 Hz, 1 H), 7.33 (d, *J* = 5.7 Hz, 1 H), 7.28–7.19 (m, 3 H), 6.96 (t, *J* = 7.3 Hz, 1 H), 6.90 (d, *J* = 7.9 Hz, 2 H), 3.59 (s, 3 H). ^{13}CNMR (101 MHz, $CDCl_3$) δ 158.65, 150.97, 141.31, 138.53, 129.73, 129.41, 127.11, 126.96, 126.32, 123.13, 122.37, 121.36, 116.92, 41.54. ESI: Calcd. for $C_{16}H_{14}N_2$ $[M+H]^+$: 235.1235; found: 235.1224.

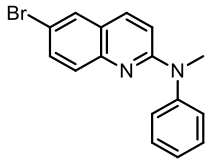


6-bromo-*N*-methyl-*N*-phenylisoquinolin-1-amine (12c) The product is obtained as white soild (isolated yield: 55%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, *J* = 5.6 Hz, 1 H), 7.88 (s, 1 H), 7.48 (d, *J* = 9.0 Hz, 1 H), 7.30–7.18 (m, 4 H), 7.02 (t, *J* = 7.3 Hz, 1 H), 6.93 (d, *J* = 7.8 Hz, 2 H), 3.58 (s, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.39, 150.69, 142.17, 139.57, 129.47, 129.37, 129.02, 128.68, 124.23, 123.10, 122.17, 120.86, 115.20, 41.73. ESI: Calcd. for $C_{16}H_{13}BrN_2$ $[M+H]^+$: 314.0340; found: 313.0331.

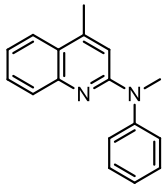


***N*-methyl-*N*-phenylquinolin-2-amine (13c)** The product is obtained as white soild (isolated yield: 70%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.2 Hz, 1 H), 7.67 (d, *J* = 9.1 Hz, 1 H),

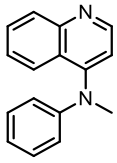
7.55 (t, *J* = 8.4 Hz, 2 H), 7.42 (t, *J* = 7.8 Hz, 2 H), 7.33–7.18 (m, 4 H), 6.73 (d, *J* = 9.1 Hz, 1 H), 3.63 (s, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.14, 147.96, 146.60, 136.32, 129.84, 129.44, 127.30, 126.74, 126.69, 125.92, 123.39, 122.49, 112.13, 38.67. ESI: Calcd. for $C_{16}H_{14}N_2$ $[M+H]^+$: 235.1235; found: 235.1221.



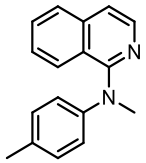
6-bromo-*N*-methyl-*N*-phenylquinolin-2-amine (14c) The product is obtained as white soild (isolated yield: 51%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76–7.56 (m, 4 H), 7.45 (t, *J* = 7.6 Hz, 2 H), 7.34–7.26 (m, 3 H), 6.73 (d, *J* = 9.1 Hz, 1 H), 3.62 (s, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.26, 157.50, 141.51, 140.16, 138.06, 134.42, 129.25, 126.76, 126.67, 126.59, 126.09, 126.05, 125.68, 122.75, 121.59, 116.61, 53.64, 33.57. ^{13}C NMR (101 MHz, Chloroform-*d*) δ 157.17, 146.67, 146.11, 135.33, 132.60, 129.96, 129.30, 128.37, 126.79, 126.32, 124.48, 115.24, 112.80, 38.71. ESI: Calcd. for $C_{16}H_{13}BrN_2$ $[M+H]^+$:314.0340; found: 313.0328.



***N*,4-dimethyl-*N*-phenylquinolin-2-amine (15c)** The product is obtained as white soild (isolated yield: 85%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86–7.74 (m, 2 H), 7.58 (t, *J* = 7.5 Hz, 1 H), 7.45 (t, *J* = 7.5 Hz, 2 H), 7.34–7.25 (m, 4 H), 6.62 (s, 1H), 3.65 (s, 3 H), 2.46 (s, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.95, 147.88, 146.68, 144.05, 129.81, 129.24, 127.16, 126.65, 125.78, 123.80, 123.55, 122.33, 112.19, 38.61, 18.93. ESI: Calcd. for $C_{17}H_{16}N_2$ $[M+H]^+$: 249.1392; found: 249.1379.

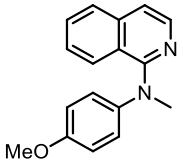


***N*-methyl-*N*-phenylquinolin-4-amine (16c)** The product is obtained as white soild (isolated yield: 50%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.83 (d, *J* = 4.9 Hz, 1 H), 8.09 (d, *J* = 8.5 Hz, 1 H), 7.71 (d, *J* = 8.5 Hz, 1 H), 7.62 (t, *J* = 7.6 Hz, 1 H), 7.31 (t, *J* = 7.6 Hz, 1 H), 7.27–7.21 (m, 2 H), 7.13 (d, *J* = 4.9 Hz, 1 H), 6.96 (t, *J* = 7.3 Hz, 1 H), 6.88 (d, *J* = 8.2 Hz, 2 H), 3.48 (s, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.82, 150.91, 149.86, 149.66, 129.77, 129.33, 129.27, 125.65, 124.68, 124.50, 121.61, 119.30, 114.23, 41.87. ESI: Calcd. for $C_{16}H_{14}N_2$ $[M+H]^+$: 235.1235; found: 235.1220.



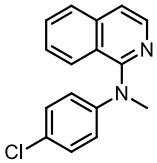
***N*-methyl-*N*-(*p*-tolyl)isoquinolin-1-amine (17c)** The product is obtained as white soild (isolated yield: 92%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, *J* = 5.7 Hz, 1 H), 7.68 (dd, *J* = 12.4, 8.5 Hz, 2 H), 7.48 (t, *J* = 7.5 Hz, 1 H), 7.34–7.12 (m, 2 H), 7.02 (d, *J* = 7.9 Hz, 2 H), 6.84 (d, *J* = 7.7 Hz, 2 H), 3.55 (s, 3 H), 2.27 (s, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.56, 148.69, 141.02, 138.27,

132.31, 129.93, 129.35, 126.94, 126.88, 125.87, 122.52, 122.23, 116.13, 41.94, 20.76. ESI: Calcd. for $C_{17}H_{16}N_2$ [M+H] $^+$: 249.1392; found: 249.1376.

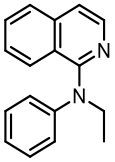


***N*-(4-methoxyphenyl)-*N*-methylisoquinolin-1-amine (18c)** The product is obtained as white soild (isolated yield: 94%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 5.6 Hz, 1 H), 7.64 (dd, *J* = 17.2, 8.4 Hz, 2 H), 7.45 (t, *J* = 7.4 Hz, 1 H), 7.30–7.10 (m, 2 H), 6.93 (d, *J* = 8.5 Hz, 2 H), 6.78 (d, *J* = 8.5 Hz, 2 H), 3.74 (s, 3 H), 3.52 (s, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.47, 155.91, 144.80, 140.73, 138.30, 129.22, 126.99, 126.86, 125.67, 124.62, 122.00, 115.57, 114.75, 55.44, 42.64. ESI: Calcd. for $C_{17}H_{16}N_2O$ [M+H] $^+$: 265.1341; found: 265.1331.

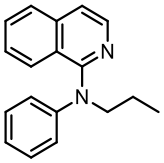
***N*-(4-fluorophenyl)-*N*-methylisoquinolin-1-amine (19c)** The product is obtained as white soild (isolated yield: 92%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 5.7 Hz, 1 H), 7.72 (d, *J* = 8.2 Hz, 1 H), 7.65 (d, *J* = 8.6 Hz, 1 H), 7.51 (t, *J* = 7.5 Hz, 1 H), 7.31 (d, *J* = 5.7 Hz, 1 H), 7.25 (t, *J* = 7.7 Hz, 1 H), 6.98–6.84 (m, 4 H), 3.54 (s, 3 H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 158.63 (d, *J* = 242.4 Hz) , 158.39, 147.28 (d, *J* = 3.1 Hz), 141.02, 138.34, 129.52, 127.01, 126.63, 126.11, 123.42 (d, *J* = 8.3 Hz), 122.40, 116.56, 116.01 (d, *J* = 22.5 Hz), 42.06. ^{19}F NMR (377 MHz, $CDCl_3$) δ -120.50. ESI: Calcd. for $C_{16}H_{13}FN_2$ [M+H]$^+$: 253.1141; found: 253.1123.



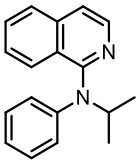
***N*-(4-chlorophenyl)-*N*-methylisoquinolin-1-amine (20c)** The product is obtained as white soild (isolated yield: 89%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, *J* = 5.7 Hz, 1 H), 7.77 (d, *J* = 8.2 Hz, 1 H), 7.70 (d, *J* = 8.5 Hz, 1 H), 7.57 (t, *J* = 7.5 Hz, 1 H), 7.39 (d, *J* = 5.7 Hz, 1 H), 7.33 (t, *J* = 7.7 Hz, 1 H), 7.16 (d, *J* = 8.7 Hz, 2 H), 6.80 (d, *J* = 8.7 Hz, 2 H), 3.56 (s, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.10, 149.06, 141.15, 138.39, 129.86, 129.19, 127.10, 126.82, 126.58, 126.43, 122.98, 121.52, 117.43, 41.13. ESI: Calcd. for $C_{16}H_{13}ClN_2$ [M+H] $^+$: 269.0846; found: 269.0833.



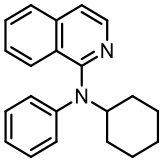
***N*-ethyl-*N*-phenylisoquinolin-1-amine (21c)** The product is obtained as white soild (isolated yield: 98%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, *J* = 5.7 Hz, 1 H), 7.69 (dd, *J* = 13.0, 8.4 Hz, 2 H), 7.49 (t, *J* = 7.5 Hz, 1 H), 7.31 (d, *J* = 5.7 Hz, 1 H), 7.25–7.12 (m, 3 H), 6.93 (t, *J* = 7.3 Hz, 1 H), 6.86 (d, *J* = 8.0 Hz, 2 H), 4.16 (q, *J* = 7.0 Hz, 2 H), 1.32 (t, *J* = 7.0 Hz, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.59, 149.63, 141.26, 138.47, 129.42, 129.21, 126.91, 126.88, 126.02, 123.34, 121.91, 121.54, 116.58, 47.96, 13.72. ESI: Calcd. for $C_{17}H_{16}N_2$ [M+H] $^+$: 249.1392; found: 249.1381.



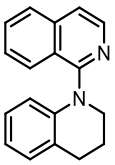
***N*-phenyl-N-propylisoquinolin-1-amine (22c)** The product is obtained as white soild (isolated yield: 96%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, *J* = 5.7 Hz, 1 H), 7.70 (t, *J* = 9.0 Hz, 2 H), 7.50 (t, *J* = 7.5 Hz, 1 H), 7.32 (d, *J* = 5.7 Hz, 1 H), 7.27–7.14 (m, 3 H), 6.92 (t, *J* = 7.3 Hz, 1 H), 6.85 (d, *J* = 7.8 Hz, 2 H), 4.14–3.95 (m, 2 H), 1.83–1.72 (m, 2 H), 0.98 (t, *J* = 7.4 Hz, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.53, 150.42, 141.17, 138.48, 129.47, 129.17, 126.93, 126.86, 126.12, 123.50, 121.72, 121.19, 116.71, 55.36, 21.73, 11.79. ESI: Calcd. for $C_{18}H_{18}N_2$ $[M+H]^+$: 263.1548; found: 263.1542.



***N*-isopropyl-*N*-phenylisoquinolin-1-amine (23c)** The product is obtained as white soild (isolated yield: 96%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (d, *J* = 5.7 Hz, 1 H), 7.78 (d, *J* = 8.5 Hz, 1 H), 7.69 (d, *J* = 8.2 Hz, 1 H), 7.53–7.43 (m, 1 H), 7.34 (d, *J* = 5.7 Hz, 1 H), 7.27–7.12 (m, 3 H), 6.94 (t, *J* = 7.4 Hz, 1 H), 6.89–6.80 (m, 2 H), 4.88 (hept, *J* = 6.7 Hz, 1 H), 1.34 (d, *J* = 6.7 Hz, 6 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.18, 148.22, 141.21, 138.63, 129.39, 129.07, 127.06, 126.87, 126.28, 124.90, 123.66, 122.34, 117.07, 51.53, 21.48. ESI: Calcd. for $C_{18}H_{18}N_2$ $[M+H]^+$: 263.1548; found: 263.1537.

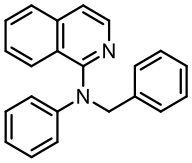


***N*-cyclohexyl-*N*-phenylisoquinolin-1-amine (24c)** The product is obtained as white soild (isolated yield: 96%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (d, *J* = 5.6 Hz, 1 H), 7.83 (d, *J* = 8.5 Hz, 1 H), 7.71 (d, *J* = 8.2 Hz, 1 H), 7.50 (t, *J* = 7.5 Hz, 1 H), 7.38 (d, *J* = 5.6 Hz, 1 H), 7.25 (t, *J* = 7.7 Hz, 1 H), 7.16 (t, *J* = 7.5 Hz, 2 H), 6.91 (t, *J* = 7.2 Hz, 1 H), 6.80 (d, *J* = 7.9 Hz, 2 H), 4.42 (t, *J* = 10.9 Hz, 1 H), 2.05 (d, *J* = 11.5 Hz, 2 H), 1.78 (d, *J* = 12.4 Hz, 2 H), 1.63 (d, *J* = 13.0 Hz, 1 H), 1.46 (dp, *J* = 25.6, 12.6 Hz, 4 H), 1.09 (q, *J* = 12.5 Hz, 1 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.85, 148.11, 141.22, 138.49, 129.48, 128.93, 126.95, 126.76, 126.39, 125.36, 122.30, 121.55, 117.44, 59.50, 31.93, 26.41, 25.97. ESI: Calcd. for $C_{21}H_{22}N_2$ $[M+H]^+$: 303.1861; found: 303.1849.

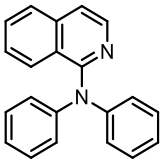


1-(isoquinolin-1-yl)-1,2,3,4-tetrahydroquinoline (25c) The product is obtained as white soild (isolated yield: 95%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (d, *J* = 4.6 Hz, 1 H), 7.95 (d, *J* = 8.4 Hz, 1 H), 7.80 (d, *J* = 8.1 Hz, 1 H), 7.61 (t, *J* = 7.3 Hz, 1 H), 7.54–7.35 (m, 2 H), 7.11 (d, *J* = 7.1 Hz, 1 H), 6.78 (dt, *J* = 21.2, 7.1 Hz, 2 H), 6.24 (d, *J* = 7.9 Hz, 1 H), 3.98–3.72 (m, 2 H), 2.97 (t, *J* = 6.1 Hz, 2 H), 2.23–2.03 (m, 2 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.32, 144.86, 141.95,

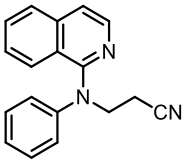
138.35, 130.12, 129.29, 127.11, 126.82, 126.38, 126.18, 125.20, 124.32, 119.63, 118.06, 117.05, 49.29, 27.56, 23.28. ESI: Calcd. for $C_{18}H_{16}N_2$ $[M+H]^+$: 261.1392; found: 261.1380.



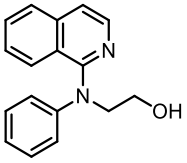
***N*-benzyl-*N*-phenylisoquinolin-1-amine (26c)** The product is obtained as white soild (isolated yield: 92%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 5.6 Hz, 1 H), 7.82 (d, *J* = 8.5 Hz, 1 H), 7.72 (d, *J* = 8.2 Hz, 1 H), 7.51 (t, *J* = 7.5 Hz, 1 H), 7.45 (d, *J* = 7.5 Hz, 2 H), 7.32 (d, *J* = 5.7 Hz, 1 H), 7.25 (p, *J* = 6.4, 5.6 Hz, 3 H), 7.18–7.11 (m, 3 H), 6.90 (t, *J* = 7.3 Hz, 1 H), 6.84 (d, *J* = 7.9 Hz, 2 H), 5.43 (s, 2 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.34, 150.43, 141.31, 140.36, 138.63, 129.68, 129.21, 128.47, 127.29, 127.17, 126.83, 126.75, 126.42, 123.37, 122.05, 120.79, 117.29, 57.05. ESI: Calcd. for $C_{22}H_{18}N_2$ $[M+H]^+$: 311.1548; found: 311.1537.



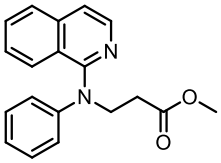
***N*,*N*-diphenylisoquinolin-1-amine (27c)** The product is obtained as white soild (isolated yield: 99%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (d, *J* = 5.7 Hz, 1 H), 7.98 (d, *J* = 8.5 Hz, 1 H), 7.85 (d, *J* = 8.2 Hz, 1 H), 7.68–7.59 (m, 1 H), 7.52 (d, *J* = 5.6 Hz, 1 H), 7.44–7.36 (m, 1 H), 7.29 (t, *J* = 7.8 Hz, 4 H), 7.13–7.00 (m, 6 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.04, 148.21, 142.12, 138.92, 130.02, 129.29, 127.09, 127.05, 126.4 , 124.72, 123.79, 123.17, 118.56. ESI: Calcd. for $C_{21}H_{16}N_2$ $[M+H]^+$: 297.1392; found: 297.1379.



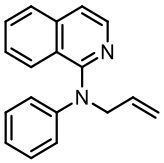
3-(isoquinolin-1-yl(phenyl)amino)propanenitrile (28c) The product is obtained as white soild (isolated yield: 94%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 5.1 Hz, 1 H), 7.71 (d, *J* = 8.0 Hz, 1 H), 7.58 (d, *J* = 8.5 Hz, 1 H), 7.49 (t, *J* = 7.3 Hz, 1 H), 7.36–7.16 (m, 4 H), 7.08–6.98 (m, 3 H), 4.37 (t, *J* = 6.6 Hz, 2 H), 2.89 (t, *J* = 6.5 Hz, 2 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.06, 148.99, 140.56, 138.39, 129.75, 129.63, 126.98, 126.63, 126.27, 124.10, 123.53, 122.24, 119.09, 117.03, 49.90, 16.67. ESI: Calcd. for $C_{18}H_{15}N_3$ $[M+Na]^+$: 296.1164; found: 296.1153.



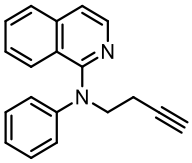
2-(isoquinolin-1-yl(phenyl)amino)ethanol (29c) The product is obtained as white soild (isolated yield: 90%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 5.8 Hz, 1 H), 7.70 (dd, *J* = 21.0, 8.4 Hz, 2 H), 7.57–7.45 (m, 1 H), 7.35 (d, *J* = 5.8 Hz, 1 H), 7.23 (qd, *J* = 7.1, 1.4 Hz, 3 H), 7.07 (bs, 1 H), 6.99 (t, *J* = 7.4 Hz, 1 H), 6.95–6.88 (m, 2 H), 4.33–4.24 (m, 2 H), 3.84–3.74 (m, 2 H). ^{13}C NMR (101 MHz, $CDCl_3$)δ 157.84, 147.84, 139.79, 138.81, 130.13, 129.66, 127.18, 127.15, 126.64, 123.09, 122.93, 122.64, 117.46, 60.38, 55.87. ESI: Calcd. for $C_{17}H_{16}N_2O$ $[M+Na]^+$: 287.1160; found: 287.1149.



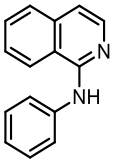
Methyl 3-(isoquinolin-1-yl(phenyl)amino)propanoate (30c) The product is obtained as white soild (isolated yield: 70%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, *J* = 5.4 Hz, 1 H), 7.70 (d, *J* = 8.1 Hz, 1 H), 7.59 (d, *J* = 8.5 Hz, 1 H), 7.48 (t, *J* = 7.5 Hz, 1 H), 7.31 (d, *J* = 5.5 Hz, 1 H), 7.22–7.15 (m, 3 H), 7.06–6.82 (m, 3 H), 4.40 (t, *J* = 6.9 Hz, 2 H), 3.60 (s, 3 H), 2.83 (t, *J* = 6.8 Hz, 2 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.10, 156.88, 149.70, 140.93, 138.36, 129.44, 129.38, 126.91, 126.72, 126.06, 122.91, 122.61, 116.73, 51.50, 49.48, 33.00. ESI: Calcd. for $C_{19}H_{18}N_2O_2$ $[M+H]^+$: 307.1447; found: 307.1431.



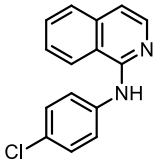
***N*-allyl-*N*-phenylisoquinolin-1-amine (31c)** The product is obtained as white soild (isolated yield: 82%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, *J* = 5.6 Hz, 1 H), 7.73 (t, *J* = 7.3 Hz, 2 H), 7.52 (t, *J* = 7.5 Hz, 1 H), 7.34 (d, *J* = 5.7 Hz, 1 H), 7.26 (t, *J* = 7.7 Hz, 1 H), 7.18 (t, *J* = 7.5 Hz, 2 H), 6.94 (t, *J* = 7.3 Hz, 1 H), 6.88 (d, *J* = 7.9 Hz, 2 H), 6.12 (ddt, *J* = 15.9, 10.1, 5.0 Hz, 1 H), 5.30 (d, *J* = 17.2 Hz, 1 H), 5.10 (d, *J* = 10.3 Hz, 1 H), 4.79 (d, *J* = 4.2 Hz, 2 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.19, 149.76, 141.00, 138.53, 135.64, 129.63, 129.12, 127.03, 126.79, 126.21, 123.08, 122.06, 121.09, 116.92, 116.12, 55.76. ESI: Calcd. for $C_{18}H_{16}N_2$ $[M+H]^+$: 261.1392; found: 261.1381.



***N*-(but-3-yn-1-yl)-*N*-phenylisoquinolin-1-amine (32c)** The product is obtained as white soild (isolated yield: 73%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, *J* = 5.6 Hz, 1 H), 7.73 (d, *J* = 8.1 Hz, 1 H), 7.66 (d, *J* = 8.5 Hz, 1 H), 7.51 (t, *J* = 7.5 Hz, 1 H), 7.34 (d, *J* = 5.6 Hz, 1 H), 7.22 (t, *J* = 7.4 Hz, 3 H), 7.04–6.89 (m, 3 H), 4.31 (t, *J* = 7.2 Hz, 2 H), 2.71 (t, *J* = 6.0 Hz, 2 H), 2.01 (s, 1 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.76, 149.63, 141.04, 138.44, 129.46, 129.36, 126.91, 126.84, 126.05, 122.88, 122.71, 122.26, 116.78, 82.89, 69.50, 52.46, 18.09. ESI: Calcd. for $C_{19}H_{16}N_2$ $[M+H]^+$: 273.1392; found: 273.1379.

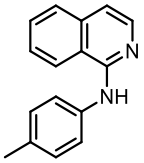


***N*-phenylisoquinolin-1-amine (33c)** The product is obtained as white soild (isolated yield: 89%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 5.8 Hz, 1 H), 7.92 (d, *J* = 8.4 Hz, 1 H), 7.74 (d, *J* = 8.1 Hz, 1 H), 7.69–7.61 (m, 3 H), 7.53 (t, *J* = 7.6 Hz, 1 H), 7.36 (t, *J* = 7.8 Hz, 2 H), 7.13 (d, *J* = 5.8 Hz, 1 H), 7.06 (t, *J* = 7.4 Hz, 1 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.26, 140.82, 140.45, 137.50, 129.95, 129.03, 127.49, 126.52, 122.75, 121.52, 120.31, 118.85, 113.47. ESI: Calcd. for $C_{15}H_{12}N_2$ $[M+H]^+$: 221.1079; found: 221.1070.

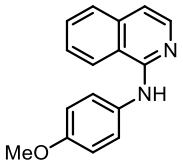


***N*-(4-chlorophenyl)isoquinolin-1-amine (34c)** The product is obtained as white soild (isolated yield: 90%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 5.8 Hz, 1 H), 7.90 (d, *J* = 8.4 Hz, 1 H), 7.75 (d, *J* = 8.1 Hz, 1 H), 7.64 (dd, *J* = 17.3, 8.2 Hz, 3 H), 7.54 (t, *J* = 7.6 Hz, 1 H), 7.30 (d, *J* = 8.8 Hz, 2 H), 7.15 (d, *J* = 5.8 Hz, 1 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.95, 140.71, 139.07, 137.48, 130.05, 128.92, 127.55, 127.40, 126.66, 121.46, 121.33, 118.77, 113.84. ESI: Calcd. for $C_{15}H_{11}ClN_2$ $[M+H]^+$: 255.0689; found: 255.0677.

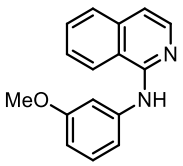
***N*-(4-bromophenyl)isoquinolin-1-amine (35c)** The product is obtained as white soild (isolated yield: 93%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 5.8 Hz, 1 H), 7.91 (d, *J* = 8.4 Hz, 1 H), 7.76 (d, *J* = 8.1 Hz, 1 H), 7.66 (t, *J* = 7.5 Hz, 1 H), 7.57 (d, *J* = 8.5 Hz, 3 H), 7.44 (d, *J* = 8.5 Hz, 2 H), 7.15 (d, *J* = 5.8 Hz, 1 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.98, 140.66, 139.74, 137.63, 131.95, 130.15, 127.65, 126.77, 121.89, 121.48, 118.94, 115.02, 113.98. ESI: Calcd. for $C_{15}H_{11}BrN_2$ $[M+H]^+$: 299.0184; found: 299.0176.



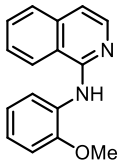
***N*-(*p*-tolyl)isoquinolin-1-amine (36c)** The product is obtained as white solid (isolated yield: 89%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 5.8 Hz, 1 H), 7.89 (d, *J* = 8.4 Hz, 1 H), 7.71 (d, *J* = 8.1 Hz, 1 H), 7.63–7.57 (m, 1 H), 7.50 (dd, *J* = 8.4, 2.4 Hz, 3 H), 7.15 (d, *J* = 8.2 Hz, 2 H), 7.08 (d, *J* = 5.8 Hz, 1 H), 2.32 (s, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.69, 140.99, 137.81, 137.49, 132.50, 129.86, 129.53, 127.40, 126.37, 121.59, 120.97, 118.78, 113.09, 20.87. ESI: Calcd. for $C_{16}H_{14}N_2$ $[M+H]^+$: 235.1235; found: 235.1224.



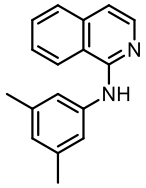
***N*-(4-methoxyphenyl)isoquinolin-1-amine (37c)** The product is obtained as white solid (isolated yield: 93%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 5.8 Hz, 1 H), 7.85 (d, *J* = 8.4 Hz, 1 H), 7.68 (d, *J* = 8.1 Hz, 1 H), 7.59 (d, *J* = 7.3 Hz, 1 H), 7.47 (t, *J* = 8.7 Hz, 3 H), 7.03 (d, *J* = 5.8 Hz, 1 H), 6.87 (d, *J* = 8.8 Hz, 2 H), 3.76 (s, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.81, 153.07, 141.09, 137.45, 133.45, 129.83, 127.35, 126.30, 123.20, 121.57, 118.58, 114.33, 112.74, 55.57. ESI: Calcd. for $C_{16}H_{14}N_2O$ $[M+H]^+$: 251.1184; found: 251.1174.



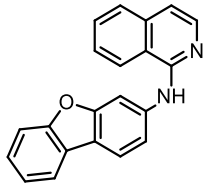
***N*-(3-methoxyphenyl)isoquinolin-1-amine (38c)** The product is obtained as white soild (isolated yield: 90%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 5.8 Hz, 1 H), 7.92 (d, *J* = 8.4 Hz, 1 H), 7.74 (d, *J* = 8.1 Hz, 1 H), 7.67–7.58 (m, 1 H), 7.57–7.47 (m, 1 H), 7.43 (s, 1 H), 7.24 (d, *J* = 8.3 Hz, 1 H), 7.18–7.09 (m, 2 H), 6.66–6.48 (m, 1 H), 3.83 (s, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.31, 152.18, 141.79, 140.85, 137.49, 129.94, 129.64, 127.47, 126.53, 121.53, 118.94, 113.57, 112.58, 108.12, 106.18, 55.30. ESI: Calcd. for $C_{16}H_{14}N_2O$ $[M+H]^+$: 251.1184; found: 251.1173.



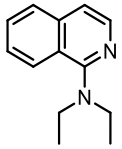
***N*-(2-methoxyphenyl)isoquinolin-1-amine (39c)** The product is obtained as white soild (isolated yield: 92%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 (d, *J* = 7.7 Hz, 1 H), 8.12 (d, *J* = 5.8 Hz, 1 H), 8.06–7.89 (m, 2 H), 7.72 (d, *J* = 8.1 Hz, 1 H), 7.62 (t, *J* = 7.5 Hz, 1 H), 7.54 (t, *J* = 7.6 Hz, 1 H), 7.14–6.84 (m, 4 H), 3.96 (s, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.03, 148.20, 140.94, 137.37, 130.20, 129.77, 127.41, 126.47, 121.51, 121.37, 121.17, 119.36, 118.90, 113.01, 109.91, 55.94. ESI: Calcd. for $C_{16}H_{14}N_2O$ $[M+H]^+$: 251.1184; found: 251.1171.



***N*-(3,5-dimethylphenyl)isoquinolin-1-amine (40c)** The product is obtained as white soild (isolated yield: 89%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 5.7 Hz, 1 H), 7.90 (d, *J* = 8.4 Hz, 1 H), 7.74 (d, *J* = 8.1 Hz, 1 H), 7.63 (t, *J* = 7.5 Hz, 1 H), 7.52 (t, *J* = 7.6 Hz, 1 H), 7.30–7.24 (m, 2 H), 7.10 (d, *J* = 5.7 Hz, 1 H), 6.71 (s, 1 H), 2.32 (s, 6 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.51, 140.87, 140.30, 138.64, 137.51, 129.92, 127.43, 126.43, 124.75, 121.65, 118.95, 118.22, 113.23, 21.51. ESI: Calcd. for $C_{17}H_{16}N_2$ $[M+H]^+$: 249.1392; found: 249.1382.

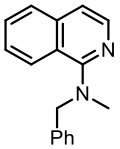


***N*-(dibenzo[b,d]furan-3-yl)isoquinolin-1-amine (41c)** The product is obtained as white soild (isolated yield: 63%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (s, 1 H), 8.09–8.03 (m, , 2 H), 7.92–7.81 (m, 2 H), 7.73 (d, *J* = 8.1 Hz, 1 H), 7.66 (t, *J* = 7.4 Hz, 1 H), 7.53 (dd, *J* = 19.5, 7.8 Hz, 2 H), 7.40 (dd, *J* = 20.5, 8.1 Hz, 2 H), 7.31 (t, *J* = 7.4 Hz, 1 H), 7.11 (d, *J* = 5.5 Hz, 1 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.11, 156.52, 151.96, 140.10, 139.93, 137.54, 130.24, 127.58, 126.76, 126.08, 124.43, 122.67, 121.65, 120.67, 119.96, 119.25, 118.86, 115.77, 113.78, 111.46, 103.61. ESI: Calcd. for $C_{21}H_{14}N_2O$ $[M+H]^+$: 311.1184; found: 311.1173.

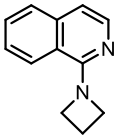


***N*,*N*-diethylisoquinolin-1-amine (42c)** The product is obtained as white soild (isolated yield: 33%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16–8.10 (m, 2 H), 7.72 (d, *J* = 8.1 Hz, 1 H), 7.58 (t, *J* =

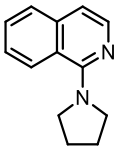
7.4 Hz, 1 H), 7.48 (t, *J* = 7.6 Hz, 1 H), 7.18 (d, *J* = 5.7 Hz, 1 H), 3.48 (q, *J* = 7.0 Hz, 4 H), 1.20 (t, *J* = 7.0 Hz, 6 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.18, 140.52, 138.31, 129.40, 126.91, 125.86, 125.63, 122.94, 114.85, 46.11, 13.08. ESI: Calcd. for $C_{17}H_{16}N_3$ $[M+H]^+$: 201.1392; found: 201.1388.



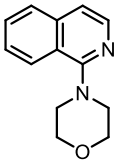
***N*-benzyl-*N*-methylisoquinolin-1-amine (43c)** The product is obtained as white soild (isolated yield: 37%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20–8.12 (m, 2 H), 7.75 (d, *J* = 8.1 Hz, 1 H), 7.60 (t, *J* = 7.5 Hz, 1 H), 7.51 – 7.29 (m, 6 H), 7.23 (d, *J* = 5.7 Hz, 1 H), 4.64 (s, 2 H), 3.02 (s, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.82, 140.55, 138.82, 138.38, 129.57, 128.59, 127.66, 127.08, 125.86, 125.60, 121.60, 115.07, 59.23, 40.05.ESI: Calcd.for $C_{17}H_{16}N_2$ $[M+H]^+$: 249.1392; found: 249.1386.



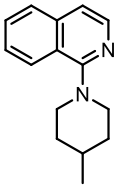
1-(azetidin-1-yl)isoquinoline (44c) The product is obtained as white soild (isolated yield: 48%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 5.8 Hz, 1 H), 7.93 (d, *J* = 8.4 Hz, 1 H), 7.67 (d, *J* = 8.1 Hz, 1 H), 7.55 (t, *J* = 7.5 Hz, 1 H), 7.40 (t, *J* = 7.6 Hz, 1 H), 6.97 (d, *J* = 5.8 Hz, 1 H), 4.46 (t, *J* = 7.5 Hz, 4 H), 2.46 (p, *J* = 7.5 Hz, 2 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.71, 140.95, 137.98, 129.57, 126.87, 125.11, 124.86, 119.03, 111.73, 53.96, 17.41. ESI: Calcd. for $C_{12}H_{12}N_2$ $[M+H]^+$: 185.1079; found: 185.1075.



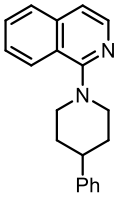
1-(pyrrolidin-1-yl)isoquinoline (45c) The product is obtained as white soild (isolated yield: 75%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 8.6 Hz, 1 H), 7.99 (d, *J* = 5.7 Hz, 1 H), 7.65 (d, *J* = 8.1 Hz, 1 H), 7.53 (t, *J* = 7.5 Hz, 1 H), 7.38 (t, *J* = 7.7 Hz, 1 H), 6.96 (d, *J* = 5.7 Hz, 1 H), 3.84 (t, *J* = 6.3 Hz, 4 H), 2.03–1.96 (m, 4 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.96, 140.78, 138.79, 129.13, 126.64, 126.19, 124.35, 120.14, 111.62, 51.53, 25.98. ESI: Calcd. for $C_{13}H_{14}N_2$ $[M+H]^+$: 199.1235; found: 199.1230.



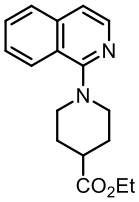
4-(isoquinolin-1-yl)morpholine (46c) The product is obtained as white soild (isolated yield: 54%): ^{1}H NMR (400 MHz, $CDCl_3$) 8.16 (d, *J* = 5.8 Hz, 1 H), 8.11 (d, *J* = 8.4 Hz, 1 H), 7.77 (d, *J* = 8.1 Hz, 1 H), 7.63 (t, *J* = 7.5 Hz, 1 H), 7.53 (t, *J* = 7.6 Hz, 1 H), 7.28 (d, *J* = 5.8 Hz, 1 H), 4.02 – 3.92 (m, 4 H), 3.47–3.38 (m, 4 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.48, 139.96, 137.67, 129.19, 126.62, 125.62, 124.80, 121.09, 115.54, 66.51, 51.33. ESI: Calcd. for $C_{13}H_{14}N_2O$ $[M+H]^+$: 215.1184; found: 215.1180.



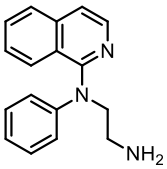
1-(4-methylpiperidin-1-yl)isoquinoline (47c) The product is obtained as white soild (isolated yield: 47%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 5.8 Hz, 1 H), 8.09 (d, *J* = 8.4 Hz, 1 H), 7.73 (d, *J* = 8.1 Hz, 1 H), 7.59 (t, *J* = 7.5 Hz, 1 H), 7.49 (t, *J* = 7.6 Hz, 1 H), 7.21 (d, *J* = 5.8 Hz, 1 H), 3.80 (d, *J* = 12.8 Hz, 2 H), 2.96 (t, *J* = 12.3 Hz, 2 H), 1.83 (d, *J* = 12.6 Hz, 2 H), 1.73–1.47 (m, 3 H), 1.06 (d, *J* = 6.3 Hz, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.25, 140.62, 138.12, 129.58, 126.98, 125.91, 125.85, 122.09, 115.37, 52.07, 34.65, 31.30, 22.05. ESI: Calcd. for $C_{15}H_{18}N_2$ $[M+H]^+$: 227.1548; found: 227.1543.



1-(4-phenylpiperidin-1-yl)isoquinoline (48c) The product is obtained as white soild (isolated yield: 35%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21–8.12 (m, 2 H), 7.76 (d, *J* = 8.1 Hz, 1 H), 7.62 (t, *J* = 7.5 Hz, 1 H), 7.53 (t, *J* = 7.6 Hz, 1 H), 7.40–7.32 (m, 4 H), 7.28–7.23 (q, *J* = 4.2 Hz, 2 H), 3.97 (d, *J* = 12.7 Hz, 2 H), 3.10 (td, *J* = 12.5, 2.8 Hz, 2 H), 2.88–2.72 (m, 1 H), 2.17–1.99 (m, 4 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.10, 146.23, 140.74, 138.16, 129.64, 128.50, 127.08, 126.94, 126.28, 126.06, 125.74, 122.08, 115.67, 52.46, 43.03, 33.77. ESI: Calcd. for $C_{20}H_{20}N_2$ $[M+H]^+$: 289.1705; found: 289.1698.

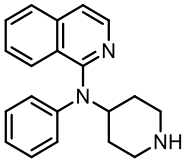


Ethyl 1-(isoquinolin-1-yl)piperidine-4-carboxylate (49c) The product is obtained as white soild (isolated yield: 43%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 5.8 Hz, 1 H), 8.08 (d, *J* = 8.4 Hz, 1 H), 7.74 (d, *J* = 8.1 Hz, 1 H), 7.61 (t, *J* = 7.5 Hz, 1 H), 7.51 (t, *J* = 7.6 Hz, 1 H), 7.24 (d, *J* = 5.7 Hz, 1 H), 4.19 (q, *J* = 7.1 Hz, 2 H), 3.81 (d, *J* = 12.8 Hz, 2 H), 3.11–2.94 (m, 2 H), 2.56 (tt, *J* = 10.4, 4.5 Hz, 1 H), 2.09 (qd, *J* = 12.0, 10.9, 3.4 Hz, 4 H), 1.30 (t, *J* = 7.1 Hz, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.04, 161.86, 140.57, 138.11, 129.72, 127.06, 126.18, 125.60, 122.03, 115.88, 60.47, 51.23, 41.60, 28.60, 14.28. ESI: Calcd. for $C_{17}H_{20}N_2O_2$ $[M+H]^+$: 285.1603; found: 285.1597.

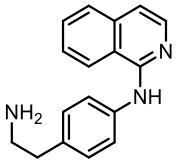


***N*^{1}-(isoquinolin-1-yl)-*N*^{1}-phenylethane-1,2-diamine (50c)** The product is obtained as white soild (isolated yield: 78%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 5.8 Hz, 1 H), 7.79 (d, *J* = 8.3 Hz, 1 H), 7.68 (d, *J* = 8.0 Hz, 1 H), 7.60 (t, *J* = 7.4 Hz, 1 H), 7.46 (t, *J* = 7.6 Hz, 1 H), 7.16 (t, *J* = 7.4 Hz, 2 H), 6.96 (d, *J* = 5.8 Hz, 1 H), 6. 75–6.62 (m, 3 H), 5.86 (bs, 1 H), 3.92 (d, *J* = 5.1

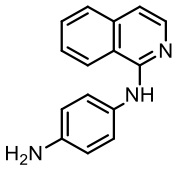
Hz, 2 H), 3.51 (t, *J* = 5.3 Hz, 2 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.23, 148.52, 140.25, 137.27, 130.22, 129.46, 127.40, 126.34, 121.87, 118.38, 117.74, 113.16, 111.49, 44.44, 41.75. ESI: Calcd. for $C_{17}H_{17}N_3$ $[M+H]^+$: 264.1501; found: 264.1489.



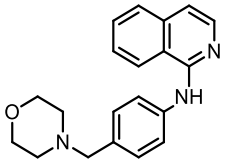
***N*-phenyl-*N*-(piperidin-4-yl)isoquinolin-1-amine (51c)** The product is obtained as white soild (isolated yield: 60%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.60–9.15 (m, 1 H), 8.25 (d, *J* = 4.9 Hz, 1 H), 7.77 (d, *J* = 8.3 Hz, 1 H), 7.68 (d, *J* = 7.9 Hz, 1 H), 7.47 (t, *J* = 7.1 Hz, 1 H), 7.33 (d, *J* = 4.8 Hz, 1 H), 7.25–7.16 (m, 3 H), 7.08–6.94 (m, 3 H), 4.75–4.65 (m, 1 H), 3.56 (d, *J* = 11.4 Hz, 2 H), 3.03 (t, *J* = 10.1 Hz, 2 H), 2.32–2.06 (m, 4 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.73, 147.14, 140.69, 138.67, 129.64, 129.52, 126.99, 126.60, 126.53, 126.17, 124.78, 124.11, 117.49, 55.80, 44.18, 28.30. ESI: Calcd. for $C_{20}H_{21}N_3$ $[M+H]^+$: 304.1814; found: 304.1799.



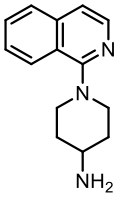
***N*-(4-(2-aminoethyl)phenyl)isoquinolin-1-amine (52c)** The product is obtained as white soild (isolated yield: 75%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 5.8 Hz, 1 H), 7.92 (d, *J* = 8.4 Hz, 1 H), 7.72 (d, *J* = 8.1 Hz, 1 H), 7.69–7.45 (m, 4 H), 7.24–7.14 (m, 3 H), 7.10 (d, *J* = 5.8 Hz, 1 H), 3.00–2.89 (m, 2 H), 2.71 (t, *J* = 6.8 Hz, 2 H), 1.38 (b, 2 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.46, 141.01, 138.58, 137.46, 134.17, 129.87, 129.35, 127.41, 126.41, 121.51, 120.74, 118.80, 113.21, 43.66, 39.53. ESI: Calcd. for $C_{17}H_{17}N_3$ $[M+H]^+$: 264.1501; found: 264.1483.



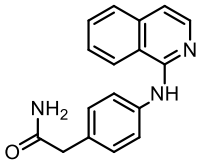
***N*^{1}-(isoquinolin-1-yl)benzene-1,4-diamine (53c)** The product is obtained as white soild (isolated yield: 68%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 5.8 Hz, 1 H), 7.90 (d, *J* = 8.3 Hz, 1 H), 7.72 (d, *J* = 8.1 Hz, 1 H), 7.62 (t, *J* = 7.5 Hz, 1 H), 7.51 (t, *J* = 7.6 Hz, 1 H), 7.38 (d, *J* = 8.4 Hz, 2 H), 7.04 (d, *J* = 5.8 Hz, 1 H), 6.72 (d, *J* = 8.5 Hz, 2 H), 3.56 (bs, 2 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.28, 142.68, 141.13, 137.47, 131.64, 129.79, 127.35, 126.20, 123.62, 121.57, 118.49 , 115.82, 112.38. ESI: Calcd. for $C_{15}H_{13}N_3$ $[M+H]^+$: 236.1188; found: 236.1177.



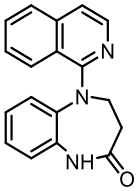
***N*-(4-(morpholinomethyl)phenyl)isoquinolin-1-amine (54c)** The product is obtained as white soild (isolated yield: 74%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 5.5 Hz, 1 H), 7.91 (d, *J* = 8.3 Hz, 1 H), 7.72 (d, *J* = 8.1 Hz, 1 H), 7.62 (t, *J* = 6.6 Hz, 3 H), 7.51 (t, *J* = 7.6 Hz, 1 H), 7.29 (d, *J* = 7.6 Hz, 2 H), 7.20 (bs, 1 H), 7.11 (d, *J* = 5.6 Hz, 1 H), 3.70 (s, 4 H), 3.46 (s, 2 H), 2.45 (s, 4 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.30, 140.95, 139.54, 137.47, 131.74, 129.91, 127.44, 126.47, 121.49, 120.16, 118.83, 113.37, 67.02, 63.03, 53.57. ESI: Calcd. for $C_{20}H_{21}N_3O$ $[M+H]^+$: 320.1763; found:320.1747.



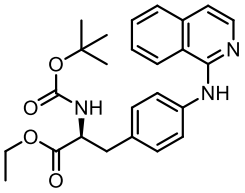
1-(isoquinolin-1-yl)piperidin-4-amine (55c) The product is obtained as white soild (isolated yield: 29%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 5.7 Hz, 1 H), 8.05 (d, *J* = 8.3 Hz, 1 H), 7.71 (d, *J* = 8.2 Hz, 1 H), 7.57 (t, *J* = 7.4 Hz, 1 H), 7.48 (t, *J* = 7.6 Hz, 1 H), 7.21 (d, *J* = 5.8 Hz, 1 H), 4.29 (bs H), 3.80 (d, *J* = 12.5 Hz, 2 H), 3.12 (t, *J* = 10.3 Hz, 1 H), 3.01 (t, *J* = 11.9 Hz, 2 H), 2.13 (d, *J* = 9.9 Hz, 2 H), 1.86 (q, *J* = 10.6, 9.6 Hz, 2 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.61, 140.62, 138.07, 129.69, 127.05, 126.20, 125.54, 121.95, 115.95, 50.29, 49.31, 34.16. ESI: Calcd. for $C_{14}H_{17}N_3$ $[M+H]^+$: 228.1501; found: 228.1496.



2-(4-(isoquinolin-1-ylamino)phenyl)acetamide (56c) The product is obtained as white soild (isolated yield: 64%): ^{1}H NMR (400 MHz, Methanol-d_4) δ 8.32 (d, *J* = 8.4 Hz, 1 H), 7.85–7.65 (m, 3 H), 7.62–7.50 (m, 3 H), 7.30 (d, *J* = 8.0 Hz, 2 H), 7.11 (d, *J* = 5.7 Hz, 1 H), 4.88 (s, 2 H) 3.51 (s, 2 H). ^{13}C NMR (101 MHz, Methanol-d_4) δ 175.90, 153.52, 139.31, 138.60, 137.63, 130.34, 130.30, 129.38, 126.70, 126.42, 122.76, 122.02, 119.22, 112.65, 41.63. ESI: Calcd. for $C_{17}H_{15}N_3O$ $[M+H]^+$: 278.1293; found: 278.1334.

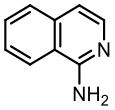


5-(isoquinolin-1-yl)-4,5-dihydro-1H-benzo[b][1,4]diazepin-2(3H)-one (57c) The product is obtained as white soild (isolated yield: 89%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.33 (s, 1 H), δ 8.19 (d, *J* = 5.6 Hz, 1 H), 7.57 (d, *J* = 8.1 Hz, 1 H), 7.33 (t, *J* = 7.3 Hz, 1 H), 7.25 (d, *J* = 8.3 Hz, 2 H), 7.17–6.95 (m, 3 H), 6.87 (t, *J* = 7.6 Hz, 1 H), 6.56 (d, *J* = 7.9 Hz, 1 H), 4.42 (t, *J* = 6.8 Hz, 2 H), 2.79 (t, *J* = 6.8 Hz, 2 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.26, 157.50, 141.51, 140.16, 138.06, 134.42, 129.25, 126.76, 126.67, 126.59, 126.09, 126.05, 125.68, 122.75, 121.59, 116.61, 53.64, 33.57. ESI: Calcd. for $C_{18}H_{15}N_3O$ $[M+H]^+$: 290.1293; found: 290.1280.

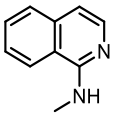


(S)-ethyl 2-((tert-butoxycarbonyl)amino)-3-(4-(isoquinolin-1-ylamino)phenyl)propanoate (58c) The product is obtained as white soild (isolated yield: 77%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 5.1 Hz, 1 H), 7.96 (d, *J* = 8.0 Hz, 1 H), 7.74 (d, *J* = 7.9 Hz, 1 H), 7.66–7.57 (m, 3 H), 7.53 (t, *J* = 7.2 Hz, 1 H), 7.11 (d, *J* = 6.5 Hz, 3 H), 5.02 (d, *J* = 7.1 Hz, 1 H), 4.61–4.47 (m, 1 H), 4.18 (d, *J* = 6.8 Hz, 2 H), 3.29–3.15 (m, 2 H), 1.43 (s, 9 H), 1.25 (t, *J* = 6.9 Hz, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.98, 155.25, 152.21, 140.35, 139.31, 137.47, 130.25, 130.07, 129.92,

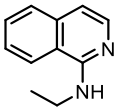
127.44, 126.57, 121.73, 120.44, 118.83, 113.38, 79.84, 61.33, 54.56, 37.58, 28.35, 14.20. ESI: Calcd. for $C_{25}H_{29}N_3O_4$ $[M+H]^+$: 436.2236; found: 436.2214.



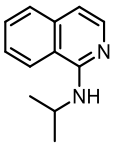
isoquinolin-1-amine (59c) The product is obtained as white liquid (isolated yield: 15%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 6.0 Hz, 1 H), 7.84 (d, *J* = 8.3 Hz, 1 H), 7.71 (d, *J* = 8.1 Hz, 1 H), 7.64 (t, *J* = 7.5 Hz, 1 H), 7.51 (t, *J* = 7.6 Hz, 1 H), 7.05 (d, *J* = 5.9 Hz, 1 H), 5.49 (bs, 2 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.16, 140.20, 137.59, 130.61, 127.33, 126.49, 122.86, 118.01, 112.71. ESI: Calcd. for $C_9H_8N_2$ $[M+H]^+$: 145.0766; found: 145.0754.



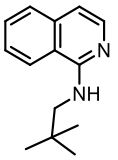
***N*-methylisoquinolin-1-amine (60c)** The product is obtained as white liquid (isolated yield: 80%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, *J* = 7.7 Hz, 1 H), 7.87 (d, *J* = 5.6 Hz, 1 H), 7.76–7.39 (m, 4 H), 6.92 (d, *J* = 5.9 Hz, 1 H), 3.27 (s, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.47, 136.62, 135.19, 131.55, 127.22, 127.17, 123.48, 118.47, 110.96, 29.55. ESI: Calcd. for $C_{10}H_{10}N_2$ $[M+H]^+$: 159.0922; found: 159.0911.



***N*-ethylisoquinolin-1-amine (61c)** The product is obtained as white liquid (isolated yield: 64%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 5.9 Hz, 1 H), 7.76 (d, *J* = 8.3 Hz, 1 H), 7.67 (d, *J* = 8.1 Hz, 1 H), 7.58 (t, *J* = 7.5 Hz, 1 H), 7.45 (t, *J* = 7.6 Hz, 1 H), 6.92 (d, *J* = 5.9 Hz, 1 H), 5.24 (bs, 1 H), 3.70–3.60 (m, 2 H), 1.36 (t, *J* = 7.2 Hz, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.43, 142.48, 138.47, 131.02, 128.55, 127.18, 122.75, 119.54, 112.08, 38.04, 16.29. ESI: Calcd. for $C_{11}H_{12}N_2$ $[M+H]^+$: 173.1079; found: 173.0793.

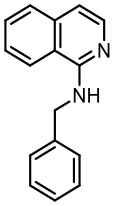


***N*-isopropylisoquinolin-1-amine (62c)** The product is obtained as white liquid (isolated yield: 49%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 5.9 Hz, 1 H), 7.76 (d, *J* = 8.4 Hz, 1 H), 7.65 (d, *J* = 8.1 Hz, 1 H), 7.57 (t, *J* = 7.5 Hz, 1 H), 7.45 (t, *J* = 7.6 Hz, 1 H), 6.89 (d, *J* = 5.9 Hz, 1 H), 5.19 (bs, 1 H), 4.56–4.42 (m, 1 H), 1.34 (d, *J* = 6.4 Hz, 6 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.23, 140.72, 137.11, 129.78, 127.20, 125.86, 121.46, 118.10, 110.48, 42.86, 23.07. ESI: Calcd. for $C_{12}H_{14}N_2$ $[M+H]^+$: 187.1235; found: 187.1223.

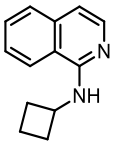


***N*-neopentylisoquinolin-1-amine (63c)** The product is obtained as white liquid (isolated yield: 53%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 5.9 Hz, 1 H), 7.76 (d, *J* = 8.3 Hz, 1 H), 7.67 (d, *J* = 8.1 Hz, 1 H), 7.58 (t, *J* = 7.5 Hz, 1 H), 7.47 (t, *J* = 7.5 Hz, 1 H), 6.90 (d, *J* = 5.8 Hz, 1 H), 5.29 (bs, 1 H), 3.48 (d, *J* = 5.3 Hz, 2 H), 1.07 (s, 9 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.26,

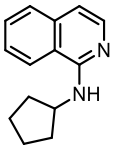
140.59, 137.13, 129.88, 127.31, 125.97, 121.25, 118.11, 110.60, 52.81, 31.86, 27.62. ESI: Calcd. for $C_{14}H_{18}N_2$ $[M+H]^+$: 215.1548; found: 215.1536.



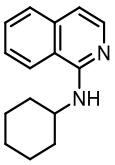
***N*-benzylisoquinolin-1-amine (64c)** The product is obtained as white soild (isolated yield: 72%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 5.8 Hz, 1 H), 7.77 (d, *J* = 8.3 Hz, 1 H), 7.69 (d, *J* = 8.1 Hz, 1 H), 7.59 (t, *J* = 7.5 Hz, 1 H), 7.48–7.42 (m, 3 H), 7.39–7.28 (m, 3 H), 6.97 (d, *J* = 5.8 Hz, 1 H), 5.56 (bs, 1 H), 4.83 (d, *J* = 4.5 Hz, 2 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.76, 140.94, 139.30, 137.09, 129.86, 128.71, 128.10, 127.43, 127.23, 126.03, 121.50, 118.08, 111.29, 46.08. ESI: Calcd. for $C_{16}H_{14}N_2$ $[M+H]^+$: 235.1235; found: 235.1221.



***N*-cyclobutylisoquinolin-1-amine (65c)** The product is obtained as white liquid (isolated yield: 51%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 5.8 Hz, 1 H), 7.83 (d, *J* = 8.2 Hz, 1 H), 7.70 (d, *J* = 8.1 Hz, 1 H), 7.62 (t, *J* = 7.5 Hz, 1 H), 7.50 (t, *J* = 7.6 Hz, 1 H), 6.95 (d, *J* = 5.9 Hz, 1 H), 5.56 (bs, 1 H), 4.78 (h, *J* = 7.5 Hz, 1 H), 2.70–2.47 (m, 2 H), 2.01 (p, *J* = 8.7 Hz, 2 H), 1.92–1.76 (m, 2 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.24, 141.40, 137.11, 129.60, 127.16, 125.78, 121.37, 117.95, 110.84, 46.92, 31.88, 15.39. ESI: Calcd. for $C_{13}H_{14}N_2$ $[M+H]^+$: 199.1235; found: 199.1230.

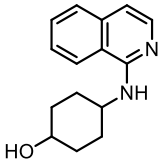


***N*-cyclopentylisoquinolin-1-amine (66c)** The product is obtained as white liquid (isolated yield: 60%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 5.9 Hz, 1 H), 7.72 (d, *J* = 8.4 Hz, 1 H), 7.66 (d, *J* = 8.1 Hz, 1 H), 7.56 (t, *J* = 7.4 Hz, 1 H), 7.44 (t, *J* = 7.4 Hz, 1 H), 6.90 (d, *J* = 5.9 Hz, 1 H), 5.37–5.02 (m, 1 H), 4.57 (h, *J* = 6.6 Hz, 1 H), 2.20 (dq, *J* = 12.0, 6.2 Hz, 2 H), 1.92–1.63 (m, 4 H), 1.55 (dq, *J* = 12.6, 6.4 Hz, 2 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.87, 141.51, 137.06, 129.51, 127.17, 125.69, 121.28, 118.13, 110.46, 53.03, 33.60, 23.89. EI: Calcd. for $C_{14}H_{16}N_2$ $[M]^+$: 212.1313; found: 212.1310.

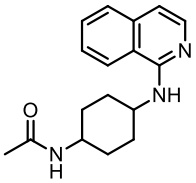


***N*-cyclohexylisoquinolin-1-amine (67c)** The product is obtained as white liquid (isolated yield: 58%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 5.8 Hz, 1 H), 7.75 (d, *J* = 8.4 Hz, 1 H), 7.66 (d, *J* = 8.1 Hz, 1 H), 7.58 (t, *J* = 7.5 Hz, 1 H), 7.46 (t, *J* = 7.6 Hz, 1 H), 6.89 (d, *J* = 5.8 Hz, 1 H), 5.19 (bs, 1 H), 4.22 (s, 1 H), 2.18 (d, *J* = 10.1 Hz, 2 H), 1.82–1.75 (m, 2 H), 1.73–1.64 (m, 1 H), 1.52 (q, *J* = 12.1 Hz, 2 H), 1.36–1.28 (m, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.35, 141.47,

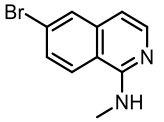
137.18, 129.51, 127.17, 125.63, 121.27, 118.09, 110.31, 49.42, 33.55, 25.98, 25.09. EI: Calcd. for $C_{15}H_{18}N_2$ [M] $^+$: 226.1470; found: 226.1466.



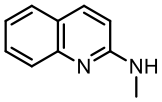
4-(isoquinolin-1-ylamino)cyclohexanol (68c) The product is obtained as white liquid (isolated yield: 55%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 5.9 Hz, 1 H), 7.67 (dd, *J* = 17.4, 8.2 Hz, 2 H), 7.56 (t, *J* = 7.5 Hz, 1 H), 7.43 (t, *J* = 7.6 Hz, 1 H), 6.90 (d, *J* = 5.9 Hz, 1 H), 5.01 (bs, 1 H), 4.24–4.12 (m, 1 H), 3.71 (td, *J* = 10.6, 5.2 Hz, 1 H), 2.27 (d, *J* = 11.8 Hz, 2 H), 2.04 (d, *J* = 12.2 Hz, 2 H), 1.74 (bs, 1 H), 1.60–1.47 (m, 2 H), 1.42–1.27 (m, 2 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.33, 141.35, 137.15, 129.60, 127.24, 125.76, 121.18, 118.03, 110.66, 70.37, 48.90, 34.25, 31.24. EI: Calcd. for $C_{15}H_{18}N_2O$ [M] $^+$: 242.1419; found: 242.1418.



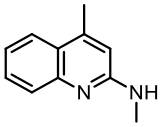
***N*-(4-(isoquinolin-1-ylamino)cyclohexyl)acetamide (69c)** The product is obtained as white soild (isolated yield: 25%): ^{1}H NMR (400 MHz, Methanol-d_4) δ 8.13 (d, *J* = 8.4 Hz, 1 H), 7.73 (d, *J* = 6.0 Hz, 1 H), 7.69–7.53 (m, 2 H), 7.46 (t, *J* = 7.6 Hz, 1 H), 6.87 (d, *J* = 6.0 Hz, 1 H), 4.08–3.91 (m, 1 H), 3.79–3.61 (m, 1 H), 2.13 (d, *J* = 12.2 Hz, 2 H), 1.97 (d, *J* = 12.0 Hz, 2 H), 1.92 (s, 3 H), 1.61–1.36 (m, 4 H). ^{13}C NMR (101 MHz, Methanol-d_4) δ 171.10, 154.95, 139.17, 137.24 , 129.88, 126.41, 125.70, 122.46, 118.60, 109.82, 49.05, 31.15, 31.01, 21.28. ESI: Calcd. for $C_{17}H_{21}N_3O$ [M+H]$^+$: 284.1763; found: 284.1758.



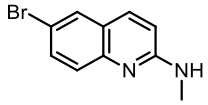
6-bromo-*N*-methylisoquinolin-1-amine (70c) The product is obtained as white soild (isolated yield: 25%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 5.9 Hz, 1 H), 7.83 (d, *J* = 1.4 Hz, 1 H), 7.62 (d, *J* = 8.8 Hz, 1 H), 7.53 (dd, *J* = 8.8, 1.7 Hz, 1 H), 6.83 (d, *J* = 5.9 Hz, 1 H), 5.36 (bs, 1 H), 3.17 (d, *J* = 3.9 Hz, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.68, 142.45, 138.37, 129.35, 129.13, 124.33, 123.24, 116.67, 109.74, 28.90. ESI: Calcd. for $C_{10}H_9BrN_2$ [M+H]$^+$: 237.0027; found: 237.0016.



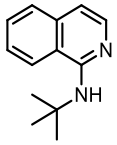
***N*-methylquinolin-2-amine (71c)** The product is obtained as white soild (isolated yield: 62%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.9 Hz, 1 H), 7.74 (d, *J* = 8.4 Hz, 1 H), 7.67–7.45 (m, 2 H), 7.24 (t, *J* = 7.4 Hz, 1 H), 6.66 (d, *J* = 8.9 Hz, 1 H), 4.96 (bs, 1 H), 3.11 (d, *J* = 3.8 Hz, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.59, 147.85, 137.38, 129.63, 127.48, 125.92, 123.30, 122.04, 111.15, 28.71. ESI: Calcd. for $C_{10}H_{10}N_2$ [M+H] $^+$: 159.0922; found: 159.0911.



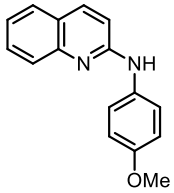
***N*,4-dimethylquinolin-2-amine (72c)** The product is obtained as white soild (isolated yield: 65%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (dd, *J* = 17.0, 8.3 Hz, 2 H), 7.52 (t, *J* = 7.6 Hz, 1 H), 7.23 (t, *J* = 7.5 Hz, 1 H), 6.48 (s, 1 H), 5.06 (bs, 1 H), 3.06 (s, 3 H), 2.54 (s, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.30, 147.33, 145.42, 129.49, 126.02, 123.66, 123.57, 121.93, 111.06, 28.66, 18.89. ESI: Calcd. for $C_{11}H_{12}N_2$ [M+H] $^{+}$: 173.1079; found: 173.0779.



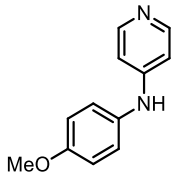
6-bromo-*N*-methylquinolin-2-amine (73c) The product is obtained as white soild (isolated yield: 28%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 7.6 Hz, 2 H), 7.61–7.53 (m, 2 H), 6.64 (d, *J* = 9.0 Hz, 1 H), 5.05 (bs, 1 H), 3.08 (d, *J* = 4.5 Hz, 3 H).^{13}C NMR (101 MHz, $CDCl_3$) δ 157.77, 146.71, 136.49, 132.88, 129.60, 127.85, 124.66, 114.98, 112.17, 28.76. ESI: Calcd. for $C_{10}H_9BrN_2$ [M+H]$^{+}$: 237.0027; found: 237.0014.



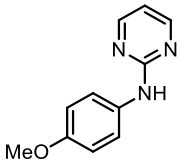
***N*-(tert-butyl)isoquinolin-1-amine (74c)** The product is obtained as white liquid (isolated yield: 48%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (d, *J* = 5.9 Hz, 2 H), 7.96 (d, *J* = 8.2 Hz, 1 H), 7.81 (t, *J* = 7.4 Hz, 1 H), 7.74 (dd, *J* = 16.8, 6.6 Hz, 2 H), 1.59 (s, 9 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.81, 141.90, 138.00, 130.62, 127.62, 126.57, 125.03, 124.28, 121.82, 70.30, 27.11. ESI: Calcd. for $C_{13}H_{16}N_2$ [M+H] $^{+}$: 201.1392; found: 201.1390.



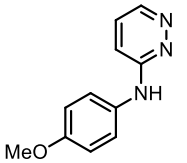
***N*-(4-methoxyphenyl)quinolin-2-amine (75c)** The product is obtained as white soild (isolated yield: 72%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 9.0 Hz, 1 H), 7.73 (d, *J* = 8.4 Hz, 1 H), 7.65–7.49 (m, 2 H), 7.39 (d, *J* = 8.8 Hz, 2 H), 7.33–7.24 (m, 1 H), 6.91 (d, *J* = 8.8 Hz, 2 H), 6.86 (d, *J* = 9.0 Hz, 1 H), 3.81 (s, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.59, 155.33, 147.02, 138.11, 132.64, 130.01, 127.50, 125.85, 124.16, 123.80, 122.94, 114.63, 110.91, 55.58. ESI: Calcd. for $C_{16}H_{13}N_2O$ [M+H] $^{+}$: 251.1184; found: 251.1172.



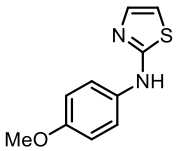
***N*-(4-methoxyphenyl)pyridin-4-amine (76c)** The product is obtained as white soild (isolated yield: 77%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 6.6 Hz, 2 H), 7.24 (d, *J* = 9.0 Hz, 2 H), 6.97 (d, *J* = 8.8 Hz, 2 H), 6.85 (d, *J* = 6.5 Hz, 2 H), 4.44 (bs, 1 H), 3.83 (s, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.13, 157.09, 145.98, 137.48, 127.21, 115.63, 107.98, 55.62. ESI: Calcd. for $C_{12}H_{12}N_2O$ [M+H] $^{+}$: 201.1028; found: 201.1014.



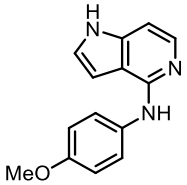
***N*-(4-methoxyphenyl)pyrimidin-2-amine (77c)** The product is obtained as white soild (isolated yield: 50%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (d, *J* = 4.7 Hz, 2 H), 7.55–7.43 (m, 3 H), 6.90 (d, *J* = 8.7 Hz, 2 H), 6.66 (t, *J* = 4.7 Hz, 1 H), 3.80 (s, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.47, 157.99, 155.88, 132.22, 122.34, 114.27, 111.93, 55.55. ESI: Calcd. for $C_{11}H_{11}N_3O$ $[M+H]^+$: 202.0980; found: 202.0973.



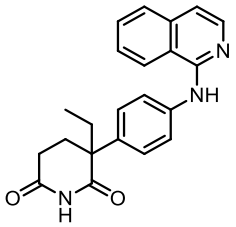
***N*-(4-methoxyphenyl)pyridazin-3-amine (78c)** The product is obtained as white soild (isolated yield: 35%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (d, *J* = 4.4 Hz, 1 H), 7.38 (bs, 1 H), 7.26 (d, *J* = 8.9 Hz, 2 H), 7.18 (dd, *J* = 9.1, 4.5 Hz, 1 H), 6.92 (dd, *J* = 9.3, 2.9 Hz, 3 H), 3.82 (s, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.70, 156.58, 143.68, 131.15, 127.02, 124.29, 114.33, 111.83, 54.93. ESI: Calcd. for $C_{11}H_{11}N_3O$ $[M+H]^+$: 202.0980; found: 202.0968.



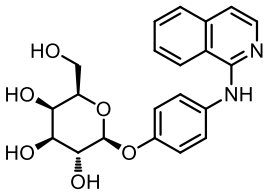
***N*-(4-methoxyphenyl)thiazol-2-amine (79c)** The product is obtained as white soild (isolated yield: 33%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 8.8 Hz, 2 H), 7.23 (s, 1 H), 6.91 (d, *J* = 8.7 Hz, 2 H), 6.55 (s, 1 H), 3.81 (s, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.05, 156.55, 137.95, 133.60, 121.98, 114.83, 106.84, 55.57. ESI: Calcd. for $C_{10}H_{10}N_2OS$ $[M+H]^+$: 207.0592; found: 207.0582.



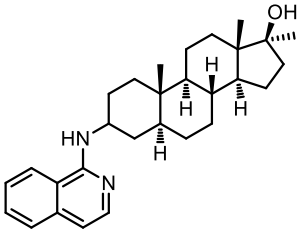
***N*-(4-methoxyphenyl)-1H-pyrrolo[3,2-c]pyridin-4-amine (80c)** The product is obtained as white soild (isolated yield: 56%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.97 (bs, 1 H), 7.60 (s, 1 H), 7.34 (d, *J* = 7.5 Hz, 2 H), 6.96 (s, 1 H), 6.85 (d, *J* = 8.0 Hz, 2 H), 6.81 (d, *J* = 6.0 Hz, 1 H), 6.04 (s, 1 H), 3.78 (s, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.74, 150.27, 140.74, 135.57, 132.66, 125.03, 123.18, 114.35, 110.72, 101.48, 100.34, 55.56. ESI: Calcd. for $C_{14}H_{13}N_3O$ $[M+H]^+$: 240.1137; found: 240.1121.



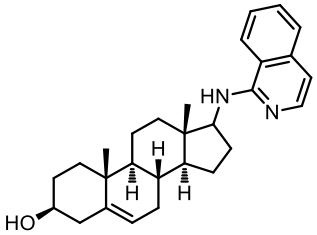
3-ethyl-3-(4-(isoquinolin-1-ylamino)phenyl)piperidine-2,6-dione (81c) The product is obtained as white soild (isolated yield: 53%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27–8.02 (m, 2 H), 7.95 (d, *J* = 8.4 Hz, 1 H), 7.79–7.61 (m, 4 H), 7.54 (t, *J* = 7.6 Hz, 1 H), 7.41–7.20 (m, 3 H), 7.15 (d, *J* = 5.7 Hz, 1 H), 2.69–2.31 (m, 3 H), 2.29–2.16 (m, 1 H), 2.06 (dq, *J* = 14.6, 7.3 Hz, 1H), 1.92 (dq, *J* = 14.5, 7.3 Hz, 1H), 0.89 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.37, 172.44, 151.91, 140.76, 139.97, 137.50, 132.27, 130.03, 127.52, 126.82, 126.64, 121.47, 120.13, 118.90, 113.84, 50.68, 32.96, 29.38, 27.07, 9.09. ESI: Calcd. for $C_{22}H_{21}N_3O_2$ $[M+H]^+$: 360.1712; found: 360.1689.



(2R,3R,4S,5R,6S)-2-(hydroxymethyl)-6-(4-(isoquinolin-1-ylamino)phenoxy)tetrahydro-2H-pyran-3,4,5-triol (82c) The product is obtained as white soild (isolated yield: 35%): ^{1}H NMR (400 MHz, Methanol-d_4) δ 8.35 (d, *J* = 8.4 Hz, 1 H), 7.81–7.68 (m, 3 H), 7.60 (t, *J* = 7.6 Hz, 1 H), 7.49 (d, *J* = 8.8 Hz, 2 H), 7.17 (d, *J* = 8.9 Hz, 2 H), 7.10 (d, *J* = 6.1 Hz, 1 H), 4.88 (s, 1 H), 3.92 (d, *J* = 3.2 Hz, 1 H), 3.85–3.74 (m, 3 H), 3.69 (t, *J* = 6.0 Hz, 1 H), 3.60 (dd, *J* = 9.7, 3.3 Hz, 1 H). ^{13}C NMR (101 MHz, Methanol-d_4) δ 154.59, 153.71, 137.61, 134.24, 130.68, 126.77, 126.58, 123.93, 122.86, 118.95, 117.27, 112.20, 102.14, 75.55, 73.50, 70.96, 68.85, 61.03. ESI: Calcd. for $C_{21}H_{22}N_2O_6$ $[M+H]^+$:399.1556; found: 399.1540.

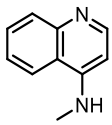


(5S,8R,9S,10S,13S,14S,17S)-3-(isoquinolin-1-ylamino)-10,13,17-trimethylhexadecahydro-1H-cyclopenta[a]phenanthren-17-ol (83c) The product is obtained as white soild (isolated yield: 56%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 5.9 Hz, 1 H), 7.85 (s, 1 H), 7.71–7.54 (m, 2 H), 7.47 (t, *J* = 7.4 Hz, 1 H), 6.89 (d, *J* = 5.9 Hz, 1 H), 5.35 (bs, 1 H), 4.25 (s, 1 H), 2.07 (d, *J* = 11.5 Hz, 1 H), 1.90–1.10 (m, 23 H), 0.93–0.80 (m, 7 H), 0.67 (t, *J* = 8.6 Hz, 1 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.48, 141.40, 137.28, 129.57, 127.21, 125.68, 121.31, 118.16, 110.40, 81.74, 54.62, 50.81, 50.31, 45.68, 45.62, 39.14, 37.76, 36.59, 35.94, 35.90, 31.85, 31.79, 29.41, 28.73, 25.92, 23.33, 20.88, 14.02, 12.45. EI: Calcd. for $C_{29}H_{40}N_2O$ $[M]^+$: 432.3141; found: 432.3142.



(3S,8R,9S,10R,13S,14S)-17-(isoquinolin-1-ylamino)-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-ol (84c) The product is obtained as white soild (isolated yield: 45%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 5.8 Hz, 1 H), 7.78 (d, *J* = 8.3 Hz, 1 H), 7.70 (d, *J* = 8.0 Hz, 1 H), 7.62 (t, *J* = 7.4 Hz, 1 H), 7.50 (t, *J* = 7.6 Hz, 1

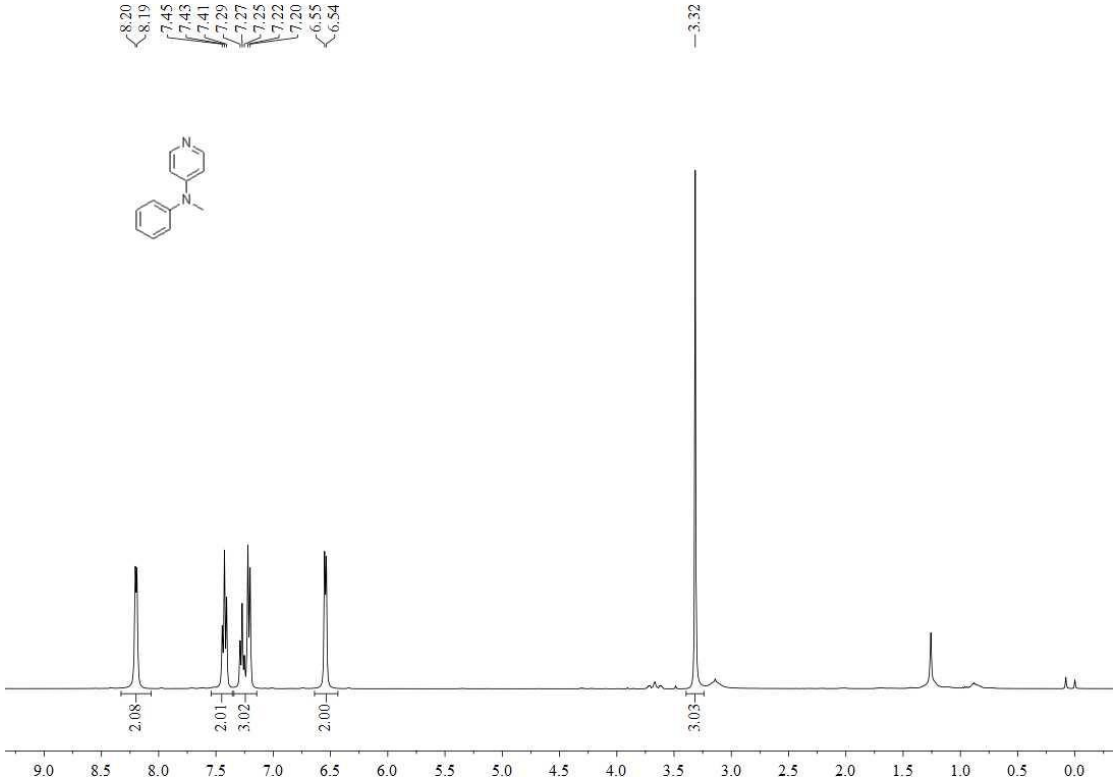
H), 6.92 (d, *J* = 5.8 Hz, 1 H), 5.54–5.19 (m, 2 H), 4.45 (q, *J* = 8.4 Hz, 1 H), 3.57 (dt, *J* = 11.1, 6.2 Hz, 1 H), 2.53–2.21 (m, 3 H), 2.12–2.00 (m 1 H), 1.83 (dd, *J* = 32.6, 8.5 Hz, 4 H), 1.70–1.23 (m, 10 H), 1.19–0.97 (m, 5 H), 0.93 (s, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.13, 141.01, 137.28, 129.84, 127.36, 125.91, 121.44, 121.43, 121.27, 118.17, 110.54, 71.77, 60.57, 53.06, 50.42, 43.07 , 42.41, 37.37, 37.25, 36.69, 32.30, 31.77, 31.68, 29.50, 23.90, 20.85, 19.49, 12.27. ESI: Calcd. for $C_{28}H_{36}N_2O$ $[M+H]^+$: 417.2906; found: 417.2904.

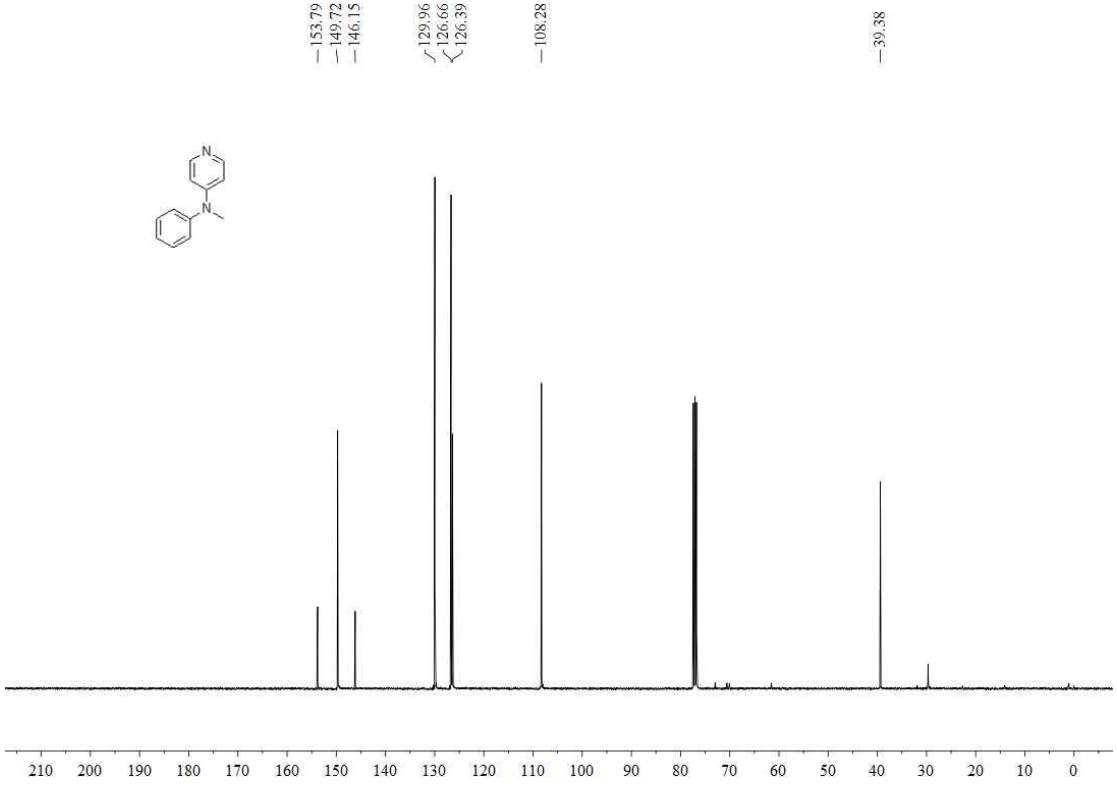


***N*-methylquinolin-4-amine (85c)** The product is obtained as white soild (isolated yield: 87%): ^{1}H NMR (400 MHz, CD_3OD) δ 8.42 (d, *J* = 7.1 Hz, 1 H), 8.34 (d, *J* = 8.5 Hz, 1 H), 7.97 (t, *J* = 7.6 Hz, 1 H), 7.87 (d, *J* = 8.4 Hz, 1 H), 7.73 (t, *J* = 7.7 Hz, 1 H), 6.83 (d, *J* = 7.1 Hz, 1 H), 3.23 (s, 3 H). ^{13}C NMR (101 MHz, CD_3OD) δ 158.49, 143.22, 139.20, 134.84, 128.22, 123.68, 121.13, 118.34, 98.97, 30.56. ESI: Calcd. for $C_{10}H_{10}N_2$ $[M+H]^+$: 159.0917; found: 159.0919.

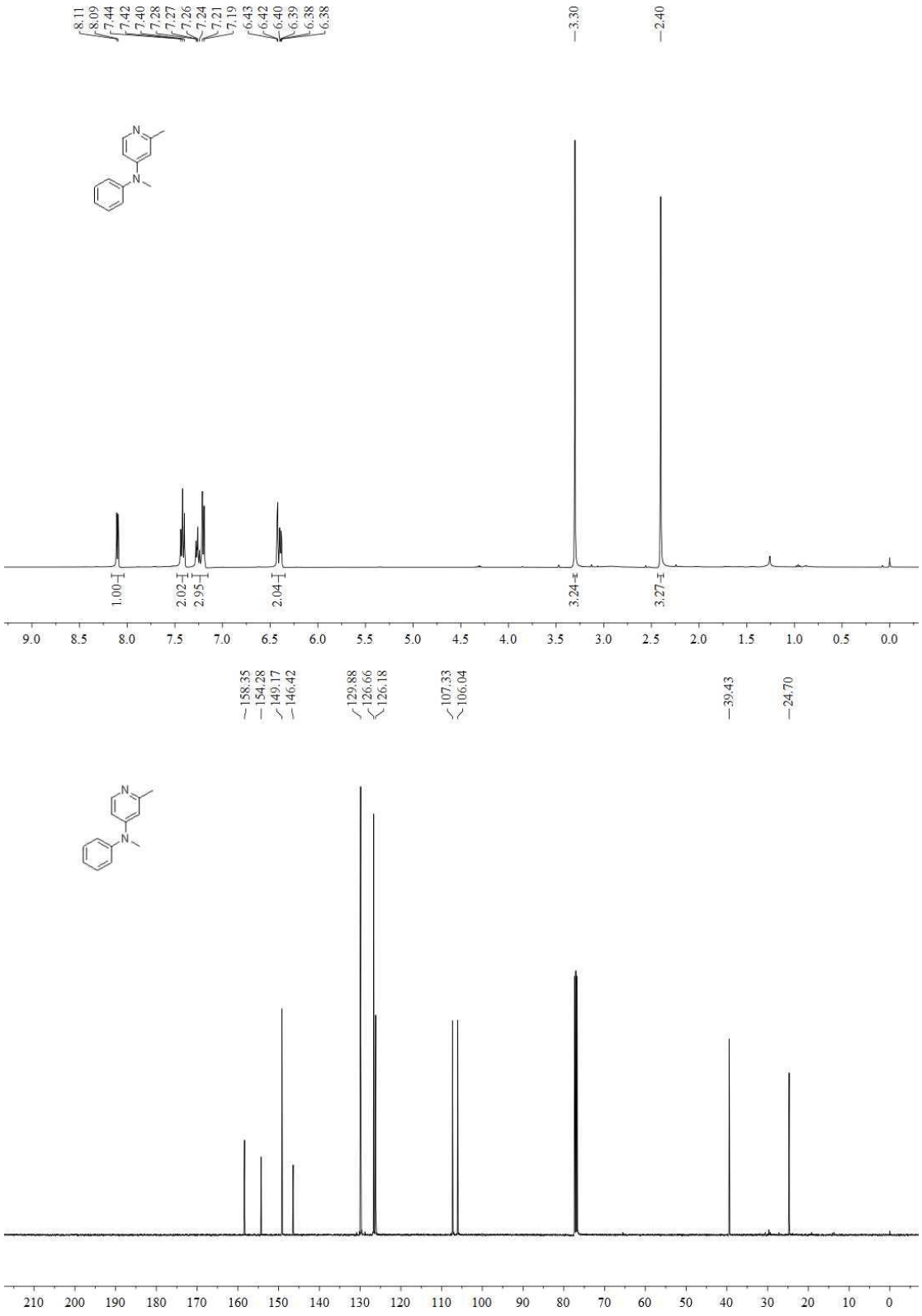
7. ^{1}H and ^{13}C spectra of products

N-methyl-*N*-phenylpyridin-4-amine (1c)

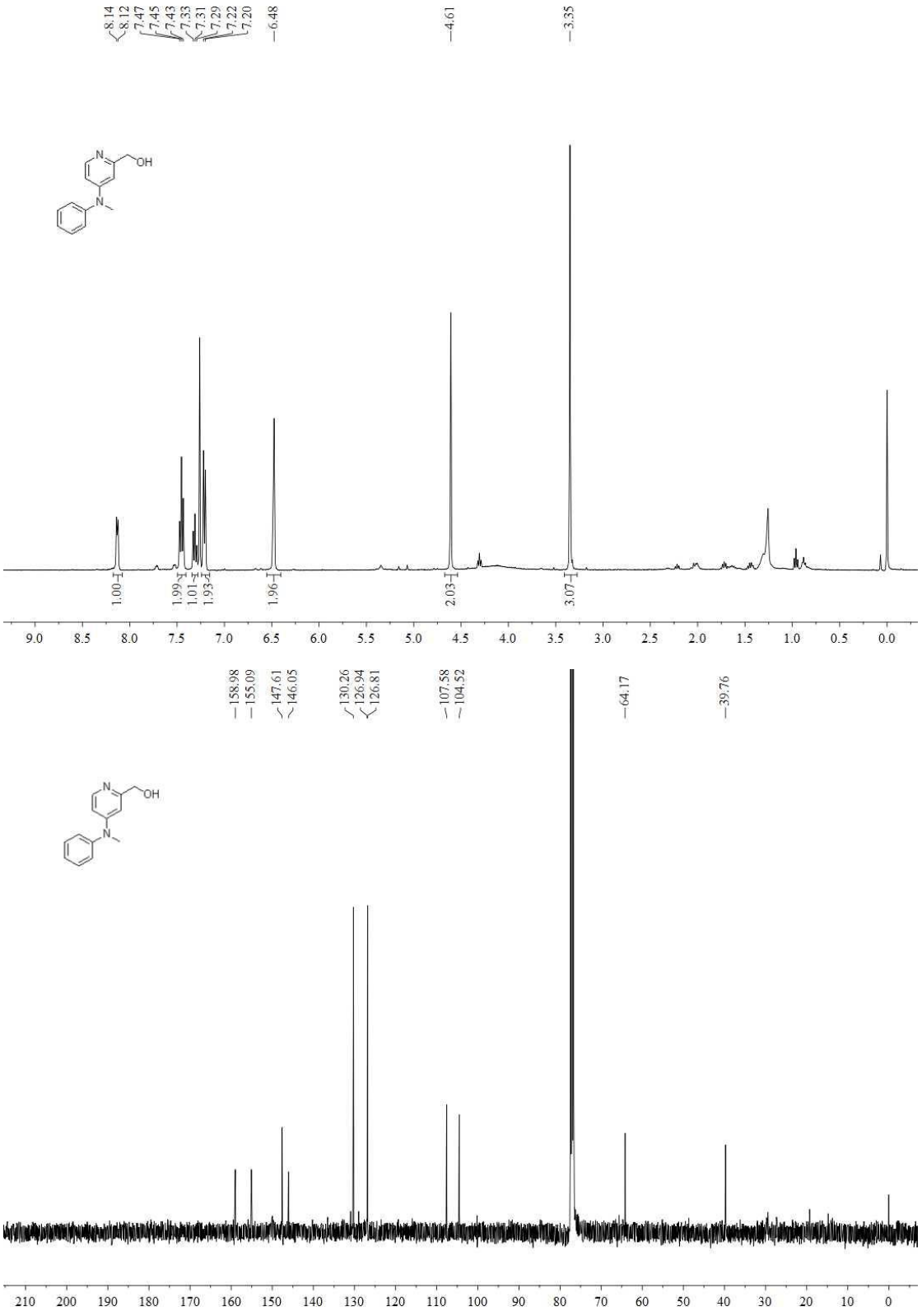




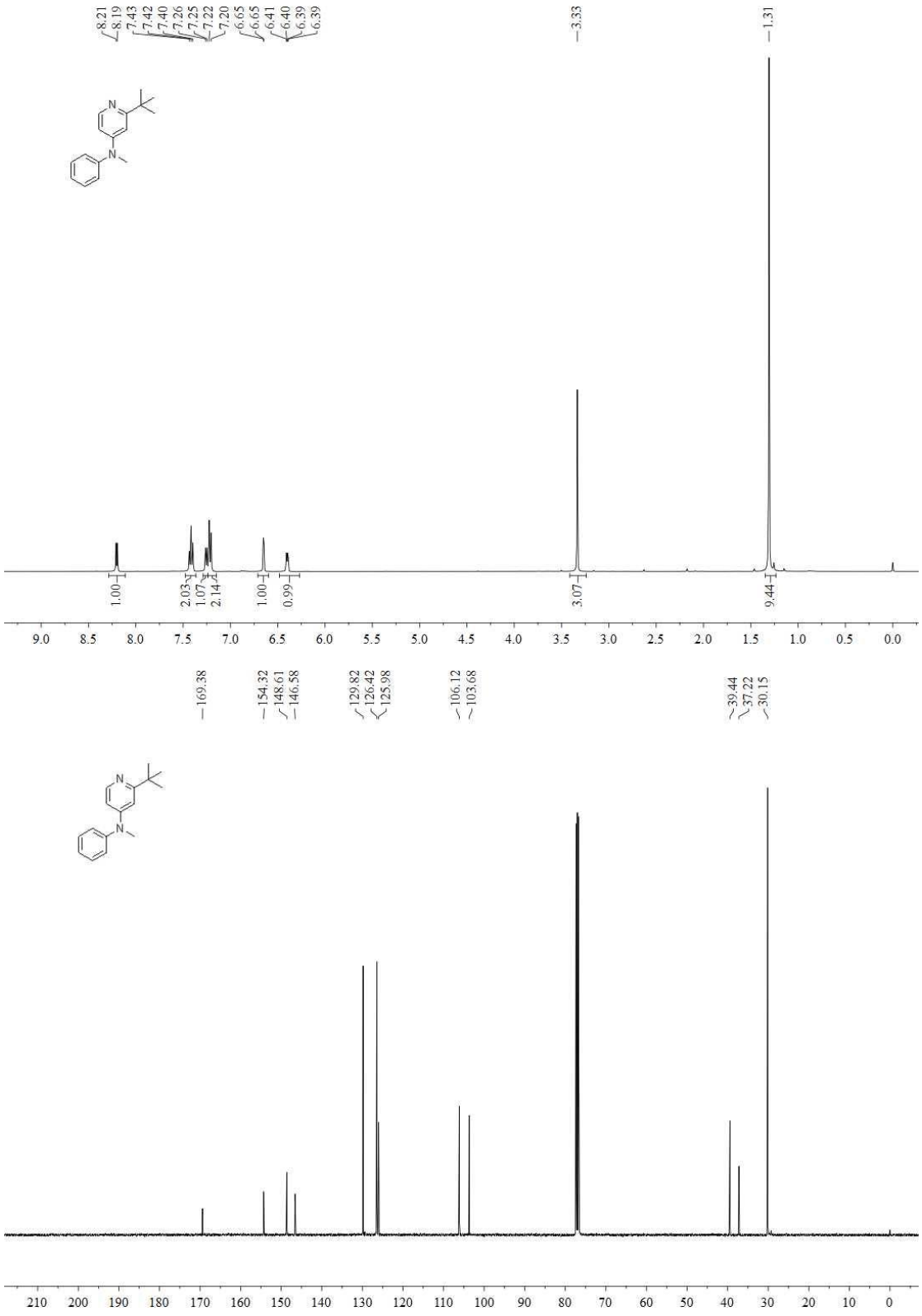
N,2-dimethyl-*N*-phenylpyridin-4-amine (2c)



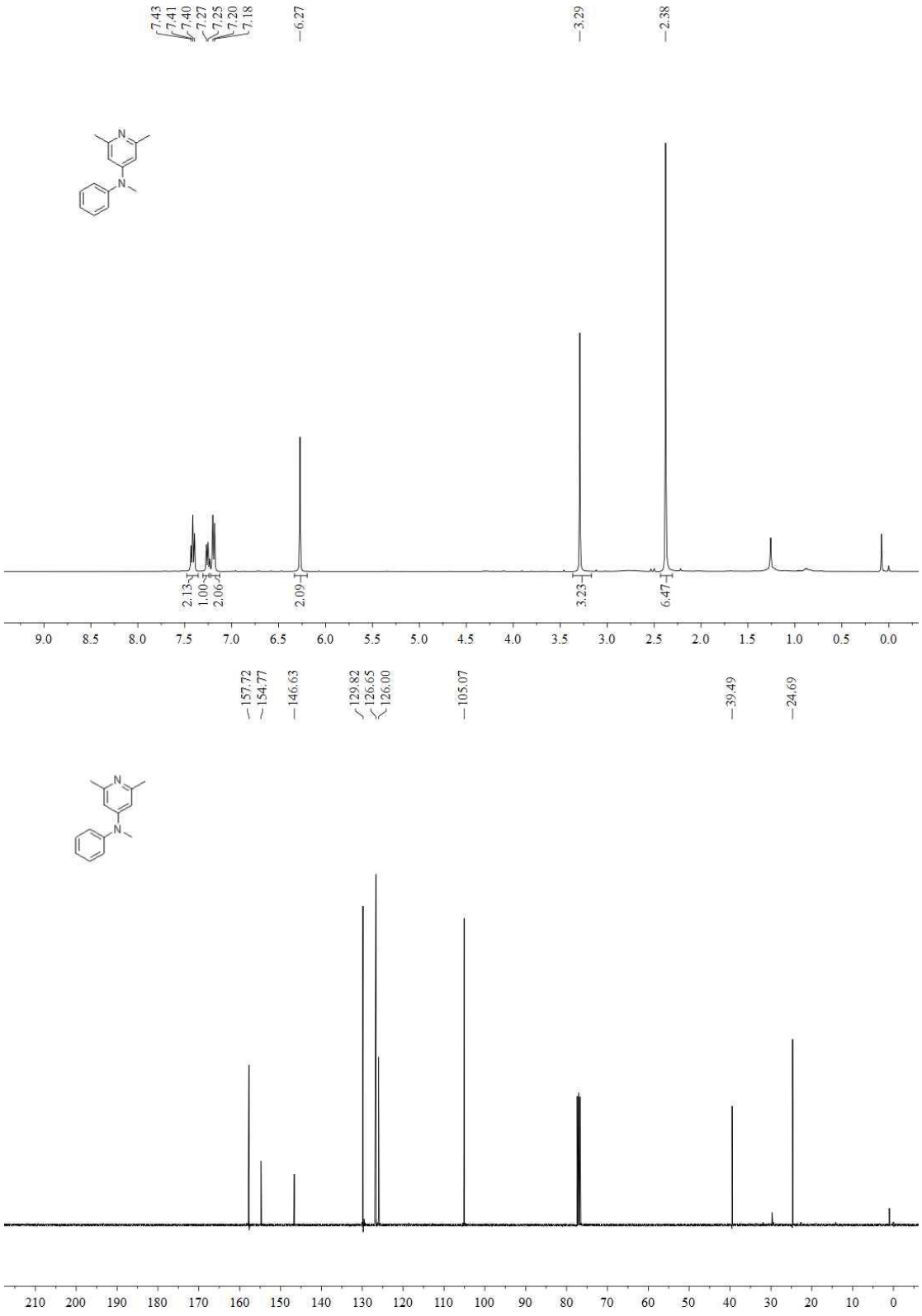
(4-(methyl(phenyl)amino)pyridin-2-yl)methanol (3c)



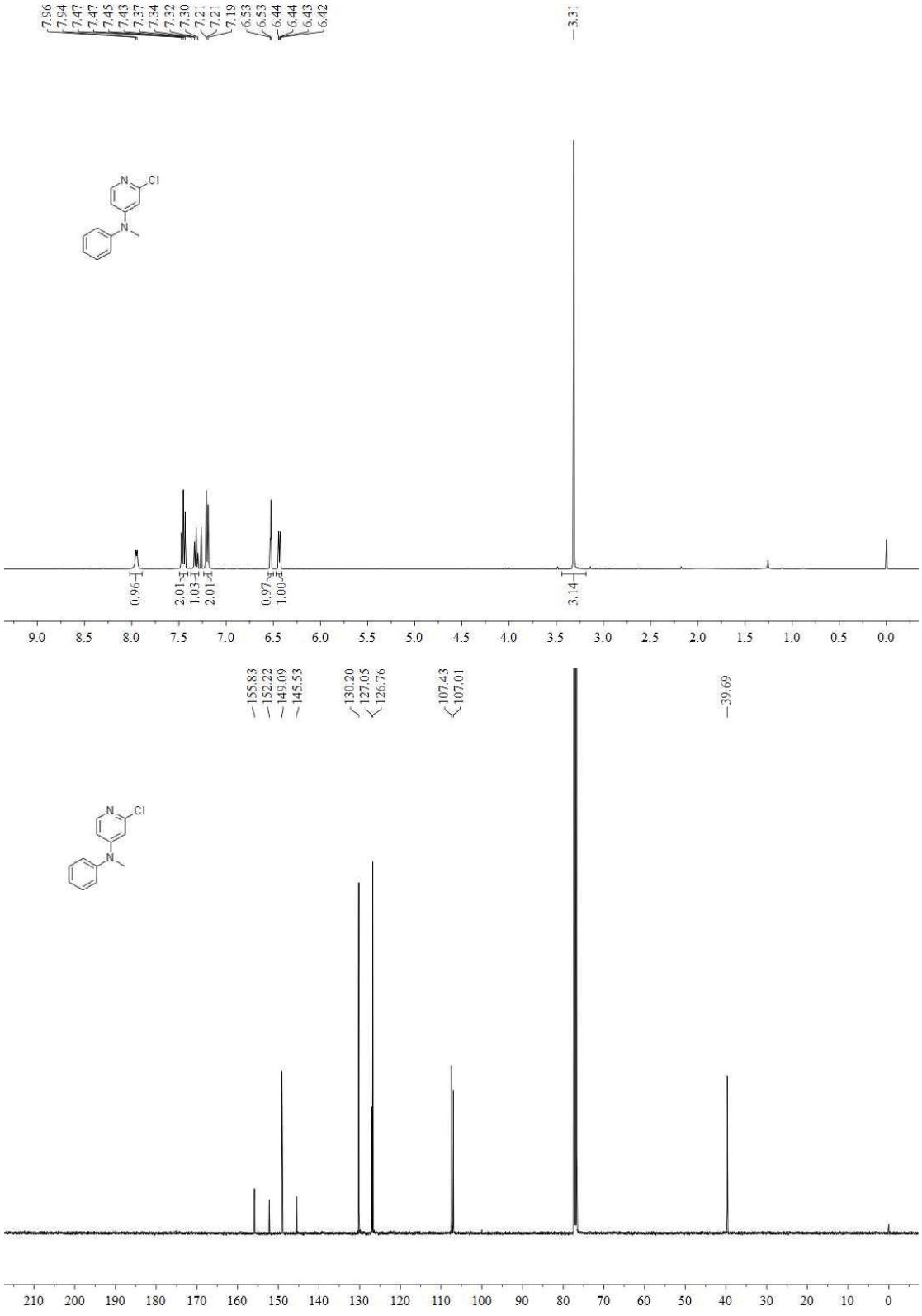
2-(tert-butyl)-*N*-methyl-*N*-phenylpyridin-4-amine (4c)



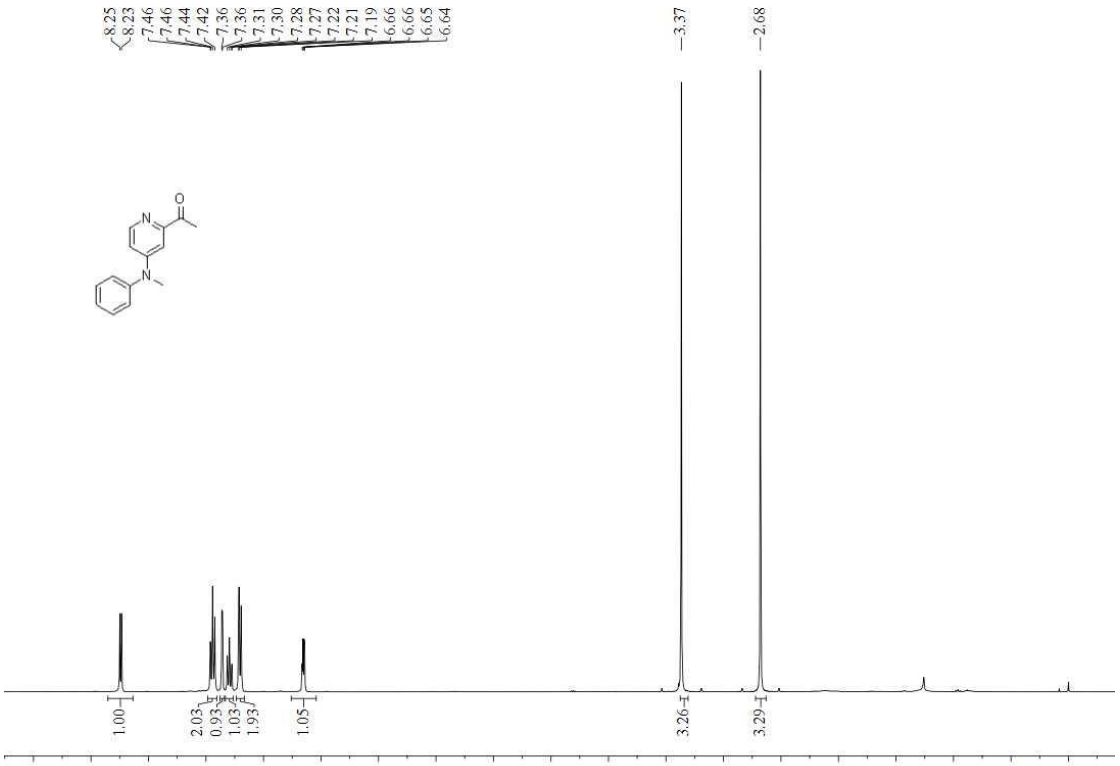
N,2,6-trimethyl-*N*-phenylpyridin-4-amine (5c)

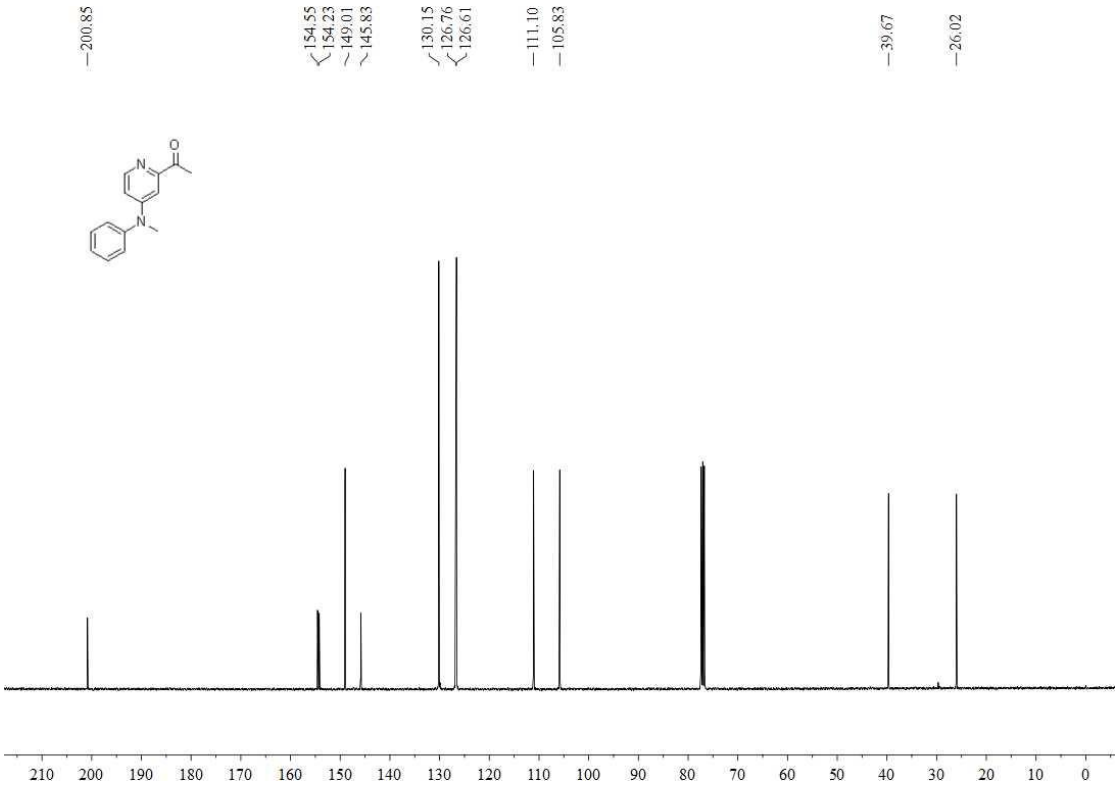


2-chloro-*N*-methyl-*N*-phenylpyridin-4-amine (6c)

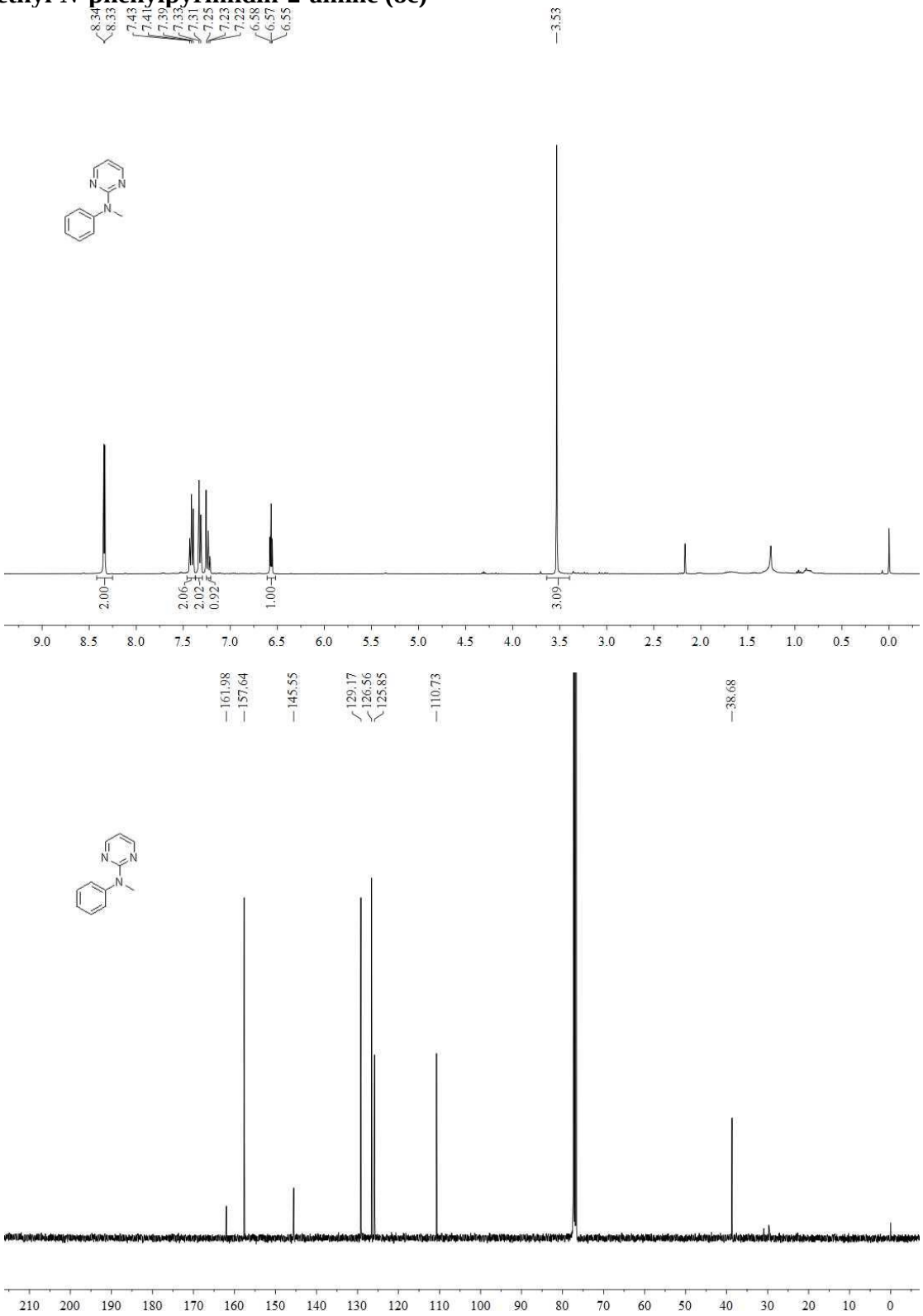


1-(4-(methyl(phenyl)amino)pyridin-2-yl)ethanone (7c)

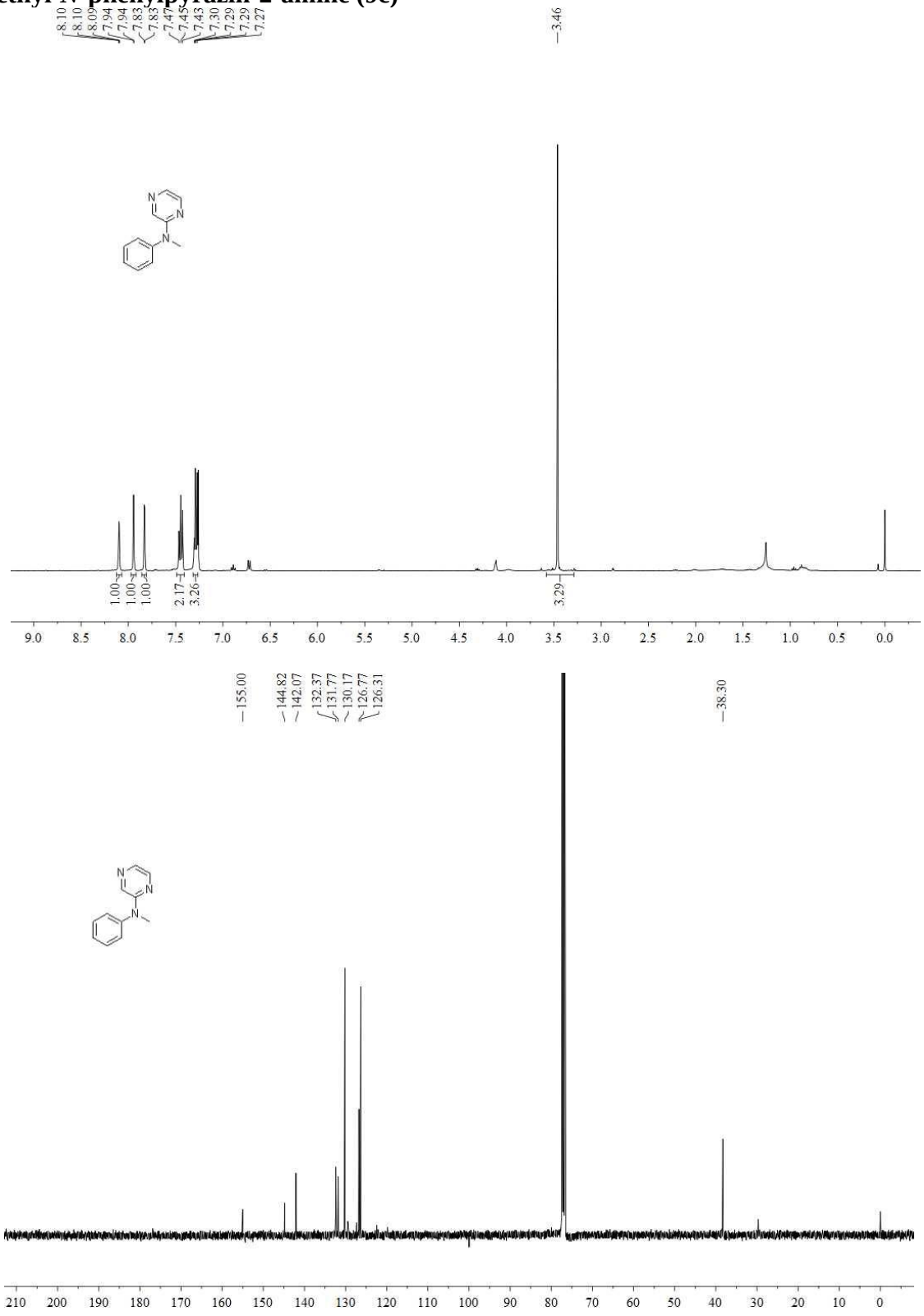




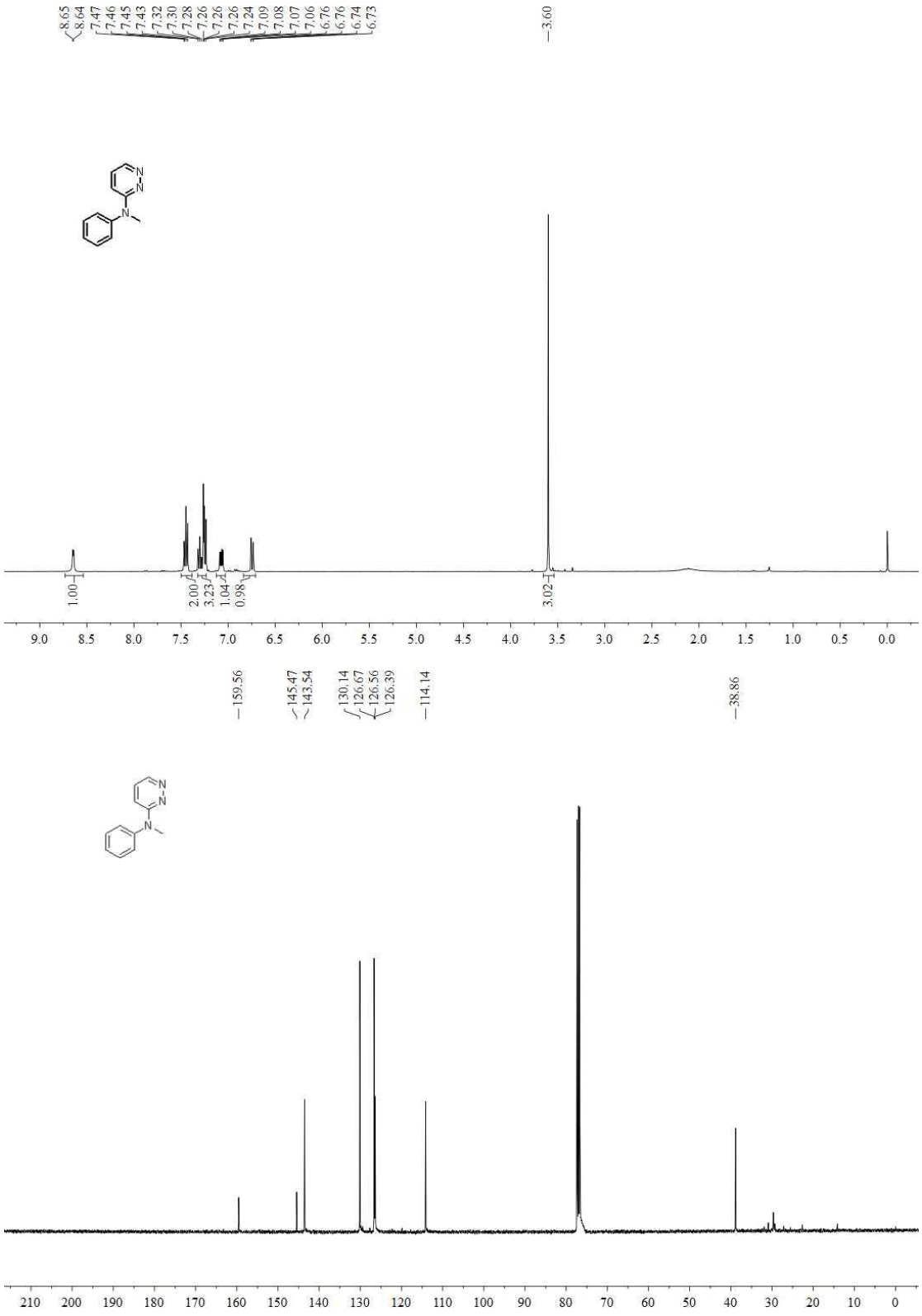
***N*-methyl-*N*-phenylpyrimidin-2-amine (8c)**



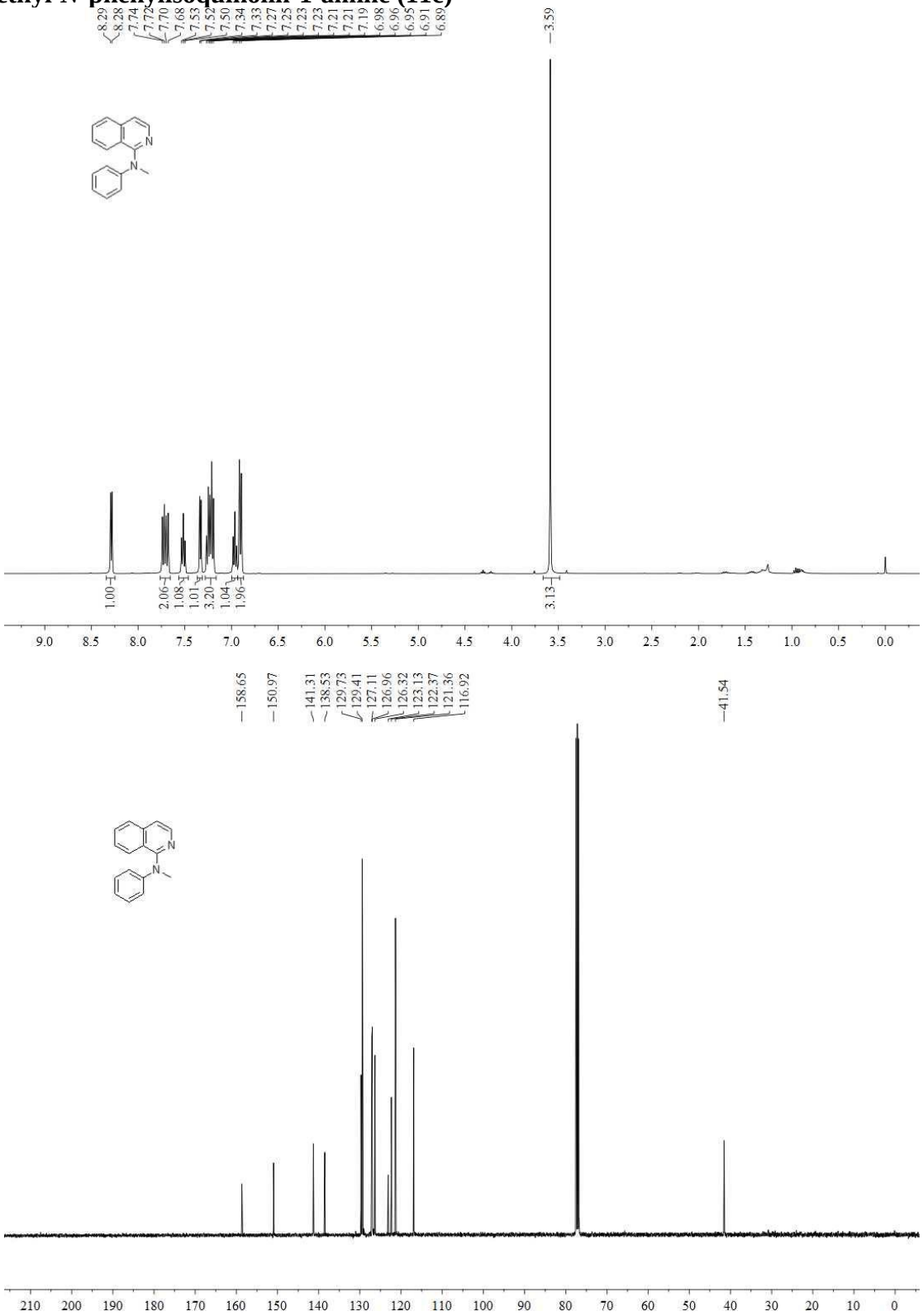
***N*-methyl-*N*-phenylpyrazin-2-amine (9c)**



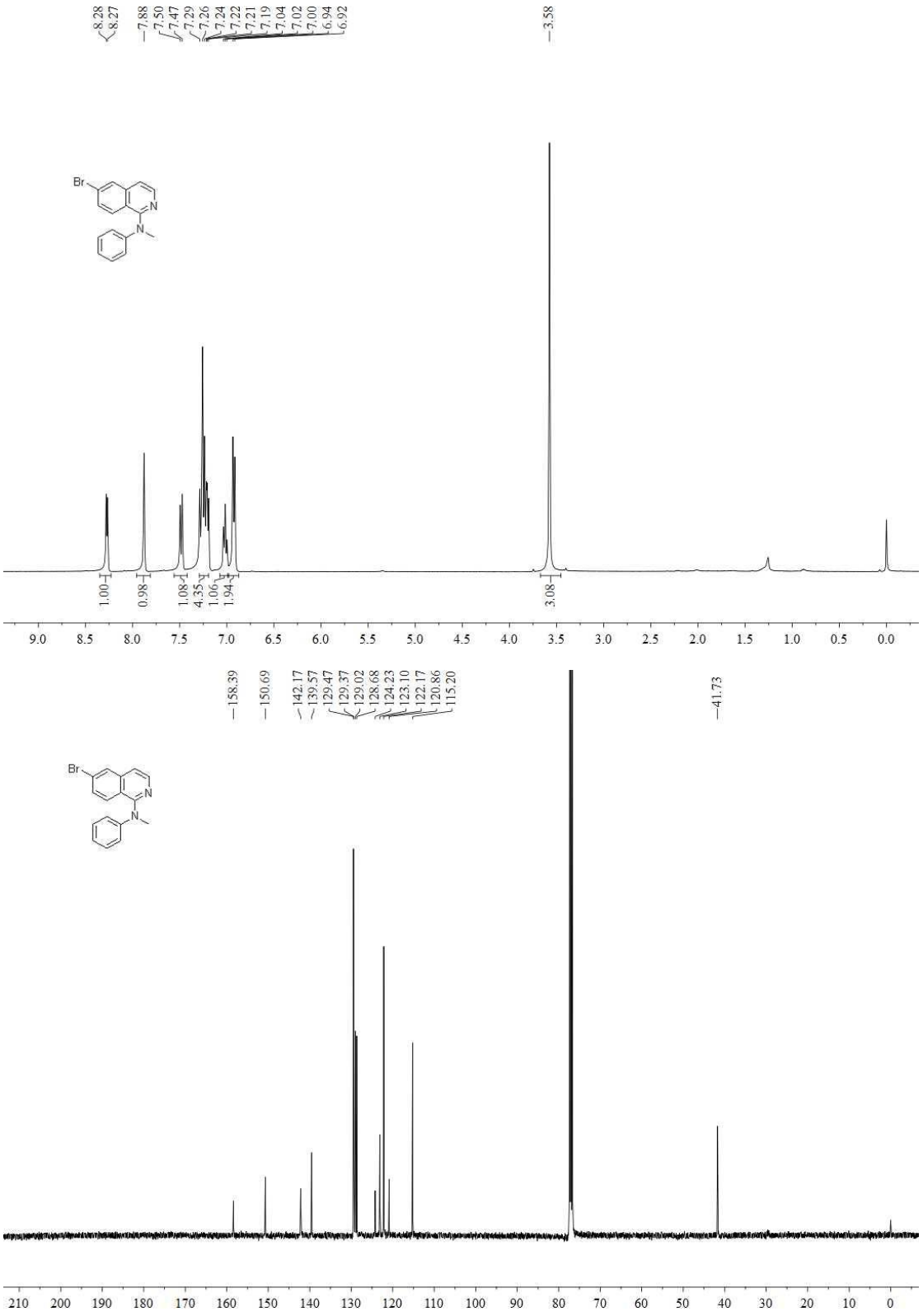
N-methyl-*N*-phenylpyridazin-3-amine (10c)



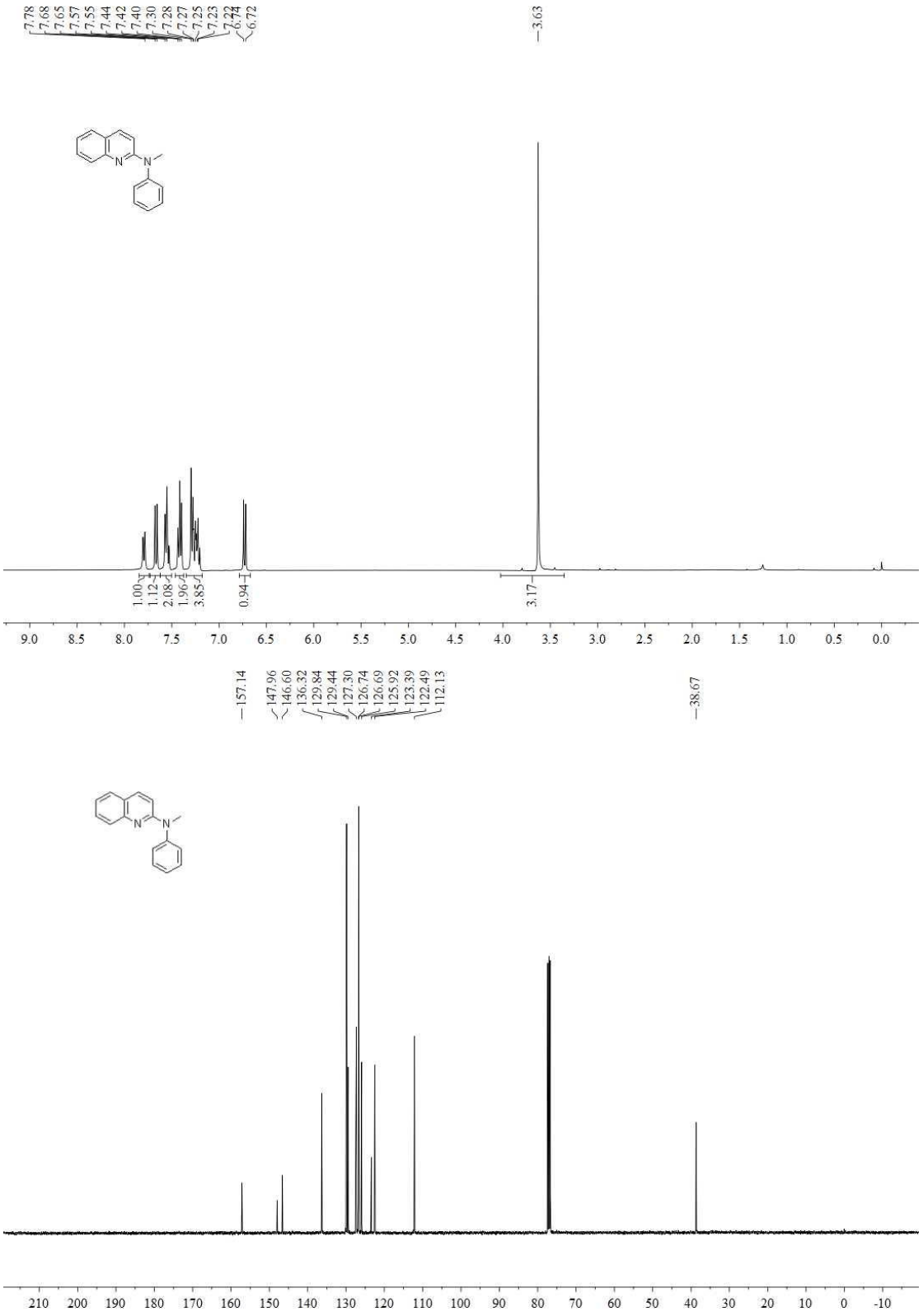
***N*-methyl-*N*-phenylisoquinolin-1-amine (11c)**



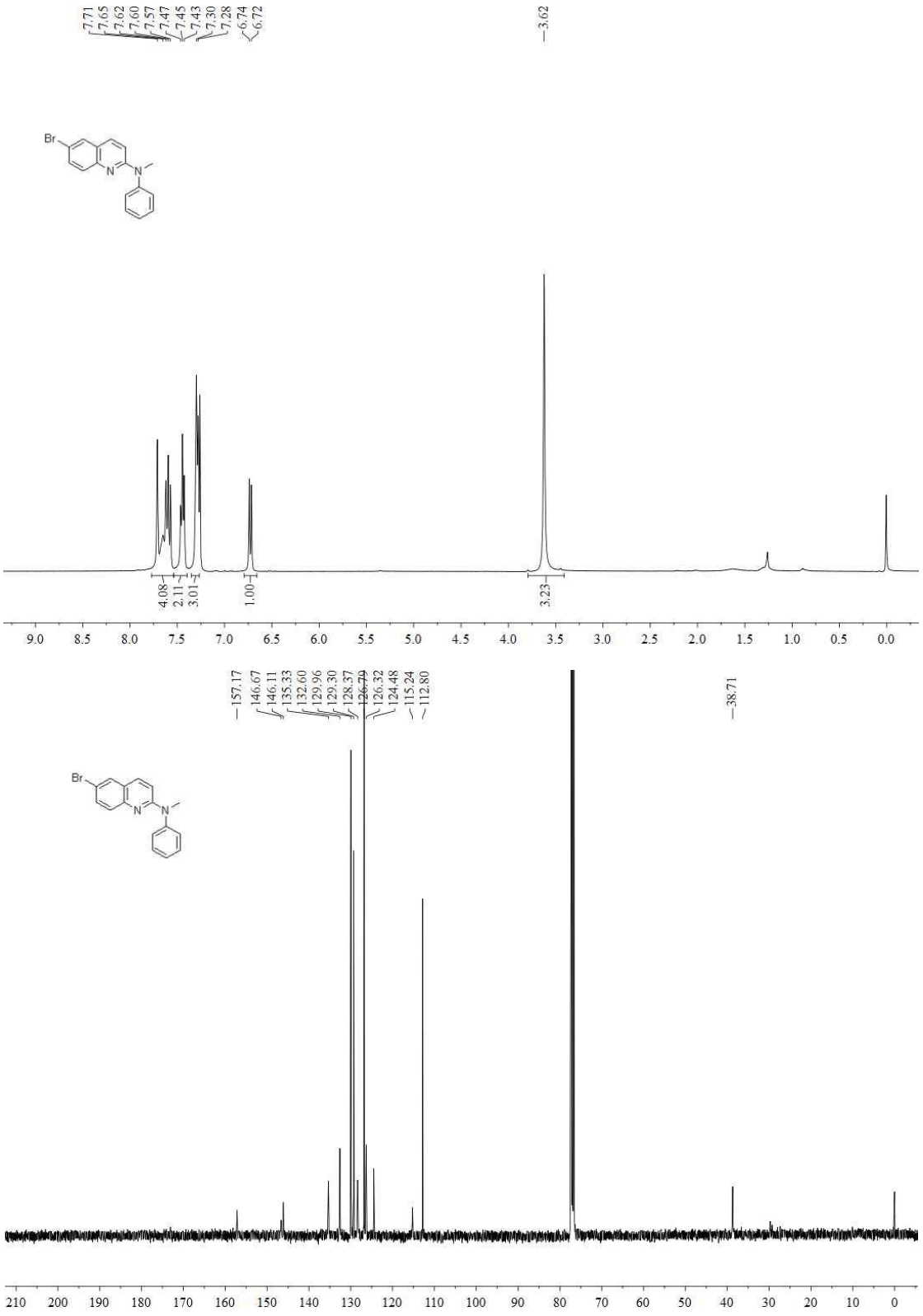
6-bromo-*N*-methyl-*N*-phenylisoquinolin-1-amine (12c)



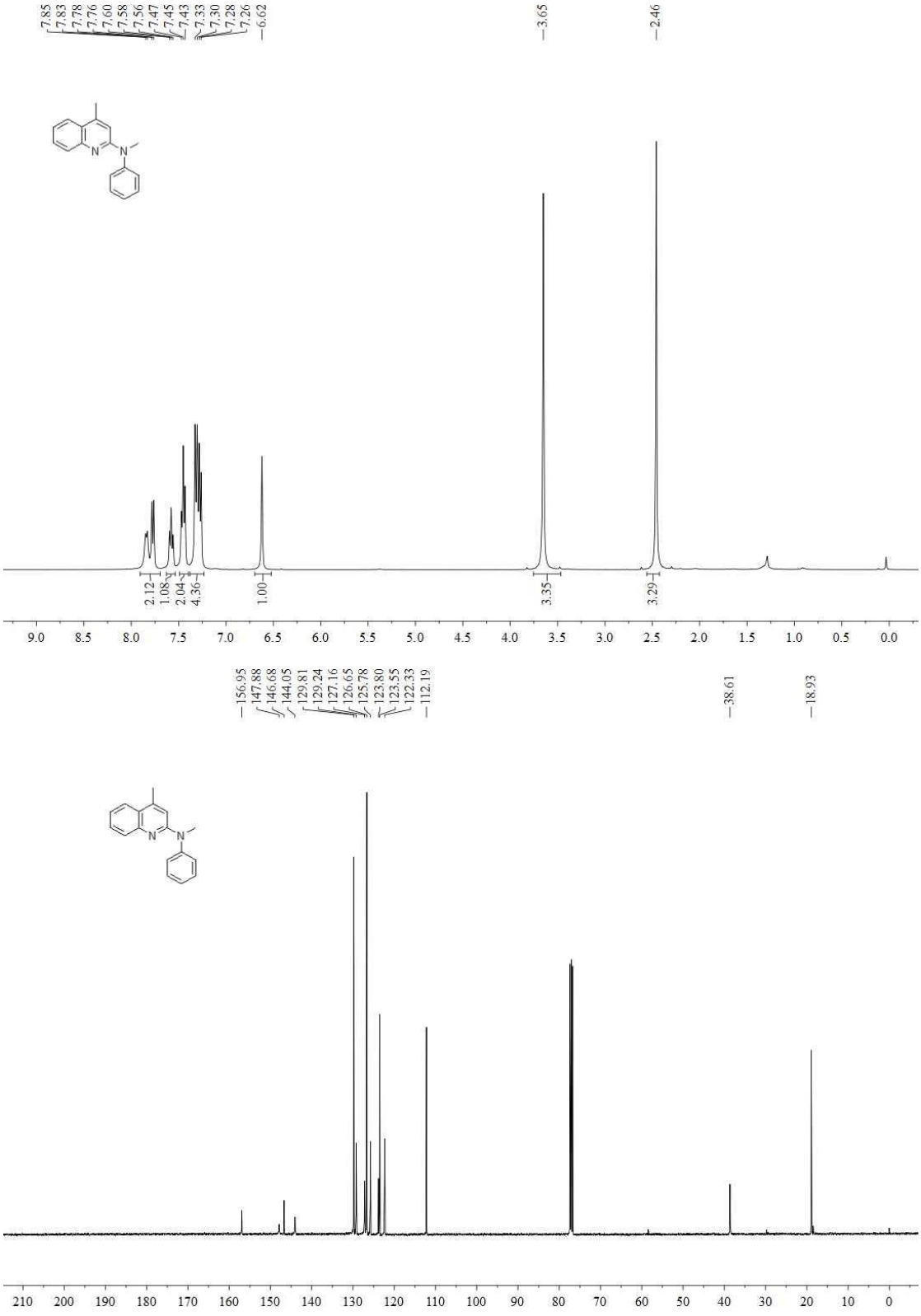
N-methyl-*N*-phenylquinolin-2-amine (13c)



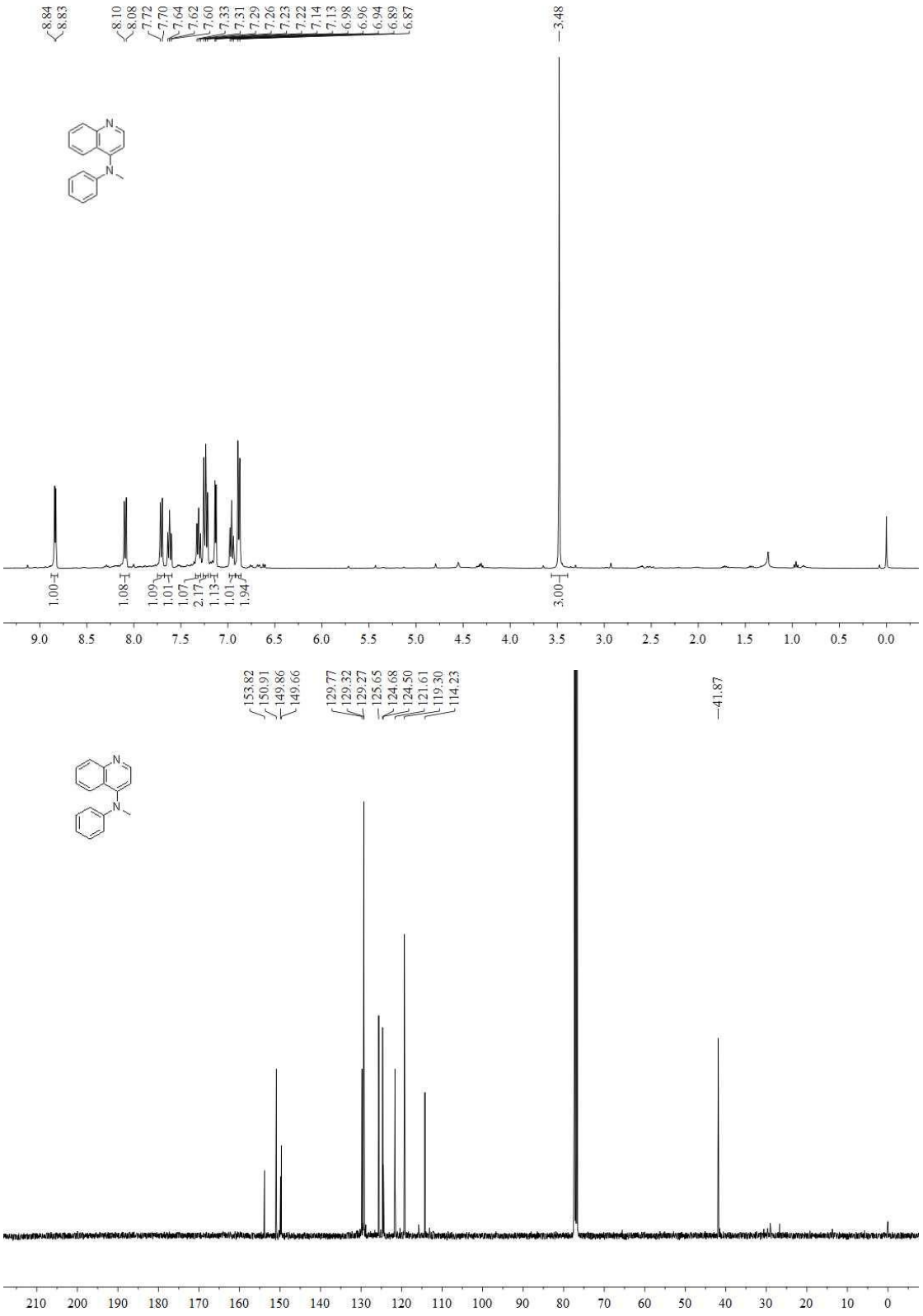
6-bromo-*N*-methyl-*N*-phenylquinolin-2-amine (14c)



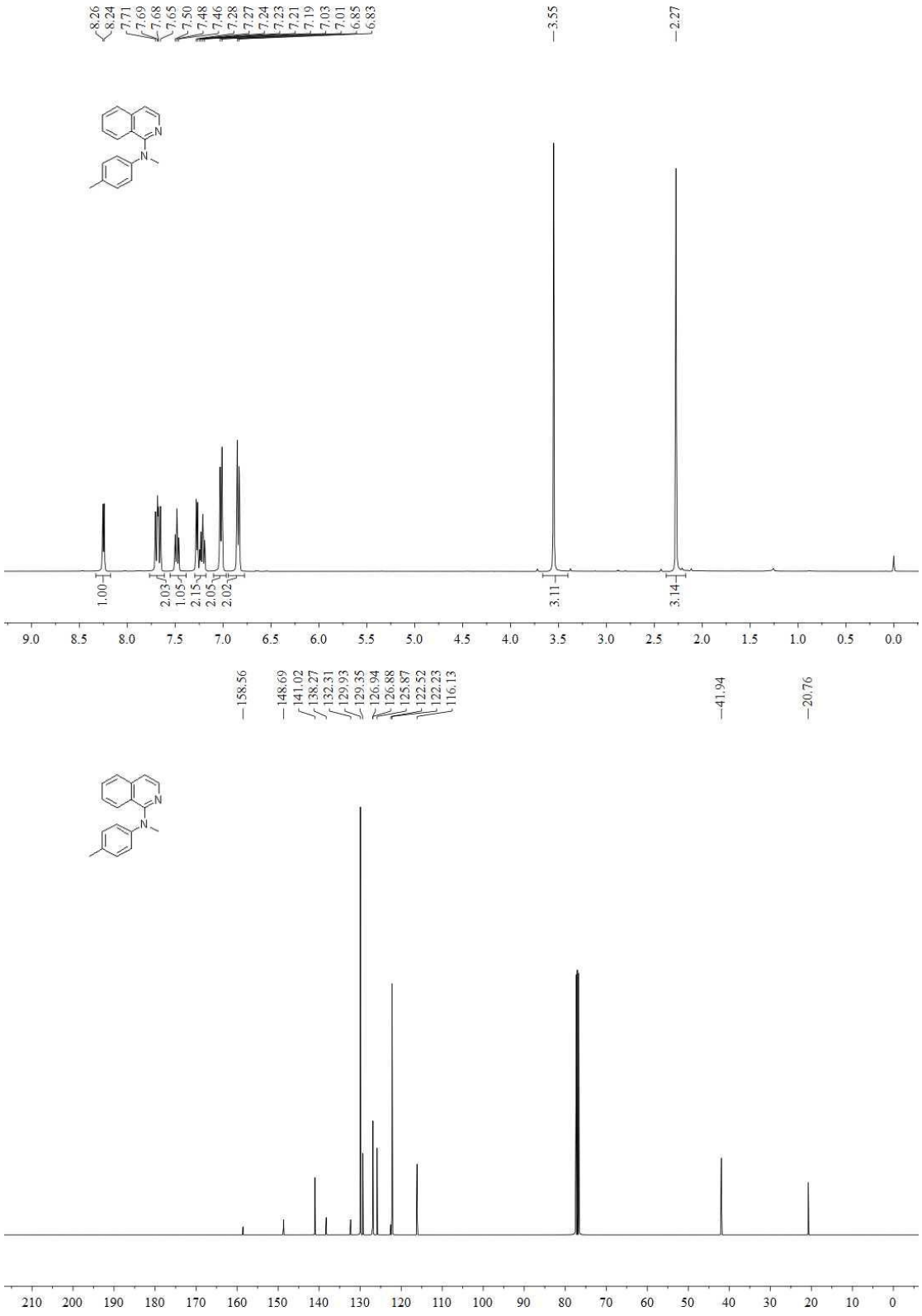
N,4-dimethyl-*N*-phenylquinolin-2-amine (15c)



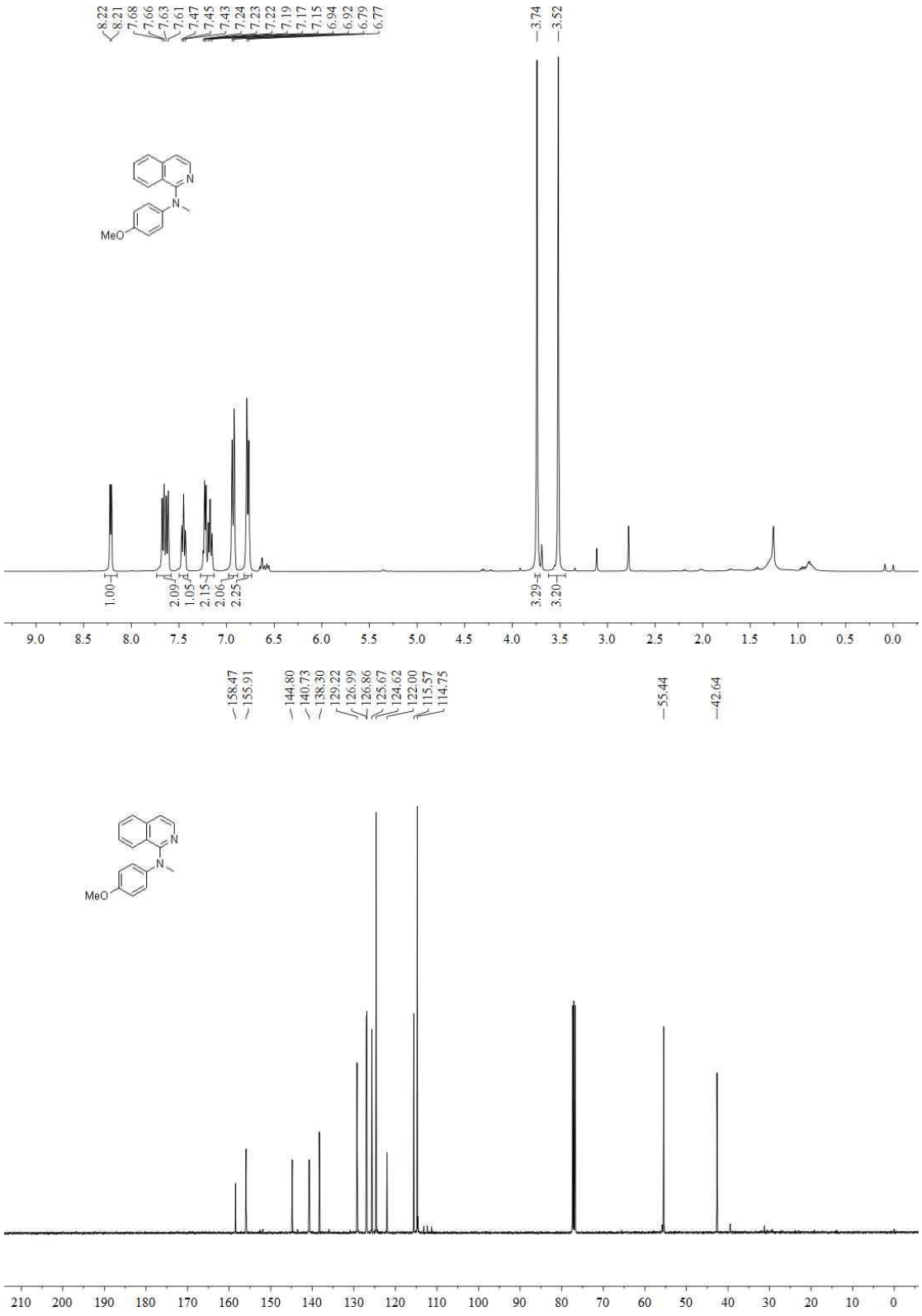
N-methyl-*N*-phenylquinolin-4-amine (16c)



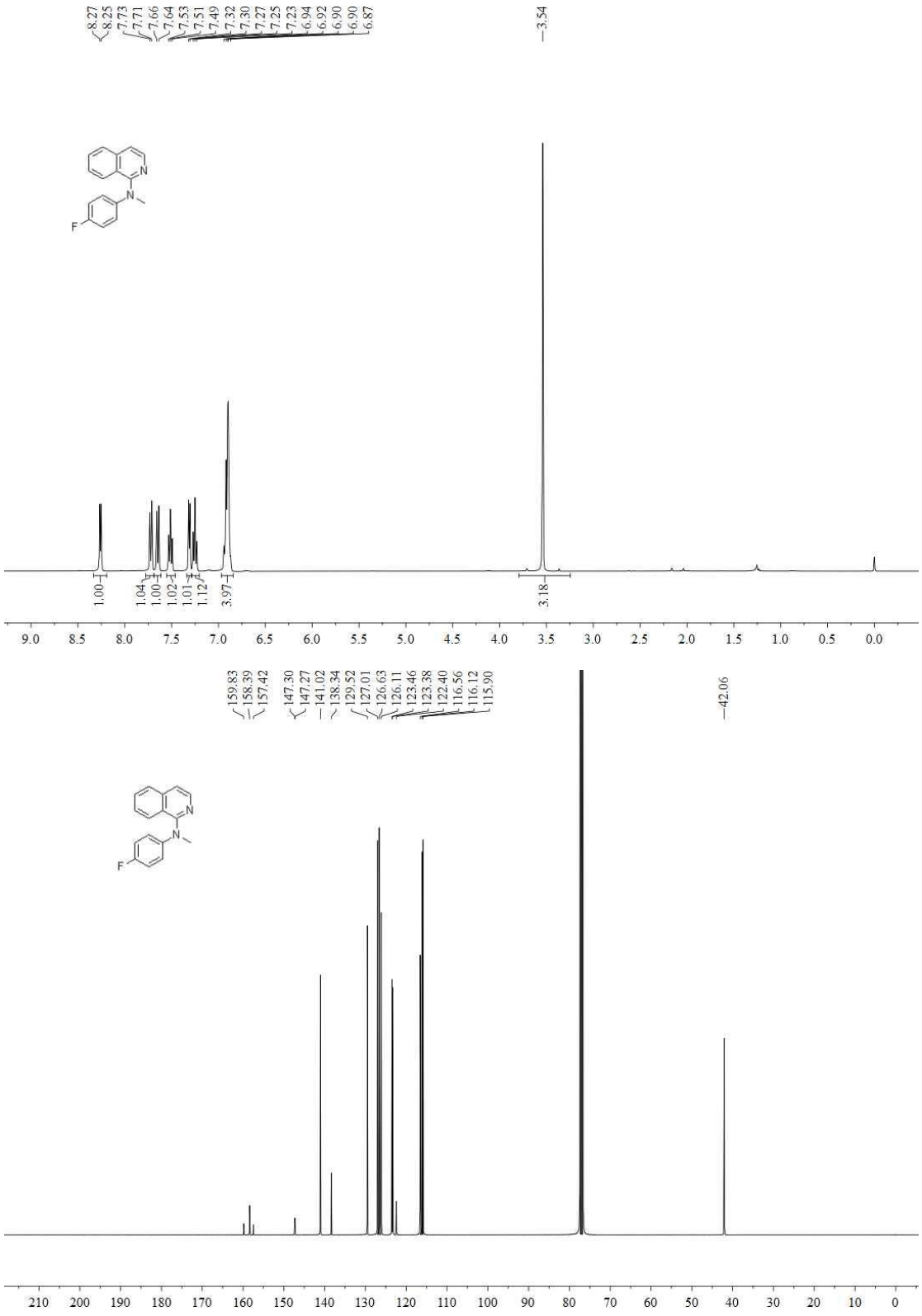
***N*-methyl-*N*-(*p*-tolyl)isoquinolin-1-amine (17c)**

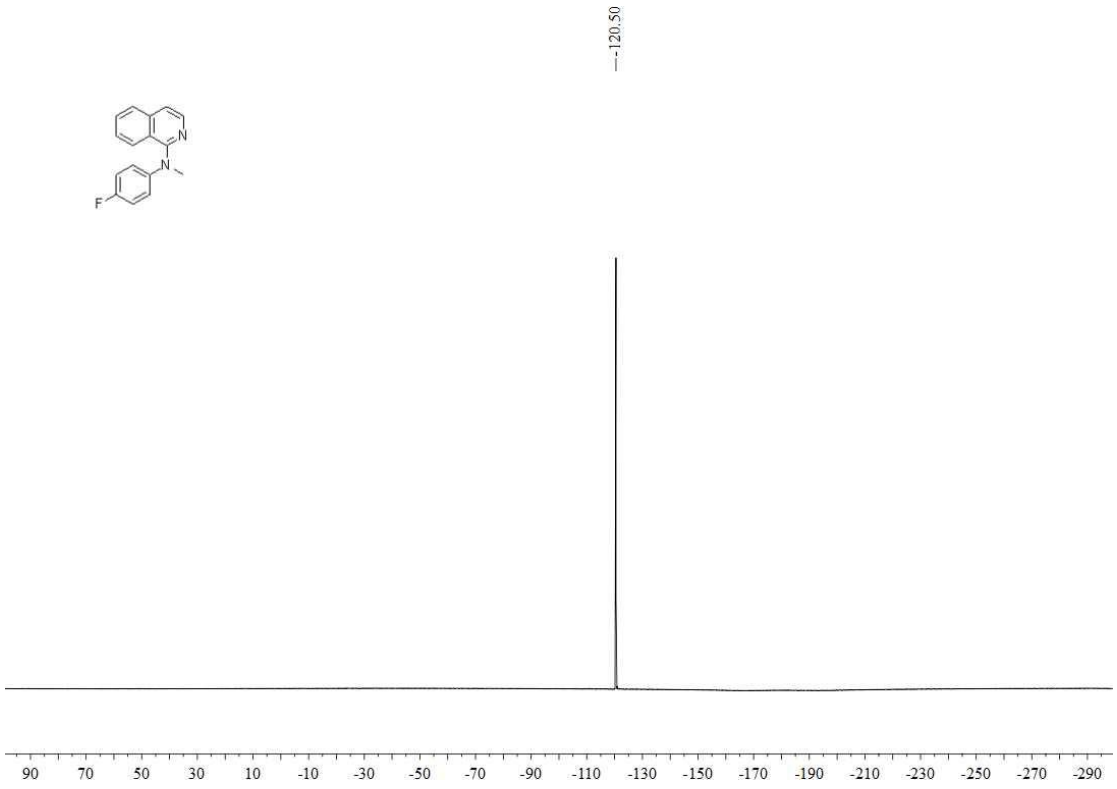


N-(4-methoxyphenyl)-*N*-methylisoquinolin-1-amine (18c)



***N*-(4-fluorophenyl)-*N*-methylisoquinolin-1-amine (19c)**

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70
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-70
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-190
-210
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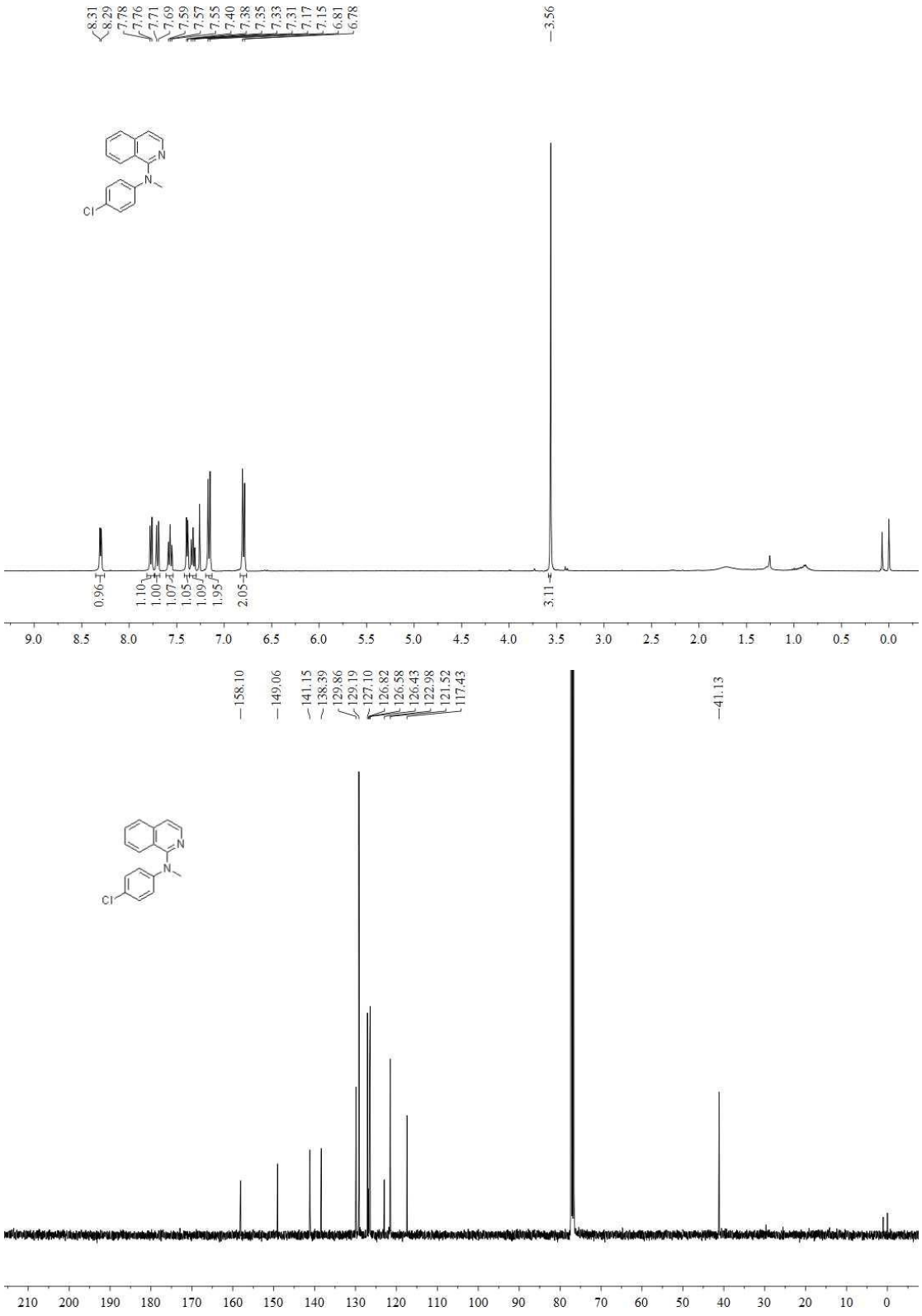
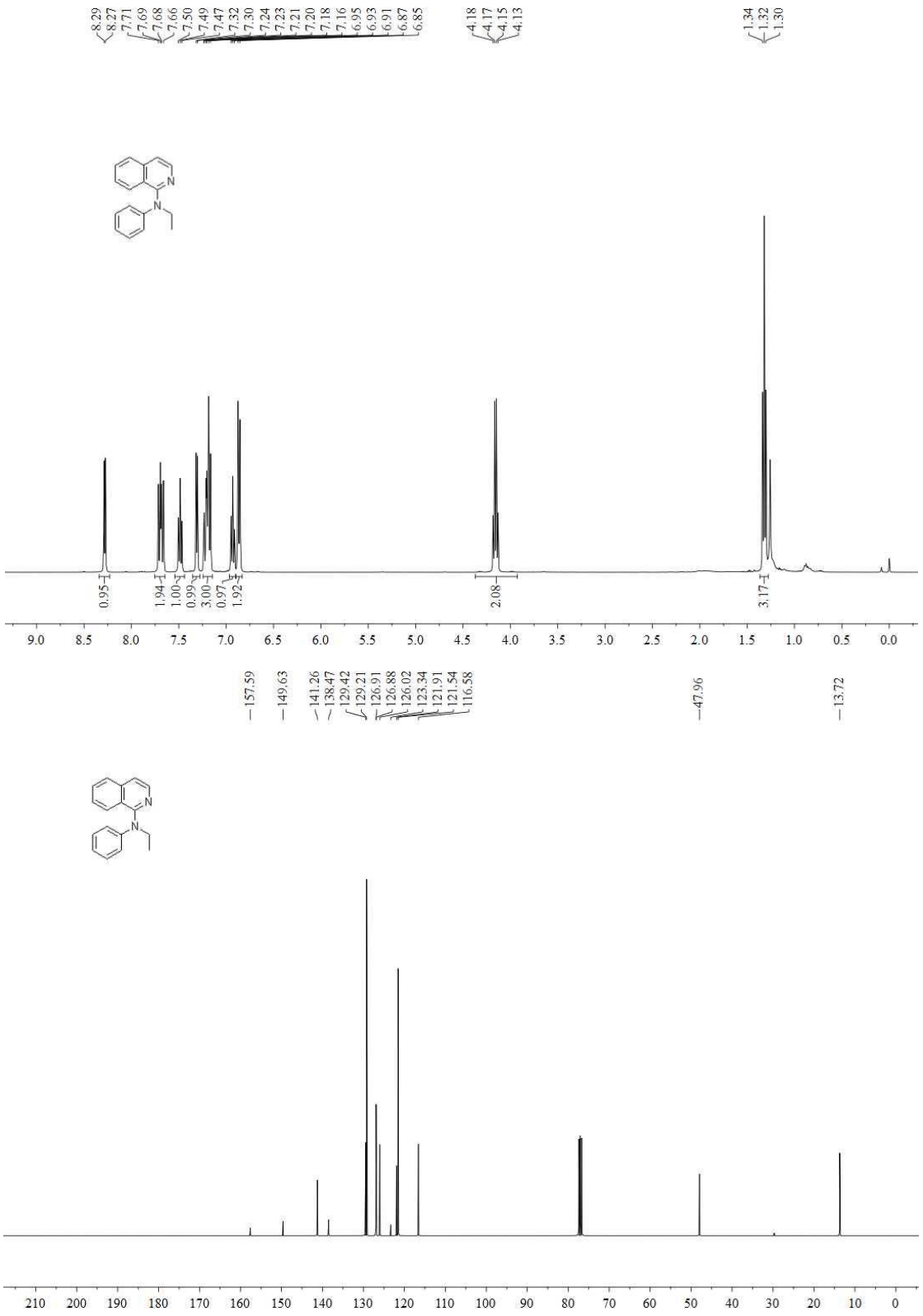
-250
-270
-290

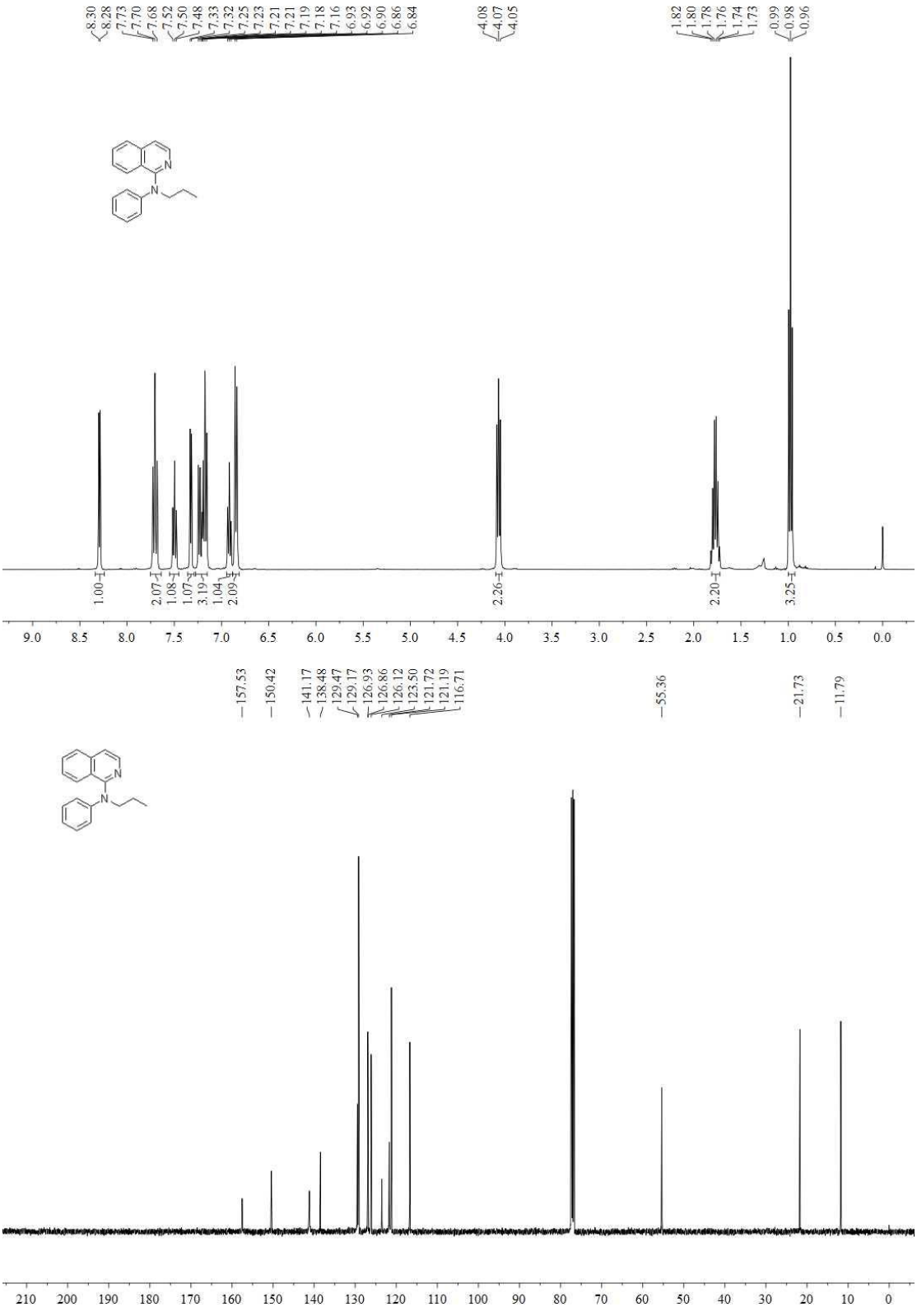
***N*-(4-chlorophenyl)-*N*-methylisoquinolin-1-amine (20c)**



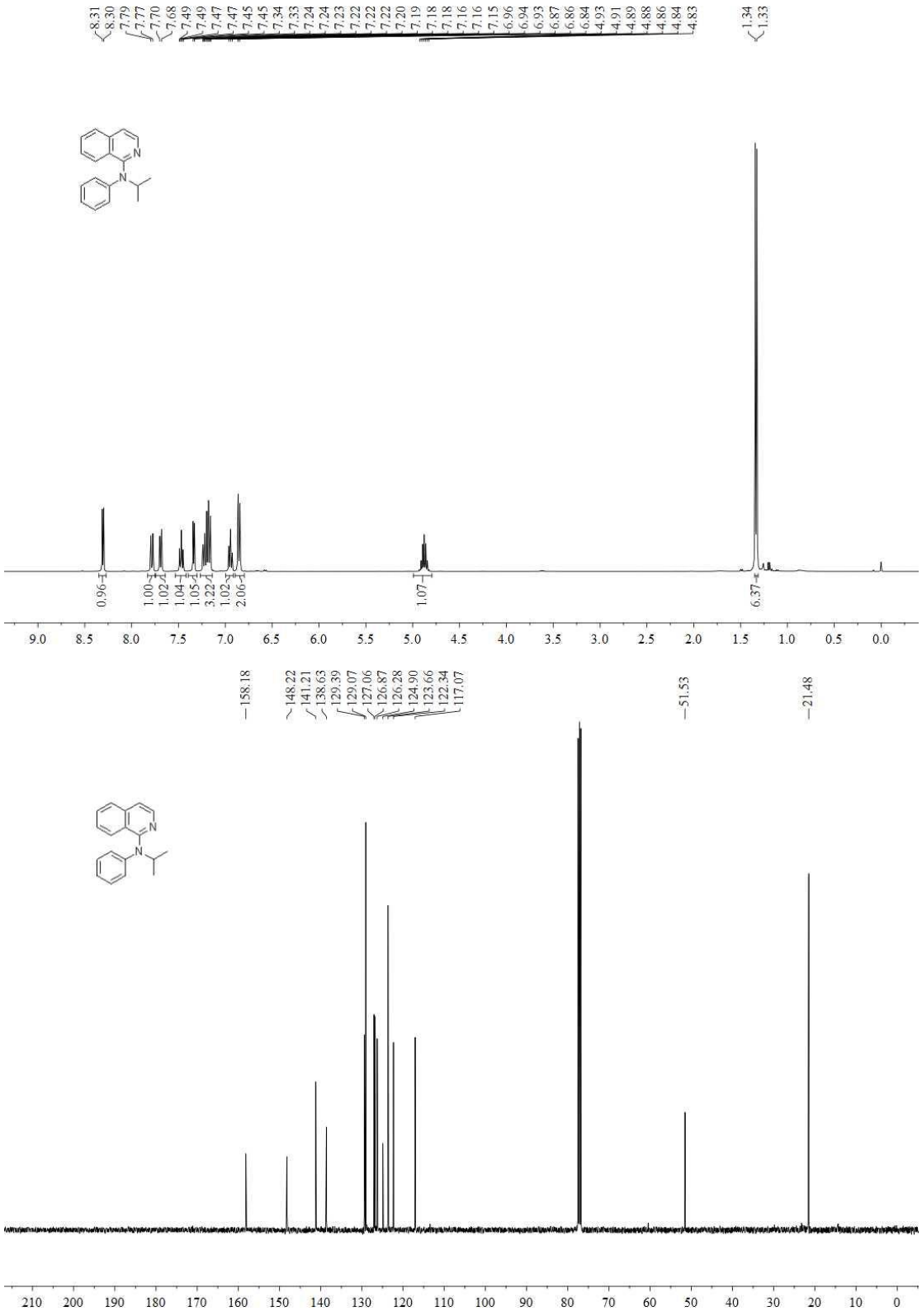
N-ethyl-*N*-phenylisoquinolin-1-amine (21c)



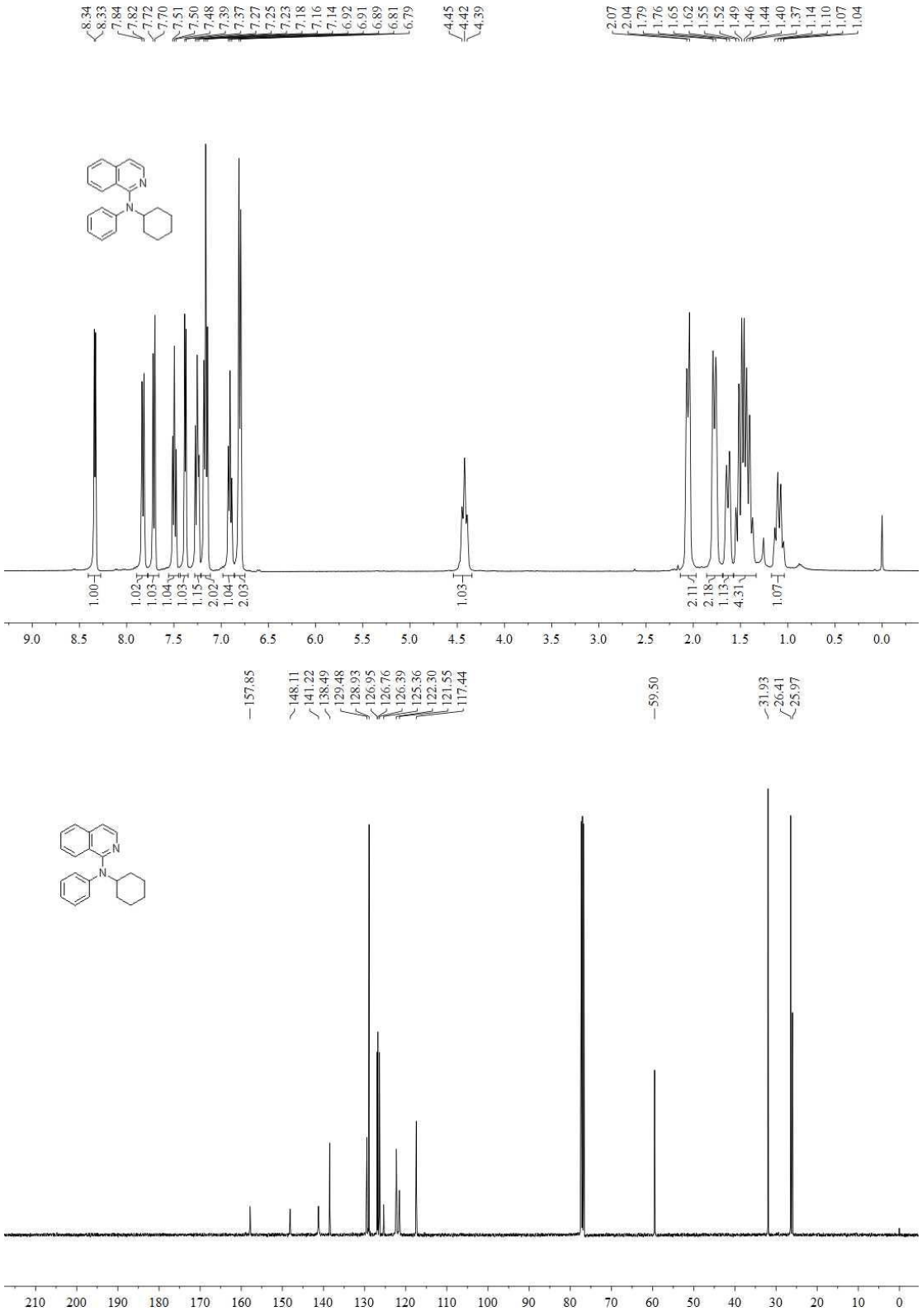
N-phenyl-N-propylisoquinolin-1-amine (22c)



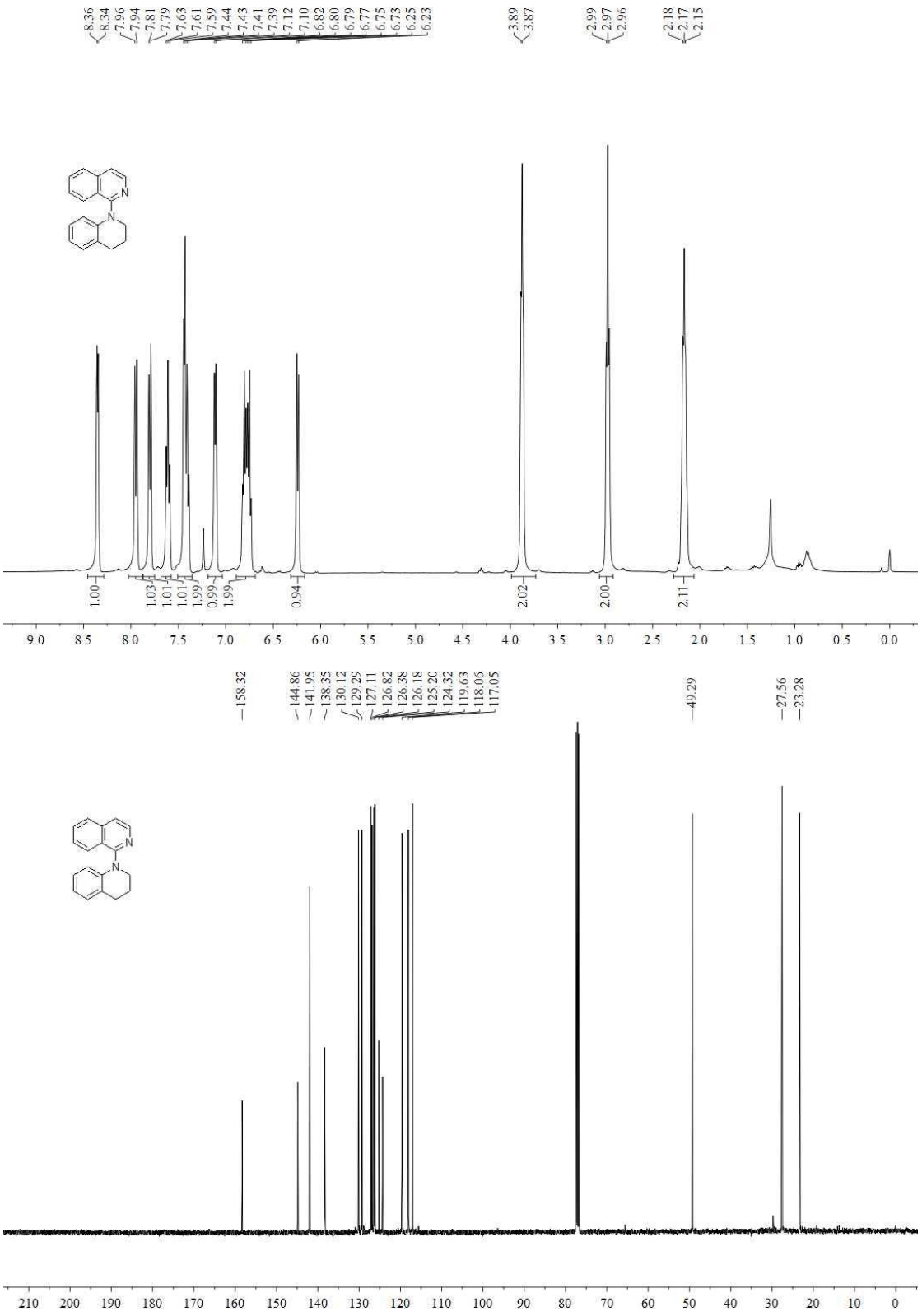
***N*-isopropyl-*N*-phenylisoquinolin-1-amine (23c)**



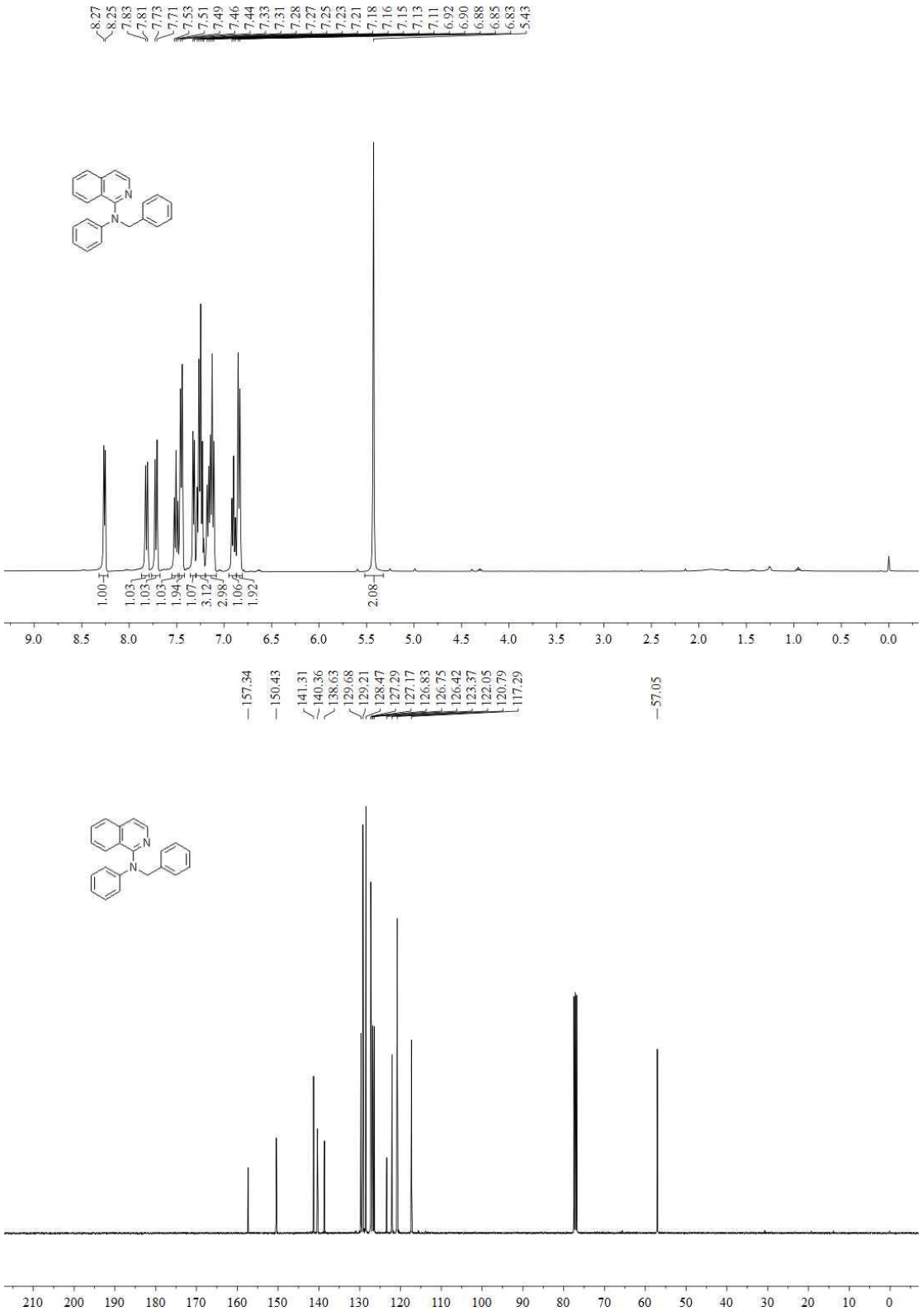
N-cyclohexyl-*N*-phenylisoquinolin-1-amine (24c)



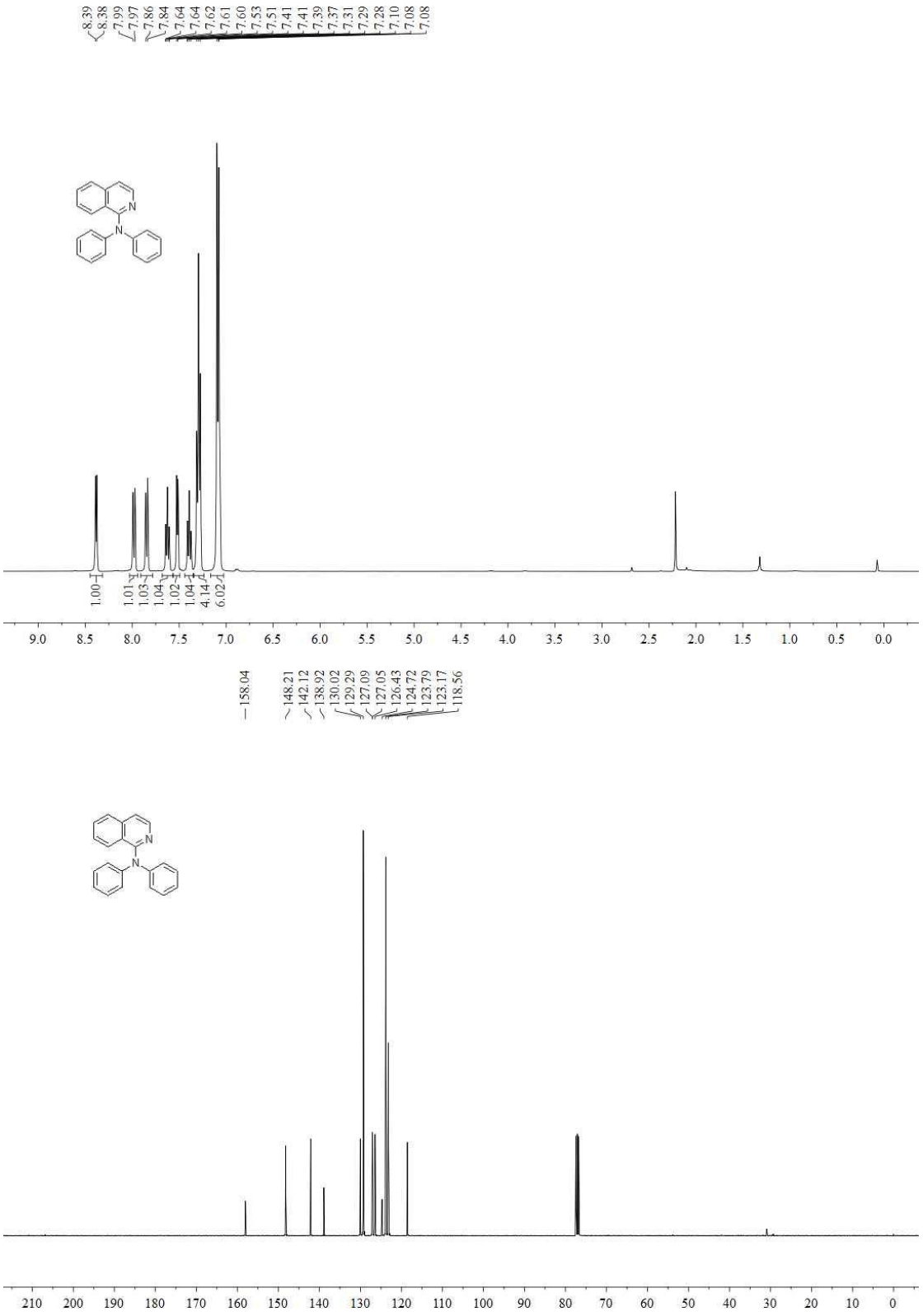
1-(isoquinolin-1-yl)-1,2,3,4-tetrahydroquinoline (25c)



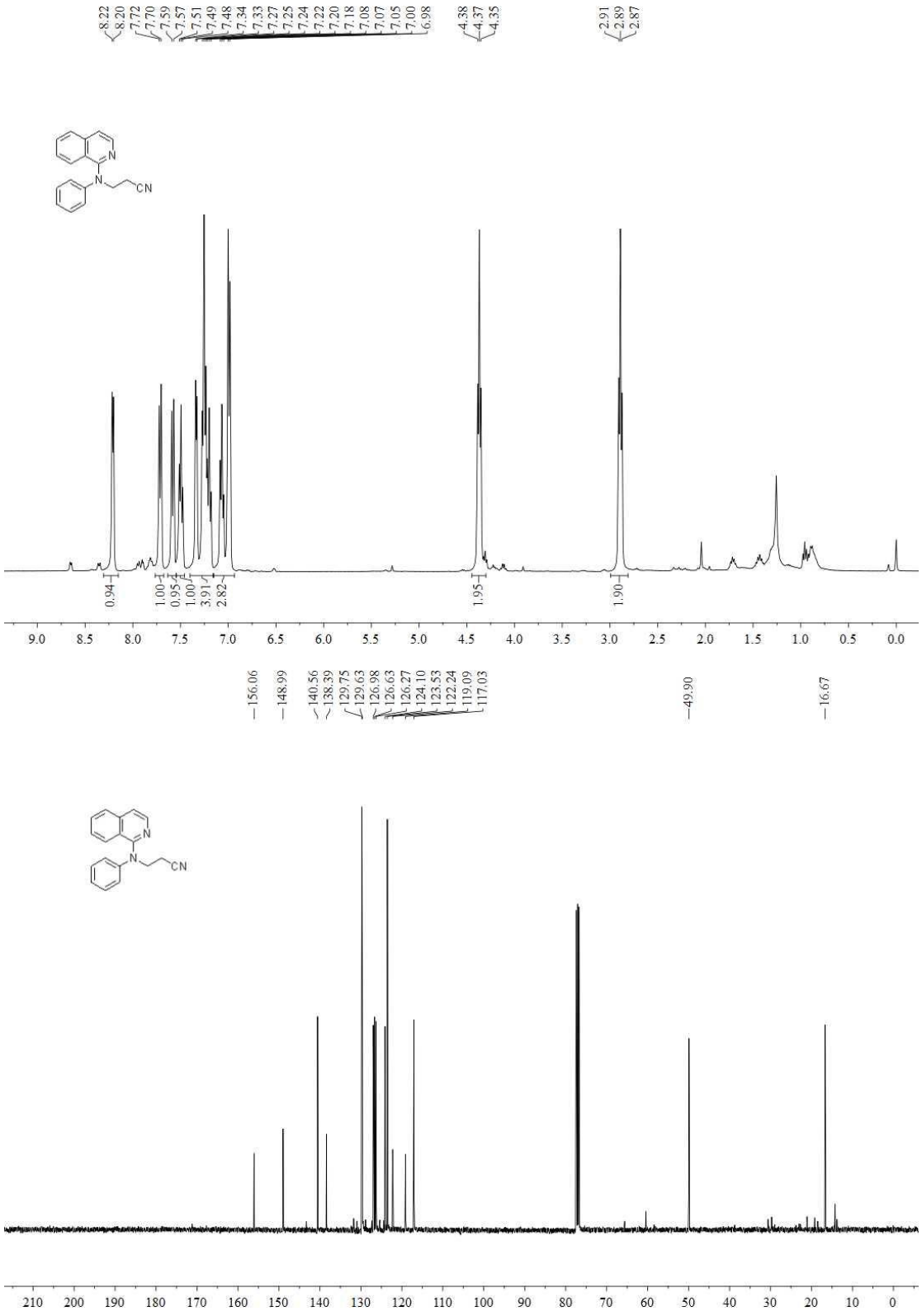
***N*-benzyl-*N*-phenylisoquinolin-1-amine (26c)**



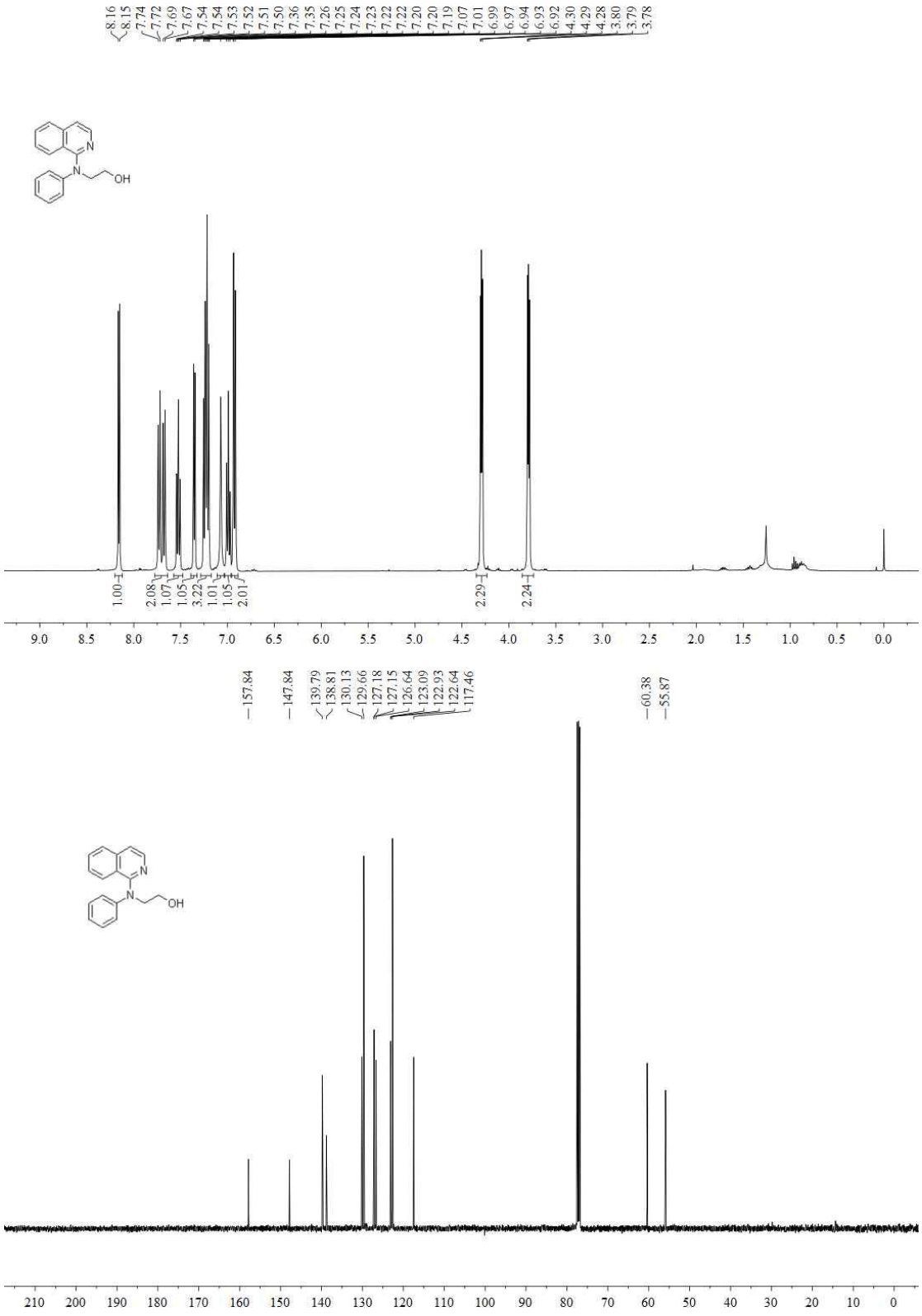
***N*,*N*-diphenylisoquinolin-1-amine (27c)**



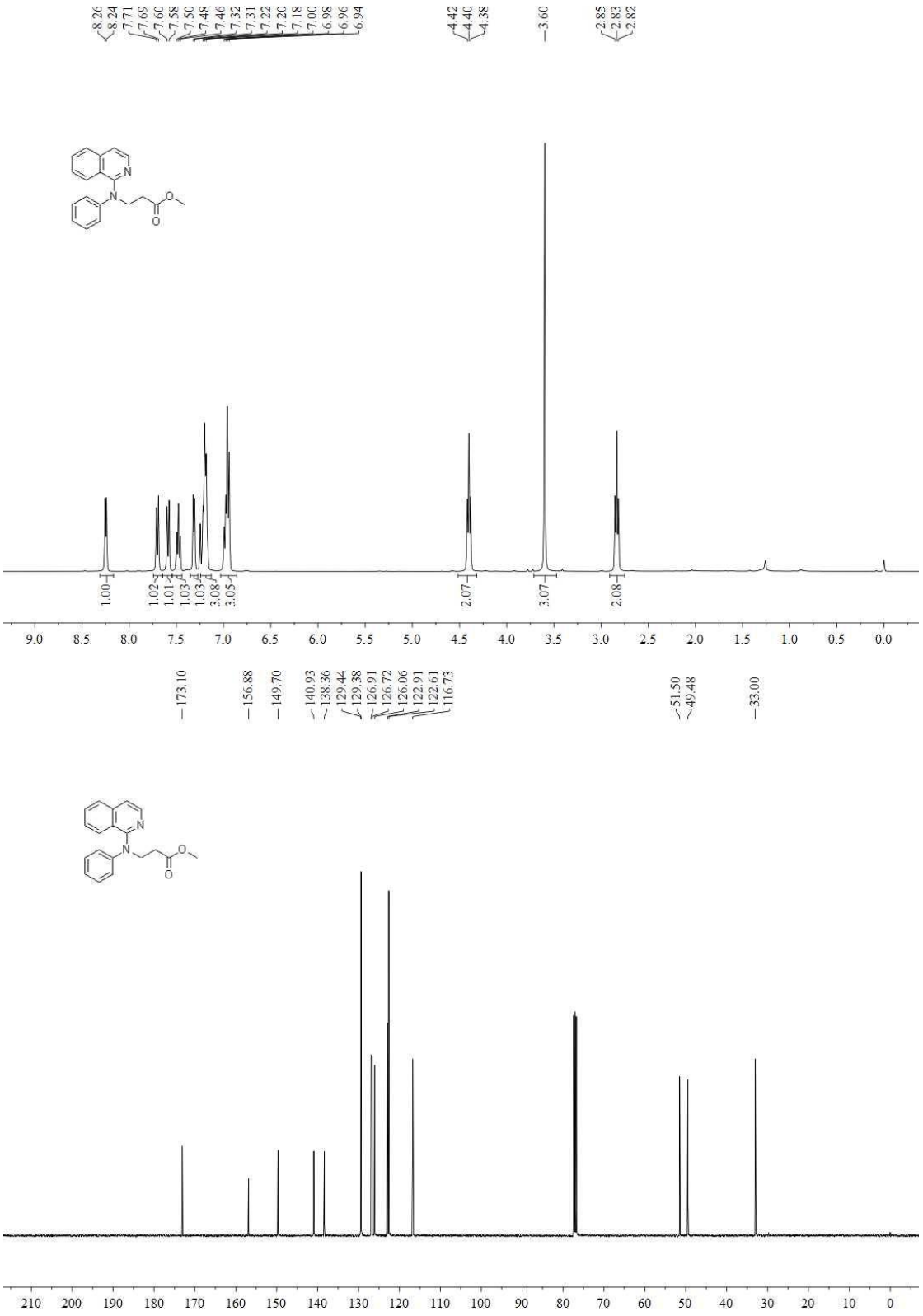
3-(isoquinolin-1-yl(phenyl)amino)propanenitrile (28c)



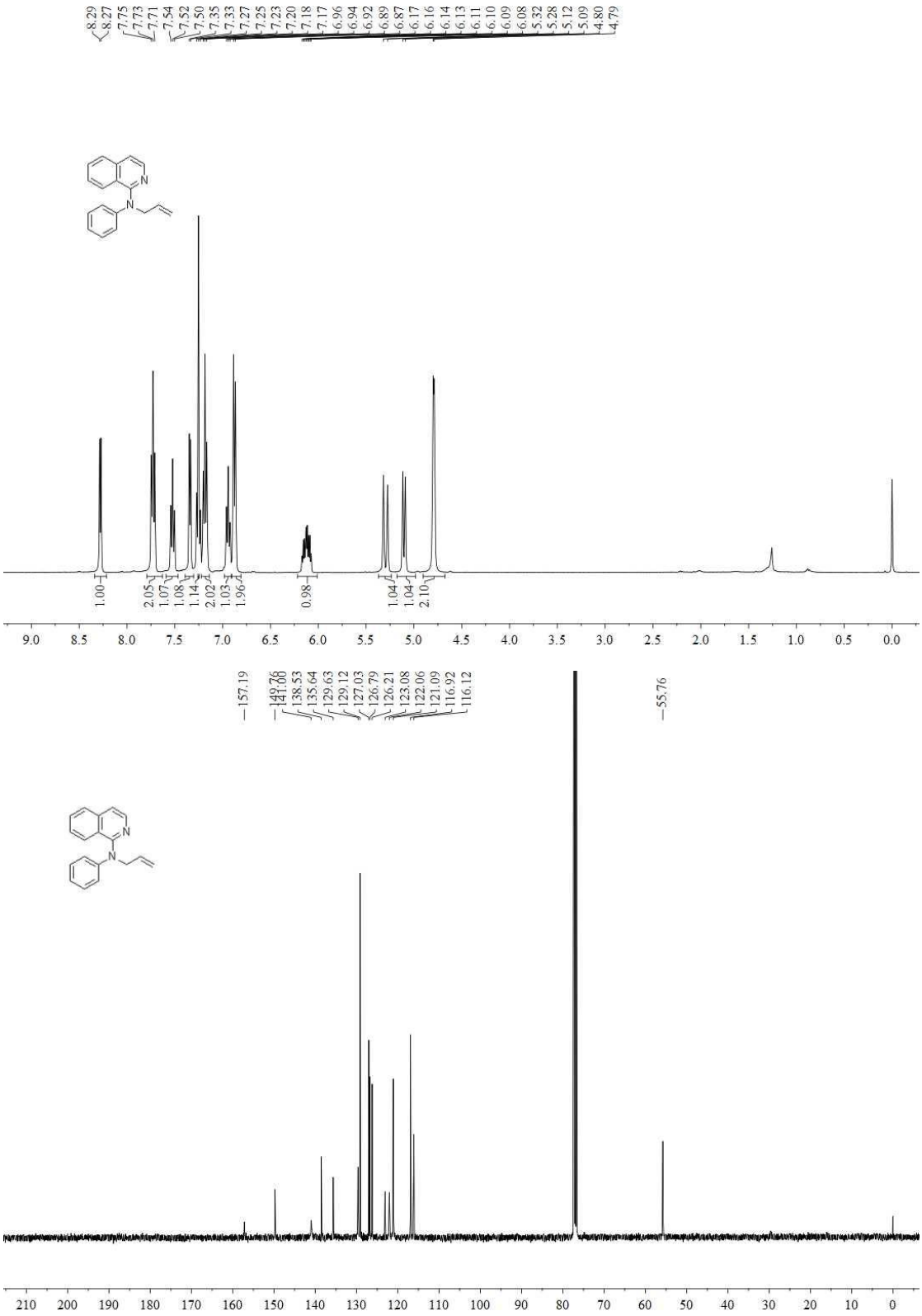
2-(isoquinolin-1-yl(phenyl)amino)ethanol (29c)



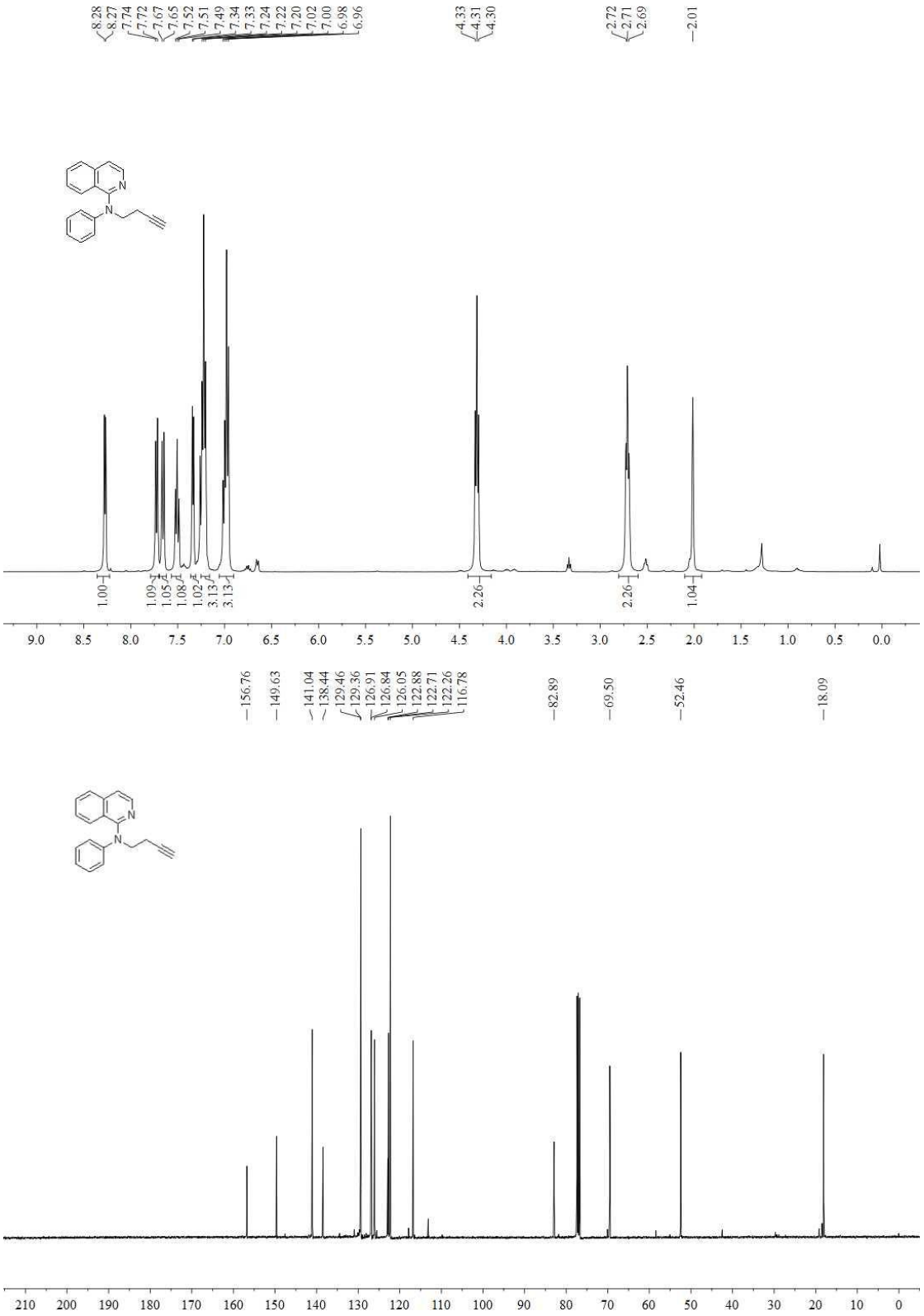
Methyl 3-(isoquinolin-1-yl(phenyl)amino)propanoate (30c)



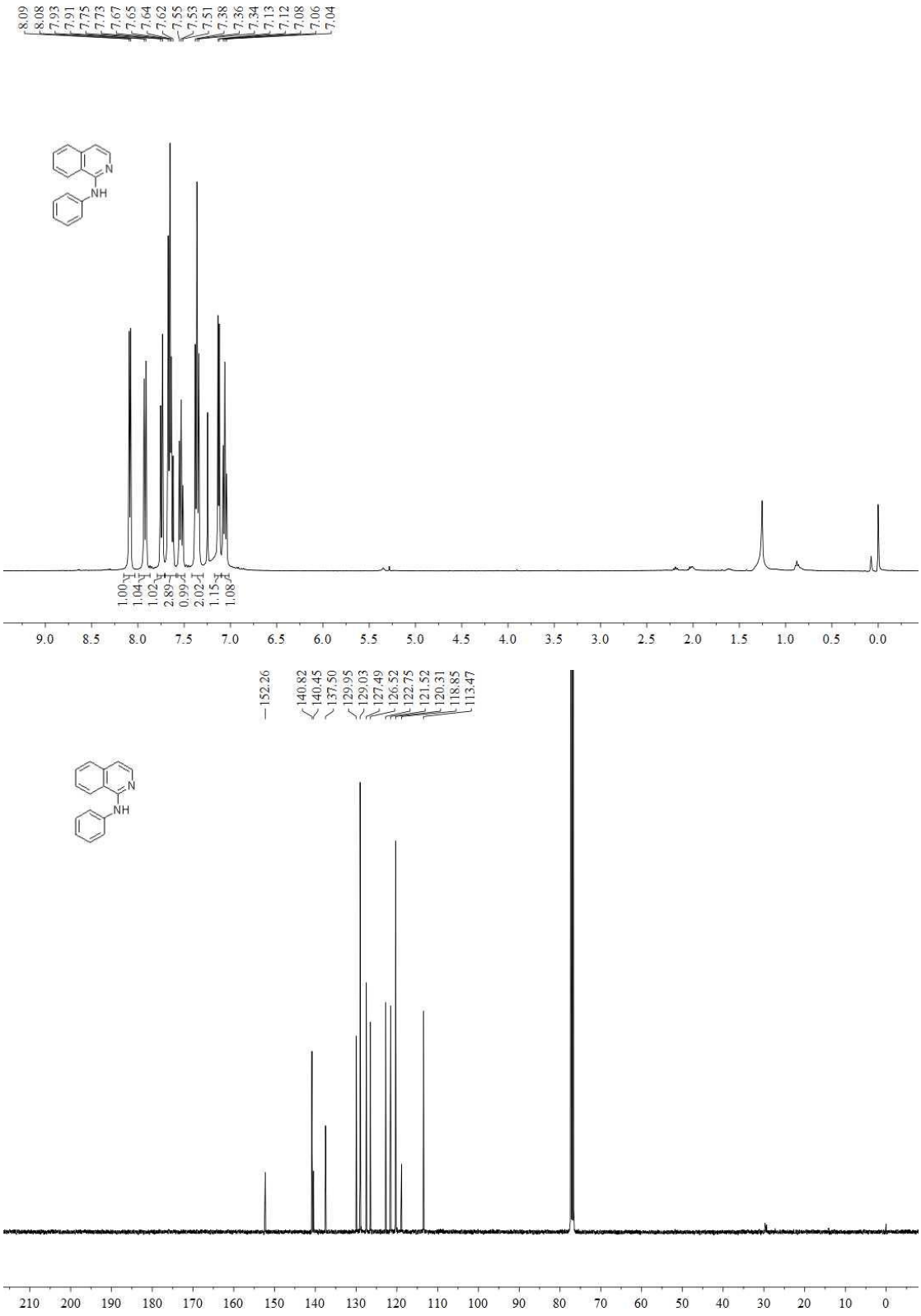
N-allyl-*N*-phenylisoquinolin-1-amine (31c)



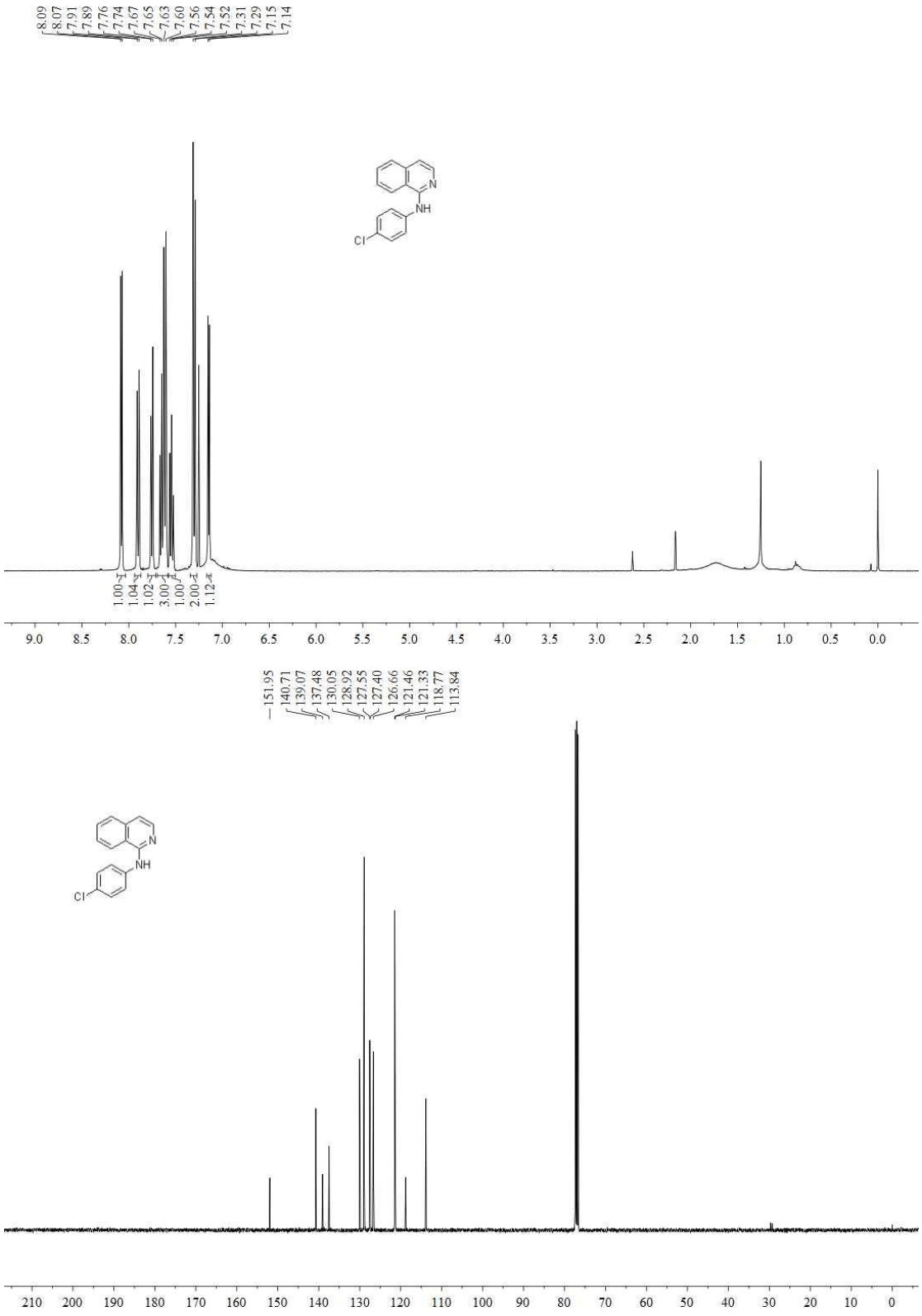
N-(but-3-yn-1-yl)-*N*-phenylisoquinolin-1-amine (32c)



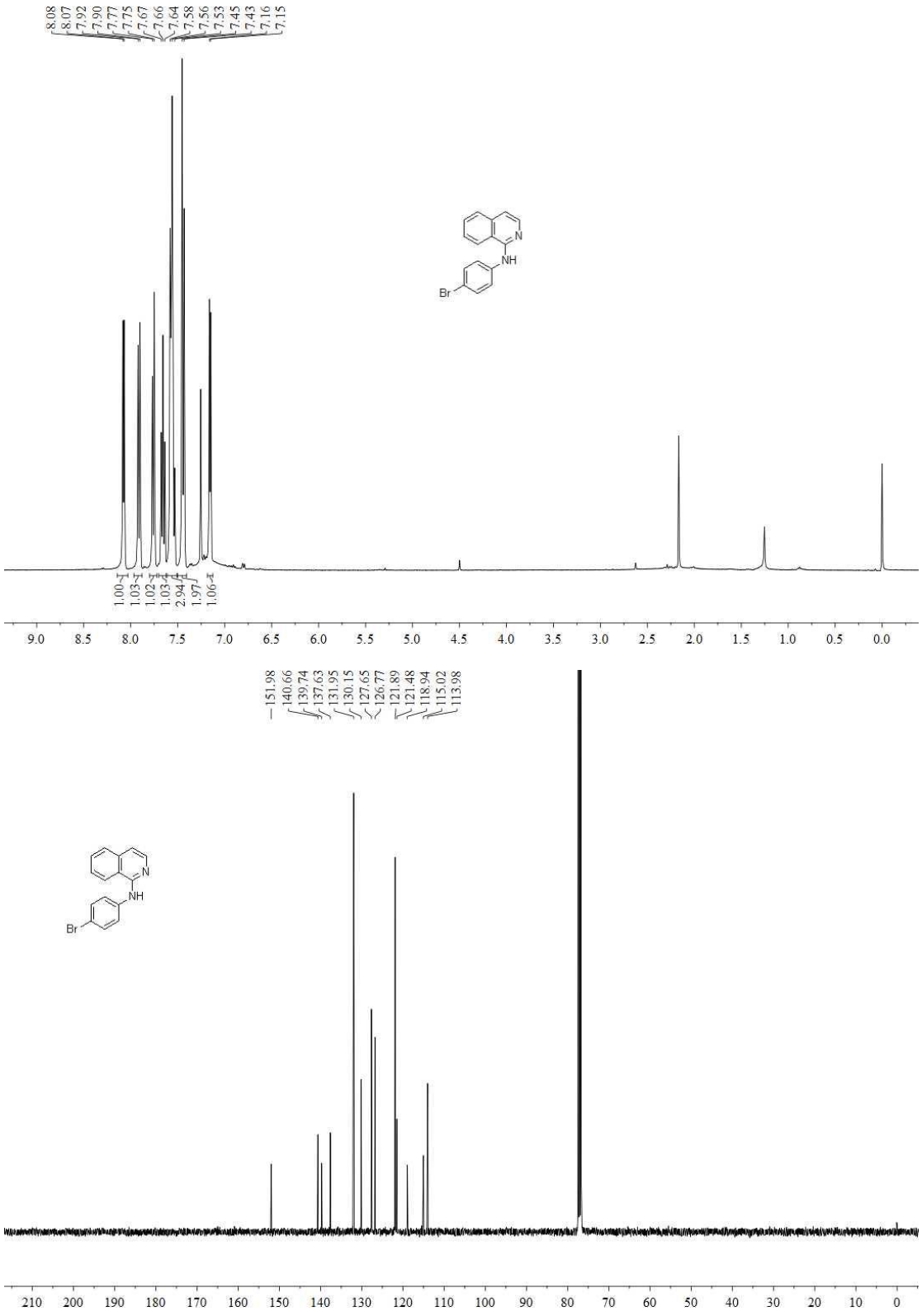
N-phenylisoquinolin-1-amine (33c)



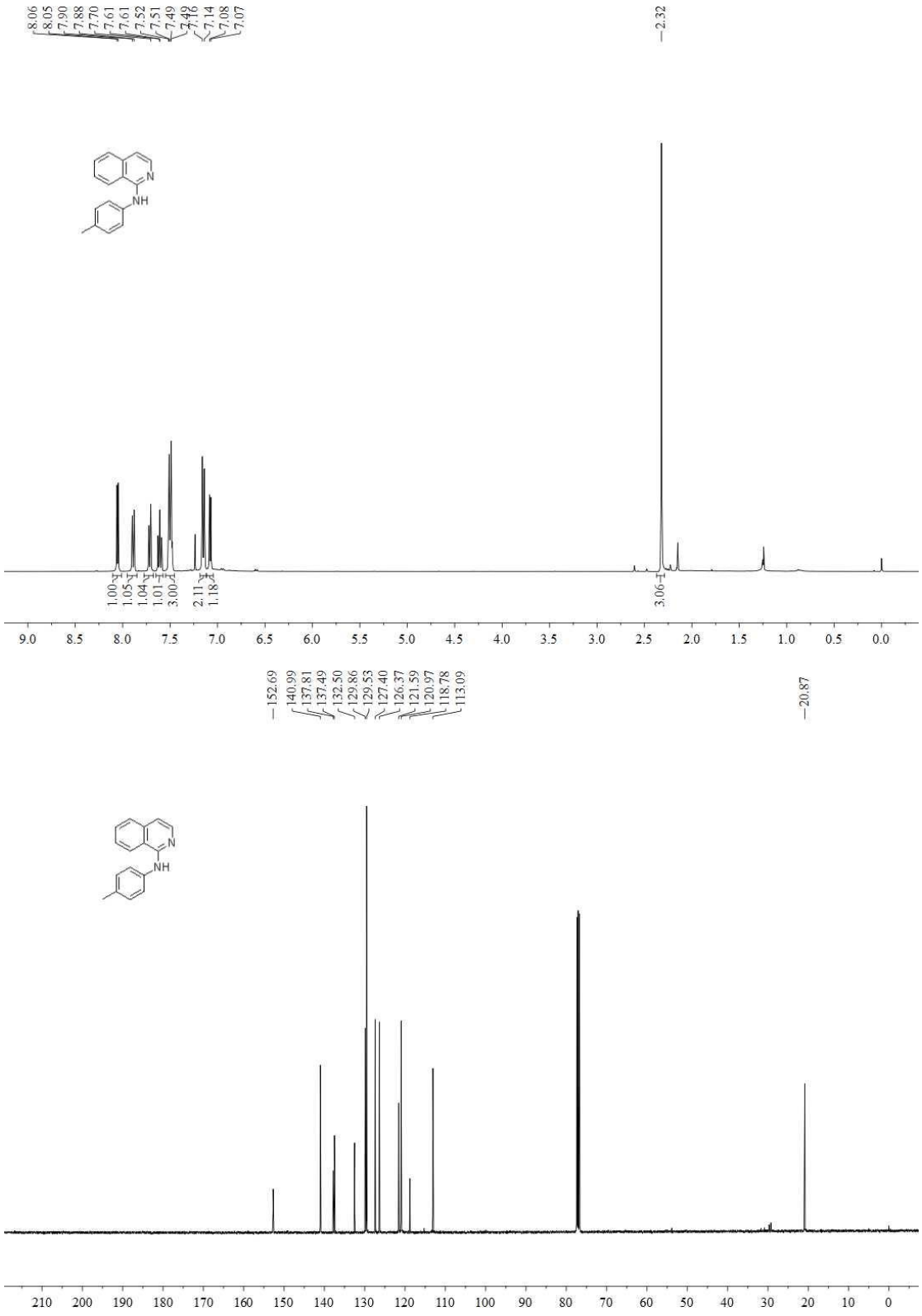
***N*-(4-chlorophenyl)isoquinolin-1-amine (34c)**



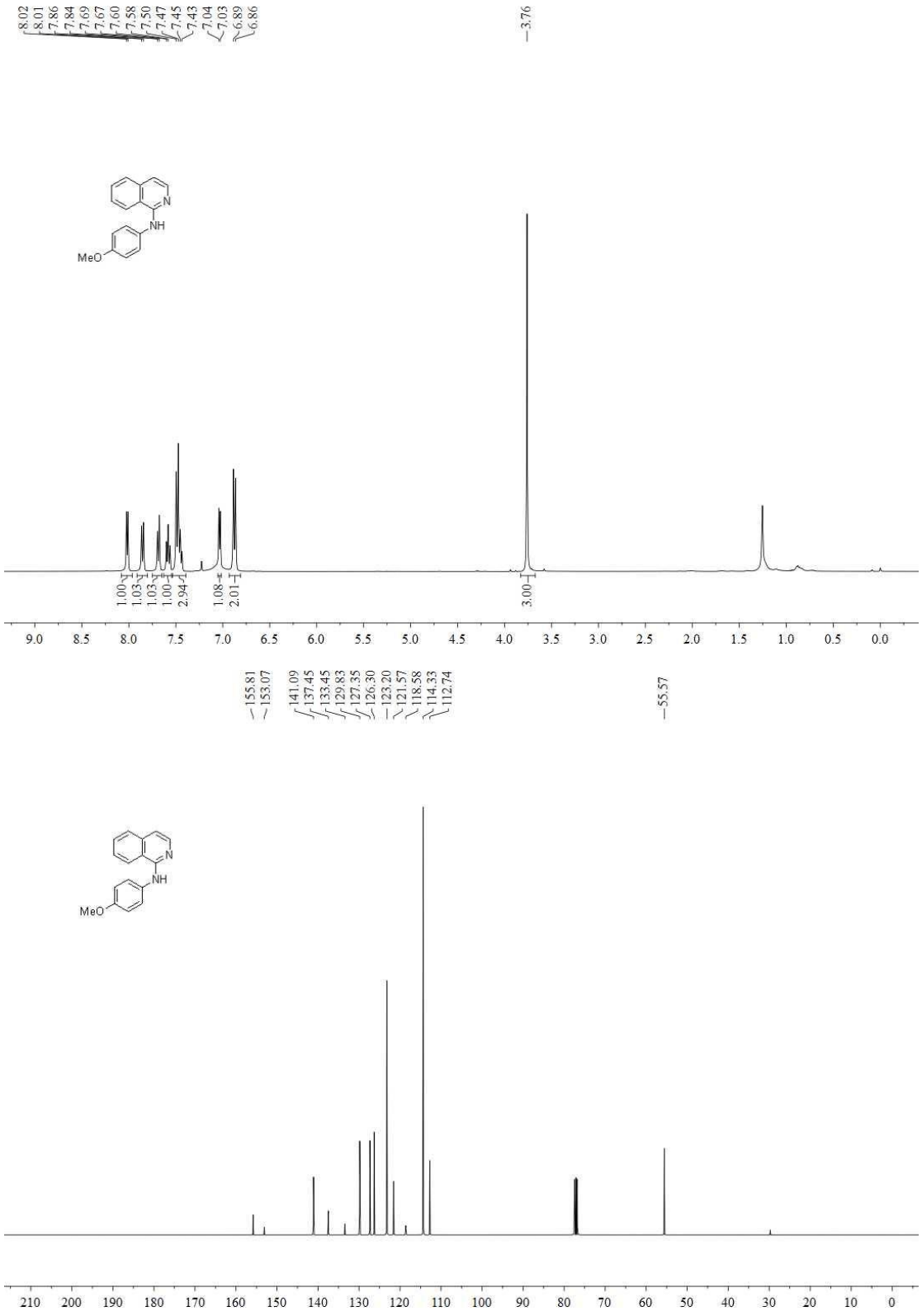
***N*-(4-bromophenyl)isoquinolin-1-amine (35c)**



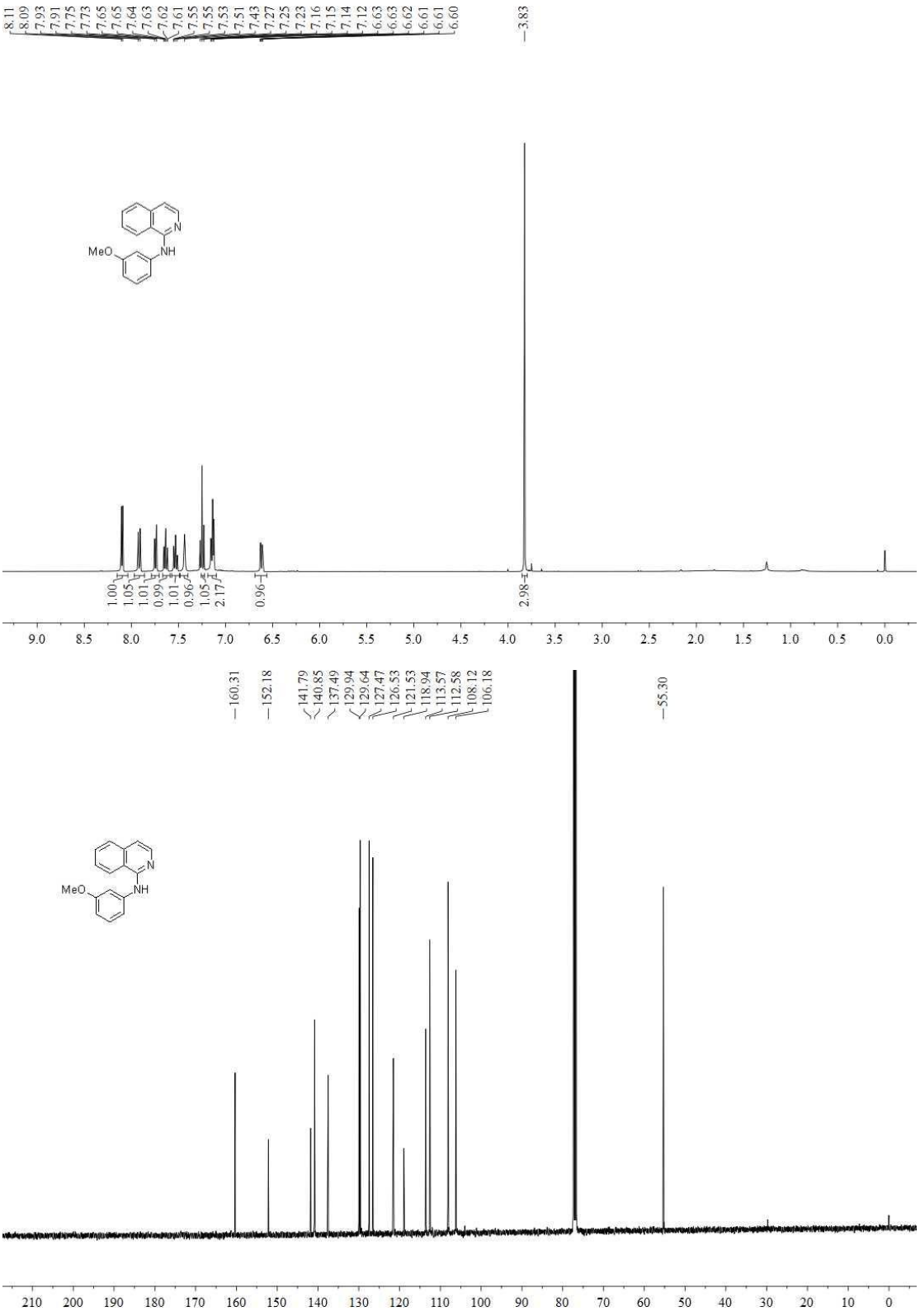
***N*-(*p*-tolyl)isoquinolin-1-amine (36c)**



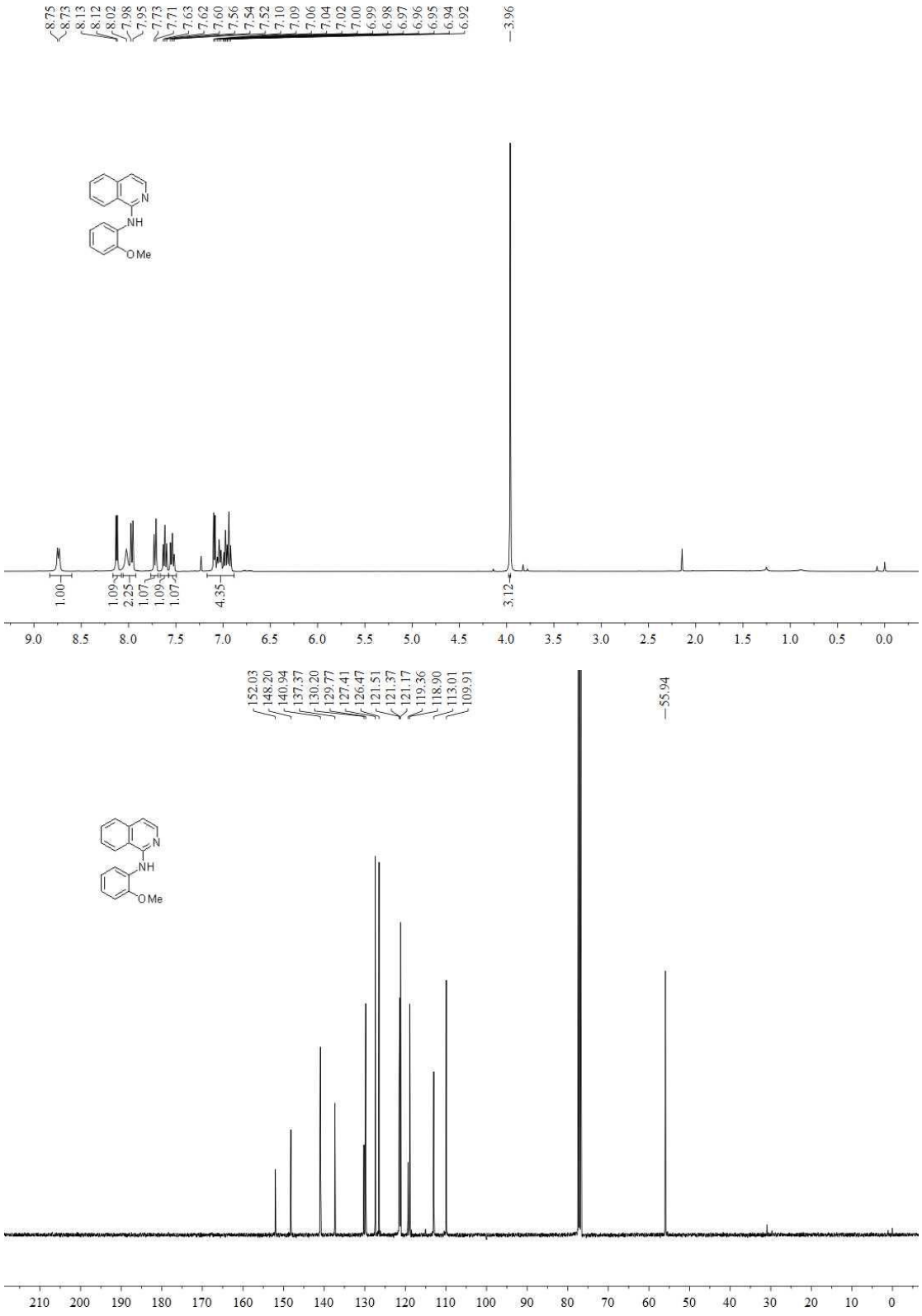
***N*-(4-methoxyphenyl)isoquinolin-1-amine (37c)**



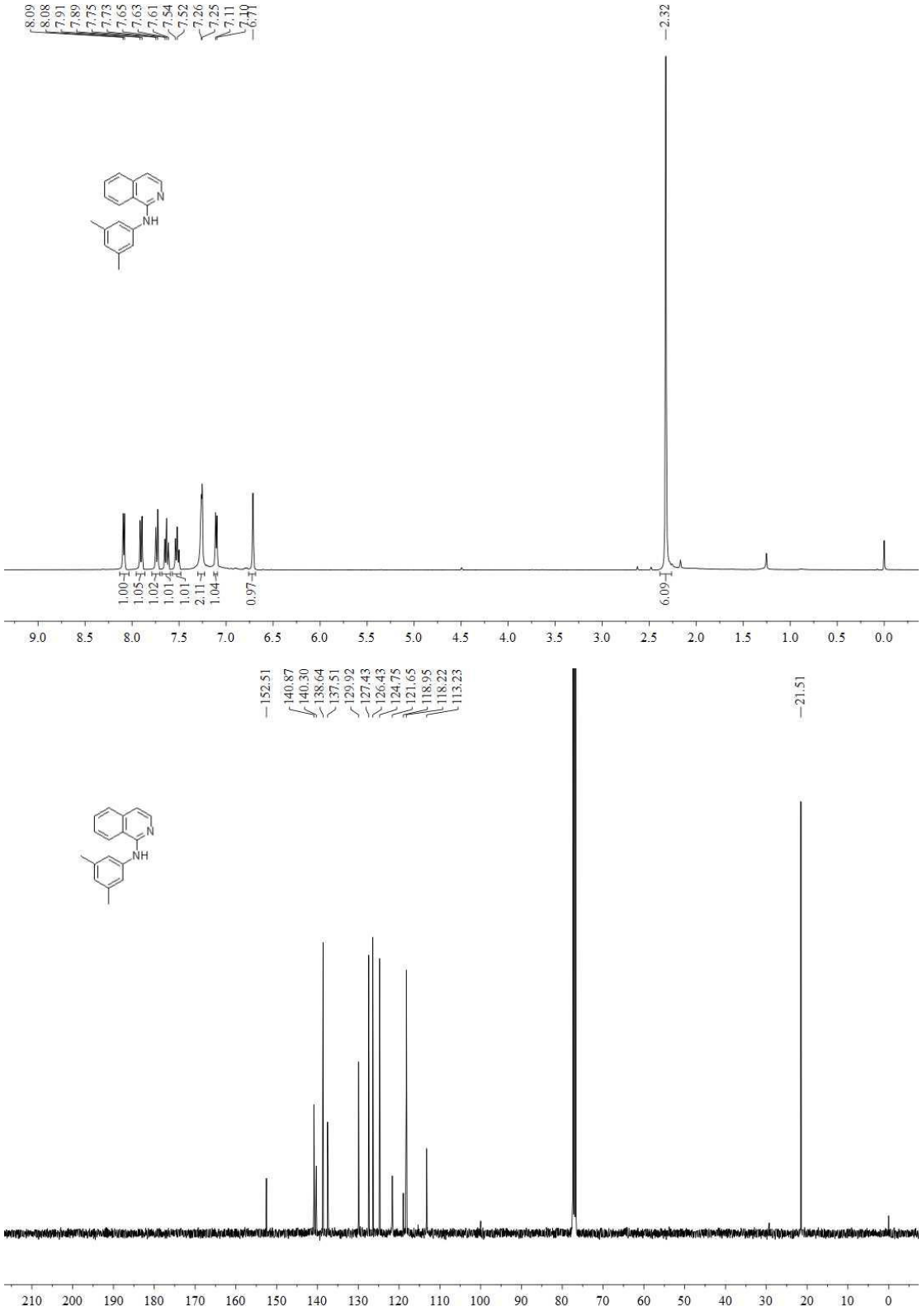
N-(3-methoxyphenyl)isoquinolin-1-amine (38c)



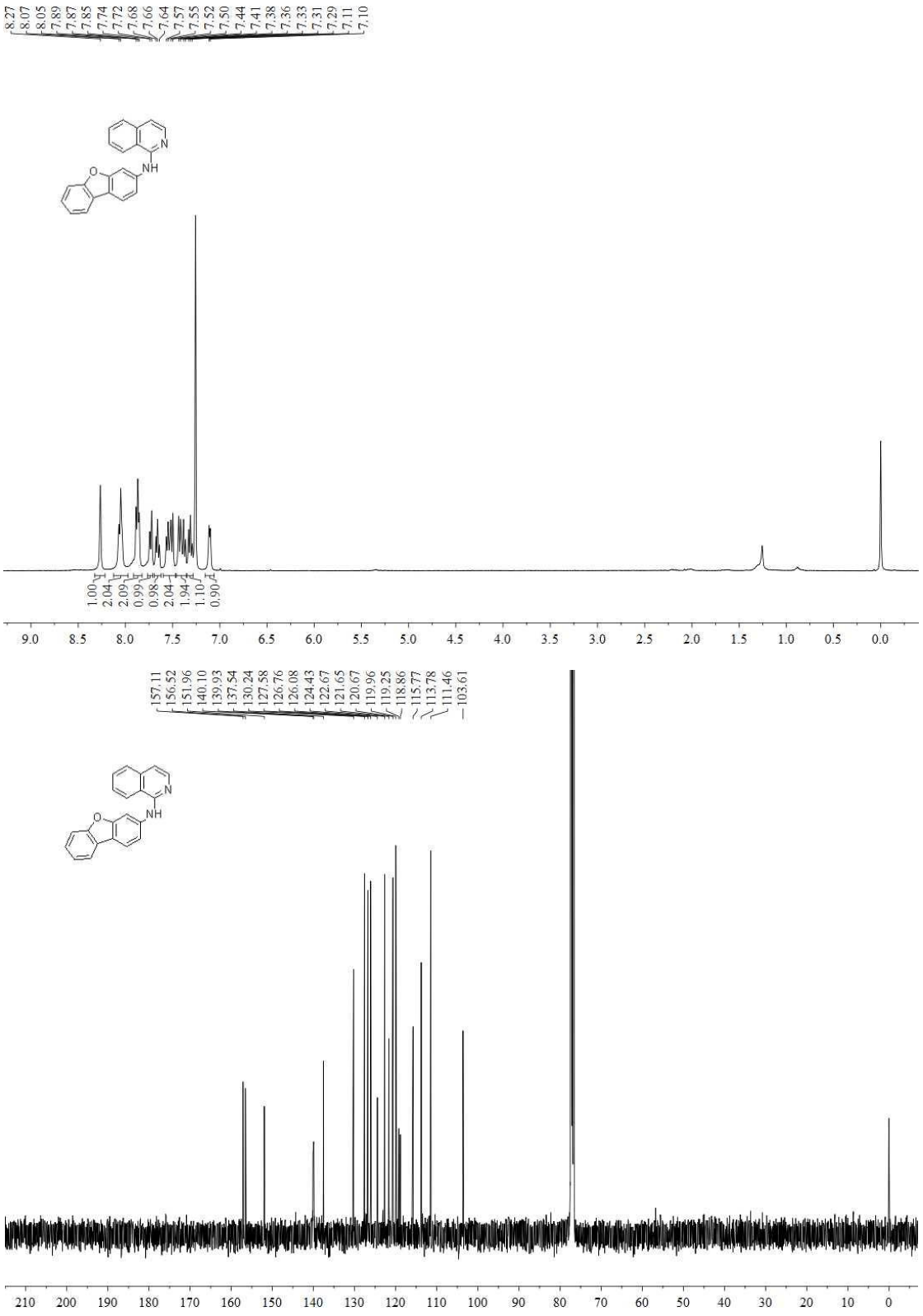
N-(2-methoxyphenyl)isoquinolin-1-amine (39c)



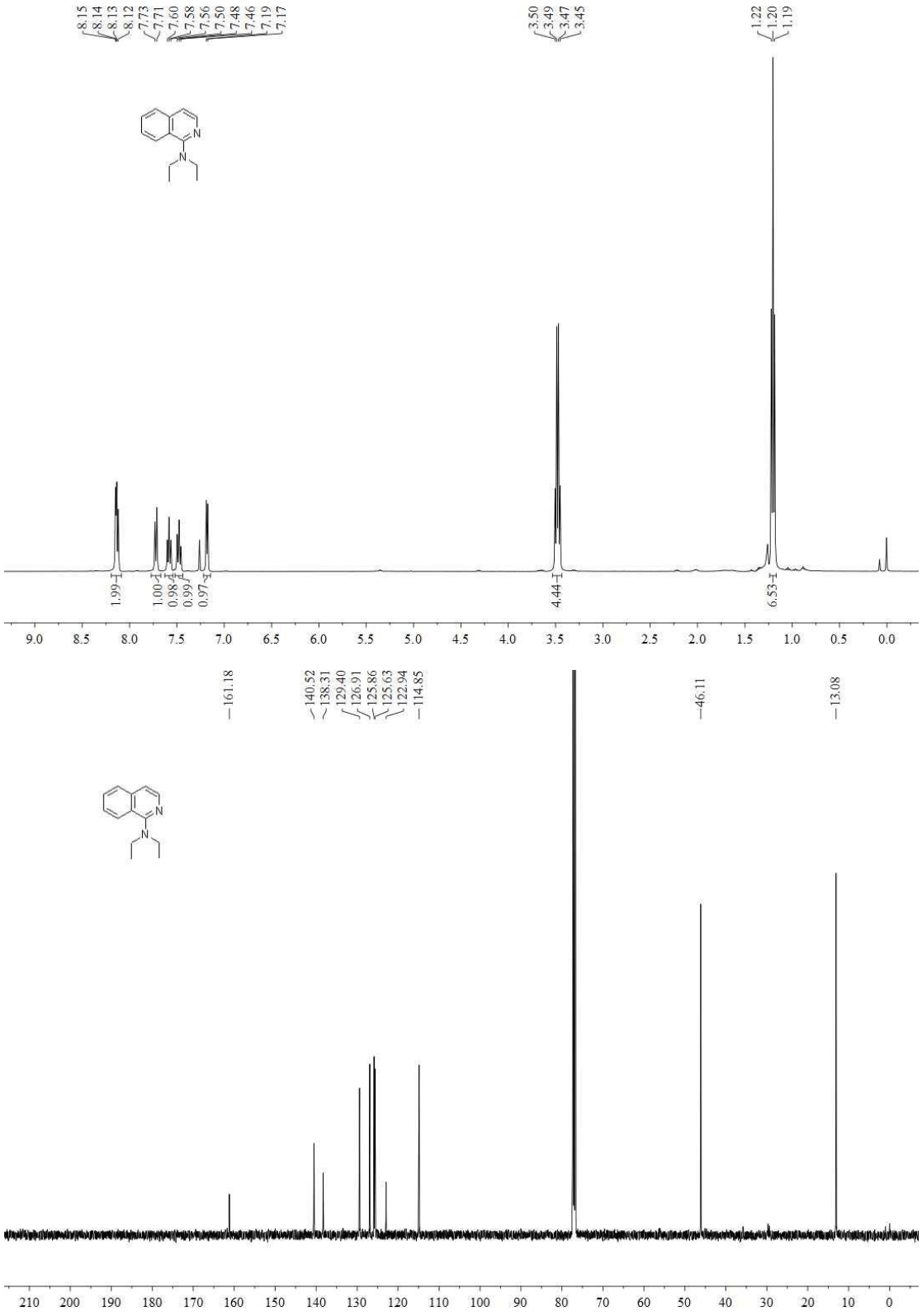
***N*-(3,5-dimethylphenyl)isoquinolin-1-amine (40c)**



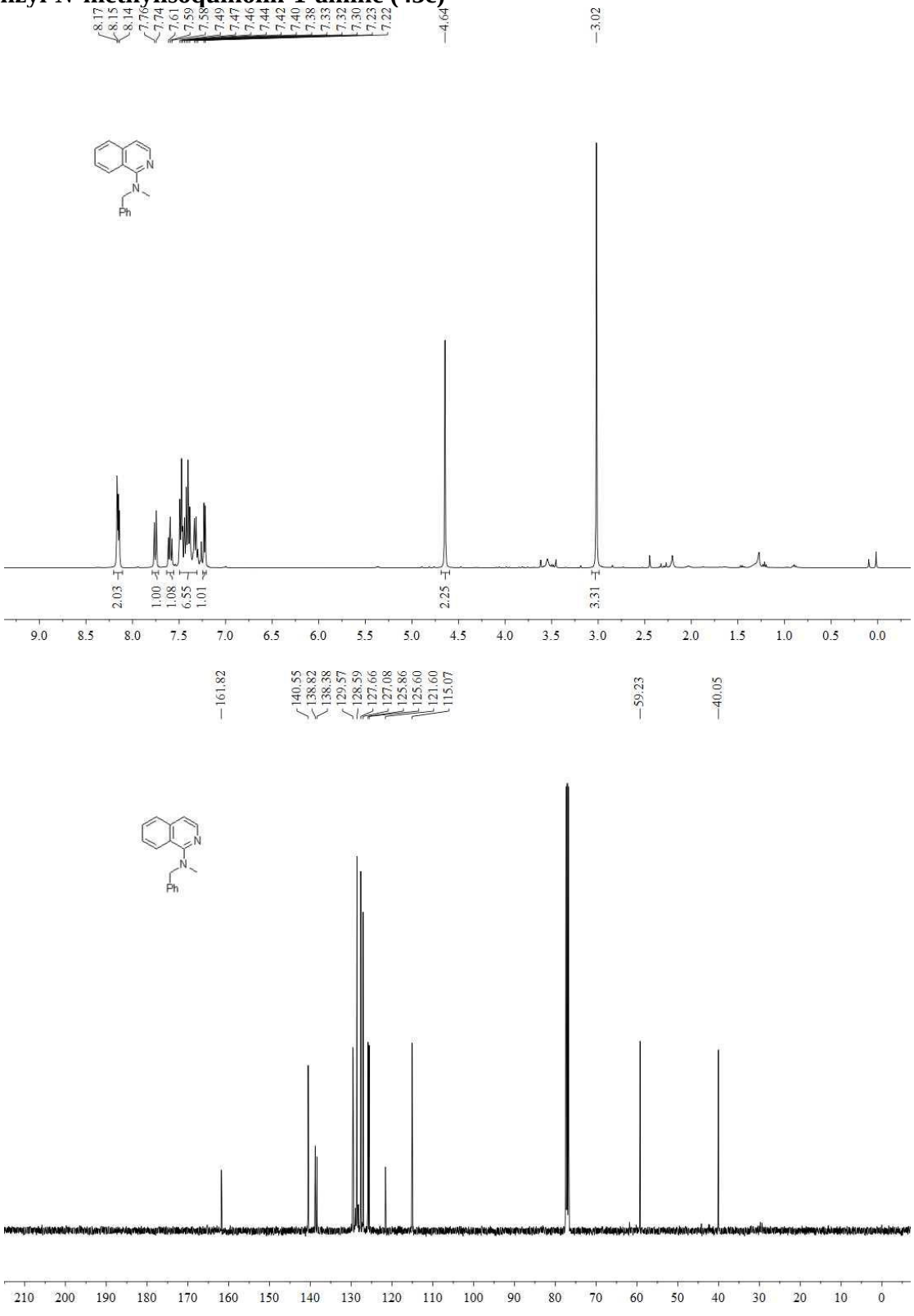
***N*-(dibenzo[b,d]furan-3-yl)isoquinolin-1-amine (41c)**



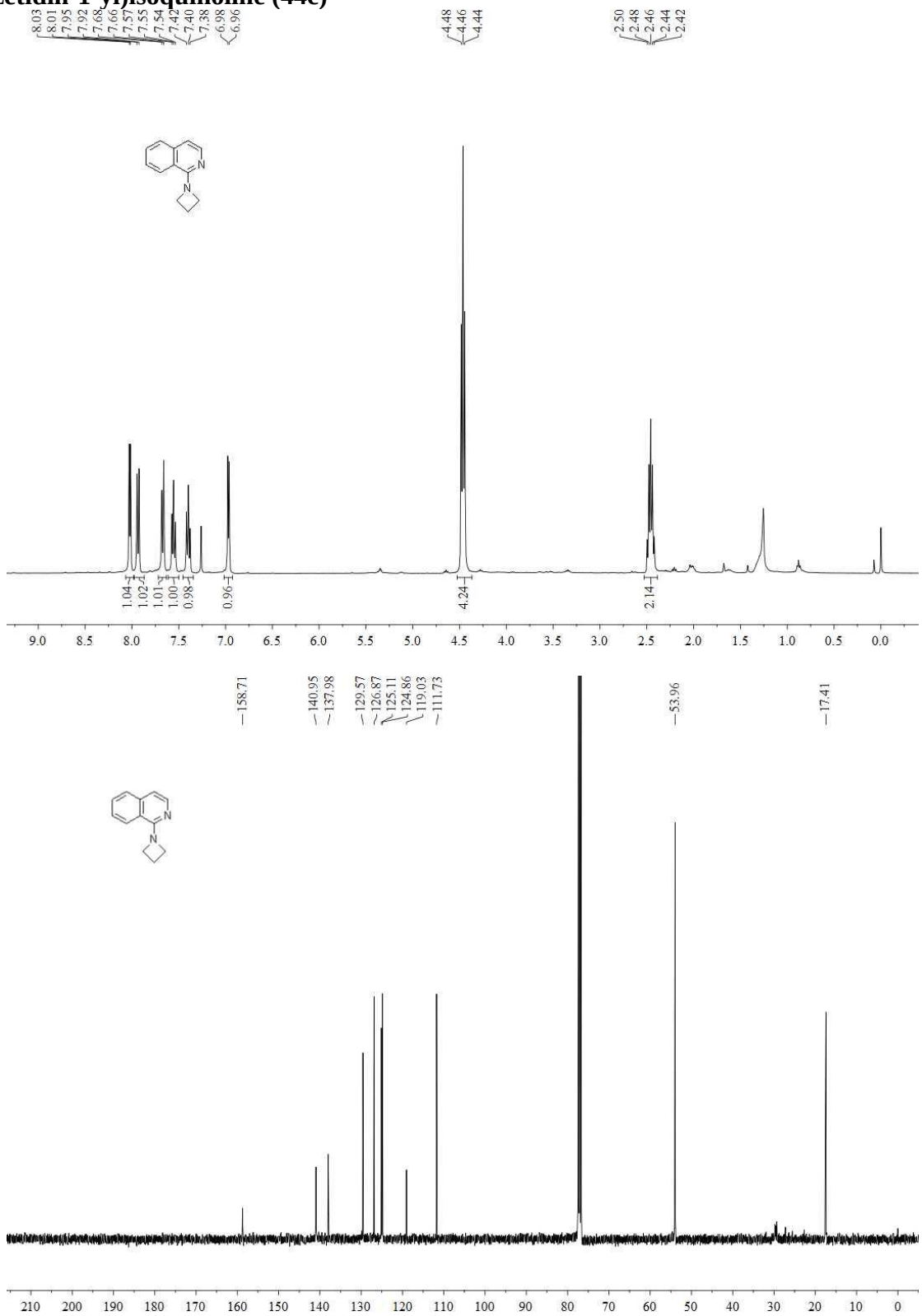
***N,N*-diethylisoquinolin-1-amine (42c)**



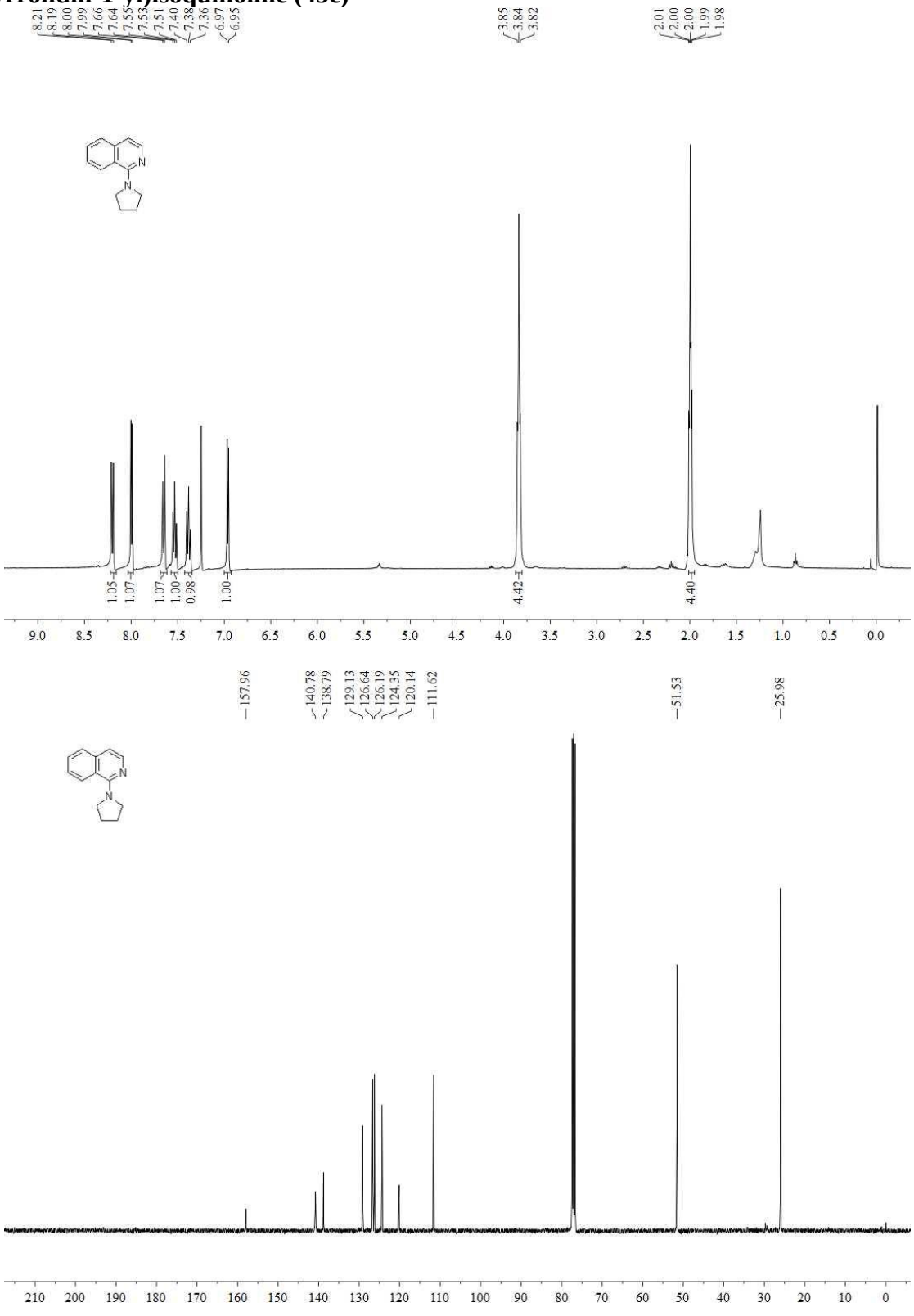
***N*-benzyl-*N*-methylisoquinolin-1-amine (43c)**



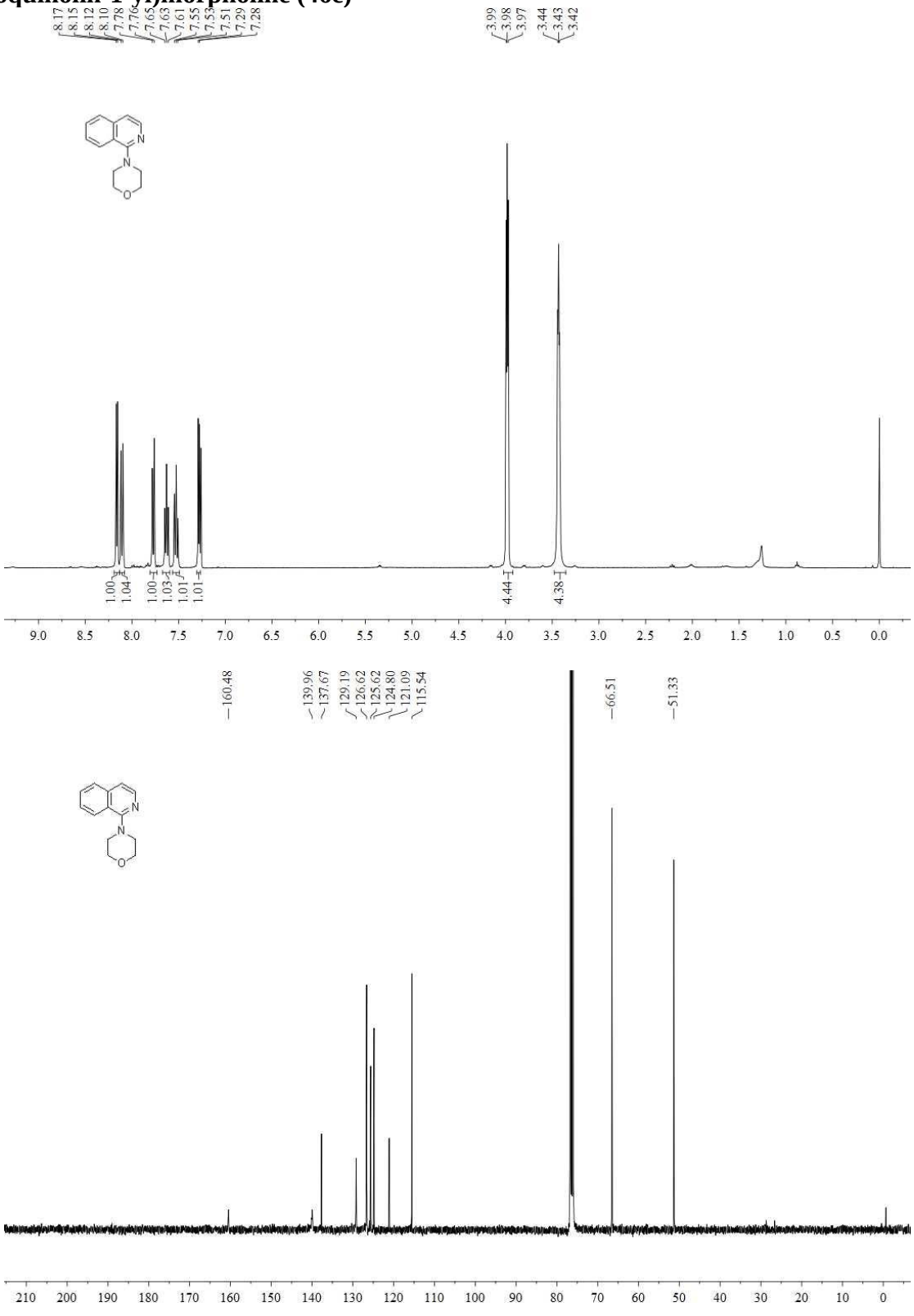
1-(azetidin-1-yl)isoquinoline (44c)



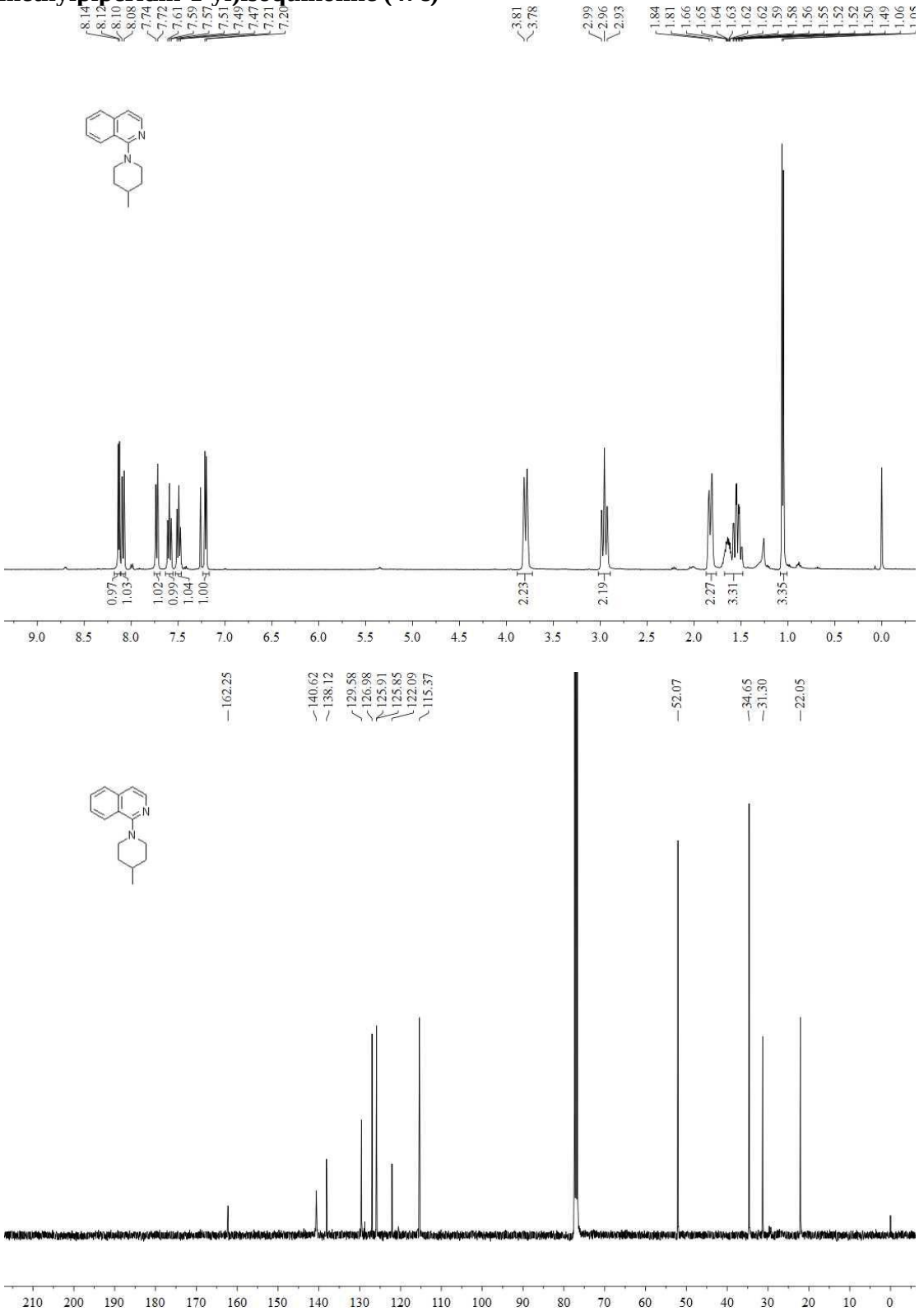
1-(pyrrolidin-1-yl)isoquinoline (45c)



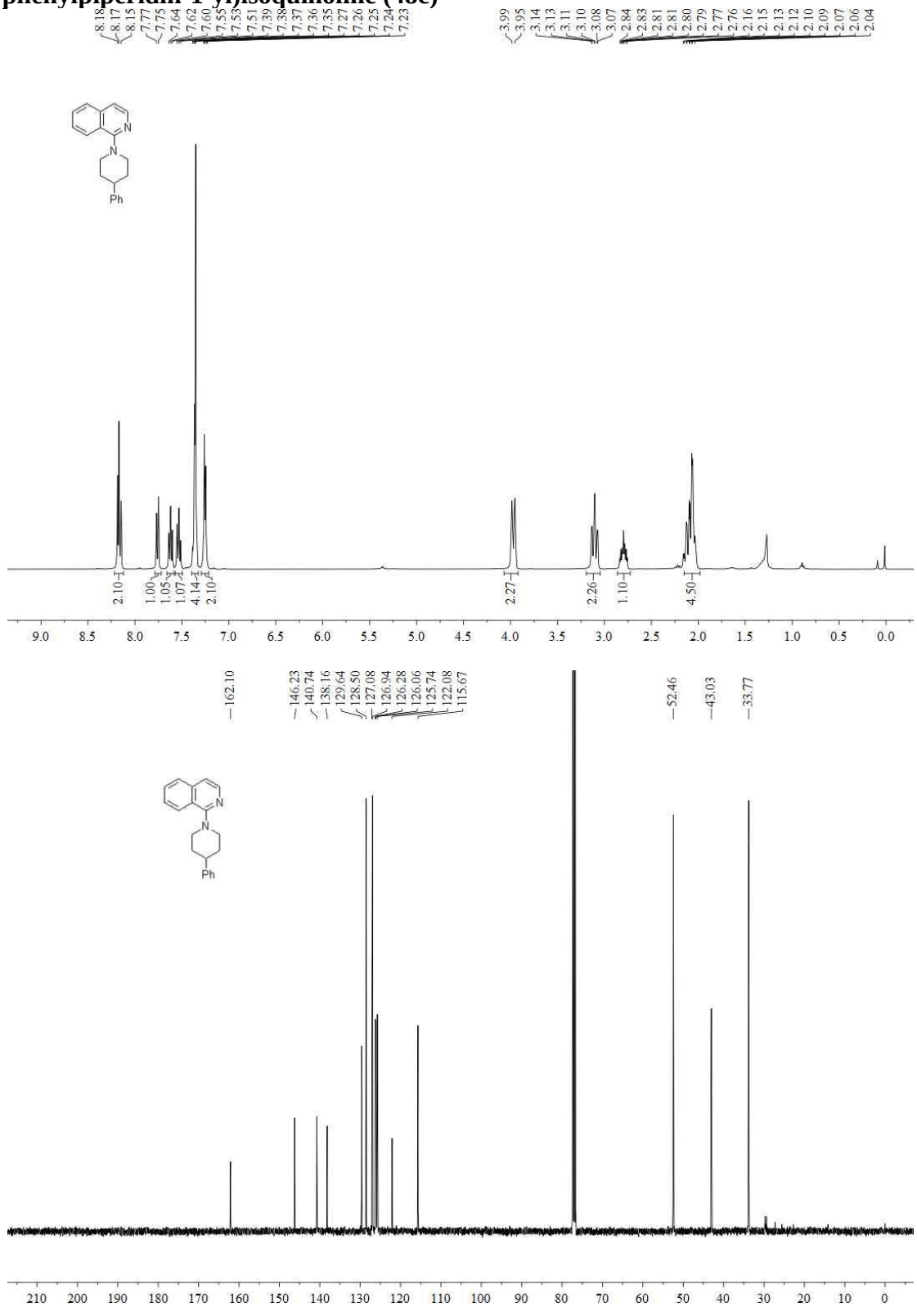
4-(isoquinolin-1-yl)morpholine (46c)



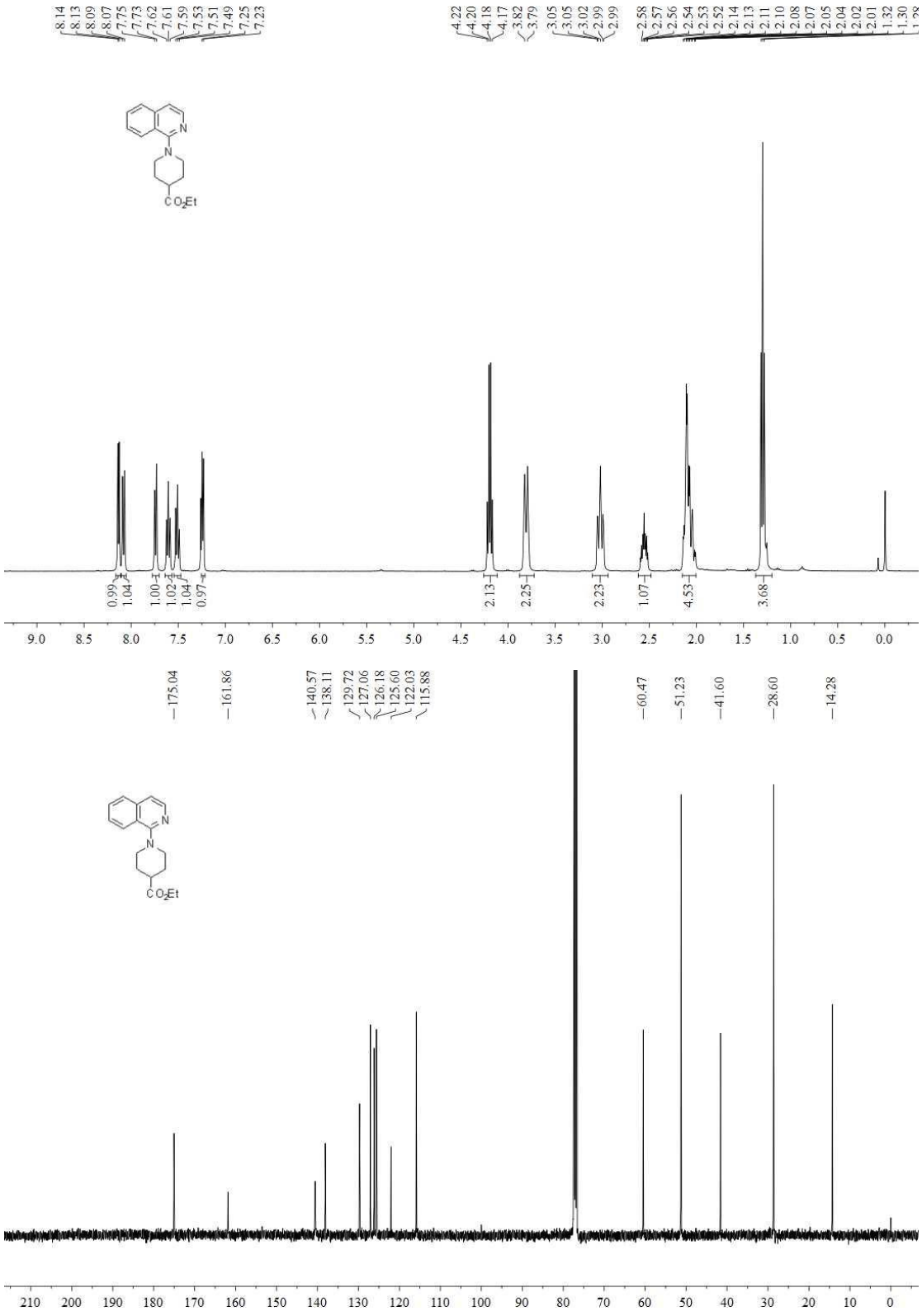
1-(4-methylpiperidin-1-yl)isoquinoline (47c)



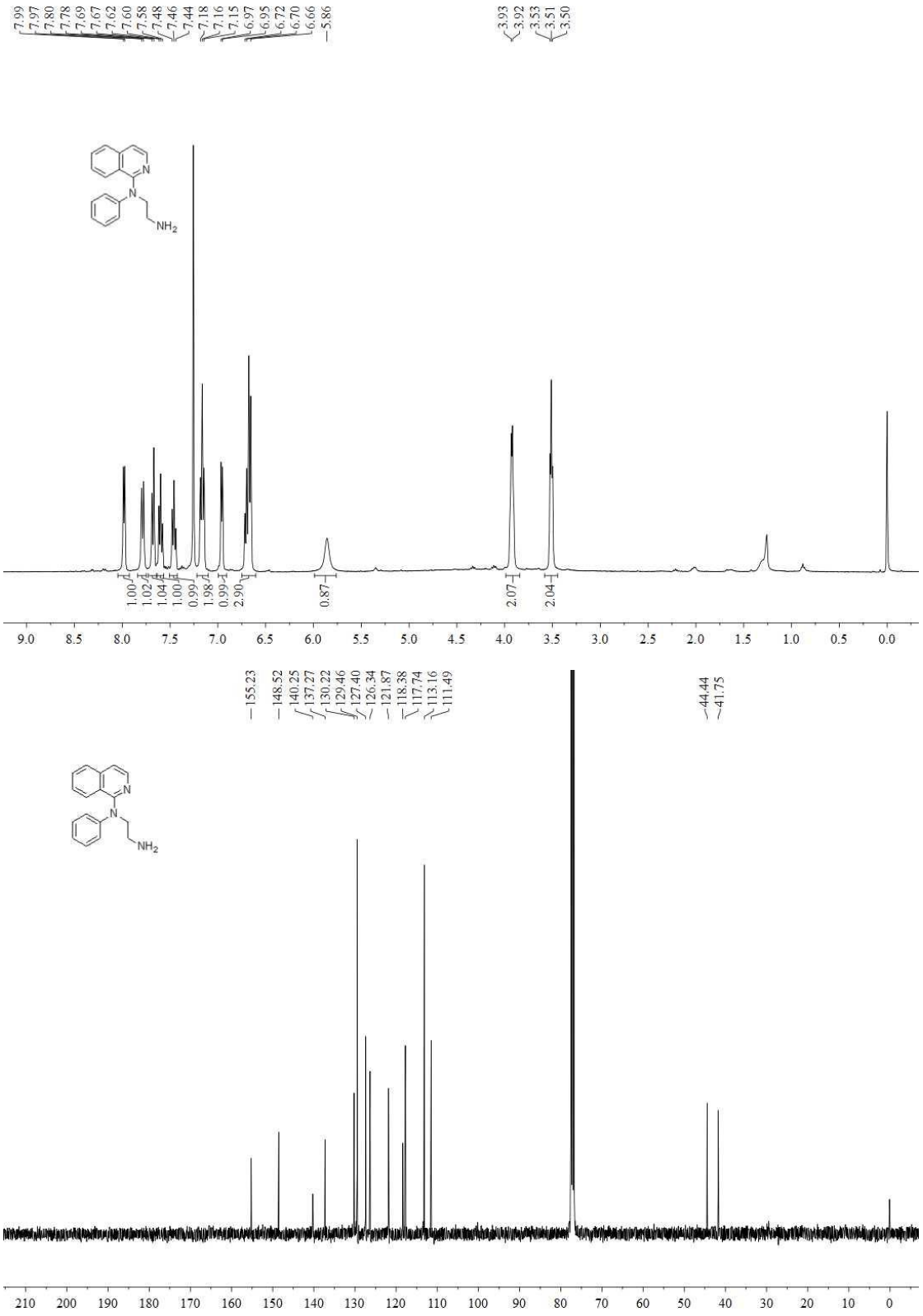
1-(4-phenylpiperidin-1-yl)isoquinoline (48c)



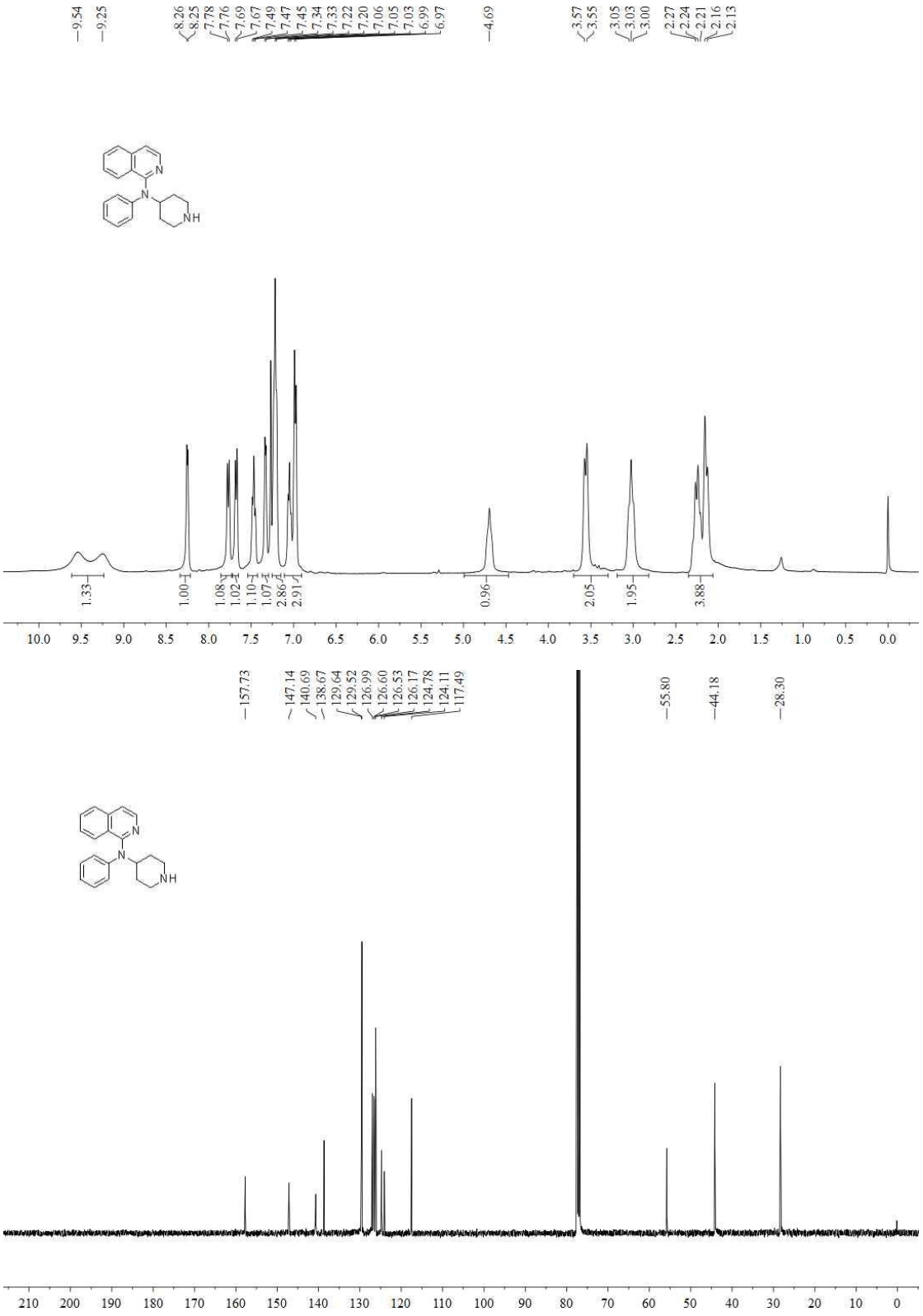
Ethyl 1-(isoquinolin-1-yl)piperidine-4-carboxylate (49c)



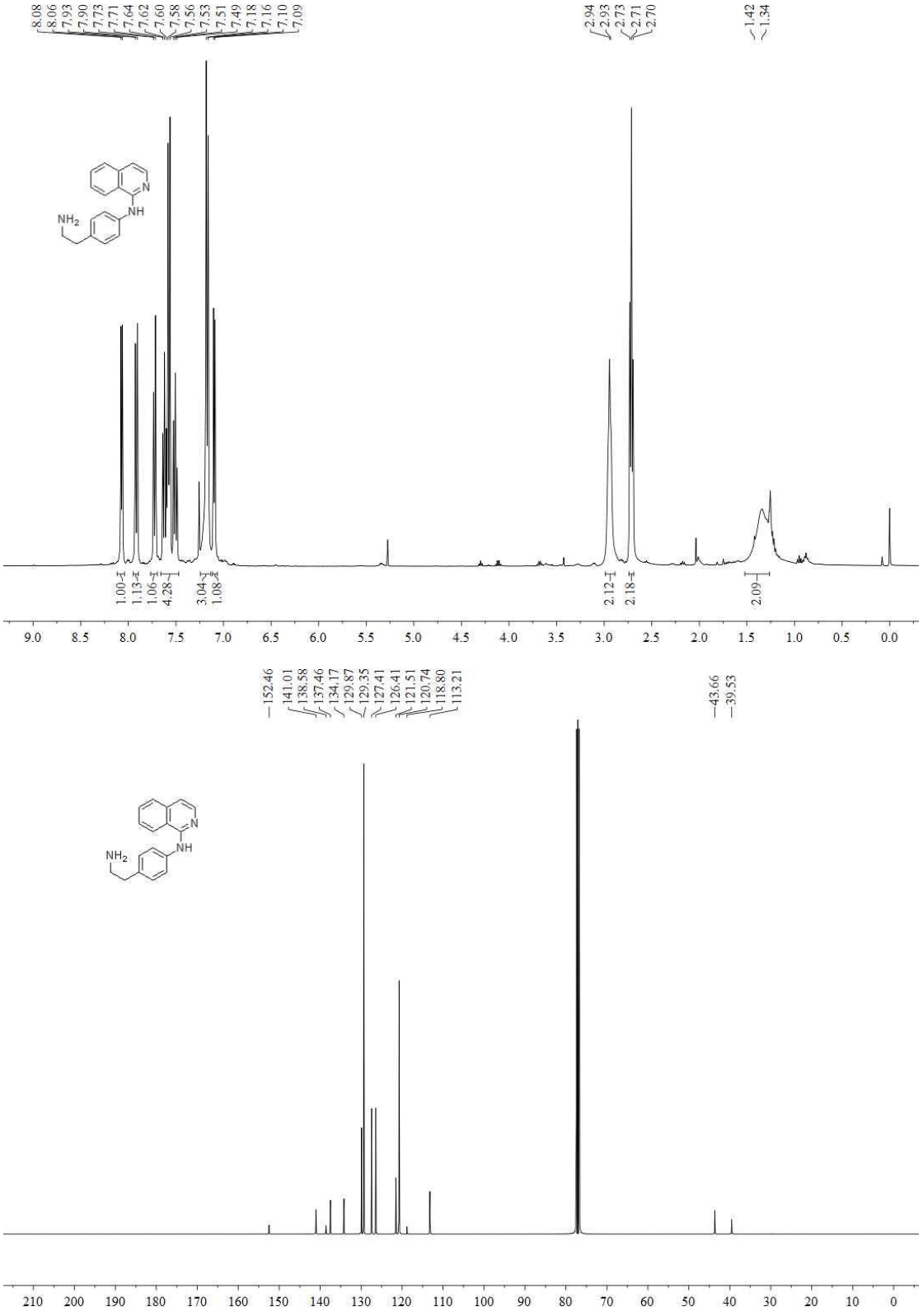
N^1-(isoquinolin-1-yl)-N^1-phenylethane-1,2-diamine (50c)



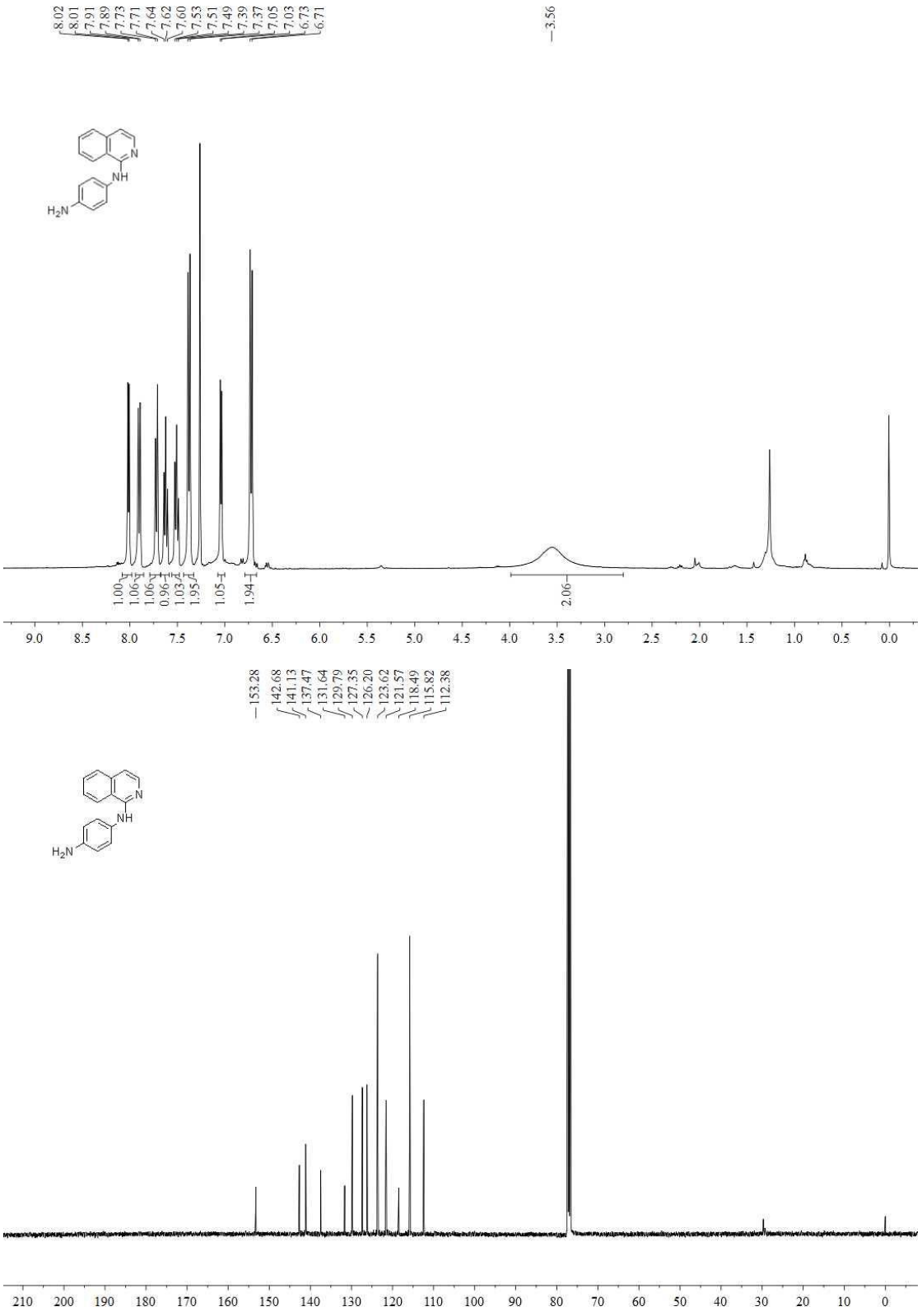
N-phenyl-*N*-(piperidin-4-yl)isoquinolin-1-amine (51c)



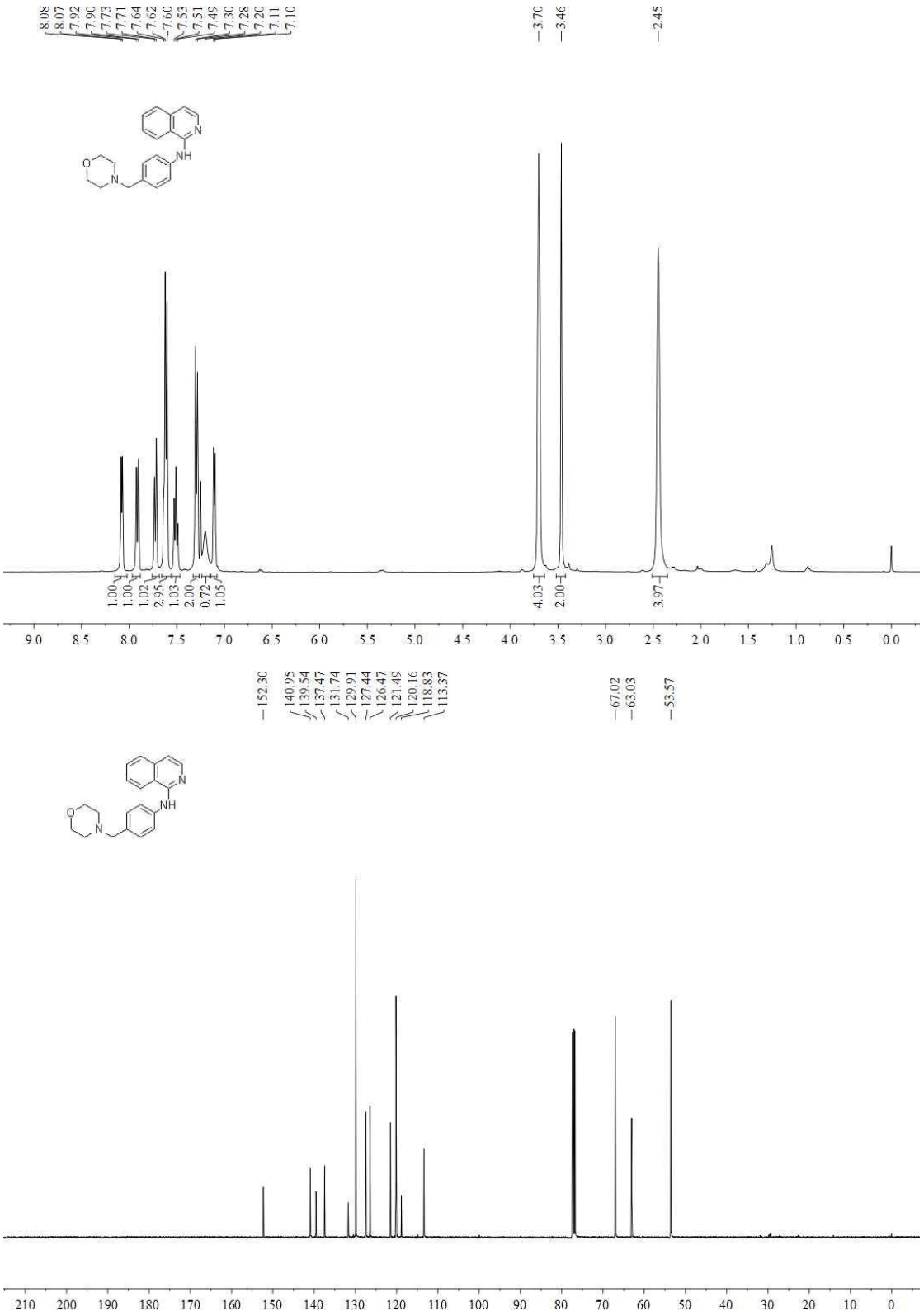
***N*-(4-(2-aminoethyl)phenyl)isoquinolin-1-amine (52c)**



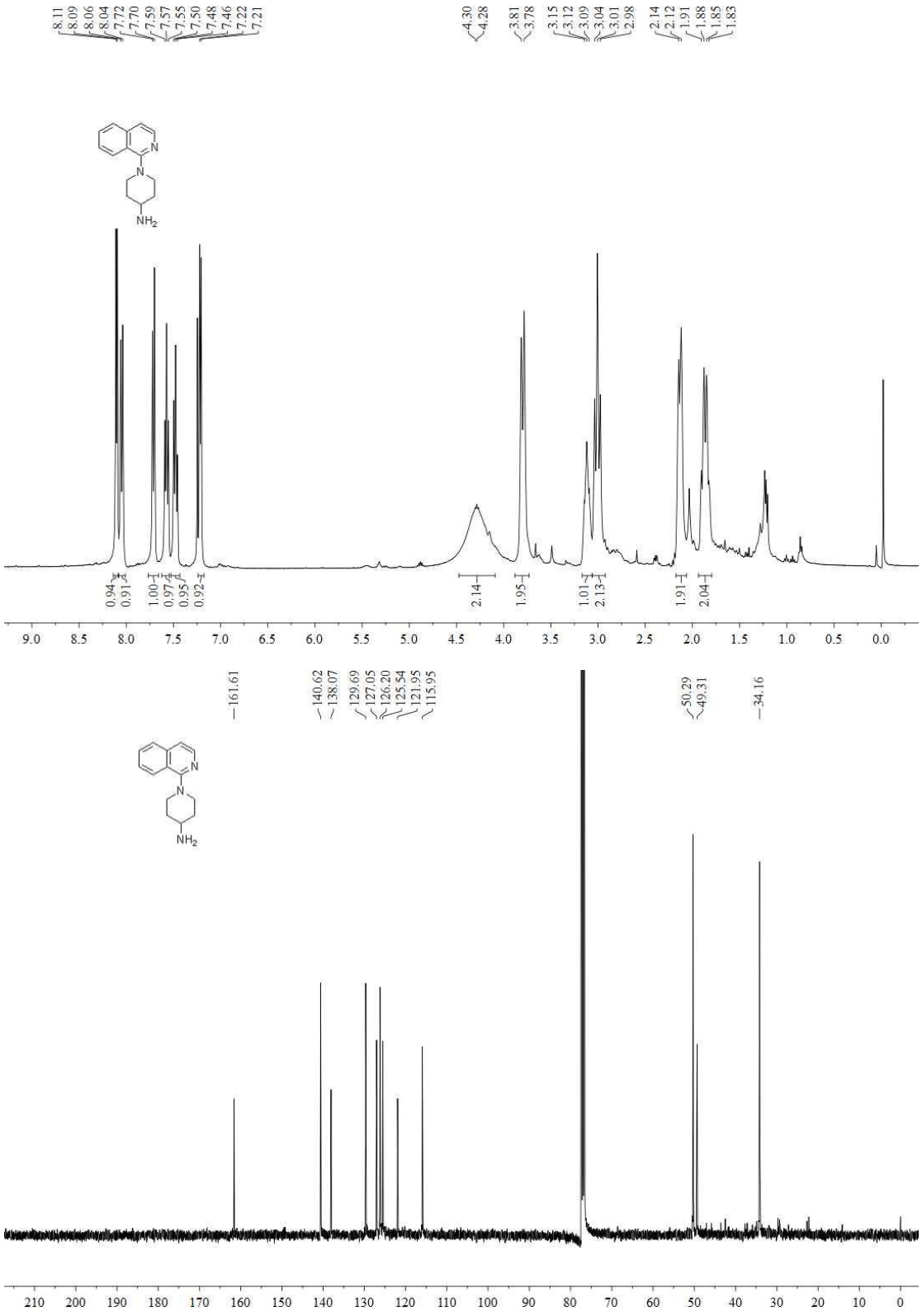
N^1-(isoquinolin-1-yl)benzene-1,4-diamine (53c)



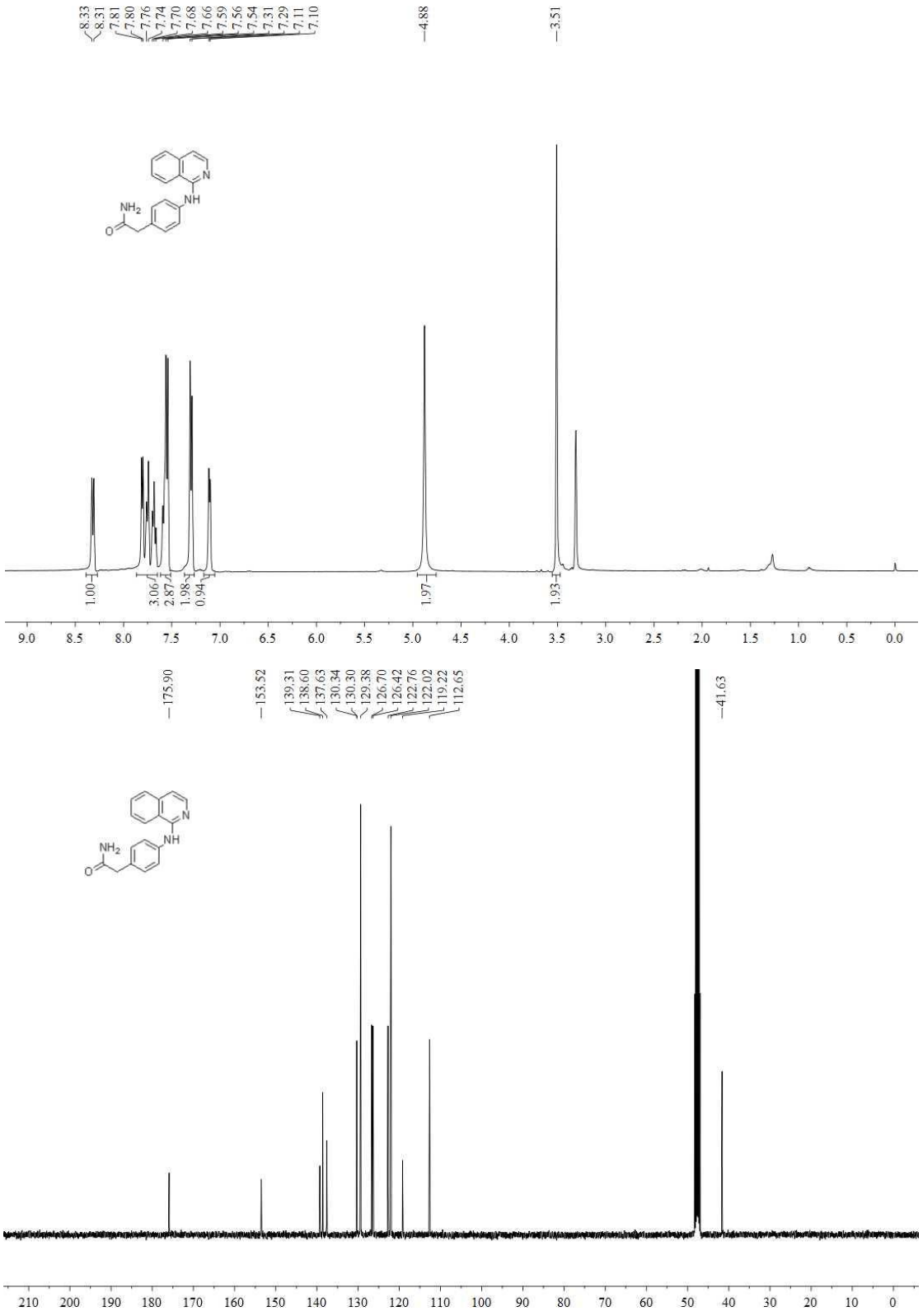
N-(4-(morpholinomethyl)phenyl)isoquinolin-1-amine (54c)



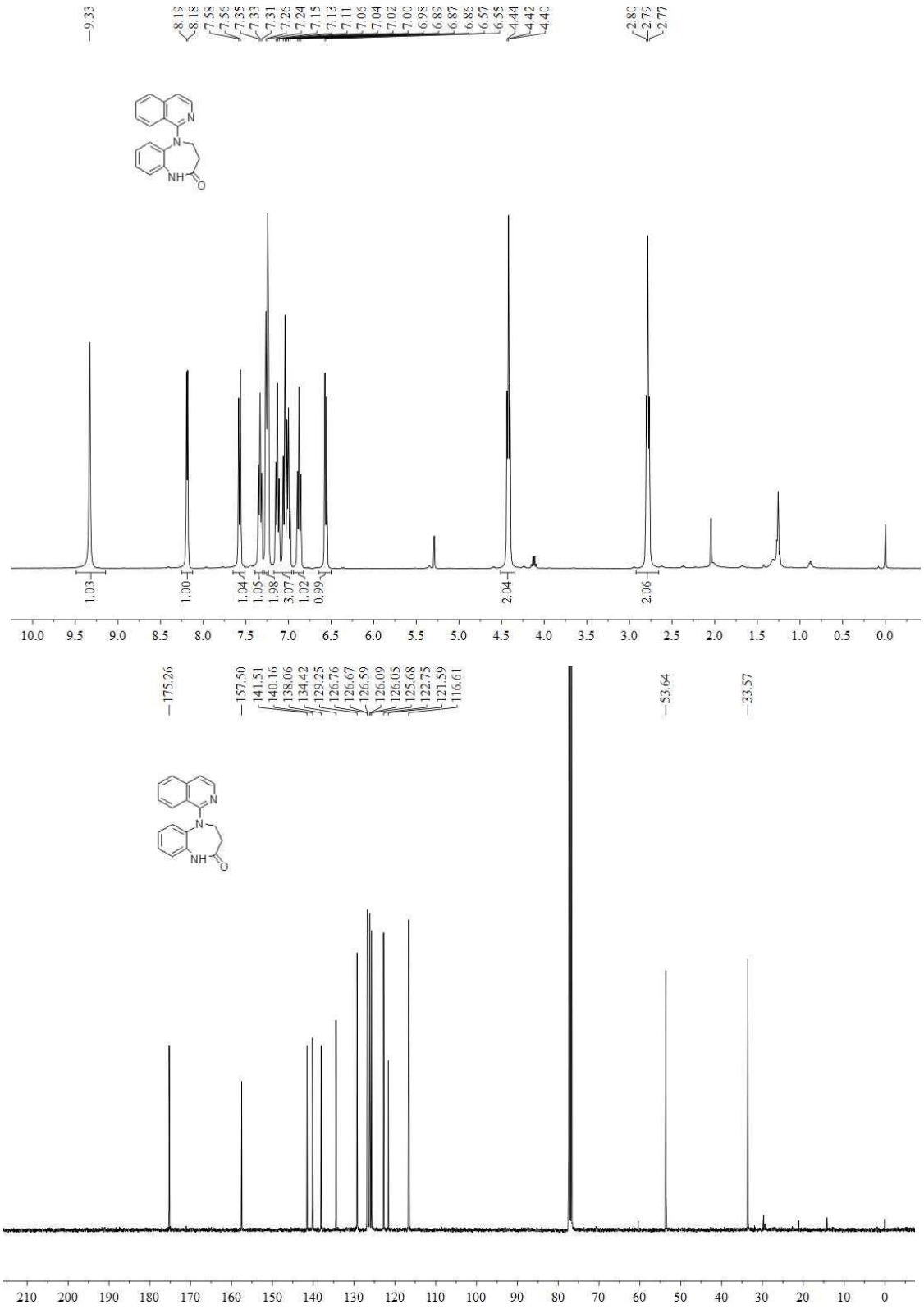
1-(isoquinolin-1-yl)piperidin-4-amine (55c)



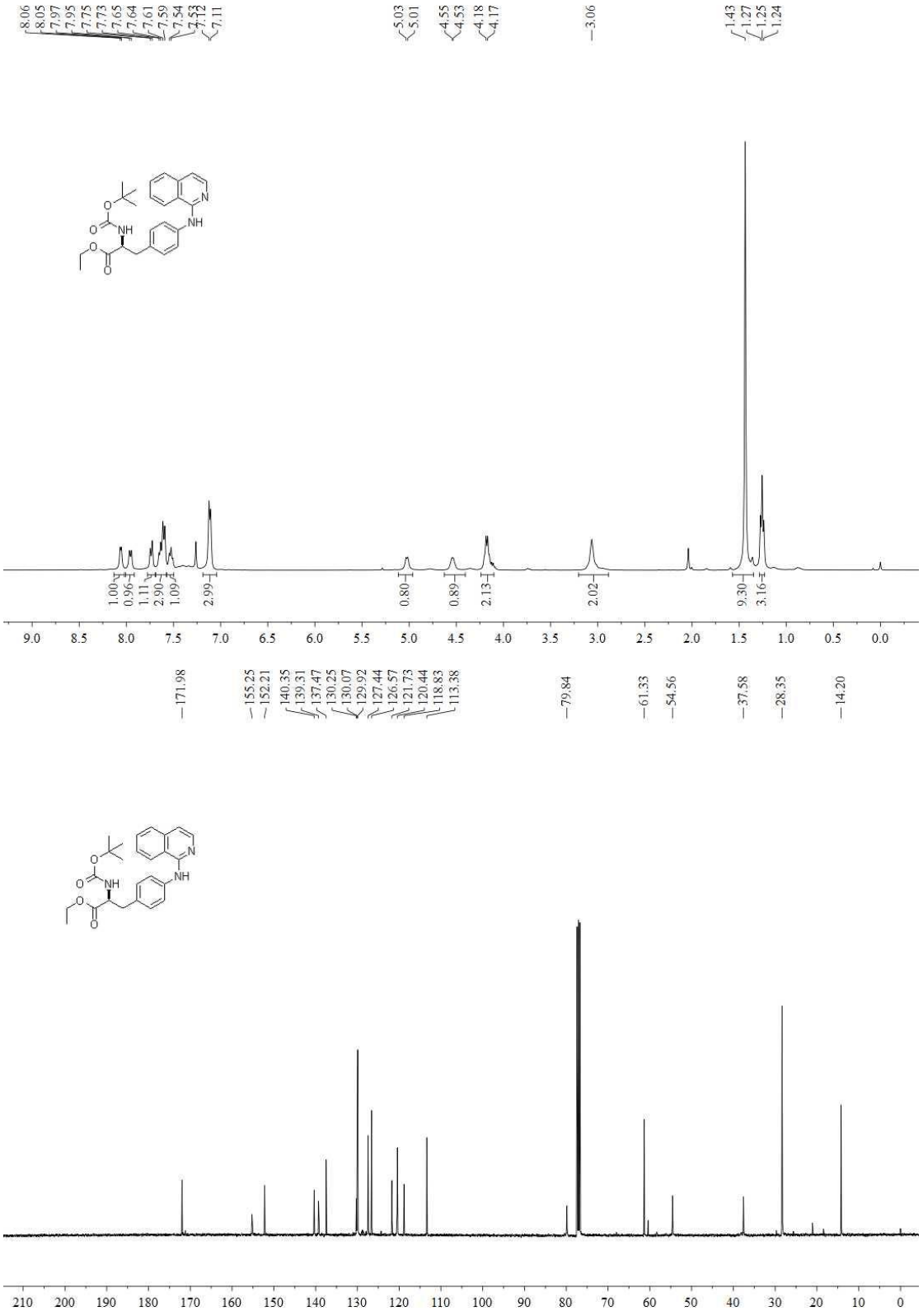
2-(4-(isoquinolin-1-ylamino)phenyl)acetamide (56c)



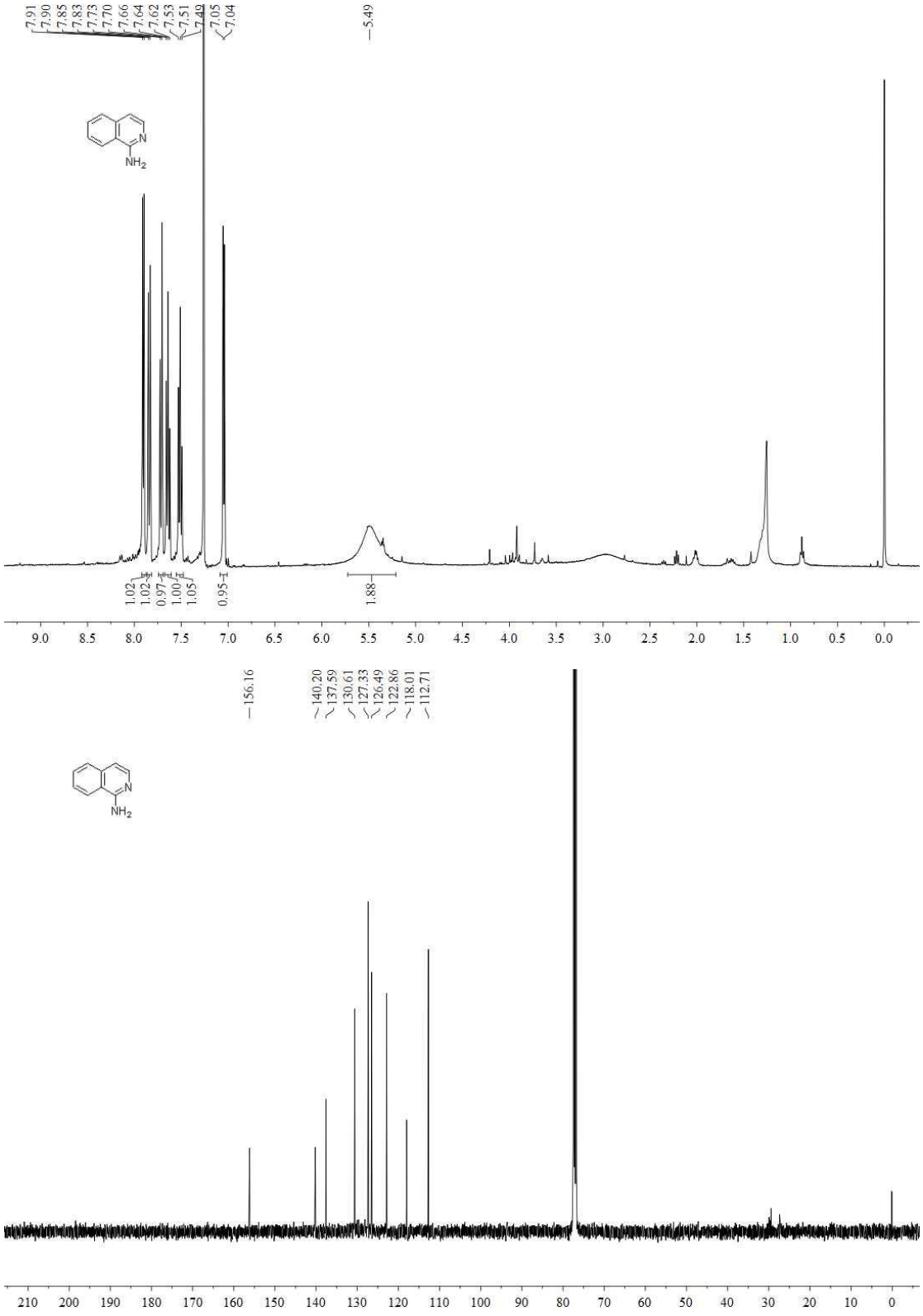
5-(isoquinolin-1-yl)-4,5-dihydro-1H-benzo[b][1,4]diazepin-2(3H)-one (57c)



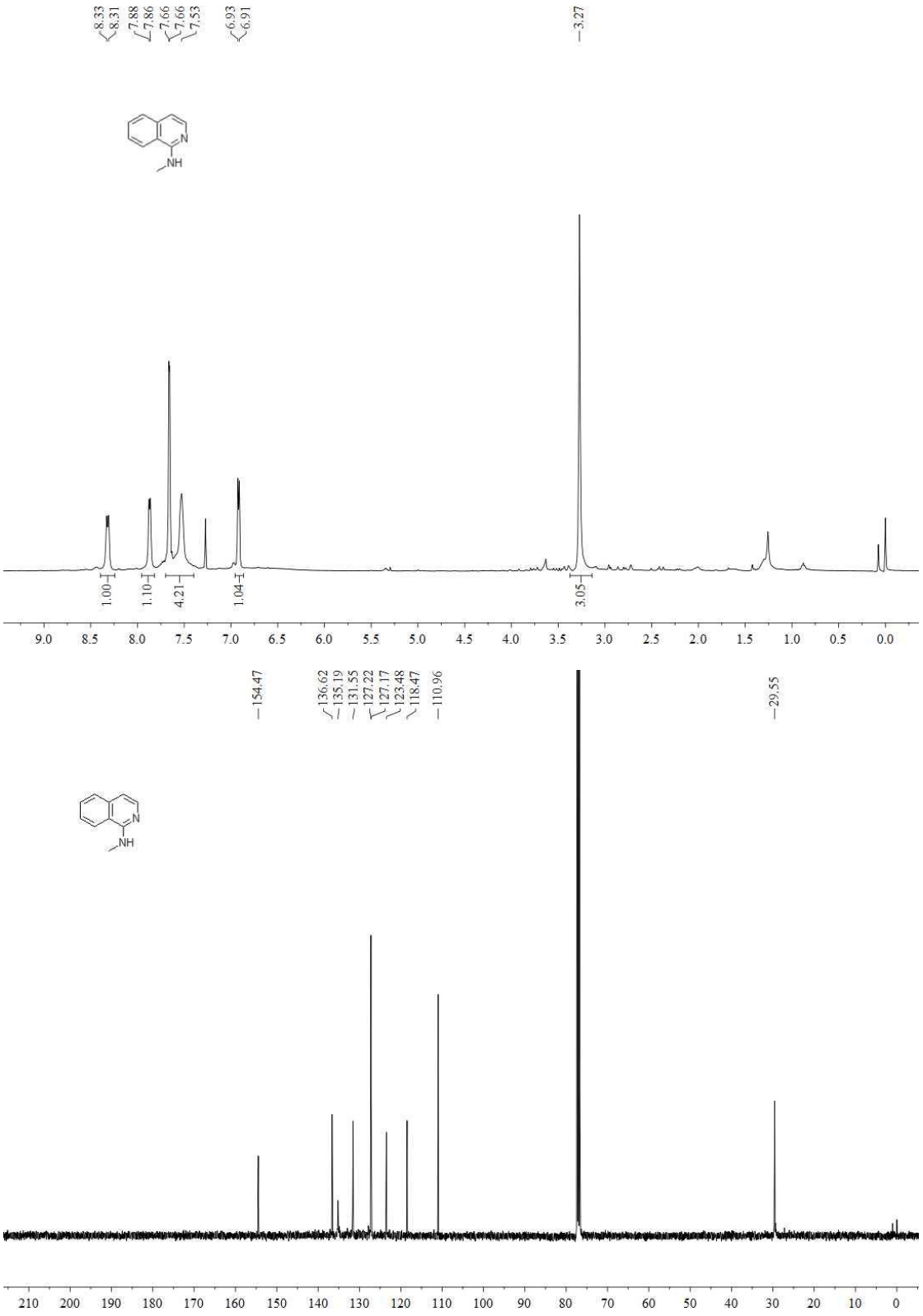
(S)-ethyl 2-((tert-butoxycarbonyl)amino)-3-(4-(isoquinolin-1-ylamino)phenyl)propanoate (58c)



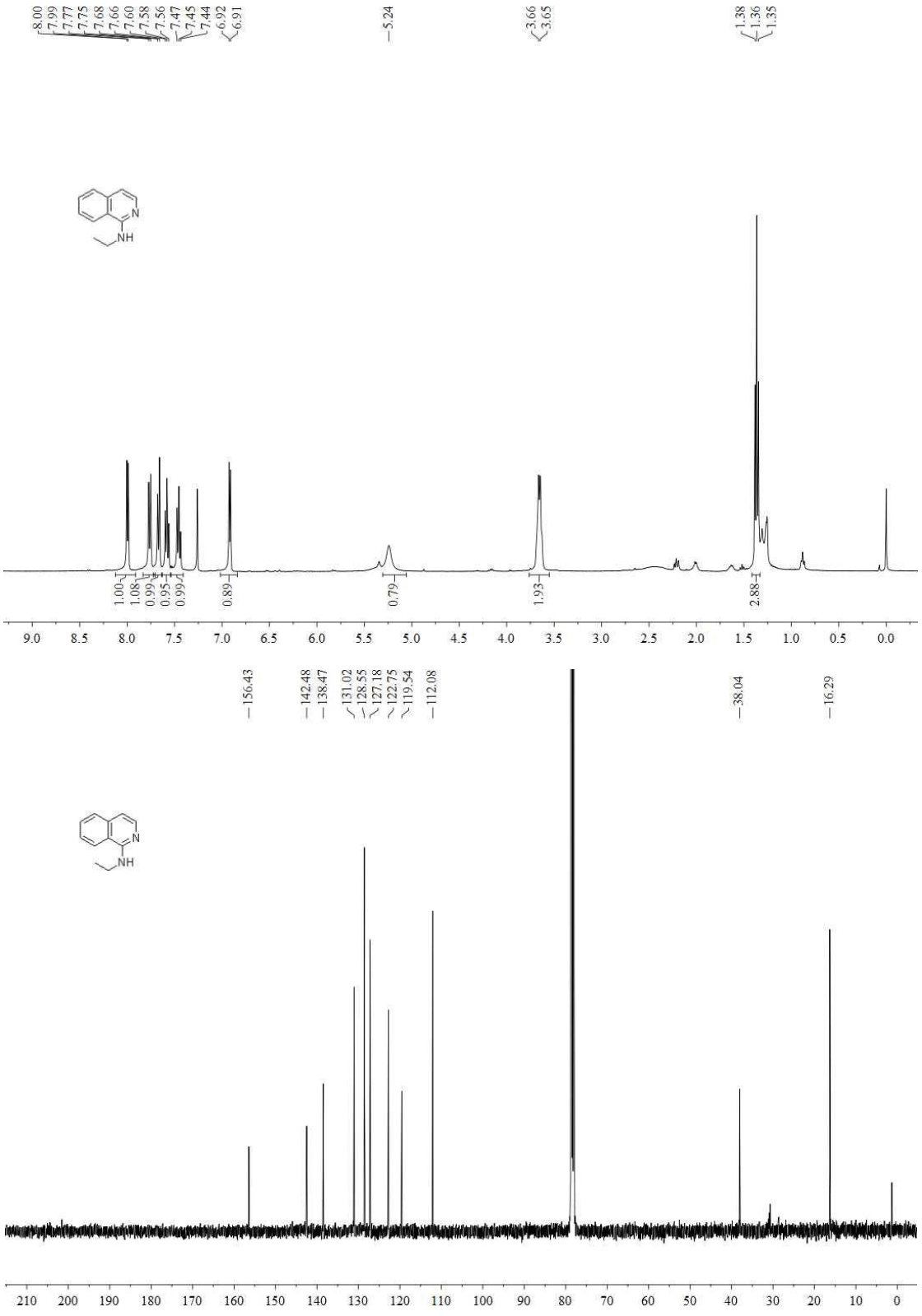
isoquinolin-1-amine (59c)



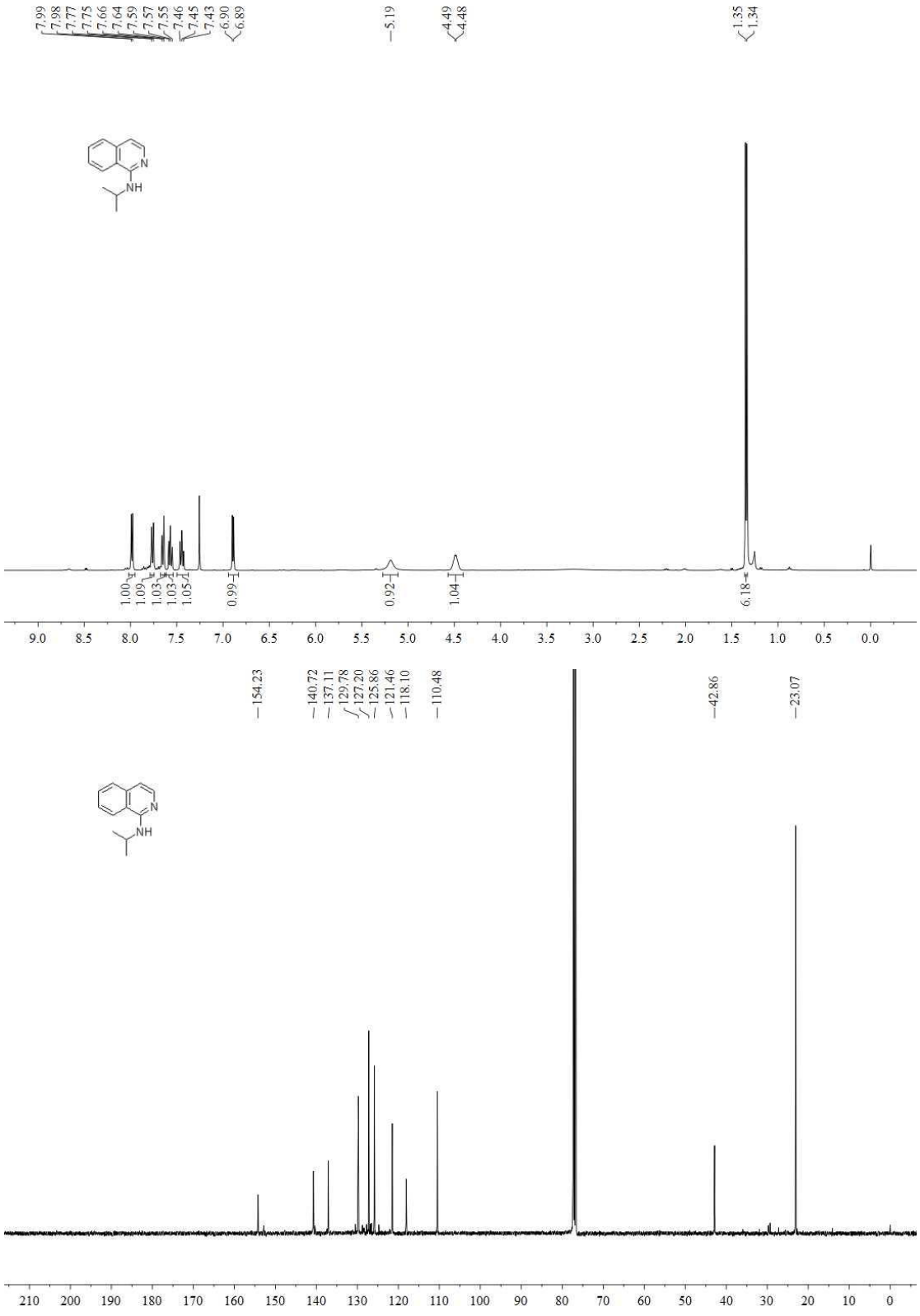
***N*-methylisoquinolin-1-amine (60c)**



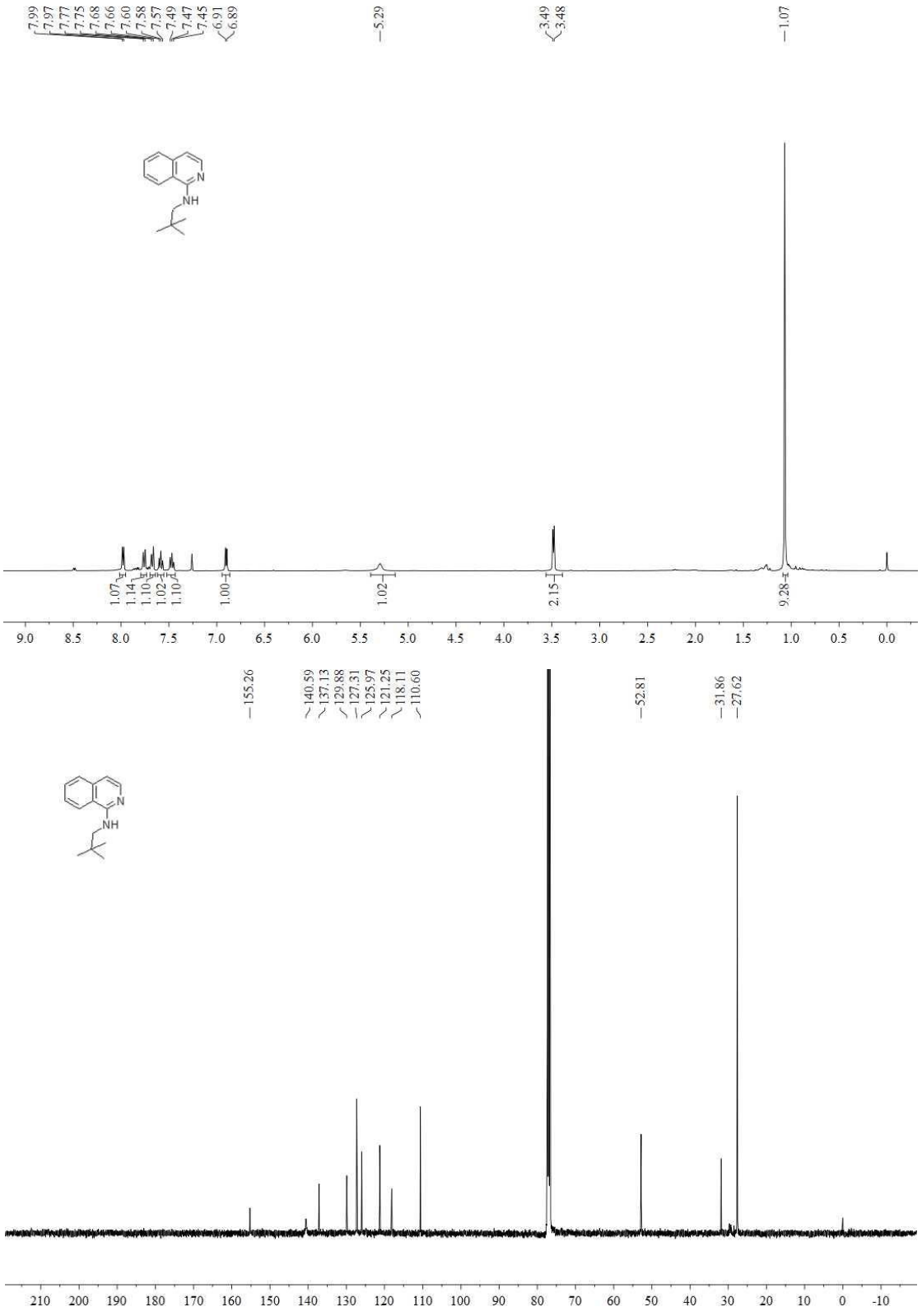
***N*-ethylisoquinolin-1-amine (61c)**



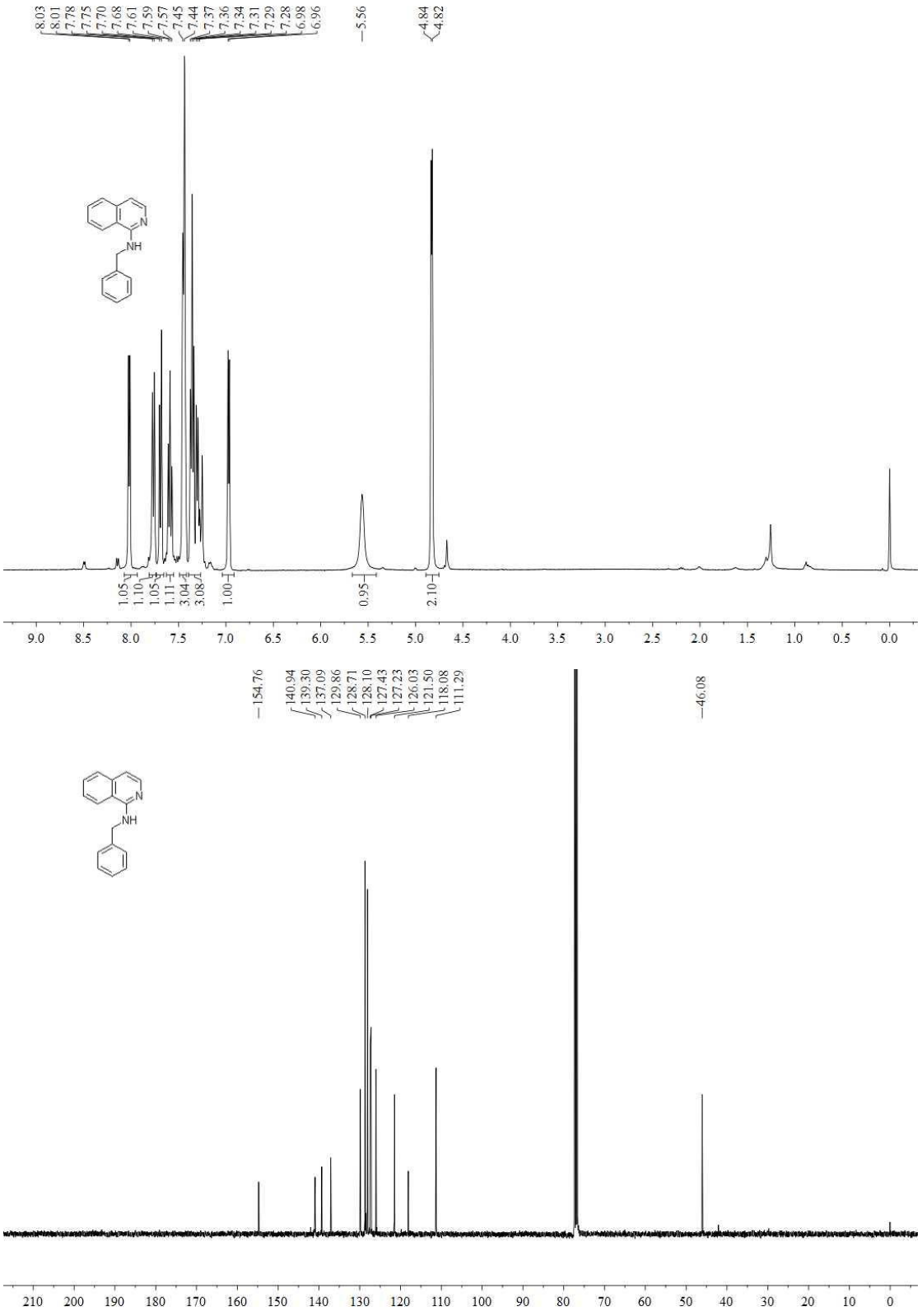
***N*-isopropylisoquinolin-1-amine (62c)**



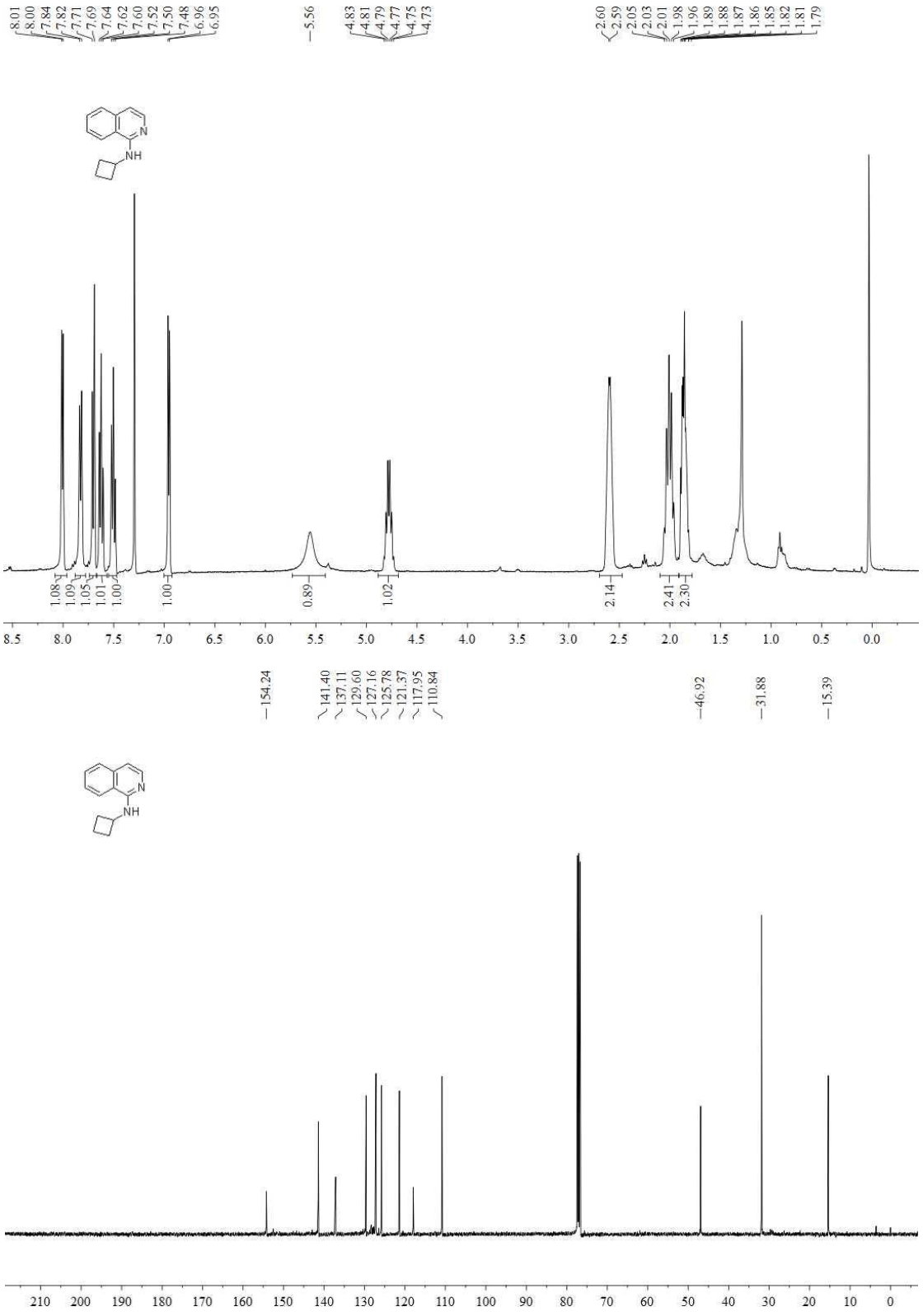
***N*-neopentylisoquinolin-1-amine (63c)**



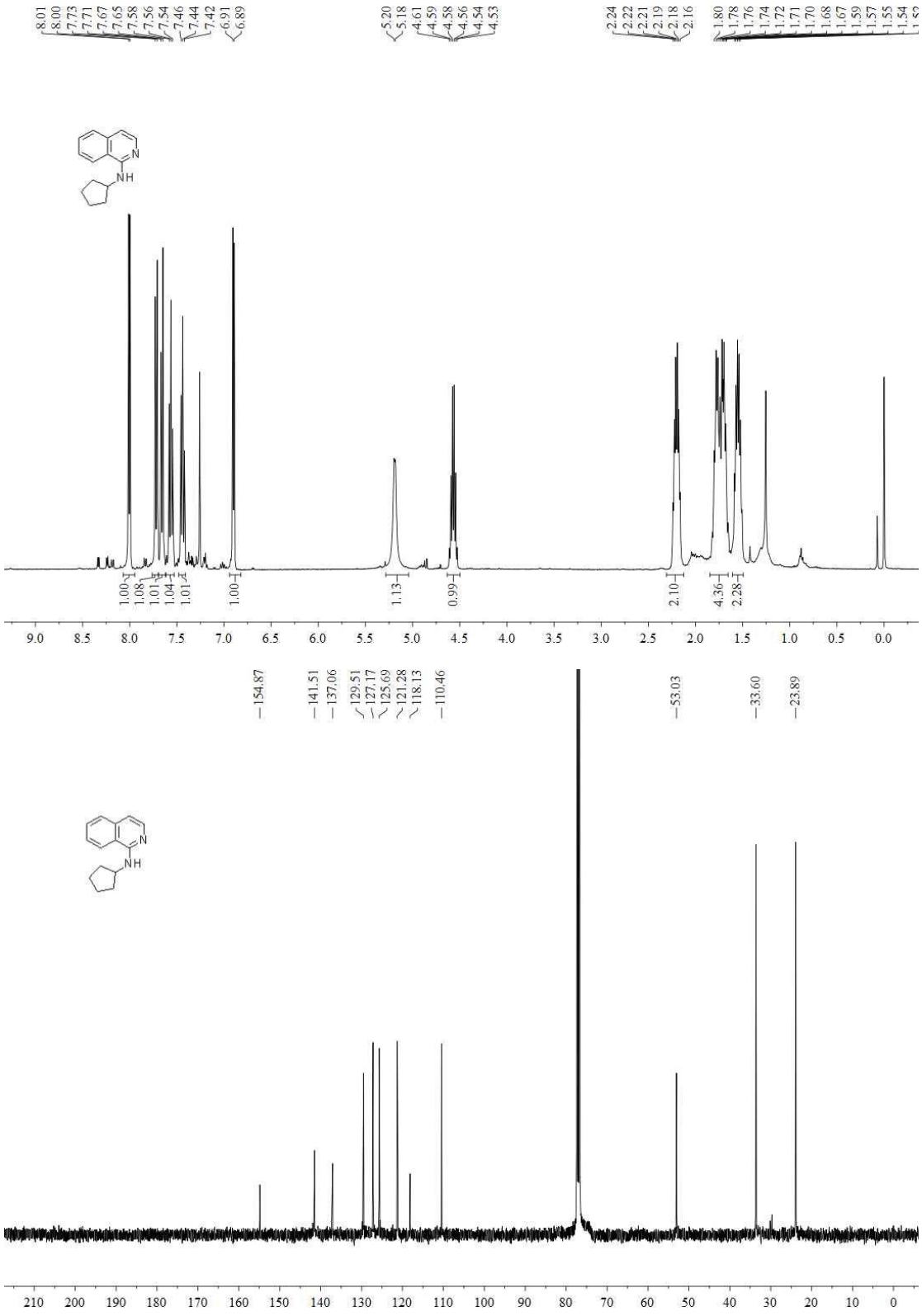
***N*-benzylisoquinolin-1-amine (64c)**



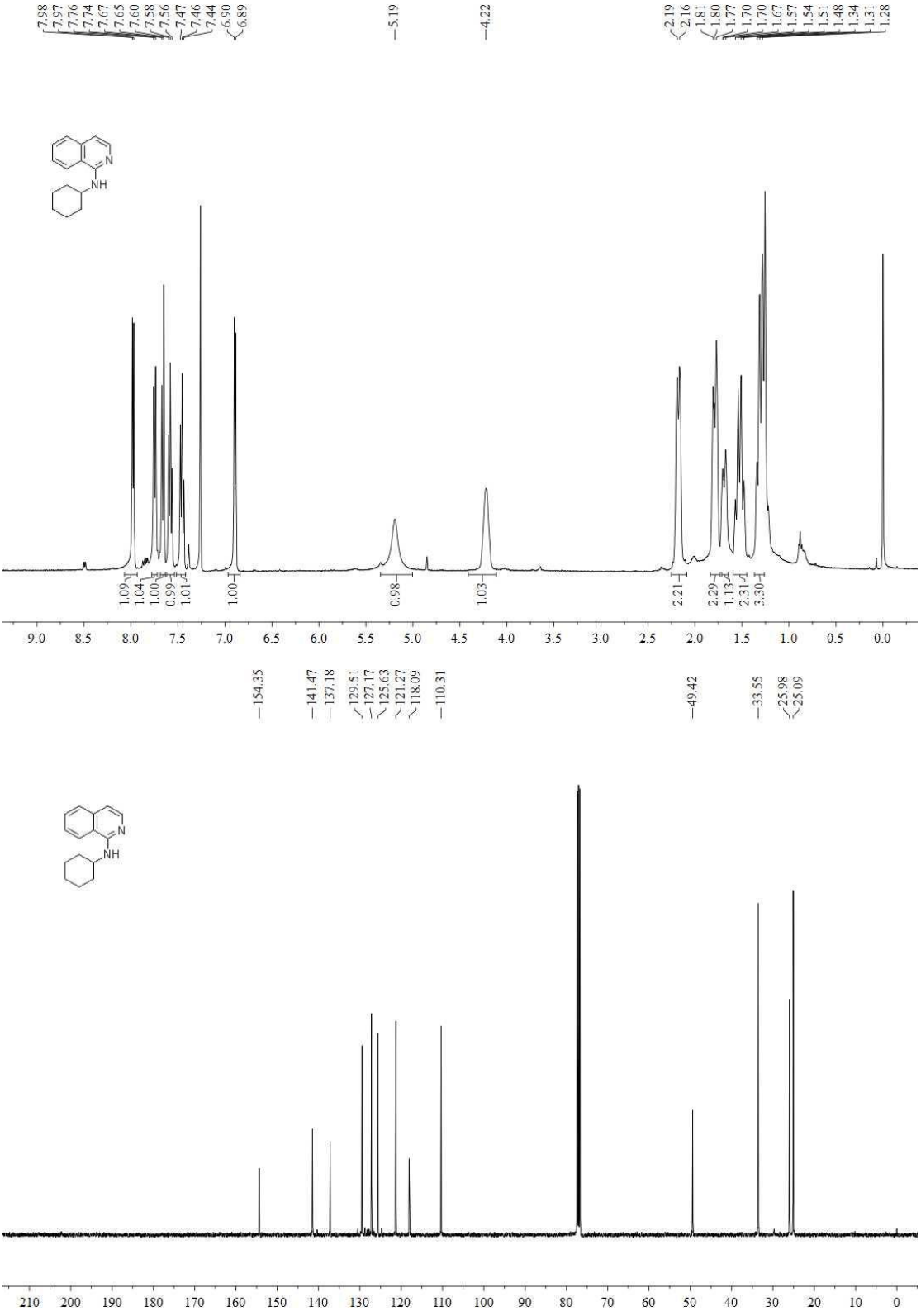
***N*-cyclobutylisoquinolin-1-amine (65c)**



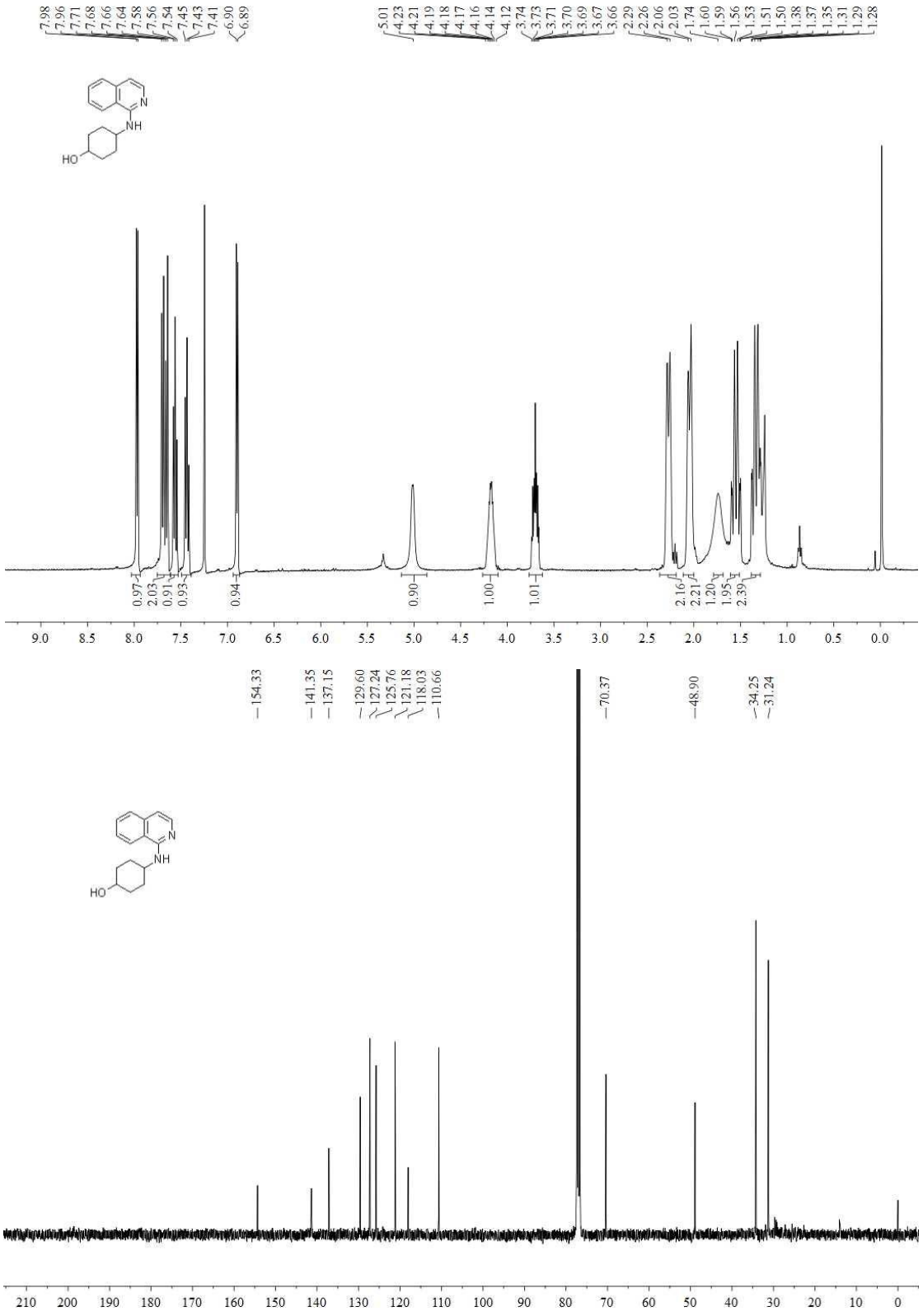
***N*-cyclopentylisoquinolin-1-amine (66c)**



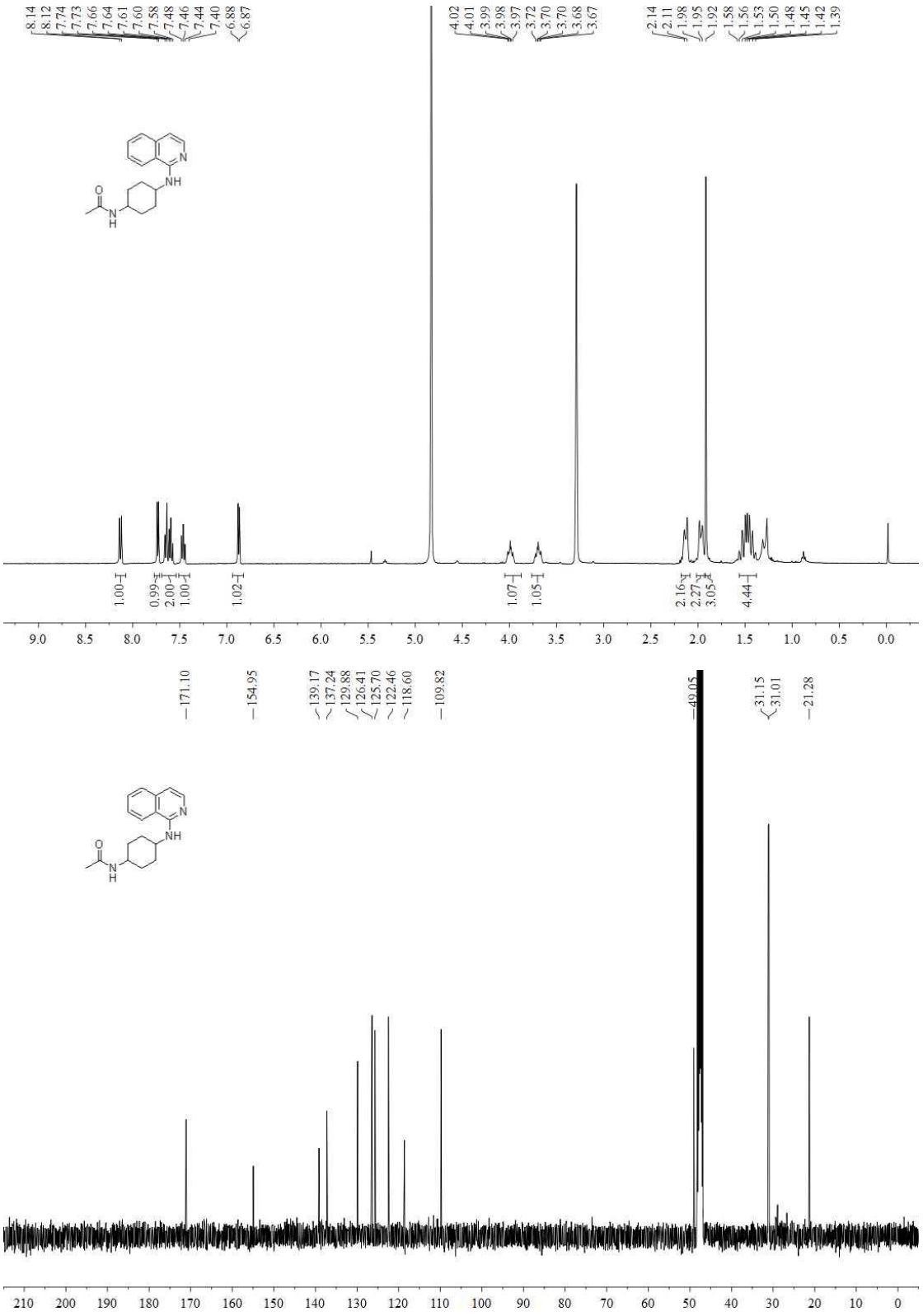
***N*-cyclohexylisoquinolin-1-amine (67c)**



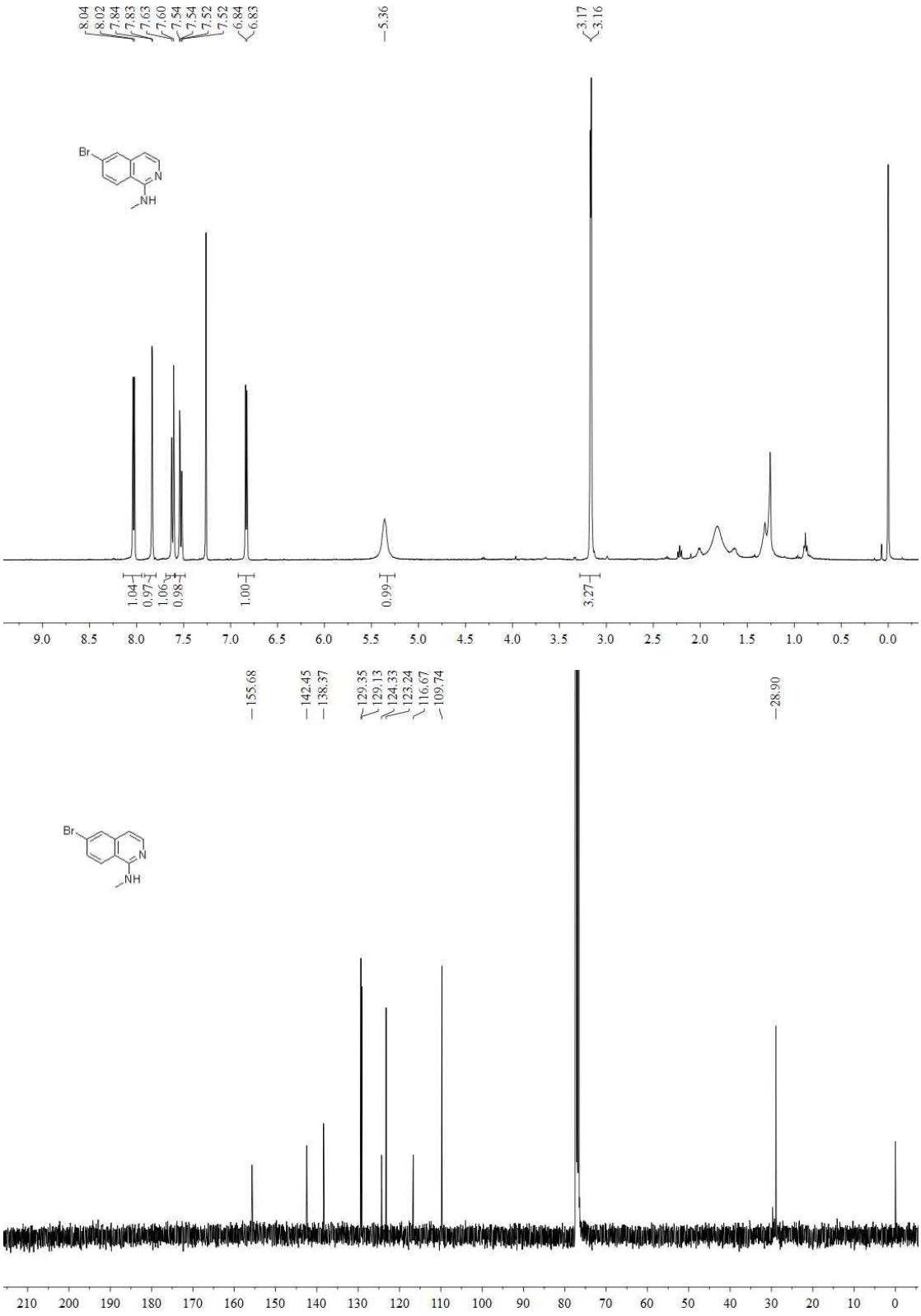
4-(isoquinolin-1-ylamino)cyclohexanol (68c)



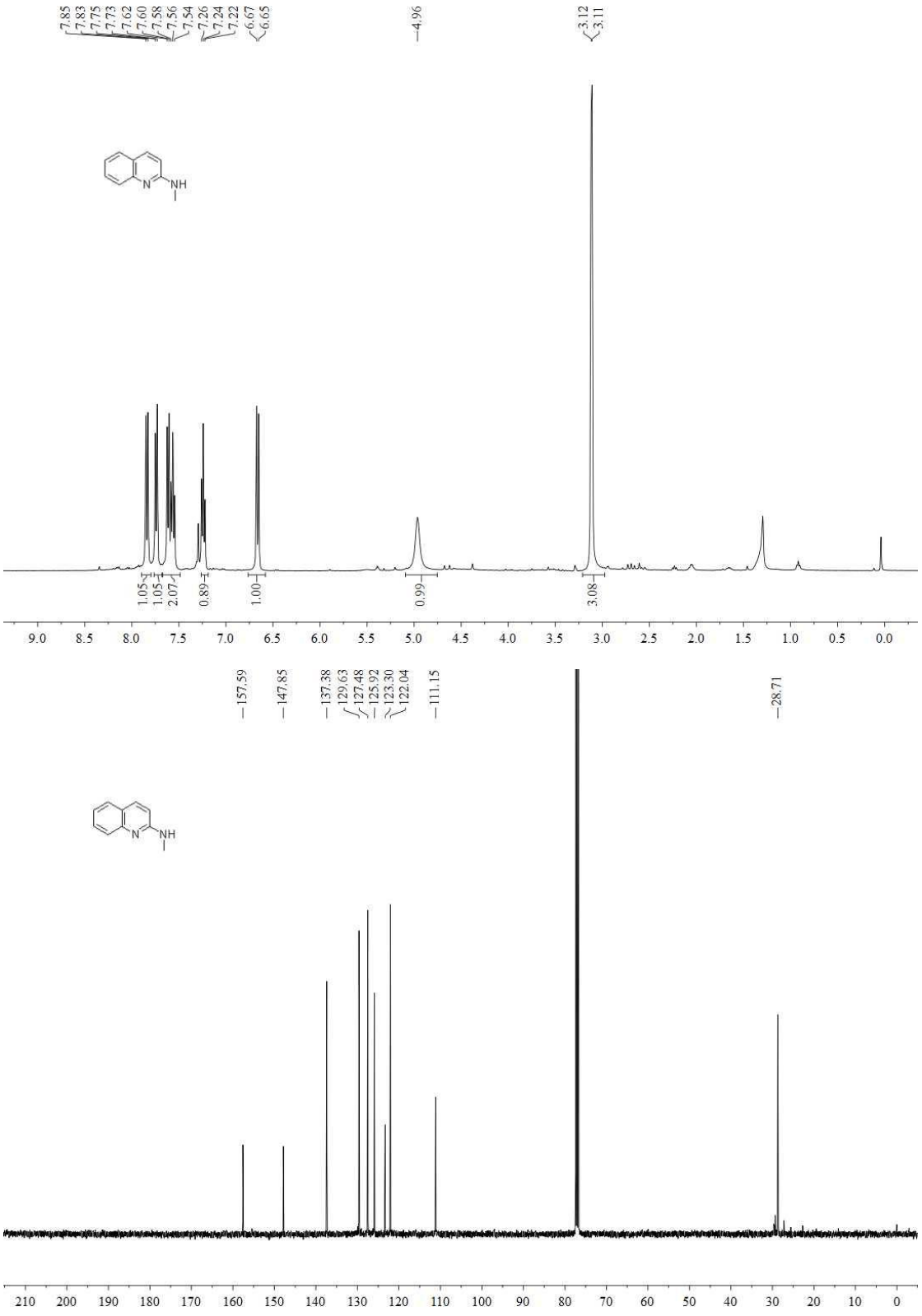
***N*-(4-(isoquinolin-1-ylamino)cyclohexyl)acetamide (69c)**



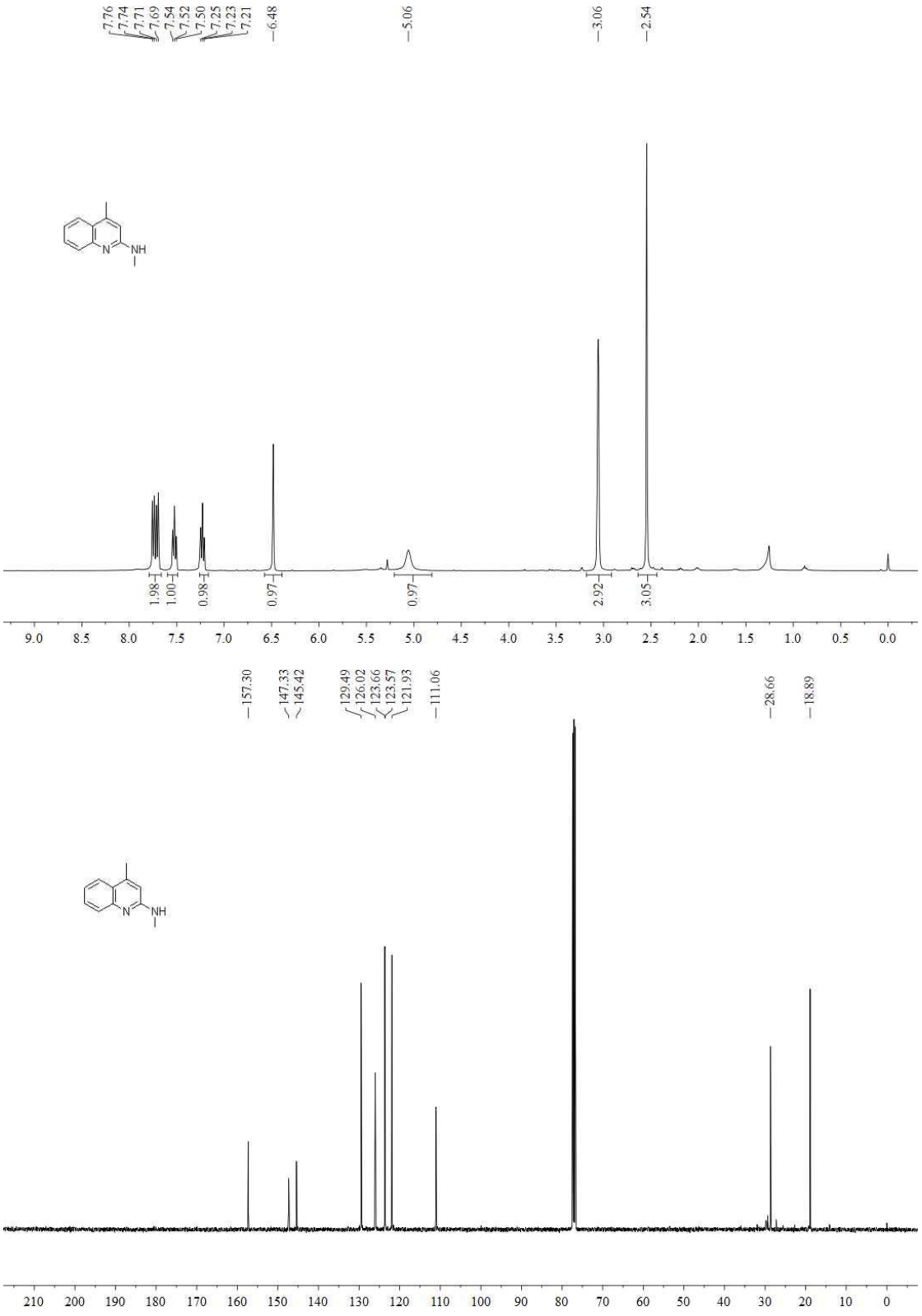
6-bromo-*N*-methylisoquinolin-1-amine (70c)



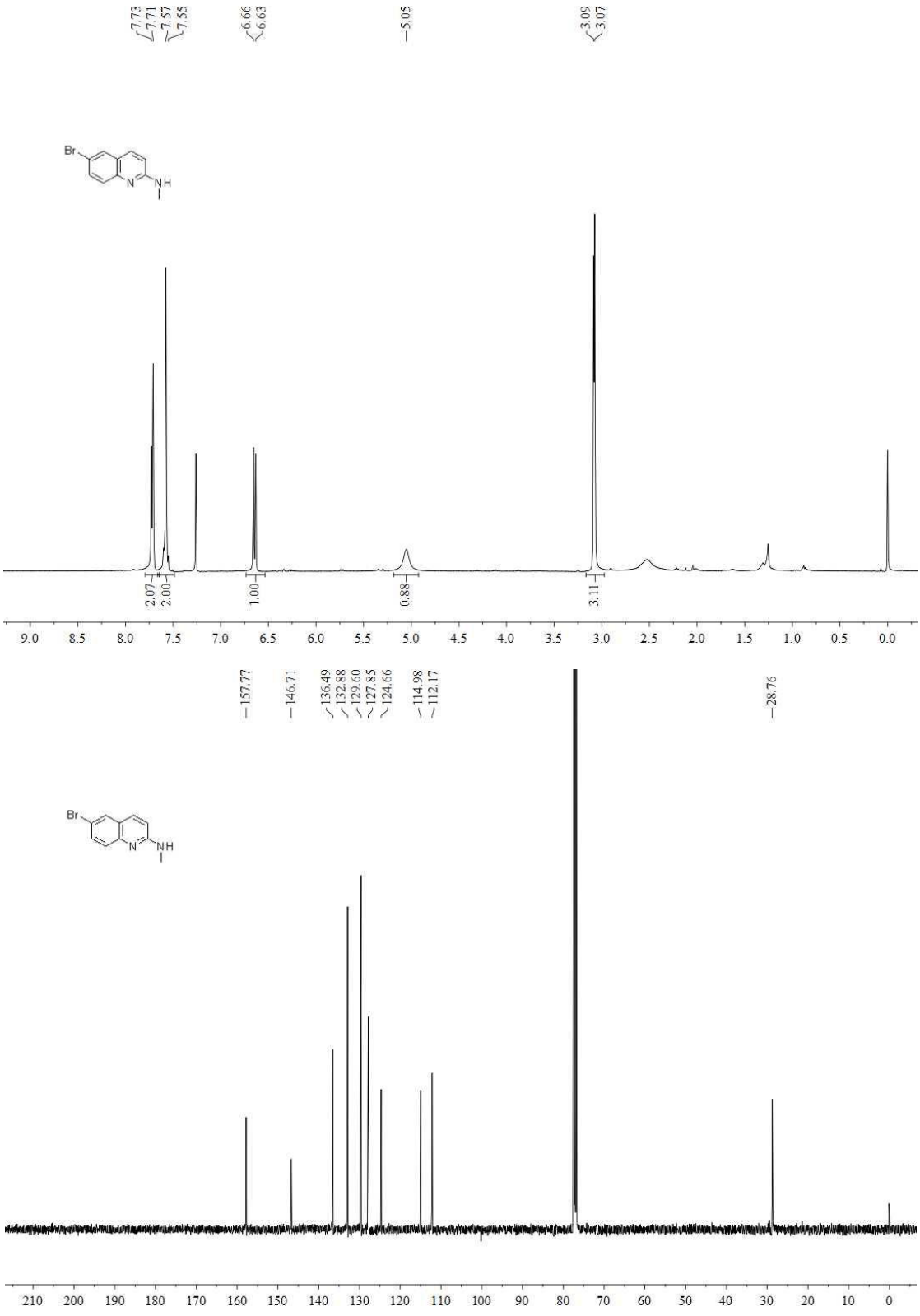
***N*-methylquinolin-2-amine (71c)**



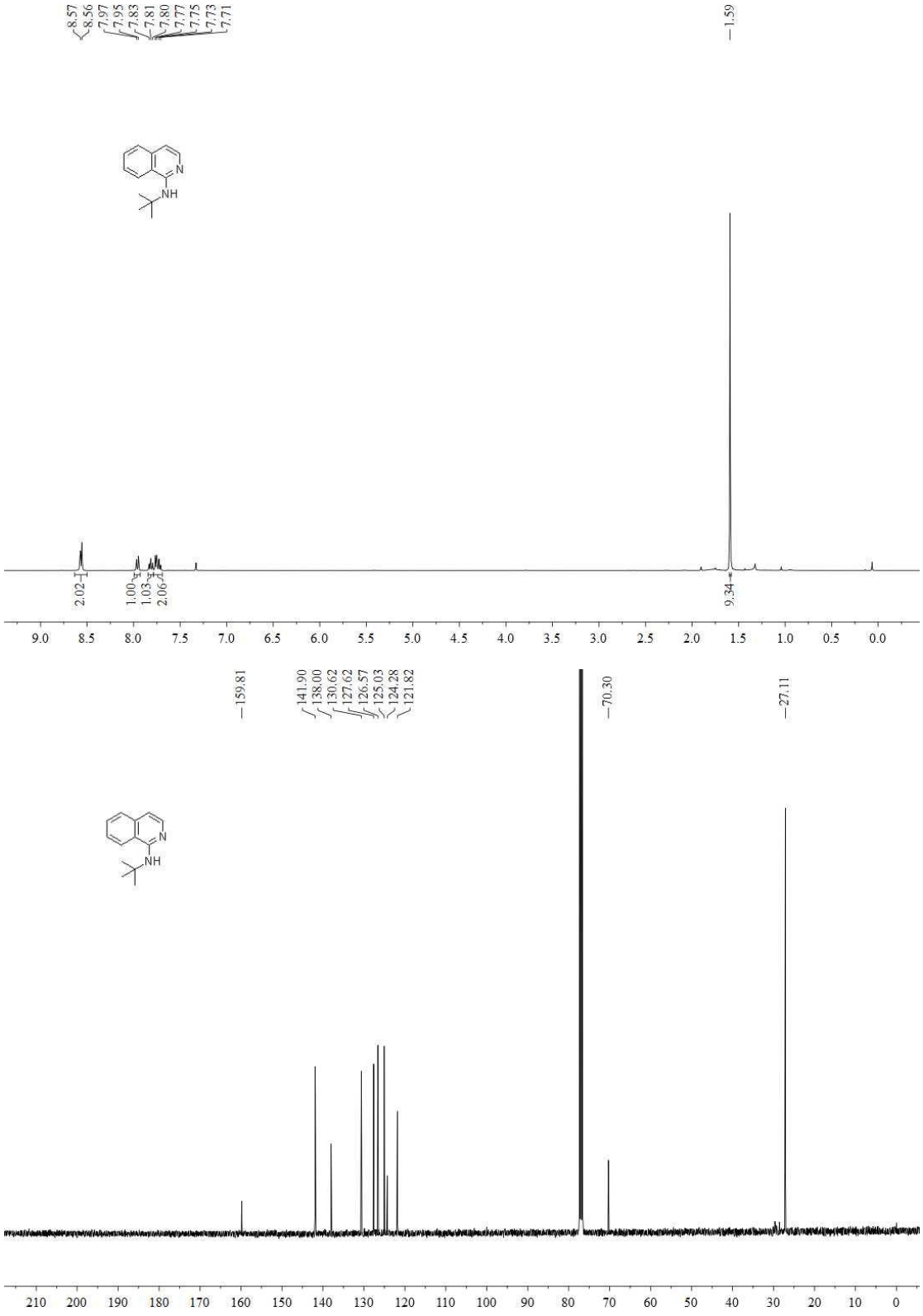
***N*,4-dimethylquinolin-2-amine (72c)**



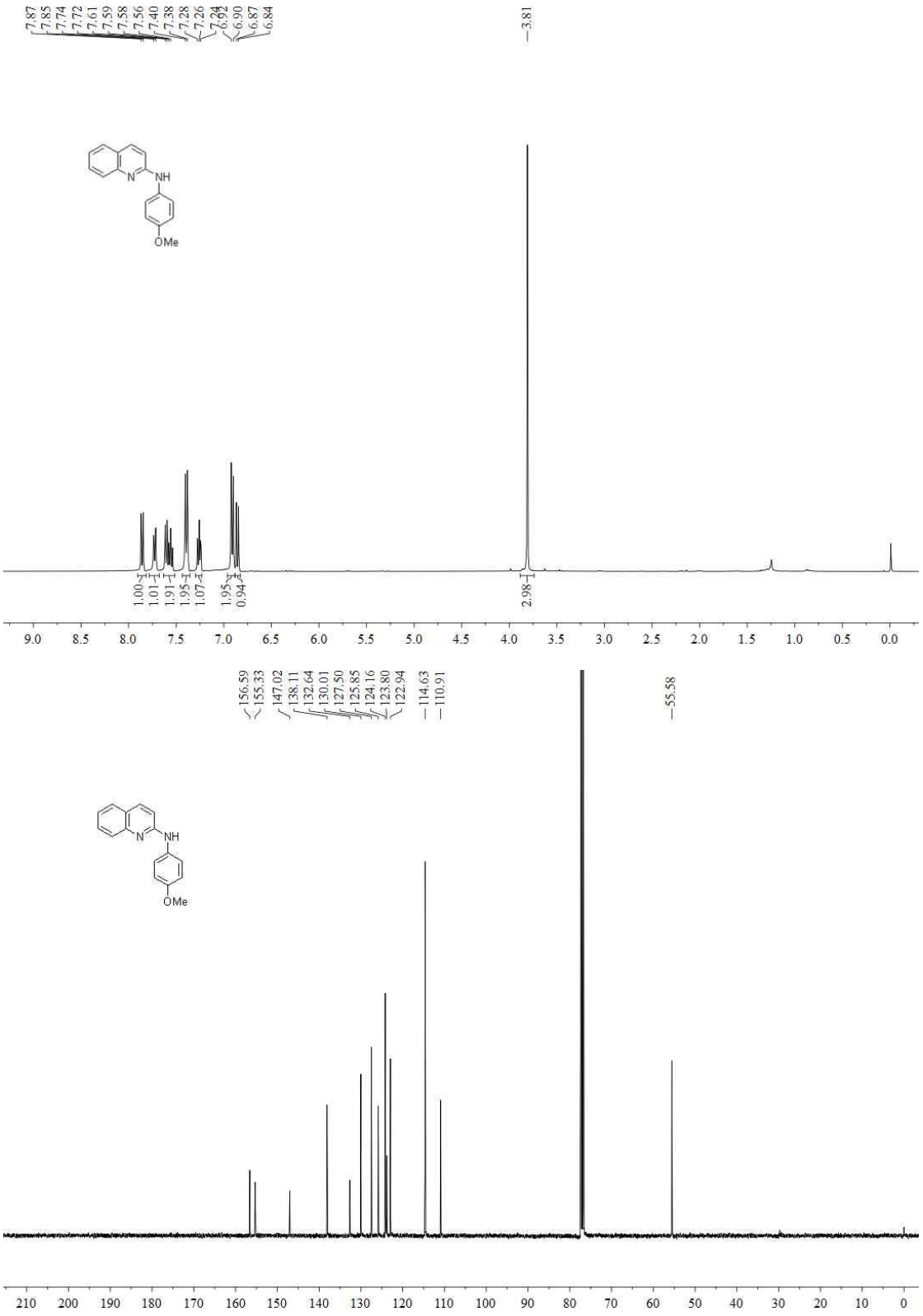
6-bromo-*N*-methylquinolin-2-amine (73c)



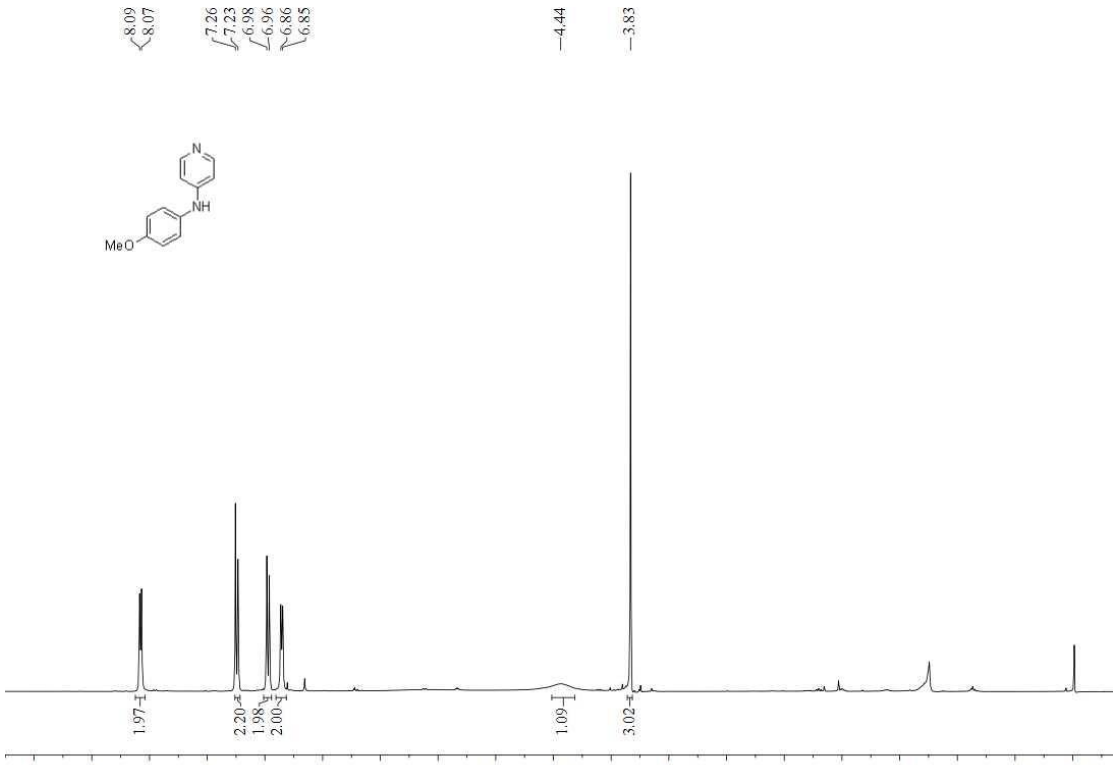
***N*-(tert-butyl)isoquinolin-1-amine (74c)**

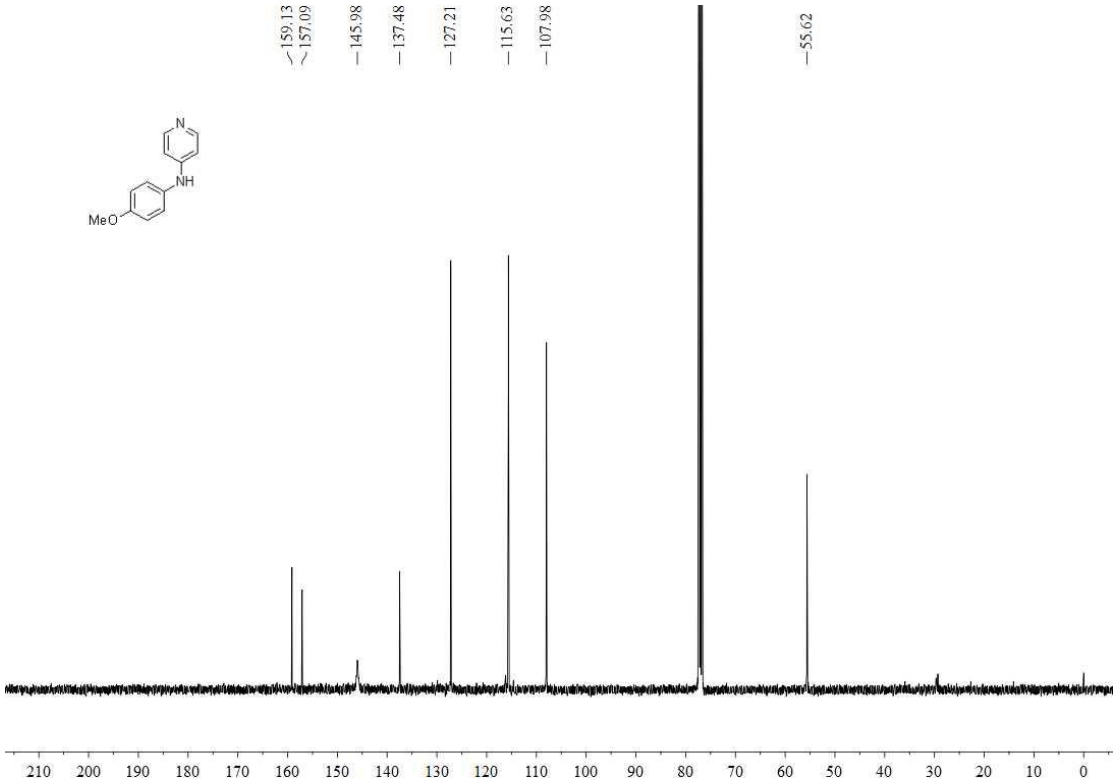


N-(4-methoxyphenyl)quinolin-2-amine (75c)

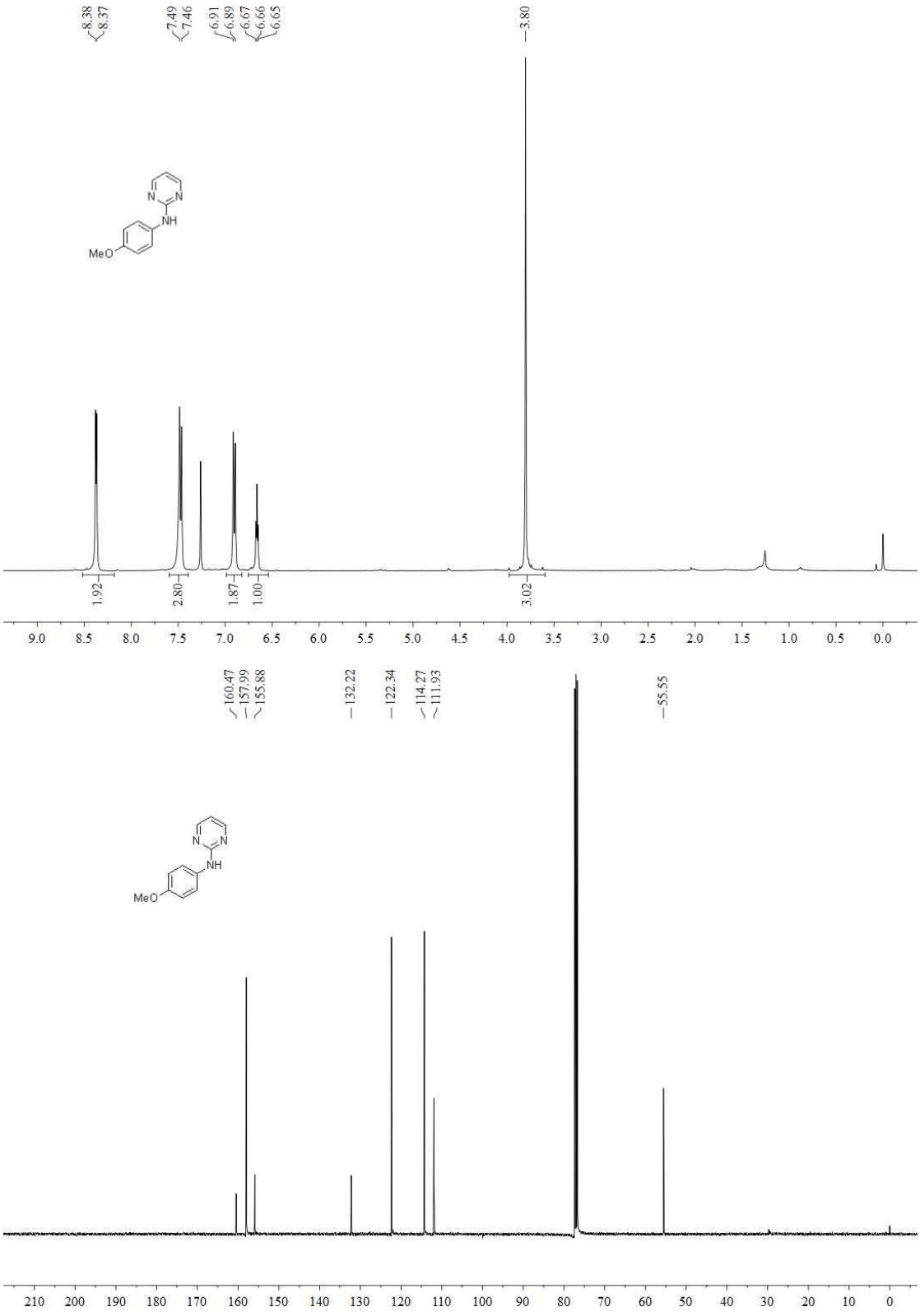


***N*-(4-methoxyphenyl)pyridin-4-amine (76c)**

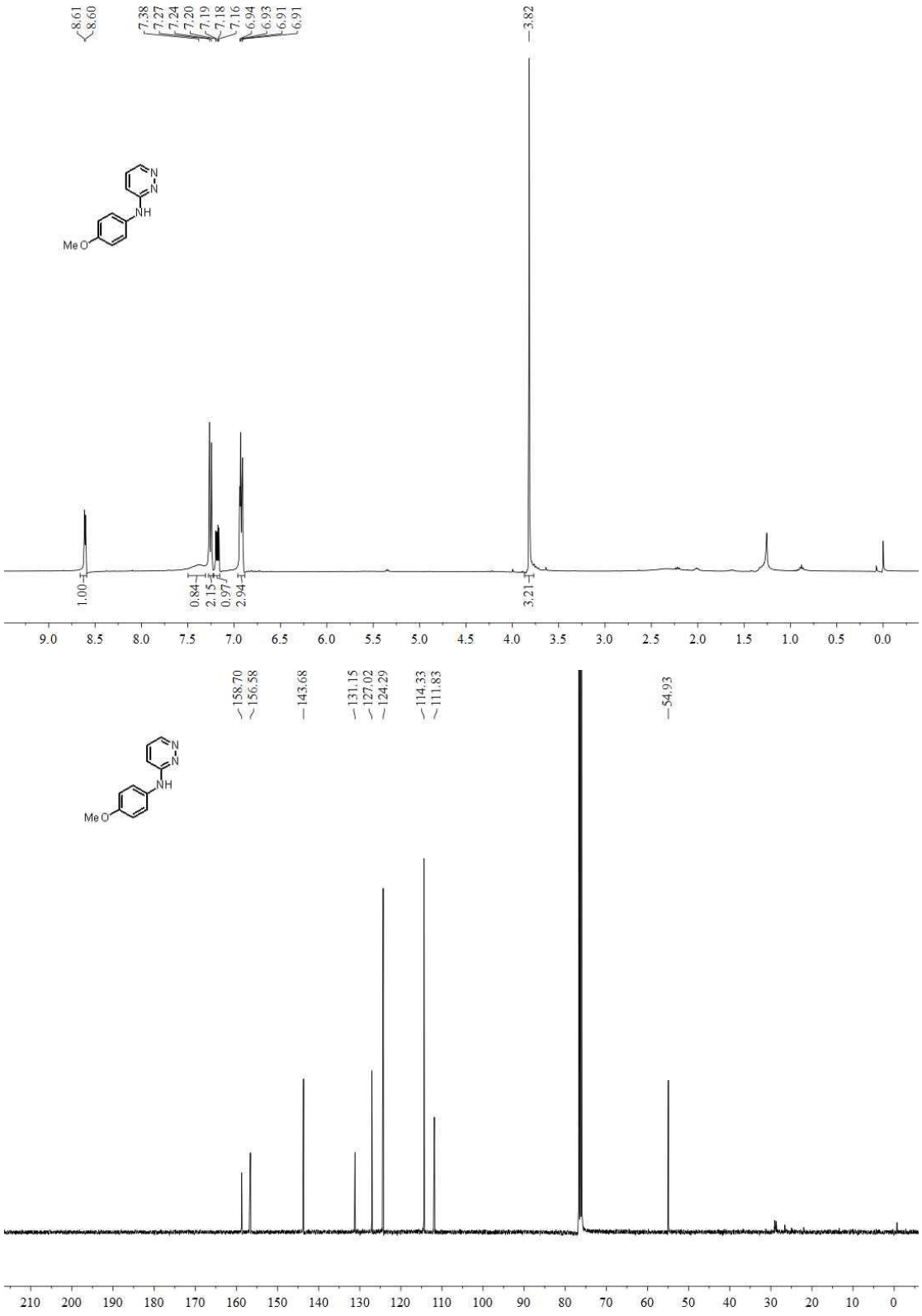




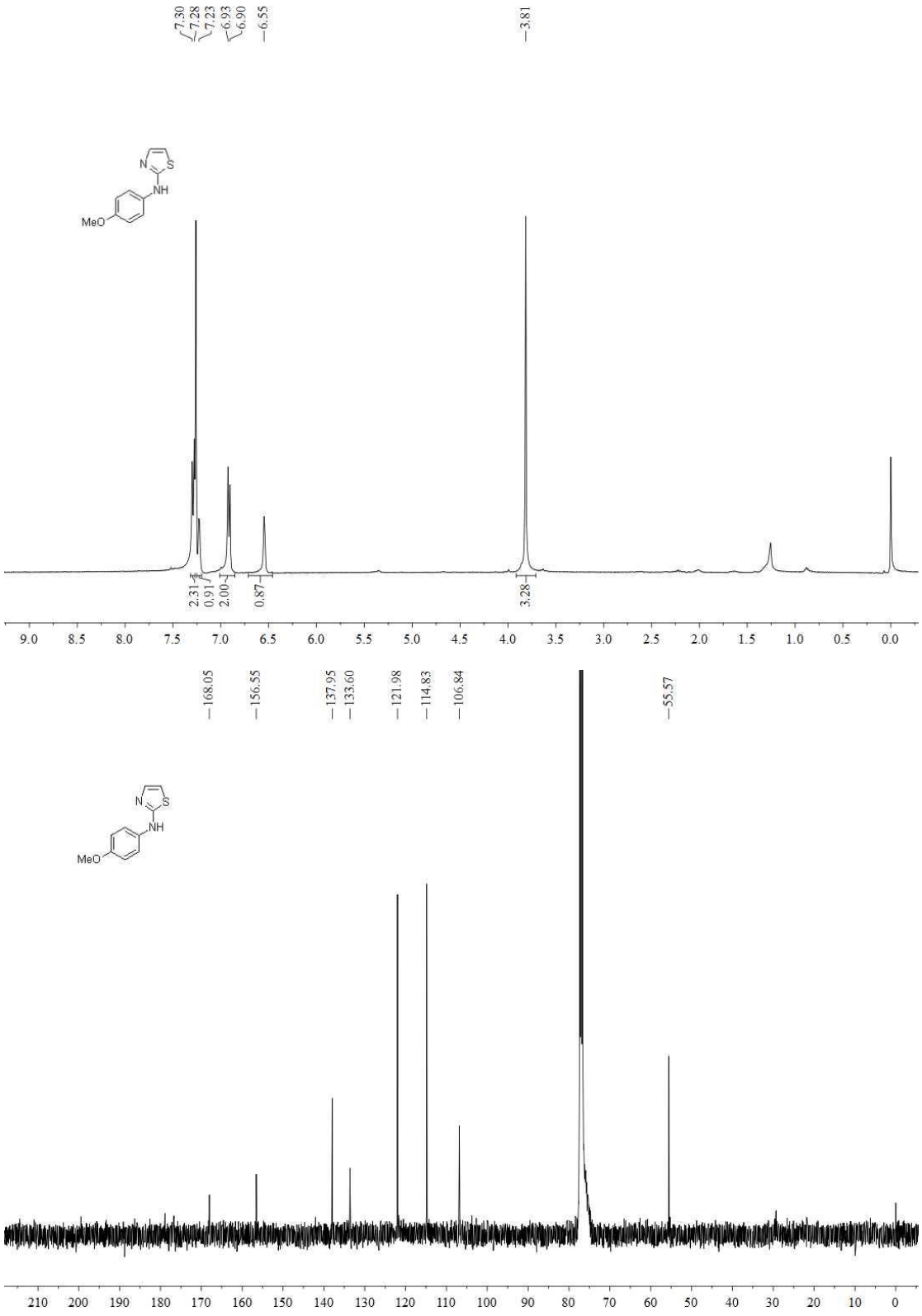
***N*-(4-methoxyphenyl)pyrimidin-2-amine (77c)**



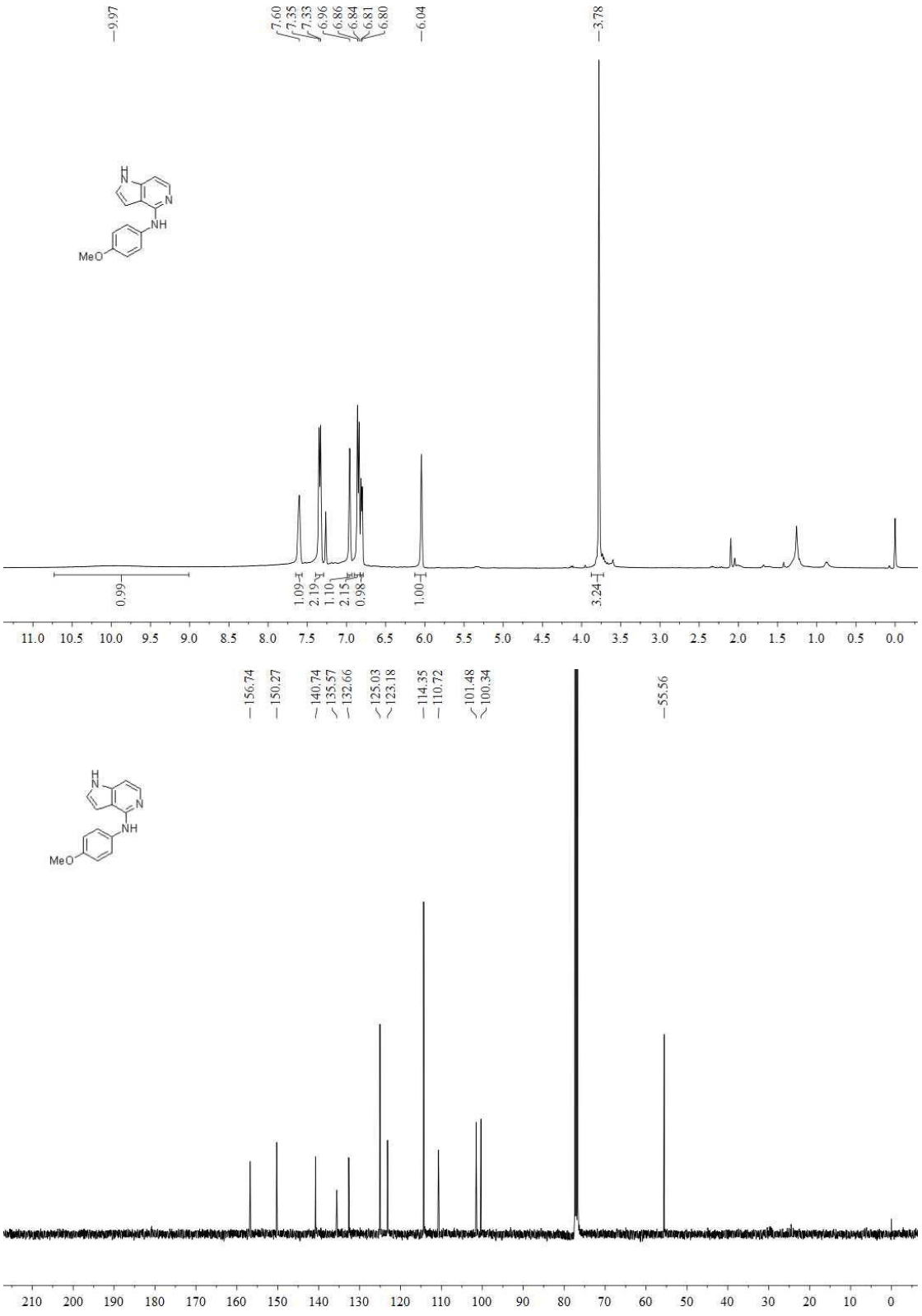
N-(4-methoxyphenyl)pyridazin-3-amine (78c)



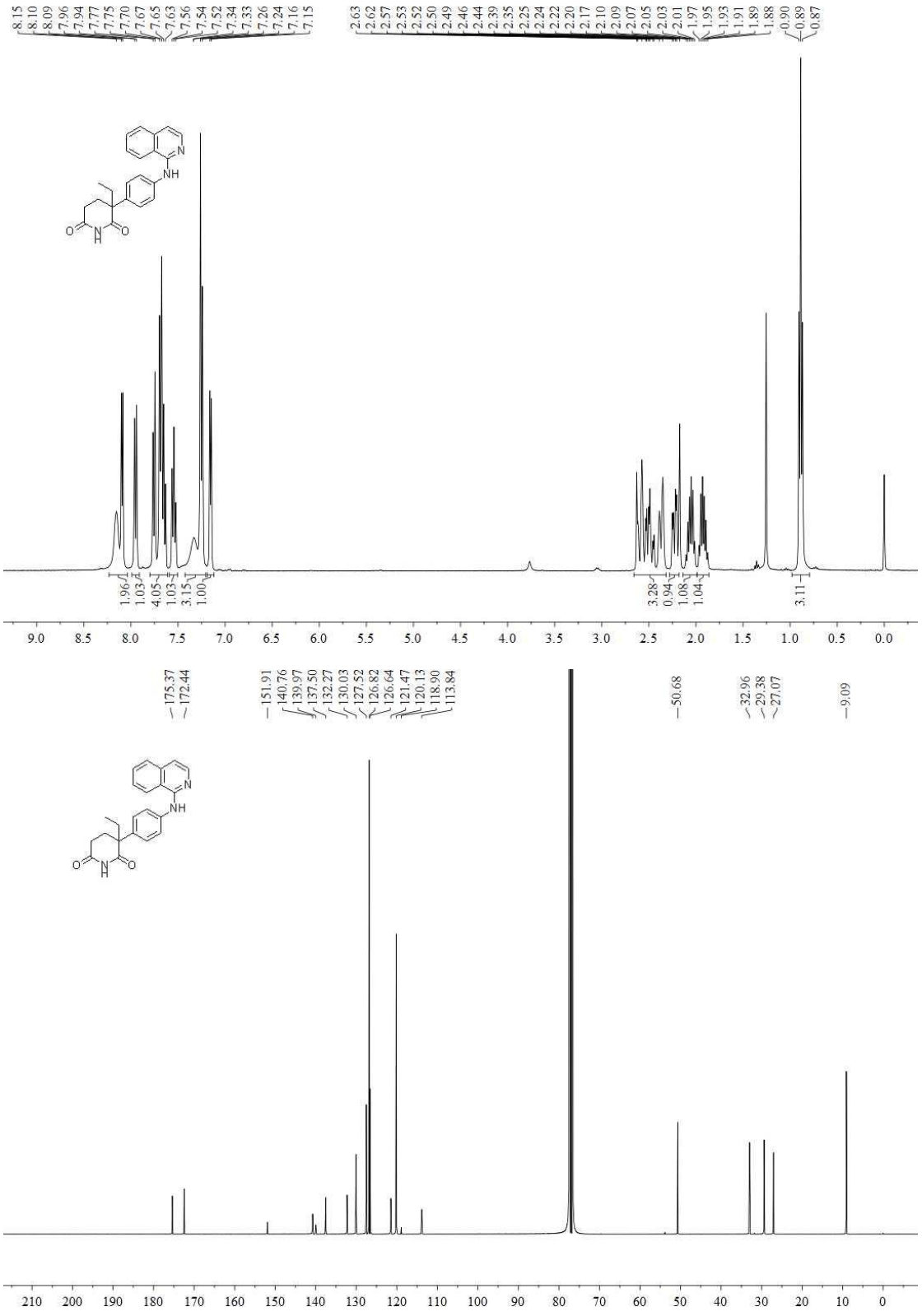
***N*-(4-methoxyphenyl)thiazol-2-amine (79c)**



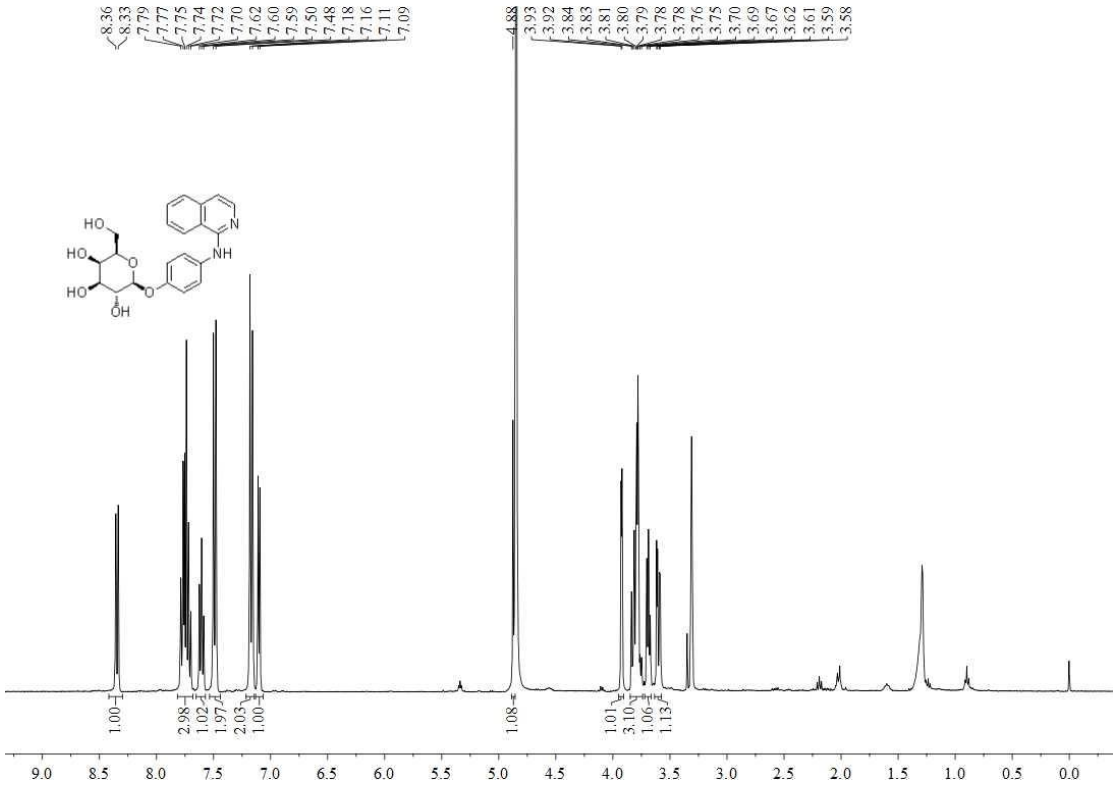
***N*-(4-methoxyphenyl)-1H-pyrrolo[3,2-c]pyridin-4-amine (80c)**

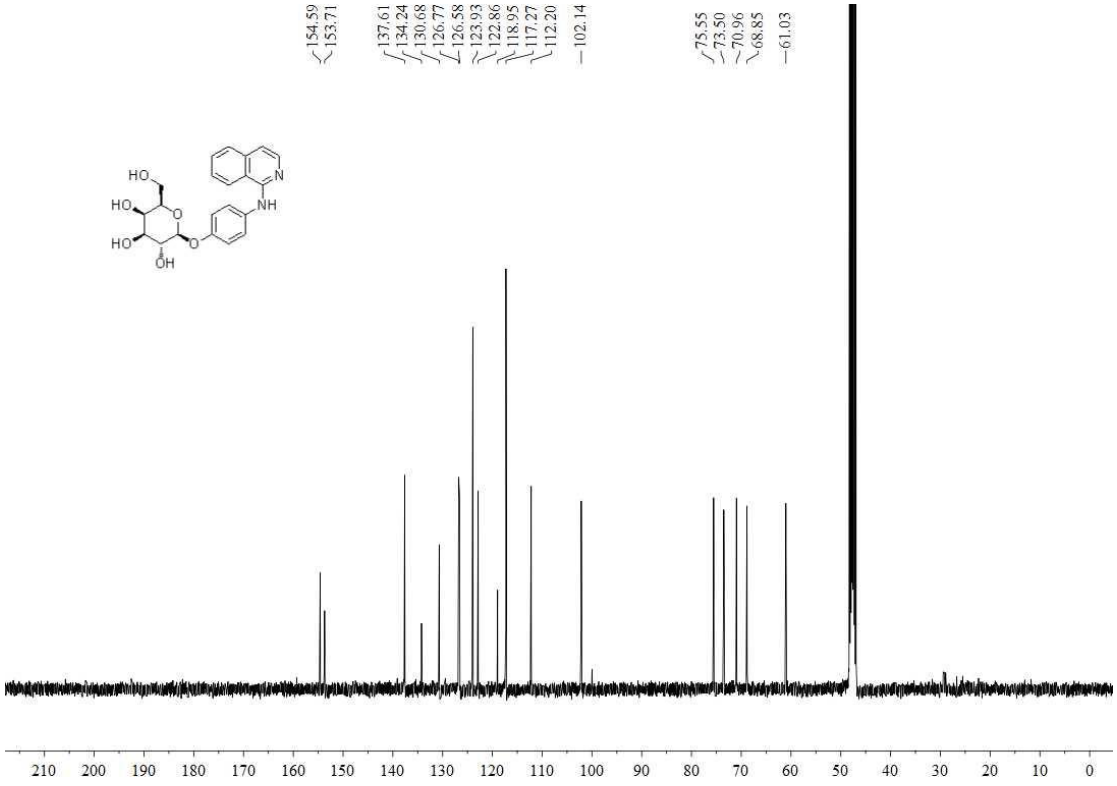


3-ethyl-3-(4-(isoquinolin-1-ylamino)phenyl)piperidine-2,6-dione (81c)

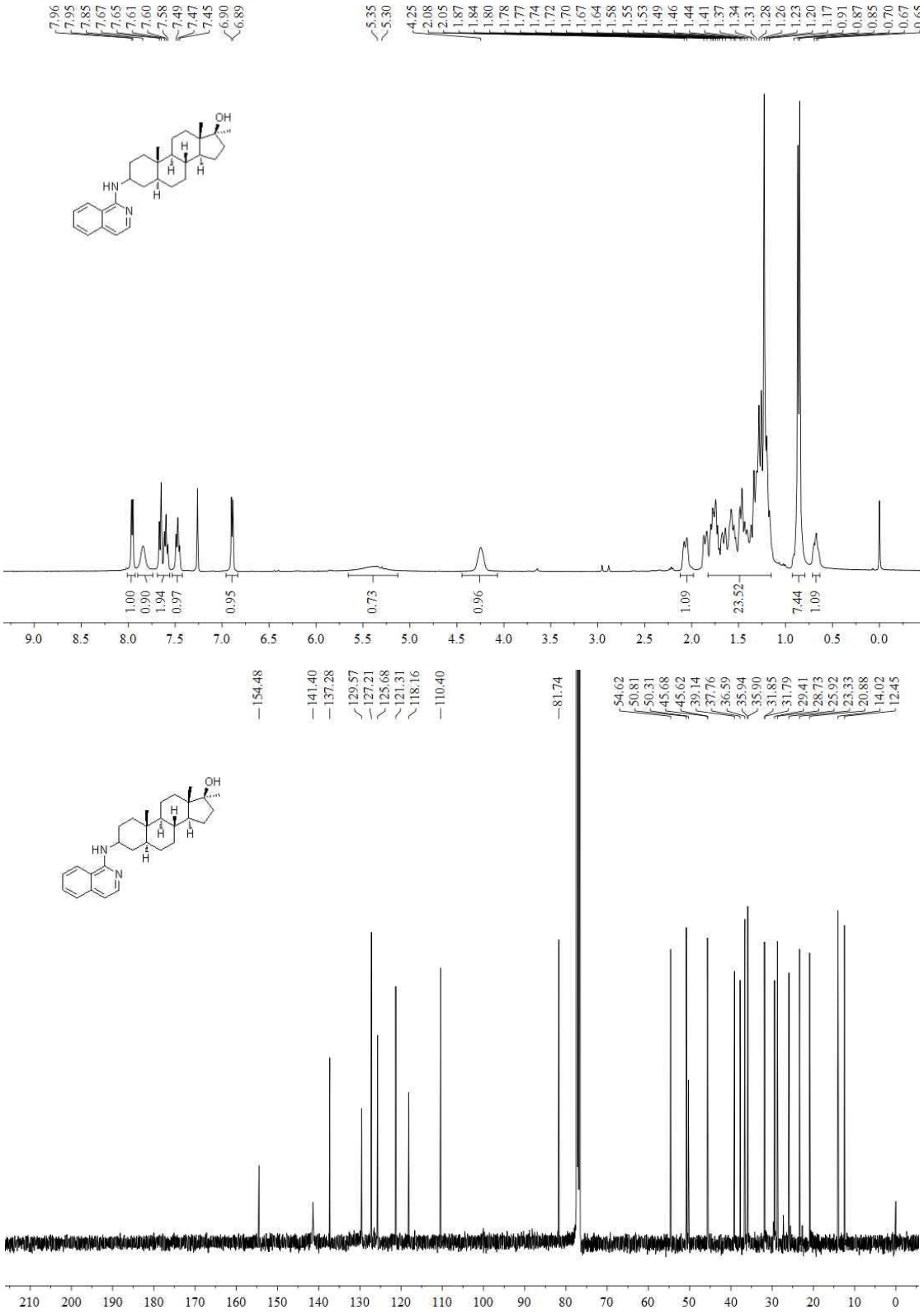


(2R,3R,4S,5R,6S)-2-(hydroxymethyl)-6-(4-(isoquinolin-1-ylamino)phenoxy)tetrahydro-2H-pyran-3,4,5-triol (82c)

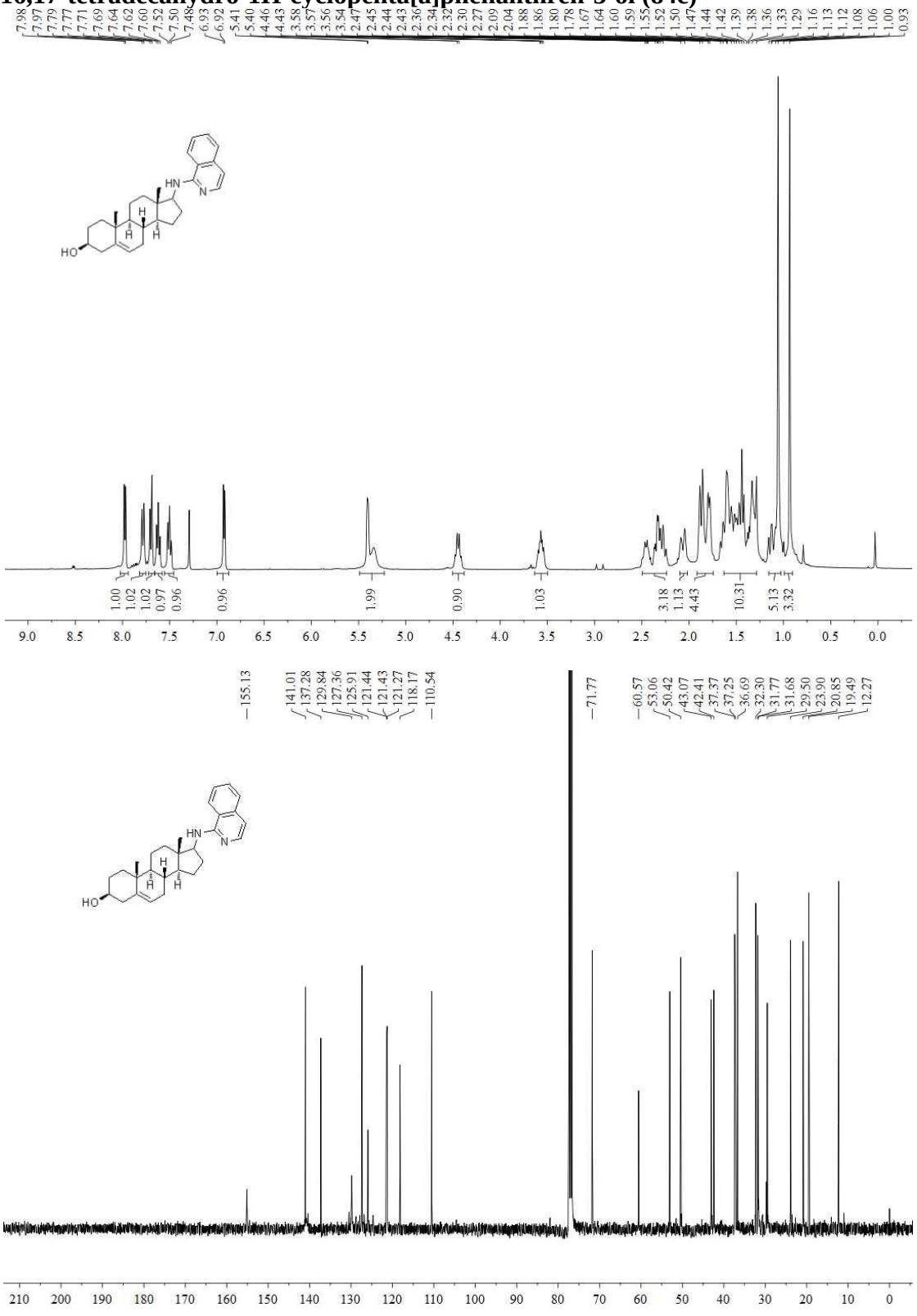




(5S,8R,9S,10S,13S,14S,17S)-3-(isoquinolin-1-ylamino)-10,13,17-trimethylhexadecahydro-1H-cyclopenta[a]phenanthren-17-ol (83c)



(3S,8R,9S,10R,13S,14S)-17-(isoquinolin-1-ylamino)-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-ol (84c)



***N*-methylquinolin-4-amine (85c)**