Supporting information

Metal-free electrochemistry promoted denitrogenative [4+2] annulation of 1,2,3-benzotriazinones with alkynes

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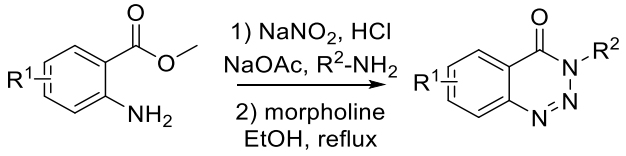
1. General Information

Unless otherwise noted, all reactions were carried out without exclusion of air or moisture. Commercial solvents and reagents were used without further purification. Analytical thin layer chromatography (TLC) was performed using silica gel GF254 plates. Column chromatography was performed using silica gel (300-400 mesh) eluting with petroleum ether and ethyl acetate. Nuclear magnetic resonance spectra (^{1}H NMR, ^{13}C NMR and ^{19}F NMR) were recorded with a Bruker Magnet system 400' 54 Ascend (^{1}H at 400 MHz, ^{13}C at 100 MHz and ^{19}F at 376 MHz). Unless otherwise noted, all spectra were acquired in $CDCl_3$. Chemical shifts are reported in parts per million (ppm, δ), downfield from tetramethylsilane (TMS, δ = 0.00 ppm) and are referenced to residual solvent ($CDCl_3$, δ = 7.26 ppm (^{1}H), 77.0 ppm (^{13}C)). Coupling constants were reported in hertz (Hz). High-resolution mass spectrometry was performed on an Agilent 1290-6540 UHPLC Q-Tof HR-MS System ESI spectrometer.

2. General Procedure for the Synthesis of 1,2,3-benzotriazin-4(3H)-ones [1]



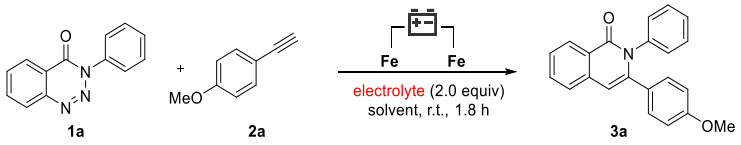
1a - 1j

To a mixture of methyl anthranilate (10 mmol, 1.0 equiv) in HCl (con., 2.5 mL) was drop-wise added a solution of $NaNO_2$ (11 mmol, 1.1 equiv) in water (5 mL) at 0 °C. The resulting solution was stirred for 30 min. Then, a solution of NaOAc (38 mmol, 3.8 equiv) in water (10 mL) was slowly added followed by addition of aryl amine (15 mmol, 1.5 equiv) at 0 °C. The resulting mixture was stirred at 0 °C for 5 h. The precipitate was collected by filtration, washed with cold water (50 ml), and purified by recrystallization from ethanol to afford triazene. The above triazene and morpholine (2.70 g, 30 mmol, 3.0 equiv.) were refluxed (oil bath) in ethanol (100 mL) until triazene was completely consumed by TLC. The reaction mixture was cooled to afford 1,2,3-benzotriazinones via crystallization.

3. Experimental Section

1) Conditions optimizing

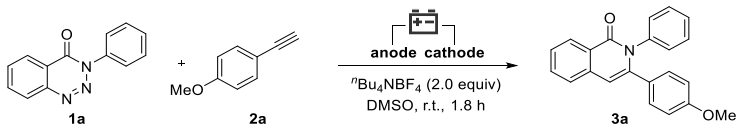
Table SI-1 Optimization of electrolytes and solvents[a]



entry	electrolytes	solvent	yield[b]
1	$^{n}Bu_4NBF_4$	DMSO	44
2	$^{n}Bu_4NBF_4$	DMF	trace
4	$^{n}Bu_4NBF_4$	MeCN	42
6	$^{n}Bu_4NBF_4$	THF	22
7	$^{n}Bu_4NBF_4$	1,4-dioxane	trace
8	$^{n}Bu_4NBF_4$	HFIP	Trace
14	$^{n}Bu_4NBF_4$	DMSO:H_2O = 40:1	55
15	$^{n}Bu_4NBF_4$	DMSO:H_2O = 20:1	68
16	$^{n}Bu_4NBF_4$	DMSO:H_2O = 10:1	70
17	$^{n}Bu_4NBF_4$	DMSO:H_2O = 8:1	78
18	$^{n}Bu_4NBF_4$	DMSO:H_2O = 8:1	64[c]
19	$^{n}Bu_4NBF_4$	DMSO:H_2O = 8:1	67[d]
	$^{n}Bu_4NPF_6$	DMSO:H_2O = 8:1	51
9	$^{n}Bu_4NClO_4$	DMSO:H_2O = 8:1	62
10	$^{n}Bu_4NOAc$	DMSO:H_2O = 8:1	36
11	KPF_6	DMSO:H_2O = 8:1	0
13	$^{n}Bu_4NBr$	DMSO	41
14	$^{n}Bu_4NBF_4$	DMSO:H_2O = 8:1	62[e]

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.4 mmol), electrolytes (2.0 equiv), solvent (4.5 mL), 10 mA, 1.8 h (3.4 F/mol), under Air. [b] Isolated yields. [c] 5 mA, 3.6 h was used. [d] 20 mA, 0.9 h. [e] DIPEA (2.0 equiv) was used.

Table SI-2 Optimization of electrodes[a]

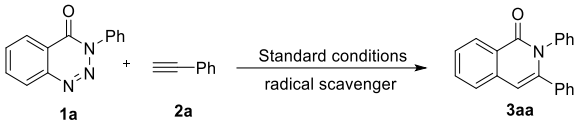


entry	anode	cathode	yield[b]
1	Fe	Graphite rod	42
2	Pt	Fe	39
3	Fe	Pt	49

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.4 mmol), $^{n}Bu_4NBF_4$ (0.4 mmol), DMSO:H_2O = 8:1 (4.5 mL), 10 mA, 1.8 h (3.4 F/mol), under Air. [b] Isolated yields.

2) Mechanism Studies

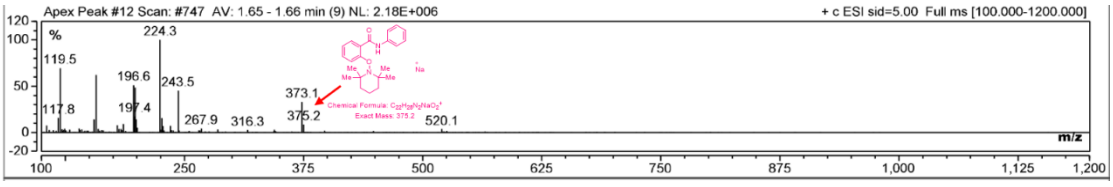
(1) radical trapping experiments



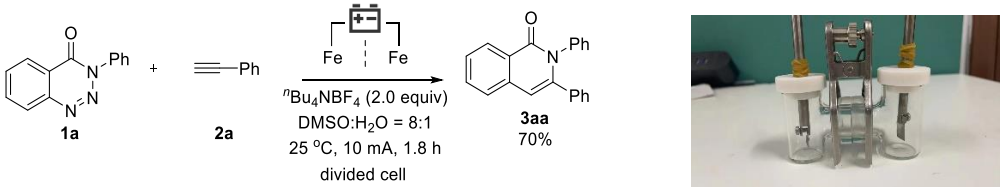
1a 2a 3aa

entry	radical scavenger	yield
1	TEMPO (2.0 equiv)	-
2	BHT (2.0 equiv)	-

A mixture of **1a** (1.0 equiv, 0.2 mmol), **2a** (3 equiv, 0.6 mmol), TEMPO or BHT (2.0 equiv, 0.4 mmol), and $^{n}Bu_4NBF_4$ (0.4 mmol, 2.0 equiv) in mixed DMSO (4.0 mL) and H_2O (0.5 mL) solution was added to a 20 mL oven-dried sealed tube with a magnetic stir bar. Subsequently, the tube was equipped with a Fe plate (anode, 20 mm × 10 mm × 0.1 mm) and a Fe plate (cathode, 20 mm × 10 mm × 5 mm), the distance between which was approximately 0.8 cm. All operations are performed in air. The constant current (10 mA) electrolysis was then performed at room temperature (Sealed tube) with vigorous stirring 1.8 h. Upon completion, the reaction mixture was poured into 20 mL H_2O and extracted with 50 mL EtOAc for three times. The combined organic layer was washed with 20 mL H_2O for two times and dried over anhydrous Na_2SO_4. Subsequently, the solvent was removed under reduced pressure. The resulting mixture was anlyzed by LC-MS. When TEMPO or BHT was present, the corresponding product **3aa** was not detected. Instead, the radical-trapped product **4** could be detected by LC-MS in the presence of TEMPO.



(2) divided cell experiments



1a 2a 3aa 70%

The reaction vessel is an H-type divided electrolytic cell (10 mL+ 10 mL) separated by a hydrogen

ion permeable membranel (Dupont N-117). And this H-type cell was equipped with a Fe anode (20 mm × 10 mm × 0.1 mm) and a Fe cathode (20 mm × 10 mm × 0.1 mm) and connected to a direct current (DC) regulated power supply. To the anodic chamber was added $^{n}Bu_4NBF_4$ (0.4 mmol, 2.0 equiv) in mixed DMSO (4.0 mL) and H_2O (0.5 mL). To the cathodic chamber was added **1a** (1.0 equiv, 0.2 mmol), **2a** (3 equiv, 0.6 mmol), and $^{n}Bu_4NBF_4$ (0.4 mmol, 2.0 equiv) in mixed DMSO (4.0 mL) and H_2O (0.5 mL). The resulting mixture was electrolyzed under constant current conditions (I = 10 mA) at room temperature for 1.8 h under magnetic stirring (air atmosphere). Upon completion of the reaction, the reaction mixture was poured into 20 mL H_2O and extracted with 50 mL EtOAc for three times. The combined organic layer was washed with 20 mL H_2O for two times and dried over anhydrous Na_2SO_4. Subsequently, the solvent was removed under reduced pressure. The resulting mixture was purified by chromatography on silica gel with PE/EA (40:1 to 20:1) to give the **3aa** (41.6 mg, 70%).

(3) CV experiments

The general procedure for cyclic voltammetry experiments: Cyclic voltammetry (CV) experiments were conducted in a 20 mL glass vial fitted with a platinum wire working electrode, a Ag/AgCl reference electrode, and a glassy carbon counter electrode (3 mm in diameter). All measurements were carried out in 20 mL anhydrous DMSO:H_2O = 8:1 with an electrolyte ($^{n}Bu_4NBF_4$, 2.0 equiv), using a scan rate of 100 mV/s.

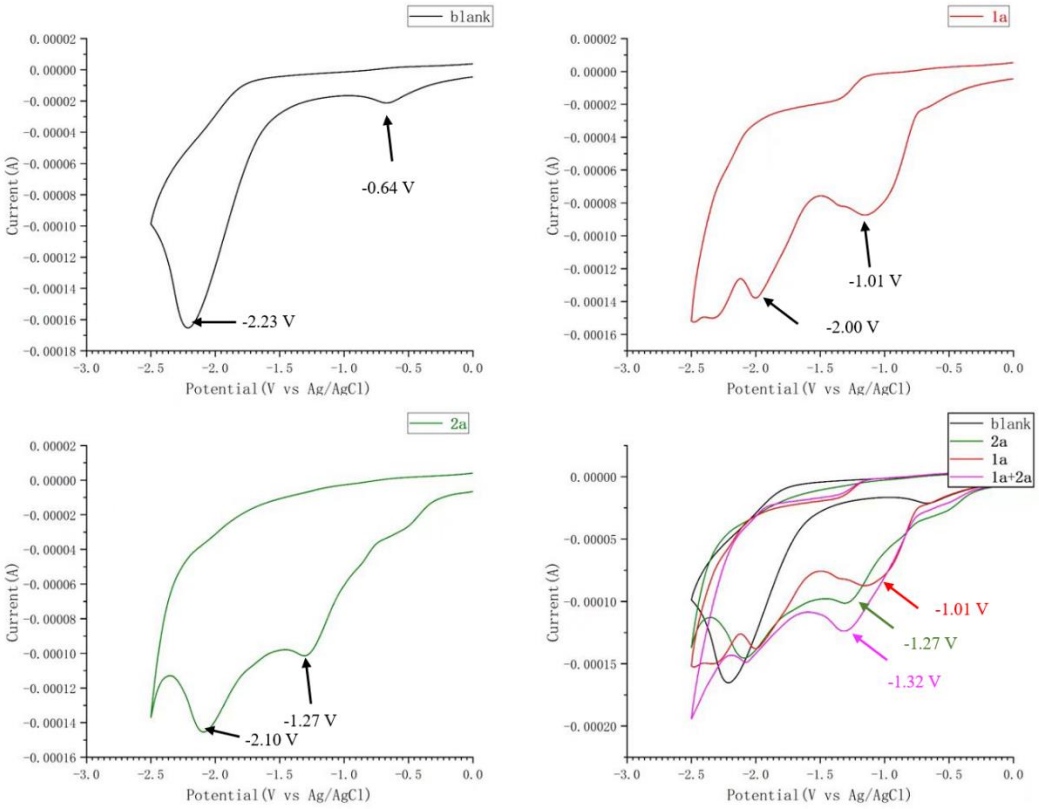
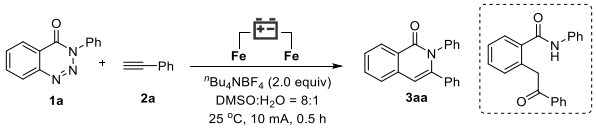


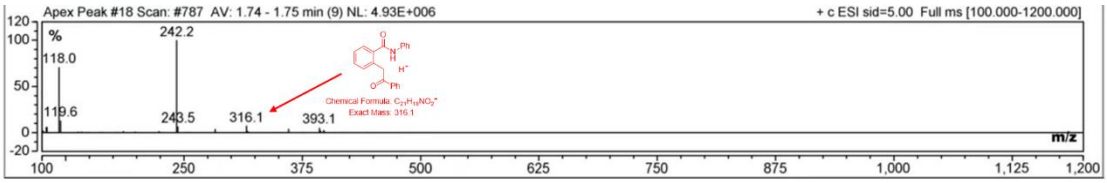
Figure SI-1 CV experiments of blank, **1a**, **2a,** and **1a**+**2a** in an electrolyte of $^{n}Bu_4NBF_4$ from -3.0V to 0.0 V at room temperature

(4) intermediate trapping experiments

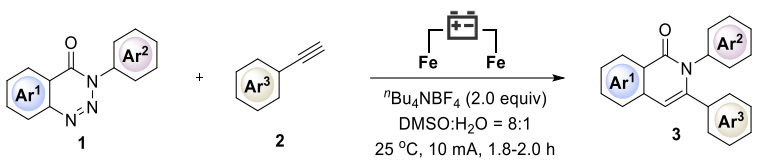


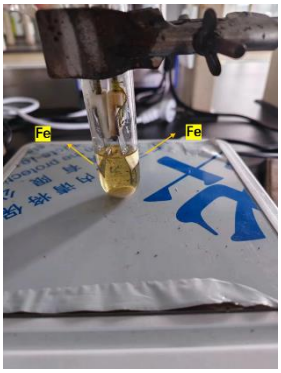
A mixture of **1a** (1.0 equiv, 0.2 mmol), alkyne **2a** (3 equiv, 0.6 mmol), and $^{n}Bu_4NBF_4$ (0.4 mmol, 2.0 equiv) in mixed DMSO (4.0 mL) and H_2O (0.5 mL) solution was added to a 20 mL oven-dried sealed tube with a magnetic stir bar. Subsequently, the tube was equipped with a Fe plate (anode, 20 mm × 10 mm × 0.1 mm) and a Fe plate (cathode, 20 mm × 10 mm × 5 mm), the distance between which was approximately 0.8 cm. All operations are performed in air. The constant current (10 mA) electrolysis was then performed at room temperature (Sealed tube) with vigorous stirring 0.5 h. Upon completion, the reaction mixture was poured into 20 mL H_2O and extracted with 50 mL

EtOAc for three times. The combined organic layer was washed with 20 mL H_2O for two times and dried over anhydrous Na_2SO_4. Subsequently, the solvent was removed under reduced pressure. The resulting mixture was anlyzed by LC-MS, the intermediate could be detected by LC-MS.



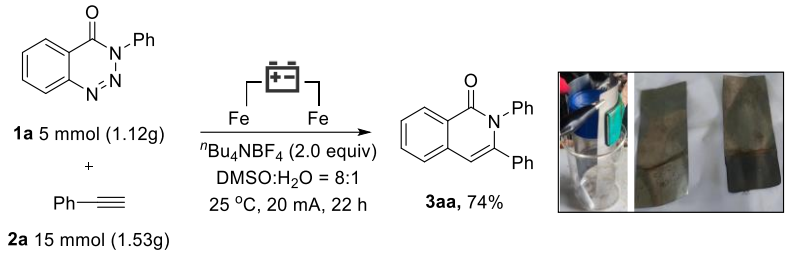
4. General Procedure for the Synthesis of Products 3





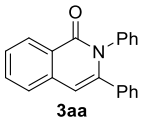
A mixture of **1** (1.0 equiv, 0.2 mmol), alkyne **2** (3 equiv, 0.6 mmol), and $^{n}Bu_4NBF_4$ (0.4 mmol, 2.0 equiv) in mixed DMSO (4.0 mL) and H_2O (0.5 mL) solution was added to a 20 mL oven-dried sealed tube with a magnetic stir bar. Subsequently, the tube was equipped with a Fe plate (anode, 20 mm × 10 mm × 0.1 mm) and a Fe plate (cathode, 20 mm × 10 mm × 5 mm), the distance between which was approximately 0.8 cm. All operations are performed in air. The constant current (10 mA) electrolysis was then performed at room temperature (Sealed tube) with vigorous stirring 1.8-2.0 h, 3.4-3.7 F/mol. Upon completion, the reaction mixture was poured into 20 mL H_2O and extracted with 50 mL EtOAc for three times. The combined organic layer was washed with 20 mL H_2O for two times and dried over anhydrous Na_2SO_4. Subsequently, the solvent was removed under reduced pressure. The resulting mixture was purified by chromatography on silica gel with PE/EA (100:1 to 6:1) to give the **3**.

Gram-scale:



A mixture of **1a** (1.0 equiv, 5.0 mmol), alkyne **2a** (3 equiv, 15 mmol), and $^{n}Bu_4NBF_4$ (10 mmol, 2.0 equiv) in mixed DMSO (80 mL) and H_2O (10 mL) solution was added to a 150 mL oven-dried beaker with a magnetic stir bar. Subsequently, the beaker was equipped with a Fe plate (anode, 20 cm × 10 cm × 0.1 mm) and a Fe plate (cathode, 20 cm × 10 cm × 0.1 mm), the distance between which was approximately 2.5cm. All operations are performed in air. The constant current (20 mA) electrolysis was then performed at room temperature with vigorous stirring 22 h. Upon completion, the reaction mixture was poured into 100 mL H_2O and extracted with 150 mL EtOAc for three times. The combined organic layer was washed with 100 mL H_2O for two times and dried over anhydrous Na_2SO_4. Subsequently, the solvent was removed under reduced pressure. The resulting mixture was purified by chromatography on silica gel with PE/EA (50:1 to 30:1) to give the **3aa** (1.10 g, 74%).

5. Characterization Data of the Product

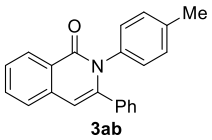


3aa

2,3-diphenylisoquinolin-1(2*H*)-one (3aa)

3aa was prepared according to general procedure; Eluent: petroleum ether/ethyl acetate (50:1); White solid (46.4 mg, 78%). M.P.: 177.4-178.7 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (d, J = 7.9 Hz, 1H), 7.72-7.68 (m, 1H), 7.56 (d, J = 7.9 Hz, 1H), 7.51 (t, J = 7.5 Hz, 1H), 7.29-7.25 (m, 2H),

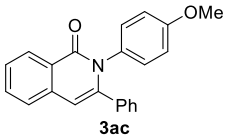
7.23-7.03 (m, 8H), 6.60 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.1, 143.5, 139.0, 136.7, 136.2, 132.8, 129.4, 129.2, 128.6, 128.3, 128.0, 127.8, 127.6, 126.9, 126.0, 125.4, 107.9. These data are consistent with that in the literature.[2]



3ab

3-phenyl-2-(*p*-tolyl)isoquinolin-1(2*H*)-one (3ab)

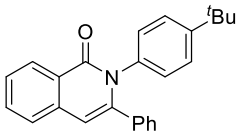
3ab was prepared according to general procedure; Eluent: petroleum ether/ethyl acetate (50:1); White solid (38.6 mg, 62%). M.P.: 157.4-159.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.66-7.70 (m, 1H), 7.61-7.43 (m, 2H), 7.23-7.12 (m, 5H), 7.06 (d, *J* = 8.1 Hz, 2H), 7.00 (d, *J* = 8.3 Hz, 2H), 6.59 (s, 1H), 2.28 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.2, 143.7, 137.4, 136.7, 136.4, 136.3, 132.7, 129.3, 129.3, 129.0, 128.4, 127.9, 127.8, 126.8, 126.0, 125.4, 107.8, 21.1. These data are consistent with that in the literature.[2]



3ac

2-(4-methoxyphenyl)-3-phenylisoquinolin-1(2*H*)-one (3ac)

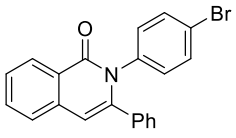
3ac was prepared according to general procedure; Eluent: petroleum ether/ethyl acetate (10:1); White solid (36.7 mg, 56%). M.P.: 173.5-175.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (d, *J* = 8.0 Hz, 1H), 7.66-7.70 (m, 1H), 7.60-7.43 (m, 2H), 7.23-7.14 (m, 5H), 7.03 (d, *J* = 8.9 Hz, 2H), 6.78 (d, *J* = 8.9 Hz, 2H), 6.59 (s, 1H), 3.75 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.3, 158.5, 143.9, 136.7, 136.3, 132.7, 131.8, 130.2, 129.2, 128.3, 127.9, 127.8, 126.8, 126.0, 125.4, 113.9, 107.7, 55.3. These data are consistent with that in the literature.[2]



3ad

2-(4-(*tert*-butyl)phenyl)-3-phenylisoquinolin-1(2*H*)-one (3ad)

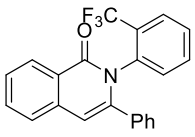
3ad was prepared according to general procedure; Eluent: petroleum ether/ethyl acetate (50:1); White solid (48.8 mg, 69%). M.P.: 161.2-164.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.71-7.61 (m, 1H), 7.59-7.45 (m, 2H), 7.29-7.21 (m, 2H), 7.18-7.11 (m, 5H), 7.06-6.96 (m, 2H), 6.59 (s, 1H), 1.24 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.2, 150.5, 143.8, 136.8, 136.3, 136.3, 132.7, 129.2, 128.7, 128.4, 127.9, 127.7, 126.8, 126.0, 125.5, 125.4, 107.8, 34.5, 31.2. These data are consistent with that in the literature.[3]



3ae

2-(4-bromophenyl)-3-phenylisoquinolin-1(2*H*)-one (3ae)

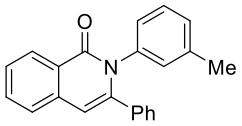
3ae was prepared according to general procedure; Eluent: petroleum ether/ethyl acetate (50:1); White solid (38.4 mg, 51%). M.P.: 164.5-167.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (d, *J* = 8.0 Hz, 1H), 7.73-7.66 (m, 1H), 7.59-7.49 (m, 2H), 7.39 (d, *J* = 8.6 Hz, 2H), 7.25-7.09 (m, 5H), 7.01 (d, *J* = 8.6 Hz, 2H), 6.61 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.9, 143.1, 138.1, 136.7, 135.8, 133.0, 131.8, 131.0, 129.2, 128.3, 128.3, 128.1, 127.1, 126.1, 125.2, 121.6, 108.2. These data are consistent with that in the literature.[3]



3af

3-phenyl-2-(2-(trifluoromethyl)phenyl)isoquinolin-1(2*H*)-one (3af)

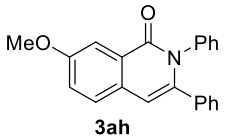
3af was prepared according to general procedure; Eluent: petroleum ether/ethyl acetate (50:1); White solid (29.9 mg, 41%). M.P.: 167.1-169.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (d, *J* = 7.8 Hz, 1H), 7.77-7.66 (m, 1H), 7.66-7.45 (m, 4H), 7.42-7.35 (m, 1H), 7.28-7.24 (m, 1H), 7.23-7.13 (m, 5fH), 6.59 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.2, 143.4, 136.8, 135.3, 133.6, 133.0, 132.6, 132.2, 129.7, 128.8, 128.4 (q, *J* = 32.8 Hz), 127.6, 127.8, 127.1 (q, *J* = 4.1 Hz), 126.1, 126.1, 122.9 (q, *J* = 270.4 Hz), 108.1. HRMS calcd. for: $C_{22}H_{15}F_3NO$ $[M+H]^+$ 366.1100, found 366.1097.



3ag

3-phenyl-2-(*m*-tolyl)isoquinolin-1(2*H*)-one (3ag)

3ag was prepared according to general procedure; Eluent: petroleum ether/ethyl acetate (50:1); White solid (41.1 mg, 66%). M.P.: 164.1-167.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.72-7.66 (m, 1H), 7.62-7.46 (m, 2H), 7.31-7.24 (m, 2H), 7.24-7.16 (m, 1H), 7.16-7.10 (m, 2H), 7.08-6.96 (m, 3H), 6.96-6.91 m, 1H), 6.60 (s, 1H), 2.22 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.1, 143.7, 139.1, 137.5, 136.8, 136.1, 132.7, 129.9, 129.4, 128.7, 128.5, 128.3, 127.6, 126.8, 126.4, 126.0, 125.4, 107.7, 21.2. HRMS calcd. for:$C_{22}H_{18}NO$ $[M+H]^+$ 283.1264, found 283.1264.

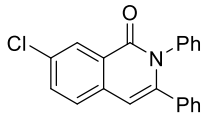


3ah

7-methoxy-2,3-diphenylisoquinolin-1(2*H*)-one (3ah)

3ag was prepared according to general procedure; Eluent: petroleum ether/ethyl acetate (10:1); Yellow solid (41.8 mg, 64%). M.P.: 200.4-203.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 2.7

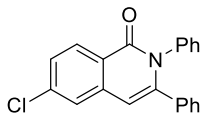
Hz, 1H), 7.50 (d, *J* = 8.7 Hz, 1H), 7.35-7.22 (m, 3H), 7.22-7.18 (m, 1H), 7.18-7.10 (m, 7H), 6.58 (s, 1H), 3.94 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.8, 158.9, 141.3, 139.2, 136.3, 130.8, 129.4, 129.3, 128.5, 127.8, 127.7, 127.7, 127.6, 126.5, 123.3, 108.1, 107.7, 55.6. These data are consistent with that in the literature.[3]



3ai

7-chloro-2,3-diphenylisoquinolin-1(2*H*)-one (3ai)

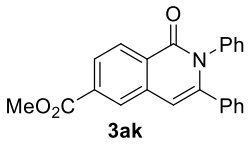
3ai was prepared according to general procedure; Eluent: petroleum ether/ethyl acetate (50:1); White solid (44.5 mg, 67%). M.P.: 184.3-186.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (d, *J* = 2.2 Hz, 1H), 7.66-7.60 (m, 1H), 7.54-7.48 (m, 1H), 7.32-7.23 (m, 2H), 7.24-7.13 (m, 7H), 7.13-7.08 (m, 1H), 6.57 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.1, 144.0, 138.8, 135.9, 135.1, 133.2, 132.8, 129.3, 129.2, 128.7, 128.2, 127.9, 127.8, 127.8, 127.6, 126.5, 107.1. HRMS calcd. for: $C_{21}H_{14}ClNNaO$ $[M+Na]^+$ 354.0662, found 354.0655.



3aj

6-chloro-2,3-diphenylisoquinolin-1(2*H*)-one (3aj)

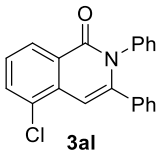
3ai was prepared according to general procedure; Eluent: petroleum ether/ethyl acetate (50:1); Yellow solid (39.1 mg, 59%). M.P.: 195.3-198.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (d, *J* = 8.6 Hz, 1H), 7.54 (d, *J* = 1.9 Hz, 1H), 7.45 (dd, *J* = 8.6, 2.0 Hz, 1H), 7.30-7.24 (m, 2H), 7.23-7.05 (m, 8H), 6.51 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.5, 145.1, 139.2, 138.7, 138.0, 135.8, 130.2, 129.3, 129.2, 128.7, 128.3, 127.9, 127.8, 127.4, 125.2, 123.7, 106.7. These data are consistent with that in the literature.[3]



3ak

methyl 1-oxo-2,3-diphenyl-1,2-dihydroisoquinoline-6-carboxylate (3ak)

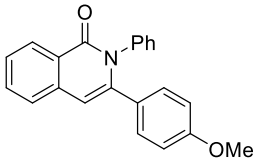
3ak was prepared according to general procedure; Eluent: petroleum ether/ethyl acetate (10:1); Colorless liquid (26.3 mg, 37%).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (d, *J* = 8.4 Hz, 1H), 8.27 (d, *J* = 1.6 Hz, 1H), 8.10 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.31-7.26 (m, 2H), 7.24-7.15 (m, 6H), 7.15-7.08 (m, 2H), 6.66 (s, 1H), 4.00 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.5, 162.6, 144.5, 138.8, 136.5, 135.8, 133.8, 129.2, 129.2, 128.7, 128.7, 128.2, 128.2, 128.1, 127.9, 127.9, 126.8, 107.7, 52.6. HRMS calcd. for: $C_{23}H_{18}NO_3$ $[M+H]^+$ 356.1281, found 356.1287.



3al

5-chloro-2,3-diphenylisoquinolin-1(2*H*)-one (3al)

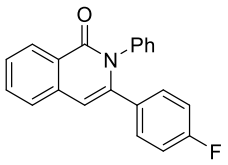
3al was prepared according to general procedure; Eluent: petroleum ether/ethyl acetate (50:1); White solid (41.8 mg, 63%). M.P.: 190.7-194.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (d, *J* = 8.0 Hz, 1H), 7.75 (dd, *J* = 7.7, 1.1 Hz, 1H), 7.43 (t, *J* = 7.9 Hz, 1H), 7.32-7.25 (m, 2H), 7.24-7.16 (m, 6H), 7.14-7.07 (m, 2H), 6.96 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.5, 144.8, 138.7, 136.0, 134.6, 132.9, 130.5, 129.2, 128.7, 128.3, 127.9, 127.9, 127.3, 127.0, 126.9, 125.9, 103.9. These data are consistent with that in the literature.[3]



3ba

3-(4-methoxyphenyl)-2-phenylisoquinolin-1(2*H*)-one (3ba)

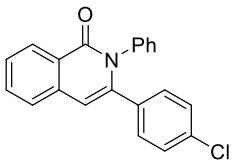
3al was prepared according to general procedure; Eluent: petroleum ether/ethyl acetate (10:1); Colorless liquid (47.4 mg, 72%).[1]H NMR (400 MHz, $CDCl_3$) δ 8.45 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.73-7.64 (m, 1H), 7.60-7.54 (m, 1H), 7.53-7.46 (m, 1H), 7.33-7.24 (m, 2H), 7.25-7.19 (m, 1H), 7.15-7.10 (m, 2H), 7.10-7.04 (m, 2H), 6.72-6.67 (m, 2H), 6.58 (s, 1H), 3.74 (s, 3H). [13]C NMR (100 MHz, $CDCl_3$) δ 163.2, 159.1, 143.3, 139.1, 136.8, 132.7, 130.5, 129.3, 128.6, 128.6, 128.3, 127.6, 126.7, 125.9, 125.2, 113.2, 107.7, 55.1. These data are consistent with that in the literature.[2]



3ca

3-(4-fluorophenyl)-2-phenylisoquinolin-1(2*H*)-one (3ca)

3ca was prepared according to general procedure; Eluent: petroleum ether/ethyl acetate (50:1); White solid (42.9 mg, 68%). M.P.: 206.7-208.5 °C. [1]H NMR (400 MHz, $CDCl_3$) δ 8.44 (d, *J* = 9.3 Hz, 1H), 7.67 (t, *J* = 8.2 Hz, 1H), 7.56-7.44 (m, 2H), 7.31-7.22 (m, 2H), 7.22-7.16 (m, 1H), 7.14-7.02 (m, 4H), 6.84 (t, *J* = 8.6 Hz, 2H), 6.56 (s, 1H). [13]C NMR (100 MHz, $CDCl_3$) δ 162.2 (d, *J* = 248.9 Hz), 163.0, 142.5, 139.0, 136.6, 132.8, 132.3 (d, *J* = 3.6 Hz), 131.1 (d, *J* = 8.3 Hz), 129.3, 128.7, 128.4, 127.8, 127.1, 126.0, 125.5, 114.9 (d, *J* = 21.7 Hz), 108.0. These data are consistent with that in the literature.[3]

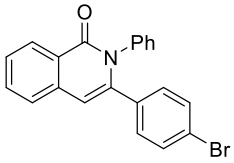


3da

3-(4-chlorophenyl)-2-phenylisoquinolin-1(2*H*)-one (3da)

3da was prepared according to general procedure; Eluent: petroleum ether/ethyl acetate (50:1); White solid (45.8 mg, 69%). M.P.: 190.7-193.5 °C. [1]H NMR (400 MHz, $CDCl_3$) δ 8.42 (dd, *J* = 8.1,

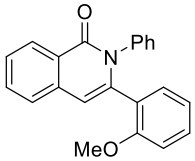
1.2 Hz, 1H), 7.73-7.58 (m, 1H), 7.58-7.44 (m, 2H), 7.34-7.16 (m, 3H), 7.15-7.02 (m, 6H), 6.54 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.9, 142.3, 138.8, 136.5, 134.6, 134.1, 132.8, 130.4, 129.3, 128.8, 128.3, 128.1, 127.8, 127.1, 126.0, 125.4, 108.1. These data are consistent with that in the literature.[3]



3ea

3-(4-bromophenyl)-2-phenylisoquinolin-1(2*H*)-one (3ea)

3ea was prepared according to general procedure; Eluent: petroleum ether/ethyl acetate (50:1); White solid (30.8 mg, 41%). M.P.: 188.3-191.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.75-7.66 (m, 1H), 7.61-7.45 (m, 2H), 7.34-7.27 (m, 4H), 7.26-7.19 (m, 1H), 7.15-7.08 (m, 2H), 7.06-6.99 (m, 2H), 6.58 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.0, 142.3, 138.8, 136.5, 135.1, 132.9, 131.1, 130.7, 129.3, 128.8, 128.4, 127.9, 127.2, 126.1, 125.5, 122.4, 108.1. These data are consistent with that in the literature.[2]

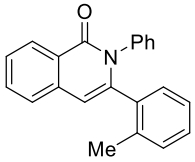


3fa

3-(2-methoxyphenyl)-2-phenylisoquinolin-1(2*H*)-one (3fa)

3fa was prepared according to general procedure; Eluent: petroleum ether/ethyl acetate (10:1); White solid (27.5 mg, 42%). M.P.: 139.1-141.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.68-7.63 (m, 1H), 7.60-7.45 (m, 2H), 7.45-7.04 (m, 6H), 6.88-6.83 (m, 2H), 6.60-6.53 (m, 2H), 3.57 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.0, 156.0, 141.2, 138.8, 136.9,

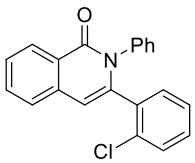
132.5, 131.1, 130.4, 128.2, 127.5, 126.7, 125.9, 125.7, 125.3, 120.0, 110.0, 107.5, 54.7. These data are consistent with that in the literature.[4]



3ga

2-phenyl-3-(*o*-tolyl)isoquinolin-1(2*H*)-one (3ga)

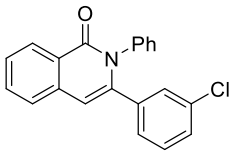
3ga was prepared according to general procedure; Eluent: petroleum ether/ethyl acetate (50:1); White solid (37.4 mg, 60%). M.P.: 139.1-141.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.78-7.65 (m, 1H), 7.59-7.48 (m, 2H), 7.25-7.07 (m, 7H), 7.03 (t, *J* = 6.8 Hz, 2H), 6.51 (s, 1H), 2.21 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.1, 142.7, 138.6, 136.7, 136.0, 135.4, 132.7, 130.6, 129.8, 128.5, 128.4, 128.3, 127.8, 126.8, 125.9, 125.5, 125.0, 107.4, 20.1. HRMS calcd. for:$C_{22}H_{18}NO$ $[M+H]^+$ 283.1264, found 283.1268.



3ha

3-(2-chlorophenyl)-2-phenylisoquinolin-1(2*H*)-one (3ha)

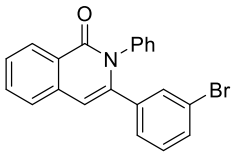
3ha was prepared according to general procedure; Eluent: petroleum ether/ethyl acetate (50:1); White solid (44.5 mg, 67%). M.P.: 186.4-188.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.75-7.67 (m, 1H), 7.61-7.48 (m, 2H), 7.43-7.32 (m, 1H), 7.25-6.99 (m, 8H), 6.56 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.9, 140.3, 138.5, 136.5, 134.9, 133.5, 132.7, 132.0, 129.9, 129.3, 129.2, 128.7, 128.4, 128.3, 128.0, 127.2, 126.1, 126.0, 125.8, 108.0. These data are consistent with that in the literature.[5]



3ia

3-(3-chlorophenyl)-2-phenylisoquinolin-1(2*H*)-one (3ia)

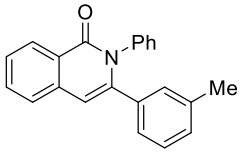
3ia was prepared according to general procedure; Eluent: petroleum ether/ethyl acetate (50:1); White solid (40.5 mg, 61%). M.P.: 166.4-169.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (d, *J* = 8.1 Hz, 1H), 7.74-7.67 (m, 1H), 7.64-7.47 (m, 2H), 7.38-7.20 (m, 4H), 7.19-7.05(m, 4H), 7.04-6.98 (m, 1H), 6.60 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.9, 142.0, 138.7, 137.8, 136.5, 133.8, 132.9, 129.3, 129.3, 129.0, 128.8, 128.4, 128.2, 127.9, 127.5, 127.3, 126.1, 125.6, 108.2. These data are consistent with that in the literature.[6]



3ja

3-(3-bromophenyl)-2-phenylisoquinolin-1(2*H*)-one (3ja)

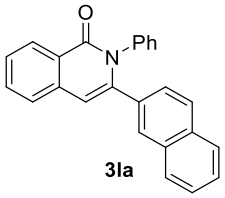
3ja was prepared according to general procedure; Eluent: petroleum ether/ethyl acetate (50:1); White solid (32.3 mg, 43%). M.P.: 186.7-189.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.69-7.62 (m, 1H), 7.57-7.45 (m, 2H), 7.35-7.31 (m, 1H), 7.30-7.16 (m, 4H), 7.12-7.05 (m, 2H), 7.04-6.93 (m, 2H), 6.55 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.9, 141.9, 138.7, 138.0, 136.4, 132.9, 132.1, 131.1, 129.3, 129.2, 128.8, 128.4, 127.9, 127.9, 127.3, 126.1, 125.5, 121.8, 108.2. These data are consistent with that in the literature.[5]



3ka

2-phenyl-3-(*m*-tolyl)isoquinolin-1(2*H*)-one (3ka)

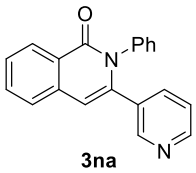
3ka was prepared according to general procedure; Eluent: petroleum ether/ethyl acetate (50:1); White solid (38.6 mg, 62%). M.P.: 125.8-128.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.72-7.66 (m, 1H), 7.62-7.47 (m, 2H), 7.31-7.24 (m, 2H), 7.23-7.17 (m, 1H), 7.15-7.11 (m, 2H), 7.08-6.97 (m, 3H), 6.96-6.91 (m, 1H), 6.60 (s, 1H), 2.22 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.1, 143.7, 139.1, 137.5, 136.8, 136.1, 132.7, 129.9, 129.4, 128.7, 128.5, 128.3, 127.6, 126.8, 126.4, 126.0, 125.4, 107.7, 21.2. These data are consistent with that in the literature.[5]



3la

3-(naphthalen-2-yl)-2-phenylisoquinolin-1(2*H*)-one (3la)

3la was prepared according to general procedure; Eluent: petroleum ether/ethyl acetate (50:1); White solid (52.8 mg, 76%). M.P.: 196.1-198.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (d, *J* = 8.0 Hz, 1H), 7.84-7.67 (m, 4H), 7.64-7.51 (m, 3H), 7.50-7.44 (m, 2H), 7.29-7.11 (m, 6H), 6.71 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.1, 143.5, 139.0, 136.8, 133.8, 132.8, 132.7, 132.4, 129.4, 128.6, 128.5, 128.4, 128.0, 127.7, 127.6, 127.2, 127.0, 126.6, 126.5, 126.4, 126.1, 125.4, 108.4. These data are consistent with that in the literature.[2]

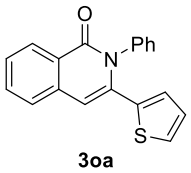


3na

2-phenyl-3-(pyridin-3-yl)isoquinolin-1(2*H*)-one (3na)

3na was prepared according to general procedure; Eluent: petroleum ether/ethyl acetate (10:1 - 2:1); White solid (43.7 mg, 73%). M.P.: 193.4-194.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55-8.51 (m, 1H), 8.50-8.45 (m, 1H), 8.43 (dd, *J* = 4.9, 1.7 Hz, 1H), 7.76-7.69 (m, 1H), 7.64-7.51 (m, 2H), 7.43-

7.36 (m, 1H), 7.36-7.27 (m, 2H), 7.26-7.21 (m, 1H), 7.16-7.11 (m, 2H), 7.10-7.05 (m, 1H), 6.63 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.9, 149.5, 149.1, 140.0, 138.5, 136.4, 136.3, 133.0, 132.2, 129.4, 129.0, 128.4, 128.1, 127.5, 126.2, 125.7, 122.5, 108.7. These data are consistent with that in the literature.[5]



3oa

2-phenyl-3-(thiophen-2-yl)isoquinolin-1(2*H*)-one (3oa)

3oa was prepared according to general procedure; Eluent: petroleum ether/ethyl acetate (40:1 - 20:1); White solid (42.5 mg, 70%). M.P.: 179.2-179.6 °C.^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.76-7.66 (m, 1H), 7.62-7.55 (m, 1H), 7.55-7.49 (m, 1H), 7.42-7.30 (m, 3H), 7.25-7.18 (m, 3H), 6.83-6.79 (m, 2H), 6.74 (dd, *J* = 3.6, 1.3 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.1, 139.1, 137.2, 136.7, 136.5, 132.9, 129.3, 129.0, 128.8, 128.3, 128.3, 127.3, 127.2, 126.6, 126.1, 125.5, 108.7. HRMS calcd. for: C19H14NOS $[M+H]^+$ 304.0791, found 304.0791.

6. References

[1] K. Madasamy, M. H. Balakrishnan, R. Korivi, S. Mannathan, *J. Org. Chem.* **2022**, *87*, 8752-8756.

[2] D. Y. Li, X. S. Shang, G. R. Chen, P. N. Liu, *Org. Lett.* **2013**, *15*, 3848-3851.

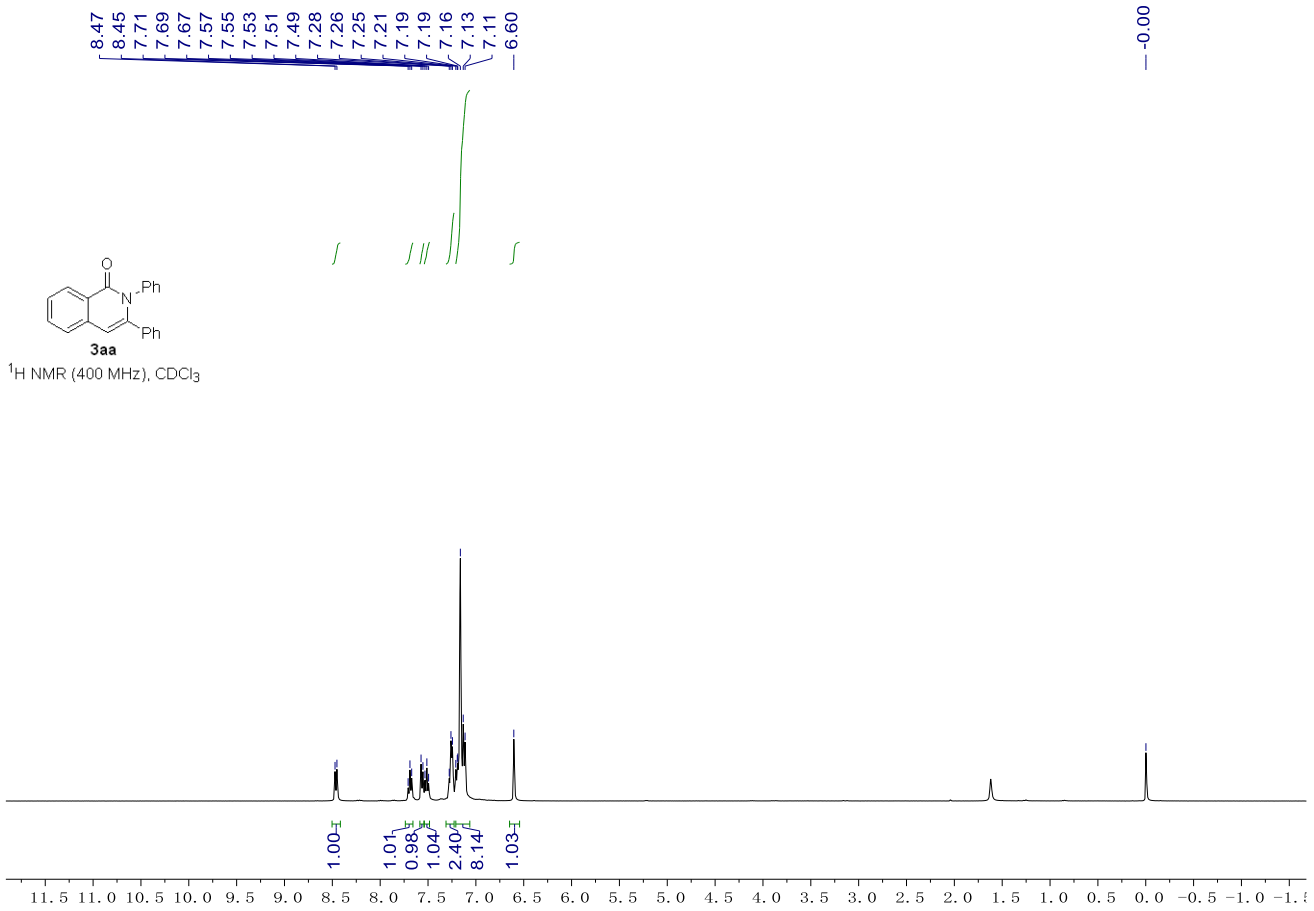
[3] M. Zhang, H.-J. Zhang, W. Ruan, T.-B. Wen, *Eur. J. Org. Chem.* **2015**, *2015*, 5914-5918.

[4] H. Wang, S. Yu, *Org. Lett.* **2015**, *17*, 4272-4275.

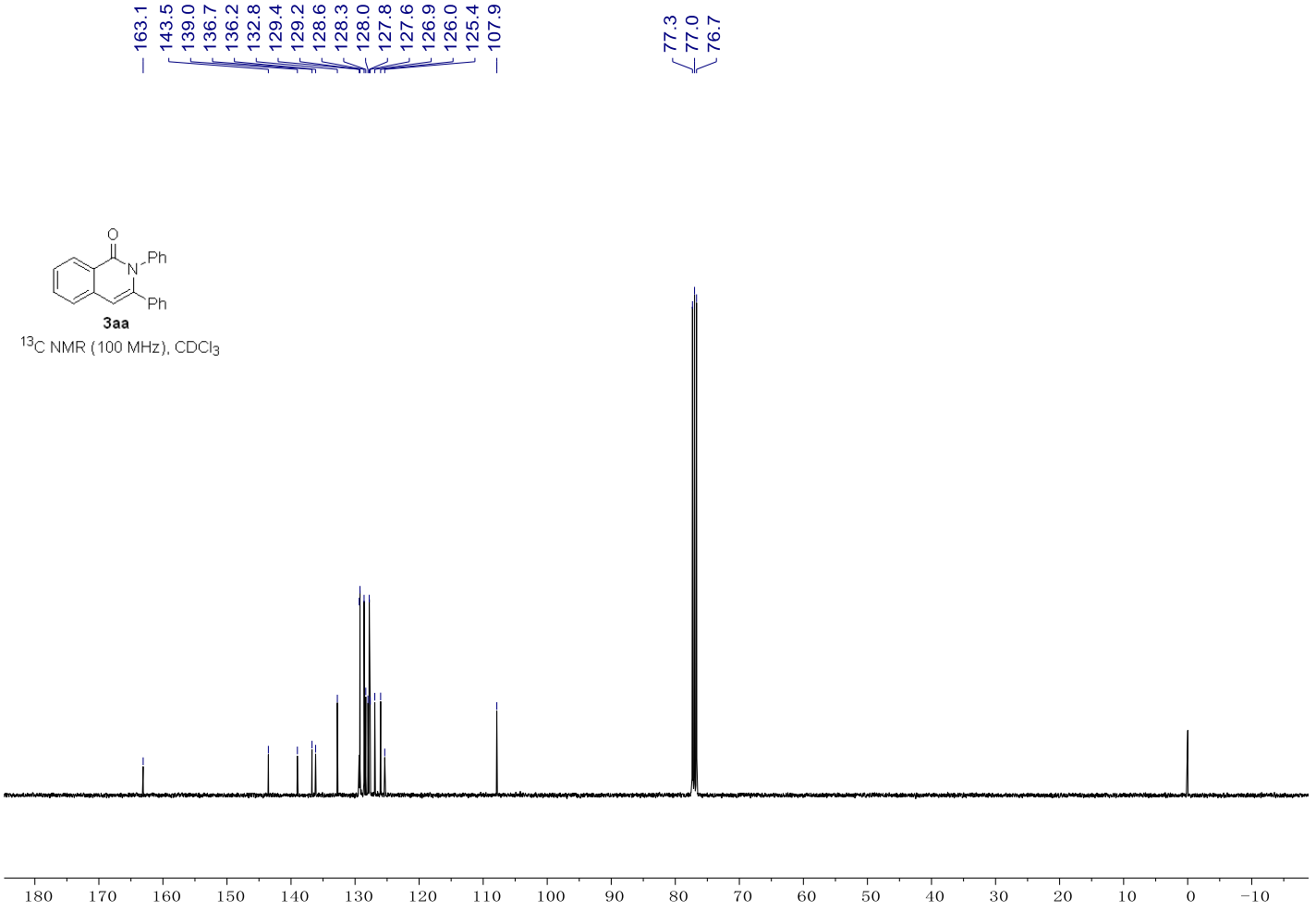
[5] H. Xie, Q. Xing, Z. Shan, F. Xiao, G.-J. Deng, *Adv. Synth. Catal.* **2019**, *361*, 1896-1901.

7. ^{1}H and ^{13}C Spectrums of Compounds

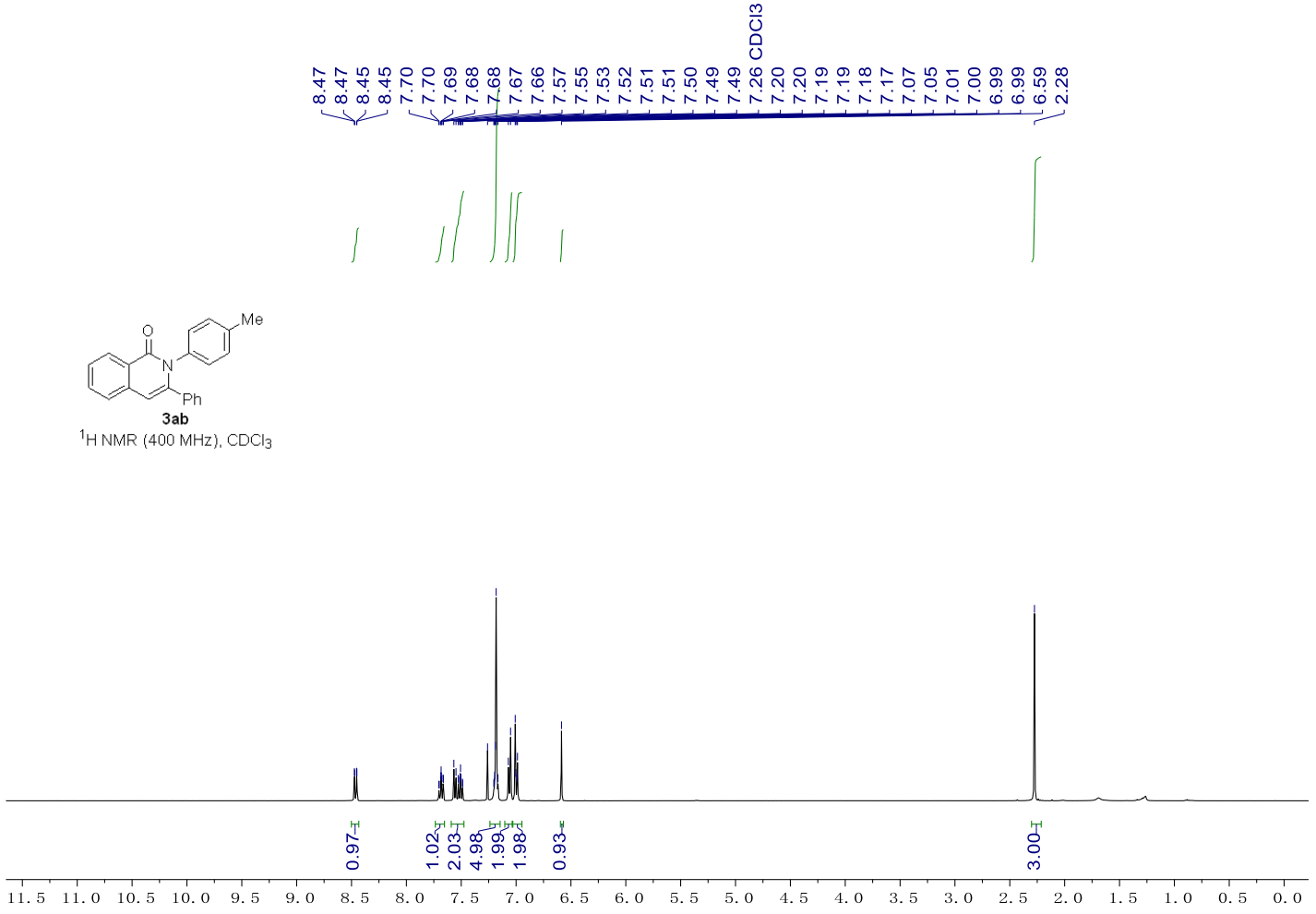
^{1}H NMR of 2,3-diphenylisoquinolin-1(2*H*)-one (3aa)



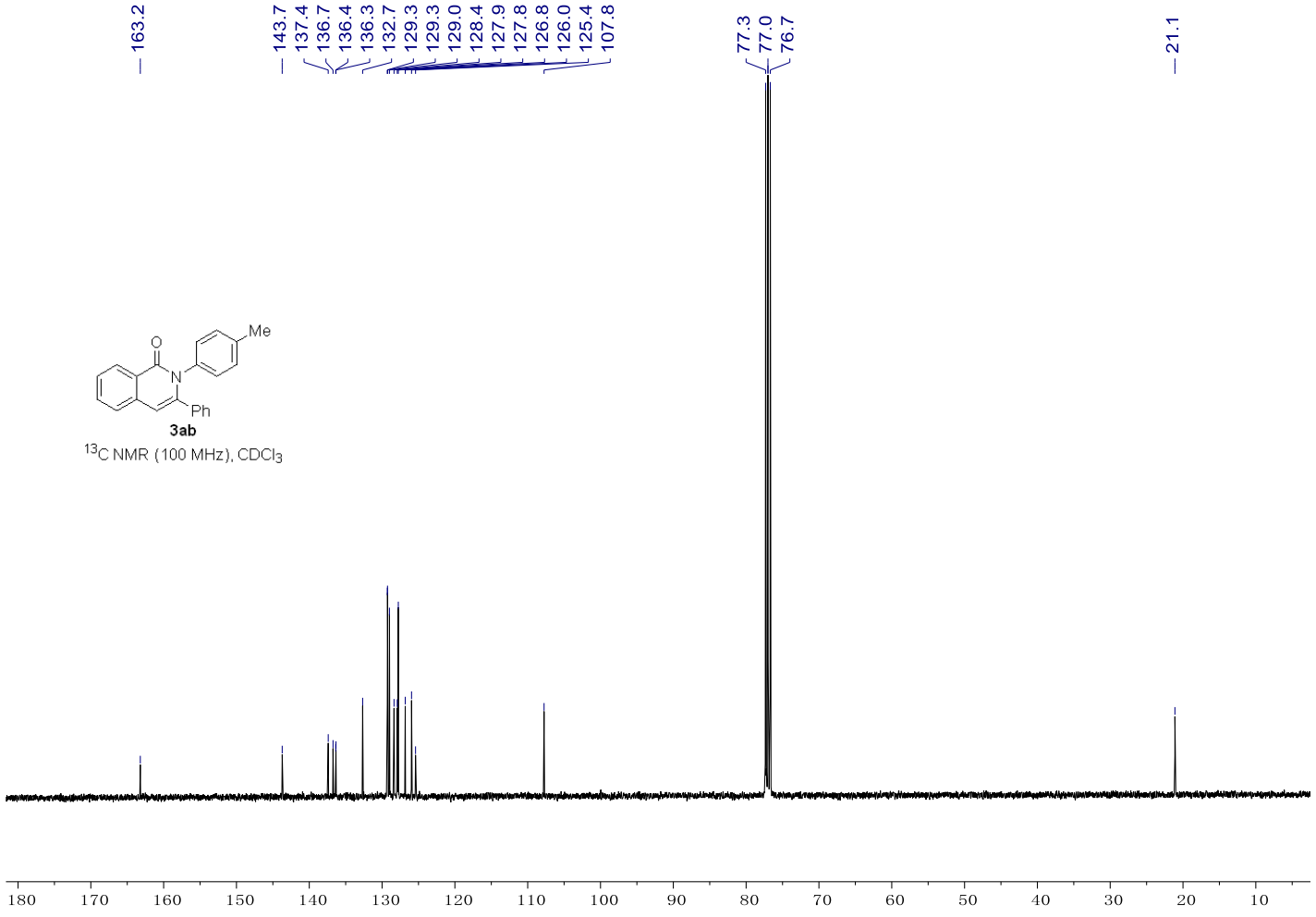
^{13}C NMR of 2,3-diphenylisoquinolin-1(2*H*)-one (3aa)



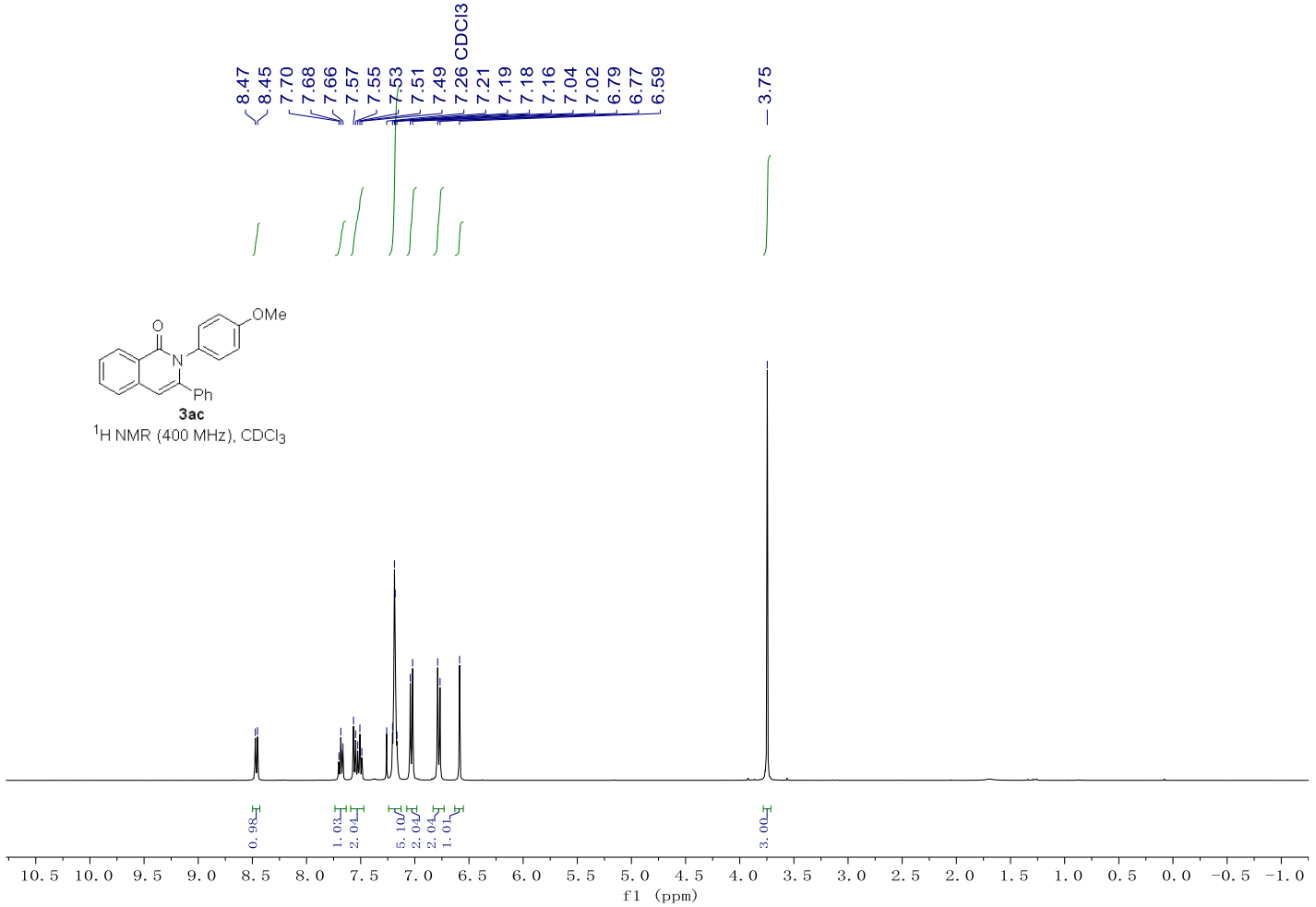
^{1}H NMR of 3-phenyl-2-(*p*-tolyl)isoquinolin-1(2*H*)-one (3ab)



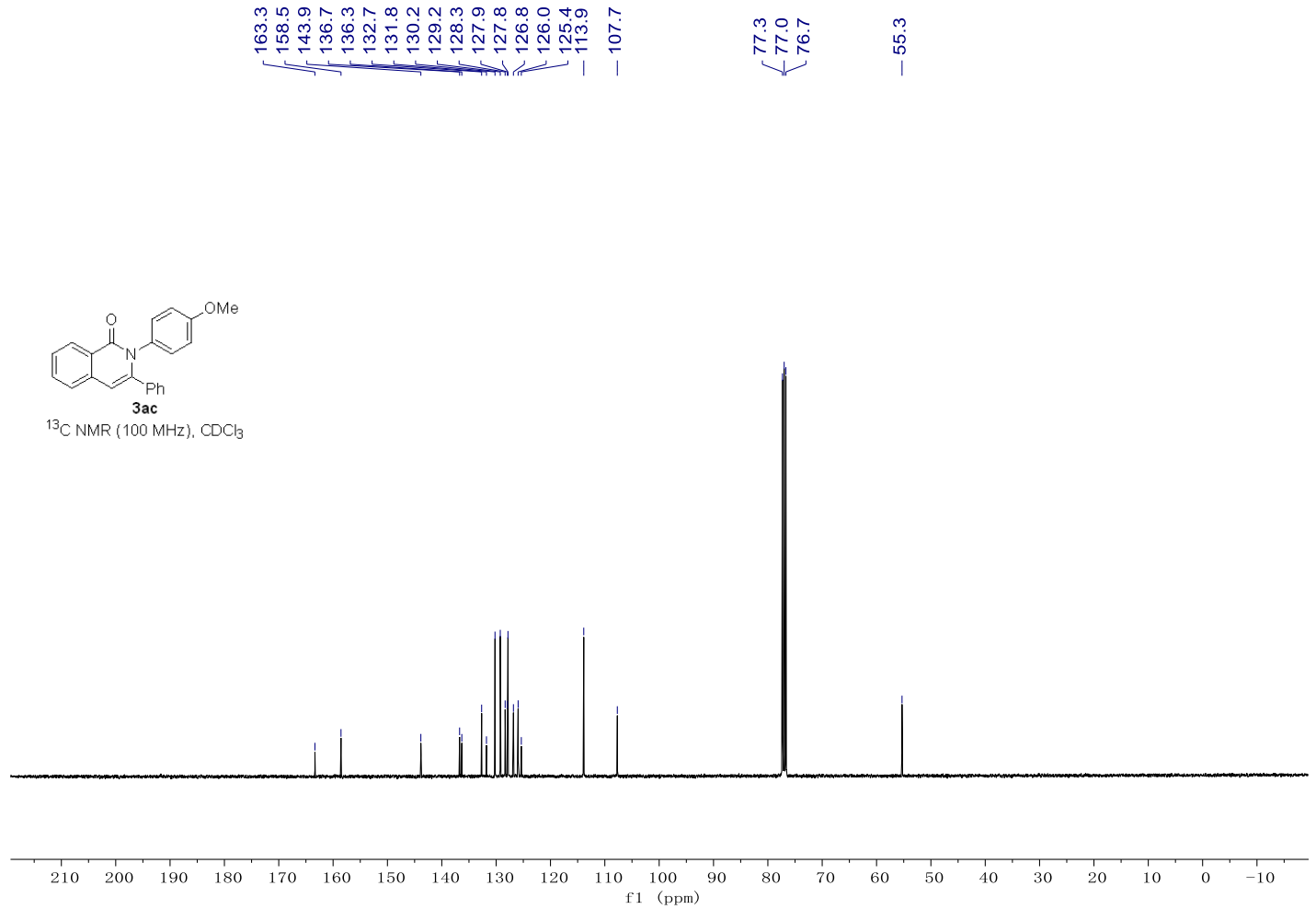
^{13}C NMR of 3-phenyl-2-(*p*-tolyl)isoquinolin-1(2*H*)-one (3ab)



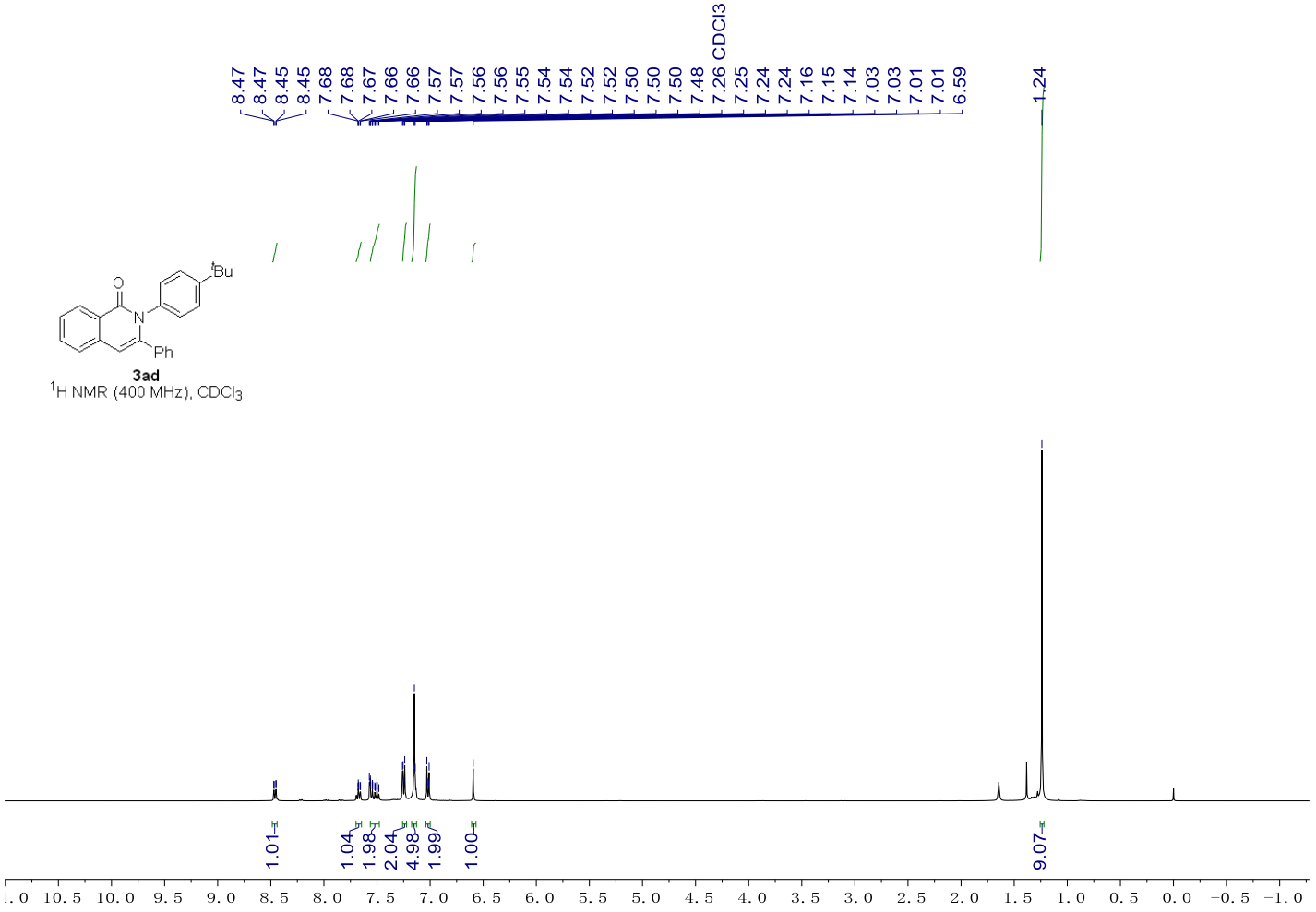
^{1}H NMR of 2-(4-methoxyphenyl)-3-phenylisoquinolin-1(2*H*)-one (3ac)



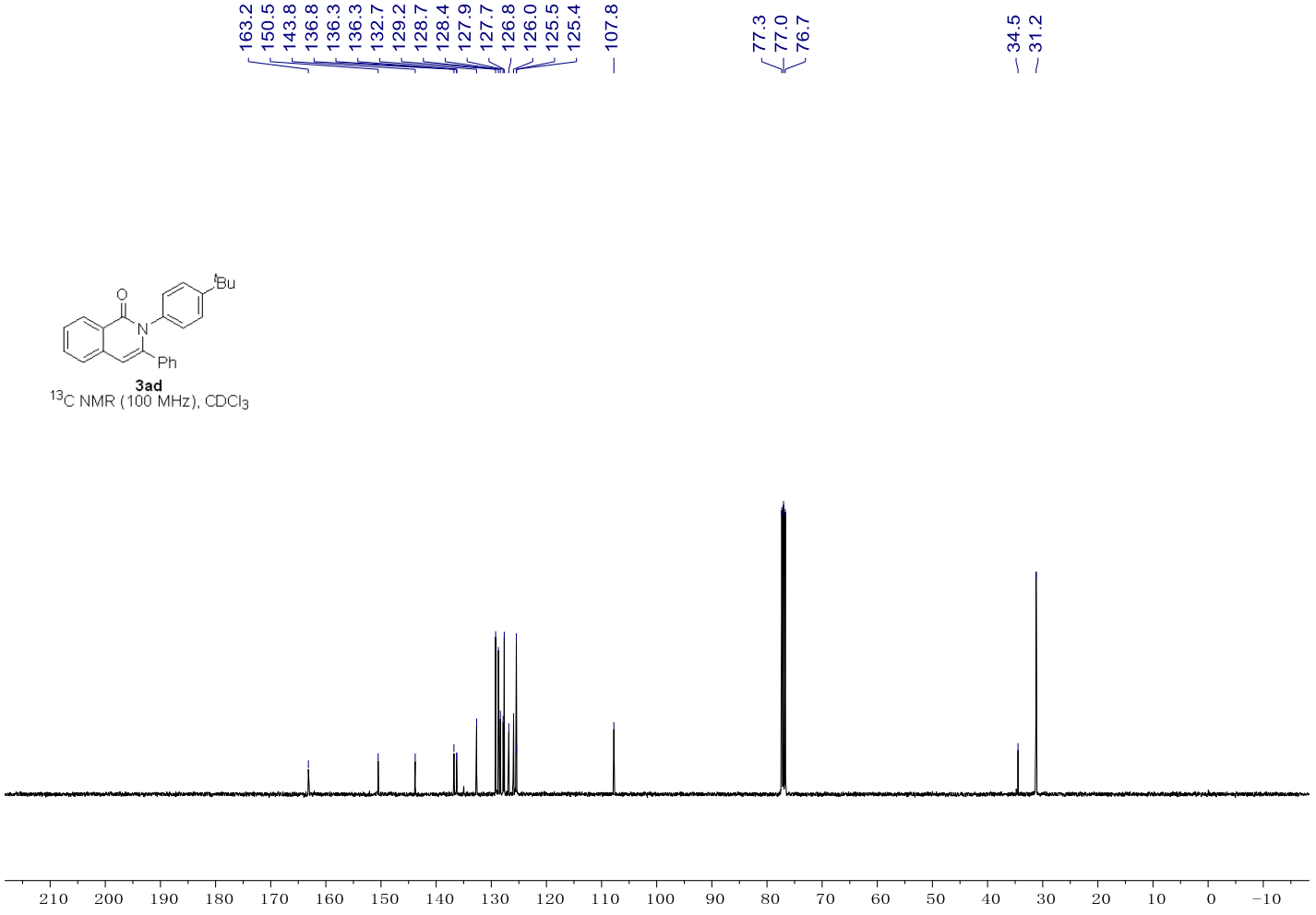
^{13}C NMR of 2-(4-methoxyphenyl)-3-phenylisoquinolin-1(2*H*)-one (3ac)



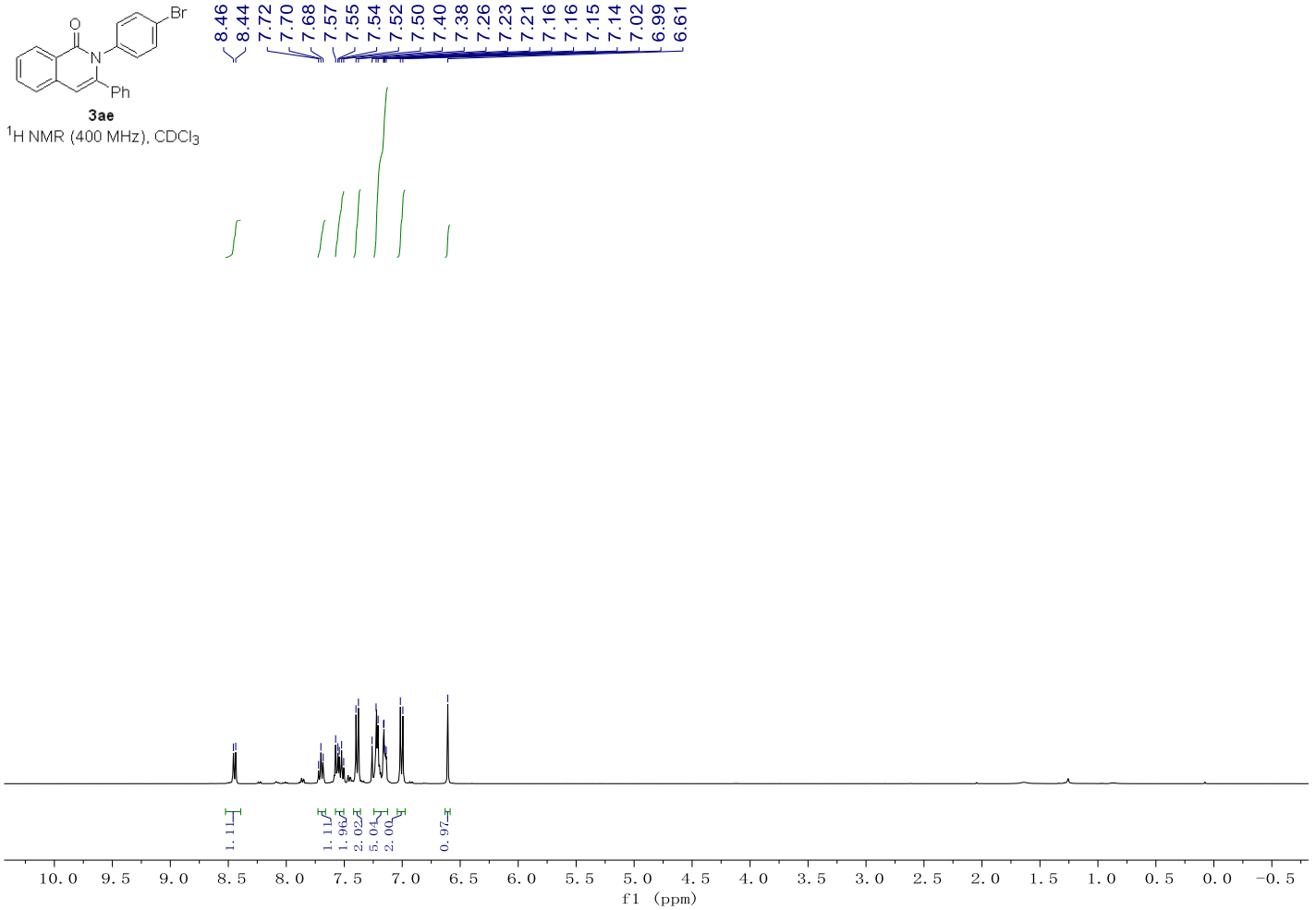
^{1}H NMR of 2-(4-(*tert*-butyl)phenyl)-3-phenylisoquinolin-1(2*H*)-one (3ad)



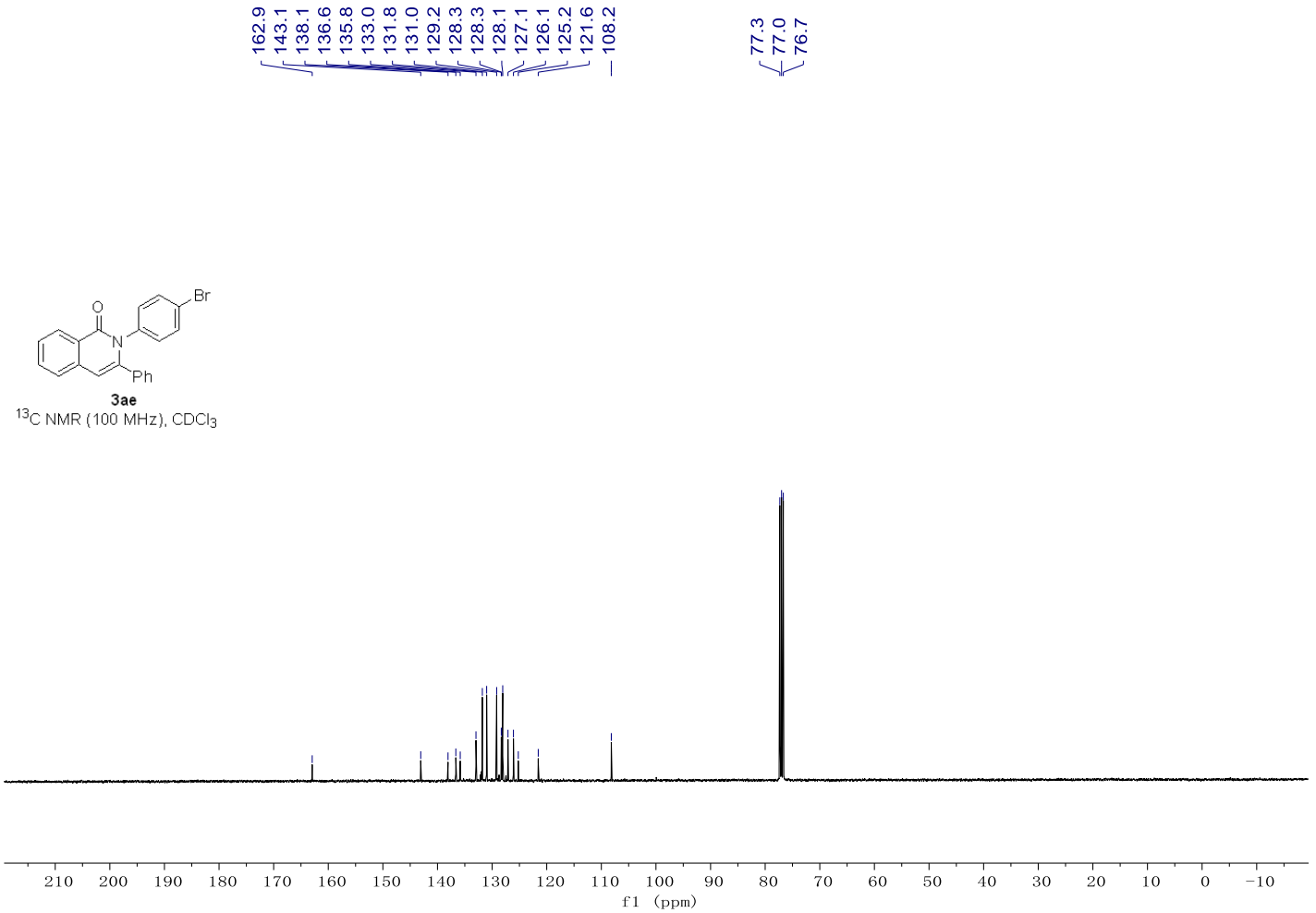
^{13}C NMR of 2-(4-(*tert*-butyl)phenyl)-3-phenylisoquinolin-1(2*H*)-one (3ad)



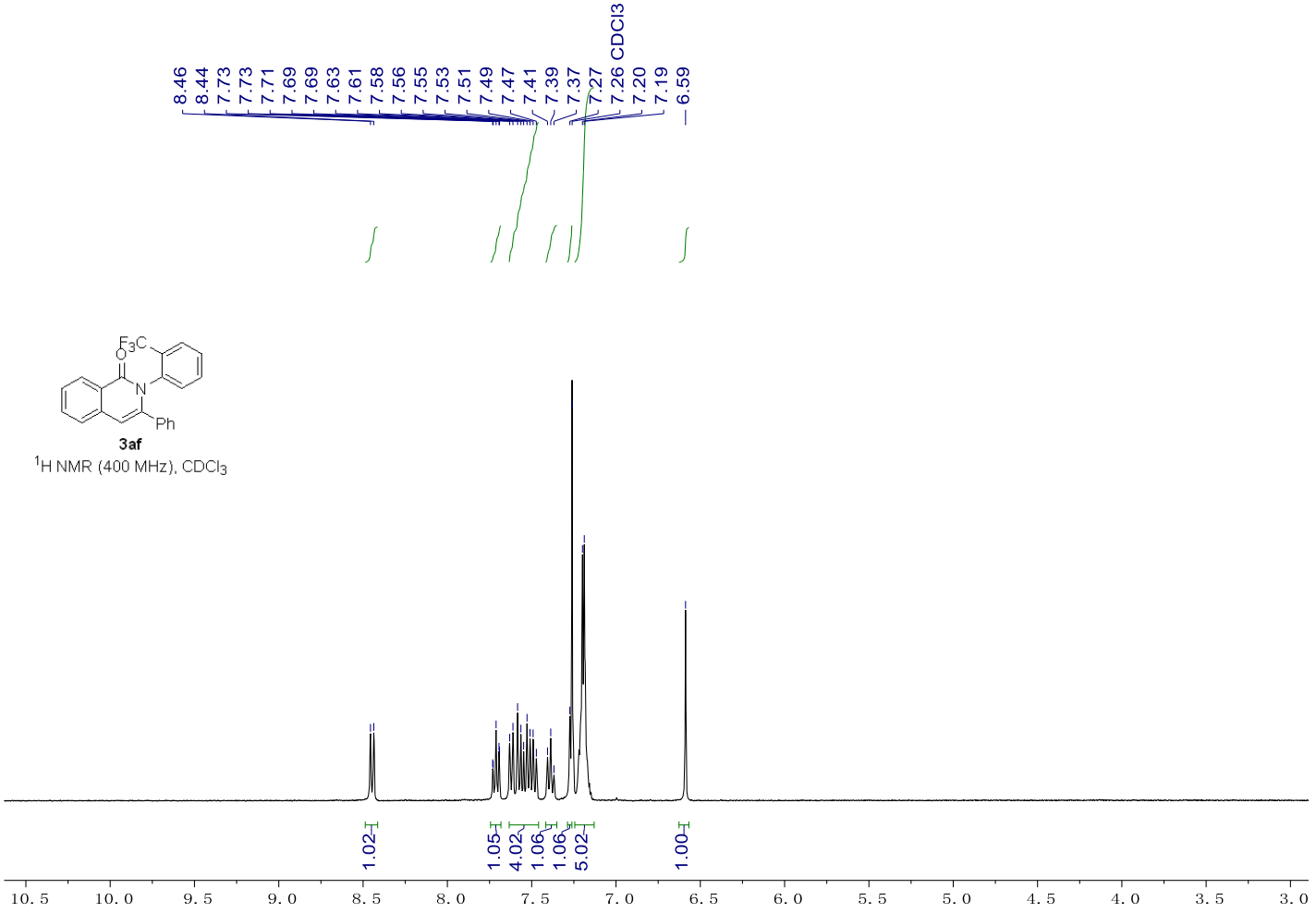
^{1}H NMR of 2-(4-bromophenyl)-3-phenylisoquinolin-1(2*H*)-one (3ae)



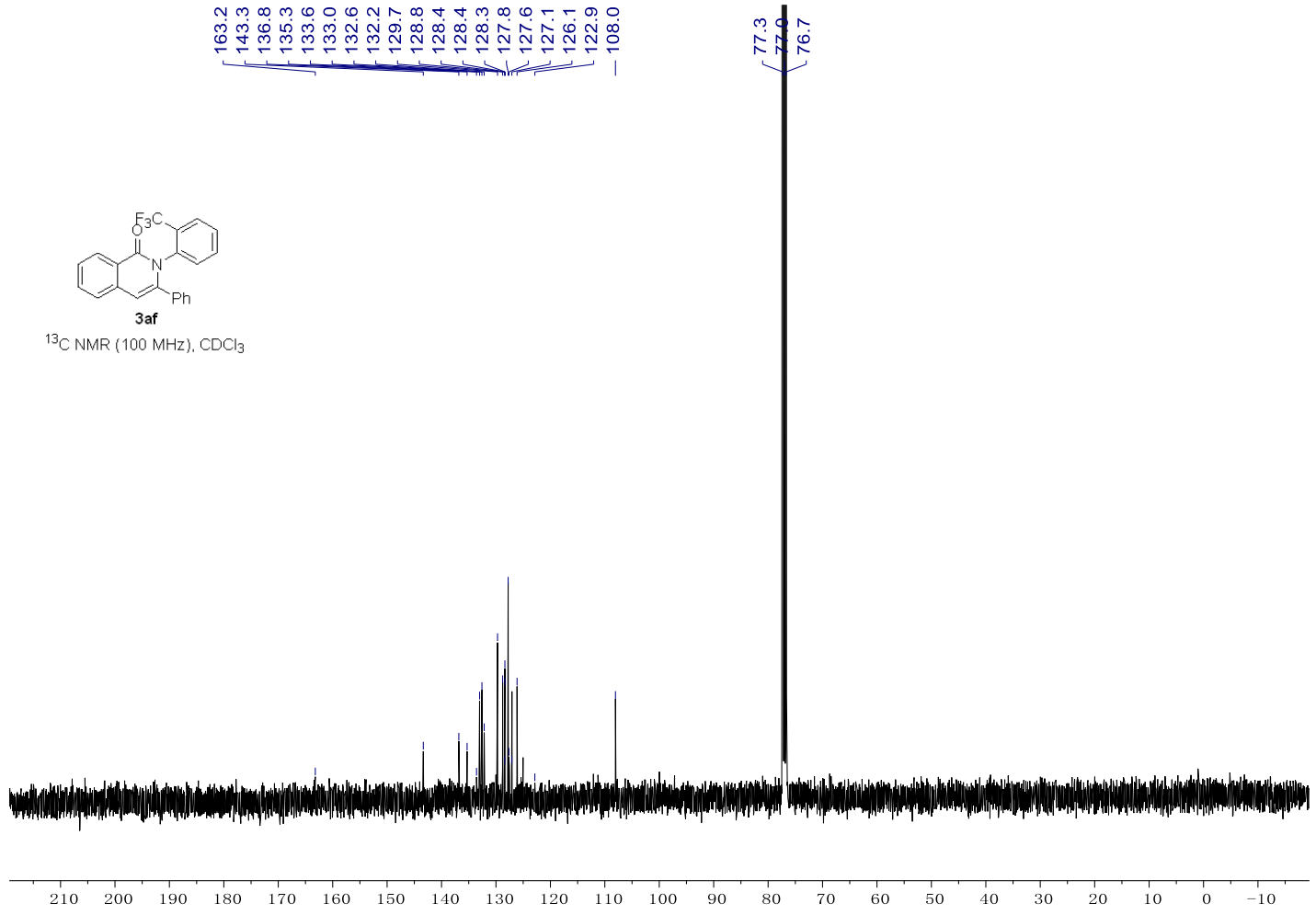
^{13}C NMR of 2-(4-bromophenyl)-3-phenylisoquinolin-1(2*H*)-one (3ae)



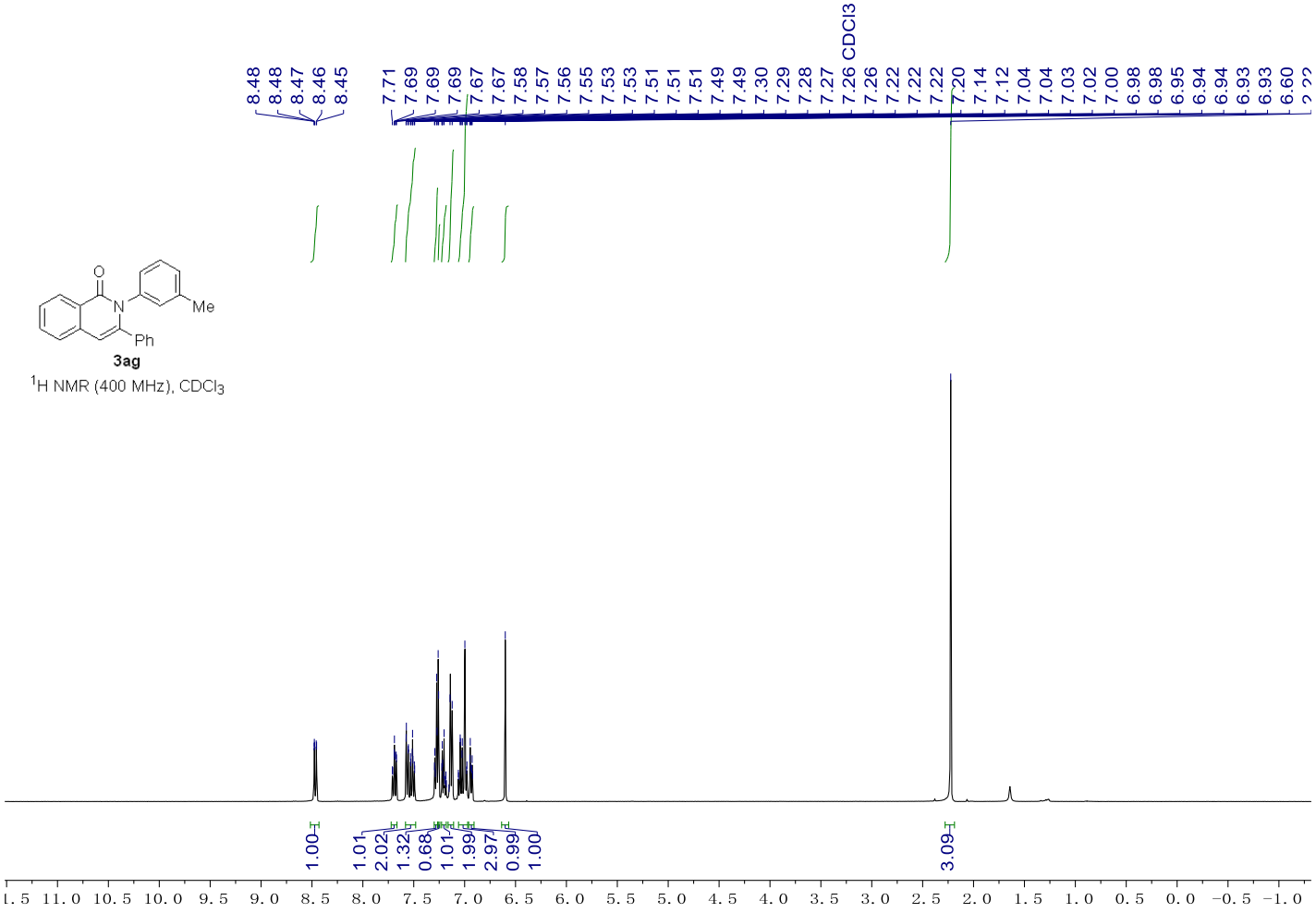
^{1}H NMR of 3-phenyl-2-(2-(trifluoromethyl)phenyl)isoquinolin-1(2*H*)-one (3af)



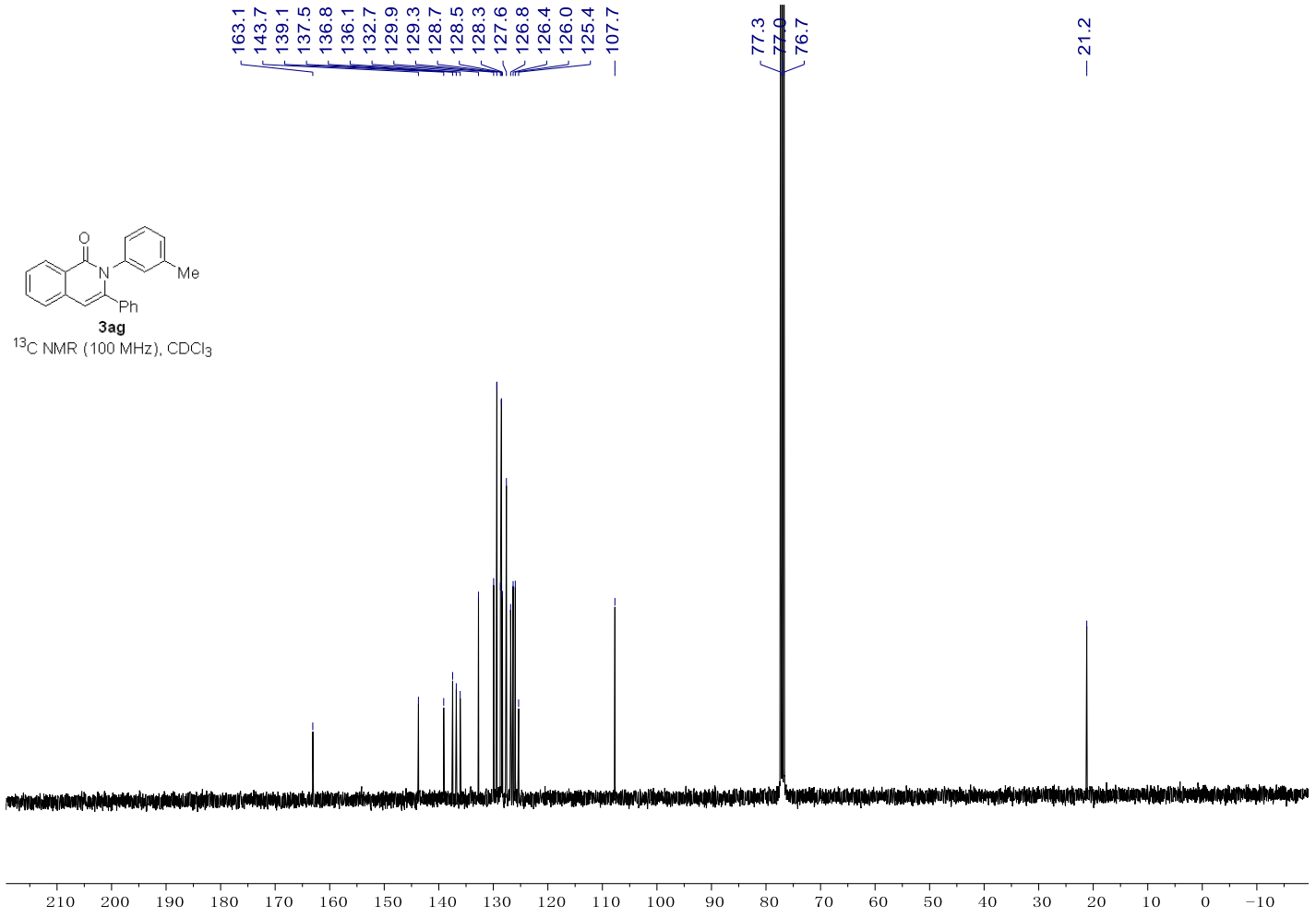
^{13}C NMR of 3-phenyl-2-(2-(trifluoromethyl)phenyl)isoquinolin-1(2*H*)-one (3af)



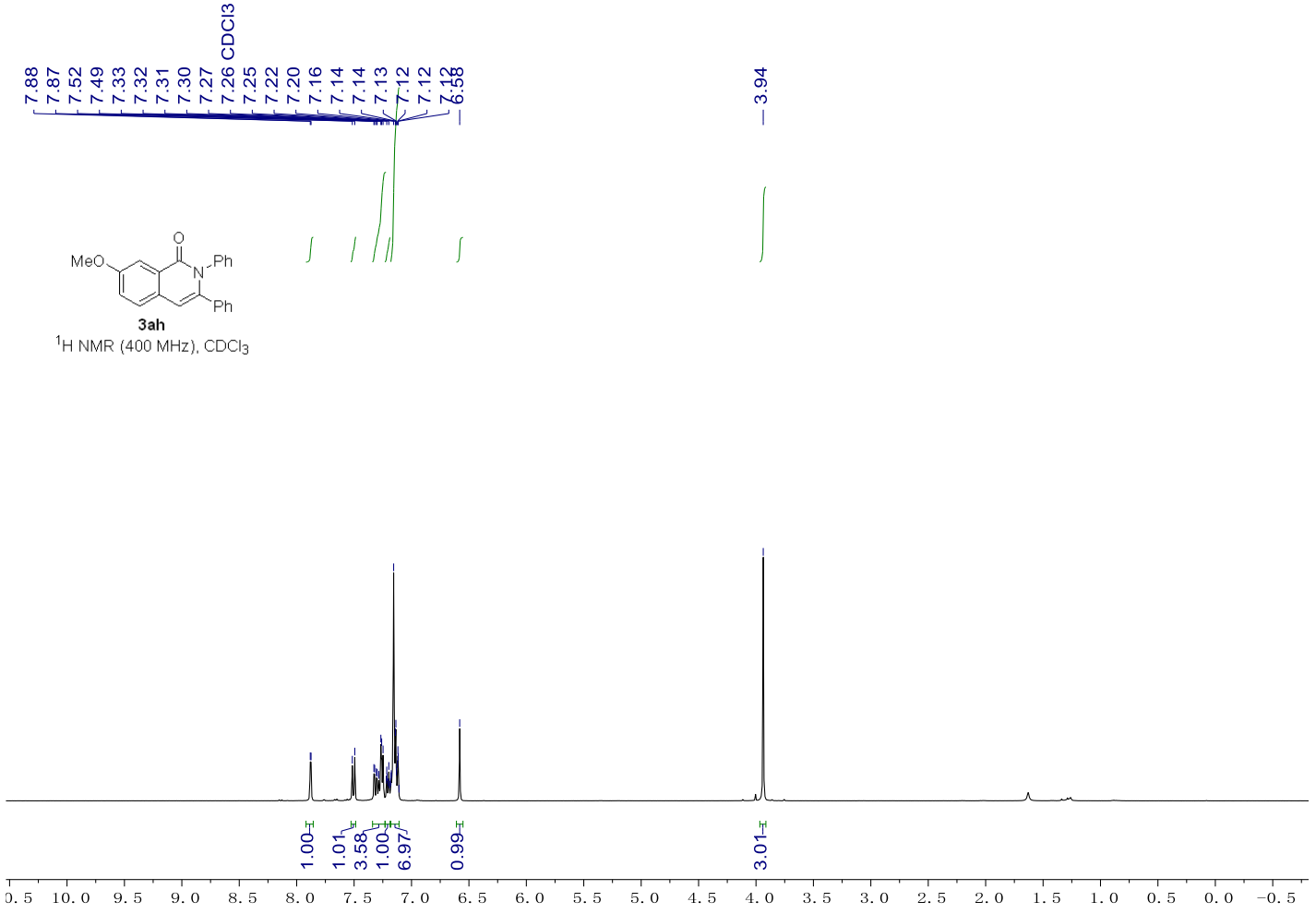
^{1}H NMR of 3-phenyl-2-(*m*-tolyl)isoquinolin-1(2*H*)-one (3ag)



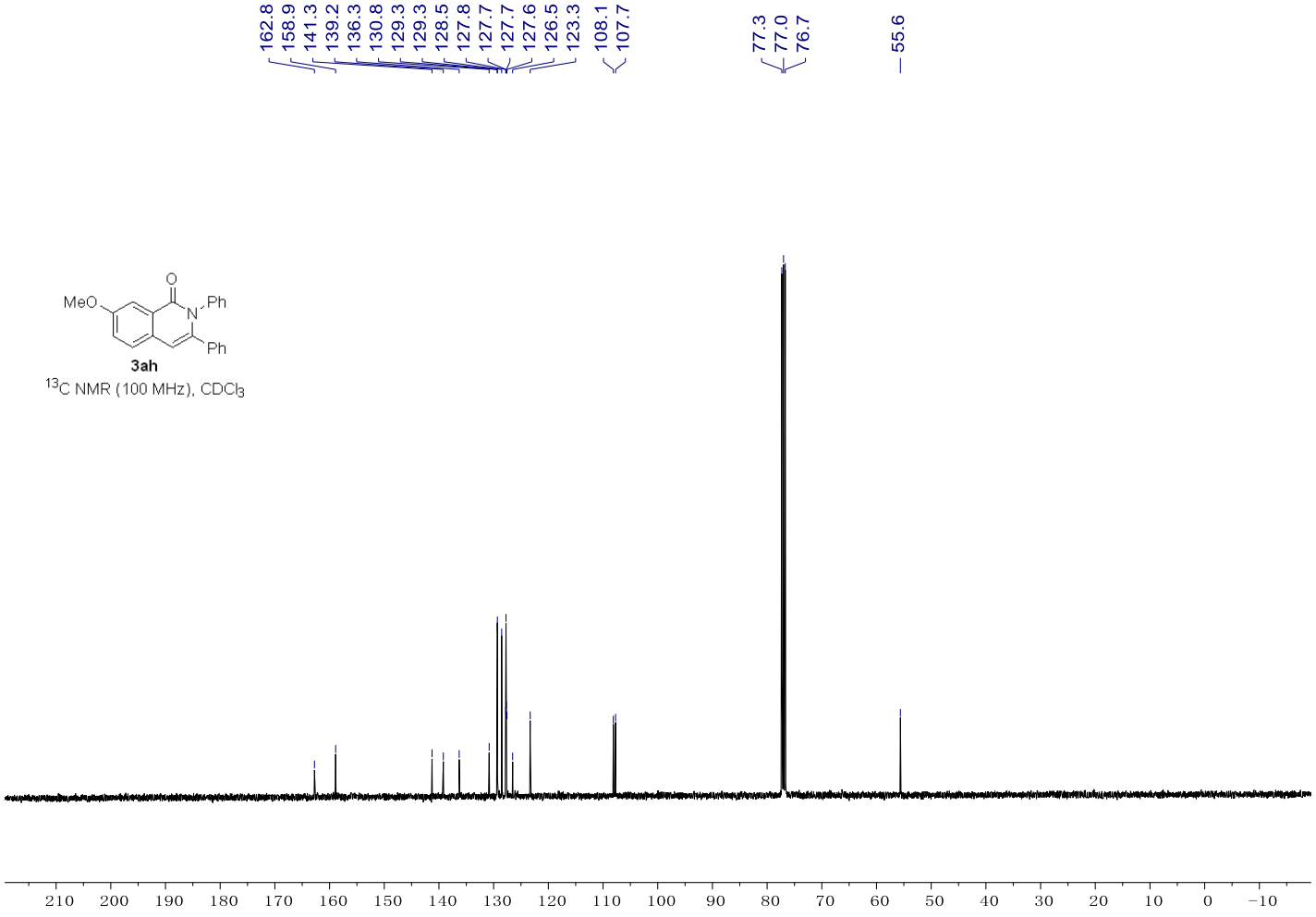
^{13}C NMR of 3-phenyl-2-(*m*-tolyl)isoquinolin-1(2*H*)-one (3ag)



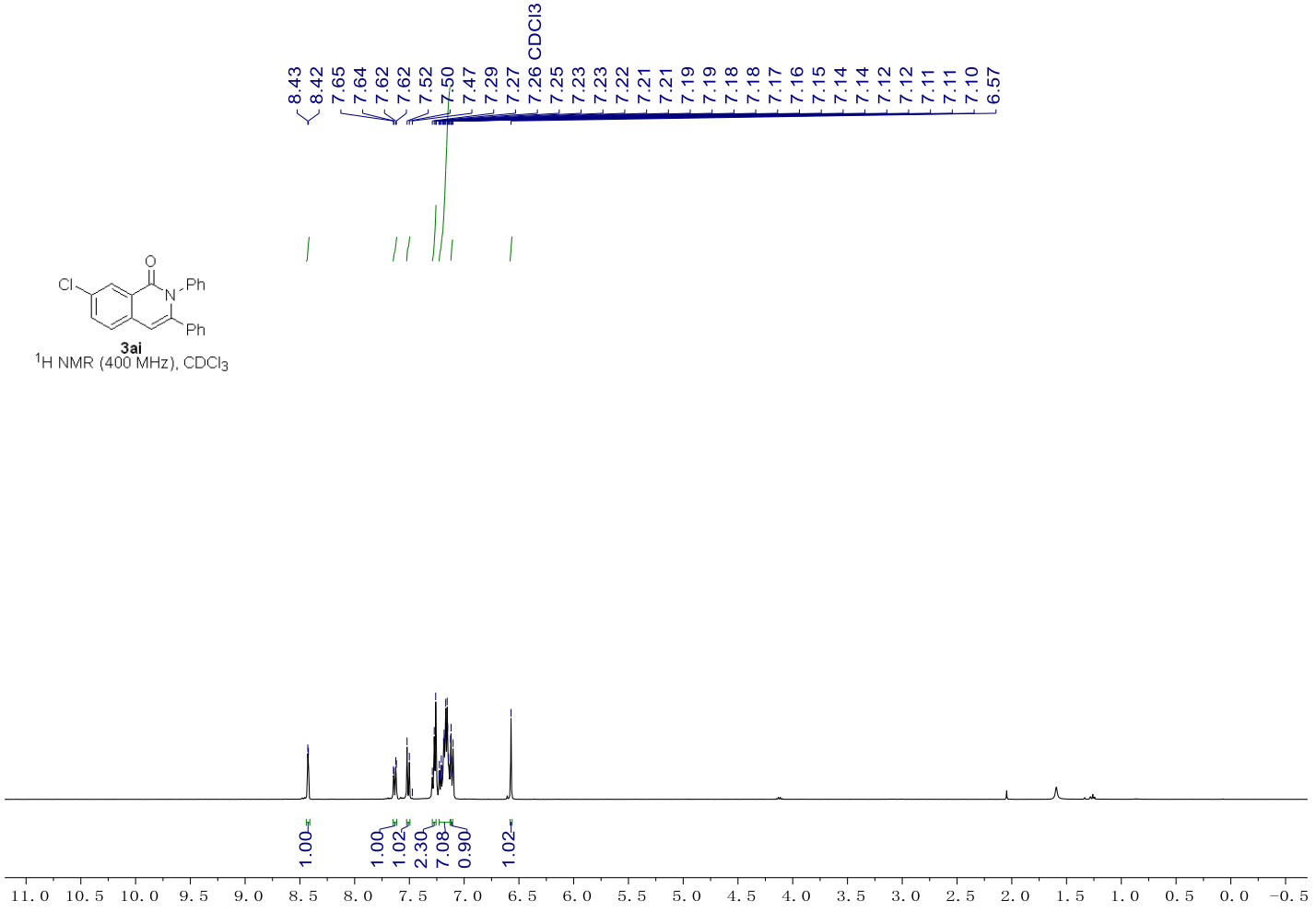
^{1}H NMR of 7-methoxy-2,3-diphenylisoquinolin-1(2*H*)-one (3ah)



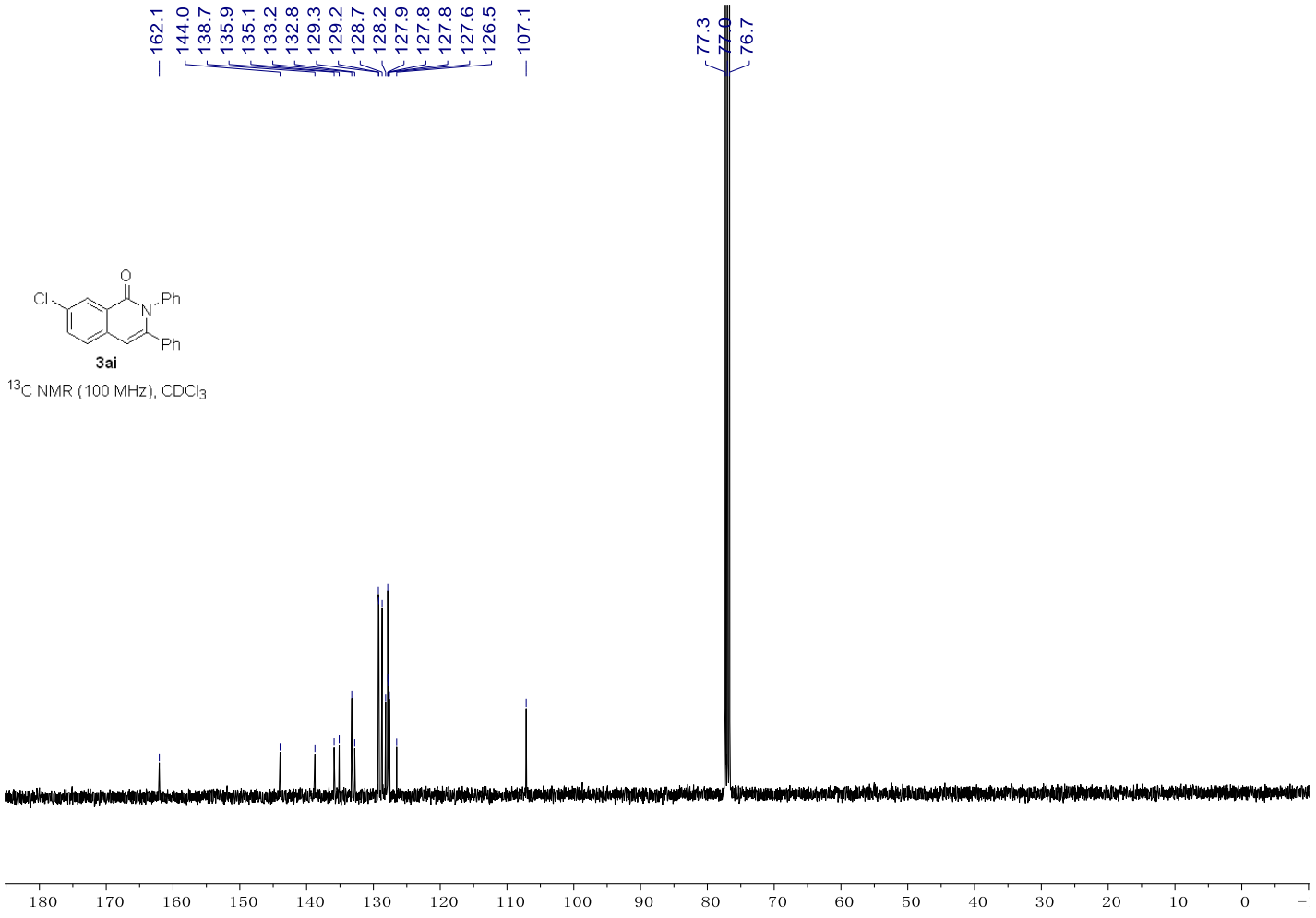
^{13}C NMR of 7-methoxy-2,3-diphenylisoquinolin-1(2*H*)-one (3ah)



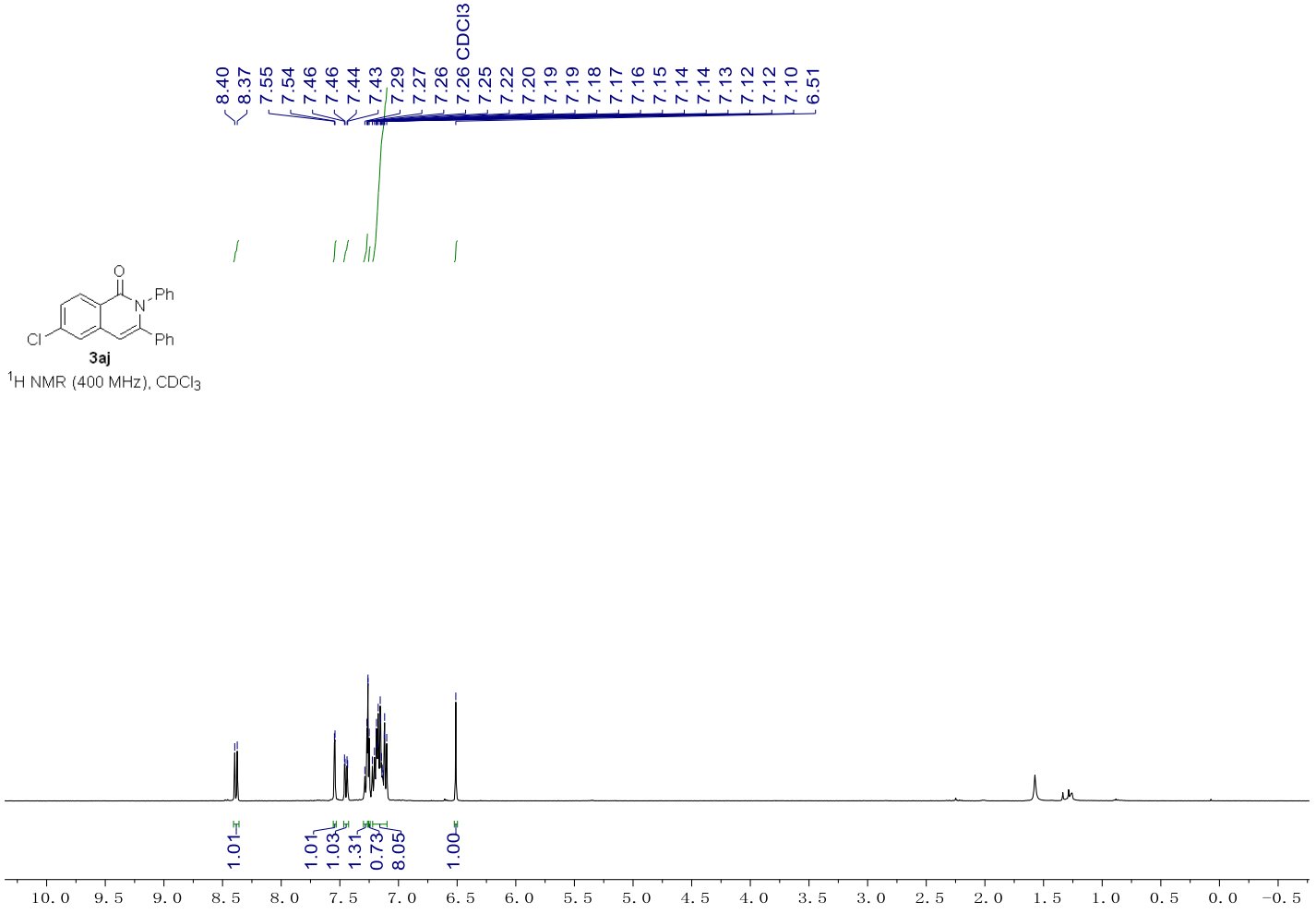
^{1}H NMR of 7-chloro-2,3-diphenylisoquinolin-1(2*H*)-one (3ai)



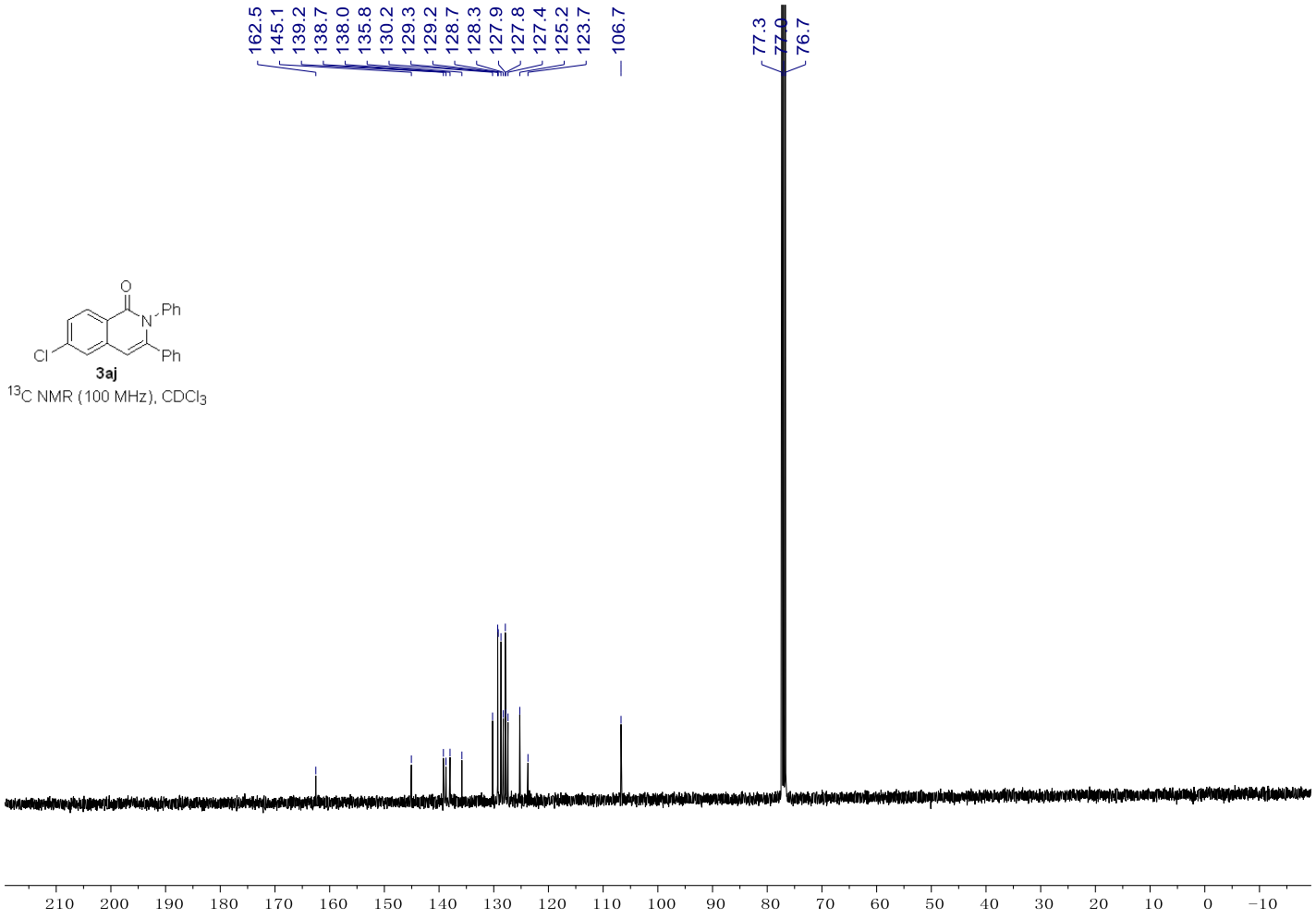
^{13}C NMR of 7-chloro-2,3-diphenylisoquinolin-1(2*H*)-one (3ai)



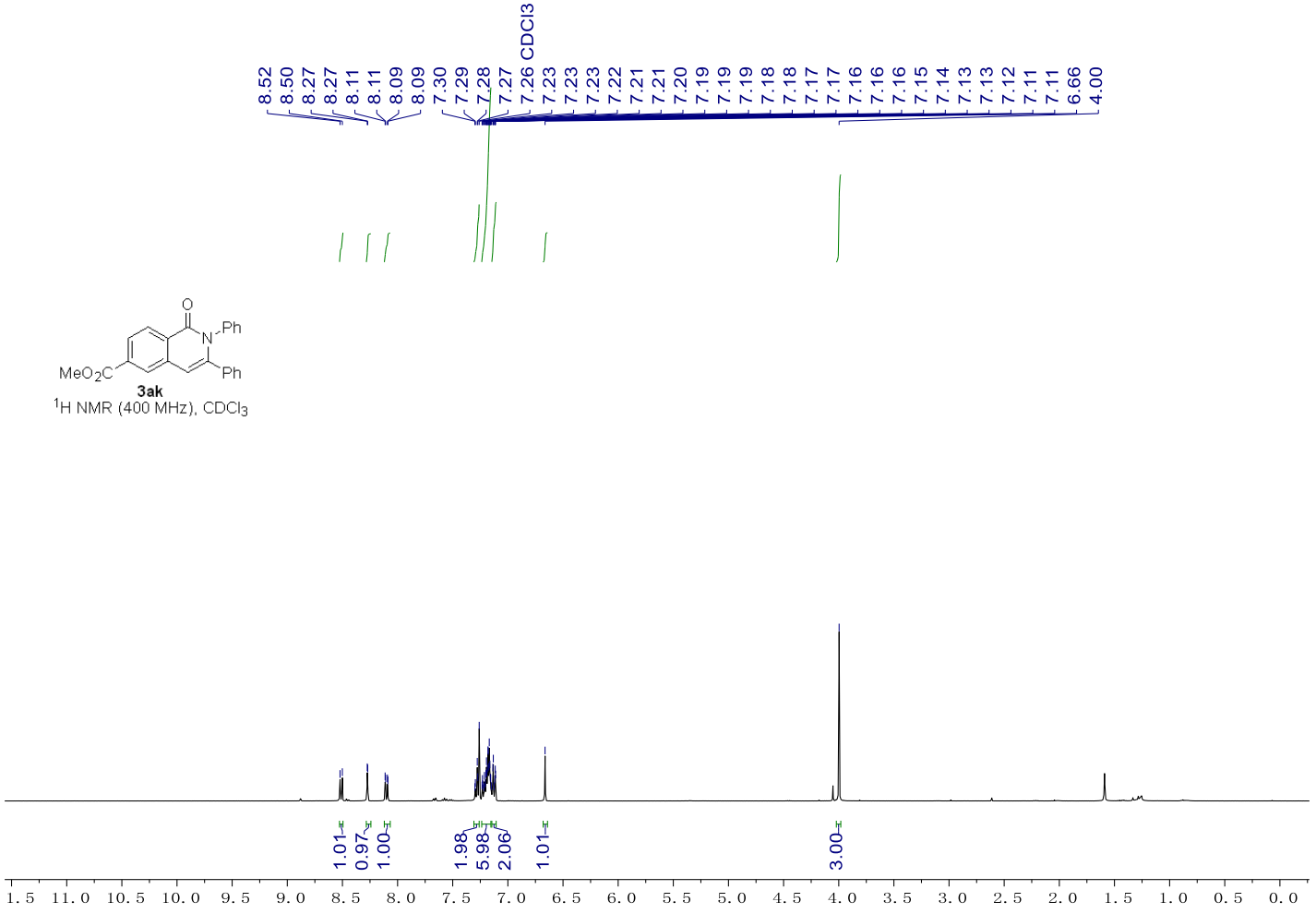
^{1}H NMR of 6-chloro-2,3-diphenylisoquinolin-1(2*H*)-one (3aj)



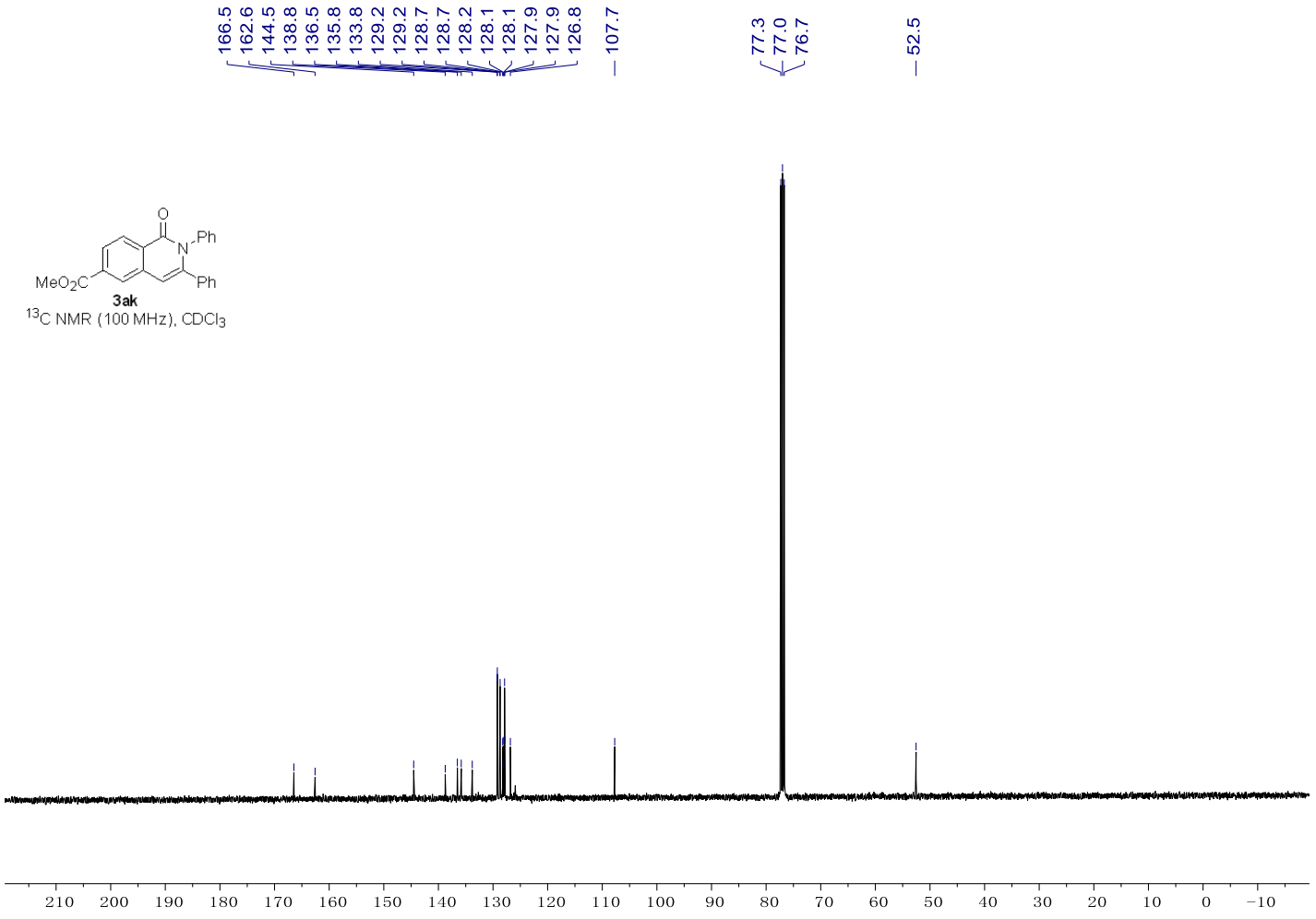
^{13}C NMR of 6-chloro-2,3-diphenylisoquinolin-1(2*H*)-one (3aj)



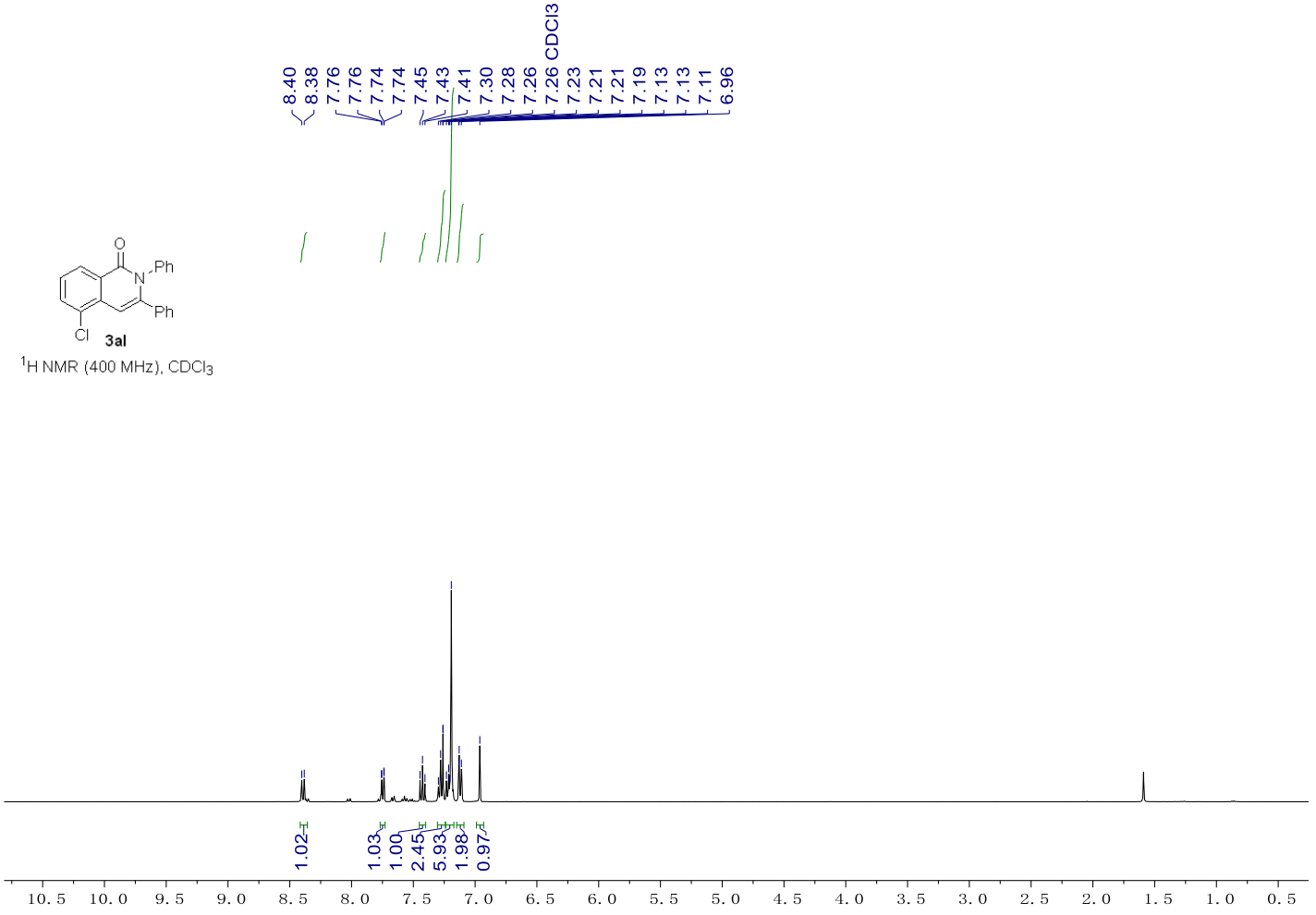
^{1}H NMR of methyl 1-oxo-2,3-diphenyl-1,2-dihydroisoquinoline-6-carboxylate (3ak)



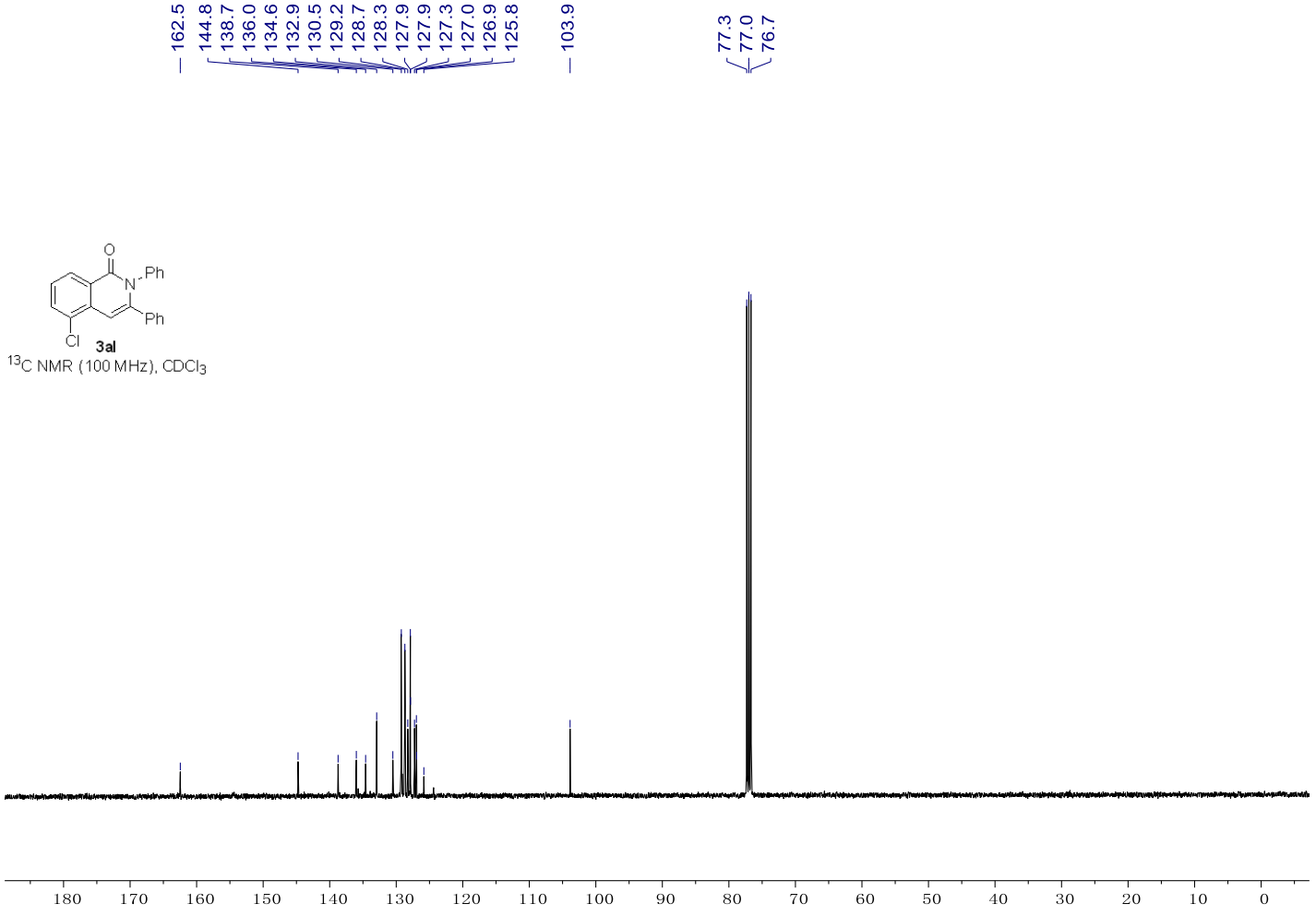
^{13}C NMR of methyl 1-oxo-2,3-diphenyl-1,2-dihydroisoquinoline-6-carboxylate (3ak)



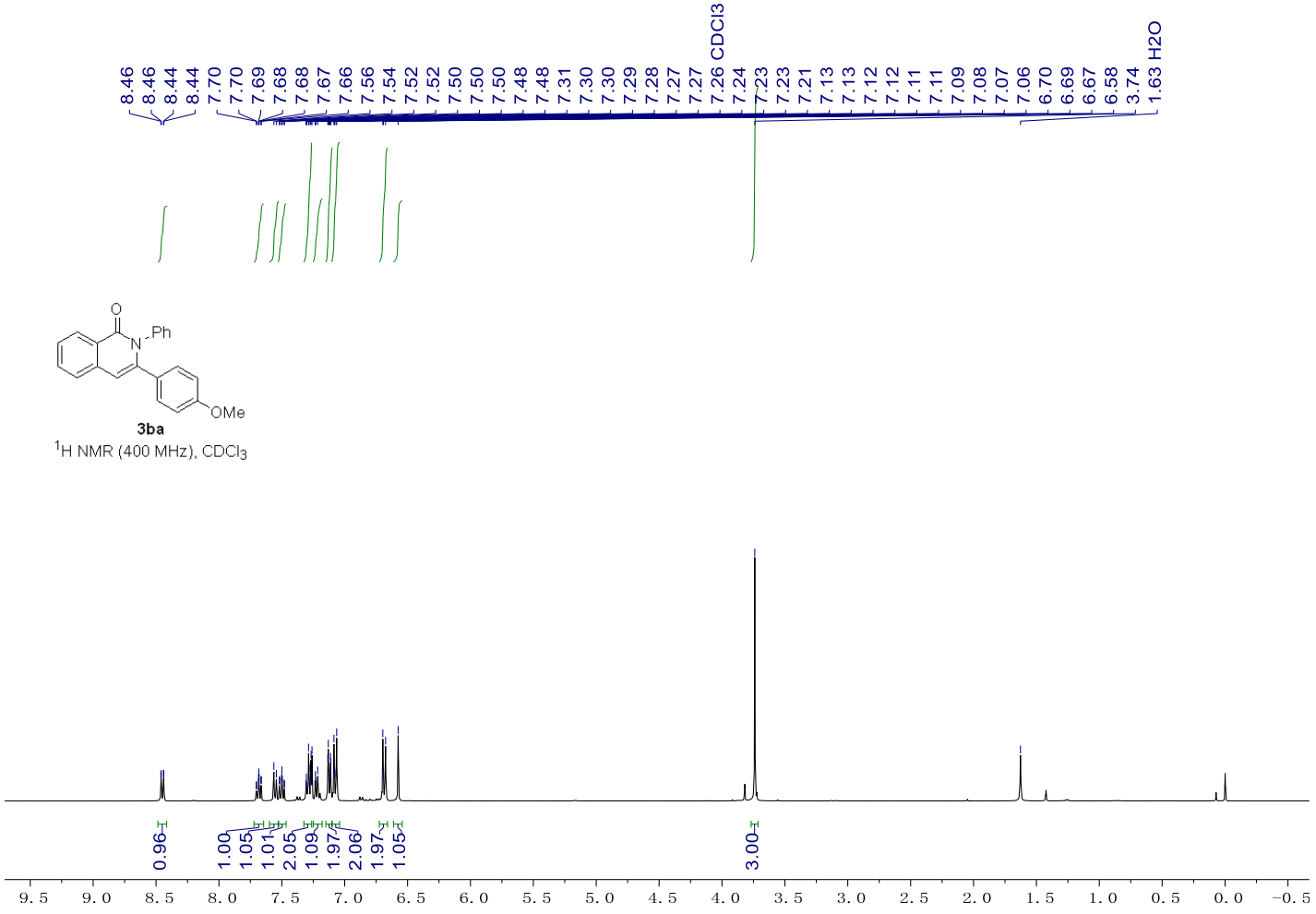
^{1}H NMR of 5-chloro-2,3-diphenylisoquinolin-1(2*H*)-one (3al)



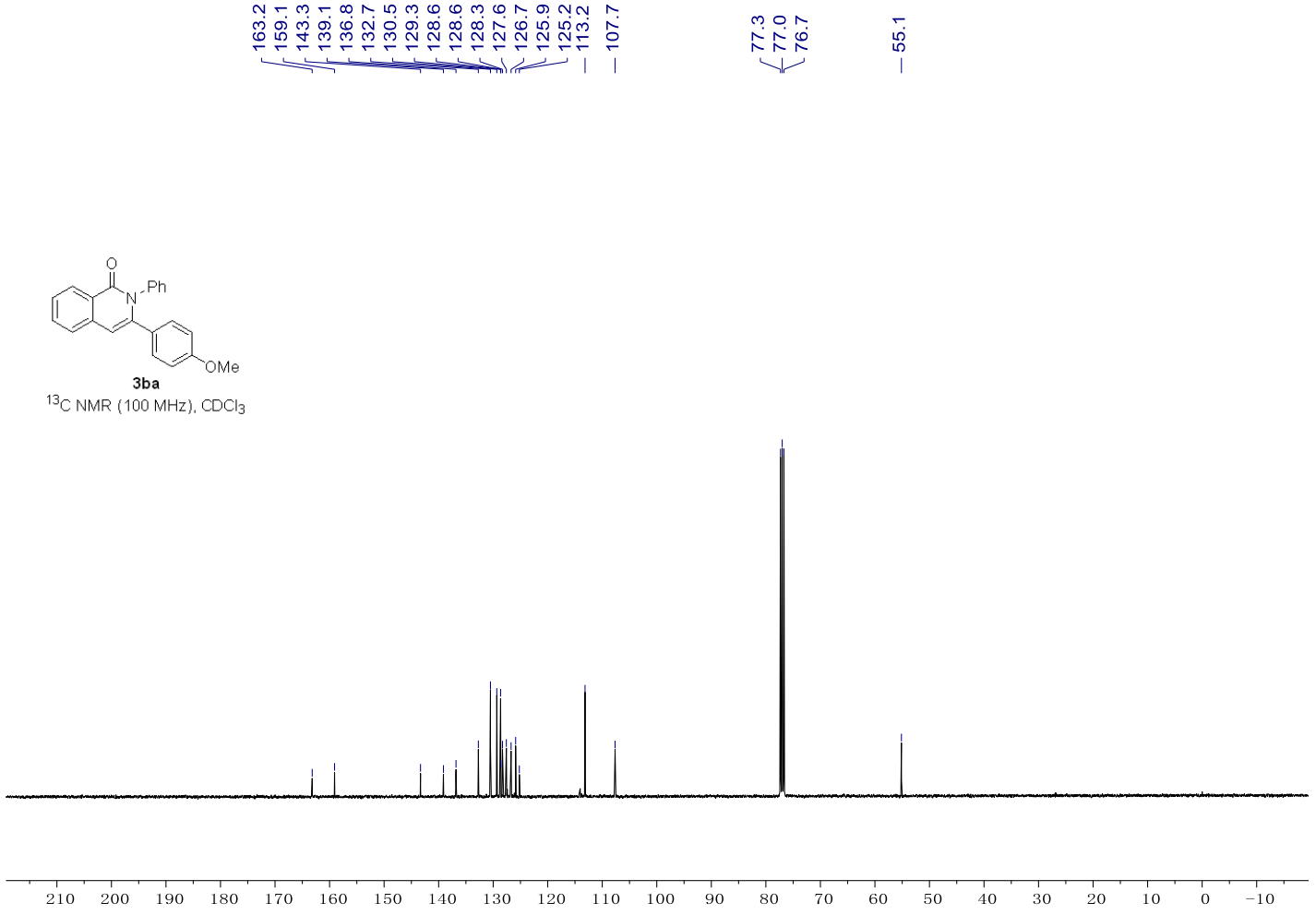
^{13}C NMR of 5-chloro-2,3-diphenylisoquinolin-1(2*H*)-one (3al)



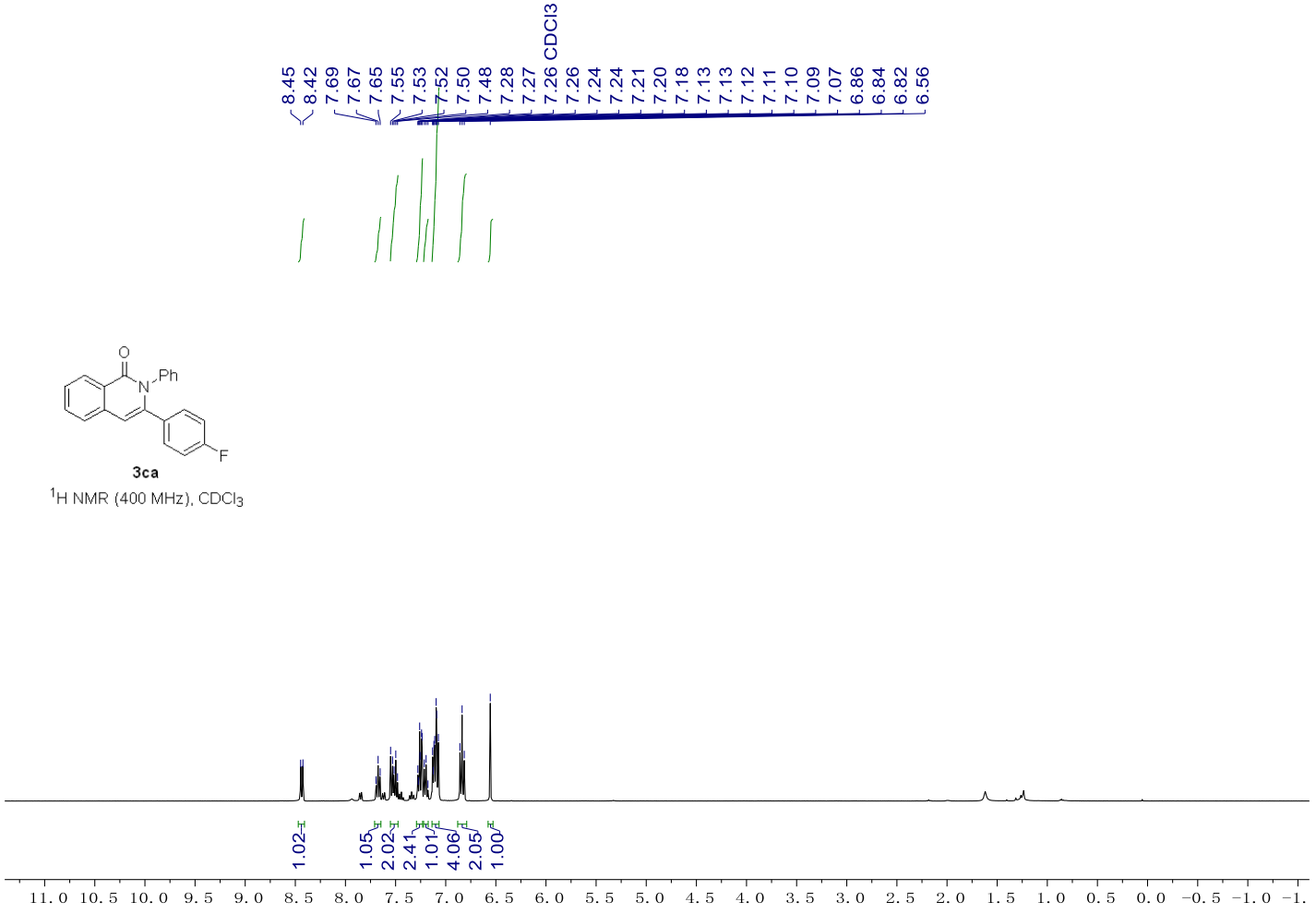
^{1}H NMR of 3-(4-methoxyphenyl)-2-phenylisoquinolin-1(2*H*)-one (3ba)



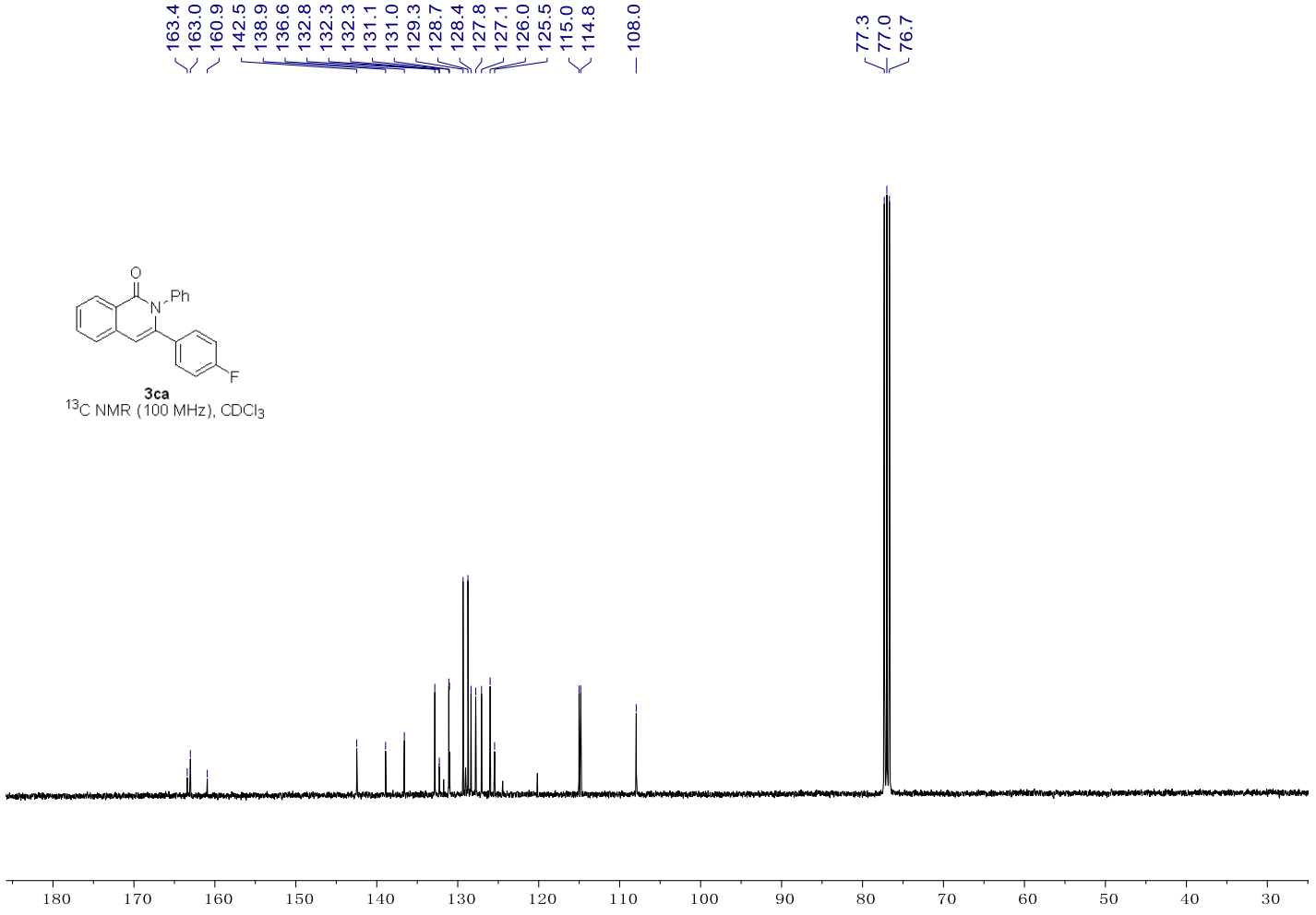
^{13}C NMR of 3-(4-methoxyphenyl)-2-phenylisoquinolin-1(2*H*)-one (3ba)



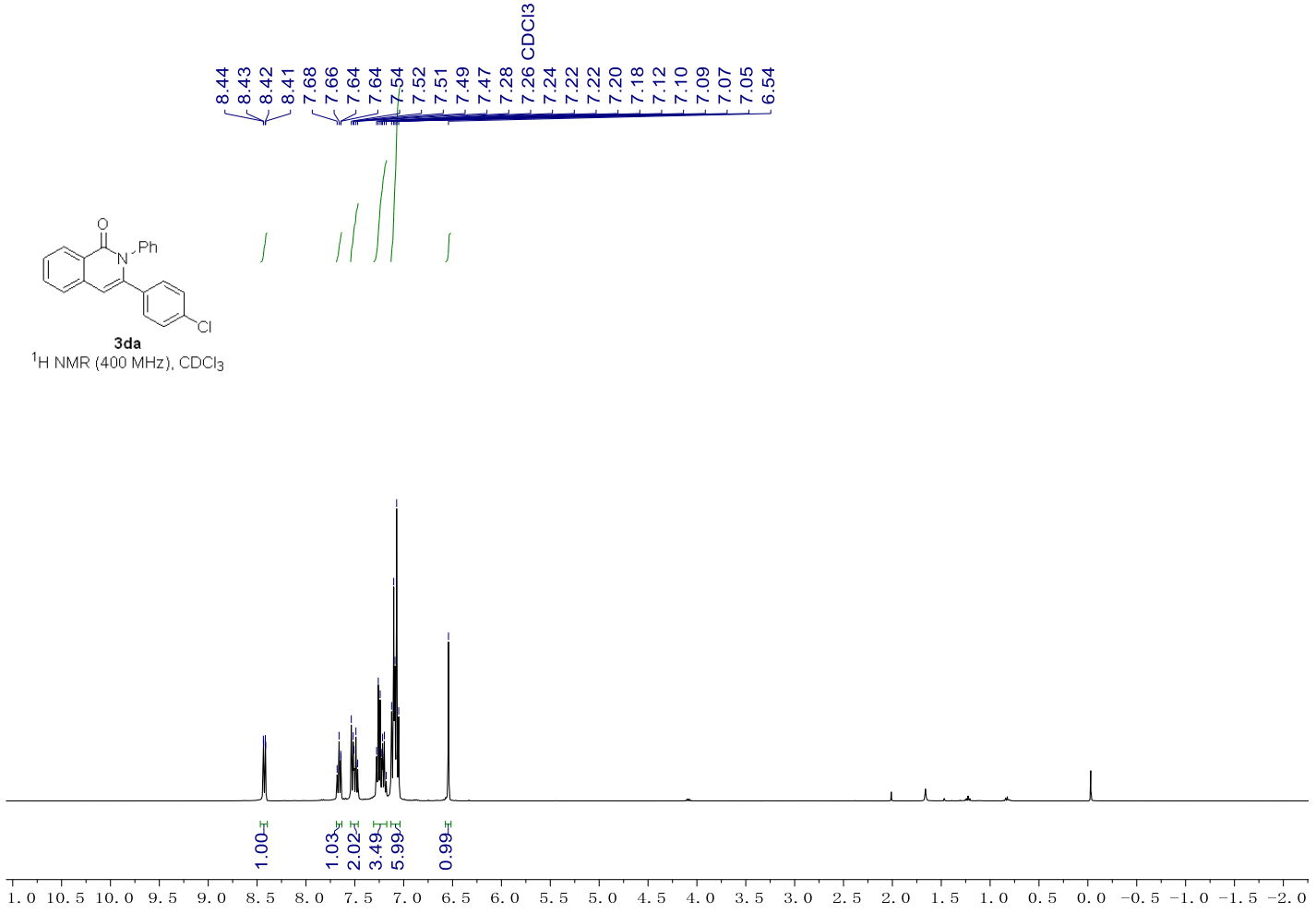
^{1}H NMR of 3-(4-fluorophenyl)-2-phenylisoquinolin-1(2*H*)-one (3ca)



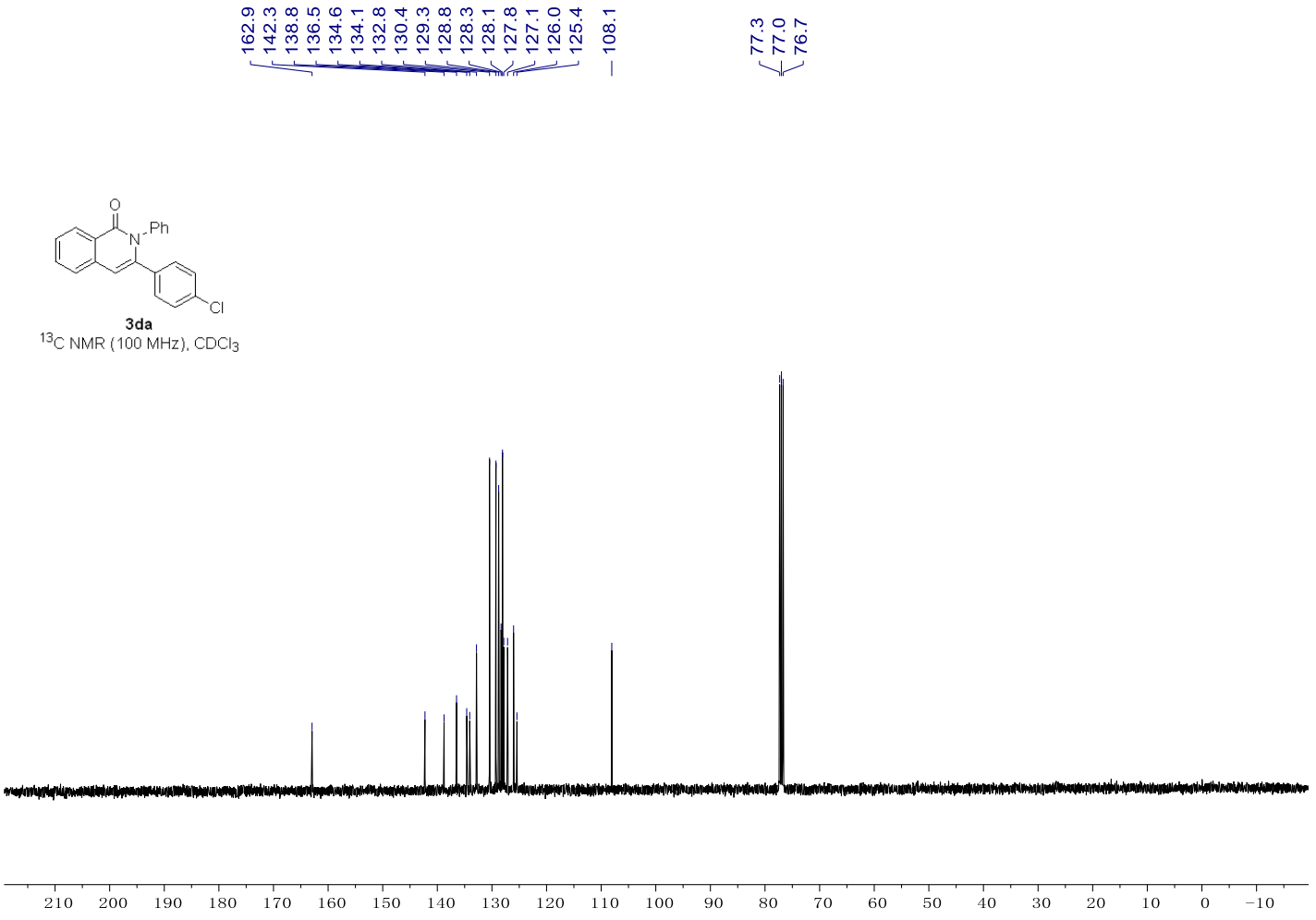
^{13}C NMR of 3-(4-fluorophenyl)-2-phenylisoquinolin-1(2*H*)-one (3ca)



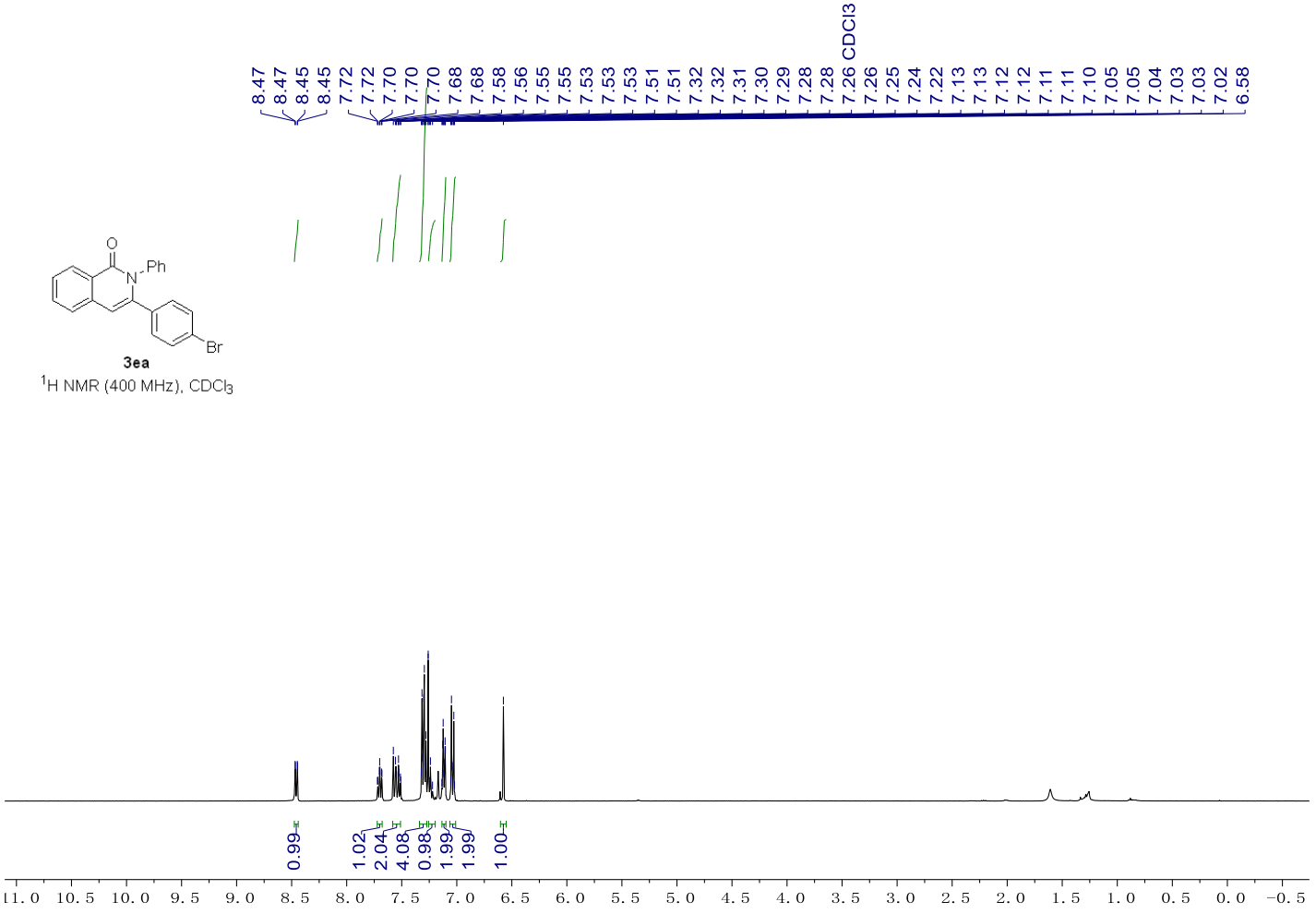
^{1}H NMR of 3-(4-chlorophenyl)-2-phenylisoquinolin-1(2*H*)-one (3da)



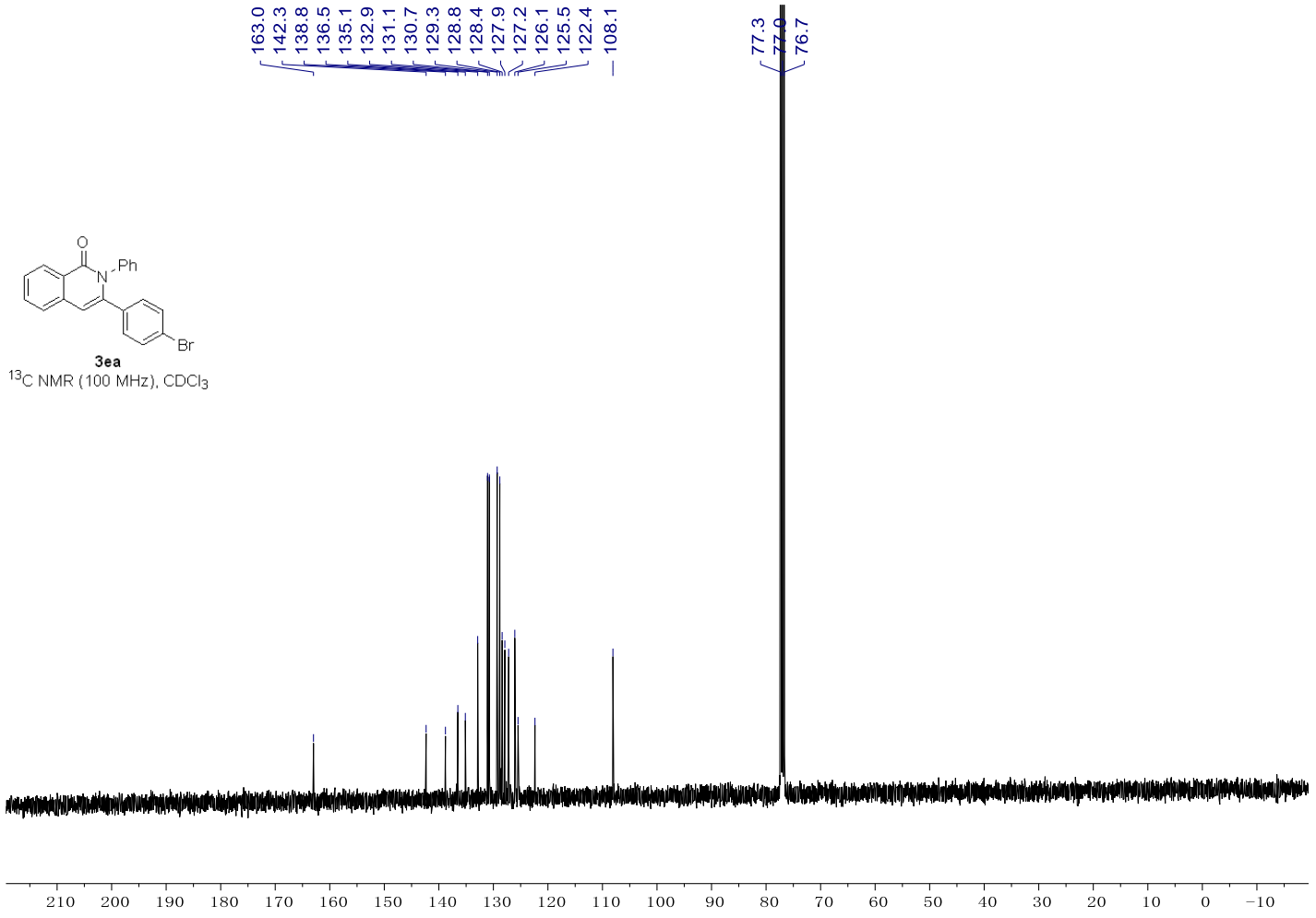
^{13}C NMR of 3-(4-chlorophenyl)-2-phenylisoquinolin-1(2*H*)-one (3da)



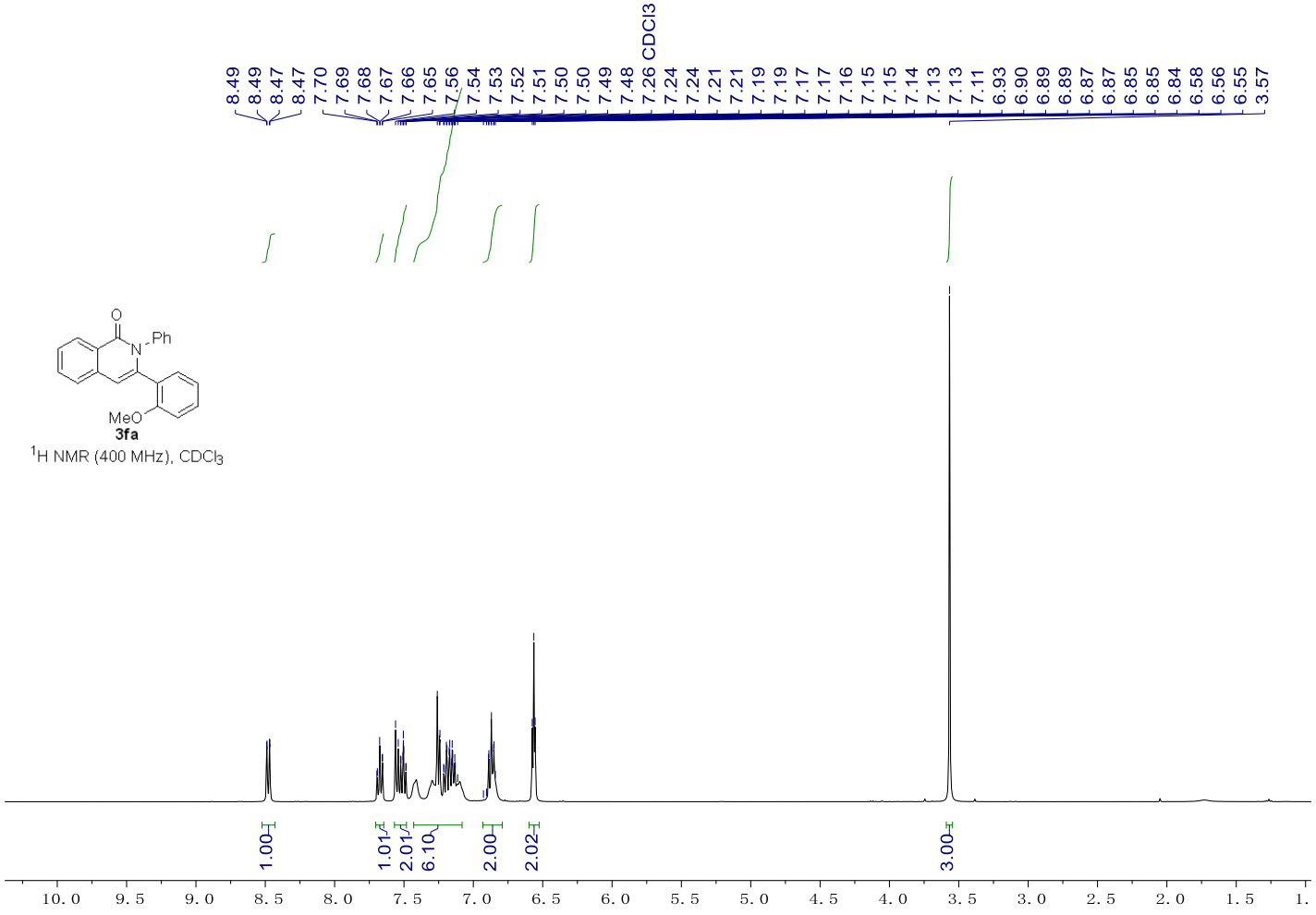
^{1}H NMR of 3-(4-bromophenyl)-2-phenylisoquinolin-1(2*H*)-one (3ea)



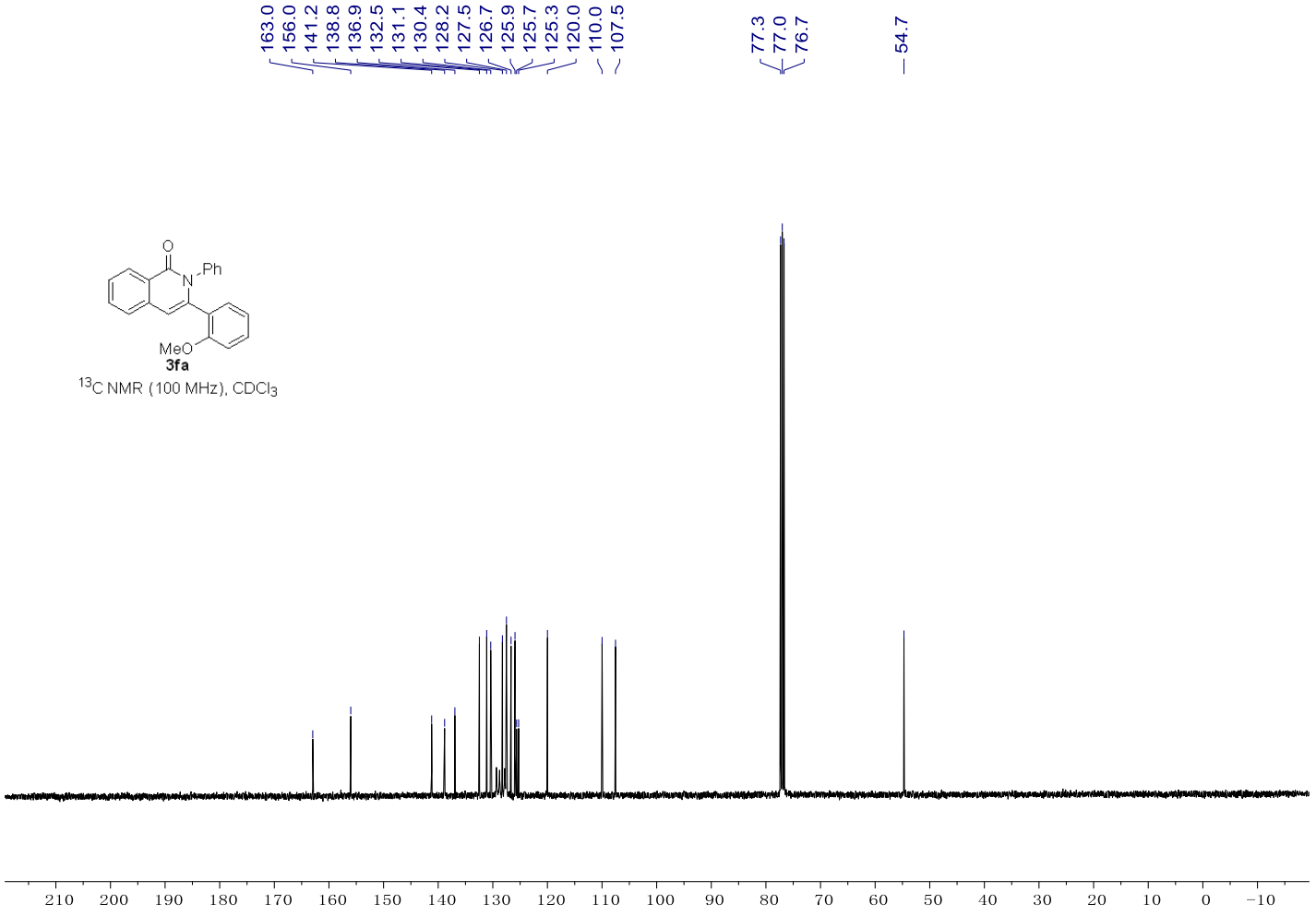
^{13}C NMR of 3-(4-bromophenyl)-2-phenylisoquinolin-1(2*H*)-one (3ea)



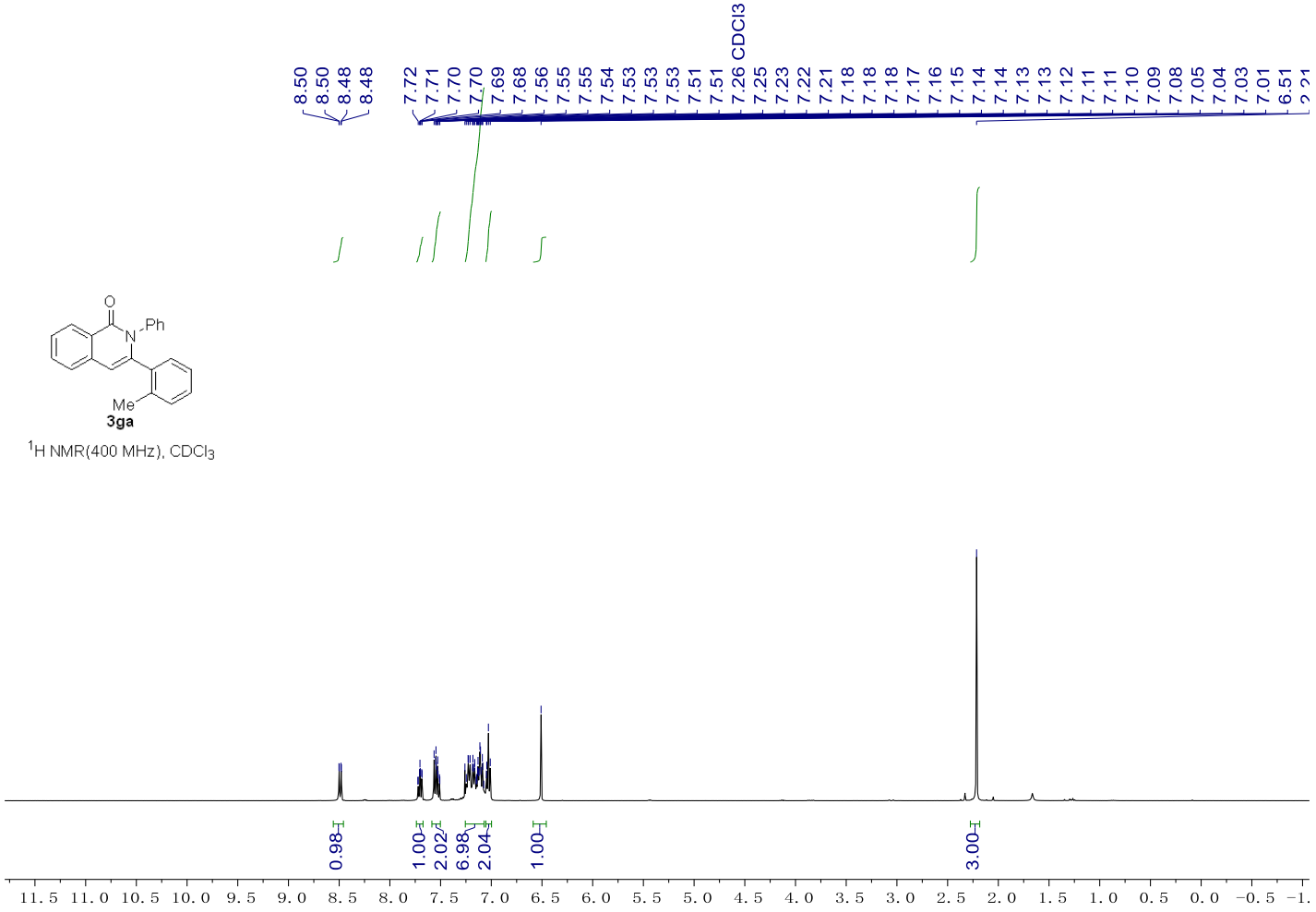
^{1}H NMR of 3-(2-methoxyphenyl)-2-phenylisoquinolin-1(2*H*)-one (3fa)



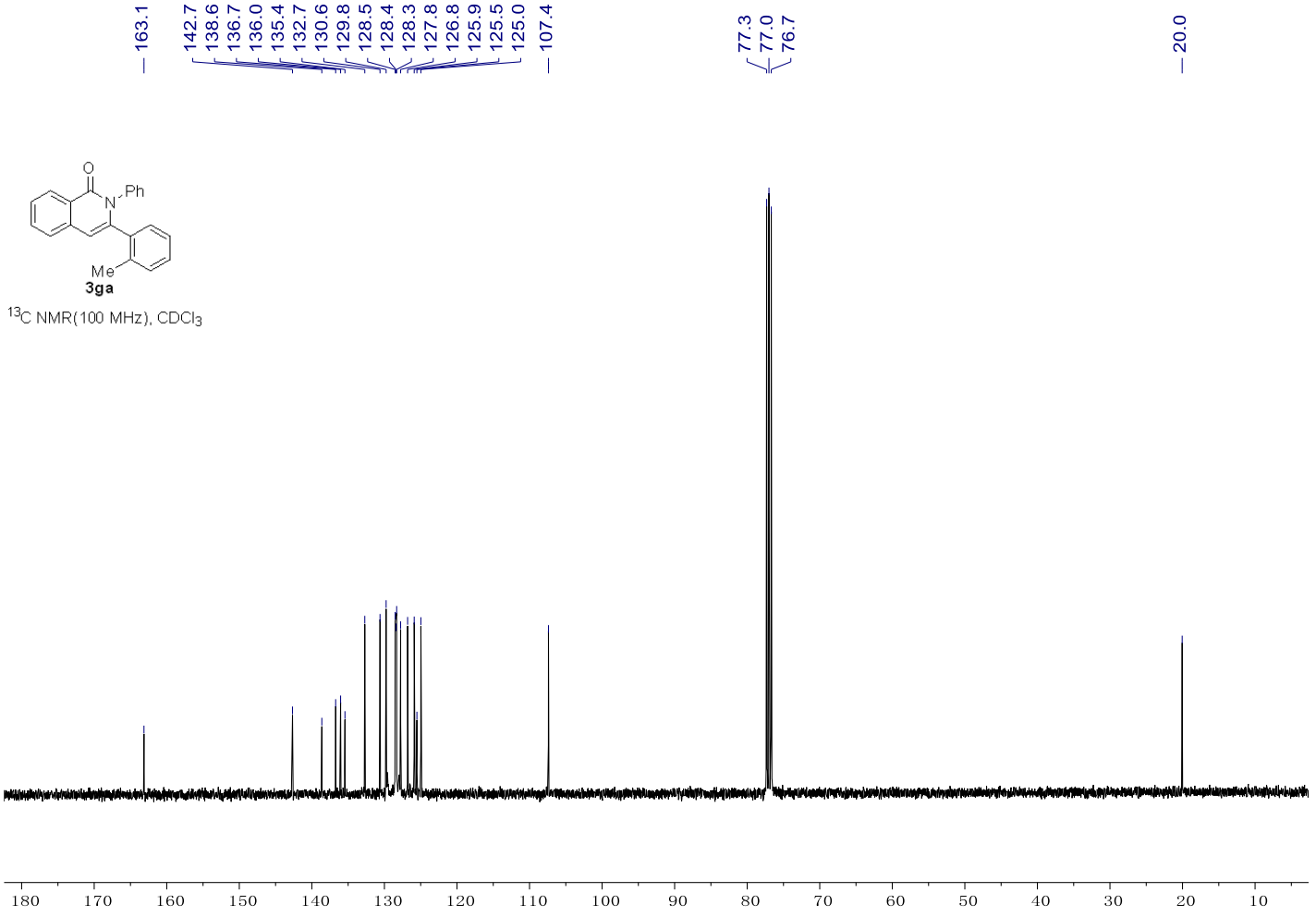
^{13}C NMR of 3-(2-methoxyphenyl)-2-phenylisoquinolin-1(2*H*)-one (3fa)



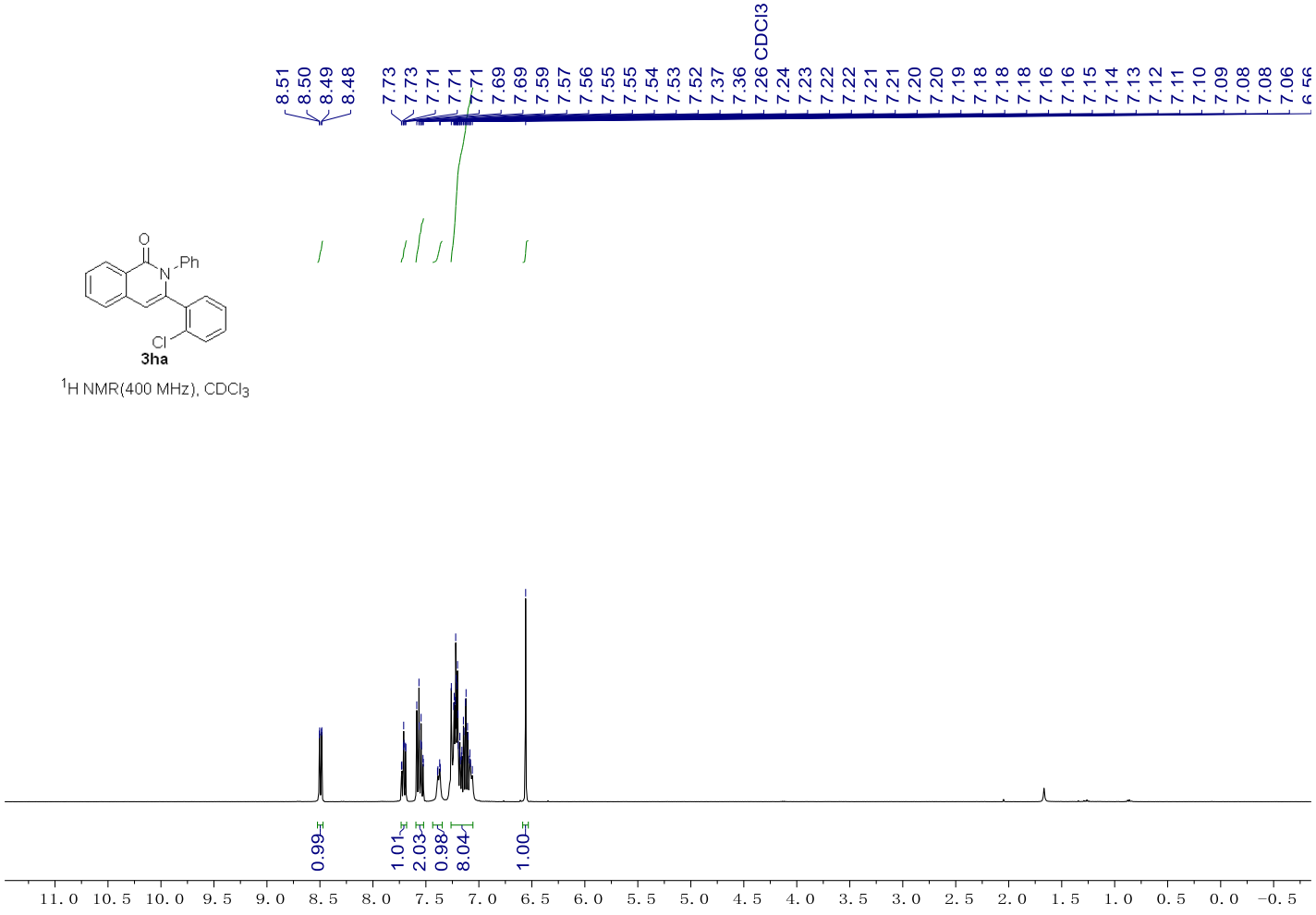
^{1}H NMR of 2-phenyl-3-(*o*-tolyl)isoquinolin-1(2*H*)-one (3ga)



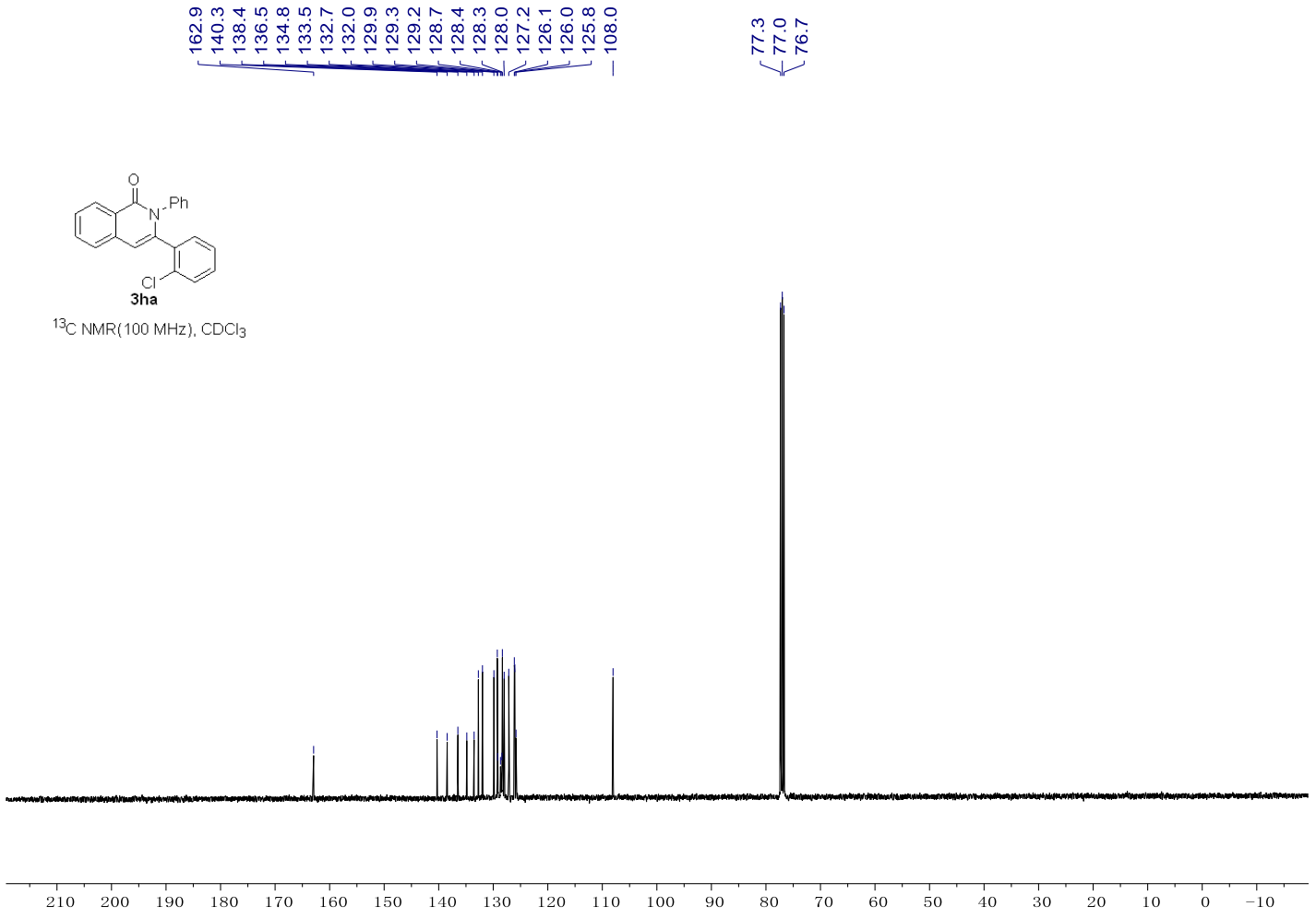
^{13}C NMR of 2-phenyl-3-(*o*-tolyl)isoquinolin-1(2*H*)-one (3ga)



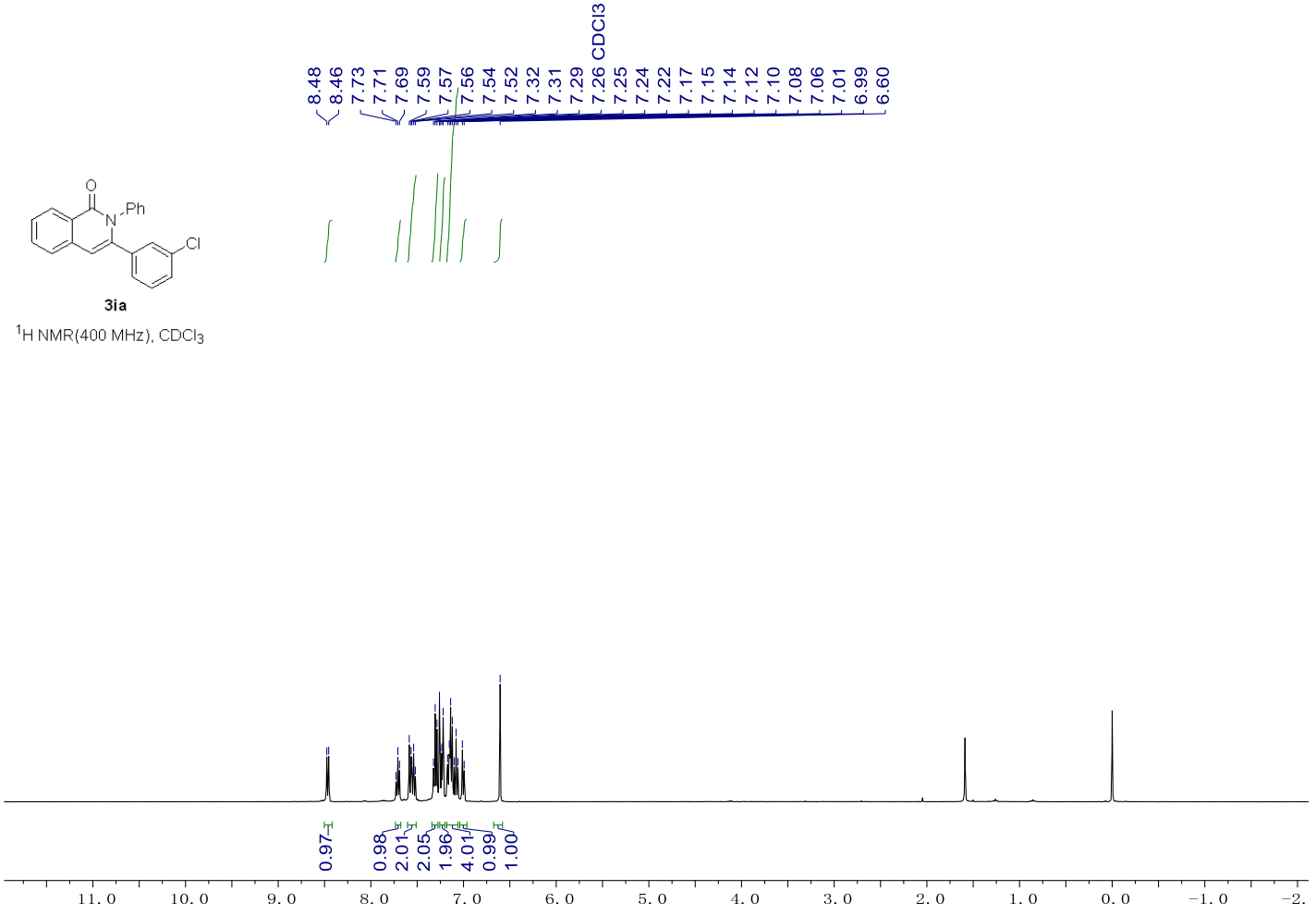
^{1}H NMR of 3-(2-chlorophenyl)-2-phenylisoquinolin-1(2*H*)-one (3ha)



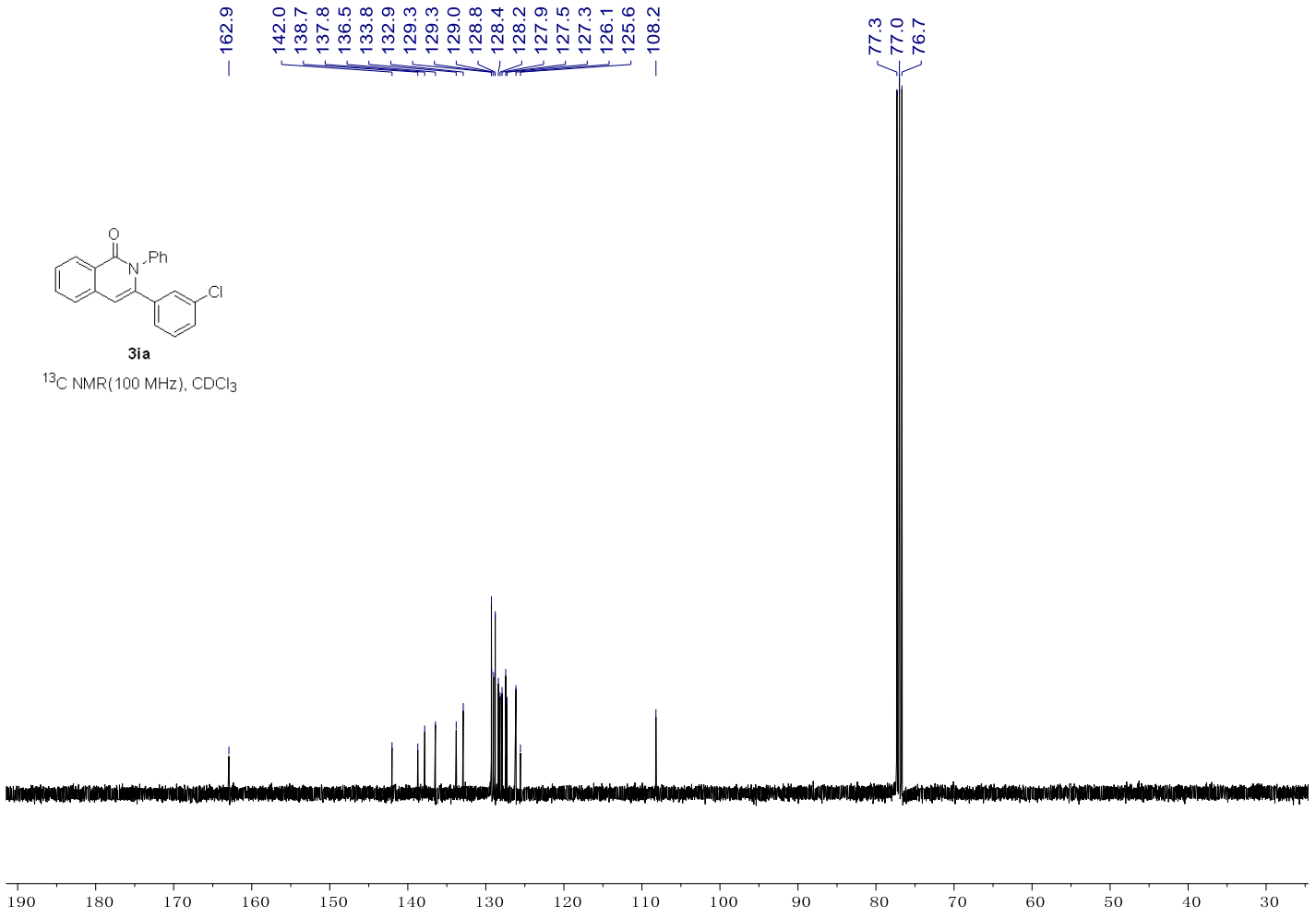
^{13}C NMR of 3-(2-chlorophenyl)-2-phenylisoquinolin-1(2*H*)-one (3ha)



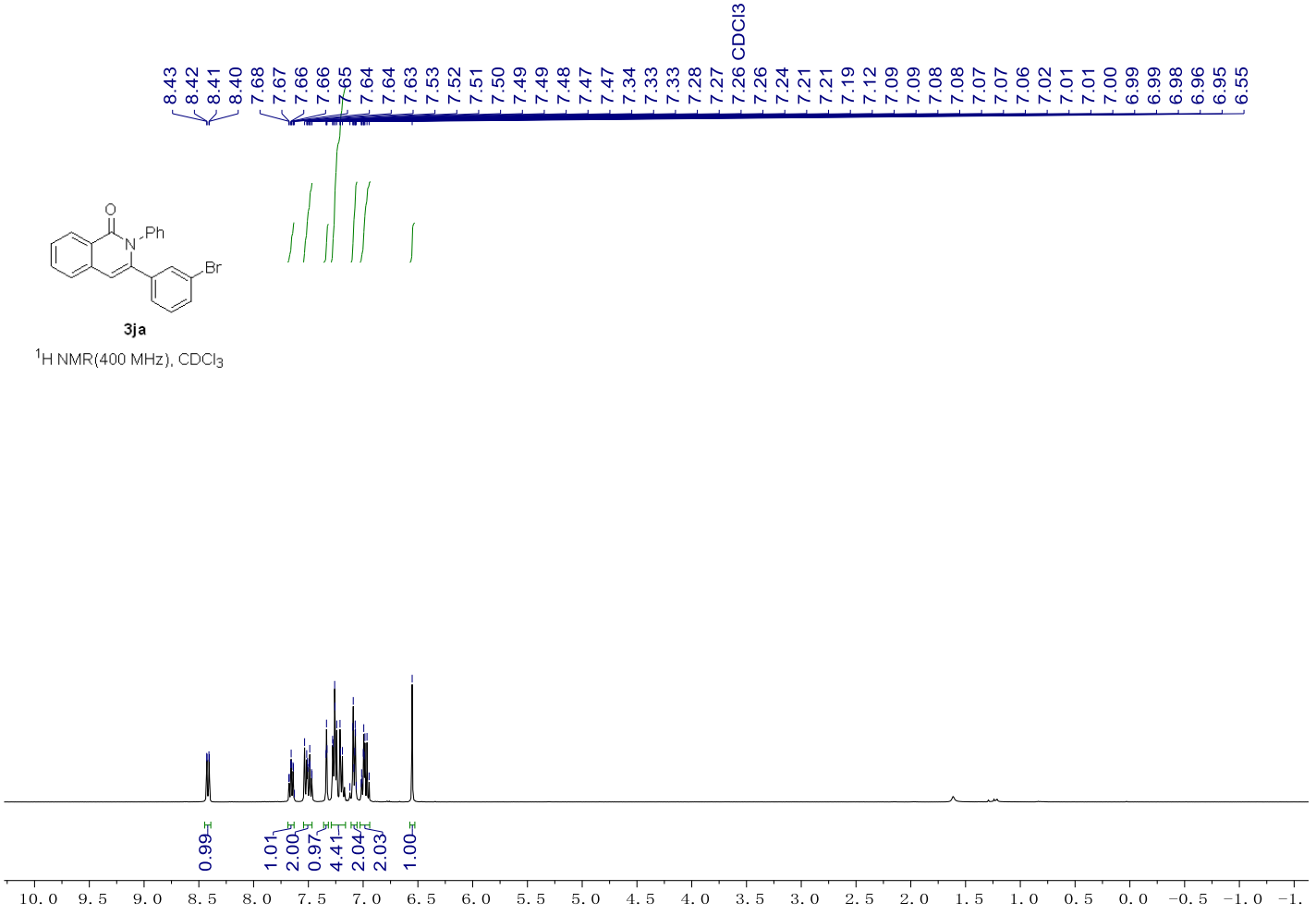
^{1}H NMR of 3-(3-chlorophenyl)-2-phenylisoquinolin-1(2*H*)-one (3ia)



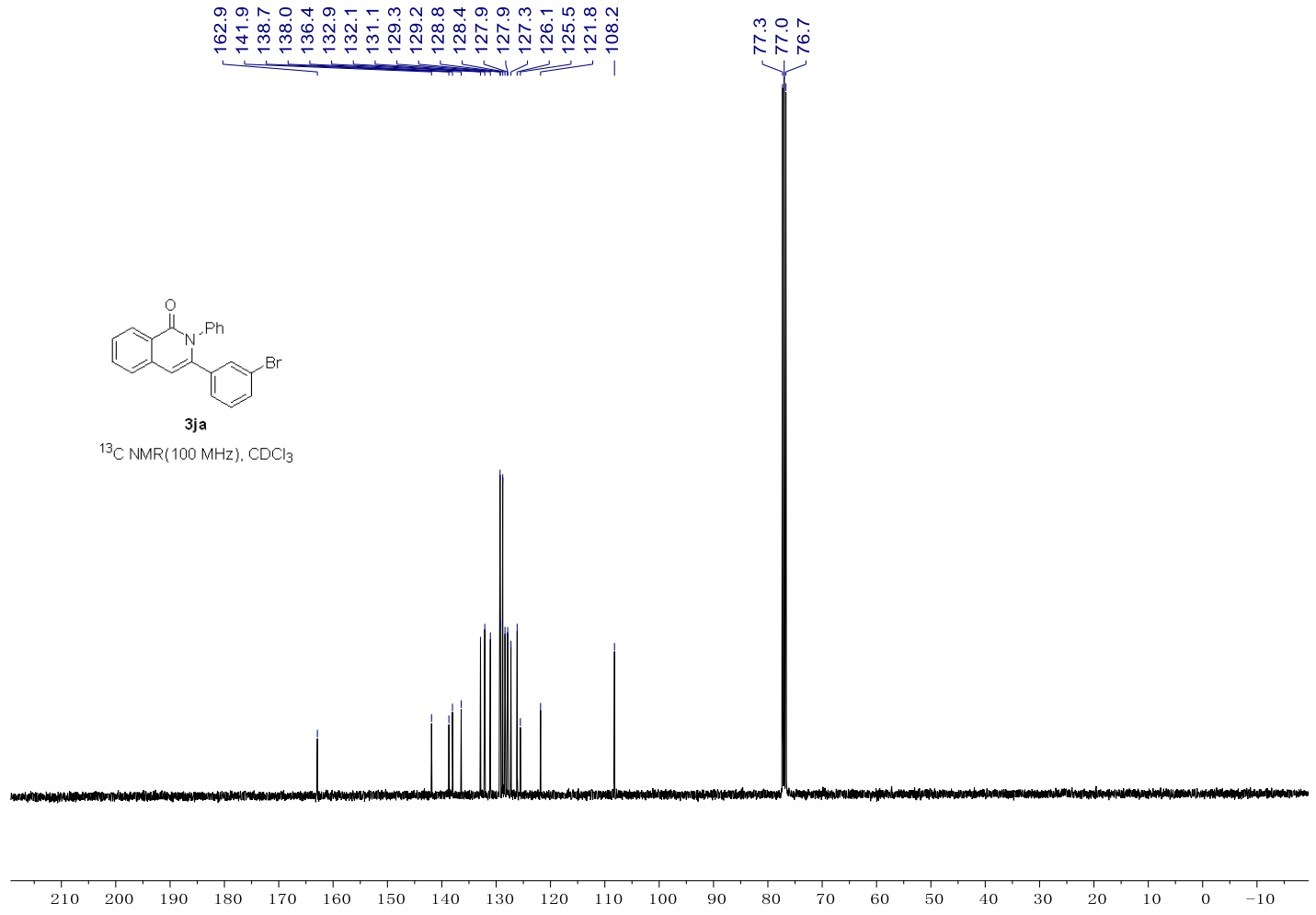
^{13}C NMR of 3-(3-chlorophenyl)-2-phenylisoquinolin-1(2*H*)-one (3ia)



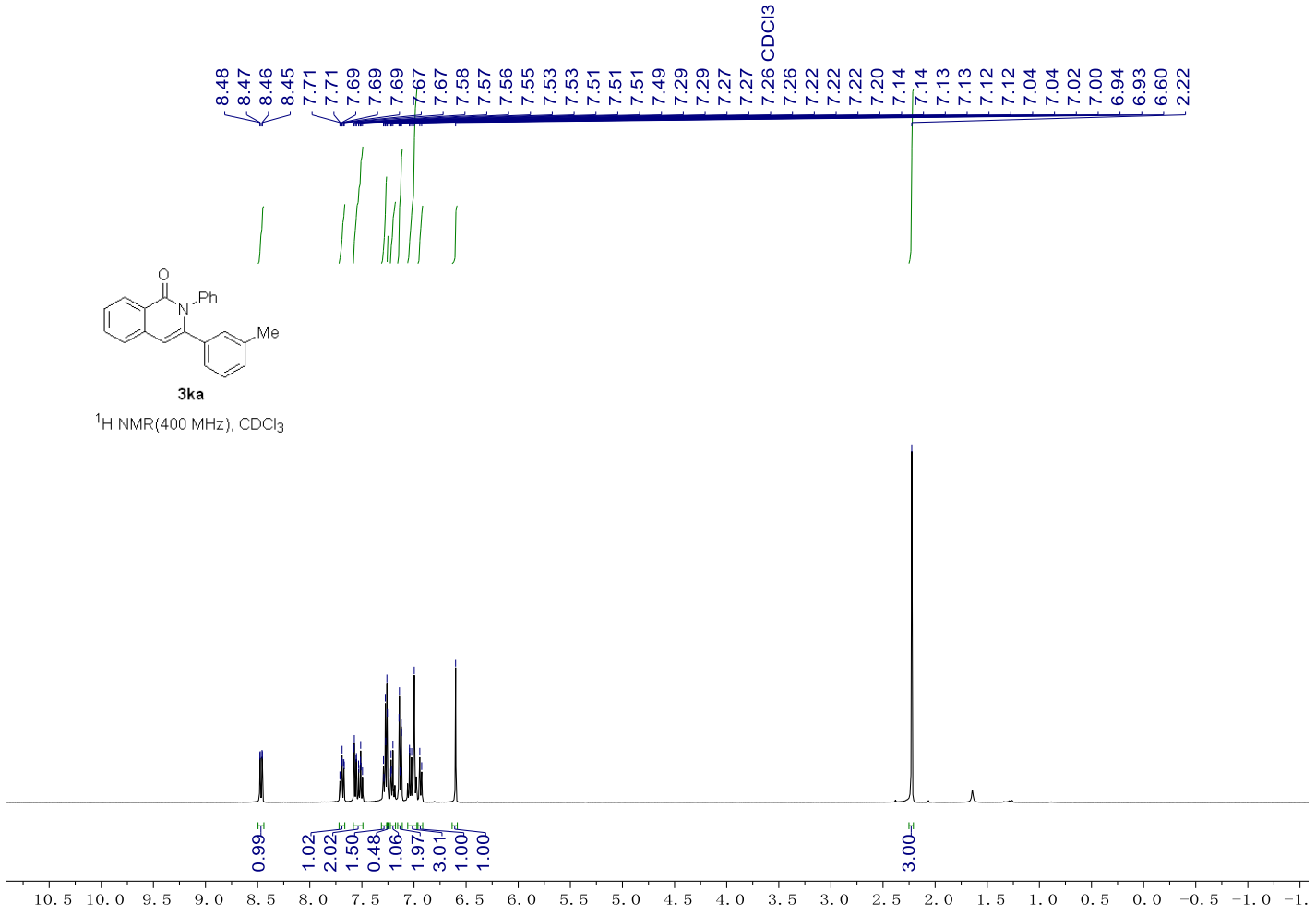
^{1}H NMR of 3-(3-bromophenyl)-2-phenylisoquinolin-1(2*H*)-one (3ja)



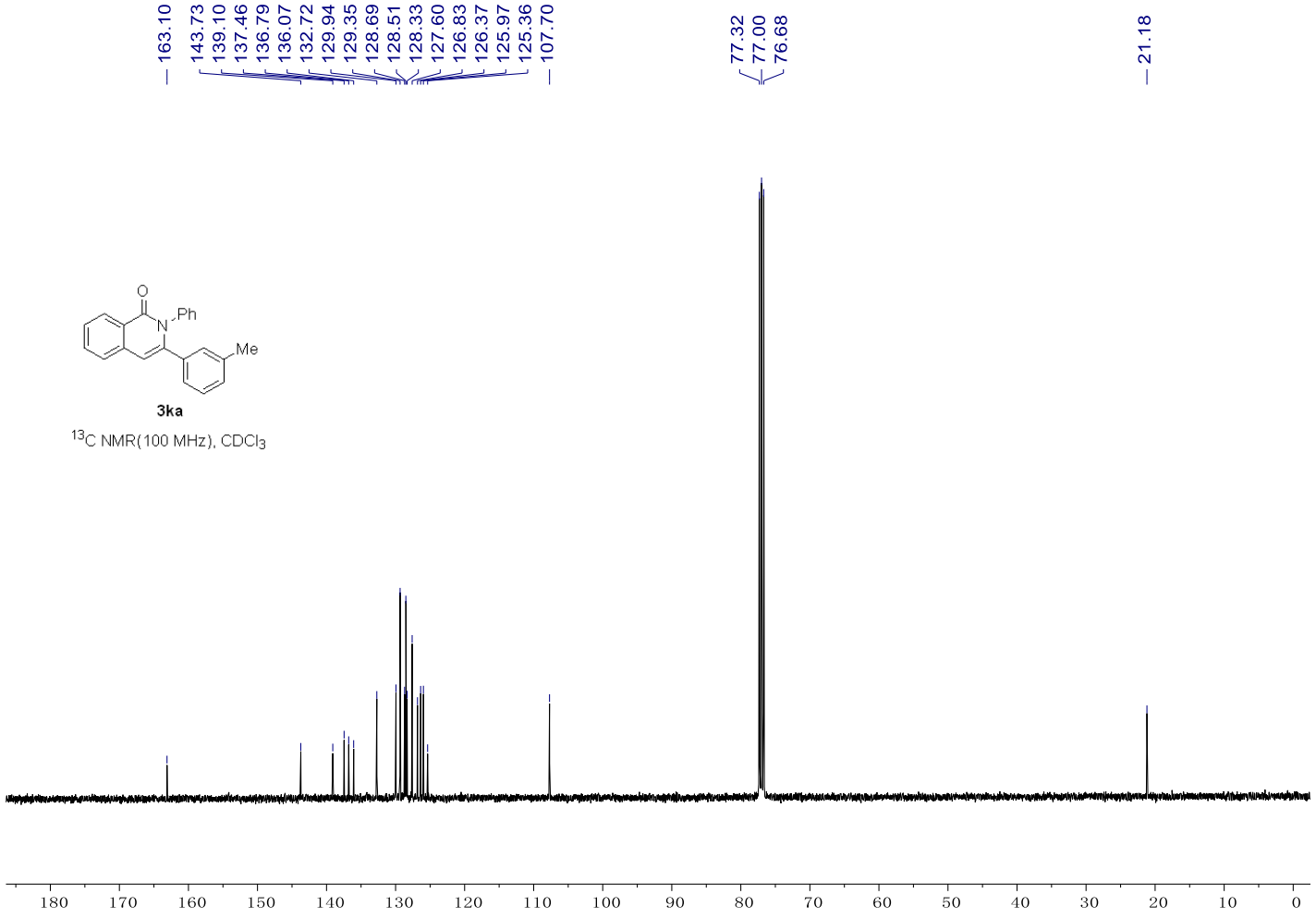
^{13}C NMR of 3-(3-bromophenyl)-2-phenylisoquinolin-1(2*H*)-one (3ja)



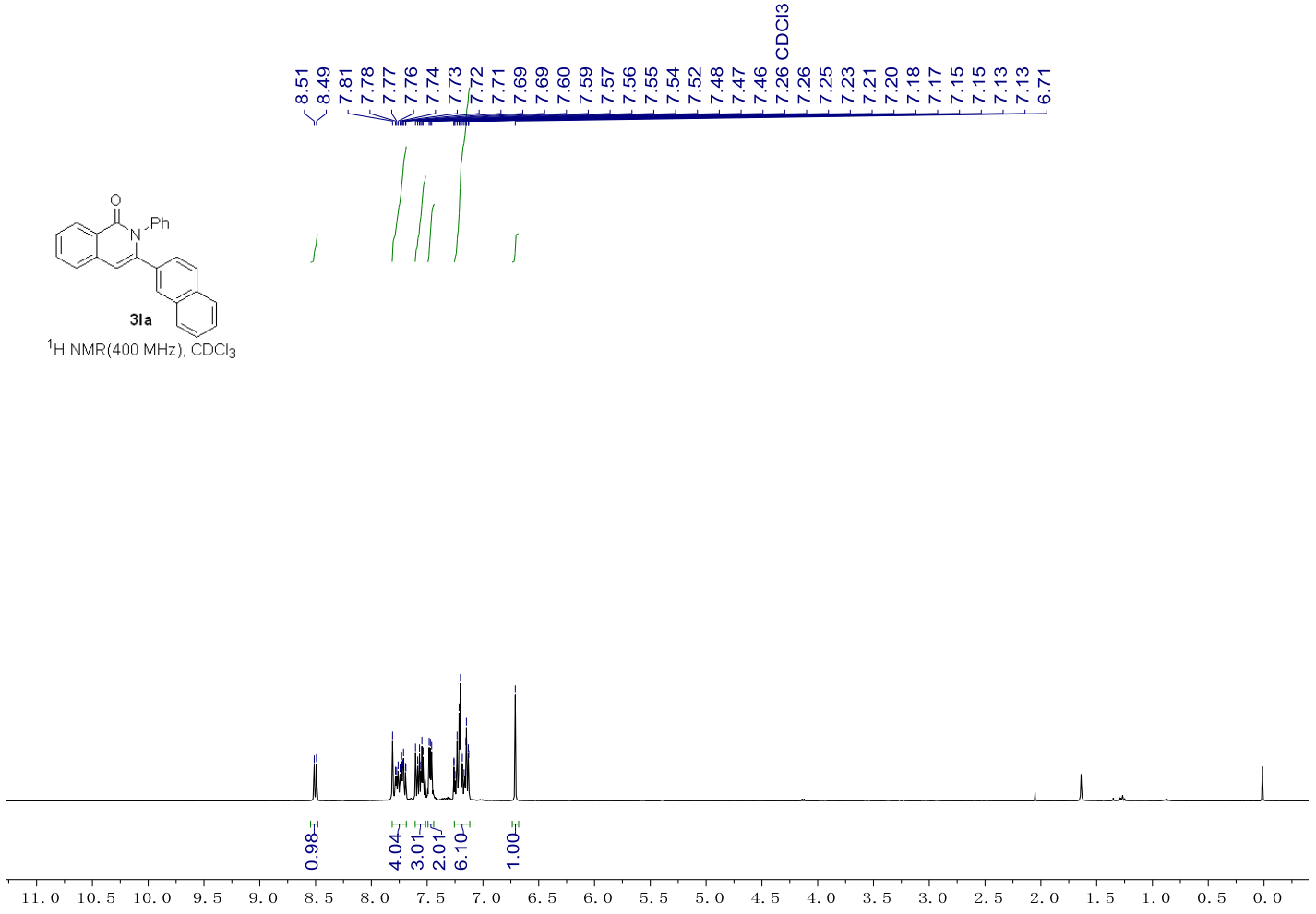
^{1}H NMR of 2-phenyl-3-(*m*-tolyl)isoquinolin-1(2*H*)-one (3ka)



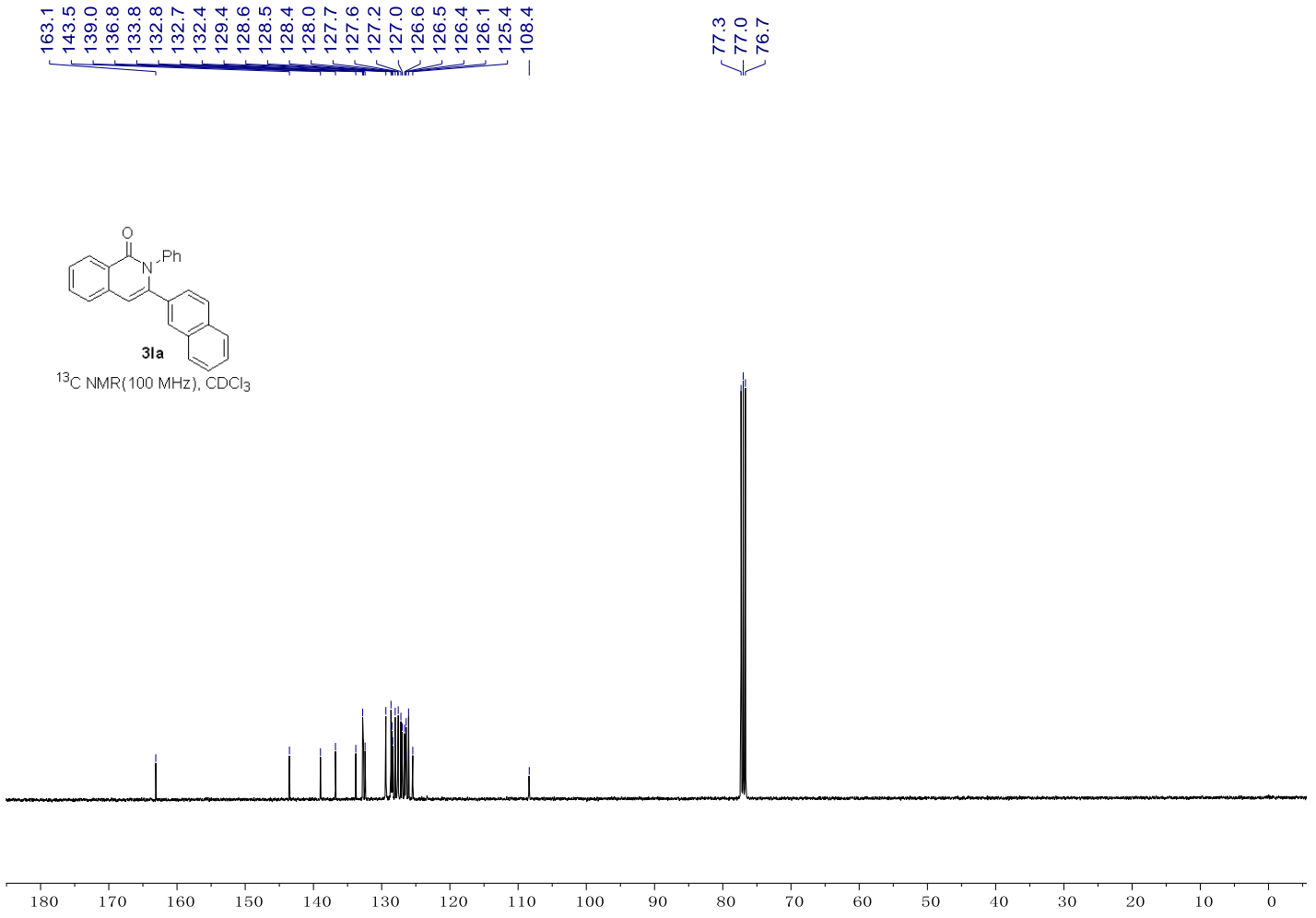
^{13}C NMR of 2-phenyl-3-(*m*-tolyl)isoquinolin-1(2*H*)-one (3ka)



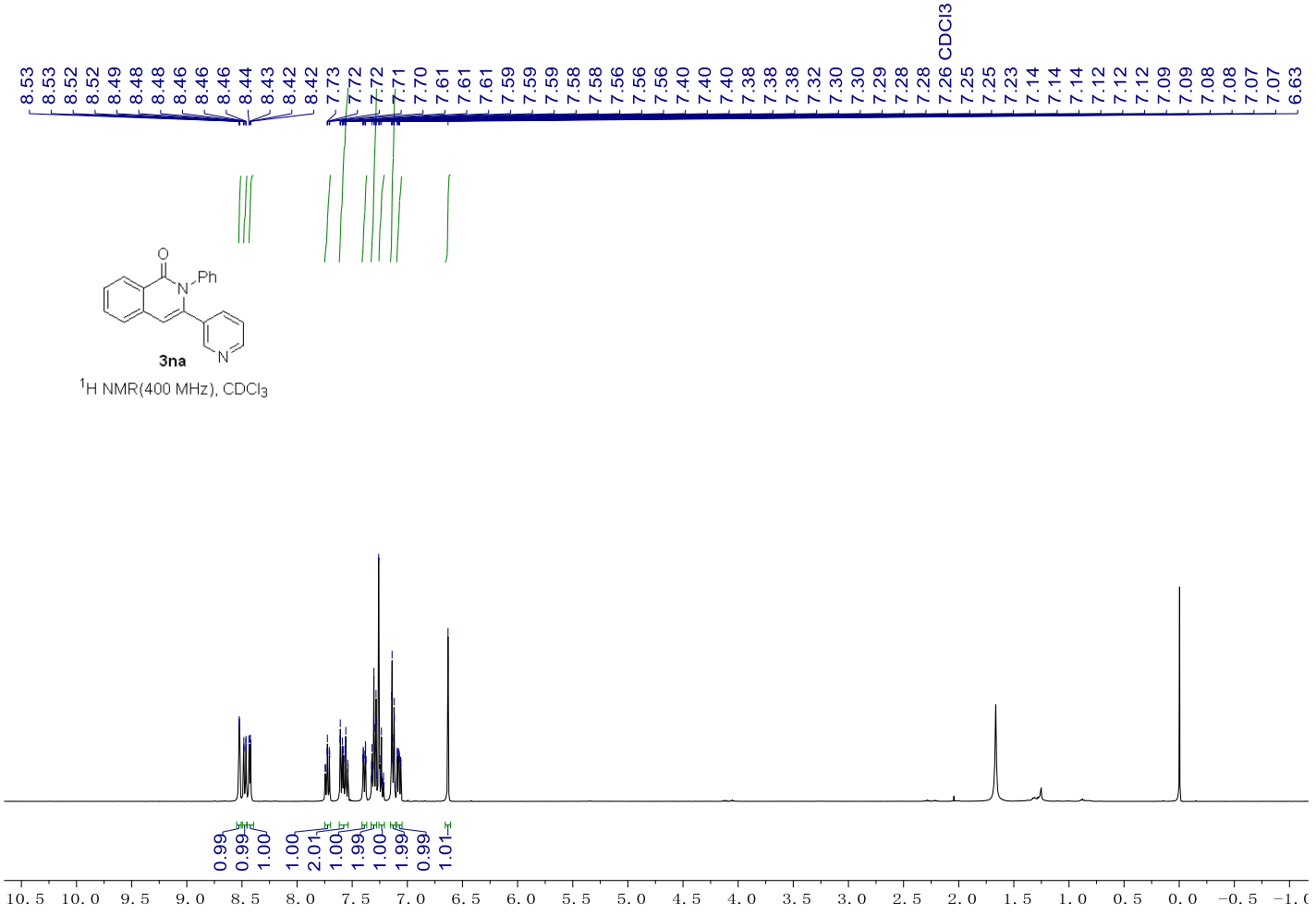
^{1}H NMR of 3-(naphthalen-2-yl)-2-phenylisoquinolin-1(2*H*)-one (3la)



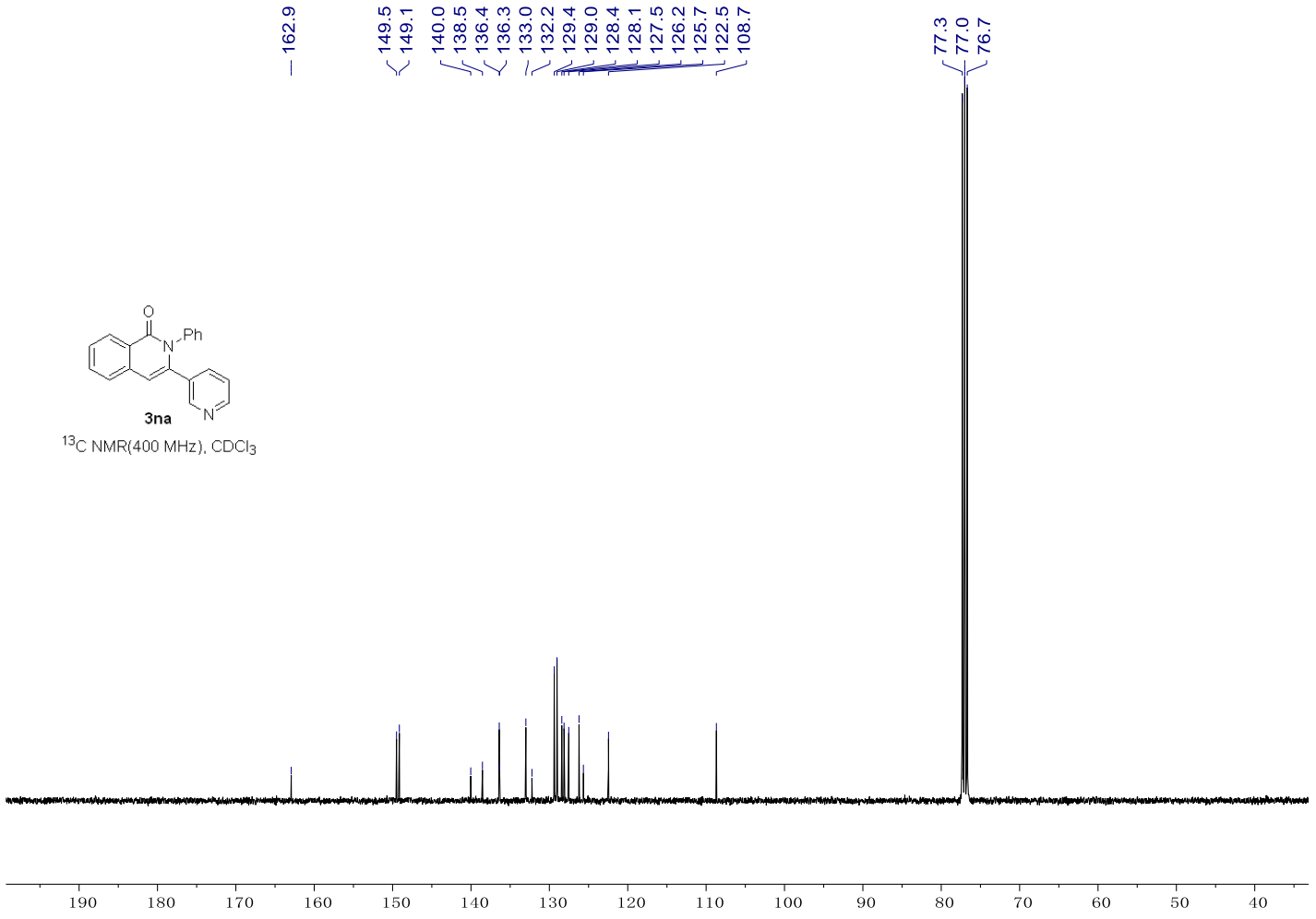
^{13}C NMR of 3-(naphthalen-2-yl)-2-phenylisoquinolin-1(2*H*)-one (3la)



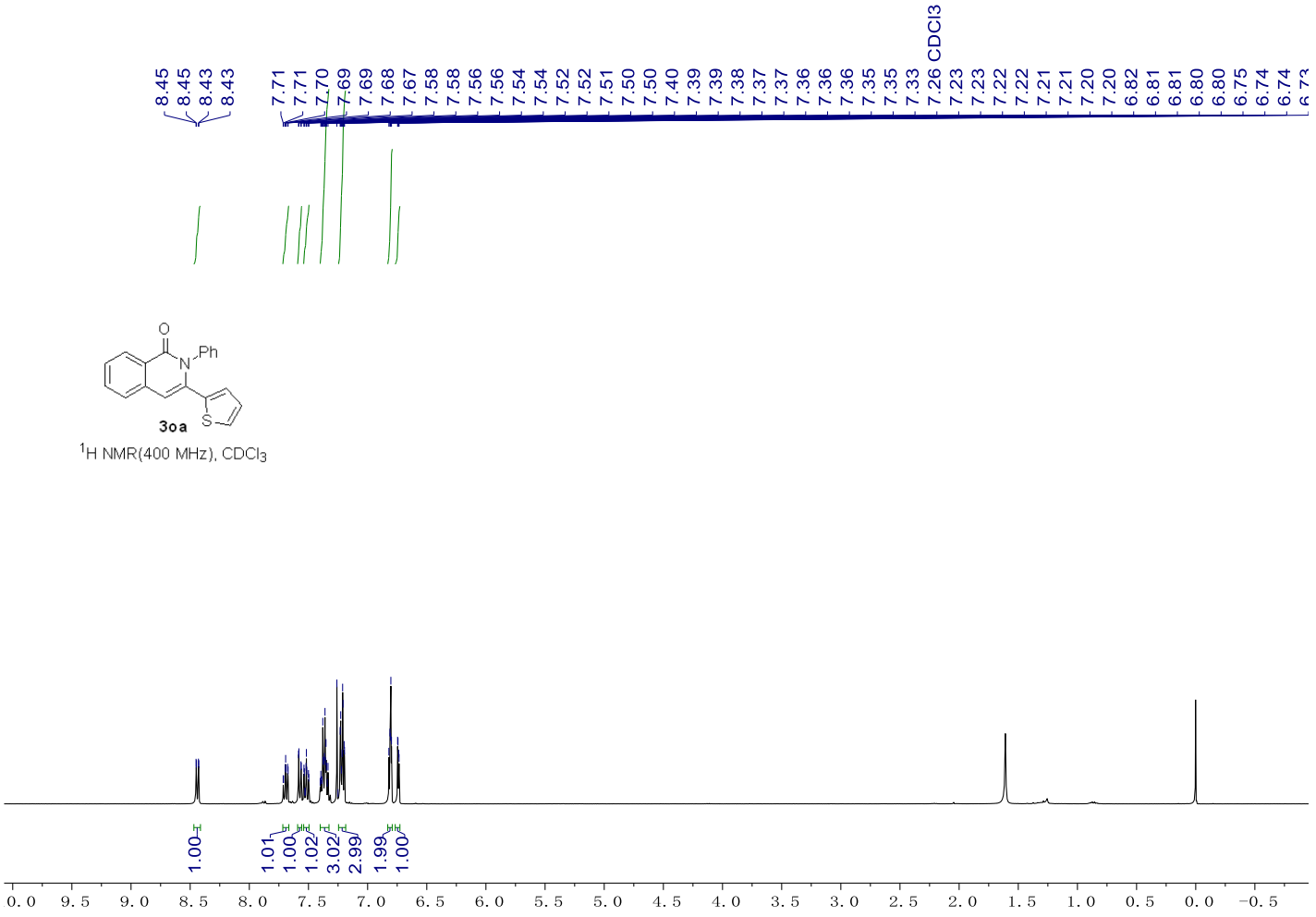
^{1}H NMR of 2-phenyl-3-(pyridin-3-yl)isoquinolin-1(2*H*)-one (3na)



^{13}C NMR of 2-phenyl-3-(pyridin-3-yl)isoquinolin-1(2*H*)-one (3na)



^{1}H NMR of 2-phenyl-3-(thiophen-2-yl)isoquinolin-1(2*H*)-one (3oa)



^{13}C NMR of 2-phenyl-3-(thiophen-2-yl)isoquinolin-1(2*H*)-one (3oa)