Supporting Information

For

Synthesis of Poly-substituted Oxazolidinones via Regioselective Addition of Azonaphthalenes

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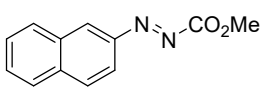
Contents

1. General Information:

All template reaction experiments were carried out under atmospheric conditions. Commercially available reagents were used without further purification. Solvents were treated prior to use according to the standard methods. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded at 300 or 400MHz on an Agilent spectrometer. $CDCl_3$ was used as solvent. Chemical shifts were referenced relative to residual solvent. Coupling constants (J) were reported in Hertz (Hz). Thin layer chromatography was carried out in the ultraviolet light using a GF-254 silica gel plate. Melting points were measured with micro melting point apparatus. HRMS were performed on an Agilent 6210 ESI/TOF.

2. Substrate of synthesis:



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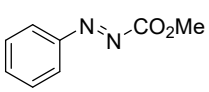

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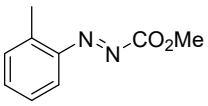

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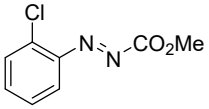

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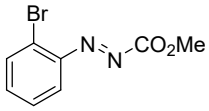

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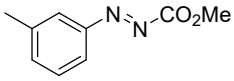

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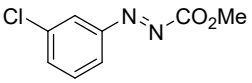

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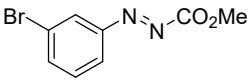

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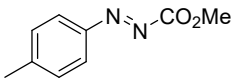

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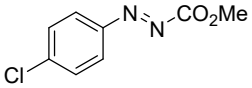

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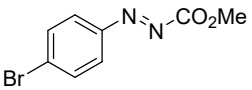

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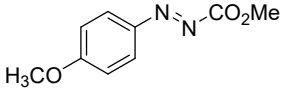

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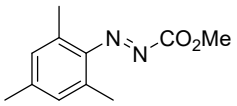

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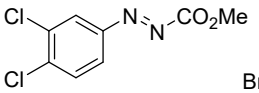

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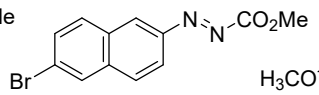

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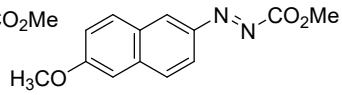

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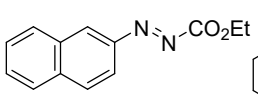
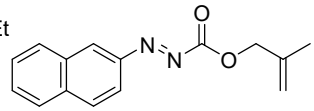
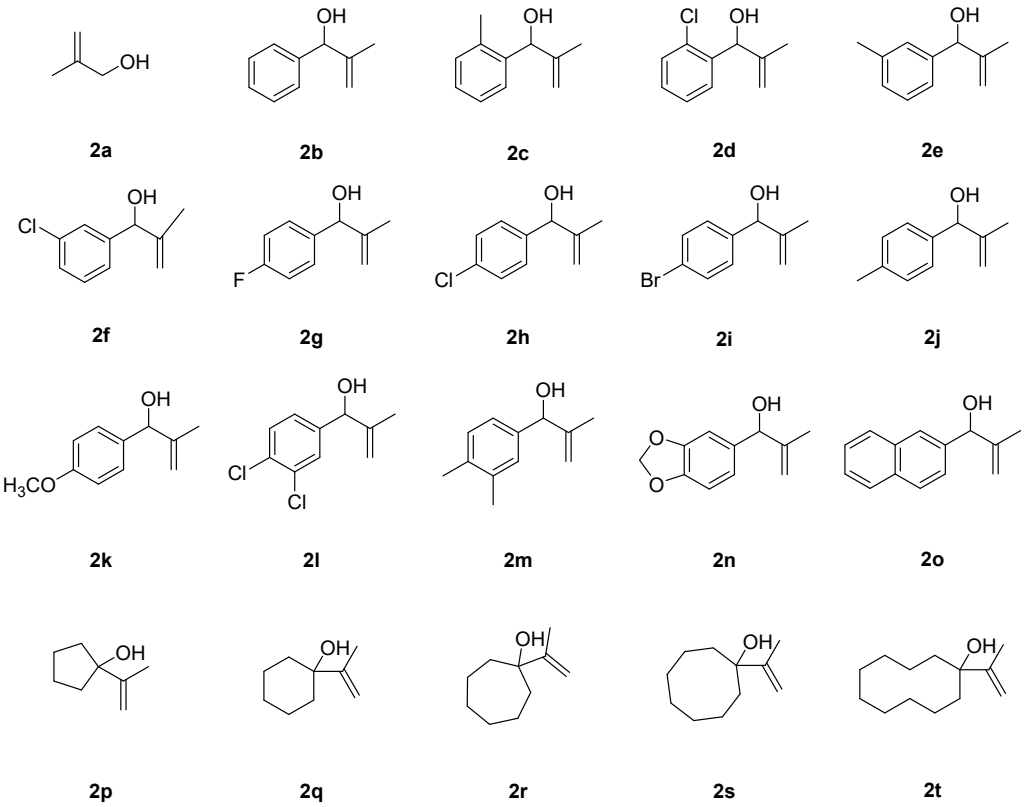


1q



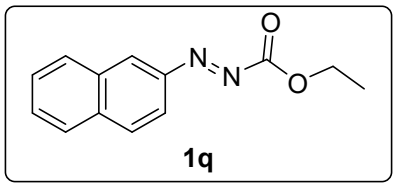
1r

All starting materials **1a-1q** are known compounds and are prepared according to literature. [1]**1r** is new compound and is prepared according to literatures. [2]



All starting materials **2a-2t** are known compounds. **2a** is commercially available. **2b-2t** are prepared according to literature.[3]

Ethyl (E)-2-(naphthalen-2-yl)diazene-1-carboxylate （1q）

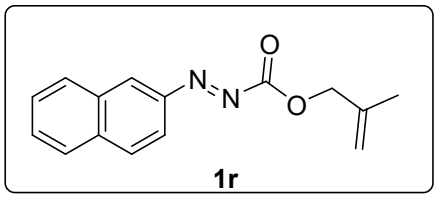


^{1}H NMR (400 MHz, $CDCl_3$): δ 8.60 (d, *J* = 1.82 Hz, 1H), 8.03 (d, *J* = 7.87 Hz, 1H), 7.92 – 7.87 (m, 3H), 7.65 – 7.56 (m, 2H), 4.56 (t, *J* = 7.14 Hz, 2H), 1.49 (t, *J* = 7.12 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 162.2, 149.3, 136.1, 133.1, 130.0, 129.5, 129.1, 128.1, 127.2, 115.5, 64.4, 14.2.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{13}H_{12}N_2O_2Na$ 251.0796; found 251.0797.

2-methylallyl (E)-2-(naphthalen-2-yl)diazene-1-carboxylate （1r）

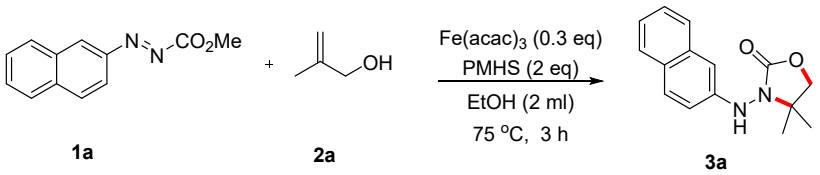


Yellow liquid, yield: 65%; R_f = 0.51 (EtOAc/Petroleum ether 1:7).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.58 (s, 1H), 8.00 (d, *J* = 7.90 Hz, 1H), 7.94 – 7.83 (m,

3H), 7.63 – 7.52 (m, 2H), 5.18 (s, 1H), 5.07 (s, 1H), 4.90 (s, 2H), 1.88 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 162.2, 149.3, 138.7, 136.1, 133.1, 132.5, 130.0, 129.5, 129.1, 128.1, 127.3, 115.3, 114.7, 71.3, 19.5.
HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{15}H_{14}N_2O_2Na$ 277.0947; found 277.0948.

3. Typical Procedure for Synthesis of 3a:

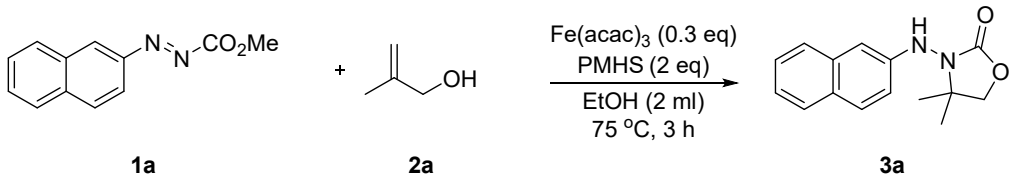


1a **2a** **3a**

$Fe(acac)_3$ (32 mg, 0.09 mmol) and methyl-2-(naphthalen-2-yl)diazene-1-carboxylate **1a** (64.2 mg, 0.3 mmol) are added to the reaction tube and dissolve with ethanol (2 ml). Afterwards, 2-Methyl-2-propen-1-ol **2a** (64.9 mg, 0.9 mmol), and PMHS (36 mg, 0.6 mmol) were added via syringe. The solution was heated to 75 °C for 3 h. After the reaction completed and quenched with water, then ethyl acetate extracted the solution. Finally, the purification by column chromatography on silica gel using ethyl acetate/petroleum ether (v/v, 1:4) as eluent to give **3a** as a white solid. (70 mg, 91% yield).

4. Optimization of the Reaction Conditions.

Table 1. Optimization of the Reaction Conditions [a, b]



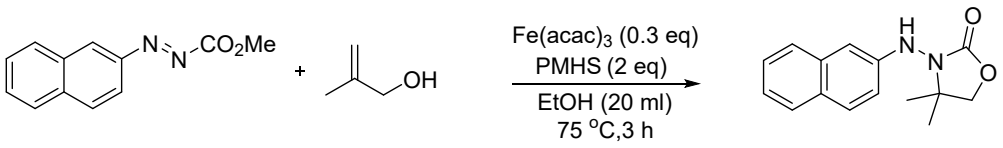
1a **2a** **3a**

entry	Variation from the Standard Conditions	Yield (%) **3a**
1	None	91
2	Without $Fe(acac)_3$	0
3	$Fe_2(ox)_3 \cdot 6H_2O$ instead of $Fe(acac)_3$	0
4	$Cu(acac)_2$ instead of $Fe(acac)_3$	0
5	$Co(acac)_2$ instead of $Fe(acac)_3$	0
6	$Ni(acac)_2$ instead of $Fe(acac)_3$	0
7	$Pd(OAc)_2$ instead of $Fe(acac)_3$	0
8	$FeCl_3$ instead of $Fe(acac)_3$	0
9	$PhSiH_3$ instead of PMHS	50
10	$(EtO)_3SiH$ instead of PMHS	86
11	Et_3SiH instead of PMHS	0

12	$NaBH_4$ instead of PMHS	0
13	THF instead of EtOH	30
14	CH_3CN instead of EtOH	15
15	CH_3OH instead of EtOH	31
16	Toluene instead of EtOH	0
17	At 90 °C,	58
18	At 60 °C,	trace
19	$Fe(acac)_3$ (20 mol %)	38
20	$Fe(acac)_3$ (40 mol %)	78
21	PMHS (2 equiv)	68
22	PMHS (4 equiv)	62

[a] Reaction conditions: **1a** (0.1 mmol), **2a** (0.3 mmol), catalyst (30 mol %), reductant (2 equiv), solvent (2 mL), 75 °C, 3h; [b] yield refers to isolated product.

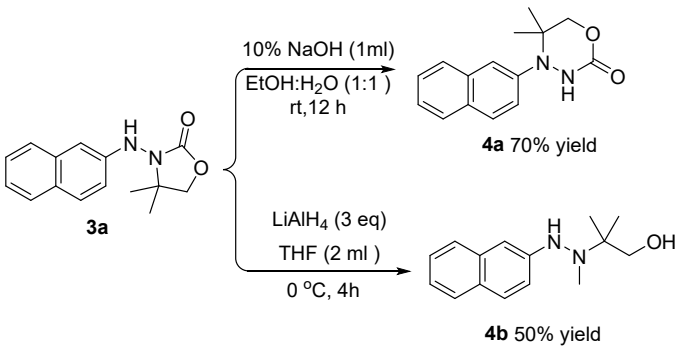
5. Scale-up Reaction



1a 5 mmol 1.07g **2a** **3a** 84 % yield

$Fe(acac)_3$ (529 mg, 0.3 eq) and methyl-2-(naphthalen-2-yl)diazene-1-carboxylate **1a** (1070 mg, 5 mmol) are added to the reaction tube and dissolve with ethanol (20 ml). Afterwards, 2-Methyl-2-propen-1-ol **2a** (1081 mg, 3 eq), and PMHS (600 mg, 2 eq) were added via syringe. The solution was heated to 75 °C for 3 h. After the reaction completed and quenched with water, then ethyl acetate extracted the solution. Finally, the purification by column chromatography on silica gel using ethyl acetate/petroleum ether (v/v, 1:4) as eluent to give **3a** as a white solid. (1075 mg, 84% yield).

6. Typical Procedure for Synthesis of 4a,4b

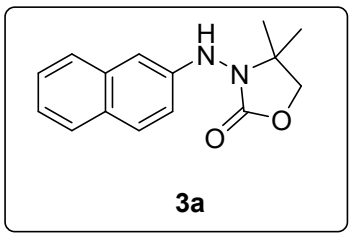


4a: Oxazolidinone **3a** (51.2 mg, 0.2 mmol), 10% NaOH aqueous solution (1.0 mL) and EtOH (1 mL) was added. The reaction mixture was stirred for 12 h at room temperature (monitored by TLC). After the reaction completed and then extracted with EtOAc three times. Finally, the purification by column chromatography on silica gel using ethyl acetate/petroleum ether (v/v, 1:1) as eluent to give **4a** as a white solid. (35.8 mg, 70% yield).

4b: Oxazolidinone **3a** (51.2 mg, 0.2 mmol), $LiAlH_4$ (24 mg, 3 eq) was added and dissolve with THF (2 ml) under argon atmosphere. The reaction mixture was stirred for 4 h at 0 °C (monitored by TLC). After the reaction completed and then extracted with EtOAc three times. Finally, the purification by column chromatography on silica gel using ethyl acetate/petroleum ether (v/v, 1:5) as eluent to give **4a** as a colorless liquid. (24.4 mg, 50% yield).

7. Characterization of 3, 4a, 4b, 5a:

4,4-dimethyl-3-(naphthalen-2-ylamino) oxazolidin-2-one (3a)



3a

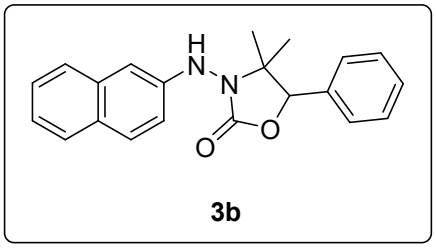
White solid, m.p.124-127 °C, 70 mg, yield: 91%; R_f = 0.35 (EtOAc/Petroleum ether 1:3).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.74 – 7.64 (m, 3H), 7.40 (ddd, *J* = 8.24, 6.83, 1.37 Hz, 1H), 7.35 – 7.27 (m, 1H), 7.20 (d, *J* = 2.32 Hz, 1H), 7.07 (dd, *J* = 8.81, 2.34 Hz, 1H), 5.99 (s, 1H), 4.24 (s, 2H), 1.39 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 158.0, 145.1, 134.3, 129.4, 129.1, 127.7, 126.6, 126.4, 123.4, 115.9, 107.5, 74.2, 60.0, 23.5.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{15}H_{16}N_2O_2Na$ 279.1109; found 279.1112.

4,4-dimethyl-3-(naphthalen-2-ylamino)-5-phenyloxazolidin-2-one (3b)



3b

White solid, m.p.184-187 °C, 48 mg, yield: 48 %; R_f = 0.40 (EtOAc/Petroleum ether 1:3).

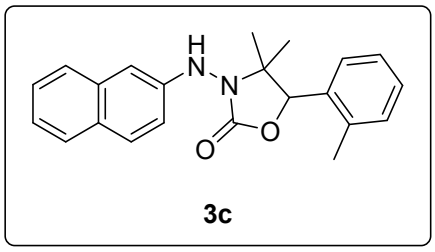
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (dt, *J* = 15.52, 7.73 Hz, 3H), 7.43 (q, *J* = 8.05, 7.50 Hz, 6H), 7.34 – 7.25 (m, 2H), 7.10 (d, *J* = 8.79 Hz, 1H), 6.12 (s, 1H), 5.47 (s, 1H), 1.52 (s, 3H), 0.90 (s, 3H).

^{13}C NMR (101 MHz, DMSO-d_6): δ 156.9, 146.8, 134.8, 129.1, 129.1, 129.0, 128.6, 128.0, 126.8, 126.5, 123.0, 116.2, 105.7, 83.6, 64.2, 23.6, 19.8.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{21}H_{20}N_2O_2Na$ 355.1422; found

355.1429.

4,4-dimethyl-3-(naphthalen-2-ylamino)-5-(o-tolyl)oxazolidin-2-one (3c)



3c

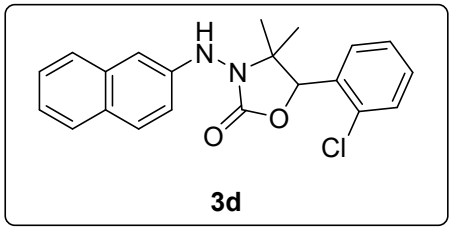
White solid, m.p.220-223 ^{o}C, 46 mg, yield: 45 %; R_f = 0.32 (EtOAc/Petroleum ether 1:3).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 – 7.58 (m, 3H), 7.55 (d, *J* = 6.95 Hz, 1H), 7.37 (dt, *J* = 32.38, 7.46 Hz, 4H), 7.25 (d, *J* = 6.93 Hz, 2H), 7.07 (d, *J* = 8.82 Hz, 1H), 6.38 (s, 1H), 5.75 (s, 1H), 2.42 (s, 3H), 1.54 (s, 3H), 0.99 (s, 3H).

^{13}C NMR (101 MHz, DMSO-d_6): δ 156.9, 146.9, 136.0, 134.8, 133.2, 131.2, 129.1, 128.9, 128.6, 128.0, 127.4, 126.8, 126.5, 123.0, 116.2, 105.8, 80.9, 64.4, 24.8, 20.8, 19.8.

HRMS (ESI-TOF) m/z: [M + Na]$^{+}$ Calcd for $C_{22}H_{22}N_2O_2Na$ 369.1579; found 369.1578.

5-(2-chlorophenyl)-4,4-dimethyl-3-(naphthalen-2-ylamino)oxazolidin-2-one (3d)



3d

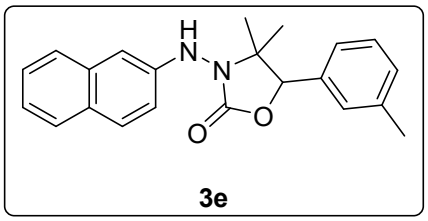
White solid, m.p.240-240 ^{o}C, 43 mg, yield: 40 %; R_f = 0.35 (EtOAc/Petroleum ether 1:3).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 – 7.64 (m, 3H), 7.41 (dd, *J* = 14.15, 5.86 Hz, 4H), 7.34 – 7.25 (m, 3H), 7.10 (dd, *J* = 8.73, 2.34 Hz, 1H), 6.05 (s, 1H), 5.42 (s, 1H), 1.54 (s, 3H), 0.91 (s, 3H).

^{13}C NMR (101 MHz, DMSO-d_6): δ 156.2, 146.6, 132.1, 130.9, 130.3, 129.1, 128.6, 128.0, 126.7, 126.5, 123.1, 116.1, 105.9, 80.6, 64.1,25.3,20.9.

HRMS (ESI-TOF) m/z: [M + Na]$^{+}$ Calcd for $C_{21}H_{19}ClN_2O_2Na$ 389.1032; found 389.1034.

4,4-dimethyl-3-(naphthalen-2-ylamino)-5-(m-tolyl)oxazolidin-2-one (3e)



3e

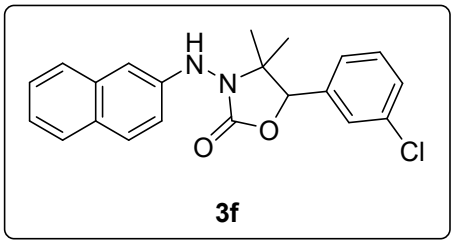
White solid, m.p.176-179 °C, 67 mg, yield: 65 %; R_f = 0.36 (EtOAc/Petroleum ether 1:3).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 – 7.59 (m, 3H), 7.42 (t, *J* = 7.66 Hz, 1H), 7.31 (dt, *J* = 12.48, 6.33 Hz, 4H), 7.19 (d, *J* = 8.67 Hz, 2H), 7.11 (d, *J* = 8.83 Hz, 1H), 6.01 (s, 1H), 5.43 (s, 1H), 2.42 (s, 3H), 1.53 (s, 3H), 0.91 (s, 3H).

^{13}C NMR (101 MHz, DMSO-d_6): δ 156.9, 146.8, 138.2, 134.8, 129.7, 129.1, 128.9, 128.6, 128.0, 126.9, 126.8, 126.5, 123.6, 123.0, 116.2, 105.7, 83.6, 64.1, 23.6, 21.5, 19.8.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{22}H_{22}N_2O_2Na$ 369.1579; found 369.1573.

5-(3-chlorophenyl)-4,4-dimethyl-3-(naphthalen-2-ylamino)oxazolidin-2-one (3f)



3f

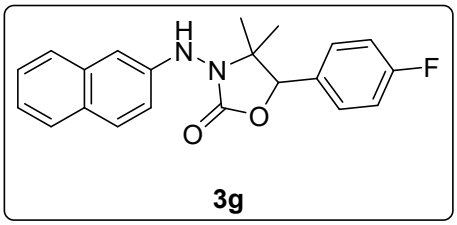
White solid, m.p.175-178 °C, 65 mg, yield: 60 %; R_f = 0.32(EtOAc/Petroleum ether 1:3).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (d, *J* = 8.13 Hz, 1H), 7.67 (d, *J* = 8.50 Hz, 2H), 7.49 – 7.33 (m, 4H), 7.34 – 7.21 (m, 3H), 7.08 (d, *J* = 8.74 Hz, 1H), 6.16 (s, 1H), 5.42 (s, 1H), 1.53 (s, 3H), 0.91 (s, 3H).

^{13}C NMR (101 MHz, DMSO-d_6): δ 156.5, 146.7, 137.4, 134.7, 133.9, 131.0, 129.1, 128.6, 128.0, 126.8, 126.5, 126.2, 125.3, 123.1, 116.2, 105.7, 82.8, 64.1, 23.6, 19.8.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{21}H_{19}ClN_2O_2Na$ 389.1032; found 389.1034.

5-(4-fluorophenyl)-4,4-dimethyl-3-(naphthalen-2-ylamino)oxazolidin-2-one (3g)



3g

White solid, m.p.180-182 °C, 57 mg, yield: 55 %; R_f = 0.31 (EtOAc/Petroleum ether 1:3).

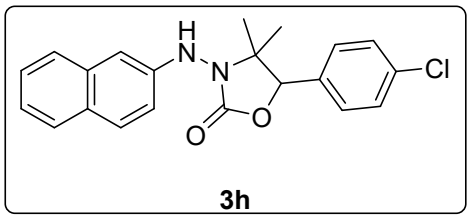
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 – 7.66 (m, 3H), 7.41 (dt, *J* = 8.27, 5.36 Hz, 3H), 7.31 (t, *J* = 7.51 Hz, 2H), 7.15 (d, *J* = 8.41 Hz, 2H), 7.12 – 7.09 (m, 1H), 6.06 (s, 1H), 5.44 (s, 1H), 1.51 (s, 3H), 0.89 (s, 3H).

^{13}C NMR (101 MHz, DMSO-d_6): δ 163.8, 161.4, 156.7, 146.8, 134.8, 129.1, 128.8, 128.7, 128.6, 128.0, 126.8, 126.5, 123.0, 116.2, 116.1, 115.8, 105.7, 83.0 23.5, 19.8.

^{19}F NMR (376 MHz, DMSO-d_6): δ -112.55

HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for $C_{21}H_{19}FN_2O_2Na$ 373.1328; found 373.1327.

5-(4-chlorophenyl)-4,4-dimethyl-3-(naphthalen-2-ylamino)oxazolidin-2-one (3h)



3h

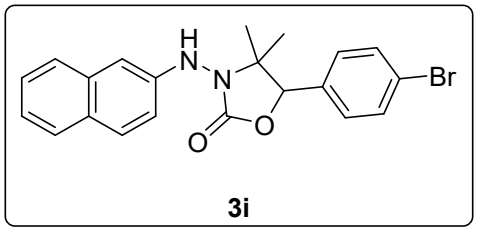
White solid, m.p.151-153 °C, 71 mg, yield: 65 %; R_f = 0.33 (EtOAc/Petroleum ether 1:3).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 – 7.63 (m, 3H), 7.50 – 7.39 (m, 3H), 7.39 – 7.20 (m, 5H), 7.11 (d, *J* = 8.79 Hz, 1H), 5.97 (s, 1H), 5.43 (s, 1H), 1.52 (s, 3H), 0.90 (s, 3H).

^{13}C NMR (101 MHz, DMSO-d_6): δ 156.6, 146.7, 134.8, 133.7, 129.1, 128.6, 128.4, 128.0, 126.8, 126.5, 123.0, 116.2, 105.7, 82.9, 64.0, 23.4, 19.7.

HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for $C_{21}H_{19}ClN_2O_2Na$ 389.1032; found 389.1036.

5-(4-bromophenyl)-4,4-dimethyl-3-(naphthalen-2-ylamino) oxazolidine-2-one (3i)



3i

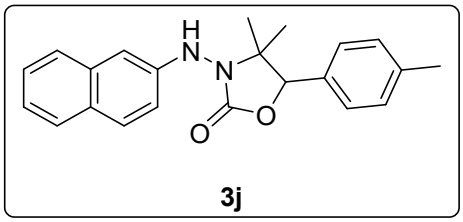
White solid, m.p.160-162 °C, 67 mg, yield: 55 %; R_f = 0.35 (EtOAc/Petroleum ether 1:3).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 – 7.71 (m, 2H), 7.68 (d, *J* = 8.30 Hz, 1H), 7.59 (d, *J* = 8.07 Hz, 2H), 7.42 (t, *J* = 7.60 Hz, 1H), 7.31 (dd, *J* = 12.30, 7.92 Hz, 4H), 7.11 (d, *J* = 8.81 Hz, 1H), 5.95 (s, 1H), 5.42 (s, 1H), 1.52 (s, 3H), 0.90 (s, 3H).

^{13}C NMR (101 MHz, DMSO-d_6): δ 156.6, 146.7, 134.7, 132.0, 129.1, 128.7, 128.6,

128.0, 126.8, 126.5, 123.0, 122.3, 116.2, 105.7, 82.9, 64.0, 23.5, 19.8.
HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for $C_{21}H_{19}BrN_2O_2Na$ 433.0527; found 433.0528.

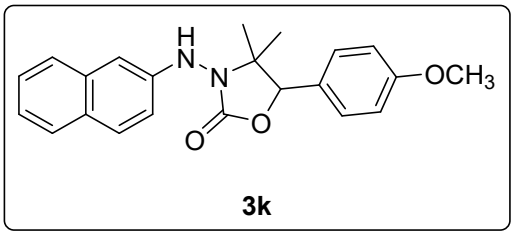
4,4-dimethyl-3-(naphthalen-2-ylamino)-5-(p-tolyl)oxazolidin-2-one (3j)



3j

White solid, m.p.157-159 ^oC, 62 mg, yield: 60 %; R_f = 0.32 (EtOAc/Petroleum ether 1:3).
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (d, *J* = 8.53 Hz, 2H), 7.68 (d, *J* = 8.33 Hz, 1H), 7.42 (t, *J* = 7.57 Hz, 1H), 7.32 – 7.24 (m, 7H), 7.12 (d, *J* = 8.88 Hz, 1H), 5.95 (s, 1H), 5.43 (s, 1H), 2.40 (s, 3H), 1.51 (s, 3H), 0.90 (s, 3H).
^{13}C NMR (101 MHz, DMSO-d_6): δ δ 156.9, 146.8, 138.4, 134.8, 129.6, 129.1, 128.6, 128.0, 126.7, 126.5, 123.0, 116.2, 105.7, 83.7, 64.2, 23.6, 21.2, 19.8.
HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for $C_{22}H_{22}N_2O_2Na$ 369.1579; found 369.1584.

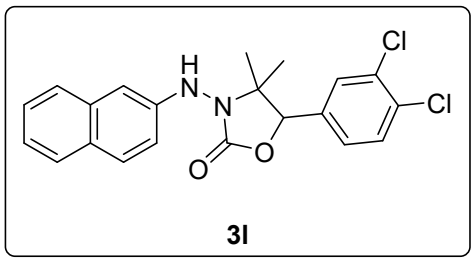
5-(4-methoxyphenyl)-4,4-dimethyl-3-(naphthalen-2-ylamino) oxazolidine-2-one (3k)



3k

White solid, m.p.184-186 ^oC, 54 mg, yield: 50 %; R_f = 0.35 (EtOAc/Petroleum ether 1:3).
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (dt, *J* = 14.68, 7.24 Hz, 3H), 7.41 (t, *J* = 7.58 Hz, 1H), 7.35 – 7.22 (m, 4H), 7.10 (d, *J* = 8.88 Hz, 1H), 6.96 (d, *J* = 8.16 Hz, 2H), 6.12 (s, 1H), 5.41 (s, 1H), 3.85 (s, 3H), 1.49 (s, 3H), 0.91 (s, 3H).
^{13}C NMR (101 MHz, DMSO-d_6): δ 159.9, 157.0, 146.8, 134.8, 129.1, 128.6, 128.0, 126.7, 126.5, 123.0, 116.2, 114.4, 105.7, 83.6, 64.1, 55.6, 23.6, 19.7.
HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for $C_{22}H_{22}N_2O_3Na$ 385.1528; found 385.1531.

5-(3,4-dichlorophenyl)-4,4-dimethyl-3-(naphthalen-2-ylamino) oxazolidin-2-one (3l)



3l

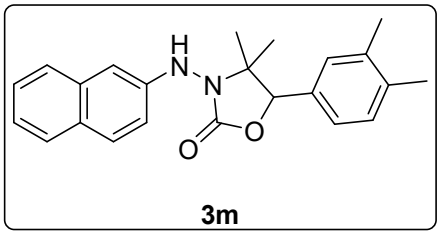
White solid, m.p.194-196 °C, 54 mg, yield: 45 %; R_f = 0.40 (EtOAc/Petroleum ether 1:3).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71 (dt, *J* = 16.06, 7.93 Hz, 3H), 7.65 – 7.37 (m, 3H), 7.32 (t, *J* = 7.48 Hz, 1H), 7.26 – 7.22 (m, 2H), 7.10 (d, *J* = 8.76 Hz, 1H), 6.00 (s, 1H), 5.40 (s, 1H), 1.53 (s, 3H), 0.92 (s, 3H).

^{13}C NMR (101 MHz, DMSO-d_6): δ 156.3, 146.6, 134.7, 132.0, 131.8, 131.4, 129.1, 128.6, 128.0, 126.9, 126.8, 126.5, 123.1, 116.2, 105.7, 82.2, 64.0, 23.6, 19.7.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{21}H_{18}Cl_2N_2O_2Na$ 423.0643; found 423.0648.

5-(3,4-dimethylphenyl)-4,4-dimethyl-3-(naphthalen-2-ylamino) oxazolidin-2-one (3m)



3m

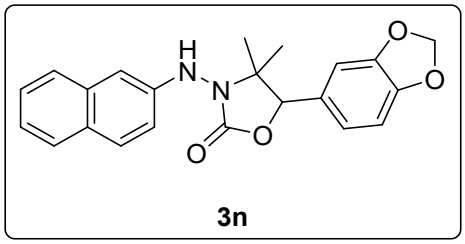
White solid, m.p.178-180 °C, 59 mg, yield: 55%; R_f = 0.35 (EtOAc/Petroleum ether 1:3).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71 (dd, *J* = 22.52, 8.35 Hz, 3H), 7.42 (t, *J* = 7.54 Hz, 1H), 7.35 – 7.26 (m, 3H), 7.24 – 7.05 (m, 4H), 5.92 (s, 1H), 5.40 (s, 1H), 2.31 (d, *J* = 6.23 Hz, 6H), 1.51 (s, 3H), 0.91 (s, 3H).

^{13}C NMR (101 MHz, DMSO-d_6): δ 156.9, 146.9, 137.1, 136.9, 134.8, 130.0, 129.1, 128.6, 128.0, 127.5, 126.8, 126.5, 123.9, 123.0, 116.2, 105.7, 83.7, 64.2, 23.6, 19.9, 19.6.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{23}H_{24}N_2O_2Na$ 383.1735; found 383.1741.

5-(benzo[d][1,3]dioxol-5-yl)-4,4-dimethyl-3-(naphthalen-2-ylamino) oxazolidin-2-one (3n)



3n

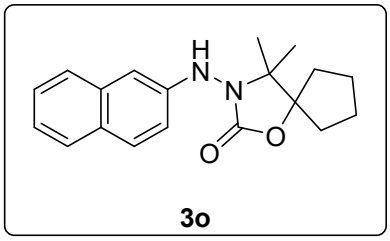
White solid, m.p.190-192 ^{o}C, 67 mg, yield: 60 %; R_f = 0.31 (EtOAc/Petroleum ether 1:3).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.74 – 7.62 (m, 3H), 7.41 (ddd, *J* = 8.23, 6.81, 1.34 Hz, 1H), 7.35 – 7.25 (m, 2H), 7.08 (dd, *J* = 8.85, 2.31 Hz, 1H), 6.89 (d, *J* = 15.71 Hz, 3H), 6.21 (s, 1H), 6.02 (s, 2H), 5.36 (s, 1H), 1.48 (s, 3H), 0.93 (s, 3H).

^{13}C NMR (101 MHz, DMSO-d_6): δ 156.8, 148.0, 147.9, 146.8, 134.8, 129.1, 128.6, 128.0, 126.7, 126.5, 123.0, 120.2, 116.2, 108.8, 107.0, 105.7, 101.8, 83.6, 64.2, 23.6, 19.7.

HRMS (ESI-TOF) m/z: [M + Na]$^{+}$ Calcd for $C_{22}H_{20}N_2O_4Na$ 399.1320; found 399.1313.

4,4-dimethyl-3-(naphthalen-2-ylamino)-1-oxa-3-azaspiro[4.4]nonan-2-one (3o)



3o

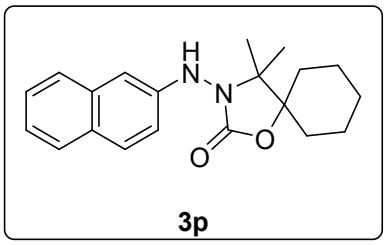
White solid, m.p.211-214 ^{o}C, 30 mg, yield: 32 %; R_f = 0.30 (EtOAc/Petroleum ether 1:3).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 (dd, *J* = 22.32, 8.34 Hz, 3H), 7.39 (t, *J* = 7.60 Hz, 1H), 7.29 (d, *J* = 7.69 Hz, 1H), 7.19 (s, 1H), 7.11 – 7.00 (m, 1H), 6.03 (s, 1H), 2.03 (d, *J* = 52.38 Hz, 4H), 1.85 (d, *J* = 24.10 Hz, 4H), 1.30 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 158.1, 145.5, 134.3, 129.5, 129.1, 127.7, 126.6, 126.4, 123.4, 115.9, 107.8, 95.7, 64.1, 22.7, 20.6.

HRMS (ESI-TOF) m/z: [M + Na]$^{+}$ Calcd for $C_{19}H_{22}N_2O_2Na$ 333.1579; found 333.1585.

4,4-dimethyl-3-(naphthalen-2-ylamino)-1-oxa-3-azaspiro[4.5]decan-2-one (3p)



3p

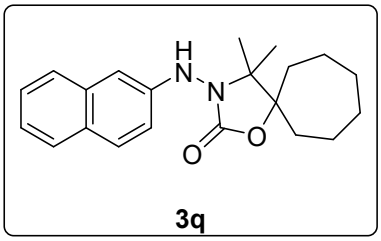
White solid, m.p.216-218 ^{o}C, 43 mg, yield: 45 %; R_f = 0.32(EtOAc/Petroleum ether 1:3).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 – 7.55 (m, 3H), 7.38 (t, *J* = 7.52 Hz, 1H), 7.30 – 7.25 (m, 1H), 7.18 (s, 1H), 7.04 (dd, *J* = 8.85, 2.25 Hz, 1H), 6.14 (s, 1H), 2.16 (d, *J* = 88.91 Hz, 2H), 1.95 – 1.58 (m, 6H), 1.47 (d, *J* = 24.60 Hz, 2H), 1.23 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 158.2, 145.8, 134.3, 129.4, 129.1, 127.7, 126.6, 126.3, 123.3, 115.9, 107.6, 84.7, 65.9, 25.2, 21.8, 19.9.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{20}H_{24}N_2O_2Na$ 347.1735; found 347.1732.

4,4-dimethyl-3-(naphthalen-2-ylamino)-1-oxa-3-azaspiro [4.6] undec-ane-2-one (3q)



3q

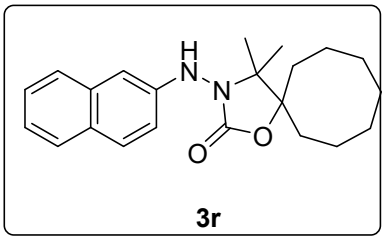
White solid, m.p.220-224 ^{o}C, 36 mg, yield: 36 %; R_f = 0.32 (EtOAc/Petroleum ether 1:3).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 – 7.61 (m, 3H), 7.39 (t, *J* = 7.54 Hz, 1H), 7.33 – 7.26 (m, 1H), 7.20 (s, 1H), 7.07 (dd, *J* = 8.87, 2.29 Hz, 1H), 5.92 (d, *J* = 5.99 Hz, 1H), 2.15 (dd, *J* = 14.40, 8.65 Hz, 2H), 1.96 – 1.72 (m, 4H), 1.58 (s, 6H), 1.26 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 145.8, 134.3, 129.5, 129.2, 127.7, 126.7, 126.4, 123.5, 116.0, 107.9, 88.8, 66.8, 34.5, 29.8, 22.3, 19.7.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{21}H_{26}N_2O_2Na$ 361.1892; found 361.1899.

4,4-dimethyl-3-(naphthalen-2-ylamino)-1-oxa-3-azaspiro[4.7] dodecan-2-one (3r)



3r

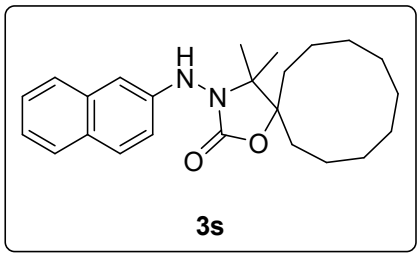
White solid, m.p.207-210 °C, 44 mg, yield: 42 %; R_f = 0.35 (EtOAc/Petroleum ether 1:3).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 – 7.53 (m, 3H), 7.39 (t, *J* = 7.51 Hz, 1H), 7.33 – 7.24 (m, 1H), 7.18 (d, *J* = 2.30 Hz, 1H), 7.03 (dd, *J* = 8.72, 2.29 Hz, 1H), 6.13 (s, 1H), 2.63 – 1.86 (m, 4H), 1.85 – 1.66 (m, 6H), 1.56 (d, *J* = 14.18 Hz, 4H), 1.30 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 158.1, 145.8, 134.3, 129.4, 129.1, 127.7, 126.6, 126.3, 123.3, 115.9, 107.6, 88.6, 66.3, 25.0, 21.9, 20.8.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{22}H_{22}N_2O_2Na$ 375.2048; found 375.2051.

4,4-dimethyl-3-(naphthalen-2-ylamino)-1-oxa-3-azaspiro[4.9]tetradecan-2-one (3s)



3s

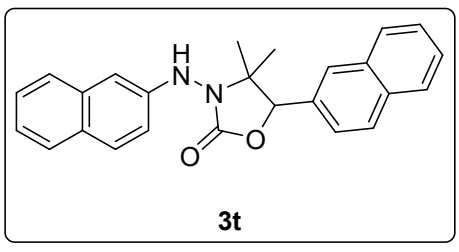
White solid, m.p.215-217 °C, 41 mg, yield: 36 %; R_f = 0.36 (EtOAc/Petroleum ether 1:3).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 – 7.57 (m, 3H), 7.39 (t, *J* = 7.56 Hz, 1H), 7.30 – 7.24 (m, 1H), 7.19 (s, 1H), 7.05 (dd, *J* = 8.88, 2.15 Hz, 1H), 6.03 (s, 1H), 2.27 (d, *J* = 14.46 Hz, 2H), 2.08 (s, 4H), 1.67 (s, 6H), 1.61 (d, *J* = 9.66 Hz, 6H), 1.30 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 158.2, 145.8, 134.3, 129.4, 129.1, 127.7, 126.6, 126.4, 123.4, 116.0, 107.8, 89.2, 66.4, 28.4, 26.9, 26.8, 23.9, 21.0, 20.3.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{22}H_{22}N_2O_2Na$ 403.2361; found 403.2361.

4,4-dimethyl-5-(naphthalen-2-yl)-3-(naphthalen-2-ylamino) oxazolidin-2-one (3t)



3t

White solid, m.p.190-192 °C, 55 mg, yield: 48 %; R_f = 0.35 (EtOAc/Petroleum ether 1:3).

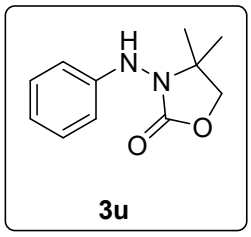
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 – 7.87 (m, 4H), 7.71 (dt, *J* = 17.14, 7.30 Hz, 3H), 7.56 (dt, *J* = 5.62, 2.72 Hz, 2H), 7.49 (d, *J* = 8.55 Hz, 1H), 7.42 (t, *J* = 7.58 Hz, 1H),

7.32 (d, *J* = 8.58 Hz, 2H), 7.14 (d, *J* = 8.80 Hz, 1H), 6.07 (s, 1H), 5.64 (s, 1H), 1.60 (s, 3H), 0.93 (s, 3H).

^{13}C NMR (101 MHz, DMSO-d_6): δ 156.8, 146.8, 134.8, 133.3, 133.1, 129.1, 128.7, 128.6, 128.5, 128.1, 128.0, 127.1, 127.0, 126.8, 126.5, 125.5, 124.2, 123.0, 116.2, 105.7, 83.7, 64.2, 23.8, 20.0.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{25}H_{22}N_2O_2Na$ 405.1579; found 405.1577.

4,4-dimethyl-3-(phenylamino)oxazolidin-2-one (3u)



3u

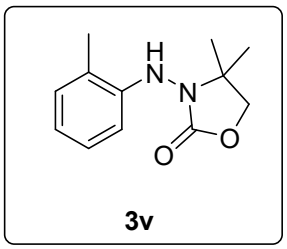
Colorless liquid, 30 mg, yield: 50 %; R_f = 30 (EtOAc/Petroleum ether 1:3).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.20 (t, *J* = 7.83 Hz, 2H), 6.91 – 6.81 (m, 3H), 6.04 (s, 1H), 4.15 (s, 2H), 1.32 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 157.9, 147.4, 129.1, 121.0, 113.3, 74.2, 59.8, 23.5, 14.5.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{13}H_{14}N_2O_2Na$ 229.0953; found 229.0957.

4,4-dimethyl-3-(o-tolylamino)oxazolidin-2-one (3v)



3v

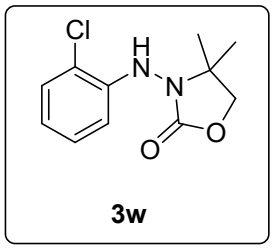
White solid, m.p.120-123 ^oC, 49 mg, yield: 75 %; R_f = 0.35 (EtOAc/Petroleum ether 1:3).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.12 (t, *J* = 7.75 Hz, 1H), 7.05 (d, *J* = 7.34 Hz, 1H), 6.93 (d, *J* = 8.02 Hz, 1H), 6.84 (t, *J* = 7.39 Hz, 1H), 5.66 (s, 1H), 4.19 (s, 2H), 2.18 (s, 3H), 1.36 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 157.9, 145.0, 130.5, 126.8, 123.0, 120.9, 111.8, 74.1, 60.0, 23.5, 17.0.

HRMS (ESI-TOF) m/z: $[M + Na]^+$Calcd for $C_{12}H_{16}N_2O_2Na$ 243.1109; found 243.1104.

3-((2-chlorophenyl)amino)-4,4-dimethyloxazolidin-2-one (3w)



3w

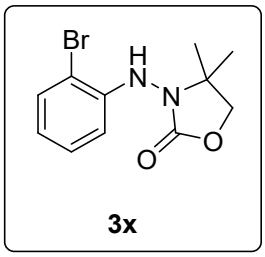
White solid, m.p.167-169 ^{o}C, 43 mg, yield: 60 %; R_f = 0.34 (EtOAc/Petroleum ether 1:3).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28 (d, *J* = 8.74 Hz, 1H), 7.16 (t, *J* = 7.73 Hz, 1H), 6.99 (d, *J* = 8.11 Hz, 1H), 6.84 (t, *J* = 7.64 Hz, 1H), 6.10 (s, 1H), 4.19 (s, 2H), 1.37 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 157.4, 143.2, 129.5, 127.7, 121.5, 119.3, 113.4, 74.2, 60.0 23.4.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{11}H_{13}ClN_2O_2Na$ 263.0563; found 263.0567.

3-((2-bromophenyl)amino)-4,4-dimethyloxazolidin-2-one (3x)



3x

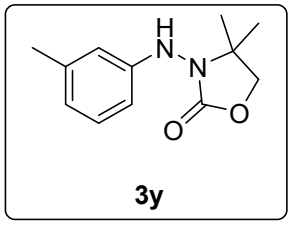
White solid, m.p.184-186 ^{o}C, 54 mg, yield: 62 %; R_f = 0.33 (EtOAc/Petroleum ether 1:3).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 (d, *J* = 7.91 Hz, 1H), 7.20 (t, *J* = 7.76 Hz, 1H), 6.97 (d, *J* = 8.16 Hz, 1H), 6.78 (t, *J* = 7.65 Hz, 1H), 6.05 (s, 1H), 4.19 (s, 2H), 1.37 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 157.4, 144.1, 132.7, 128.4, 122.1, 113.7, 108.9, 74.1, 60.0, 23.4.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{11}H_{13}BrN_2O_2Na$ 307.0058; found 307.0061.

4,4-dimethyl-3-(m-tolylamino)oxazolidin-2-one (3y)

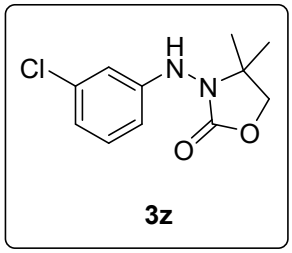


3y

White solid, m.p.108-111 ^{o}C, 36 mg, yield: 56 %; R_f = 0.31 (EtOAc/Petroleum ether 1:3).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.10 (t, *J* = 8.09 Hz, 1H), 6.81 – 6.56 (m, 3H), 5.94 (s, 1H), 4.16 (s, 2H), 2.28 (s, 3H), 1.33 (s, 6H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 158.0, 147.4, 139.0, 129.0, 122.0, 114.1, 110.4, 74.2, 59.8, 23.5, 21.5.
HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{12}H_{16}N_2O_2Na$ 243.1109; found 243.1114.

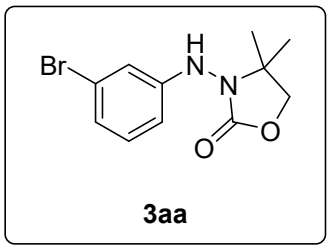
3-((3-chlorophenyl)amino)-4,4-dimethyloxazolidin-2-one (3z)



3z

White solid, m.p.120-123 °C, 49 mg, yield: 69 %; R_f = 0.32 (EtOAc/Petroleum ether 1:3).
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.08 (t, *J* = 8.29 Hz, 1H), 6.83 (d, *J* = 7.29 Hz, 2H), 6.74 – 6.66 (m, 1H), 6.21 (s, 1H), 4.17 (s, 2H), 1.31 (s, 6H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 157.9, 148.8, 134.9, 130.2, 121.0, 113.2, 111.6, 74.2, 60.0, 23.3.
HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{11}H_{13}ClN_2O_2Na$ 263.0563; found 263.0568.

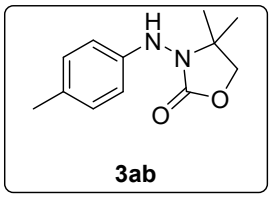
3-((3-bromophenyl)amino)-4,4-dimethyloxazolidin-2-one (3aa)



3aa

White solid, m.p. 132-134 °C, 54 mg, yield: 64 %; R_f = 0.32 (EtOAc/Petroleum ether 1:3).
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28 (d, *J* = 7.93 Hz, 1H), 7.16 (t, *J* = 7.60 Hz, 1H), 6.99 (d, *J* = 8.14 Hz, 1H), 6.85 (t, *J* = 7.65 Hz, 1H), 6.08 (s, 1H), 4.20 (s, 2H), 1.38 (s, 6H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 157.4, 143.2, 129.5, 127.7, 121.5, 119.3, 113.4, 74.1, 60.0, 23.4.
HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{11}H_{13}BrN_2O_2Na$ 307.0058; found 307.0060.

4,4-dimethyl-3-(p-tolylamino)oxazolidin-2-one (3ab)



3ab

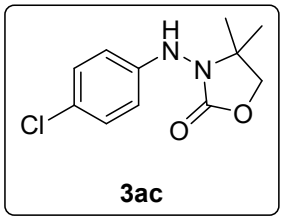
White solid, m.p.97-100 °C, 57 mg, yield: 87 %; R_f = 0.33 (EtOAc/Petroleum ether 1:3).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.03 (d, *J* = 8.07 Hz, 2H), 6.79 (d, *J* = 8.45 Hz, 2H), 5.77 (s, 1H), 4.15 (s, 2H), 2.27 (s, 3H), 1.33 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 157.9, 145.0, 130.6, 129.6, 113.6, 74.1, 59.8, 23.5, 20.5.

HRMS (ESI-TOF) m/z: $[M + Na]^+$Calcd for $C_{12}H_{16}N_2O_2Na$ 243.1109; found 243.1108.

3-((4-chlorophenyl)amino)-4,4-dimethyloxazolidin-2-one (3ac)



3ac

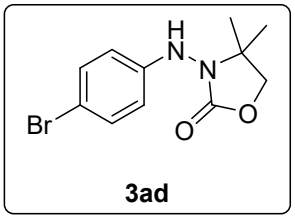
White solid, m.p.105-107 °C, 59 mg, yield: 82 %; R_f = 0.32 (EtOAc/Petroleum ether 1:3).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.12 (d, *J* = 8.59 Hz, 2H), 6.75 (d, *J* = 8.59 Hz, 2H), 6.18 (s, 1H), 4.15 (s, 2H), 1.30 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 157.9, 146.1, 129.0, 125.7, 114.5, 74.2, 59.9, 23.5.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{11}H_{13}ClN_2O_2Na$ 263.0563; found 263.0564.

3-((4-bromophenyl)amino)-4,4-dimethyloxazolidin-2-one (3ad)



3ad

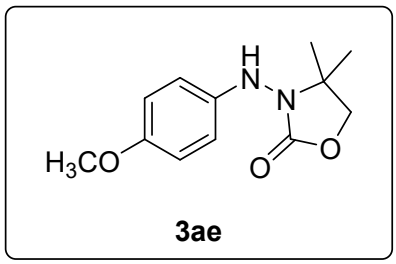
White solid, m.p.110-112 °C, 57 mg, yield: 67 %; R_f = 0.34 (EtOAc/Petroleum ether 1:3).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26 (d, *J* = 8.51 Hz, 2H), 6.70 (d, *J* = 8.54 Hz, 2H), 6.20 (s, 1H), 4.15 (s, 2H), 1.30 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 157.9, 146.6, 131.9, 114.9, 112.9, 74.2, 59.9, 23.4,14.5.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{11}H_{13}BrN_2O_2Na$ 307.0058; found 307.0063.

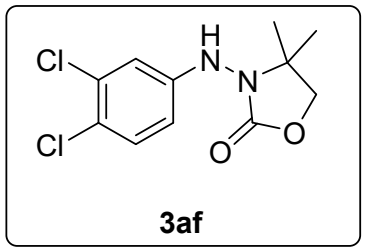
3-((4-methoxyphenyl)amino)-4,4-dimethyloxazolidin-2-one (3ae)



3ae

Colorless liquid, 24 mg, yield: 35 %; R_f = 0.30 (EtOAc/Petroleum ether 1:3).
^{1}H NMR (400 MHz, $CDCl_3$): δ 6.84 – 6.75 (m, 4H), 5.82 (s, 1H), 4.12 (s, 2H), 3.73 (s, 3H), 1.30 (s, 6H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 158.1, 154.6, 141.0, 114.5, 74.1, 59.8, 55.6, 23.5,14.5.
HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{12}H_{16}N_2O_3Na$ 259.1058, found 259.1060.

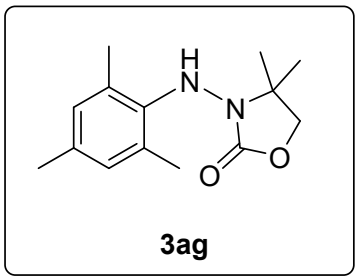
3-((3,4-dichlorophenyl)amino)-4,4-dimethyloxazolidin-2-one (3af)



3af

White solid, m.p.110-112 °C, 41 mg, yield: 50 %; R_f = 0.29 (EtOAc/Petroleum ether 1:3).
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.21 (d, *J* = 8.71 Hz, 1H), 6.92 (d, *J* = 2.68 Hz, 1H), 6.67 – 6.63 (m, 1H), 6.19 (s, 1H), 4.18 (s, 2H), 1.32 (s, 6H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 157.9, 147.1, 133.0, 130.6, 124.0, 114.9, 112.9, 74.2, 60.1, 23.4.
HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{11}H_{12}Cl_2N_2O_2Na$ 297.0173,found 297.0180.

3-(mesitylamino)-4,4-dimethyloxazolidin-2-one (3ag)



3ag

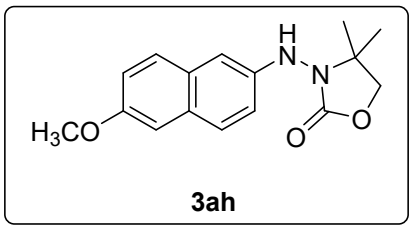
White solid, m.p.102-104 °C, 37 mg, yield: 50%; R_f = 0.28 (EtOAc/Petroleum ether 1:3).
^{1}H NMR (300 MHz, $CDCl_3$): δ 6.76 (s, 2H), 5.42 (s, 1H), 3.98 (s, 2H), 2.31 (s, 6H),

2.21 (s, 3H), 1.21 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 157.8, 139.8, 132.2, 130.1, 127.5, 73.0, 60.8, 23.0, 20.5, 18.6.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{14}H_{20}N_2O_2Na$ 271.1422, found 271.1418.

3-((6-methoxynaphthalen-2-yl)amino)-4,4-dimethyloxazolidin-2-one (3ah)



3ah

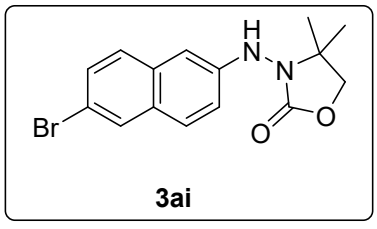
White solid, m.p.131-133 °C, 64 mg, yield: 75 %; R_f = 0.21 (EtOAc/Petroleum ether 1:3).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.56 (dd, *J* = 8.80, 4.90 Hz, 2H), 7.16 (d, *J* = 2.37 Hz, 1H), 7.07 (ddd, *J* = 11.32, 7.16, 2.58 Hz, 3H), 5.93 (s, 1H), 4.22 (s, 2H), 3.89 (s, 3H), 1.38 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ158.0, 156.1, 143.3, 130.4, 129.6, 128.1, 127.9, 119.1, 116.5, 108.4, 106.0, 74.2, 60.0, 55.3, 23.4.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{16}H_{18}N_20_3Na$ 309.1215, found 309.1216.

3-((6-bromonaphthalen-2-yl)amino)-4,4-dimethyloxazolidin-2-one (3ai)



3ai

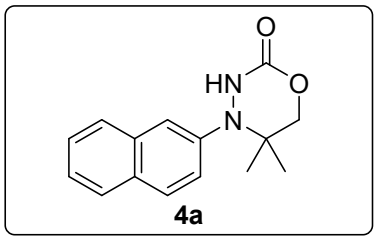
White solid, m.p.145-147 °C, 82 mg, yield: 82%; R_f = 0.25 (EtOAc/Petroleum ether 1:3).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.79 (s, 1H), 7.40 (d, *J* = 11.26 Hz, 3H), 7.08 (s, 1H), 6.98 (d, *J* = 10.35 Hz, 1H), 6.35 (s, 1H), 4.23 (s, 2H), 1.36 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 158.0, 145.5, 132.7, 130.3, 129.6, 129.6, 128.2, 128.1, 116.8, 116.7, 107.3, 74.3, 60.1, 22.6.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{15}H_{15}N_20_2BrNa$ 357.0214, found 357.0216.

5,5-dimethyl-4-(naphthalen-2-yl)-1,3,4-oxadiazinan-2-one (4a)



4a

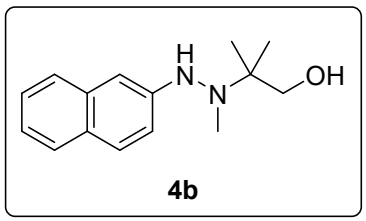
White solid, m.p.132-135 °C, 38 mg, yield: 70%; R_f = 0.50 (EtOAc/Petroleum ether 1:1).

^{1}H NMR (400 MHz, DMSO-d_6): δ 9.37 (s, 1H), 7.95 – 7.79 (m, 3H), 7.58 (s, 1H), 7.46 (p, *J* = 6.84 Hz, 2H), 7.27 (d, *J* = 8.77 Hz, 1H), 4.01 (s, 2H), 1.18 (s, 6H).

^{13}C NMR (101 MHz, DMSO-d_6): δ 151.4, 145.3, 133.5, 131.4, 128.2, 128.1, 127.8, 126.9, 126.0, 125.6, 122.3, 70.5, 54.0, 23.8.

HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for $C_{15}H_{16}N_2O_2Na$ 279.1109; found 279.1110.

2-methyl-2-(2-(naphthalen-2-yl)hydrazineyl)propan-1-ol (4b)



4b

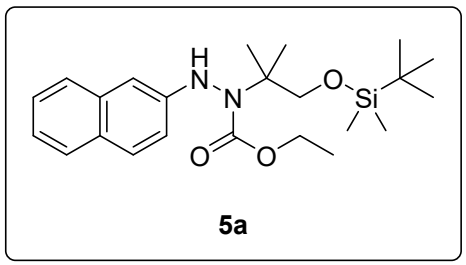
Colorless liquid, 24 mg, yield: 50%; R_f = 0.51 (EtOAc/Petroleum ether 1:3).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.73 – 7.66 (m, 3H), 7.43 – 7.37 (m, 1H), 7.30 – 7.24 (m, 2H), 7.06 (dd, *J* = 8.86, 2.16 Hz, 1H), 4.57 (s, 1H), 3.56 (s, 2H), 2.75 (s, 1H), 2.53 (s, 3H), 1.16 (s, 6H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 145.7, 134.8, 129.1, 129.0, 127.6, 126.3, 122.8, 116.7, 107.3, 70.4, 60.1, 37.5,19.4.

HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for $C_{15}H_{21}N_2O$ 245.1648; found 245.1655.

ethyl 1-(1-((tert-butyldimethylsilyl)oxy)-2-methylpropan-2-yl)-2-(naphthalen-2-yl)hydrazine-1-carboxylate (5a)



5a

Colorless liquid, 54 mg, yield: 43%; R_f = 0.62 (EtOAc/Petroleum ether 1:7).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.75 – 7.64 (m, 3H), 7.39 (ddd, *J* = 8.21, 6.83, 1.33 Hz, 1H), 7.27 – 7.22 (m, 1H), 7.07 – 6.93 (m, 2H), 6.03 (s, 1H), 4.08 (qd, *J* = 7.08, 1.94

Hz, 2H), 4.00 (d, J = 9.68 Hz, 1H), 3.61 (d, J = 9.70 Hz, 1H), 1.61 (s, 3H), 1.36 (s, 3H), 1.11 (t, J = 7.09 Hz, 3H), 0.96 (s, 9H), 0.09 (d, J = 4.60 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 157.2, 147.0, 134.7, 128.9, 128.8, 127.7, 126.3, 126.3, 122.7, 115.2, 105.9, 68.3, 63.7, 61.6, 25.9, 24.3, 24.1, 18.2, 14.4.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{23}H_{36}N_20_3Si$ 439.2392, found 439.2390.

8. X-Ray Analysis

Single crystals of $C_{15}H_{16}N_2O_2$ **3a** were grown from ethyl acetate and PE. A suitable crystal was selected and collected on a SuperNova, Dual, Cu at zero, AtlasS2 diffractometer. The crystal was kept at 149.99(10) K during data collection. The data were collected and processed using CrysAlisPro. The structures were solved by direct methods using Olex2 software with the SHELXT structure solution program via intrinsic phasing algorithm, and the non-hydrogen atoms were located from the trial structure and then refined anisotropically with SHELXL-2018 using a full-matrix least squares procedure based on F^2. The weighted R factor, wR and goodness-of-fit S values were obtained based on F^2. The hydrogen atom positions were fixed geometrically at the calculated distances and allowed to ride on their parent atoms.

Crystallographic data for the structure reported in this paper have been deposited at the Cambridge Crystallographic Data Center and allocated with the deposition numbers: CCDC 2240182 for compounds **3a**

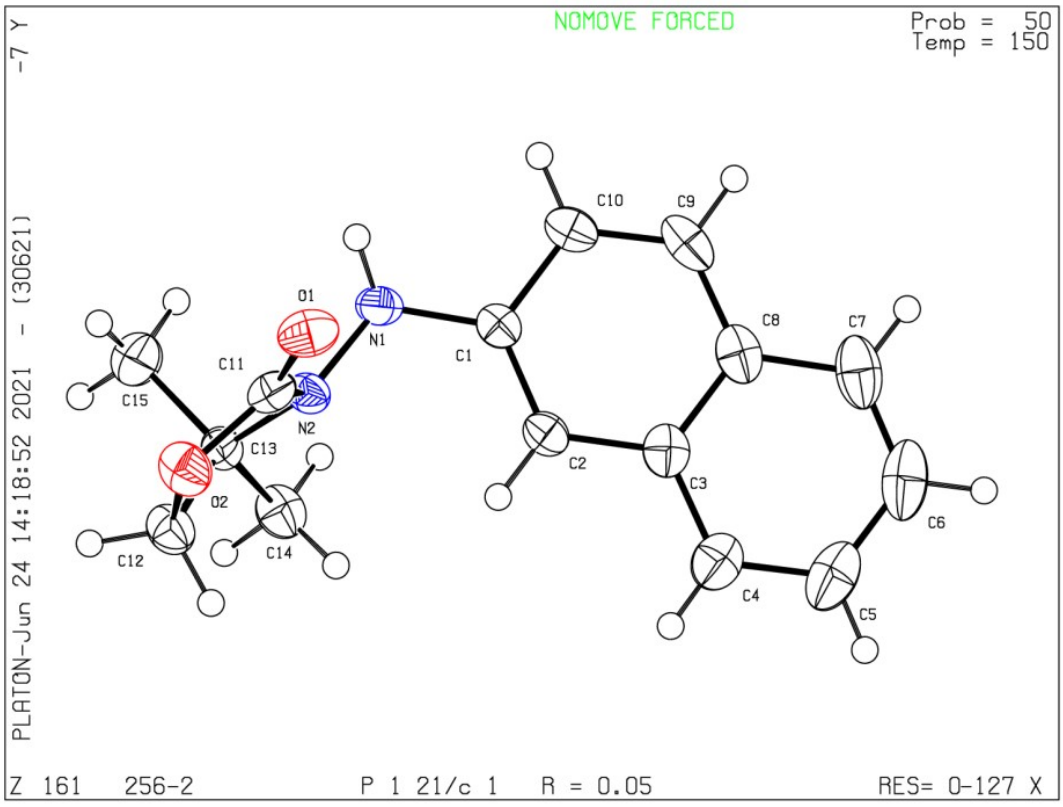


Figure S1. ORTEP Drawing of **3a** (The ellipsoids are shown at 50% probability levels)

Table 1 Crystal data and structure refinement for 3a.

Identification code	**3a**
Empirical formula	$C_{15}H_{16}N_2O_2$
Formula weight	256.30
Temperature/K	149.99(10)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	10.9803(9)
b/Å	10.5194(6)
c/Å	12.5582(12)
α/°	90
β/°	112.748(11)
γ/°	90
Volume/Å^3	1337.7(2)
Z	4
ρ_{calc}g/cm^3	1.273
μ/mm^{-1}	0.086
F(000)	544.0
Crystal size/mm^3	0.15 × 0.12 × 0.11
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.022 to 49.996
Index ranges	$-13 \le h \le 10$, $-12 \le k \le 11$, $-14 \le l \le 13$
Reflections collected	6236
Independent reflections	2354 [R_{int} = 0.0348, R_{sigma} = 0.0459]
Data/restraints/parameters	2354/0/178
Goodness-of-fit on F^2	1.069
Final R indexes [I>=2σ (I)]	R_1 = 0.0453, wR_2 = 0.0920
Final R indexes [all data]	R_1 = 0.0641, wR_2 = 0.1046
Largest diff. peak/hole / e Å^{-3}	0.14/-0.21

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 3a. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
O1	4564.6(13)	9963.4(11)	3491.1(11)	37.5(4)
O2	6146.6(12)	8977.8(11)	3071.7(11)	37.0(4)
N1	4710.7(14)	7875.9(15)	4951.4(14)	28.8(4)
N2	5310.8(13)	7950.1(13)	4162.1(12)	25.1(4)
C1	3415.7(16)	7399.9(15)	4547.7(15)	25.1(4)
C2	2862.0(16)	6717.7(16)	3550.1(15)	27.5(4)

Table 2 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for 3a. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
C3	1605.9(17)	6152.9(16)	3242.3(17)	30.1(4)
C4	1034.2(18)	5393.6(18)	2245.0(18)	38.9(5)
C5	-160(2)	4821.3(19)	1989(2)	49.4(6)
C6	-855(2)	4988(2)	2711(2)	52.2(6)
C7	-336.1(18)	5719.6(19)	3672(2)	45.3(6)
C8	903.8(17)	6314.2(17)	3972.0(18)	33.2(5)
C9	1493.6(18)	7049.4(18)	4987.3(18)	37.5(5)
C10	2710.5(18)	7571.1(17)	5271.0(17)	32.5(5)
C11	5267.0(17)	9042.4(17)	3579.7(16)	28.9(4)
C12	6734.7(18)	7712.9(17)	3287.4(17)	34.3(5)
C13	6537.8(16)	7234.1(16)	4358.8(16)	26.4(4)
C14	6290.9(18)	5821.7(17)	4338.7(18)	35.0(5)
C15	7625.6(18)	7659(2)	5470.5(18)	44.8(5)

Table 3 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for 3a. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O1	49.3(8)	24.3(7)	35.6(8)	-0.9(6)	12.9(7)	5.6(6)
O2	45.6(8)	30.3(7)	42.0(8)	7.0(6)	24.8(7)	-1.7(6)
N1	33.6(9)	28.6(9)	27.4(9)	-5.2(8)	15.2(7)	-1.3(7)
N2	29.8(8)	22.9(8)	26.4(8)	0.2(7)	15.1(7)	-0.8(6)
C1	27.9(9)	20.9(9)	28.5(10)	4.1(8)	13.0(8)	4.2(7)
C2	28.5(10)	27.8(10)	28.1(11)	2.9(9)	13.2(8)	4.5(8)
C3	27.2(9)	24.0(9)	36.5(11)	7.6(9)	9.4(9)	6.3(8)
C4	34.1(11)	31.8(10)	43.5(13)	1.2(10)	7.1(9)	3.3(9)
C5	37.2(12)	35.6(12)	58.6(15)	2.0(11)	0.2(11)	-2.2(9)
C6	28.3(11)	42.8(13)	75.6(18)	18.2(13)	9.3(12)	-1.0(9)
C7	29.3(11)	40.7(12)	65.8(16)	20.2(12)	18.1(11)	6.2(9)
C8	28.8(10)	27.6(10)	44.4(12)	12.9(10)	15.4(9)	7.9(8)
C9	38.7(11)	37.4(11)	47.9(13)	11.6(11)	29.4(10)	11.7(9)
C10	38.4(11)	30.7(10)	32.9(11)	1.8(9)	18.6(9)	7.1(8)
C11	34.7(10)	25.2(10)	24.5(10)	-3.6(8)	9.0(8)	-4.6(8)
C12	36.4(10)	32.0(10)	40.0(12)	1.6(9)	20.9(9)	-0.2(8)
C13	24.7(9)	27.2(9)	28.5(10)	-0.8(8)	11.7(8)	0.6(7)
C14	34.8(10)	30.0(10)	42.5(12)	5.6(9)	17.4(9)	6.2(8)
C15	33.0(11)	57.9(14)	38.3(12)	-8.6(11)	8.1(10)	-1.6(10)

Table 4 Bond Lengths for 3a.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	C11	1.216(2)	C3	C8	1.417(3)
O2	C11	1.349(2)	C4	C5	1.364(3)
O2	C12	1.458(2)	C5	C6	1.403(3)
N1	N2	1.3885(19)	C6	C7	1.358(3)
N1	C1	1.404(2)	C7	C8	1.411(3)
N2	C11	1.353(2)	C8	C9	1.416(3)
N2	C13	1.479(2)	C9	C10	1.358(3)
C1	C2	1.366(2)	C12	C13	1.528(3)
C1	C10	1.415(2)	C13	C14	1.509(2)
C2	C3	1.411(2)	C13	C15	1.512(3)
C3	C4	1.412(3)			

Table 5 Bond Angles for 3a.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C11	O2	C12	107.73(13)	C7	C8	C3	119.0(2)
N2	N1	C1	117.13(15)	C7	C8	C9	122.72(19)
N1	N2	C13	120.36(14)	C9	C8	C3	118.29(16)
C11	N2	N1	120.41(14)	C10	C9	C8	121.19(17)
C11	N2	C13	111.26(13)	C9	C10	C1	120.49(18)
N1	C1	C10	116.88(16)	O1	C11	O2	122.77(16)
C2	C1	N1	123.23(16)	O1	C11	N2	127.93(17)
C2	C1	C10	119.72(16)	O2	C11	N2	109.30(15)
C1	C2	C3	120.91(17)	O2	C12	C13	105.14(14)
C2	C3	C8	119.39(17)	N2	C13	C12	96.61(13)
C4	C3	C2	122.23(17)	N2	C13	C14	110.65(13)
C4	C3	C8	118.35(17)	N2	C13	C15	110.32(14)
C5	C4	C3	121.1(2)	C14	C13	C12	113.30(16)
C4	C5	C6	120.4(2)	C14	C13	C15	112.27(16)
C7	C6	C5	119.95(19)	C15	C13	C12	112.67(15)
C6	C7	C8	121.2(2)				

Table 6 Torsion Angles for 3a.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
O2	C12	C13	N2	29.39(16)	C3	C4	C5	C6	0.7(3)
O2	C12	C13	C14	145.26(14)	C3	C8	C9	C10	-1.1(3)
O2	C12	C13	C15	-85.90(17)	C4	C3	C8	C7	-0.4(3)
N1	N2	C11	O1	-13.9(3)	C4	C3	C8	C9	178.42(16)
N1	N2	C11	O2	166.47(14)	C4	C5	C6	C7	-0.2(3)

Table 6 Torsion Angles for 3a.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
N1	N2	C13	C12	-177.98(14)	C5	C6	C7	C8	-0.5(3)
N1	N2	C13	C14	64.0(2)	C6	C7	C8	C3	0.8(3)
N1	N2	C13	C15	-60.8(2)	C6	C7	C8	C9	-177.93(18)
N1	C1	C2	C3	173.60(15)	C7	C8	C9	C10	177.60(17)
N1	C1	C10	C9	-174.66(16)	C8	C3	C4	C5	-0.4(3)
N2	N1	C1	C2	17.6(2)	C8	C9	C10	C1	0.6(3)
N2	N1	C1	C10	-167.10(14)	C10	C1	C2	C3	-1.5(3)
C1	N1	N2	C11	94.29(19)	C11	O2	C12	C13	-22.42(19)
C1	N1	N2	C13	-119.51(16)	C11	N2	C13	C12	-28.96(17)
C1	C2	C3	C4	-177.00(17)	C11	N2	C13	C14	-146.94(16)
C1	C2	C3	C8	1.0(3)	C11	N2	C13	C15	88.20(18)
C2	C1	C10	C9	0.8(3)	C12	O2	C11	O1	-175.74(17)
C2	C3	C4	C5	177.62(17)	C12	O2	C11	N2	3.88(19)
C2	C3	C8	C7	-178.41(16)	C13	N2	C11	O1	-162.94(18)
C2	C3	C8	C9	0.4(2)	C13	N2	C11	O2	17.47(19)

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 3a.

Atom	*x*	*y*	*z*	U(eq)
H1	4869(18)	8540(20)	5397(18)	38(6)
H2	3318.81	6623.85	3066.96	33
H4	1479.35	5281.67	1754.55	47
H5	-516.59	4317.32	1332.26	59
H6	-1671.24	4598.42	2530.05	63
H7	-806.5	5830.71	4142.6	54
H9	1039.72	7177.39	5468.7	45
H10	3082.63	8044.28	5945.73	39
H12A	7666.59	7753.6	3427.17	41
H12B	6297.05	7157.29	2634.02	41
H14A	6064.63	5595.39	4980	53
H14B	7073.82	5372.52	4393.15	53
H14C	5577.08	5598.51	3630.36	53
H15A	7774.57	8553.87	5433.11	67
H15B	8422	7203.12	5577.33	67
H15C	7371.08	7488.73	6106.89	67

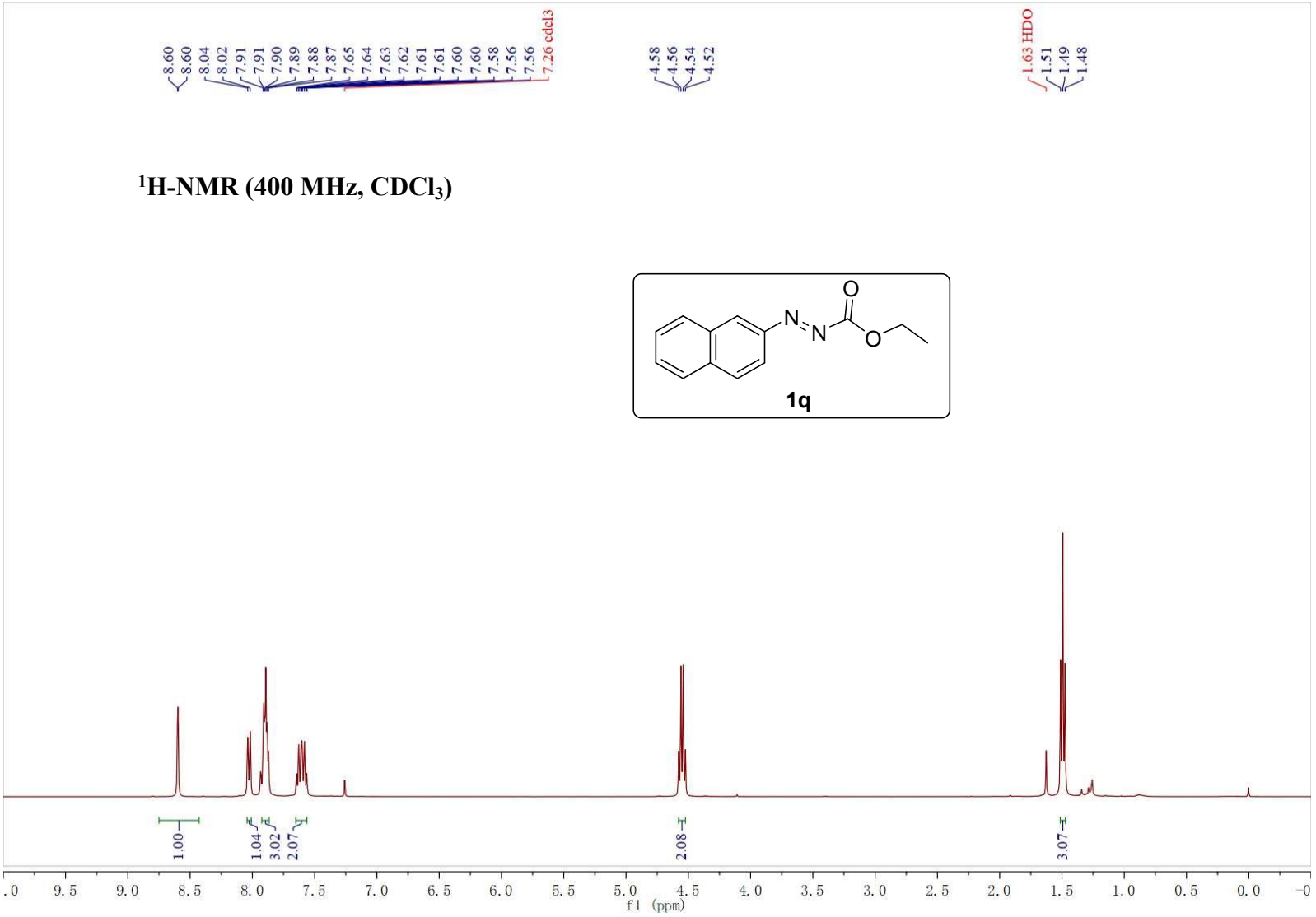
9. Reference

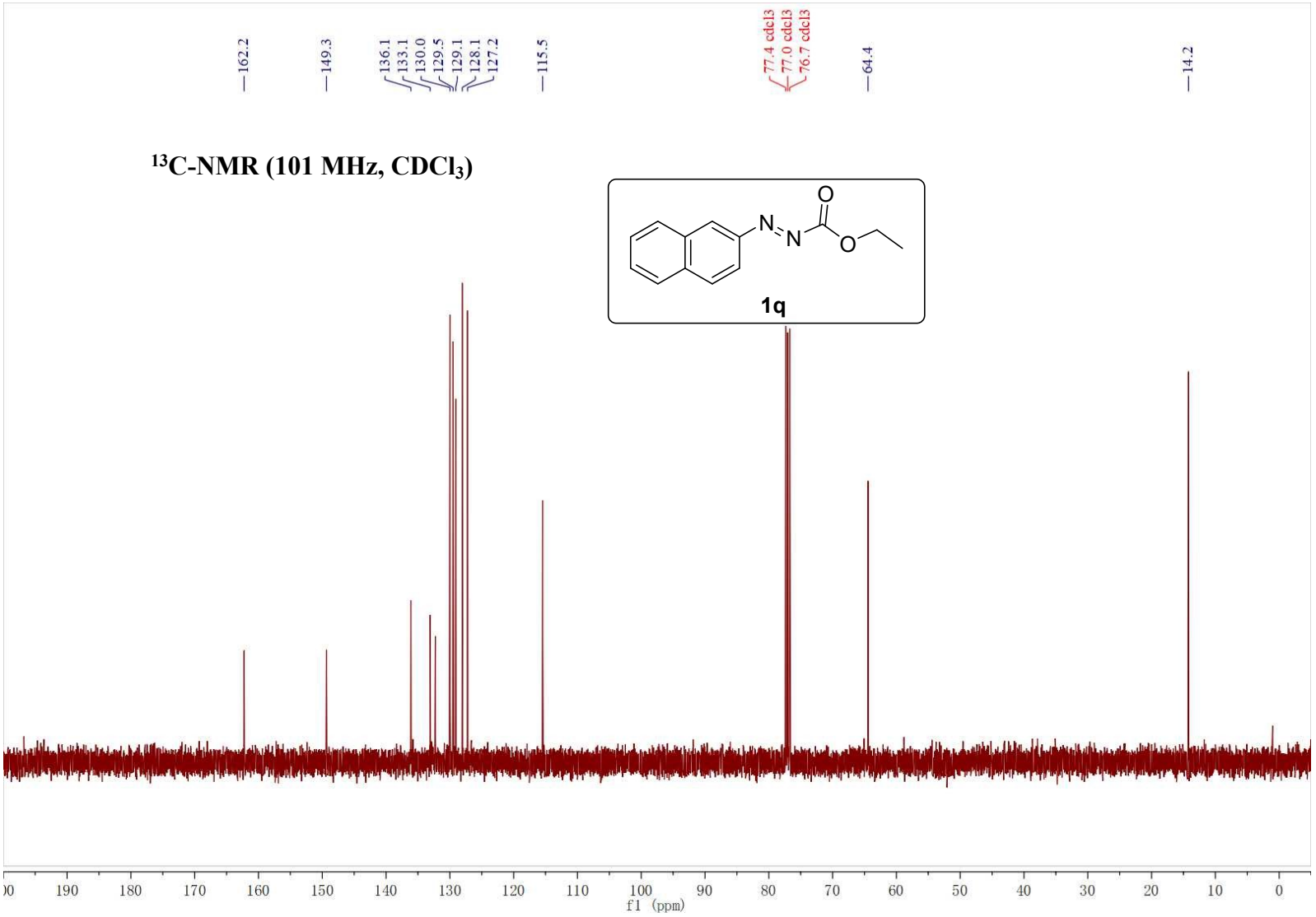
1. (a) J. Giwon, H. K. Min and K. Jinho, *Org. Chem. Front*., 2020, **7**, 834; (b) J.-Y. Zhang, M. Liu, M. Huang, H. Liu, Y.-K. Yan, Z.-Y. Wang and X.-M. Zhang. *Org. Chem. Front*., 2020, **7**, 3160.

2. S. Ghosh, S. Chaudhuri and A. Bisai. *Chem. Eur. J*., 2015, **21**, 17479.

3. B. M. Loertscher, P. R. Young, P. R. Evans and S. L. Castle, *Org. Lett.,* 2013, **15**, 1930; (b) J. Barluenga, F. J. Fañanás, R. Sanz, C. Marcos and M. Trabada, *Org. Lett.,* 2002, **4**, 1587.

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

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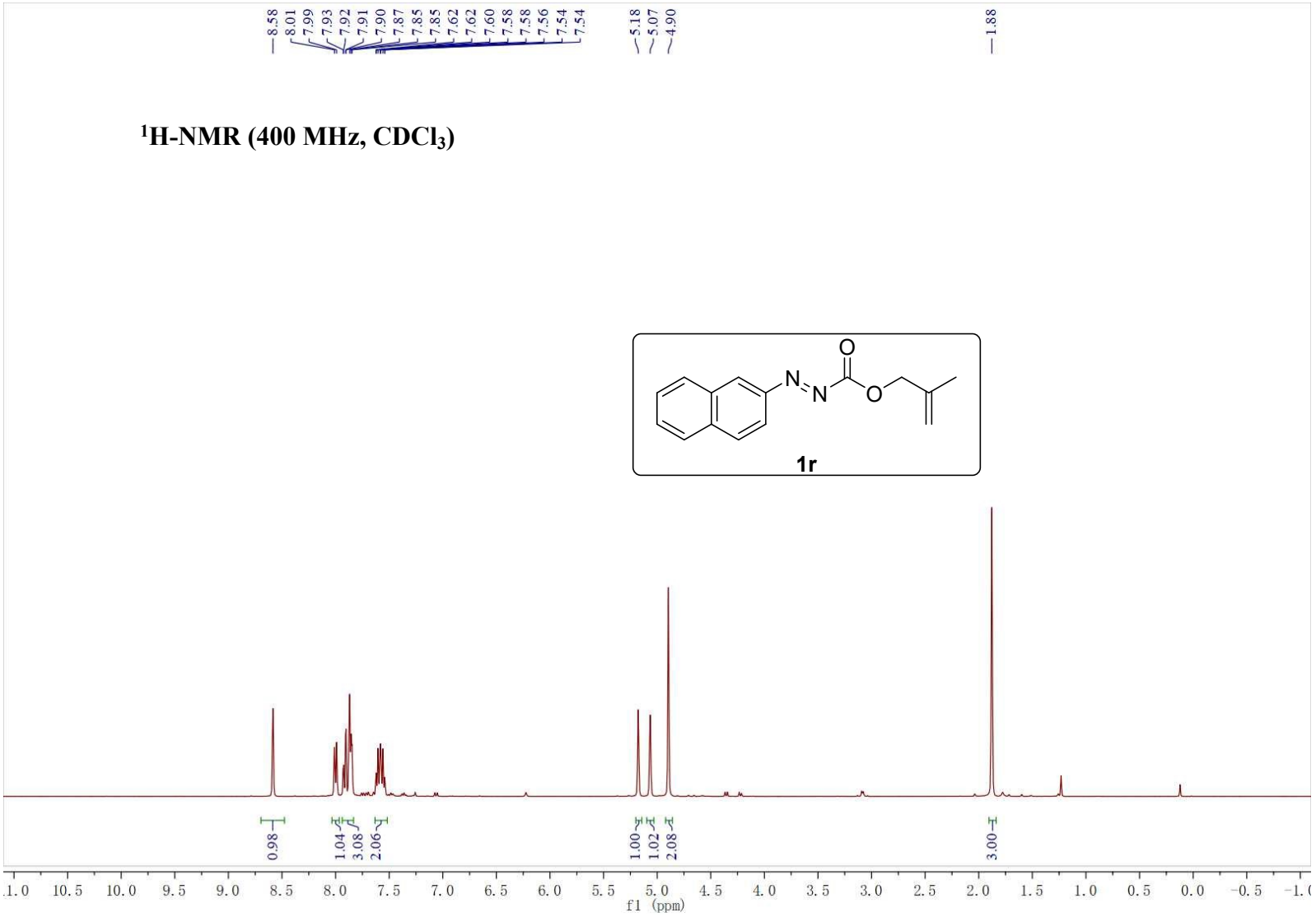
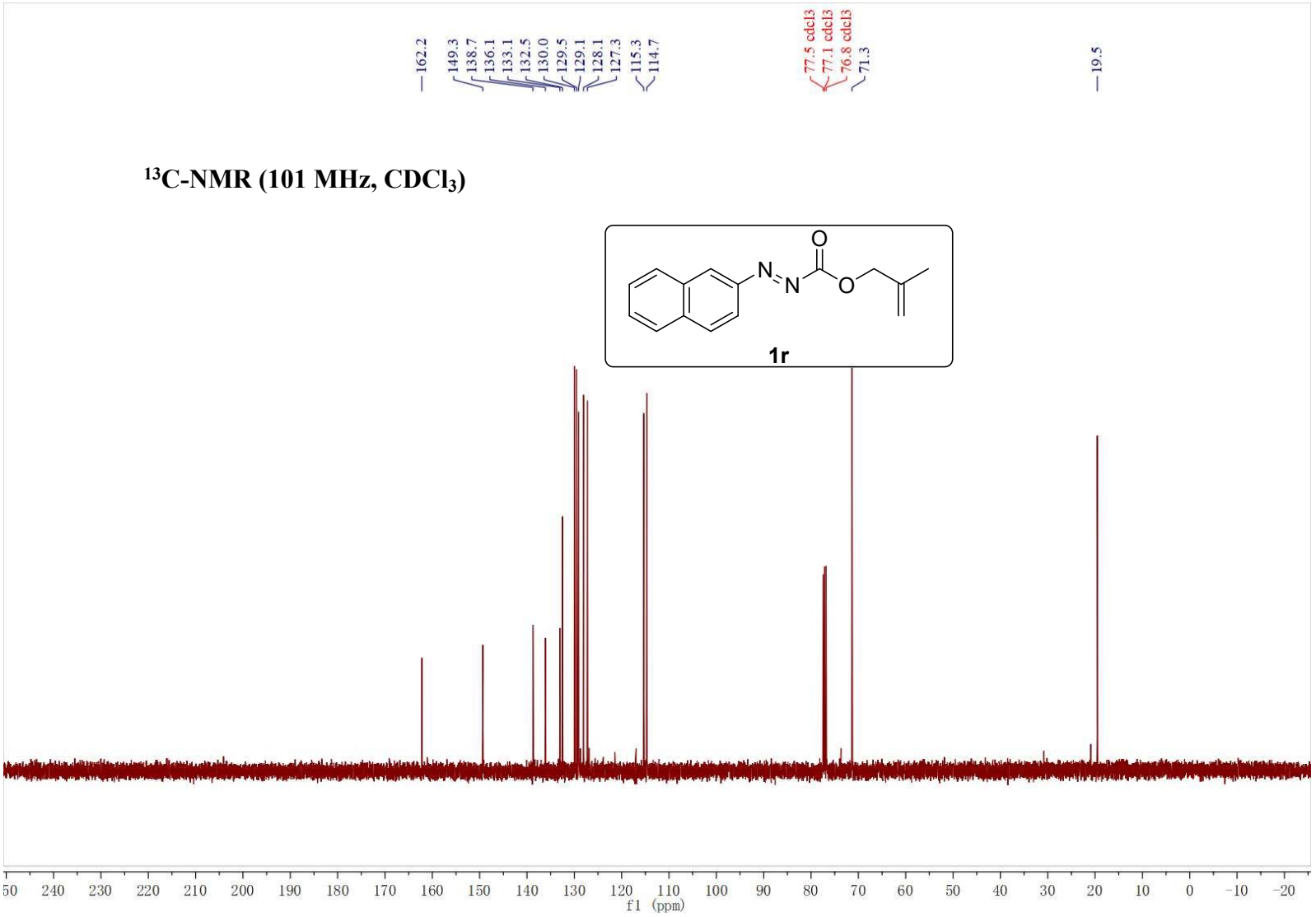
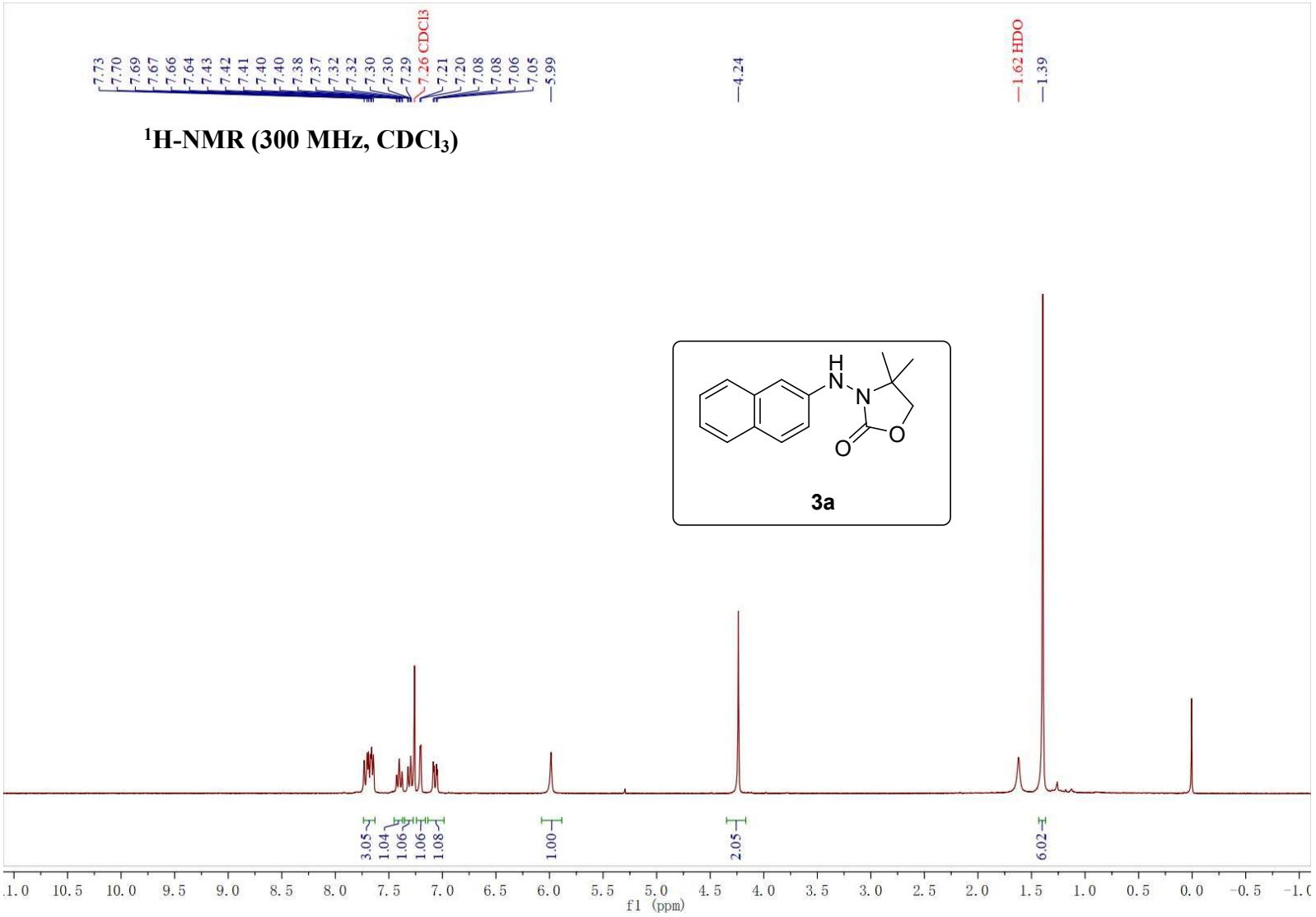
129.5
129.1
128.1
127.2
115.5
77.4 cdcl3
77.0 cdcl3
76.7 cdcl3
64.4
14.2
13C-NMR (101 MHz, CDCl3)
O
N
N
O
1q
f1 (ppm)

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



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





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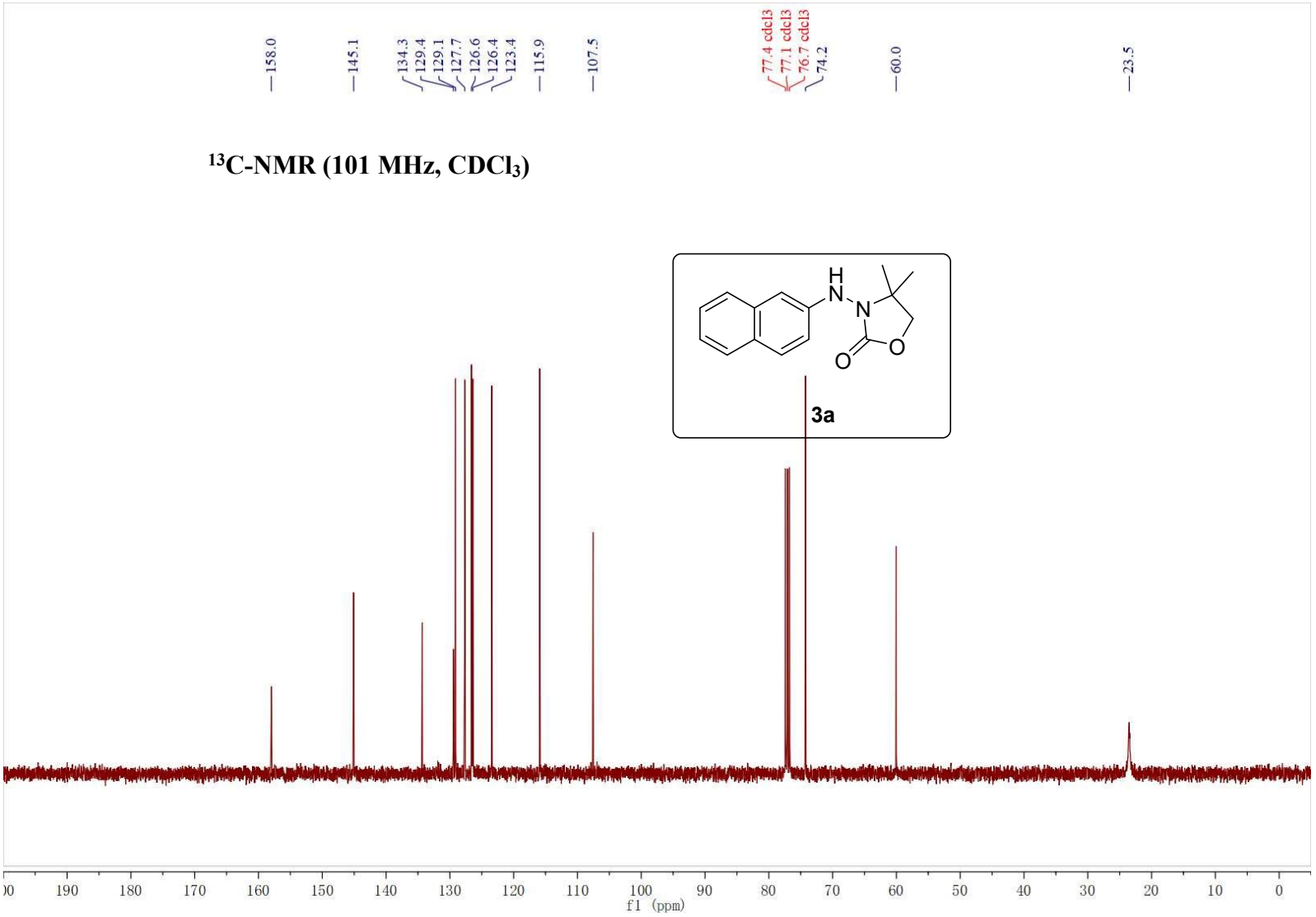

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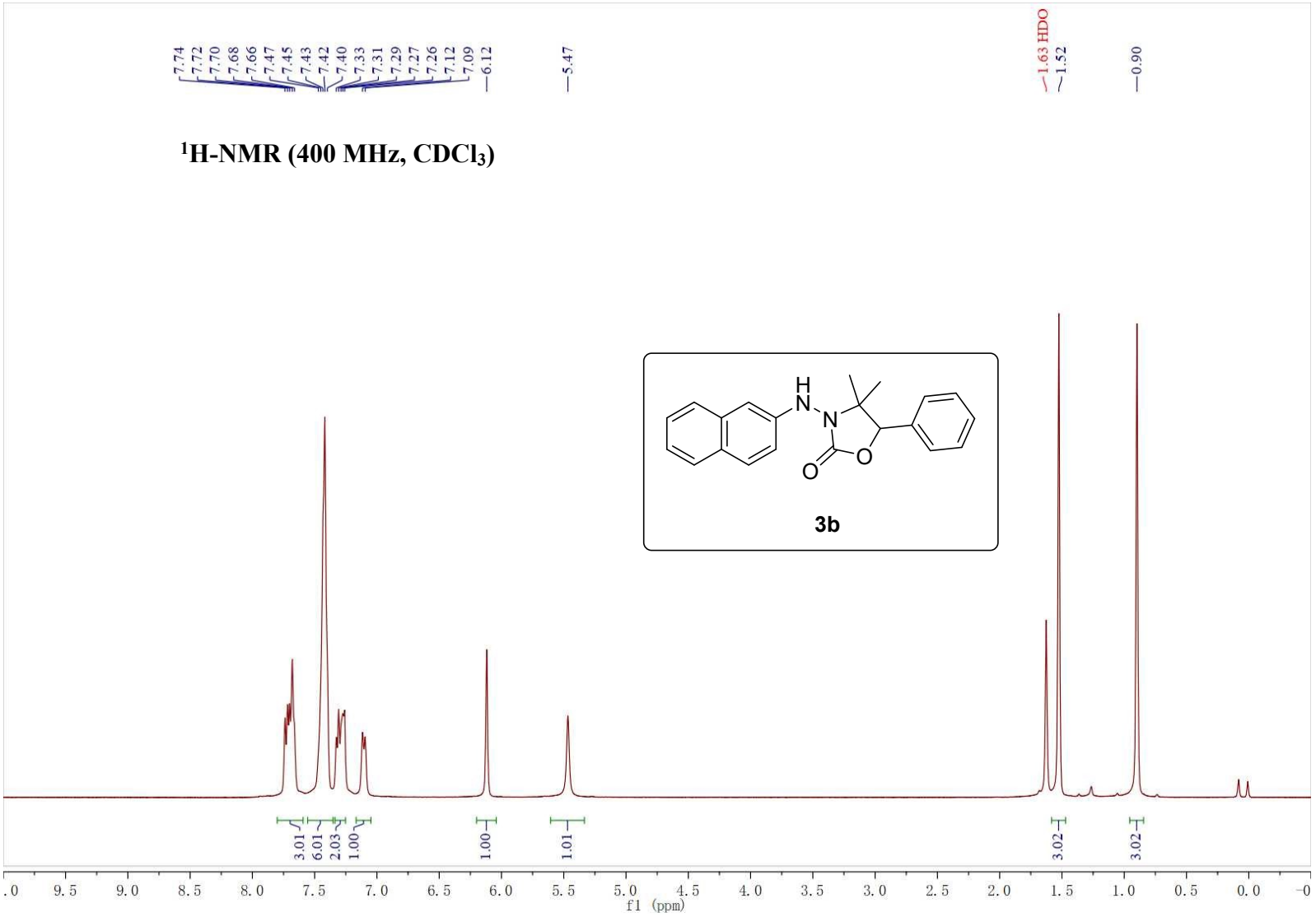
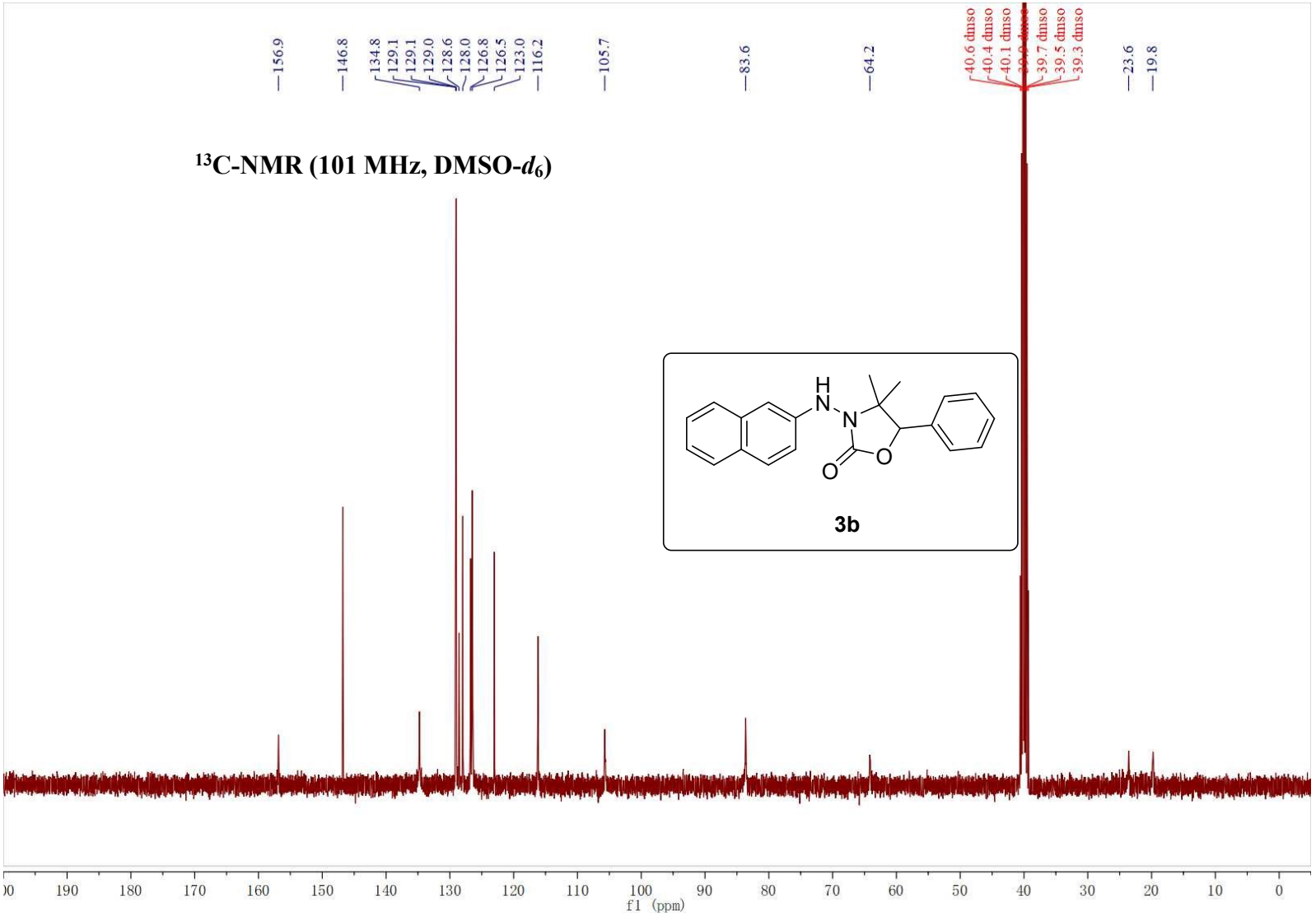


^{1}H-NMR (400 MHz, $CDCl_3$)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129.1
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129.0
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128.0
126.8
126.5
123.0
116.2
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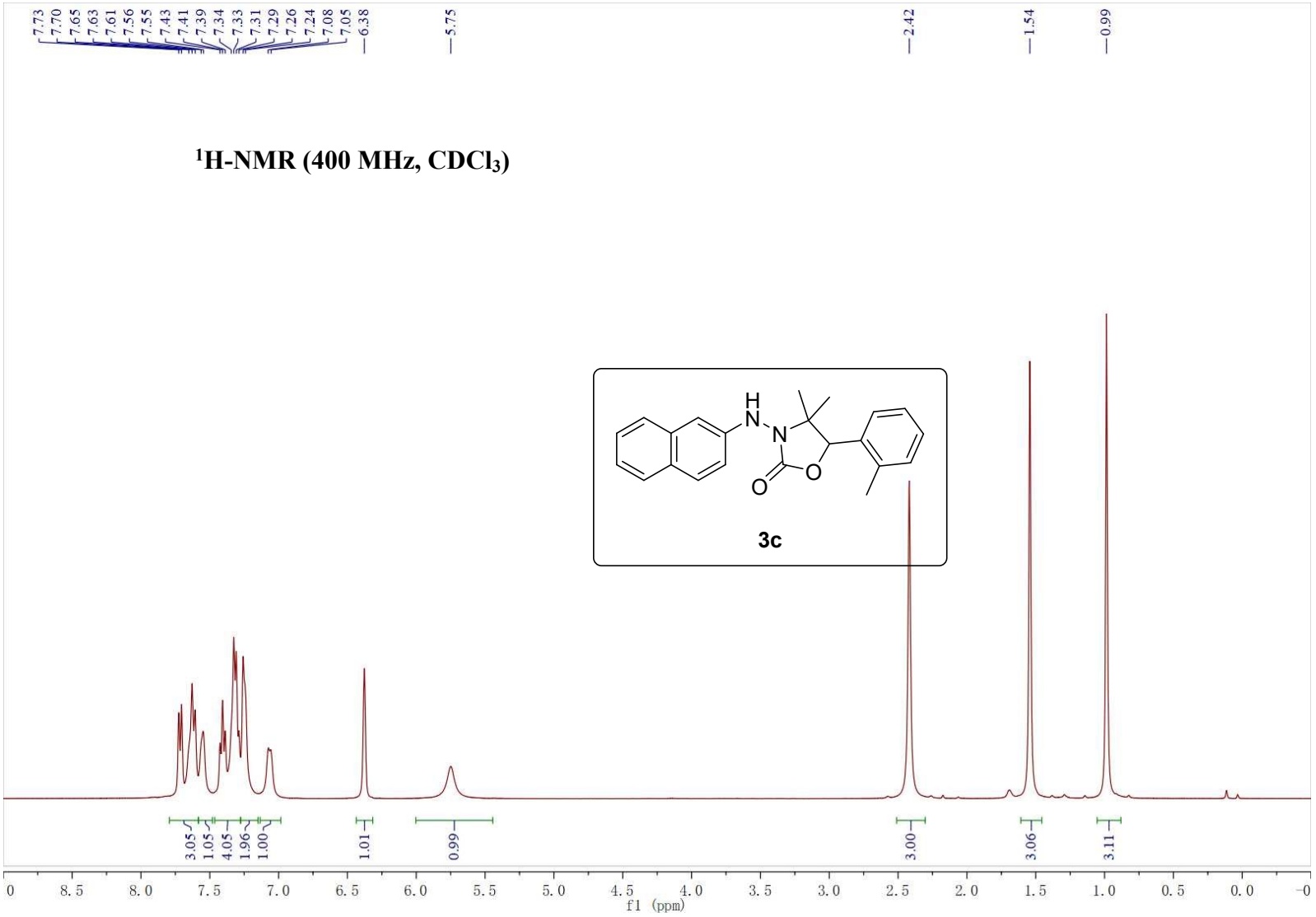
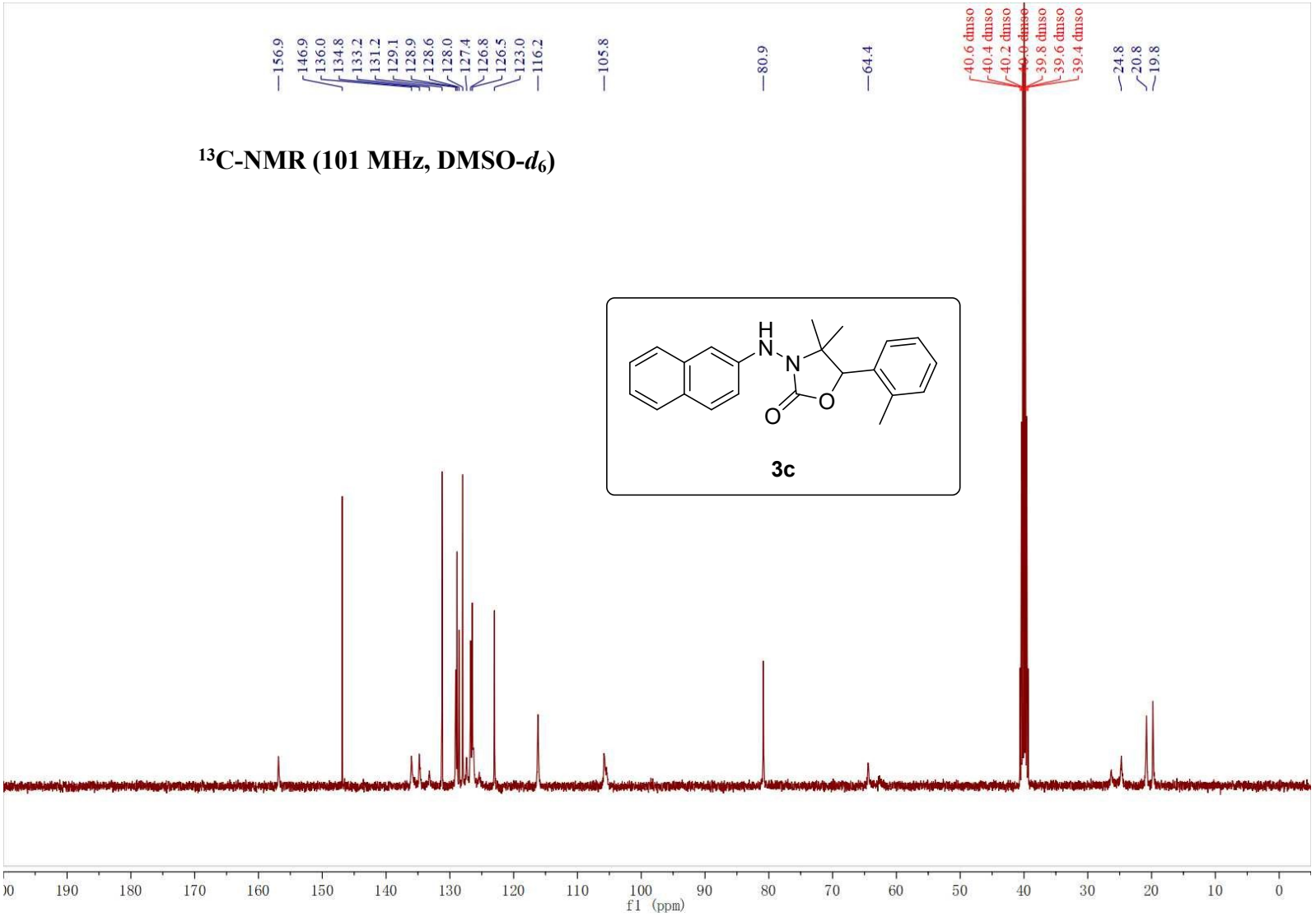
83.6
64.2
40.6 dmso
40.4 dmso
40.1 dmso
39.7 dmso
39.5 dmso
39.3 dmso
23.6
19.8
13C-NMR (101 MHz, DMSO-d6)
H
N
N
O
O
3b
f1 (ppm)

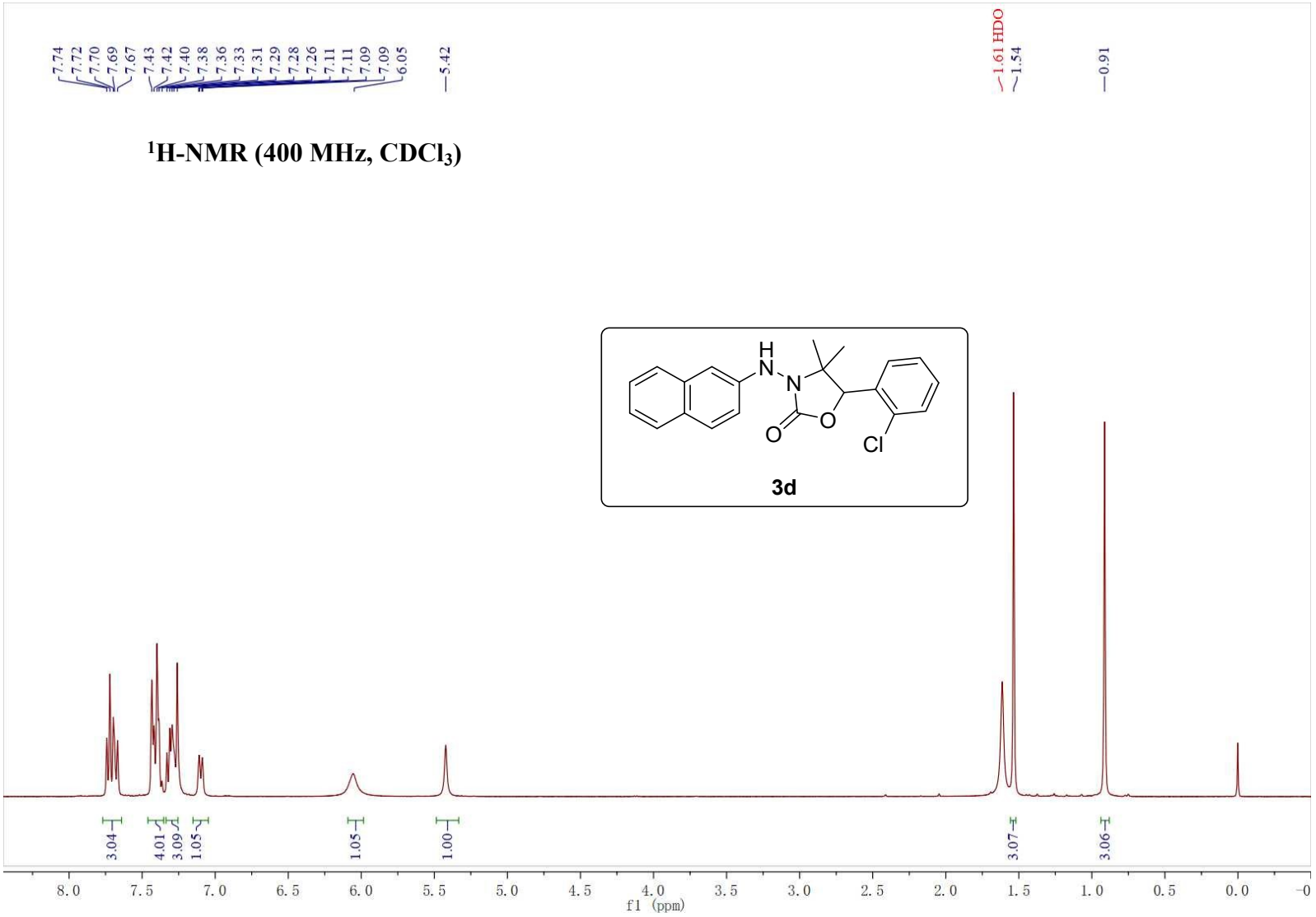
^{1}H-NMR (400 MHz, $CDCl_3$)



3c

^{13}C-NMR (101 MHz, DMSO-d_6)

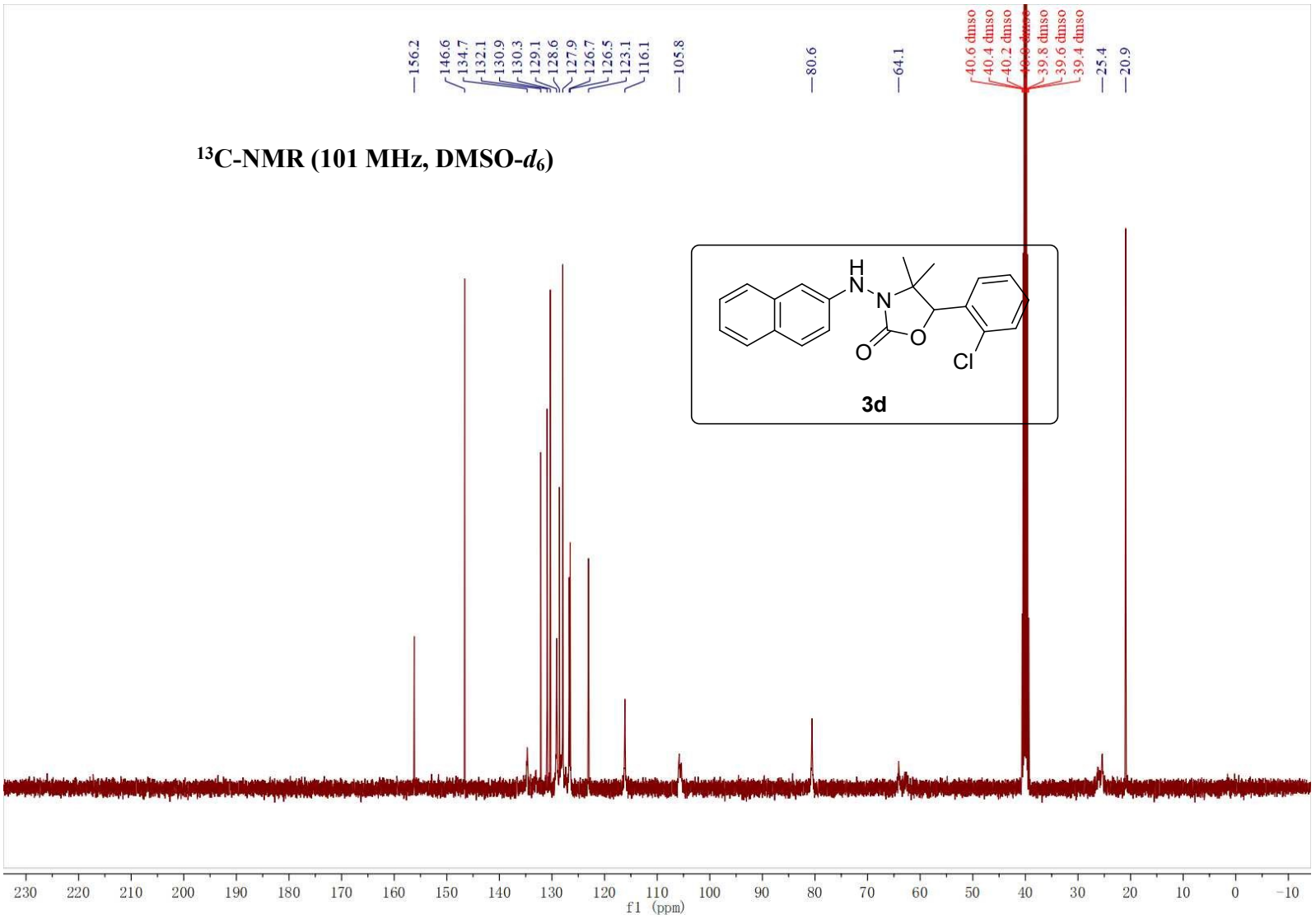




^{1}H-NMR (400 MHz, $CDCl_3$)

3d

^{13}C-NMR (101 MHz, DMSO-d_6)



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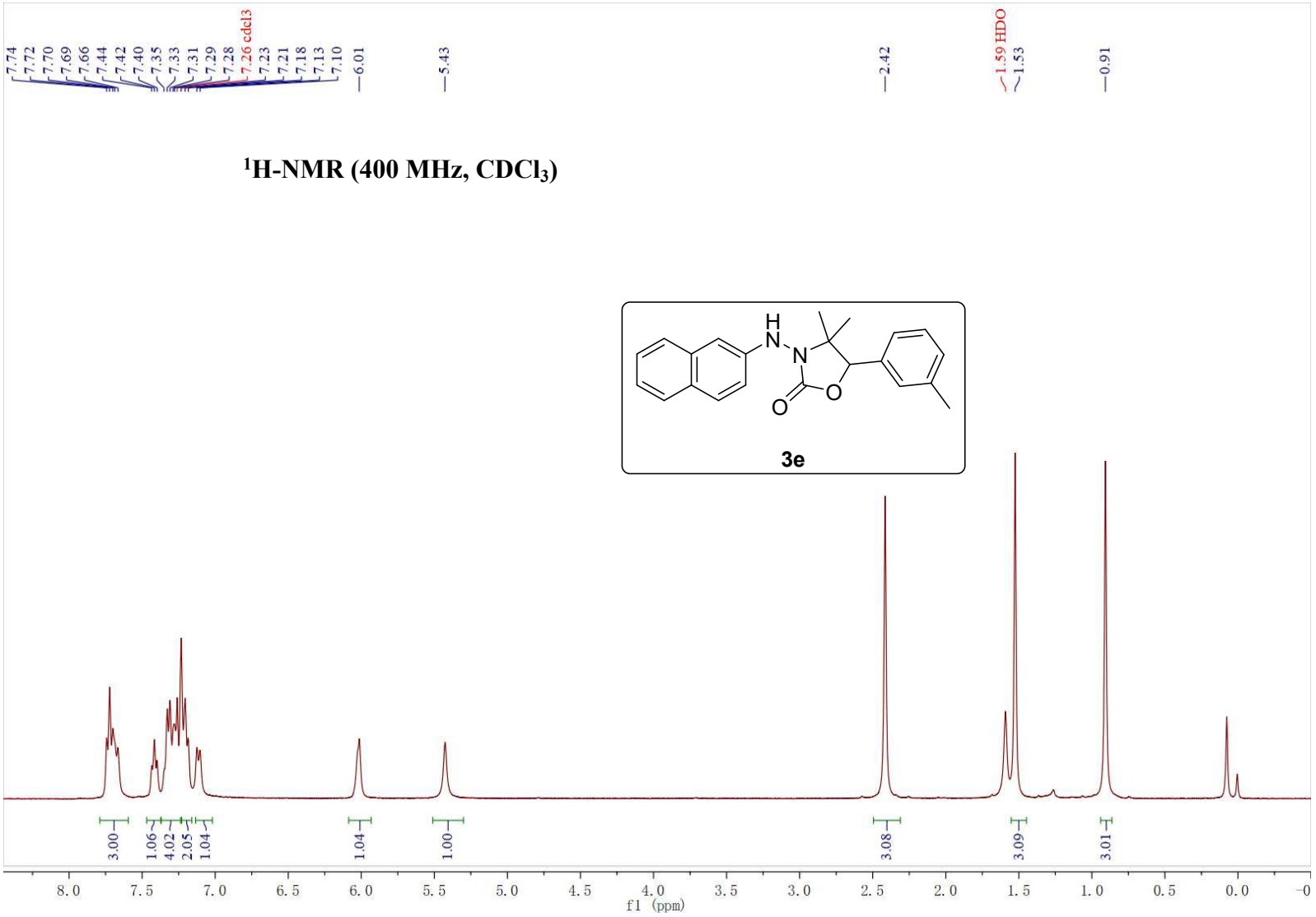

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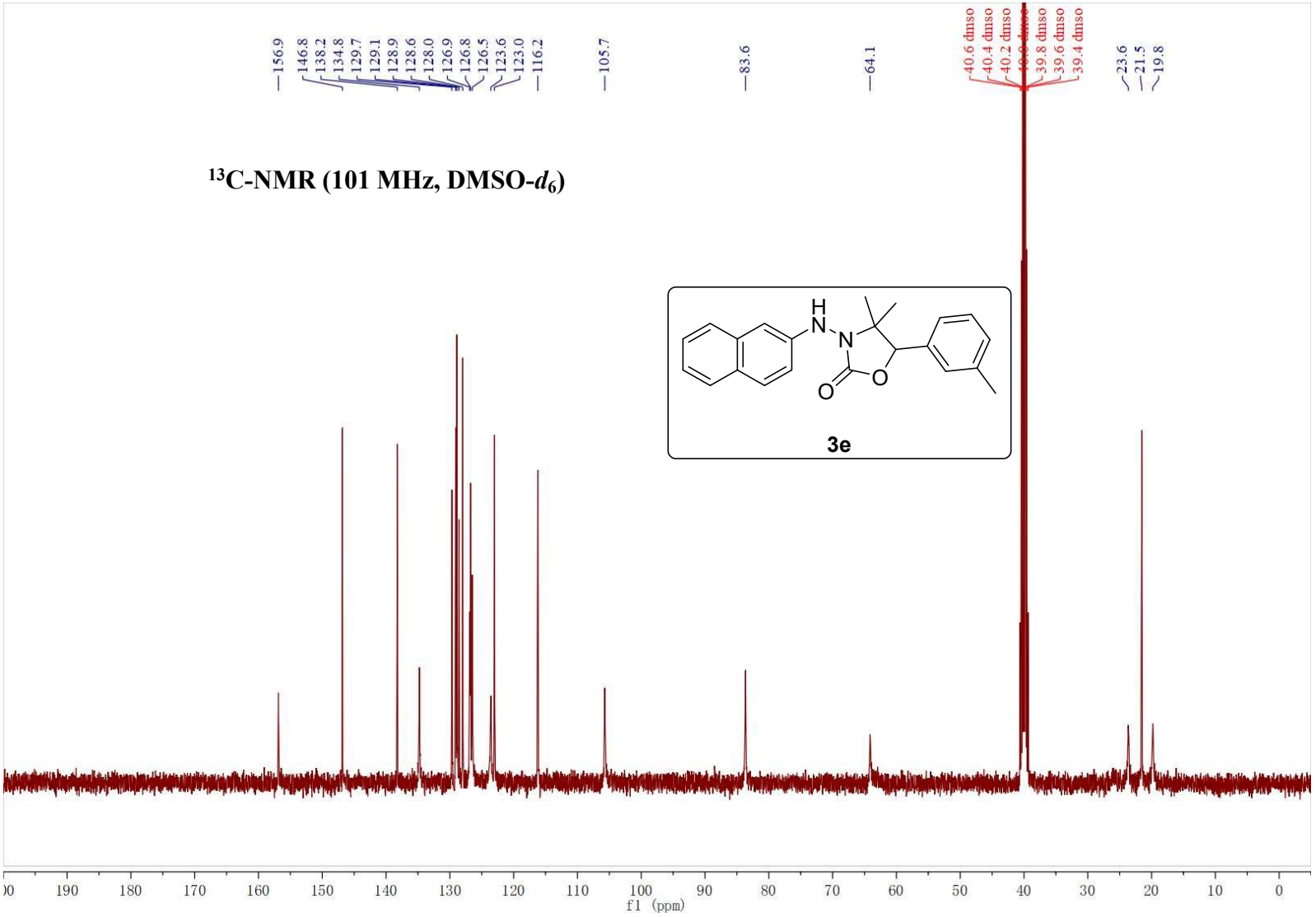
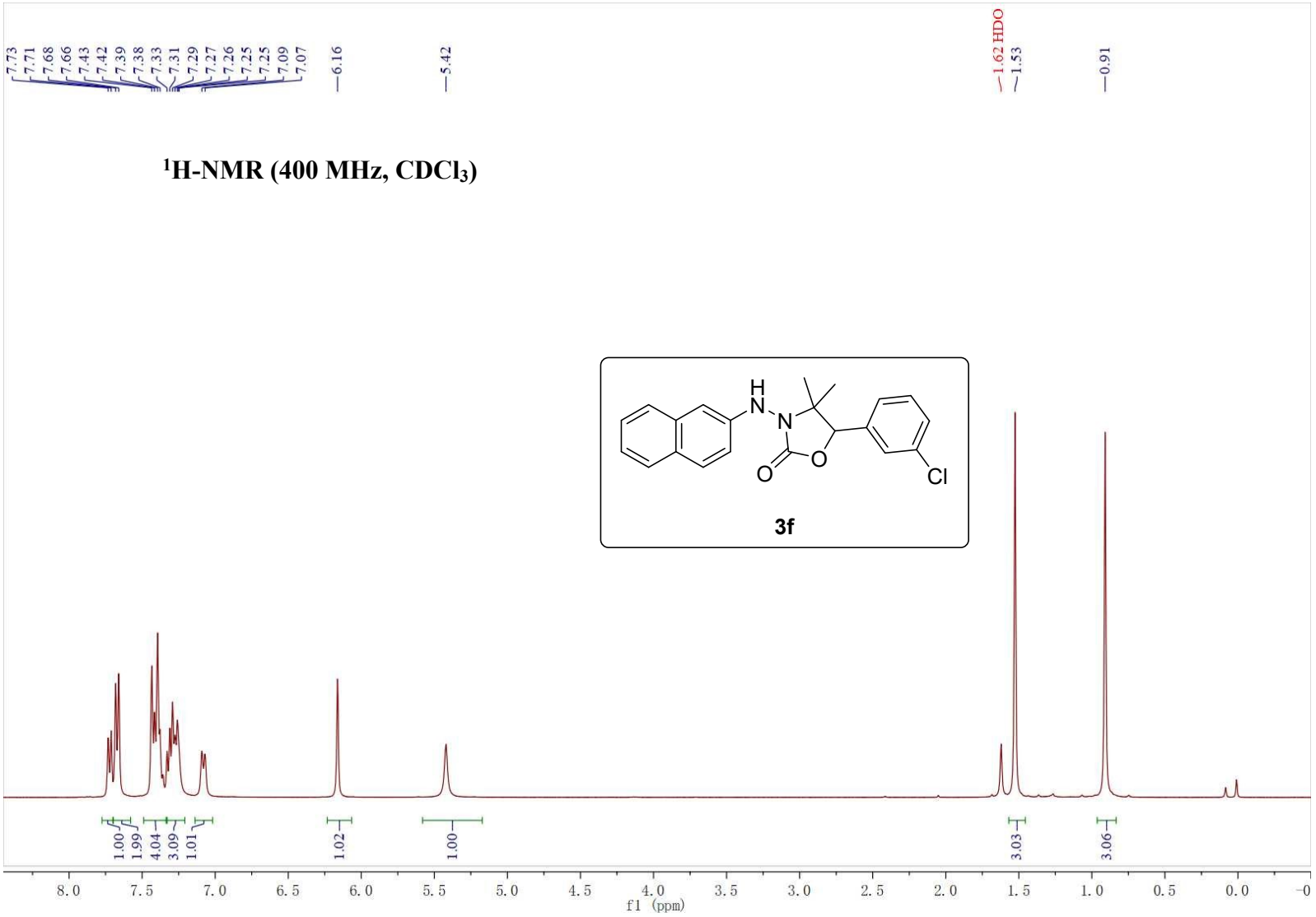


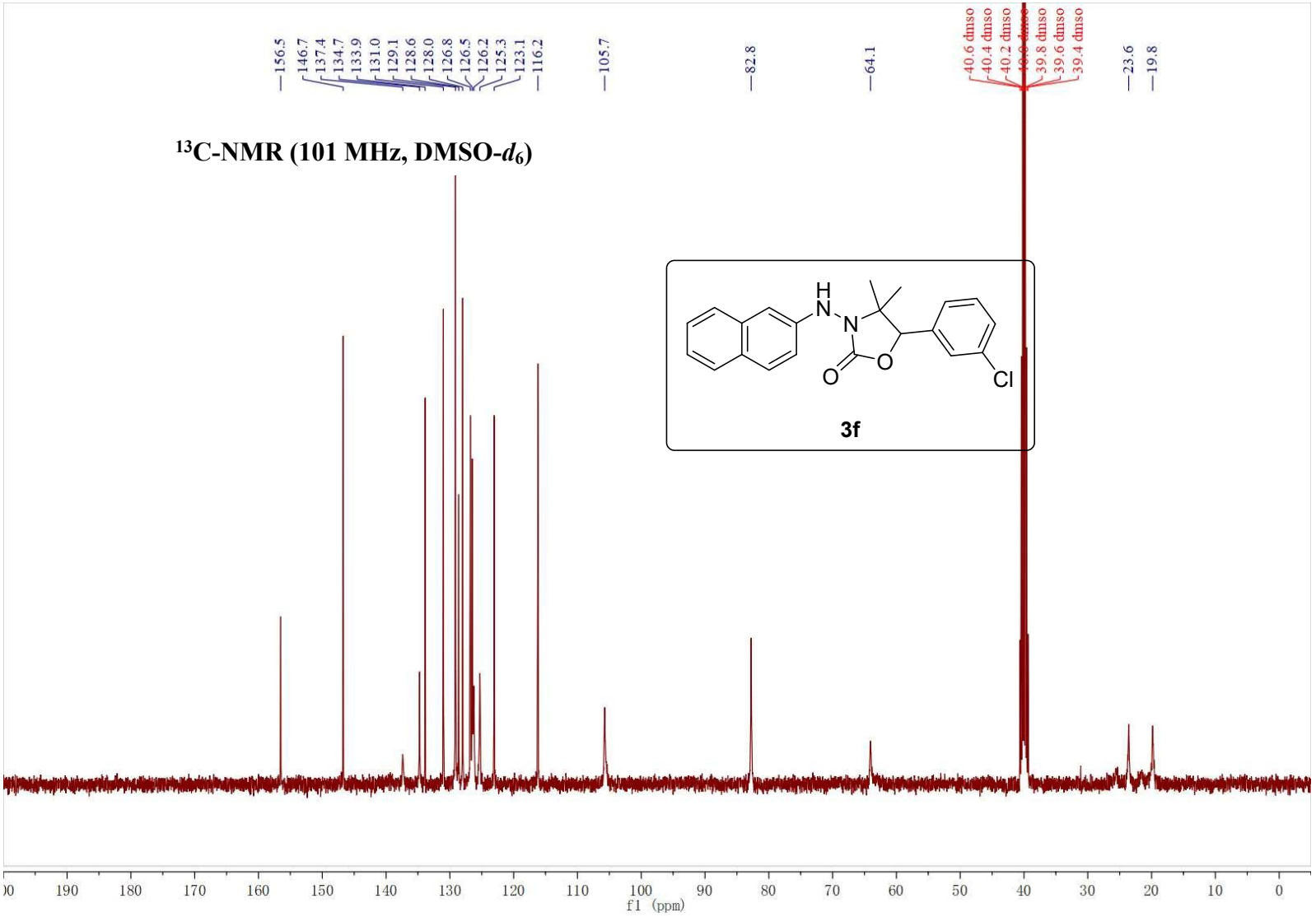
^{13}C-NMR (101 MHz, DMSO-d_6)

3e



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

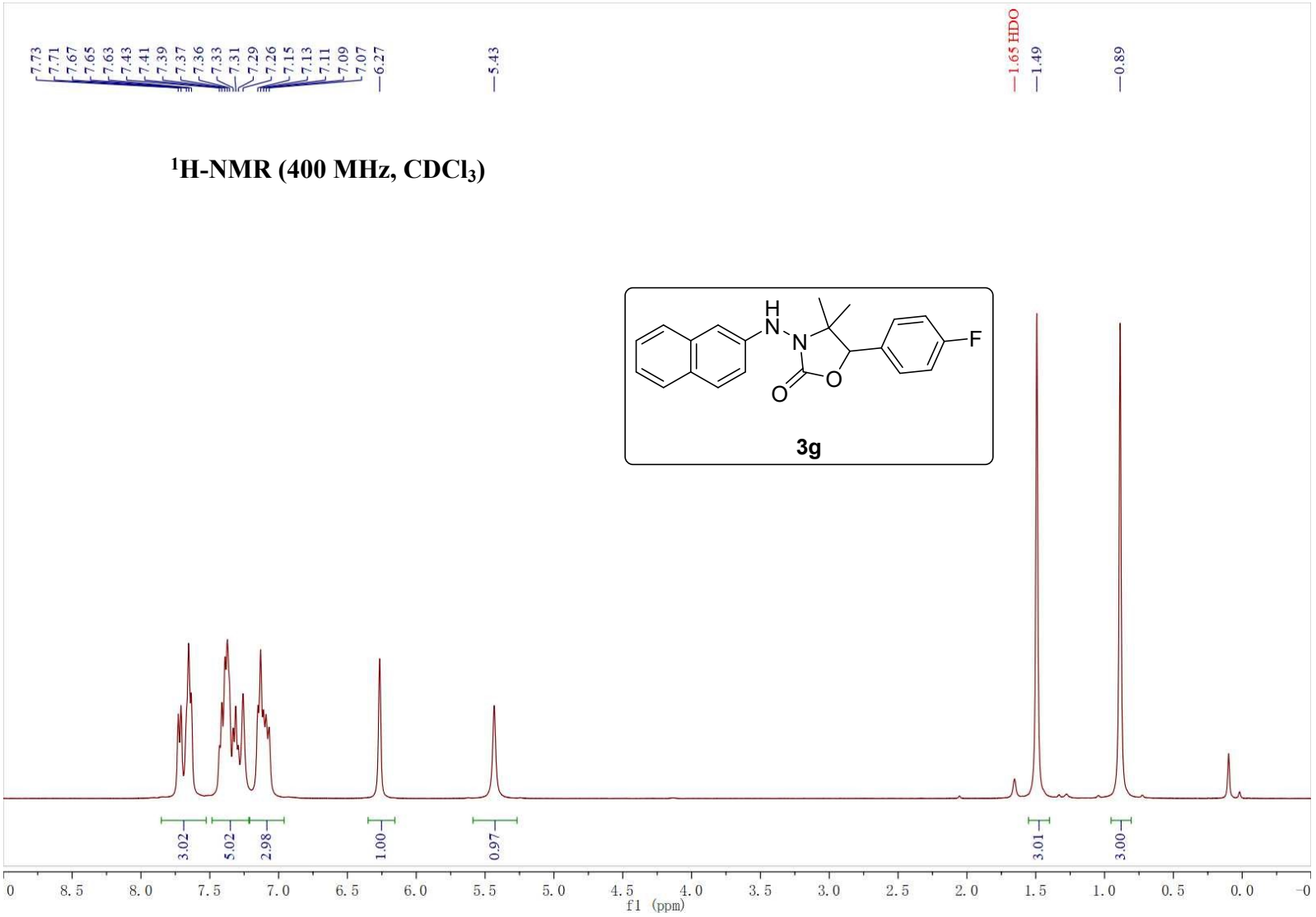
3f

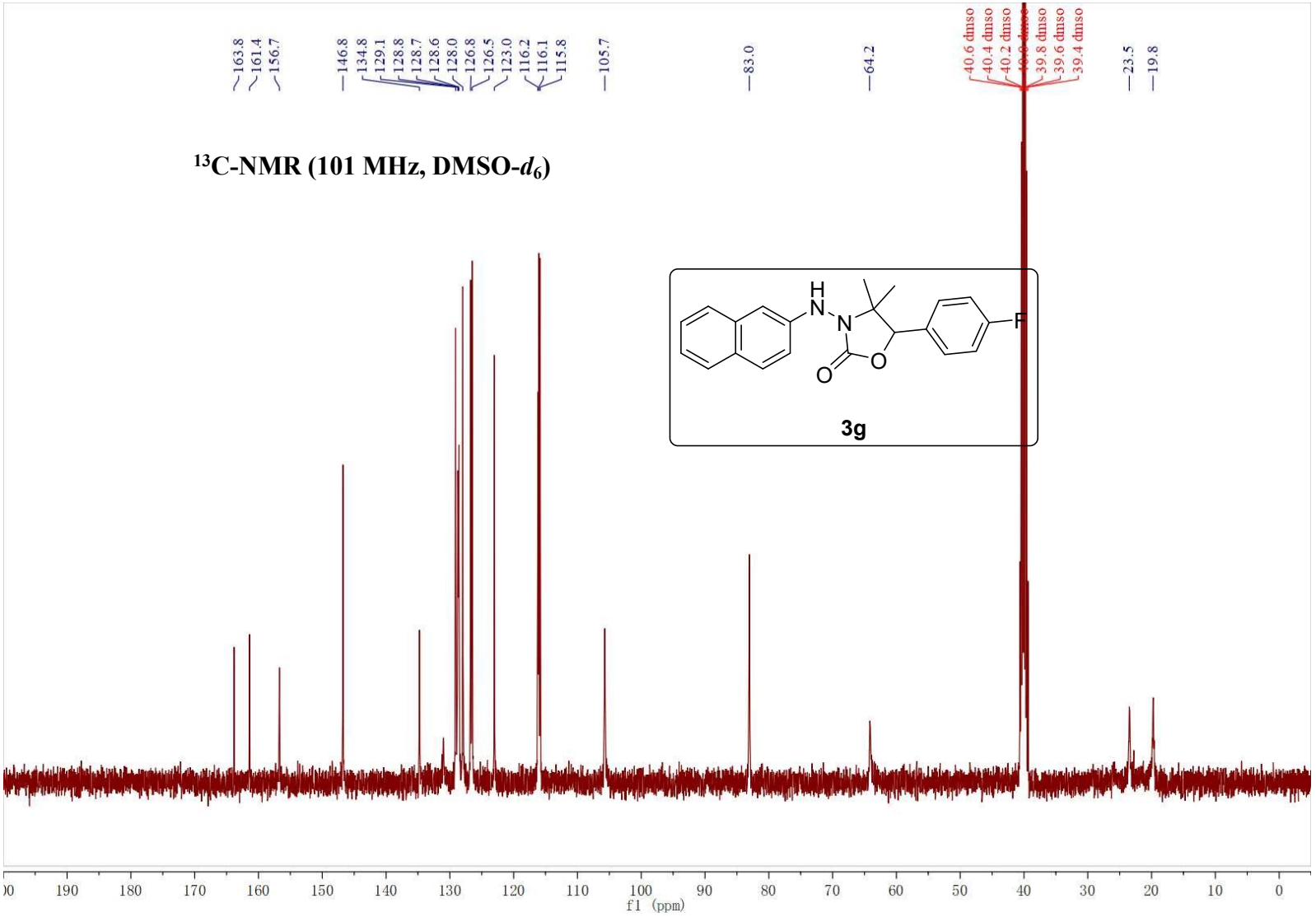


^{13}C-NMR (101 MHz, DMSO-d_6)

3f

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

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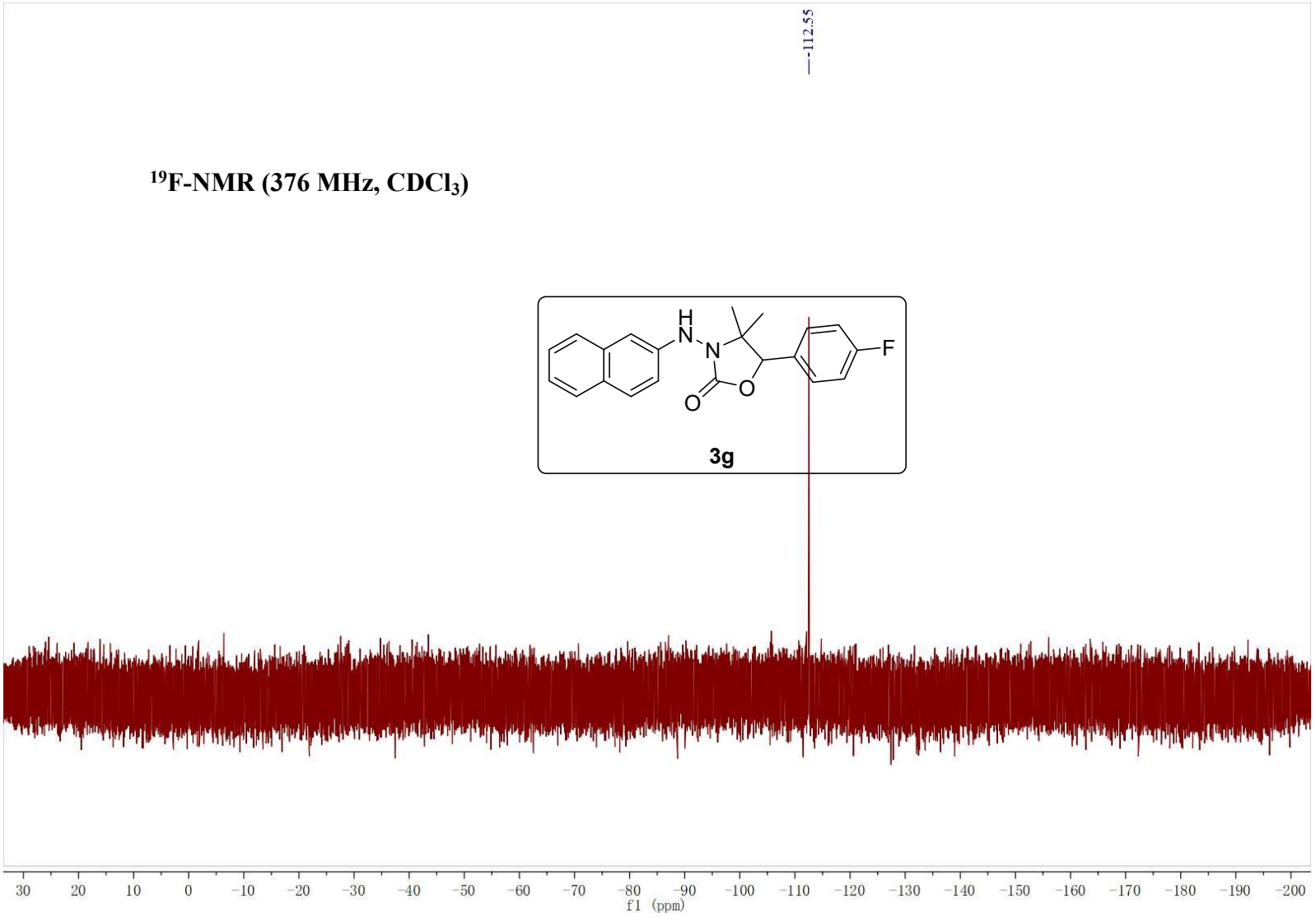
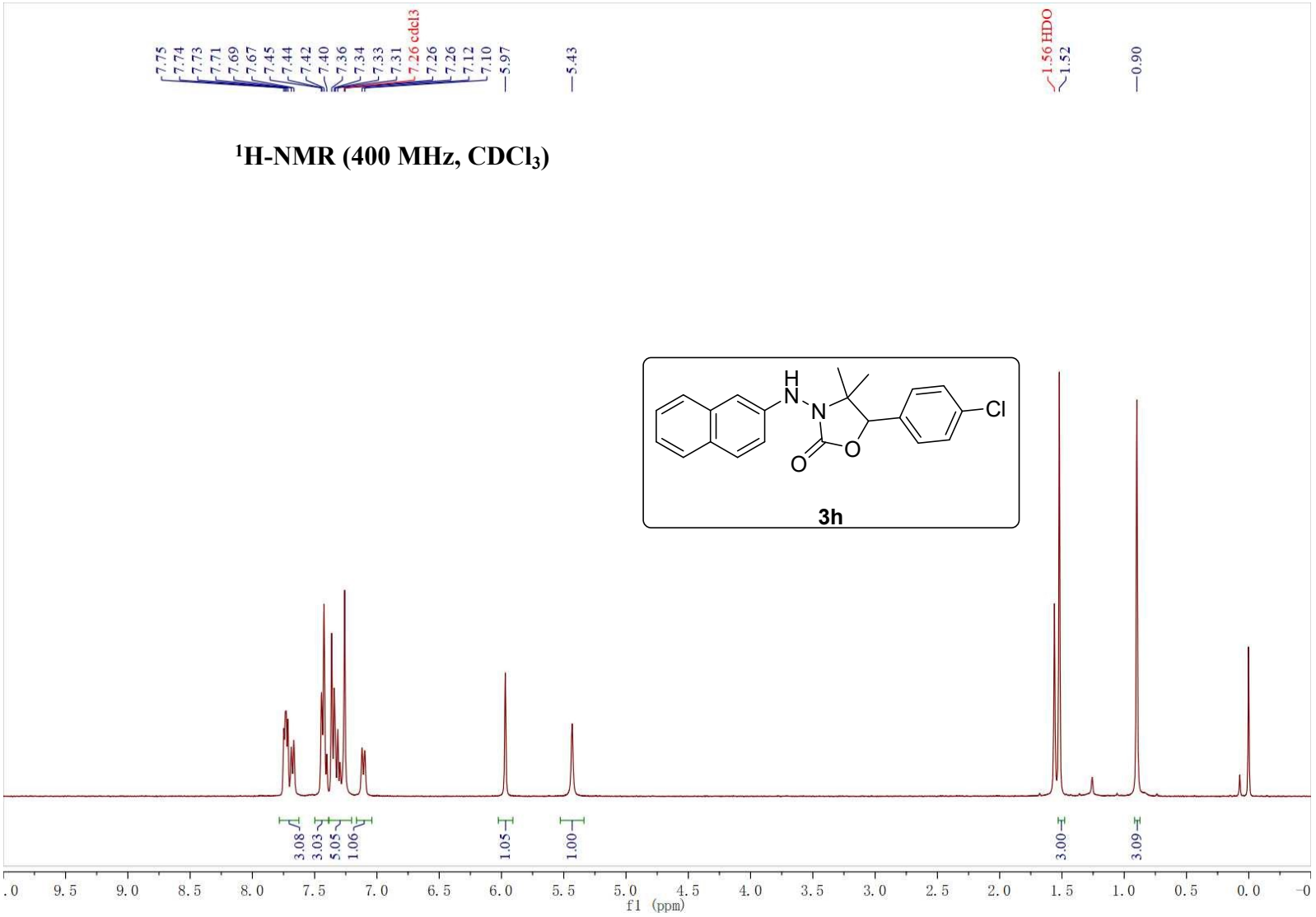
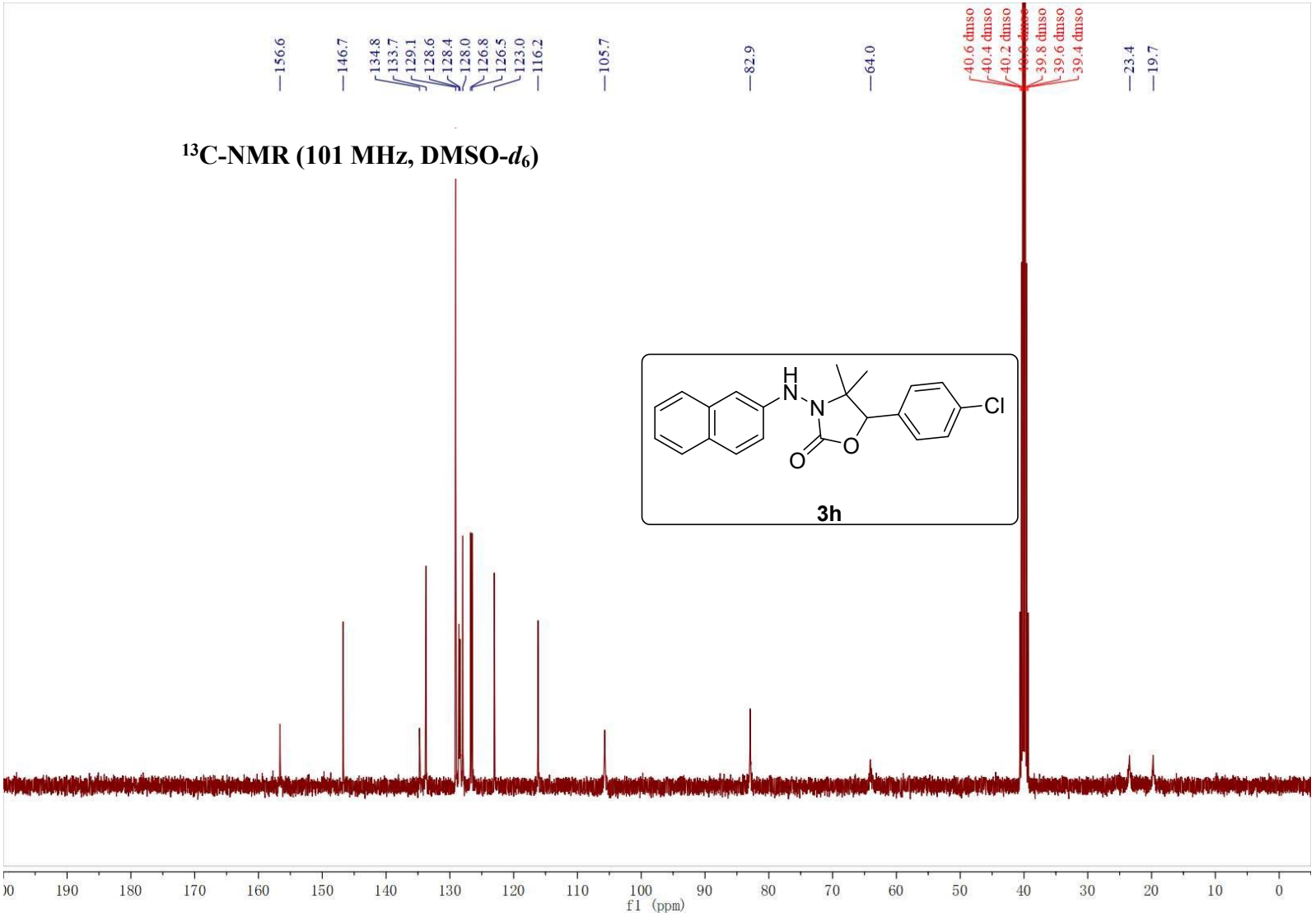
134.8
129.1
128.8
128.7
128.6
128.0
126.8
126.5
123.0
116.2
116.1
115.8
105.7
83.0
64.2
40.6 dmso
40.4 dmso
40.2 dmso
39.8 dmso
39.6 dmso
39.4 dmso
23.5
19.8
13C-NMR (101 MHz, DMSO-d6)
H
N
N
O
O
F
3g
f1 (ppm)

^{19}F-NMR (376 MHz, $CDCl_3$)





^{1}H-NMR (400 MHz, $CDCl_3$)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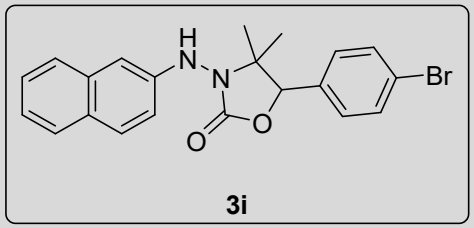
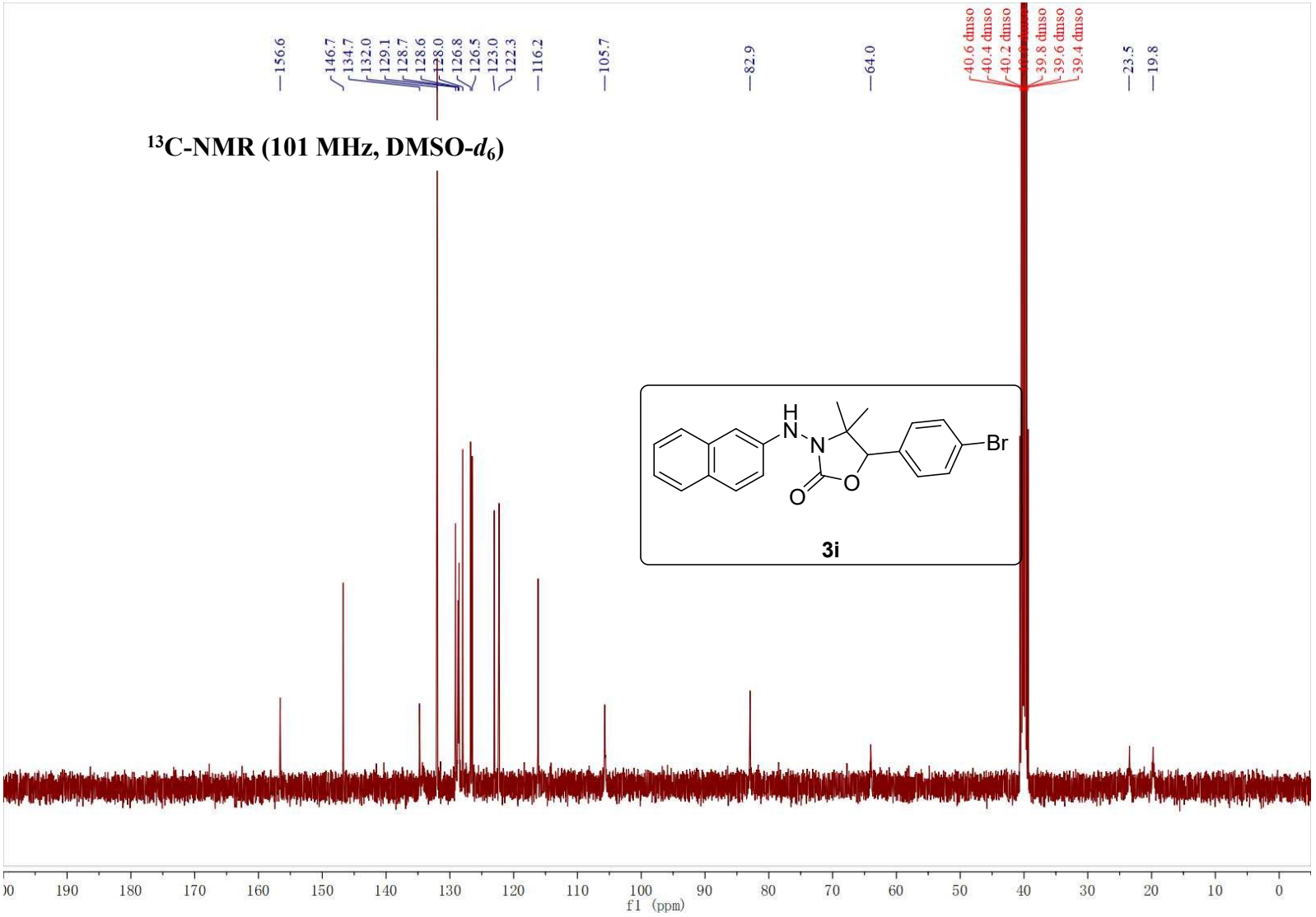
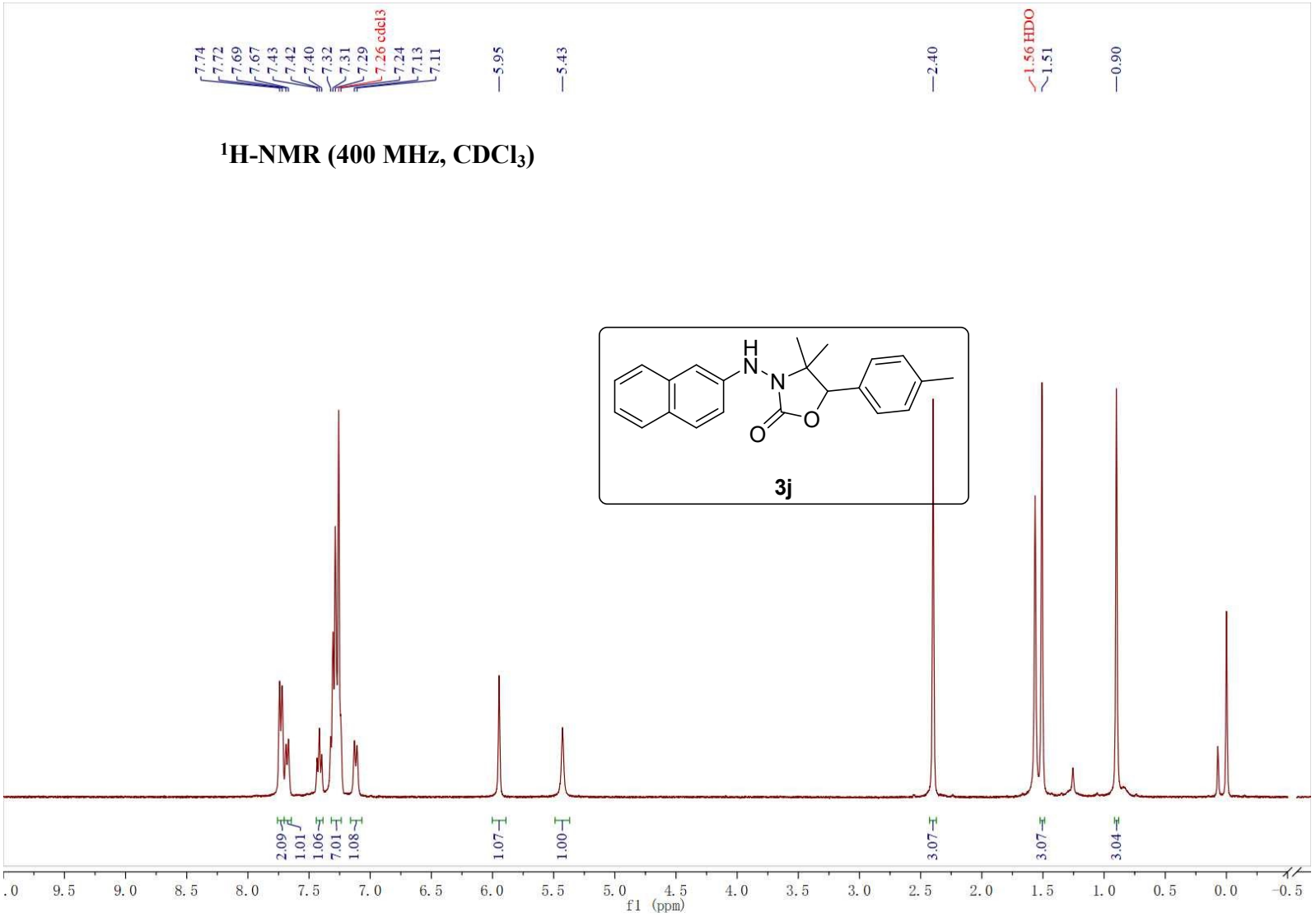
134.8
133.7
129.1
128.6
128.4
128.0
126.8
126.5
123.0
116.2
105.7
82.9
64.0
40.6 dmso
40.4 dmso
40.2 dmso
39.8 dmso
39.6 dmso
39.4 dmso
23.4
19.7
13C-NMR (101 MHz, DMSO-d6)
H
N
N
O
O
Cl
3h
f1 (ppm)

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

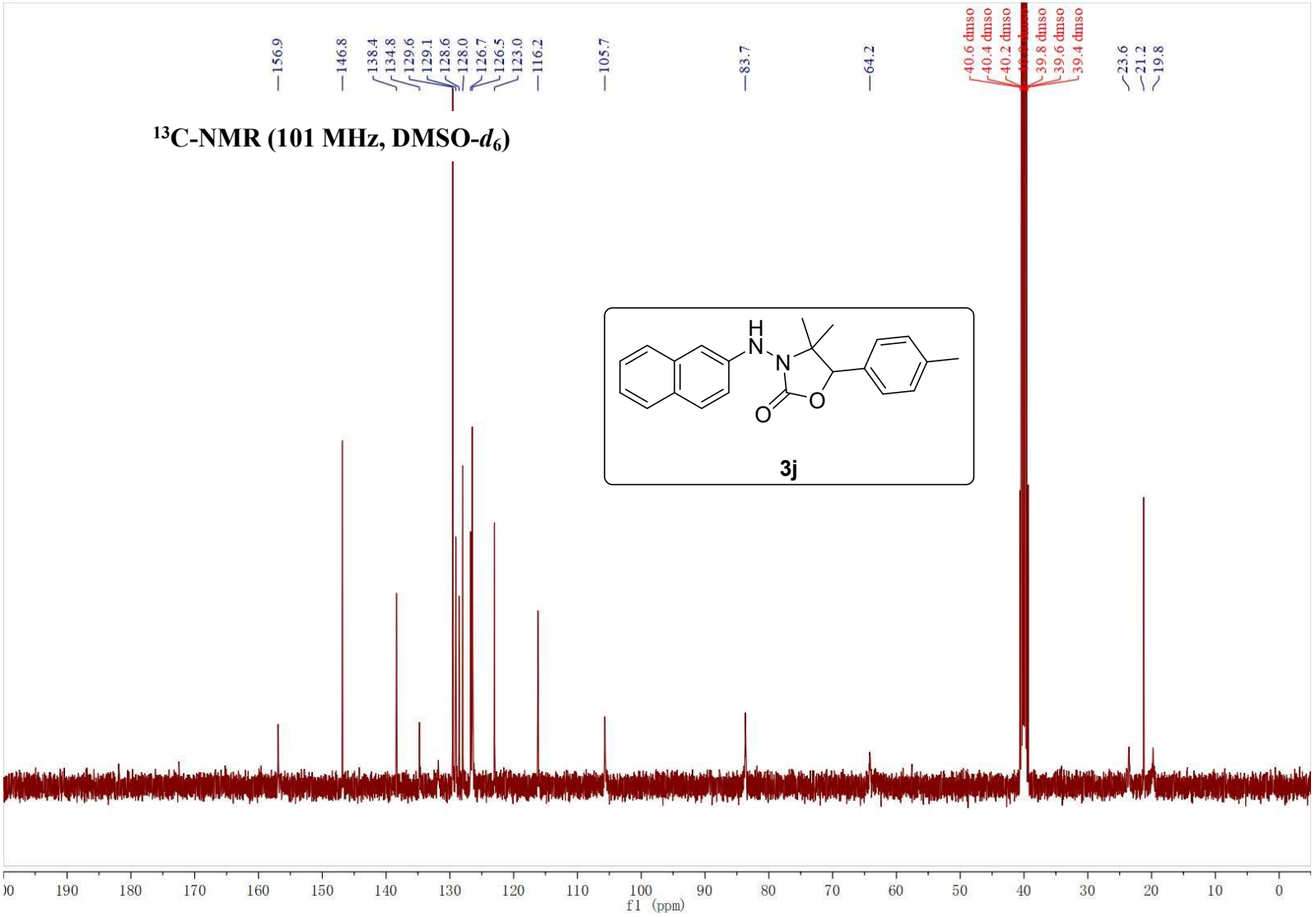


3i


156.6
146.7
134.7
132.0
129.1
128.7
128.6
128.0
126.8
126.5
123.0
122.3
116.2
105.7
82.9
64.0
40.6 dmso
40.4 dmso
40.2 dmso
39.8 dmso
39.6 dmso
39.4 dmso
23.5
19.8
13C-NMR (101 MHz, DMSO-d6)
H
N
N
O
O
Br
3i
f1 (ppm)

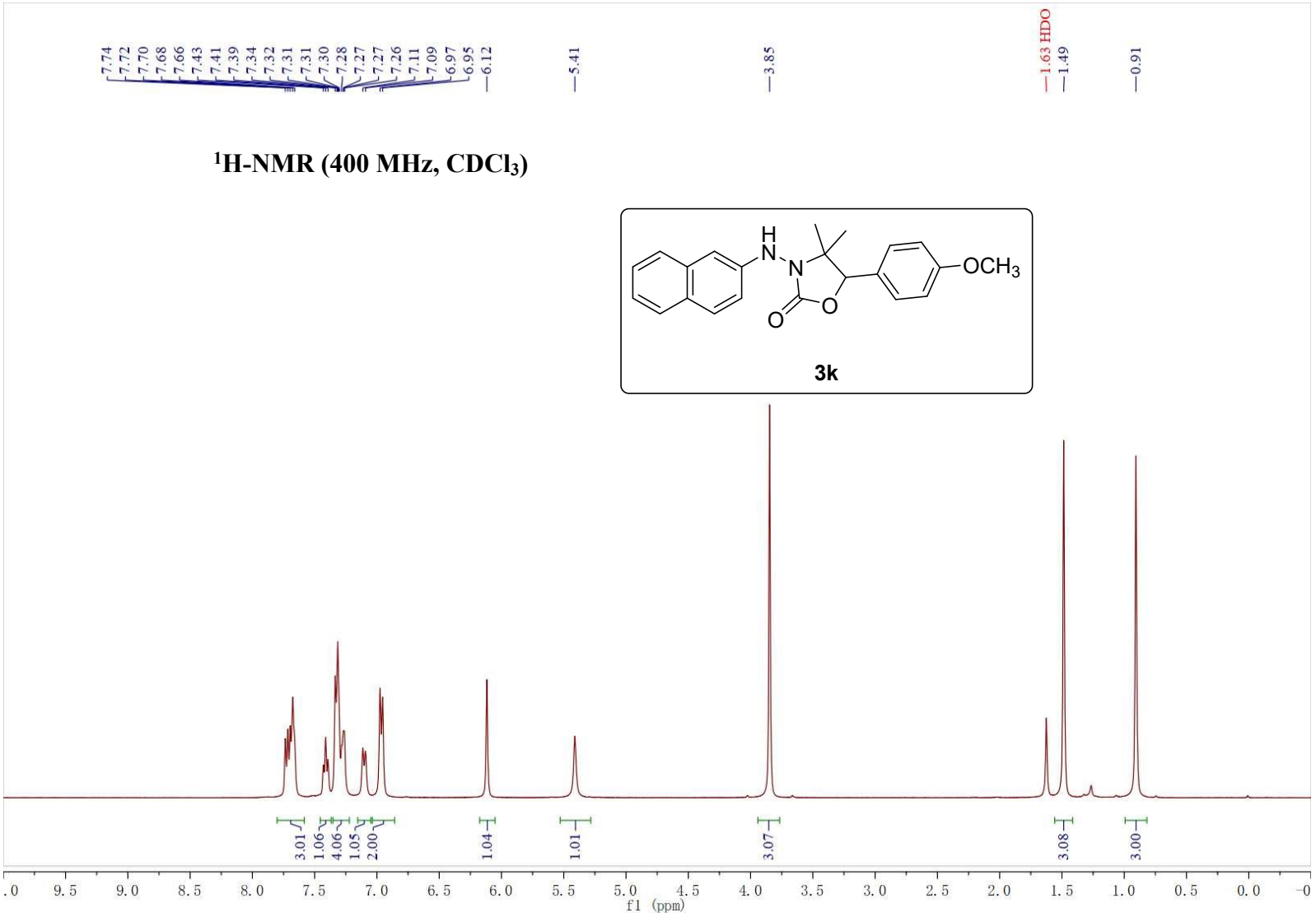


^{1}H-NMR (400 MHz, $CDCl_3$)



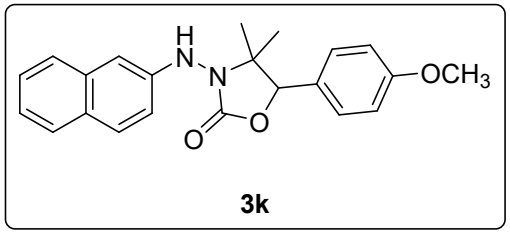
^{13}C-NMR (101 MHz, DMSO-d_6)

3j

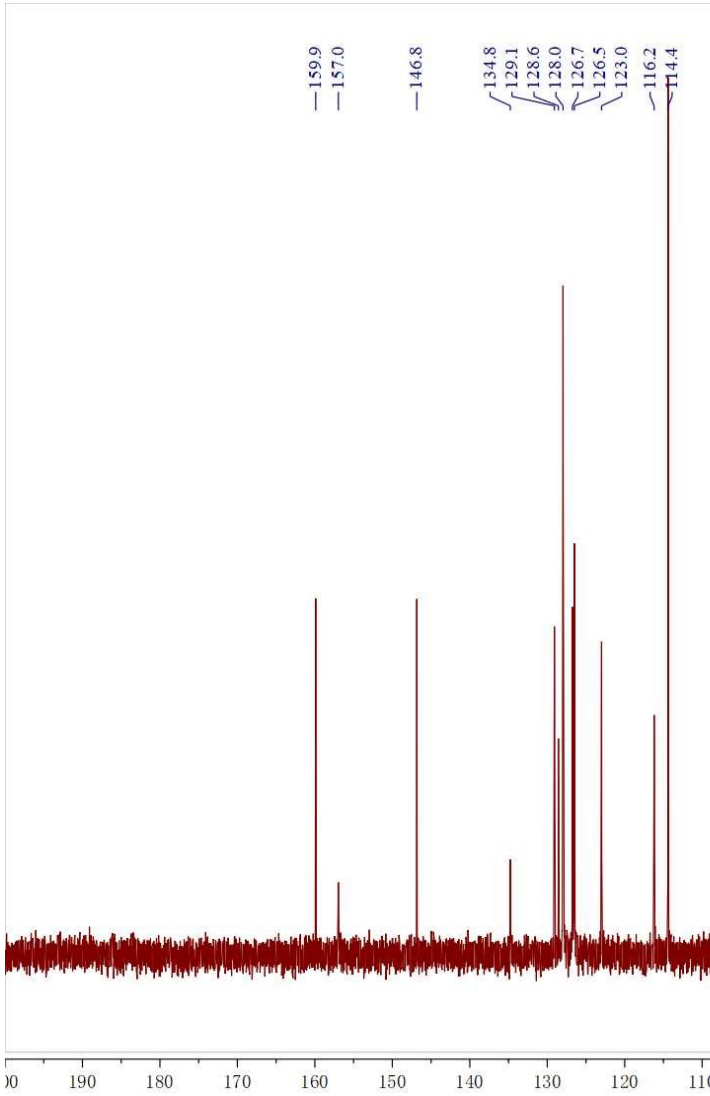


^{1}H-NMR (400 MHz, $CDCl_3$)

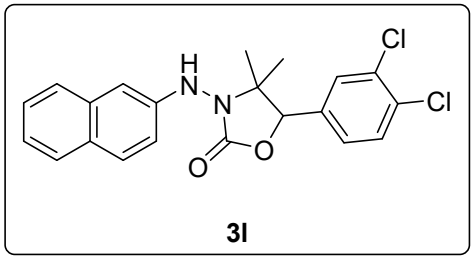
^{13}C-NMR (101 MHz, DMSO-d_6)



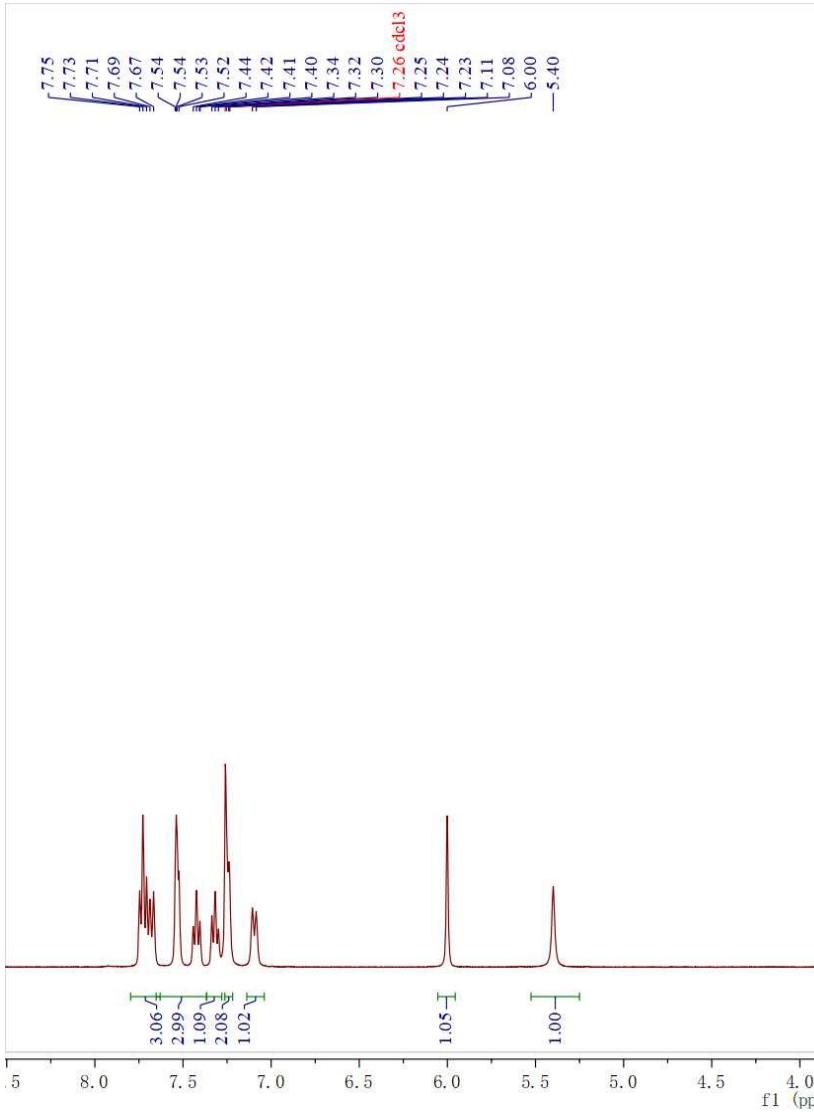
3k

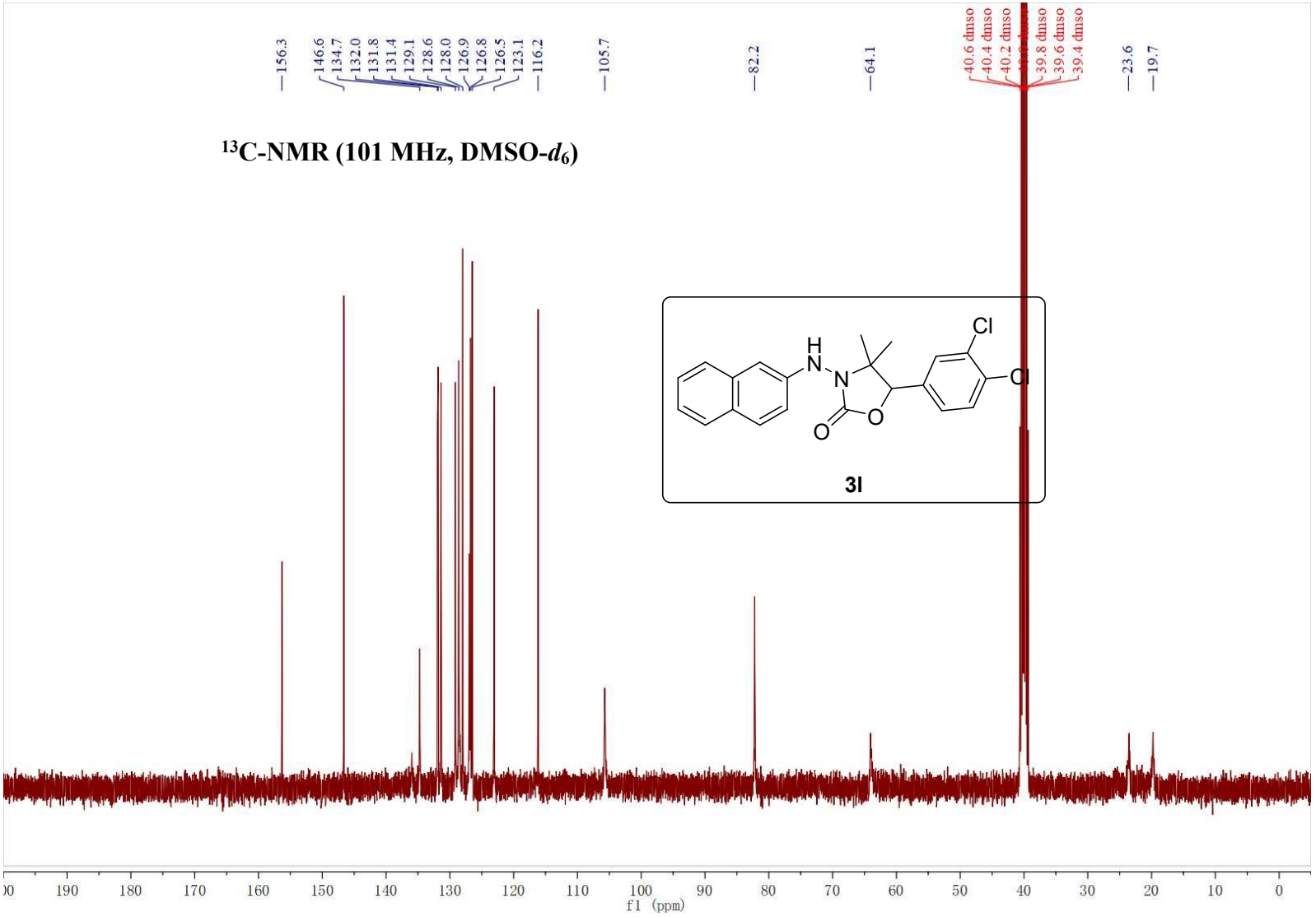


^{1}H-NMR (400 MHz, $CDCl_3$)

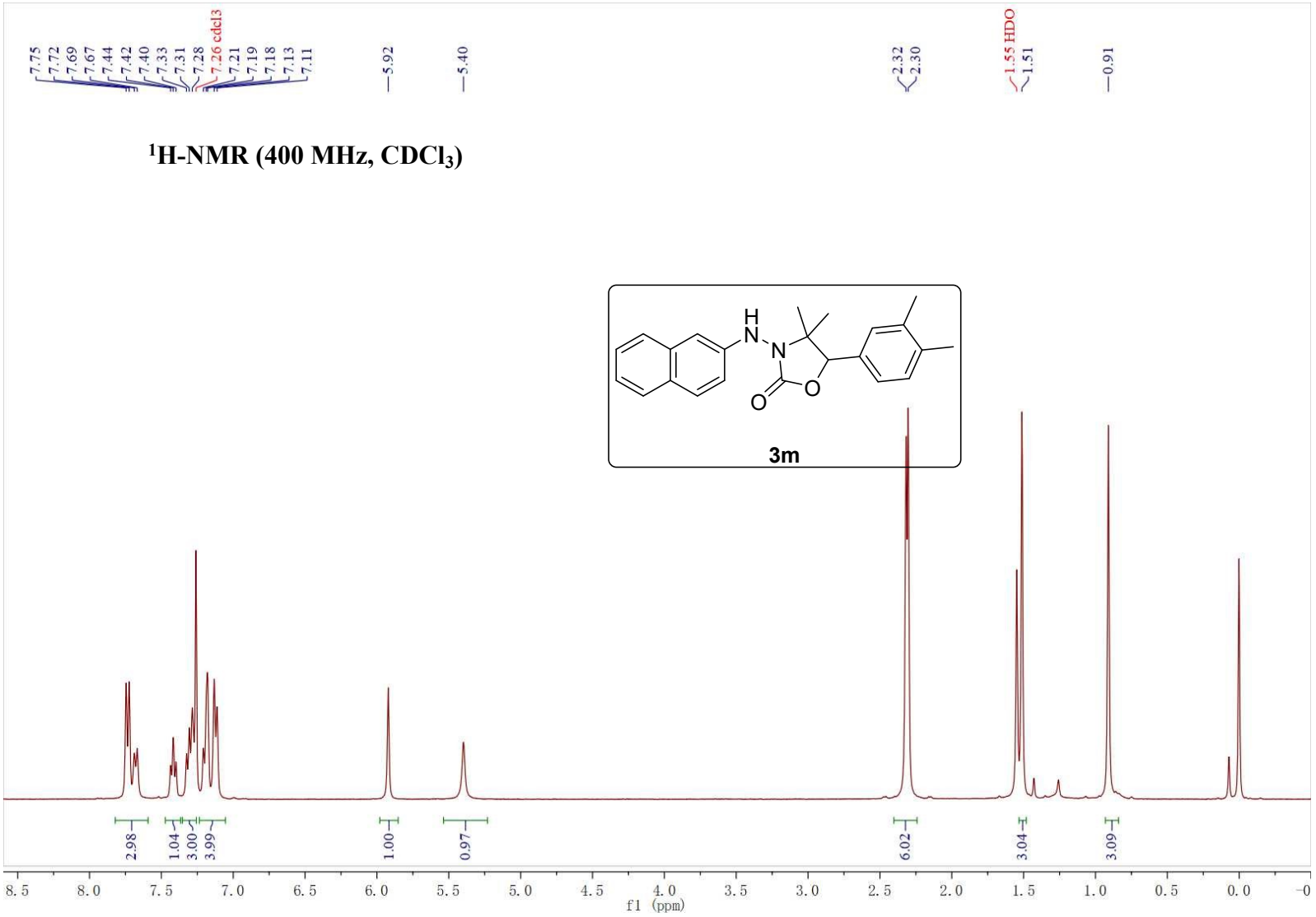


3l

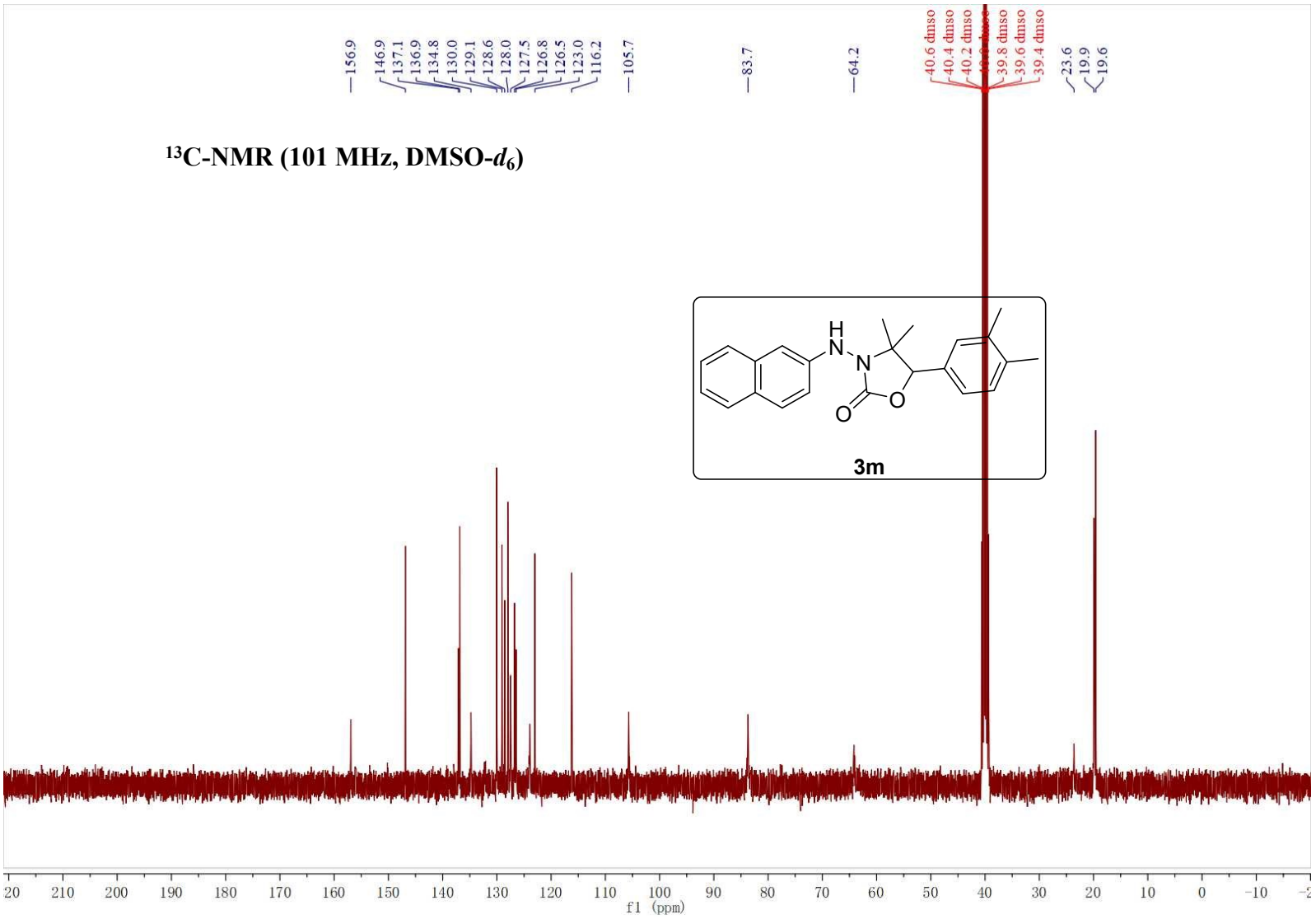


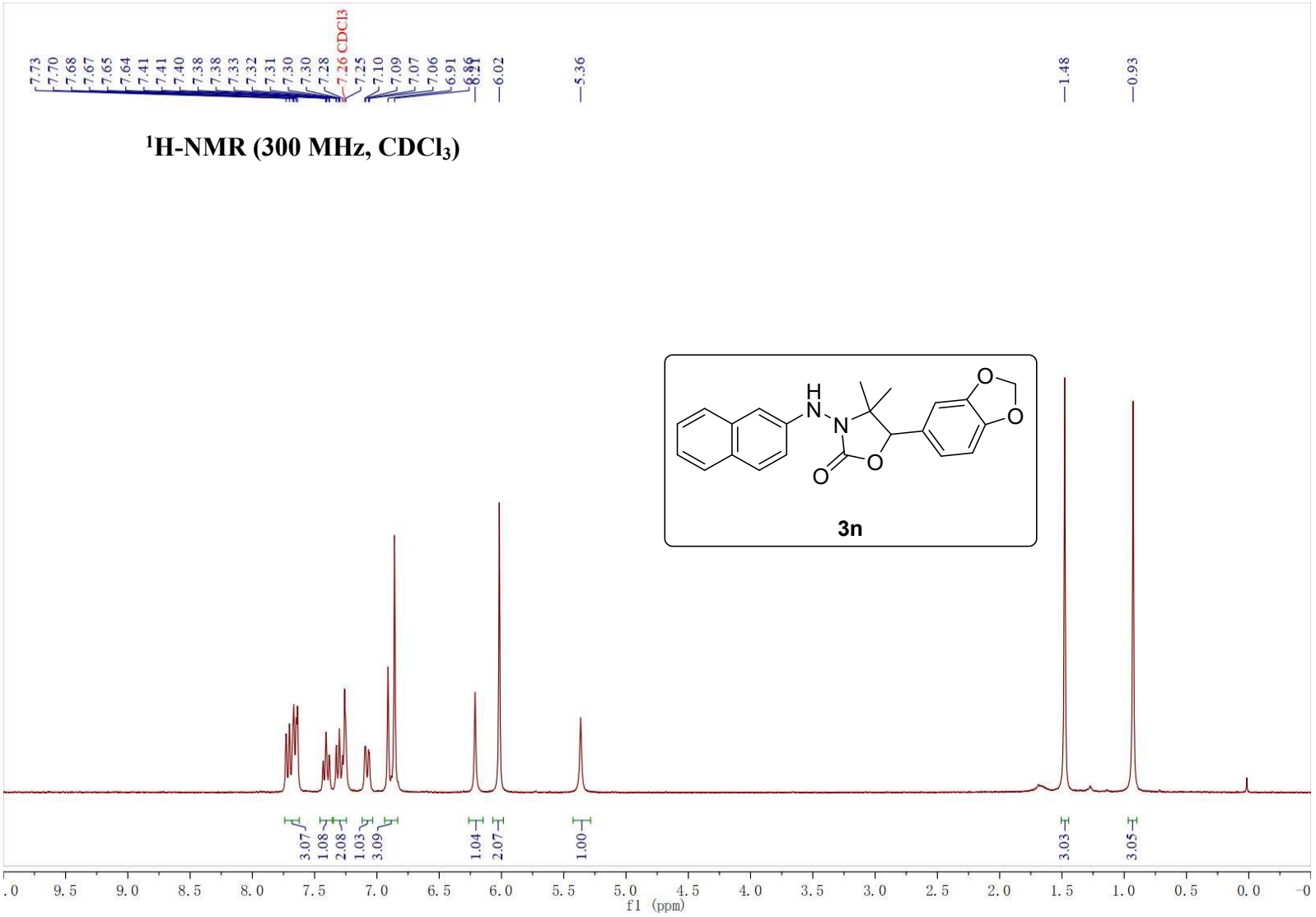

156.3
146.6
134.7
132.0
131.8
131.4
129.1
128.6
128.0
126.9
126.8
126.5
123.1
116.2
105.7
82.2
64.1
40.6 dmso
40.4 dmso
40.2 dmso
39.8 dmso
39.6 dmso
39.4 dmso
23.6
19.7
13C-NMR (101 MHz, DMSO-d6)
H
N
N
O
O
Cl
Cl
3l
f1 (ppm)

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



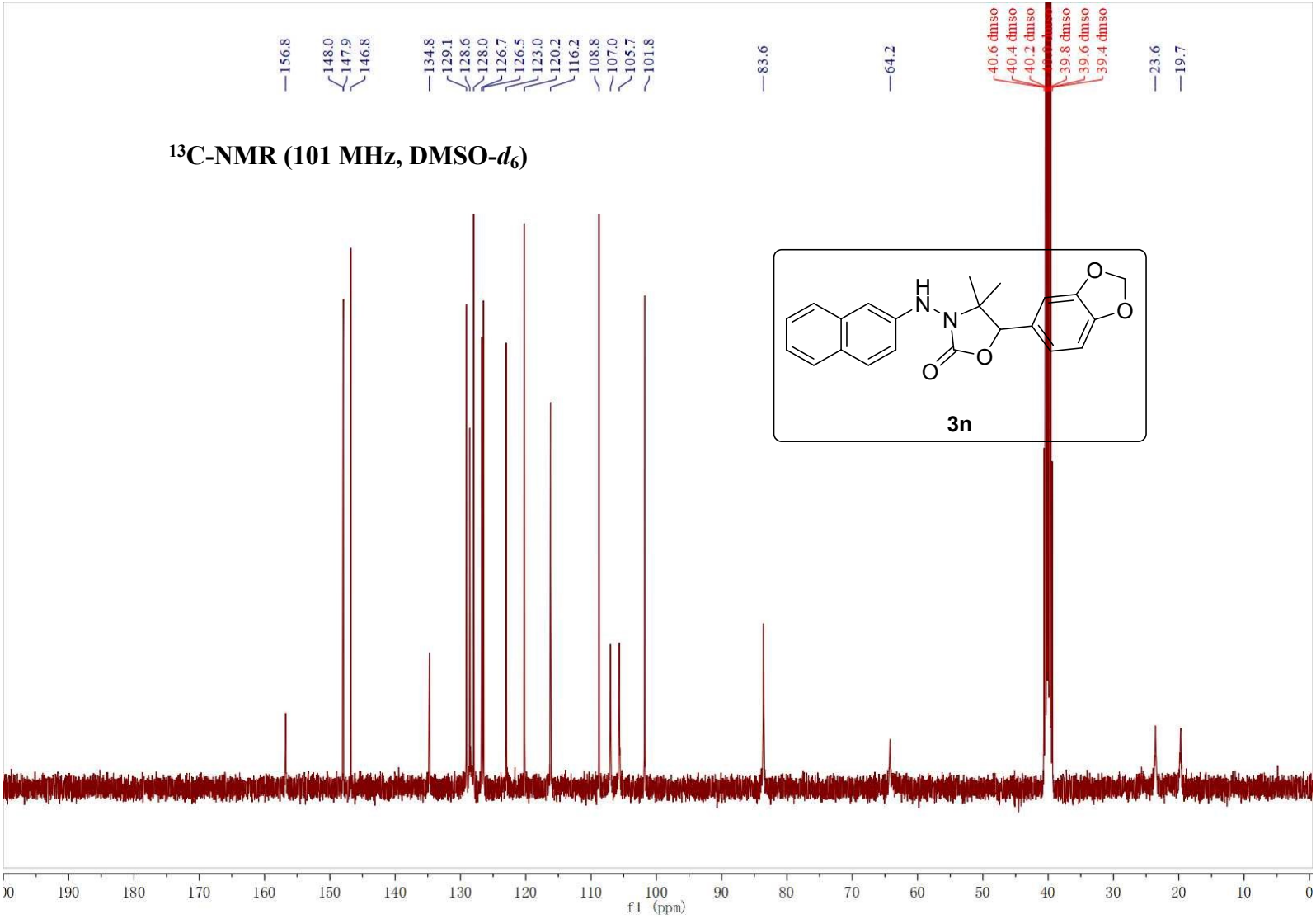
^{13}C-NMR (101 MHz, DMSO-d_6)





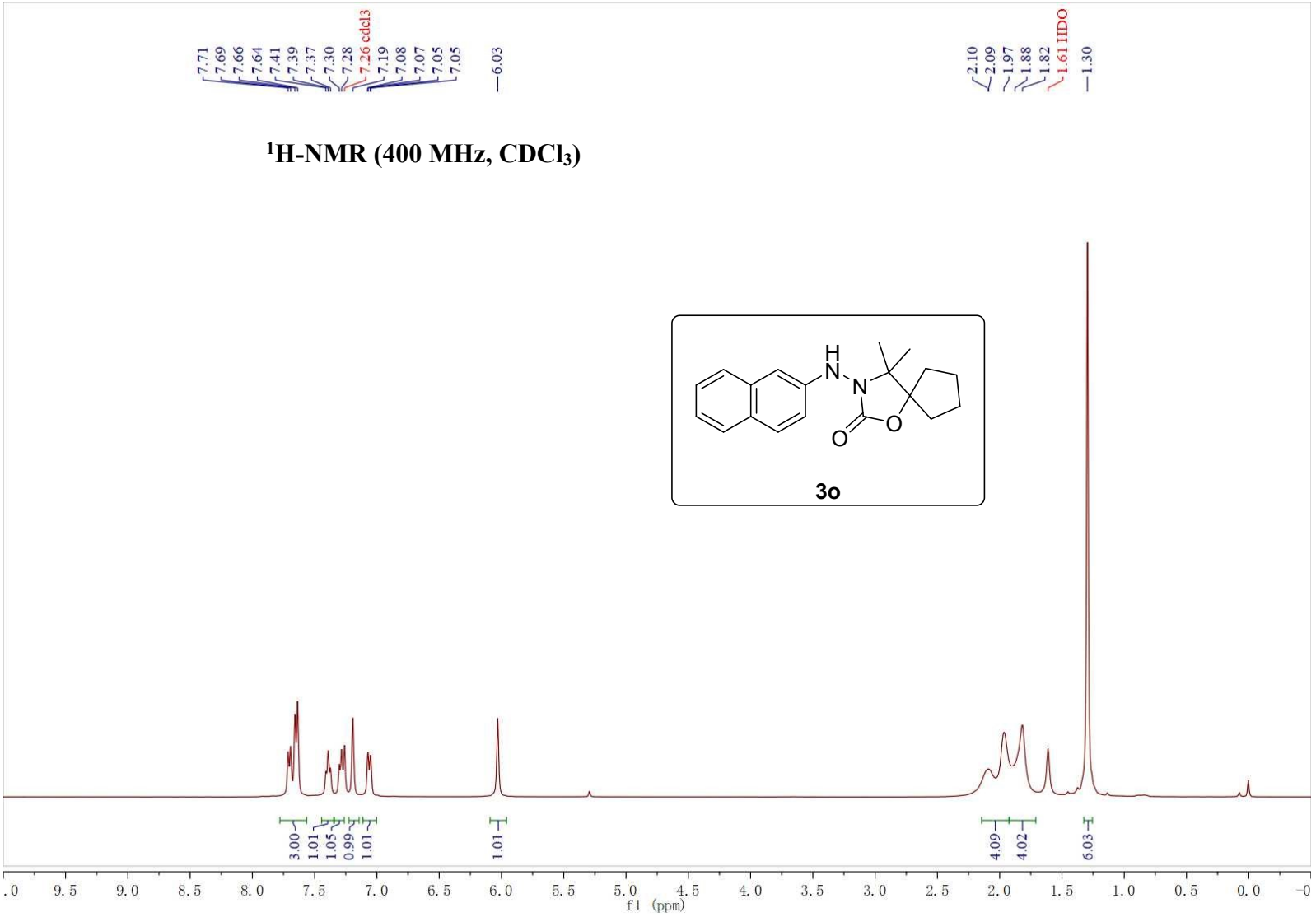
^{1}H-NMR (300 MHz, $CDCl_3$)

3n

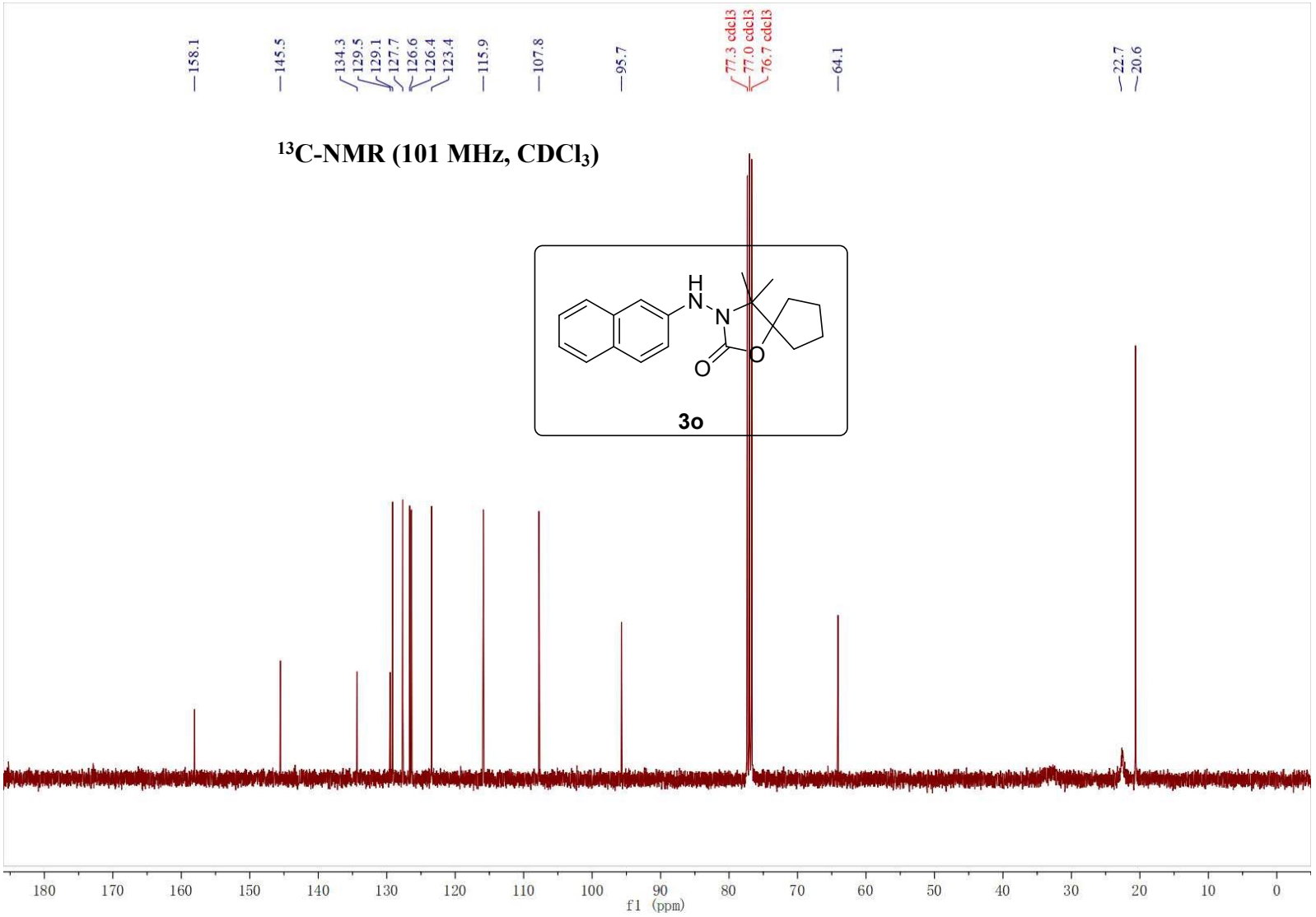


^{13}C-NMR (101 MHz, DMSO-d_6)

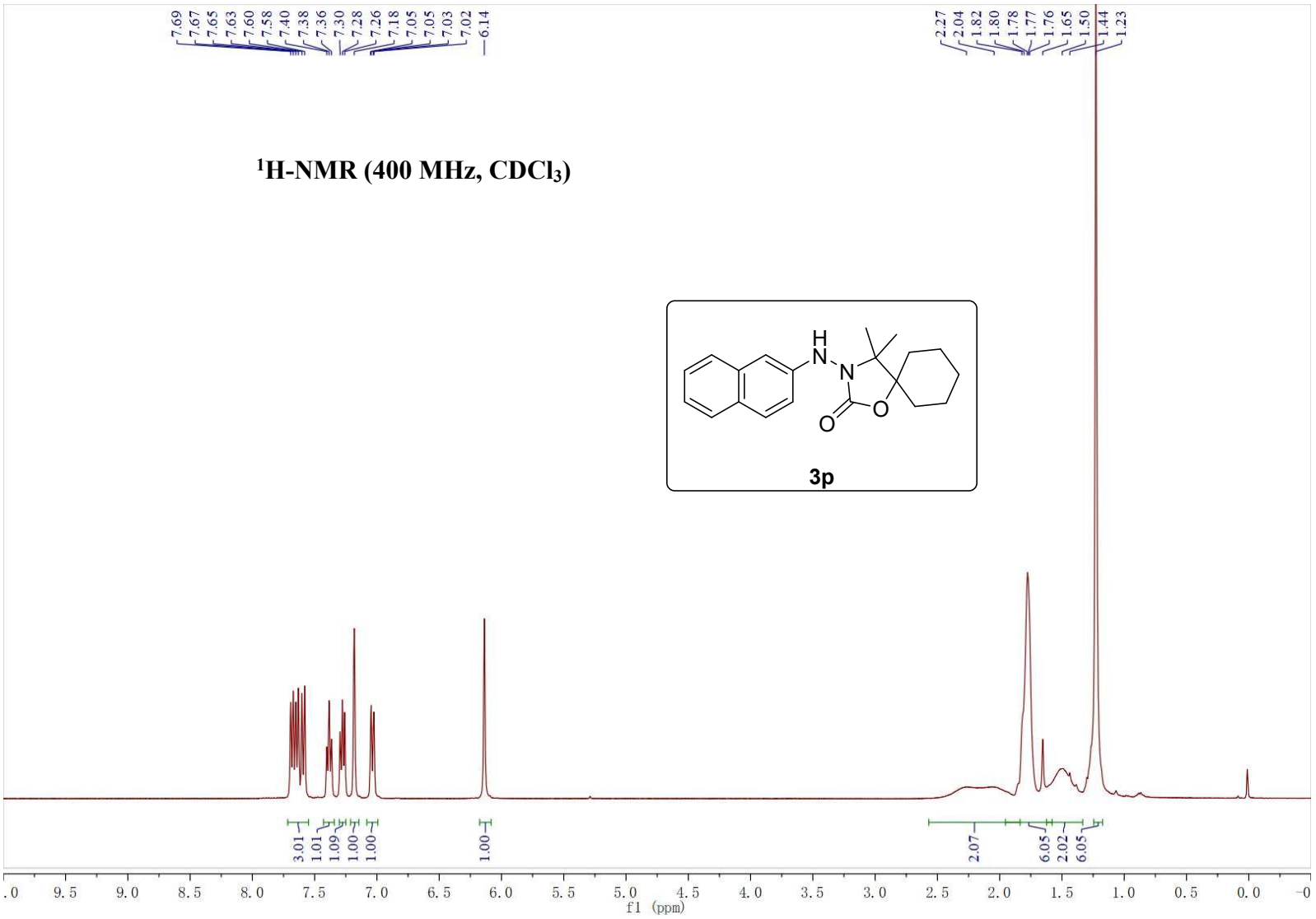
3n



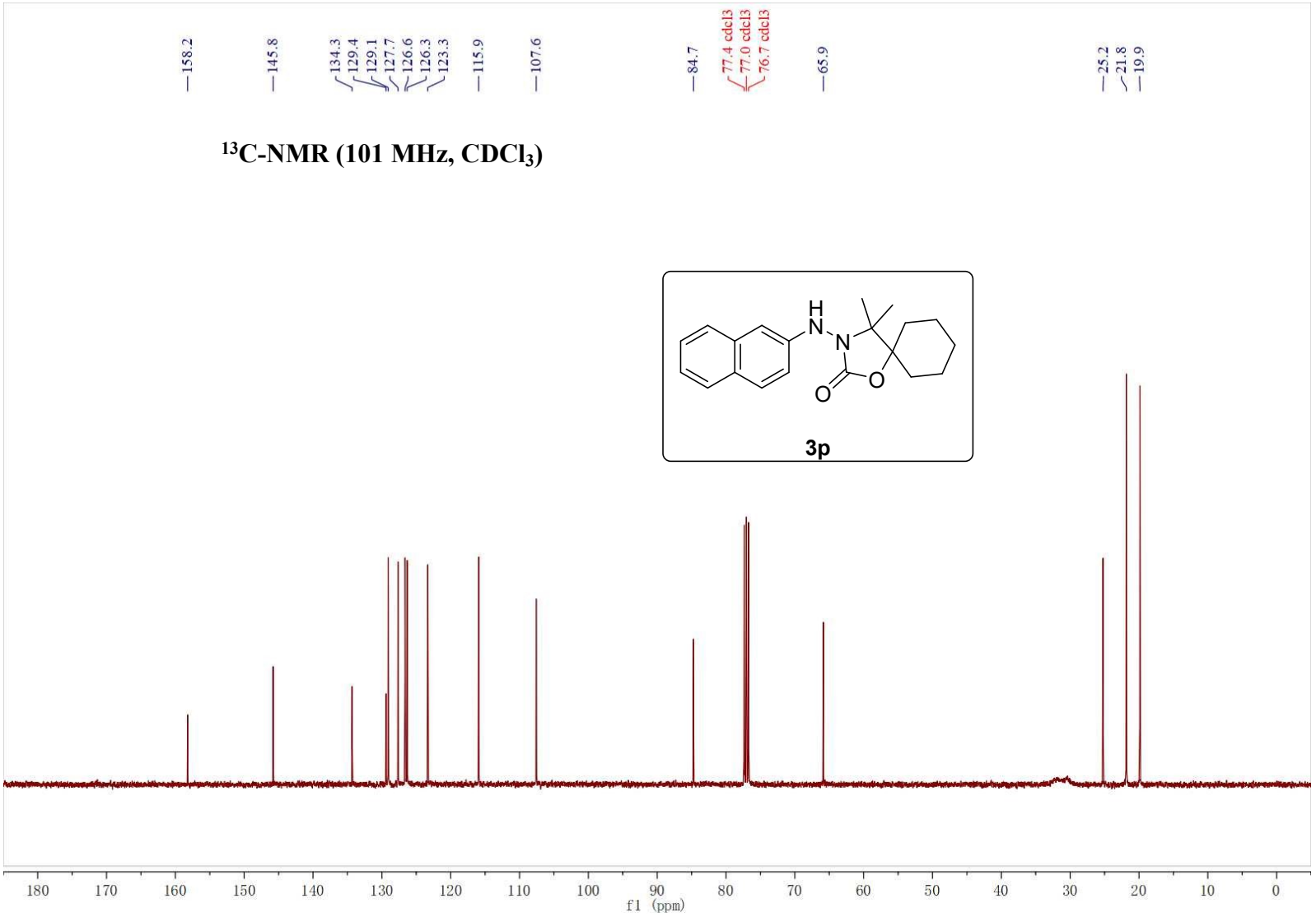
^{1}H-NMR (400 MHz, $CDCl_3$)


158.1
145.5
134.3
129.5
129.1
127.7
126.6
126.4
123.4
115.9
107.8
95.7
77.3 cdcl3
77.0 cdcl3
76.7 cdcl3
64.1
22.7
20.6
13C-NMR (101 MHz, CDCl3)
H
N
N
O
O
3o
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

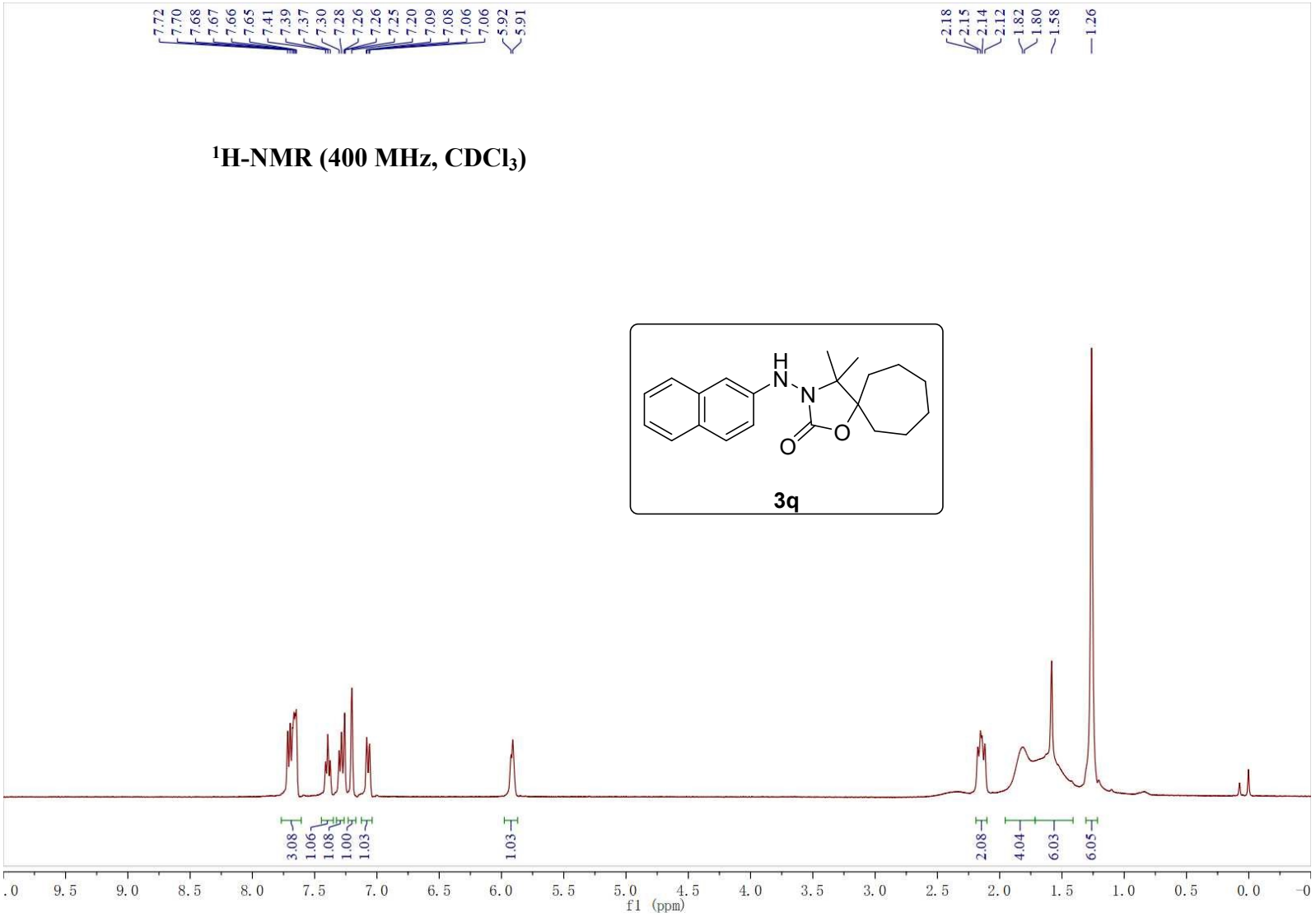
^{1}H-NMR (400 MHz, $CDCl_3$)



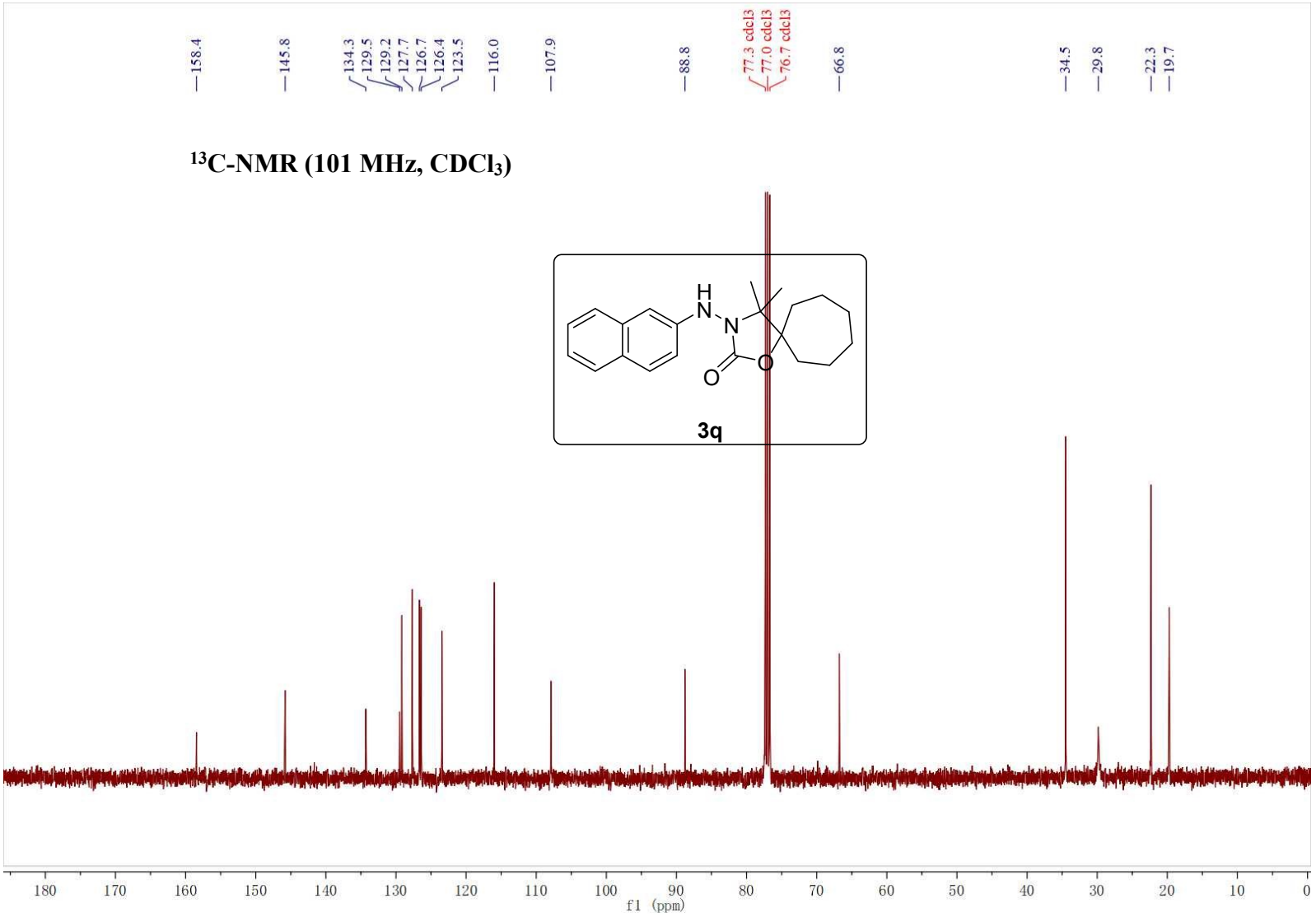
3p



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

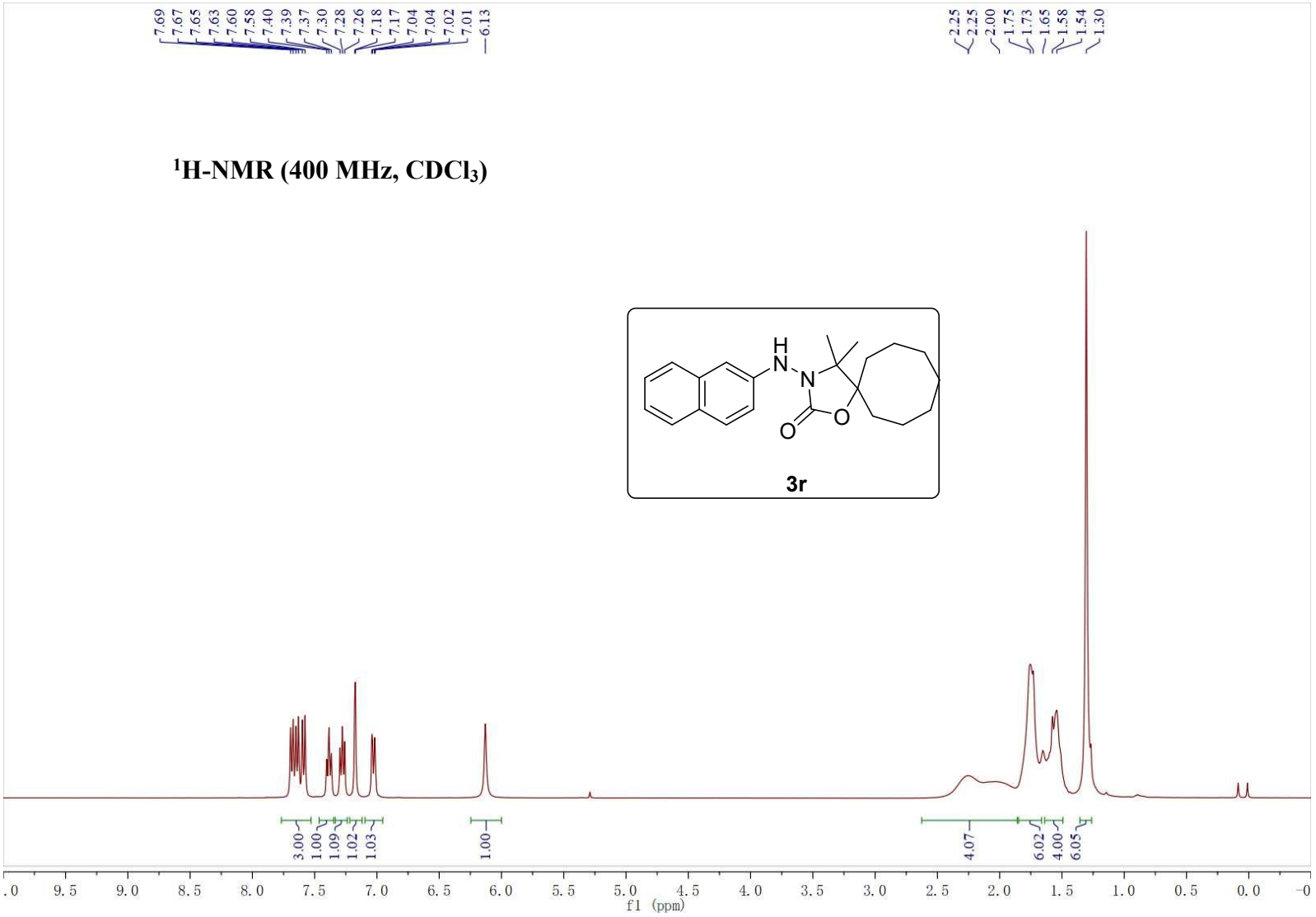


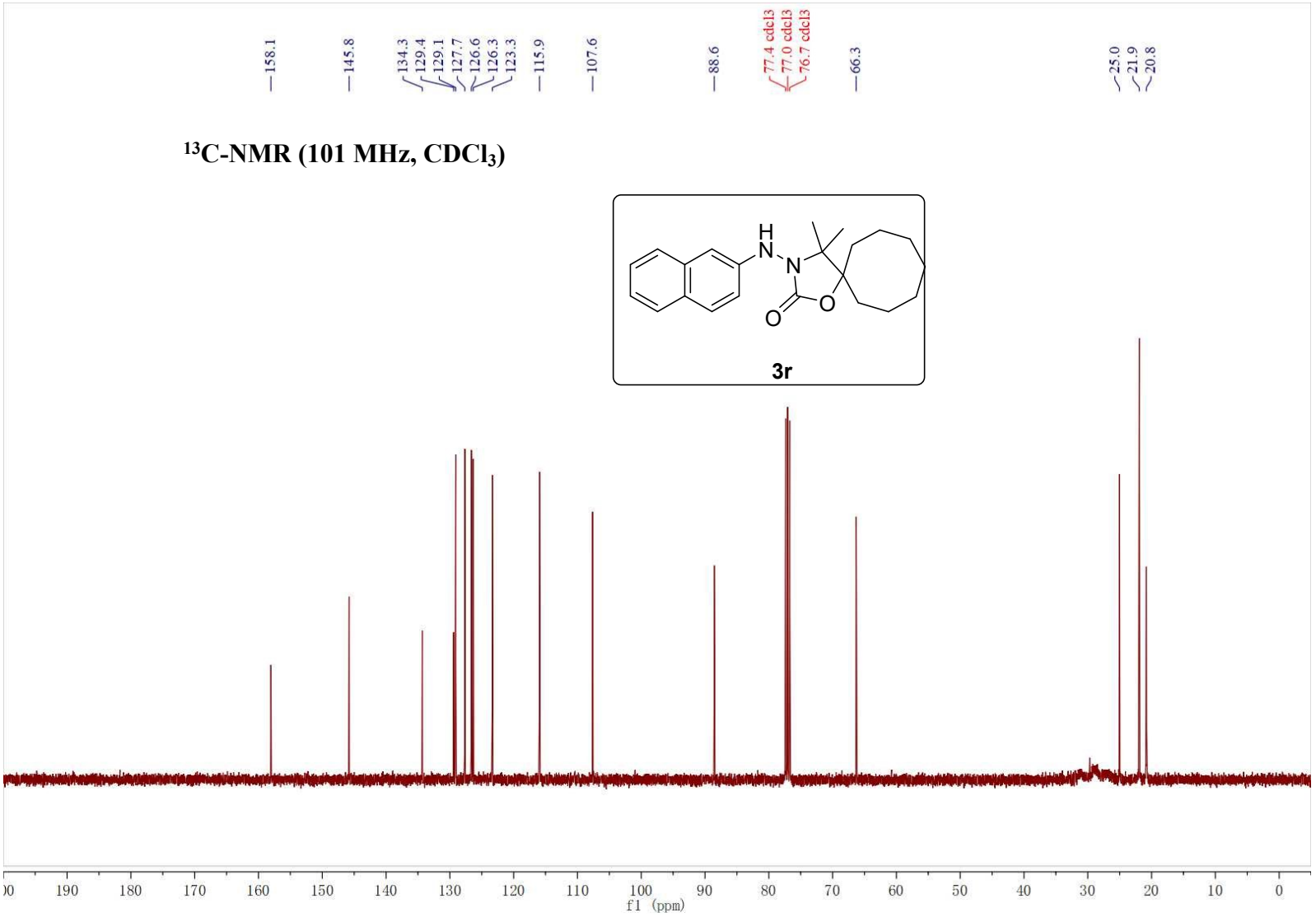
^{1}H-NMR (400 MHz, $CDCl_3$)



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

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

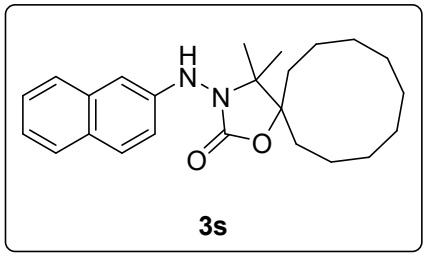




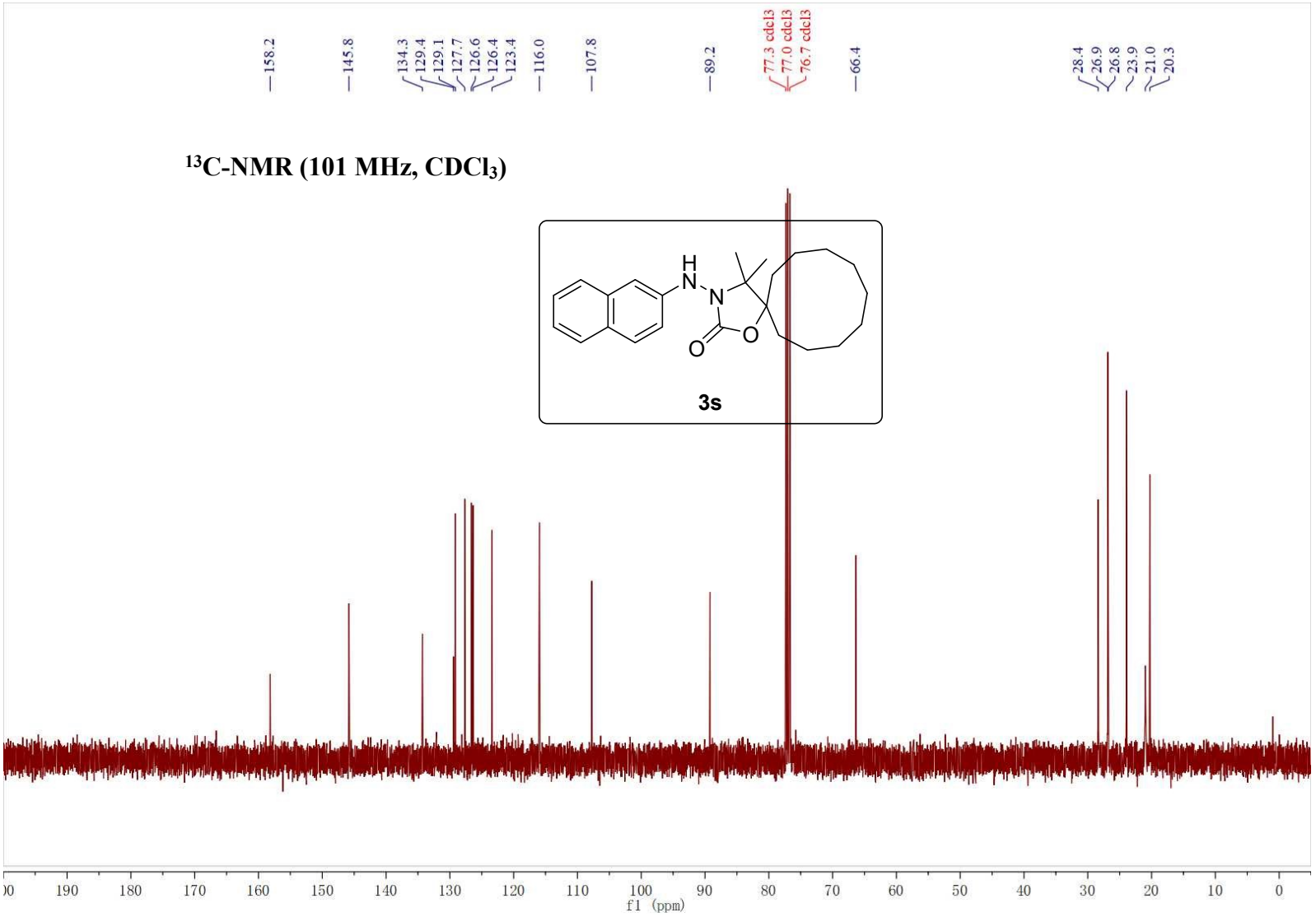
^{13}C-NMR (101 MHz, $CDCl_3$)

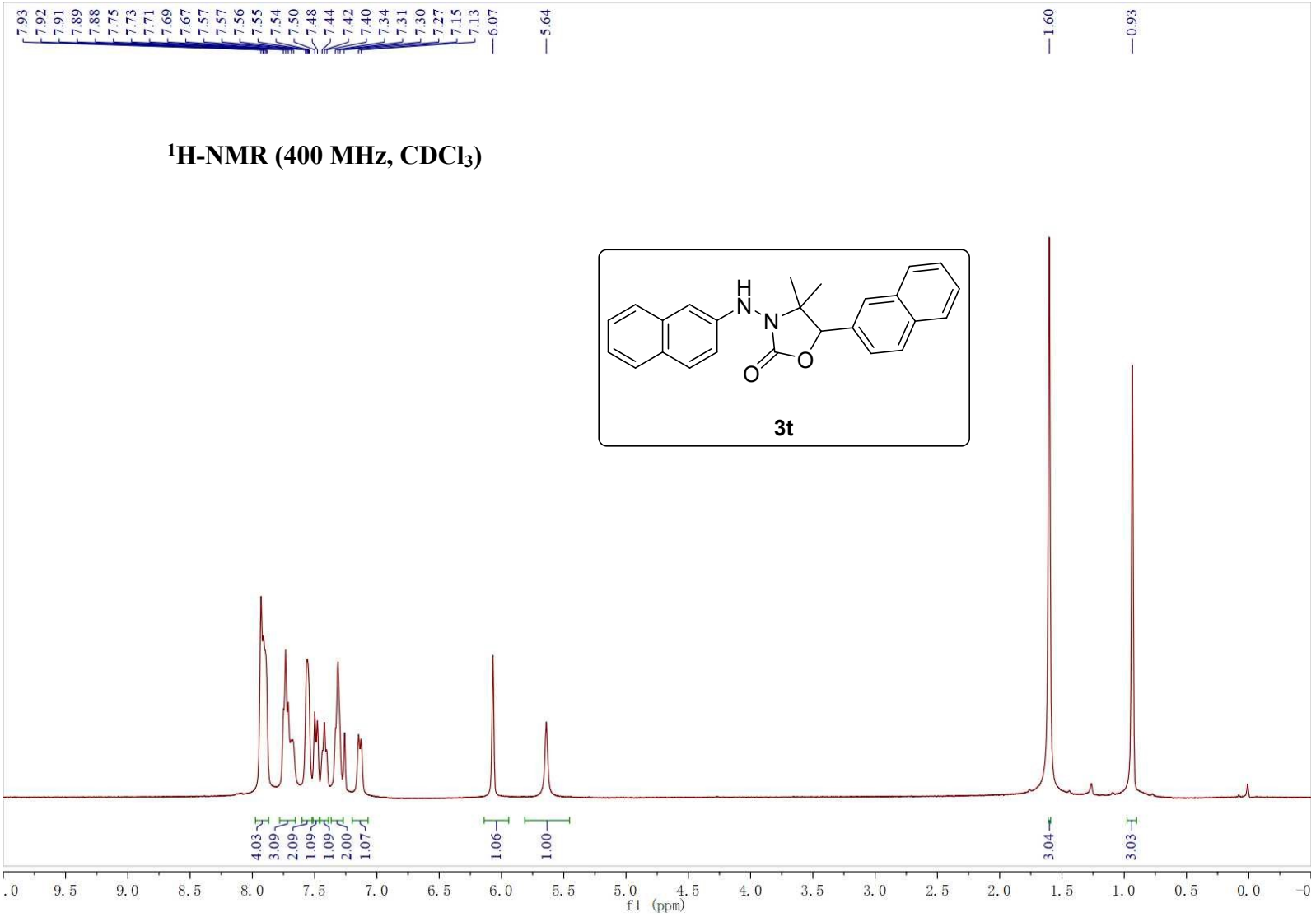
3r

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



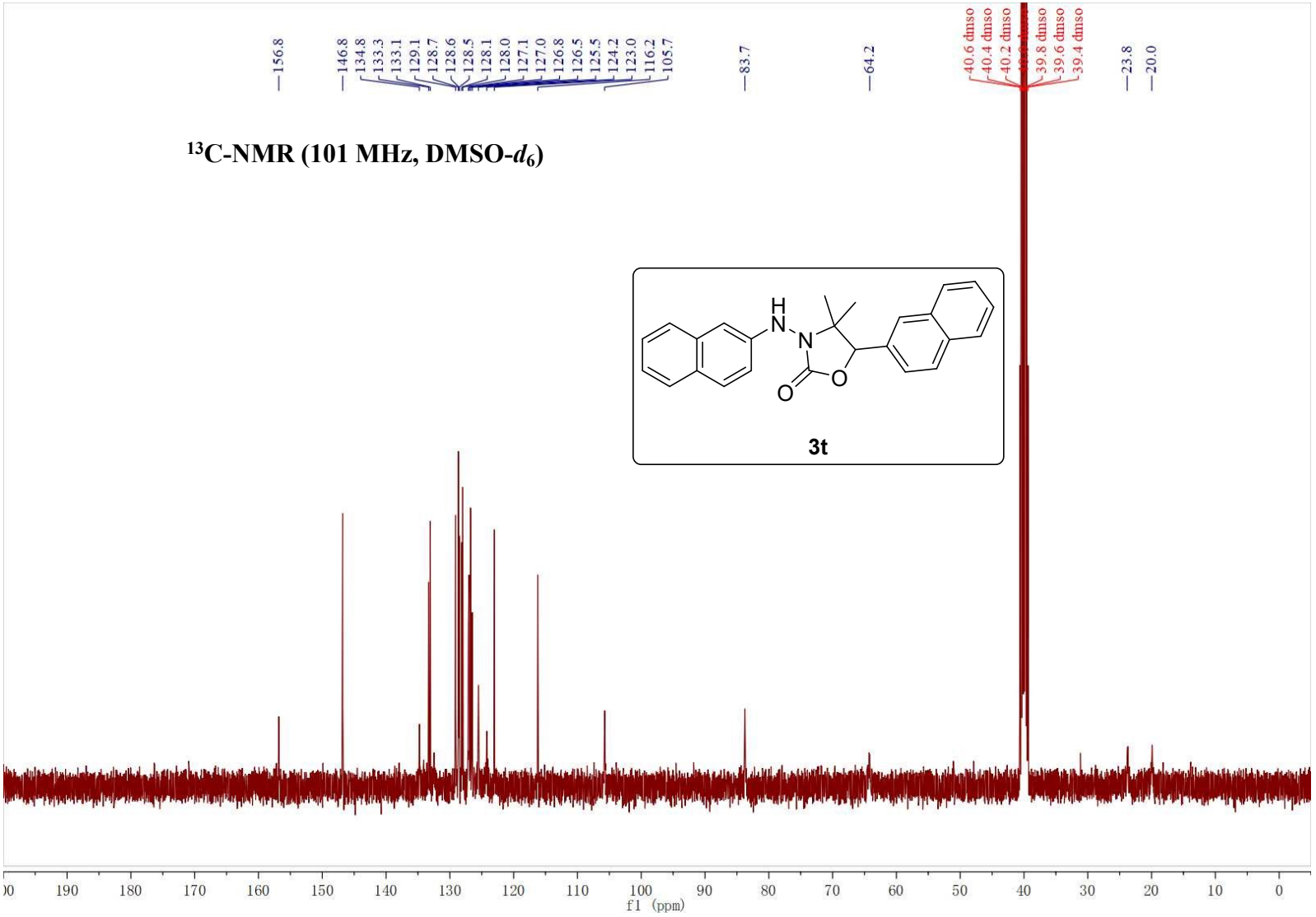
3s


158.2
145.8
134.3
129.4
129.1
127.7
126.6
126.4
123.4
116.0
107.8
89.2
77.3 cdcl3
77.0 cdcl3
76.7 cdcl3
66.4
28.4
26.9
26.8
23.9
21.0
20.3
13C-NMR (101 MHz, CDCl3)
H
N
N
O
O
3s
f1 (ppm)

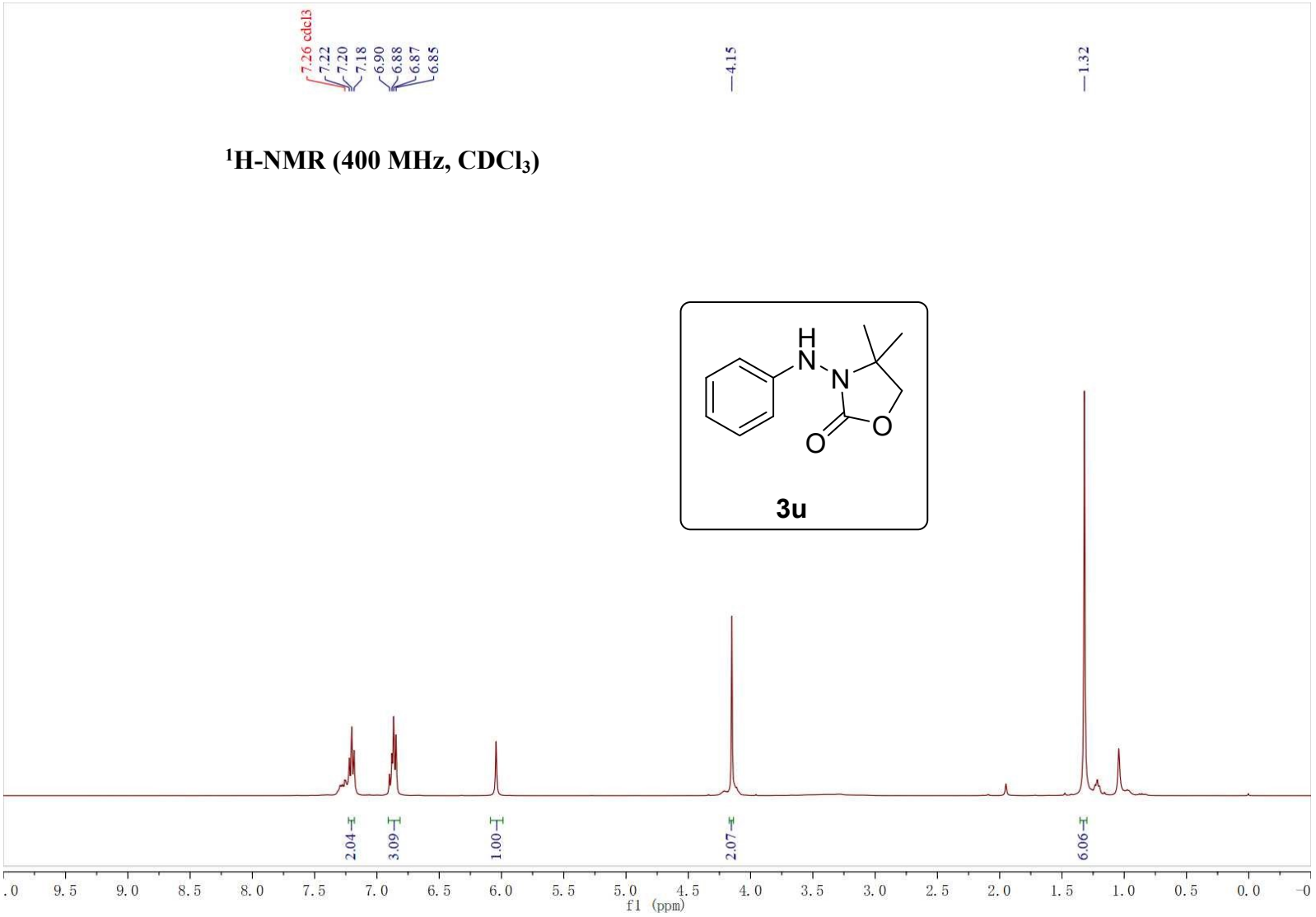


^{1}H-NMR (400 MHz, $CDCl_3$)

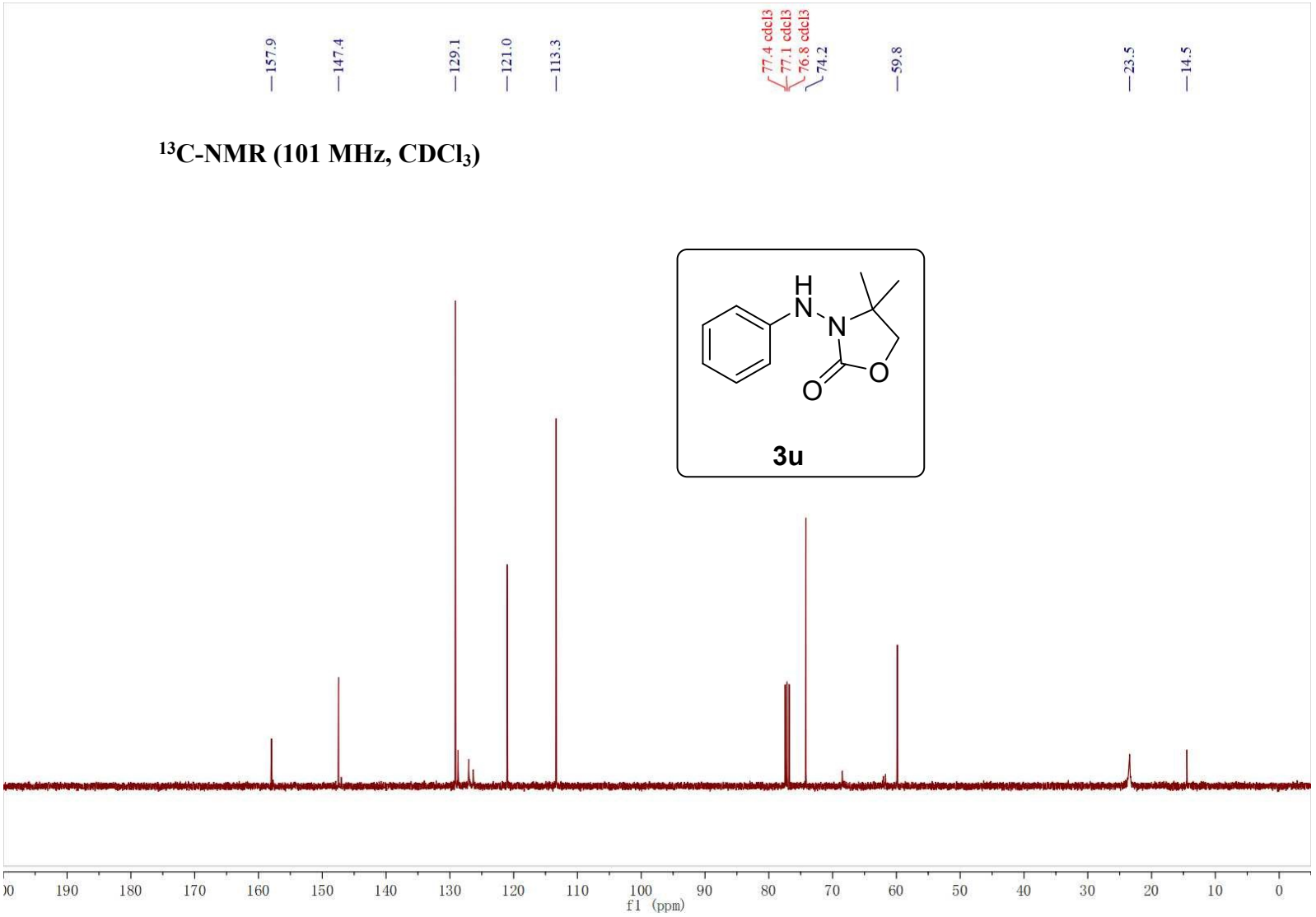
3t


156.8
146.8
134.8
133.3
133.1
129.1
128.7
128.6
128.5
128.1
128.0
127.1
127.0
126.8
126.5
125.5
124.2
123.0
116.2
105.7
83.7
64.2
40.6 dmso
40.4 dmso
40.2 dmso
39.8 dmso
39.6 dmso
39.4 dmso
23.8
20.0
13C-NMR (101 MHz, DMSO-d6)
H
N
N
O
O
3t
f1 (ppm)

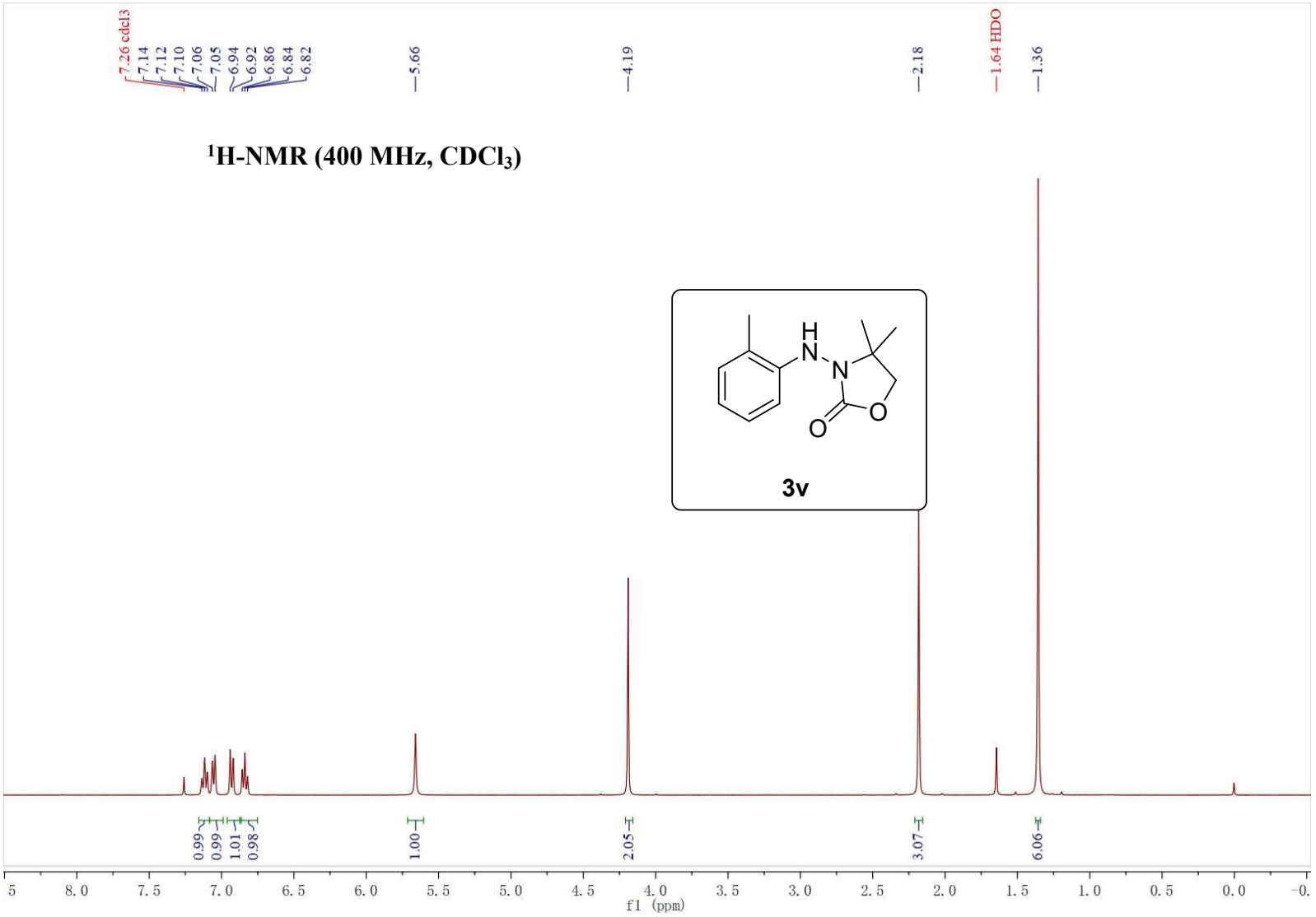
^{1}H-NMR (400 MHz, $CDCl_3$)



3u

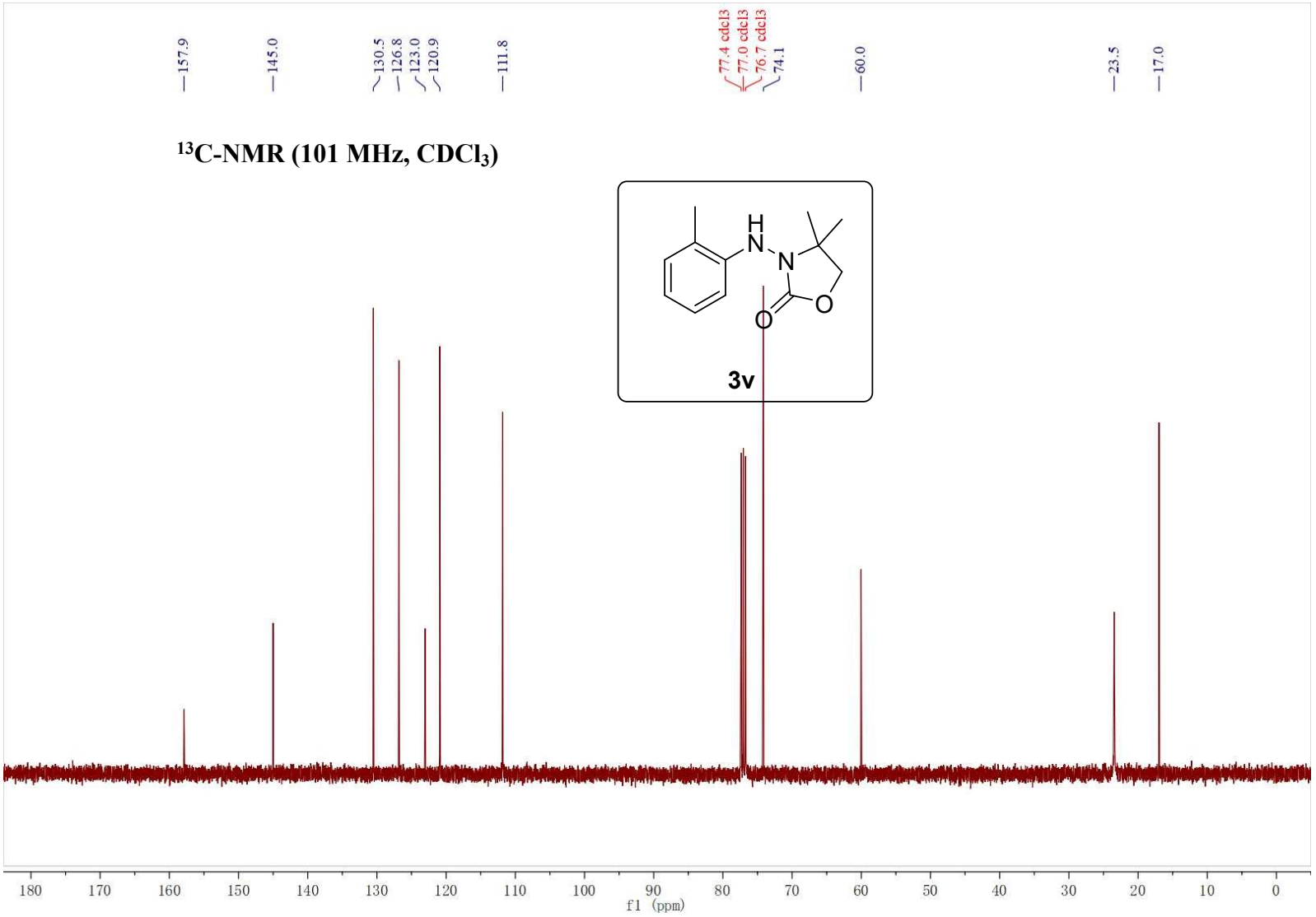


^{13}C-NMR (101 MHz, $CDCl_3$)

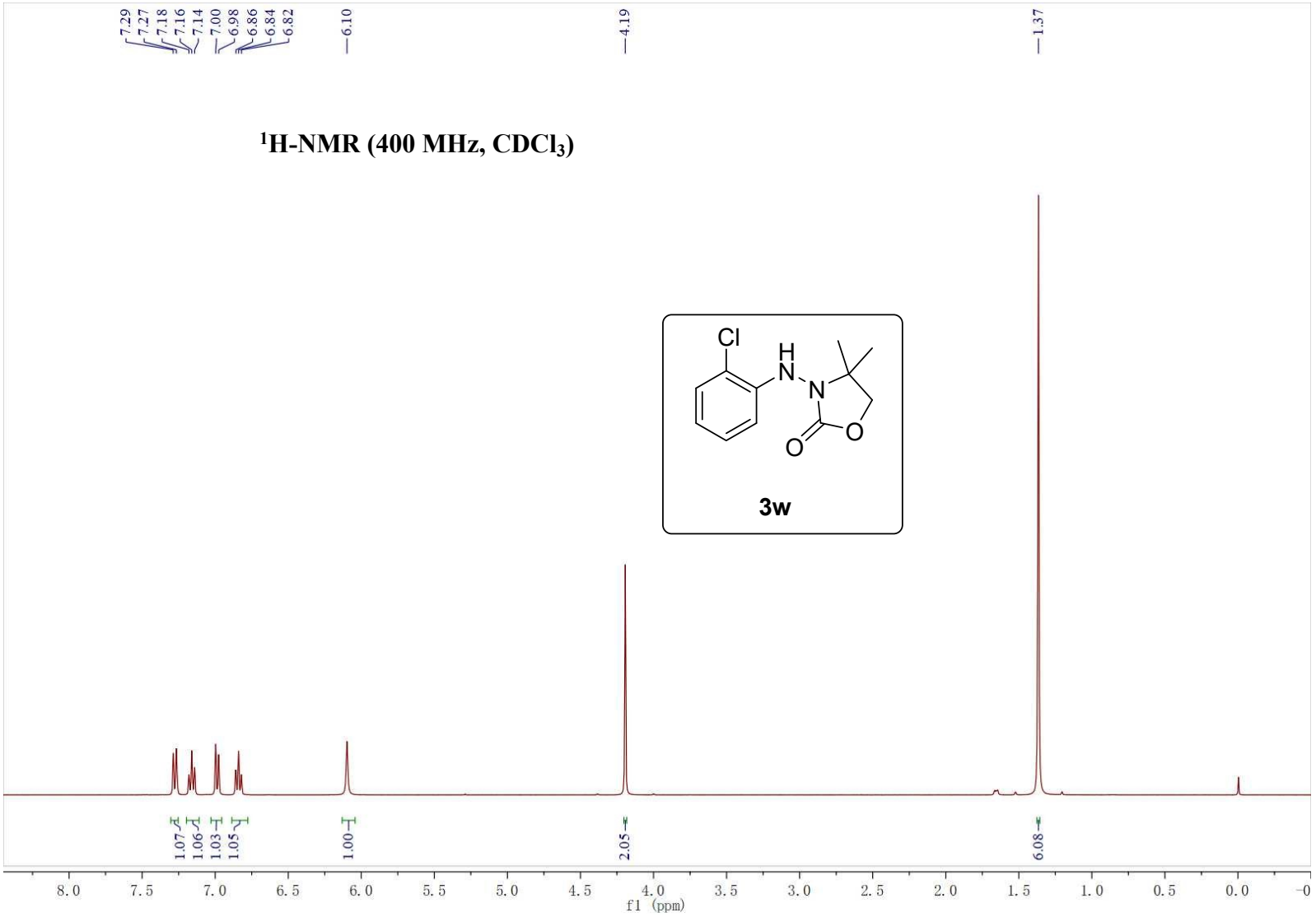


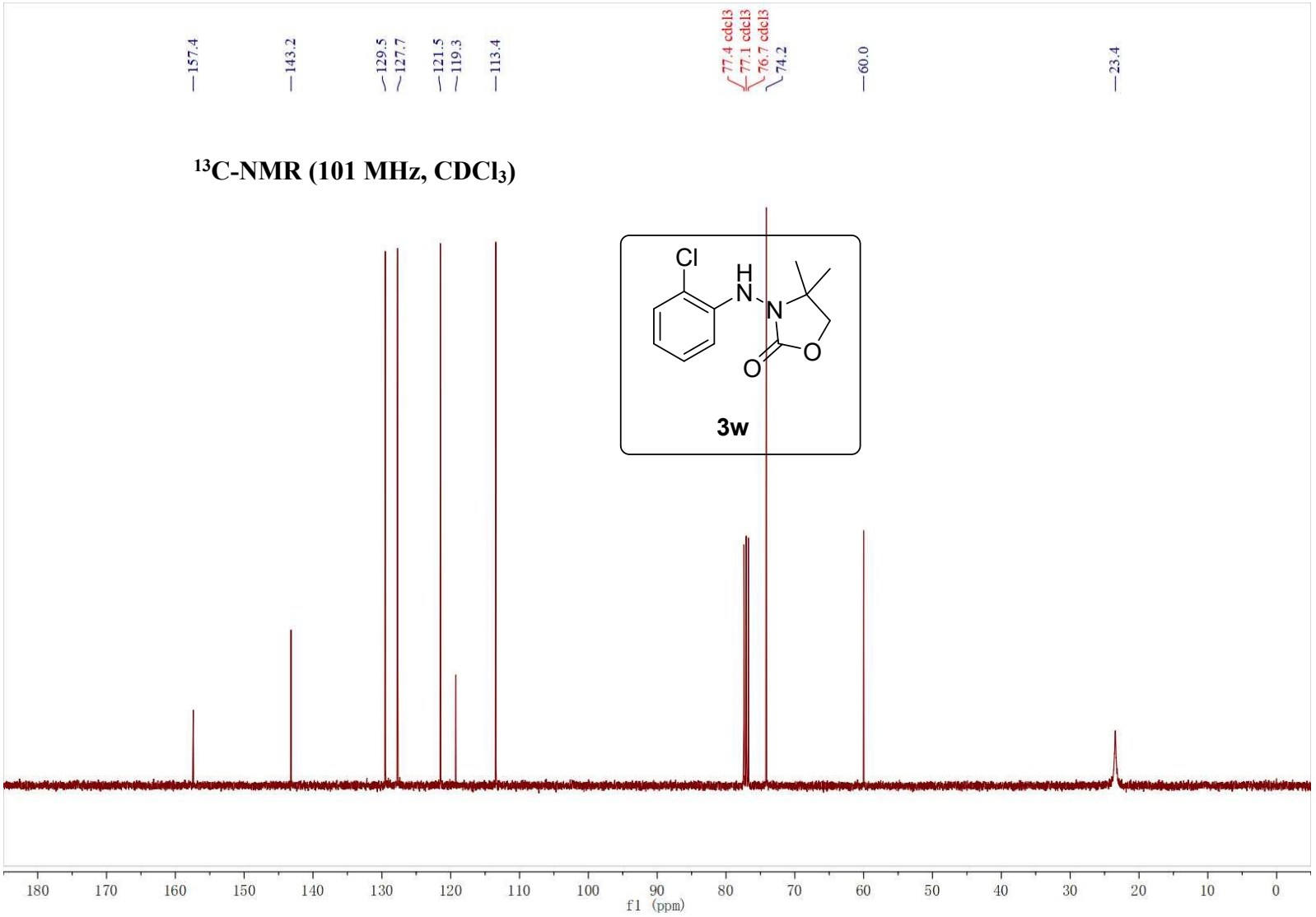
^{1}H-NMR (400 MHz, $CDCl_3$)

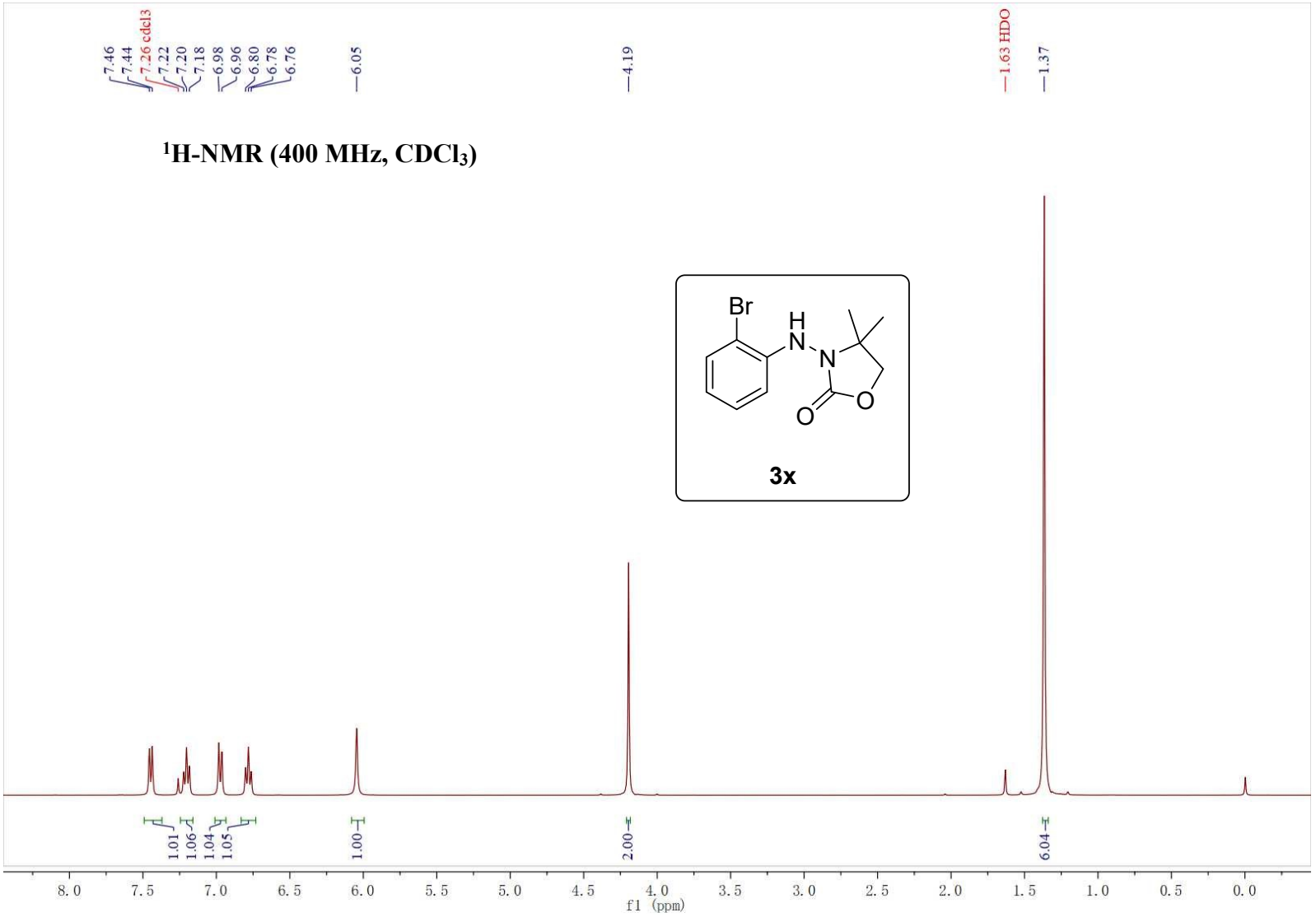
3v


157.9
145.0
130.5
126.8
123.0
120.9
111.8
77.4 cdcl3
77.0 cdcl3
76.7 cdcl3
74.1
60.0
23.5
17.0
13C-NMR (101 MHz, CDCl3)
H
N
N
O
O
O
3v
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

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

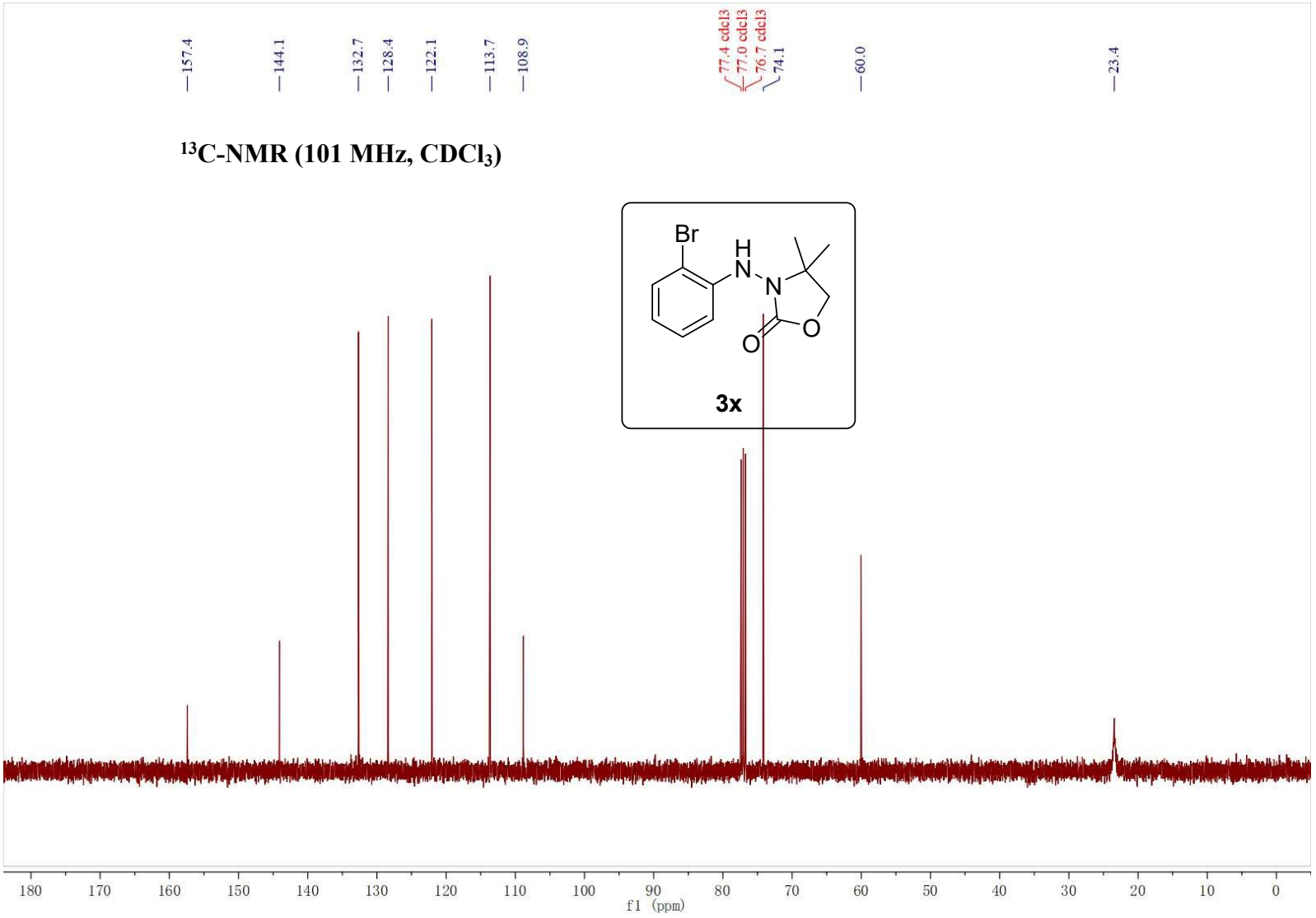



157.4
143.2
129.5
127.7
121.5
119.3
113.4
77.4 cdcl3
77.1 cdcl3
76.7 cdcl3
74.2
60.0
23.4
13C-NMR (101 MHz, CDCl3)
Cl
H
N
N
O
O
3w
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

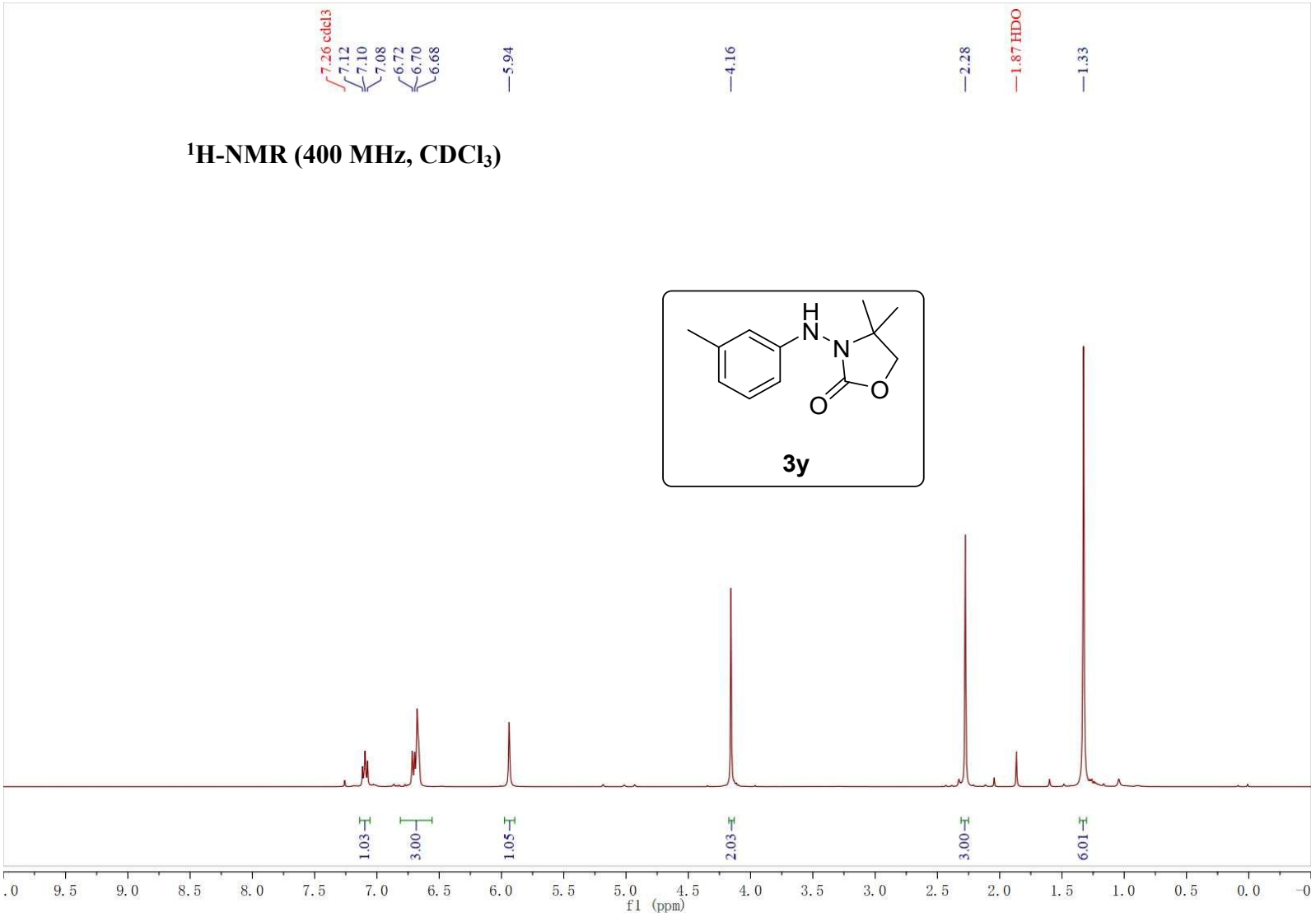


^{1}H-NMR (400 MHz, $CDCl_3$)

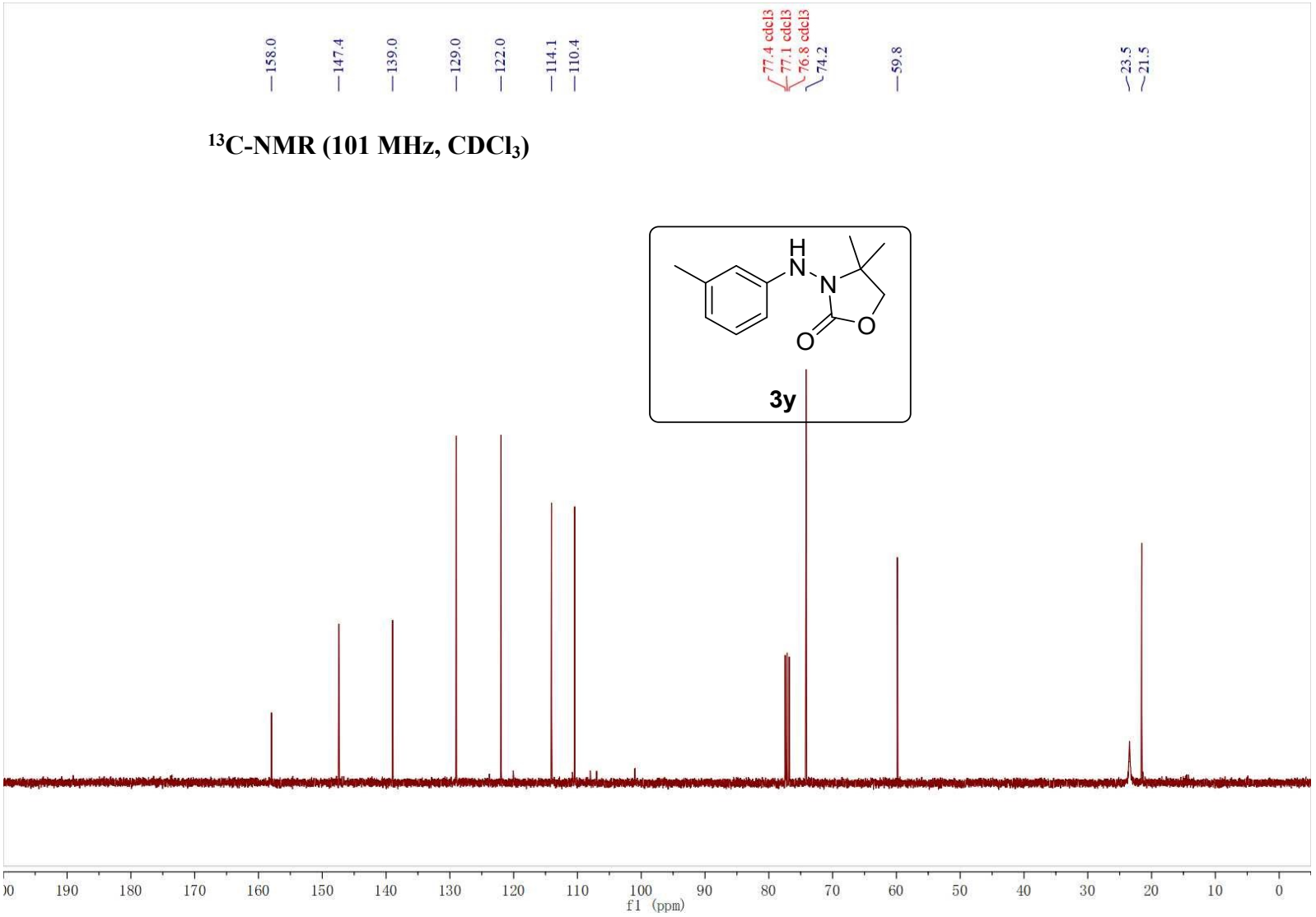
3x


157.4
144.1
132.7
128.4
122.1
113.7
108.9
77.4 cdcl3
77.0 cdcl3
76.7 cdcl3
74.1
60.0
23.4
13C-NMR (101 MHz, CDCl3)
Br
H
N
N
O
O
3x
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

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

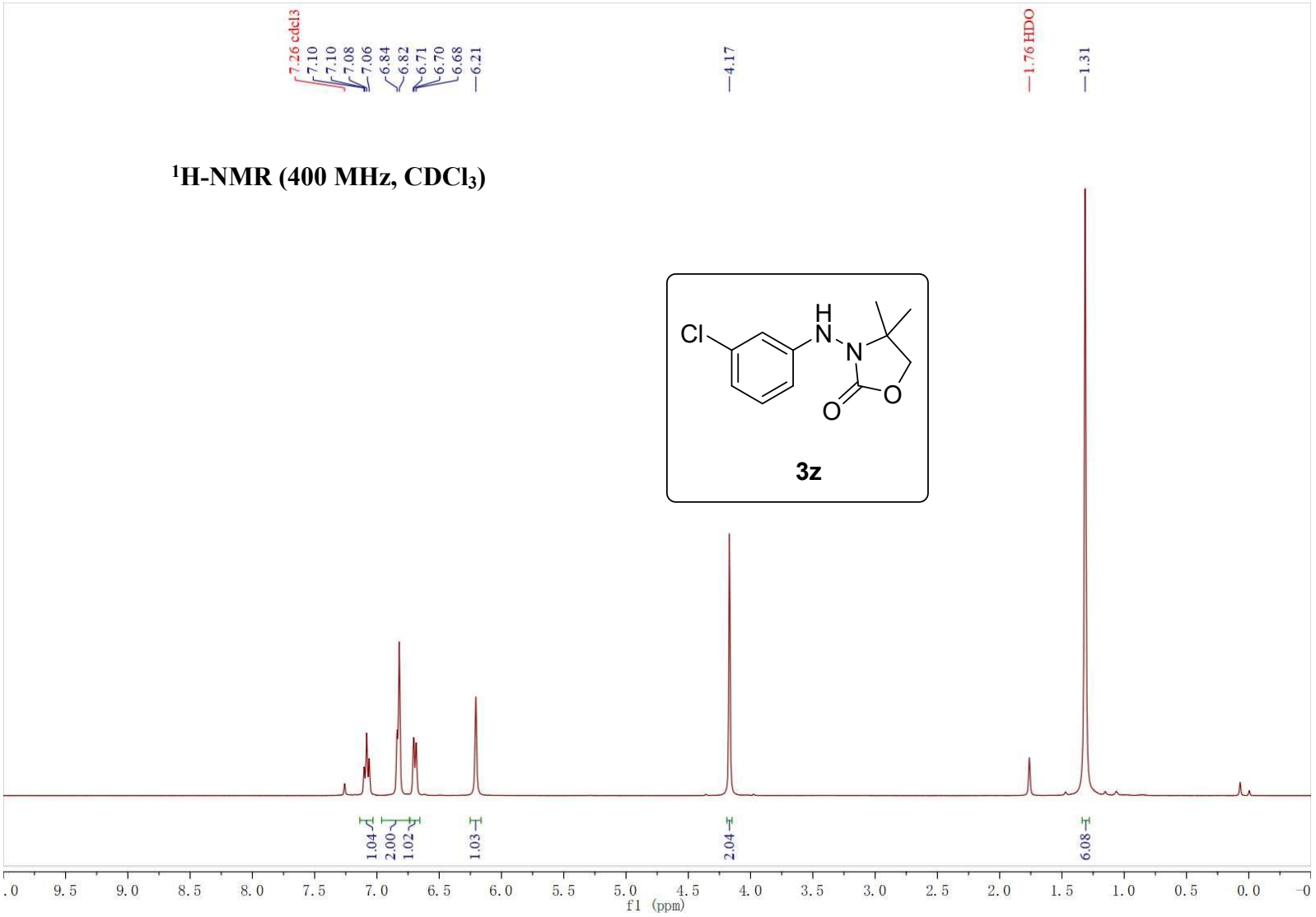


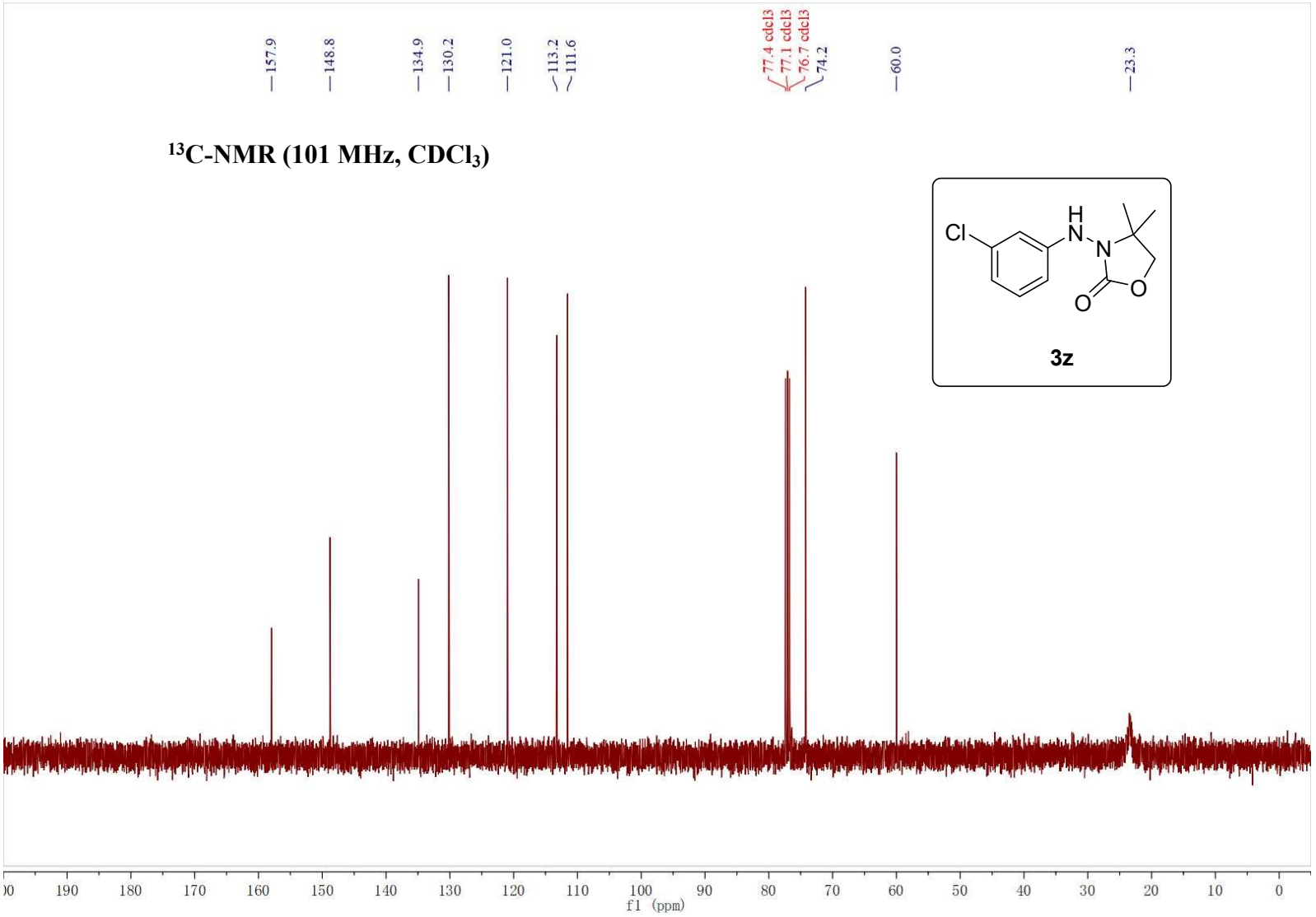
3y



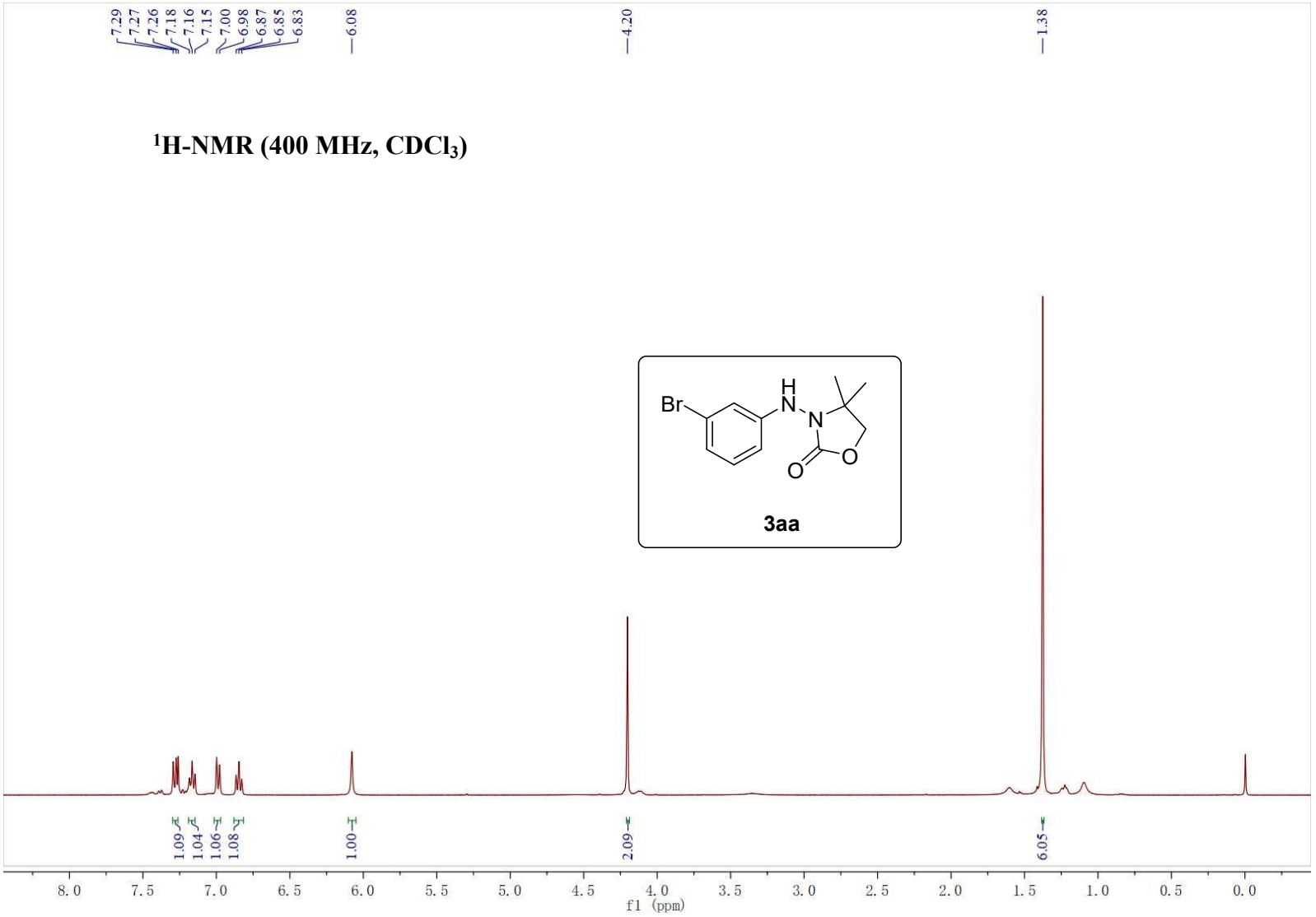
^{13}C-NMR (101 MHz, $CDCl_3$)

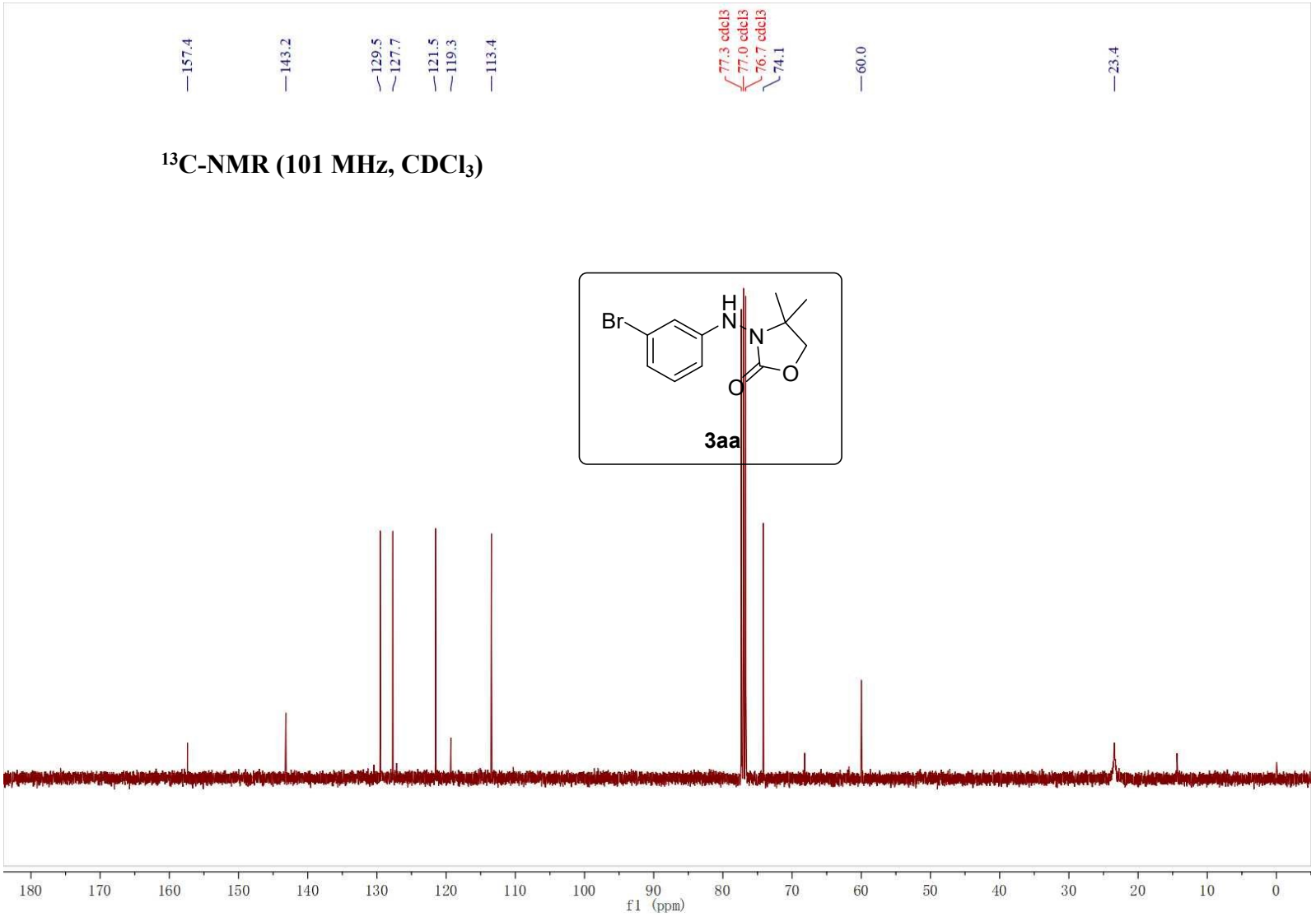
^{1}H-NMR (400 MHz, $CDCl_3$)



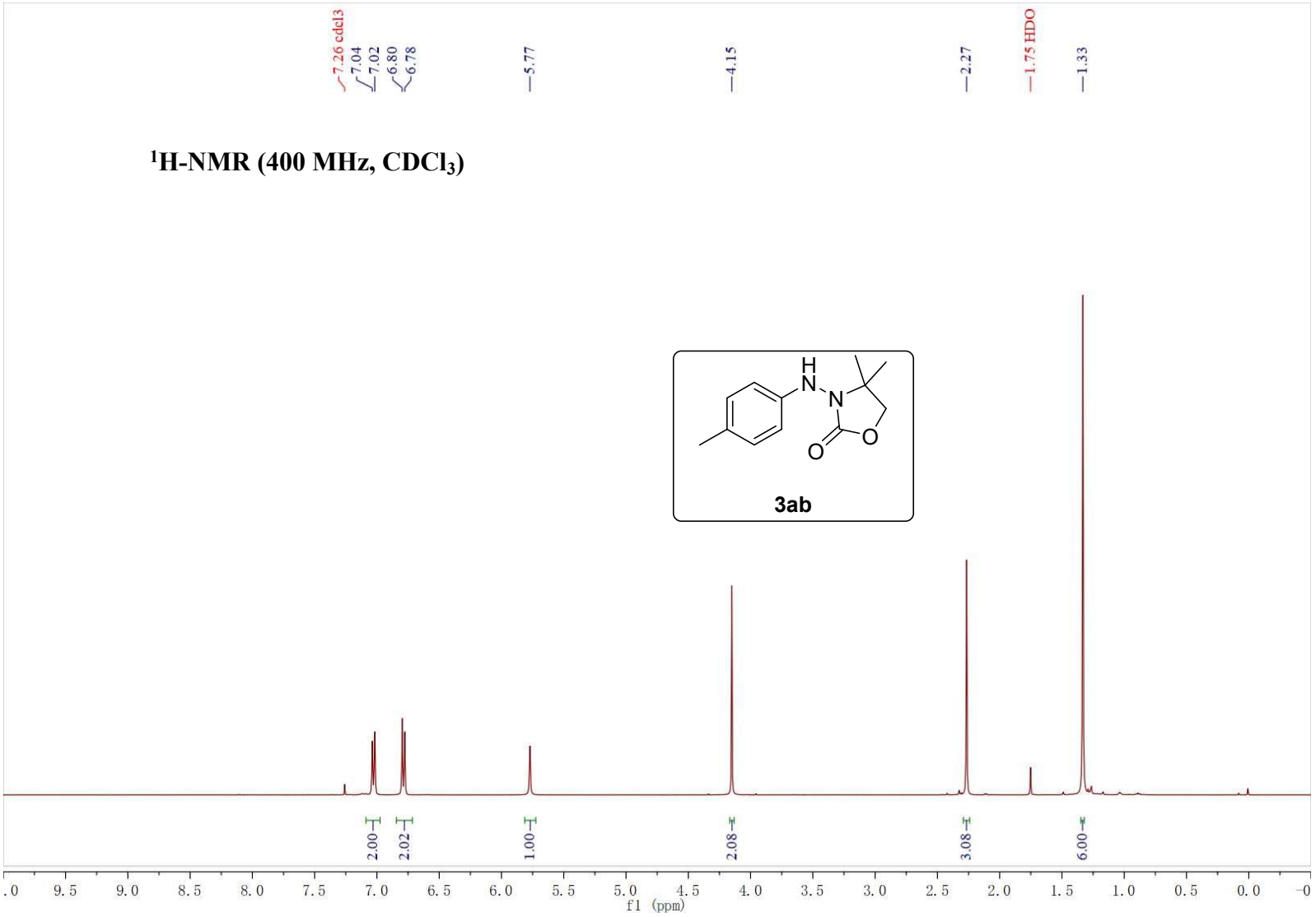

157.9
148.8
134.9
130.2
121.0
113.2
111.6
77.4 cdcl3
77.1 cdcl3
76.7 cdcl3
74.2
60.0
23.3
13C-NMR (101 MHz, CDCl3)
Cl
H
N
N
O
O
3z
f1 (ppm)

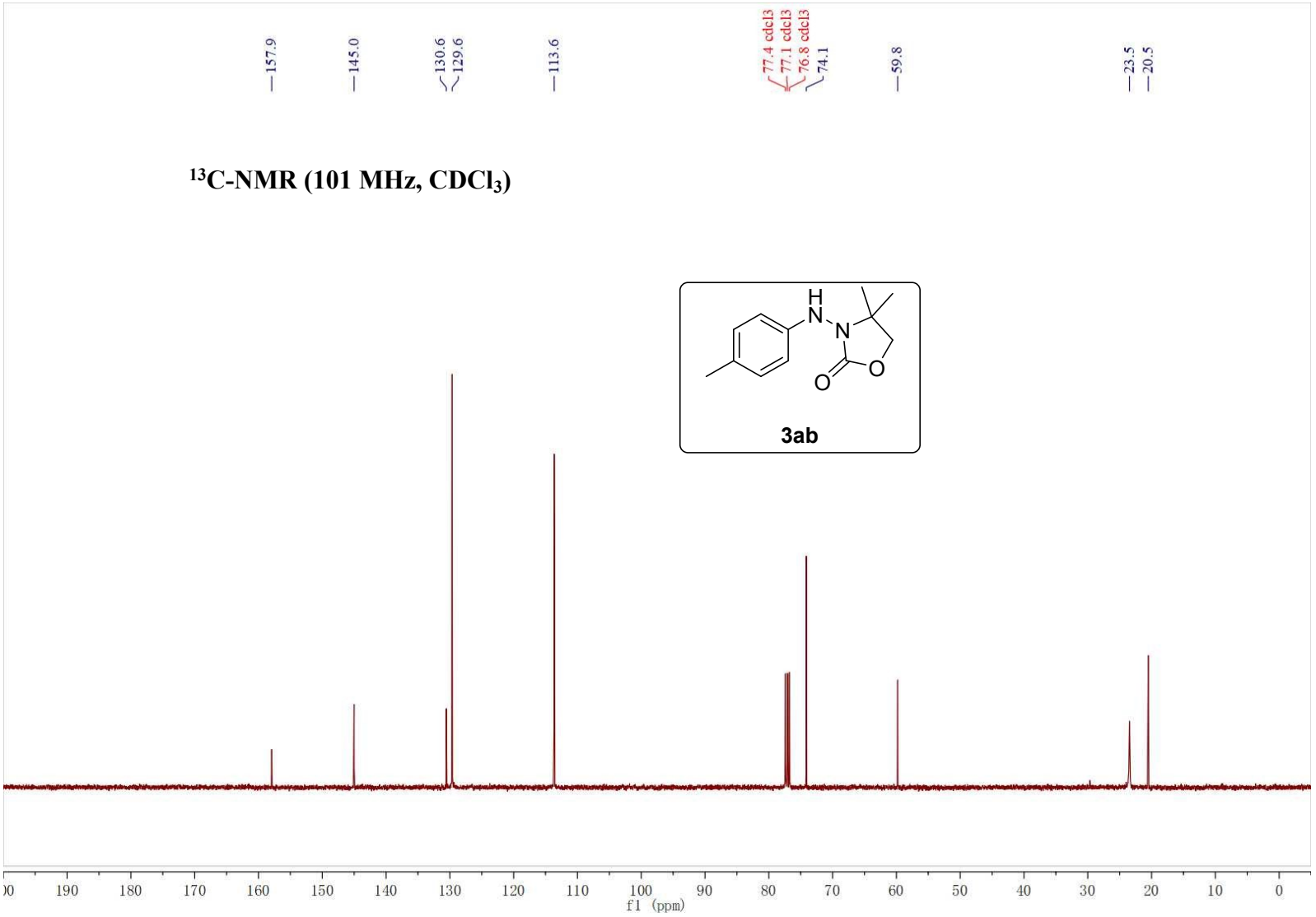
^{1}H-NMR (400 MHz, $CDCl_3$)




157.4
143.2
129.5
127.7
121.5
119.3
113.4
77.3 cdcl3
77.0 cdcl3
76.7 cdcl3
74.1
60.0
23.4
13C-NMR (101 MHz, CDCl3)
Br
H
N
N
O
O
3aa
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

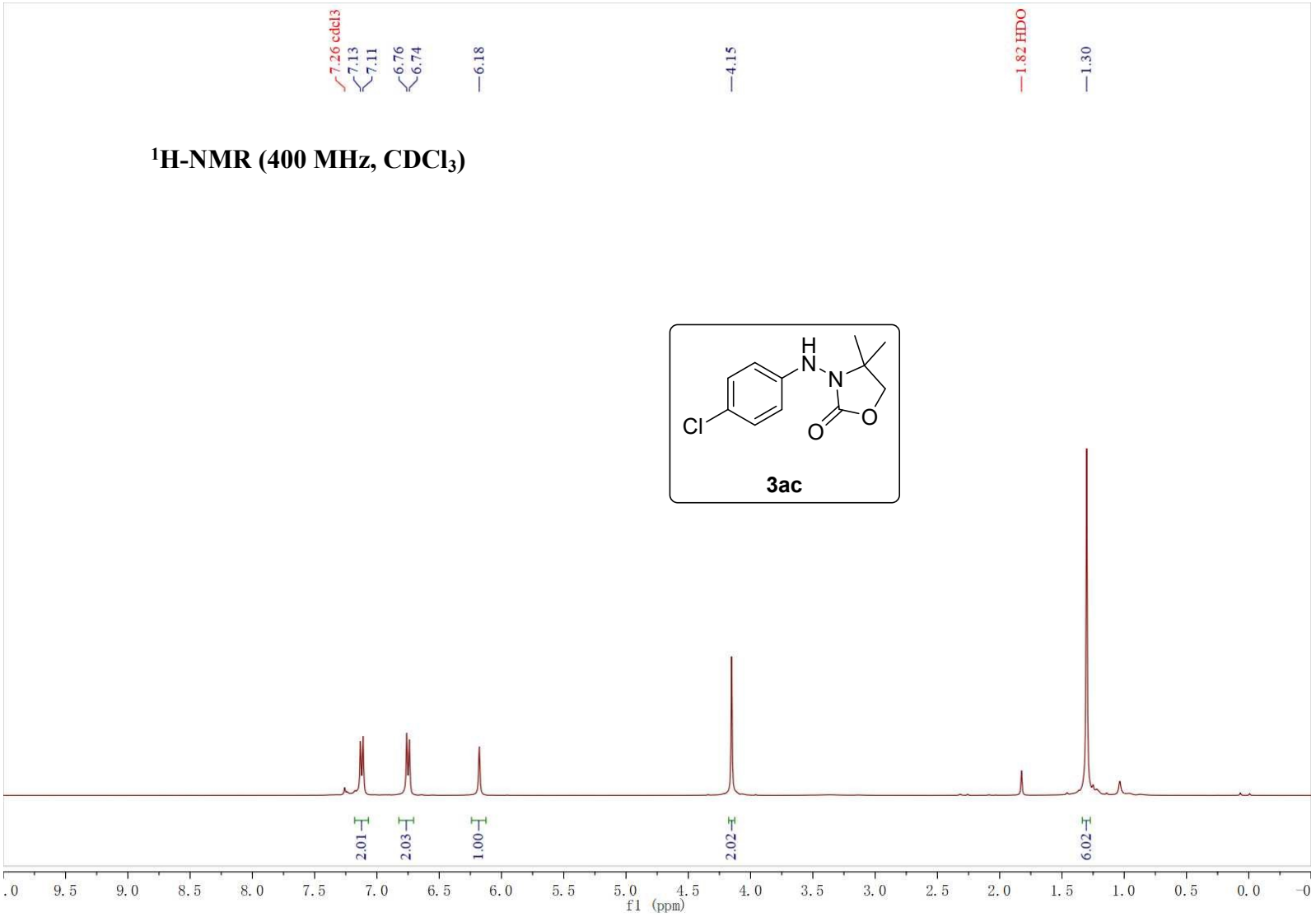
^{1}H-NMR (400 MHz, $CDCl_3$)



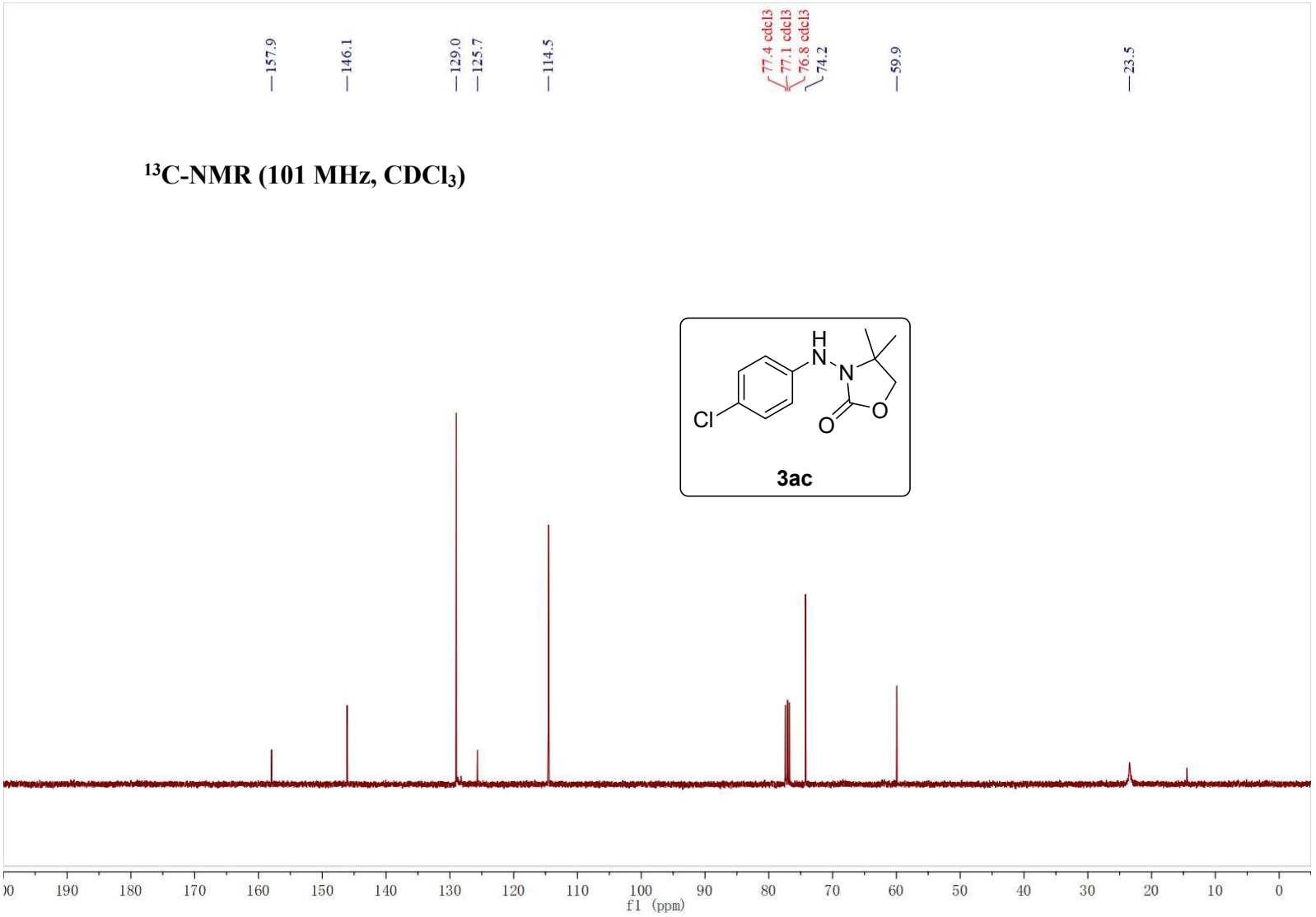


^{13}C-NMR (101 MHz, $CDCl_3$)

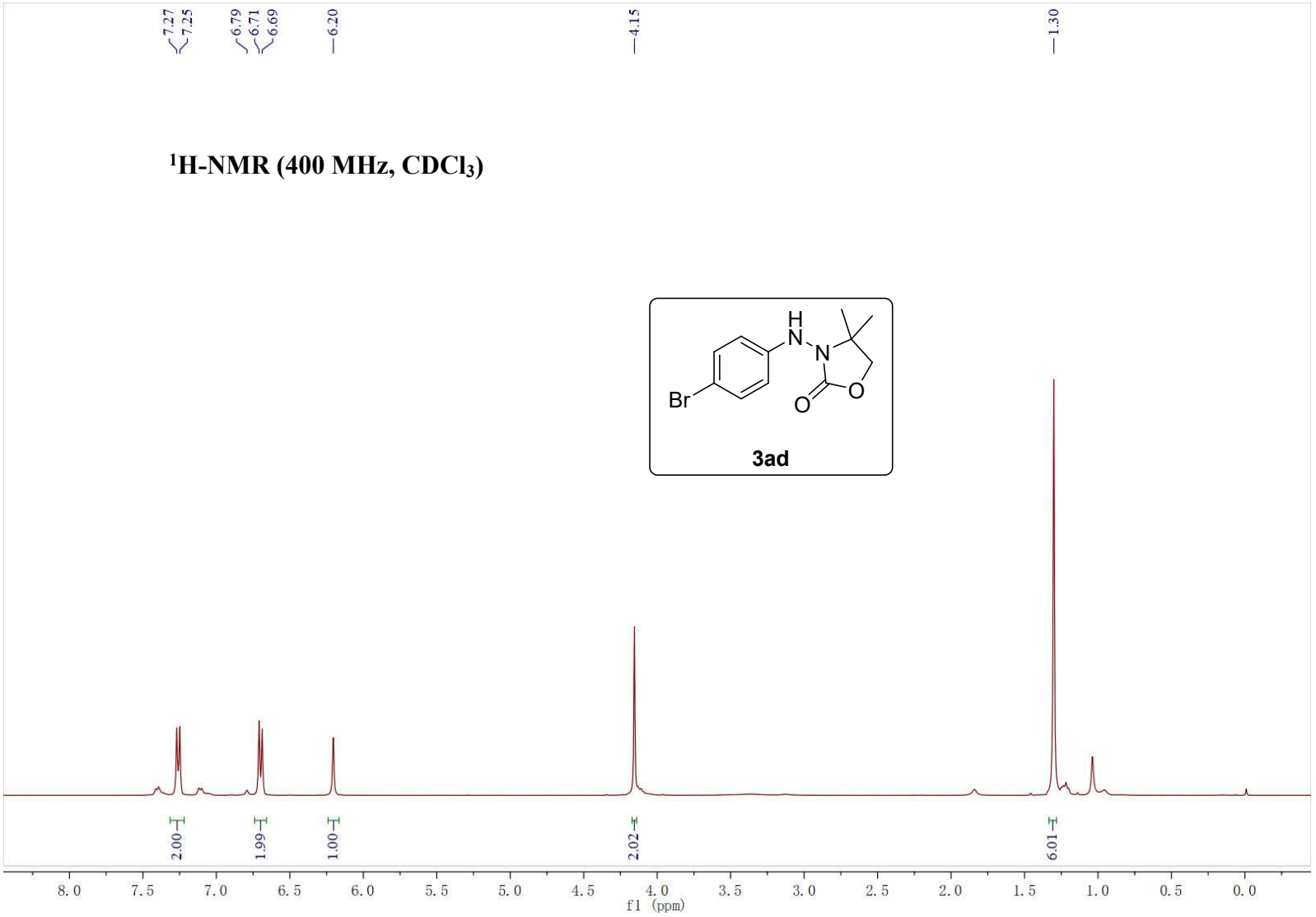
^{1}H-NMR (400 MHz, $CDCl_3$)



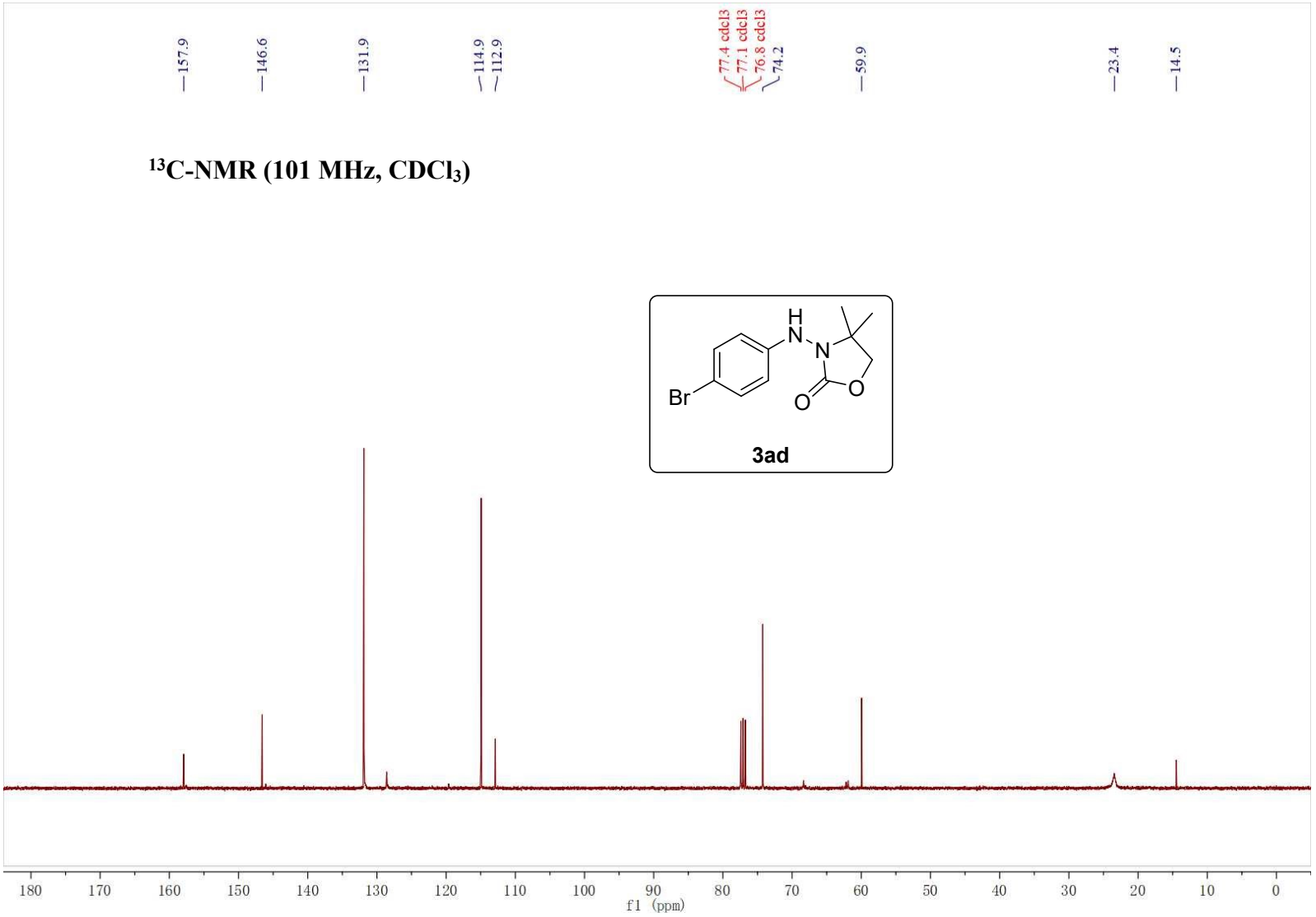
^{13}C-NMR (101 MHz, $CDCl_3$)



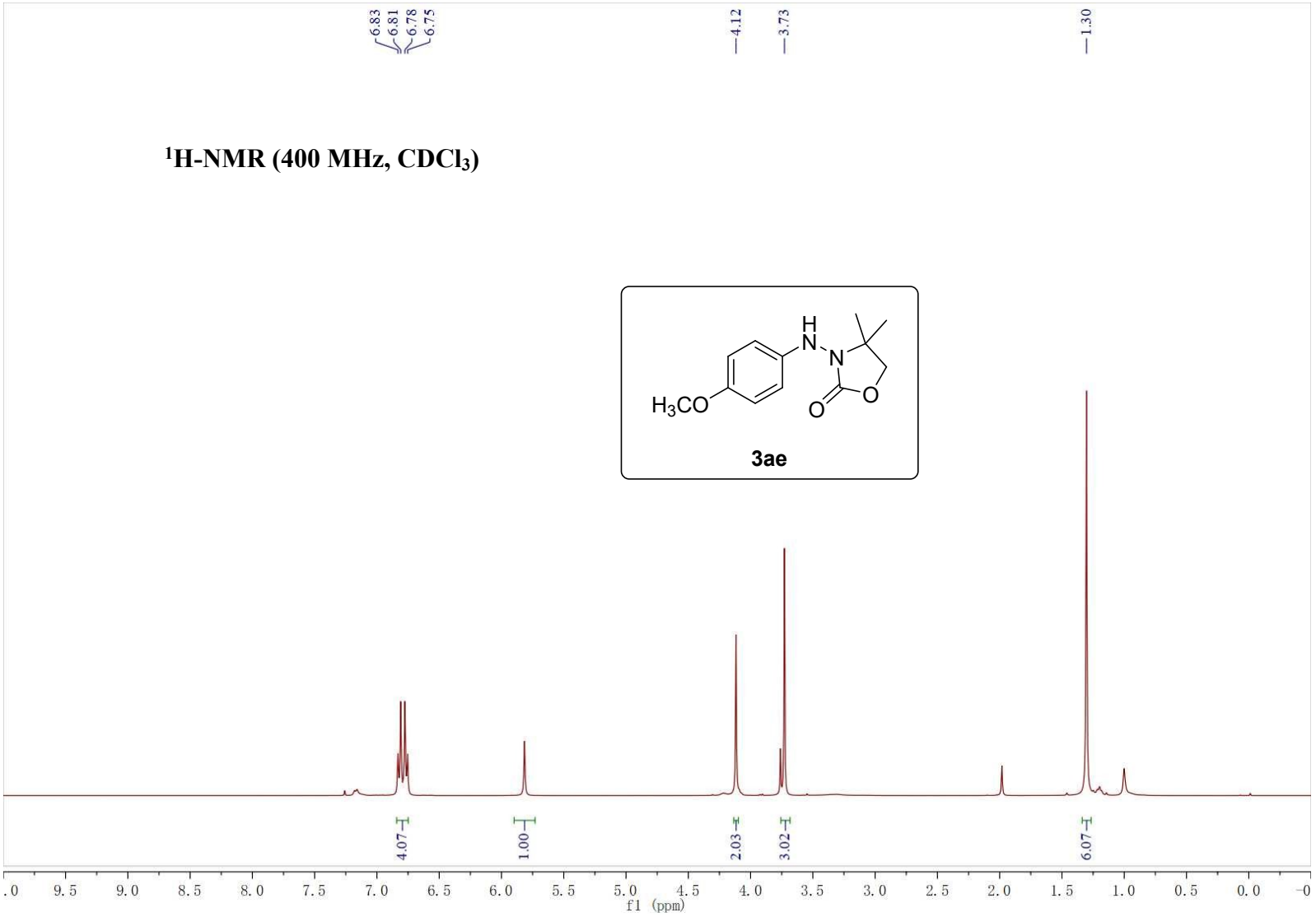
^{1}H-NMR (400 MHz, $CDCl_3$)



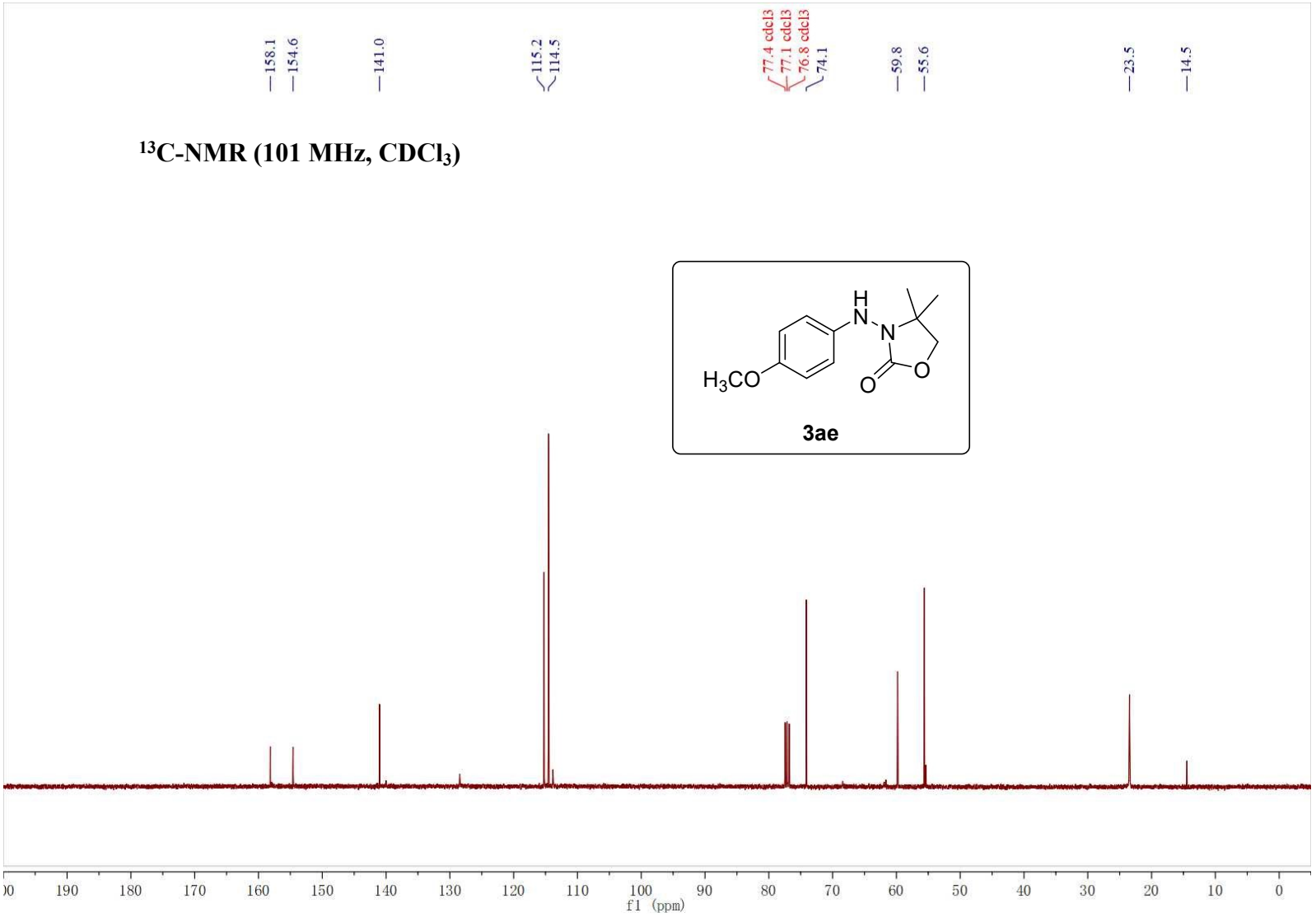
^{13}C-NMR (101 MHz, $CDCl_3$)



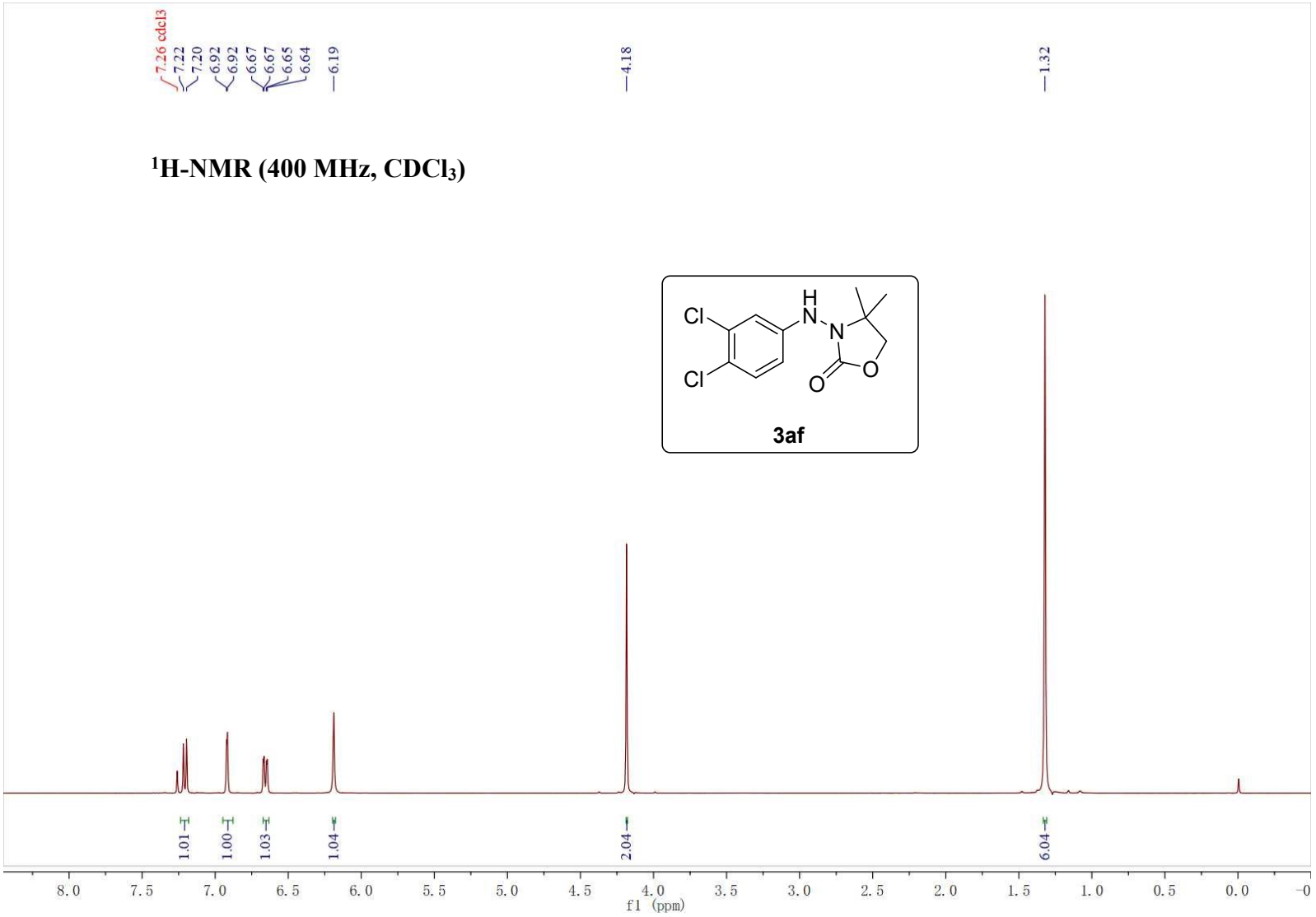
^{1}H-NMR (400 MHz, $CDCl_3$)

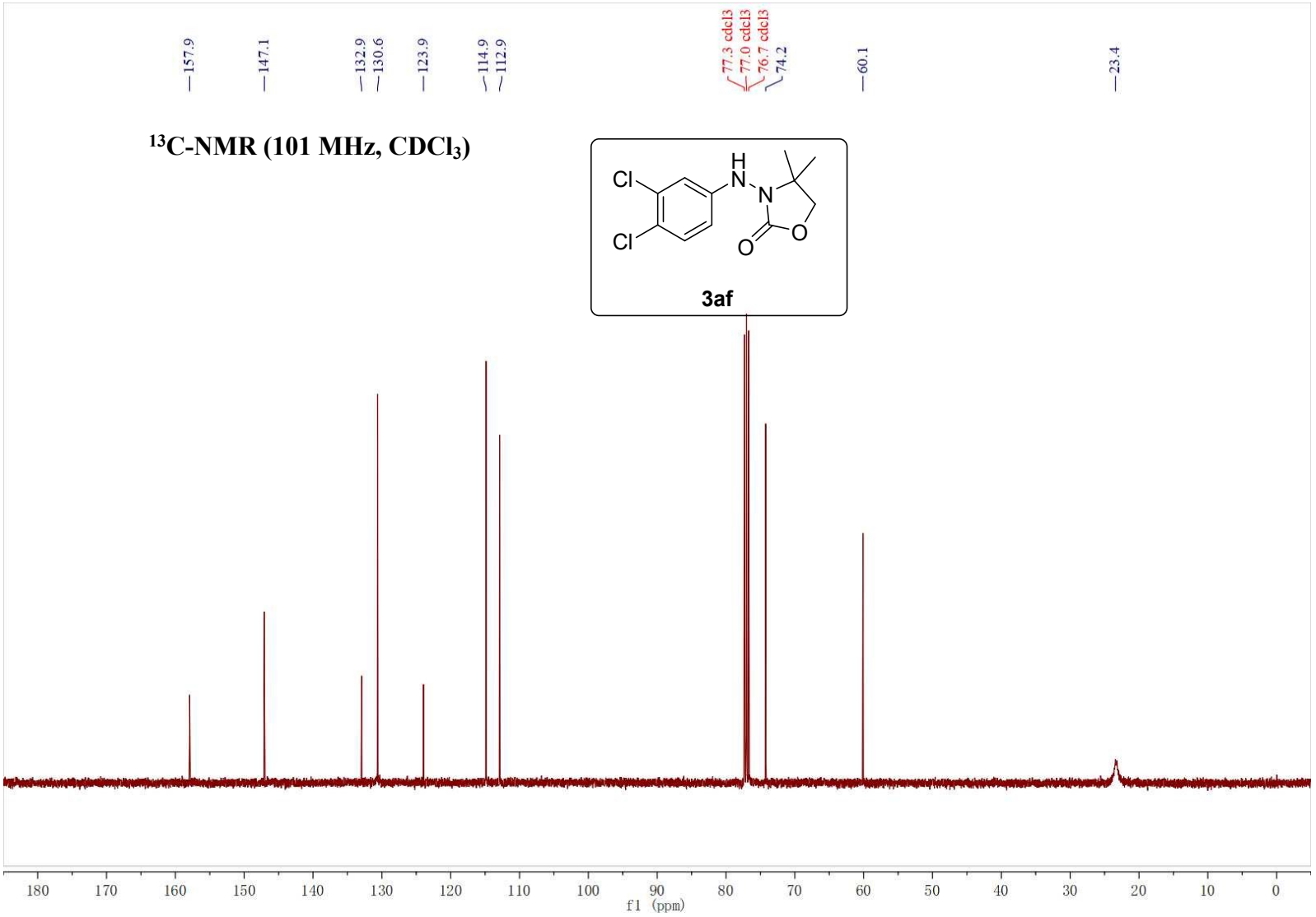


^{13}C-NMR (101 MHz, $CDCl_3$)

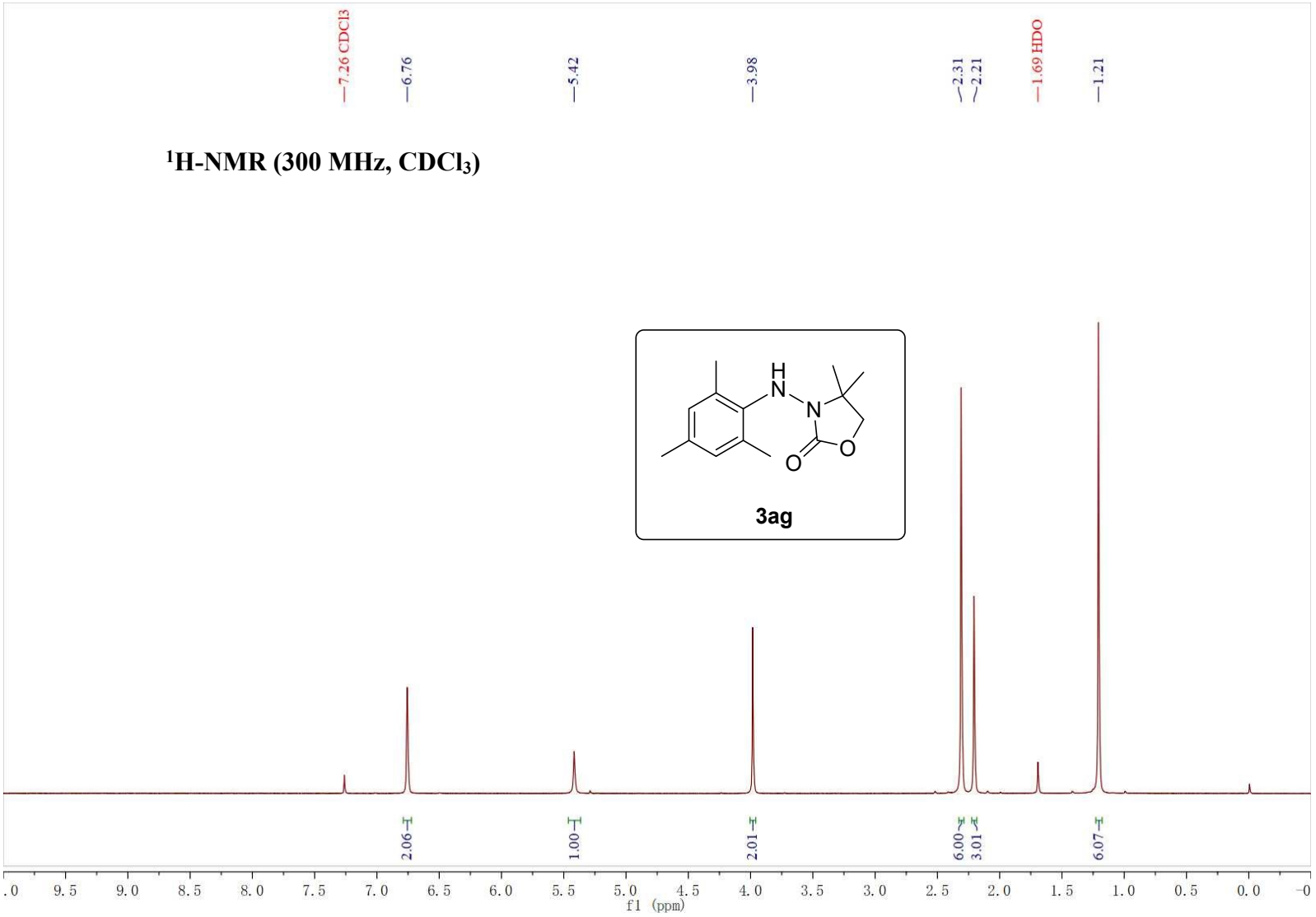


^{1}H-NMR (400 MHz, $CDCl_3$)

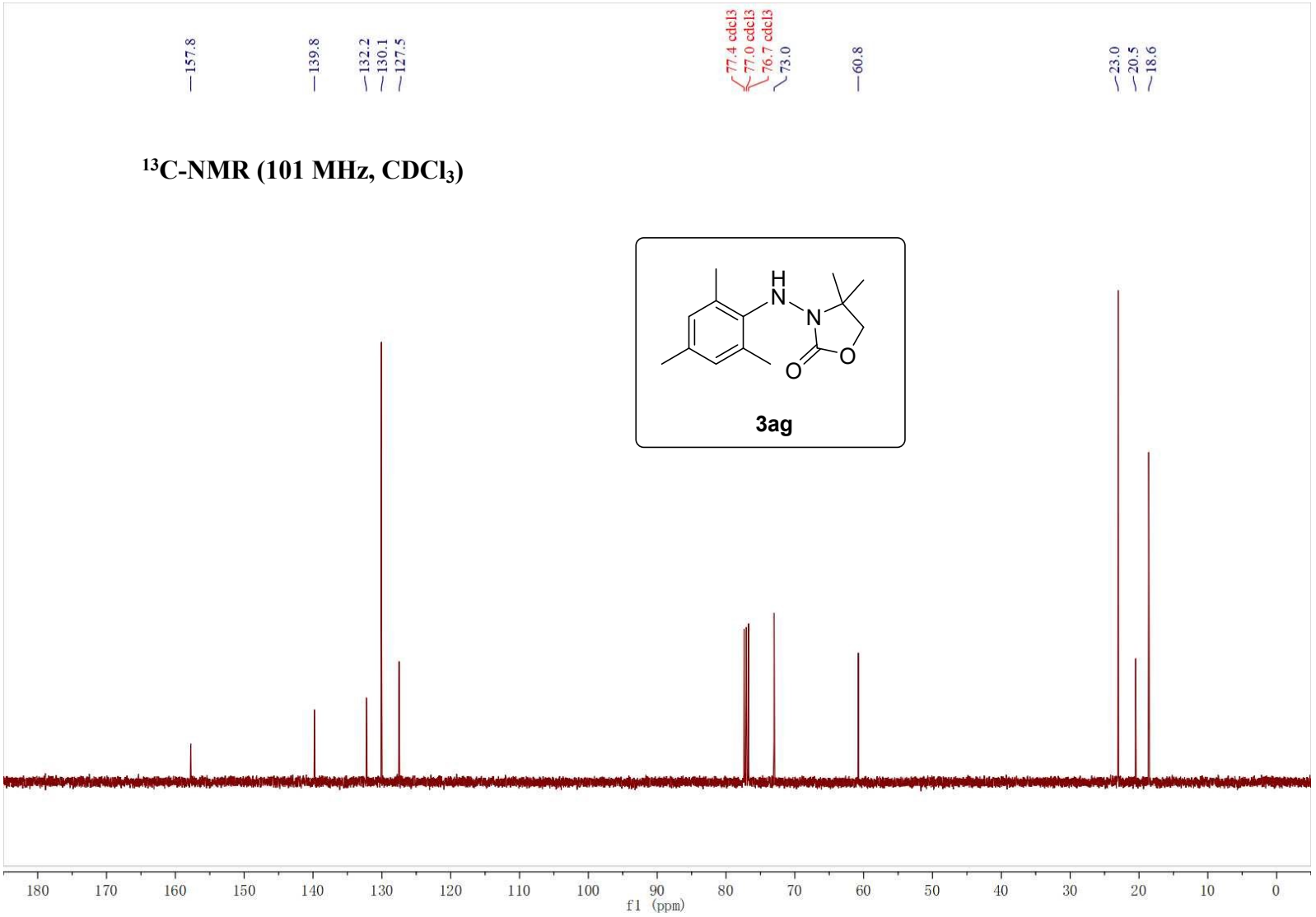



157.9
147.1
132.9
130.6
123.9
114.9
112.9
77.3 cdcl3
77.0 cdcl3
76.7 cdcl3
74.2
60.1
23.4
13C-NMR (101 MHz, CDCl3)
Cl
Cl
H
N
N
O
O
3af
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

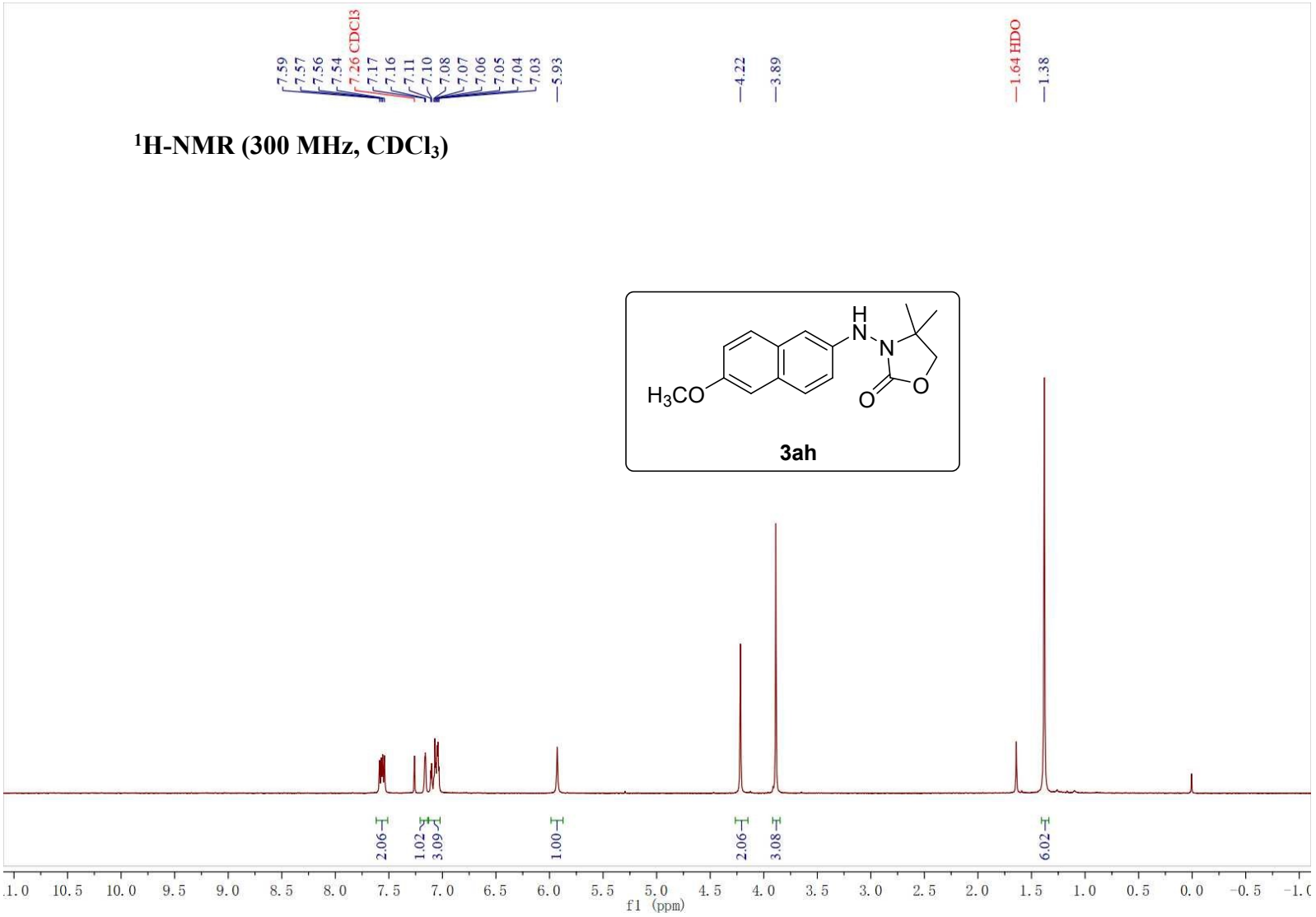
^{1}H-NMR (300 MHz, $CDCl_3$)

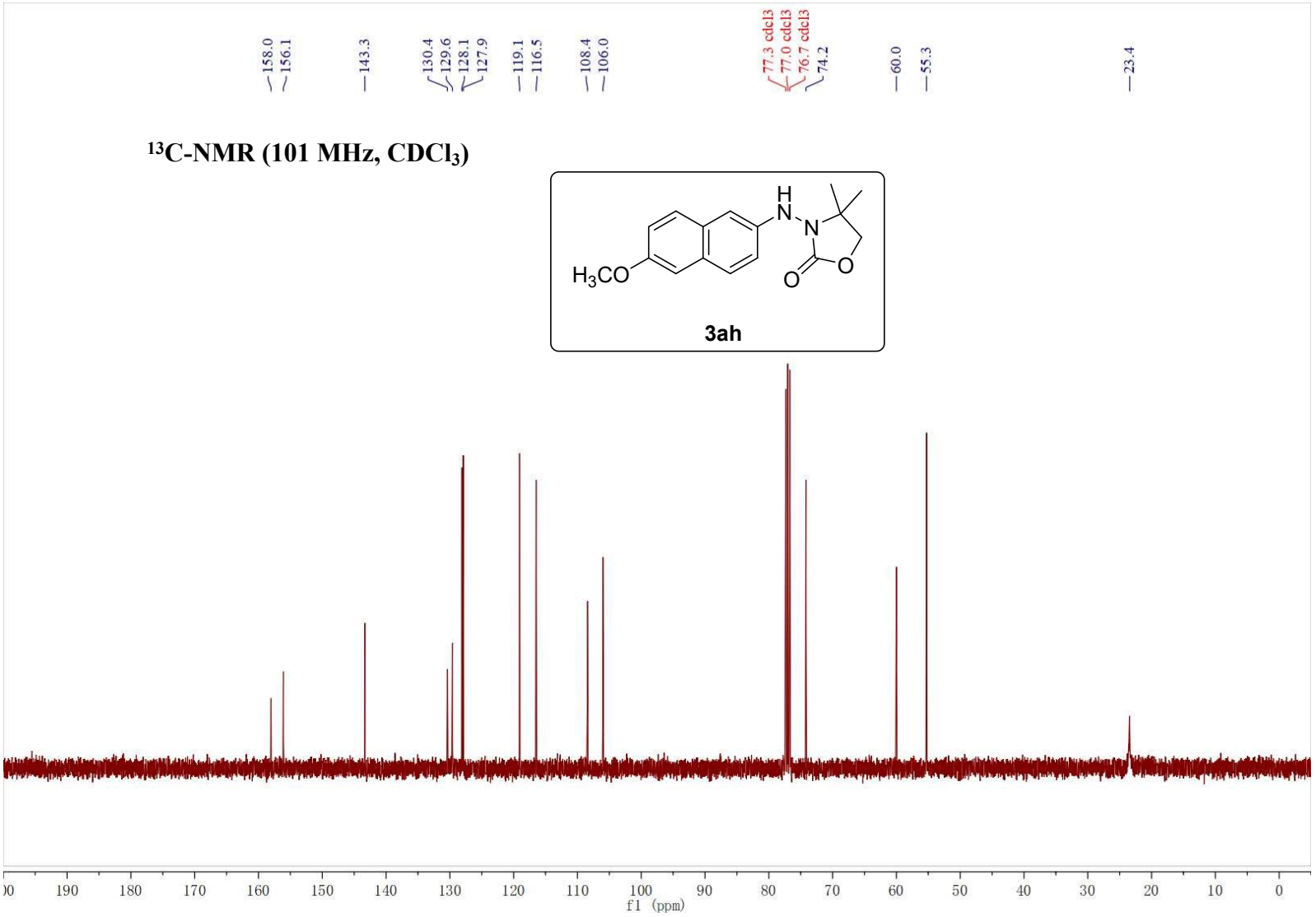


^{13}C-NMR (101 MHz, $CDCl_3$)



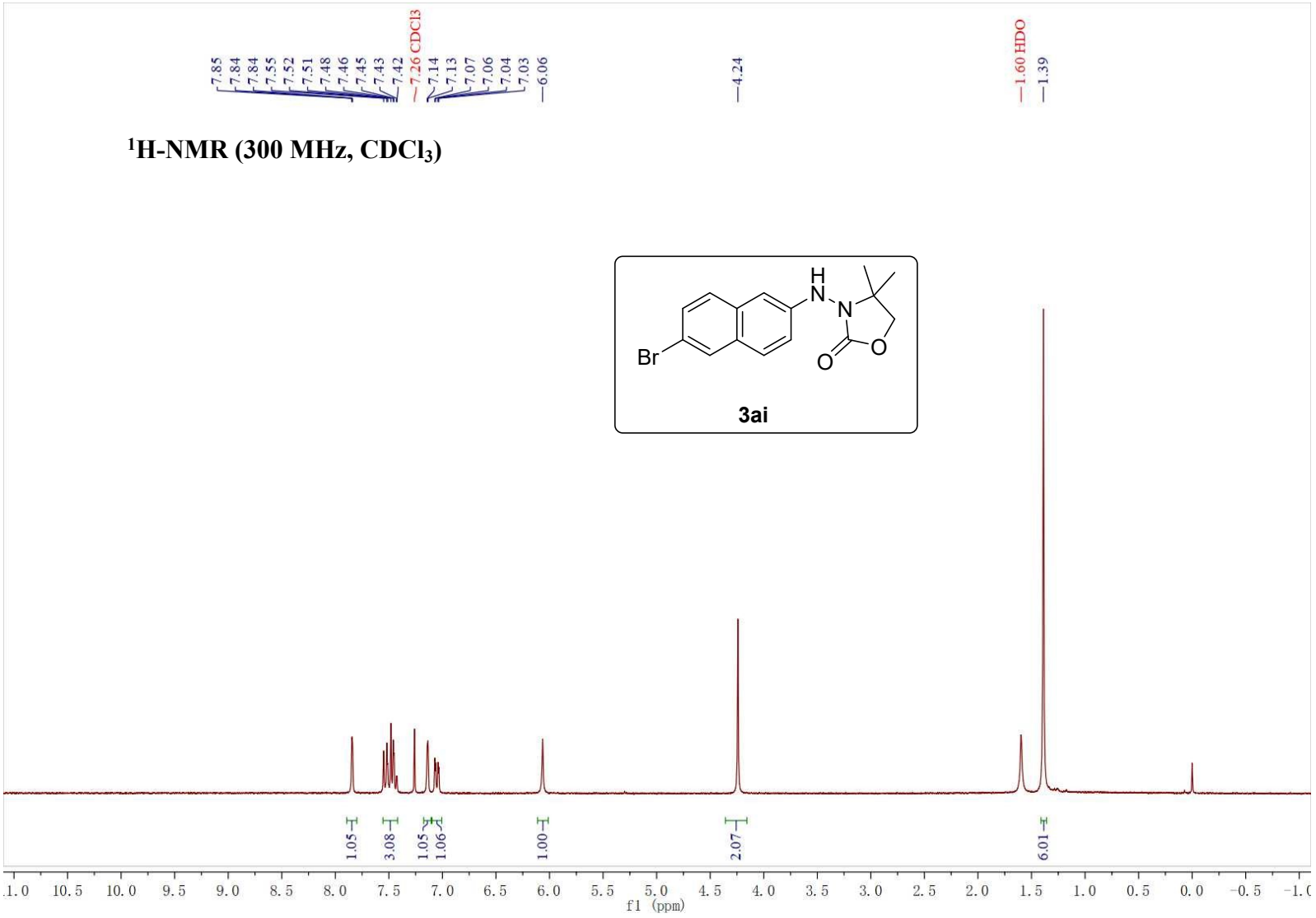
^{1}H-NMR (300 MHz, $CDCl_3$)

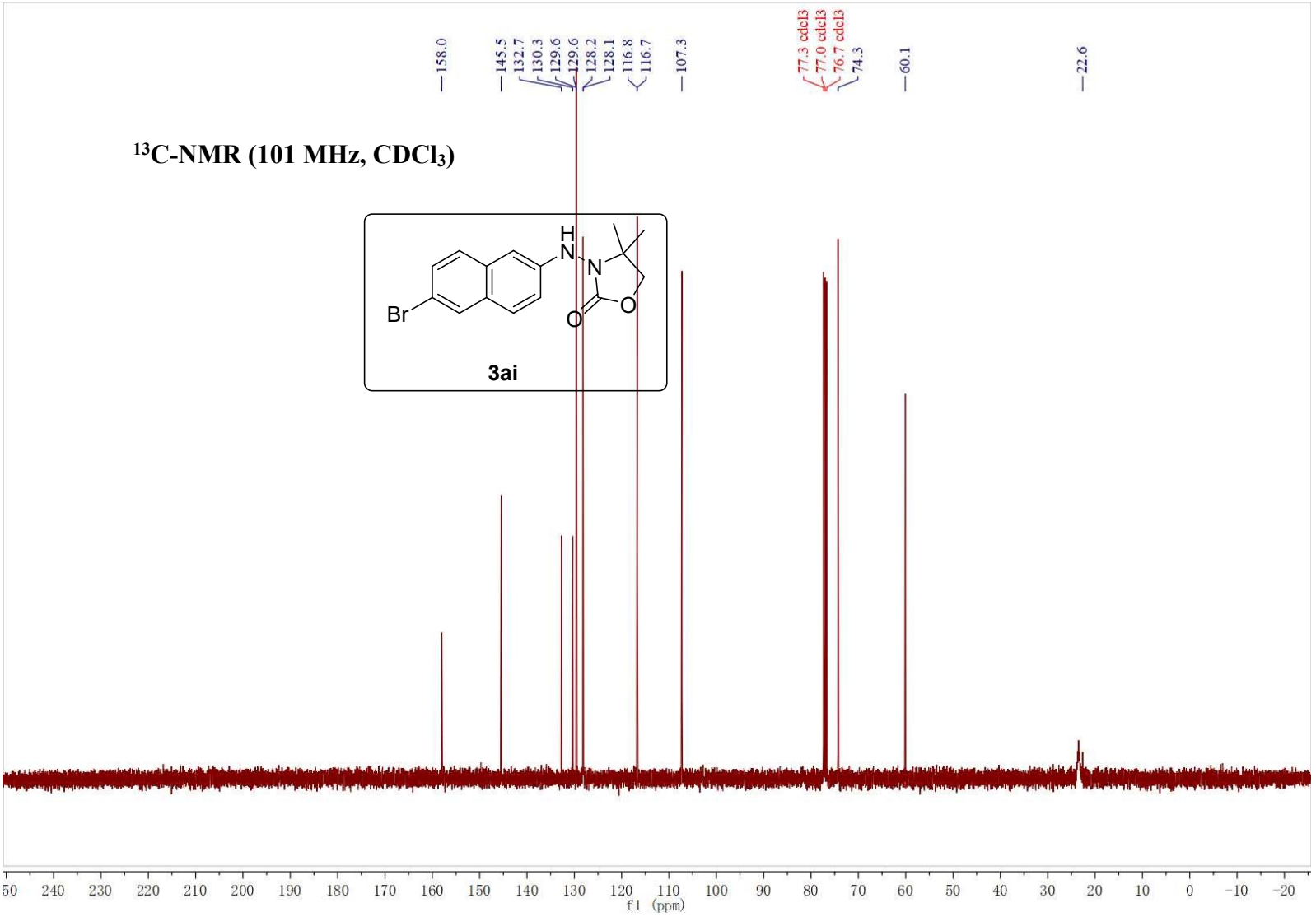




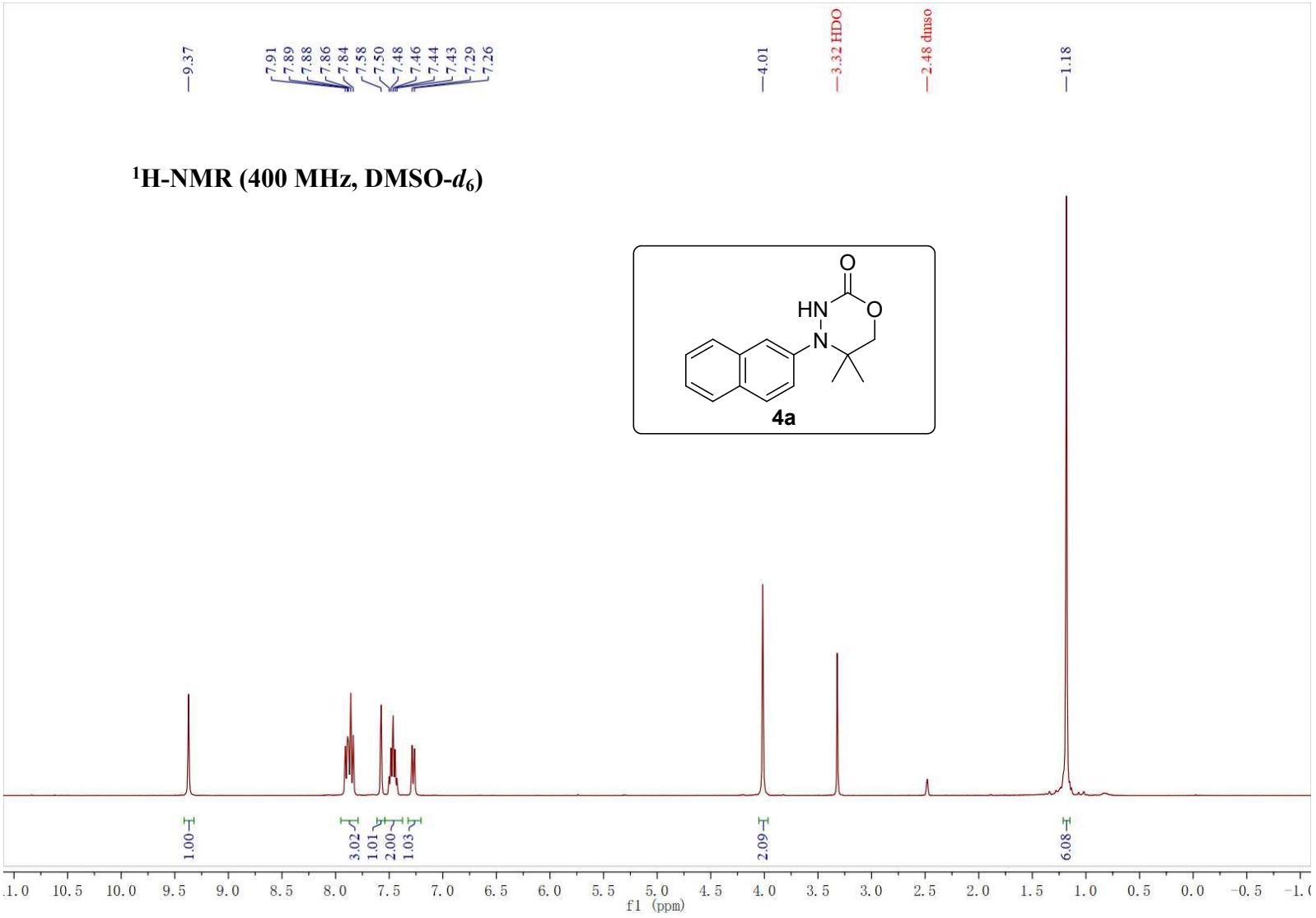
^{13}C-NMR (101 MHz, $CDCl_3$)

3ah

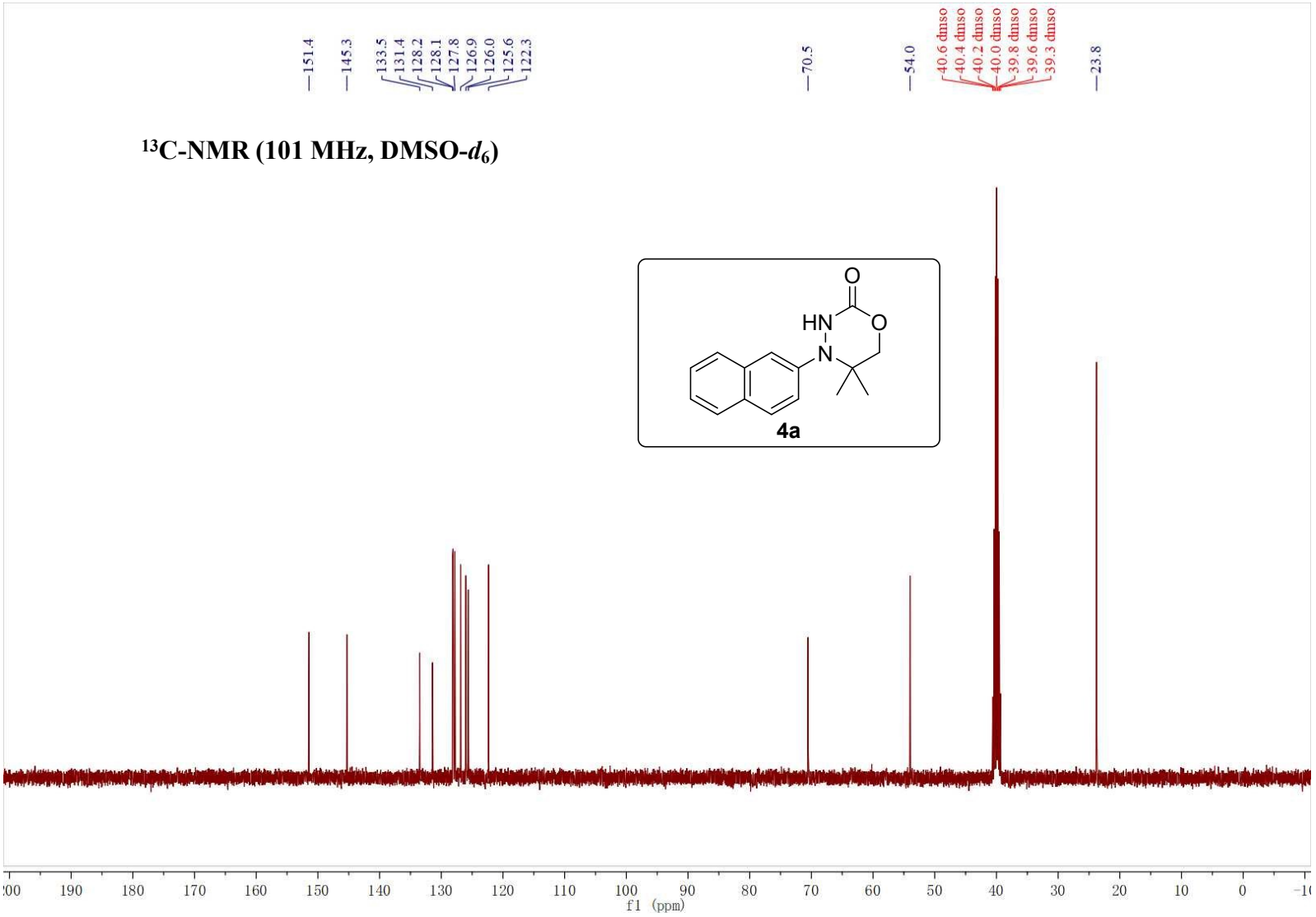

7.85
7.84
7.84
7.55
7.52
7.51
7.48
7.46
7.45
7.43
7.42
7.26 CDCl3
7.14
7.13
7.07
7.06
7.04
7.03
6.06
4.24
1.60 HDO
1.39
1H-NMR (300 MHz, CDCl3)
H
N
N
O
O
Br
3ai
1.05
3.08
1.05
1.06
1.00
2.07
6.01
f1 (ppm)

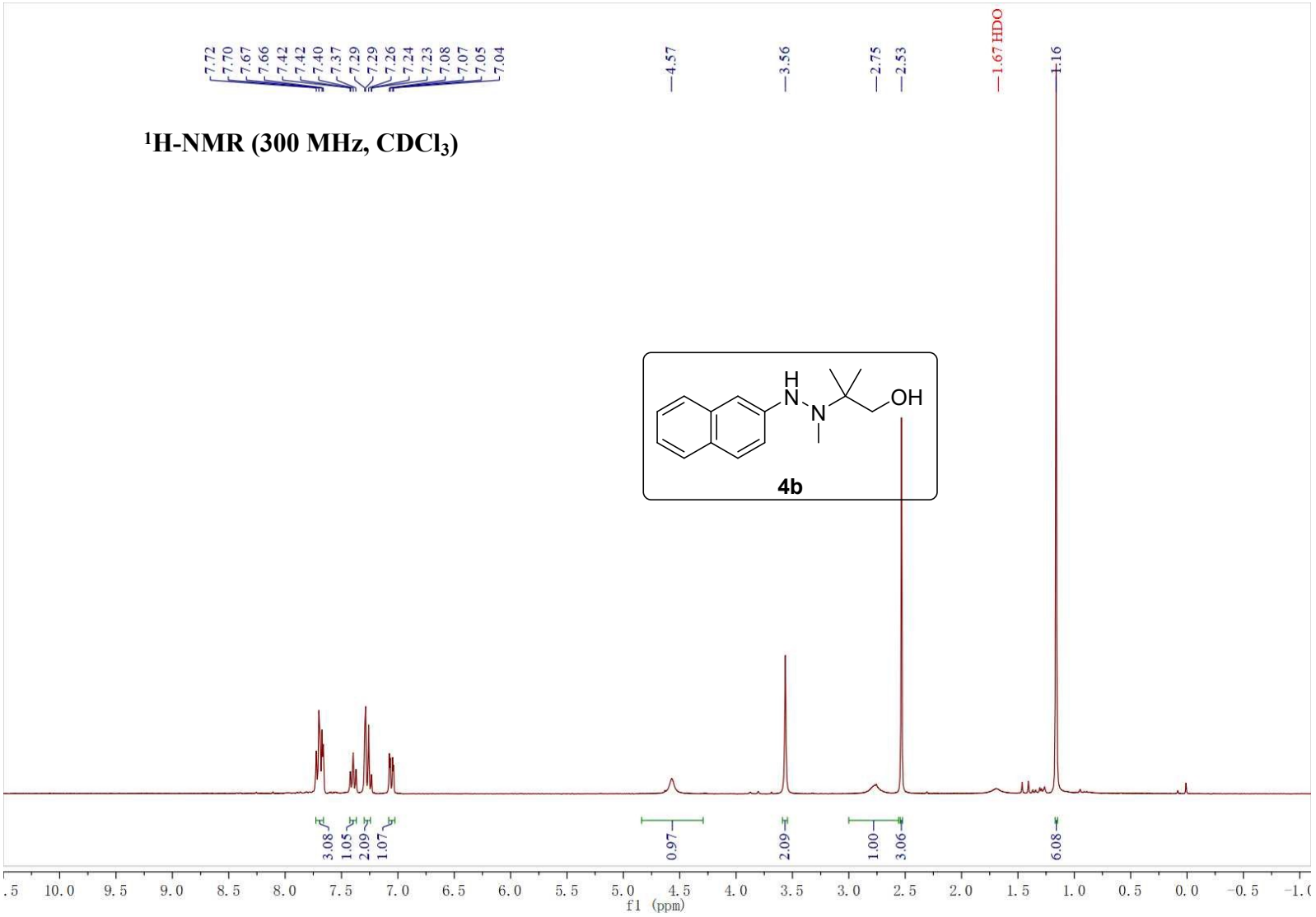

158.0
145.5
132.7
130.3
129.6
129.6
128.2
128.1
116.8
116.7
107.3
77.3 cdcl3
77.0 cdcl3
76.7 cdcl3
74.3
60.1
22.6
13C-NMR (101 MHz, CDCl3)
H
N
N
O
O
O
Br
3ai
50 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

^{1}H-NMR (400 MHz, DMSO-d_6)



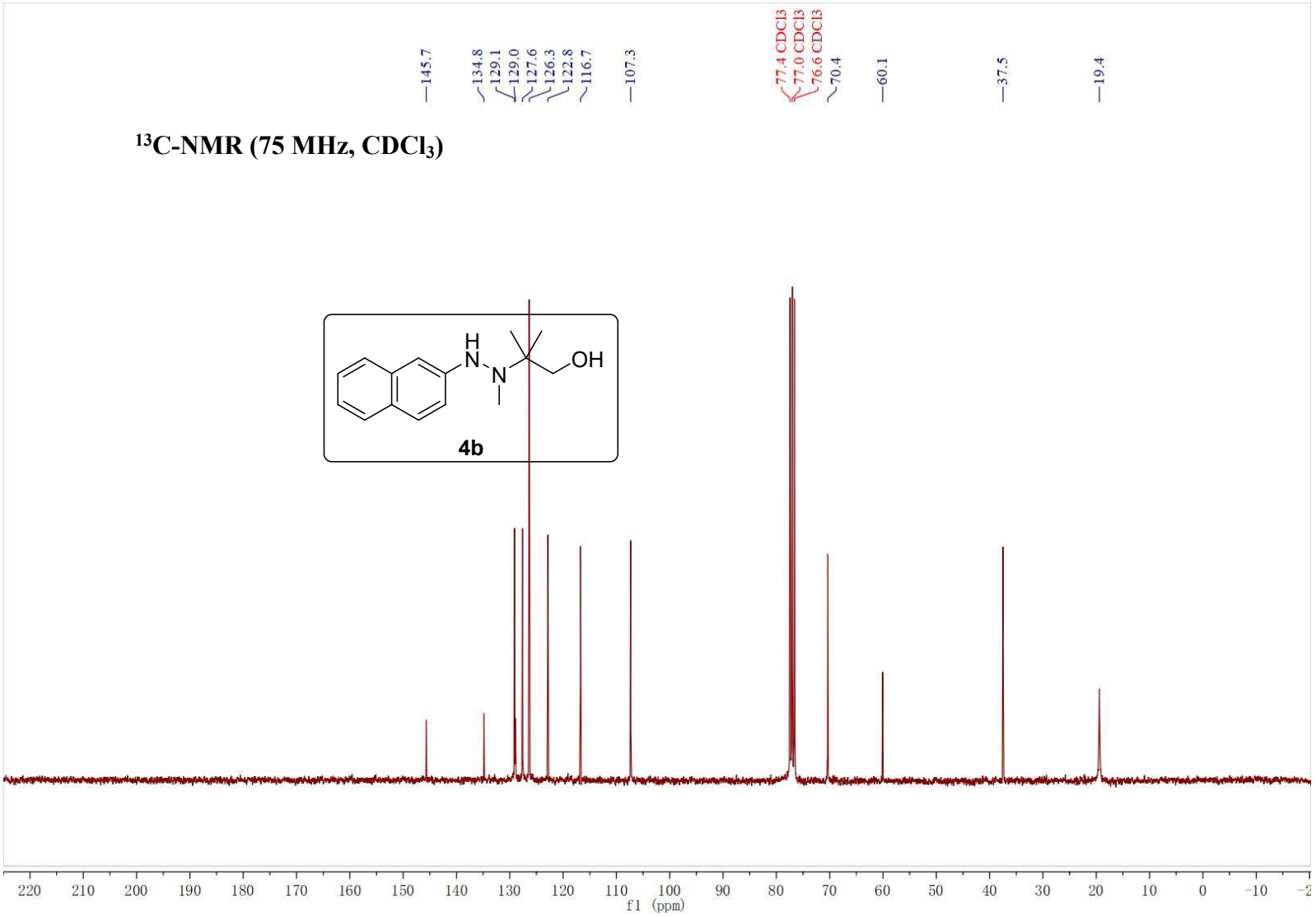
^{13}C-NMR (101 MHz, DMSO-d_6)

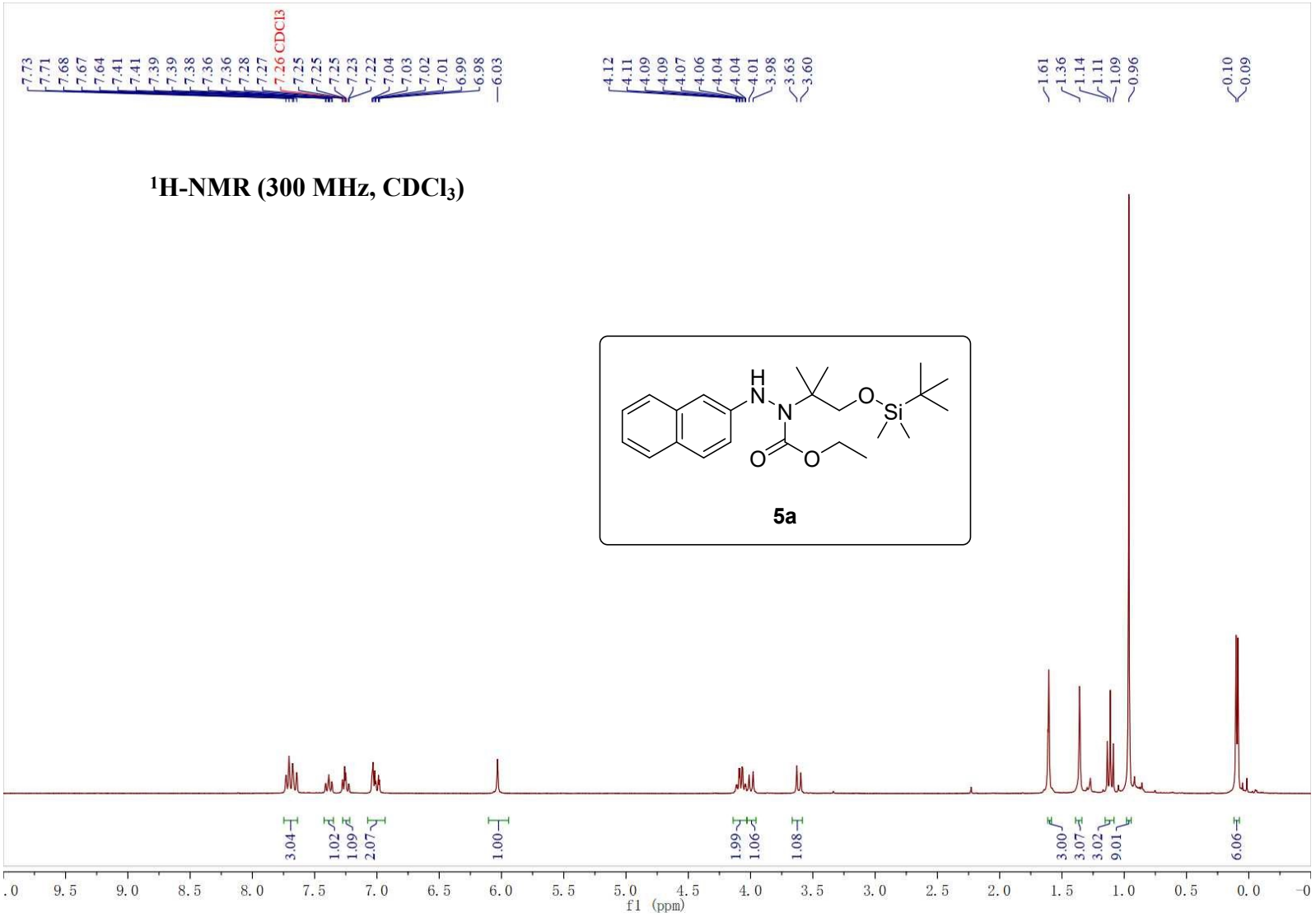




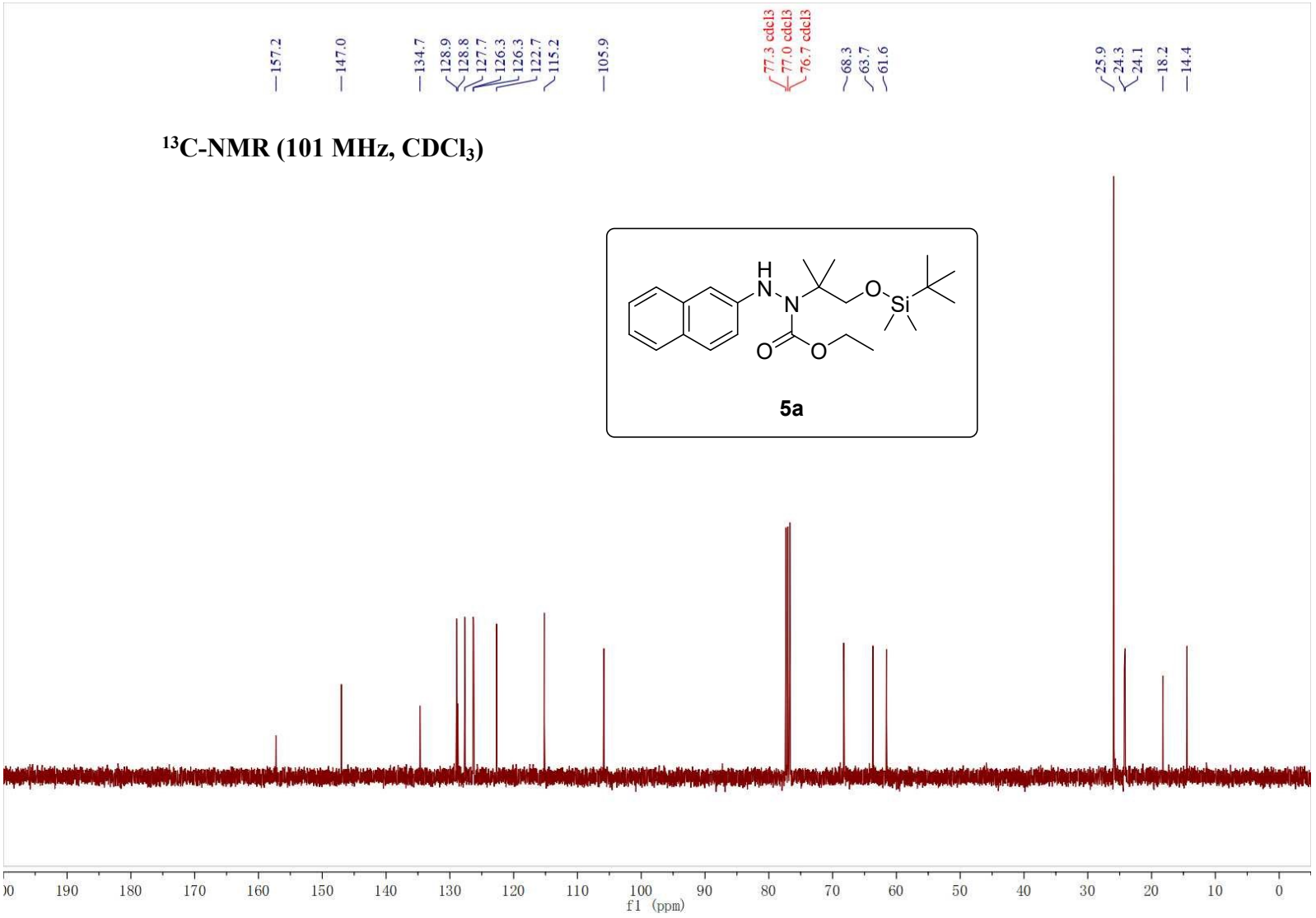
^{1}H-NMR (300 MHz, $CDCl_3$)

^{13}C-NMR (75 MHz, $CDCl_3$)





^{1}H-NMR (300 MHz, $CDCl_3$)



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