Supporting Information

For

Synthesis of Naphthodihydrofurans via Iron(III)-catalyzed Reduction Radical Cascade Reaction

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Contents

1. General Information S2-S3

2. Substrate of Synthesis S3-S5

3. Typical Synthesis Procedure of 3 S6

4. Optimization of the Reaction Conditions S6-S7

5. Typical Synthesis Procedure of 5a S7-S8

6. Typical Synthesis Procedure of 6a S8

7. Characterization of 3, 4a, 5a, 6a S8-S28

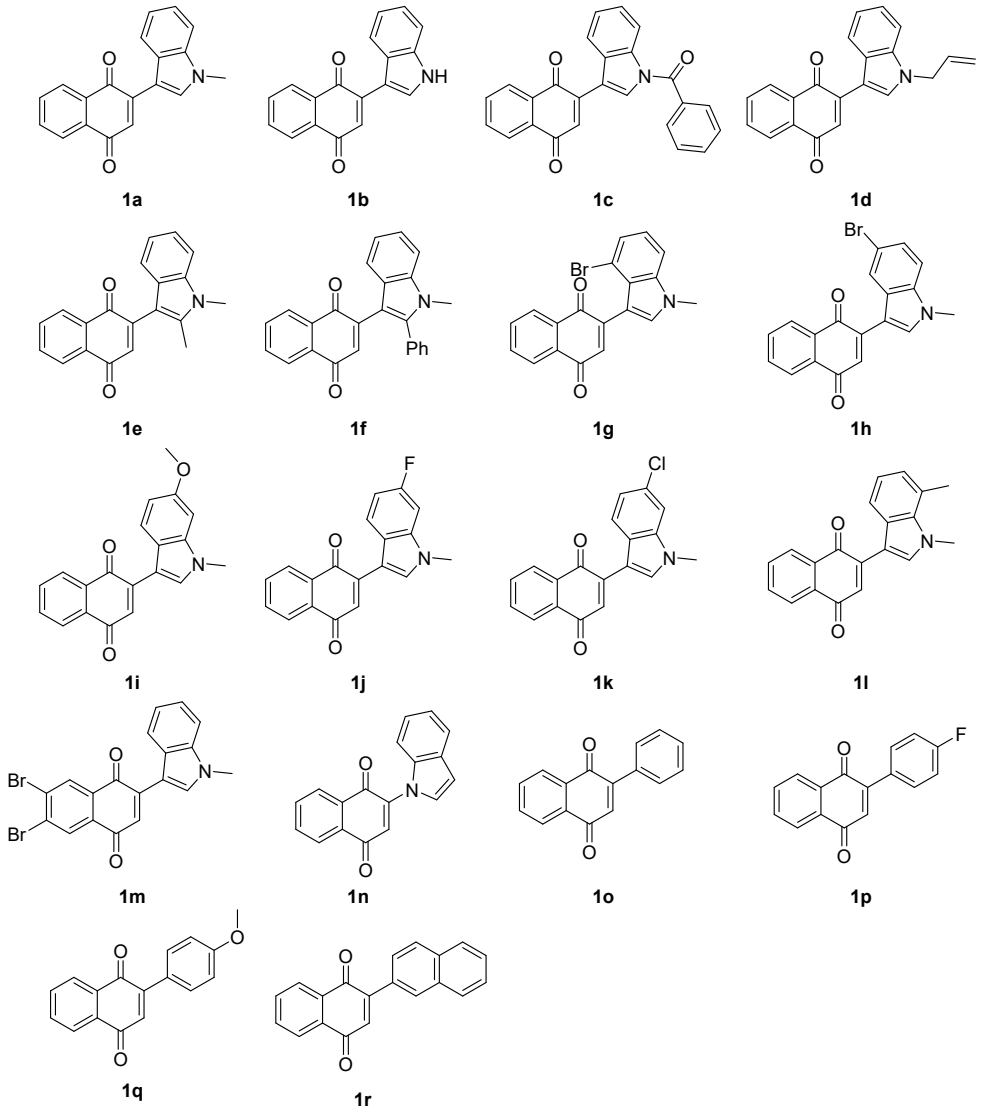
8. X-Ray Analysis S29-S46

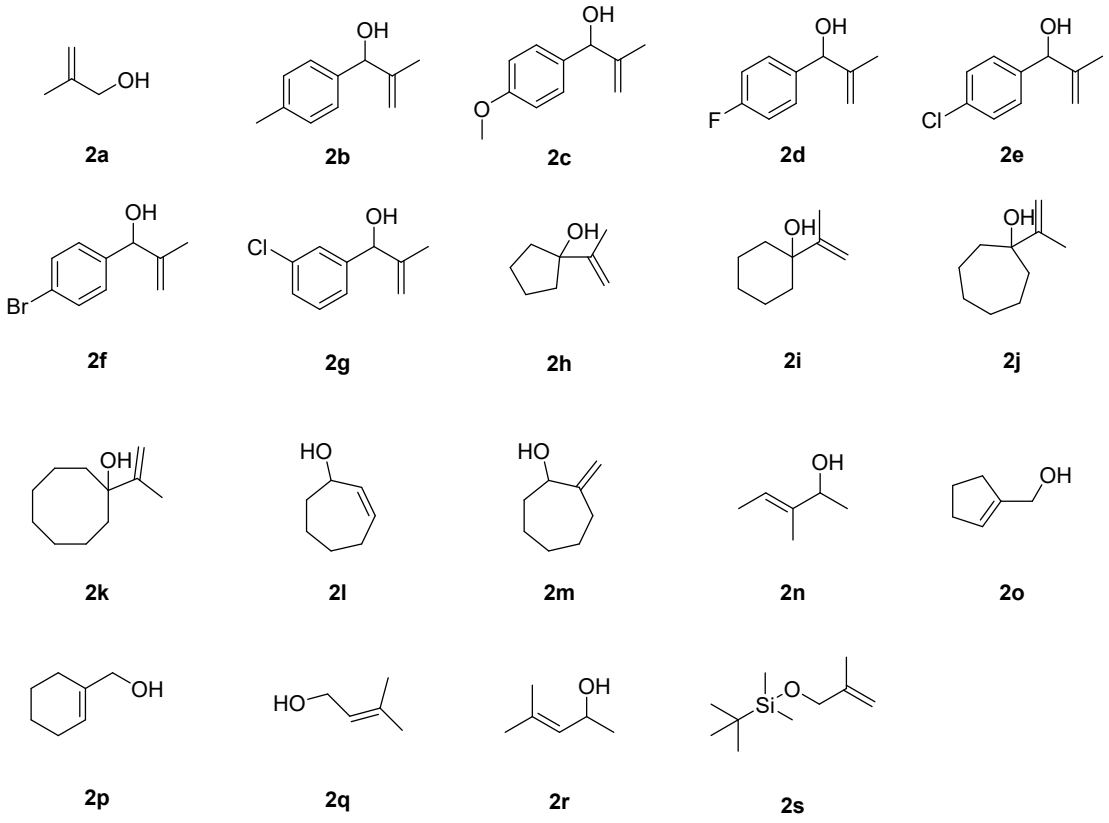
9. References S46-S47

10. Copies of NMR Spectra S48-S125

1. General Information:

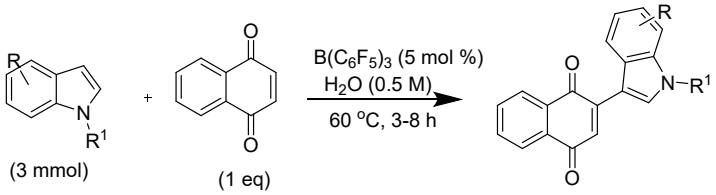
All template reaction experiments were carried out under atmospheric conditions. Thin layer chromatography was carried out in the ultraviolet light using a GF-254 silica gel plate. Column chromatography was carried out using 200-300 mesh silica gel. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded at 400 MHz on an Agilent spectrometer. $CDCl_3$ and DMSO-d_6 were used as solvent. Chemical shifts were referenced relative to residual solvent. Coupling constants (J) were reported in Hertz (Hz). HRMS were performed on a Thermo Scientific LTQ Orbitrap XL instrument. Melting points were measured with micro melting point apparatus. $FeCl_3$ (Adamas, 99%), $Fe(acac)_3$ (HX-R, 99.5%), $Fe(ox)_3{\cdot}6H_2O$ (Alfa Aesar), $PhSiH_3$(Adamas, 97%), Ph_2SiH_2 (Adamas, 97%), EtOH (GHTECH, 99.7%), 2-methylprop-2-en-1-ol (**2a**, Adamas, 98%), 3-methylbut-2-en-1-ol (**2q**, Macklin, 98%) were commercial available, and the naphthoquinone derivatives (**1a-1r)** were prepared according to literature.[1, 2, 3] The allyl alcohols (**2b-2p, 2r-2s**) could be easily prepared according to literature.[4, 5, 6, 7]





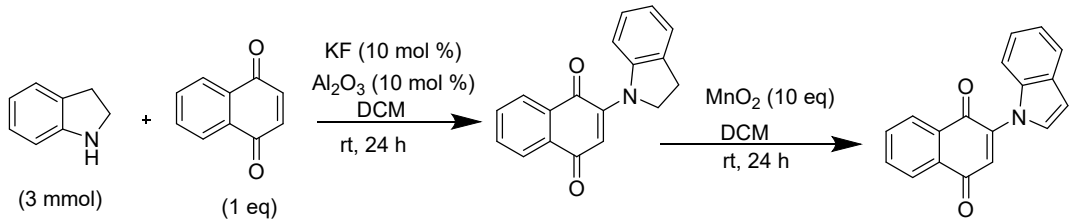
2. Substrate synthesis:

(a) Synthesis of compounds 1a-1m[1]



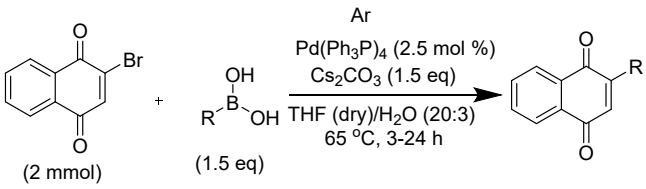
Indole (3 mmol), naphthoquinone (3 mmol), $(C_6F_5)_3B$ (77 mg, 5 mol%) were sequentially weighed into the reaction flask, then 6ml of water was added, and the reaction was heated to 60°C for 3-8h. After the reaction was completed, the aqueous phase was extracted three times with ethyl acetate. The organic phase was dried with anhydrous magnesium sulfate. The solvent was evaporated to dryness under reduced pressure, and the product was purified by column chromatography using ethyl acetate/petroleum ether as the eluent to obtain **1a-1m**. If the product is not pure, it can be recrystallized with ethyl acetate**.**

(b) Synthesis of compounds 1n[2]



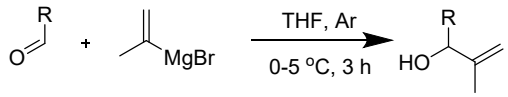
Indoline (3 mmol), naphthoquinone (3 mmol), KF (17 mg, 10 mol%), Al_2O_3 (31 mg, 10 mol%) were sequentially weighed into the reaction flask. Then 15ml of dichloromethane was added and incubated at room temperature for 24h. After the reaction was completed, it was filtered, and the filtrate was evaporated to dryness under reduced pressure. The residue was dissolved in ethyl acetate and frozen in the refrigerator to recrystallize. Filter and dry the filter cake. Add the obtained filter cake to the reaction flask and dissolve it with dichloromethane. Add manganese dioxide to the reaction flask and keep it warm at room temperature for 24 hours. After the reaction was completed, the aqueous phase was extracted three times with DCM. The organic phase was dried with anhydrous magnesium sulfate. The solvent was evaporated to dryness under reduced pressure, and the product was purified by column chromatography using ethyl acetate/petroleum ether as the eluent to obtain **1n.**

(a) Synthesis of compounds 1o-1r[3]



Indole (3 mmol), naphthoquinone (3 mmol), $(C_6F_5)_3B$ (77 mg, 5 mol%) were sequentially weighed into the reaction flask, then 6ml of water was added, and the reaction was heated to 60°C for 3-8h. After the reaction was completed, the aqueous phase was extracted three times with ethyl ace

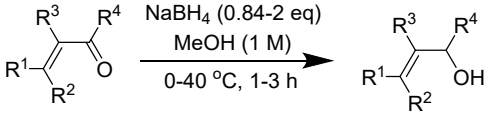
(b) Synthesis of compounds 2b-2k[4]



The reaction tube was filled with argon gas, and aldehyde (3 mmol) was added and dissolved in 1 ml of THF. The reaction tube was cooled to 0-5°C with an ice water bath, and 4.5 ml of isopropene magnesium bromide (1 mol/L solution of isopropene magnesium bromide dissolved in THF) was added. The reaction solution was kept at

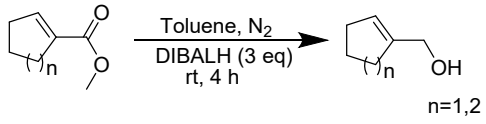
0-5°C for 3 h. After the reaction was completed, it was quenched with water and extracted with ethyl acetate. The solvent was evaporated to dryness under reduced pressure and the product was purified by column chromatography using ethyl acetate/petroleum ether as eluent to give **2b-2k**.

(c) Synthesis of compounds 2l-n, 2r [5]



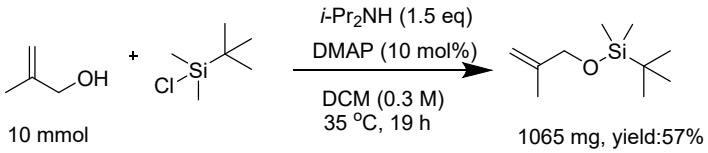
Add α,β-unsaturated ketone (10 mmol) to the reaction flask and dissolve with methanol. Control the temperature at 0-40°C, add sodium borohydride(8.4-20 mmol). The reaction system was kept at 0-40°C for 1-3 h. It was quenched with water and extracted with methylene chloride. The organic phase was dried over anhydrous magnesium sulfate and filtered, and the solvent was distilled off under reduced pressure to obtain the product(**2l-2n, 2r)**.

(d) Synthesis of compounds 2o-2p[6]



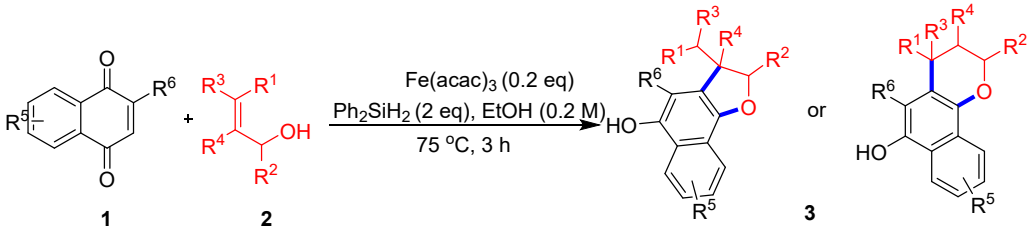
Carboxylate (2 mmol) was added to a reaction tube filled with nitrogen and dissolved in 2 ml of toluene. The reaction tube was cooled to 0-5°C with an ice water bath, and 6 ml of diisobutylaluminum hydride (1 mol/L solution of diisobutylaluminum hydride dissolved in toluene) was added. The reaction tube was incubated at room temperature for 4 h. It was quenched with water and extracted with ethyl acetate. The solvent was evaporated to dryness under reduced pressure and the product was purified by column chromatography using ethyl acetate/petroleum ether as eluent to give **2o-2p**.

(e) Synthesis of compounds 2s[7]



Weigh 2-methylallyl alcohol (721 mg, 10 mmol), diisopropylamine (1518 mg, 15 mmol), DMAP (122 mg, 1 mmol) into the reaction flask, and add 20 mL of dichloromethane to dissolve. Take another reaction flask, weigh in bis(methyl)tert-butylchlorosilane (1808 mg, 12 mmol), and dissolve it with 10 mL of dichloromethane to prepare solution A. Drop solution A into the reaction flask, and keep the reaction at 35 °C for 19 h. After the reaction was completed, it was quenched with water and extracted with ethyl acetate. The organic phase was evaporated to dryness under reduced pressure. The product was purified by column chromatography using petroleum ether as the eluent to obtain **2s** as a colorless liquid (1065 mg, Yield 57%).

3. Typical Procedure for Synthesis of 3a:

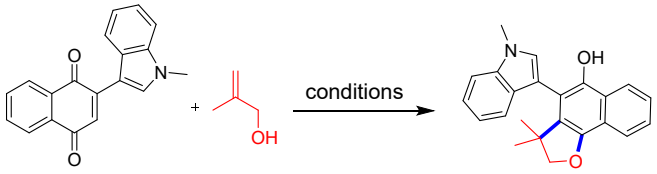


1 2 3

Add $Fe(acac)_3$ (32 mg, 0.09 mmol) and naphthoquinone **1** (0.3 mmol) to the reaction tube and immediately dissolve it with ethanol (1.5 mL). Then, allyl alcohol **2** (0.9 mmol) and Ph_2SiH_2 (110 mg, 0.6 mmol) were added via a syringe. Heat the solution to 75 °C. And react at 75 °C for 3 hours. The solution was then diluted with water. Extract with ethyl acetate and transfer to a round bottom flask. Silica gel was added to the flask, and the solvent was evaporated under vacuum. Purified by silica gel column chromatography using ethyl acetate/petroleum ether as eluent to obtain compound **3**.

4. Optimization of the Reaction Conditions.

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



1a 2a 3a

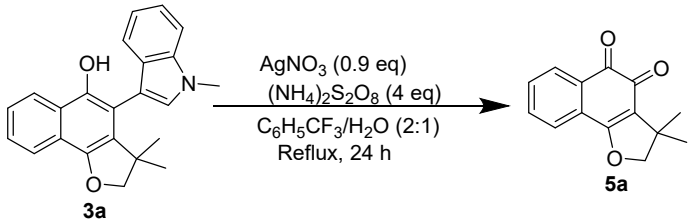
entry	catalyst	reductant	solvent	T (°C)	Yield(%) 3a
1	$Fe(acac)_3$	$PhSiH_3$	EtOH	60	42
2	$Cu(OAc)_2$	$PhSiH_3$	EtOH	60	0
3	$CoCl_2·6H_2O$	$PhSiH_3$	EtOH	60	0
4	$Ni(acac)_2$	$PhSiH_3$	EtOH	60	0
5	$FeBr_3$	$PhSiH_3$	EtOH	60	trace
6	$FeCl_3$	$PhSiH_3$	EtOH	60	23
7	$Fe(ox)_3·6H_2O$	$PhSiH_3$	EtOH	60	trace
8	$Fe(acac)_3$	$HSiCl_3$	EtOH	60	trace
9	$Fe(acac)_3$	Et_3SiH	EtOH	60	0
10	$Fe(acac)_3$	$(EtO)_3SiH$	EtOH	60	9
12	$Fe(acac)_3$	Ph_2SiH_2	EtOH	60	62
13	$Fe(acac)_3$	$PhSiH(CH_3)_2$	EtOH	60	0
14	$Fe(acac)_3$	PMHS	EtOH	60	44
15	$Fe(acac)_3$	Ph_3SiH	EtOH	60	0
16	$Fe(acac)_3$	Et_2SiH_2	EtOH	60	0
17	$Fe(acac)_3$	$NaBH_4$	EtOH	60	0
18	$Fe(acac)_3$	$NaBH_3CN$	EtOH	60	trace
19	$Fe(acac)_3$	Ph_2SiH_2	cyclohexane	60	33

20	$Fe(acac)_3$	Ph_2SiH_2	MeOH	60	51
21	$Fe(acac)_3$	Ph_2SiH_2	THF	60	16
22	$Fe(acac)_3$	Ph_2SiH_2	Toluene	60	31
23	$Fe(acac)_3$	Ph_2SiH_2	EtOH	75	69
24	$Fe(acac)_3$	Ph_2SiH_2	EtOH	100（seal）	60
25[c]	$Fe(acac)_3$	Ph_2SiH_2	EtOH	75	72
26[c, d]	$Fe(acac)_3$	Ph_2SiH_2	EtOH	75	45
27[c, d]	$Fe(acac)_3$	Ph_2SiH_2	EtOH	75	51

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.6 mmol), catalyst (30 mol%), reductant (2 equiv), solvent (1 mL), 3h; [b]yield refers to isolated product. [c] $Fe(acac)_3$ (20 mol %) was used; [d]Argon atmosphere; [e]Oxygen atmosphere.

We used 2-(1-methyl-1H-indol-3-yl)naphthalene-1,4-dione (**1a**) and 2-methylallyl alcohol (**2a**) to explore optimal conditions (**Table 1**). Gratifyingly, when the reaction was carried out under Baran's conditions,[8] the product could be obtained in a moderate yield (entry 1). Other metal Lewis acids have almost no catalytic activity (entries 2-6). Regrettably, the reaction was carried out under Boger's conditions[9] and only a trace amount of product was obtained (entry 7). Examination of a series of reducing agents found that, except for diphenylsilane and polymethylhydrogensiloxane, other reducing agents can hardly produce naphthodihydrofuran (entries 8-18). Interestingly, when Ph_2SiH_2 was used instead of $PhSiH_3$, the yield of the reaction could be dramatically increased to 62% (entry 12). When $NaBH_4$ was used as the reductant, only the raw materials remained in the reaction system (entry 17). We have also examined a series of solvents, although the naphthodihydrofuran can be obtained, but the yield has not been significantly improved (entries 19-22). What's more, when the reaction temperature was increased to 75°C, the yield of the reaction could be increased to 69% (entry 23). When the temperature continued to increase, the yield of the product did not increase (entry 24). When methanol was used as solvent, 2,3-dihydronaphtho[1,2-*b*]furan could be obtained in moderate yield (entry 20). To our surprise, when the catalyst loading was reduced to 20%, the yield could miraculously increase to 72% (entry 25). Finally, whether the reaction was carried out under an oxygen atmosphere or an inert gas atmosphere, the reaction yield could not be improved (entries 26-27). This proved that the reaction was not sensitive to air and moisture.

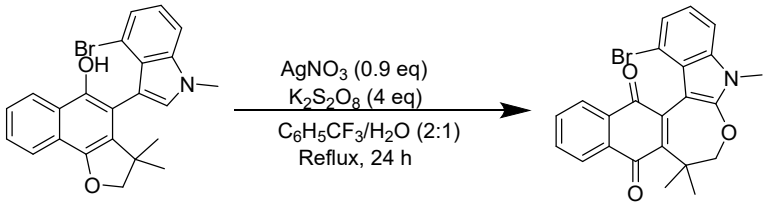
5. Typical Procedure for Synthesis of 5a.



Add $AgNO_3$ (15 mg, 0.09 mmol), **3a** (0.1 mmol), ammonium persulfate (91 mg, 0.4 mmol) to the reaction tube and add 1 mL benzotrifluoride and 0.6 mL purified water. Heat the solution to 110 °C. And reflux for 24 hours at 110 °C. The solution

was then diluted with water. Extract with ethyl acetate and transfer to a round bottom flask. Silica gel was added to the flask, and the solvent was evaporated under vacuum. Purified by silica gel column chromatography using ethyl acetate/petroleum ether as eluent to obtain compound **5a** (3,3-dimethyl-2,3-dihydronaphtho[1,2-*b*]furan-4,5-dione) as a yellow solid (18 mg, 78% yield).

6. Typical Procedure for Synthesis of 6a.

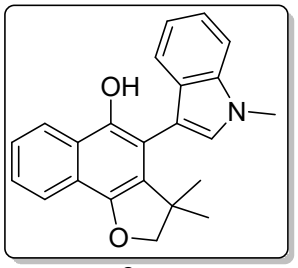


3x **6a**

Add $AgNO_3$ (15 mg, 0.09 mmol), **3x** (0.1 mmol), potassium persulfate (108 mg, 0.4 mmol) to the reaction tube and add 1 mL of trifluorotoluene and 0.6 mL of purified water. Heat the solution to 110 °C. And reflux for 24 hours at 110 °C. The solution was then diluted with water. Extract with ethyl acetate and transfer to a round bottom flask. Silica gel was added to the flask, and the solvent was evaporated under vacuum. Purify by silica gel column chromatography using ethyl acetate/petroleum ether as eluent to obtain compound **6a** (1-bromo-5,8,8-trimethyl-7,8-dihydro-5*H*-naphtho[2',3':4,5]oxepino[2,3-*b*]indole-9,14-dione) as a red solid (23 mg, 53% yield).

7. Characterization of 3, 4a, 5a, 6a:

3,3-dimethyl-4-(1-methyl-1H-indol-3-yl)-2,3-dihydronaphtho[1,2-*b*]furan-5-ol (3a)



3a

White solid, m.p. 122-123°C, 74 mg, yield: 72%; R_f = 0.54 (EtOAc/Petroleum ether 1:7).

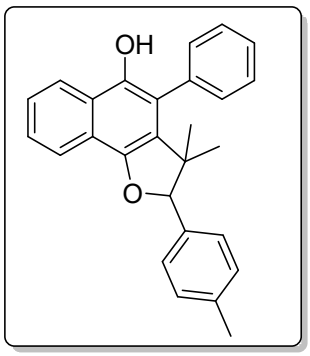
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19 (d, *J* = 8.0 Hz, 1H), 7.97 (d, *J* = 8.0 Hz, 1H), 7.50 (ddd, *J* = 8.2, 6.8, 1.5 Hz, 1H), 7.49-7.41 (m, 2H), 7.36-7.28 (m, 2H), 7.17-7.09 (m, 2H), 5.22 (s, 1H), 4.35-4.28 (dd, *J* = 8.0, 8.0 Hz, 2H), 3.93 (s, 3H), 1.27 (s, 3H), 0.94 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 147.5, 144.9, 137.0, 129.6, 128.5, 128.4, 125.8,

124.9, 123.1, 122.9, 122.5, 121.2, 120.8, 120.3, 120. 1, 110.4, 109.5, 106.0, 84.9, 44.5, 33.1, 28.0, 26.4.

HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{23}H_{22}NO_2$ 344.1645; found 344.1649.

3,3-dimethyl-4-phenyl-2-(p-tolyl)-2,3-dihydronaphtho[1,2-b]furan-5-ol (3b)



3b

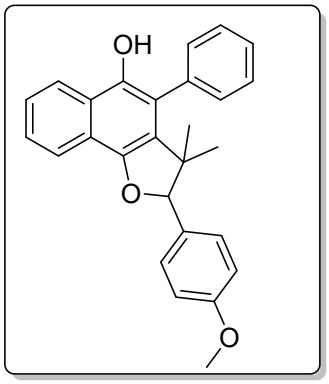
White solid, m.p. 111-112°C, 84 mg, yield: 74%; R_f = 0.51 (EtOAc/Petroleum ether 1:15).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21 (d, *J* = 8.9 Hz, 1H), 8.08 (d, *J* = 7.6 Hz, 1H), 7.59-7.42 (m, 6H), 7.35 (dd, *J* = 12.5, 7.1 Hz, 3H), 7.19 (d, *J* = 7.8 Hz, 2H), 5.37 (s, 1H), 4.81 (s, 1H), 2.38 (s, 3H), 1.07 (s, 3H), 0.68 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 147.1, 142.7, 137.6, 134.4, 133.7, 131.5, 131.2, 129.1, 129.0, 128.8, 128.7, 127.0, 126.7, 125.9, 125.4, 123.4, 122.7, 121.6, 120.6, 119.5, 94.6, 48.0, 26.6, 24.7, 21.2.

HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{27}H_{25}O_2$ 381.1849; found 381.1859.

2-(4-methoxyphenyl)-3,3-dimethyl-4-phenyl-2,3-dihydronaphtho[1,2-b]furan-5-ol (3c)



3c

White solid, m.p. 108-109°C, 74 mg, yield: 62%; R_f = 0.51 (EtOAc/Petroleum ether 1:15).

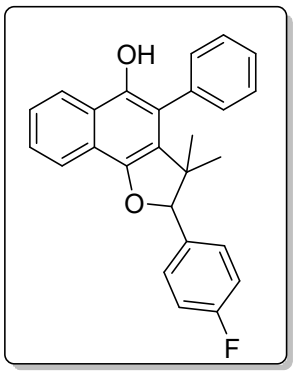
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21 (d, *J* = 7.4 Hz, 1H), 8.07 (d, *J* = 9.2 Hz, 1H),

7.58-7.43 (m, 6H), 7.36 (d, *J* = 8.0 Hz, 3H), 6.92 (d, *J* = 8.3 Hz, 2H), 5.35 (s, 1H), 4.82 (s, 1H), 3.83 (s, 3H), 1.05 (s, 3H), 0.68 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 159.4, 147.1, 142.7, 135.2, 133.7, 131.5, 131.2, 129.5, 129.4, 129.1, 129.0, 128.7, 128.5, 128.0, 127.0, 125.9, 125.4, 123.4, 122.7, 121.6, 120.6, 119.5, 113.5, 94.4, 55.3, 48.0, 26.5, 24.7.

HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{27}H_{25}O_3$ 397.1798; found 397.1797.

2-(4-fluorophenyl)-3,3-dimethyl-4-phenyl-2,3-dihydronaphtho[1,2-b]furan-5-ol (3d)



3d

White solid, m.p. 105-106°C, 74 mg, yield: 64%; R_f = 0.51 (EtOAc/Petroleum ether 1:15).

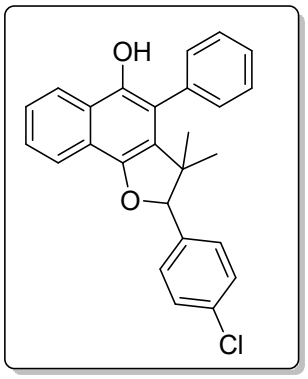
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22 (d, *J* = 8.2 Hz, 1H), 8.07 (d, *J* = 7.8 Hz, 1H), 7.59-7.46 (m, 5H), 7.48-7.38 (m, 3H), 7.36 (d, *J* = 7.0 Hz, 1H), 7.16-7.01 (m, 2H), 5.37 (s, 1H), 4.83 (s, 1H), 1.07 (s, 3H), 0.66 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 163.8-161.3 (*J*=252.5 Hz), 146.9, 142.9, 134.6, 133.5, 133.3, 131.5, 131.2, 129.1, 129.1, 128.8, 128.4, 128.3, 126.7, 126.0, 125.5, 123.5, 122.7, 121.5, 120.6, 119.3, 115.1-114.9 (*J*=20.2 Hz), 93.9, 77.3, 77.0, 76.7, 48.0, 26.5, 24.7.

^{19}F NMR (376 MHz, $CDCl_3$) δ -114.46

HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{26}H_{22}FO_2$ 385.1598; found 385.1591.

2-(4-chlorophenyl)-3,3-dimethyl-4-phenyl-2,3-dihydronaphtho[1,2-b]furan-5-ol (3e)



3e

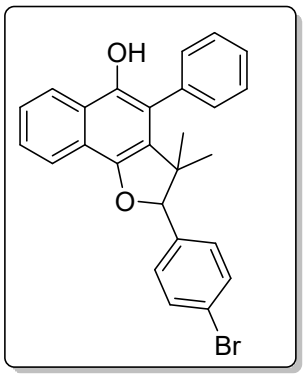
White solid, m.p. 113-114°C, 70 mg, yield: 58%; R_f = 0.51 (EtOAc/Petroleum ether 1:15).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21 (d, *J* = 7.3 Hz, 1H), 8.05 (d, *J* = 8.6 Hz, 1H), 7.59-7.40 (m, 6H), 7.41-7.30 (m, 5H), 5.36 (s, 1H), 4.82 (s, 1H), 1.07 (s, 3H), 0.65 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 146.8, 142.9, 136.1, 133.7, 133.5, 131.5, 131.2, 129.1, 129.1, 128.8, 128.3, 128.1, 126.6, 126.0, 125.5, 123.5, 122.7, 121.4, 120.6, 119.3, 93.8, 48.1, 26.6, 24.7.

HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{26}H_{22}ClO_2$ 401.1303; found 401.1312.

2-(4-bromophenyl)-3,3-dimethyl-4-phenyl-2,3-dihydronaphtho[1,2-b]furan-5-ol (3f)



3f

White solid, m.p. 101-102°C, 95 mg, yield: 71%; R_f = 0.51 (EtOAc/Petroleum ether 1:15).

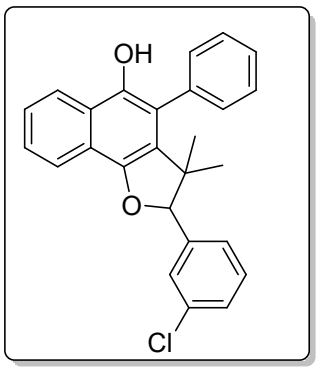
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21 (d, *J* = 7.7 Hz, 1H), 8.05 (d, *J* = 8.5 Hz, 1H), 7.55-7.48 (m, 7H), 7.44 (d, *J* = 8.0 Hz, 1H), 7.36-7.33 (m, 3H), 5.34 (s, 1H), 4.82 (s, 1H), 1.07 (s, 3H), 0.65 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 146.8, 142.9, 136.7, 134.6, 133.5, 131.5, 131.2, 131.2, 129.2, 129.1, 128.8, 128.4, 127.8, 126.6, 126.0, 125.5, 123.5, 122.7, 121.8, 121.4, 120.6, 119.3, 93.8, 48.1, 26.6, 24.7.

HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{26}H_{22}BrO_2$ 445.0798; found 445.0804.

2-(3-chlorophenyl)-3,3-dimethyl-4-phenyl-2,3-dihydronaphtho[1,2-

b]furan-5-ol (3g)



3g

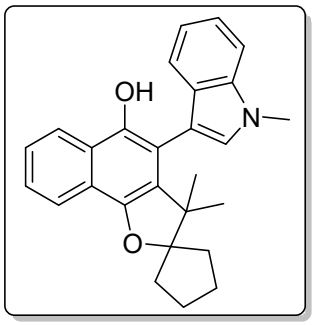
White solid, m.p. 136-137°C, 76 mg, yield: 63%; R_f = 0.51 (EtOAc/Petroleum ether 1:15).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22 (d, *J* = 7.5 Hz, 1H), 8.07 (d, *J* = 9.3 Hz, 1H), 7.58-7.43 (m, 7H), 7.36 (d, *J* = 7.1 Hz, 1H), 7.33-7.30 (m, 3H), 5.36 (s, 1H), 4.83 (s, 1H), 1.09 (s, 3H), 0.68 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 146.7, 143.0, 139.8, 134.2, 133.4, 131.5, 131.2, 129.4, 129.2, 129.1, 128.8, 128.1, 126.8, 126.6, 126.0, 125.5, 124.9, 123.5, 122.7, 121.5, 120.6, 119.2, 93.7, 48.2, 26.6, 24.8.

HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{26}H_{22}ClO_2$ 401.1303; found 401.1304.

3',3'-dimethyl-4'-(1-methyl-1H-indol-3-yl)-3'H-spiro[cyclopentane-1,2'-naphtho[1,2-*b*]furan]-5'-ol (3h)



3h

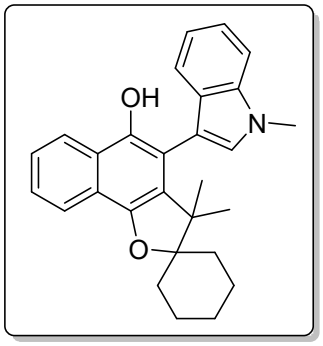
White solid, m.p. 183-184°C, 84 mg, yield: 70%; R_f = 0.62 (EtOAc/Petroleum ether 1:7).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19 (d, *J* = 8.1 Hz, 1H), 8.00 (d, *J* = 8.0 Hz, 1H), 7.46 (m, 3H), 7.34 (t, *J* = 7.5 Hz, 2H), 7.16 (d, *J* = 6.9 Hz, 2H), 5.20 (s, 1H), 3.96 (s, 3H), 2.02-1.94 (m, 3H), 1.90-1.85 (m, 1H), 1.66-1.63 (m, 2H), 1.45-1.29 (m, 2H), 1.12 (s, 3H), 0.82 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 146.0, 144.5, 137.0, 134.3, 130.0, 129.6, 128.7, 125.4, 124.7, 122.7, 122.4, 121.5, 121.0, 120.3, 120.1, 110.6, 109.5, 106.4, 103.8, 46.5, 33.2, 32.6, 32.1, 31.5, 25.2, 23.3, 23.2.

HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{27}H_{28}NO_2$ 398.2115; found 398.2111.

3',3'-dimethyl-4'-(1-methyl-1H-indol-3-yl)-3'H-spiro[cyclohexane-1,2'-naphtho[1,2-b]furan]-5'-ol (3i)



3i

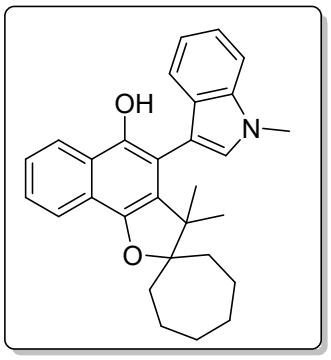
White solid, m.p. 139-140°C, 72 mg, yield: 58%; R_f = 0.62 (EtOAc/Petroleum ether 1:15).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11 (d, *J* = 7.8 Hz, 1H), 7.82 (ddt, *J* = 7.9, 2.3, 0.9 Hz, 2H), 7.74 (s, 1H), 7.61 (ddd, *J* = 7.9, 7.3, 1.3 Hz, 1H), 7.48 (td, *J* = 7.5, 1.2 Hz, 1H), 7.39-7.35 (m, 2H), 7.23-7.18 (m, 1H), 3.84 (s, 3H), 2.20-2.14 (m, 2H), 1.90-1.80 (m, 1H), 1.78-1.70 (m, 4H), 1.51-1.50 (m, 1H), 1.48 (s, 3H), 1.45 (s, 3H), 1.41-1.37 (m, 1H), 1.30-1.22 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 184.7, 142.3, 141.5, 136.9, 132.5, 132.5, 132.1, 131.2, 128.8, 127.0, 126.6, 126.3, 121.8, 120.1, 119.5, 109.7, 108.0, 99.6, 85.7, 85.0, 34.3, 34.1, 33.0, 25.9, 25.8, 25.5, 22.8, 22.6.

HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{28}H_{30}NO_2$ 412.2271; found 412.2275.

3',3'-dimethyl-4'-(1-methyl-1H-indol-3-yl)-3'H-spiro[cycloheptane-1,2'-naphtho[1,2-b]furan]-5'-ol (3j)



3j

White solid, m.p. 106-107°C, 66 mg, yield: 52%; R_f = 0.62 (EtOAc/Petroleum ether 1:7).

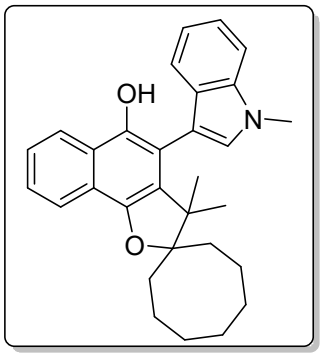
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19 (d, *J* = 8.2 Hz, 1H), 8.05 (d, *J* = 8.2 Hz, 1H), 7.53-7.40 (m, 3H), 7.34 (d, *J* = 7.8 Hz, 2H), 7.19-7.09 (m, 2H), 5.20 (s, 1H), 3.95 (s,

3H), 2.17 (dd, *J* = 14.7, 7.9 Hz, 1H), 2.06 (dd, *J* = 14.7, 8.1 Hz, 1H), 1.88 (q, *J* = 11.8, 11.2 Hz, 2H), 1.71 (td, *J* = 17.7, 14.8, 7.9 Hz, 4H), 1.53-1.44 (m, 2H), 1.40-1.29 (m, 2H), 1.07 (s, 3H), 0.78 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 145.9, 144.4, 137.0, 134.3, 129.9, 129.5, 128.7, 128.0, 125.4, 124.6, 122.7, 122.4, 121.4, 120.3, 120.1, 111.0, 109.4, 106.4, 94.9, 50.7, 33.5, 33.3, 33.2, 29.1, 29.0, 24.5, 22.7, 22.4, 22.2.

HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{29}H_{32}NO_2$ 426.2428; found 426.2427.

3',3'-dimethyl-4'-(1-methyl-1H-indol-3-yl)-3'H-spiro[cyclooctane-1,2'-naphtho[1,2-*b*]furan]-5'-ol (3k)



3k

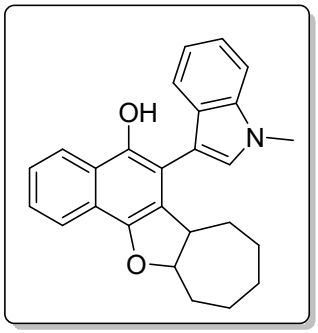
White solid, m.p. 100-102°C, 81 mg, yield: 61%; R_f = 0.61 (EtOAc/Petroleum ether 1:7).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.30-8.27 (m, 1H), 8.21-8.19 (m, 1H), 7.65-7.63 (m, 1H), 7.53-7.47 (m, 2H), 7.46-7.43 (m, 1H), 7.38-7.33 (ddd, *J* = 8.2, 6.9, 1.1 Hz, 1H), 7.27-7.26 (d, *J* = 4 Hz, 1H), 7.22 (ddd, *J* = 8.0, 7.0, 1.1 Hz, 1H), 7.16 (s, 1H), 5.85 (s, 1H), 3.90 (s, 3H), 2.19-2.07 (m, 2H), 1.97-1.86 (m, 3H), 1.77-1.63 (m, 4H), 1.60-1.48 (m, 3H), 1.36 (s, 6H), 1.04-0.97 (m, 1H), 0.93-0.84 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 144.9, 143.1, 137.4, 130.7, 127.9, 126.8, 125.6, 125.4, 125.0, 123.1, 122.7, 122.4, 122.1, 120.3, 119.9, 113.4, 110.7, 109.8, 88.1, 78.7, 34.7, 33.0, 31.4, 28.2, 26.9, 25.3, 24.8, 22.4, 22.2, 18.8.

HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{30}H_{34}NO_2$ 440.2584; found 440.2586.

6-(1-methyl-1H-indol-3-yl)-6b,8,9,10,11,11a-hexahydro-7H-cyclohepta[*b*]naphtho[2,1-*d*]furan-5-ol (3l)



3l

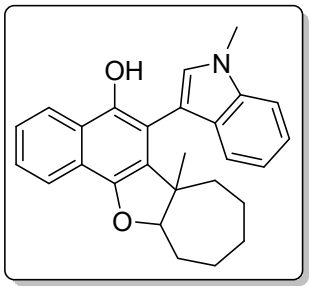
White solid, m.p. 176-177°C, 54 mg, yield: 47%; d.r. = 6:5:1, R_f = 0.40 (EtOAc/Petroleum ether 1:7).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21 (d, *J* = 8.1 Hz, 1H), 7.96 (d, *J* = 7.7 Hz, 1H), 7.45 (d, *J* = 8.2 Hz, 3H), 7.34 (t, *J* = 7.6 Hz, 2H), 7.26-7.03 (m, 2H), 5.34 (s, 1H), 4.59 (dt, *J* = 12.3, 5.1 Hz, 1H), 3.91 (s, 3H), 3.73-3.52 (m, 1H), 2.51 (dt, *J* = 16.6, 5.5 Hz, 1H), 1.96 (tt, *J* = 12.1, 7.3 Hz, 1H), 1.86-1.70 (m, 1H), 1.68-1.05 (m, 7H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 148.0, 143.5, 137.5, 137.0, 134.3, 130.3, 128.6, 128.1, 127.9, 127.8, 125.6, 124.9, 124.4, 124.3, 123.3, 123.1, 122.9, 122.8, 122.6, 122.4, 121.3, 120.3, 120.1, 120.0, 119.9, 111.1, 109.7, 109.6, 107.6, 89.8, 89.8, 86.6, 49.1, 48.9, 33.1, 32.9, 31.7, 28.4, 28.3, 27.5, 27.3, 25.9, 25.8, 24.9, 24.7, 23.6.

HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{26}H_{26}NO_2$ 384.1958; found 384.1955.

6b-methyl-6-(1-methyl-1H-indol-3-yl)-6b,8,9,10,11,11a-hexahydro-7*H*-cyclohepta[*b*]naphtho[2,1-*d*]furan-5-ol (3m)



3m

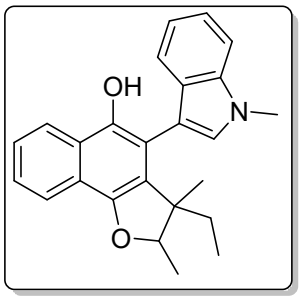
White solid, m.p. 187-188°C, 63 mg, yield: 53%; d.r. = 1:3:2, R_f = 0.40 (EtOAc/Petroleum ether 1:7).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.2 (d, *J* = 7.9 Hz, 1H), 8.0 (d, *J* = 8.8 Hz, 1H), 7.52-7.42 (m, 3H), 7.37-7.29 (m, 2H), 7.16-7.09 (m, 2H), 5.2 (s, 1H), 4.6 (t, *J* = 17.1 Hz, 1H), 3.9 (s, 3H), 2.39-2.30 (m, 1H), 2.13-2.01 (m, 1H), 1.92-1.85 (m, 1H), 1.66- 1.55 (m, 3H), 1.49-1.37 (m, 2H), 1.34-1.26 (m, 3H), 1.01-0.86 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 146.9, 145.0, 144.9, 137.1, 137.0, 131.8, 131.6, 130.0, 129.8, 129.2, 128.6, 128.3, 125.6, 125.6, 124.9, 124.8, 122.8, 122.5, 122.4, 122.4, 121.5, 121.4, 121.3, 120.7, 120.3, 120.3, 120.1, 120.1, 120.0, 110.5, 110.4, 109.5, 109.4, 106.7, 92.8, 90.2, 89.8, 50.8, 50.4, 38.5, 38.0, 37.2, 35.4, 33.2, 31.2,

30.5, 30.1, 27.2, 27.0, 25.5, 25.2, 25.1, 25.1, 23.6, 23.5, 23.2, 20.1, 19.4.
HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{27}H_{28}NO_2$ 398.2115; found 398.2120.

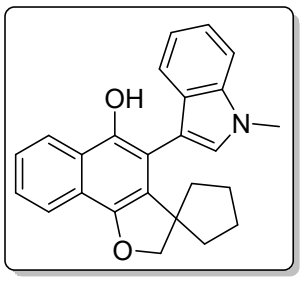
3-ethyl-2,3-dimethyl-4-(1-methyl-1H-indol-3-yl)-2,3-dihydronaphtho[1,2-*b*]furan-5-ol (3n)



3n

White solid, m.p. 216-217°C, 79 mg, yield: 71%; d.r. = 1:2, R_f = 0.40 (EtOAc/Petroleum ether 1:15).
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.31 (d, *J* = 12.4 Hz, 1H), 8.13 (d, *J* = 10.4 Hz, 1H), 7.56-7.40 (m, 3H), 7.36-7.26 (m, 2H), 7.18-7.06 (m, 2H), 5.04 (d, *J* = 4.4 Hz, 1H), 4.40 (dddd, *J* = 11.5, 5.4, 3.5, 1.8 Hz, 1H), 3.93 (s, 3H), 1.89-1.77 (m, 1H), 1.62-1.55 (m, 1H), 1.53-1.50 (m, 3H), 1.47-1.19 (d, *J* = 2.9 Hz, 3H), 1.10-0.79 (d, *J* = 3.6 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 144.8, 144.5, 142.8, 136.9, 130.8, 130.3, 129.1, 128.6, 126.0, 125.9, 125.8, 125.3, 125.0, 124.8, 122.8, 122.5, 122.4, 122.2, 122.0, 122.0, 120.8, 120.5, 120.3, 120.1, 112.4, 112.4, 109.5, 109.4, 68.2, 67.9, 49.6, 49.1, 33.5, 33.3, 33.1, 32.2, 31.2, 31.2, 29.6, 21.8, 21.7.
HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{25}H_{26}NO_2$ 372.1958; found 372.1963.

4'-(1-methyl-1H-indol-3-yl)-2'H-spiro[cyclopentane-1,3'-naphtho[1,2-*b*]furan]-5'-ol (3o)

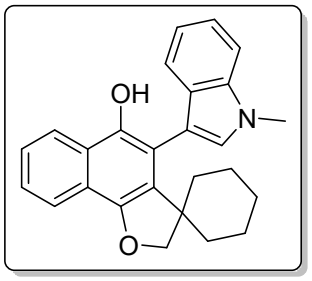


3o

White solid, m.p. 147-148°C, 64 mg, yield: 58%; R_f = 0.55 (EtOAc/Petroleum ether 1:7).
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.18 (d, *J* = 8.2 Hz, 1H), 7.96 (d, *J* = 7.4 Hz, 1H), 7.51-7.42 (m, 3H), 7.34-7.30 (m, 2H), 7.16-7.09 (m, 2H), 5.21 (s, 1H), 4.38 (d, *J* = 8.3 Hz, 1H), 4.28 (d, *J* = 8.2 Hz, 1H), 3.92 (s, 3H), 2.00-1.93 (m, 1H), 1.88 -1.79 (m,

1H), 1.59-1.55 (m, 1H), 1.47-1.35 (m, 2H), 1.33-1.23 (m, 2H), 1.01- 0.94 (m, 1H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 148.2, 145.1, 137.0, 134.6, 129.6, 128.3, 126.7, 125.8, 124.9, 122.8, 122.5, 121.1, 120.6, 120.2, 120.1, 110.2, 109.5, 106.0, 85.6, 54.7, 39.9, 37.1, 33.1, 25.5, 25.4.
HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{25}H_{24}NO_2$ 370.1802; found 370.1807.

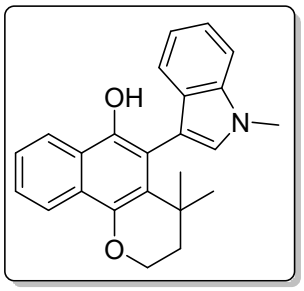
4'-(1-methyl-1H-indol-3-yl)-2'H-spiro[cyclohexane-1,3'-naphtho[1,2-*b*]furan]-5'-ol (3p)



3p

White solid, m.p. 198-199°C, 78 mg, yield: 68%; R_f = 0.54 (EtOAc/Petroleum ether 1:15).
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.17 (d, *J* = 7.7 Hz, 1H), 7.97 (d, *J* = 7.0 Hz, 1H), 7.51-7.42 (m, 3H), 7.34-7.29 (m, 2H), 7.15-7.11 (m, 2H), 5.17 (s, 1H), 4.59 (d, *J* = 8.6 Hz, 1H), 4.41 (d, *J* = 8.6 Hz, 1H), 3.95 (s, 3H), 1.82-1.68 (m, 2H), 1.57-1.51 (m, 3H), 1.38-1.28 (m, 2H), 1.26-1.08 (m, 2H), 0.77-.68 (m, 1H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 147.6, 144.9, 137.1, 134.6, 129.7, 128.6, 125.7, 124.9, 123.1, 122.8, 122.5, 121.2, 120.8, 120.3, 120.2, 110.5, 109.5, 106.1, 80.3, 49.4, 35.9, 34.4, 33.2, 25.2, 23.3, 23.1.
HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{26}H_{26}NO_2$ 384.1958; found 384.1966.

4,4-dimethyl-5-(1-methyl-1H-indol-3-yl)-3,4-dihydro-2H-benzo[*h*]chromen-6-ol (3q)



3q

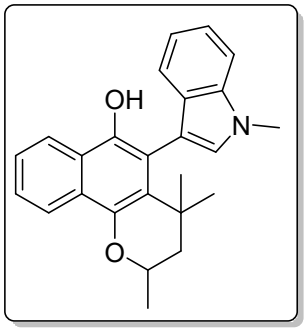
White solid, m.p. 239-240°C, 71 mg, yield: 66%; R_f = 0.40 (EtOAc/Petroleum ether 1:15).
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.25 (d, *J* = 7.2 Hz, 1H), 8.13 (d, *J* = 7.6 Hz, 1H), 7.55-7.41 (m, 3H), 7.36-7.27 (m, 2H), 7.18-7.09 (m, 2H), 5.07 (s, 1H), 4.42-4.31 (m,

2H), 3.93 (s, 3H), 1.96 (td, *J* = 8.8, 4.6 Hz, 1H), 1.77 (ddd, *J* = 13.7, 5.0, 3.0 Hz, 1H), 1.39 (s, 3H), 0.91 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 144.5, 142.8, 136.9, 130.8, 130.3, 129.1, 128.6, 126.0, 125.9, 125.8, 125.8, 125.3, 124.8, 122.8, 122.5, 122.4, 122.2, 122.0, 122.0, 120.8, 120.5, 120.3, 120.1, 112.4, 109.5, 109.4, 109.1, 68.2, 67.9, 49.6, 49.1, 33.5, 33.3, 33.1, 32.2, 31.2, 31.2, 29.6, 21.8, 21.7.

HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{24}H_{24}NO_2$ 358.1802; found 358.1799.

2,4,4-trimethyl-5-(1-methyl-1H-indol-3-yl)-3,4-dihydro-2H-benzo[*h*]chromen-6-ol (3r)



3r

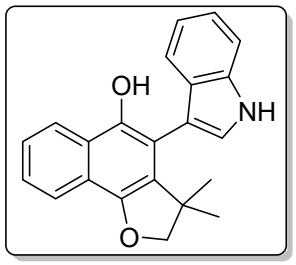
White solid, m.p. 213-214°C, 59 mg, yield: 53%, d.r. = 2:1, R_f = 0.66 (EtOAc/Petroleum ether 1:7).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.30 (d, *J* = 8.8 Hz, 1H), 8.12 (d, *J* = 7.8 Hz, 1H), 7.54-7.40 (m, 3H), 7.31 (m, 2H), 7.17-7.06 (m, 2H), 5.04 (s, 1H), 4.34 (ddd, *J* = 35.7, 11.6, 6.1 Hz, 1H), 3.93 (s, 3H), 1.91-1.74 (m, 1H), 1.59 (dd, *J* = 13.3, 6.3 Hz, 1H), 1.51 (d, *J* = 6.1 Hz, 3H), 1.46 (s, 3H), 0.79 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 172.62, 141.77, 140.09, 137.80, 135.08, 133.04, 130.10, 129.21, 128.91, 128.75, 127.81, 127.03, 126.91, 79.04, 39.53, 25.68.

HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{25}H_{26}NO_2$ 372.1958; found 372.1964.

4-(1H-indol-3-yl)-3,3-dimethyl-2,3-dihydronaphtho[1,2-*b*]furan-5-ol (3s)

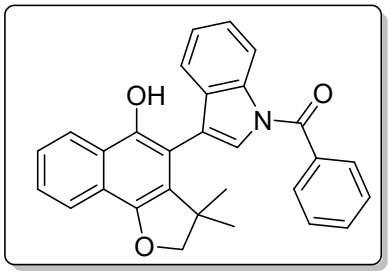


3s

White solid, m.p. 142-143°C, 56 mg, yield: 57%; R_f = 0.24 (EtOAc/Petroleum ether 1:7).

^{1}H NMR (400 MHz, DMSO-d_6): δ 11.27 (s, 1H), 8.09 (d, *J* = 7.3 Hz, 1H), 7.82 (d, *J* = 8.8 Hz, 1H), 7.70 (s, 1H), 7.51-7.36 (m, 3H), 7.32 (d, *J* = 2.4 Hz, 1H), 7.09 (dd, *J* = 14.4, 7.5 Hz, 2H), 6.93 (t, *J* = 7.5 Hz, 1H), 4.23 (d, *J* = 8.3 Hz, 1H), 4.16 (d, *J* = 8.3 Hz, 1H), 1.15 (s, 3H), 0.75 (s, 3H).
^{13}C NMR (101 MHz, DMSO-d_6): δ 146.7, 146.0, 136.4, 129.5, 129.0, 126.3, 125.8, 125.0, 124.6, 123.4, 121.4, 121.3, 120.3, 119.7, 119.1, 113.6, 111.9, 108.1, 84.4, 44.5, 28.1, 26.3.
HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{22}H_{20}NO_2$ 330.1489; found 330.1494.

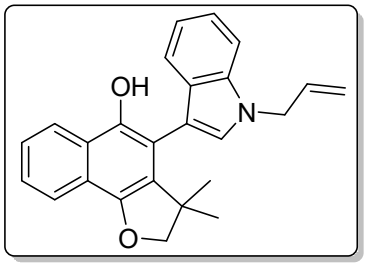
(3-(5-hydroxy-3,3-dimethyl-2,3-dihydronaphtho[1,2-b]furan-4-yl)-1H-indol-1-yl)(phenyl)methanone (3t)



3t

White solid, m.p. 130-131°C, 113 mg, yield: 87%; R_f = 0.60 (EtOAc/Petroleum ether 1:7).
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.52 (d, *J* = 8.3 Hz, 1H), 8.20 (d, *J* = 8.2 Hz, 1H), 7.99 (d, *J* = 8.1 Hz, 1H), 7.83-7.73 (m, 2H), 7.73-7.58 (m, 2H), 7.58-7.43 (m, 5H), 7.36 (d, *J* = 4.3 Hz, 2H), 5.09 (s, 1H), 4.37 (d, *J* = 8.3 Hz, 1H), 4.33 (d, *J* = 8.3 Hz, 1H), 1.32 (s, 3H), 1.04 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 168.6, 148.0, 144.5, 136.2, 134.6, 134.4, 134.1, 132.3, 130.9, 130.3, 130.2, 129.2, 128.8, 128.1, 127.8, 126.3, 126.1, 125.4, 124.7, 122.8, 121.3, 120.4, 116.6, 114.3, 108.3, 84.9, 44.4, 28.0, 26.5.
HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{29}H_{24}NO_3$ 434.1751; found 434.1759.

4-(1-allyl-1H-indol-3-yl)-3,3-dimethyl-2,3-dihydronaphtho[1,2-b]furan-5-ol (3u)

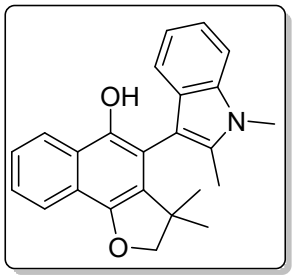


3u

White solid, m.p. 125-126°C, 56 mg, yield: 50%; R_f = 0.32 (EtOAc/Petroleum ether 1:7).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21 (d, *J* = 8.2 Hz, 1H), 7.99 (d, *J* = 8.1 Hz, 1H), 7.58-7.41 (m, 3H), 7.39-7.28 (m, 2H), 7.21 (s, 1H), 7.15 (t, *J* = 7.5 Hz, 1H), 6.10 (ddt, *J* = 16.3, 10.4, 5.2 Hz, 1H), 5.30 (d, *J* = 10.2 Hz, 1H), 5.25 (s, 1H), 5.19 (d, *J* = 17.1 Hz, 1H), 4.96-4.80 (m, 2H), 4.36 (d, *J* = 8.2 Hz, 1H), 4.31 (d, *J* = 8.2 Hz, 1H), 1.29 (s, 3H), 0.96 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 147.5, 144.8, 136.4, 133.1, 128.7, 128.6, 128.3, 125.8, 125.0, 123.1, 122.8, 122.6, 121.2, 120.8, 120.3, 120.3, 117.6, 110.4, 109.9, 106.5, 84.9, 48.9, 44.5, 28.0, 26.4.
HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{25}H_{24}NO_2$ 370.1802; found 370.1796.

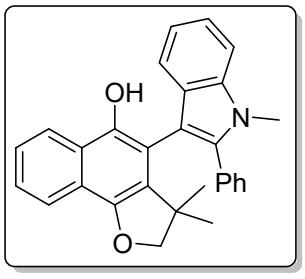
4-(1,2-dimethyl-1H-indol-3-yl)-3,3-dimethyl-2,3-dihydronaphtho[1,2-b]furan-5-ol (3v)



3v

White solid, m.p. 212-213°C, 54 mg, yield: 50%; R_f = 0.32 (EtOAc/Petroleum ether 1:7).
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22 (d, *J* = 7.9 Hz, 1H), 8.00 (d, *J* = 7.5 Hz, 1H), 7.56-7.42 (m, 2H), 7.15 (dd, *J* = 7.5, 1.7 Hz, 1H), 7.02 (dd, *J* = 9.9, 7.9 Hz, 3H), 5.25 (s, 1H), 4.36 (d, *J* = 8.2 Hz, 1H), 4.32 (d, *J* = 8.2 Hz, 1H), 4.20 (s, 3H), 2.89 (s, 3H), 1.31 (s, 3H), 0.98 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 147.5, 144.9, 135.8, 131.2, 129.5, 128.4, 125.7, 125.1, 124.9, 123.1, 122.9, 121.4, 121.2, 120.8, 120.4, 118.4, 110.5, 105.8, 84.9, 44.5, 37.0, 28.1, 26.4, 19.7.
HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{24}H_{24}NO_2$ 358.1802; found 358.1799.

3,3-dimethyl-4-(1-methyl-2-phenyl-1H-indol-3-yl)-2,3-dihydronaphtho[1,2-b]furan-5-ol (3w)



3w

White solid, m.p. 204-205°C, 78 mg, yield: 62%; R_f = 0.40 (EtOAc/Petroleum ether

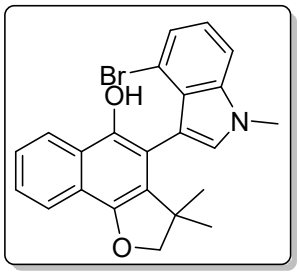
1:7).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.26 (d, *J* = 7.8 Hz, 1H), 7.93 (d, *J* = 7.9 Hz, 1H), 7.54-7.43 (m, 3H), 7.40-7.24 (m, 7H), 7.19-7.10 (m, 1H), 5.44 (s, 1H), 4.20 (d, *J* = 8.2 Hz, 1H), 4.09 (d, *J* = 8.1 Hz, 1H), 3.87 (s, 3H), 0.93 (s, 3H), 0.71 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 147.5, 145.8, 140.5, 138.0, 131.2, 129.9, 128.8, 128.5, 128.1, 128.1, 125.7, 124.8, 123.1, 123.0, 122.7, 121.2, 121.0, 120.5, 120.2, 111.0, 109.7, 104.9, 84.7, 44.3, 31.9, 27.2, 26.0.

HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{29}H_{26}NO_2$ 420.1958; found 420.1969.

4-(4-bromo-1-methyl-1H-indol-3-yl)-3,3-dimethyl-2,3-dihydronaphtho[1,2-b]furan-5-ol (3x)



3x

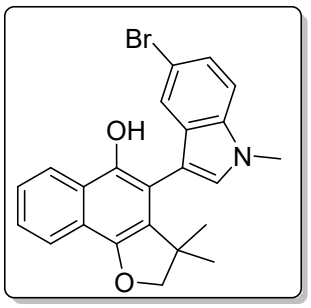
White solid, m.p. 166-167°C, 69 mg, yield: 54%; R_f = 0.32 (EtOAc/Petroleum ether 1:7).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22 (d, *J* = 8.2 Hz, 1H), 7.98 (d, *J* = 7.9 Hz, 1H), 7.57-7.44 (m, 2H), 7.41 (d, *J* = 8.2 Hz, 1H), 7.31 (d, *J* = 7.5 Hz, 1H), 7.19-7.12 (m, 2H), 5.07 (s, 1H), 4.34 (s, 2H), 3.93 (s, 3H), 1.26 (s, 3H), 1.02 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 147.3, 145.5, 137.9, 131.2, 128.3, 126.4, 125.8, 124.9, 124.6, 123.3, 123.0, 122.9, 121.2, 121.0, 114.9, 111.0, 109.0, 106.2, 84.9, 44.5, 33.4, 28.6, 25.6.

HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{23}H_{21}BrNO_2$ 422.0750; found 422.0754.

4-(5-bromo-1-methyl-1H-indol-3-yl)-3,3-dimethyl-2,3-dihydronaphtho[1,2-b]furan-5-ol (3y)



3y

White solid, m.p. 243-244°C, 75 mg, yield: 59%; R_f = 0.32 (EtOAc/Petroleum ether

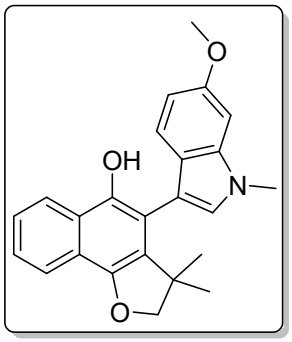
1:7).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.18 (d, *J* = 8.2 Hz, 1H), 7.97 (d, *J* = 8.1 Hz, 1H), 7.54-7.42 (m, 3H), 7.39 (d, *J* = 8.8 Hz, 1H), 7.30 (d, *J* = 8.7 Hz, 1H), 5.11 (s, 1H), 4.33 (d, *J* = 8.2 Hz, 1H), 4.29 (d, *J* = 8.2 Hz, 1H), 3.91 (s, 3H), 1.26 (s, 3H), 0.93 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 147.6, 144.9, 135.7, 130.7, 130.1, 128.1, 126.0, 125.5, 125.1, 123.2, 122.8, 122.6, 121.3, 120.9, 113.8, 111.1, 109.5, 105.8, 84.9, 44.4, 33.3, 28.1, 26.4.

HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{23}H_{21}BrNO_2$ 422.0750; found 422.0757.

4-(6-methoxy-1-methyl-1H-indol-3-yl)-3,3-dimethyl-2,3-dihydronaphtho[1,2-b]furan-5-ol (3z)



3z

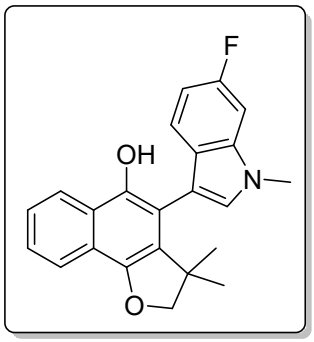
White solid, m.p. 170-171°C, 55 mg, yield: 49%; R_f = 0.26 (EtOAc/Petroleum ether 1:7).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.18 (d, *J* = 8.1 Hz, 1H), 7.96 (d, *J* = 8.0 Hz, 1H), 7.46 (m, 2H), 7.19 (d, *J* = 8.6 Hz, 1H), 7.01 (s, 1H), 6.87 (d, *J* = 2.2 Hz, 1H), 6.79 (dd, *J* = 8.7, 2.2 Hz, 1H), 5.27 (s, 1H), 4.33 (d, *J* = 8.2 Hz, 1H), 4.28 (d, *J* = 8.2 Hz, 1H), 3.91 (s, 3H), 3.87 (s, 3H), 1.27 (s, 3H), 0.96 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 157.0, 147.5, 144.9, 137.8, 134.3, 128.4, 127.7, 125.7, 124.9, 123.1, 122.8, 121.2, 121.0, 120.7, 110.5, 110.1, 106.1, 92.9, 84.9, 77.3, 77.0, 76.7, 55.7, 44.5, 33.1, 28.0, 26.4.

HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{24}H_{24}NO_3$ 374.1751; found 374.1761.

4-(6-fluoro-1-methyl-1H-indol-3-yl)-3,3-dimethyl-2,3-dihydronaphtho[1,2-b]furan-5-ol (3aa)



3aa

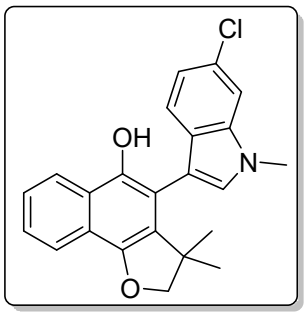
White solid, m.p. 251-252°C, 72 mg, yield: 66%; R_f = 0.38 (EtOAc/Petroleum ether 1:7).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.17 (d, *J* = 8.1 Hz, 1H), 7.96 (d, *J* = 7.4 Hz, 1H), 7.54-7.41 (m, 2H), 7.22 (dd, *J* = 8.7, 5.3 Hz, 1H), 7.13-7.07 (m, 2H), 6.89 (td, *J* = 9.1, 2.3 Hz, 1H), 5.17 (s, 1H), 4.33 (d, *J* = 8.2 Hz, 1H), 4.29 (d, *J* = 8.2 Hz, 1H), 3.88 (s, 3H), 1.26 (s, 3H), 0.93 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 161.5-159.2 (*J* = 232.3 Hz), 147.6, 144.8, 137.1-137.0 (*J* = 10.1 Hz), 134.6, 134.3 (*J* = 2.6 Hz), 129.9 (*J* = 3.6 Hz), 128.2, 127.8, 125.9, 125.0, 123.1, 122.8, 121.2 (*J* = 2.6 Hz), 121.1, 120.9, 109.9, 109.2-108.9 (*J* = 30.3 Hz), 106.5, 96.1-95.8 (*J* = 30.3 Hz), 84.9, 44.4, 33.2, 28.0, 26.4.

HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{23}H_{21}FNO_2$ 362.1551; found 362.1564.

4-(6-chloro-1-methyl-1H-indol-3-yl)-3,3-dimethyl-2,3-dihydronaphtho[1,2-b]furan-5-ol (3ab)



3ab

White solid, m.p. 253-254°C, 76 mg, yield: 67%; R_f = 0.38 (EtOAc/Petroleum ether 1:7).

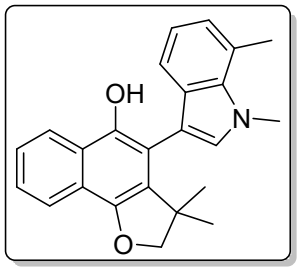
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21 (d, *J* = 8.2 Hz, 1H), 8.00 (d, *J* = 8.1 Hz, 1H), 7.58-7.42 (m, 3H), 7.30-7.22 (m, 1H), 7.18-7.08 (m, 2H), 5.17 (s, 1H), 4.35 (d, *J* = 8.2 Hz, 1H), 4.31 (d, *J* = 8.6 Hz, 1H), 3.90 (s, 3H), 1.28 (s, 3H), 0.95 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 147.6, 144.9, 137.4, 130.3, 128.7, 128.2, 127.0, 126.0, 125.1, 123.2, 122.8, 121.3, 121.2, 121.0, 120.9, 109.7, 109.7, 106.5, 84.9, 44.4, 33.2, 28.0, 26.4.

HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{23}H_{21}ClNO_2$ 378.1255; found 378.1253.

4-(1,7-dimethyl-1H-indol-3-yl)-3,3-dimethyl-2,3-dihydronaphtho[1,2-

b]furan-5-ol (3ac)



3ac

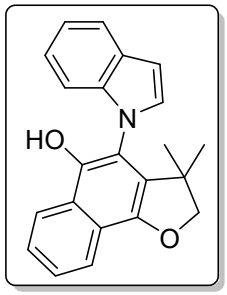
White solid, m.p. 196-197°C, 75 mg, yield: 70%; R_f = 0.33 (EtOAc/Petroleum ether 1:7).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.20 (d, *J* = 7.3 Hz, 1H), 7.97 (d, *J* = 8.0 Hz, 1H), 7.54-7.40 (m, 2H), 7.16-7.08 (m, 1H), 7.02 (s, 1H), 7.02-6.92 (m, 2H), 5.23 (s, 1H), 4.34 (d, *J* = 8.3 Hz, 1H), 4.29 (d, *J* = 8.2 Hz, 1H), 4.18 (s, 3H), 2.86 (s, 3H), 1.29 (s, 3H), 0.96 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 147.5, 144.9, 135.8, 131.2, 129.5, 128.4, 125.7, 125.1, 124.9, 123.1, 122.9, 121.4, 121.2, 120.8, 120.3, 118.4, 110.5, 105.8, 84.9, 44.5, 37.0, 28.1, 26.4, 19.7.

HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{24}H_{24}NO_2$ 358.1802; found 358.1800.

4-(1H-indol-1-yl)-3,3-dimethyl-2,3-dihydronaphtho[1,2-b]furan-5-ol (3ad)



3ad

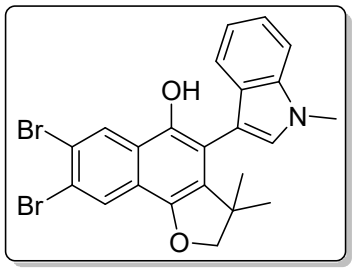
White solid, m.p. 138-139°C, 69 mg, yield: 70%; R_f = 0.53 (EtOAc/Petroleum ether 1:15).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22 (d, *J* = 8.3 Hz, 1H), 7.99 (d, *J* = 7.8 Hz, 1H), 7.77-7.69 (m, 1H), 7.61-7.47 (m, 2H), 7.25- 7.14 (m, 3H), 7.04-6.99 (m, 1H), 6.80 (d, *J* = 2.3 Hz, 1H), 4.88 (s, 1H), 4.34 (d, *J* = 8.3 Hz, 1H), 4.30 (d, *J* = 8.3 Hz, 1H), 1.22 (s, 3H), 0.79 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 148.6, 143.6, 137.6, 134.6, 129.6, 128.3, 127.7, 126.8, 125.8, 123.9, 123.1, 122.9, 121.4, 121.1, 120.7, 115.9, 110.7, 104.0, 85.2, 44.4, 27.3, 26.0.

HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{22}H_{20}NO_2$ 330.1489; found 330.1490.

7,8-dibromo-3,3-dimethyl-4-(1-methyl-1H-indol-3-yl)-2,3-dihydronaphtho[1,2-b]furan-5-ol (3ae)



3ae

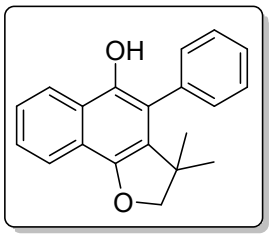
White solid, m.p. 195-196°C, 111 mg, yield: 74%; R_f = 0.23 (EtOAc/Petroleum ether 1:7).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.5 (s, 1H), 8.3 (s, 1H), 7.4 (d, *J* = 8.3 Hz, 1H), 7.4-7.3 (m, 1H), 7.3 (d, *J* = 8.2 Hz, 1H), 7.2-7.1 (m, 2H), 5.2 (s, 1H), 4.3 (d, *J* = 8.3 Hz, 1H), 4.3 (d, *J* = 8.3 Hz, 1H), 3.9 (s, 3H), 1.3 (s, 3H), 0.9 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 146.6, 144.1, 137.0, 130.3, 129.5, 128.1, 127.9, 126.2, 122.7, 121.9, 121.0, 120.3, 120.2, 120.0, 112.3, 109.6, 105.2, 85.1, 44.6, 33.2, 27.9, 26.2.

HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{23}H_{20}Br_2NO_2$ 499.9855; found 499.9856.

3,3-dimethyl-4-phenyl-2,3-dihydronaphtho[1,2-b]furan-5-ol (3af)



3af

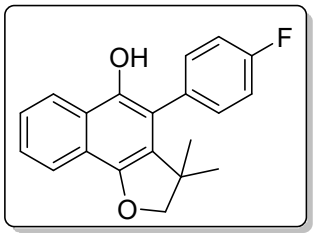
White solid, m.p. 150-151°C, 63 mg, yield: 72%; R_f = 0.51 (EtOAc/Petroleum ether 1:15).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.17 (d, *J* = 8.0 Hz, 1H), 7.95 (d, *J* = 8.2 Hz, 1H), 7.58-7.41 (m, 5H), 7.40 (d, *J* = 7.9 Hz, 2H), 4.79 (s, 1H), 4.30 (s, 2H), 1.10 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 147.8, 142.4, 133.7, 131.3, 129.0, 128.7, 127.8, 126.4, 125.8, 125.3, 123.5, 122.7, 121.3, 120.6, 119.2, 85.0, 44.4, 27.2.

HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{20}H_{19}O_2$ 291.1380; found 291.1389.

4-(4-fluorophenyl)-3,3-dimethyl-2,3-dihydronaphtho[1,2-b]furan-5-ol (3ag)



3ag

White solid, m.p. 156-158°C, 86 mg, yield: 93%; R_f = 0.51 (EtOAc/Petroleum ether 1:15).

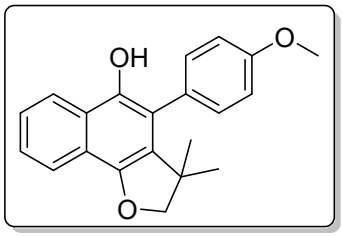
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16 (d, *J* = 7.2 Hz, 1H), 7.95 (d, *J* = 7.8 Hz, 1H), 7.51-7.44 (m, 2H), 7.42-7.31 (m, 2H), 7.22 (d, *J* = 8.8 Hz, 2H), 4.72 (s, 1H), 4.30 (s, 2H), 1.09 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 164.1-161.6 (d, *J* = 11.0 Hz), 147.9, 142.6, 134.6, 134.4 (*J* = 11.0 Hz), 133.1, 130.1, 127.8, 127.7, 126.0, 125.4, 123.5, 122.7, 121.3, 120.8, 118.1, 116.2 (*J* = 21.6 Hz), 85.0, 58.9, 27.2, 18.3.

^{19}F NMR (376 MHz, $CDCl_3$): δ -112.75.

HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{20}H_{18}FO_2$ 309.1285; found 309.1288.

4-(4-methoxyphenyl)-3,3-dimethyl-2,3-dihydronaphtho[1,2-b]furan-5-ol (3ah)



3ah

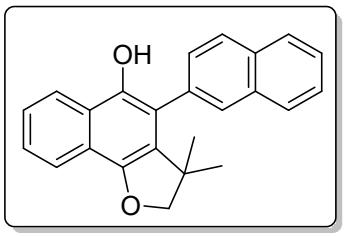
White solid, m.p. 166-167°C, 48 mg, yield: 50%; R_f = 0.33 (EtOAc/Petroleum ether 1:15).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.2 (d, *J* = 7.4 Hz, 1H), 7.9 (d, *J* = 9.3 Hz, 1H), 7.5 (m, 2H), 7.3 (d, *J* = 8.5 Hz, 2H), 7.1 (d, *J* = 8.6 Hz, 2H), 4.9 (s, 1H), 4.3 (s, 2H), 3.9 (s, 3H), 1.1 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 159.8, 147.7, 142.9, 132.5, 126.9, 125.8, 125.3, 125.2, 123.3, 122.7, 121.2, 120.6, 118.8, 114.4, 85.0, 55.3, 44.4, 27.2.

HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{21}H_{21}O_3$ 321.1485; found 321.1485.

3,3-dimethyl-4-(naphthalen-2-yl)-2,3-dihydronaphtho[1,2-b]furan-5-ol (3ai)



3ai

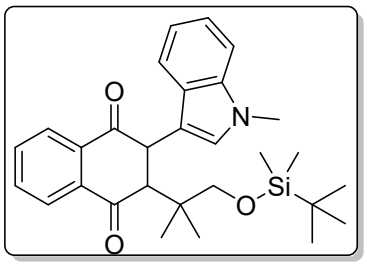
White solid, m.p. 142-143°C, 62 mg, yield: 61%; R_f = 0.37 (EtOAc/Petroleum ether 1:15).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.2 (d, *J* = 7.7 Hz, 1H), 8.0 (d, *J* = 8.3 Hz, 1H), 8.0-7.9 (m, 2H), 7.9 (d, *J* = 5.7 Hz, 2H), 7.6 (m, 2H), 7.5-7.4 (m, 3H), 4.8 (s, 1H), 4.3 (s, 2H), 1.1 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 147.9, 142.7, 134.7, 134.5, 133.9, 133.1, 131.3, 130.4, 130.0, 128.8, 127.9, 127.7, 126.8, 125.9, 125.4, 123.6, 122.7, 121.3, 120.8, 119.1, 85.1, 77.3, 77.0, 76.7, 44.5, 27.5, 18.1.

HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{24}H_{21}O_2$ 341.1536; found 341.1541.

2-(1-((*tert*-butyldimethylsilyl)oxy)-2-methylpropan-2-yl)-3-(1-methyl-1*H*-indol-3-yl)-2,3-dihydronaphthalene-1,4-dione (4a)



4a

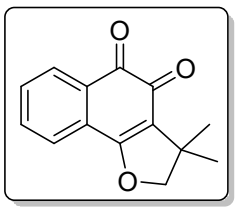
Yellow solid, m.p. 190-192°C, 90 mg, yield: 63%; R_f = 0.53 (EtOAc/Petroleum ether 1:7).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10 (d, *J* = 7.9 Hz, 1H), 7.97 (d, *J* = 7.6 Hz, 1H), 7.81 (d, *J* = 7.5 Hz, 1H) , 7.76-7.72 (m, 1H) , 7.70-7.66 (m, 1H), 7.24-7.18 (m, 3H), 6.49 (s, 1H), 4.89 (d, *J* = 4.5 Hz, 1H), 3.80 (d, *J* = 4.5 Hz, 1H), 3.58 (s, 3H), 3.54 (d, *J* = 8.7 Hz, 1H), 3.40 (d, *J* = 9.5 Hz, 1H) , 1.02 (s, 3H) , 0.91 (s, 3H) , 0.86 (s, 9H), 0.08 (s, 3H) , 0.01 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 199.0, 194.2, 137.3, 136.4, 133.8, 133.8, 127.9, 127.8, 126.9, 126.0, 122.3, 119.8, 118.9, 109.3, 108.8, 70.9, 47.6, 38.4, 32.9, 25.9, 23.8, 22.8, 18.2, -5.4, -5.6.

HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{29}H_{38}NO_3Si$ 476.2616; found 476.2616.

3,3-dimethyl-2,3-dihydronaphtho[1,2-*b*]furan-4,5-dione (5a)



5a

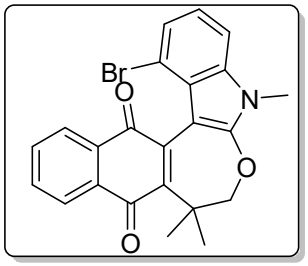
Yellow solid, m.p. 101-102°C, 18 mg, yield: 78%; R_f = 0.34 (EtOAc/Petroleum ether 1:3).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 (d, *J* = 8.4 Hz, 1H), 7.69-7.59 (m, 2H), 7.56 (m, 1H), 4.47 (s, 2H), 1.48 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 181.4, 175.3, 169.0, 134.5, 131.7, 130.8, 129.3, 127.8, 124.4, 122.8, 87.3, 42.5, 25.9.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{14}H_{12}O_3Na$ 251.0679; found 251.0683.

1-bromo-5,8,8-trimethyl-7,8-dihydro-5*H*-naphtho[2',3':4,5]oxepino[2,3-*b*]indole-9,14-dione (6a)



6a

Red solid, m.p. 209-210°C, 23 mg, yield: 53%; R_f = 0.33 (EtOAc/Petroleum ether 1:7).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (m, 2H), 7.75-7.63 (m, 2H), 7.32-7.26 (m, 1H), 7.16 (d, *J* = 8.1 Hz, 1H), 7.03 (m, 1H), 4.38 (d, *J* = 11.7 Hz, 1H), 4.22 (d, *J* = 11.6 Hz, 1H), 3.63 (s, 3H), 1.71 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 187.5, 183.1, 155.5, 145.0, 144.6, 134.4, 133.6, 133.0, 132.5, 126.7, 126.1, 125.9, 125.5, 122.2, 113.8, 107.9, 90.6, 82.9, 42.0, 28.0, 27.0, 20.6.

HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{23}H_{19}BrNO_3$ 436.0543; found 436.0544.

8. X-Ray Analysis

Compound **3a** X-Ray crystal diffraction data: Crystals were grown in slow diffusion with EA as clusters of colorless prisms. The ellipsoids are shown at 30% probability levels. Compounds **3a** was collected at 100 K on a Rigaku Oxford Diffraction Supernova Dual Source, Cu at Zero equipped with an AtlasS2 CCD using Cu Kα radiation. The data were collected and processed using CrysAlisPro. The structure was solved by direct methods using Olex2 software, 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 2079811 for compounds **3a**.

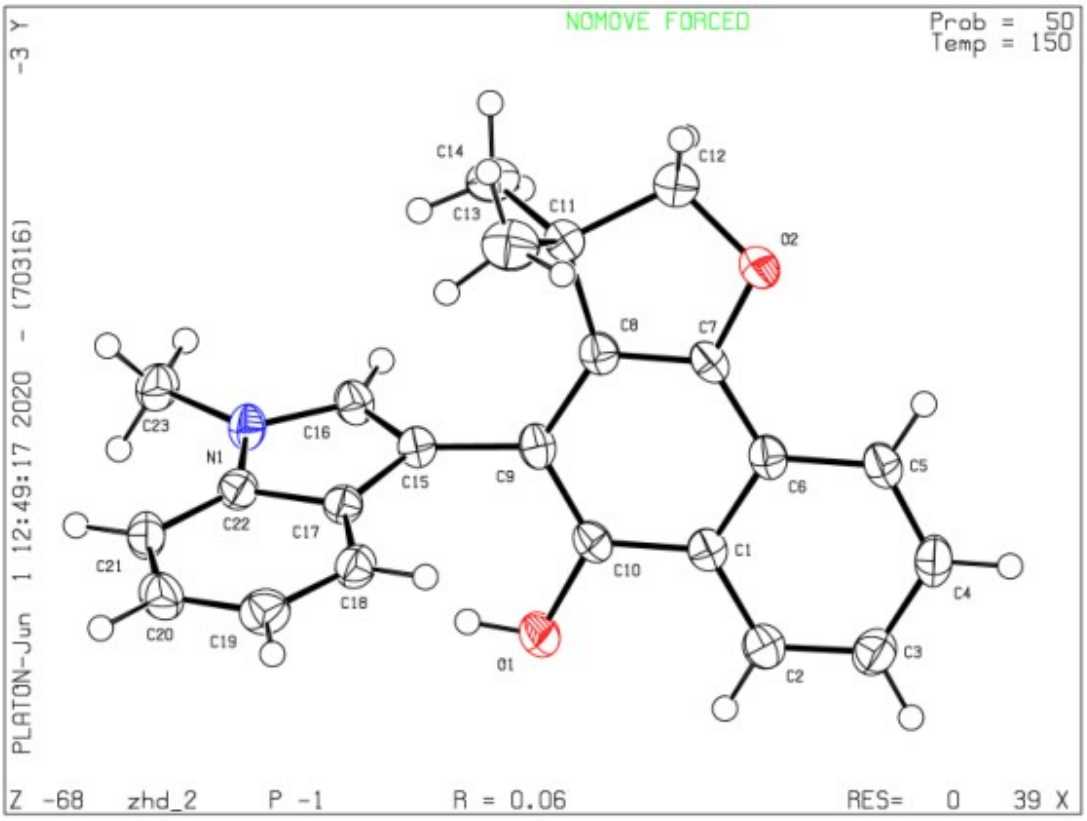


Figure S1. ORTEP Drawing of **3a** (The ellipsoids are shown at 30% probability levels)

Table 1 Crystal data and structure refinement for 3a.

Identification code	3a
Empirical formula	$C_{23}H_{21}NO_2$
Formula weight	343.41
Temperature/K	150.00(16)
Crystal system	triclinic
Space group	P-1

a/Å	9.3482(13)
b/Å	9.9667(14)
c/Å	11.3283(15)
α/°	111.927(13)
β/°	101.129(12)
γ/°	108.193(13)
Volume/Å^3	870.9(2)
Z	2
ρ_{calc}g/cm^3	1.310
μ/mm^{-1}	0.083
F(000)	364.0
Crystal size/mm^3	0.14 × 0.13 × 0.12
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.14 to 49.994
Index ranges	-11 ≤ h ≤ 10, -11 ≤ k ≤ 11, -11 ≤ l ≤ 13
Reflections collected	6225
Independent reflections	3034 [R_{int} = 0.0477, R_{sigma} = 0.0640]
Data/restraints/parameters	3034/0/242
Goodness-of-fit on F^2	1.054
Final R indexes [I>=2σ (I)]	R_1 = 0.0585, wR_2 = 0.1441
Final R indexes [all data]	R_1 = 0.0787, wR_2 = 0.1644
Largest diff. peak/hole / e Å^{-3}	0.27/-0.25

Crystal structure determination of [3a]

Crystal Data for $C_{23}H_{21}NO_2$ (*M* =343.41 g/mol): triclinic, space group P-1 (no. 2), *a* = 9.3482(13) Å, *b* = 9.9667(14) Å, *c* = 11.3283(15) Å, *α* = 111.927(13)°, *β* = 101.129(12)°, *γ* = 108.193(13)°, *V* = 870.9(2) Å^3, *Z* = 2, *T* = 150.00(16) K, μ(Mo Kα) = 0.083 mm^{-1}, *Dcalc* = 1.310 g/cm^3, 6225 reflections measured (4.14° ≤ 2Θ ≤ 49.994°), 3034 unique (R_{int} = 0.0477, R_{sigma} = 0.0640) which were used in all calculations. The final R_1 was 0.0585 (I > 2σ(I)) and wR_2 was 0.1644 (all data).

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)
C1	-8542(3)	-13042(3)	-5251(2)	24.4(5)
C2	-10053(3)	-14243(3)	-6219(2)	29.1(6)
C3	-10262(3)	-15783(3)	-6920(3)	34.6(6)
C4	-8970(3)	-16202(3)	-6690(3)	34.1(6)
C5	-7483(3)	-15077(3)	-5792(2)	28.5(6)
C6	-7226(3)	-13461(3)	-5056(2)	25.5(5)

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)
C7	-5737(3)	-12226(3)	-4124(2)	24.6(5)
C8	-5481(3)	-10672(3)	-3407(2)	25.6(5)
C9	-6795(3)	-10240(3)	-3576(2)	24.5(5)
C10	-8285(3)	-11432(3)	-4490(2)	25.4(5)
C11	-3748(3)	-9708(3)	-2433(2)	27.4(6)
C12	-3060(3)	-10937(3)	-2978(3)	43.1(7)
C13	-3678(3)	-9315(4)	-974(3)	42.7(7)
C14	-2821(3)	-8201(3)	-2511(3)	37.7(7)
C15	-6664(3)	-8597(3)	-2823(2)	25.7(5)
C16	-5984(3)	-7299(3)	-3011(2)	28.4(6)
C17	-7375(3)	-8097(3)	-1809(2)	24.9(5)
C18	-8242(3)	-8850(3)	-1182(2)	29.5(6)
C19	-8768(3)	-7994(3)	-230(3)	35.9(6)
C20	-8439(3)	-6400(3)	116(3)	35.8(6)
C21	-7587(3)	-5622(3)	-470(2)	30.9(6)
C22	-7047(3)	-6483(3)	-1436(2)	25.8(5)
C23	-5548(3)	-4426(3)	-2062(3)	33.3(6)
N1	-6201(2)	-6026(2)	-2189(2)	27.8(5)
O1	-9611(2)	-11120(2)	-4726.1(19)	34.8(5)
O2	-4378.5(19)	-12496.5(19)	-3823.1(17)	31.7(4)

Table 3 Anisotropic Displacement Parameters (Å^2×10^3) 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}
C1	29.2(13)	24.9(13)	25.9(13)	15.3(11)	13.4(10)	12.9(10)
C2	31.8(13)	30.1(14)	29.0(14)	15.4(12)	11.6(11)	15.1(11)
C3	33.5(14)	29.6(15)	32.0(14)	9.4(13)	10.7(12)	9.4(11)
C4	43.0(15)	23.2(14)	35.6(15)	10.4(12)	19.6(12)	13.8(12)
C5	34.5(13)	27.0(14)	33.7(14)	16.7(12)	18.2(11)	18.0(11)
C6	32.2(13)	24.7(13)	27.5(13)	14.9(11)	17.6(11)	14.1(11)
C7	28.6(12)	27.8(14)	28.5(13)	16.5(12)	15.9(10)	17.5(11)
C8	29.4(13)	26.3(13)	25.8(13)	13.7(11)	13.5(10)	12.9(10)
C9	33.7(13)	23.8(13)	23.5(12)	14.1(11)	12.4(10)	16.0(11)
C10	28.2(12)	27.8(14)	28.4(13)	15.9(12)	12.7(10)	16.4(11)
C11	27.2(12)	26.8(14)	29.2(13)	12.2(12)	11.0(11)	13.1(10)
C12	30.5(14)	33.2(16)	52.3(18)	9.6(14)	8.5(13)	13.7(12)
C13	40.2(15)	52.8(19)	36.5(16)	23.4(15)	11.9(13)	19.2(14)

Table 3 Anisotropic Displacement Parameters ($Å^2×10^3$) 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}
C14	29.5(14)	39.6(17)	42.1(16)	21.3(14)	11.5(12)	10.2(12)
C15	26.5(12)	24.1(13)	26.4(13)	10.7(11)	9.4(10)	11.7(10)
C16	32.1(13)	28.6(14)	27.8(13)	12.6(12)	14.0(11)	15.4(11)
C17	23.0(12)	24.0(13)	25.4(13)	10.7(11)	5.2(10)	10.1(10)
C18	29.9(13)	24.1(14)	31.4(14)	12.3(12)	8.3(11)	9.7(11)
C19	33.1(14)	39.3(16)	34.5(15)	17.4(13)	15.6(12)	11.8(12)
C20	37.0(14)	39.5(16)	30.5(14)	11.0(13)	15.3(12)	19.9(12)
C21	35.5(14)	24.6(14)	29.4(14)	8.8(12)	9.7(11)	14.5(11)
C22	25.9(12)	24.4(13)	25.6(13)	11.2(11)	6.9(10)	10.8(10)
C23	35.1(14)	24.7(14)	40.3(15)	17.3(13)	11.5(12)	11.3(11)
N1	33.2(11)	21.0(11)	30.4(11)	12.4(10)	11.8(9)	12.1(9)
O1	31.7(9)	29.8(11)	40.3(11)	12.4(10)	6.9(8)	18.2(8)
O2	28.6(9)	28.3(10)	41.6(11)	15.5(9)	13.9(8)	16.1(8)

Table 4 Bond Lengths for 3a.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C1	C2	1.413(3)	C11	C12	1.541(3)
C1	C6	1.422(3)	C11	C13	1.532(3)
C1	C10	1.422(3)	C11	C14	1.527(3)
C2	C3	1.367(3)	C12	O2	1.445(3)
C3	C4	1.405(3)	C15	C16	1.367(3)
C4	C5	1.361(4)	C15	C17	1.443(3)
C5	C6	1.423(3)	C16	N1	1.367(3)
C6	C7	1.400(3)	C17	C18	1.402(3)
C7	C8	1.368(3)	C17	C22	1.412(3)
C7	O2	1.384(3)	C18	C19	1.382(3)
C8	C9	1.425(3)	C19	C20	1.398(4)
C8	C11	1.521(3)	C20	C21	1.371(4)
C9	C10	1.384(3)	C21	C22	1.403(3)
C9	C15	1.488(3)	C22	N1	1.373(3)
C10	O1	1.371(3)	C23	N1	1.458(3)

Table 5 Bond Angles for 3a.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C2	C1	C6	118.4(2)	C8	C11	C14	115.09(19)
C2	C1	C10	122.5(2)	C13	C11	C12	111.4(2)
C6	C1	C10	119.1(2)	C14	C11	C12	109.3(2)
C3	C2	C1	120.9(2)	C14	C11	C13	110.7(2)

Table 5 Bond Angles for 3a.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C2	C3	C4	120.4(2)	O2	C12	C11	108.83(19)
C5	C4	C3	120.7(2)	C16	C15	C9	128.2(2)
C4	C5	C6	120.1(2)	C16	C15	C17	105.8(2)
C1	C6	C5	119.3(2)	C17	C15	C9	125.8(2)
C7	C6	C1	116.7(2)	C15	C16	N1	111.1(2)
C7	C6	C5	124.0(2)	C18	C17	C15	134.2(2)
C8	C7	C6	124.4(2)	C18	C17	C22	119.0(2)
C8	C7	O2	113.7(2)	C22	C17	C15	106.7(2)
O2	C7	C6	121.9(2)	C19	C18	C17	118.9(2)
C7	C8	C9	119.5(2)	C18	C19	C20	121.1(2)
C7	C8	C11	109.13(19)	C21	C20	C19	121.6(2)
C9	C8	C11	131.1(2)	C20	C21	C22	117.6(2)
C8	C9	C15	124.1(2)	C21	C22	C17	121.7(2)
C10	C9	C8	117.6(2)	N1	C22	C17	108.04(19)
C10	C9	C15	118.3(2)	N1	C22	C21	130.2(2)
C9	C10	C1	122.7(2)	C16	N1	C22	108.37(19)
O1	C10	C1	115.8(2)	C16	N1	C23	125.8(2)
O1	C10	C9	121.5(2)	C22	N1	C23	125.74(19)
C8	C11	C12	99.66(19)	C7	O2	C12	105.75(18)
C8	C11	C13	110.19(19)				

Table 6 Torsion Angles for 3a.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C1	C2	C3	C4	-0.1(4)	C9	C15	C17	C22	-175.9(2)
C1	C6	C7	C8	-0.2(3)	C10	C1	C2	C3	-179.1(2)
C1	C6	C7	O2	178.31(18)	C10	C1	C6	C5	178.6(2)
C2	C1	C6	C5	-2.7(3)	C10	C1	C6	C7	-0.9(3)
C2	C1	C6	C7	177.8(2)	C10	C9	C15	C16	-106.5(3)
C2	C1	C10	C9	-177.7(2)	C10	C9	C15	C17	67.5(3)
C2	C1	C10	O1	1.7(3)	C11	C8	C9	C10	-174.9(2)
C2	C3	C4	C5	-1.5(4)	C11	C8	C9	C15	4.5(4)
C3	C4	C5	C6	1.0(4)	C11	C12	O2	C7	16.3(3)
C4	C5	C6	C1	1.1(3)	C13	C11	C12	O2	99.6(3)
C4	C5	C6	C7	-179.4(2)	C14	C11	C12	O2	-137.7(2)
C5	C6	C7	C8	-179.7(2)	C15	C9	C10	C1	-179.43(19)
C5	C6	C7	O2	-1.2(3)	C15	C9	C10	O1	1.2(3)
C6	C1	C2	C3	2.2(3)	C15	C16	N1	C22	-0.1(3)
C6	C1	C10	C9	1.0(3)	C15	C16	N1	C23	175.9(2)

Table 6 Torsion Angles for 3a.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C6	C1	C10	O1	-179.61(18)	C15	C17	C18	C19	-179.6(2)
C6	C7	C8	C9	1.2(3)	C15	C17	C22	C21	179.3(2)
C6	C7	C8	C11	176.3(2)	C15	C17	C22	N1	0.7(2)
C6	C7	O2	C12	172.5(2)	C16	C15	C17	C18	179.6(2)
C7	C8	C9	C10	-1.1(3)	C16	C15	C17	C22	-0.7(2)
C7	C8	C9	C15	178.3(2)	C17	C15	C16	N1	0.5(3)
C7	C8	C11	C12	11.5(2)	C17	C18	C19	C20	-0.4(4)
C7	C8	C11	C13	-105.8(2)	C17	C22	N1	C16	-0.3(3)
C7	C8	C11	C14	128.2(2)	C17	C22	N1	C23	-176.4(2)
C8	C7	O2	C12	-8.8(3)	C18	C17	C22	C21	-1.0(3)
C8	C9	C10	C1	0.0(3)	C18	C17	C22	N1	-179.63(19)
C8	C9	C10	O1	-179.32(19)	C18	C19	C20	C21	0.0(4)
C8	C9	C15	C16	74.0(3)	C19	C20	C21	C22	-0.1(4)
C8	C9	C15	C17	-111.9(3)	C20	C21	C22	C17	0.6(3)
C8	C11	C12	O2	-16.7(2)	C20	C21	C22	N1	178.9(2)
C9	C8	C11	C12	-174.3(2)	C21	C22	N1	C16	-178.9(2)
C9	C8	C11	C13	68.5(3)	C21	C22	N1	C23	5.1(4)
C9	C8	C11	C14	-57.5(3)	C22	C17	C18	C19	0.8(3)
C9	C15	C16	N1	175.5(2)	O2	C7	C8	C9	-177.37(18)
C9	C15	C17	C18	4.5(4)	O2	C7	C8	C11	-2.3(3)

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

Atom	*x*	*y*	*z*	U(eq)
H2	-10936.59	-13976.53	-6384.98	35
H3	-11286.59	-16576.06	-7565.47	42
H4	-9136.07	-17281.11	-7167.56	41
H5	-6615.17	-15371.67	-5655.99	34
H12A	-2414.82	-10648.6	-3514.57	52
H12B	-2351.46	-10944.33	-2210.14	52
H13A	-2556.2	-8692.83	-355.29	64
H13B	-4134.23	-10307.18	-916.36	64
H13C	-4297.41	-8691.89	-716.81	64
H14A	-3174.54	-7375.42	-2073	57
H14B	-3026.62	-8442.67	-3465.21	57
H14C	-1667.27	-7817.43	-2044.2	57
H16	-5433.97	-7283.38	-3632.2	34
H18	-8465.18	-9930.73	-1407.96	35

Table 7 Hydrogen Atom Coordinates (Å×10⁴) and Isotropic Displacement Parameters (Å²×10³) for 3a.

Atom	*x*	*y*	*z*	U(eq)
H19	-9361.9	-8496.78	195.44	43
H20	-8816.33	-5842.57	773.12	43
H21	-7369.39	-4539.91	-231.57	37
H23A	-6431.38	-4140.67	-2314.26	50
H23B	-4930.03	-4398.73	-2667.23	50
H23C	-4842.77	-3661.72	-1120.94	50
H1	-9330(50)	-10080(50)	-4170(50)	116(16)

Compound **5a** X-Ray crystal diffraction data: Crystals were grown in slow diffusion with EA as clusters of colorless prisms. The ellipsoids are shown at 30% probability levels. Compounds **5a** was collected at 100 K on a Rigaku Oxford Diffraction Supernova Dual Source, Cu at Zero equipped with an AtlasS2 CCD using Cu Kα radiation. The data were collected and processed using CrysAlisPro. The structure was solved by direct methods using Olex2 software, 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 2079812 for compounds **5a**.

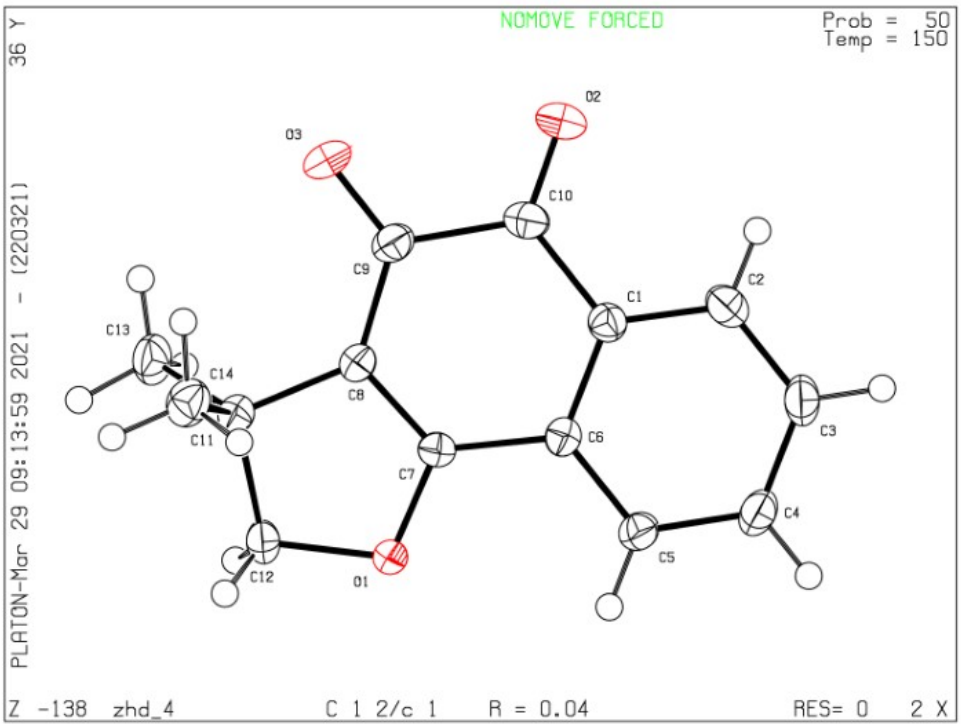


Figure S2. ORTEP Drawing of **5a** (The ellipsoids are shown at 30% probability levels)

Table 8 Crystal data and structure refinement for 5a.

Identification code	5a
Empirical formula	$C_{14}H_{12}O_3$
Formula weight	228.24
Temperature/K	149.99(10)
Crystal system	monoclinic
Space group	C2/c
a/Å	11.3788(6)
b/Å	16.9785(9)
c/Å	11.7105(7)
α/°	90
β/°	103.517(6)
γ/°	90
Volume/Å^3	2199.7(2)
Z	8
ρ_{calc}g/cm^3	1.378
μ/mm^{-1}	0.097
F(000)	960.0
Crystal size/mm^3	0.14 × 0.13 × 0.12
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.394 to 49.974
Index ranges	-13 ≤ h ≤ 11, -20 ≤ k ≤ 20, -13 ≤ l ≤ 13
Reflections collected	4318
Independent reflections	1938 [R_{int} = 0.0157, R_{sigma} = 0.0219]
Data/restraints/parameters	1938/0/157
Goodness-of-fit on F^2	1.014
Final R indexes [I>=2σ (I)]	R_1 = 0.0379, wR_2 = 0.1010
Final R indexes [all data]	R_1 = 0.0427, wR_2 = 0.1052
Largest diff. peak/hole / e Å^{-3}	0.27/-0.17

Crystal structure determination of [5a]

Crystal Data for $C_{14}H_{12}O_3$ (*M* =228.24 g/mol): monoclinic, space group C2/c (no. 15), *a* = 11.3788(6) Å, *b* = 16.9785(9) Å, *c* = 11.7105(7) Å, *β* = 103.517(6)°, *V* = 2199.7(2) Å^3, *Z* = 8, *T* = 149.99(10) K, μ(Mo Kα) = 0.097 mm^{-1}, *Dcalc* = 1.378 g/cm^3, 4318 reflections measured (4.394° ≤ 2Θ ≤ 49.974°), 1938 unique (R_{int} = 0.0157, R_{sigma} = 0.0219) which were used in all calculations. The final R_1 was 0.0379 (I > 2σ(I)) and wR_2 was 0.1052 (all data).

Table 9 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for 5a. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
O1	6015.8(8)	4796.8(5)	3812.3(8)	21.3(3)
O2	7187.1(11)	1858.8(6)	2781.3(10)	41.9(3)
O3	8302.9(10)	3129.0(6)	2078.6(10)	37.2(3)
C1	6107.4(11)	2634.9(8)	3873.2(11)	20.9(3)
C2	5626.8(13)	1998.9(8)	4355.4(13)	28.7(4)
C3	4860.6(13)	2115.8(9)	5097.4(13)	30.8(4)
C4	4569.0(13)	2870.9(9)	5374.7(13)	29.7(4)
C5	5030.0(11)	3516.7(8)	4895.2(11)	23.8(3)
C6	5795.0(11)	3402.2(8)	4143.4(11)	18.5(3)
C7	6332.1(11)	4051.1(7)	3628.0(10)	17.2(3)
C8	7174.6(11)	3989.3(7)	2989.6(11)	19.1(3)
C9	7558.3(12)	3235.2(8)	2661.9(12)	23.7(3)
C10	6953.8(12)	2507.0(8)	3089.7(12)	25.4(3)
C11	7608.0(11)	4802.1(8)	2747.1(11)	20.7(3)
C12	6672.0(12)	5311.9(8)	3163.2(12)	25.0(3)
C13	7575.0(14)	4939.2(8)	1453.4(12)	30.4(4)
C14	8881.8(12)	4944.6(8)	3505.0(13)	29.2(4)

Table 10 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for 5a. 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	26.1(5)	16.5(5)	24.9(5)	1.5(4)	13.3(4)	1.5(4)
O2	56.6(8)	21.7(6)	56.8(8)	-7.8(5)	32.4(6)	2.3(5)
O3	43.1(7)	34.0(6)	44.8(7)	-4.3(5)	31.0(5)	3.5(5)
C1	20.4(7)	20.2(7)	22.1(7)	0.1(5)	4.7(5)	-0.3(6)
C2	30.0(8)	18.9(7)	38.6(8)	0.1(6)	10.7(6)	0.2(6)
C3	30.6(8)	25.9(8)	39.2(9)	9.7(6)	14.5(7)	-2.5(6)
C4	29.5(8)	31.7(8)	32.9(8)	7.8(6)	17.5(6)	2.7(6)
C5	25.0(7)	23.0(7)	26.2(7)	3.8(6)	11.4(6)	4.7(6)
C6	17.1(6)	20.7(7)	17.1(6)	1.9(5)	3.1(5)	0.1(5)
C7	17.8(6)	17.4(7)	15.7(6)	-0.5(5)	2.7(5)	1.3(5)
C8	18.7(6)	21.4(7)	17.6(6)	0.2(5)	5.2(5)	-0.3(5)
C9	23.8(7)	26.4(7)	22.8(7)	-2.1(6)	9.2(5)	0.6(6)
C10	27.8(7)	21.1(7)	27.9(7)	-3.5(6)	7.8(6)	2.9(6)
C11	21.9(7)	21.4(7)	20.1(7)	0.2(5)	7.5(5)	-1.2(5)
C12	26.2(7)	20.1(7)	31.5(8)	5.3(6)	12.4(6)	-1.7(6)
C13	40.6(9)	29.9(8)	22.9(8)	1.8(6)	11.9(6)	-7.5(7)

Table 10 Anisotropic Displacement Parameters ($Å^2×10^3$) for 5a. 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}
C14	24.5(7)	33.2(8)	30.7(8)	-1.7(6)	7.8(6)	-4.6(6)

Table 11 Bond Lengths for 5a.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	C7	1.3473(15)	C5	C6	1.3888(18)
O1	C12	1.4715(16)	C6	C7	1.4573(18)
O2	C10	1.2071(16)	C7	C8	1.3506(18)
O3	C9	1.2196(17)	C8	C9	1.4337(18)
C1	C2	1.3887(19)	C8	C11	1.5145(17)
C1	C6	1.4059(18)	C9	C10	1.5538(19)
C1	C10	1.4931(18)	C11	C12	1.5375(19)
C2	C3	1.382(2)	C11	C13	1.5245(19)
C3	C4	1.382(2)	C11	C14	1.5316(19)
C4	C5	1.389(2)			

Table 12 Bond Angles for 5a.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C7	O1	C12	106.79(9)	C7	C8	C11	109.72(11)
C2	C1	C6	119.00(12)	C9	C8	C11	129.09(12)
C2	C1	C10	120.58(12)	O3	C9	C8	125.23(13)
C6	C1	C10	120.42(12)	O3	C9	C10	118.74(12)
C3	C2	C1	120.69(13)	C8	C9	C10	116.03(11)
C4	C3	C2	120.17(13)	O2	C10	C1	122.34(13)
C3	C4	C5	120.20(13)	O2	C10	C9	118.96(13)
C6	C5	C4	119.84(13)	C1	C10	C9	118.70(11)
C1	C6	C7	117.05(12)	C8	C11	C12	99.99(10)
C5	C6	C1	120.08(12)	C8	C11	C13	113.08(11)
C5	C6	C7	122.85(12)	C8	C11	C14	109.92(11)
O1	C7	C6	119.37(11)	C13	C11	C12	111.78(11)
O1	C7	C8	114.36(11)	C13	C11	C14	110.61(11)
C8	C7	C6	126.23(11)	C14	C11	C12	111.06(11)
C7	C8	C9	121.17(12)	O1	C12	C11	107.57(10)

Table 13 Torsion Angles for 5a.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
O1	C7	C8	C9	-176.50(10)	C7	O1	C12	C11	-10.36(13)
O1	C7	C8	C11	4.89(15)	C7	C8	C9	O3	179.23(13)
O3	C9	C10	O2	-4.0(2)	C7	C8	C9	C10	-0.31(19)

Table 13 Torsion Angles for 5a.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
O3	C9	C10	C1	175.78(12)	C7	C8	C11	C12	-10.45(13)
C1	C2	C3	C4	-0.4(2)	C7	C8	C11	C13	-129.44(12)
C1	C6	C7	O1	176.74(10)	C7	C8	C11	C14	106.41(12)
C1	C6	C7	C8	-5.55(19)	C8	C9	C10	O2	175.60(13)
C2	C1	C6	C5	0.89(19)	C8	C9	C10	C1	-4.65(18)
C2	C1	C6	C7	179.31(11)	C8	C11	C12	O1	12.24(12)
C2	C1	C10	O2	5.2(2)	C9	C8	C11	C12	171.09(13)
C2	C1	C10	C9	-174.56(12)	C9	C8	C11	C13	52.10(18)
C2	C3	C4	C5	1.0(2)	C9	C8	C11	C14	-72.05(16)
C3	C4	C5	C6	-0.6(2)	C10	C1	C2	C3	178.83(13)
C4	C5	C6	C1	-0.35(19)	C10	C1	C6	C5	-178.46(11)
C4	C5	C6	C7	-178.67(12)	C10	C1	C6	C7	-0.04(18)
C5	C6	C7	O1	-4.88(18)	C11	C8	C9	O3	-2.5(2)
C5	C6	C7	C8	172.82(12)	C11	C8	C9	C10	178.00(11)
C6	C1	C2	C3	-0.5(2)	C12	O1	C7	C6	-178.45(10)
C6	C1	C10	O2	-175.47(13)	C12	O1	C7	C8	3.58(14)
C6	C1	C10	C9	4.78(19)	C13	C11	C12	O1	132.18(11)
C6	C7	C8	C9	5.7(2)	C14	C11	C12	O1	-103.77(12)
C6	C7	C8	C11	-172.92(11)					

Table 14 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 5a.

Atom	*x*	*y*	*z*	U(eq)
H2	5822.7	1488.87	4176.98	34
H3	4540.23	1685.17	5411.04	37
H4	4062.54	2947.01	5883.82	36
H5	4826.88	4024.33	5077.22	29
H12A	7073.1	5732	3668.43	30
H12B	6114.54	5545.69	2494.57	30
H13A	8140.09	4592.81	1214.57	46
H13B	7788.2	5475.87	1340.58	46
H13C	6775.82	4835.2	990.31	46
H14A	8873.44	4892.6	4319.37	44
H14B	9142.34	5465.54	3361.85	44
H14C	9428.19	4564.86	3308.87	44

Compound **6a** X-Ray crystal diffraction data: Crystals were grown in slow diffusion with EA as clusters of colorless prisms. The ellipsoids are shown at 30% probability levels. Compounds **6a** was collected at 100 K on a Rigaku Oxford Diffraction

Supernova Dual Source, Cu at Zero equipped with an AtlasS2 CCD using Cu Kα radiation. The data were collected and processed using CrysAlisPro. The structure was solved by direct methods using Olex2 software, 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 2079813 for compounds **6a**.

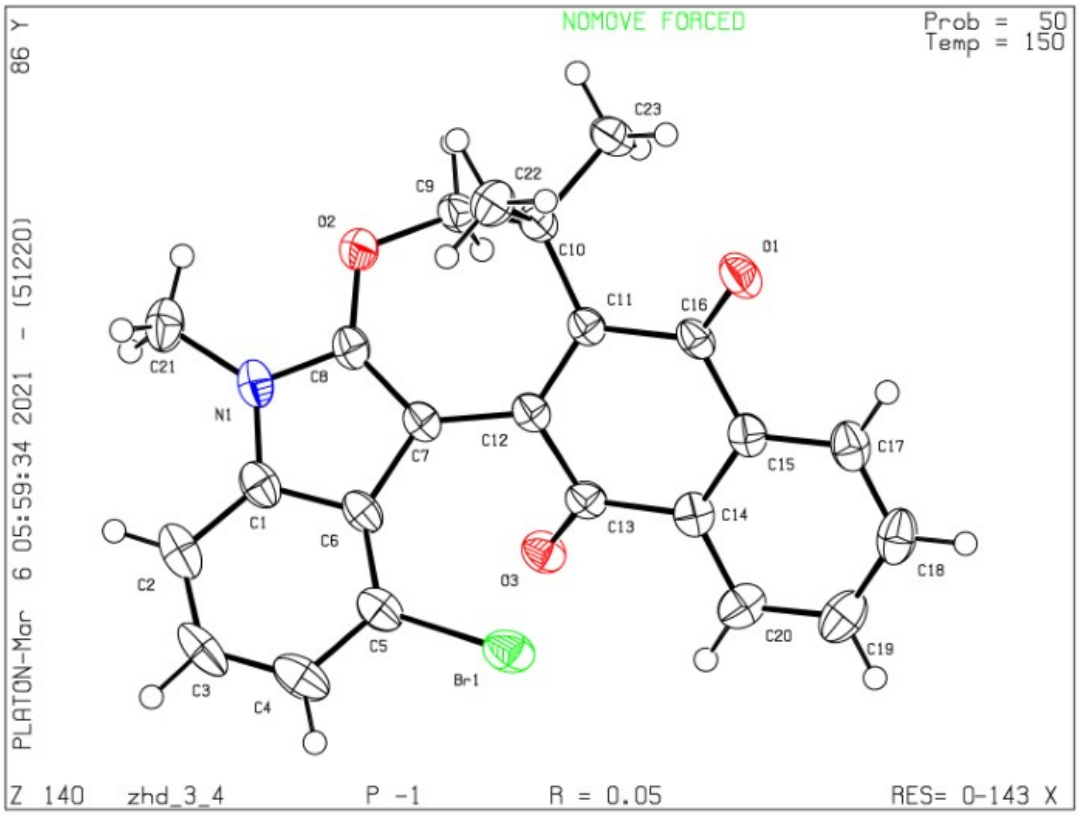


Figure S3. ORTEP Drawing of **6a** (The ellipsoids are shown at 30% probability levels)

Table 15 Crystal data and structure refinement for 6a.

Identification code	6a
Empirical formula	$C_{23}H_{18}BrNO_3$
Formula weight	436.29
Temperature/K	149.99(10)
Crystal system	triclinic
Space group	P-1
a/Å	7.5489(4)
b/Å	9.1816(6)
c/Å	13.9165(8)
α/°	89.982(5)

β/°	85.879(4)
γ/°	71.987(5)
Volume/Å^3	914.67(10)
Z	2
ρ_{calc}g/cm^3	1.584
μ/mm^{-1}	3.272
F(000)	444.0
Crystal size/mm^3	0.13 × 0.11 × 0.09
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	6.37 to 133.202
Index ranges	-8 ≤ h ≤ 7, -10 ≤ k ≤ 9, -16 ≤ l ≤ 16
Reflections collected	5619
Independent reflections	3214 [R_{int} = 0.0585, R_{sigma} = 0.0488]
Data/restraints/parameters	3214/0/256
Goodness-of-fit on F^2	1.075
Final R indexes [I>=2σ (I)]	R_1 = 0.0480, wR_2 = 0.1318
Final R indexes [all data]	R_1 = 0.0518, wR_2 = 0.1356
Largest diff. peak/hole / e Å^{-3}	0.64/-1.03

Crystal structure determination of [6a]

Crystal Data for $C_{23}H_{18}BrNO_3$ (*M* =436.29 g/mol): triclinic, space group P-1 (no. 2), *a* = 7.5489(4) Å, *b* = 9.1816(6) Å, *c* = 13.9165(8) Å, *α* = 89.982(5)°, *β* = 85.879(4)°, *γ* = 71.987(5)°, *V* = 914.67(10) Å^3, *Z* = 2, *T* = 149.99(10) K, μ(Cu Kα) = 3.272 mm^{-1}, *Dcalc* = 1.584 g/cm^3, 5619 reflections measured (6.37° ≤ 2Θ ≤ 133.202°), 3214 unique (R_{int} = 0.0585, R_{sigma} = 0.0488) which were used in all calculations. The final R_1 was 0.0480 (I > 2σ(I)) and wR_2 was 0.1356 (all data).

Table 16 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 6a. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Br1	10215.9(5)	2382.4(4)	7483.2(3)	40.28(18)
O1	7670(4)	7830(3)	5132.6(17)	37.0(6)
O2	5063(4)	8518(3)	8843.4(16)	34.8(6)
O3	5829(3)	3699(3)	7239.0(17)	32.4(5)
N1	6285(4)	6606(4)	9868.7(19)	33.0(7)
C1	7333(5)	5087(4)	9849(2)	32.3(7)
C2	7911(6)	4165(5)	10631(3)	41.4(9)
C3	9033(6)	2678(5)	10439(3)	45.7(10)
C4	9640(5)	2170(5)	9495(3)	43.2(9)
C5	9047(5)	3112(4)	8724(3)	34.7(8)
C6	7785(4)	4584(4)	8875(2)	27.9(7)

Table 16 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for 6a. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
C7	6863(5)	5875(4)	8285(2)	27.4(7)
C8	6041(5)	7055(4)	8944(2)	29.8(7)
C9	4457(5)	8955(4)	7897(2)	31.0(7)
C10	6032(5)	8791(4)	7087(2)	29.0(7)
C11	6627(4)	7162(4)	6665(2)	24.9(6)
C12	6811(4)	5901(4)	7239(2)	25.1(6)
C13	6605(4)	4490(4)	6777(2)	26.2(7)
C14	7179(4)	4177(4)	5739(2)	29.2(7)
C15	7408(4)	5355(4)	5172(2)	28.5(7)
C16	7202(4)	6881(4)	5615(2)	27.2(7)
C17	7862(5)	5100(5)	4183(2)	34.7(8)
C18	8122(5)	3667(5)	3785(3)	40.0(9)
C19	7955(5)	2483(5)	4353(3)	41.6(9)
C20	7452(5)	2727(4)	5329(3)	36.0(8)
C21	5545(6)	7571(5)	10724(2)	40.5(9)
C22	7674(5)	9199(4)	7451(3)	36.3(8)
C23	5038(5)	10002(4)	6362(3)	35.0(8)

Table 17 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for 6a. 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}
Br1	29.8(2)	34.6(3)	48.5(3)	7.28(17)	0.36(16)	0.71(17)
O1	38.8(14)	39.3(14)	30.5(12)	11.3(10)	0.6(10)	-9.3(12)
O2	39.8(14)	32.5(13)	26.8(12)	0.6(10)	2.7(10)	-4.4(11)
O3	31.0(13)	32.4(13)	34.3(12)	5.5(10)	0.6(10)	-11.3(11)
N1	35.4(16)	42.7(18)	23.2(13)	5.0(12)	-1.7(11)	-15.6(14)
C1	29.8(17)	41(2)	30.7(17)	10.0(14)	-5.9(13)	-16.9(16)
C2	41(2)	58(3)	33.1(18)	17.7(17)	-11.3(15)	-25.0(19)
C3	44(2)	56(3)	44(2)	31.1(19)	-20.0(17)	-22(2)
C4	30.8(19)	43(2)	57(2)	21.8(18)	-13.0(17)	-11.0(17)
C5	30.4(18)	36.4(19)	38.7(19)	11.1(15)	-7.5(14)	-11.4(15)
C6	22.4(15)	34.3(18)	29.1(16)	10.3(13)	-6.0(12)	-10.7(14)
C7	27.3(16)	29.2(17)	25.8(16)	5.6(13)	-2.2(12)	-9.1(14)
C8	30.3(17)	34.5(19)	25.1(16)	4.2(13)	0.0(13)	-11.1(15)
C9	27.1(17)	29.4(17)	30.0(17)	4.3(13)	-0.9(13)	0.6(14)
C10	29.6(17)	28.0(17)	27.0(16)	5.4(13)	-0.9(13)	-5.8(14)
C11	20.7(15)	27.3(16)	25.9(16)	3.4(12)	-2.6(12)	-5.9(13)

Table 17 Anisotropic Displacement Parameters ($Å^2×10^3$) for 6a. 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}
C12	17.9(14)	29.1(17)	26.5(15)	4.4(12)	-1.4(11)	-4.5(13)
C13	17.2(14)	26.6(16)	31.2(16)	3.1(13)	-2.4(12)	-1.1(12)
C14	21.3(15)	37.1(19)	29.6(16)	1.8(14)	-0.7(12)	-9.9(14)
C15	19.1(14)	36.2(18)	27.1(16)	2.4(13)	-2.6(12)	-3.7(14)
C16	20.9(15)	31.3(18)	26.6(16)	8.3(13)	-3.9(12)	-3.7(13)
C17	26.2(17)	47(2)	28.2(17)	4.0(15)	0.3(13)	-7.9(16)
C18	29.0(18)	58(2)	29.7(17)	-7.6(16)	0.4(14)	-9.8(17)
C19	32.9(19)	48(2)	44(2)	-14.5(18)	4.2(16)	-15.4(18)
C20	31.2(18)	35.7(19)	42(2)	-6.0(15)	3.8(15)	-12.7(16)
C21	47(2)	52(2)	26.0(17)	-1.9(16)	3.9(15)	-23.1(19)
C22	33.7(19)	39(2)	35.8(18)	-3.4(15)	-0.1(14)	-11.9(16)
C23	40(2)	29.5(18)	35.0(18)	8.7(14)	-5.6(15)	-9.5(16)

Table 18 Bond Lengths for 6a.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Br1	C5	1.904(4)	C7	C12	1.459(4)
O1	C16	1.221(4)	C9	C10	1.551(4)
O2	C8	1.331(4)	C10	C11	1.526(5)
O2	C9	1.441(4)	C10	C22	1.521(5)
O3	C13	1.222(4)	C10	C23	1.552(4)
N1	C1	1.373(5)	C11	C12	1.383(4)
N1	C8	1.358(4)	C11	C16	1.494(4)
N1	C21	1.454(5)	C12	C13	1.501(5)
C1	C2	1.390(5)	C13	C14	1.480(4)
C1	C6	1.415(5)	C14	C15	1.385(5)
C2	C3	1.380(6)	C14	C20	1.398(5)
C3	C4	1.391(6)	C15	C16	1.490(5)
C4	C5	1.388(5)	C15	C17	1.396(5)
C5	C6	1.398(5)	C17	C18	1.379(6)
C6	C7	1.461(4)	C18	C19	1.376(6)
C7	C8	1.380(5)	C19	C20	1.384(5)

Table 19 Bond Angles for 6a.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C8	O2	C9	116.4(3)	C22	C10	C9	111.6(3)
C1	N1	C21	126.4(3)	C22	C10	C11	111.7(3)

Table 19 Bond Angles for 6a.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C8	N1	C1	108.0(3)	C22	C10	C23	109.9(3)
C8	N1	C21	125.6(3)	C12	C11	C10	122.1(3)
N1	C1	C2	127.5(3)	C12	C11	C16	117.8(3)
N1	C1	C6	108.4(3)	C16	C11	C10	119.9(3)
C2	C1	C6	124.1(4)	C7	C12	C13	115.6(3)
C3	C2	C1	117.5(4)	C11	C12	C7	126.3(3)
C2	C3	C4	120.4(3)	C11	C12	C13	117.2(3)
C5	C4	C3	121.0(4)	O3	C13	C12	119.6(3)
C4	C5	Br1	116.8(3)	O3	C13	C14	121.2(3)
C4	C5	C6	120.8(4)	C14	C13	C12	118.8(3)
C6	C5	Br1	122.0(3)	C15	C14	C13	118.9(3)
C1	C6	C7	106.9(3)	C15	C14	C20	120.3(3)
C5	C6	C1	115.7(3)	C20	C14	C13	120.8(3)
C5	C6	C7	137.2(3)	C14	C15	C16	120.3(3)
C8	C7	C6	104.1(3)	C14	C15	C17	119.7(3)
C8	C7	C12	128.1(3)	C17	C15	C16	120.0(3)
C12	C7	C6	127.8(3)	O1	C16	C11	121.0(3)
O2	C8	N1	115.2(3)	O1	C16	C15	119.2(3)
O2	C8	C7	132.3(3)	C15	C16	C11	119.5(3)
N1	C8	C7	112.4(3)	C18	C17	C15	119.6(3)
O2	C9	C10	115.9(3)	C19	C18	C17	120.7(3)
C9	C10	C23	101.9(3)	C18	C19	C20	120.4(4)
C11	C10	C9	108.8(3)	C19	C20	C14	119.3(3)
C11	C10	C23	112.5(3)				

Table 20 Hydrogen Bonds for 6a.

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
C23	H23A	O1	0.96	2.21	2.813(5)	120.2

Table 21 Torsion Angles for 6a.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
Br1	C5	C6	C1	-167.1(2)	C9	C10	C11	C16	145.0(3)
Br1	C5	C6	C7	6.1(6)	C10	C11	C12	C7	-13.5(5)
O2	C9	C10	C11	87.0(3)	C10	C11	C12	C13	155.1(3)
O2	C9	C10	C22	-36.7(4)	C10	C11	C16	O1	19.0(5)
O2	C9	C10	C23	-153.9(3)	C10	C11	C16	C15	-167.7(3)
O3	C13	C14	C15	156.7(3)	C11	C12	C13	O3	-142.9(3)
O3	C13	C14	C20	-22.0(5)	C11	C12	C13	C14	31.0(4)

Table 21 Torsion Angles for 6a.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
N1	C1	C2	C3	-177.1(3)	C12	C7	C8	O2	-3.0(6)
N1	C1	C6	C5	172.3(3)	C12	C7	C8	N1	176.5(3)
N1	C1	C6	C7	-2.9(4)	C12	C11	C16	O1	-155.5(3)
C1	N1	C8	O2	-179.2(3)	C12	C11	C16	C15	17.8(4)
C1	N1	C8	C7	1.2(4)	C12	C13	C14	C15	-17.1(4)
C1	C2	C3	C4	3.8(5)	C12	C13	C14	C20	164.2(3)
C1	C6	C7	C8	3.5(3)	C13	C14	C15	C16	4.0(5)
C1	C6	C7	C12	-175.9(3)	C13	C14	C15	C17	-176.9(3)
C2	C1	C6	C5	-6.7(5)	C13	C14	C20	C19	178.8(3)
C2	C1	C6	C7	178.1(3)	C14	C15	C16	O1	169.5(3)
C2	C3	C4	C5	-3.8(6)	C14	C15	C16	C11	-3.9(4)
C3	C4	C5	Br1	172.3(3)	C14	C15	C17	C18	-1.6(5)
C3	C4	C5	C6	-1.6(6)	C15	C14	C20	C19	0.1(5)
C4	C5	C6	C1	6.5(5)	C15	C17	C18	C19	-0.5(5)
C4	C5	C6	C7	179.8(4)	C16	C11	C12	C7	160.9(3)
C5	C6	C7	C8	-170.1(4)	C16	C11	C12	C13	-30.6(4)
C5	C6	C7	C12	10.4(6)	C16	C15	C17	C18	177.5(3)
C6	C1	C2	C3	1.6(5)	C17	C15	C16	O1	-9.5(5)
C6	C7	C8	O2	177.6(3)	C17	C15	C16	C11	177.1(3)
C6	C7	C8	N1	-3.0(4)	C17	C18	C19	C20	2.5(6)
C6	C7	C12	C11	-152.2(3)	C18	C19	C20	C14	-2.2(6)
C6	C7	C12	C13	39.1(4)	C20	C14	C15	C16	-177.2(3)
C7	C12	C13	O3	26.9(4)	C20	C14	C15	C17	1.8(5)
C7	C12	C13	C14	-159.2(3)	C21	N1	C1	C2	-0.4(6)
C8	O2	C9	C10	-63.3(4)	C21	N1	C1	C6	-179.4(3)
C8	N1	C1	C2	-179.9(3)	C21	N1	C8	O2	1.3(5)
C8	N1	C1	C6	1.2(4)	C21	N1	C8	C7	-178.2(3)
C8	C7	C12	C11	28.4(5)	C22	C10	C11	C12	82.9(4)
C8	C7	C12	C13	-140.3(3)	C22	C10	C11	C16	-91.4(3)
C9	O2	C8	N1	-167.9(3)	C23	C10	C11	C12	-152.9(3)
C9	O2	C8	C7	11.6(5)	C23	C10	C11	C16	32.8(4)
C9	C10	C11	C12	-40.7(4)					

Table 22 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 6a.

Atom	*x*	*y*	*z*	U(eq)
H2	7554.71	4535.2	11260.59	50
H3	9385.23	2010.88	10943.65	55

Table 22 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 6a.

Atom	*x*	*y*	*z*	U(eq)
H4	10455.82	1185.11	9377.72	52
H9A	3668.84	10014.34	7933.06	37
H9B	3693.27	8336.98	7716.55	37
H17	7987.76	5892.64	3794.77	42
H18	8414.54	3499.15	3125.14	48
H19	8181.27	1512.58	4078.41	50
H20	7296.73	1934.8	5708.63	43
H21A	4909.77	8594.61	10536.47	61
H21B	6552.97	7581.14	11105.13	61
H21C	4685.14	7173.13	11096.86	61
H22A	8279.33	8448.48	7901.1	54
H22B	7232.89	10190.34	7765.04	54
H22C	8547.43	9216.37	6918.02	54
H23A	5895.78	10007.7	5819.17	53
H23B	4617.84	10996.35	6671.95	53
H23C	3985.37	9751.58	6146.25	53

8. References

1. Y. Dong, H. Zhang, J. Yang, S. He, Z.-C. Shi, X.-M. Zhang and J.-Y. Wang, B(C_6F_5)$_3$-Catalyzed C–C Coupling of 1,4-Naphthoquinones with the C-3 Position of Indole Derivatives in Water, *ACS Omega*., 2019, **4**, 21567-21577.

2. H. Kilic, S. Bayindir, E. Erdogan and N. Saracoglu, Synthesis of Highly N-substituted Indole Library via Conjugate Additions of Indoline and Their Synthetic Tool Potentials, *Tetrahedron,* 2012, **68**, 5619-5630.

3. M.-M. Kalt, W. Schuehly, R. Saf, S. Ochensberger, J. Solnier, F. Bucar, M. Kaiser and A. Presser, Palladium-catalysed Synthesis of Arylnaphthoquinones as Antiprotozoal and Antimycobacterial Agents, *Eur J Med Chem*., **2020**, *207*, 112837.

4. (a) B. M. Loertscher, P. R. Young, P. R. Evans and S. L. Castle, Diastereoselective Synthesis of Vicinal Tertiary Diols, *Org. Lett*., 2013, **15**, 1930-1933. (b) J. Barluenga, F. J. Fañanás, R. Sanz, C. Marcos, M. Trabada, On the Reactivity of o-Lithioaryl Ethers: Tandem Anion Translocation and Wittig Rearrangement, *Org. Lett.,* 2002, **4**, 1587-1590.

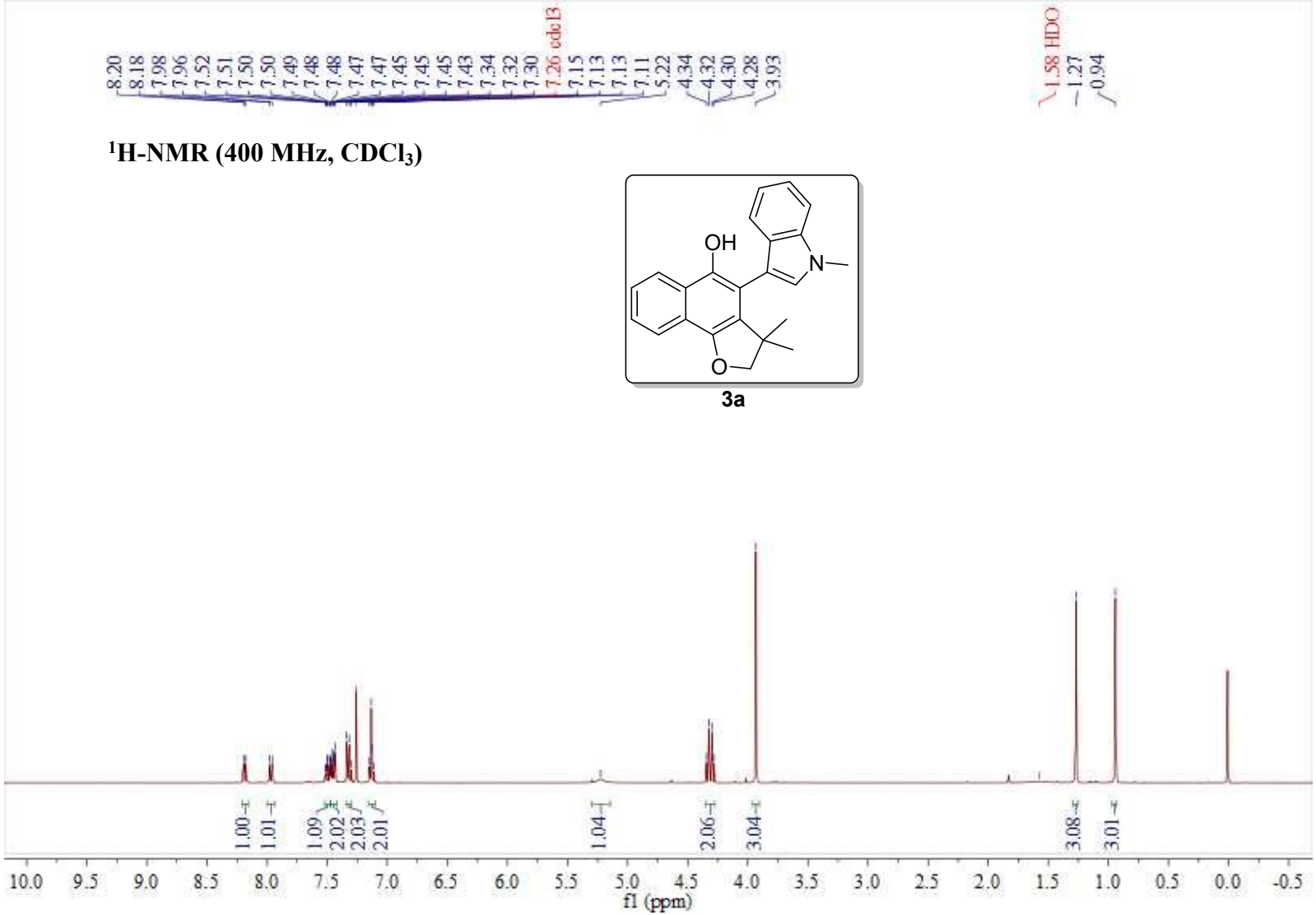
5. W. Gladkowski, A. Skrobiszewski, M. Mazur, M. Siepka, A. Pawlak, B. O. nska-Mrukowicz, A. Bialonska, D. Poradowski, A. Drynda and M. Urbaniak, Synthesis and Anticancer Activity of Novel Halolactones with β-aryl Substituents from Simple Aromatic Aldehydes, *Tetrahedron*, 2013, **69**, 10414-10423.

6. A. Kapat, E. Nyfeler, G. T. Giuffredi and Renaud, P, Intramolecular Schmidt Reaction Involving Primary Azidoalcohols under Nonacidic Conditions: Synthesis of Indolizidine (−)-167B, *J. Am. Chem. Soc.* 2009, **131**, 17746-17747.

7. (a) C. Su and P. G. Williard, Isomerization of Allyl Ethers Initiated by Lithium Diisopropylamide, *Org. Lett*., 2010, **12**, 5378-5381. (b) L. Bunch, P.-O. Norrby, K. Frydenvang, P. Krogsgaard-Larsen and U. Madsen, Unprecedented Migration of N-Alkoxycarbonyl Groups in Protected Pyroglutaminol, *Org. Lett*., 2001, **3**, 433-435.

8. (a) J. C. Lo, Y. Yabe and P. S. Baran, A Practical and Catalytic Reductive Olefin Coupling, *J. Am. Chem. Soc*. 2014, **136**, 1304-1307; (b) J. C. Lo, J. Gui, Y. Yabe, C.-M. Pan, Baran, P. S. Functionalized Olefin Cross-coupling to Construct Carbon-carbon Bonds, *Nature* 2014, **516**, 343-348; (c) H. T. Dao, C. Li, Q. Michaudel, B. D. Maxwell and P. S. Baran, Hydromethylation of Unactivated Olefins, *J. Am. Chem. Soc*. 2015, **137**, 8046-8049; (d) J. Gui, C.-M. Pan, Y. Jin, T. Qin, J. C. Lo, B. J. Lee, S. H. Spergel, M. E. Mertzman, W. J. Pitts, T. E. L. Cruz, M. A. Schmidt, N. Darvatkar, S. R. Natarajan and P. S. Baran, Practical Olefin Hydroamination with Nitroarenes, *Science* 2015, **348**, 886-891; (e) J. C. Lo, D. Kim, C.-M. Pan, J. T. Edwards, Y. Yabe, J. Gui, T. Qin, S. Gutiérrez, J. Giacoboni, M. W. Smith, P. L. Holland and P. S. Baran, Fe-Catalyzed C-C Bond Construction from Olefins via Radicals, *J. Am. Chem. Soc*. 2017, **139**, 2484-2503.

9. (a) H. Ishikawa, D. A. Colby and Boger, D. L, Direct Coupling of Catharanthine and Vindoline to Provide Vinblastine: Total Synthesis of (+)- and ent-(−)-Vinblastine, *J. Am. Chem. Soc*., 2008, **130**, 420-421; (b) H. Ishikawa, D. A. Colby, S. Seto, P. Va, A. Tam, H. Kakei, T. J. Rayl, I. Hwang and Boger, D. L, Total Synthesis of Vinblastine, Vincristine, Related Natural Products, and Key Structural Analogues, *J. Am. Chem. Soc*., 2009, **131**, 4904-4916; (c) T. J. Barker and D. L. Boger, Fe(III)/$NaBH_4$-Mediated Free Radical Hydrofluorination of Unactivated Alkenes, *J. Am. Chem. Soc*. 2012, **134**, 13588-13591; (b) E. K. Leggans, T. J. Barker, K. K. Duncan and D. L. Boger, Iron(III)/$NaBH_4$-Mediated Additions to Unactivated Alkenes: Synthesis of Novel 20'-Vinblastine Analogues, *Org. Lett*. 2012, **14**, 1428-1431.



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

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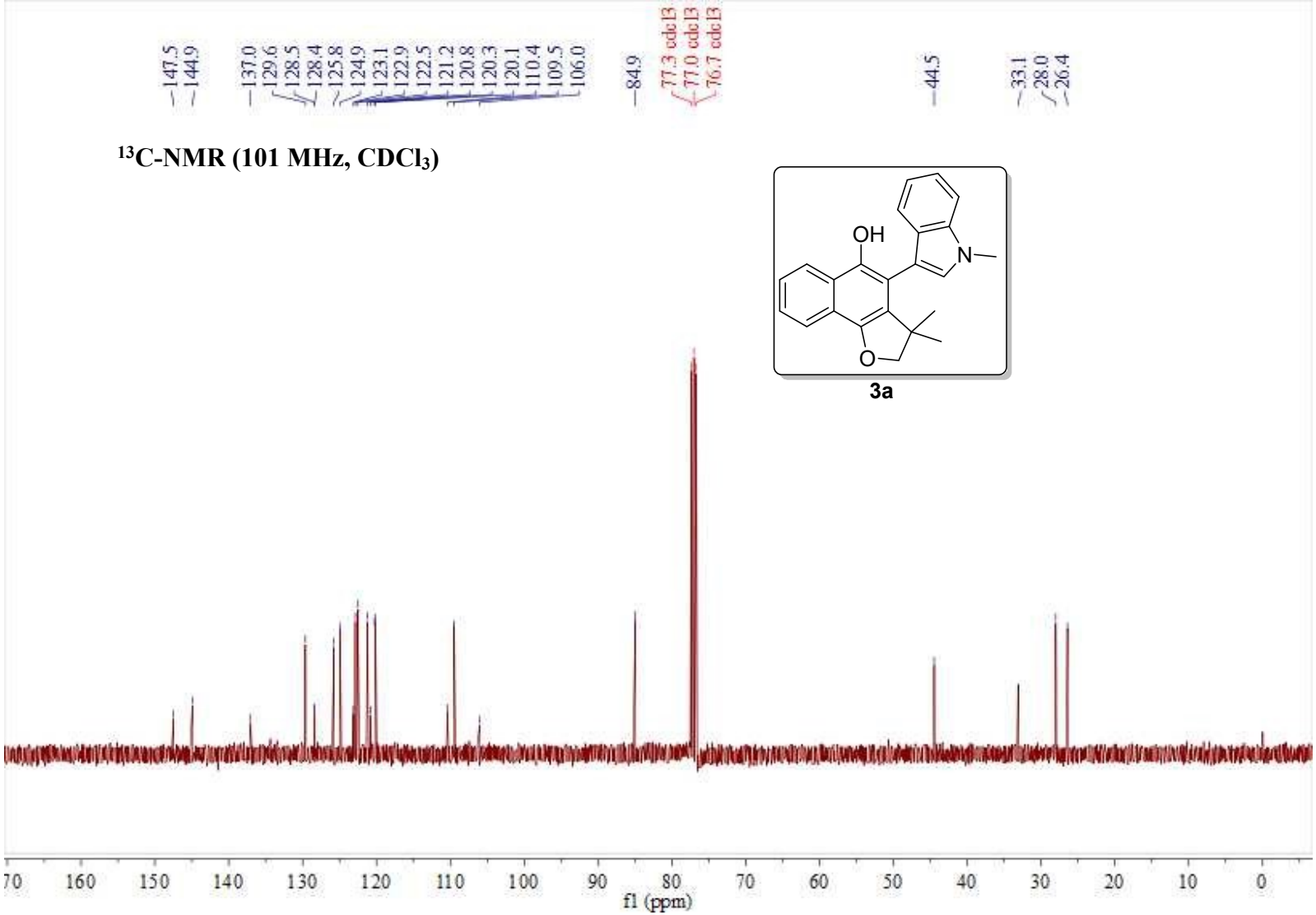

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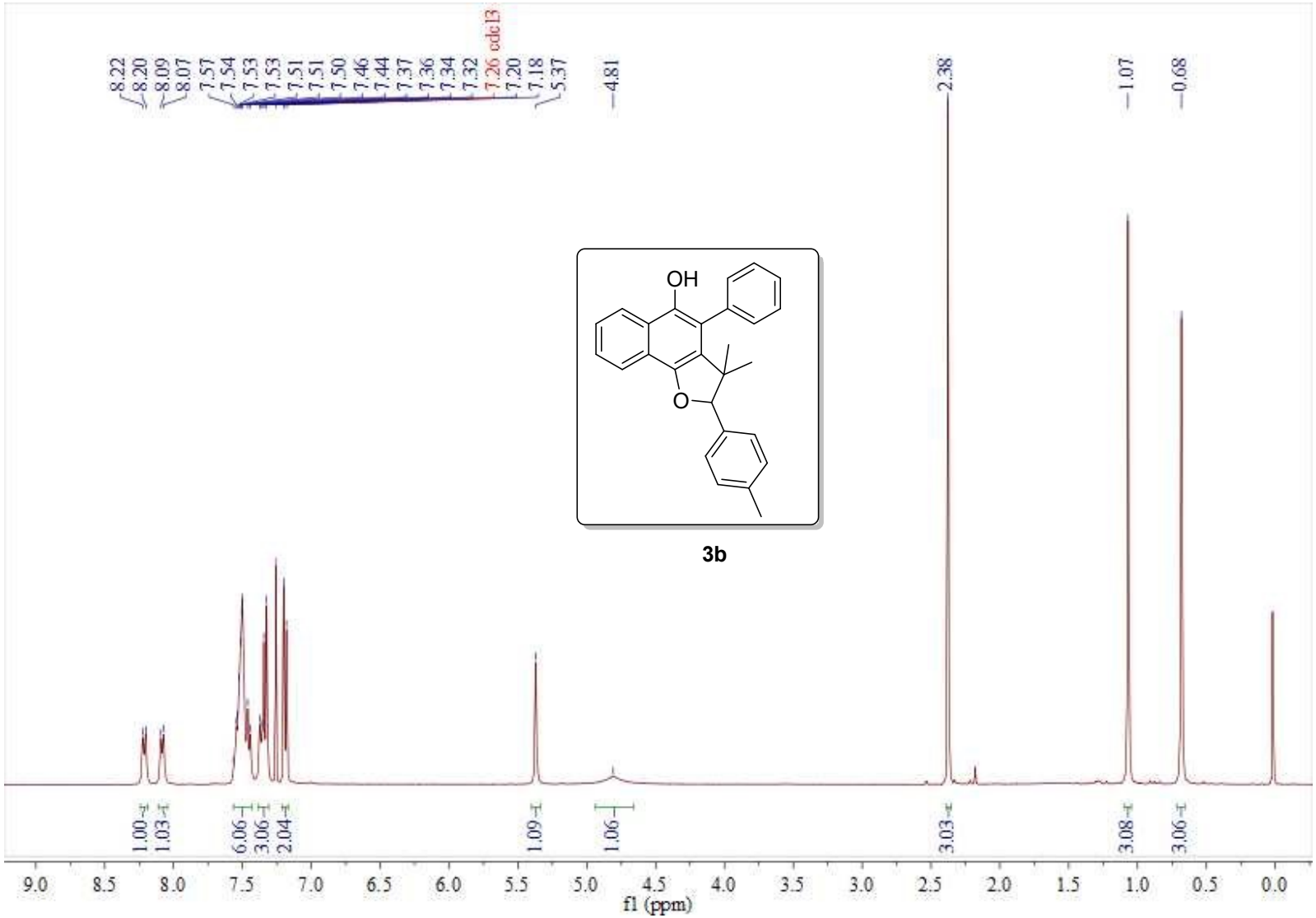
3a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OH
O
1.00
1.03
6.06
3.06
2.04
1.09
1.06
3.03
3.08
3.06
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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5.0
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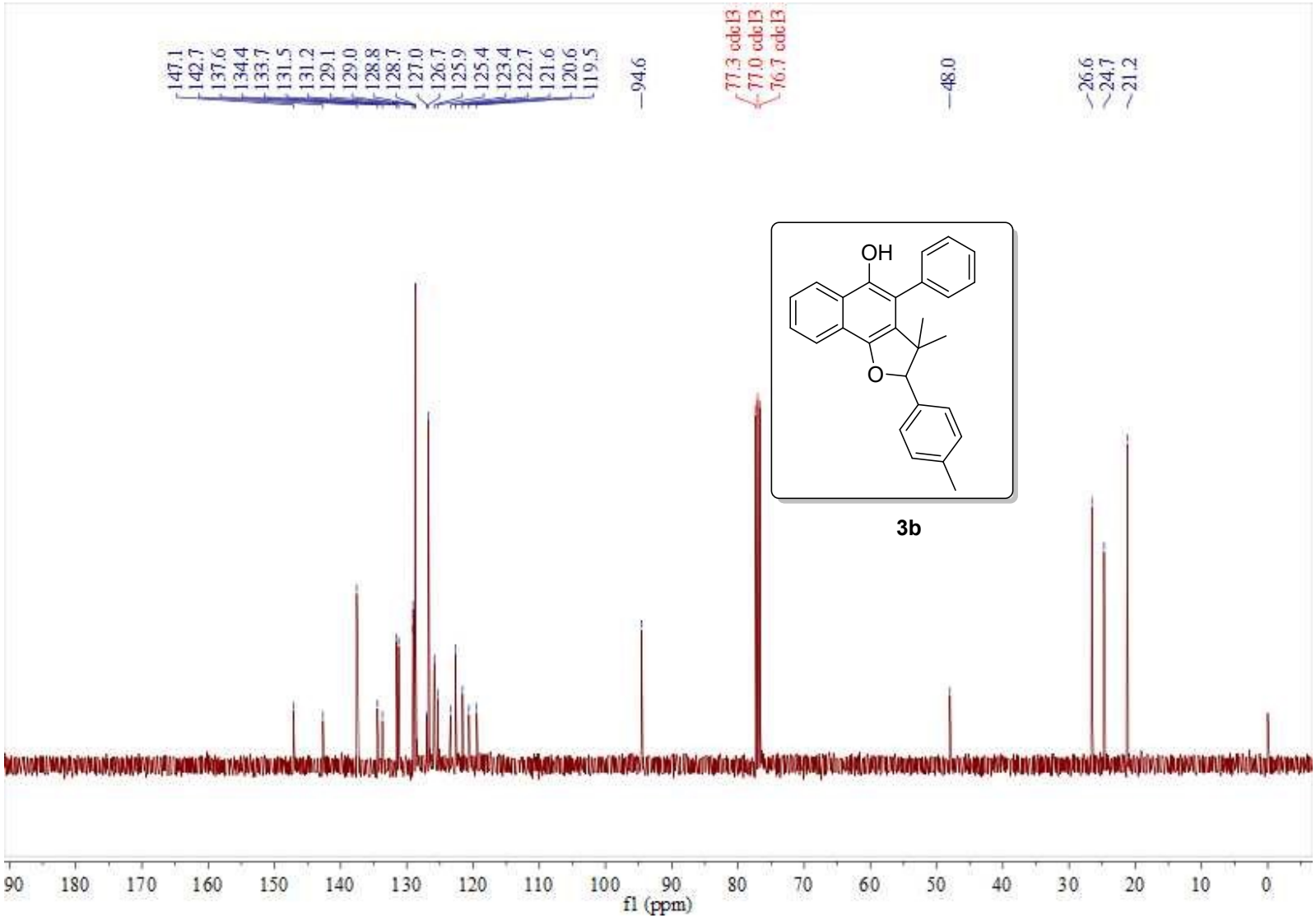
f1 (ppm)

3b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125.4
123.4
122.7
121.6
120.6
119.5
94.6
77.3 cdcl3
77.0 cdcl3
76.7 cdcl3
48.0
26.6
24.7
21.2
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O
3b
90
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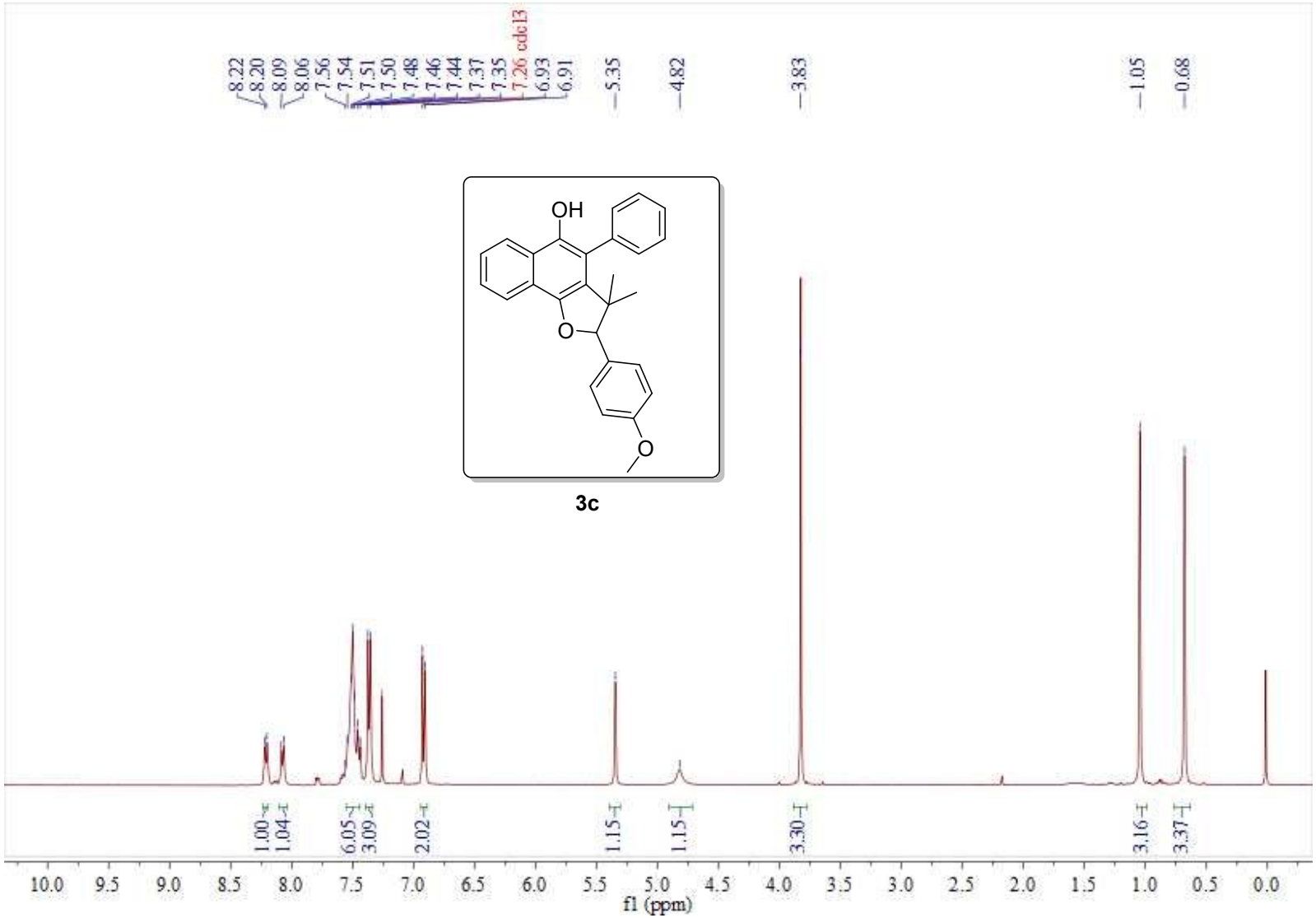
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7.35
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6.91
5.35
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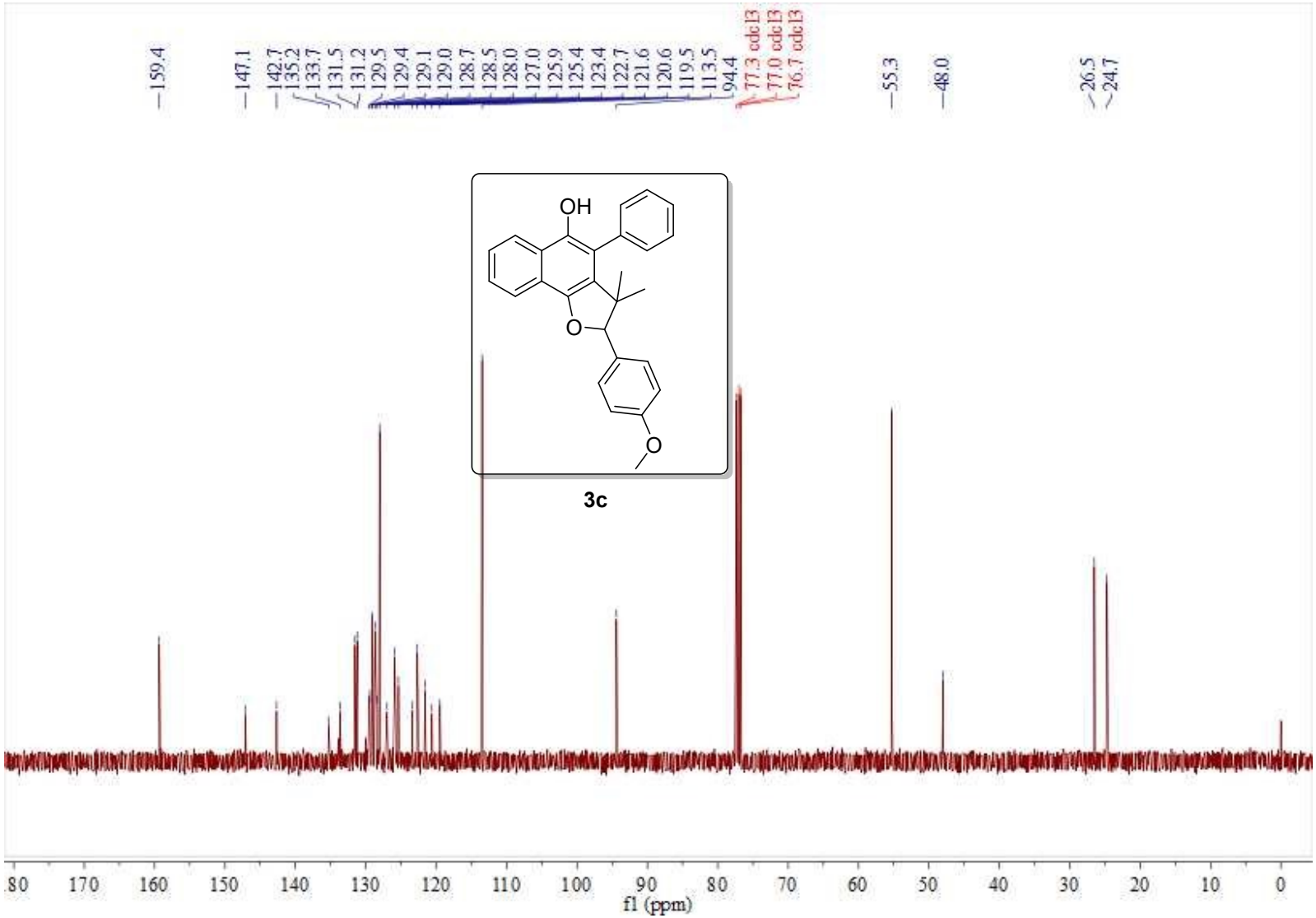
3.83
1.05
0.68
OH
O
O
1.00
1.04
6.05
3.09
2.02
1.15
1.15
3.30
3.16
3.37
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

3c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123.4
122.7
121.6
120.6
119.5
113.5
94.4
77.3 cdcl3
77.0 cdcl3
76.7 cdcl3
55.3
48.0
26.5
24.7
OH
O
O
3c
80
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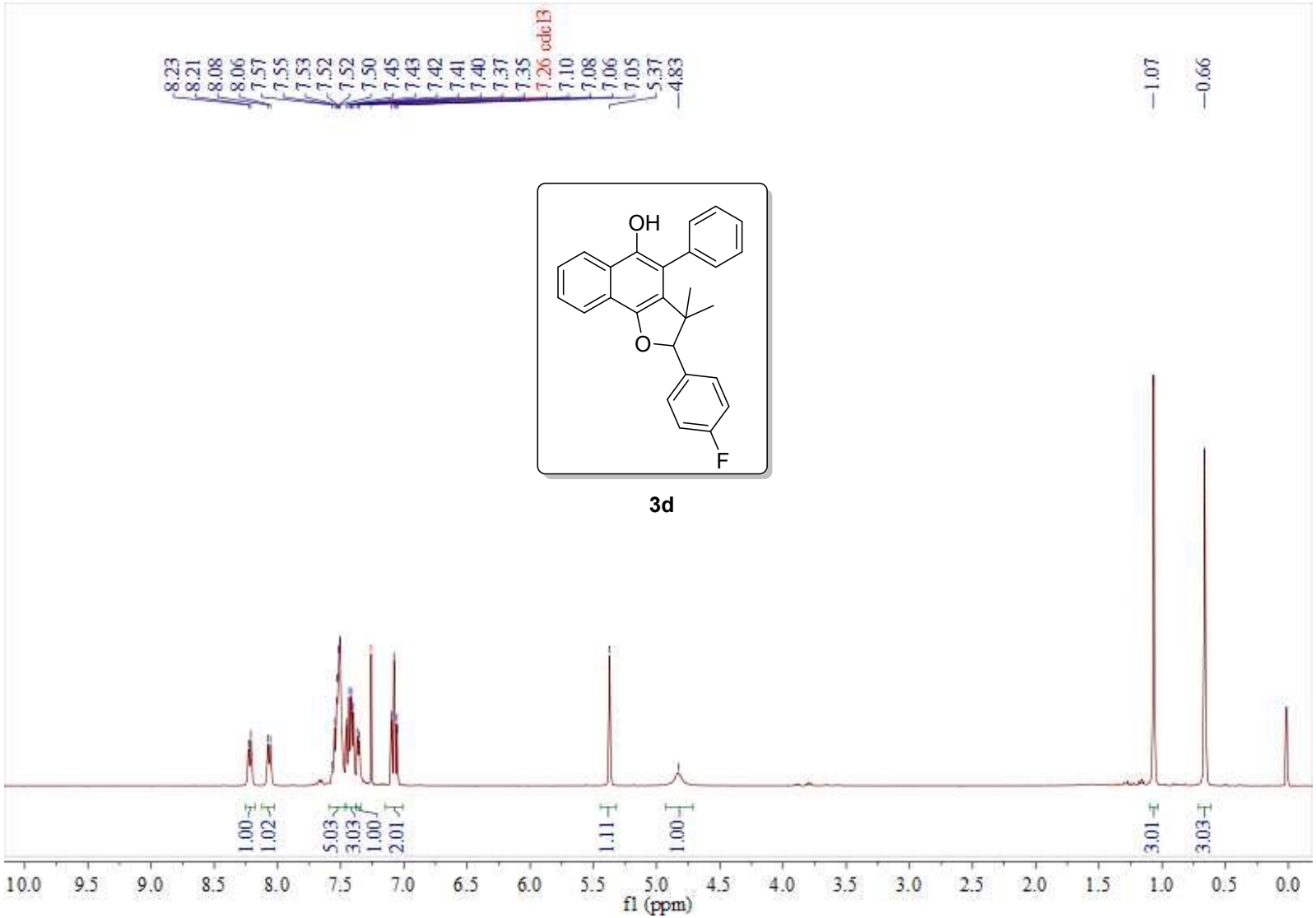
f1 (ppm)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7.40
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7.35
7.26 cdcl3
7.10
7.08
7.06
7.05
5.37
4.83
1.07
0.66
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O
F
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1.02
5.03
3.03
1.00
2.01
1.11
1.00
3.01
3.03
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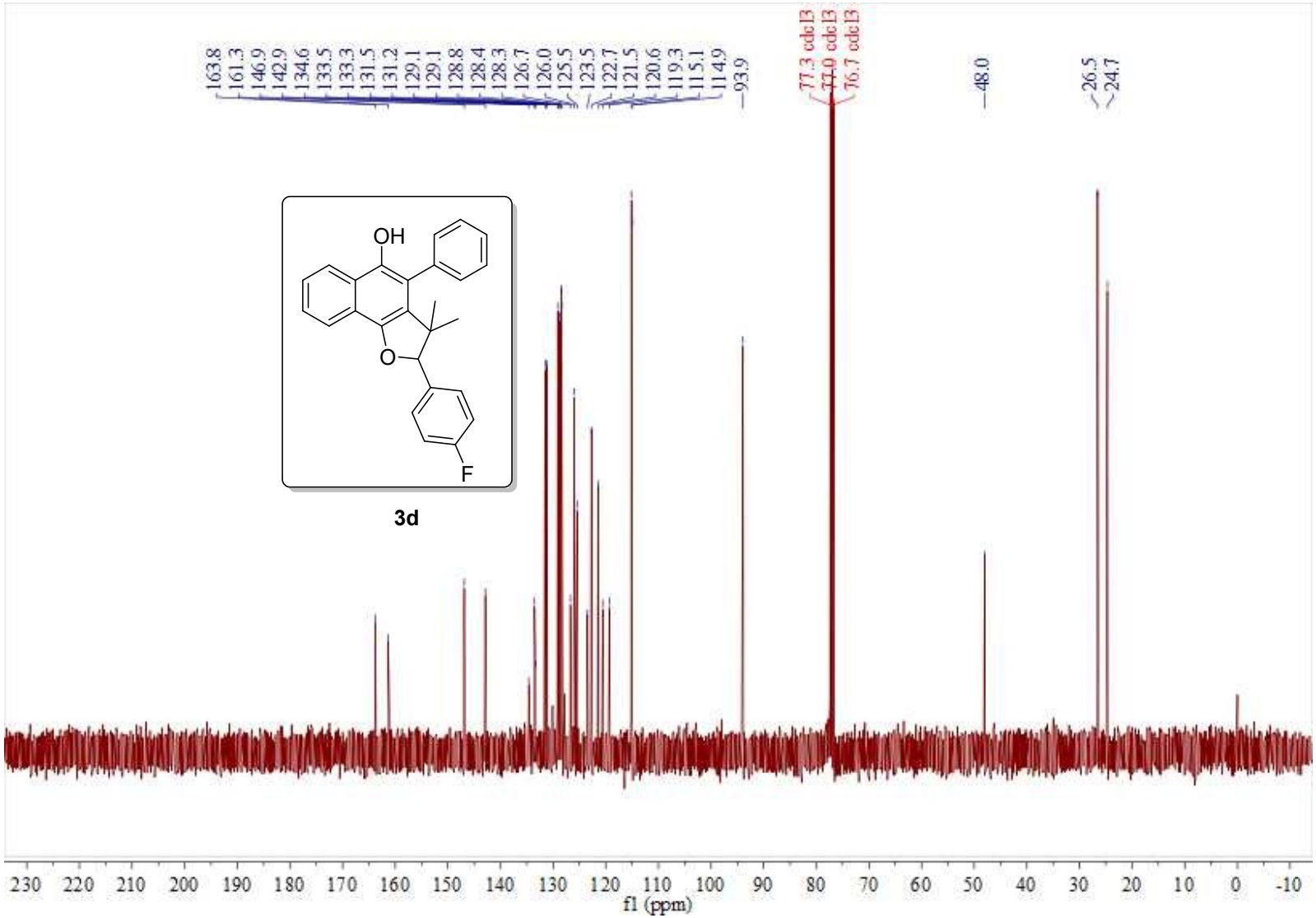
f1 (ppm)

3d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122.7
121.5
120.6
119.3
115.1
114.9
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77.3 cdcl3
77.0 cdcl3
76.7 cdcl3
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OH
O
F
3d
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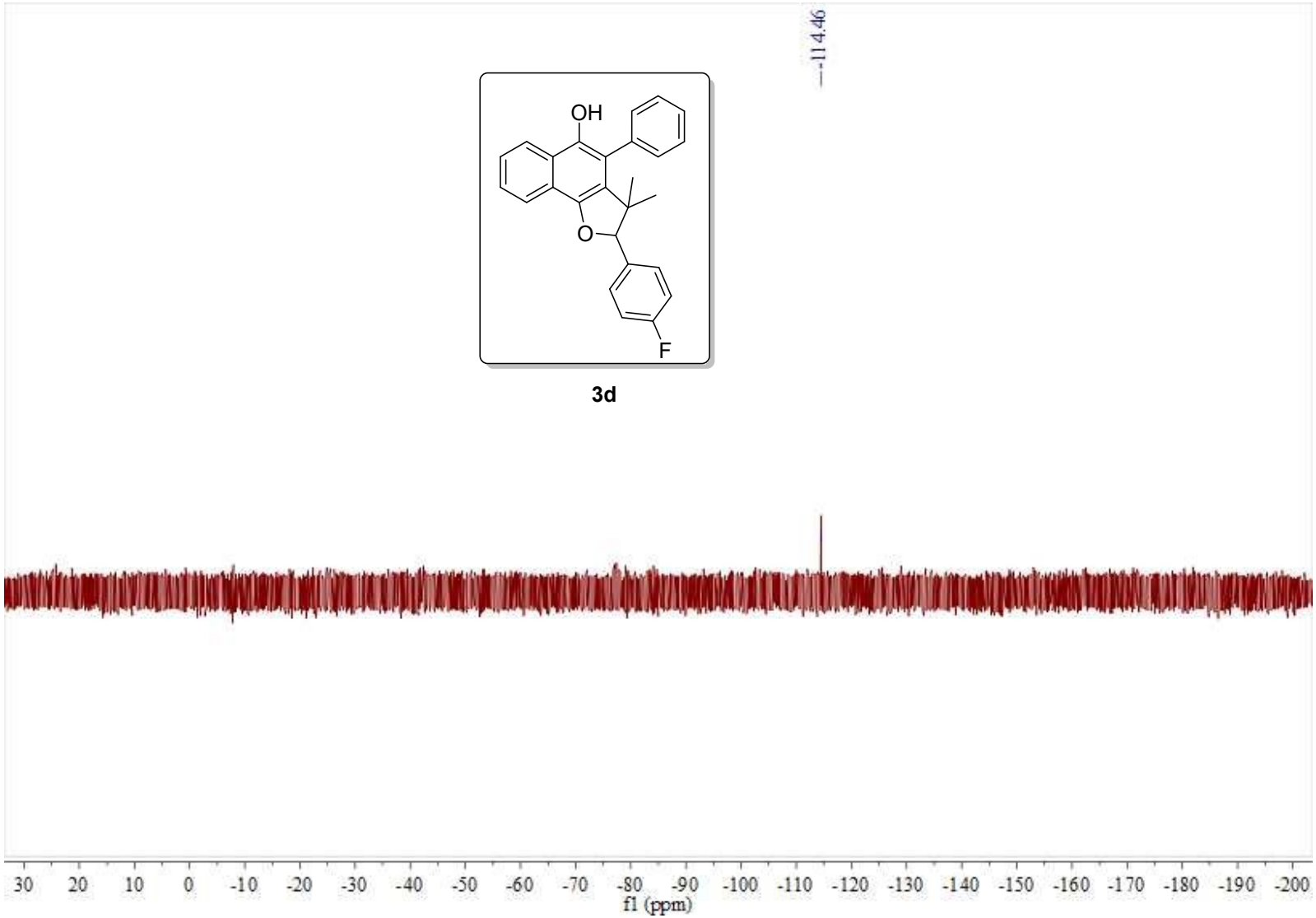
f1 (ppm)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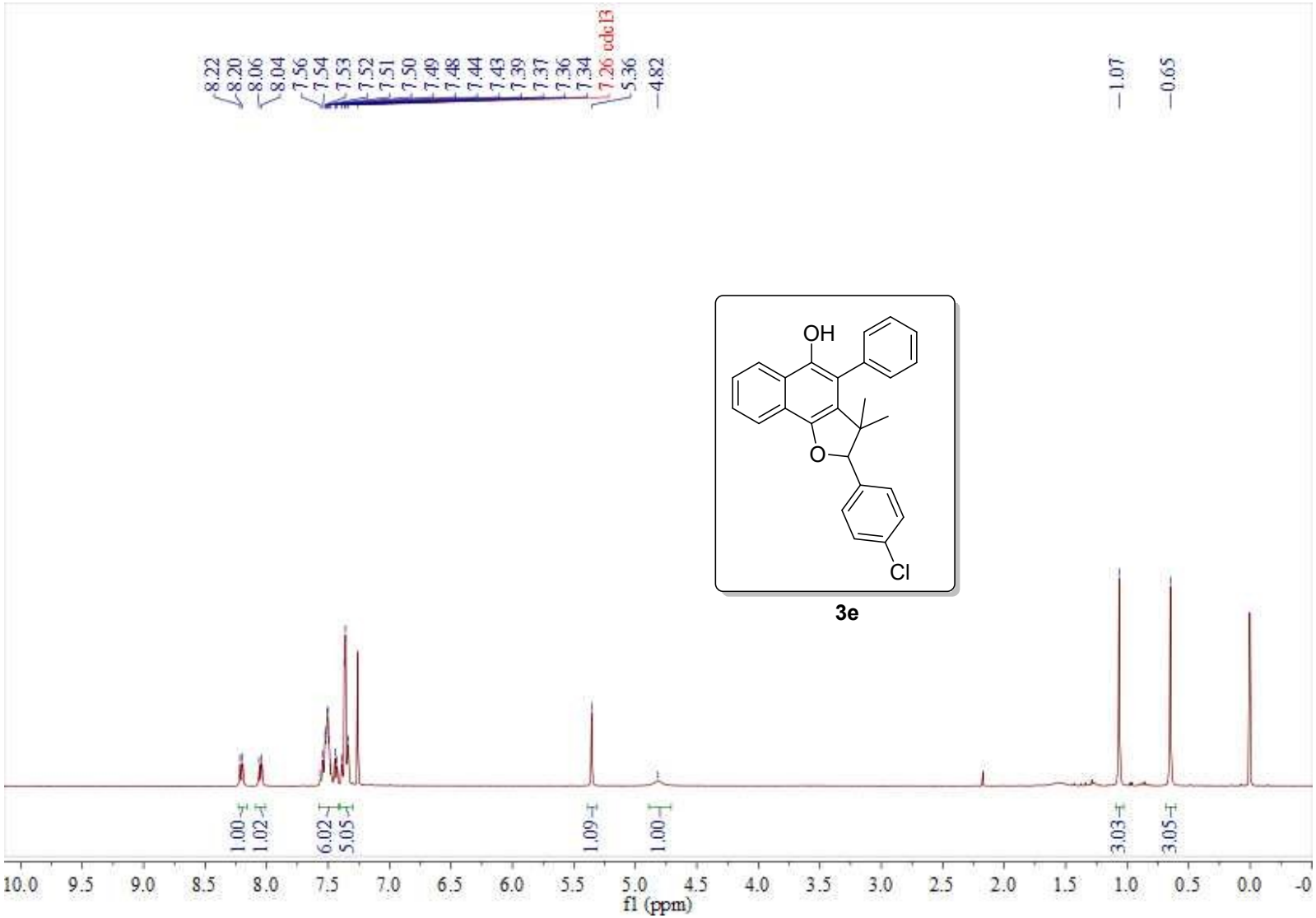
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7.36
7.34
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4.82
1.07
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O
Cl
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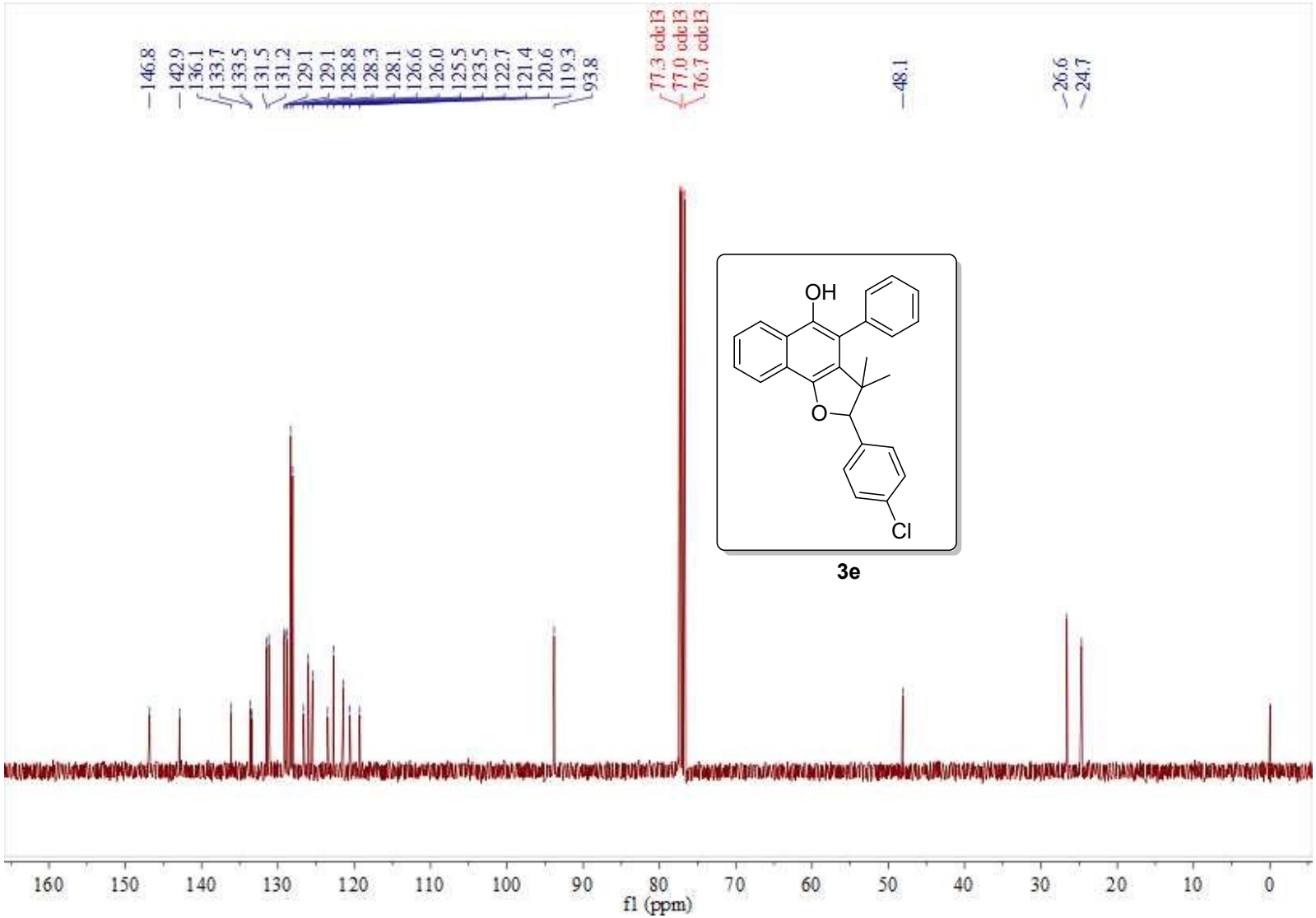
1.02
6.02
5.05
1.09
1.00
3.03
3.05
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)

3e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119.3
93.8
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76.7 cdcl3
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OH
O
Cl
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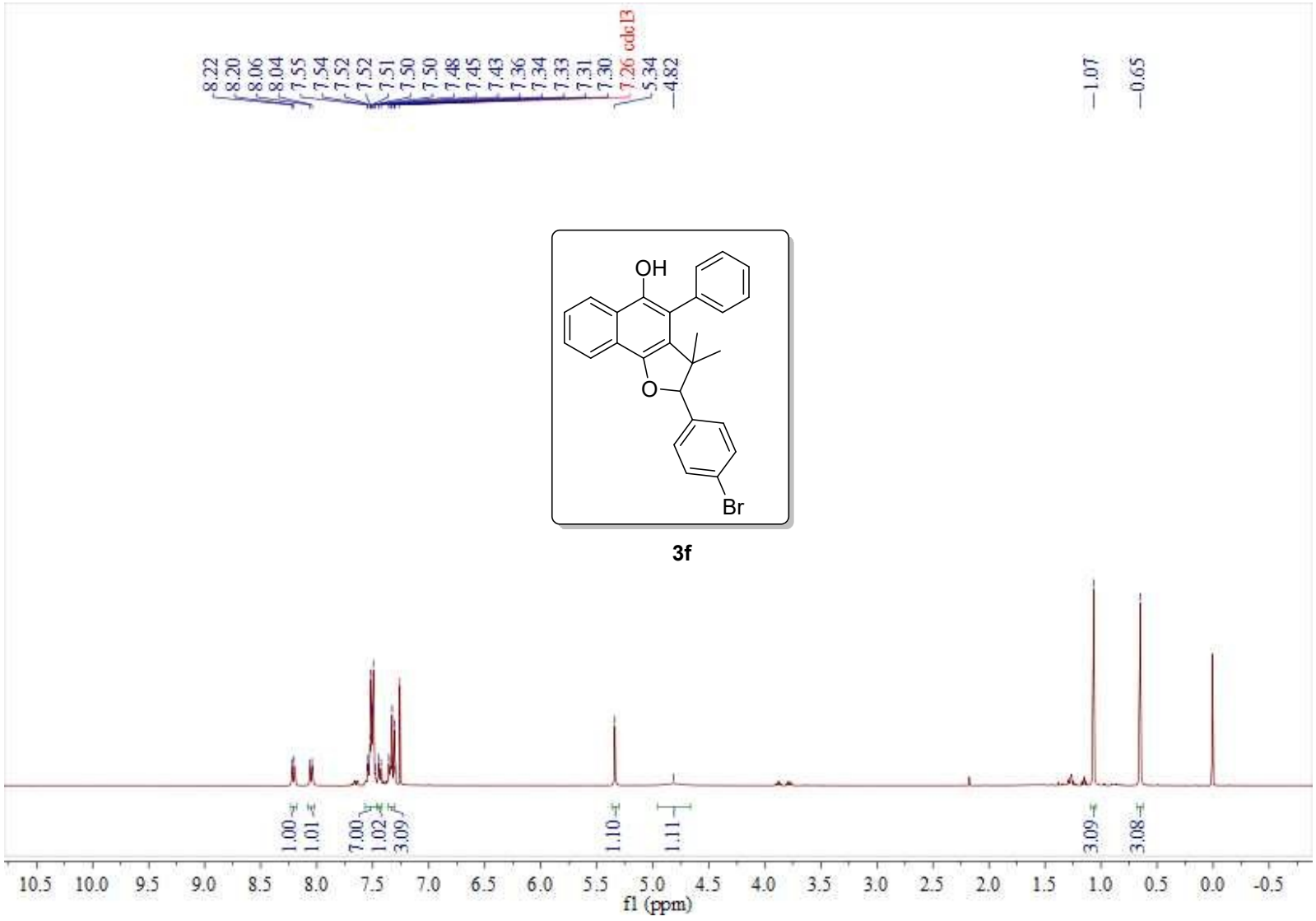
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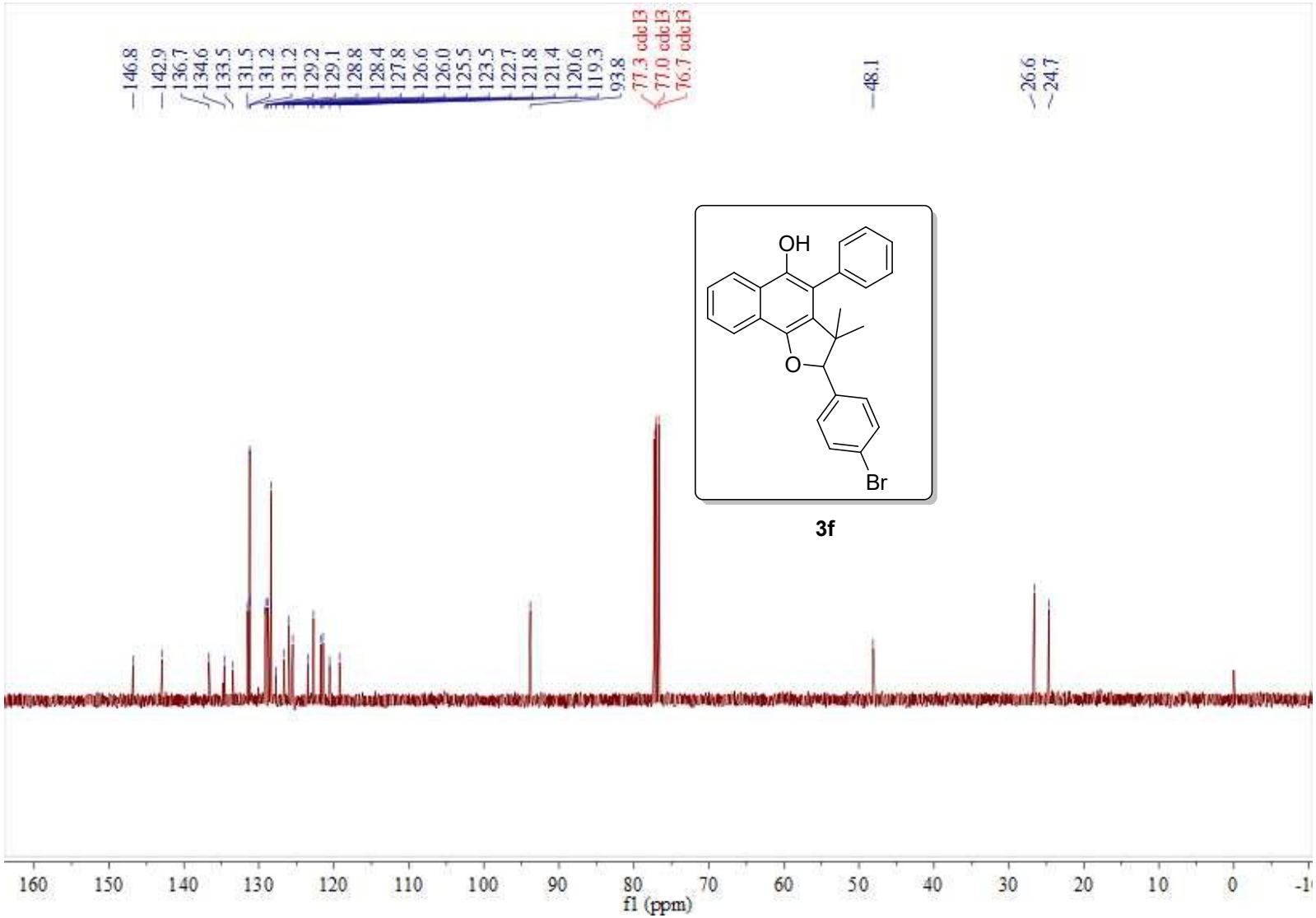
3f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76.7 cdcl3
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24.7
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O
Br
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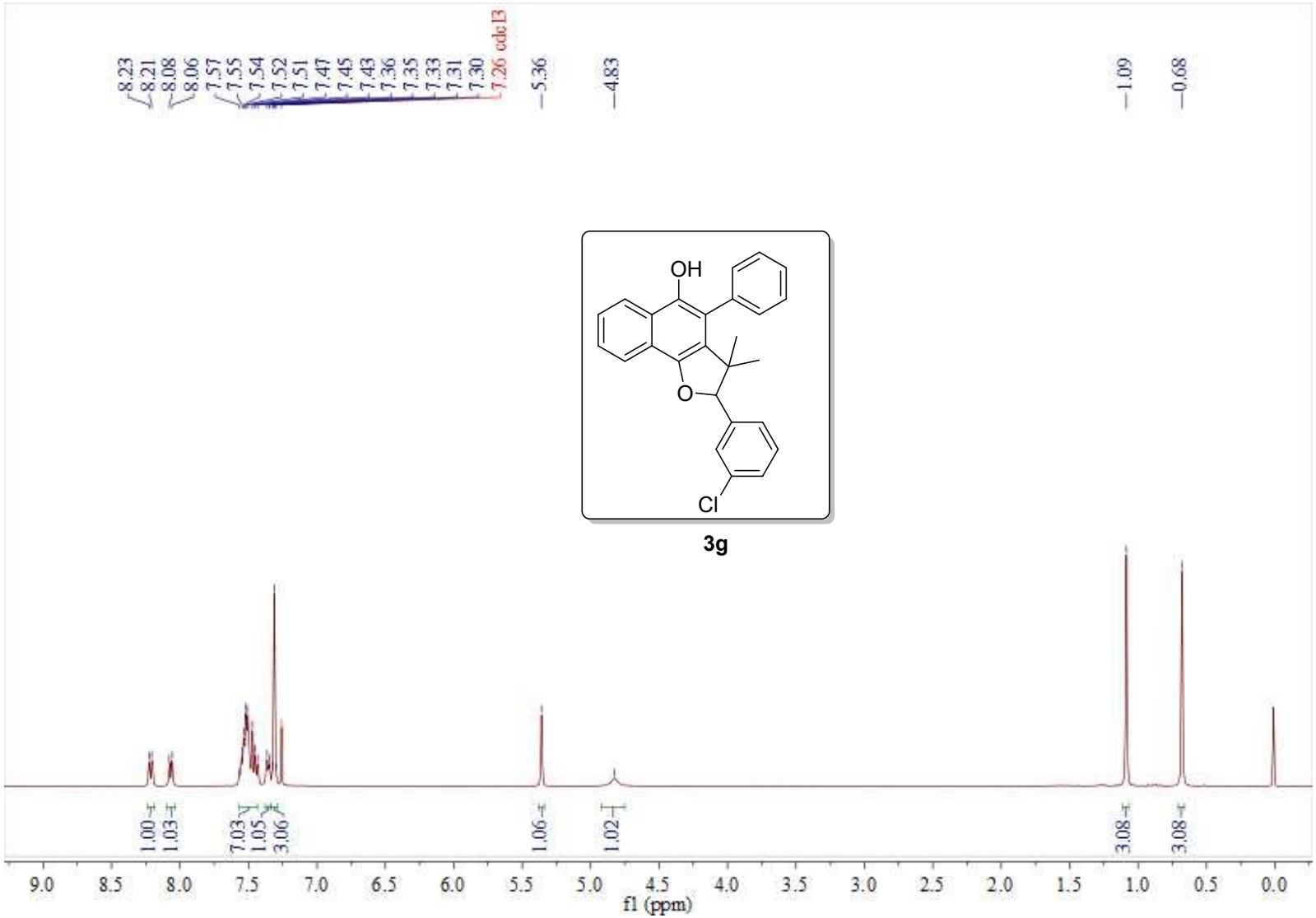
f1 (ppm)

3f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Cl
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1.02
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3.08
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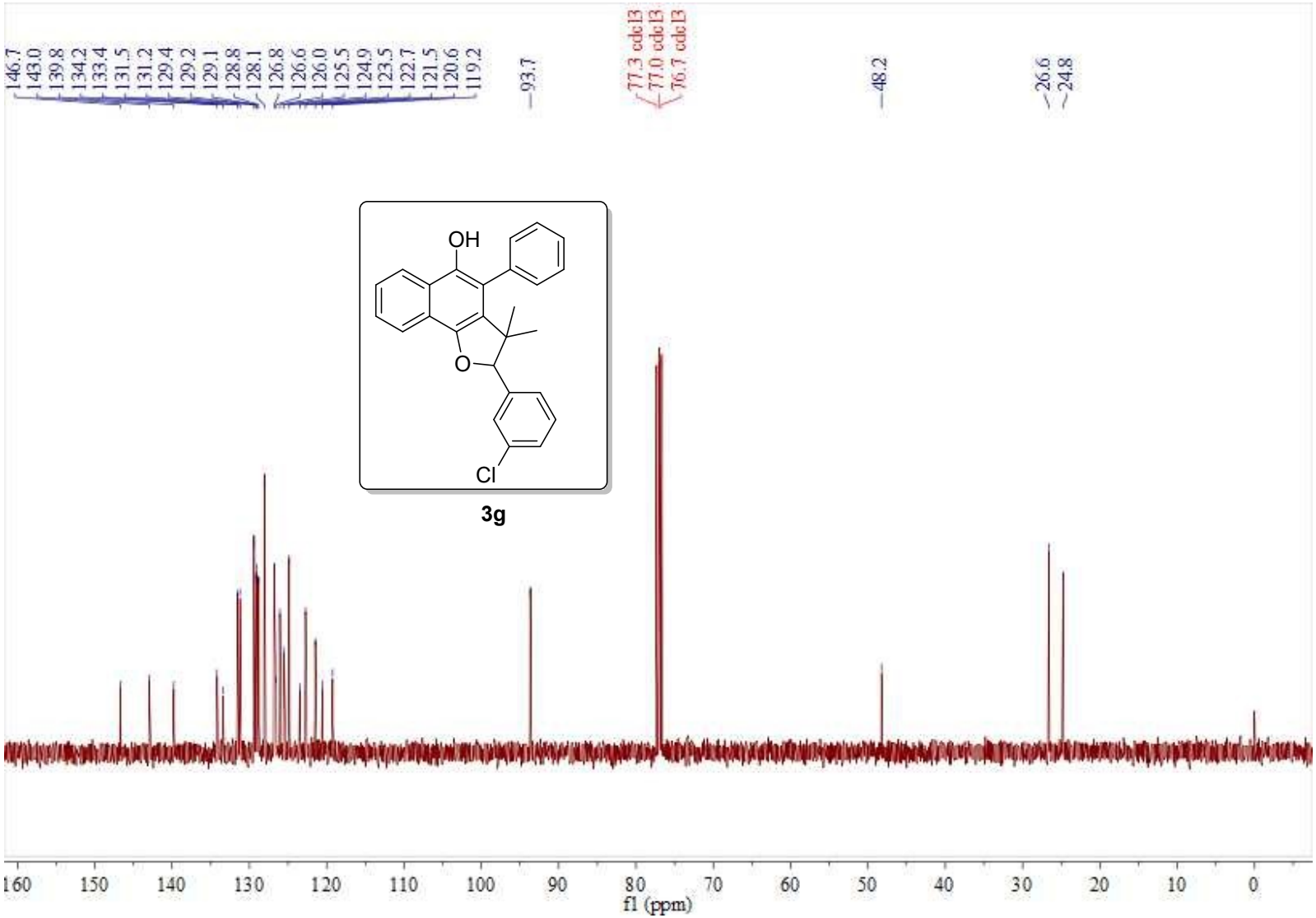
f1 (ppm)

3g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119.2
93.7
77.3 cdcl3
77.0 cdcl3
76.7 cdcl3
48.2
26.6
24.8
OH
O
Cl
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100
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30
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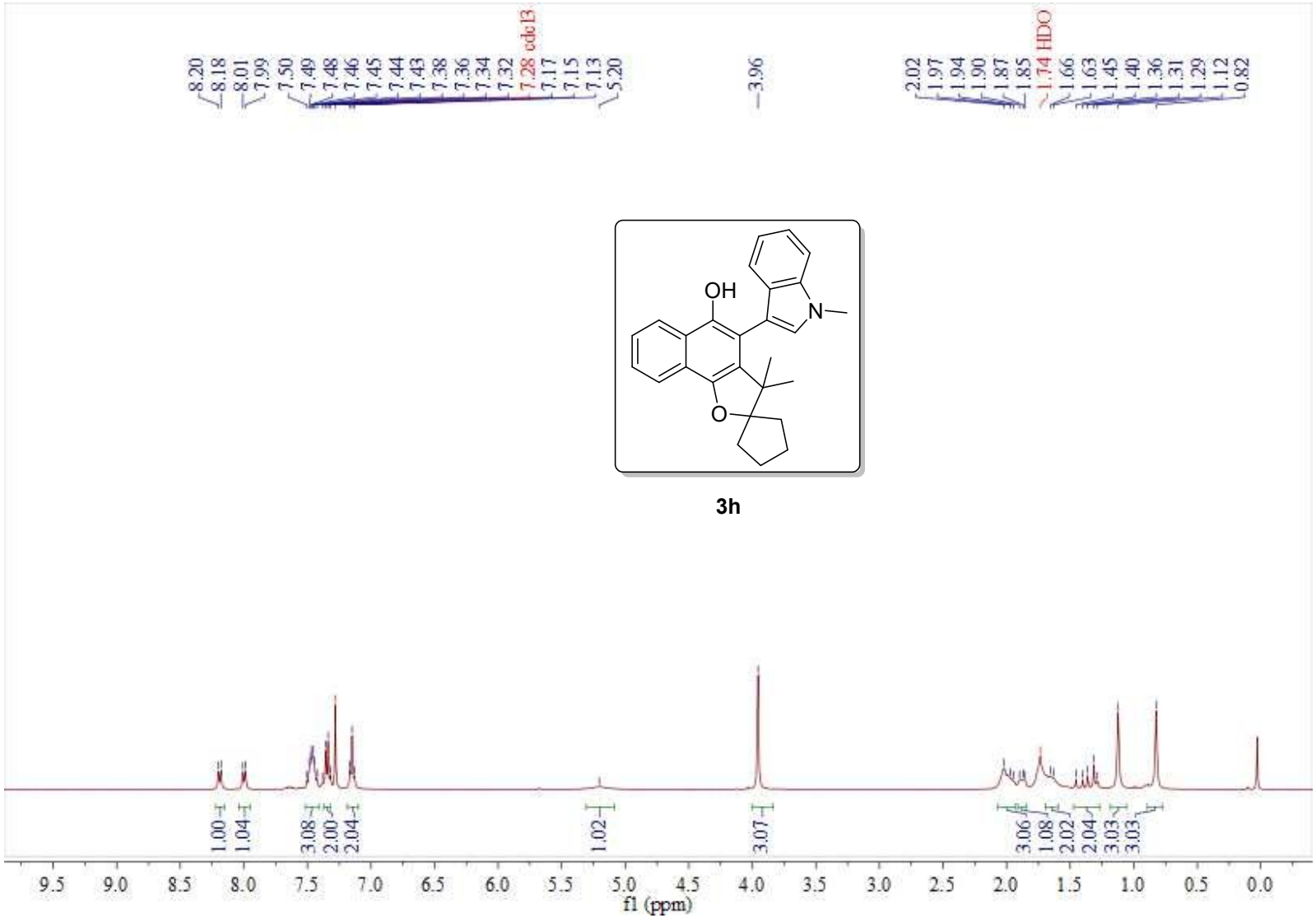
0
f1 (ppm)

3g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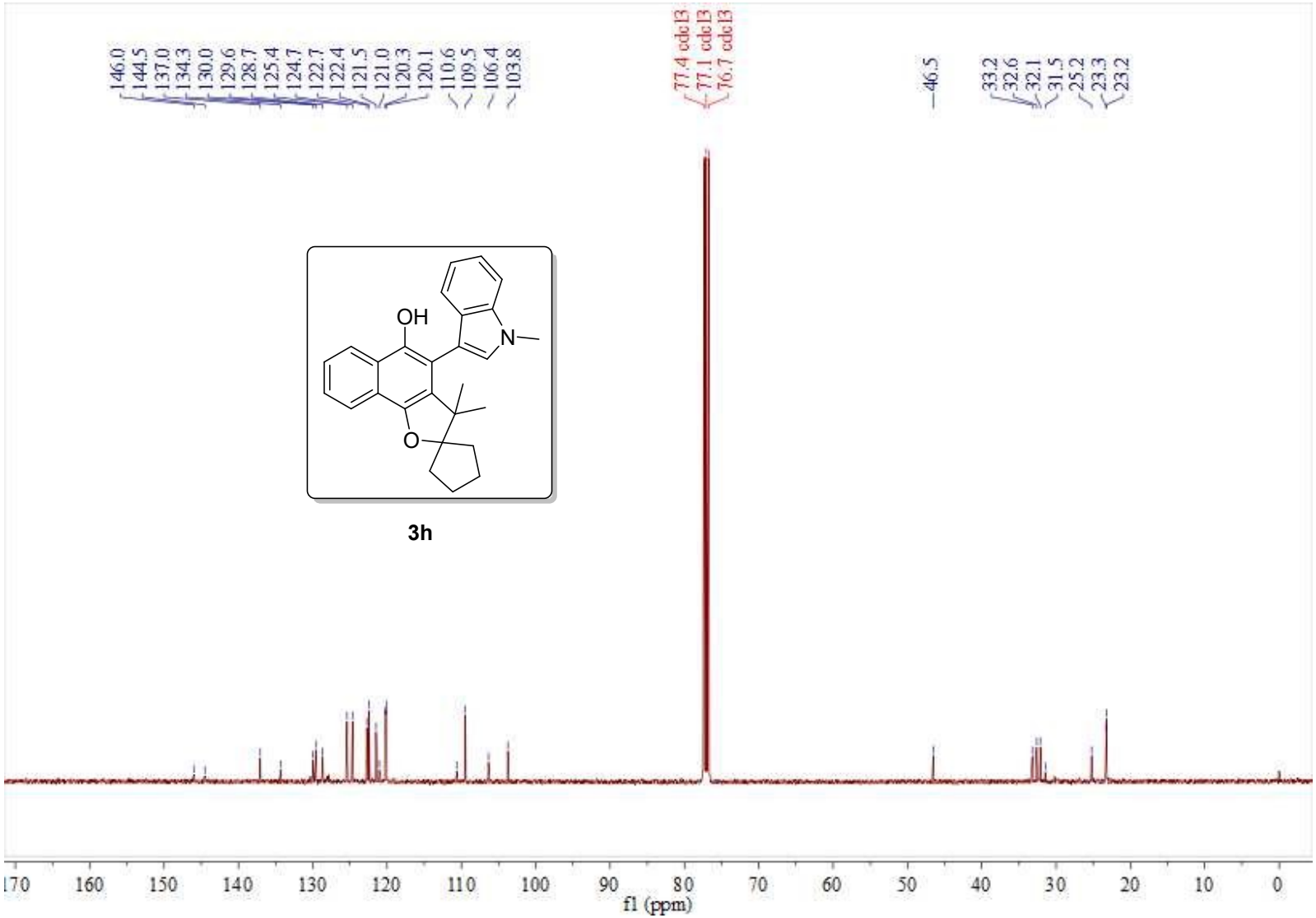
3h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77.1 cdcl3
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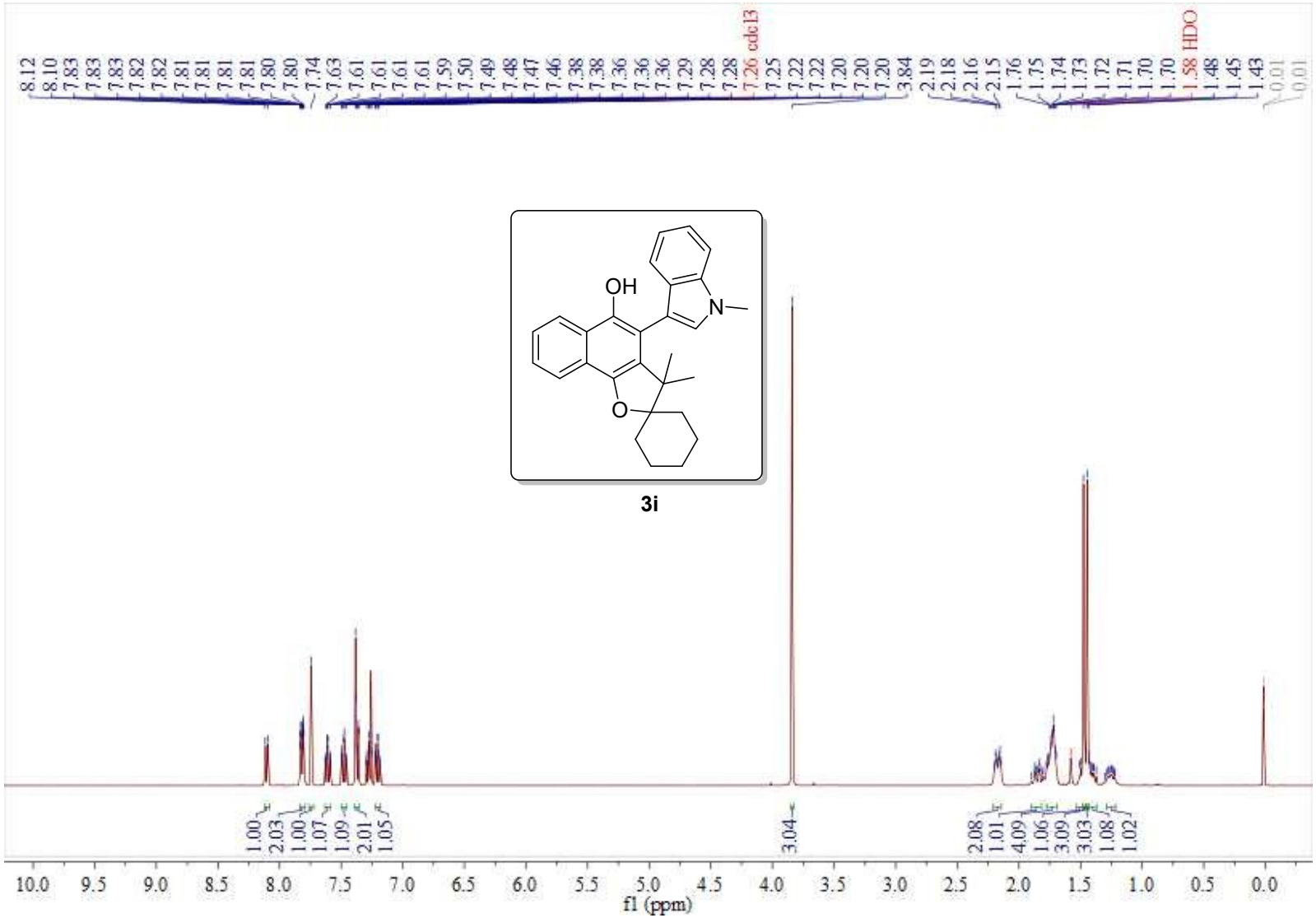
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OH
N
O
3i
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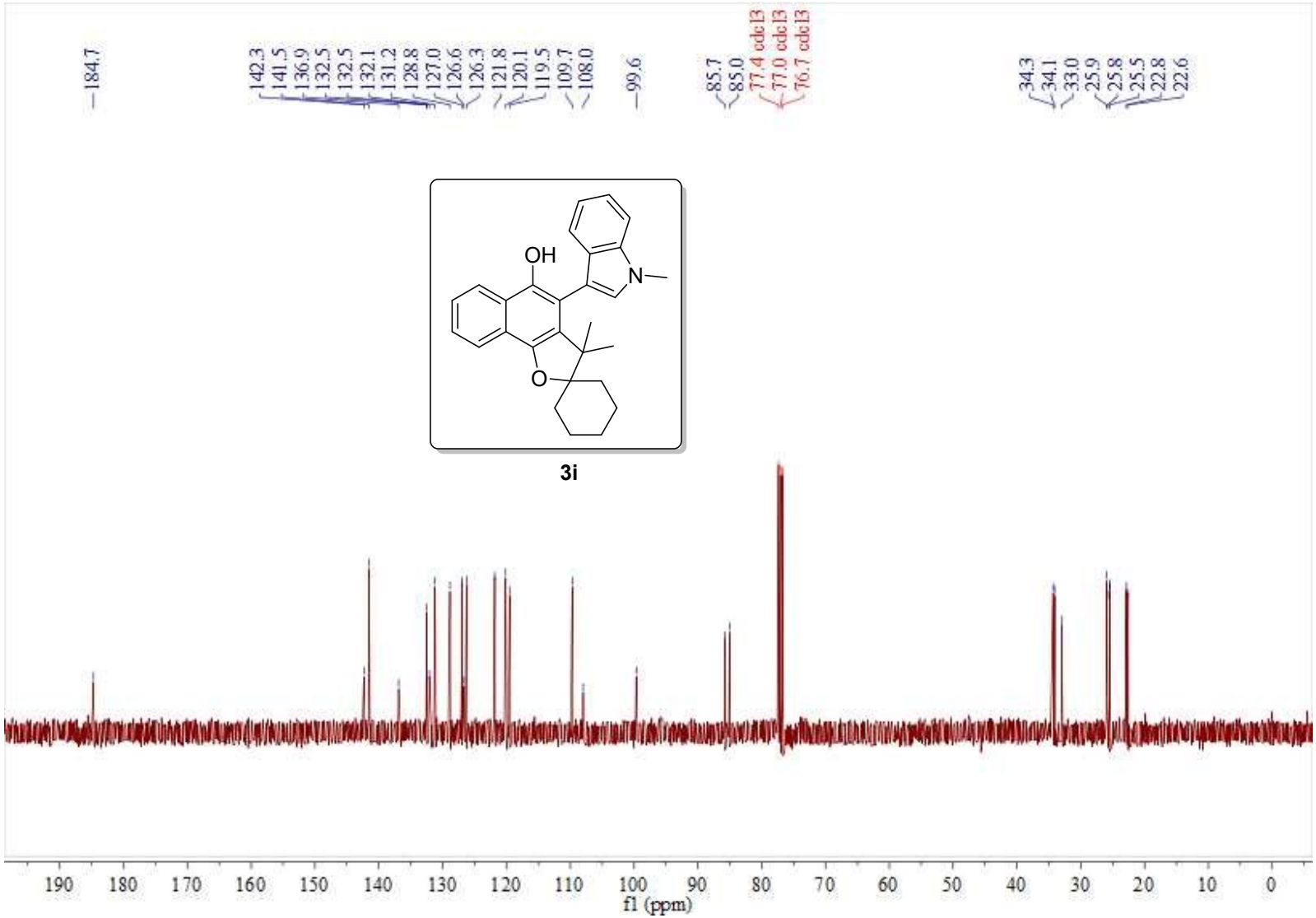
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85.7
85.0
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77.0 cdcl3
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33.0
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O
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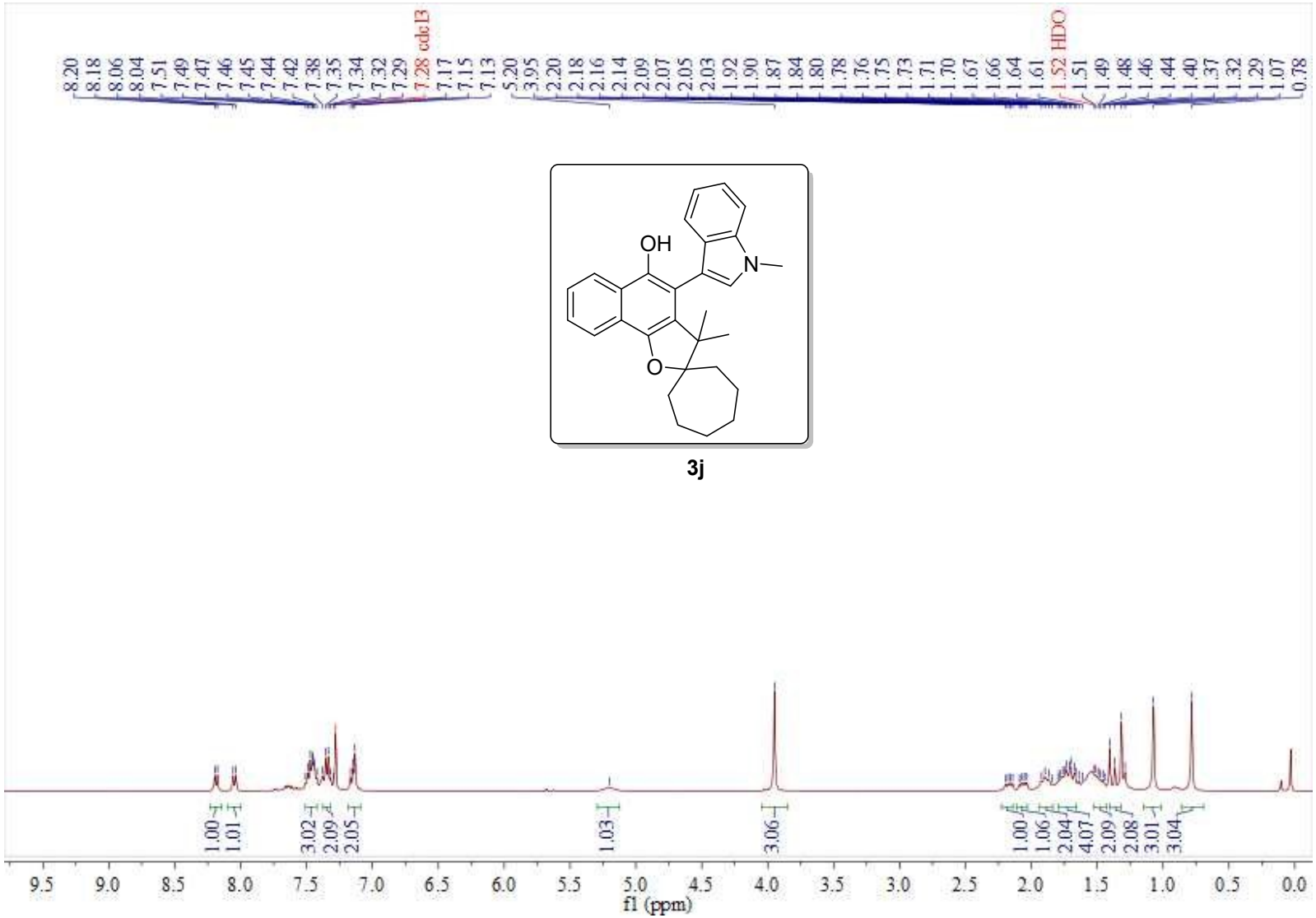
f1 (ppm)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O
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2.04
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2.08
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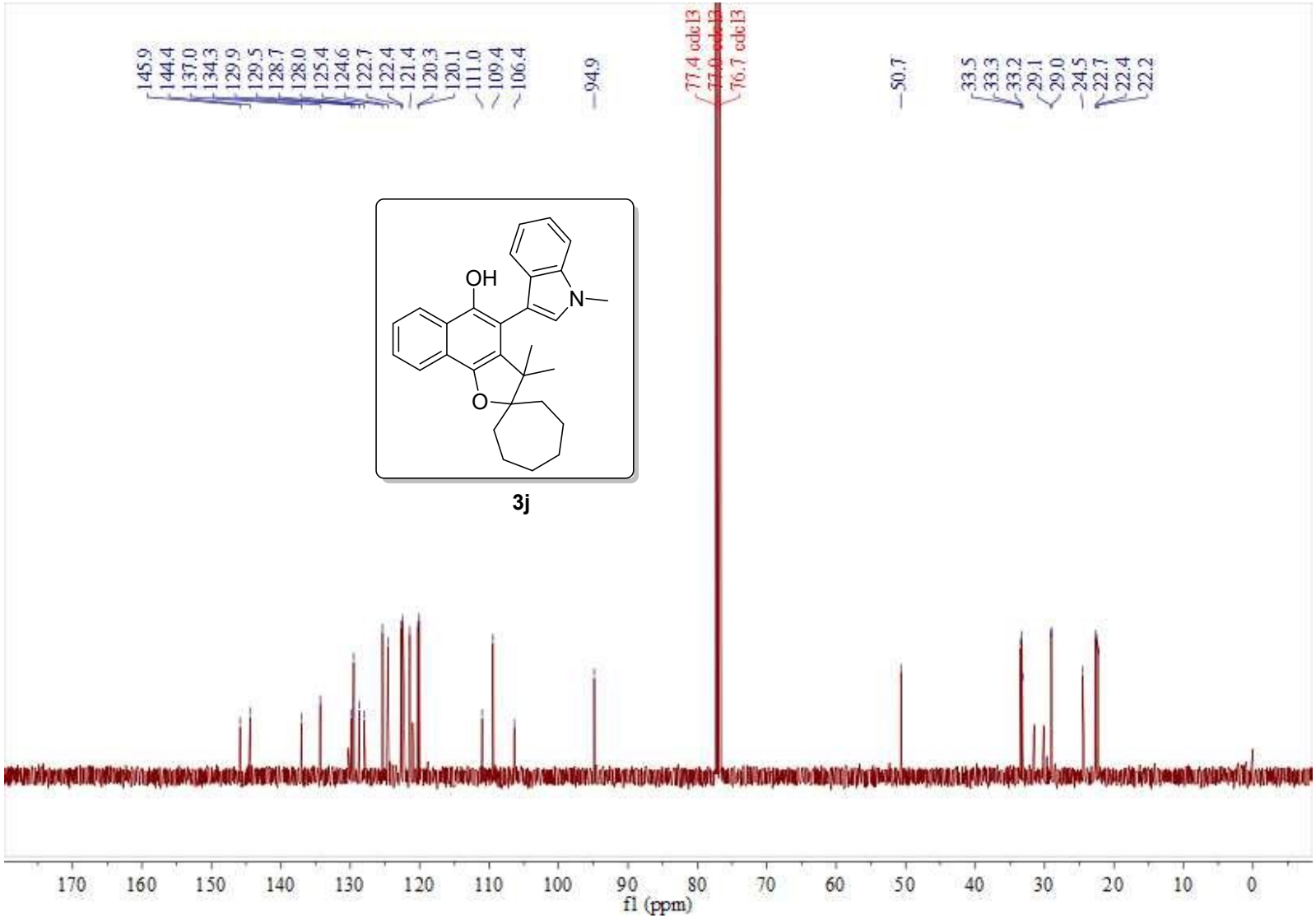
f1 (ppm)

3j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128.7
128.0
125.4
124.6
122.7
122.4
121.4
120.3
120.1
111.0
109.4
106.4
94.9
77.4 cdcl3
77.0 cdcl3
76.7 cdcl3
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33.5
33.3
33.2
29.1
29.0
24.5
22.7
22.4
22.2
OH
N
O
3j
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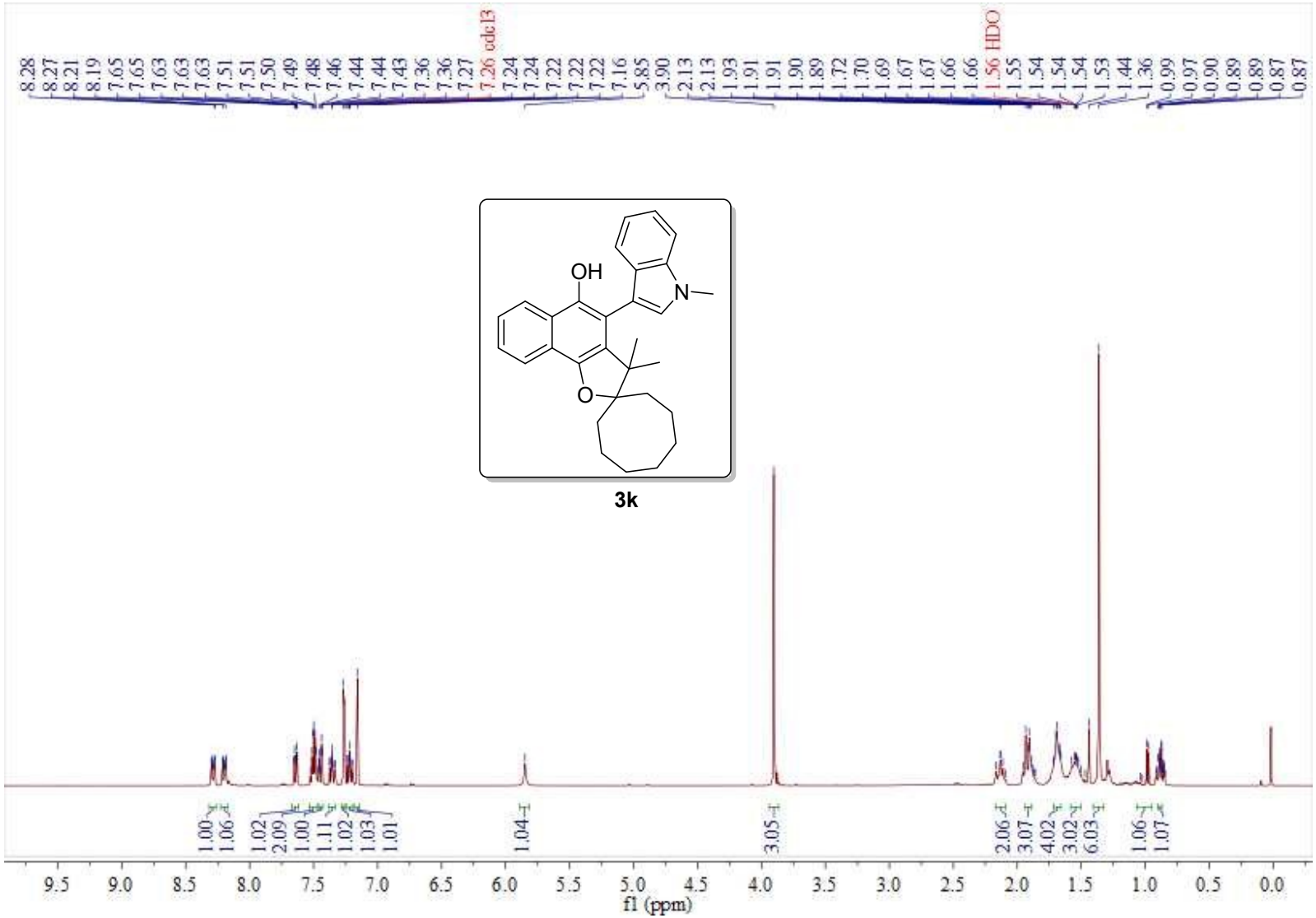
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7.48
7.46
7.44
7.44
7.43
7.36
7.36
7.27
7.26 cdcl3
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7.22
7.22
7.22
7.16
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3.90
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2.13
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1.91
1.91
1.90
1.89
1.72
1.70
1.69
1.67
1.67
1.66
1.66
1.56 HDO
1.55
1.54
1.54
1.54
1.53
1.44
1.36
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0.90
0.89
0.89
0.87
0.87
OH
N
O
3k
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1.06
1.02
2.09
1.00
1.11
1.02
1.03
1.01
1.04
3.05
2.06
3.07
4.02
3.02
6.03
1.06
1.07
9.5
9.0
8.5
8.0
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7.0
6.5
6.0
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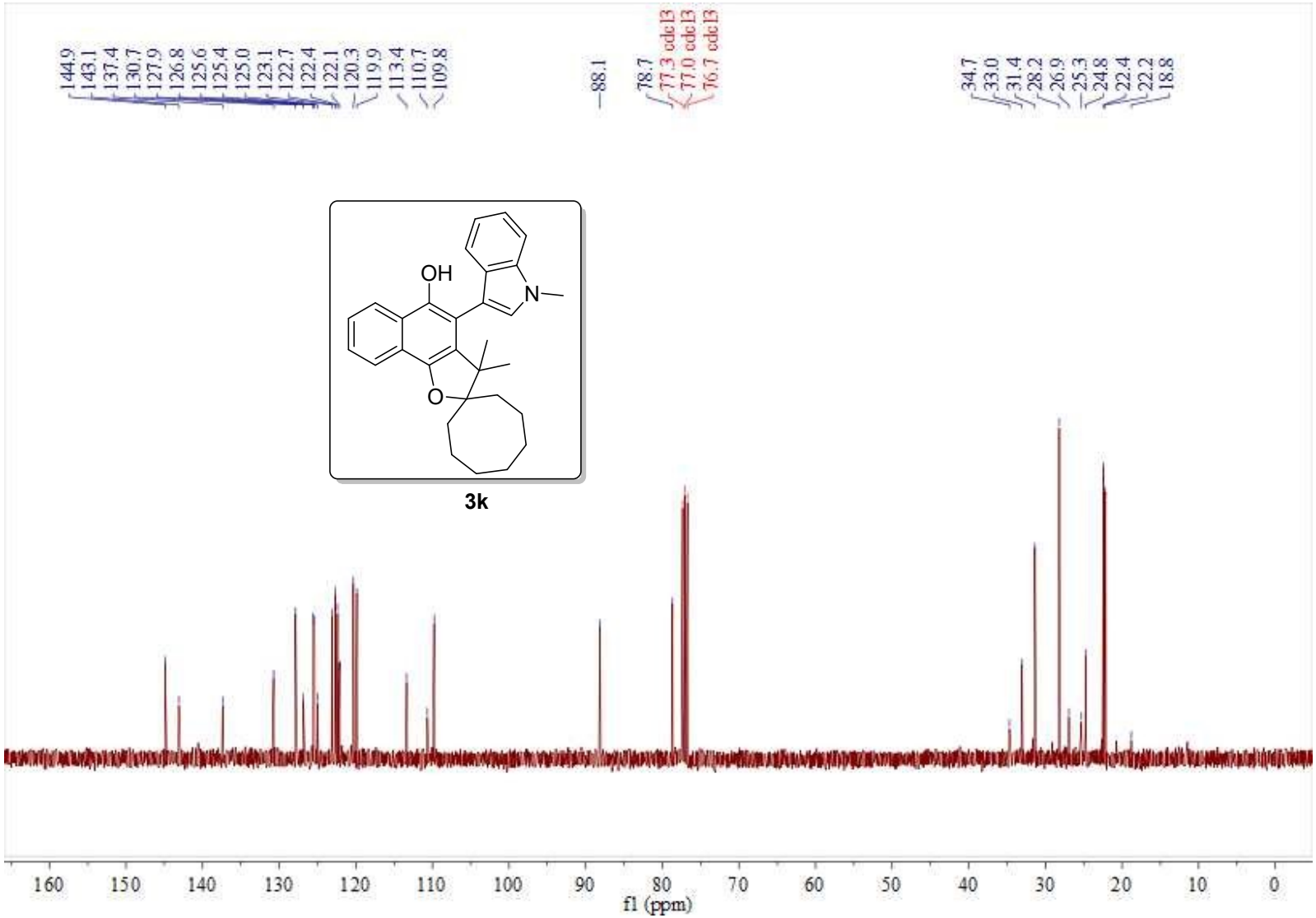
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120.3
119.9
113.4
110.7
109.8
88.1
78.7
77.3 cdcl3
77.0 cdcl3
76.7 cdcl3
34.7
33.0
31.4
28.2
26.9
25.3
24.8
22.4
22.2
18.8
OH
N
O
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120
110
100
90
80
70
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50
40
30
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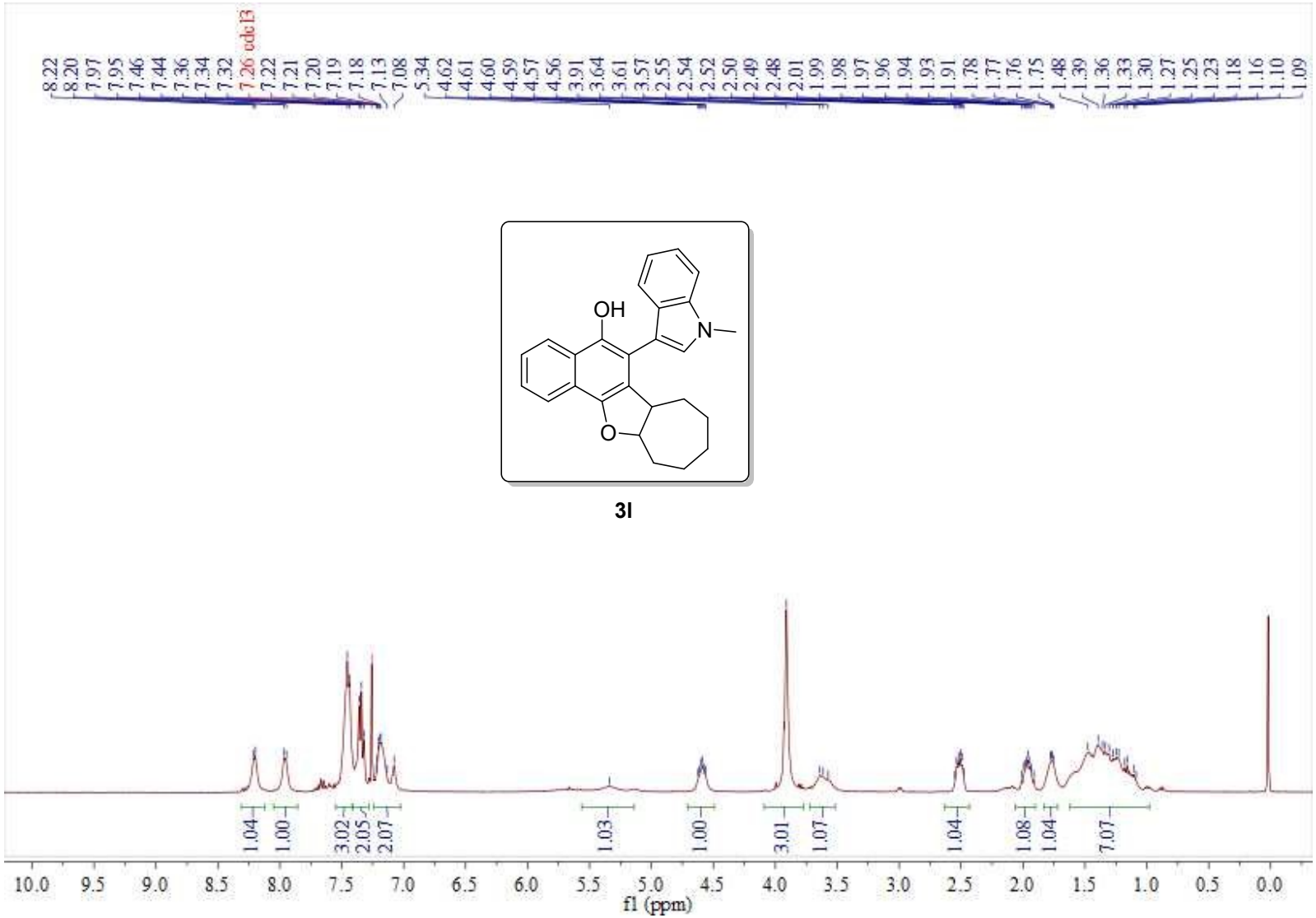
10
0
f1 (ppm)

3k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7.21
7.20
7.19
7.18
7.13
7.08
5.34
4.62
4.61
4.60
4.59
4.57
4.56
3.91
3.64
3.61
3.57
2.55
2.54
2.52
2.50
2.49
2.48
2.01
1.99
1.98
1.97
1.96
1.94
1.93
1.91
1.78
1.77
1.76
1.75
1.48
1.39
1.36
1.33
1.30
1.27
1.25
1.23
1.18
1.16
1.10
1.09
OH
N
O
1.04
1.00
3.02
2.05
2.07
1.03
1.00
3.01
1.07
1.04
1.08
1.04
7.07
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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3.0
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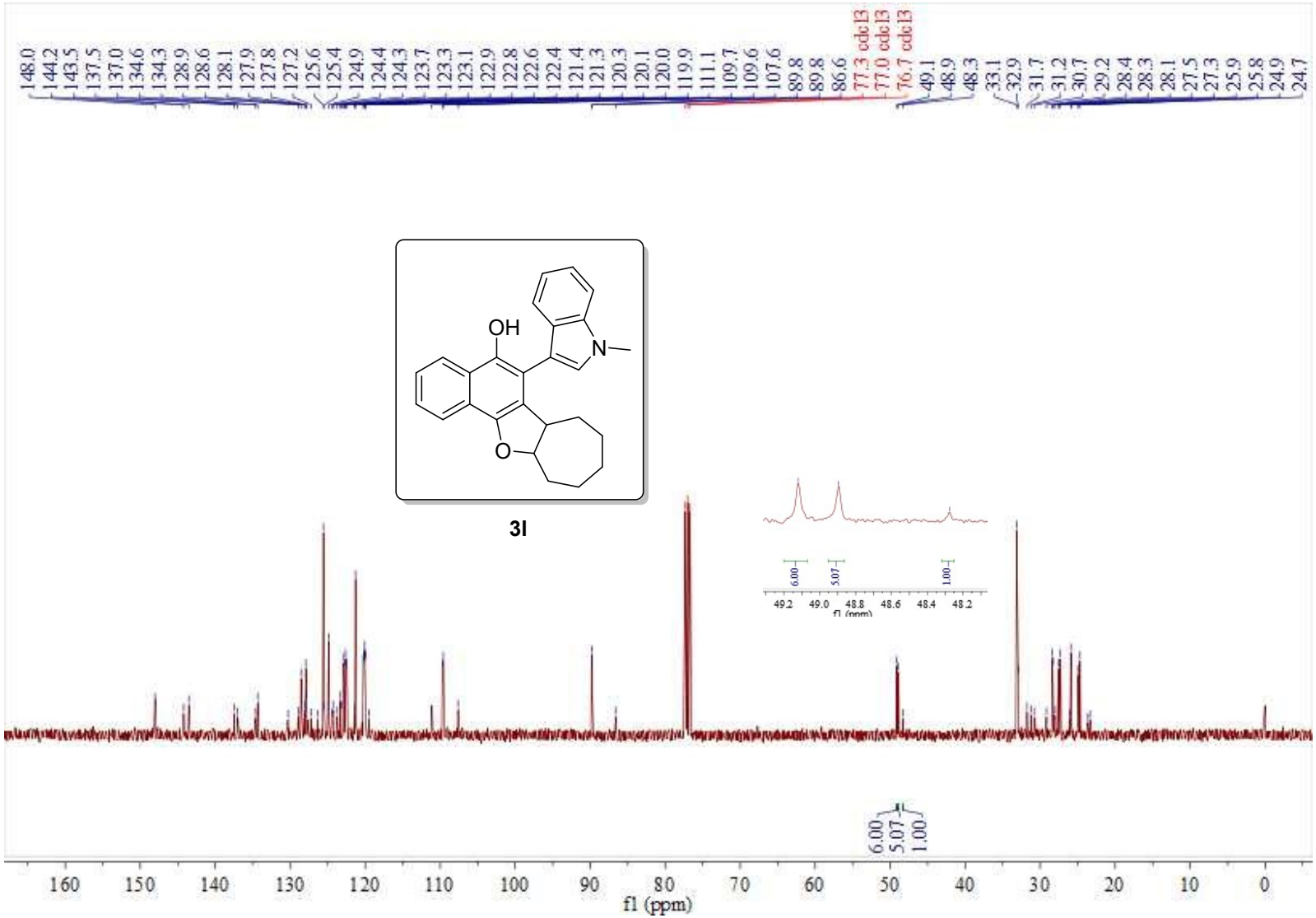
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

3l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125.4
124.9
124.4
124.3
123.7
123.3
123.1
122.9
122.8
122.6
122.4
121.4
121.3
120.3
120.1
120.0
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111.1
109.7
109.6
107.6
89.8
89.8
86.6
77.3 cdcl3
77.0 cdcl3
76.7 cdcl3
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48.9
48.3
33.1
32.9
31.7
31.2
30.7
29.2
28.4
28.3
28.1
27.5
27.3
25.9
25.8
24.9
24.7
OH
N
O
6.00
5.07
1.00
49.2
49.0
48.8
48.6
48.4
48.2
f1 (ppm)
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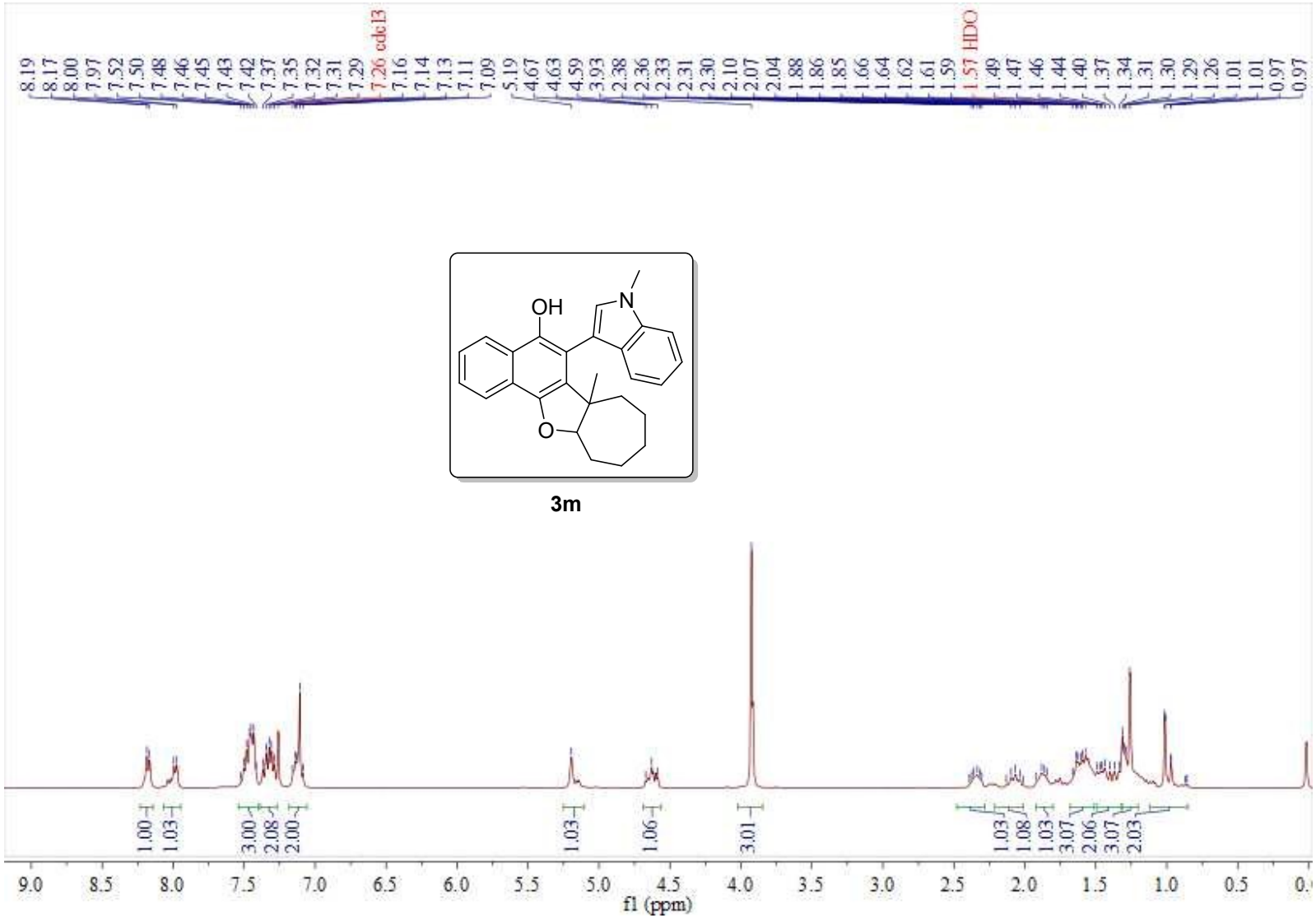
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

3l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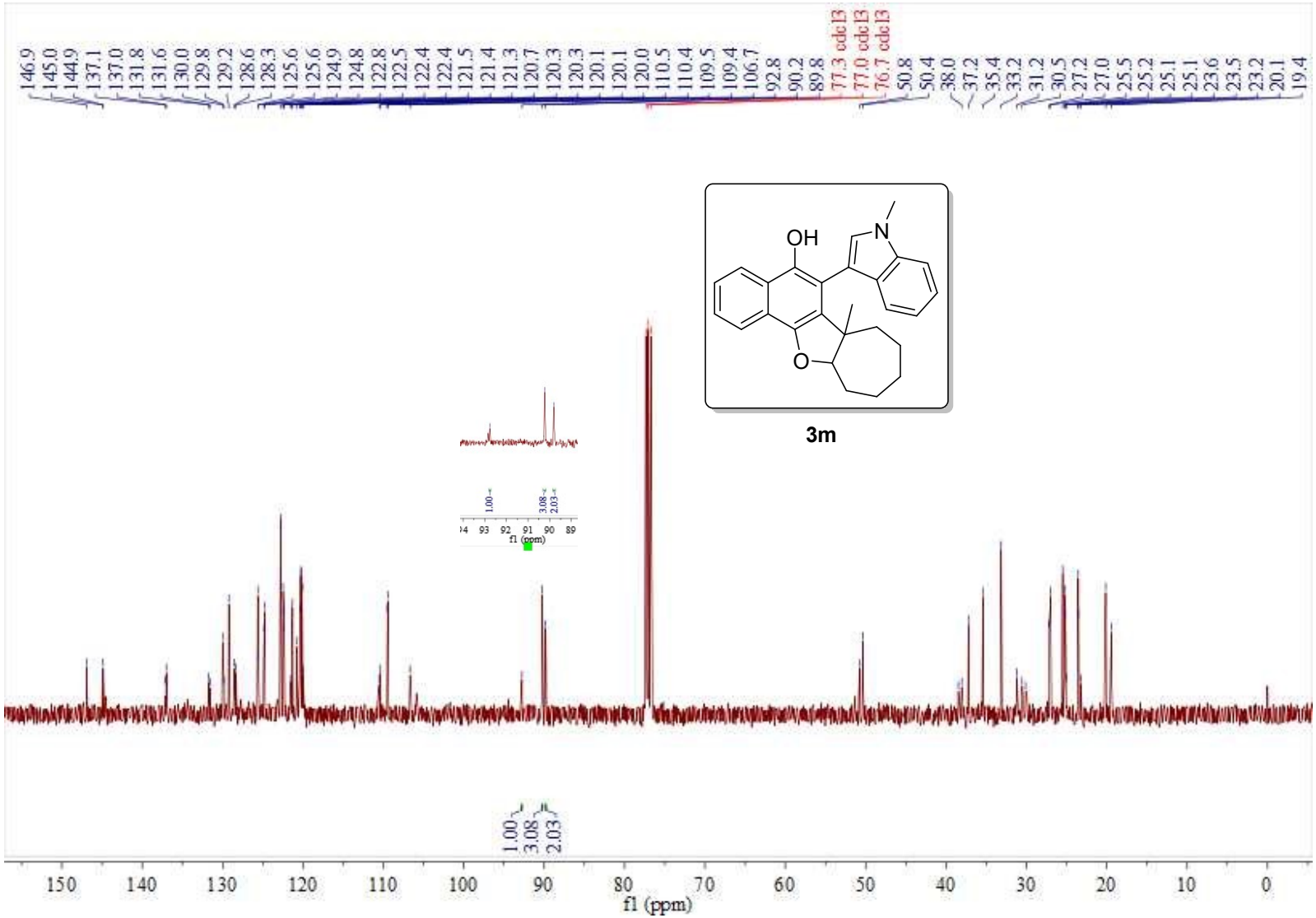
7.43
7.42
7.37
7.35
7.32
7.31
7.29
7.26 cdcl3
7.16
7.14
7.13
7.11
7.09
5.19
4.67
4.63
4.59
3.93
2.38
2.36
2.33
2.31
2.30
2.10
2.07
2.04
1.88
1.86
1.85
1.66
1.64
1.62
1.61
1.59
1.57 HDO
1.49
1.47
1.46
1.44
1.40
1.37
1.34
1.31
1.30
1.29
1.26
1.01
1.01
0.97
0.97
OH
N
O
1.00
1.03
3.00
2.08
2.00
1.03
1.06
3.01
1.03
1.08
1.03
3.07
2.06
3.07
2.03
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

3m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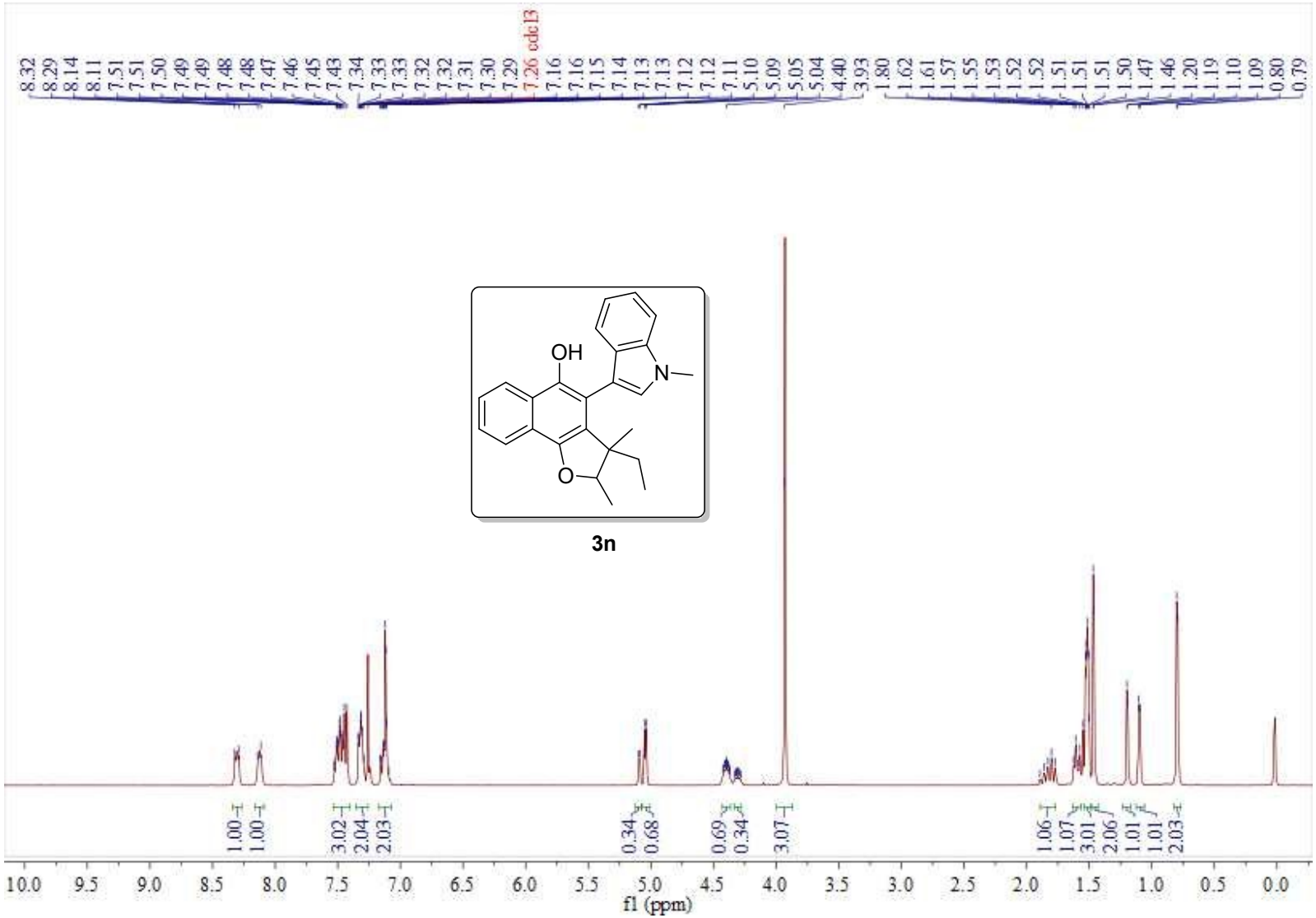
130.0
129.8
129.2
128.6
128.3
125.6
125.6
124.9
124.8
122.8
122.5
122.4
122.4
121.5
121.4
121.3
120.7
120.3
120.3
120.1
120.1
120.0
110.5
110.4
109.5
109.4
106.7
92.8
90.2
89.8
77.3 cdcl3
77.0 cdcl3
76.7 cdcl3
50.8
50.4
38.0
37.2
35.4
33.2
31.2
30.5
27.2
27.0
25.5
25.2
25.1
25.1
23.6
23.5
23.2
20.1
19.4
OH
N
O
1.00
3.08
2.03
f1 (ppm)

3m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7.48
7.48
7.47
7.46
7.45
7.43
7.34
7.33
7.33
7.32
7.32
7.31
7.30
7.29
7.26 cdcl3
7.16
7.16
7.15
7.14
7.13
7.13
7.12
7.12
7.11
5.10
5.09
5.05
5.04
4.40
3.93
1.80
1.62
1.61
1.57
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1.52
1.52
1.51
1.51
1.51
1.50
1.47
1.46
1.20
1.19
1.10
1.09
0.80
0.79
OH
N
O
3n
1.00
1.00
3.02
2.04
2.03
0.34
0.68
0.69
0.34
3.07
1.06
1.07
3.01
2.06
1.01
1.01
2.03
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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4.5
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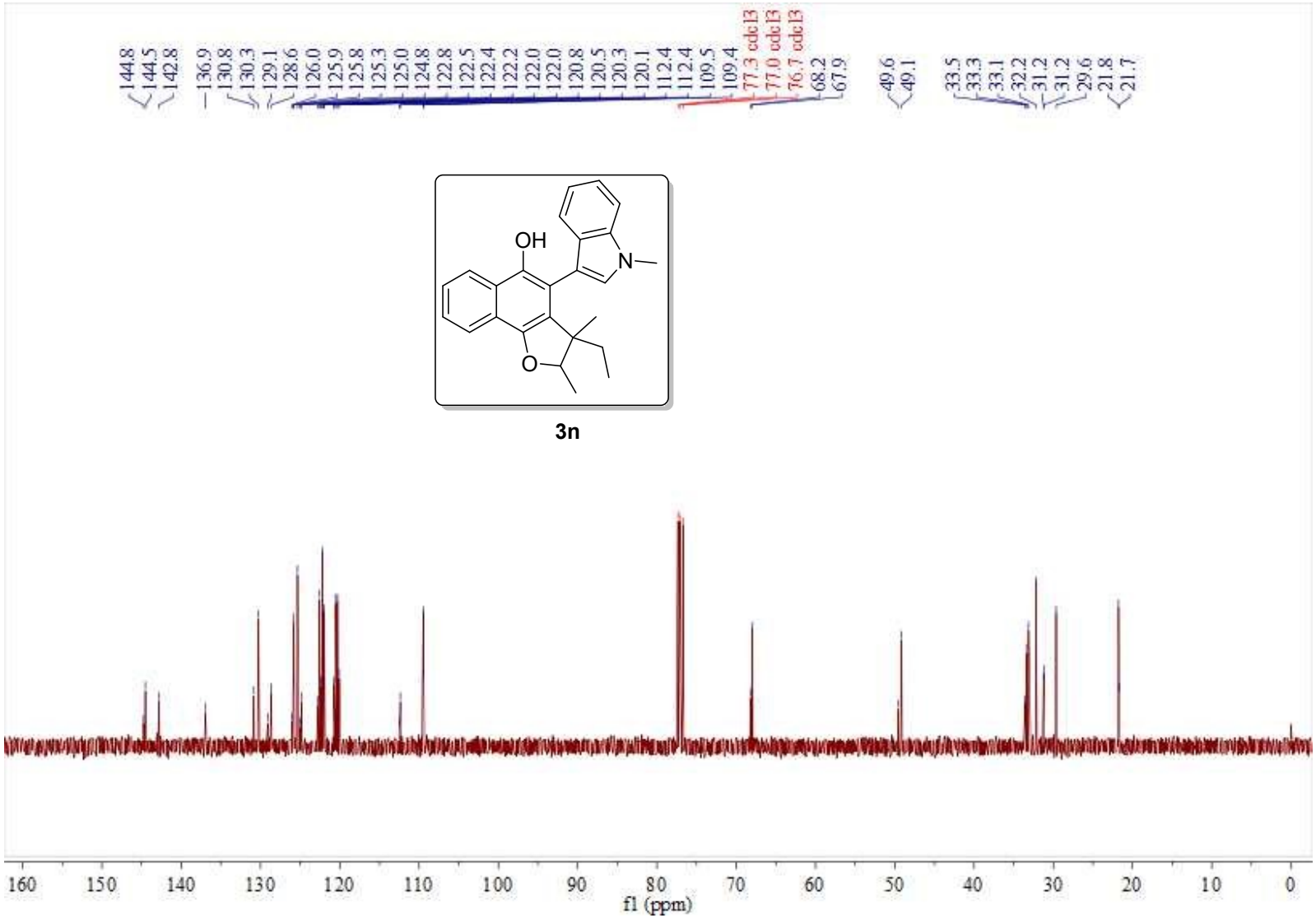
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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125.8
125.3
125.0
124.8
122.8
122.5
122.4
122.2
122.0
122.0
120.8
120.5
120.3
120.1
112.4
112.4
109.5
109.4
77.3 cdcl3
77.0 cdcl3
76.7 cdcl3
68.2
67.9
49.6
49.1
33.5
33.3
33.1
32.2
31.2
31.2
29.6
21.8
21.7
OH
N
O
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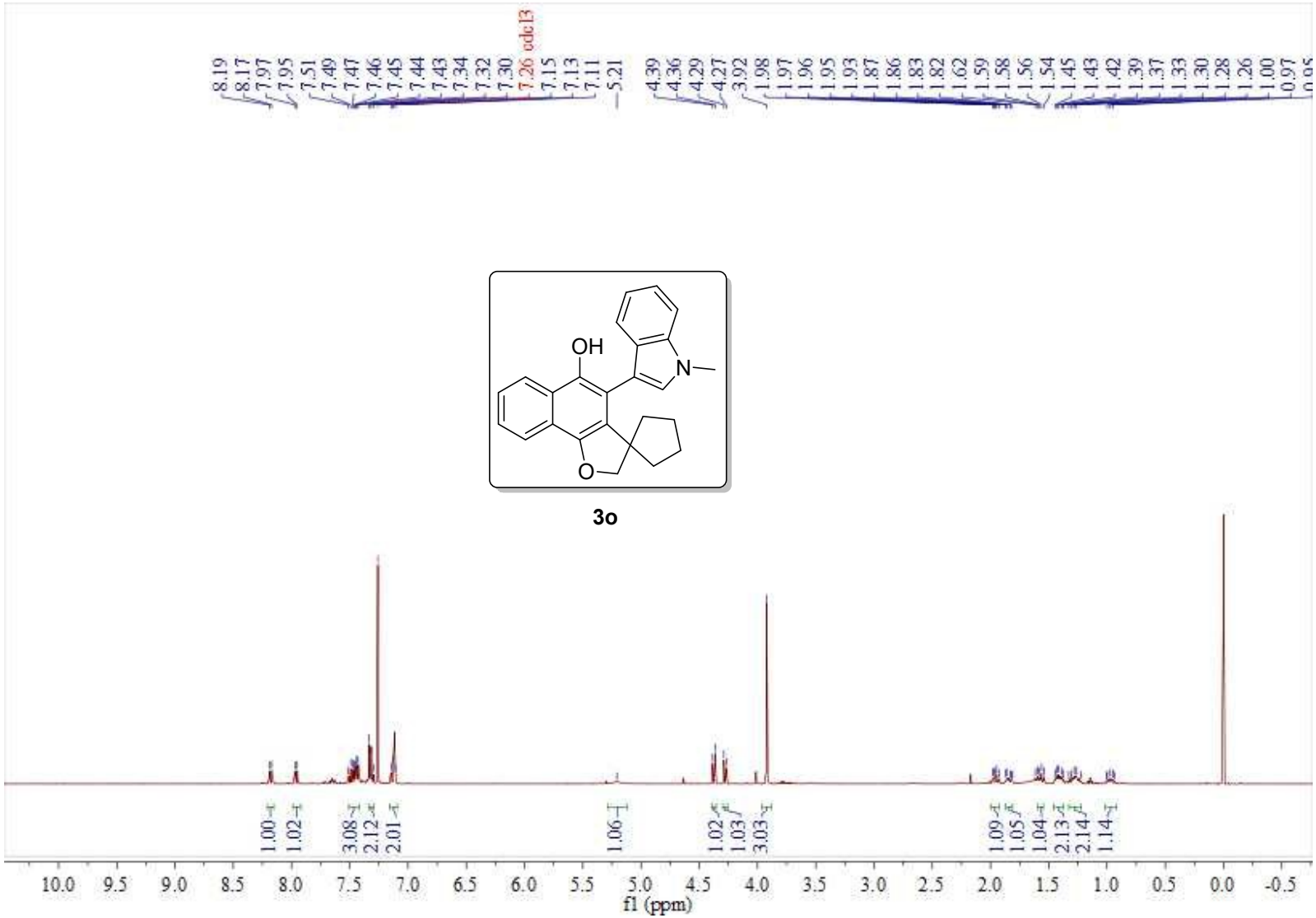
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

3n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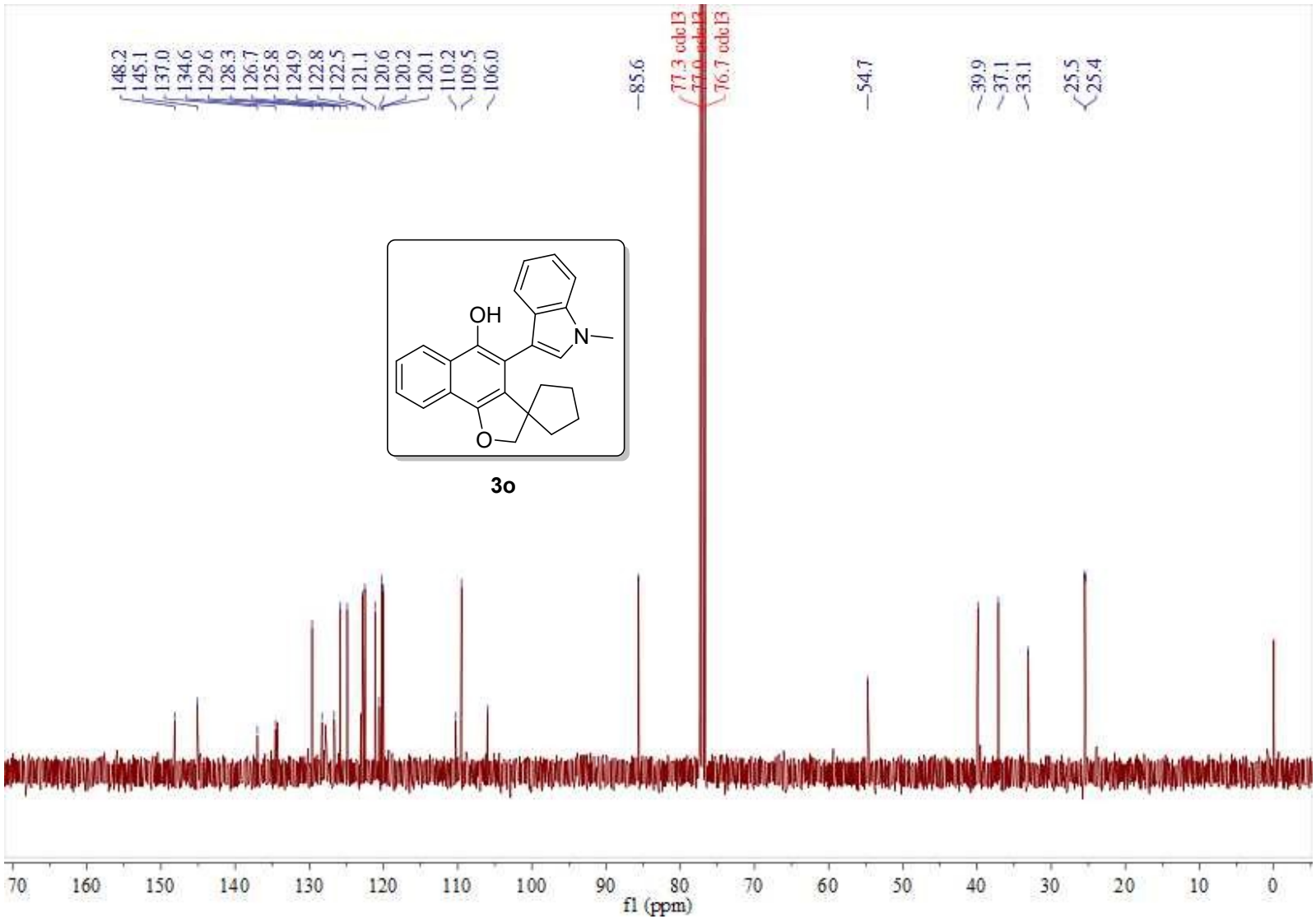
7.45
7.44
7.43
7.34
7.32
7.30
7.26 cdcl3
7.15
7.13
7.11
5.21
4.39
4.36
4.29
4.27
3.92
1.98
1.97
1.96
1.95
1.93
1.87
1.86
1.83
1.82
1.62
1.59
1.58
1.56
1.54
1.45
1.43
1.42
1.39
1.37
1.33
1.30
1.28
1.26
1.00
0.97
OH
N
O
1.00
1.02
3.08
2.12
2.01
1.06
1.02
1.03
3.03
1.09
1.05
1.04
2.13
2.14
1.14
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

3o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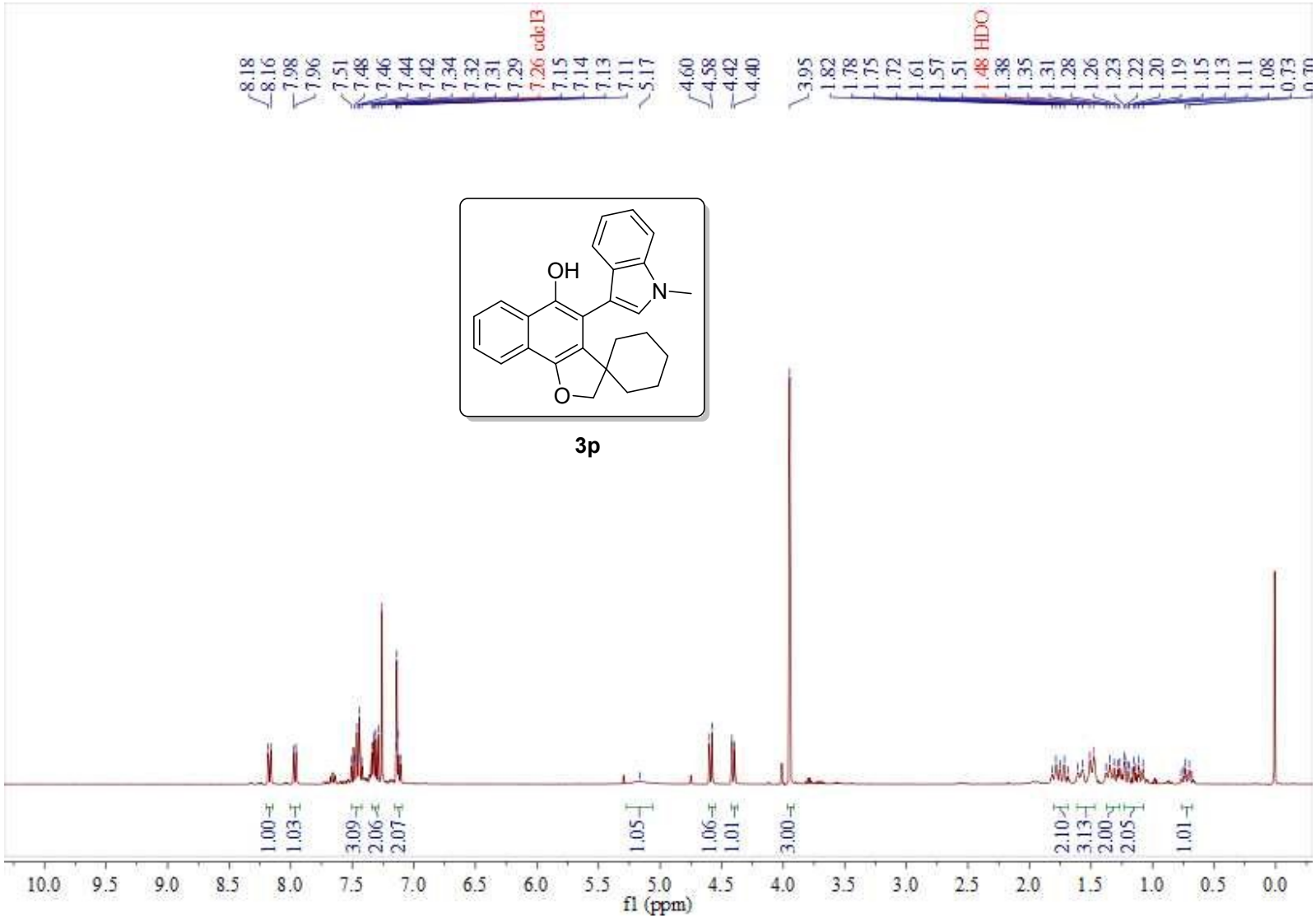
125.8
124.9
122.8
122.5
121.1
120.6
120.2
120.1
110.2
109.5
106.0
85.6
77.3 cdcl3
76.7 cdcl3
54.7
39.9
37.1
33.1
25.5
25.4
OH
N
O
70
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

3o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7.98
7.96
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7.44
7.42
7.34
7.32
7.31
7.29
7.26 cdcl3
7.15
7.14
7.13
7.11
5.17
4.60
4.58
4.42
4.40
3.95
1.82
1.78
1.75
1.72
1.61
1.57
1.51
1.48 HDO
1.38
1.35
1.31
1.28
1.26
1.23
1.22
1.20
1.19
1.15
1.13
1.11
1.08
0.73
OH
N
O
1.00
1.03
3.09
2.06
2.07
1.05
1.06
1.01
3.00
2.10
3.13
2.00
2.05
1.01
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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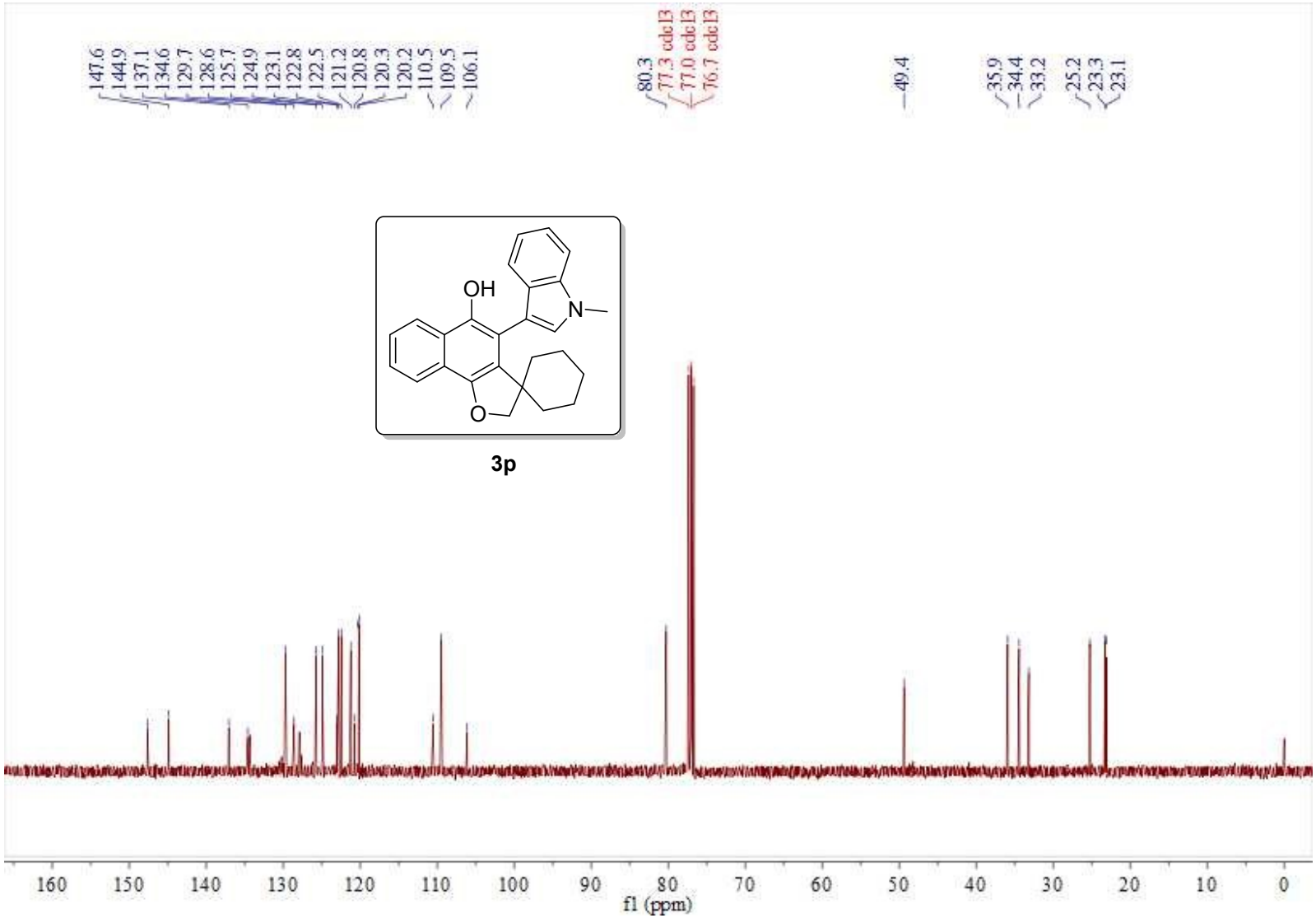
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

3p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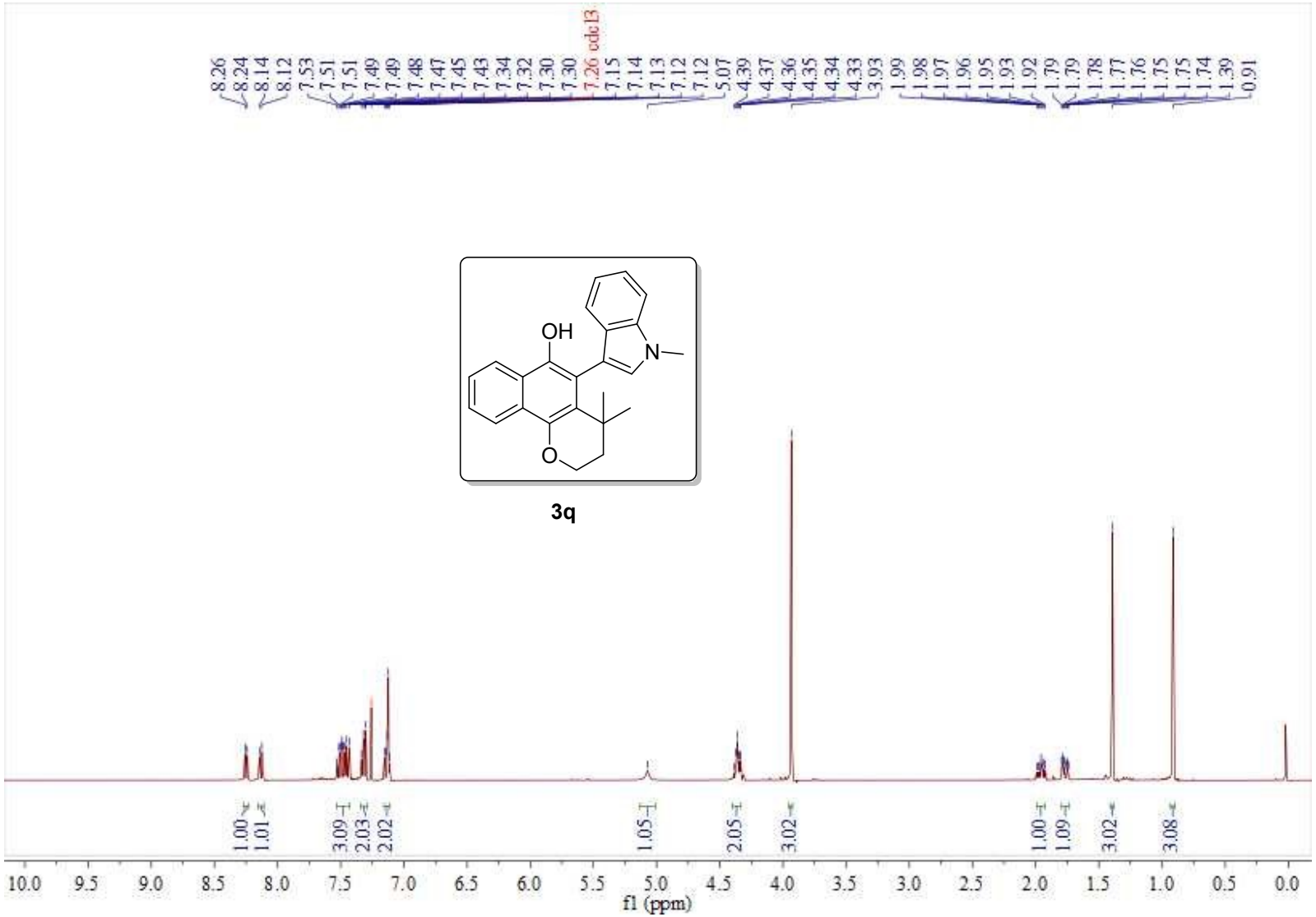
128.6
125.7
124.9
123.1
122.8
122.5
121.2
120.8
120.3
120.2
110.5
109.5
106.1
80.3
77.3 cdcl3
77.0 cdcl3
76.7 cdcl3
49.4
35.9
34.4
33.2
25.2
23.3
23.1
OH
N
O
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

3p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7.51
7.51
7.49
7.49
7.48
7.47
7.45
7.43
7.34
7.32
7.30
7.30
7.26 cdcl3
7.15
7.14
7.13
7.12
7.12
5.07
4.39
4.37
4.36
4.35
4.34
4.33
3.93
1.99
1.98
1.97
1.96
1.95
1.93
1.92
1.79
1.79
1.78
1.77
1.76
1.75
1.75
1.74
1.39
0.91
OH
N
O
1.00
1.01
3.09
2.03
2.02
1.05
2.05
3.02
1.00
1.09
3.02
3.08
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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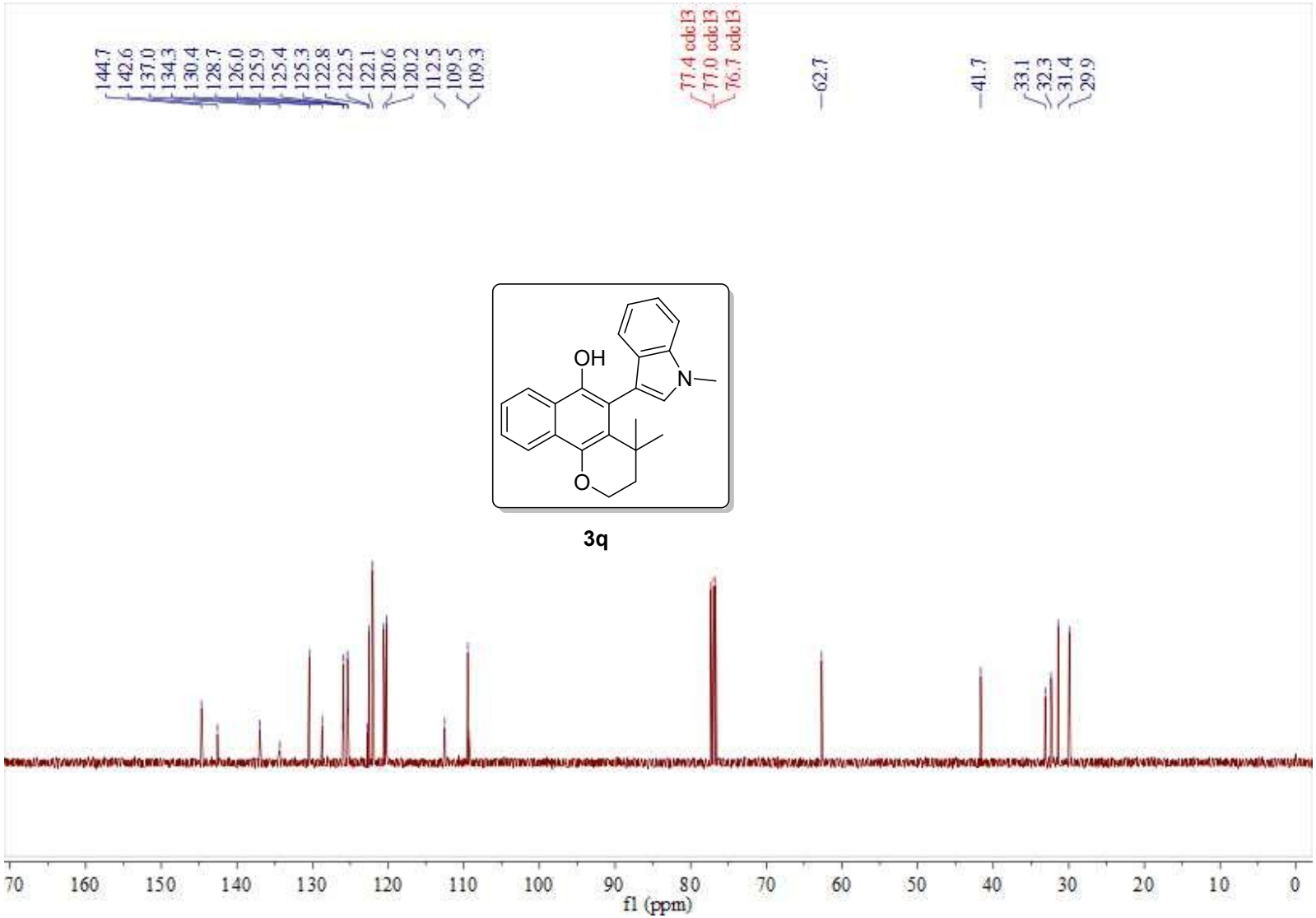
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

3q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128.7
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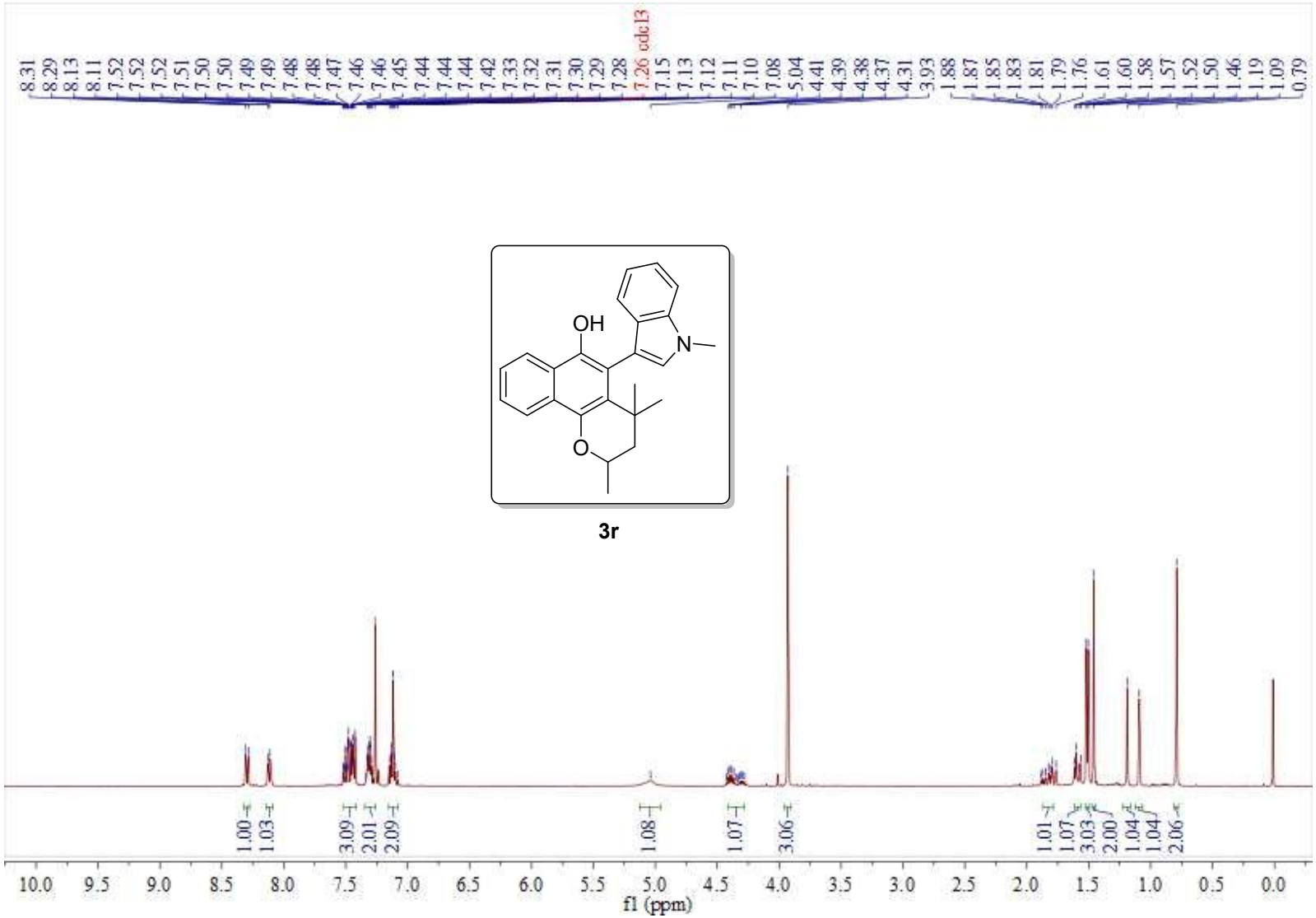
125.9
125.4
125.3
122.8
122.5
122.1
120.6
120.2
112.5
109.5
109.3
77.4 cdcl3
77.0 cdcl3
76.7 cdcl3
62.7
41.7
33.1
32.3
31.4
29.9
OH
N
O
3q
70
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.52
7.52
7.51
7.50
7.50
7.49
7.49
7.48
7.48
7.47
7.46
7.46
7.45
7.44
7.44
7.44
7.42
7.33
7.32
7.31
7.30
7.29
7.28
7.26 cdcl3
7.15
7.13
7.12
7.11
7.10
7.08
5.04
4.41
4.39
4.38
4.37
4.31
3.93
1.88
1.87
1.85
1.83
1.81
1.79
1.76
1.61
1.60
1.58
1.57
1.52
1.50
1.46
1.19
1.09
0.79
OH
N
O
3r
1.00
1.03
3.09
2.01
2.09
1.08
1.07
3.06
1.01
1.07
3.03
2.00
1.04
1.04
2.06
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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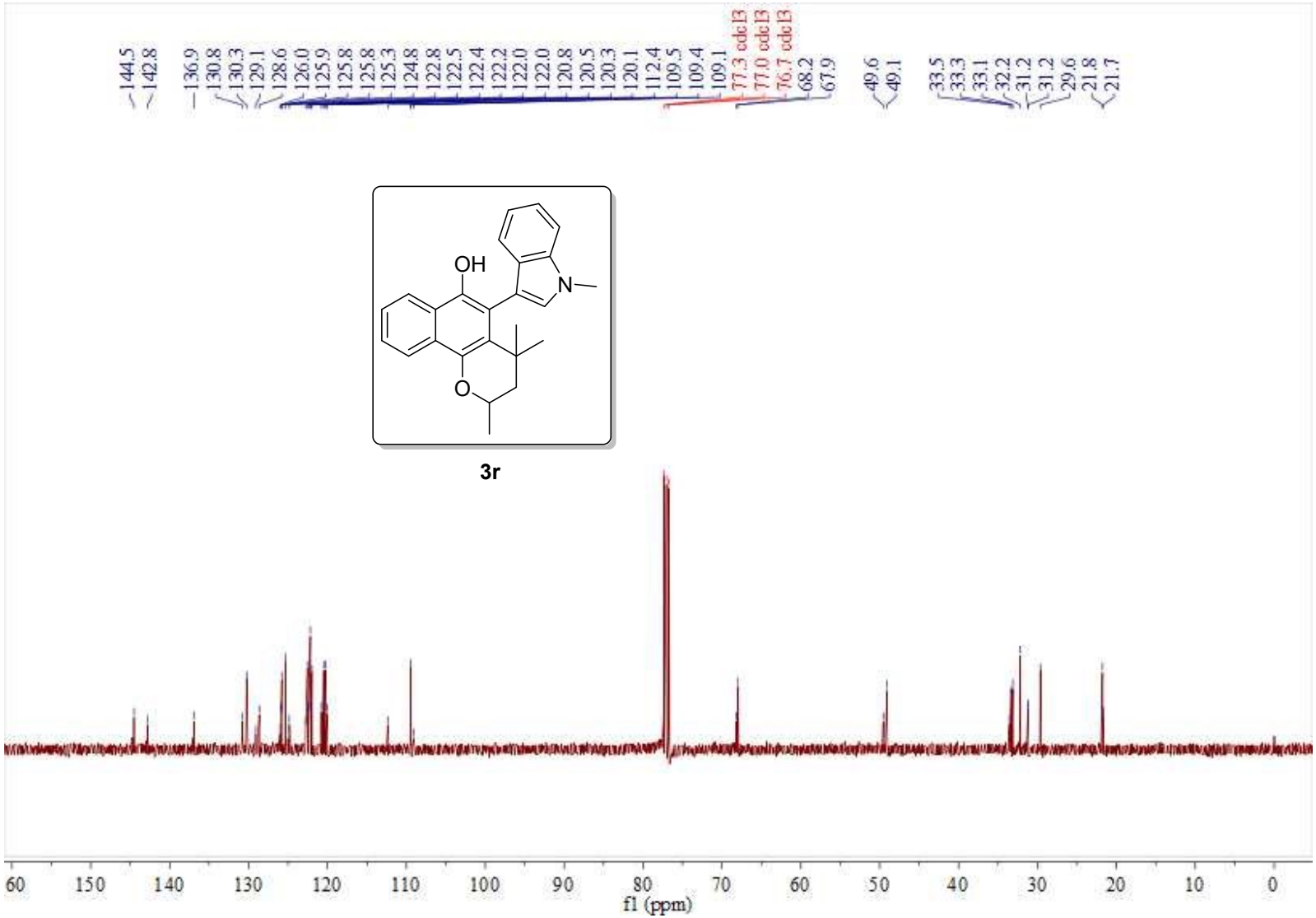
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


144.5
142.8
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130.8
130.3
129.1
128.6
126.0
125.9
125.8
125.8
125.3
124.8
122.8
122.5
122.4
122.2
122.0
122.0
120.8
120.5
120.3
120.1
112.4
109.5
109.4
109.1
77.3 cdcl3
77.0 cdcl3
76.7 cdcl3
68.2
67.9
49.6
49.1
33.5
33.3
33.1
32.2
31.2
31.2
29.6
21.8
21.7
OH
N
O
60
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140
130
120
110
100
90
80
70
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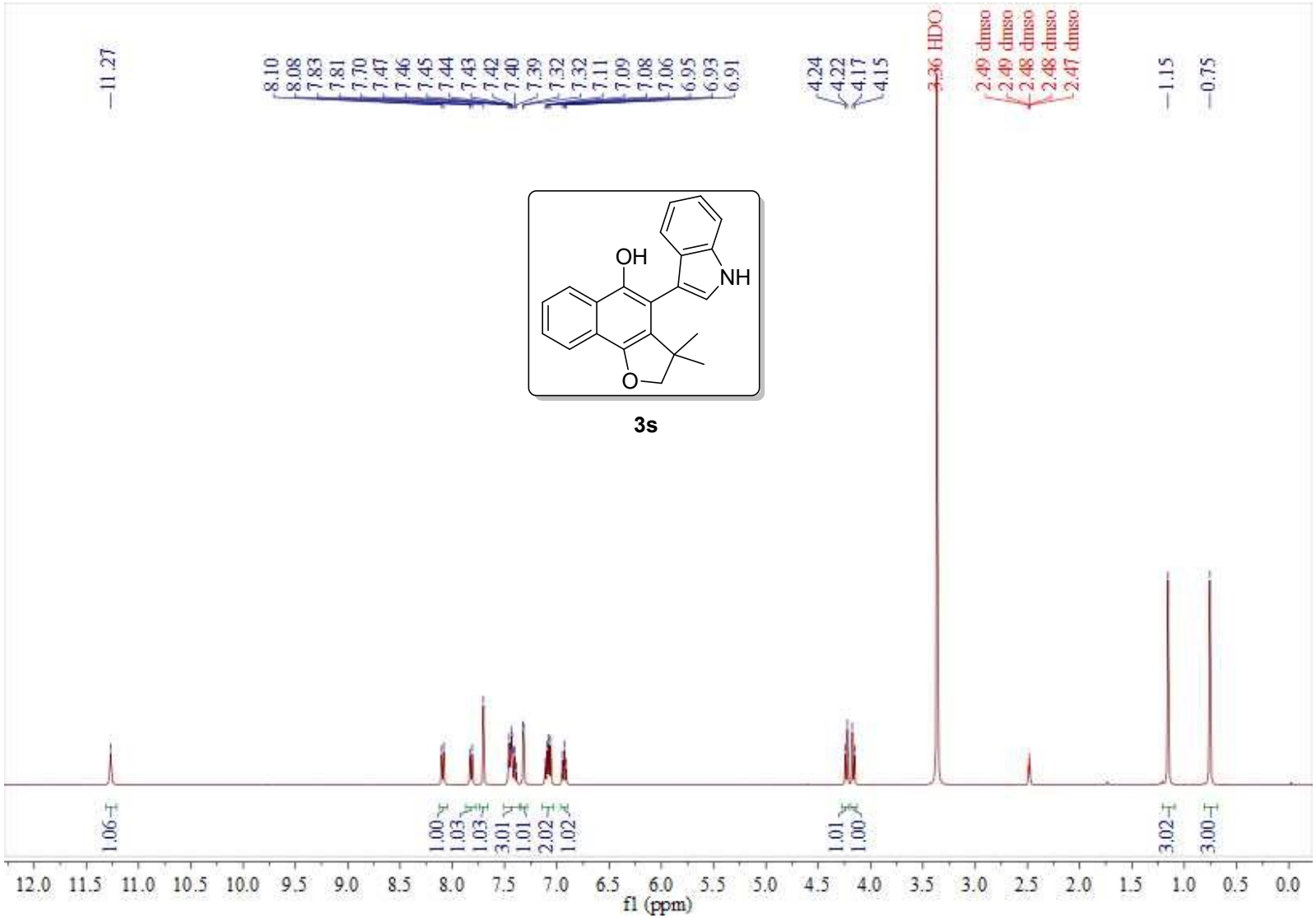
50
40
30
20
10
0
f1 (ppm)

3r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8.08
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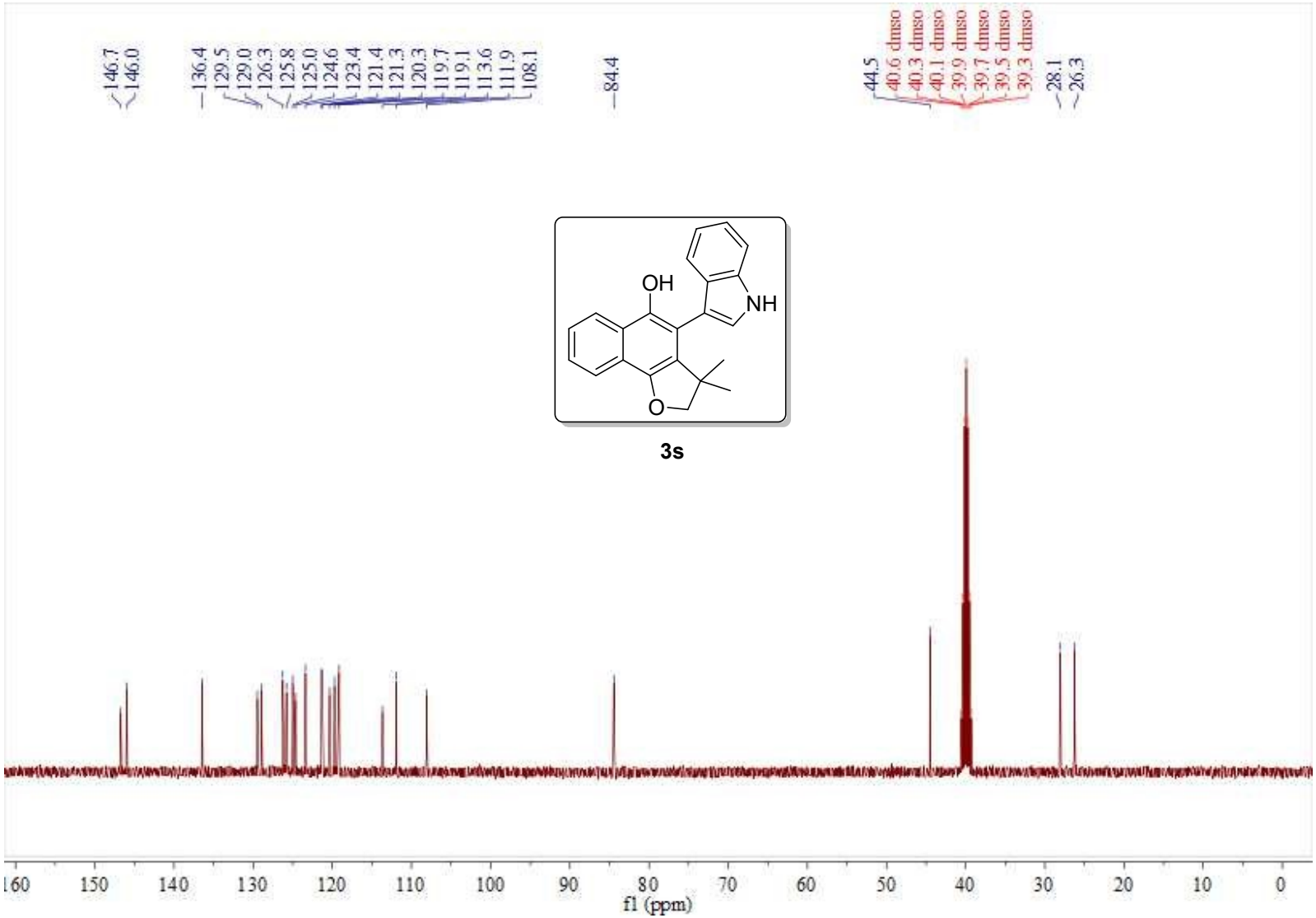
7.81
7.70
7.47
7.46
7.45
7.44
7.43
7.42
7.40
7.39
7.32
7.32
7.11
7.09
7.08
7.06
6.95
6.93
6.91
4.24
4.22
4.17
4.15
3.36 HDO
2.49 dmso
2.49 dmso
2.48 dmso
2.48 dmso
2.47 dmso
1.15
0.75
OH
NH
O
1.06
1.00
1.03
1.03
3.01
1.01
2.02
1.02
1.01
1.00
3.02
3.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

3s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126.3
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125.0
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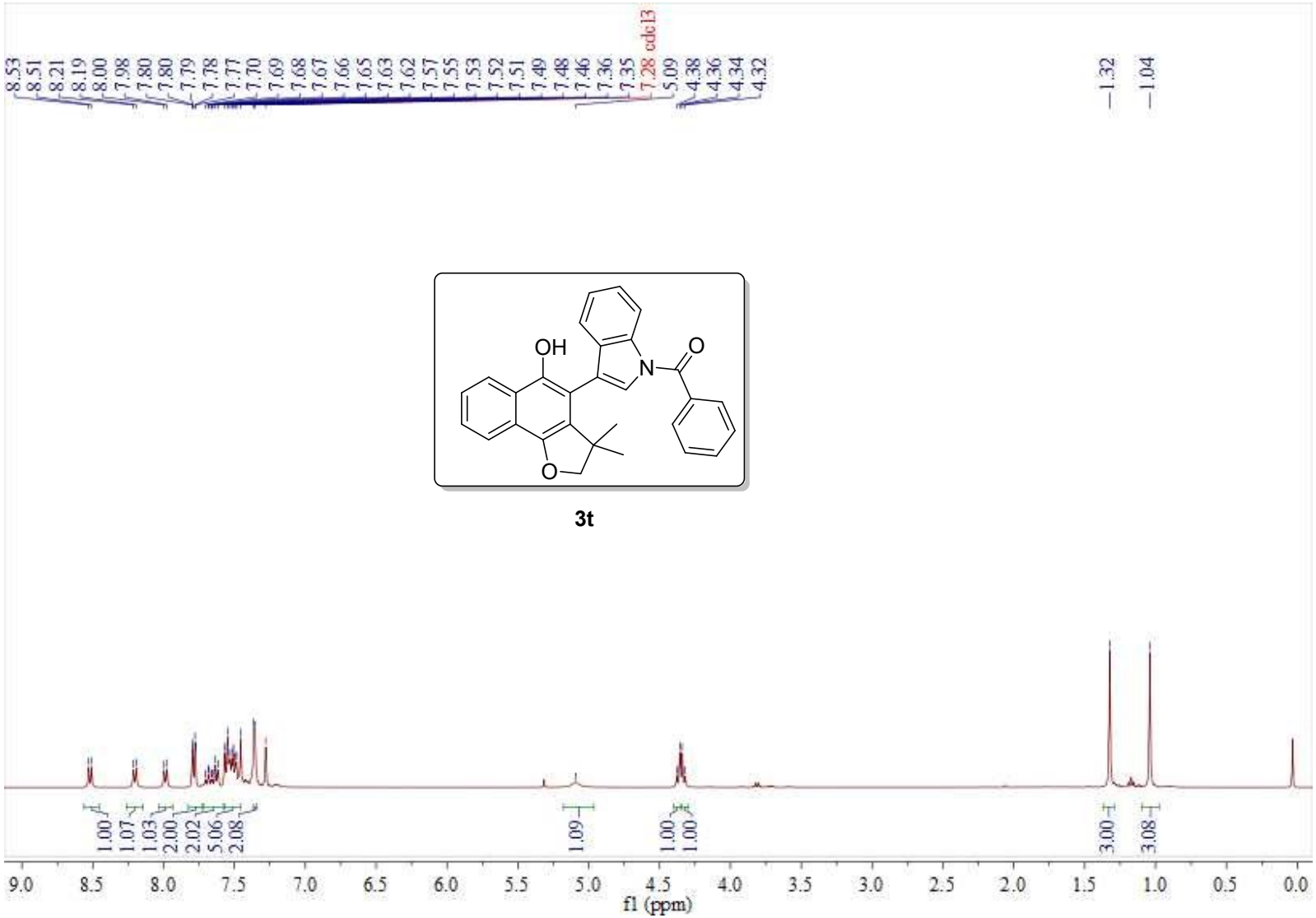
123.4
121.4
121.3
120.3
119.7
119.1
113.6
111.9
108.1
84.4
44.5
40.6 dmso
40.3 dmso
40.1 dmso
39.9 dmso
39.7 dmso
39.5 dmso
39.3 dmso
28.1
26.3
OH
NH
O
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

3s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8.51
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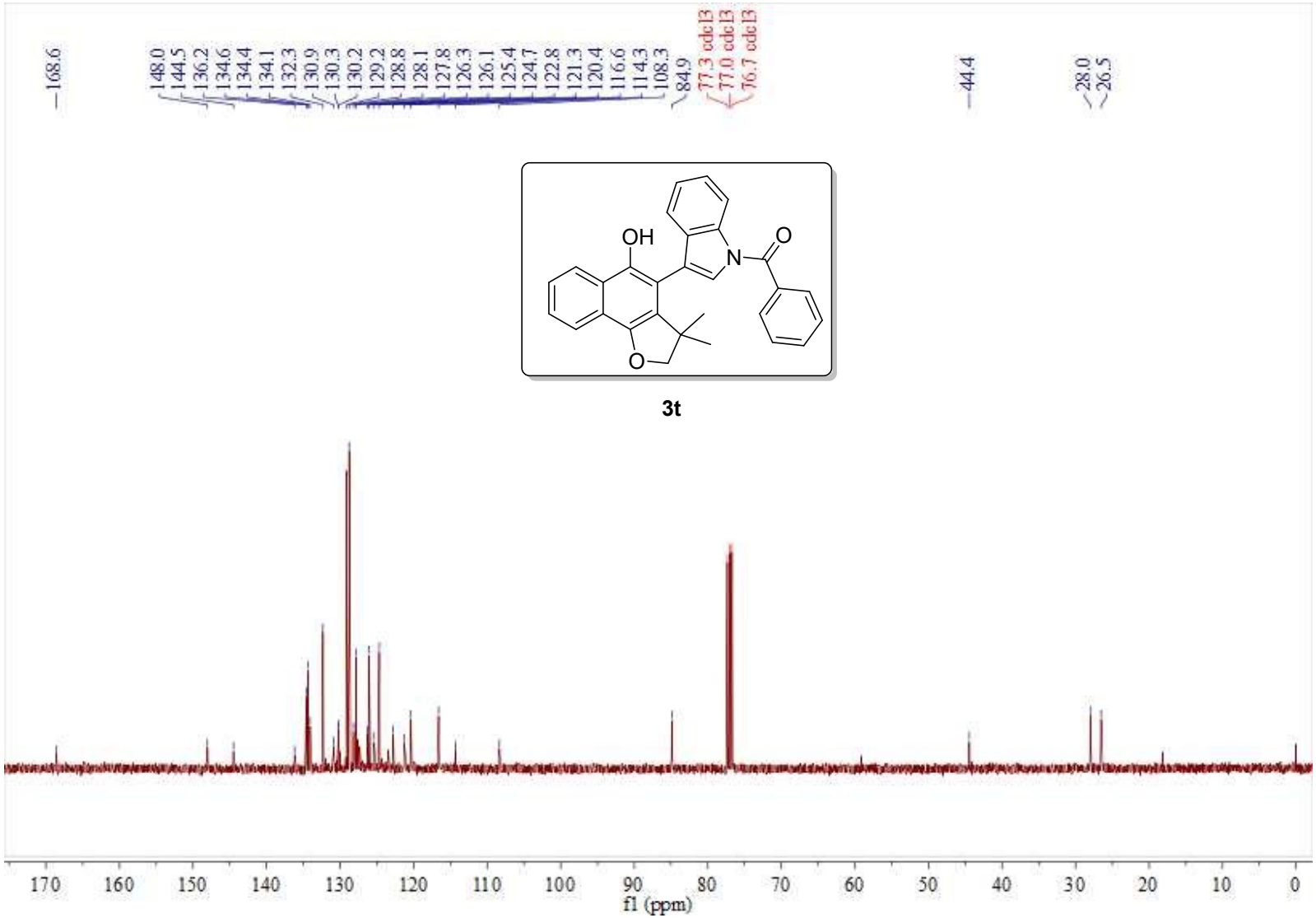
7.80
7.79
7.78
7.77
7.70
7.69
7.68
7.67
7.66
7.65
7.63
7.62
7.57
7.55
7.53
7.52
7.51
7.49
7.48
7.46
7.36
7.35
7.28 cdcl3
5.09
4.38
4.36
4.34
4.32
1.32
1.04
OH
O
N
O
1.00
1.07
1.03
2.00
2.02
5.06
2.08
1.09
1.00
1.00
3.00
3.08
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

3t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148.0
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134.6
134.4
134.1
132.3
130.9
130.3
130.2
129.2
128.8
128.1
127.8
126.3
126.1
125.4
124.7
122.8
121.3
120.4
116.6
114.3
108.3
84.9
77.3 cdcl3
77.0 cdcl3
76.7 cdcl3
44.4
28.0
26.5
OH
N
O
O
3t
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
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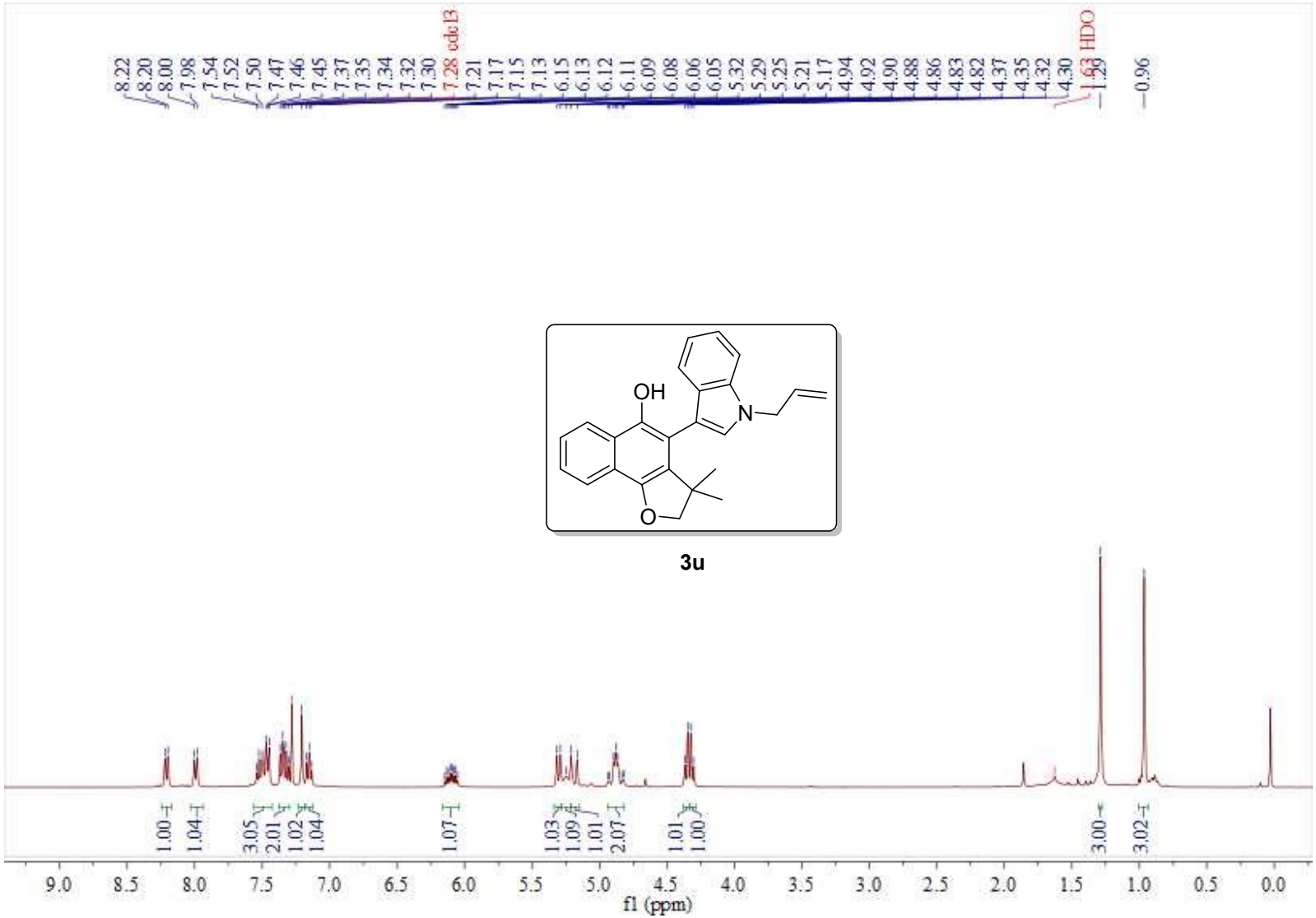
f1 (ppm)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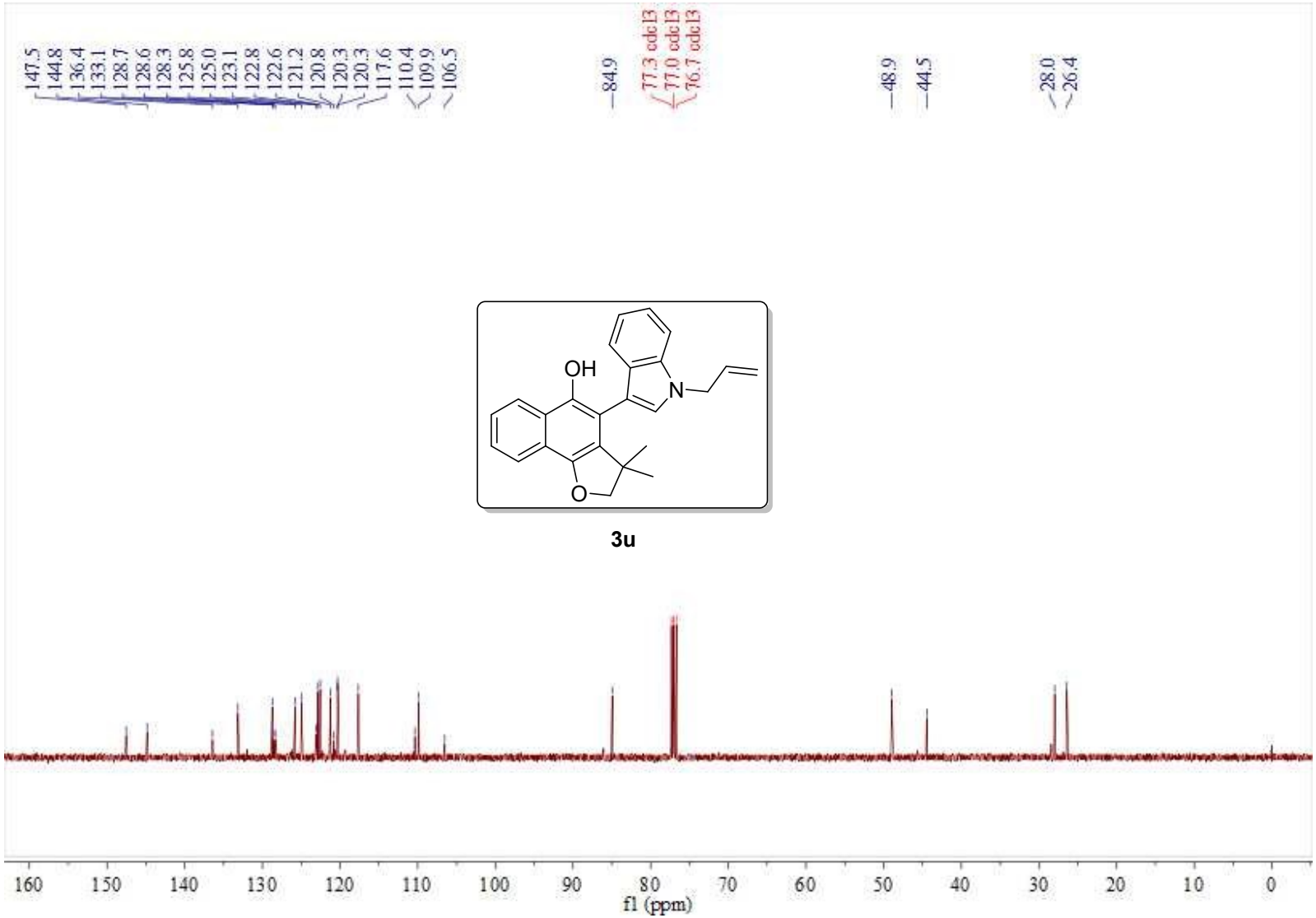
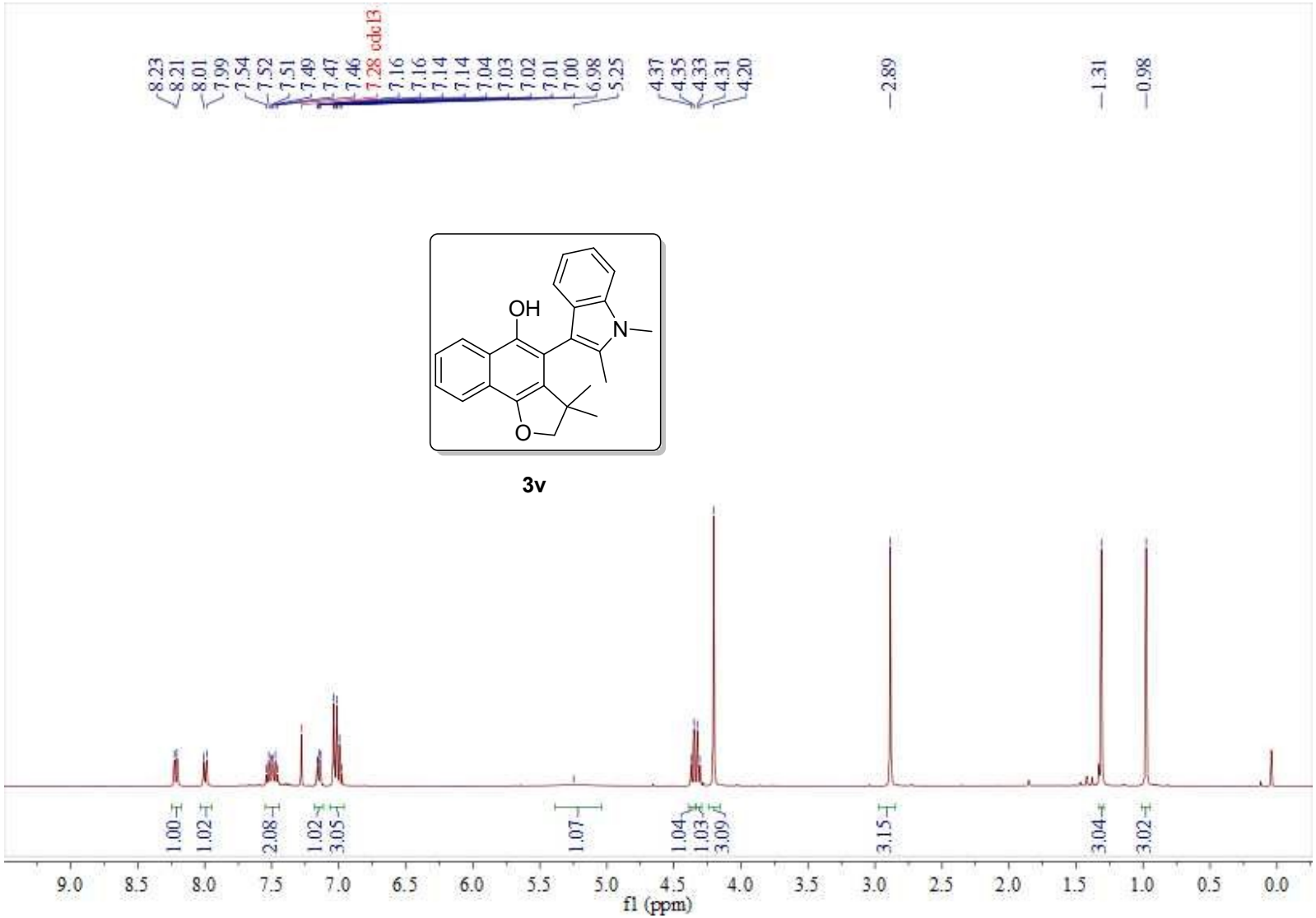
8.20
8.00
7.98
7.54
7.52
7.50
7.47
7.46
7.45
7.37
7.35
7.34
7.32
7.30
7.28 cdcl3
7.21
7.17
7.15
7.13
6.15
6.13
6.12
6.11
6.09
6.08
6.06
6.05
5.32
5.29
5.25
5.21
5.17
4.94
4.92
4.90
4.88
4.86
4.83
4.82
4.37
4.35
4.32
4.30
1.63 HDO
1.26
0.96
OH
N
O
1.00
1.04
3.05
2.01
1.02
1.04
1.07
1.03
1.09
1.01
2.07
1.01
1.00
3.00
3.02
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

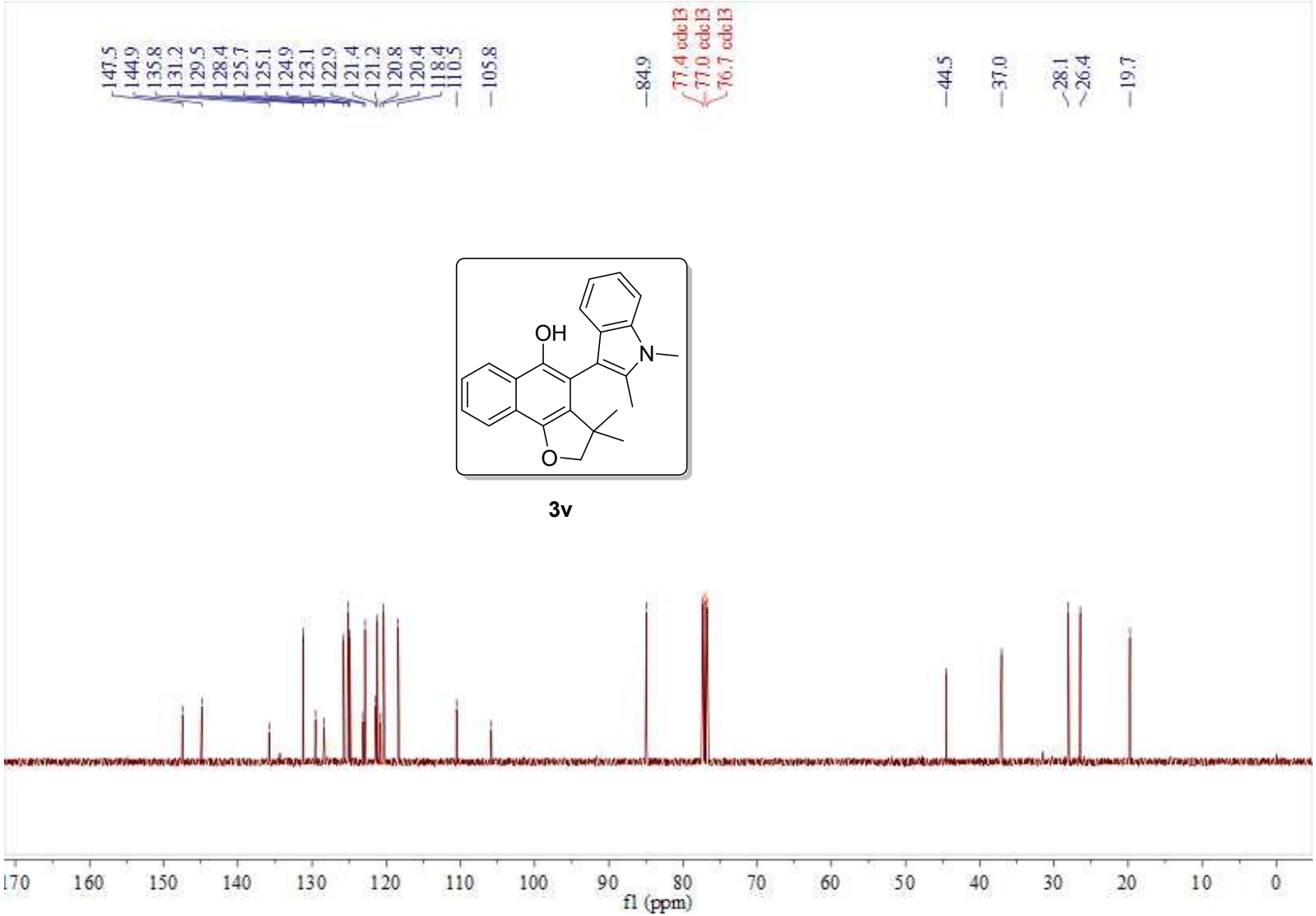
3u


147.5
144.8
136.4
133.1
128.7
128.6
128.3
125.8
125.0
123.1
122.8
122.6
121.2
120.8
120.3
120.3
117.6
110.4
109.9
106.5
84.9
77.3 cdcl3
77.0 cdcl3
76.7 cdcl3
48.9
44.5
28.0
26.4
OH
N
O
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

3u


8.23
8.21
8.01
7.99
7.54
7.52
7.51
7.49
7.47
7.46
7.28 cdcl3
7.16
7.16
7.14
7.14
7.04
7.03
7.02
7.01
7.00
6.98
5.25
4.37
4.35
4.33
4.31
4.20
2.89
1.31
0.98
OH
N
O
1.00
1.02
2.08
1.02
3.05
1.07
1.04
1.03
3.09
3.15
3.04
3.02
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

3v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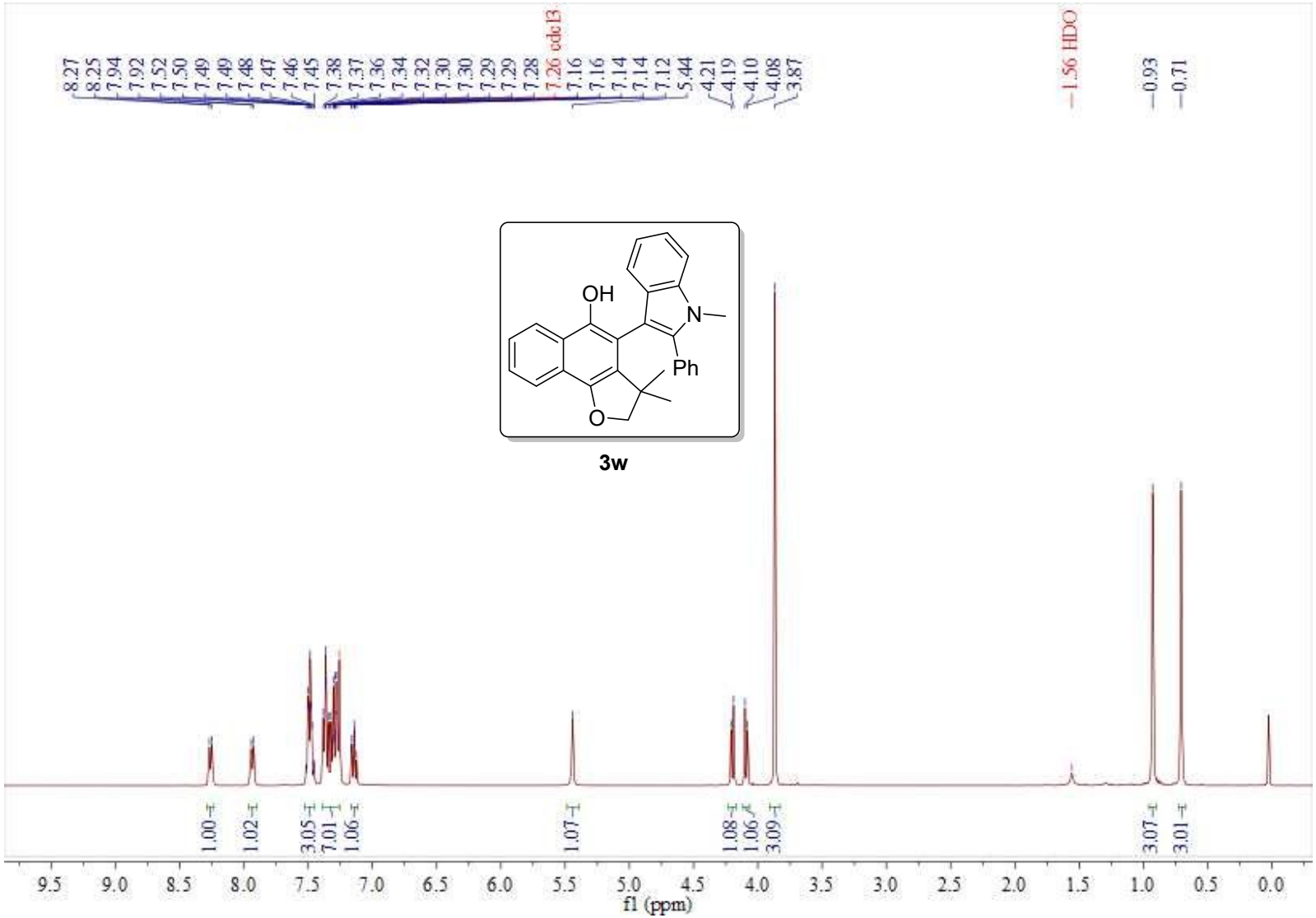
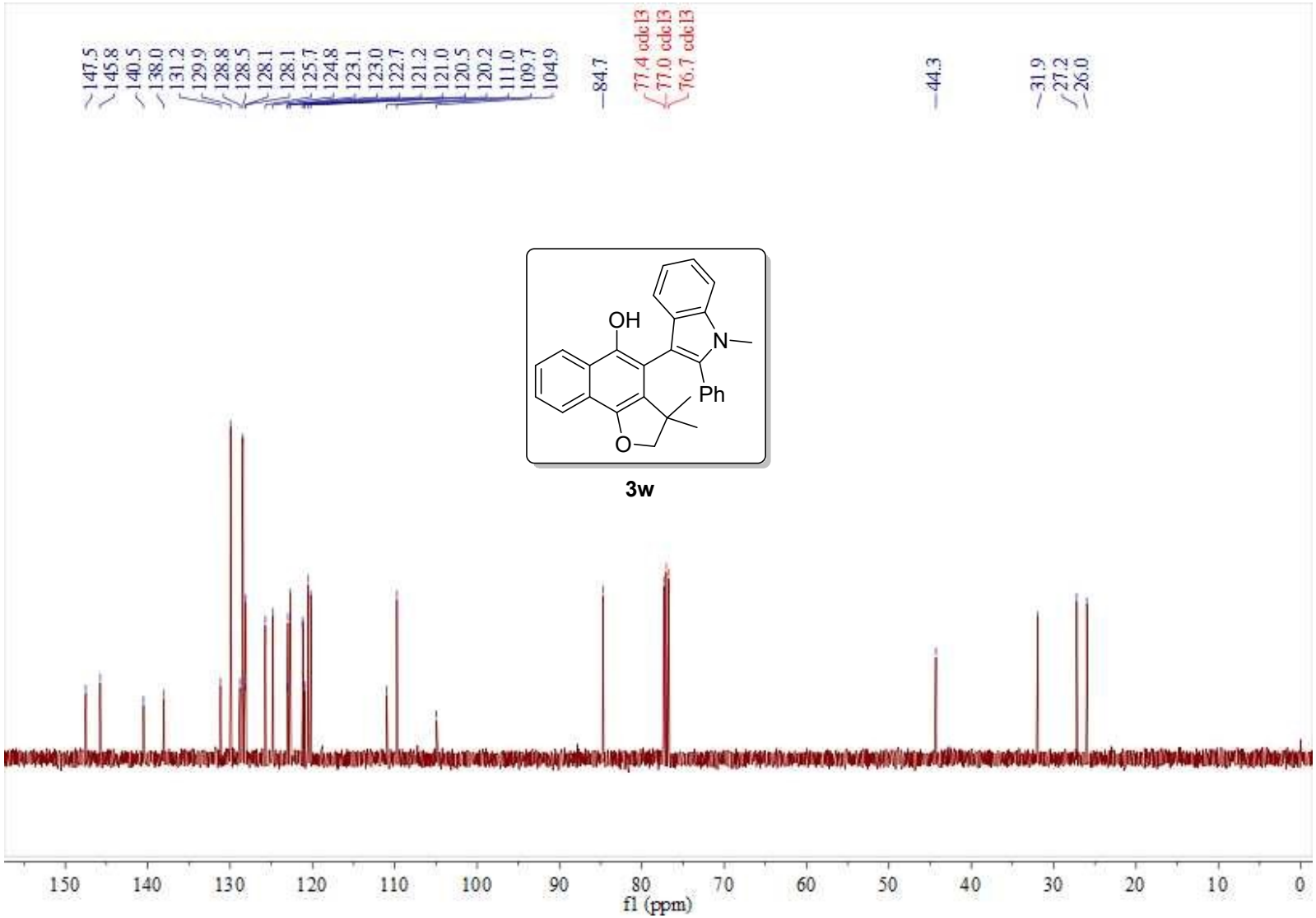
144.9
135.8
131.2
129.5
128.4
125.7
125.1
124.9
123.1
122.9
121.4
121.2
120.8
120.4
118.4
110.5
105.8
84.9
77.4 cdcl3
77.0 cdcl3
76.7 cdcl3
44.5
37.0
28.1
26.4
19.7
OH
N
O
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

3v


8.27
8.25
7.94
7.92
7.52
7.50
7.49
7.49
7.48
7.47
7.46
7.45
7.38
7.37
7.36
7.34
7.32
7.30
7.30
7.29
7.29
7.28
7.26 cdcl3
7.16
7.16
7.14
7.14
7.12
5.44
4.21
4.19
4.10
4.08
3.87
1.56 HDO
0.93
0.71
OH
N
Ph
O
1.00
1.02
3.05
7.01
1.06
1.07
1.08
1.06
3.09
3.07
3.01
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

3w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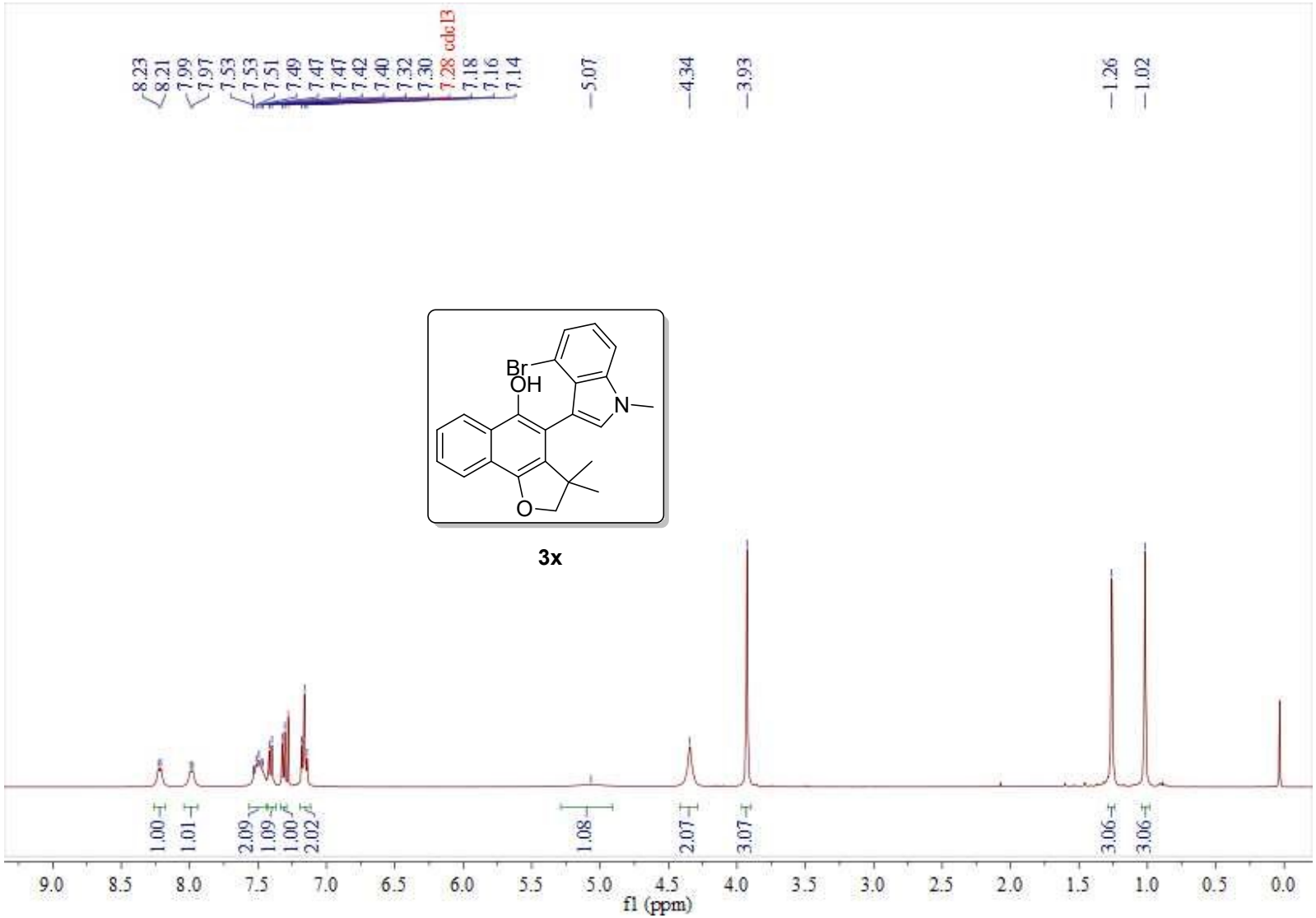
145.8
140.5
138.0
131.2
129.9
128.8
128.5
128.1
128.1
125.7
124.8
123.1
123.0
122.7
121.2
121.0
120.5
120.2
111.0
109.7
104.9
84.7
77.4 cdcl3
77.0 cdcl3
76.7 cdcl3
44.3
31.9
27.2
26.0
OH
N
Ph
O
3w
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.23
8.21
7.99
7.97
7.53
7.53
7.51
7.49
7.47
7.47
7.42
7.40
7.32
7.30
7.28 cdcl3
7.18
7.16
7.14
5.07
4.34
3.93
1.26
1.02
Br
OH
N
O
1.00
1.01
2.09
1.09
1.00
2.02
1.08
2.07
3.07
3.06
3.06
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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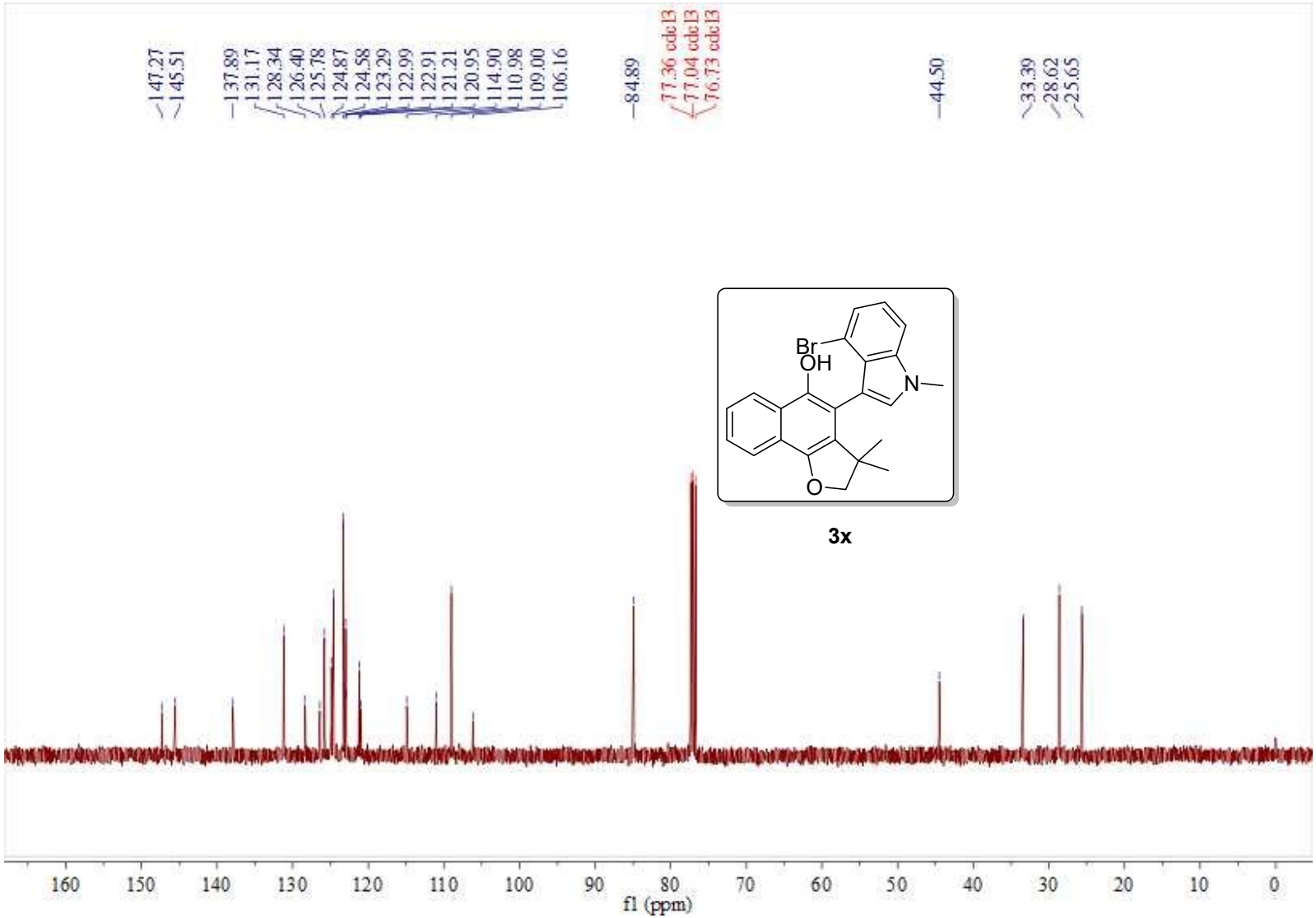
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

3x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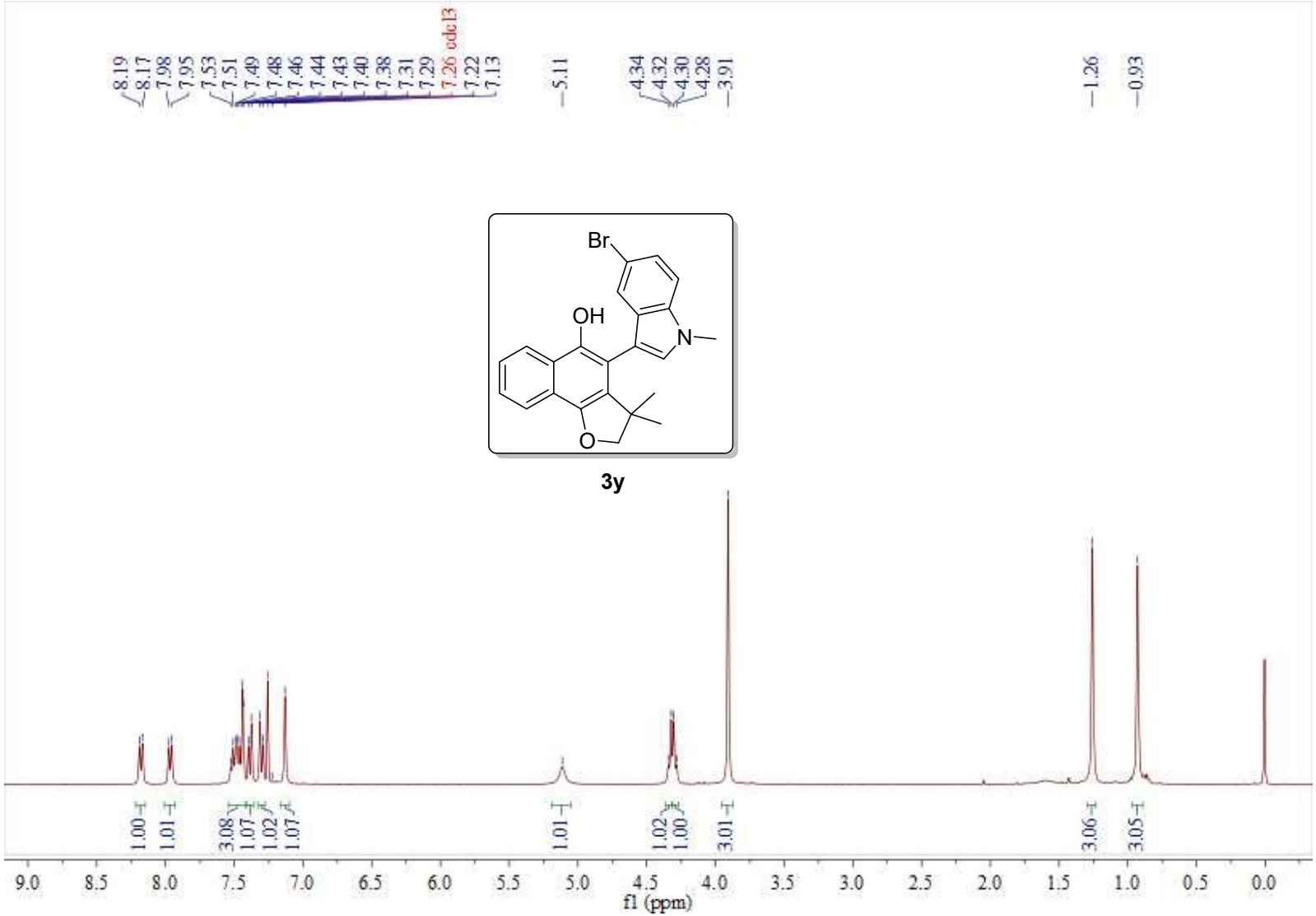
131.17
128.34
126.40
125.78
124.87
124.58
123.29
122.99
122.91
121.21
120.95
114.90
110.98
109.00
106.16
84.89
77.36 cdcl3
77.04 cdcl3
76.73 cdcl3
44.50
33.39
28.62
25.65
Br
OH
N
O
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

3x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8.17
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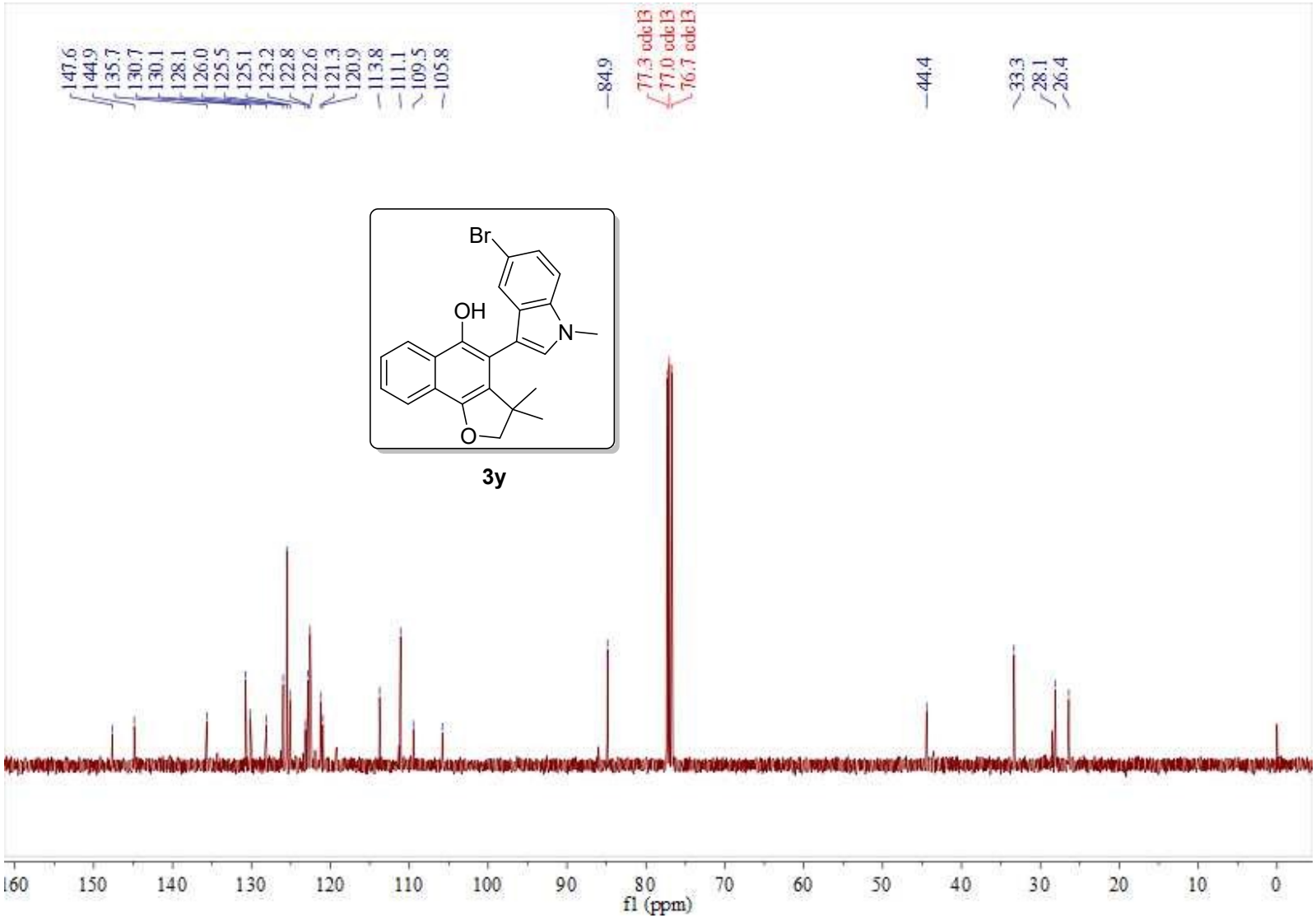
7.51
7.49
7.48
7.46
7.44
7.43
7.40
7.38
7.31
7.29
7.26 cdcl3
7.22
7.13
5.11
4.34
4.32
4.30
4.28
3.91
1.26
0.93
Br
OH
N
O
3y
1.00
1.01
3.08
1.07
1.02
1.07
1.01
1.02
1.00
3.01
3.06
3.05
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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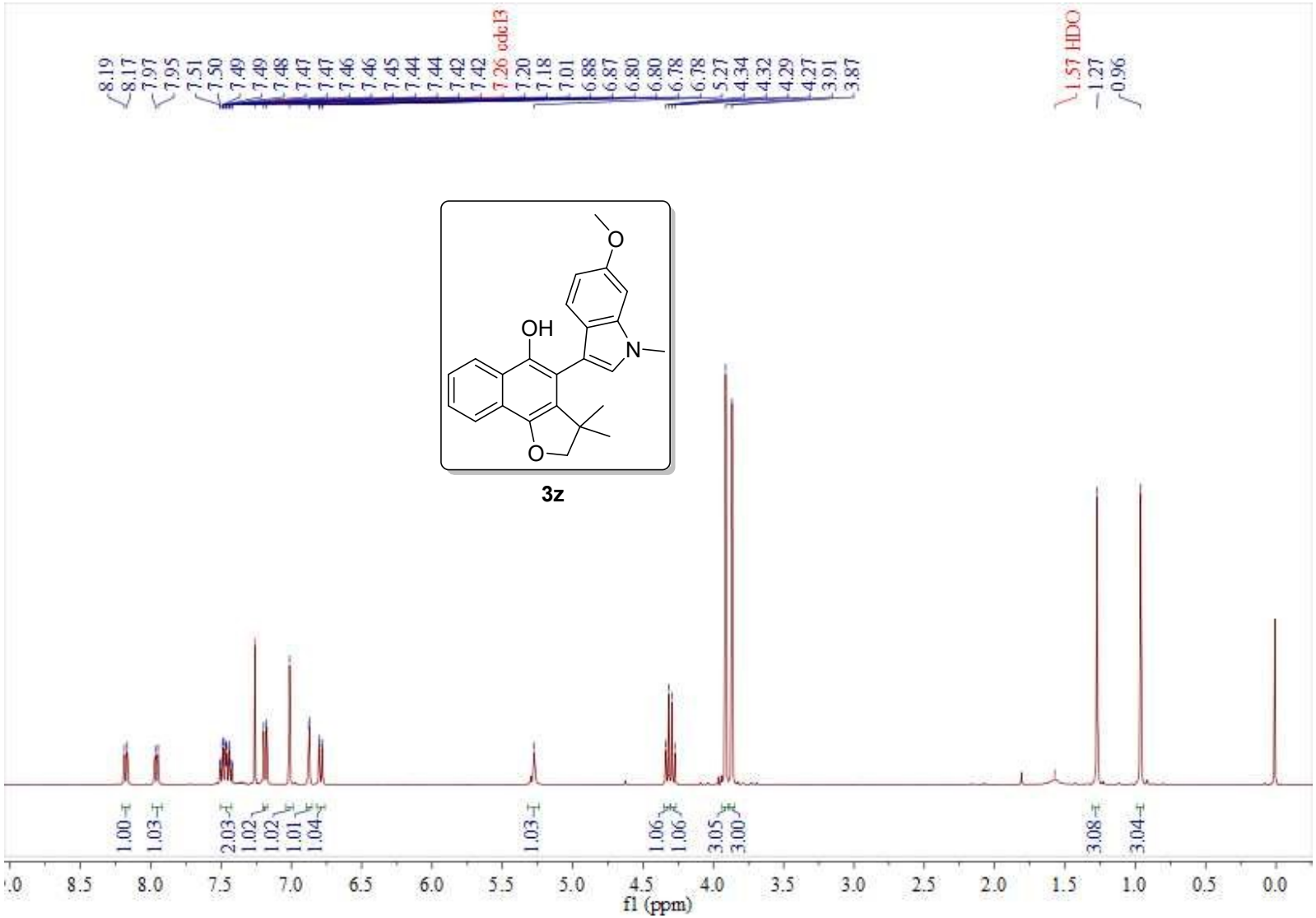
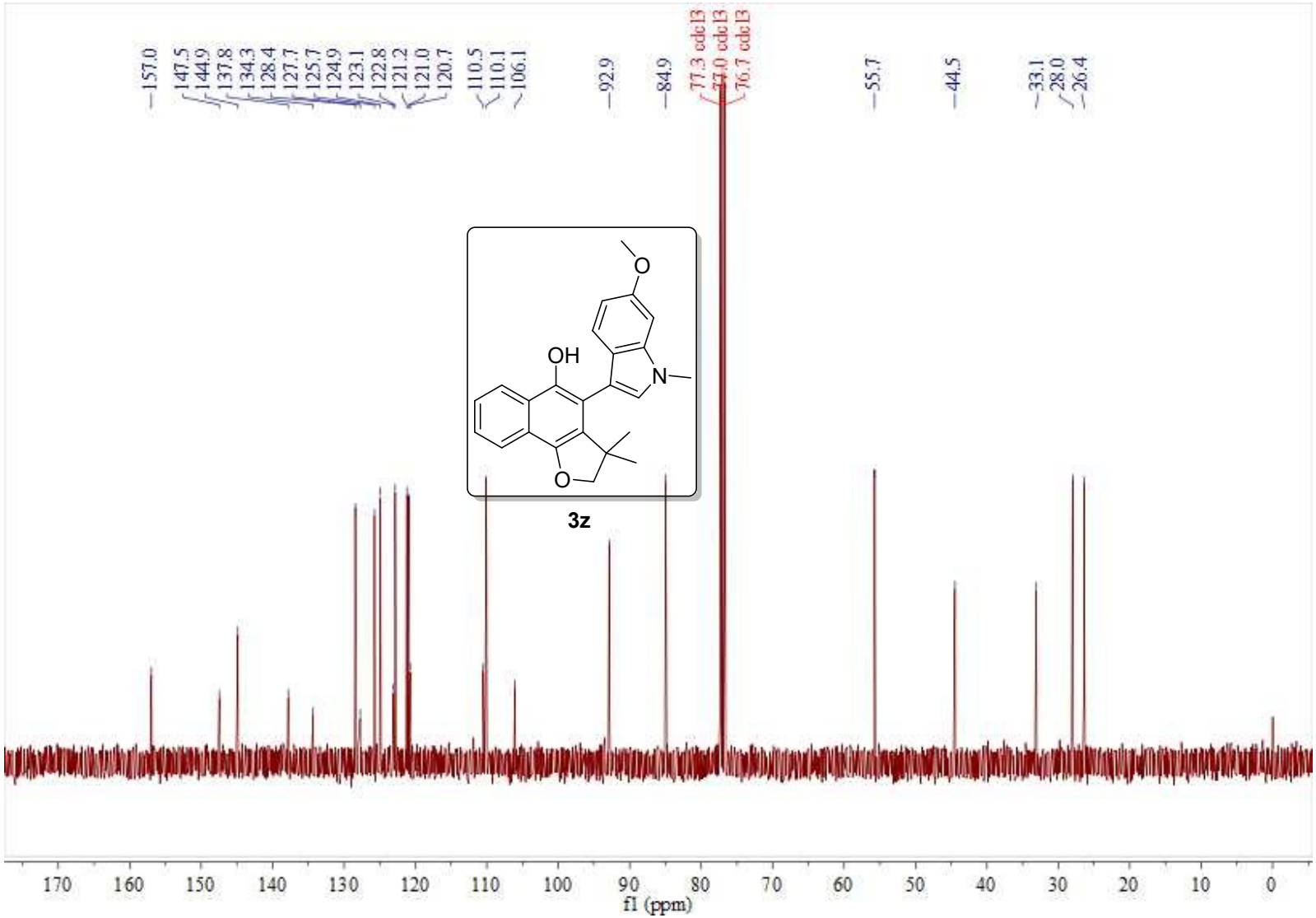
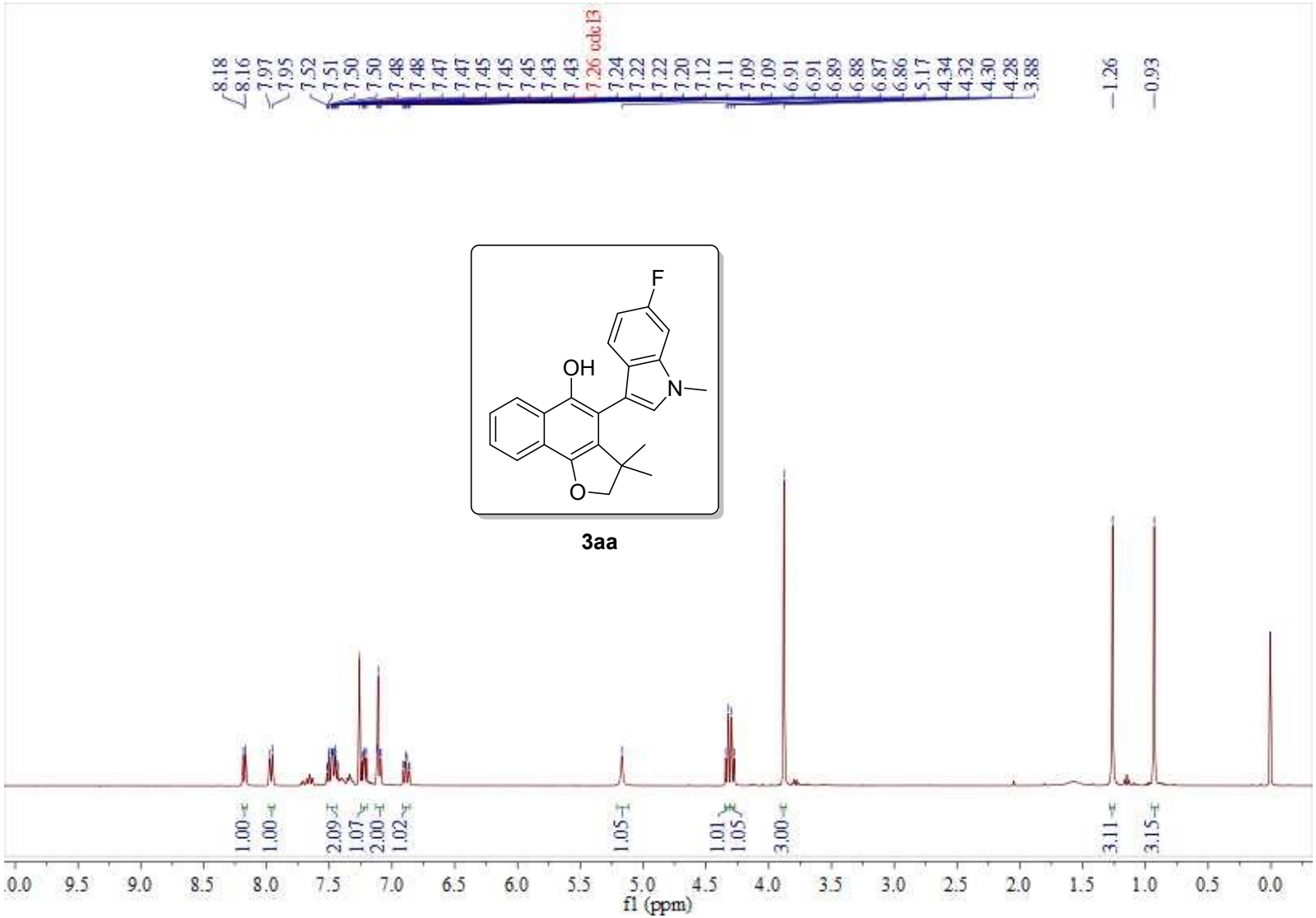
130.1
128.1
126.0
125.5
125.1
123.2
122.8
122.6
121.3
120.9
113.8
111.1
109.5
105.8
84.9
77.3 cdcl3
77.0 cdcl3
76.7 cdcl3
44.4
33.3
28.1
26.4
Br
OH
N
O
3y
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.19
8.17
7.97
7.95
7.51
7.50
7.49
7.49
7.48
7.47
7.47
7.46
7.46
7.45
7.44
7.44
7.42
7.42
7.26 cdcl3
7.20
7.18
7.01
6.88
6.87
6.80
6.80
6.78
6.78
5.27
4.34
4.32
4.29
4.27
3.91
3.87
1.57 HDO
1.27
0.96
O
OH
N
O
3z
1.00
1.03
2.03
1.02
1.02
1.01
1.04
1.03
1.06
1.06
3.05
3.00
3.08
3.04
f1 (ppm)


157.0
147.5
144.9
137.8
134.3
128.4
127.7
125.7
124.9
123.1
122.8
121.2
121.0
120.7
110.5
110.1
106.1
92.9
84.9
77.3 cdcl3
77.0 cdcl3
76.7 cdcl3
55.7
44.5
33.1
28.0
26.4
O
OH
N
O
3z
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.18
8.16
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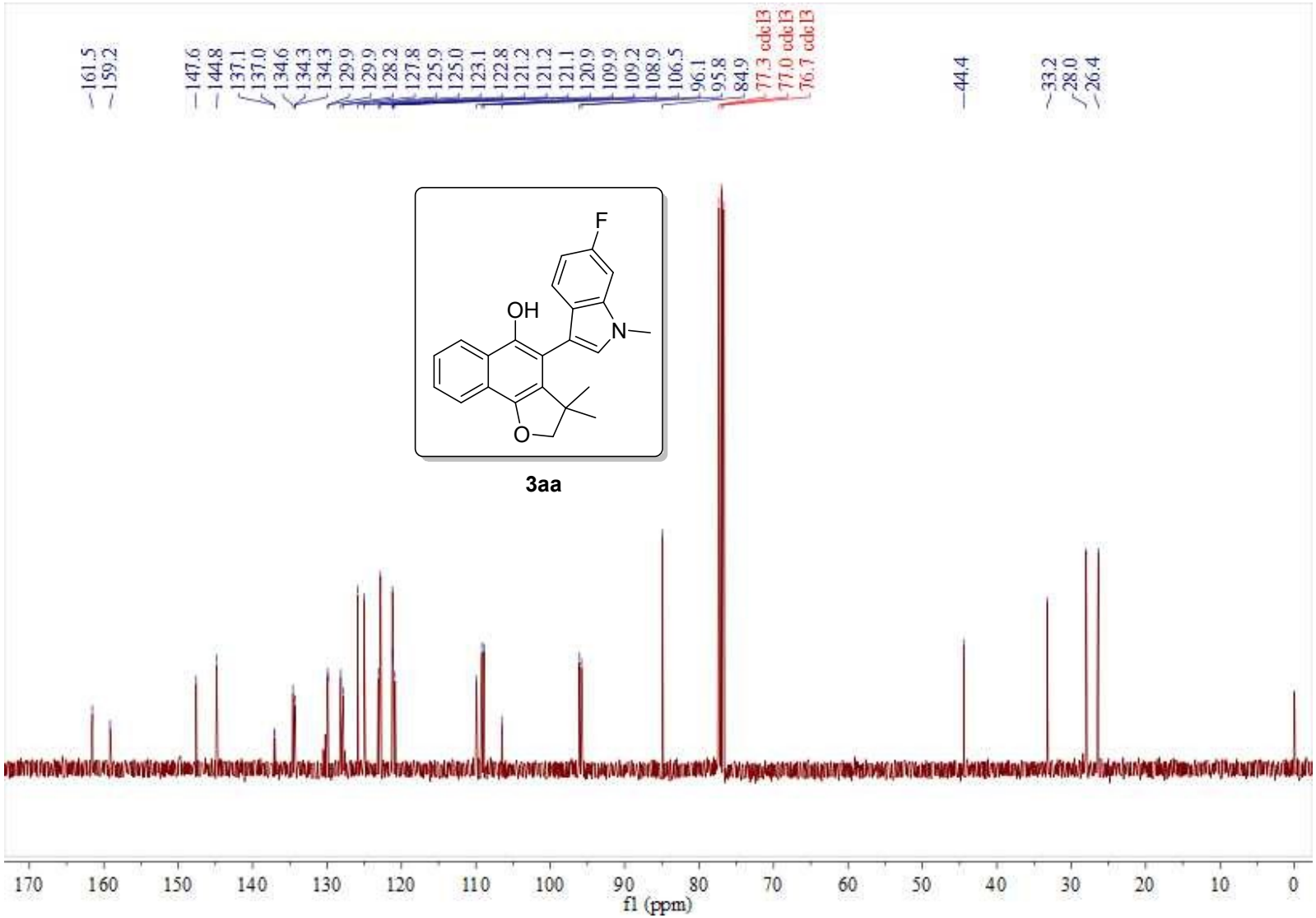
7.51
7.50
7.50
7.48
7.48
7.47
7.47
7.45
7.45
7.45
7.43
7.43
7.26 cdcl3
7.24
7.22
7.22
7.20
7.12
7.11
7.09
7.09
6.91
6.91
6.89
6.88
6.87
6.86
5.17
4.34
4.32
4.30
4.28
3.88
1.26
0.93
F
OH
N
O
3aa
1.00
1.00
2.09
1.07
2.00
1.02
1.05
1.01
1.05
3.00
3.11
3.15
f1 (ppm)


161.5
159.2
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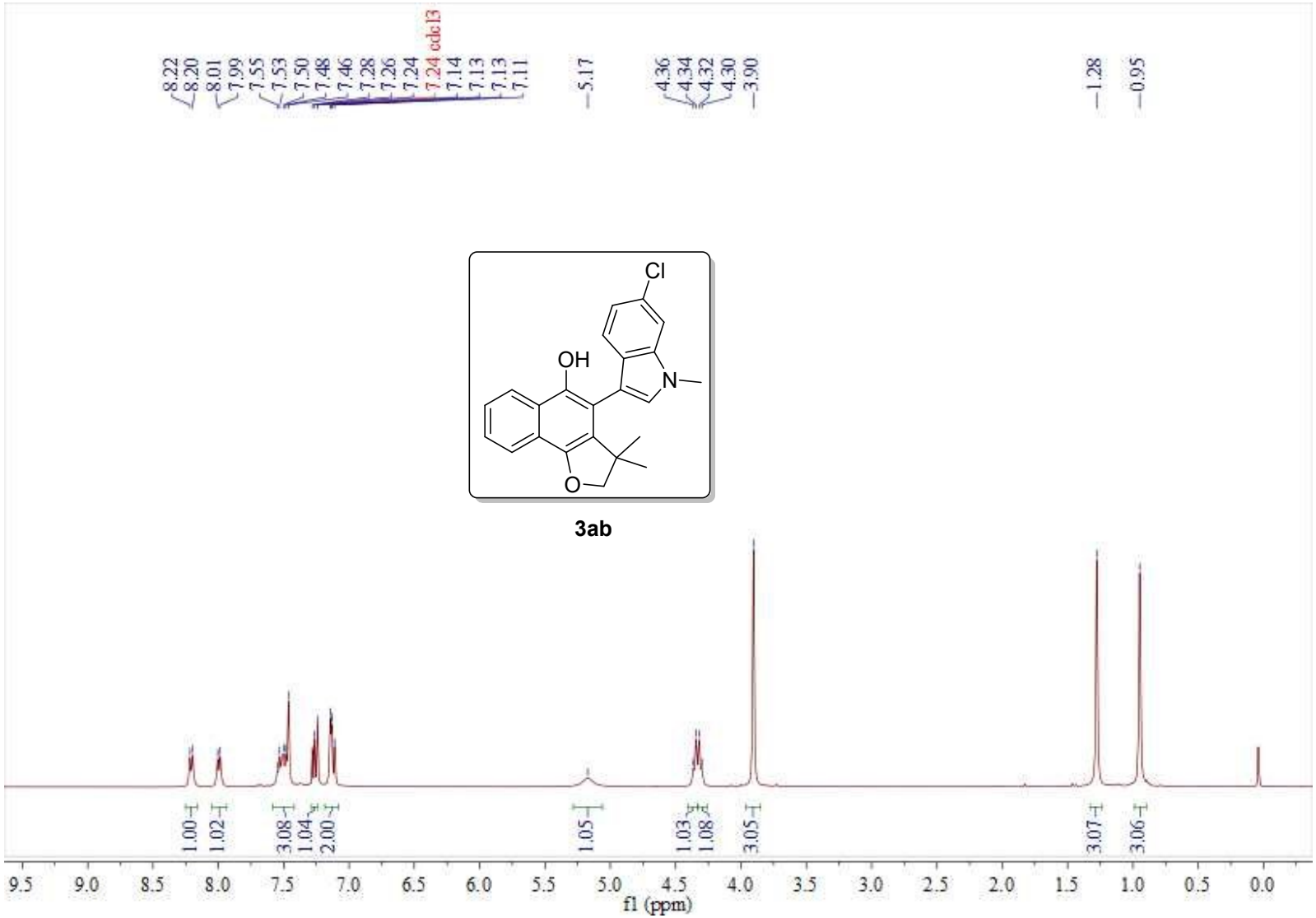
144.8
137.1
137.0
134.6
134.3
134.3
129.9
129.9
128.2
127.8
125.9
125.0
123.1
122.8
121.2
121.2
121.1
120.9
109.9
109.2
108.9
106.5
96.1
95.8
84.9
77.3 cdcl3
77.0 cdcl3
76.7 cdcl3
44.4
33.2
28.0
26.4
F
OH
N
O
3aa
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.22
8.20
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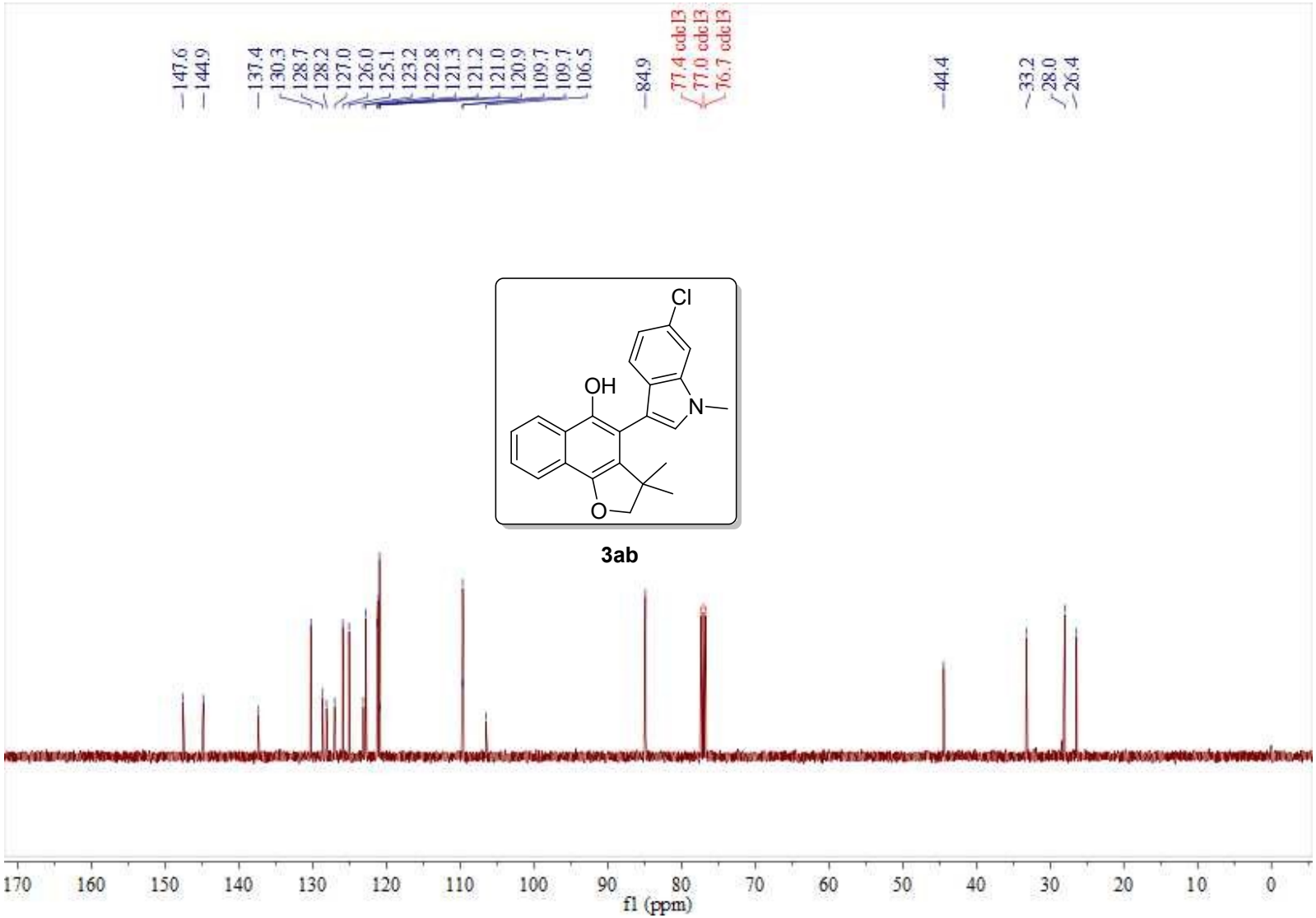
7.99
7.55
7.53
7.50
7.48
7.46
7.28
7.26
7.24
7.24 cdcl3
7.14
7.13
7.13
7.11
5.17
4.36
4.34
4.32
4.30
3.90
1.28
0.95
Cl
OH
N
O
1.00
1.02
3.08
1.04
2.00
1.05
1.03
1.08
3.05
3.07
3.06
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

3ab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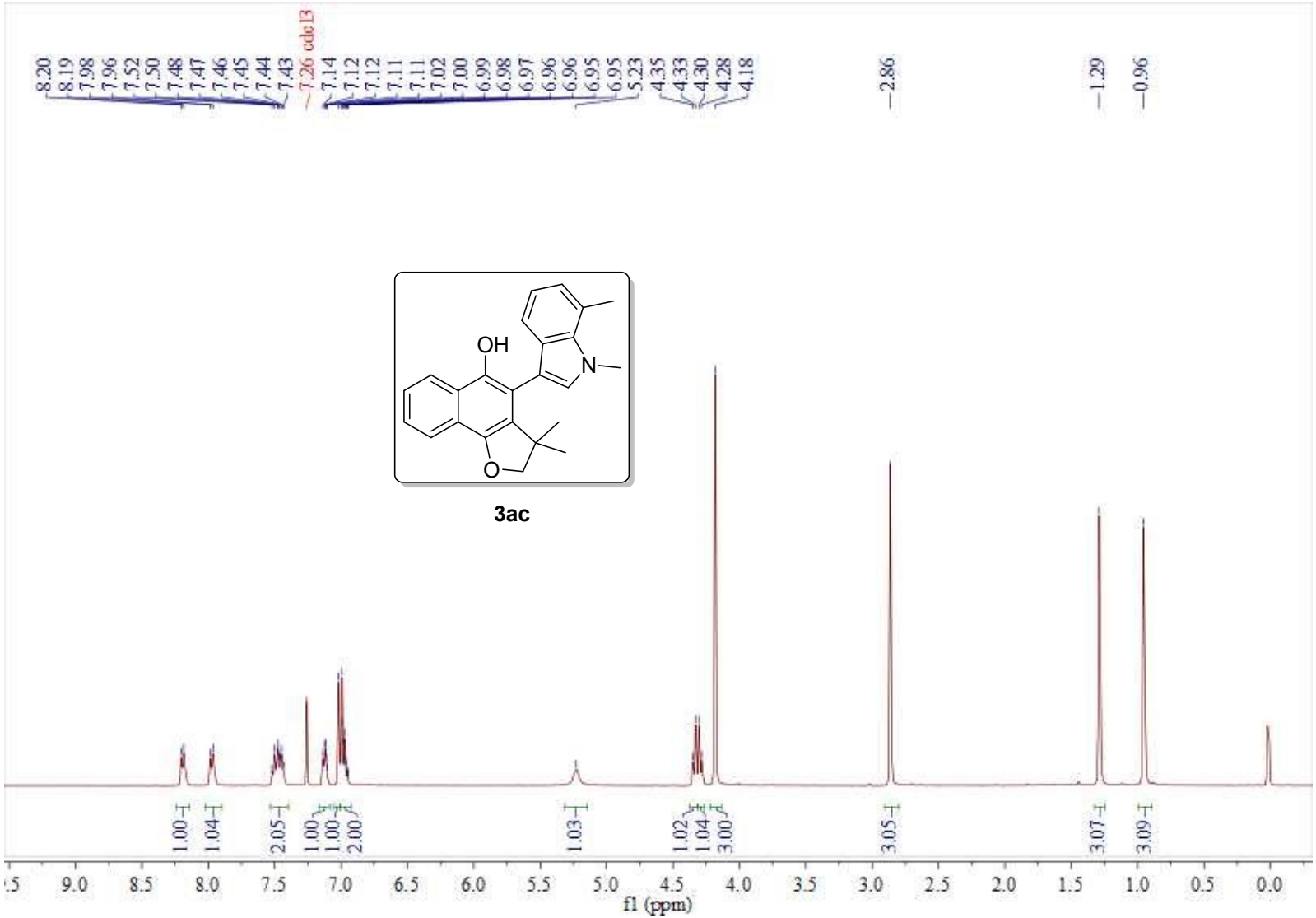
144.9
137.4
130.3
128.7
128.2
127.0
126.0
125.1
123.2
122.8
121.3
121.2
121.0
120.9
109.7
109.7
106.5
84.9
77.4 cdcl3
77.0 cdcl3
76.7 cdcl3
44.4
33.2
28.0
26.4
Cl
OH
N
O
3ab
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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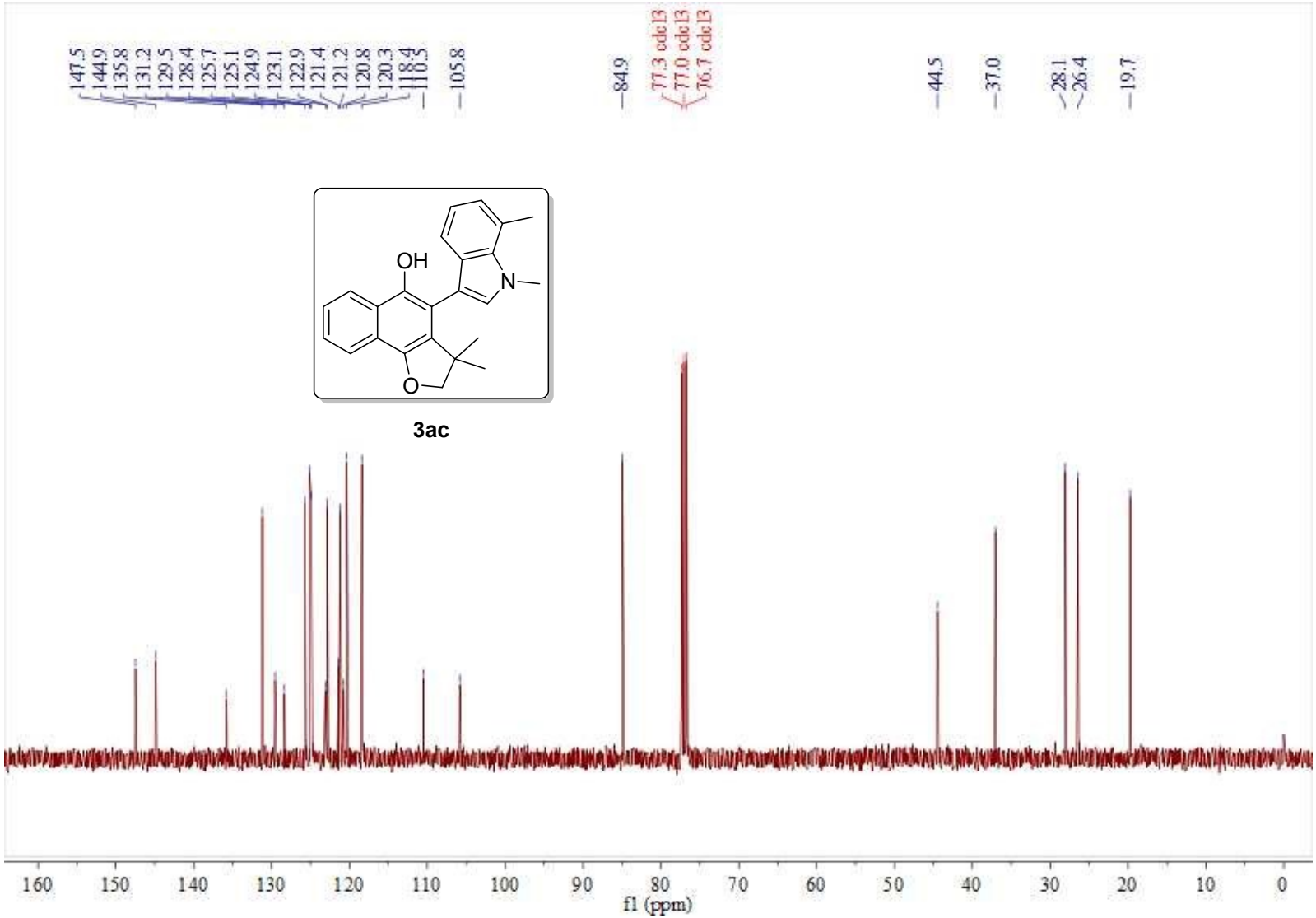
8.19
7.98
7.96
7.52
7.50
7.48
7.47
7.46
7.45
7.44
7.43
7.26 cdcl3
7.14
7.12
7.12
7.11
7.11
7.02
7.00
6.99
6.98
6.97
6.96
6.96
6.95
6.95
5.23
4.35
4.33
4.30
4.28
4.18
2.86
1.29
0.96
OH
N
O
1.00
1.04
2.05
1.00
1.00
2.00
1.03
1.02
1.04
3.00
3.05
3.07
3.09
f1 (ppm)

3ac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144.9
135.8
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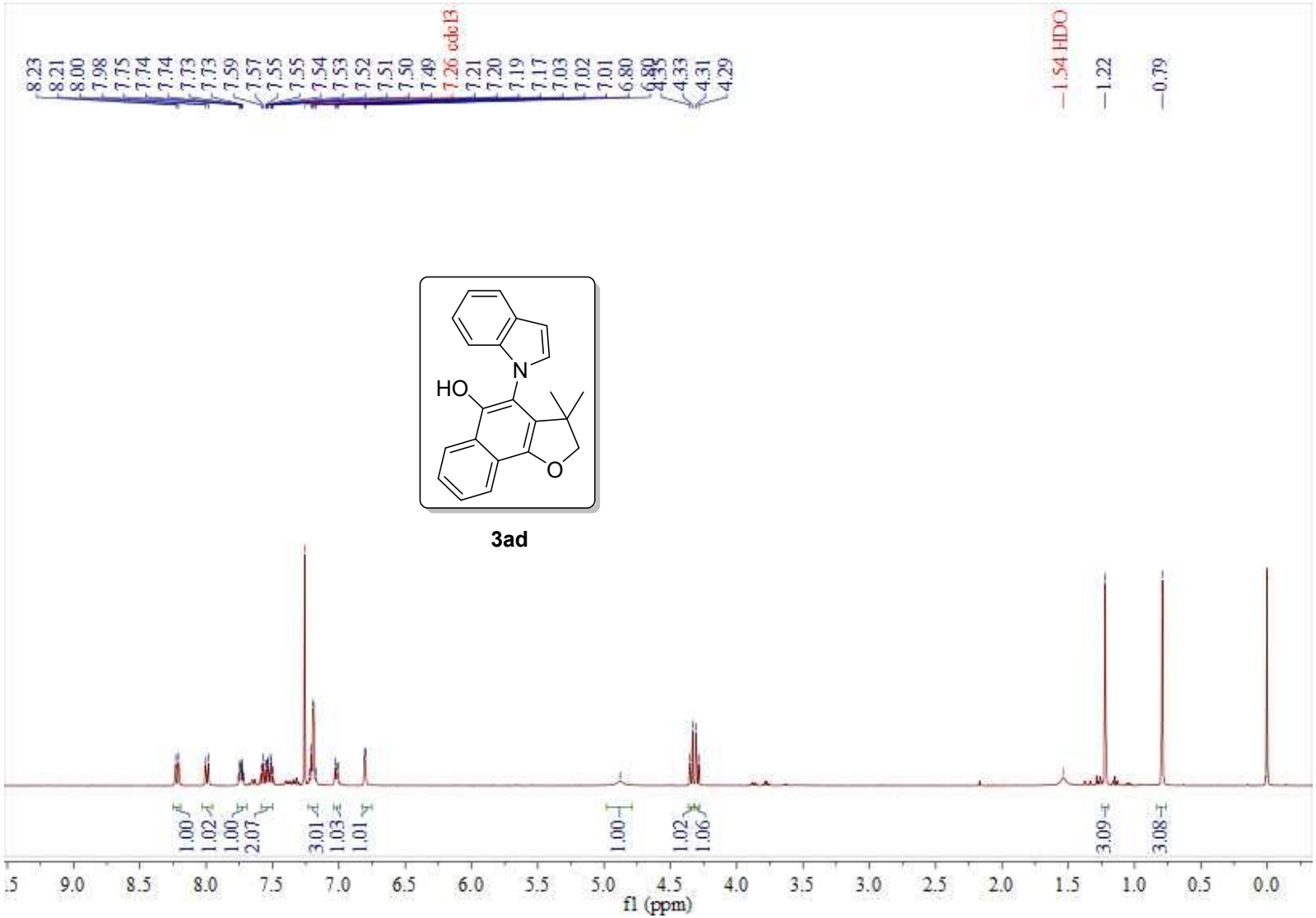
129.5
128.4
125.7
125.1
124.9
123.1
122.9
121.4
121.2
120.8
120.3
118.4
110.5
105.8
84.9
77.3 cdcl3
77.0 cdcl3
76.7 cdcl3
44.5
37.0
28.1
26.4
19.7
OH
N
O
3ac
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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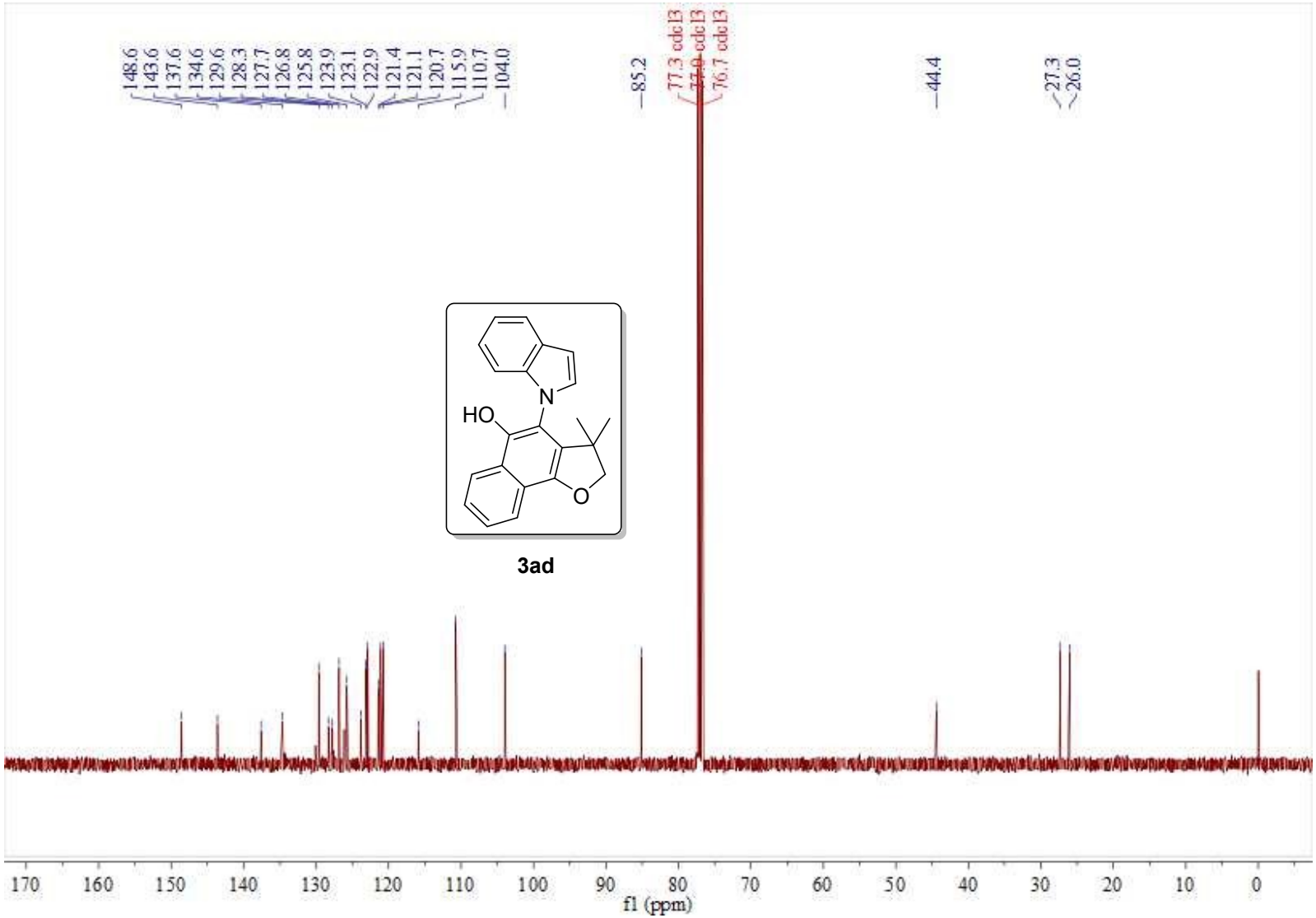
8.21
8.00
7.98
7.75
7.74
7.74
7.73
7.73
7.59
7.57
7.55
7.55
7.54
7.53
7.52
7.51
7.50
7.49
7.26 cdcl3
7.21
7.20
7.19
7.17
7.03
7.02
7.01
6.80
4.33
4.31
4.29
1.54 HDO
1.22
0.79
HO
N
O
1.00
1.02
1.00
2.07
3.01
1.03
1.01
1.00
1.02
1.06
3.09
3.08
f1 (ppm)

3ad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143.6
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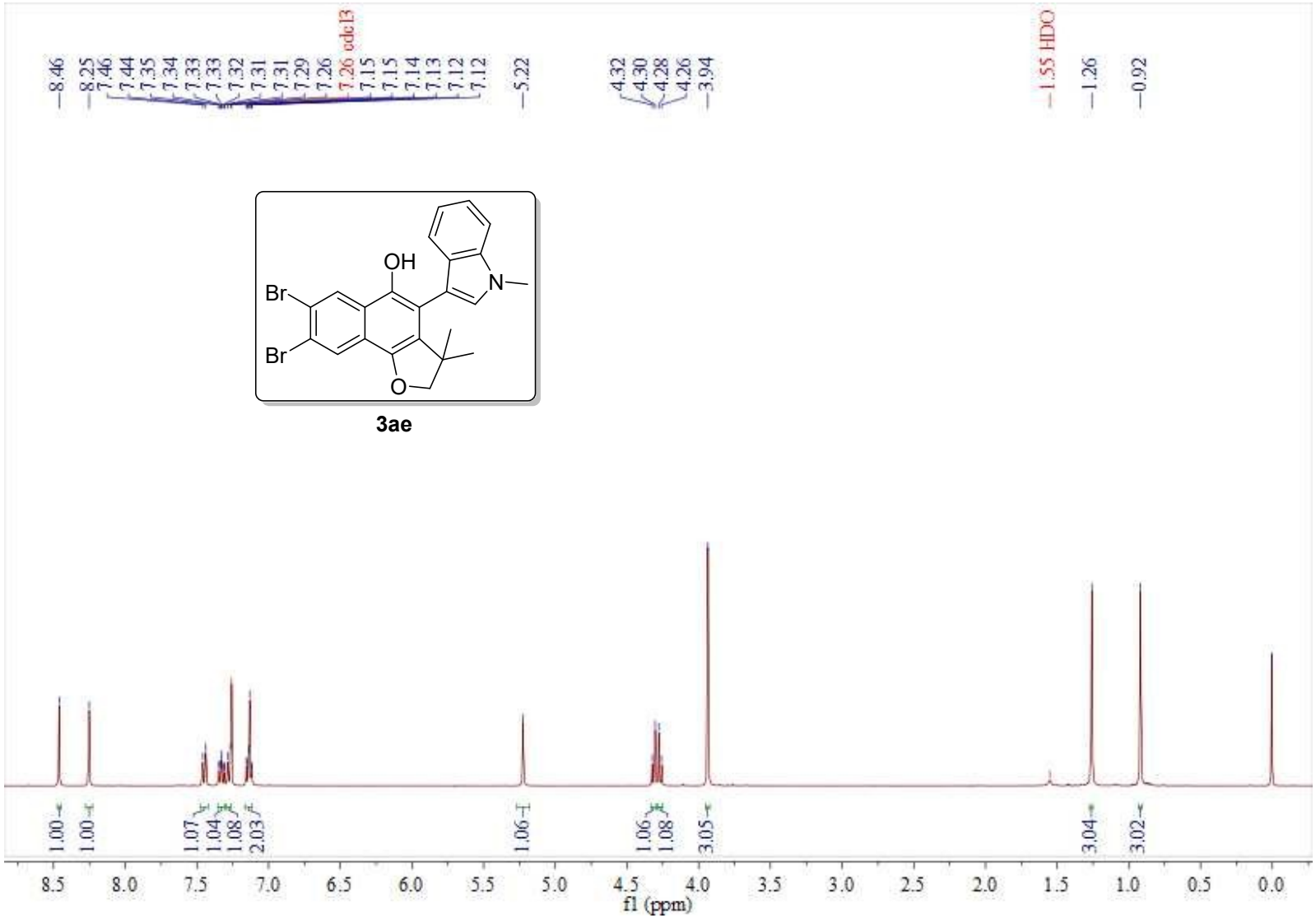
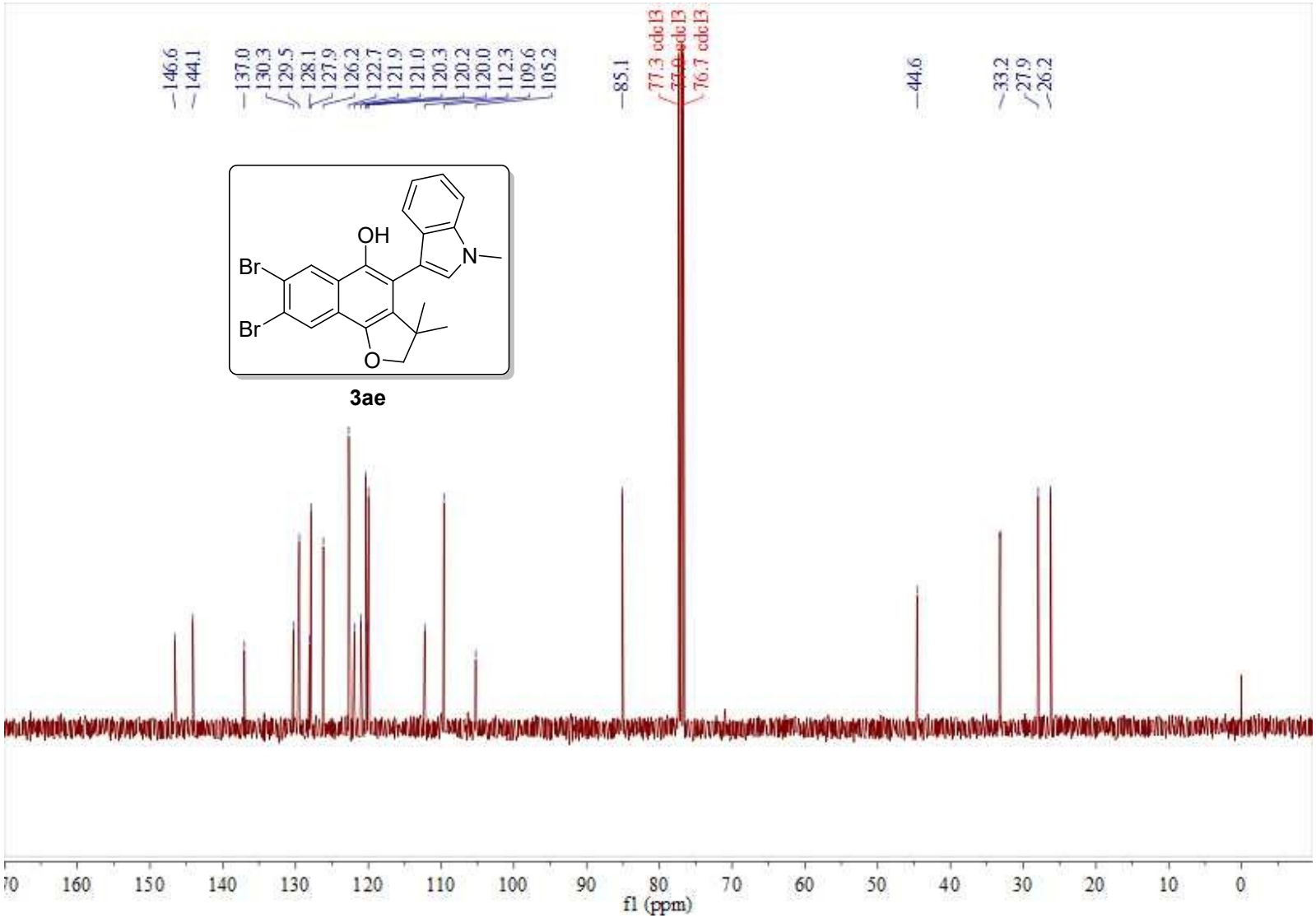
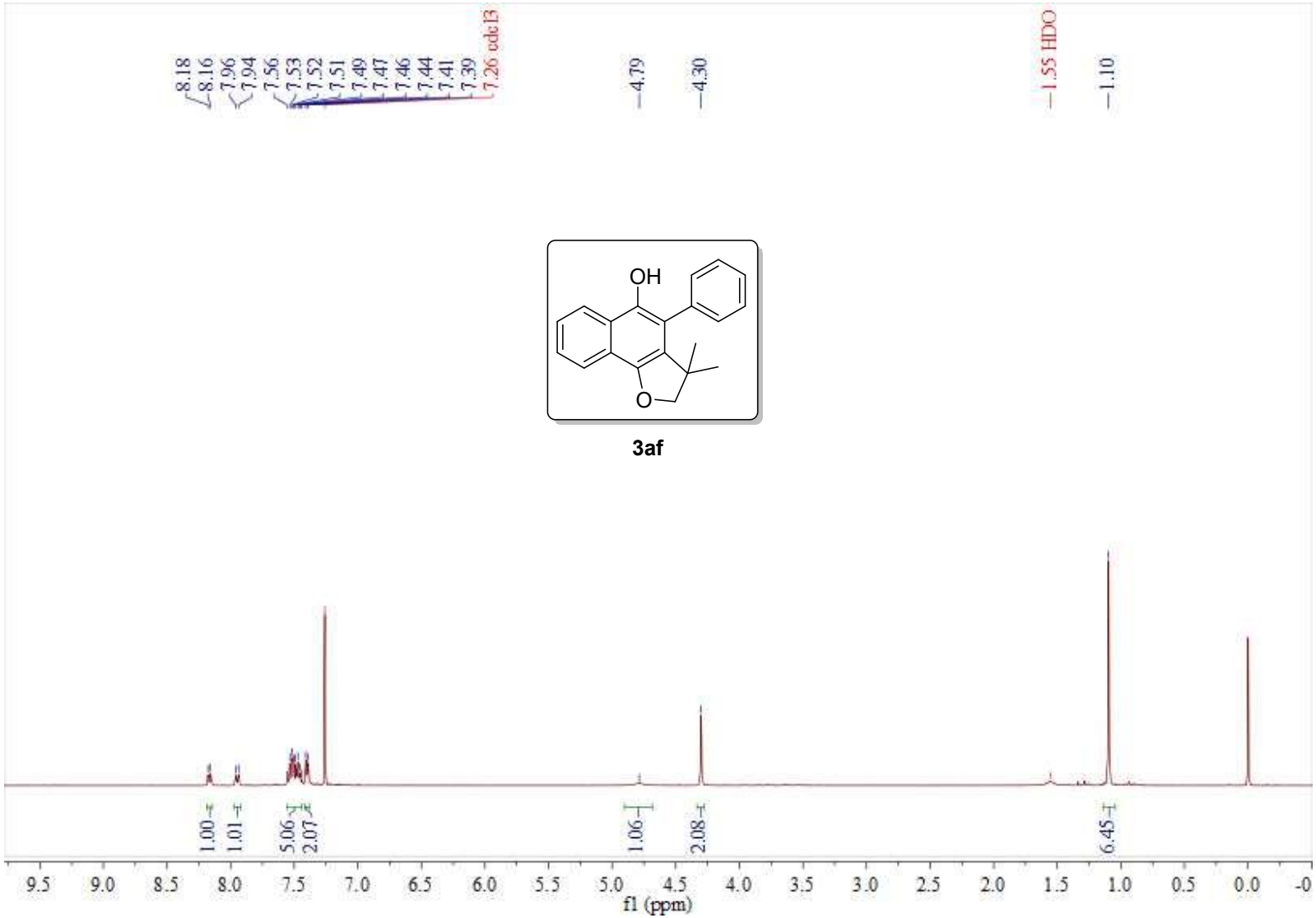
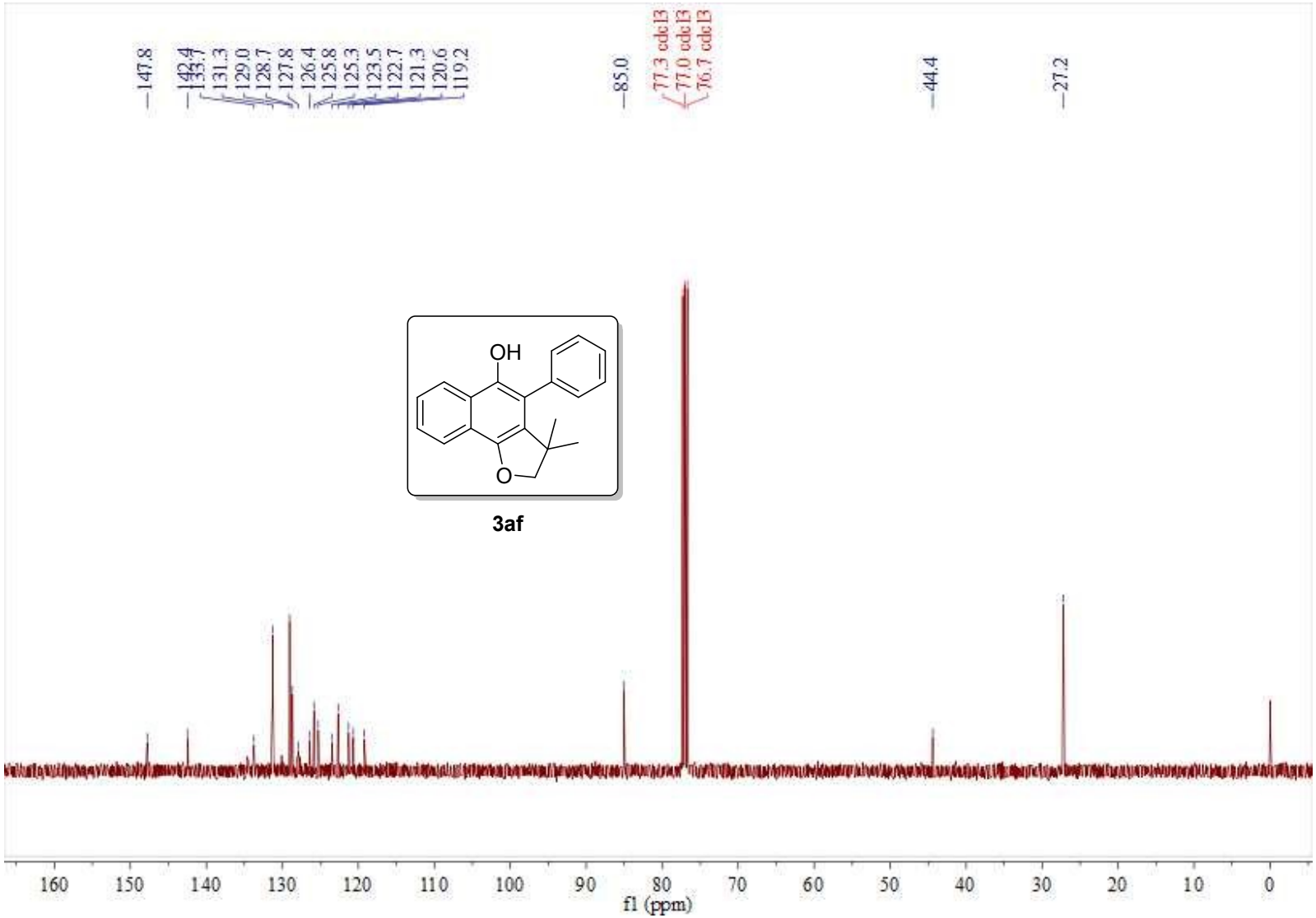
134.6
129.6
128.3
127.7
126.8
125.8
123.9
123.1
122.9
121.4
121.1
120.7
115.9
110.7
104.0
85.2
77.3 cdcl3
76.7 cdcl3
44.4
27.3
26.0
HO
N
O
3ad
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.46
8.25
7.46
7.44
7.35
7.34
7.33
7.33
7.32
7.31
7.31
7.29
7.26
7.26 cdcl3
7.15
7.15
7.14
7.13
7.12
7.12
5.22
4.32
4.30
4.28
4.26
3.94
1.55 HDO
1.26
0.92
OH
Br
Br
N
O
3ae
1.00
1.00
1.07
1.04
1.08
2.03
1.06
1.06
1.08
3.05
3.04
3.02
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

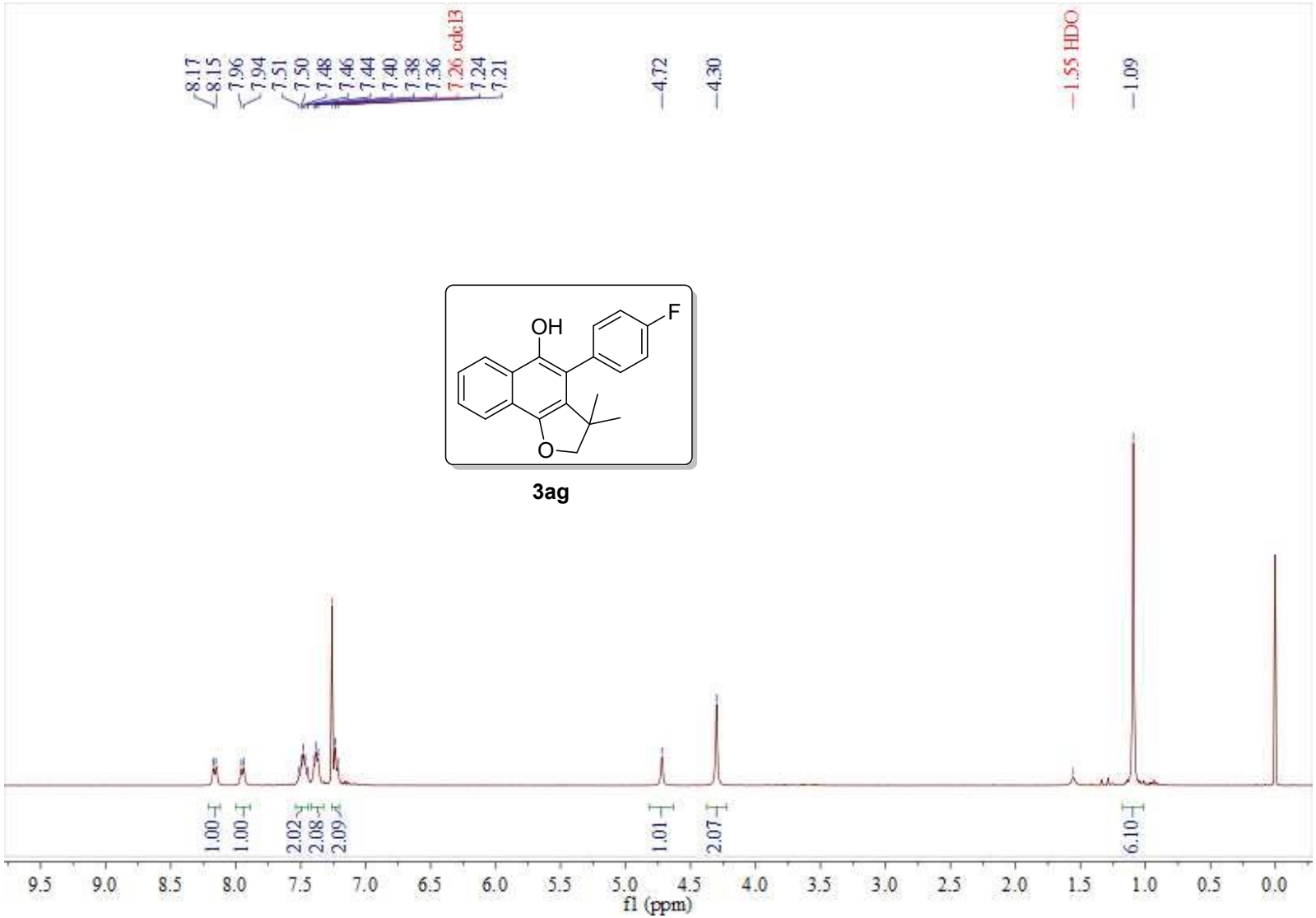

146.6
144.1
137.0
130.3
129.5
128.1
127.9
126.2
122.7
121.9
121.0
120.3
120.2
120.0
112.3
109.6
105.2
85.1
77.3 cdcl3
76.7 cdcl3
44.6
33.2
27.9
26.2
OH
N
Br
Br
O
3ae
f1 (ppm)


8.18
8.16
7.96
7.94
7.56
7.53
7.52
7.51
7.49
7.47
7.46
7.44
7.41
7.39
7.26 cdcl3
4.79
4.30
1.55 HDO
1.10
OH
O
1.00
1.01
5.06
2.07
1.06
2.08
6.45
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)

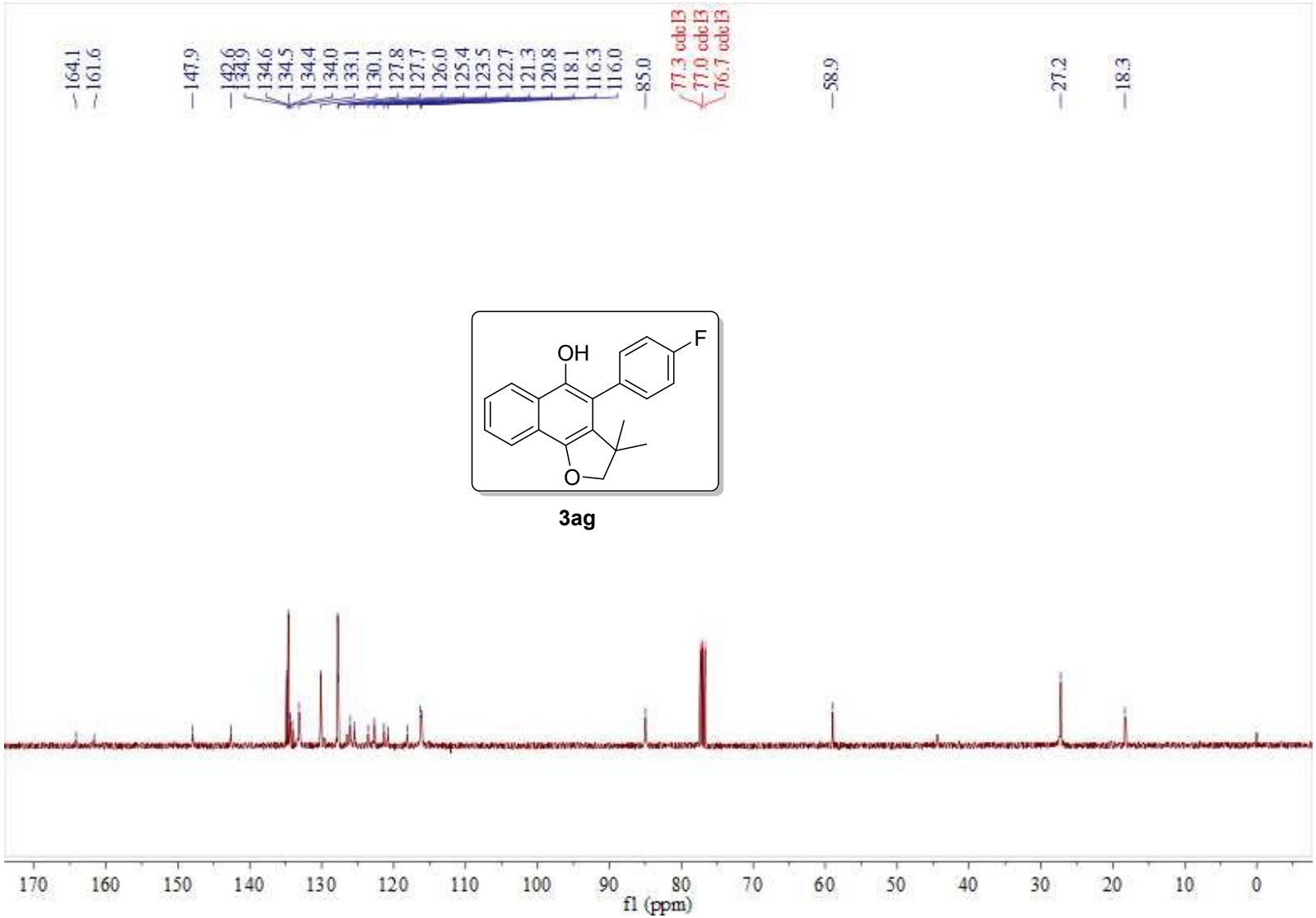
3af


147.8
142.4
133.7
131.3
129.0
128.7
127.8
126.4
125.8
125.3
123.5
122.7
121.3
120.6
119.2
85.0
77.3 cdcl3
77.0 cdcl3
76.7 cdcl3
44.4
27.2
OH
O
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

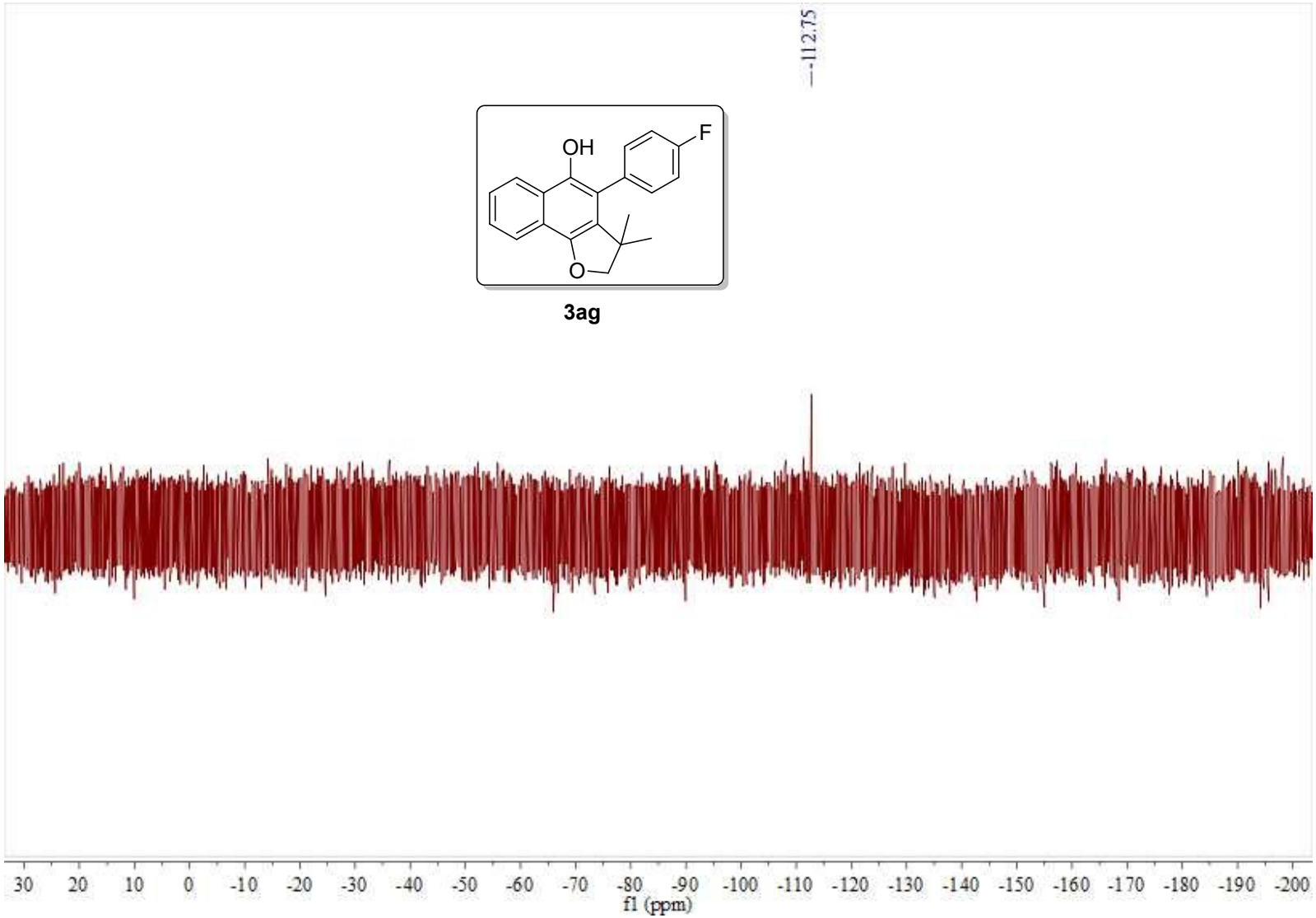
3af

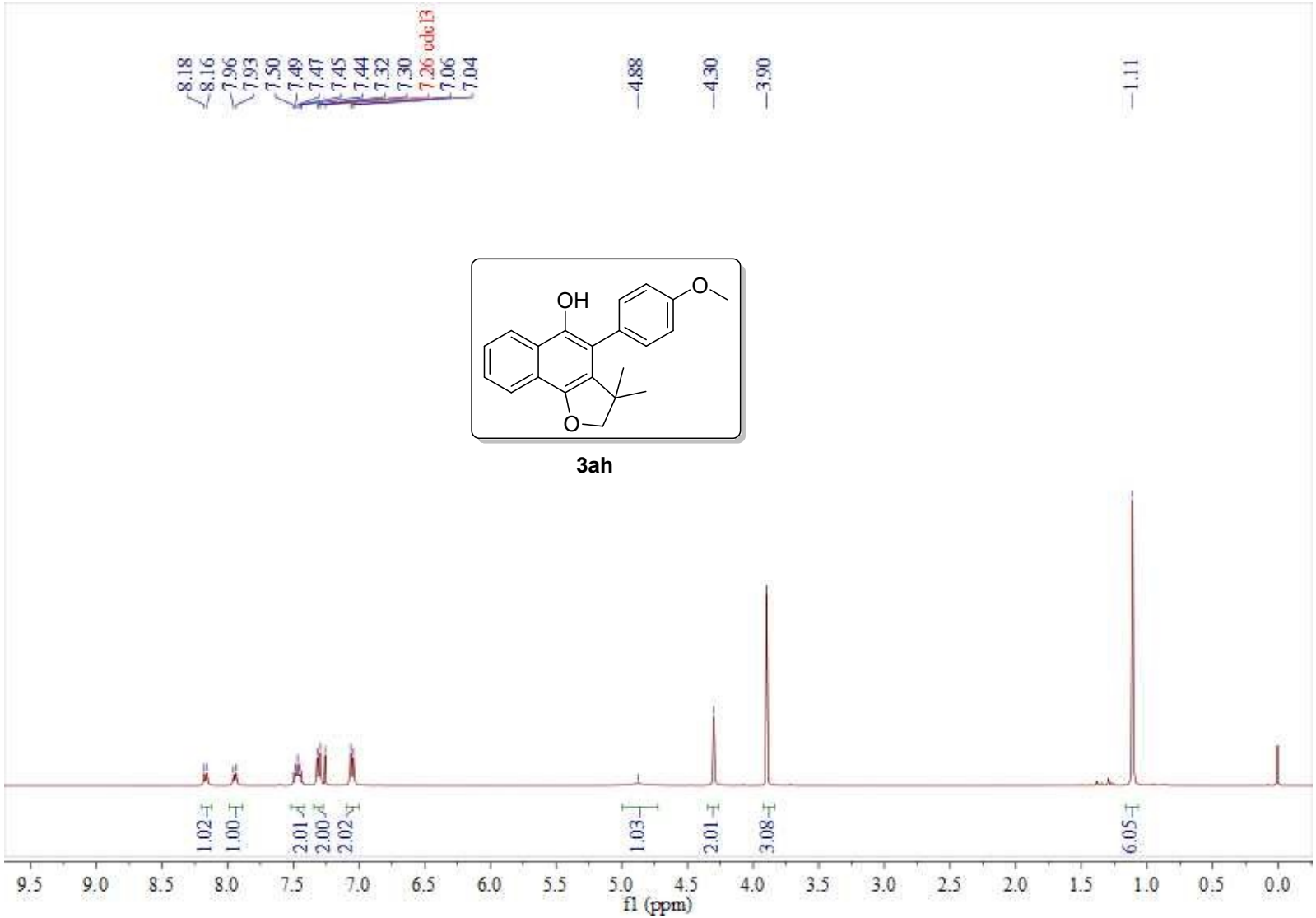

8.17
8.15
7.96
7.94
7.51
7.50
7.48
7.46
7.44
7.40
7.38
7.36
7.26 cdcl3
7.24
7.21
4.72
4.30
1.55 HDO
1.09
OH
F
O
1.00
1.00
2.02
2.08
2.09
1.01
2.07
6.10
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

3ag

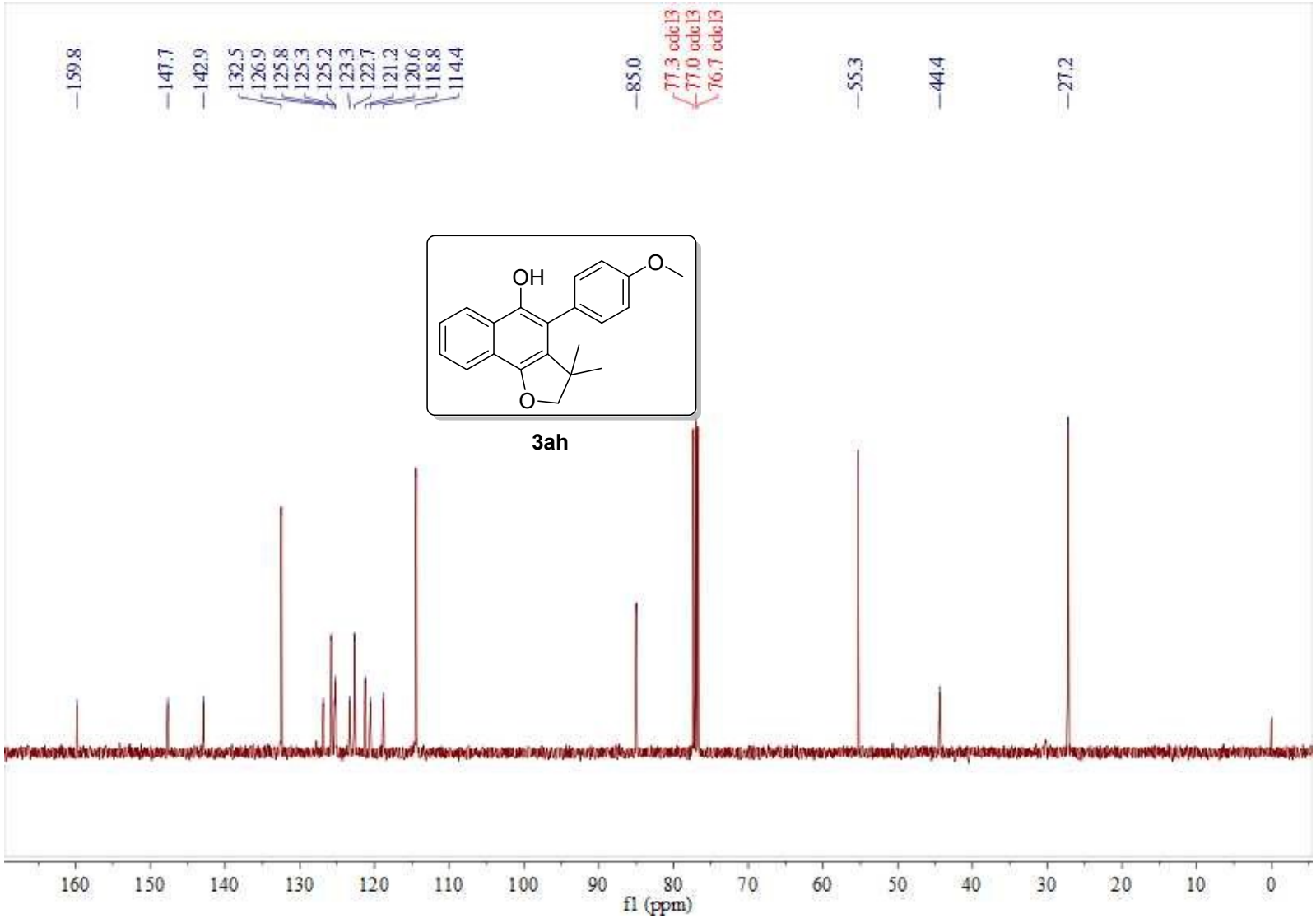

164.1
161.6
147.9
142.6
134.9
134.6
134.5
134.4
134.0
133.1
130.1
127.8
127.7
126.0
125.4
123.5
122.7
121.3
120.8
118.1
116.3
116.0
85.0
77.3 cdcl3
77.0 cdcl3
76.7 cdcl3
58.9
27.2
18.3
OH
F
O
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

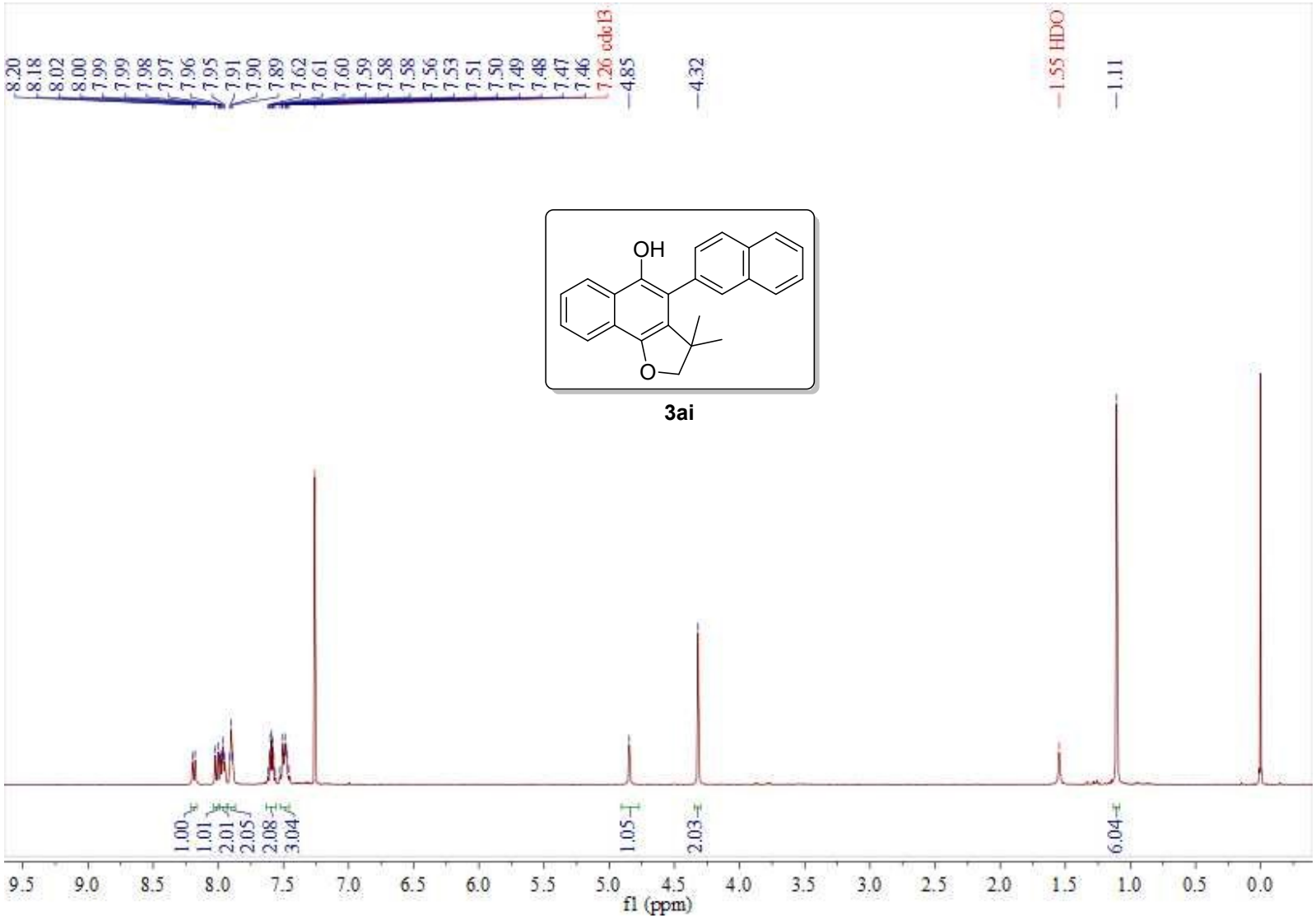
3ag


-112.75
OH
F
O
3ag
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

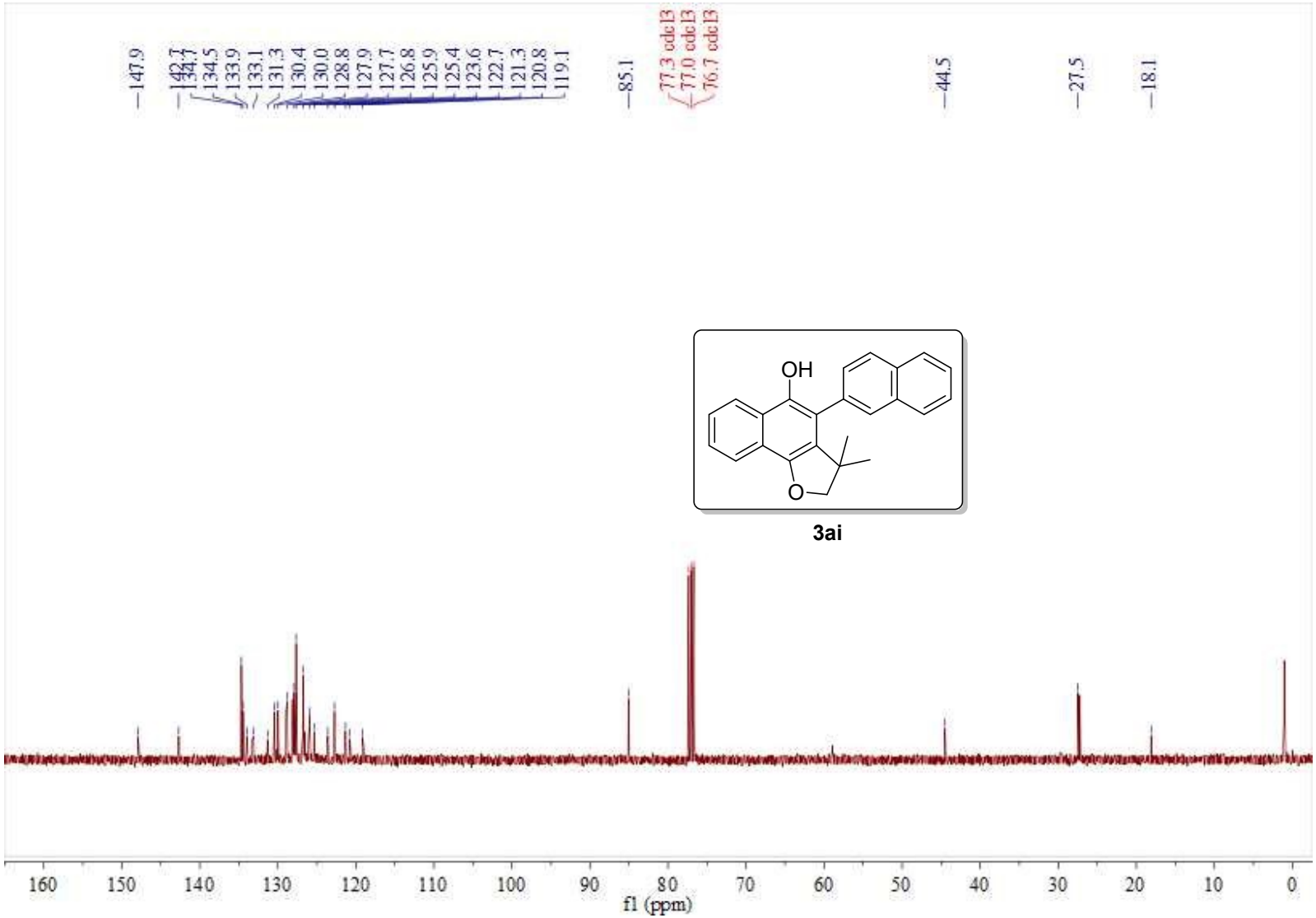

8.18
8.16
7.96
7.93
7.50
7.49
7.47
7.45
7.44
7.32
7.30
7.26 cdcl3
7.06
7.04
4.88
4.30
3.90
1.11
OH
O
O
1.02
1.00
2.01
2.00
2.02
1.03
2.01
3.08
6.05
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

3ah

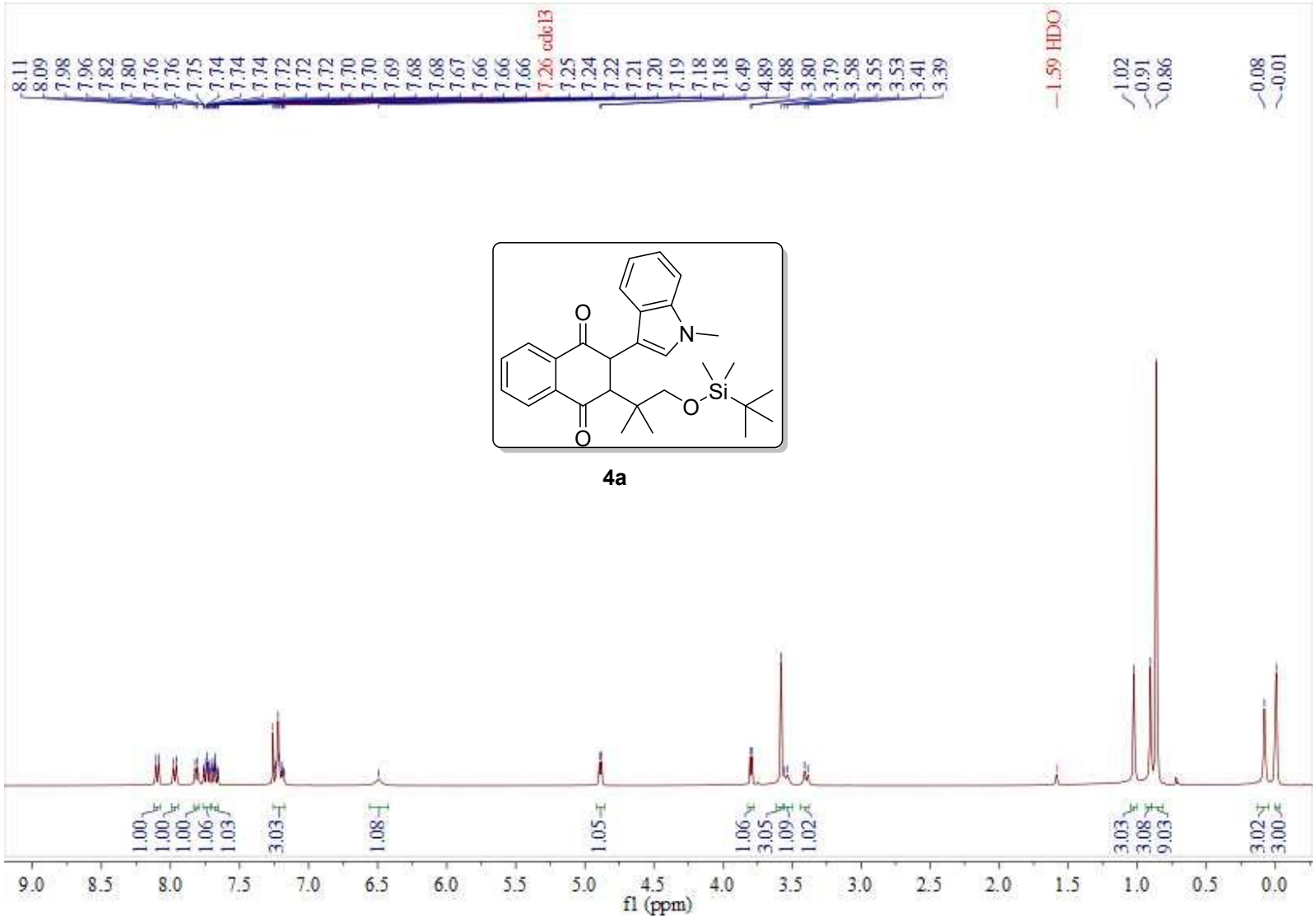

159.8
147.7
142.9
132.5
126.9
125.8
125.3
125.2
123.3
122.7
121.2
120.6
118.8
114.4
85.0
77.3 cdcl3
77.0 cdcl3
76.7 cdcl3
55.3
44.4
27.2
OH
O
O
3ah
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.20
8.18
8.02
8.00
7.99
7.99
7.98
7.97
7.96
7.95
7.91
7.90
7.89
7.62
7.61
7.60
7.59
7.58
7.58
7.56
7.53
7.51
7.50
7.49
7.48
7.47
7.46
7.26 cdcl3
4.85
4.32
1.55 HDO
1.11
OH
O
1.00
1.01
2.01
2.05
2.08
3.04
1.05
2.03
6.04
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

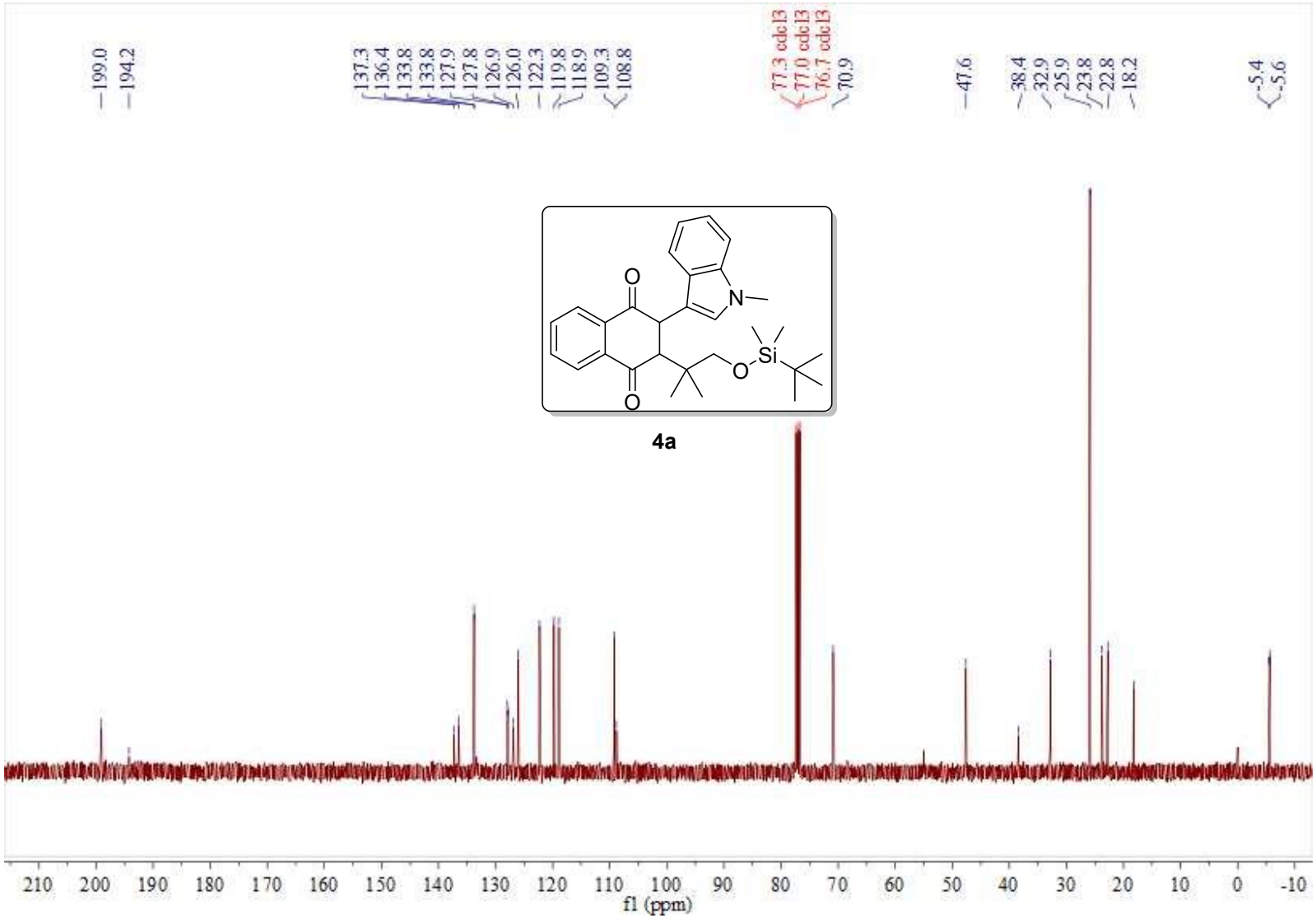
3ai

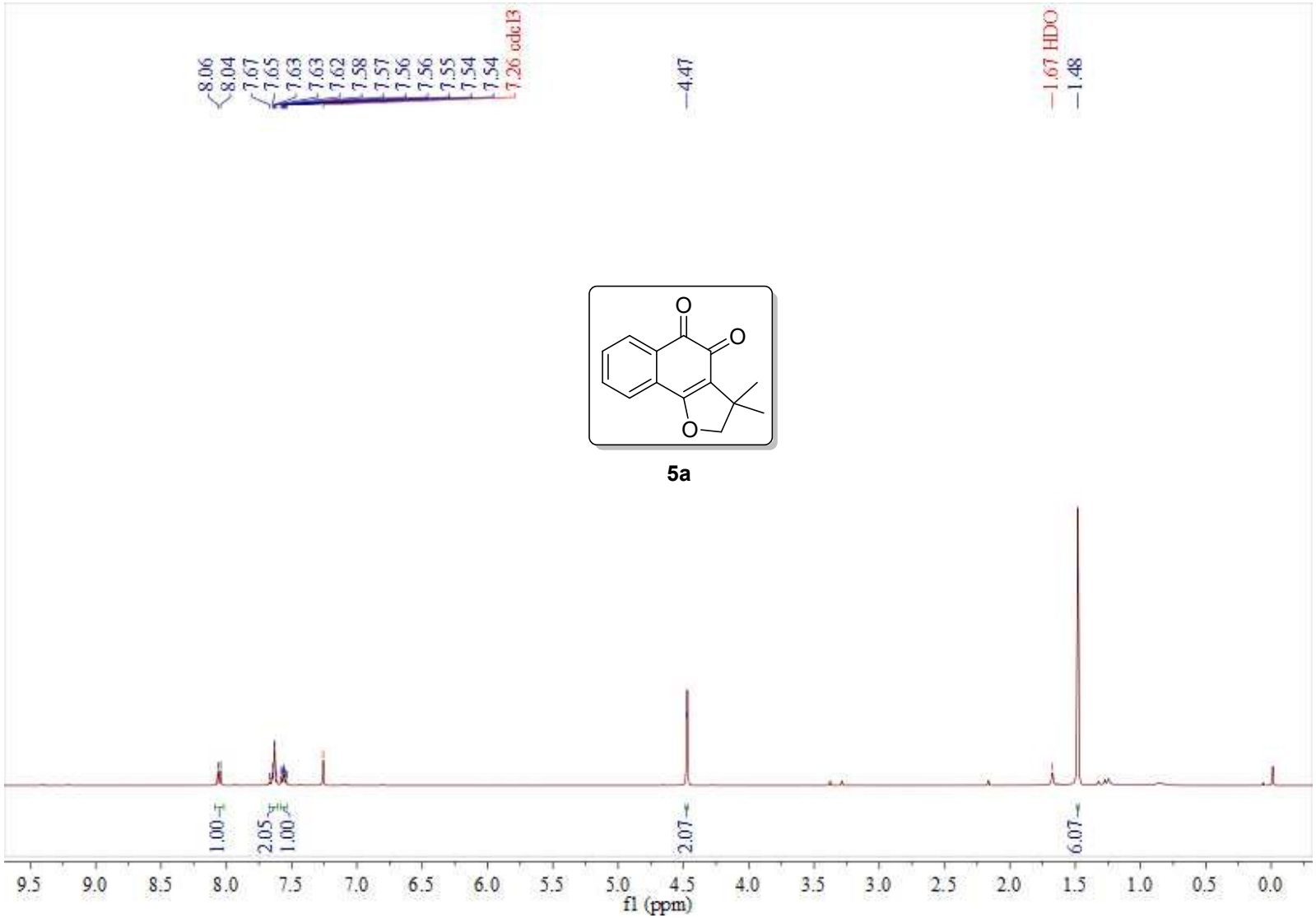

147.9
142.7
134.7
134.5
133.9
133.1
131.3
130.4
130.0
128.8
127.9
127.7
126.8
125.9
125.4
123.6
122.7
121.3
120.8
119.1
85.1
77.3 cdcl3
77.0 cdcl3
76.7 cdcl3
44.5
27.5
18.1
OH
O
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

3ai

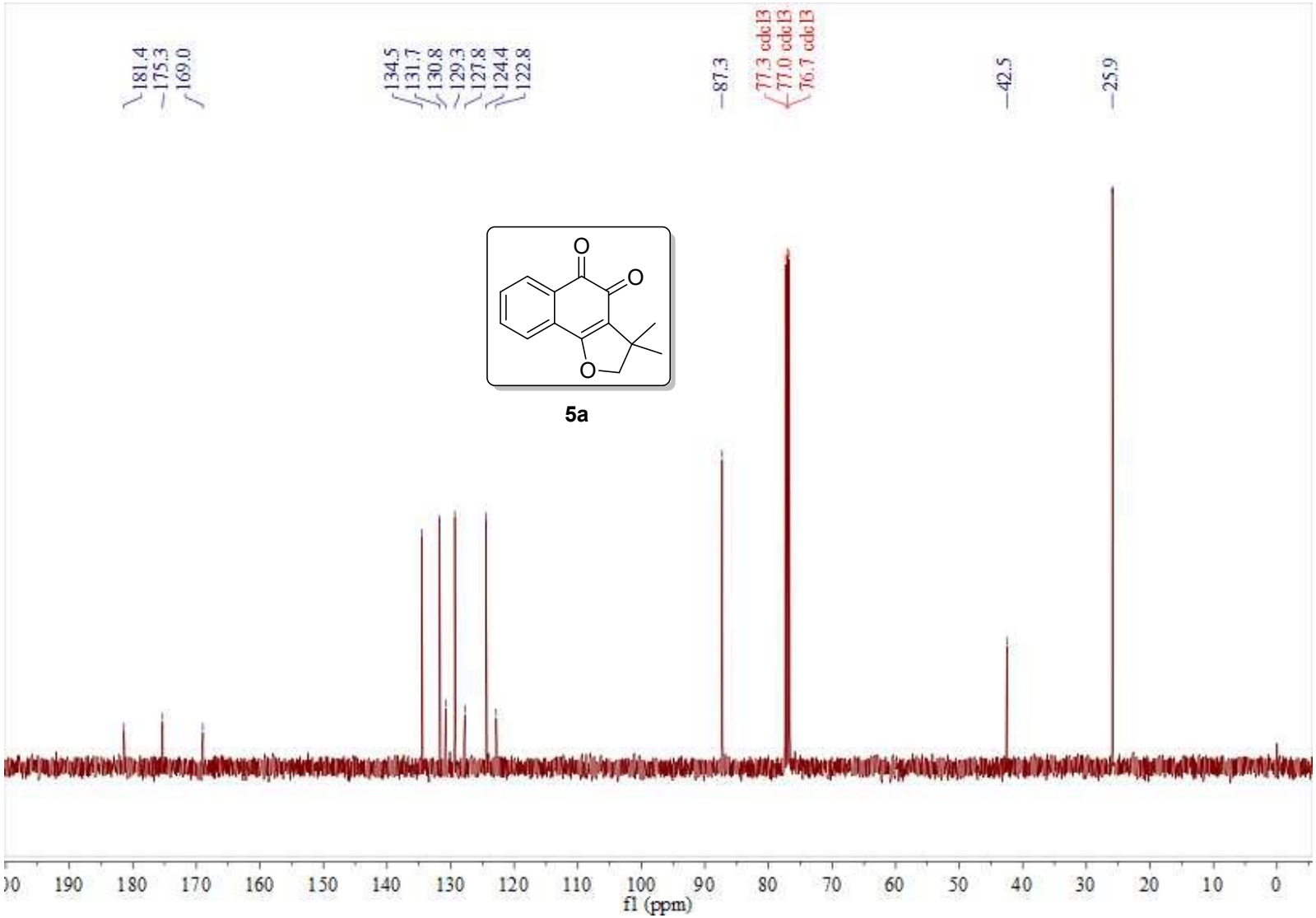

8.11
8.09
7.98
7.96
7.82
7.80
7.76
7.76
7.75
7.74
7.74
7.74
7.72
7.72
7.72
7.70
7.70
7.69
7.68
7.68
7.67
7.66
7.66
7.66
7.26 cdcl3
7.25
7.24
7.22
7.21
7.20
7.19
7.18
7.18
6.49
4.89
4.88
3.80
3.79
3.58
3.55
3.53
3.41
3.39
1.59 HDO
1.02
0.91
0.86
0.08
-0.01
O
N
Si
O
O
1.00
1.00
1.00
1.06
1.03
3.03
1.08
1.05
1.06
3.05
1.09
1.02
3.03
3.08
9.03
3.02
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

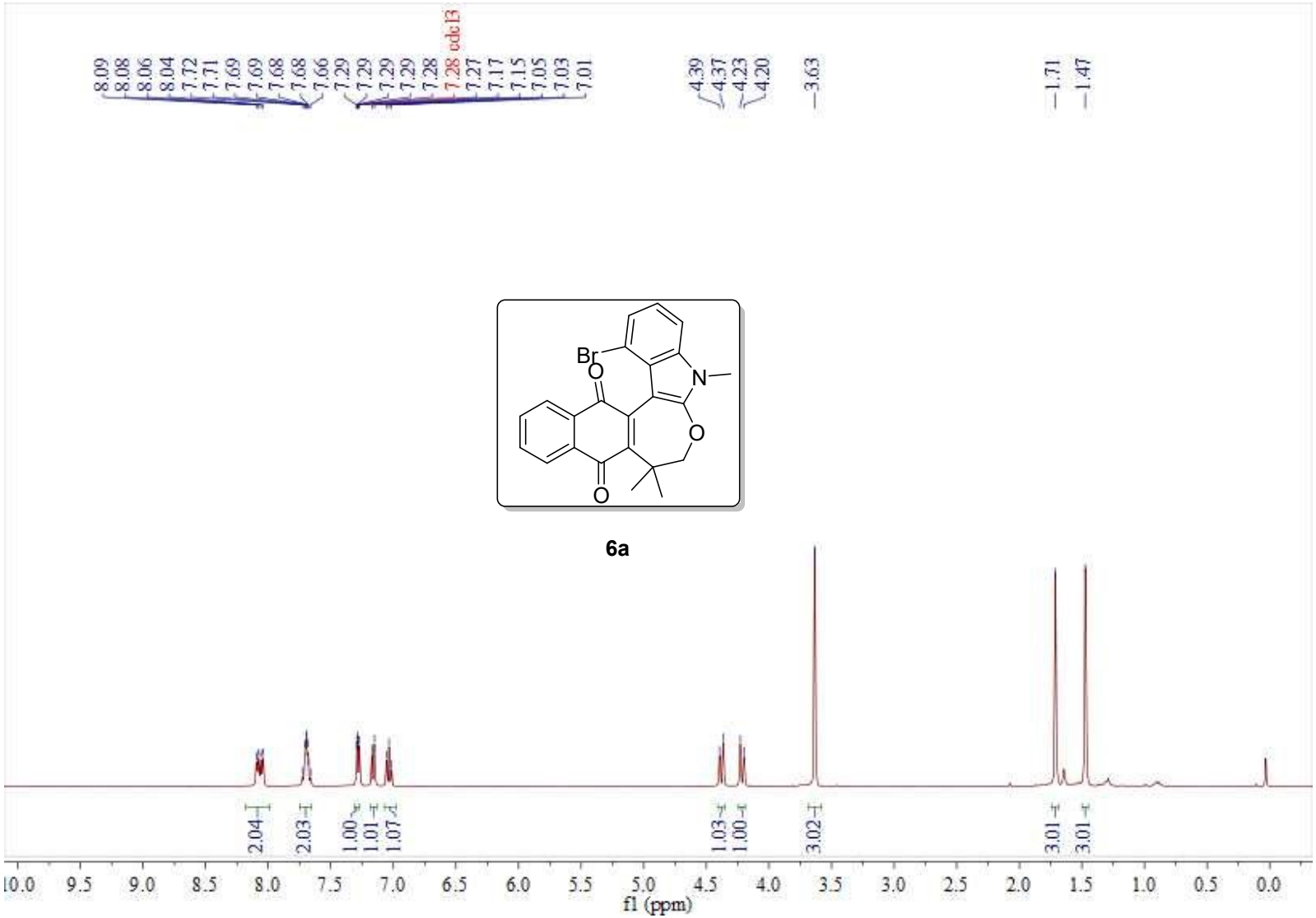
4a


199.0
194.2
137.3
136.4
133.8
133.8
127.9
127.8
126.9
126.0
122.3
119.8
118.9
109.3
108.8
77.3 cdcl3
77.0 cdcl3
76.7 cdcl3
70.9
47.6
38.4
32.9
25.9
23.8
22.8
18.2
-5.4
-5.6
O
N
O
Si
O
4a
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

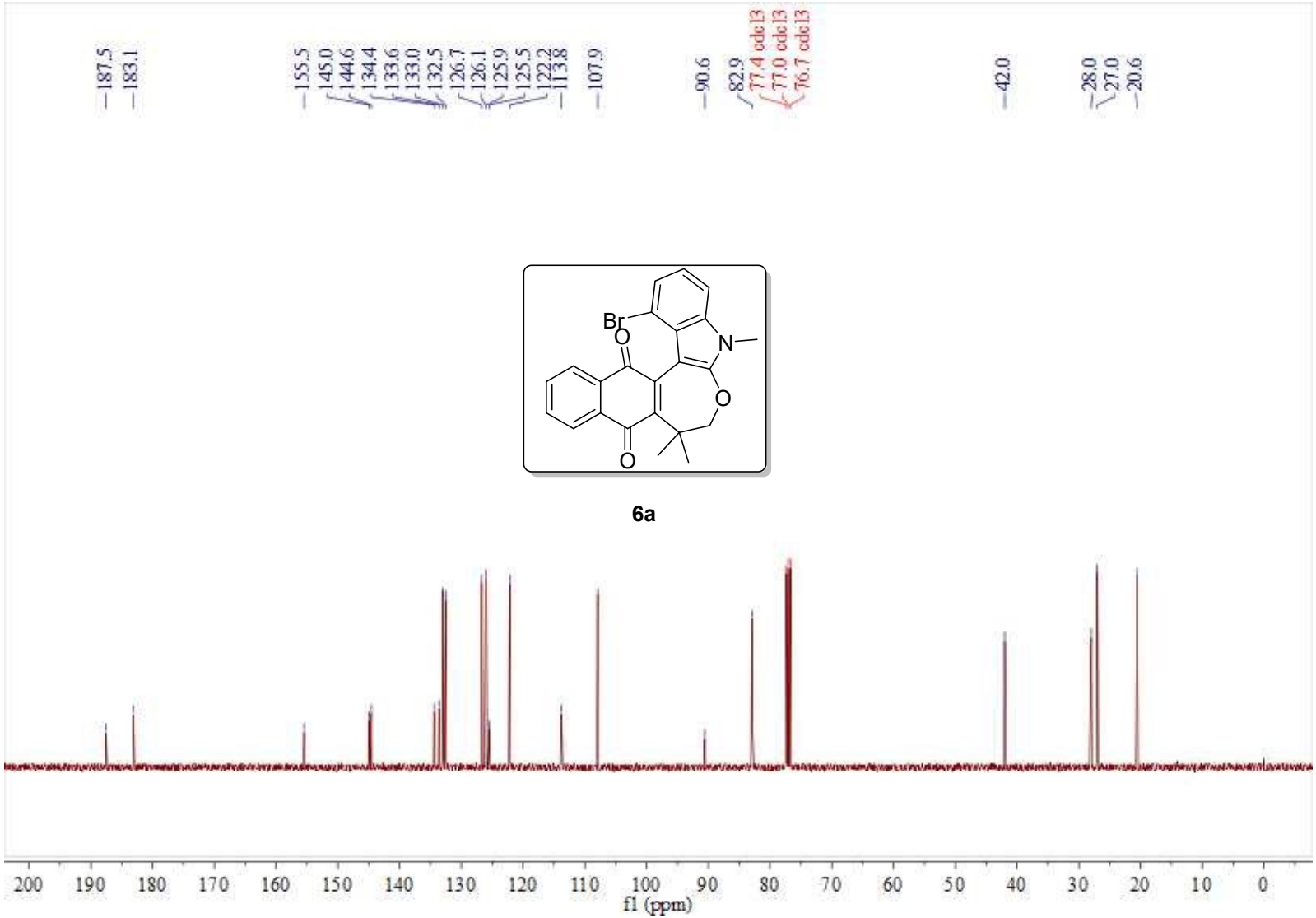

8.06
8.04
7.67
7.65
7.63
7.63
7.62
7.58
7.57
7.56
7.56
7.55
7.54
7.54
7.26 cdcl3
4.47
1.67 HDO
1.48
O
O
O
1.00
2.05
1.00
2.07
6.07
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

5a


181.4
175.3
169.0
134.5
131.7
130.8
129.3
127.8
124.4
122.8
87.3
77.3 cdcl3
77.0 cdcl3
76.7 cdcl3
42.5
25.9
O
O
O
5a
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.09
8.08
8.06
8.04
7.72
7.71
7.69
7.69
7.68
7.68
7.66
7.29
7.29
7.29
7.29
7.28
7.28 cdcl3
7.27
7.17
7.15
7.05
7.03
7.01
4.39
4.37
4.23
4.20
3.63
1.71
1.47
Br
O
N
O
O
2.04
2.03
1.00
1.01
1.07
1.03
1.00
3.02
3.01
3.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

6a


187.5
183.1
155.5
145.0
144.6
134.4
133.6
133.0
132.5
126.7
126.1
125.9
125.5
122.2
113.8
107.9
90.6
82.9
77.4 cdcl3
77.0 cdcl3
76.7 cdcl3
42.0
28.0
27.0
20.6
Br
O
N
O
O
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

6a