Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

For

Fe (III)-Catalyzed Reduction Radical Tandem Strategy to Access Poly-Substituted β-Alkenyl Valerolactones

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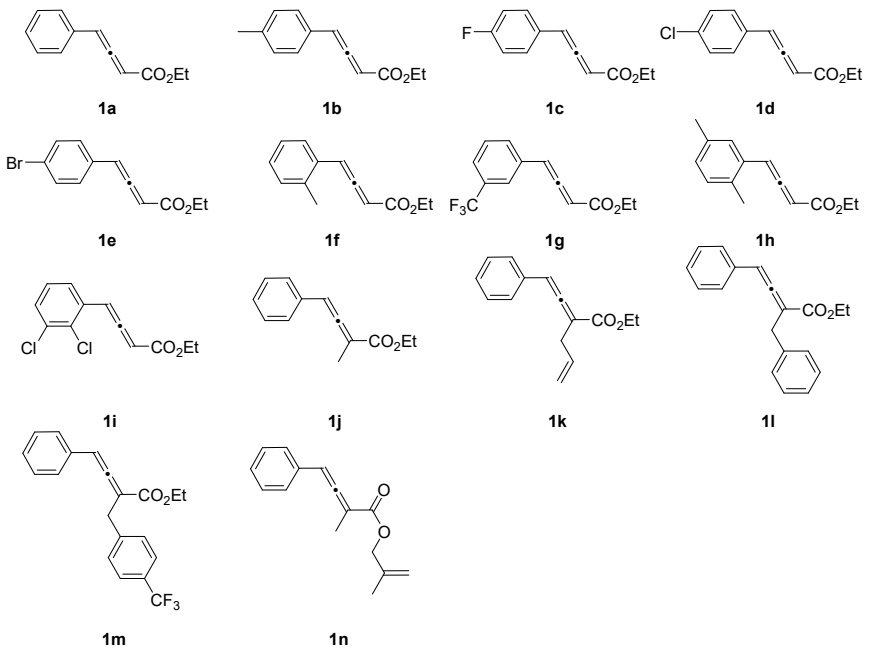
Contents

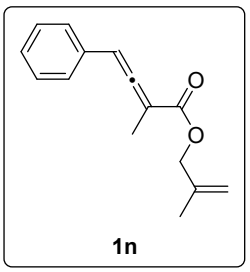
1. General Information:

All template reaction experiments were carried out under atmospheric conditions. Commercially available reagents were used without further purification. Solvents were treated prior to use according to the standard methods. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded at 300 or 400MHz on an Agilent spectrometer. $CDCl_3$ was used as solvent. Chemical shifts were referenced relative to residual solvent. Coupling constants (J) were reported in Hertz (Hz). Thin layer chromatography was carried out in the ultraviolet light using a GF-254 silica gel plate. Melting points were measured with micro melting point apparatus. HRMS were performed on an Agilent 6210 ESI/TOF. Infrared (IR) spectra were recorded on Nicolet 380. Samples were scanned in the 400-4000 cm^{-1} region with KBr pellet

2. Substrate synthesis:

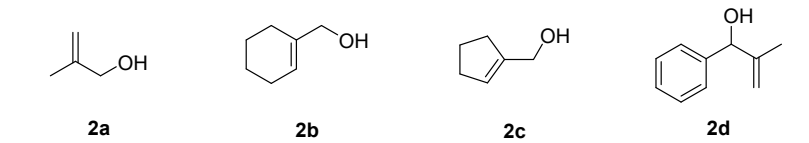


All starting materials **1a-1m** are known compounds and are prepared according to literature. [1,2]**1n** is new compound and is prepared according to literatures.[3]



Colorless liquid, yield: 70%; R_f = 0.45 (EtOAc/Petroleum ether 1:7).
IR (KBr) 3023, 2969, 2928, 1705, 1491, 1447, 1368, 1297, 1268, 1137, 1031, 985, 950, 906, 756, 698 cm^{-1}

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.34 (q, *J* = 2.64, 2.11 Hz, 1H), 7.32 (d, *J* = 2.12 Hz, 2H), 7.31 – 7.24 (m, 2H), 6.51 (q, *J* = 2.94 Hz, 1H), 4.97 (dd, *J* = 1.61, 0.86 Hz, 1H), 4.89 (q, *J* = 1.33 Hz, 1H), 4.66 – 4.53 (m, 2H), 2.04 (d, *J* = 2.97 Hz, 3H), 1.75 – 1.71 (m, 3H).
^{13}C NMR (75 MHz, $CDCl_3$): δ 212.5, 166.5, 139.8, 132.3, 128.7, 127.6, 127.2, 112.3, 99.1, 97.2, 67.9, 19.3, 14.9.
HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{15}H_{17}O_2$ 229.1228 ; found 229.1231.

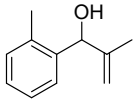


2a

2b

2c

2d



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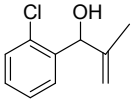

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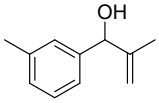

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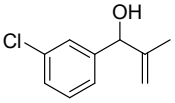

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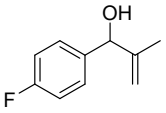

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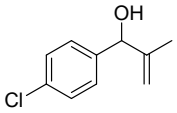
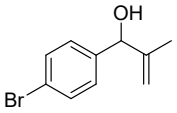
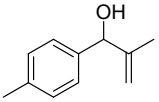


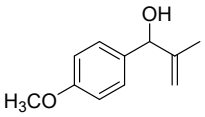
2j



2k



2l



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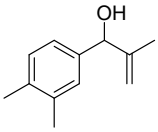
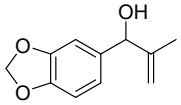
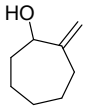


2n



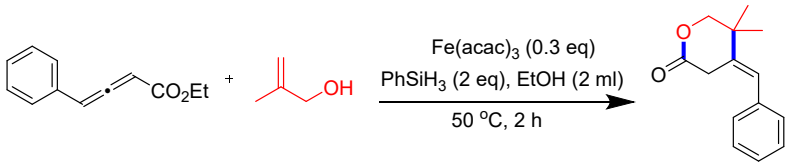
2o



2p

All starting materials **2a-2p** are known compounds. **2a** is commercially available. **2b-2c** are prepared according to literature.[4] **2d-2o** are prepared according to literature.[5] **2p** is prepared according to literature.[6]

3. Typical Procedure for Synthesis of 3a:



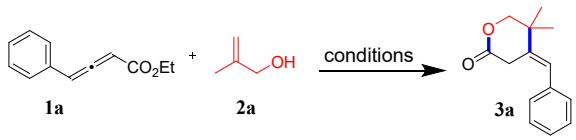
1a **2a** **3a**

$Fe(acac)_3$ (32 mg, 0.09 mmol) and 2,3-dienoates **1a** (56.4 mg,0.3 mmol) was added to the reaction tube and dissolved with ethanol (2 ml). Afterwards, 2-Methyl-2-propen-1-ol **2a** (64.9 mg, 0.9 mmol), and $PhSiH_3$ (64.9 mg, 0.6 mmol) were added via syringe. The solution was heated to 50°C for 2 h. After the reaction completed and quenched

with water, then ethyl acetate extracted the solution. Finally, the purification by column chromatography on silica gel using ethyl acetate/petroleum ether (v/v, 1:20) as eluent to give **3a** as a colorless liquid. (53 mg, 82% yield).

4. Optimization of the Reaction Conditions.

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

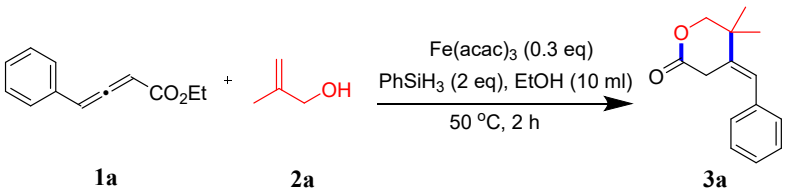


1a 2a 3a

entry	catalyst	reductant	solvent	T(°C)	Yield(%) 3a
1	$Fe(acac)_3$	$PhSiH_3$	EtOH	60	60
2	$Fe_2(ox)_3{\cdot}6H_2O$	$PhSiH_3$	EtOH	60	0
3	$CoCl_2$	$PhSiH_3$	EtOH	60	trace
4	$Cu(acac)_2$	$PhSiH_3$	EtOH	60	trace
5	$Ni(acac)_2$	$PhSiH_3$	EtOH	60	0
6	$FeCl_3$	$PhSiH_3$	EtOH	60	0
7	$Fe(acac)_3$	$NaBH_4$	EtOH	60	trace
8	$Fe(acac)_3$	Et_3SiH	EtOH	60	0
9	$Fe(acac)_3$	$(EtO)_3SiH$	EtOH	60	30
10	$Fe(acac)_3$	Ph_2SiH_2	EtOH	60	60
11	$Fe(acac)_3$	$PhSiH_3$	MeOH	60	20
12	$Fe(acac)_3$	$PhSiH_3$	THF	60	0
13	$Fe(acac)_3$	$PhSiH_3$	CH_3CN	60	48
14	$Fe(acac)_3$	$PhSiH_3$	1,4-Dioxane	60	35
15	$Fe(acac)_3$	$PhSiH_3$	EtOH	75	30
16	$Fe(acac)_3$	$PhSiH_3$	EtOH	50	82
17	$Fe(acac)_3$	$PhSiH_3$	EtOH	30	15
18[c]	$Fe(acac)_3$	$PhSiH_3$	EtOH	50	34
19[d]	$Fe(acac)_3$	$PhSiH_3$	EtOH	50	24

[a] Reaction conditions: **1a** (0.3 mmol), **2a** (0.9 mmol), catalyst (30 mol %), reductant (2 equiv), solvent (2 mL), 2h; [b] yield refers to isolated product. [c] $Fe(acac)_3$ (10 mol %) was used. [d] conducted the reaction in an argon atmosphere.

5. Scale-up Reaction

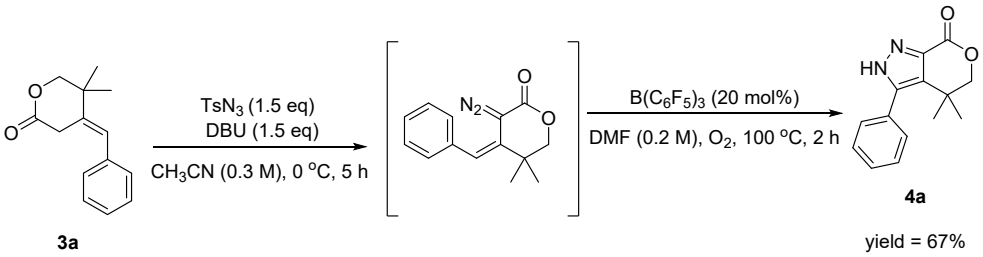


1a 2a 3a

$Fe(acac)_3$ (160 mg, 0.45 mmol) and 2,3-dienoates **1a** (282 mg, 1.5 mmol) was added to the reaction tube and dissolved with ethanol (10 ml). Afterwards, 2-Methyl-2-

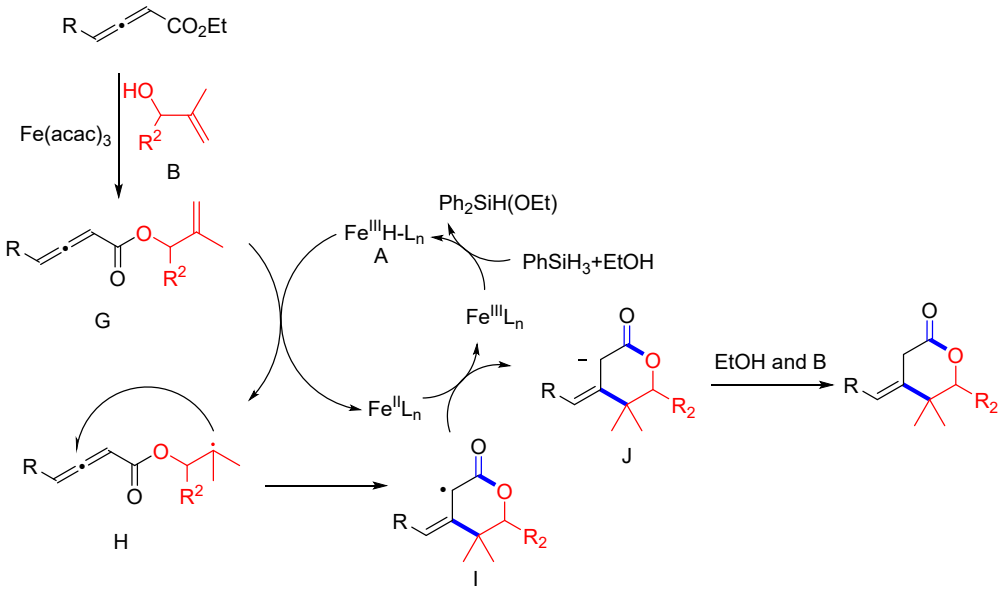
propen-1-ol **2a** (324.5 mg, 4.5 mmol), and $PhSiH_3$ (324.5 mg, 3.0 mmol) were added via syringe. The solution was heated to 50°C for 2 h. After the reaction completed and quenched with water, then ethyl acetate extracted the solution. Finally, the purification by column chromatography on silica gel using ethyl acetate/petroleum ether (v/v, 1:20) as eluent to give **3a** as a colorless liquid. (200 mg, 62% yield).

6. Typical Procedure for Synthesis of 4a.



3a (106 mg, 0.5 mmol), TsN_3 (130 mg, 1.5 eq), DBU (110 mg, 1.5 eq) are added to reaction tube under argon atmosphere, then dissolve with anhydrous acetonitrile (0.3 M). The solution was reacted for 5 hours in 0 °C. After the reaction was completed, it was quenched with water and extracted with ethyl acetate to obtain azo ester compound intermediate, which was added to the next step without purification. Add azo ester intermediate, $B(C_6F_5)_3$ (50 mg, 0.2 eq) to a dry reaction tube in an argon atmosphere, then dissolve with anhydrous DMF (0.2 M). The solution was reacted for 2 hours in 100 °C in an oxygen atmosphere. After the reaction is completed, it was quenched with water and extracted with ethyl acetate. Finally, the purification by column chromatography on silica gel using ethyl acetate/petroleum ether (v/v, 1:30) as eluent to give **4a** as white solid. (81 mg, 67% yield).

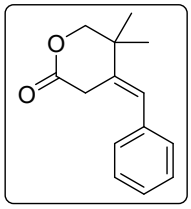
7. Proposed Mechanism



The reaction went through second path: 2,3-dienoates and allyl alcohol **B** formed allyl ester intermediate **G** under Fe (III) catalysis. Then allyl ester intermediate **G** and ferrohydride species **A** underwent hydrogen atom transfer to form radical intermediates **H**, which underwent intramolecular Michael addition to form radicals **I.** Finally, **I** formed anionic intermediates **J** through single electron transfer and **J** abstracted the proton from the ethanol and **B** to generate product.

8. Characterization of 3, 4a, 5a:

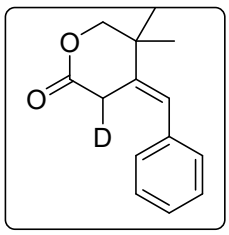
(E)-4-benzylidene-5,5-dimethyltetrahydro-2H-pyran-2-one (3a)



3a

Colorless liquid, 53 mg, yield: 82%; R_f = 0.26 (EtOAc/Petroleum ether 1:7).
IR (KBr) 3034, 2971, 2928, 1718, 1462, 1389, 1256, 1241, 1129, 1064, 1023, 860, 802, 744, 706, 577, 492 cm^{-1}
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 (t, *J* = 7.56 Hz, 2H), 7.24 (d, *J* = 7.29 Hz, 1H), 7.16 (d, *J* = 7.50 Hz, 2H), 6.50 (d, *J* = 2.45 Hz, 1H), 4.08 (s, 2H), 3.57 – 3.52 (m, 2H), 1.28 (s, 6H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 170.6, 137.9, 136.2, 128.6, 128.4, 127.1, 125.2, 77.0, 36.4, 33.8, 25.6.
HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{14}H_{17}O_2$ 217.1228; found 217.1230.

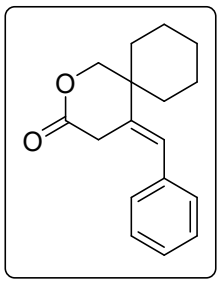
(E)-4-benzylidene-5,5-dimethyltetrahydro-2H-pyran-2-one-3-dc (3aD)



3aD

Colorless liquid, 13 mg, yield: 20%; R_f = 0.33 (EtOAc/Petroleum ether 1:7).
IR (KBr) 3025, 2960, 2928, 1746, 1492, 1376, 1294, 1254, 1195, 1057, 966, 920, 859, 761, 702 cm^{-1}
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 – 7.32 (m, 2H), 7.26 – 7.21 (m, 1H), 7.16 (d, *J* = 7.58 Hz, 2H), 6.51 (s, 1H), 4.08 (s, 2H), 3.53 (d, *J* = 11.76 Hz, 1H), 1.27 (s, 6H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 170.6, 137.9, 136.2, 128.6, 128.4, 127.1, 125.2, 77.0, 36.4, 33.9, 25.6.
HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{14}H_{16}DO_2$ 218.1291; found 218.1281.

(E)-5-benzylidene-2-oxaspiro[5.5]undecan-3-one (3b)



3b

White crystalline solid, m.p. 104-106°C, 57 mg, yield: 75%; R_f = 0.45 (EtOAc/Petroleum ether 1:7).

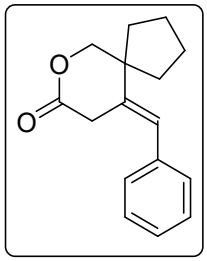
IR (KBr) 3007, 2936, 2853, 1745, 1485, 1456, 1385, 1243, 1164, 1135, 1056, 914, 871, 837, 756, 729, 704, 594, 550 cm^{-1}

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.35 (t, *J* = 7.35 Hz, 2H), 7.23 (d, *J* = 6.10 Hz, 1H), 7.15 (d, *J* = 7.30 Hz, 2H), 6.56 (s, 1H), 4.30 (s, 2H), 3.53 (s, 2H), 1.73 (s, 4H), 1.67 (d, *J* = 9.09 Hz, 3H), 1.46 (dt, *J* = 22.30, 10.16 Hz, 4H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 170.9, 138.5, 136.4, 128.7, 128.4, 127.0, 125.5, 72.3, 39.3, 33.8, 33.4, 25.8, 21.8.

HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{17}H_{21}O_2$ 257.1541; found 257.1546.

(E)-10-benzylidene-7-oxaspiro[4.5]decan-8-one (3c)



3c

White crystalline solid, m.p. 135-138°C, 53 mg, yield: 74%; R_f = 0.35 (EtOAc/Petroleum ether 1:7).

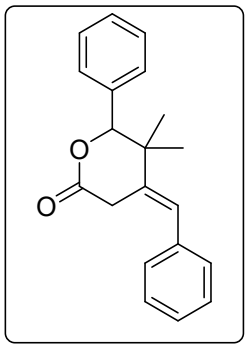
IR (KBr) 3061, 2959, 2865, 1728, 1660, 1597, 1447, 1391, 1260, 1231, 1102, 1052, 889, 802, 741, 691, 610 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 (t, *J* = 7.51 Hz, 2H), 7.23 (d, *J* = 7.42 Hz, 1H), 7.15 (d, *J* = 7.29 Hz, 2H), 6.50 (s, 1H), 4.11 (s, 2H), 3.58 (d, *J* = 2.10 Hz, 2H), 1.91 – 1.83 (m, 4H), 1.82 – 1.70 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 170.7, 138.6, 136.3, 128.7, 128.4, 127.0, 124.5, 74.7, 48.2, 36.6, 34.8, 24.8.

HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{16}H_{19}O_2$ 243.1385; found 243.1389.

(E)-4-benzylidene-5,5-dimethyl-6-phenyltetrahydro-2H-pyran-2-one (3d)



3d

White crystalline solid, m.p. 140-142°C, 44 mg, yield: 50%; R_f = 0.35 (EtOAc/Petroleum ether 1:7).

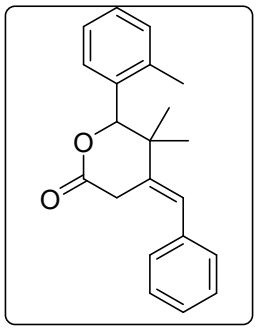
IR (KBr) 3053, 3028, 2978, 1730, 1495, 1451, 1368, 1364, 1295, 1258, 1170, 1039, 1002, 929, 908, 868, 748, 691, 592 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 (d, *J* = 6.20 Hz, 5H), 7.30 (dd, *J* = 16.00, 7.38 Hz, 4H), 7.19 (d, *J* = 7.42 Hz, 2H), 6.53 (s, 1H), 5.23 (s, 1H), 3.83 – 3.62 (m, 2H), 1.23 (s, 3H), 1.10 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 170.1, 138.0, 136.4, 135.4, 128.7, 128.5, 128.5, 128.0, 127.9, 127.1, 125.6, 87.3, 40.5, 34.0, 25.4, 22.0.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{20}H_{20}O_2Na$ 315.1361; found 315.1363.

(E)-4-benzylidene-5-(o-tolyl)tetrahydro-2H-pyran-2-one (3e)



3e

White crystalline solid, m.p. 138-140°C, 36 mg, yield: 40%; R_f = 0.35 (EtOAc/Petroleum ether 1:7).

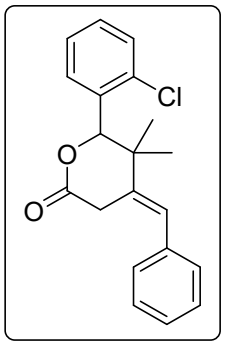
IR (KBr) 3055, 3019, 2967, 1733, 1493, 1470, 1393, 1360, 1327, 1264, 1170, 1035, 1008, 925, 902, 868, 748, 694, 594, 560, 508 cm^{-1}

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.40 (td, *J* = 6.71, 2.66 Hz, 3H), 7.33 – 7.27 (m, 2H), 7.23 (dt, *J* = 8.59, 4.12 Hz, 4H), 6.53 (s, 1H), 5.61 (s, 1H), 3.86 – 3.68 (m, 2H), 2.43 (s, 3H), 1.26 (s, 3H), 1.21 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 170.2, 138.2, 136.3, 136.0, 133.9, 130.5, 128.7, 128.4, 128.3, 128.2, 127.1, 125.6, 125.1, 82.4, 41.4, 34.1, 25.0, 22.3, 20.3.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{21}H_{23}O_2$ 307.1698; found 307.1692.

(E)-4-benzylidene-5-(2-chlorophenyl)tetrahydro-2H-pyran-2-one (3f)



3f

White crystalline solid, m.p. 155-158°C, 39 mg, yield: 40%; R_f = 0.34 (EtOAc/Petroleum ether 1:7).

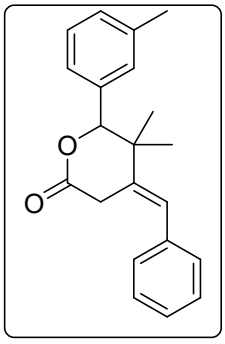
IR (KBr) 3067, 3028, 2971, 2936, 2869, 1735, 1576, 1476, 1443, 1406, 1329, 1291, 1268, 1166, 1048, 1033, 1004, 923, 900, 868, 771, 746, 733, 694, 650, 598, 569, 512 cm^{-1}

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.52 – 7.45 (m, 1H), 7.45 – 7.37 (m, 3H), 7.35 – 7.27 (m, 3H), 7.22 (d, *J* = 7.34 Hz, 2H), 6.55 (s, 1H), 5.91 (s, 1H), 3.87 – 3.67 (m, 2H), 1.31 (s, 3H), 1.20 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 169.8, 137.6, 136.2, 133.6, 133.4, 129.9, 129.6, 129.5, 128.7, 128.4, 127.1, 126.5, 125.5, 82.0, 41.5, 34.0, 24.6, 22.1.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{20}H_{21}ClO_2$ 349.0971; found 349.0968.

(E)-4-benzylidene-5,5-dimethyl-6-(m-tolyl)tetrahydro-2H-pyran-2-one (3g)



3g

White crystalline solid, m.p. 143-146°C, 53 mg, yield: 58%; R_f = 0.36 (EtOAc/Petroleum ether 1:7).

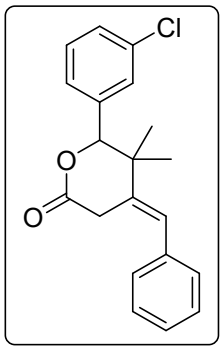
IR (KBr) 3053, 3028, 2965, 2919, 1737, 1597, 1451, 1406, 1333, 1260, 1172, 1029, 1004, 925, 871, 794, 741, 691, 589, 502 cm^{-1}

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.37 (t, *J* = 7.38 Hz, 2H), 7.30 – 7.27 (m, 1H), 7.24 (s, 1H), 7.22 – 7.15 (m, 3H), 7.15 – 7.07 (m, 2H), 6.53 (s, 1H), 5.20 (s, 1H), 3.78 (dd, *J* = 19.53, 1.10 Hz, 1H), 3.64 (dd, *J* = 19.04, 2.68 Hz, 1H), 2.38 (s, 3H), 1.23 (s, 3H), 1.10 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 170.1, 138.1, 137.5, 136.4, 135.3, 129.2, 128.7, 128.7,

128.4, 127.7, 127.1, 125.5, 125.2, 87.4, 87.4, 40.5, 34.0, 25.5, 22.1, 21.5.
HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{21}H_{23}O_2$ 307.1698; found 307.1697.

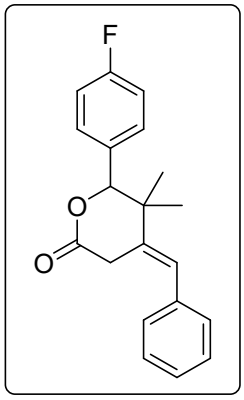
(E)-4-benzylidene-6-(3-chlorophenyl)-5,5-dimethyltetrahydro-2H-pyran-2-one (3h)



3h

White crystalline solid, m.p. 157-160°C, 48 mg, yield: 50%; R_f = 0.32 (EtOAc/Petroleum ether 1:7).
IR (KBr) 3065, 3028, 2976, 2965, 1739, 1595, 1574, 1431, 1366, 1322, 1260, 1177, 1033, 918, 808, 771, 750, 696, 508 cm^{-1}
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.41 – 7.34 (m, 4H), 7.33 – 7.25 (m, 3H), 7.23 – 7.16 (m, 3H), 6.55 (s, 1H), 5.20 (s, 1H), 3.84 – 3.72 (m, 1H), 3.64 (dd, *J* = 19.30, 2.55 Hz, 1H), 1.24 (s, 3H), 1.10 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 169.6, 137.5, 137.4, 136.2, 134.0, 129.2, 128.7, 128.7, 128.5, 128.2, 127.2, 126.2, 125.9, 86.5, 86.4, 40.5, 33.9, 25.3, 21.9.
HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{20}H_{21}ClO_2$ 327.1151 ; found 327.1154.

(E)-4-benzylidene-6-(4-fluorophenyl)-5,5-dimethyltetrahydro-2H-pyran-2-one (3i)



3i

White crystalline solid, m.p. 127-130°C, 55 mg, yield: 60%; R_f = 0.24 (EtOAc/Petroleum ether 1:7).
IR (KBr) 3055, 2976, 2930, 1737, 1608, 1510, 1418, 1289, 1247, 1156, 1027, 904,

835, 777, 604, 508 cm^{-1}

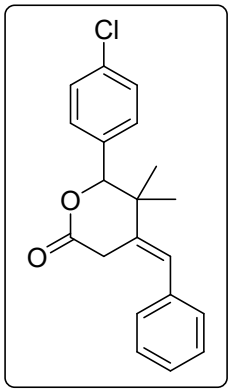
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 (t, *J* = 7.48 Hz, 2H), 7.28 (td, *J* = 7.65, 6.63, 4.42 Hz, 3H), 7.18 (d, *J* = 7.43 Hz, 2H), 7.07 (t, *J* = 8.61 Hz, 2H), 6.53 (s, 1H), 5.22 (s, 1H), 3.82 – 3.71 (m, 1H), 3.64 (dd, *J* = 19.26, 2.46 Hz, 1H), 1.21 (s, 3H), 1.08 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 169.8, 137.7, 136.3, 131.3, 129.8, 129.7, 128.7, 128.5, 127.2, 125.7, 115.0, 114.8, 86.6, 40.5, 33.9, 25.3, 21.9.

^{19}F NMR (376 MHz, $CDCl_3$): δ -113.30.

HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{20}H_{21}FO_2$ 311.1447 ; found 311.1449.

(E)-4-benzylidene-6-(4-chlorophenyl)-5,5-dimethyltetrahydro-2H-pyran-2-one (3j)



3j

White crystalline solid, m.p. 145-148°C, 63 mg, yield: 65%; R_f = 0.24 (EtOAc/Petroleum ether 1:7).

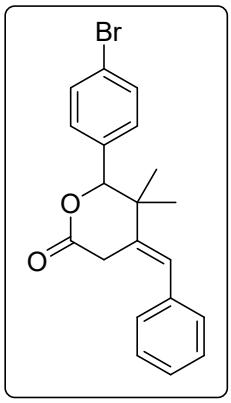
IR (KBr) 3053, 3028, 2976, 2921, 1741, 1599, 1495, 1410, 1283, 1250, 1160, 1089, 1033, 1008, 906, 833, 771, 702 cm^{-1}

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.34 (d, *J* = 8.13 Hz, 4H), 7.24 (t, *J* = 9.05 Hz, 3H), 7.16 (d, *J* = 7.57 Hz, 2H), 6.51 (s, 1H), 5.19 (s, 1H), 3.75 (d, *J* = 19.30 Hz, 1H), 3.62 (dd, *J* = 19.28, 2.09 Hz, 1H), 1.19 (s, 3H), 1.05 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 169.7, 137.6, 136.2, 134.4, 134.0, 129.3, 128.7, 128.5, 128.1, 127.2, 125.8, 86.5, 40.5, 33.9, 25.3, 21.9.

HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{20}H_{21}ClO_2$ 327.1151 ; found 327.1156.

(E)-4-benzylidene-6-(4-bromophenyl)-5,5-dimethyltetrahydro-2H-pyran-2-one (3k)



3k

White crystalline solid, m.p. 154-157°C, 66 mg, yield: 60%; R_f = 0.32 (EtOAc/Petroleum ether 1:7).

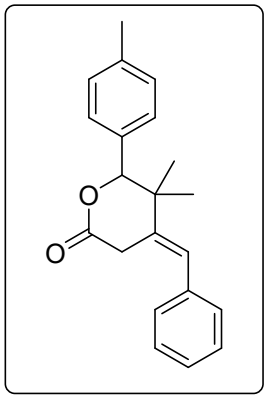
IR (KBr) 3051, 3023, 2971, 2932, 1730, 1597, 1489, 1410, 1289, 1243, 1168, 1073, 1033, 1008, 906, 827, 775, 706, 550, 481 cm^{-1}

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.52 (d, *J* = 8.47 Hz, 2H), 7.37 (t, *J* = 7.27 Hz, 2H), 7.29 (d, *J* = 7.33 Hz, 1H), 7.23 – 7.14 (m, 4H), 6.54 (s, 1H), 5.20 (s, 1H), 3.78 (dd, *J* = 19.22, 1.46 Hz, 1H), 3.64 (dd, *J* = 19.25, 2.50 Hz, 1H), 1.21 (s, 3H), 1.07 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 169.7, 137.5, 136.2, 134.5, 131.1, 129.7, 128.7, 128.5, 127.2, 125.8, 122.6, 86.5, 40.4, 33.9, 25.3, 21.9.

HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{20}H_{21}BrO_2$ 371.0646; found 371.0649.

(E)-4-benzylidene-5,5-dimethyl-6-(p-tolyl)tetrahydro-2H-pyran-2-one (3l)



3l

White crystalline solid, m.p. 140-142°C, 71 mg, yield: 78%; R_f = 0.35 (EtOAc/Petroleum ether 1:7).

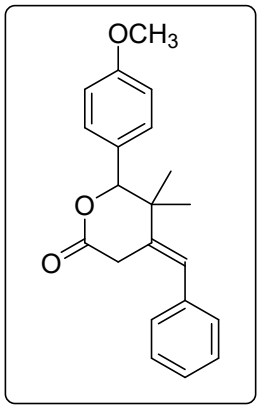
IR (KBr) 3030, 2974, 2924, 2878, 1728, 1520, 1470, 1358, 1293, 1264, 1172, 1035, 1008, 906, 835, 762, 737, 700, 600, 510 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 (t, *J* = 7.47 Hz, 2H), 7.29 – 7.20 (m, 2H), 7.22 – 7.08 (m, 6H), 6.52 (t, *J* = 2.12 Hz, 1H), 5.20 (s, 1H), 3.77 (dd, *J* = 19.25, 1.46 Hz, 1H), 3.64 (dd, *J* = 19.26, 2.61 Hz, 1H), 2.37 (s, 3H), 1.22 (s, 3H), 1.09 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 170.1, 138.3, 138.1, 136.4, 132.5, 128.7, 128.5, 128.4,

127.9, 127.1, 125.5, 87.3, 87.3, 40.5, 34.0, 25.5, 22.0, 21.2.
HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{21}H_{23}O_2$ 307.1698 ; found 307.1693.

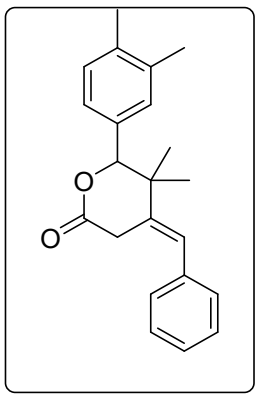
(E)-4-benzylidene-6-(4-methoxyphenyl)-5,5-dimethyltetrahydro-2H-pyran-2-one (3m)



3m

White crystalline solid, m.p. 104-106°C, 67 mg, yield: 70%; R_f = 0.29 (EtOAc/Petroleum ether 1:7).
IR (KBr) 3048, 2959, 2838, 1741, 1616, 1552, 1308, 1256, 1179, 1035, 993, 831, 764, 698, 594 cm^{-1}
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 (t, *J* = 7.46 Hz, 2H), 7.31 – 7.21 (m, 4H), 7.18 (d, *J* = 7.24 Hz, 2H), 6.90 (d, *J* = 8.68 Hz, 2H), 6.52 (s, 1H), 5.19 (s, 1H), 3.83 (s, 3H), 3.79 – 3.72 (m, 1H), 3.64 (dd, *J* = 19.26, 2.40 Hz, 1H), 1.21 (s, 3H), 1.09 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 170.1, 159.7, 138.1, 136.4, 129.2, 128.7, 128.4, 127.6, 127.1, 125.5, 113.3, 87.1, 87.1, 55.3, 40.6, 34.0, 25.5, 22.0.
HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{21}H_{22}O_3$ 323.1647 ,found 323.1646.

(E)-4-benzylidene-6-(3,4-dimethylphenyl)-5,5-dimethyltetrahydro-2H-pyran-2-one (3n)

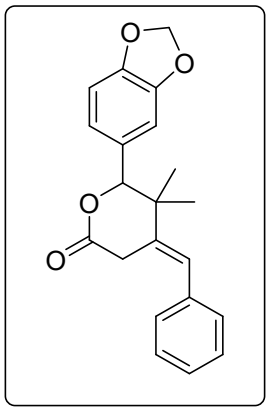


3n

White crystalline solid, m.p. 145-148°C, 76 mg, yield: 80%; R_f = 0.37

(EtOAc/Petroleum ether 1:7).
IR (KBr) 3026, 2971, 2921, 1737, 1639, 1443, 1354, 1262, 1170, 1039, 1002, 918, 827, 739, 694, 510 cm^{-1}
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 (t, *J* = 7.50 Hz, 2H), 7.28 (s, 1H), 7.22 – 7.15 (m, 2H), 7.15 – 7.06 (m, 2H), 7.02 (dd, *J* = 7.59, 1.60 Hz, 1H), 6.52 (s, 1H), 5.17 (s, 1H), 3.76 (dd, *J* = 19.26, 1.47 Hz, 1H), 3.63 (dd, *J* = 19.21, 2.63 Hz, 1H), 2.27 (s, 6H), 1.22 (s, 3H), 1.09 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 170.2, 138.2, 136.9, 136.5, 136.1, 132.8, 129.2, 129.0, 128.7, 128.4, 127.1, 125.5, 125.4, 87.4, 40.5, 34.0, 25.5, 22.1, 19.8, 19.5.
HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{22}H_{25}O_2$ 321.1854 ,found 321.1855.

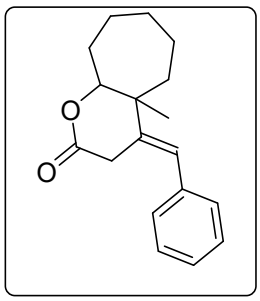
(E)-6-(benzo[d][1,3]dioxol-5-yl)-4-benzylidene-5,5-dimethyltetrahydro-2H-pyran-2-one (3o)



3o

White crystalline solid, m.p. 103-105^{o}C, 65 mg, yield: 65%; R_f = 0.28 (EtOAc/Petroleum ether 1:7).
IR (KBr) 3053, 2976, 2909, 1728, 1497, 1439, 1254, 1204, 1162, 1102, 1039, 1010, 937, 831, 769, 696 cm^{-1}
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 (t, *J* = 7.48 Hz, 2H), 7.26 (d, *J* = 14.65 Hz, 2H), 7.18 (d, *J* = 7.32 Hz, 2H), 6.85 – 6.82 (m, 1H), 6.82 – 6.73 (m, 2H), 6.53 (t, *J* = 2.10 Hz, 1H), 5.99 (s, 2H), 5.14 (s, 1H), 3.75 (dd, *J* = 19.26, 1.38 Hz, 1H), 3.62 (dd, *J* = 19.30, 2.41 Hz, 1H), 1.21 (s, 3H), 1.11 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 169.9, 147.7, 147.4, 138.0, 129.2, 128.7, 128.5, 127.1, 125.5, 121.8, 108.5, 107.6, 101.2, 87.1, 87.1, 40.6, 33.9, 25.5, 22.0.
HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{21}H_{21}O_4$ 337.1440, found 337.1438.

(E)-4-benzylidene-4a-methyloctahydrocyclohepta[b]pyran-2(3H)-one (3p)



3p

White crystalline solid, m.p. 150-152°C, 34 mg, yield: 34%; R_f = 0.35 (EtOAc/Petroleum ether 1:7).

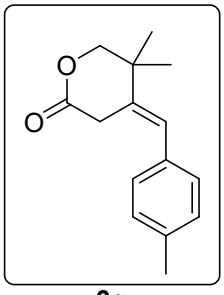
IR (KBr) 3073, 2973, 2934, 2876, 1742, 1651, 1598, 1507, 1485, 1411, 1383, 1301, 1220, 1161, 1046, 1103, 942, 878, 820, 780, 743 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 (t, *J* = 7.48 Hz, 2H), 7.25 (s, 1H), 7.15 (d, *J* = 7.38 Hz, 2H), 6.50 (s, 1H), 4.31 – 4.23 (m, 1H), 3.72 – 3.52 (m, 1H), 3.46 (dd, *J* = 18.57, 2.06 Hz, 1H), 2.02 – 1.88 (m, 3H), 1.86 – 1.67 (m, 3H), 1.59 (dd, *J* = 25.70, 13.10 Hz, 4H), 1.15 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 171.2, 170.8, δ 139.9, 138.8, 136.6, 136.6, 128.7, 128.7, 128.5, 128.4, 126.9, 126.5, 125.8, 124.4, 86.3, 85.2, 43.1, 42.7, 37.3, 37.1, 34.2, 33.8, 30.2, 28.6, 28.1, 27.5, 26.8, 24.0, 23.1, 22.1, 22.0, 20.4.

HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{18}H_{23}O_2$ 271.1698 ,found 271.1697.

(E)-5,5-dimethyl-4-(4-methylbenzylidene)tetrahydro-2H-pyran-2-one (3q)



3q

White crystalline solid, m.p. 85-89°C, 48 mg, yield: 70%; R_f = 0.27 (EtOAc/Petroleum ether 1:7).

IR (KBr) 3023, 2971, 2936, 1724, 1601, 1520, 1468, 1377, 1295, 1245, 1179, 1114, 1060, 1018, 887, 864, 831, 777, 752, 552 cm^{-1}

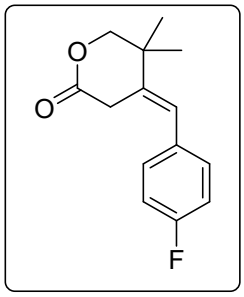
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.15 (d, *J* = 7.70 Hz, 2H), 7.05 (d, *J* = 7.75 Hz, 2H), 6.46 (s, 1H), 4.07 (s, 2H), 3.54 (d, *J* = 2.21 Hz, 2H), 2.34 (s, 3H), 1.26 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 170.7, 137.1, 136.8, 133.3, 129.1, 128.6, 125.1, 125.1, 77.0, 36.3, 33.9, 33.9, 25.5, 21.1.

HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{15}H_{19}O_2$ 231.1385 ; found 231.1387.

(E)-4-(4-fluorobenzylidene)-5,5-dimethyltetrahydro-2H-pyran-2-one

(3r)

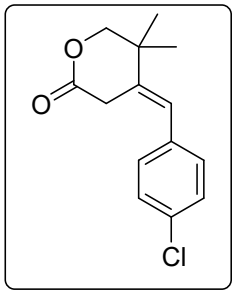


3r

Colorless liquid, 47 mg, yield: 68%; R_f = 0.26 (EtOAc/Petroleum ether 1:7).
IR (KBr) 3058, 3026, 2936, 2854, 1742, 1594, 1498, 1448, 1381, 1259, 1155, 1020, 868, 748, 702 cm^{-1}
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.17 – 7.06 (m, 2H), 7.03 (t, *J* = 8.60 Hz, 2H), 6.45 (s, 1H), 4.07 (s, 2H), 3.50 – 3.48 (m, 2H), 1.26 (s, 6H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 170.4, 160.5, 138.1, 132.1, 130.3, 130.2, 124.2, 115.5, 115.3, 76.9, 36.4, 33.8, 25.6.
^{19}F NMR (376 MHz, $CDCl_3$): δ -114.71.
HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{14}H_{16}FO_2$ 235.1134; found 235.1131.

(E)-4-(4-chlorobenzylidene)-5,5-dimethyltetrahydro-2H-pyran-2-one

(3s)

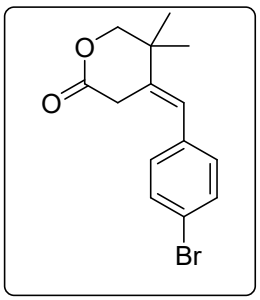


3s

White crystalline solid, m.p. 95-98°C, 45 mg, yield: 60%; R_f = 0.25 (EtOAc/Petroleum ether 1:7).
IR (KBr) 3073, 2967, 2884, 1745, 1485, 1404, 1377, 1306, 1239, 1156, 1093, 1050, 1014, 879, 816, 748, 604, 519 cm^{-1}
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30 (d, *J* = 8.22 Hz, 2H), 7.08 (d, *J* = 8.22 Hz, 2H), 6.43 (s, 1H), 4.07 (s, 2H), 3.49 (s, 2H), 1.26 (s, 6H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 170.3, 138.8, 134.6, 132.9, 130.0, 128.6, 124.1, 76.9, 36.5, 33.8, 25.5.
HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{14}H_{16}ClO_2$ 251.0838; found 251.0835.

(E)-4-(4-bromobenzylidene)-5,5-dimethyltetrahydro-2H-pyran-2-one

(3t)



3t

White crystalline solid, m.p. 110-114°C, 55 mg, yield: 63%; R_f = 0.28 (EtOAc/Petroleum ether 1:7).

IR (KBr) 3071, 2969, 2932, 2894, 1718, 1597, 1493, 1470, 1387, 1291, 1243, 1137, 1068, 1010, 860, 821, 769, 702, 498 cm^{-1}

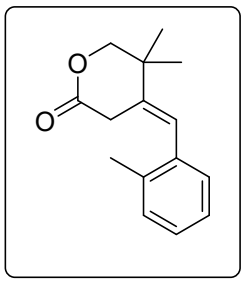
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 (d, *J* = 8.27 Hz, 2H), 7.02 (d, *J* = 8.13 Hz, 2H), 6.42 (s, 1H), 4.08 (s, 2H), 3.49 (s, 2H), 1.27 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 170.2, 138.9, 135.1, 131.6, 130.3, 124.2, 121.0, 76.8, 36.5, 33.8, 25.5.

HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{20}H_{21}BrO_2$ 295.0333 ; found 295.0339.

(E)-5,5-dimethyl-4-(2-methylbenzylidene)tetrahydro-2H-pyran-2-one

(3u)



3u

Colorless liquid, 34 mg, yield: 50%; R_f = 0.22 (EtOAc/Petroleum ether 1:7).

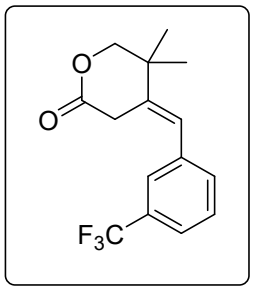
IR (KBr) 3063, 3021, 2965, 2930, 1747, 1462, 1372, 1272, 1231, 1154, 1058, 850, 754, 737, 554, 452 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.16 (d, *J* = 6.30 Hz, 3H), 7.03 – 6.95 (m, 1H), 6.50 (s, 1H), 4.08 (s, 2H), 3.34 – 3.31 (m, 2H), 2.20 (s, 3H), 1.30 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 170.9, 138.1, 136.2, 135.2, 130.1, 128.7, 127.4, 125.7, 124.8, 77.0, 36.3, 33.6, 25.8, 19.7.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{15}H_{18}O_2Na$ 253.1204; found 253.1208.

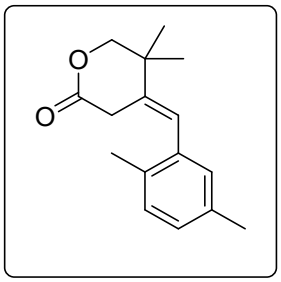
(E)-5,5-dimethyl-4-(3-(trifluoromethyl)benzylidene)tetrahydro-2H-pyran-2-one (3v)



3v

Colorless liquid, 42 mg, yield: 50%; R_f = 0.18 (EtOAc/Petroleum ether 1:7).
IR (KBr) 3061, 3019, 2969, 2926, 1758, 1462, 1379, 1272, 1235, 1150, 1110,1045, 946, 848, 756, 735, 562, 446 cm^{-1}
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 (dt, *J* = 15.34, 7.72 Hz, 2H), 7.39 (s, 1H), 7.34 (d, *J* = 7.38 Hz, 1H), 6.52 (s, 1H), 4.09 (s, 2H), 3.52 – 3.48 (m, 2H), 1.29 (s, 6H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 170.1, 140.0, 136.9, 131.8, 131.8, 128.9, 125.4, 125.4, 124.0, 123.9, 123.8, 123.8, 76.8, 36.5, 33.8, 25.5
^{19}F NMR (376 MHz, $CDCl_3$): δ -62.74.
HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{15}H_{16}F_3O_2$ 285.1102; found 285.1102.

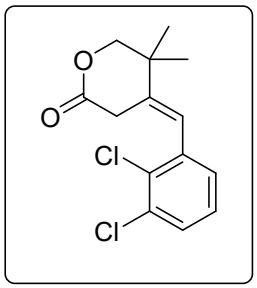
(E)-4-(2,5-dimethylbenzylidene)-5,5-dimethyltetrahydro-2H-pyran-2-one (3w)



3w

Colorless liquid, 29 mg, yield: 40%; R_f = 0.23 (EtOAc/Petroleum ether 1:7).
IR (KBr) 3013, 2974, 2926, 1718, 1479, 1383, 1283, 1241, 1056, 943, 864, 810, 769, 677, 592, 496 cm^{-1}
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.07 (d, *J* = 7.68 Hz, 1H), 6.98 (d, *J* = 7.78 Hz, 1H), 6.82 (s, 1H), 6.48 (s, 1H), 4.08 (s, 2H), 3.35 – 3.33 (m, 2H), 2.30 (s, 3H), 2.15 (s, 3H), 1.29 (s, 6H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 170.9, 137.8, 135.0, 132.9, 129.9, 129.2, 128.0, 124.8, 77.0, 36.2, 33.6, 25.7, 20.9, 19.1.
HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{16}H_{20}O_2Na$ 267.1361; found 267.1367.

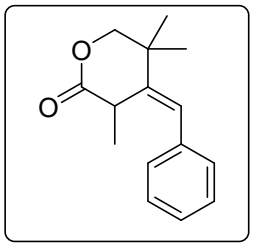
(E)-4-(2,3-dichlorobenzylidene)-5,5-dimethyltetrahydro-2H-pyran-2-one (3x)



3x

Colorless liquid, 56 mg, yield: 66%; R_f = 0.20 (EtOAc/Petroleum ether 1:7).
IR (KBr) 3076, 2969, 2934, 2884, 1716, 1476, 1418, 1381, 1237, 1133, 1064, 939, 860, 789, 746, 704, 498 cm^{-1}
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 (d, *J* = 8.05 Hz, 1H), 7.18 (t, *J* = 7.85 Hz, 1H), 7.03 (d, *J* = 7.60 Hz, 1H), 6.52 (s, 1H), 4.09 (s, 2H), 3.34 (s, 2H), 1.31 (s, 6H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 170.2, 140.5, 136.7, 133.5, 132.0, 129.4, 129.4, 128.3, 127.0, 123.0, 76.8, 36.6, 33.7, 25.5.
HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{14}H_{15}Cl_2O_2$ 285.0449; found 285.0452.

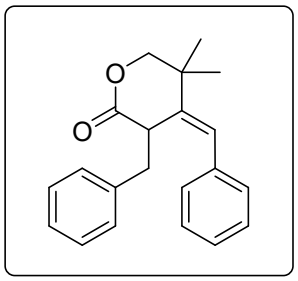
(E)-4-benzylidene-3,5,5-trimethyltetrahydro-2H-pyran-2-one (3y)



3y

Colorless liquid, 30 mg, yield: 44%; R_f = 0.32 (EtOAc/Petroleum ether 1:7).
IR (KBr) 3053, 2976, 2934, 2886, 1701, 1474, 1379, 1295, 1250, 1147, 1039, 989, 921, 846, 733, 689, 577,490 cm^{-1}
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.34 (t, *J* = 7.49 Hz, 2H), 7.25 (d, *J* = 7.28 Hz, 1H), 7.19 (d, *J* = 7.41 Hz, 2H), 6.49 (s, 1H), 4.29 (d, *J* = 11.26 Hz, 1H), 3.99 (d, *J* = 11.26 Hz, 1H), 3.86 (q, *J* = 6.82 Hz, 1H), 1.38 (d, *J* = 7.63 Hz, 3H), 1.27 (s, 6H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 174.1, 144.2, 136.4, 128.6, 128.2, 127.1, 125.5, 76.1, 38.0, 36.3, 27.4, 25.3, 19.1.
HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{15}H_{19}O_2$ 231.1385; found 231.1385.

(E)-*3-benzyl-4-benzylidene-5,5-dimethyltetrahydro-2H-pyran-2-one* (3z)



3z

White crystalline solid, m.p. 100-102°C, 45 mg, yield: 50%; R_f = 0.33 (EtOAc/Petroleum ether 1:7).

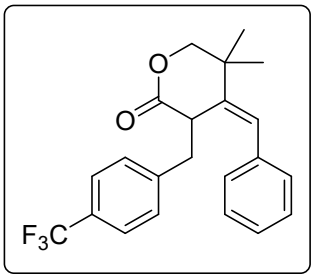
IR (KBr) 3065, 3028, 2967, 2930, 1739, 1606, 1491, 1454, 1374, 1252, 1145, 1064, 1031, 960, 921, 754, 702, 567, 500 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 (t, *J* = 7.38 Hz, 2H), 7.26 (d, *J* = 14.65 Hz, 2H), 7.23 – 7.16 (m, 5H), 6.93 (dd, *J* = 6.59, 2.77 Hz, 2H), 6.61 (s, 1H), 4.27 – 4.16 (m, 1H), 3.78 – 3.70 (m, 2H), 2.92 (dd, *J* = 6.74, 2.04 Hz, 2H), 1.26 (s, 3H), 1.18 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 172.4, 142.7, 137.2, 136.7, 129.2, 128.7, 128.4, 128.2, 127.1, 127.0, 126.4, 75.3, 45.6, 38.5, 36.0, 28.8, 24.5.

HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{21}H_{23}O_2$ 307.1698; found 307.1700.

(E)-4-benzylidene-5,5-dimethyl-3-(4-(trifluoromethyl)benzyl)tetra-hydro-2H-pyran-2-one (3aa)



3aa

White crystalline solid, m.p. 110-112°C, 37 mg, yield: 33%; R_f = 0.36 (EtOAc/Petroleum ether 1:7).

IR (KBr) 3019, 2976, 2928, 2874, 1735, 1620, 1422, 1322, 1287, 1170, 1127, 1068, 1043, 1018, 835, 769, 700, 635, 502 cm^{-1}

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.39 (d, *J* = 8.04 Hz, 2H), 7.36 – 7.26 (m, 3H), 7.10 (d, *J* = 6.97 Hz, 2H), 6.94 (d, *J* = 8.03 Hz, 2H), 6.62 (s, 1H), 4.27 – 4.18 (m, 1H), 4.03 (d, *J* = 11.44 Hz, 1H), 3.91 (d, *J* = 11.38 Hz, 1H), 2.95 (dd, *J* = 7.00, 3.50 Hz, 2H), 1.29 (s, 3H), 1.23 (s, 3H).

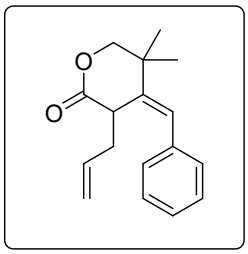
^{13}C NMR (101 MHz, $CDCl_3$): δ 172.0, 142.1, 141.3, 136.4, 129.4, 128.8, 128.1, 127.2, 127.0, 125.2, 125.2, 75.7, 45.1, 38.4, 36.1, 28.5, 24.7.

^{19}F NMR (376 MHz, $CDCl_3$): -62.53.

HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{22}H_{22}BF_3O_2$ 375.15719; found 375.1570.

(E)-3-allyl-4-benzylidene-5,5-dimethyltetrahydro-2H-pyran-2-one

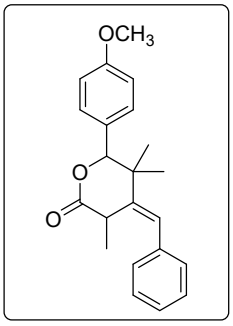
(3ab)



3ab

Colorless liquid, 38 mg, yield: 50%; R_f = 0.32 (EtOAc/Petroleum ether 1:7).
IR (KBr) 3073, 3055, 2980, 2928, 1724, 1599, 1443, 1368, 1291, 1135, 998, 918, 858, 741, 696, 639, 492 cm^{-1}
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.34 (t, *J* = 7.44 Hz, 2H), 7.24 (d, *J* = 7.44 Hz, 1H), 7.19 (d, *J* = 7.59 Hz, 2H), 6.56 (s, 1H), 5.67 (td, *J* = 17.16, 7.44 Hz, 1H), 5.04 – 4.95 (m, 2H), 4.39 – 4.33 (m, 1H), 3.95 (d, *J* = 11.42 Hz, 1H), 3.93 – 3.87 (m, 1H), 2.45 (dt, *J* = 14.03, 6.47 Hz, 2H), 1.30 (s, 3H), 1.27 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 172.2, 142.9, 136.4, 133.8, 128.6, 128.3, 127.1, 126.4, 117.8, 75.7, 44.1, 37.3, 36.2, 28.6, 25.2.
HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{17}H_{21}O_2$ 257.1541 ; found 257.1541.

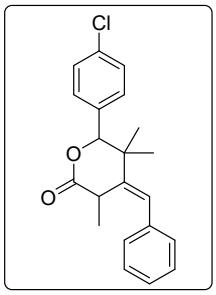
(E)-4-benzylidene-6-(4-methoxyphenyl)-3,5,5-trimethyltetrahydro-2H-pyran-2-one (3ac)



3ac

White crystalline solid, m.p. 145-148 °C, 55 mg, yield:55%; R_f = 0.25 (EtOAc/Petroleum ether 1:7).
IR (KBr) 3061, 3001, 2974, 2934, 2901, 2884, 1726, 1610, 1512, 1464, 1387, 1362, 1324, 1272, 1239, 1177, 1120, 1056, 1033, 889, 837, 748, 691, 552 cm^{-1}
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 (t, *J* = 7.47 Hz, 2H), 7.27 (d, *J* = 11.38 Hz, 2H), 7.24 – 7.20 (m, 3H), 6.90 (d, *J* = 8.62 Hz, 2H), 6.50 (s, 1H), 5.35 (s, 1H), 3.98 (q, *J* = 7.41 Hz, 1H), 3.83 (s, 3H), 1.48 (d, *J* = 7.62 Hz, 3H), 1.26 (s, 3H), 1.07 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 174.0, 144.1, 136.8, 129.2, 128.6, 128.2, 127.8, 127.1, 126.2, 113.2, 85.8, 55.3, 40.9, 38.2, 26.2, 23.6, 19.8.
HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{22}H_{25}O_3$ 337.1803; found 337.1800.

(E)-4-benzylidene-6-(4-chlorophenyl)-3,5,5-trimethyltetrahydro-2H-pyran-2-one (3ad)



3ad

White crystalline solid, m.p. 152-156°C, 51 mg, yield: 50%; R_f = 0.24 (EtOAc/Petroleum ether 1:7).

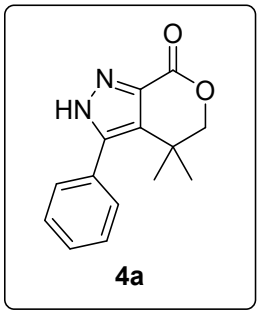
IR (KBr) 3057, 3028, 2974, 2934, 2878, 1739, 1599, 1491, 1385, 1281, 1260, 1093, 1054, 1012, 846, 766, 698, 637, 548, 506, 456 cm^{-1}

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.37 (d, *J* = 6.40 Hz, 2H), 7.35 (s, 2H), 7.28 (s, 3H), 7.20 (d, *J* = 7.49 Hz, 2H), 6.52 (s, 1H), 5.37 (s, 1H), 3.98 (q, *J* = 7.50 Hz, 1H), 1.48 (d, *J* = 7.61 Hz, 3H), 1.27 (s, 3H), 1.05 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 173.6, 143.7, 136.6, 134.4, 134.2, 129.4, 128.7, 128.2, 128.1, 127.2, 126.6, 85.3, 40.7, 38.2, 26.2, 23.5, 19.8

HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{21}H_{22}ClO_2$ 341.1308; found 341.1303.

4,4-dimethyl-3-phenyl-4,5-dihydropyrano[3,4-c]pyrazol-7(2H)-one (4a)



4a

White crystalline solid, m.p. 83-85°C, 81 mg, yield: 67%; R_f = 0.20 (EtOAc/Petroleum ether 1:7).

IR (KBr) 3282, 3061, 2980, 2936, 2876, 1735, 1489, 1462, 1441, 1370, 1283, 1250, 1137, 1056, 1014, 971, 769, 719, 696, 552 cm^{-1}

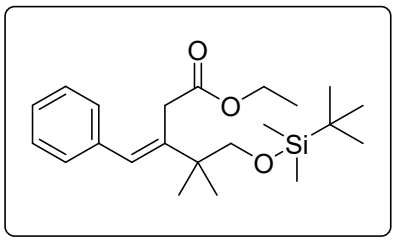
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.55 – 7.38 (m, 5H), 4.14 (s, 2H), 1.29 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 160.4, 130.5, 129.2, 129.1, 128.6, 128.1, 80.3, 32.1, 24.6.

HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{14}H_{15}N_2O_2$ 243.1133; found 243.1132.

ethyl 3-benzylidene-5-((tert-butyldimethylsilyl)oxy)-4,4-dimethyl-

pentanoate (5a)



5a

Colorless liquid, 90 mg, yield: 80%; R_f = 0.45 (EtOAc/Petroleum ether 1:15).
IR (KBr) 3061, 2963, 2938, 2863, 1730, 1470, 1370, 1250, 1154, 1077, 1020, 837, 775, 702, 662, 575 cm^{-1}
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.31 (d, *J* = 7.50 Hz, 1H), 7.26 (dd, *J* = 7.89, 4.21 Hz, 3H), 7.20 (t, *J* = 6.83 Hz, 1H), 6.67 (s, 1H), 4.12 (q, *J* = 7.13 Hz, 2H), 3.47 (s, 2H), 3.23 (s, 2H), 1.24 (t, *J* = 7.13 Hz, 3H), 1.13 (s, 6H), 0.90 (s, 9H), 0.03 (s, 6H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 172.7, 140.4, 138.5, 129.2, 128.5, 128.1, 126.4, 71.3, 60.5, 41.8, 35.0, 25.9, 24.2, 18.2, 14.1, -5.5.
HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{22}H_{37}O_3Si$ 377.2512; found 377.2504

9. X-Ray Analysis

9.1 X-Ray Analysis for 3b

Single crystals of $C_{17}H_{20}O_2$ **3b** were grown from ethyl acetate and PE. A suitable crystal was selected and collected on a SuperNova, Dual, Cu at zero, AtlasS2 diffractometer. The crystal was kept at 149.99(10) K during data collection. The data were collected and processed using CrysAlisPro. The structures were solved by direct methods using Olex2 software with the SHELXT structure solution program via intrinsic phasing algorithm, and the non-hydrogen atoms were located from the trial structure and then refined anisotropically with SHELXL-2018 using a full-matrix least squares procedure based on F^2. The weighted *R* factor, *wR* and goodness-of-fit *S* values were obtained based on F^2. The hydrogen atom positions were fixed geometrically at the calculated distances and allowed to ride on their parent atoms.

Crystallographic data for the structure reported in this paper have been deposited at the Cambridge Crystallographic Data Center and allocated with the deposition numbers: CCDC 2167329 for compounds **3b**

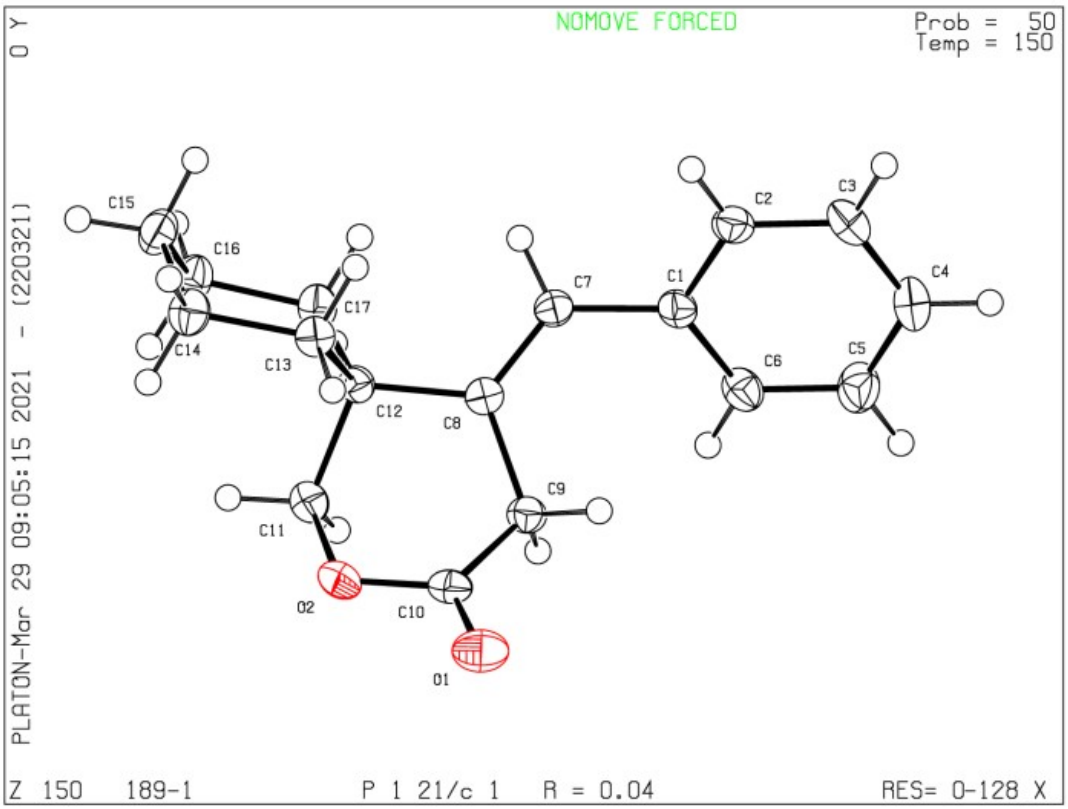


Figure S1. ORTEP Drawing of **3b** (The ellipsoids are shown at 50% probability levels)

Table 1 Crystal data and structure refinement for 3b.

Identification code	3b
Empirical formula	$C_{17}H_{20}O_2$
Formula weight	256.33
Temperature/K	149.99(10)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	10.8532(7)
b/Å	15.9018(9)
c/Å	8.3007(5)
α/°	90
β/°	108.936(7)
γ/°	90
Volume/Å^3	1355.05(16)
Z	4
ρ_{calc}g/cm^3	1.256
μ/mm^{-1}	0.081
F(000)	552.0
Crystal size/mm^3	0.14 × 0.13 × 0.12

Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	3.968 to 49.998
Index ranges	$-12 \leq h \leq 12$, $-18 \leq k \leq 18$, $-9 \leq l \leq 6$
Reflections collected	5432
Independent reflections	2378 [R_{int} = 0.0212, R_{sigma} = 0.0313]
Data/restraints/parameters	2378/0/172
Goodness-of-fit on F^2	1.079
Final R indexes [I>=2σ (I)]	R_1 = 0.0409, wR_2 = 0.0923
Final R indexes [all data]	R_1 = 0.0491, wR_2 = 0.0977
Largest diff. peak/hole / e $Å^{-3}$	0.17/-0.26

Table 2 Fractional Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters (Å²×10³) for 3b. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
O1	5663.4(11)	3548.7(7)	2328.5(14)	36.5(3)
O2	7212.4(10)	3594.4(7)	4811.9(13)	28.7(3)
C1	2843.6(14)	3510.1(9)	6158.8(17)	21.4(3)
C2	1846.1(14)	4074.3(10)	6105.8(18)	25.0(3)
C3	554.2(14)	3853.9(10)	5366(2)	28.7(4)
C4	222.9(15)	3068.5(10)	4653(2)	32.5(4)
C5	1197.6(15)	2499.6(10)	4701(2)	32.7(4)
C6	2493.3(14)	2712.3(9)	5460.9(19)	26.3(4)
C7	4212.4(13)	3770.3(9)	6960.4(18)	21.7(3)
C8	5218.2(13)	3623.4(8)	6411.1(17)	19.0(3)
C9	5065.4(14)	3160.5(9)	4764.9(18)	22.3(3)
C10	5966.3(15)	3454.3(9)	3847.2(19)	24.3(3)
C11	7513.2(14)	3460.3(10)	6625.4(19)	25.5(4)
C12	6592.4(13)	3948.3(9)	7335.6(17)	19.4(3)
C13	6650.9(14)	4901.3(9)	7004.3(18)	22.3(3)
C14	7952.4(15)	5302.0(9)	7994.1(19)	26.8(4)
C15	8266.9(15)	5143.2(10)	9893.9(19)	29.0(4)
C16	8288.6(15)	4208.3(10)	10282.7(19)	27.5(4)
C17	7007.2(14)	3787.7(9)	9267.8(18)	24.0(3)

Table 3 Anisotropic Displacement Parameters (Å²×10³) for 3b. 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	47.2(7)	43.8(7)	23.1(6)	0.5(5)	17.9(5)	1.6(6)
O2	26.1(6)	36.7(6)	28.3(6)	-3.3(5)	15.7(5)	-0.6(5)
C1	22.3(8)	26.3(8)	17.5(7)	2.4(6)	8.9(6)	-1.2(6)

Table 3 Anisotropic Displacement Parameters ($Å^2×10^3$) for 3b. 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}
C2	26.9(8)	26.0(8)	25.0(8)	-2.5(6)	12.4(6)	-1.0(7)
C3	21.8(8)	33.5(9)	33.3(9)	5.5(7)	12.5(7)	5.4(7)
C4	19.9(8)	37.4(10)	37.1(9)	2.7(8)	5.1(7)	-3.7(7)
C5	29.2(9)	26.7(9)	40.7(10)	-2.1(7)	9.4(7)	-5.4(7)
C6	23.6(8)	24.0(8)	32.7(9)	2.1(7)	11.2(7)	2.2(7)
C7	22.6(8)	24.8(8)	18.0(7)	-0.9(6)	6.8(6)	-0.6(6)
C8	21.8(8)	17.2(7)	17.7(7)	2.9(6)	6.2(6)	1.1(6)
C9	22.3(8)	24.2(8)	20.7(7)	-0.9(6)	7.7(6)	1.2(6)
C10	28.2(8)	22.2(8)	25.2(8)	-3.4(6)	12.5(7)	2.9(7)
C11	20.9(8)	28.8(8)	26.7(8)	-1.2(7)	7.5(6)	1.3(7)
C12	19.1(7)	20.2(7)	19.3(7)	1.3(6)	6.8(6)	-0.2(6)
C13	23.3(8)	22.1(8)	21.0(7)	2.8(6)	6.6(6)	0.6(6)
C14	28.0(8)	21.1(8)	30.2(9)	2.5(6)	8.2(7)	-3.0(7)
C15	26.6(8)	31.2(9)	25.7(8)	-4.7(7)	3.8(7)	-5.5(7)
C16	27.6(8)	31.0(9)	20.6(8)	3.2(7)	3.1(6)	-3.8(7)
C17	23.3(8)	25.9(8)	22.1(8)	5.2(6)	6.2(6)	-2.5(7)

Table 4 Bond Lengths for 3b.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	C10	1.2045(18)	C8	C9	1.5131(19)
O2	C10	1.3479(18)	C8	C12	1.5289(19)
O2	C11	1.4488(18)	C9	C10	1.496(2)
C1	C2	1.396(2)	C11	C12	1.527(2)
C1	C6	1.395(2)	C12	C13	1.5451(19)
C1	C7	1.476(2)	C12	C17	1.5400(19)
C2	C3	1.381(2)	C13	C14	1.524(2)
C3	C4	1.379(2)	C14	C15	1.522(2)
C4	C5	1.383(2)	C15	C16	1.520(2)
C5	C6	1.383(2)	C16	C17	1.527(2)
C7	C8	1.333(2)			

Table 5 Bond Angles for 3b.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C10	O2	C11	115.93(11)	O1	C10	C9	124.77(14)
C2	C1	C7	119.40(13)	O2	C10	C9	116.40(12)
C6	C1	C2	117.86(13)	O2	C11	C12	111.80(11)
C6	C1	C7	122.73(13)	C8	C12	C13	109.38(11)
C3	C2	C1	121.08(14)	C8	C12	C17	112.00(11)

Table 5 Bond Angles for 3b.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C4	C3	C2	120.42(15)	C11	C12	C8	106.77(11)
C3	C4	C5	119.33(14)	C11	C12	C13	111.10(12)
C4	C5	C6	120.54(15)	C11	C12	C17	108.12(12)
C5	C6	C1	120.75(14)	C17	C12	C13	109.45(11)
C8	C7	C1	127.79(13)	C14	C13	C12	113.48(11)
C7	C8	C9	122.16(13)	C15	C14	C13	110.24(12)
C7	C8	C12	122.88(13)	C16	C15	C14	111.41(12)
C9	C8	C12	114.89(12)	C15	C16	C17	111.27(12)
C10	C9	C8	114.19(12)	C16	C17	C12	114.09(12)
O1	C10	O2	118.80(14)				

Table 6 Torsion Angles for 3b.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
O2	C11	C12	C8	60.84(15)	C8	C9	C10	O1	-138.78(15)
O2	C11	C12	C13	-58.35(15)	C8	C9	C10	O2	43.38(18)
O2	C11	C12	C17	-178.48(11)	C8	C12	C13	C14	175.14(12)
C1	C2	C3	C4	-0.3(2)	C8	C12	C17	C16	-171.77(12)
C1	C7	C8	C9	1.7(2)	C9	C8	C12	C11	-18.47(16)
C1	C7	C8	C12	178.29(13)	C9	C8	C12	C13	101.84(14)
C2	C1	C6	C5	1.7(2)	C9	C8	C12	C17	-136.64(12)
C2	C1	C7	C8	-138.28(16)	C10	O2	C11	C12	-52.76(16)
C2	C3	C4	C5	0.6(2)	C11	O2	C10	O1	-179.34(13)
C3	C4	C5	C6	0.3(2)	C11	O2	C10	C9	-1.36(18)
C4	C5	C6	C1	-1.5(2)	C11	C12	C13	C14	-67.24(15)
C6	C1	C2	C3	-0.9(2)	C11	C12	C17	C16	70.86(16)
C6	C1	C7	C8	42.6(2)	C12	C8	C9	C10	-30.26(17)
C7	C1	C2	C3	179.96(13)	C12	C13	C14	C15	-56.37(17)
C7	C1	C6	C5	-179.10(14)	C13	C12	C17	C16	-50.29(16)
C7	C8	C9	C10	146.56(14)	C13	C14	C15	C16	57.21(17)
C7	C8	C12	C11	164.74(13)	C14	C15	C16	C17	-55.67(17)
C7	C8	C12	C13	-74.96(17)	C15	C16	C17	C12	53.12(18)
C7	C8	C12	C17	46.56(19)	C17	C12	C13	C14	52.09(16)

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

Atom	*x*	*y*	*z*	U(eq)
H2	2054.83	4607.33	6576.38	30
H3	-96.62	4237.74	5348.47	34
H4	-647.3	2922.84	4145.63	39

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

Atom	*x*	*y*	*z*	U(eq)
H5	980.43	1969.72	4217.95	39
H6	3138.04	2318.98	5507.19	32
H7	4394.99	4072.87	7969.65	26
H9A	5214.67	2565.93	5012.9	27
H9B	4174.94	3225.51	4016.77	27
H11A	8402.29	3636.03	7210.33	31
H11B	7449.24	2865.04	6841.04	31
H13A	6486.15	4990.85	5796.58	27
H13B	5964.28	5180.93	7310.93	27
H14A	8635.17	5066.94	7613.07	32
H14B	7914.11	5902.63	7779.25	32
H15A	9109.44	5385.85	10503.92	35
H15B	7619.11	5417.52	10287.89	35
H16A	8439.64	4129.38	11490.39	33
H16B	8999.79	3944.13	10004.92	33
H17A	6325.34	3989.5	9689.06	29
H17B	7089.18	3186.15	9467.54	29

9.2 X-Ray Analysis for 3ad

Single crystals of $C_{21}H_{21}ClO_2$ **3ad** were grown from ethyl acetate and PE. A suitable crystal was selected and collected on a SuperNova, Dual, Cu at zero, AtlasS2 diffractometer. The crystal was kept at 149.99(10) K during data collection. The data were collected and processed using CrysAlisPro. The structures were solved by direct methods using Olex2 software with the SHELXT structure solution program via intrinsic phasing algorithm, and the non-hydrogen atoms were located from the trial structure and then refined anisotropically with SHELXL-2018 using a full-matrix least squares procedure based on F^2. The weighted *R* factor, *wR* and goodness-of-fit *S* values were obtained based on F^2. The hydrogen atom positions were fixed geometrically at the calculated distances and allowed to ride on their parent atoms.

Crystallographic data for the structure reported in this paper have been deposited at the Cambridge Crystallographic Data Center and allocated with the deposition numbers: CCDC 2167331 for compounds **3ad**

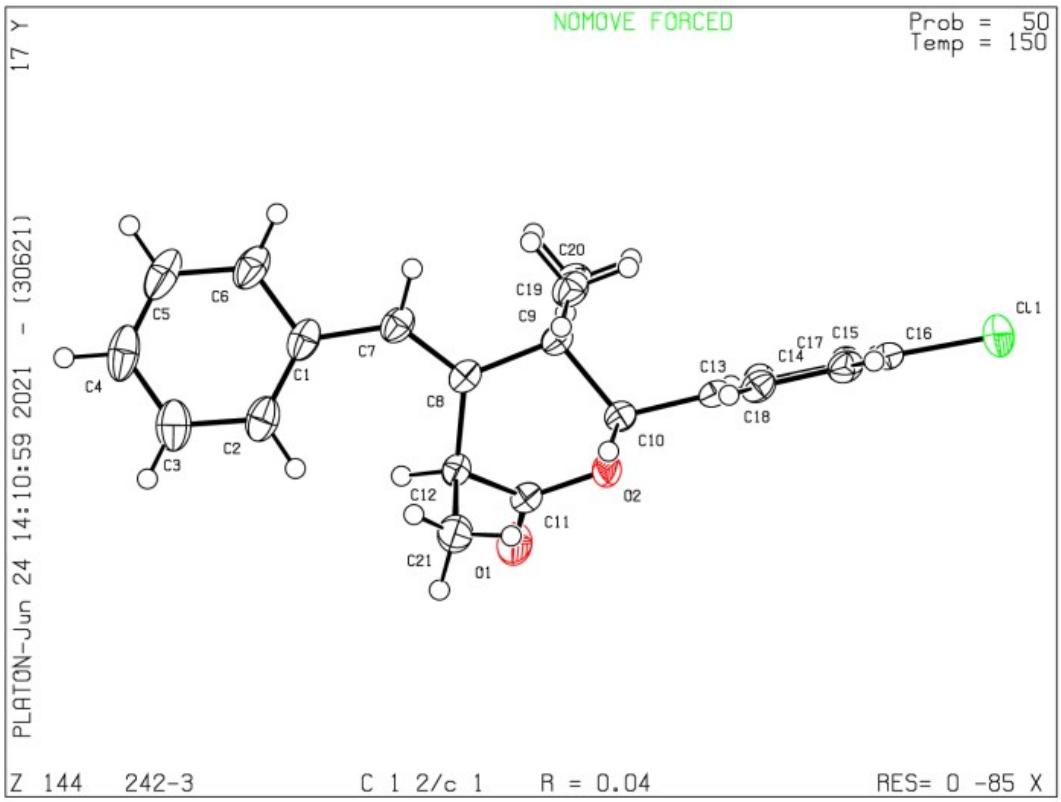


Figure S2. ORTEP Drawing of **3ad** (The ellipsoids are shown at 50% probability levels)

Table 1 Crystal data and structure refinement for 3ad.

Identification code	3ad
Empirical formula	$C_{21}H_{21}ClO_2$
Formula weight	340.83
Temperature/K	149.99(10)
Crystal system	monoclinic
Space group	C2/c
a/Å	10.2977(7)
b/Å	17.5607(12)
c/Å	19.3729(13)
α/°	90
β/°	96.121(6)
γ/°	90
Volume/Å^3	3483.3(4)
Z	8
ρ_{calc}g/cm^3	1.300
μ/mm^{-1}	0.229
F(000)	1440.0
Crystal size/mm^3	0.15 × 0.13 × 0.12
Radiation	Mo Kα (λ = 0.71073)

2Θ range for data collection/°	4.23 to 49.99
Index ranges	$-12 \le h \le 12$, $-20 \le k \le 20$, $-23 \le l \le 17$
Reflections collected	7517
Independent reflections	3066 [R_{int} = 0.0221, R_{sigma} = 0.0284]
Data/restraints/parameters	3066/0/220
Goodness-of-fit on F^2	1.023
Final R indexes [I>=2σ (I)]	R_1 = 0.0372, wR_2 = 0.0879
Final R indexes [all data]	R_1 = 0.0444, wR_2 = 0.0920
Largest diff. peak/hole / e Å^{-3}	0.18/-0.23

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

Atom	*x*	*y*	*z*	U(eq)
Cl1	1655.9(4)	5239.9(3)	2707.6(2)	40.27(16)
O1	8497.0(12)	2475.6(7)	3392.3(6)	42.0(3)
O2	7173.1(10)	3432.2(6)	3522.1(5)	27.5(3)
C1	10435.3(17)	3413.9(9)	5808.9(8)	30.4(4)
C2	11559.2(17)	3319.0(10)	5475.6(9)	36.0(4)
C3	12714.4(19)	3059.3(11)	5832.2(11)	42.6(5)
C4	12776(2)	2883.1(10)	6527.5(10)	43.7(5)
C5	11681(2)	2971.5(11)	6867.4(10)	46.2(5)
C6	10528(2)	3236.4(10)	6515.3(9)	40.1(5)
C7	9172.6(16)	3710.6(9)	5490.3(8)	28.9(4)
C8	8622.0(15)	3735.1(9)	4833.6(8)	23.0(3)
C9	7230.8(15)	4048.0(9)	4666.8(8)	23.3(3)
C10	6972.2(15)	4149.7(9)	3873.0(8)	22.6(3)
C11	8301.1(15)	3057.8(10)	3689.0(8)	27.0(4)
C12	9273.3(15)	3413.3(9)	4232.5(8)	25.9(4)
C13	5625.7(15)	4416.9(9)	3598.8(7)	23.1(3)
C14	4617.4(15)	3904.8(10)	3422.2(8)	27.6(4)
C15	3396.1(15)	4157.0(10)	3151.9(8)	28.3(4)
C16	3184.5(15)	4926.5(10)	3068.5(8)	26.9(4)
C17	4159.7(16)	5452.9(10)	3245.1(8)	28.8(4)
C18	5380.6(16)	5188.3(9)	3503.9(8)	26.7(4)
C19	7090.9(18)	4829.4(10)	5000.3(9)	31.6(4)
C20	6247.5(16)	3488.7(10)	4930.0(9)	32.1(4)
C21	10094.7(17)	3999.3(12)	3870.2(9)	39.0(5)

Table 3 Anisotropic Displacement Parameters (Å^2×10^3) for 3ad. 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}
Cl1	31.5(3)	46.0(3)	42.1(3)	6.2(2)	-1.78(18)	12.0(2)
O1	45.9(8)	42.5(8)	34.9(7)	-16.2(6)	-8.2(6)	16.0(6)
O2	26.0(6)	31.3(7)	23.9(6)	-6.7(5)	-3.4(4)	5.0(5)
C1	40.7(10)	20.3(9)	27.5(9)	-4.2(7)	-9.2(7)	-1.3(8)
C2	37.4(10)	32.1(10)	35.7(10)	2.8(8)	-9.4(8)	-7.1(8)
C3	36.5(10)	34.3(11)	53.5(12)	-0.1(9)	-12.1(8)	-4.8(9)
C4	50.6(12)	23.9(10)	50.1(12)	-3.5(8)	-24.9(10)	2.3(9)
C5	71.5(14)	30.4(10)	31.2(10)	-4.5(8)	-19.5(9)	10.6(10)
C6	57.9(12)	33.2(10)	26.2(9)	-6.0(8)	-9.4(8)	9.8(9)
C7	37.8(9)	24.0(9)	23.9(8)	-1.8(7)	-1.8(7)	1.2(8)
C8	29.1(8)	17.7(8)	21.7(8)	1.0(6)	0.1(6)	-4.6(7)
C9	27.9(8)	21.8(8)	20.0(8)	-0.4(6)	1.3(6)	-1.2(7)
C10	25.5(8)	20.5(8)	21.6(8)	-2.0(6)	1.9(6)	-1.6(7)
C11	28.3(9)	31.9(10)	20.6(8)	-0.3(7)	1.6(6)	2.2(8)
C12	24.2(8)	31.3(9)	21.3(8)	1.3(7)	-1.1(6)	0.3(7)
C13	27.4(8)	26.2(9)	15.9(7)	0.1(6)	3.5(6)	-0.2(7)
C14	29.8(9)	23.2(8)	29.3(9)	-0.3(7)	1.1(7)	1.6(7)
C15	25.4(8)	31.1(10)	28.2(9)	-2.0(7)	2.1(6)	-1.1(7)
C16	27.0(9)	35.7(10)	18.5(8)	2.1(7)	4.9(6)	6.1(8)
C17	38.0(9)	24.5(9)	24.6(8)	5.0(7)	6.1(7)	4.9(8)
C18	31.5(9)	26.0(9)	22.7(8)	2.9(7)	3.0(6)	-3.5(7)
C19	40.7(10)	28.8(10)	24.7(9)	-4.0(7)	0.0(7)	3.3(8)
C20	34.5(9)	34.4(10)	27.5(9)	5.9(7)	4.7(7)	-4.7(8)
C21	28.4(9)	53.8(12)	34.8(10)	11.7(9)	3.2(7)	-4.2(9)

Table 4 Bond Lengths for 3ad.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cl1	C16	1.7421(16)	C8	C12	1.514(2)
O1	C11	1.200(2)	C9	C10	1.543(2)
O2	C10	1.4569(18)	C9	C19	1.530(2)
O2	C11	1.3439(19)	C9	C20	1.536(2)
C1	C2	1.394(3)	C10	C13	1.506(2)
C1	C6	1.397(2)	C11	C12	1.509(2)
C1	C7	1.474(2)	C12	C21	1.547(2)
C2	C3	1.387(2)	C13	C14	1.389(2)
C3	C4	1.377(3)	C13	C18	1.387(2)
C4	C5	1.374(3)	C14	C15	1.383(2)
C5	C6	1.385(3)	C15	C16	1.375(2)
C7	C8	1.337(2)	C16	C17	1.381(2)

Table 4 Bond Lengths for 3ad.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C8	C9	1.536(2)	C17	C18	1.383(2)

Table 5 Bond Angles for 3ad.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C11	O2	C10	118.23(12)	O2	C10	C9	110.30(12)
C2	C1	C6	116.97(16)	O2	C10	C13	106.02(12)
C2	C1	C7	125.96(15)	C13	C10	C9	116.24(12)
C6	C1	C7	117.03(16)	O1	C11	O2	119.11(15)
C3	C2	C1	121.24(17)	O1	C11	C12	123.63(15)
C4	C3	C2	120.55(19)	O2	C11	C12	117.24(14)
C5	C4	C3	119.29(17)	C8	C12	C21	114.16(14)
C4	C5	C6	120.39(18)	C11	C12	C8	112.08(13)
C5	C6	C1	121.54(19)	C11	C12	C21	108.23(13)
C8	C7	C1	132.50(16)	C14	C13	C10	121.43(14)
C7	C8	C9	120.19(14)	C18	C13	C10	119.92(14)
C7	C8	C12	122.83(15)	C18	C13	C14	118.63(15)
C12	C8	C9	116.84(12)	C15	C14	C13	120.80(16)
C8	C9	C10	107.99(12)	C16	C15	C14	119.04(16)
C8	C9	C20	109.54(13)	C15	C16	Cl1	118.85(13)
C19	C9	C8	111.08(13)	C15	C16	C17	121.78(15)
C19	C9	C10	107.64(13)	C17	C16	Cl1	119.34(13)
C19	C9	C20	109.76(13)	C16	C17	C18	118.28(16)
C20	C9	C10	110.80(13)	C17	C18	C13	121.45(15)

Table 6 Torsion Angles for 3ad.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
Cl1	C16	C17	C18	-177.35(12)	C8	C9	C10	C13	177.06(13)
O1	C11	C12	C8	-139.75(17)	C9	C8	C12	C11	-31.77(19)
O1	C11	C12	C21	93.5(2)	C9	C8	C12	C21	91.73(16)
O2	C10	C13	C14	34.07(18)	C9	C10	C13	C14	-88.89(17)
O2	C10	C13	C18	-144.50(14)	C9	C10	C13	C18	92.54(17)
O2	C11	C12	C8	42.03(19)	C10	O2	C11	O1	-178.12(14)
O2	C11	C12	C21	-84.74(17)	C10	O2	C11	C12	0.2(2)
C1	C2	C3	C4	0.4(3)	C10	C13	C14	C15	-178.08(14)
C1	C7	C8	C9	176.52(16)	C10	C13	C18	C17	179.20(14)
C1	C7	C8	C12	1.0(3)	C11	O2	C10	C9	-51.59(17)
C2	C1	C6	C5	-0.6(3)	C11	O2	C10	C13	-178.22(12)
C2	C1	C7	C8	24.1(3)	C12	C8	C9	C10	-15.06(18)

Table 6 Torsion Angles for 3ad.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C2	C3	C4	C5	-0.4(3)	C12	C8	C9	C19	-132.88(14)
C3	C4	C5	C6	-0.1(3)	C12	C8	C9	C20	105.70(15)
C4	C5	C6	C1	0.6(3)	C13	C14	C15	C16	-0.9(2)
C6	C1	C2	C3	0.0(3)	C14	C13	C18	C17	0.6(2)
C6	C1	C7	C8	-158.25(18)	C14	C15	C16	Cl1	178.41(12)
C7	C1	C2	C3	177.67(16)	C14	C15	C16	C17	0.2(2)
C7	C1	C6	C5	-178.41(16)	C15	C16	C17	C18	0.8(2)
C7	C8	C9	C10	169.11(14)	C16	C17	C18	C13	-1.2(2)
C7	C8	C9	C19	51.29(19)	C18	C13	C14	C15	0.5(2)
C7	C8	C9	C20	-70.13(18)	C19	C9	C10	O2	176.37(12)
C7	C8	C12	C11	143.94(16)	C19	C9	C10	C13	-62.93(17)
C7	C8	C12	C21	-92.56(19)	C20	C9	C10	O2	-63.60(16)
C8	C9	C10	O2	56.37(15)	C20	C9	C10	C13	57.09(18)

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

Atom	*x*	*y*	*z*	U(eq)
H2	11534.2	3431.82	5005.33	43
H3	13453.6	3003.73	5599.7	51
H4	13549.8	2706.14	6764.48	52
H5	11713.78	2852.78	7336.78	55
H6	9798.97	3297.42	6754.73	48
H7	8658.91	3921.96	5807.6	35
H10	7604.87	4519.2	3730.12	27
H12	9867.29	3009.16	4418.22	31
H14	4765.35	3385.93	3486.38	33
H15	2727.26	3811.41	3028.24	34
H17	3999.73	5971.92	3191.54	35
H18	6051.87	5535.47	3616.62	32
H19A	7272.17	4785.93	5495.17	47
H19B	6216.32	5013.36	4886.78	47
H19C	7696.42	5179.18	4828.22	47
H20A	6329.2	3001.65	4713.85	48
H20B	5377.18	3679.2	4816.23	48
H20C	6421.73	3435.88	5424.43	48
H21A	9523.97	4361	3620.91	59
H21B	10596.18	3739.97	3552.09	59
H21C	10673.59	4260.39	4212.69	59

9.3 X-Ray Analysis for 4a

Single crystals of $C_{14}H_{14}N_2O_2$ **4a** were grown from ethyl acetate and PE. A suitable crystal was selected and collected on a SuperNova, Dual, Cu at zero, AtlasS2 diffractometer. The crystal was kept at 179.99(10) K during data collection. The data were collected and processed using CrysAlisPro. The structures were solved by direct methods using Olex2 software with the SHELXT structure solution program via intrinsic phasing algorithm, and the non-hydrogen atoms were located from the trial structure and then refined anisotropically with SHELXL-2018 using a full-matrix least squares procedure based on F^2. The weighted R factor, wR and goodness-of-fit S values were obtained based on F^2. The hydrogen atom positions were fixed geometrically at the calculated distances and allowed to ride on their parent atoms.

Crystallographic data for the structure reported in this paper have been deposited at the Cambridge Crystallographic Data Center and allocated with the deposition numbers: CCDC 2167332 for compounds **4a**

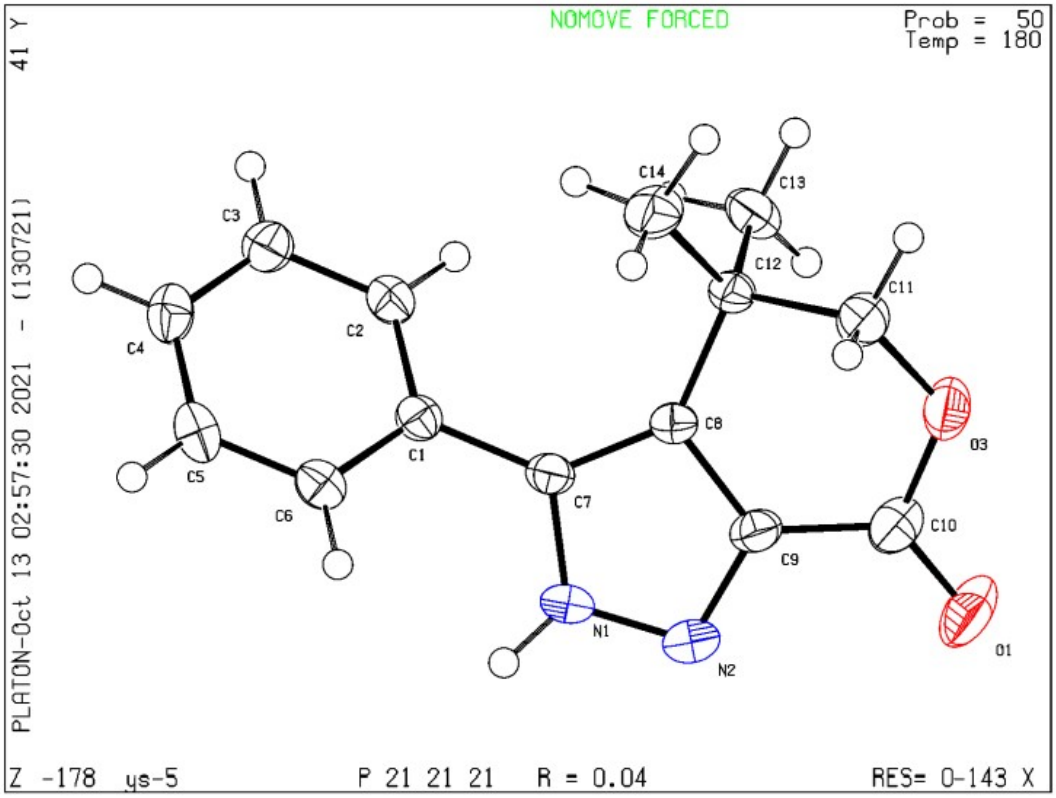


Figure S3. ORTEP Drawing of **4a** (The ellipsoids are shown at 50% probability levels)

Table 1 Crystal data and structure refinement for 4a.

Identification code	4a
Empirical formula	$C_{14}H_{14}N_2O_2$
Formula weight	242.27
Temperature/K	179.99(10)
Crystal system	orthorhombic

Space group	$P2_12_12_1$
a/Å	6.4356(3)
b/Å	12.2960(5)
c/Å	15.5108(7)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1227.40(9)
Z	4
ρ_{calc}g/cm^3	1.311
μ/mm^{-1}	0.724
F(000)	512.0
Crystal size/mm^3	0.14 × 0.1 × 0.08
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	9.178 to 147.64
Index ranges	$-7 \le h \le 4$, $-15 \le k \le 6$, $-13 \le l \le 18$
Reflections collected	3039
Independent reflections	2152 [R_{int} = 0.0281, R_{sigma} = 0.0462]
Data/restraints/parameters	2152/0/169
Goodness-of-fit on F^2	1.092
Final R indexes [I>=2σ (I)]	R_1 = 0.0415, wR_2 = 0.1058
Final R indexes [all data]	R_1 = 0.0465, wR_2 = 0.1106
Largest diff. peak/hole / e Å^{-3}	0.15/-0.23
Flack parameter	0.0(3)

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

Atom	*x*	*y*	*z*	U(eq)
O1	137(4)	4444(2)	4399.8(17)	51.0(7)
O3	1222(3)	5969.9(18)	5020.4(15)	38.7(5)
N1	5192(4)	3143(2)	5690.6(17)	34.9(6)
N2	3644(4)	3325(2)	5135.7(18)	37.2(6)
C1	7369(4)	3947(2)	6835.8(18)	23.6(5)
C2	7139(4)	4394(2)	7657.7(18)	27.0(6)
C3	8748(5)	4344(2)	8248.4(19)	31.2(6)
C4	10585(5)	3811(2)	8030(2)	31.8(6)
C5	10801(4)	3342(2)	7224(2)	29.9(6)
C6	9205(4)	3406(2)	6629.0(19)	26.6(6)
C7	5684(4)	4018(2)	6195.9(18)	24.2(5)
C8	4331(4)	4835(2)	5945.0(17)	21.6(5)

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

Atom	*x*	*y*	*z*	U(eq)
C9	3127(4)	4360(2)	5290.9(18)	27.5(6)
C10	1409(5)	4885(2)	4857(2)	33.7(7)
C11	3032(5)	6533(2)	5378(2)	34.6(7)
C12	3967(4)	6007(2)	6183.4(17)	23.7(5)
C13	2444(5)	6120(2)	6939(2)	33.7(7)
C14	5978(5)	6628(2)	6376(2)	36.4(7)

Table 3 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for 4a. 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	51.1(14)	50.4(14)	51.4(14)	7.8(13)	-28.4(12)	-16.7(12)
O3	37.3(11)	35.8(11)	42.9(12)	5.8(10)	-15.6(10)	0.2(9)
N1	41.8(15)	25.8(11)	37.0(14)	-14.0(11)	-7.7(11)	8.2(11)
N2	43.8(14)	31.9(13)	36.0(14)	-12.9(12)	-9.3(12)	2.4(11)
C1	26.8(13)	19.1(11)	24.8(13)	2.2(11)	-0.3(11)	-0.8(10)
C2	25.7(12)	25.6(12)	29.6(14)	-1.0(12)	1.4(11)	3.5(11)
C3	37.5(14)	30.5(14)	25.7(13)	0.3(12)	-2.2(12)	3.0(12)
C4	30.5(14)	32.7(14)	32.1(15)	7.7(13)	-5.2(12)	0.8(12)
C5	23.9(13)	29.3(13)	36.5(15)	8.6(13)	3.4(12)	4.7(11)
C6	28.1(13)	23.9(12)	27.9(14)	1.9(11)	4.4(11)	1.1(11)
C7	25.2(12)	21.3(11)	26.2(13)	-4.7(11)	1.0(11)	0.9(10)
C8	22.6(12)	20.3(11)	21.9(12)	-2.1(10)	1.4(10)	-2.1(10)
C9	30.5(14)	25.9(12)	26.2(14)	-5.6(12)	-3.2(11)	-3.1(11)
C10	37.8(15)	33.5(14)	29.7(15)	3.9(13)	-7.0(13)	-8.0(12)
C11	42.7(16)	25.3(12)	35.7(16)	3.5(12)	-9.6(14)	-3.2(13)
C12	28.0(13)	17.9(11)	25.3(13)	-1.0(10)	-2.5(11)	-0.9(10)
C13	39.9(16)	26.5(12)	34.6(16)	-2.0(13)	3.9(13)	8.8(12)
C14	42.3(17)	24.4(14)	42.5(17)	0.7(13)	-8.5(14)	-9.6(13)

Table 4 Bond Lengths for 4a.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	C10	1.211(4)	C3	C4	1.393(4)
O3	C10	1.364(4)	C4	C5	1.384(4)
O3	C11	1.465(4)	C5	C6	1.384(4)
N1	N2	1.336(4)	C7	C8	1.385(4)

Table 4 Bond Lengths for 4a.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
N1	C7	1.368(4)	C8	C9	1.403(4)
N2	C9	1.337(4)	C8	C12	1.506(3)
C1	C2	1.396(4)	C9	C10	1.446(4)
C1	C6	1.393(4)	C11	C12	1.530(4)
C1	C7	1.473(4)	C12	C13	1.534(4)
C2	C3	1.384(4)	C12	C14	1.532(4)

Table 5 Bond Angles for 4a.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C10	O3	C11	117.6(2)	C7	C8	C12	136.3(2)
N2	N1	C7	114.2(2)	C9	C8	C12	119.3(2)
N1	N2	C9	103.2(2)	N2	C9	C8	112.9(3)
C2	C1	C7	120.9(2)	N2	C9	C10	122.0(3)
C6	C1	C2	119.2(3)	C8	C9	C10	124.9(3)
C6	C1	C7	119.9(3)	O1	C10	O3	119.1(3)
C3	C2	C1	120.5(3)	O1	C10	C9	126.2(3)
C2	C3	C4	119.7(3)	O3	C10	C9	114.7(3)
C5	C4	C3	120.0(3)	O3	C11	C12	115.0(2)
C6	C5	C4	120.3(3)	C8	C12	C11	105.4(2)
C5	C6	C1	120.2(3)	C8	C12	C13	111.9(2)
N1	C7	C1	120.6(2)	C8	C12	C14	113.2(2)
N1	C7	C8	105.3(2)	C11	C12	C13	109.5(2)
C8	C7	C1	134.1(2)	C11	C12	C14	106.3(2)
C7	C8	C9	104.4(2)	C14	C12	C13	110.2(2)

Table 6 Torsion Angles for 4a.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
O3	C11	C12	C8	52.3(3)	C6	C1	C7	N1	40.8(4)
O3	C11	C12	C13	-68.3(3)	C6	C1	C7	C8	-138.7(3)
O3	C11	C12	C14	172.7(2)	C7	N1	N2	C9	0.2(3)
N1	N2	C9	C8	-0.4(3)	C7	C1	C2	C3	-178.6(3)
N1	N2	C9	C10	-176.5(3)	C7	C1	C6	C5	179.6(2)
N1	C7	C8	C9	-0.3(3)	C7	C8	C9	N2	0.4(3)
N1	C7	C8	C12	-178.2(3)	C7	C8	C9	C10	176.4(3)
N2	N1	C7	C1	-179.6(3)	C7	C8	C12	C11	152.6(3)
N2	N1	C7	C8	0.1(3)	C7	C8	C12	C13	-88.4(4)
N2	C9	C10	O1	8.8(5)	C7	C8	C12	C14	36.8(4)
N2	C9	C10	O3	-173.5(3)	C8	C9	C10	O1	-166.9(3)

Table 6 Torsion Angles for 4a.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C1	C2	C3	C4	-2.2(4)	C8	C9	C10	O3	10.8(4)
C1	C7	C8	C9	179.3(3)	C9	C8	C12	C11	-25.1(3)
C1	C7	C8	C12	1.4(6)	C9	C8	C12	C13	93.9(3)
C2	C1	C6	C5	-1.8(4)	C9	C8	C12	C14	-140.9(3)
C2	C1	C7	N1	-137.7(3)	C10	O3	C11	C12	-52.1(4)
C2	C1	C7	C8	42.7(5)	C11	O3	C10	O1	-164.4(3)
C2	C3	C4	C5	0.5(4)	C11	O3	C10	C9	17.7(4)
C3	C4	C5	C6	0.5(4)	C12	C8	C9	N2	178.8(3)
C4	C5	C6	C1	0.2(4)	C12	C8	C9	C10	-5.2(4)
C6	C1	C2	C3	2.9(4)					

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

Atom	*x*	*y*	*z*	U(eq)
H1	5960(60)	2540(40)	5650(30)	55(12)
H2	5895.32	4727.35	7809.56	32
H3	8604.28	4664.34	8788.13	37
H4	11666.4	3770.16	8426.75	38
H5	12024.46	2981.3	7082.39	36
H6	9358.25	3087.3	6088.97	32
H11A	2632.31	7273.02	5519	41
H11B	4098.13	6571.16	4937.4	41
H13A	1160.36	5764.69	6797.12	51
H13B	2187.44	6876.25	7049.01	51
H13C	3031.48	5789	7443.98	51
H14A	6520	6399.52	6923.46	55
H14B	5693.54	7394.28	6392.36	55
H14C	6980.42	6479.9	5933.02	55

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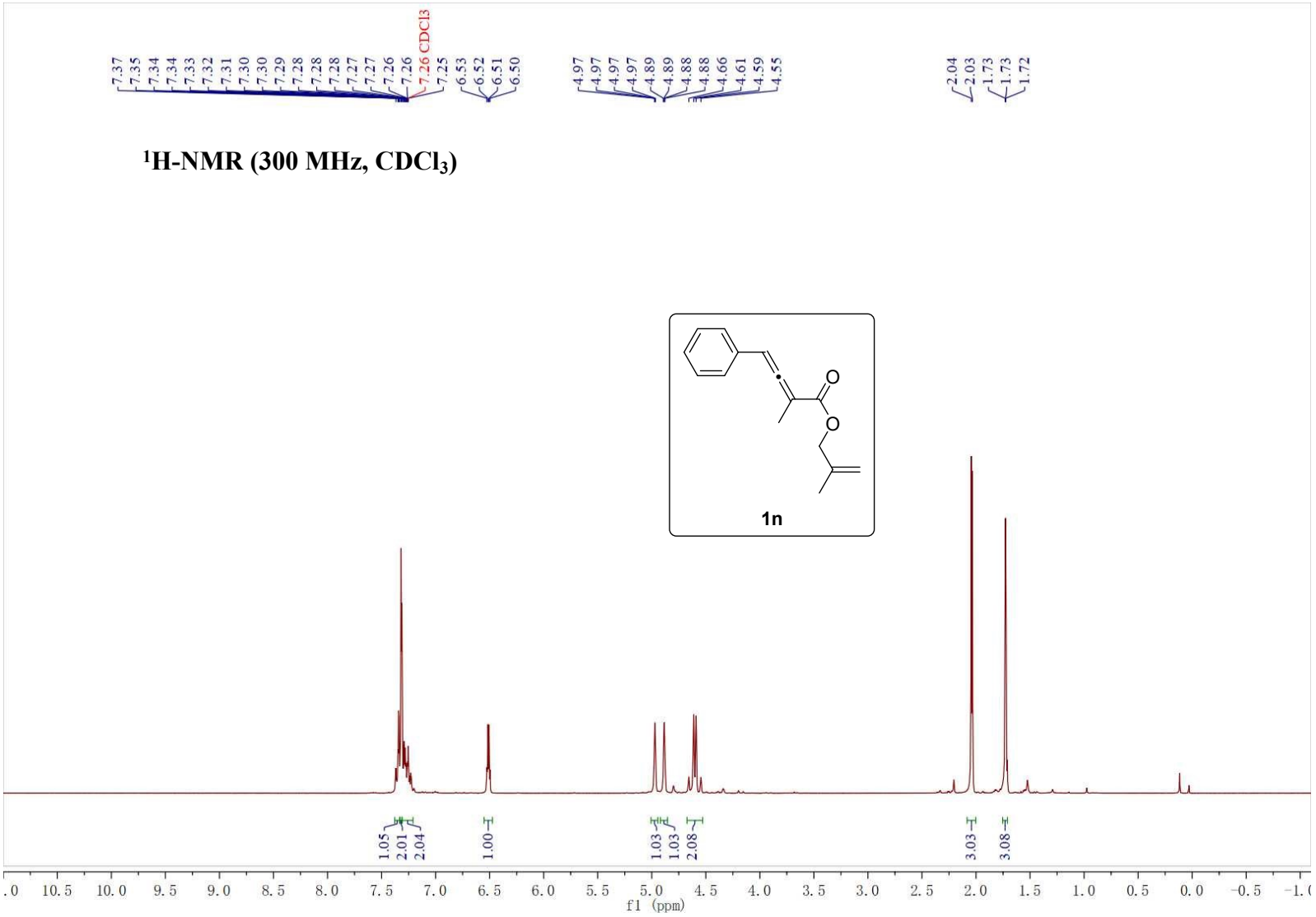
11. Copies of NMR and IR Spectra



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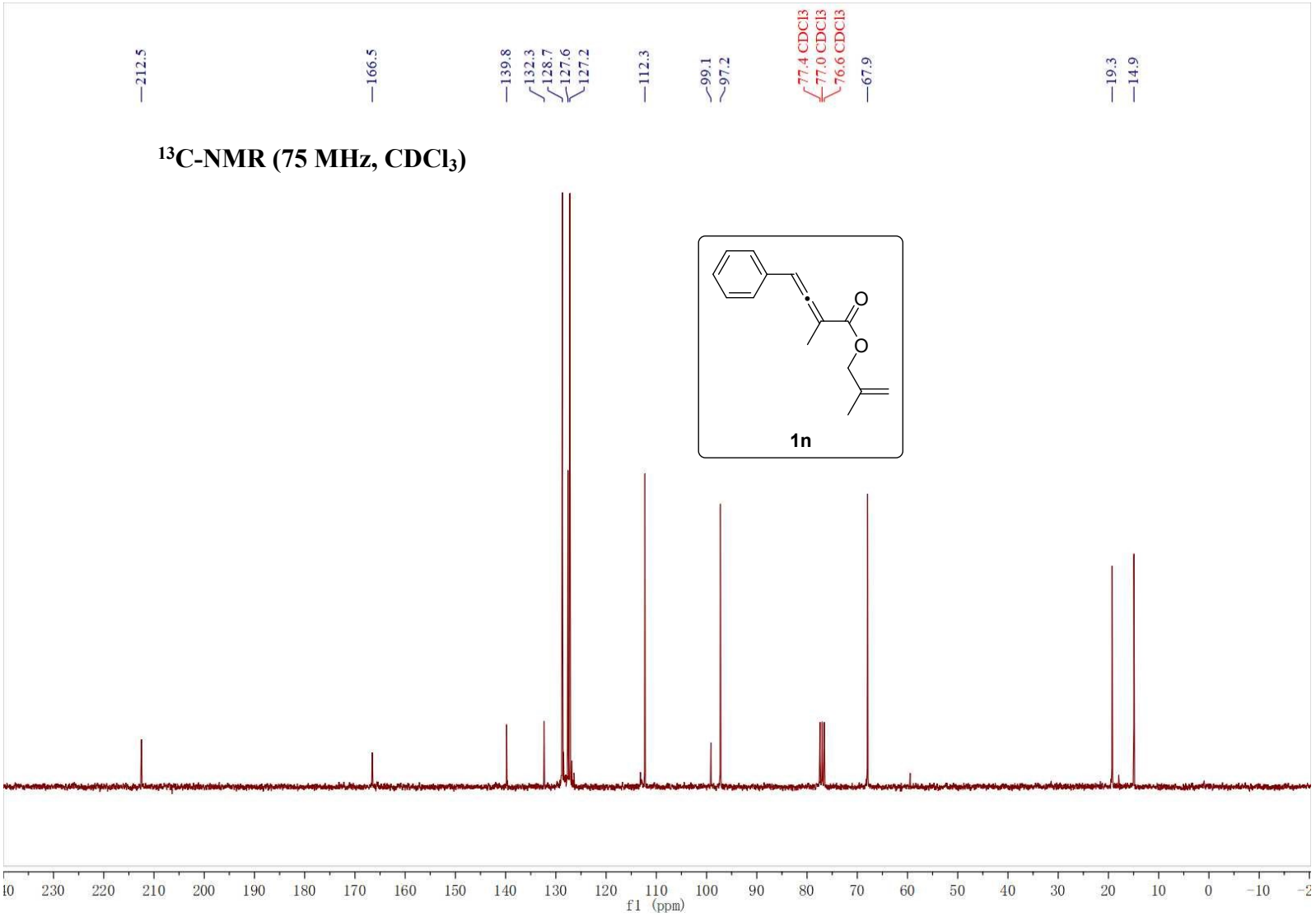
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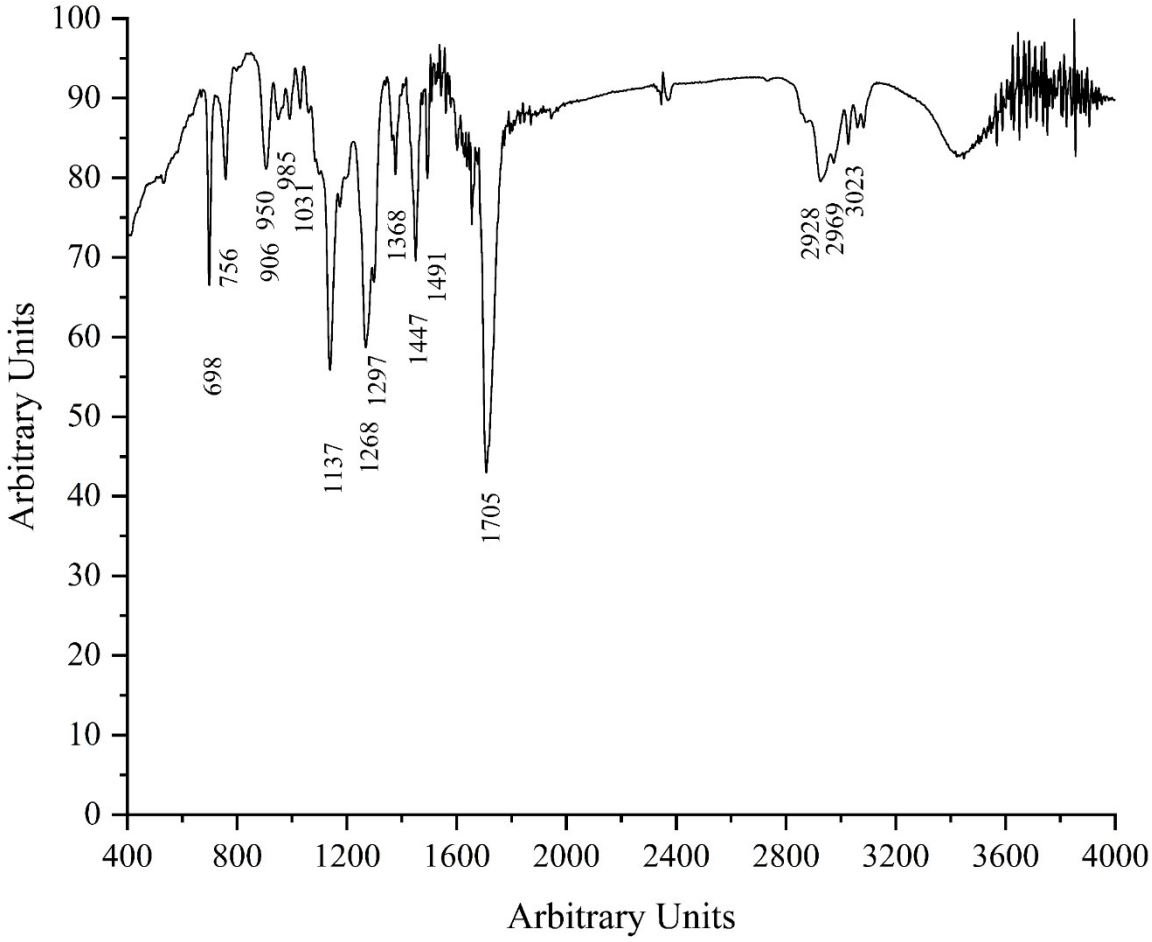
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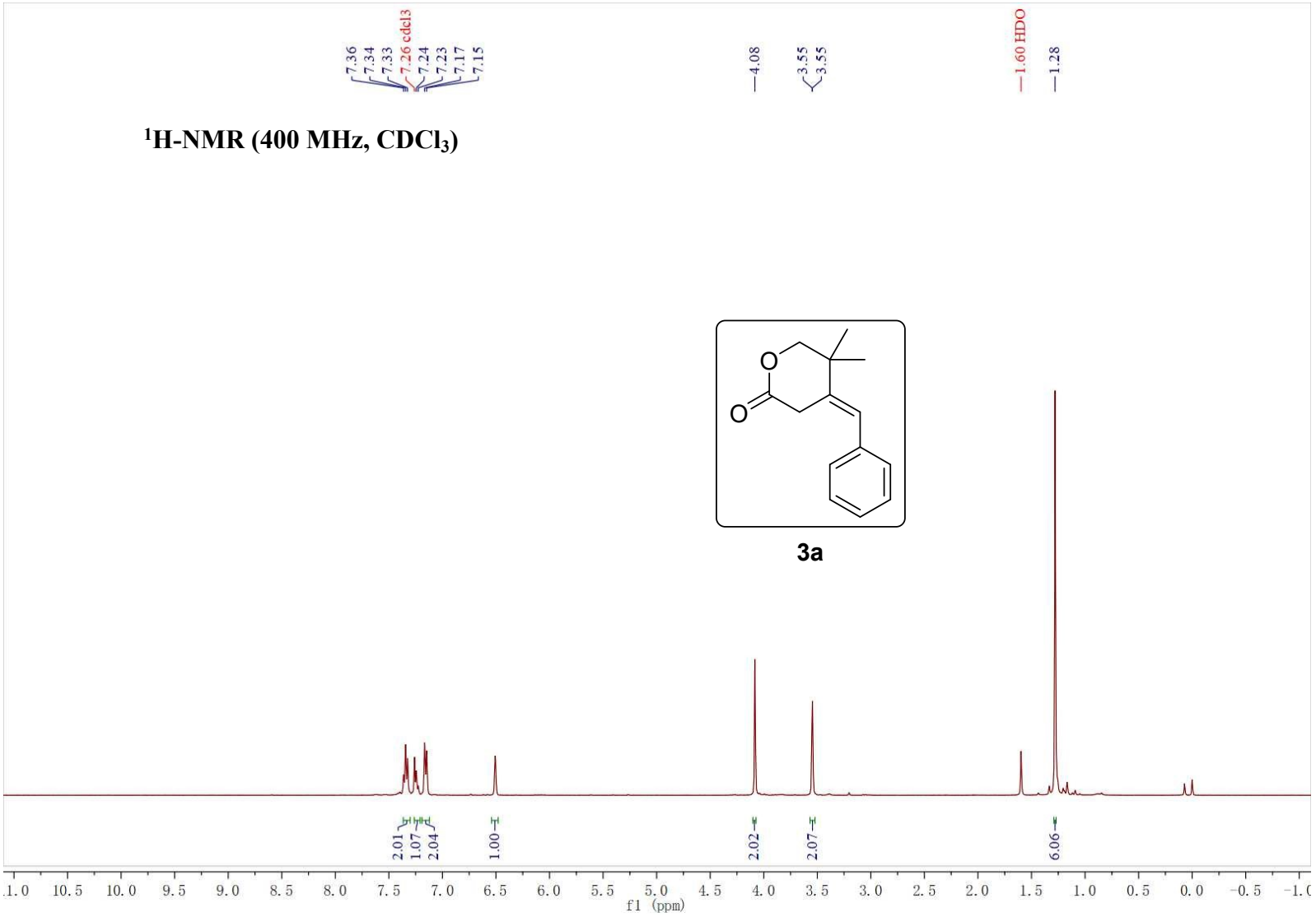

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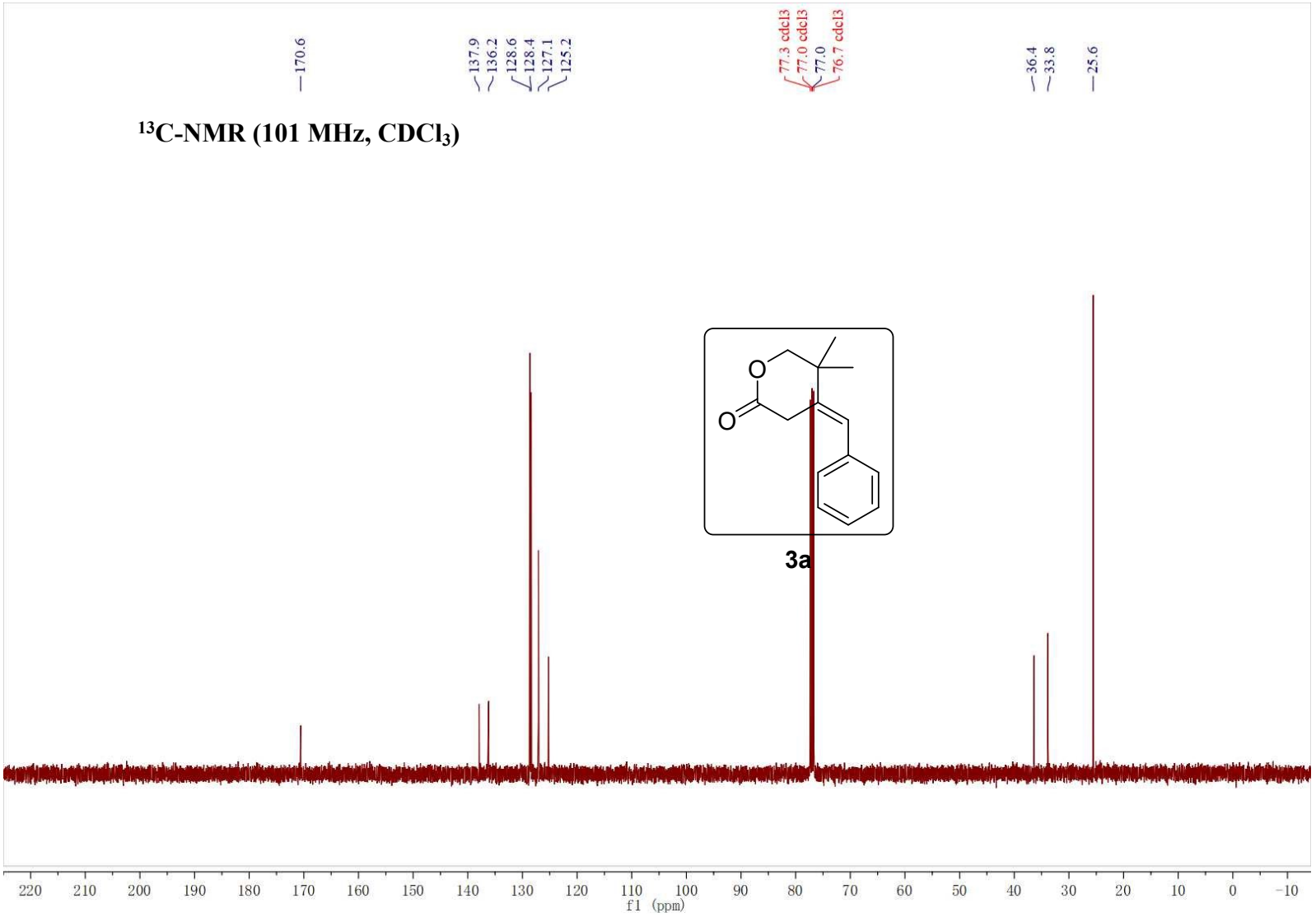

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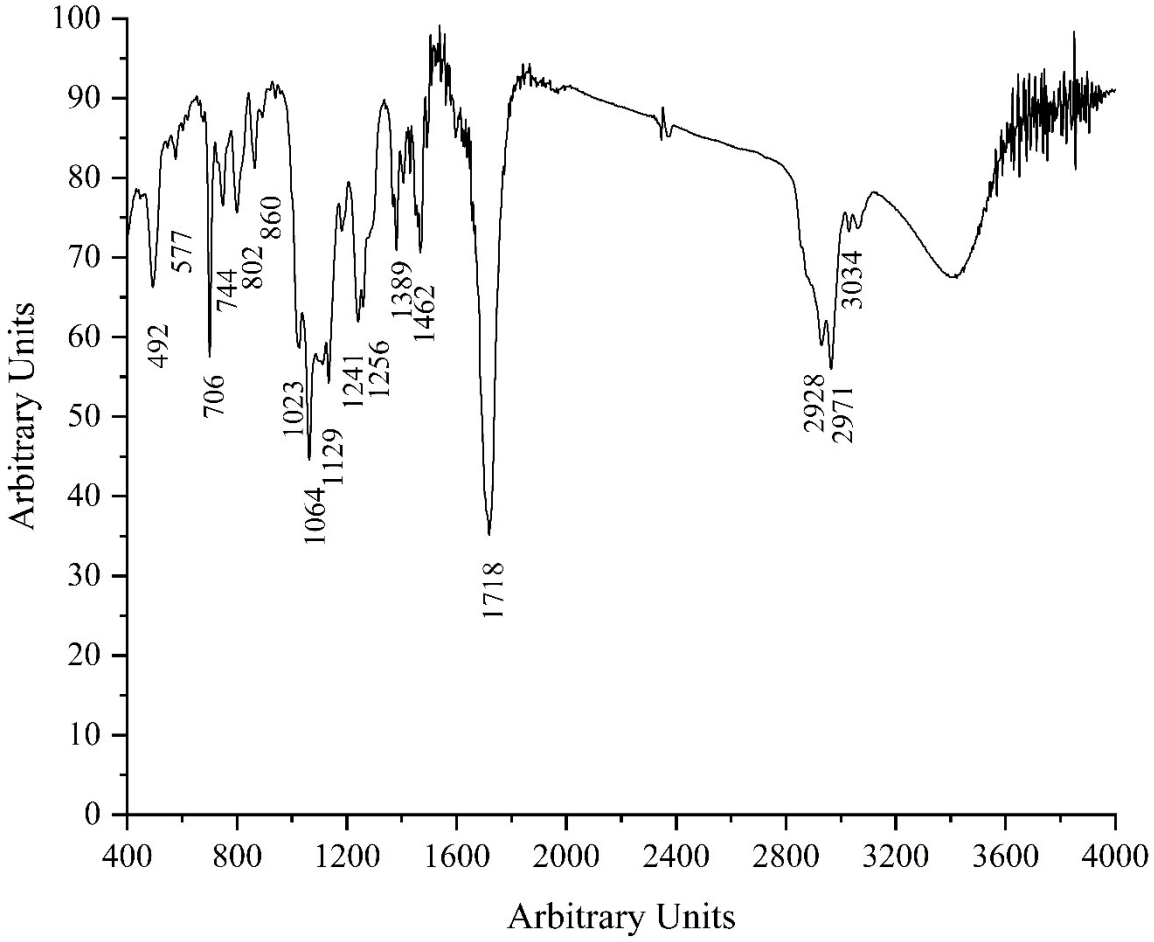
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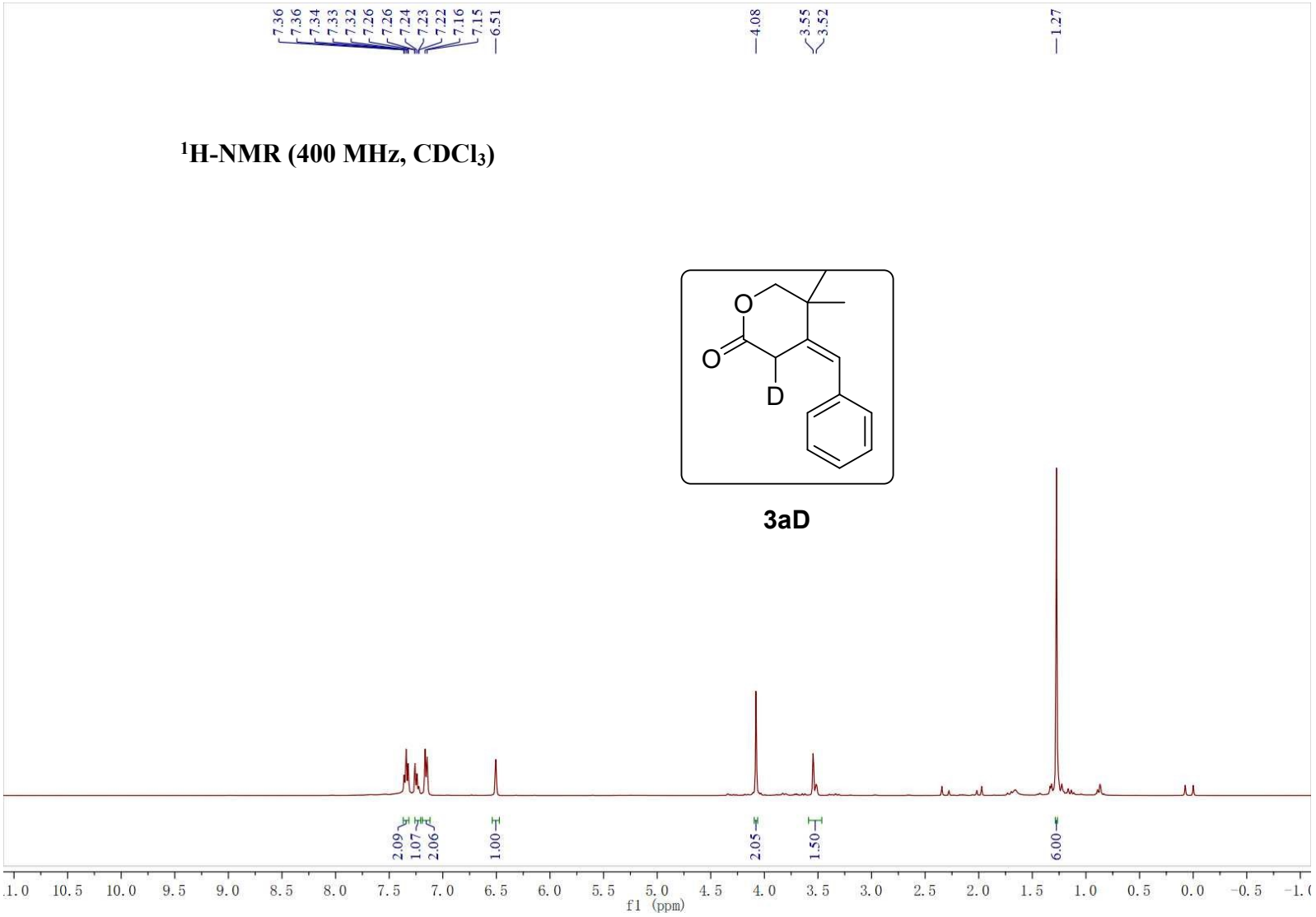
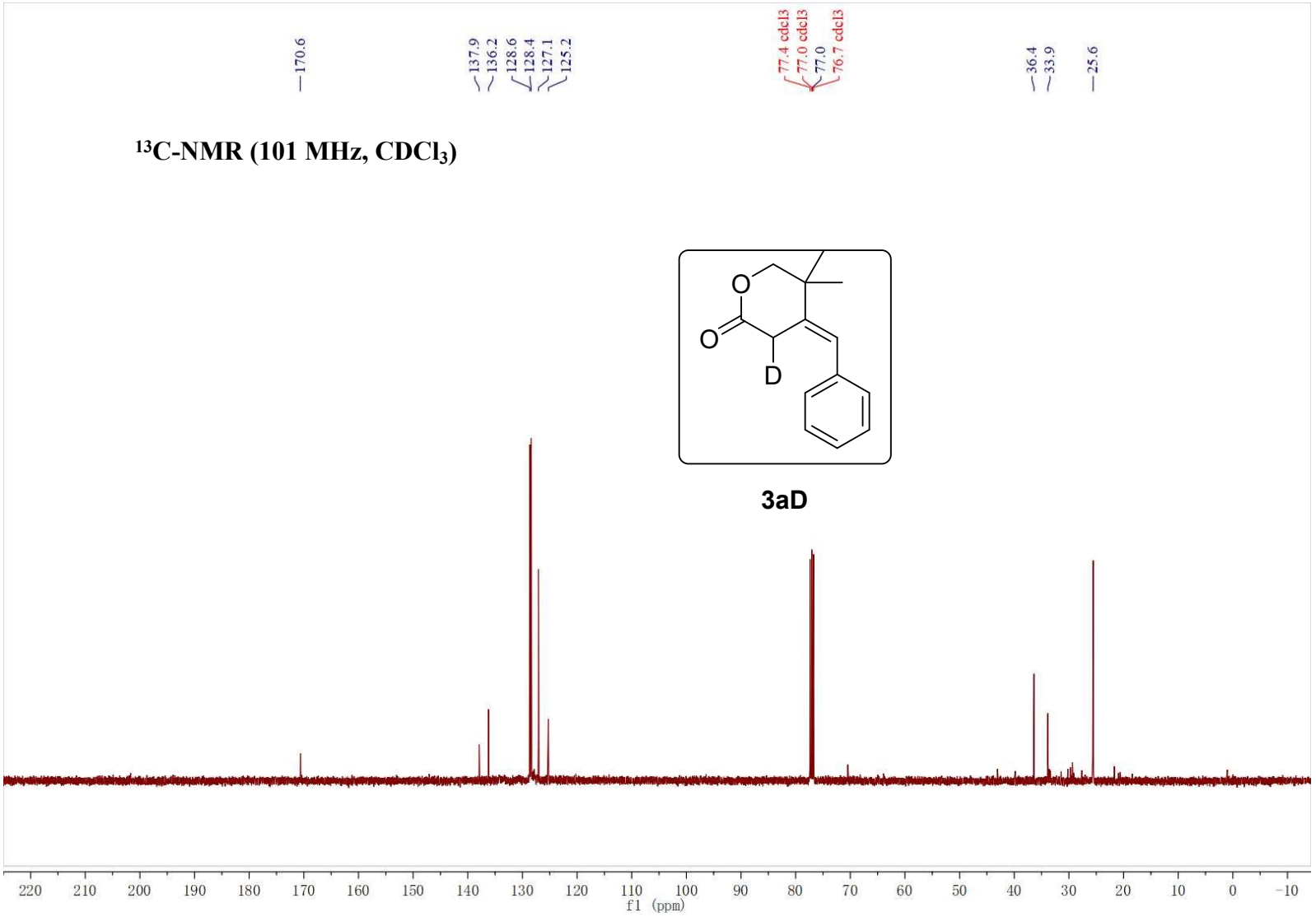
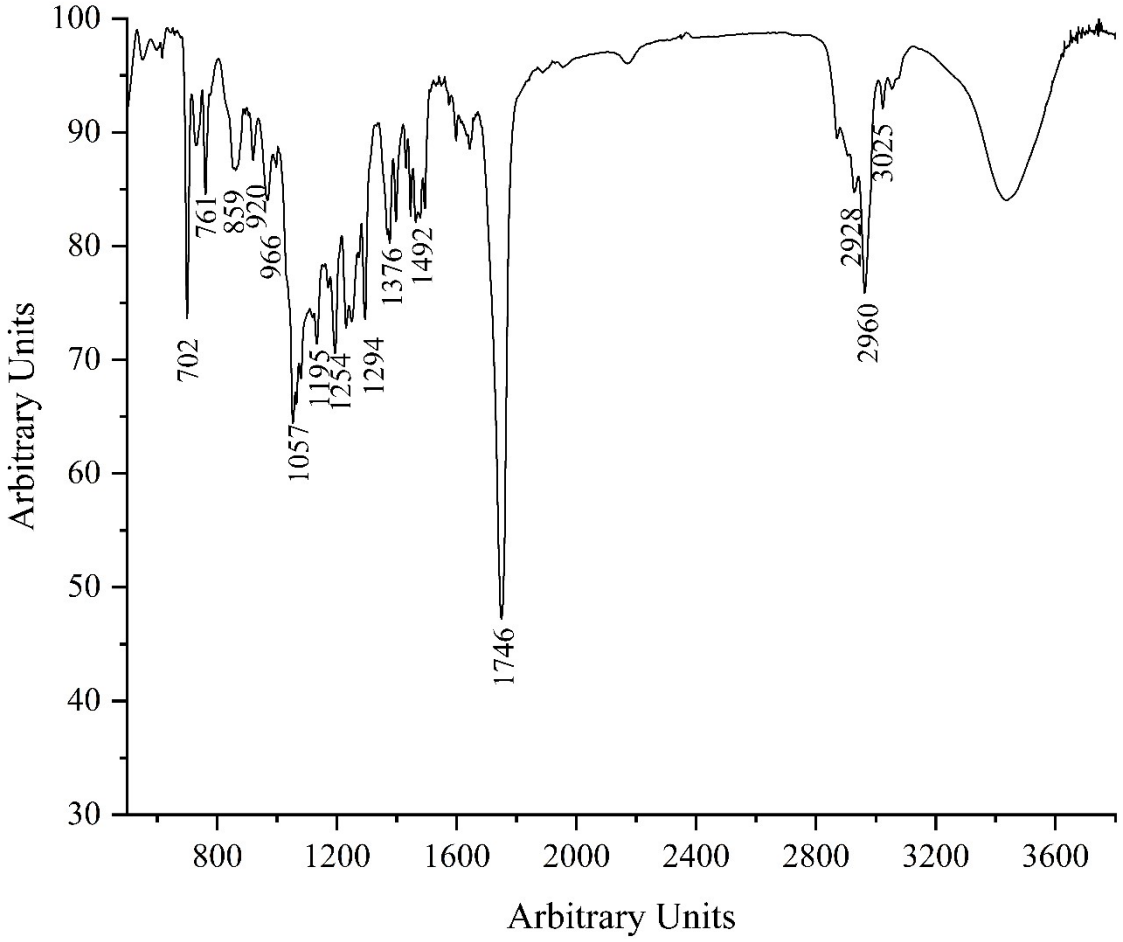


3aD

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



3aD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50
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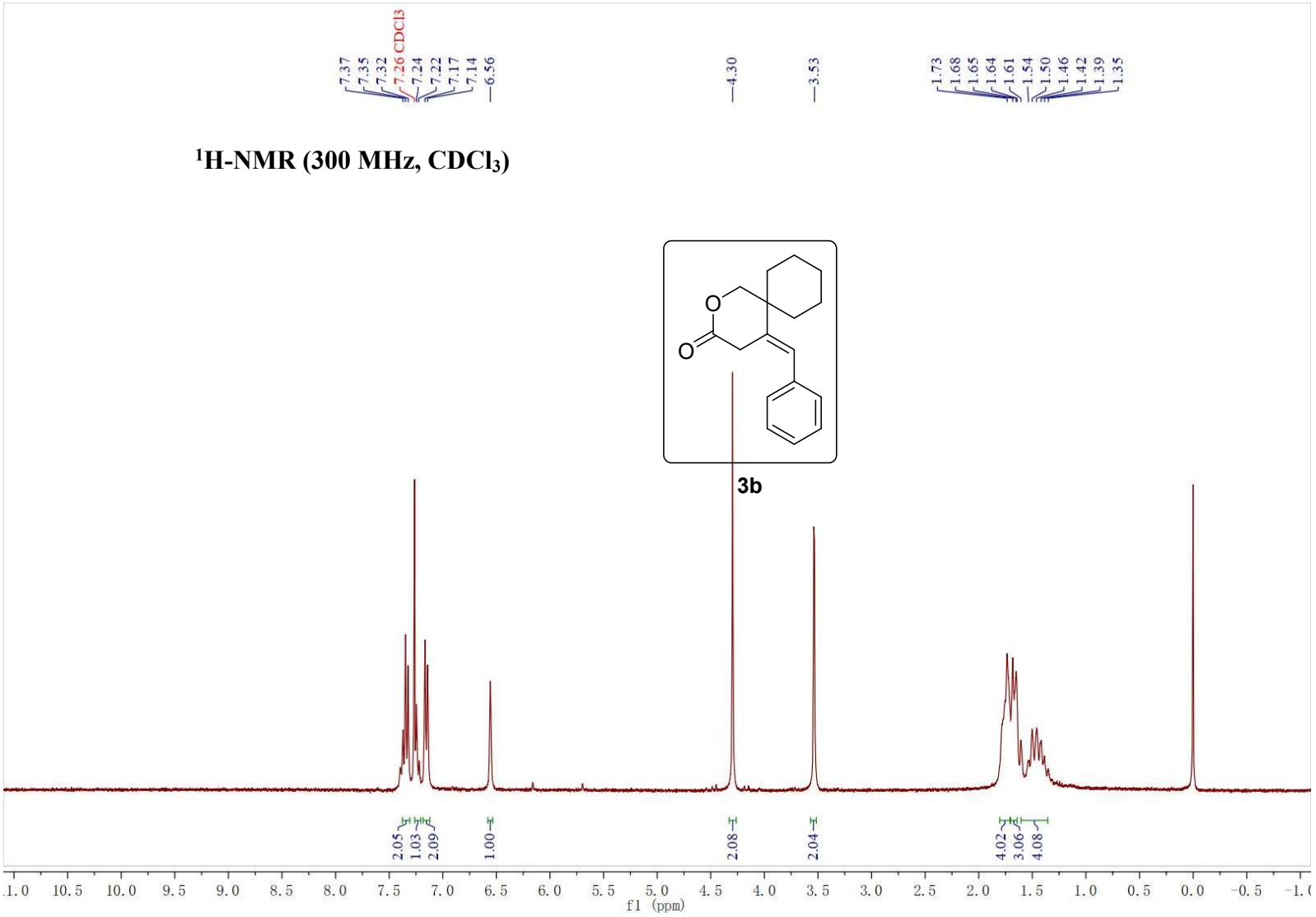
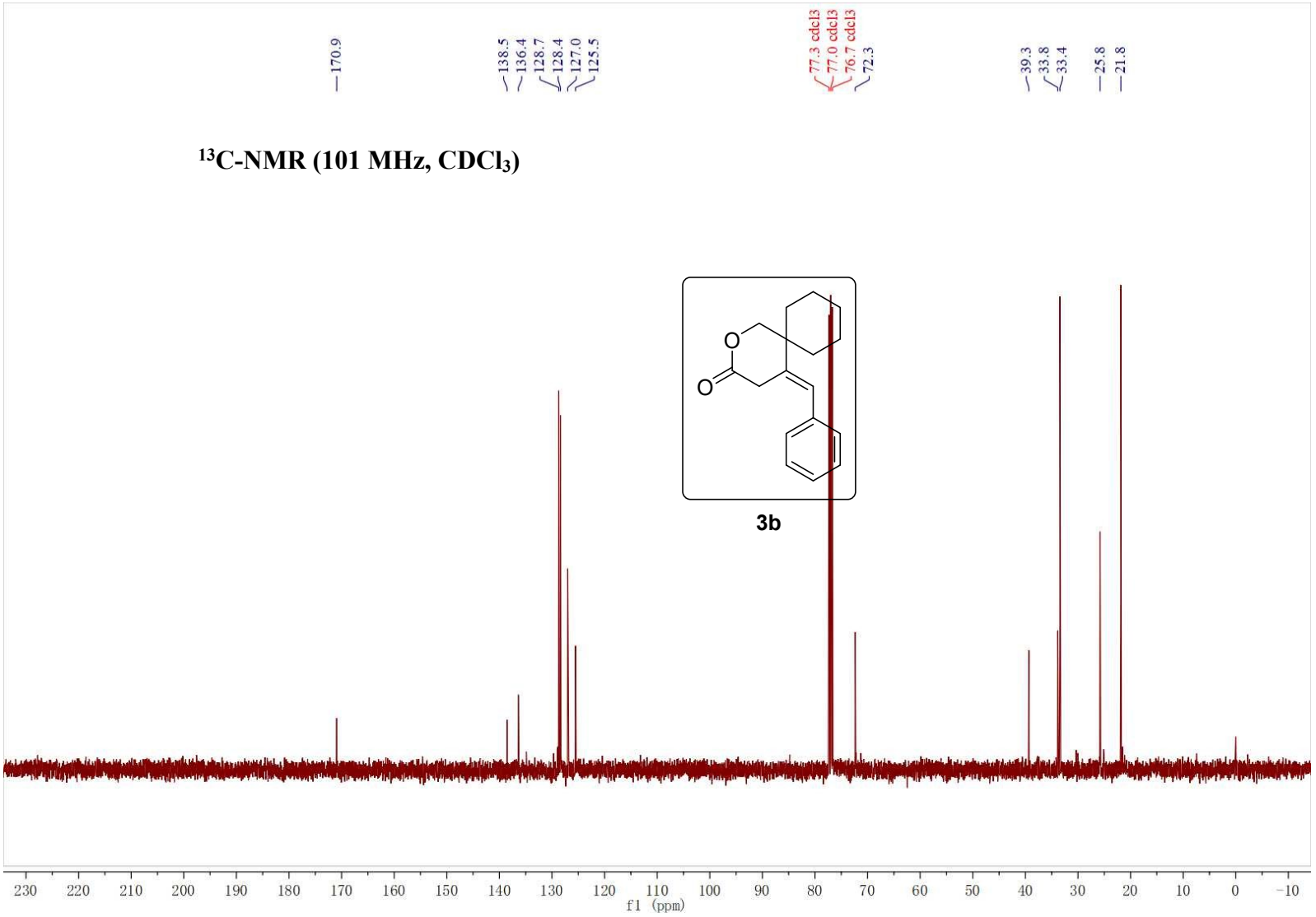
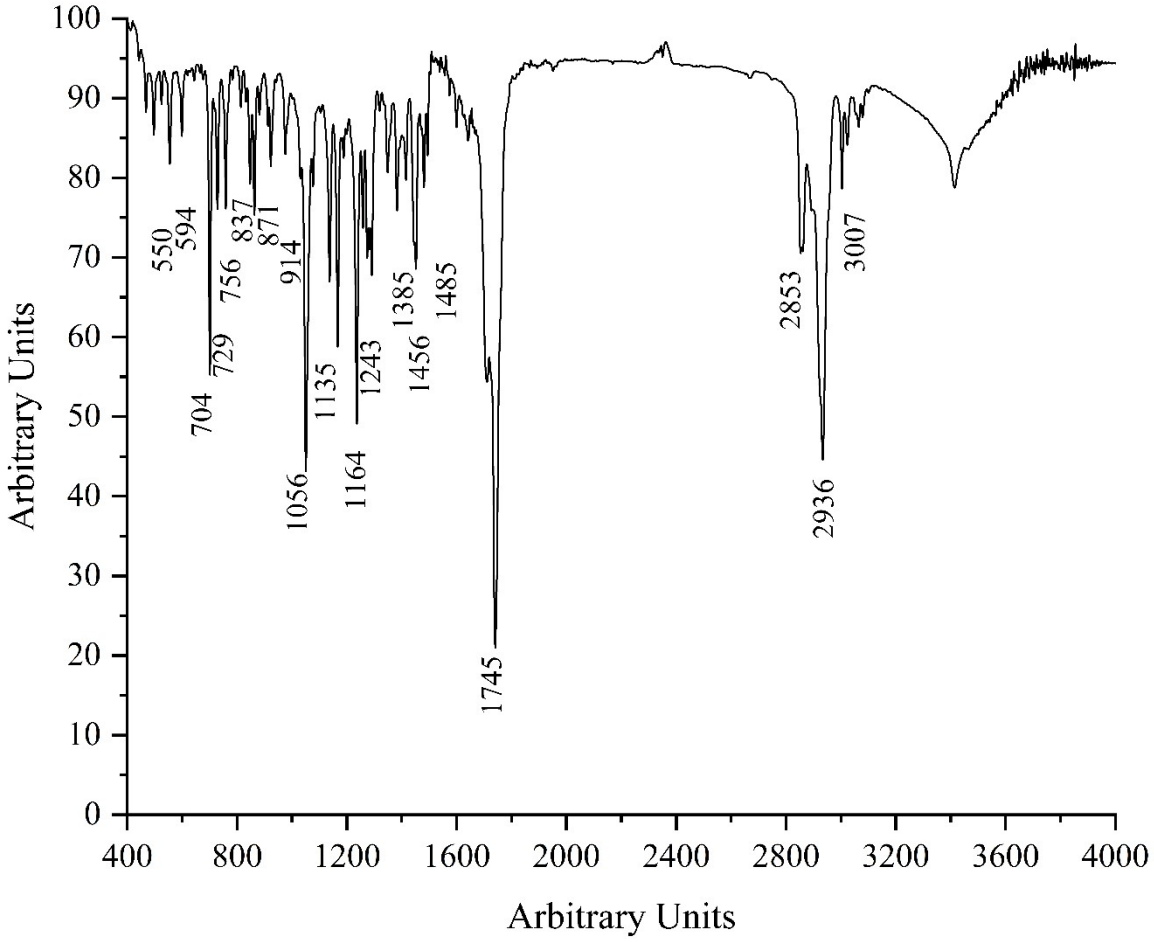
Arbitrary Units
800
1200
1600
2000
2400
2800
3200
3600
Arbitrary Units
702
761
859
920
966
1057
1195
1254
1294
1376
1492
1746
2928
2960
3025

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



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

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2400
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3200
3600
4000
Arbitrary Units
550
594
704
729
756
837
871
914
1056
1135
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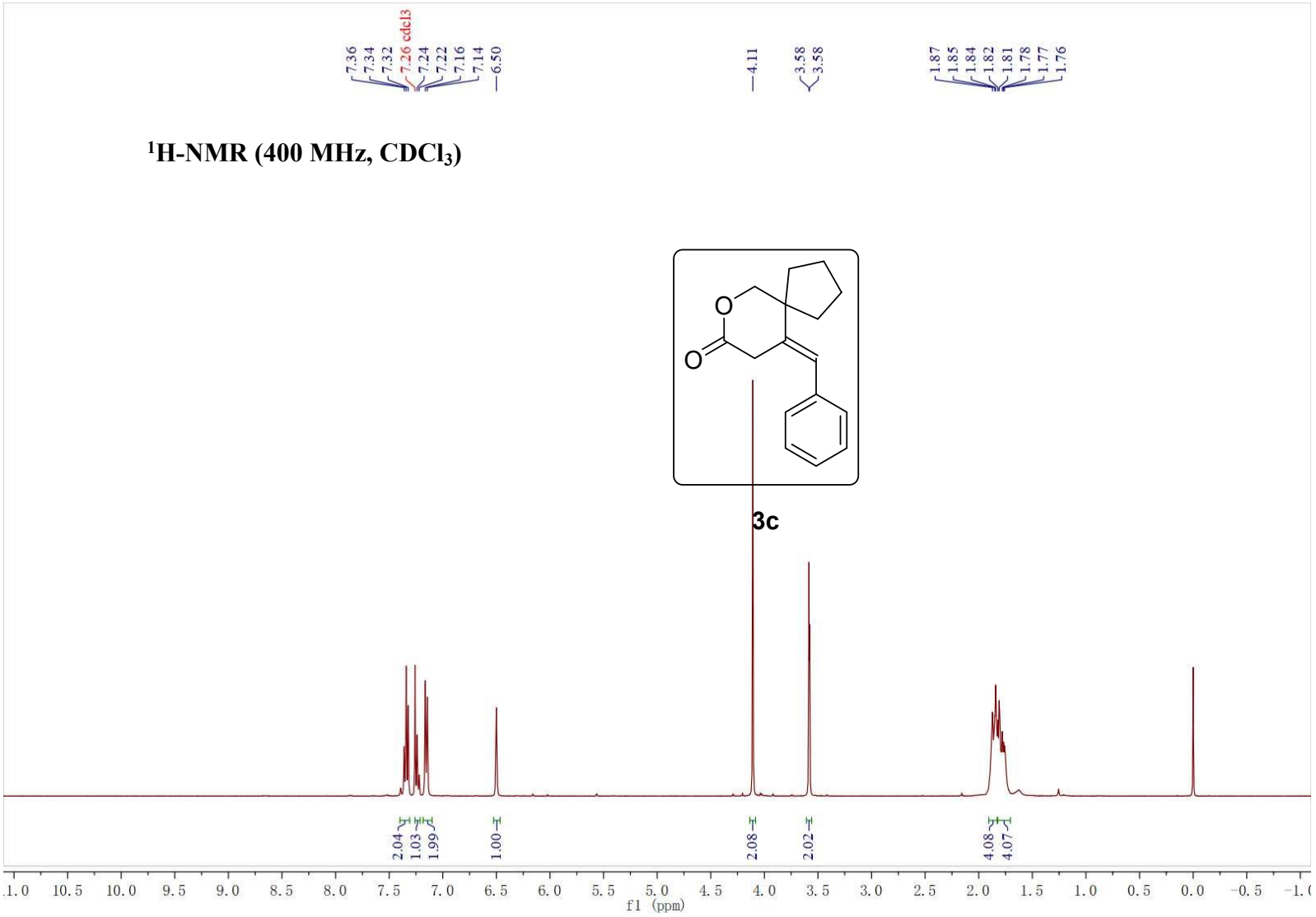
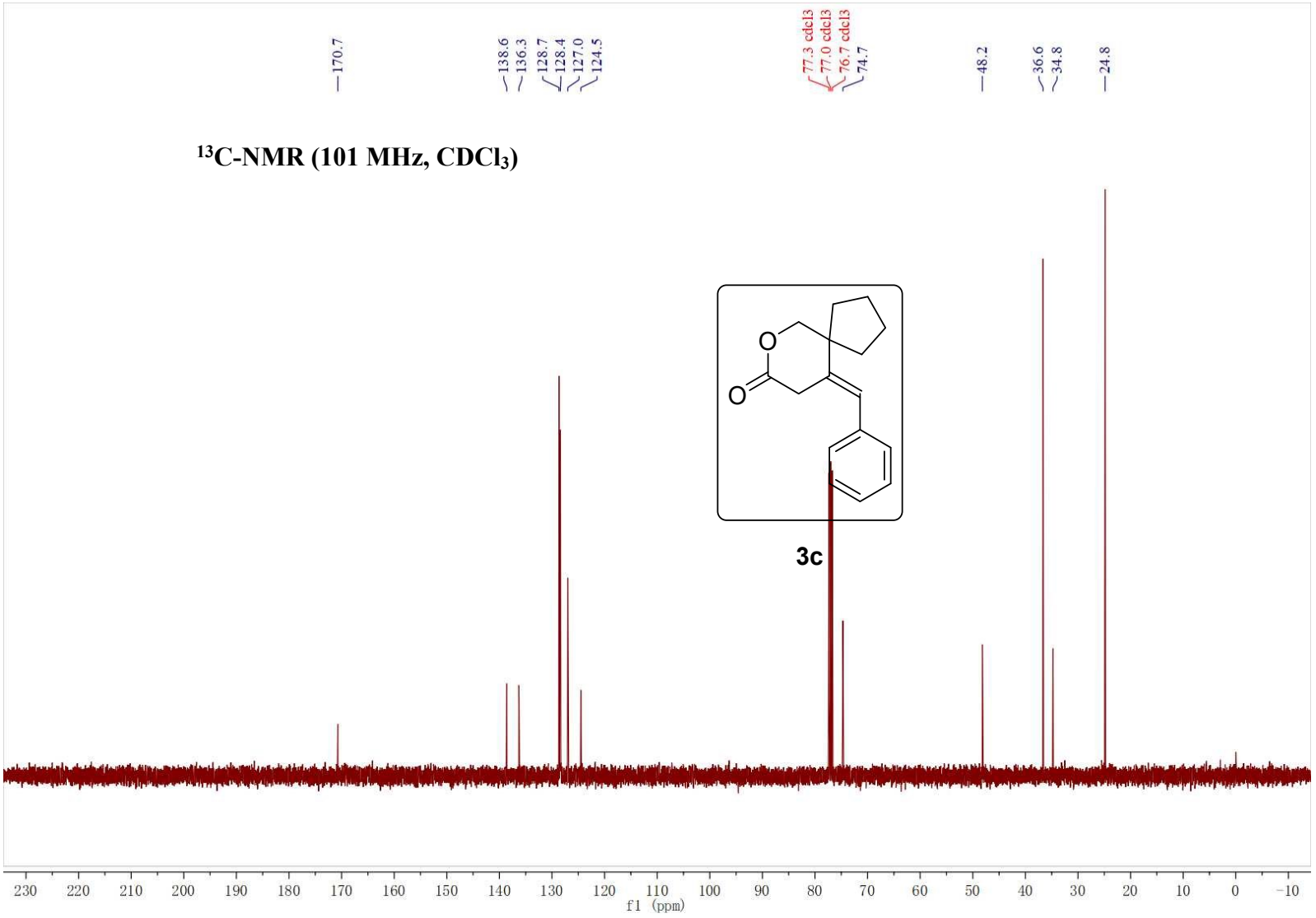
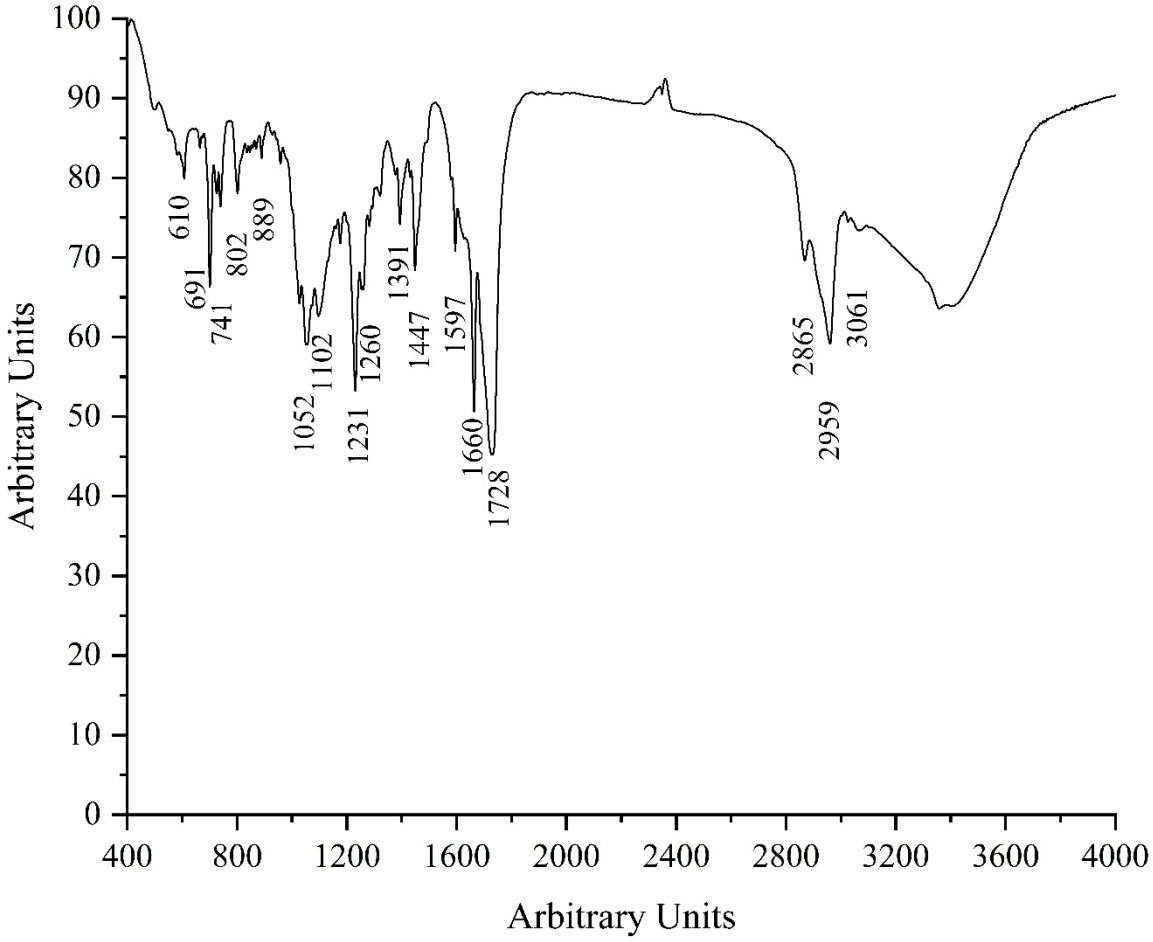
1243
1385
1456
1485
1745
2853
2936
3007

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




170.7
138.6
136.3
128.7
128.4
127.0
124.5
77.3 cdcl3
77.0 cdcl3
76.7 cdcl3
74.7
48.2
36.6
34.8
24.8
13C-NMR (101 MHz, CDCl3)
O
O
3c
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


Arbitrary Units
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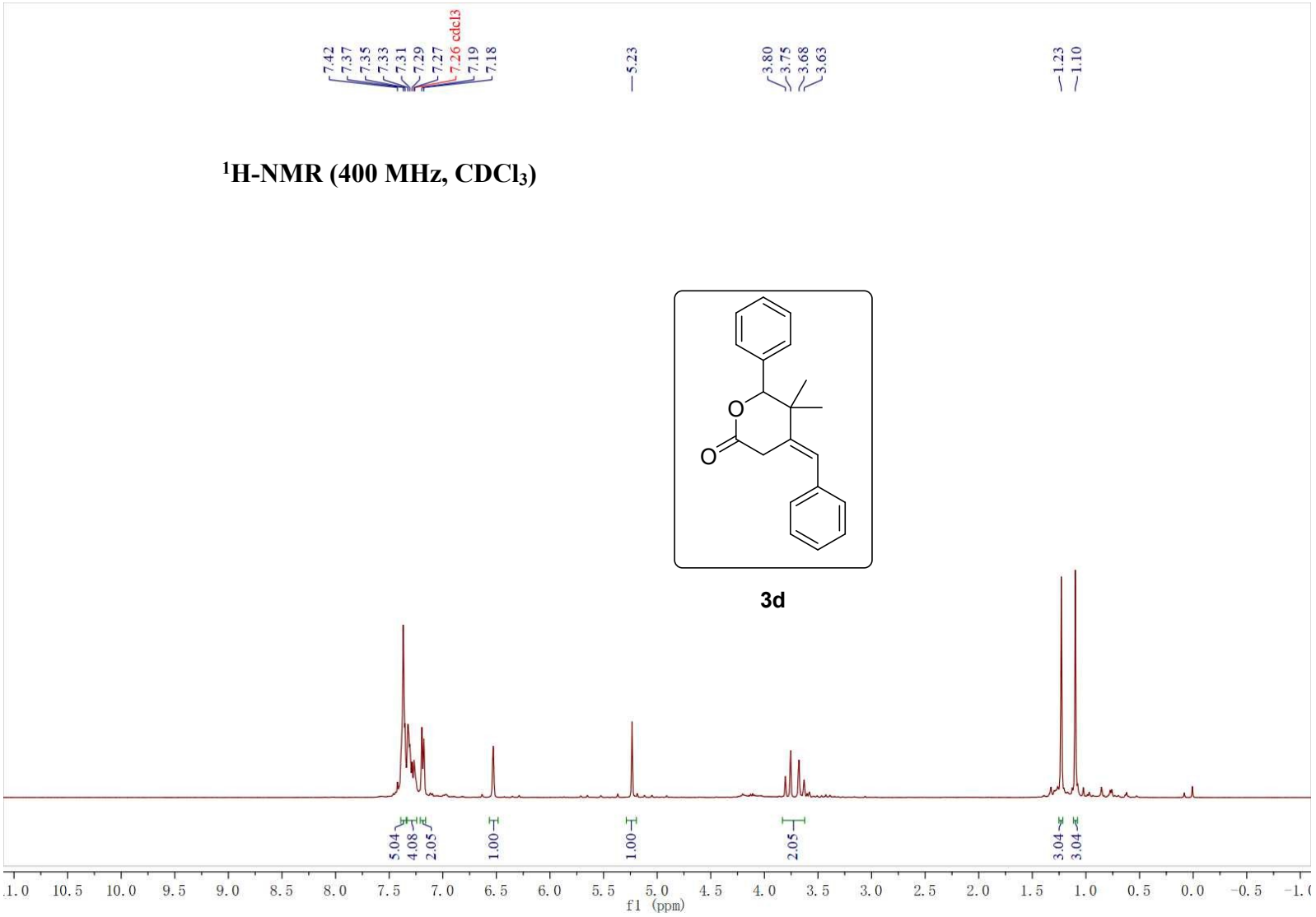
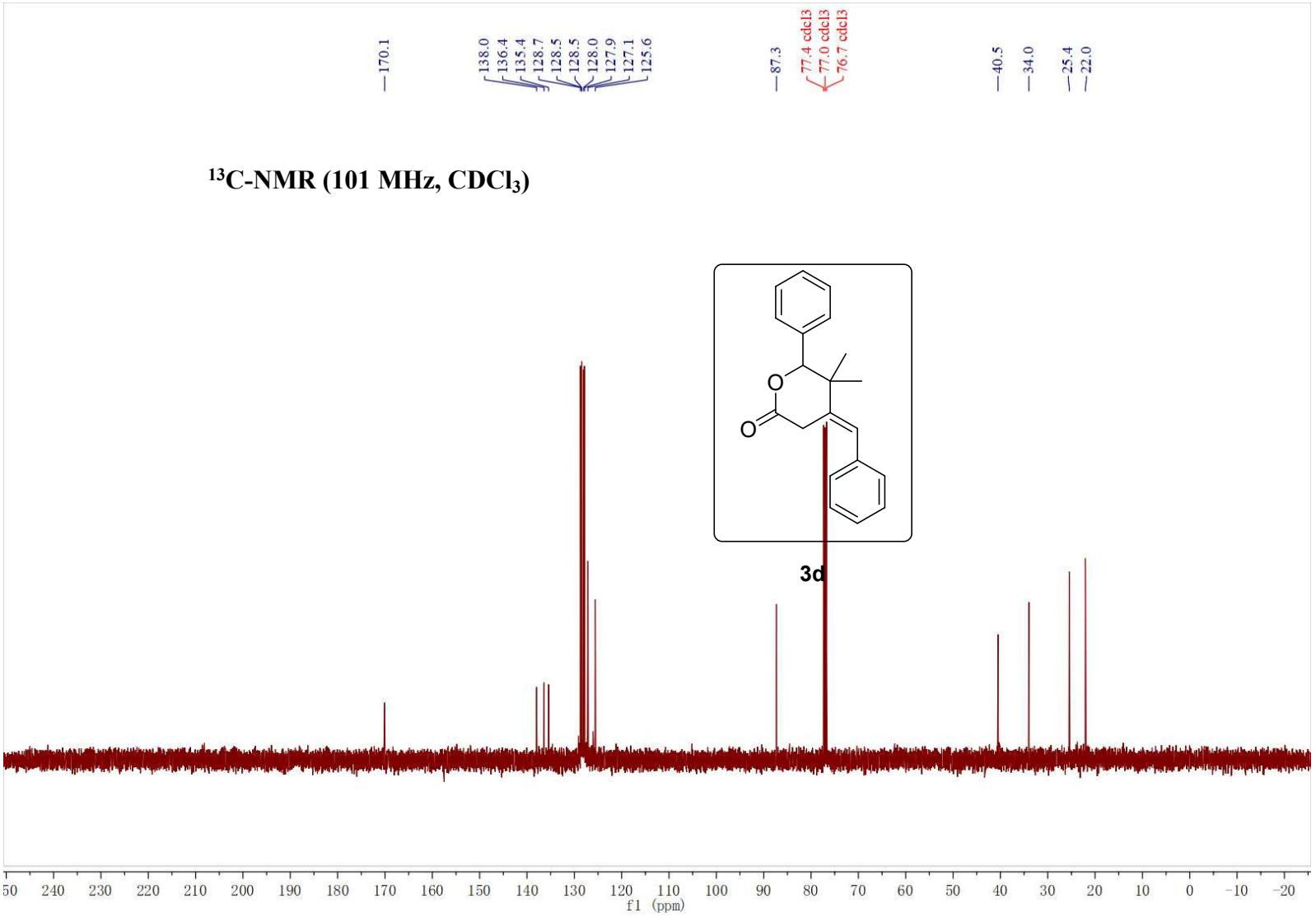
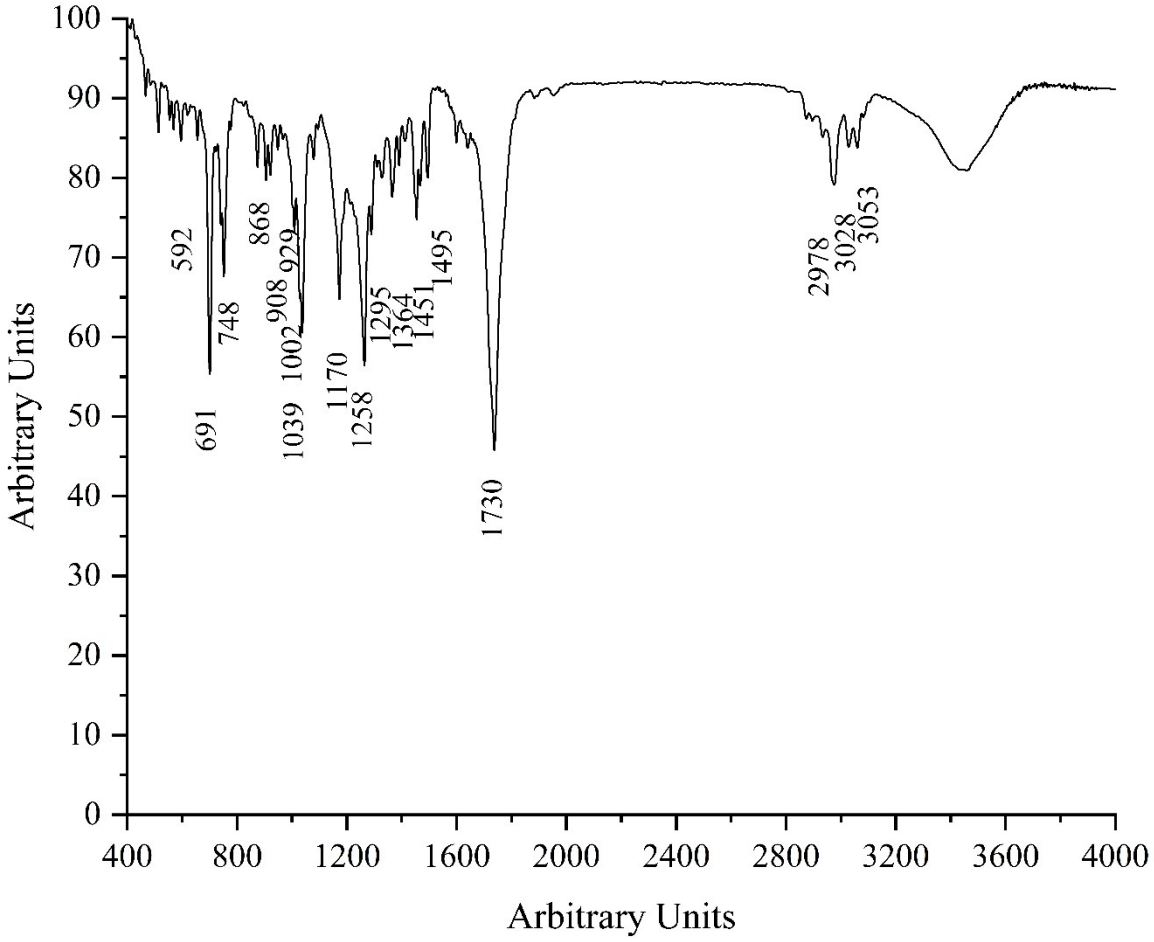
1200
1600
2000
2400
2800
3200
3600
4000
Arbitrary Units
610
691
741
802
889
1052
1102
1231
1260
1391
1447
1597
1660
1728
2865
2959
3061

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



3d


170.1
138.0
136.4
135.4
128.7
128.5
128.5
128.0
127.9
127.1
125.6
87.3
77.4 cdcl3
77.0 cdcl3
76.7 cdcl3
40.5
34.0
25.4
22.0
13C-NMR (101 MHz, CDCl3)
O
O
3d
f1 (ppm)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0
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800
1200
1600
2000
2400
2800
3200
3600
4000
Arbitrary Units
592
691
748
868
908
929
1002
1039
1170
1258
1295
1364
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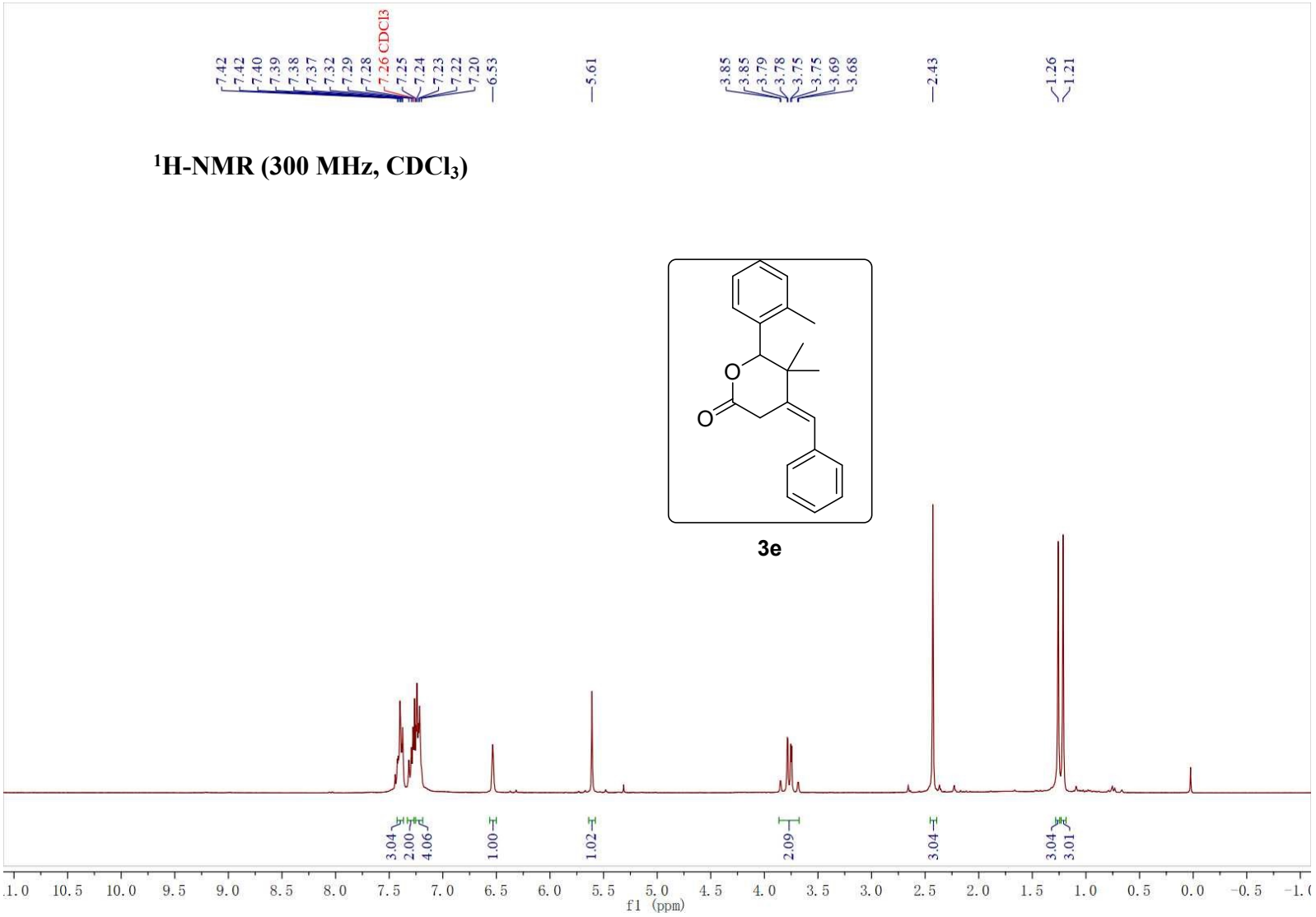
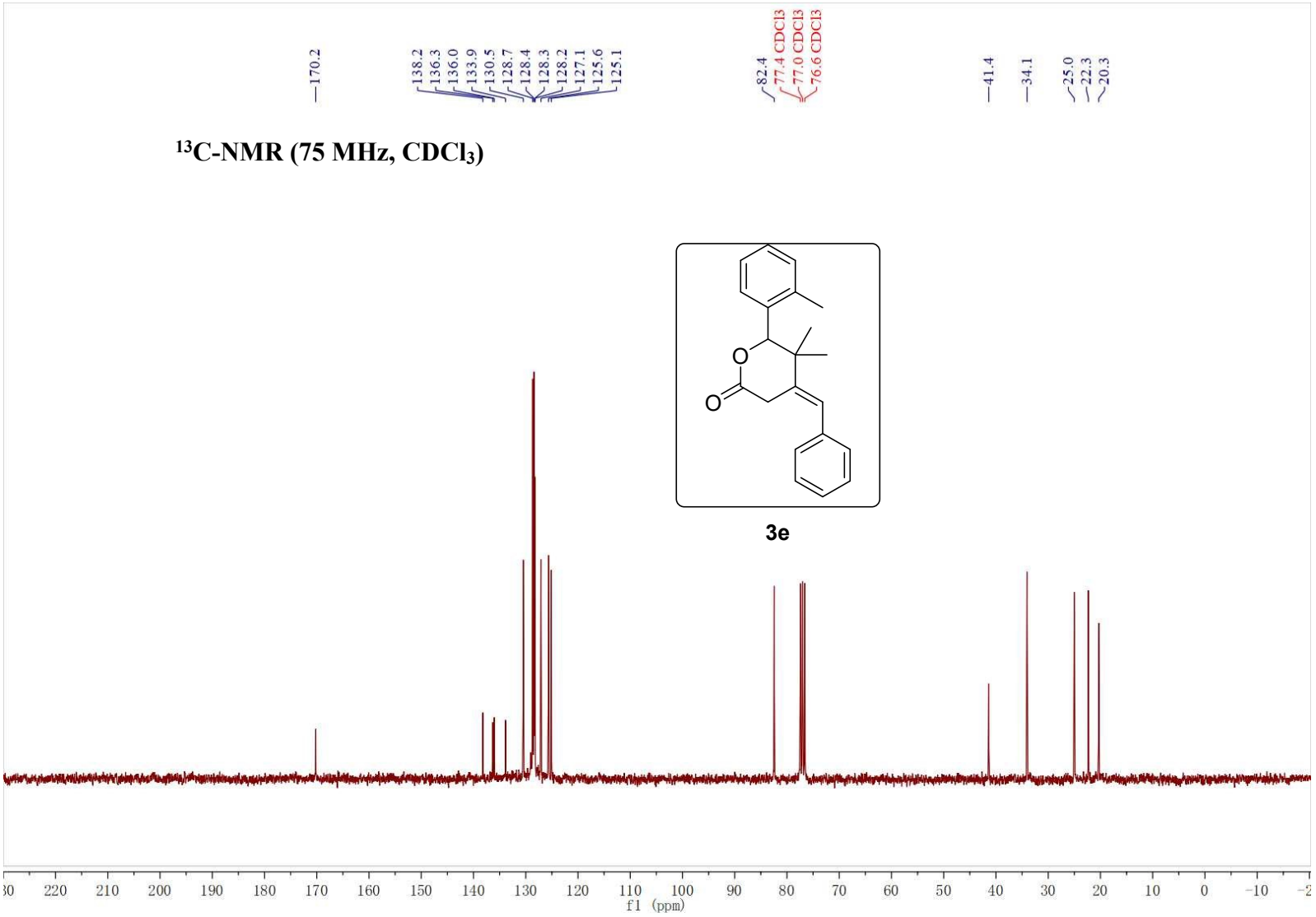
1730
2978
3028
3053

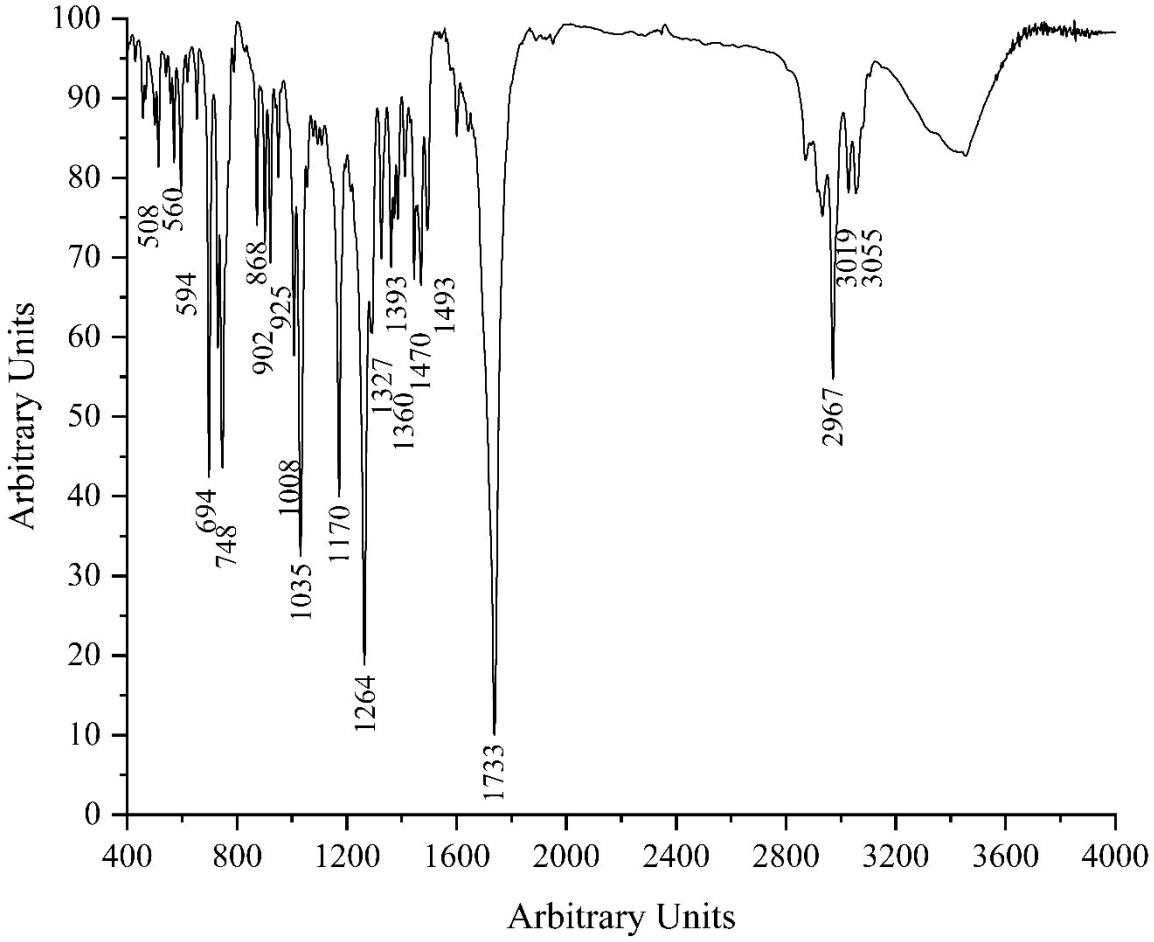


^{1}H-NMR (300 MHz, $CDCl_3$)



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

3e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0
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1200
1600
2000
2400
2800
3200
3600
4000
Arbitrary Units
508
560
594
694
748
868
902
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1170
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1327
1360
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1470
1493
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2967
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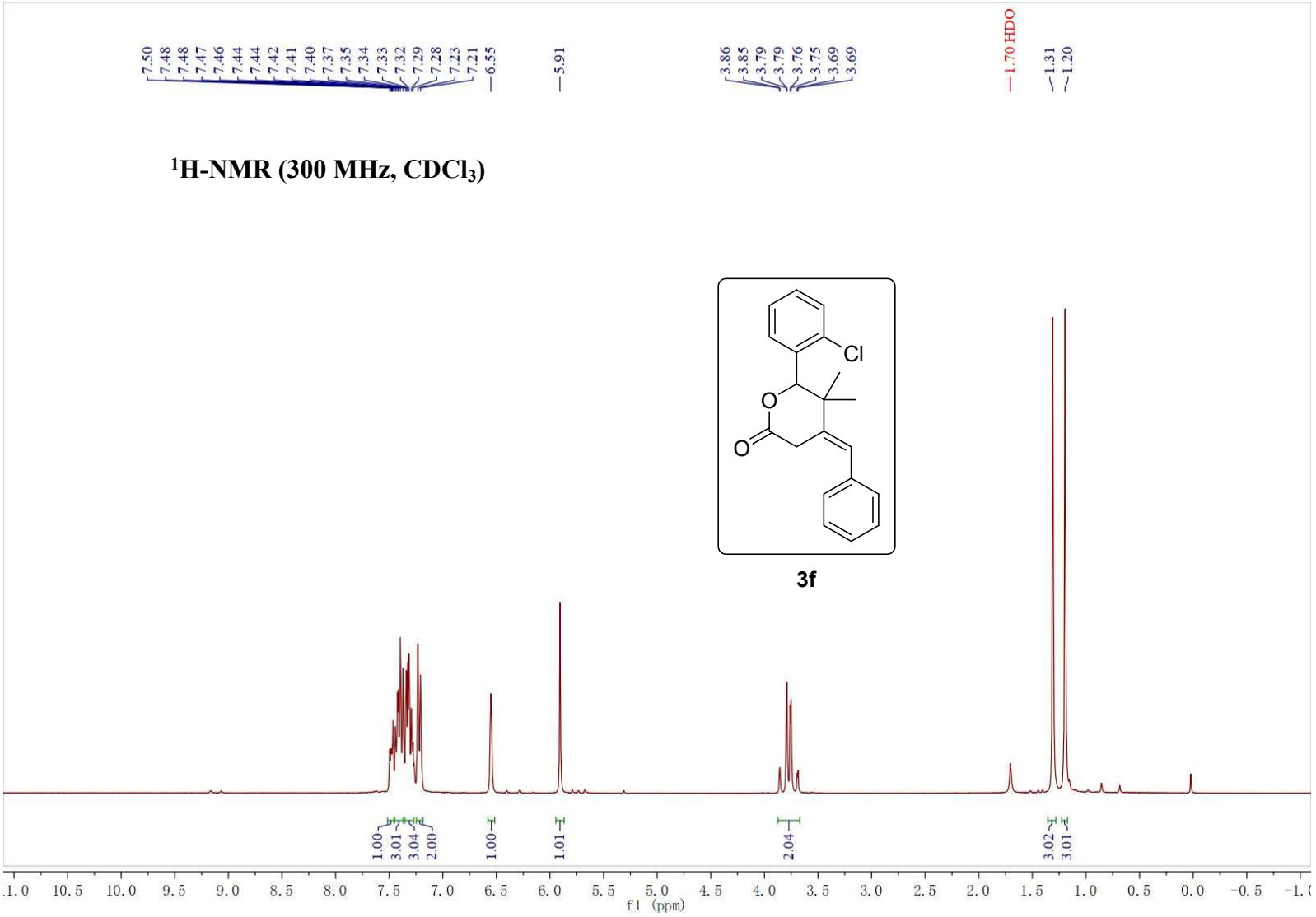
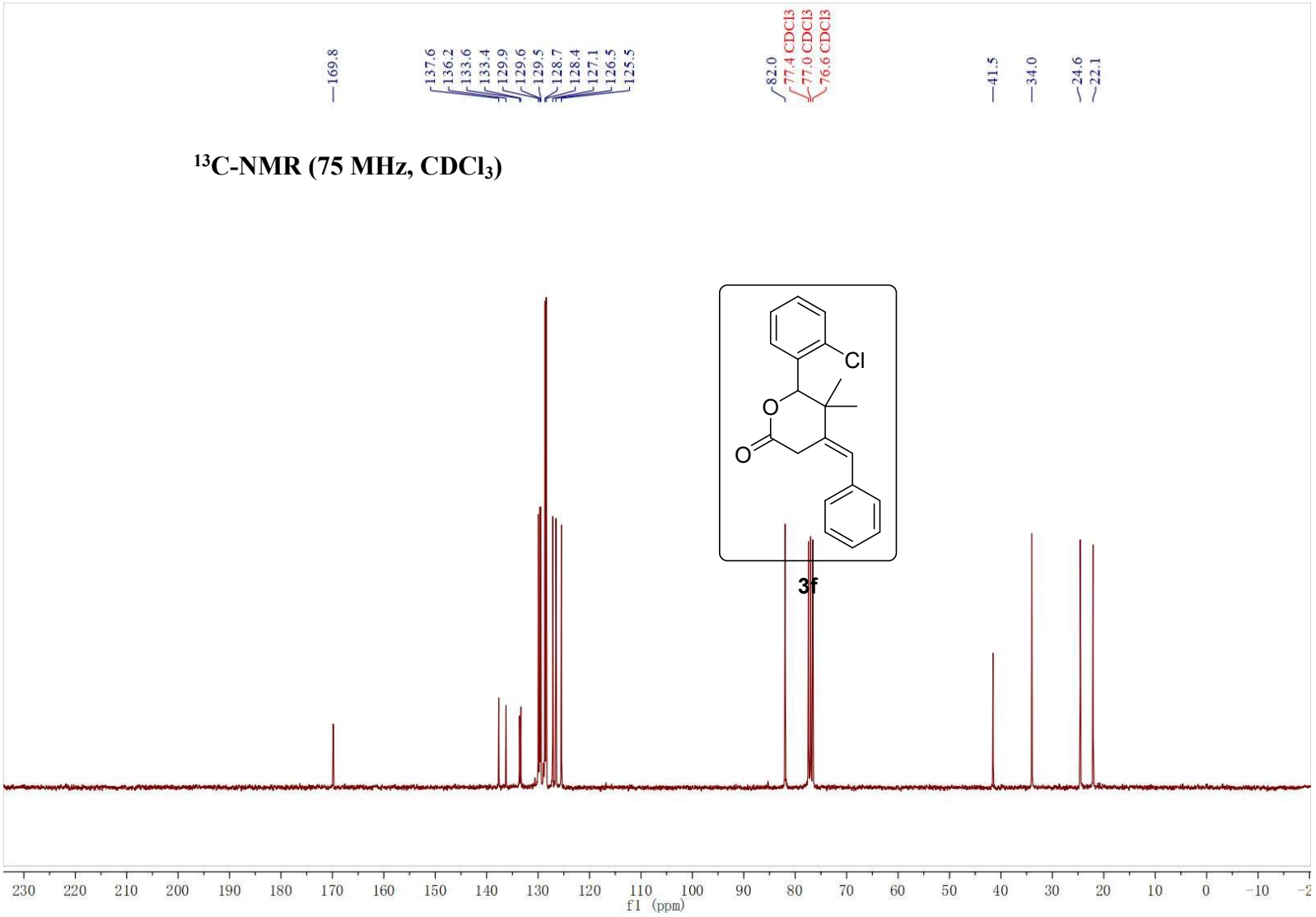
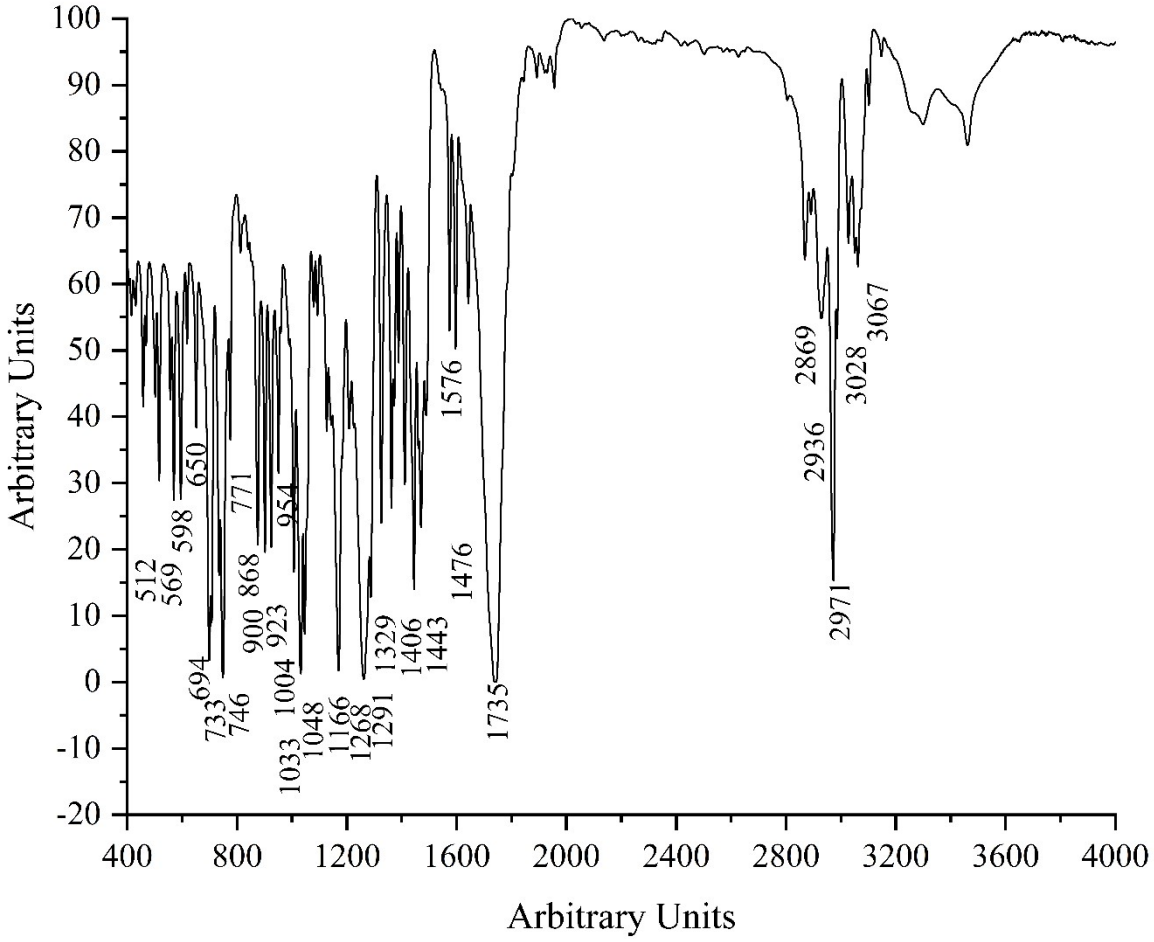


^{1}H-NMR (300 MHz, $CDCl_3$)

3f

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




Arbitrary Units
Arbitrary Units
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20
10
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400
800
1200
1600
2000
2400
2800
3200
3600
4000
512
569
598
650
694
733
746
771
868
900
923
954
1004
1033
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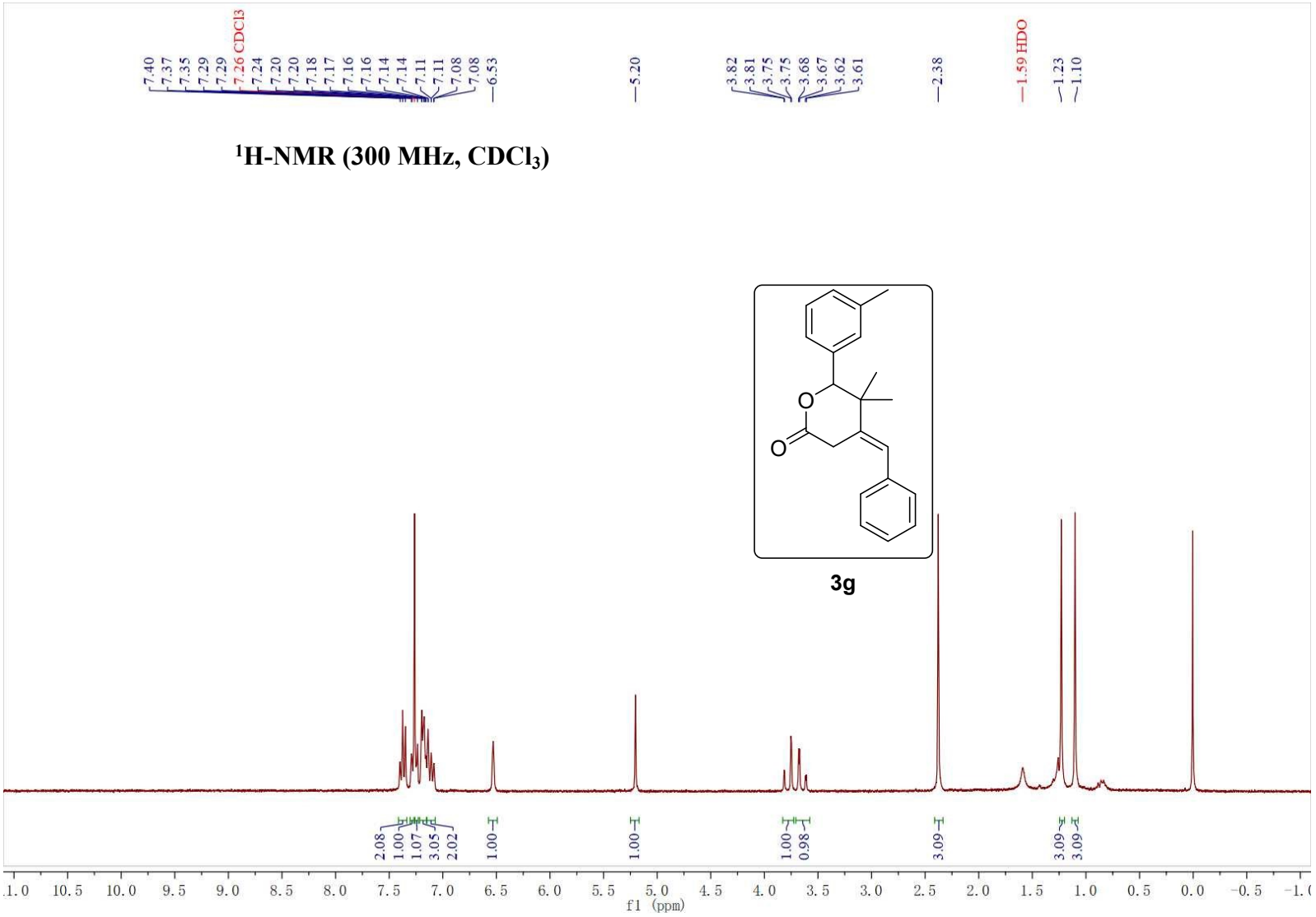
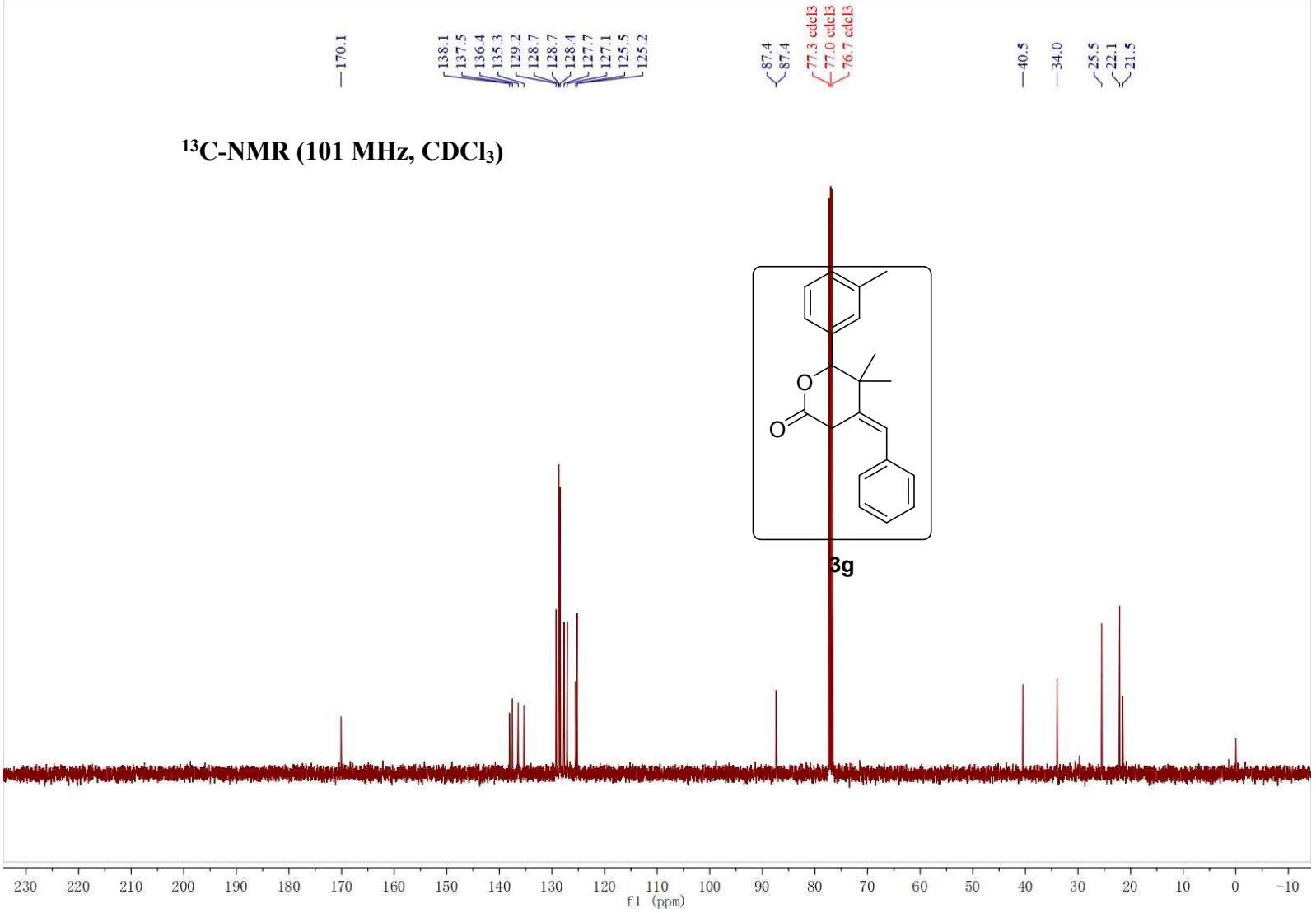
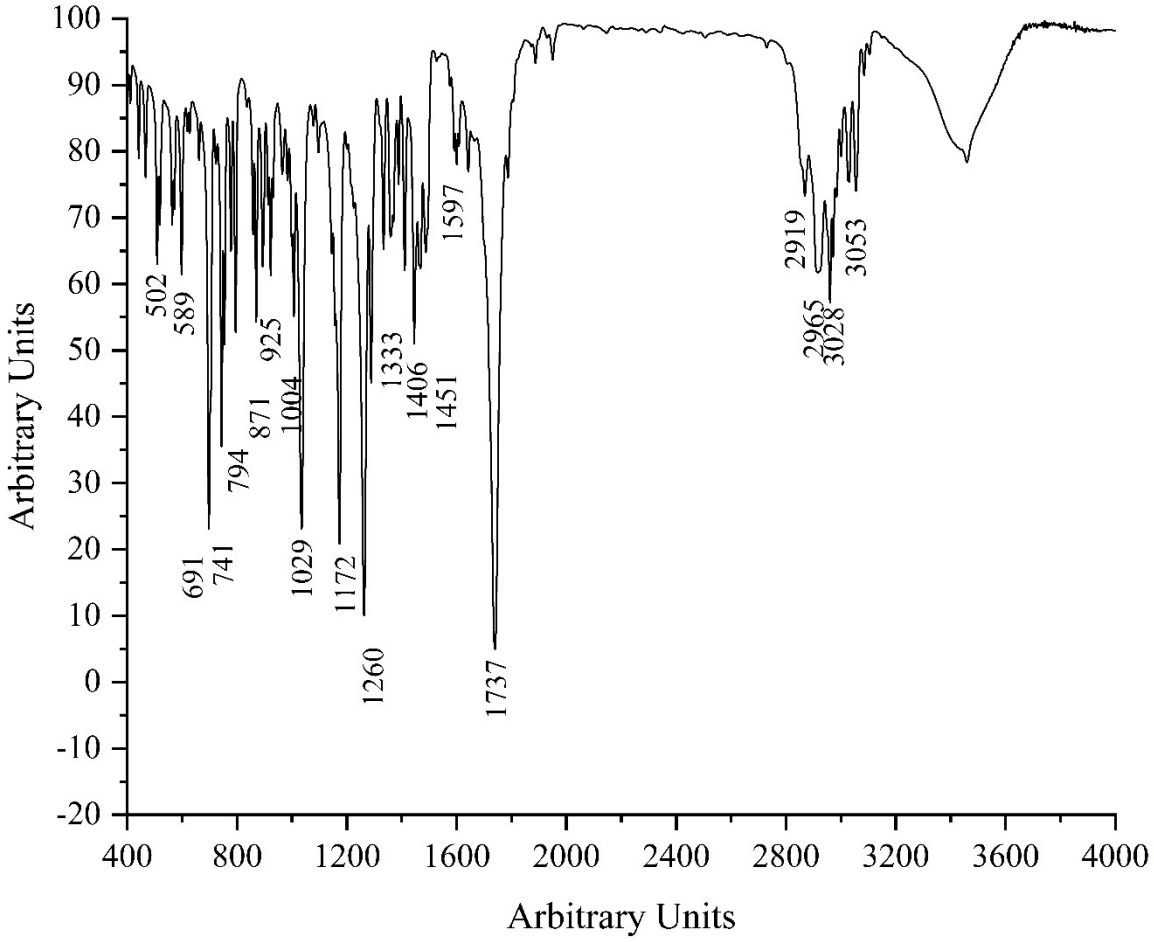


^{1}H-NMR (300 MHz, $CDCl_3$)

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




Arbitrary Units
Arbitrary Units
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1200
1600
2000
2400
2800
3200
3600
4000
502
589
691
741
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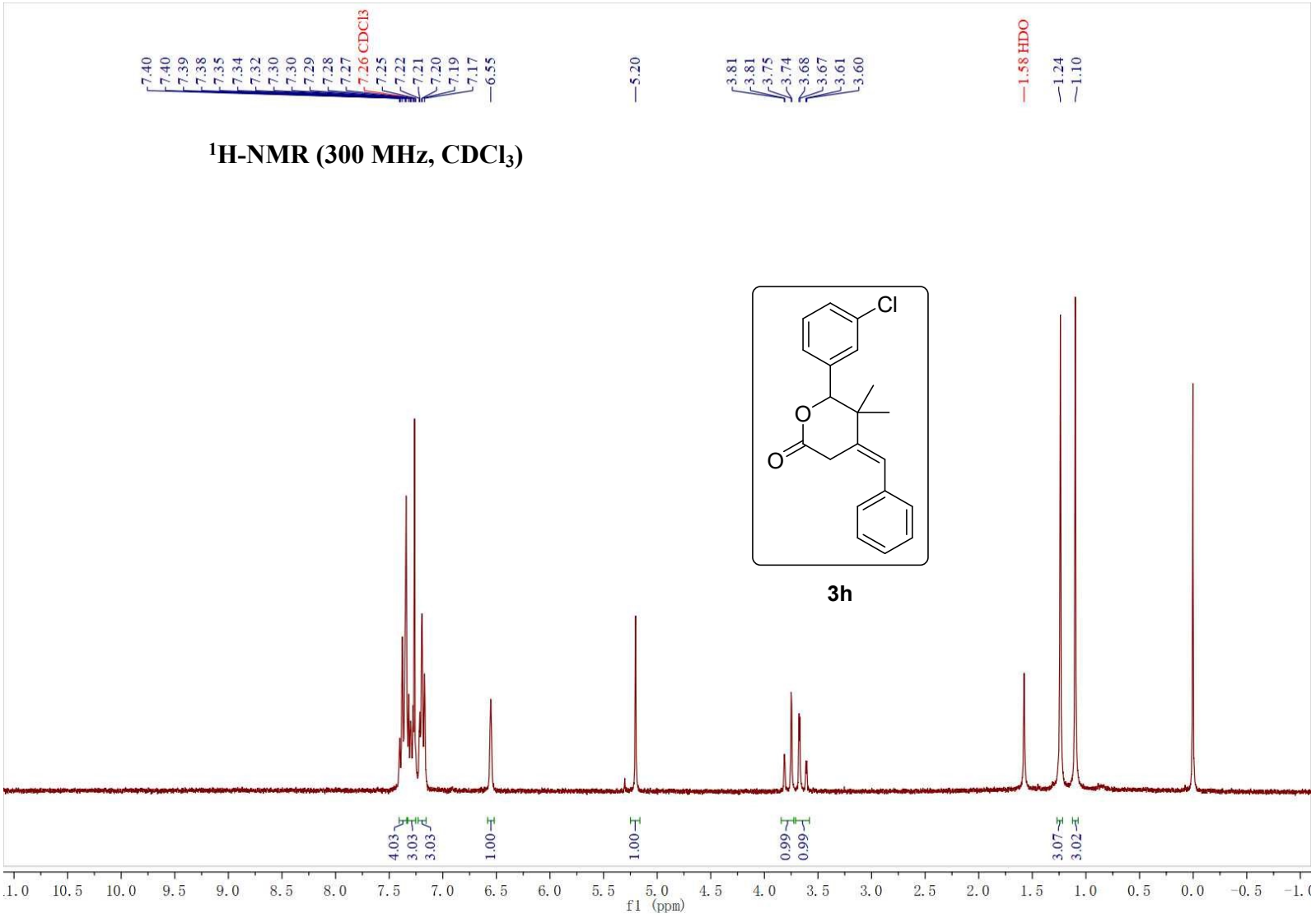
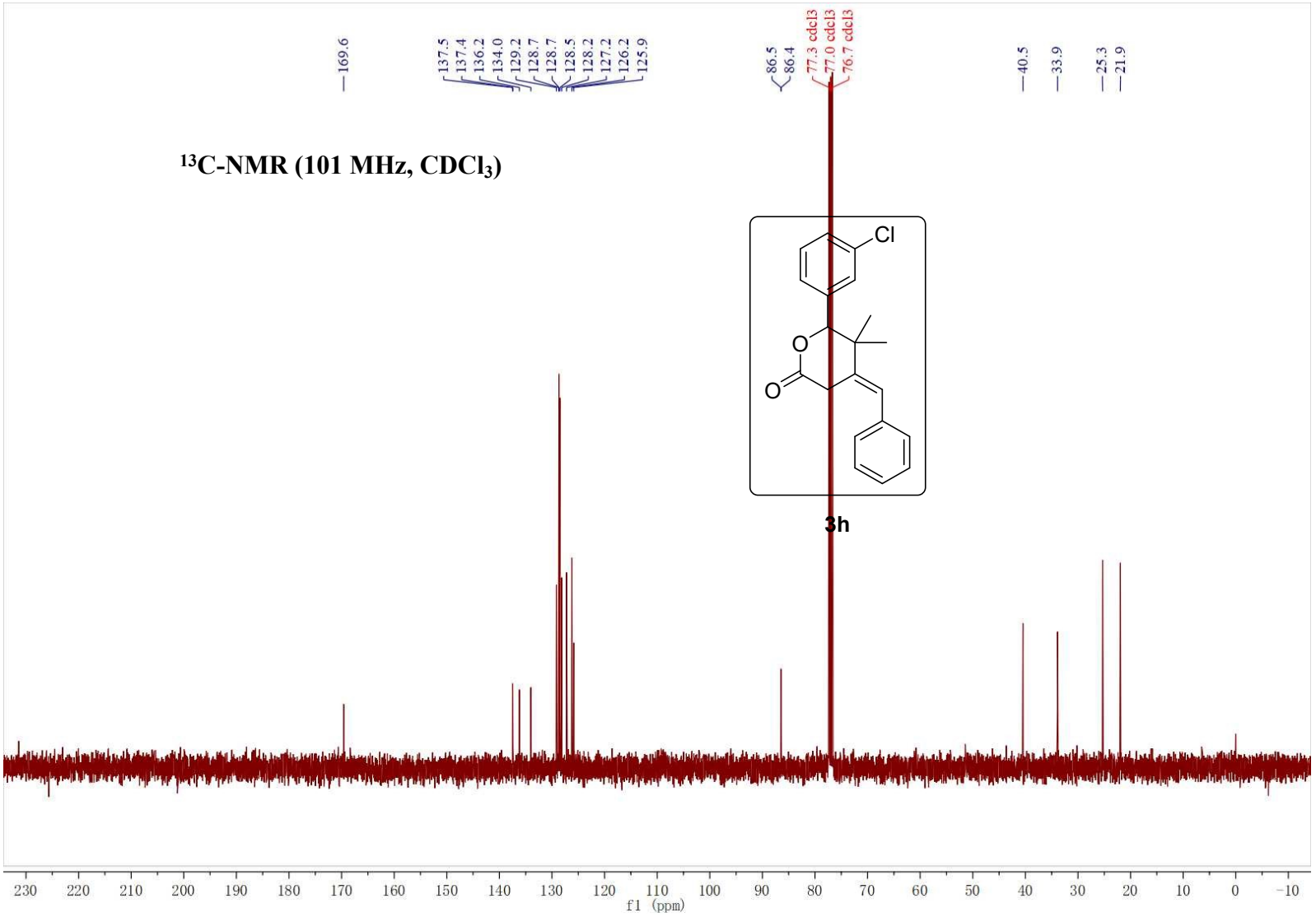
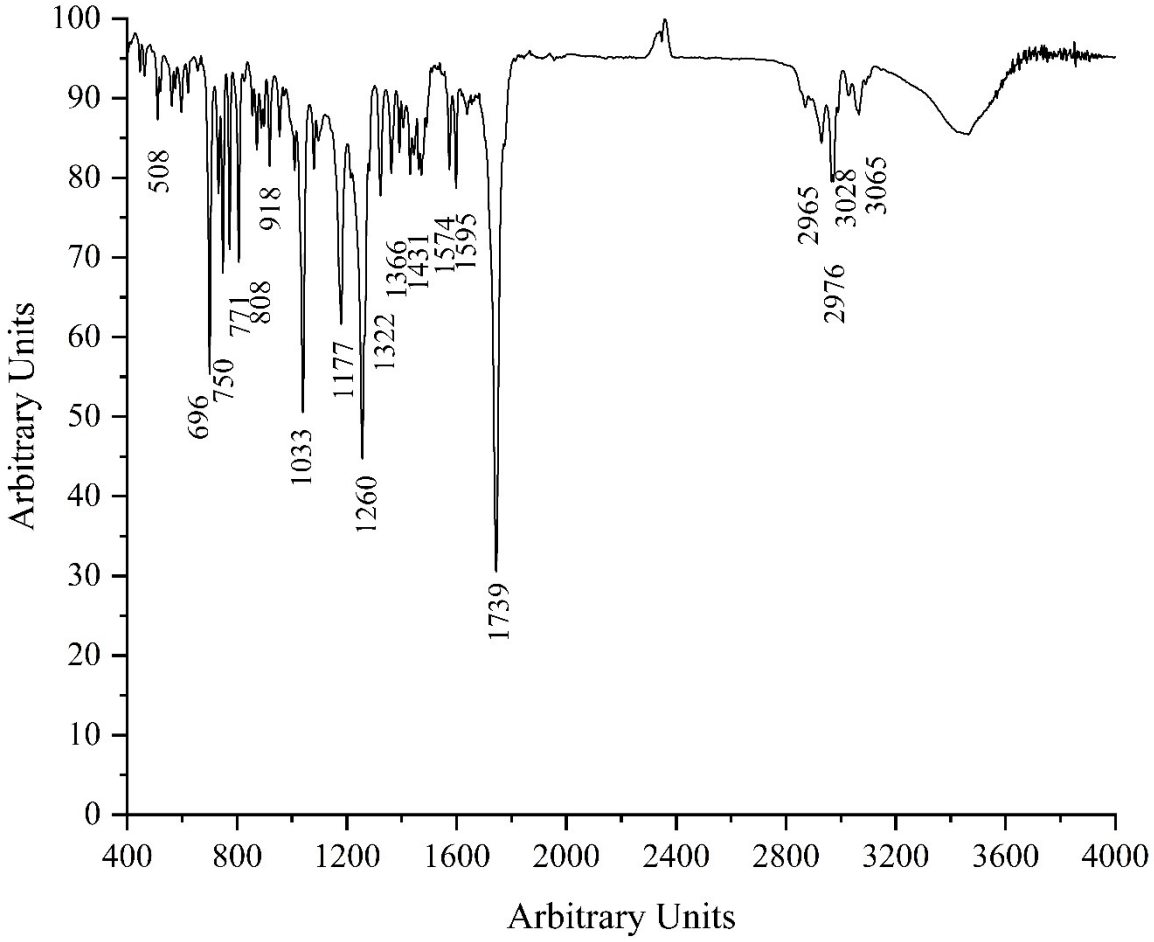


^{1}H-NMR (300 MHz, $CDCl_3$)

3h

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




100
90
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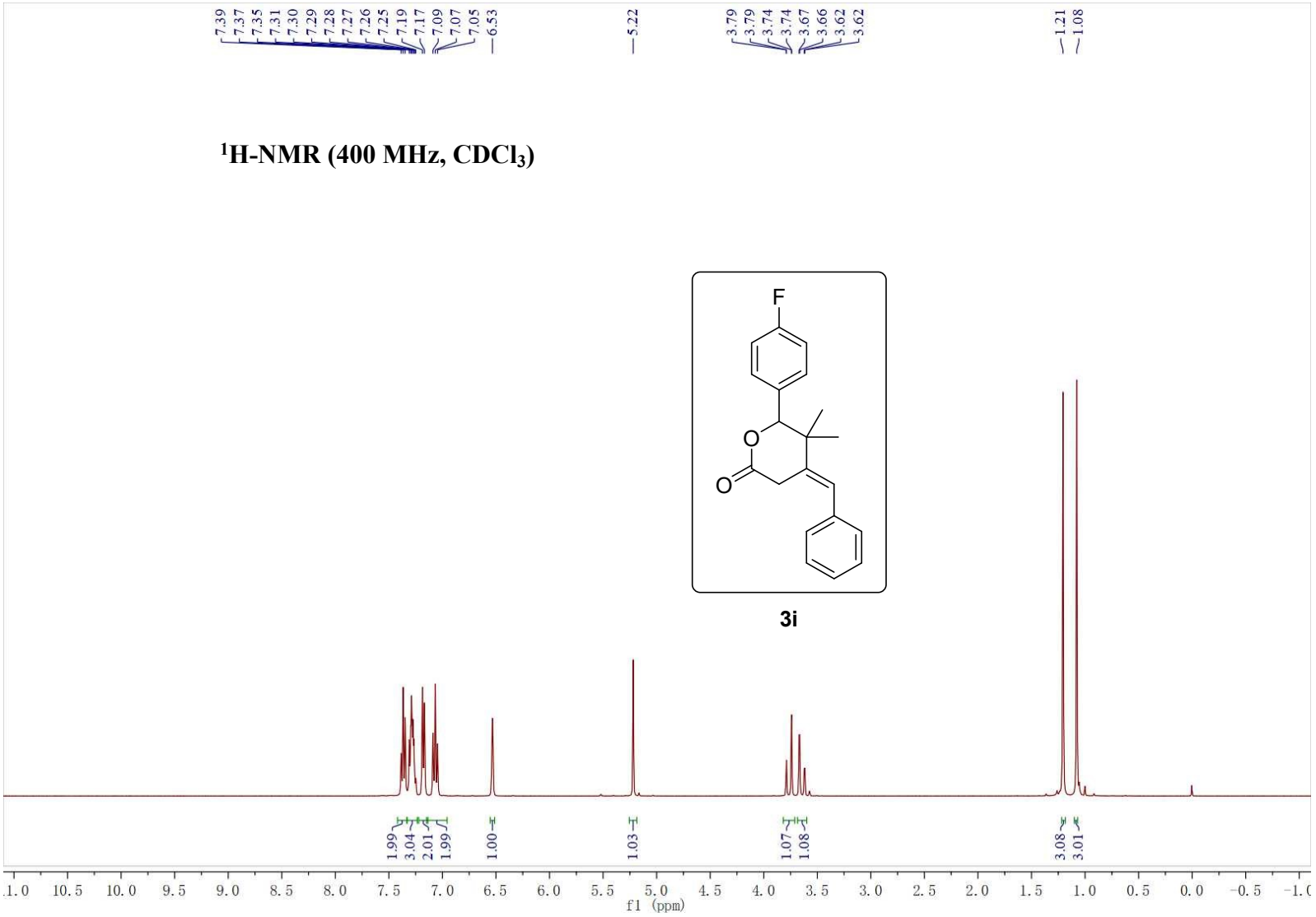
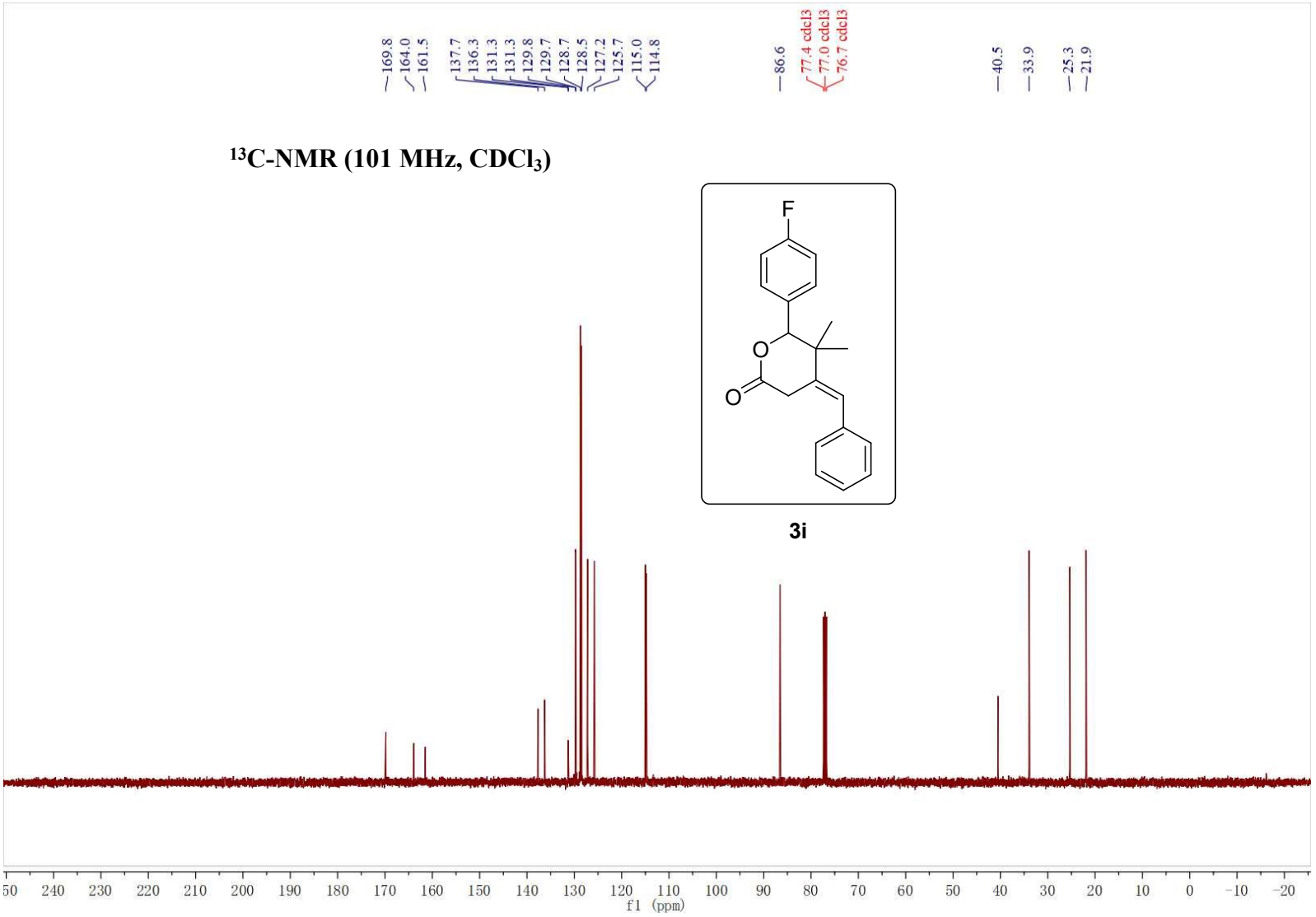
70
60
50
40
30
20
10
0
Arbitrary Units
400
800
1200
1600
2000
2400
2800
3200
3600
4000
Arbitrary Units
508
696
750
771
808
918
1033
1177
1260
1322
1366
1431
1574
1595
1739
2965
2976
3028
3065

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

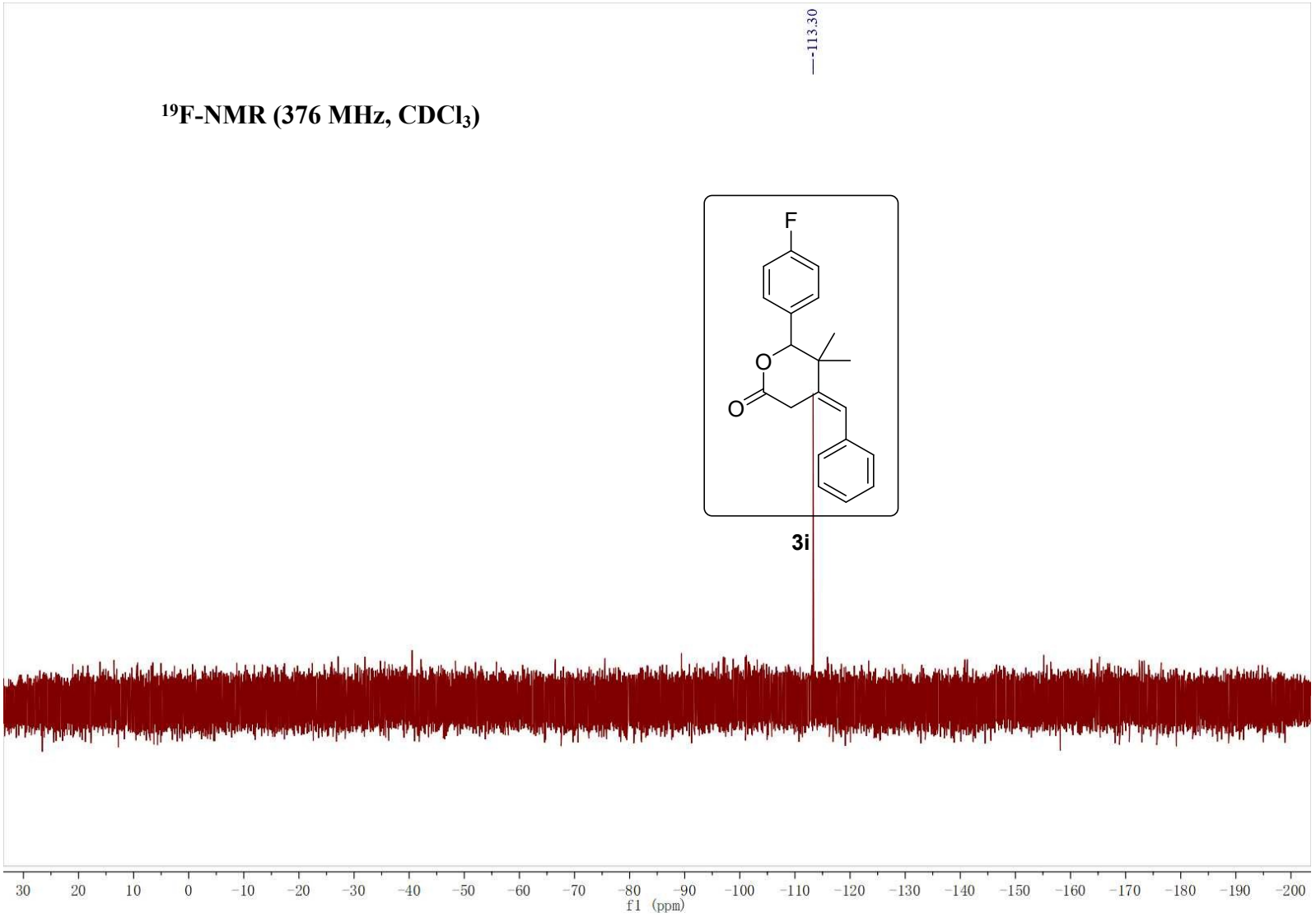


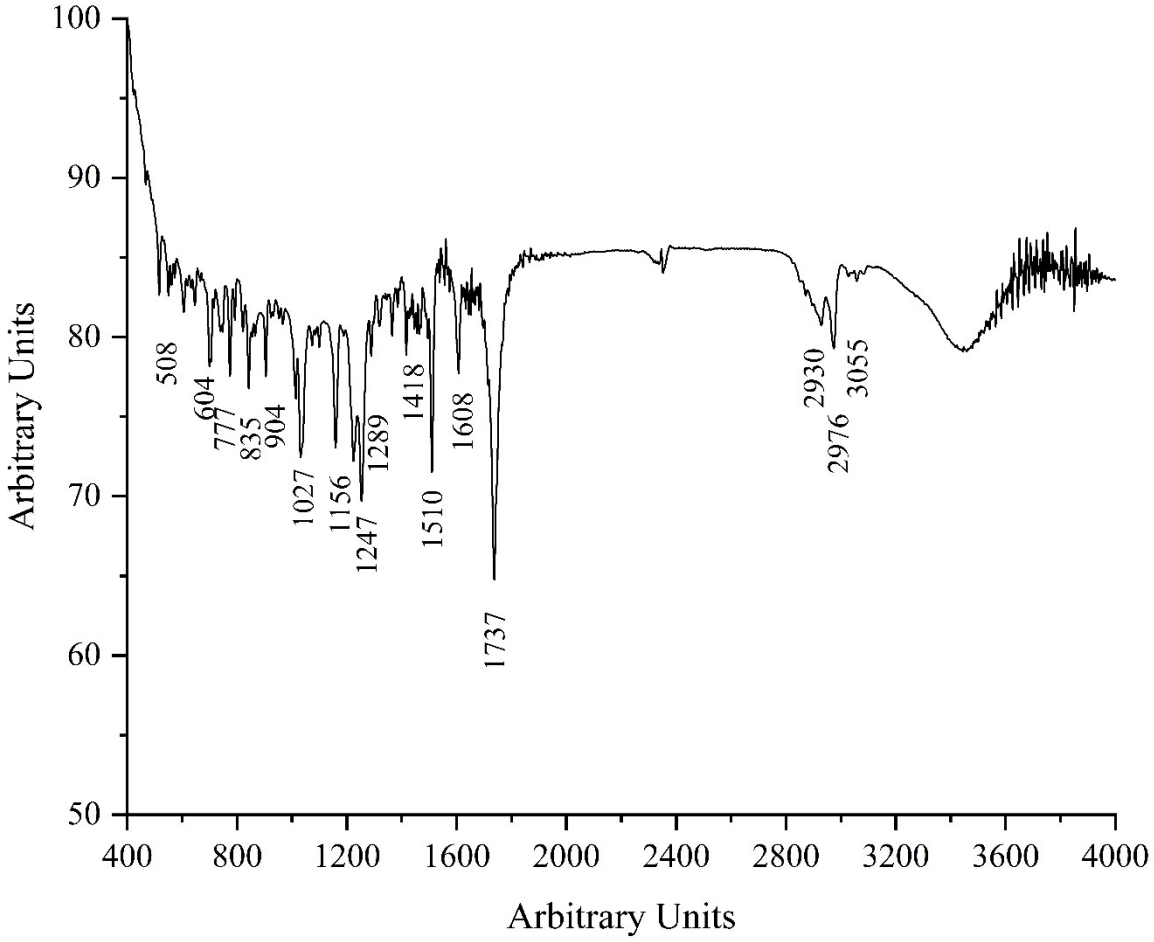
^{13}C-NMR (101 MHz, $CDCl_3$)



3i

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




100
90
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50
Arbitrary Units
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604
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904
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1247
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1418
1510
1608
1737
2930
2976
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400
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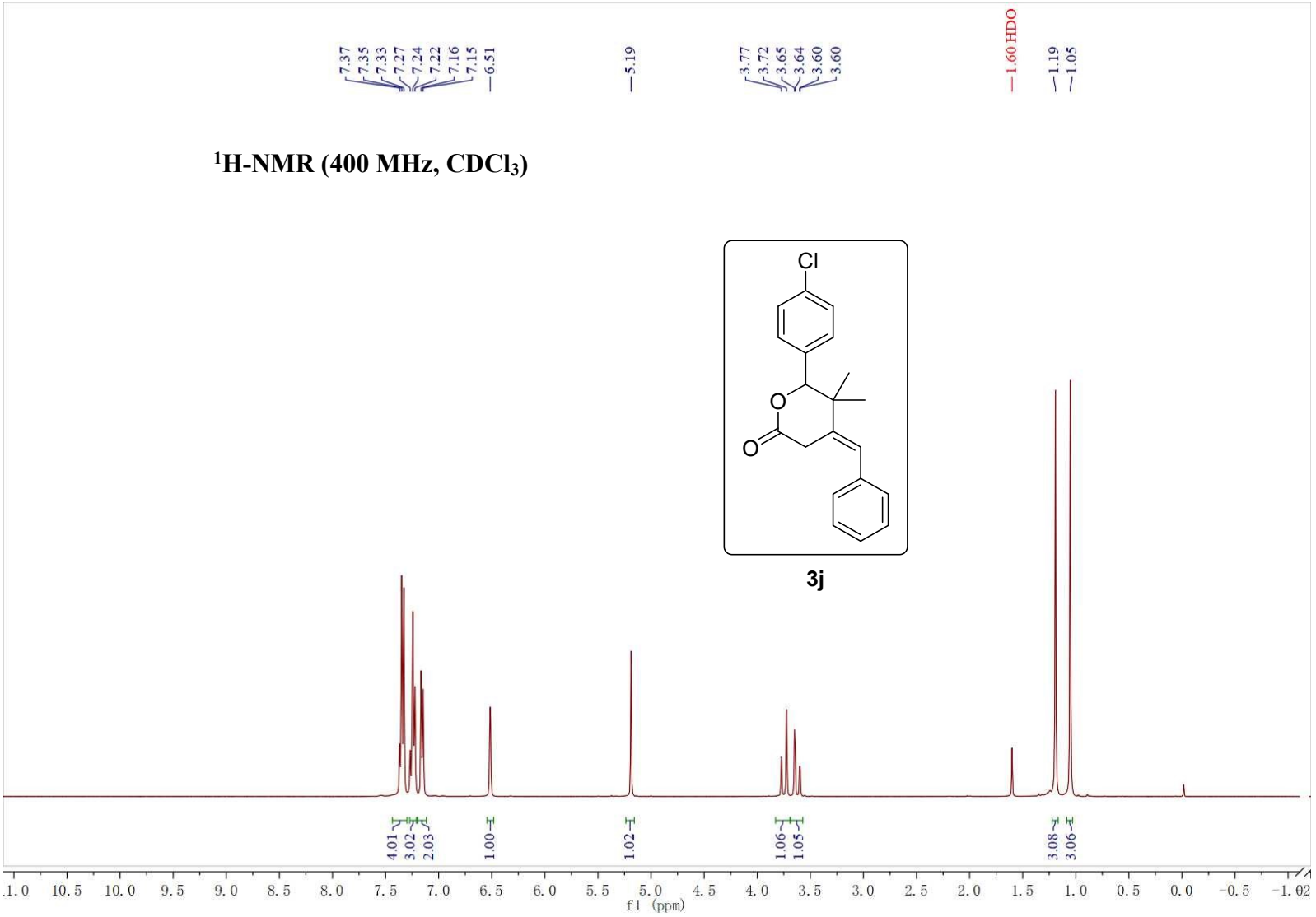
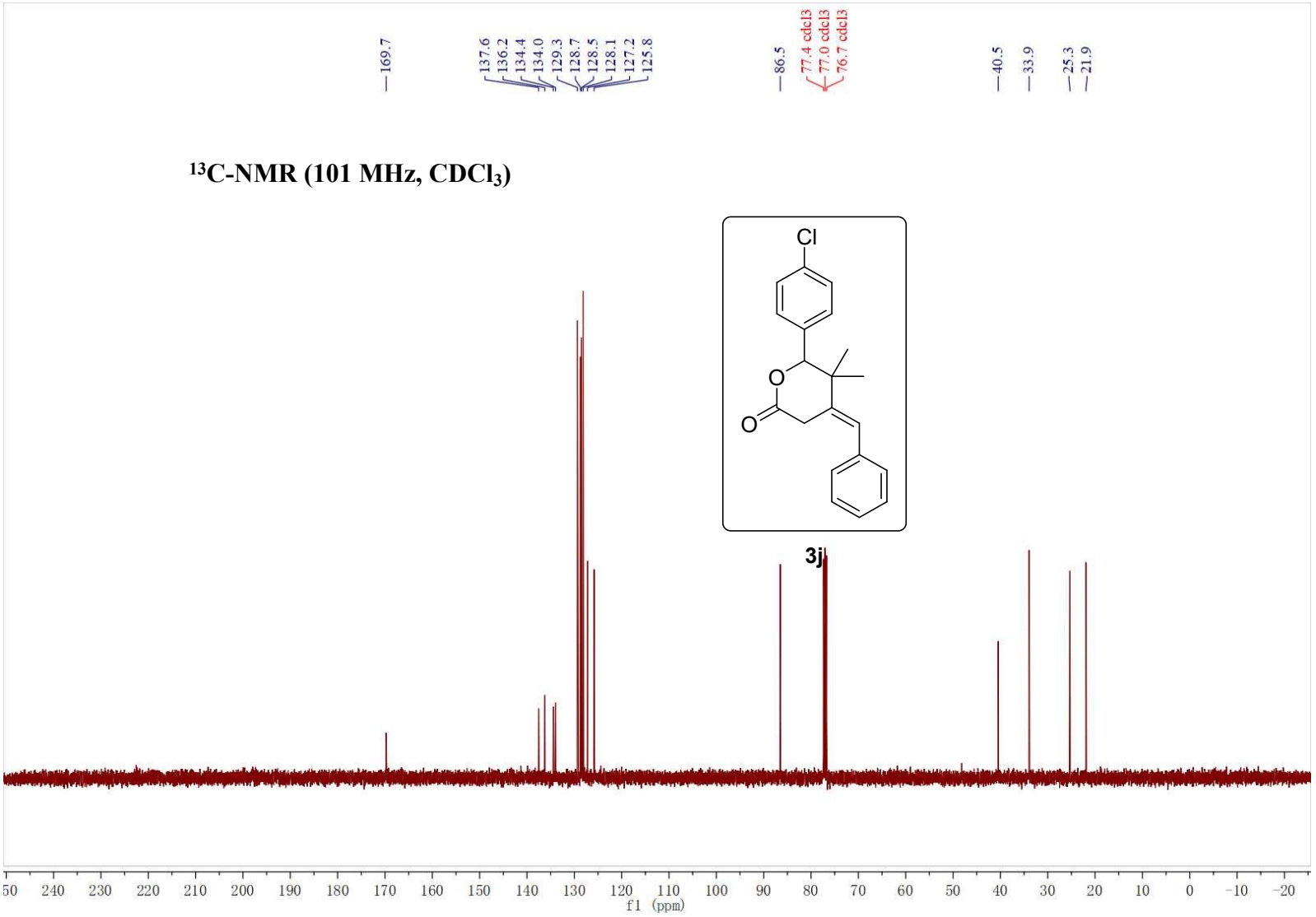
1600
2000
2400
2800
3200
3600
4000
Arbitrary Units

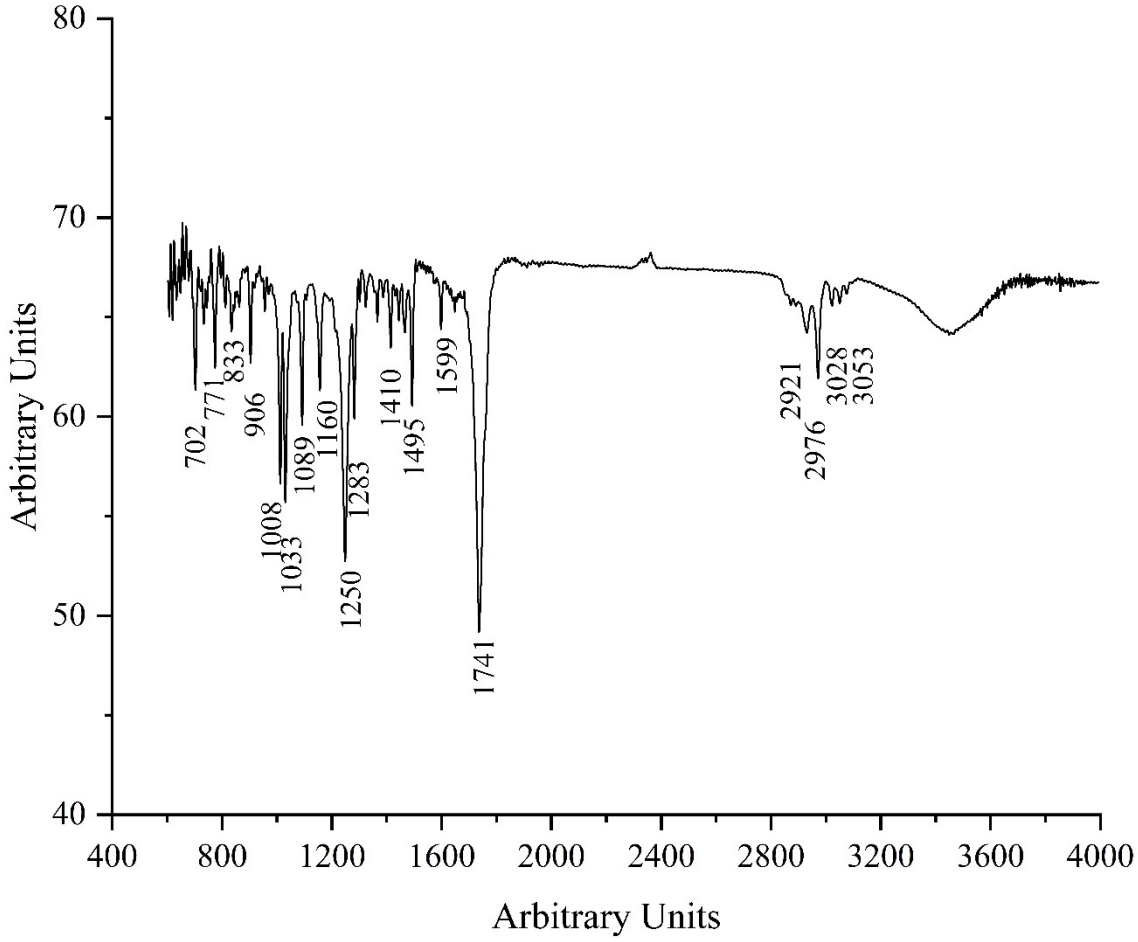
^{1}H-NMR (400 MHz, $CDCl_3$)



3j



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


80
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40
Arbitrary Units
400
800
1200
1600
2000
2400
2800
3200
3600
4000
Arbitrary Units
702
771
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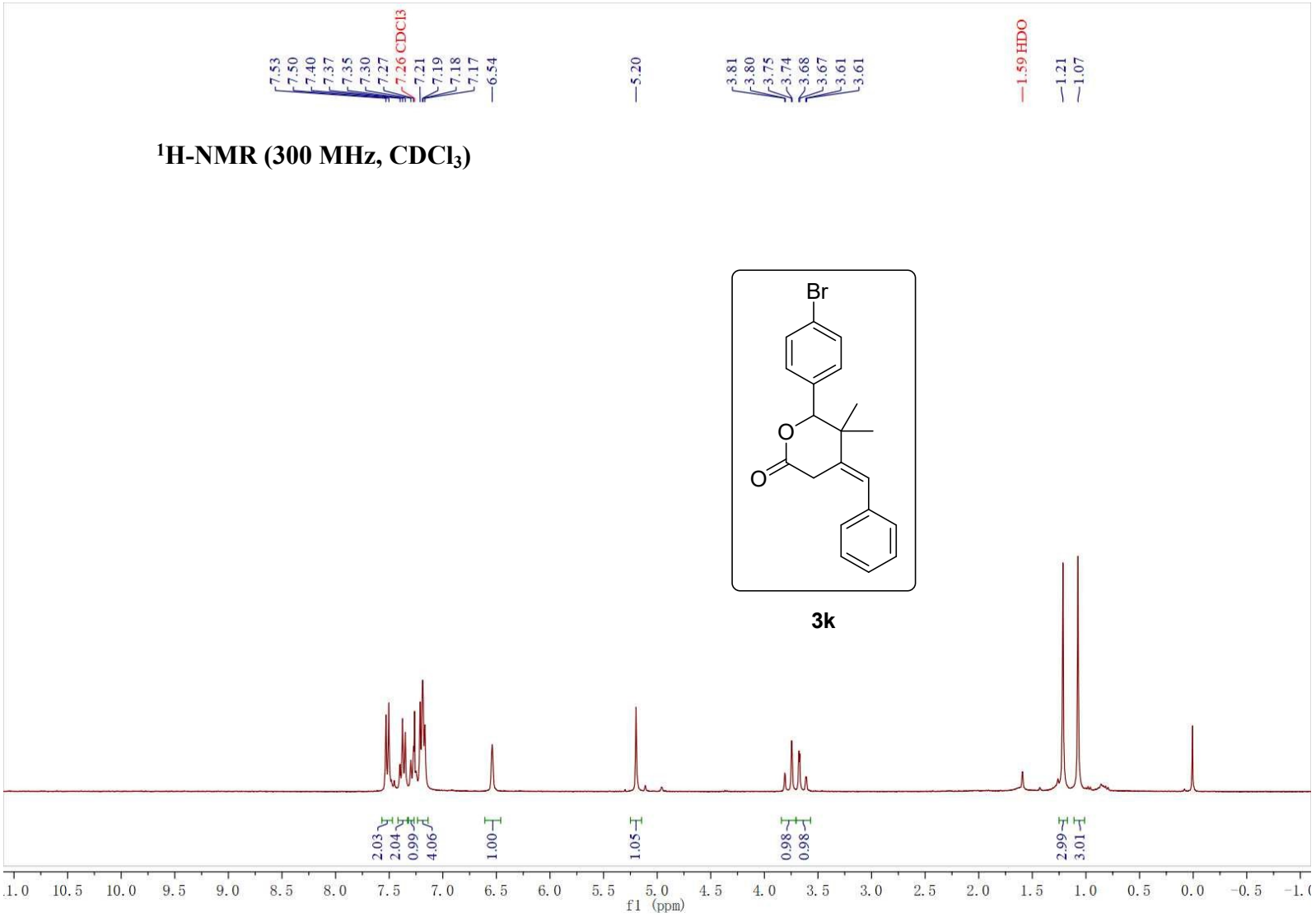
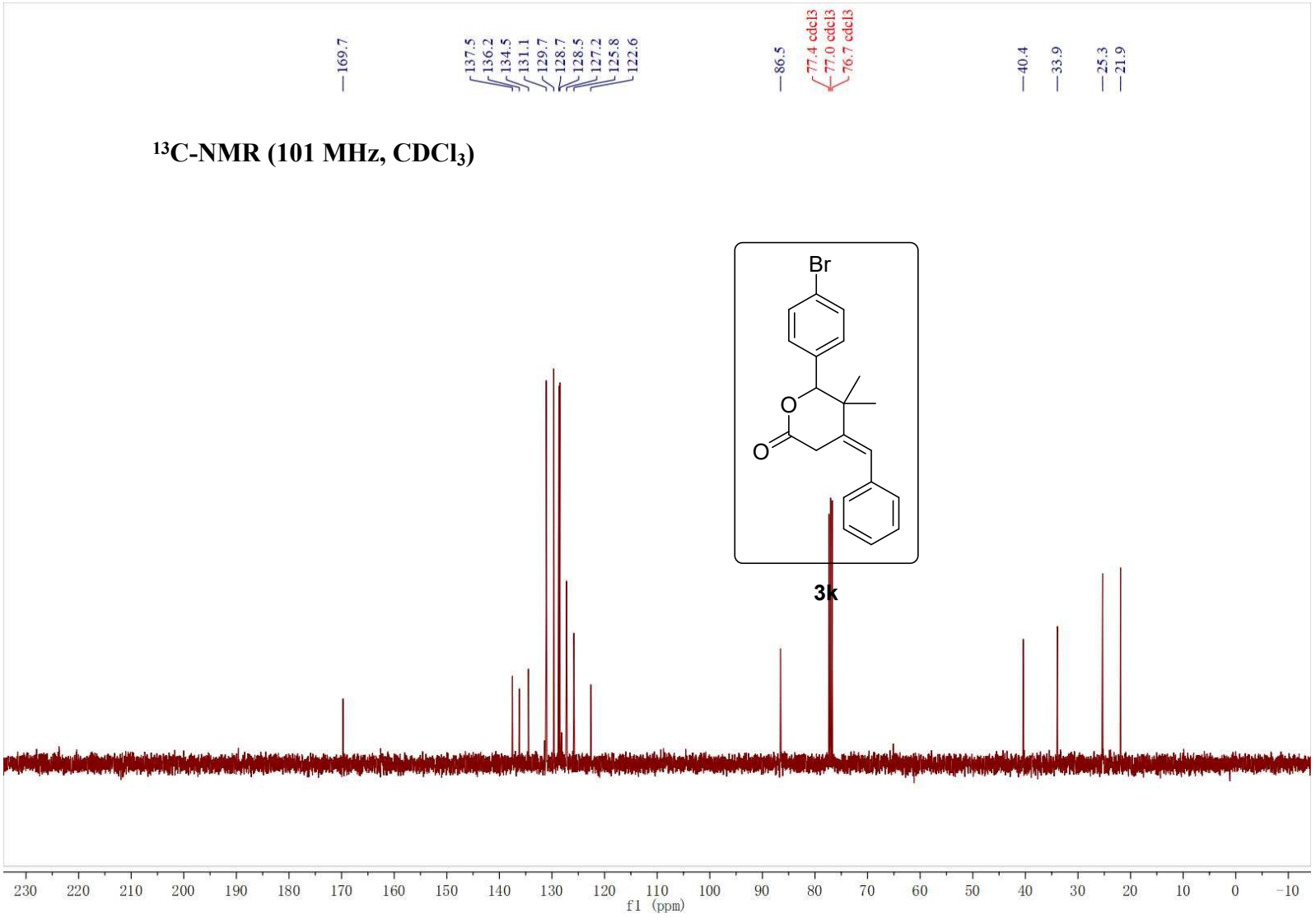
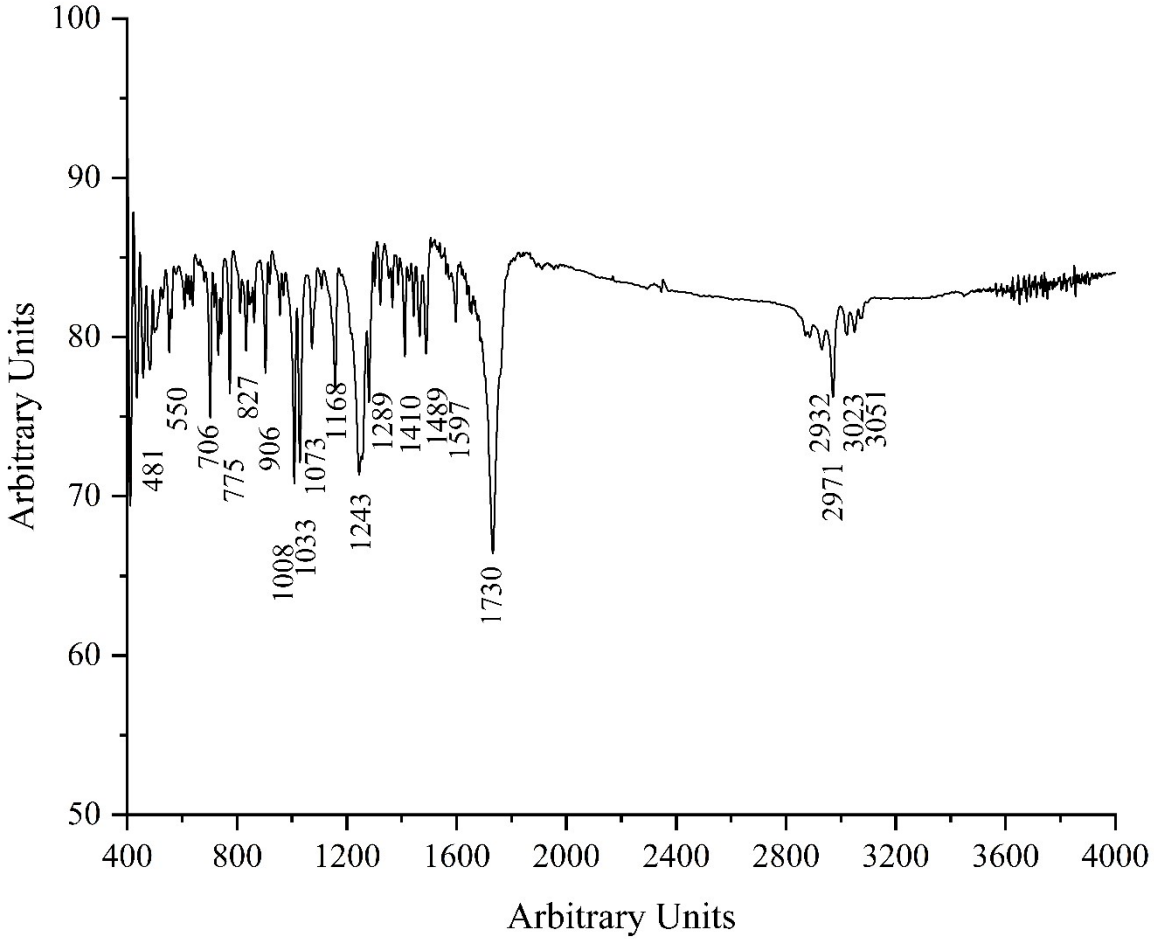


^{1}H-NMR (300 MHz, $CDCl_3$)

3k

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




100
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50
Arbitrary Units
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2000
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2800
3200
3600
4000
Arbitrary Units
481
550
706
775
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906
1008
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1073
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2971
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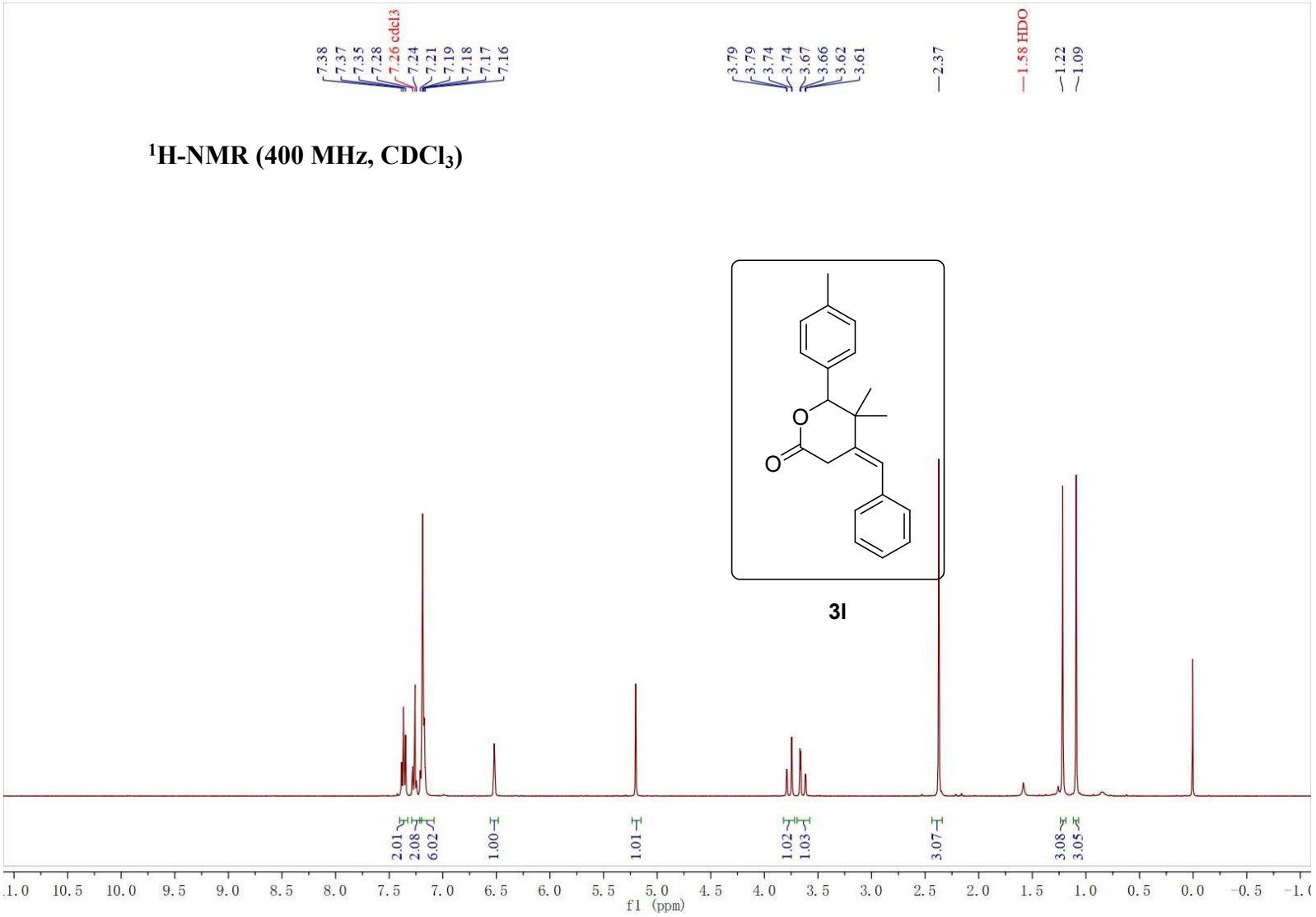
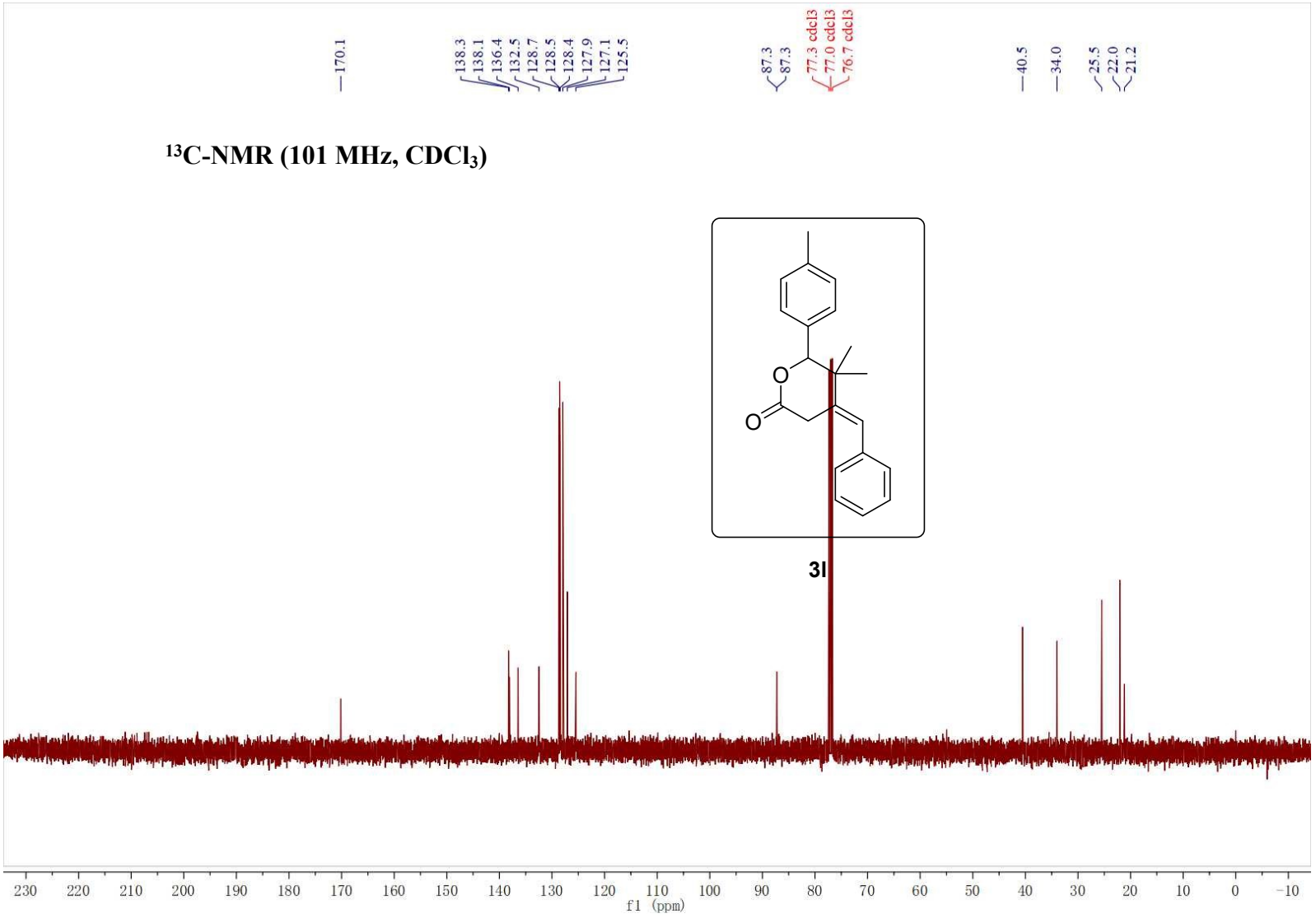
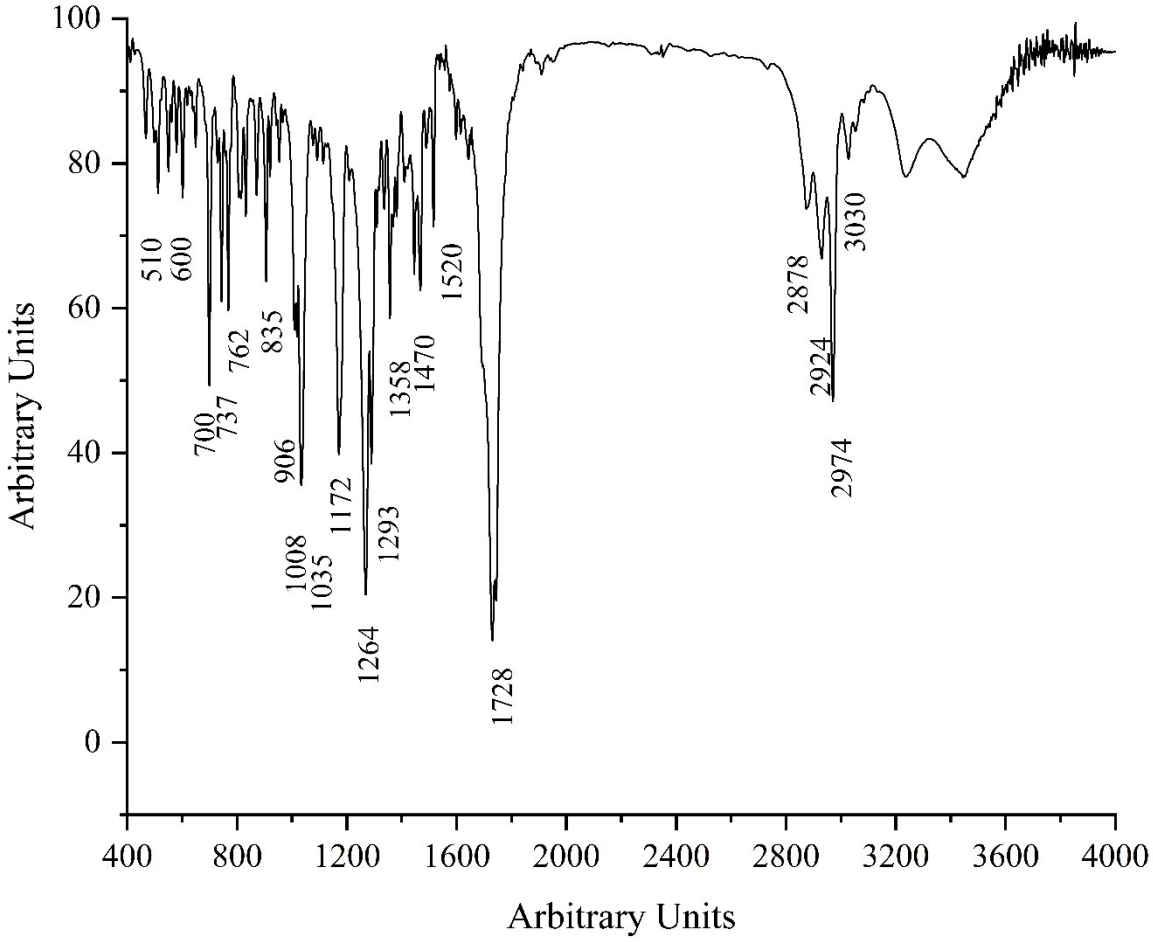
3051

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



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

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20
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Arbitrary Units
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1200
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2000
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2800
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Arbitrary Units
510
600
700
737
762
835
906
1008
1035
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1728
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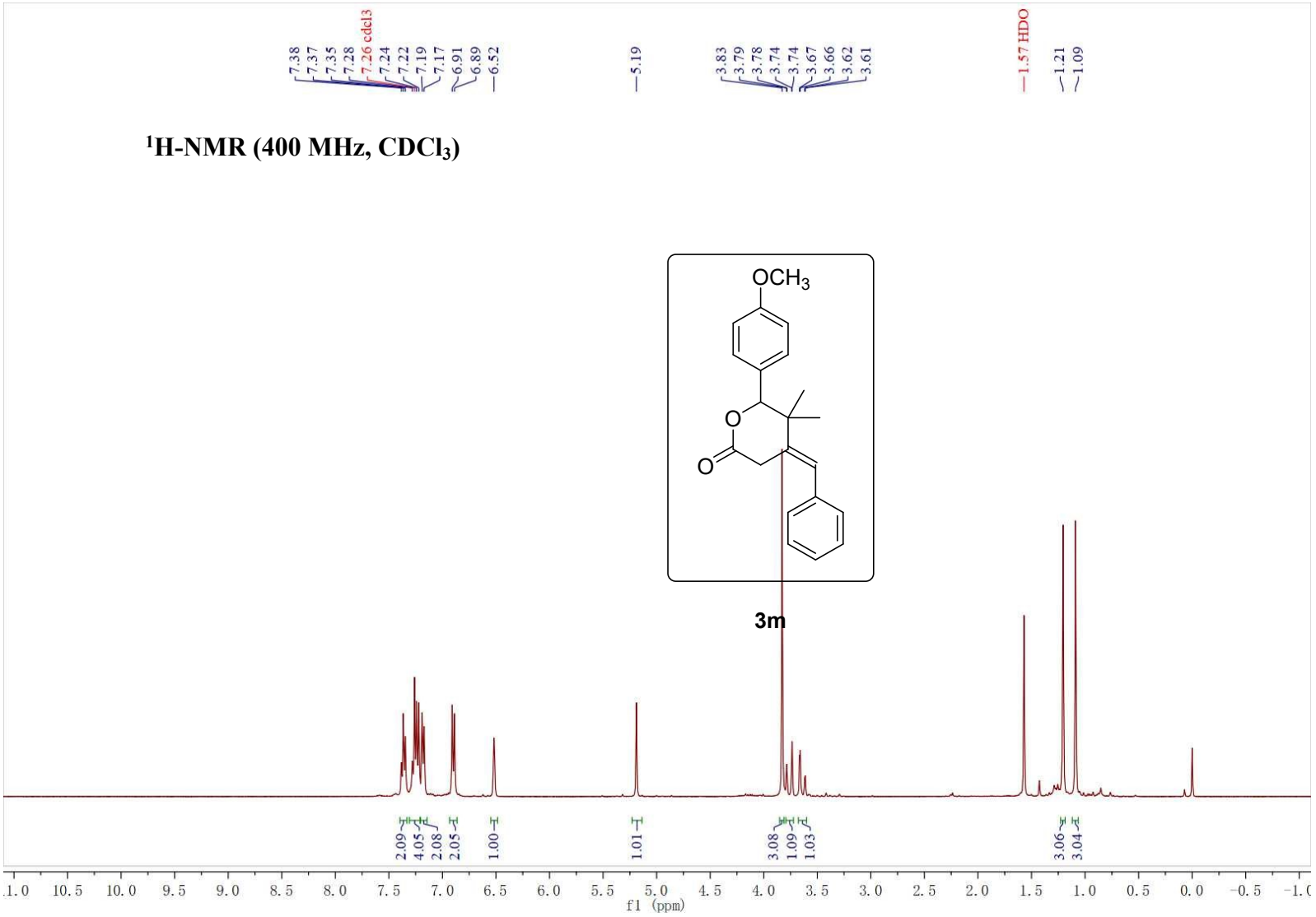
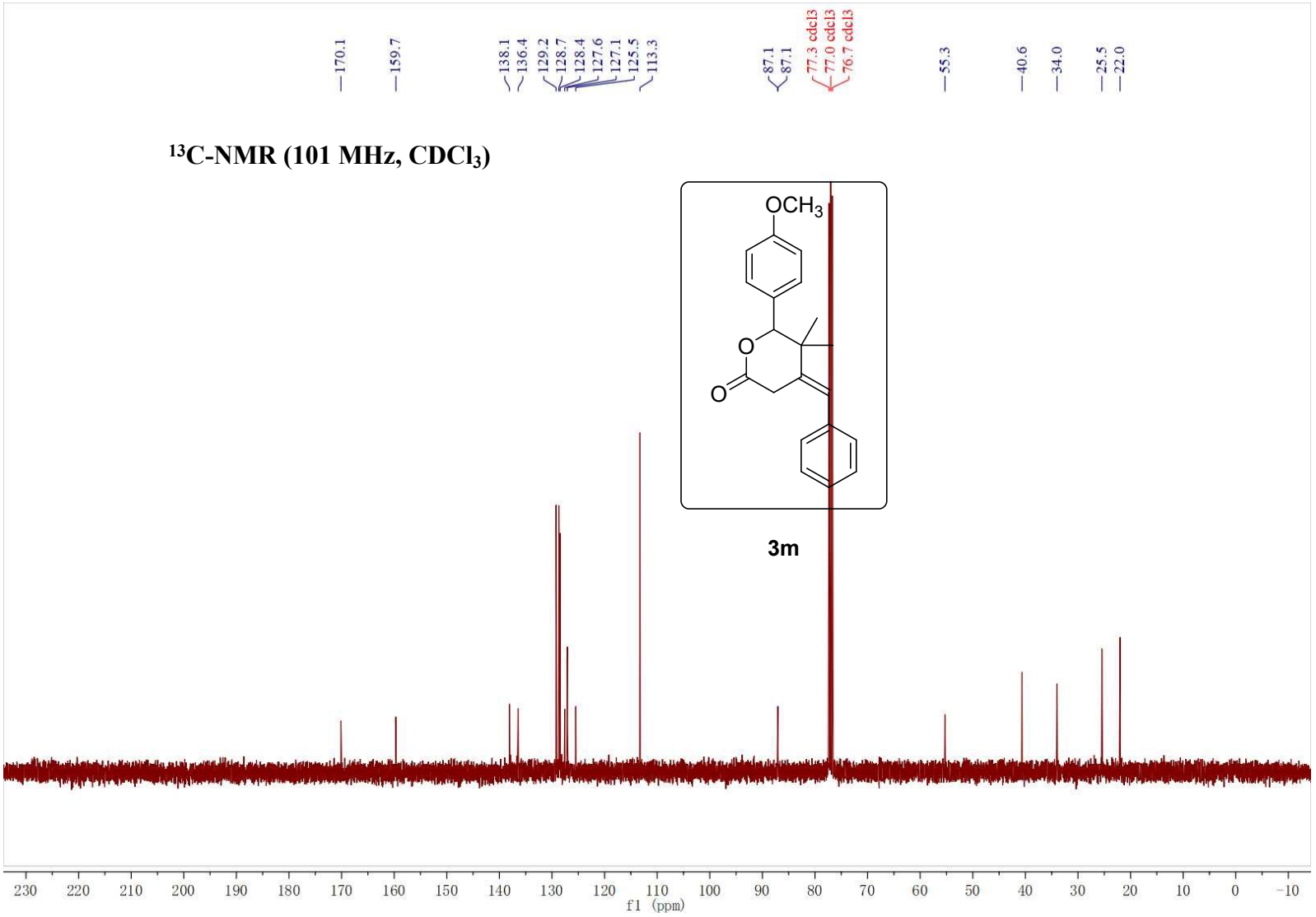
3030

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

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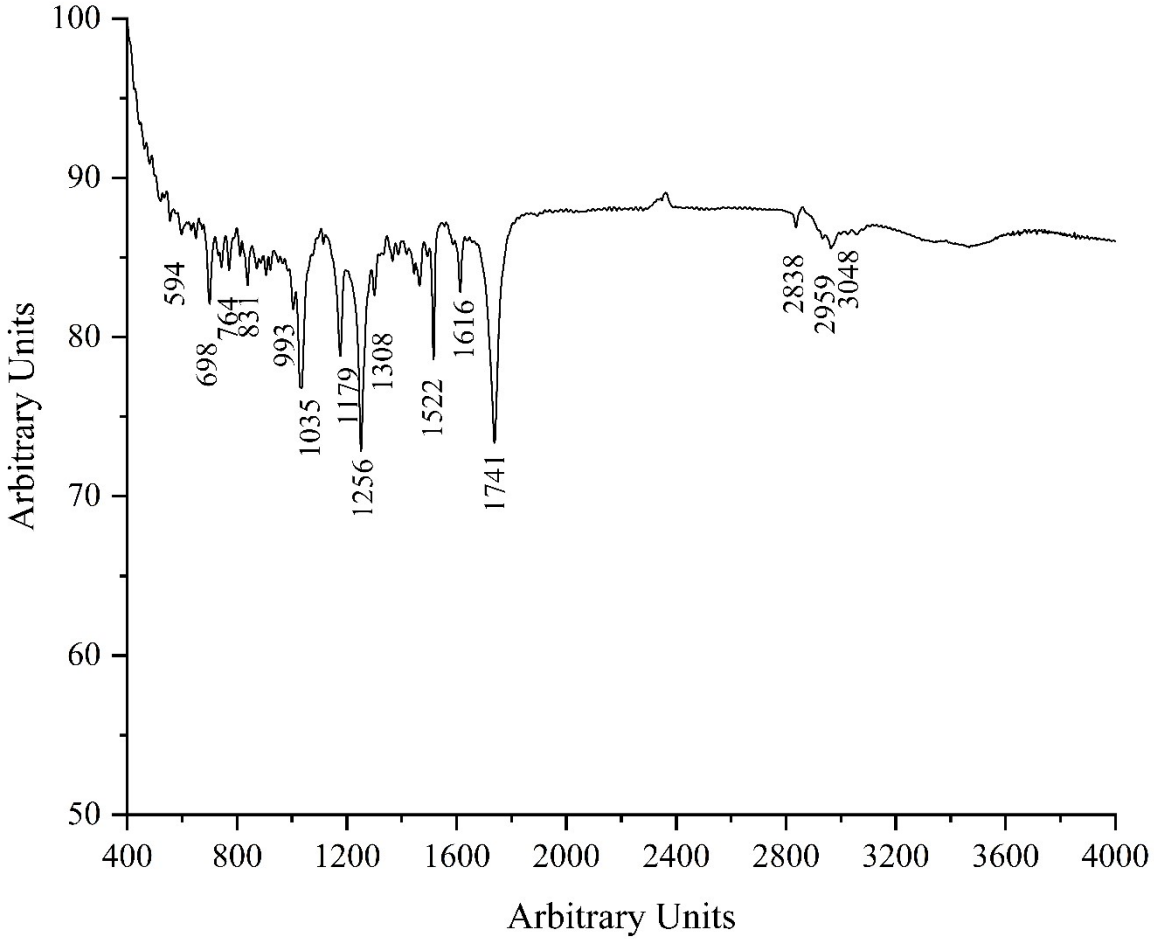
138.1
136.4
129.2
128.7
128.4
127.6
127.1
125.5
113.3
87.1
87.1
77.3 cdcl3
77.0 cdcl3
76.7 cdcl3
55.3
40.6
34.0
25.5
22.0
13C-NMR (101 MHz, CDCl3)
OCH3
O
O
3m
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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70
60
50
Arbitrary Units
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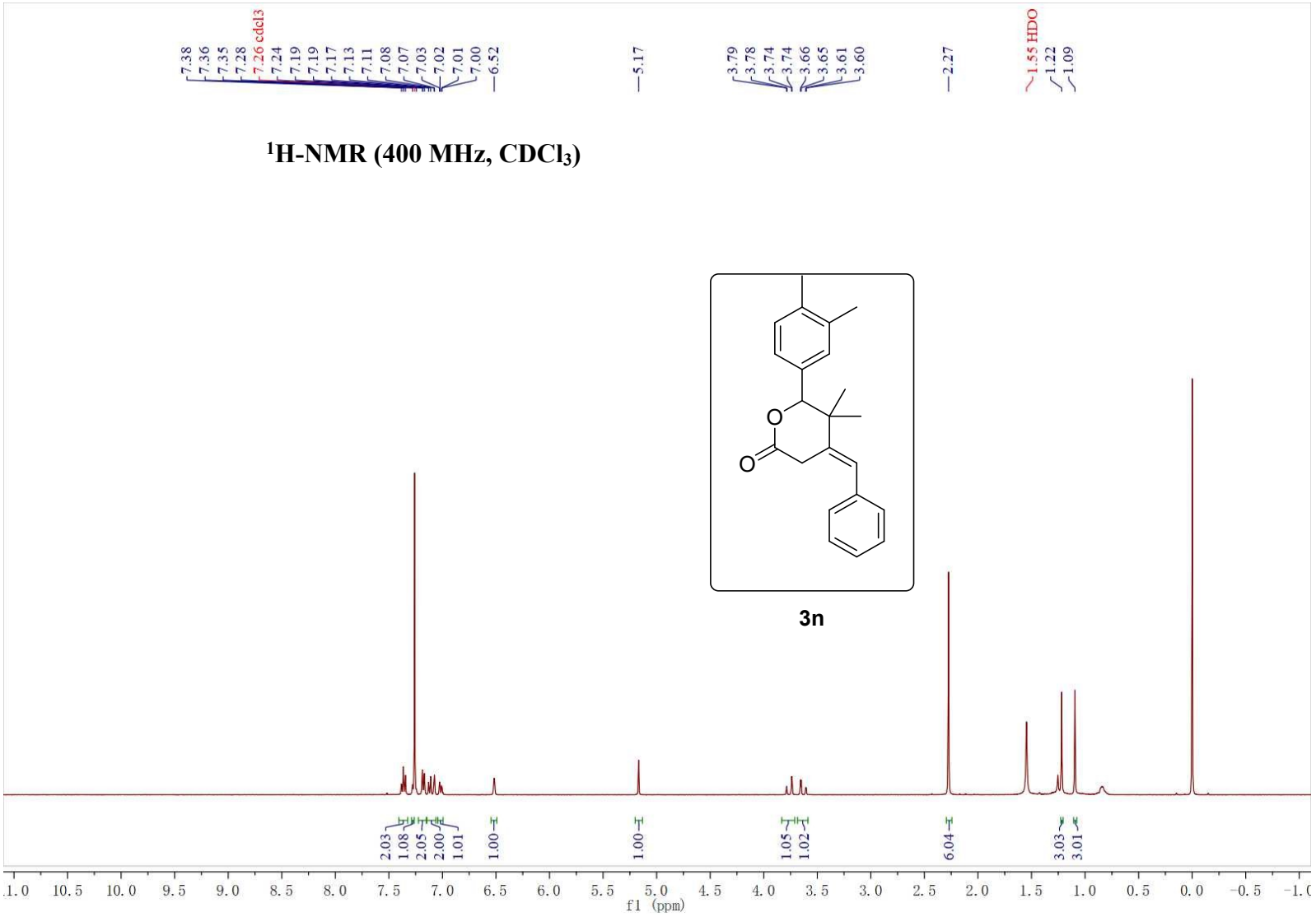
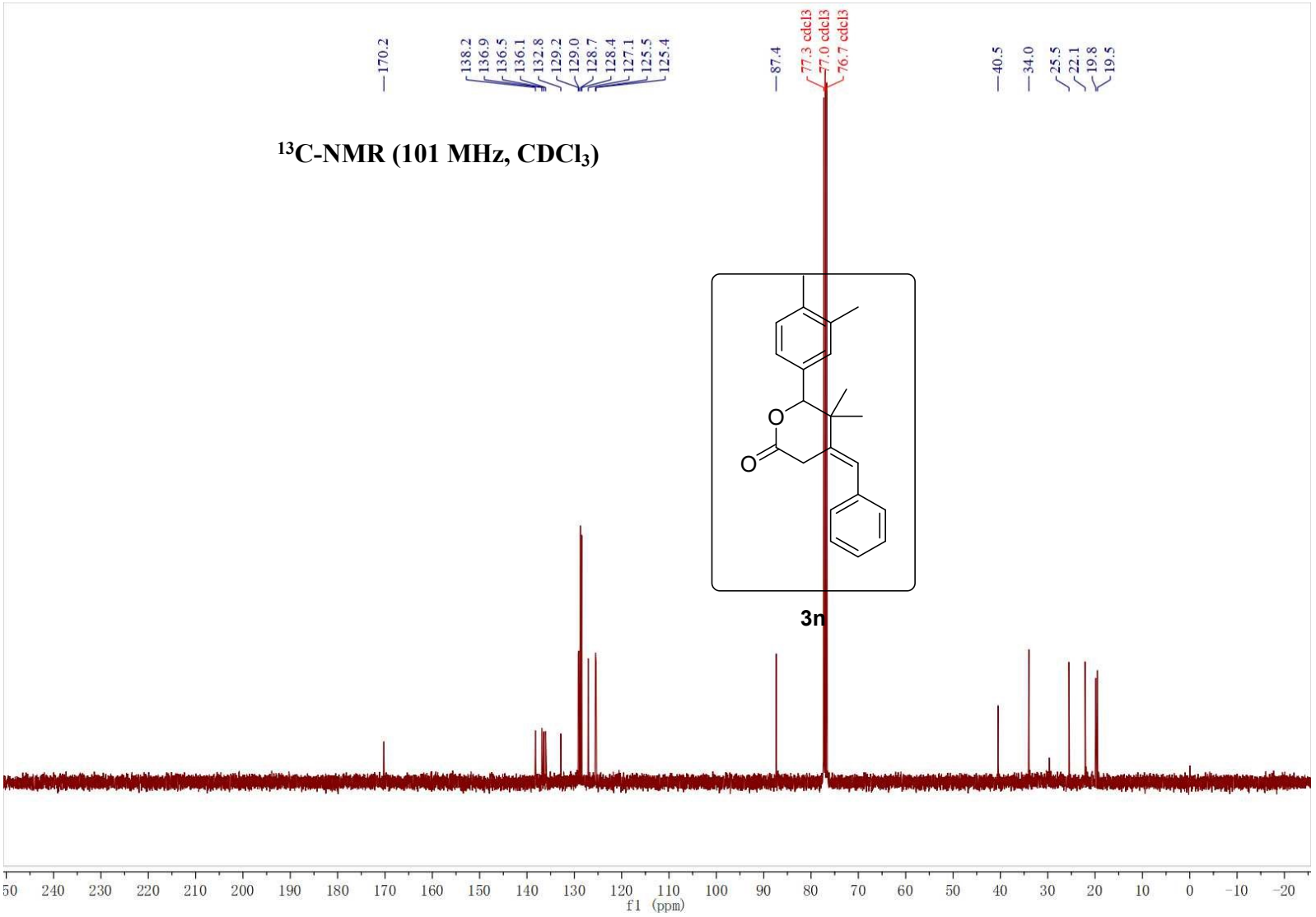
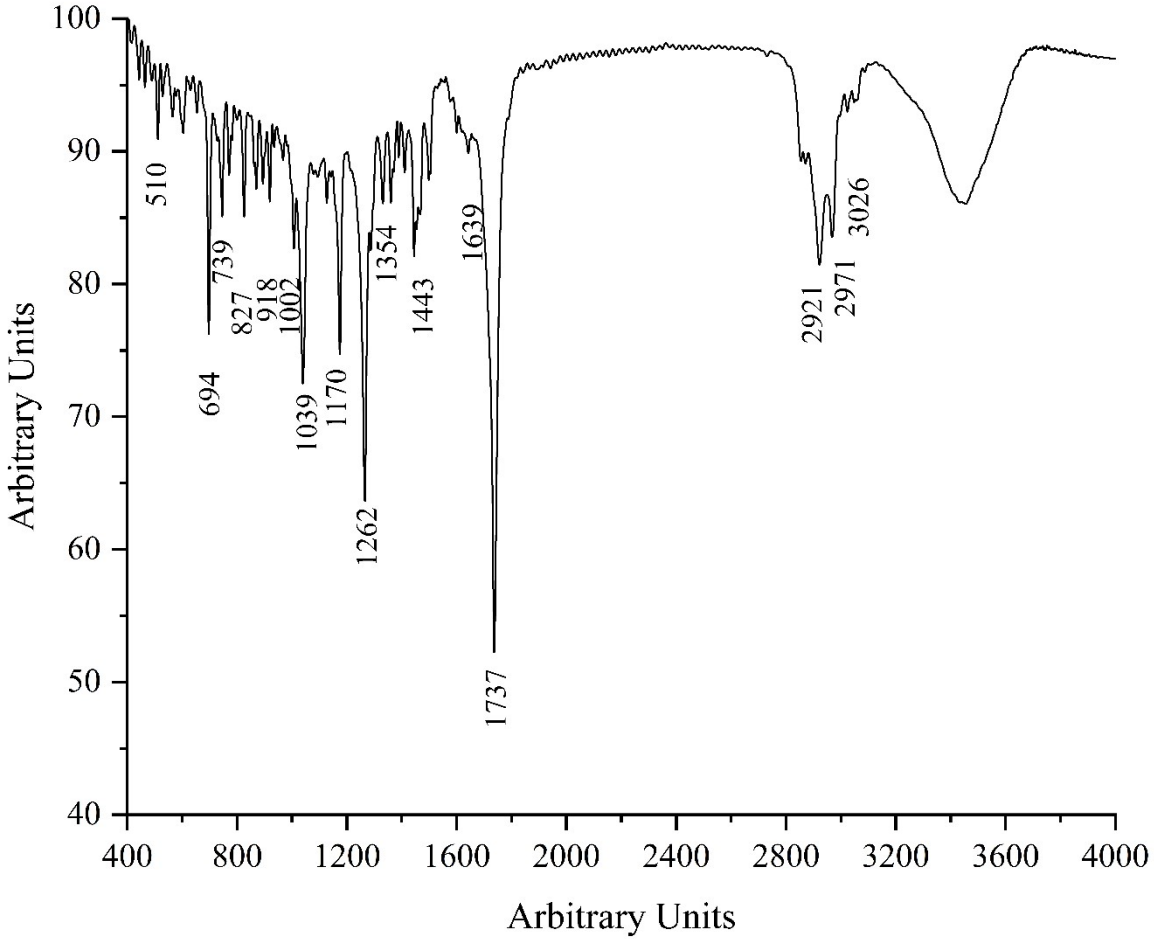
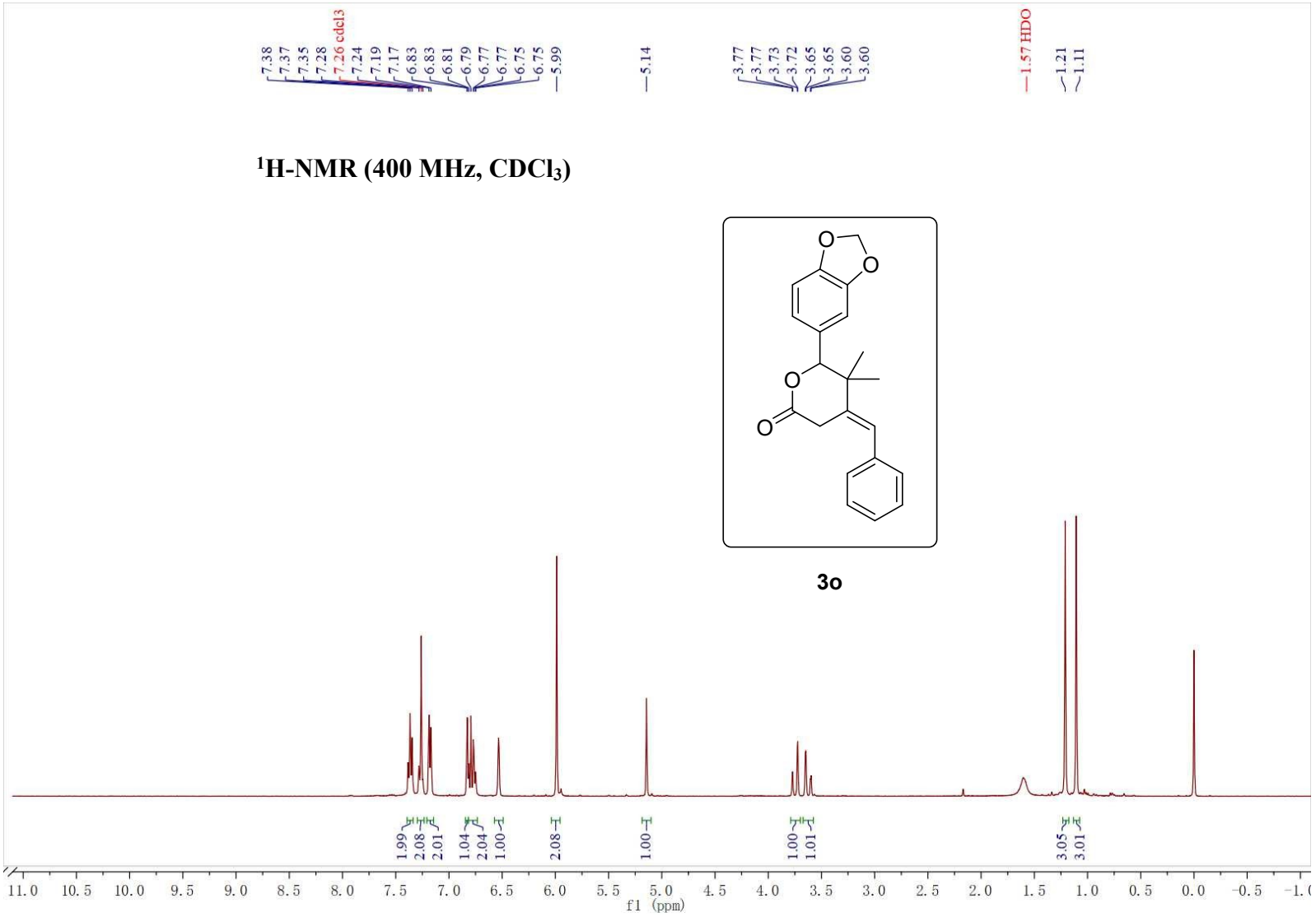


^{1}H-NMR (400 MHz, $CDCl_3$)

3n

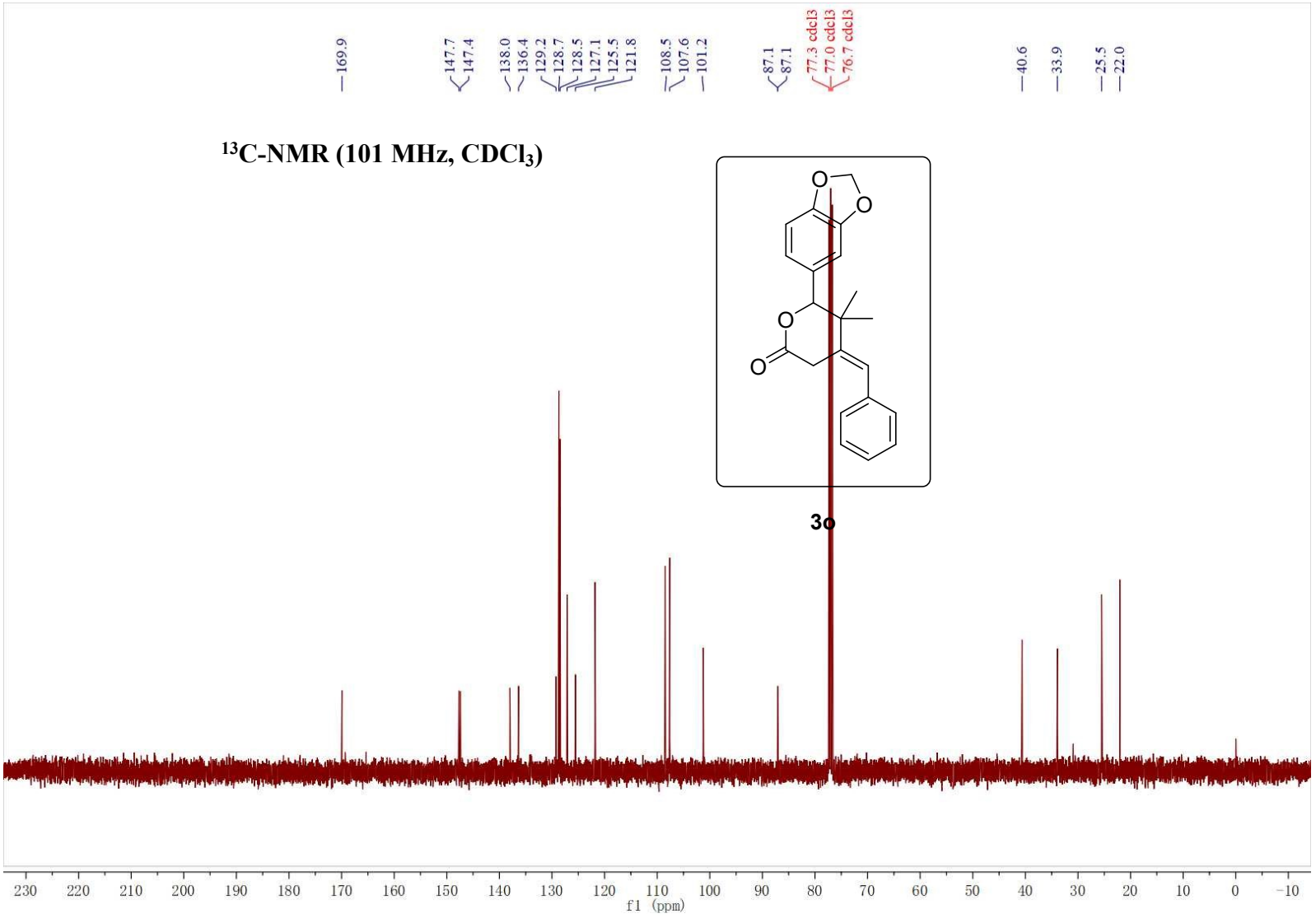

170.2
138.2
136.9
136.5
136.1
132.8
129.2
129.0
128.7
128.4
127.1
125.5
125.4
87.4
77.3 cdcl3
77.0 cdcl3
76.7 cdcl3
40.5
34.0
25.5
22.1
19.8
19.5
13C-NMR (101 MHz, CDCl3)
O
O
3n
f1 (ppm)

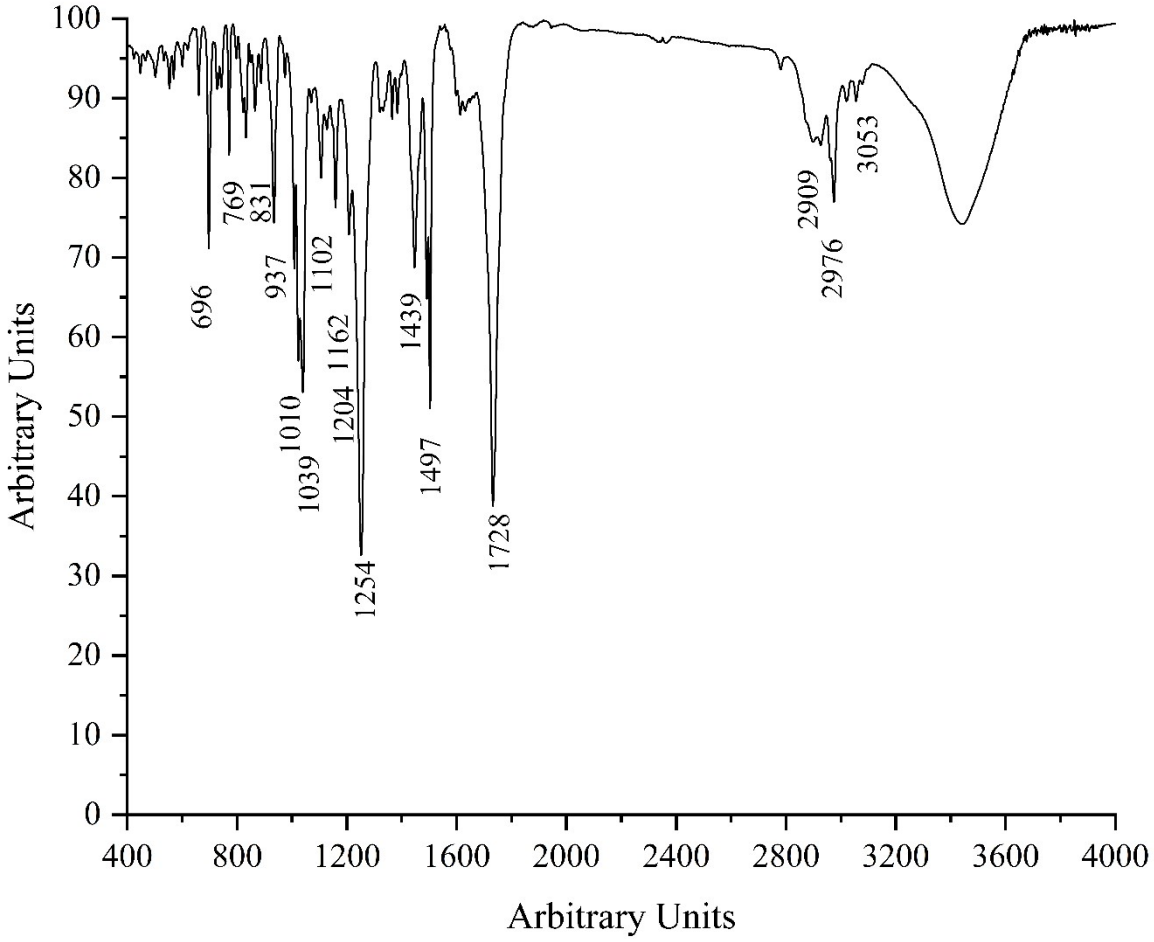

100
90
80
70
60
50
40
Arbitrary Units
510
694
739
827
918
1002
1039
1170
1262
1354
1443
1639
1737
2921
2971
3026
400
800
1200
1600
2000
2400
2800
3200
3600
4000
Arbitrary Units



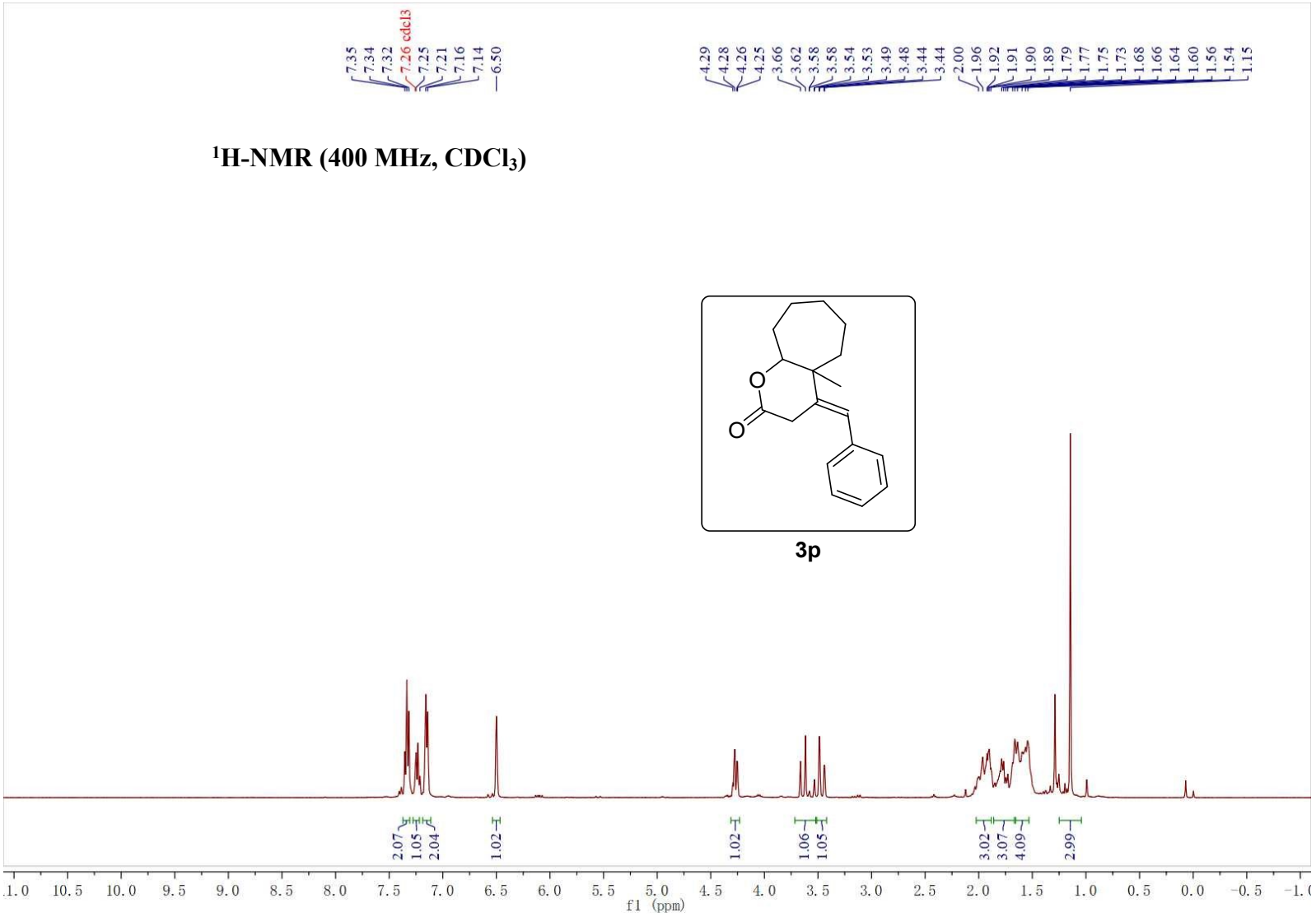
^{1}H-NMR (400 MHz, $CDCl_3$)

3o


169.9
147.7
147.4
138.0
136.4
129.2
128.7
128.5
127.1
125.5
121.8
108.5
107.6
101.2
87.1
87.1
77.3 cdcl3
77.0 cdcl3
76.7 cdcl3
40.6
33.9
25.5
22.0
13C-NMR (101 MHz, CDCl3)
O
O
O
O
3o
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

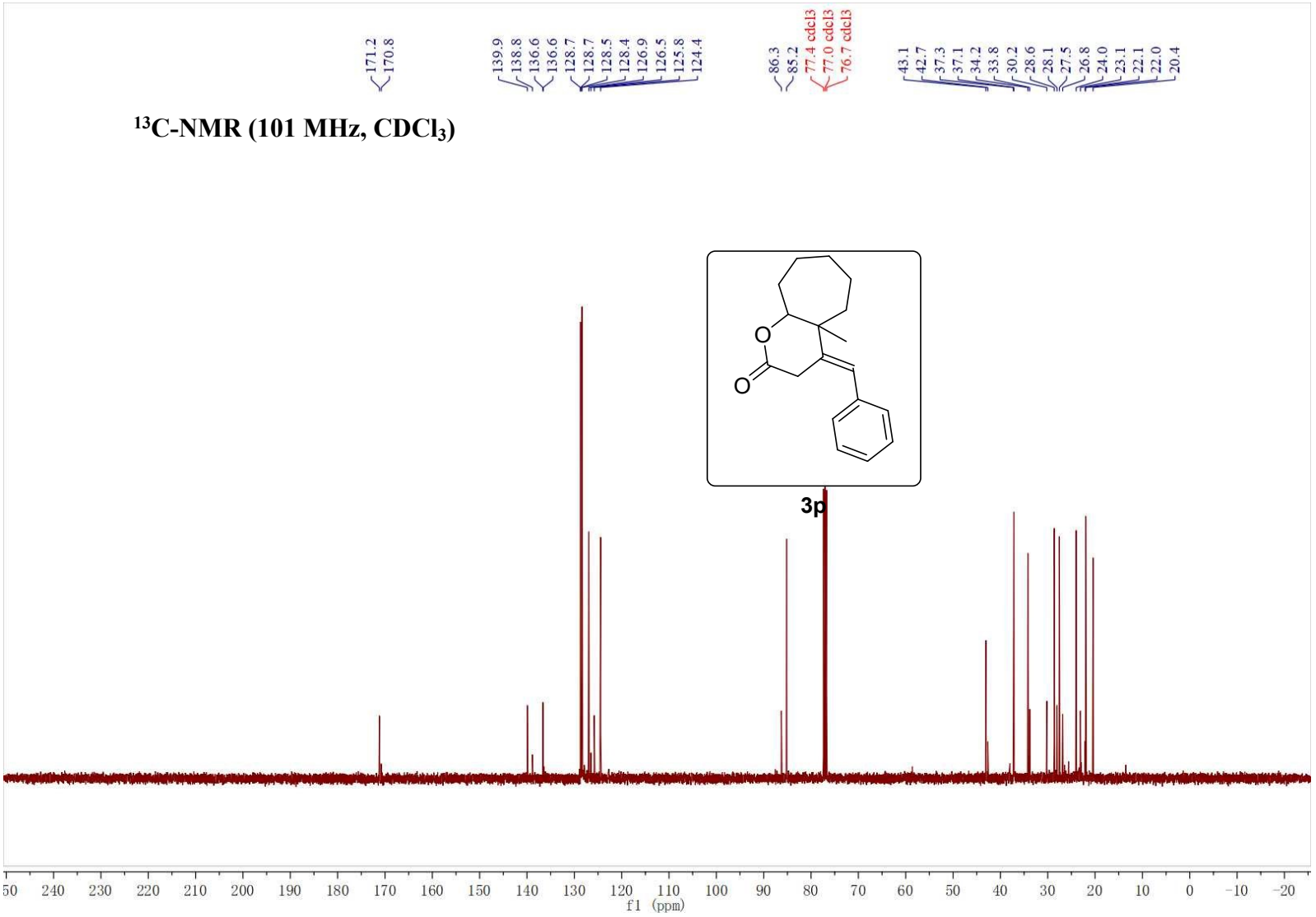

Arbitrary Units
100
90
80
70
60
50
40
30
20
10
0
400
800
1200
1600
2000
2400
2800
3200
3600
4000
Arbitrary Units
696
769
831
937
1010
1039
1102
1162
1204
1254
1439
1497
1728
2909
2976
3053

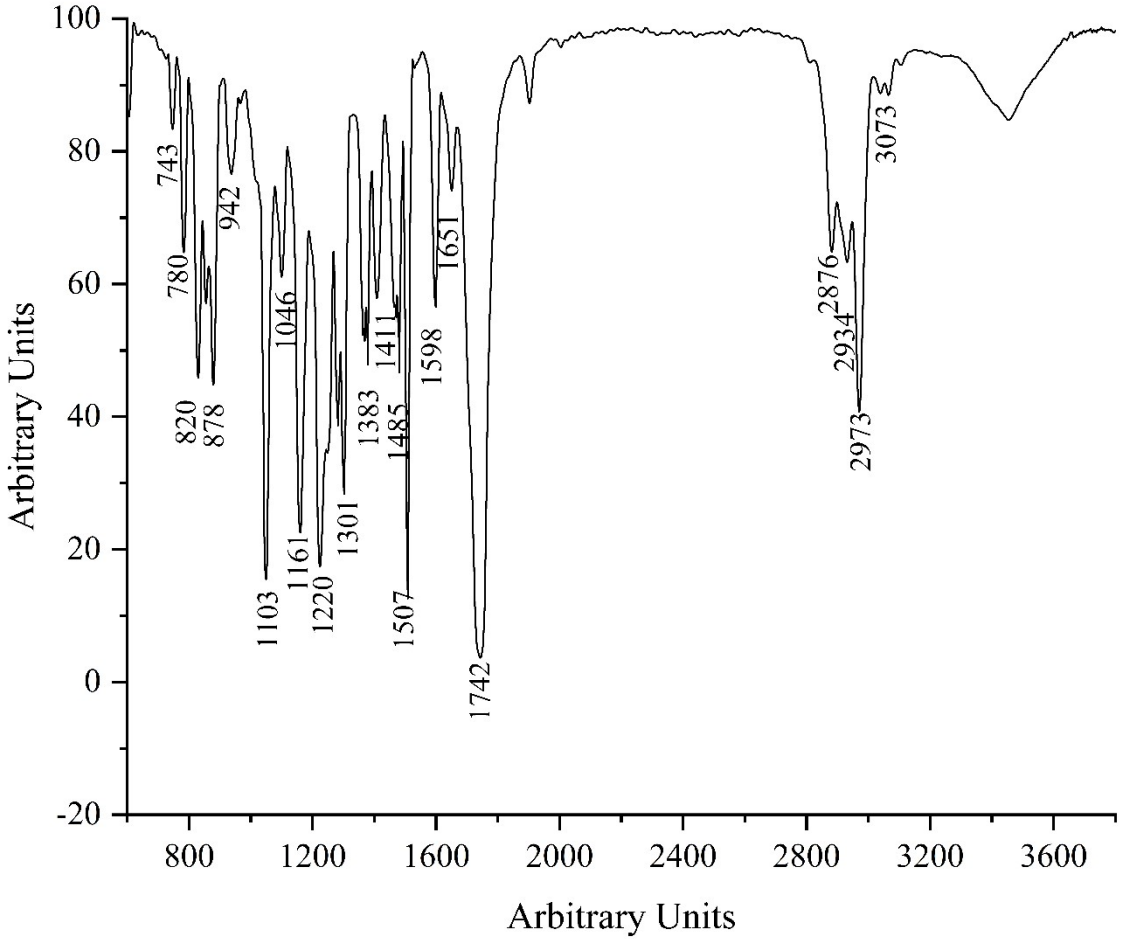
^{1}H-NMR (400 MHz, $CDCl_3$)



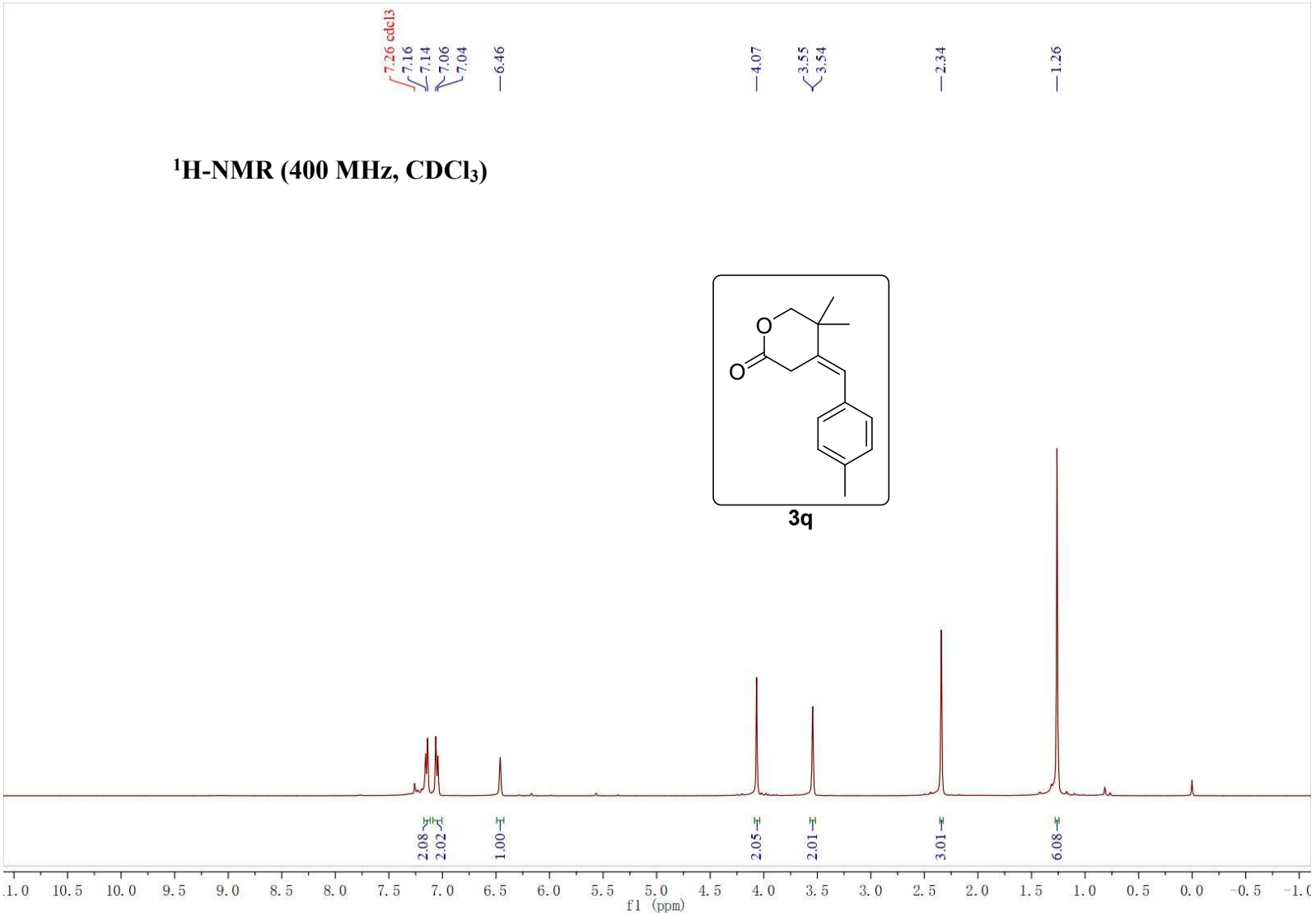
3p

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



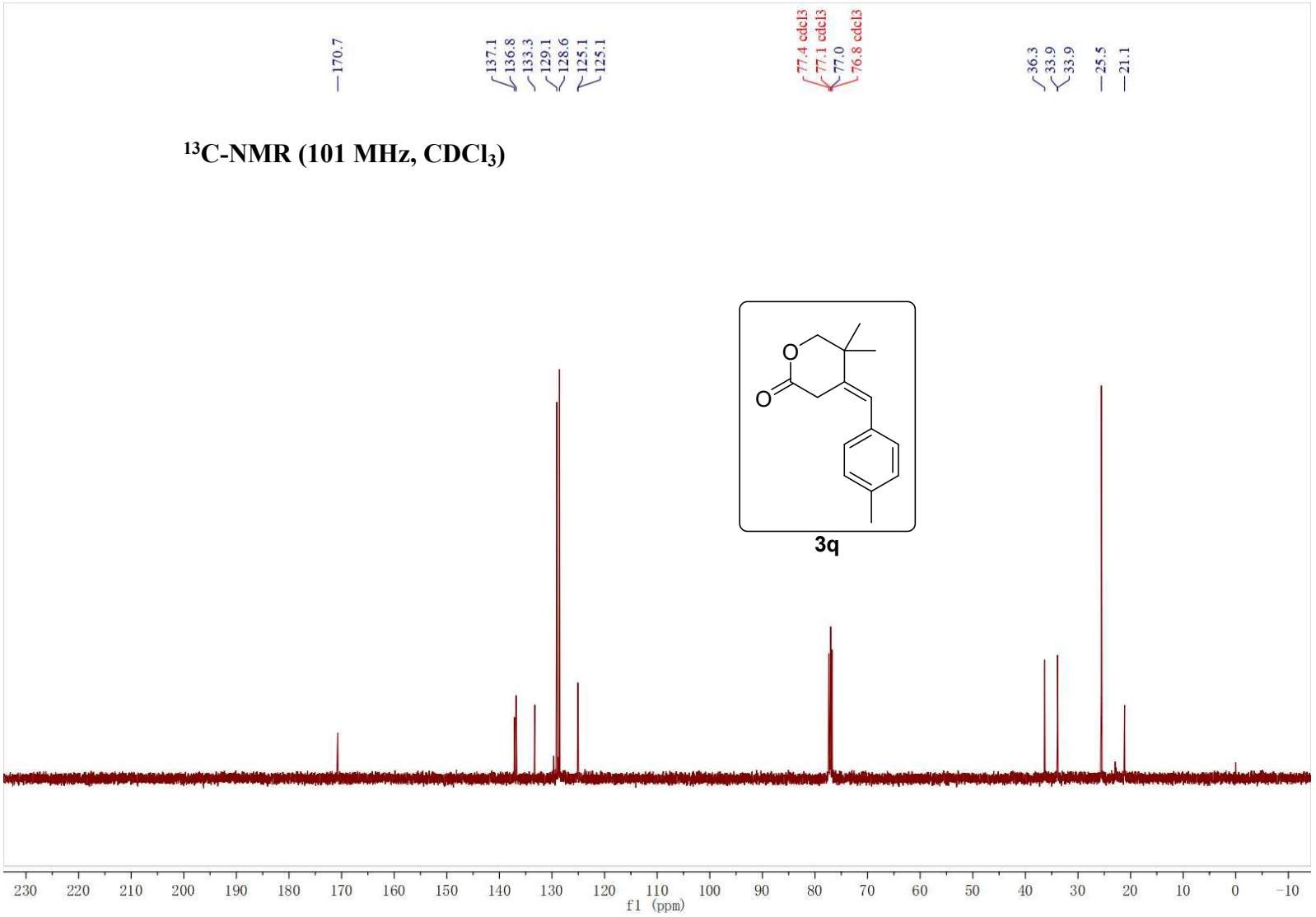

100
80
60
40
20
0
-20
Arbitrary Units
800
1200
1600
2000
2400
2800
3200
3600
Arbitrary Units
743
780
820
878
942
1046
1103
1161
1220
1301
1383
1411
1485
1507
1598
1651
1742
2876
2934
2973
3073

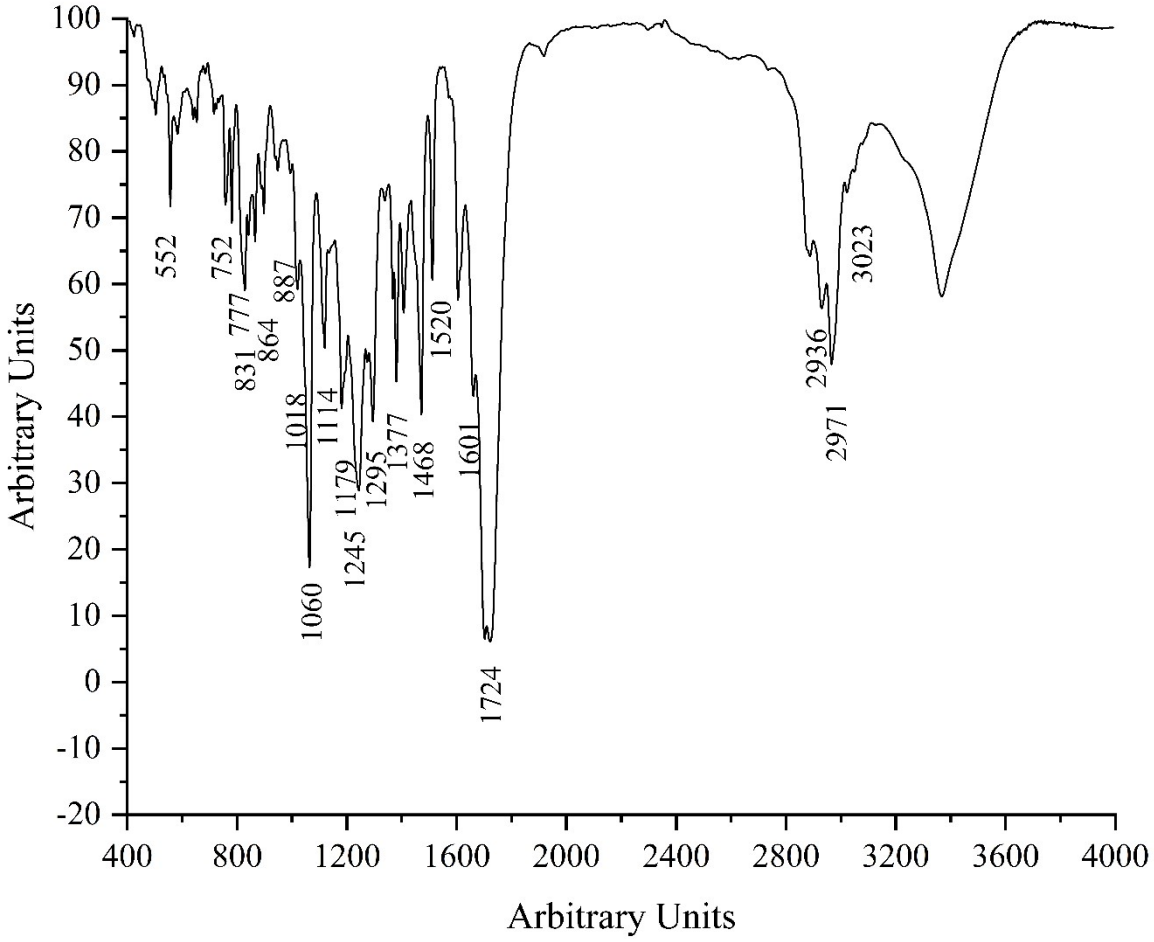
^{1}H-NMR (400 MHz, $CDCl_3$)



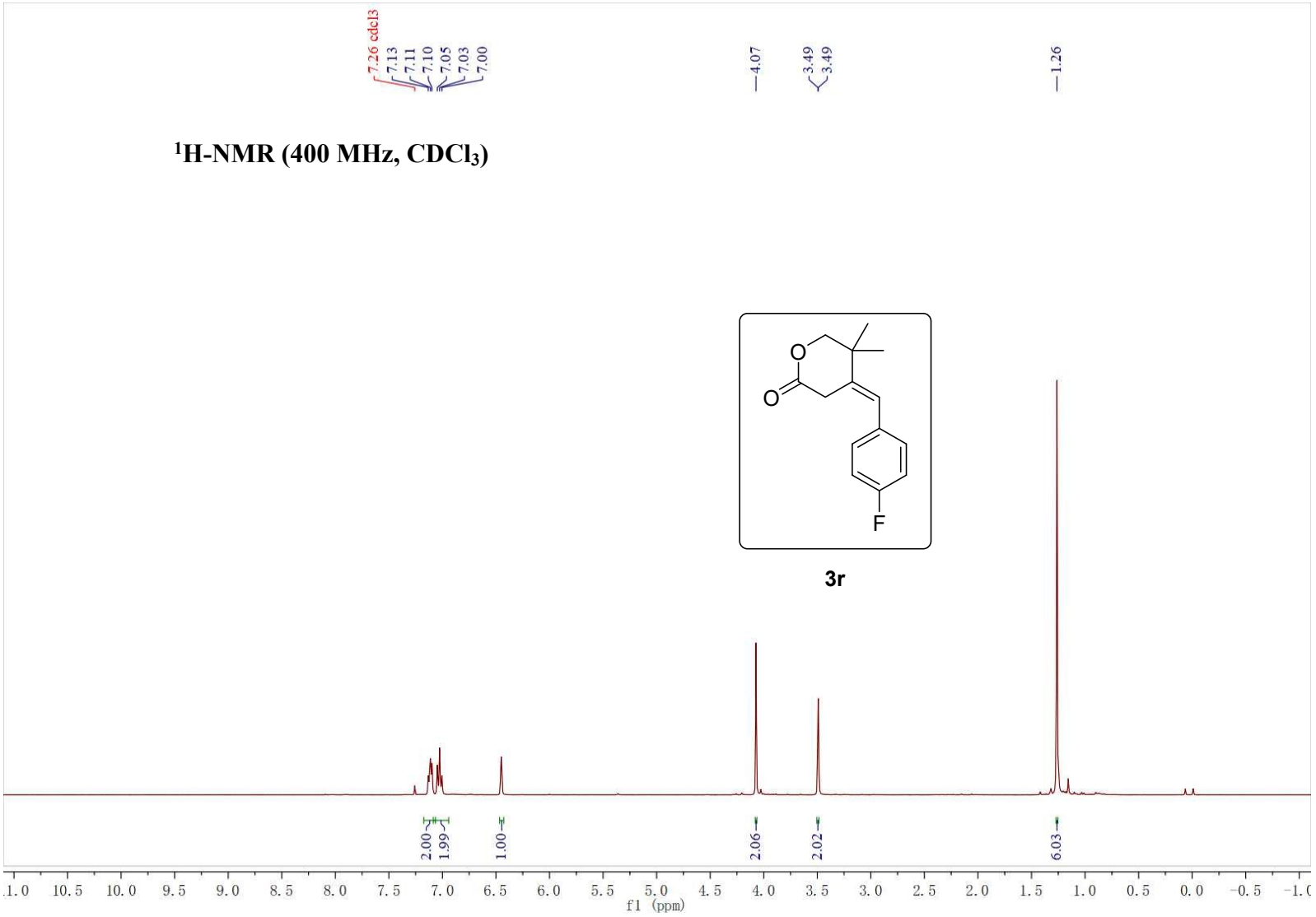
3q

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

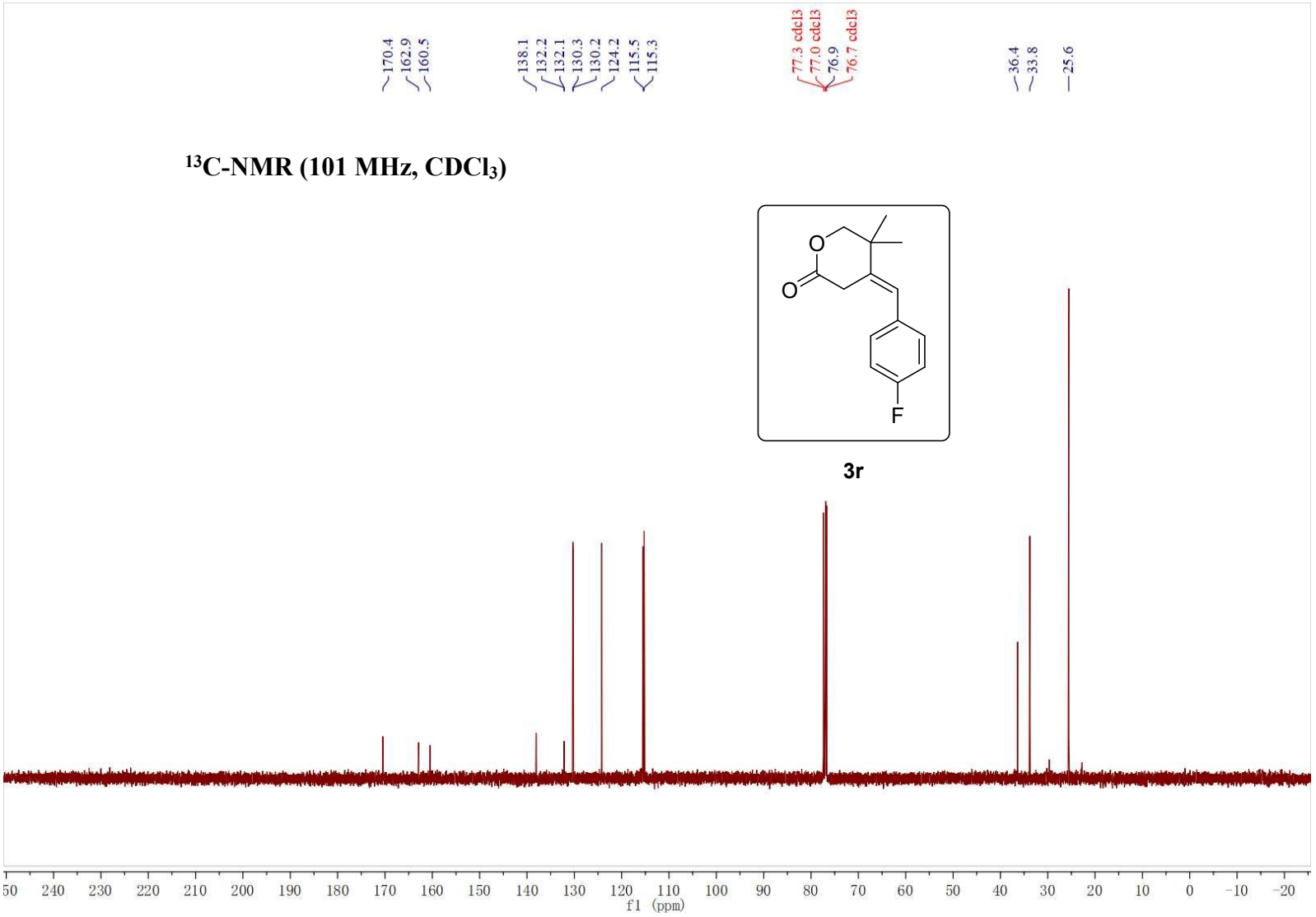



Arbitrary Units
100
90
80
70
60
50
40
30
20
10
0
-10
-20
400
800
1200
1600
2000
2400
2800
3200
3600
4000
Arbitrary Units
552
752
777
831
864
887
1018
1060
1114
1179
1245
1295
1377
1468
1520
1601
1724
2936
2971
3023

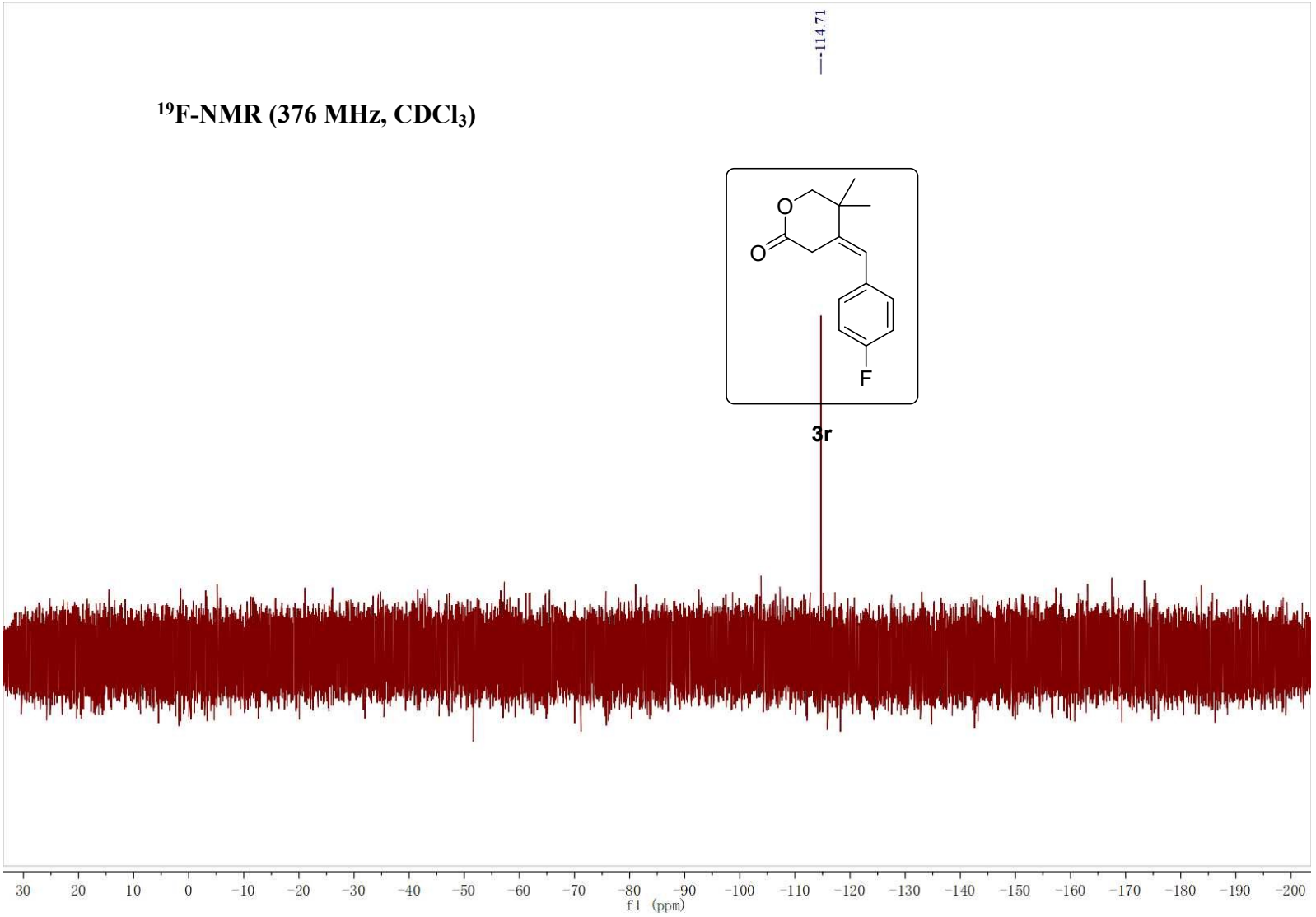
^{1}H-NMR (400 MHz, $CDCl_3$)

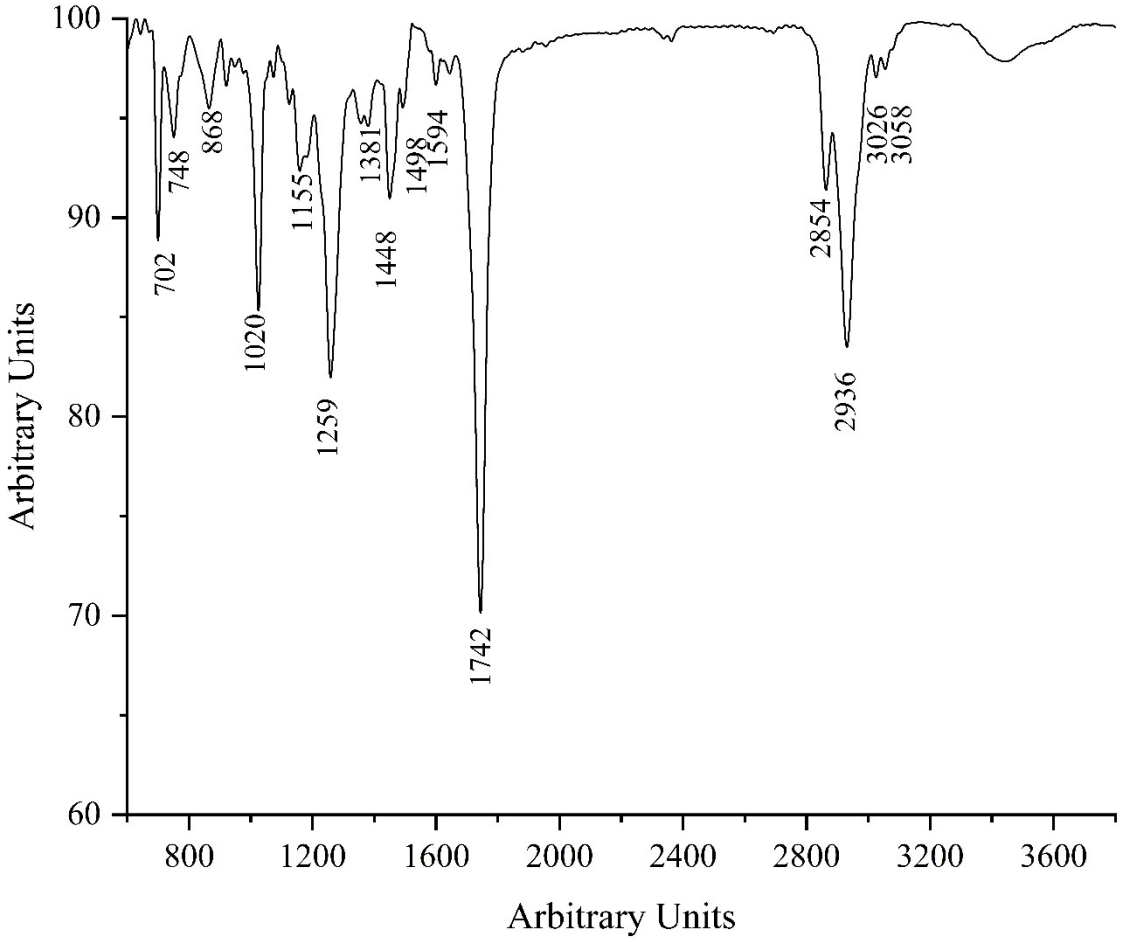


^{13}C-NMR (101 MHz, $CDCl_3$)

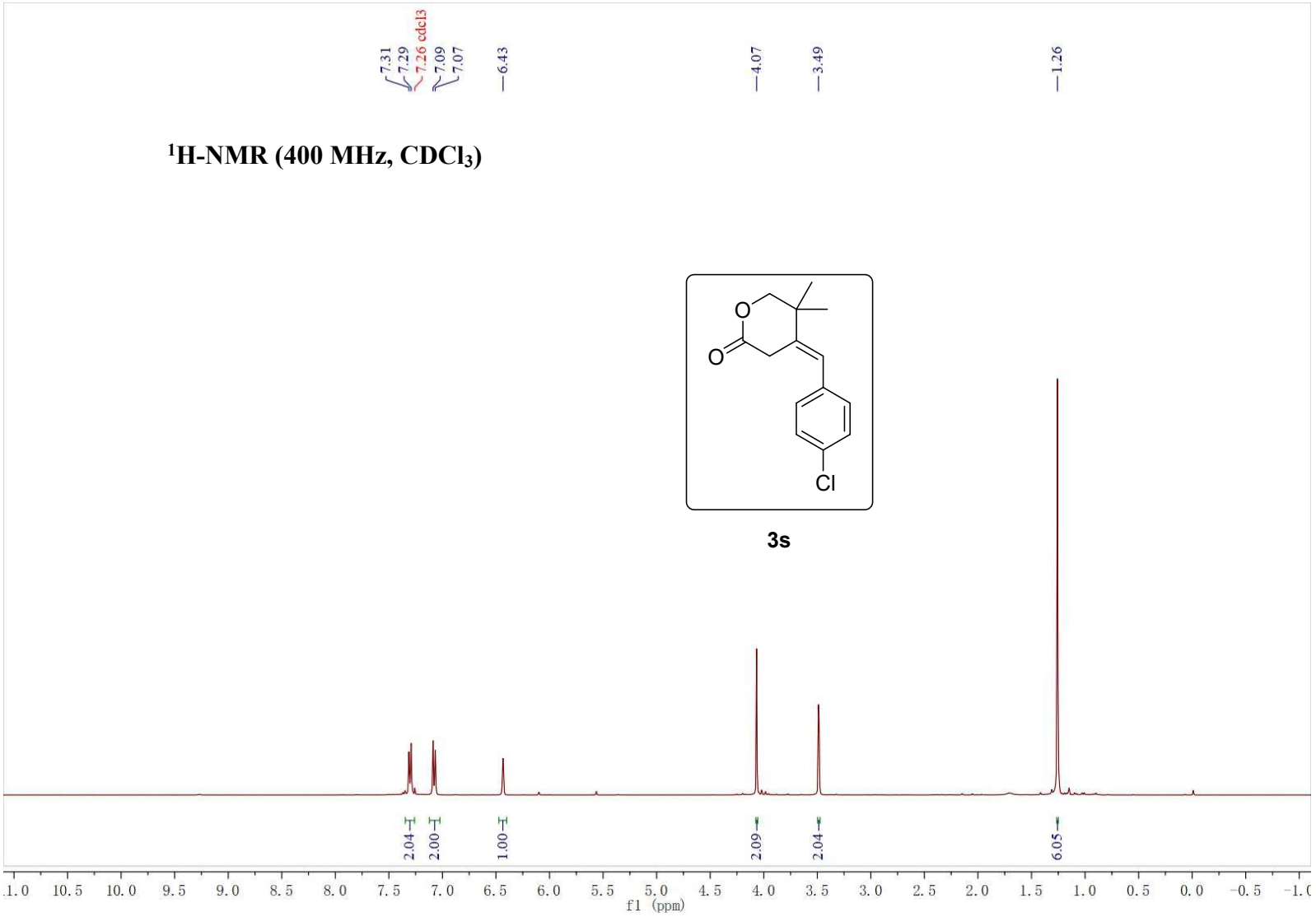


^{19}F-NMR (376 MHz, $CDCl_3$)



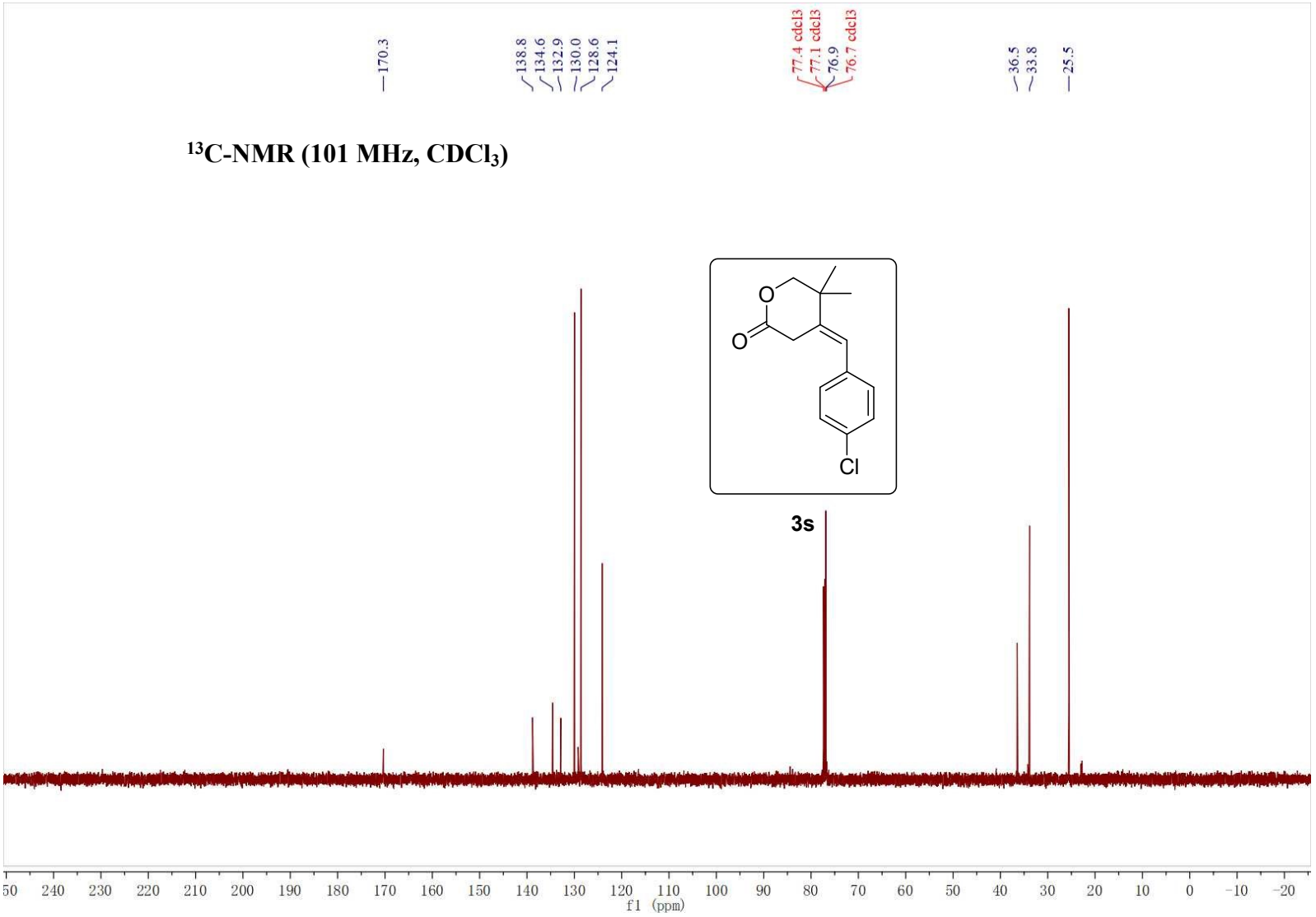

100
90
80
70
60
Arbitrary Units
800
1200
1600
2000
2400
2800
3200
3600
Arbitrary Units
702
748
868
1020
1155
1259
1381
1448
1498
1594
1742
2854
2936
3026
3058

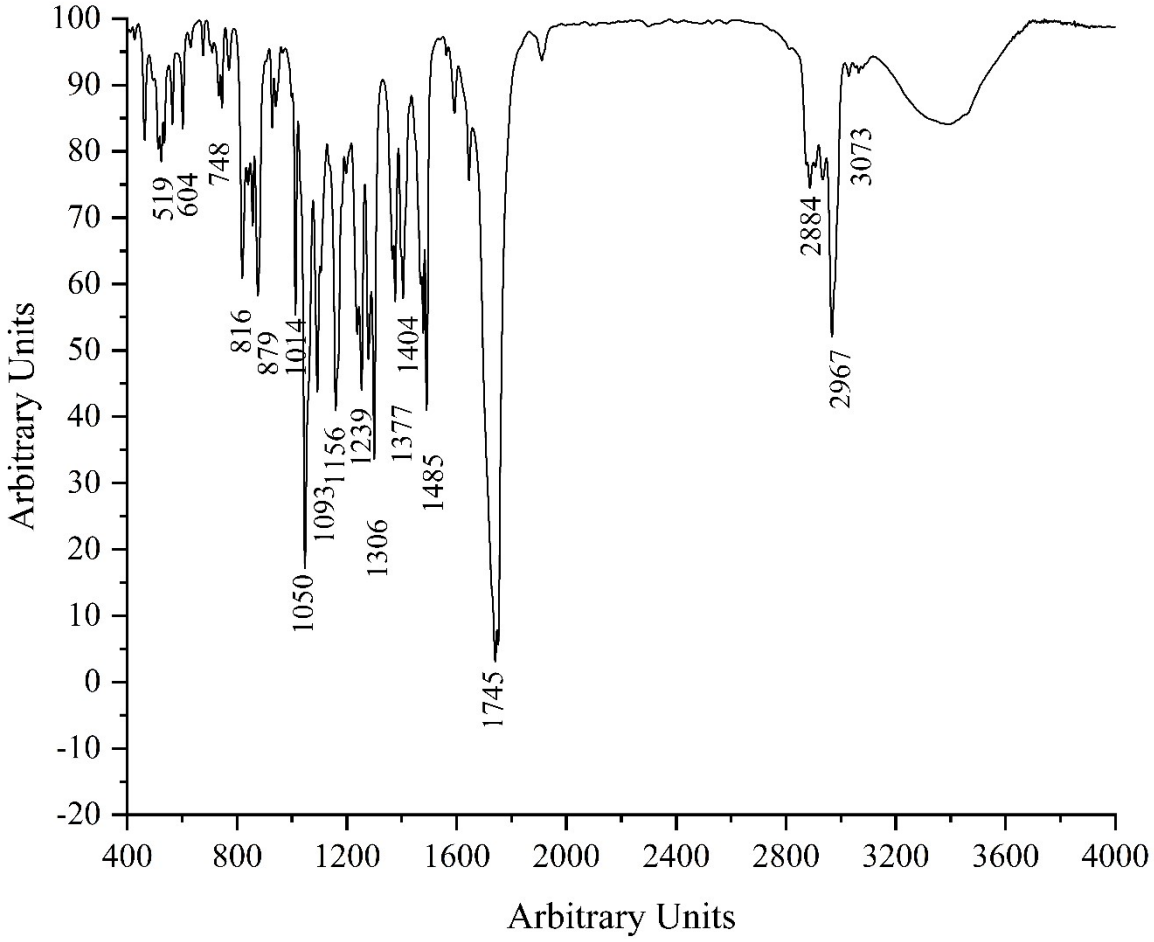
^{1}H-NMR (400 MHz, $CDCl_3$)



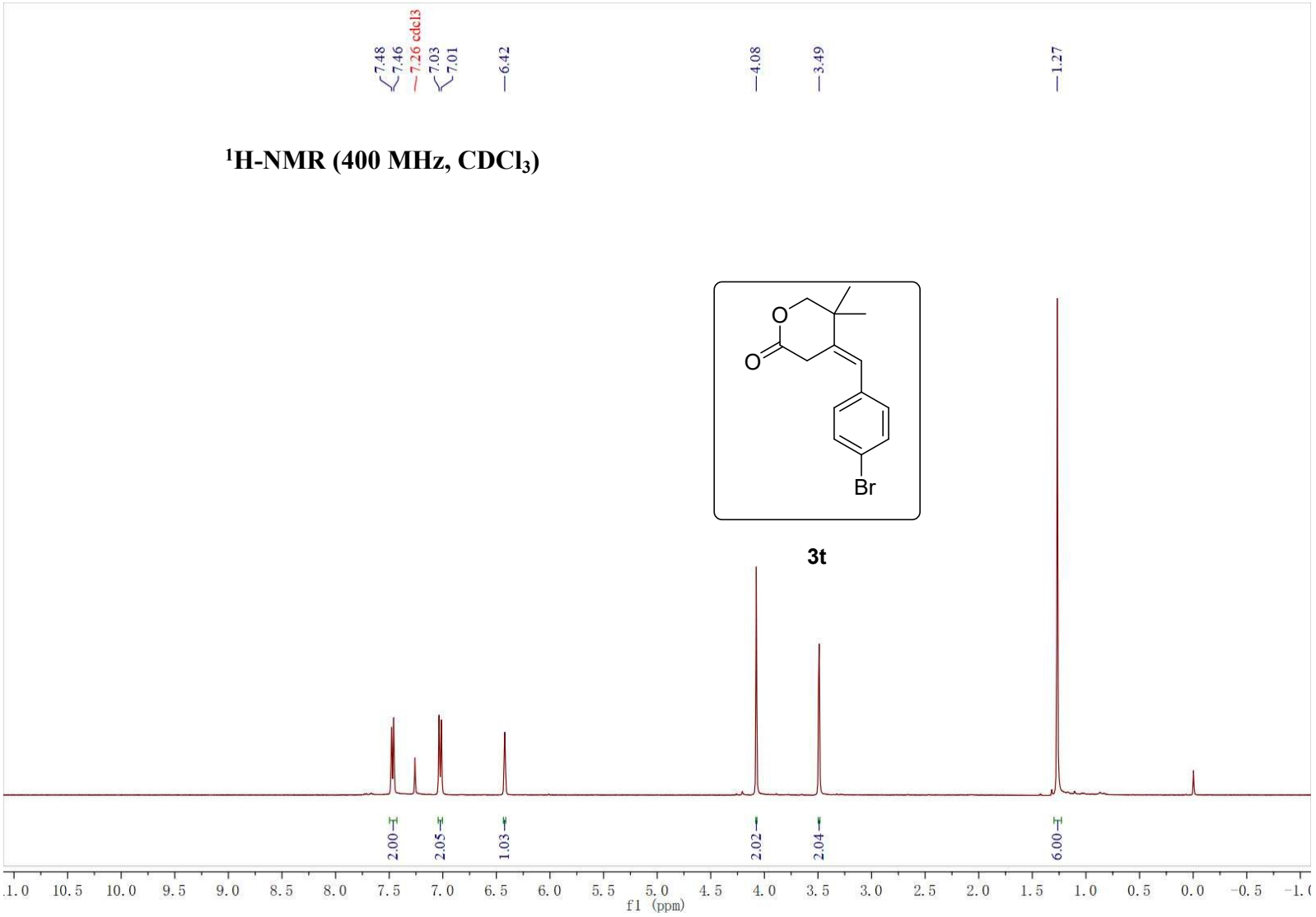
3s

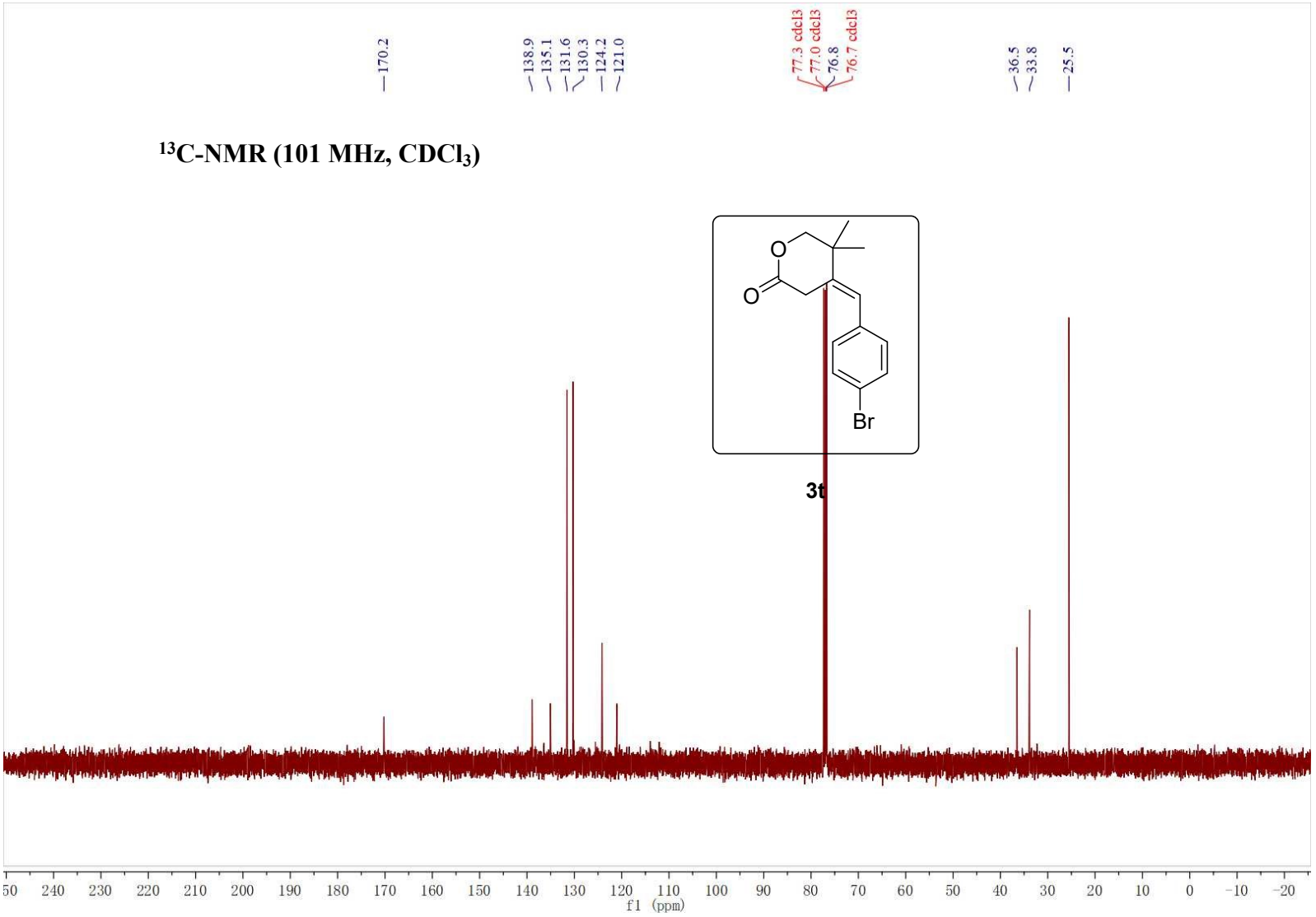
^{13}C-NMR (101 MHz, $CDCl_3$)



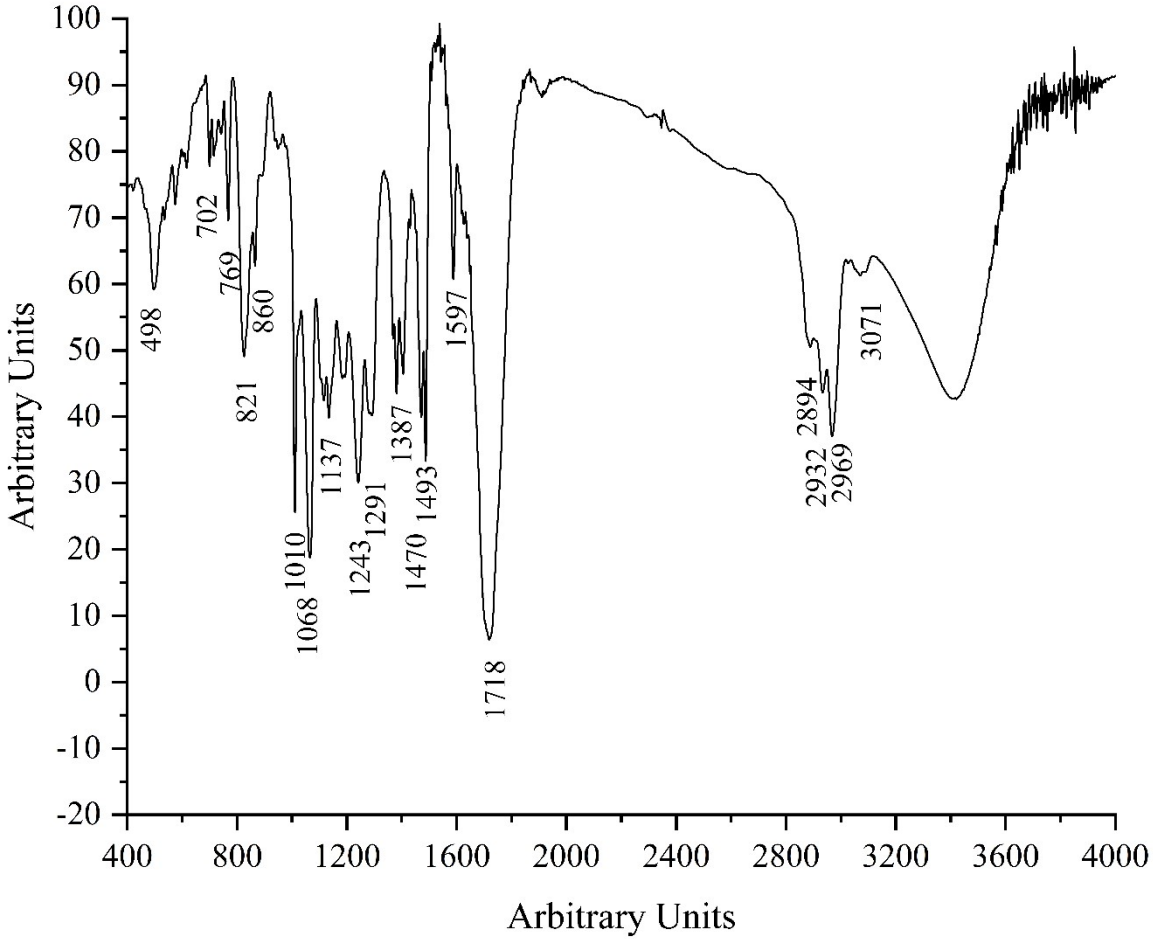

Arbitrary Units
Arbitrary Units
100
90
80
70
60
50
40
30
20
10
0
-10
-20
400
800
1200
1600
2000
2400
2800
3200
3600
4000
519
604
748
816
879
1014
1050
1093
1156
1239
1306
1377
1404
1485
1745
2884
2967
3073

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

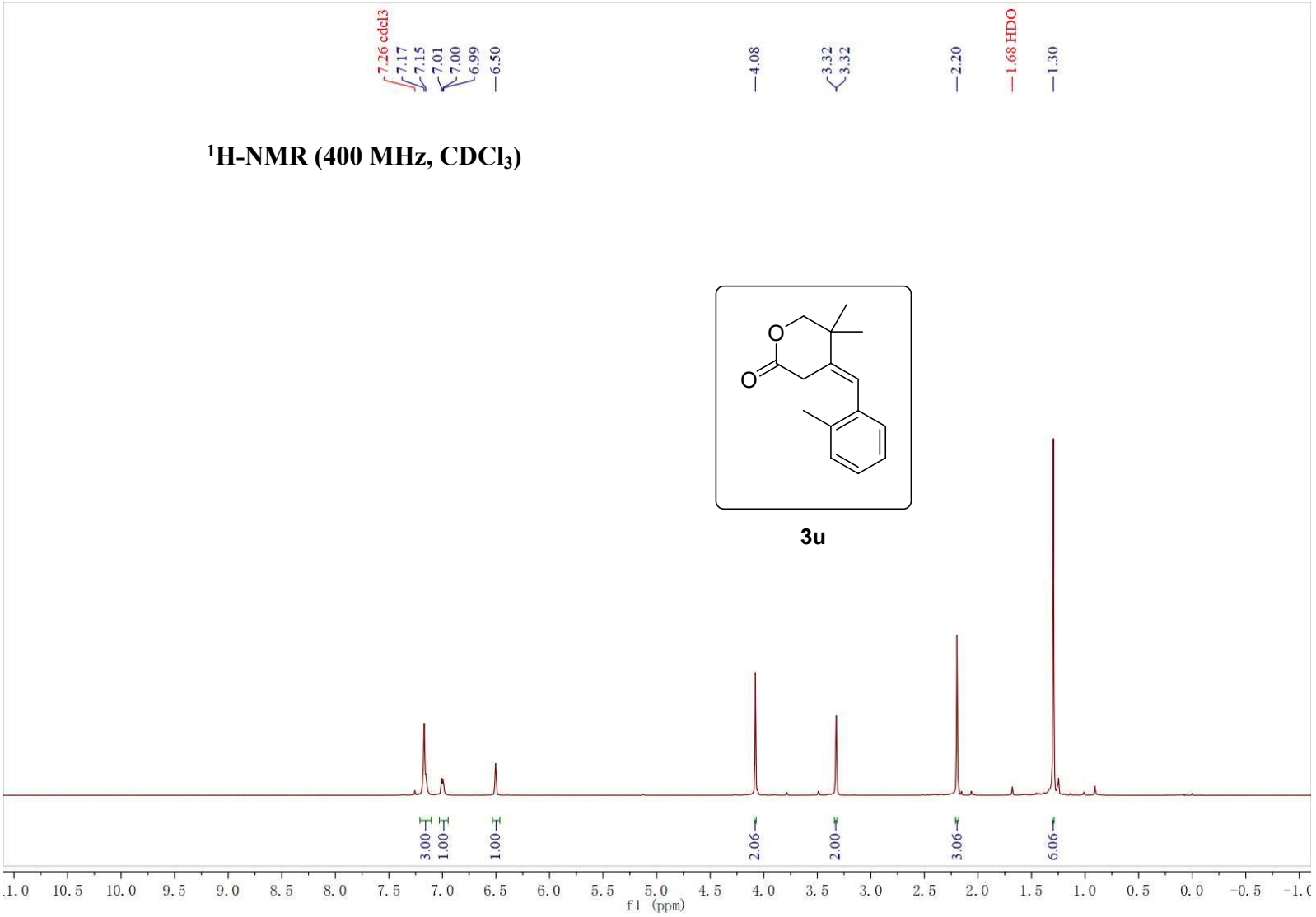




^{13}C-NMR (101 MHz, $CDCl_3$)

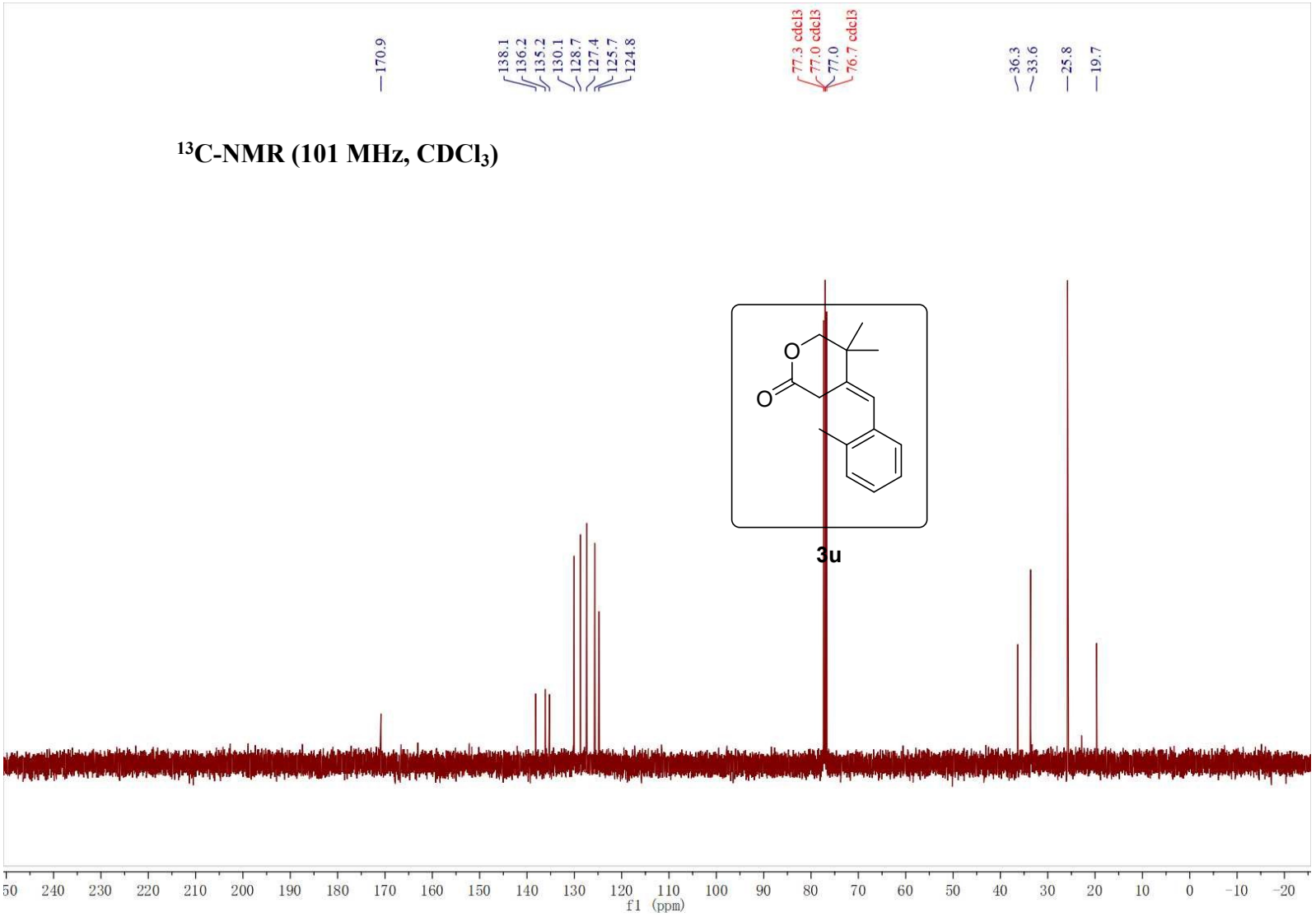

Arbitrary Units
100
90
80
70
60
50
40
30
20
10
0
-10
-20
400
800
1200
1600
2000
2400
2800
3200
3600
4000
Arbitrary Units
498
702
769
821
860
1010
1068
1137
1243
1291
1387
1470
1493
1597
1718
2894
2932
2969
3071

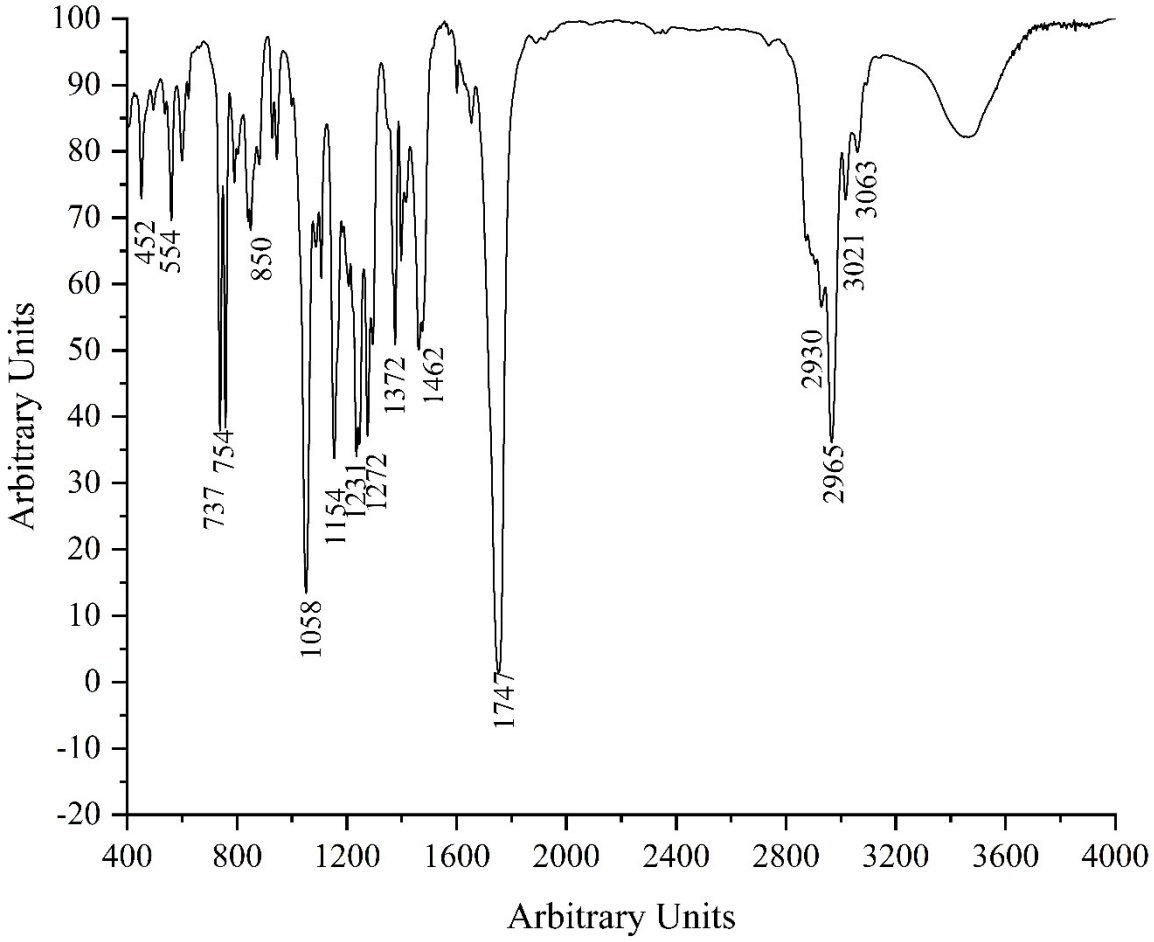
^{1}H-NMR (400 MHz, $CDCl_3$)

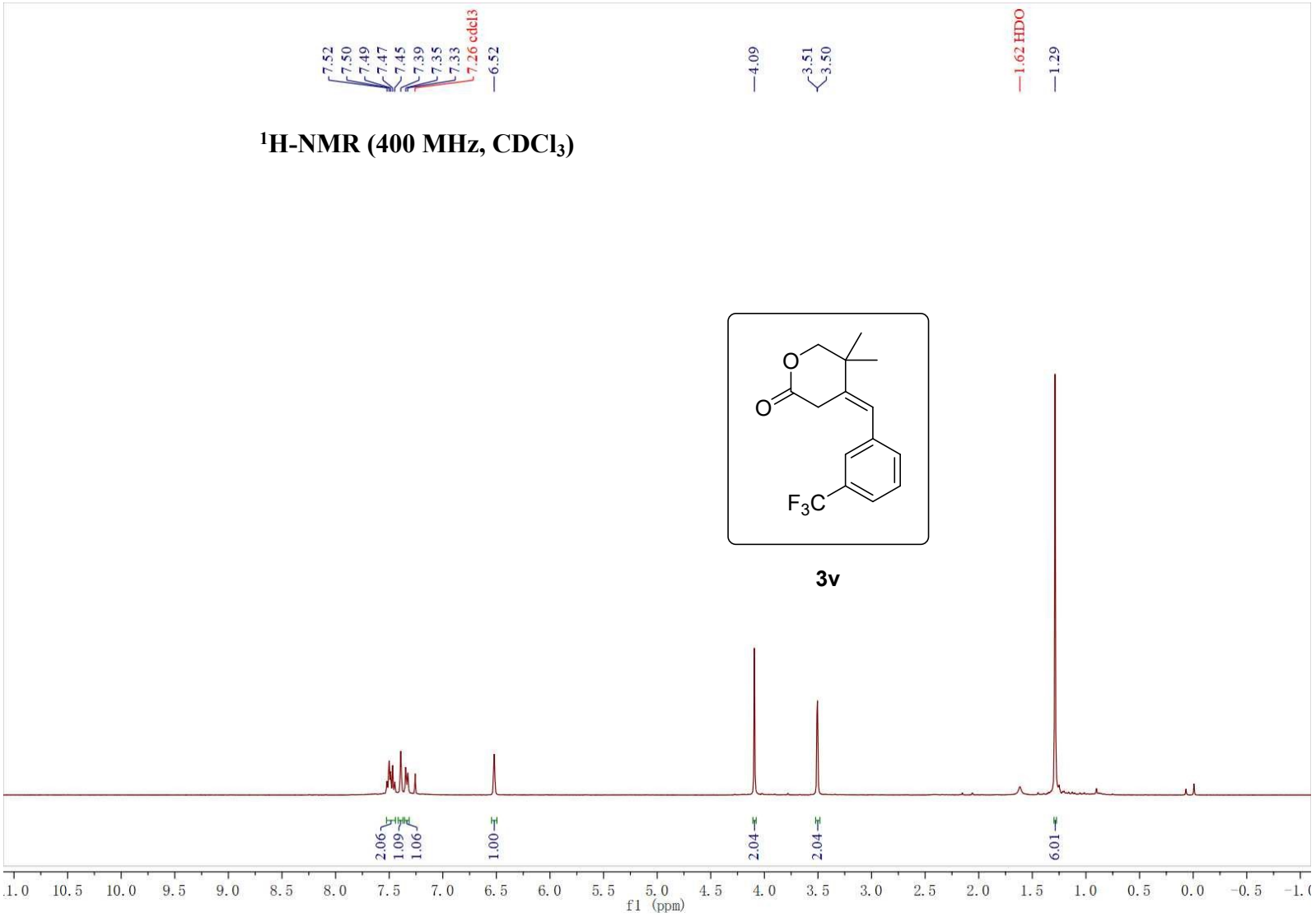


3u

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

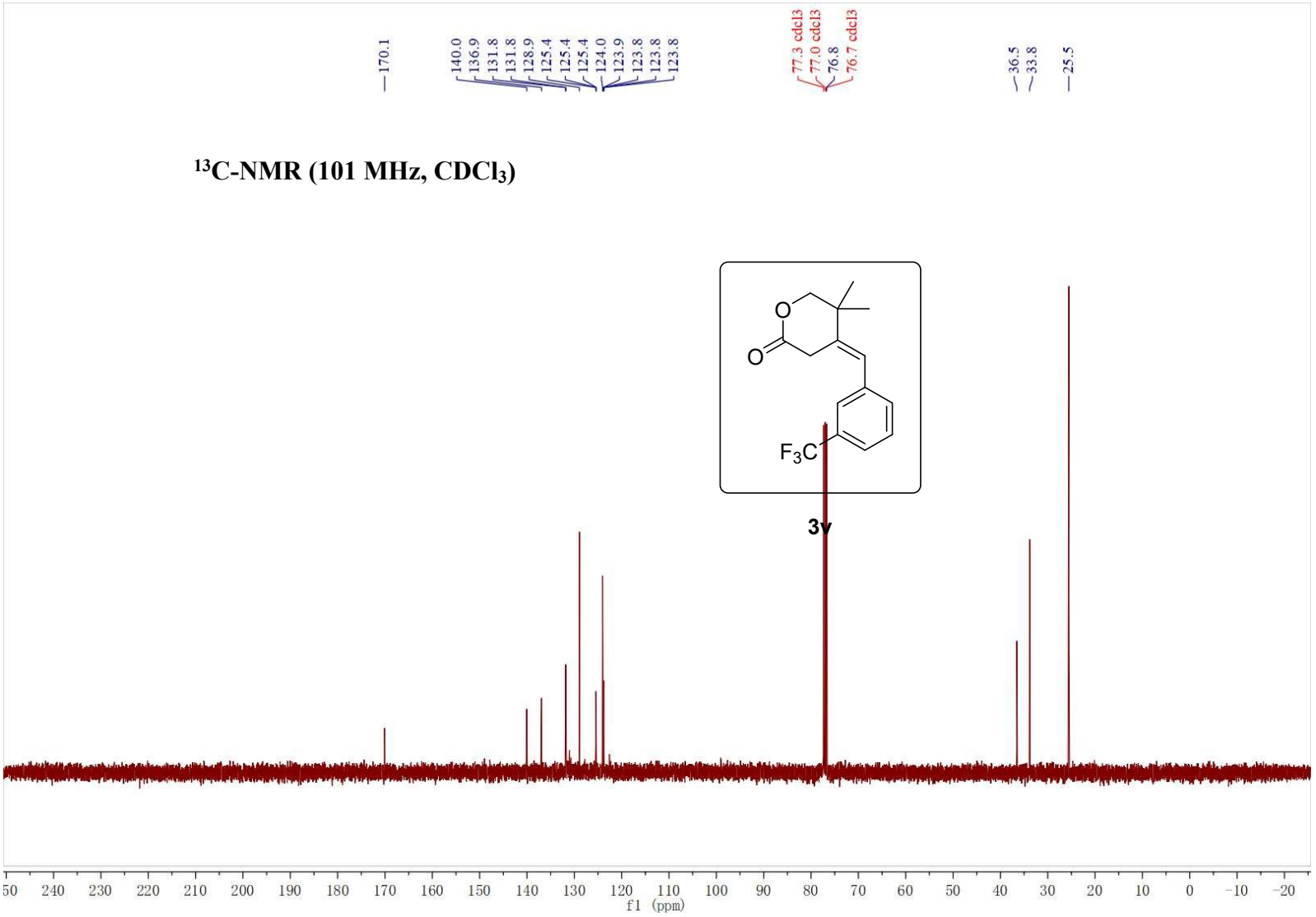



Arbitrary Units
100
90
80
70
60
50
40
30
20
10
0
-10
-20
400
800
1200
1600
2000
2400
2800
3200
3600
4000
Arbitrary Units
452
554
737
754
850
1058
1154
1231
1272
1372
1462
1747
2930
2965
3021
3063



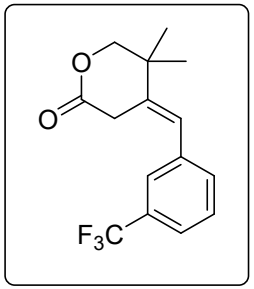
^{1}H-NMR (400 MHz, $CDCl_3$)

3v

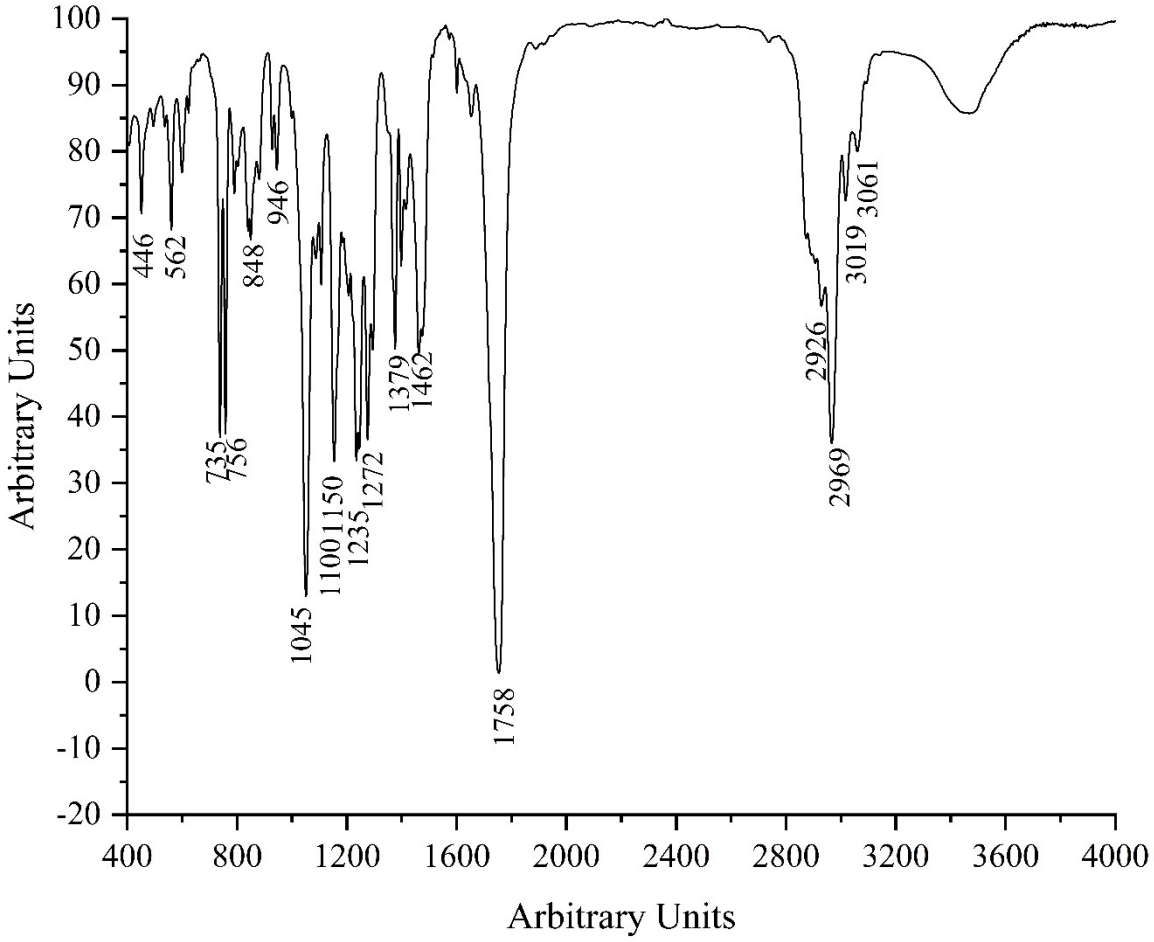


^{13}C-NMR (101 MHz, $CDCl_3$)

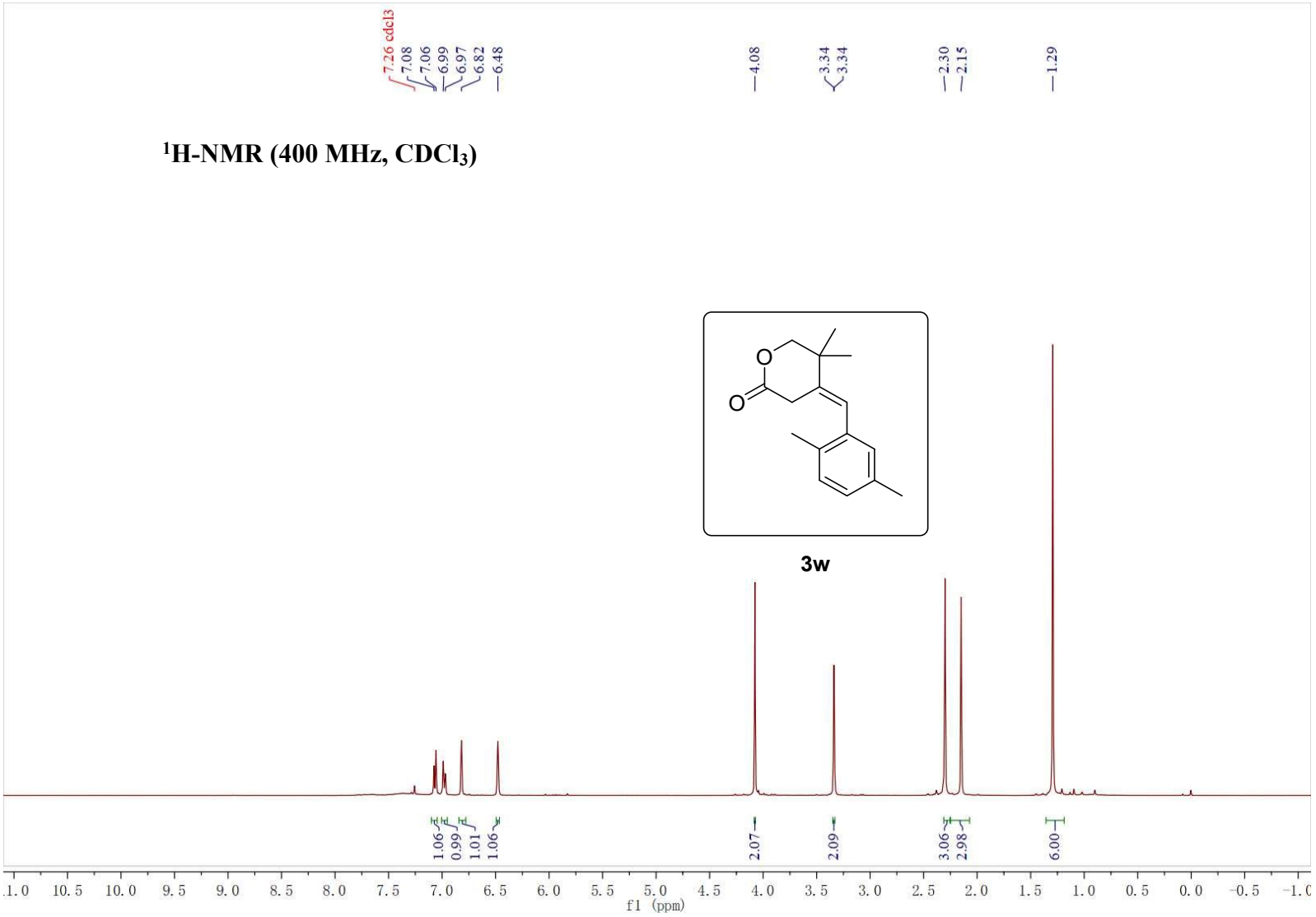
^{19}F-NMR (376 MHz, $CDCl_3$)



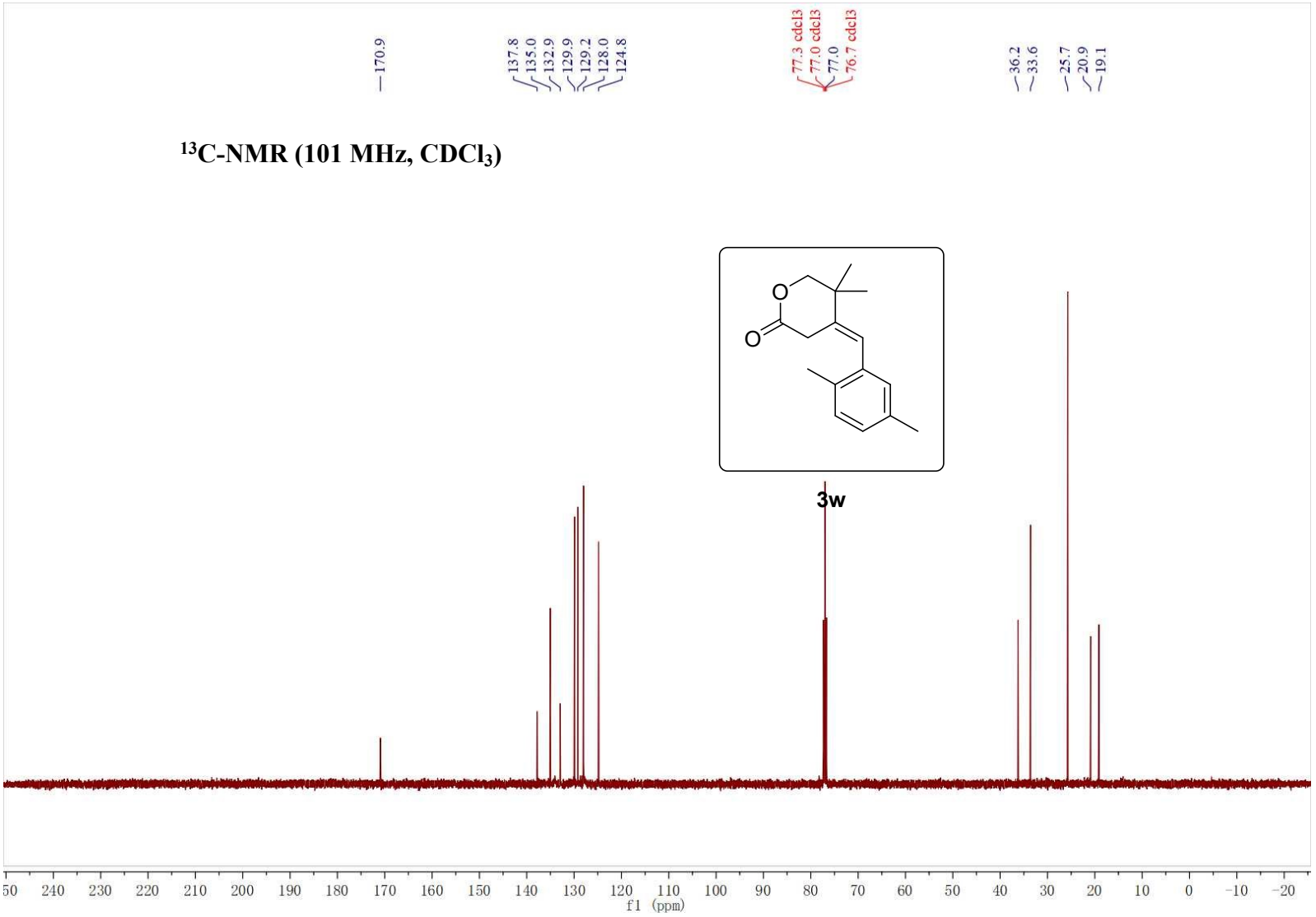
3v

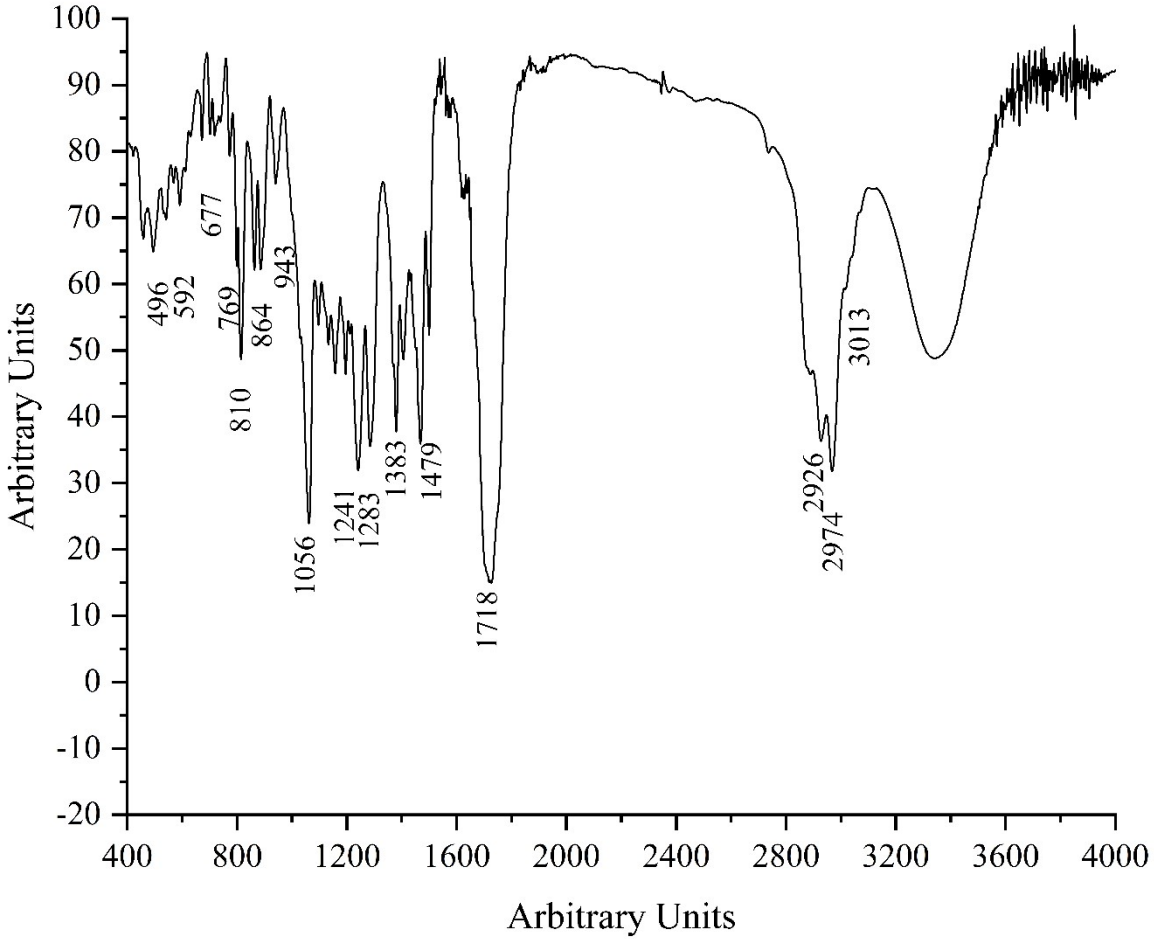

Arbitrary Units
100
90
80
70
60
50
40
30
20
10
0
-10
-20
400
800
1200
1600
2000
2400
2800
3200
3600
4000
Arbitrary Units
446
562
735
756
848
946
1045
1100
1150
1235
1272
1379
1462
1758
2926
2969
3019
3061

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

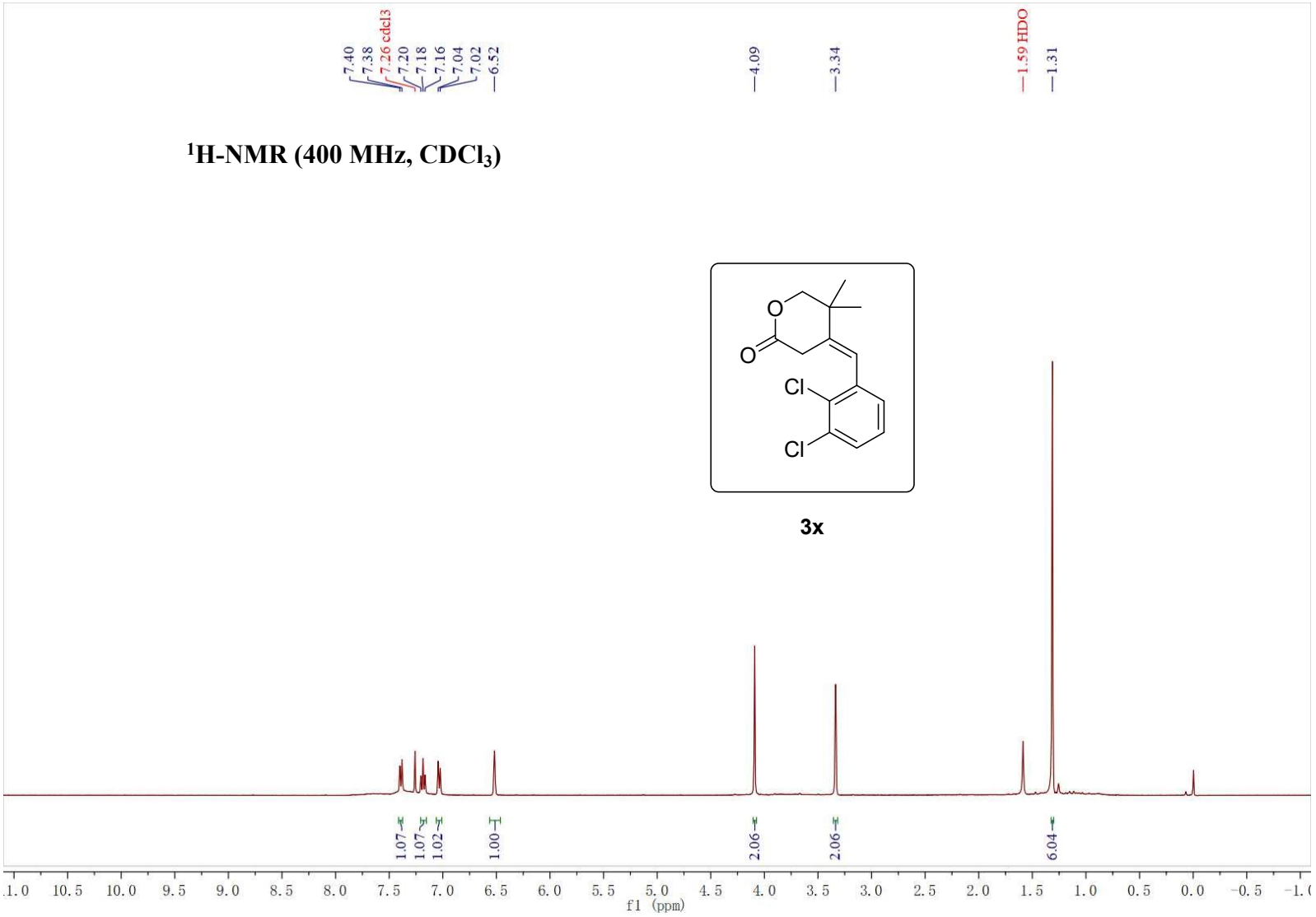


^{13}C-NMR (101 MHz, $CDCl_3$)



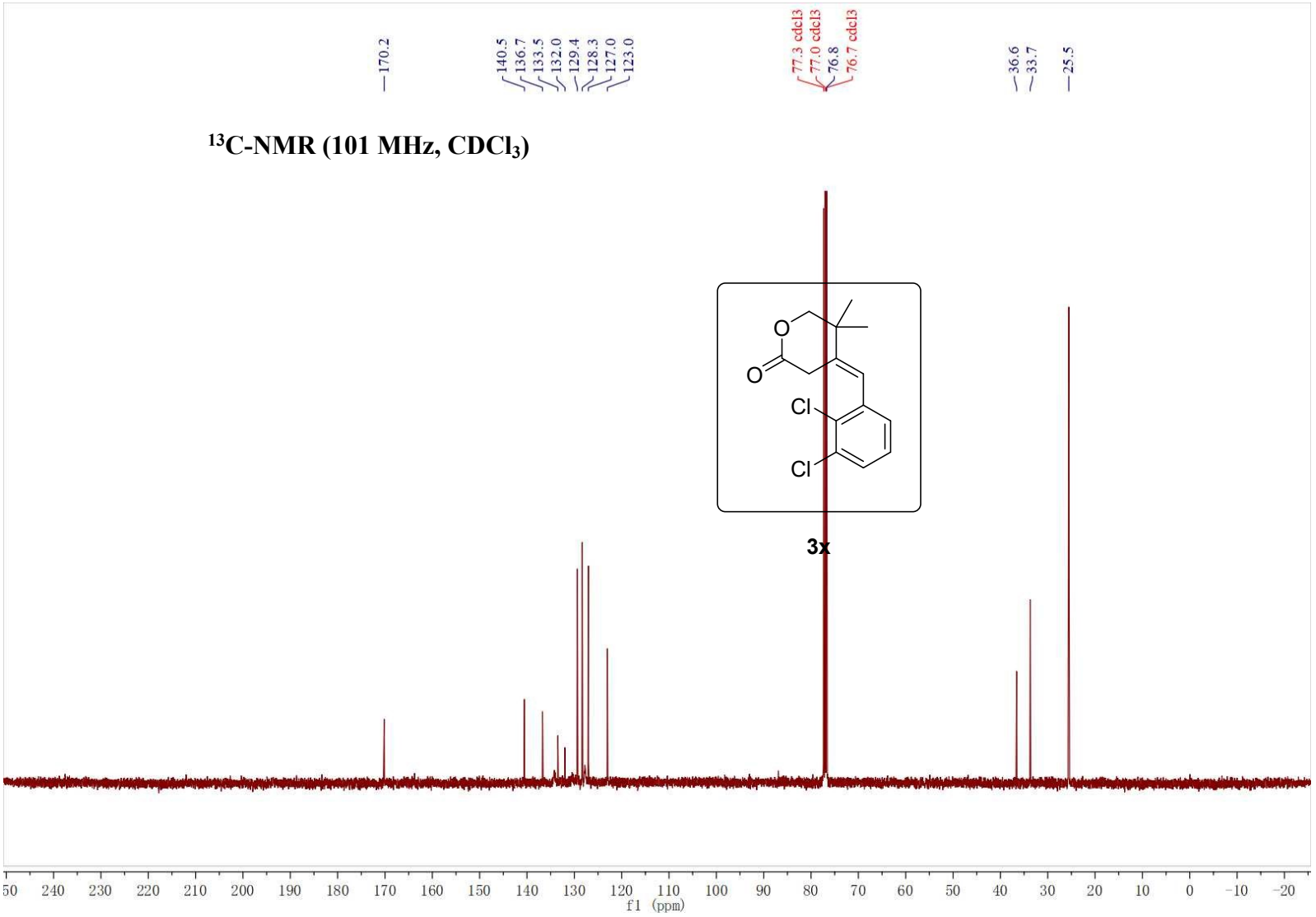

Arbitrary Units
100
90
80
70
60
50
40
30
20
10
0
-10
-20
400
800
1200
1600
2000
2400
2800
3200
3600
4000
Arbitrary Units
496
592
677
769
810
864
943
1056
1241
1283
1383
1479
1718
2926
2974
3013

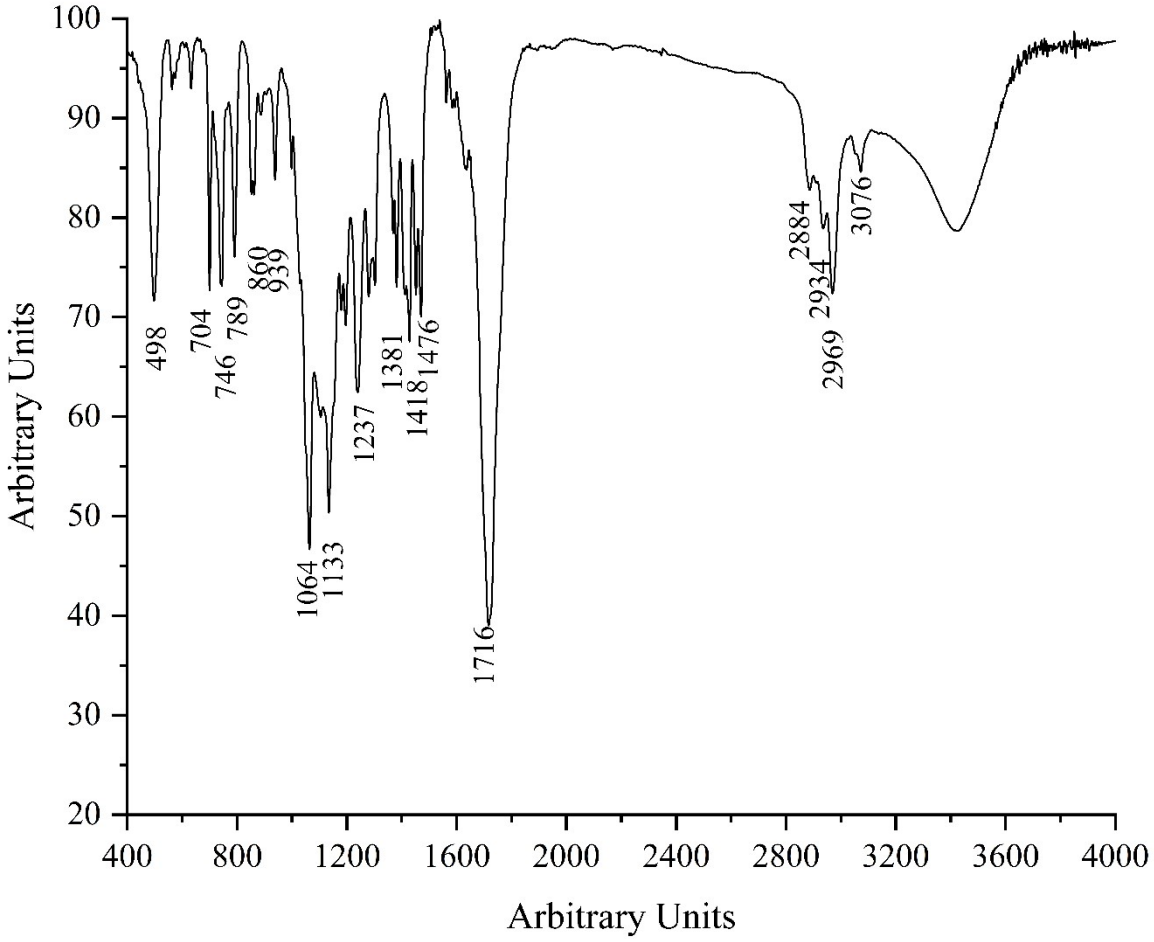
^{1}H-NMR (400 MHz, $CDCl_3$)



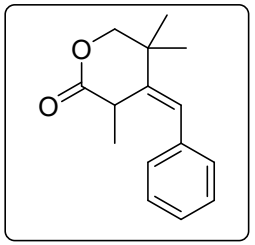
3x

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

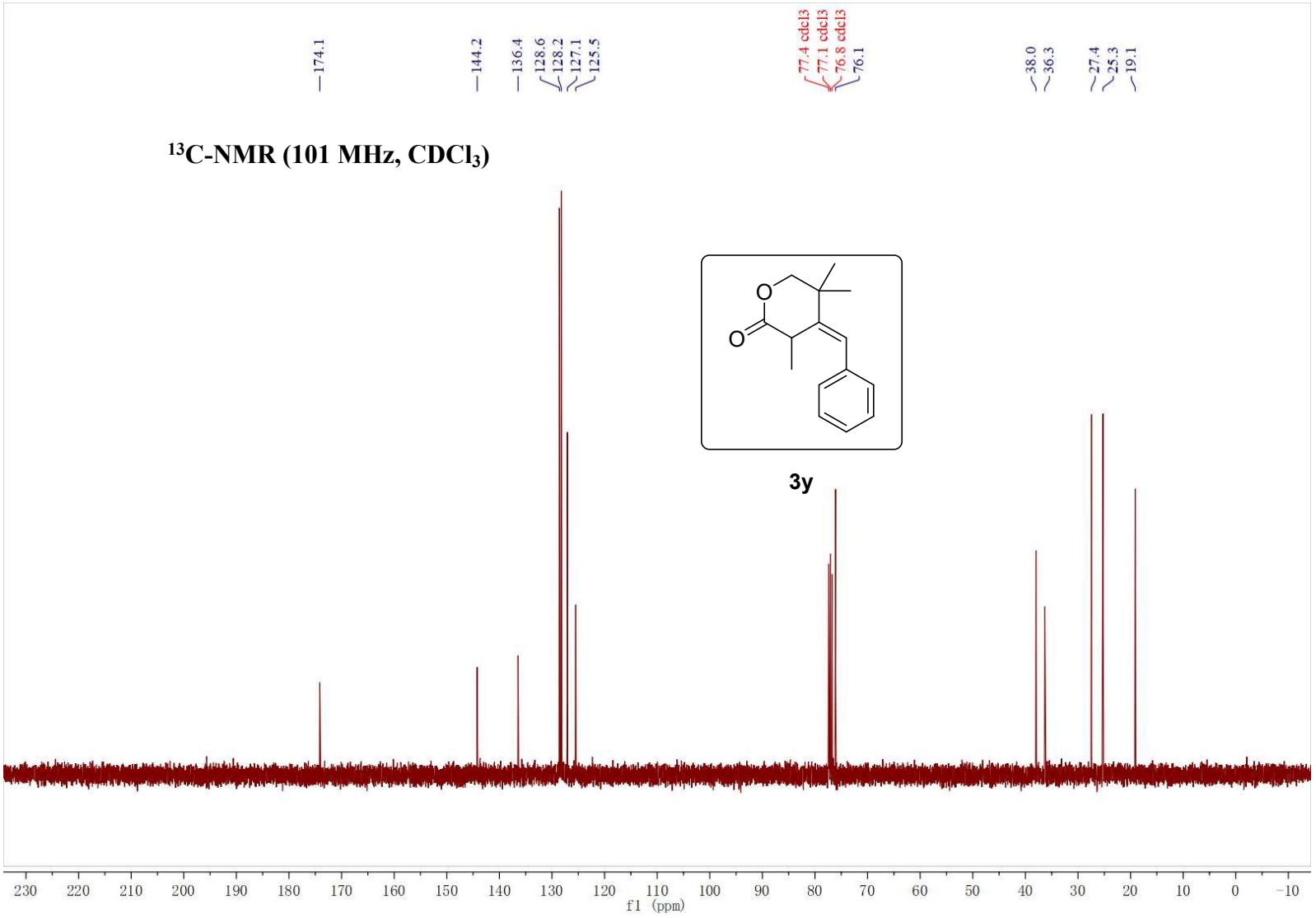


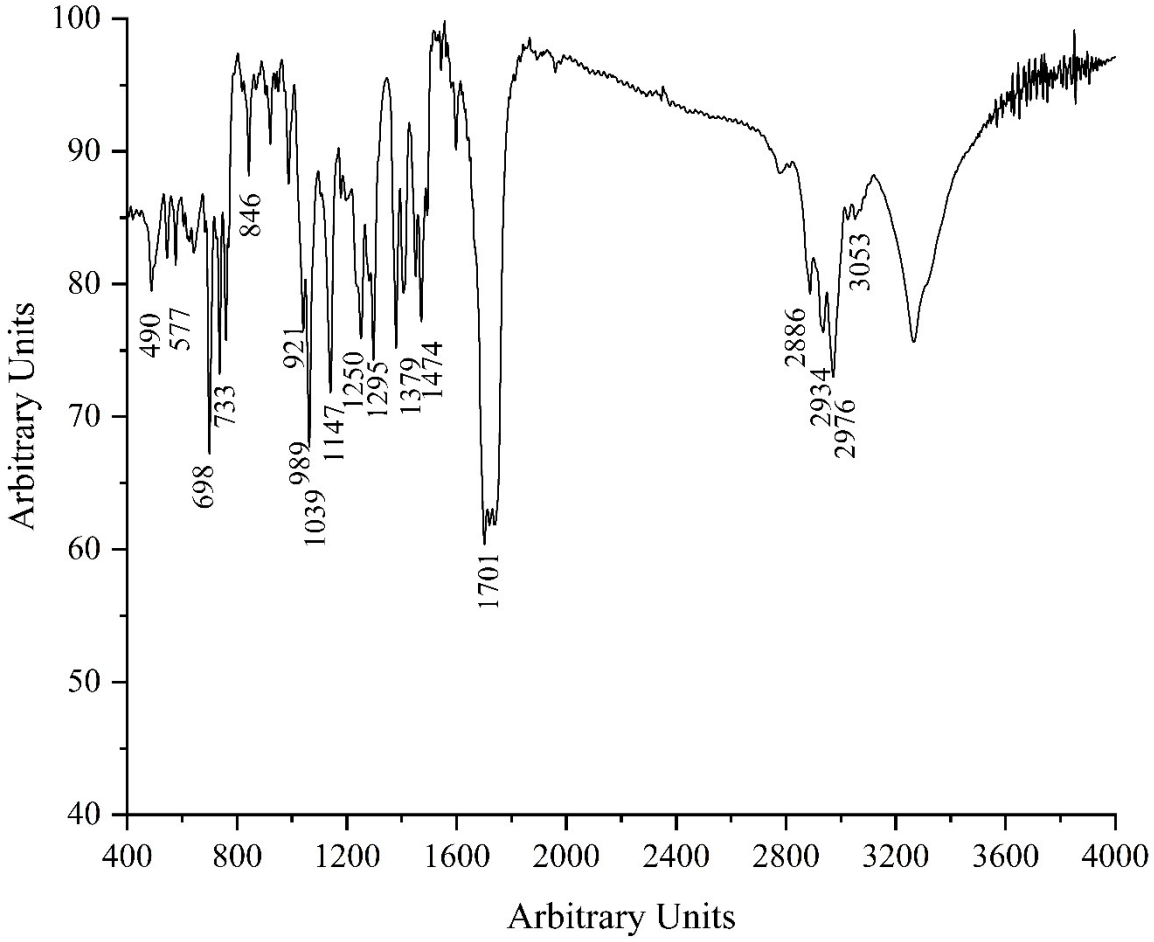

100
90
80
70
60
50
40
30
20
Arbitrary Units
400
800
1200
1600
2000
2400
2800
3200
3600
4000
Arbitrary Units
498
704
746
789
860
939
1064
1133
1237
1381
1418
1476
1716
2884
2934
2969
3076

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

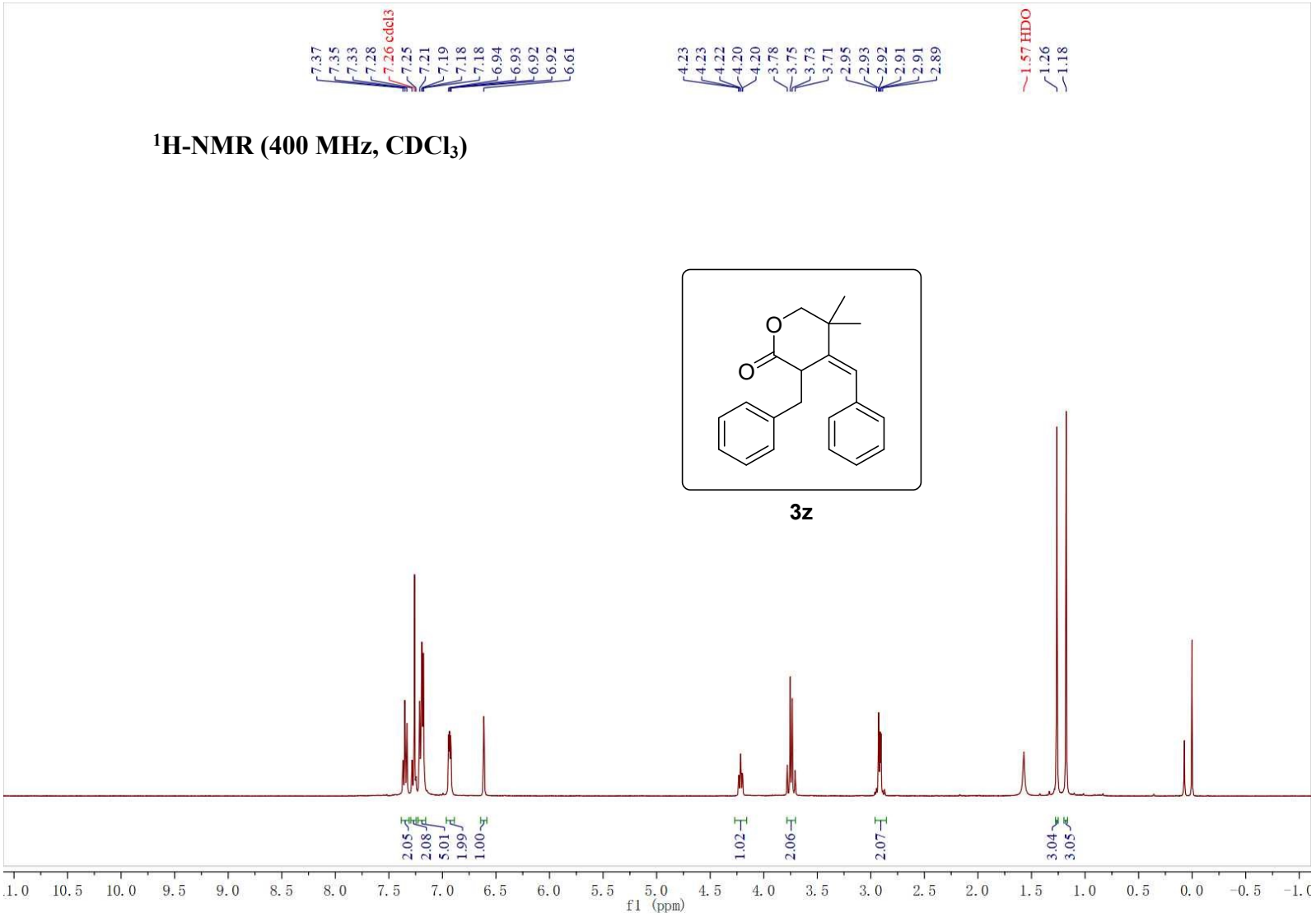


3y

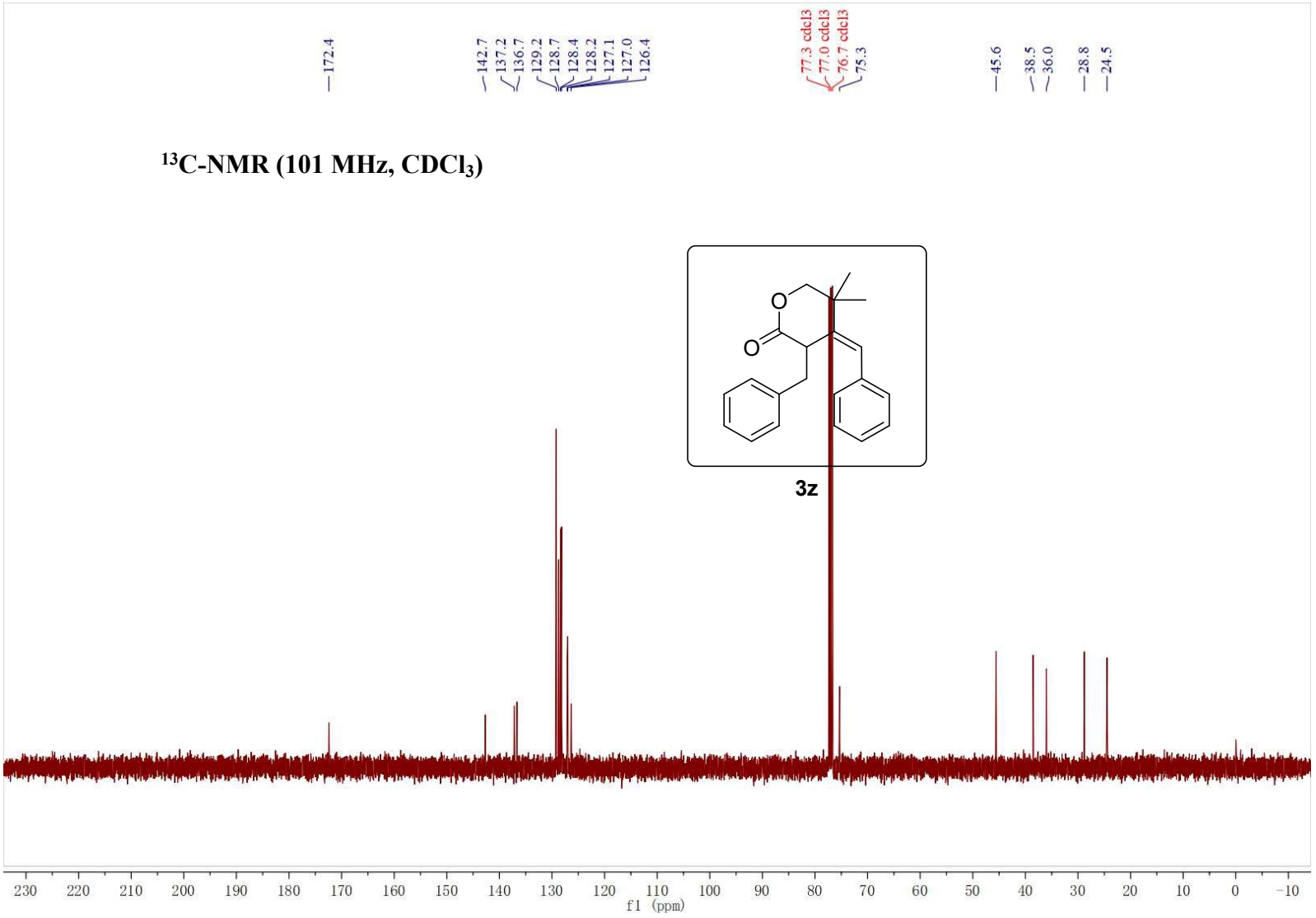

174.1
144.2
136.4
128.6
128.2
127.1
125.5
77.4 cdcl3
77.1 cdcl3
76.8 cdcl3
76.1
38.0
36.3
27.4
25.3
19.1
13C-NMR (101 MHz, CDCl3)
O
O
3y
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


100
90
80
70
60
50
40
Arbitrary Units
490
577
698
733
846
921
989
1039
1147
1250
1295
1379
1474
1701
2886
2934
2976
3053
400
800
1200
1600
2000
2400
2800
3200
3600
4000
Arbitrary Units

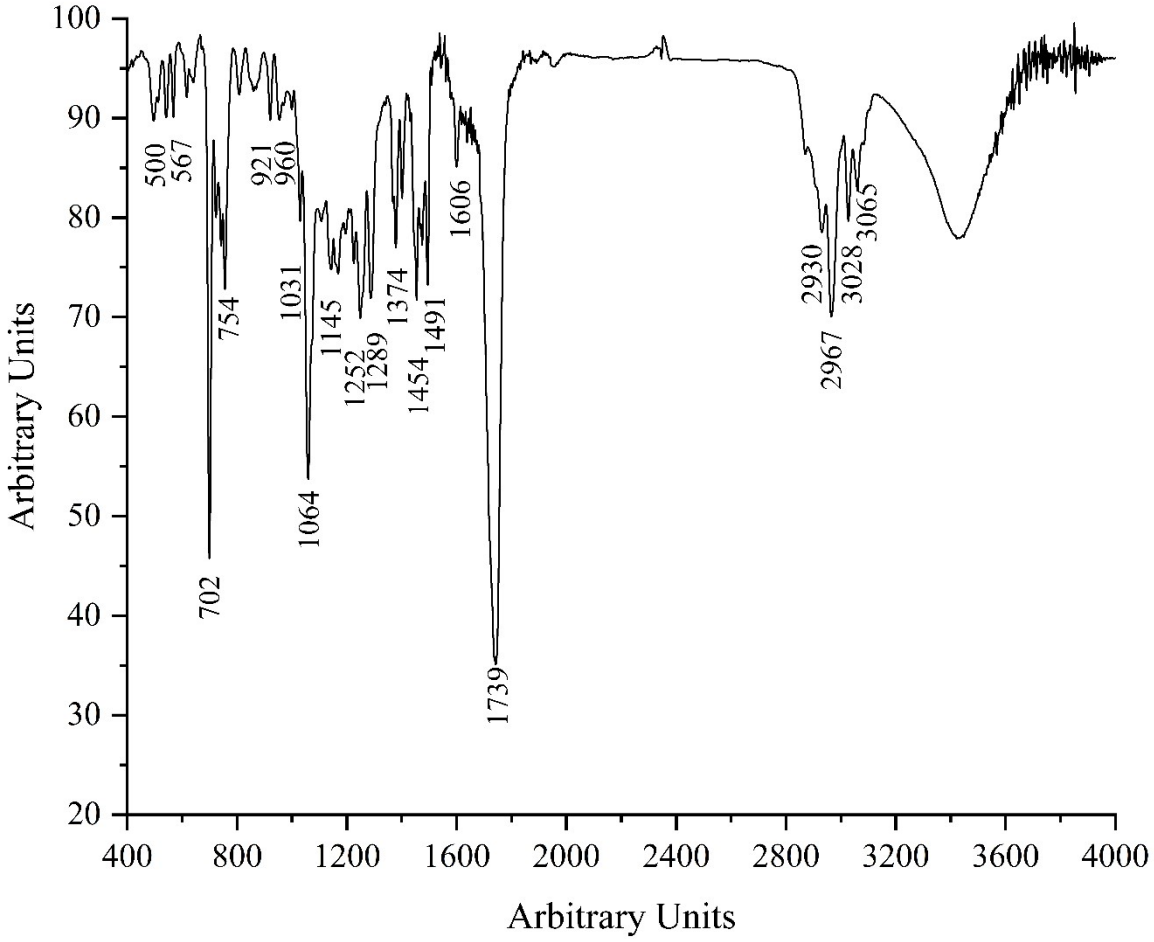
^{1}H-NMR (400 MHz, $CDCl_3$)



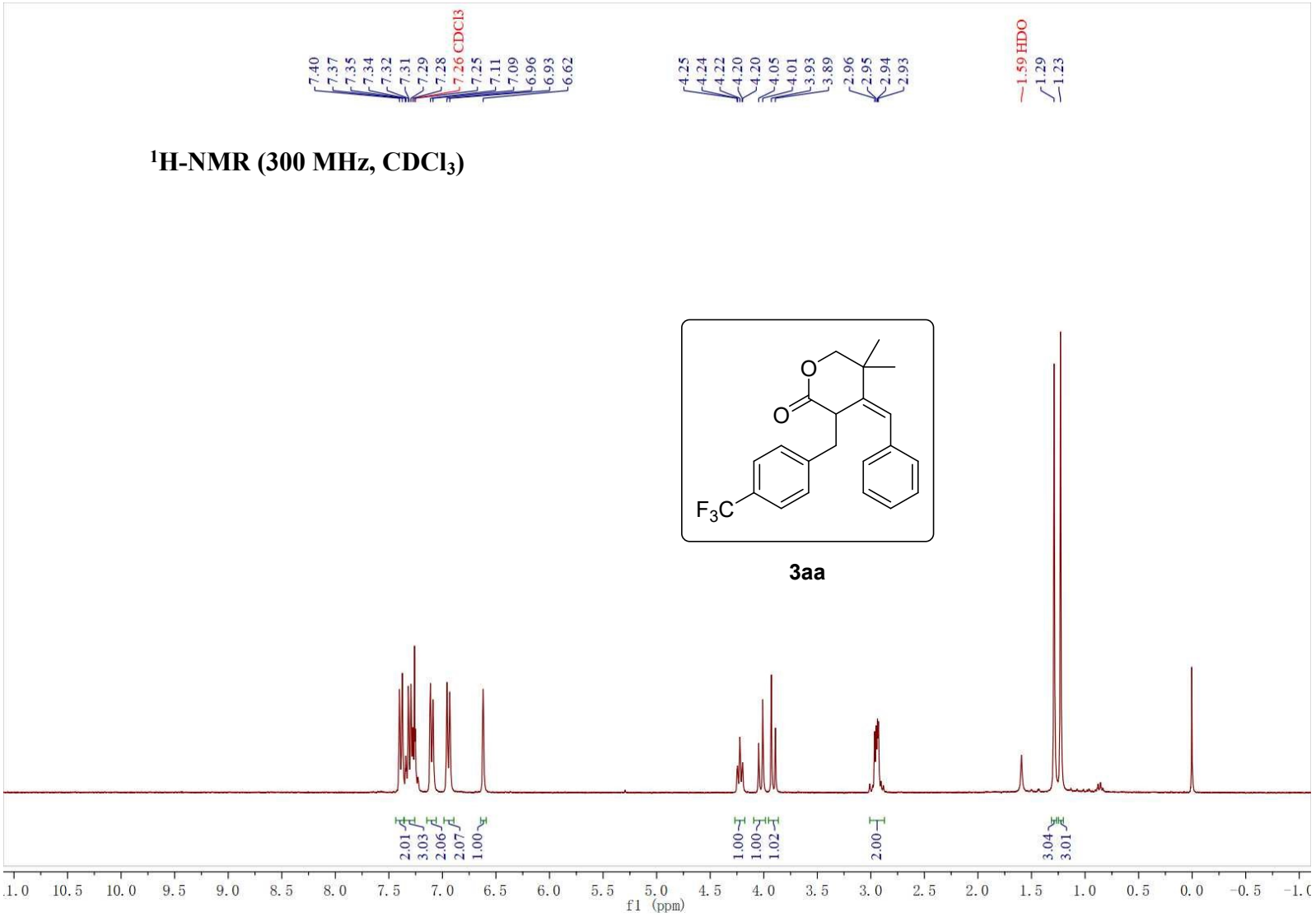
3z



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

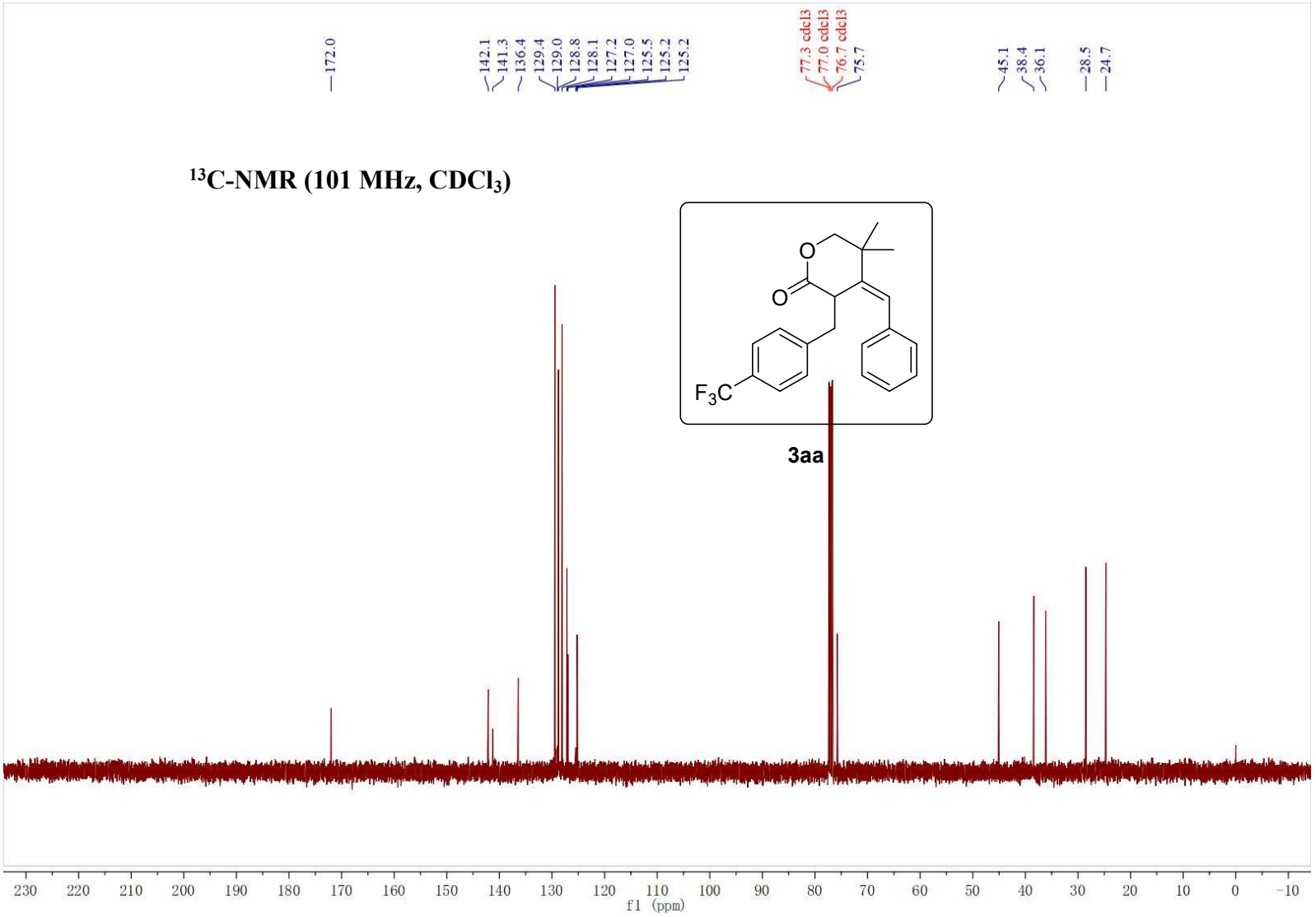

100
90
80
70
60
50
40
30
20
Arbitrary Units
400
800
1200
1600
2000
2400
2800
3200
3600
4000
Arbitrary Units
500
567
702
754
921
960
1031
1064
1145
1252
1289
1374
1454
1491
1606
1739
2930
2967
3028
3065

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

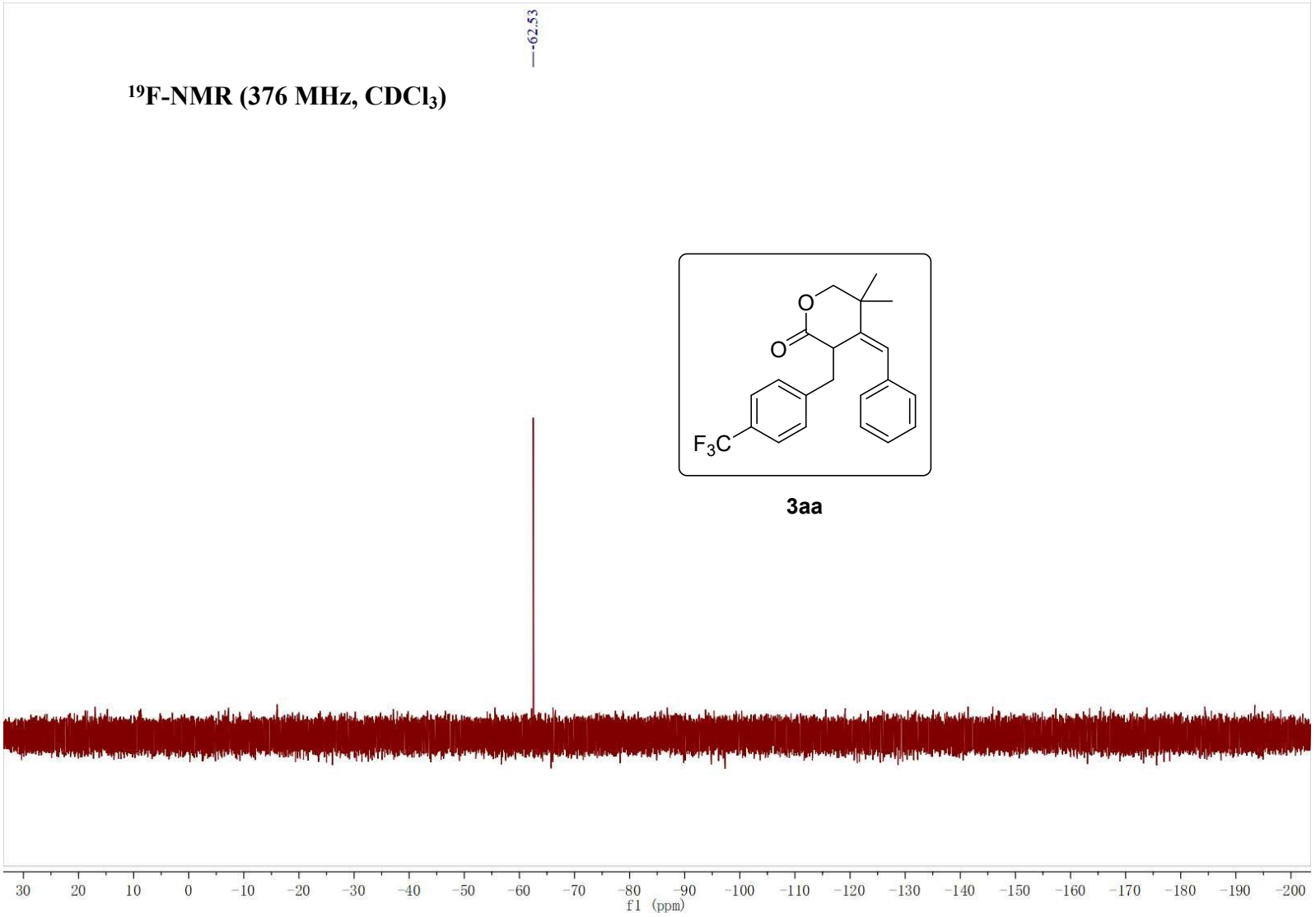


3aa

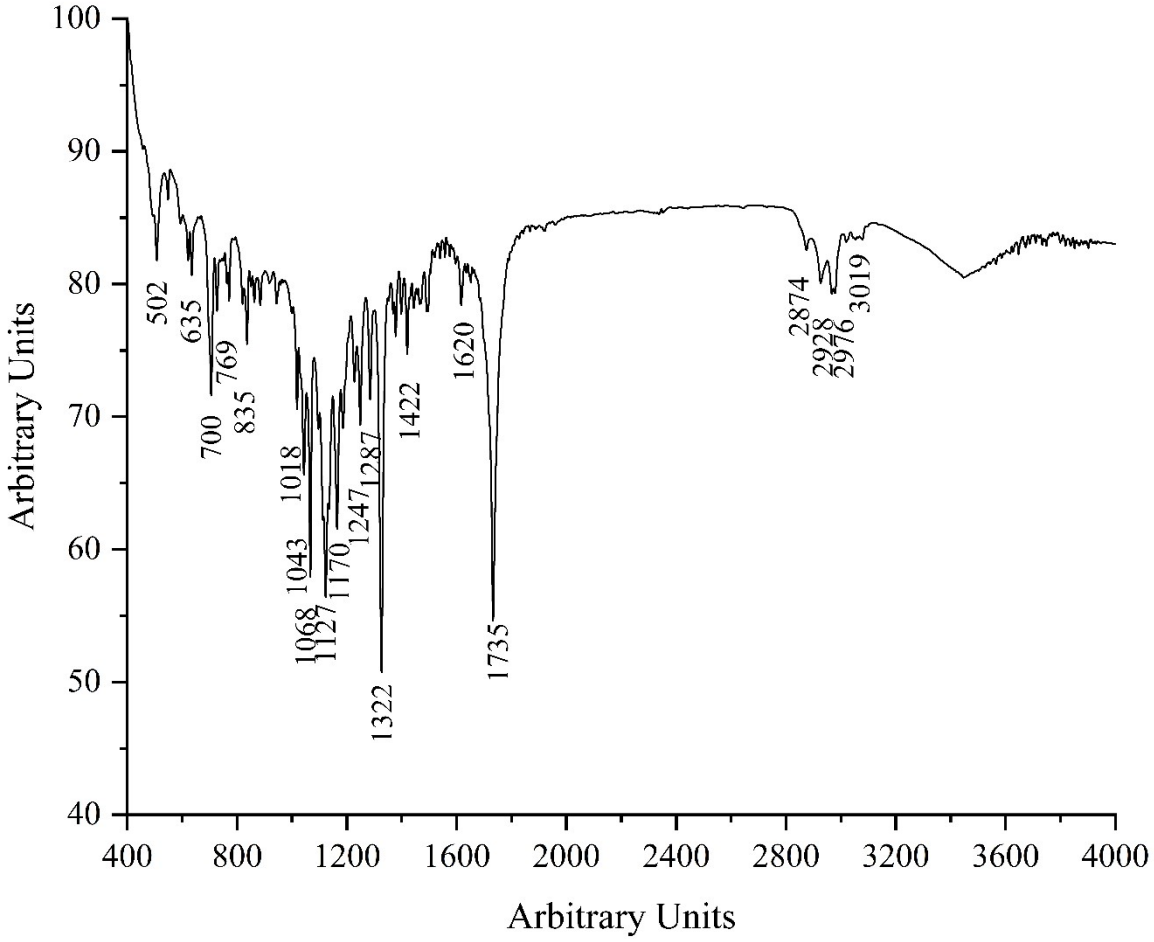
^{13}C-NMR (101 MHz, $CDCl_3$)



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



3aa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40
Arbitrary Units
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800
1200
1600
2000
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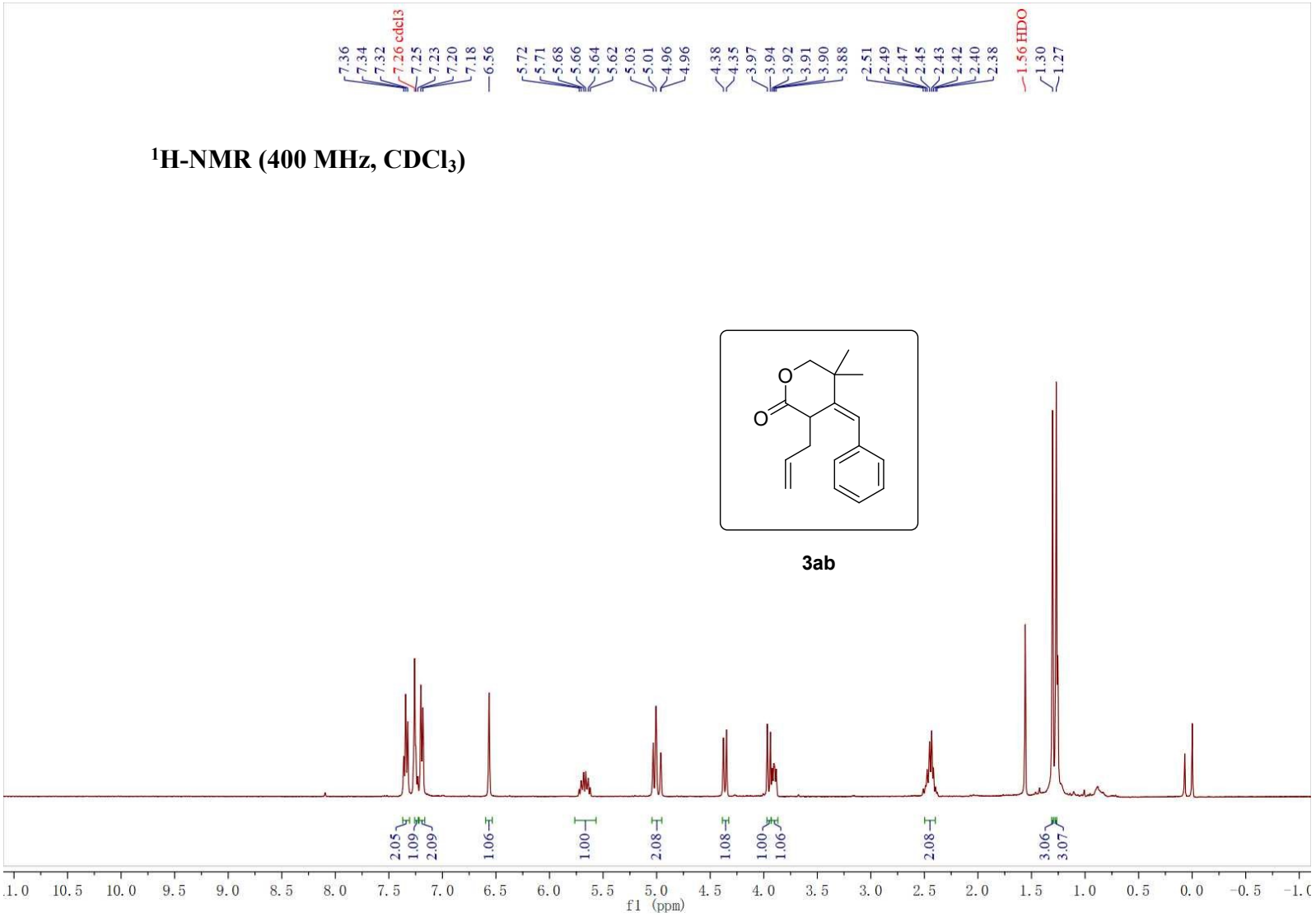
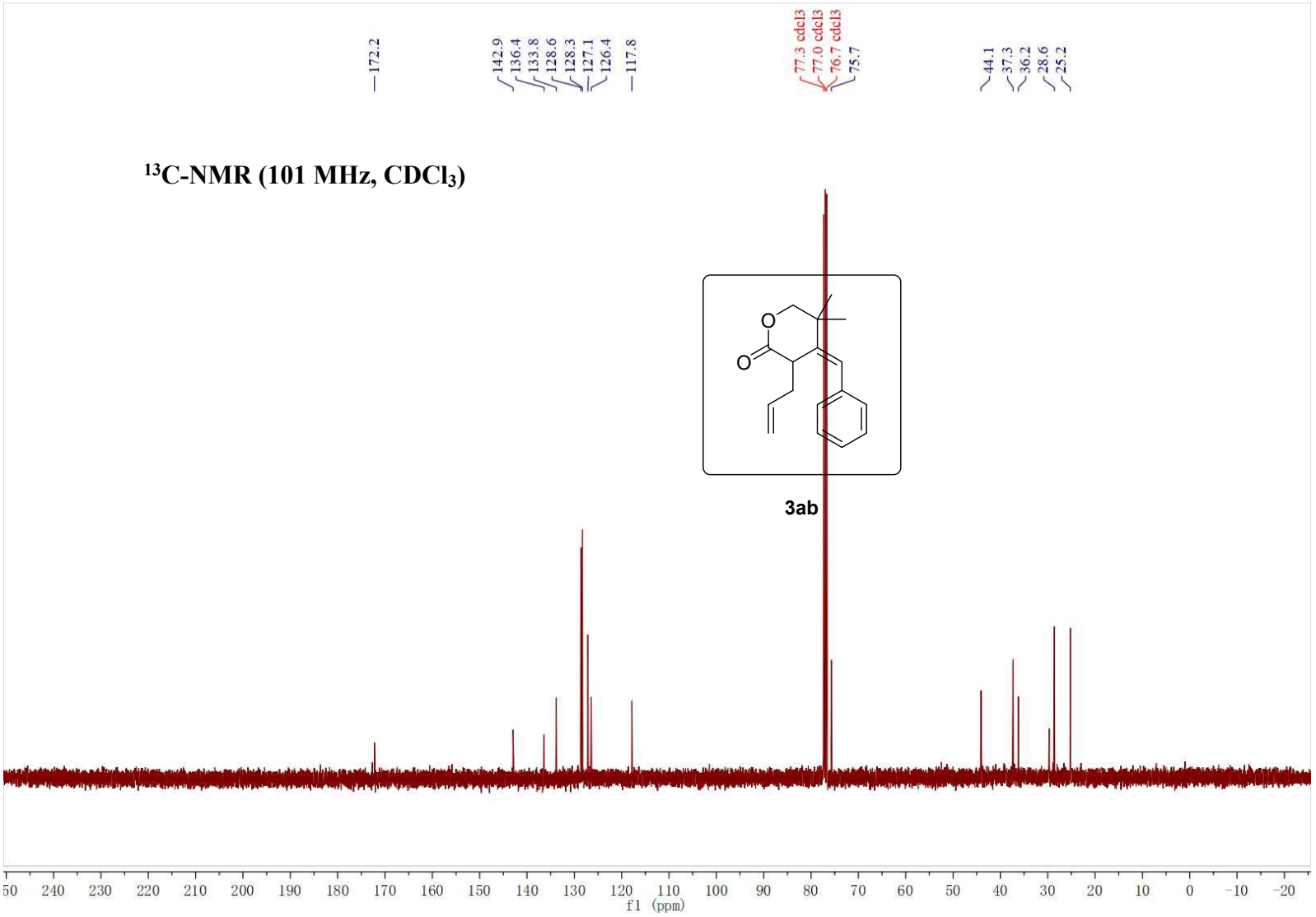
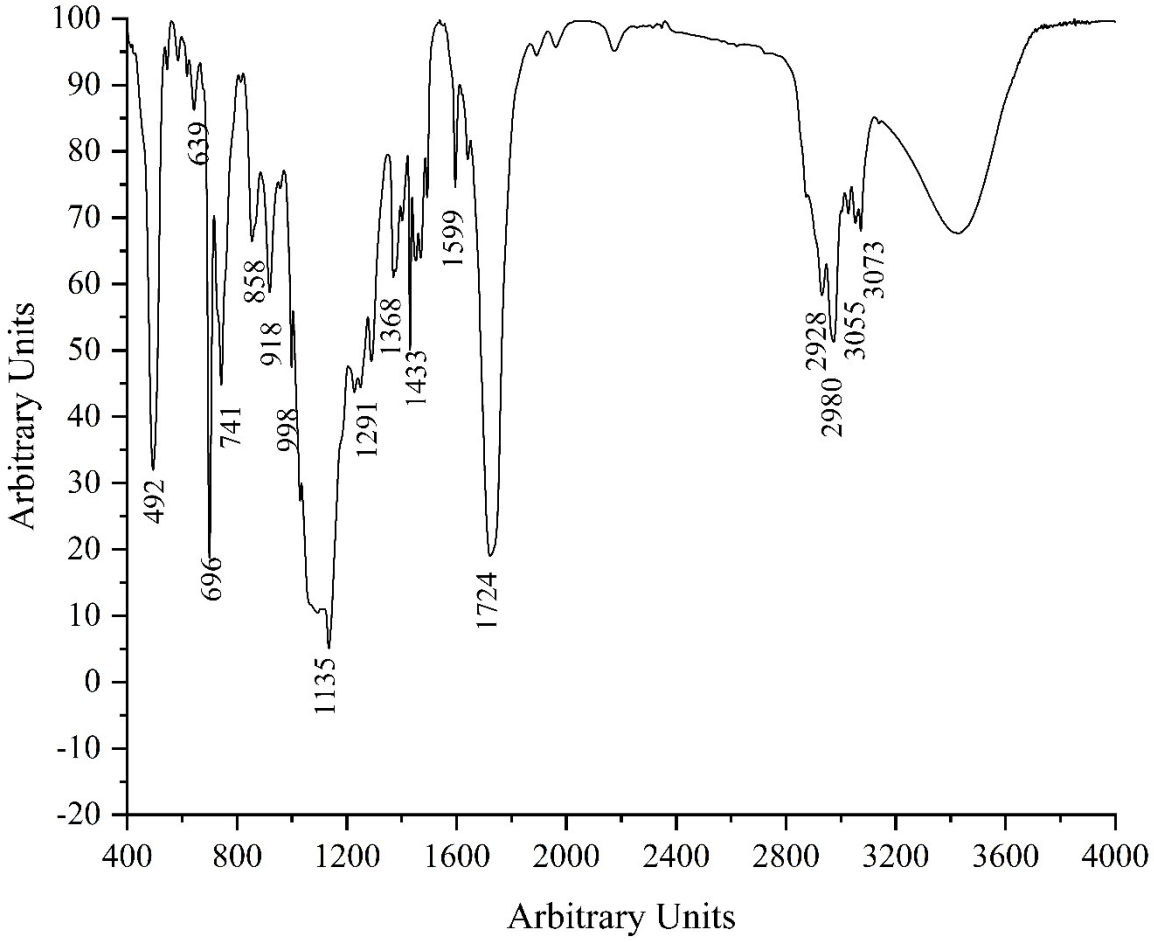
2800
3200
3600
4000
Arbitrary Units
502
635
700
769
835
1018
1043
1068
1087
1127
1170
1247
1287
1322
1422
1620
1735
2874
2928
2976
3019

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



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

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-20
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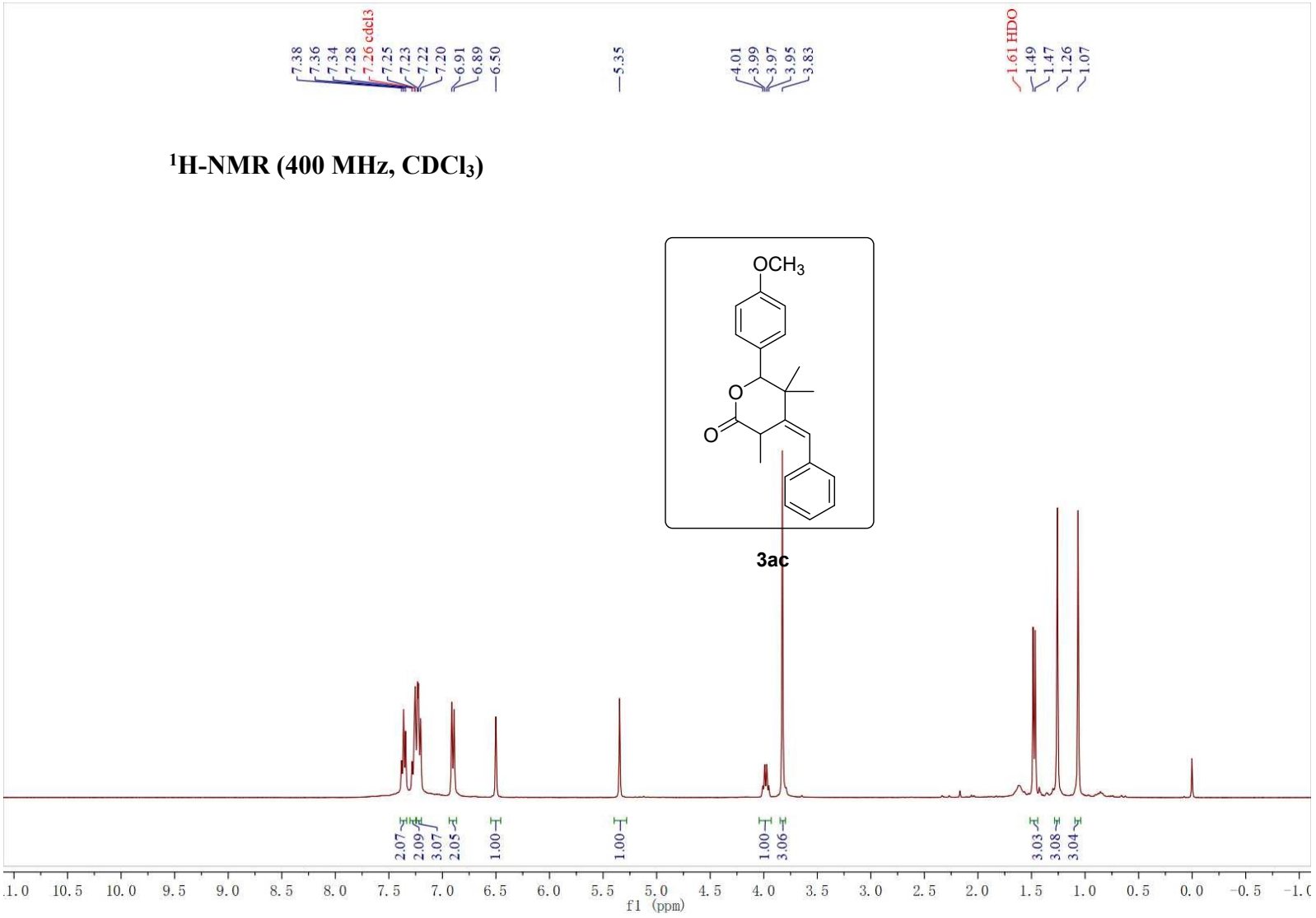
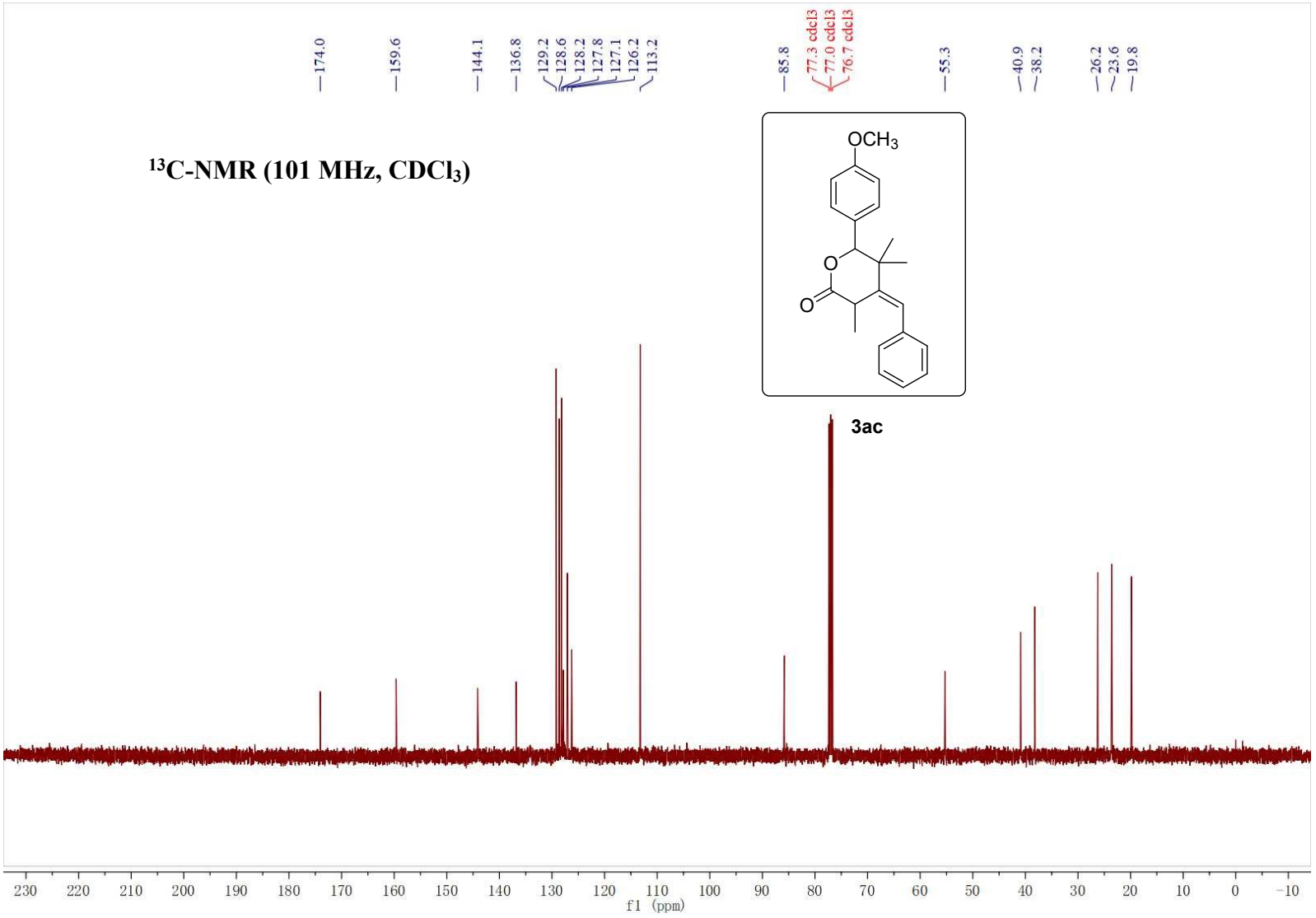
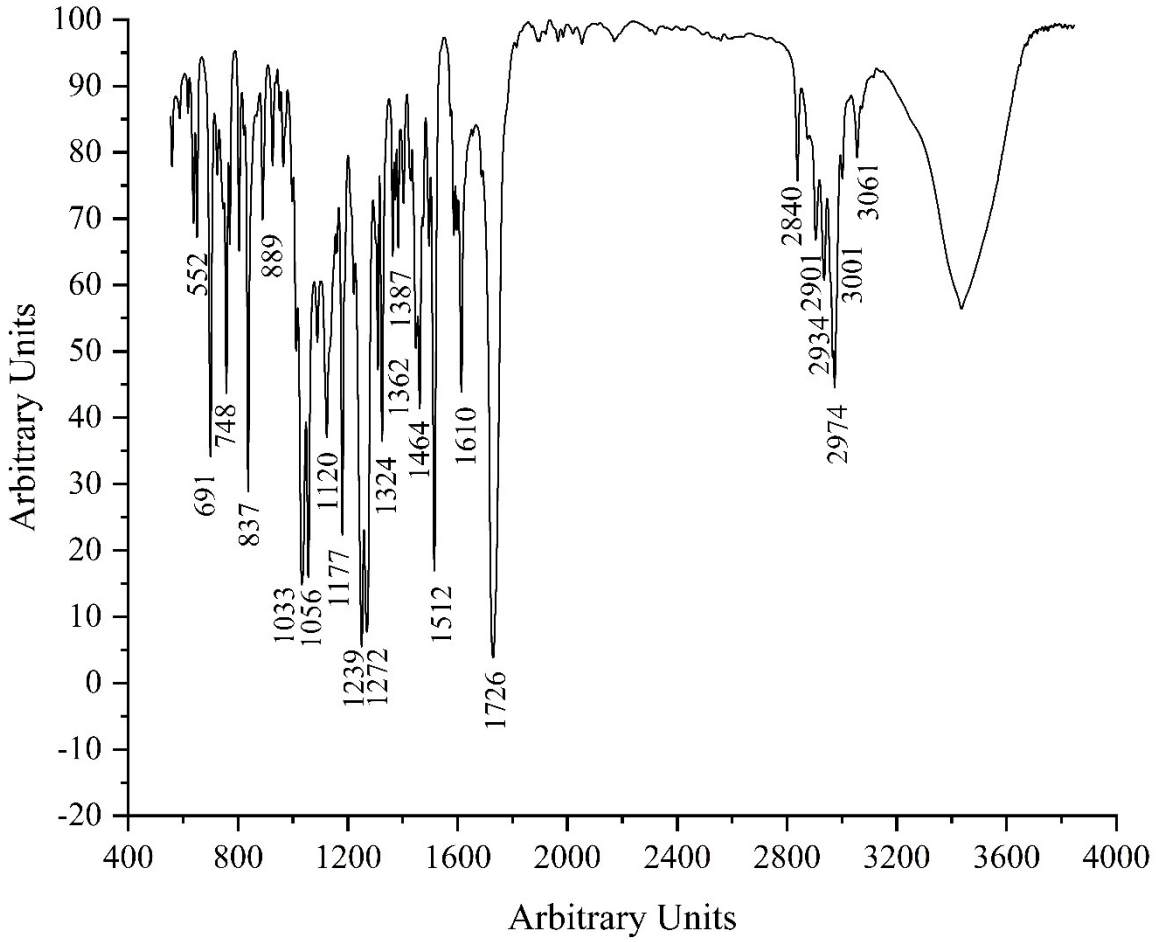
1600
2000
2400
2800
3200
3600
4000
Arbitrary Units
492
639
696
741
858
918
998
1135
1291
1368
1433
1599
1724
2928
2980
3055
3073



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

3ac


174.0
159.6
144.1
136.8
129.2
128.6
128.2
127.8
127.1
126.2
113.2
85.8
77.3 cdcl3
77.0 cdcl3
76.7 cdcl3
55.3
40.9
38.2
26.2
23.6
19.8
13C-NMR (101 MHz, CDCl3)
OCH3
O
O
3ac
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


Arbitrary Units
Arbitrary Units
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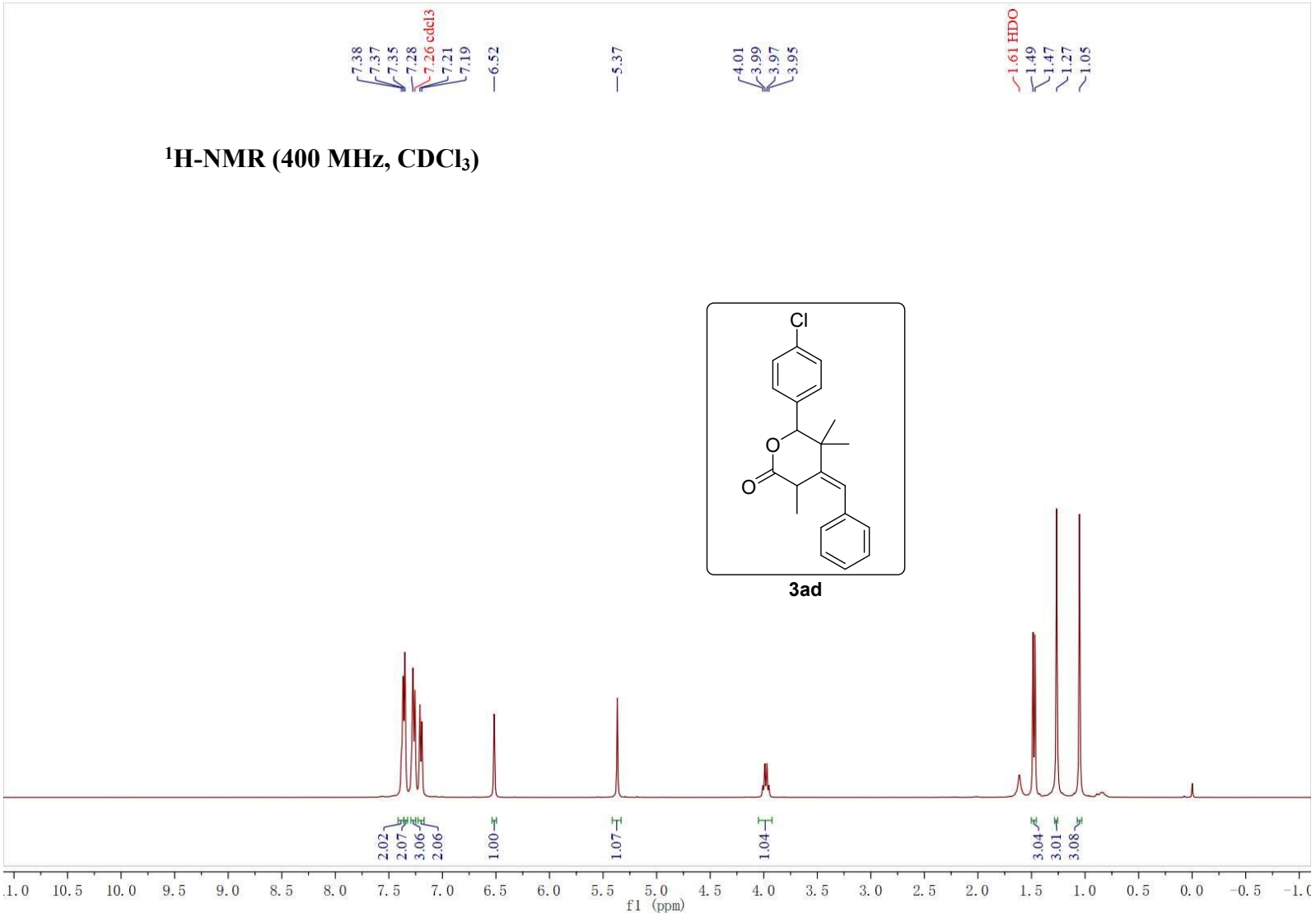
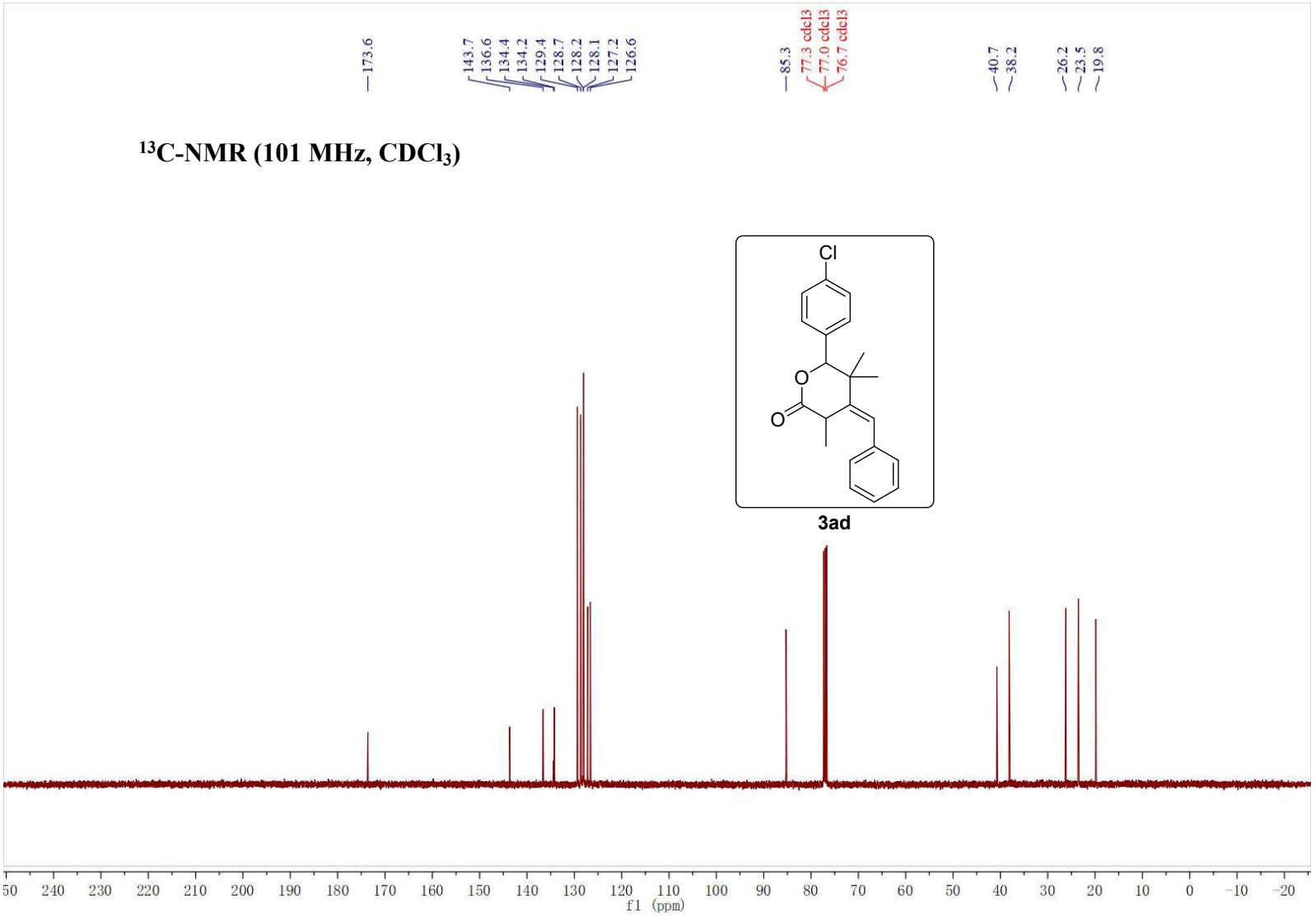
10
0
-10
-20
400
800
1200
1600
2000
2400
2800
3200
3600
4000
552
691
748
837
889
1033
1056
1120
1177
1239
1272
1324
1362
1387
1464
1512
1610
1726
2840
2901
2934
2974
3001
3061

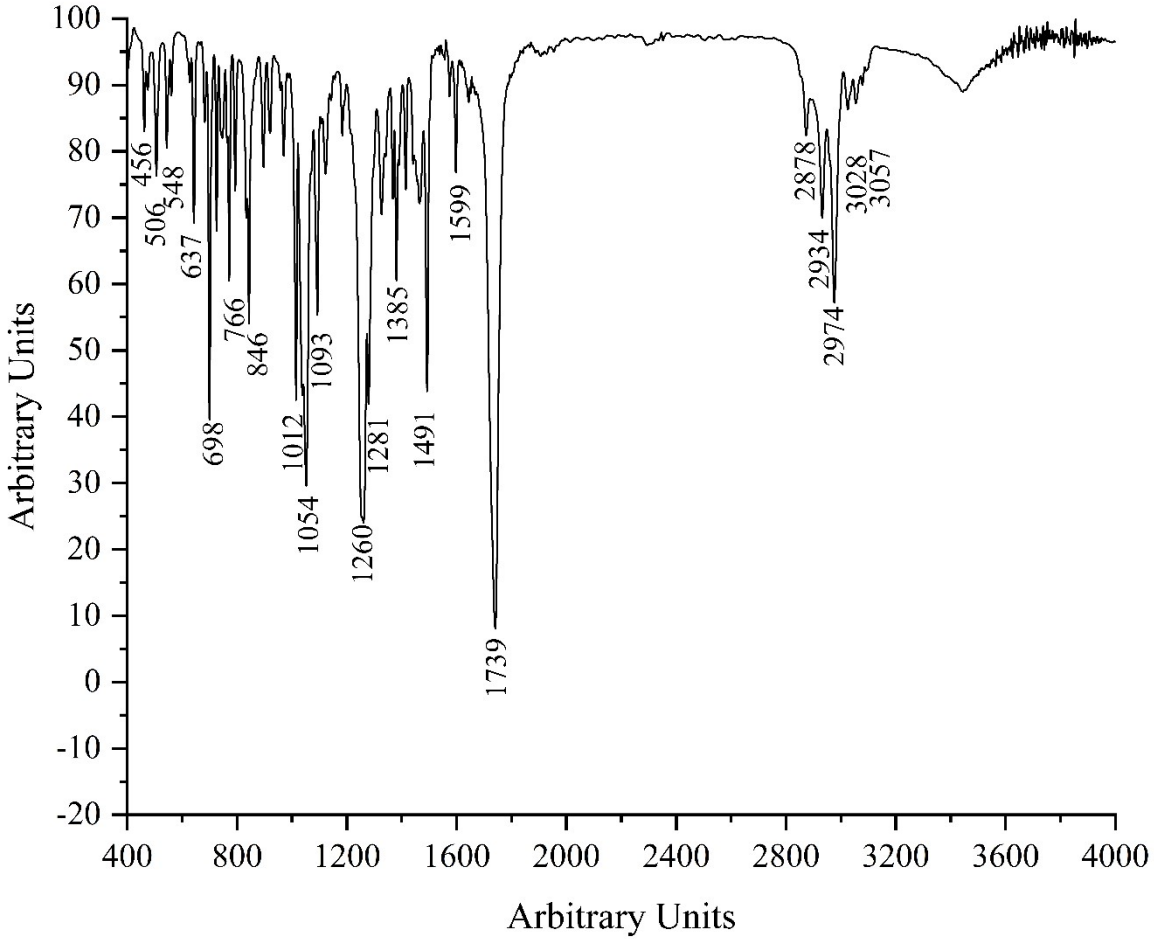
9

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



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




Arbitrary Units
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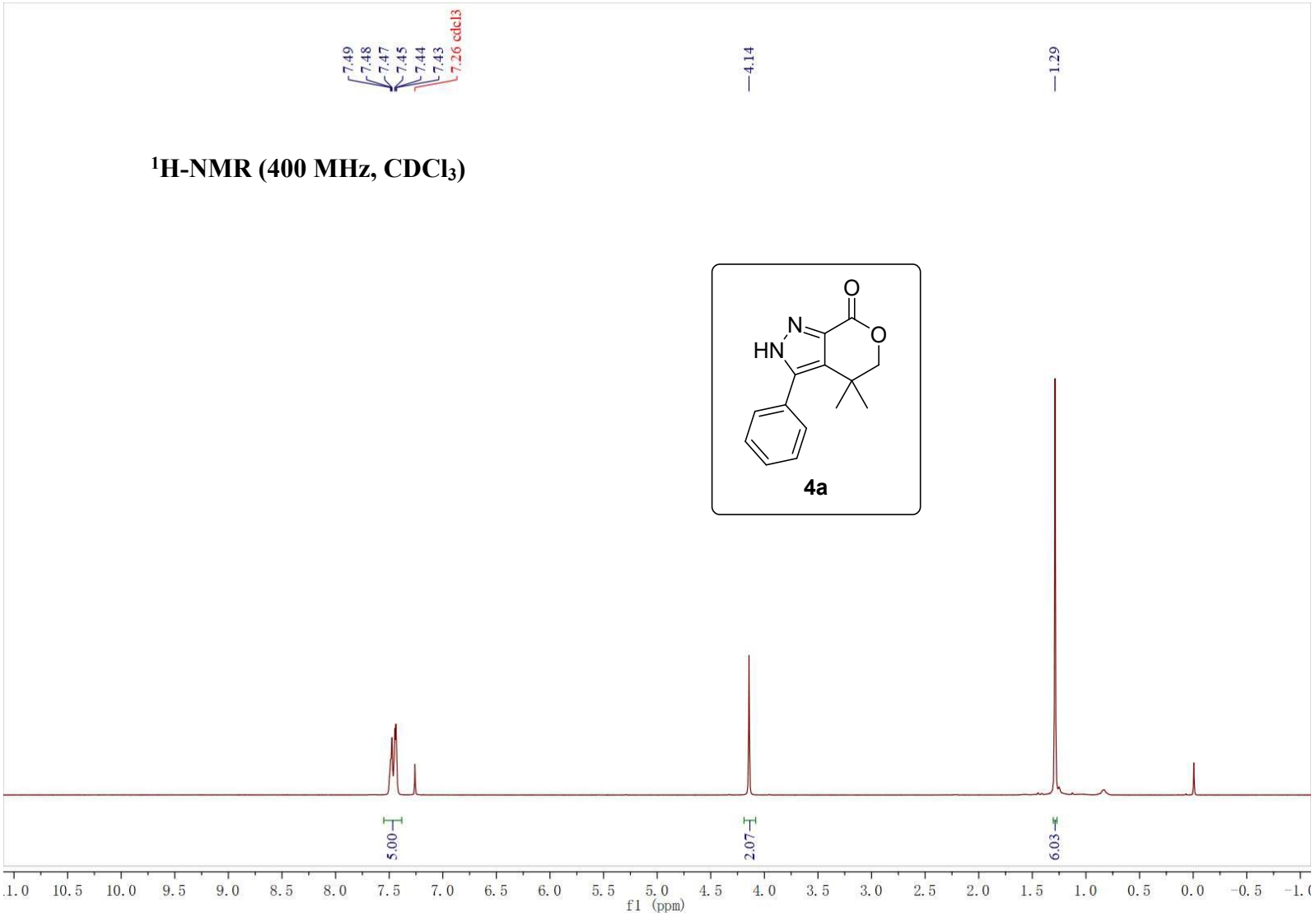
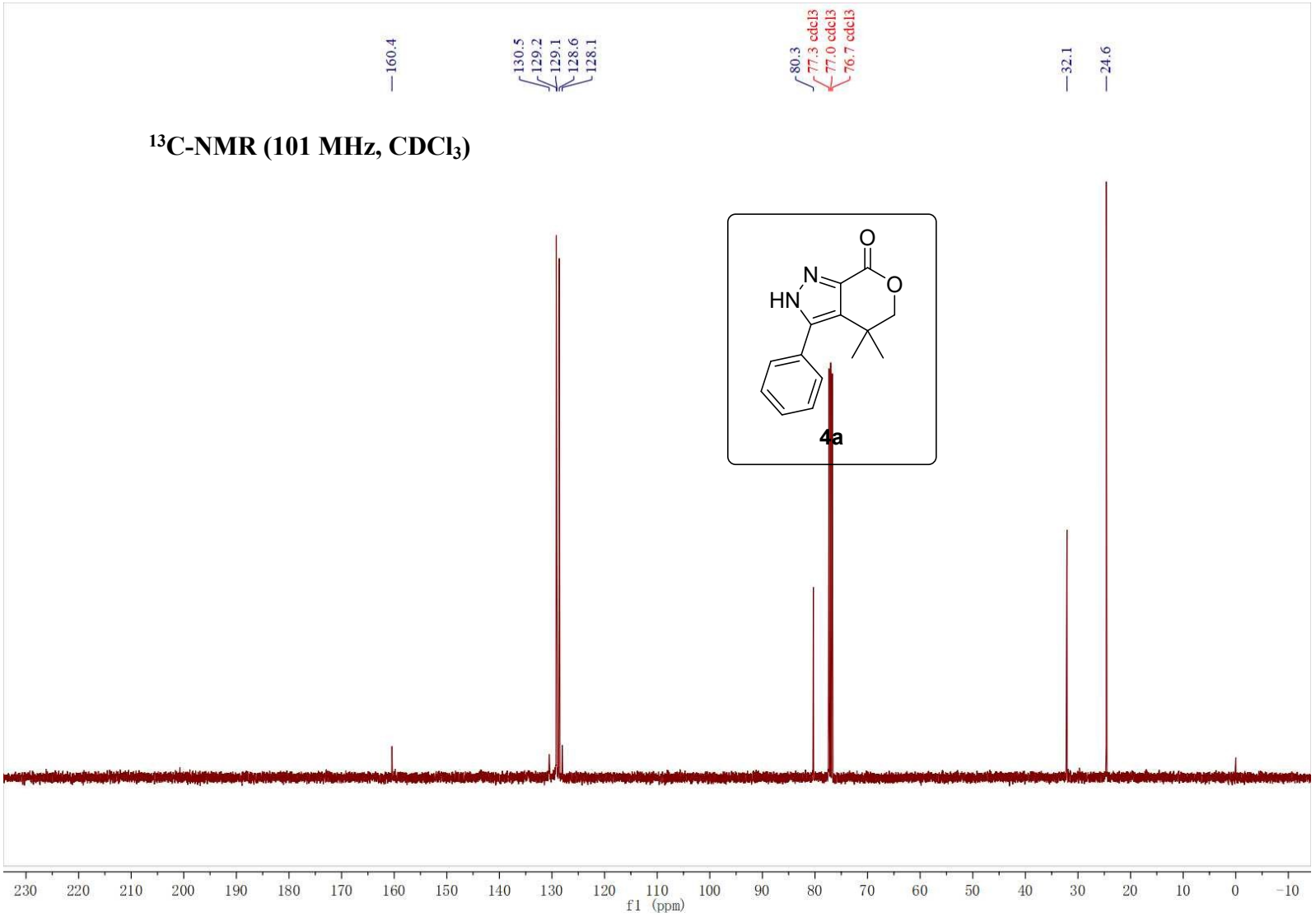
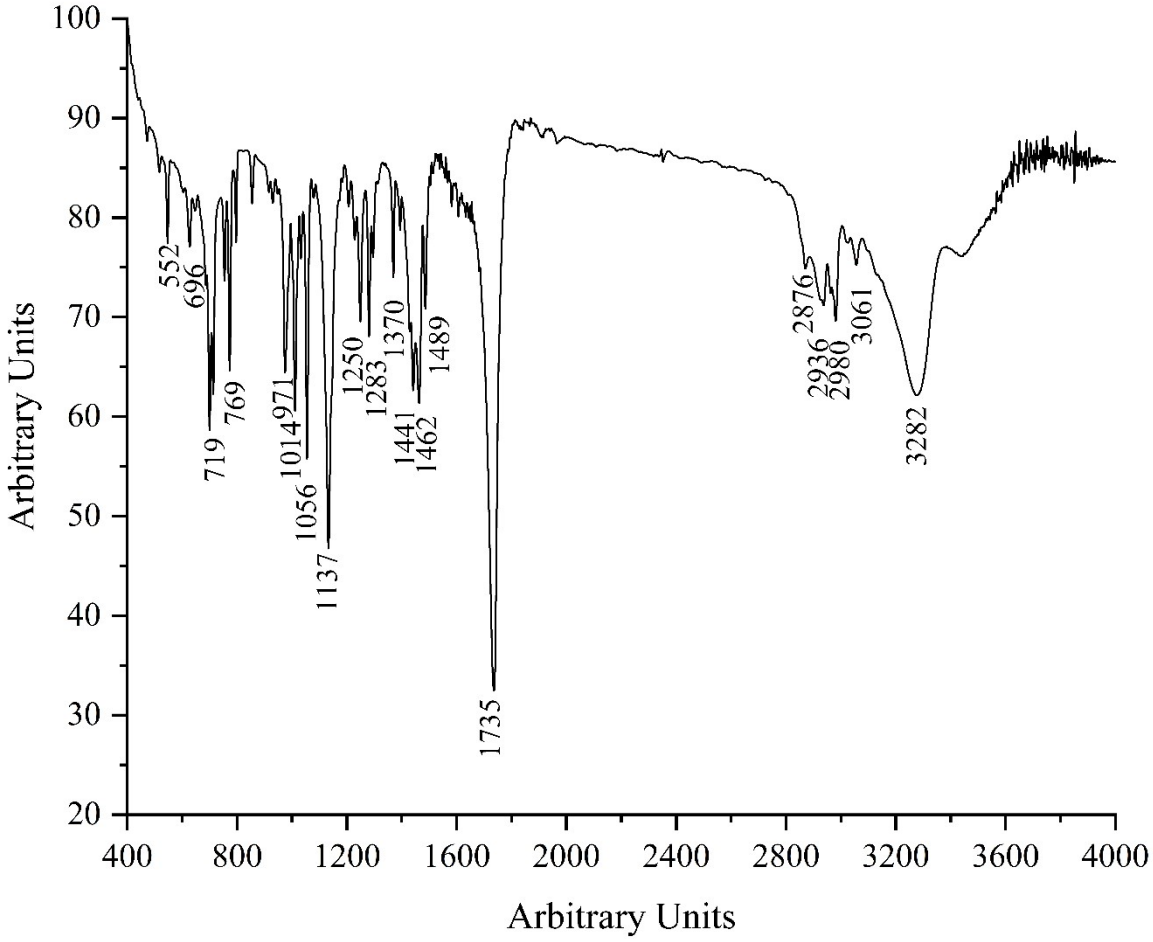
0
-10
-20
400
800
1200
1600
2000
2400
2800
3200
3600
4000
Arbitrary Units
456
506
548
637
698
766
846
1012
1054
1093
1260
1281
1385
1491
1599
1739
2878
2934
2974
3028
3057

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



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




Arbitrary Units
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60
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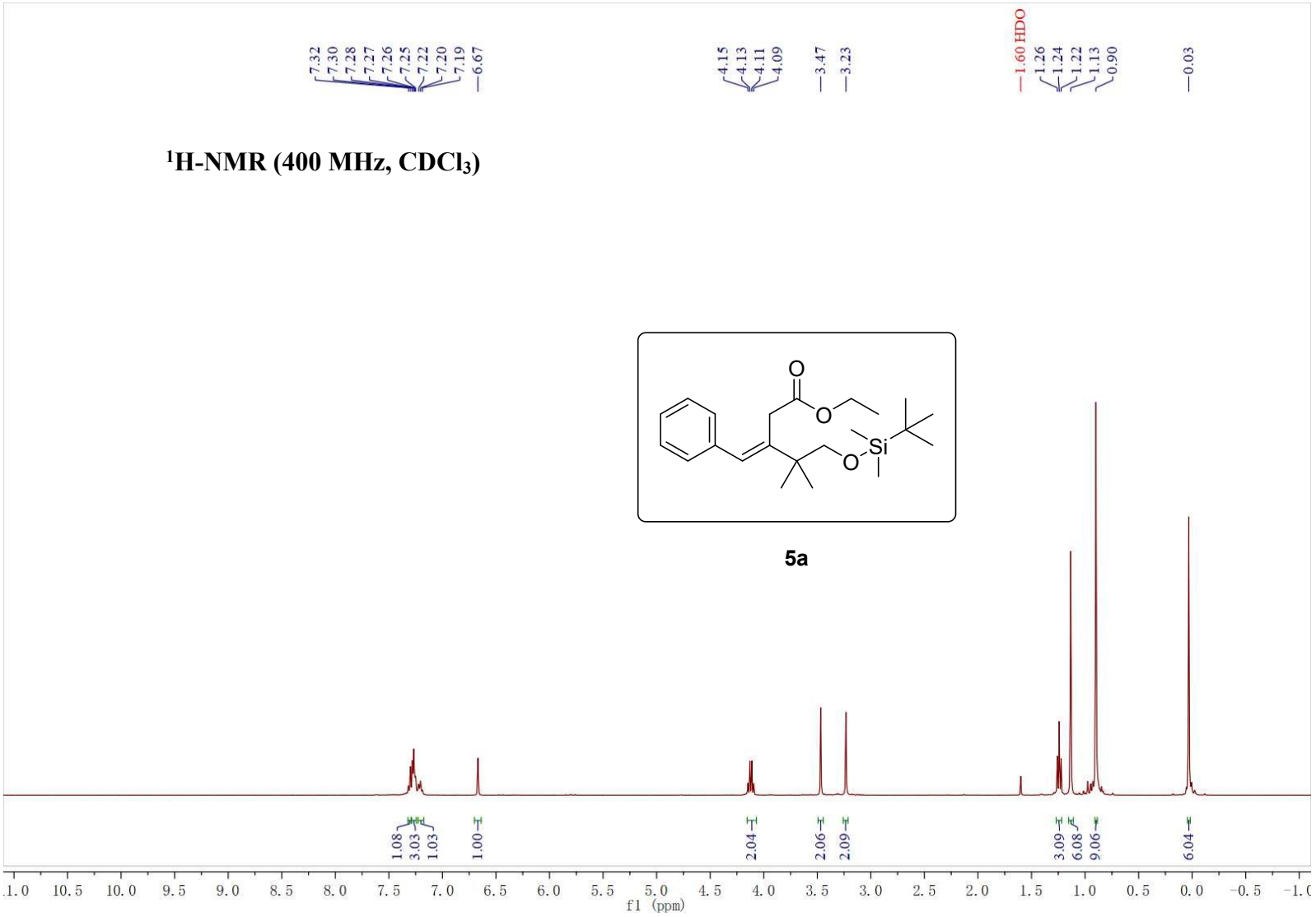
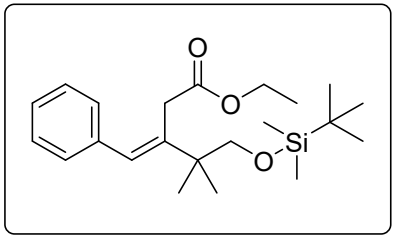
30
20
400
800
1200
1600
2000
2400
2800
3200
3600
4000
Arbitrary Units
552
696
719
769
971
1014
1056
1137
1250
1283
1370
1441
1462
1489
1735
2876
2936
2980
3061
3282

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

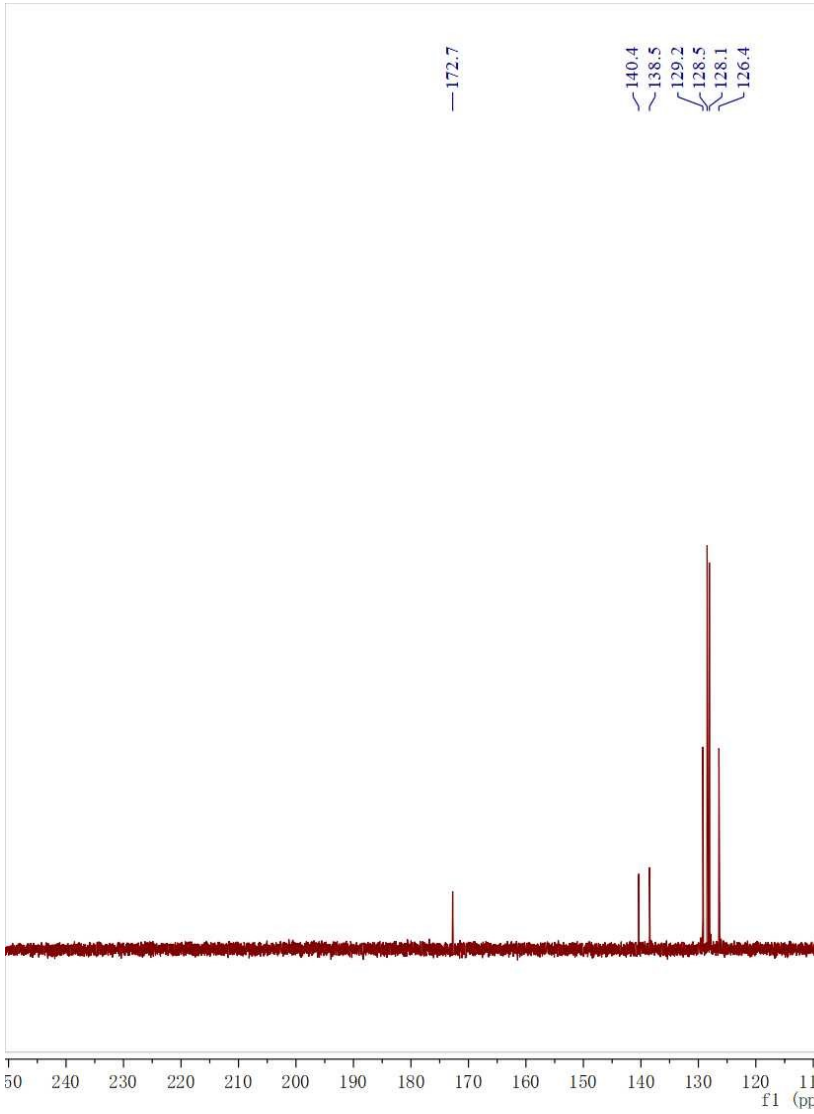


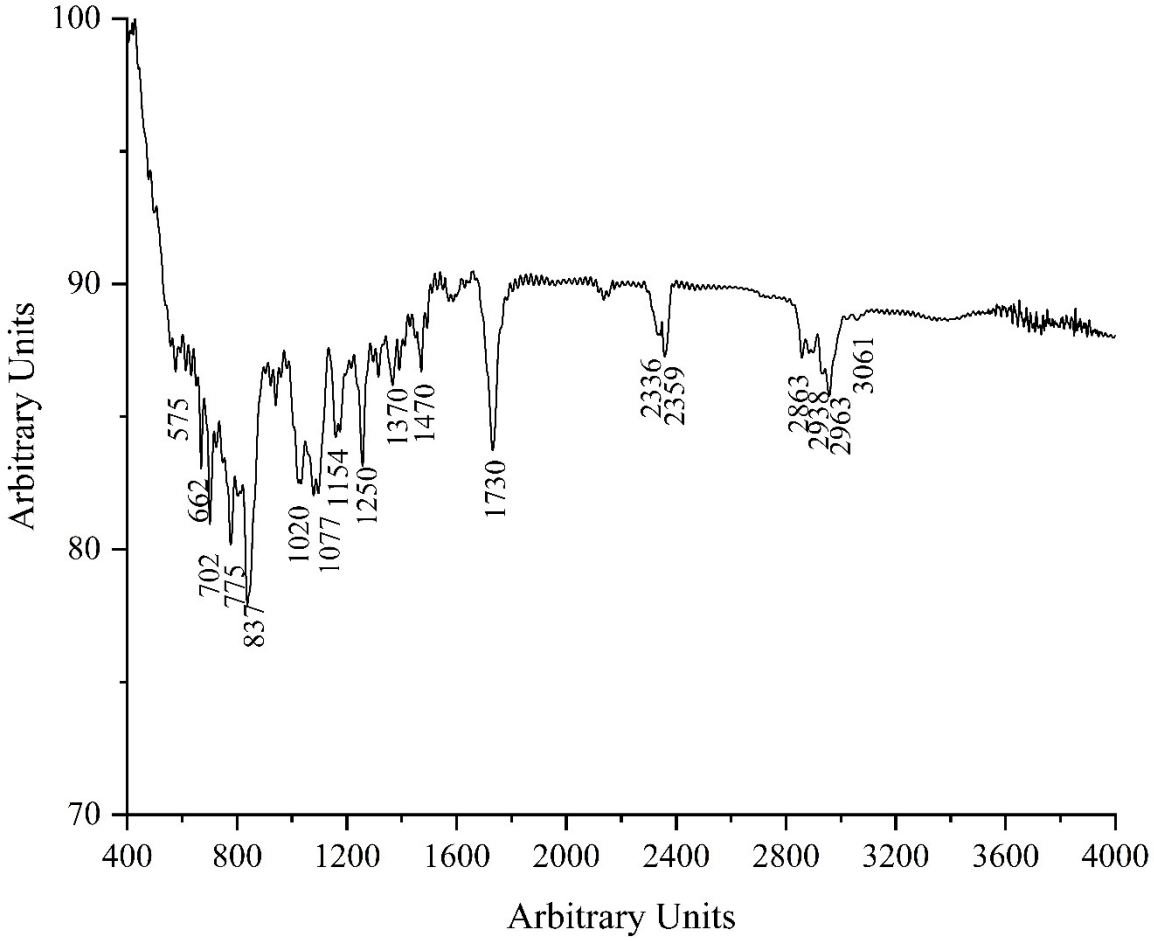
5a

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



5a




100
90
80
70
Arbitrary Units
400
800
1200
1600
2000
2400
2800
3200
3600
4000
Arbitrary Units
575
662
702
775
837
1020
1077
1154
1250
1370
1470
1730
2336
2359
2863
2938
2963
3061