Supporting Information

Mild and efficient synthesis of carbamates using dioxazolones as bench-stable isocyanate surrogates: Application in AChE-inhibiting agent development

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Table S1. Docking scores (kcal/mol) of carbamate compounds with AChE (PDB: 6TT0, 7D9O).

Compd.	6TT0	7D9O
1a	–5.3129	–5.4369
1b	–5.8117	–6.0918
1c	–5.9608	–6.0454
1d	–6.1716	–6.3851
1e	–6.1507	–6.3418
1f	–6.0331	–6.1067
2a	–5.9676	–6.1189
2b	–6.4757	–6.6822
2c	–6.7661	–6.7778
2d	–7.1777	–7.0168
2e	–7.2480	–6.9662
2f	–6.8856	–6.6223
3a	–6.4029	–6.2284
3b	–6.6376	–6.3183
3c	–6.8289	–6.7875
3d	–7.1724	–7.0586
3e	–6.9189	–6.8828
3f	–6.8455	–6.4411
4a	–5.6083	–5.7529
4b	–6.1481	–6.3998
4c	–6.4141	–6.5733
4d	–6.6313	–6.6033
4e	–6.5182	–6.8393
4f	–6.4459	–6.5258
5a	–6.2165	–6.2958
5b	–6.6315	–6.4171

5c	–6.8136	–6.9055
5d	–7.1976	–6.9236
5e	–7.0987	–7.1120
5f	–7.0161	–6.5891

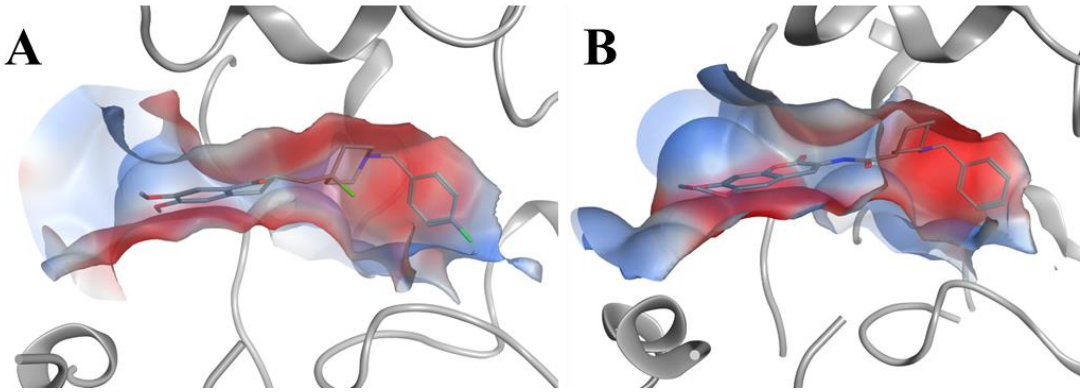


Fig. S1. Schematic diagram of the interaction (VDW) in the active pocket of human *h*AChE (**A**) (PDB: 7D9O, ligand: (2*R*)-2-[[4-fluoro-1-[(4-fluorophenyl)methyl]piperidin-4-yl]methyl]-5,6-dimethoxy-2,3-dihydroinden-1-one) and electric eel AChE (**B**) (PDB: 6TT0, ligand: (1*R*,3*S*)-*N*-(6,7-dimethoxy-2-oxochromen-3-yl)-3-[(phenylmethyl)amino]cyclohexane-1-carboxamide. Hydrophilic regions of the pocket are shown in blue, and hydrophobic regions in red.

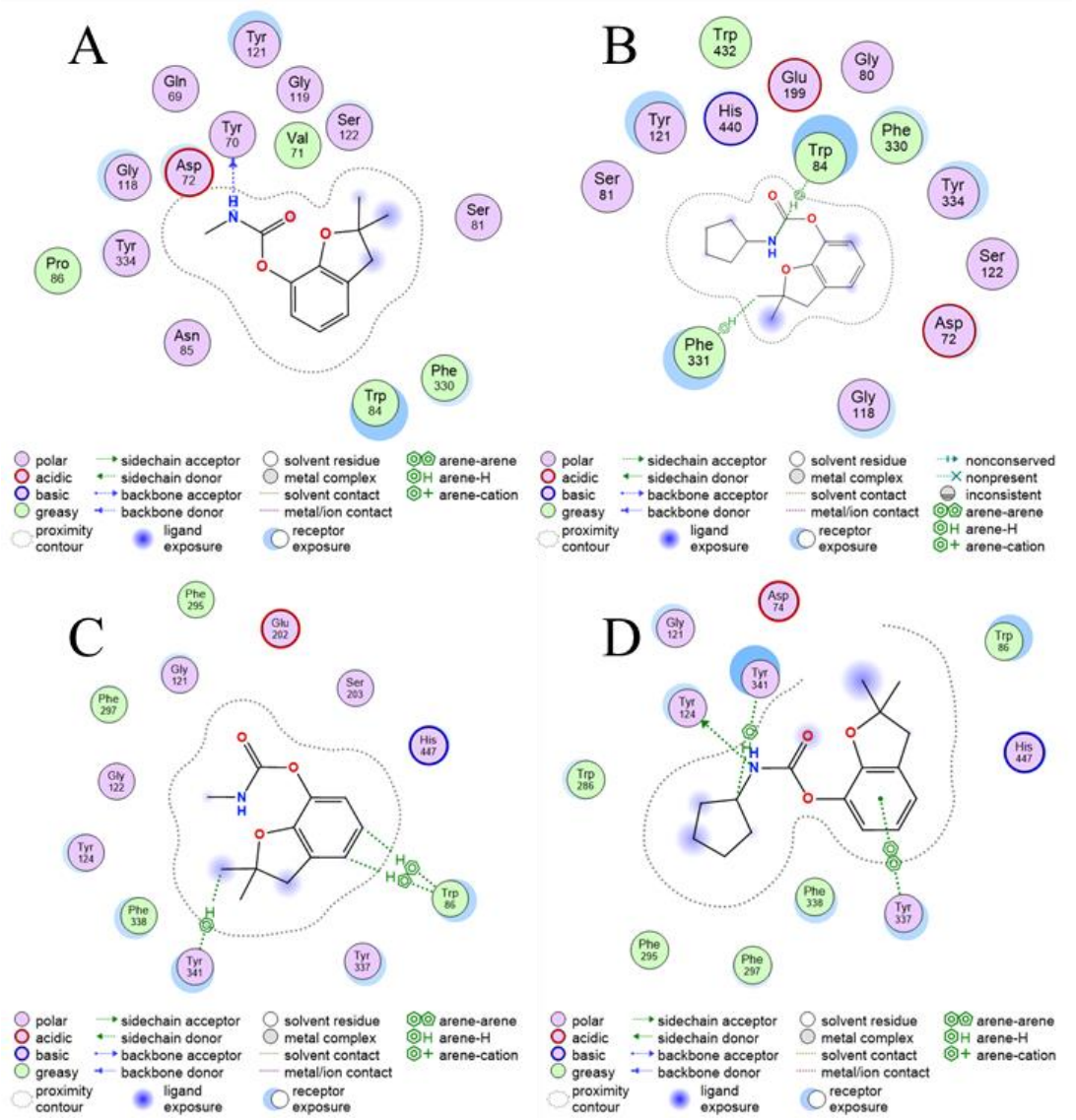


Fig. S2. 2D mode (**A**) of interactions of **5a** with receptor eeAChE (PDB: 6TT0) and 2D mode (**B**) of interactions of **5d** with receptor eeAChE (PDB: 6TT0); 2D mode (**C**) of interactions of **5a** with receptor AChE (PDB: 7D9O) and 2D mode (**D**) of interactions of **5d** with receptor AChE (PDB: 7D9O).

1. General information

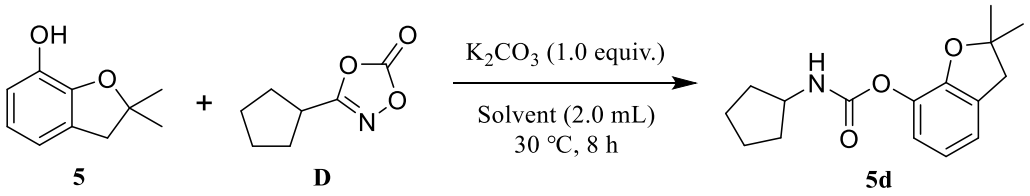
All reactions were carried out under an air atmosphere unless otherwise specified. Oil bath was used for the heating reactions. NMR spectra were recorded in $CDCl_3$ / DMSO-d_6 on a 500 MHz (for ^1H/ for ^{13}C) or 400 MHz (for ^1H/ for ^{13}C) spectrometer. All chemical shifts are reported in ppm relative to TMS (0 ppm) as an internal standard. The following abbreviations were used to explain the multiplicities: *s* = singlet, *d* = doublet, *t* = triplet, *q* = quartet, *m* = multiplet. The coupling constants were reported in Hertz (Hz).

The reaction between 2,2-dimethyl-2,3-dihydrobenzofuran-7-ol (**5**) and 3-cyclopentyl-1,4,2-dioxazol-5-one (**D**) to form 2,2-dimethyl-2,3-dihydrobenzofuran-7-yl cyclopentylcarbamate (**5d**) was selected as the model for optimization. To monitor and quantify the yield under optimized conditions, high-performance liquid chromatography (HPLC) was preferred for the detection of both reactants and products. HPLC analysis was performed on a Shimadzu system equipped with a J&K RP-C18 column (5 μm, 4.6 × 150 mm). A pure, independently synthesized sample of **5d** was used as an external standard for quantification.

Unless otherwise specified, an acetonitrile (A)-water (B) gradient was applied as follows: 0-2 min, 60% A; 2-3 min, linear increase to 80% A; 3-7 min, maintained at 80% A; 7-8 min, increase to 90% A; 8-10 min, maintained at 90% A; 10-11 min, decrease to 60% A; and 11-14 min, re-equilibration at 60% A. The total run time was 20 min with a flow rate of 1.0 mL/min. The retention times and detection wavelength were: TR, **5d** = 6.520 min, **5** = 3.526 min at λ_{max} = 254.0 nm. All other reagents were obtained from commercial sources and used without further purification.

2. Optimization of the reaction conditions

Table S2. Screening of the solvent [a]

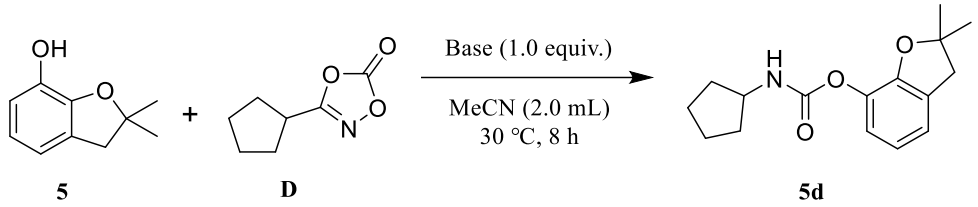


5 **D** **5d**

Entry	Solvent	Yield (**5d**, %) [b]
1	DCM	9
2	Ethyl acetate	6
3	MeOH	14
4	**MeCN**	**22**
5	THF	5
6	**Acetone**	**25**
7	Toluene	10
8	1,4-Dioxane	3
9	DMF	12
10	DMSO	5

[a] Dissolve 2,2-dimethyl-2,3-dihydrobenzofuran-7-ol (**5**, 32.8 mg, 0.2 mmol), 3-cyclopentyl-1,4,2-dioxazol-5-one (**D**, 31.1 mg, 0.2 mmol, 1.0 equiv.) in solvent (2.0 mL) by stirring with anhydrous potassium carbonate (27.6 mg, 1.0 equiv.) and react at 30 degrees Celsius for 8 h. [b] The yield was determined by high-performance liquid chromatography, using pure **5d** as an external standard.

Table S3. Screening of the base [a]



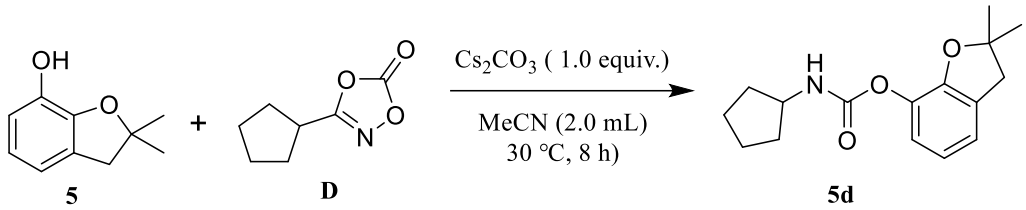
5 **D** **5d**

Entry	Base	Yield (**5d**, %) [b]
1	KOAc	13
2	Et_3N	6
3	DIPEA	4
4	DBU	8
5	Na_2CO_3	15
6	K_2CO_3	21
7	**Cs_2CO_3**	**29**
8	NaOH	12

[a] Dissolve 2,2-dimethyl-2,3-dihydrobenzofuran-7-ol (**5**, 32.8 mg, 0.2 mmol), 3-cyclopentyl-1,4,2-dioxazol-5-one (**D**, 31.1 mg, 0.2 mmol, 1.0 equiv.) in MeCN (2.0 mL) by stirring with anhydrous base (27.6 mg, 1.0 equiv.) and react at 30 degrees Celsius for 8 h.

[b] The yield was determined by high-performance liquid chromatography, using pure **5d** as an external standard.

Table S4. Screening of the **D** equivalent [a]



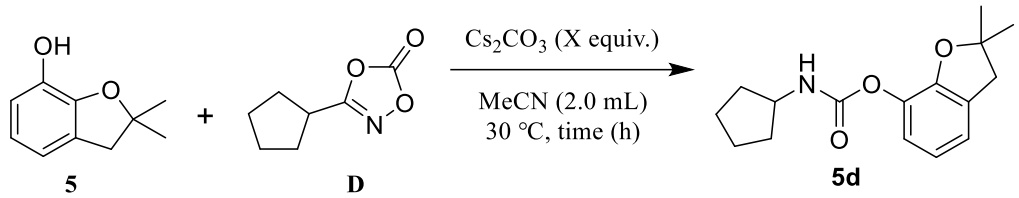
5 **D** **5d**

Entry	**D** (X equiv.)	Yield (**5d**, %) [b]
1	1	29
2	1.2	32
3	1.5	47
4	2	59
5	3	61
6	4	63

[a] Dissolve 2,2-dimethyl-2,3-dihydrobenzofuran-7-ol (**5**, 32.8 mg, 0.2 mmol), 3-cyclopentyl-1,4,2-dioxazol-5-one (**D**) in MeCN (2.0 mL) by stirring with anhydrous cesium carbonate (65.2 mg, 1.0 equiv.) and react at 30 degrees Celsius for 8 h.

[b] The yield was determined by high-performance liquid chromatography, using pure **5d** as an external standard.

Table S5. Screening of the effects of base equivalent and reaction time [a]



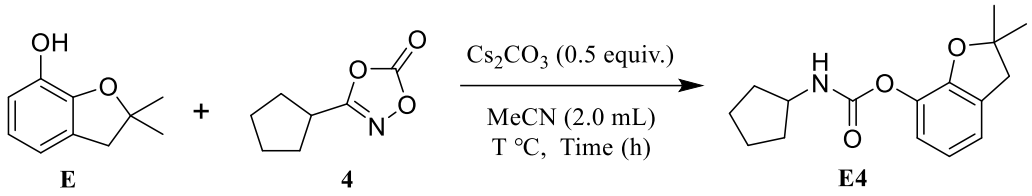
5 **D** **5d**

Entry	Cs_2CO_3 (X equiv.)	Yield (**5d**, 2h, %)	Yield (**5d**, 4h, %)	Yield (**5d**, 6h, %)	Yield (**5d**, 8h, %)	Yield (**5d**, 12h, %) [b]
1	0.1	23	35	45	51	54
2	0.2	26	37	46	53	55
3	0.5	34	46	53	58	57
4	1	47	55	58	58	53
5	2	57	55	52	49	44

[a] Dissolve 2,2-dimethyl-2,3-dihydrobenzofuran-7-ol (**5**, 32.8 mg, 0.2 mmol), 3-cyclopentyl-1,4,2-dioxazol-5-one (**D**, 62.2 mg, 0.4 mmol, 2.0 equiv.) in MeCN (2.0 mL) by stirring with anhydrous cesium carbonate and react at 40 degrees Celsius.

[b] The yield was determined by high-performance liquid chromatography at 2 h, 4 h, 6 h, 8 h, and 12 h, using pure **5d** as an external standard.

Table S6. Screening of the highest yield corresponding to different reaction temperatures [a]



E **4** **E4**

Entry	Temperature (℃)	Yield (**5d**, 7 min, %)	Yield (**5d**, 20 min, %)	Yield (**5d**, 1h, %)	Yield (**5d**, 2h, %)	Yield (**5d**, 4h, %) [b]
1	40	\	\	\	\	60
2	50	\	\	\	67	
3	60	\	\	73	\	\
4	70	\	86	\	\	\
5	80	74	\	\	\	\

[a] A mixture of 2,2-dimethyl-2,3-dihydrobenzofuran-7-ol (**5**, 32.8 mg, 0.2 mmol), 3-cyclopentyl-1,4,2-dioxazol-5-one (**D**, 62.2 mg, 0.4 mmol, 2.0 equiv.), and cesium carbonate (32.6 mg, 0.1 mmol, 0.5 equiv.) was stirred and dissolved in acetonitrile (2.0 mL), and the reaction was conducted at 40, 50, 60, 70, and 80 ℃, respectively.

The reaction mixture at 40 ℃ was sampled every 30 min over 3-5 h, and the yield was determined by high-performance liquid chromatography (HPLC). The yield reached its maximum at 4 h. For the 50 ℃ system, sampling was performed every 15 min within 1–3 h, with the highest yield observed at 2 h. At 60 C, samples were taken every 10 min during 0.5–1.5 h, and the maximum yield was achieved at 1 h. For the 70 °C condition, the mixture was sampled every 2 min between 15–30 min, and the yield peaked at 21 min. At 80 °C, sampling was carried out every 1 min within 5–15 min, with the highest yield attained at 8 min. Pure compound **5d** was used as an external standard for all HPLC analyses.

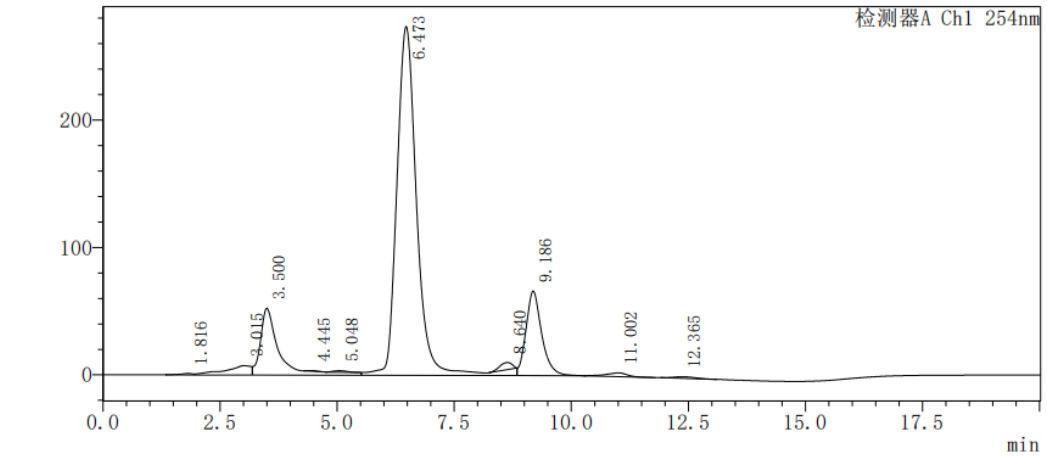
3. HPLC Chromatograms

SHIMADZU LabSolutions Analysis Report

<Sample message>

Sample	: 21min		
ID	: 21min		
Data Name	: 21min.lcd		
Method Name	: 60%MeCN to 80% MeCN to 60%MeCN.lcm		
Batch Name	: MeCN 1mmol 10ml 70℃.lcb		
Sample Number	: 1-5		
Injection volume	: 10 uL		
Acquisition Date	: 2025/7/18 16:34:39	Operator	: System Administrator
Modified Date	: 2025/7/18 16:54:46	Modified by	: System Administrator

<Chromatogram>



<峰表>

检测器A Ch1 254nm

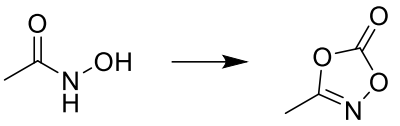
peak	retention time	square	height	concentration	sign
1	1.816	20082	1104	0.000	
2	3.015	288129	7321	0.000	V
3	3.500	1468815	52442	0.000	SV
4	4.445	8292	561	0.000	T
5	5.048	23798	1210	0.000	T
6	6.473	8137939	273795	0.000	SV
7	8.640	106706	5611	0.000	T
8	9.186	1549977	66354	0.000	V
9	11.002	89688	2943	0.000	
10	12.365	39793	1186	0.000	
总计		11733219	412528		

HPLC Chromatograms

In the HPLC chromatogram, the peak corresponding to the starting material, 2,2-dimethyl-2,3-dihydrobenzofuran-7-ol (**5**), appeared at a retention time (Rt) of 3.500 min. In contrast, the target product, 2,2-dimethyl-2,3-dihydrobenzofuran-7-yl cyclopentylcarbamate (**5d**), exhibited a sharp and well-defined peak at R_t = 6.473 min, with good baseline separation between the two compounds.

4. Experimental procedures

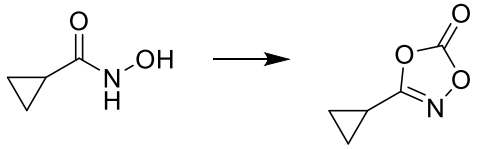
4.1 Synthesis of 3-methyl-1,4,2-dioxazol-5-one (**A**)



I **A**

Triethylamine (1.5 mL) was added dropwise to a mixture of acetohydroxamic acid (**I**, 750 mg, 10 mmol) and triphosgene (1.2 g, 4 mmol) in dichloromethane at 0 °C (ice bath). The reaction mixture was stirred for 30 min. The mixture was then washed with 1N HCl (50 mL) and saturated NaCl solution (2 × 40 mL). The organic phase was collected, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure to afford pure 3-methyl-1,4,2-dioxazol-5-one (**A**).

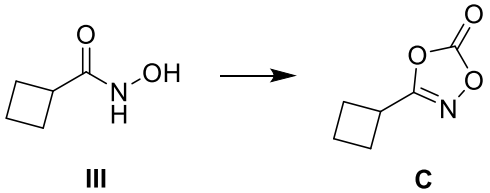
4.2 Synthesis of 3-cyclopropyl-1,4,2-dioxazol-5-one (**B**)



II **B**

Triethylamine (1.5 mL) was added dropwise to a mixture of *N*-hydroxycyclopropanecarboxamide (**II**, 1.01 g, 10 mmol) and triphosgene (1.2 g, 4 mmol) in dichloromethane at 0 °C (ice bath). The reaction mixture was stirred for 30 min. The mixture was then washed with 1N HCl (50 mL) and saturated NaCl solution (2 × 40 mL). The organic phase was collected, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure to afford pure 3-cyclopropyl-1,4,2-dioxazol-5-one (**B**).

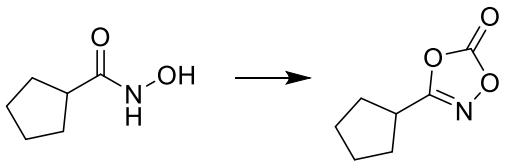
4.3 Synthesis of 3-cyclobutyl-1,4,2-dioxazol-5-one (**C**)



III **C**

Triethylamine (1.5 mL) was added dropwise to a mixture of *N*-hydroxycyclobutanecarboxamide (**III**, 1.15 g, 10 mmol) and triphosgene (1.2 g, 4 mmol) in dichloromethane at 0 °C (ice bath). The reaction mixture was stirred for 30 min. The mixture was then washed with 1N HCl (50 mL) and saturated NaCl solution (2 × 40 mL). The organic phase was collected, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure to afford pure 3-cyclobutyl-1,4,2-dioxazol-5-one (**C**).

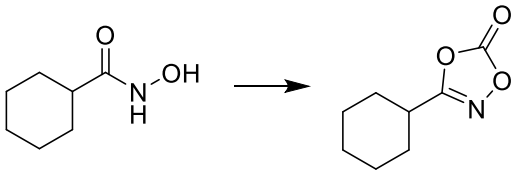
4.4 Synthesis of 3-cyclopentyl-1,4,2-dioxazol-5-one (**D**)



IV **D**

Triethylamine (1.5 mL) was added dropwise to a mixture of *N*-hydroxycyclopentanecarboxamide (**IV**, 1.29 g, 10 mmol) and triphosgene (1.2 g, 4 mmol) in dichloromethane at 0 °C (ice bath). The reaction mixture was stirred for 30 min. The mixture was then washed with 1N HCl (50 mL) and saturated NaCl solution (2 × 40 mL). The organic phase was collected, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure to afford pure 3-cyclopentyl-1,4,2-dioxazol-5-one (**D**).

4.5 Synthesis of 3-cyclohexyl-1,4,2-dioxazol-5-one (**E**)

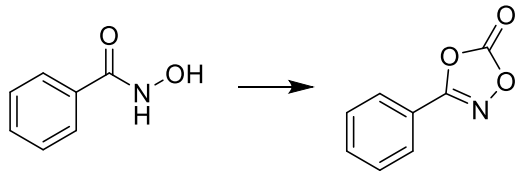


V **E**

Triethylamine (1.5 mL) was added dropwise to a mixture of *N*-hydroxycyclohexanecarboxamide (**V**, 1.43 g, 10 mmol) and triphosgene (1.2 g, 4 mmol) in dichloromethane at 0 °C (ice bath). The reaction mixture was stirred for 30 min. The

mixture was then washed with 1N HCl (50 mL) and saturated NaCl solution (2 × 40 mL). The organic phase was collected, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure to afford pure 3-cyclohexyl-1,4,2-dioxazol-5-one (**E**).

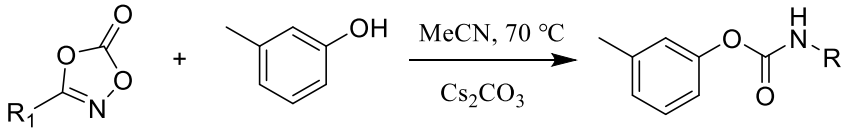
4.6 Synthesis of 3-phenyl-1,4,2-dioxazol-5-one (**F**)



VI **F**

Triethylamine (1.5 mL) was added dropwise to a mixture of *N*-hydroxybenzamide (**VI**, 1.37 g, 10 mmol) and triphosgene (1.2 g, 4 mmol) in dichloromethane at 0 °C (ice bath). The reaction mixture was stirred for 30 min. The mixture was then washed with 1N HCl (50 mL) and saturated NaCl solution (2 × 40 mL). The organic phase was collected, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure to afford pure 3-phenyl-1,4,2-dioxazol-5-one (**F**).

4.7 Synthesis of m -tolyl-substituted carbamates (**1a–1f**)

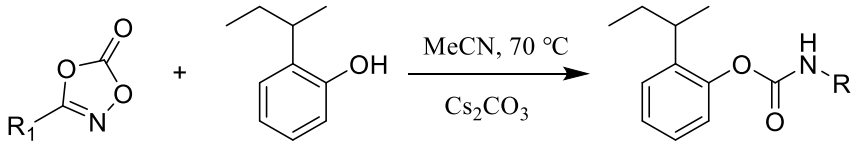


A-F **1** **1a–1f**

A mixture of m -cresol (**1**, 216 mg, 2 mmol), 3-substituted-1,4,2-dioxazol-5-one (**A-F**, 6 mmol), and cesium carbonate (325 mg, 1 mmol) in acetonitrile was stirred and heated at 70 °C for 21 min. After completion of the reaction, the mixture was extracted with ethyl acetate (30 mL) and washed with saturated sodium chloride solution (2 × 30 mL). The organic phase was dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography using a mixture of petroleum ether and ethyl acetate (petroleum ether / ethyl acetate = 15: 1) as the eluent. The resulting product was recrystallized from a mixture of petroleum ether and ethyl acetate (30: 1) to afford pure solid products (**1a–**

5f).

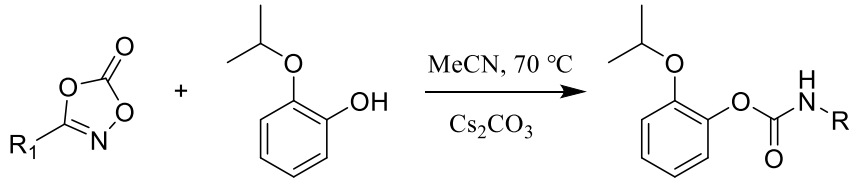
4.8 Synthesis of 2 - (sec-butyl) phenyl *N*-substituted carbamates (**2a–2f**)



A-F **2** **2a–2f**

A mixture of 2-(sec-butyl) phenol (**2**, 300 mg, 2 mmol), 3-substituted-1,4,2-dioxazol -5-one (**A-F**, 4 mmol), and cesium carbonate (325 mg, 1 mmol) in acetonitrile was stirred and heated at 70 °C for 21 min. After completion of the reaction, the mixture was extracted with ethyl acetate (30 mL) and washed with saturated sodium chloride solution (2 × 30 mL). The organic phase was dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography using a mixture of petroleum ether and ethyl acetate (petroleum ether / ethyl acetate =10: 1) as the eluent to give the target compounds (**2a–2f**).

4.9 Synthesis of 2-isopropoxyphenyl *N*-substituted carbamates (**3a–3f**)

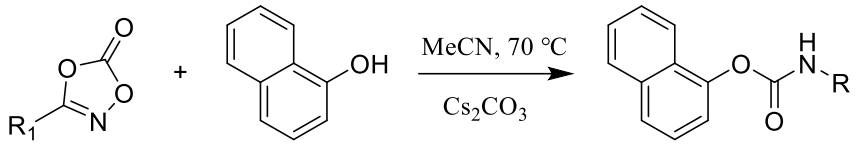


A-F **3** **3a–3f**

A mixture of 2-isopropoxyphenol (**3**, 304 mg, 2 mmol), 3-substituted-1,4,2-dioxazol-5-one (**A-F**, 4 mmol), and cesium carbonate (325 mg, 1 mmol) in acetonitrile was stirred and heated at 70 °C for 21 min. After completion of the reaction, the mixture was extracted with ethyl acetate (30 mL) and washed with saturated sodium chloride solution (2 × 30 mL). The organic phase was dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography using a mixture of petroleum ether and ethyl acetate

(petroleum ether / ethyl acetate = 10: 1) as the eluent to give the target compounds (**3a–3f**).

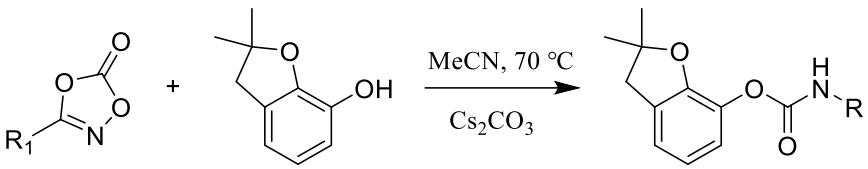
4.10 Synthesis of 1-naphthyl *N*-substituted carbamates (**4a–4f**)



A-F **4** **4a–4f**

A mixture of 1-naphthol (**4**, 288 mg, 2 mmol), 3-substituted-1,4,2-dioxazol-5-one (**A-F**, 4 mmol), and cesium carbonate (325 mg, 1 mmol) in acetonitrile was stirred and heated at 70 °C for 21 min. After completion of the reaction, the mixture was extracted with ethyl acetate (30 mL) and washed with saturated sodium chloride solution (2 × 30 mL). The organic phase was dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography using a mixture of petroleum ether and ethyl acetate (petroleum ether / ethyl acetate = 10: 1) as the eluent to give the target compounds (**4a–4f**).

4.11 Synthesis of 2,2-dimethyl-2,3-dihydrobenzofuran-7-yl *N*-substituted carbamates (**5a–5f**)



A-F **5** **5a–5f**

A mixture of 2,2-dimethyl-2,3-dihydrobenzofuran-7-ol (**5**, 328 mg, 2.0 mmol), 3-substituted-1,4,2-dioxazol-5-one (**A-F**, 4 mmol), and cesium carbonate (325 mg, 1 mmol) in acetonitrile was stirred and heated at 70 °C for 21 min. After completion of the reaction, the mixture was extracted with ethyl acetate (30 mL) and washed with saturated sodium chloride solution (2 × 30 mL). The organic phase was dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. The crude

product was purified by column chromatography using a mixture of petroleum ether and ethyl acetate (petroleum ether / ethyl acetate = 10: 1) as the eluent to give the target compounds (**5a–5f**).

5. Characterization

m-tolyl methylcarbamate (**1a**). White solid, 238 mg, 72 % yield. $C_9H_{11}NO_2$; M W: 165.19. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23 (dd, J = 15.2, 7.4 Hz, 1H), 7.00 (d, J = 7.6 Hz, 1H), 6.97 – 6.86 (m, 2H), 5.02 (s, 1H), 2.86 (d, J = 4.9 Hz, 3H, CH_3), 2.34 (s, 3H, CH_3). ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.61 (C=O), 151.18, 139.60, 129.18, 126.29, 122.44, 118.73, 27.86, 21.48; TOF-HRMS (ESI): *m/z* [M + Na]$^+$ calcd for $[C_9H_{11}NO_2Na]^+$: 188.0682; found: 188.0367.

m-tolyl cyclopropylcarbamate (**1b**). White solid, 288 mg, 75 % yield. $C_{11}H_{13}NO_2$; M W: 191.23. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23 (dd, J = 15.9, 8.4 Hz, 1H), 7.05 – 6.86 (m, 3H), 5.26 (s, 1H), 2.67 (s, 1H), 2.34 (s, 3H, CH_3), 0.76 (q, J = 6.8 Hz, 2H), 0.67 – 0.55 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.50 (C=O), 151.05, 139.58, 129.16, 126.28, 122.41, 118.71, 23.41, 21.48, 6.97 (2C). TOF-HRMS (ESI): *m/z* [M + Na]$^+$ calcd for $[C_{11}H_{13}NO_2Na]^+$: 214.0838; found: 188.0367.

m-tolyl cyclobutylcarbamate (**1c**). White solid. 284 mg, 69% yield. $C_{12}H_{15}NO_2$; M W: 205.26. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (t, J = 7.8 Hz, 1H), 7.00 (d, J = 7.7 Hz, 1H), 6.94 (s, 1H), 6.91 (d, J = 8.7 Hz, 1H), 5.26 (d, J = 8.3 Hz, 1H), 4.22 (h, J = 8.3 Hz, 1H), 2.42 – 2.35 (m, 2H), 2.35 – 2.32 (m, 3H, CH_3), 1.98 – 1.87 (m, 2H), 1.70 (dd, J = 11.0, 6.6 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.68 (C=O), 151.00, 139.47, 129.07, 126.17, 122.39, 118.69, 46.39, 31.37 (2C), 21.40, 14.86. TOF-HRMS (ESI): *m/z* [M + Na]$^+$ calcd for $[C_{12}H_{15}NO_2Na]^+$: 228.0995; found: 228.0998.

m-tolyl cyclopentylcarbamate (**1d**). White solid, 340 mg, 78% yield. $C_{13}H_{17}NO_2$; M W: 219.28. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (t, J = 7.8 Hz, 1H), 7.00 (d, J = 7.8 Hz,

1H), 6.95 (s, 1H), 6.92 (d, J = 8.3 Hz, 1H), 5.01 (d, J = 7.5 Hz, 1H), 4.05 (h, J = 7.2 Hz, 1H), 2.35 (s, 3H, CH_3), 2.01 (dq, J = 12.5, 6.4 Hz, 2H), 1.81 – 1.68 (m, 2H),1.61 (td, J = 7.5, 3.9 Hz, 2H), 1.48 (dq, J = 13.3, 6.6 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.28 (C=O), 151.09, 139.47, 129.07, 126.10, 122.40, 118.70, 53.07, 33.25 (2C), 23.66 (2C), 21.42. TOF-HRMS (ESI): *m/z* $[M + Na]^+$ calcd for $[C_{13}H_{17}NO_2Na]^+$: 242.1151; found: 242.0836.

m-tolyl cyclohexylcarbamate (**1e**). White solid. 372 mg, 80% yield. $C_{14}H_{19}NO_2$; M W: 233.31. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (t, J = 7.8 Hz, 1H), 7.00 (d, J = 7.8 Hz, 1H), 6.95 (s, 1H), 6.92 (d, J = 7.8 Hz, 1H), 5.21 – 4.81 (m, 1H), 3.62 – 3.50 (m, 1H), 2.35 (s, 3H, CH_3), 2.00 (dd, J = 12.4, 4.3 Hz, 2H), 1.80 – 1.71 (m, 2H), 1.71 – 1.45 (m, 2H), 1.42 – 1.31 (m, 2H), 1.25 – 1.17 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.93 (C=O), 151.12, 139.45, 129.05, 126.06, 122.38, 118.68, 50.19, 33.36, 25.56 (2C), 24.87 (2C), 21.42. TOF-HRMS (ESI): *m/z* $[M + H]^+$ calcd for $[C_{14}H_{20}NO_2]^+$: 234.1489; found: 234.1489.

m-tolyl phenylcarbamate (**1f**). White solid. 295 mg, 65% yield. $C_{14}H_{13}NO_2$; M W: 227.26. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 (d, J = 7.8 Hz, 2H), 7.35 – 7.28 (m, 2H), 7.28 – 7.22 (m, 1H), 7.09 (t, J = 7.4 Hz, 1H), 7.06 – 6.94 (m, 4H), 2.35 (s, 3H, CH_3). ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.99 (C=O), 150.66, 139.80, 137.62, 129.31 (3C), 126.73, 124.02, 122.48 (2C), 118.87, 118.79, 21.51. TOF-HRMS (ESI): *m/z* $[M + Na]^+$ calcd for $[C_{14}H_{13}NO_2Na]^+$: 250.0838; found: 250.0831.

2-(sec-butyl)phenyl methylcarbamate (**2a**). Colorless oil. 364 mg, 88% yield. $C_{12}H_{17}NO_2$; M W: 207.27. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (dd, J = 5.8, 3.6 Hz, 1H), 7.19 (t, J = 3.7 Hz, 1H), 7.17 (t, J = 3.7 Hz, 1H), 7.06 (d, J = 9.4 Hz, 1H), 5.00 (m, 1H), 2.90 (d, J = 4.9 Hz, 3H, CH_3), 2.89 – 2.82 (m, 1H), 1.62 – 1.53 (m, 2H), 1.20 (d, J = 6.9 Hz, 3H, CH_3), 0.83 (t, J = 7.4 Hz, 3H, CH_3). TOF-HRMS (ESI): *m/z* $[M + H]^+$ calcd for $[C_{12}H_{18}NO_2]^+$: 208.1332; found: 208.1332.

2-(sec-butyl)phenyl cyclopropylcarbamate (**2b**). White solid. 414mg, 89% yield. $C_{14}H_{19}NO_2$; M W: 233.31. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (d, J = 6.7 Hz, 1H), 7.19 (s, 1H), 7.17 (s, 1H), 7.07 (s, 1H), 5.18 (d, J = 77.0 Hz, 1H), 2.94 – 2.79 (m, 1H), 2.70 (s, 1H), 1.66 – 1.47 (m, 2H), 1.20 (d, J = 7.0 Hz, 3H, CH_3), 0.83 (t, J = 7.6 Hz, 3H, CH_3), 0.78 (dt, J = 6.9, 3.3 Hz, 2H), 0.63 (d, J = 7.6 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.49 (C=O), 148.67, 139.59, 127.16, 126.54, 125.92, 122.65, 34.38, 30.28, 23.41, 20.93, 12.34, 7.04 (2C). TOF-HRMS (ESI): *m/z* $[M + H]^+$ calcd for $[C_{14}H_{20}NO_2]^+$: 234.1489; found: 234.1457.

2-(sec-butyl)phenyl cyclobutylcarbamate (**2c**). White solid. 386mg, 83% yield. $C_{15}H_{21}NO_2$; M W: 247.34. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (t, J = 4.7 Hz, 1H), 7.18 (s, 1H), 7.18 – 7.13 (m, 1H), 7.11 – 6.96 (m, 1H), 5.22 (d, J = 8.4 Hz, 1H), 4.23 (h, J = 8.2 Hz, 1H), 2.86 (h, J = 7.0 Hz, 1H), 2.44 – 2.33 (m, 2H), 1.94 (dt, J = 20.5, 9.8 Hz, 2H), 1.70 (q, J = 9.4 Hz, 2H), 1.58 (dq, J = 16.4, 6.9 Hz, 2H), 1.20 (d, J = 6.9 Hz, 3H, CH_3), 0.83 (t, J = 7.3 Hz, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.72 (C=O), 148.71, 139.65, 127.14, 126.51, 125.85, 122.68, 46.50, 34.32, 31.50, 31.43, 30.30, 20.95, 14.86, 12.34. TOF-HRMS (ESI): *m/z* $[M + H]^+$ calcd for $[C_{15}H_{22}NO_2]^+$: 248.1645; found: 248.1607.

2-(sec-butyl)phenyl cyclopentylcarbamate (**2d**). White solid. 480mg, 92% yield. $C_{16}H_{23}NO_2$; M W: 261.37. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 – 7.22 (m, 1H), 7.19 (d, J = 4.3 Hz, 1H), 7.17 (d, J = 5.1 Hz, 1H), 7.09 – 7.04 (m, 1H), 5.02 (d, J = 7.7 Hz, 1H), 4.06 (h, J = 6.9 Hz, 1H), 2.86 (h, J = 7.1 Hz, 1H), 2.02 (dq, J = 12.8, 6.5 Hz, 2H), 1.75 – 1.68 (m, 2H), 1.62 (dd, J = 10.3, 4.9 Hz, 2H), 1.56 (q, J = 6.3 Hz, 2H), 1.49 (dt, J = 12.6, 6.2 Hz, 2H), 1.20 (d, J = 7.0 Hz, 3H, CH_3), 0.83 (t, J = 7.4 Hz, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.38 (C=O), 148.78, 139.69, 127.11, 126.50, 125.80, 122.74, 53.12, 34.36, 33.93, 33.30, 33.26, 30.31, 23.66, 20.93, 12.36. TOF-HRMS (ESI): *m/z* $[M + H]^+$ calcd for $[C_{16}H_{24}NO_2]^+$: 262.1802; found: 262.1766.

2-(sec-butyl)phenyl cyclohexylcarbamate (**2e**). White solid. 471mg, 86% yield. $C_{17}H_{25}NO_2$; M W: 275.39. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.26 (m, 1H), 7.22 (s, 1H), 7.21 – 7.17 (m, 1H), 7.12 – 7.07 (m, 1H), 5.02 (d, J = 8.2 Hz, 1H), 3.60 (td, J = 13.5, 8.1 Hz, 1H), 2.90 (h, J = 7.0 Hz, 1H), 2.04 (dd, J = 12.4, 4.3 Hz, 2H), 1.81 – 1.73 (m, 2H), 1.72 – 1.63 (m, 2H), 1.58 (dt, J = 13.7, 6.9 Hz, 2H), 1.38 (t, J = 12.5 Hz, 2H), 1.33 – 1.25 (m, 2H), 1.25 – 1.22 (m, 3H, CH_3), 0.87 (t, J = 7.5 Hz, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.05 (C=O), 148.78, 139.70, 127.10, 126.47, 125.77, 122.75, 50.20, 34.38, 33.37, 30.30, 25.55 (2C), 24.88 (2C), 20.90, 12.35. TOF-HRMS (ESI): *m/z* $[M + H]^+$ calcd for $[C_{17}H_{26}NO_2]^+$: 276.1958; found: 276.1910.

2-(sec-butyl)phenyl phenylcarbamate (**2f**). White solid. 436mg, 82% yield. $C_{17}H_{19}NO_2$; M W: 269.34. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, J = 8.0 Hz, 2H), 7.38 – 7.31 (m, 2H), 7.32 – 7.27 (m, 1H), 7.26 – 7.19 (m, 2H), 7.18 – 7.11 (m, 2H), 7.11 (d, 1H), 2.93 (h, J = 7.1 Hz, 1H), 1.61 (ddt, J = 16.8, 9.4, 4.2 Hz, 2H), 1.23 (d, J = 6.9 Hz, 3H, CH_3), 0.85 (t, J = 7.4 Hz, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.88 (C=O), 148.26, 139.73, 137.63, 129.27 (2C), 127.32, 126.68, 126.36, 123.90, 122.66, 118.68 (2C), 34.36, 30.31, 21.09, 12.34. TOF-HRMS (ESI): *m/z* $[M + H]^+$ calcd for $[C_{17}H_{20}NO_2]^+$: 270.1489; found: 270.1472.

2-isopropoxyphenyl methylcarbamate (**3a**). White solid. 322 mg, 77% yield. $C_{11}H_{15}NO_3$; M W: 209.25. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 – 7.11 (m, 1H), 7.08 (dd, J = 8.0, 1.7 Hz, 1H), 6.96 (dd, J = 8.2, 1.5 Hz, 1H), 6.91 (td, J = 7.7, 1.5 Hz, 1H), 5.05 (s, 1H), 4.51 (hept, J = 6.1 Hz, 1H), 2.88 (d, J = 4.9 Hz, 3H, CH_3), 1.33 (d, J = 6.0 Hz, 6H, $2CH_3$). TOF-HRMS (ESI): *m/z* $[M + Na]^+$ calcd for $[C_{11}H_{15}NO_3Na]^+$: 232.0944; found: 232.0948.

2-isopropoxyphenyl cyclopropylcarbamate (**3b**). White solid. 383mg, 81% yield. $C_{13}H_{17}NO_3$; M W: 235.28. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.17 – 7.11 (m, 1H), 7.08 (d,

J = 8.3 Hz, 1H), 6.95 (dd, *J* = 8.2, 1.4 Hz, 1H), 6.90 (t, *J* = 7.7 Hz, 1H), 5.31 (d, *J* = 19.9 Hz, 1H), 4.51 (p, *J* = 4.9 Hz, 1H), 2.68 (s, 1H), 1.33 (d, *J* = 6.1 Hz, 6H, $2CH_3$), 0.80 – 0.73 (m, 2H), 0.66 (dd, *J* = 54.1, 5.2 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.10 (C=O), 150.15, 141.29, 126.35, 123.50, 120.82, 115.50, 71.50, 23.34, 22.25 (2C), 6.97 (2C). TOF-HRMS (ESI): *m/z* [M -C_3H_6+ H]$^+$ calcd for $[C_{10}H_{11}NO_3]^+$: 194.0812; found: 194.0816.

2-isopropoxyphenyl cyclobutylcarbamate (**3c**). White solid. 368mg, 74% yield. $C_{14}H_{19}NO_3$; M W: 249.31. ^1H NMR (500 MHz, $CDCl_3$) δ 7.15 – 7.10 (m, 1H), 7.08 (d, *J* = 7.9 Hz, 1H), 6.95 (dd, *J* = 8.2, 1.5 Hz, 1H), 6.94 – 6.87 (m, 1H), 5.26 (d, *J* = 8.0 Hz, 1H), 4.50 (hept, *J* = 6.1 Hz, 1H), 4.21 (h, *J* = 8.3 Hz, 1H), 2.36 (q, *J* = 7.7 Hz, 2H), 1.99 – 1.88 (m, 2H), 1.75 – 1.65 (m, 2H), 1.32 (d, *J* = 6.1 Hz, 6H, $2CH_3$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.37 (C=O), 150.23, 141.38, 126.30, 123.53, 120.88, 115.62, 71.63, 46.52, 31.37 (2C), 22.26 (2C), 14.89. TOF-HRMS (ESI): *m/z* [M + H]$^+$ calcd for $[C_{14}H_{20}NO_3]^+$: 250.1438; found: 250.1440.

2-isopropoxyphenyl cyclopentylcarbamate (**3d**). White solid. 447mg, 85% yield. $C_{15}H_{21}NO_3$; M W: 263.34. ^1H NMR (600 MHz, $CDCl_3$) δ 7.17 – 7.04 (m, 2H), 6.99 – 6.93 (m, 1H), 6.90 (t, *J* = 7.7 Hz, 1H), 4.04 – 5.05 (d, 1H), 4.51 (p, *J* = 6.0 Hz, 1H), 4.03 - 4.06 (q, 1H), 2.00 (dt, *J* = 12.5, 6.2 Hz, 2H), 1.76 – 1.44 (m, 6H, $3CH_2$), 1.33 (d, *J* = 6.1 Hz, 6H, $2CH_3$). ^{13}C NMR (151 MHz, $CDCl_3$) δ 154.03 (C=O), 150.33, 141.56, 126.31, 123.64, 120.94, 115.66, 71.63, 53.20, 33.29 (2C), 23.69 (2C), 22.33 (2C). TOF-HRMS (ESI): *m/z* [M + H]$^+$ calcd for $[C_{15}H_{22}NO_3]^+$: 264.1594; found: 264.1597.

2-isopropoxyphenyl cyclohexylcarbamate (**3e**). White solid. 428mg, 77% yield. $C_{16}H_{23}NO_3$; M W: 277.36. ^1H NMR (600 MHz, $CDCl_3$) δ 7.18 – 7.04 (m, 2H), 6.98 – 6.86 (m, 2H), 4.51 (p, *J* = 6.0 Hz, 1H), 2.00 (d, *J* = 9.9 Hz, 1H), 1.77 – 1.67 (m, 1H), 1.61 (dt, *J* = 12.5, 3.6 Hz, 2H), 1.47 – 1.29 (m, 3H), 1.35 – 1.38 (dt, 2H), 1.32 – 1.33 (d, 6H, $2CH_3$), 1.26 – 1.10 (m, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 153.70 (C=O),

150.37, 141.60, 126.31, 123.67, 120.97, 115.73, 71.64, 50.20, 33.43, 25.69 (2C), 24.92 (2C), 22.34 (2C). TOF-HRMS (ESI): *m/z* $[M + H]^+$ calcd for $[C_{16}H_{24}NO_3]^+$: 278.1751; found: 278.1751.

2-isopropoxyphenyl phenylcarbamate (**3f**). White solid. 384mg, 71% yield. $C_{16}H_{17}NO_3$; M W: 271.32. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 – 7.46 (m, 1H), 7.45 (s, 1H), 7.34 (d, J = 7.3 Hz, 1H), 7.32 (d, J = 7.4 Hz, 1H), 7.20 (d, J = 7.9 Hz, 1H), 7.18 – 7.15 (m, 1H), 7.12 – 7.08 (m, 2H), 7.00 (d, J = 6.8 Hz, 1H), 6.95 (t, J = 7.7 Hz, 1H), 4.56 (hept, J = 6.1 Hz, 1H), 1.33 (d, J = 6.0 Hz, 6H, $2CH_3$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.23 (C=O), 149.90, 140.56, 137.54, 128.95 (2C), 126.51, 123.54, 123.28 (2C), 120.60, 118.46, 115.18, 71.31, 21.97 (2C). TOF-HRMS (ESI): *m/z* $[M + H]^+$ calcd for $[C_{16}H_{18}NO_3]^+$: 272.1281; found: 272.1291.

naphthalen-1-yl methylcarbamate (**4a**). White solid. 307mg, 76% yield. $C_{12}H_{11}NO_2$; M W: 201.22. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.93 (m, 1H), 7.89 – 7.84 (m, 1H), 7.72 (d, J = 8.2 Hz, 1H), 7.52 (d, J = 5.5 Hz, 1H), 7.50 (d, J = 4.9 Hz, 1H), 7.48 – 7.44 (m, 1H), 7.30 (d, J = 7.5 Hz, 1H), 5.21 (s, 1H), 2.95 (d, J = 4.9 Hz, 3H, CH_3). TOF-HRMS (ESI): *m/z* $[M + H]^+$ calcd for $[C_{12}H_{12}NO_2]^+$: 202.0863; found: 202.0785.

naphthalen-1-yl cyclopropylcarbamate (**4b**). White solid. 381mg, 84% yield. $C_{14}H_{13}NO_2$; M W: 227.26. ^{1}H NMR (400 MHz, DMSO) δ 8.26 (d, J = 3.3 Hz, 1H), 8.02 – 7.95 (m, 1H), 7.92 – 7.86 (m, 1H), 7.80 (d, J = 8.2 Hz, 1H), 7.58 (d, J = 2.5 Hz, 1H), 7.57 – 7.53 (m, 1H), 7.51 (t, J = 7.9 Hz, 1H), 7.30 (d, J = 7.5 Hz, 1H), 2.63 (tq, J = 7.2, 3.6 Hz, 1H), 0.67 (dt, J = 6.8, 3.3 Hz, 2H), 0.57 (dd, J = 5.1, 2.4 Hz, 2H). ^{13}C NMR (101 MHz, DMSO) δ 155.20 (C=O), 146.69, 134.16, 127.97, 127.28, 126.49 (2C), 125.80, 125.19, 121.15, 118.58, 23.24, 5.98 (2C). TOF-HRMS (ESI): *m/z* $[M + H]^+$ calcd for $[C_{14}H_{14}NO_2]^+$: 228.1019; found: 228.0999.

naphthalen-1-yl cyclobutylcarbamate (**4c**). White solid. 379mg, 79% yield.

$C_{15}H_{15}NO_2$; M W: 241.29. ^{1}H NMR (500 MHz, DMSO) δ 8.36 (d, J = 8.0 Hz, 1H), 7.99 – 7.96 (m, 1H), 7.88 (d, J = 6.6 Hz, 1H), 7.80 (d, J = 8.2 Hz, 1H), 7.60 – 7.57 (m, 1H), 7.57 – 7.54 (m, 1H), 7.52 – 7.47 (m, 1H), 7.29 (d, J = 7.5 Hz, 1H), 4.06 (h, J = 8.0 Hz, 1H), 2.28 – 2.19 (m, 2H), 2.09 – 1.99 (m, 2H), 1.64 (dd, J = 24.9, 10.0 Hz, 2H). ^{13}C NMR (126 MHz, DMSO) δ 153.76 (C=O), 147.10, 134.57, 128.38, 127.73, 126.90, 126.88, 126.20, 125.56, 121.53, 118.99, 46.34, 30.69 (2C), 14.86. TOF-HRMS (ESI): *m/z* $[M + H]^+$ calcd for $[C_{15}H_{16}NO_2]^+$: 242.1176; found: 242.1178.

naphthalen-1-yl cyclopentylcarbamate (**4d**). White solid. 448mg, 88% yield. $C_{16}H_{17}NO_2$; M W: 255.32. ^{1}H NMR (400 MHz, DMSO) δ 8.07 (d, J = 7.2 Hz, 1H), 7.97 (d, J = 8.9 Hz, 1H), 7.90 (d, J = 7.3 Hz, 1H), 7.79 (d, J = 8.2 Hz, 1H), 7.61 – 7.53 (m, 2H), 7.50 (t, J = 7.9 Hz, 1H), 7.30 (d, J = 7.6 Hz, 1H), 3.89 (h, J = 7.2 Hz, 1H), 1.87 (dd, J = 9.2, 5.4 Hz, 2H), 1.70 (d, J = 7.7 Hz, 2H), 1.61 – 1.48 (m, 4H). ^{13}C NMR (101 MHz, DMSO) δ 153.95 (C=O), 146.79, 134.13, 127.92, 127.33, 126.41 (2C), 125.76, 125.02, 121.14, 118.50, 52.46, 32.31 (2C), 23.37 (2C). TOF-HRMS (ESI): *m/z* $[M + H]^+$ calcd for $[C_{16}H_{18}NO_2]^+$: 256.1332; found: 256.1311.

naphthalen-1-yl cyclohexylcarbamate (**4e**). White solid. 441mg, 82% yield. $C_{17}H_{19}NO_2$; M W: 269.34. ^{1}H NMR (400 MHz, DMSO) δ 7.97 (dd, J = 6.3, 3.1 Hz, 2H), 7.79 (d, J = 8.2 Hz, 1H), 7.59 – 7.53 (m, 1H), 7.50 (t, J = 7.9 Hz, 2H), 7.49 (t, 1H), 7.29 (dd, J = 7.5, 0.8 Hz, 1H), 3.35 (d, J = 7.7 Hz, 1H), 1.89 (d, J = 8.1 Hz, 2H), 1.80 – 1.67 (m, 3H), 1.39 – 1.07 (m, 5H). ^{13}C NMR (101 MHz, DMSO) δ 153.61 (C=O), 146.79, 134.10, 127.87, 127.29, 126.35, 126.32, 125.70, 124.95, 121.10, 118.39, 49.83, 32.54, 25.13 (2C), 24.52 (2C). TOF-HRMS (ESI): *m/z* $[M + H]^+$ calcd for $[C_{17}H_{20}NO_2]^+$: 270.1489; found: 270.1450.

naphthalen-1-yl phenylcarbamate (**4f**). White solid. 396mg, 75% yield. $C_{17}H_{13}NO_2$; M W: 263.30. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.13 (d, J = 1.6 Hz, 1H), 8.67 (s, 1H), 8.14 (d, J = 7.8 Hz, 1H), 7.81 (d, J = 8.4 Hz, 1H), 7.57 (d, J = 8.8 Hz, 1H), 7.49 – 7.46

(m, 1H), 7.46 – 7.44 (m, 1H), 7.43 (d, J = 1.6 Hz, 1H), 7.33 – 7.31 (m, 1H), 7.30 (d, J = 1.6 Hz, 1H), 7.28 (d, J = 2.2 Hz, 1H), 6.97 (t, J = 7.4 Hz, 1H), 6.88 (d, J = 7.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.19 (C=O), 152.58, 139.75, 134.45, 128.84 (2C), 127.41, 126.46, 126.12, 124.58, 122.00 (2C), 121.86, 118.35, 118.22, 113.90, 108.05. TOF-HRMS (ESI): *m/z* $[M + H]^+$ calcd for $[C_{17}H_{14}NO_2]^+$: 264.1019; found: 264.1017.

2,2-dimethyl-2,3-dihydrobenzofuran-7-yl methylcarbamate (**5a**). White solid. 358 mg, 81% yield. $C_{12}H_{15}NO_3$; M W: 221.26. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.97 (dd, J = 7.3, 1.2 Hz, 1H), 6.94 (d, J = 7.5 Hz, 1H), 6.82 – 6.74 (m, 1H), 5.03 (s, 1H), 3.03 (d, J = 1.0 Hz, 2H), 2.88 (d, J = 4.9 Hz, 3H, CH_3), 1.49 (s, 6H, $2CH_3$). TOF-HRMS (ESI): *m/z* $[M + H]^+$ calcd for $[C_{12}H_{16}NO_3]^+$: 222.1125; found: 222.1124.

2,2-dimethyl-2,3-dihydrobenzofuran-7-yl cyclopropylcarbamate (**5b**). White solid. 420 mg, 85% yield. $C_{14}H_{17}NO_3$; M W: 247.29. ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.93 (t, J = 7.3 Hz, 2H), 6.75 (t, 1H), 5.29(s, 1H), 3.01 (s, 2H), 2.66 (s, 1H), 1.46 (s, 6H, $2CH_3$), 0.79 – 0.69 (m, 2H), 0.60 (s, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 154.79 (C=O), 150.32, 134.93, 129.60, 122.20, 121.95, 120.22, 88.37, 43.28, 28.33 (2C), 23.46, 6.95 (2C). TOF-HRMS (ESI): *m/z* $[M + H]^+$ calcd for $[C_{14}H_{18}NO_3]^+$: 248.1281; found: 248.1281.

2,2-dimethyl-2,3-dihydrobenzofuran-7-yl cyclobutylcarbamate (**5c**). White solid. 397mg, 76% yield. $C_{15}H_{19}NO_3$; M W: 261.32. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.00 – 6.91 (m, 2H), 6.77 (t, J = 7.7 Hz, 1H), 5.26 (d, 1H), 4.19 – 4.24 (m, 1H),3.02 (s, 2H), 2.36 (q, J = 7.8 Hz, 2H), 1.99 – 1.85 (m, 2H), 1.77 – 1.60 (m, 2H), 1.48 (s, 6H, $2CH_3$). ^{13}C NMR (151 MHz, $CDCl_3$) δ 153.04 (C=O), 150.34, 134.94, 129.58, 122.16, 122.03, 120.22, 88.34, 46.61, 43.28, 31.44 (2C), 28.33 (2C), 14.99. TOF-HRMS (ESI): *m/z* $[M + H]^+$ calcd for $[C_{15}H_{20}NO_3]^+$: 262.1438; found: 262.1437.

2,2-dimethyl-2,3-dihydrobenzofuran-7-yl cyclopentylcarbamate (**5d**). White solid.

473 mg, 86% yield. $C_{16}H_{21}NO_3$; M W: 275.35. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.97 (d, J = 7.3 Hz, 1H), 6.95 (d, J = 1.1 Hz, 1H), 6.77 (t, J = 7.7 Hz, 1H), 5.24 – 4.81 (m, 1H), 4.04 (h, J = 6.8 Hz, 1H), 3.03 (s, 2H), 2.00 (dq, J = 12.7, 6.8 Hz, 2H), 1.69 (dd, J = 7.5, 4.3 Hz, 2H), 1.64 – 1.57 (m, 2H), 1.51 (d, J = 5.5 Hz, 2H), 1.49 (s, 6H, $2CH_3$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.85 (C=O), 150.45, 135.23, 129.73, 122.24, 122.17, 120.40, 88.51, 53.43, 43.45, 33.43 (2C), 28.52 (2C), 23.89 (2C). TOF-HRMS (ESI): *m/z* $[M + H]^+$ calcd for $[C_{16}H_{22}NO_3]^+$: 276.1594; found: 276.1597.

2,2-dimethyl-2,3-dihydrobenzofuran-7-yl cyclohexylcarbamate (**5e**). White solid. 462 mg, 73% yield. $C_{17}H_{23}NO_3$; M W: 289.38. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.97 (d, J = 5.2 Hz, 1H), 6.95 (d, J = 5.0 Hz, 1H), 6.77 (t, J = 7.7 Hz, 1H), 5.00 (d, J = 8.0 Hz, 1H), 3.64 – 3.49 (m, 1H), 3.03 (s, 2H), 2.01 (dd, J = 12.9, 3.9 Hz, 2H), 1.72 (dd, J = 9.6, 4.1 Hz, 2H), 1.68 – 1.55 (m, 2H), 1.49 (s, 6H, $2CH_3$), 1.40 – 1.31 (m, 2H), 1.22 – 1.17 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.24 (C=O), 150.23, 135.02, 129.47, 121.97, 121.90, 120.14, 88.24, 50.30, 43.21, 33.28 (2C), 28.28 (2C), 25.60, 24.87 (2C). TOF-HRMS (ESI): *m/z* $[M + H]^+$ calcd for $[C_{17}H_{24}NO_3]^+$: 290.1751; found: 290.1751.

2,2-dimethyl-2,3-dihydrobenzofuran-7-yl phenylcarbamate (**5f**). White solid. 413 mg, 73 % yield. $C_{17}H_{17}NO_3$; M W: 283.33. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.42 (d, J = 7.9 Hz, 2H), 7.30 (t, J = 8.0 Hz, 2H), 7.07 (t, J = 7.4 Hz, 2H), 7.02 – 6.97 (m, 2H), 6.80 (t, 1H), 3.04 (s, 2H), 1.48 (s, 6H, $2CH_3$). ^{13}C NMR (151 MHz, $CDCl_3$) δ 151.15 (C=O), 150.42, 137.75, 134.48, 129.84 (2C), 129.27, 123.89, 122.67, 122.01 (2C), 120.37, 118.82, 88.67, 43.28, 28.33 (2C). TOF-HRMS (ESI): *m/z* $[M + H]^+$ calcd for $[C_{17}H_{18}NO_3]^+$: 284.1281; found: 284.1283.

6. ^{1}H-NMR and ^{13}C-NMR spectra

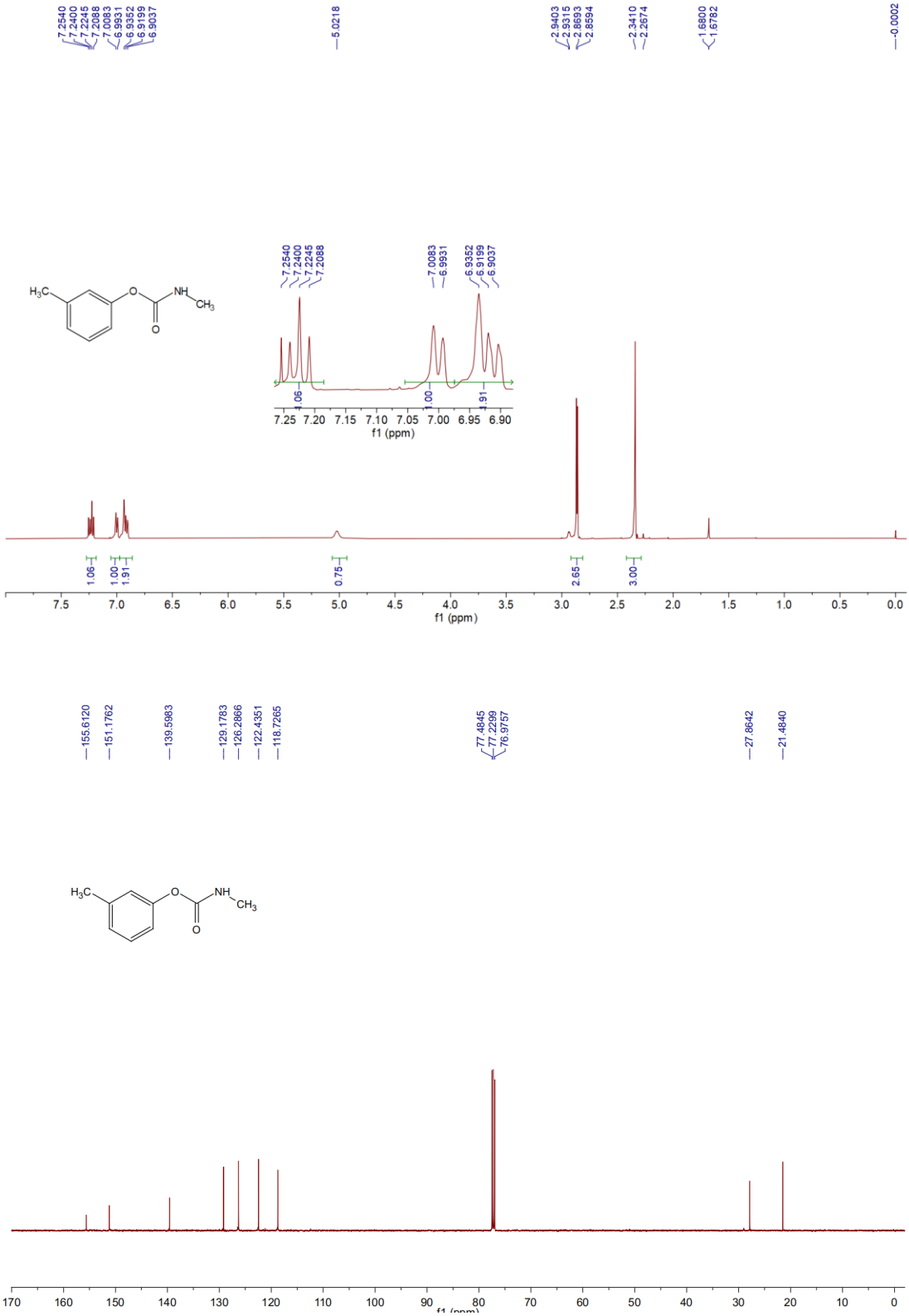


Figure S1. ^{1}H-NMR and ^{13}C-NMR spectra of compound **1a**.

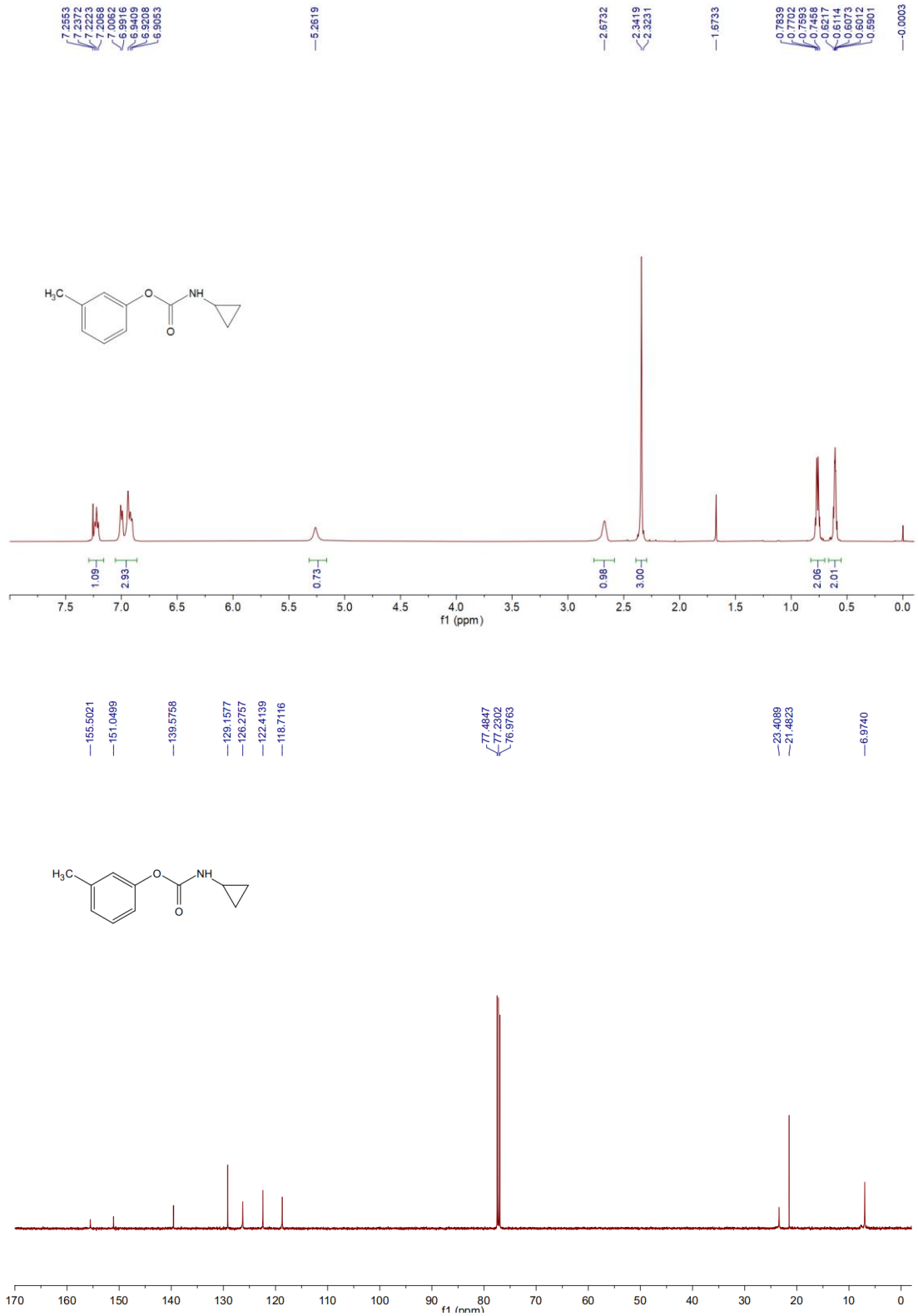


Figure S2. ^{1}H-NMR and ^{13}C-NMR spectra of compound **1b**.

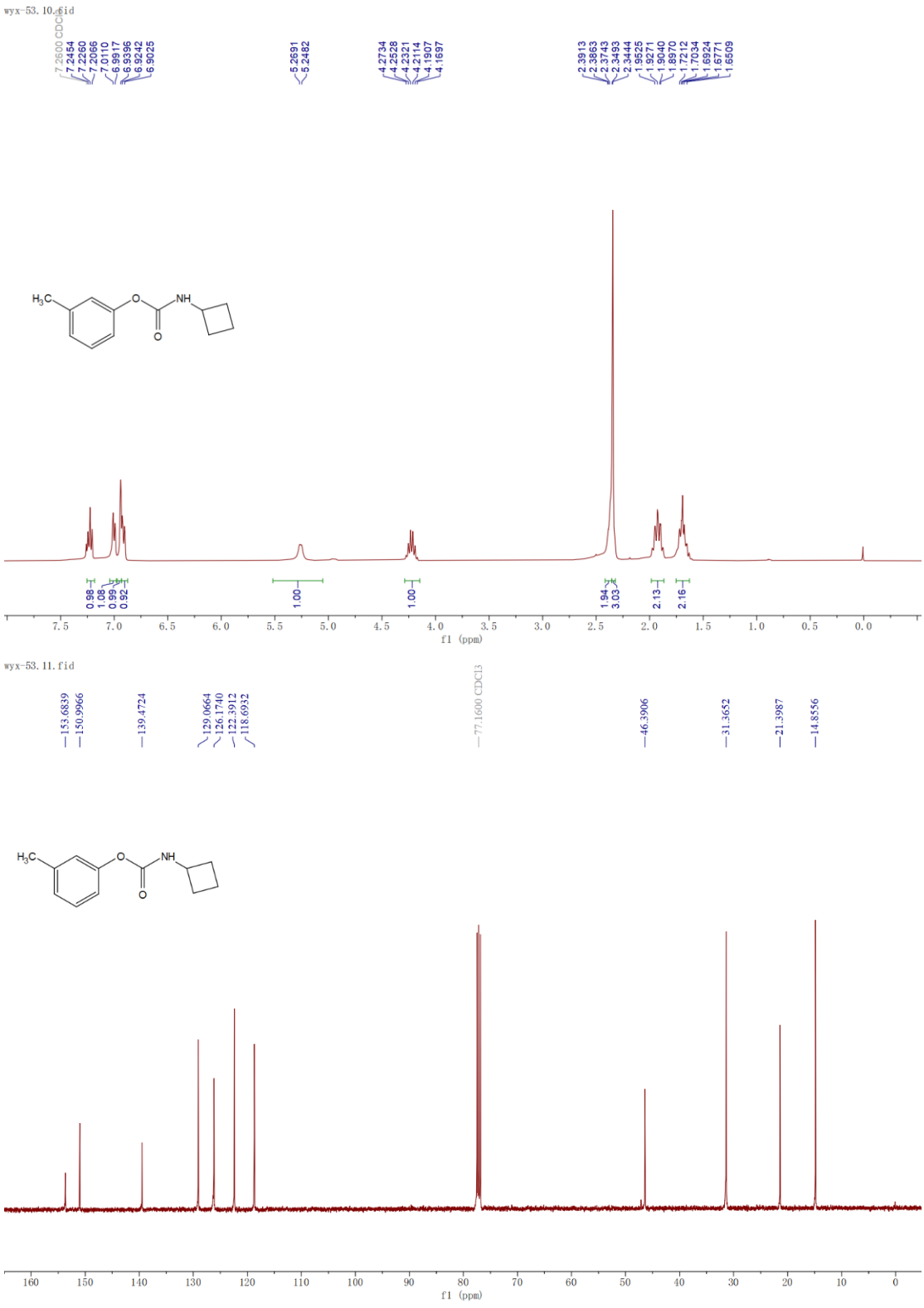


Figure S3. ^{1}H-NMR and ^{13}C-NMR spectra of compound **1c**.

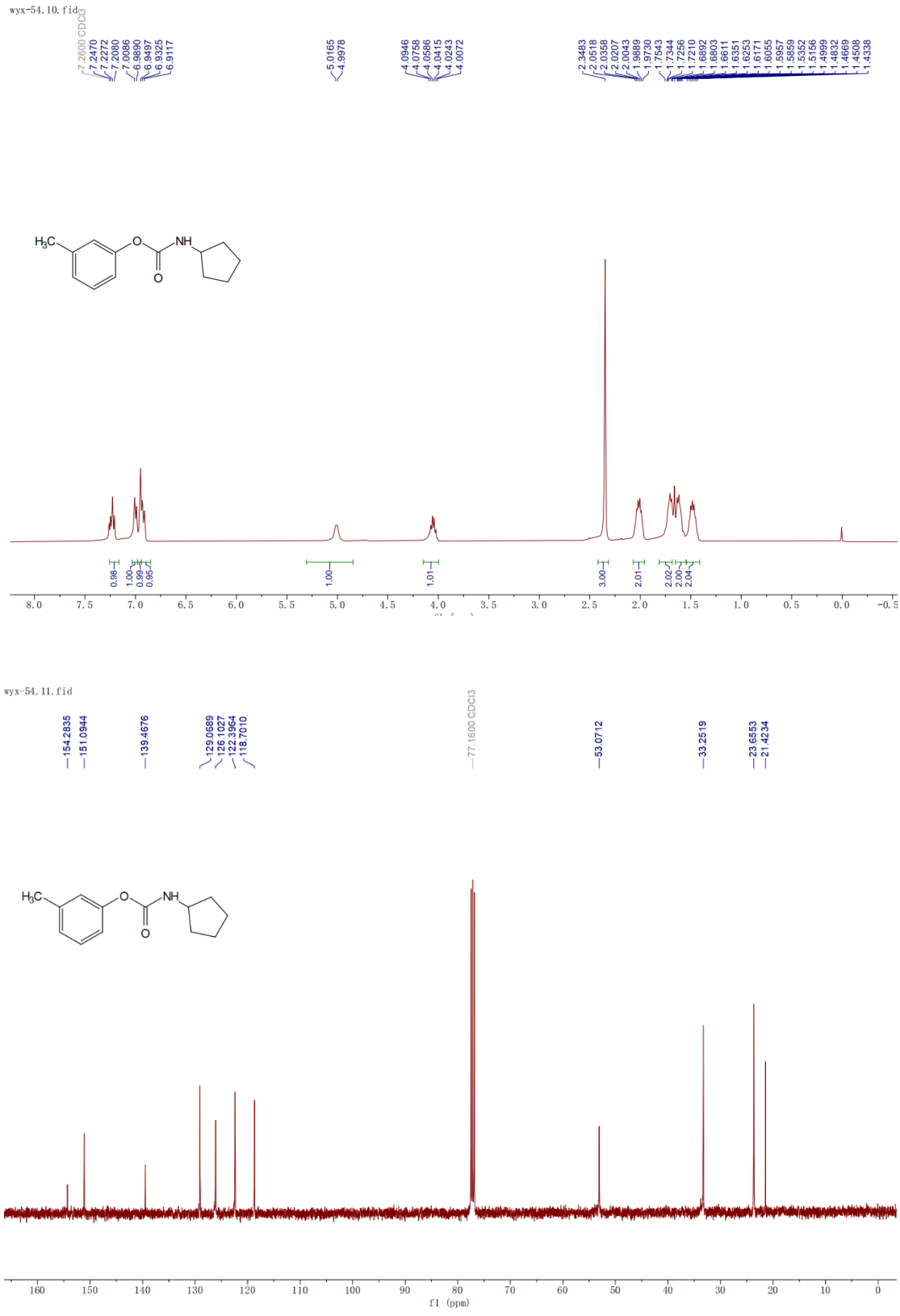


Figure S4. ^{1}H-NMR and ^{13}C-NMR spectra of compound **1d**.

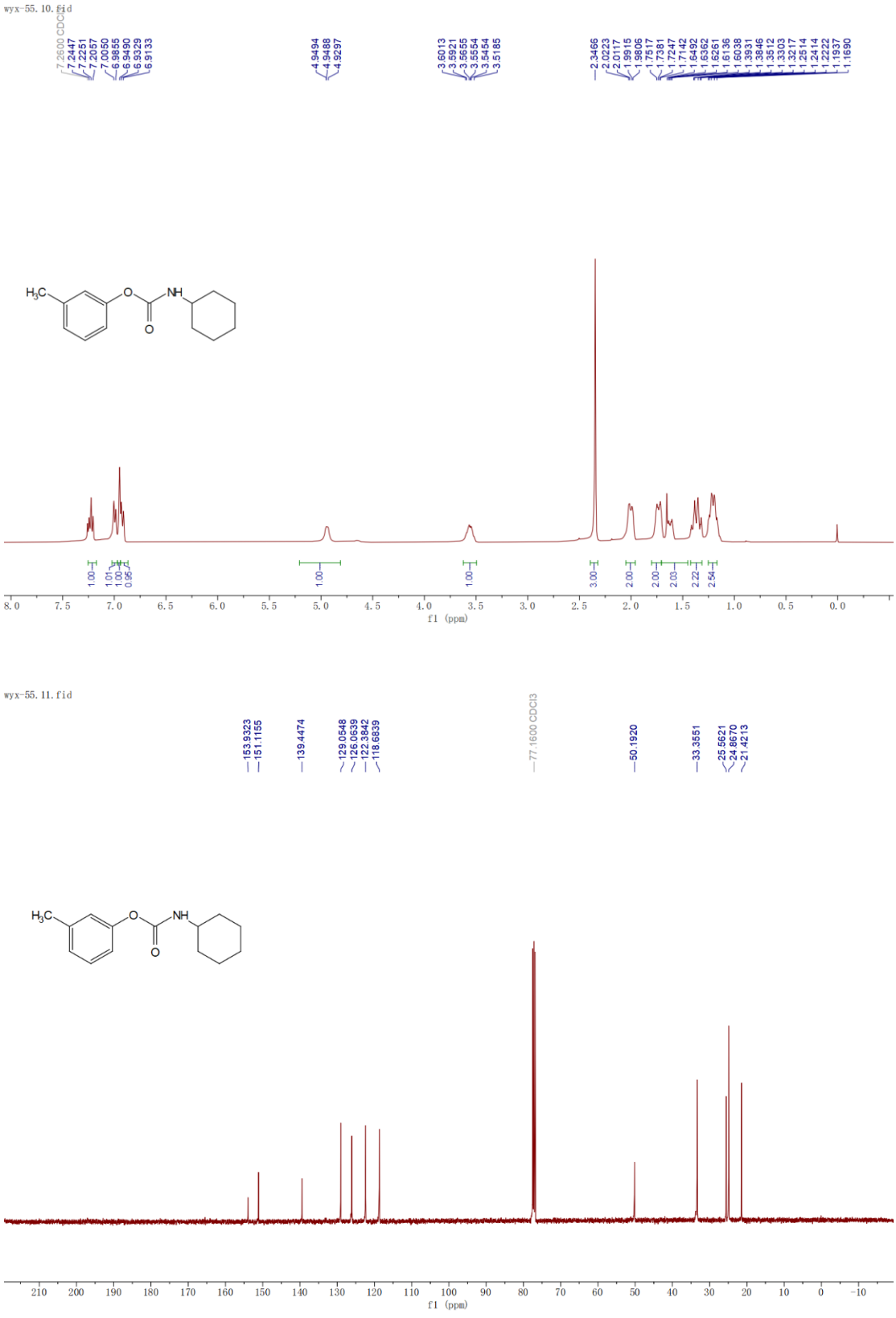


Figure S5. ^{1}H-NMR and ^{13}C-NMR spectra of compound **1e**.

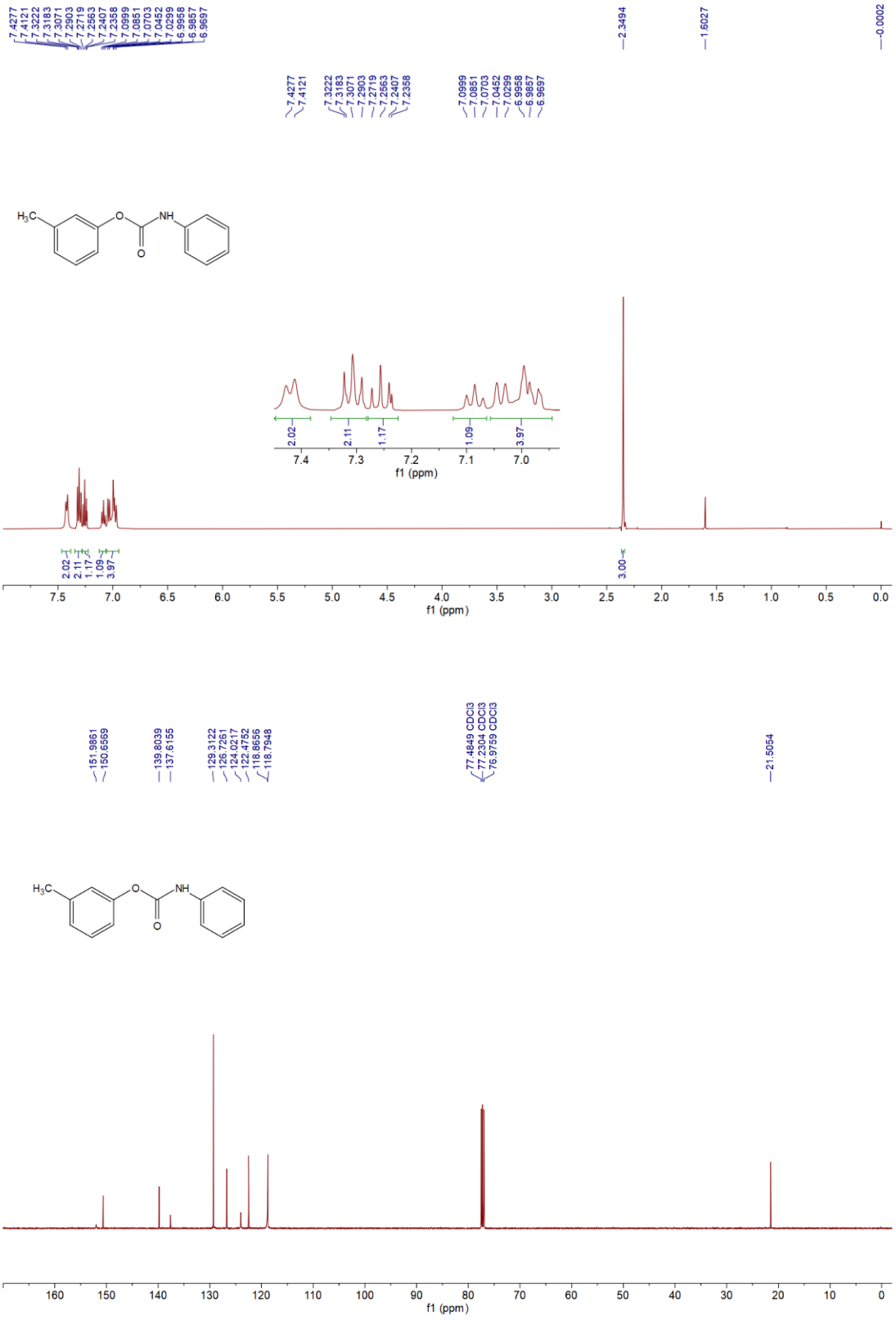


Figure S6. ^{1}H-NMR and ^{13}C-NMR spectra of compound **1f**.

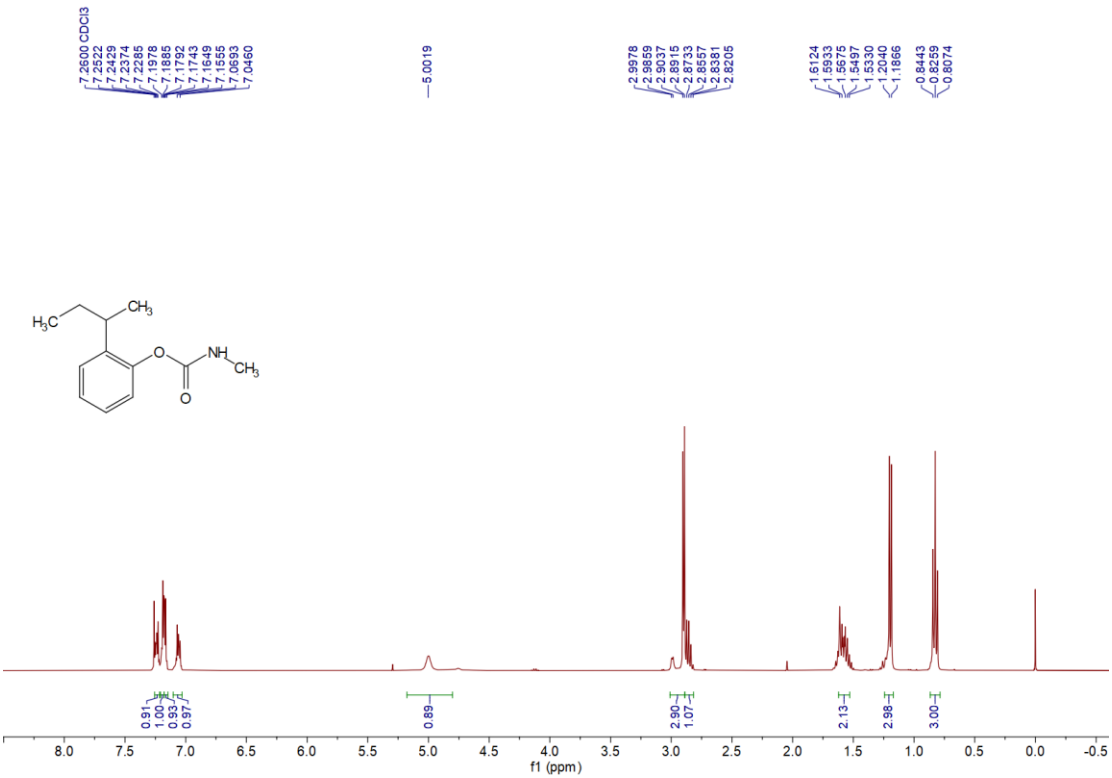


Figure S7. ^{1}H-NMR spectra of compound **2a**.

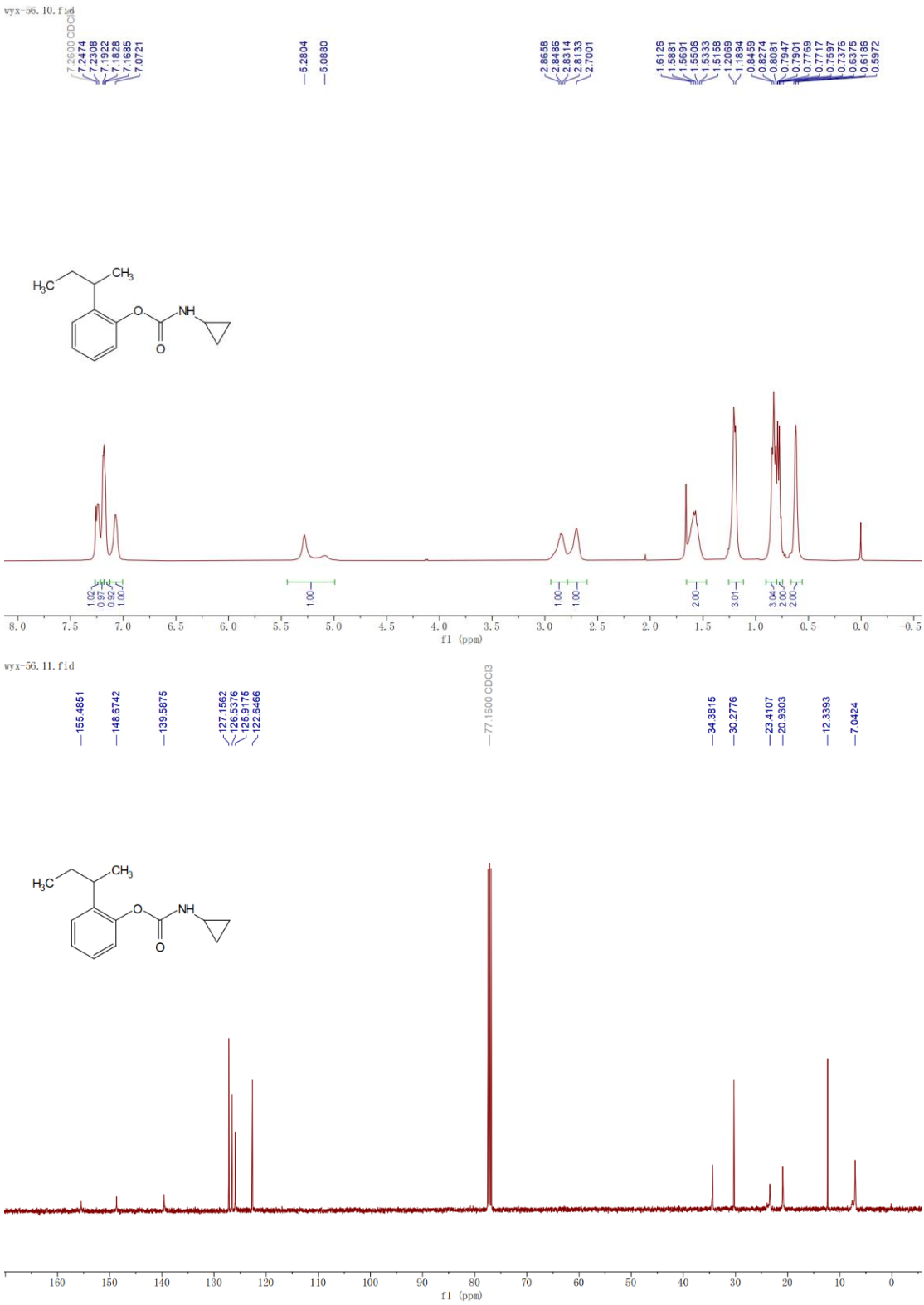


Figure S8. ^{1}H-NMR and ^{13}C-NMR spectra of compound **2b**.

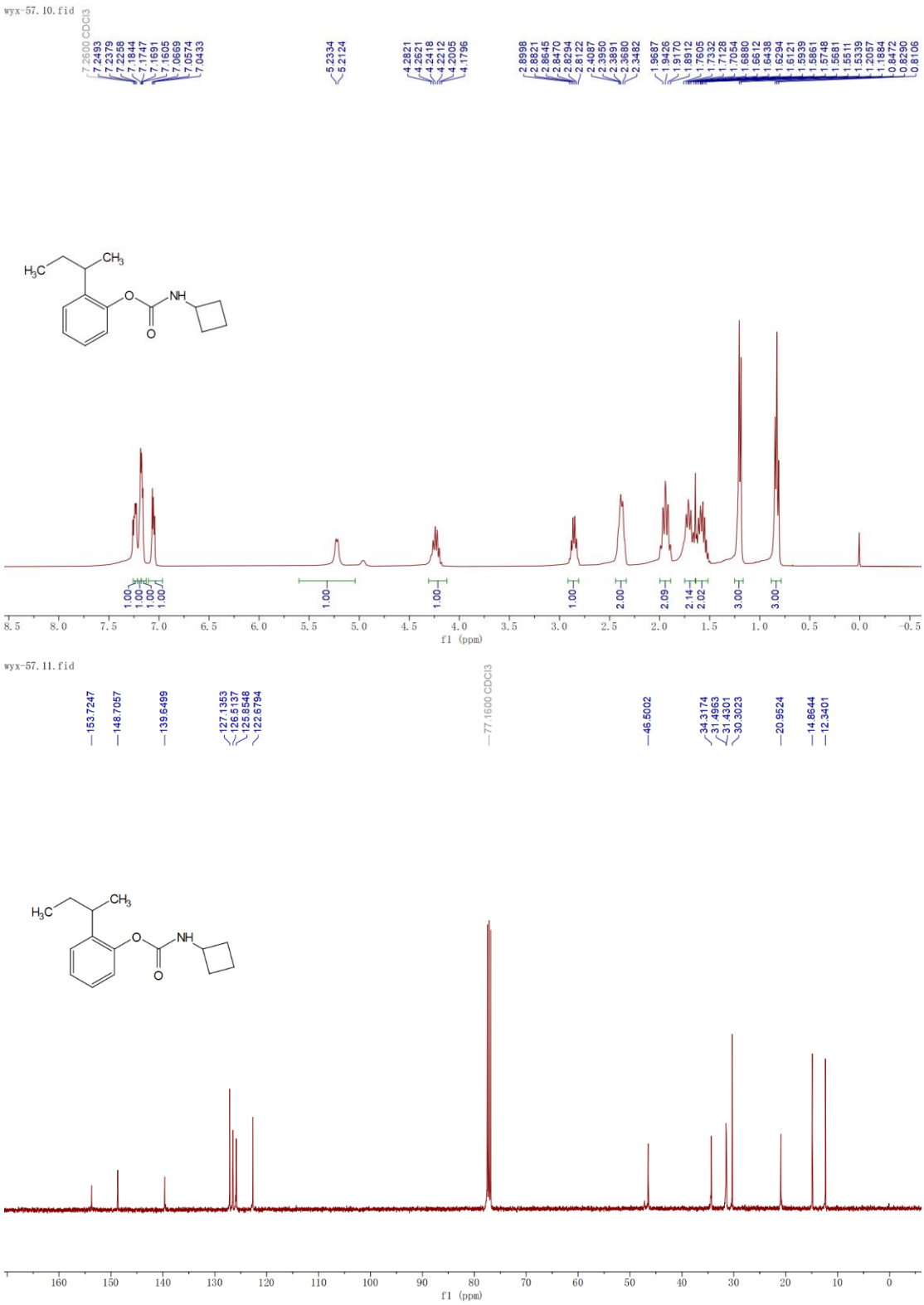


Figure S9. ^{1}H-NMR and ^{13}C-NMR spectra of compound **2c**.

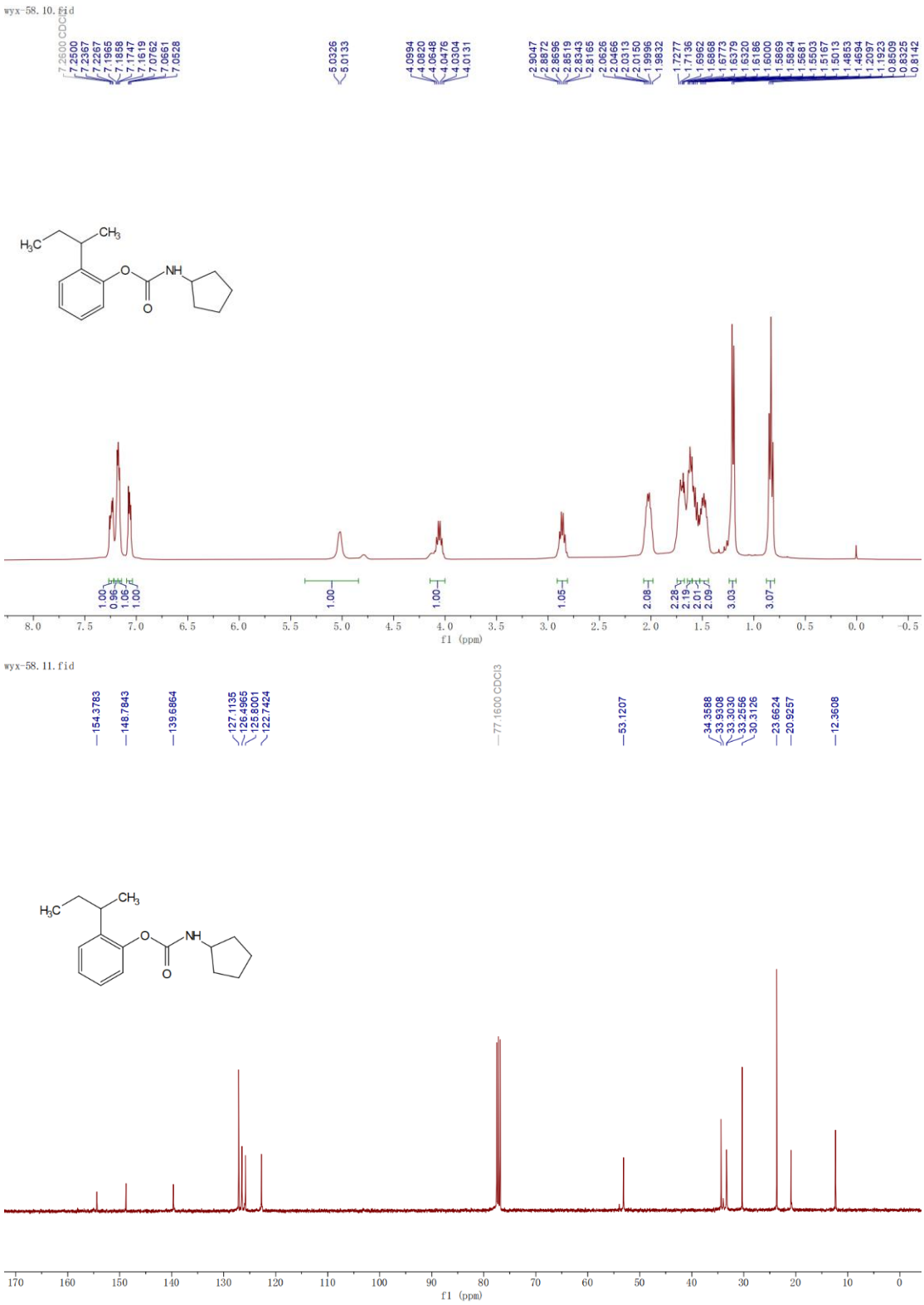


Figure S10. ^{1}H-NMR and ^{13}C-NMR spectra of compound **2d**.

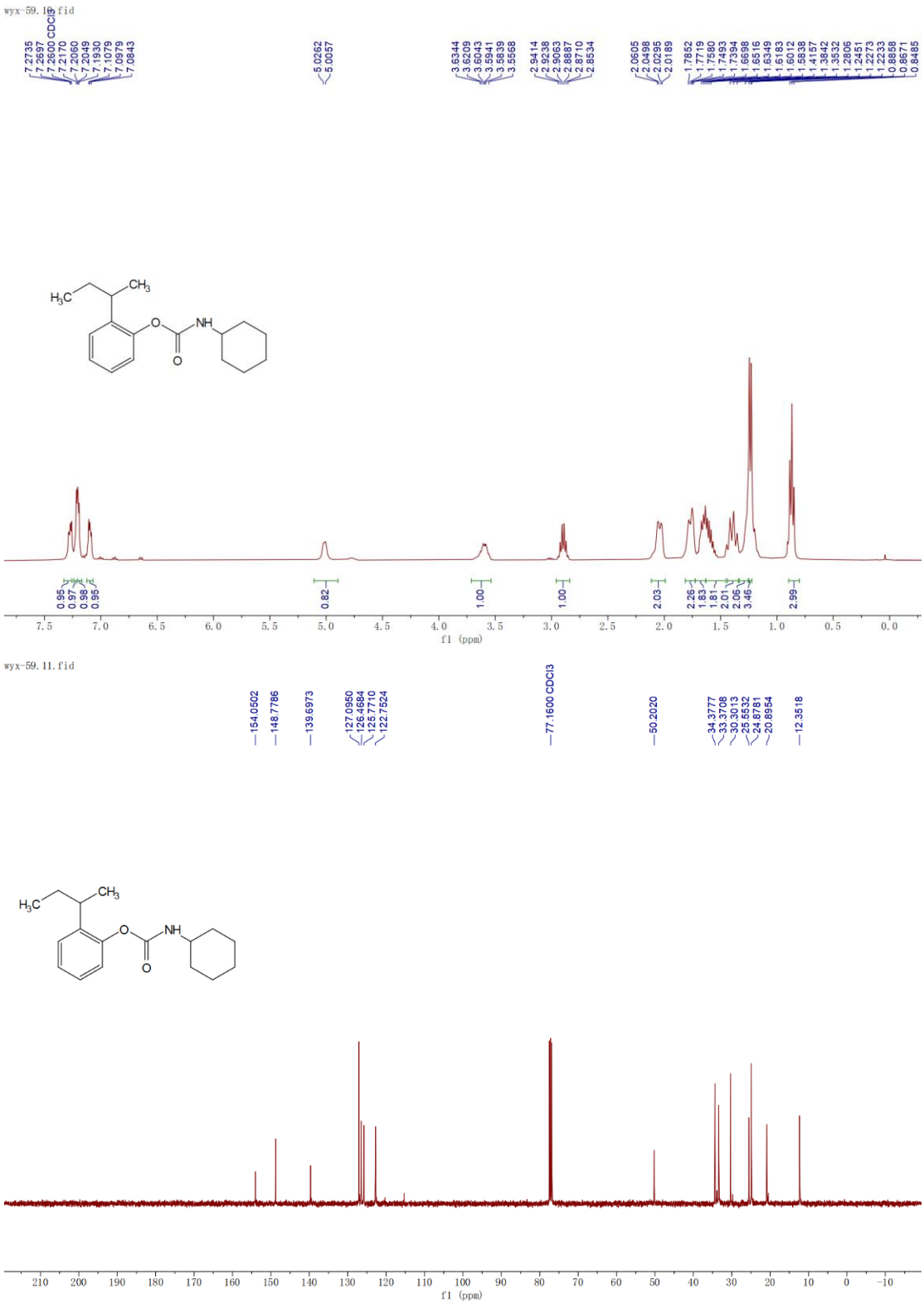


Figure S11. ^{1}H-NMR and ^{13}C-NMR spectra of compound **2e**.

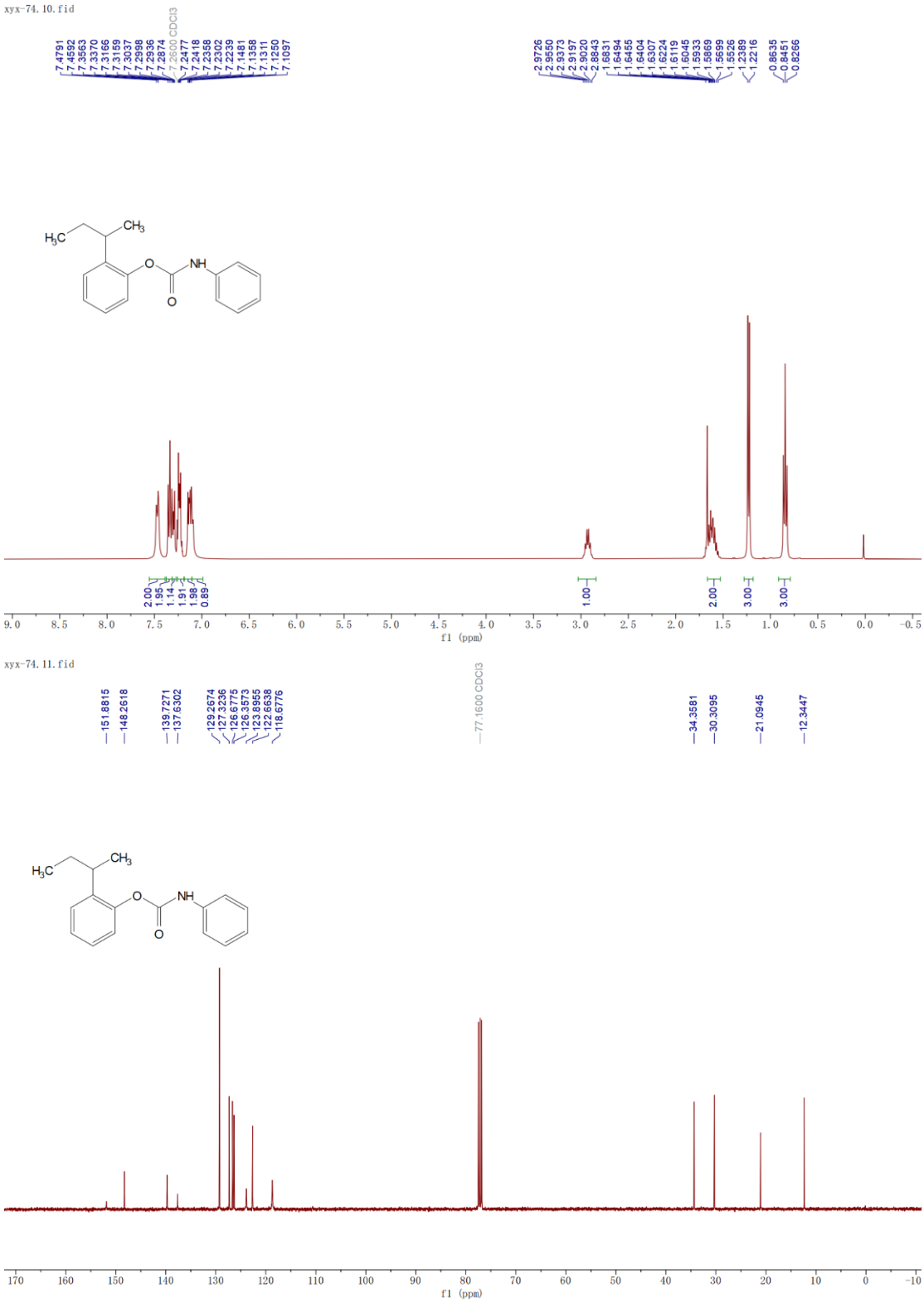


Figure S12. ^{1}H-NMR and ^{13}C-NMR spectra of compound **2f**.

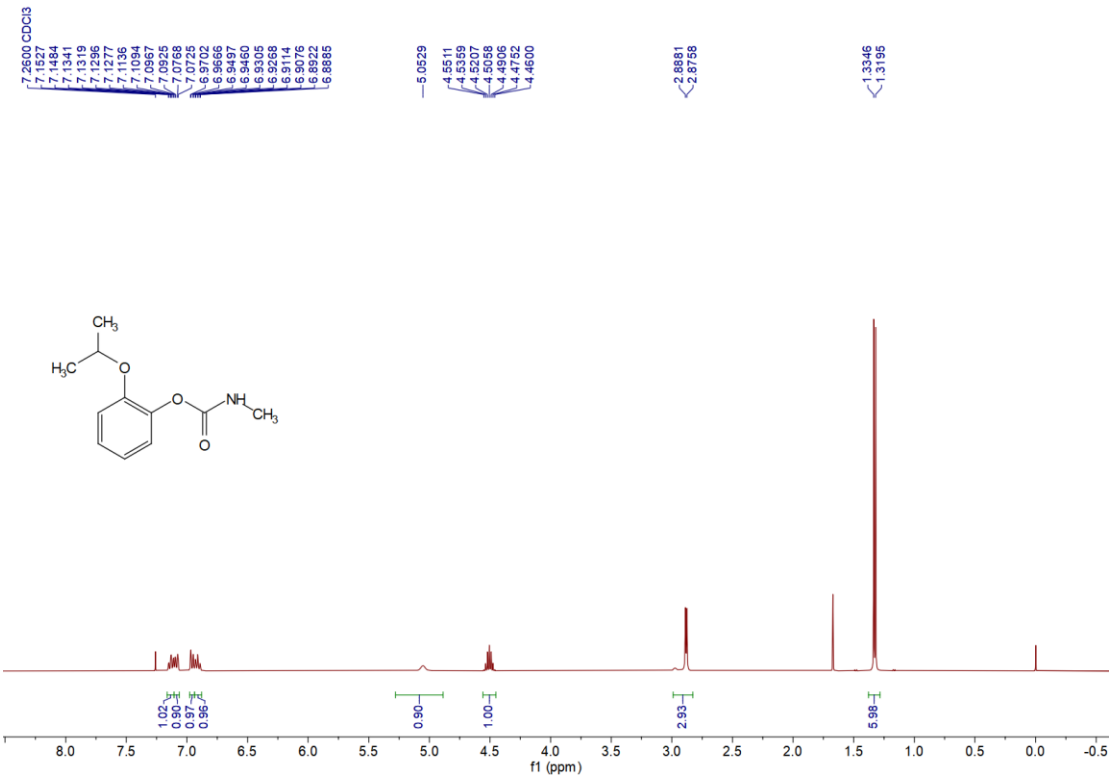


Figure S13. ^{1}H-NMR spectra of compound **3a**.

Figure S14. ^{1}H-NMR and ^{13}C-NMR spectra of compound **3b**.

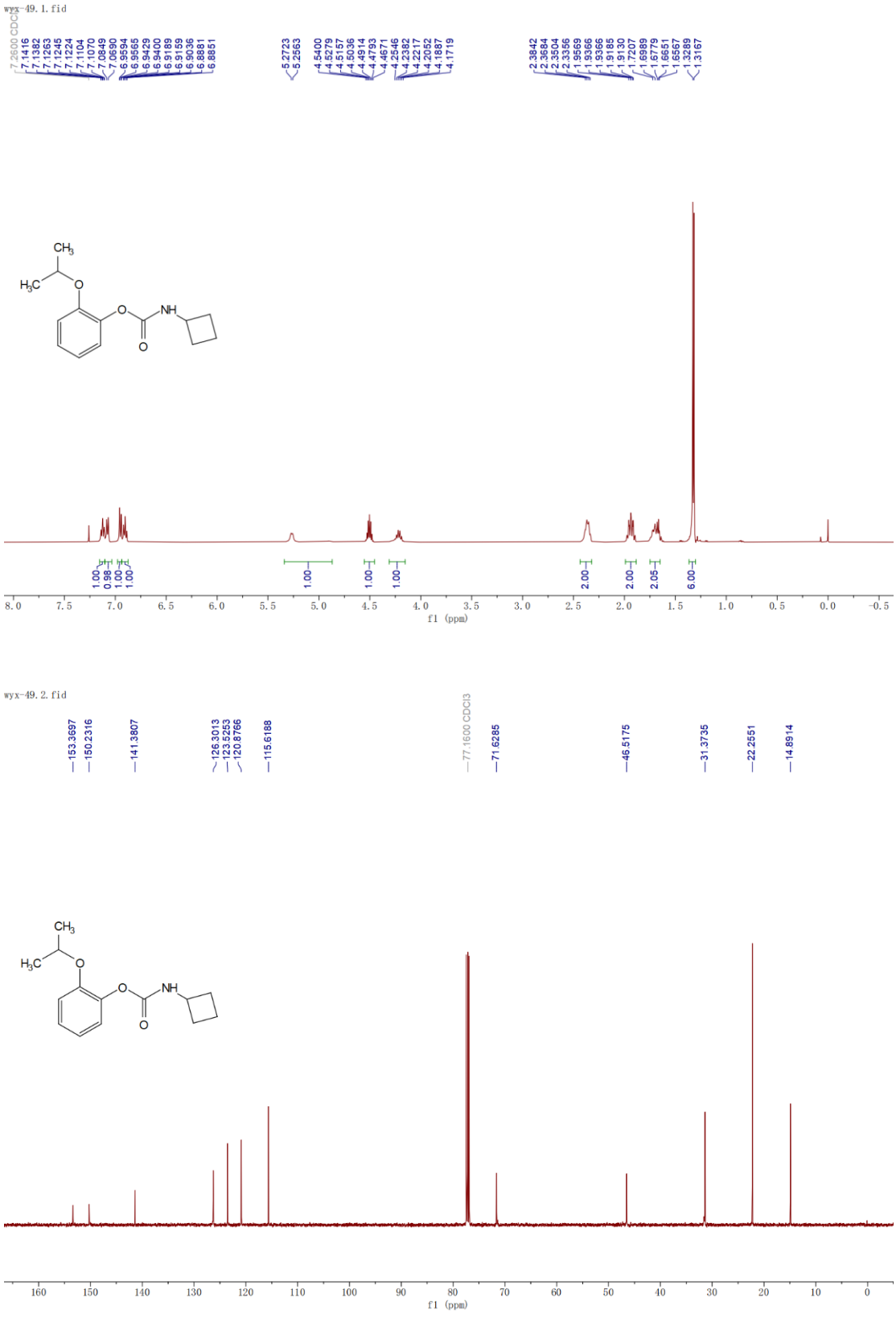


Figure S15. ^{1}H-NMR and ^{13}C-NMR spectra of compound **3c**.

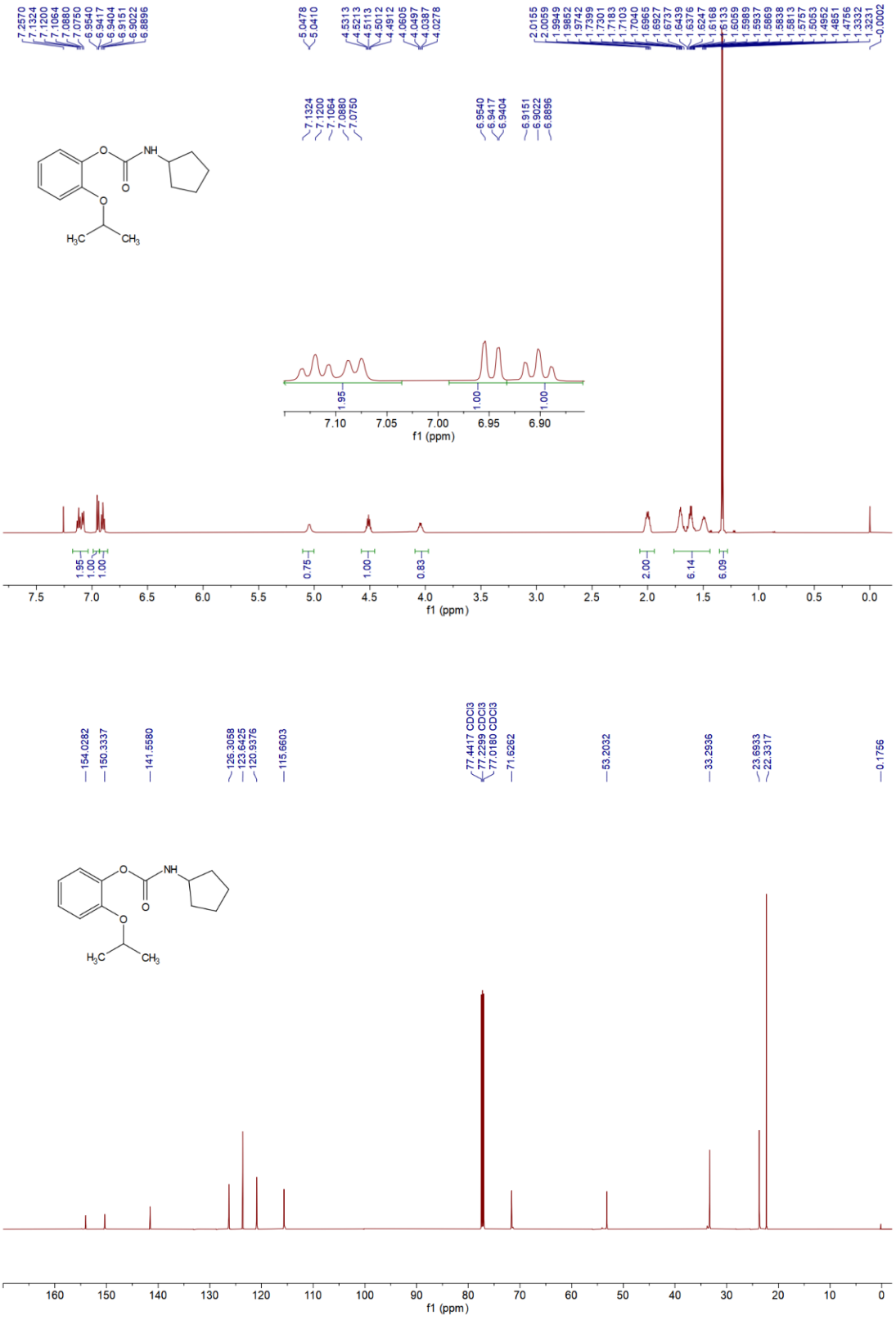


Figure S16. ^{1}H-NMR and ^{13}C-NMR spectra of compound **3d**.

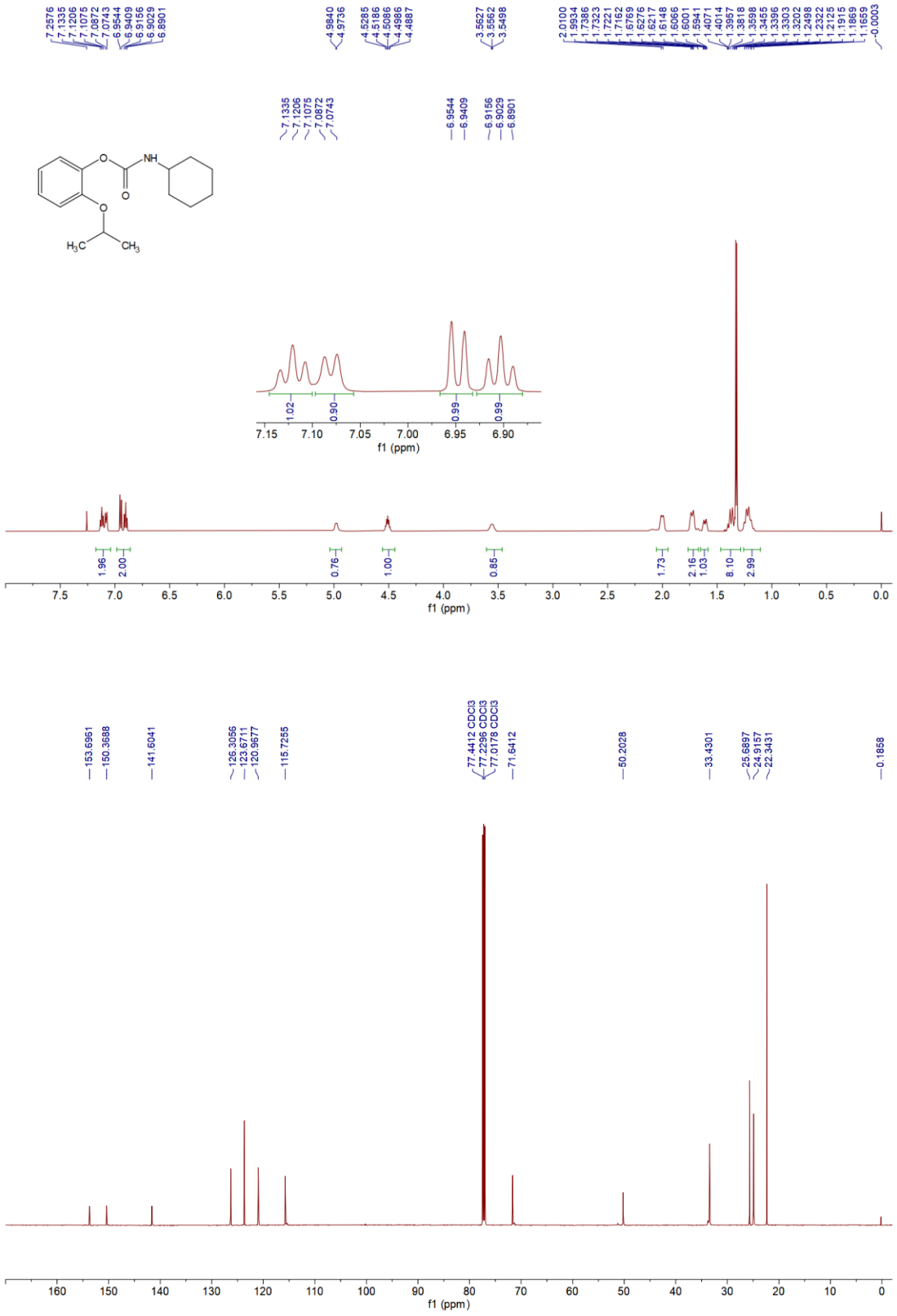


Figure S17. ^{1}H-NMR and ^{13}C-NMR spectra of compound **3e**.

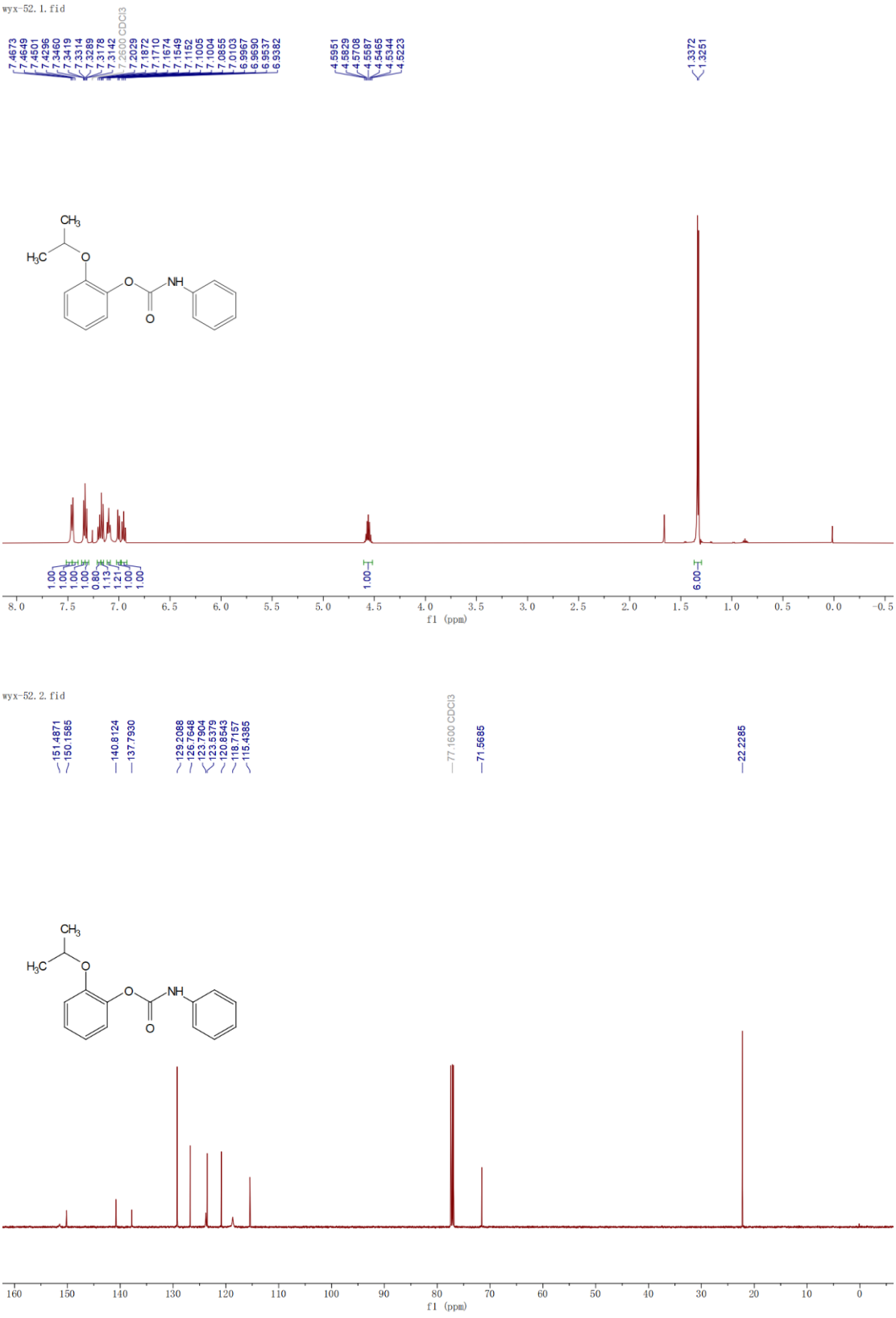


Figure S18. ^{1}H-NMR and ^{13}C-NMR spectra of compound **3f**.

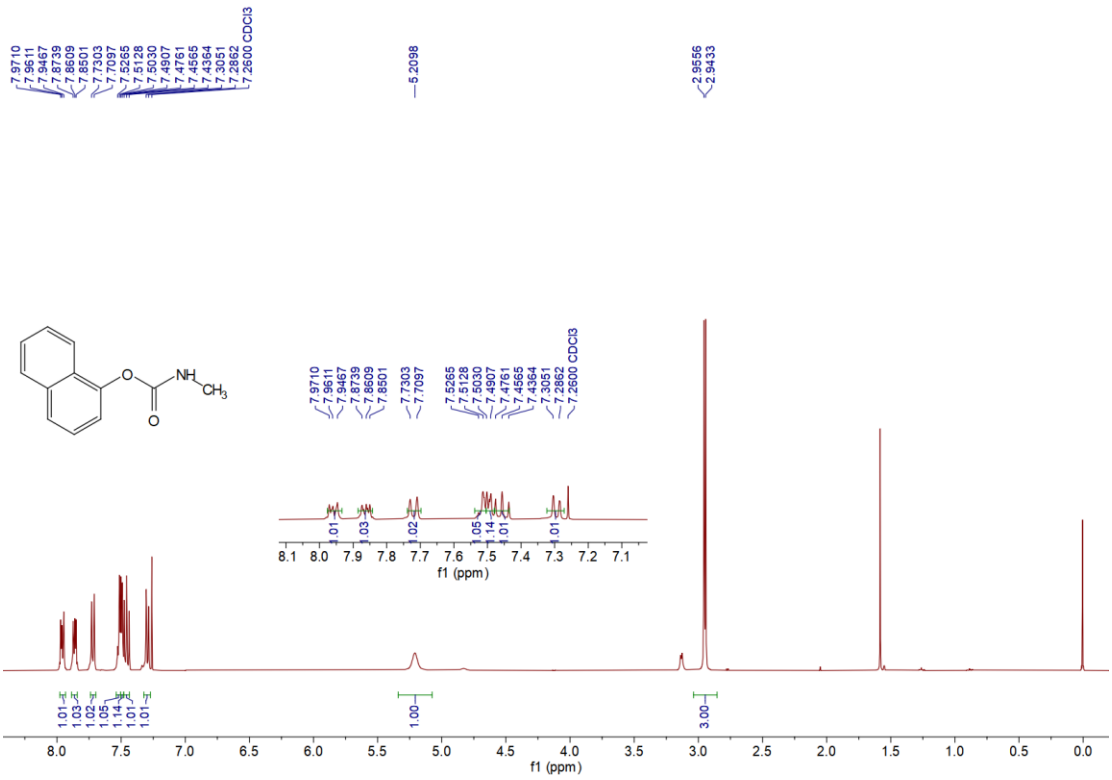


Figure S19. ^{1}H-NMR spectra of compound **4a**.

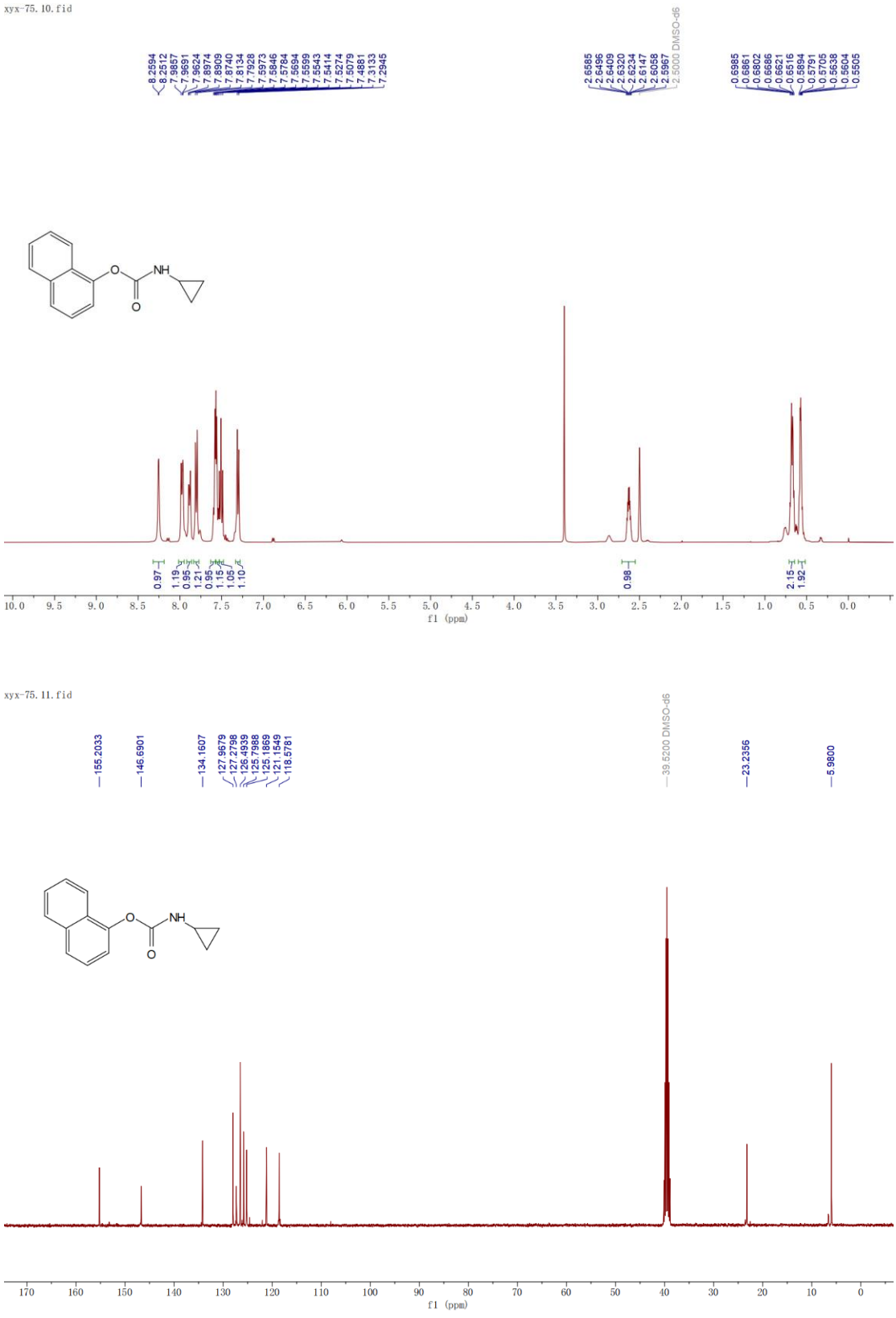


Figure S20. ^{1}H-NMR and ^{13}C-NMR spectra of compound **4b**.

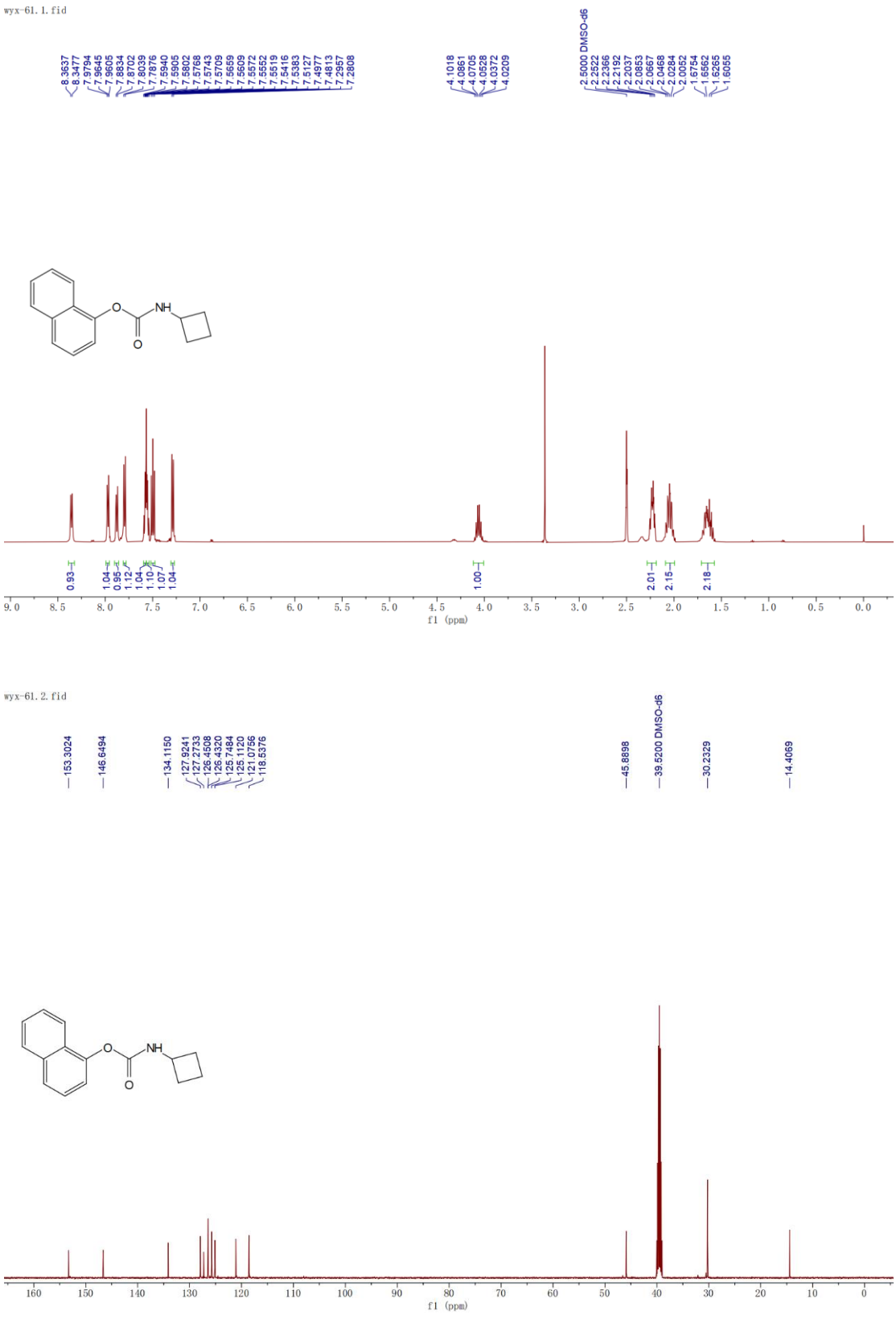


Figure S21. ^{1}H-NMR and ^{13}C-NMR spectra of compound **4c**.

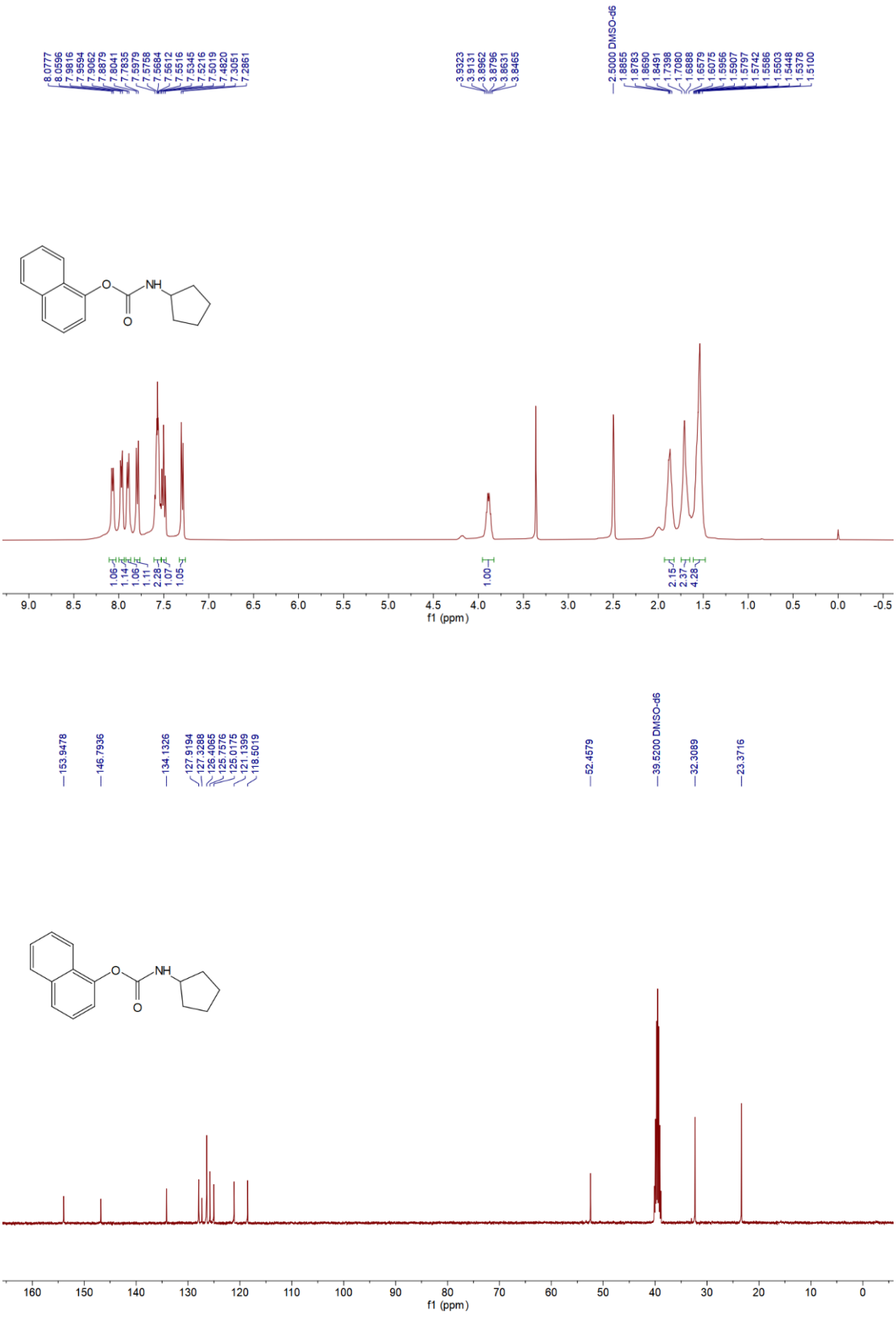


Figure S22. ^{1}H-NMR and ^{13}C-NMR spectra of compound **4d**.

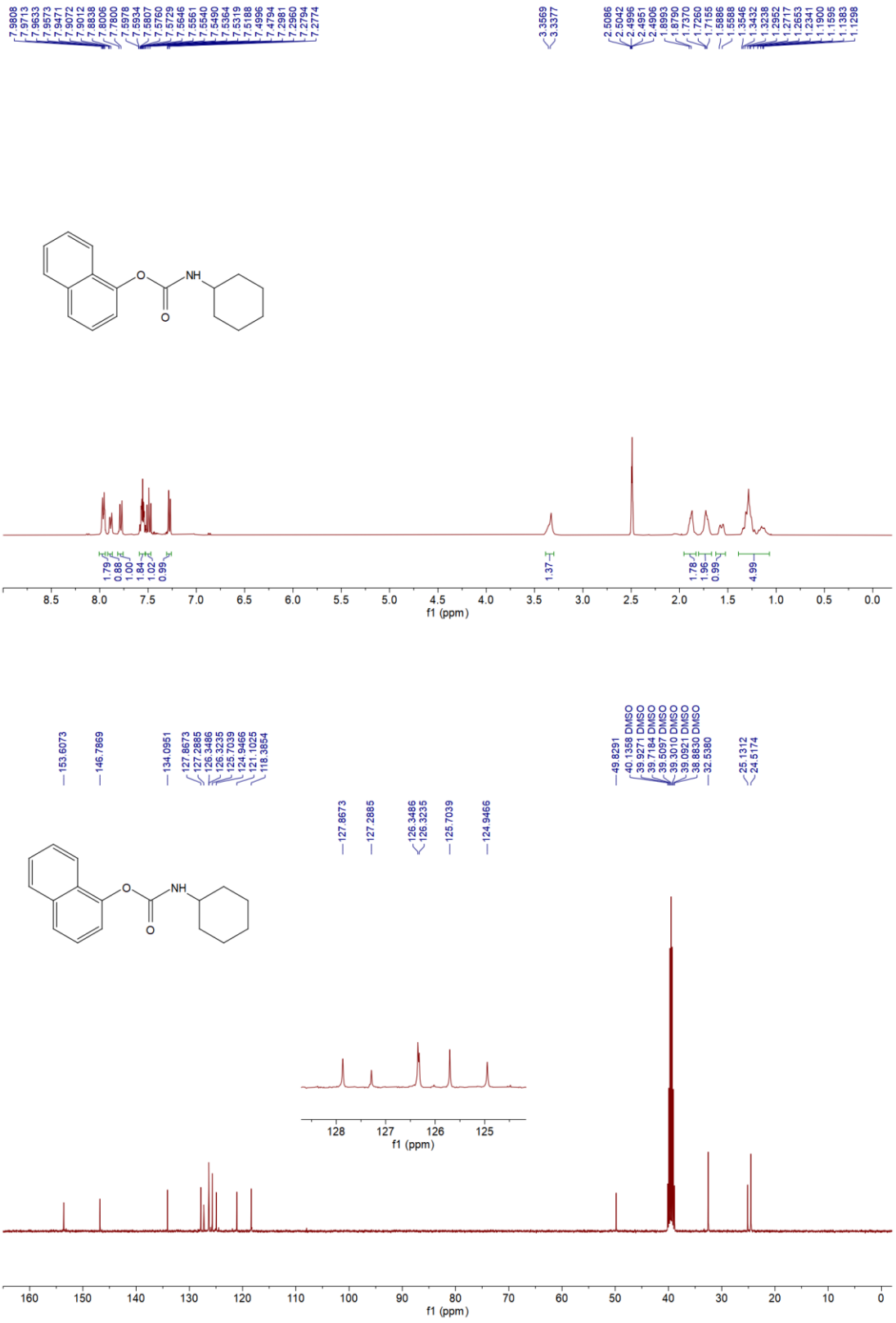


Figure S23. ^{1}H-NMR and ^{13}C-NMR spectra of compound **4e**.

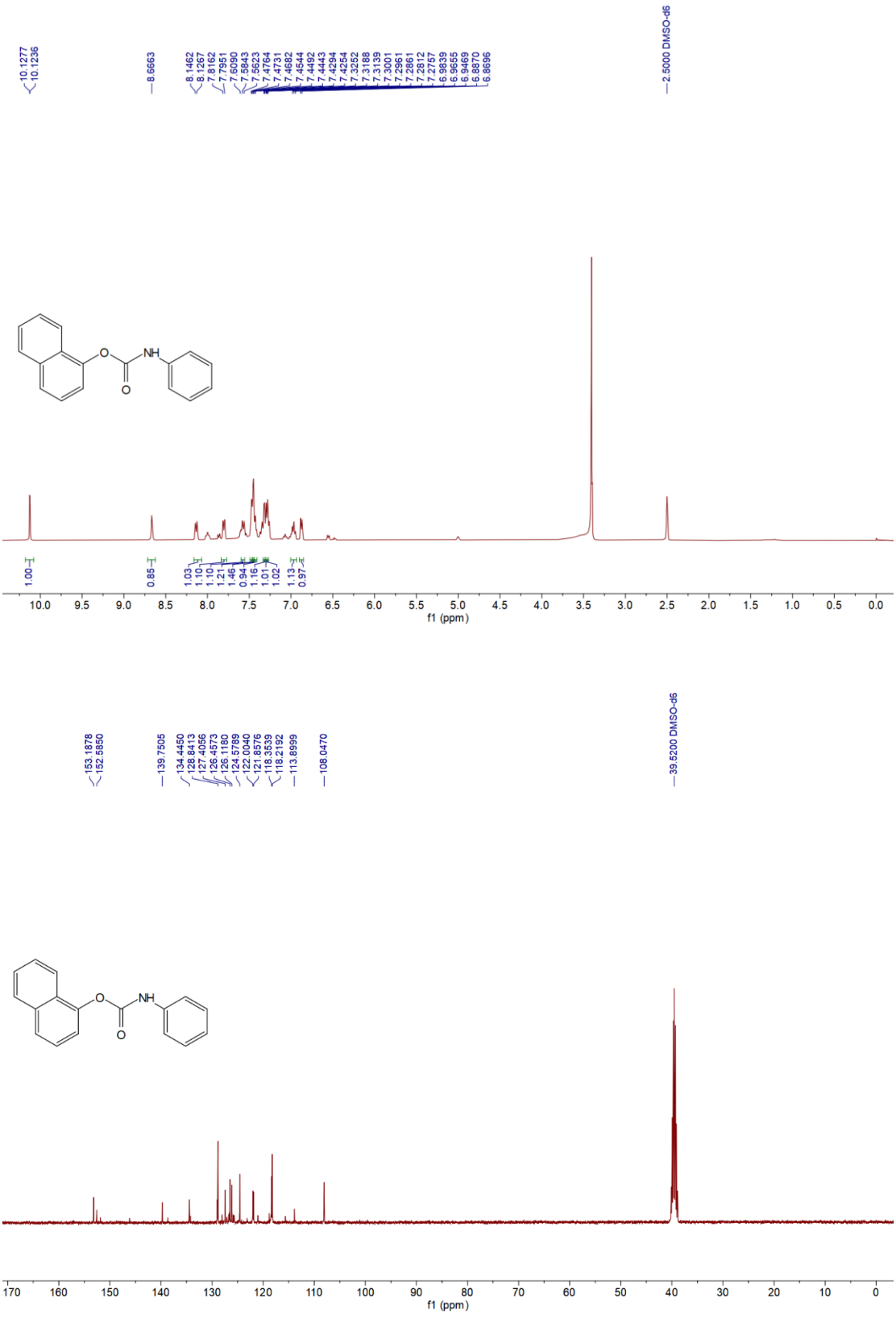


Figure S24. ^{1}H-NMR and ^{13}C-NMR spectra of compound **4f**.

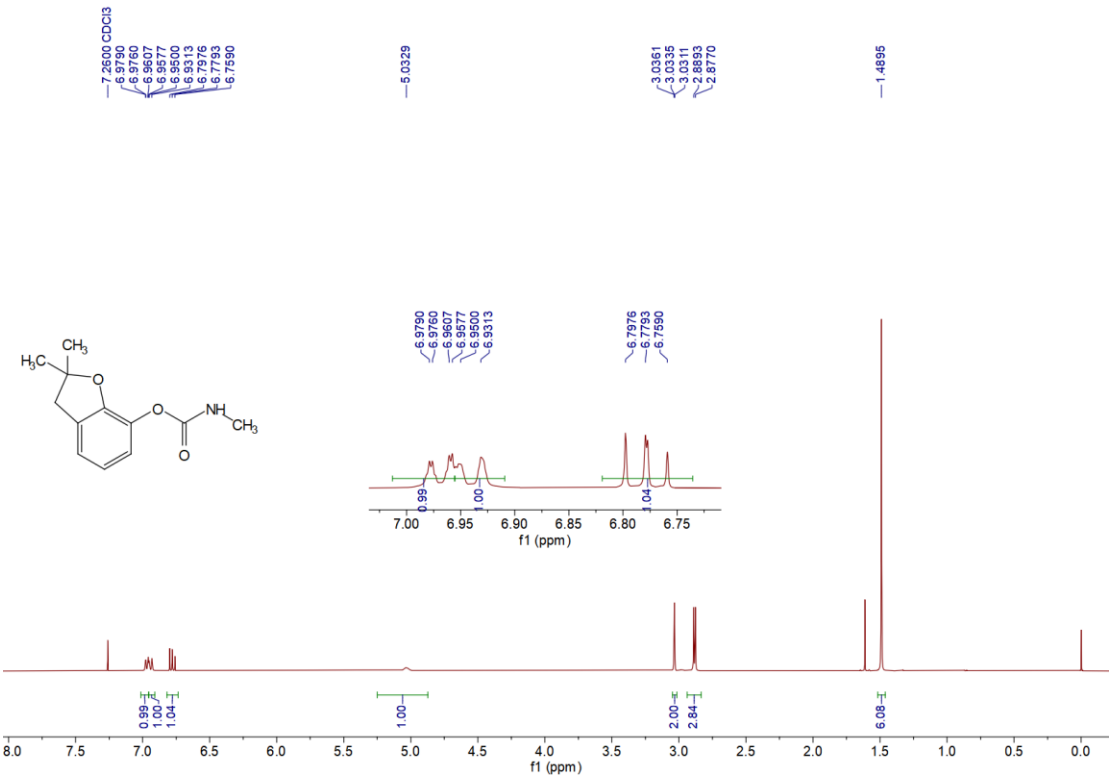


Figure S25. ^{1}H-NMR spectra of compound **5a**.

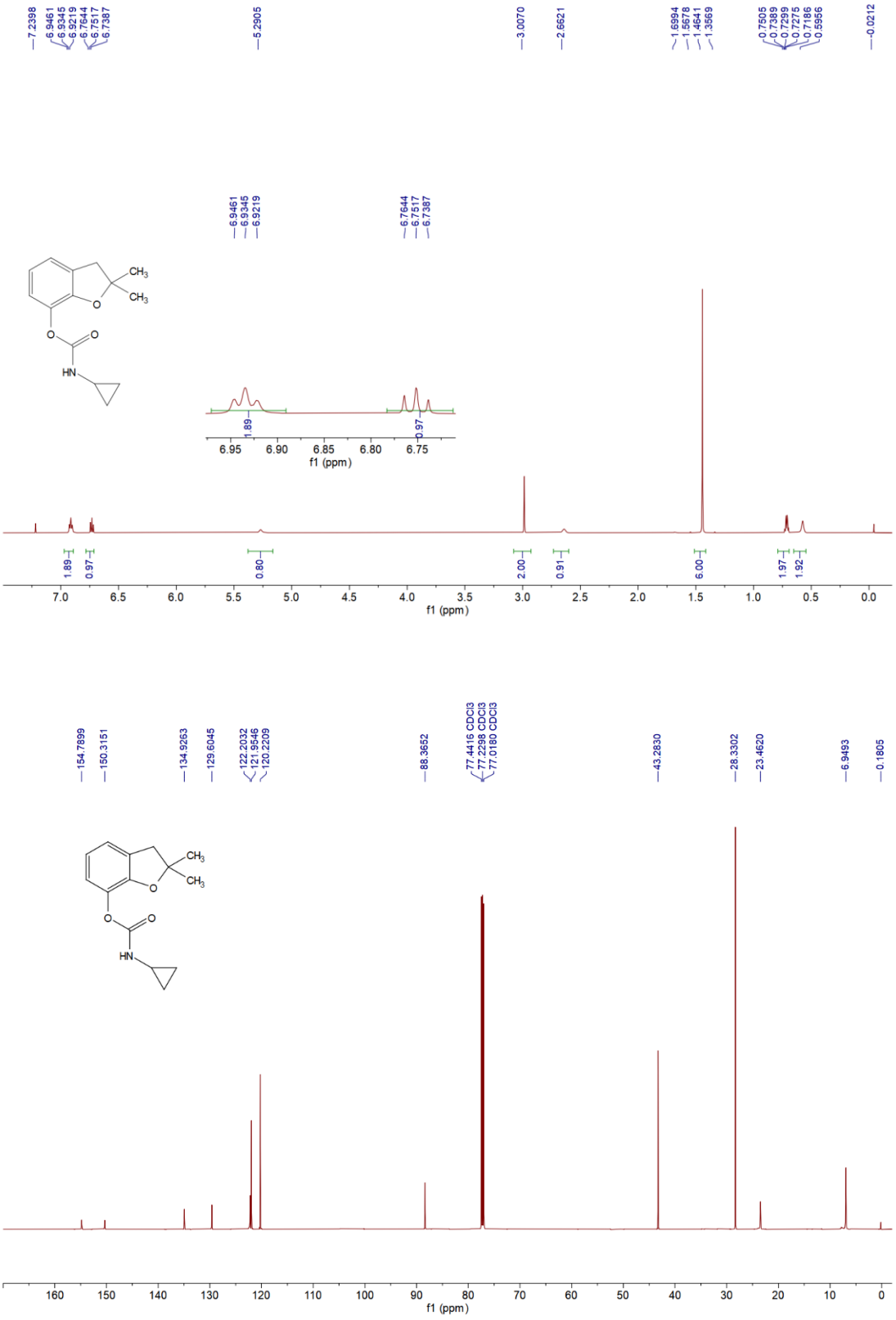


Figure S26. ^{1}H-NMR and ^{13}C-NMR spectra of compound **5b**.

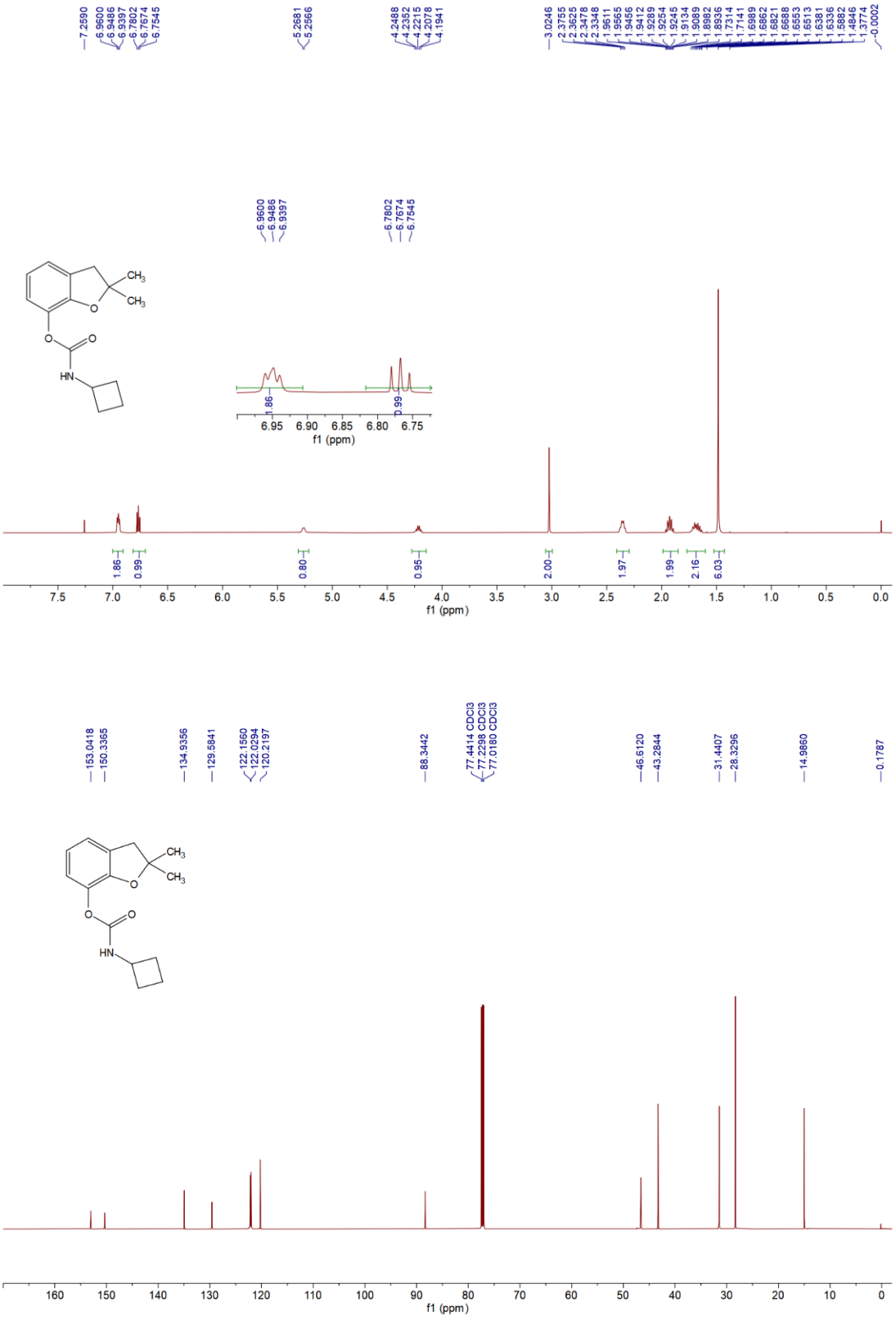


Figure S27. ^{1}H-NMR and ^{13}C-NMR spectra of compound **5c**.

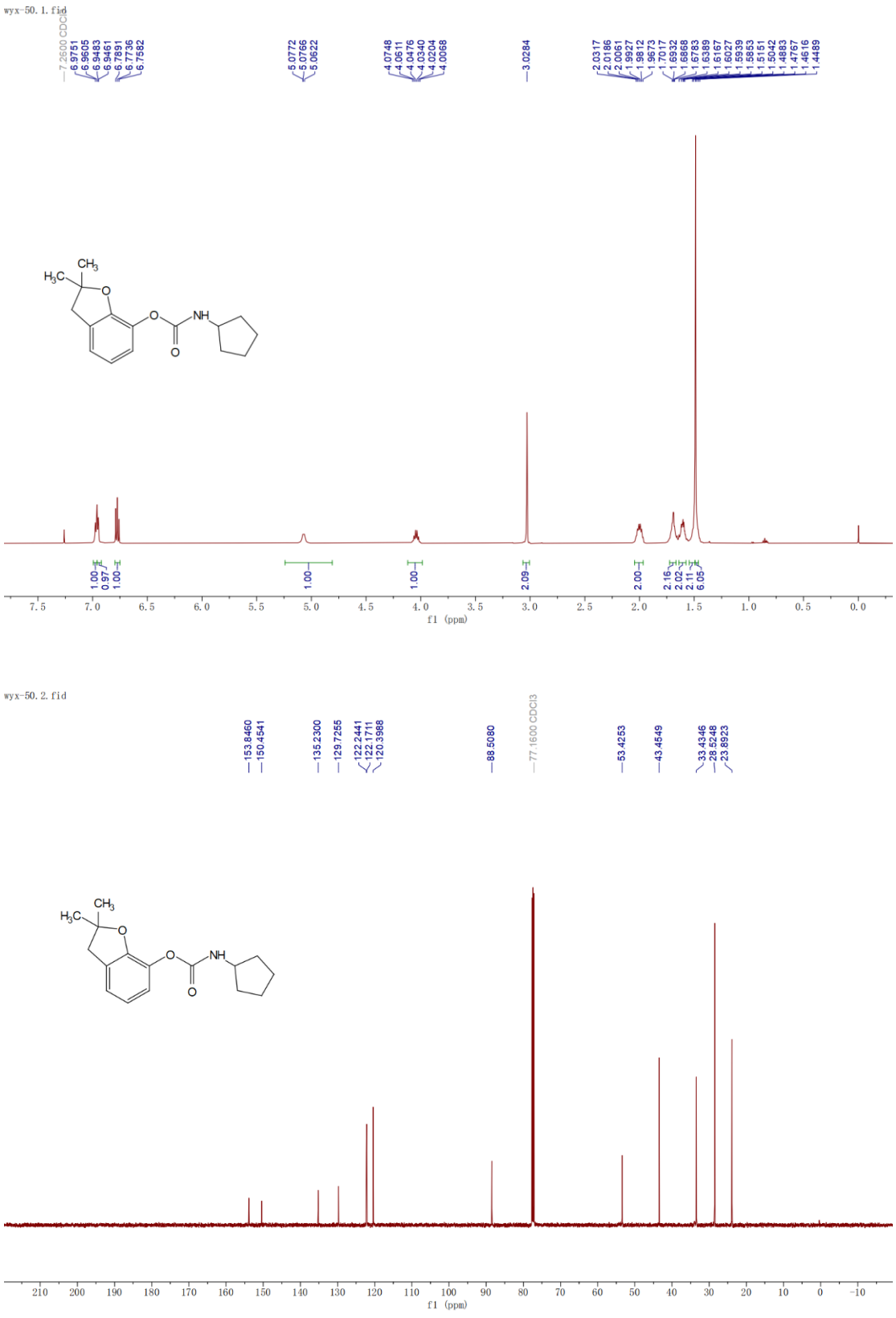


Figure S28. ^{1}H-NMR and ^{13}C-NMR spectra of compound **5d.**

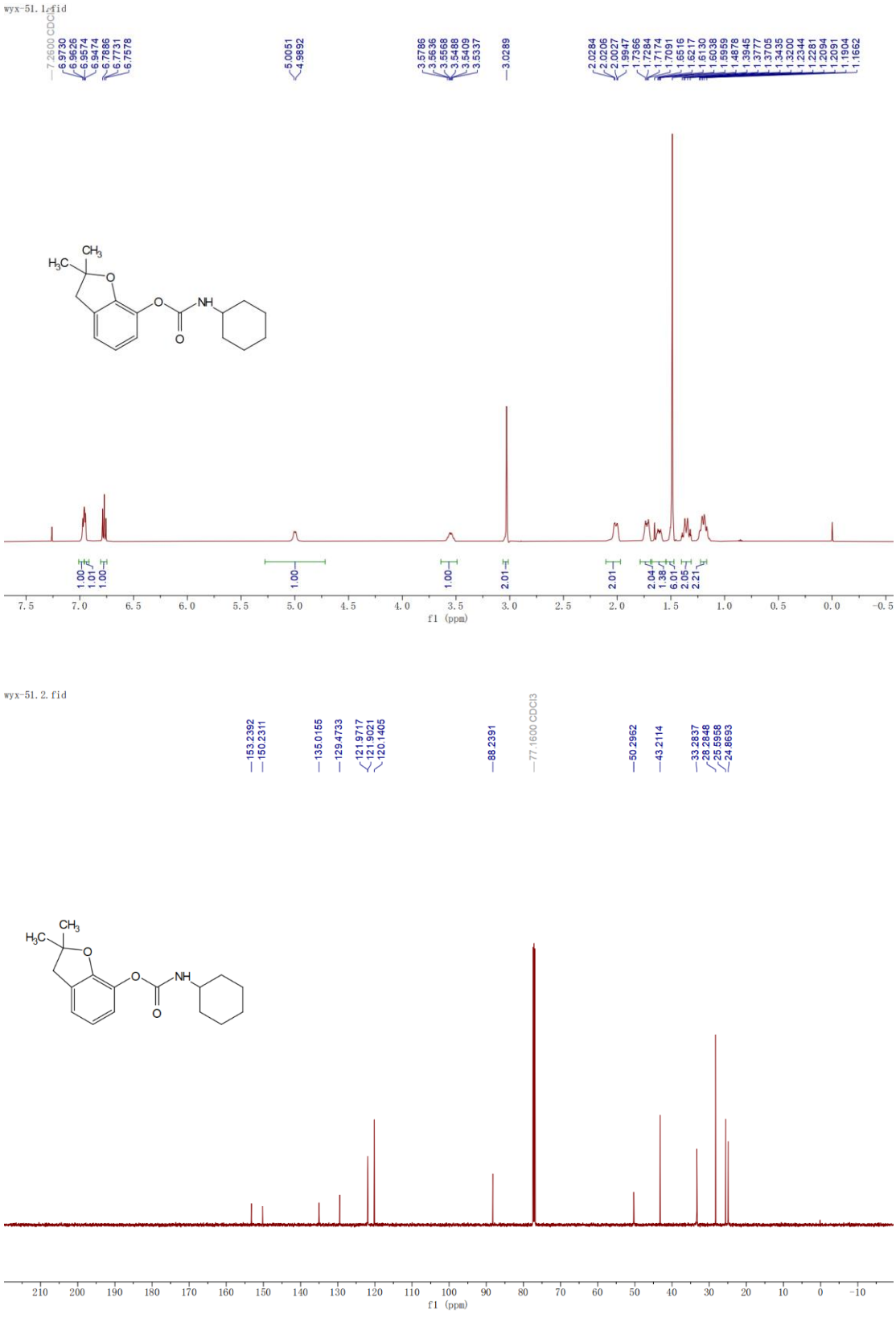


Figure S29. ^{1}H-NMR and ^{13}C-NMR spectra of compound **5e**.

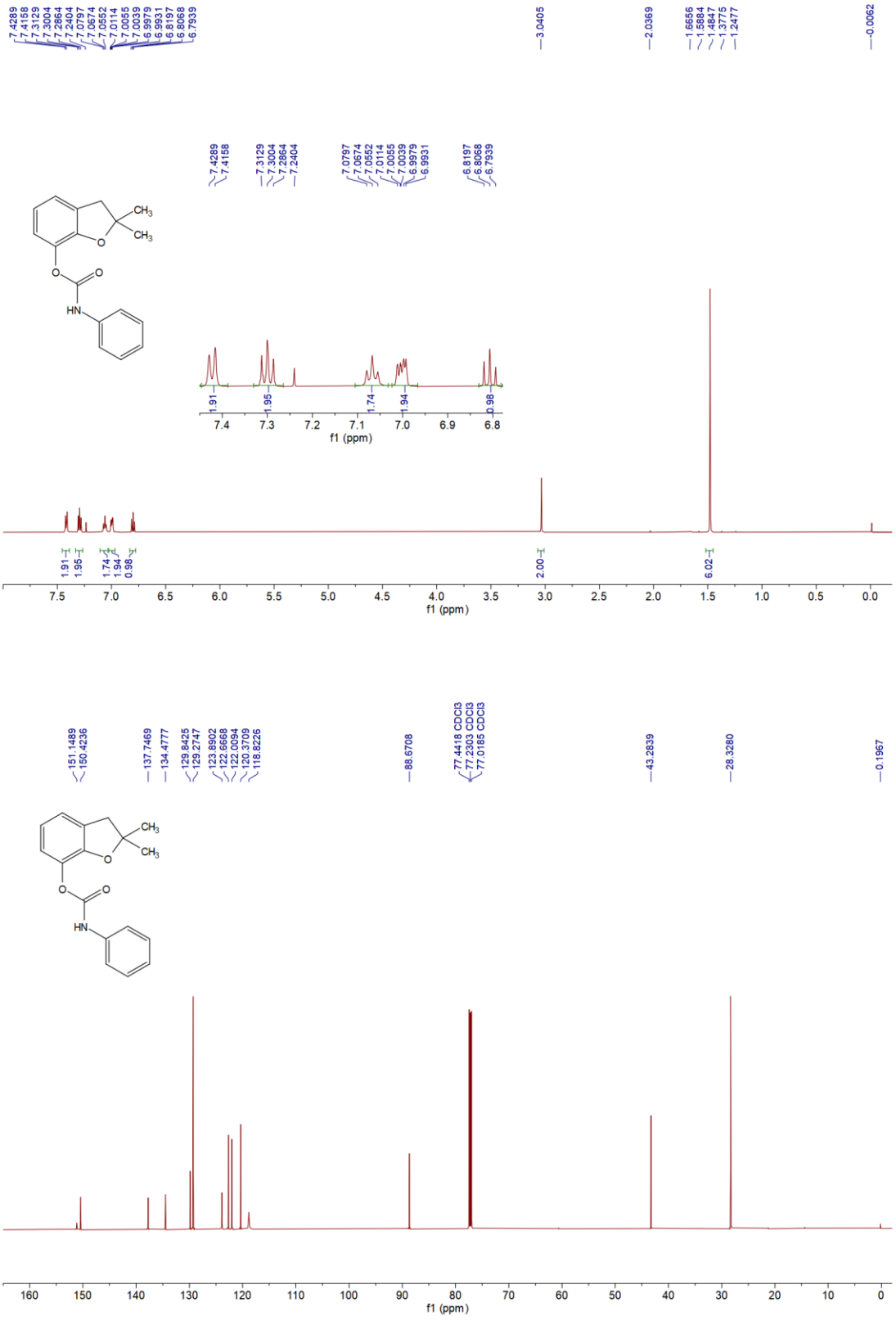


Figure S30. ^{1}H-NMR and ^{13}C-NMR spectra of compound **5f**.

7. TOF-HRMS (ESI) spectra

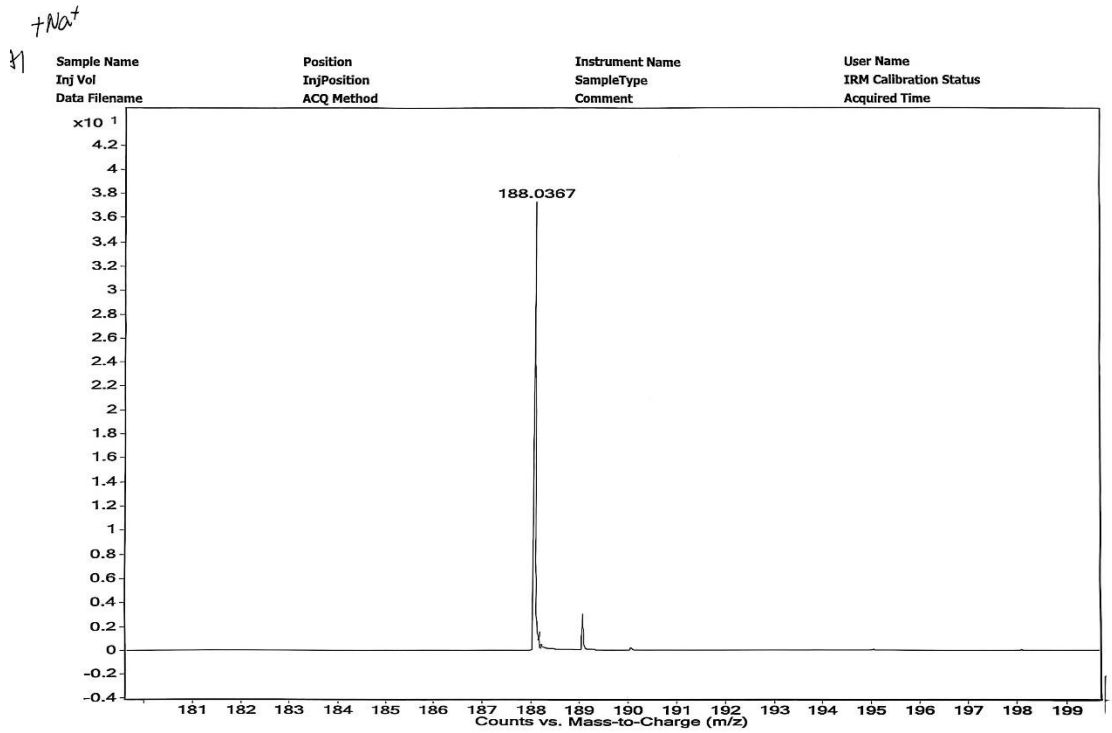


Figure S31. TOF-HRMS (ESI) spectra of compound **1a**.

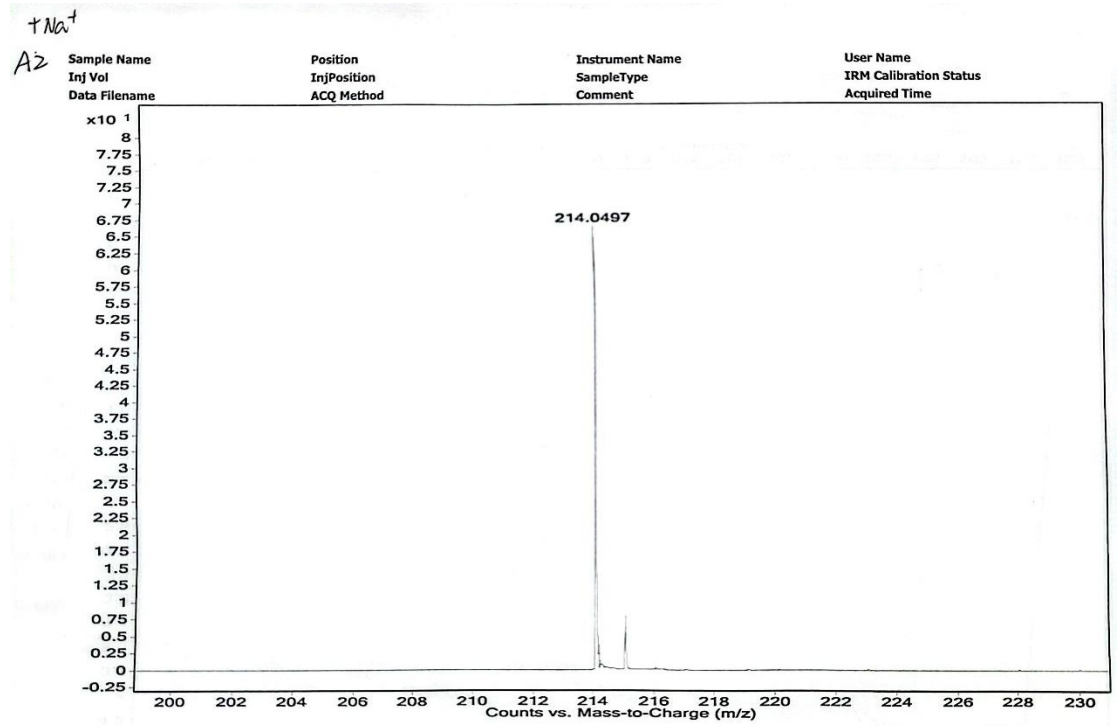


Figure S32. TOF-HRMS (ESI) spectra of compound **1b**.

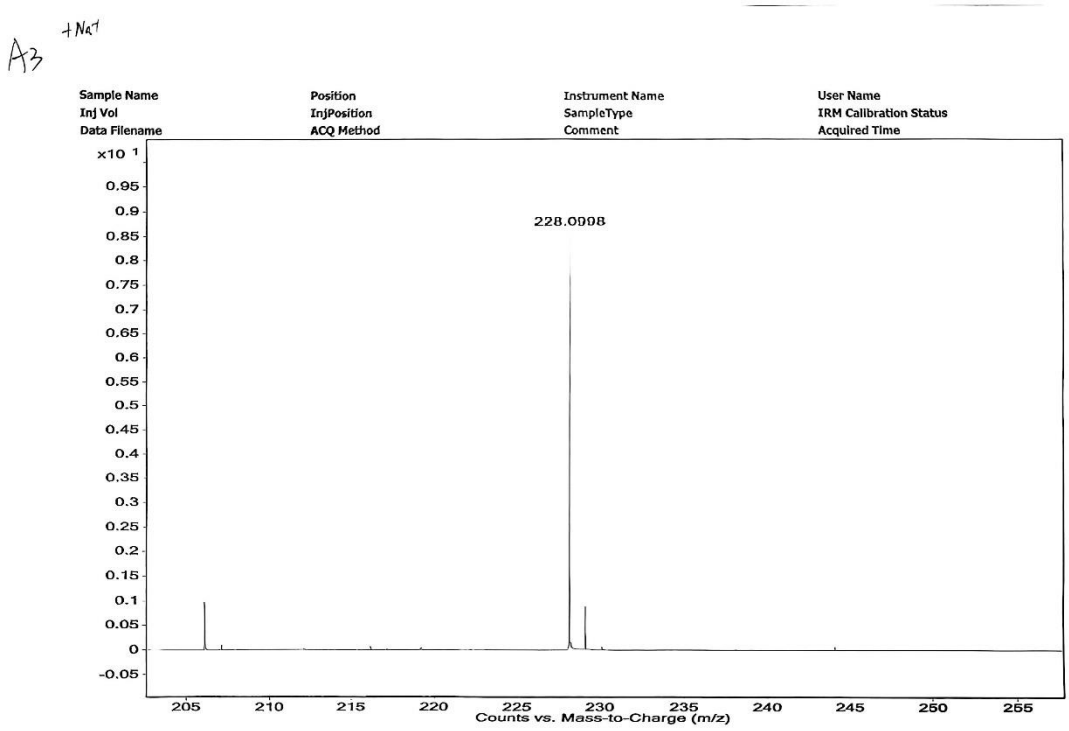


Figure S33. TOF-HRMS (ESI) spectra of compound **1c**.

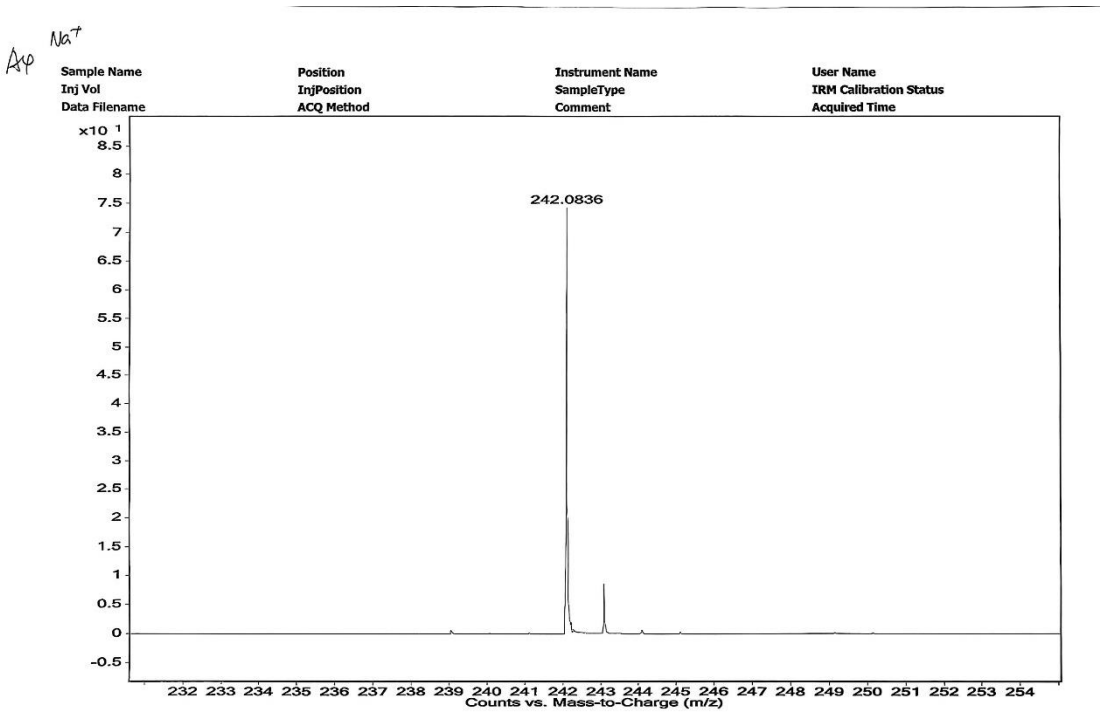


Figure S34. TOF-HRMS (ESI) spectra of compound **1d**.

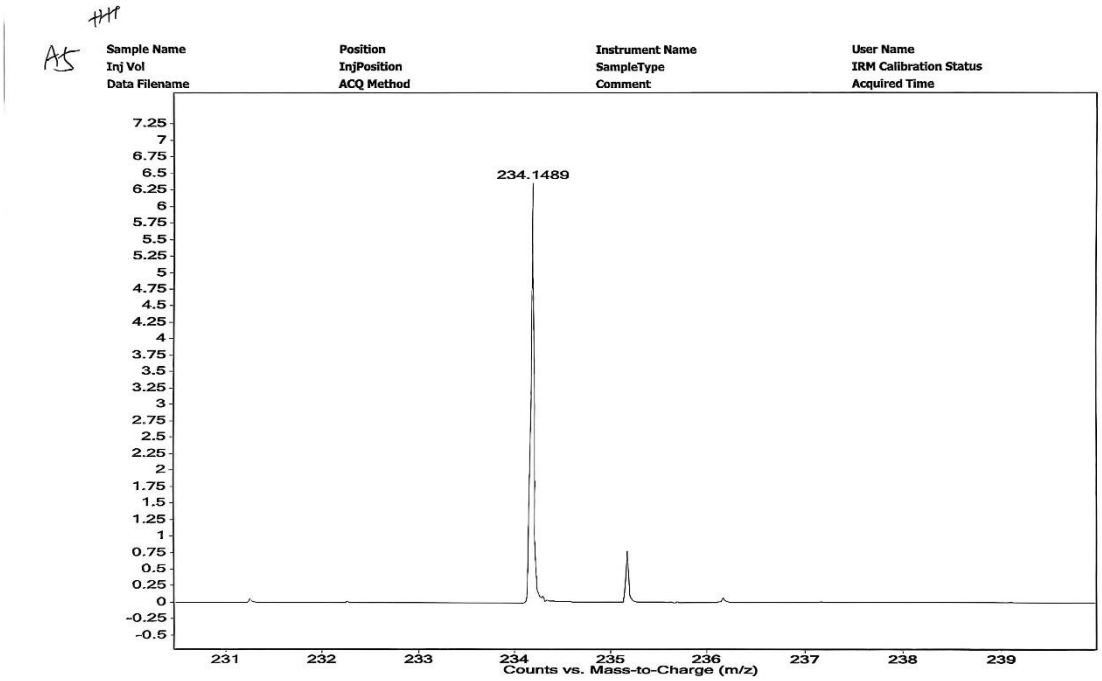


Figure S35. TOF-HRMS (ESI) spectra of compound **1e**.

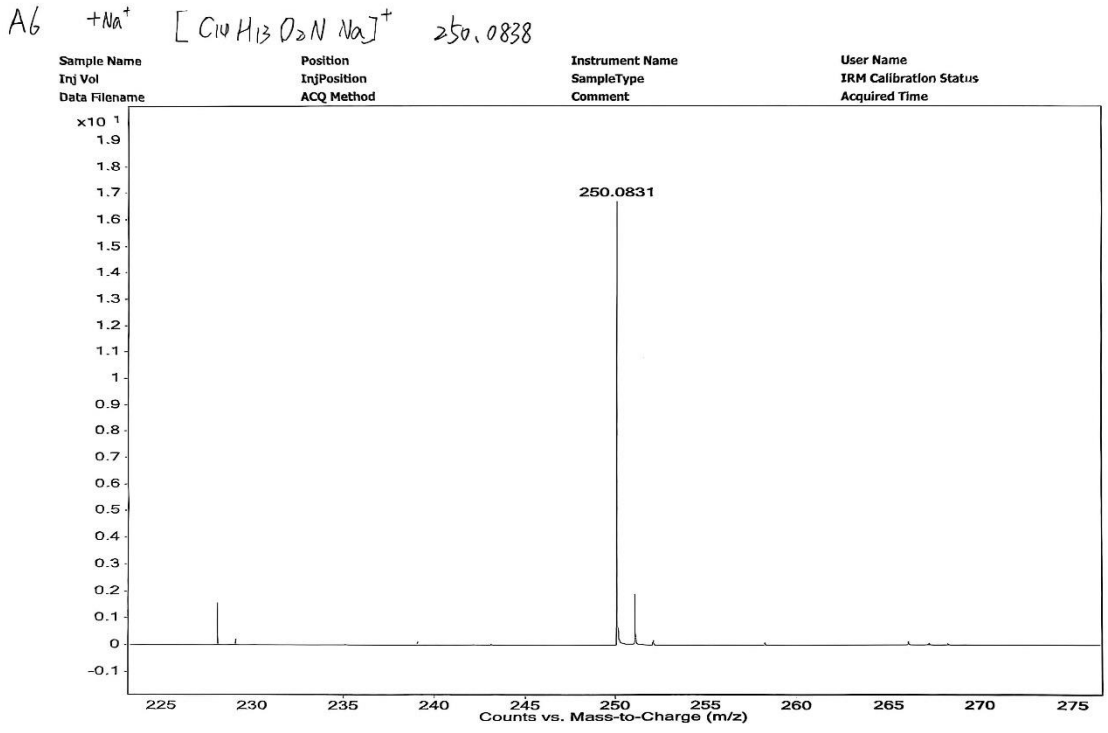


Figure S36. TOF-HRMS (ESI) spectra of compound **1f**.

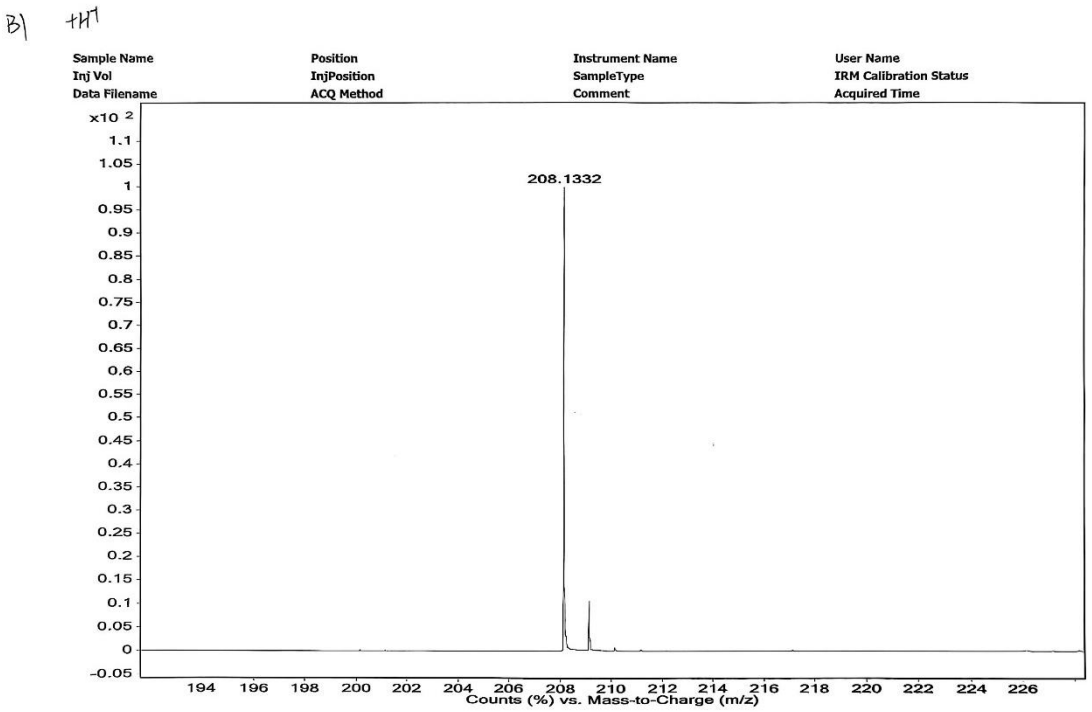


Figure S37. TOF-HRMS (ESI) spectra of compound **2a**.

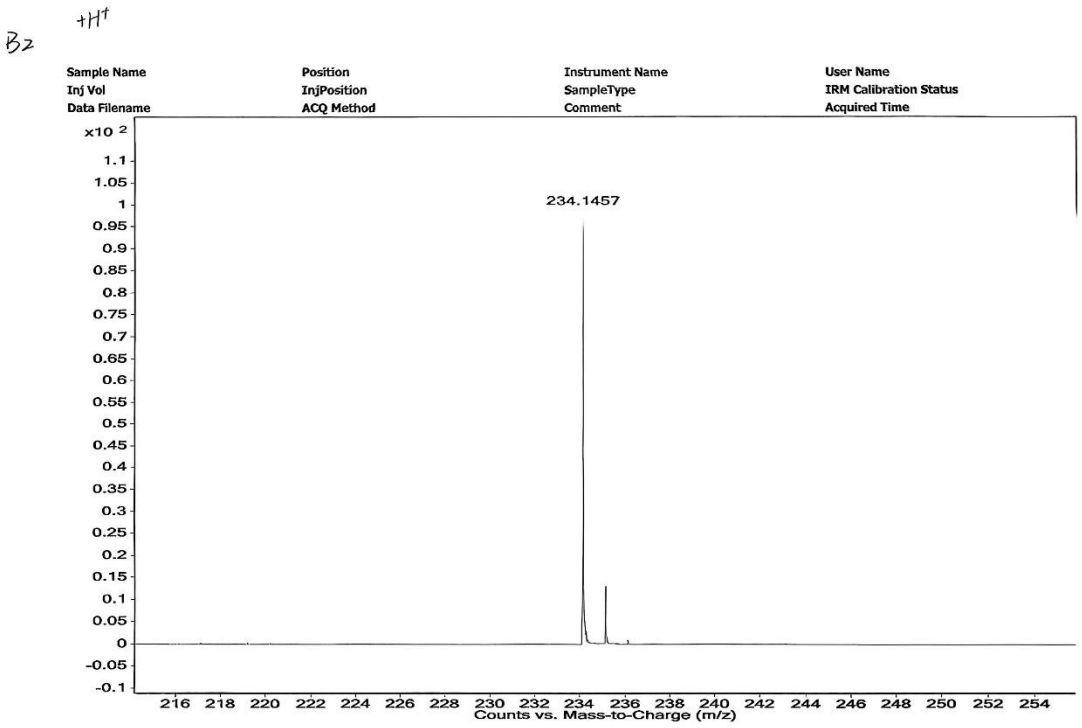


Figure S38. TOF-HRMS (ESI) spectra of compound **2b**.

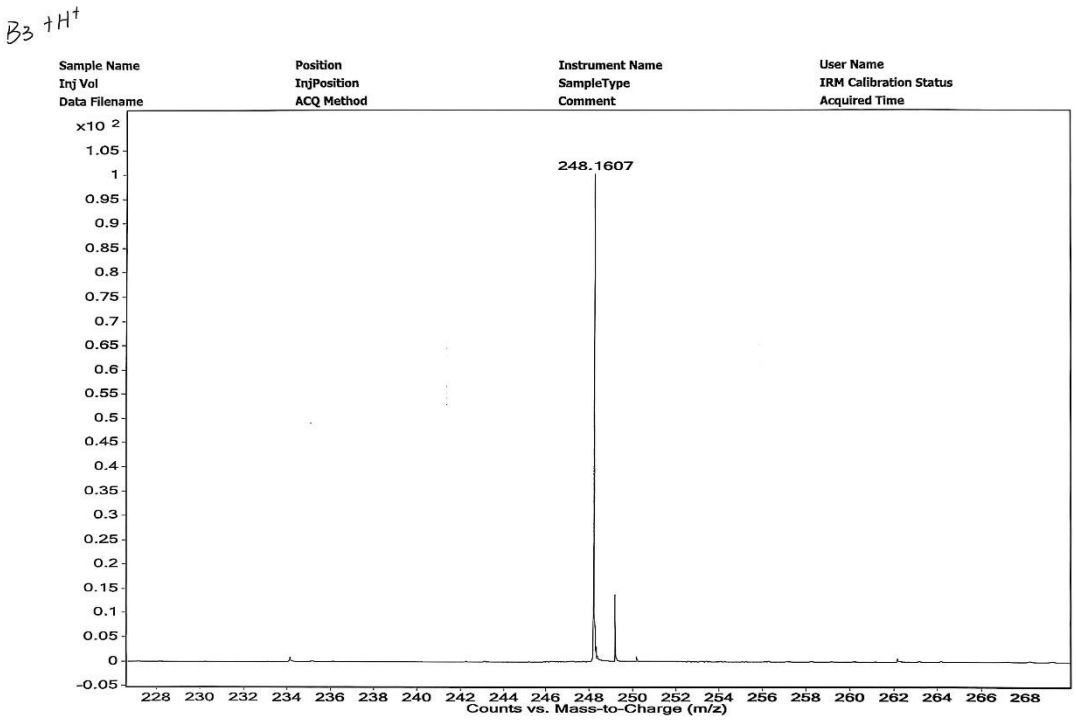


Figure S39. TOF-HRMS (ESI) spectra of compound **2c**.

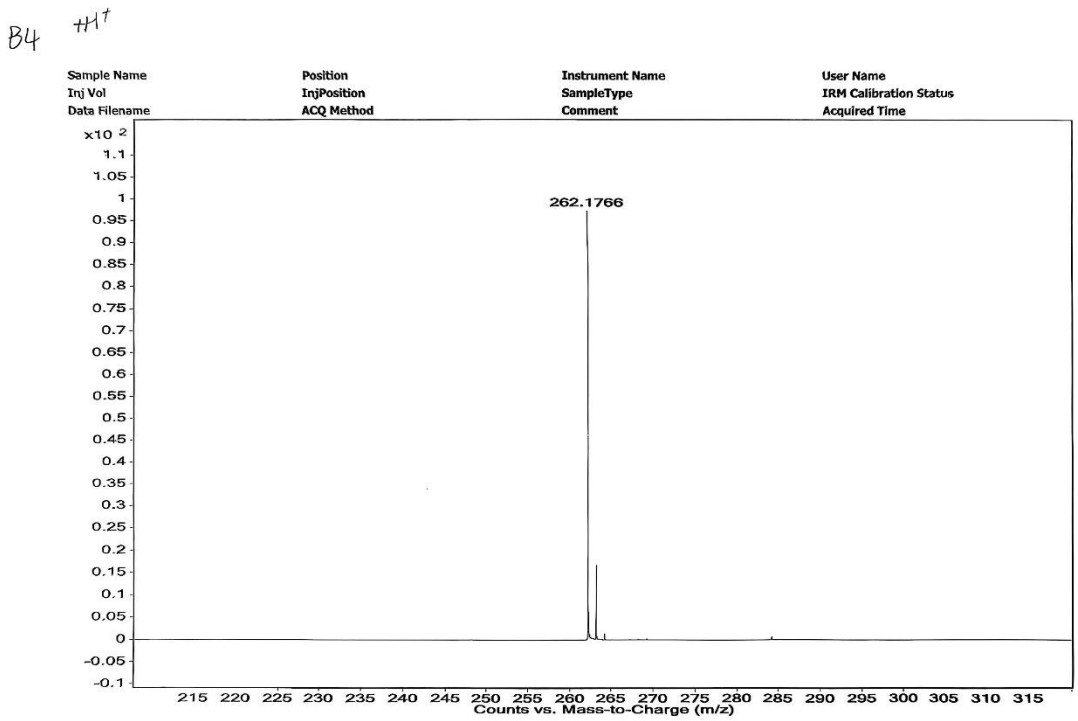


Figure S40. TOF-HRMS (ESI) spectra of compound **2d**.

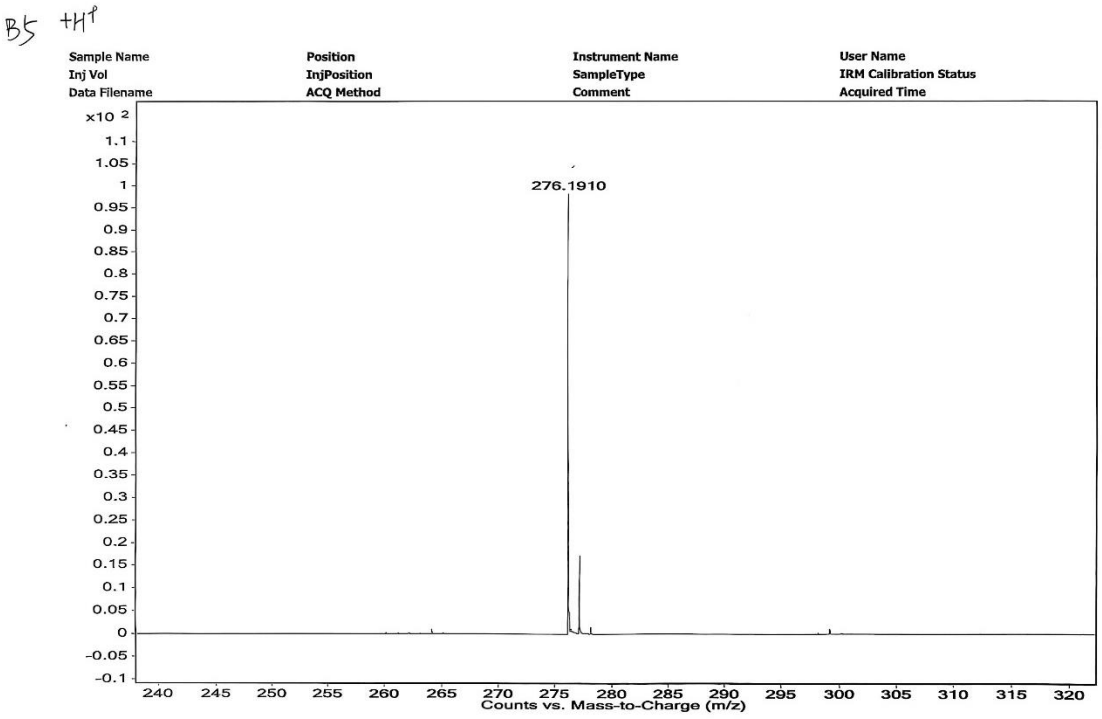


Figure S41. TOF-HRMS (ESI) spectra of compound **2e**.

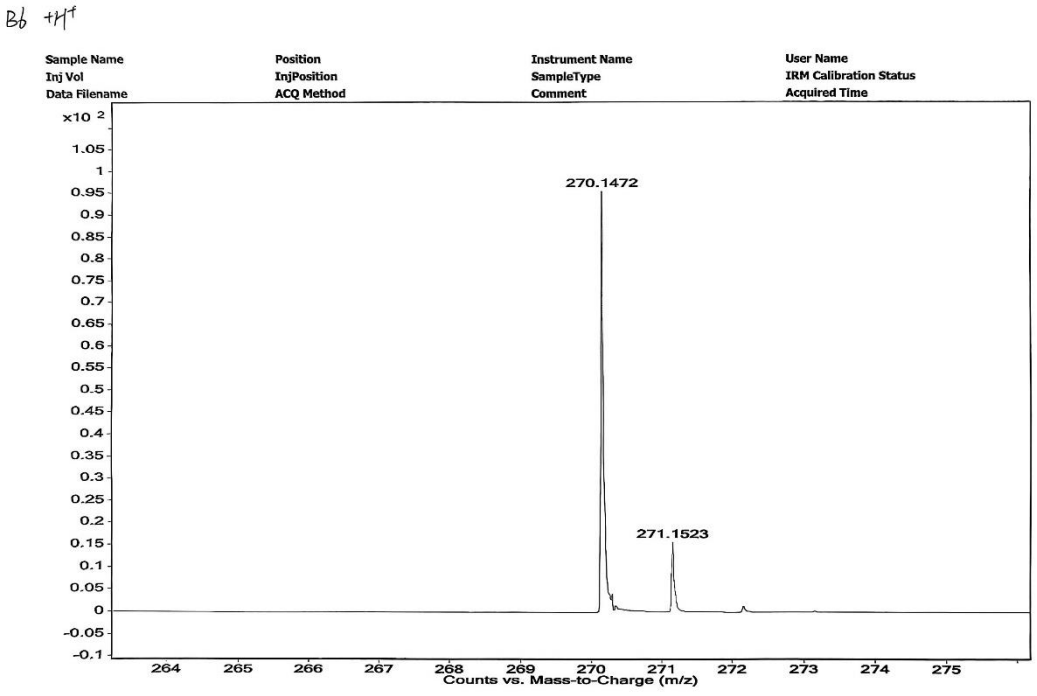


Figure S42. TOF-HRMS (ESI) spectra of compound **2f**.

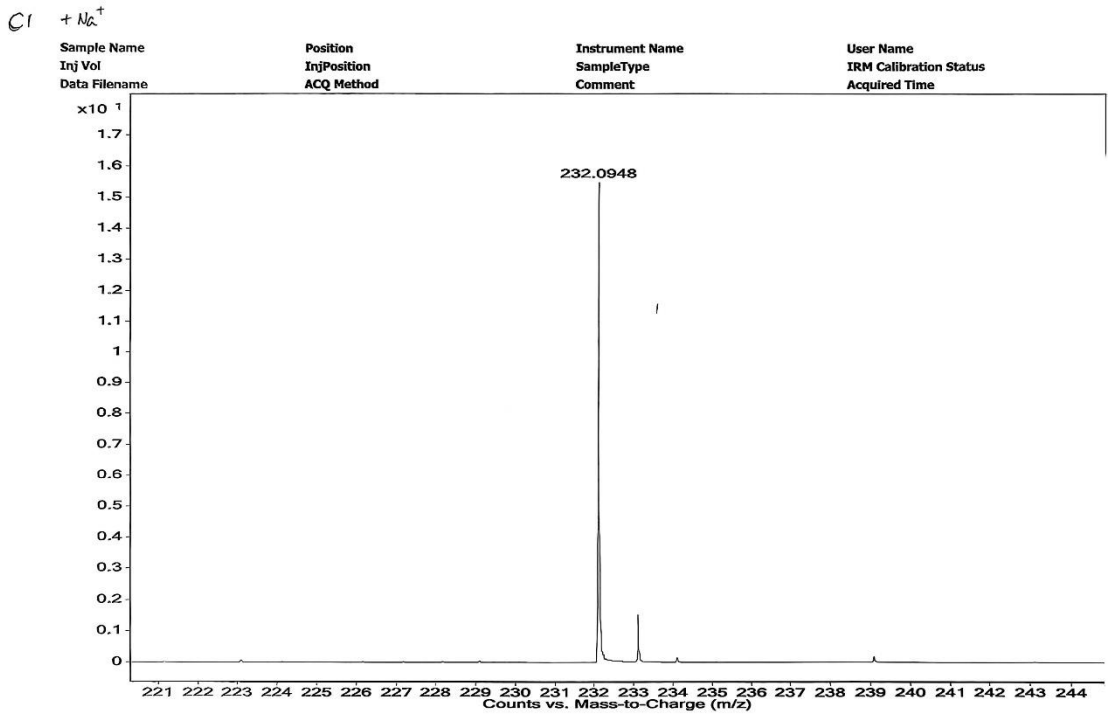


Figure S43. TOF-HRMS (ESI) spectra of compound **3a**.

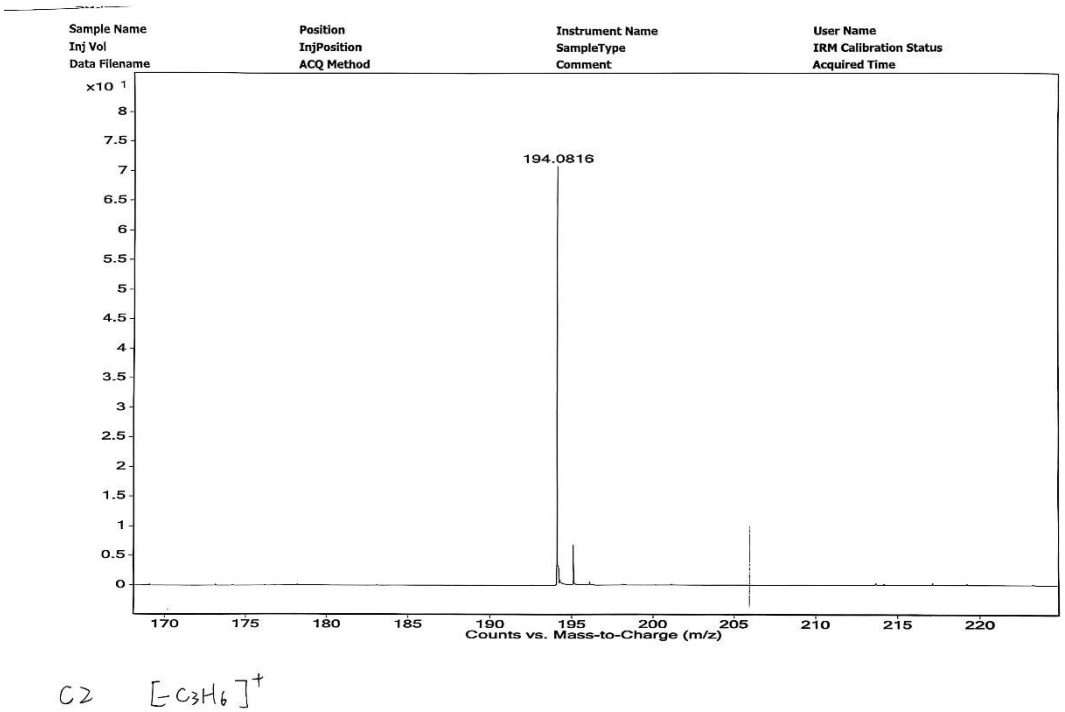


Figure S44. TOF-HRMS (ESI) spectra of compound **3b**.

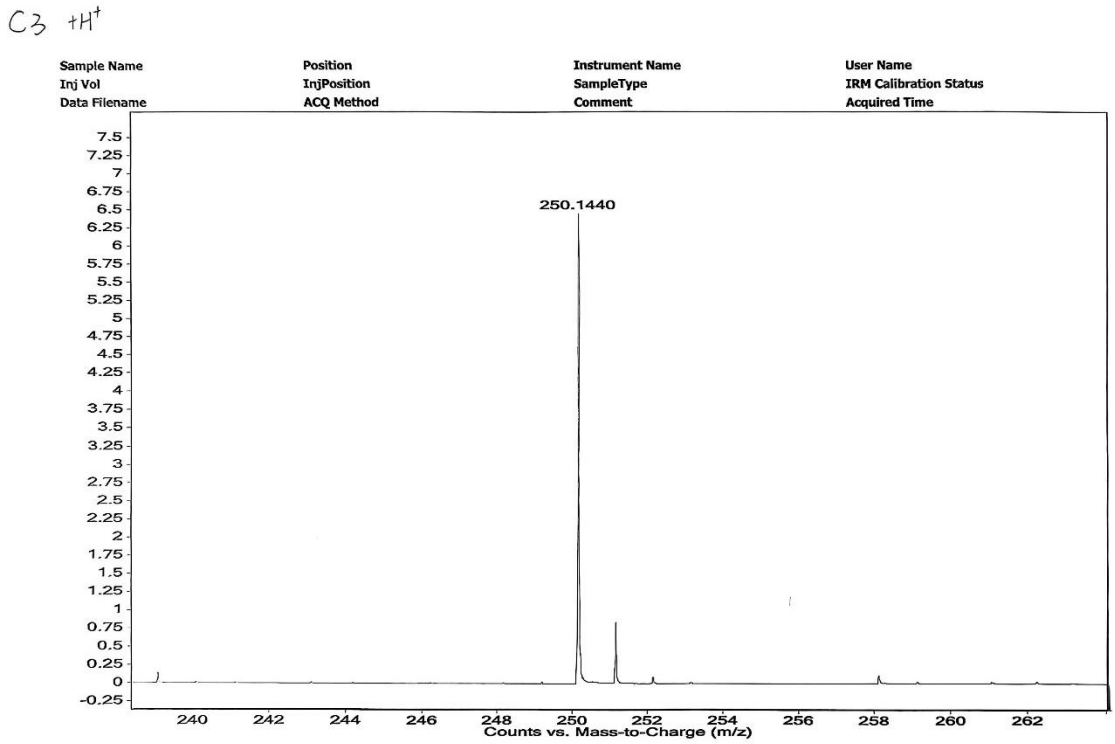


Figure S45. TOF-HRMS (ESI) spectra of compound **3c**.

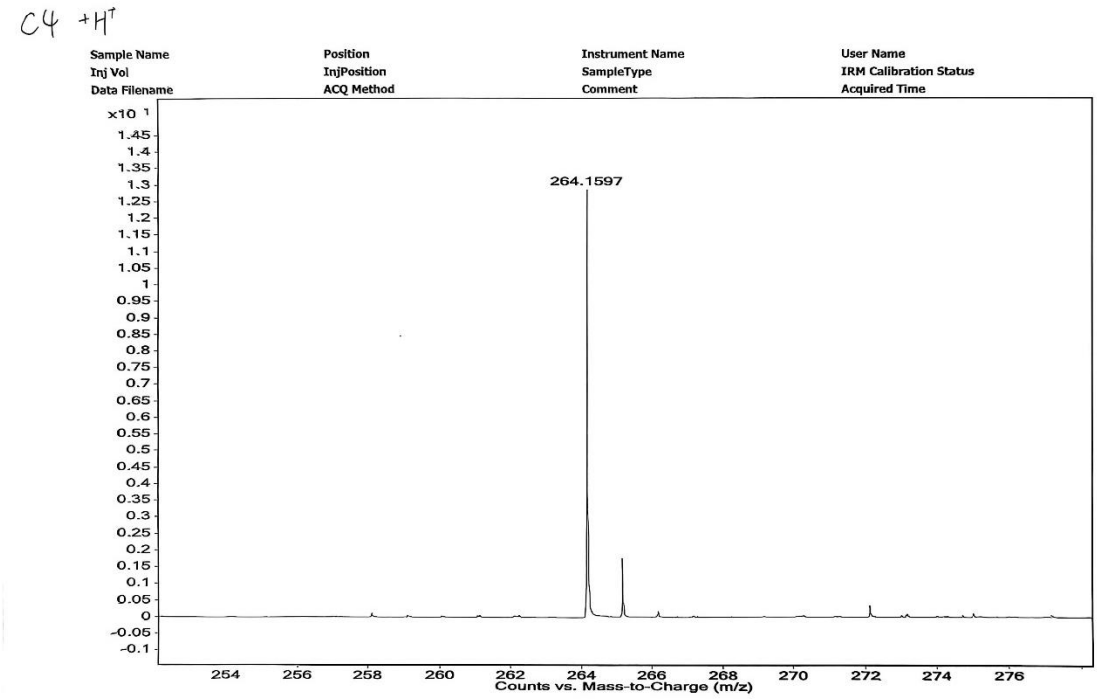


Figure S46. TOF-HRMS (ESI) spectra of compound **3d**.

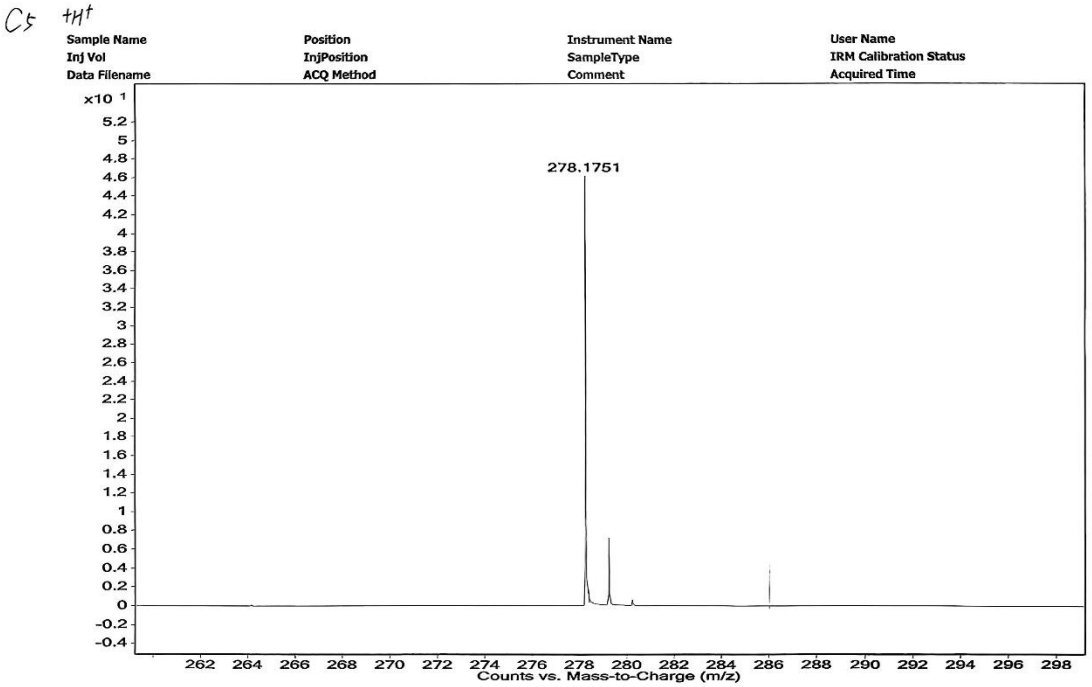


Figure S47. TOF-HRMS (ESI) spectra of compound **3e.**

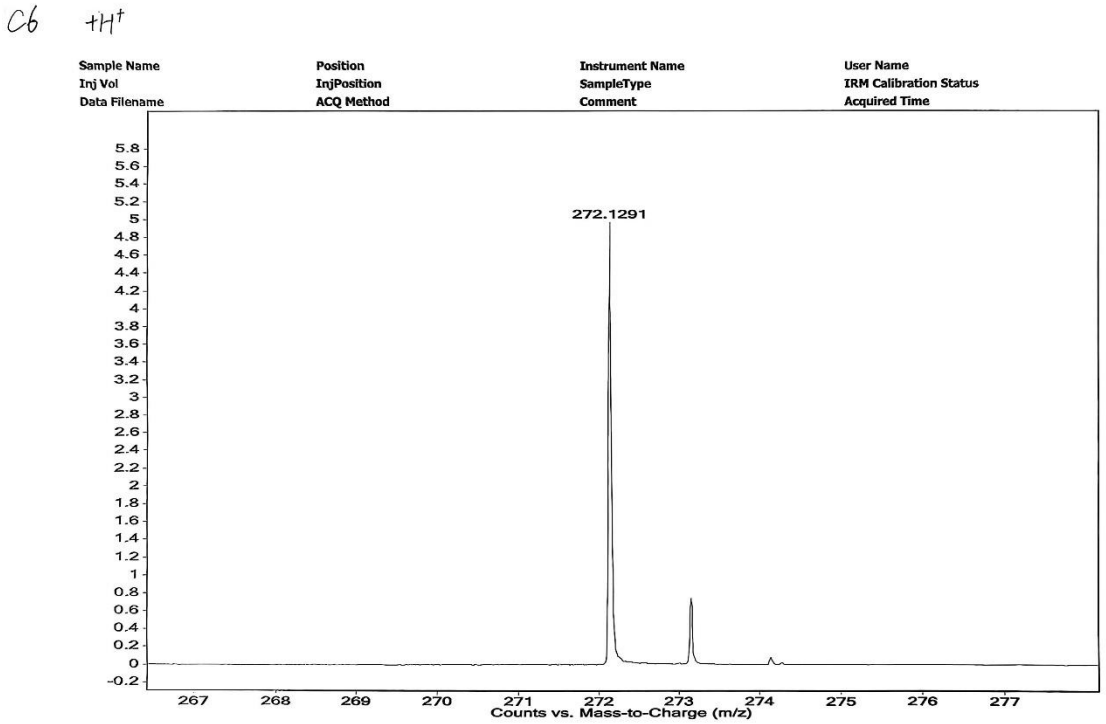


Figure S48. TOF-HRMS (ESI) spectra of compound **3f**.

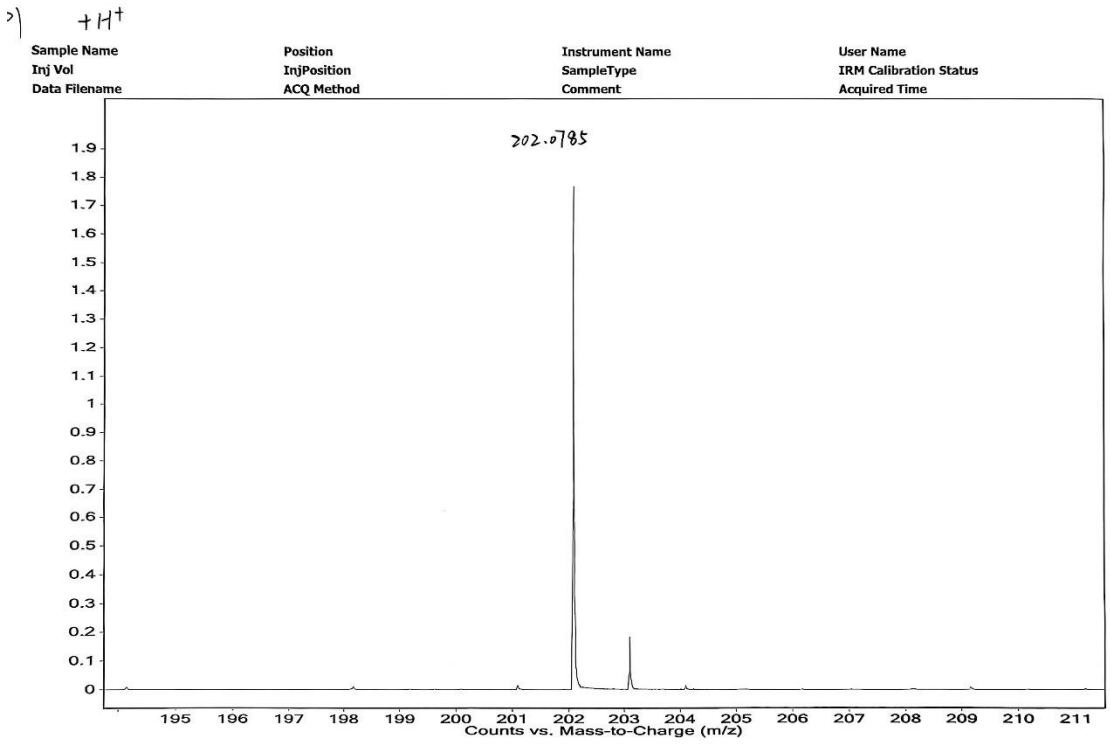


Figure S49. TOF-HRMS (ESI) spectra of compound **4a**.

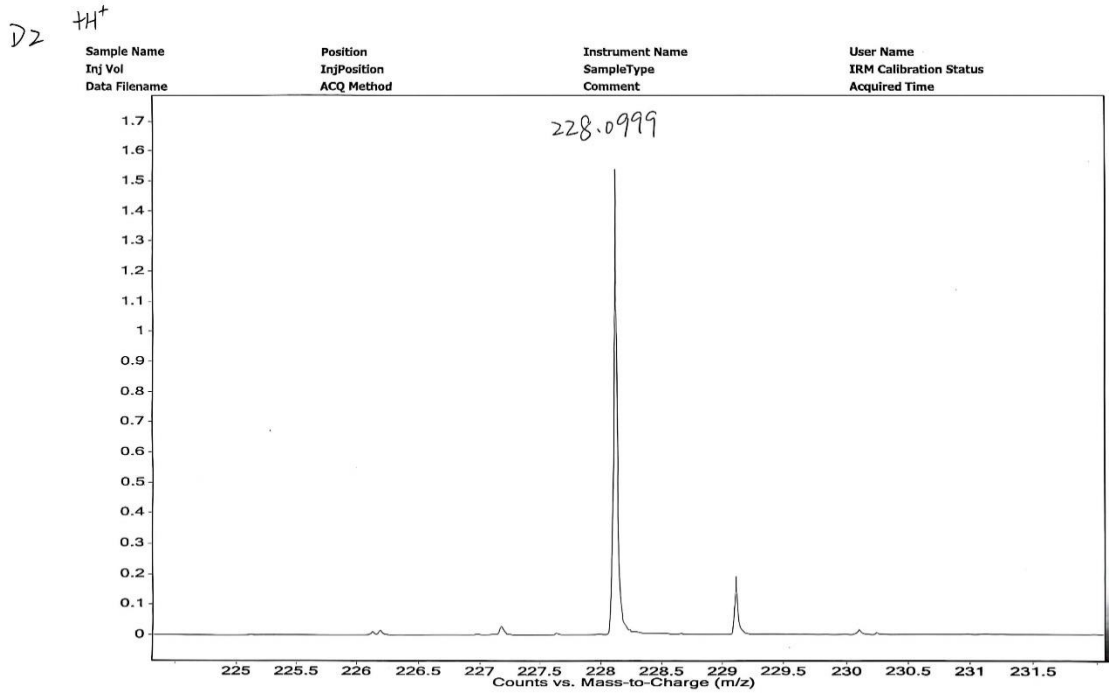


Figure S50. TOF-HRMS (ESI) spectra of compound **4b**.

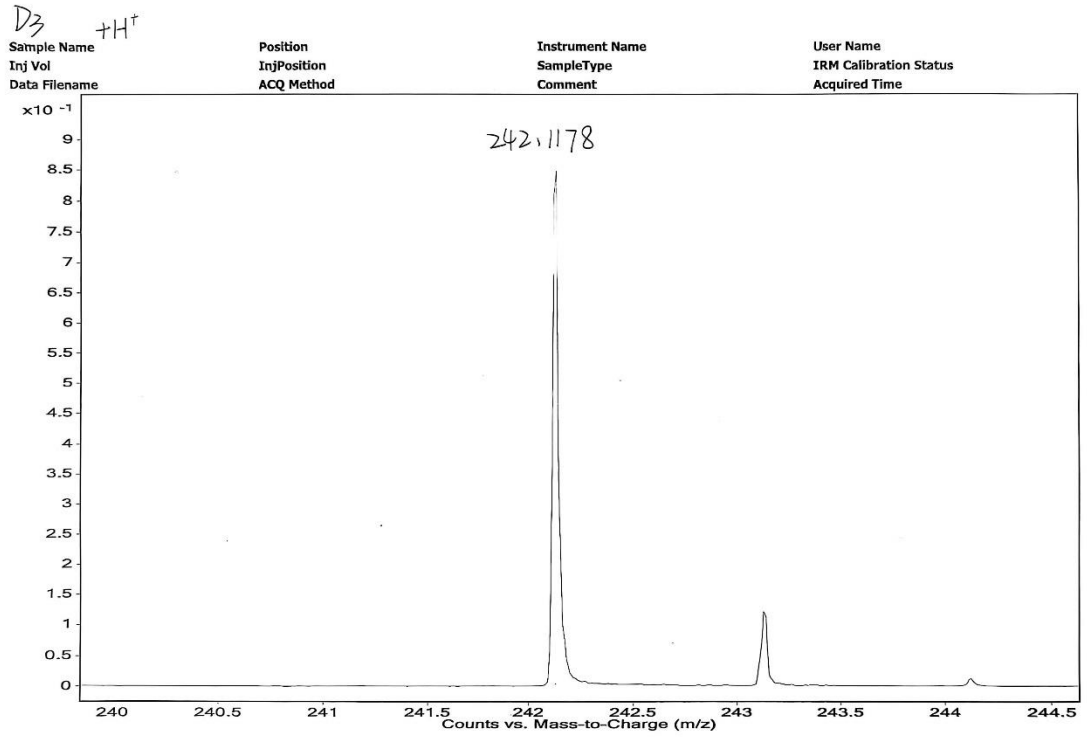


Figure S51. TOF-HRMS (ESI) spectra of compound **4c**.

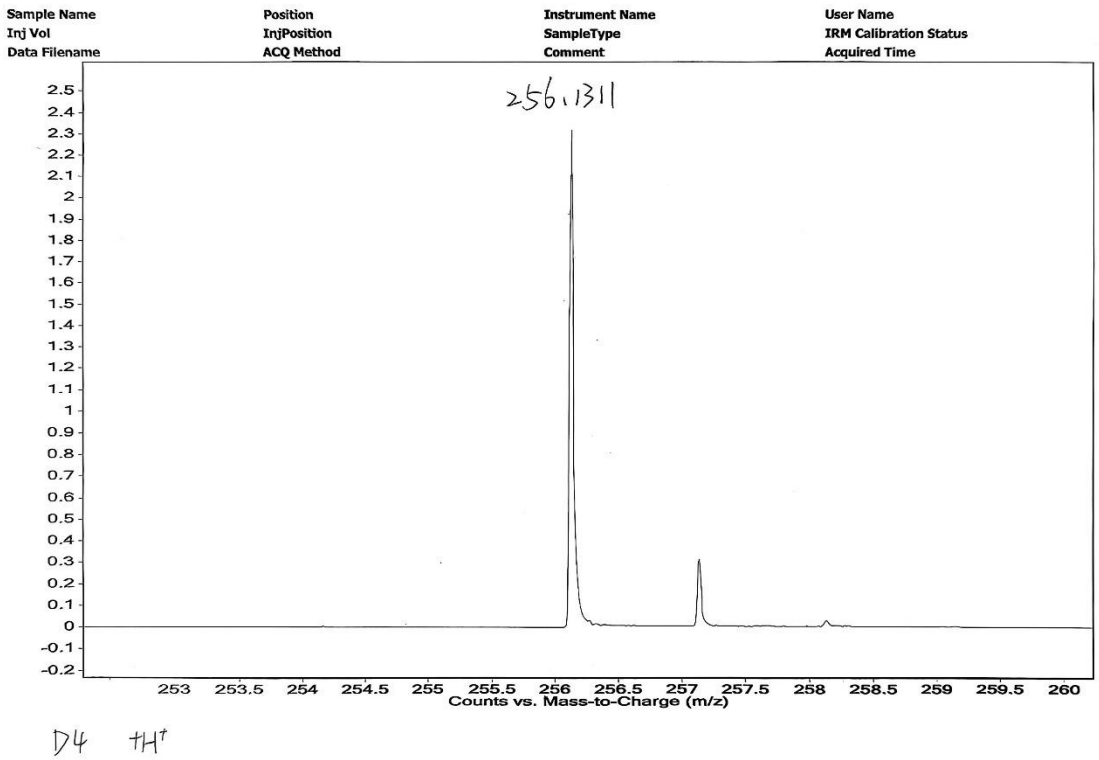


Figure S52. TOF-HRMS (ESI) spectra of compound **4d**.

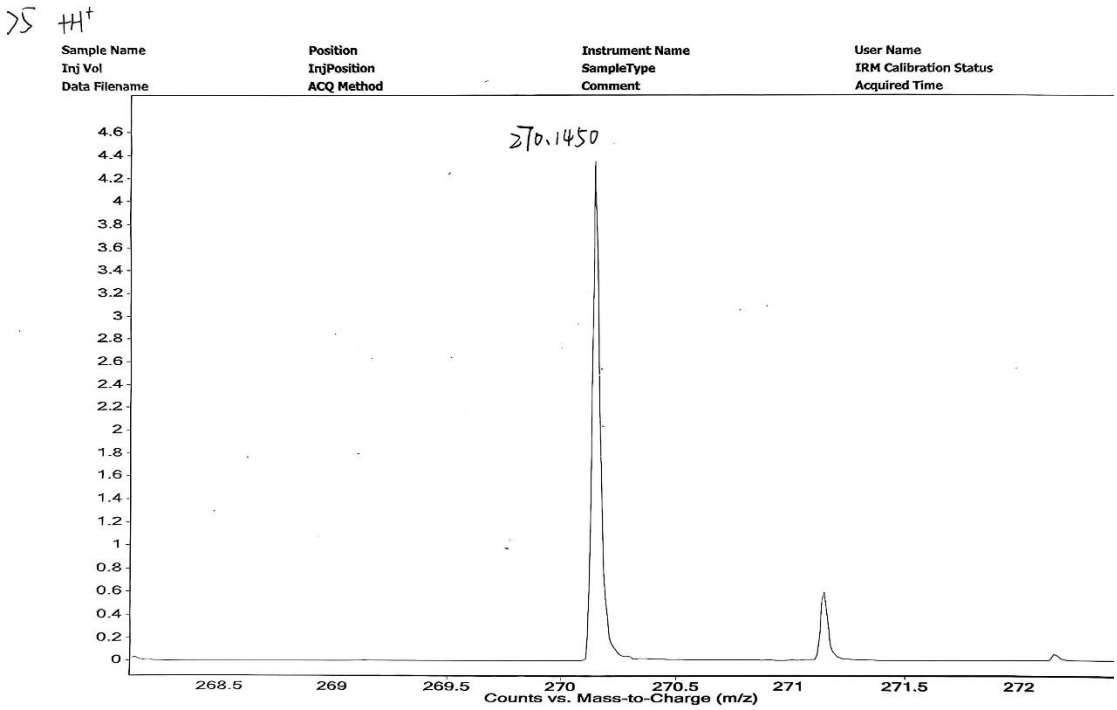


Figure S53. TOF-HRMS (ESI) spectra of compound **4e**.

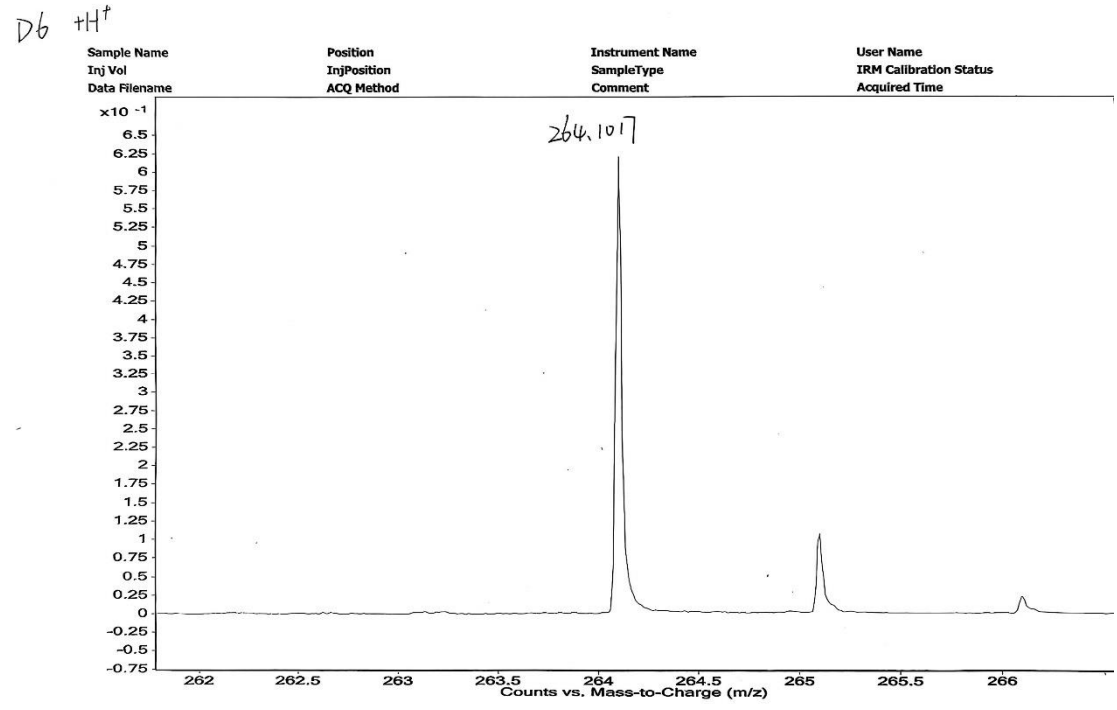


Figure S54. TOF-HRMS (ESI) spectra of compound **4f**.

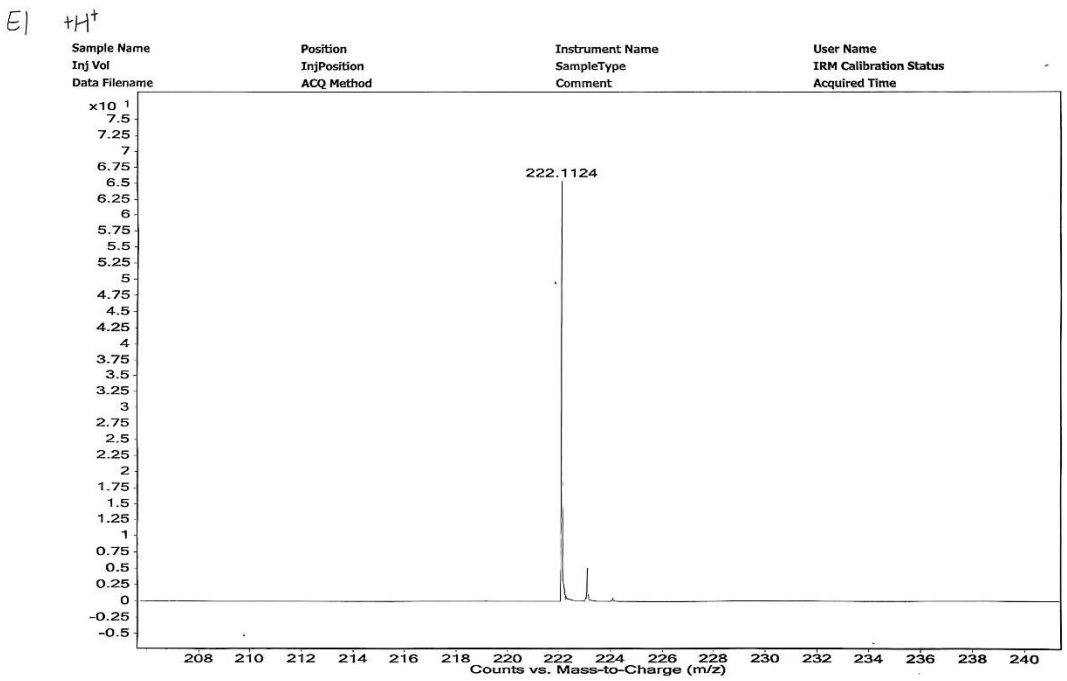


Figure S55. TOF-HRMS (ESI) spectra of compound **5a**.

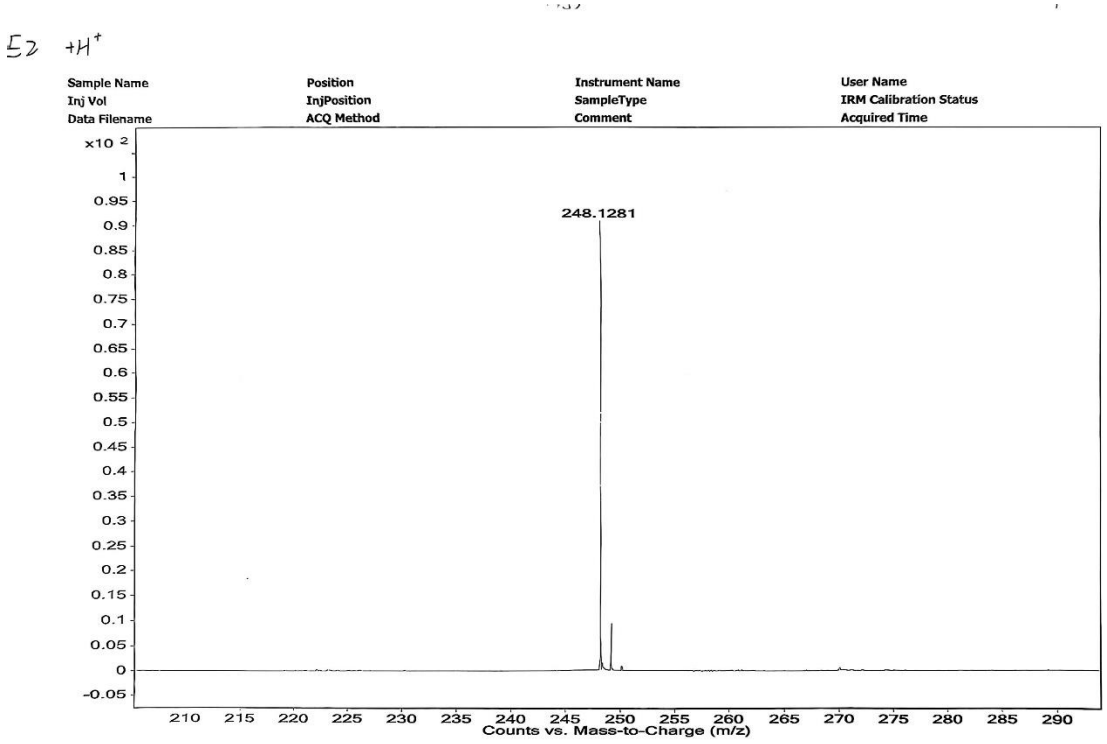


Figure S56. TOF-HRMS (ESI) spectra of compound **5b.**

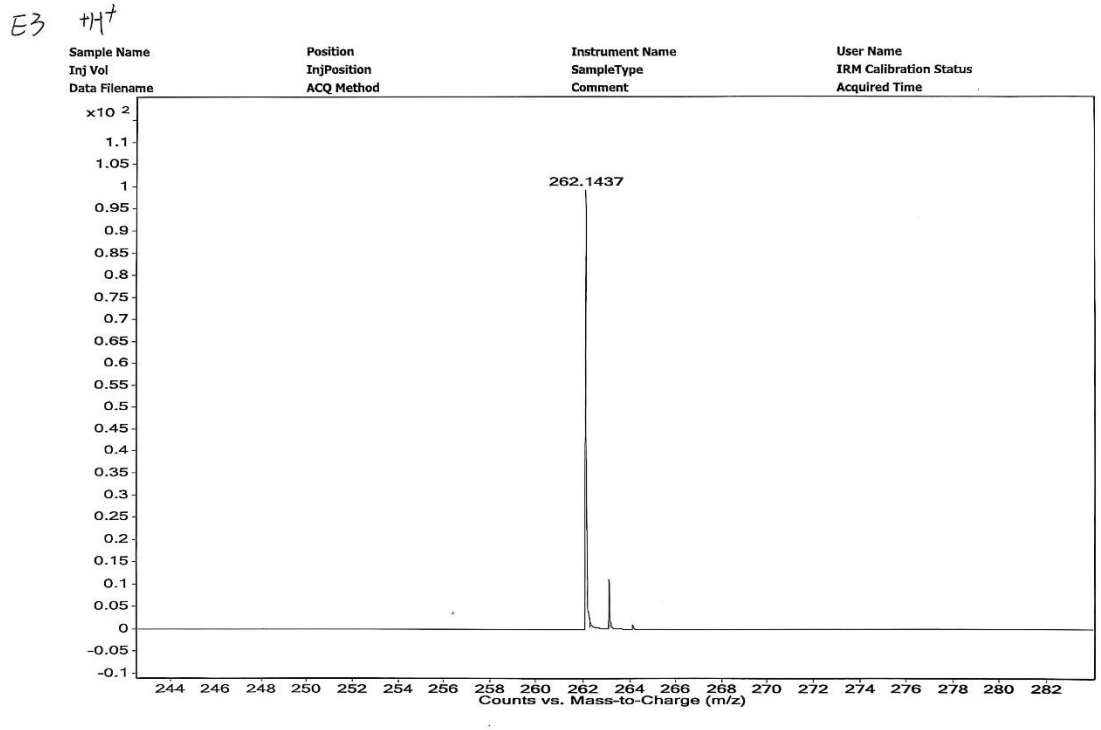


Figure S57. TOF-HRMS (ESI) spectra of compound **5c**.

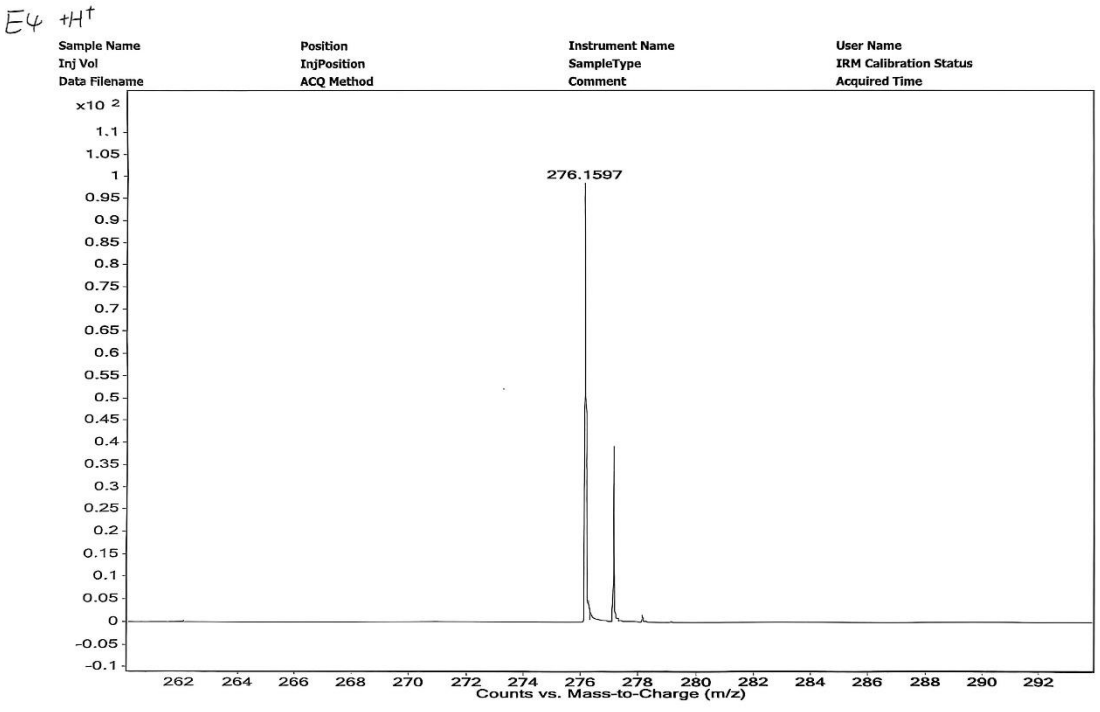


Figure S58. TOF-HRMS (ESI) spectra of compound **5d**.

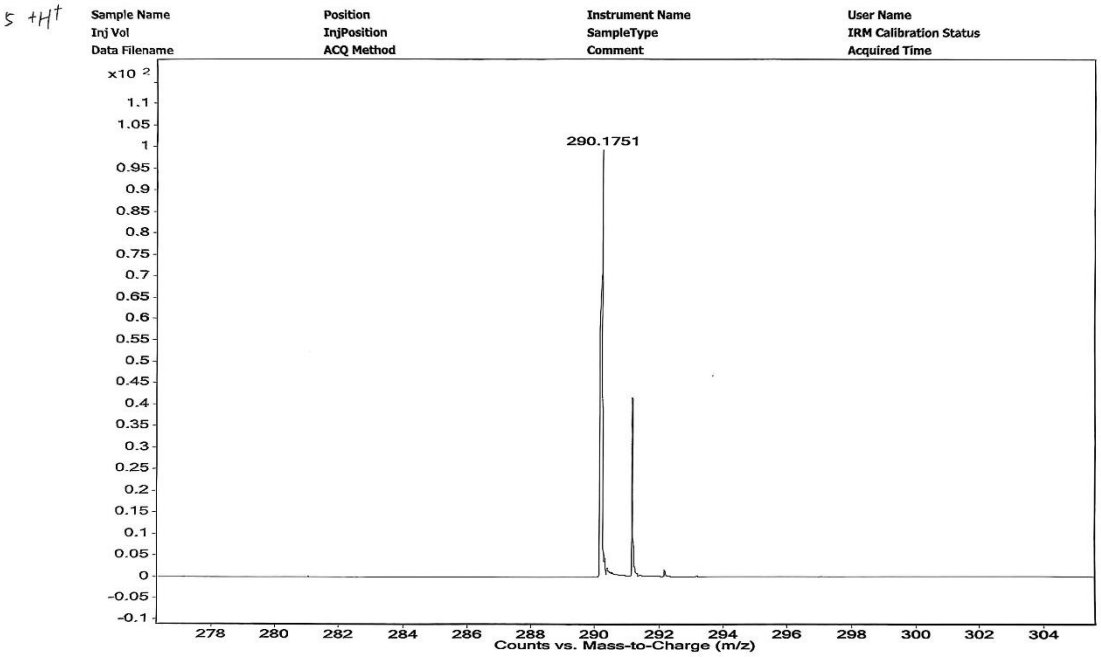


Figure S59. TOF-HRMS (ESI) spectra of compound **5e**.

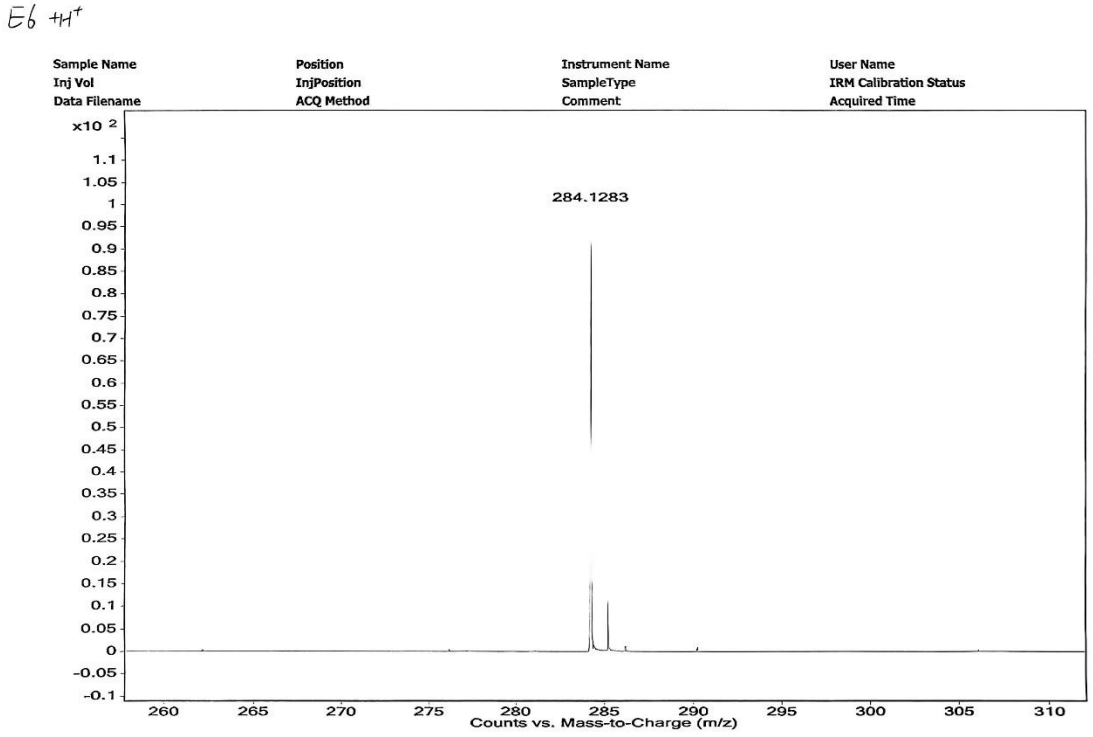


Figure S60. TOF-HRMS (ESI) spectra of compound **5f**.