Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Carbon Atom Insertion into *N*-heterocyclic Carbenes to Yield 3,4-Dihydroquinoxalin-2(1*H*)-ones

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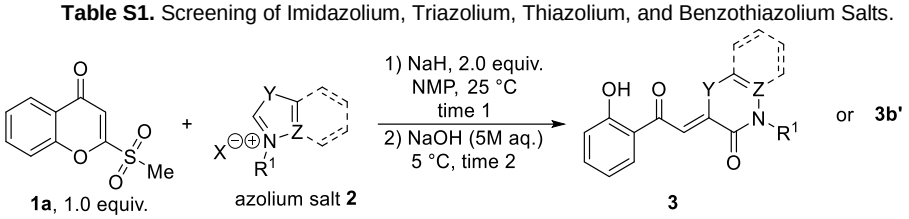
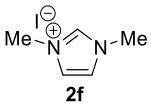
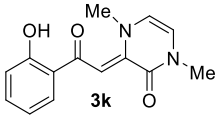
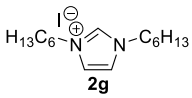
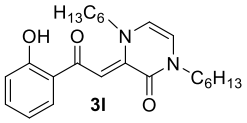
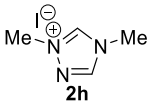
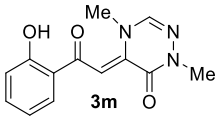
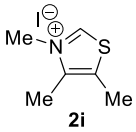
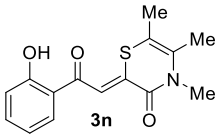
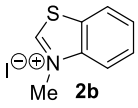
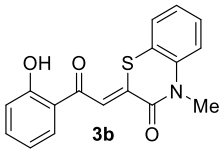
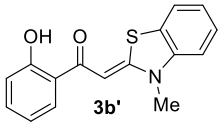
Table S1. Screening of Imidazolium, Triazolium, Thiazolium, and Benzothiazolium Salts.

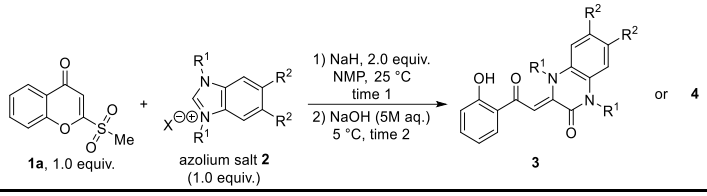


1a, 1.0 equiv. azolium salt **2** (1.0 equiv.) Y = N-R^2 or S, Z = C or N. **3**

Entry	Azolium Salt **2**	Time 1 (h)	Time 2 (h)	Desired Product	Obtained Product	Yield of Obtained Product (%)
1[a]	 **2f**	21	48	 **3k**	complex mixture	-
2[a]	 **2g**	21	48	 **3l**	complex mixture	-
3[a]	 **2h**	24	26	 **3m**	complex mixture	-
4[a,b]	 **2i**	24	26	 **3n**	complex mixture	-
5[c]	 **2b**	24	48	 **3b**	 **3b'**	28

[a]For convenience, only one of the expected product isomers is shown. [b]Et_3N (2.0 equiv.) instead of NaH in step 1 [c]step 2 conditions: H_2O, Et_3N (2 equiv.), 5 °C

Table S2. Screening of Benzimidazolium Salts



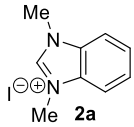
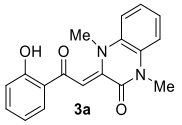
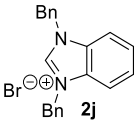
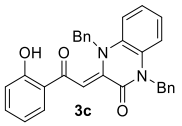
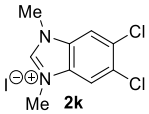
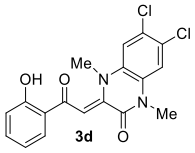
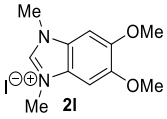
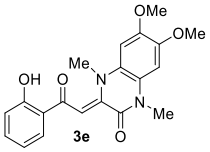
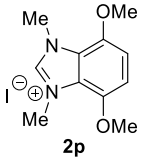
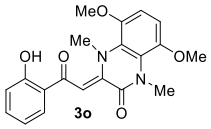
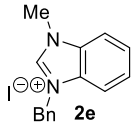
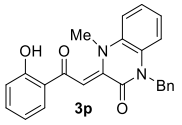
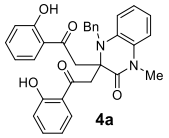
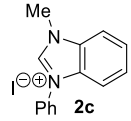
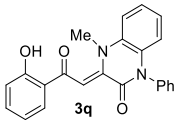
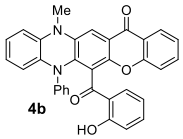
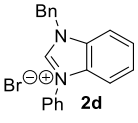
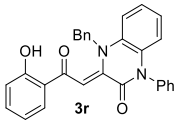
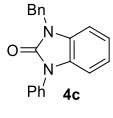
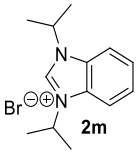
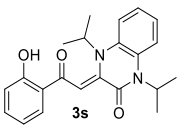
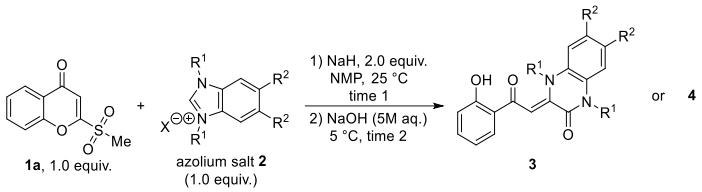
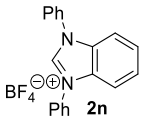
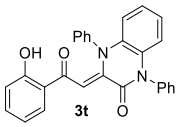
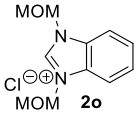
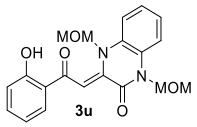
Entry	Azolium Salt **2**	Time 1 (h)	Time 2 (h)	Desired Product	Obtained Product	Yield of Obtained Product (%)
1	 **2a**	24	48	 **3a**	**3a**	99
2	 **2j**	25	72	 **3c**	**3c**	54
3[a]	 **2k**	18	48	 **3d**	**3d**	81
4	 **2l**	12	10	 **3e**	**3e**	78
5	 **2p**	21	41	 **3o**	complex mixture	-
6	 **2e**	18	24	 **3p**	 **4a**	25
7	 **2c**	21	72	 **3q**	 **4b**	94
8	 **2d**	20	72	 **3r**	 **4c**	55
9[b]	 **2m**	18	24	 **3s**	complex mixture	-

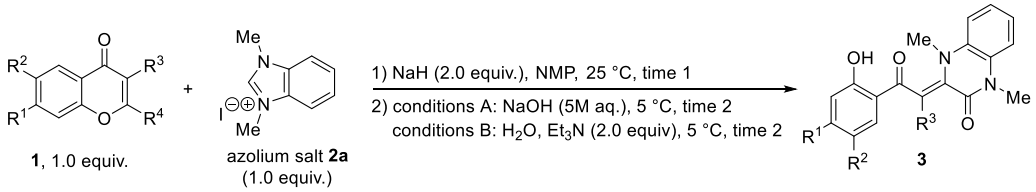
Table S2 (Continued). Screening of Benzimidazolium Salts



Entry	Azolium Salt **2**	Time 1 (h)	Time 2 (h)	Desired Product	Obtained Product	Yield of Obtained Product (%)
10[b]	 **2n**	20	72	 **3t**	complex mixture	-
11[b]	 **2o**	18	24	 **3u**	complex mixture	-

. [a]Conditions for step 2: H_2O, Et_3N (2.0 equiv.), 5 °C [b]For convenience, only one of the expected product isomers is shown.

Table S3. Screening of Chromones.



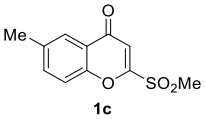
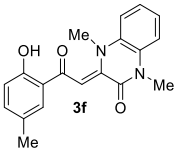
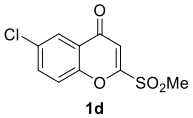
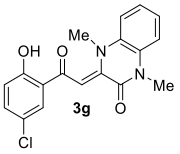
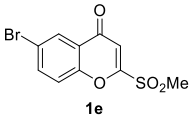
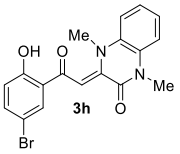
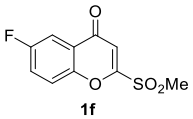
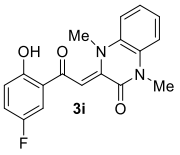
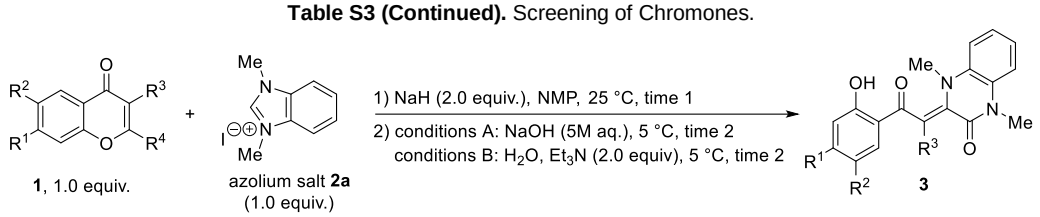
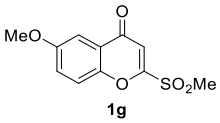
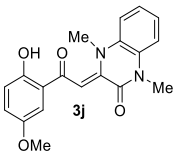
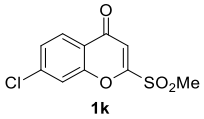
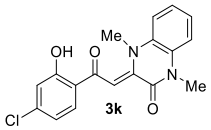
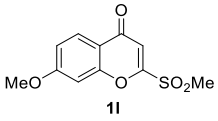
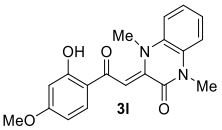
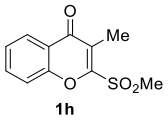
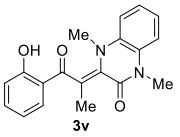
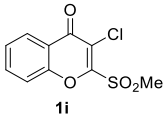
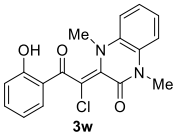
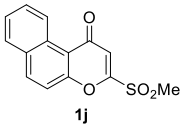
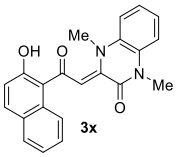
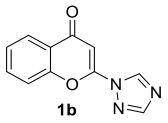
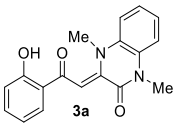
Entry	Chromone **1**	Conditions	Time 1 (h)	Time 2 (h)	Desired Product	Yield of Desired Product (%)
1	 **1c**	A	24	26	 **3f**	45
2	 **1d**	A and B	conditions A: 18 conditions B: 18	conditions A: 40 conditions B: 24	 **3g**	conditions A: 42 conditions B: 57
3	 **1e**	A and B	conditions A: 18 conditions B: 28	conditions A: 18 conditions B: 80	 **3h**	conditions A: 18 conditions B: 80
4	 **1f**	B	18	10	 **3i**	46

Table S3 (Continued). Screening of Chromones.

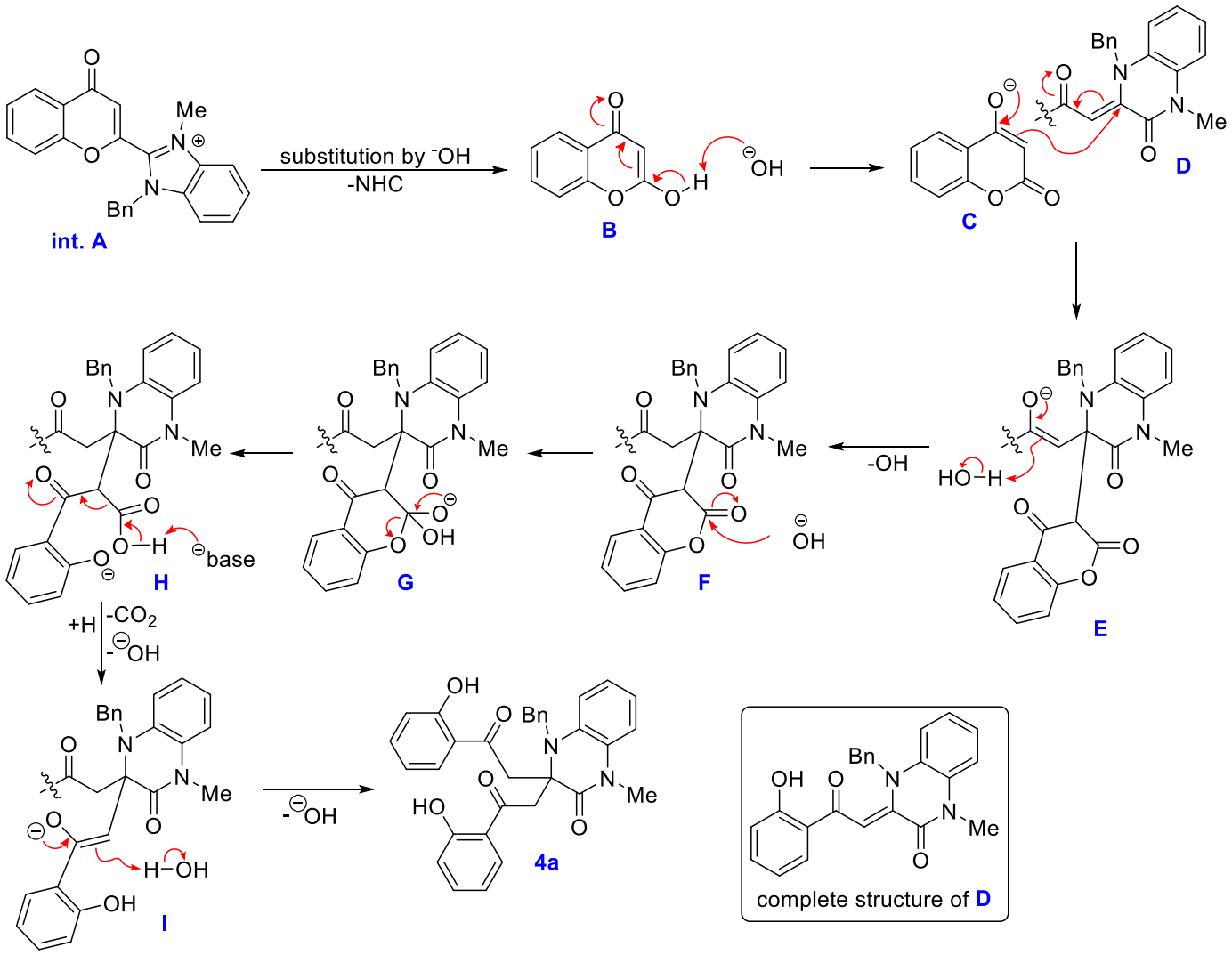


1, 1.0 equiv. + azolium salt **2a** (1.0 equiv.) → **3**

Entry	Chromone **1**	Conditions	Time 1 (h)	Time 2 (h)	Desired Product	Yield of Desired Product (%)
5	 **1g**	A	18	72	 **3j**	73
6	 **1k**	B	24	24	 **3k**	74
7	 **1l**	A	24	24	 **3l**	85
9[a]	 **1h**	A	18	72	 **3v**	- (complex mixture)
10[a]	 **1i**	B	21	24	 **3w**	- (complex mixture)
11	 **1j**	B	24	24	 **3x**	- (complex mixture)
12	 **1b**	A	18	24	 **3a**	18

[a]For convenience, only one of the expected product isomers is shown.

2. Possible Mechanism for the Formation of 4a



Scheme S1. Possible Mechanism for the Synthesis of **4a**

Compound **4a** could potentially be synthesized through the mechanism shown above. Intermediate **int. A** could be attacked by a hydroxide anion to form **B**. Based on thin-layer chromatography analysis, no starting methylsulfonyl chromone remained by the time the NaOH solution was added, thus it is unlikely **B** would originate from the starting methylsulfonyl chromone. Deprotonation of **B** would lead to the enolate **C** which would attack one molecule of the quinoxalinone product **D** to form **E**. The enolate of **E** would be protonated with water to form **F** which could be attacked by another hydroxide anion at the lactone moiety to form **G**. The formation of a carboxylic acid group then leads to the generation of intermediate **H**, which is quickly deprotonated to form **I** through the loss of CO_2. Protonation of **I** affords the observed quinoxalinone **4a**.

3. Experimental Procedures

3.1 General Information

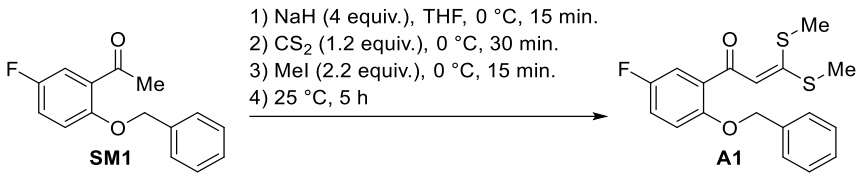
Reagents and solvents were purchased from commercial sources and were used as is. All solvents were of the dehydrated or super dehydrated form. All reactions were performed under argon and stirring. Column chromatography was performed using spherical silica gel (63–219 μm) (Kanto Chemicals). Medium-pressure liquid chromatography was performed using a Yamazen EPC LC W-Prep 2XY system equipped with a Yamazen Ultra Pack B silica column or a Yamazen Hi-Flash silica column. Recycling size-exclusion chromatography was conducted using a Japan Analytical Industry (JAI) recycling preparative high-performance liquid chromatography (HPLC) LC-918 system equipped with JAIGEL-1HR and JAIGEL-2HR columns using chloroform as the solvent. Merck thin-layer chromatography (TLC) plates (silica gel 60G F254 0.25 mm) were used. TLC plates were visualized by fluorescence under a UV lamp (254 or 365 nm). ^{1}H NMR was recorded on a JEOL JNM-ECX (500 MHz) or a Bruker Ascend 400 (400 MHz) spectrometer. Chemical shifts were recorded in parts per million (ppm, δ), relative to tetramethylsilane (δ 0.00). ^{1}H NMR splitting patterns are reported as singlet (s), doublet (d), triplet (t), dd (doublet of doublets), dt (doublet of triplets), m (multiplet), etc. ^{13}C NMR spectra were recorded on a JEOL JNM-ECX (125 MHz) spectrometer or a Bruker Ascend 400 (100 MHz) spectrometer. Mass spectra were recorded using a TOF (ESI) analyzer or a magnetic sector (FAB) analyzer. Melting points were measured using an ATM-02, AS ONE melting point apparatus and were uncorrected.

3.2 Synthetic Procedures

3.2.1 General Note on the Synthesis of Propenones and Synthetic Procedure for Propenone A1

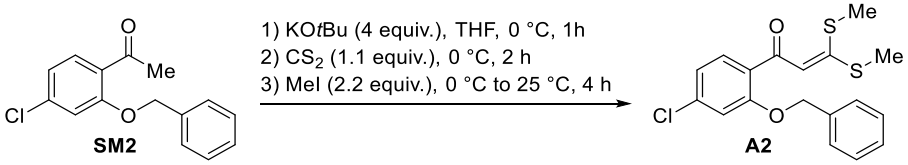
1-(2-Benzyloxyphenyl)-3,3-bis(methylthio)propenones were synthesized according to the procedure reported by Pratap and coworkers.[1] It should be noted that, for the synthesis of the propenones, the reported reaction times of 5-6 hours should be strictly kept. Longer reaction times (i.e. overnight) lead to a sticky oil being formed which is difficult to purify.

Synthesis of 1-[2-(benzyloxy)-5-fluorophenyl]-3,3-bis(methylthio)prop-2-en-1-one (A1)



2-(Benzyloxy)-5-fluoroacetophenone[2] (**SM1**, 3.67 g, 15 mmol) was added dropwise to a dispersion of NaH (2.40 g, 4 equiv., 60% dispersion in paraffin liquid) in THF (50 mL) at 0 °C under argon. The resulting mixture was stirred for 15 minutes at 0 °C. Next, carbon disulfide (1.10 mL, 1.2 equiv.) was added dropwise and the mixture was stirred for 30 minutes at 0 °C. Methyl iodide (2.06 mL, 2.2 equiv.) was then added dropwise followed by stirring at 0 °C for 15 minutes. The mixture was warmed to 25 °C and stirred for 5 h at that temperature. Volatiles were then removed under reduced pressure. Ice-cold water was then slowly added to quench residual NaH. The mixture was vacuum filtered and the obtained solid was further washed with cold water. The solid was then washed with *n*-hexane to afford **A1** in 89% yield (4.64 g). Analytically pure **A1** was obtained through recrystallization from a mixture of CH_2Cl_2 and *n*-hexane which afforded **A1** as yellow columnar crystals.
R*f* (9:1 *n*-hexane/EtOAc): 0.36
Melting point: 159-160 °C (from CH_2Cl_2/*n*-hexane)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (dd, J = 9.2, 3.3 Hz, 1H), 7.46 – 7.30 (m, 5H), 7.12–7.05 (m, 1H), 6.97 (dd, J = 9.0, 4.2 Hz, 1H), 6.92 (s, 1H), 5.05 (s, 2H), 2.48 (s, 3H), 1.93 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 183.9 (d, $J_{C\text{-}F}$ = 1.7 Hz)., 165.7, 157.5 (d, $J_{C\text{-}F}$ = 240.5 Hz), 153.1 (d, $J_{C\text{-}F}$ = 1.8 Hz), 136.3, 131.2 (d, $J_{C\text{-}F}$ = 6.2 Hz), 128.8, 128.6, 128.3, 118.9 (d, $J_{C\text{-}F}$ = 23.3 Hz), 117.9 (d, $J_{C\text{-}F}$ = 23.3 Hz)., 114.6 (d, $J_{C\text{-}F}$ = 7.5 Hz)., 114.5, 71.9, 16.6, 15.3.
HRMS (FAB): *m/z*: $[M+H]^+$ calculated for $C_{18}H_{18}FO_2S_2^+$: 349.0727, found 349.0726

Synthesis of 1-[2-(benzyloxy)-4-chlorophenyl]-3,3-bis(methylthio)prop-2-en-1-one (A2)

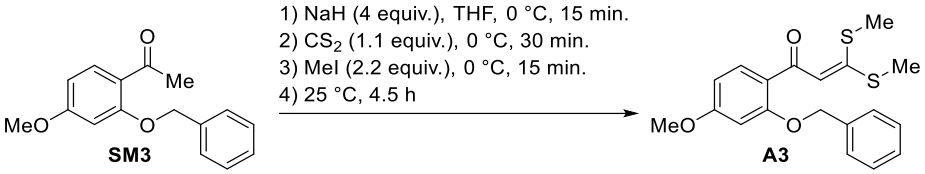


A solution of 2-(benzyloxy)-4-chloroacetophenone (**SM2**, 3.00 g, 11.5 mmol) in dry THF (10 mL) was added dropwise to a dispersion of KO*t*Bu (5.20 g, 4 equiv.) in THF (35 mL) at 0 °C under argon. The resulting mixture was stirred for 1 h at 0 °C. Carbon disulfide (770 μL, 1.1 equiv.) was added dropwise and the mixture was stirred for 2 h at 0 °C. Methyl iodide (1.58 mL, 2.2 equiv.) was then added dropwise followed by stirring at 0 °C for 15 minutes. The mixture was warmed to 25 °C and stirred for 4 h at that temperature. The mixture was then filtered (with thorough washing of the insoluble components with CH_2Cl_2), and the filtrate was concentrated under reduced pressure to afford **A2** as a red-orange solid in 44% yield (1.85 g), which was used in the next step without further purification. Analytically pure **A2** was obtained by recrystallization using the vapor diffusion method (chloroform and *n*-hexane as the solvents) to afford **A2** as an orange solid. *Note: when this reaction was conducted using NaH instead of KOtBu, a black tar containing a complex mixture of products was obtained rather than the desired product.*

R*f* (9:1 *n*-hexane/EtOAc): 0.85
Melting Point: 134-135 °C (from chloroform/*n*-hexane)

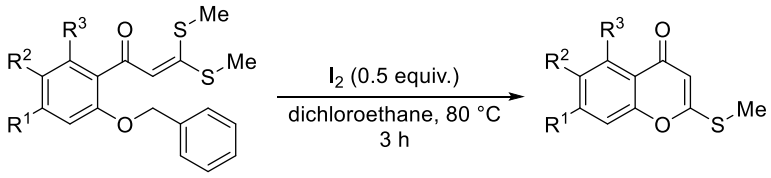
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86-7.81 (m, 1H), 7.47 – 7.31 (m, 5H), 7.06-7.01 (m, 2H), 6.87 (s, 1H), 5.08 (s, 2H), 2.47 (s, 3H), 1.87 (s, 3H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 184.1, 165.0, 157.3, 138.2, 135.7, 132.8, 128.8, 128.6, 128.3, 128.1, 121.6, 114.7, 113.3, 71.3, 16.4, 15.2.
HRMS (FAB): *m/z*: $[M+H]^+$ calculated for $C_{18}H_{18}{}^{35}ClO_2S_2^+$: 365.0431, found 365.0435

Synthesis of 1-[2-(benzyloxy)-4-methoxyphenyl]-3,3-bis(methylthio)prop-2-en-1-one (A3)



A solution of 2-(benzyloxy)-4-methoxyacetophenone (**SM3**, 6.84 g, 26.7 mmol) in dry THF (20 mL) was added dropwise to a dispersion of NaH (4.27 g, 4 equiv., 60% dispersion in paraffin liquid) in THF (75 mL) at 0 °C under argon. The resulting mixture was stirred for 15 minutes at 0 °C. Carbon disulfide (1.78 mL, 1.1 equiv.) was added dropwise and the mixture was stirred for 30 minutes at 0 °C. Methyl iodide (3.66 mL, 2.2 equiv.) was then added dropwise followed by stirring at 0 °C for 15 minutes. The mixture was warmed to 25 °C and stirred for 4.5 h at that temperature. Volatiles were then removed under reduced pressure. Ice-cold water was then slowly added to quench residual NaH. The mixture was vacuum filtered and the obtained solid was further washed with cold water. The solid was then washed with *n*-hexane to afford **A3** in 94% yield (9.00 g). Analytically pure **A3** was obtained through recrystallization using the vapor diffusion method ($CHCl_3$ and *n*-hexane as the solvents) which afforded **A3** as yellow columnar crystals.
R*f* (8:2 *n*-hexane/EtOAc): 0.32
Melting Point: 131-132 °C
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, J = 8.7 Hz, 1H), 7.46-7.41 (m, 2H), 7.40-7.31 (m, 3H), 6.96 (s, 1H), 6.58 (dd, J = 8.7, 2.3 Hz, 1H), 6.54 (d, J = 2.3 Hz, 1H), 5.05 (s, 2H), 3.83 (s, 3H), 2.44 (s, 3H), 1.81 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 184.4, 163.7, 163.1, 158.7, 136.2, 133.7, 128.8, 128.6, 128.6, 122.7, 115.4, 105.8, 99.7, 71.1, 55.6, 16.5, 15.3.
HRMS (FAB): *m/z*: $[M+H]^+$ calculated for $C_{19}H_{21}O_3S_2^+$: 361.0927, found 361.0922

3.2.2 Synthetic Procedure for 2-(Methylthio)chromones

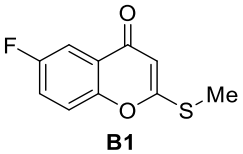


Chromones were synthesized based on the procedure reported by Pratap and coworkers.[1]

General procedure A (synthesis of chromones):

The corresponding propenone (1 equiv.) was added to a flask containing I_2 (0.5 equiv.). A reflux condenser was then attached, and the flask was then purged with argon. Dichloroethane was then added, and the mixture was stirred at 80 °C for 3 h. The reaction mixture was transferred to a separatory funnel and washed with a 5% aqueous solution of $Na_2S_2O_3$. The aqueous layer was washed with CH_2Cl_2 three times. The combined organic layers were washed with brine and dried over anhydrous Na_2SO_4. Volatiles were then removed under reduced pressure and the remaining residue was purified by silica gel chromatography to afford the corresponding chromones.

Synthesis of 6-fluoro-2-(methylthio)chromone (B1)

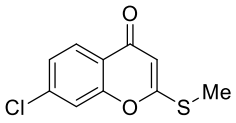


B1

Propenone **A1** (4.64 g, 13.3 mmol, 1 equiv.) was added to a flask containing I_2 (1.69 g, 0.5 equiv.). A reflux condenser was then attached, and the flask was then purged with argon. Dichloroethane (40 mL) was then added, and the mixture was stirred at 80 °C for 3 h. The reaction mixture was transferred to a separatory funnel and washed with a 5% aqueous solution of $Na_2S_2O_3$. The aqueous layer was washed with CH_2Cl_2 three times. The combined organic layers were washed with brine and dried over anhydrous Na_2SO_4. Volatiles were then removed under reduced pressure and the remaining residue was purified by silica gel chromatography (5% EtOAc/95% *n*-hexane) to afford **B1** in 90% yield (2.52 g).

Data for chromone B1
brown solid
R*f* (8:2 *n*-hexane/EtOAc): 0.20
Melting Point: 126-127 °C
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (dd, J = 8.2, 3.1 Hz, 1H), 7.41 (ddd, J = 9.2, 4.2, 0.5 Hz, 1H), 7.37-7.31 (m, 1H), 6.20 (s, 1H), 2.55 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 174.8 (d, $J_{C\text{-}F}$ = 2.2 Hz)., 170.4, 159.6 (d, $J_{C\text{-}F}$ = 246.9) 153.0 (d, $J_{C\text{-}F}$ = 1.8 Hz), 124.9 (d, $J_{C\text{-}F}$ = 7.3 Hz), 121.3 (d, $J_{C\text{-}F}$ = 25.5 Hz), 119.3 (d, $J_{C\text{-}F}$ = 8.1 Hz), 111.0 (d, $J_{C\text{-}F}$ = 23.8 Hz), 106.8, 13.8.
HRMS (FAB): *m/z*: $[M+H]^+$ calculated for $C_{10}H_8FO_2S^+$: 211.0224, found 211.0235

Synthesis of 7-chloro-2-(methylthio)chromone (B2)

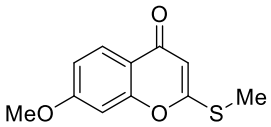


B2

Propenone **A2** (1.5 g, 4.11 mmol, 1 equiv.) was added to a flask containing I_2 (520 mg, 0.5 equiv.). A reflux condenser was then attached, and the flask was then purged with argon. Dichloroethane (10 mL) was then added, and the mixture was stirred at 80 °C for 3 h. The reaction mixture was transferred to a separatory funnel and washed with a 5% aqueous solution of $Na_2S_2O_3$. The aqueous layer was washed with CH_2Cl_2 three times. The combined organic layers were washed with brine and dried over anhydrous Na_2SO_4. Volatiles were then removed under reduced pressure and the remaining residue was purified by silica gel chromatography (20% EtOAc/80% *n*-hexane) to afford **B2** in 48% yield (447 mg).

Data for chromone B2
orange-brown solid
R*f* (1:1 *n*-hexane/EtOAc): 0.74
Melting Point: 154-155 °C (from chloroform/*n*-hexane)
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, J = 8.5 Hz, 1H), 7.41 (d, J = 2.0 Hz, 1H), 7.34 (dd, J = 8.5, 1.9 Hz, 1H), 6.18 (s, 1H), 2.53 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 173.8, 169.3, 155.8, 138.4, 126.2, 125.1, 121.1, 116.4, 106.6, 12.8.
HRMS (FAB): *m/z*: $[M+H]^+$ calculated for $C_{10}H_8{}^{35}ClO_2S^+$: 226.9928, found 226.9922

Synthesis of 7-methoxy-2-(methylthio)chromone (B3)



B3

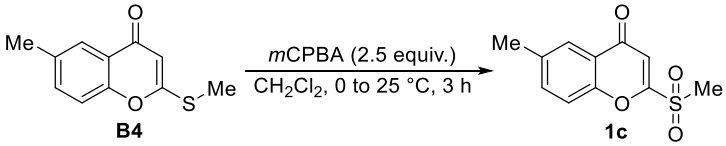
Propenone **A3** (2.75 g, 7.63 mmol, 1 equiv.) was added to a flask containing I_2 (970 mg, 0.5 equiv.). A reflux condenser was then attached, and the flask was then purged with argon. Dichloroethane (20 mL) was then added, and the mixture was stirred at 80 °C for 3 h. The reaction mixture was transferred to a separatory funnel and washed with a 5% aqueous solution of $Na_2S_2O_3$. The aqueous layer was washed with CH_2Cl_2 three times. The combined organic layers were washed with brine and dried over anhydrous Na_2SO_4. Volatiles were then removed under reduced pressure and the remaining residue was purified by silica gel chromatography (20% EtOAc/80% *n*-hexane) to afford **B3** in 43% yield (727 mg).

Data for chromone B3
brown solid
R*f* (8:2 *n*-hexane/EtOAc): 0.13
Melting Point: 144-145 °C
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (d, J = 8.8 Hz, 1H), 6.93 (dd, J = 8.9, 2.4 Hz, 1H), 6.79 (d, J = 2.3 Hz, 1H), 6.12 (s, 1H), 3.87 (s, 3H), 2.51 (s, 3H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 175.5, 169.4, 164.0, 158.5, 127.3, 117.3, 114.3, 107.4, 100.1, 55.9, 14.0.
HRMS (FAB): *m/z*: $[M+H]^+$ calculated for $C_{11}H_{11}O_3S^+$: 223.0424, found 223.0429

3.2.3 Synthetic Procedures for 2-(Methylsulfonyl)chromones

1a[3], **1g**[4], and **1h**[5] were synthesized according to the representative procedure reported by Pak and coworkers[3].
Note: 2-(Methylsulfonyl)chromones decompose over time even if kept in a desiccator. During multiple melting point measurements of compounds whose melting point is labeled as "decomposes", decomposition was observed at varying temperatures above 40 °C. Thus, a precise decomposition point could not be measured for these compounds.

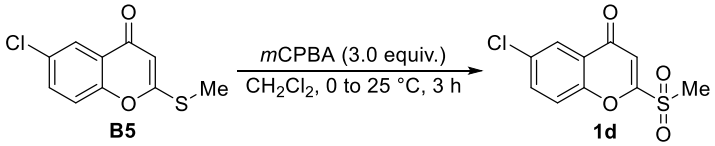
Synthesis of 6-methyl-2-(methylsulfonyl)chromone (1c)



B4 **1c**

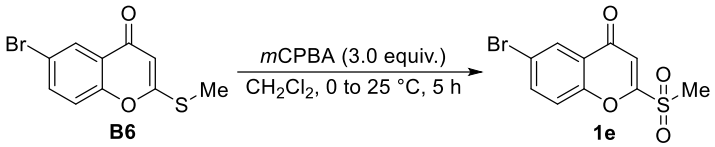
6-Methyl-2-(methylthio)chromone (**B4**, 1.04 g, 5.0 mmol) and *m*-chloroperoxybenzoic acid (70% mixture with water; 2.5 equiv.; 3.11 g) were added to a flask. The flask was purged with argon and cooled to 0 °C in an ice bath. Then, 15 mL of CH_2Cl_2 was added. The mixture was left in the ice bath (which slowly warmed to room temperature) and stirred for 3 h. The mixture was washed with a saturated $Na_2S_2O_3$ solution, followed by a wash with a saturated $NaHCO_3$ solution and extracted with CH_2Cl_2. The aqueous layer was washed with CH_2Cl_2 three times. The combined organic fractions were dried over anhydrous Na_2SO_4. The volatiles were removed under reduced pressure. The residue was subjected to silica gel chromatography (7:3 to 1:1 *n*-hexane:EtOAc). The product was obtained as a colorless solid (745 mg, 62% yield).
R*f* (7:3 *n*-hexane/EtOAc): 0.26; (1:1 *n*-hexane/EtOAc): 0.63
Melting point: decomposes
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (d, J = 2.3 Hz, 2H), 7.59 (dd, J = 8.6, 2.3 Hz, 1H), 7.47 (d, J = 8.6 Hz, 1H), 7.05 (s, 1H), 3.24 (s, 3H), 2.48 (s, 3H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 177.0, 160.7, 154.2, 137.2, 136.7, 125.6, 123.8, 118.3, 112.0, 40.9, 21.1.
HRMS (FAB): *m/z*: $[M+H]^+$ calculated for $C_{11}H_{11}O_4S^+$: 239.0373 , found 239.0368

Synthesis of 6-chloro-2-(methylsulfonyl)-chromone (1d)



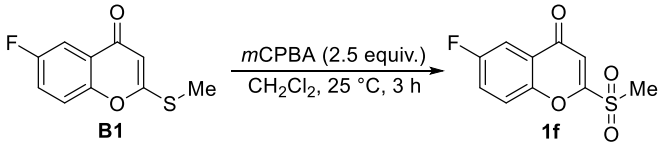
6-Chloro-2-(methylthio)chromone (**B5**, 500 mg, 2.21 mmol) and *m*-chloroperoxybenzoic acid (70% mixture with water; 3.0 equiv.; 1.64 g) were added to a flask. The flask was purged with argon and cooled to 0 °C in an ice bath. Then, 10 mL of CH_2Cl_2 was added. The mixture was left in the ice bath (which slowly warmed to room temperature) and stirred for 3 h. The mixture was washed with a saturated $Na_2S_2O_3$ solution, followed by a wash with a saturated $NaHCO_3$ solution and extracted with CH_2Cl_2. The aqueous layer was washed with CH_2Cl_2 three times. The combined organic fractions were dried over anhydrous Na_2SO_4. The volatiles were removed under reduced pressure. The residue was subjected to silica gel chromatography (7:3 to 1:1 *n*-hexane:EtOAc). The product was obtained as a colorless solid (285 mg, 50% yield).
R*f* (1:1 *n*-hexane/EtOAc): 0.44
Melting point: decomposes
^{1}H NMR (500 MHz, acetone-d_6) δ 8.02 (d, J = 2.7 Hz, 1H), 7.93 – 7.87 (m, 1H), 7.80 (d, J = 9.0 Hz, 1H), 6.90 (s, 1H), 3.41 (s, 3H).
^{13}C NMR (125 MHz, acetone-d_6) δ 176.3, 162.8, 155.4, 136.2, 132.6, 126.0, 125.4, 122.0, 111.8, 40.9.
HRMS (FAB): *m/z*: $[M+H]^+$ calculated for $C_{10}H_8{}^{35}ClO_4S^+$: 258.9832, found 258.9824

Synthesis of 6-bromo-2-(methylsulfonyl)chromone (1e)



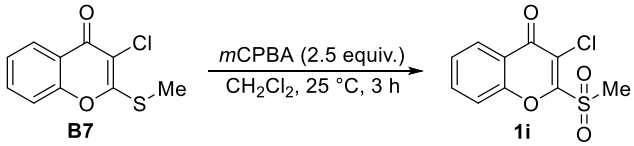
6-Bromo-2-(methylthio)chromone (**B6**, 718 mg, 2.65 mmol) and *m*-chloroperoxybenzoic acid (70% mixture with water; 3.0 equiv.; 1.96 g) were added to a flask. The flask was purged with argon and cooled to 0 °C in an ice bath. Then, 15 mL of CH_2Cl_2 was added. The mixture was left in the ice bath (which slowly warmed to room temperature) and stirred for 5 h. The mixture was washed with a saturated $Na_2S_2O_3$ solution, followed by a wash with a saturated $NaHCO_3$ solution and extracted with CH_2Cl_2. The aqueous layer was washed with CH_2Cl_2 three times. The combined organic fractions were dried over anhydrous Na_2SO_4. The volatiles were removed under reduced pressure. The residue was subjected to silica gel chromatography (8:2 to 1:1 *n*-hexane:EtOAc). The product was obtained as a colorless solid (450 mg, 56% yield).
R*f* (1:1 *n*-hexane/EtOAc): 0.44
Melting point: decomposes
^{1}H NMR (500 MHz, acetone-d_6) δ 8.17 (d, J = 2.5 Hz, 1H), 8.03 (dd, J = 9.0, 2.5 Hz, 1H), 7.73 (d, J = 9.0 Hz, 1H), 6.90 (s, 1H), 3.41 (s, 3H).
^{13}C NMR (125 MHz, acetone-d_6) δ 175.4, 161.9, 155.0, 138.2, 127.8, 125.5, 121.3, 119.3, 111.2, 40.1.
HRMS (FAB) *m/z*: $[M+H]^+$ calculated for $C_{10}H_8{}^{81}BrO_4S^+$: 304.9306; found 304.9307

Synthesis of 6-fluoro-2-(methylsulfonyl)chromone (1f)



6-Fluoro-2-(methylthio)chromone (**B1**, 1.00 g, 4.76 mmol) and *m*-chloroperoxybenzoic acid (70% mixture with water; 2.5 equiv.; 2.93 g) were added to a flask. The flask was purged with argon and then 15 mL of CH_2Cl_2 was added. The mixture was stirred for 3 h at 25 ˚C. The mixture was washed with a saturated $Na_2S_2O_3$ solution, followed by a wash with a saturated $NaHCO_3$ solution and extracted with CH_2Cl_2. The aqueous layer was washed with CH_2Cl_2 three times. The combined organic fractions were dried over anhydrous Na_2SO_4. The volatiles were removed under reduced pressure. The residue was subjected to silica gel chromatography (1:1 *n*-hexane:EtOAc). The obtained colorless solid was then subjected to size-exclusion HPLC (eluent: chloroform). The product was obtained as a colorless solid (517 mg, 45% yield).
R*f* (1:1 *n*-hexane/EtOAc): 0.51
Melting point: decomposes
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (dd, J = 7.8, 3.1 Hz, 1H), 7.62 (dd, J = 9.2, 4.1 Hz, 1H), 7.52 (ddd, J = 9.2, 7.4, 3.1 Hz, 1H), 7.07 (s, 1H), 3.26 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 176.0 (d, $J_{C\text{-}F}$ = 2.6 Hz)., 161.1, 160.3 (d, $J_{C\text{-}F}$ = 250.2 Hz), 151.9 (d, $J_{C\text{-}F}$ = 1.9 Hz), 125.4 (d, $J_{C\text{-}F}$ = 7.7 Hz), 123.6 (d, $J_{C\text{-}F}$ = 25.6 Hz), 120.7 (d, $J_{C\text{-}F}$ = 8.3 Hz), 111.3, 111.3 (d, $J_{C\text{-}F}$ = 23.8 Hz), 40.8.
HRMS (FAB): *m/z*: $[M+H]^+$ calculated for $C_{10}H_8FO_4S^+$: 243.0122, found 243.0135

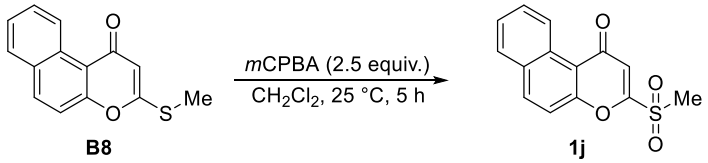
Synthesis of 3-chloro-2-(methylsulfonyl)chromone (1i)



3-chloro-2-(methylthio)chromone[1] (**B7**, 940 mg, 4.15 mmol) and *m*-chloroperoxybenzoic acid (70% mixture with water; 2.5 equiv.; 2.56 g) were added to a flask. The flask was purged with argon. Then, 20 mL of CH_2Cl_2 was added, and the mixture was stirred for 3 h. The mixture was washed with a saturated $Na_2S_2O_3$ solution, followed by a wash with a saturated $NaHCO_3$ solution and extracted with CH_2Cl_2. The aqueous layer was washed with CH_2Cl_2 three times. The combined organic fractions were dried over Na_2SO_4. The volatiles were removed under reduced pressure. The residue was subjected to silica gel chromatography (8:2 to 1:1 *n*-hexane:EtOAc). The product was obtained as a colorless solid (800 mg, 75% yield).
R*f* of 1i (1:1 *n*-hexane/EtOAc): 0.47
Melting point: decomposes
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.29 – 8.23 (m, 1H), 7.85-7.80 (m, 1H), 7.62 (dd, J = 8.6, 1.2 Hz, 1H), 7.57-7.52 (m, 1H), 3.41 (s, 3H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 172.1, 156.6, 154.8, 135.8, 127.2, 126.7, 122.3, 120.6, 118.6, 42.0.

HRMS (FAB) *m/z*: $[M+H]^+$ calculated for $C_{10}H_8ClO_4S^+$: 258.9828; found 258.9829

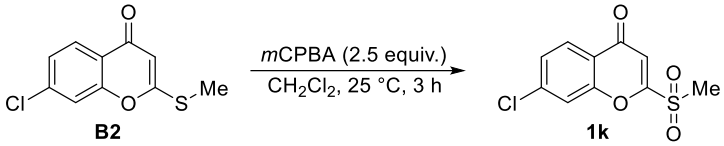
Synthesis of 3-(methylsulfonyl)-1*H*-naphtho[2,1-*b*]pyran-1-one (1j)



B8 **1j**

3-(Methylthio)-1*H*-naphtho[2,1-*b*]pyran-1-one[1] (**B8**, 750 mg, 3.10 mmol) and *m*-chloroperoxybenzoic acid (70% mixture with water; 2.5 equiv.; 1.90 g) were added to a flask. The flask was purged with argon. Then, 20 mL of CH_2Cl_2 was added, and the mixture was stirred for 5 h. The mixture was washed with a saturated $Na_2S_2O_3$ solution, followed by a wash with a saturated $NaHCO_3$ solution and extracted with CH_2Cl_2. The aqueous layer was washed with CH_2Cl_2 three times. The combined organic fractions were dried over Na_2SO_4. The volatiles were removed under reduced pressure. The residue was subjected to silica gel chromatography (8:2 to 1:1 *n*-hexane:EtOAc). The product was obtained as a tan solid (387 mg, 46% yield).
R*f* (1:1 *n*-hexane/EtOAc): 0.61
Melting point: 187-188 °C
^{1}H NMR (500 MHz, $CDCl_3$) δ 9.89 (d, J = 8.7 Hz, 1H), 8.19 (d, J = 9.5 Hz, 1H), 7.94 (d, J = 8.0 Hz, 1H), 7.85 – 7.76 (m, 1H), 7.71 – 7.64 (m, 1H), 7.59 (d, J = 9.1 Hz, 1H), 7.21 (s, 1H), 3.28 (s, 3H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 178.4, 158.4, 157.4, 137.3, 131.1, 130.3, 130.0, 128.6, 127.7, 127.0, 118.0, 117.2, 115.2, 41.1.
HRMS (FAB) *m/z*: $[M+H]^+$ calculated for $C_{14}H_{11}O_4S^+$: 275.0373, found 275.0363

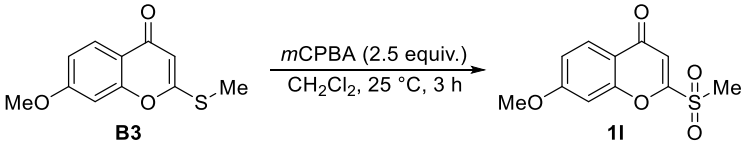
Synthesis of 7-chloro-2-(methylsulfonyl)chromone (1k)



B2 **1k**

7-Chloro-2-(methylthio)chromone (**B2**, 300 mg, 1.32 mmol) and *m*-chloroperoxybenzoic acid (70% mixture with water; 2.5 equiv.; 816 mg) were added to a flask. The flask was purged with argon and then 10 mL of CH_2Cl_2 was added. The mixture was stirred for 3 h at 25 ˚C. The mixture was washed with a saturated $Na_2S_2O_3$ solution, followed by a wash with a saturated $NaHCO_3$ solution and extracted with CH_2Cl_2. The aqueous layer was washed with CH_2Cl_2 three times. The combined organic fractions were dried over anhydrous Na_2SO_4. The volatiles were removed under reduced pressure. The residue was subjected to silica gel chromatography (1:1 *n*-hexane:EtOAc). The product was obtained as a colorless solid (311 mg, 91% yield).
R*f* (1:1 *n*-hexane/EtOAc): 0.71
Melting point: 171-172 °C
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, J = 8.6 Hz, 1H), 7.63 (d, J = 1.8 Hz, 1H), 7.48 (dd, J = 8.6, 1.9 Hz, 1H), 7.07 (s, 1H), 3.25 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 175.9, 160.9, 155.8, 141.6, 127.7, 127.5, 122.6, 118.6, 112.5, 40.8.
HRMS (FAB): *m/z*: $[M+H]^+$ calculated for $C_{10}H_8{}^{35}ClO_4S^+$: 258.9827, found 258.9828

Synthesis of 7-methoxy-2-(methylsulfonyl)chromone (1l)

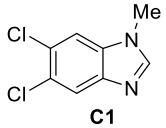


B3 **1l**

7-Methoxy-2-(methylthio)chromone (**B3**, 500 mg, 2.25 mmol) and *m*-chloroperoxybenzoic acid (70% mixture with water; 2.5 equiv.; 1.39 g) were added to a flask. The flask was purged with argon and then 10 mL of CH_2Cl_2 was added. The mixture was stirred for 3 h at 25 ˚C. The mixture was washed with a saturated $Na_2S_2O_3$ solution, followed by a wash with a saturated $NaHCO_3$ solution and extracted with CH_2Cl_2. The aqueous layer was washed with CH_2Cl_2 three times. The combined organic fractions were dried over anhydrous Na_2SO_4. The volatiles were removed under reduced pressure. The residue was subjected to silica gel chromatography (1:1 *n*-hexane:EtOAc). The product was obtained as a colorless solid (510 mg, 89% yield).
R*f* (1:1 *n*-hexane/EtOAc): 0.45
Melting point: 180-181 °C
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, J = 8.9 Hz, 1H), 7.05 (dd, J = 8.9, 2.4 Hz, 1H), 7.01 (s, 1H), 6.97 (d, J = 2.4 Hz, 1H), 3.94 (s, 3H), 3.24 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 175.9, 165.3, 160.3, 157.7, 127.5, 117.9, 116.0, 112.4, 100.7, 56.1, 40.9.
HRMS (FAB): *m/z*: $[M+H]^+$ calculated for $C_{11}H_{11}O_5S^+$: 255.0322, found 255.0318

3.2.4 Synthetic Procedures for Benzimidazoles

Synthesis of 5,6-dichloro-1-methylbenzimidazole (C1)[6]

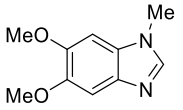


C1

5,6-Dichlorobenzimidazole[7] (654 mg; 3.5 mmol) and NaH (212 mg; 60% dispersion in paraffin liquid; 5.3 mmol; 1.5 equivalents) were added to a flask which was then purged with argon. Dehydrated THF (10 mL) was then added and the mixture was stirred at 25 °C for 5 minutes. Methyl iodide (240 μL; 3.86 mmol; 1.1 equivalents) was then added. The mixture was stirred at 25 °C for 12 h. Volatiles were evaporated under reduced pressure,

and the residue was extracted with CH_2Cl_2 (3 times). The combined organic layers were washed with brine and dried over anhydrous Na_2SO_4. The volatiles were removed under reduced pressure and the residue was subjected to silica gel medium-pressure liquid chromatography (eluent: 5% MeOH/95% CH_2Cl_2) to afford **C1** as a brown solid (552 mg; 78% yield).
^{1}H NMR (500 MHz, DMSO-d_6) δ 8.27 (s, 1H), 7.94 (s, 1H), 7.89 (s, 1H), 3.80 (s, 3H).
^{13}C NMR (125 MHz, DMSO-d_6) δ 147.7, 143.3, 134.7, 125.3, 124.6, 121.0, 112.8, 31.6.

Synthesis of 5,6-dimethoxy-1-methylbenzimidazole (C2)[8]



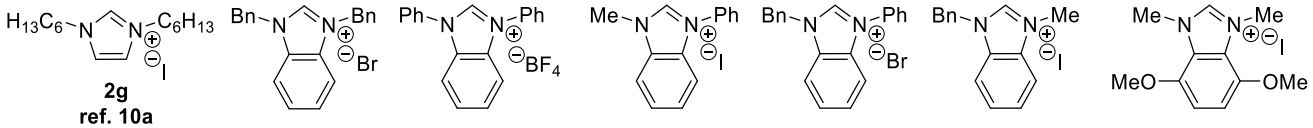
C2

A 25 mL flask containing a solution of 5,6-dimethoxybenzimidazole[9] (1.52 g; 8.5 mmol) in dehydrated DMF (10 mL) was placed into a water bath. Then, sodium hydride (60% dispersion in paraffin liquid; 408 mg; 1.2 equivalents) was added portionwise with constant stirring. The mixture was stirred for 15 minutes at 25 °C. The atmosphere in the flask was then replaced by flushing with argon. Methyl iodide (530 μL; 1 equivalent) was then added dropwise. The mixture was stirred under an argon atmosphere at 25 °C for 18 h. Water was added, and the mixture was extracted with CH_2Cl_2 three times. The combined organic layers were washed with brine and dried over anhydrous Na_2SO_4. The volatiles were evaporated under reduced pressure, and the remaining residue was subjected to silica gel medium-pressure column chromatography (eluent: 3% MeOH/97% CH_2Cl_2) to afford the titled product as a yellow-orange solid (388 mg; 24% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (s, 1H), 7.26 (s, 1H), 6.81 (s, 1H), 3.95 (s, 3H), 3.93 (s, 3H), 3.79 (s, 3H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 147.6, 146.8, 142.1, 137.3, 128.4, 102.2, 92.2, 56.5, 56.4, 31.3.

3.2.5 Synthetic Procedures for Azolium Salts

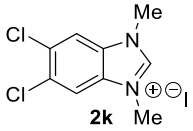
Known azolium salts were synthesized according to their respective literature procedures:



2g ref. 10a | **2j** ref. 10b | **2n** ref. 10c | **2c** ref. 10d | **2d** ref. 10e | **2e** ref. 10f | **2p** ref. 10g

Figure S1. Structures and reference numbers for azolium salts **2g**, **2j**, **2n**, **2c**, **2d**, **2e**, and **2p**

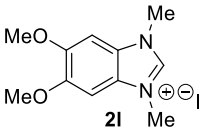
Synthesis of 5,6-dichloro-1,3-dimethylbenzimidazolium iodide (2k)[11]



2k

5,6-Dichloro-1-methylbenzimidazole **C1** (454 mg; 2.26 mmol) was added to a flask which was then purged with argon. CH_2Cl_2 (5 mL) and methyl iodide (510 μL; 8.19 mmol; 3.62 equivalents) were then added. The mixture was stirred at 25 °C for 48 h. The precipitated solid was vacuum filtered off and washed with a small amount of cool diethyl ether to afford **2k** as a colorless solid (419 mg; 54% yield).
R*f* (9:1 CH_2Cl_2/MeOH): 0.22
^{1}H NMR (500 MHz, DMSO-d_6) δ 9.71 (s, 1H), 8.48 (s, 2H), 4.02 (s, 6H).
^{13}C NMR (125 MHz, DMSO-d_6) δ 145.9, 131.8, 130.0, 116.2, 34.3.
HRMS (FAB) *m/z*: $[M]^+$ calculated for $C_9H_9{}^{35}Cl^{37}ClN_2{}^+$: 217.0114, found: 217.0108.

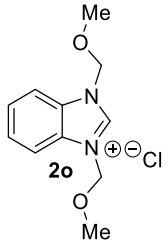
Synthesis of 5,6-dimethoxy-1,3-dimethylbenzimidazolium iodide (2l)[12]



2l

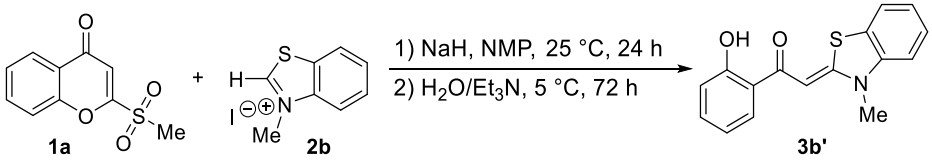
5,6-Dimethoxy-1-methylbenzimidazole **C2** (388 mg; 2.0 mmol) was added to a flask which was then purged with argon. Dehydrated CH_2Cl_2 (8 mL) and methyl iodide (150 μL; 2.4 mmol; 1.2 equivalents) were then added. The mixture was stirred under an argon atmosphere at 25 °C for 72 h. The precipitated solid was filtered off and washed with diethyl ether to afford the **2l** as a tan solid (376 mg; 56% yield).
R*f* (9:1 CH_2Cl_2/MeOH): 0.30
Melting point: 275-276 °C
^{1}H NMR (500 MHz, DMSO-d_6) δ 9.36 (s, 1H), 7.52 (s, 2H), 3.99 (s, 6H), 3.88 (s, 6H).
^{13}C NMR (125 MHz, DMSO-d_6) δ 150.1, 140.8, 126.2, 95.9, 57.0, 33.8.
HRMS (FAB) *m/z*: $[M]^+$ calculated for $C_{11}H_{15}N_2O_2{}^+$: 207.1128, found: 207.1143

Synthesis of 1,3-dimethoxymethylbenzimidazolium chloride (2o)



1-Methoxymethylbenzimidazole[13] (873 mg; 5.38 mmol) was added to a flask which was then purged with argon. CH_2Cl_2 (3 mL) was then added. The mixture was stirred at 25 °C until the starting material fully dissolved. MOM-Cl (449 μL; 5.91 mmol; 1.1 equiv.) was then added dropwise. After complete addition of MOM-Cl, the mixture was stirred at 25 °C for 3 days. H_2O (2 mL) was then added, and the mixture was stirred for 30 min. Voltiles were removed by distillation under reduced pressure. The resulting yellow oil was purified by silica gel (neutral) medium-pressure liquid chromatography (eluent: 99:1 CH_2Cl_2/MeOH to 95:5 CH_2Cl_2/MeOH) to afford **2o** as a colorless solid (32% yield; 419 mg).
R*f* (9:1 CH_2Cl_2/MeOH): 0.42
Melting point: 78-79 °C
^{1}H NMR (500 MHz, DMSO-d_6) δ 10.38 (s, 1H), 8.10 – 8.03 (m, 2H), 7.74 – 7.67 (m, 2H), 5.91 (s, 4H), 3.35 (s, 6H).
^{13}C NMR (125 MHz, DMSO-d_6) δ 144.4, 131.4, 127.7, 114.7, 78.7, 57.5.
HRMS (FAB) *m/z*: $[M]^+$ calculated for $C_{11}H_{15}N_2O_2^+$: 207.1128; found 207.1137

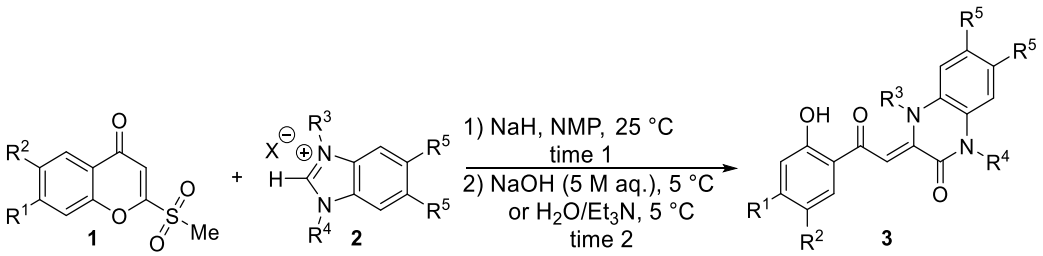
3.2.6 Synthesis of (*Z*)-1-(2-hydroxyphenyl)-2-[(3-methyl-2(3*H*)-benzothiazolylidene]ethan-1-one (3b')



Chromone **1a** (224 mg, 1 mmol, 1 equiv.), benzothiazolium salt **2b** (277 mg, 1 mmol, 1 equiv.), and NaH (160 mg, 4 mmol, 60% dispersion in paraffin liquid, 4 equiv.) were added to a flask. The flask was purged with argon. NMP (3 mL) was then added and the mixture was stirred at 25 °C in an EYELA ChemiStation PersonalSynthesizer PPS-CTRL1 machine for 24 h. The mixture was then cooled to 5 °C. H_2O (2 mL) and Et_3N (280 μL) were then added. The mixture was stirred at 5 °C in an EYELA ChemiStation PersonalSynthesizer PPS-CTRL1 machine for 72 h. The mixture was transferred to a separatory funnel. The mixture was washed with a saturated aqueous NH_4Cl solution. The aqueous layer was washed with CH_2Cl_2 three times. The combined organic layers were dried over anhydrous Na_2SO_4 and then concentrated under reduced pressure. The resulting oil was purified by silica gel medium-pressure liquid chromatography (eluent: 7:3 *n*-hexane/EtOAc). An analytically pure sample was obtained after size-exclusion HPLC (solvent: chloroform).

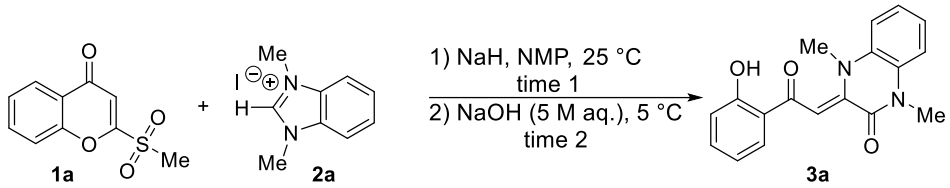
Yield of **3b'**: 28% (79 mg)
Yellow solid (recrystallized from *n*-hexane/dichloroethane using the vapor diffusion method)
R*f* (7:3 *n*-hexane/EtOAc): 0.49
^{1}H NMR (400 MHz, $CDCl_3$) δ 13.49 (s, 1H), 7.73 (dd, J = 8.0, 1.6 Hz, 1H), 7.67 – 7.60 (m, 1H), 7.44-7.38 (m, 1H), 7.37-7.31 (m, 1H), 7.30 – 7.20 (m, 2H), 6.96 (dd, J = 8.3, 1.2 Hz, 1H), 6.86-6.80 (m, 1H), 6.54 (s, 1H), 3.71 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 187.4, 162.6, 162.2, 139.9, 133.6, 127.3, 127.3, 126.8, 123.3, 122.5, 120.5, 118.3, 118.2, 110.2, 86.1, 32.7.
Melting point: 235-236 °C (from *n*-hexane/dichloroethane)
HRMS (FAB) *m/z*: $[M]^+$ calculated for $C_{16}H_{13}NO_2S^+$: 283.0667, found: 283.0664; $[M+H]^+$ calculated for $C_{16}H_{14}NO_2S^+$: 284.0745, found: 284.0739; (*Note: During mass spectrometry measurements, a m/z value of 285 was sometimes observed as the major peak. This is likely due to the reduction of **3b'** during the measurement.[14] Using the same sample in a follow up measurement showed 284 as the major peak.)*

3.2.7 Synthetic Procedures for 3,4-Dihydroquinoxalin-2(1*H*)-ones 3



General procedure B (synthesis of quinoxalinones):
Chromone **1** (1 equiv.), benzimidazolium salt **2** (1 equiv.), and NaH (2 equiv.) were added to a flask. The flask was purged with argon. NMP was then added and the mixture was stirred at 25 °C in an EYELA ChemiStation PersonalSynthesizer PPS-CTRL1 machine for the indicated time (time 1). The mixture was then cooled to 5 °C. A 5-molar aqueous NaOH solution or a H_2O/Et_3N mixture (H_2O was added first, followed by Et_3N) was then added. The mixture was stirred at 5 °C in an EYELA ChemiStation PersonalSynthesizer PPS-CTRL1 machine for the indicated time (time 2). The mixture was transferred to a separatory funnel. The mixture was washed with a saturated aqueous NH_4Cl solution. The aqueous layer was washed with CH_2Cl_2 three times. The combined organic layers were dried over anhydrous Na_2SO_4 and then concentrated under reduced pressure. The resulting oil was purified by silica gel medium-pressure liquid chromatography (eluent: 7:3 *n*-hexane/EtOAc). Analytically pure samples were obtained after size-exclusion HPLC (solvent: chloroform) and/or recrystallization from the indicated solvent(s).

Synthesis of compound (*Z*)-1,4-dimethyl-3-[(2-hydroxyphenyl]-2-oxoethylidene]-3,4-dihydroquinoxalin-2(1*H*)-one (3a)



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

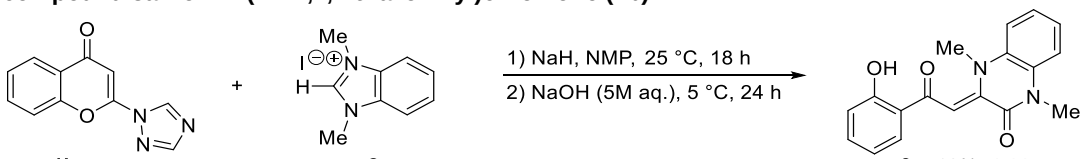
Synthesized according to general procedure B using the following amounts of reagents.

Reaction at 0.3 mmol scale:
Time 1: 18 h
Time 2: 48 h
1a: 75 mg (0.335 mmol)
2a: 92 mg (0.335 mmol)
NaH: 27 mg (60% dispersion in paraffin oil; 0.675 mmol; 2 equiv.)
NMP: 3 mL
NaOH (5 M aq.): 2 mL
Yield of **3a**: 99% (103 mg)

Reaction at 1.0 mmol scale:
Time 1: 18 h
Time 2: 24 h
1a: 224 mg (1.0 mmol)
2a: 274 mg (1.0 mmol)
NaH: 80 mg (60% dispersion in paraffin oil; 2.0 mmol; 2 equiv.)
NMP: 5 mL
NaOH (5 M aq.): 3 mL
Yield of **3a**: 94% (290 mg)

Data for Compound 3a.
Orange solid (recrystallized from EtOAc)
R*f* (1:1 *n*-hexane/EtOAc): 0.74
Melting point: 192-193 °C (from EtOAc)
^{1}H NMR (400 MHz, $CDCl_3$) δ 13.15 (s, 1H), 7.97 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.42 (ddd, *J* = 8.6, 7.1, 1.6 Hz, 1H), 7.32 (d, *J* = 0.6 Hz, 1H), 7.28 – 7.19 (m, 3H), 7.23 – 7.16 (m, 1H), 6.97 (dd, *J* = 8.4, 1.1 Hz, 1H), 6.91 (ddd, *J* = 8.2, 7.2, 1.2 Hz, 1H), 3.65 (s, 3H), 3.49 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 192.0, 162.6, 158.3, 144.6, 135.0, 130.4, 130.1, 128.7, 124.2, 123.9, 121.6, 118.7, 118.2, 116.0, 114.3, 97.8, 43.2, 30.0.
HRMS (FAB) *m/z*: $[M+H]^+$ calculated for $C_{18}H_{17}N_2O_3^+$: 309.1234, found: 309.1239

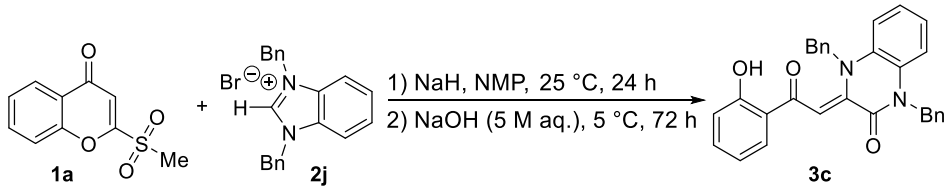
Synthesis of compound 3a from 2-(1*H*-1,2,4-triazol-1-yl)chromone (1b)



1b **2a** **3a**, 18% yield

Chromone **1b** (213 mg, 1 mmol, 1 equiv.), benzimidazolium salt **2a** (274 mg, 1 mmol, 1 equiv.), and NaH (80 mg, 2 mmol, 60% dispersion in paraffin liquid, 2 equiv.) were added to a flask. The flask was purged with argon. NMP (3 mL) was then added and the mixture was stirred at 25 °C in an EYELA ChemiStation PersonalSynthesizer PPS-CTRL1 machine for 18 h. The mixture was then cooled to 5 °C. A 5-molar aqueous NaOH solution (1.5 mL) was then added. The mixture was stirred at 5 °C in an EYELA ChemiStation PersonalSynthesizer PPS-CTRL1 machine for 24 h. The mixture was transferred to a separatory funnel. The mixture was washed with a saturated aqueous NH_4Cl solution. The aqueous layer was washed with CH_2Cl_2 three times. The combined organic layers were dried over anhydrous Na_2SO_4 and then concentrated under reduced pressure. The resulting oil was purified by silica gel medium-pressure liquid chromatography (eluent: 7:3 *n*-hexane/EtOAc) to afford **3a** in 18% yield (56 mg).

Synthesis of (*Z*)-1,4-dibenzyl-3-[(2-hydroxyphenyl)-2-oxoethylidene]-3,4-dihydroquinoxalin-2(1*H*)-one (3c)



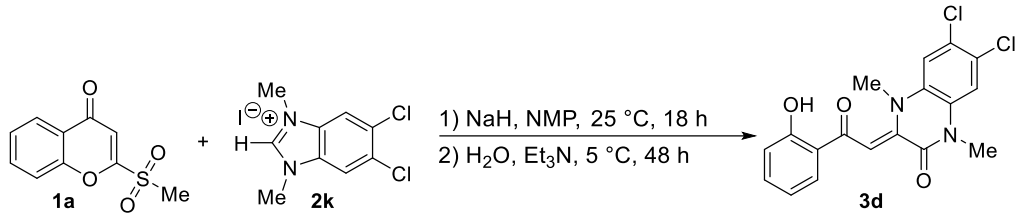
1a **2j** **3c**

Synthesized according to general procedure B (time 1 = 24 h, time 2 = 72 h) using the following amounts of reagents.
1a: 67 mg (0.3 mmol)
2j: 114 mg (0.3 mmol)
NaH: 24 mg (60% dispersion in paraffin oil; 0.6 mmol; 2 equiv.)
NMP: 3 mL
NaOH (5 M aq.): 2 mL

Yield of **3c**: 54% (75 mg)
Orange oil
R*f* (7:3 *n*-hexane/EtOAc): 0.74

^{1}H NMR (500 MHz, $CDCl_3$) δ 12.13 (s, 1H), 7.76 (dd, J = 8.1, 1.7 Hz, 1H), 7.42 (d, J = 0.5 Hz, 1H), 7.40 (ddd, J = 8.6, 7.1, 1.6 Hz, 1H), 7.34 (ddt, J = 8.0, 7.1, 1.0 Hz, 2H), 7.30 – 7.23 (m, 4H), 7.18 – 7.10 (m, 4H), 7.08 – 6.92 (m, 6H), 6.83 (ddd, J = 8.3, 7.2, 1.2 Hz, 1H), 5.48 (s, 2H), 5.19 (s, 2H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 192.3, 162.8, 159.7, 144.2, 135.5, 135.3, 135.1, 130.3, 129.5, 129.1, 128.8, 128.4, 127.8, 127.8, 127.4, 126.6, 124.0, 123.7, 121.6, 118.8, 118.2, 117.9, 115.6, 100.7, 57.8, 46.8.
HRMS (FAB) m/z: $[M+H]^+$ calculated for $C_{30}H_{25}N_2O_3^+$: 461.1860, found 461.1845

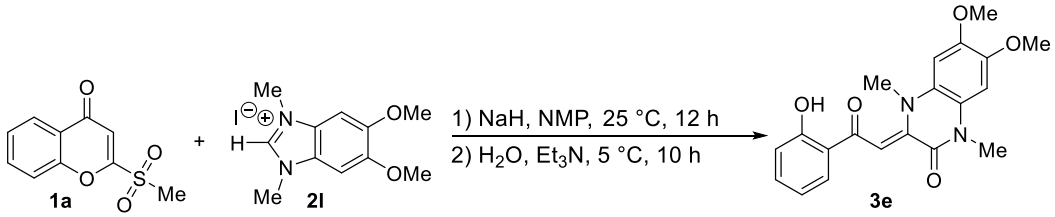
Synthesis of (*Z*)-6,7-dichloro-3-[2-(2-hydroxyphenyl)-2-oxoethylidene]-1,4-dimethyl-3,4-dihydroquinoxalin-2(1*H*)-one (3d)



Synthesized according to general procedure B (time 1 = 18 h, time 2 = 48 h) using the following amounts of reagents.
1a: 131 mg (0.58 mmol)
2k: 200 mg (0.58 mmol)
NaH: 47 mg (60% dispersion in paraffin oil; 1.2 mmol; 2 equiv.)
NMP: 2 mL
H_2O: 1 mL
Et_3N: 163 μL (1.2 mmol; 2 equiv.)

Yield of **3d**: 81% (177 mg)
Yellow-orange solid (recrystallized from *n*-pentane/chloroform using the vapor diffusion method)
Rf: 0.73 (7:3 *n*-hexane:EtOAc)
Melting point: 240-241 °C (from *n*-pentane/chloroform)
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (dd, J = 8.0, 1.6 Hz, 1H), 7.47-7.41 (m, 1H), 7.33 (s, 1H), 7.24 (s, 1H), 7.22 (s, 1H), 6.98 (dd, J = 8.3, 1.2 Hz, 1H), 6.94-6.89 (m, 1H), 3.60 (s, 3H), 3.40 (s, 3H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 192.6, 162.8, 158.1, 143.3, 135.6, 130.6, 129.8, 128.3, 127.8, 127.1, 121.5, 118.9, 118.4, 117.1, 115.8, 100.0, 43.2, 30.2.
HRMS (FAB) m/z: $[M+H]^+$ calculated for $C_{18}H_{14}Cl_2N_2O_3^+$: 377.0454, found 377.0464

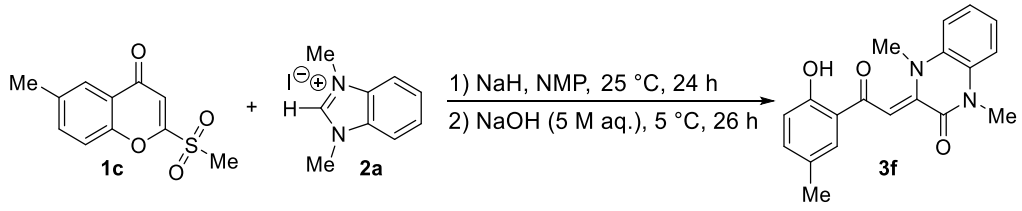
Synthesis of (*Z*)-6,7-dimethoxy-1,4-dimethyl-3-[2-(2-hydroxyphenyl)-2-oxoethylidene]-3,4-dihydroquinoxalin-2(1*H*)-one (3e)



Synthesized according to general procedure B (time 1 = 12 h, time 2 = 10 h) using the following amounts of reagents.
1a: 134 mg (0.6 mmol)
2l: 200 mg (0.6 mmol)
NaH: 48 mg (60% dispersion in paraffin oil; 1.2 mmol; 2 equiv.)
NMP: 5 mL
NaOH (5 M aq.): 2 mL

Yield of **3e**: 81% (178 mg)
Orange solid (recrystallized from *n*-pentane/chloroform using the vapor diffusion method)
Rf: 0.15 (7:3 *n*-hexane:EtOAc); 0.53 (4:6 *n*-hexane:EtOAc)
Melting point: 186-187 °C (from *n*-pentane/chloroform)
^{1}H NMR (400 MHz, $CDCl_3$) δ 13.31 (s, 1H), 7.96 (dd, J = 8.2, 1.6 Hz, 1H), 7.41 (ddd, J = 8.6, 7.1, 1.6 Hz, 1H), 7.27 (s, 1H), 6.96 (dd, J = 8.3, 1.2 Hz, 1H), 6.90 (ddd, J = 8.3, 7.2, 1.2 Hz, 1H), 6.80 (s, 1H), 6.72 (s, 1H), 3.97 (s, 3H), 3.95 (s, 3H), 3.66 (s, 3H), 3.52 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 191.2, 162.6, 157.9, 146.2, 146.1, 144.9, 134.8, 130.2, 123.7, 122.4, 121.7, 118.6, 118.1, 100.8, 99.2, 96.5, 56.7, 56.6, 43.7, 30.2.
HRMS (FAB) m/z: $[M]^+$ calculated for $C_{20}H_{20}N_2O_5^+$: 368.1372, found 368.1370; $[M+H]^+$ calculated for $C_{20}H_{21}N_2O_5^+$: 369.1445, found 369.1469

Synthesis of (*Z*)-1,4-dimethyl-3-[2-(2-hydroxy-5-methylphenyl)-2-oxoethylidene]-3,4-dihydroquinoxalin-2(1*H*)-one (3f)

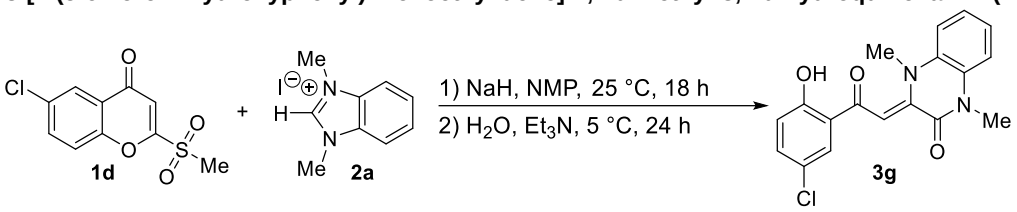


Synthesized according to general procedure B (time 1 = 24 h, time 2 = 26 h) using the following amounts of reagents.
1c: 715 mg (3 mmol)
2a: 822 mg (3 mmol)
NaH: 240 mg (60% dispersion in paraffin oil; 6 mmol; 2 equiv.)

NMP: 5 mL
NaOH (5 M aq.): 2 mL

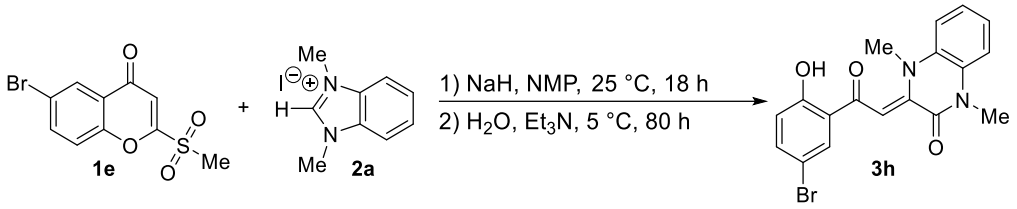
Yield of **3f**: 45% (435 mg)
Orange solid (recrystallized from *n*-pentane/chloroform using the vapor diffusion method)
Rf: 0.48 (7:3 *n*-hexane:EtOAc)
Melting point: 178-179 °C (from *n*-pentane/chloroform)
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (d, *J* = 2.2 Hz, 1H), 7.29 (s, 1H), 7.27 – 7.14 (m, 5H), 6.87 (d, *J* = 8.3 Hz, 1H), 3.64 (s, 3H), 3.45 (s, 3H), 2.32 (s, 3H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 192.2, 160.6, 158.5, 144.5, 136.1, 130.3, 130.2, 128.7, 127.9, 124.3, 123.9, 121.3, 118.0, 116.0, 114.4, 98.0, 43.2, 30.0, 20.6.
HRMS (FAB) *m/z*: $[M+H]^+$ calculated for $C_{19}H_{19}N_2O_3^+$: 323.1390, found 323.1387

Synthesis of (*Z*)-3-[2-(5-chloro-2-hydroxyphenyl)-2-oxoethylidene]-1,4-dimethyl-3,4-dihydroquinoxalin-2(1*H*)-one (3g)



Synthesized according to general procedure B (time 1 = 18 h, time 2 = 24 h) using the following amounts of reagents.
1d: 61 mg (0.24 mmol)
2a: 65 mg (0.24 mmol)
NaH: 19 mg (60% dispersion in paraffin oil; 0.47 mmol; 2 equiv.)
NMP: 2 mL
H_2O: 1 mL
Et_3N: 66 μL (0.47 mmol; 2 equiv.)
Yield of **3g**: 57% (46 mg)
Orange solid (recrystallized from *n*-pentane/chloroform using the vapor diffusion method)
Rf: 0.48 (7:3 *n*-hexane:EtOAc)
Melting point: 218-219 °C (from *n*-pentane/chloroform)
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (d, *J* = 2.6 Hz, 1H), 7.34 (dd, *J* = 8.8, 2.6 Hz, 1H), 7.29 – 7.16 (m, 5H), 6.91 (d, *J* = 8.8 Hz, 1H), 3.66 (s, 3H), 3.49 (s, 3H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 190.4, 161.1, 158.0, 145.3, 134.7, 129.8, 129.5, 128.7, 124.4, 124.3, 123.3, 122.3, 119.7, 116.2, 114.4, 96.9, 43.4, 30.0.
HRMS (FAB) *m/z*: $[M+H]^+$ calculated for $C_{18}H_{16}{}^{35}ClN_2O_3^+$: 343.0844, found 343.0840

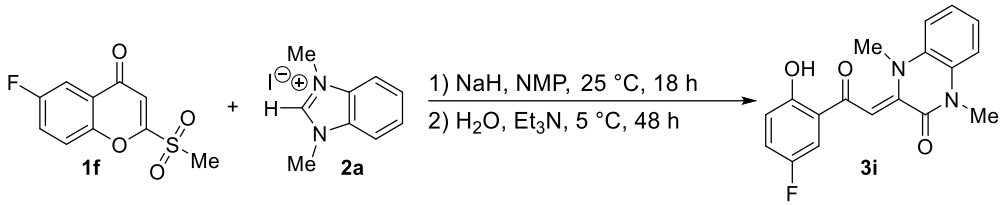
Synthesis of (*Z*)-3-[(5-bromo-2-hydroxyphenyl)-2-oxoethylidene]-1,4-dimethyl-3,4-dihydroquinoxalin-2(1*H*)-one (3h)



Synthesized according to general procedure B (time 1 = 18 h, time 2 = 80 h) using the following amounts of reagents.
1e: 84 mg (0.28 mmol)
2a: 76 mg (0.28 mmol)
NaH: 22 mg (60% dispersion in paraffin oil; 0.55 mmol; 2 equiv.)
NMP: 2 mL
H_2O: 1 mL
Et_3N: 77 μL (0.55 mmol; 2 equiv.)

Yield of **3h**: 80% (86 mg)
Orange solid (recrystallized from *n*-pentane/chloroform using the vapor diffusion method)
Rf: 0.52 (7:3 *n*-hexane:EtOAc)
Melting point: 207-208 °C (from *n*-pentane/chloroform)
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (d, *J* = 2.5 Hz, 1H), 7.47 (dd, *J* = 8.8, 2.4 Hz, 1H), 7.30 – 7.16 (m, 5H), 6.86 (d, *J* = 8.8 Hz, 1H), 3.66 (s, 3H), 3.49 (s, 3H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 190.4, 161.6, 158.0, 145.4, 137.6, 132.6, 129.9, 128.8, 124.5, 124.4, 123.0, 120.2, 116.3, 114.5, 110.4, 97.0, 43.5, 30.1.
HRMS (FAB) *m/z*: $[M+H]^+$ calculated for $C_{18}H_{16}{}^{79}BrN_2O_3^+$: 387.0339, found 387.0358

Synthesis of (*Z*)-1,4-dimethyl-3-[(5-fluoro-2-hydroxyphenyl)-2-oxoethylidene]-3,4-dihydroquinoxalin-2(1*H*)-one (3i)

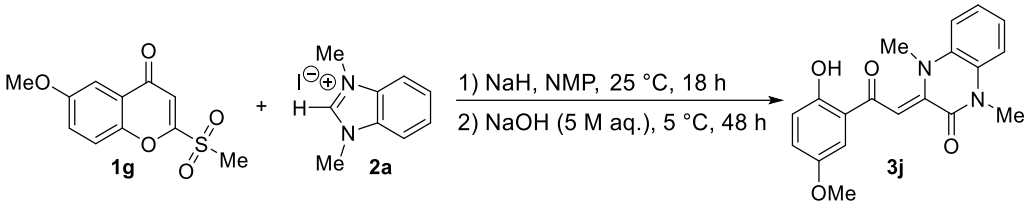


1f **2a** **3i**

Synthesized according to general procedure B (time 1 = 18 h, time 2 = 48 h) using the following amounts of reagents.
1f: 387 mg (1.6 mmol)
2a: 438 mg (1.6 mmol)
NaH: 128 mg (60% dispersion in paraffin oil; 3.2 mmol; 2 equiv.)
NMP: 3 mL
H_2O: 2 mL
Et_3N: 445 µL (3.2 mmol; 2 equiv.)

Yield of **3i**: 46% (240 mg)
Orange solid (recrystallized from *n*-pentane/chloroform using the vapor diffusion method)
Rf: 0.44 (7:3 *n*-hexane:EtOAc)
Melting point: 196-197 °C (from *n*-pentane/chloroform)
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (dd, J = 9.3, 3.1 Hz, 1H), 7.26 – 7.17 (m, 5H), 7.16-7.10 (m,1H), 6.90 (dd, J = 9.1, 4.6 Hz, 1H), 3.64 (s, 3H), 3.49 (s, 3H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 190.6 (d, $J_{C\text{-}F}$ = 3.0 Hz), 158.8, 158.0, 155.0 (d, $J_{C\text{-}F}$ = 238.1 Hz), 145.3, 129.9, 128.8, 124.4 (2C), 122.3 (d, $J_{C\text{-}F}$ = 23.4 Hz), 121.4 (d, $J_{C\text{-}F}$ = 6.6 Hz), 119.3 (d, $J_{C\text{-}F}$ = 7.2 Hz), 116.2, 115.4 (d, $J_{C\text{-}F}$ = 23.4 Hz), 114.5, 97.0, 43.5, 30.1.
HRMS (FAB) *m/z*: $[M]^+$ calculated for $C_{18}H_{15}{}^{19}FN_2O_3{}^+$: 326.1067, found: 326.1082

Synthesis of (*Z*)-1,4-dimethyl-3-[(5-methoxy-2-hydroxyphenyl)-2-oxoethylidene]-3,4-dihydroquinoxalin-2(1*H*)-one (3j)

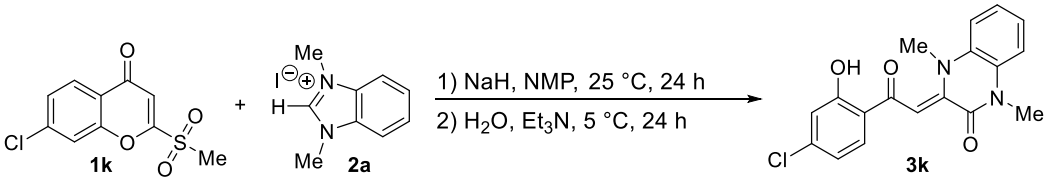


1g **2a** **3j**

Synthesized according to general procedure B (time 1 = 18 h, time 2 = 48 h) using the following amounts of reagents.
1g: 500 mg (2 mmol)
2a: 539 mg (2 mmol)
NaH: 157 mg (60% dispersion in paraffin oil; 3.9 mmol; 2 equiv.)
NMP: 8 mL
NaOH (5 M aq.): 3 mL

Yield of **3j**: 73% (486 mg)
Orange solid (recrystallized from *n*-pentane/chloroform using the vapor diffusion method)
Rf: 0.41 (7:3 *n*-hexane:EtOAc)
Melting point: 157-158 °C (from *n*-pentane/chloroform)
^{1}H NMR (400 MHz, $CDCl_3$) δ 12.76 (s, 1H), 7.41 (d, J = 3.0 Hz, 1H), 7.30 – 7.17 (m, 5H), 7.06 (dd, J = 9.0, 3.0 Hz, 1H), 6.92 (d, J = 9.0 Hz, 1H), 3.83 (s, 3H), 3.66 (s, 3H), 3.48 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 191.6, 158.3, 157.0, 151.7, 144.7, 130.0, 128.6, 124.3, 124.0, 123.2, 121.1, 119.0, 116.0, 114.4, 112.9, 97.8, 56.1, 43.2, 30.0.
HRMS (FAB) *m/z*: $[M]^+$ calculated for $C_{19}H_{18}N_2O_4{}^+$: 338.1267, found 338.1262

Synthesis of (*Z*)-1,4-dimethyl-3-[(4-chloro-2-hydroxyphenyl)-2-oxoethylidene]-3,4-dihydroquinoxalin-2(1*H*)-one (3k)



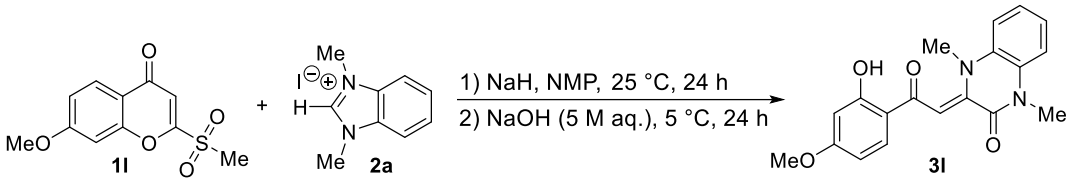
1k **2a** **3k**

Synthesized according to general procedure B (time 1 = 24 h, time 2 = 24 h) using the following amounts of reagents.
1k: 234 mg (0.91 mmol)
2a: 248 mg (0.91 mmol)
NaH: 72 mg (60% dispersion in paraffin oil; 1.8 mmol; 2 equiv.)
NMP: 3 mL
H_2O: 1.5 mL
Et_3N: 252 µL (1.8 mmol; 2 equiv.)

Yield of **3k**: 74% (230 mg)
Orange solid (recrystallized from *n*-hexane/chloroform using the vapor diffusion method)

Rf: 0.82 (1:1 *n*-hexane/EtOAc)
Melting point: 158-159 °C (from *n*-hexane/chloroform)
^{1}H NMR (400 MHz, $CDCl_3$) δ 13.38 (s, 1H), 7.87 (d, *J* = 8.6 Hz, 1H), 7.29 – 7.15 (m, 5H), 6.96 (d, *J* = 2.1 Hz, 1H), 6.87 (dd, *J* = 8.6, 2.1 Hz, 1H), 3.64 (s, 3H), 3.48 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 190.7, 163.3, 158.0, 145.0, 140.4, 131.2, 129.9, 128.7, 124.3, 124.2, 120.2, 119.2, 118.2, 116.1, 114.4, 97.1, 43.3, 30.0.
HRMS (FAB) *m/z*: $[M-H]^-$ calculated for $C_{18}H_{14}{}^{35}ClN_2O_3^-$: 341.0698, found 341.0705

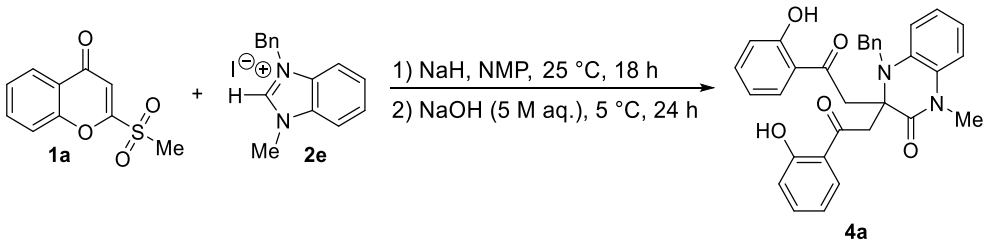
Synthesis of(*Z*)-1,4-dimethyl-3-[(4-methoxy-2-hydroxyphenyl)-2-oxoethylidene]-3,4-dihydroquinoxalin-2(1*H*)-one (3l)



Synthesized according to general procedure B (time 1 = 24 h, time 2 = 24 h) using the following amounts of reagents.
1l: 234 mg (0.92 mmol)
2a: 253 mg (0.92 mmol)
NaH: 74 mg (60% dispersion in paraffin oil; 1.8 mmol; 2 equiv.)
NMP: 3 mL
NaOH (5 M aq.): 1.5 mL

Yield of **3l**: 85% (265 mg)
Orange solid (recrystallized from *n*-hexane/chloroform using the vapor diffusion method)
Rf: 0.77 (1:1 *n*-hexane/EtOAc)
Melting point: 192-193 °C (from *n*-hexane/chloroform)
^{1}H NMR (400 MHz, $CDCl_3$) δ 13.61 (s, 1H), 7.86 (d, *J* = 8.8 Hz, 1H), 7.25 – 7.09 (m, 5H), 6.49 – 6.40 (m, 2H), 3.84 (s, 3H), 3.63 (s, 3H), 3.45 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 191.0, 165.3, 165.2, 158.5, 143.8, 132.0, 130.3, 128.5, 124.1, 123.6, 115.8, 115.7, 114.3, 107.0, 101.0, 98.1, 55.5, 42.9, 29.9.
HRMS (FAB) *m/z*: $[M]^+$ calculated for $C_{19}H_{18}N_2O_4^+$: 338.1267, found 338.1272

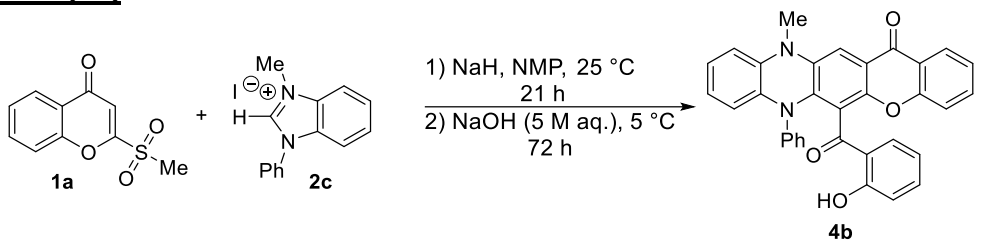
3.2.8 Synthesis of 4-Benzyl-3,3-bis[(2-hydroxybenzoyl)methyl]-1-methyl-3,4-dihydroquinoxalin-2(1*H*)-one (4a)



Chromone **1a** (345 mg, 1.5 mmol, 1 equiv.), benzimidazolium salt **2e** (539 mg, 1.5 mmol, 1 equiv.), and NaH (123 mg, 3.1 mmol, 2 equiv., 60% dispersion in paraffin oil) were added to a flask. The flask was purged with argon. NMP (3 mL) was then added and the mixture was stirred at 25 °C in an EYELA ChemiStation PersonalSynthesizer PPS-CTRL1 machine for 18 h. The mixture was then cooled to 5 °C. A 5-molar aqueous NaOH solution (2 mL) was then added. The mixture was stirred at 5 °C in an EYELA ChemiStation PersonalSynthesizer PPS-CTRL1 machine for 24 h. The mixture was transferred to a separatory funnel. The mixture was washed with a saturated aqueous NH_4Cl solution. The aqueous layer was washed with CH_2Cl_2 three times. The combined organic layers were dried over anhydrous Na_2SO_4 and then concentrated under reduced pressure. The resulting oil was purified by silica gel medium-pressure liquid chromatography (eluent: 7:3 *n*-hexane/EtOAc).

Yield of **4a**: 25% (100 mg)
Yellow solid (recrystallized from *n*-hexane/dichloroethane using the vapor diffusion method)
Rf: 0.5 (7:3 *n*-hexane/EtOAc)
Melting point: 182-183 °C (from *n*-hexane/dichloroethane)
^{1}H NMR (500 MHz, $CDCl_3$) δ 11.82 (s, 2H), 7.54 (dd, *J* = 8.4, 1.7 Hz, 2H), 7.43 – 7.36 (m, 2H), 7.15 – 7.05 (m, 4H), 6.98 (t, *J* = 7.2 Hz, 1H), 6.90 – 6.78 (m, 5H), 6.78 – 6.70 (m, 2H), 6.47 (d, *J* = 8.1 Hz, 1H), 4.64 (s, 2H), 3.88 (d, *J* = 15.6 Hz, 2H), 3.61 (d, *J* = 15.6 Hz, 2H), 3.22 (s, 3H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 202.3, 166.8, 162.6, 137.1, 136.6, 134.5, 129.9, 128.6, 127.5, 127.0, 126.4, 124.2, 119.7, 119.0, 118.7, 118.5, 114.0, 113.3, 66.1, 49.6, 44.1, 29.6.
HRMS (FAB) *m/z*: $[M]^+$ calculated for $C_{32}H_{28}N_2O_5^+$: 520.1998, found 520.2011

3.2.9 Synthesis of 6-(2-Hydroxybenzoyl)-12-methyl-7-phenyl-7,12-dihydro-14*H*-chromeno[2,3-*b*]phenazin-14-one (4b)

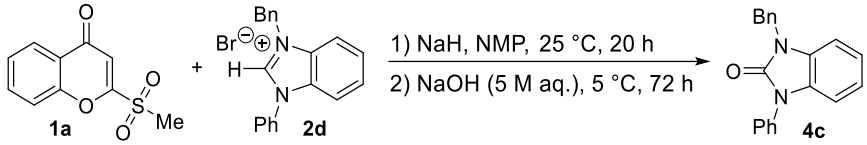


1a + **2c** → **4b**

Chromone **1a** (224 mg, 1.0 mmol, 1 equiv.), *N*-methyl-*N'*-phenylbenzimidazolium iodide **2c** (336 mg, 1.0 mmol, 1 equiv.), and NaH (80 mg, 2 mmol, 2 equiv., 60% dispersion in paraffin oil) were added to a flask. The flask was purged with argon. NMP (3 mL) was then added and the mixture was stirred at 25 °C in an EYELA ChemiStation PersonalSynthesizer PPS-CTRL1 machine for 21 h. The mixture was then cooled to 5 °C. A 5-molar aqueous NaOH solution (1.5 mL) was then added. The mixture was stirred at 5 °C in an EYELA ChemiStation PersonalSynthesizer PPS-CTRL1 machine for 72 h. The mixture was transferred to a separatory funnel. The mixture was washed with a saturated aqueous NH_4Cl solution. The aqueous layer was washed with CH_2Cl_2 three times. The combined organic layers were dried over anhydrous Na_2SO_4 and then concentrated under reduced pressure. The resulting oil was purified by silica gel medium-pressure liquid chromatography (eluent: 7:3 *n*-hexane/EtOAc). Analytically pure samples were obtained after size-exclusion HPLC (solvent: chloroform) and recrystallization from benzene.

Yield of **4b**: 94% (240 mg)
Red solid (recrystallized from benzene)
Rf: 0.70 (7:3 *n*-hexane:EtOAc)
Melting point: decomposes above 200 °C (from benzene)
^{1}H NMR (400 MHz, $CDCl_3$) δ 11.46 (s, 1H), 8.23 (dd, J = 7.9, 1.5 Hz, 1H), 7.45 (ddd, J = 8.7, 7.1, 1.7 Hz, 1H), 7.37 (ddd, J = 8.6, 7.1, 1.7 Hz, 1H), 7.28-7.23 (m, 4H; overlapped with C**H**Cl_3), 7.18 (s, 1H), 7.16 – 7.11 (m, 4H), 6.94 (dd, J = 8.5, 0.7 Hz, 1H), 6.87 (dd, J = 8.6, 1.1 Hz, 1H), 6.81 (td, J = 7.7, 1.4 Hz, 1H), 6.68 (ddd, J = 8.1, 7.1, 1.1 Hz, 1H), 6.56 – 6.45 (m, 2H), 6.17 (dd, J = 8.0, 1.3 Hz, 1H), 3.24 (s, 3H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 198.5, 174.9, 162.2, 155.6, 151.0, 143.2, 140.7, 137.3, 136.8, 136.5, 135.3, 133.7, 133.0, 132.3, 129.7, 128.7, 126.2, 124.4, 124.0, 121.7, 121.0, 120.9, 118.7, 117.9, 117.8, 116.1, 115.8, 113.2, 112.1, 105.7, 33.4.
HRMS (FAB) *m/z*: $[M]^+$ calculated for $C_{33}H_{22}N_2O_4^+$: 510.1580; found 510.1596

3.2.10 Synthesis of 1-Benzyl-3-phenyl-2*H*-benzimidazol-2-one (4c)[15]



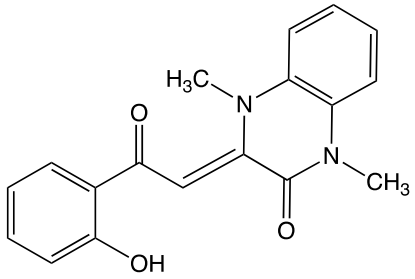
1a + **2d** → **4c**

Chromone **1a** (500 mg, 2.2 mmol, 1 equiv.), benzimidazolium salt **2d** (815 mg, 2.2 mmol, 1 equiv.), and NaH (178 mg, 4.5 mmol, 2 equiv., 60% dispersion in paraffin oil) were added to a flask. The flask was purged with argon. NMP (3 mL) was then added and the mixture was stirred at 25 °C in an EYELA ChemiStation PersonalSynthesizer PPS-CTRL1 machine for 20 h. The mixture was then cooled to 5 °C. A 5-molar aqueous NaOH solution (2 mL) was then added. The mixture was stirred at 5 °C in an EYELA ChemiStation PersonalSynthesizer PPS-CTRL1 machine for 72 h. The mixture was transferred to a separatory funnel. The mixture was washed with a saturated aqueous NH_4Cl solution. The aqueous layer was washed with CH_2Cl_2 three times. The combined organic layers were dried over anhydrous Na_2SO_4 and then concentrated under reduced pressure. The resulting oil was purified by silica gel medium-pressure liquid chromatography (eluent: 7:3 *n*-hexane/EtOAc).

Yield of **4c**: 55% (368 mg)
Data is in accordance with literature.[15]
Colorless solid
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.46 (m, 4H), 7.43 – 7.36 (m, 2H), 7.41 – 7.22 (m, 4H), 7.13 – 6.90 (m, 4H), 5.13 (s, 2H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 153.6, 136.3, 134.8, 129.5, 129.5, 129.4, 128.8, 127.8, 127.7, 127.6, 126.0, 122.0, 121.6, 108.8, 108.5, 45.1.
HRMS (ESI) *m/z*: $[M+Na]^+$ calculated for $C_{20}H_{16}N_2O^{23}Na^+$: 323.1160, found 323.1164

4. Data for X-ray Analyses

4.1 X-ray Diffraction Analysis of (*Z*)-1,4-dimethyl-3-[(2-hydroxyphenyl]-2-oxoethylidene]-3,4-dihydroquinoxalin-2(1*H*)-one (3a)



Chemical Formula: $C_{18}H_{16}N_2O_3$
Exact Mass: 308.11609
Molecular Weight: 308.33700
m/z: 308.11609 (100.0%), 309.11945 (19.5%), 310.12280 (1.8%)
Elemental Analysis: C, 70.12; H, 5.23; N, 9.09; O, 15.57

Crystals were obtained from a dichloromethane solution by exposing to hexane vapor. An orange block crystal (0.25 × 0.20 × 0.15 mm) was mounted on a polyimide film, MicroMounts™ (MiTegen), and coated with paraffin. All measurements were made on a Rigaku XtaLAB Synergy-S diffractometer using multi-layer mirror monochromated Cu-*Kα* radiation at 153K. Data were collected and processed using CrysAlisPro (Rigaku Oxford Diffraction).[16] The structure was solved by direct methods[17] and expanded using Fourier techniques. Non-hydrogen atoms were refined anisotropically. Some hydrogen atoms were refined isotropically and the rest were refined using the riding model. The final cycle of full-matrix least-squares refinement on F^2 was based on 2558 observed reflections and 214 variable parameters. All calculations were performed using the CrystalStructure[18] crystallographic software package except for refinement, which was performed using SHELXL97.[19] Crystallographic data are summarized in Table S4. CIF data were deposited in Cambridge Structural Database (CCDC-2291932).

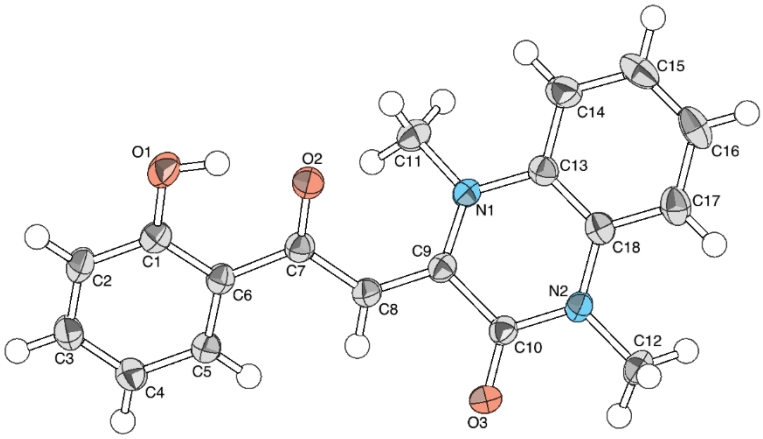
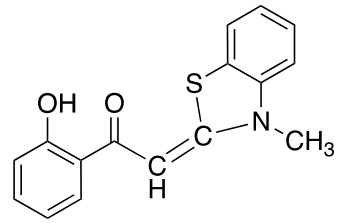


Figure S2. Molecular structure of **3a**.

Table S4. Crystal data and structure refinement for **3a**.

	Compound **3a**
Empirical Formula	$C_{18}H_{16}N_2O_3$
Formula Weight	308.34
Crystal Color, Habit	orange, block
Crystal Dimensions	0.25 × 0.20 × 0.15 mm
Crystal System	orthorhombic
Lattice Type	Primitive
Space Group	$P2_12_12_1$ (#19)
Lattice Parameters	*a* = 7.89055(11) Å *b* = 8.30596(12) Å *c* = 22.2467(4) Å *V* = 1458.02(4) Å^3
Z value	4
Absorption coefficient	7.934 cm^{-1}
Radiation	CuKα (*λ* = 1.54187 Å) multi-layer mirror monochromated
Temperature	153 K
No. Of Reflections Measured	Total: 5252 Unique: 2558 (R_{int} = 0.0323) Friedel pairs: 995
Corrections	Lorentz-polarization Absorption (trans. Factors: 0.864 – 0.888)
No. Of Reflections	2558
No. Variables	214
Reflection/Parameter Ratio	11.95
Residuals: *R*; *wR* (All data)	0.0358; 0.0883
Residuals: R_1	0.0340
No. of Reflections to calc R_1	2431
Goodness of Fit Indicator	0.983
Flack Parameter	-0.1(2)
Max Shift/Error in Final Cycle	0.000
Maximum peak in Final Diff. Map (e Å^3)	0.14
Minimum peak in Final Diff. Map (e Å^3)	–0.18
CCDC#	2291932

4.2 X-ray Diffraction Analysis of (*Z*)-1-(2-hydroxyphenyl)-2-[(3-methyl-2(3*H*)-benzothiazolylidene]ethan-1-one (3b')



Chemical Formula: $C_{16}H_{13}NO_2S$
Exact Mass: 283.06670
Molecular Weight: 283.34500

Crystals were obtained from a dichloroethane solution by exposing to hexane vapor. A yellow plate crystal (0.28 × 0.13 × 0.04 mm) was mounted on a polyimide film, MicroMounts™ (MiTegen), and coated with perfluoropolyalkyl ether (F06206R, ABCR). All measurements were made on a Rigaku XtaLAB Synergy-S diffractometer using multi-layer mirror monochromated Cu-*Kα* radiation at 153K. Data were collected and processed using CrysAlisPro (Rigaku Oxford Diffraction).[16] The structure was solved by direct methods[17] and expanded using Fourier techniques. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. The final cycle of full-matrix least-squares refinement on F^2 was based on 2317 observed reflections and 182 variable parameters. All calculations were performed using the CrystalStructure[18] crystallographic software package except for refinement, which was performed using SHELXL97.[19] Crystallographic data are summarized in Table S5. CIF data were deposited in Cambridge Structural Database (CCDC- 2291930).

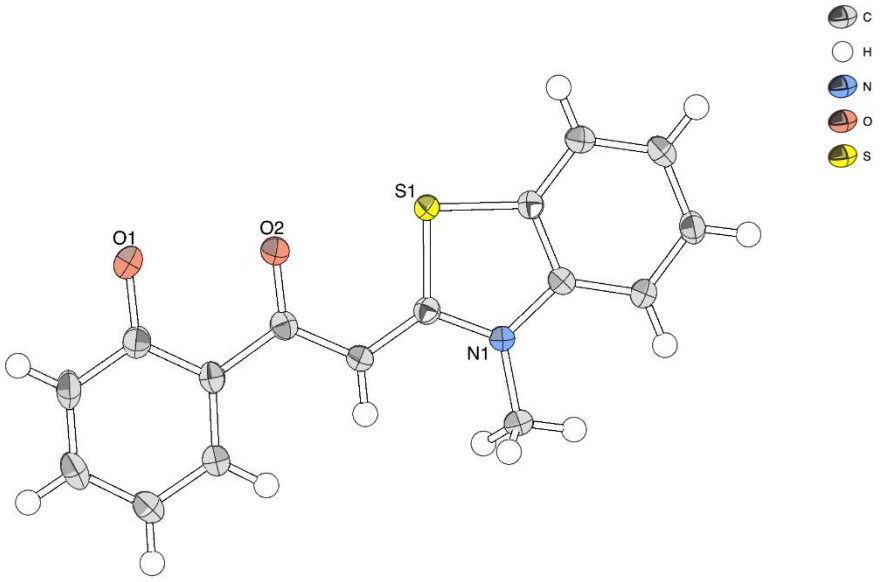
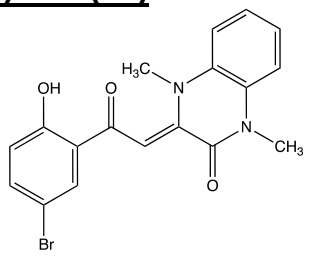


Figure S3. Molecular structure of **3b'**.

Table S5. Crystal data and structure refinement for **3b'**.

	Compound **3b'**
Empirical Formula	$C_{16}H_{12}NO_2S$
Formula Weight	282.34
Crystal Color, Habit	yellow, plate
Crystal Dimensions	0.28 × 0.13 × 0.04 mm
Crystal System	Triclinic
Lattice Type	Primitive
Space Group	P-1 (#2)
Lattice Parameters	*a* = 7.0044(4) Å *b* = 8.4419(3) Å *c* = 11.6565(4) Å *α* = 96.906(3) ° *β* = 95.814(4) ° *γ* = 109.537(4) ° *V* = 637.44(5) Å^3
Z value	2
Absorption coefficient	22.583 cm^{-1}
Radiation	CuKα (*λ* = 1.54184 Å) multi-layer mirror monochromated
Temperature	153 K
No. of Reflections Measured	Total: 6530 Unique: 2317 (R_{int} = 0.0346)
Corrections	Lorentz-polarization Absorption (trans. Factors: 0.702 – 0.914)
No. of Reflections	2317
No. Variables	182
Reflection/Parameter Ratio	12.73
Residuals: *R*; *wR* (All data)	0.0395; 0.1063
Residuals: R_1	0.0373
No. of Reflections to calc R_1	2152
Goodness of Fit Indicator	1.086
Max Shift/Error in Final Cycle	0.004
Maximum peak in Final Diff. Map (e Å^3)	0.47
Minimum peak in Final Diff. Map (e Å^3)	–0.34
CCDC#	2291930

4.3 X-ray Diffraction Analysis of (*Z*)-3-[(5-bromo-2-hydroxyphenyl)-2-oxoethylidene]-1,4-dimethyl-3,4-dihydroquinoxalin-2(1*H*)-one (3h)



Chemical Formula: $C_{18}H_{15}BrN_2O_3$
Exact Mass: 386.02660
Molecular Weight: 387.23
Elemental Analysis: C, 55.83; H, 3.90; Br, 20.63; N, 7.23; O, 12.39

Crystals were obtained from a dichloromethane solution by exposing to hexane vapor. An orange block crystal (0.27 × 0.20 × 0.16 mm) was mounted on a polyimide film, MicroMounts™ (MiTegen), and coated with paraffin. All measurements were made on a Rigaku XtaLAB Synergy-S diffractometer using multi-layer mirror monochromated Cu-*Kα* radiation at 153K. Data were collected and processed using CrysAlisPro (Rigaku Oxford Diffraction).[16] The structure was solved by direct methods[17] and expanded using Fourier techniques. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. The final cycle of full-matrix least-squares refinement on F^2 was based on 2819 observed reflections and 220 variable parameters. All calculations were performed using the CrystalStructure[18] crystallographic software package except for refinement, which was performed using SHELXL97.[19] Crystallographic data are summarized in Table S6. CIF data were deposited in Cambridge Structural Database (CCDC-2291931).

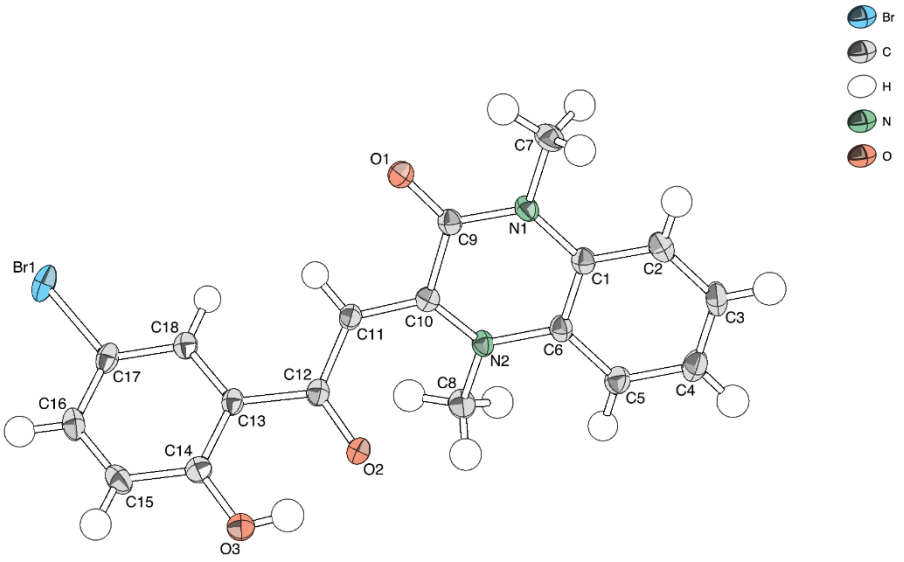
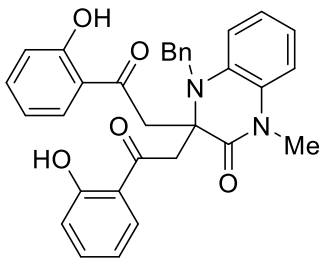


Figure S4. Molecular structure of **3h**.

Table S6. Crystal data and structure refinement for **3h**.

	Compound **3h**
Empirical Formula	$C_{18}H_{15}BrN_2O_3$
Formula Weight	387.23
Crystal Color, Habit	orange, block
Crystal Dimensions	0.27 × 0.20 × 0.16 mm
Crystal System	Triclinic
Lattice Type	Primitive
Space Group	P-1 (#2)
Lattice Parameters	*a* = 8.9075(4) Å *b* = 9.0424(5) Å *c* = 10.1037(4) Å *α* = 106.034(4) ° *β* = 92.104(3) ° *γ* = 97.174(4) ° *V* = 773.86(7) Å^3
Z value	2
Absorption coefficient	37.990 cm^{-1}
Radiation	CuKα (*λ* = 1.54184 Å) multi-layer mirror monochromated
Temperature	153 K
No. Of Reflections Measured	Total: 8549 Unique: 2819 (R_{int} = 0.0349)
Corrections	Lorentz-polarization Absorption (trans. Factors: 0.472 – 0.545)
No. Of Reflections	2819
No. Variables	220
Reflection/Parameter Ratio	12.81
Residuals: *R*; *wR* (All data)	0.0297; 0.0729
Residuals: R_1	0.0287
No. of Reflections to calc R_1	2724
Goodness of Fit Indicator	1.209
Max Shift/Error in Final Cycle	0.001
Maximum peak in Final Diff. Map (e Å^3)	0.30
Minimum peak in Final Diff. Map (e Å^3)	–0.56
CCDC#	2291931

4.4 X-ray Diffraction Analysis of 4-Benzyl-3,3-bis[(2-hydroxybenzoyl)methyl]-1-methyl-3,4-dihydroquinoxalin-2(1*H*)-one (4a)



Chemical Formula: $C_{32}H_{28}N_2O_5$
Exact Mass: 520.1998
Molecular Weight: 520.5850

Crystals were obtained from a dichloroethane solution by exposing to hexane vapor. A yellow plate crystal (0.24 × 0.12 × 0.04 mm) was mounted on a polyimide film, MicroMounts™ (MiTegen), and coated with perfluoropolyalkyl ether (F06206R, ABCR). All measurements were made on a Rigaku XtaLAB Synergy-S diffractometer using multi-layer mirror monochromated Cu-*Kα* radiation at 153K. Data were collected and processed using CrysAlisPro (Rigaku Oxford Diffraction).[16] The structure was solved by direct methods[17] and expanded using Fourier techniques. The cell units consist of two crystallographically independent molecules of **4a** which have fundamentally identical structures. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. The final cycle of full-matrix least-squares refinement on F^2 was based on 8131 observed reflections and 705 variable parameters. All calculations were performed using the CrystalStructure[18] crystallographic software package except for refinement, which was performed using SHELXL97.[19] Crystallographic data are summarized in Table S7. CIF data were deposited in Cambridge Structural Database (CCDC-2291929).

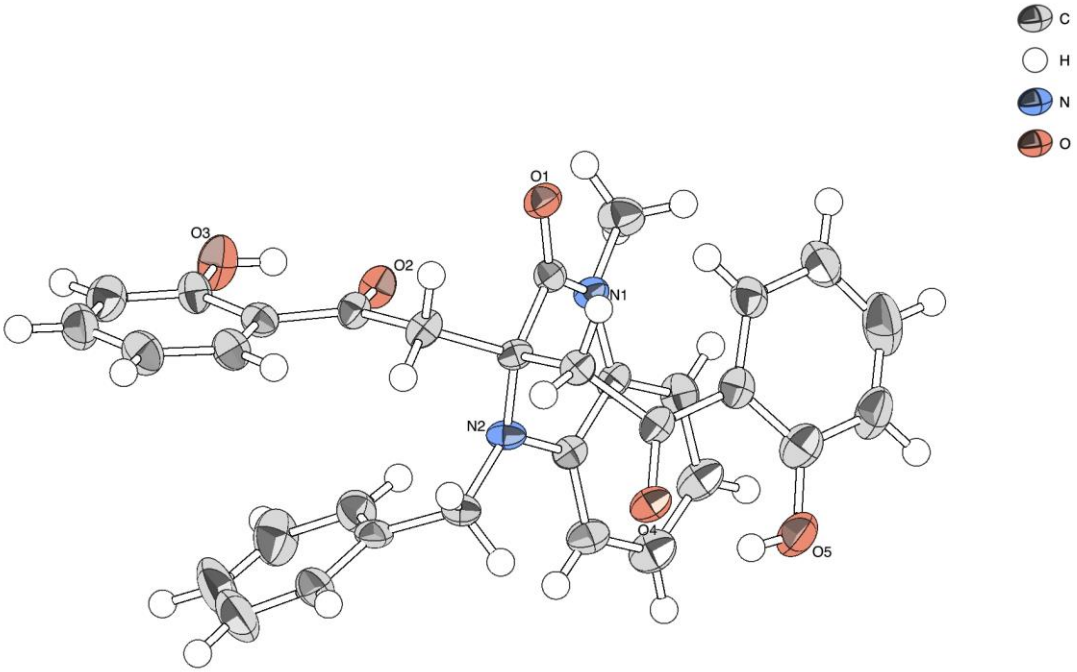
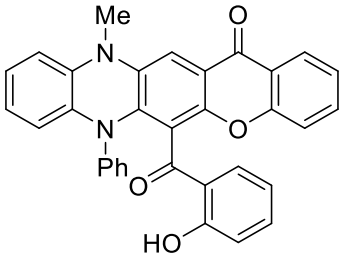


Figure S5. Molecular structure of **4a**.

Table S7. Crystal data and structure refinement for **4a**.

	Compound **4a**
Empirical Formula	$C_{32}H_{28}N_2O_3$
Formula Weight	520.58
Crystal Color, Habit	yellow, plate
Crystal Dimensions	0.24 × 0.12 × 0.04 mm
Crystal System	monoclinic
Lattice Type	Primitive
Space Group	Pn (#7)
Lattice Parameters	*a* = 8.8903(2) Å *b* = 11.6219(3) Å *c* = 25.8312(6) Å *β* = 97.715(2) ° *V* = 2644.78(11 Å^3
Z value	4
Absorption coefficient	7.214 cm^{-1}
Radiation	CuKα (*λ* = 1.54184 Å) multi-layer mirror monochromated
Temperature	153 K
No. of Reflections Measured	Total: 18280 Unique: 8131 (R_{int} = 0.0470)
Corrections	Lorentz-polarization Absorption (trans. factors: 0.813 – 0.972)
No. of Reflections	8131
No. Variables	705
Reflection/Parameter Ratio	11.53
Residuals: *R*; *wR* (All data)	0.1166; 0.3305
Residuals: R_1	0.1137
No. of Reflections to calc R_1	7599
Goodness of Fit Indicator	1.545
Max Shift/Error in Final Cycle	0.002
Maximum peak in Final Diff. Map (e Å^3)	1.30
Minimum peak in Final Diff. Map (e Å^3)	–0.43
CCDC#	2291929

4.5 X-ray Diffraction Analysis of 6-(2-Hydroxybenzoyl)-12-methyl-7-phenyl-7,12-dihydro-14*H*-chromeno[2,3-*b*]phenazin-14-one (4b)



Chemical Formula: $C_{33}H_{22}N_2O_4$
Exact Mass: 510.1580
Molecular Weight: 510.5490

Crystals were obtained from a benzene solution by slow evaporation. A brown needle crystal (0.16 × 0.01 × 0.01 mm) was mounted on a polyimide film, MicroMounts™ (MiTegen), and coated with perfluoropolyalkyl ether (F06206R, ABCR). All measurements were made on a Rigaku XtaLAB Synergy-S diffractometer using multi-layer mirror monochromated Cu-*Kα* radiation at 153K. Data were collected and processed using CrysAlisPro (Rigaku Oxford Diffraction).[16] The structure was solved by direct methods[17] and expanded using Fourier techniques. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. The final cycle of full-matrix least-squares refinement on F^2 was based on 4689 observed reflections and 380 variable parameters. All calculations were performed using the CrystalStructure[18] crystallographic software package except for refinement, which was performed using SHELXL97.[19] Crystallographic data are summarized in Table S8. CIF data were deposited in Cambridge Structural Database (CCDC-2291928).

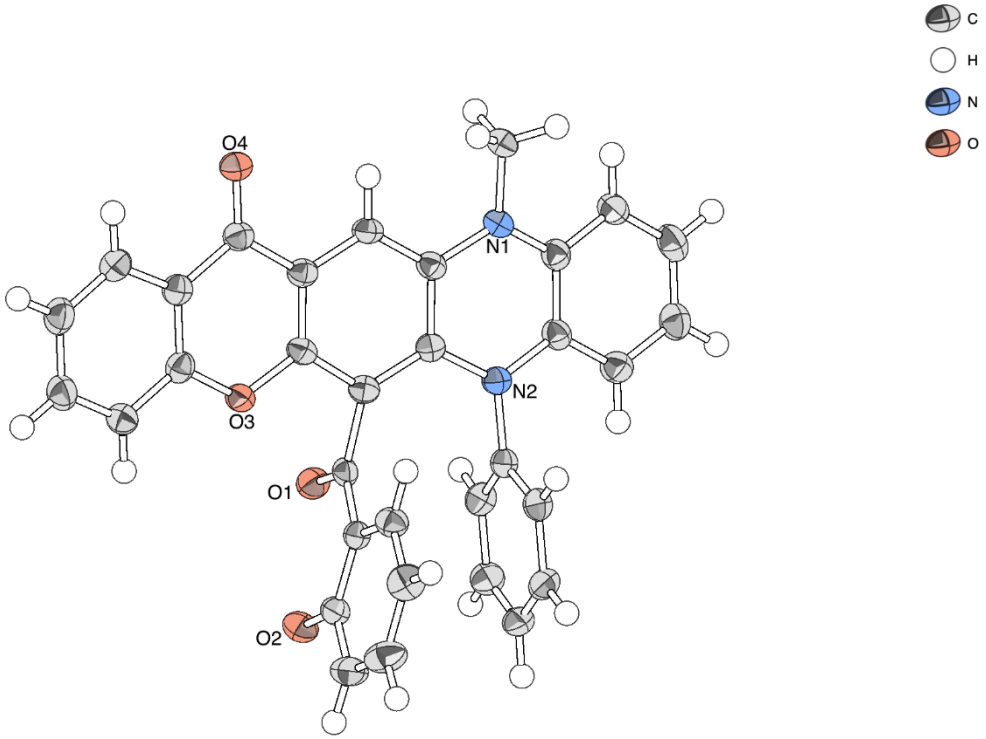


Figure S6. Molecular structure of **4b**.

Table S8. Crystal data and structure refinement for **4b**.

	Compound **4b**
Empirical Formula	$C_{36}H_{24}N_2O_4$
Formula Weight	548.60
Crystal Color, Habit	brown, needle
Crystal Dimensions	0.16 × 0.01 × 0.01 mm
Crystal System	Triclinic
Lattice Type	Primitive
Space Group	P-1 (#2)
Lattice Parameters	*a* = 7.5025(4) Å *b* = 13.4118(6) Å *c* = 14.2343(5) Å *α* = 103.527(4) ° *β* = 104.171(4) ° *γ* = 101.131(4) ° *V* = 1301.70(11) Å^3
Z value	2
Absorption coefficient	7.408 cm^{-1}
Radiation	CuKα (*λ* = 1.54184 Å) multi-layer mirror monochromated
Temperature	153 K
No. of Reflections Measured	Total: 14514 Unique: 4689 (R_{int} = 0.0524)
Corrections	Lorentz-polarization Absorption (trans. Factors: 0.5442 – 0.993)
No. of Reflections	4689
No. Variables	380
Reflection/Parameter Ratio	12.34
Residuals: *R*; *wR* (All data)	0.0728; 0.1502
Residuals: R_1	0.0555
No. of Reflections to calc R_1	3784
Goodness of Fit Indicator	1.099
Max Shift/Error in Final Cycle	0.000
Maximum peak in Final Diff. Map (e Å^3)	0.50
Minimum peak in Final Diff. Map (e Å^3)	–0.24
CCDC#	2291928

5. References

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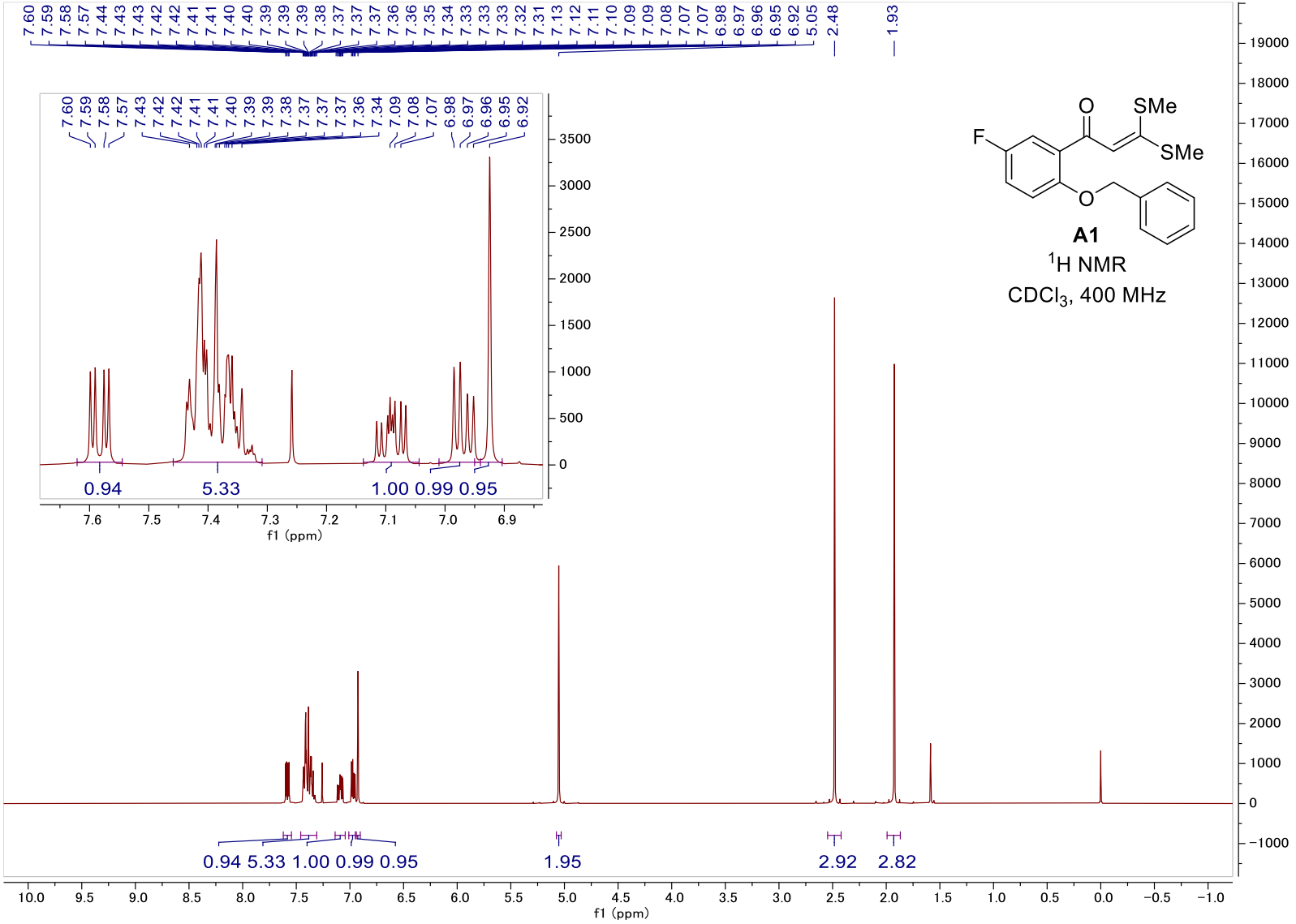
6. Spectral Data

^{1}H NMR for 1-[2-(benzyloxy)-5-fluorophenyl]-3,3-bis(methylthio)prop-2-en-1-one (**A1**) ($CDCl_3$, 400 MHz)



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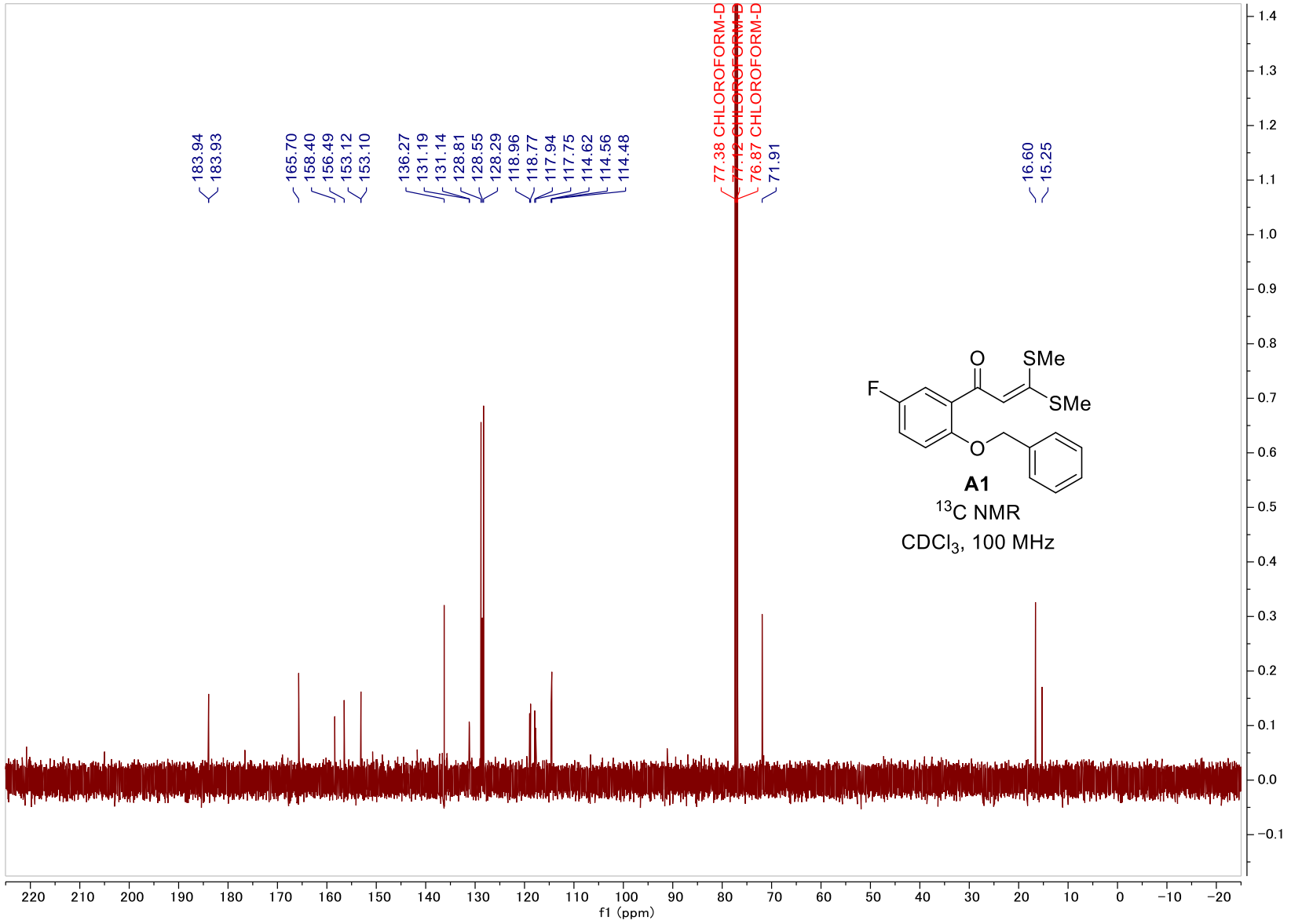
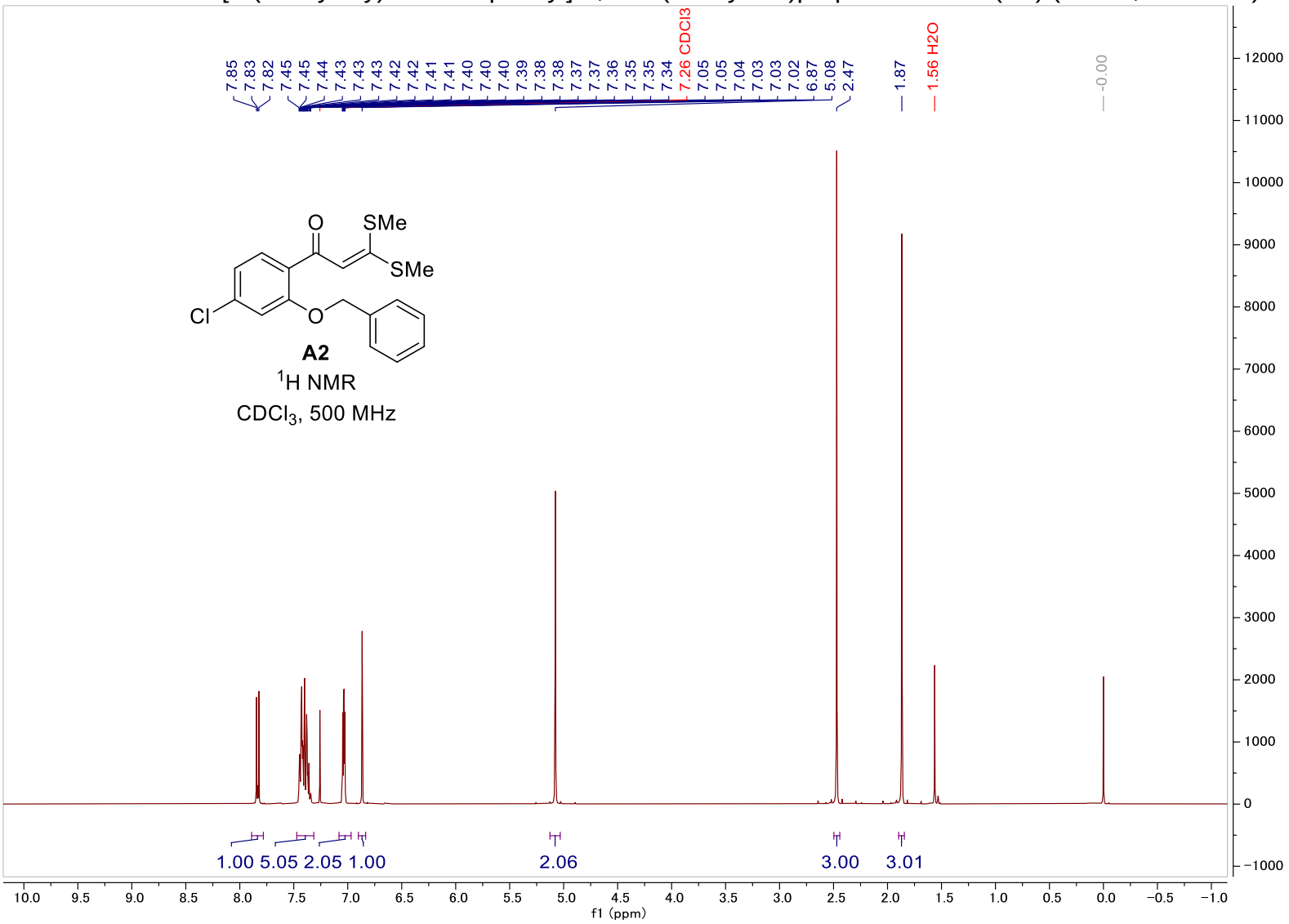


^{1}H NMR for 1-[2-(benzyloxy)-4-chlorophenyl]-3,3-bis(methylthio)prop-2-en-1-one (**A2**) ($CDCl_3$, 500 MHz)



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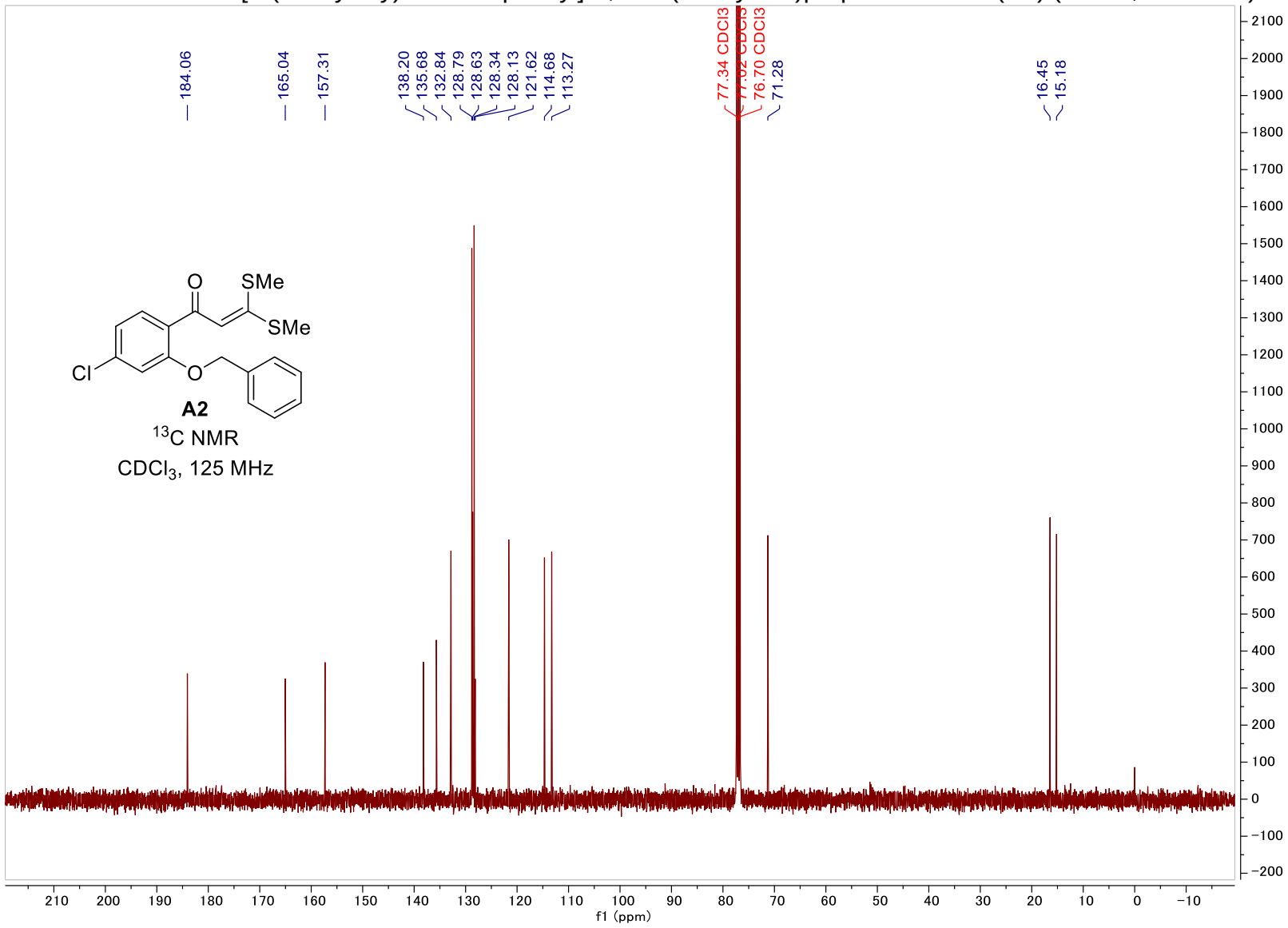

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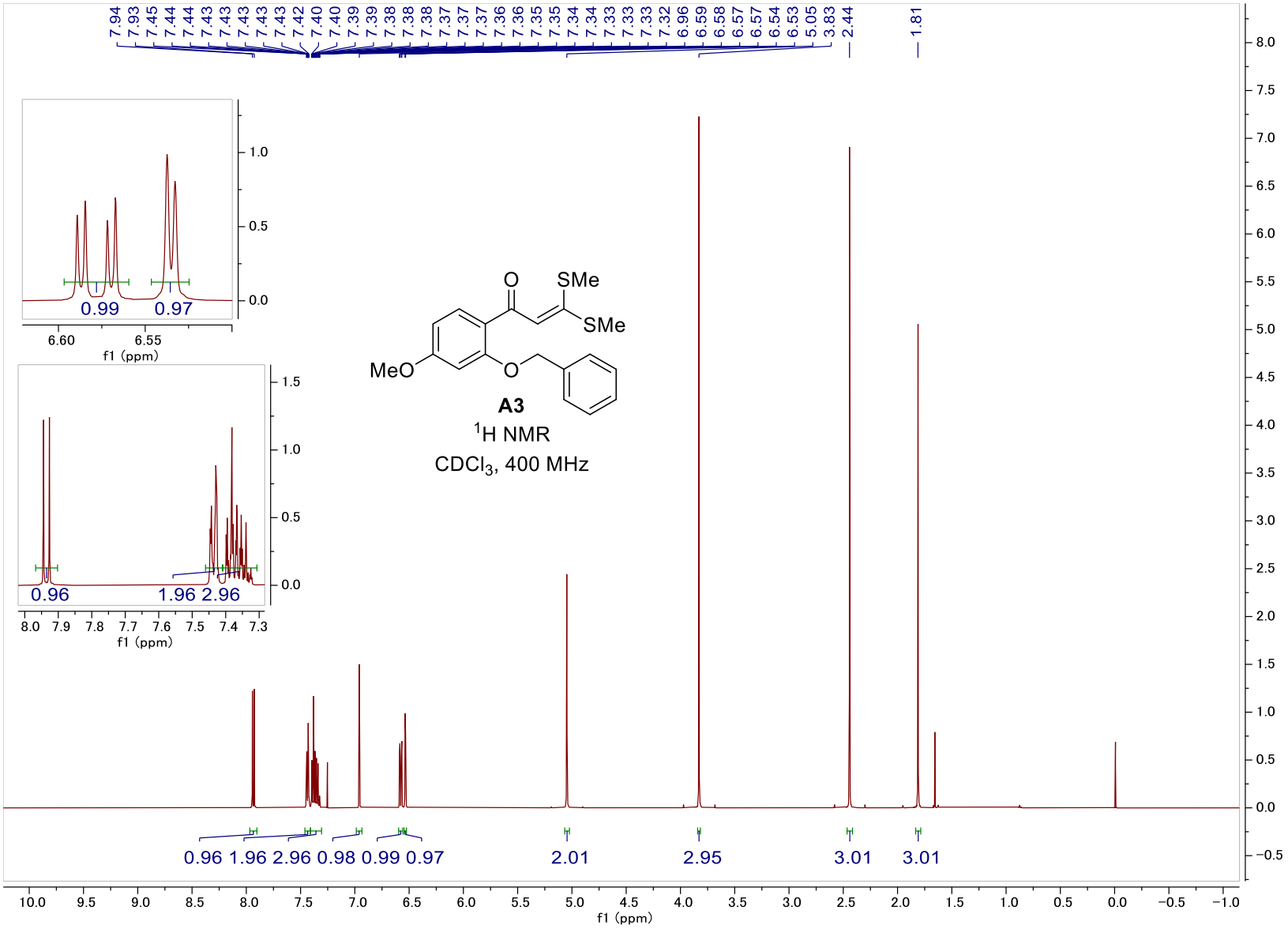

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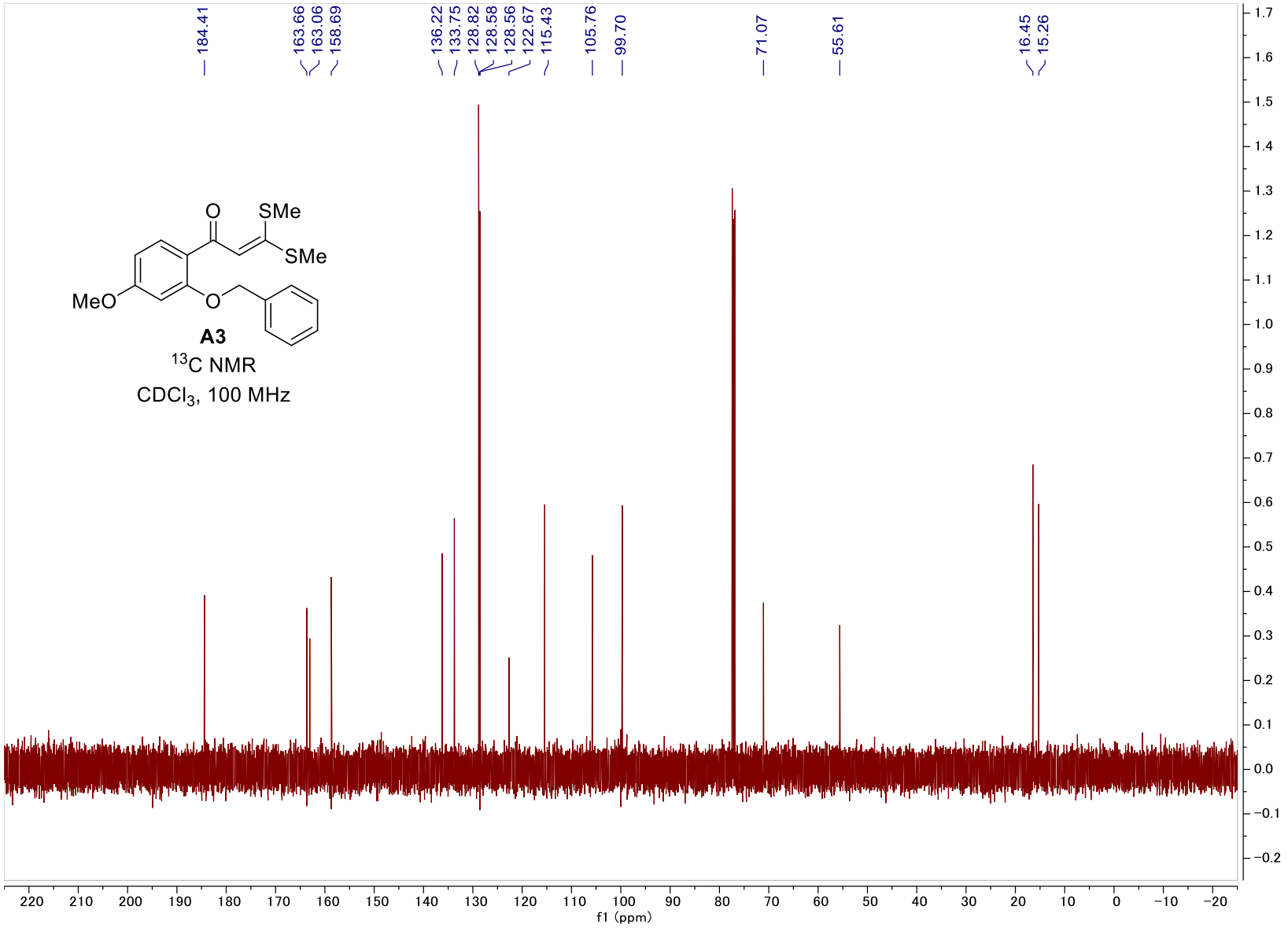
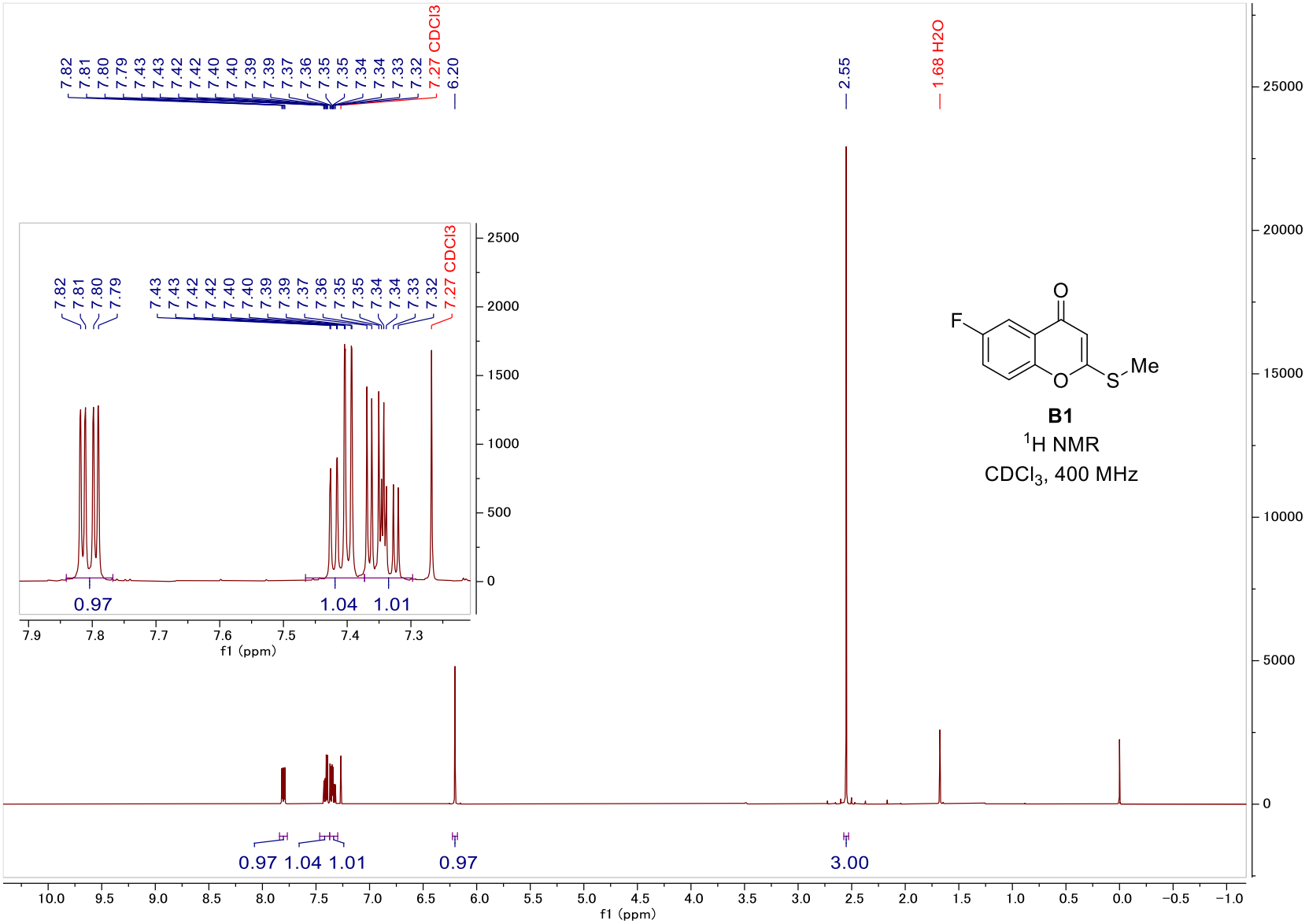


^{1}H NMR for 6-fluoro-2-(methylthio)chromone (**B1**) ($CDCl_3$, 400 MHz)



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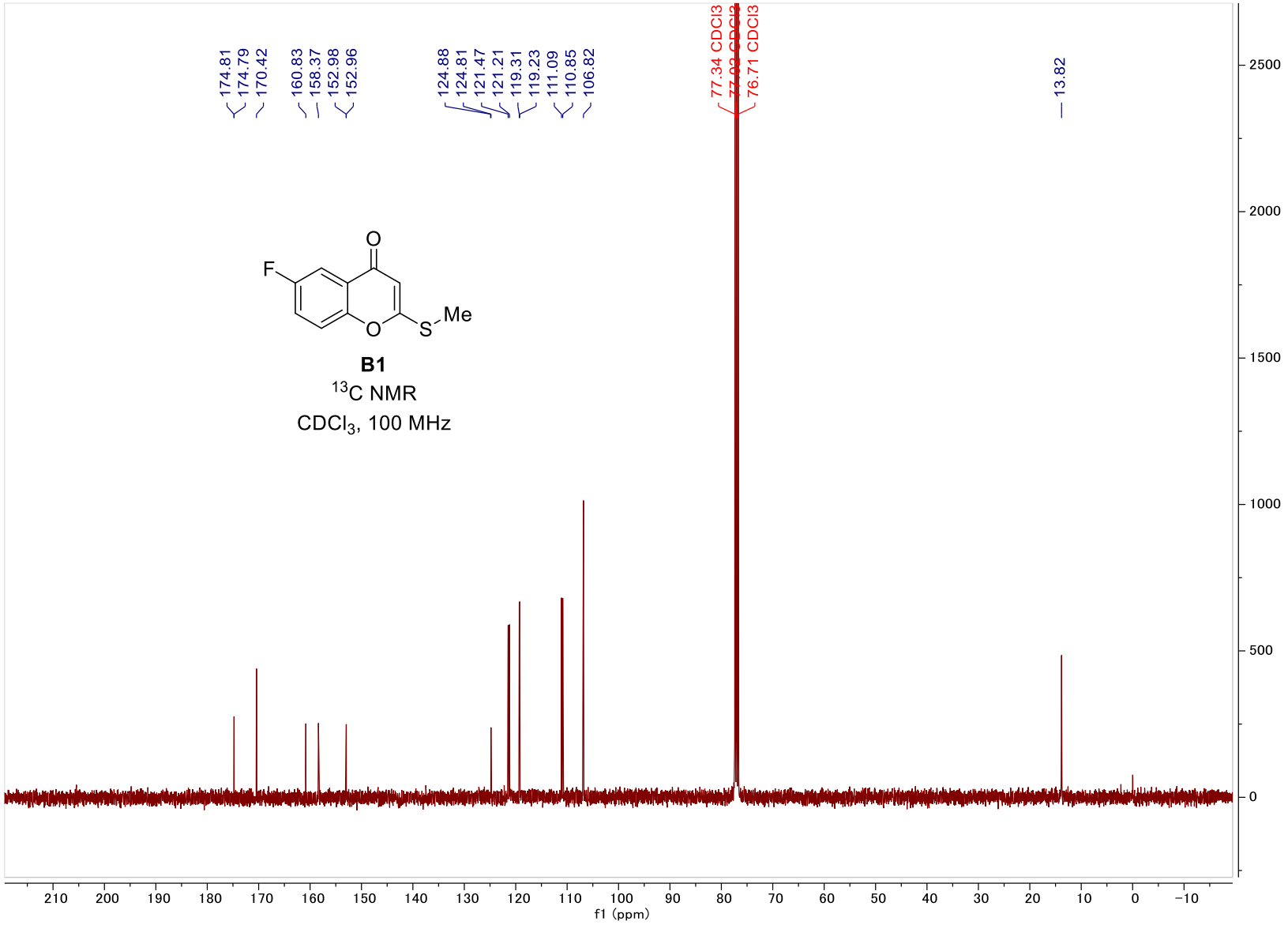

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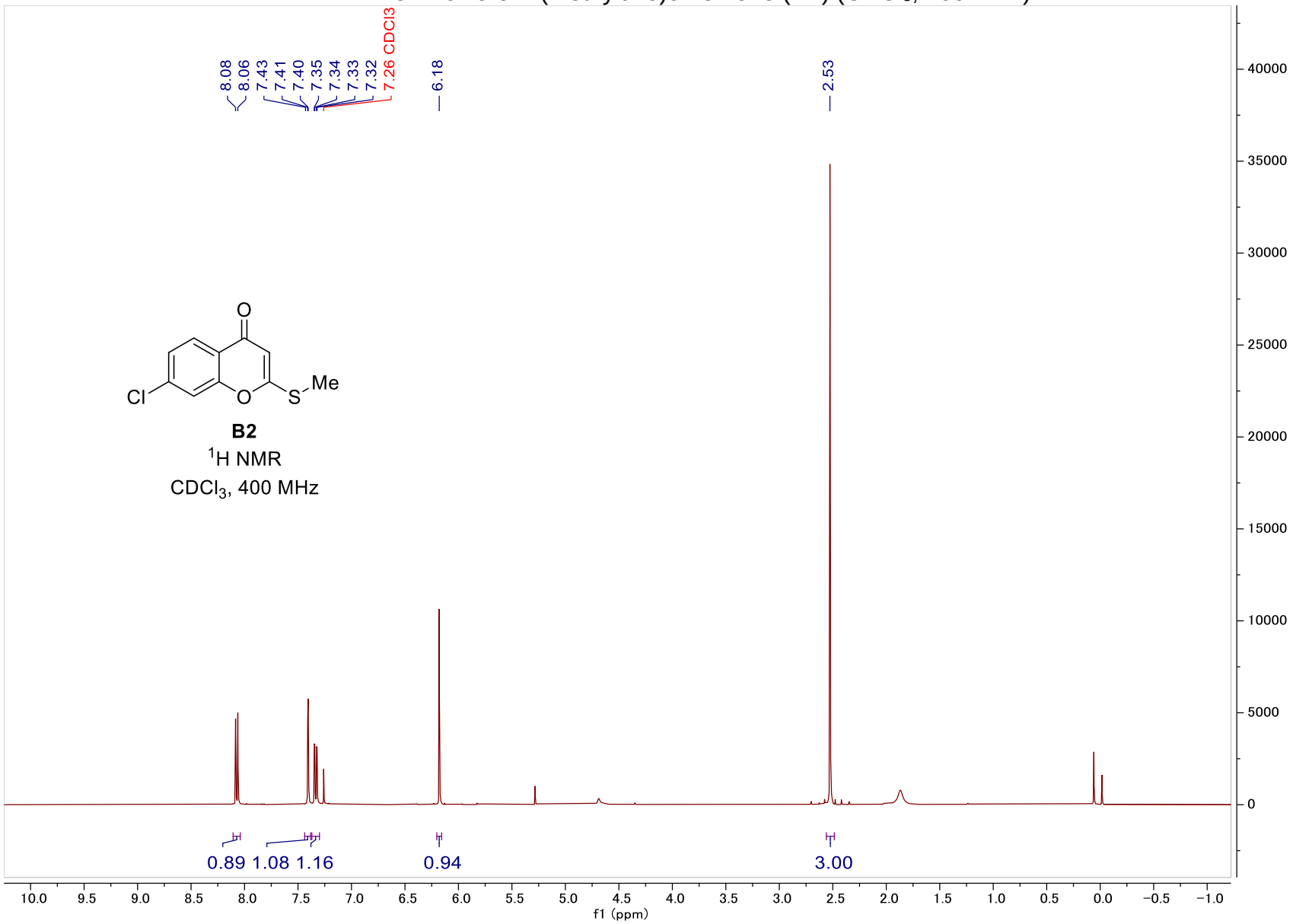

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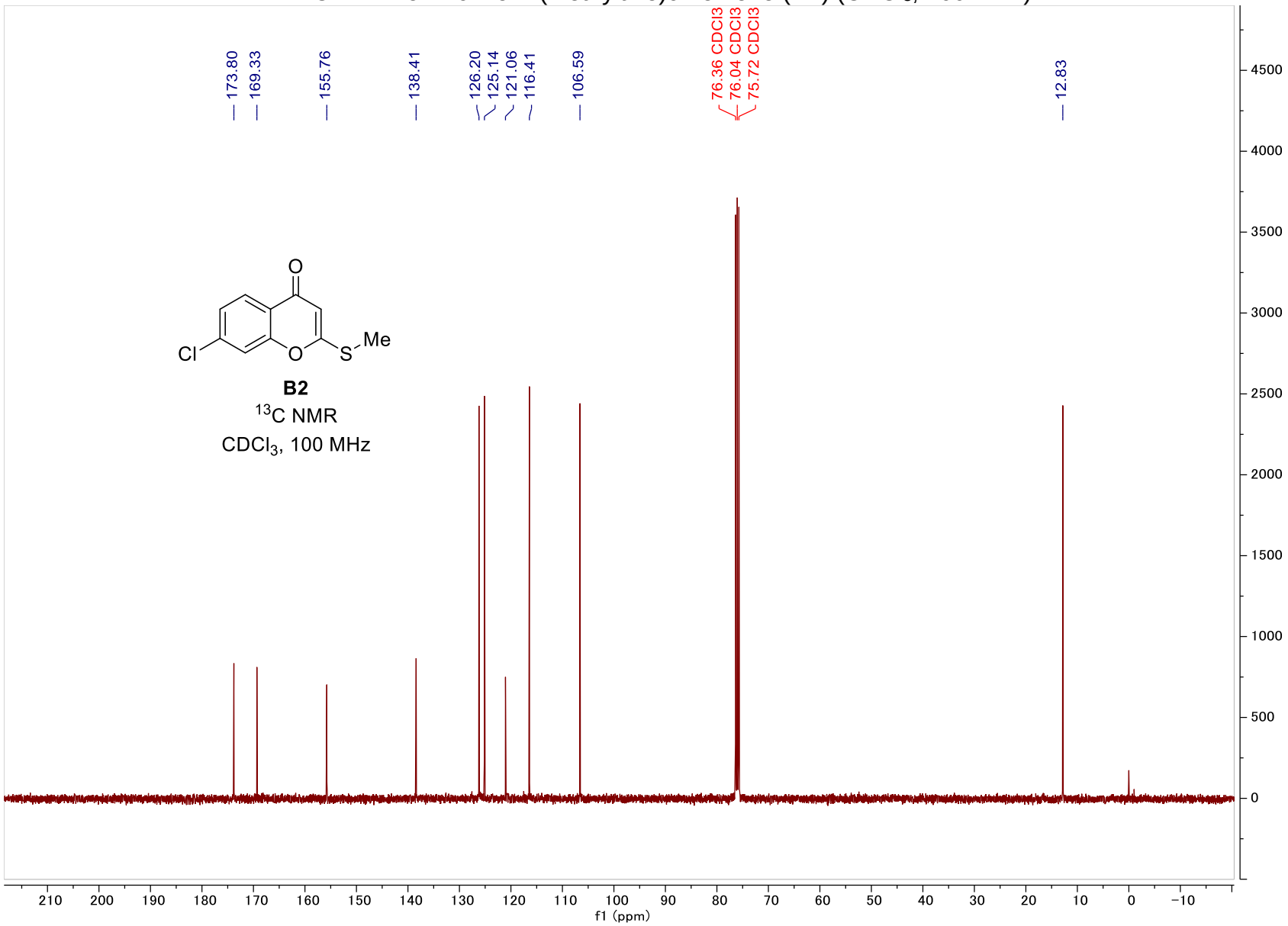

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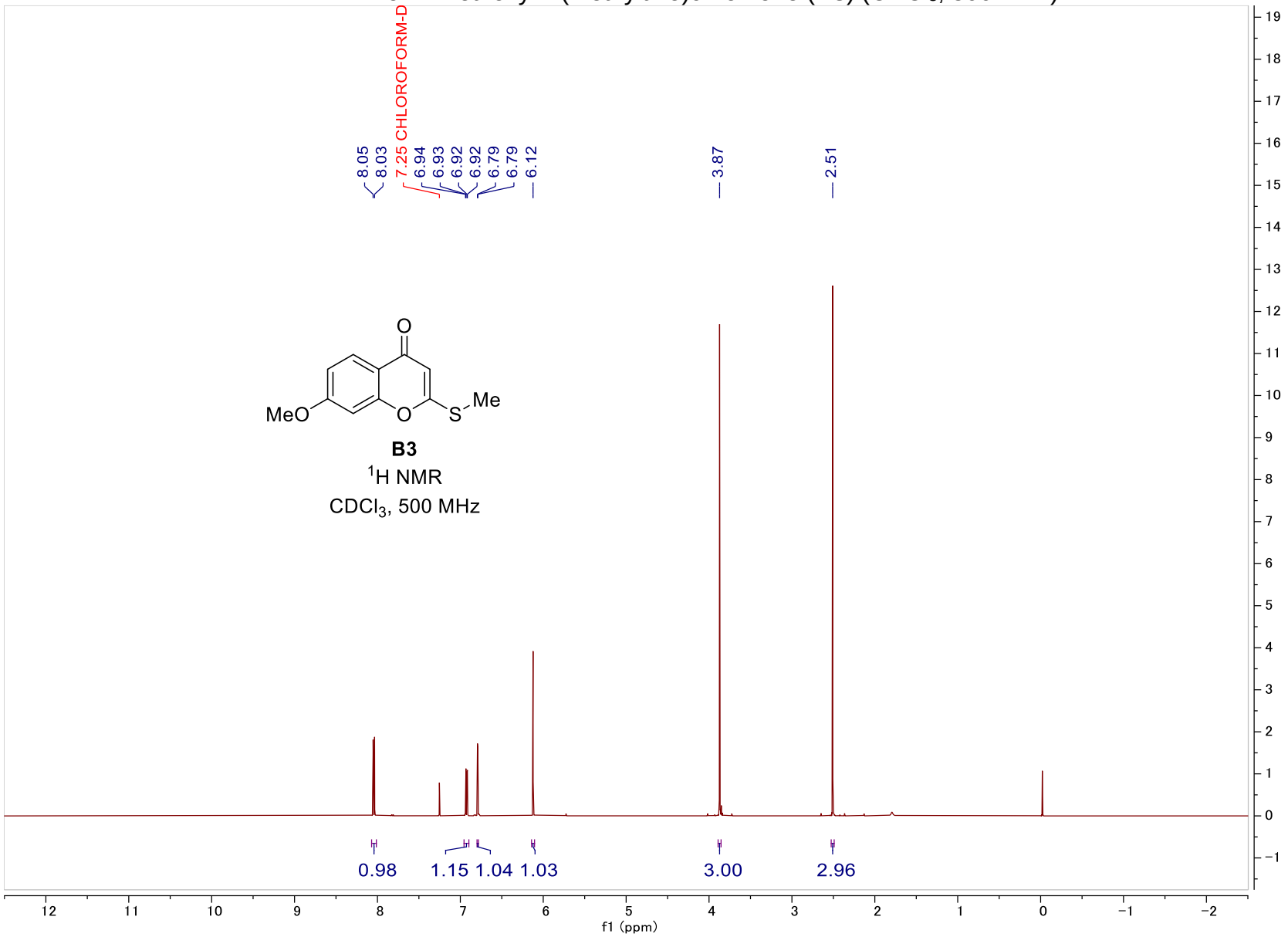

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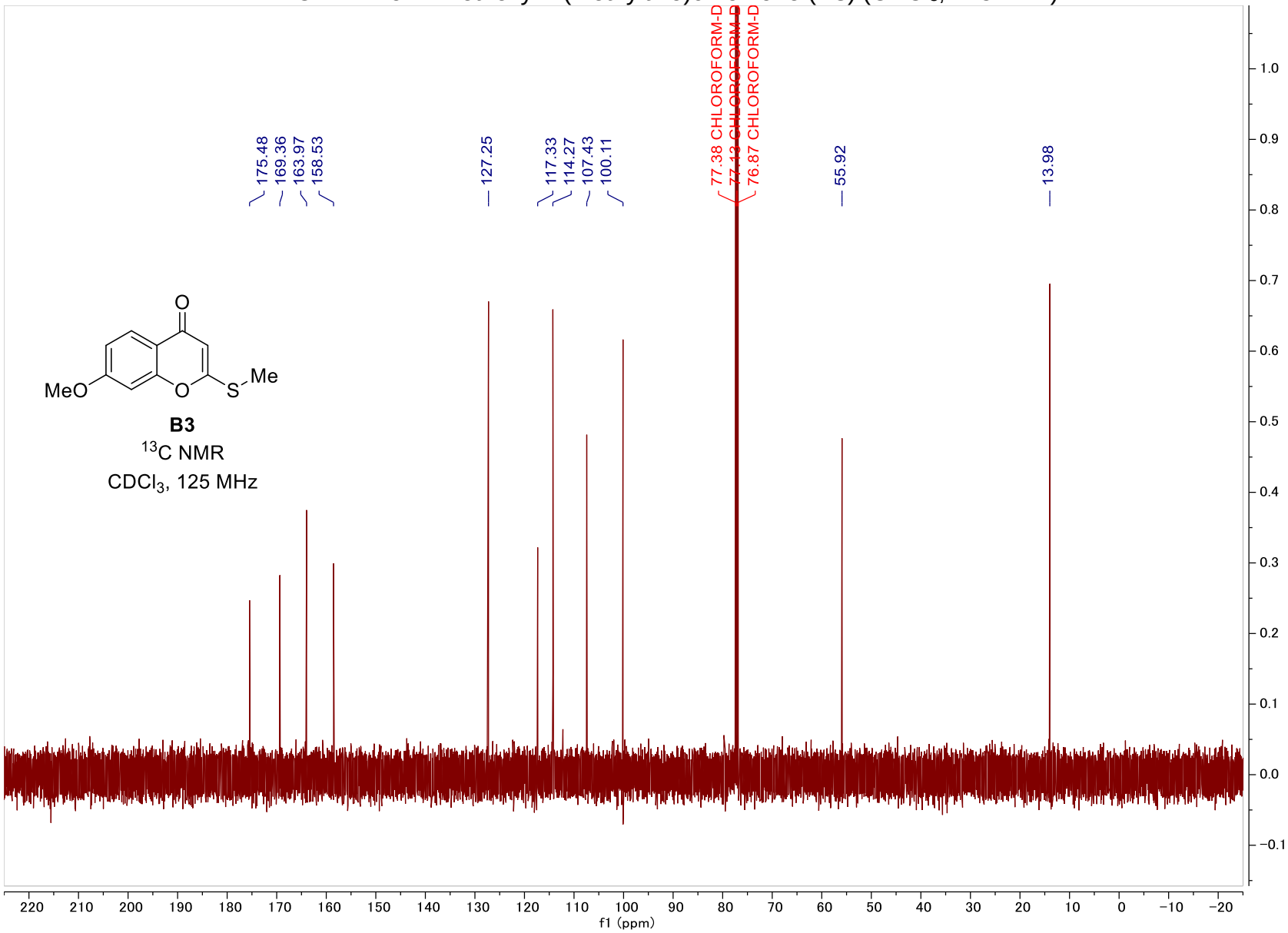
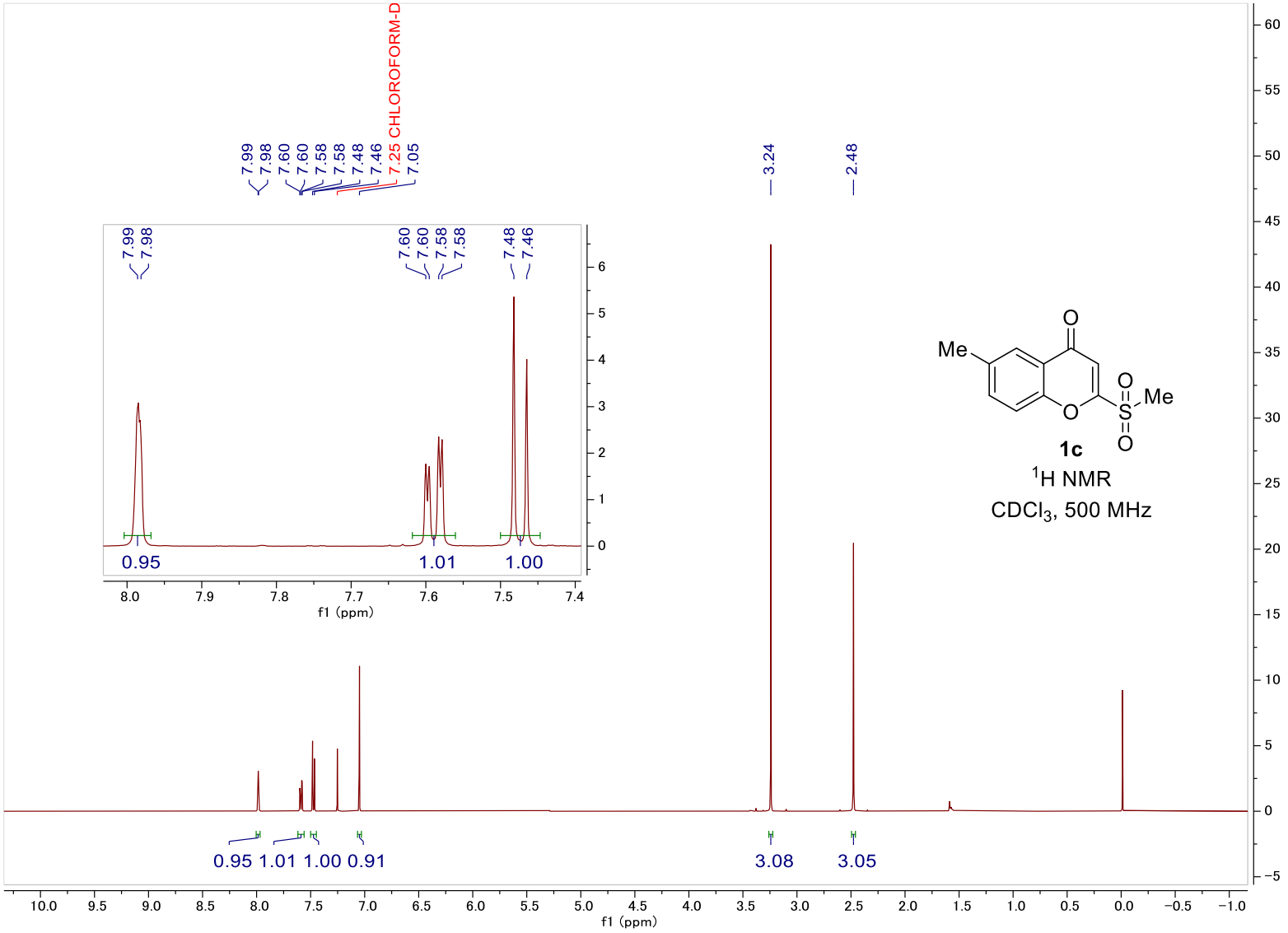
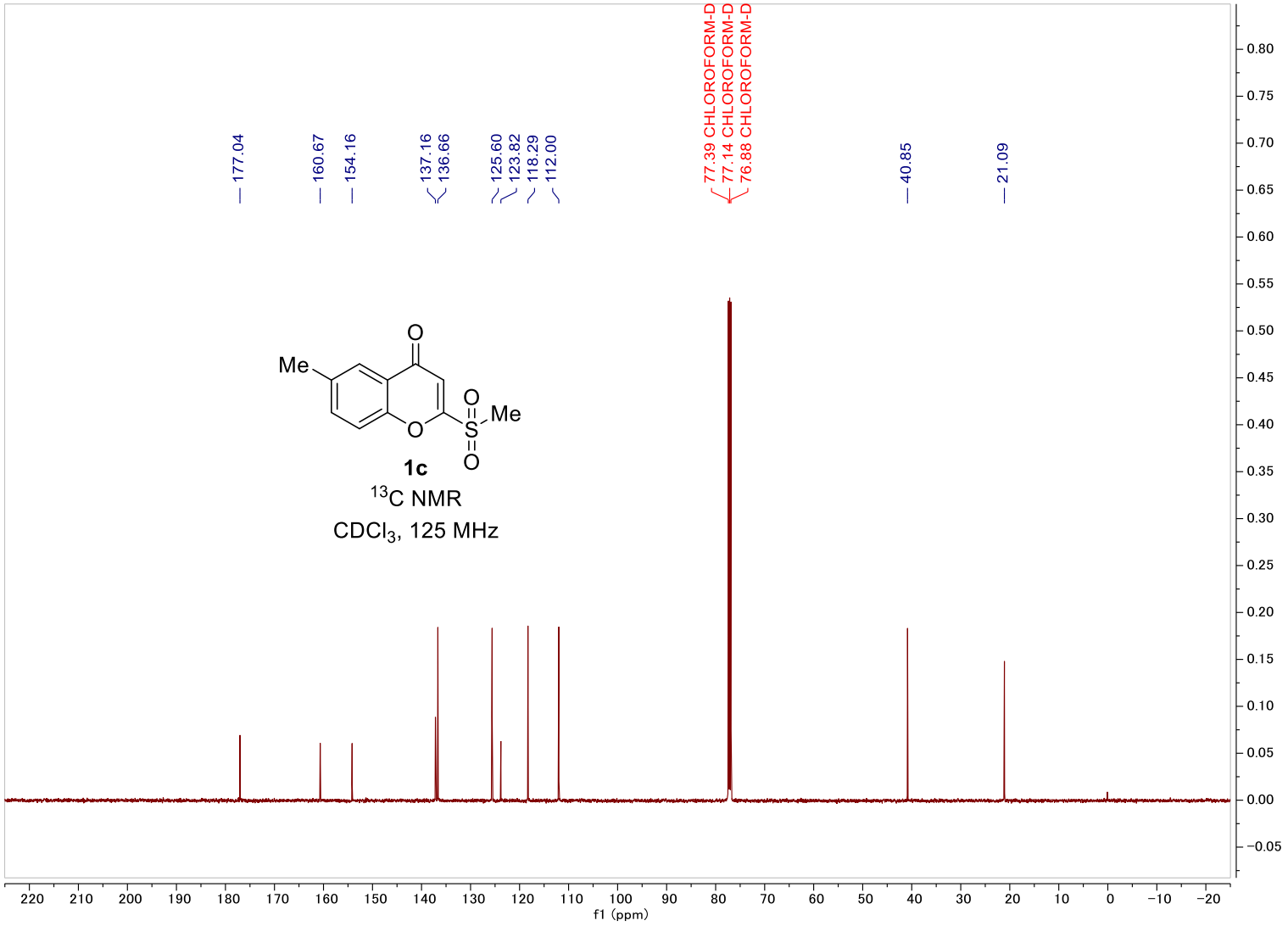


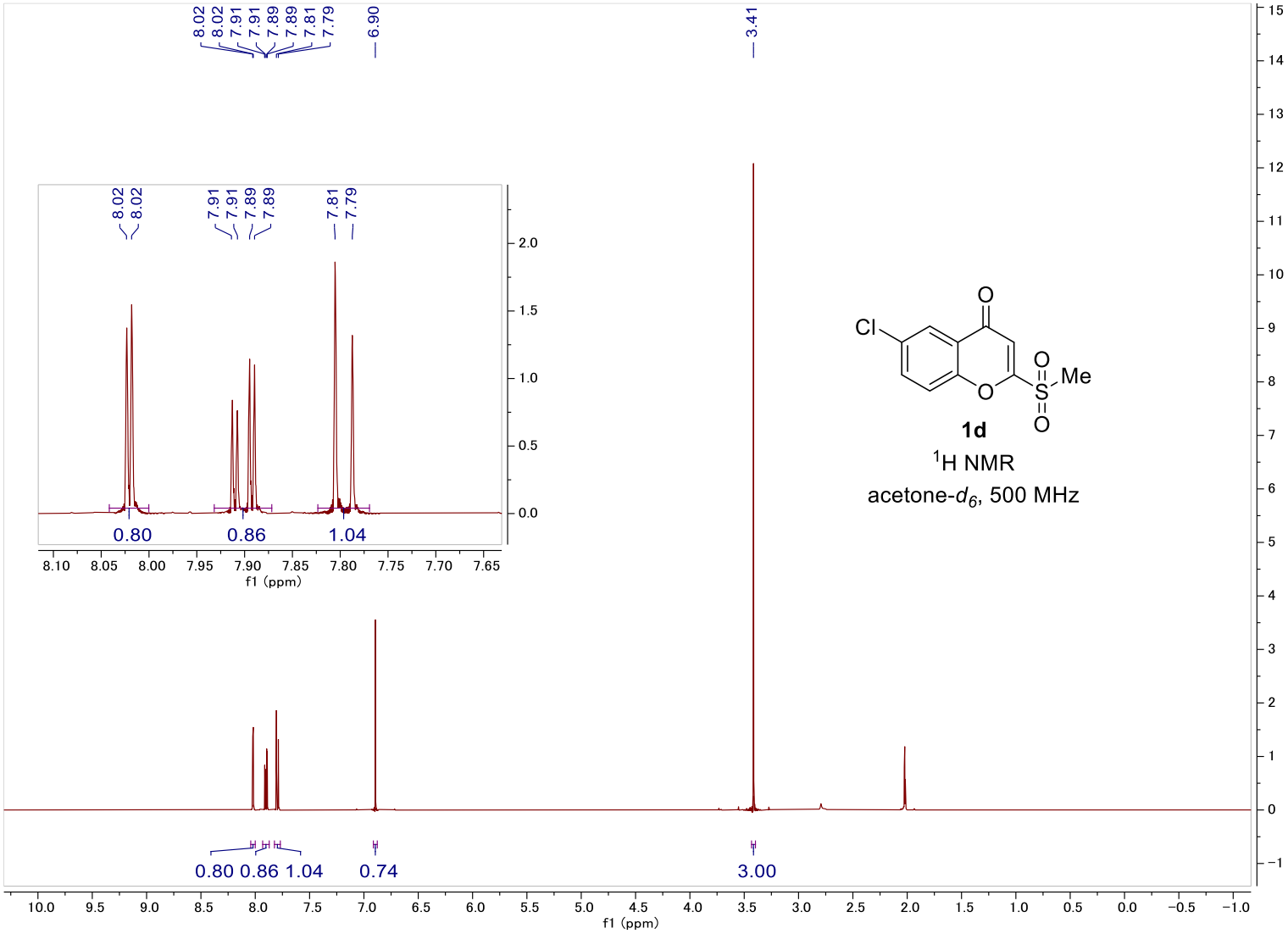
^{1}H NMR for 6-methyl-2-(methylsulfonyl)chromone (**1c**) ($CDCl_3$, 500 MHz)



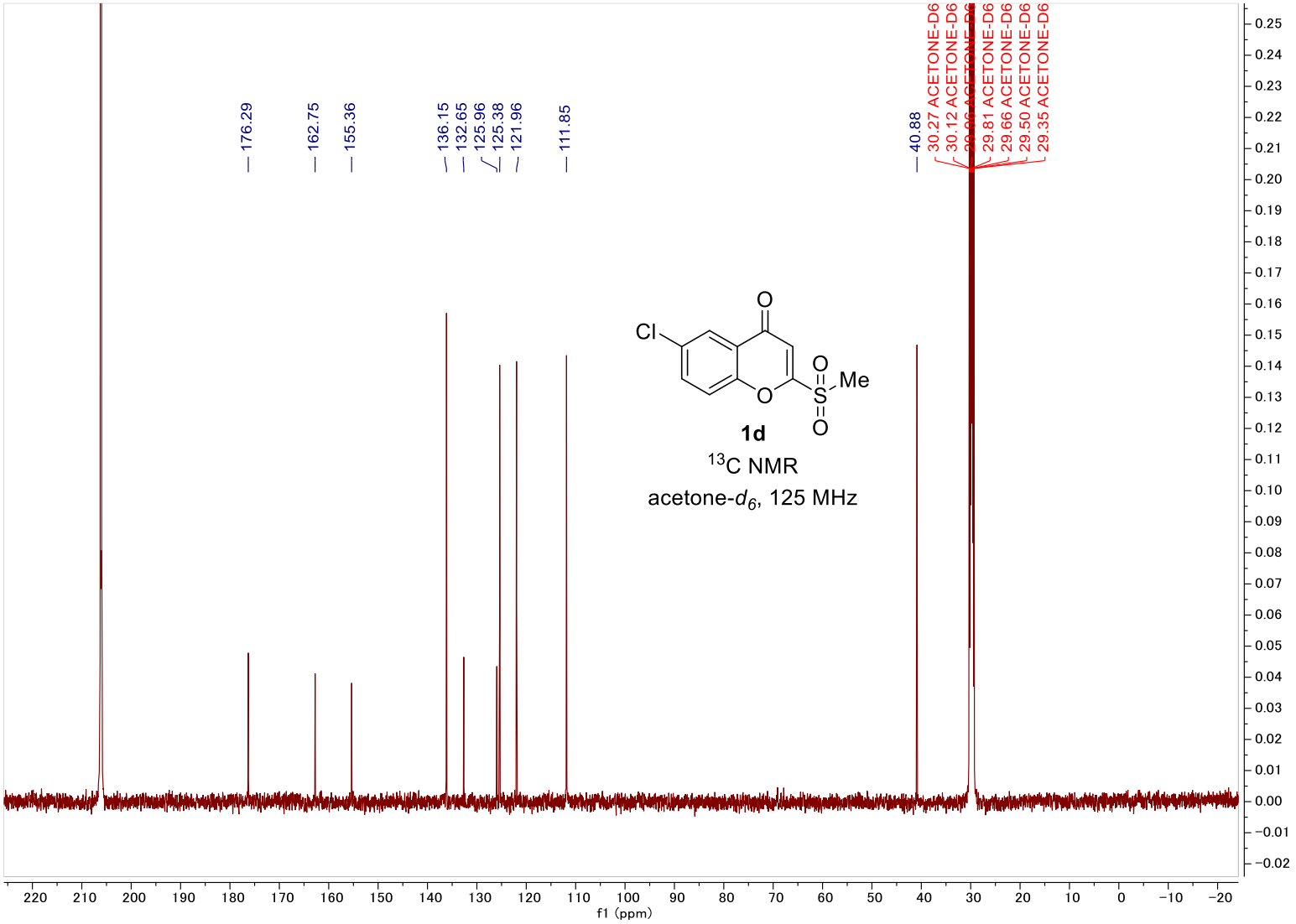
^{13}C NMR for 6-methyl-2-(methylsulfonyl)chromone (**1c**) ($CDCl_3$, 125 MHz)



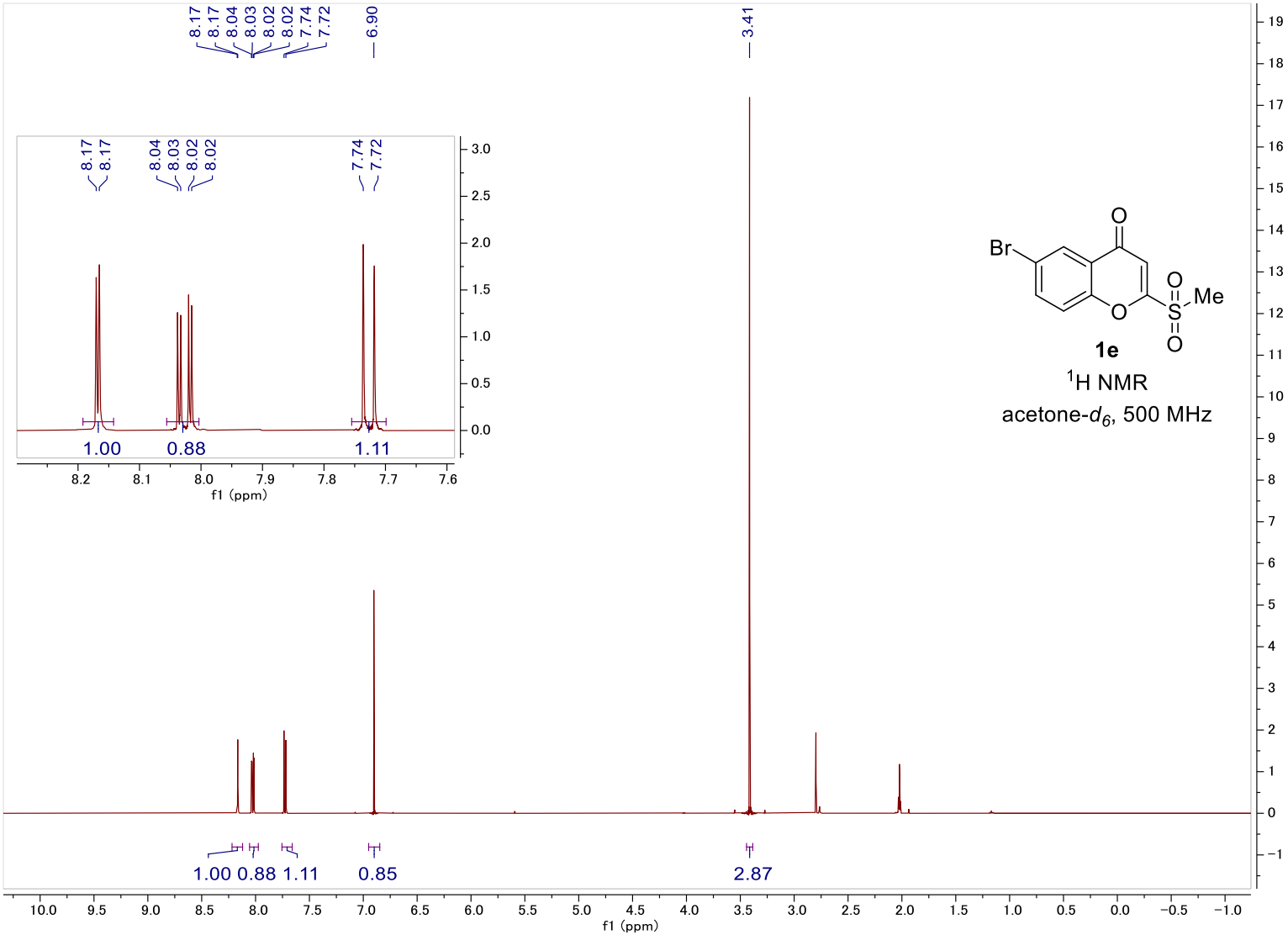
^{1}H NMR for 6-chloro-2-(methylsulfonyl)chromone (**1d**) (acetone-d_6, 500 MHz)



^{13}C NMR for 6-chloro-2-(methylsulfonyl)chromone (**1d**) (acetone-d_6, 125 MHz)



^{1}H NMR for 6-bromo-2-(methylsulfonyl)chromone (**1e**) (acetone-d_6, 500 MHz)



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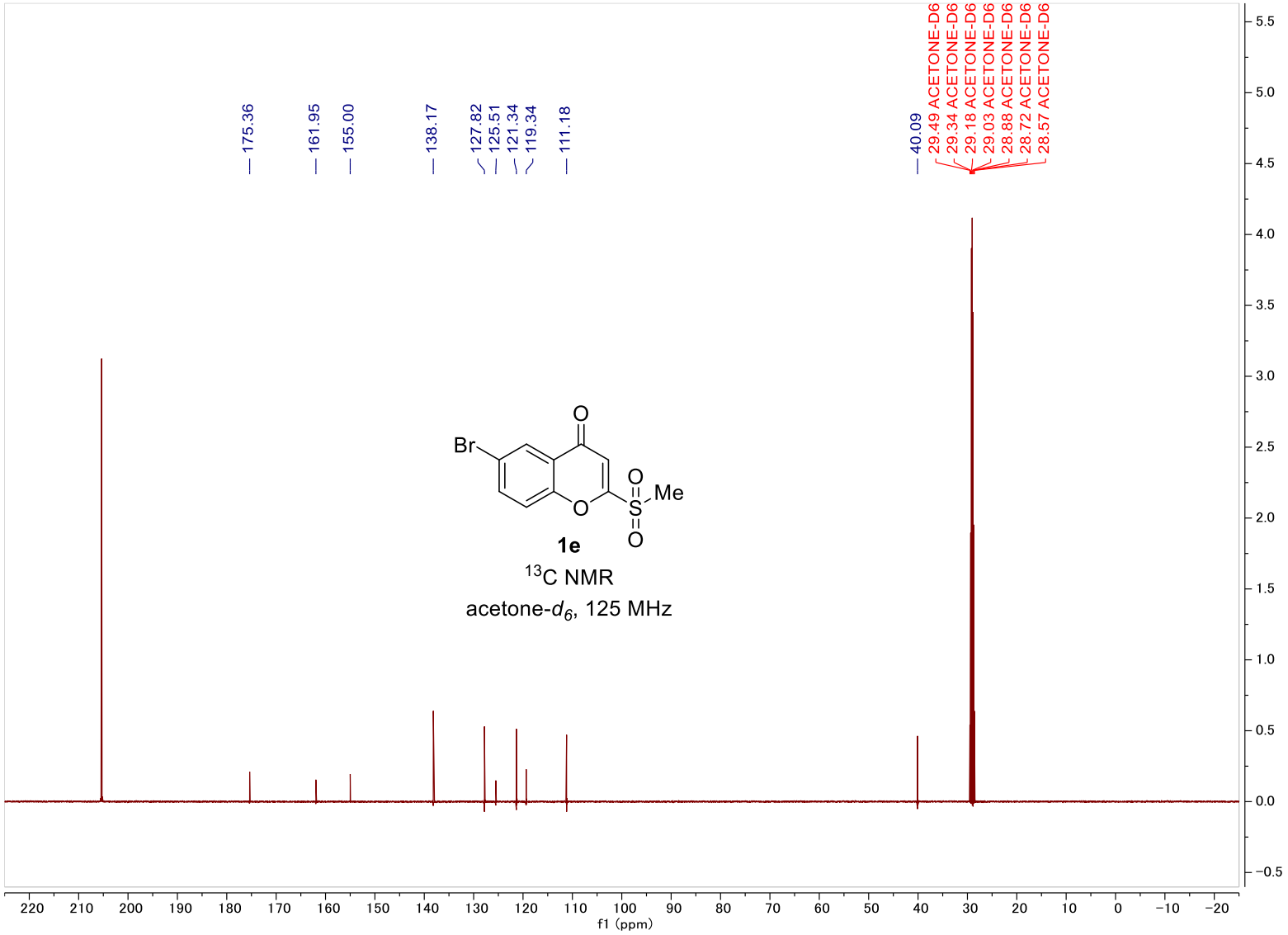

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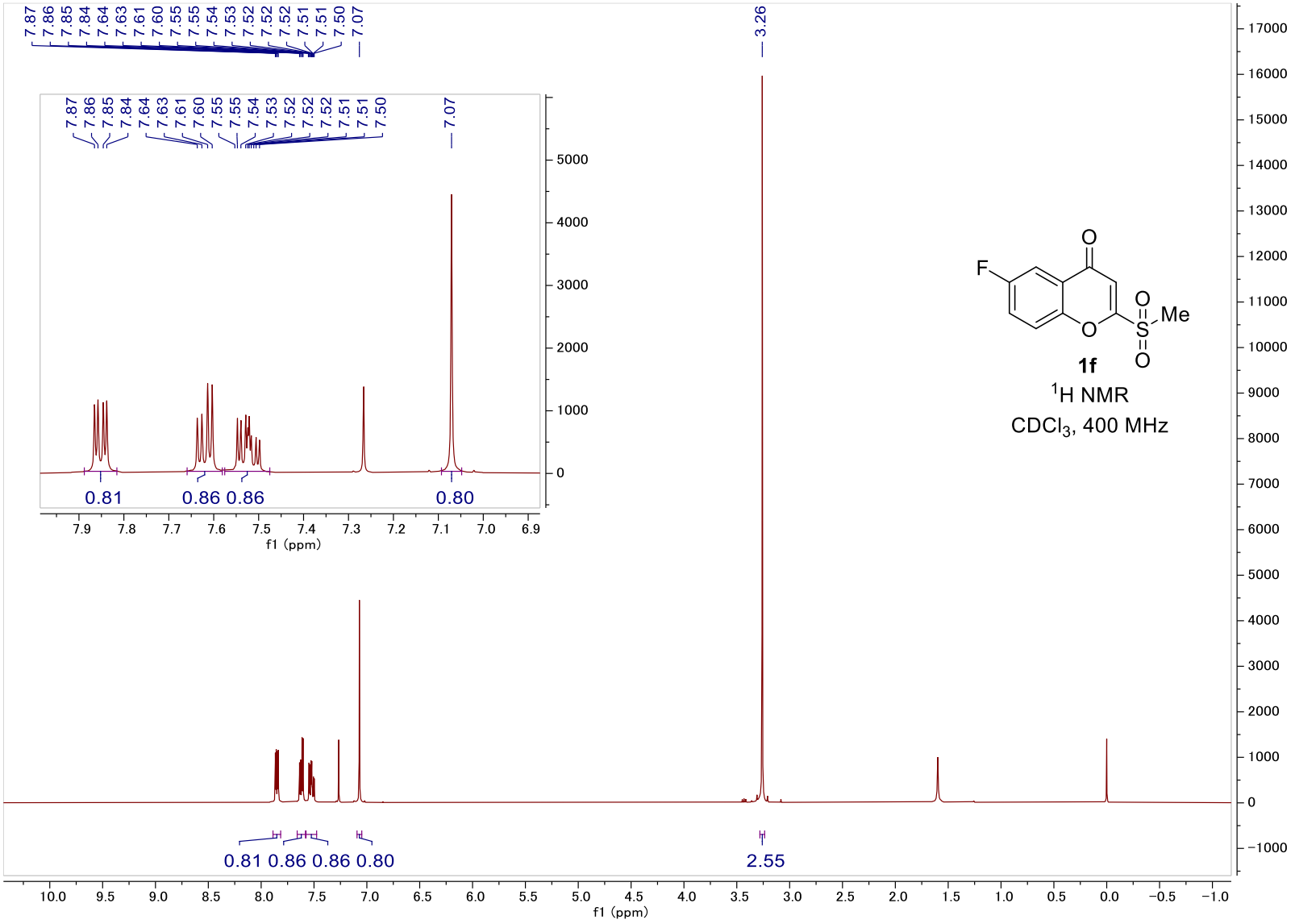

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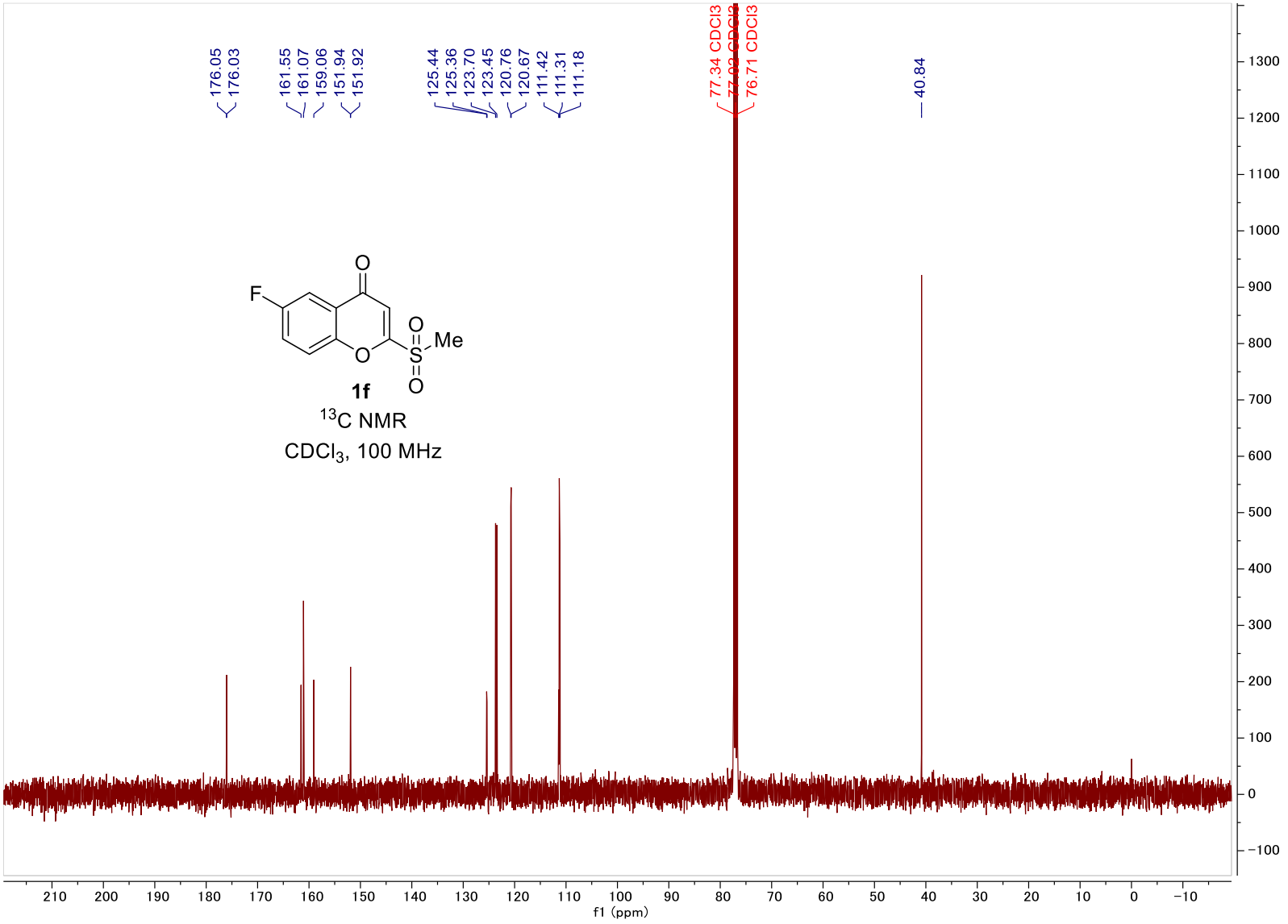

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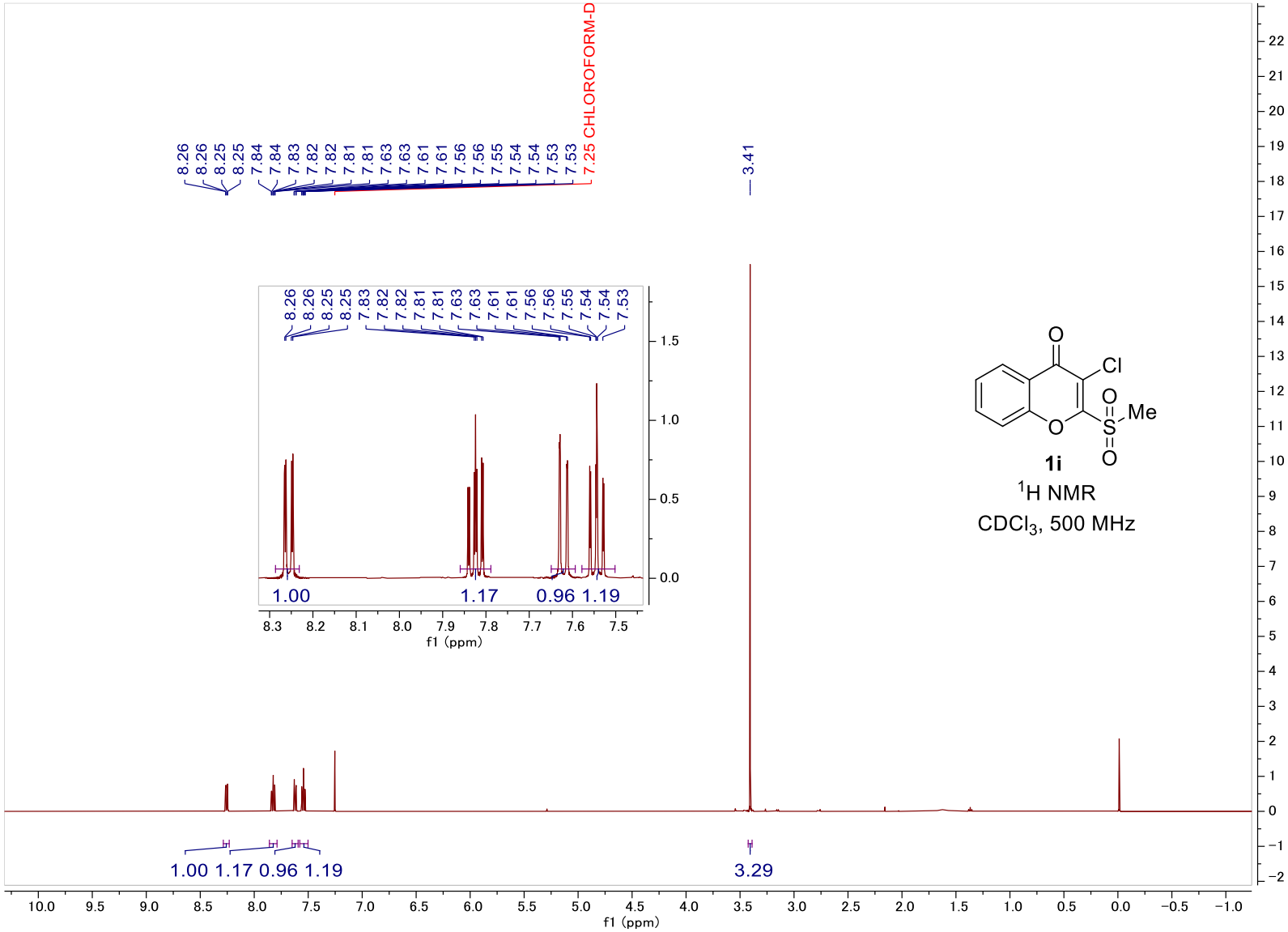

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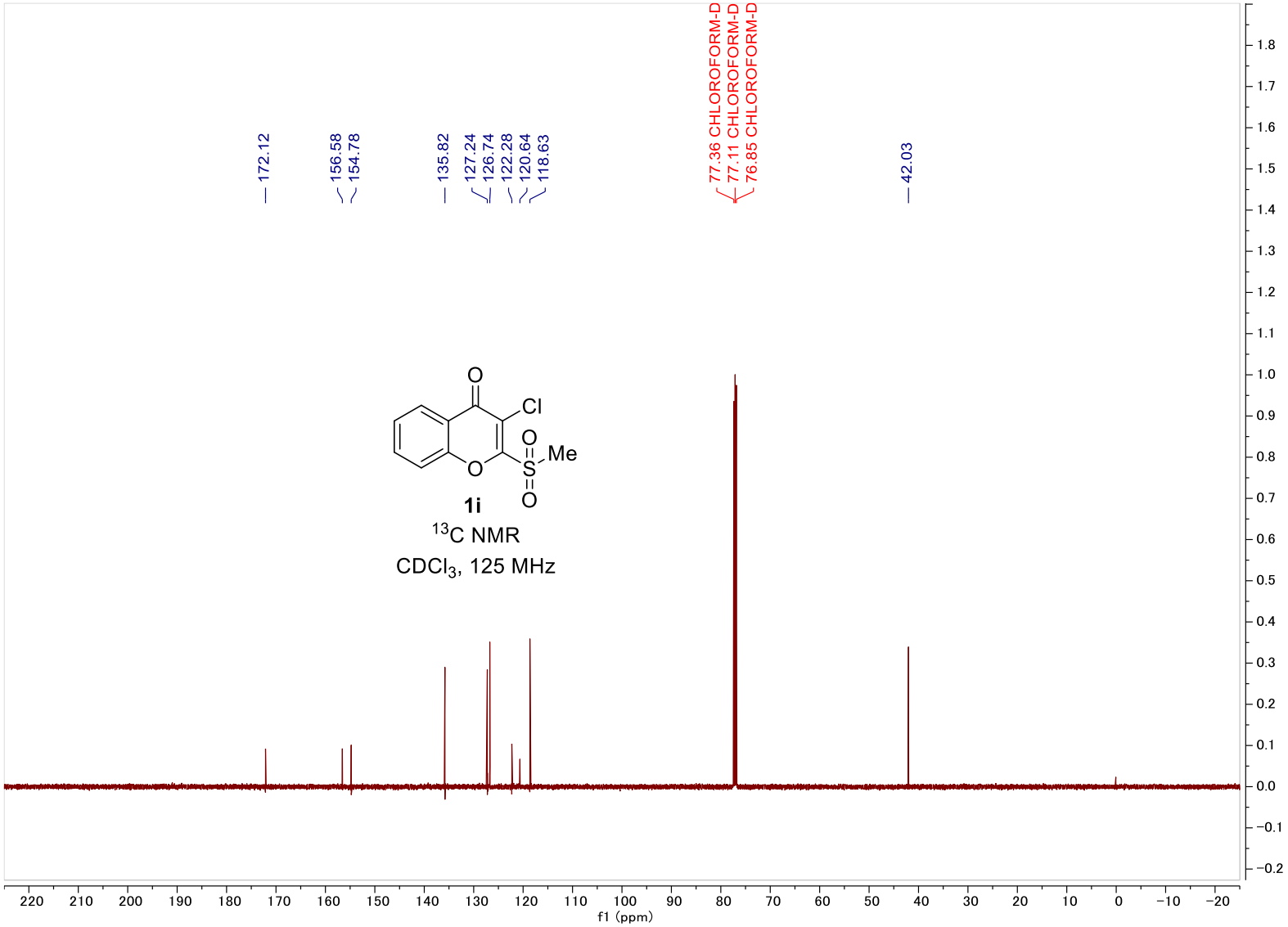
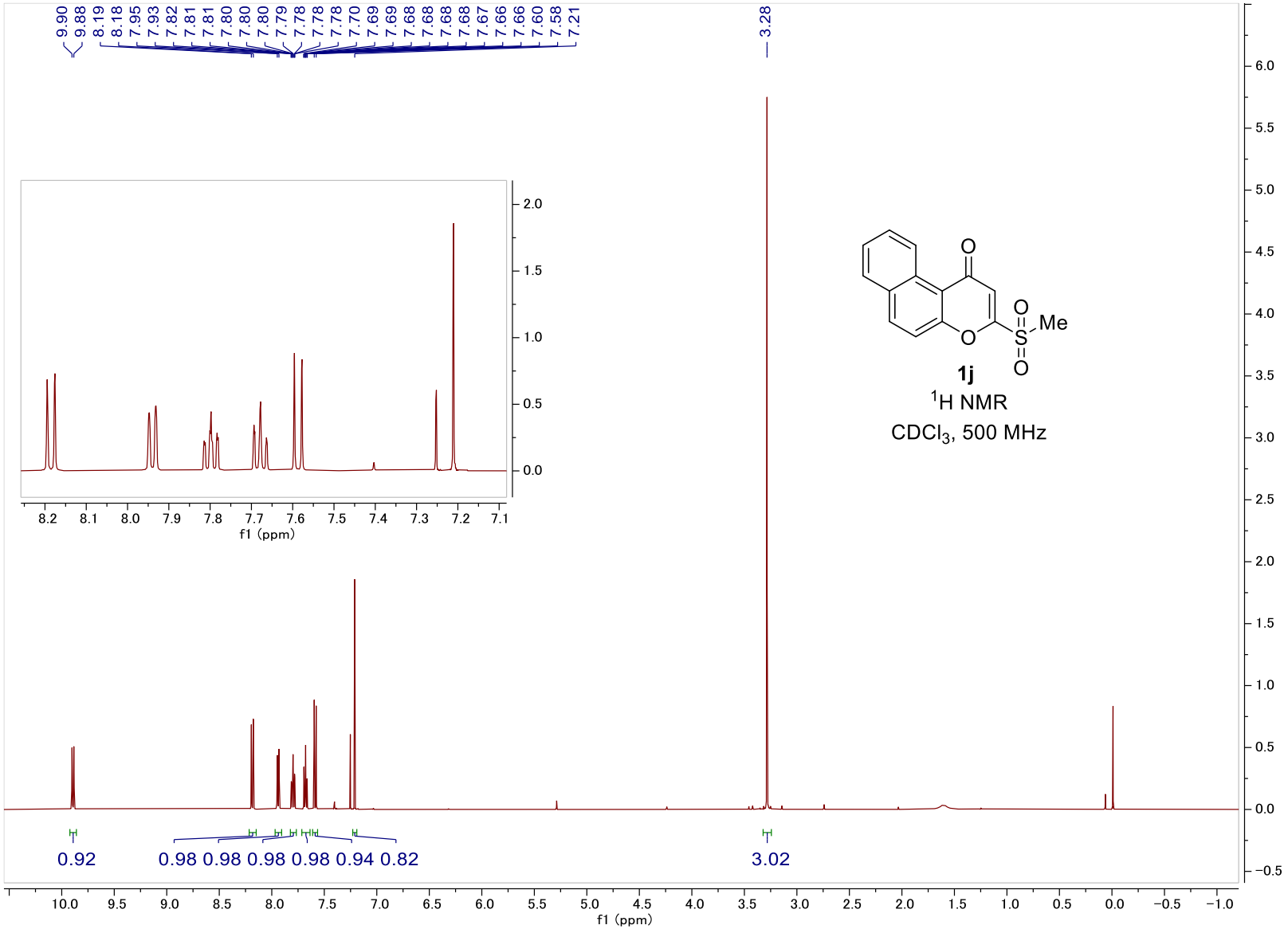
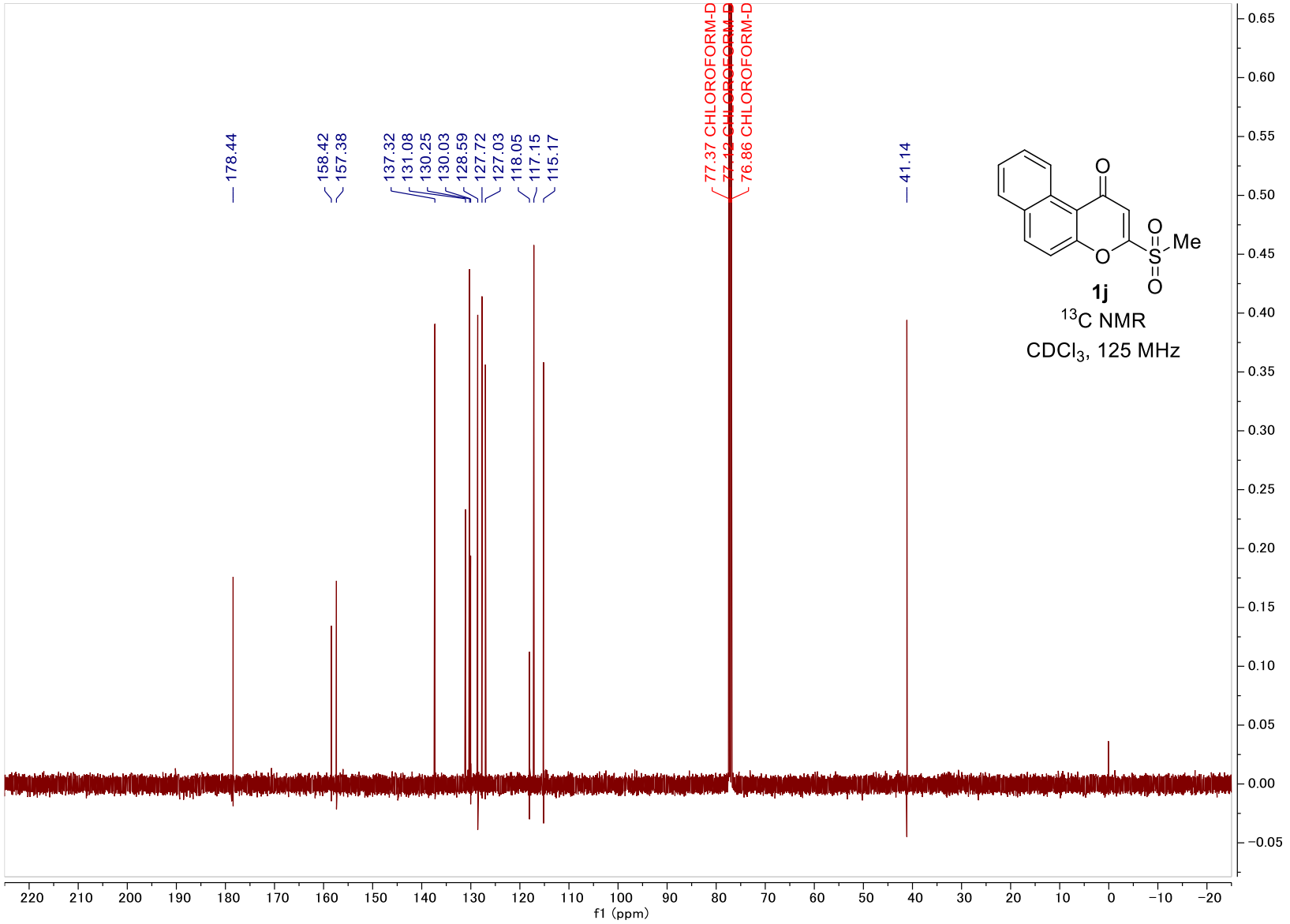


^{1}H NMR for 3-(methylsulfonyl)-1*H*-naphtho[2,1-*b*]pyran-1-one (**1j**) ($CDCl_3$, 500 MHz)



^{13}C NMR for 3-(methylsulfonyl)-1*H*-naphtho[2,1-*b*]pyran-1-one (**1j**) ($CDCl_3$, 125 MHz)



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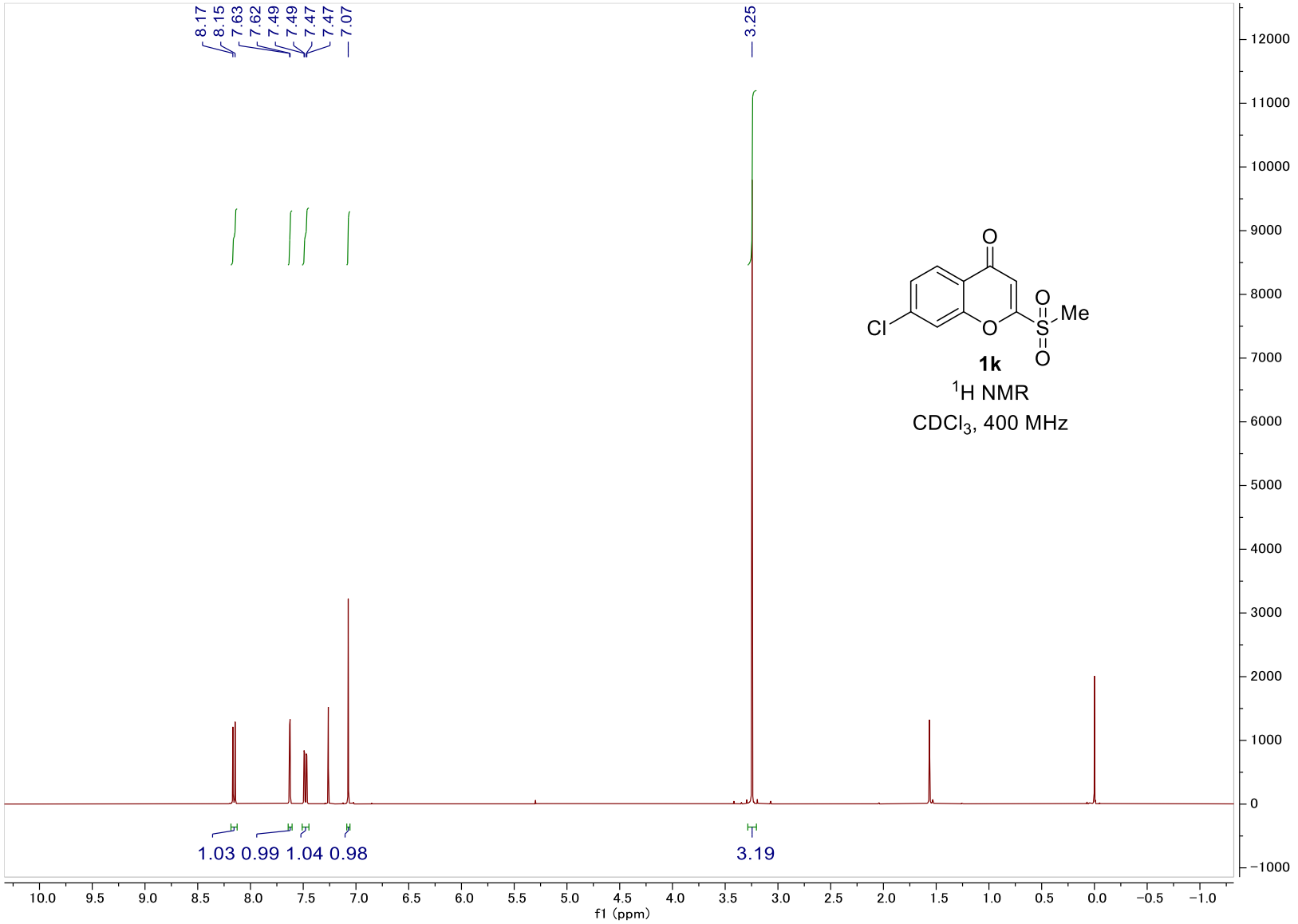
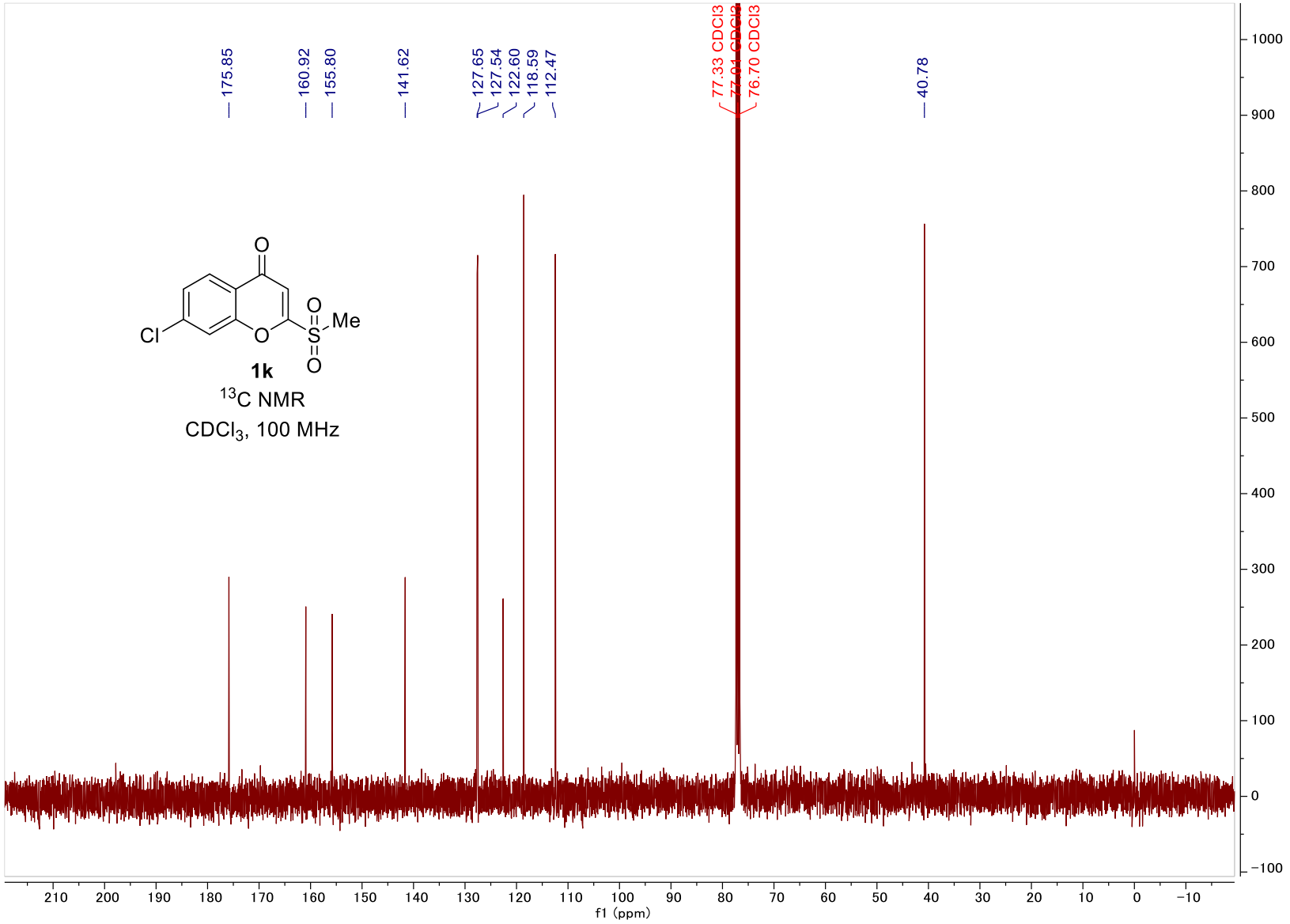


^{13}C NMR for 7-chloro-2-(methylsulfonyl)chromone (**1k**) ($CDCl_3$, 100 MHz)



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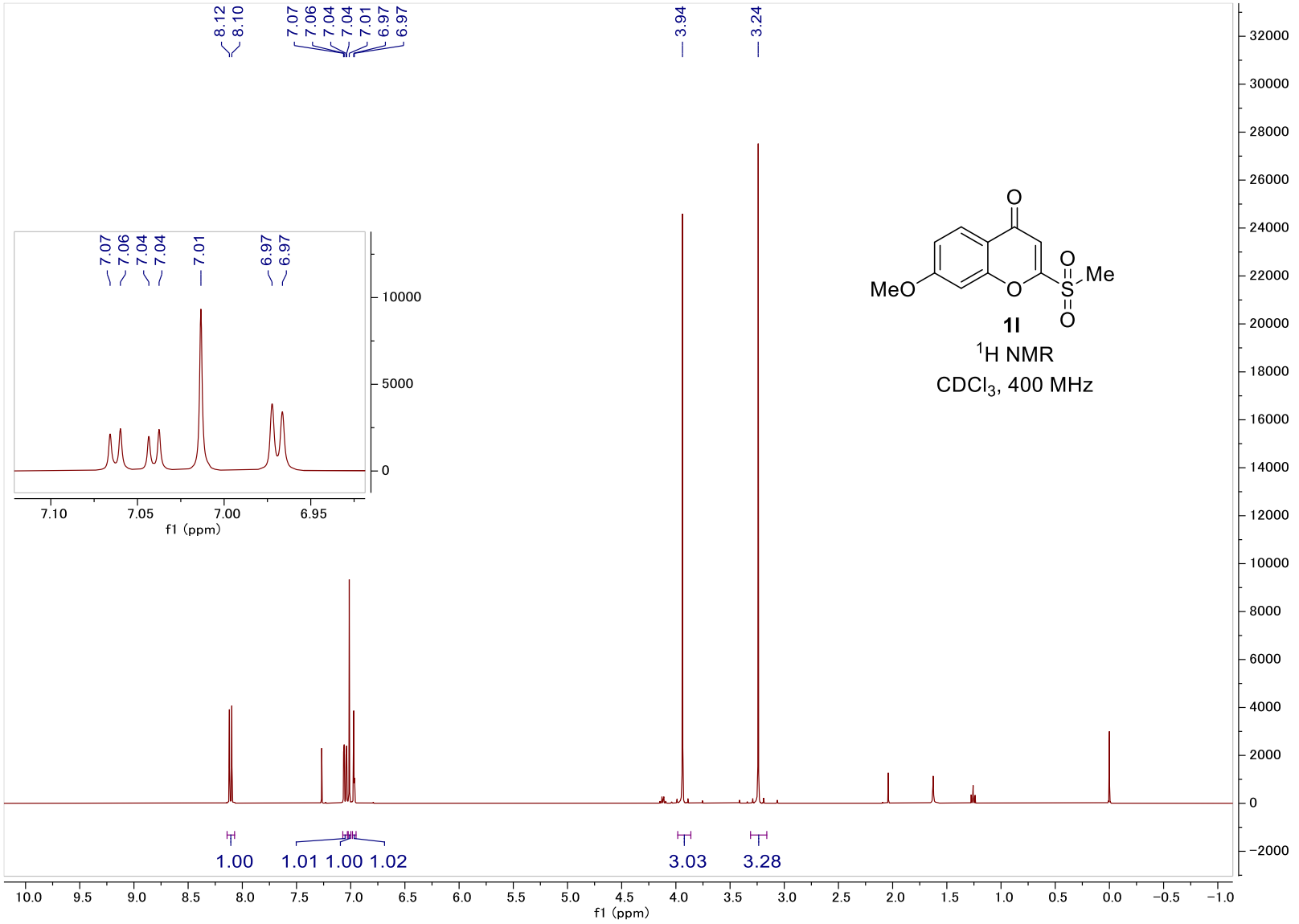
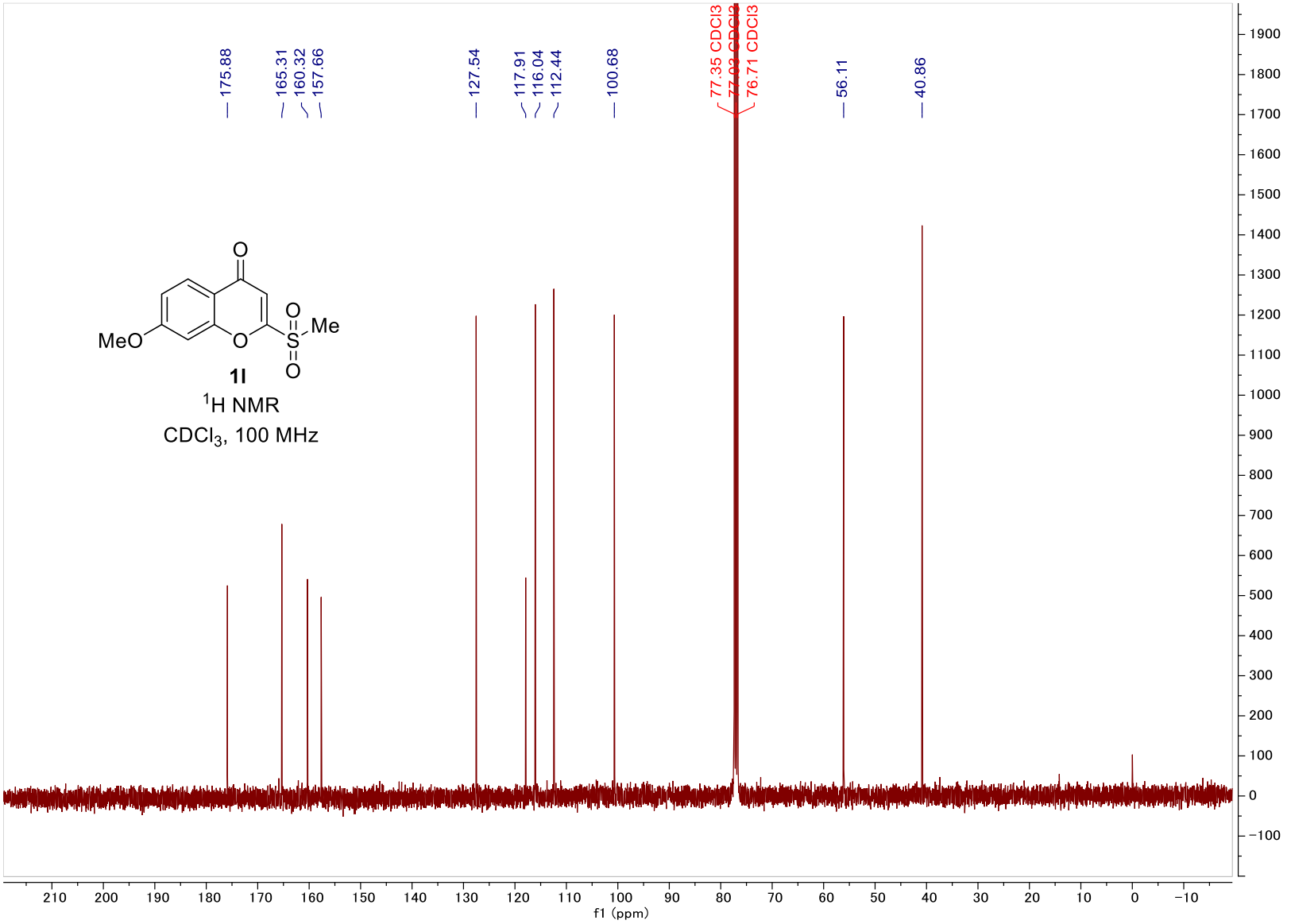
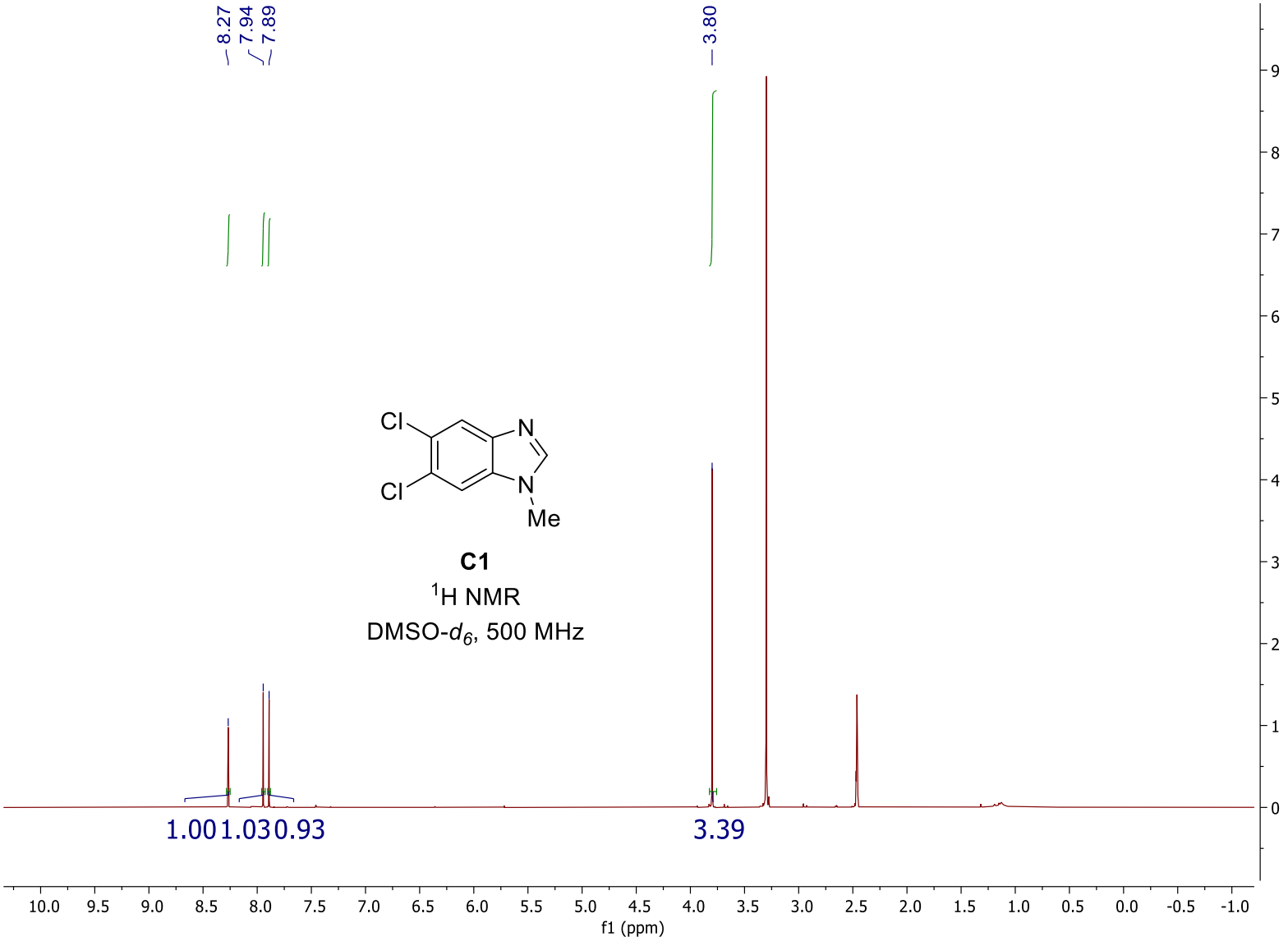


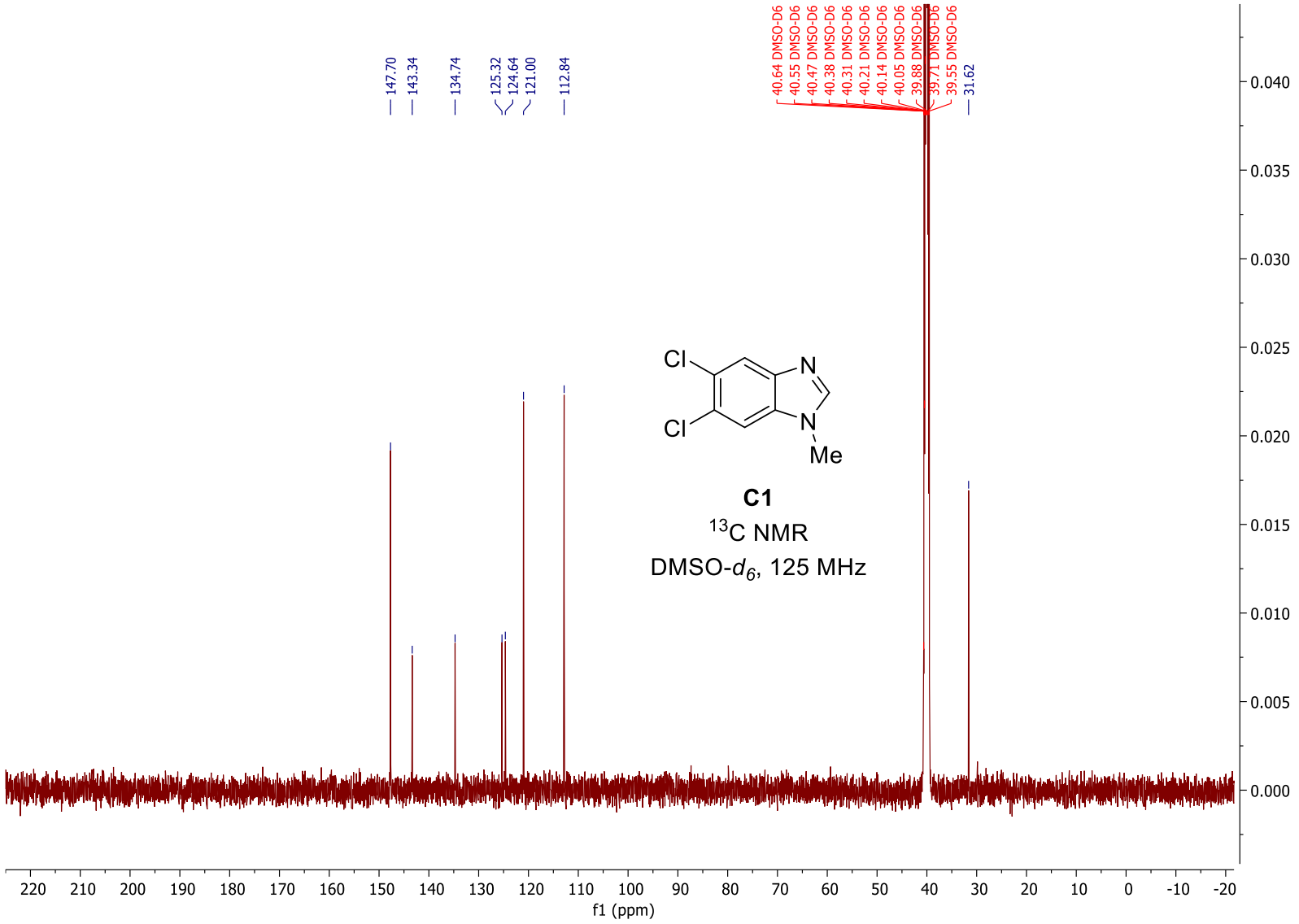
^{13}C NMR for 7-methoxy-2-(methylsulfonyl)chromone (**1l**) ($CDCl_3$, 100 MHz)



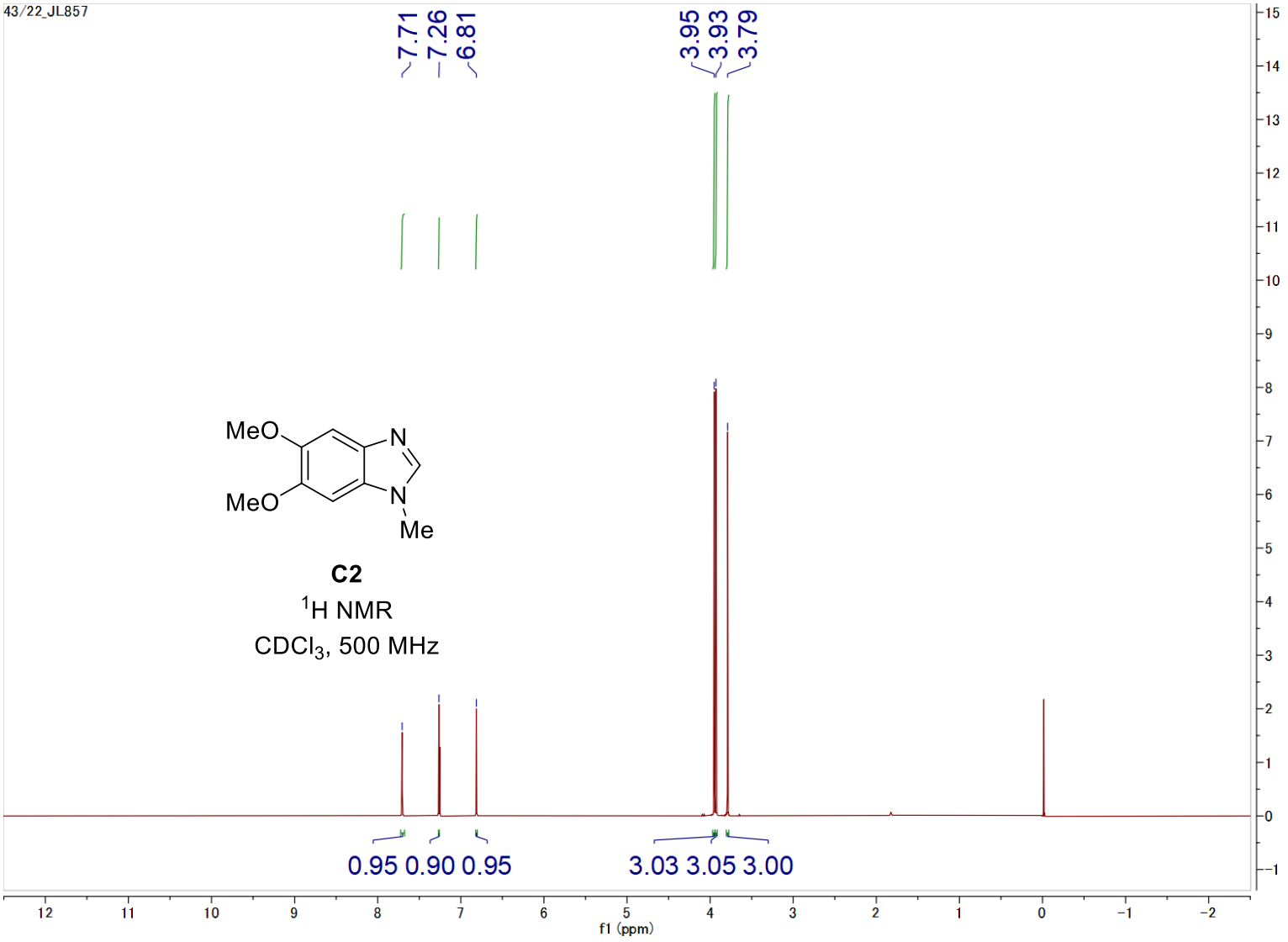
^{1}H NMR for 5,6-dichloro-1-methylbenzimidazole (**C1**) (DMSO-d_6, 500 MHz)



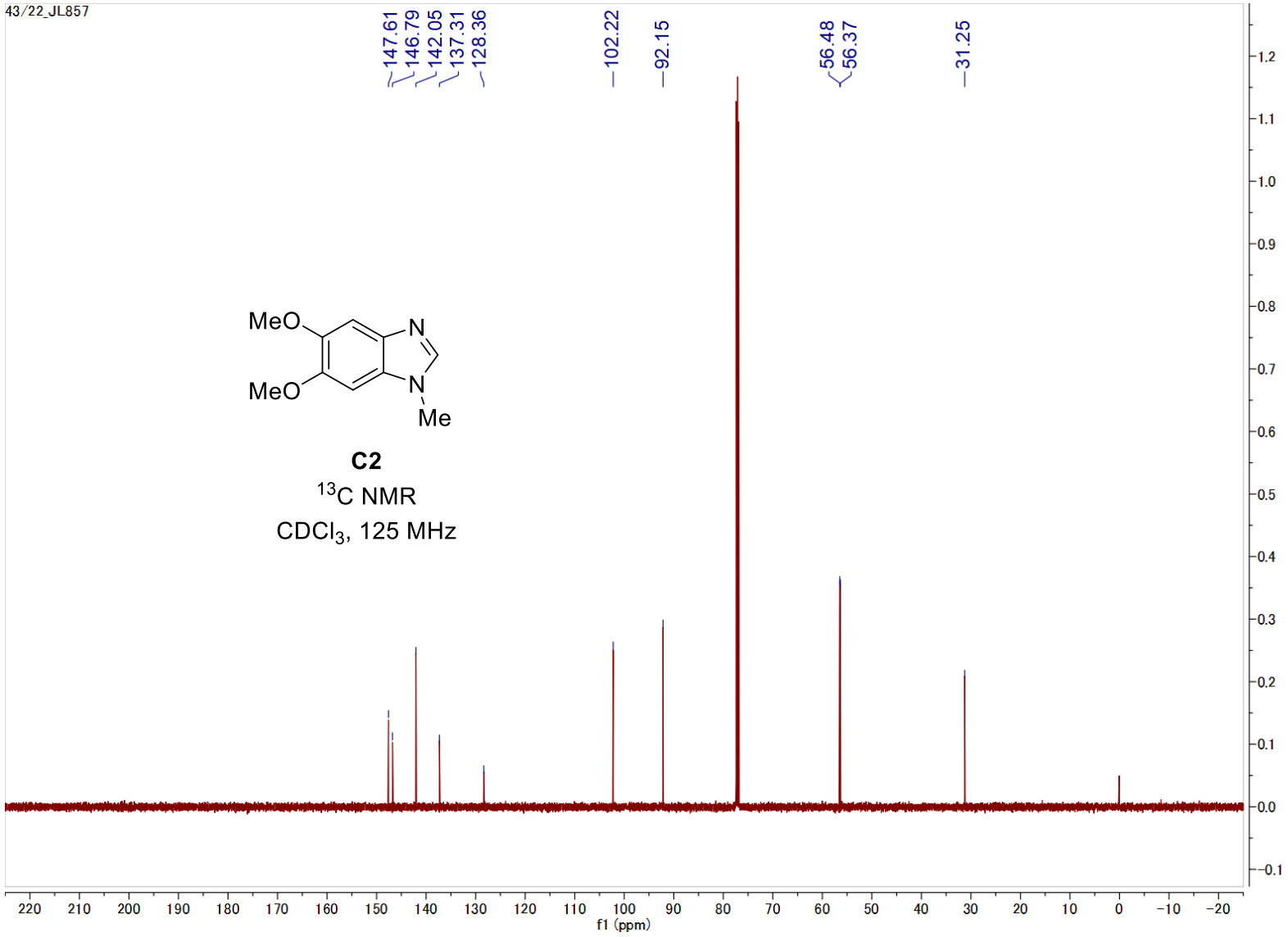
^{13}C NMR for 5,6-dichloro-1-methylbenzimidazole (**C1**) (DMSO-d_6, 125 MHz)



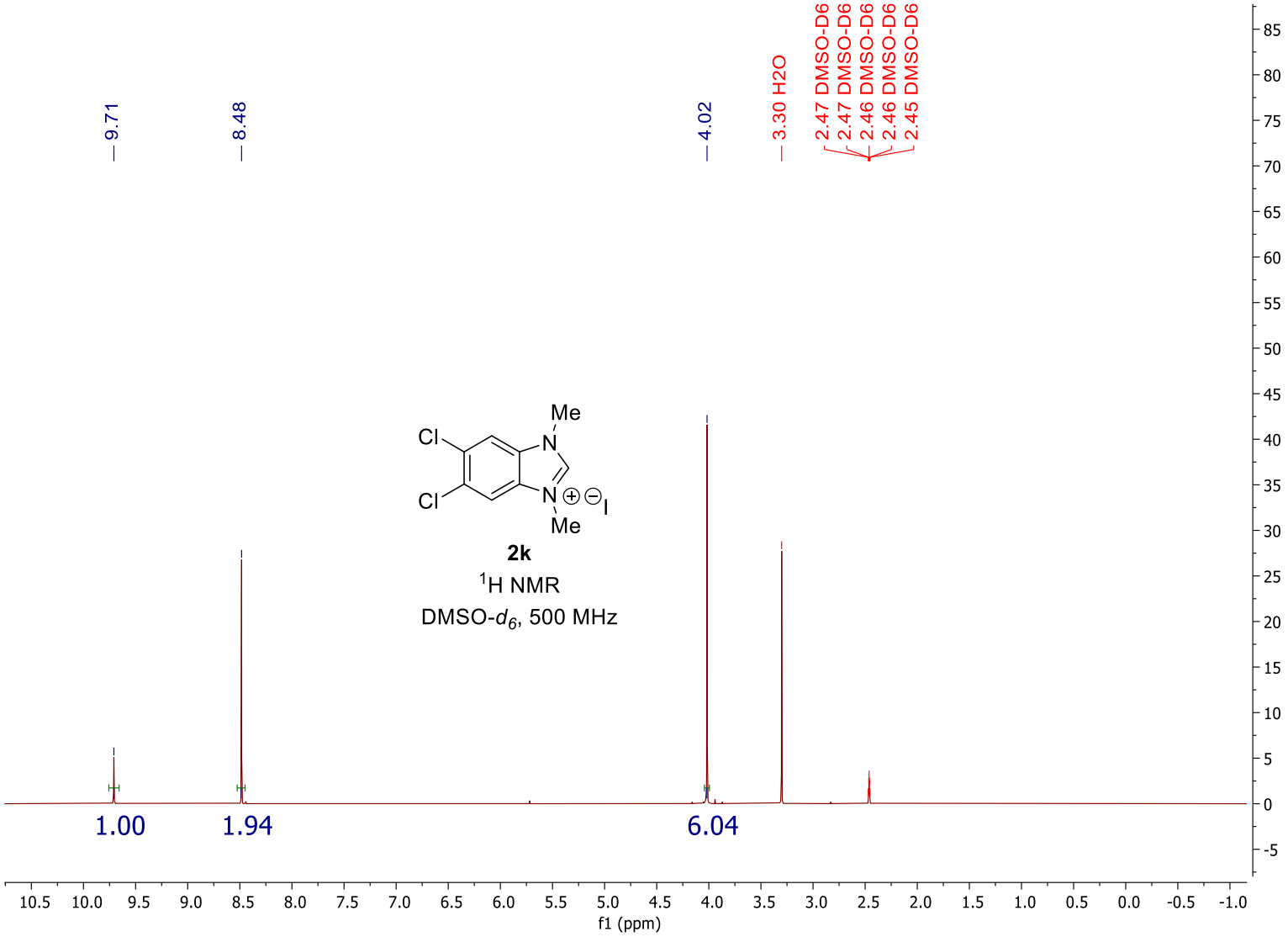
^{1}H NMR for 5,6-dimethoxy-1-methylbenzimidazole (**C2**) ($CDCl_3$, 500 MHz)



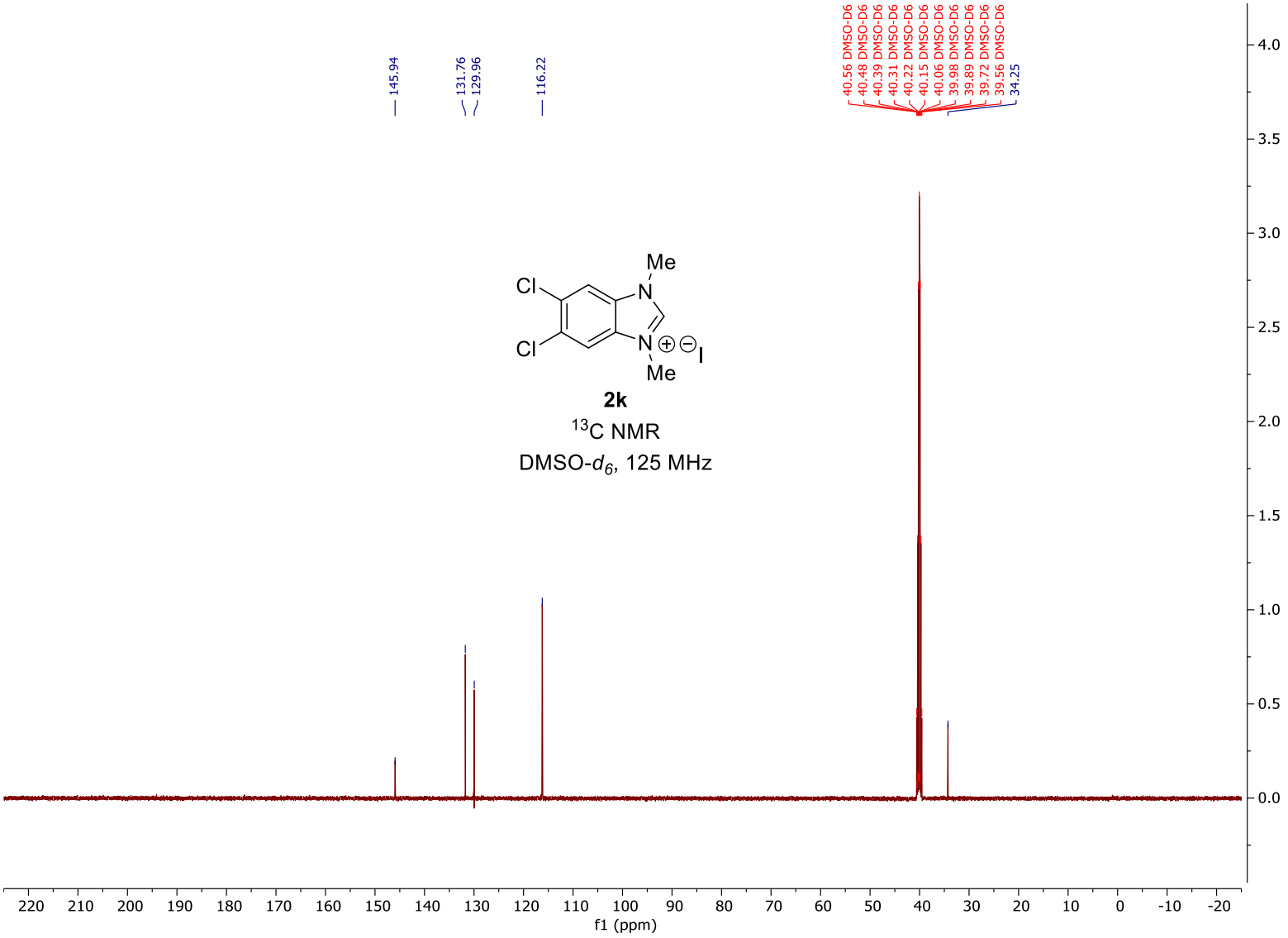
^{13}C NMR for 5,6-dimethoxy-1-methylbenzimidazole (**C2**) ($CDCl_3$, 125 MHz)



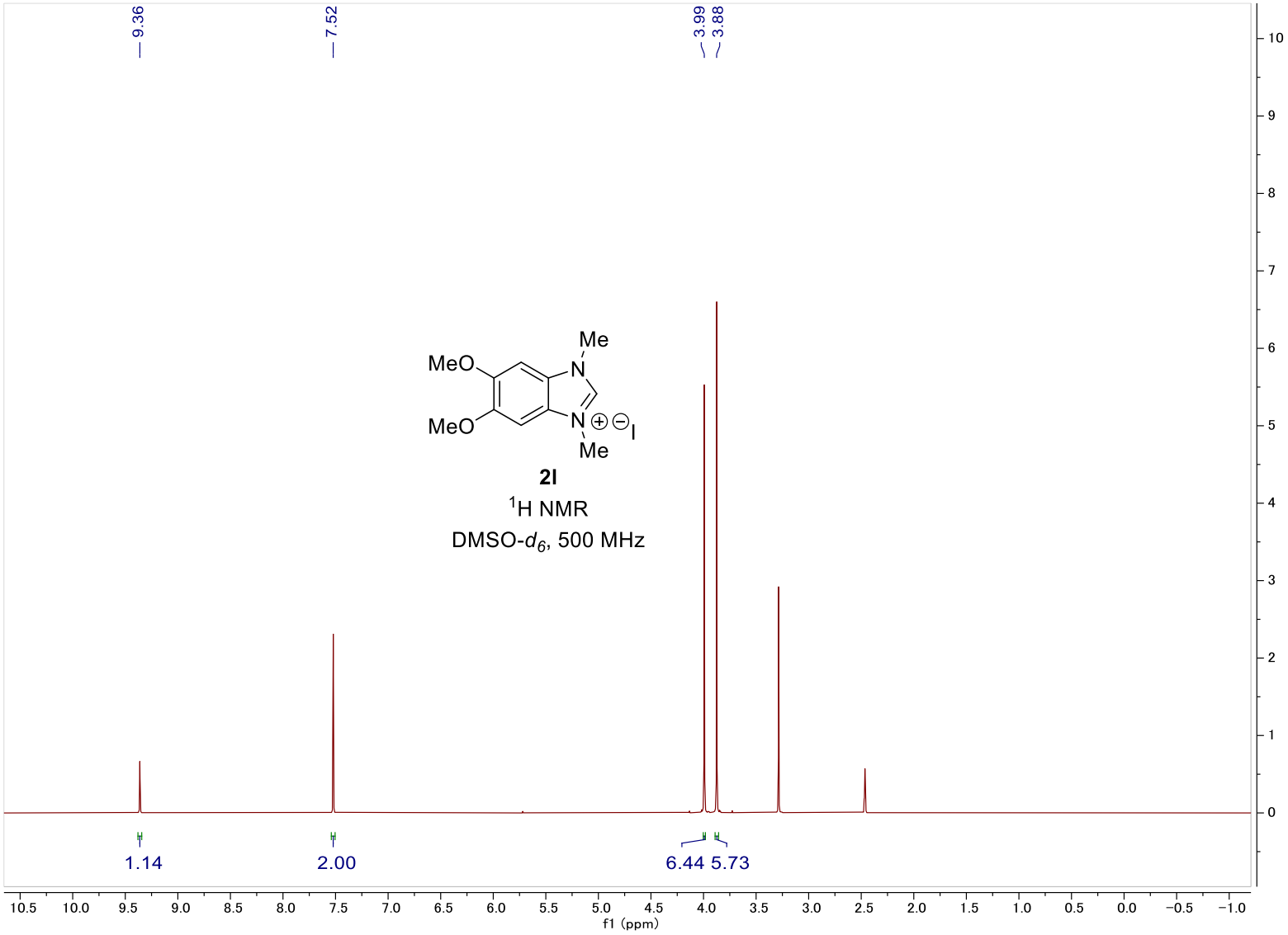
^{1}H NMR for 5,6-dichloro-1,3-dimethylbenzimidazolium iodide (**2k**) (DMSO-d_6, 500 MHz)



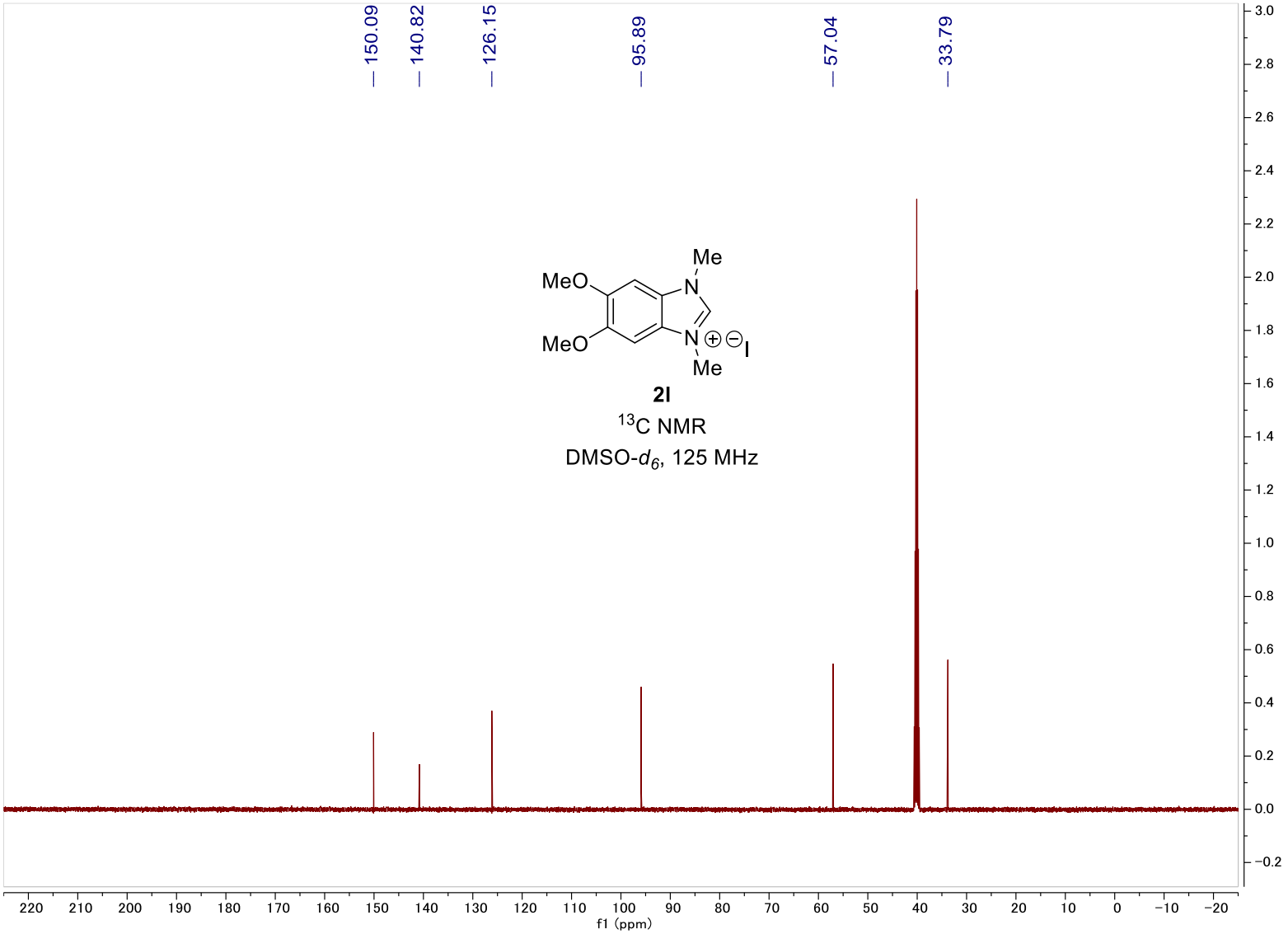
^{13}C NMR for 5,6-dichloro-1,3-dimethylbenzimidazolium iodide (**2k**) (DMSO-d_6, 125 MHz)



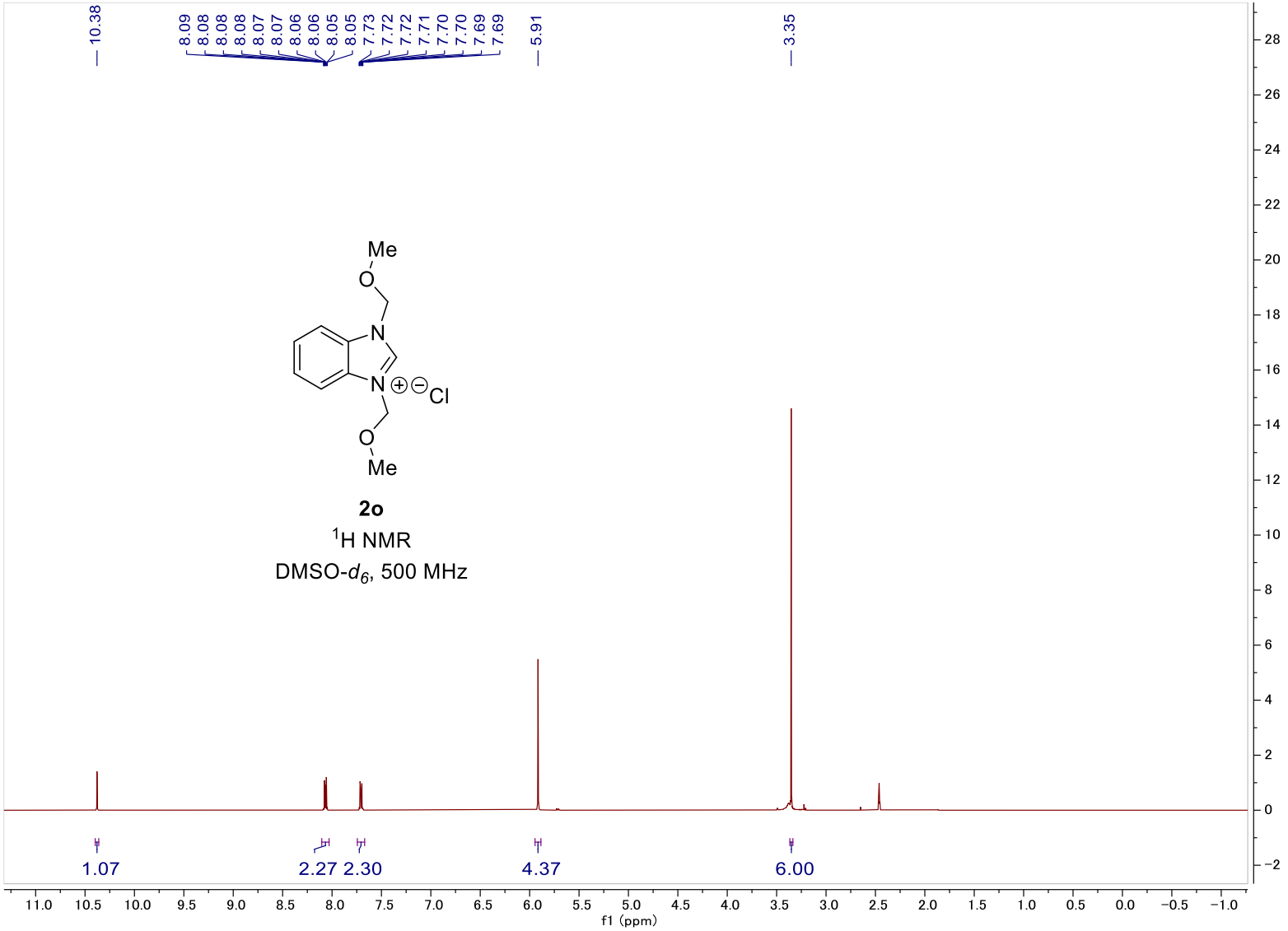
^{1}H NMR for 5,6-dimethoxy-1,3-dimethylbenzimidazolium iodide (**2l**) (DMSO-d_6, 500 MHz)



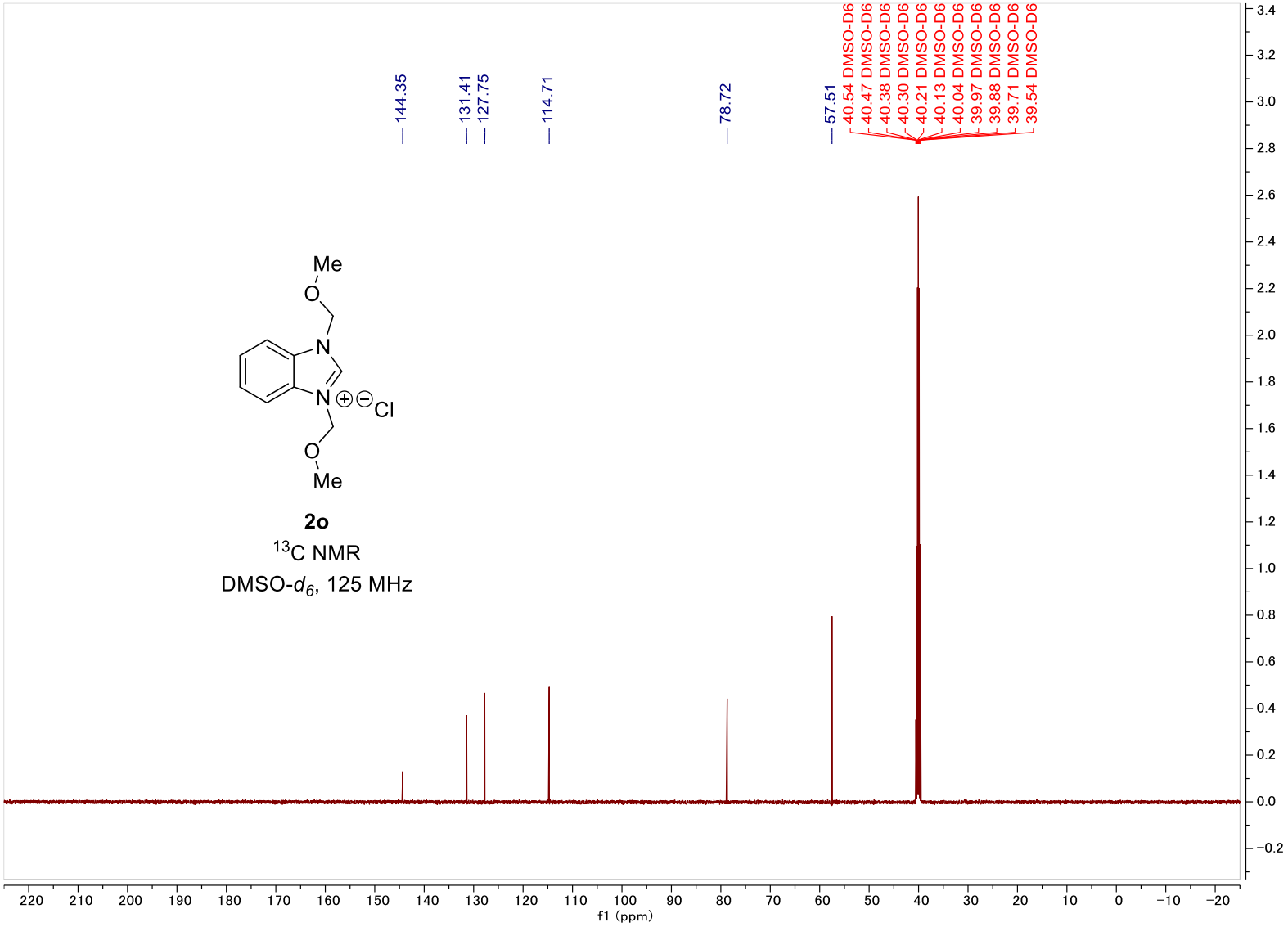
^{13}C NMR for 5,6-dimethoxy-1,3-dimethylbenzimidazolium iodide (**2l**) (DMSO-d_6, 125 MHz)



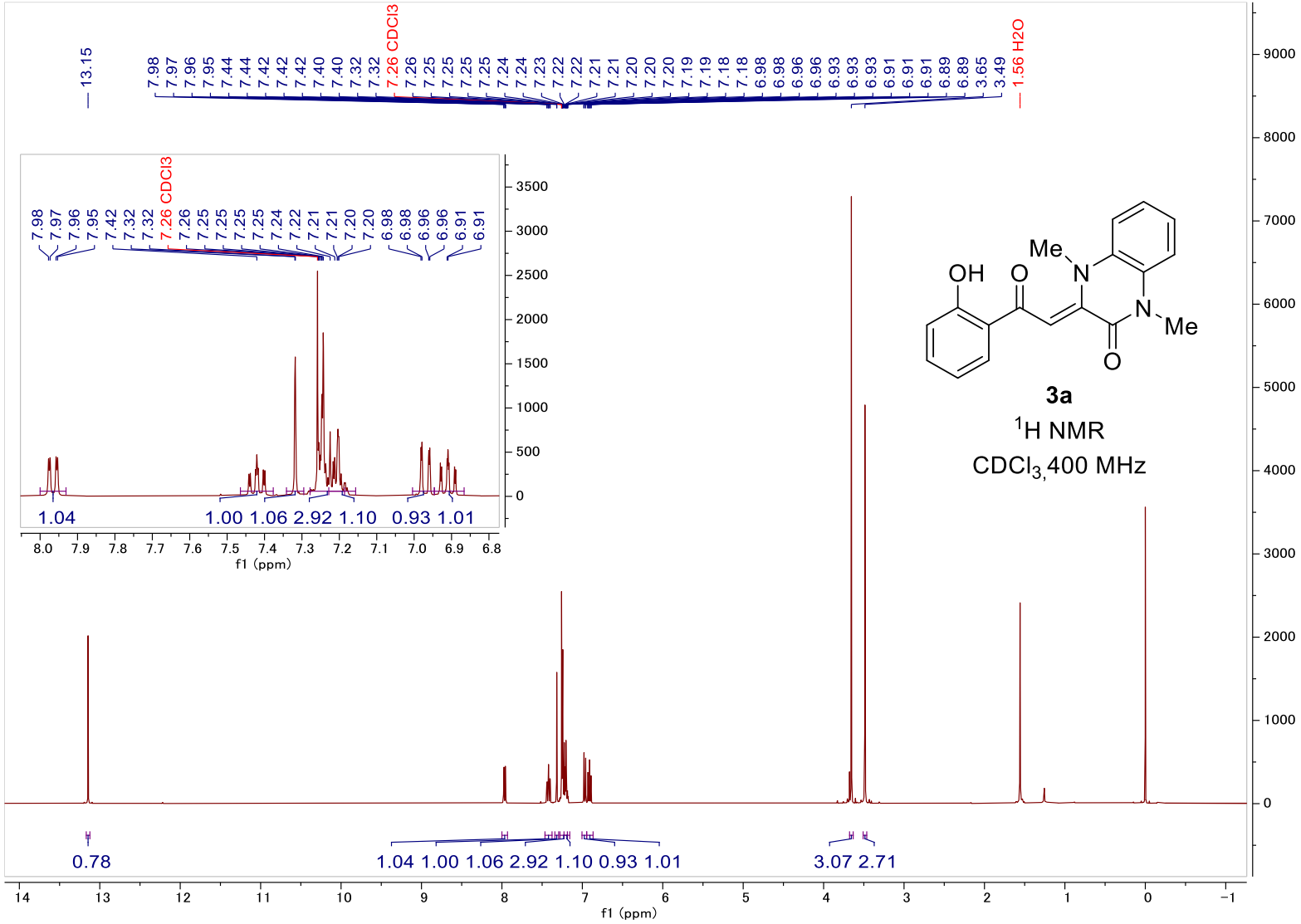
^{1}H NMR for 1,3-dimethoxymethylbenzimidazolium chloride (**2o**) (DMSO-d_6, 500 MHz)



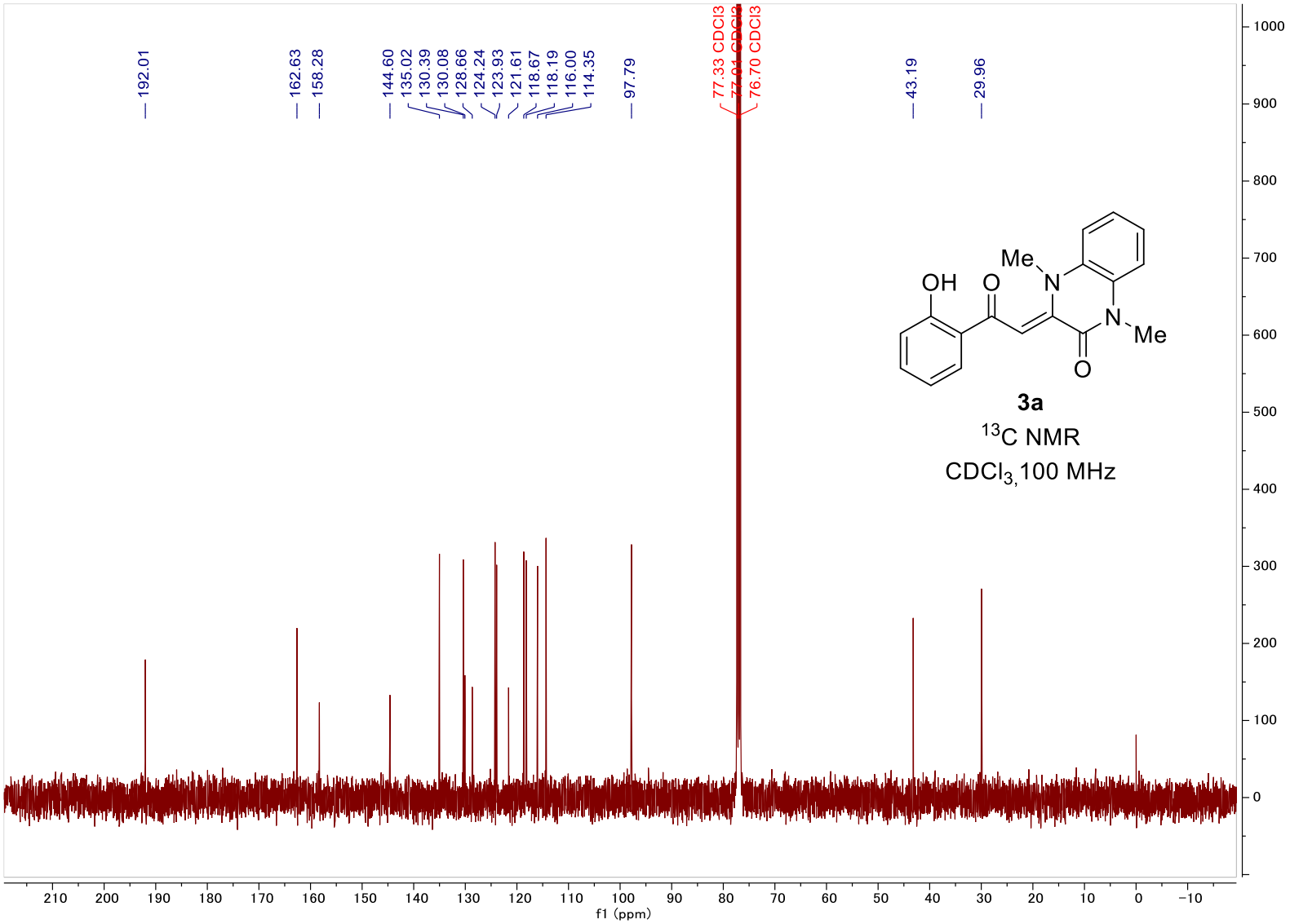
^{13}C NMR for 1,3-dimethoxymethylbenzimidazolium chloride (**2o**) (DMSO-d_6, 125 MHz)



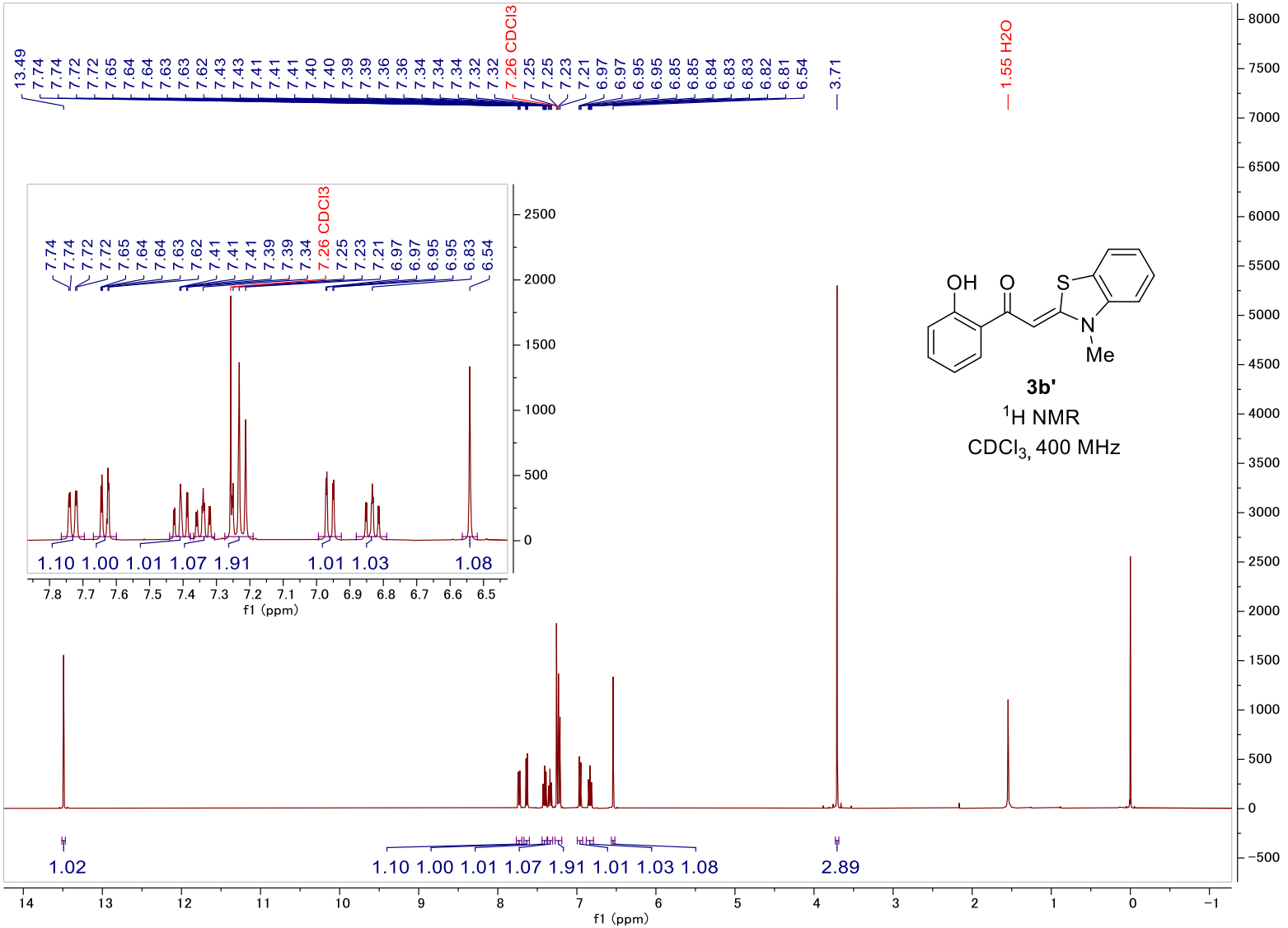
^{1}H NMR for (*Z*)-1,4-dimethyl-3-[(2-hydroxyphenyl]-2-oxoethylidene]-3,4-dihydroquinoxalin-2(1*H*)-one (**3a**)
($CDCl_3$, 400 MHz)



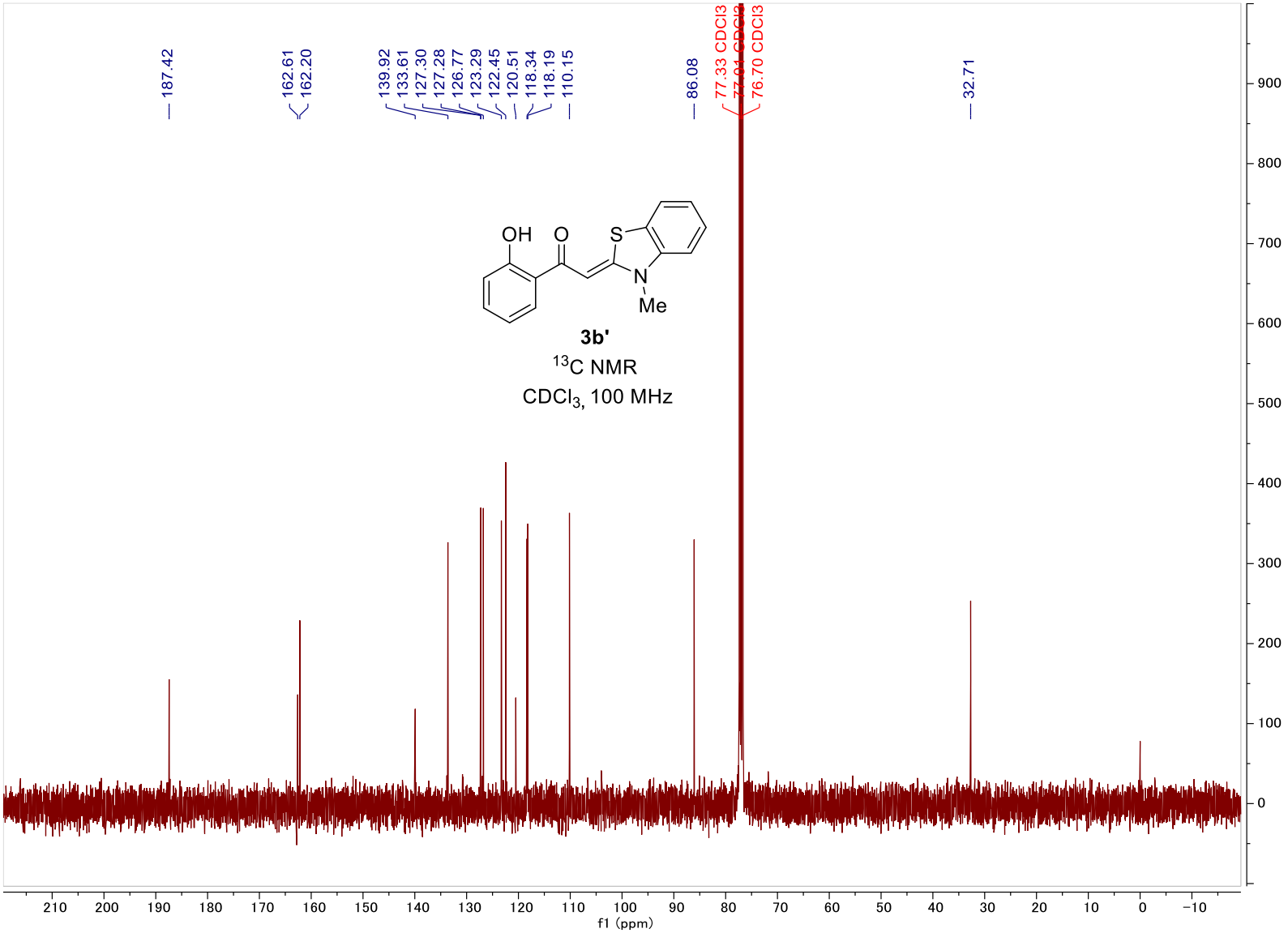
^{13}C NMR for (*Z*)-1,4-dimethyl-3-[(2-hydroxyphenyl]-2-oxoethylidene]-3,4-dihydroquinoxalin-2(1*H*)-one (**3a**)
($CDCl_3$, 100 MHz)



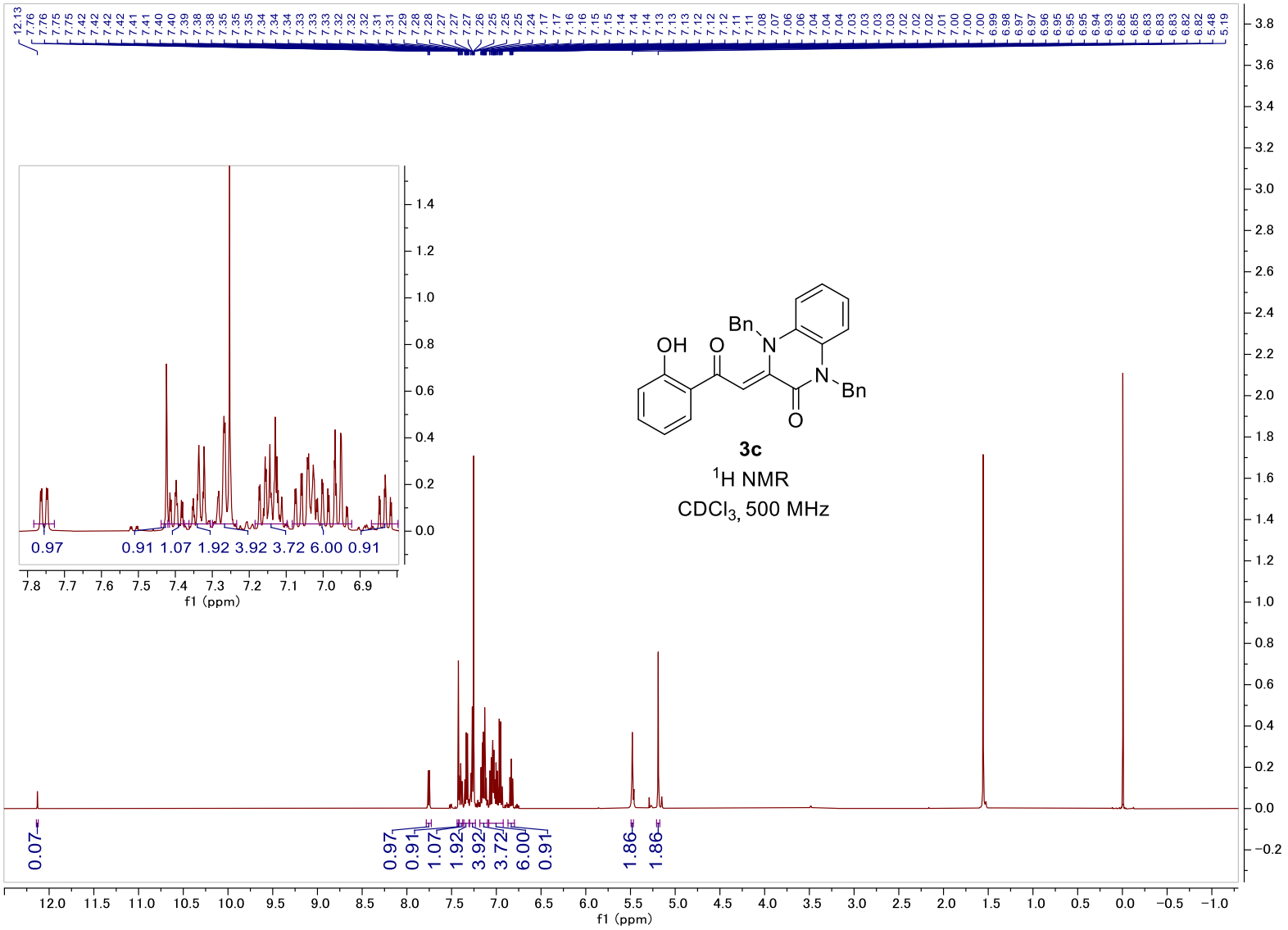
^{1}H NMR for (*Z*)-1-(2-hydroxyphenyl)-2-[(3-methyl-2(3*H*)-benzothiazolylidene]ethan-1-one (**3b'**) ($CDCl_3$, 400 MHz)



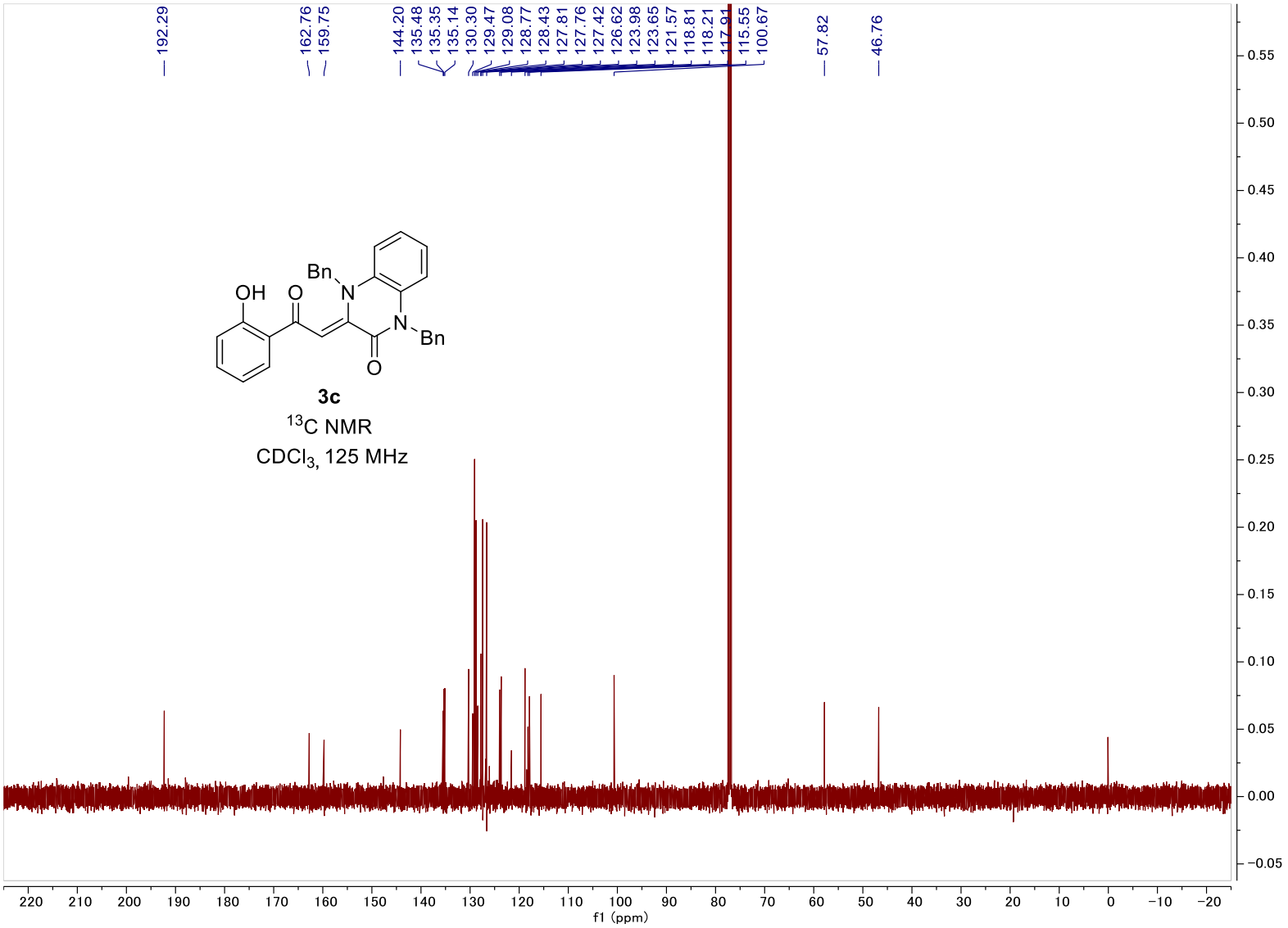
^{1}H NMR for (*Z*)-1-(2-hydroxyphenyl)-2-[(3-methyl-2(3*H*)-benzothiazolylidene]ethan-1-one (**3b'**) ($CDCl_3$, 400 MHz)



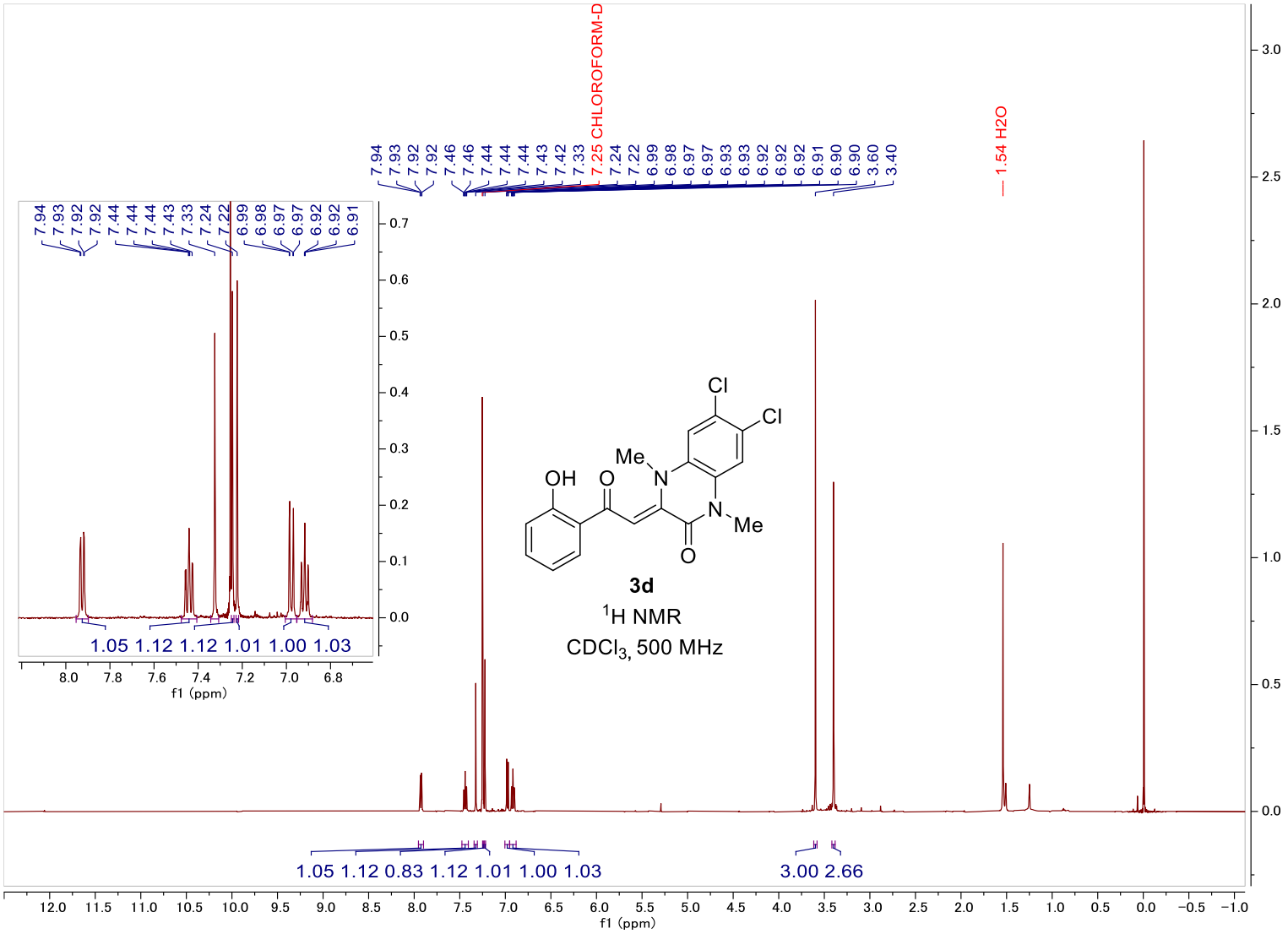
^{1}H NMR for (*Z*)-1,4-dibenzyl-3-[(2-hydroxyphenyl)-2-oxoethylidene]-3,4-dihydroquinoxalin-2(1*H*)-one (**3c**)
($CDCl_3$, 500 MHz)



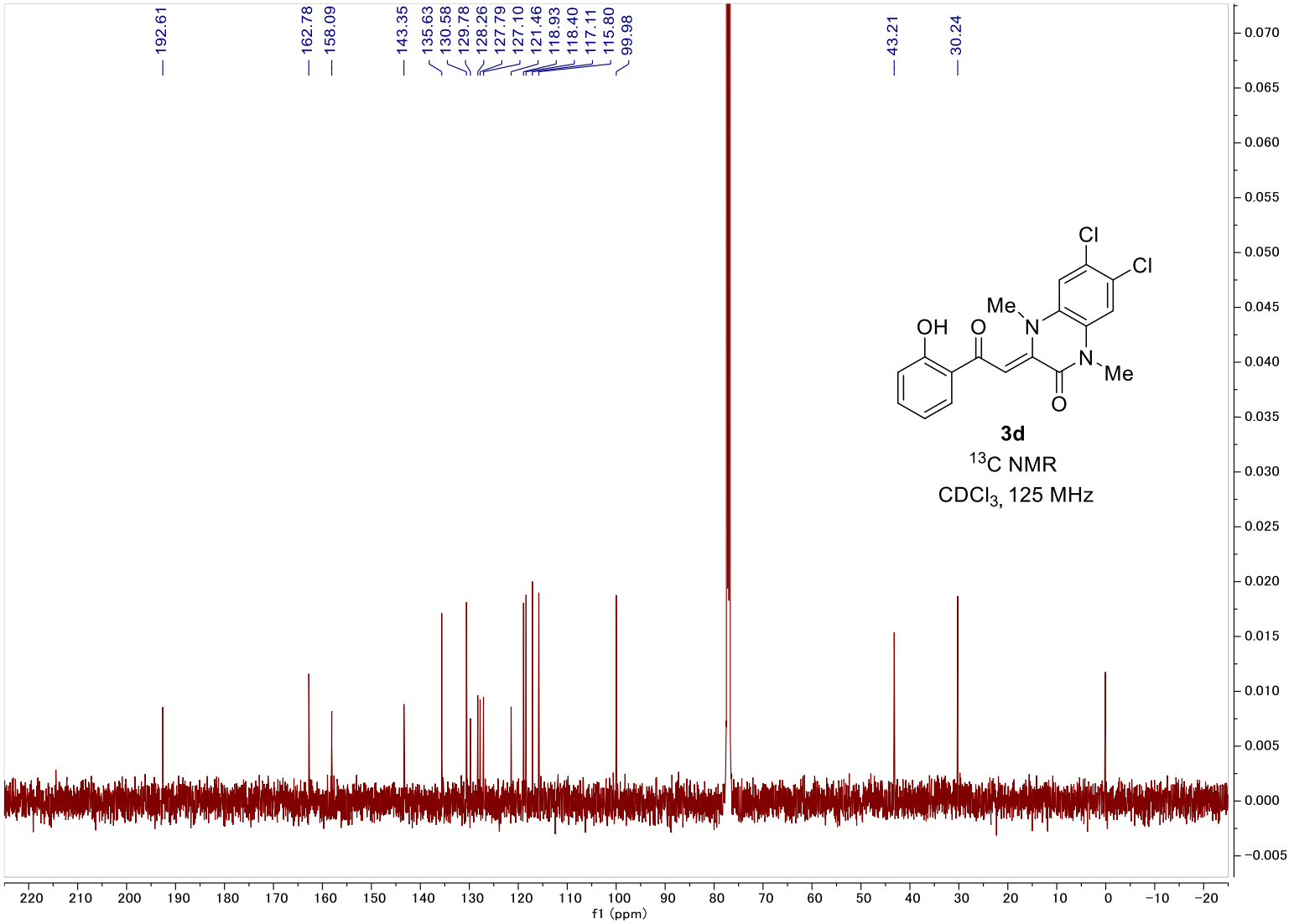
^{13}C NMR for (*Z*)-1,4-dibenzyl-3-[(2-hydroxyphenyl)-2-oxoethylidene]-3,4-dihydroquinoxalin-2(1*H*)- one (**3c**) ($CDCl_3$, 125 MHz)



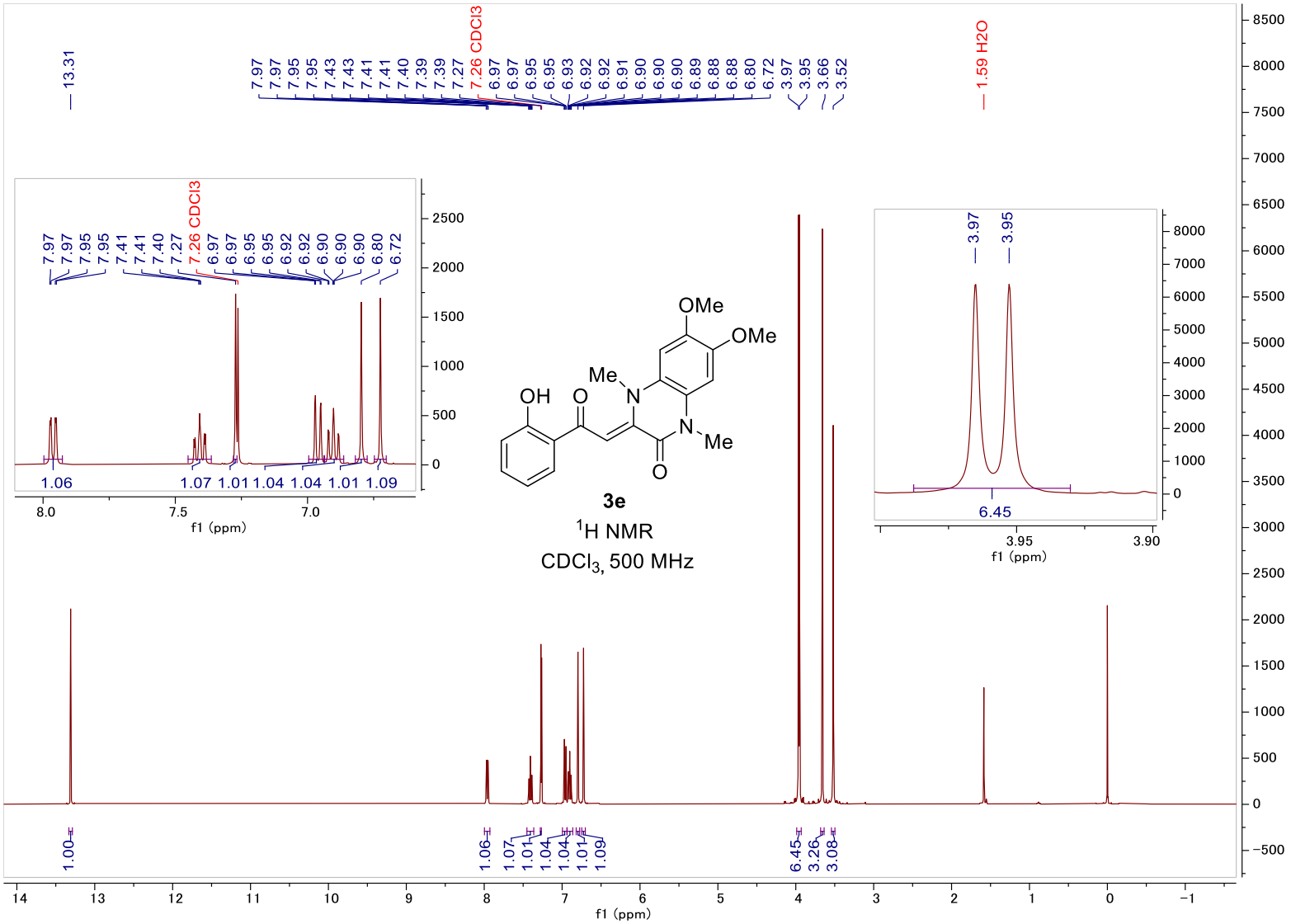
^{1}H NMR for (*Z*)-6,7-dichloro-3-[2-(2-hydroxyphenyl)-2-oxoethylidene]-1,4-dimethyl-3,4-dihydroquinoxalin-2(1*H*)-one (**3d**) ($CDCl_3$, 500 MHz)



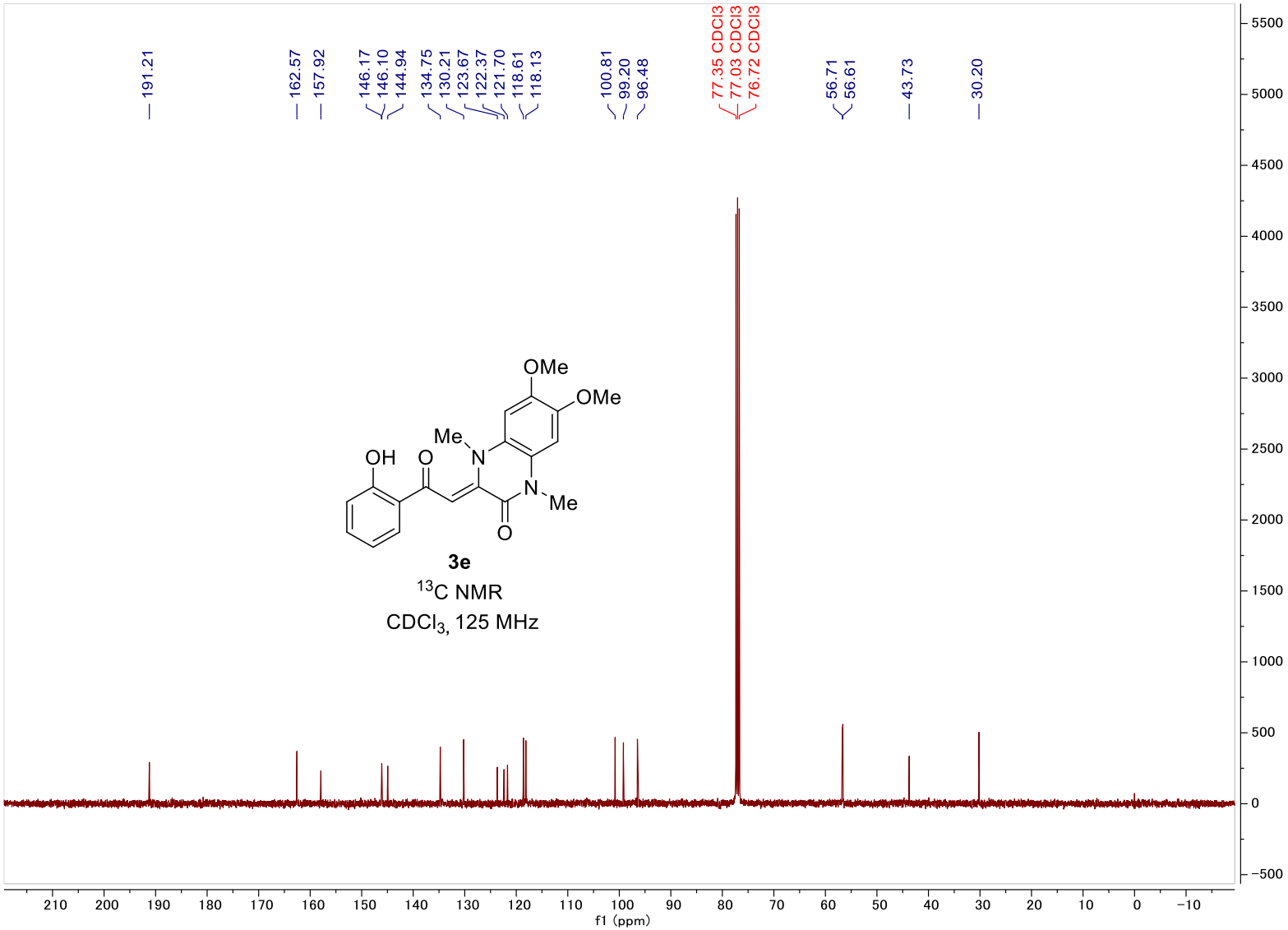
^{13}C NMR for (*Z*)-6,7-dichloro-3-[2-(2-hydroxyphenyl)-2-oxoethylidene]-1,4-dimethyl-3,4-dihydroquinoxalin-2(1*H*)-one (**3d**) ($CDCl_3$, 125 MHz)



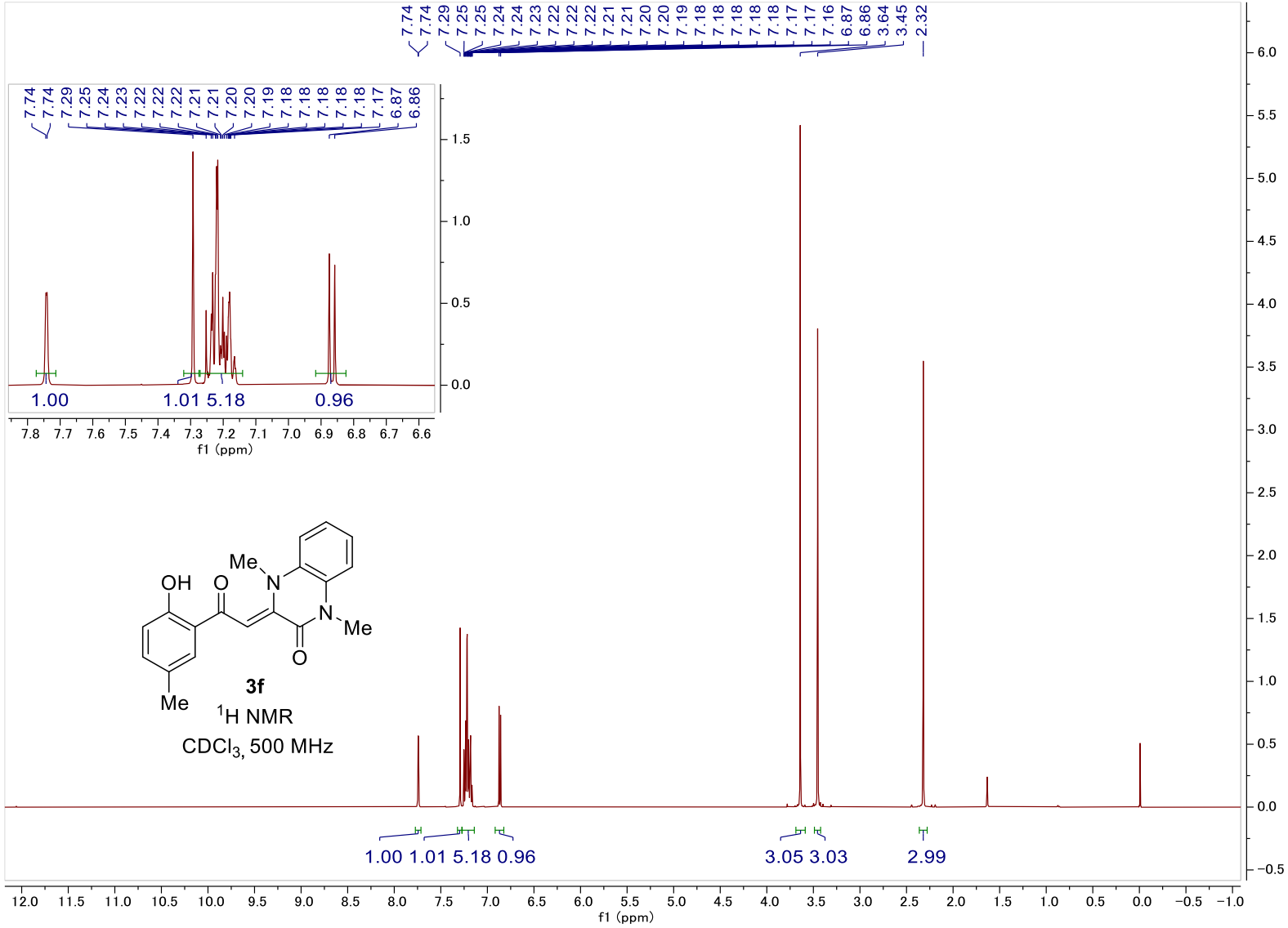
^{1}H NMR for (*Z*)-6,7-dimethoxy-1,4-dimethyl-3-[2-(2-hydroxyphenyl)-2-oxoethylidene]-3,4-dihydroquinoxalin-2(1*H*)-one (**3e**) ($CDCl_3$, 500 MHz)



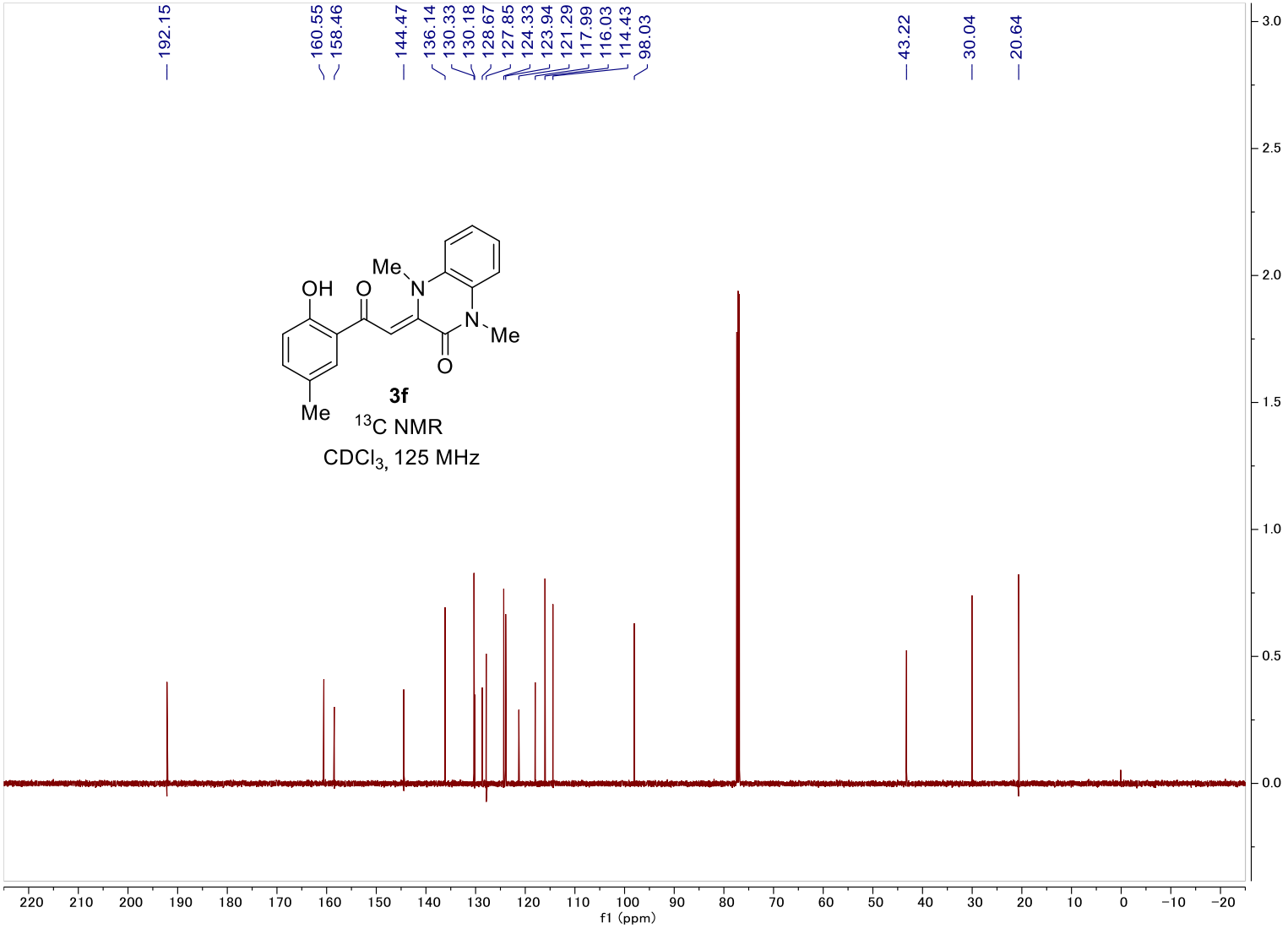
^{13}C NMR for (*Z*)-6,7-dimethoxy-1,4-dimethyl-3-[2-(2-hydroxyphenyl)-2-oxoethylidene]-3,4-dihydroquinoxalin-2(1*H*)-one (**3e**) ($CDCl_3$, 125 MHz)



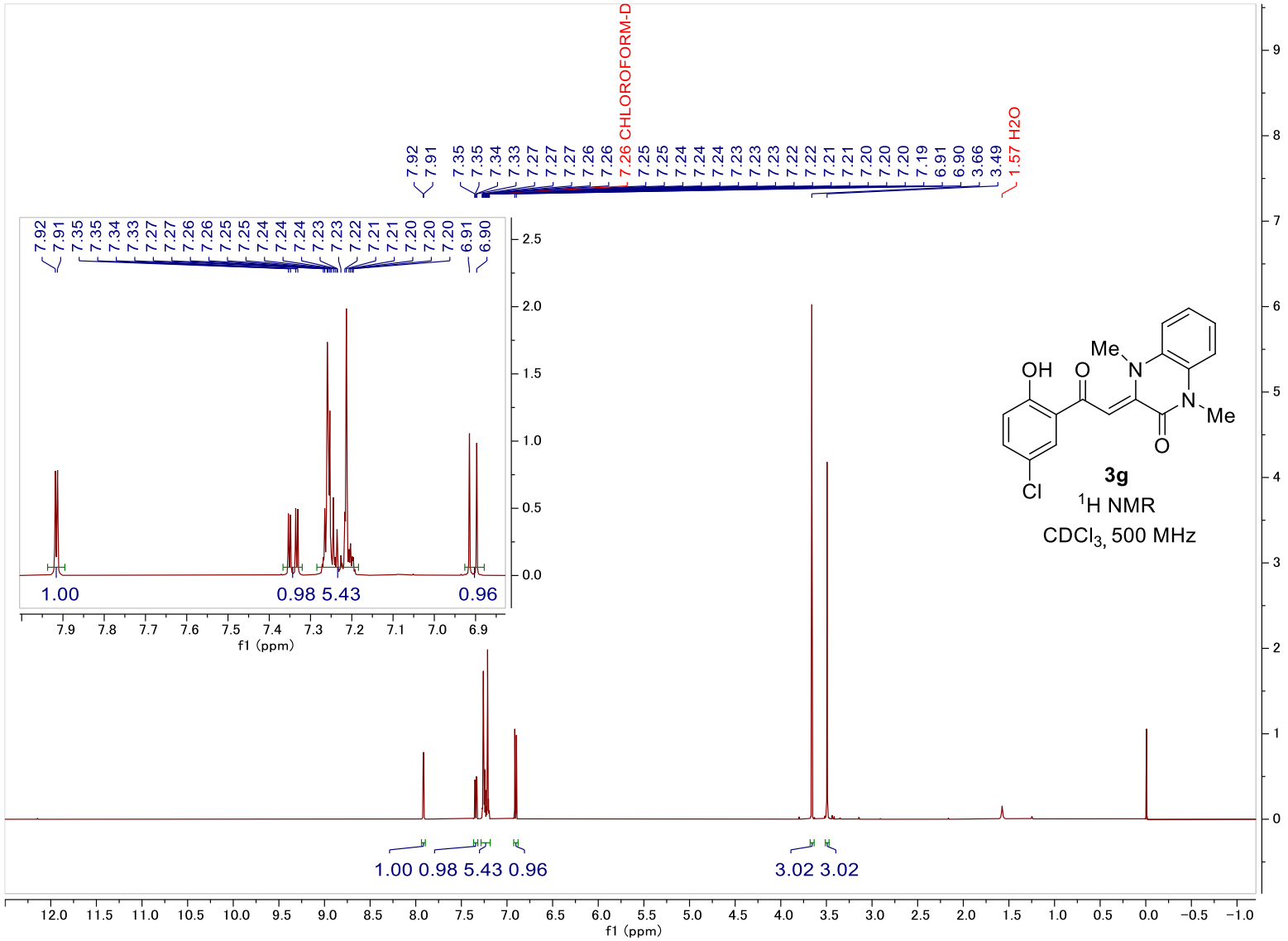
^{1}H NMR for (*Z*)-1,4-dimethyl-3-[2-(2-hydroxy-5-methylphenyl)-2-oxoethylidene]-3,4-dihydroquinoxalin-2(1*H*)-one (**3f**) ($CDCl_3$, 500 MHz)



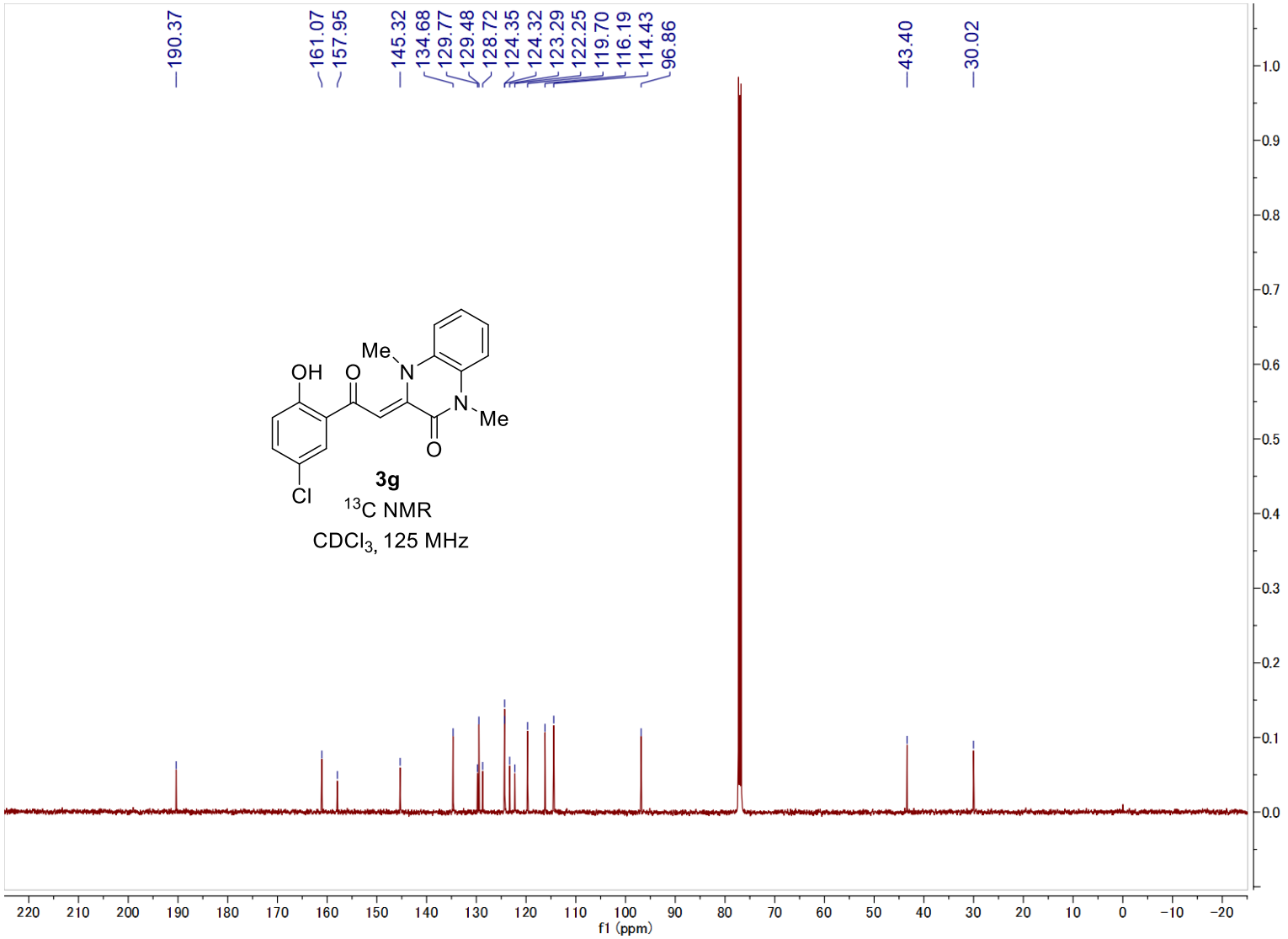
^{13}C NMR for (*Z*)-1,4-dimethyl-3-[2-(2-hydroxy-5-methylphenyl)-2-oxoethylidene]-3,4-dihydroquinoxalin-2(1*H*)-one (**3f**) ($CDCl_3$, 125 MHz)



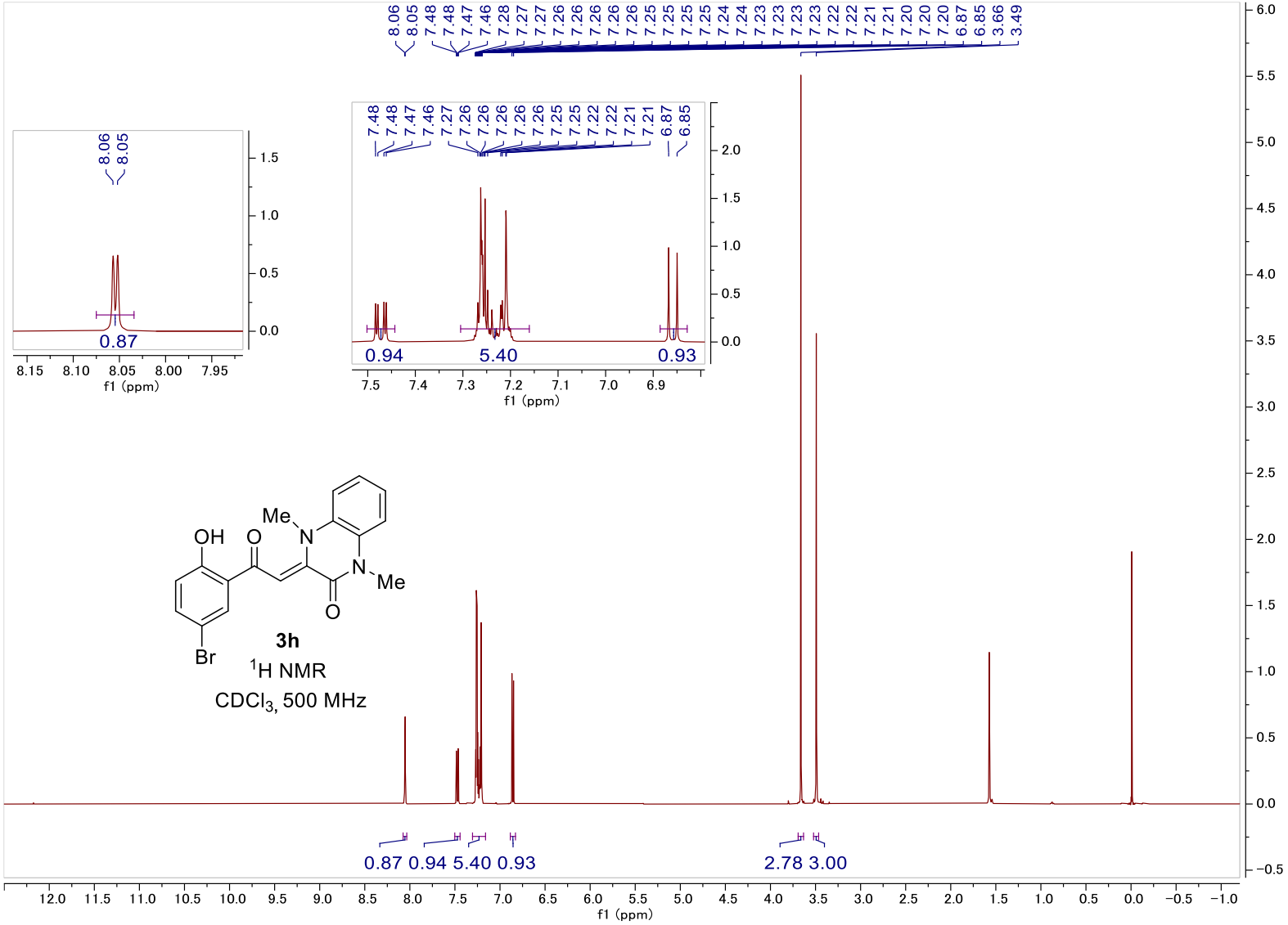
^{1}H NMR for (*Z*)-3-[2-(5-chloro-2-hydroxyphenyl)-2-oxoethylidene]-1,4-dimethyl-3,4-dihydroquinoxalin-2(1*H*)-one (**3g**) ($CDCl_3$, 500 MHz)



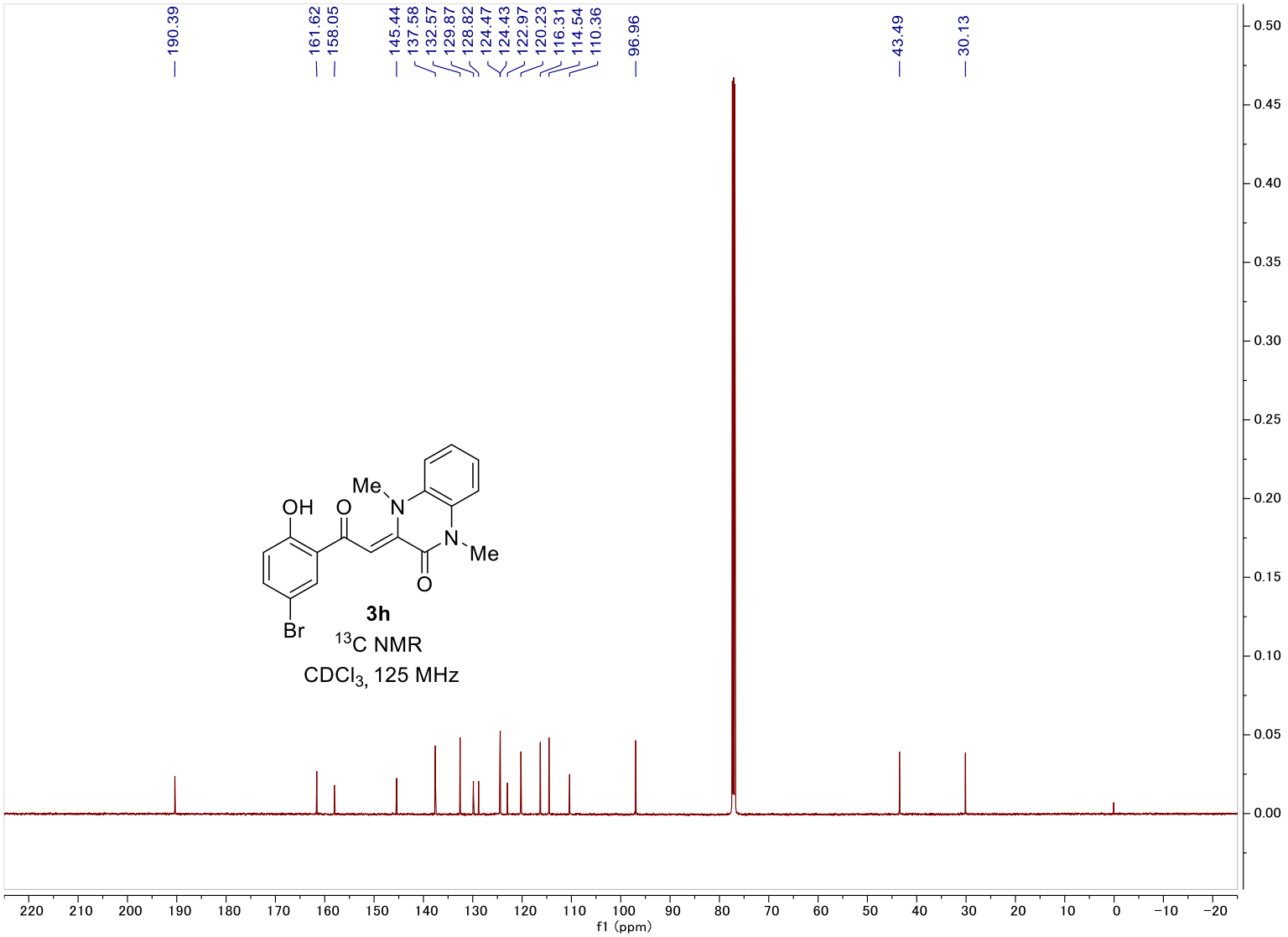
^{13}C NMR for (*Z*)-3-[2-(5-chloro-2-hydroxyphenyl)-2-oxoethylidene]-1,4-dimethyl-3,4-dihydroquinoxalin-2(1*H*)-one (**3g**) ($CDCl_3$, 125 MHz)



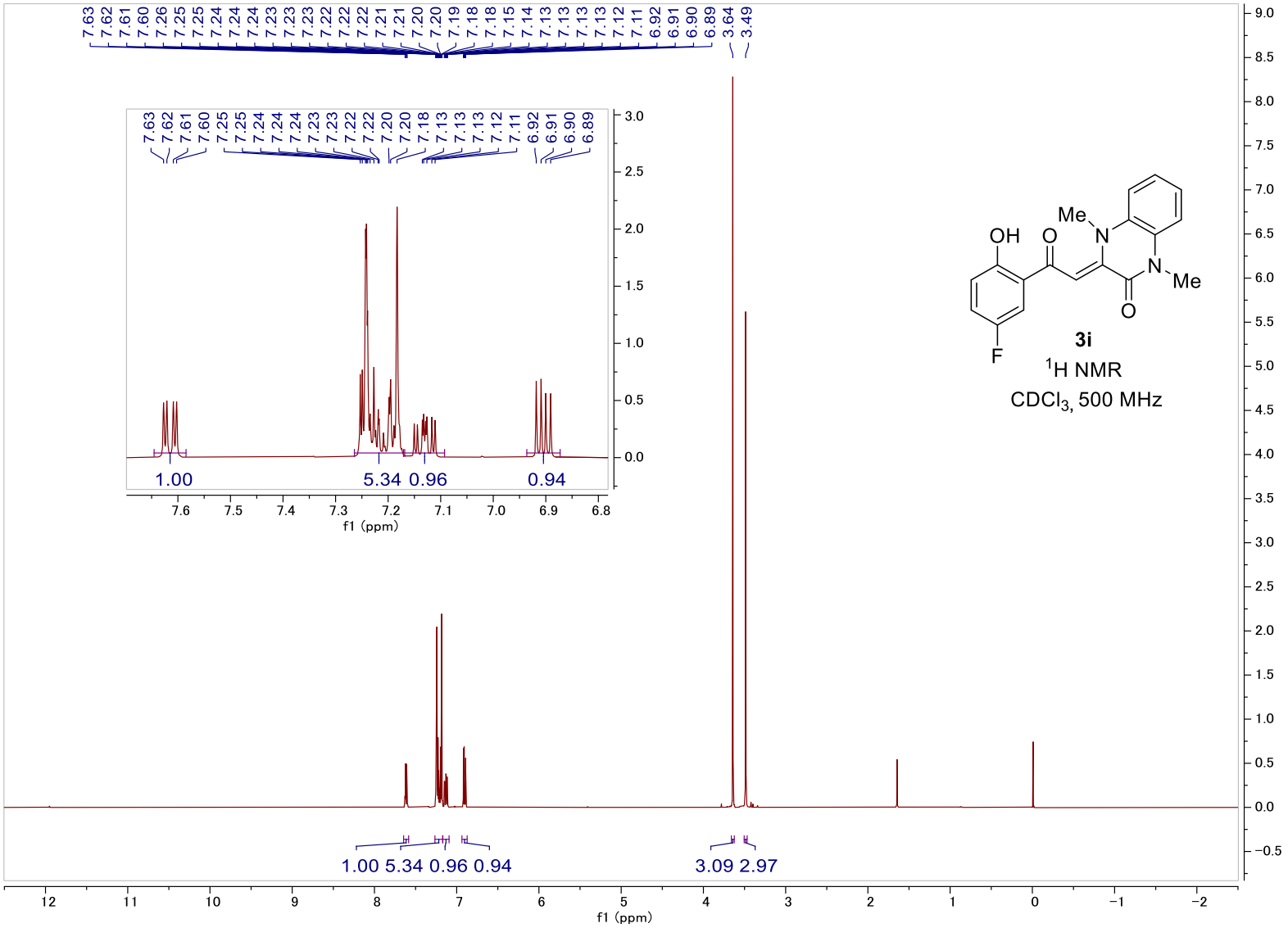
^{1}H NMR for (*Z*)-3-[(5-bromo-2-hydroxyphenyl)-2-oxoethylidene]-1,4-dimethyl-3,4-dihydroquinoxalin-2(1*H*)-one (**3h**) ($CDCl_3$, 500 MHz)



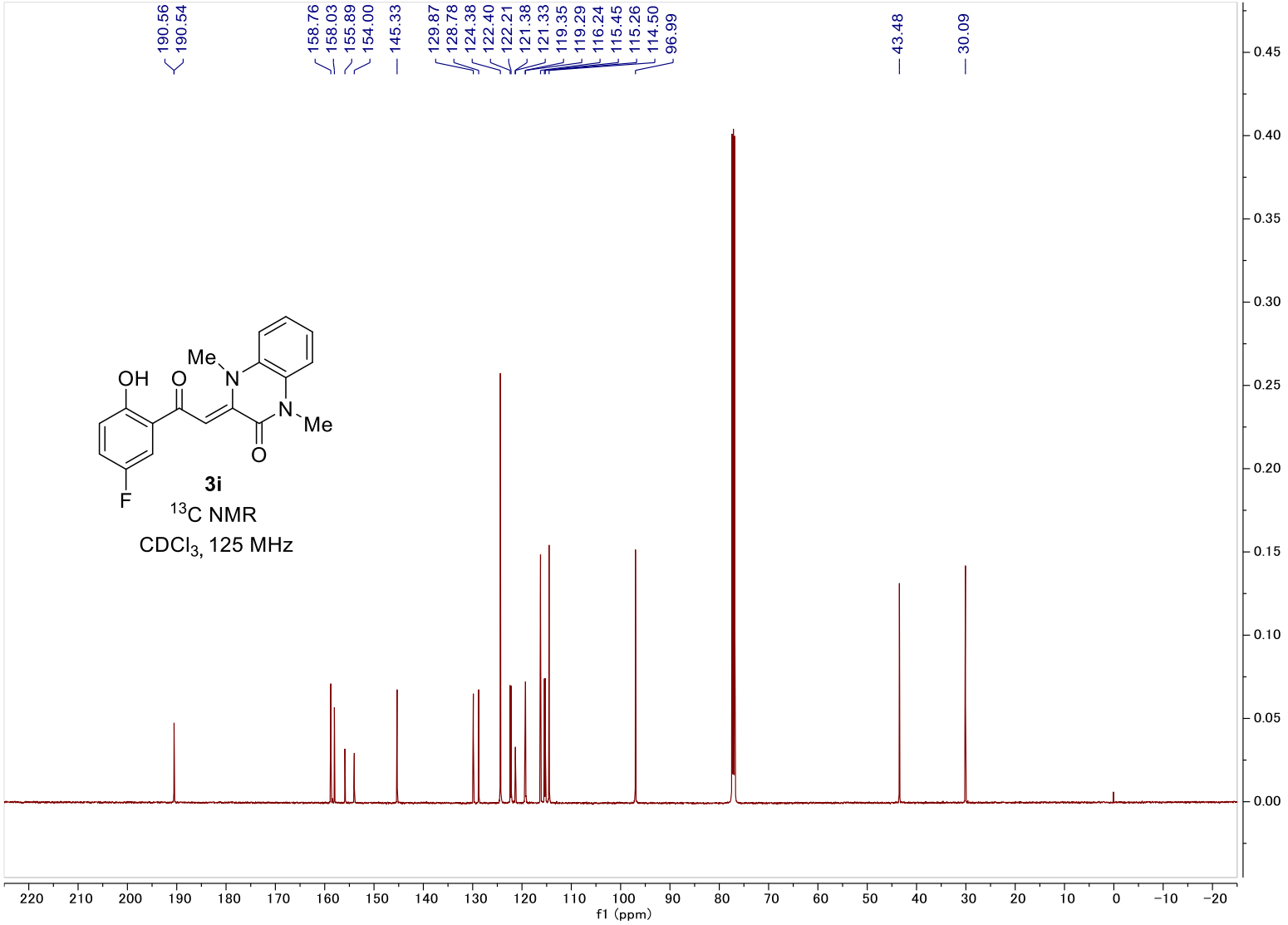
^{13}C NMR for (*Z*)-3-[(5-bromo-2-hydroxyphenyl)-2-oxoethylidene]-1,4-dimethyl-3,4-dihydroquinoxalin-2(1*H*)-one (**3h**)
($CDCl_3$, 125 MHz)



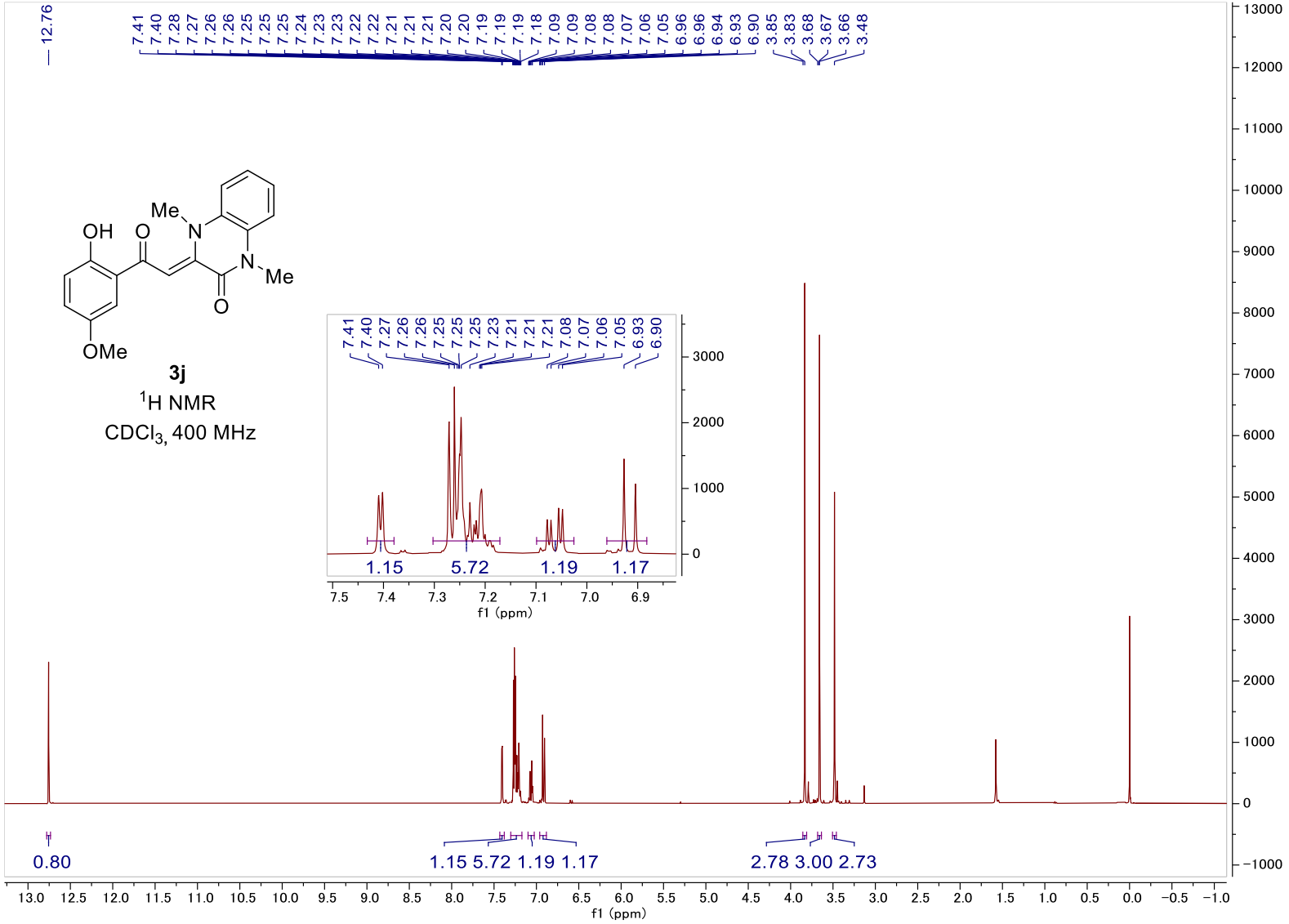
^{1}H NMR for (*Z*)-1,4-dimethyl-3-[(5-fluoro-2-hydroxyphenyl)-2-oxoethylidene]-3,4-dihydroquinoxalin-2(1*H*)-one (**3i**) ($CDCl_3$, 500 MHz)



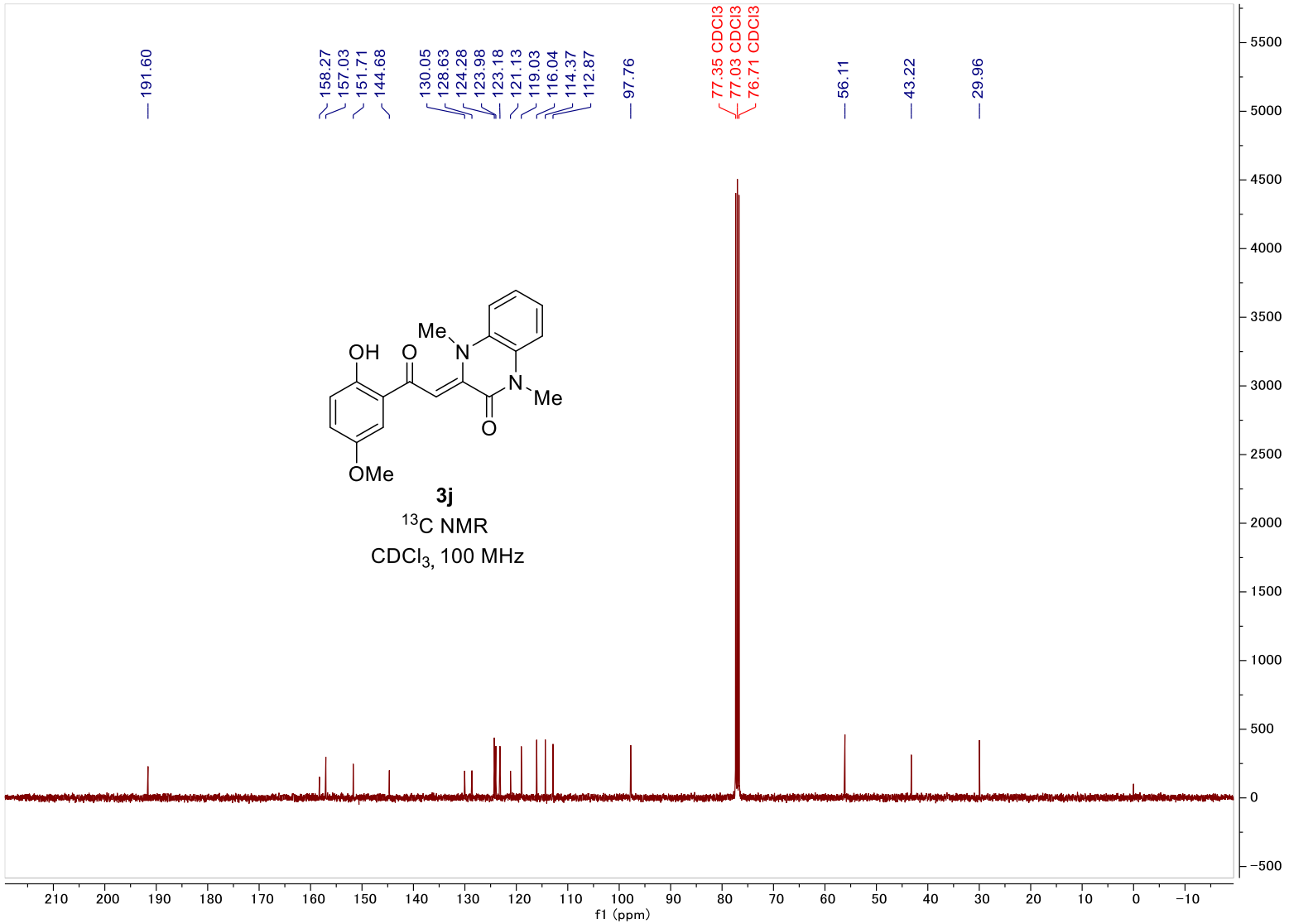
^{13}C NMR for (*Z*)-1,4-dimethyl-3-[(5-fluoro-2-hydroxyphenyl)-2-oxoethylidene]-3,4-dihydroquinoxalin-2(1*H*)-one (**3i**)
($CDCl_3$, 125 MHz)



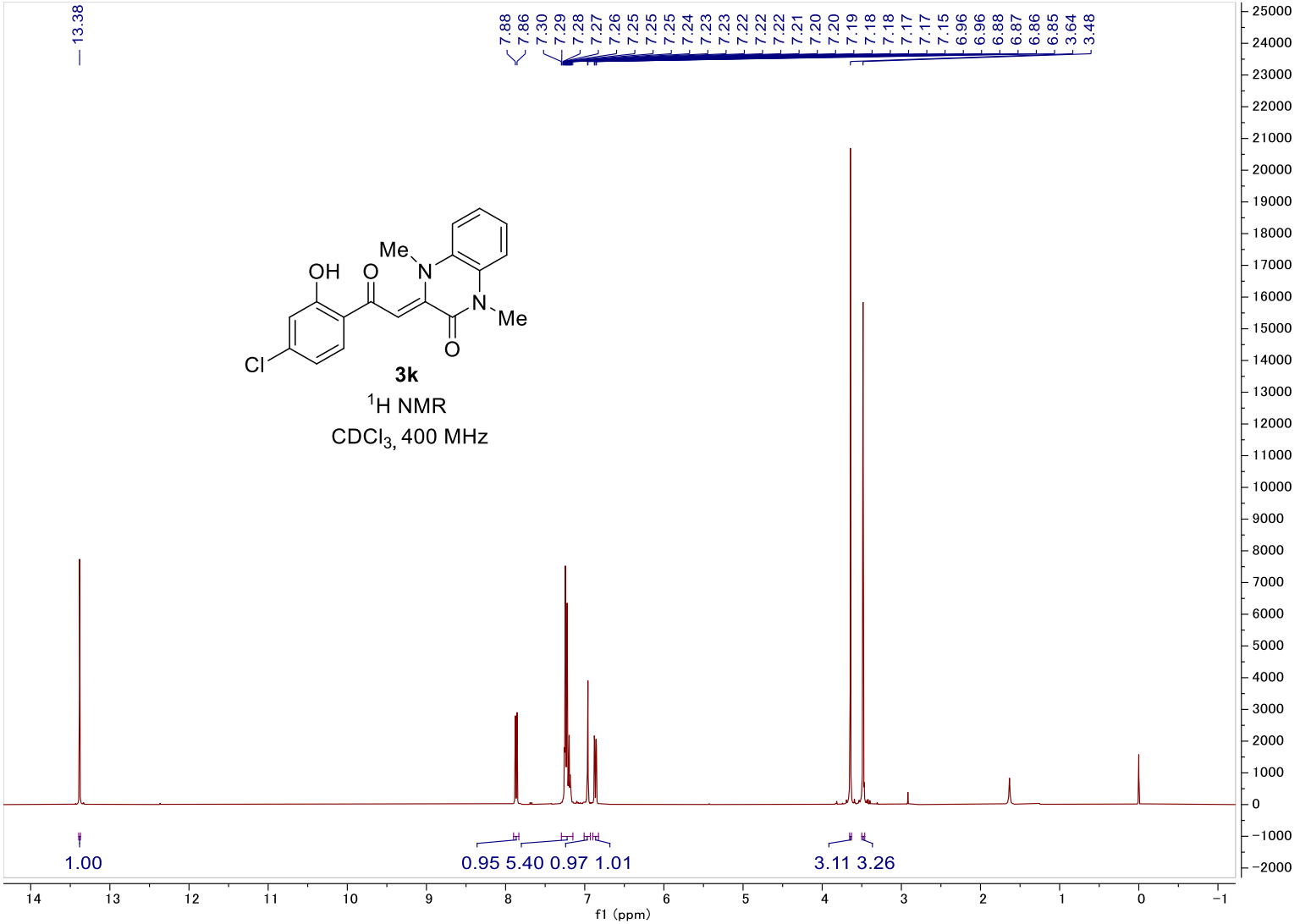
^{1}H NMR for (*Z*)-1,4-dimethyl-3-[(5-methoxy-2-hydroxyphenyl)-2-oxoethylidene]-3,4-dihydroquinoxalin-2(1*H*)-one (**3j**) ($CDCl_3$, 400 MHz)



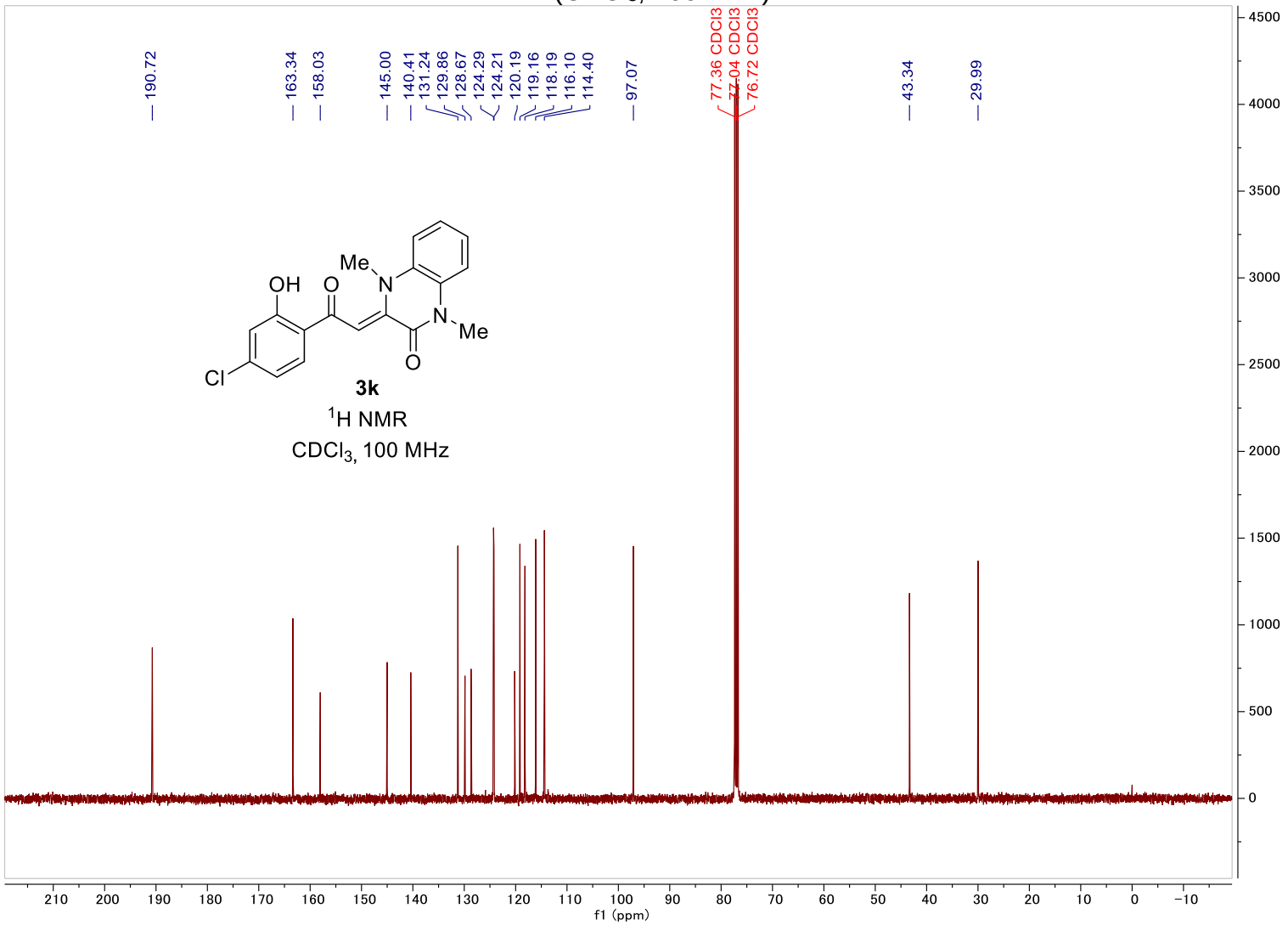
^{13}C NMR for (*Z*)-1,4-dimethyl-3-[(5-methoxy-2-hydroxyphenyl)-2-oxoethylidene]-3,4-dihydroquinoxalin-2(1*H*)-one (**3j**) ($CDCl_3$, 100 MHz)



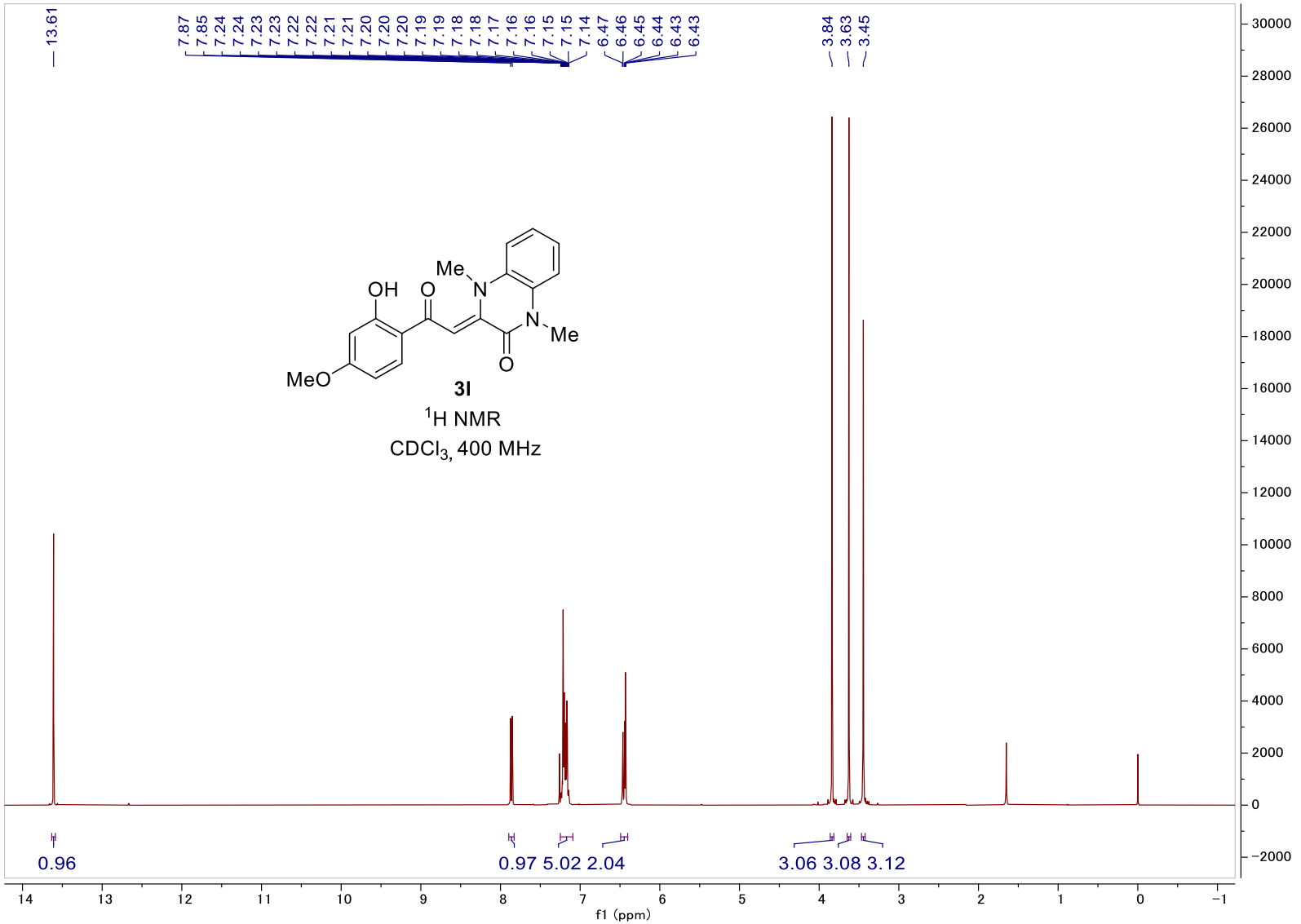
^{1}H NMR for (*Z*)-1,4-dimethyl-3-[(4-chloro-2-hydroxyphenyl)-2-oxoethylidene]-3,4-dihydroquinoxalin-2(1*H*)-one (**3k**) ($CDCl_3$, 400 MHz)



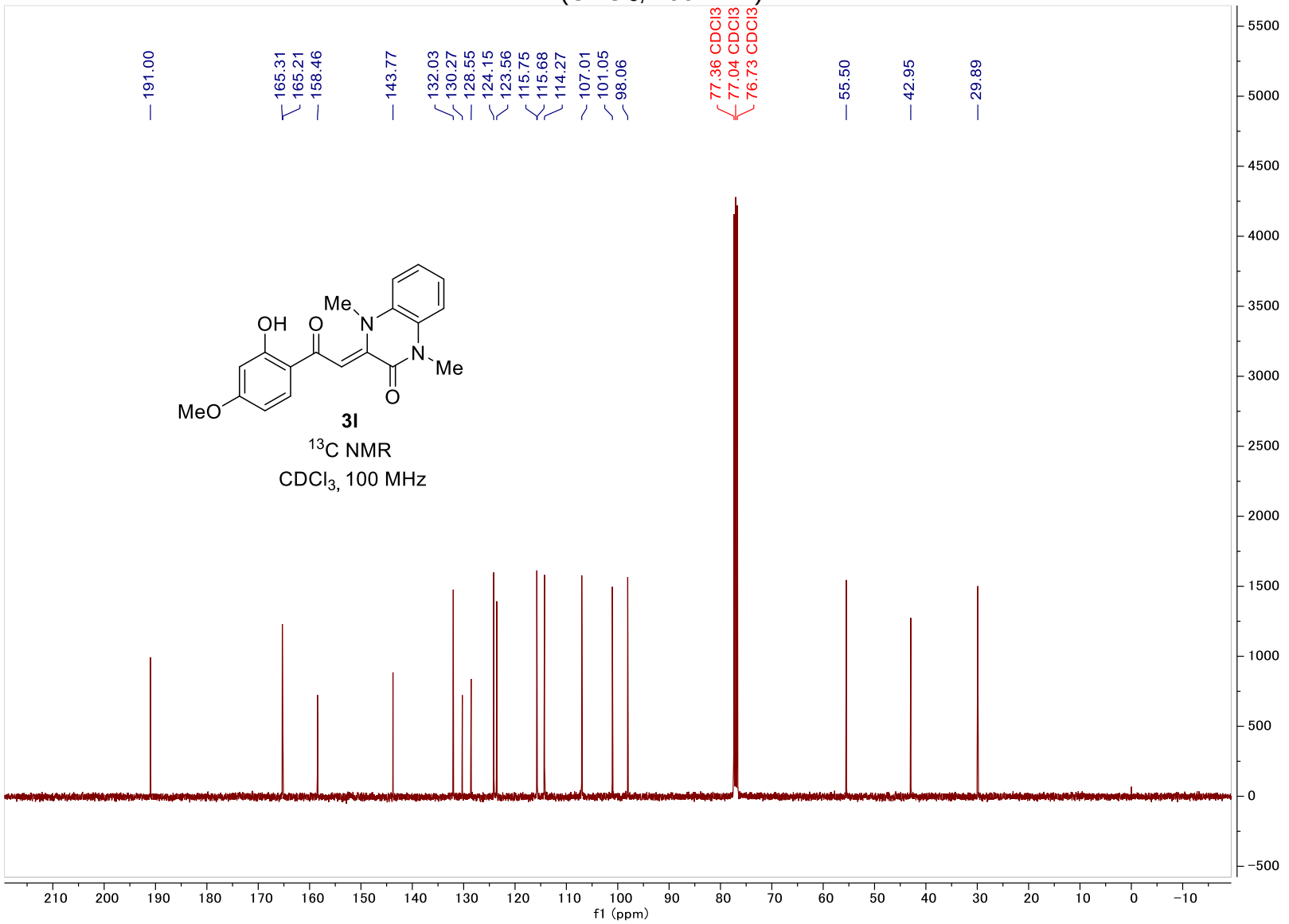
^{13}C NMR for (*Z*)-1,4-dimethyl-3-[(4-chloro-2-hydroxyphenyl)-2-oxoethylidene]-3,4-dihydroquinoxalin-2(1*H*)-one (**3k**) ($CDCl_3$, 100 MHz)



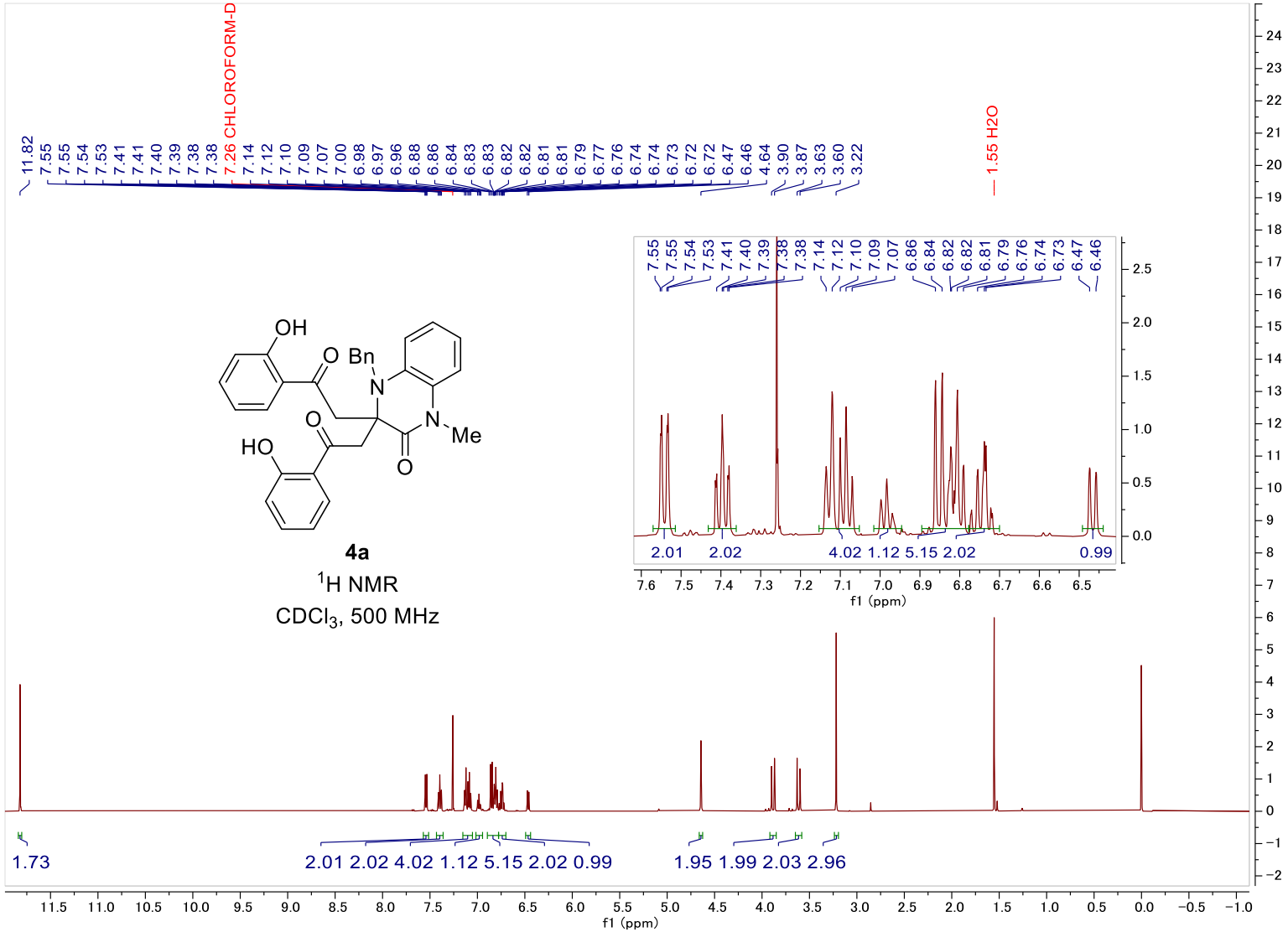
^{1}H NMR for (*Z*)-1,4-dimethyl-3-[(4-methoxy-2-hydroxyphenyl)-2-oxoethylidene]-3,4-dihydroquinoxalin-2(1*H*)-one (**3l**) ($CDCl_3$, 400 MHz)



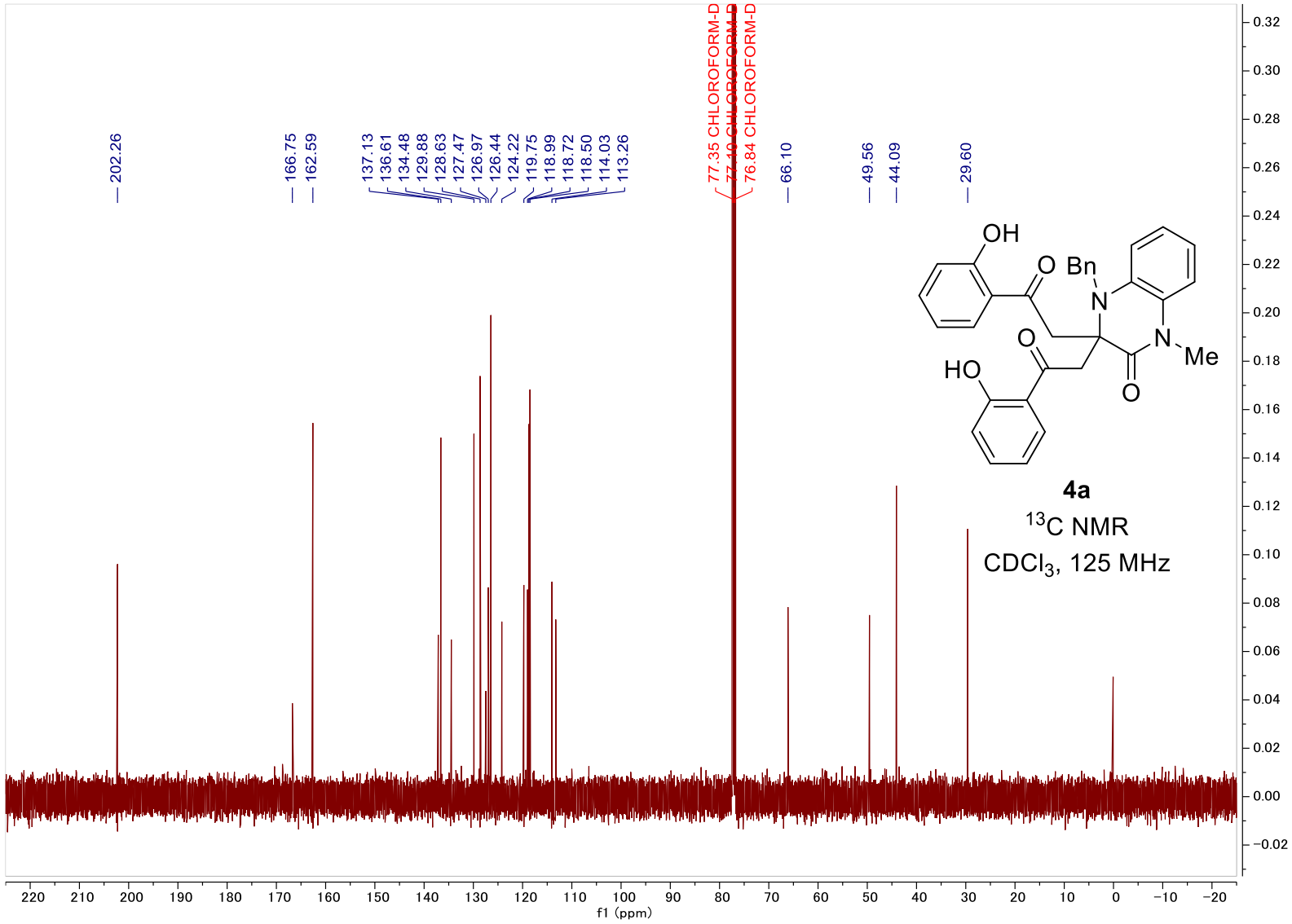
^{13}C NMR for (*Z*)-1,4-dimethyl-3-[(4-methoxy-2-hydroxyphenyl)-2-oxoethylidene]-3,4-dihydroquinoxalin-2(1*H*)-one (**3l**) ($CDCl_3$, 100 MHz)



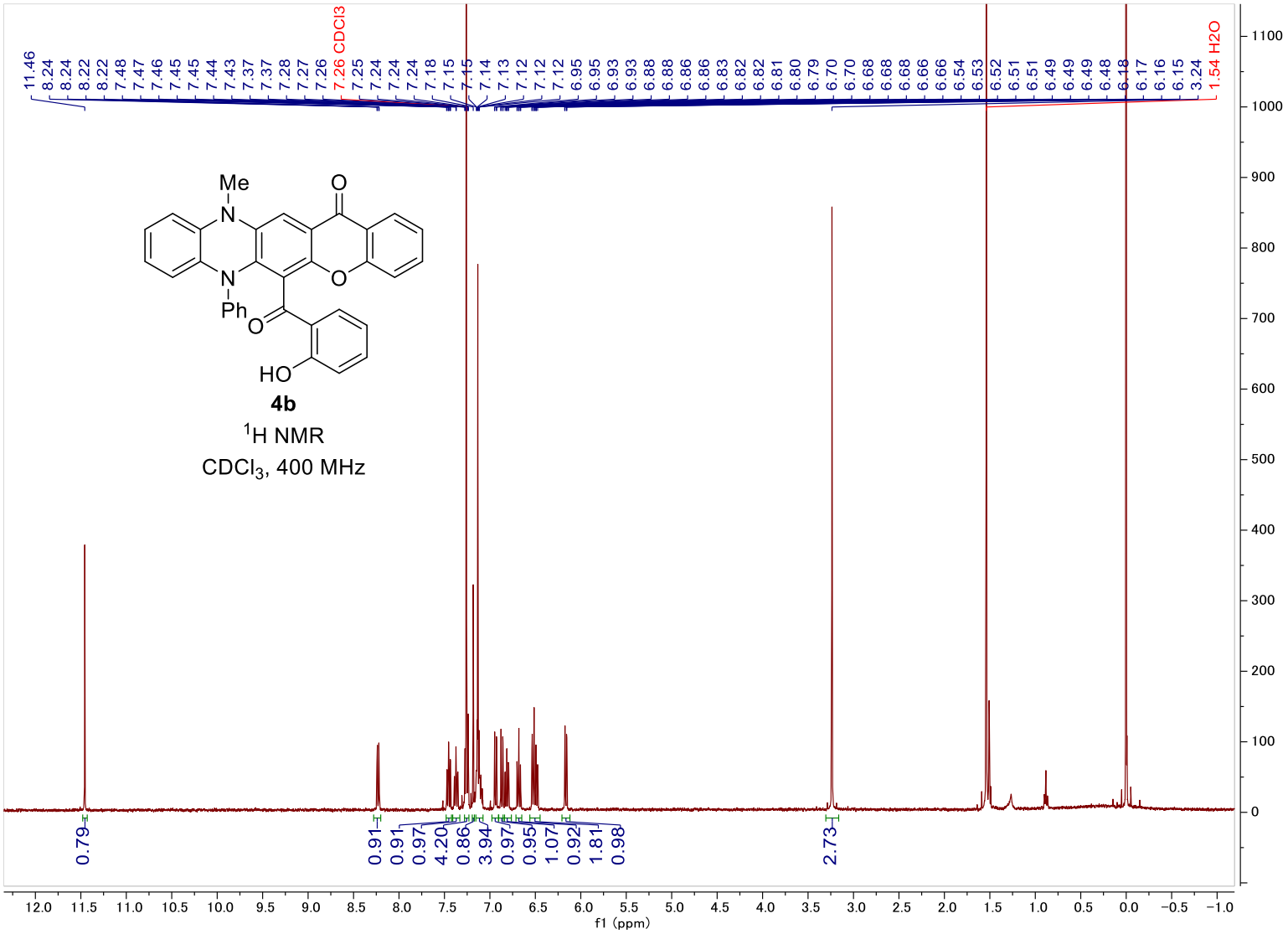
NMR for 4-benzyl-3,3-bis[(2-hydroxybenzoyl)methyl]-1-methyl-3,4-dihydroquinoxalin-2(1*H*)-one (**4a**) ($CDCl_3$, 500 MHz)



^{13}C NMR for 4-benzyl-3,3-bis[(2-hydroxybenzoyl)methyl]-1-methyl-3,4-dihydroquinoxalin-2(1*H*)-one (**4a**) ($CDCl_3$, 125 MHz)



^{1}H NMR for 6-(2-hydroxybenzoyl)-12-methyl-7-phenyl-7,12-dihydro-14*H*-chromeno[2,3-*b*]phenazin-14-one (**4b**)
($CDCl_3$, 400 MHz)



^{13}C NMR for 6-(2-hydroxybenzoyl)-12-methyl-7-phenyl-7,12-dihydro-14*H*-chromeno[2,3-*b*]phenazin-14-one (**4b**) ($CDCl_3$, 125 MHz)