

European Journal of Organic Chemistry

Supporting Information

Microwave-Assisted 1,3-Dioxa-[3,3]-Sigmatropic Rearrangement of Substituted Allylic Carbamates: Application to the Synthesis of Novel 1,3-Oxazine-2,4-dione Derivatives

Samar Bou Zeid, Samar Eid, Fadia Najjar, Aurélie Macé, Ivan Rivilla, Fernando P. Cossío,
Vincent Dorcet, Thierry Roisnel, and François Carreaux*

Contents:

I.	General information	S2
II.	General procedure for the synthesis of allylic alcohols 1a-g	S3
III.	General procedure for the synthesis of compounds 6a-i and 8a	S6
IV.	^1H NMR and ^{13}C NMR spectra of all compounds	S12
V.	X-Ray Crystallographic data for compound 7a	S115
VI.	X-Ray Crystallographic data for compound 9a	S116
VII.	Computational data	S117
VIII.	References	S140

I. General information

All air- and water-sensitive reactions were performed in flame-dried glassware under argon atmosphere. Tetrahydrofuran (THF) was distilled over sodium/benzophenone, dichloromethane (DCM) and ethanol were distilled over CaH₂ and toluene was distilled over sodium. All aldehydes were distilled prior to their used. All other commercial reagents were used as received unless otherwise.

NMR spectra were recorded on Bruker apparatus at 300, 400 or 500 MHz for ¹H and 75, 101 or 126 MHz for ¹³C. Chemical shifts are given relative to TMS or the appropriate solvent. Data are represented as follows: chemical shift (ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constant *J* (Hz) and integration. Assignments are made with the aid of DEPT 135, COSY and HMQC experiments.

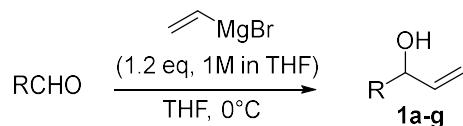
All high-resolution mass spectra (HRMS) were recorded on a Bruker Micro-Tof-Q II or on a Waters Q-Tof 2 at the CRMPO (Centre Régional de Mesures de Physiques de l'Ouest – Rennes- France) using positive ion electrospray.

Purifications on silica gel were carried out on Acros silica gel 0.006-0.200 mm, 60 Å. Flash chromatography purifications were performed on a Grace Reveleris™ apparatus. Analytical thin layer chromatography was performed on Merck Silica gel 60 F254 plates. Compounds were visualized by exposure to UV-light (254 nm) or by dipping the plates in a 7.6% solution of vanillin in a mixture of ethanol and sulfuric acid (99/1)

X-ray crystallographic data were collected on an APEXII crystal diffractometer at the Centre de Diffraction, Rennes.

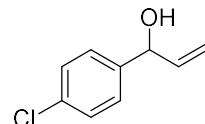
Melting points were measured on a melting point apparatus Stuart SMP10 and were not corrected.

II-General procedure for the preparation of allylic alcohols **1a-g**



To a solution of aldehyde (12.50 mmol) in THF (20 mL) was slowly added at 0° C (or -78 °C) a solution of vinyl magnesium bromide in THF (15 mmol, 1 M, 1.2 eq). The reaction mixture was stirred at room temperature for 16 hours after which a saturated NH₄Cl solution (15 mL) was added. The aqueous layer was extracted with ethyl acetate (4 x 20 mL). The organic layers were dried over MgSO₄, filtered and concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel to afford the corresponding product.

1-(4-chlorophenyl)prop-2-en-1-ol **1a**



Chemical Formula: C₉H₉ClO
MW: 168.62 g/mol

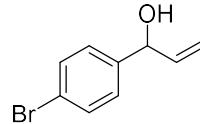
Prepared starting from 4-chlorobenzaldehyde (0 °C). The crude was purified by chromatography (silica gel, eluent: cyclohexane/AcOEt, 9/1) to give **1a** (1.14 g, 55%) as a pale yellow oil.

R_f = 0.25 (cyclohexane/EtOAc: 90/10)

¹H NMR (300 MHz, CDCl₃) δ ppm: 1.95 (d, J = 3.7 Hz, 1H), 5.20-5.26 (m, 2H), 5.37 (ddd, J = 16.9, 1.3, 1.2 Hz, 1H), 6.03 (ddd, J = 16.9, 10.2, 6.2 Hz, 1H), 7.30-7.38 (m, 4H).

Spectral data were identical to those reported in literature.¹

1-(4-Bromophenyl)prop-2-en-1-ol **1b**



Chemical Formula: C₉H₉BrO
MW: 213.07 g/mol

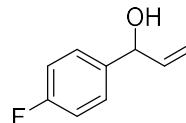
Prepared starting from 4-bromobenzaldehyde (-78 °C). The crude was purified by chromatography (silica gel, eluent: cyclohexane/AcOEt, 75/25) to give **1b** (590 mg, 22%) as a yellow oil.

R_f = 0.26 (cyclohexane/EtOAc: 75/25)

¹H NMR (300 MHz, CDCl₃) δ ppm: 1.96-2.01 (br s, 1H), 5.17-5.27 (m, 2H), 5.36 (d, J = 17.1 Hz, 1H), 6.02 (ddd, J = 17.1, 10.3, 6.1 Hz, 1H), 7.27 (d, J = 8.4 Hz, 2H), 7.50 (d, J = 8.4 Hz, 2H).

Spectral data were identical to those reported in literature.¹

1-(4-Fluorophenyl)prop-2-en-1-ol **1c**



Chemical Formula: C₉H₉FO
MW: 152.17 g/mol

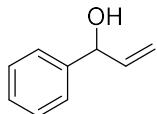
Prepared starting from 4-fluorobenzaldehyde (0 °C). The crude was purified by chromatography (silica gel, eluent: cyclohexane/AcOEt, 95/5) to give **1c** (800 mg, 42%) as a colorless oil.

R_f = 0.24 (cyclohexane/EtOAc: 95/5)

¹H NMR (300 MHz, CDCl₃) δ ppm: 1.97-2.02 (br s, 1H), 5.17-5.21 (m, 2H), 5.34 (ddd, J = 17.2 Hz, 1H), 6.02 (ddd, J = 17.2, 10.2, 6.1 Hz, 1H), 7.02-7.07 (m, 2H), 7.31-7.39 (m, 2H).

Spectral data were identical to those reported in literature.²

1-phenylprop-2-en-1-ol 1d



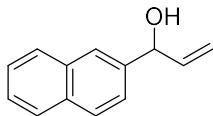
Chemical Formula: C₉H₁₀O
MW: 134.18 g/mol

Prepared starting from benzaldehyde (0 °C). The crude was purified by chromatography (silica gel, eluent: cyclohexane/AcOEt, 85/15) to give **1d** (1.02 g, 61%) as a colorless oil.

R_f = 0.25 (cyclohexane/EtOAc: 85/15)

¹H NMR (300 MHz, CDCl₃) δ ppm: 1.91 (d, J = 3.9 Hz, 1H), 5.17- 5.28 (m, 2H), 5.41 (ddd, J = 17.1, 1.3, 1.3 Hz, 1H), 6.09 (ddd, J = 17.1, 10.3, 5.9 Hz, 1H), 7.29-7.43 (m, 5H). Spectral data were identical to those reported in literature.¹

1-(naphthalen-2-yl)prop-2-en-1-ol 1e



Chemical Formula: C₁₃H₁₂O
MW: 184.24 g/mol

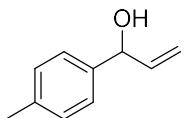
Prepared starting from 2-naphthaldehyde (0 °C). The crude was purified by chromatography (silica gel, eluent: cyclohexane/AcOEt, 85/15) to give **1e** (1.34 g, 58%) as a colorless oil.

R_f = 0.26 (cyclohexane/EtOAc: 85/15)

¹H NMR (300 MHz, CDCl₃) δ ppm: 2.16 (d, J = 3.8 Hz, 1H), 5.28 (ddd, J = 10.3, 1.2, 1.2 Hz, 1H), 5.38-5.42 (m, 1H), 5.46 (ddd, J = 17.0, 1.4, 1.4 Hz, 1H), 6.16 (ddd, J = 17.0, 10.3, 6.0 Hz, 1H), 7.48-7.54 (m, 3H), 7.82-7.89 (m, 4H).

Spectral data were identical to those reported in literature.¹

1-(p-tolyl)prop-2-en-1-ol 1f



Chemical Formula: C₁₀H₁₂O
MW: 148.21 g/mol

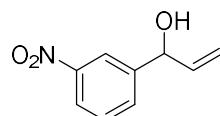
Prepared starting from 4-methylbenzaldehyde (0 °C). The crude was purified by chromatography (silica gel, eluent: cyclohexane/AcOEt, 90/10) to give **1f** (1.56 g, 84%) as a colorless oil.

R_f = 0.24 (cyclohexane/EtOAc: 90/10)

¹H NMR (300 MHz, CDCl₃) δ ppm: 1.98 (d, *J* = 3.8 Hz, 1H), 2.37 (s, 3H), 5.13-5.28 (m, 2H), 5.32-5.42 (m, 1H), 6.07 (ddd, *J* = 17.1, 10.2, 5.9 Hz, 1H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H).

Spectral data were identical to those reported in literature.²

1-(3-nitrophenyl)prop-2-en-1-ol 1g



Chemical Formula: C₉H₉NO₃
MW: 179.18 g/mol

Prepared starting from 3-nitrobenzaldehyde (0 °C). The crude was purified by chromatography (silica gel, eluent: cyclohexane/AcOEt, 75/25) to give **1g** (493 mg, 22%) as a colorless oil

R_f = 0.26 (cyclohexane/EtOAc: 75/25)

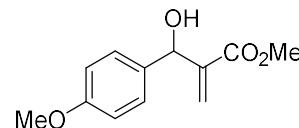
¹H NMR (300 MHz, CDCl₃) δ ppm: 2.14 (d, *J* = 3.5 Hz, 1H), 5.33 (dd, *J* = 11.1, 7.1 Hz, 2H), 5.44 (d, *J* = 17.1 Hz, 1H), 6.04 (ddd, *J* = 17.1, 10.2, 6.4 Hz, 1H), 7.55 (dd, *J* = 7.9 Hz, 1H), 8.28 (s, 1H), 7.75 (d, *J* = 7.7 Hz, 1H), 8.17 (d, *J* = 8.1 Hz, 1H).

Spectral data were identical to those reported in literature.¹

III. General procedure for the synthesis of compounds 6a-i and 8a

To the desired aldehyde (18.85 mmol) was added the required amount of DABCO (18.85 mmol). The resulting mixture was degassed under slow bubbling of argon for 5 min. Methyl acrylate (75.39 mmol) was then introduced and the mixture was stirred at 25 °C. After specified time reaction, the reaction mixture was diluted in 15 mL of dichloromethane and washed twice with 1N aqueous HCl (15 mL) and brine. The organic layers were collected, dried over anhydrous magnesium sulfate, and concentrated under reduced pressure. The residue was purified by silica gel chromatography to afford the corresponding product **6**. For the synthesis of compound **8a**, methyl acrylate was replaced by acrylonitrile.

Methyl 2-(hydroxy(4-methoxyphenyl)methyl)acrylate **6a**



Chemical Formula: C₁₂H₁₄O₄
MW: 222.24 g/mol

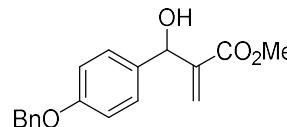
Prepared starting from 4-methoxybenzaldehyde (20 days). The crude was purified by chromatography (silica gel, eluent: cyclohexane/AcOEt, 80/20) to give **6a** (1.97 g, 47%) as a white solid.

R_f = 0.26 (cyclohexane/EtOAc: 80/20)

¹H NMR (300 MHz, CDCl₃) δ ppm: 2.85 (d, *J* = 5.7 Hz, 1H), 3.75 (s, 3H), 3.82 (s, 3H), 5.56 (d, *J* = 5.7 Hz, 1H), 5.85-5.87 (m, 1H), 6.33-6.35 (m, 1H), 6.90 (d, *J* = 8.9 Hz, 2H), 7.32 (d, *J* = 8.9 Hz, 2H).

Spectral data were identical to those reported in literature.³

Methyl 2-((4-(benzyloxy)phenyl)(hydroxy)methyl)acrylate **6b**



Chemical Formula: C₁₈H₁₈O₄
MW: 298.34 g/mol

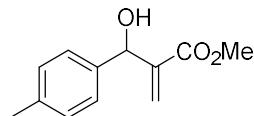
Prepared starting from 4-benzyloxybenzaldehyde (38 days). The crude was purified by chromatography (silica gel, eluent: cyclohexane/AcOEt, 75/25) to give **6b** (3.4 g, 61%) as a white amorphous solid.

R_f = 0.29 (cyclohexane/EtOAc: 75/25)

¹H NMR (300 MHz, CDCl₃) δ ppm: 2.86 (d, *J* = 5.4 Hz, 1H), 3.75 (s, 3H), 5.08 (s, 2H), 5.56 (d, *J* = 5.4 Hz, 1H), 5.86-5.88 (m, 1H), 6.34-6.36 (m, 1H), 6.93-7.02 (m, 2H) 7.25-7.51 (m, 9H).

Spectral data were identical to those reported in literature.⁴

Methyl 2-(hydroxy(*p*-tolyl)methyl)acrylate **6c**



Chemical Formula: C₁₂H₁₄O₃
MW: 206.24 g/mol

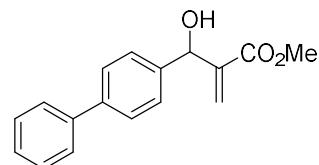
Prepared starting from 4-methylbenzaldehyde (6 days). The crude was purified by chromatography (silica gel, eluent: cyclohexane/AcOEt, 80/20) to give **6c** (2.37 g, 61%) as a colorless oil.

R_f = 0.29 (cyclohexane/EtOAc: 80/20)

¹H NMR (400 MHz, CDCl₃) δ ppm: 2.36 (s, 3H), 2.95 (d, *J* = 5.6 Hz, 1H), 3.74 (s, 3H), 5.56 (d, *J* = 5.6 Hz, 1H), 5.86-5.88 (m, 1H), 6.34-6.36 (m, 1H), 7.18 (d, *J* = 8.1 Hz, 2H), 7.28 (d, *J* = 8.1 Hz, 2H).

Spectral data were identical to those reported in literature.³

Methyl 2-([1,1'-biphenyl]-4-yl(hydroxy)methyl)acrylate **6d**



Chemical Formula: C₁₇H₁₆O₃
MW: 268.31 g/mol

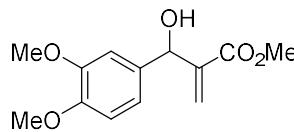
Prepared starting from [1,1'-biphenyl]-4-carbaldehyde (10 days). The crude was purified by chromatography (silica gel, eluent: cyclohexane/AcOEt, 80/20) to give **6d** (4.7 g, 93%) as a white solid.

R_f = 0.32 (cyclohexane/EtOAc: 80/20)

¹H NMR (300 MHz, CDCl₃) δ ppm: 3.02 (d, *J* = 5.8 Hz, 1H), 3.77 (s, 3H), 5.64 (d, *J* = 5.8 Hz, 1H), 5.91-5.93 (m, 1H), 6.39-6.41 (m, 1H), 7.33-7.47 (m, 5H), 7.61-7.75 (m, 4H).

Spectral data were identical to those reported in literature.³

Methyl 2-((3,4-dimethoxyphenyl)(hydroxy)methyl)acrylate **6e**



Chemical Formula: C₁₃H₁₆O₅
MW: 252.27 g/mol

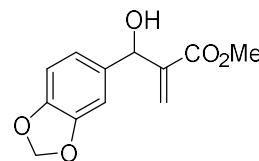
Prepared starting from 3,4-dimethoxybenzaldehyde (24 days). The crude was purified by chromatography (silica gel, eluent: cyclohexane/AcOEt, 80/20) to give **6e** (2.19g, 46%) as a white amorphous solid.

R_f = 0.3 (cyclohexane/EtOAc: 80/20)

¹H NMR (300 MHz, CDCl₃) δ ppm: 2.99 (d, *J* = 5.4 Hz, 1H), 3.75 (s, 3H), 3.88 (s, 3H), 3.89 (s, 3H), 5.54 (d, *J* = 5.4 Hz, 1H), 5.85 (dd, *J* = 1.3, 1.3 Hz, 1H), 6.34 (dd, *J* = 0.9, 0.9 Hz, 1H), 6.96-6.84 (m, 3H).

Spectral data were identical to those reported in literature.⁵

Methyl 2-(benzo[d][1,3]dioxol-5-yl(hydroxy)methyl)acrylate **6f**



Chemical Formula: C₁₂H₁₂O₅
MW: 236.22 g/mol

Prepared starting from benzo[d][1,3]dioxole-5-carbaldehyde (22 days). The crude was purified by chromatography (silica gel, eluent: cyclohexane/AcOEt, 80/20) to give **6f** (2.0 g, 45%) as a colorless oil.

R_f = 0.29 (cyclohexane/EtOAc: 80/20)

¹H NMR (300 MHz, CDCl₃) δ ppm: 2.93 (d, *J* = 5.3 Hz, 1H), 3.73 (s, 3H), 5.48 (d, *J* = 5.3 Hz, 1H), 5.85-5.87 (m, 1H), 5.94 (s, 2H), 6.33 (s, 1H), 6.74- 6.88 (m, 3H).

Spectral data were identical to those reported in literature.⁶

Methyl 2-((2,3-dihydrobenzo[b][1,4]dioxin-6-yl)(hydroxy)methyl)acrylate 6g



Chemical Formula: C₁₃H₁₄O₅
MW: 250.25 g/mol

Prepared starting from 2,3-dihydrobenzofuran-5-carbaldehyde (32 days). The crude was purified by chromatography (silica gel, eluent: cyclohexane/AcOEt, 70/30) to give **6g** (2.31 g, 49%) as a yellow oil.

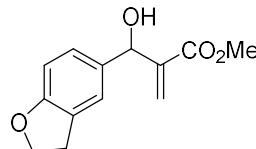
R_f = 0.25 (cyclohexane/EtOAc: 70/30)

¹H NMR (300 MHz, CDCl₃) δ ppm: 3.04 (d, *J* = 5.2 Hz, 1H), 3.72 (s, 3H), 4.23 (s, 4H), 5.46 (d, *J* = 5.2 Hz, 1H), 5.87-5.89 (m, 1H), 6.31-6.33 (m, 1H), 6.81-6.89 (m, 3H).

¹³C NMR (75 MHz, CDCl₃) δ ppm: 51.9, 64.3, 64.4, 72.6, 115.6, 117.1, 119.7, 125.7, 134.8, 142.0, 143.2, 143.4, 166.7.

Spectral data were identical to those reported in literature.⁷

Methyl 2-((2,3-dihydrobenzofuran-5-yl)(hydroxy)methyl)acrylate 6h



Chemical Formula: C₁₃H₁₄O₄
MW: 234.25 g/mol

Prepared starting from 2,3-dihydrobenzofuran-5-carbaldehyde (20 days). The crude was purified by chromatography (silica gel, eluent: cyclohexane/AcOEt, 80/20) to give **6h** (930 mg, 21%) as a colorless oil.

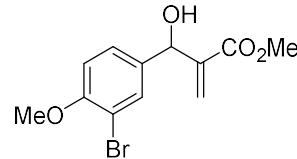
R_f = 0.32 (cyclohexane/EtOAc: 80/20)

¹H NMR (300 MHz, CDCl₃) δ ppm: 2.82 (d, *J* = 5.9 Hz, 1H), 3.21 (t, *J* = 8.7 Hz, 2H), 3.75 (s, 3H), 4.58 (t, *J* = 8.7 Hz, 2H), 5.53 (d, *J* = 5.9 Hz, 1H), 5.90 (dd, *J* = 1.3, 1.3 Hz, 1H), 6.35 (dd, *J* = 1.0, 1.0 Hz, 1H), 6.76 (d, *J* = 8.2 Hz, 1H), 7.11 (dd, *J* = 8.2, 1.9 Hz, 1H), 7.24 (d, *J* = 1.9 Hz, 1H).

¹³C NMR (75 MHz, CDCl₃) δ ppm: 29.7, 51.9, 71.4, 72.9, 109.0, 123.4, 125.4, 126.8, 127.3, 133.5, 142.3, 159.8, 166.8.

HRMS (ESI) m/z calcd for C₁₃H₁₄O₄Na [M+Na]⁺ 257.0784, Found 257.0785.

Methyl 2-((3-bromo-4-methoxyphenyl)(hydroxy)methyl)acrylate **6i**



Chemical Formula: C₁₂H₁₃BrO₄
MW: 301.14 g/mol

Prepared starting from 3-bromo-4-methoxybenzaldehyde (10 days). The crude was purified by chromatography (silica gel, eluent: cyclohexane/AcOEt, 80/20) to give **6i** (4.0 g, 71%) as a colorless oil.

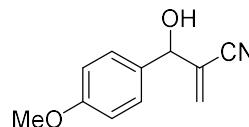
R_f = 0.35 (cyclohexane/EtOAc: 80/20)

¹H NMR (300 MHz, CDCl₃) δ ppm: 2.97-3.01 (br s, 1H), 3.77 (s, 3H), 3.91 (s, 3H), 5.50-5.52 (m, 1H), 5.87-5.89 (m, 1H), 6.36-6.38 (m, 1H), 6.89 (d, *J* = 8.5 Hz, 1H), 7.31 (dd, *J* = 8.5, 2.1 Hz, 1H), 7.57 (d, *J* = 2.1 Hz, 1H).

¹³C NMR (75 MHz, CDCl₃) δ ppm: 52.0, 56.3, 72.1, 111.6, 111.7, 126.0, 126.9, 131.6, 135.0, 141.7, 155.4, 166.6.

HRMS (ESI) m/z calcd for C₁₂H₁₃BrO₄Na [M+Na]⁺ 322.9889, Found 322.9890.

2-(hydroxy(4-methoxyphenyl)methyl)acrylonitrile **8a**



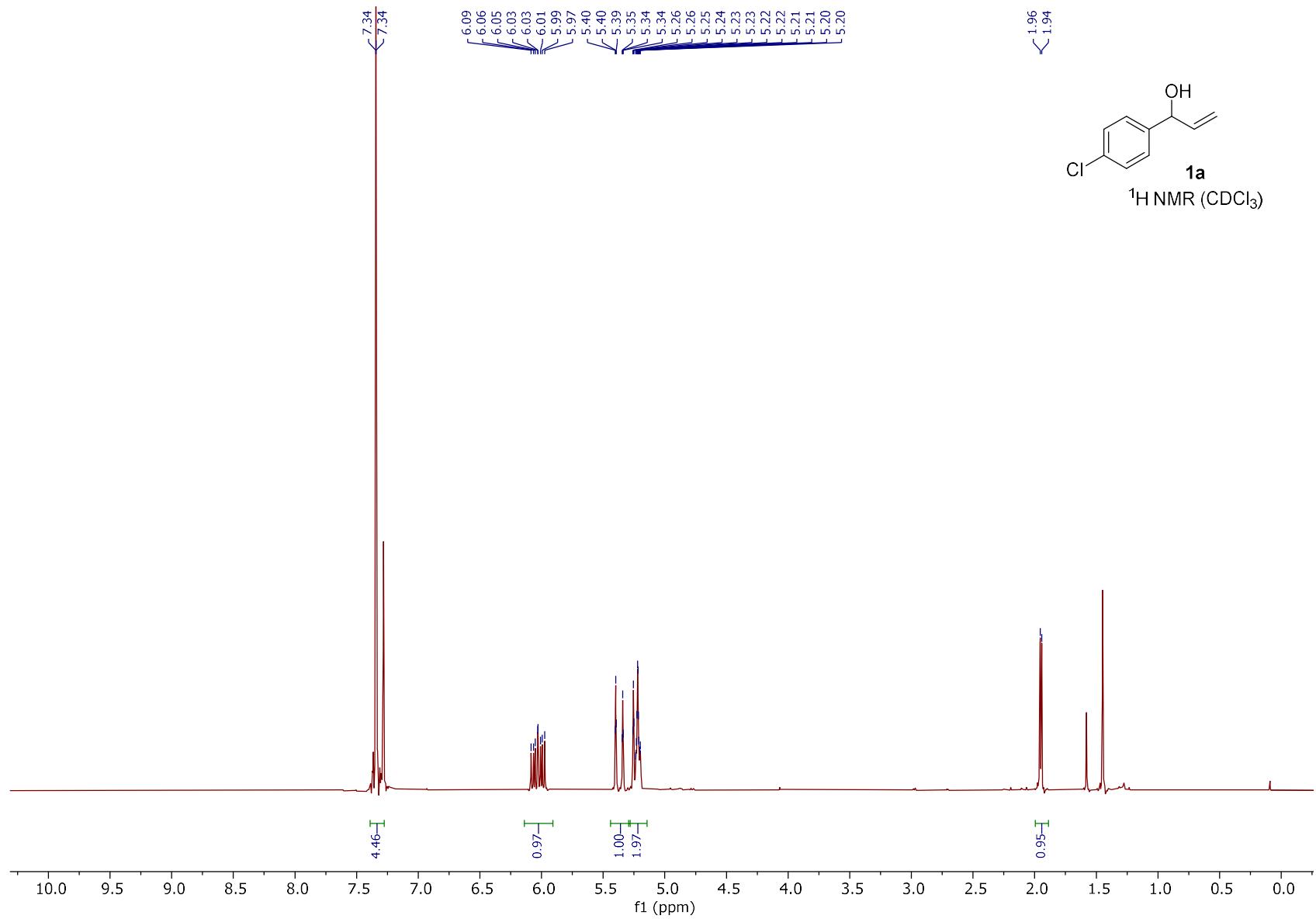
Chemical Formula: C₁₁H₁₁NO₂
MW: 189.21 g/mol

Prepared starting from 4-methoxybenzaldehyde (2 days). The crude was purified by chromatography (silica gel, eluent: cyclohexane/AcOEt, 75/25) to give **8a** (750 mg, 21%) as a colorless oil.

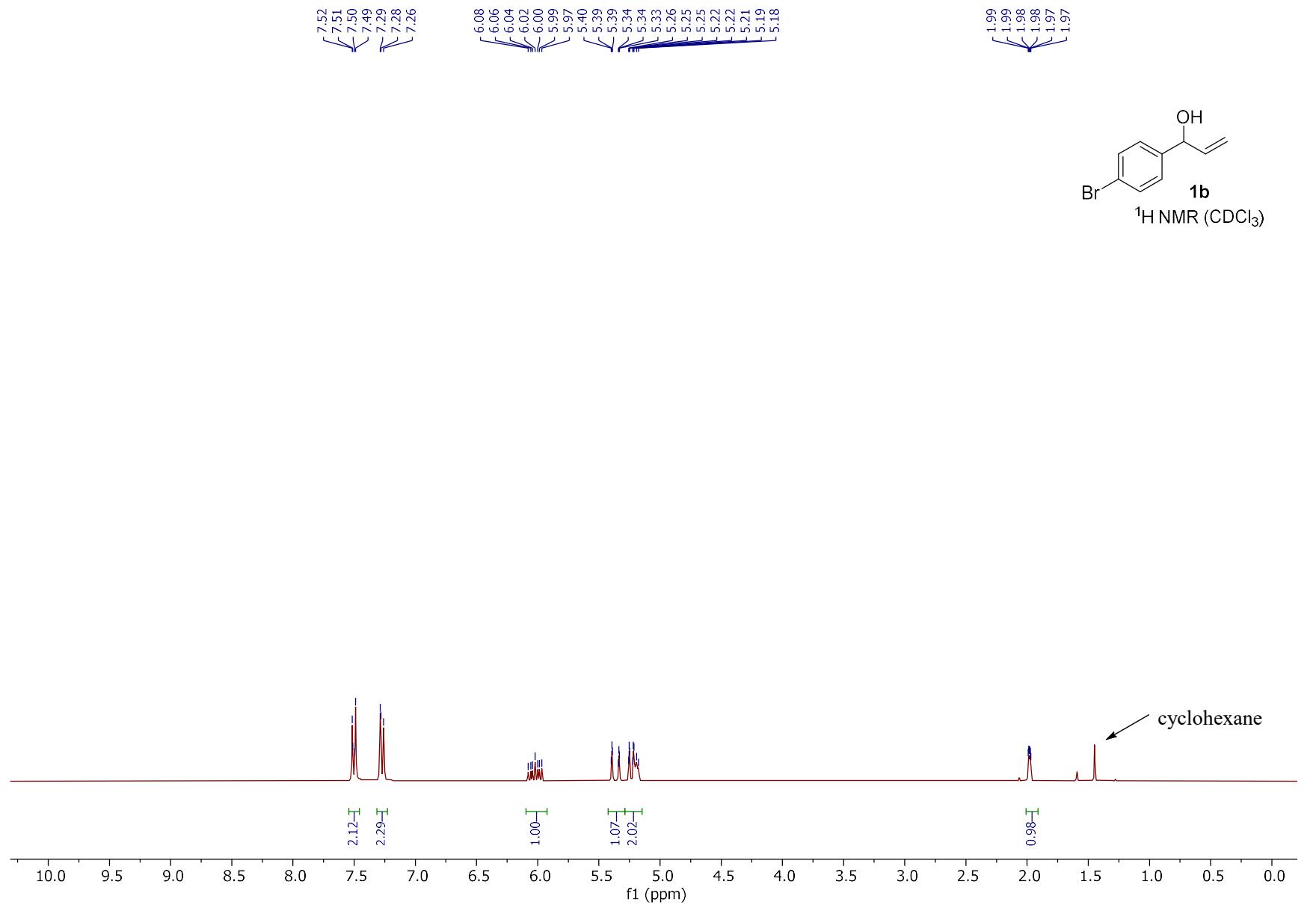
R_f = 0.28 (cyclohexane/EtOAc: 75/25)

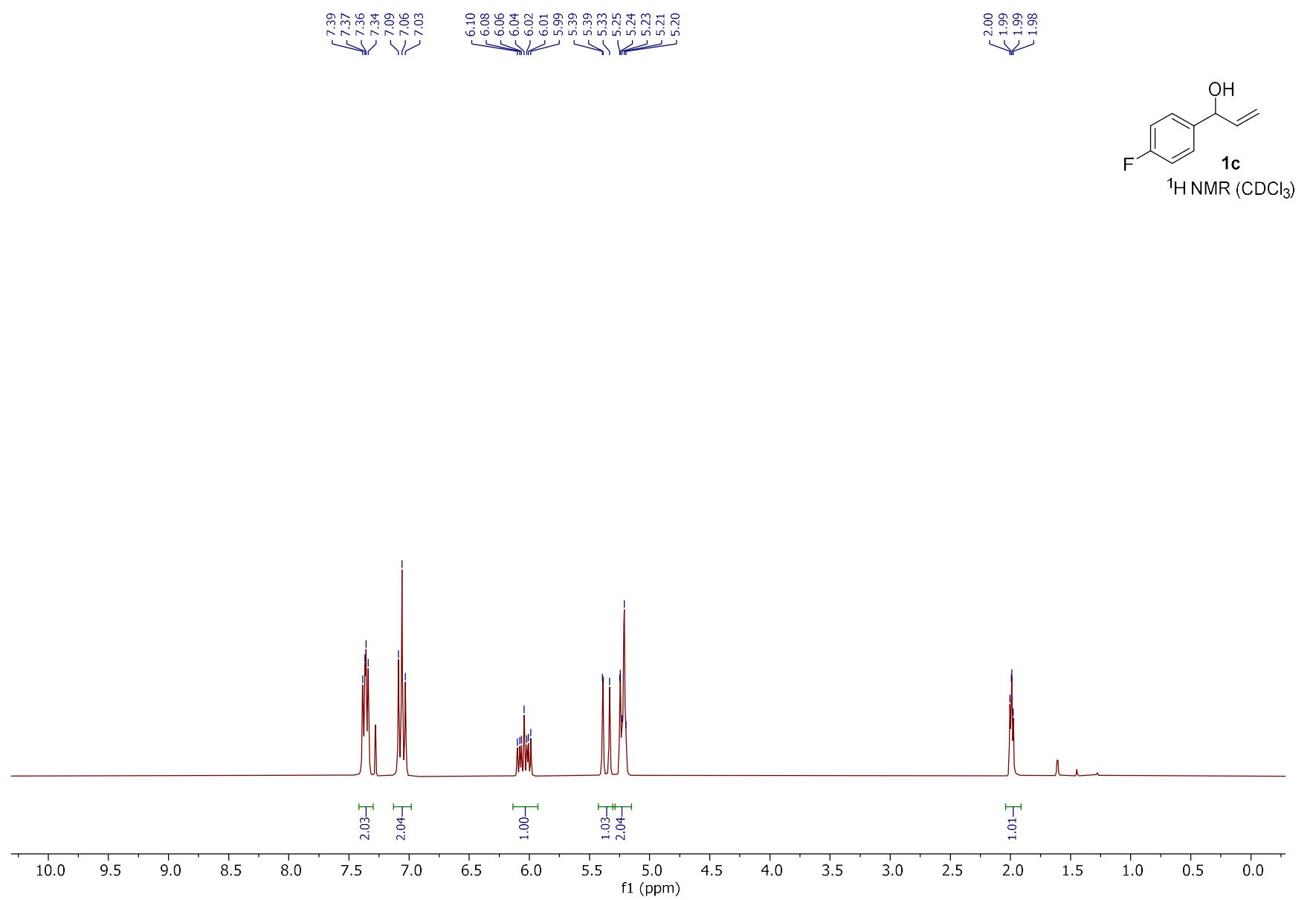
¹H NMR (300 MHz, CDCl₃) δ ppm: 2.27 (d, *J* = 3.9 Hz, 1H), 3.84 (s, 3H), 5.27-5.30 (m, 1H), 6.04-6.06 (m, 1H), 6.12-6.14 (m, 1H), 6.94 (d, *J* = 8.7 Hz, 2H), 7.33 (d, *J* = 8.7 Hz, 2H).

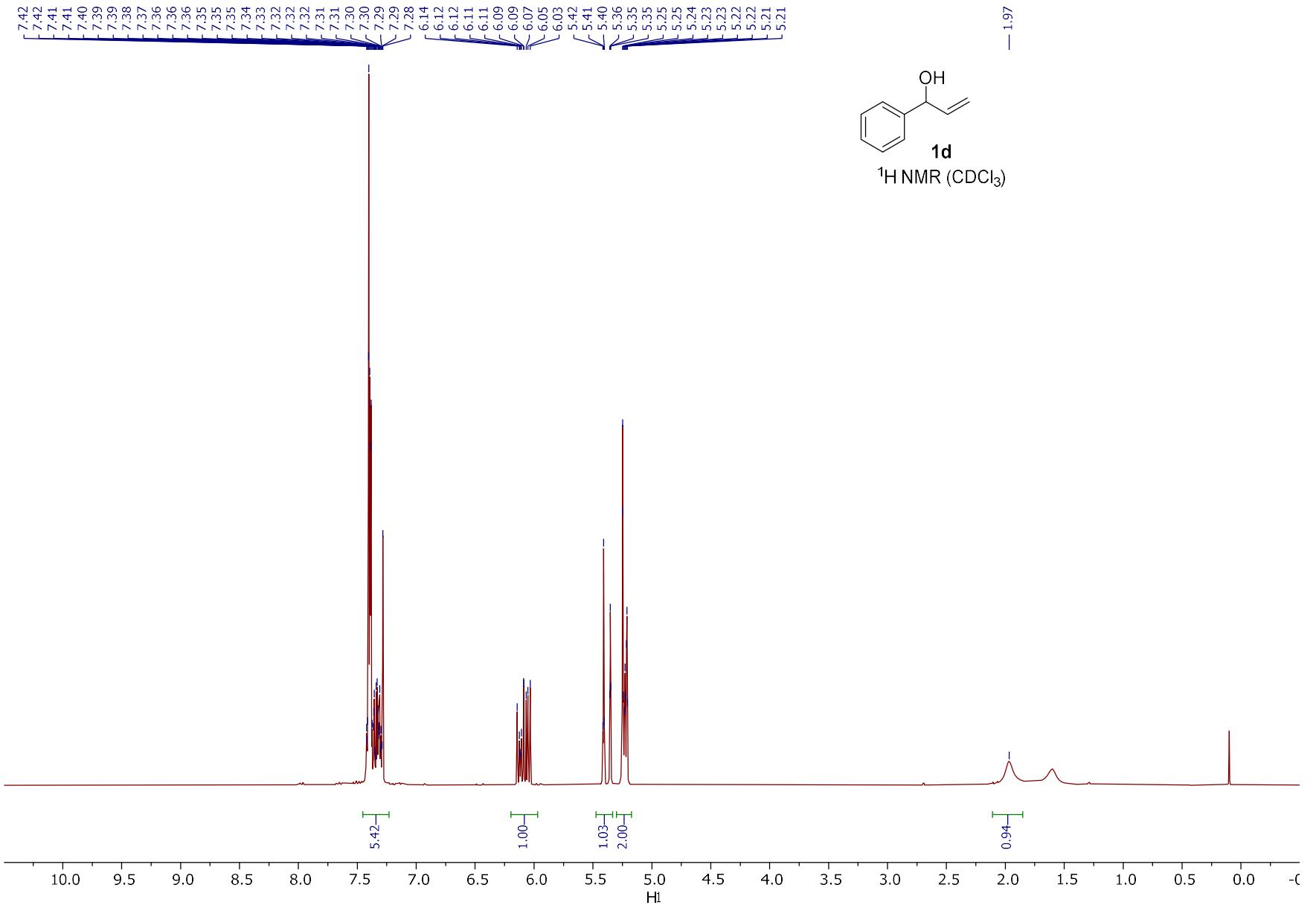
Spectral data were identical to those reported in literature.⁸

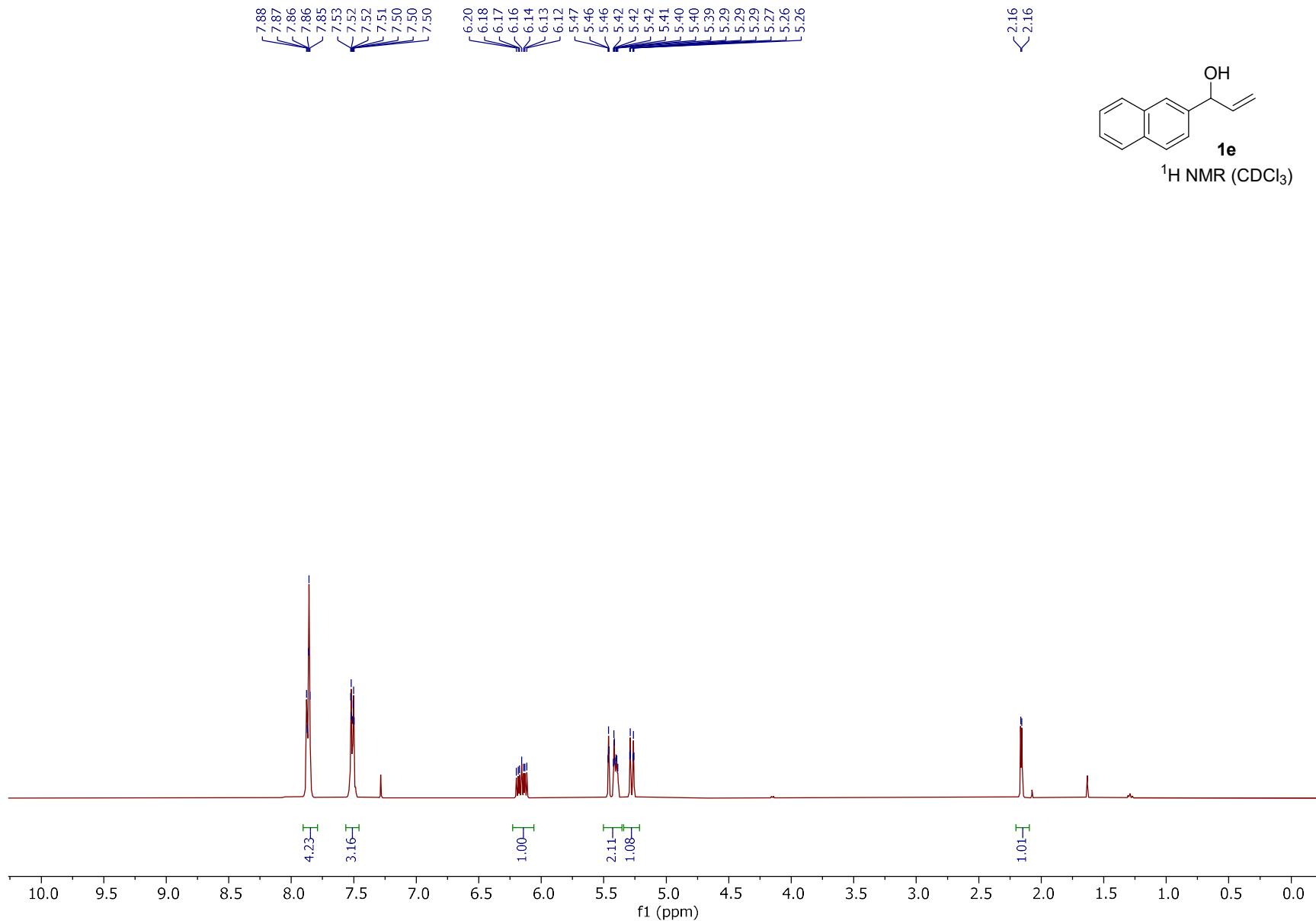


S12

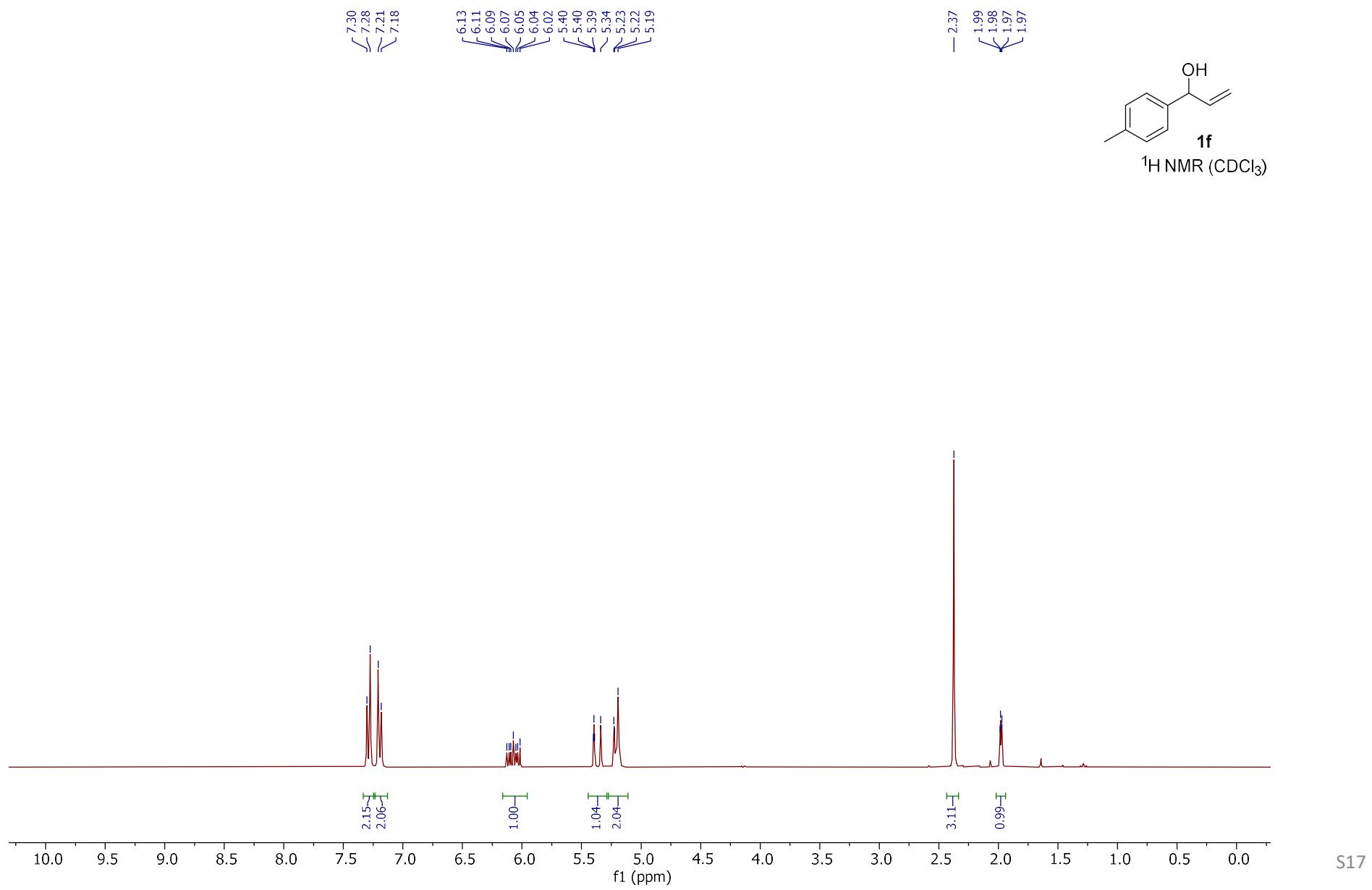


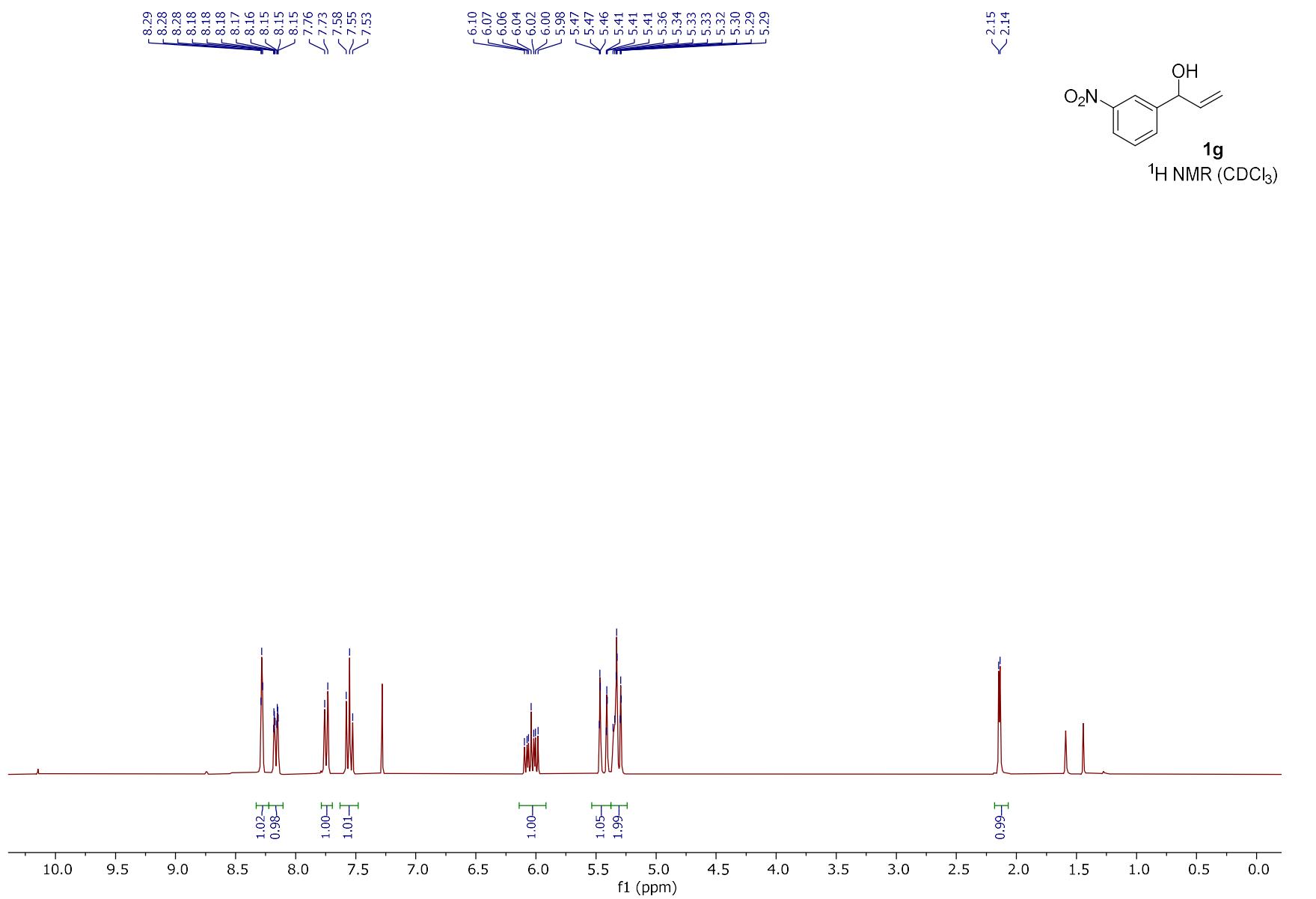


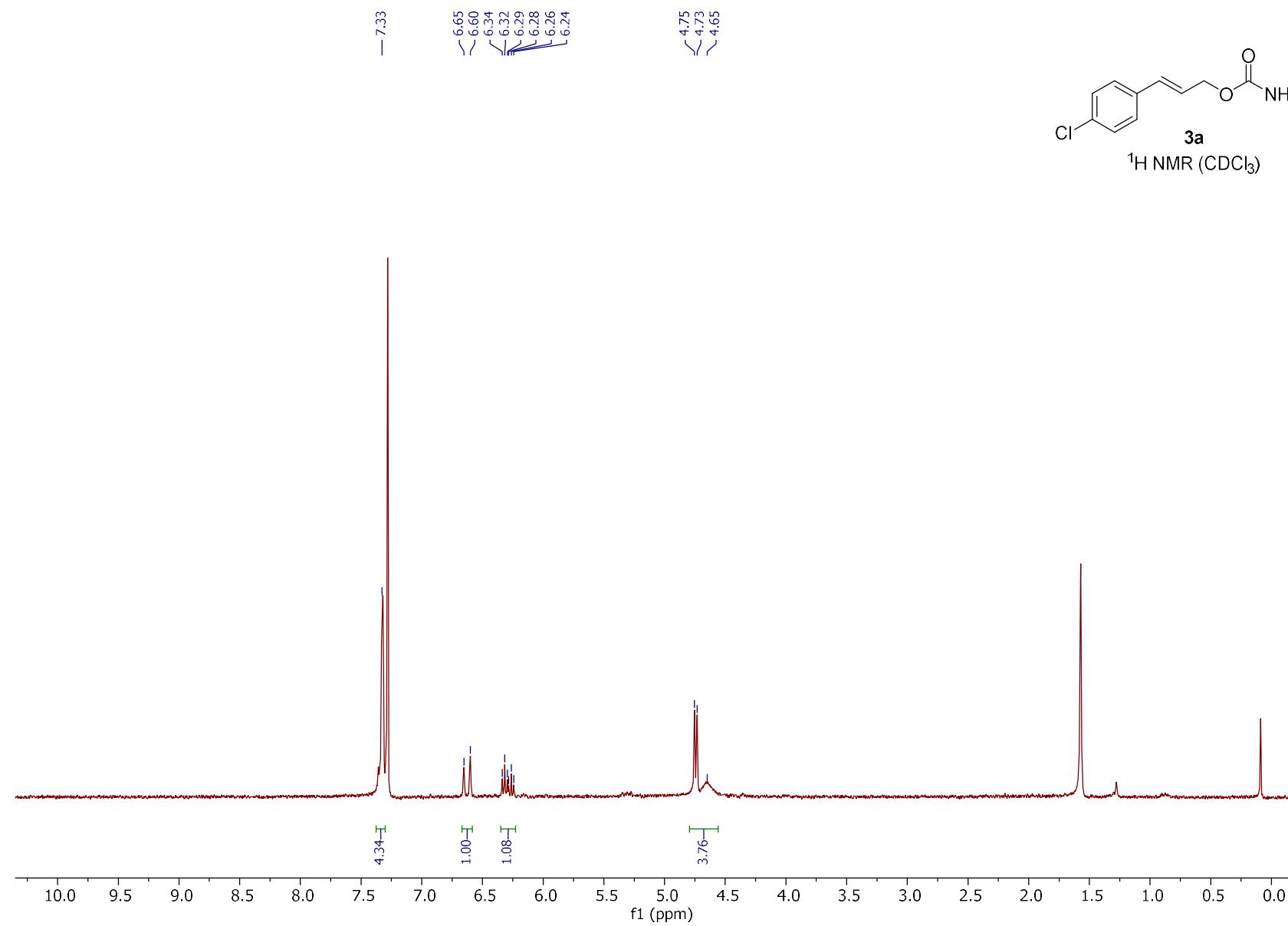


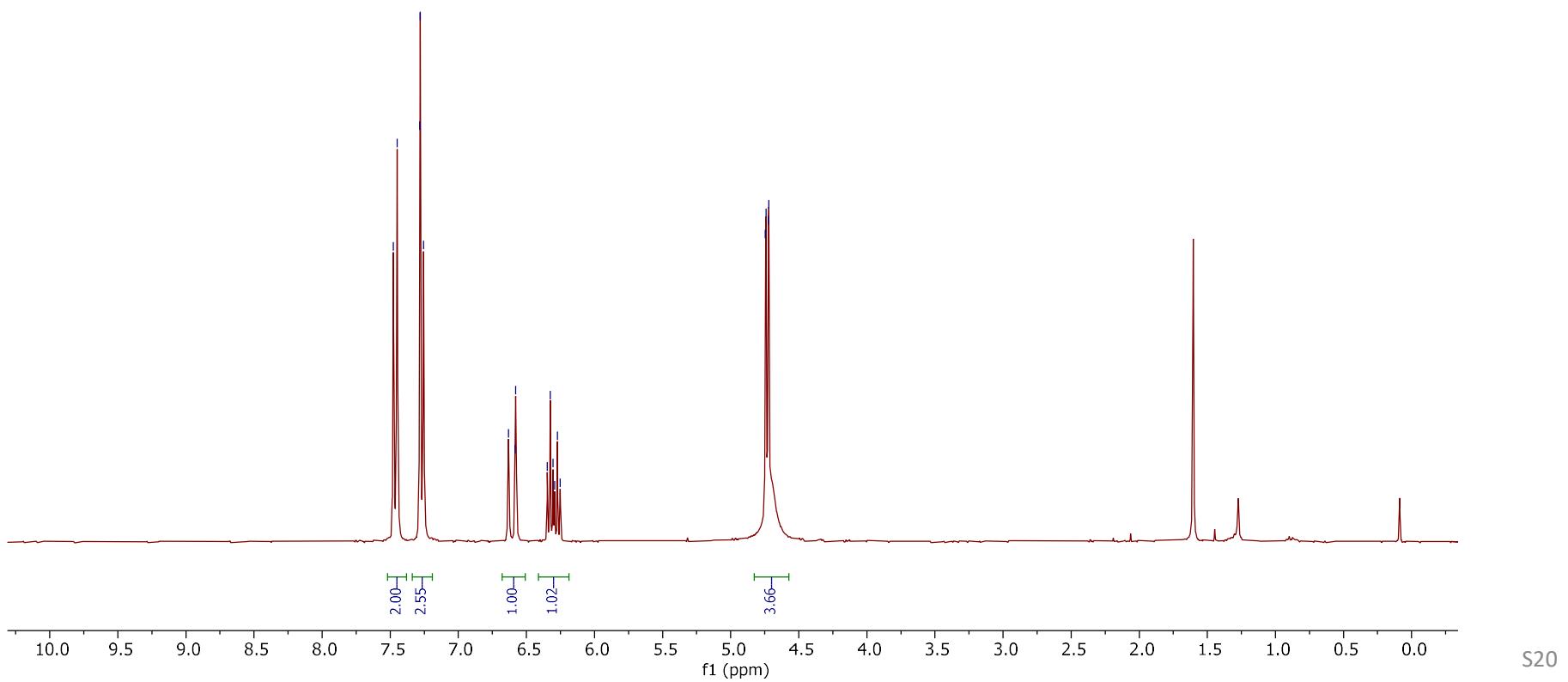


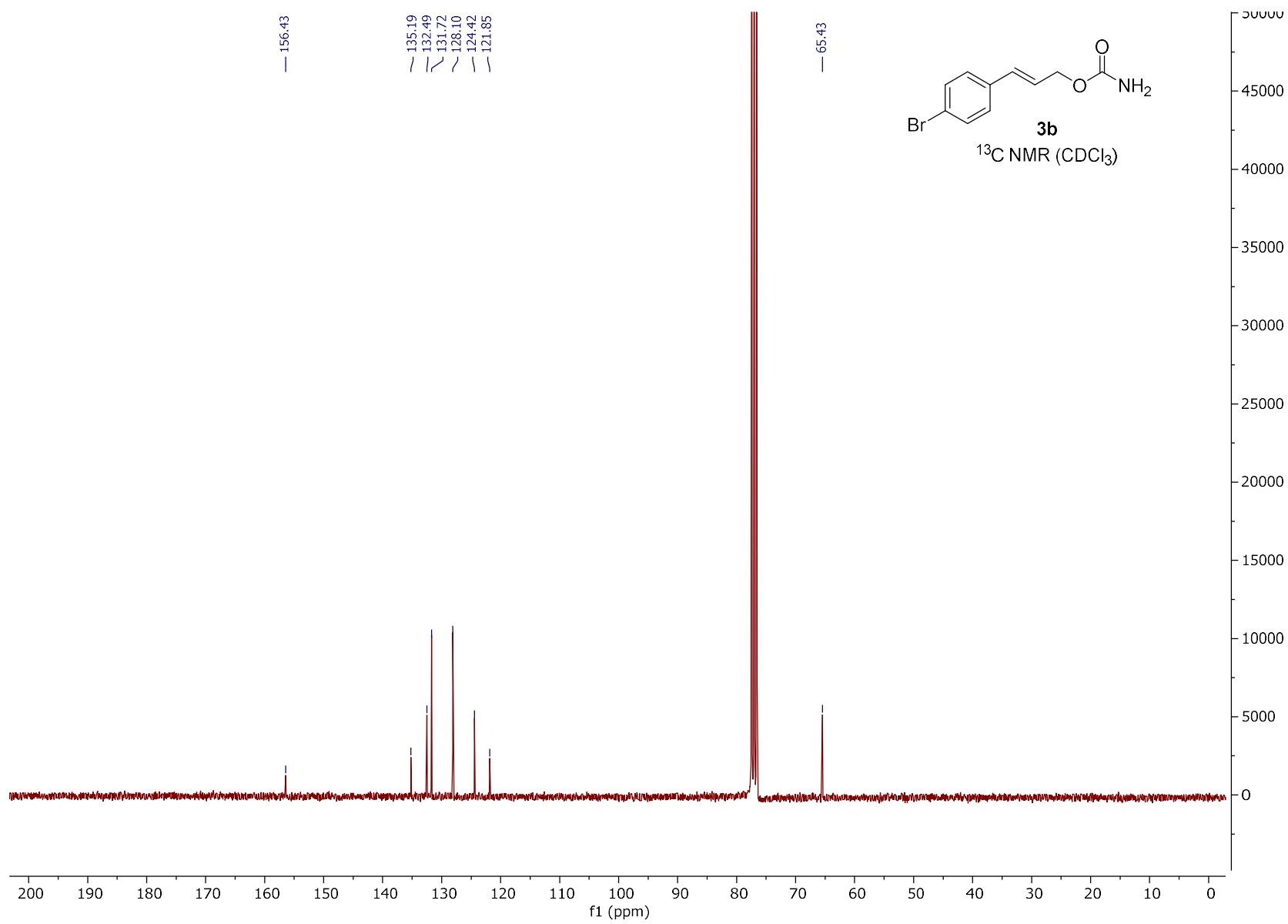
S16



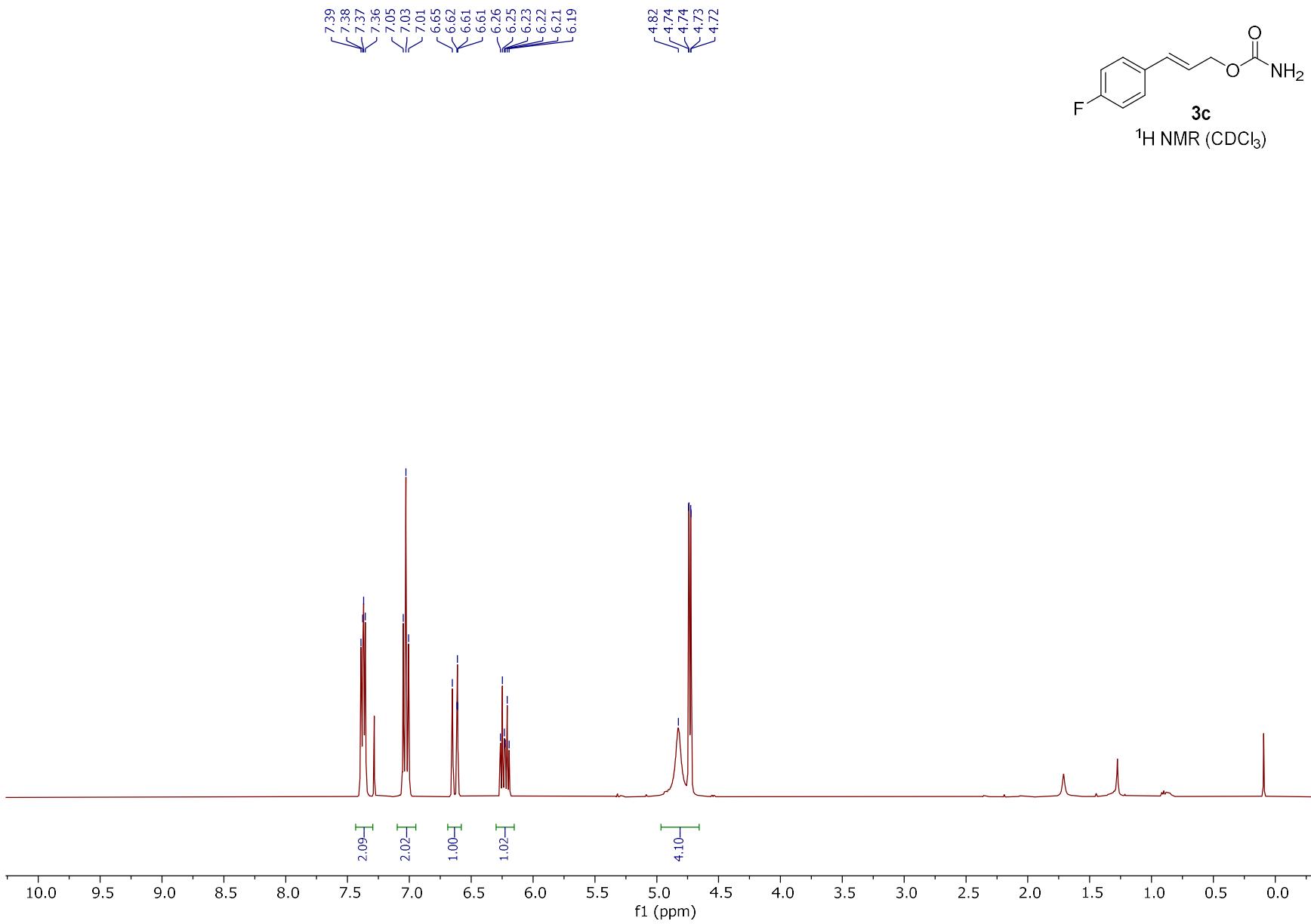


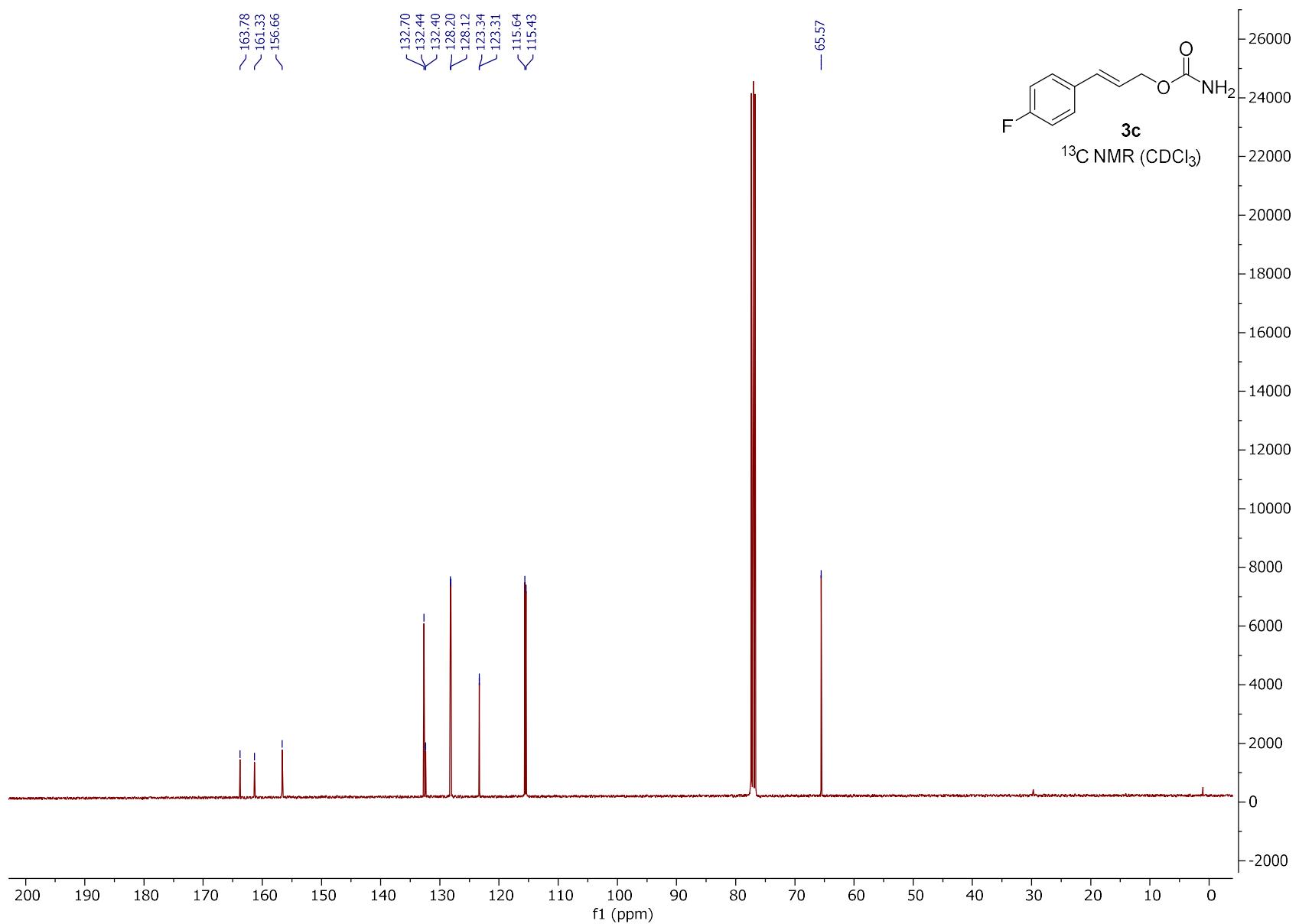


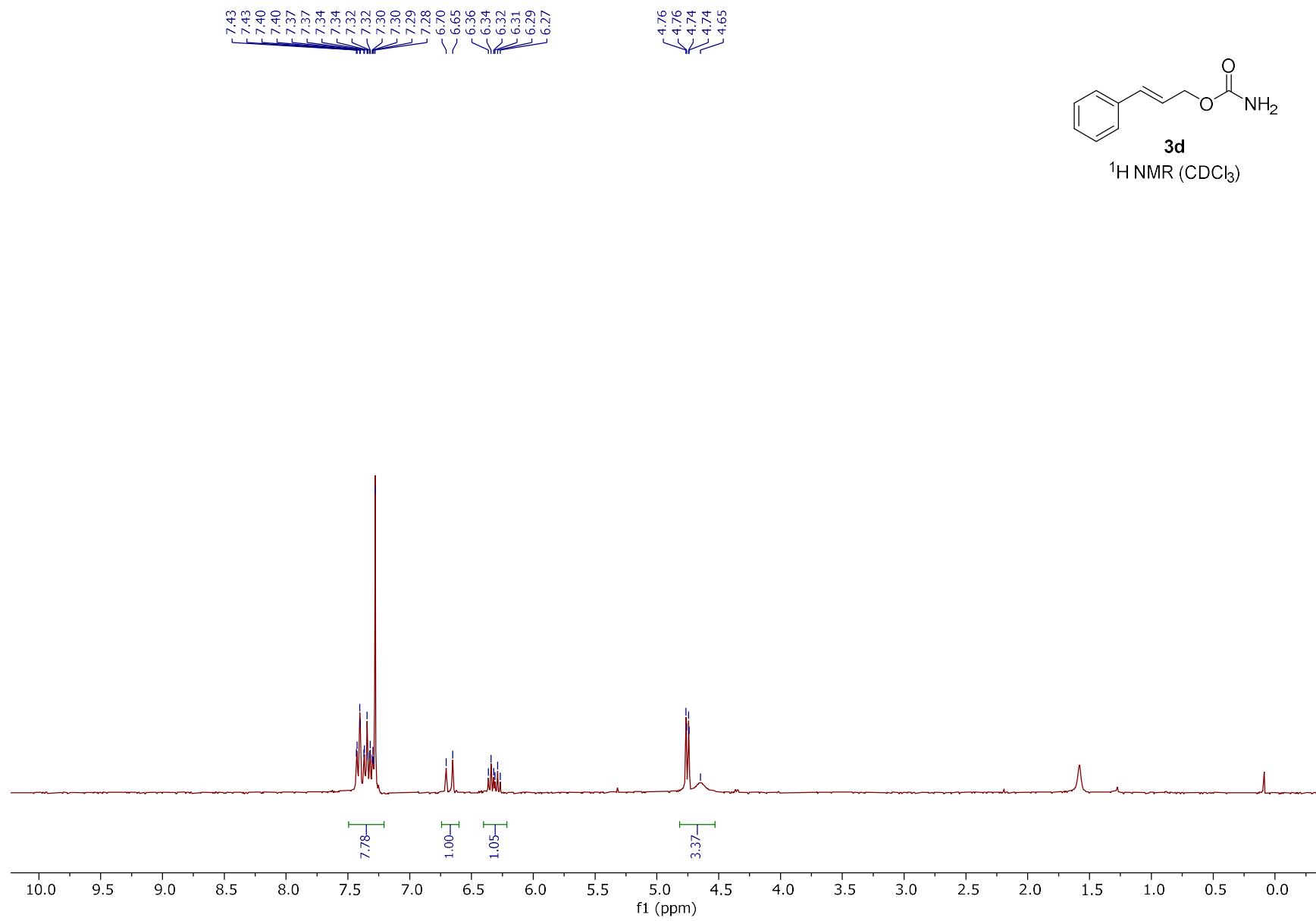


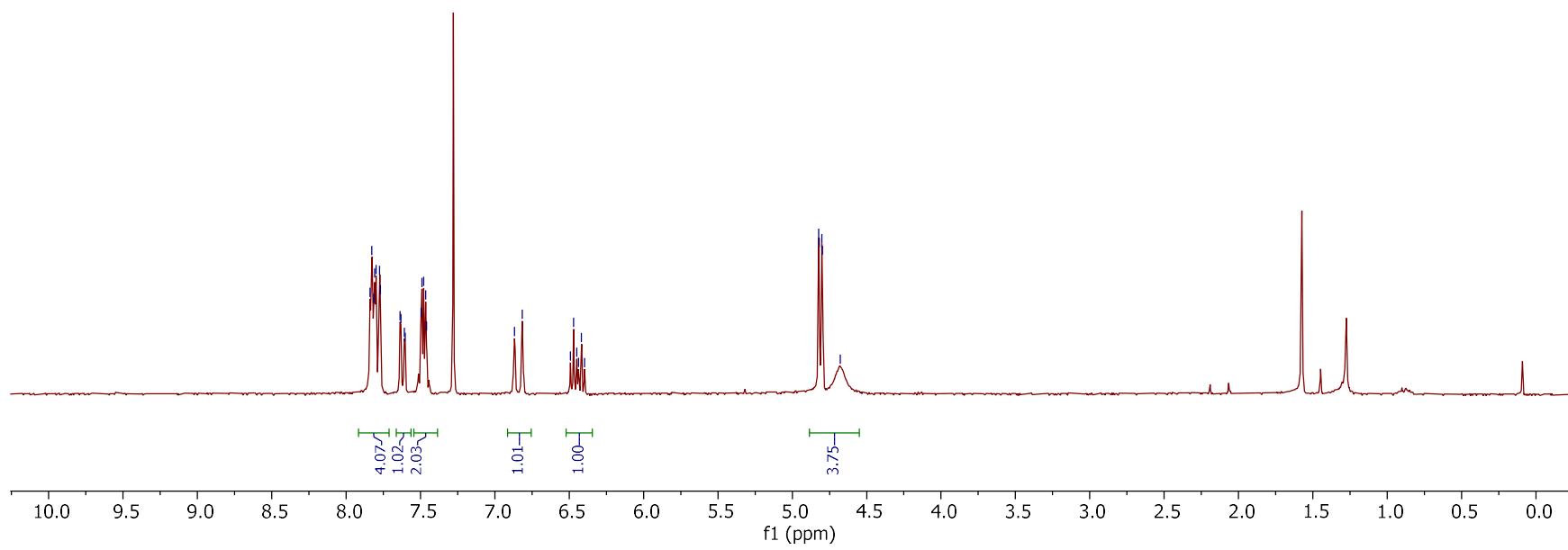


S21



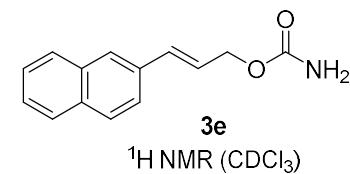


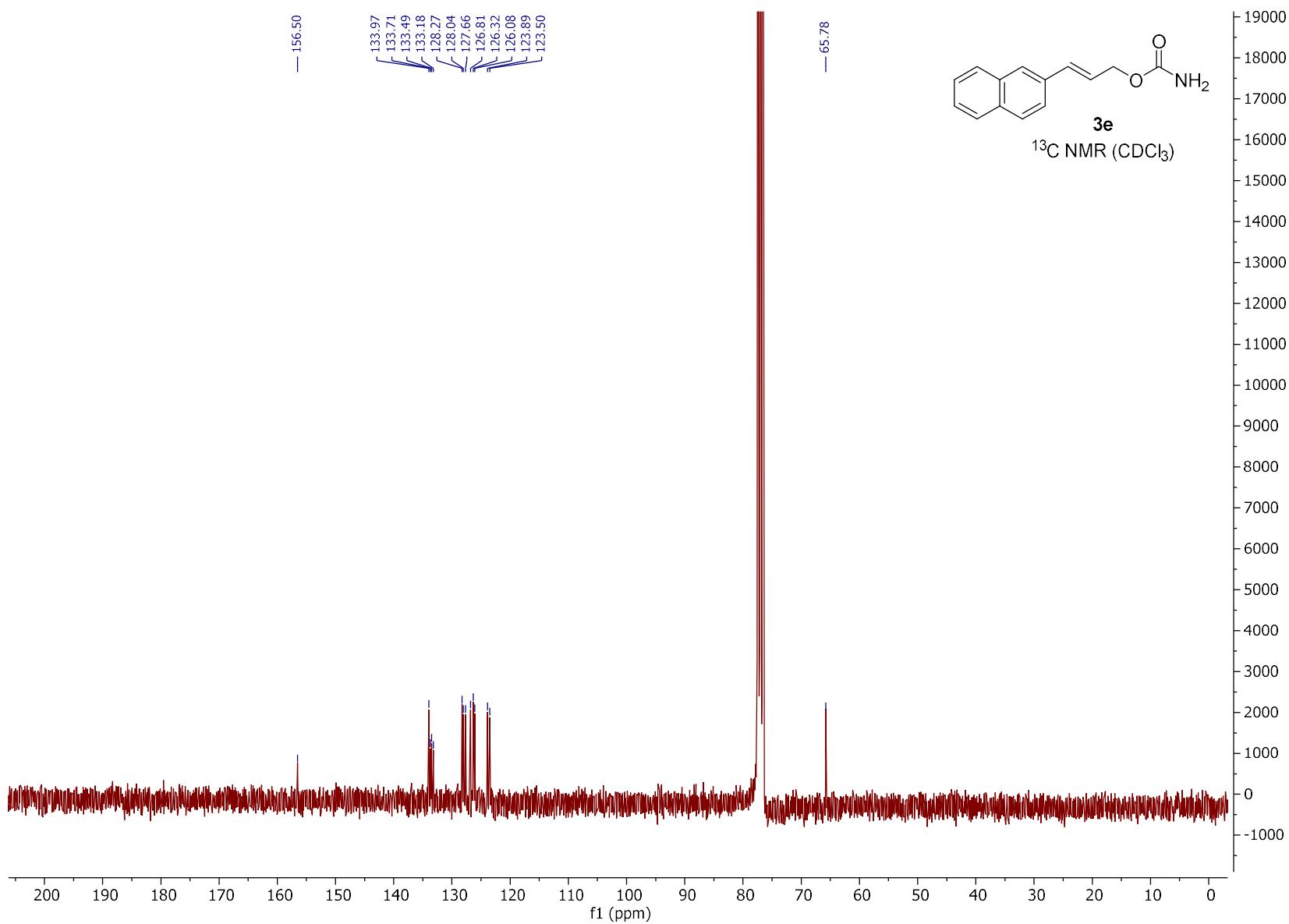


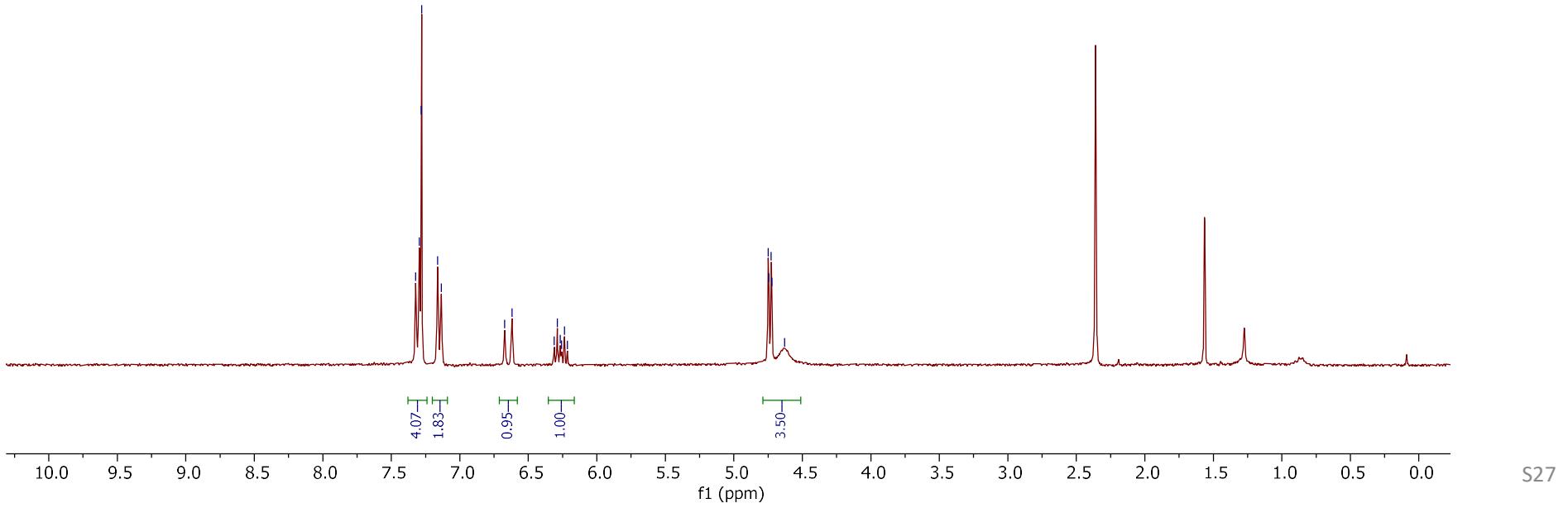


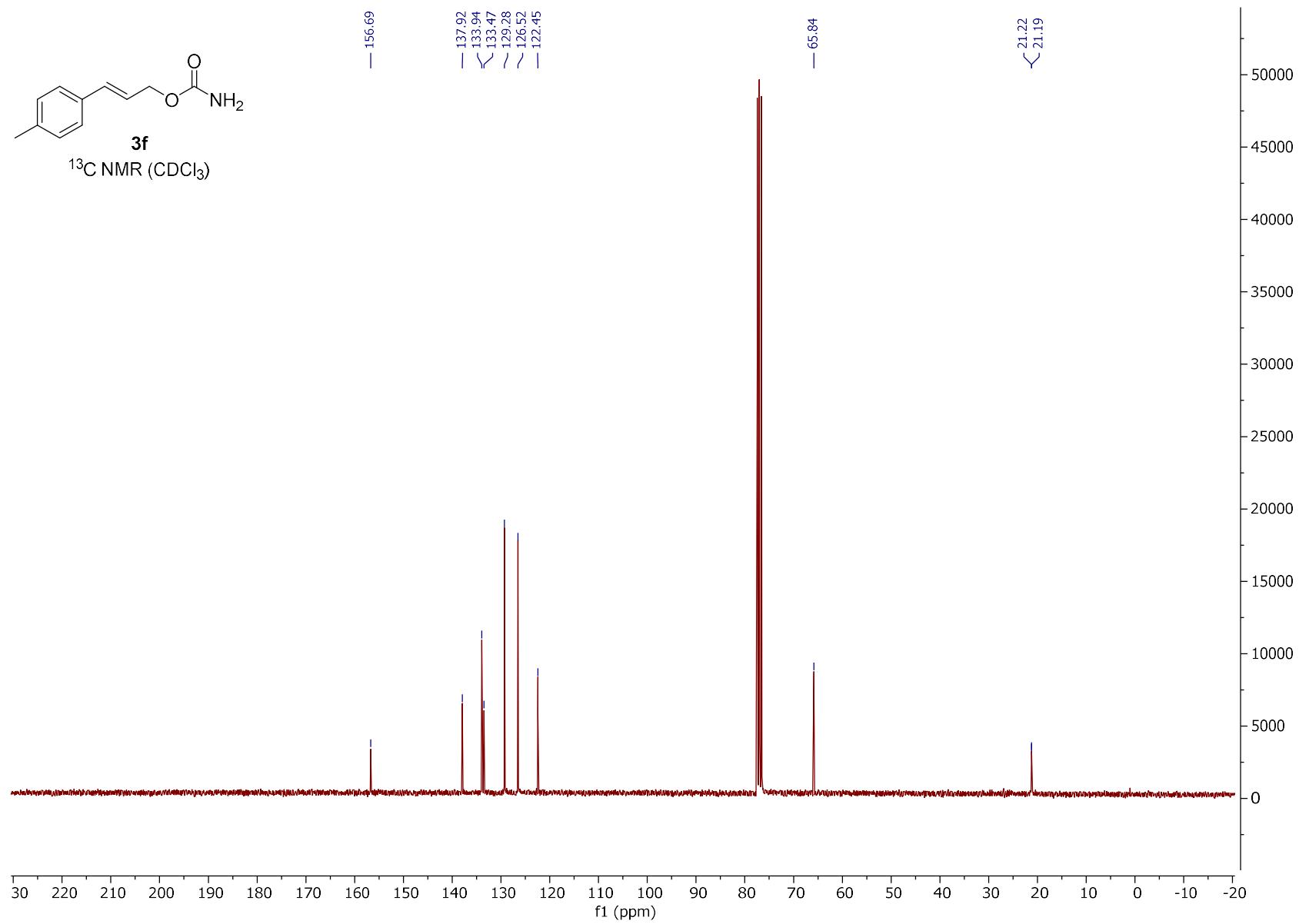
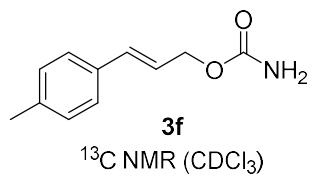
7.84
7.83
7.81
7.81
7.80
7.78
7.77
7.64
7.63
7.61
7.61
7.60
7.50
7.49
7.48
7.47
7.46
6.87
6.81
6.49
6.47
6.45
6.44
6.42
6.40

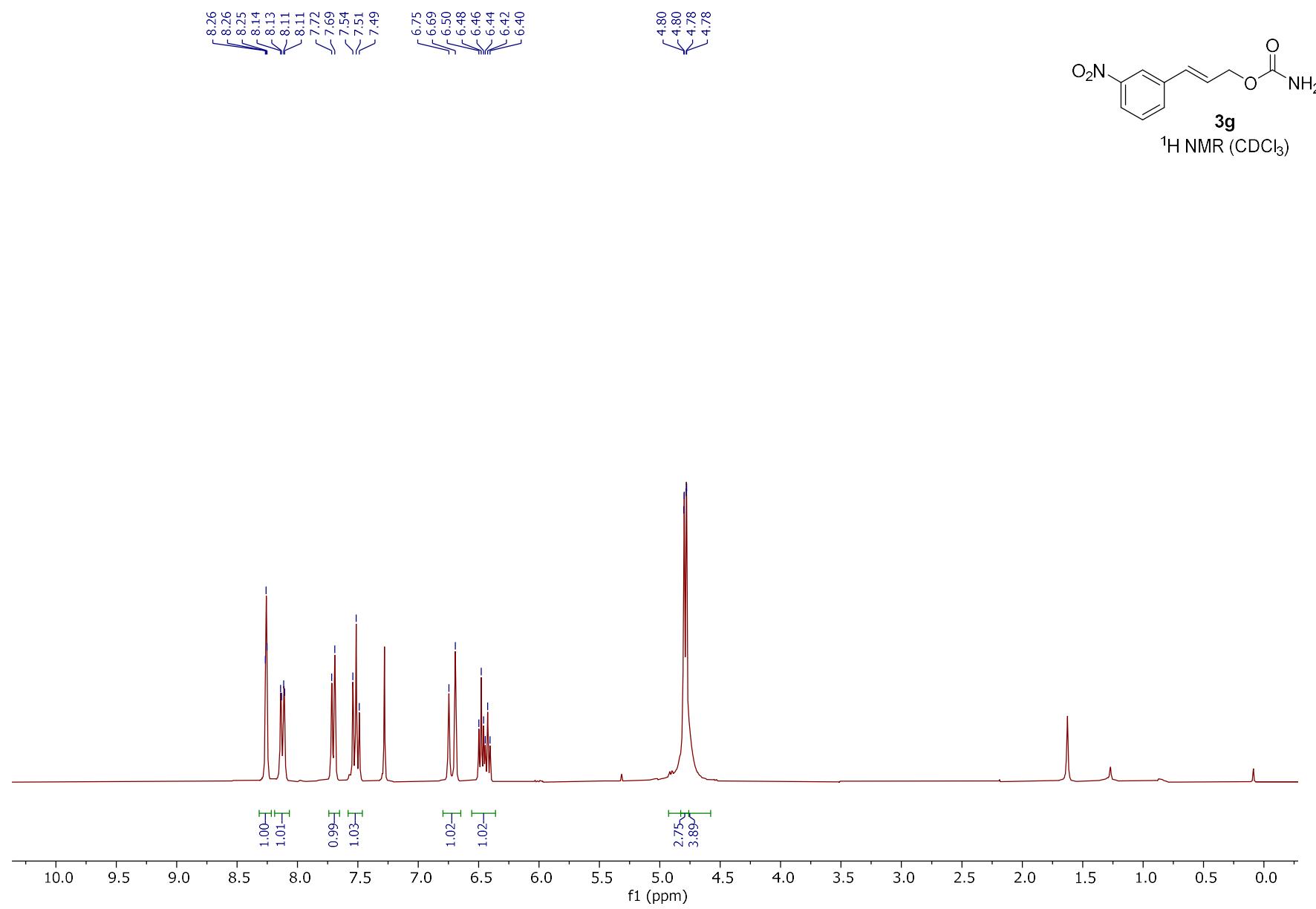
4.82
4.82
4.80
4.80
4.68

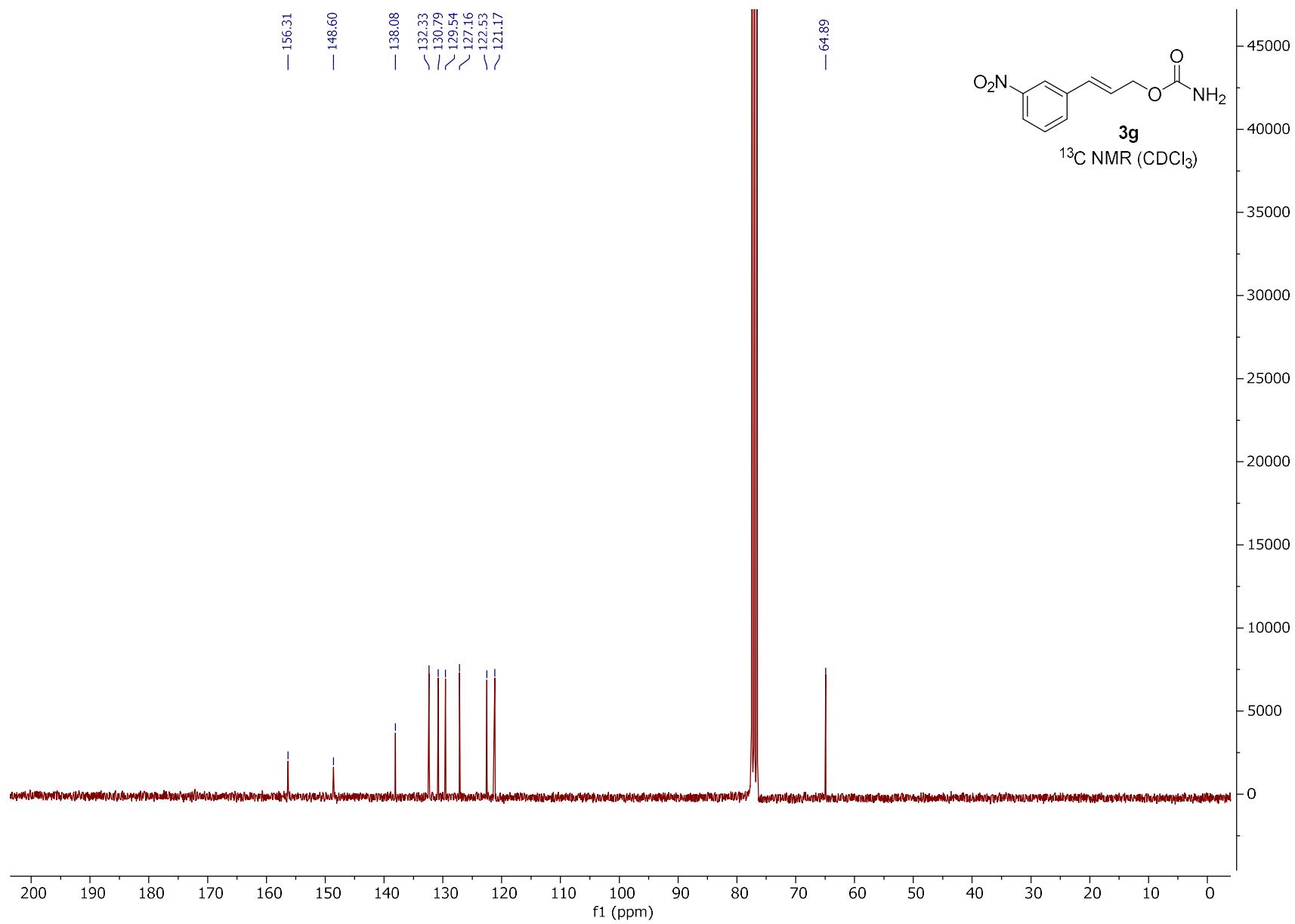


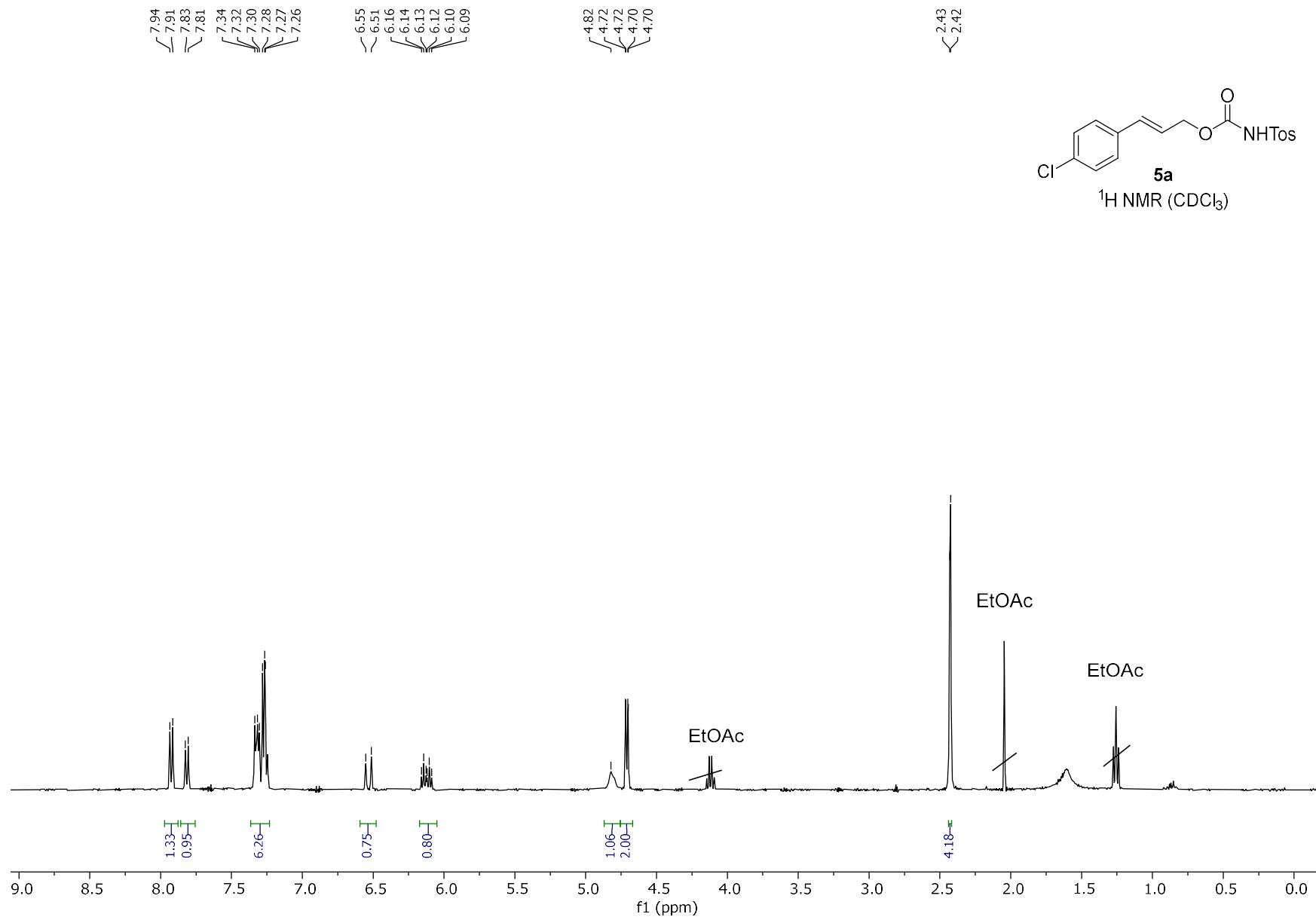


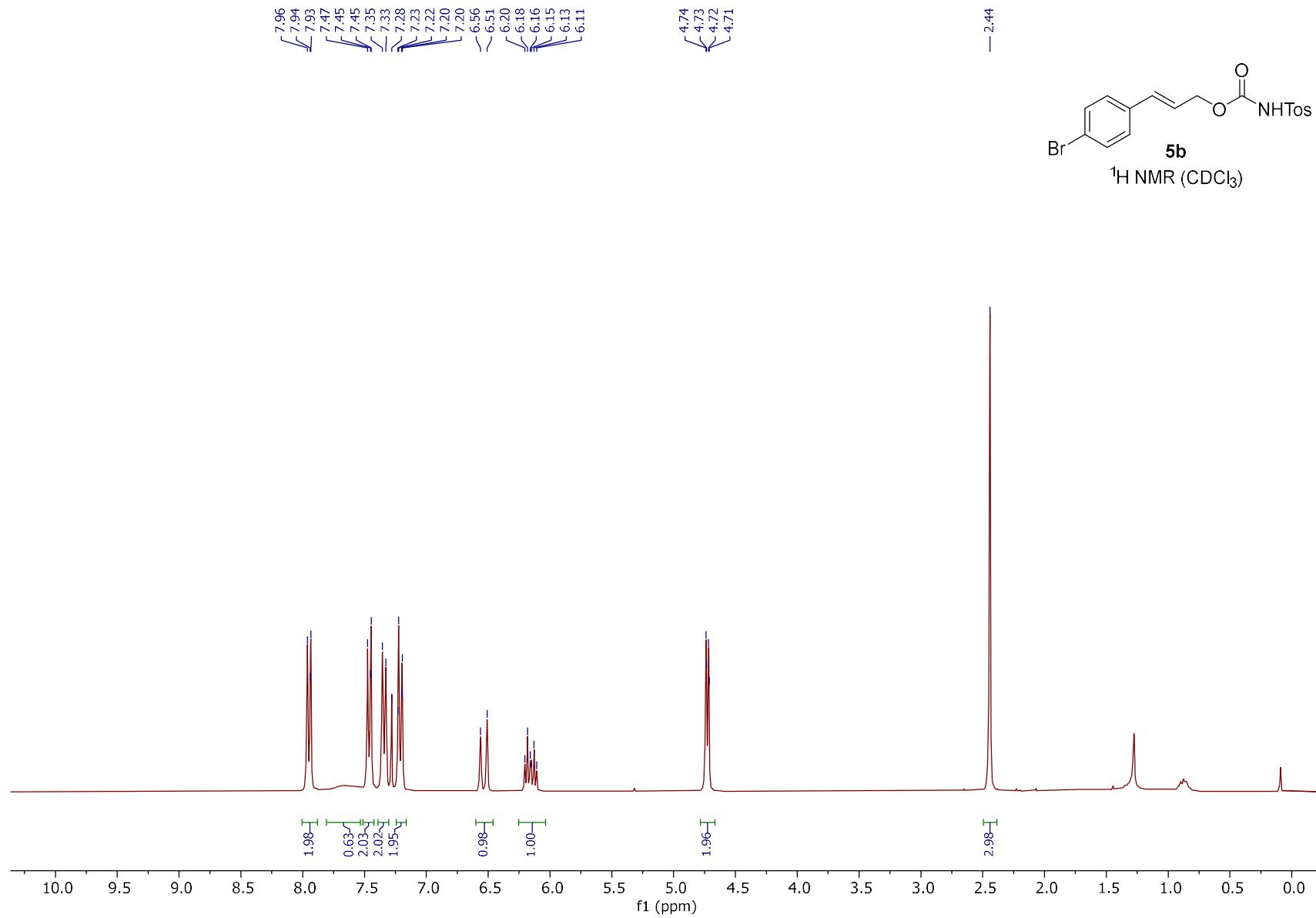


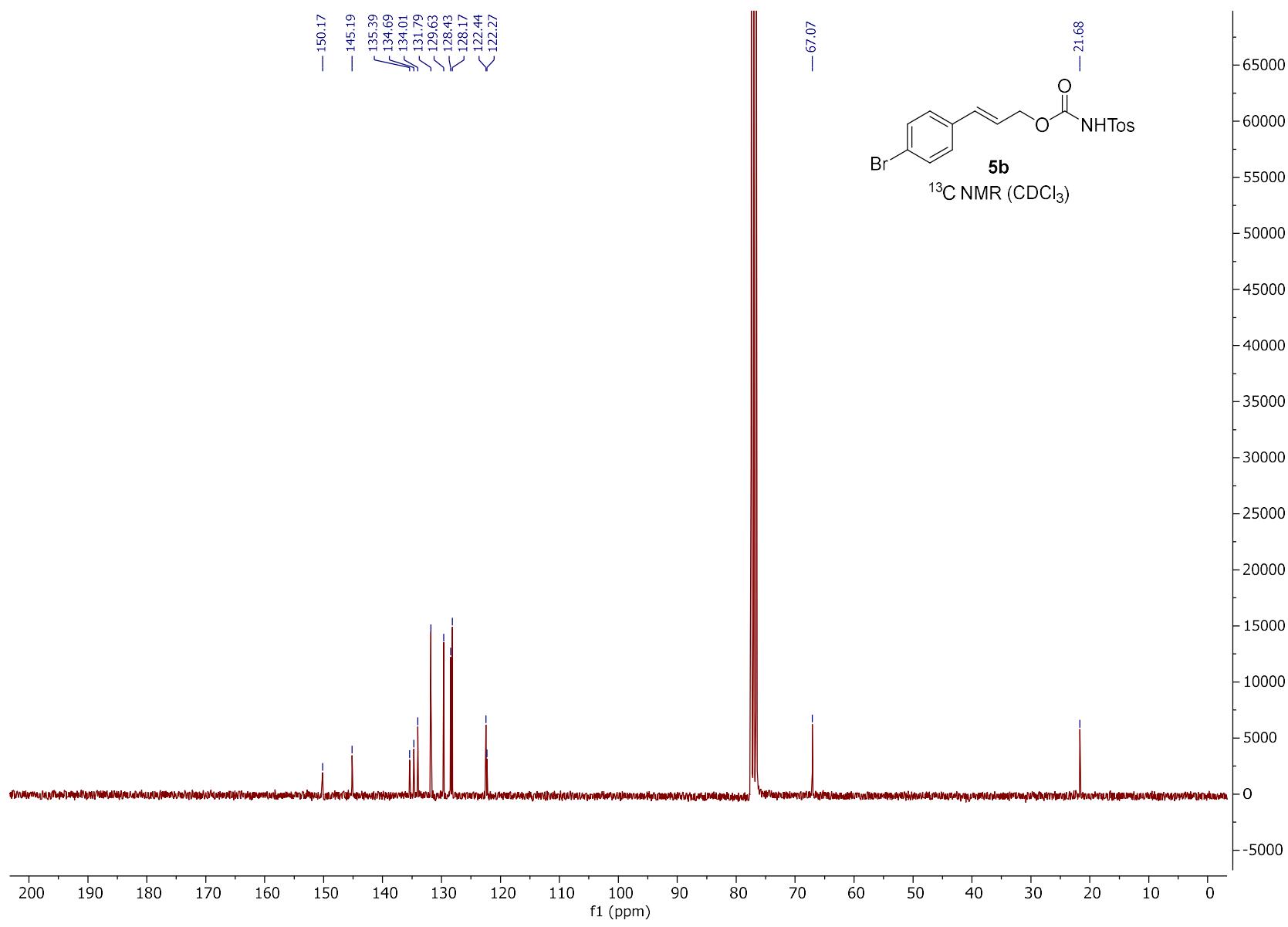


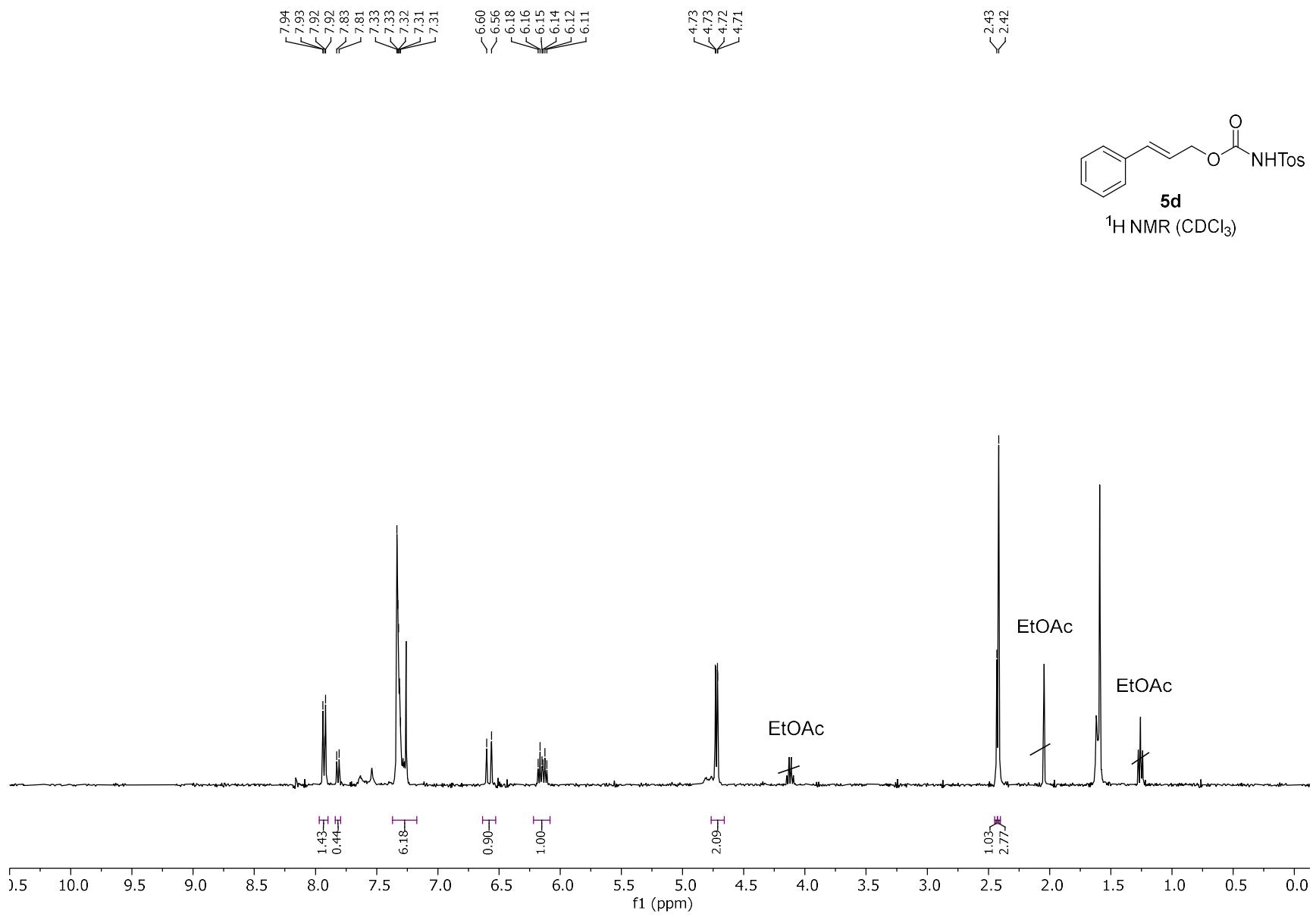


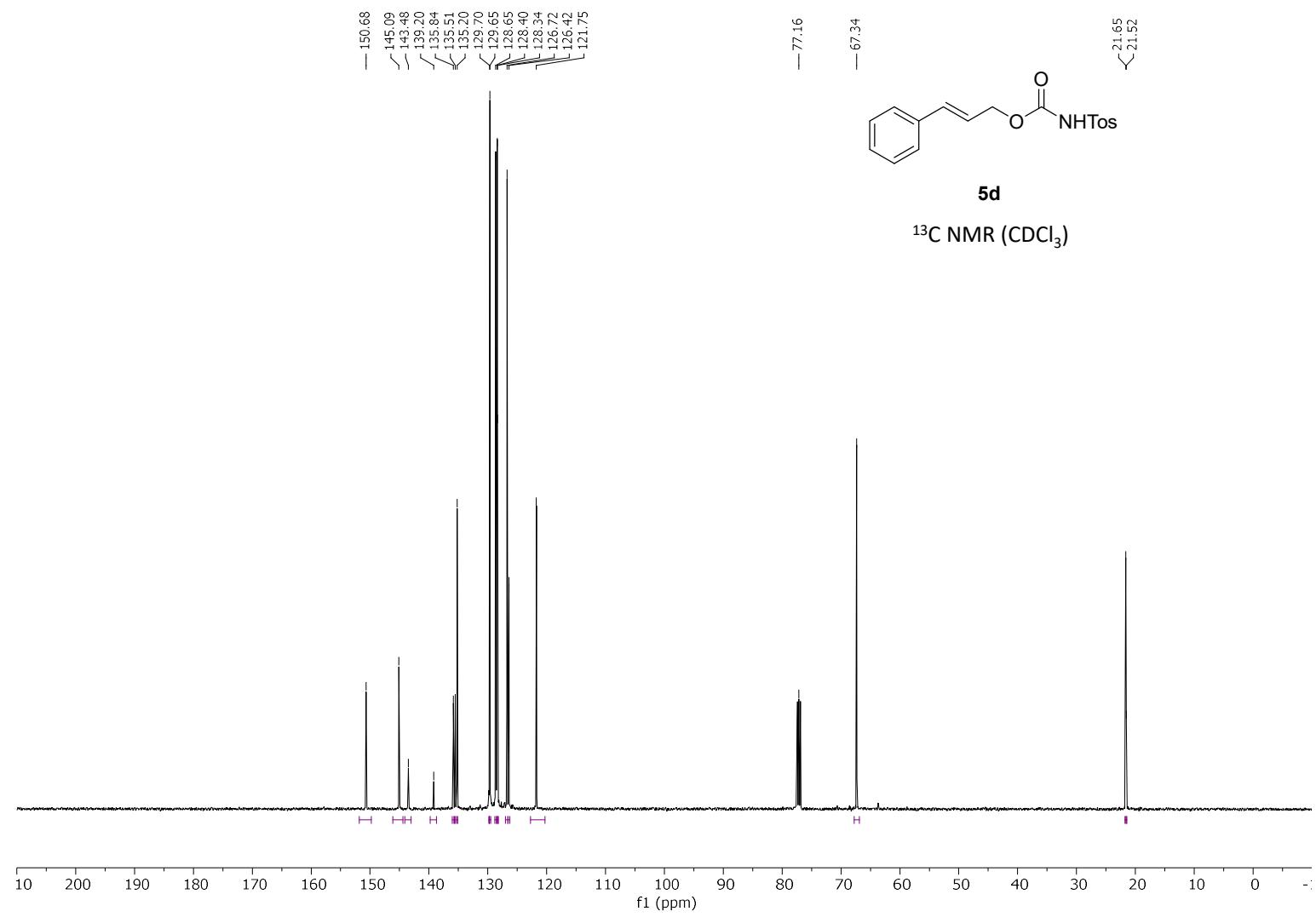


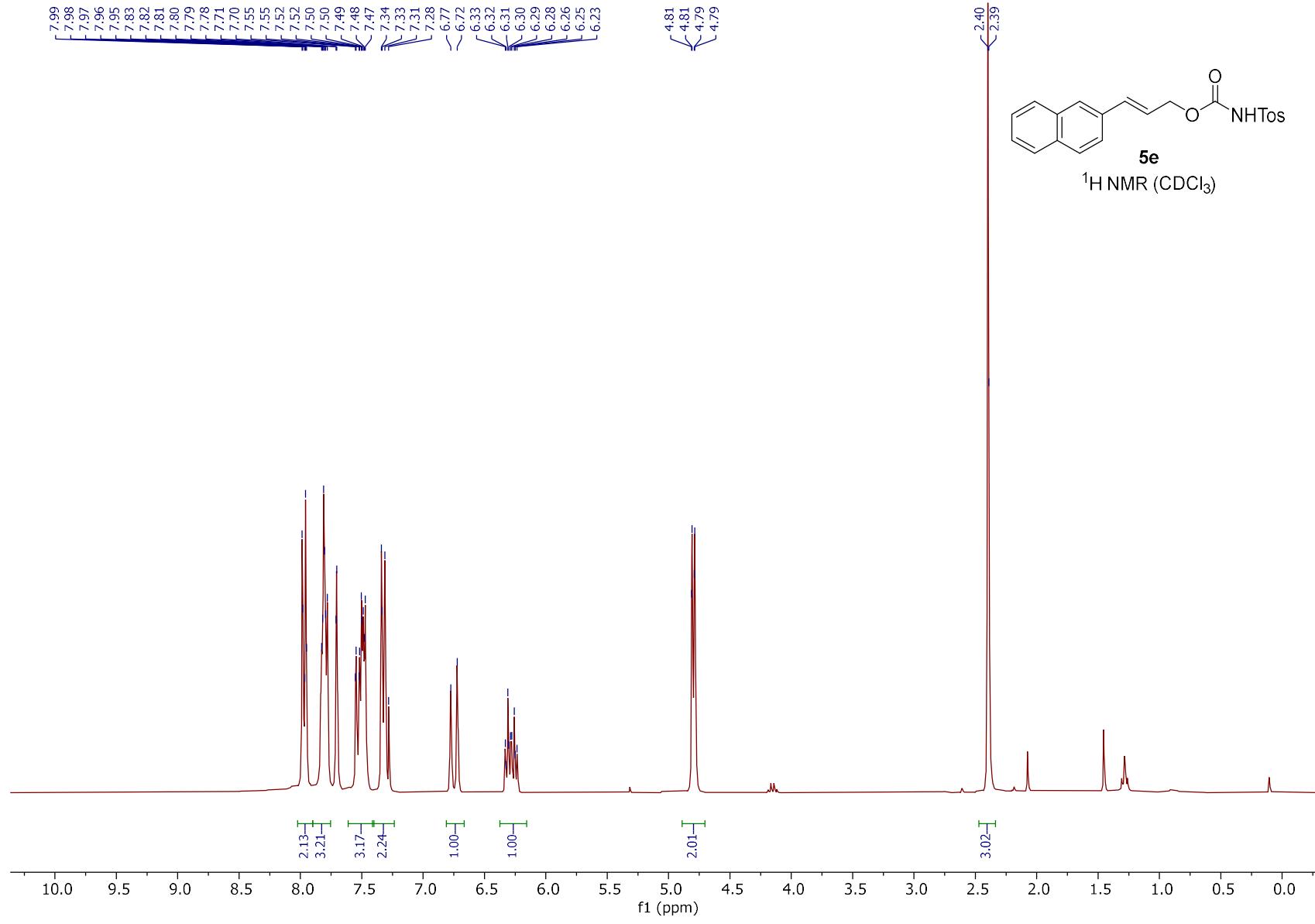


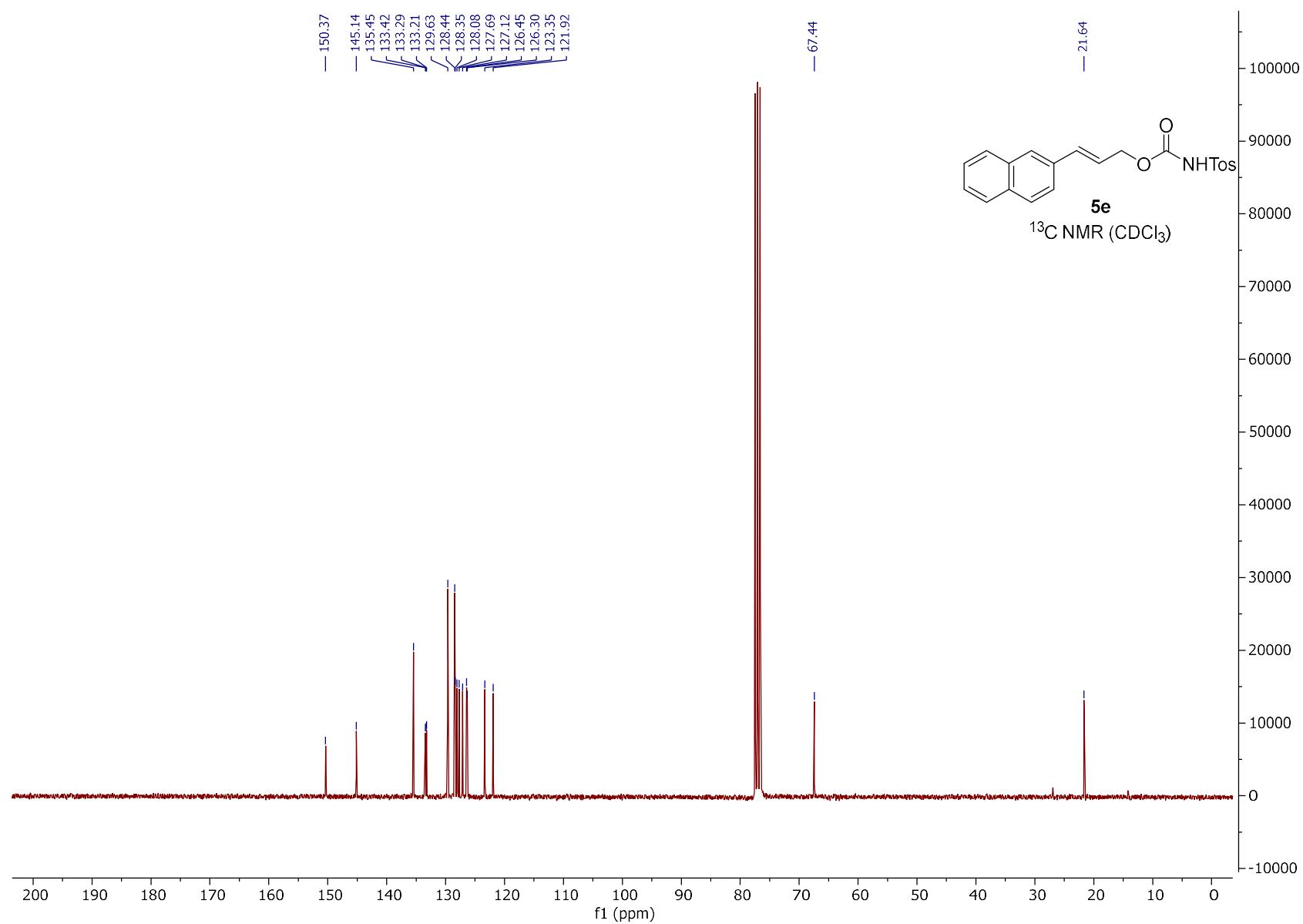


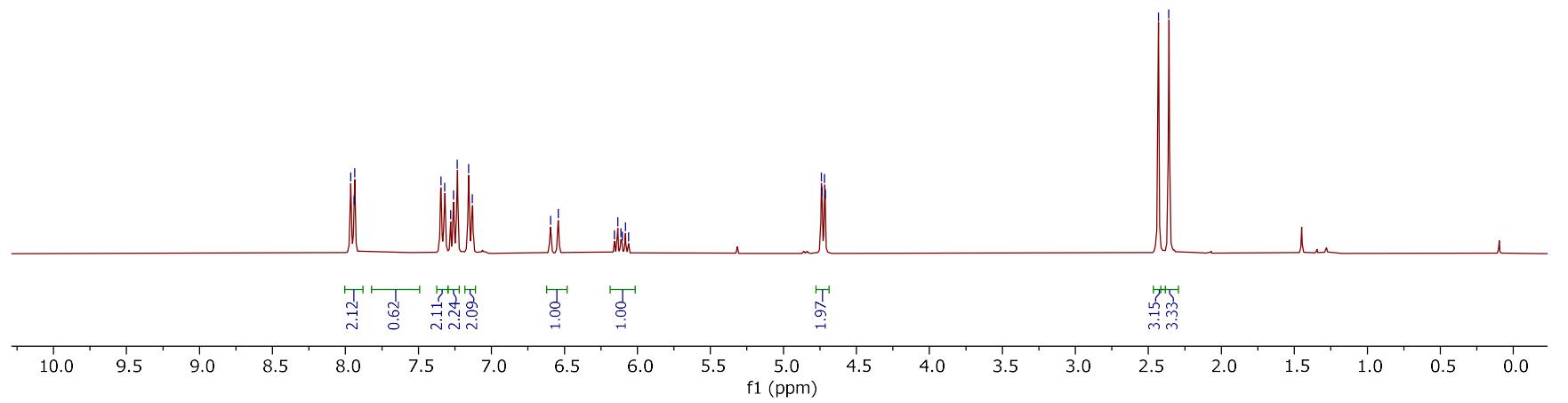




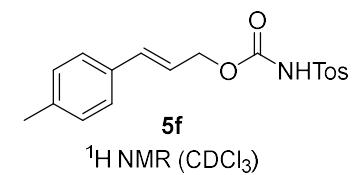






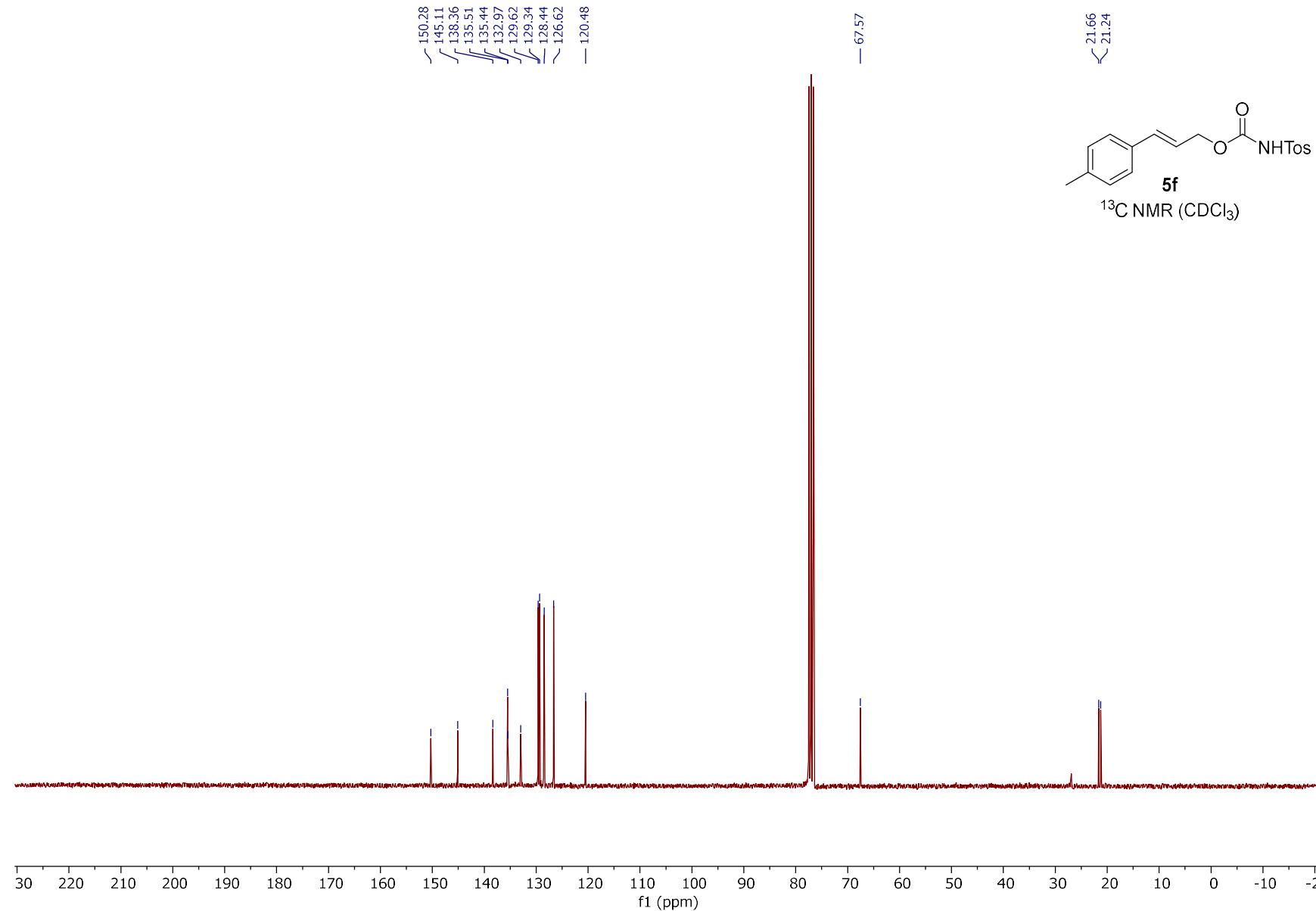


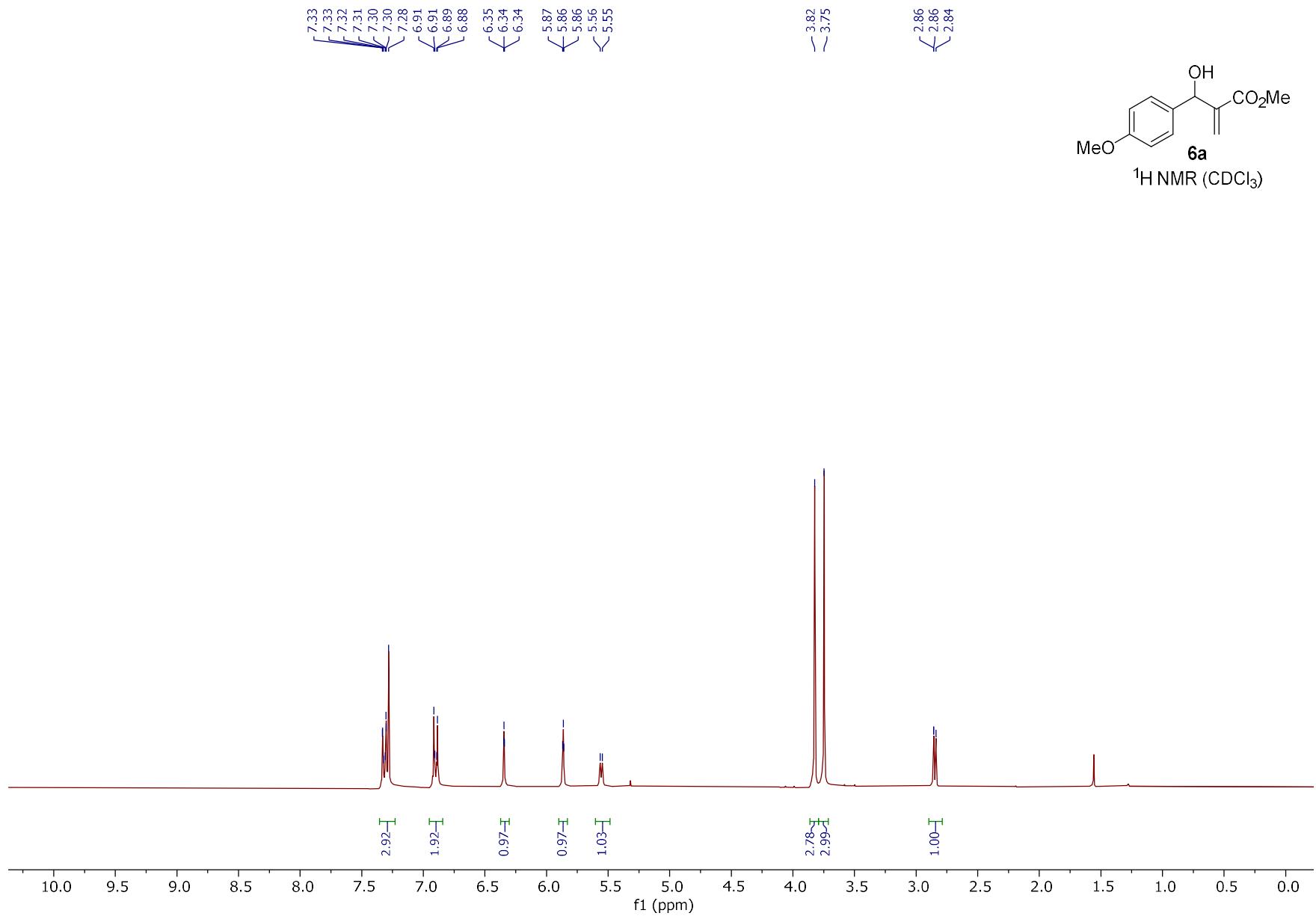
~2.43
~2.36

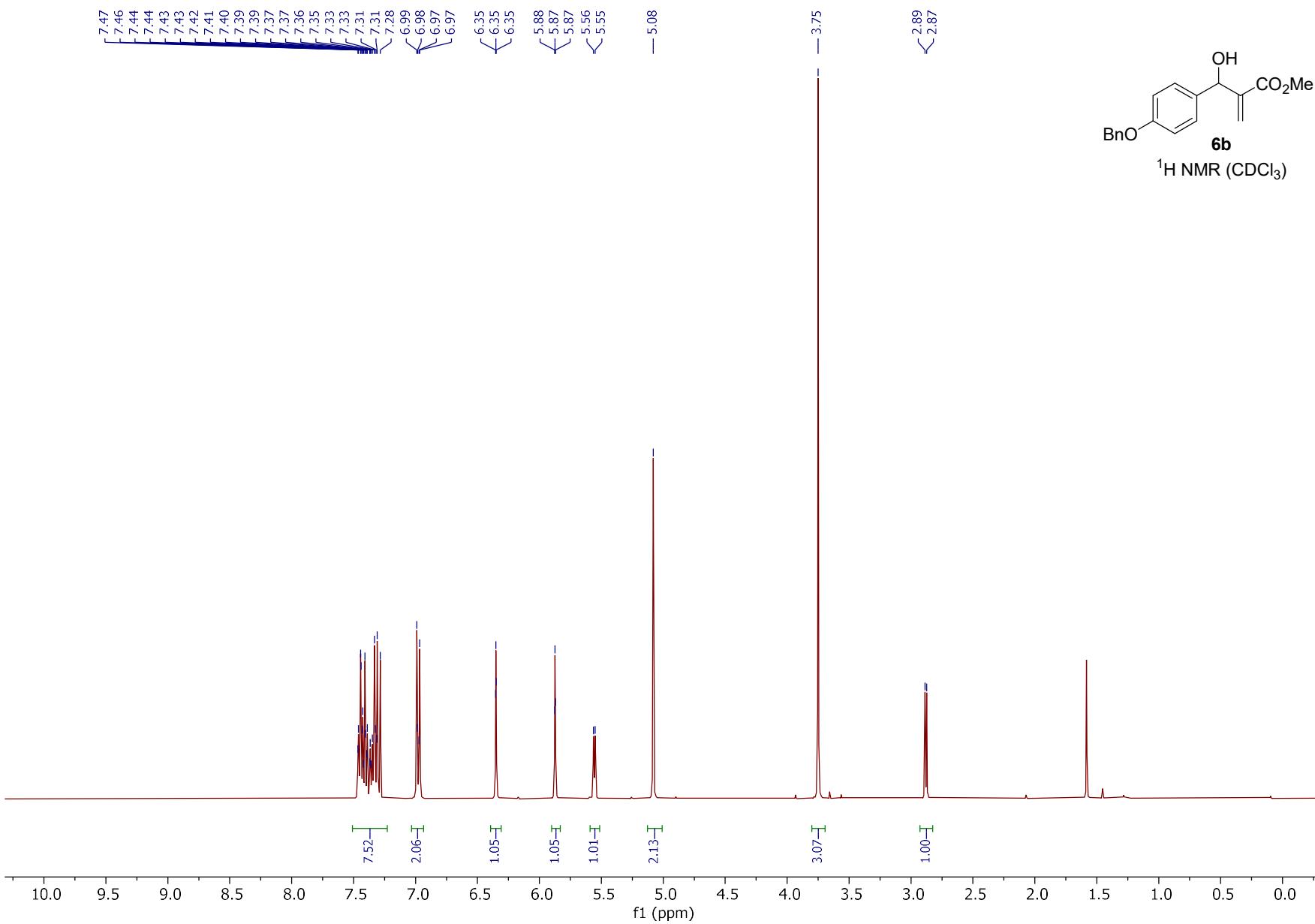


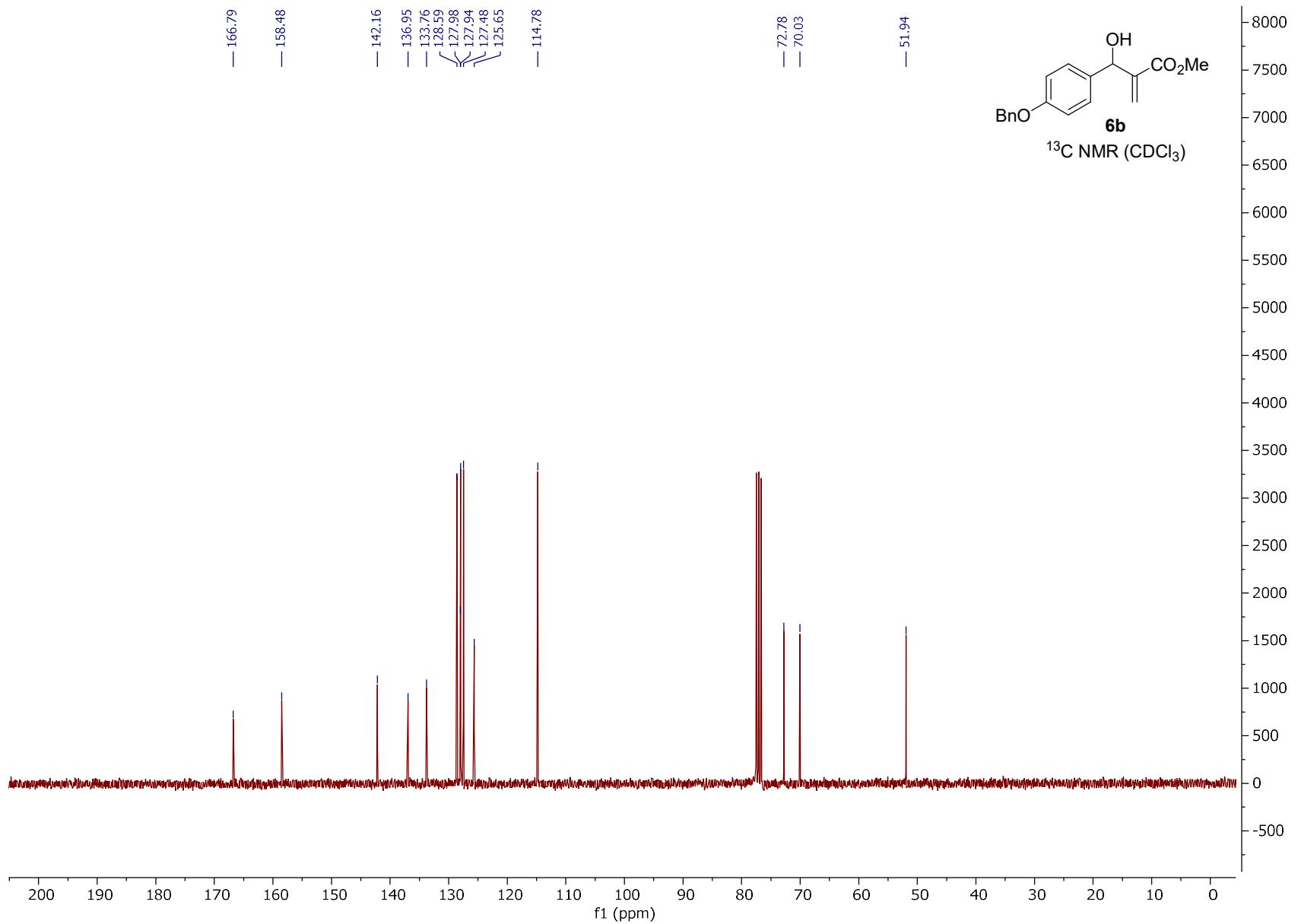
7.96
7.94
7.94
7.35
7.32
7.28
7.26
7.23
7.16
7.13
6.59
6.54
6.16
6.14
6.11
6.10
6.08
6.06

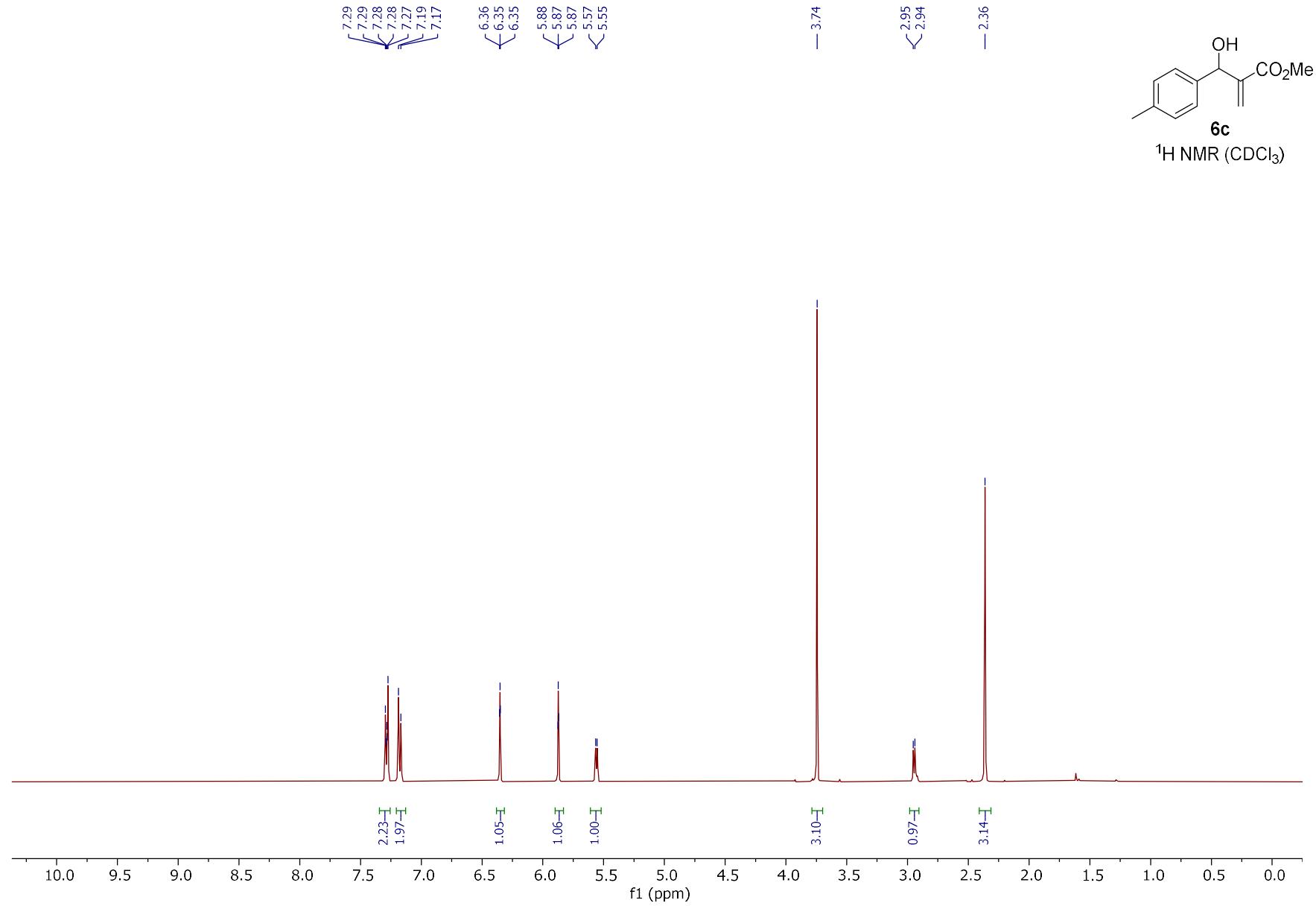
4.74
4.74
4.72
4.71

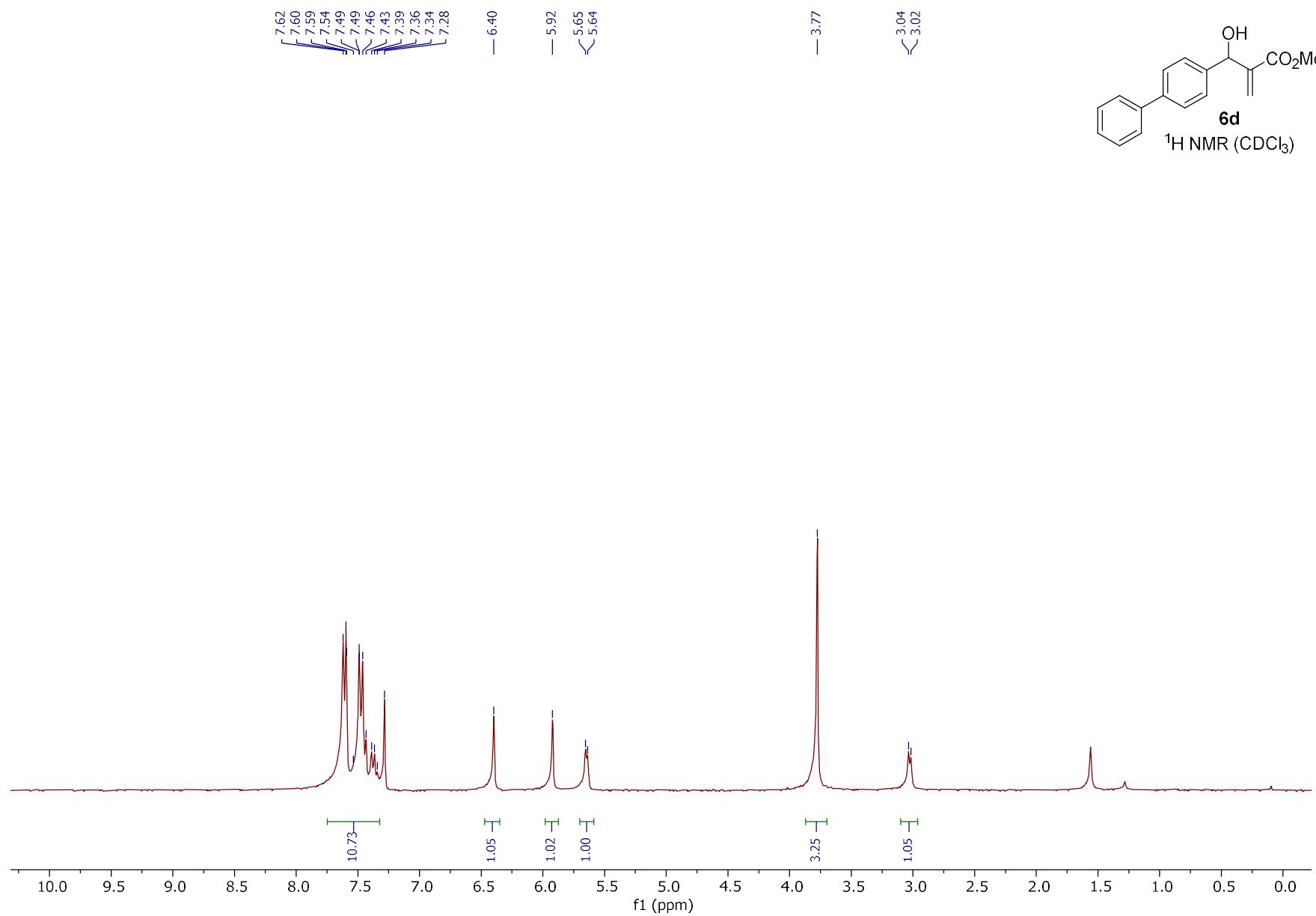


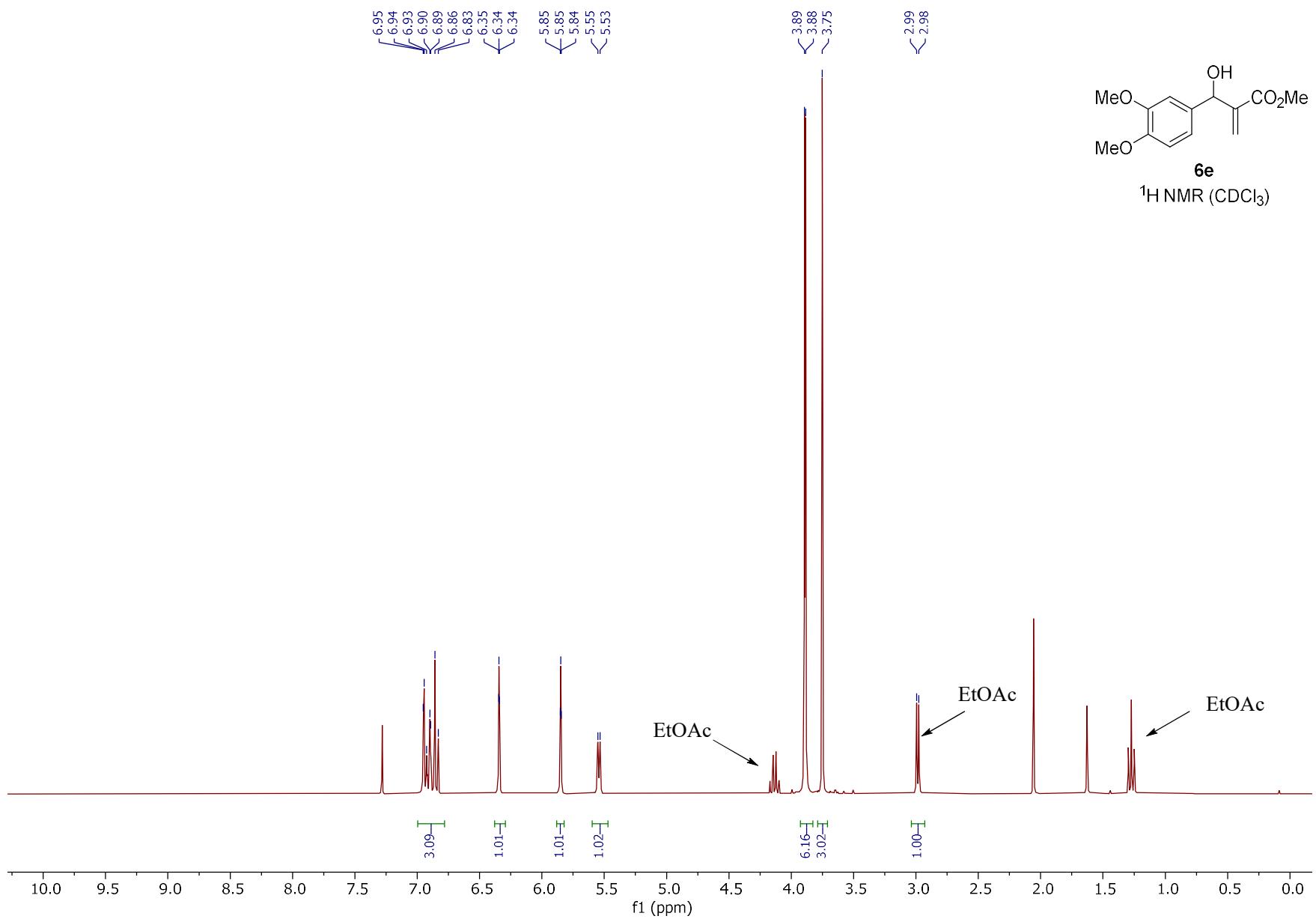


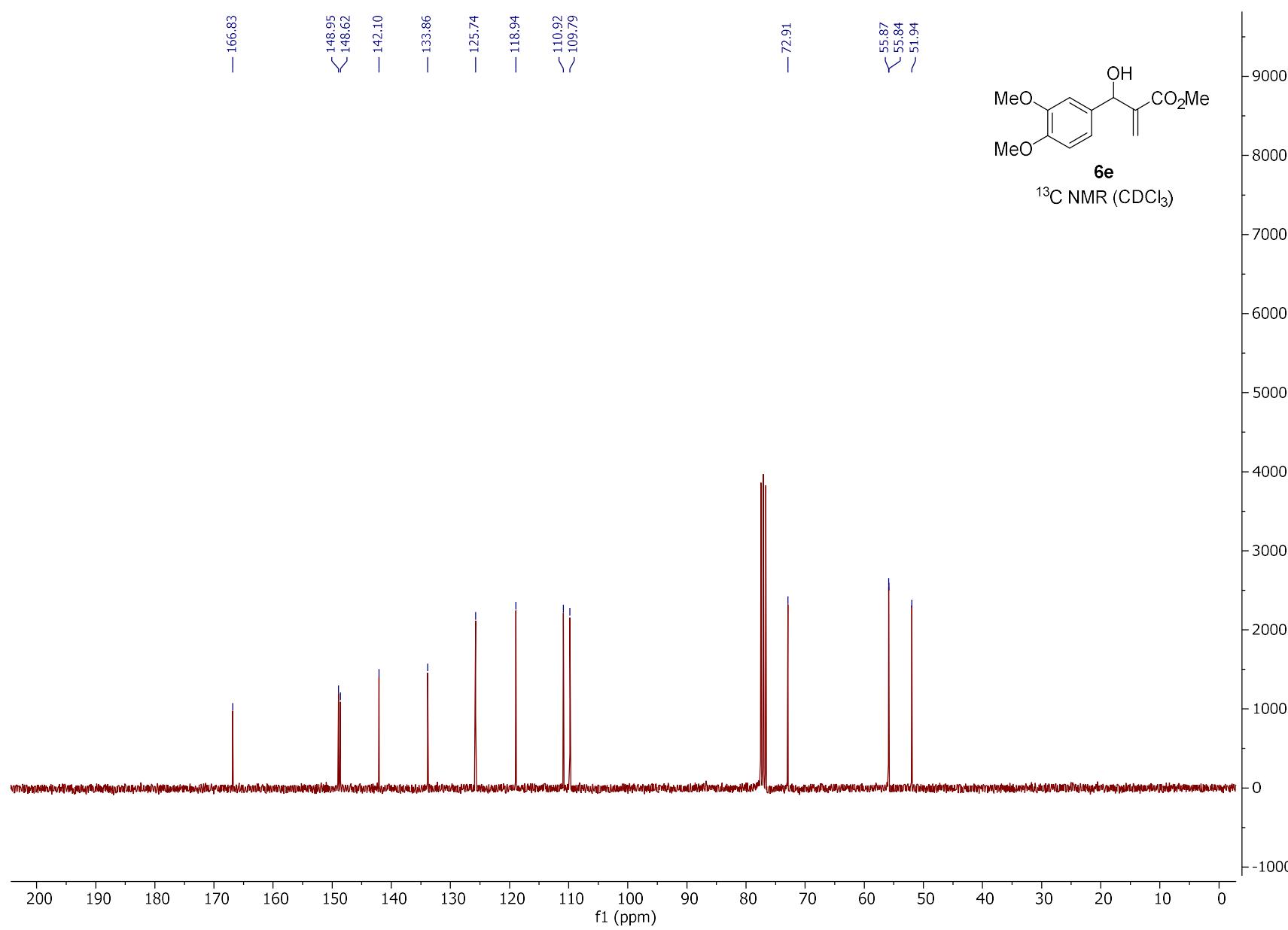


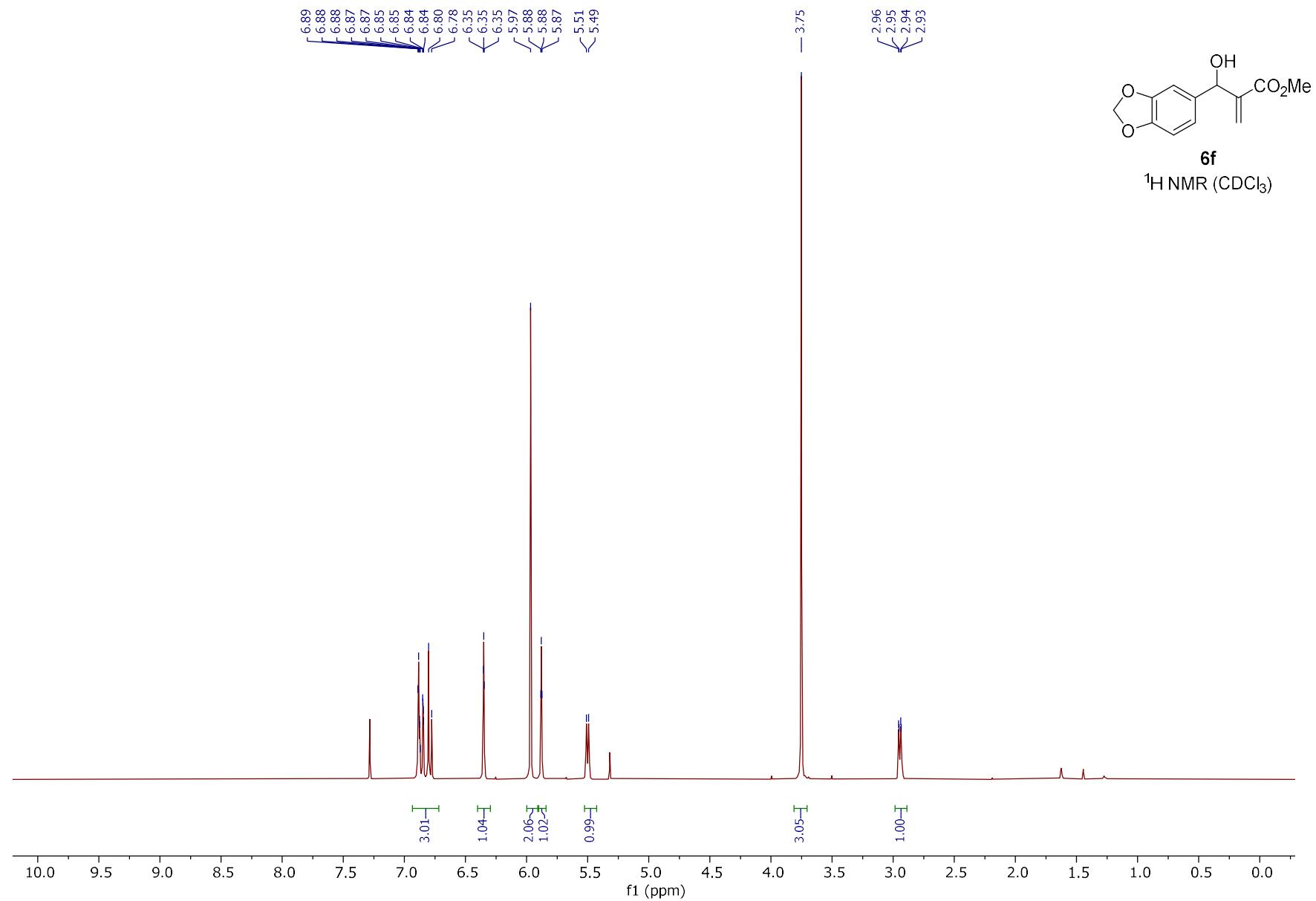


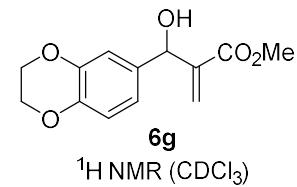
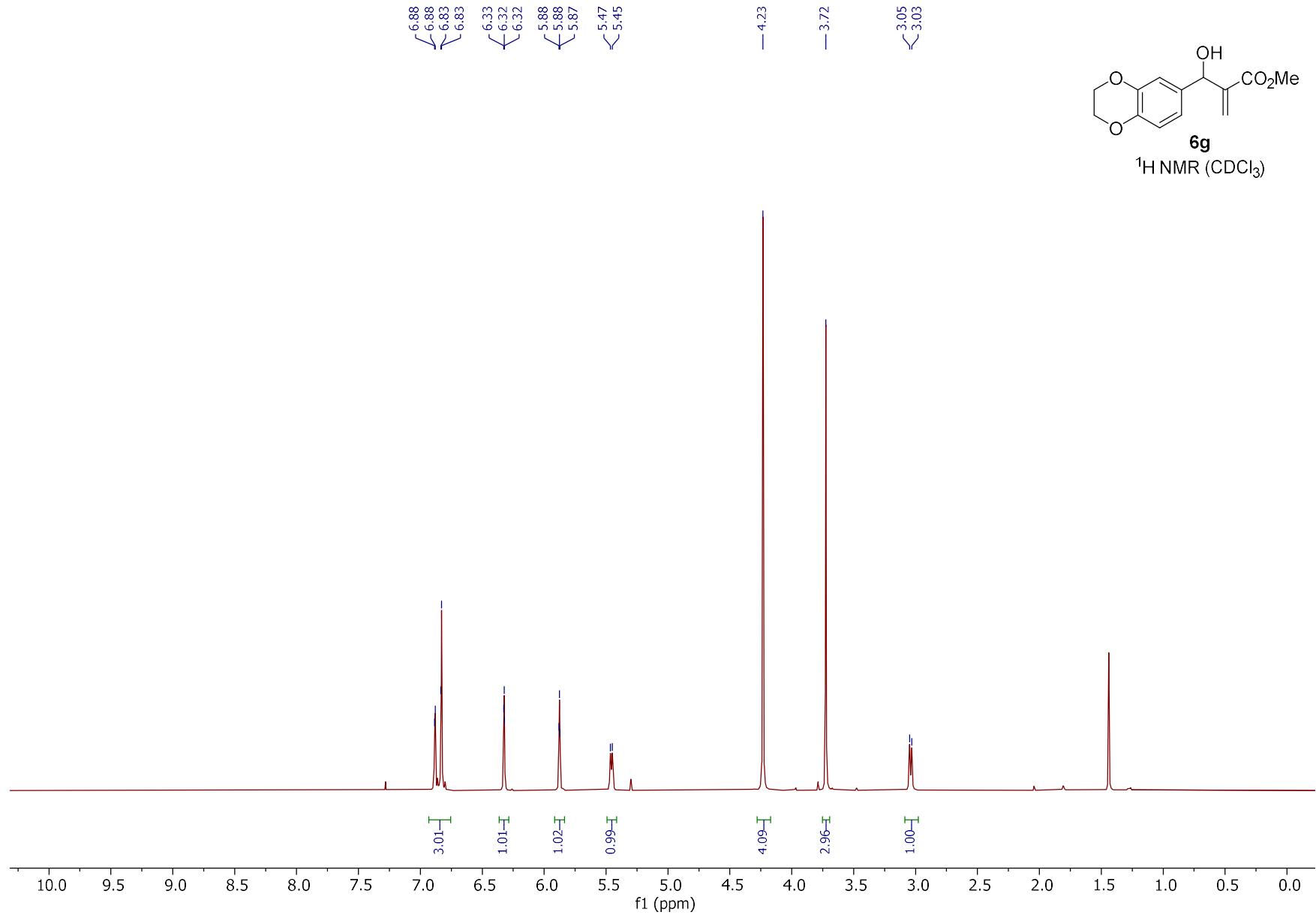


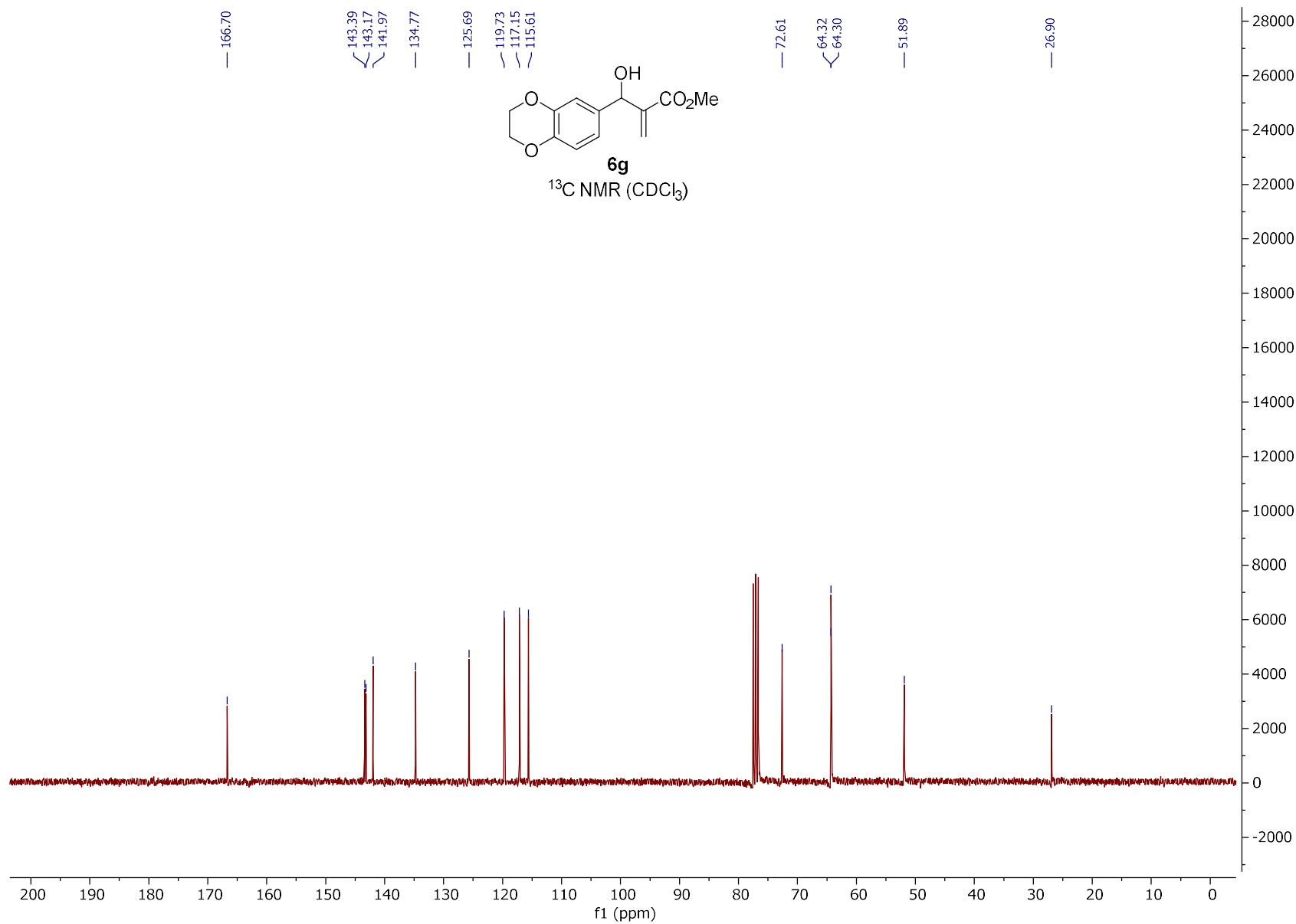


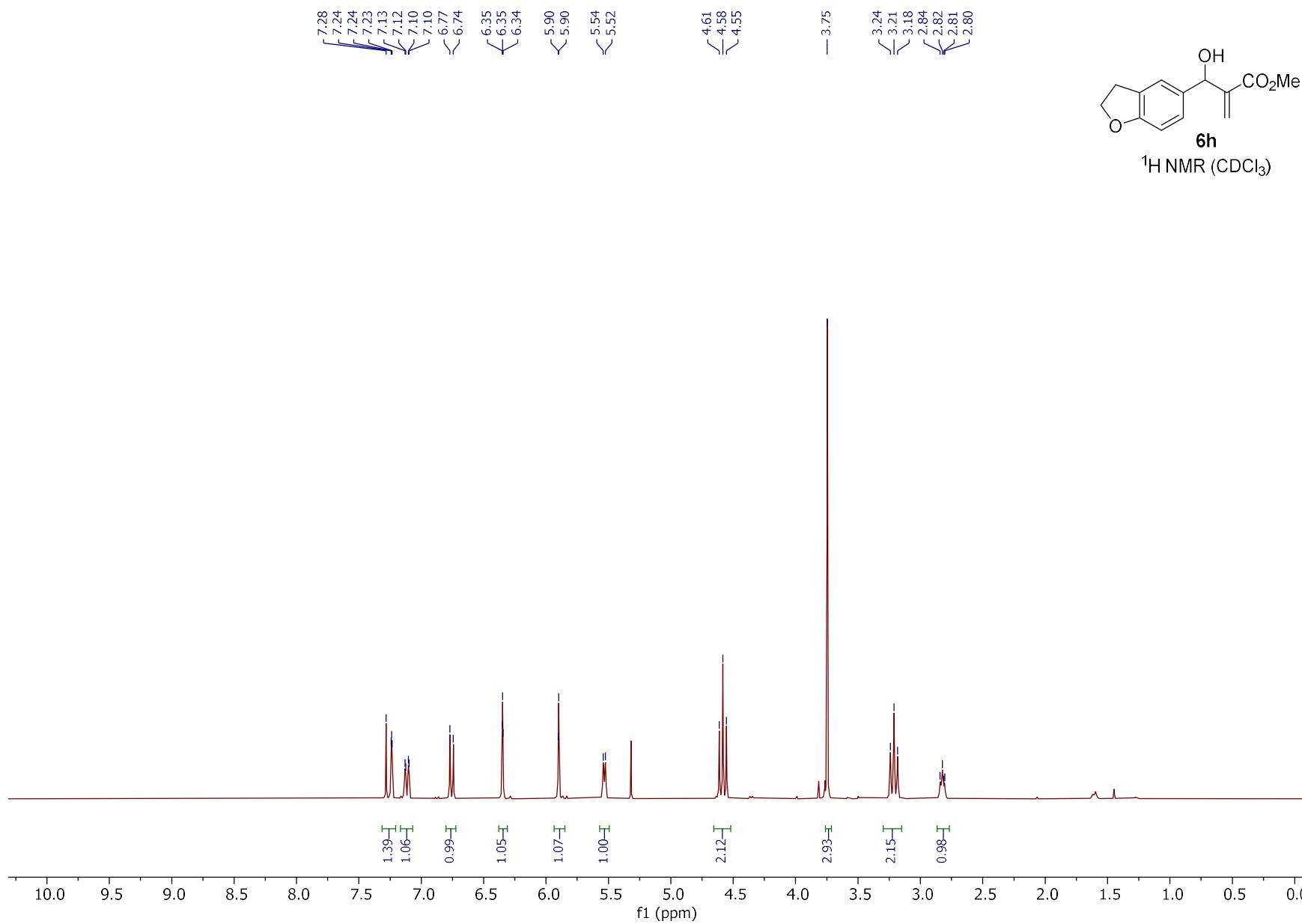


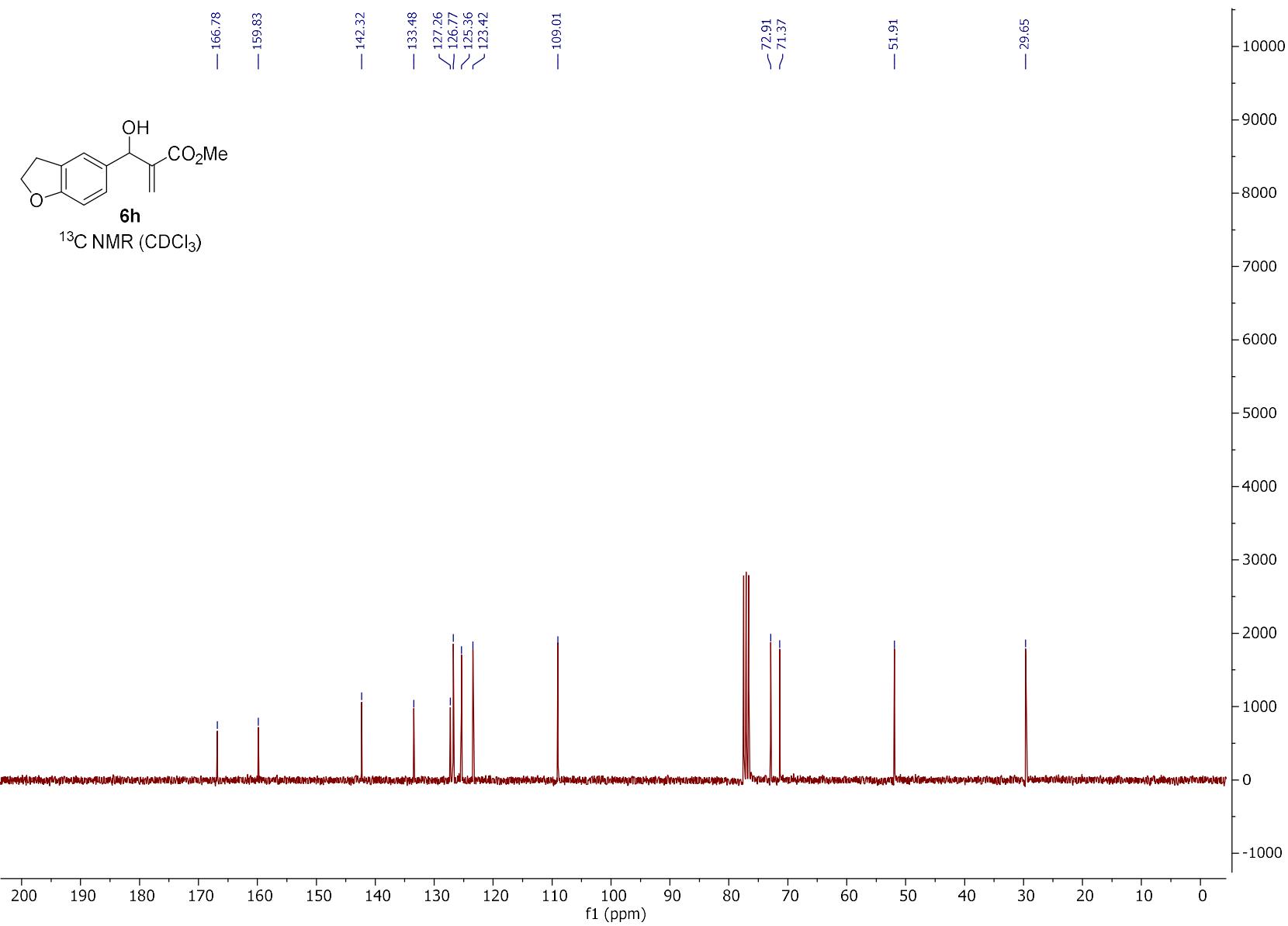


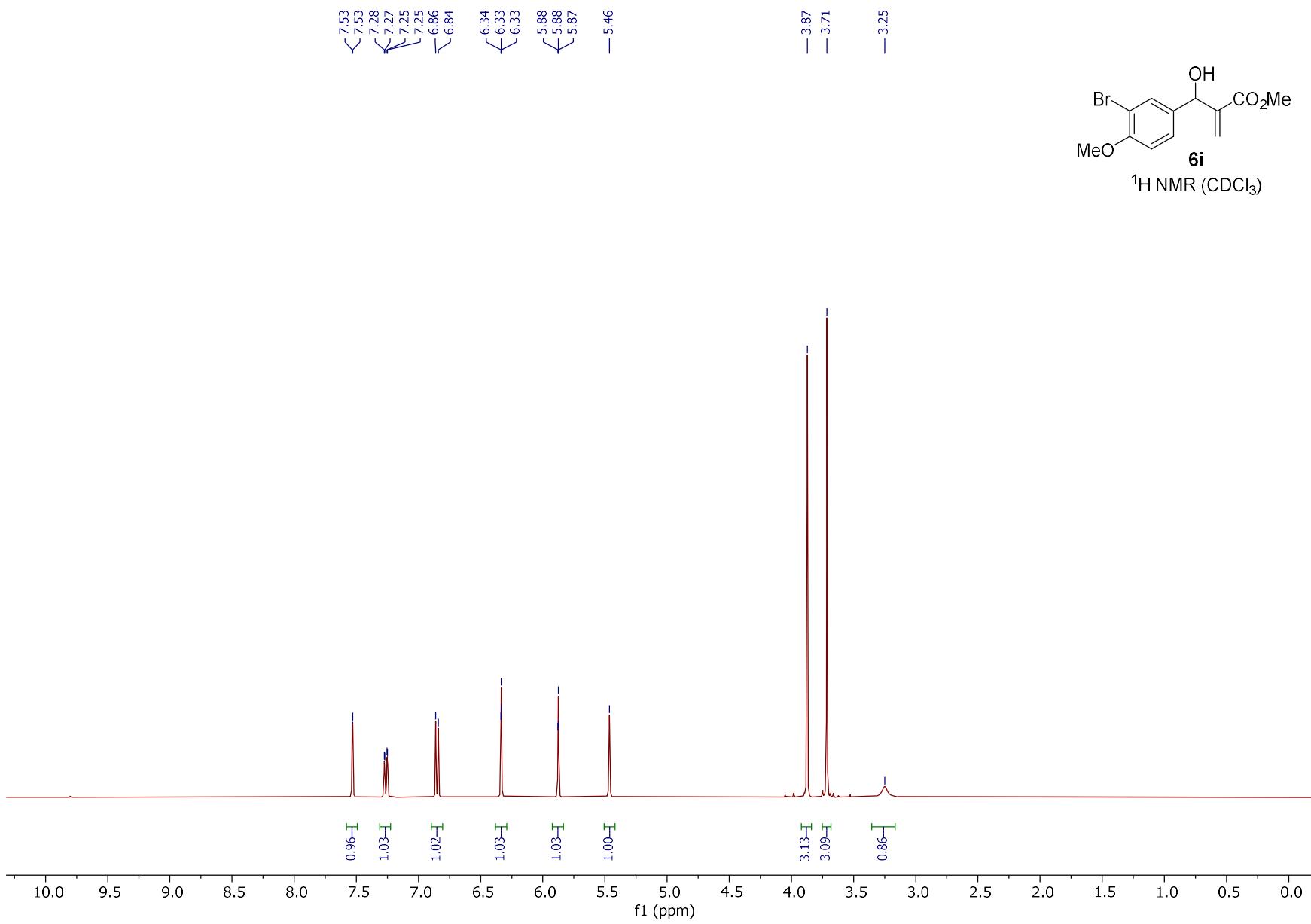


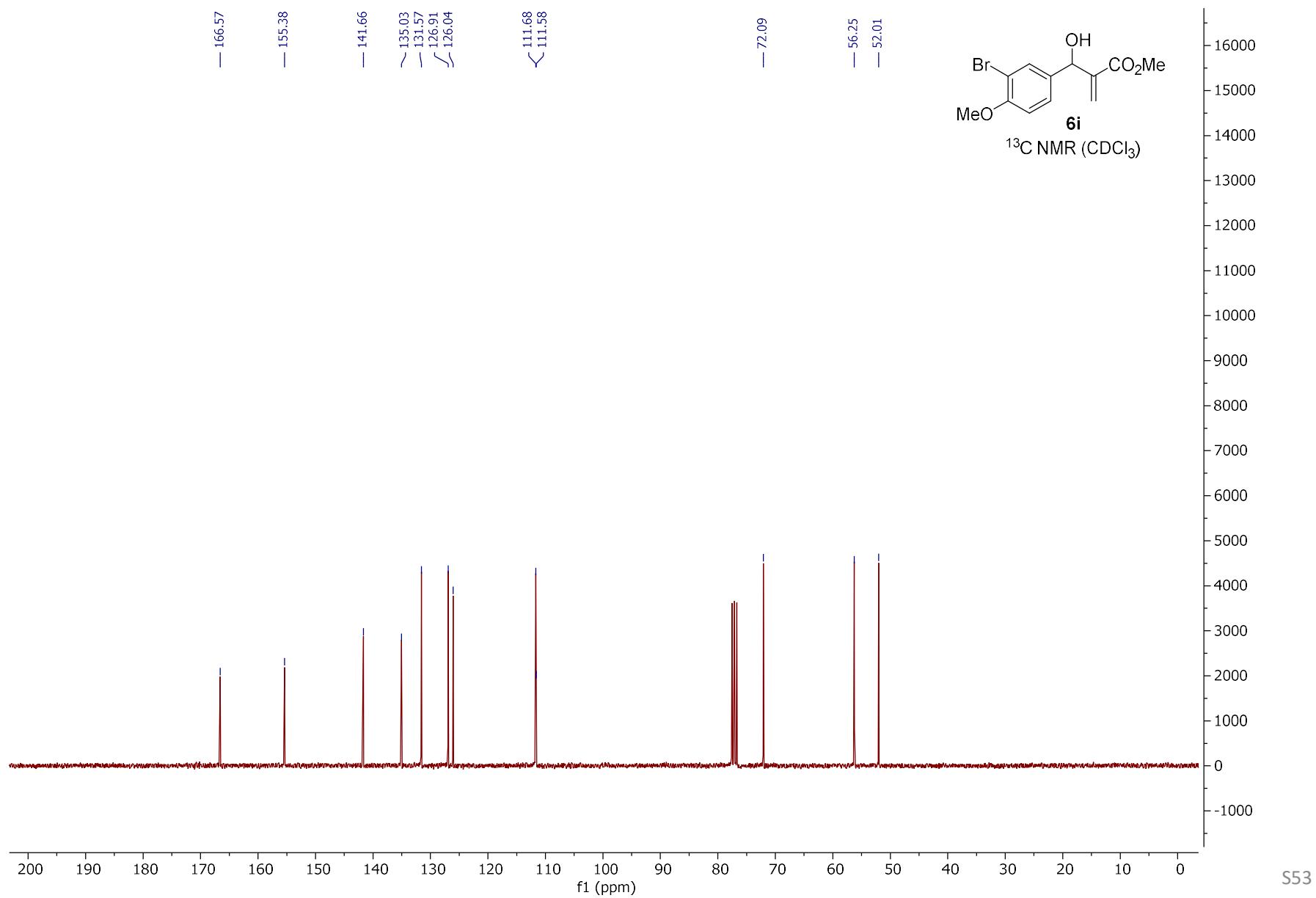


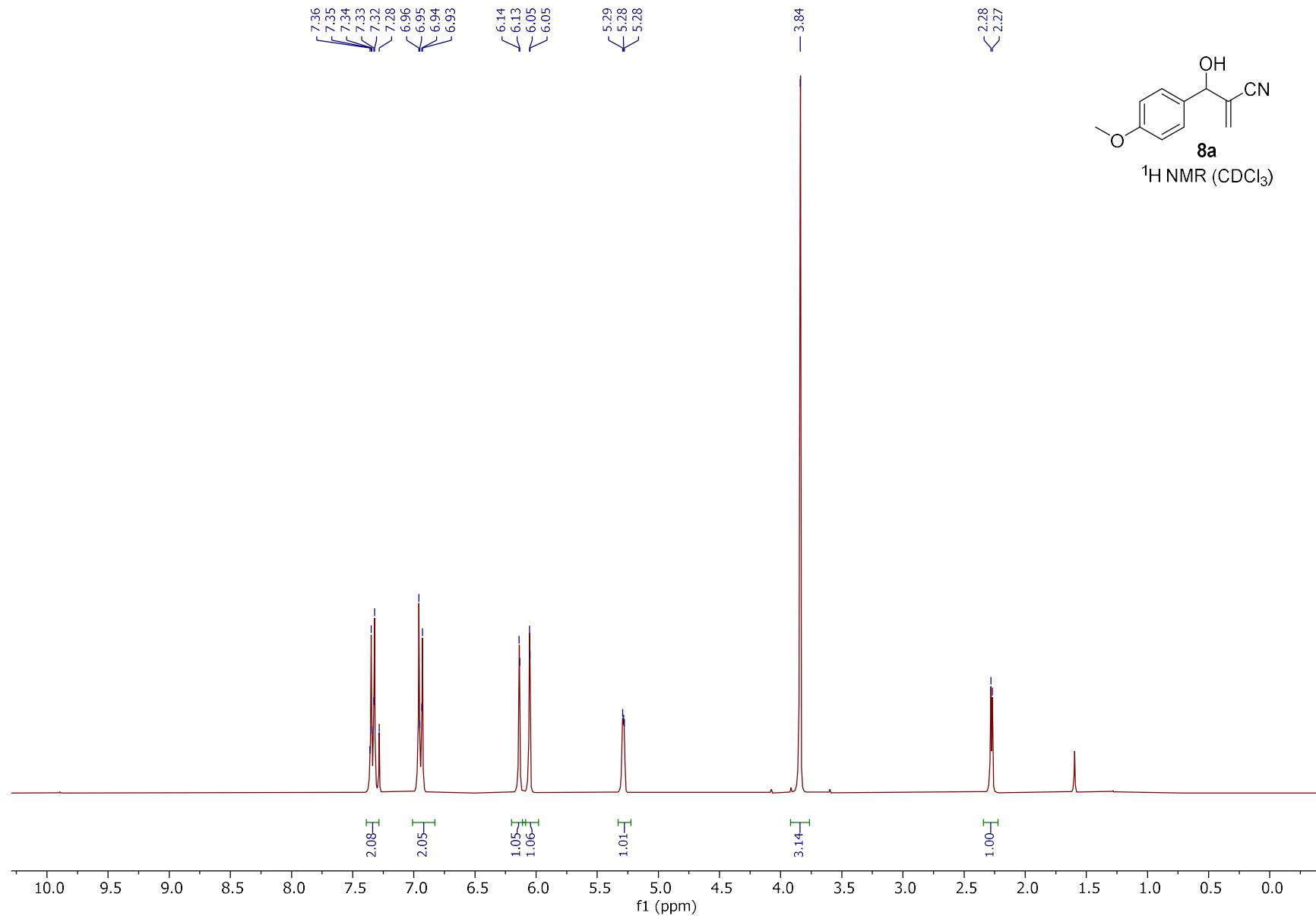


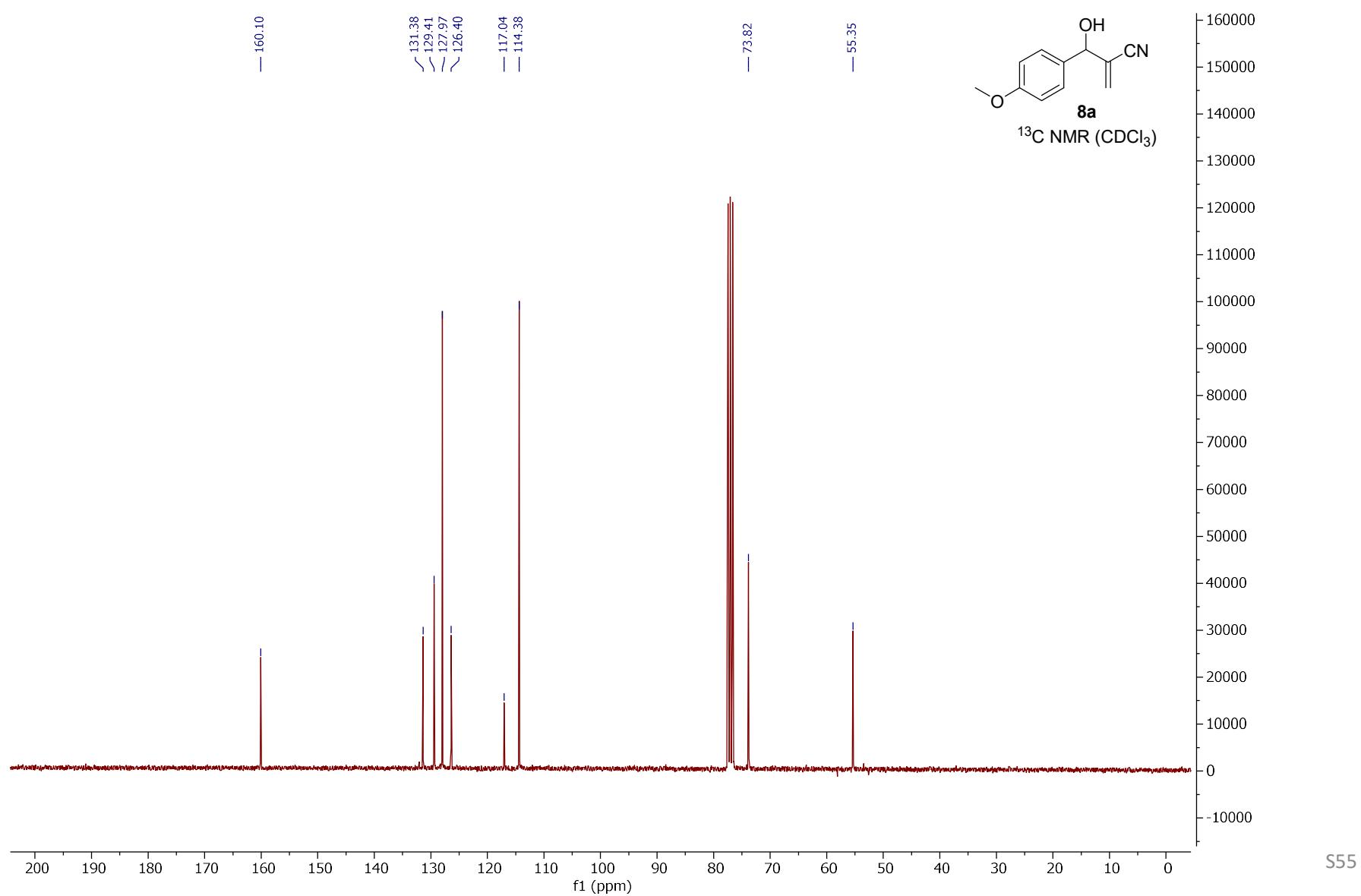


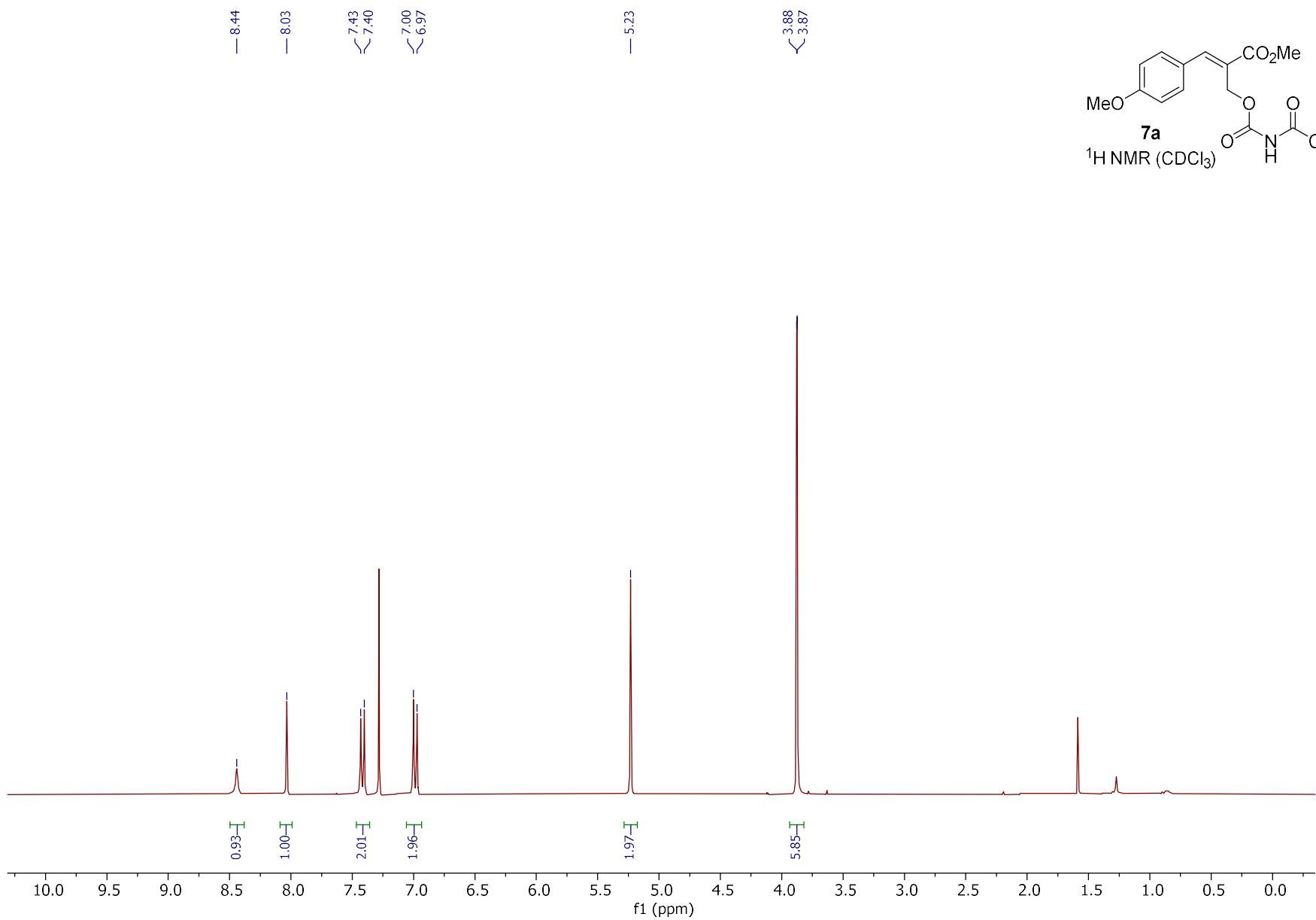


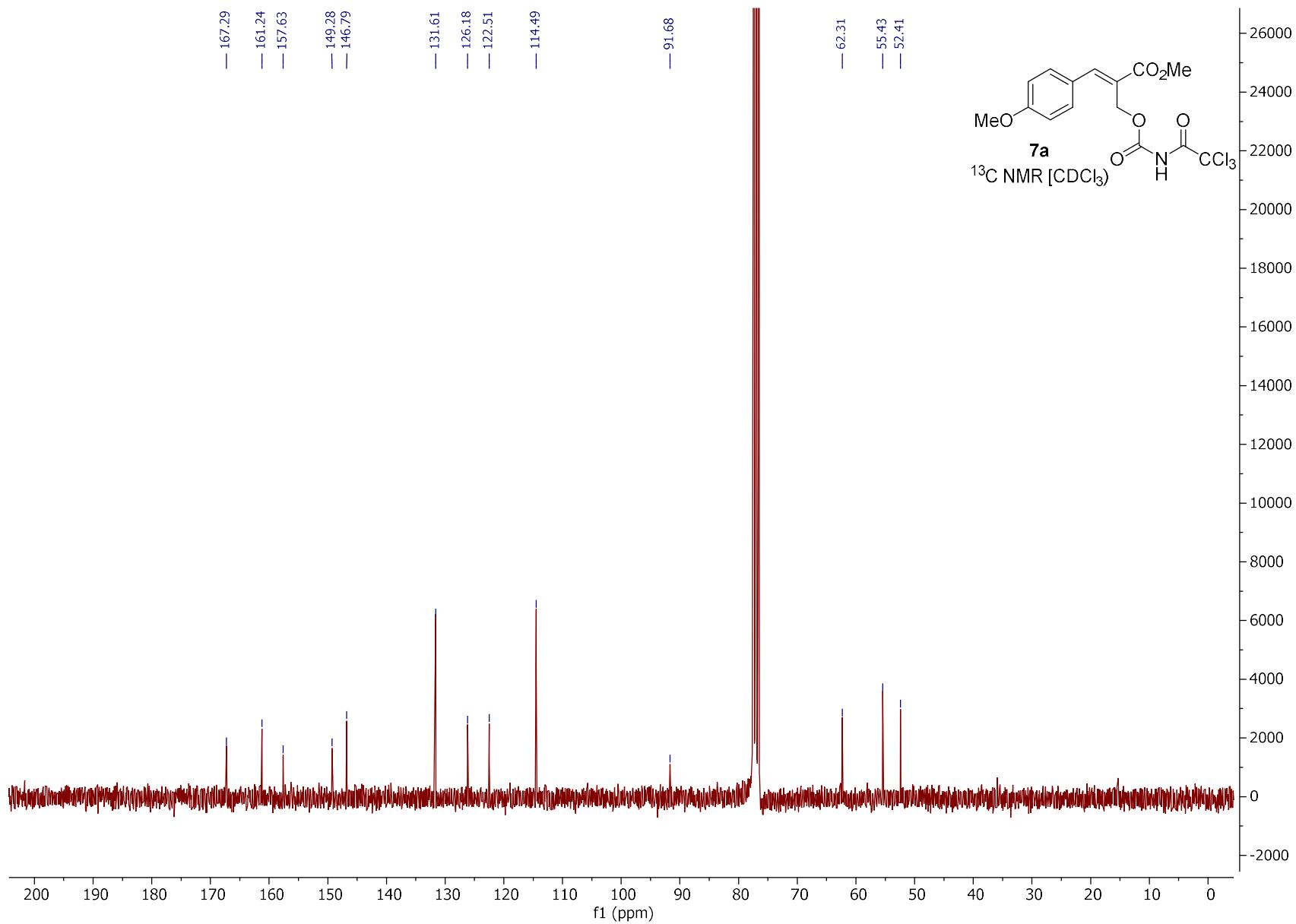


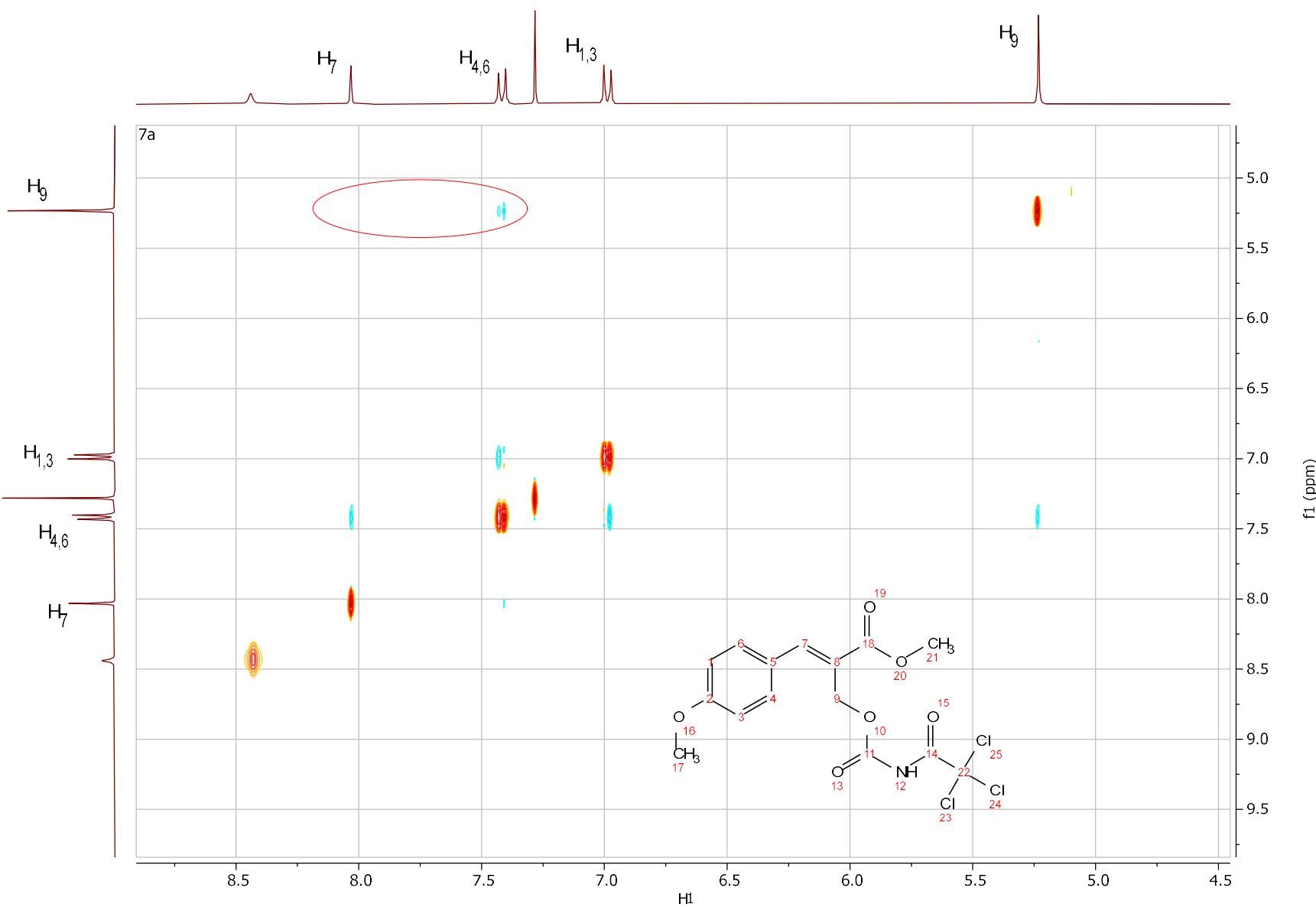
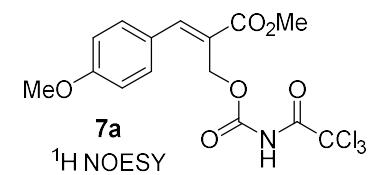


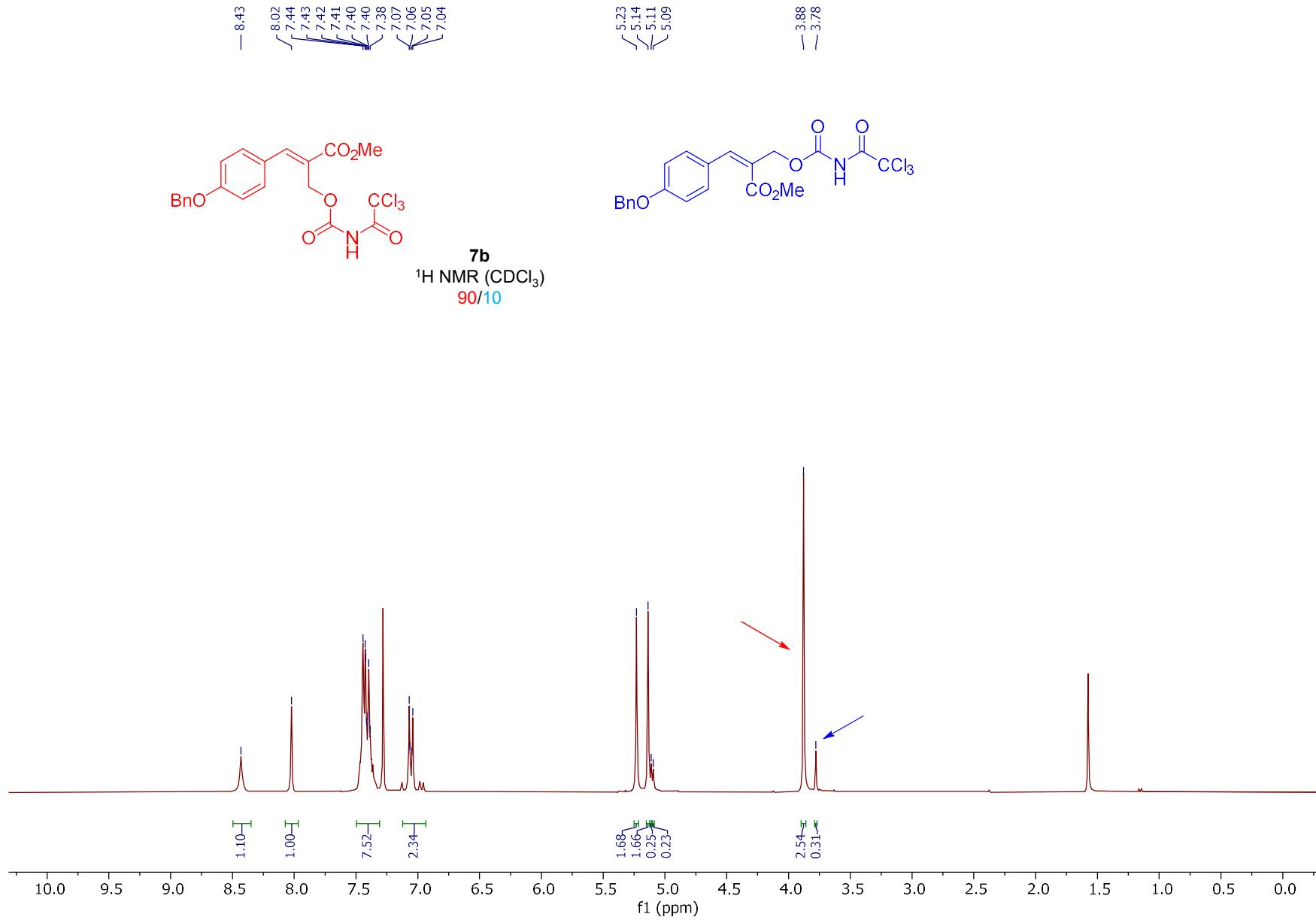


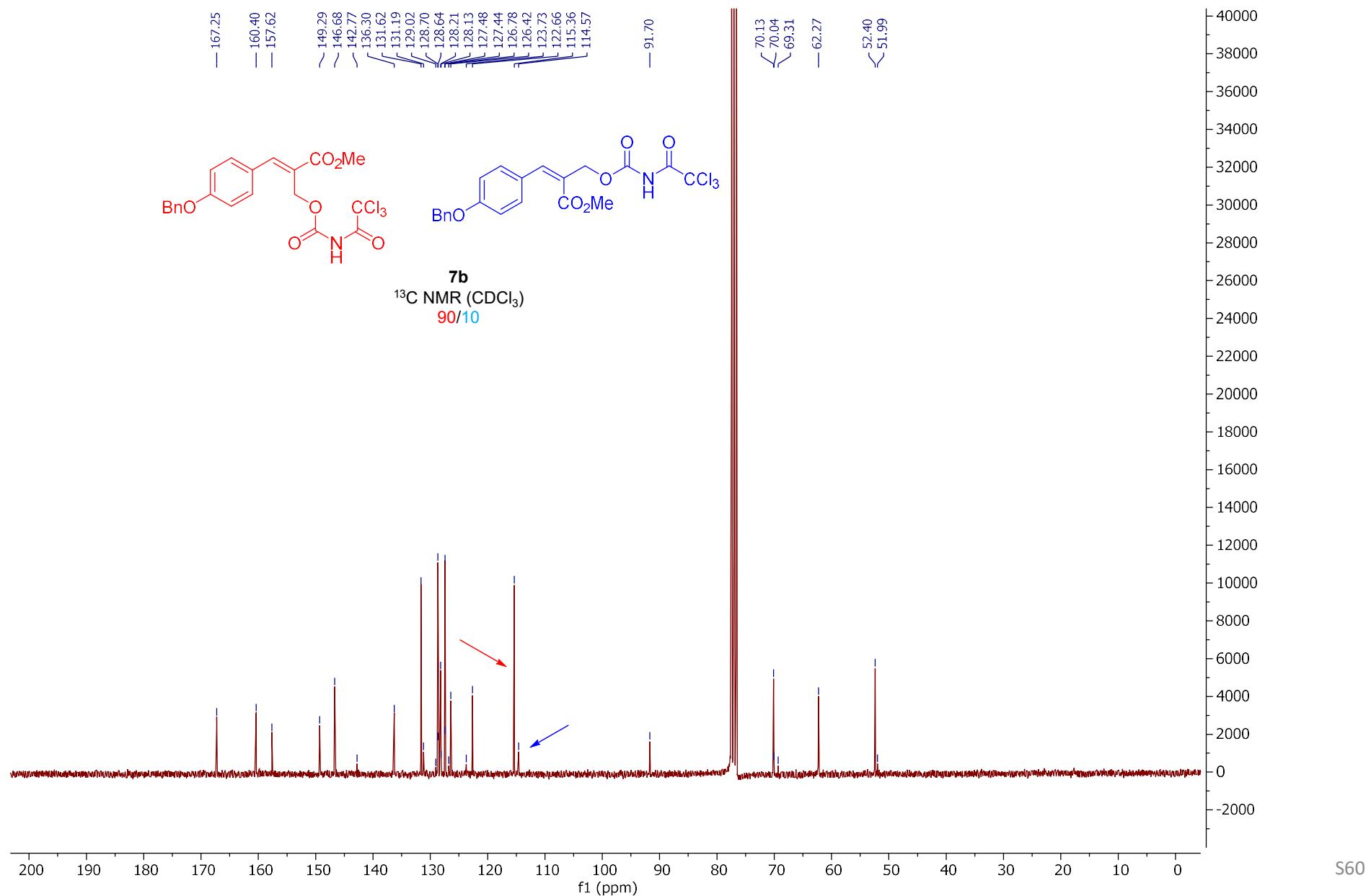


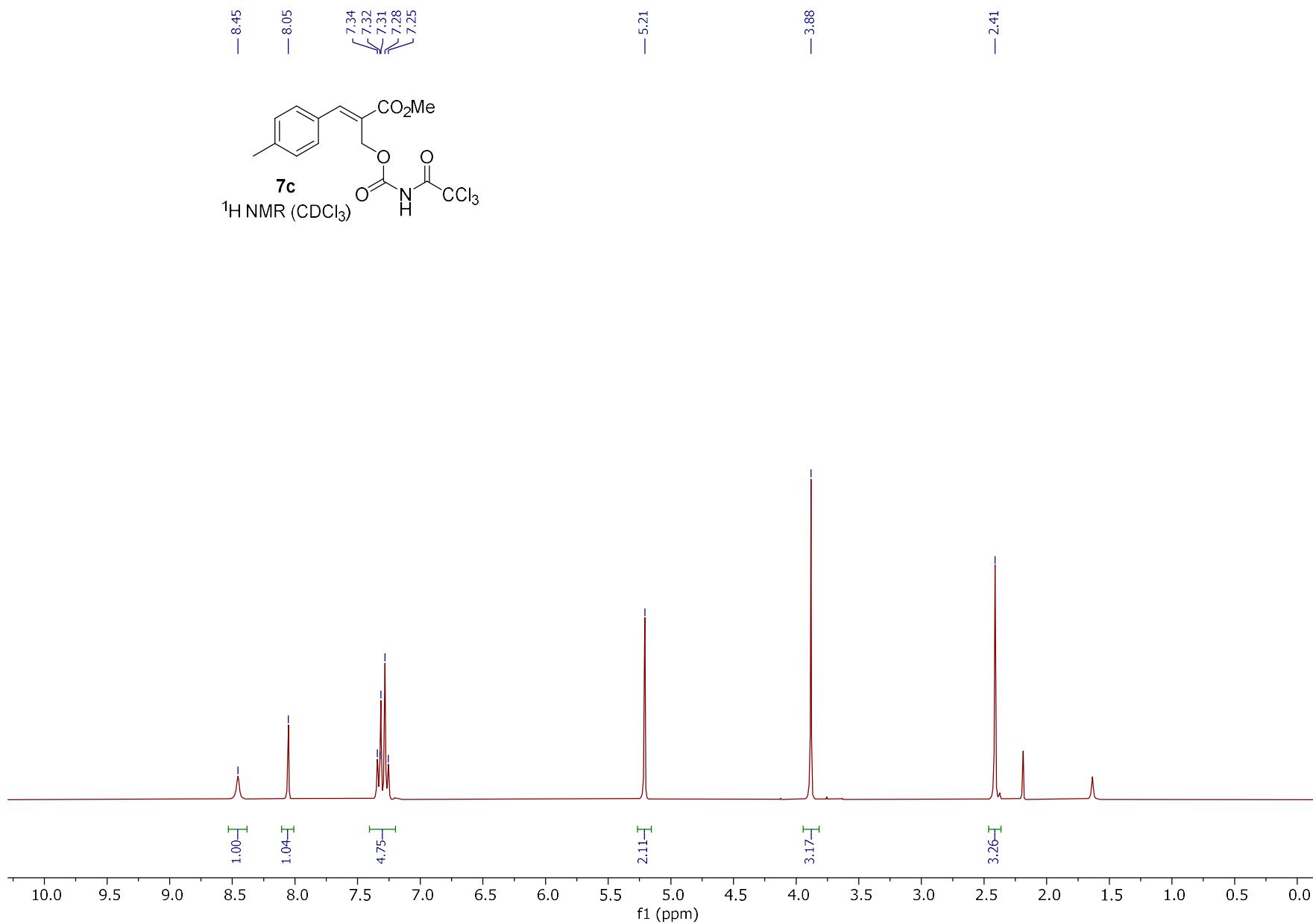


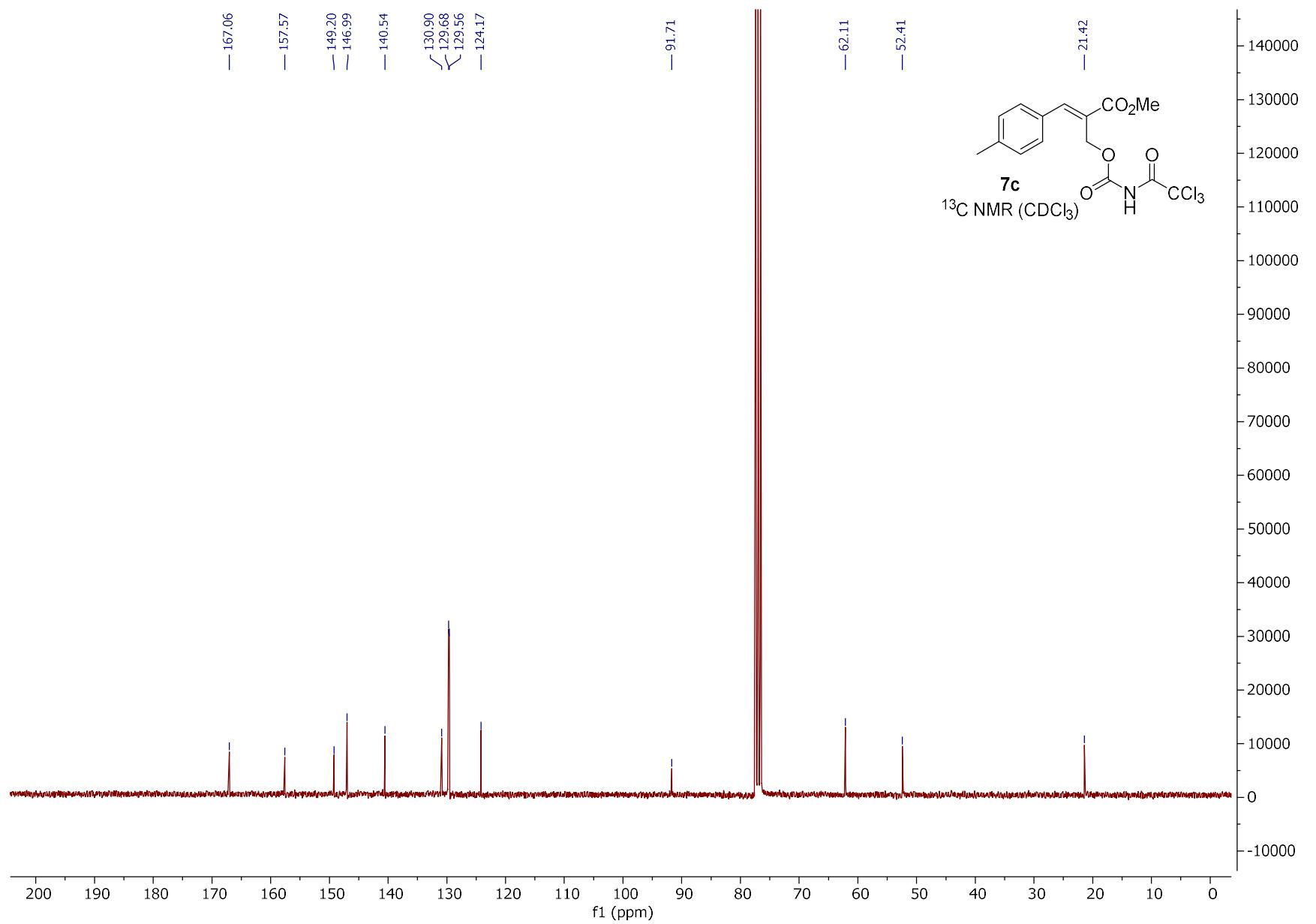


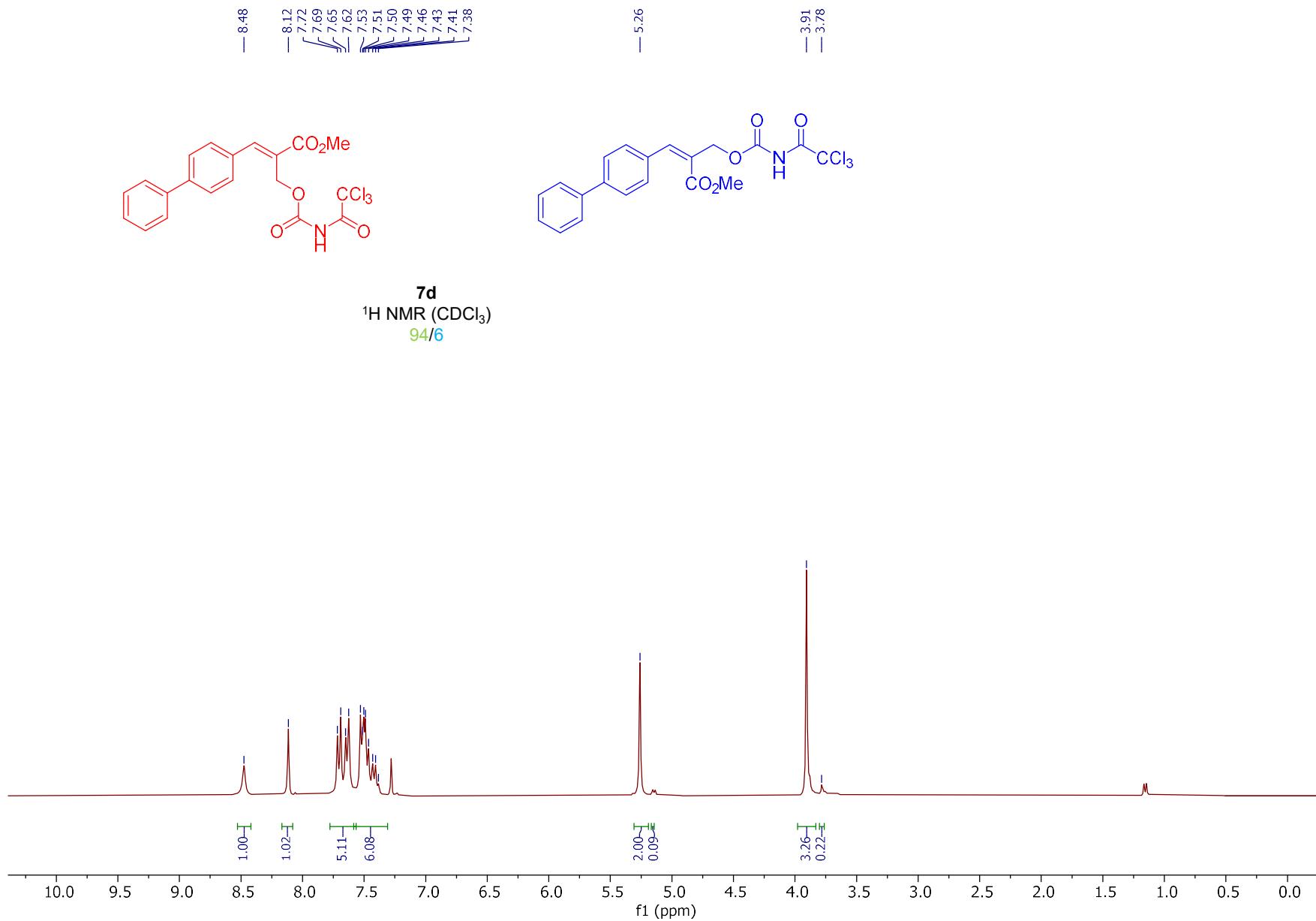


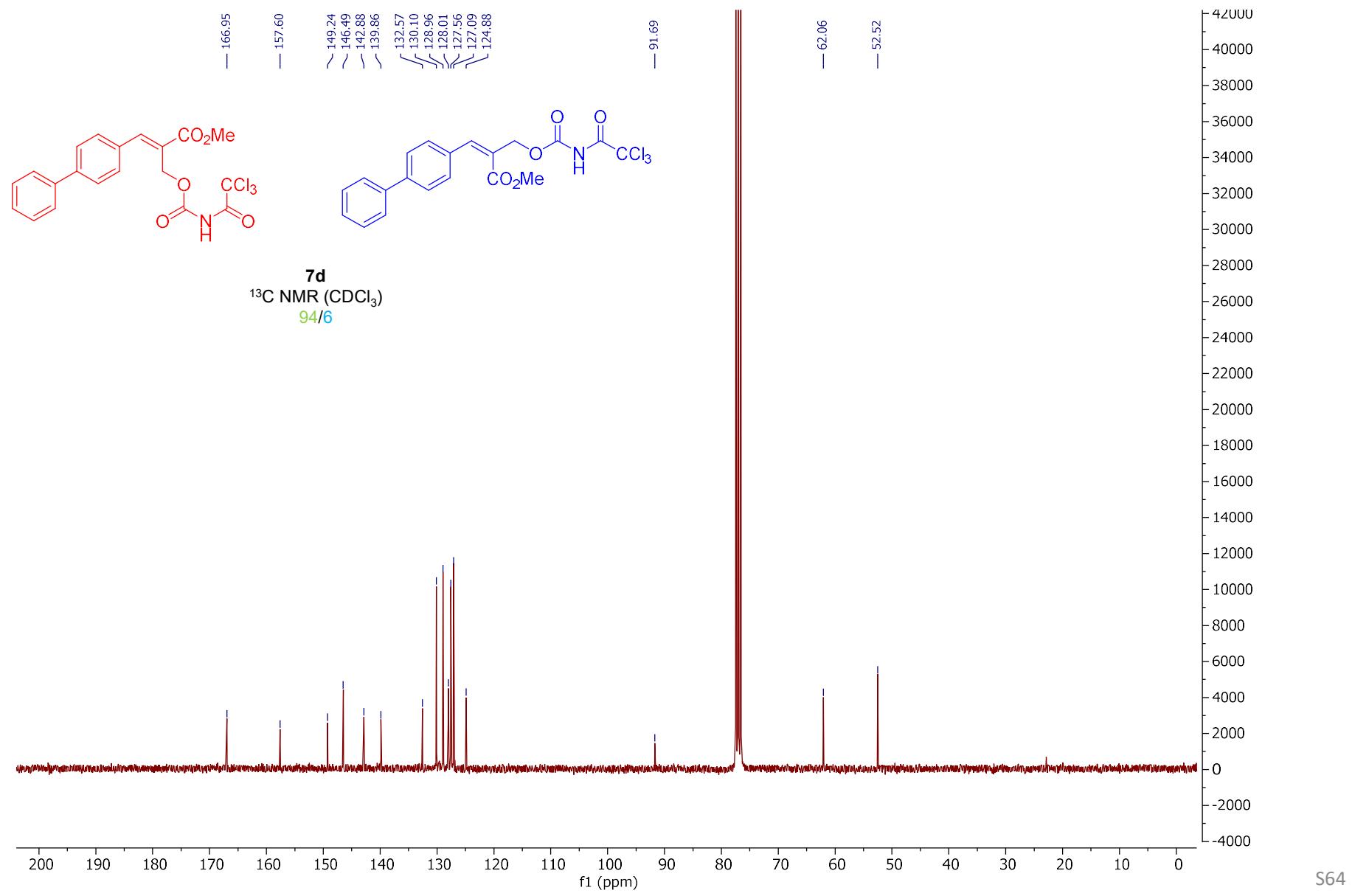


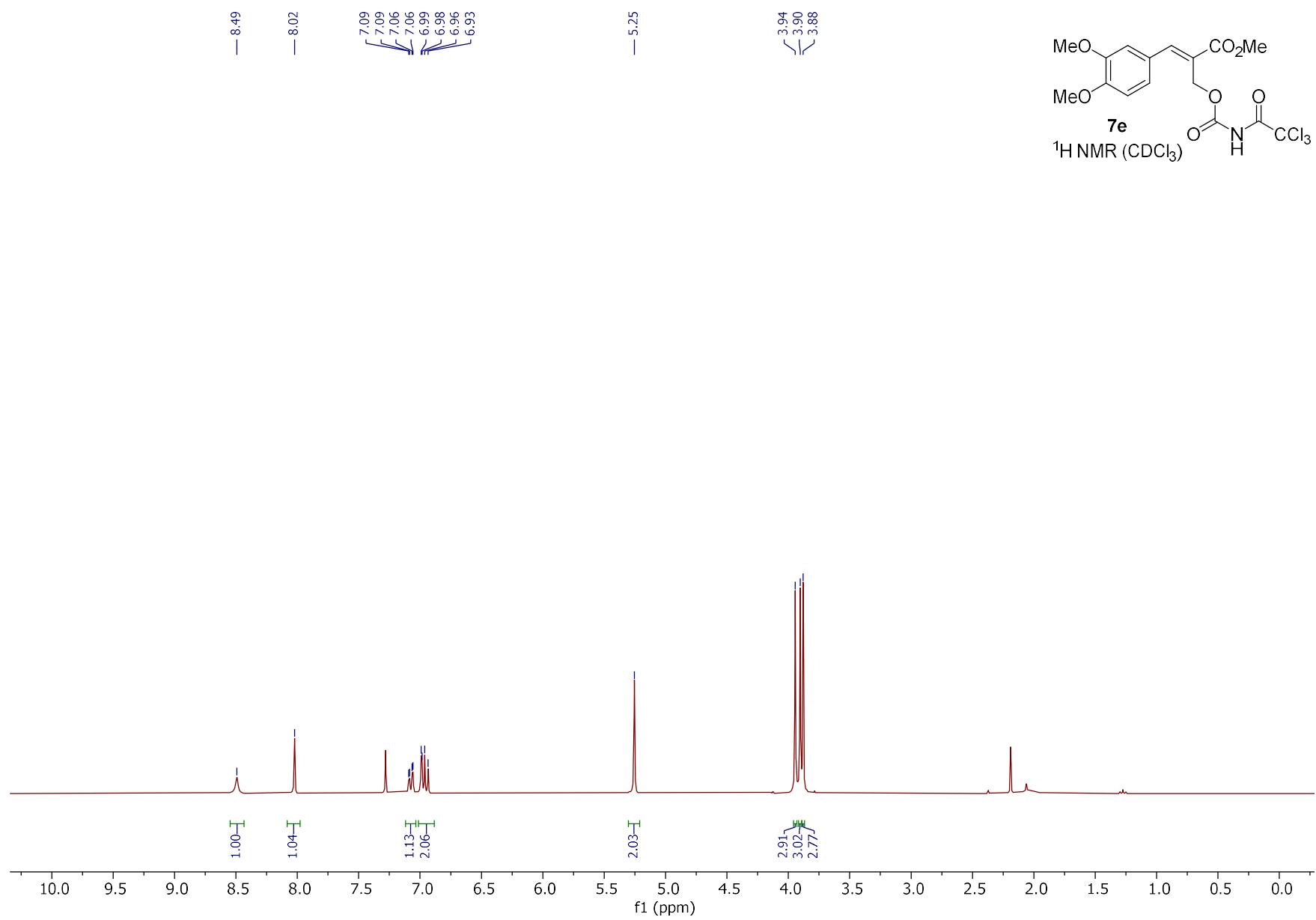


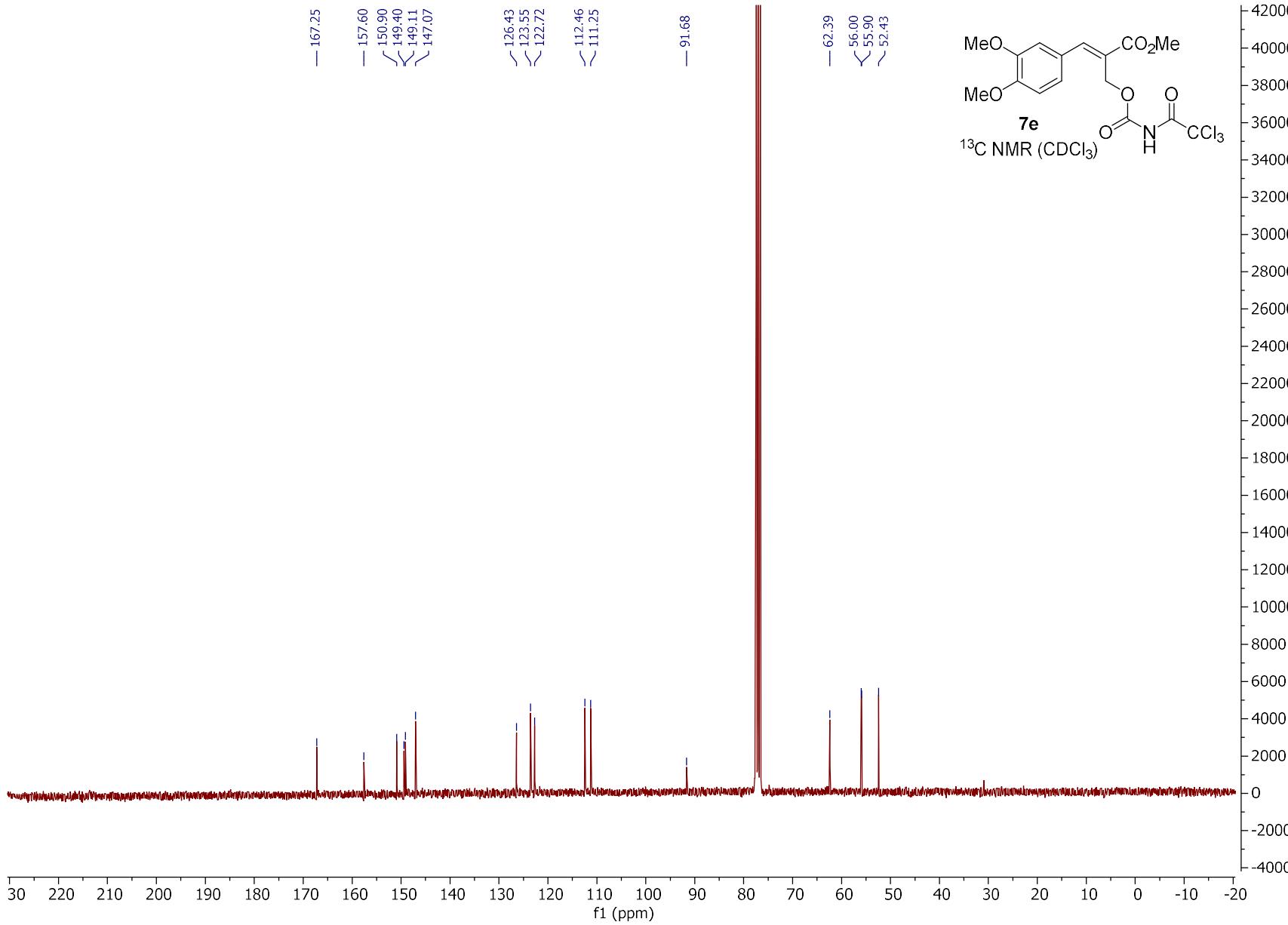


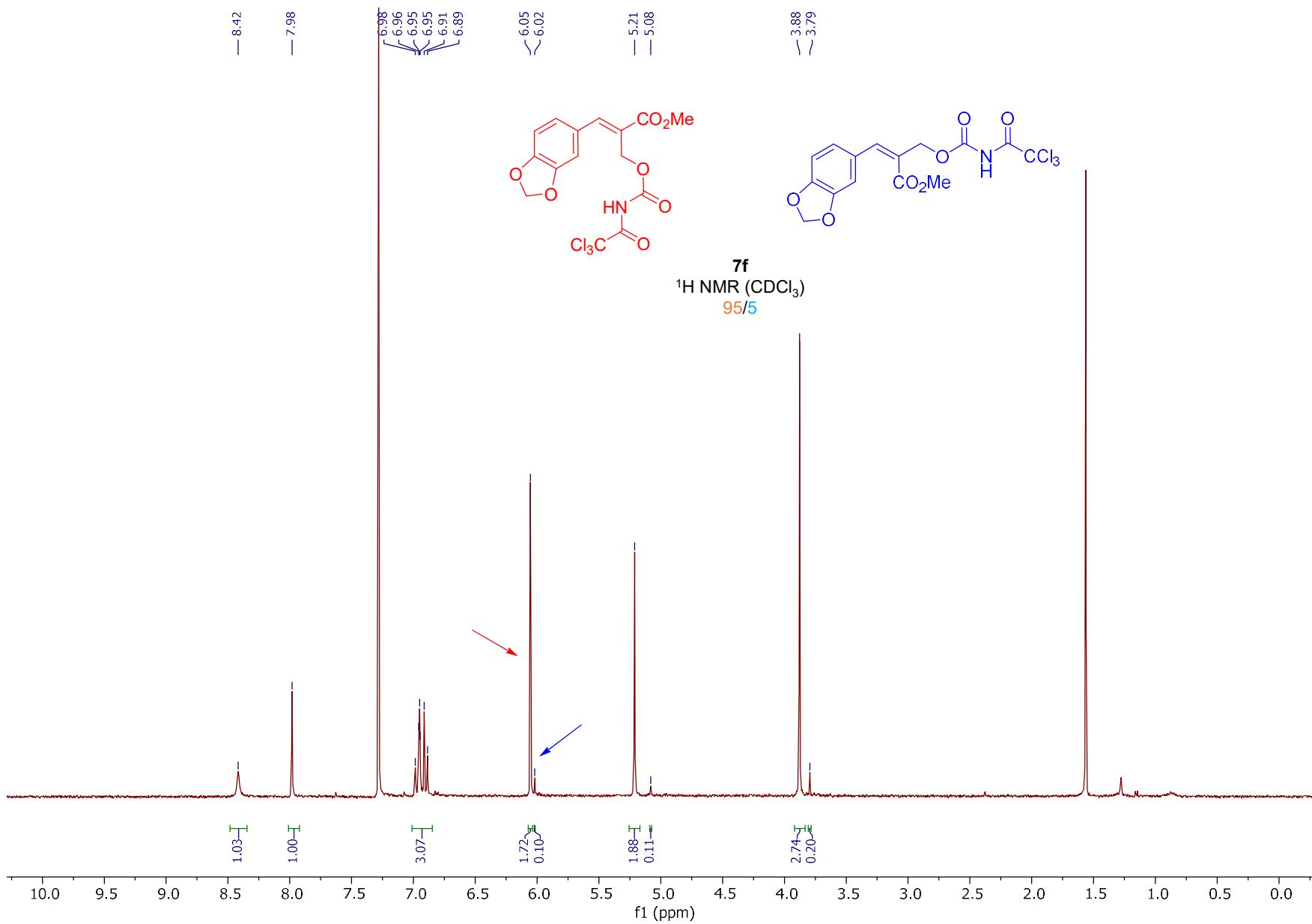


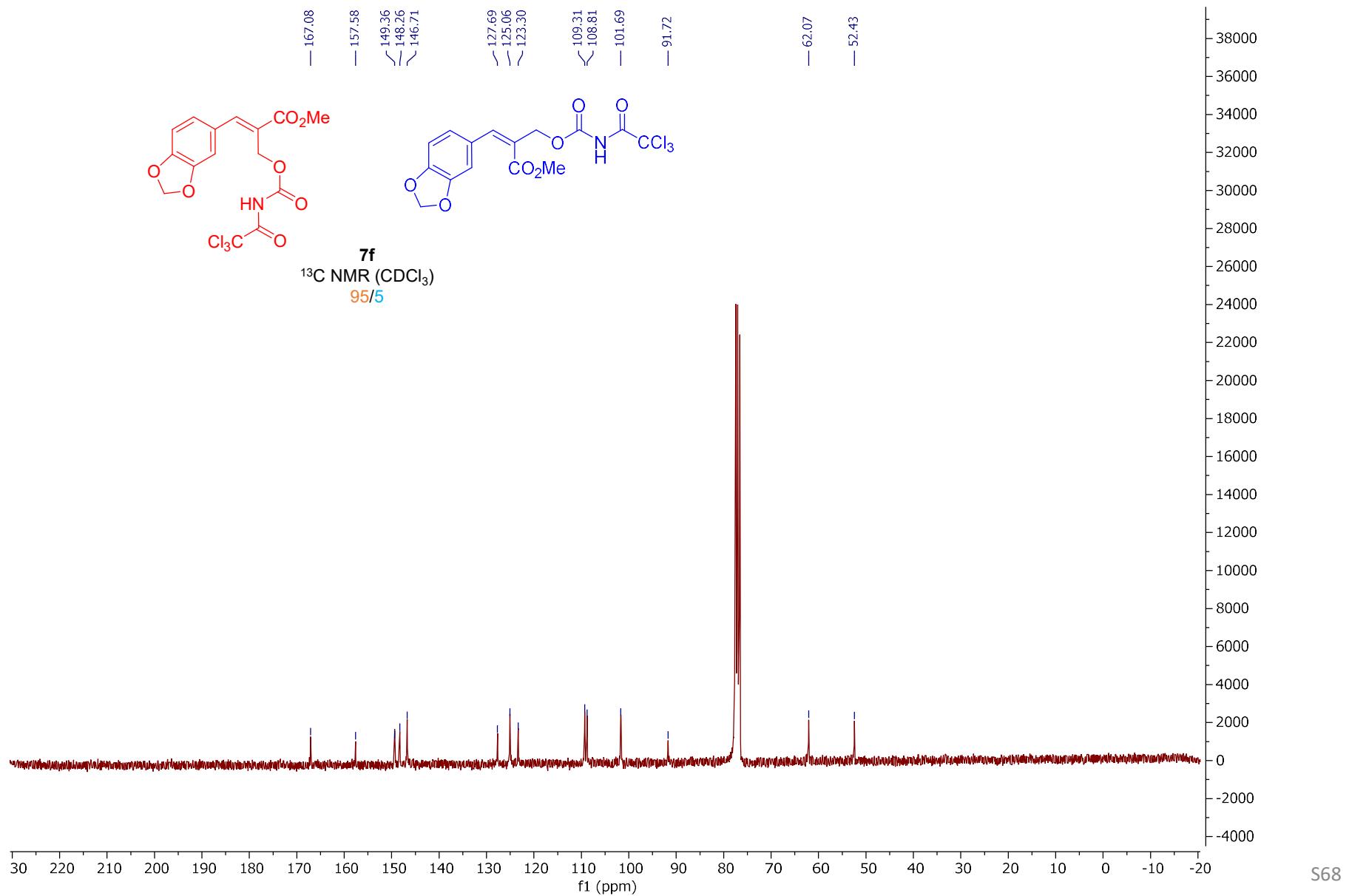












— 8.43

— 7.96

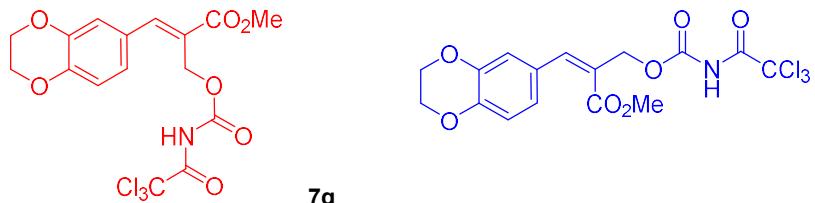
> 6.95

— 5.22

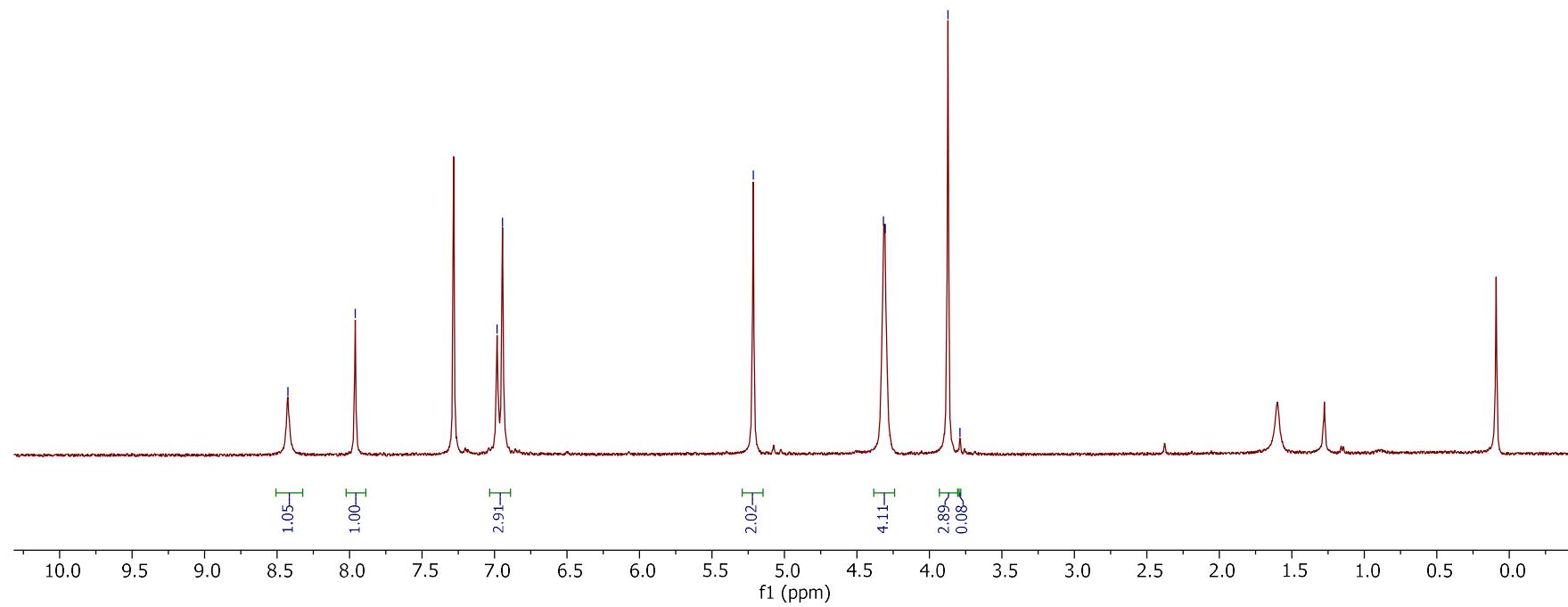
< 4.31

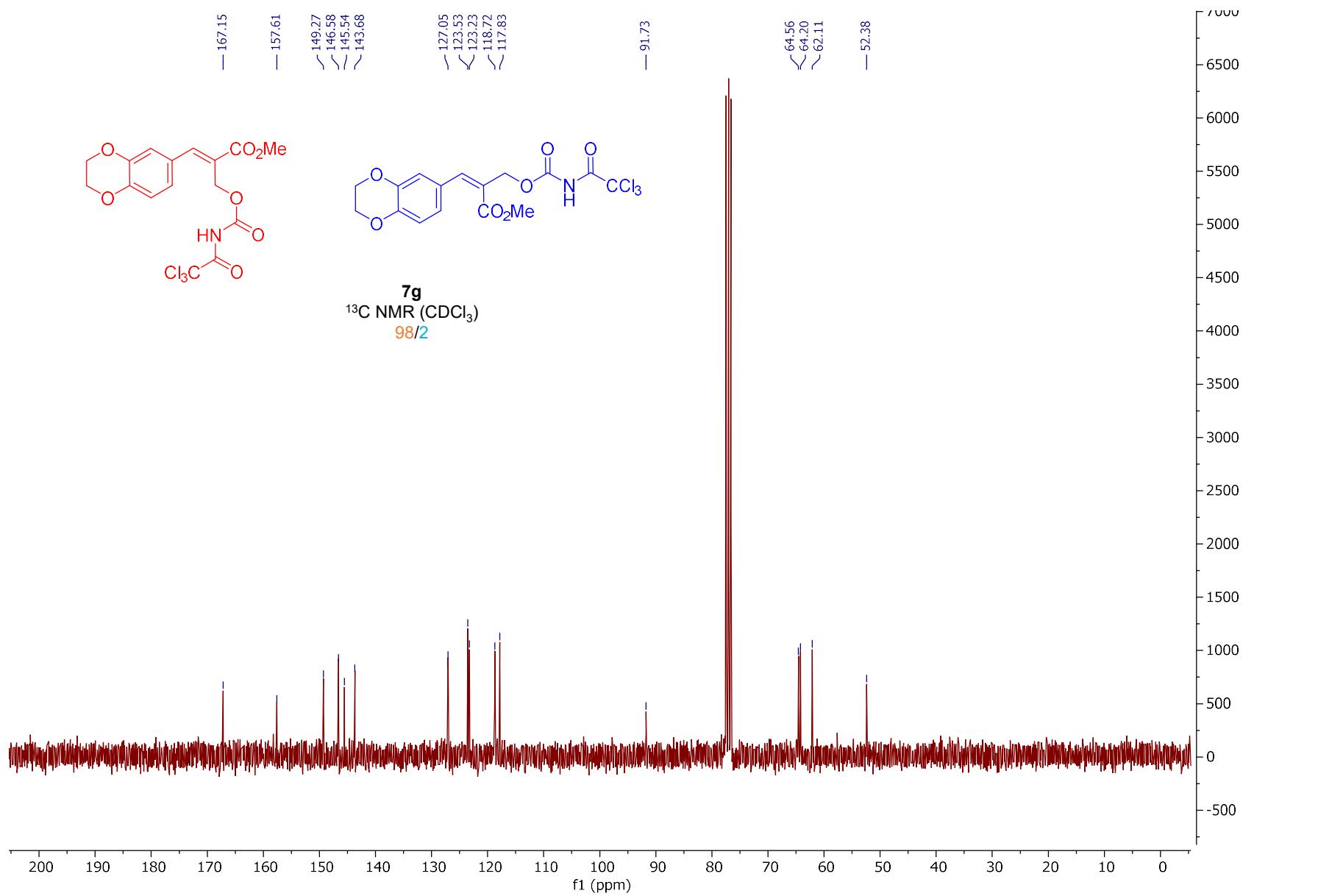
> 3.87

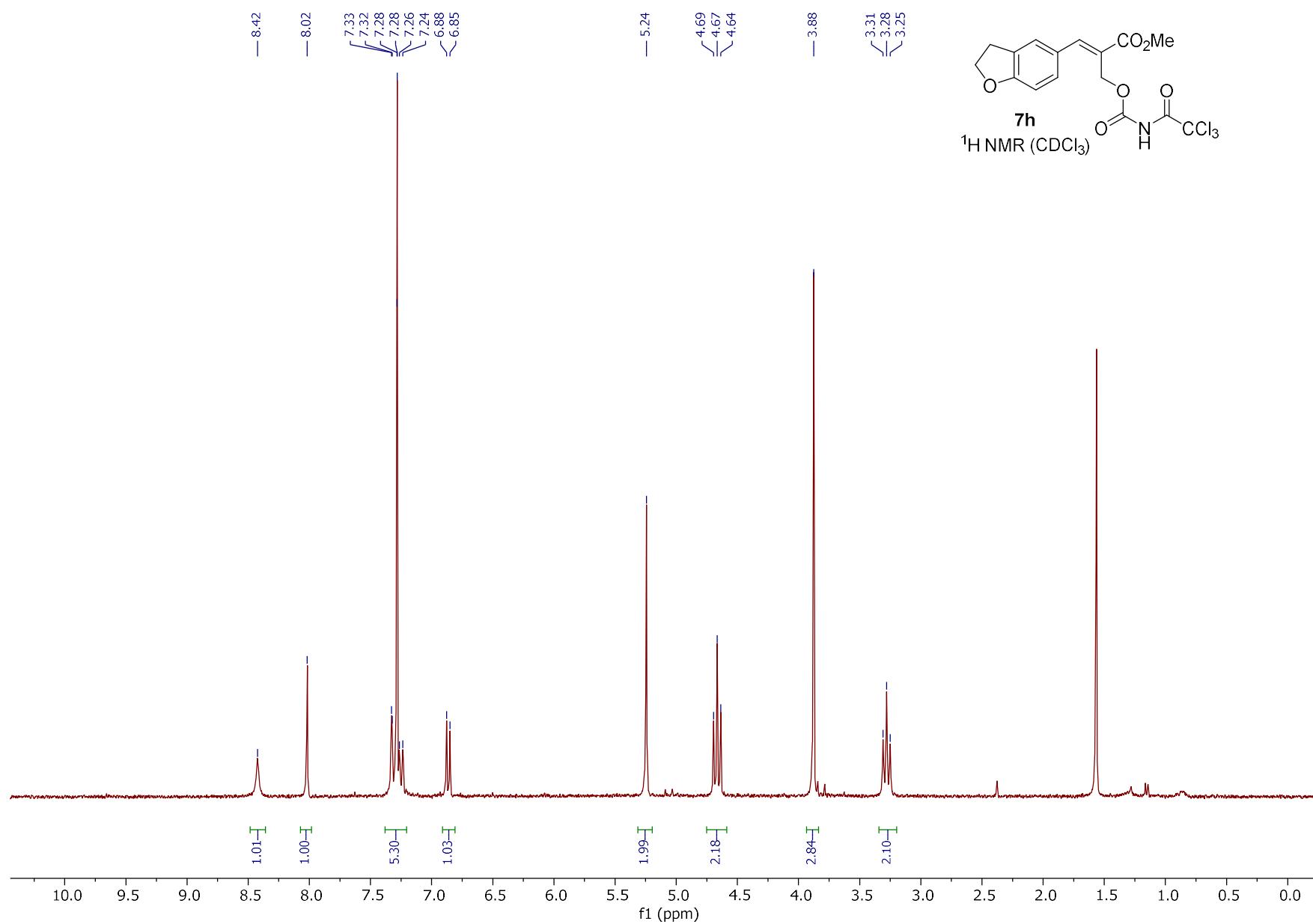
< 3.79

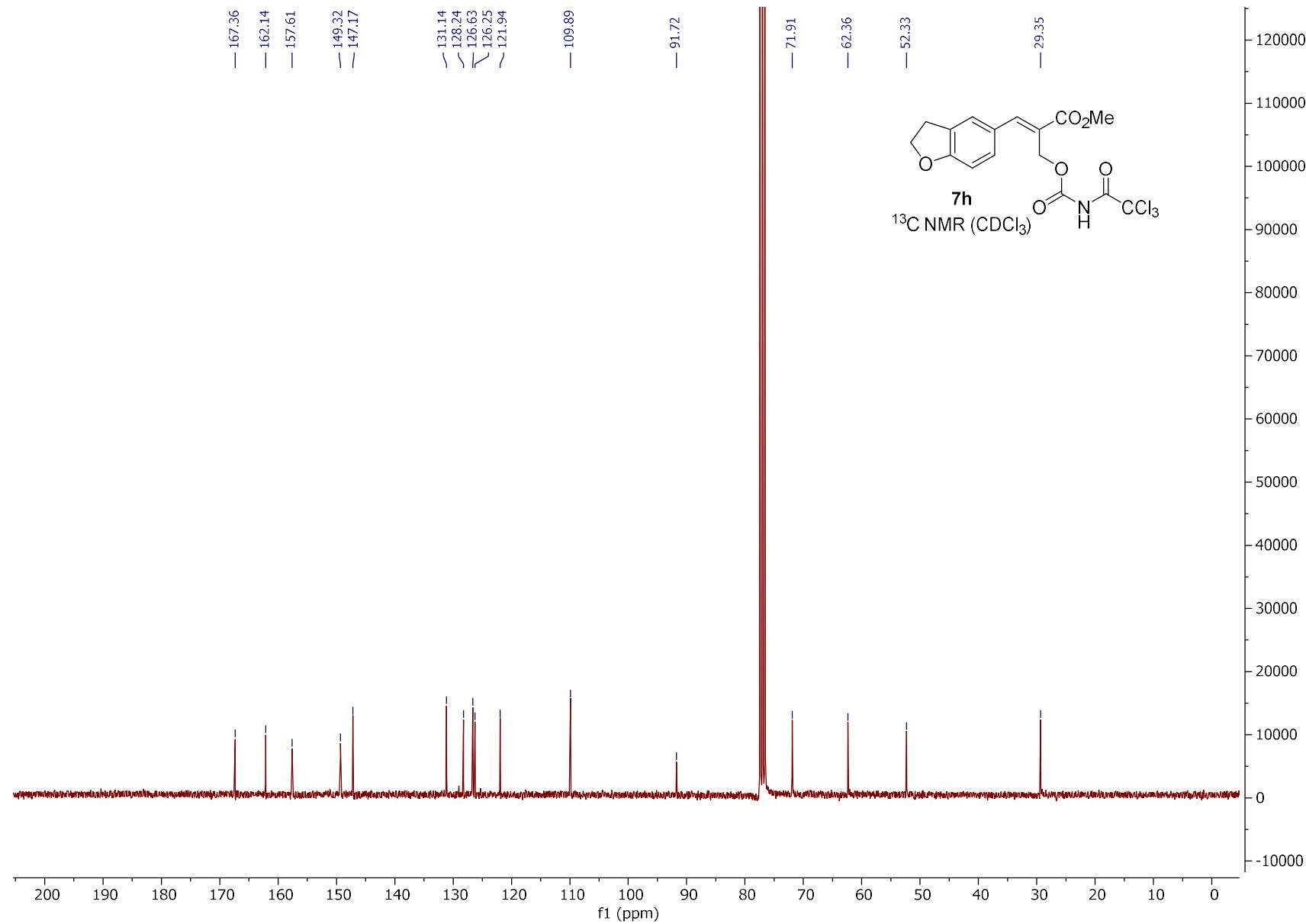


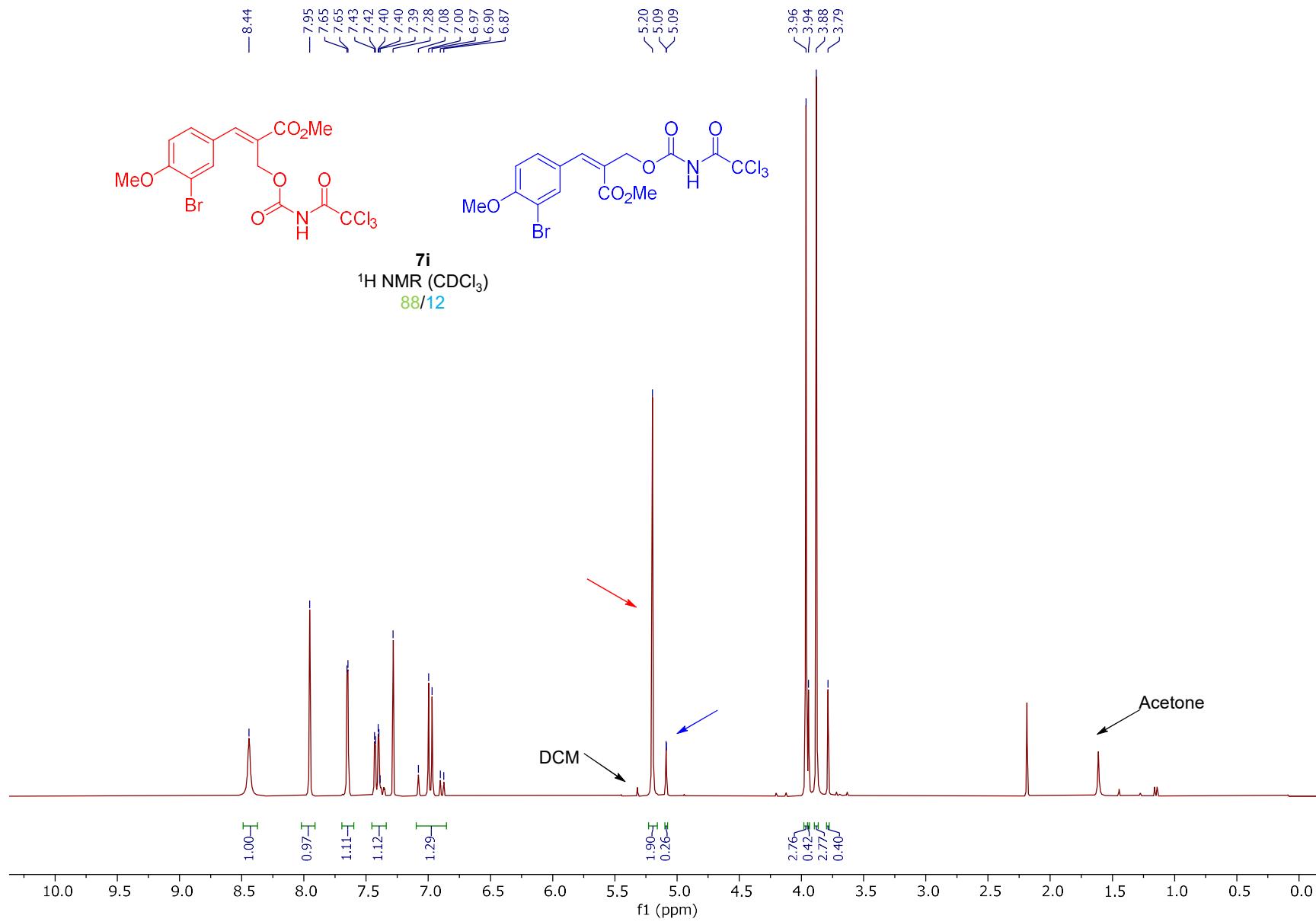
7g
 ^1H NMR (CDCl_3)
98/2

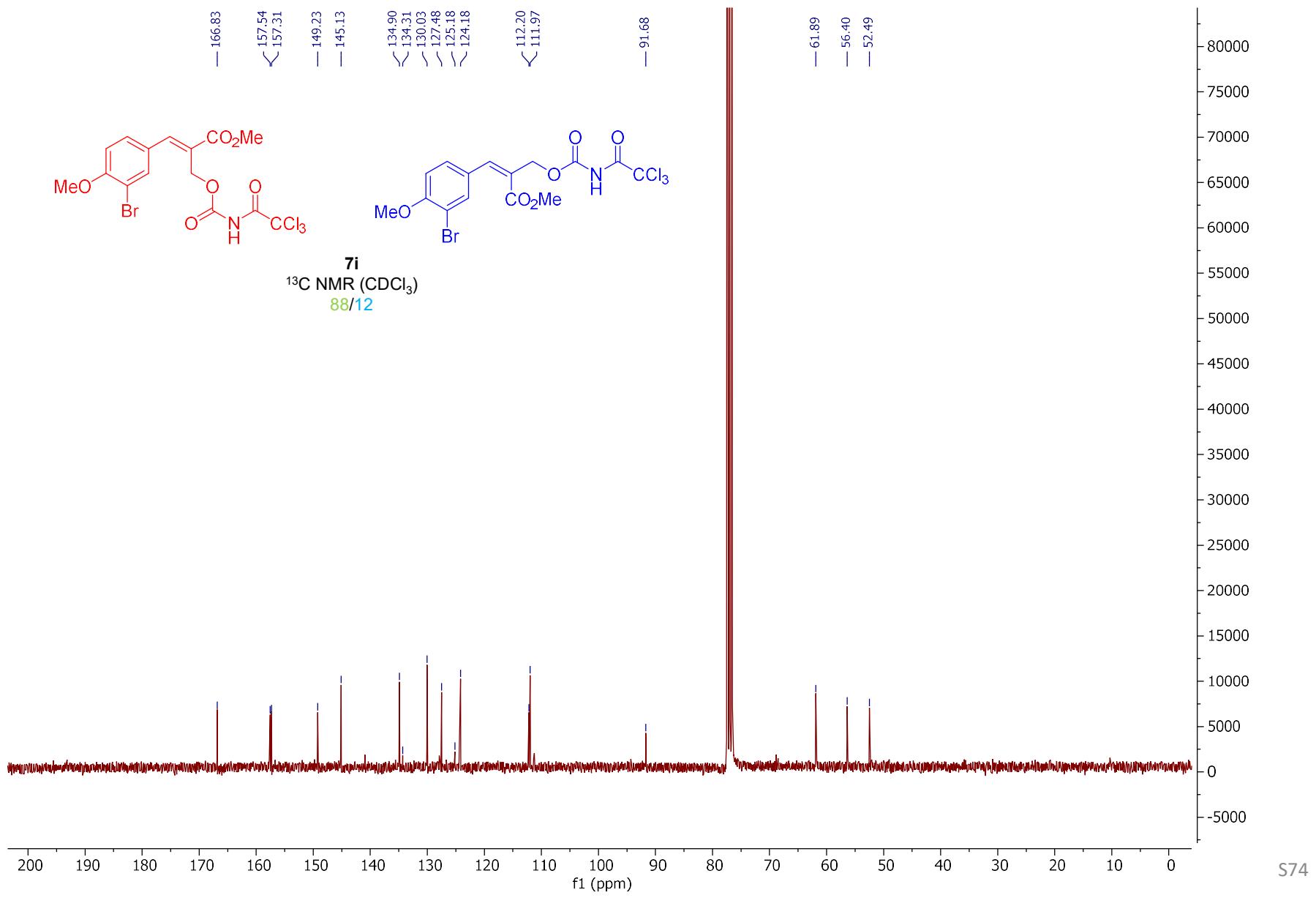


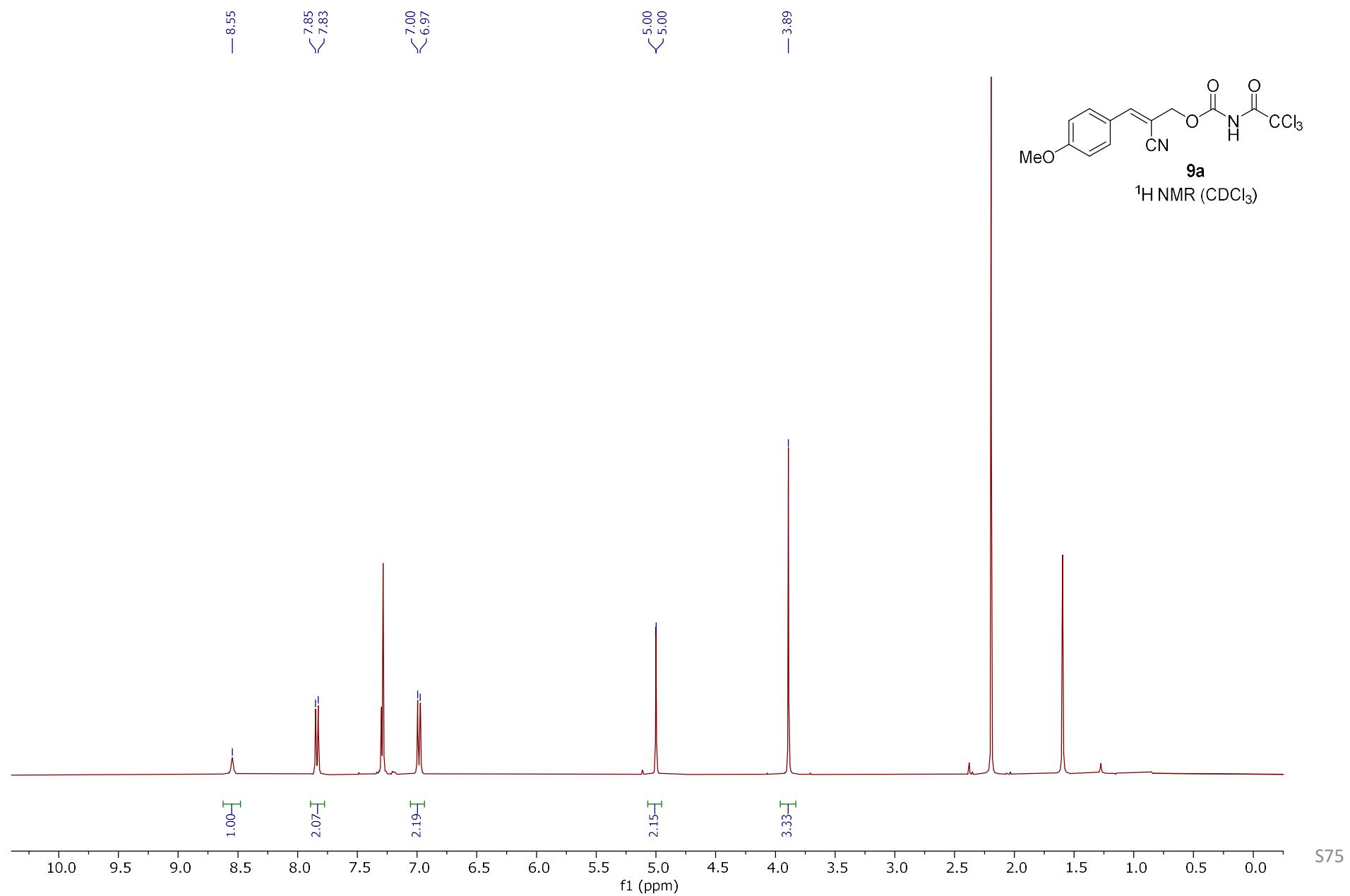


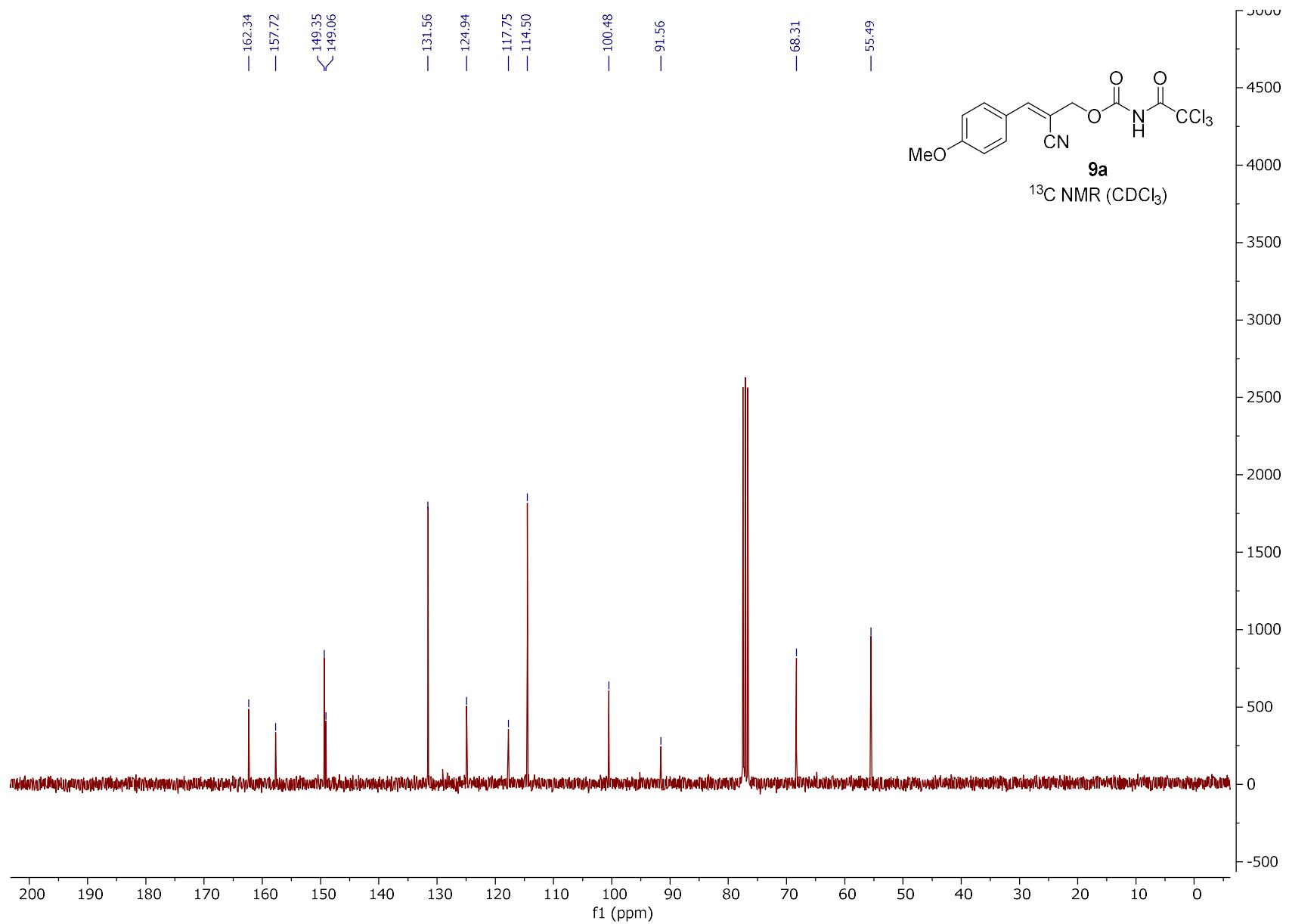


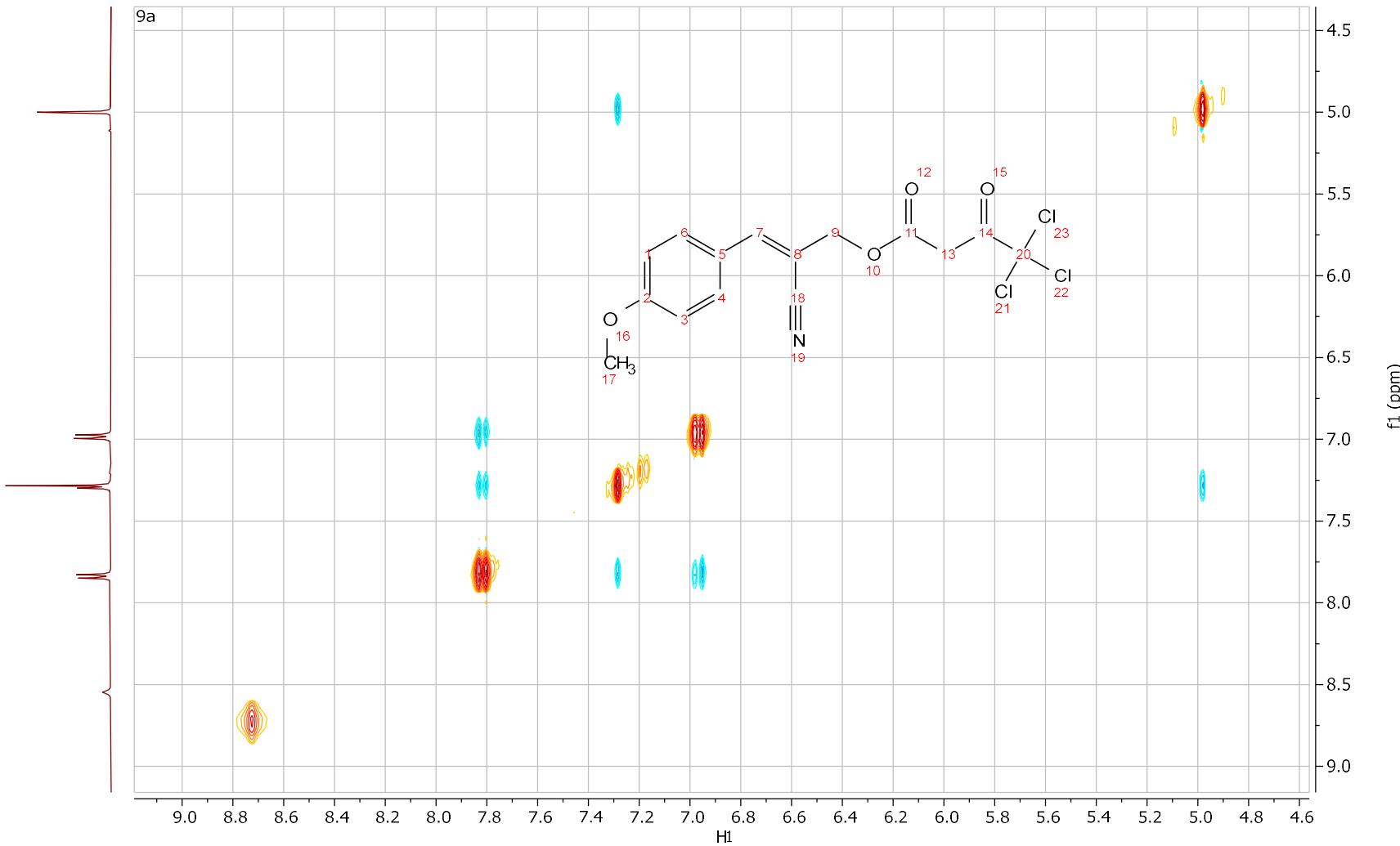
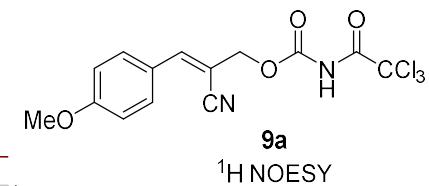


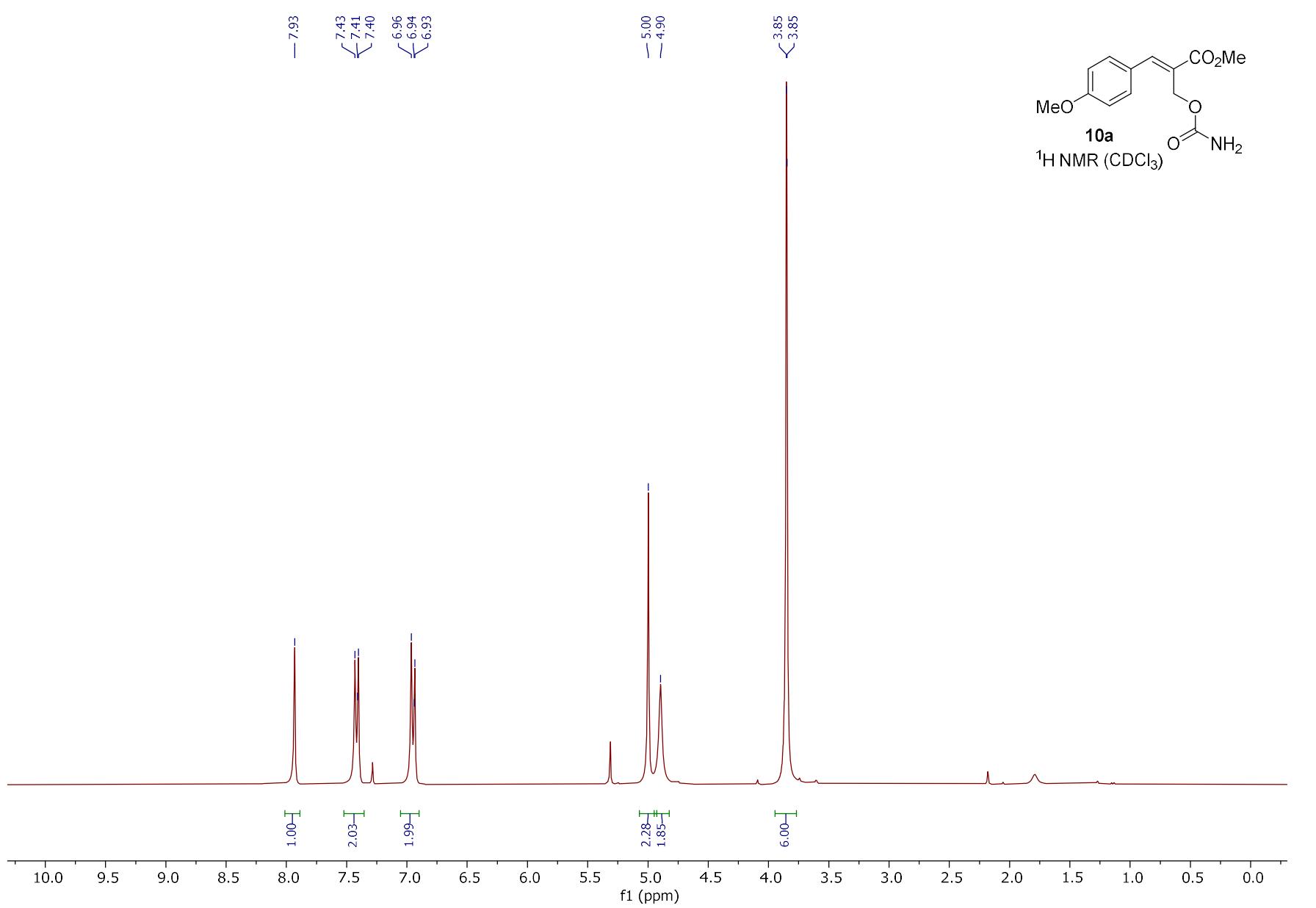


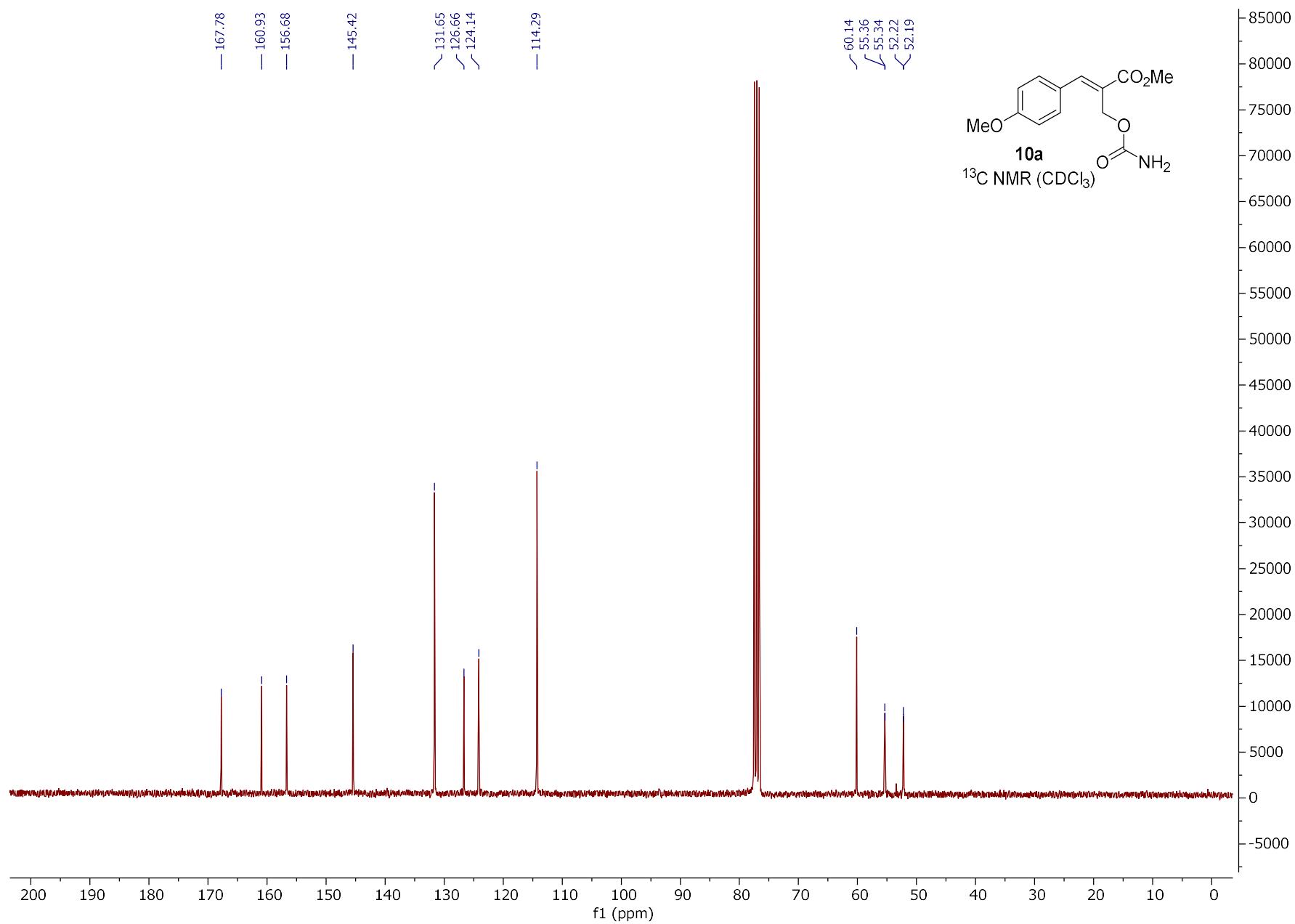


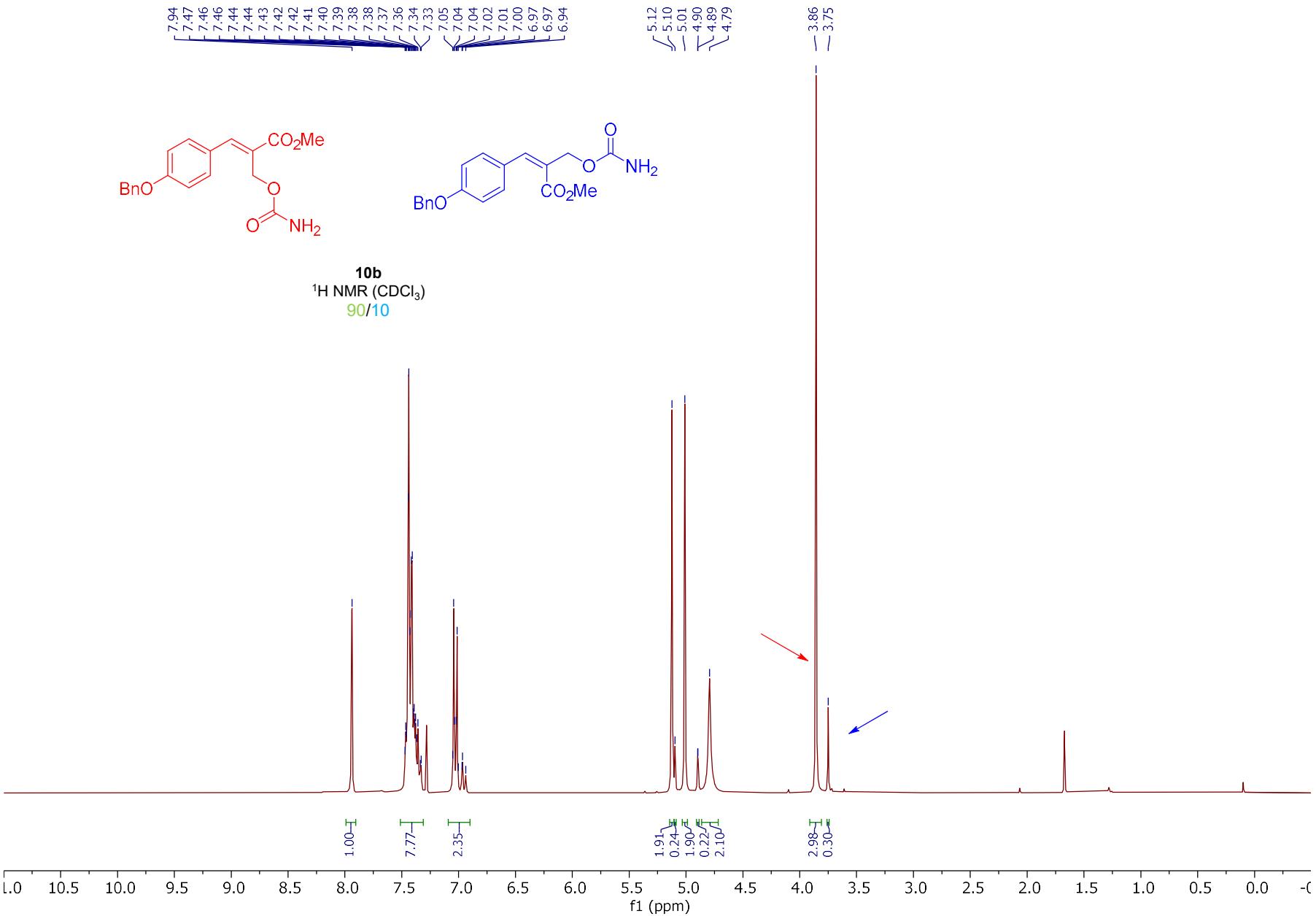


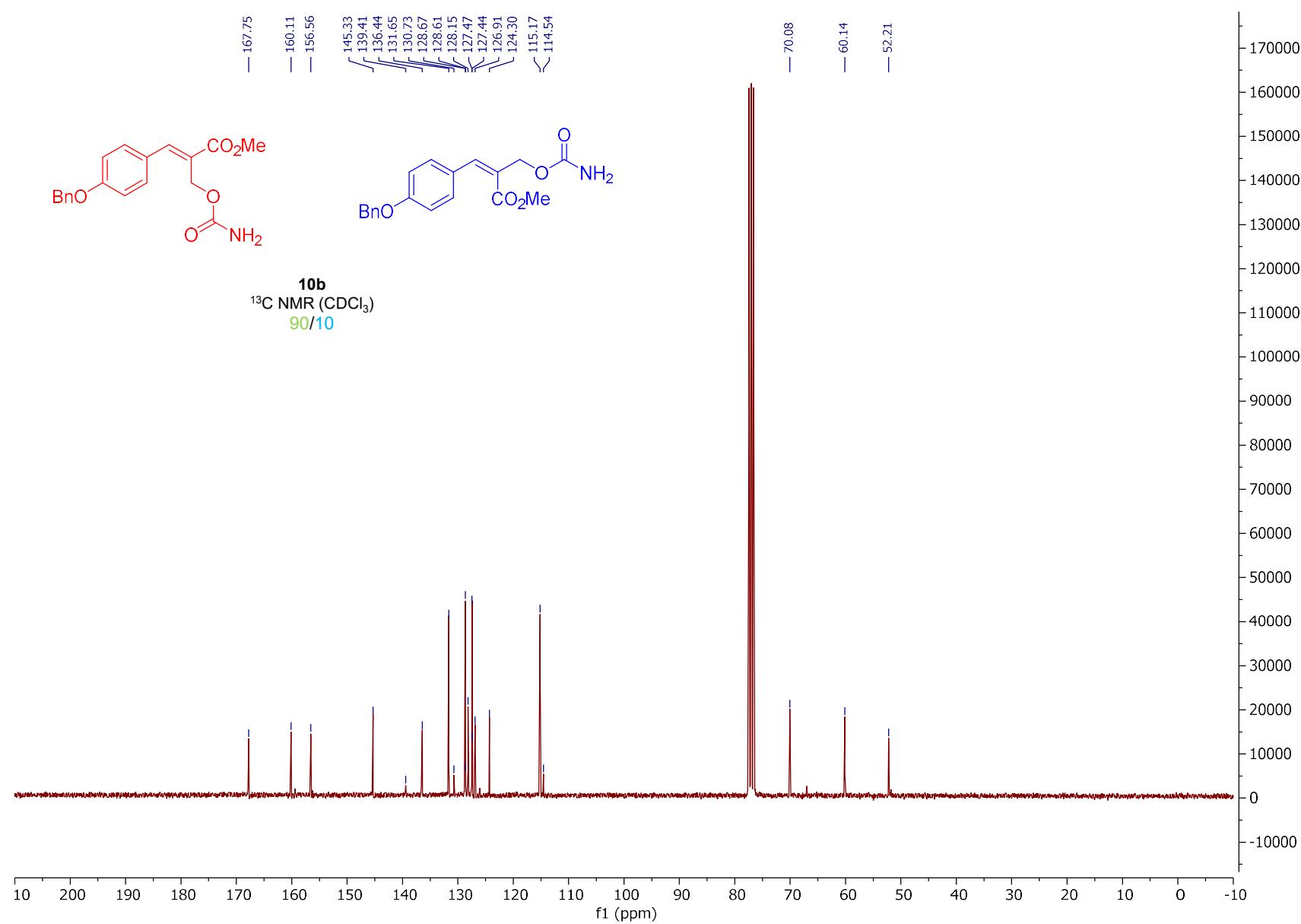


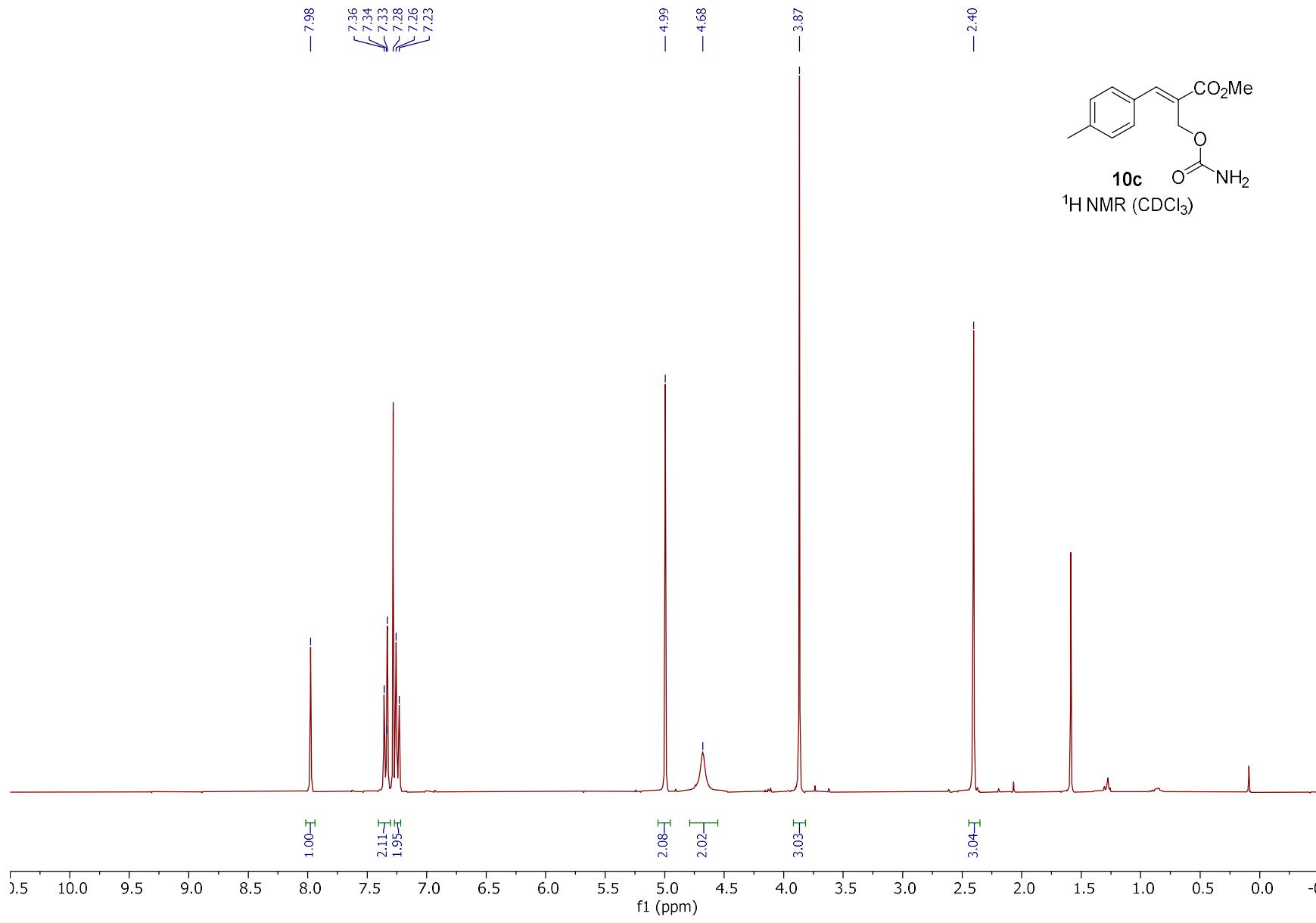


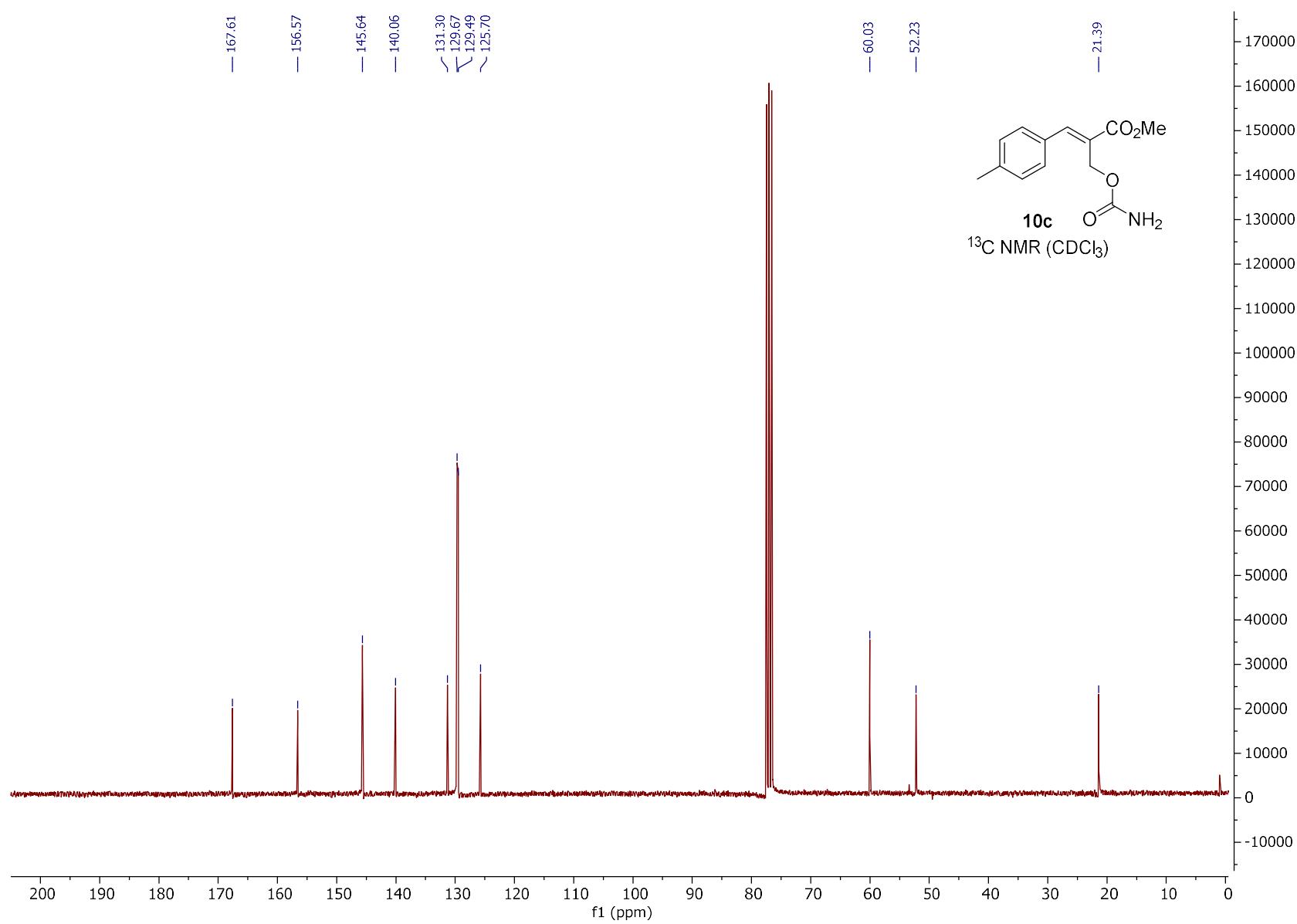


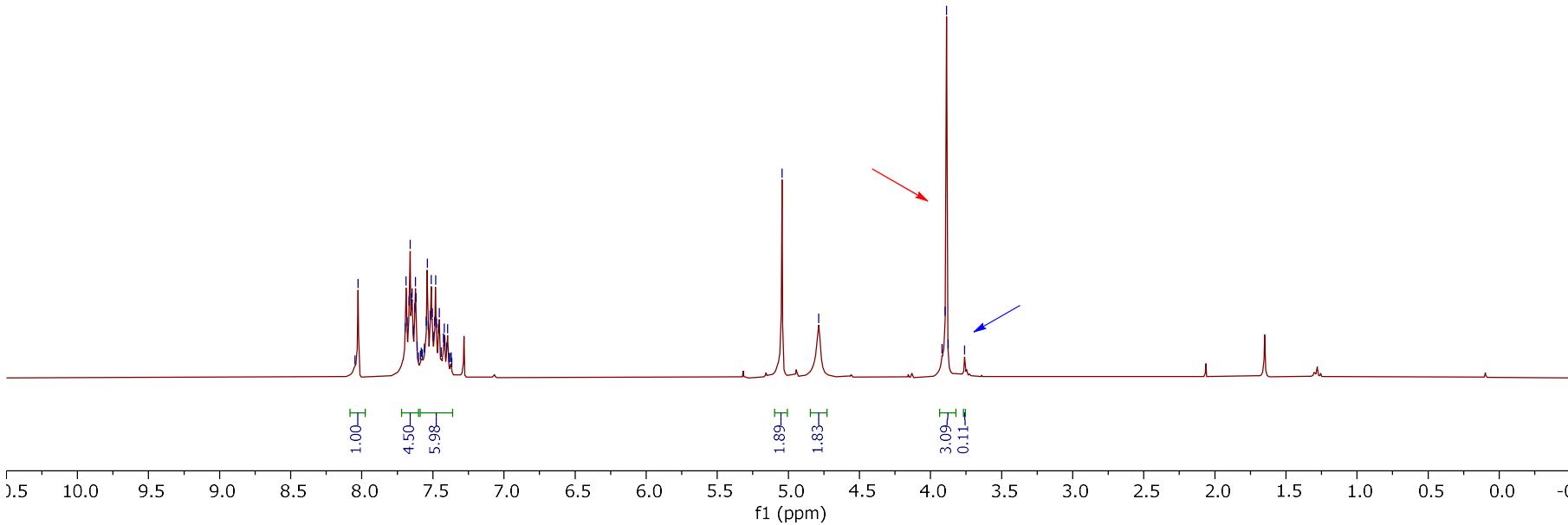
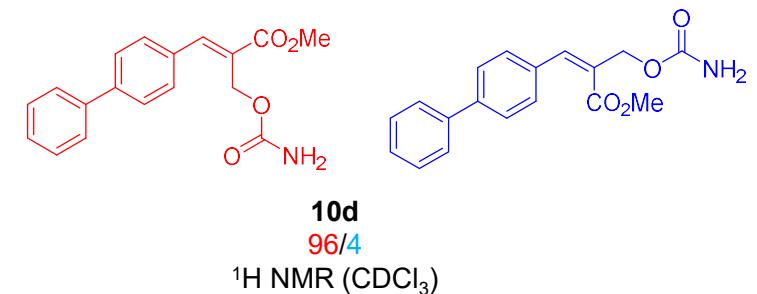


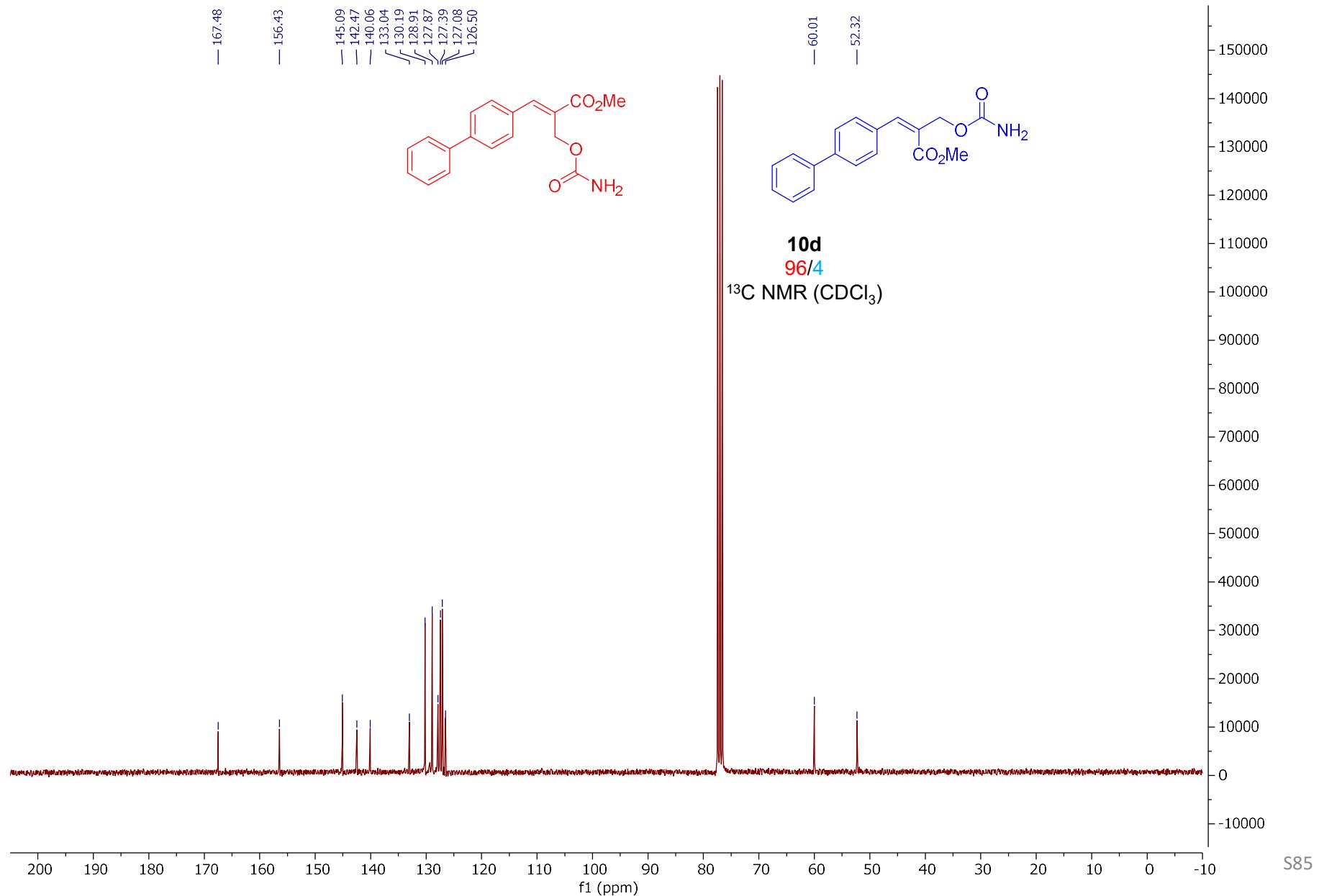


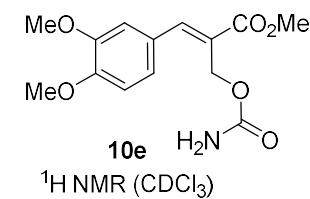
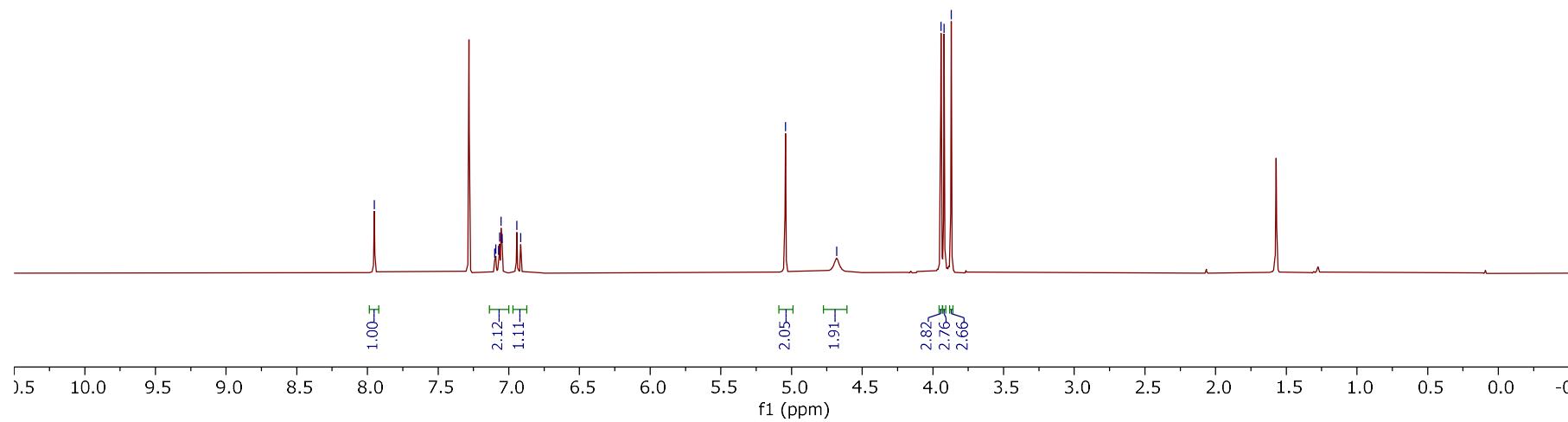


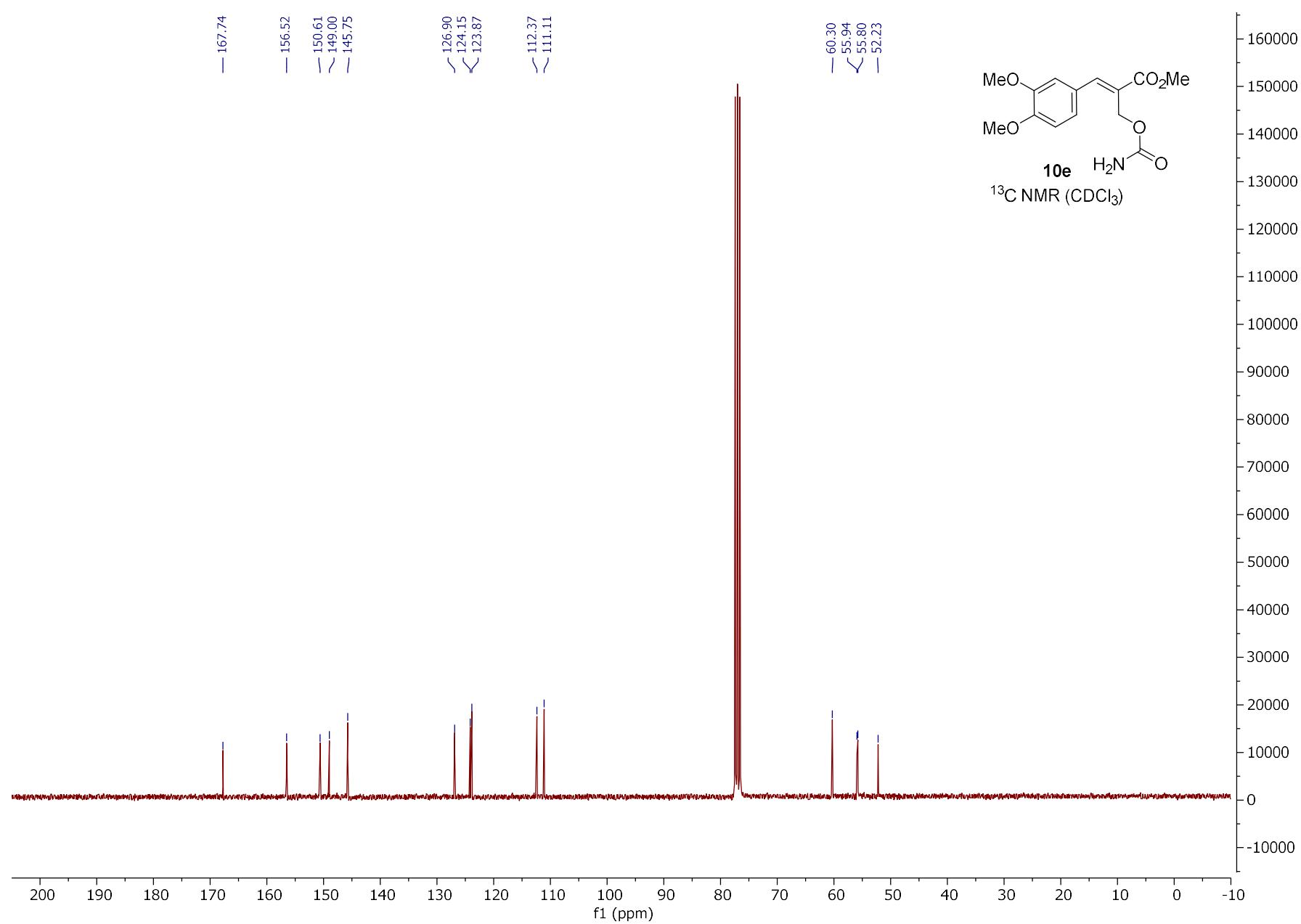


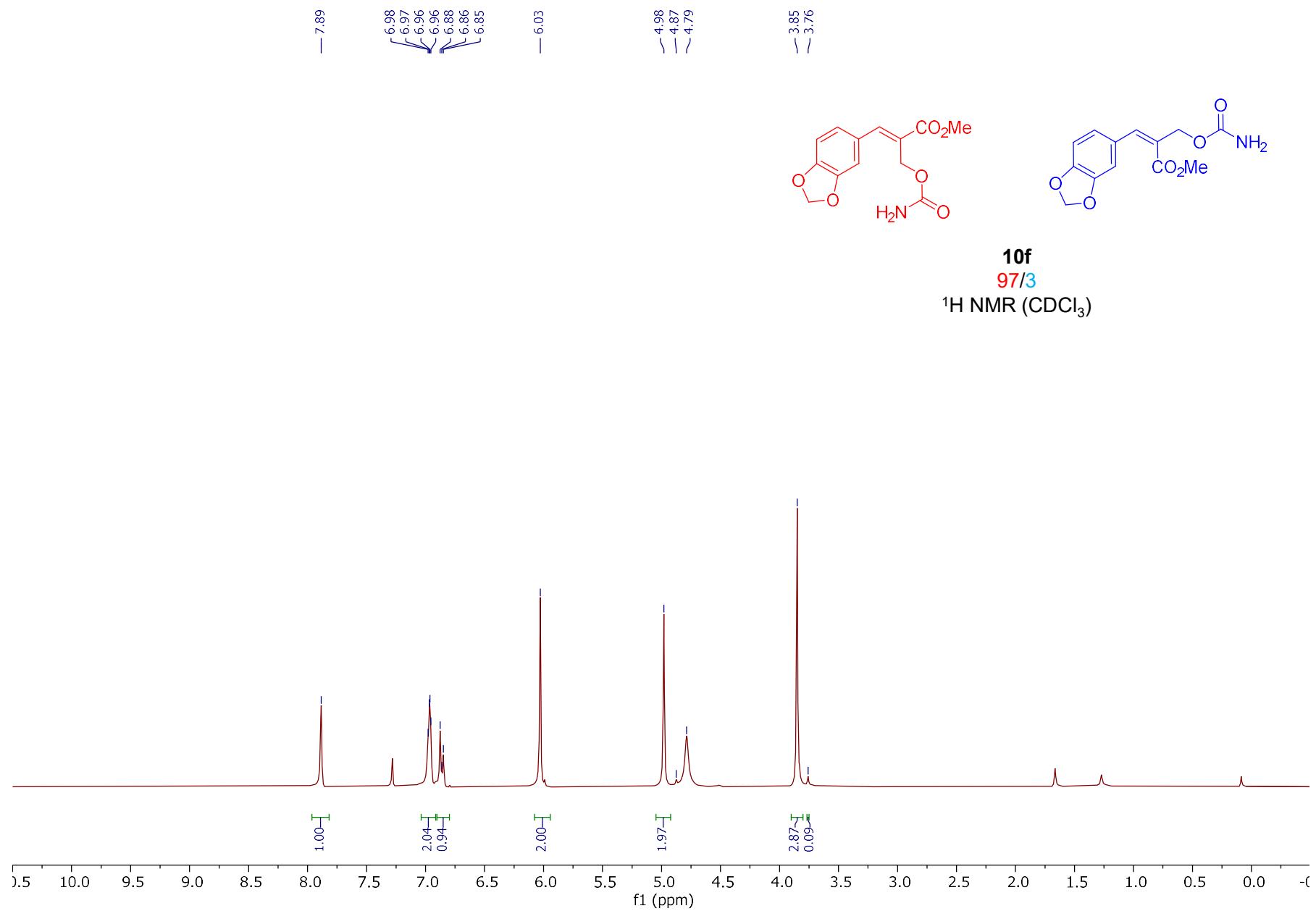


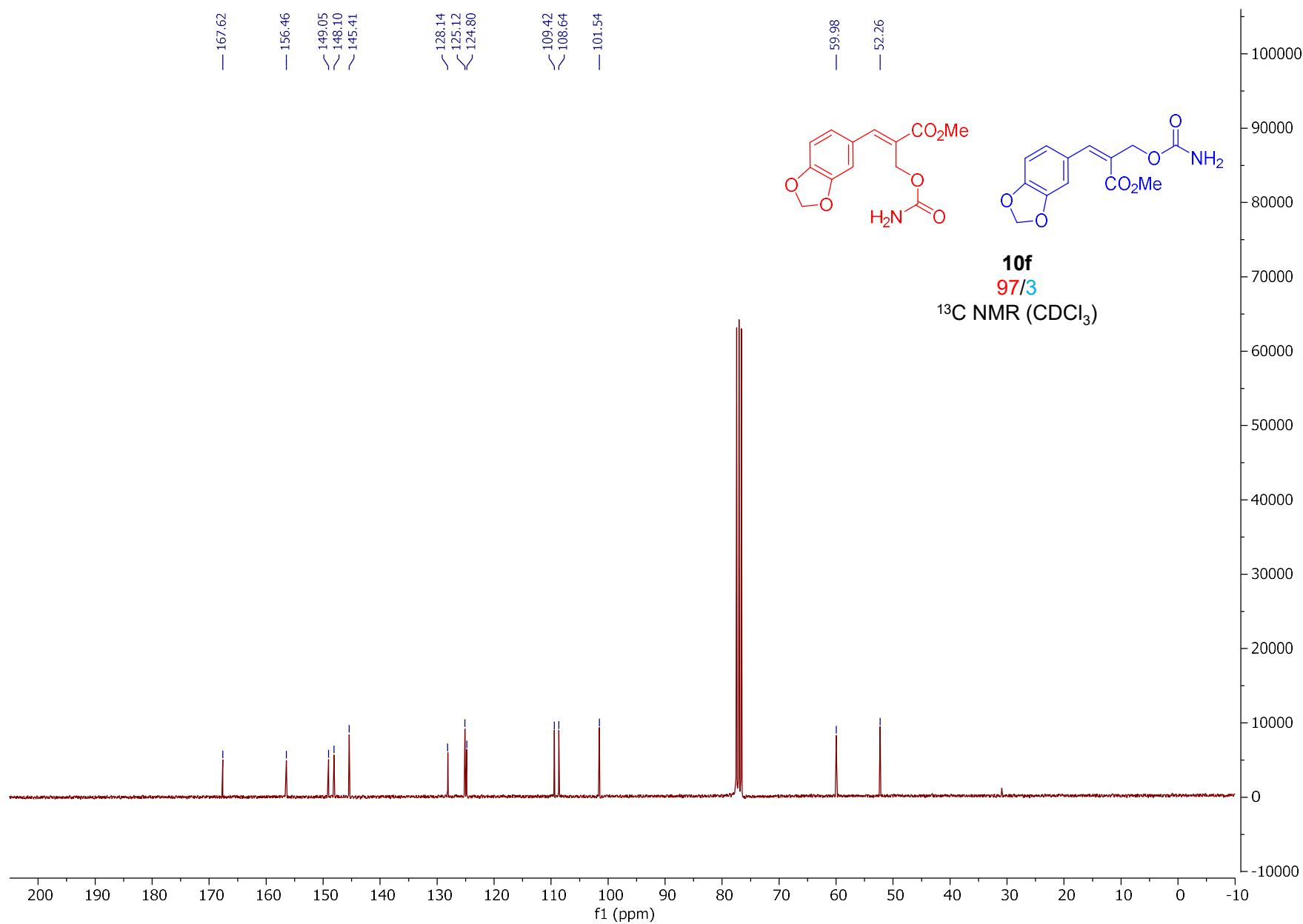


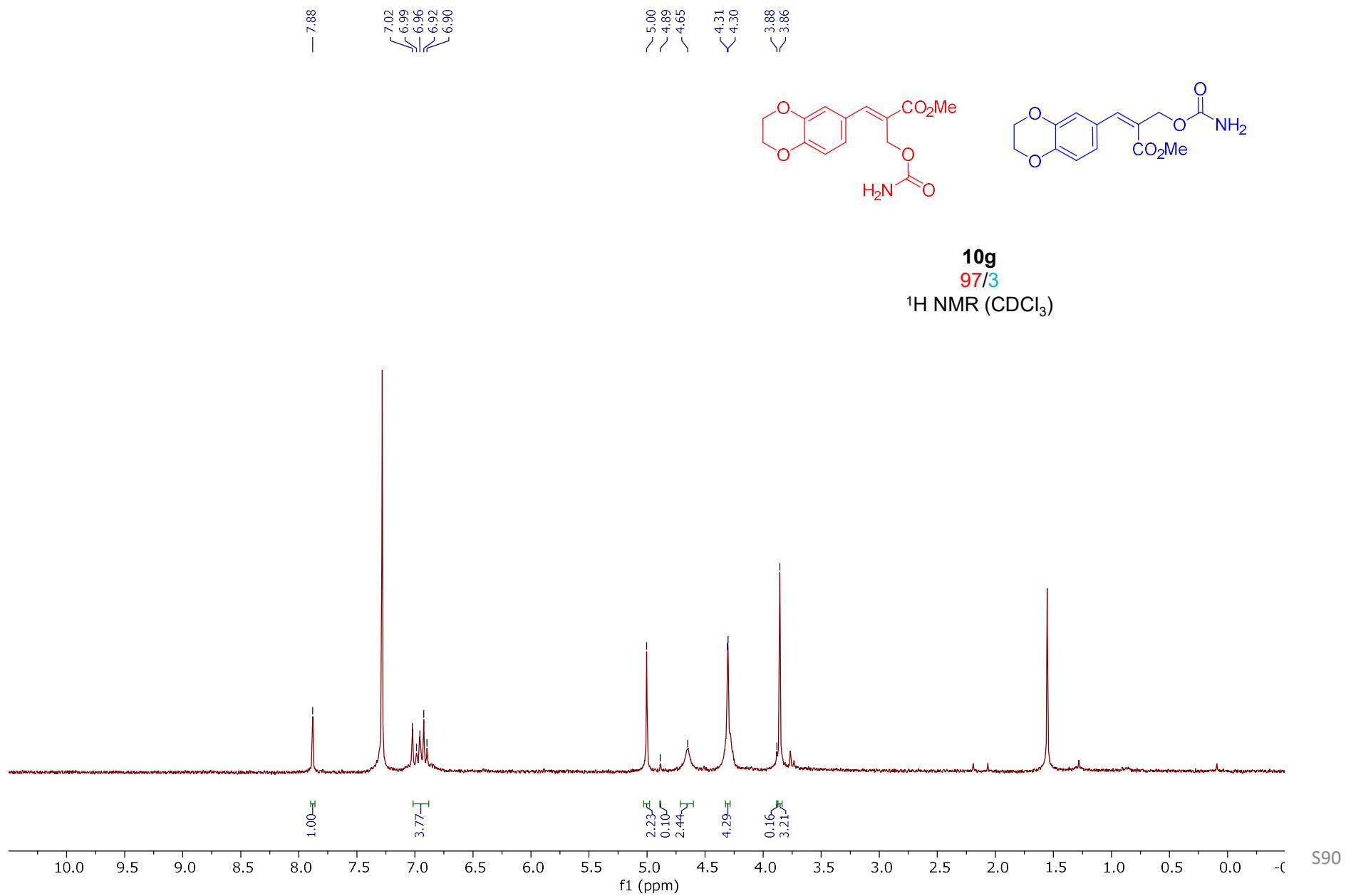


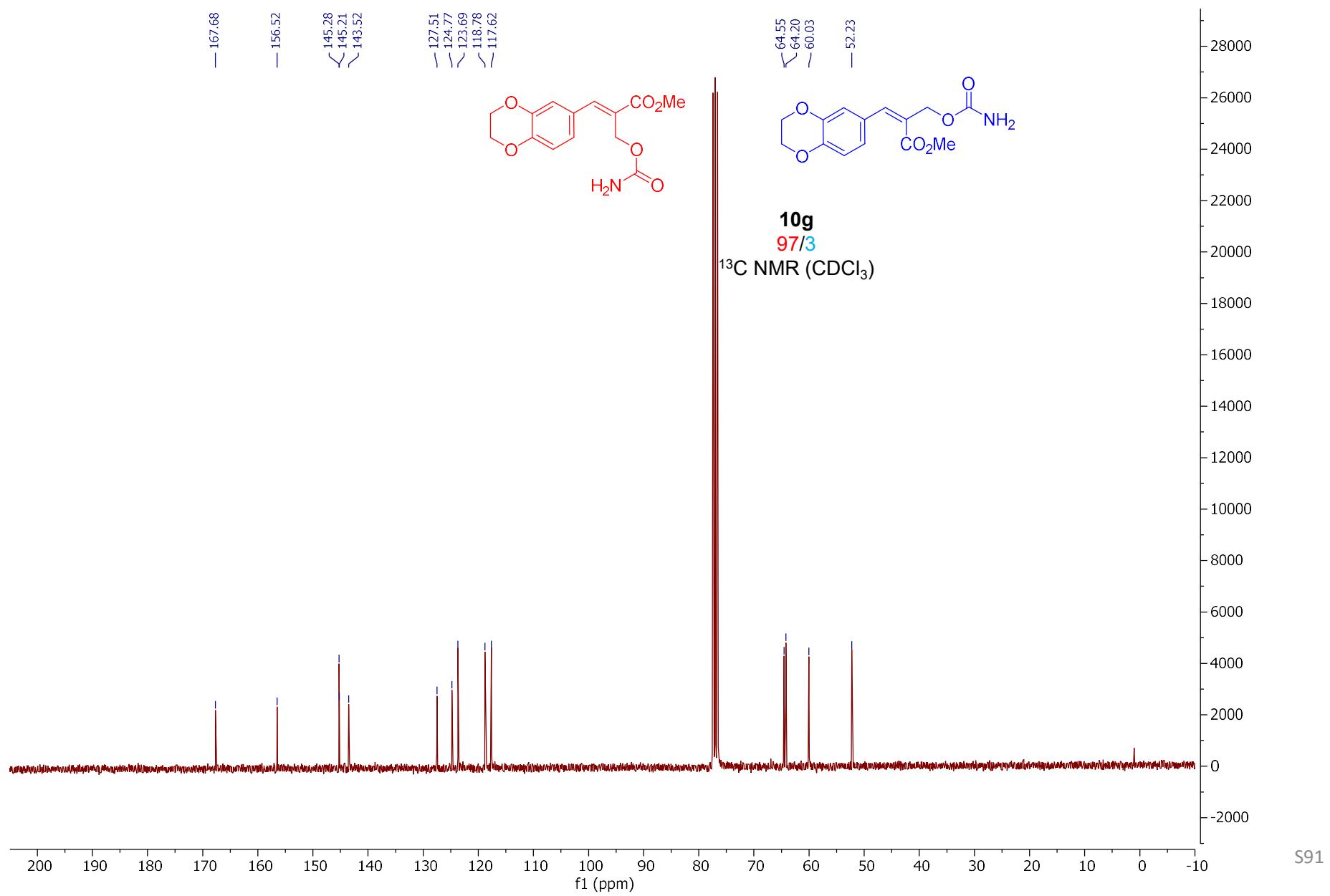


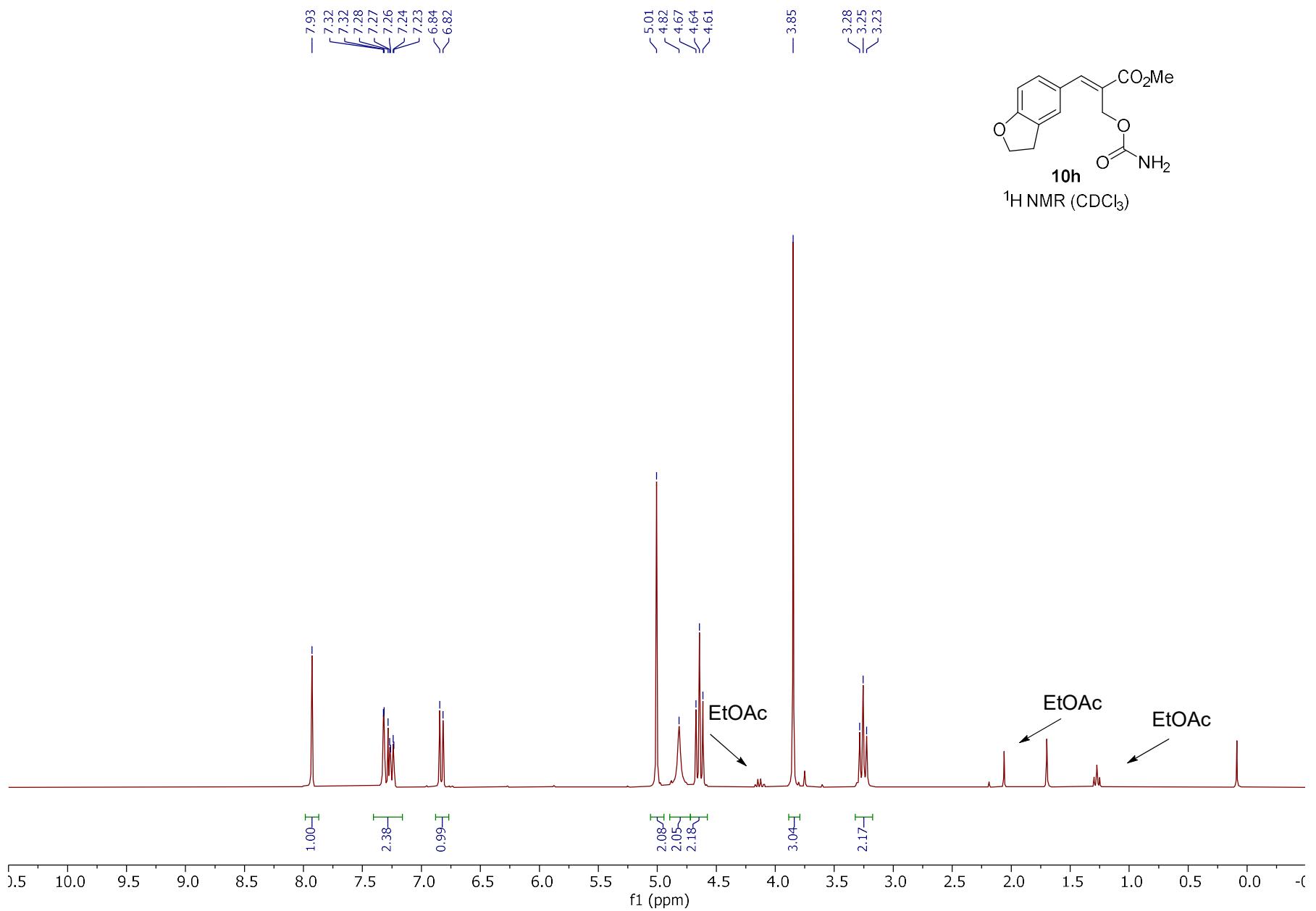


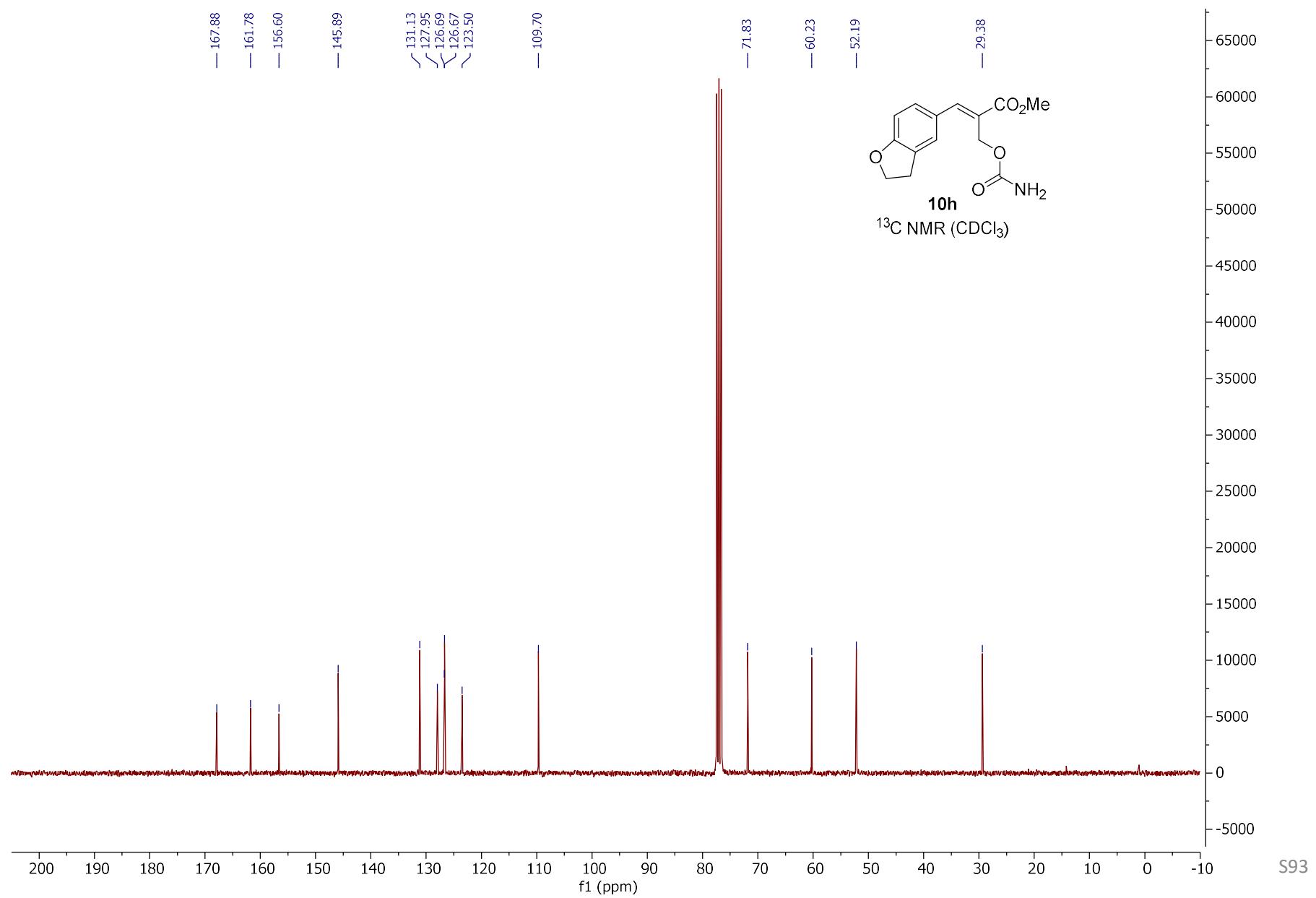


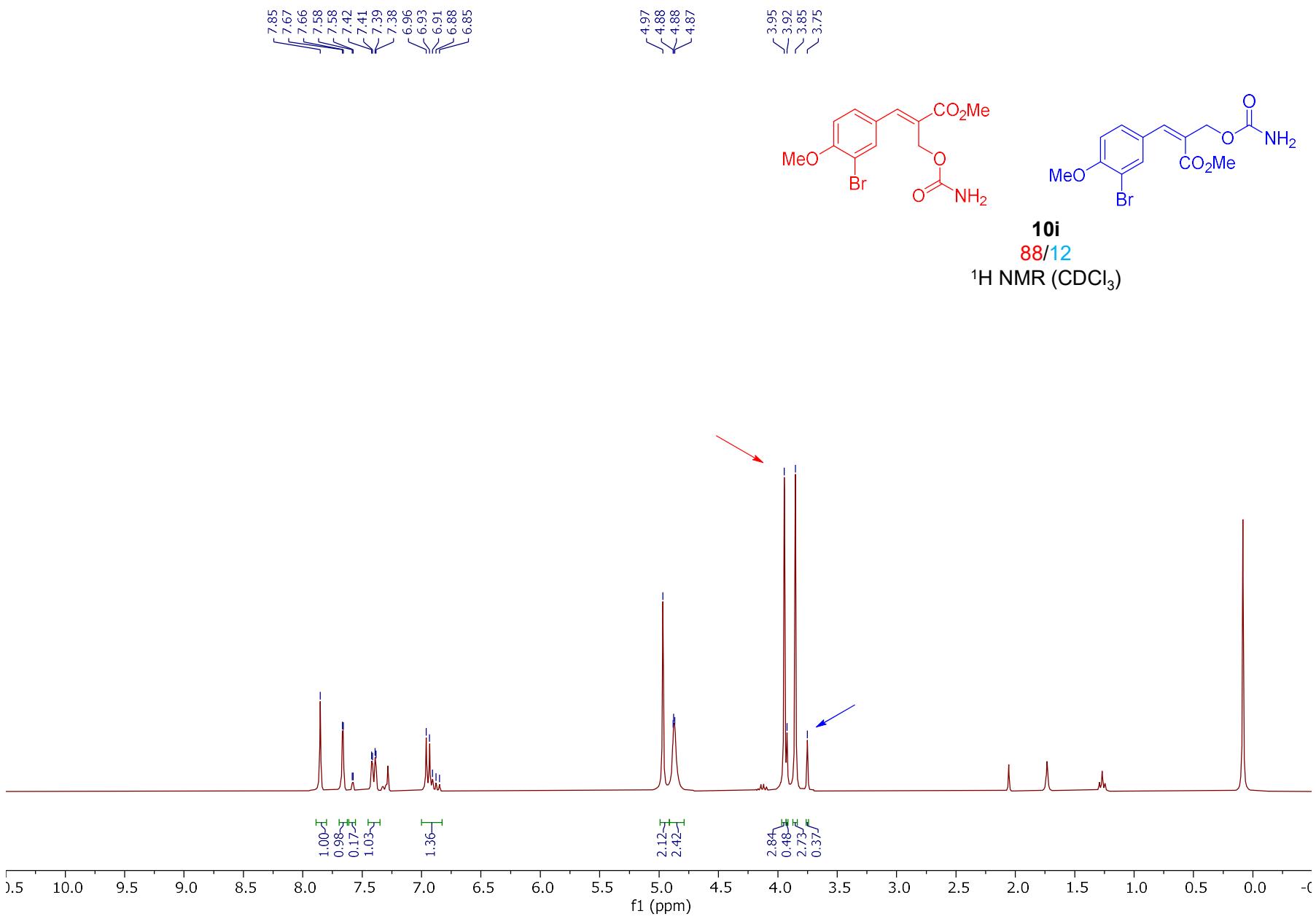


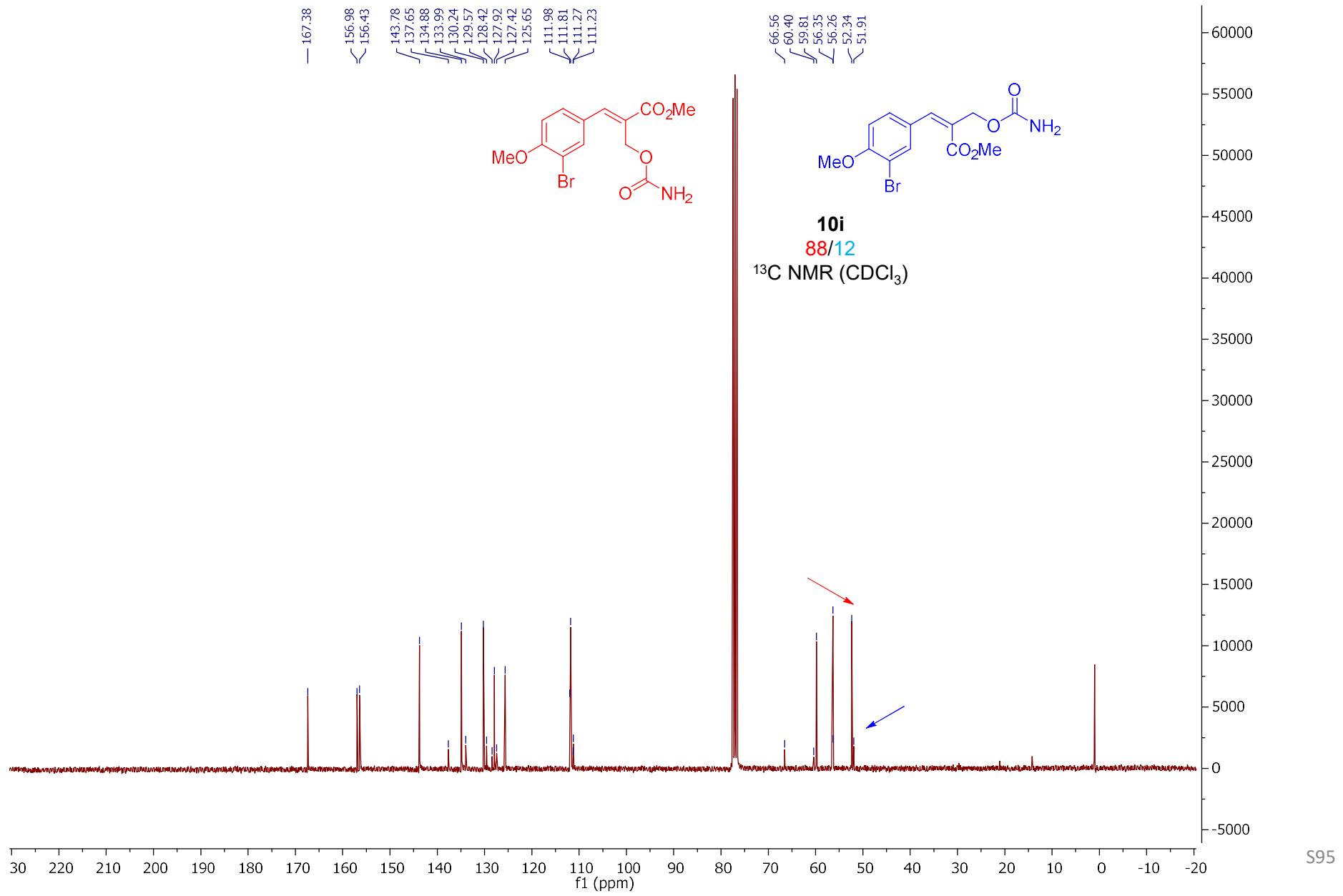


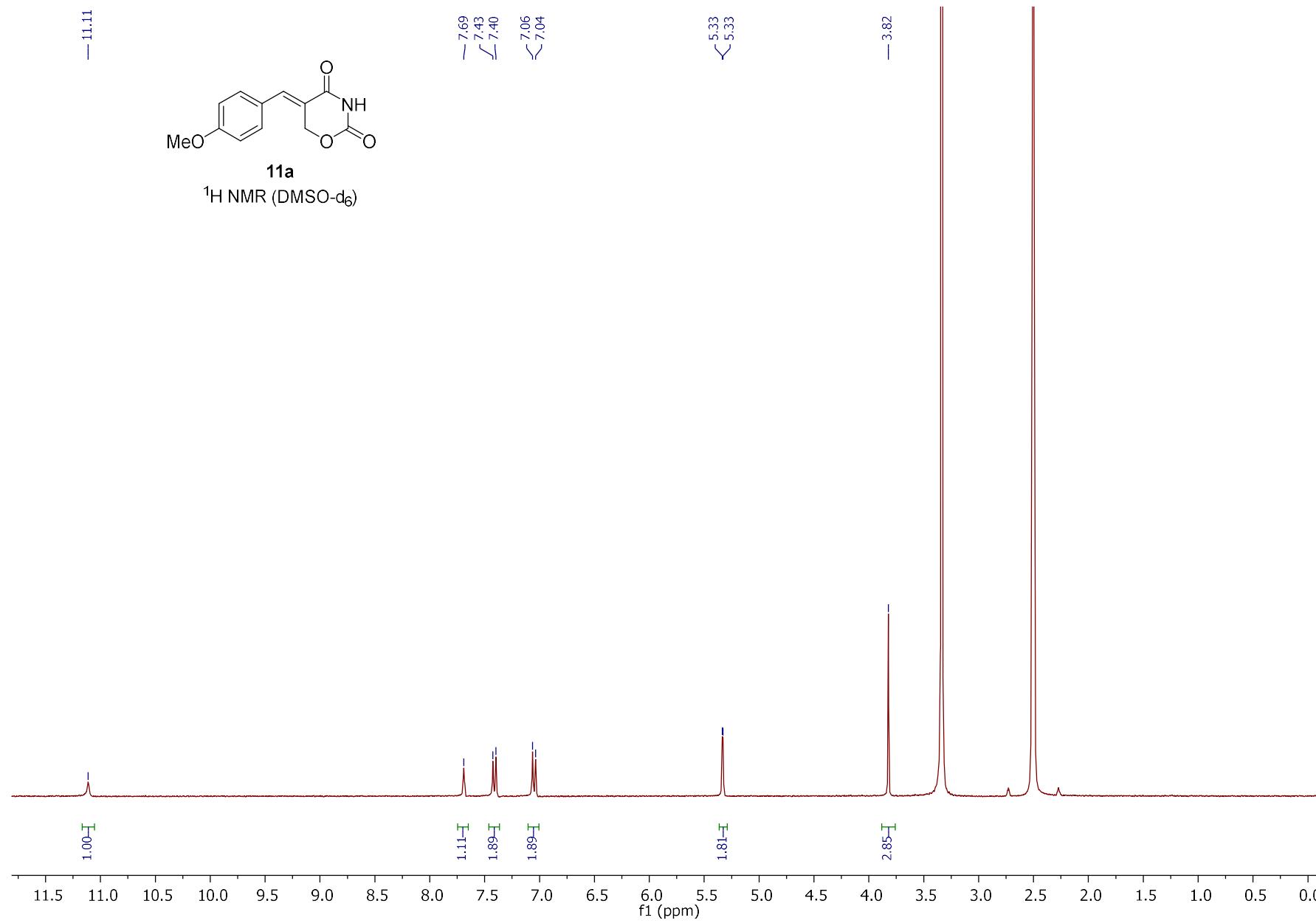


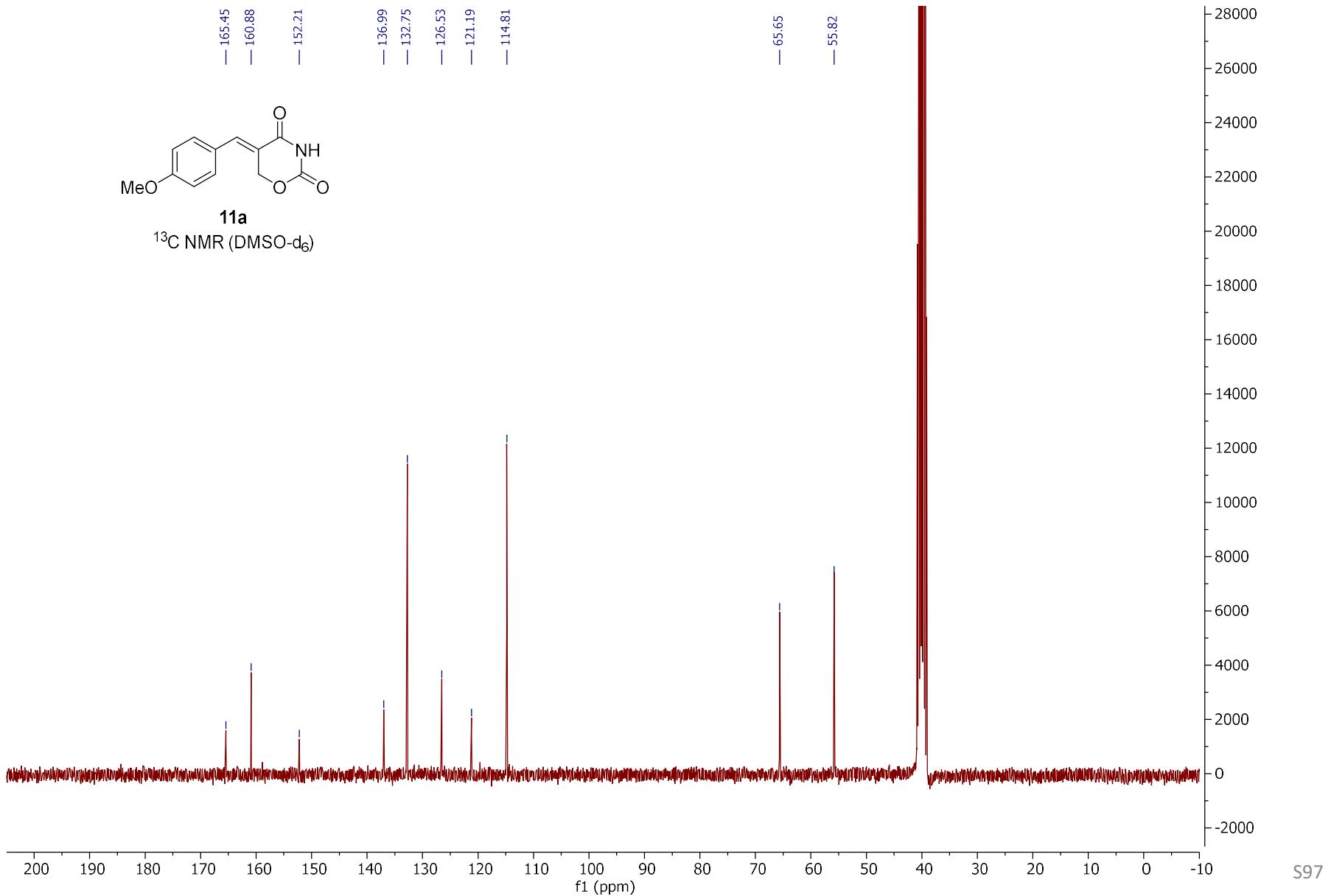


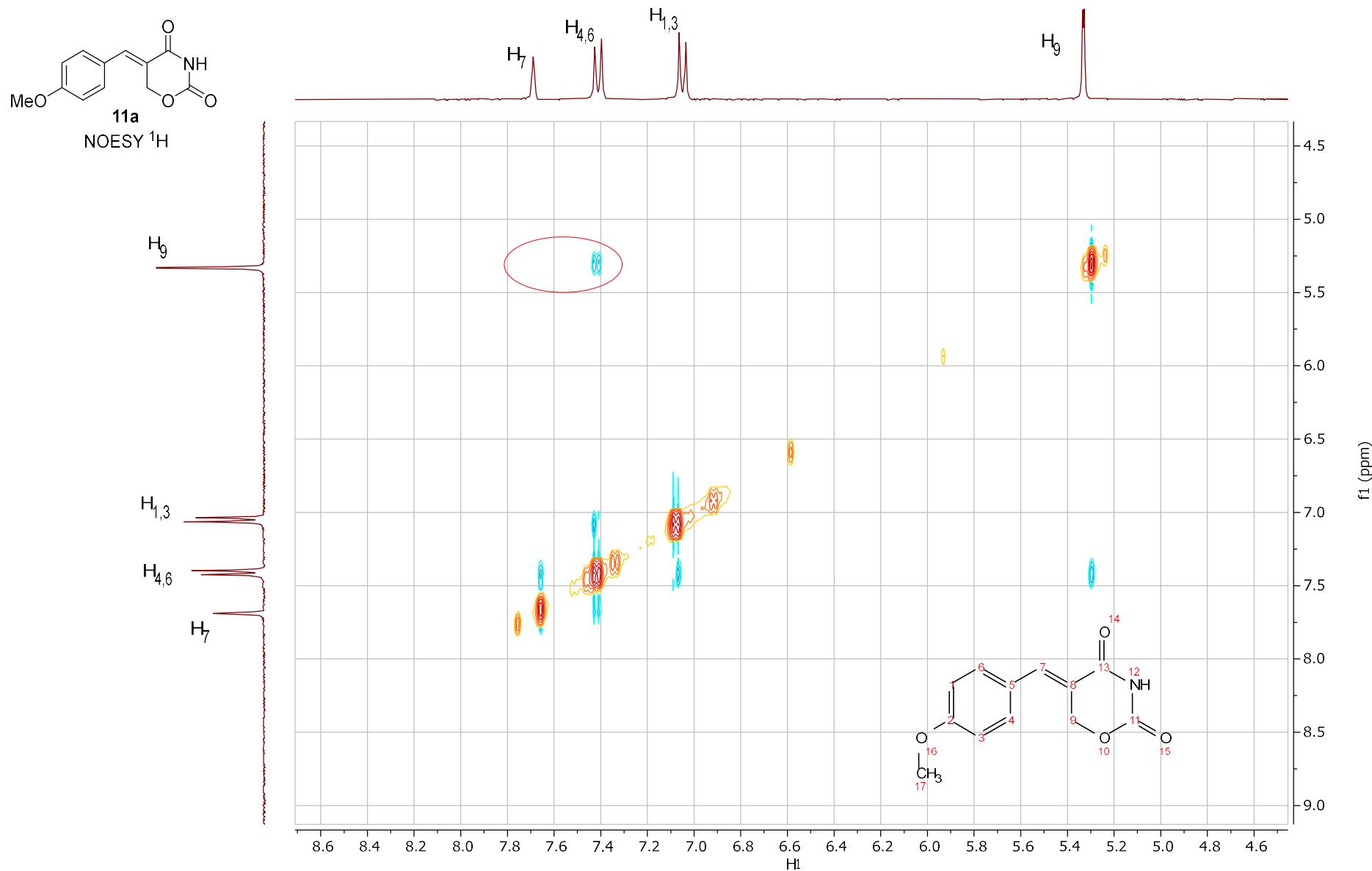


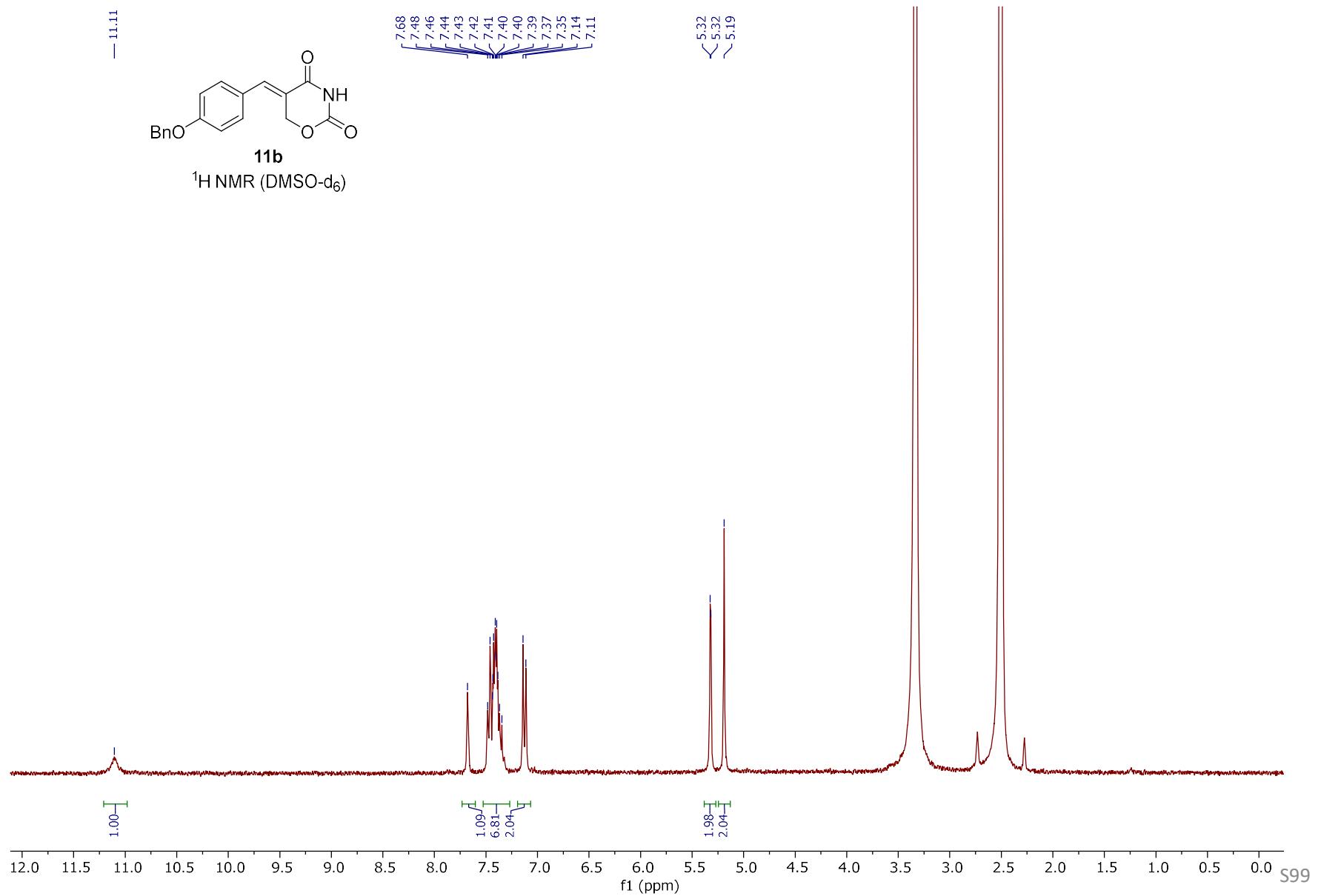


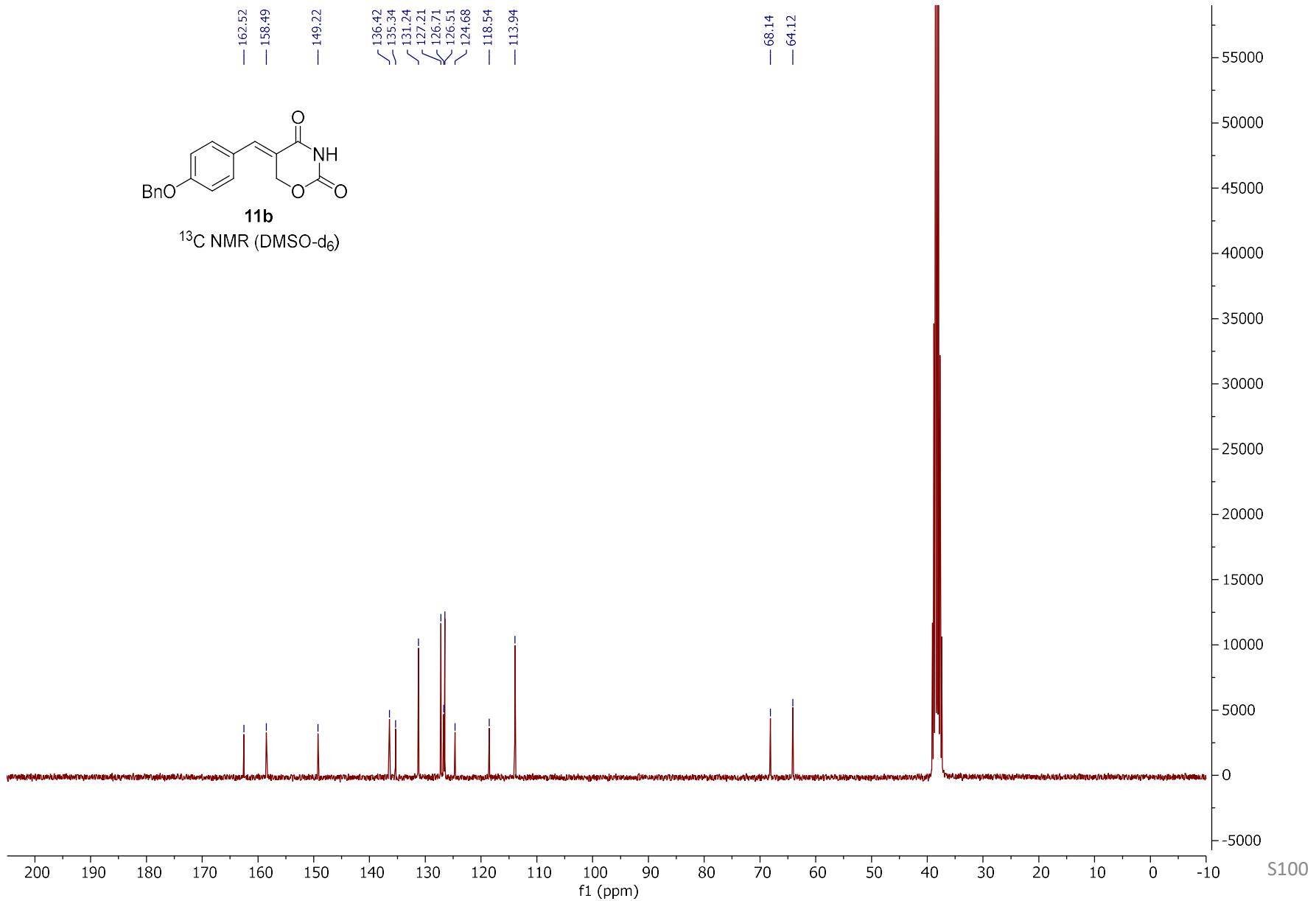
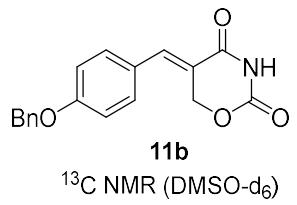


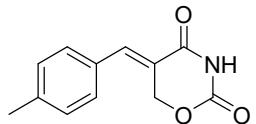




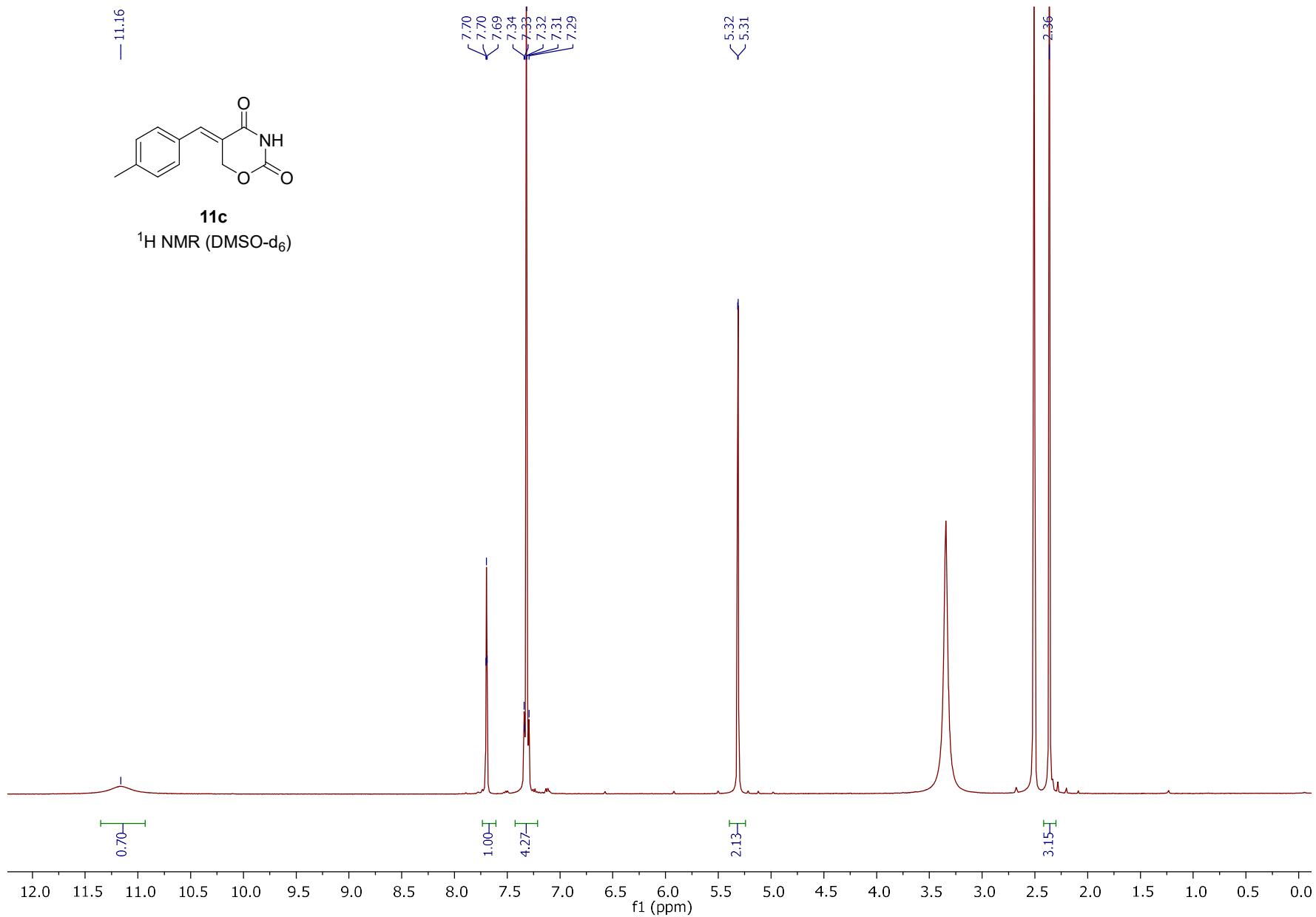


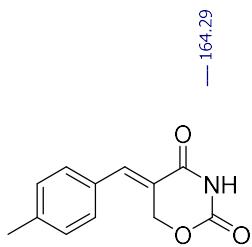




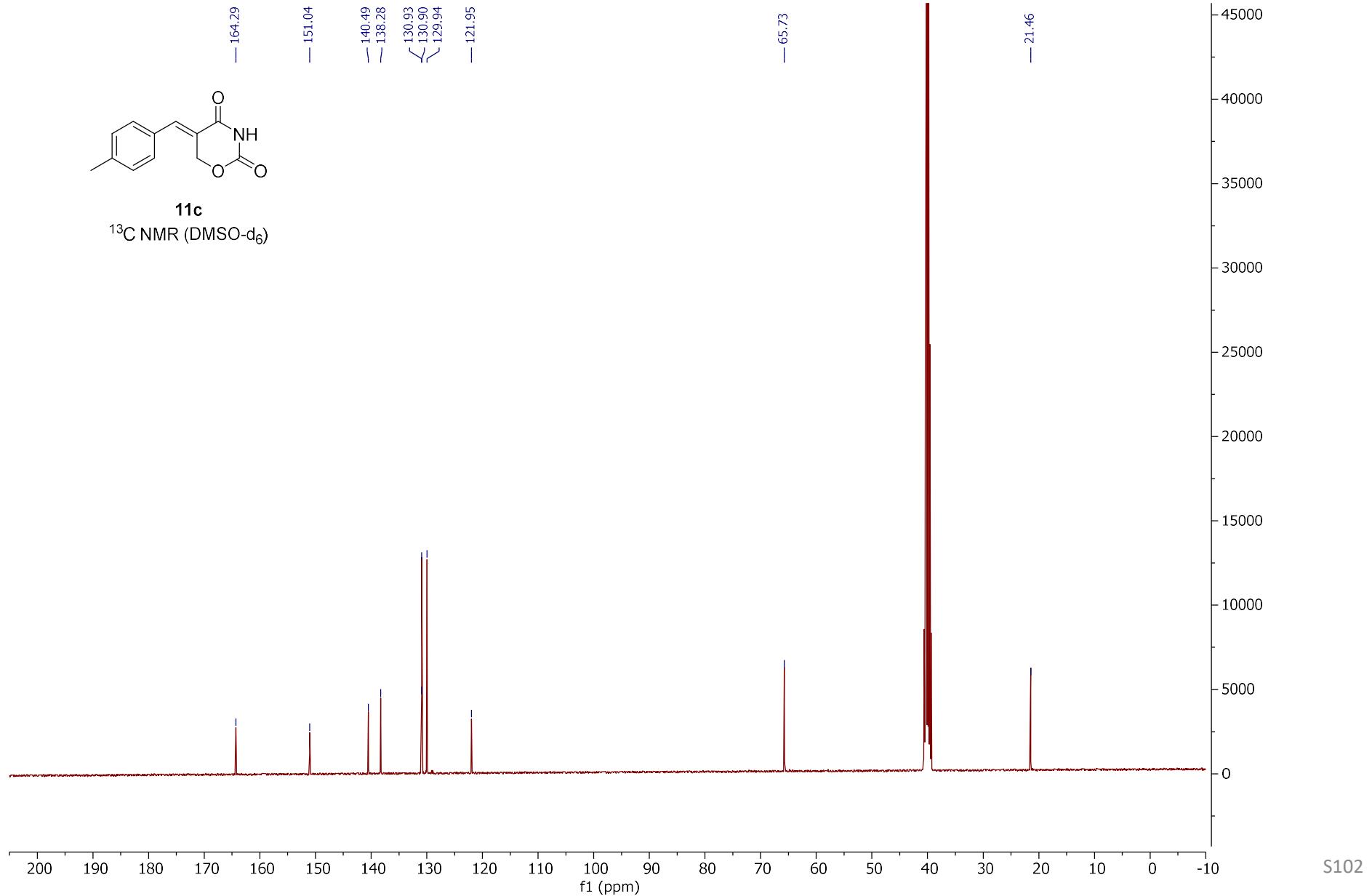


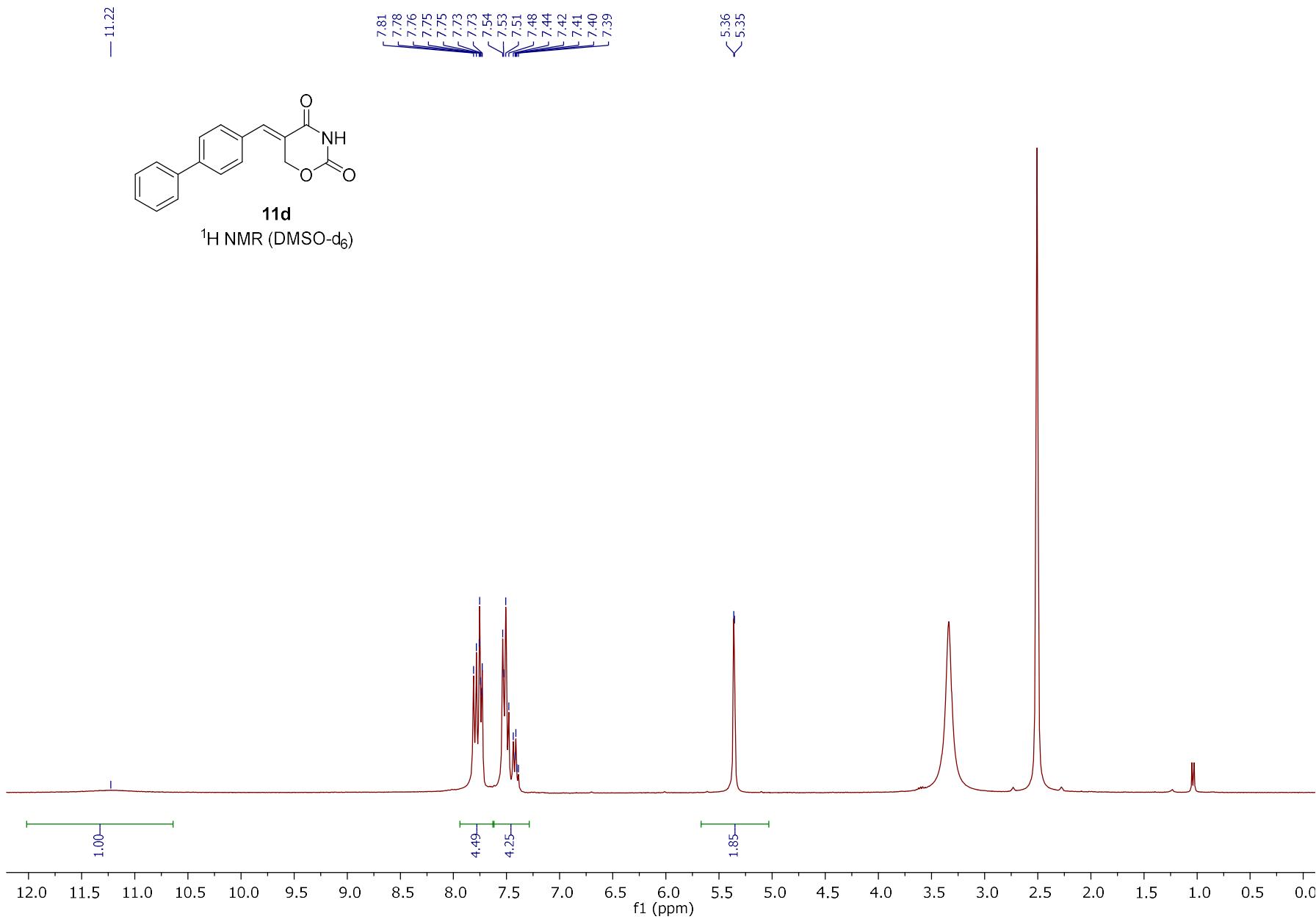
11c
¹H NMR (DMSO-d₆)

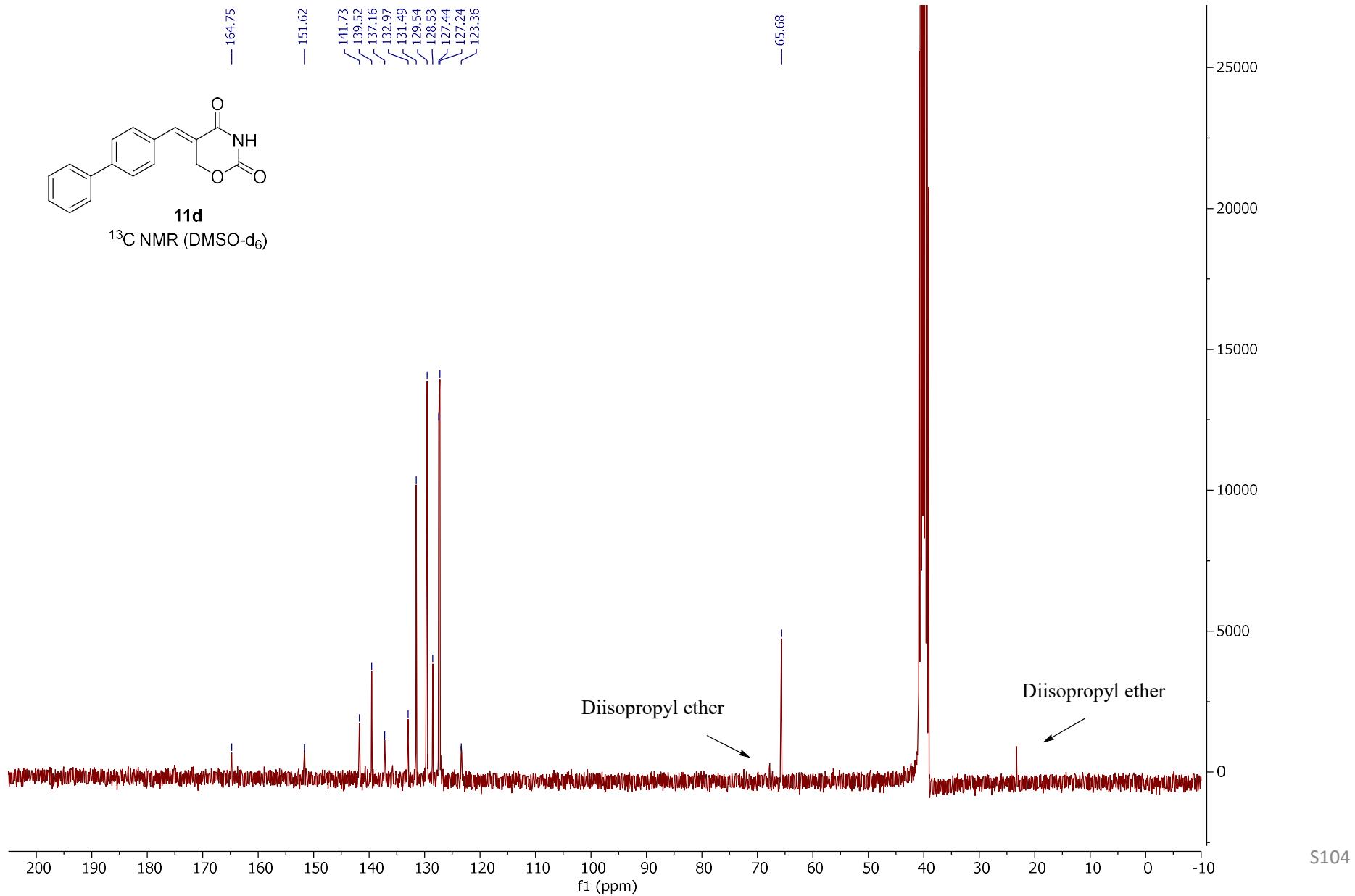
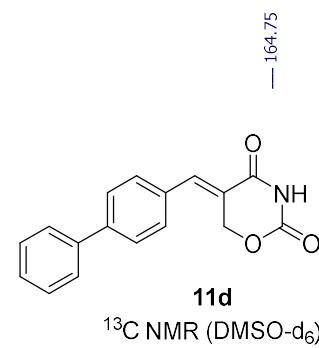


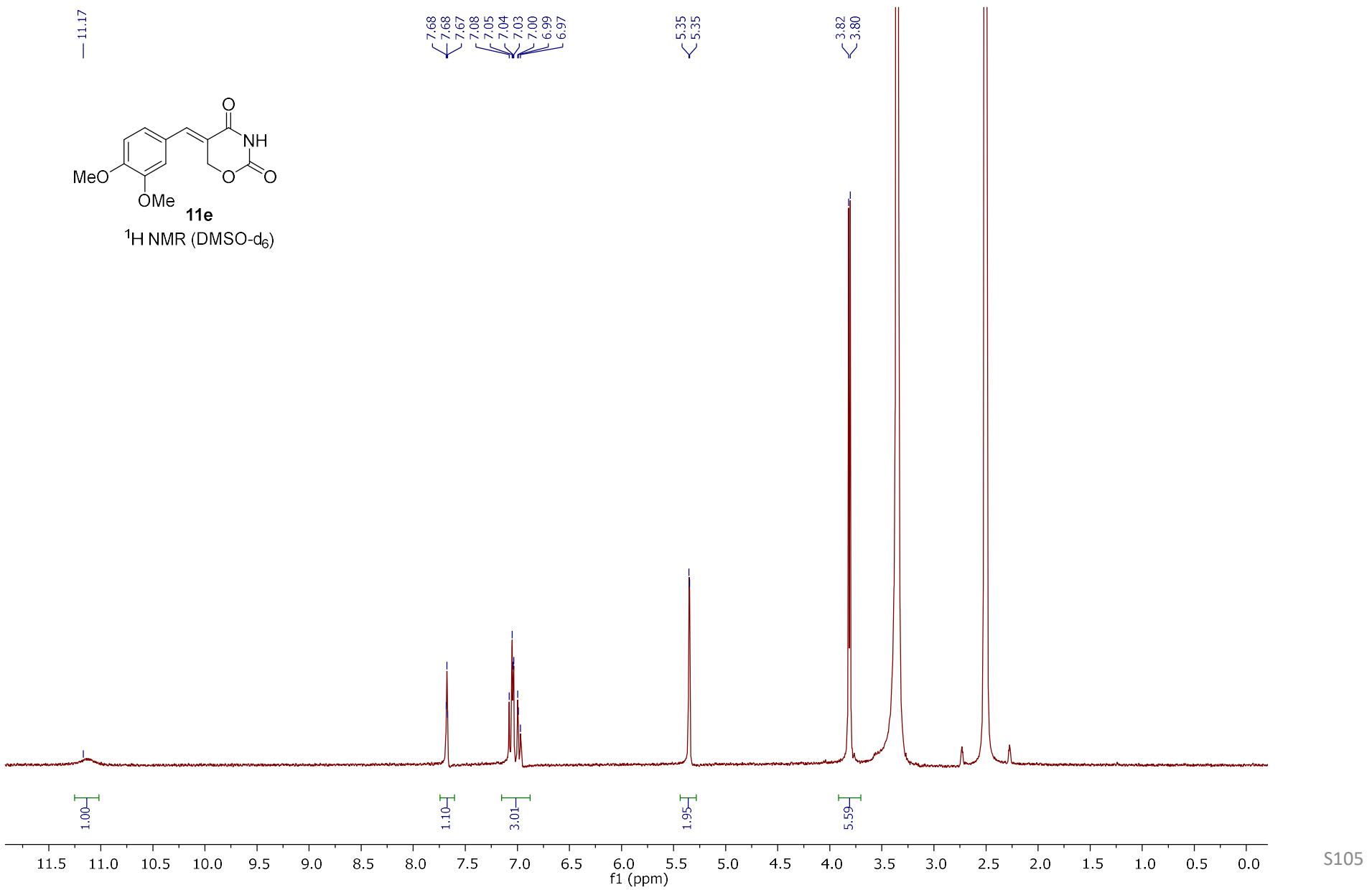


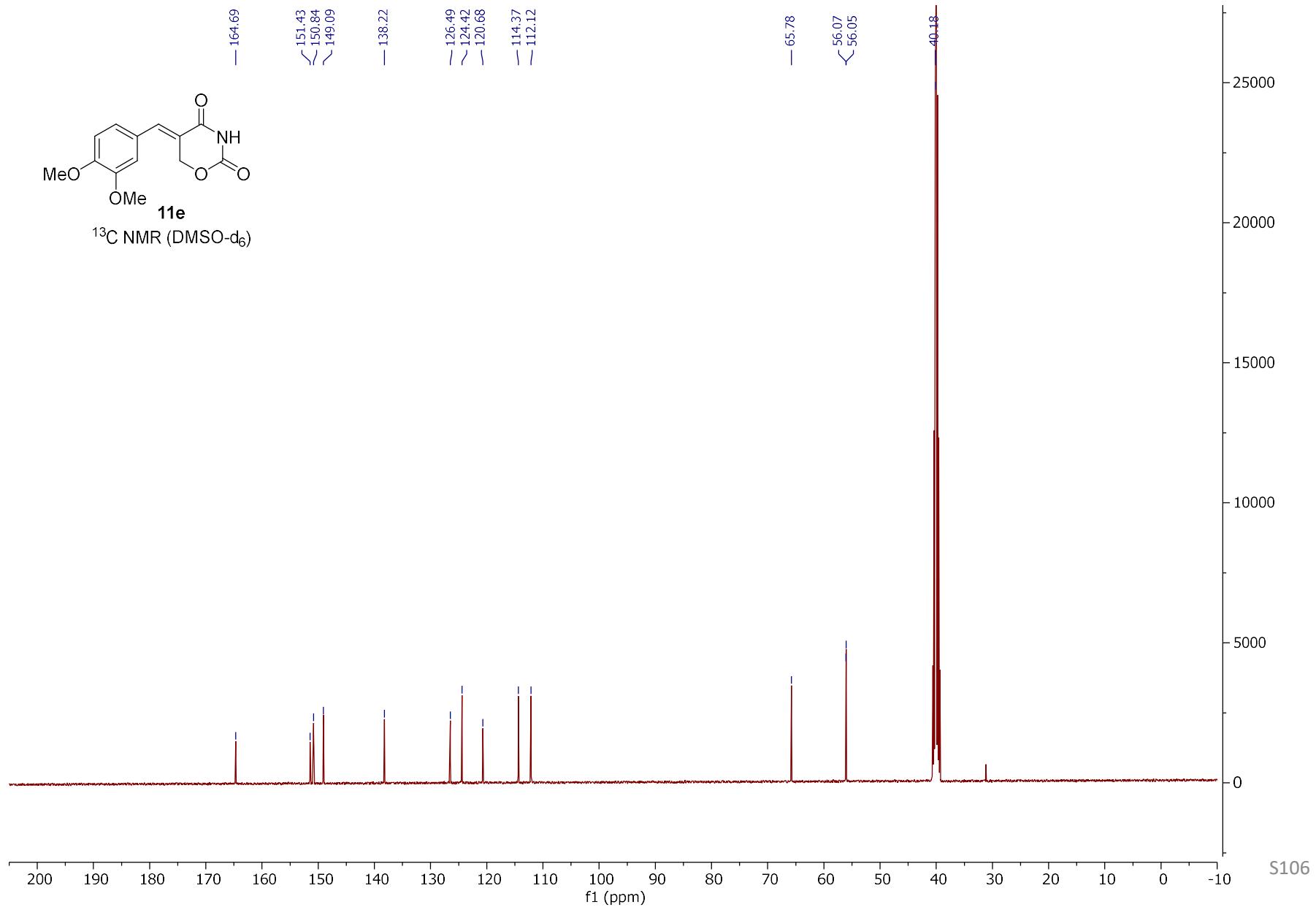
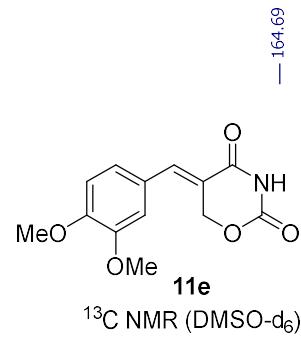
11c
 ^{13}C NMR (DMSO-d₆)

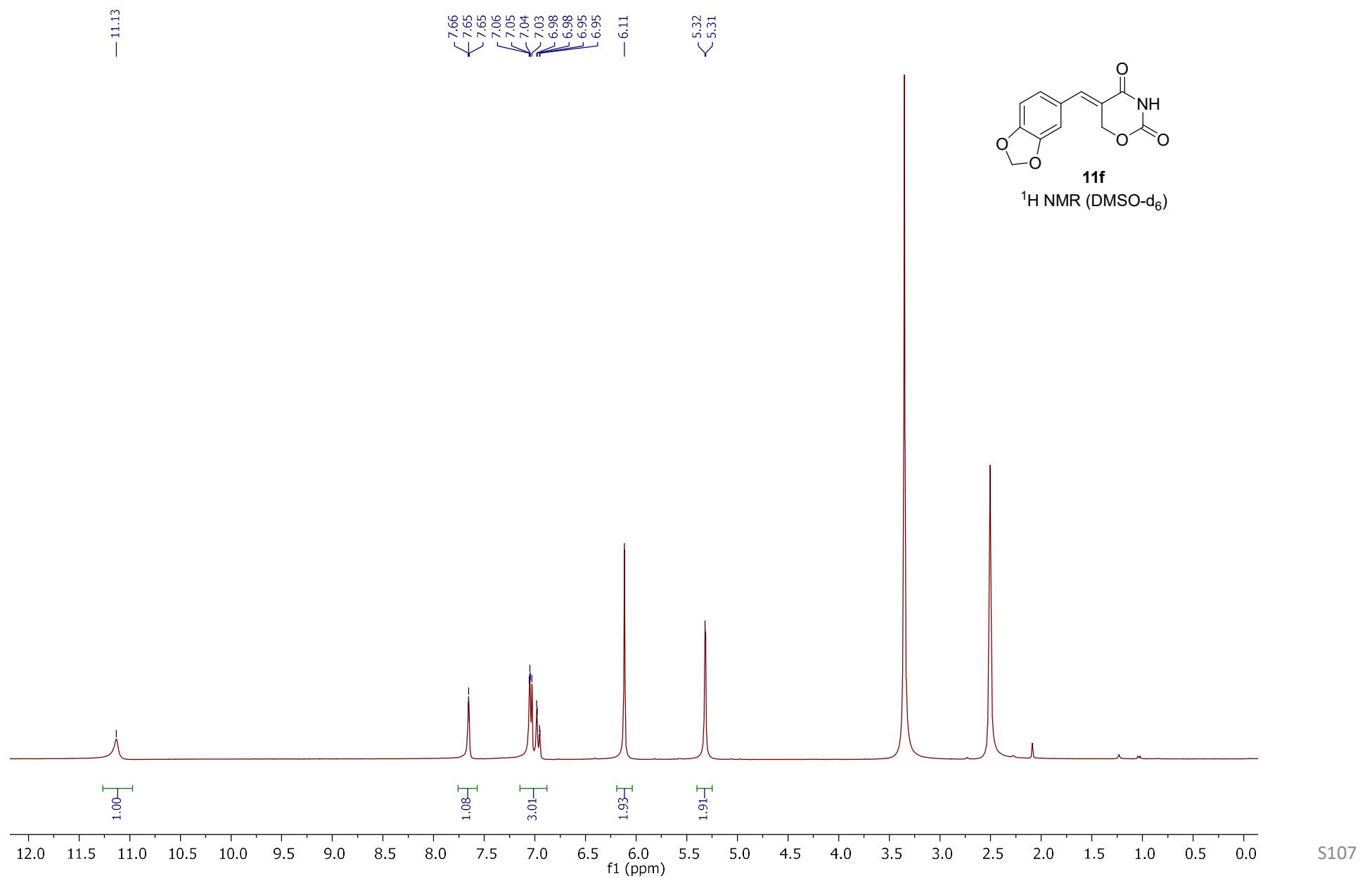


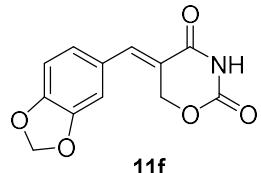




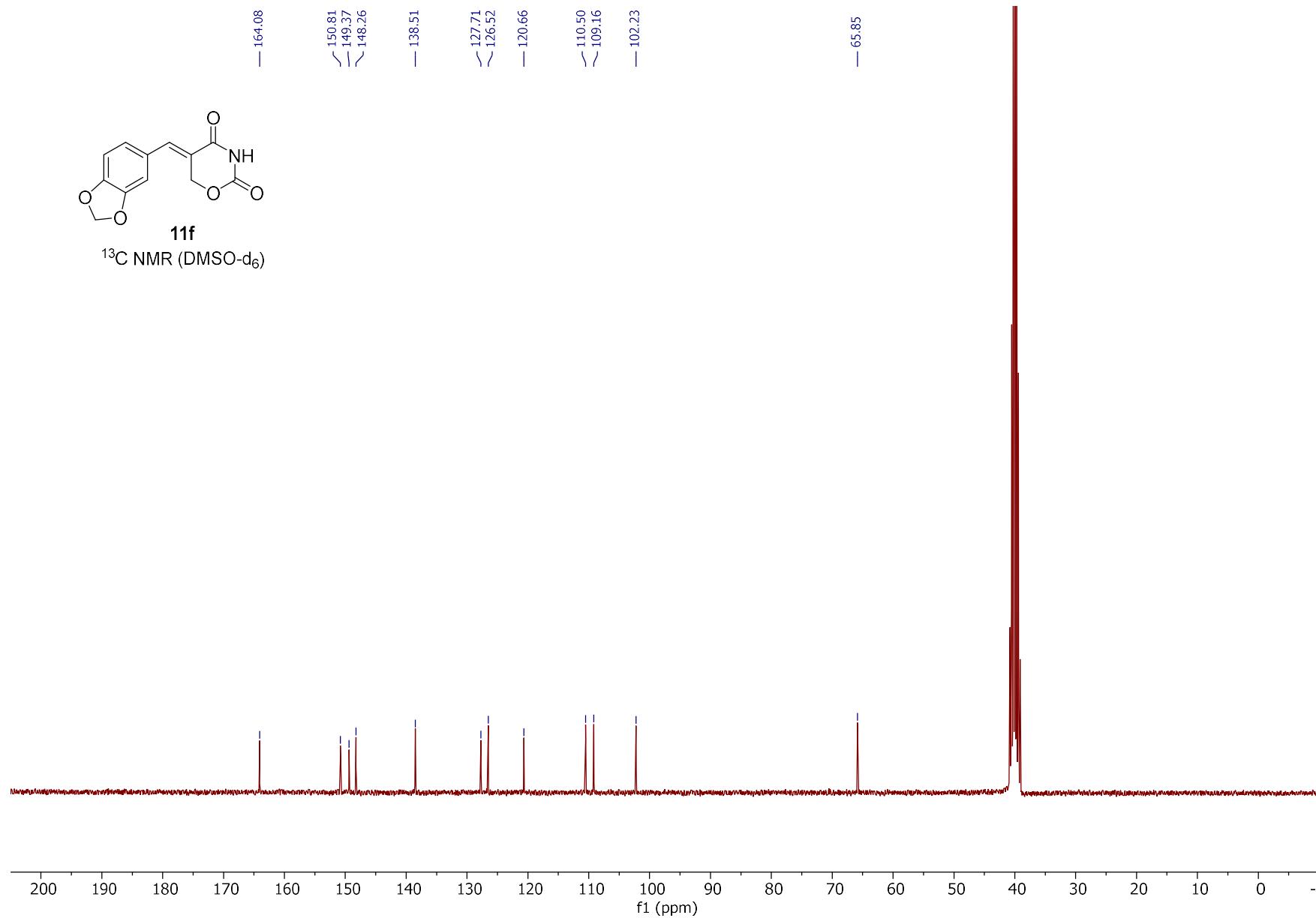


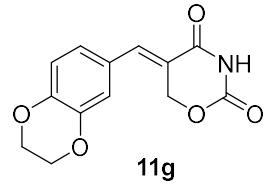






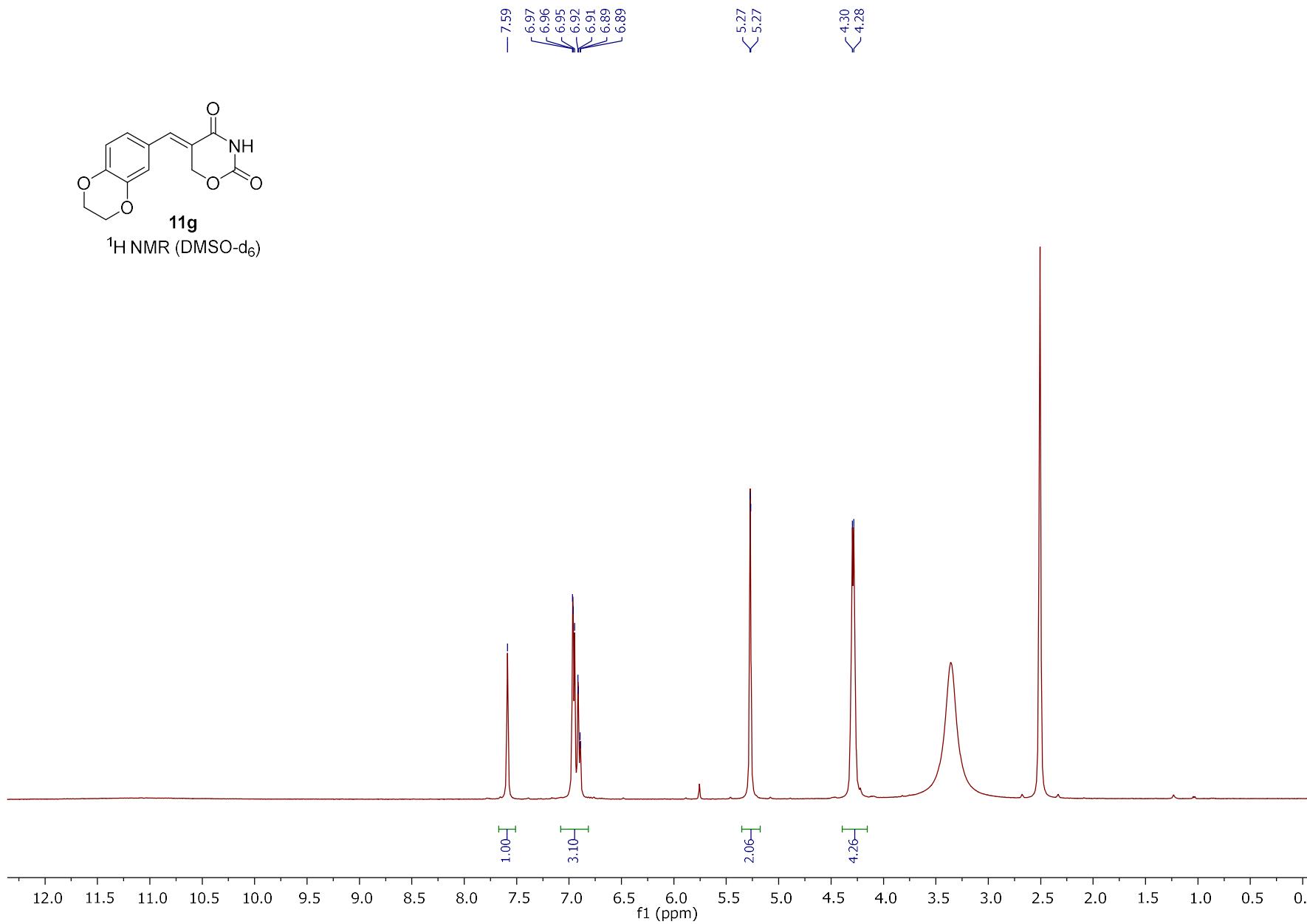
11f
 ^{13}C NMR (DMSO-d₆)

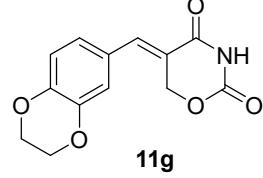




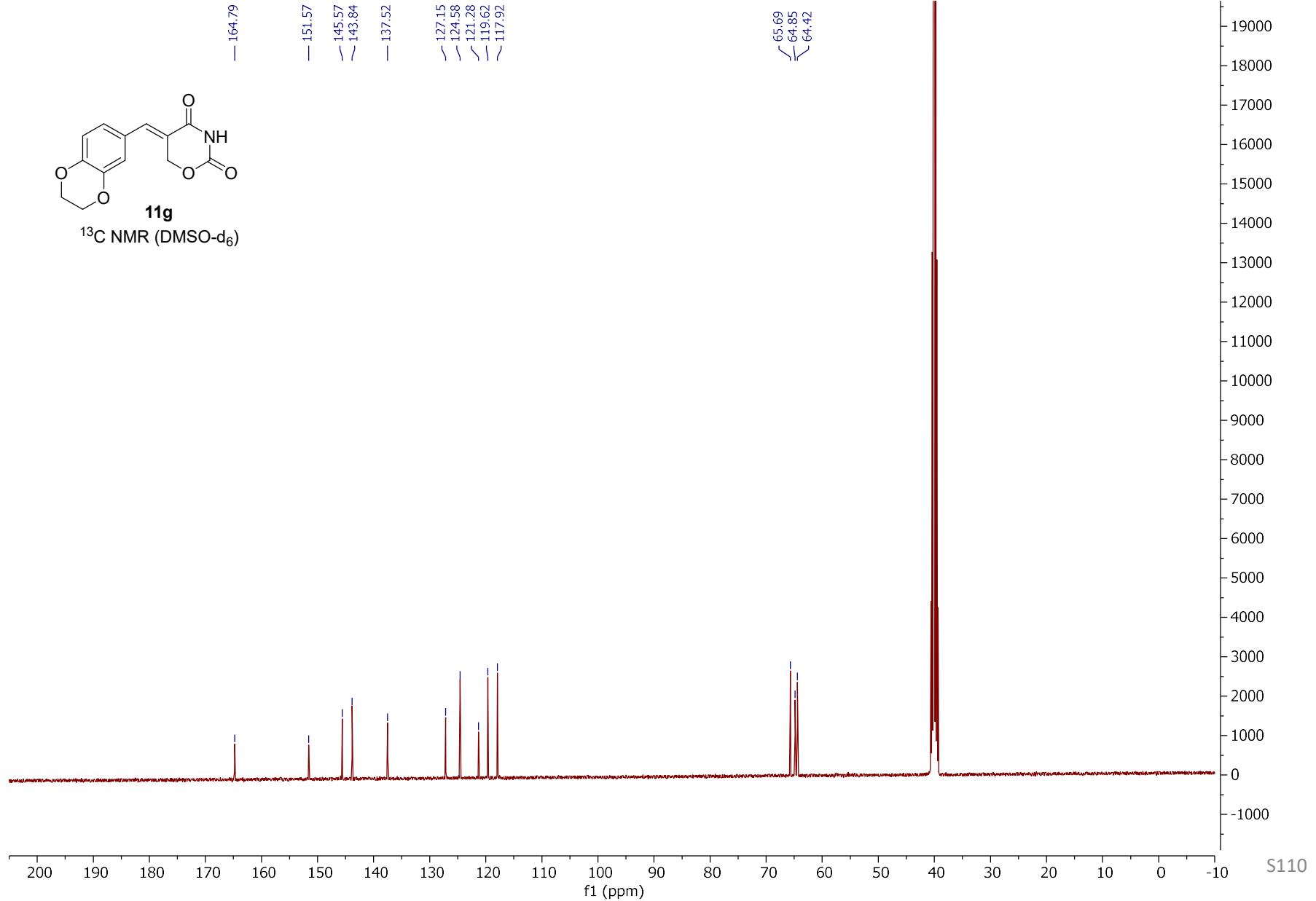
11g

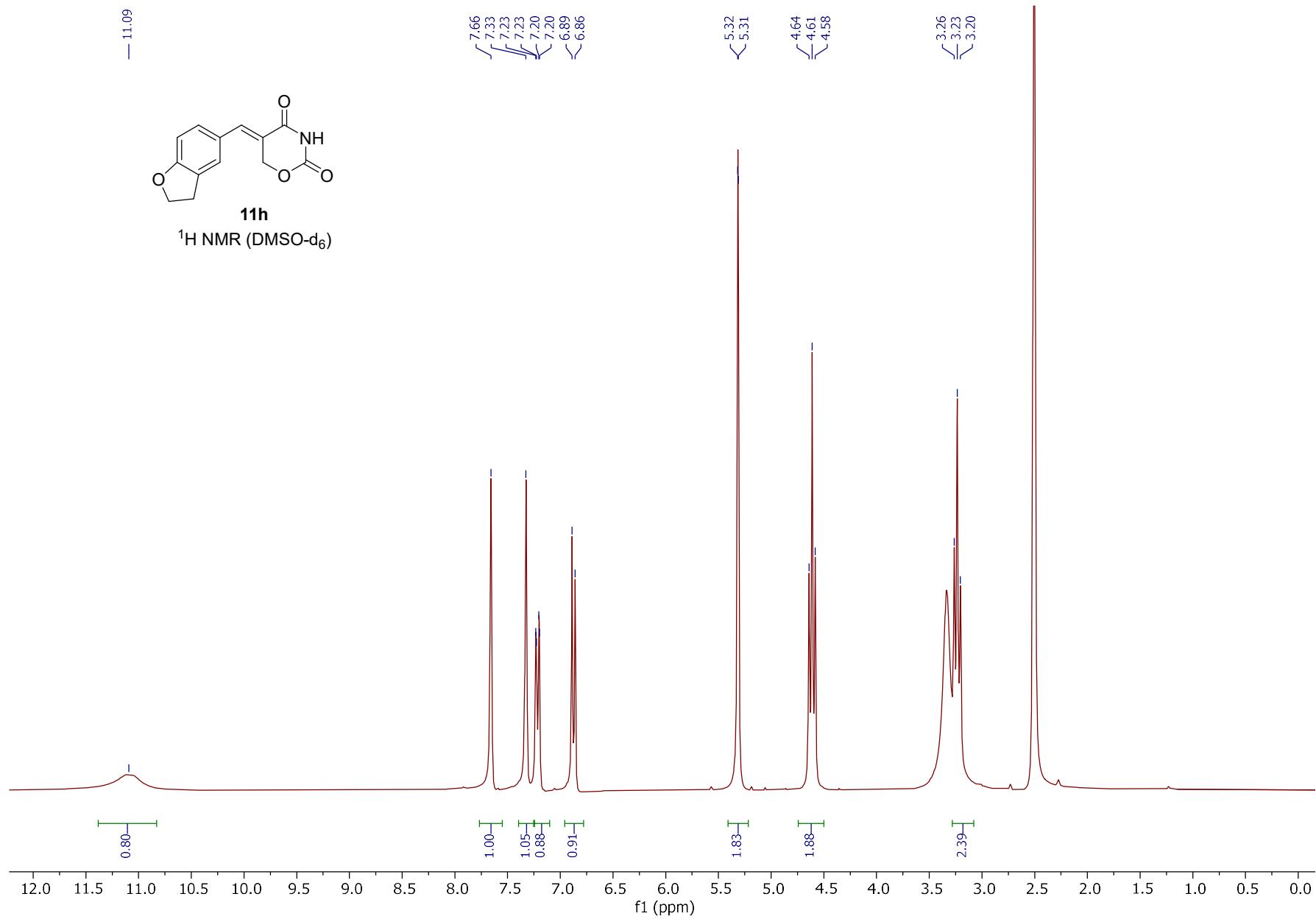
^1H NMR (DMSO- d_6)

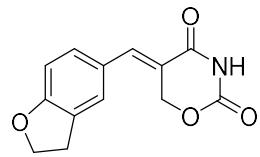




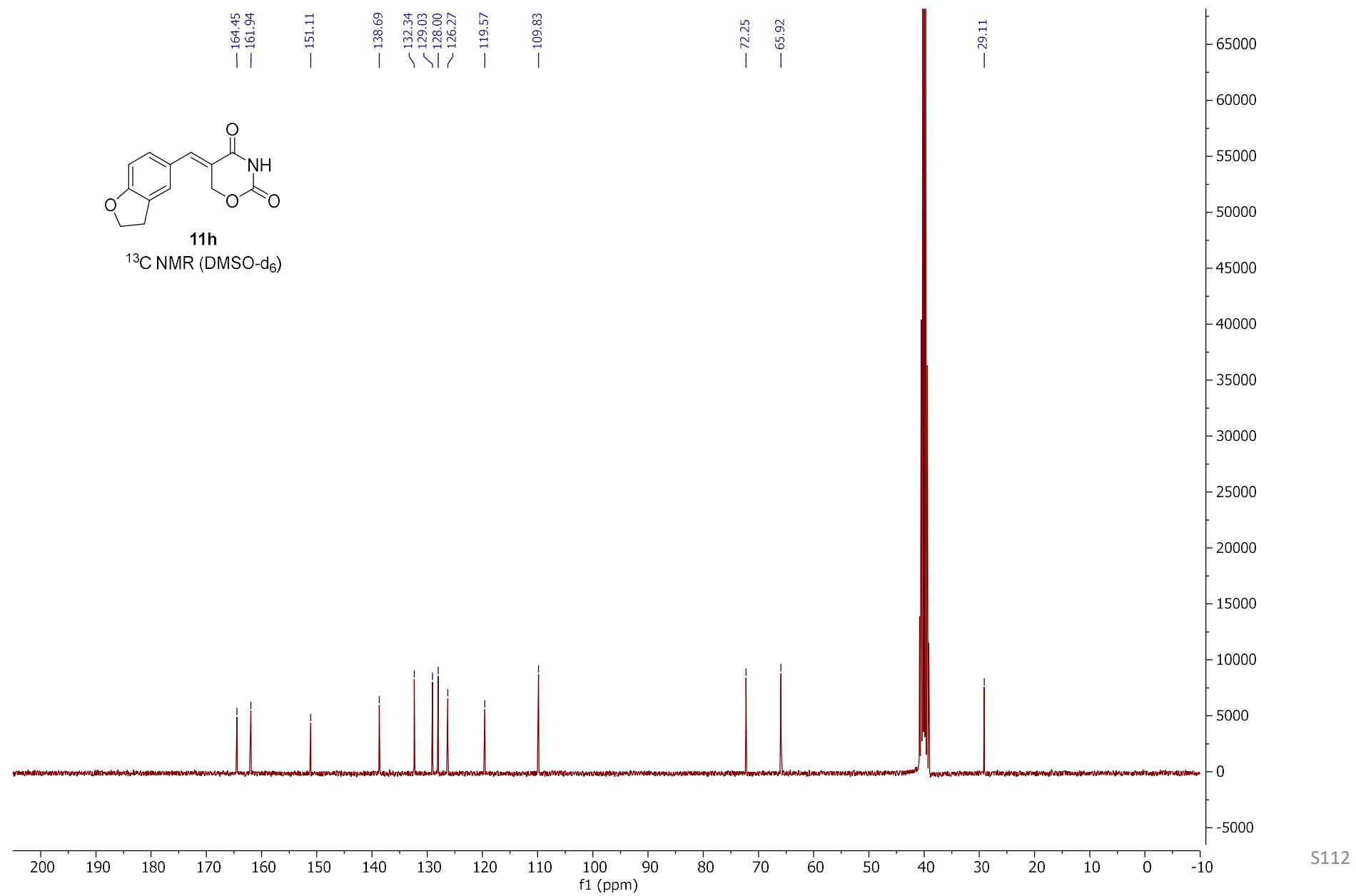
¹³C NMR (DMSO-d₆)



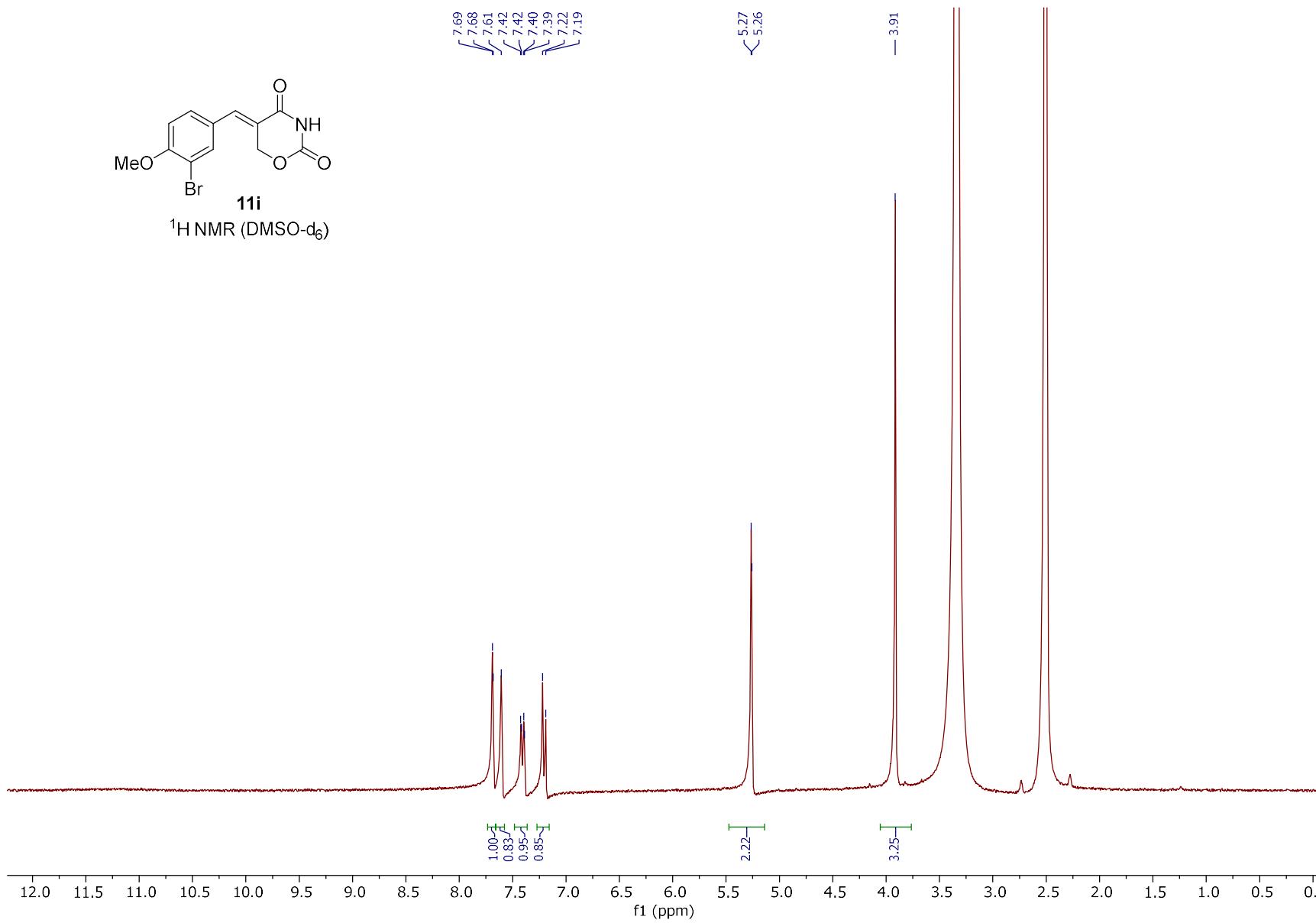
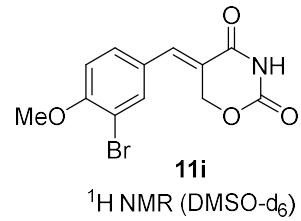


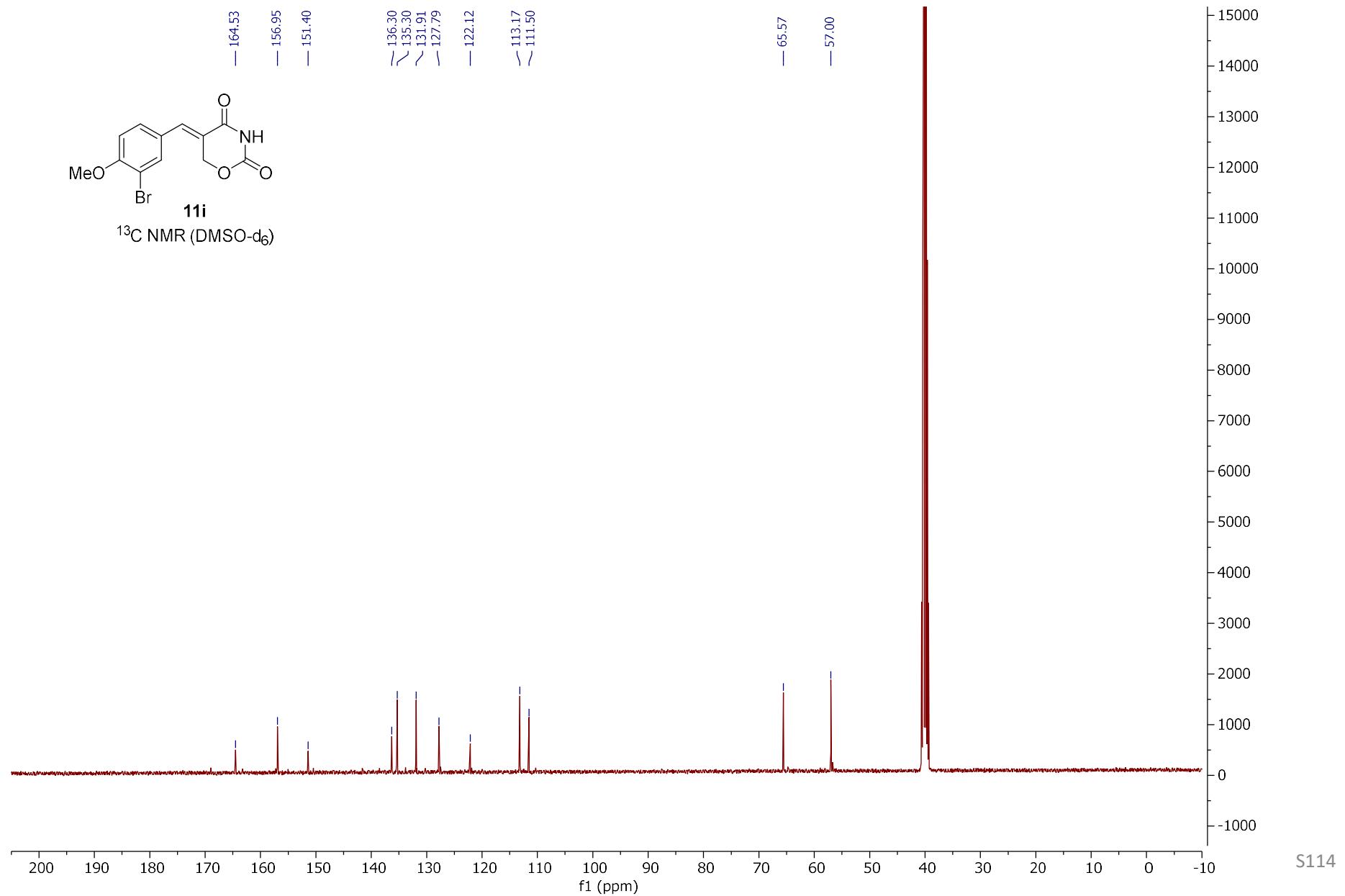
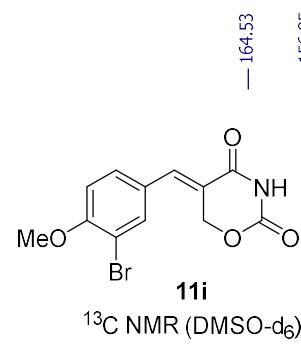


11h
 ^{13}C NMR (DMSO-d₆)



S112





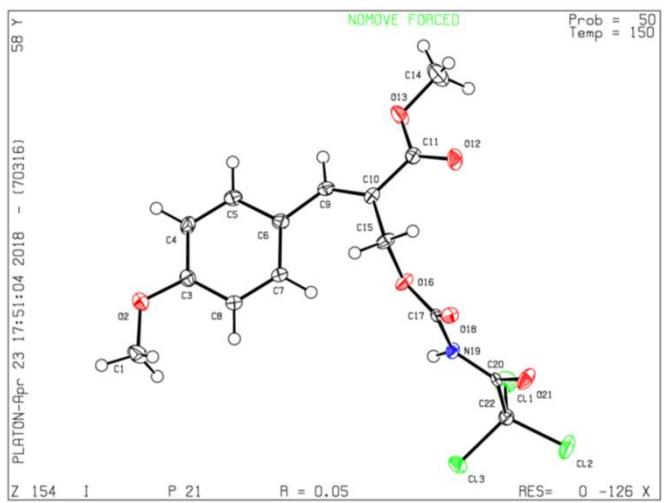


Table S1. Selected crystal parameters and refinement metrics (CCDC 2074213)

Empirical formula	C15 H14 Cl3 N O6
Formula weight	410.62
Temperature	150 K
Wavelength	0.71073 Å
Crystal system, space	monoclinic, P 2 ₁
Unit cell dimensions	a = 9.9702 (11) Å, alpha = 90 °
	b = 6.4752 (8) Å, beta = 108.868(5) °
	c = 14.4200(19) Å, gamma = 90 °
Volume	880.92(19) Å ³
Z, Calculated density	2, 1.548 (g.cm-3)
Absorption coefficient	0.552 mm ⁻¹
F(000)	420
Crystal size	0.580 x 0.080 x 0.030 mm
Crystal color	colourless

ORTEP plot of the crystal structure of 7a (at 50% probability level)

Crystal structure determination: The data were collected using graphite-monochromated Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$). The structure was solved by dual-space algorithm using the *SHELXT* program [8], and then refined with full-matrix least-square methods based on F^2 (*SHELXL*) [9]. All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. H atoms were finally included in their calculated positions.

Theta range for data collection	2.159 to 27.517 °
h_min, h_max	-12, 12
k_min, k_max	-7, 8
l_min, l_max	-18, 18
Reflections collected / unique	8617 / 3710 [R(int) = 0.0470]
Reflections [$I > 2\sigma(I)$]	3150
Completeness to theta_max	0.983
Absorption correction type	multi-scan
Max. and min. transmission	0.984 , 0.709
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3710 / 1 / 232
Goodness-of-fit	1.038
Final R indices [$I > 2\sigma(I)$]	R1= 0.0466, wR2= 0.1125
R indices (all data)	R1= 0.0622, wR2= 0.1199
Largest diff. peak and hole	0.283 and -0.329 e.Å ⁻³

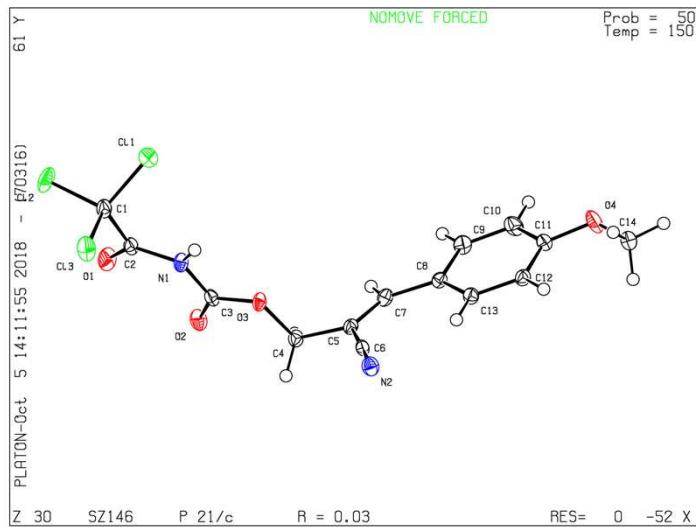


Table S2. Selected crystal parameters and refinement metrics (CCDC 2074212)

Empirical formula	C14 H11 Cl3 N2 O4
Formula weight	377.60
Temperature	150 K
Wavelength	0.71073 Å
Crystal system, space	monoclinic, P 2 ₁ /c
Unit cell dimensions	a = 11.2753 (10) Å, alpha = 90 ° b = 12.7847 (12) Å, beta = 101.537(3) ° c = 11.3373(9) Å, gamma = 90 °
Volume	1601.3(2) Å ³
Z, Calculated density	4,1.566 (g.cm ⁻³)
Absorption coefficient	0.592 mm ⁻¹
F(000)	768
Crystal size	0.350 x 0.310 x 0.080 mm
Crystal color	colourless

ORTEP plot of the crystal structure of 9a (at 50% probability level)

Crystal structure determination: The data were collected using graphite-monochromated Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$). The structure was solved by dual-space algorithm using the *SHELXT* program [8], and then refined with full-matrix least-square methods based on F^2 (*SHELXL*) [9]. All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. H atoms were finally included in their calculated positions.

Theta range for data collection	2.437 to 27.556 °
h_min, h_max	-14, 14
k_min, k_max	-16, 16
l_min, l_max	-11, 14
Reflections collected / unique	27730 / 3680 [R(int) = 0.0412]
Reflections [$I > 2\sigma(I)$]	3221
Completeness to theta_max	0.995
Absorption correction type	multi-scan
Max. and min. transmission	0.954 , 0.849
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3680 / 0 / 212
Goodness-of-fit	0.992
Final R indices [$I > 2\sigma(I)$]	R1= 0.0302, wR2= 0.0739
R indices (all data)	R1= 0.0376, wR2= 0.0780
Largest diff. peak and hole	0.384 and -0.345e.Å ⁻³

VII Computational data

Table S1. Zero-point corrected energies (E_z , in a. u.), Gibbs energies (G , at 383.15 K, in a. u.) and number of imaginary frequencies (NIMAG, imaginary frequencies in cm^{-1}) of the stationary points discussed in the main text. All values have been obtained at the M06-2X(PCM, solvent=toluene)/6-31+G* level of theory.

Stationary Point	E_z	G	NIMAG (imaginary freq.)
6a'	-2465.929826	-2466.018711	0
(E)-TS1	-2465.872060	-2465.957276	1 (-147.8876)
(Z)-TS1	-2465.871267	-2465.955221	1 (-138.8174)
(E)-7a	-2465.934024	-2466.023061	0
(Z)-7a	-2465.927441	-2466.015807	0
8a'	-2330.391560	-2330.473142	0
(E)-TS2	-2330.336042	-2330.419675	1 (-406.7865)
(Z)-TS2	-2330.332482	-2330.412545	1 (-484.0173)
(E)-9a	-2330.398197	-2330.482069	0
(Z)-9a	-2330.394395	-2330.476272	0

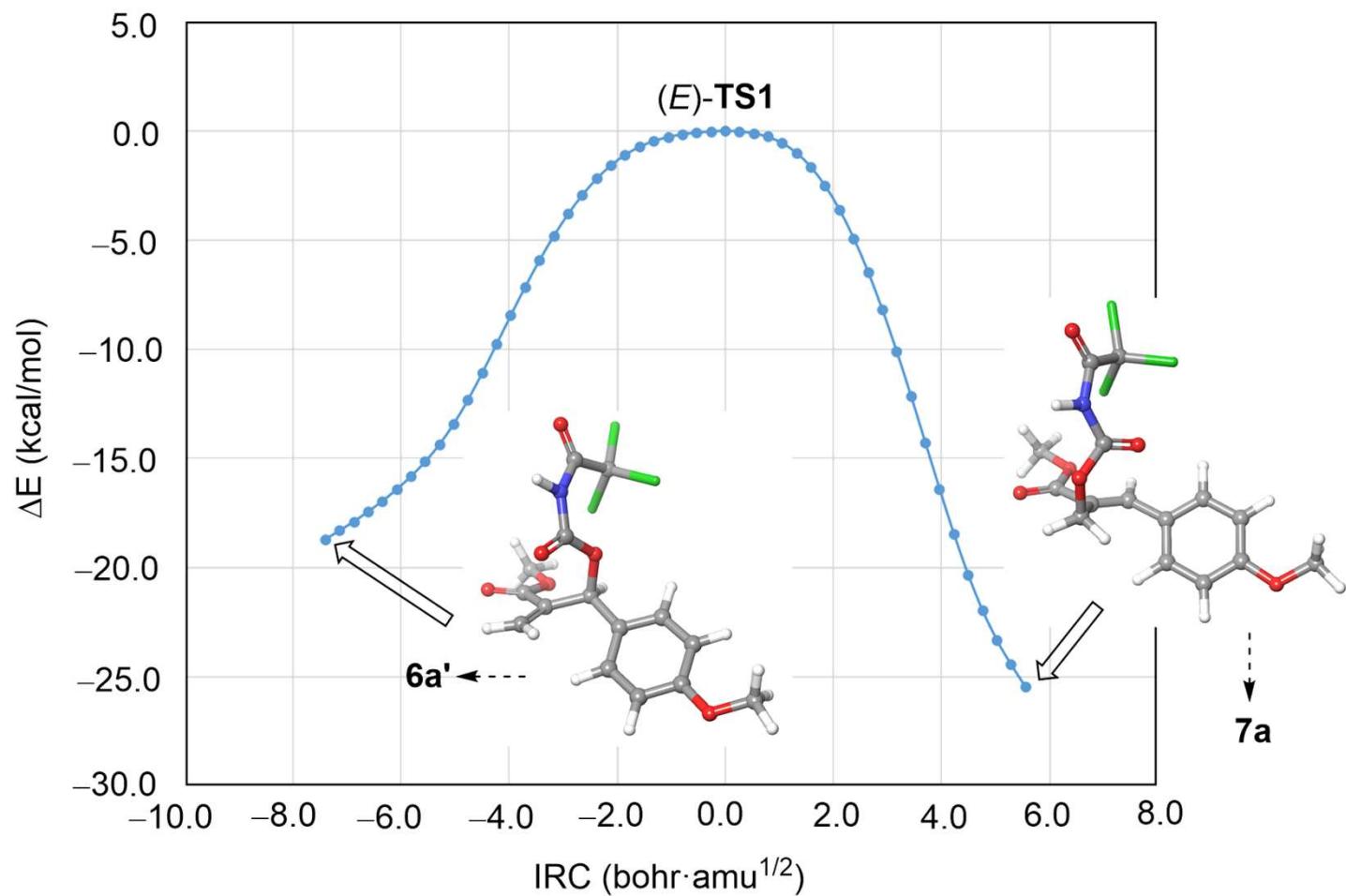


Figure S1. Intrinsic Reaction Coordinate (IRC) of concerted reaction $6\text{a}' \rightarrow 7\text{a}$, computed at the M06-2X(SCRF=Toluene)/6-31+G* level of theory.

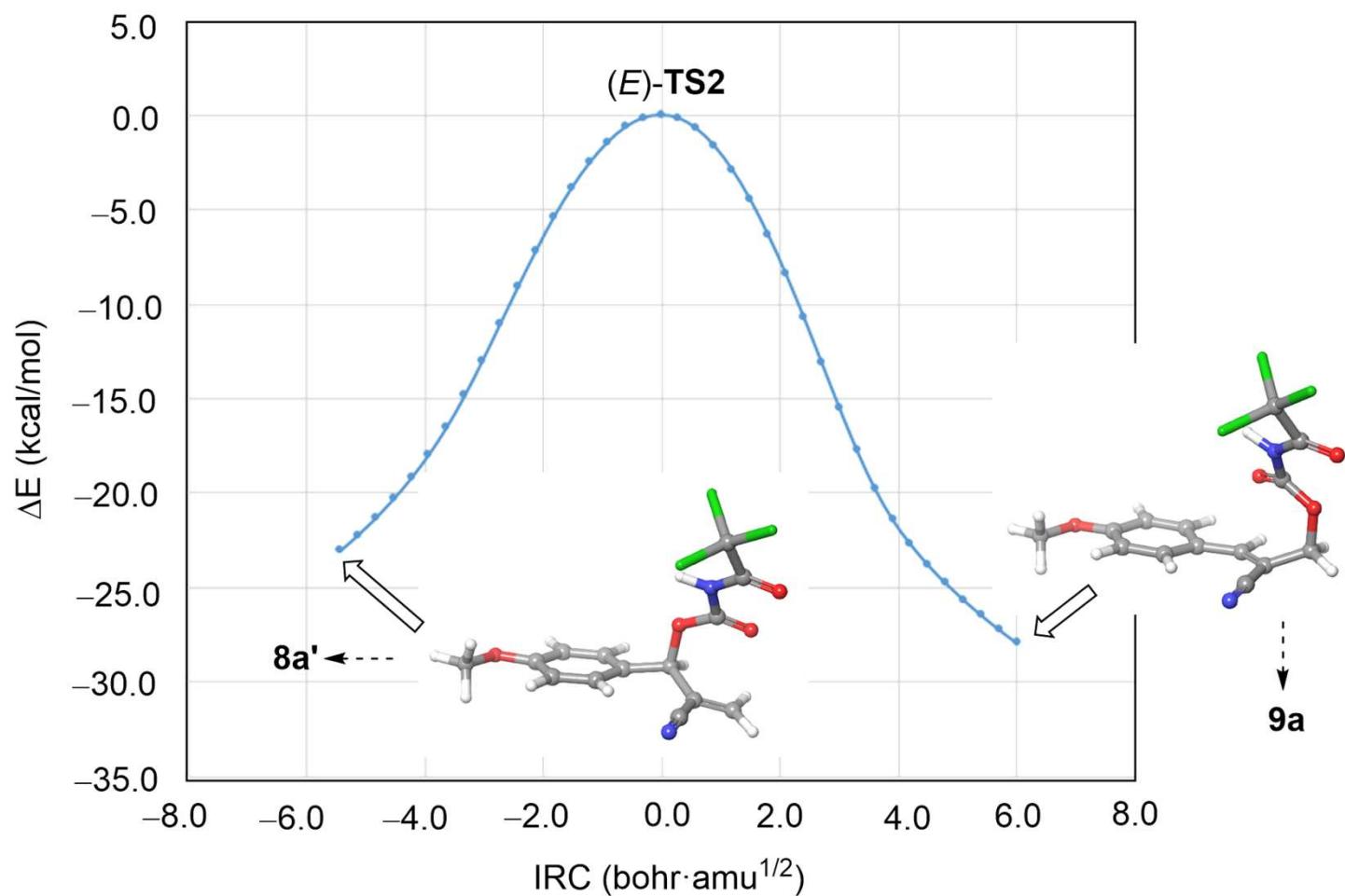


Figure S2. Intrinsic Reaction Coordinate (IRC) of concerted reaction $8a' \rightarrow 9a$, computed at the M06-2X(SCRF=Toluene)/6-31+G* level of theory.

Cartesian coordinates

6a'

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-1.453562	-1.032649	0.427792
2	1	0	-1.457087	-1.340609	1.476892
3	6	0	-2.082232	0.339897	0.309144
4	6	0	-3.205633	2.894684	0.089516
5	6	0	-2.449359	1.053355	1.454447
6	6	0	-2.286340	0.919408	-0.940243
7	6	0	-2.839969	2.194314	-1.063879
8	6	0	-3.009206	2.316895	1.350411
9	1	0	-2.289301	0.611205	2.433974
10	1	0	-2.012811	0.372126	-1.840050
11	1	0	-2.984778	2.619749	-2.050034
12	1	0	-3.299094	2.880161	2.231711
13	6	0	-2.167224	-2.068651	-0.405308
14	6	0	-1.674038	-2.643406	-1.502648
15	1	0	-2.256640	-3.372218	-2.055187
16	1	0	-0.679176	-2.402072	-1.861062
17	6	0	-3.518802	-2.414655	0.130250
18	8	0	-3.910190	-2.052258	1.218622
19	8	0	-4.243574	-3.169689	-0.701187
20	6	0	-5.535537	-3.551126	-0.215641
21	1	0	-5.434973	-4.135886	0.700862
22	1	0	-5.979518	-4.149726	-1.008654
23	1	0	-6.138281	-2.662926	-0.016690
24	8	0	-0.083275	-0.993081	-0.030374

25	6	0	0.798094	-0.474213	0.838959
26	8	0	0.568456	-0.136895	1.966907
27	7	0	2.038548	-0.403949	0.197893
28	1	0	2.057231	-0.717535	-0.766815
29	6	0	3.197208	0.045368	0.788654
30	8	0	3.315882	0.429195	1.917094
31	6	0	4.420181	0.021846	-0.195465
32	17	0	4.639093	-1.641338	-0.808012
33	17	0	5.868662	0.548039	0.646000
34	17	0	4.068574	1.117546	-1.559478
35	8	0	-3.757540	4.135334	0.086065
36	6	0	-3.965635	4.763976	-1.165031
37	1	0	-3.017884	4.902134	-1.697962
38	1	0	-4.403894	5.736199	-0.942777
39	1	0	-4.656969	4.183733	-1.786900

(E)-TS1

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-3.771816	-1.386376	-0.706263
2	6	0	-4.860772	-0.695598	-0.144932
3	6	0	-4.712296	0.636187	0.292846
4	6	0	-3.487010	1.255553	0.206198
5	6	0	-2.371464	0.571271	-0.335191
6	6	0	-2.552541	-0.743971	-0.811360
7	6	0	-1.075717	1.150103	-0.452813
8	6	0	-0.582994	2.284615	0.245569
9	6	0	0.579936	3.049047	-0.298246
10	8	0	0.888793	2.681261	-1.548476
11	6	0	2.021380	3.344962	-2.125346
12	6	0	-0.920910	2.497809	1.551772
13	8	0	1.161443	3.919688	0.307152
14	8	0	0.104100	-0.425434	0.808133
15	6	0	0.727382	0.059188	1.770807
16	7	0	2.114901	-0.311728	1.953827
17	6	0	3.038326	-1.037090	1.263477
18	6	0	2.760770	-1.457739	-0.222880
19	17	0	2.255746	-0.043333	-1.185043
20	8	0	0.322939	0.856979	2.645004
21	8	0	4.103243	-1.338696	1.759238
22	17	0	1.552073	-2.760663	-0.270211
23	17	0	4.268929	-2.079773	-0.927894

24	1	0	-1.716339	1.948781	2.035006
25	1	0	-0.434755	0.747541	-1.231944
26	1	0	-0.415980	3.271147	2.120550
27	1	0	-1.696843	-1.272219	-1.223400
28	1	0	-3.392200	2.294984	0.504285
29	1	0	-5.584109	1.151408	0.681512
30	1	0	-3.874285	-2.406962	-1.053539
31	8	0	-6.085001	-1.216147	-0.004502
32	1	0	1.835237	4.418874	-2.183224
33	1	0	2.134265	2.916874	-3.119641
34	1	0	2.910165	3.157997	-1.519210
35	1	0	2.476234	-0.015055	2.855841
36	6	0	-6.315212	-2.555554	-0.429394
37	1	0	-7.361764	-2.756868	-0.209062
38	1	0	-6.136607	-2.655220	-1.504435
39	1	0	-5.678556	-3.250773	0.126132

(Z)-TS1

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-4.599348	-0.173263	-0.702952
2	6	0	-4.264664	1.092091	-0.195927
3	6	0	-2.970102	1.337586	0.312498
4	6	0	-2.041778	0.326797	0.345578
5	6	0	-2.363157	-0.966456	-0.137450
6	6	0	-3.642123	-1.173869	-0.689490
7	6	0	-1.438679	-2.049334	-0.174394
8	6	0	-0.253391	-2.236486	0.593756
9	6	0	0.181853	-1.323566	1.702960
10	8	0	-0.802105	-1.126776	2.585303
11	6	0	-0.490062	-0.239061	3.667461
12	6	0	0.574426	-3.266800	0.256266
13	8	0	1.293026	-0.863412	1.818010
14	8	0	-0.406976	-1.430717	-2.195568
15	6	0	0.810764	-1.573244	-1.915431
16	7	0	1.405770	-0.361075	-1.394912
17	6	0	2.575856	-0.260441	-0.709499
18	6	0	2.884819	1.204793	-0.205309
19	17	0	1.418284	2.078547	0.344198
20	8	0	1.494143	-2.603335	-1.925203
21	8	0	3.394867	-1.119763	-0.512494
22	17	0	3.580181	2.083840	-1.597670
23	17	0	4.047190	1.147151	1.114899
24	1	0	0.266928	-4.015482	-0.463571

25	1	0	-1.731351	-2.901173	-0.782234
26	1	0	1.540531	-3.389811	0.736791
27	1	0	-3.886173	-2.147545	-1.105589
28	1	0	-1.039762	0.547537	0.700411
29	1	0	-2.734273	2.338886	0.657271
30	1	0	-5.579634	-0.370854	-1.118474
31	8	0	-5.100204	2.135636	-0.168403
32	1	0	0.329093	-0.646482	4.262452
33	1	0	-1.401586	-0.167491	4.257151
34	1	0	-0.201620	0.739575	3.275442
35	1	0	0.797432	0.447259	-1.451056
36	6	0	-6.416590	1.974158	-0.686339
37	1	0	-6.902650	2.939264	-0.557725
38	1	0	-6.382919	1.714132	-1.748683
39	1	0	-6.959502	1.207065	-0.125586

(E)-7a

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	2.868845	1.663247	0.537883
2	1	0	3.264451	2.386307	1.251260
3	6	0	1.706273	1.995742	-0.054316
4	6	0	3.671420	0.453108	0.337072
5	6	0	5.294690	-1.819148	-0.004739
6	6	0	3.102060	-0.808525	0.077663
7	6	0	5.062995	0.532755	0.459592
8	6	0	5.879706	-0.580780	0.277487
9	6	0	3.898953	-1.927180	-0.090387
10	1	0	2.021540	-0.919237	0.048393
11	1	0	5.522524	1.490843	0.689702
12	1	0	6.954288	-0.473427	0.366575
13	1	0	3.465383	-2.904588	-0.276949

14	8	0	5.988089	-2.966826	-0.191294
15	6	0	7.401391	-2.913475	-0.096127
16	1	0	7.819692	-2.239536	-0.851914
17	1	0	7.751224	-3.928644	-0.278120
18	1	0	7.714522	-2.590333	0.902831
19	6	0	1.031193	3.238814	0.417758
20	8	0	1.476688	4.020349	1.230772
21	8	0	-0.169535	3.387364	-0.161853
22	6	0	-0.912177	4.548303	0.221992
23	1	0	-1.107559	4.529727	1.296098
24	1	0	-1.841377	4.499160	-0.342483
25	1	0	-0.352613	5.451284	-0.030227
26	6	0	1.048605	1.230682	-1.163429
27	1	0	0.627337	1.902584	-1.911260
28	1	0	1.747787	0.545284	-1.644148
29	8	0	-0.027009	0.434737	-0.613995
30	6	0	-1.232899	0.555805	-1.189124
31	8	0	-1.501536	1.178909	-2.178352
32	7	0	-2.135173	-0.192467	-0.424518
33	1	0	-1.746788	-0.646070	0.396009
34	6	0	-3.469982	-0.345086	-0.716206
35	6	0	-4.206118	-1.272954	0.314377
36	17	0	-3.453798	-2.890984	0.254273
37	17	0	-4.015715	-0.586407	1.950852
38	17	0	-5.909679	-1.383802	-0.098044
39	8	0	-4.056403	0.142513	-1.640464

(Z)-7a

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-2.556832	0.351743	1.649233
2	1	0	-2.560998	0.069695	2.702911
3	6	0	-1.466103	0.985275	1.196774
4	6	0	-3.763564	-0.021073	0.897445
5	6	0	-6.079182	-0.832977	-0.479810
6	6	0	-4.211468	0.679564	-0.236748
7	6	0	-4.522085	-1.109893	1.335831
8	6	0	-5.665580	-1.530048	0.658119
9	6	0	-5.348050	0.280696	-0.917180
10	1	0	-3.684770	1.567579	-0.574680
11	1	0	-4.207832	-1.655231	2.222627
12	1	0	-6.218191	-2.386568	1.025983
13	1	0	-5.701060	0.823150	-1.788476
14	8	0	-7.175655	-1.146161	-1.213107
15	6	0	-7.948315	-2.261307	-0.805870
16	1	0	-7.351839	-3.180279	-0.827418
17	1	0	-8.763949	-2.338451	-1.523638
18	1	0	-8.357176	-2.109361	0.199528
19	6	0	-1.237887	1.324269	-0.247461

20	8	0	-0.948336	0.510919	-1.094880
21	8	0	-1.333442	2.637330	-0.470391
22	6	0	-0.932992	3.069086	-1.777852
23	1	0	0.110276	2.794052	-1.946392
24	1	0	-1.053510	4.150604	-1.777597
25	1	0	-1.568035	2.607961	-2.537417
26	6	0	-0.328742	1.343660	2.110966
27	1	0	-0.069278	2.402900	2.038879
28	1	0	-0.566255	1.083609	3.142401
29	8	0	0.847602	0.561974	1.796316
30	6	0	1.651427	1.056942	0.843861
31	8	0	1.503788	2.101478	0.267712
32	7	0	2.689845	0.148413	0.640852
33	1	0	2.635698	-0.712473	1.175793
34	6	0	3.729398	0.339592	-0.241112
35	6	0	4.706899	-0.886835	-0.292007
36	17	0	5.360245	-1.167293	1.346436
37	17	0	3.791601	-2.321232	-0.824600
38	17	0	6.017848	-0.552910	-1.412432
39	8	0	3.916249	1.311480	-0.916081

8a'

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-1.530022	1.348295	-0.522428
2	1	0	-1.421955	1.805259	-1.509639
3	6	0	-2.741398	0.452058	-0.483405
4	6	0	-5.065140	-1.107823	-0.377223
5	6	0	-3.820548	0.725233	-1.331943
6	6	0	-2.841802	-0.606732	0.415481
7	6	0	-3.993469	-1.392459	0.473134
8	6	0	-4.972942	-0.042276	-1.282437
9	1	0	-3.757225	1.548720	-2.039860
10	1	0	-2.014772	-0.832306	1.082517
11	1	0	-4.040265	-2.211268	1.181248
12	1	0	-5.813749	0.158372	-1.938635
13	6	0	-1.590377	2.464115	0.504849
14	6	0	-1.524471	3.759111	0.185577
15	1	0	-1.590498	4.535904	0.940002
16	1	0	-1.396347	4.060411	-0.849641
17	8	0	-0.366118	0.539772	-0.257406
18	6	0	0.804187	1.044269	-0.691762
19	8	0	0.942316	2.055663	-1.322754

20	7	0	1.818424	0.179998	-0.282564
21	1	0	1.523426	-0.621555	0.266191
22	6	0	3.155294	0.357300	-0.566822
23	8	0	3.627824	1.249076	-1.211618
24	6	0	4.054845	-0.767168	0.055016
25	17	0	3.825594	-0.769785	1.824166
26	17	0	5.739177	-0.462021	-0.336681
27	17	0	3.542603	-2.339275	-0.617741
28	8	0	-6.227960	-1.805452	-0.401747
29	6	0	-6.372176	-2.884933	0.504490
30	1	0	-5.616040	-3.656242	0.319527
31	1	0	-7.364486	-3.296202	0.323998
32	1	0	-6.300882	-2.538505	1.541600
33	6	0	-1.717931	2.049407	1.881565
34	7	0	-1.804908	1.684710	2.976949

(E)-TS2

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	3.985450	-0.954122	0.838035
2	6	0	3.054539	0.072284	0.803964
3	6	0	2.906543	0.878965	-0.338653
4	6	0	3.716344	0.602020	-1.463510
5	6	0	4.647605	-0.412499	-1.442124
6	6	0	4.791015	-1.199413	-0.285620
7	6	0	1.968592	1.963111	-0.460869
8	6	0	1.231413	2.653838	0.543539
9	6	0	0.389681	3.648364	0.106253
10	8	0	5.721036	-2.164499	-0.348118
11	6	0	5.913575	-3.000670	0.786221
12	6	0	1.075354	2.170665	1.887511
13	7	0	0.942695	1.816701	2.982542
14	8	0	0.363942	0.927626	-1.335536
15	6	0	-0.781252	1.338192	-0.987113
16	7	0	-1.673141	0.278534	-0.642254
17	6	0	-2.971382	0.390792	-0.236034
18	8	0	-3.602203	1.400621	-0.070968
19	8	0	-1.167713	2.515946	-0.885810

20	6	0	-3.639197	-1.012053	0.029886
21	17	0	-5.307385	-0.793655	0.542467
22	17	0	-3.589250	-1.974525	-1.474610
23	17	0	-2.718710	-1.857321	1.305845
24	1	0	2.039472	2.515709	-1.392141
25	1	0	-0.307794	4.135725	0.778054
26	1	0	0.541960	4.097742	-0.866361
27	1	0	3.598391	1.201575	-2.362252
28	1	0	5.276479	-0.627556	-2.299399
29	1	0	4.076072	-1.556893	1.733353
30	1	0	2.437794	0.232538	1.679844
31	1	0	-1.268258	-0.645111	-0.752300
32	1	0	6.704228	-3.695422	0.508719
33	1	0	6.226663	-2.410762	1.653538
34	1	0	4.998807	-3.555048	1.018517

(Z)-TS2

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-4.123072	1.011705	-0.998946
2	6	0	-3.046134	0.673726	-0.143469
3	6	0	-3.230294	-0.402759	0.768117
4	6	0	-4.446738	-1.040852	0.859180
5	6	0	-5.531822	-0.633783	0.050071
6	6	0	-5.360256	0.395614	-0.893879
7	6	0	-1.855223	1.441279	-0.289021
8	6	0	-0.856724	1.789149	0.669365
9	6	0	0.295171	2.650445	0.234868
10	7	0	1.213026	3.316688	-0.068346
11	8	0	-6.678874	-1.310625	0.232833
12	6	0	-7.819166	-0.988512	-0.573147
13	6	0	-0.789321	1.279850	1.931263
14	8	0	-0.445991	-0.297926	-1.058735
15	6	0	0.263556	-0.661218	-0.074190
16	7	0	1.681079	-0.559672	-0.350873
17	6	0	2.714236	-0.607454	0.532628
18	6	0	4.123427	-0.446799	-0.177645
19	17	0	4.382890	-1.863860	-1.266997

20	8	0	-0.102998	-1.014483	1.060916
21	8	0	2.662710	-0.761882	1.732258
22	17	0	4.148387	1.070170	-1.167988
23	17	0	5.417099	-0.377076	1.033243
24	1	0	-1.785248	1.989511	-1.222536
25	1	0	0.069138	1.505145	2.554128
26	1	0	-1.596921	0.716561	2.373760
27	1	0	-2.375776	-0.790194	1.309212
28	1	0	-4.588490	-1.884579	1.526521
29	1	0	-6.169614	0.700656	-1.545246
30	1	0	-3.984793	1.797587	-1.736210
31	1	0	1.883250	-0.341110	-1.319049
32	1	0	-8.608066	-1.662080	-0.240292
33	1	0	-8.124735	0.050911	-0.412578
34	1	0	-7.604479	-1.161517	-1.632893

(E)-9a

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-2.287278	1.224332	-0.934114
2	1	0	-1.966462	1.119140	-1.970001
3	6	0	-1.508398	2.038061	-0.187008
4	6	0	-3.471135	0.443532	-0.593087
5	6	0	-5.740585	-1.152040	-0.114676
6	6	0	-3.941462	-0.466927	-1.561112
7	6	0	-4.178572	0.539462	0.614345
8	6	0	-5.301140	-0.245001	0.857438
9	6	0	-5.051315	-1.257124	-1.331175
10	1	0	-3.413397	-0.554559	-2.507331
11	1	0	-3.869416	1.237899	1.383287
12	1	0	-5.823065	-0.139328	1.801021
13	1	0	-5.408364	-1.962441	-2.074475
14	8	0	-6.815204	-1.958288	0.028017
15	6	0	-7.544989	-1.892229	1.242682
16	1	0	-6.909936	-2.157138	2.094923
17	1	0	-8.349976	-2.619190	1.145746
18	1	0	-7.967638	-0.892511	1.390622
19	6	0	-0.323705	2.751179	-0.786806

20	1	0	-0.352194	2.686775	-1.875783
21	1	0	-0.280168	3.794867	-0.474518
22	8	0	0.915253	2.191768	-0.307831
23	6	0	1.296382	1.049369	-0.903228
24	8	0	0.742855	0.518874	-1.827779
25	7	0	2.451056	0.597895	-0.264319
26	1	0	2.775760	1.163949	0.513511
27	6	0	3.145361	-0.537923	-0.617400
28	6	0	4.408534	-0.772146	0.283030
29	17	0	5.501737	0.626908	0.094896
30	17	0	3.887880	-0.900331	1.984171
31	17	0	5.224439	-2.246308	-0.212214
32	8	0	2.864961	-1.291529	-1.505308
33	6	0	-1.694291	2.263021	1.217968
34	7	0	-1.791267	2.481814	2.352685

(Z)-9a

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	2.657993	2.021119	-0.549410
2	1	0	2.906009	2.757700	-1.313226
3	6	0	1.518876	2.244891	0.138561
4	6	0	3.650161	0.951859	-0.378754
5	6	0	5.646583	-1.008688	-0.116714
6	6	0	5.008233	1.273969	-0.558633
7	6	0	3.315206	-0.378589	-0.105796
8	6	0	4.299552	-1.356625	0.024414
9	6	0	5.995852	0.316297	-0.415098
10	1	0	5.288398	2.295638	-0.803513
11	1	0	2.271992	-0.671335	-0.038547
12	1	0	4.001526	-2.380331	0.218304
13	1	0	7.045254	0.563190	-0.539996
14	8	0	6.676378	-1.879561	-0.001158
15	6	0	6.372523	-3.236194	0.277121
16	1	0	5.848113	-3.331553	1.234374
17	1	0	7.330663	-3.751042	0.332066

18	1	0	5.765257	-3.673361	-0.523082
19	6	0	1.021788	1.514506	1.362586
20	1	0	1.582708	0.600251	1.548212
21	1	0	1.087100	2.168293	2.234754
22	8	0	-0.382654	1.227363	1.260501
23	6	0	-0.720239	0.150411	0.534071
24	8	0	0.044772	-0.638611	0.048409
25	7	0	-2.109541	0.107028	0.451566
26	1	0	-2.603358	0.882292	0.882984
27	6	0	-2.821543	-0.888947	-0.181760
28	6	0	-4.369131	-0.640191	-0.136939
29	17	0	-4.882483	-0.560504	1.571335
30	17	0	-4.719704	0.912798	-0.939801
31	17	0	-5.203220	-1.950027	-0.957694
32	8	0	-2.359052	-1.854833	-0.717828
33	6	0	0.717007	3.383904	-0.231430
34	7	0	0.048903	4.290193	-0.505894

VIII. References

1. A. Bouziane, M. Hélou, B. Carboni, F. Carreaux, B. Demerseman, C. Bruneau, J.-L. Renaud, *Chem. Eur. J.* **2008**, *14*, 5630-5637.
2. D. E. Latham, K. Polidano, J. M. J. Williams, L. C. Morrill, *Org. Lett.* **2019**, *21*, 7914-7918.
3. C. Rasson, A. Stouse, A. Boreux, V. Cirriez, O. Riant, *Chem. Eur. J.* **2018**, *24*, 9234-9237.
4. M. S. Santos, D. C. Fernandes, M. T. Rodrigues Jr., T. Regiani, A. D. Andricopulo, A. L. T. G. Ruiz, D. B. Vendramini-Costa, J. E. de Carvalho, M. N. Eberlin, F. Coelho, *J. Org. Chem.* **2016**, *81*, 6626-6639.
5. D. Seebach, R. Henning, T. Mukhopadhyay, *Chem. Ber.* **1982**, *115*, 1705-1720.
6. F. Coelho, W. P. Almeida, D. Veronese, C. R. Mateus, E. C. S. Lopes, R. C. Rossi, G. P. C. Silveira, C. H. Pavam, *Tetrahedron*, **2002**, *58*, 7437-7447.
7. Y.-L. Liu, X.-H. Xu, F.-L. Qing, *Tetrahedron. Lett.* **2019**, *60*, 953-956.
8. N.-F. Yang, H. Gong, W.-J. Tang, Q.-H. Fan, C.-Q. Cai, L.-W. Yang, *J. Mol. Cat. A*, **2005**, *233*, 55-59.
9. G. M. Sheldrick, *Acta Cryst.* **2015**, *A71*, 3-8.
10. G. M. Sheldrick, *Acta Cryst.* **2015**, *C71*, 3-8.