

Supporting information

Kinetic Analysis as an Optimization Tool for Catalytic Esterification with a Moisture Tolerant Zirconium Complex

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1. NMR studies of complex Zr(Cp)₂(CF₃SO₃)₂·THF

To a standard NMR tube were added ¹³C(1)-benzoic acid (0.01 mmol, 1.2 mg) and 0.5 mL d₈-toluene, and a ¹³C-NMR spectrum was recorded (Figure S1). Thereafter, the tube was opened and Zr(Cp)₂(CF₃SO₃)₂·THF (0.01 mmol, 5.9 mg) was added, followed by recording of a second ¹³C-NMR spectrum (Figure S2) at 80 °C. We observed limited solubility of the Zr-complex in d₈-toluene at low reactant concentrations, hence the subsequent NMR-experiment was effectively performed using a saturated Zr-solution with excess carboxylic acid. The ¹³C-NMR spectra were recorded at 100.6 MHz on a Bruker DRX-400 spectrometer using a 5 mm inverse broadband NMR probe head. The temperature was measured using a calibrated Pt-100 resistance thermometer and adjusted using a Bruker Eurotherm variable temperature control unit. The ¹³C-NMR spectra were referenced to the methyl signal (20.43 ppm) of the deuterated toluene solvent measured at 298 K.

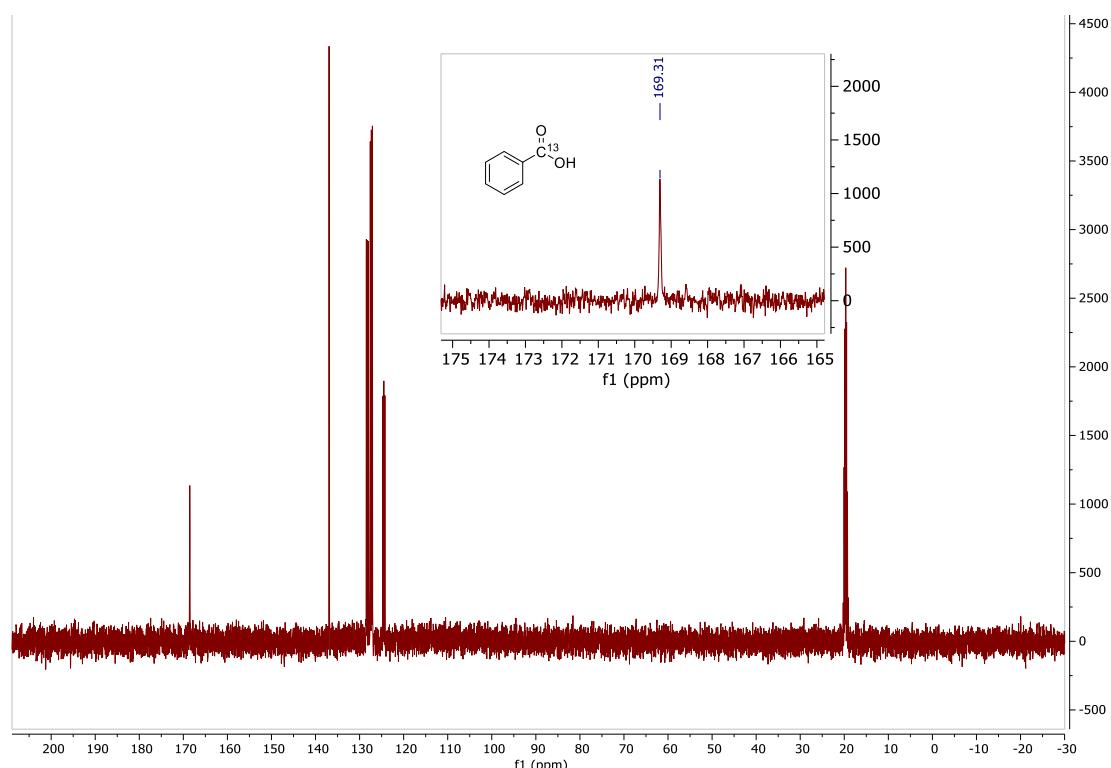


Figure S1: ¹³C-NMR of ¹³(C1)-benzoic acid (0.01 mmol, 0.02 M) in d₈-toluene at 80 °C

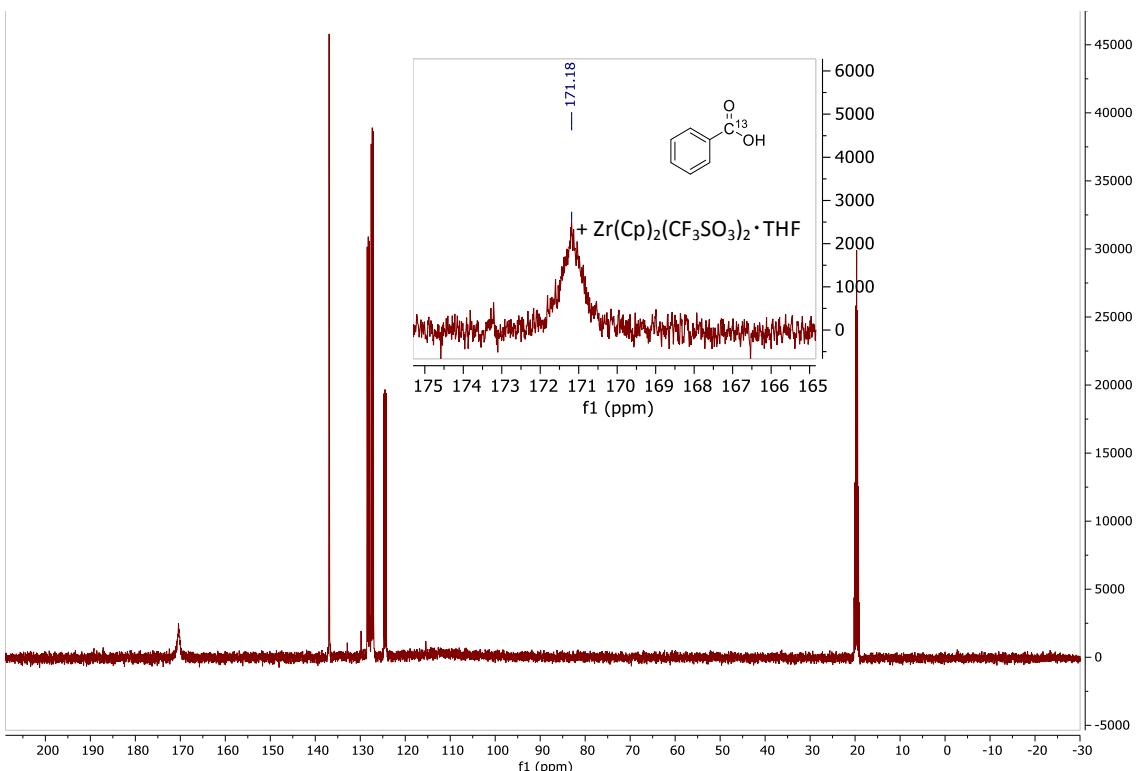


Figure S2: ^{13}C -NMR of $^{13}(\text{C1})\text{-benzoic acid}$ (0.01 mmol, 0.02 M) in d_8 -toluene at 80 °C after addition of 0.01 mmol $\text{Zr}(\text{Cp})_2(\text{CF}_3\text{SO}_3)_2\cdot\text{THF}$.

2. Kinetic evaluation of reaction parameters

2.1. Reproducibility

The reproducibility was evaluated by comparison of rate data from three identical reactions, indicating good overlay (Figure S3).

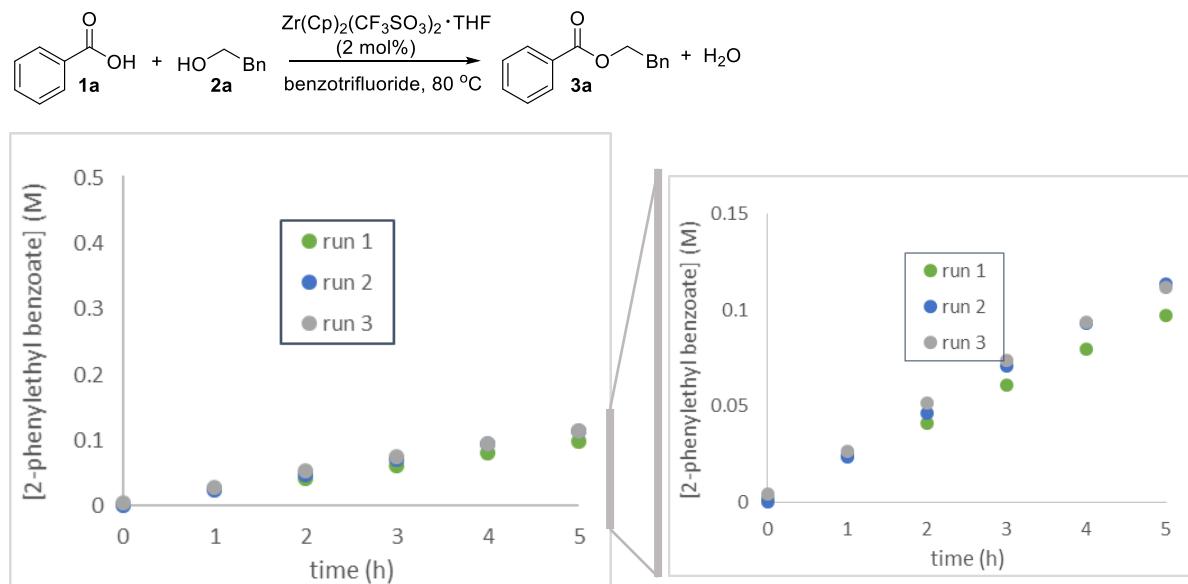


Figure S3 Left: Reproducibility of kinetic data from four individual reactions with identical conditions. Conditions: 0.5 M benzoic acid (**1a**), 0.5 M 2-phenylethanol (**2a**), 0.01 M (2 mol%) $\text{Zr}(\text{Cp})_2(\text{CF}_3\text{SO}_3)_2\cdot\text{THF}$, benzotrifluoride, 80 °C, ambient atmosphere. **Right:** Magnification of the figure on the left.

2.2. Solvent evaluation at synthetic conditions

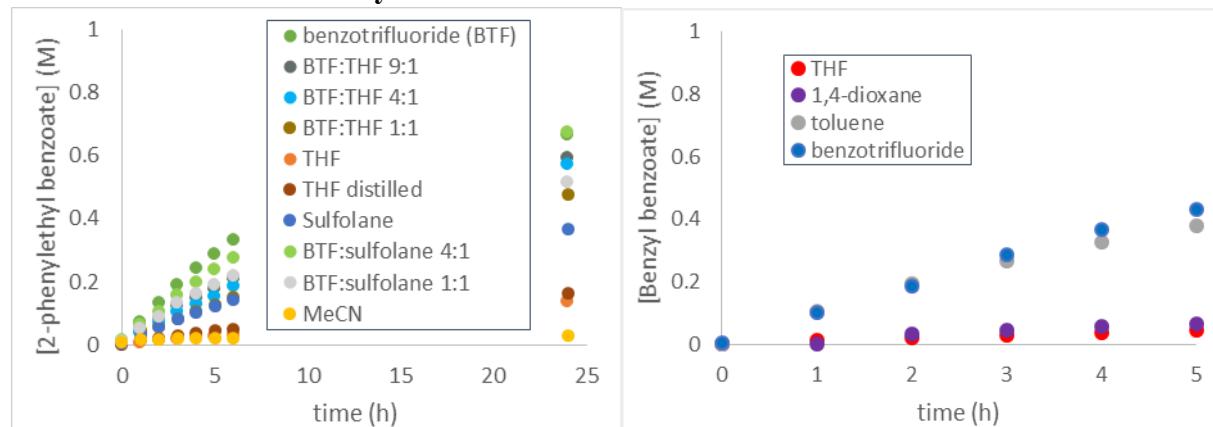


Figure S4. Solvent evaluation. Conditions: 1 M benzoic acid, 1 M 2-phenylethanol or benzyl alcohol, 0.02 M (2 mol%) $Zr(Cp)_2(CF_3SO_3)_2$ -THF, solvent(s), 80 °C, ambient atmosphere.

2.3. VTNA analysis of order in [catalyst]

The rate dependence on catalyst concentration was evaluated based on the kinetics for sets of reactions with different catalyst concentrations. Graphic analysis of the product concentration versus the time independent catalyst concentration in accordance with VTNA (Reference 13 in main text) indicated that the order in catalyst was approximately 0.75 at different global concentrations using equimolar ratios of alcohol to acid (Figure S5 and S6).

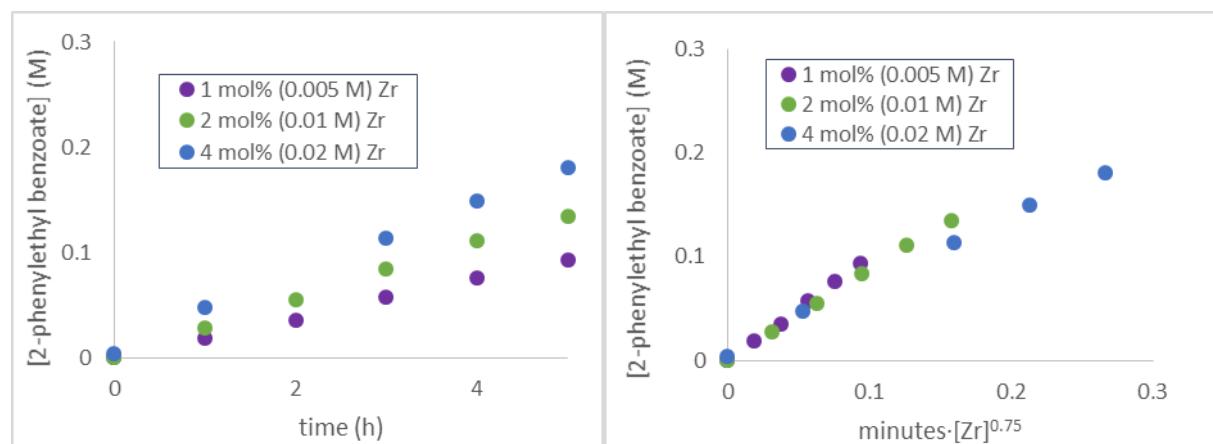


Figure S5. Different catalyst concentrations at equimolar ratios of alcohol and carboxylic acid (0.5 M global concentration). Conditions: 0.5 M benzoic acid, 0.5 M 2-phenylethanol, benzotrifluoride, 80 °C, ambient atmosphere

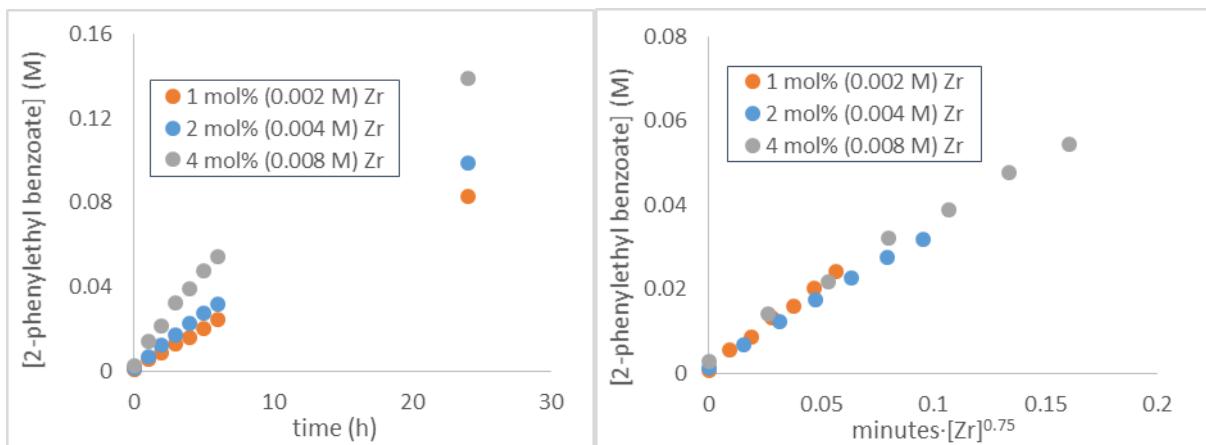


Figure S6. Different catalyst concentrations at equimolar ratios of alcohol and carboxylic acid (0.2 M global concentration). Conditions: 0.2 M benzoic acid, 0.2 M 2-phenylethanol, benzotrifluoride, 80 °C, ambient atmosphere.

2.4. Concentration experiments

Various concentrations of equimolar reactions were tested (Table S1). Due to observed side products for the initial substrate combination at high concentrations (see main article), reactant concentrations of 0.5 M were chosen to assess the kinetic profiles. After *different* and *same excess* reactions (main article) it was found that reactant concentrations of 1 M was tolerated for the benchmark substrates benzoic acid **1a** and 2-phenylethanol **2a**, resulting in increased fractional yield as a result of higher catalyst concentration due to lower solvent volume (Figure S7). Further increase of global concentrations by reduction of solvent was not beneficial to fractional product yield and reactant concentrations of 1 M was assessed to be the best for the substrate scopes.

Table S1. Reaction mixture concentration and the corresponding solvent volume for a 1 mmol scale reaction.

Entry	Substrate concentration (M)	Volume benzotrifluoride (mL)
1	2	0.5
2	1	1
3	0.5	2
4	0.2	5

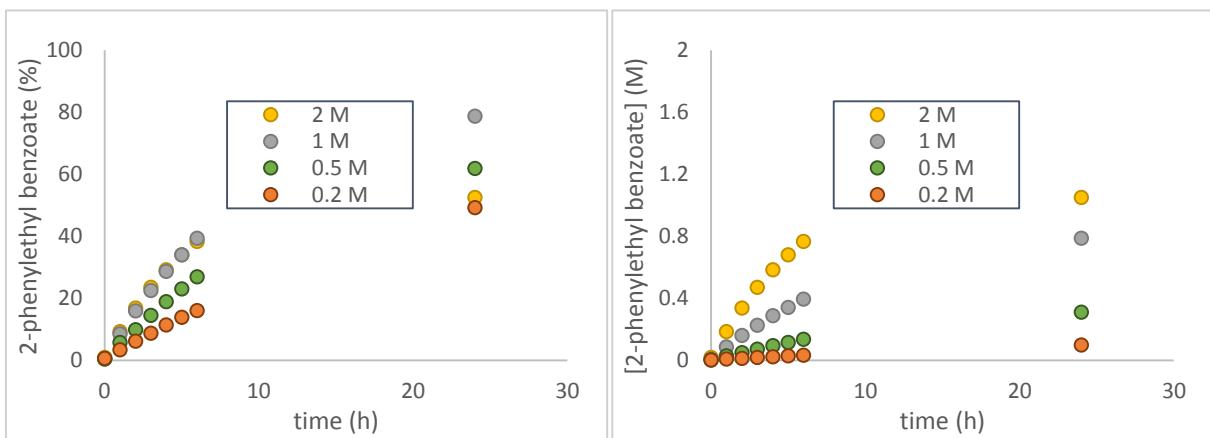


Figure S7. Variations of global concentrations as a function of solvent volume. Conditions: 1 mmol benzoic acid, 1 mmol 2-phenylethanol, 0.02 mmol (2 mol%) $Zr(Cp)_2(CF_3SO_3)_2\cdot THF$, benzotrifluoride, 80 °C, ambient atmosphere.

2.5. Effect of added water and effect of molecular sieves

Comparison of triflic acid and $Zr(Cp)_2(CF_3SO_3)_2\cdot THF$ as catalysts in the formation of 2-phenylethyl benzoate

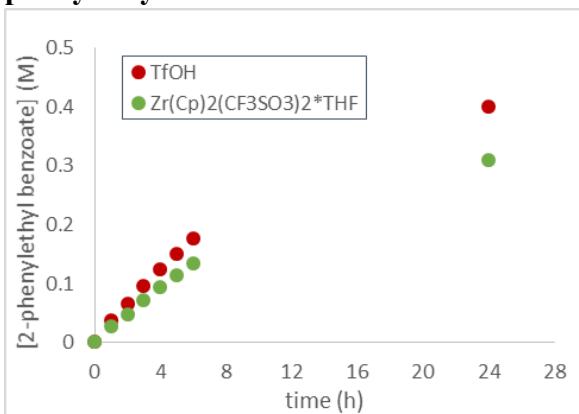


Figure S8. Formation of 2-phenylethyl benzoate catalyzed by either $Zr(Cp)_2(CF_3SO_3)_2\cdot THF$ or CF_3SO_3H (triflic acid, TfOH) - General esterification procedure A.

Effect of added water in the formation of 2-phenylethyl benzoate

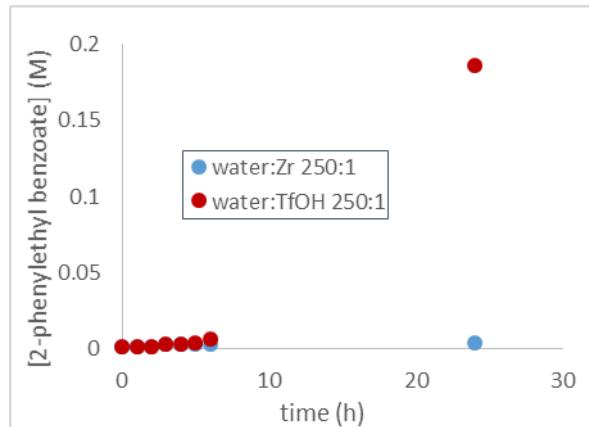


Figure S9. Comparison of the effect of water ($90 \mu\text{L}$) on the formation of 2-phenylethyl benzoate catalyzed by either $\text{Zr}(\text{Cp})_2(\text{CF}_3\text{SO}_3)_2\cdot\text{THF}$ (2 mol%) or $\text{CF}_3\text{SO}_3\text{H}$ (triflic acid, TfOH, 2 mol%) in 0.5 equimolar reaction in 1 mmol scale (General esterification procedure A).

Effect of molecular sieves in the reaction mixture

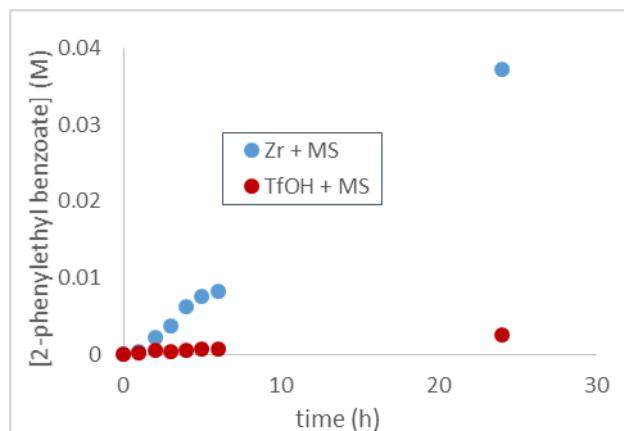
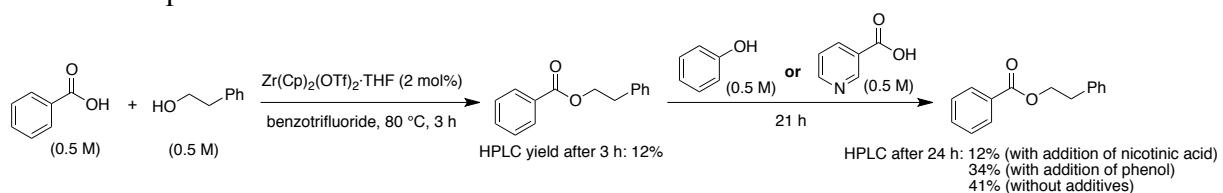


Figure S10. Comparison of the effect of molecular sieves (100 mg, 3 Å, flame-dried under vacuum) on the formation of 2-phenylethyl benzoate catalyzed by either $\text{Zr}(\text{Cp})_2(\text{CF}_3\text{SO}_3)_2\cdot\text{THF}$ (2 mol%) or $\text{CF}_3\text{SO}_3\text{H}$ (triflic acid, TfOH, 2 mol%) in 0.5 equimolar reaction in 1 mmol scale (General esterification procedure A).

2.6 Effect of phenols and pyridinic carboxylic acids on the reaction

Addition of phenol or nicotinic acid to the standard esterification reaction:



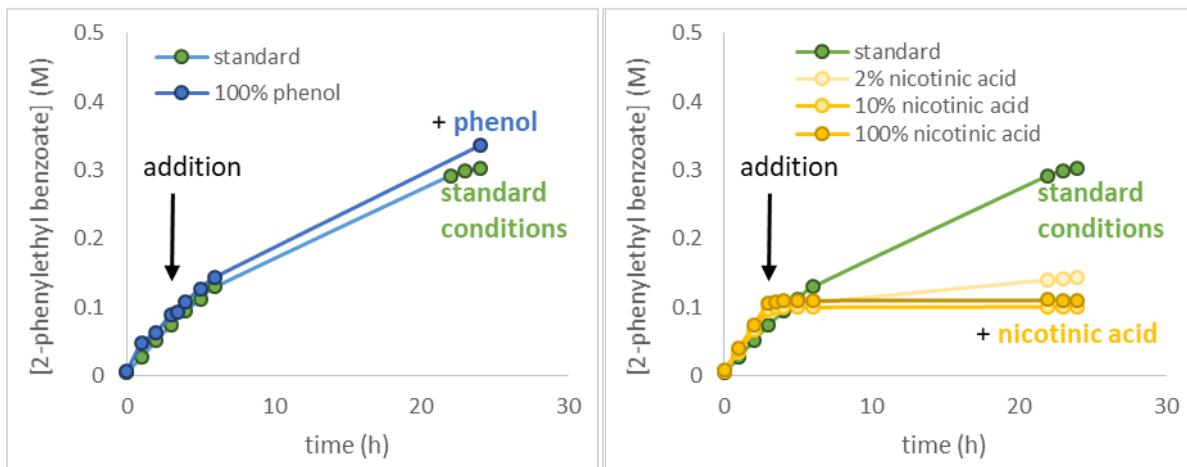
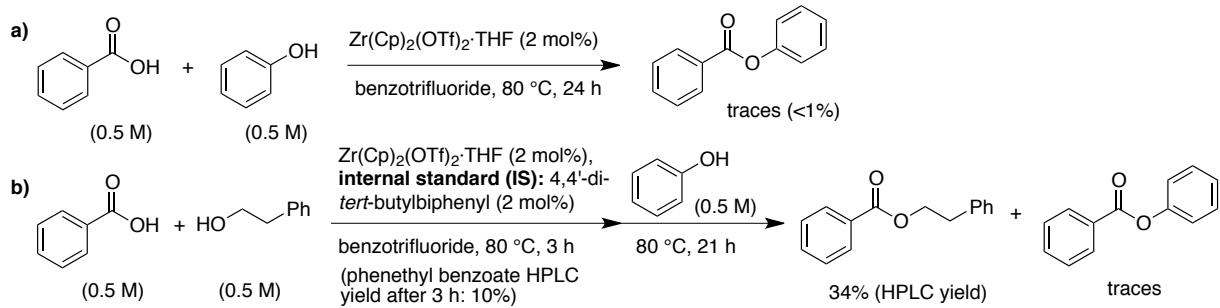
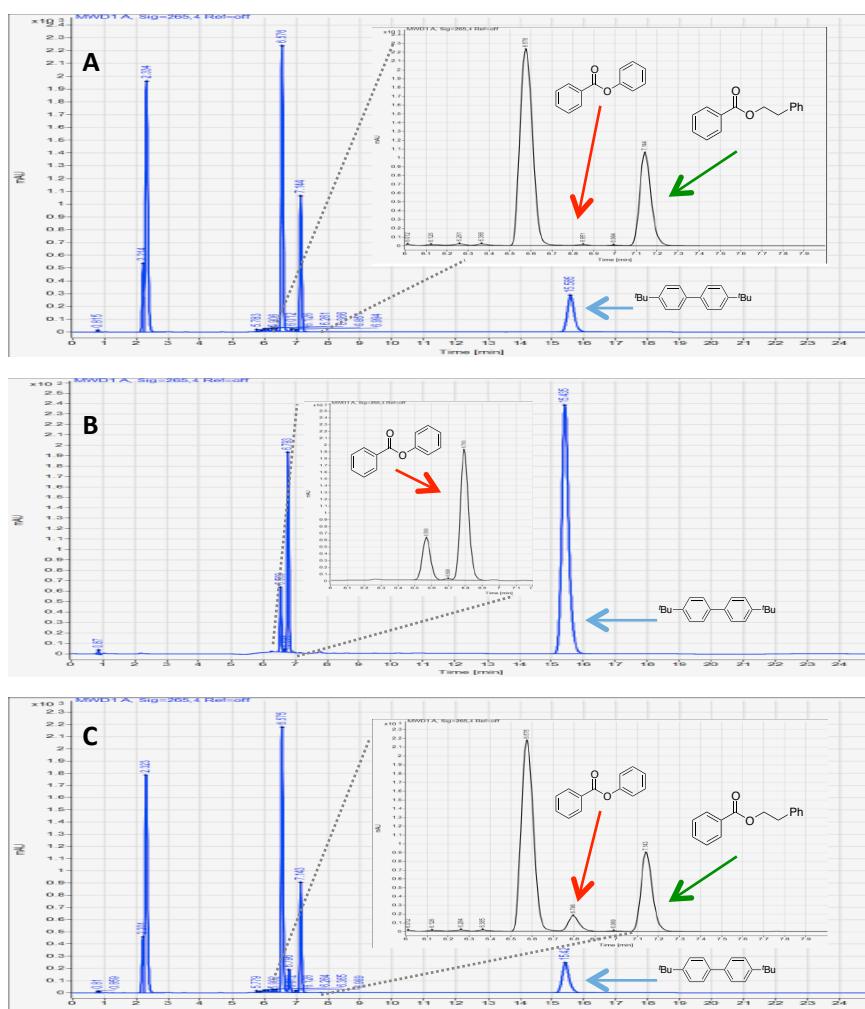


Figure S11. Formation of 2-phenylethyl benzoate as a function of the addition of phenol (1 equiv.) (left) and nicotinic acid (2 mol%, 10 mol% or 1 equiv.) (right) after three hours. Standard reaction conditions for equimolar ratios of alcohol and acid at 0.5 M global concentration.

Only traces (*ca* 1%) of phenyl benzoate was formed and isolated in the esterification attempt with phenol (Scheme S1a). In the standard reaction mixture where phenol was added after 3 hours (Scheme S1b) 2-phenylethyl benzoate was observed as the major expected product with only faint traces of phenyl benzoate (Figure S12).



Scheme S1. a) Esterification with benzoic acid and phenol; b) esterification with benzoic acid and 2-phenylethanol, addition of phenol after 3 h.



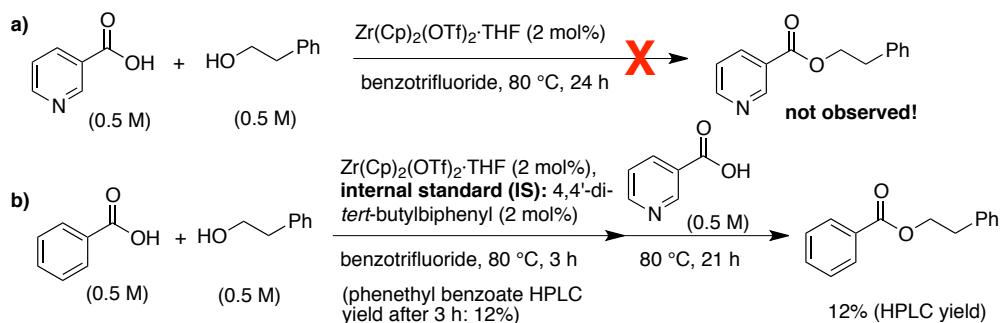
Reaction mixture
after 24 h.
Phenyl benzoate (traces,
Rt = 6.7 min),
2-phenylethyl benzoate
(34%, Rt = 7.1 min),
IS (Rt = 15.5 min).

Isolated phenyl
benzoate (Rt = 6.8 min)
with IS (Rt = 15.4 min)

Reaction mixture
**after 24 h with
added phenyl benzoate.**
phenyl benzoate
(Rt= 6.8 min),
phenethyl benzoate
(Rt = 7.1 min),
IS (Rt= 15.4 min)

Figure S12. HPLC chromatograms of the reaction mixture with added phenol and internal standard after 24 h (A), isolated phenyl benzoate with internal standard (B), isolated phenyl benzoate added to reaction mixture after 24 h (C). Enlargements of the relevant areas are shown for each chromatogram.

For the esterification reaction with nicotinic acid no product was observed and starting materials were recovered quantitatively (Scheme S2a). Similarly, we did not observe any formation of pyridinic products after addition of nicotinic acid to the standard reaction after 3 h from reaction onset (Scheme S2b). The 2-phenylethyl benzoate yield at 3 h had reached 12% (analyzed by HPLC), after addition of nicotinic acid, the 2-phenylethyl benzoate yield stayed the same over 24 h (24 h HPLC yield: 12%, Figure S13).



Scheme S2. a) Esterification attempt with nicotinic acid and 2-phenylethanol; b) esterification with benzoic acid and 2-phenylethanol, addition of nicotinic acid after 3 h.

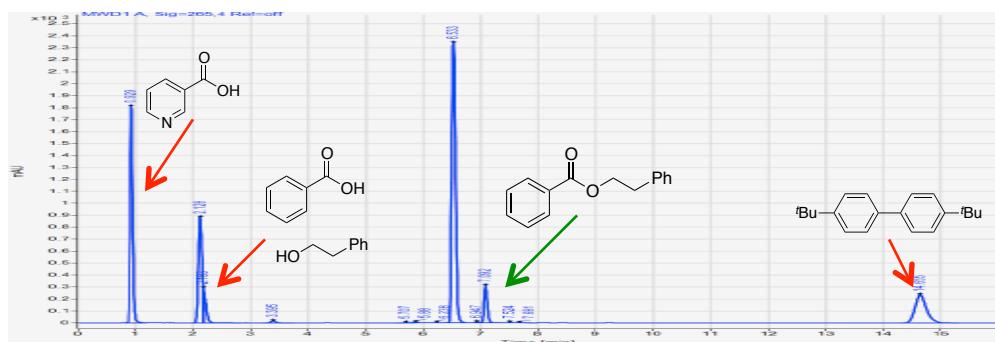
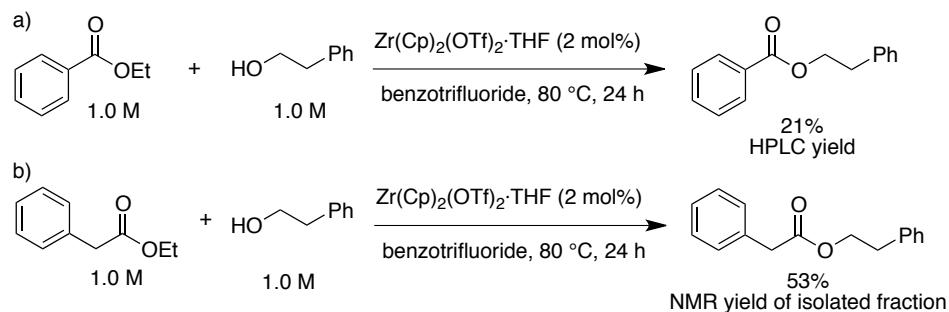


Figure S13. HPLC chromatogram of the reaction mixture with internal standard and nicotinic acid after 24 h.

3. Transesterification

Transesterification reactions were carried out according to the general esterification procedure in 1 mmol scale, with either ethyl benzoate or ethyl phenylacetate used instead of corresponding carboxylic acids (Scheme S3). The formed esters were difficult to isolate from the ester substrates due to their very similar R_f values. Thus, the transesterification was either assessed by HPLC analysis or NMR yield was given to the isolated mixture of two esters. Transesterification of ethyl benzoate with 2-phenylethanol gave the product in 21% yield (HPLC analysis, see Figure S14), and ethyl phenylacetate under same conditions gave 53% (inseparable mixture by flash chromatography, NMR yield from isolated fraction, see Figure S15).



Scheme S3. Transesterification of a) ethyl benzoate; b) ethyl phenylacetate

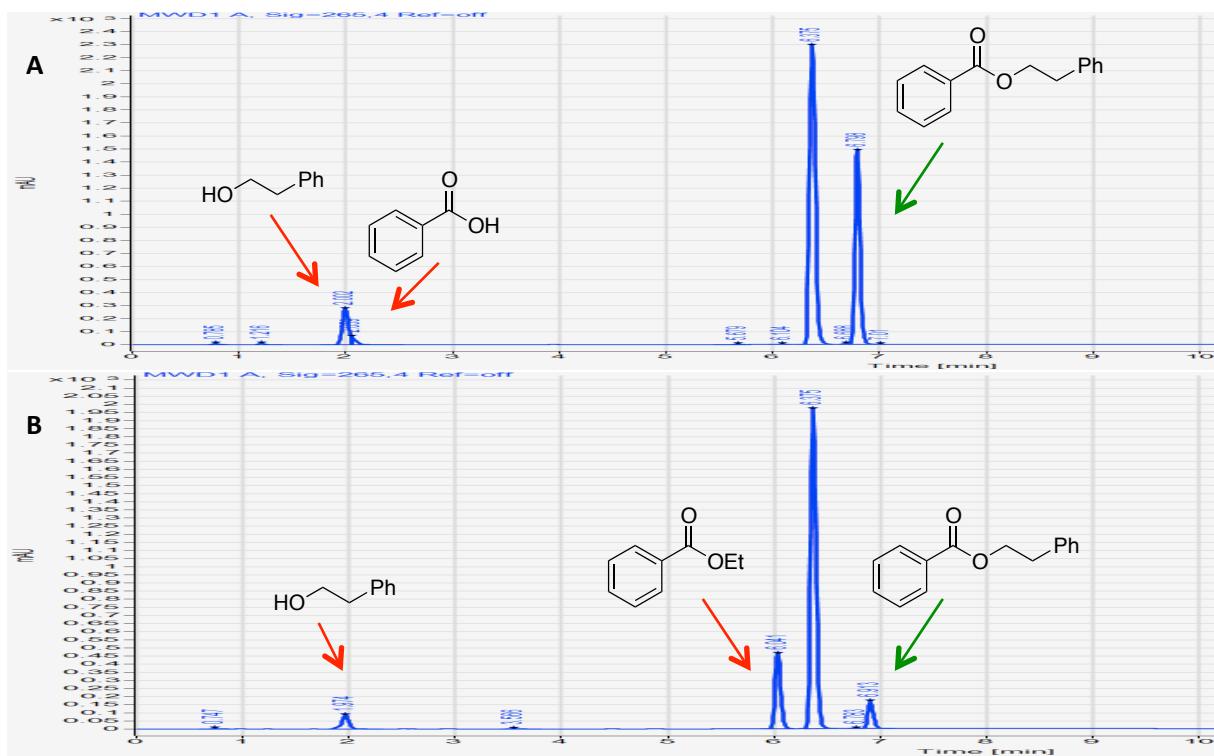


Figure S14. HPLC chromatograms for reactions after 24 h for (A) esterification of benzoic acid with 2-phenylethanol (66%); (B) transesterification of ethyl benzoate with 2-phenylethanol (21%).

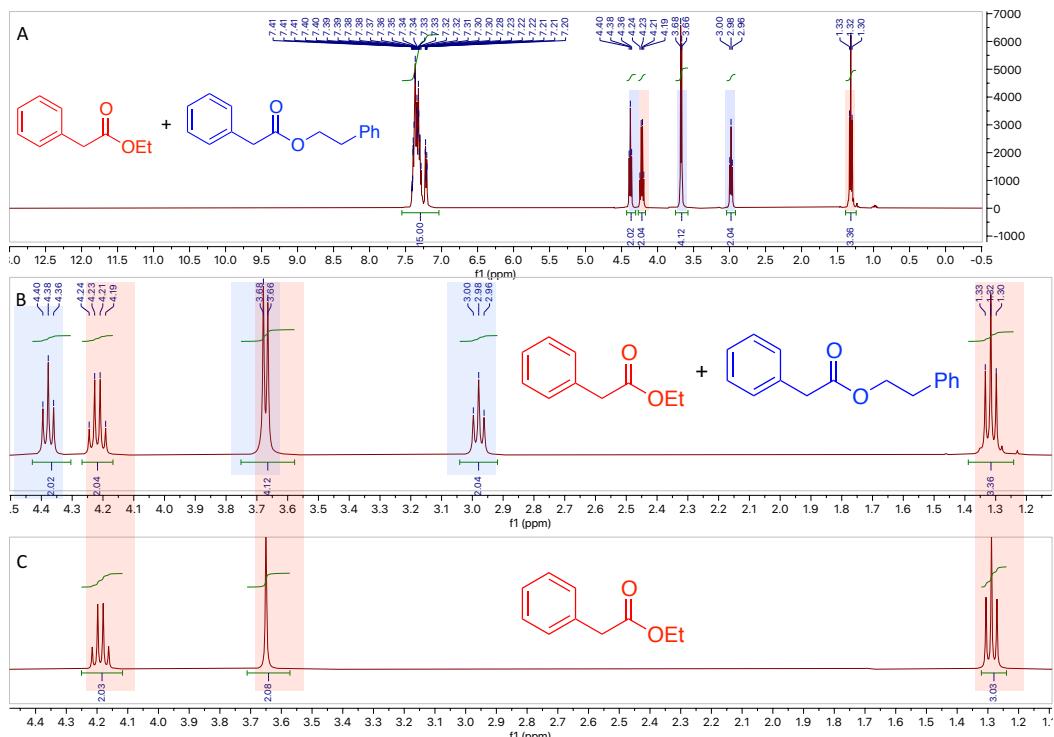
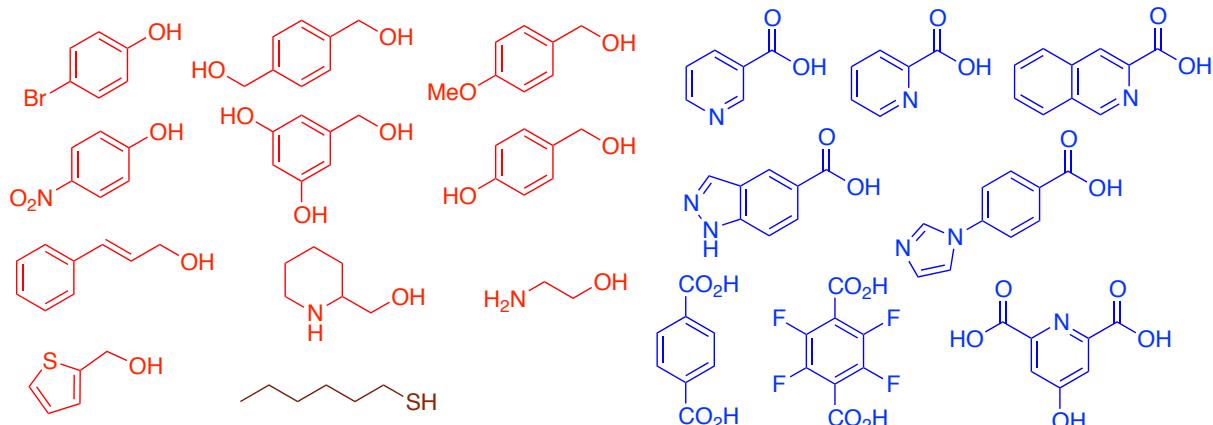


Figure S15. ^1H NMR spectrum of (A) mixture of ethyl phenylacetate and phenylethyl phenylacetate as isolated fraction, full spectrum; (B) enlargement of the spectrum in A; (C) isolated ethyl phenylacetate, enlarged spectrum.

4. Incompatible substrates

a) None or only traces of esterification products observed:



b) Low amount of esterification product observed and isolated (>1%):

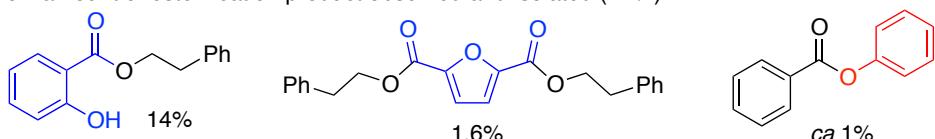


Figure S16. a) Alcohols and carboxylic acids yielding no or only faint traces (<1%) of esterification products under our conditions; b) Esterification products that were observed and isolated in low yields due to low conversion of starting material (>1% yield).

5. Turnover number and frequency

The turnover number (TON) for the first six hours was calculated to 19.7 (Eqn. 3) according to the definition in Equation 1 for a standard reaction with the following reactant concentrations: 0.02 M $\text{Zr}(\text{Cp})_2(\text{CF}_3\text{SO}_3)_2 \cdot \text{THF}$, 1 M benzoic acid and 1 M 2-phenylethanol. For the same reaction and time span this represents a turnover frequency (TOF) of around 3.3 h^{-1} (Eqn. 4) according to the definition in Equation 2. The definitions in Equation 1-2 are adapted from reference 18 of the main text.

$$TON = \frac{[\text{benzoic acid}]}{[\text{Zr}]} \quad \text{Eqn. 1}$$

$$TOF = \frac{[\text{benzoic acid}]}{[\text{Zr}] \times \text{time}} = \frac{TON}{\text{time}} \quad \text{Eqn. 2}$$

$$TON = \frac{[0.394]}{[0.02]} = 19.7 \quad (\text{during the first 6 hours of reaction time}) \quad \text{Eqn. 3}$$

$$TOF = \frac{[0.394]}{[0.02] \times 6} = 3.28 \text{ } h^{-1} \quad \text{Eqn. 4}$$

6. Estimation of activation energy using the Arrhenius equation

$$\text{Rate} = k \times [\text{catalyst}]^n \quad (n = \text{catalyst order}) \quad \text{Eqn. 5}$$

$$\text{Rate} = k \times [\text{Zr}]^{0.75} \quad \text{Eqn. 6}$$

$$k = \frac{\text{rate}}{[\text{Zr}]^{0.75}} \quad \text{Eqn. 7}$$

Units: concentration (M = mol/liter), rate (M/s), rate constant k (1/s)

Arrhenius equation: $k = A \times e^{(-E_a/RT)}$

Eqn. 8

$\ln(k) = \ln A - E_a/RT$

Eqn. 9

Units: rate constant k (s^{-1}), Activation energy E_a (J/mol), gas constant R (J/(mol·K)) = 8.314, temperature T (K)

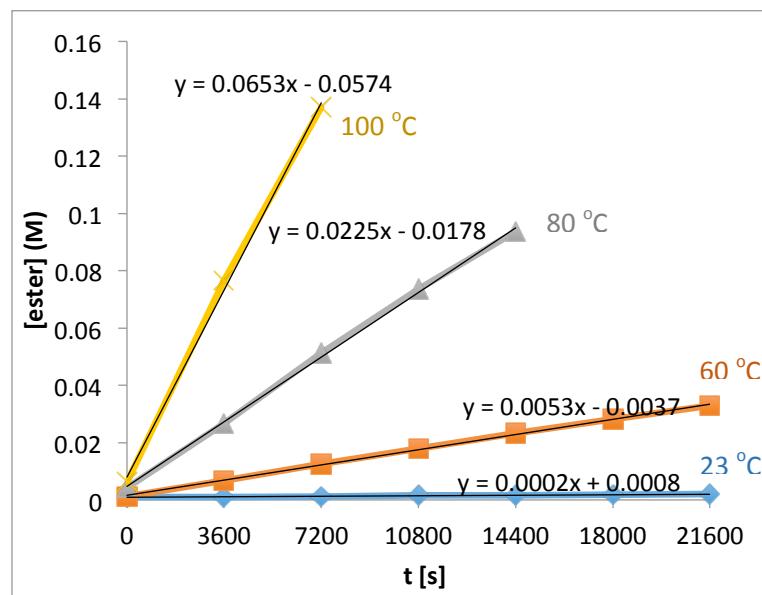


Figure S17. Linear regressions for reactions at different temperatures (replotted temperature data from Figure 1 in main article)

Table S2. Table of data derived from Figure S17

temp (K)	296	333	353	373
temp (°C)	23	60	80	100
rate	0.0002	0.0053	0.0225	0.0653
$k = \text{rate}/[\text{Zr}]^{0.75}$	0.00632456	0.16760072	0.711512474	2.06496731
1/T (1/K)	0.00337838	0.003003	0.002832861	0.00268097
$\ln(k)$	-5.0633156	-1.7861708	-0.34036233	0.7251144

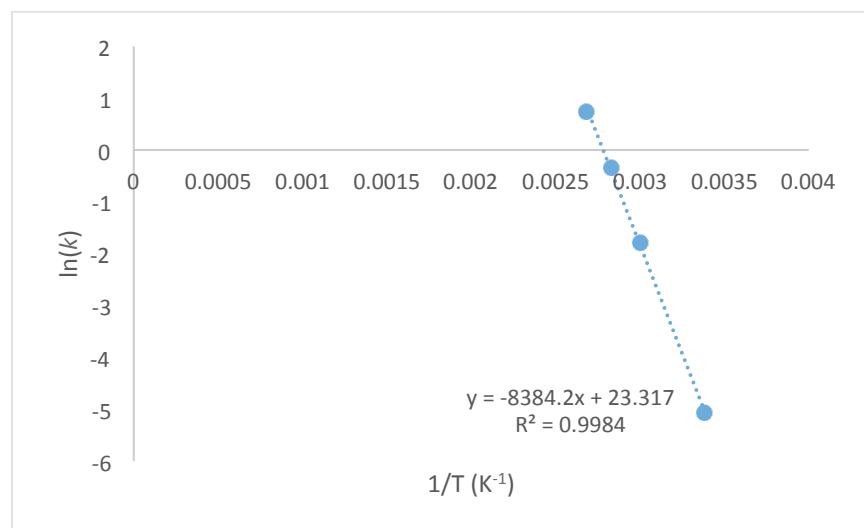


Figure S18. Arrhenius plot (data from Table S2)

Microsoft Excel Regression Analysis was used to calculate the standard error for the linear regression in Figure S18. The data output for the Regression Analysis is found in Figure S19.

SUMMARY OUTPUT							
Regression Statistics							
Multiple R	0,999198652						
R Square	0,998397947						
Adjusted R Square	-2						
Standard Error	0,123435524						
Observations	1						
ANOVA							
	df	SS	MS	F	Significance F		
Regression	4	18,9905328	4,7476332	1246,398226	#OGILTGT!		
Residual	2	0,030472657	0,01523633				
Total	6	19,02100546					
	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%	Lower 95.0% Upper 95.0%
Intercept							-1,089E-154 1,089E-154
X Variable 1							-4,3766E-153 4,3766E-153
X Variable 2							1,2503E-269 -2,0075E-269
X Variable 3	23,31690838	0,708924173	32,8905534	0,000923115	20,26665385	26,36716	20,26665385 26,36716291
X Variable 4	-8384,247624	237,4847273	-35,3043655	0,000801348	-9406,061934	-7362,43	-9406,061934 -7362,433313
Fit							
slope arrhenius (-E _a /R)	-8384,25				slope arrhenius (-E _a /R)	237,48	
R	8,31				R	8,31	
E _a	69706,63 J/mol				E _a	-1974,41 J/mol	
E _a	69,71 kJ/mol				E _a	-1,97 kJ/mol	
E _a	16,66 kcal/mol				E _a	-0,47 kcal/mol	
E _a = 16,7 kcal/mol					E _a = 16,7 ± 0,5 kcal/mol		

Figure S19. Output from Microsoft Excel Regression Analysis to estimate the activation energy for the formation of ester **3a**

7. Recycling experiments

The catalyst can be reused at least four times with negligible loss of activity for the formation of ester **3I** (Figure S20).

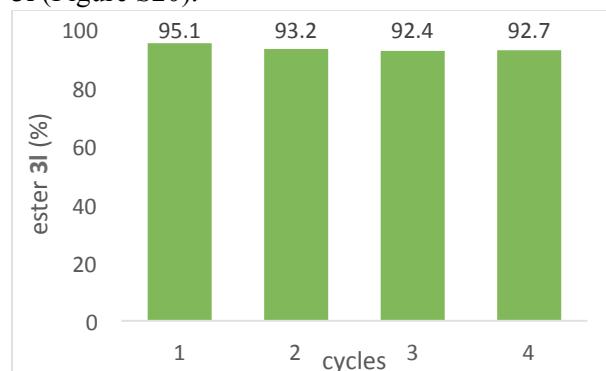


Figure S20. Recycling of catalyst for the formation of ester **3I**

Conditions: Phenylacetic acid (0.5 mmol, 1 M), 2-phenylethanol (0.5 mmol, 1 M), Zr(Cp)₂(CF₃SO₃)₂·THF (5.9 mg, 0.01 mmol, 0.02 M), benzotrifluoride, 80 °C, ambient atmosphere, 24 hours. Yields are determined by ¹H-NMR in d₄-MeOD as the product fraction of the mass of isolated product/starting material mixture after 24 hours, using the 10 protons in the aromatic region as internal standard. See Experimental Section in main article for experimental details on the recycling procedure.

8. HPLC chromatograms for esters 3t and 3ac

For **3t** the enantiomeric excess (*ee*) >99% was determined by HPLC analysis (Chiralcel OD-H 250x4.6 mm, 10% 2-propanol in hexane, 1.0 mL/min, $\lambda=225$ nm, 10 μ L injection volume, *S* isomer t(1)= 5.8 min. Compared against racemic mixture: *S* isomer t(1)= 5.8 min, *R* isomer t(2)= 6.6 min.

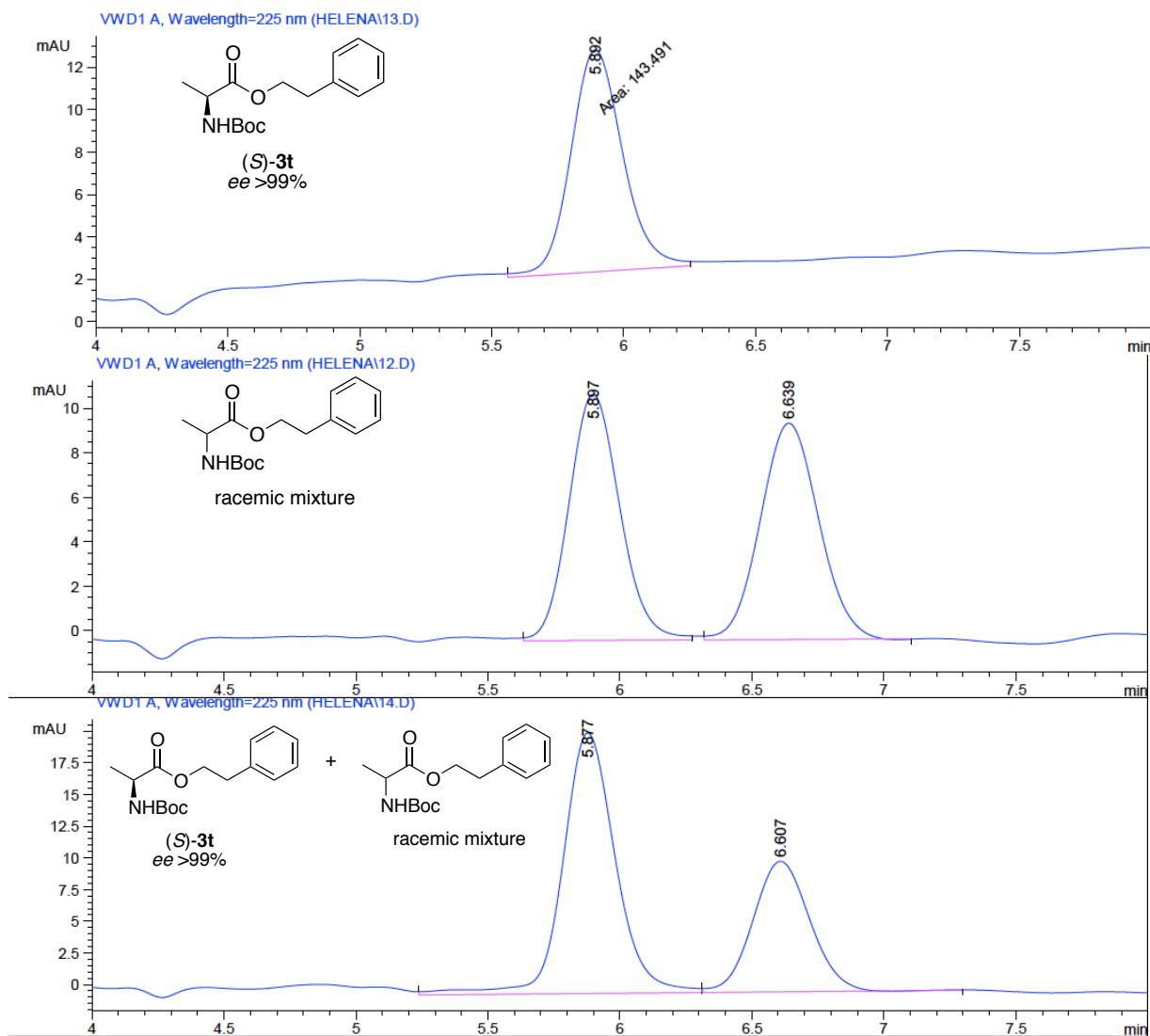


Figure S21. Chromatograms for the determination of enantiomeric excess (*ee*) of **3t**

For **3ad** the enantionmeric ratio *er* 99.18:0.82 (98.4% *ee*) was determined by HPLC analysis (ReproSil Chiral-NR 250x46 mm, 5% 2-propanol in hexane, 1.0 mL/min, $\lambda=225$ nm, 10 μ L injection volume, *R* isomer $t(1)=$ 10.2 min, *S* isomer $t(2)=$ 11.4 min. Compared against racemic mixture.

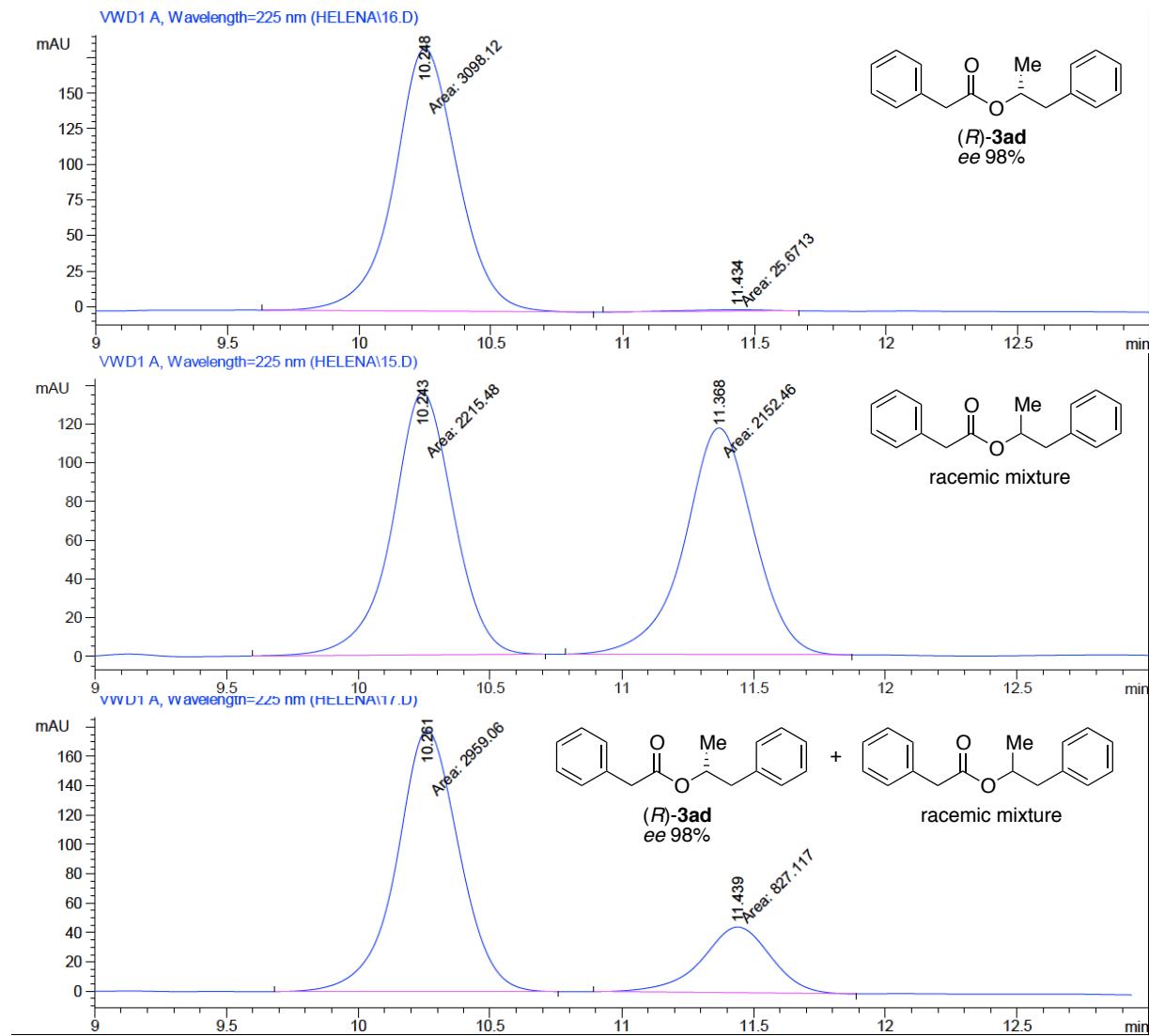
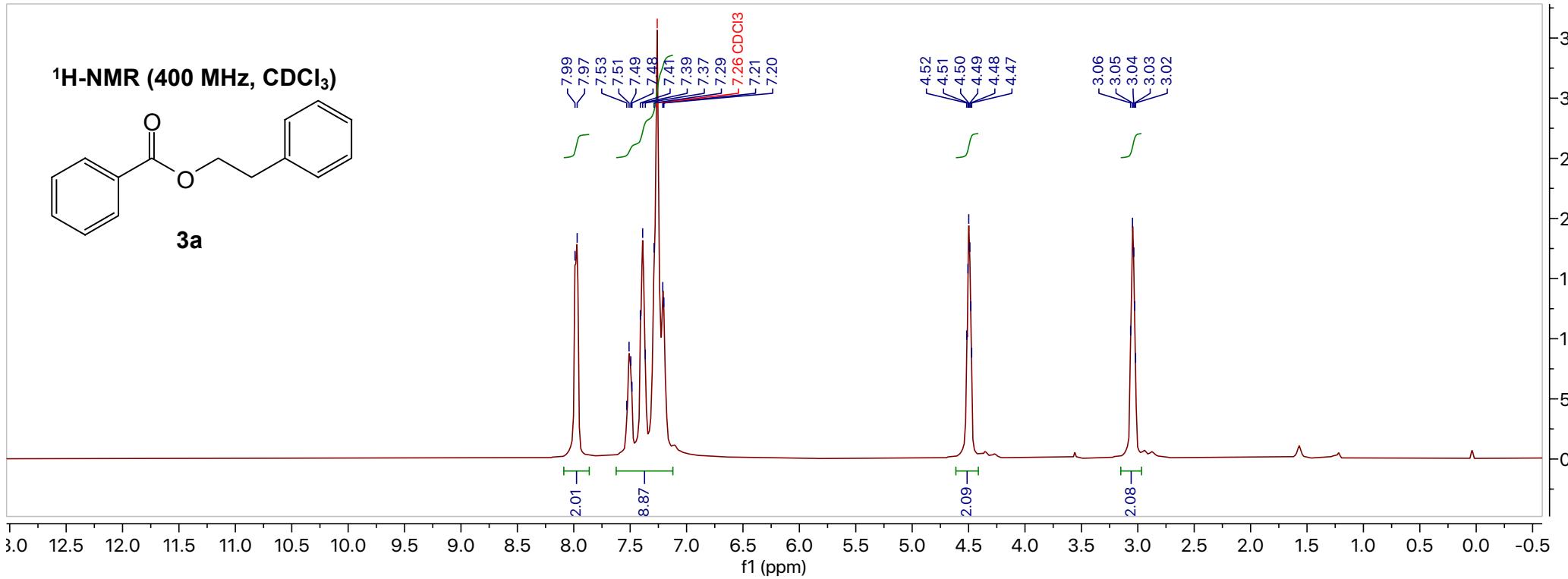
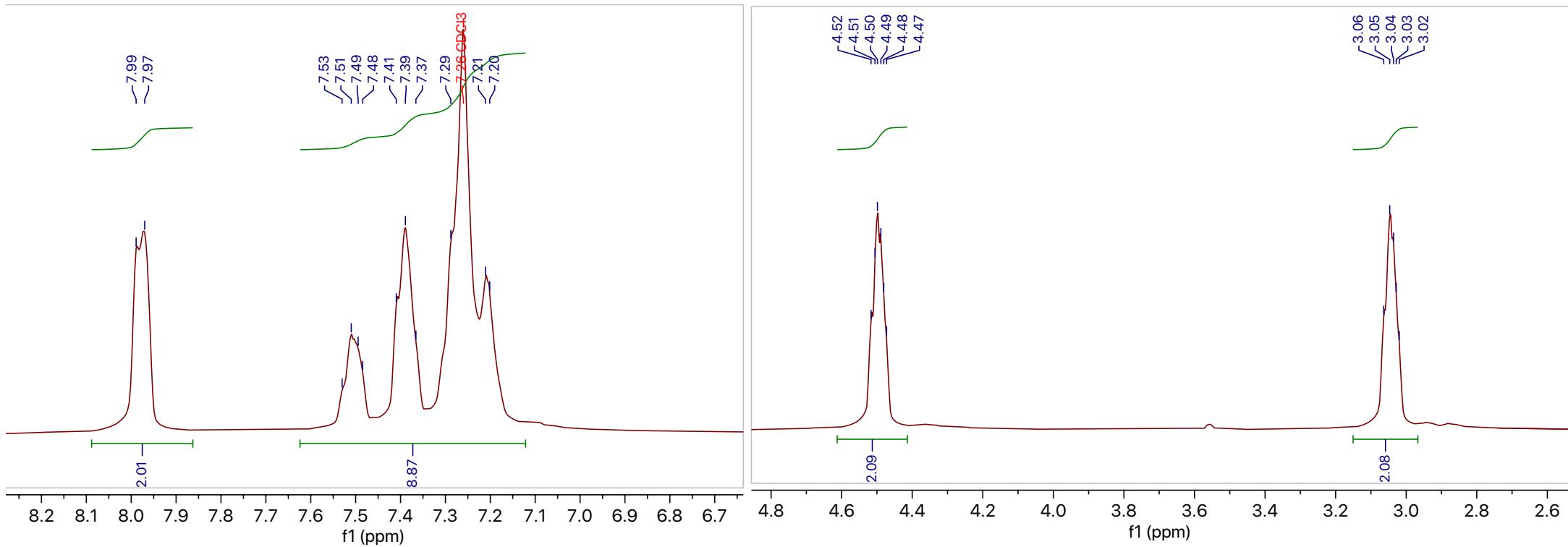
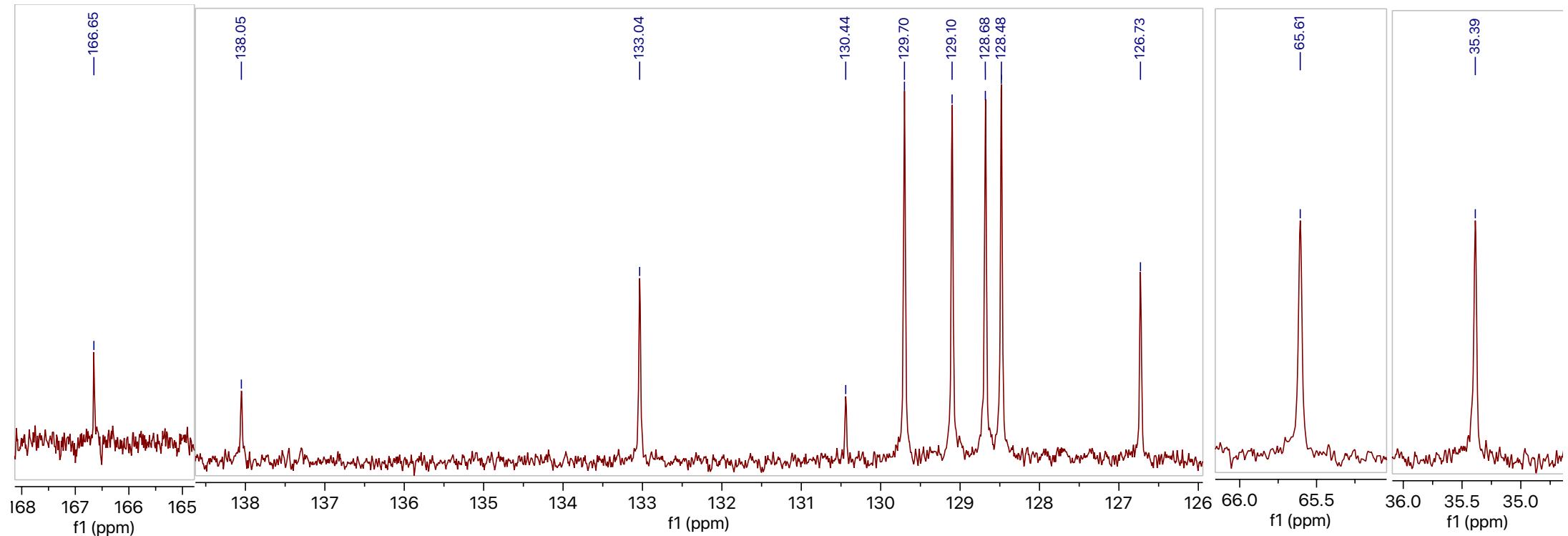


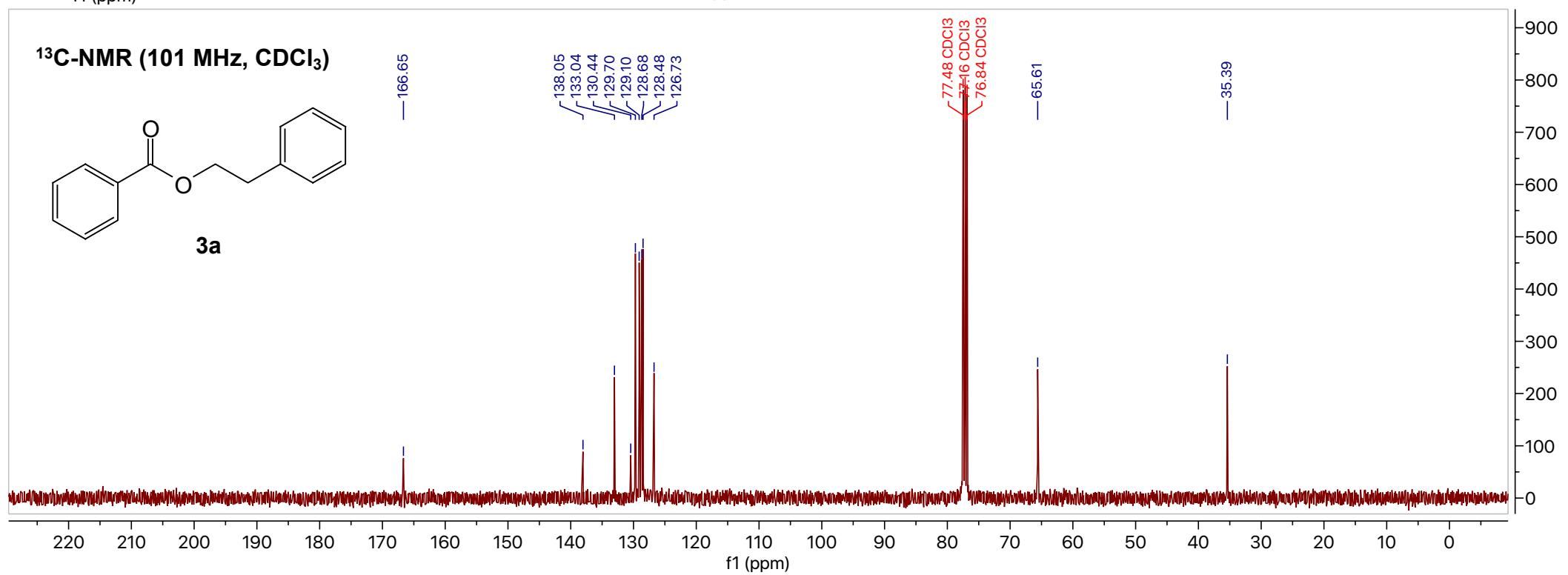
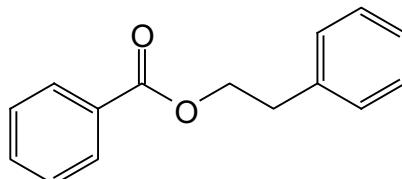
Figure S22. Chromatograms for the determination of enantiomeric excess (*ee*) of **3ad**

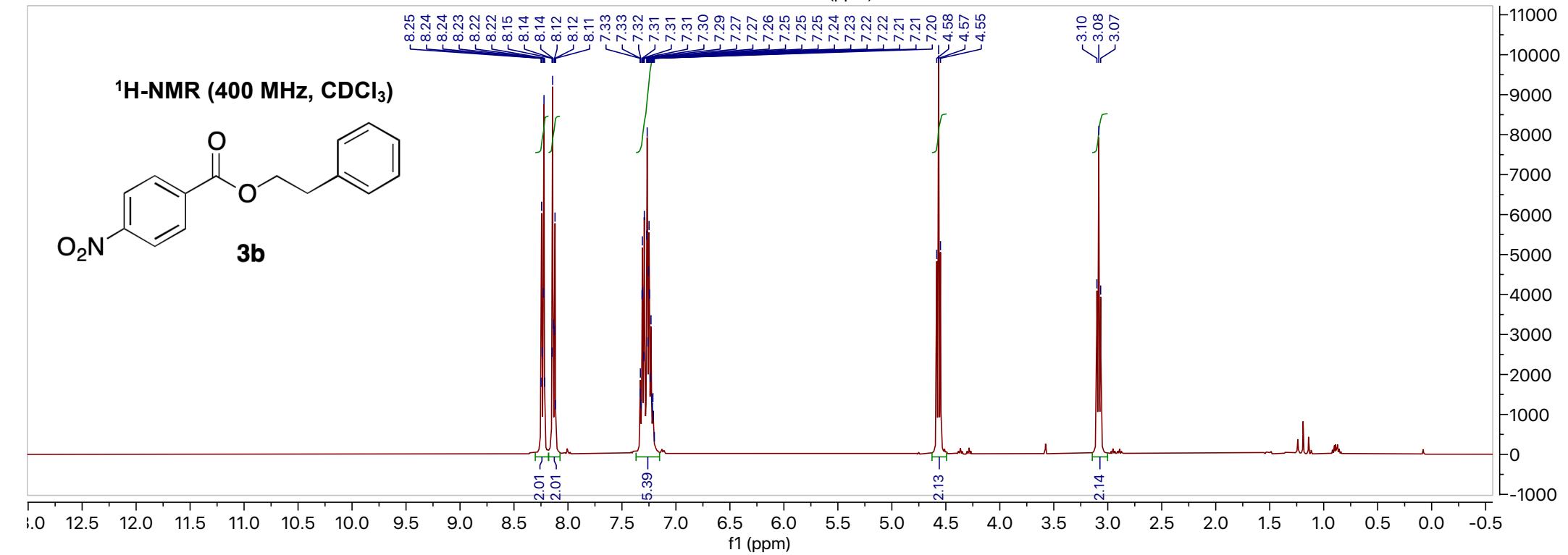
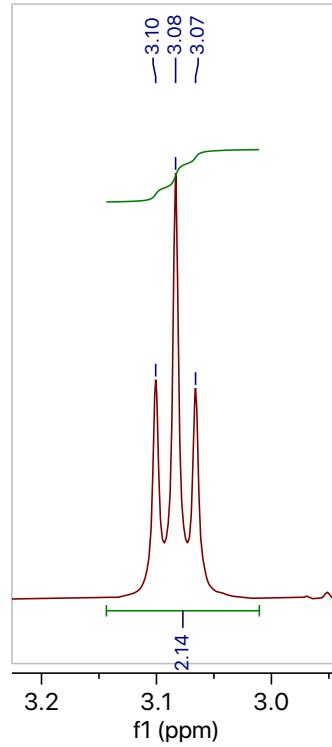
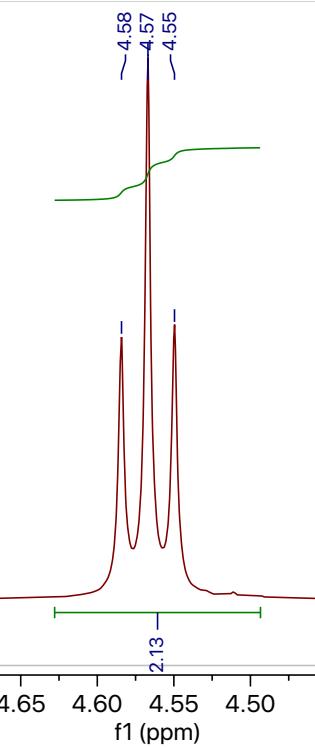
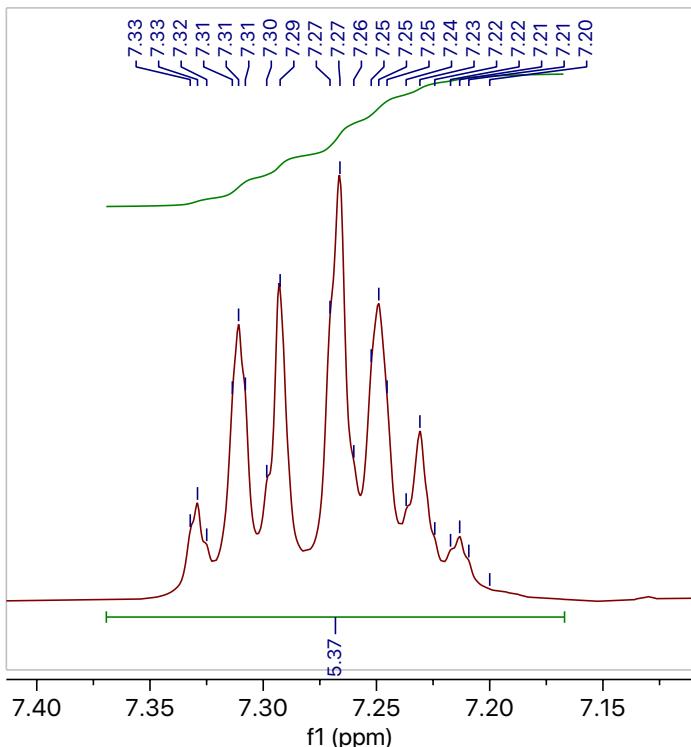
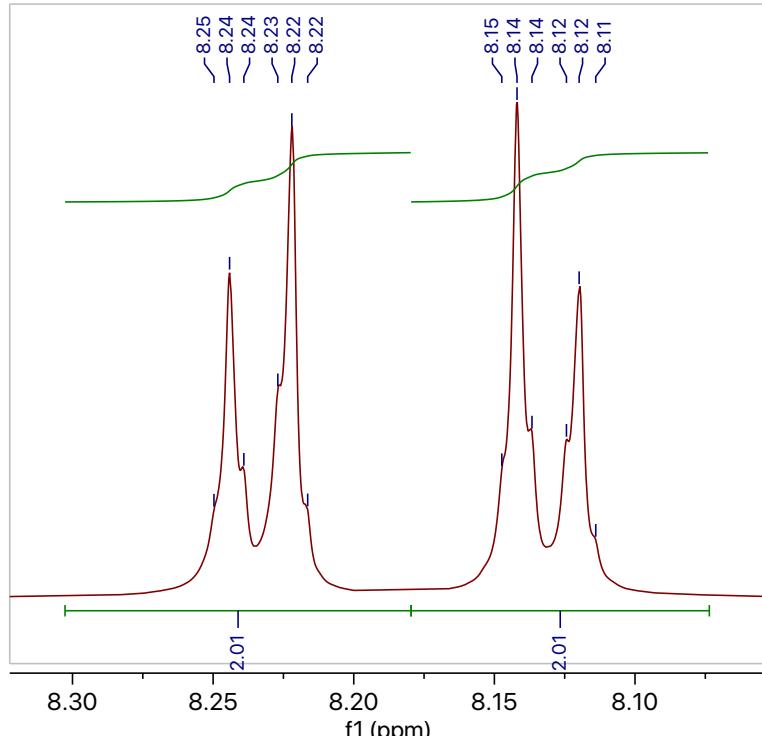
9. ^1H , ^{13}C , ^{19}F NMR spectra for esterification products 3a-3ae

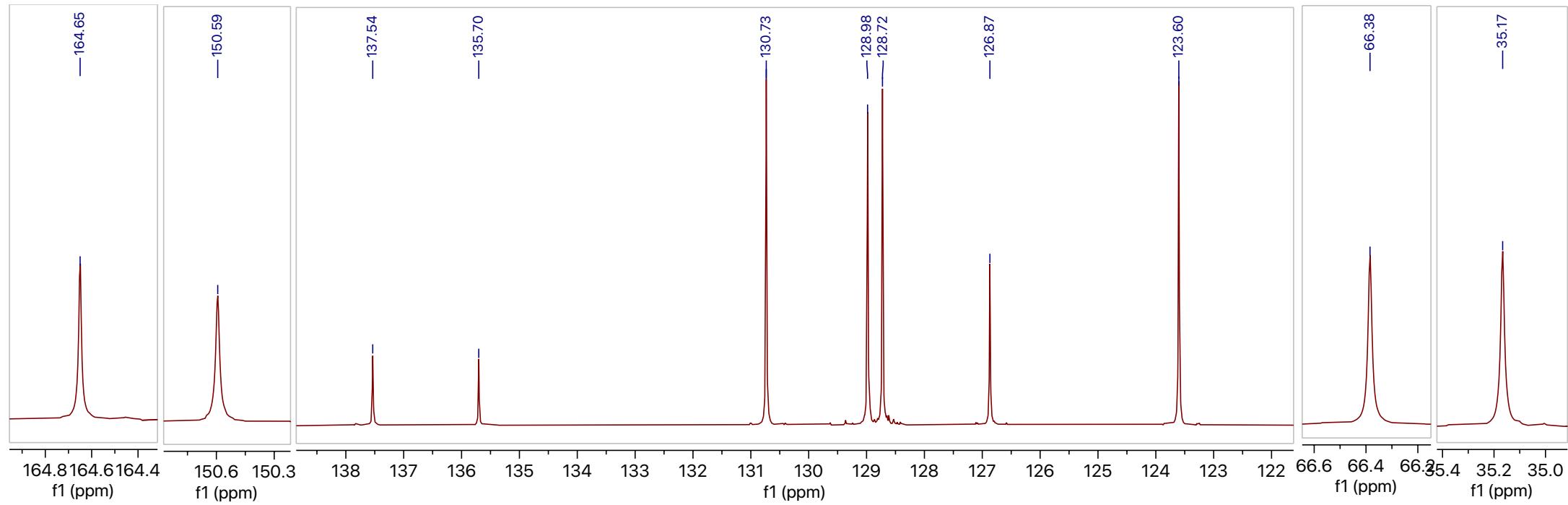




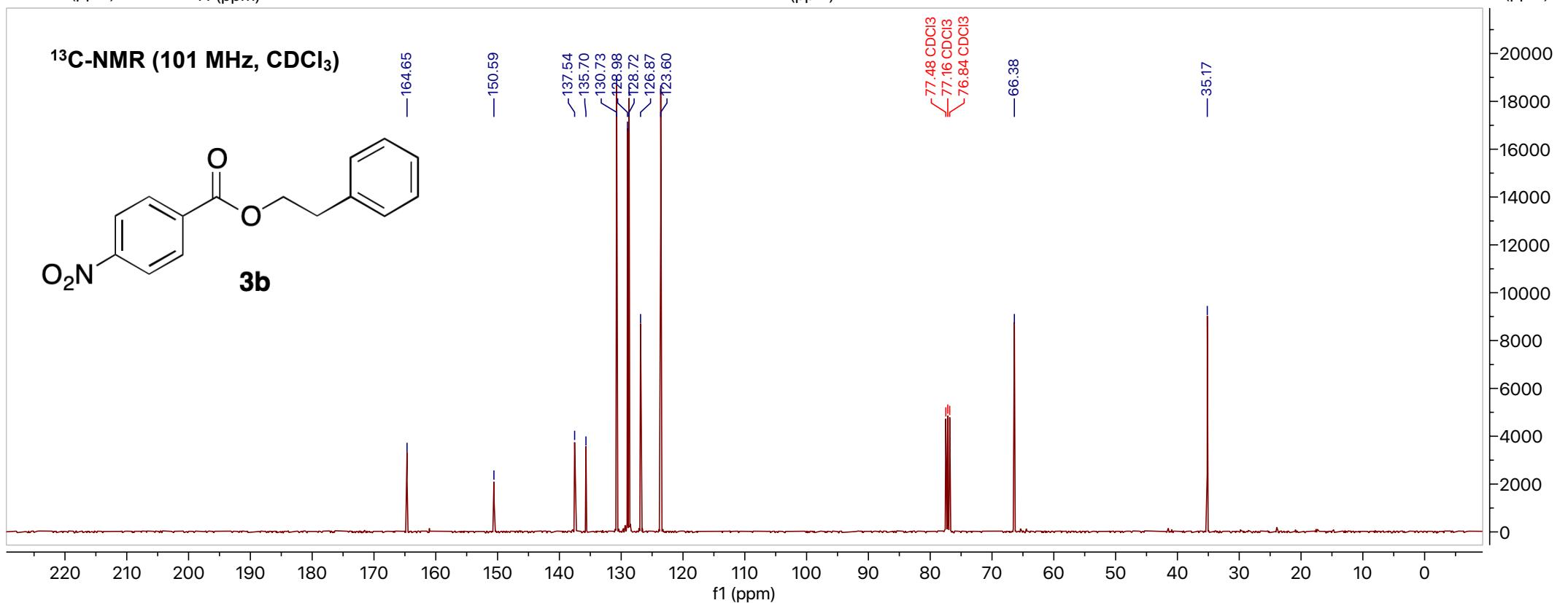
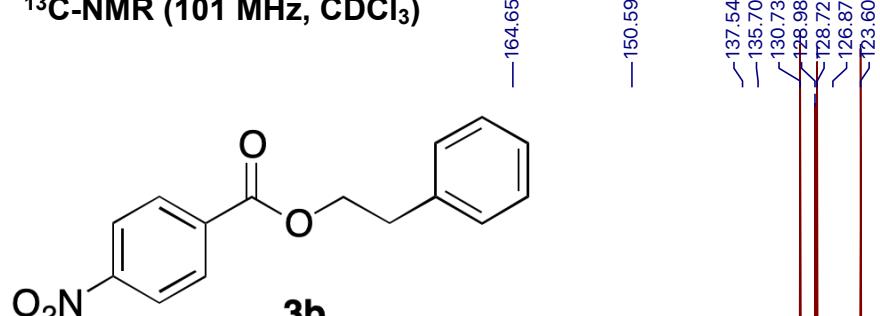
¹³C-NMR (101 MHz, CDCl₃)

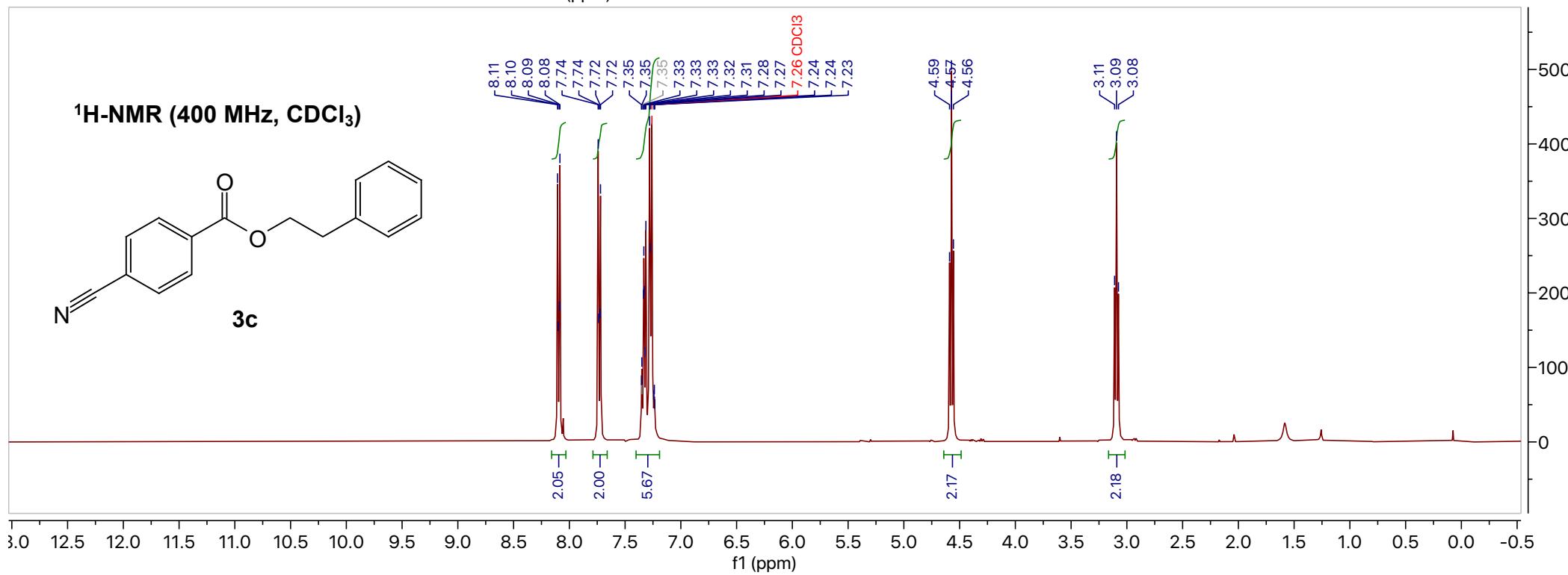
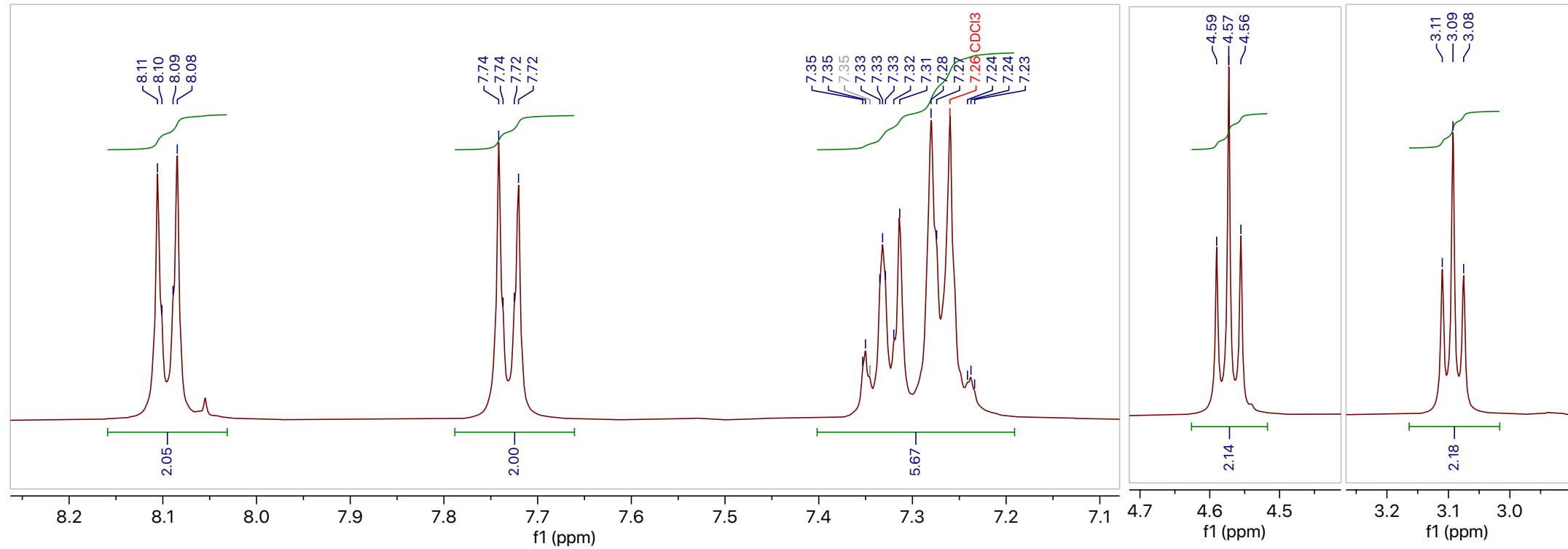


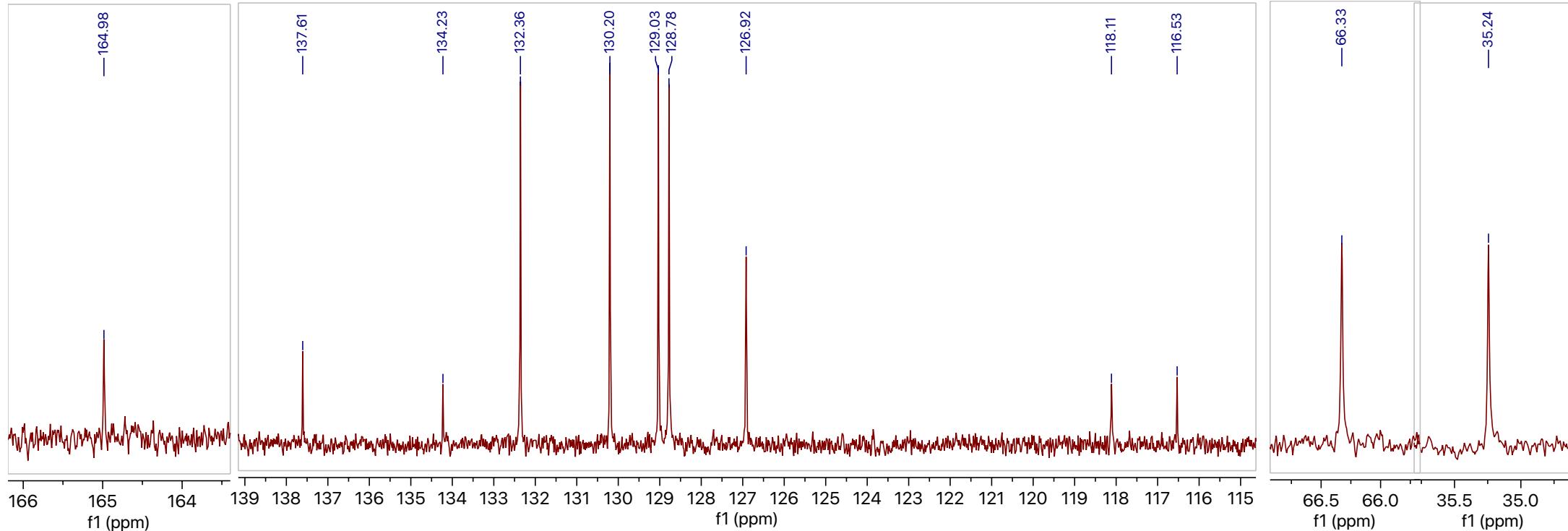




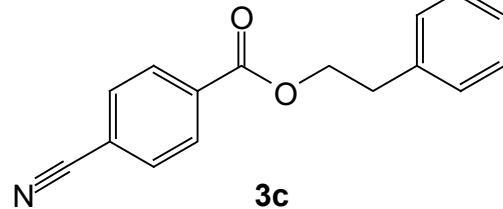
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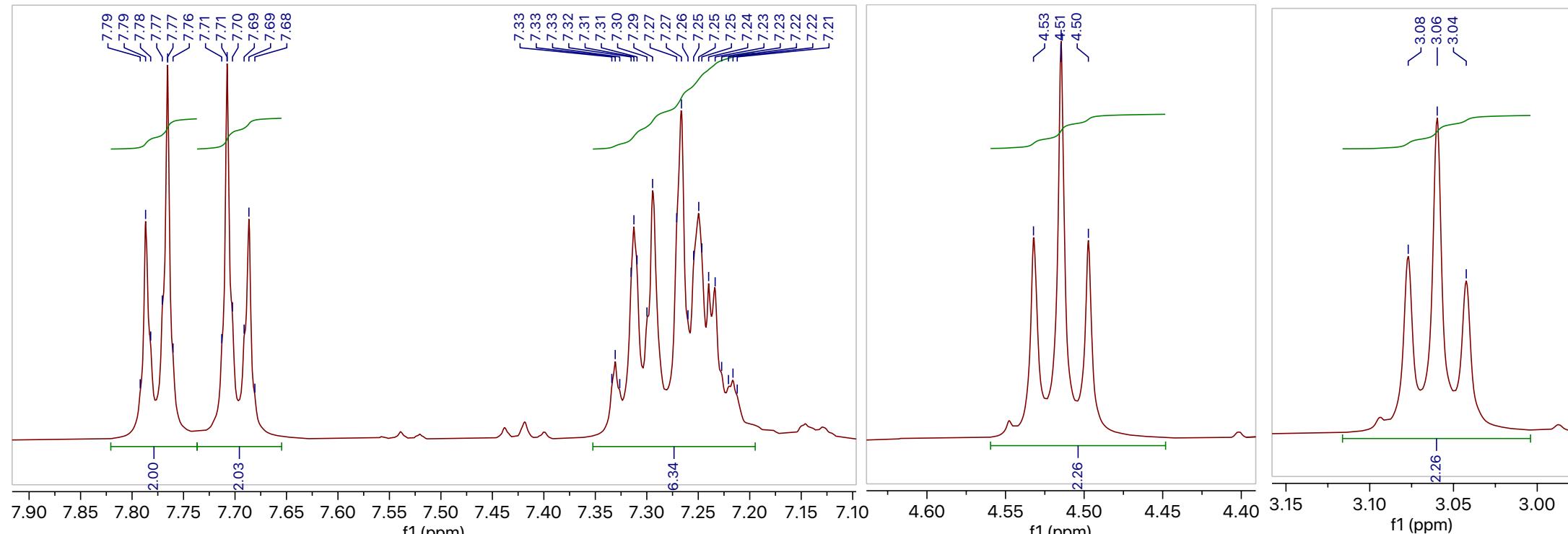




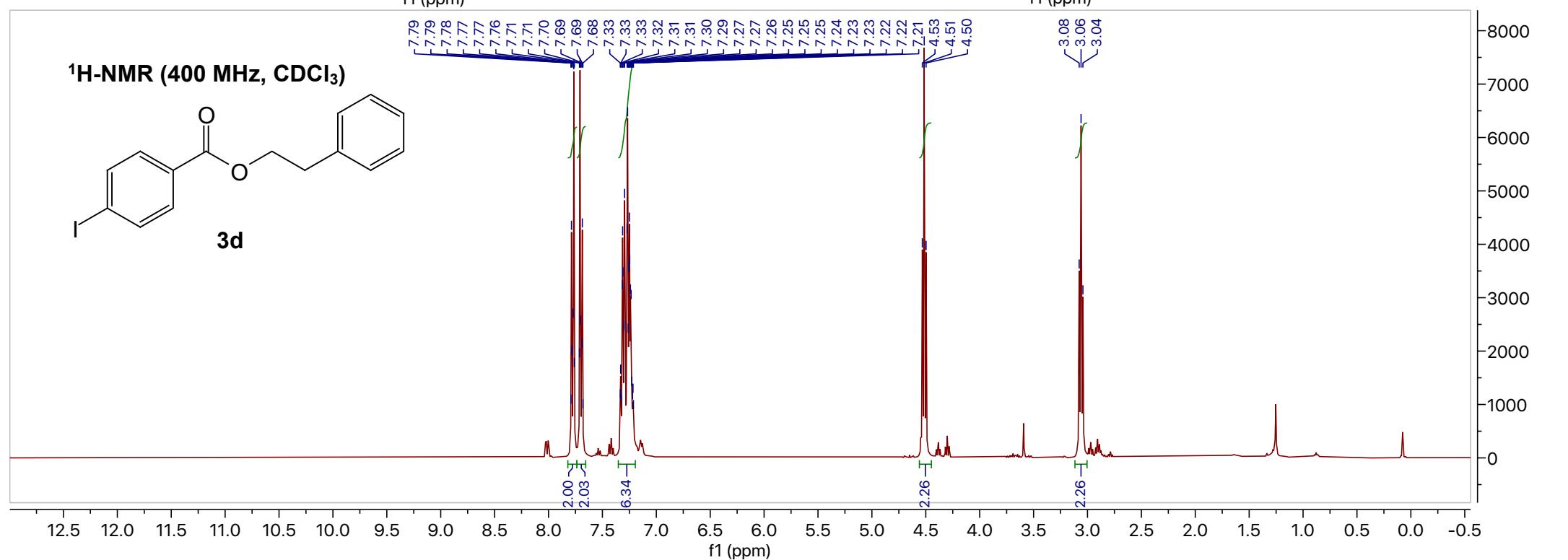
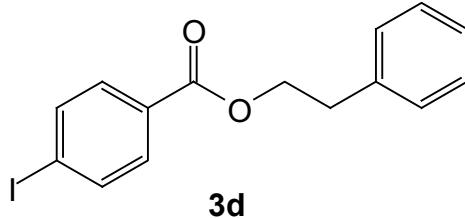


¹³C-NMR (101 MHz, CDCl₃)

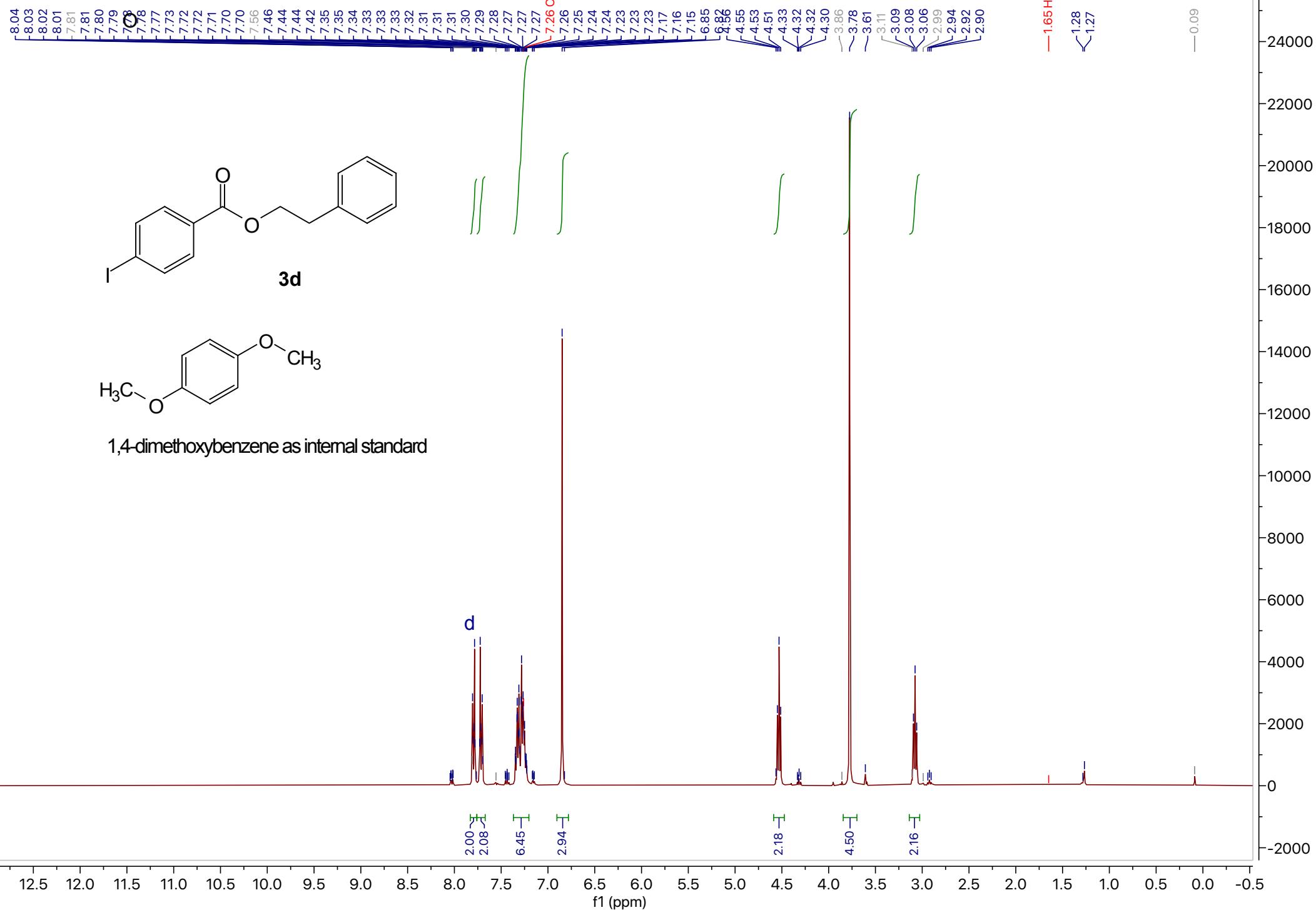


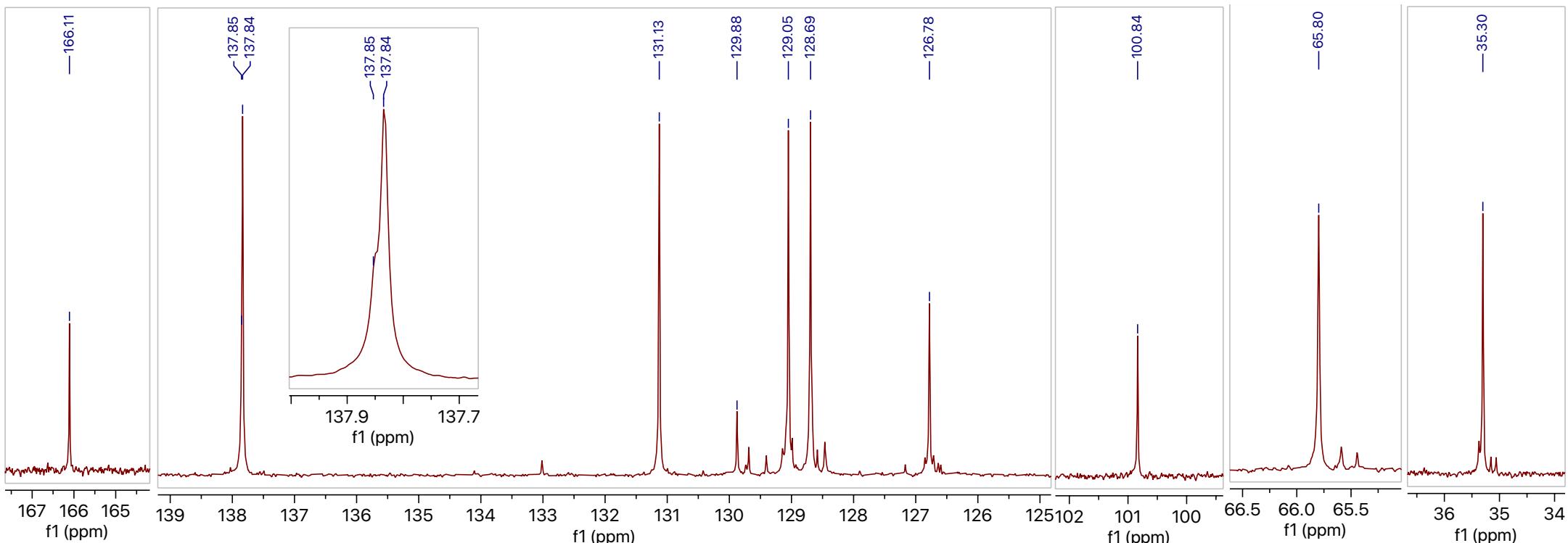


^1H -NMR (400 MHz, CDCl_3)

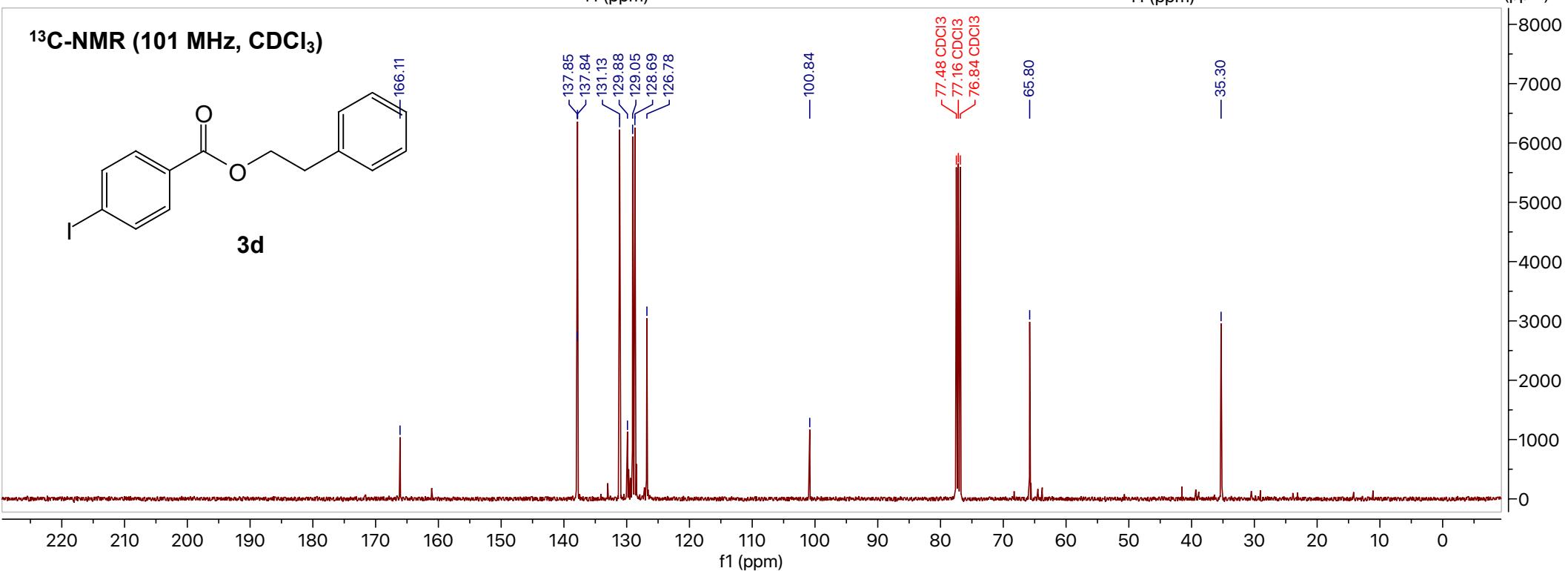
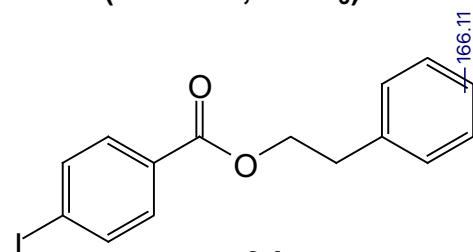


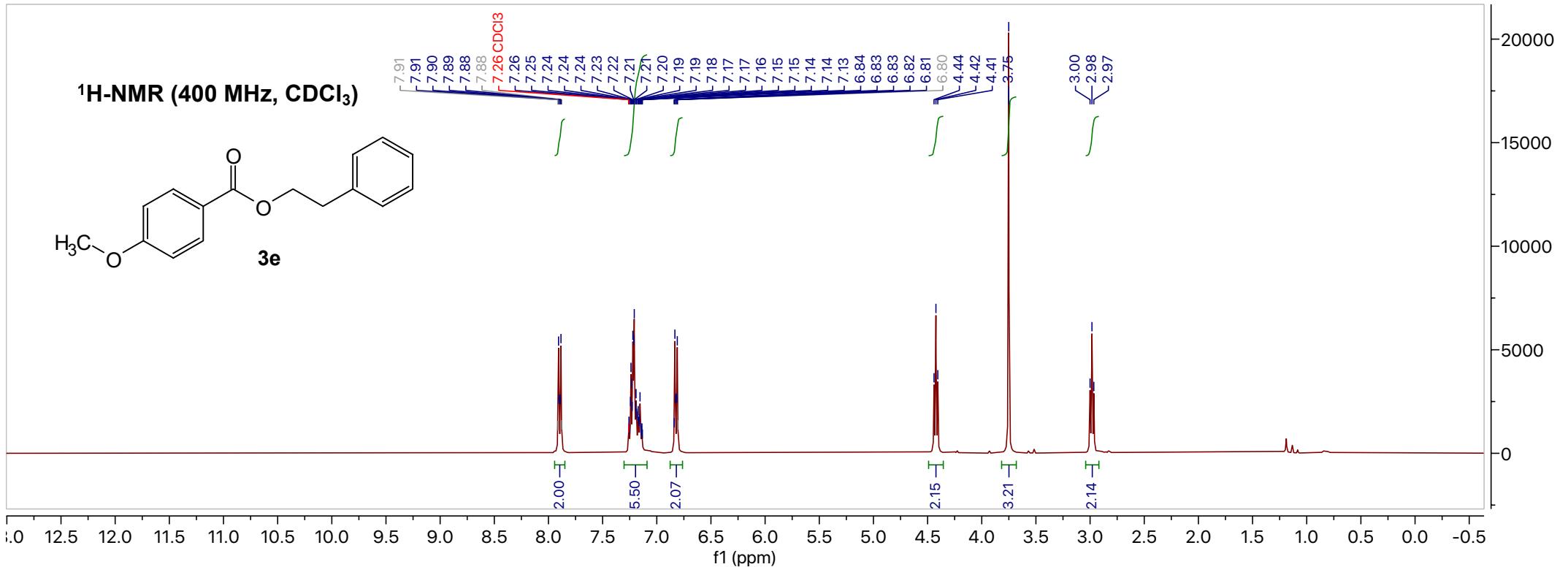
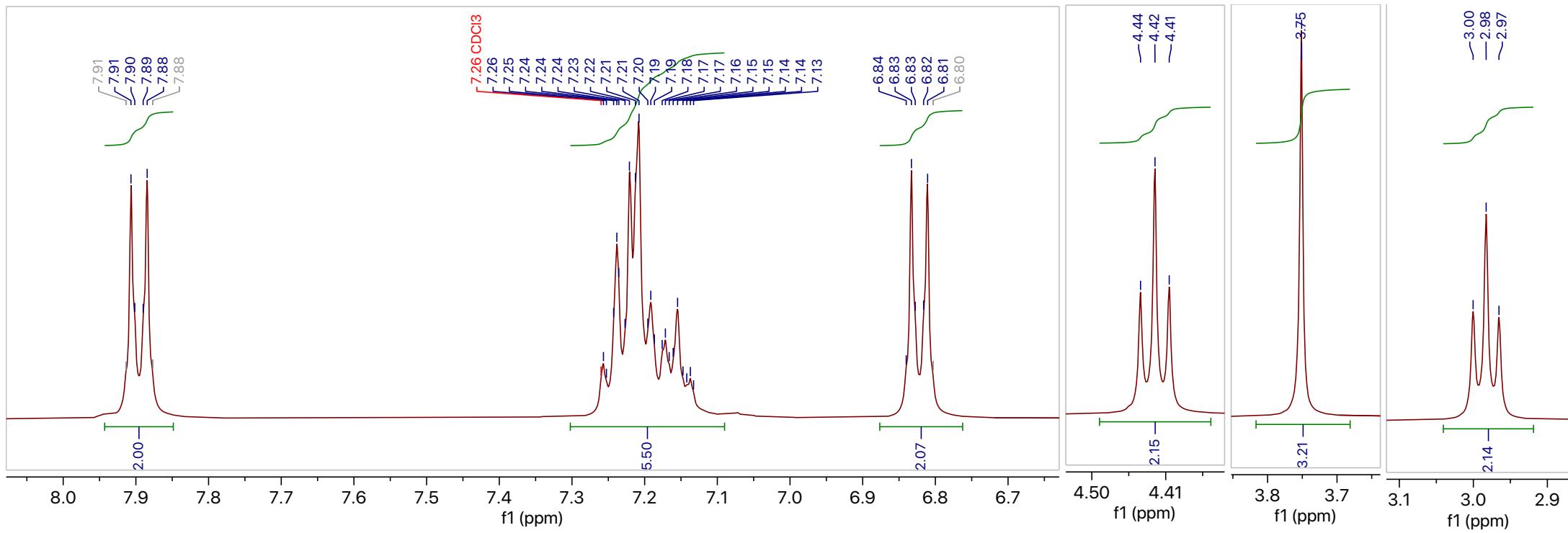
$^1\text{H-NMR}$ (400 MHz, CDCl_3)

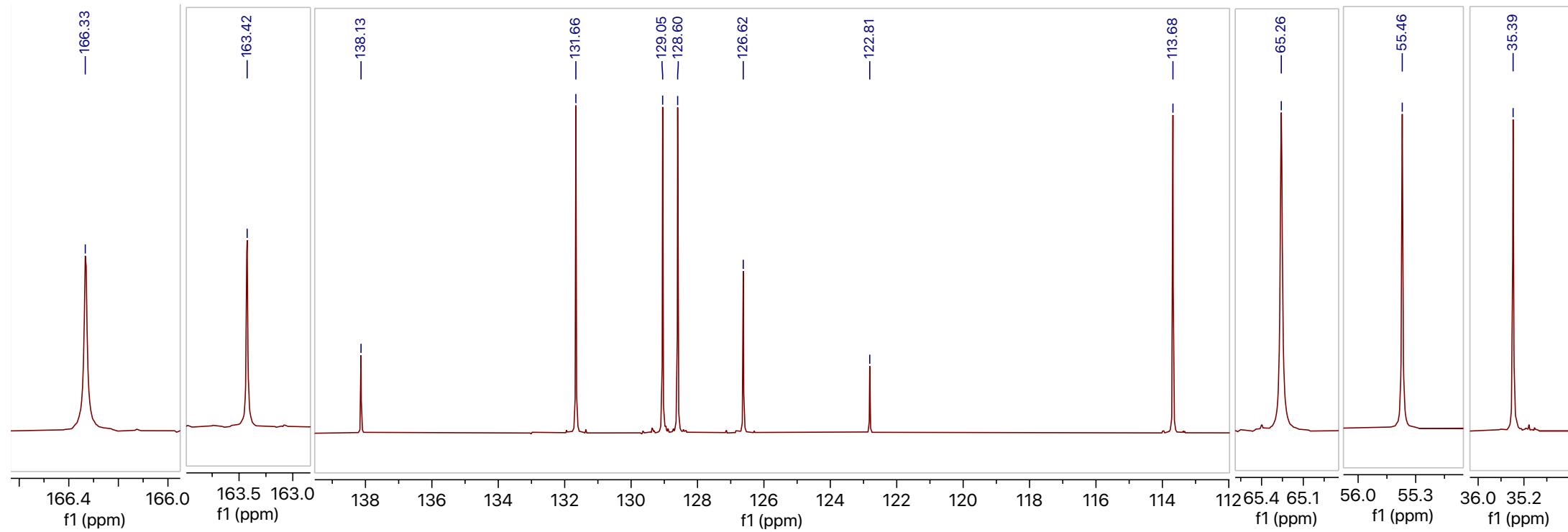




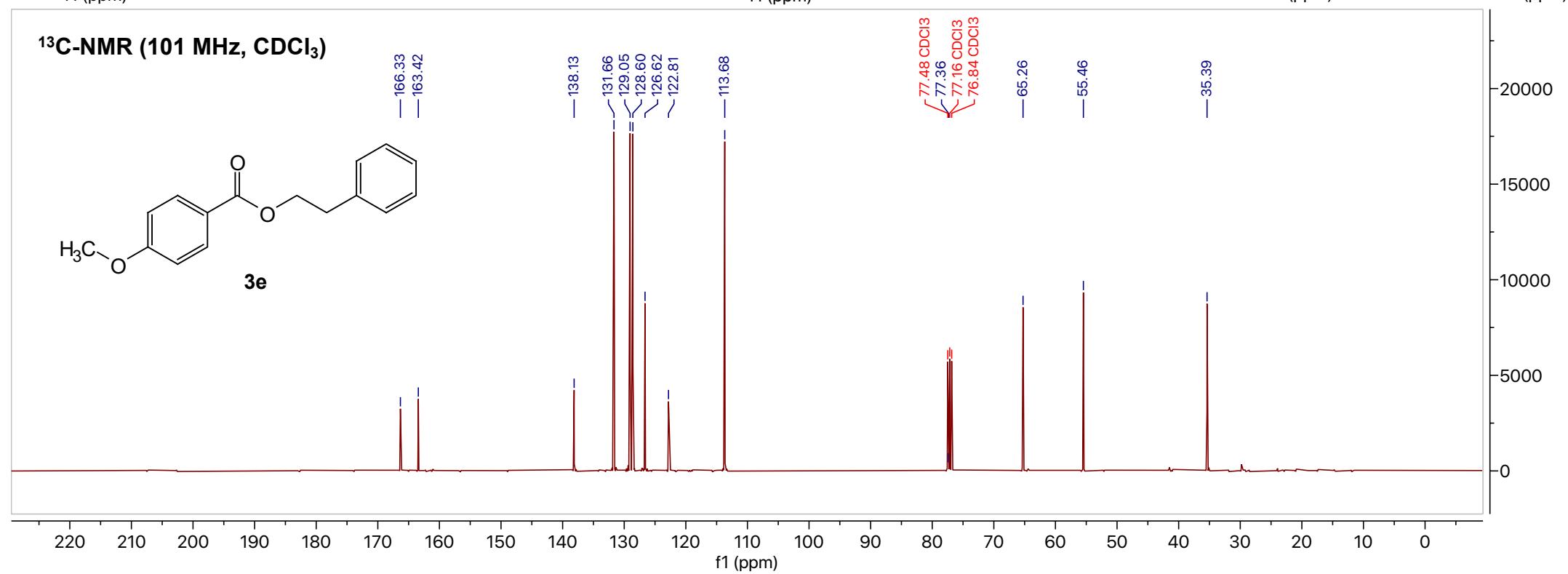
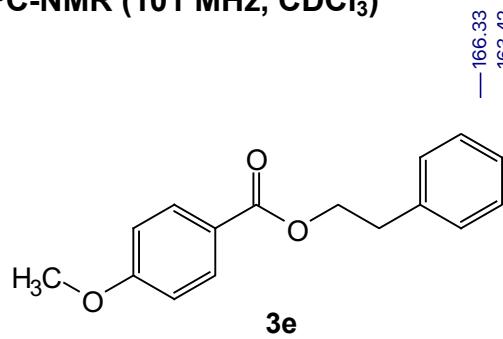
¹³C-NMR (101 MHz, CDCl₃)

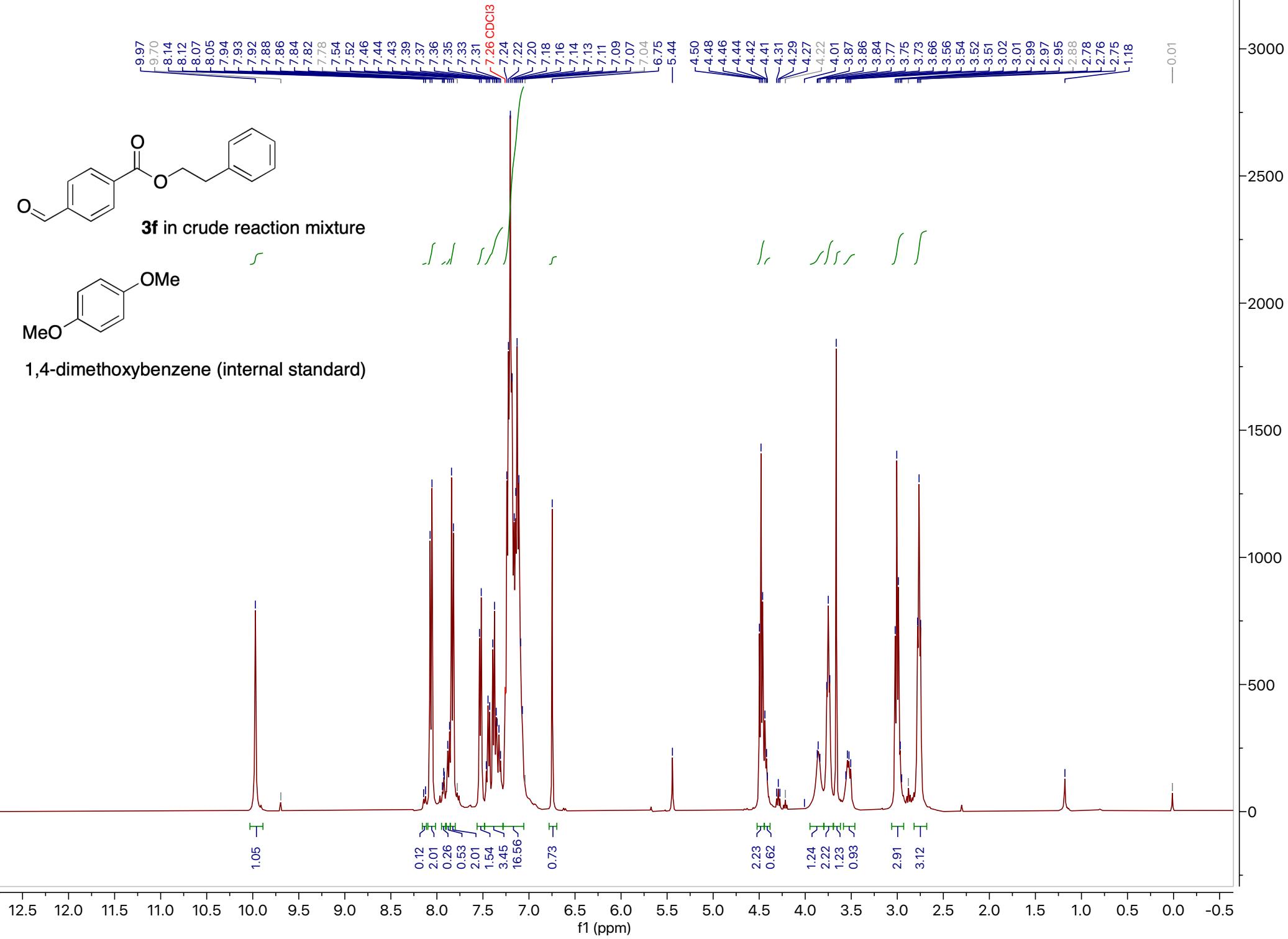


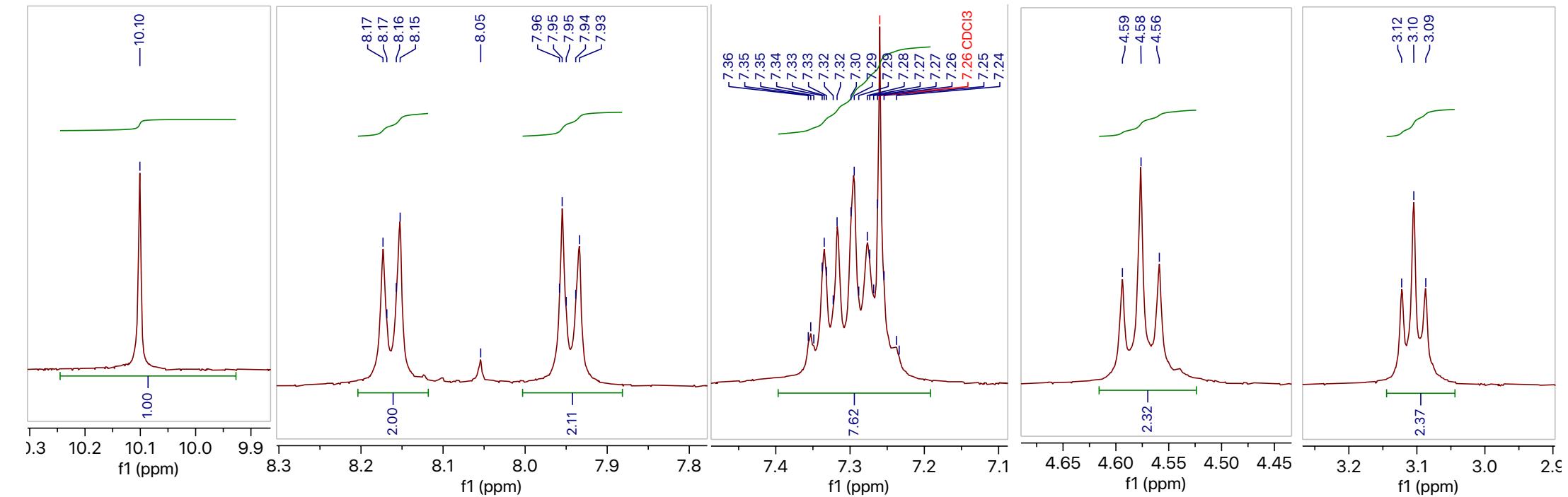




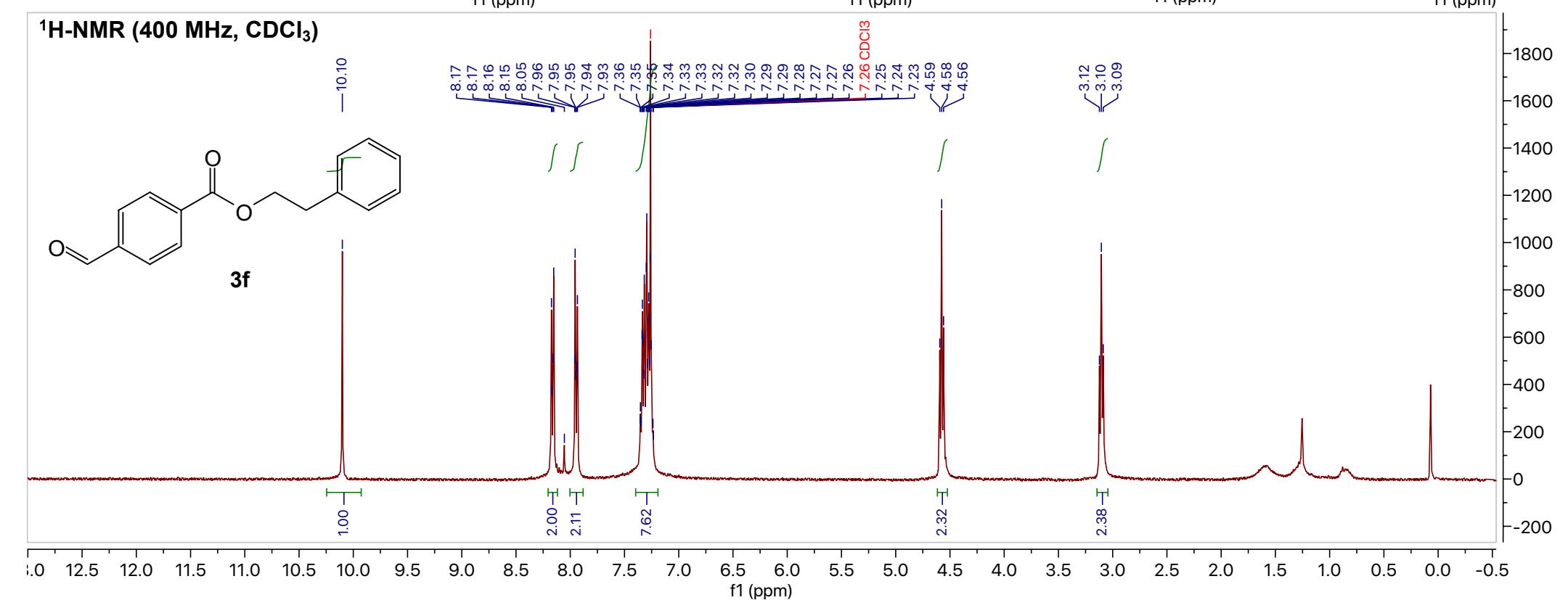
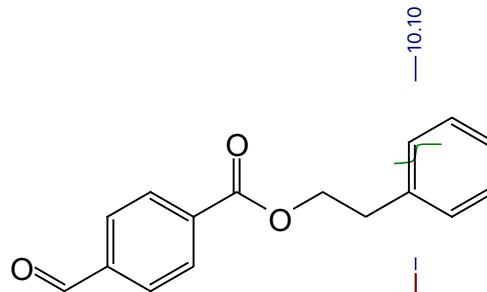
¹³C-NMR (101 MHz, CDCl_3)

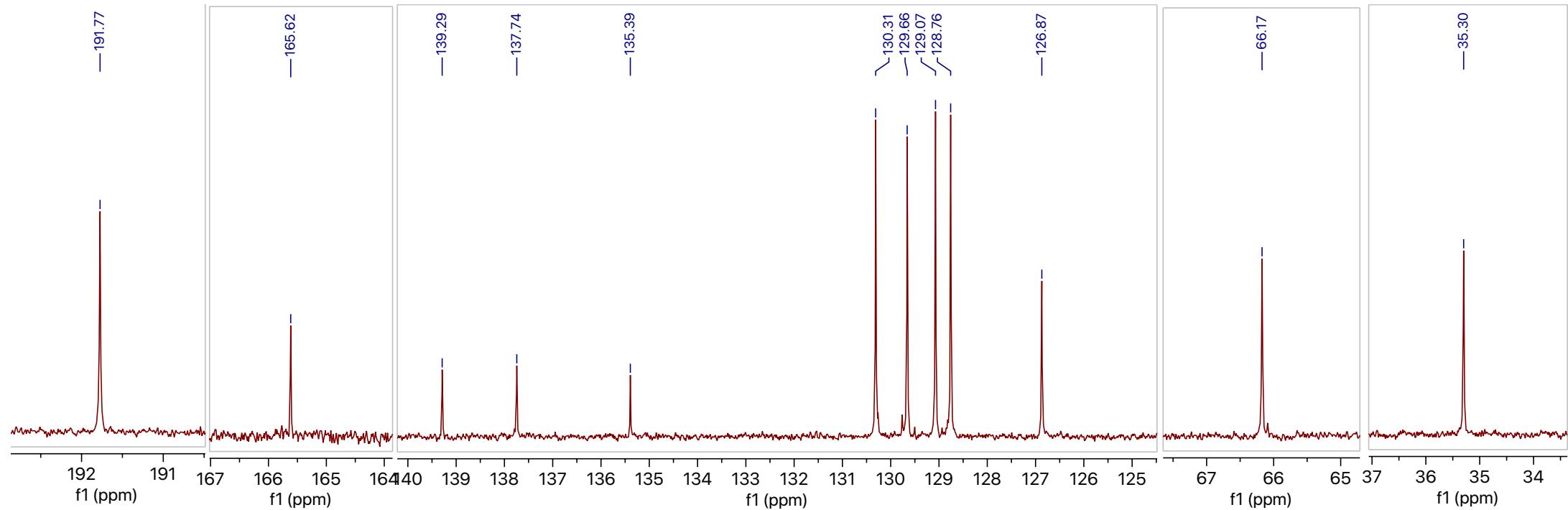




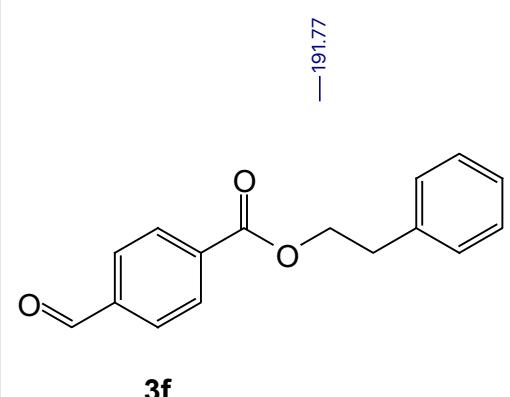


$^1\text{H-NMR}$ (400 MHz, CDCl_3)

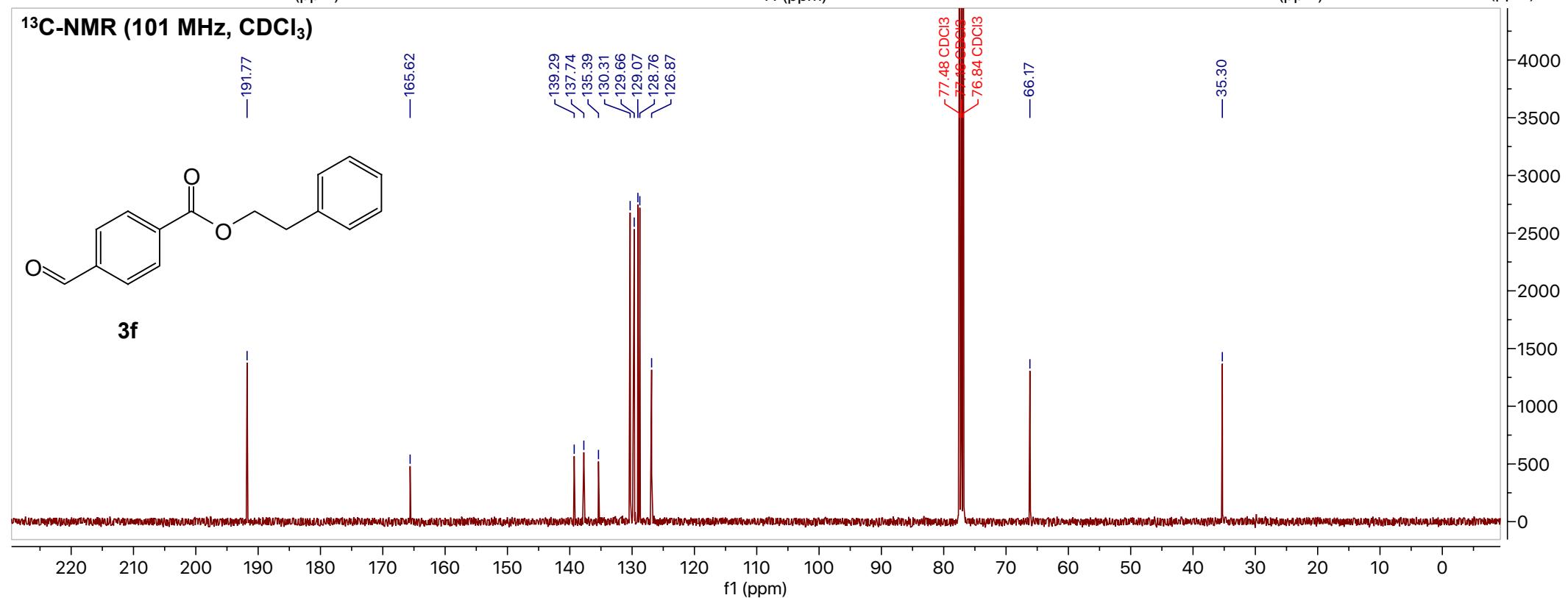


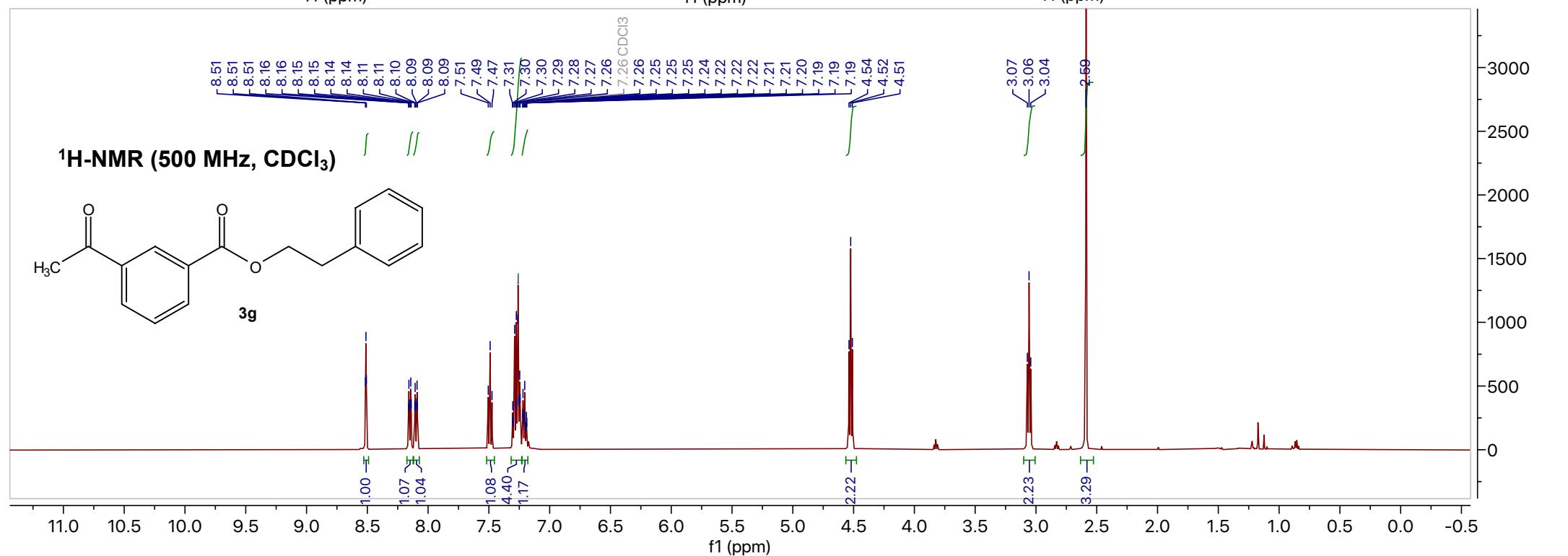
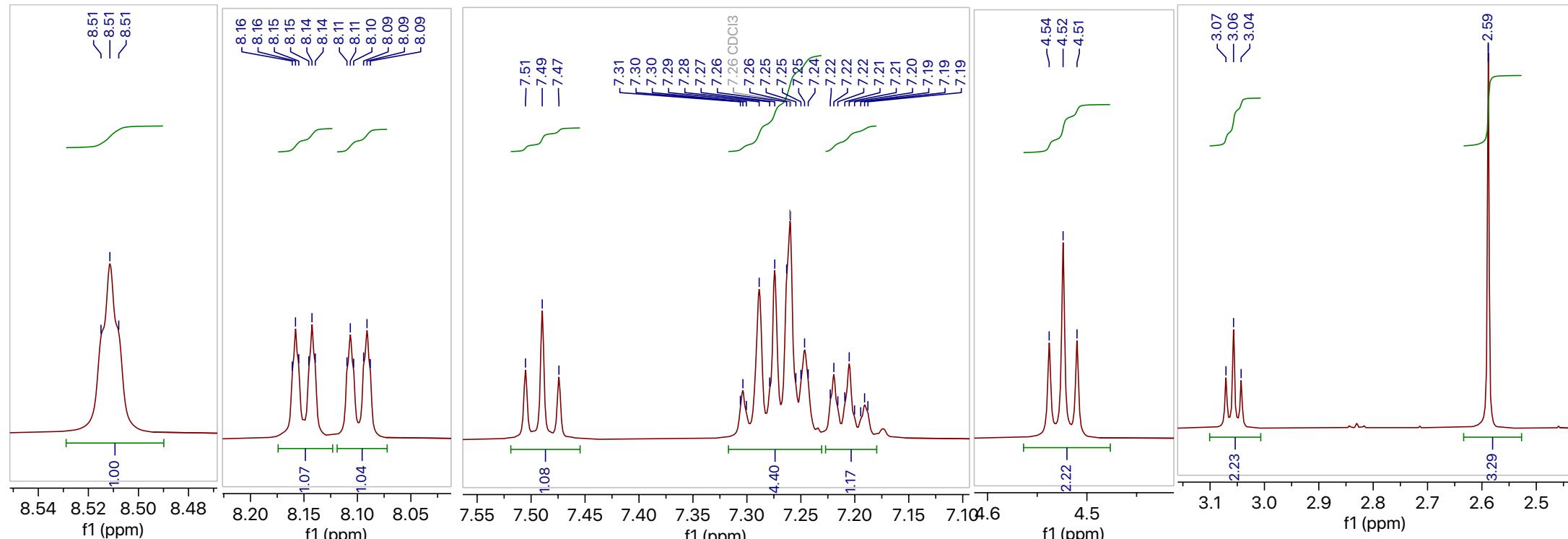


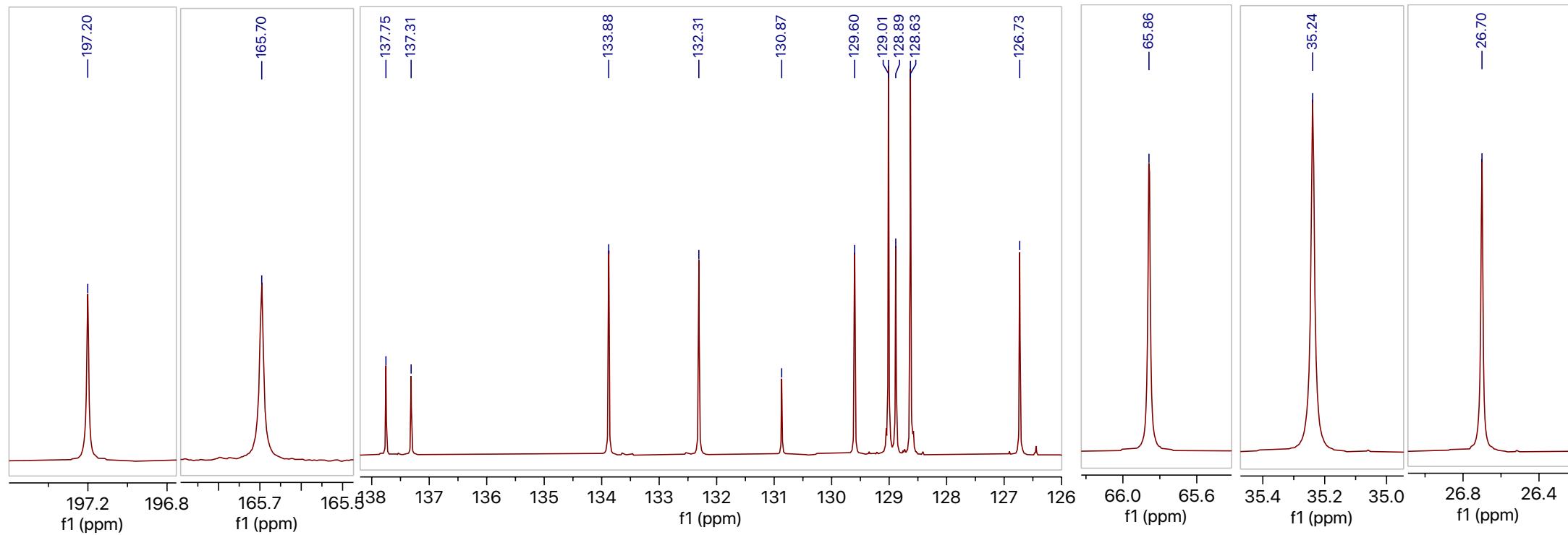
¹³C-NMR (101 MHz, CDCl₃)



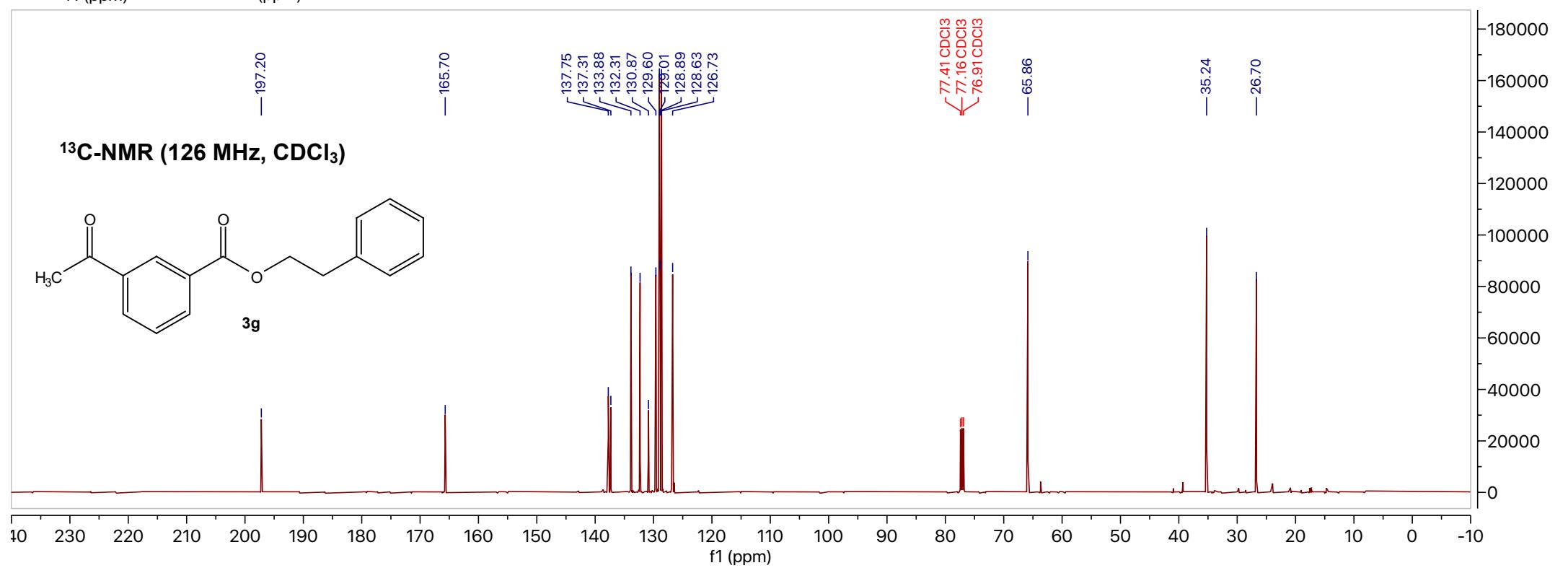
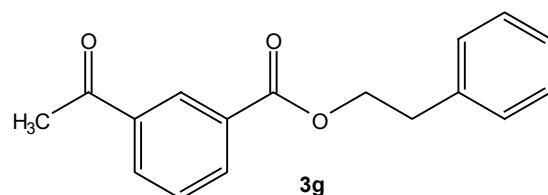
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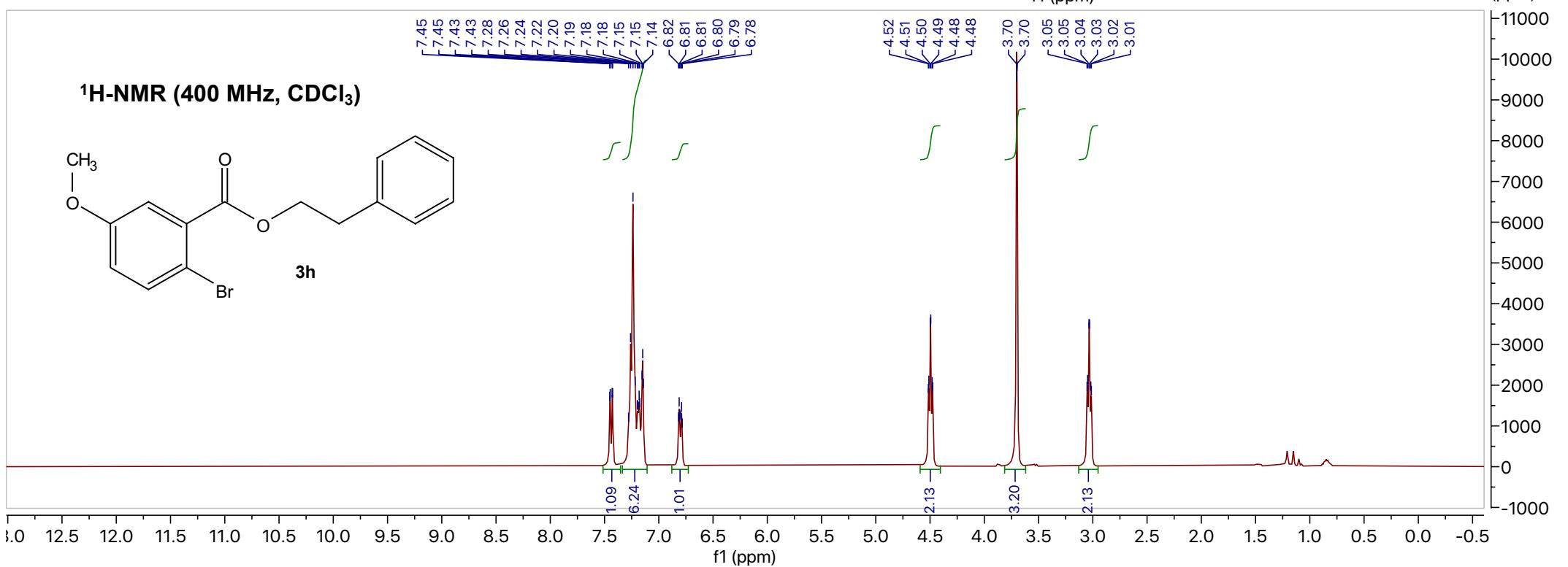
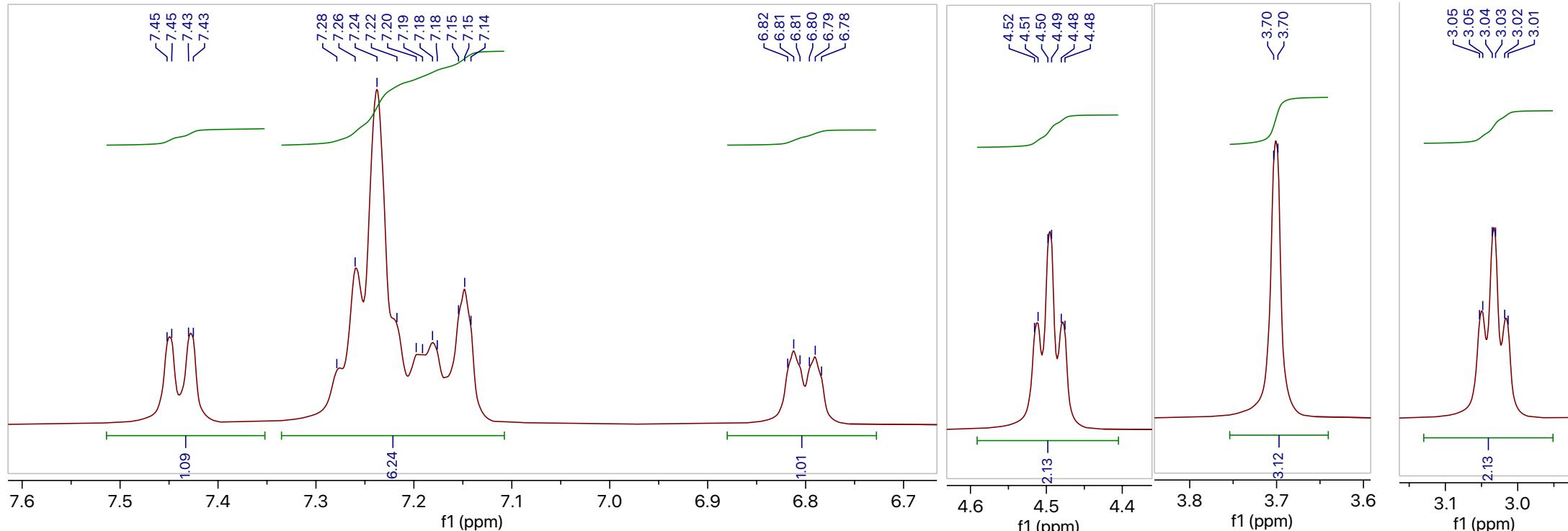


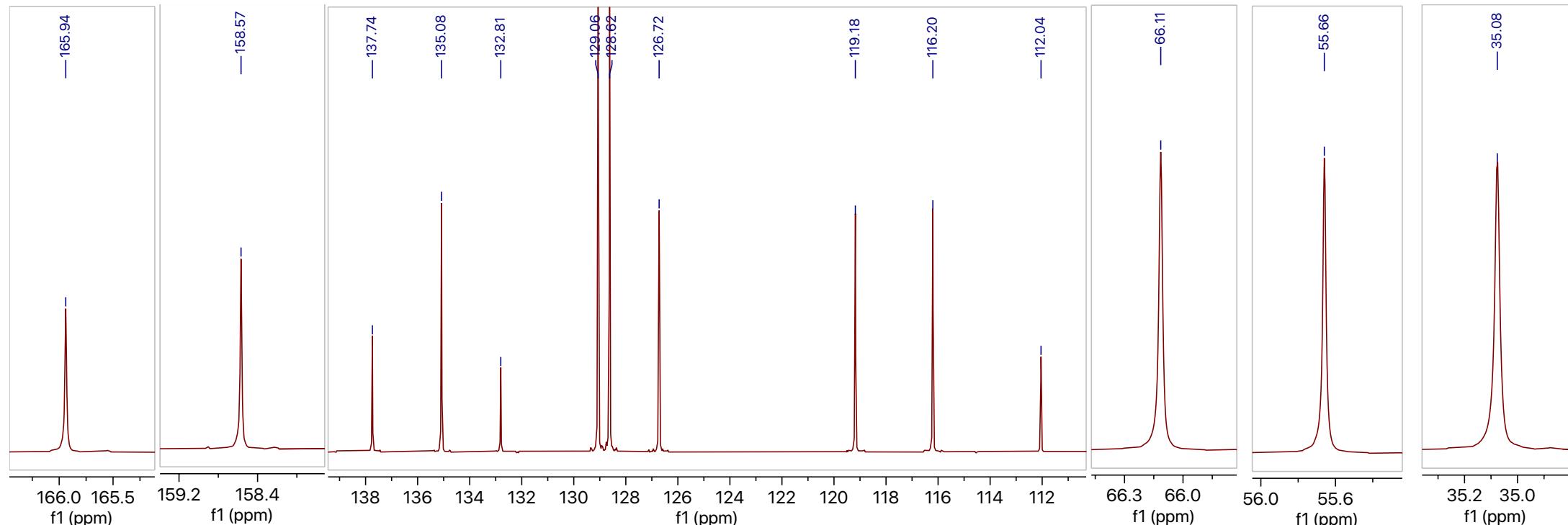




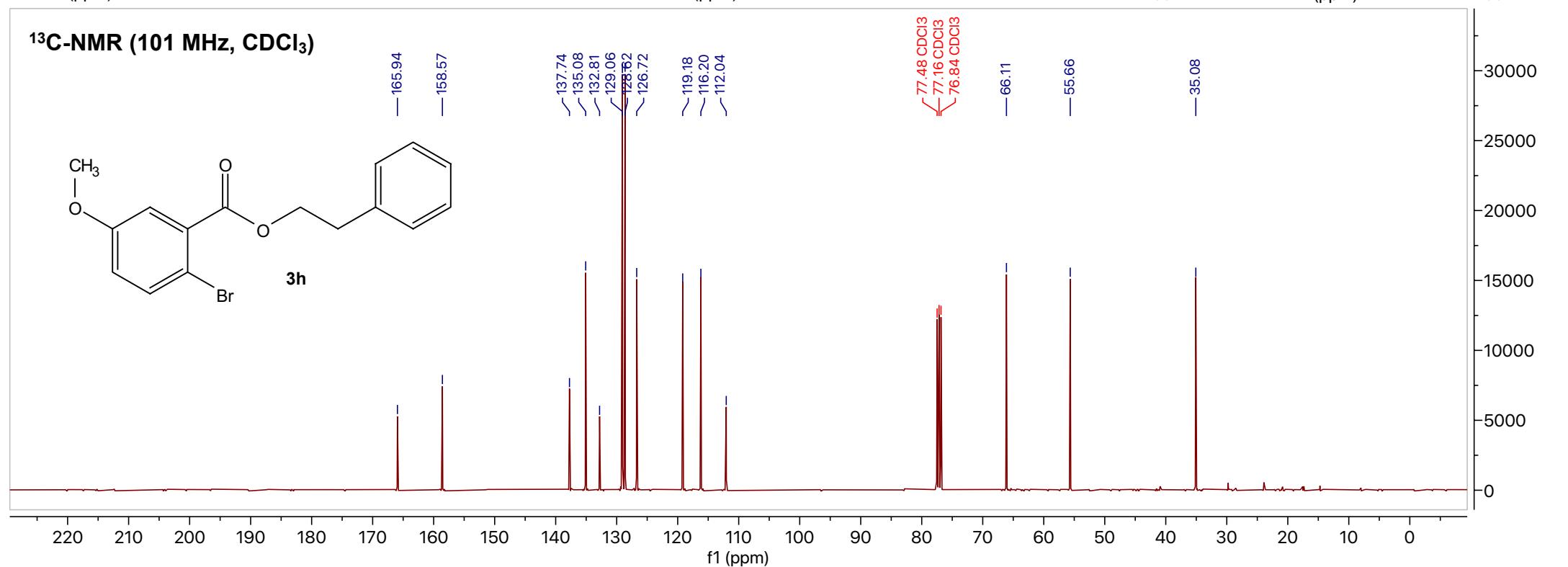
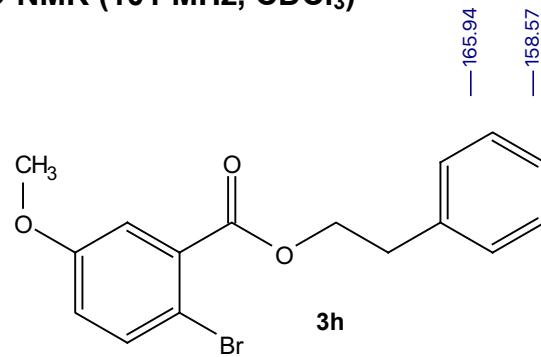
¹³C-NMR (126 MHz, CDCl₃)

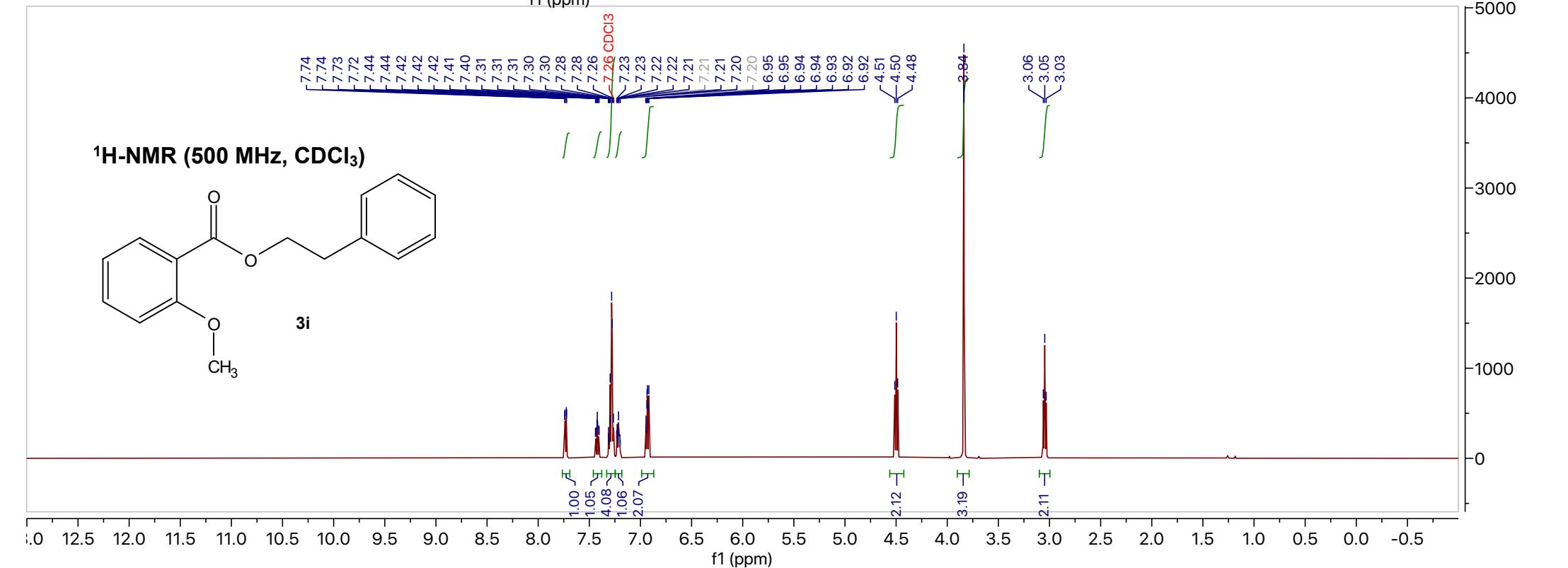
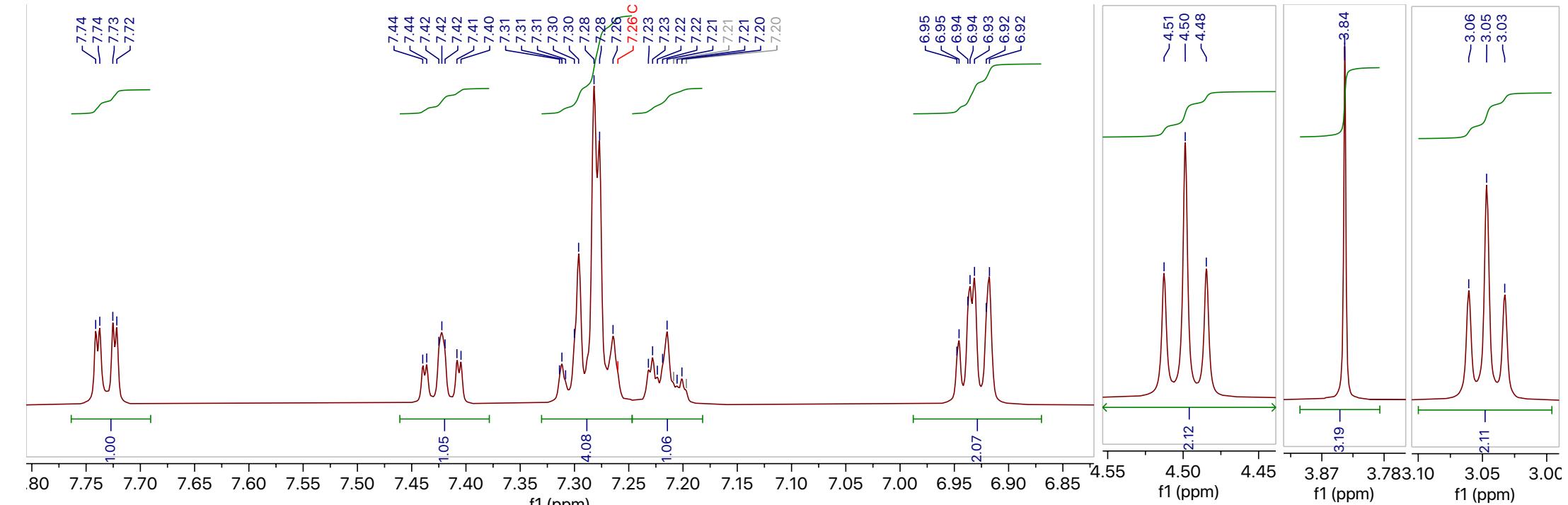


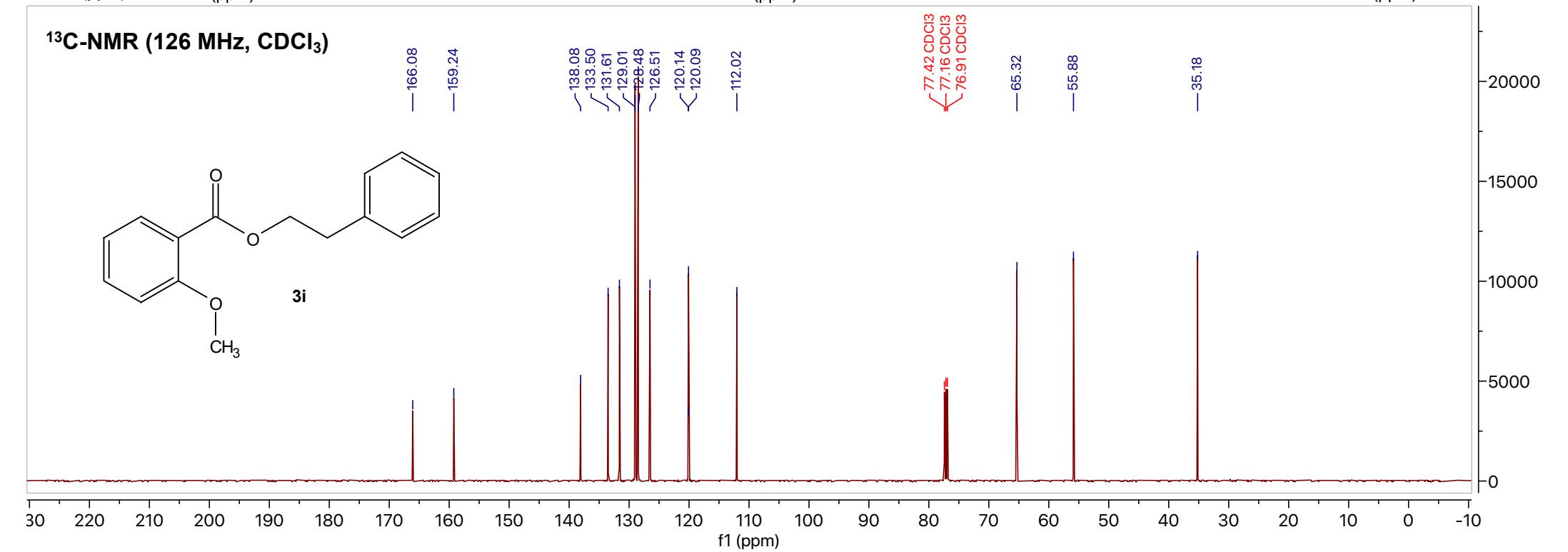
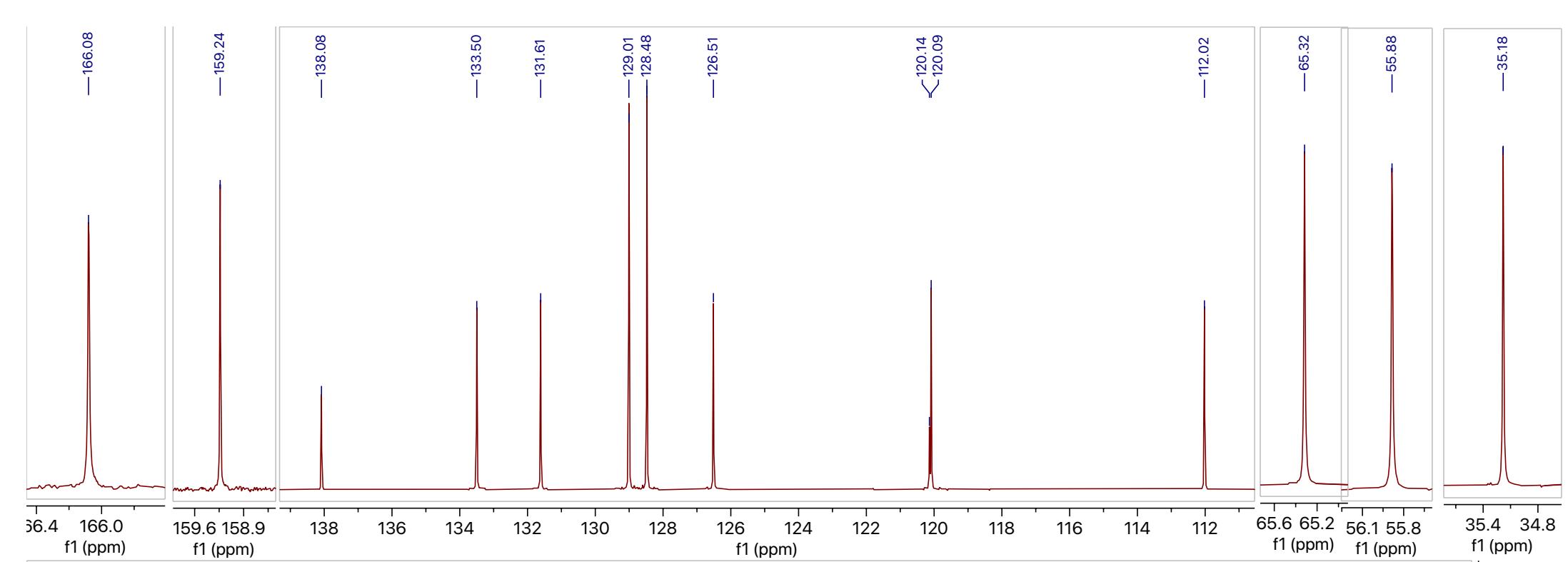


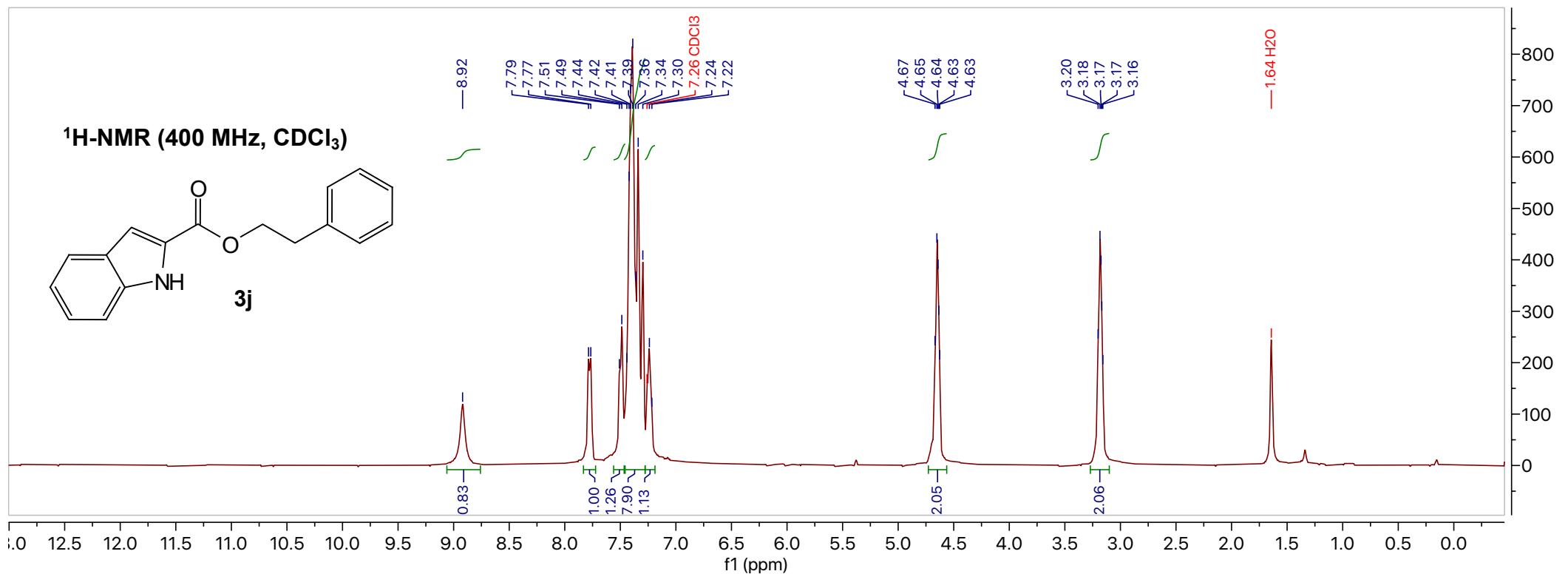
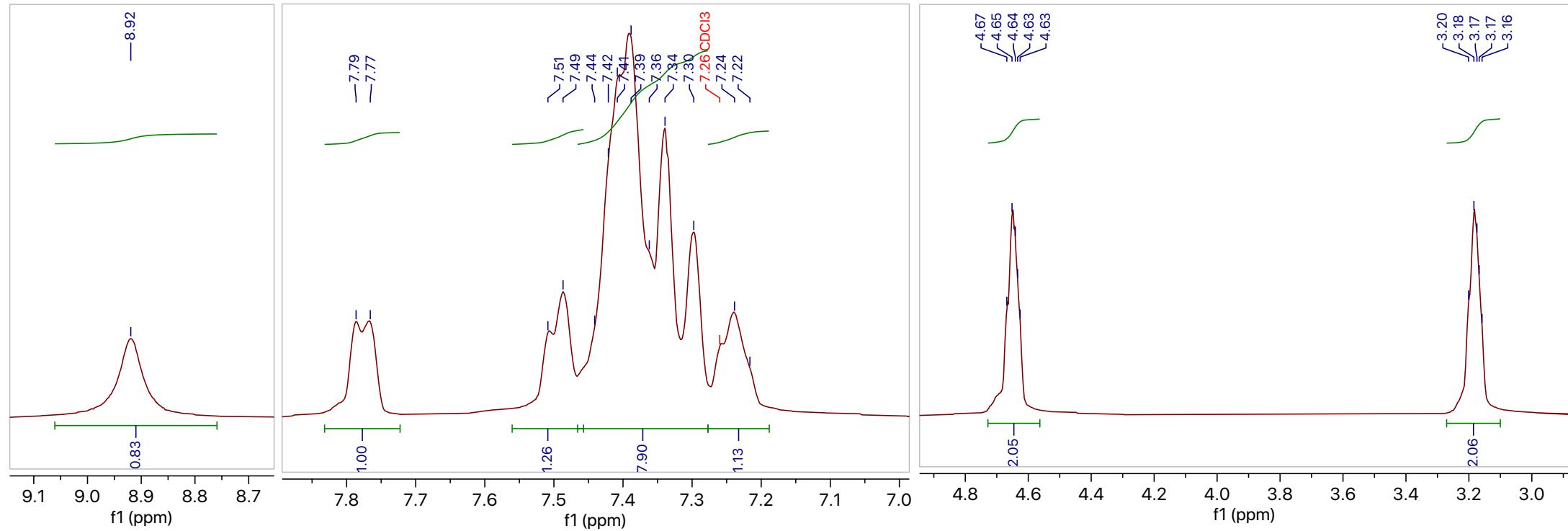


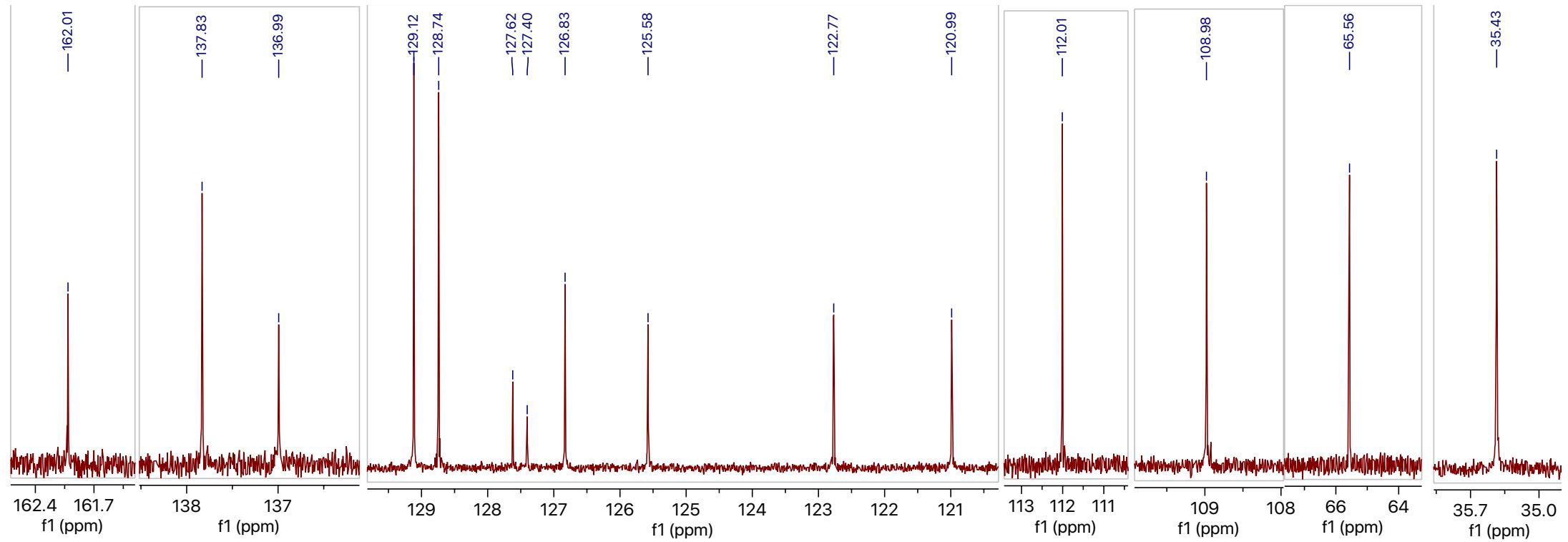
¹³C-NMR (101 MHz, CDCl_3)



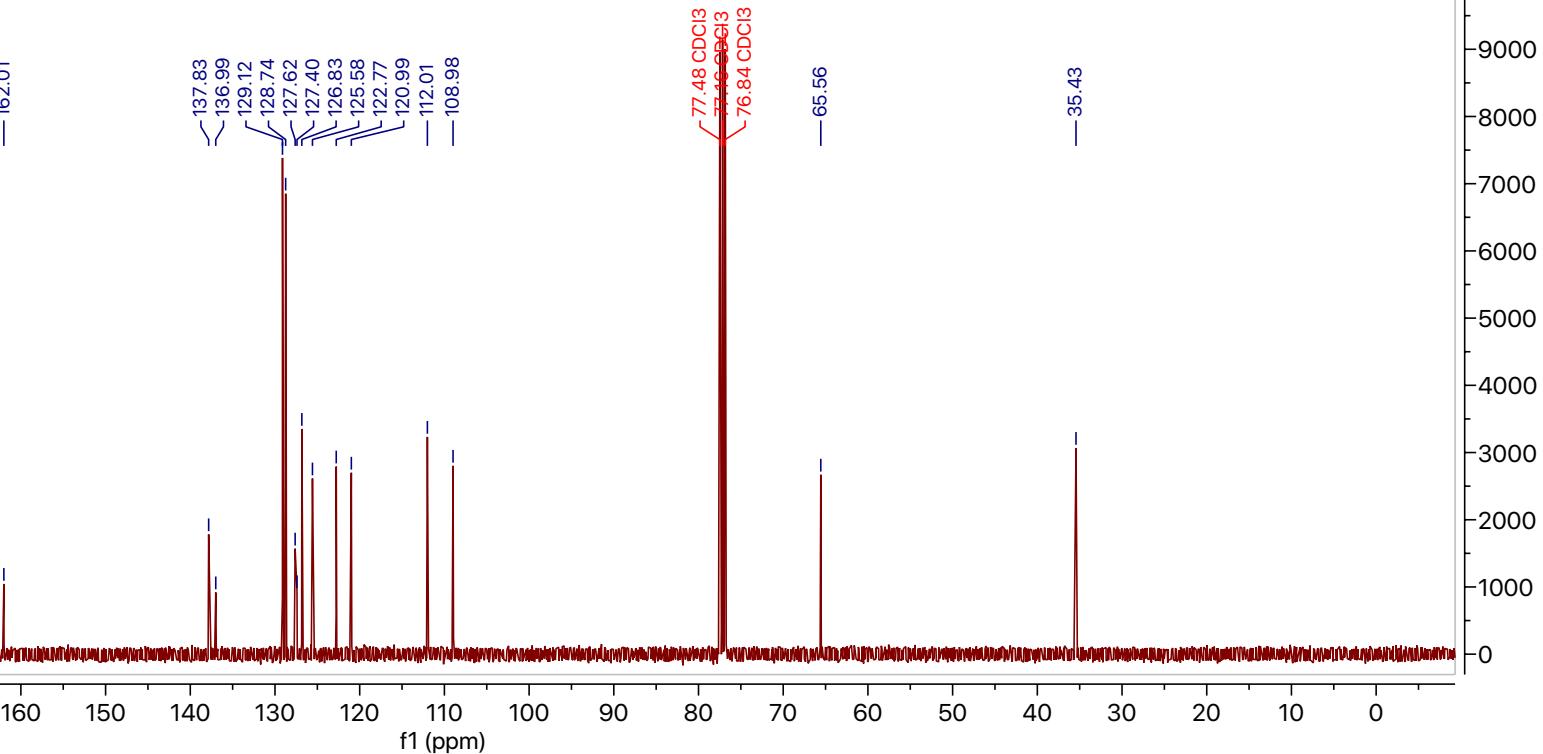
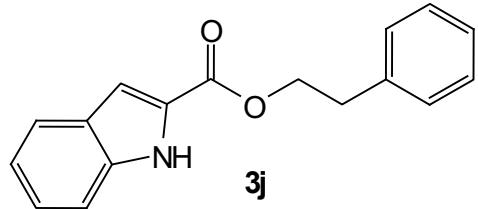


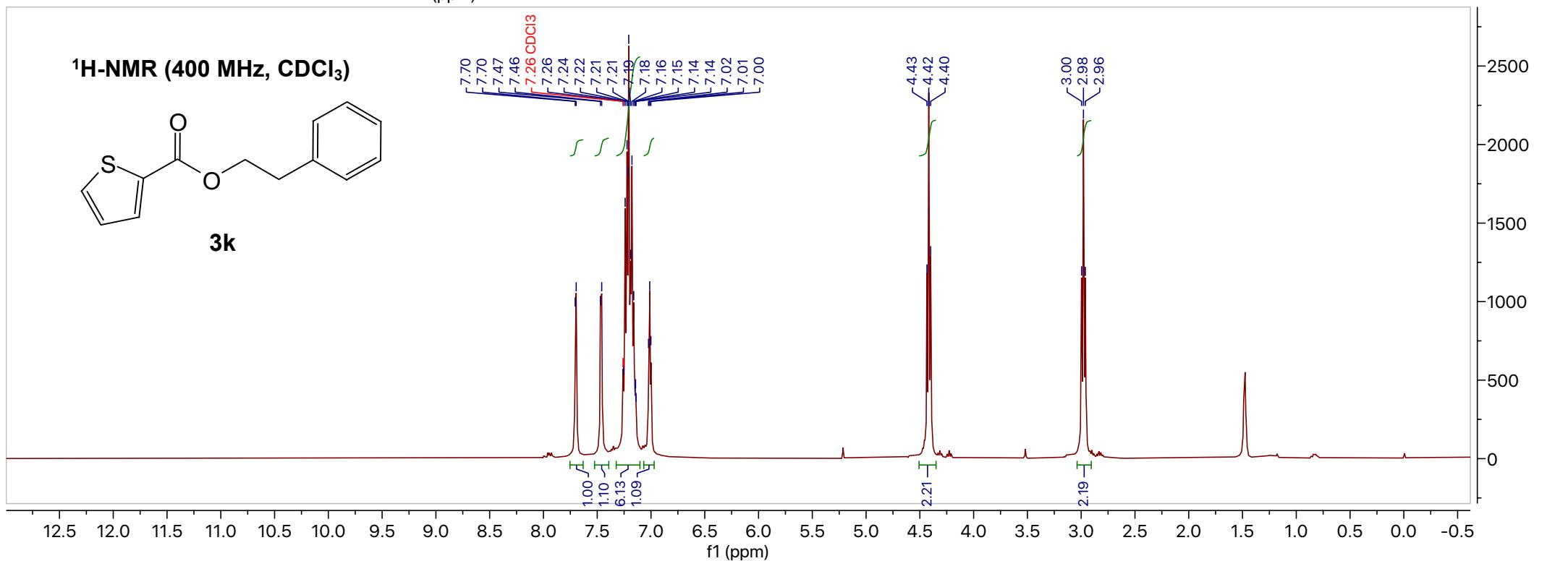
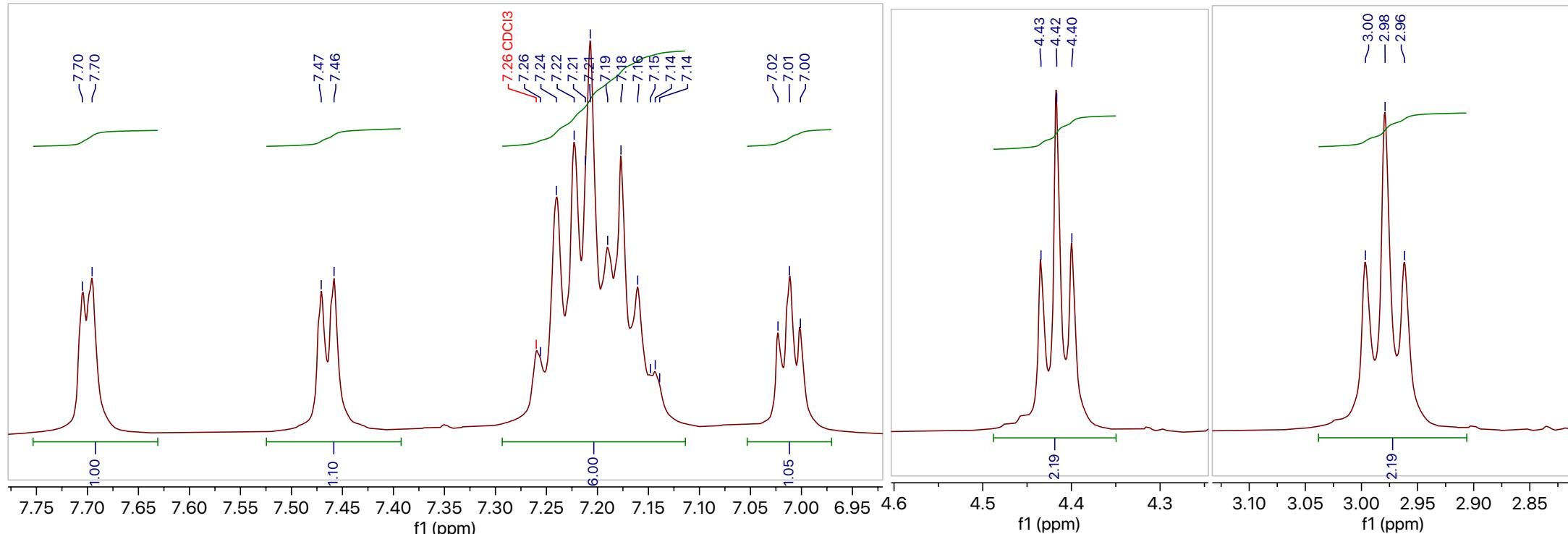


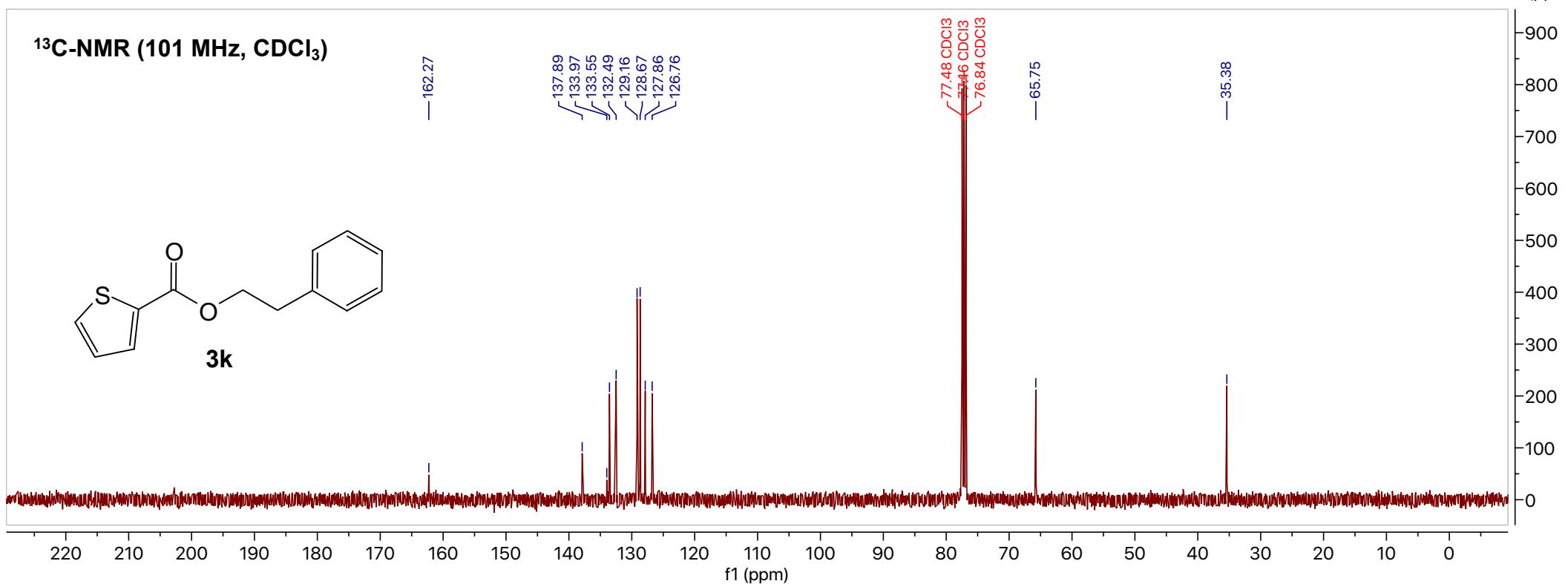
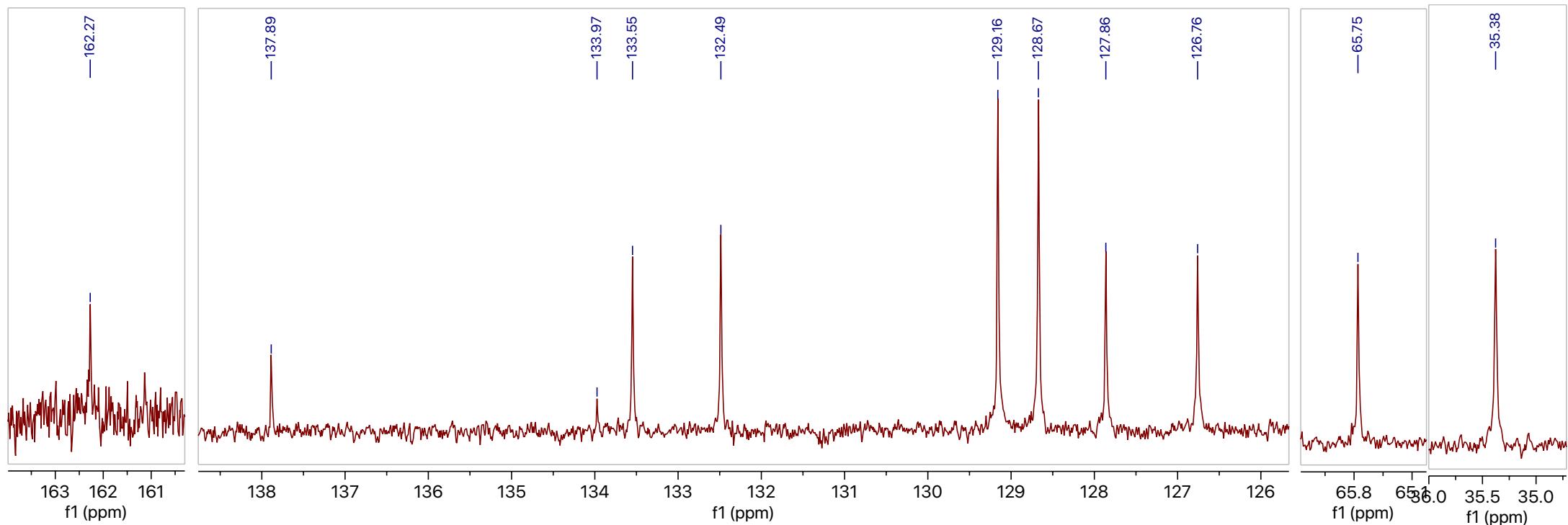


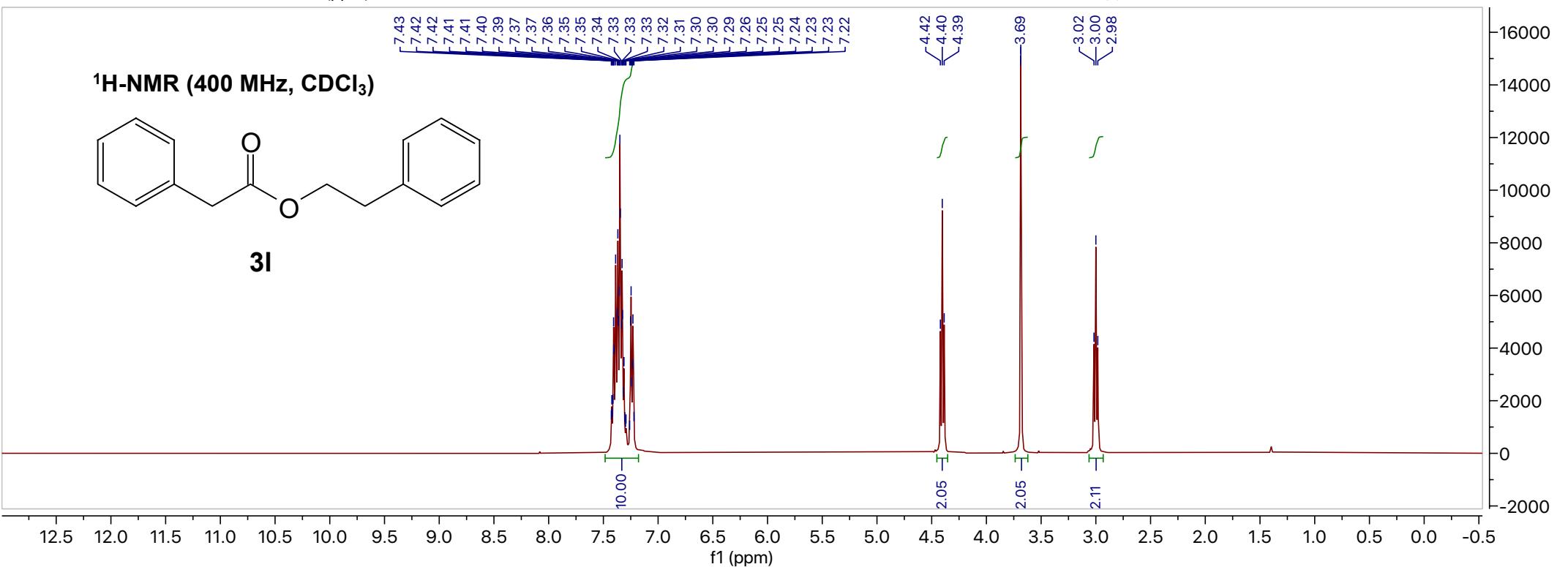
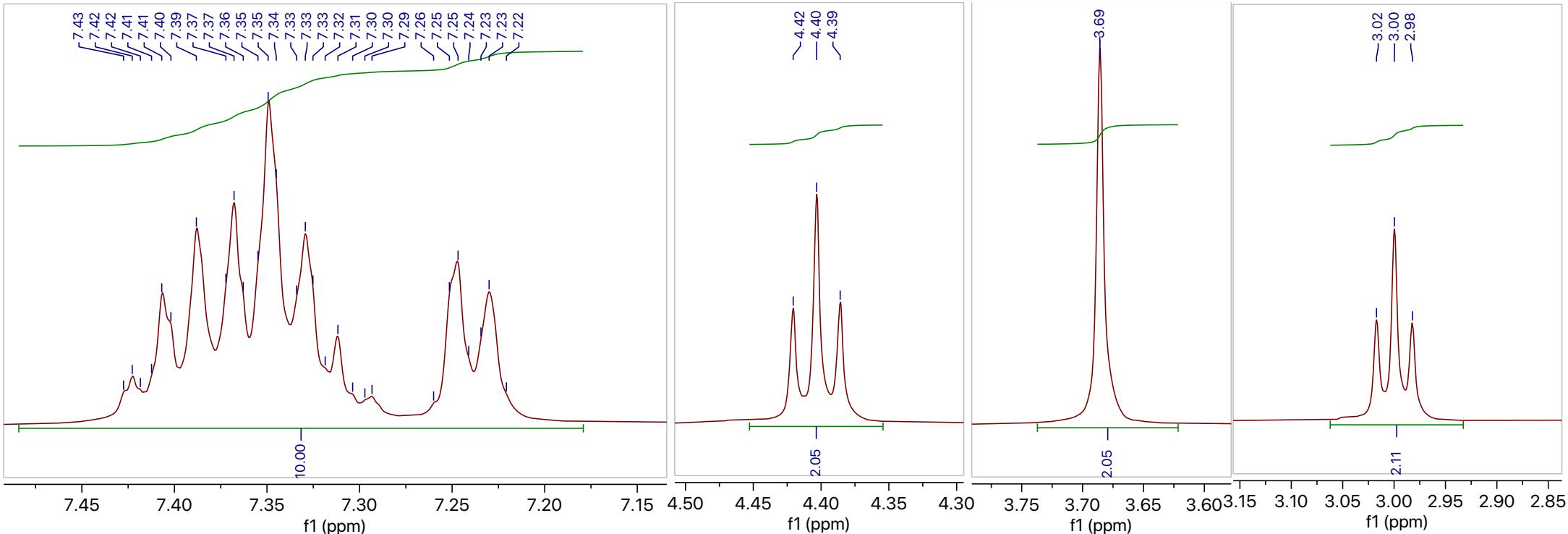


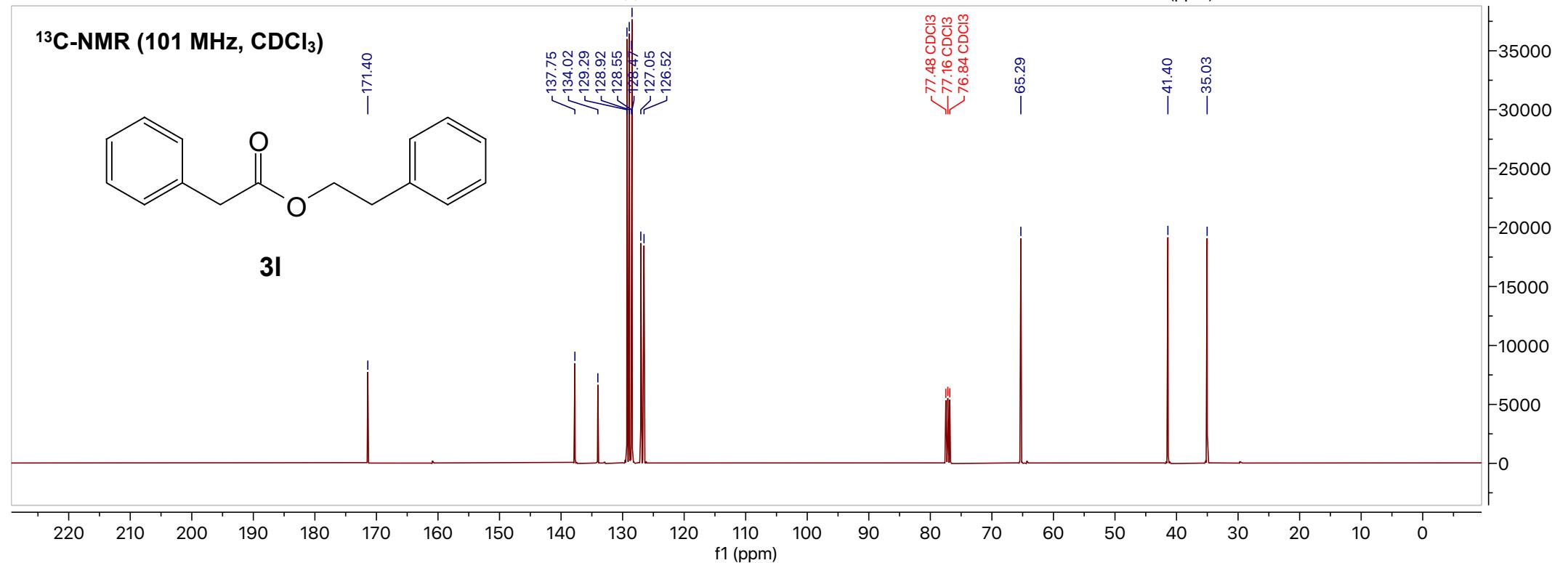
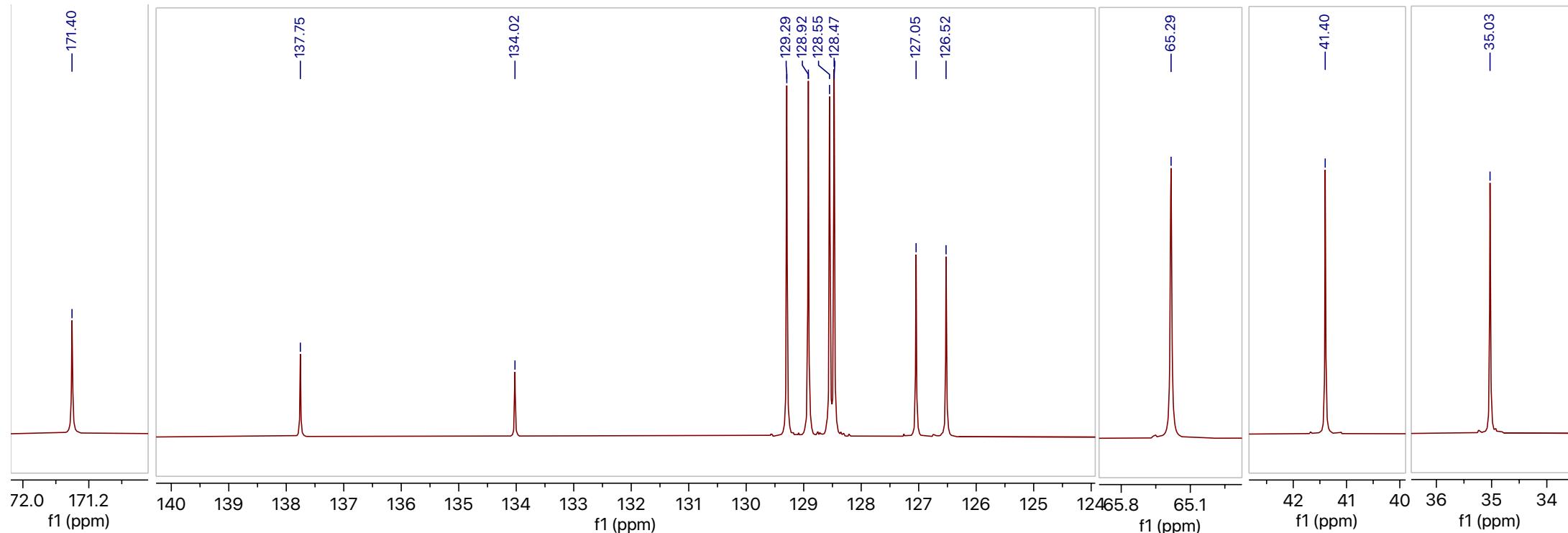
¹³C-NMR (101 MHz, CDCl₃)

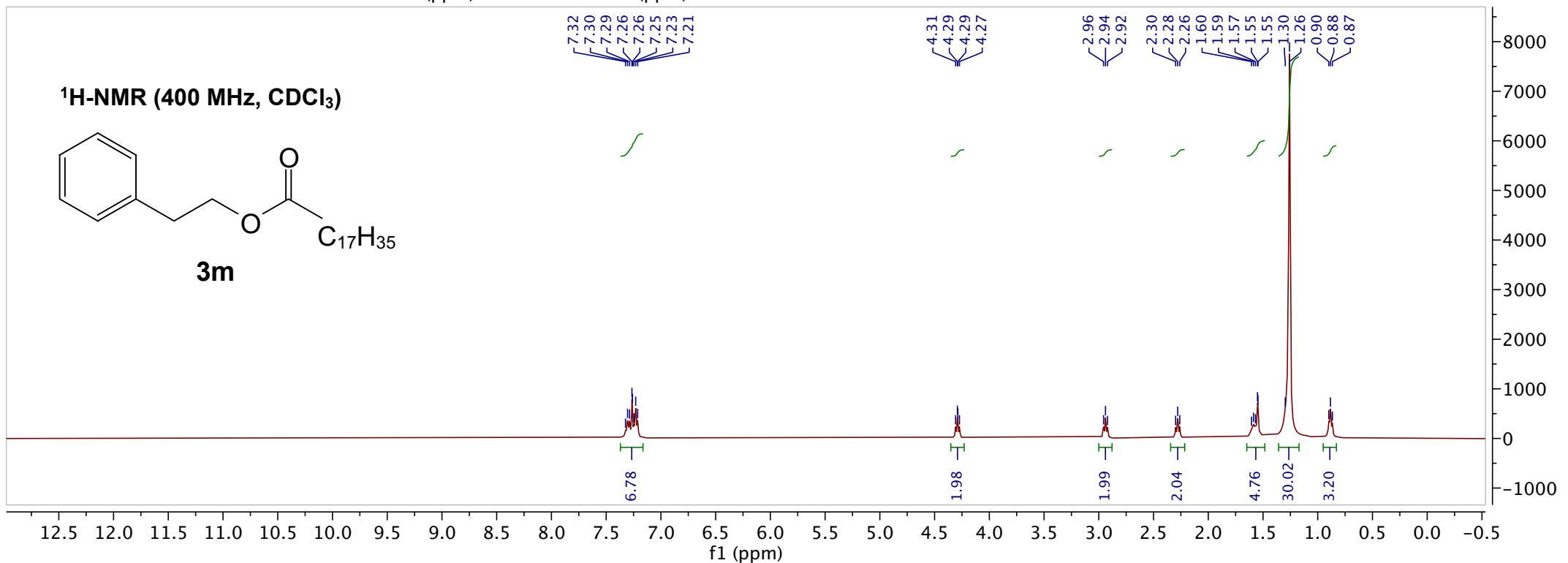
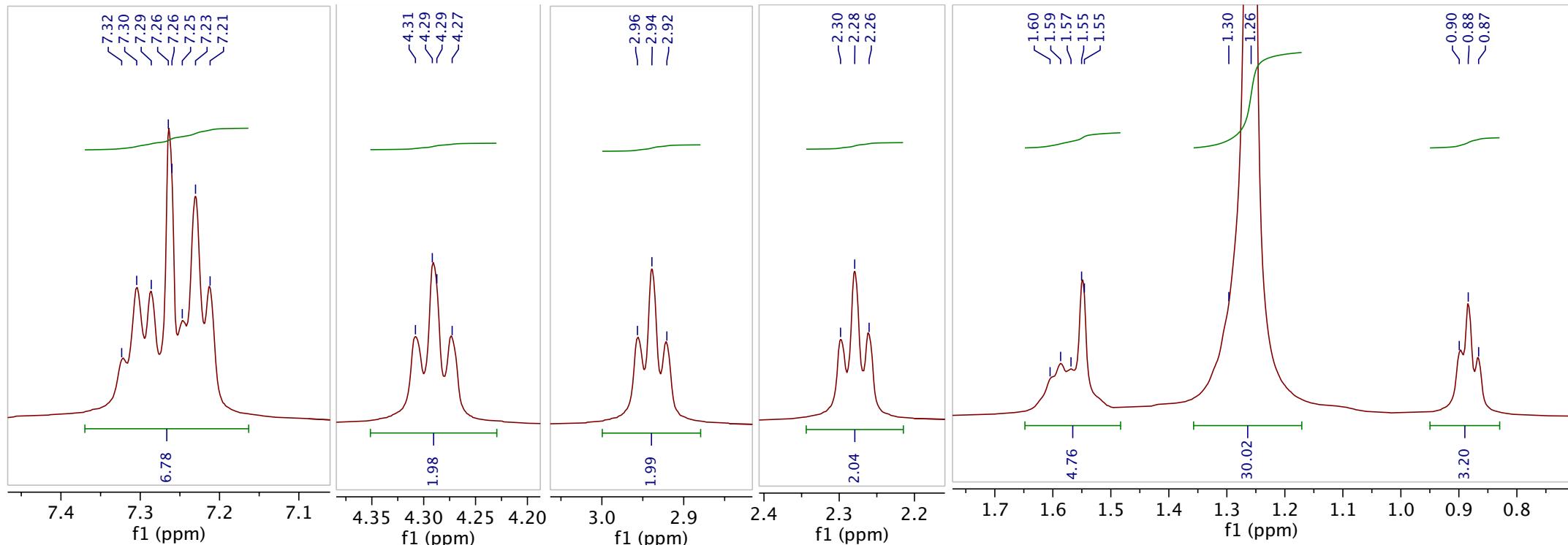


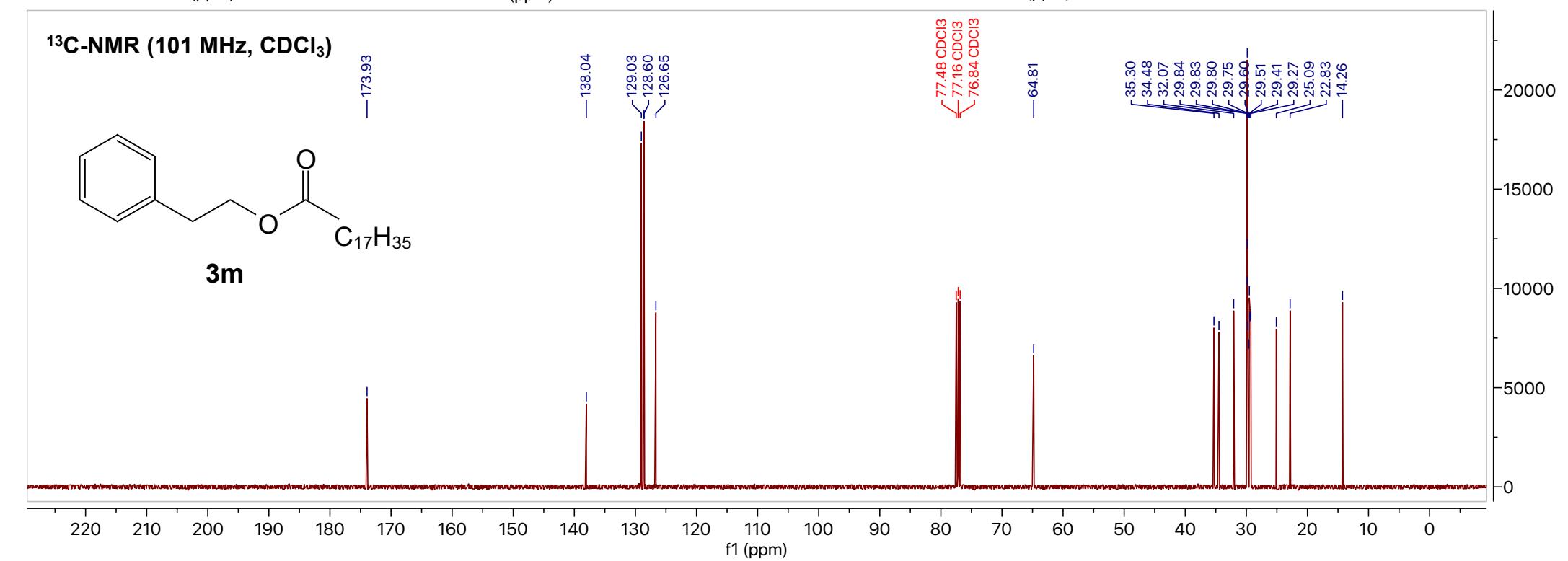
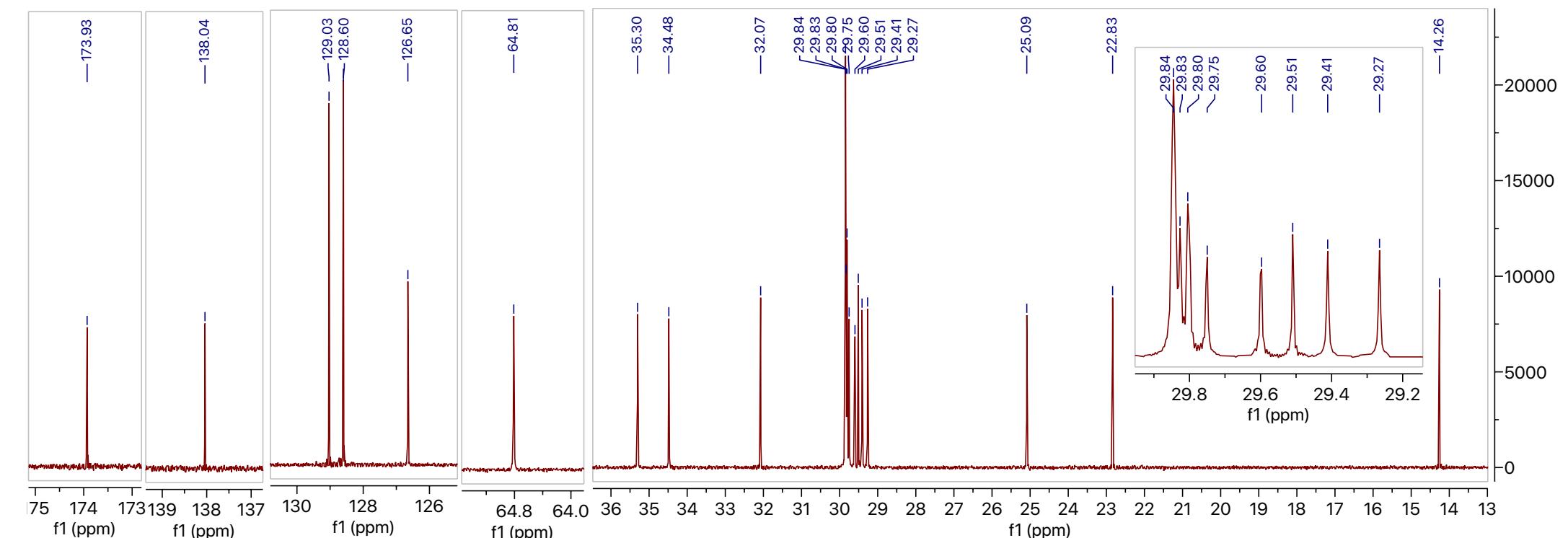


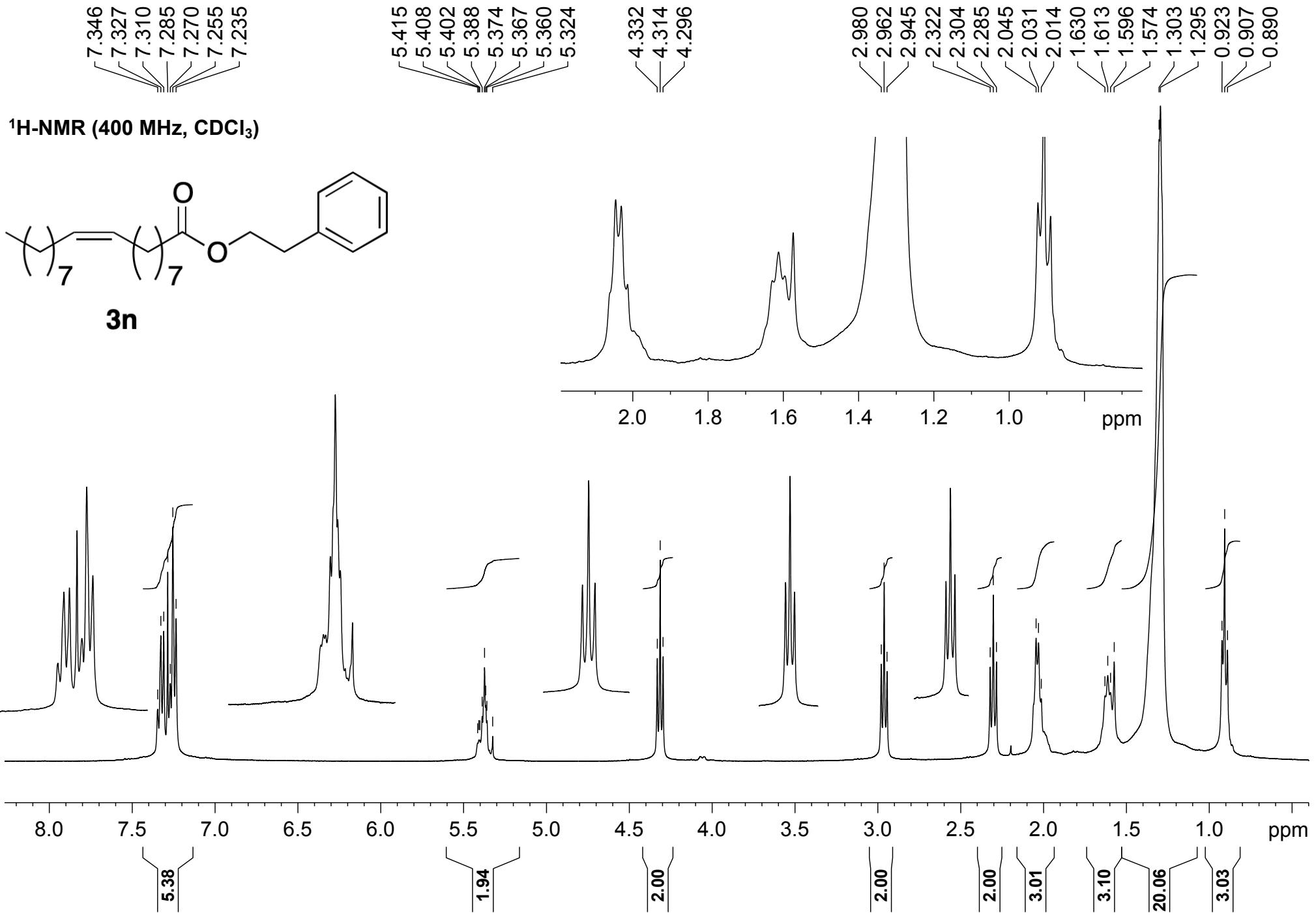


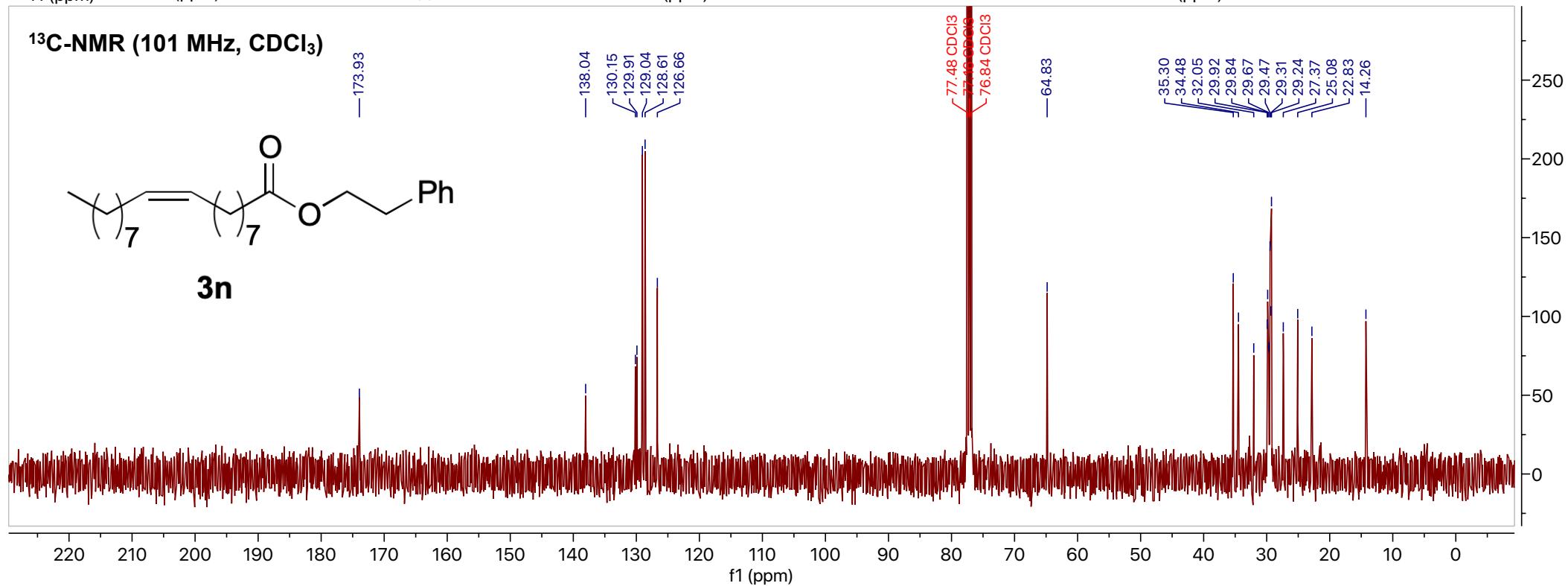
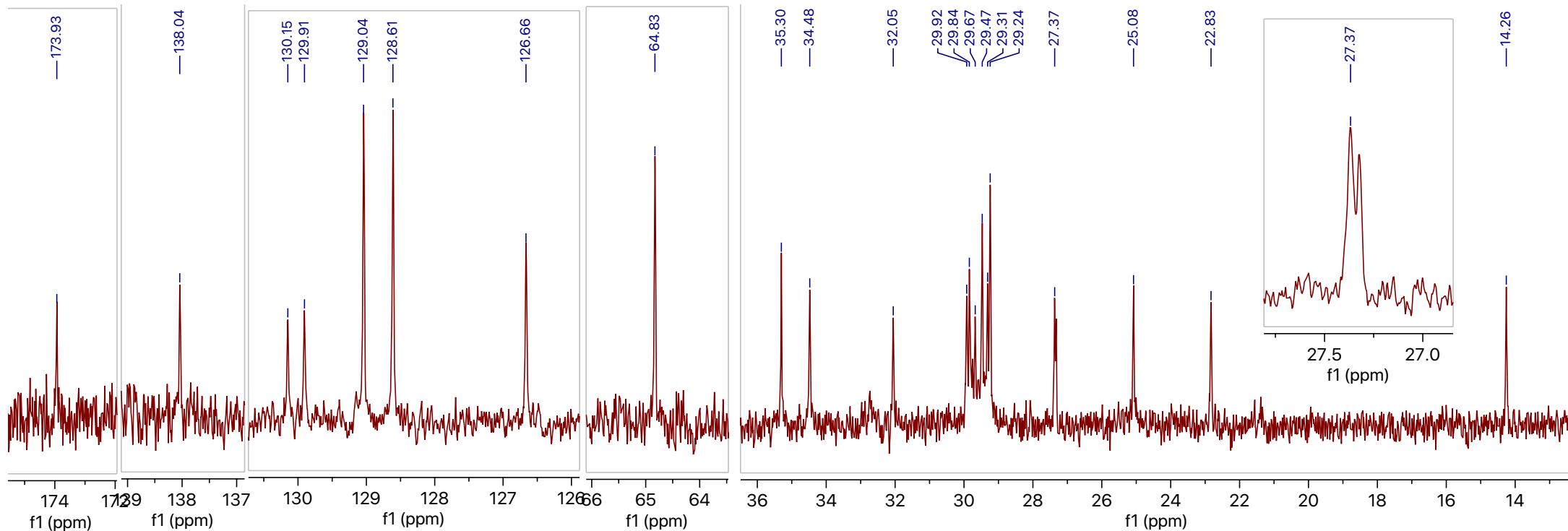


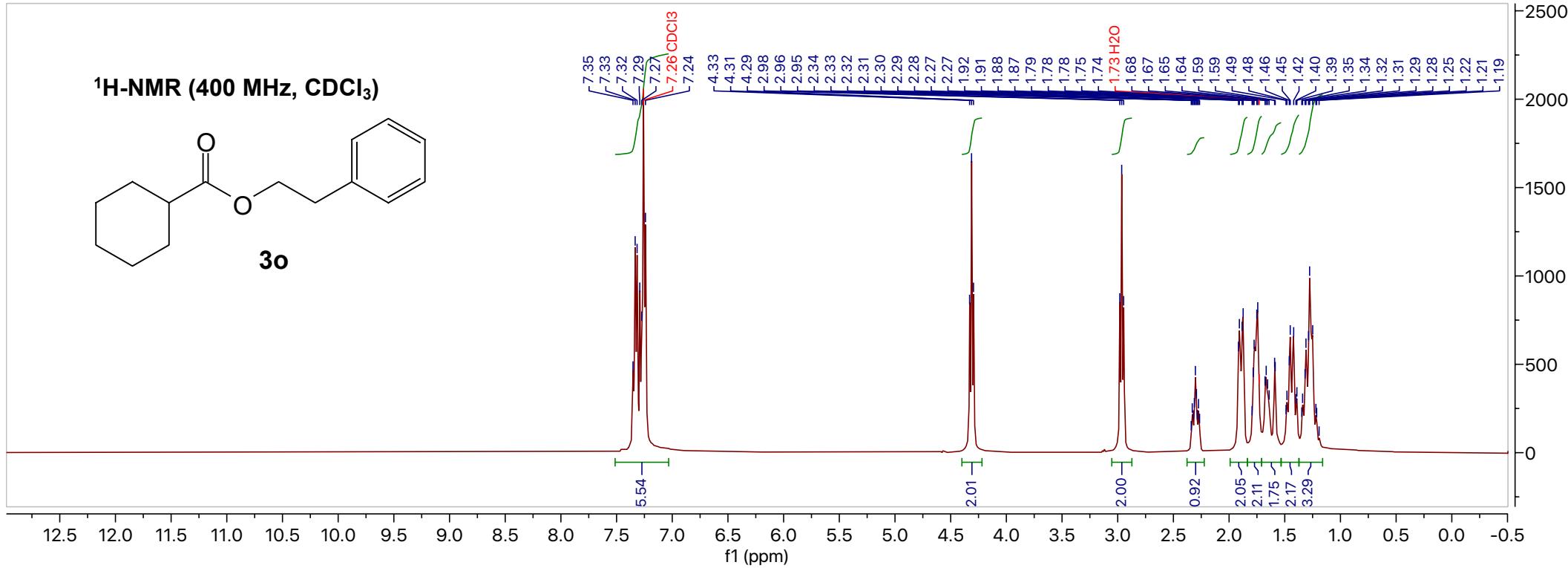
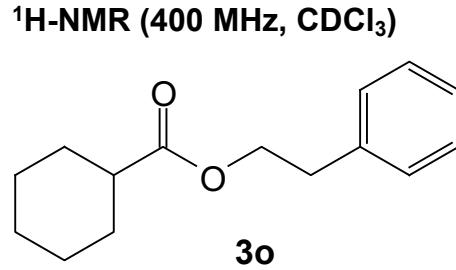
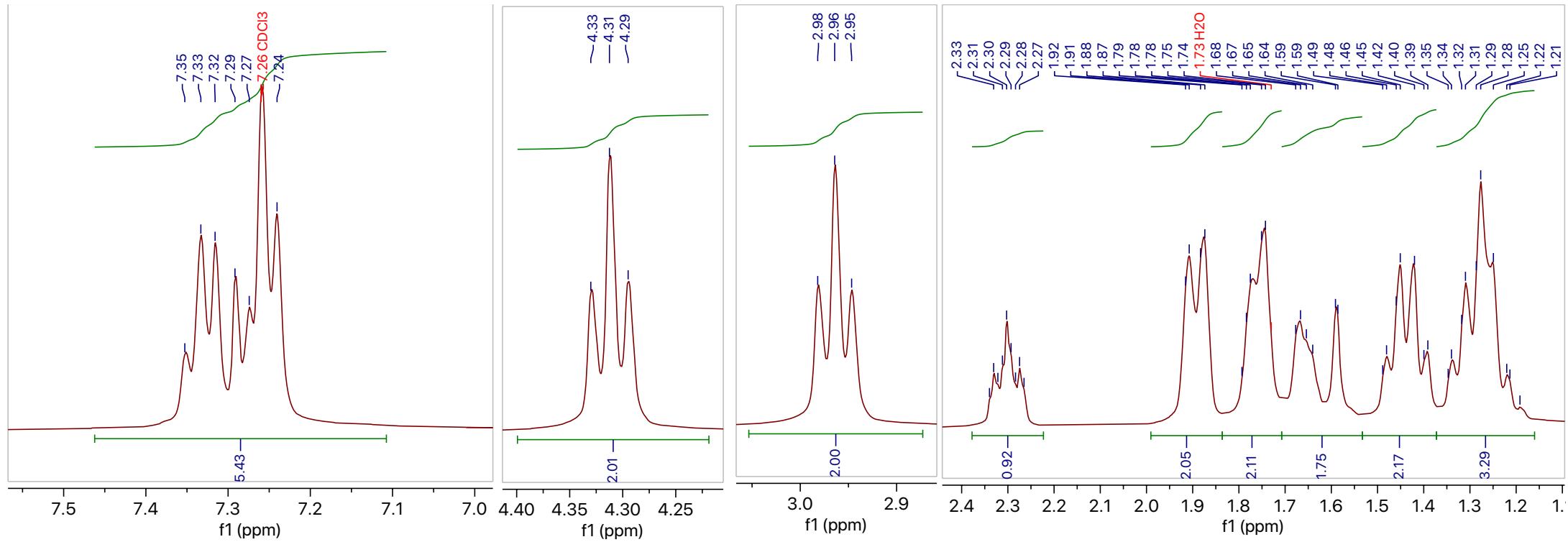


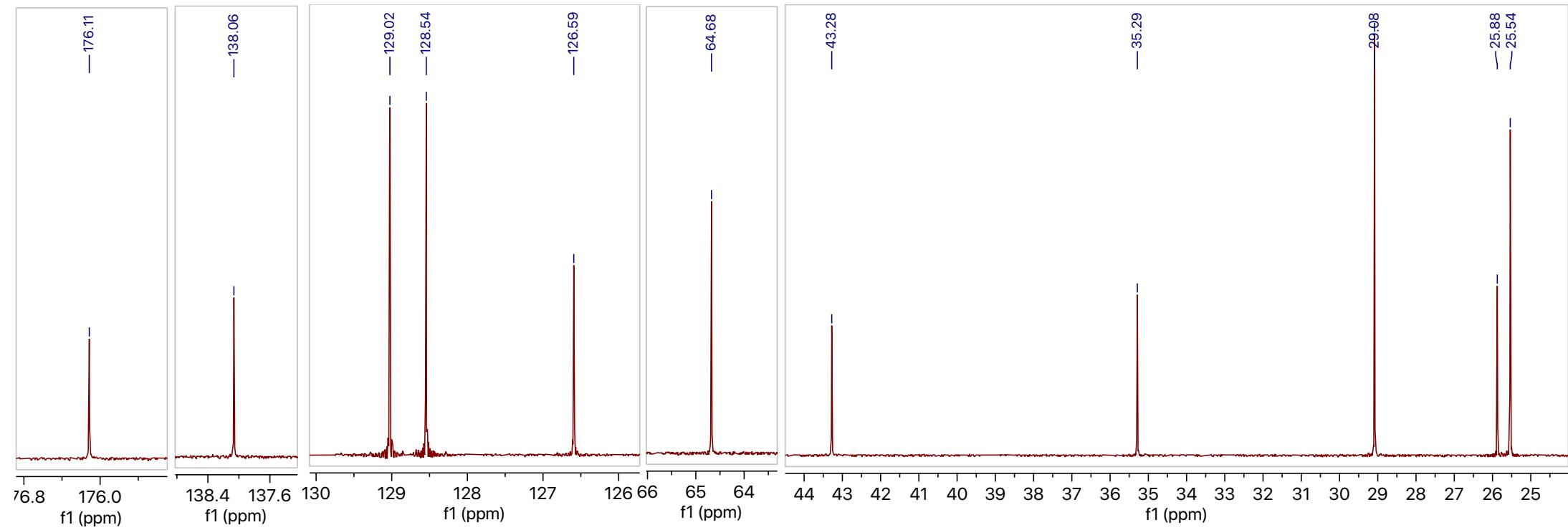




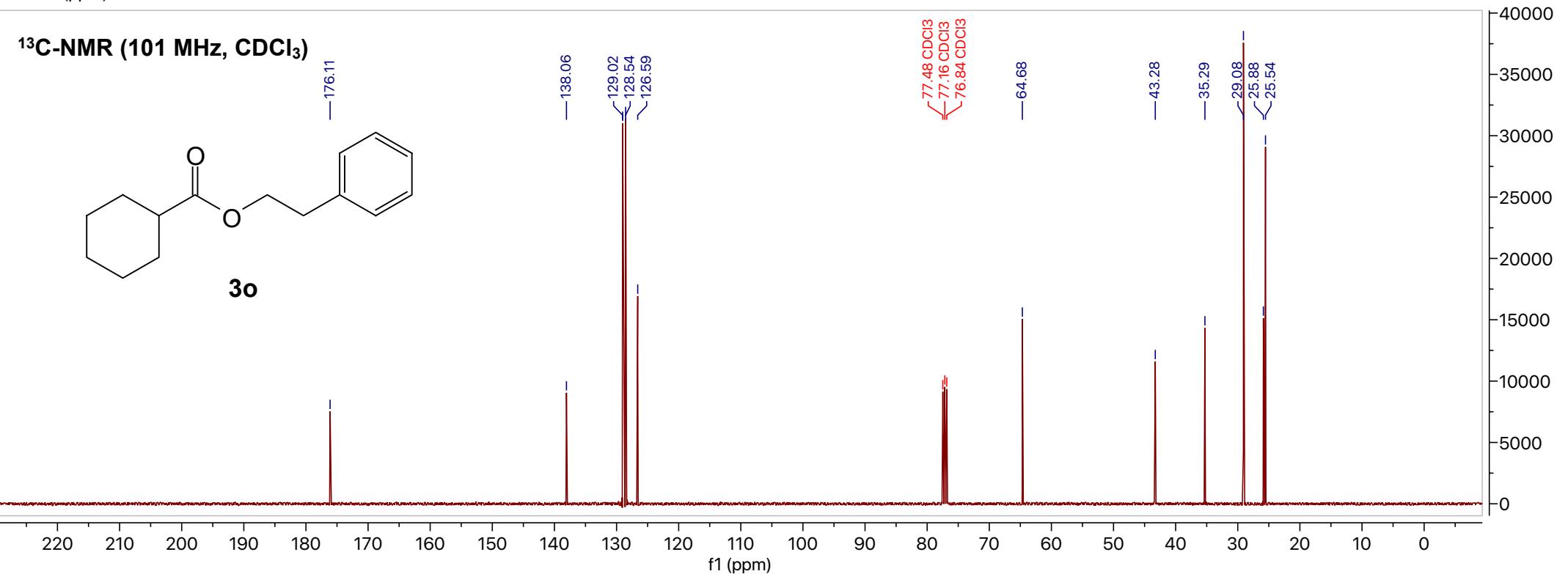
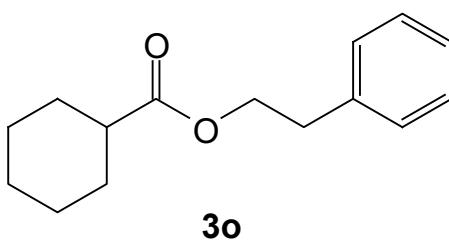


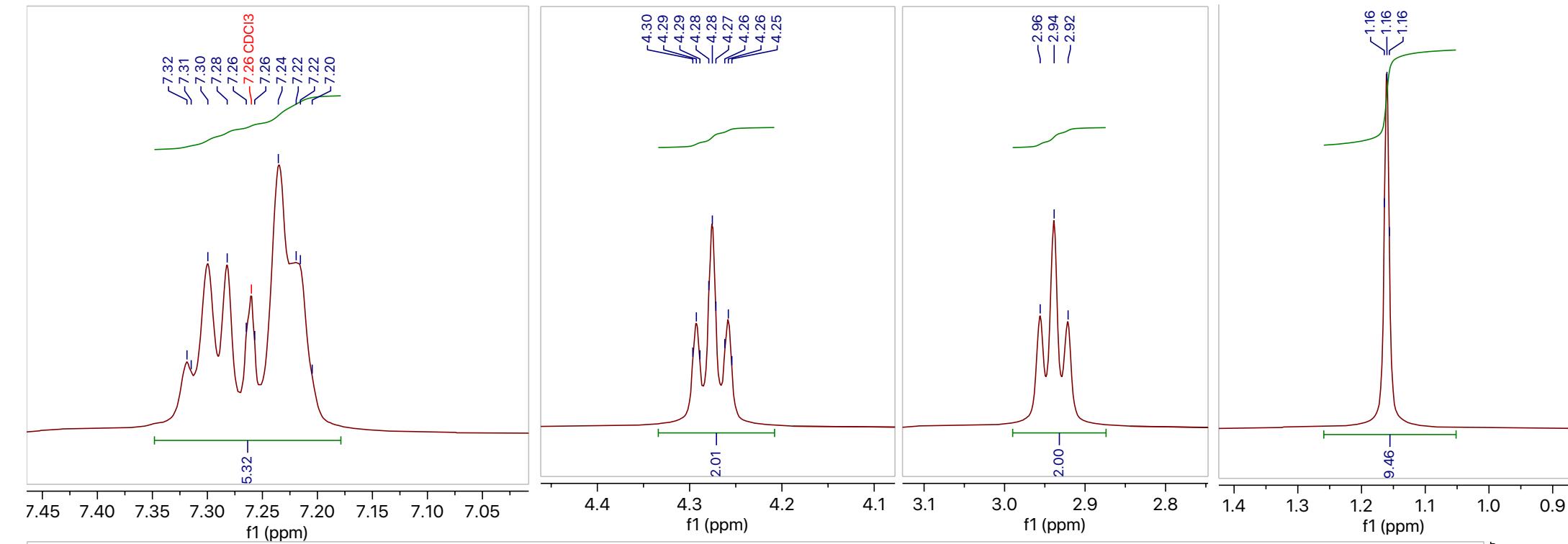




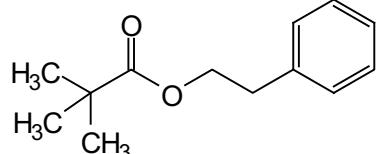


¹³C-NMR (101 MHz, CDCl₃)

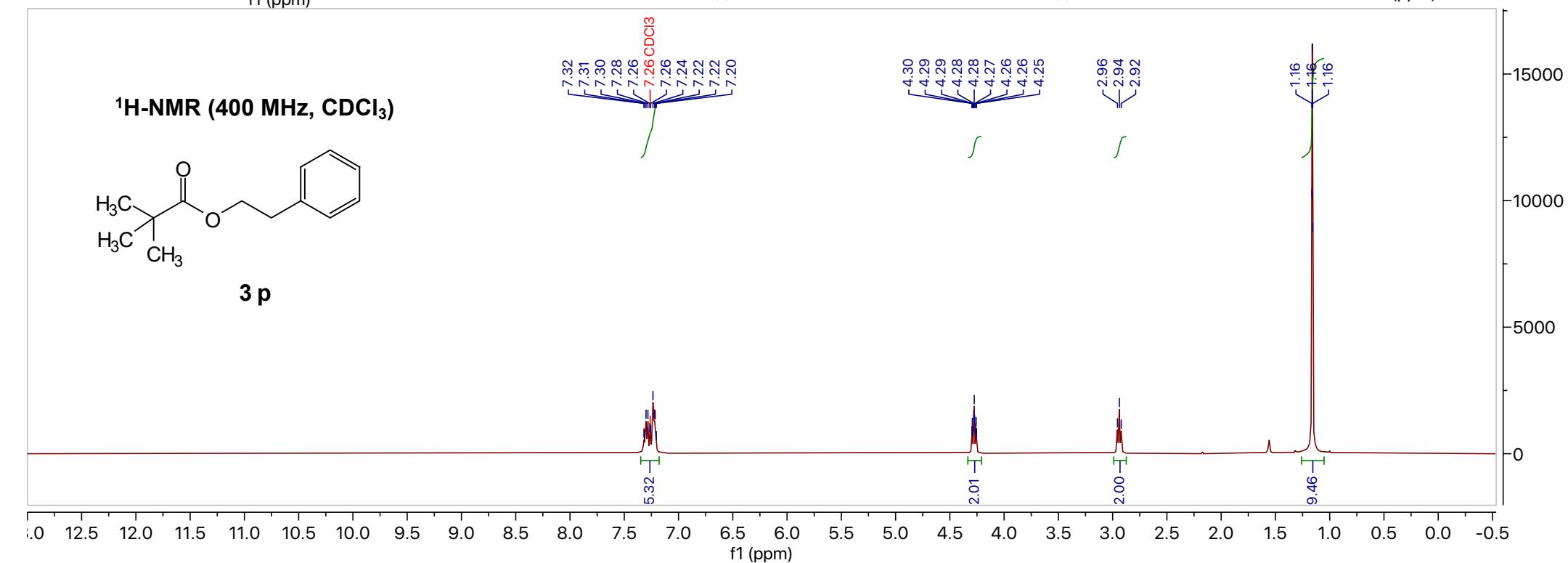


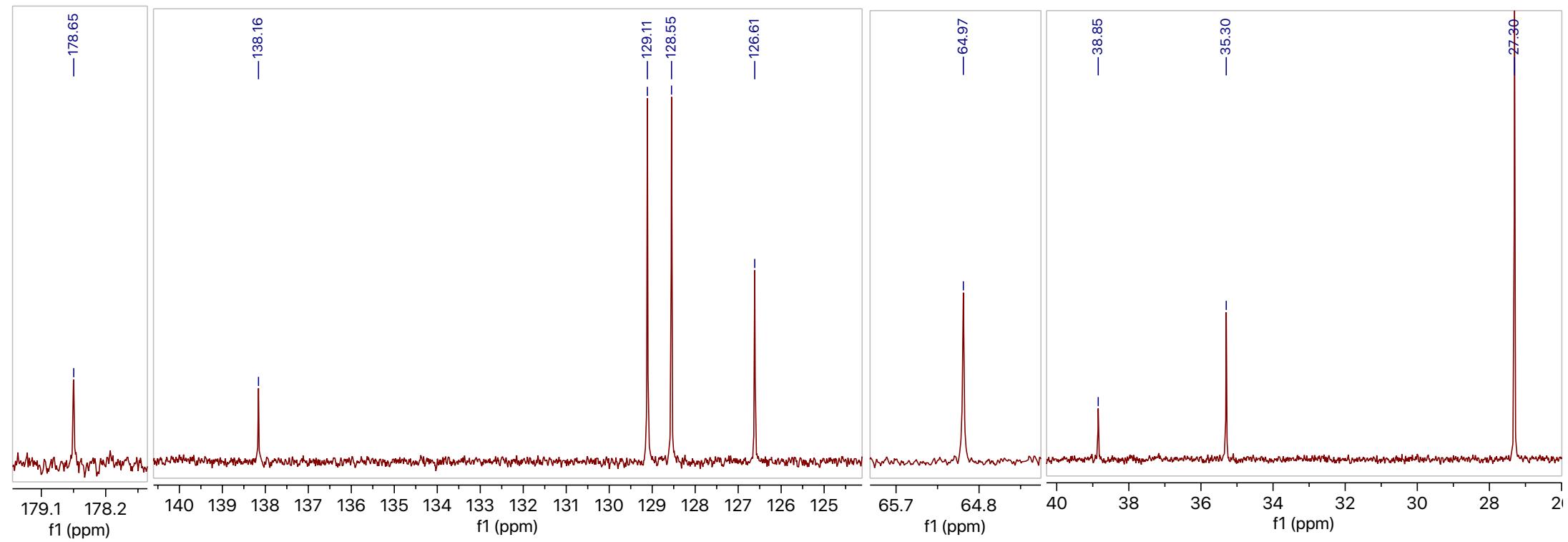


¹H-NMR (400 MHz, CDCl₃)

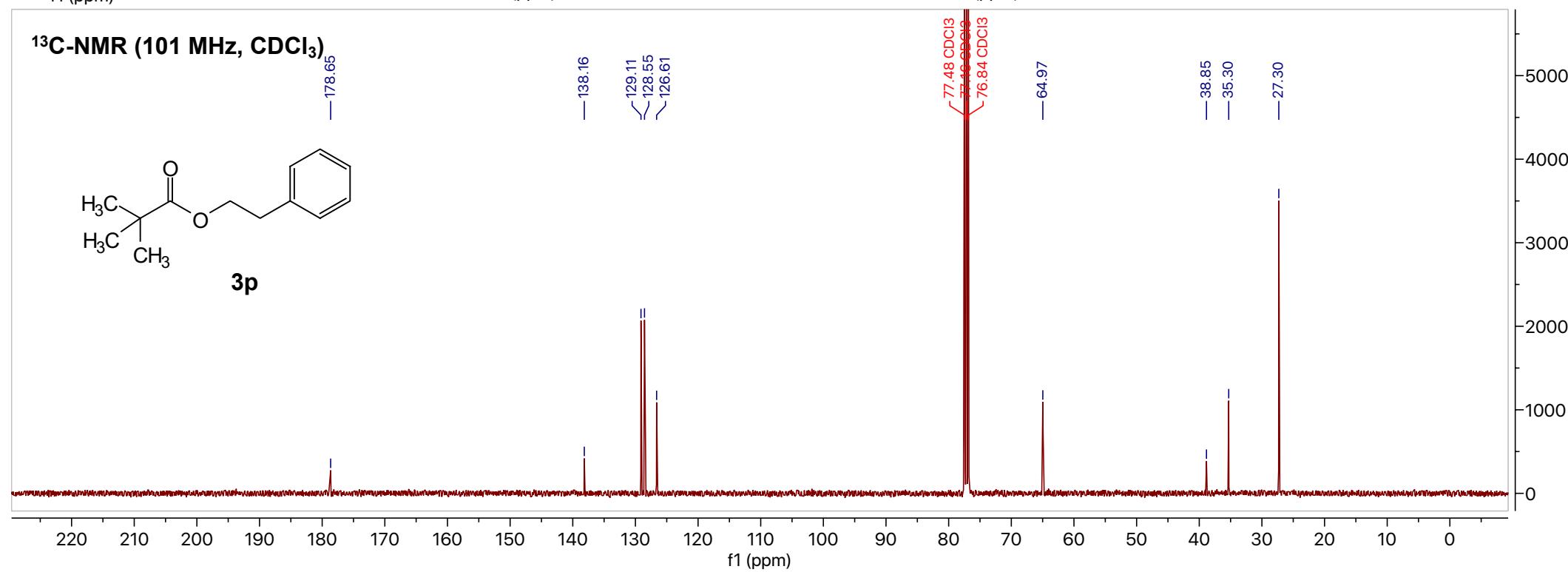
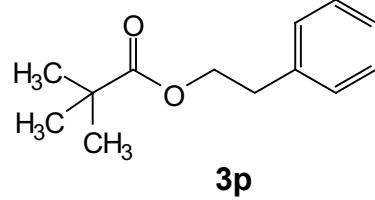


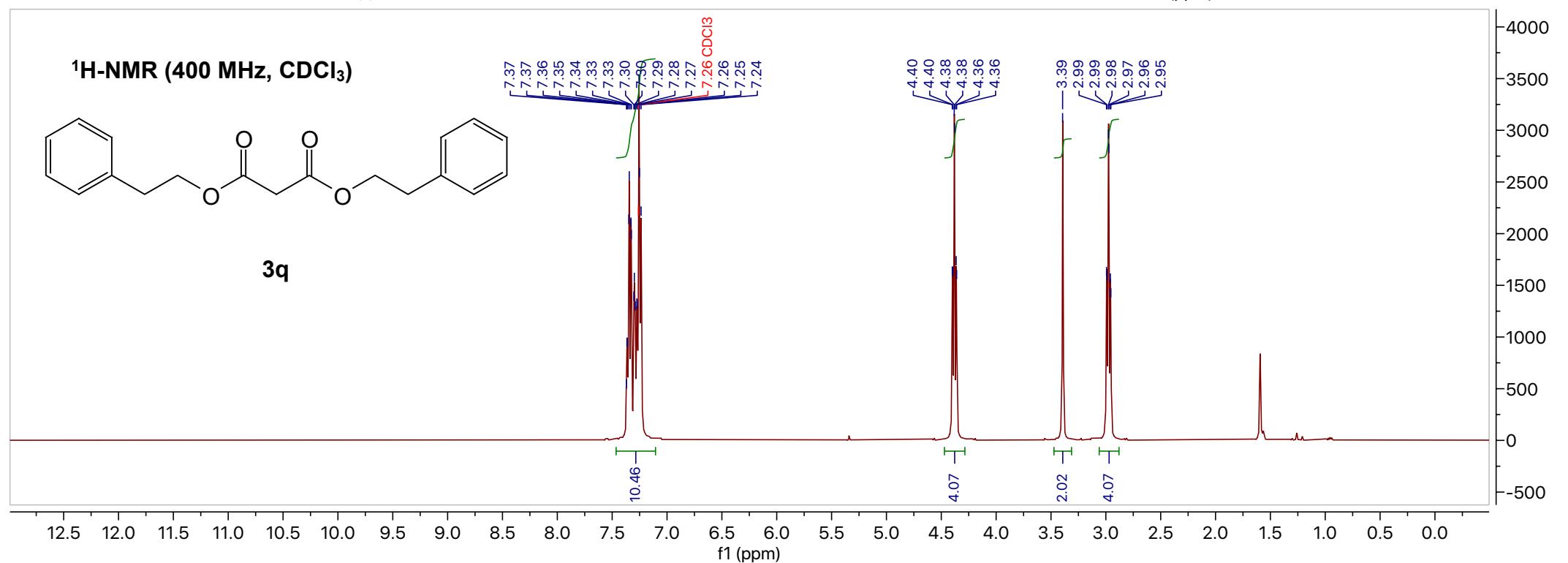
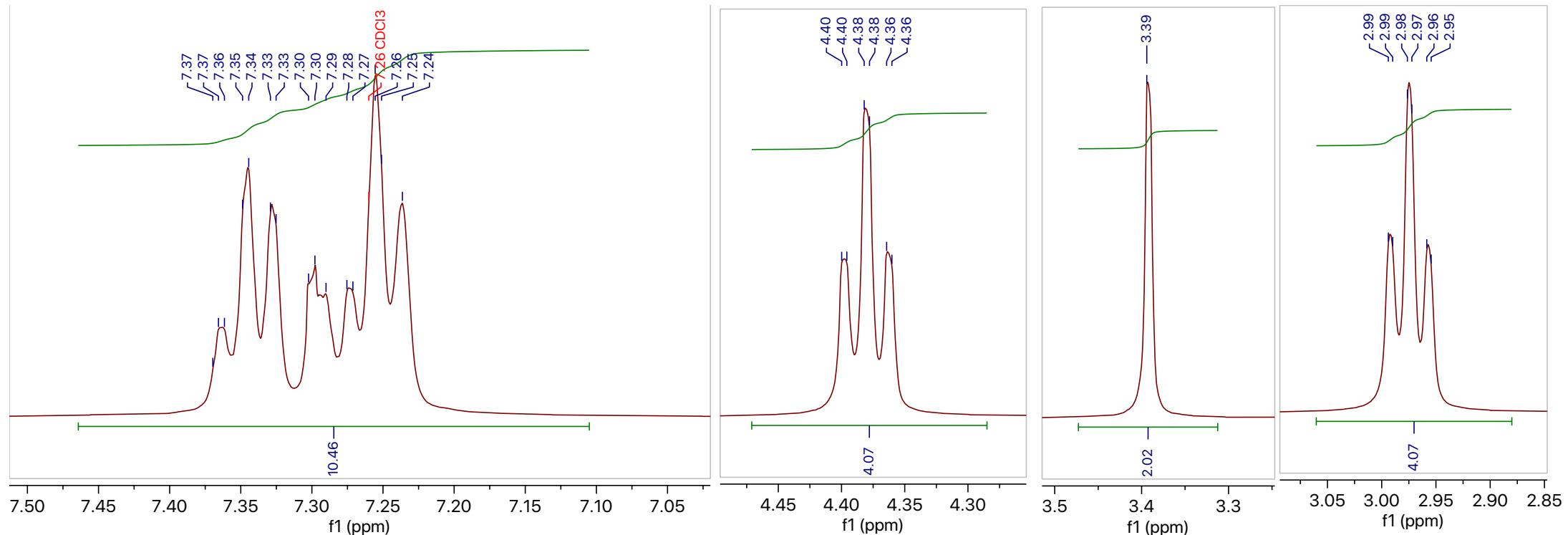
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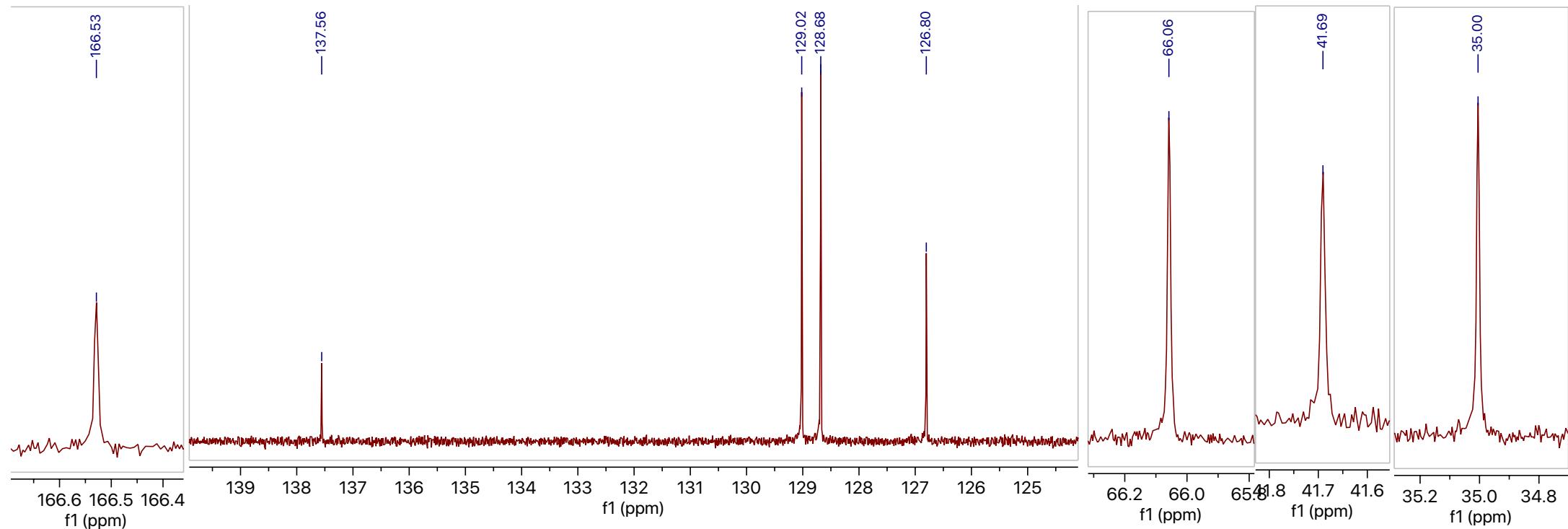




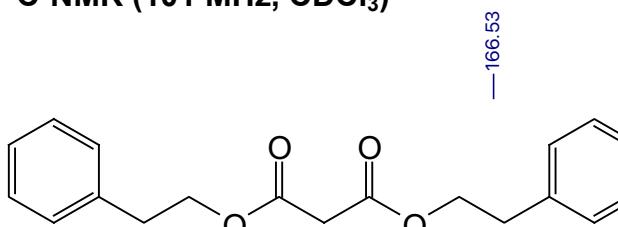
¹³C-NMR (101 MHz, CDCl₃)



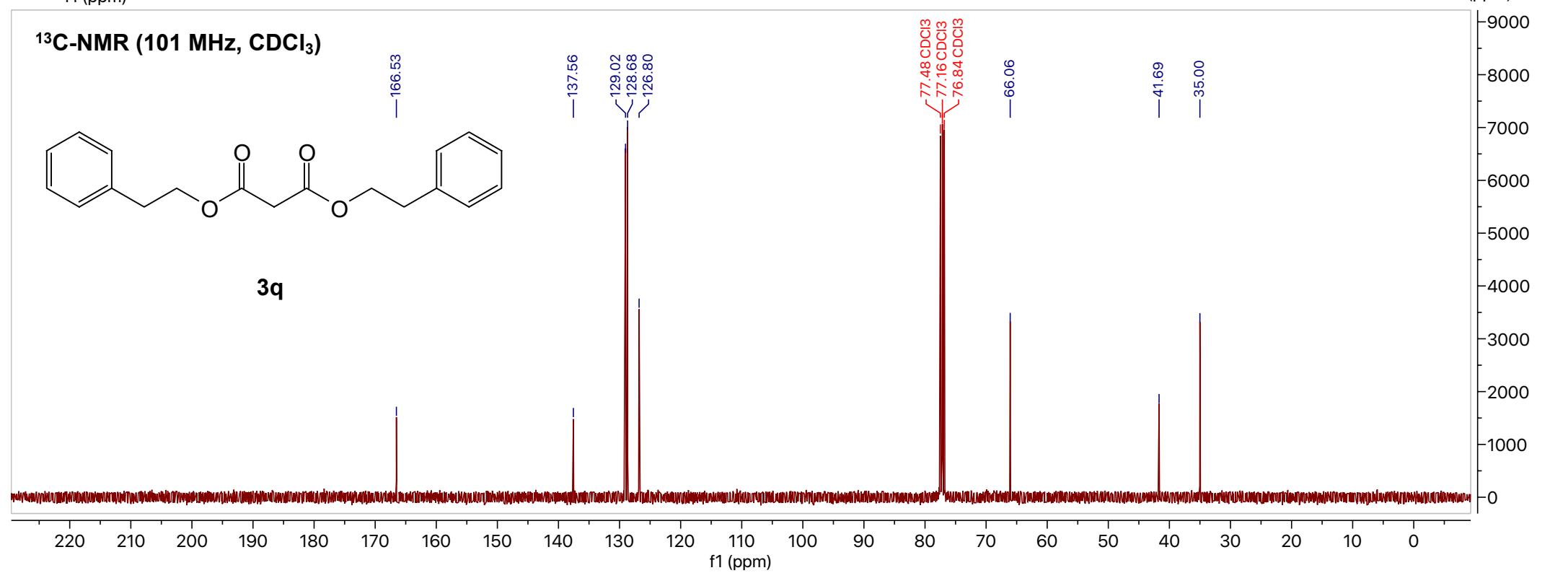


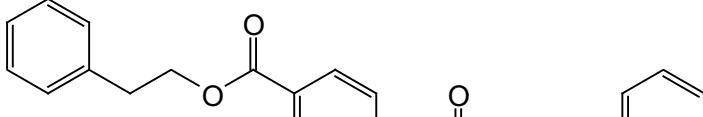
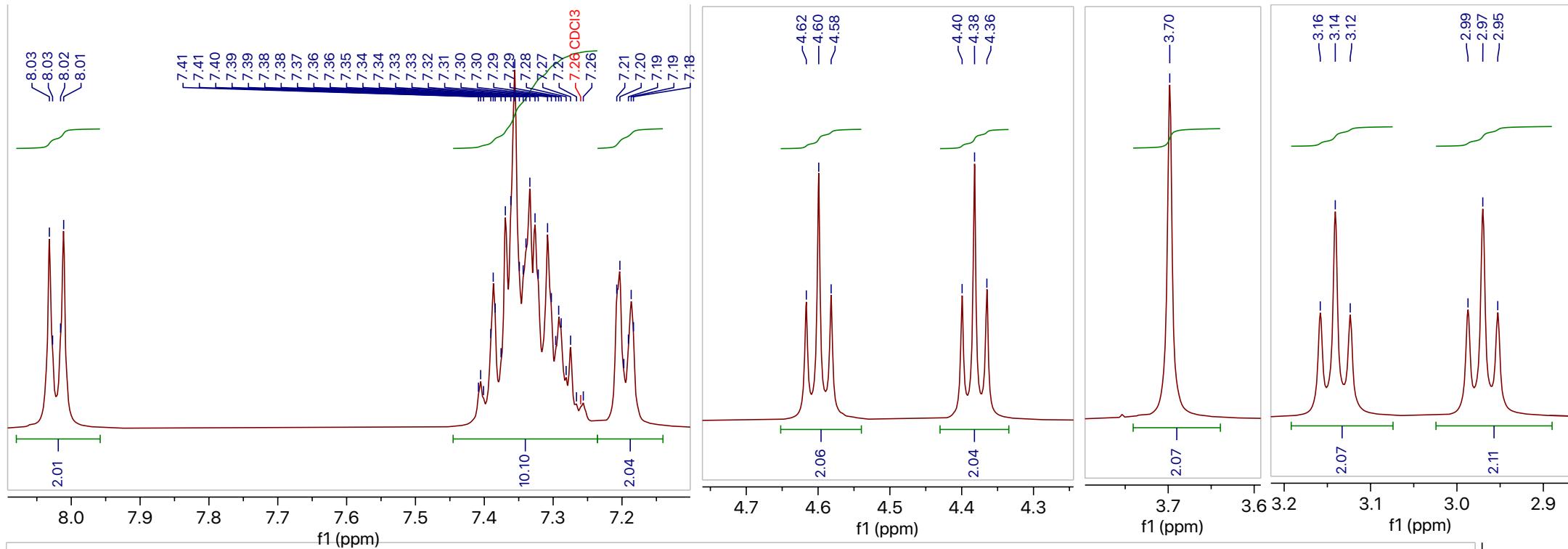


¹³C-NMR (101 MHz, CDCl₃)

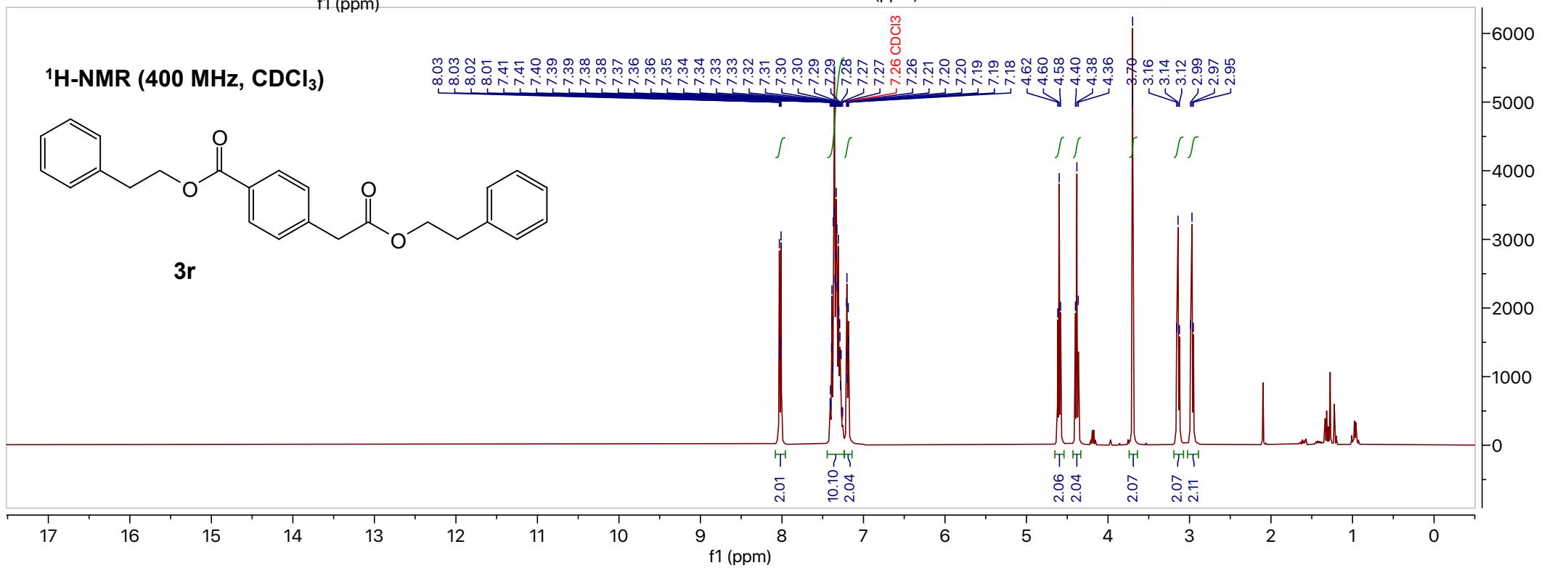


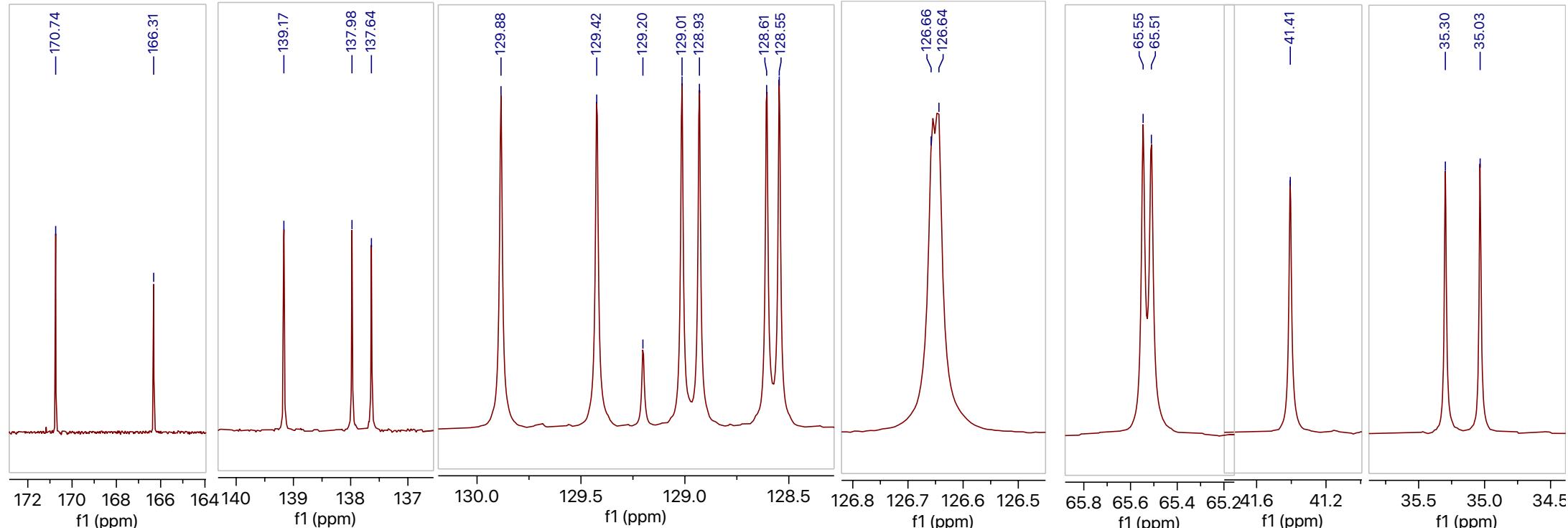
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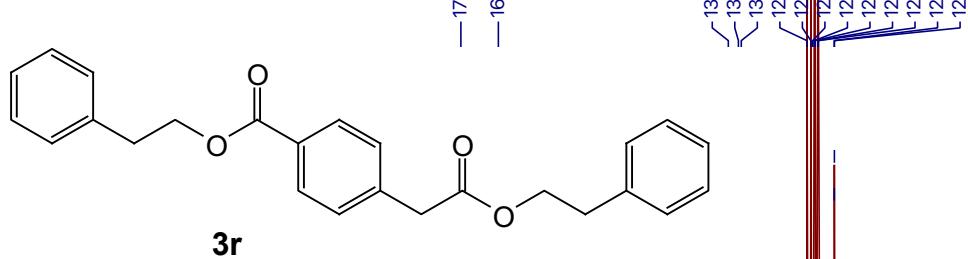


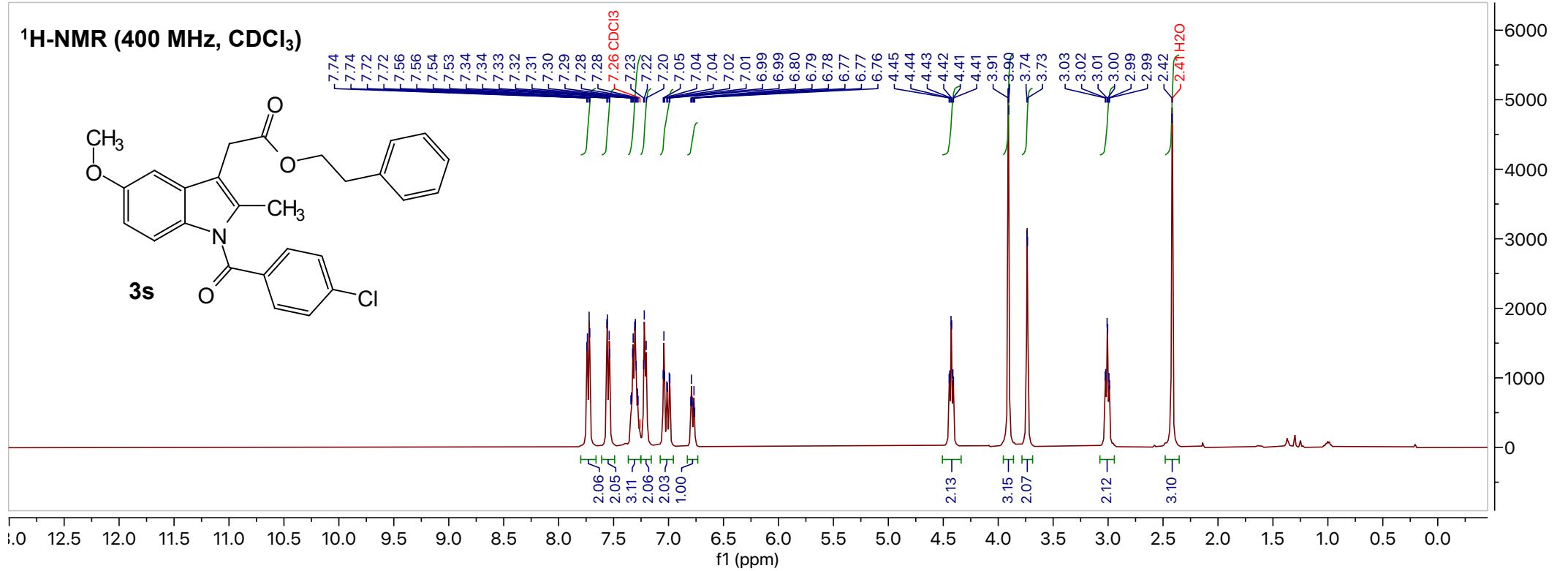
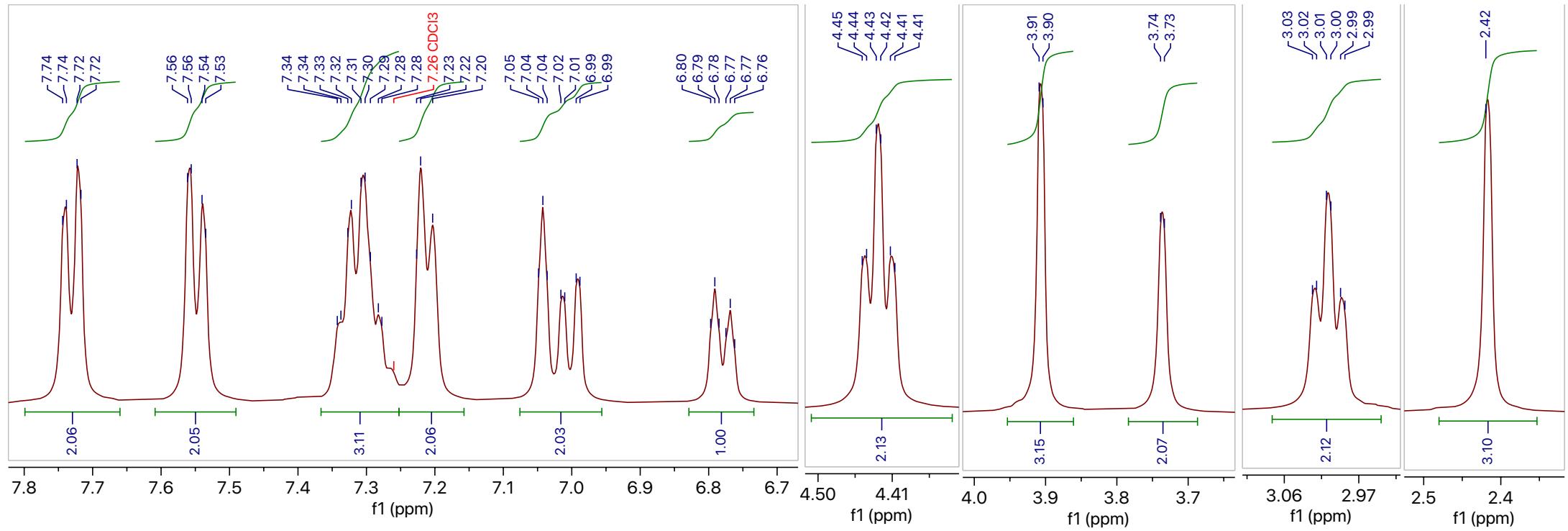
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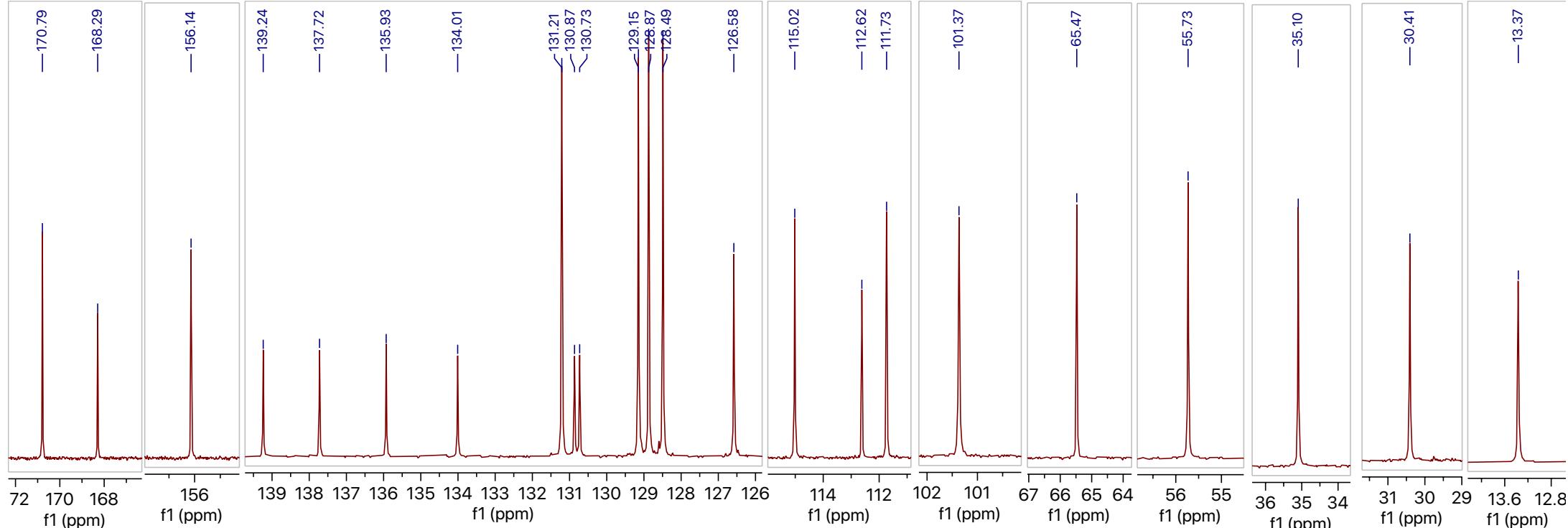




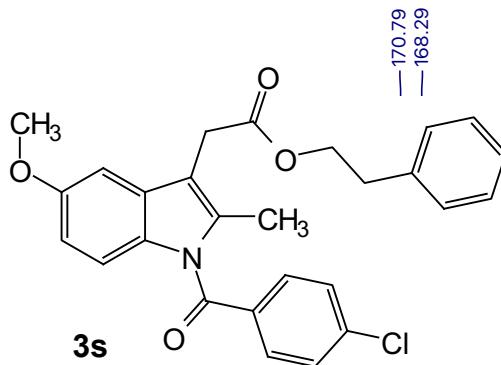
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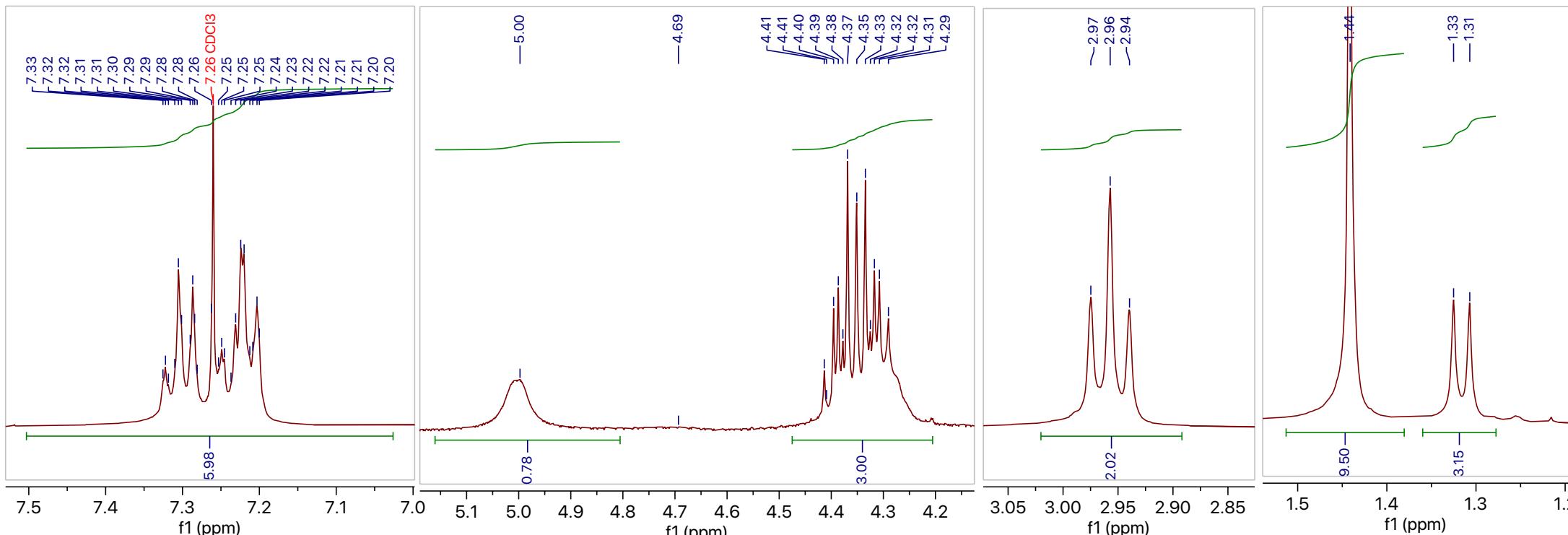




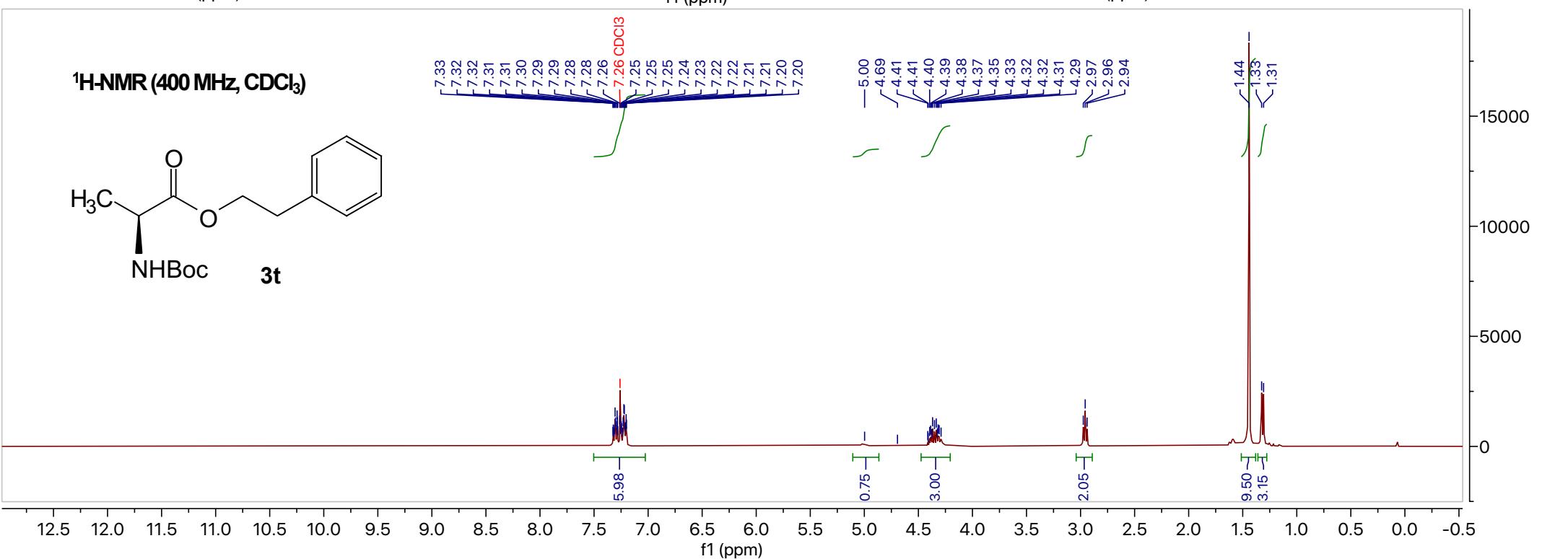
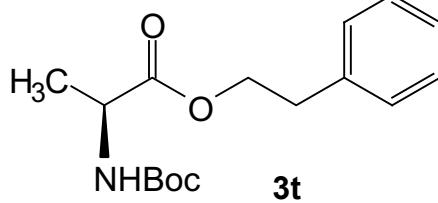


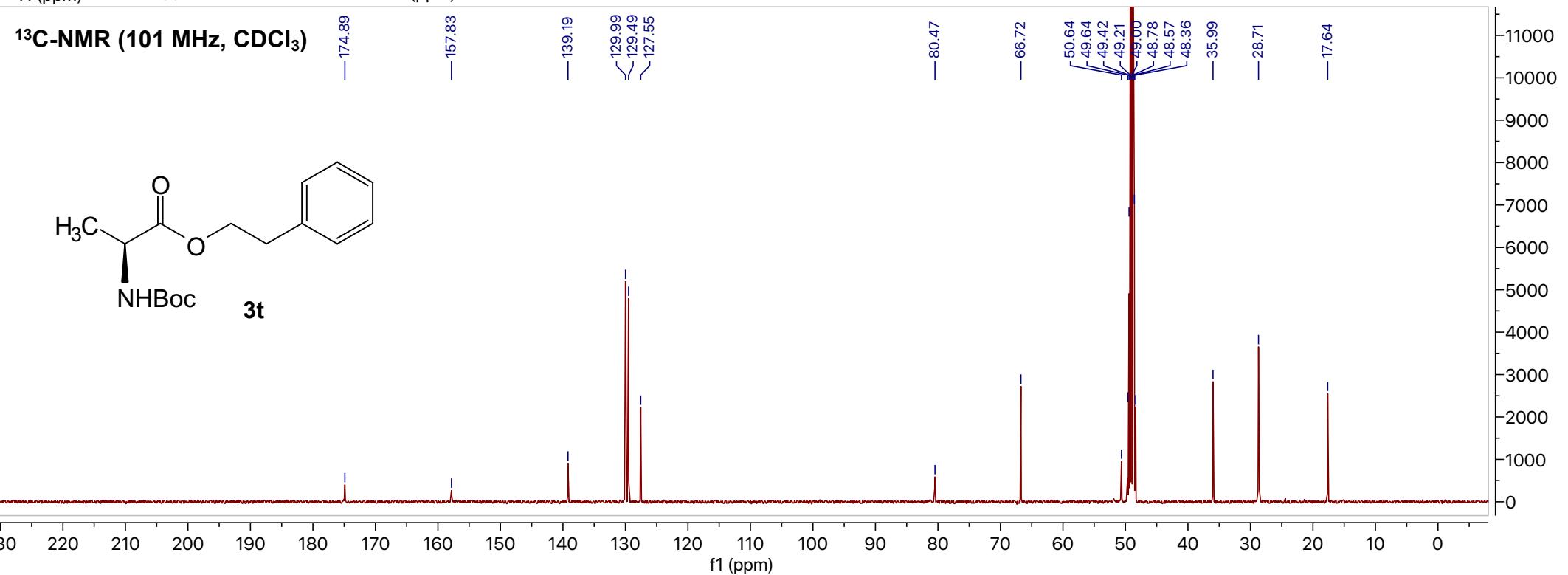
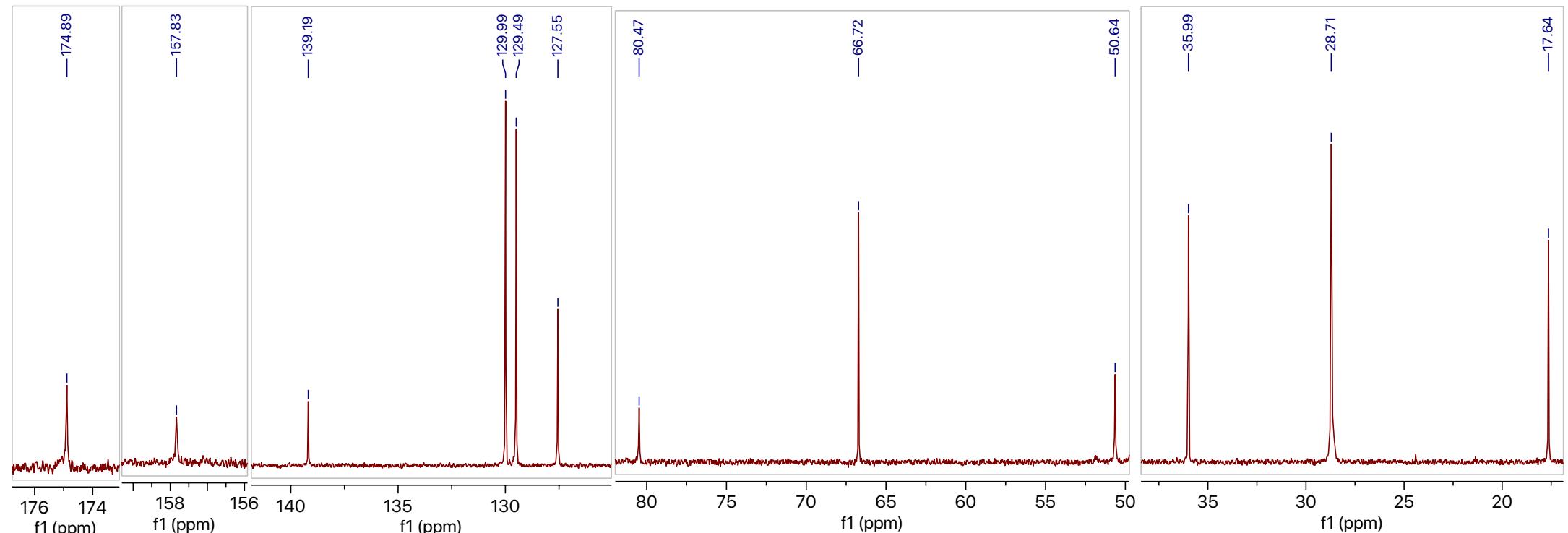
¹³C-NMR (101 MHz, CDCl₃)

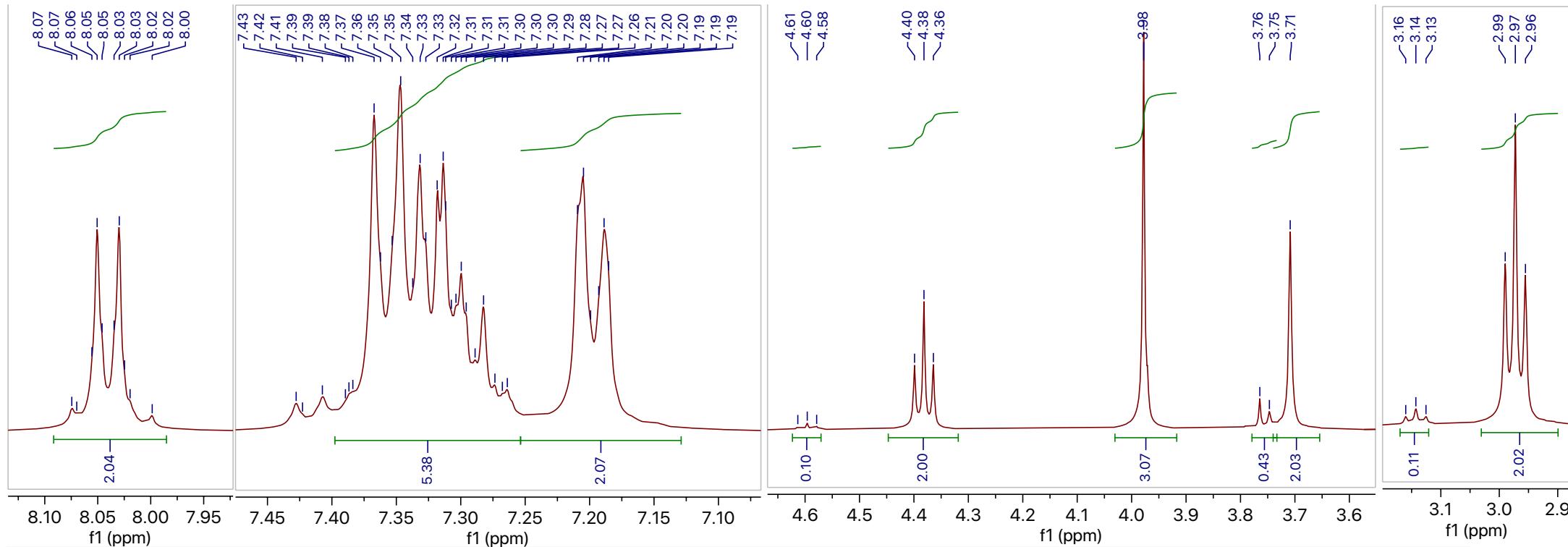




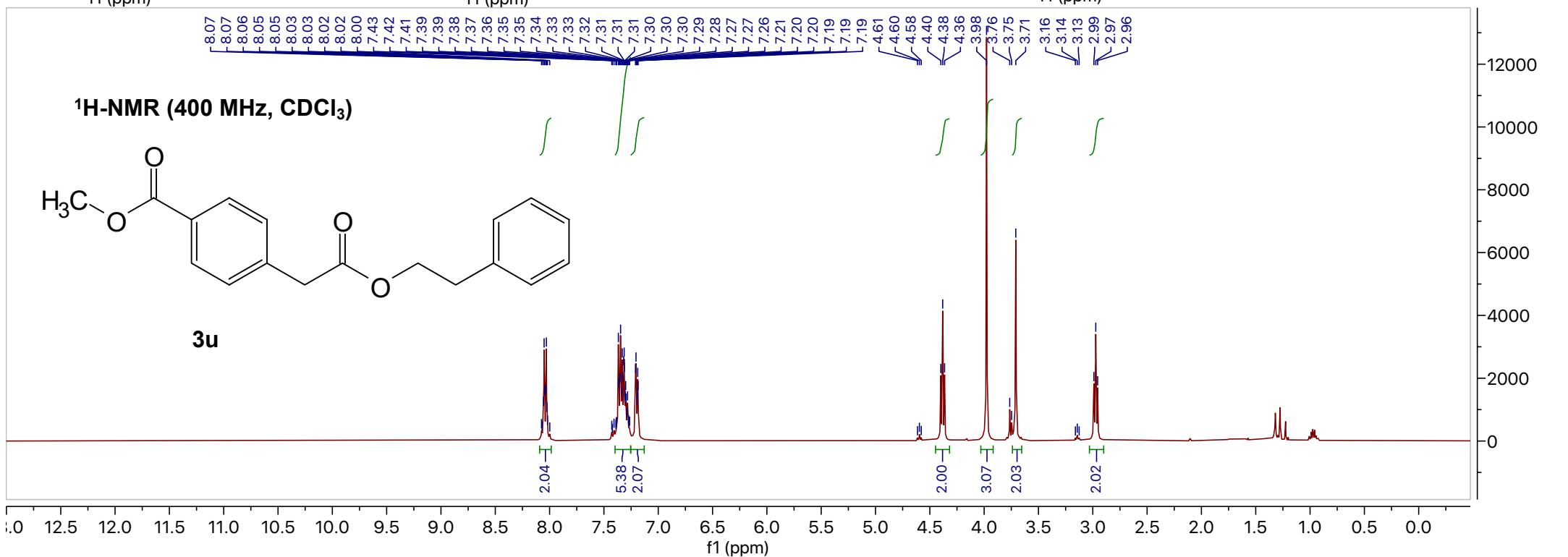
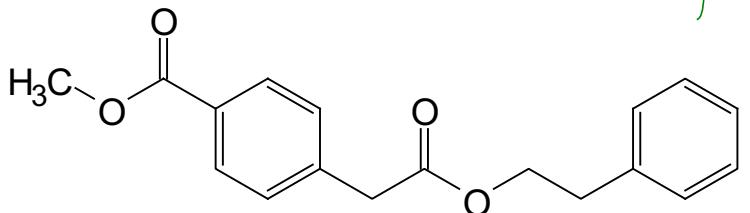
^1H -NMR (400 MHz, CDCl₃)

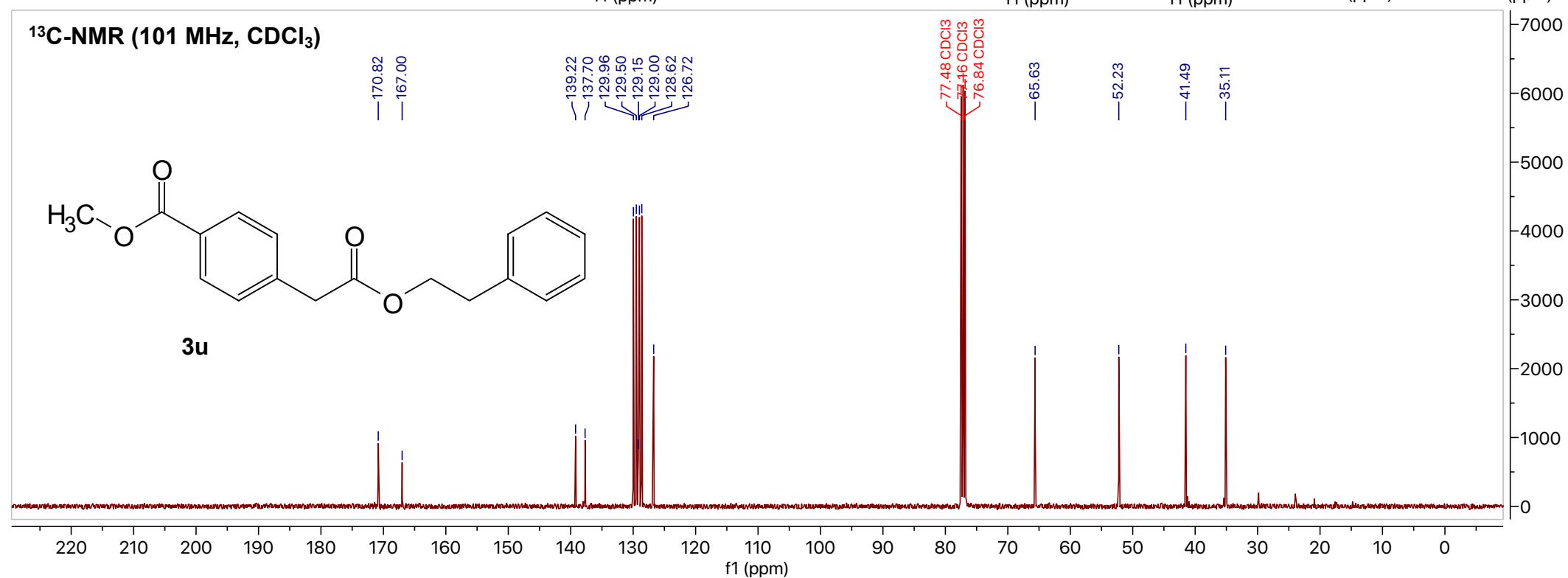
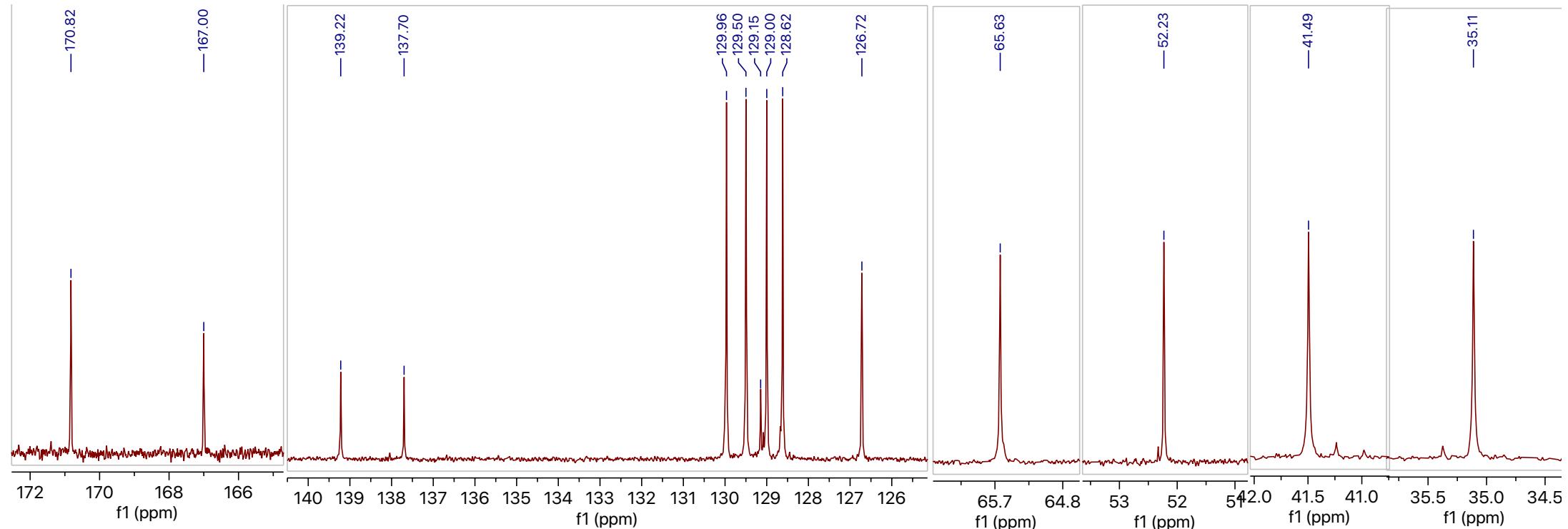


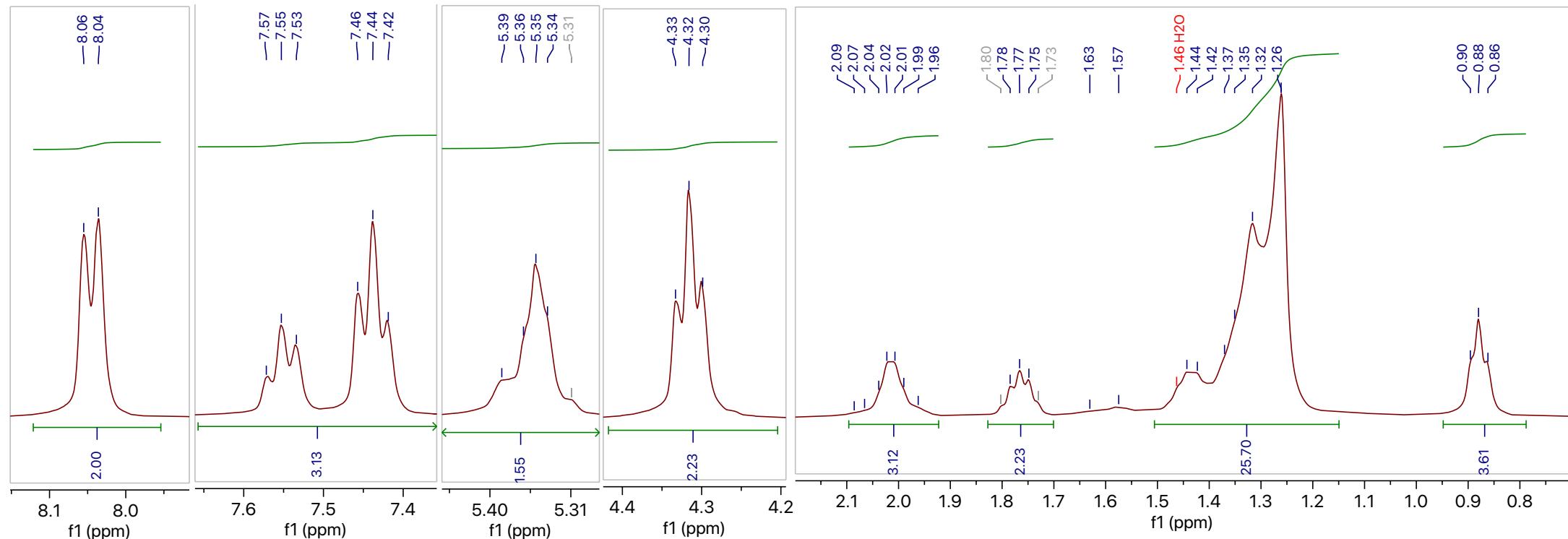




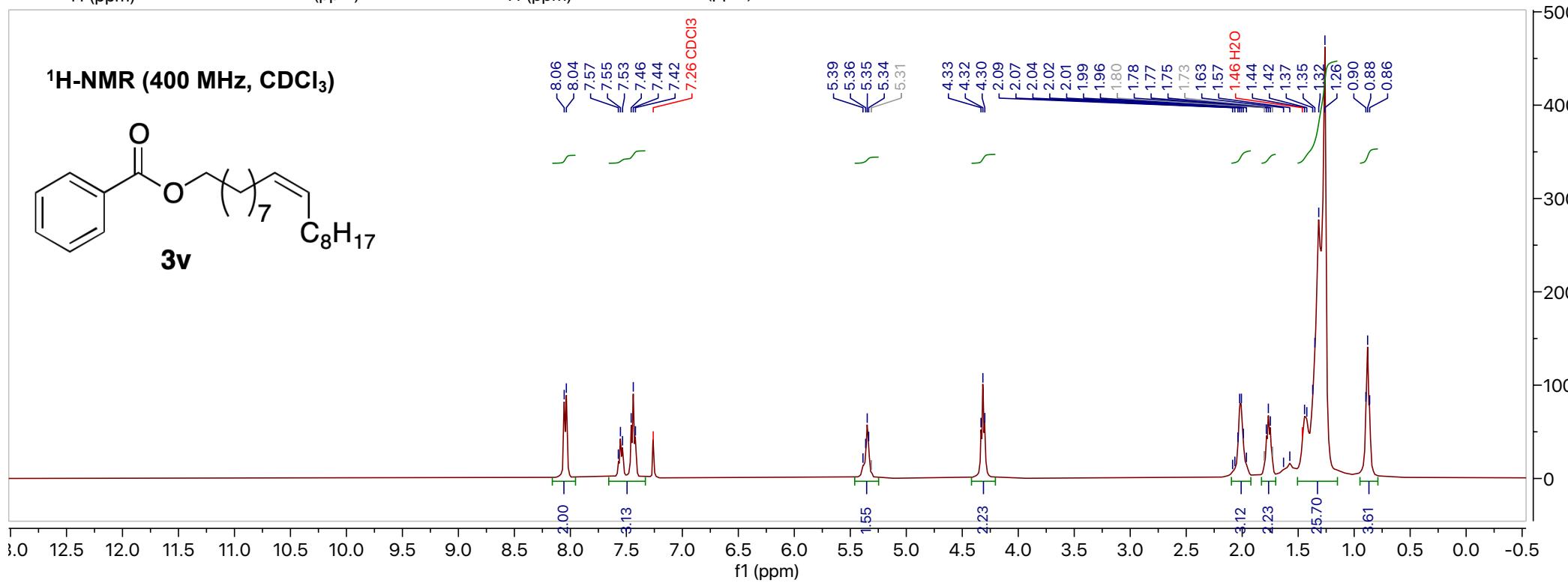
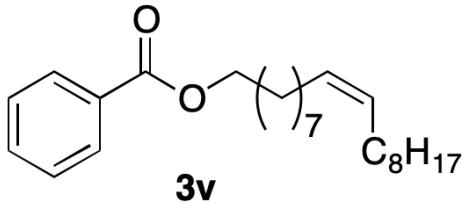
¹H-NMR (400 MHz, CDCl₃)

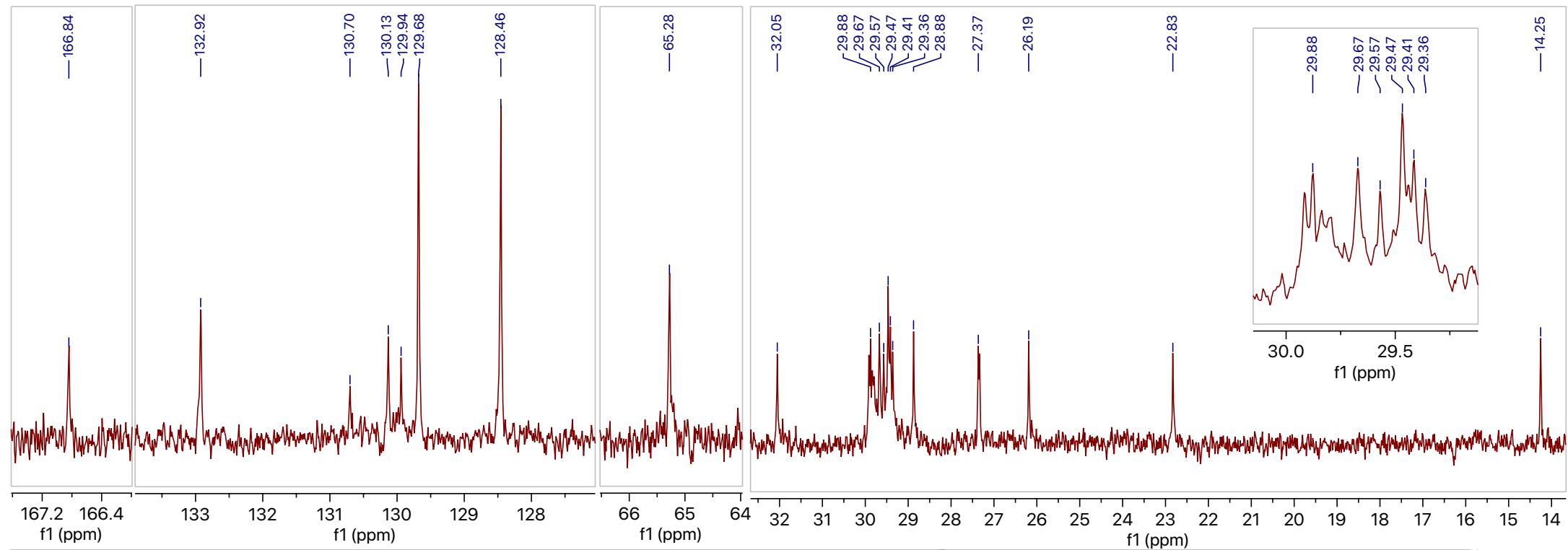




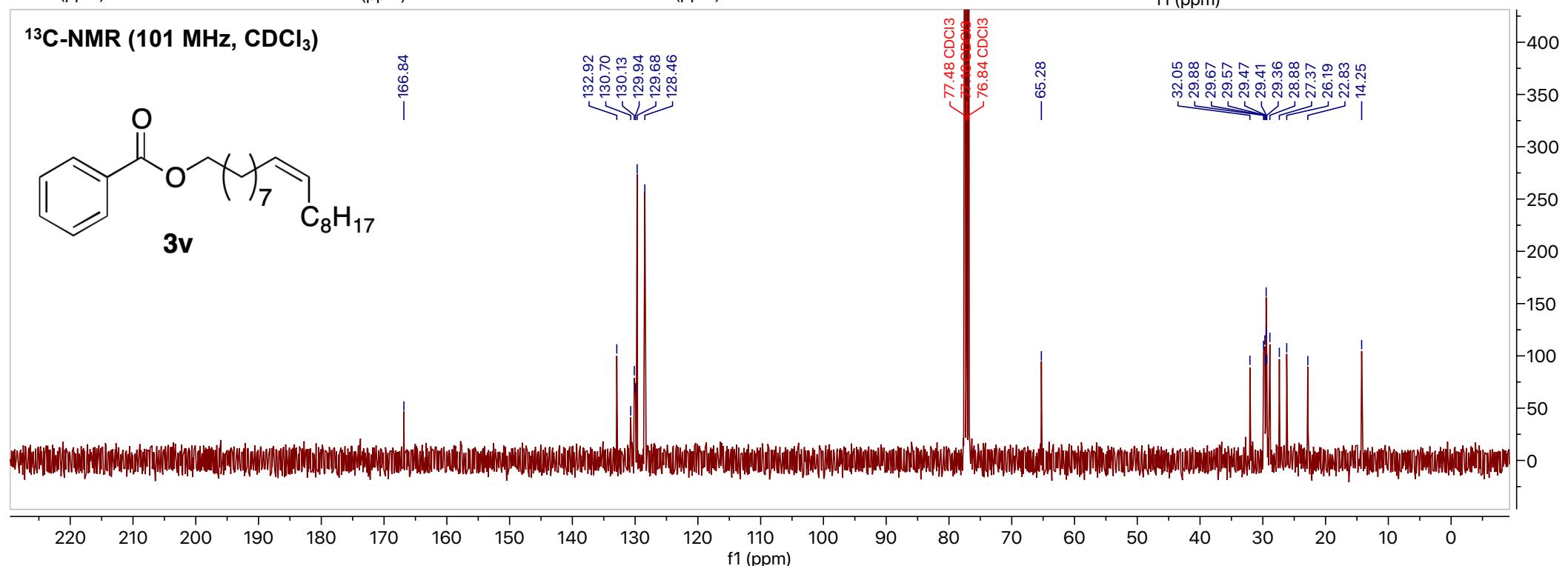
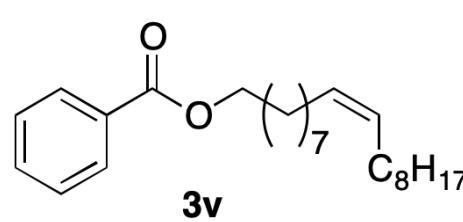


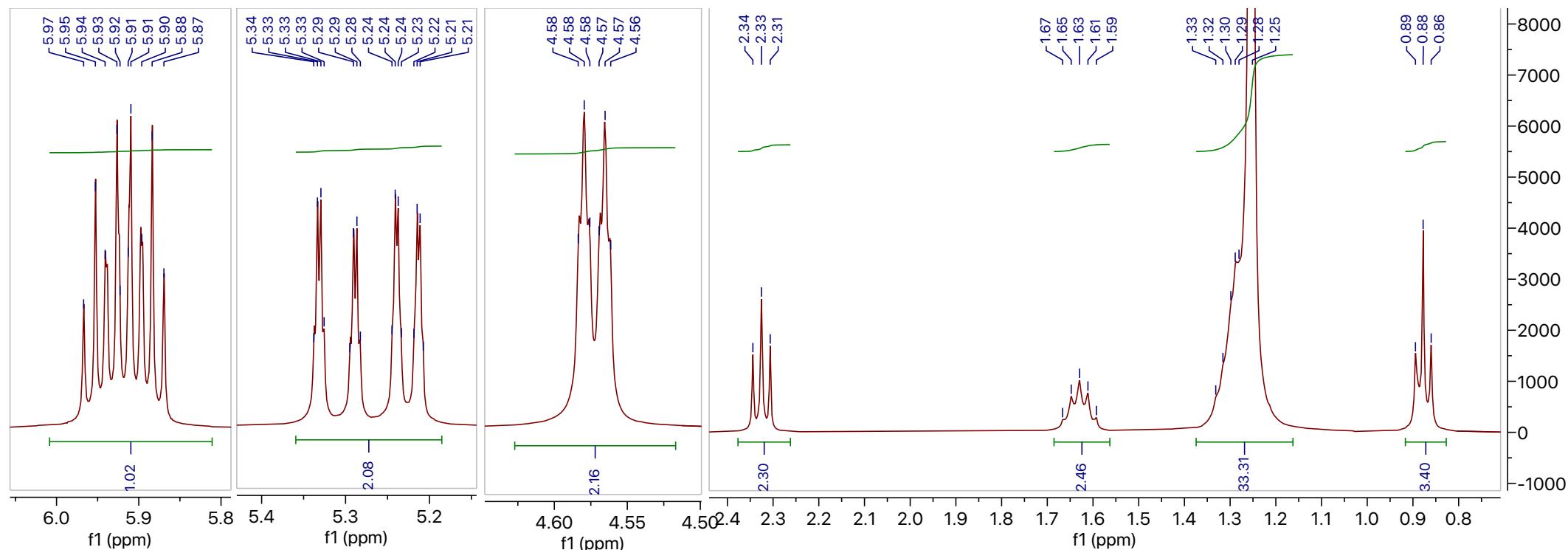
^1H -NMR (400 MHz, CDCl_3)



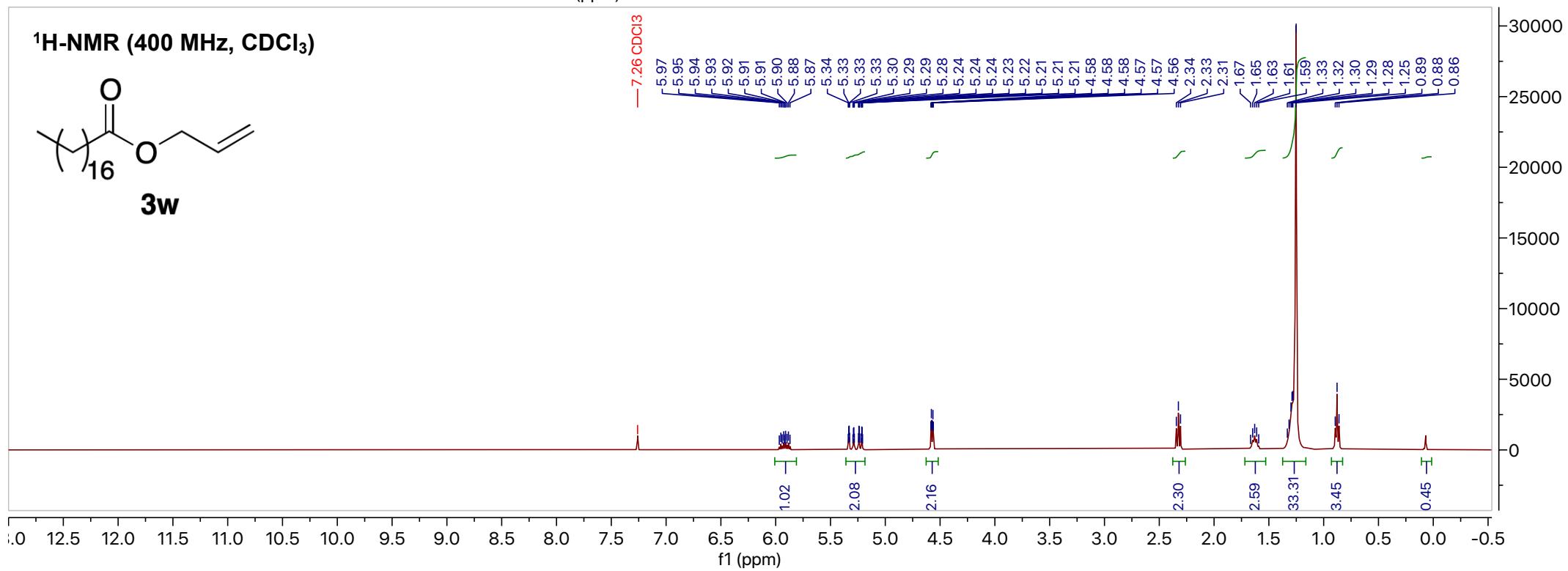
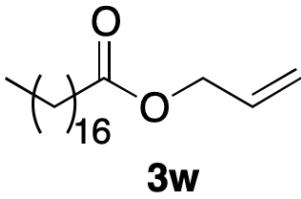


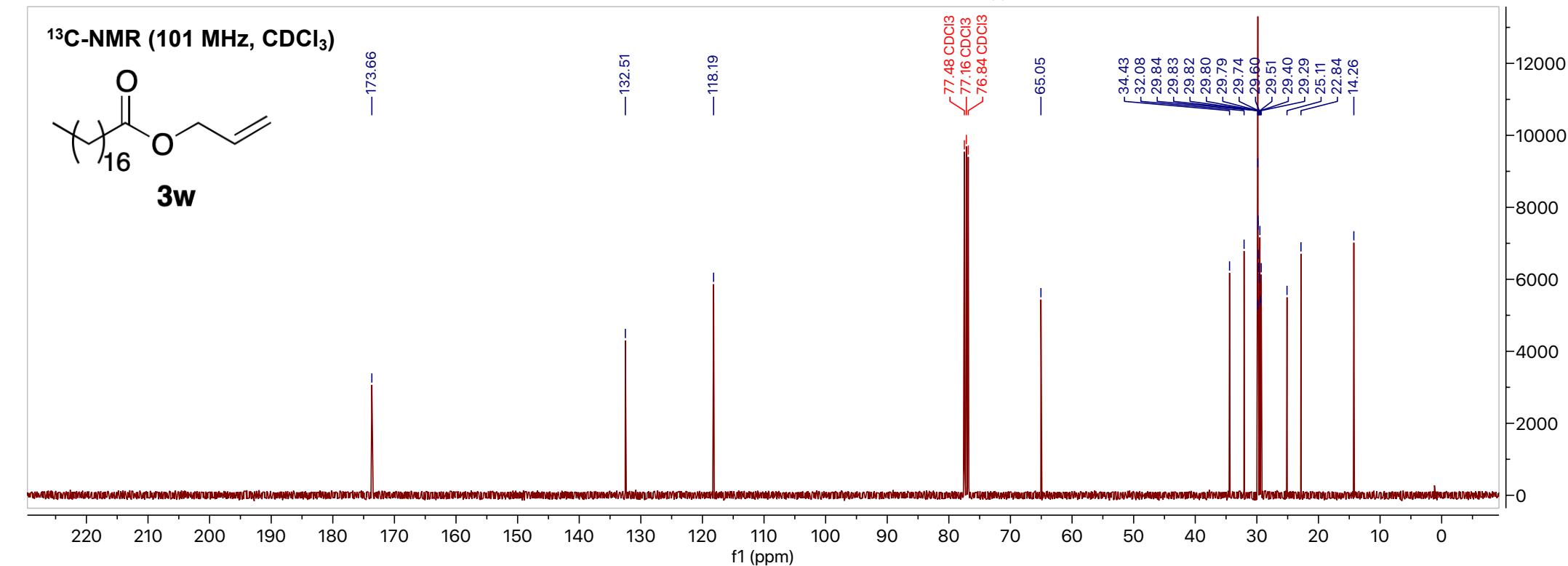
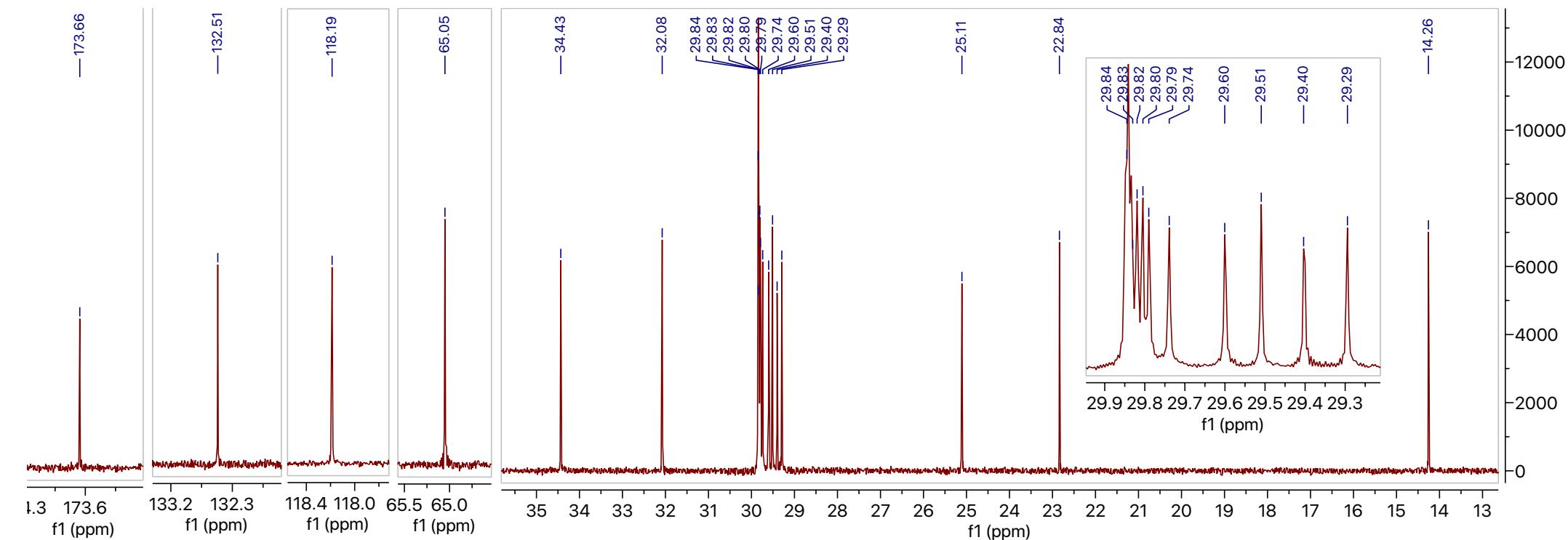
¹³C-NMR (101 MHz, CDCl₃)

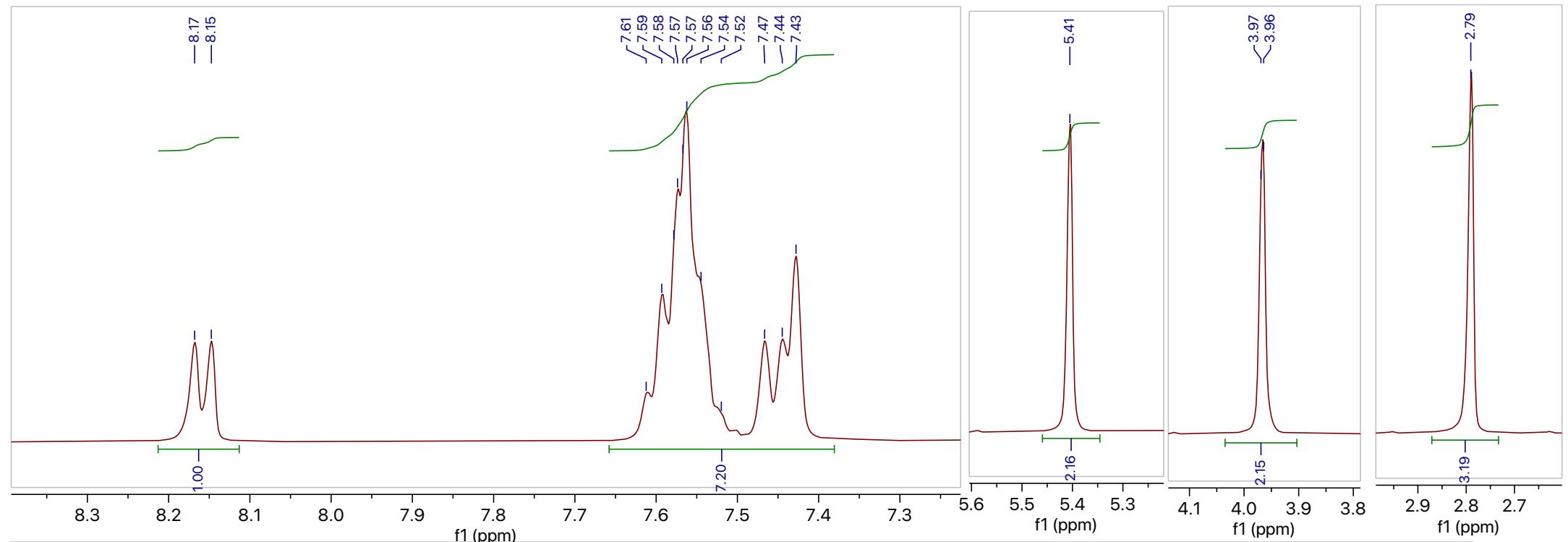




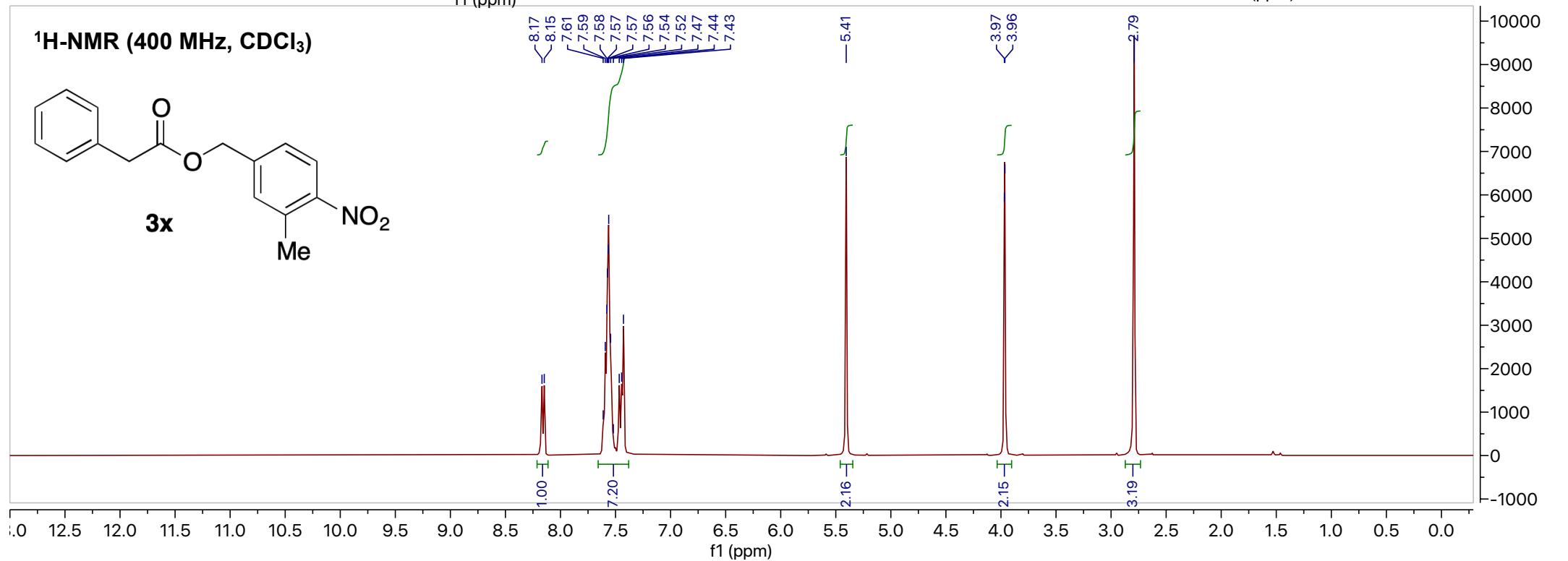
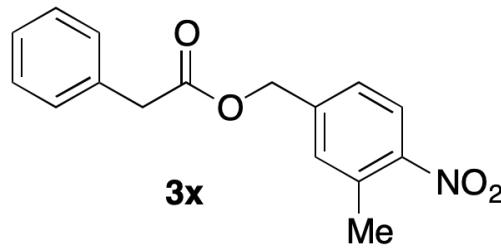
¹H-NMR (400 MHz, CDCl₃)

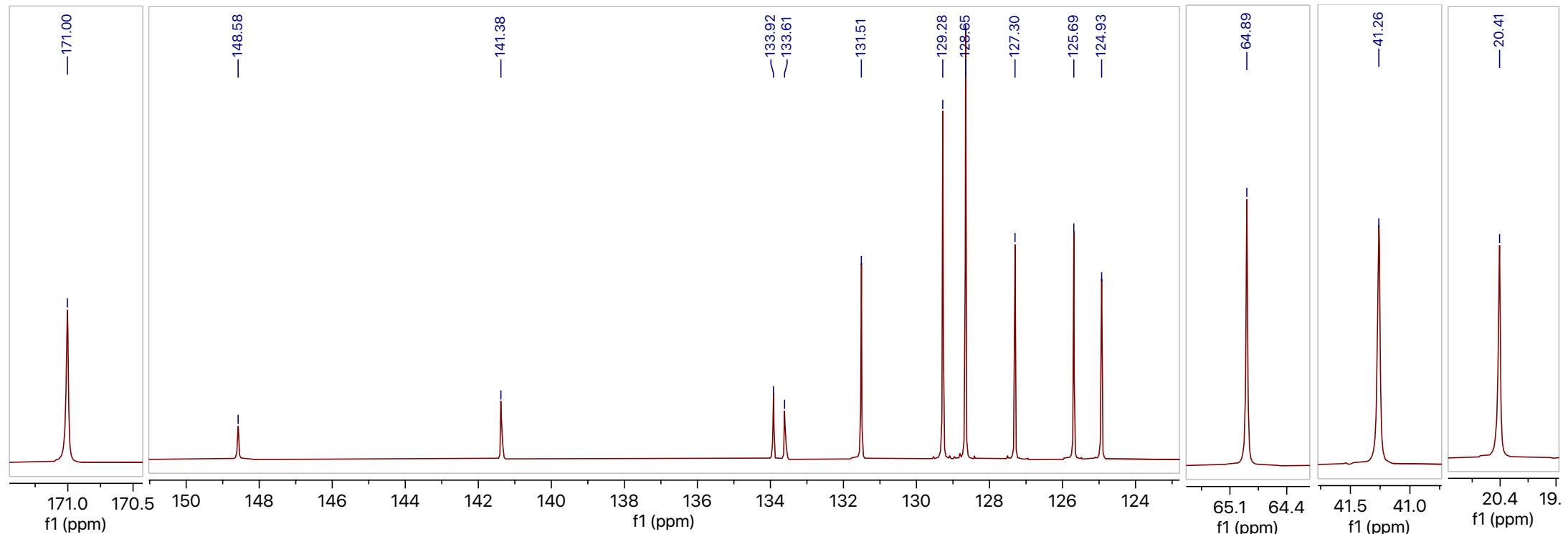




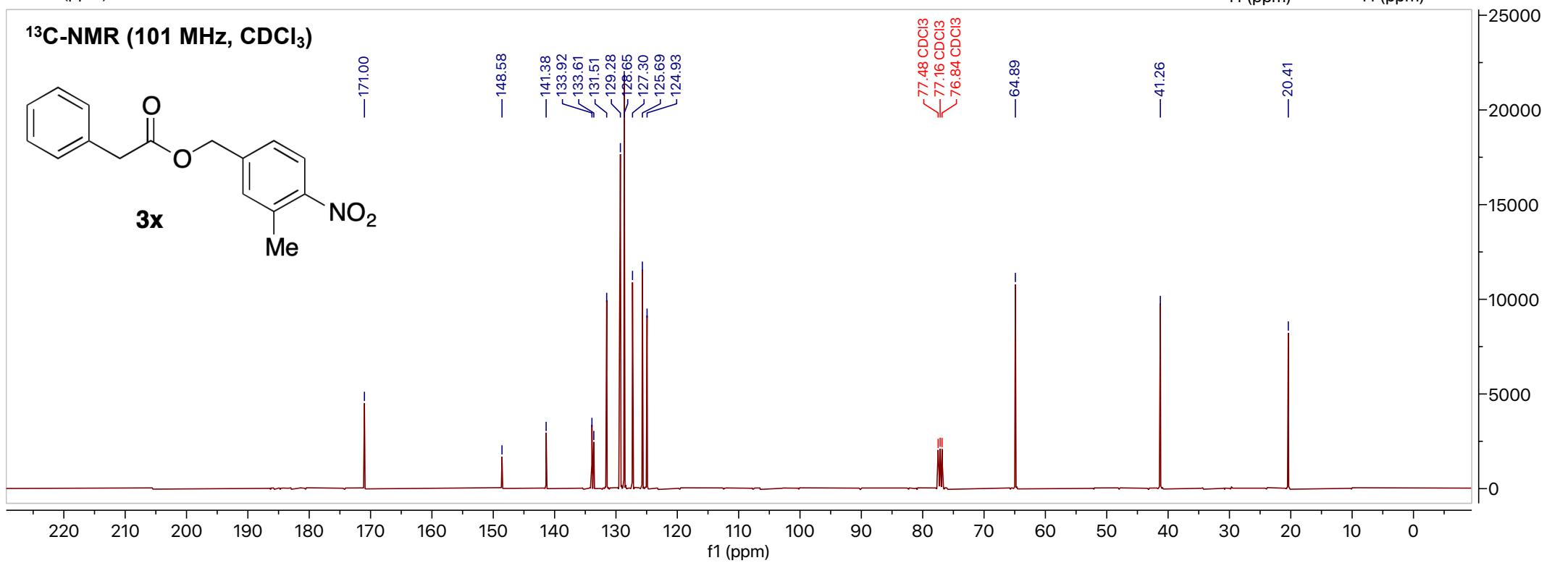
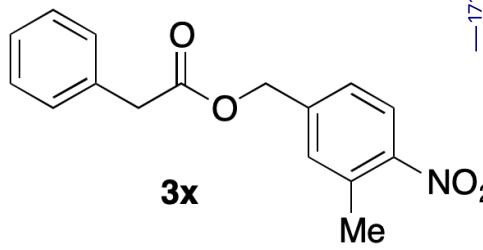


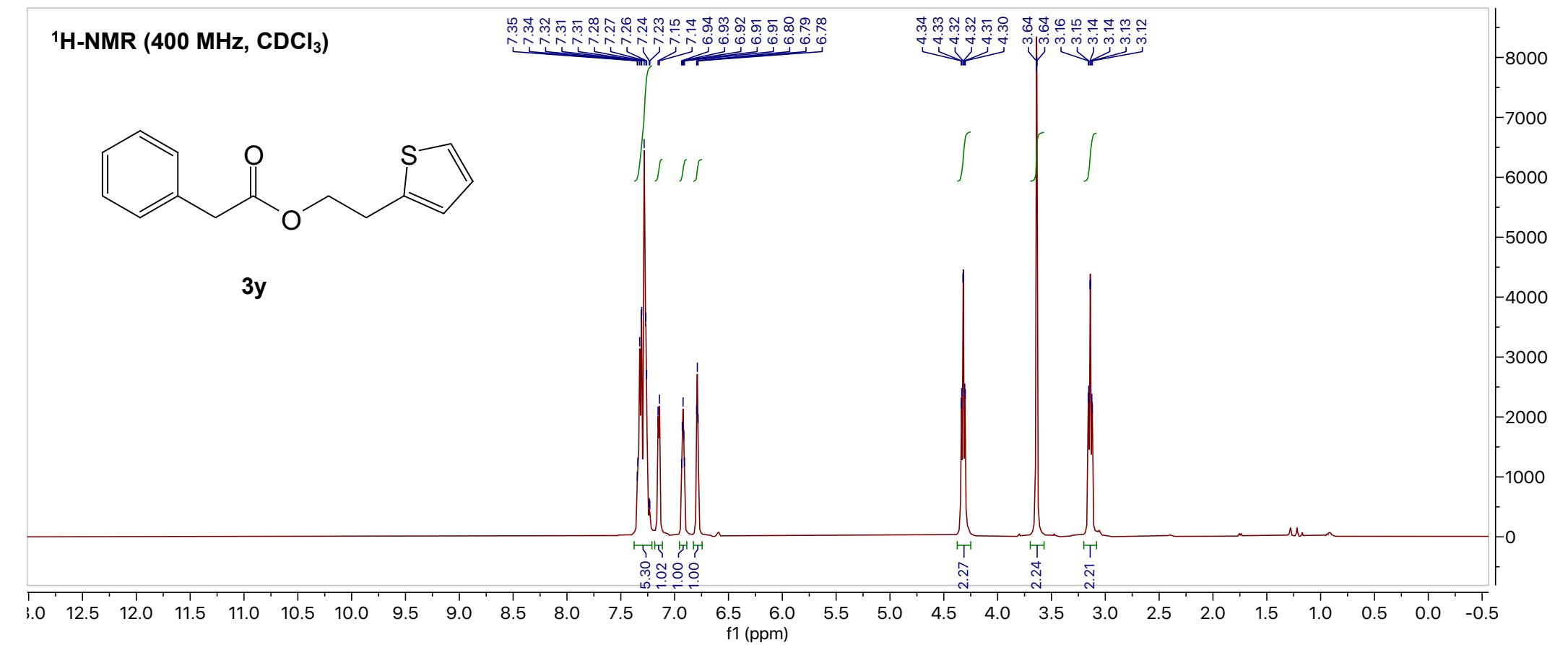
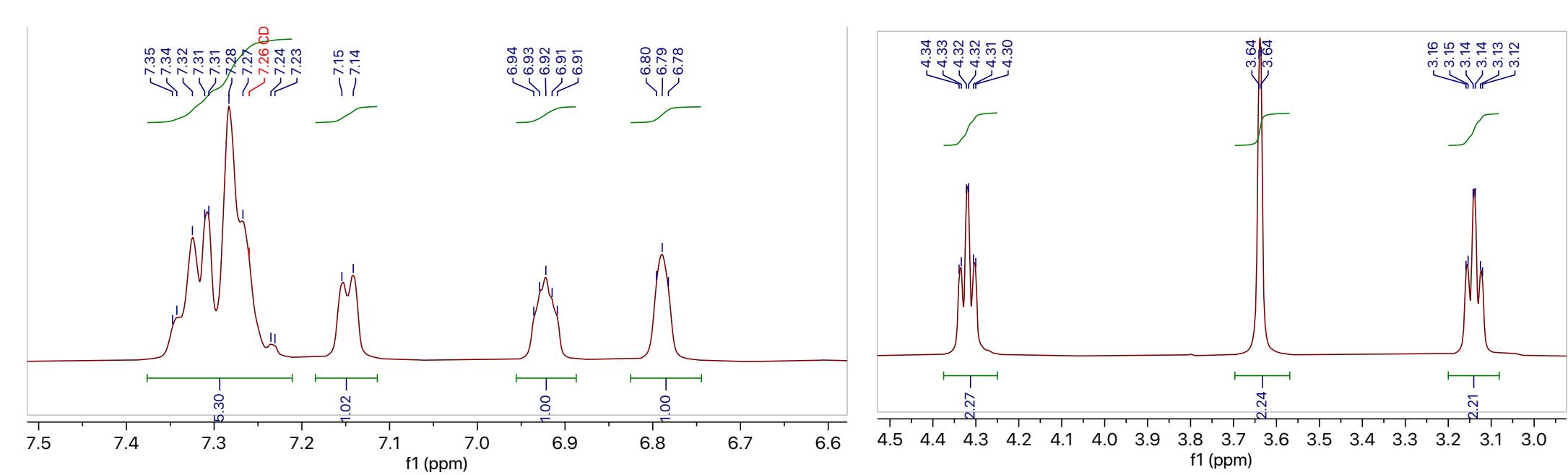
¹H-NMR (400 MHz, CDCl₃)

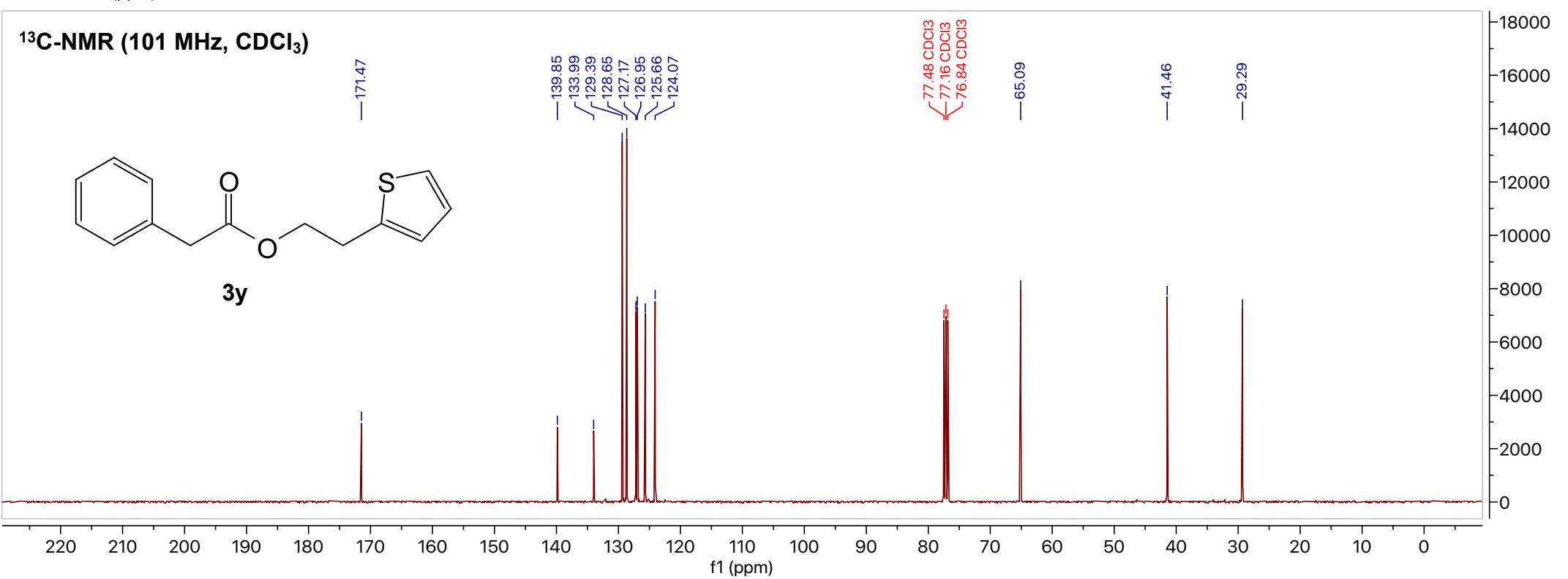
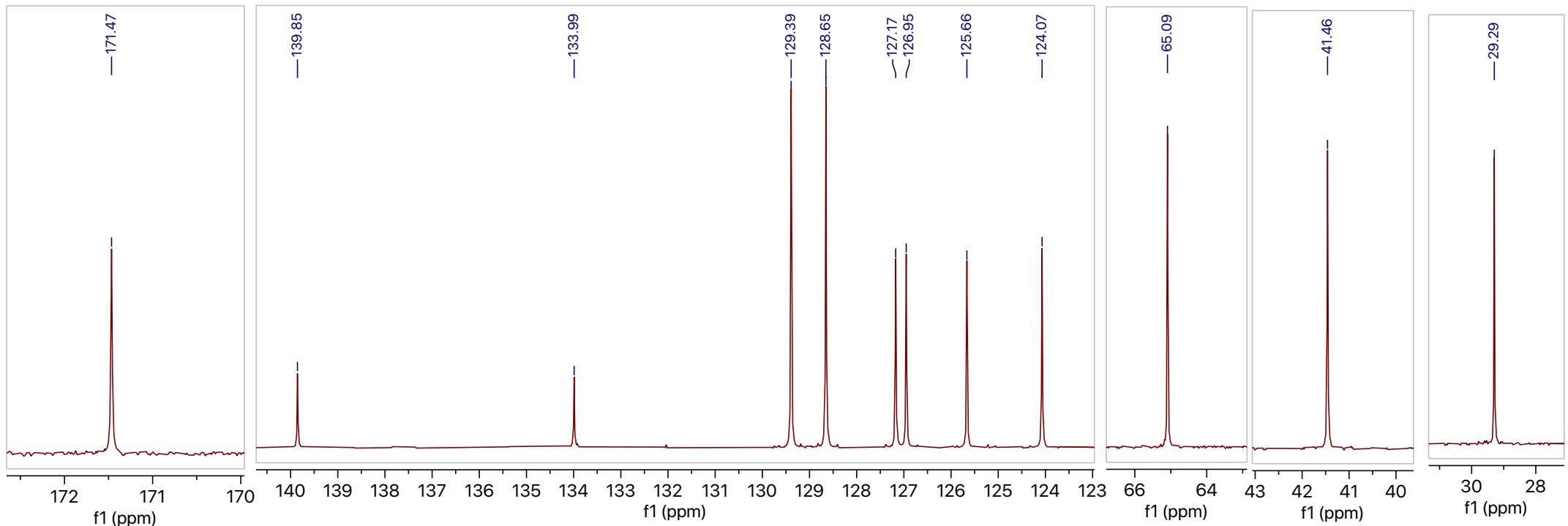


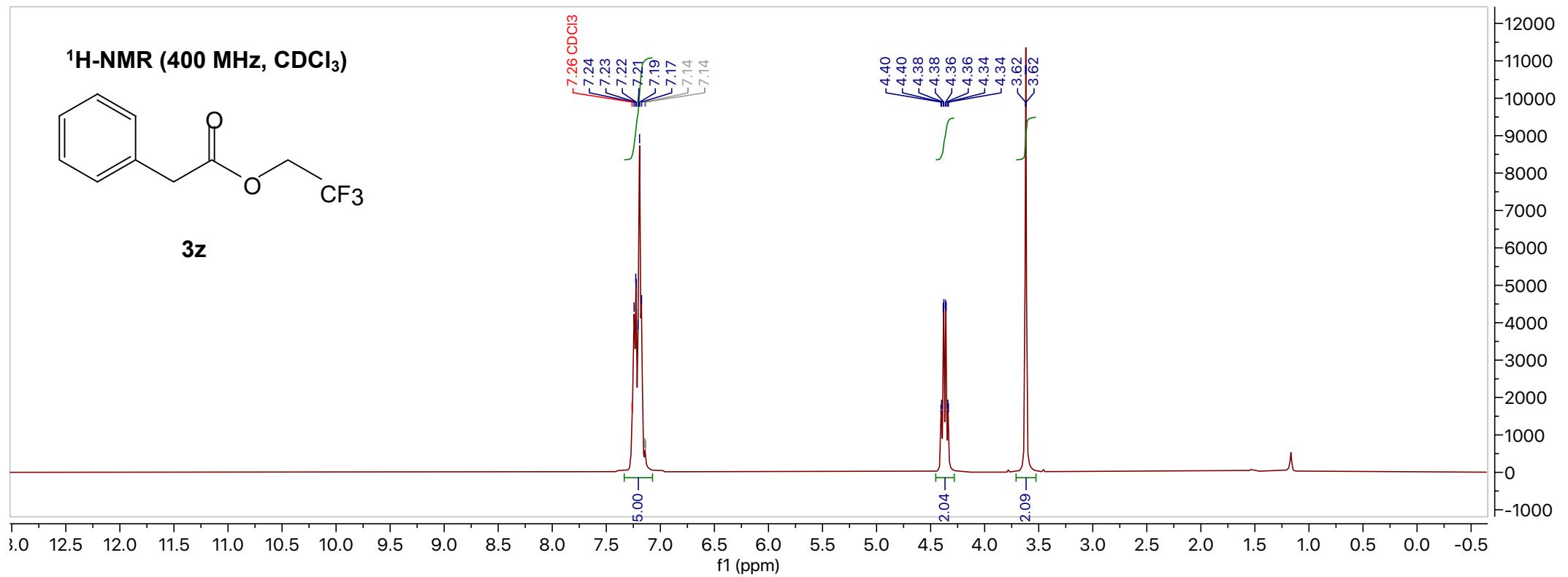
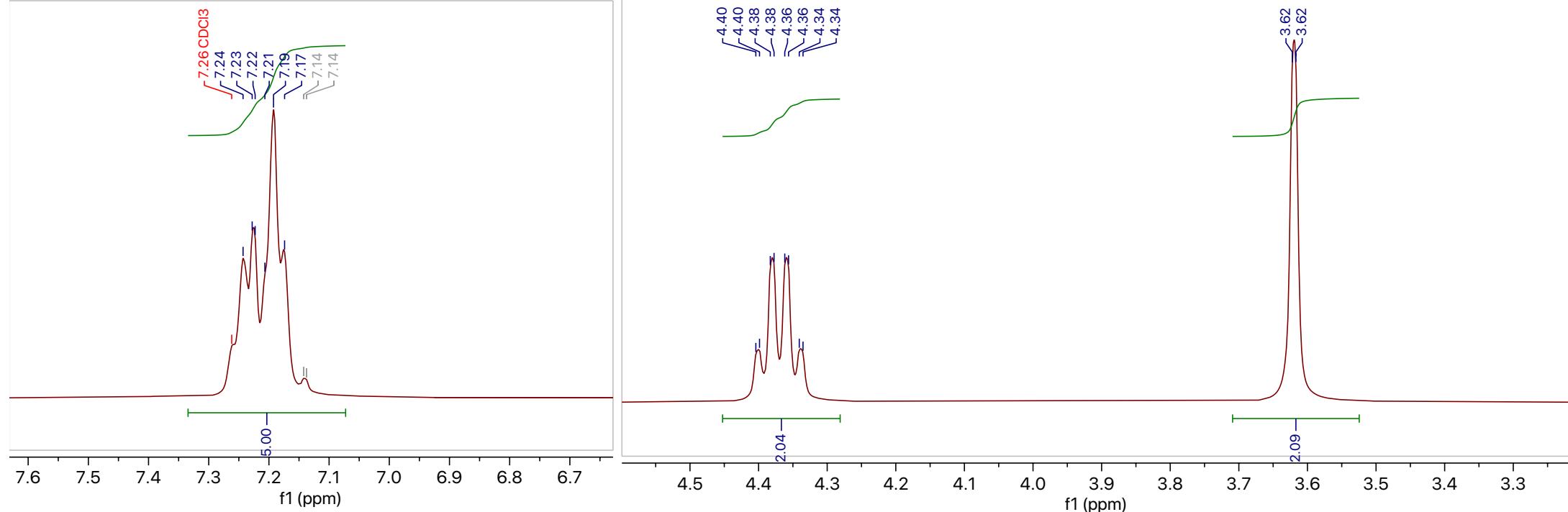


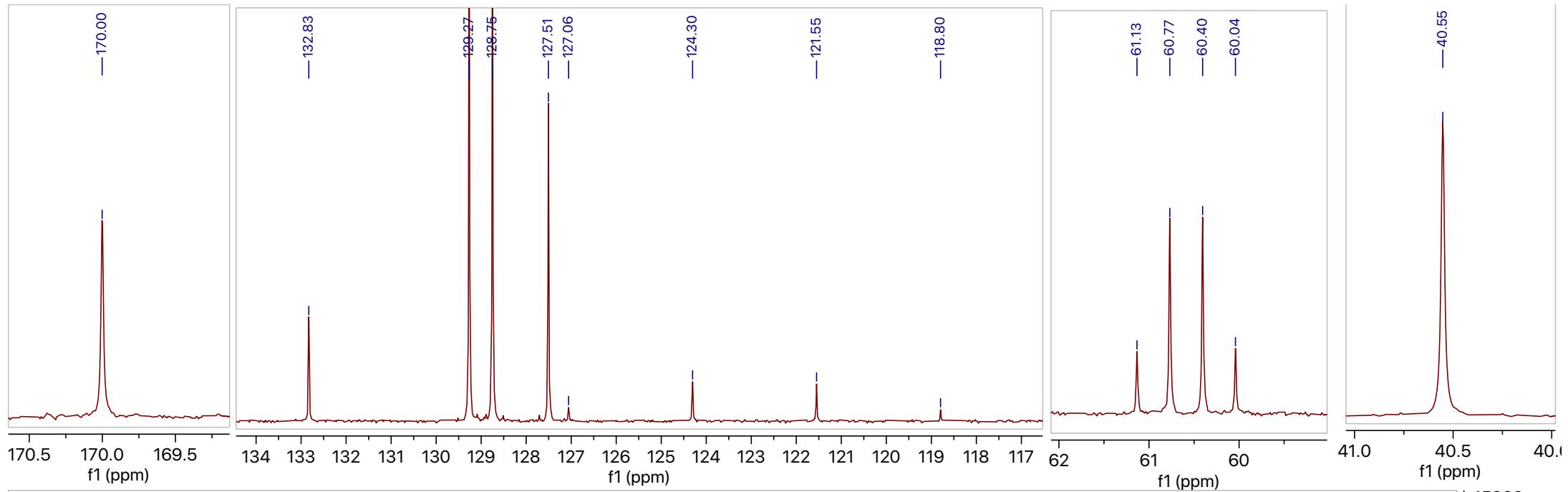
¹³C-NMR (101 MHz, CDCl₃)



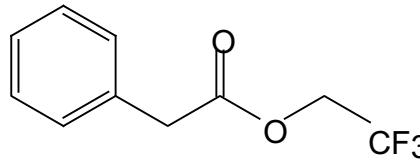




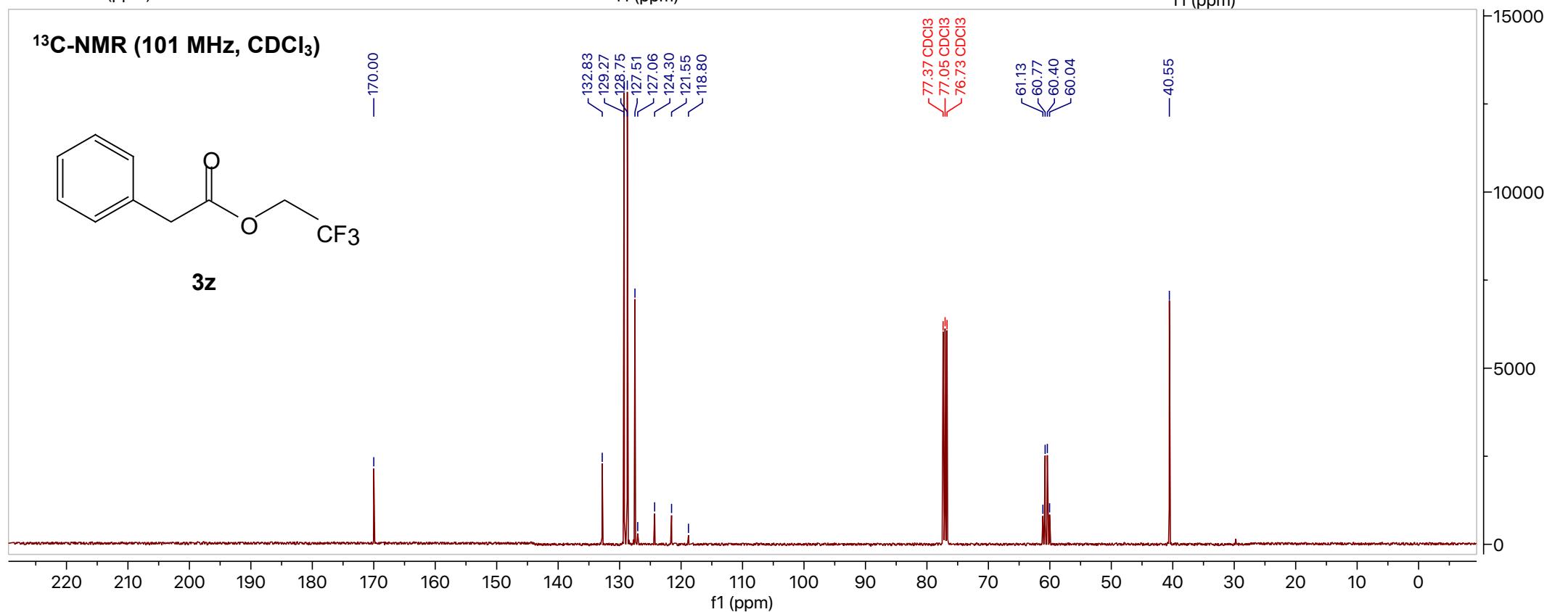




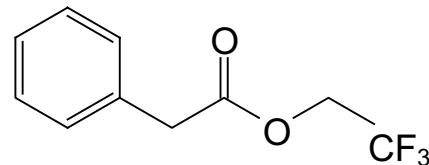
¹³C-NMR (101 MHz, CDCl₃)



3z

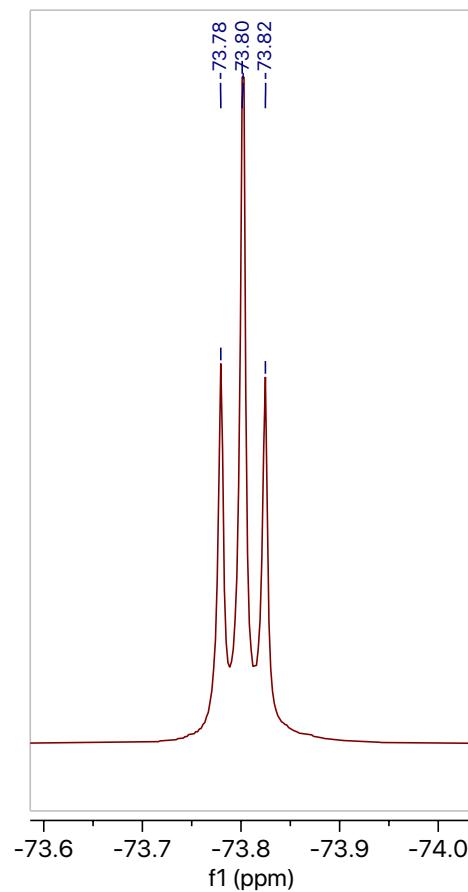


¹⁹F-NMR (377 MHz, CDCl₃)



3z

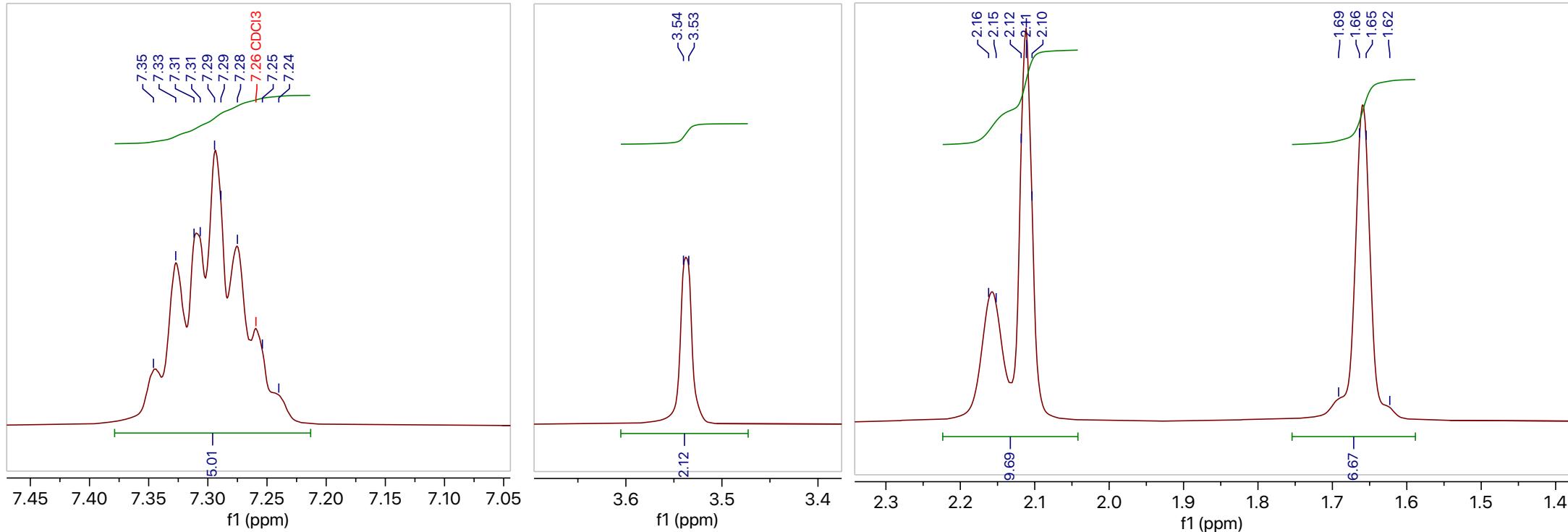
-73.78
-73.80
-73.82



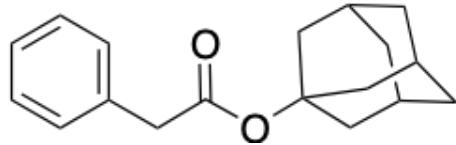
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210

f1 (ppm)

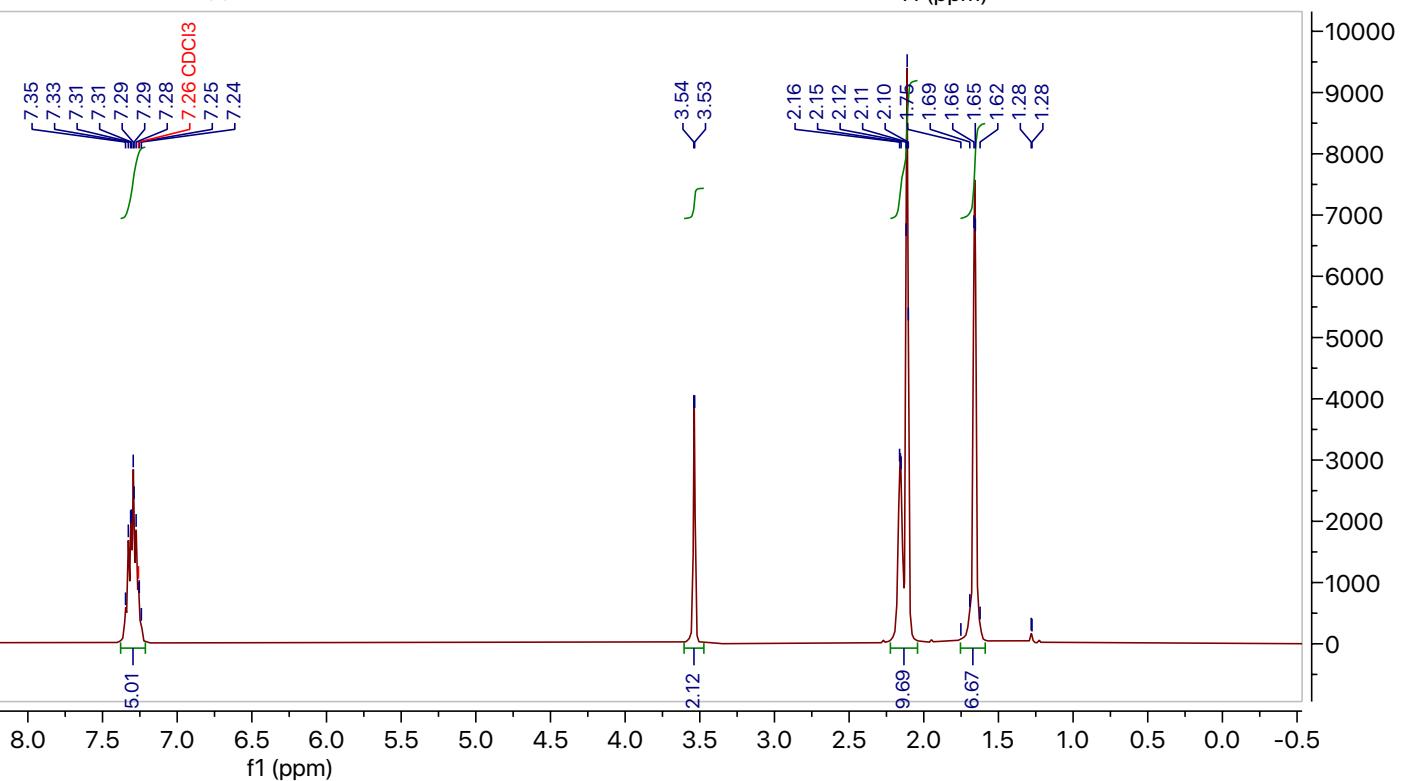
320000
300000
280000
260000
240000
220000
200000
180000
160000
140000
120000
100000
80000
60000
40000
20000
0
-20000

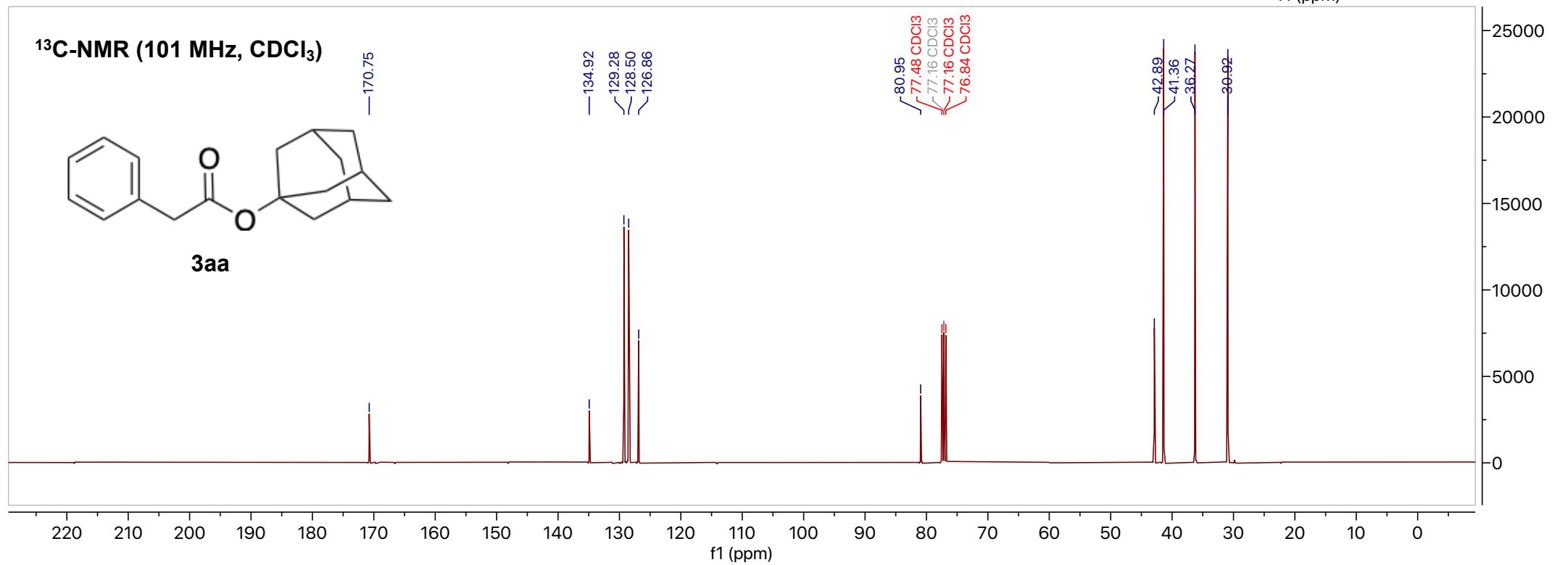
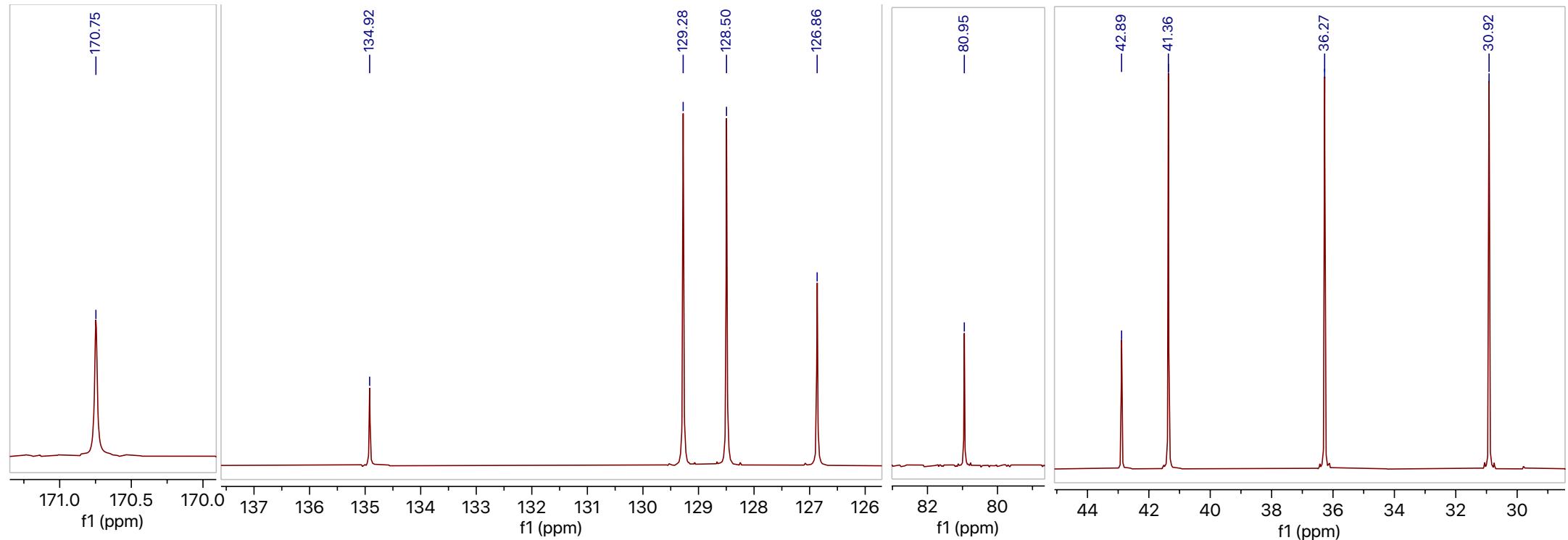


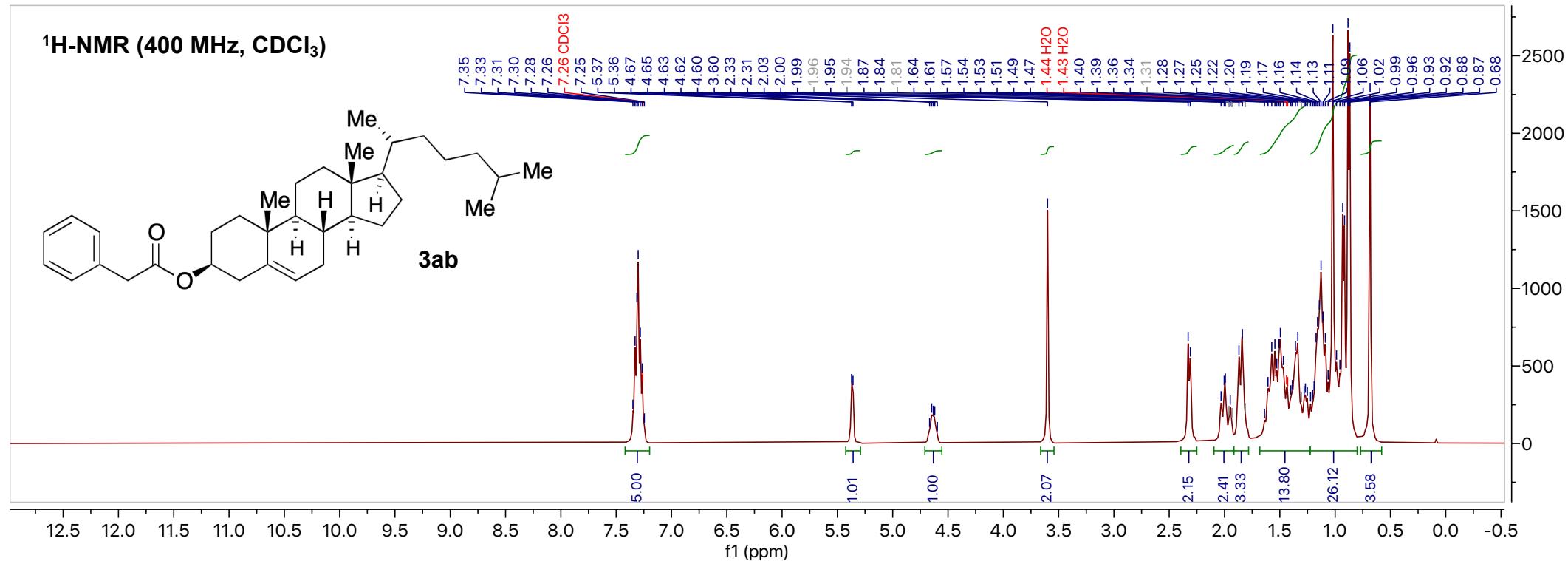
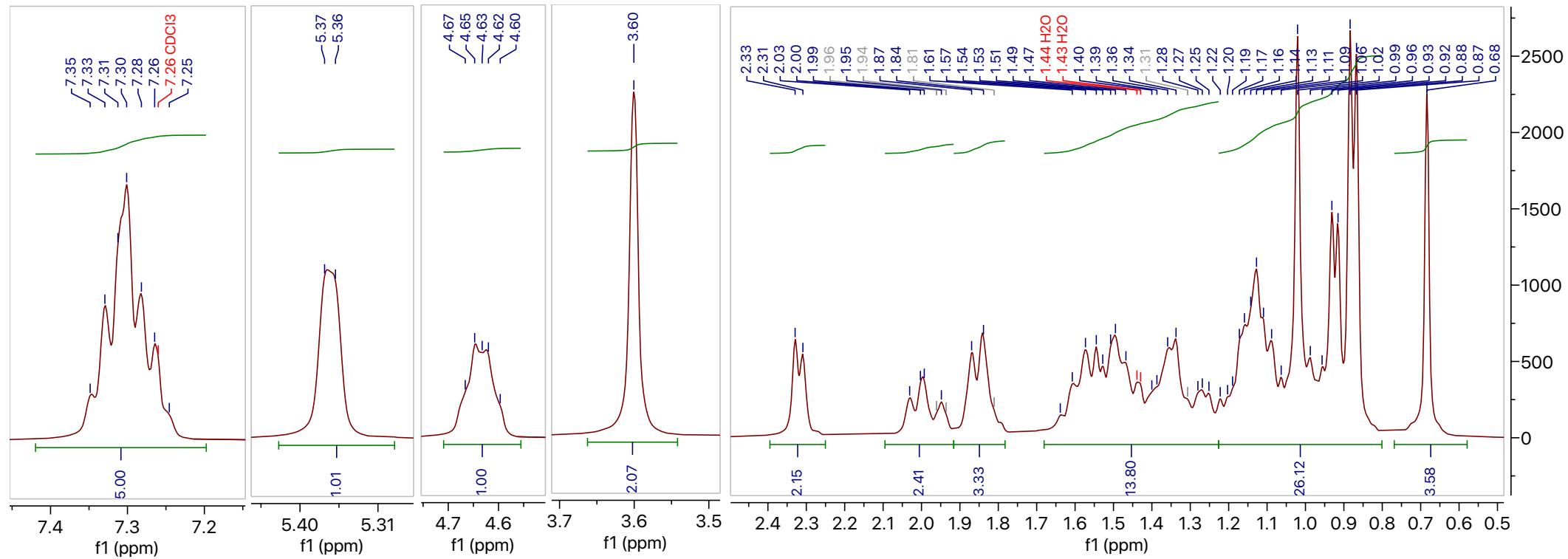
^1H -NMR (400 MHz, CDCl_3)

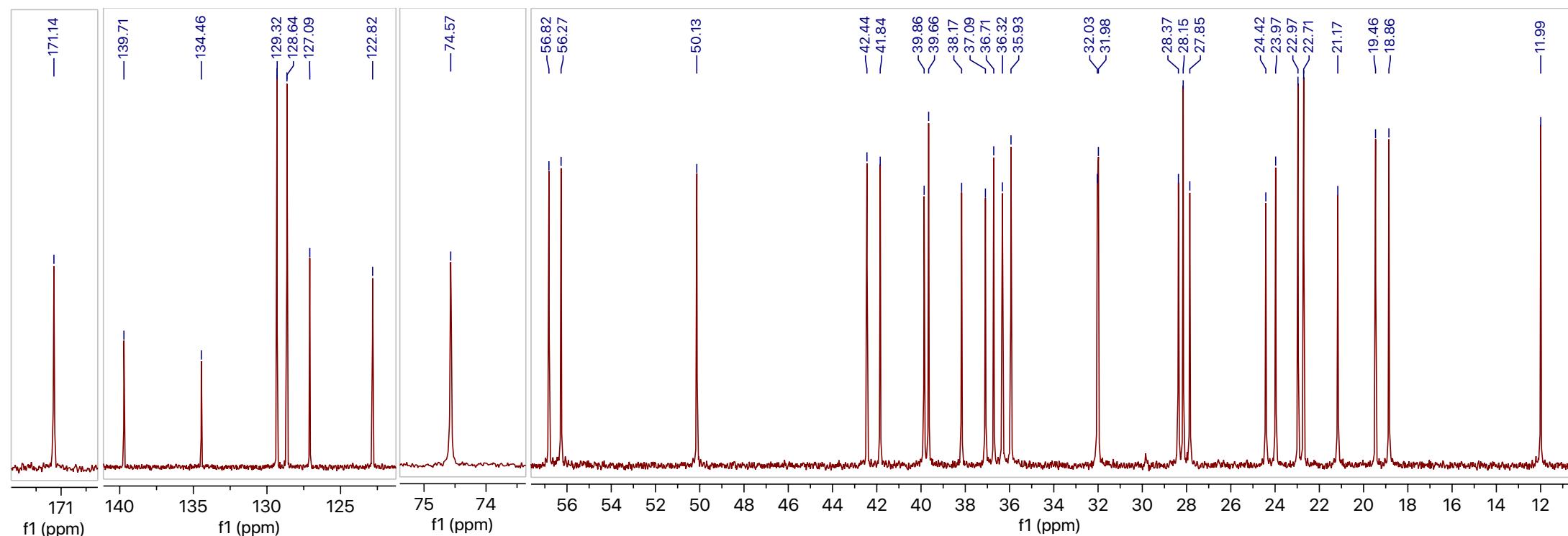


3aa

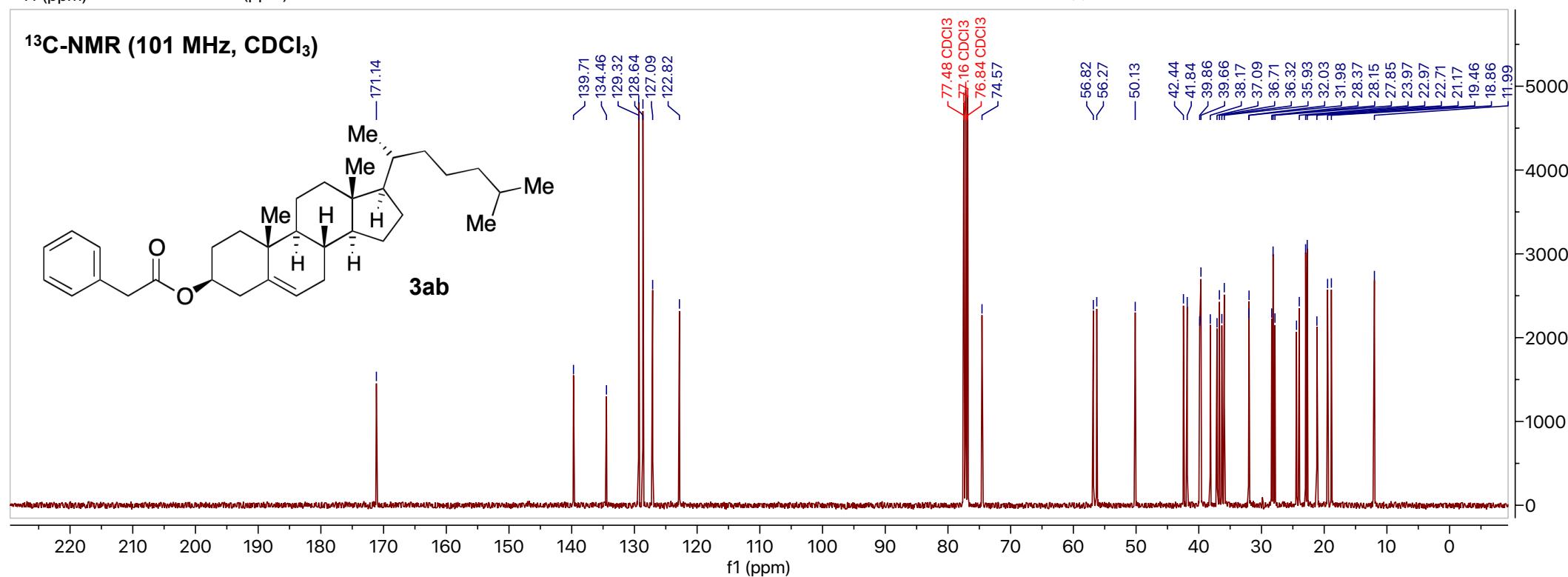
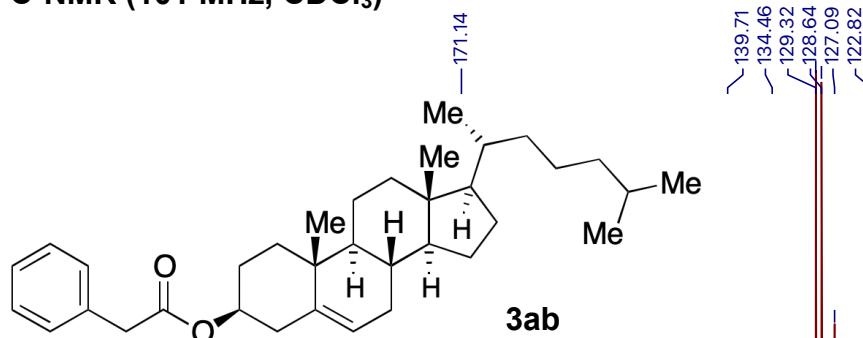


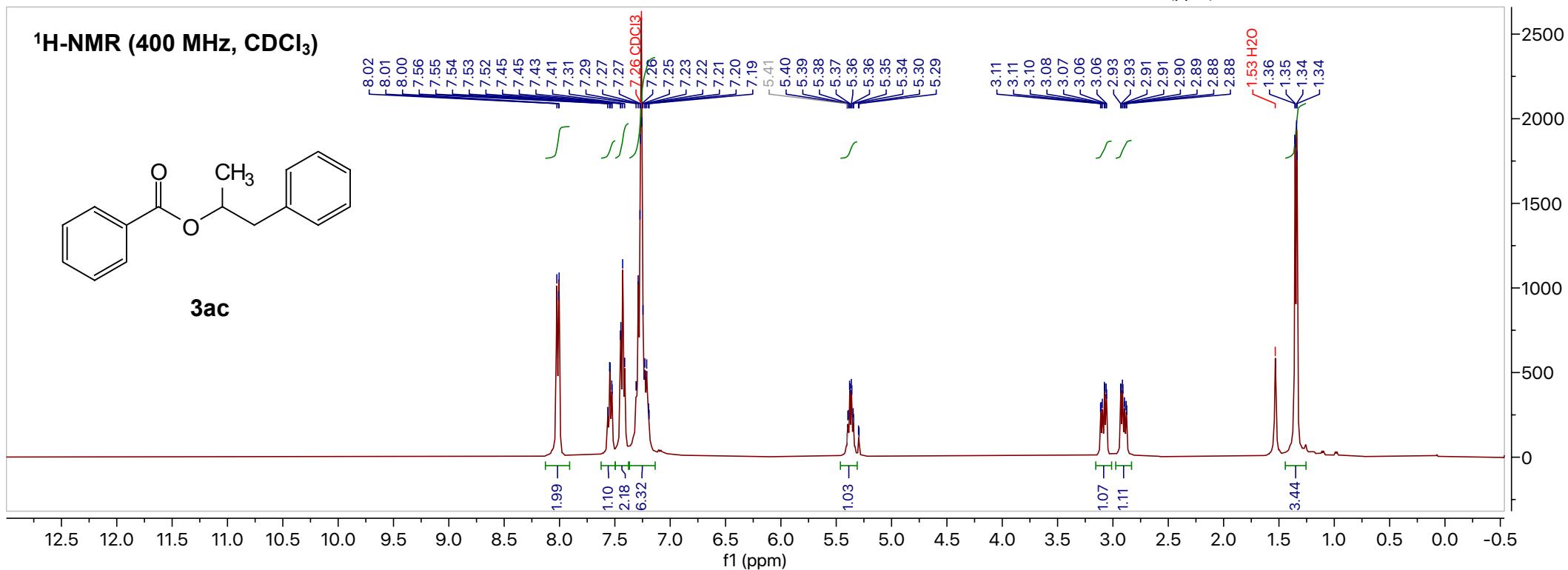
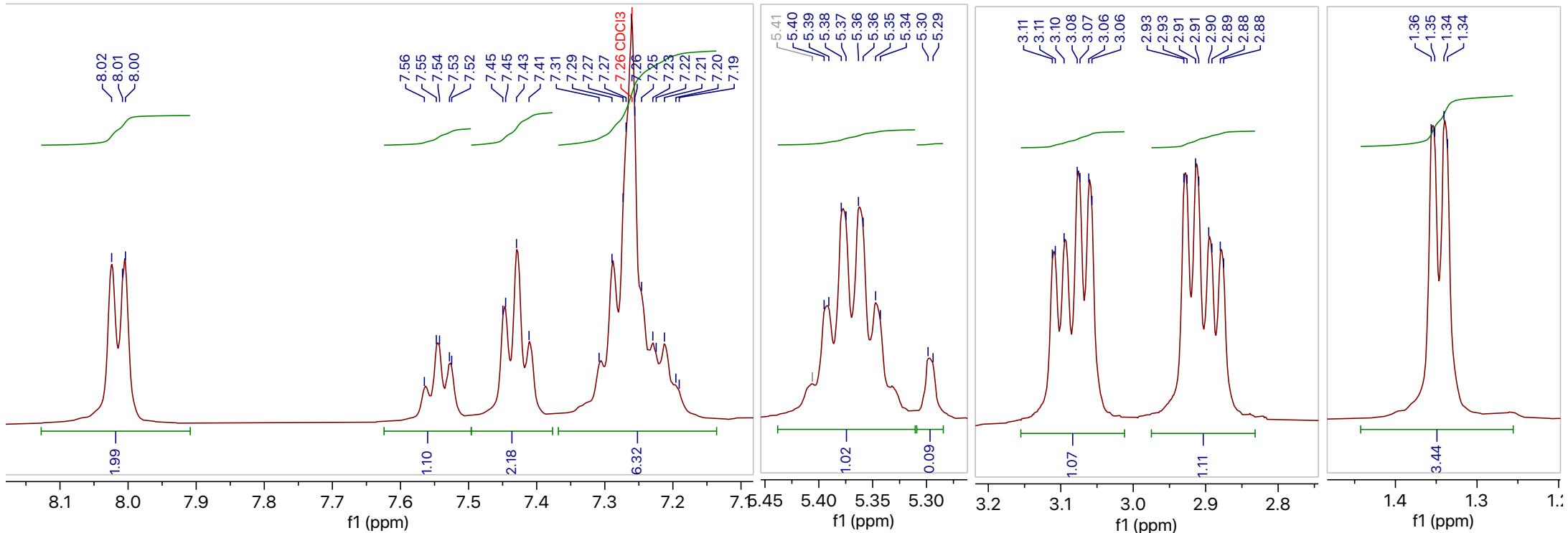


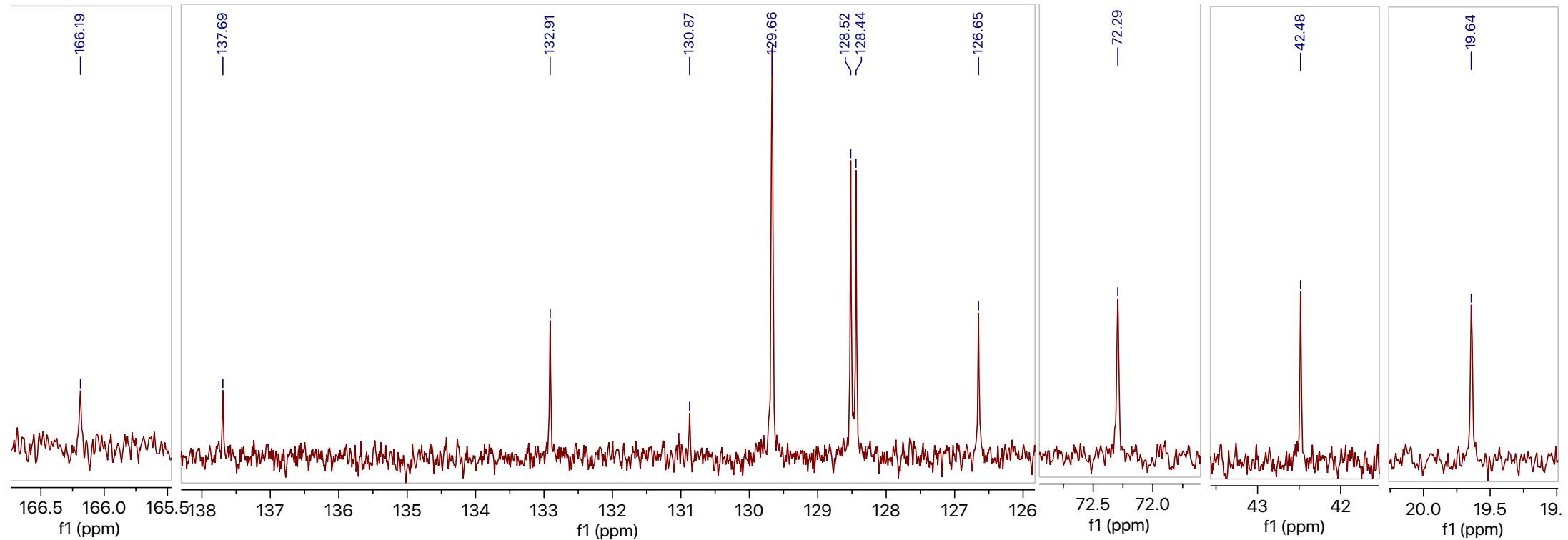




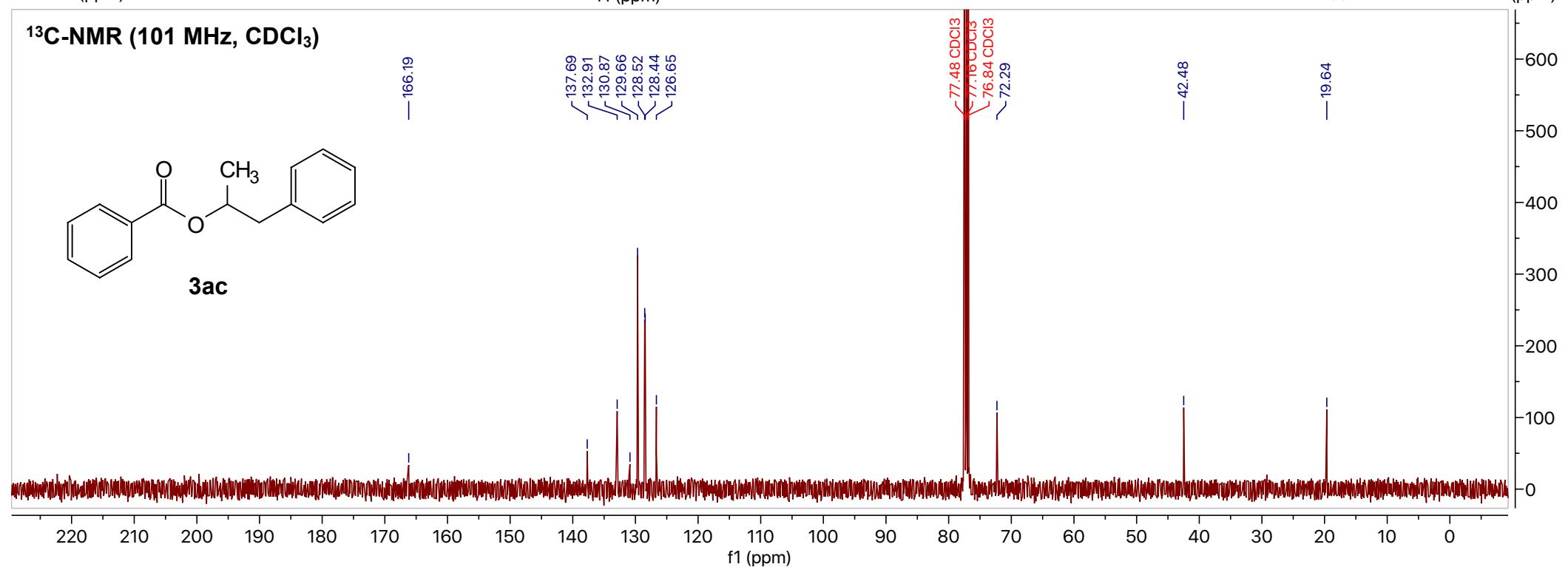
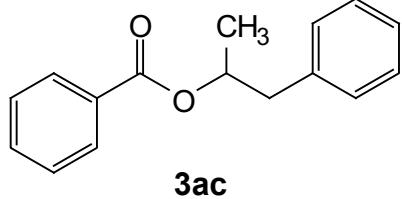
¹³C-NMR (101 MHz, CDCl₃)

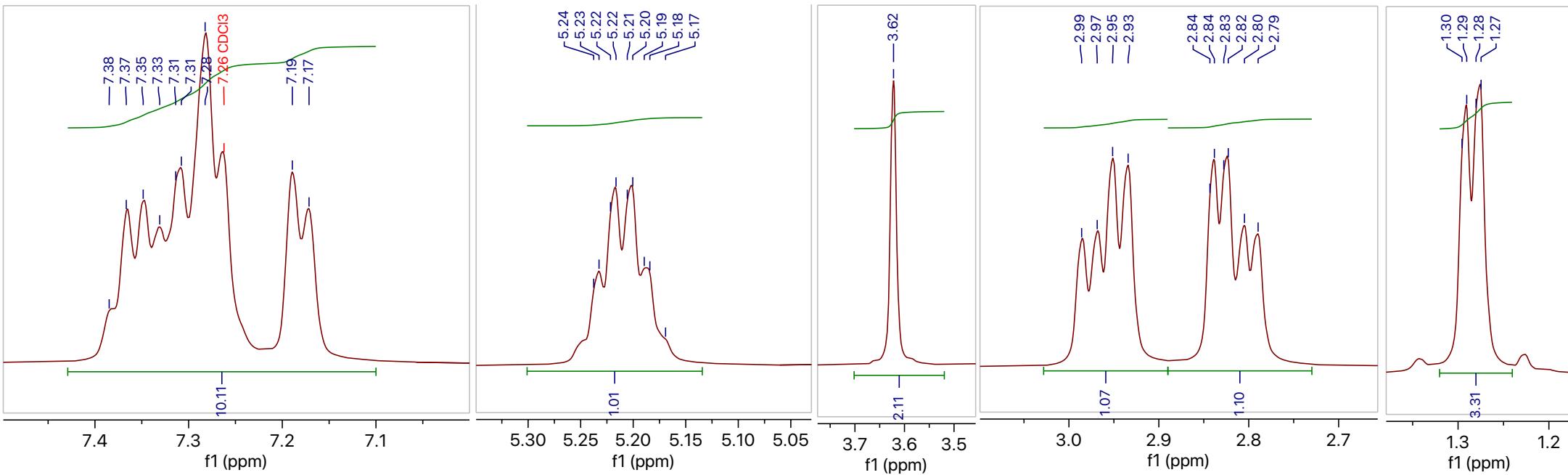




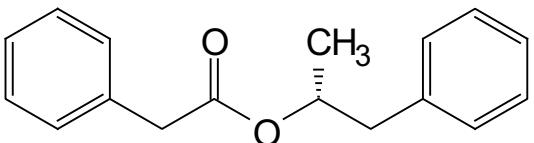


¹³C-NMR (101 MHz, CDCl₃)

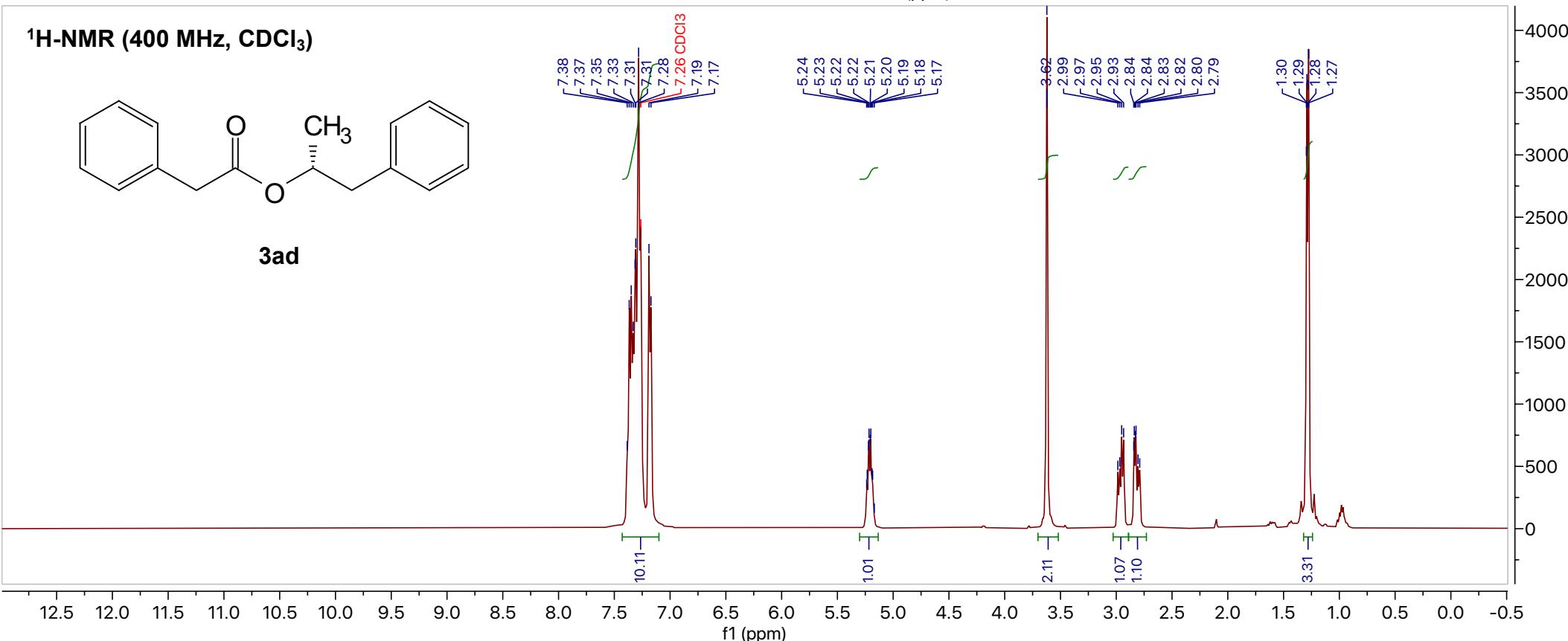


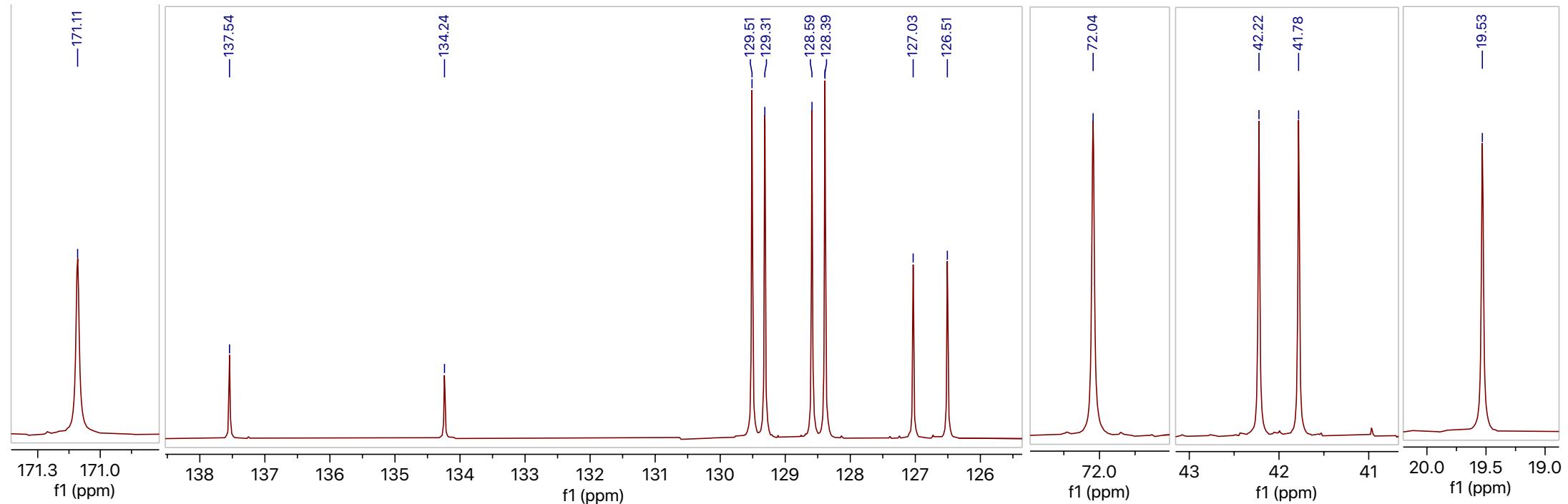


¹H-NMR (400 MHz, CDCl₃)

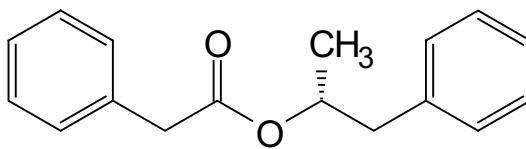


3ad

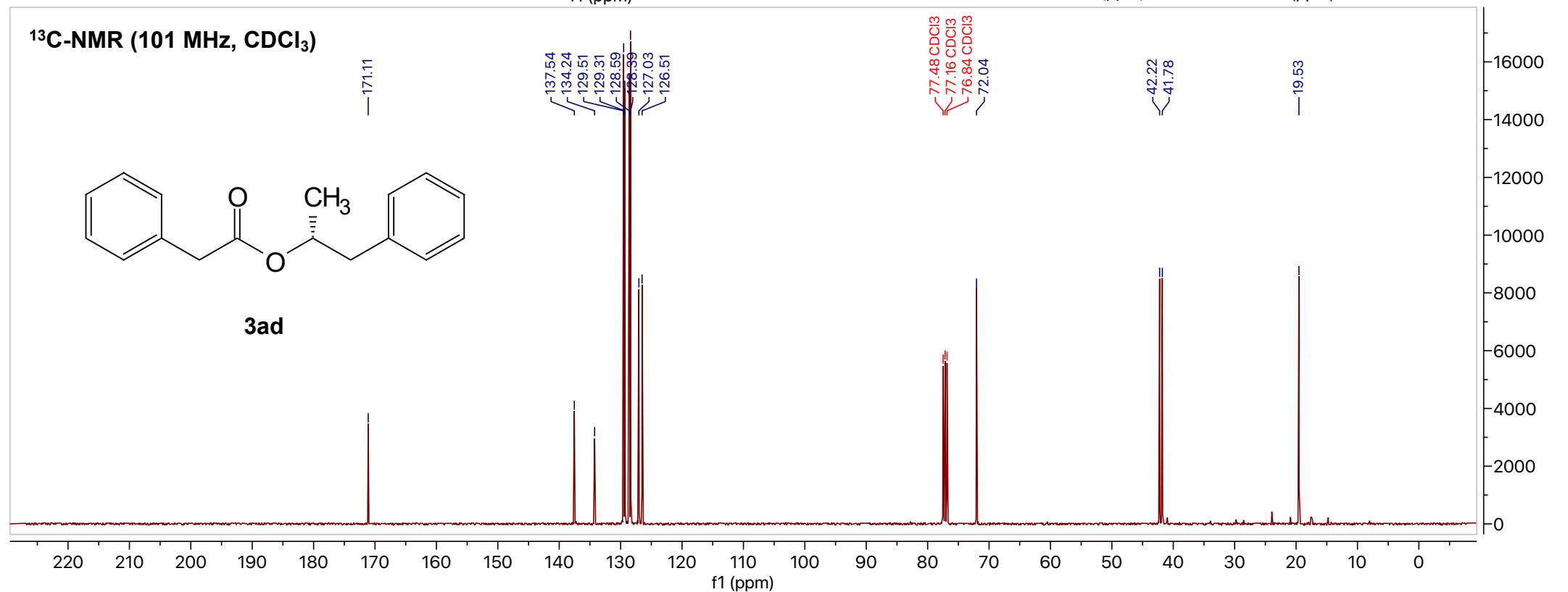


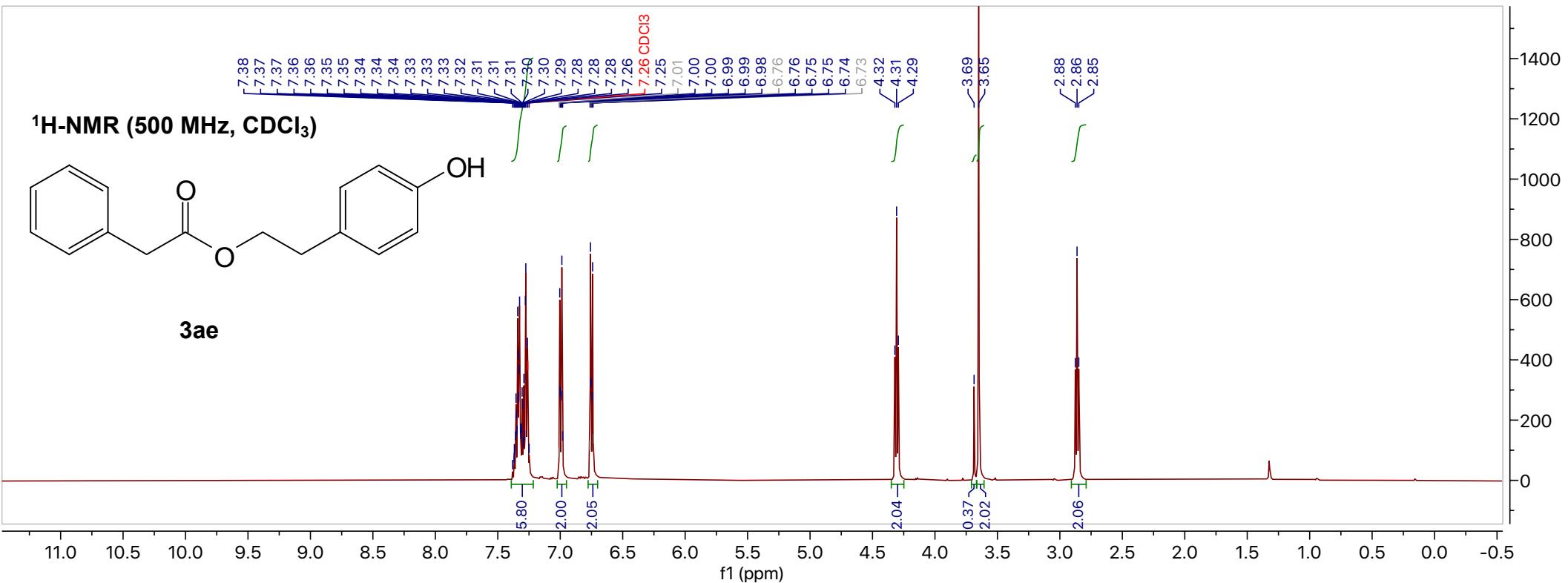
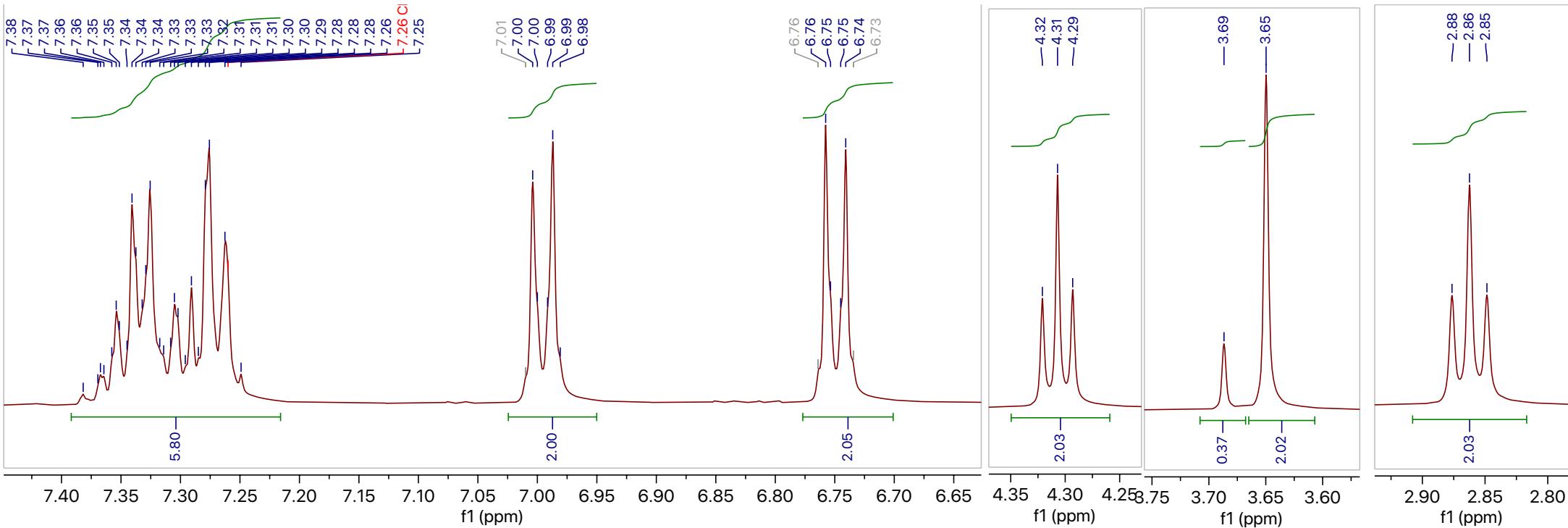


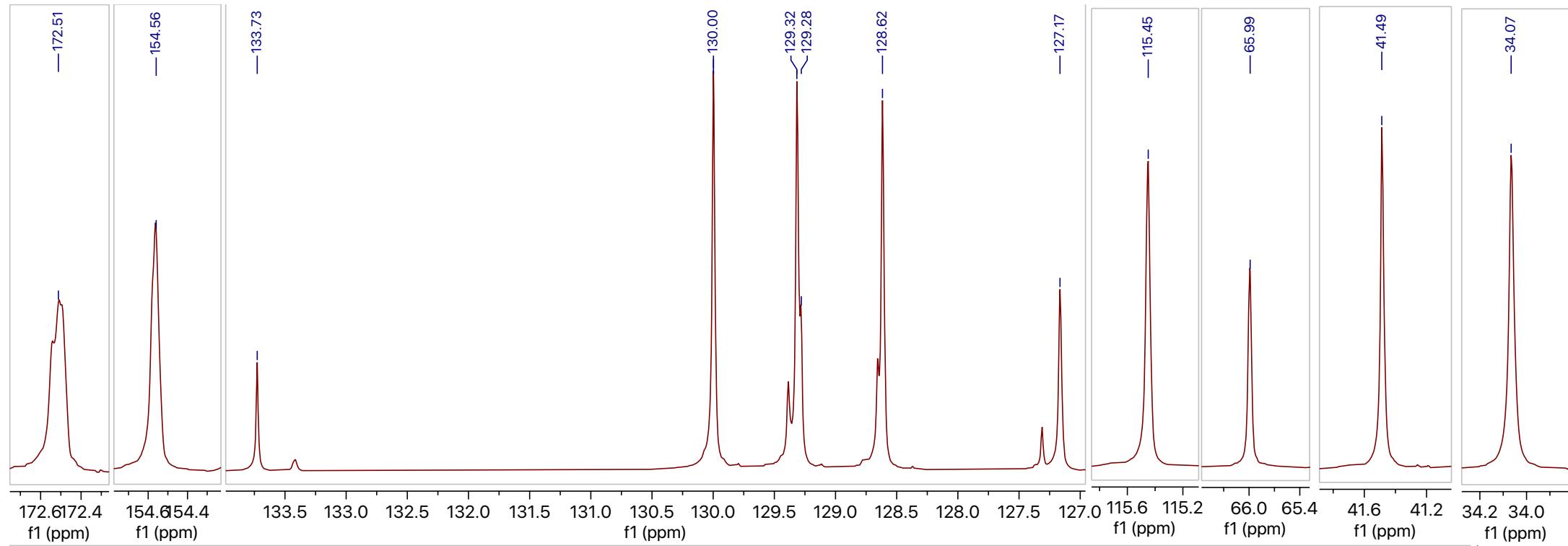
¹³C-NMR (101 MHz, CDCl₃)



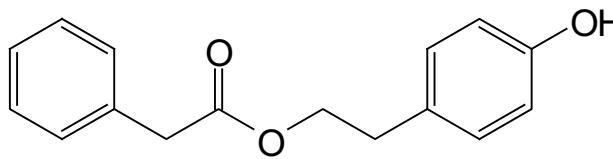
3ad







¹³C-NMR (101 MHz, CDCl₃)



3ae

