Supporting Information

Enantioselective bacterial hydrolysis of amido esters and diamides derived from (±)-*trans*-cyclopropane-1,2-dicarboxylic acid

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I. Procedures for the synthesis of racemic compounds implied in the determination of the enantiomeric excesses

*1. Mixed benzyl methyl trans-cyclopropane-1,2-dicarboxylate (**8**).*

The required racemic mixed benzyl methyl ester (±)-**8** could not be prepared by conventional methods. A nearly racemic sample was obtained as follows: first, (±)-**4b** (43 mg) was incubated with a bacterial suspension (A_{650} = 1.5) in fresh 0.10 M phosphate buffer pH 7.0 (43 mL) and ethanol (0.43 mL), at 28 ºC during 25 h. The resulting, nearly racemic, product **6b** (ee = 8%, 37 mg, 0.26 mmol) was converted into the acid chloride as described for its analogue (±)-**6a** in the first step corresponding to the synthesis of (±)-**9a-c**. Then, the crude acid chloride was dissolved in anhydrous THF (2.0 mL) and treated with benzyl alcohol (53 μL, 0.51 mmol) and triethylamine (72 mL, 0.51 mmol) at room temperature. After 12 h, aqueous 1 M HCl was added and the mixture extracted with AcOEt. Evaporation of organic solvents and purification of the residue by flash chromatography (*n*-hexane/ethyl acetate 15:1 as the eluent) yielded product **8** (ee = 8% chiral-HPLC analysis) as a colourless liquid. δ_H (300.13 MHz, $CDCl_3$) 7.43-7.30 (5 H, m, Ph), AB system

centered to 5.13 ppm ($|J_{A,B}|$ = 12.5 Hz, 2H, CH_2-Ph,), 3.70 (3 H, s, OMe), 2.38-2.17 (2 H, m, 2 x CH), 1.52-1.40 (m, 2H, CH_2); δ_C (75.5 MHz, $CDC1_3$) 172.0 (C=O), 171.5 (C=O), 135.4 (C), 128.5 (CH), 128.3 (CH), 128.2 (CH), 66.8 (CH_2), 55.1 (CH_3), 22.3 (CH), 22.2 (CH), 15.4 (CH_2). MS (ESI+) m/z 257.0 ($(M+Na)^+$, 100%).

*2. General procedure for the preparation of racemic amido esters (±)-**12a-c**.*

A mixture of dimethyl (±)-*trans*-cyclopropane-1,2-dicarboxylate ((±)-**3b**) (0.16 g, 1.0 mmol) and the corresponding amine (1.0 mmol) was heated in a sealed tube nearly to the boiling point of the amine during 20 h (for **12a**) or 60 h (for **12b,c**). Then aqueous 1 M HCl (5 mL) and CH_2Cl_2 (8 mL) were added. The organic phase was separated and the aqueous layer again extracted with CH_2Cl_2. The organic phases were combined and washed with brine. Evaporation of solvents and subsequent flash column chromatography of the residue (*n*-hexane/ethyl acetate 2:1 as the eluent) yielded the corresponding amido esters (±)-**12a-c**.

*(1) Methyl (±)-trans-2-(N-benzylcarbamoyl)cyclopropanecarboxylate ((±)-**12a**).* White solid (0.12 g, 50%); mp 104-105 ºC; δ_H (300.13 MHz, $CDC1_3$) 7.40-7.25 (5 H, m, Ph), 6.14 (1 H, br s, NH), 4.44 (2 H, d, J = 5.7 Hz, CH_2Ph), 3.67 (3 H, s, OCH_3), 2.21 (1 H, ddd, J_1 = 9.2 Hz, J_2 = 5.5 Hz, J_3 = 3.7 Hz, CH), 1.94 (1 H, ddd, , J_1 = 8.9 Hz, J_2 = 5.4 Hz, J_3 = 3.7 Hz, CH), 1.49 (1 H, ddd, J_1 = 9.1 Hz, J_2 = 5.5 Hz, J_3 = 3.6 Hz, C*H*H), 1.33 (1 H, ddd, J_1 = 9.1 Hz, J_2 = 5.5 Hz, J_3 = 3.6 Hz, CH*H*); δ_C (75.5 MHz, $CDC1_3$) 173.1 (C=O), 169.9 (C=O), 137.9 (C), 128.7 (CH), 127.8 (CH), 127.6 (CH), 52.0 (CH_3), 44.0 (CH_2), 24.2 (CH), 21.3 (CH), 14.8 (CH_2); MS (ESI+) m/z 256.0 ($(M+Na)^+$, 100%).

*(2) Methyl (±)-trans-2-(N-allylcarbamoyl)cyclopropanecarboxylate ((±)-**12b**).* White solid (62 mg, 34%); mp 86-87 ºC; δ_H (300.13 MHz, $CDC1_3$) 5.84 [2 H, ddt (J_{trans} = 17.2 Hz (d), J_{cis} = 10.2 Hz (d), J = 5.7 Hz (t), C*H*=CH_2) overlapped with br s (NH)], 5.24-5.12 (2 H, m, CH=CH_2), 3.90 (2 H, tt, J_1 = 5.8 Hz, J_2 = 1.5 Hz, NCH_2), 3.69 (3 H, s, OCH_3), 2.18 (1 H, ddd, J_1 = 8.8 Hz, J_2 = 5.7 Hz, J_3 = 3.8 Hz, CH), 1.94 (1 H, ddd, J_1 = 8.6 Hz, J_2 = 5.8 Hz, J_3 = 3.8 Hz, CH), 1.47 (1 H, ddd, J_1 = 8.8 Hz, J_2 = 5.8 Hz, J_3 = 3.8 Hz, C*H*H), 1.33 (1 H, ddd, , J_1 = 8.7 Hz, J_2 = 5.7 Hz, J_3 = 3.8 Hz, CH*H*); δ_C (75.5 MHz, $CDC1_3$) 173.1 (C=O), 169.8 (C=O), 133.8 (CH), 116.7 (CH_2), 52.0 (CH_3), 42.3 (CH_2), 24.3 (CH), 21.3 (CH), 14.7 (CH_2); MS (ESI+) m/z 389.1 ($(2M+Na)^+$, 100%; $(M+H)^+$, 85%).

*(3) Methyl (±)-trans-2-(N-allyl-N-methylcarbamoyl)cyclopropanecarboxylate ((±)-**12c**).* Colorless oil (20 mg, 10%); δ_H (300.13 MHz, $CDC1_3$) corresponding to a 47:53 mixture of rotamers: 5.90-5.61 (1 H, m, C*H*=CH_2), 5.32-5.05 (2 H, m, CH=CH_2), 4.17-3.94 (2 H, m, NCH_2), 3.70 and 3.68 (2 H, two s, OCH_3), 3.09 (3 H for minor rotamer, s, NCH_3), 2.94 (3 H for major

rotamer, s, NCH_3), 2.40-2.10 (2 H, m, 2 x CH), 1.50-1.12 (2 H, m, CH_2); δ_C (75.5 MHz, $CDC1_3$) corresponding to a mixture of rotamers: 173.3, 173.2, 170.3, 169.8, 132.7, 132.4, 117.4, 116.7, 52.2, 52.0, 50.4, 34.7, 34.2, 21.7, 21.1, 21.0, 15.4, 15.3; MS (ESI+) m/z 220.0 ($(M+Na)^+$, 100%).

*3. General procedure for the preparation of racemic carbamates (±)-**14a-c***

Racemic carbamates (±)-**14a-c** were obtained from the corresponding racemic carboxylic acid (±)-**11a-c** as described for the optically active samples. In turn, racemic carboxylic acids (±)-**11a-c** were prepared as follows: the racemic ethyl amido ester (±)-**9a-c** (0.50 mmol) was dissolved in ethanol (0.50 mL) and then aqueous 1 M NaOH (0.50 mL) was added. The mixture was heated at 80 ºC during 2 h. After this time, ethanol was removed, water (5 mL) and aqueous 1 M NaOH (0.2 mL) were added, and the mixture extracted with CH_2Cl_2. The organic phase was discarded. The aqueous phase was acidified with conc. HCl and extracted with ethyl acetate (2 × 10 mL). The combined organic phases were washed with brine and dried with Na_2SO_4. Evaporation of solvents yielded the corresponding racemic carboxylic acid. Spectroscopic data for (±)-**11a-c** matched those of the optically active samples.

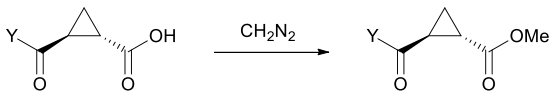
(±)-**11a**: Yield, 95%; mp 172-173 ºC.

(±)-**11b**: Yield, 90%; mp 152-153 ºC.

(±)-**11c**: Yield, 91%; mp 73-75 ºC.

4. General procedure for the derivatization of the carboxylic acids with diazomethane.

An excess of a solution of diazomethane in a mixture of diethyl ether/methanol (40 mM) was added to a sample of 1.0 mg of the corresponding carboxylic acid. After 2-3 min. solvents were evaporated and the resulting methyl ester was analysed by chiral GC or HPLC. The optically active carboxylic acids (isolated from the enzymatic reactions) and the methyl esters derivatives are collected in Scheme I.



6b (Y = OMe)
6c (Y = OBn)
11a (Y = NHBn)
11b (Y = NHAllyl)
11c (Y = NMeAllyl)

3b (Y = OMe)
8 (Y = OBn)
12a (Y = NHBn)
12b (Y = NHAllyl)
12c (Y = NMeAllyl)

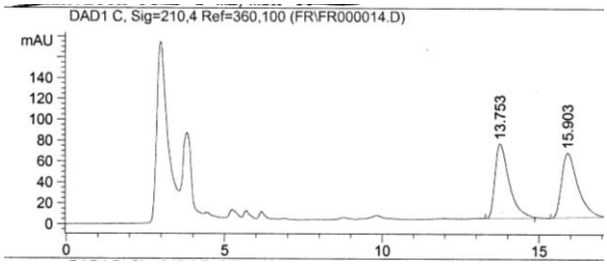
Scheme I. Methyl esters derivatives

II. Chiral HPLC conditions and chromatograms:

*1. Biotransformation of methyl (±)-trans-2-carbamoylcyclopropanecarboxylate ((±)-**4b**)* (Table 1 of the manuscript, entry 4)

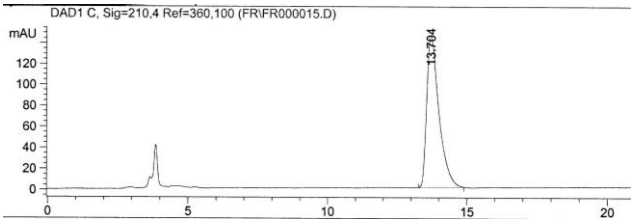
Remaining substrate (1*R*,2*R*)-**4b** was isolated with ee > 99%.
HPLC conditions: Chiralcel OD; hexane/propan-2-ol 90:10, 0.8 mL/min, 210 nm, 20 °C; t_R = 13.8 (1*R*,2*R*) and 15.9 (1*S*,2*S*) min; R_S = 2.1.

(±)-**4b**	(1*R*,2*R*)-**4b** with ee > 99%



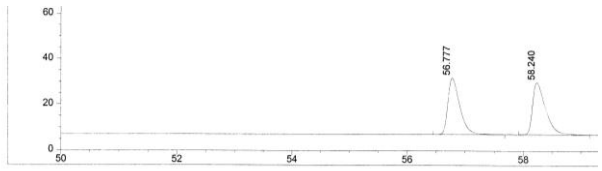
Signal 1: DAD1 C, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.753	PB	0.4731	2243.59839	71.30194	50.2058
2	15.903	PB	0.5090	2225.20654	61.95530	49.7942



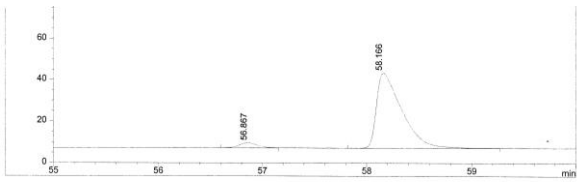
Product (1*S*,2*S*)-**6b** was isolated with ee = 91%. It was transformed into (1*S*,2*S*)-**3b** (Scheme I)
GC conditions for (±)-**3b**: RTBetaDEXse chiral column, heating at 50 ºC during 5 min, and then, a ramp of 1 ºC/min; t_R = 56.8 (1*R*,2*R*) and 58.2 (1*S*,2*S*) min; R_S = 2.9.

(±)-**3b**	(1*S*,2*S*)-**3b** with ee = 91%



Signal 1: FID1 A,

Peak #	RT [min]	Width [min]	Area	Area %
1	56.777	0.238	353.230	49.899
2	58.240	0.259	354.654	50.101

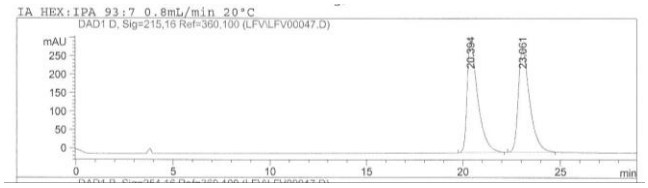
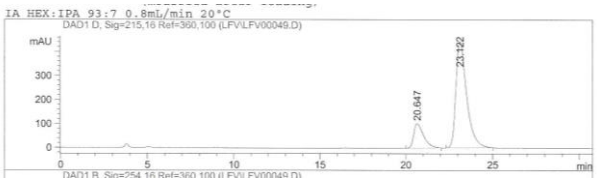


Signal 1: FID1 A,

Peak #	RT [min]	Width [min]	Area	Area %
1	56.867	0.202	29.609	4.676
2	58.166	0.277	603.585	95.324

*2. Biotransformation of benzyl (±)-trans-2-carbamoylcyclopropanecarboxylate ((±)-**4c**):*

Remaining substrate (1*R*,2*R*)-**4c** was isolated with ee = 65%.
HPLC conditions: Chiralpak IA; *n*-hexane/propan-2-ol 93:7, 0.8 mL/min, 20 °C, 215 nm; t_R = 20.4 (1*S*,2*S*) and 23.1 (1*R*,2*R*) min; R_S = 2.2.

(±)-**4c**	(1*R*,2*R*)-**4b** with ee > 99%
	

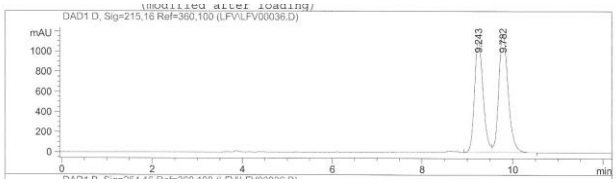
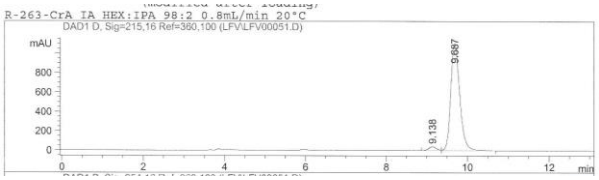
Signal 1: DAD1 D, Sig=215,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.394	BB	0.5714	1.15081e4	300.07648	50.2563
2	23.061	PB	0.6155	1.13908e4	277.13135	49.7437

Signal 1: DAD1 D, Sig=215,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.647	BB	0.5897	4076.66064	103.02068	17.5808
2	23.122	PB	0.6509	1.91114e4	443.34354	82.4192

Product (1*S*,2*S*)-**6c** was isolated with ee = 94%. For the chiral-HPLC analysis, **6c** was transformed into **8** (Scheme I).
HPLC conditions: Chiralpak IA; *n*-hexane/propan-2-ol 98:2, 0.8 mL/min, 20 °C, 215 nm; t_R = 9.2 (1*R*,2*R*) and 9.8 (1*S*,2*S*) min; R_S = 1.3.

Nearly racemic **8** (ee = 8%)	(1*S*,2*S*)-**8** with ee = 94%
	

Signal 1: DAD1 D, Sig=215,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.243	VV	0.2018	1.46398e4	1110.54370	46.2568
2	9.782	VB	0.2229	1.70092e4	1175.13623	53.7432

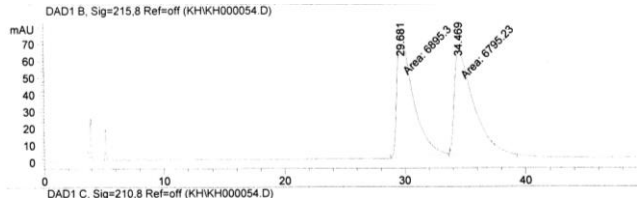
Signal 1: DAD1 D, Sig=215,16 Ref=360,100

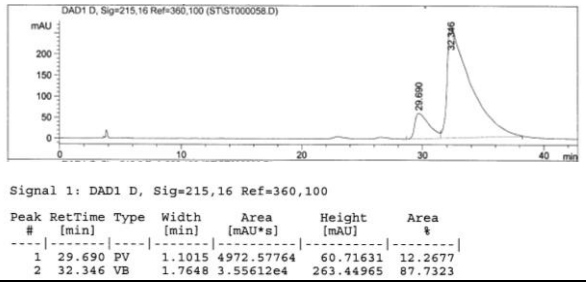
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.138	VV	0.2101	546.77722	39.84304	3.1106
2	9.687	VB	0.2378	1.70312e4	1104.97314	96.8894

*3. Biotransformation of (±)-trans-N-benzylcyclopropane-1,2-dicarboxamide ((±)-**10a**)* (Table 2 of the manuscript, entry 1):

Remaining substrate (1*R*,2*R*)-**10a** was isolated with ee = 75%.
HPLC conditions: Chiralpak IA; *n*-hexane/propan-2-ol 95:5, 0.8 mL/min, 20 °C, 215 nm; t_R = 29.7 (1*S*,2*S*) and 34.5 (1*R*,2*R*) min; R_S = 1.4.

(±)-**10a**	(1*R*,2*R*)-**10a** with ee = 75%



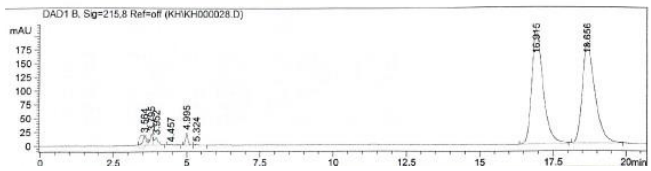


Signal 1: DAD1 D, Sig=215,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	29.690	PV	1.1015	4972.57764	60.71631	12.2677
2	32.346	VB	1.7648	3.55612e4	263.44965	87.7323

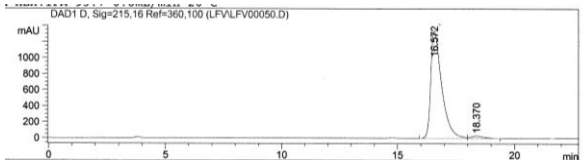
Product (1*S*,2*S*)-**11a** was isolated with ee = 95%. For the chiral-HPLC analysis, **11a** was transformed into **12a** (Scheme I).
HPLC conditions: Chiralpak IA; *n*-hexane/propan-2-ol 93:7, 0.8 mL/min, 20 °C, 215 nm; t_R = 17.0 (1*S*,2*S*) and 18.7 (1*R*,2*R*) min; R_S = 2.1.

(±)-**12a**	(1*S*,2*S*)-**12a** with ee = 95%



Signal 1: DAD1 B, Sig=215,8 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.564	BV	0.1145	141.40953	17.46466	1.2062
2	3.795	VV	0.0990	138.75882	21.03160	1.1836
3	3.952	VB	0.1297	138.00468	14.16263	1.1771
4	4.457	BB	0.1789	20.09639	1.47541	0.1714
5	4.995	BB	0.0925	137.35048	22.74512	1.1715
6	5.324	BP	0.1021	12.13186	1.85904	0.1035
7	16.915	BB	0.3980	5583.51758	208.80965	47.6250
8	18.656	BB	0.4455	5552.64844	184.30960	47.3617



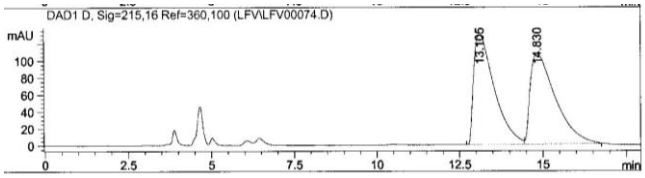
Signal 1: DAD1 D, Sig=215,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.572	BV	0.4808	4.35742e4	1335.04956	97.5456
2	18.370	VB	0.5343	1096.38733	29.86458	2.4544

*4. Biotransformation of (±)-trans-N-allylcyclopropane-1,2-dicarboxamide ((±)-**10b**)* (Table 2 of the manuscript, entry 2):

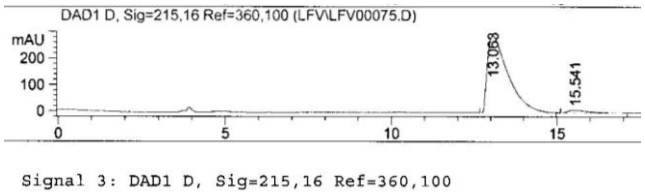
Remaining substrate (1*R*,2*R*)-**10b** was isolated with ee = 93%.
HPLC conditions: Chiralcel OD; *n*-hexane/propan-2-ol 94:6, 0.8 mL/min, 30 °C, 215 nm; t_R = 13.1 (1*R*,2*R*) and 14.8 (1*S*,2*S*) min; R_S = 1.2.

(±)-**10b**	(1*R*,2*R*)-**10b** with ee = 93%



Signal 2: DAD1 D, Sig=215,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.105	BV	0.6298	5604.49414	131.33781	50.0112
2	14.830	VB	0.7788	5601.98877	107.34842	49.9888

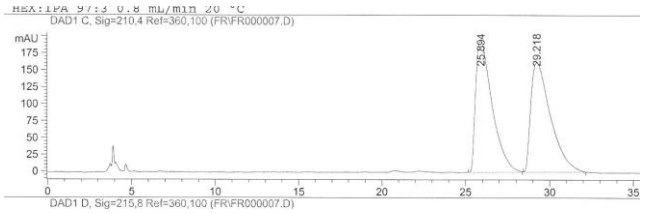


Signal 3: DAD1 D, Sig=215,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.063	BB	0.6617	1.27674e4	291.07977	96.6323
2	15.541	BB	0.5320	444.95074	10.25924	3.3677

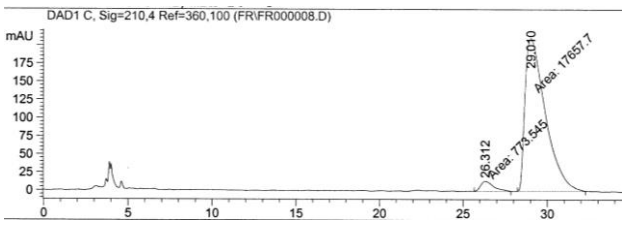
Product (1*S*,2*S*)-**11b** was isolated with ee = 92%. For the chiral-HPLC analysis, **11b** was transformed into **12b** (Scheme I).
HPLC conditions: Chiralcel OD; *n*-hexane/propan-2-ol 97:3, 0.8 mL/min, 20 °C, 210 nm; t_R = 25.9 (1*R*,2*R*) and 29.2 (1*S*,2*S*) min; R_S = 1.7.

(±)-**12b**	(1*S*,2*S*)-**12b** with ee = 92%



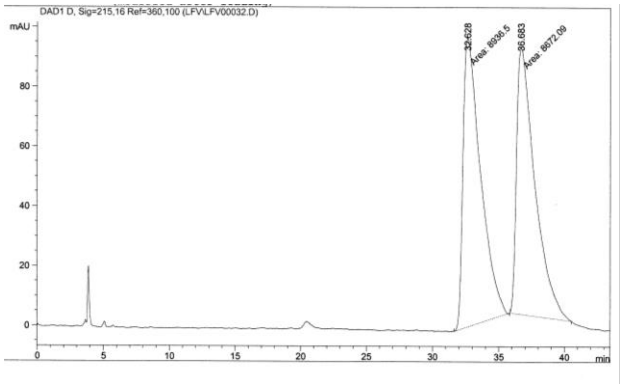
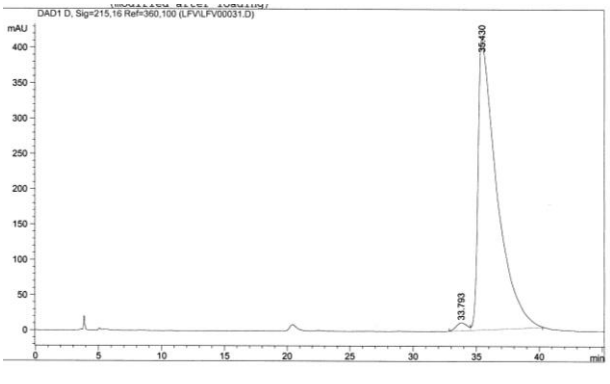
Signal 1: DAD1 C, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.894	BB	0.9202	1.32897e4	195.23094	50.0888
2	29.218	BB	1.0681	1.32426e4	161.92171	49.9112



*5. Biotransformation of (±)-trans-N-allyl-N-methylcyclopropane-1,2-dicarboxamide ((±)-**10c**)* (Table 2 of the manuscript, entry 3):

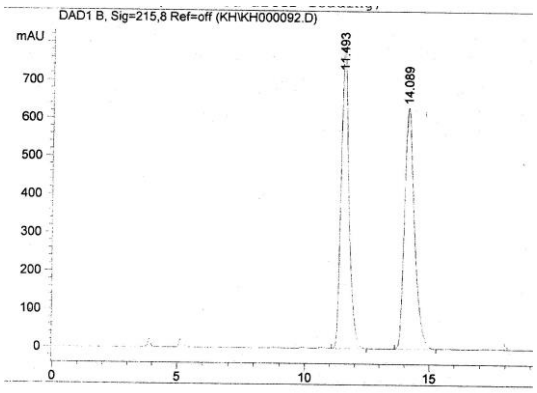
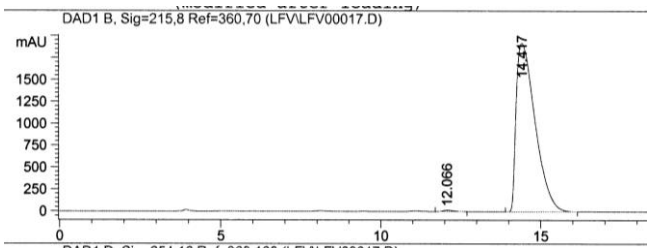
Remaining substrate (1*R*,2*R*)-**10c** was isolated with ee = 97%.
HPLC conditions: Chiralpak IA; *n*-hexane/propan-2-ol 95:5, 0.8 mL/min, 20 °C, 215 nm; t_R = 32.6 (1*S*,2*S*) and 36.7 (1*R*,2*R*) min; R_S = 1.3.

(±)-**10c**	(1*R*,2*R*)-**10c** with ee = 97%
	

Signal 1: DAD1 D, Sig=215,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	33.793	BV	0.7344	696.72559	11.57219	1.6087
2	35.430	VB	1.3694	4.26122e4	411.75284	98.3913

Product (1*S*,2*S*)-**11c** was isolated with ee = 99%. For the chiral-HPLC analysis, **11c** was transformed into **12c** (Scheme I).
HPLC conditions: Chiralcel OD; *n*-hexane/propan-2-ol 95:5, 0.8 mL/min, 20 °C, 215 nm; t_R = 11.5 (1*R*,2*R*) and 14.1 (1*S*,2*S*) min; R_S = 3.5.

(±)-**12c**	(1*S*,2*S*)-**12c** with ee = 99%
	

Signal 1: DAD1 B, Sig=215,8 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.493	VB	0.3318	1.75795e4	789.29468	49.9225
2	14.089	BB	0.4178	1.76341e4	631.42932	50.0775

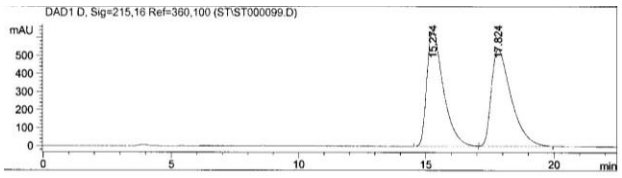
Signal 1: DAD1 B, Sig=215,8 Ref=360,70

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.066	BB	0.3421	360.70236	15.46318	0.4552
2	14.417	VB	0.6356	7.88763e4	1918.83911	99.5448

*6. The Curtius rearrangement of **11a-c**: carbamates **14a-c***

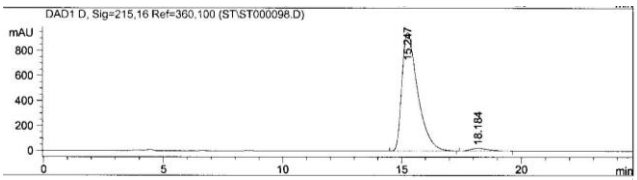
14a. HPLC conditions: Chiralcel OD; *n*-hexane/propan-2-ol 80:20, 0.8 mL/min, 20 °C, 215 nm; t_R = 15.3 (1*S*,2*S*) and 17.8 (1*R*,2*R*) min; R_S = 1.7.

(±)-**14a**	(1*S*,2*S*)-**14a** with ee = 95%



Signal 2: DAD1 D, Sig=215,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.274	BB	0.6762	2.88193e4	641.37073	49.9189
2	17.824	BB	0.7969	2.89129e4	538.04236	50.0811

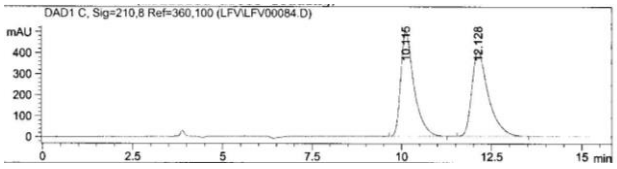


Signal 2: DAD1 D, Sig=215,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.247	BB	0.7019	4.37197e4	948.16193	97.6119
2	18.184	PB	0.7186	1069.59229	21.71792	2.3881

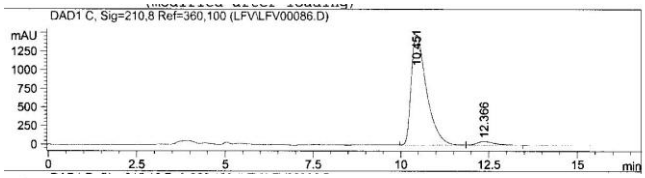
14b. HPLC conditions: Chiralcel OD; *n*-hexane/propan-2-ol 80:20, 0.8 mL/min, 20 °C, 210 nm; t_R = 10.1 (1*S*,2*S*) and 12.1 (1*R*,2*R*) min; R_S = 2.3.

(±)-**14b**	(1*S*,2*S*)-**14b** with ee = 92%



Signal 1: DAD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.115	BB	0.3831	1.28323e4	497.21582	49.9259
2	12.128	BB	0.4779	1.28704e4	401.62277	50.0741

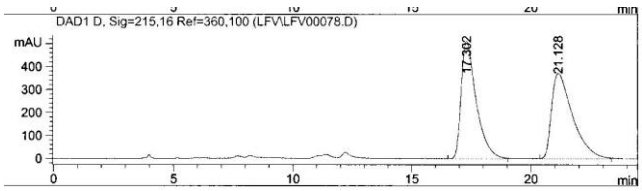


Signal 1: DAD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.451	BB	0.4593	4.50908e4	1480.49634	96.1494
2	12.366	BB	0.5150	1805.79041	51.01522	3.8506

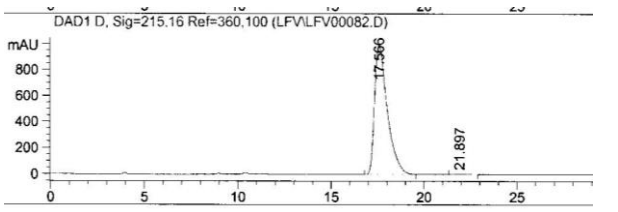
14c. HPLC conditions: Chiralcel OD; *n*-hexane/propan-2-ol 85:15, 0.8 mL/min, 20 °C, 215 nm; t_R = 17.3 (1*S*,2*S*) and 21.1 (1*R*,2*R*) min; R_S = 2.5.

(±)-**14c**	(1*S*,2*S*)-**14c** with ee = 99%



Signal 2: DAD1 D, Sig=215,16 Ref=360,100

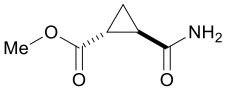
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.302	BB	0.6594	2.25085e4	511.44687	49.8933
2	21.128	VV	0.8905	2.26048e4	371.18146	50.1067

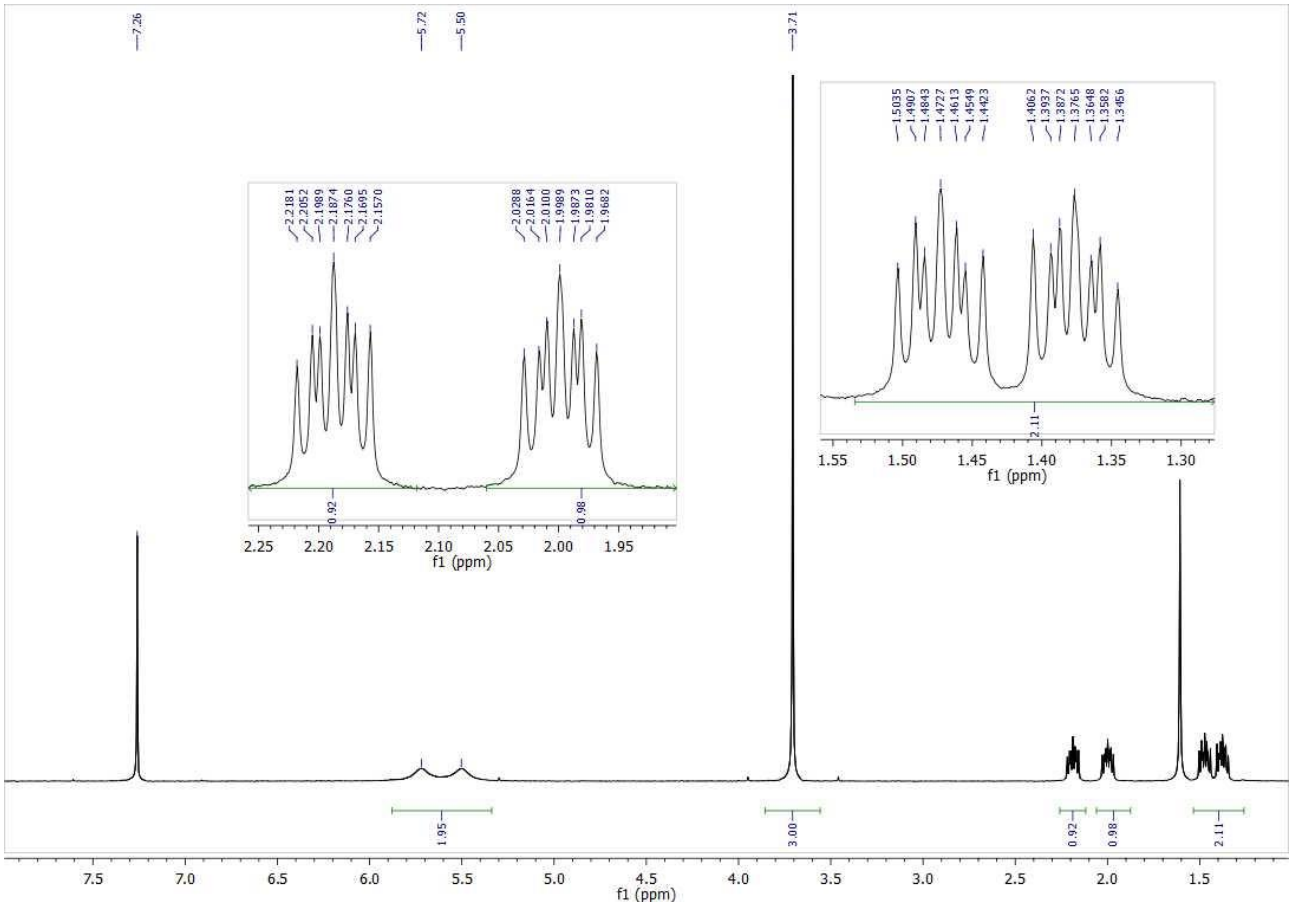


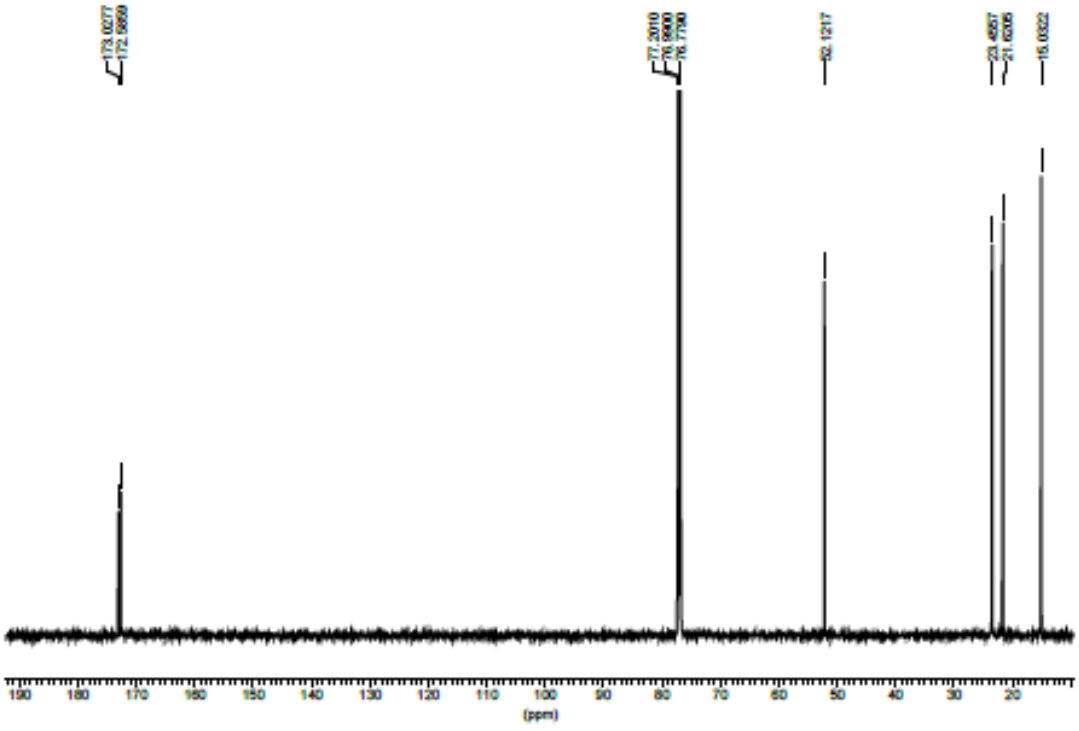
Signal 2: DAD1 D, Sig=215,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.566	BB	0.6937	4.73570e4	1001.35815	99.5437
2	21.897	VV	0.6537	217.10345	4.04823	0.4563

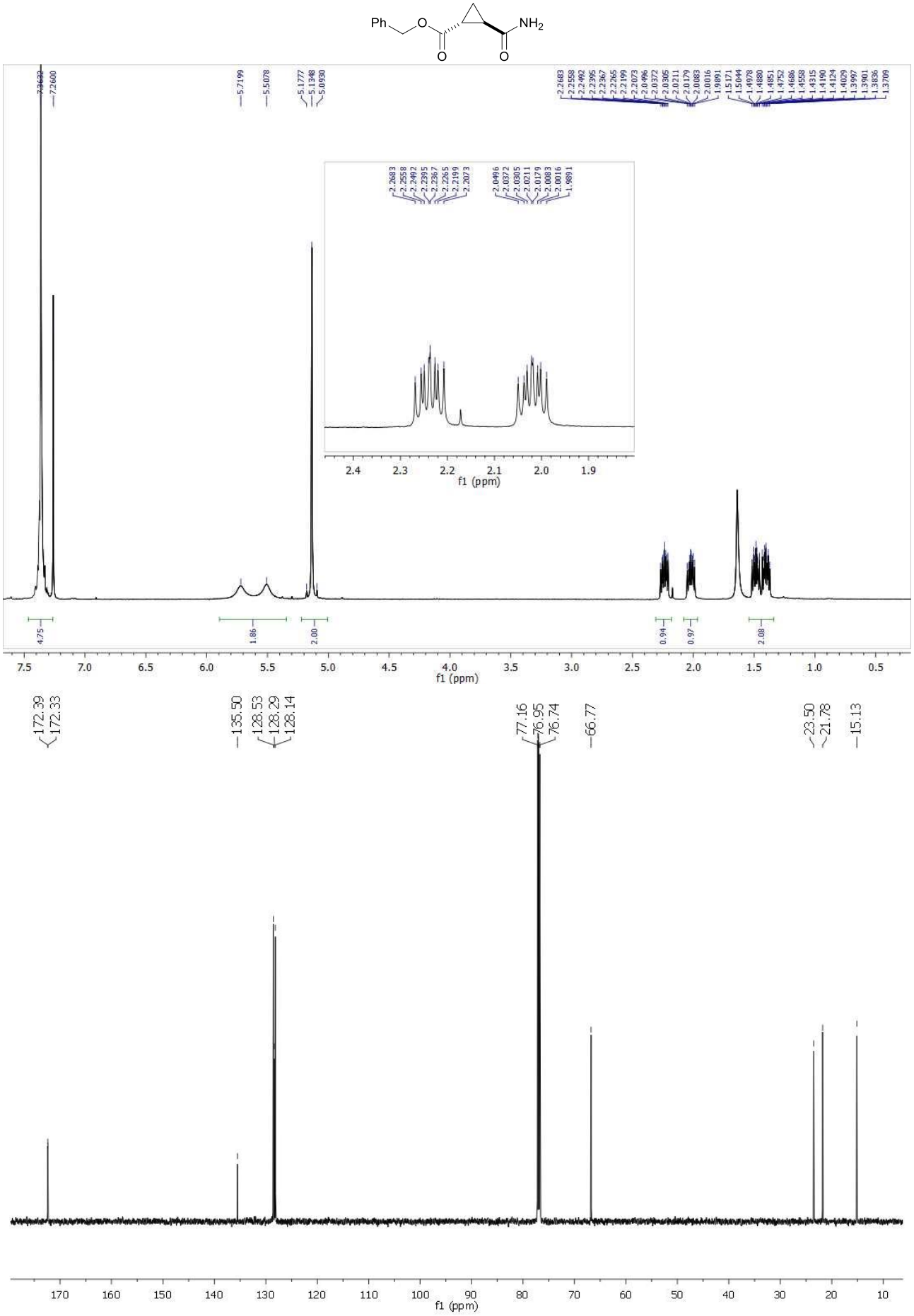
^{1}H and ^{13}C NMR spectra of **4b** in $CDCl_3$:



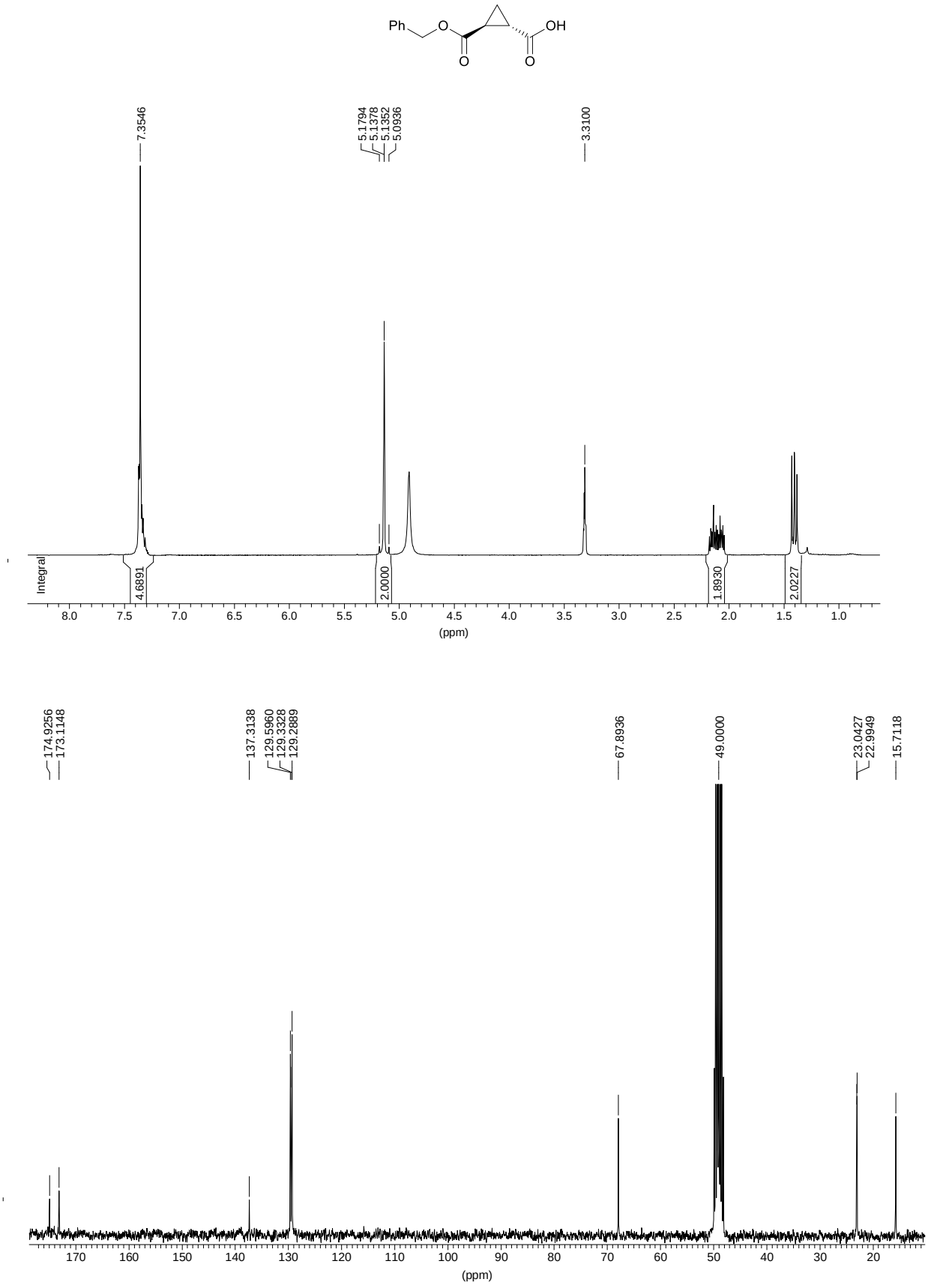




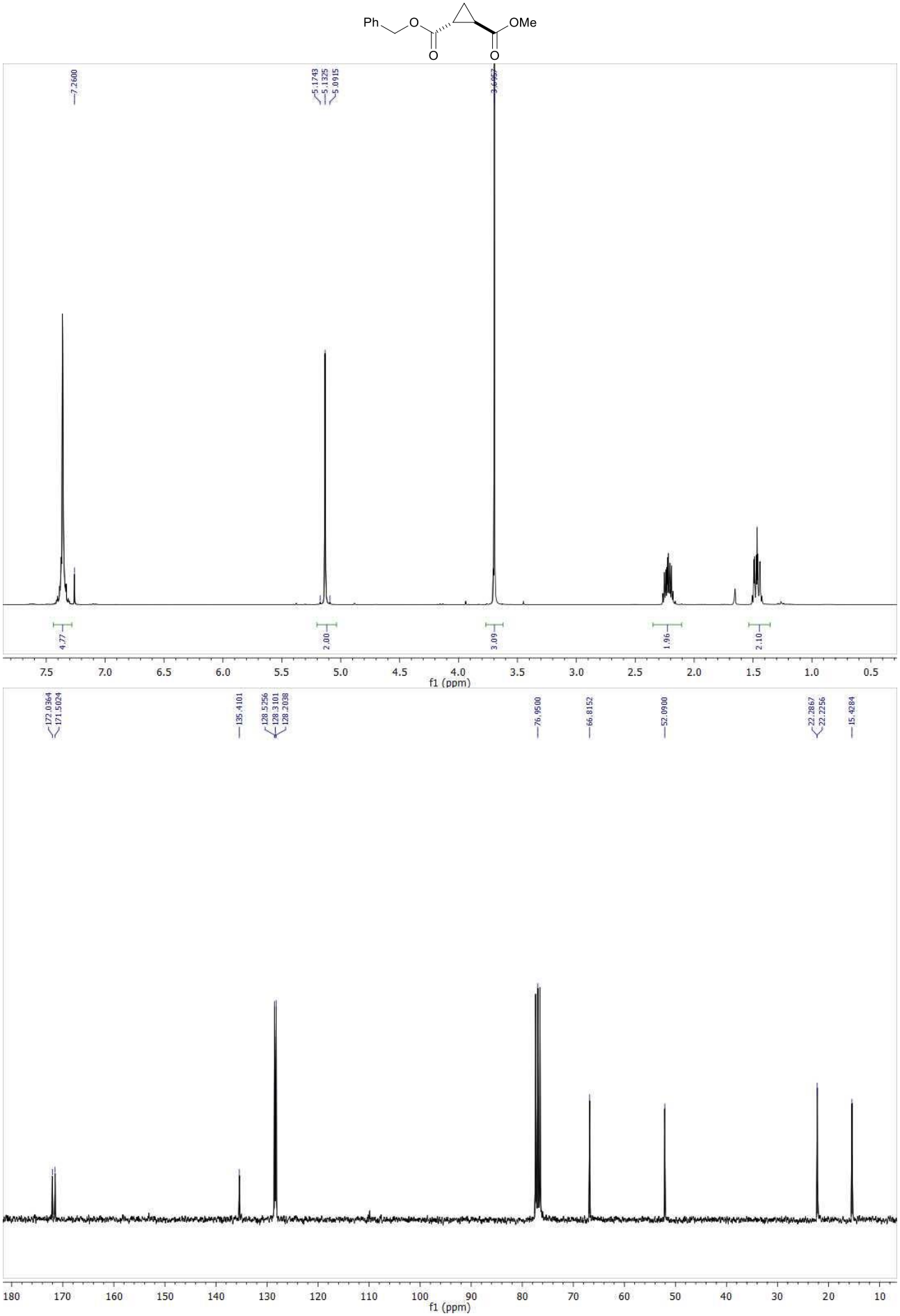
^{1}H and ^{13}C NMR spectra of **4c** in $CDCl_3$:



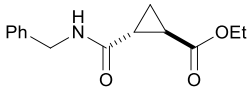
^{1}H and ^{13}C NMR spectra of **6c** in CD_3OD:

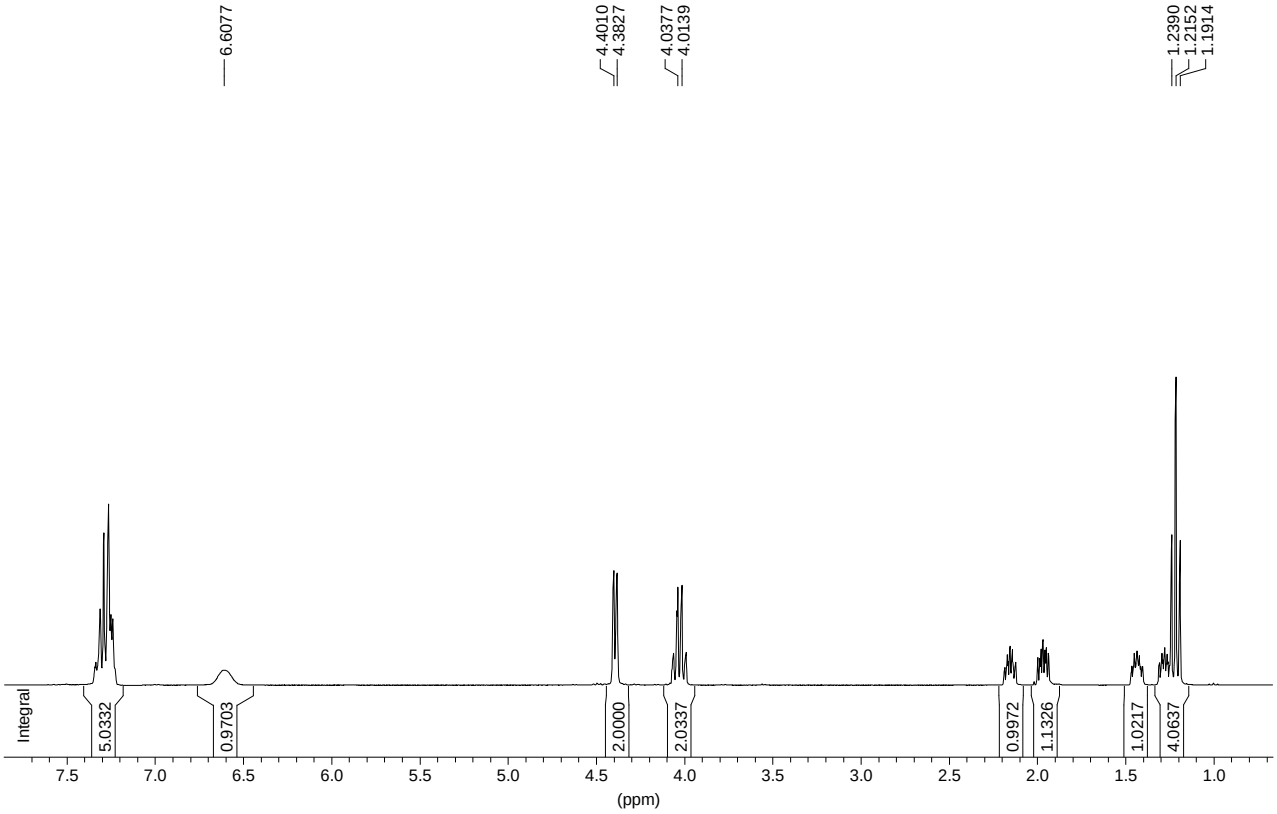


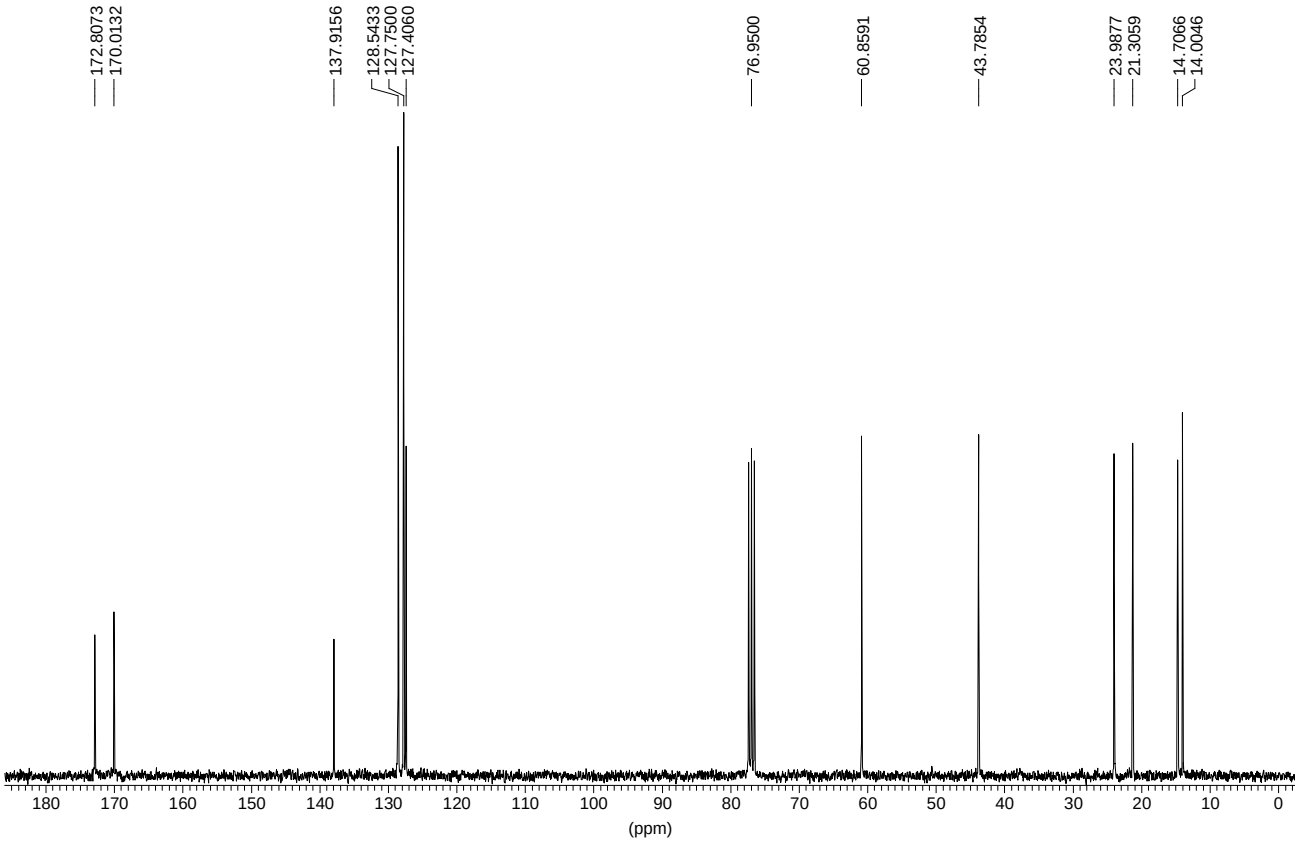
^{1}H and ^{13}C NMR spectra of **8** in $CDCl_3$:



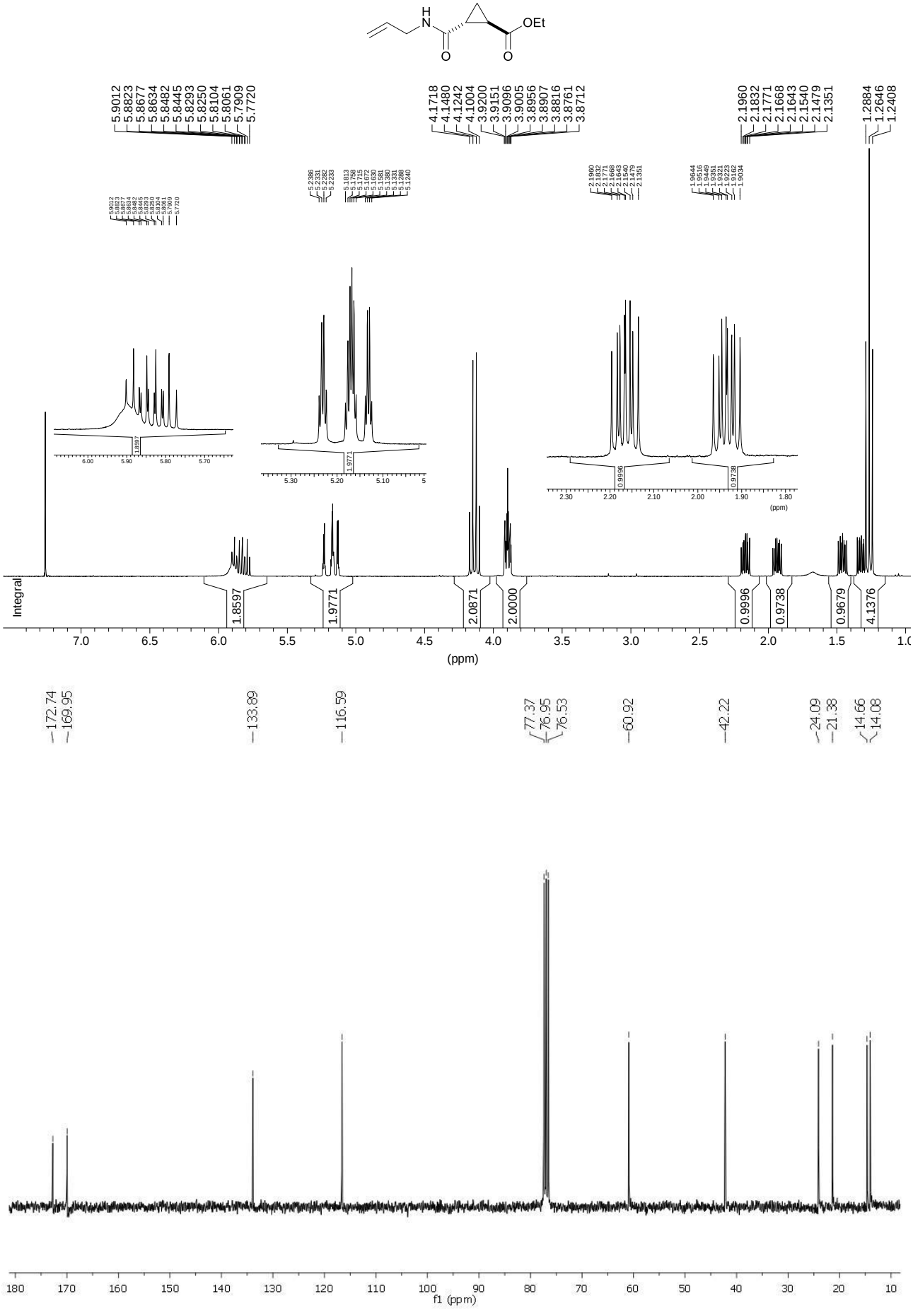
^{1}H and ^{13}C NMR spectra of **9a** in $CDCl_3$:



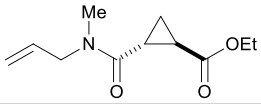


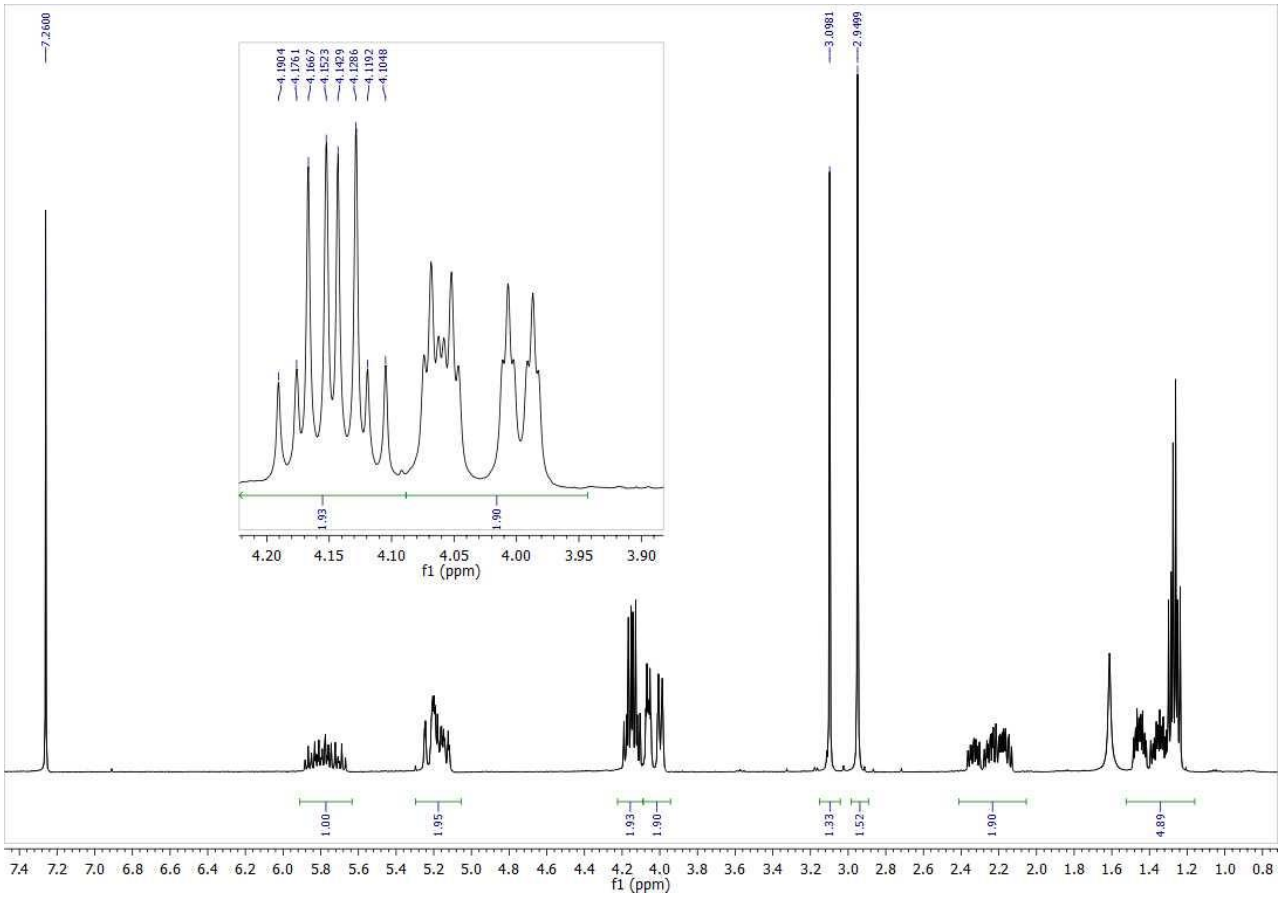


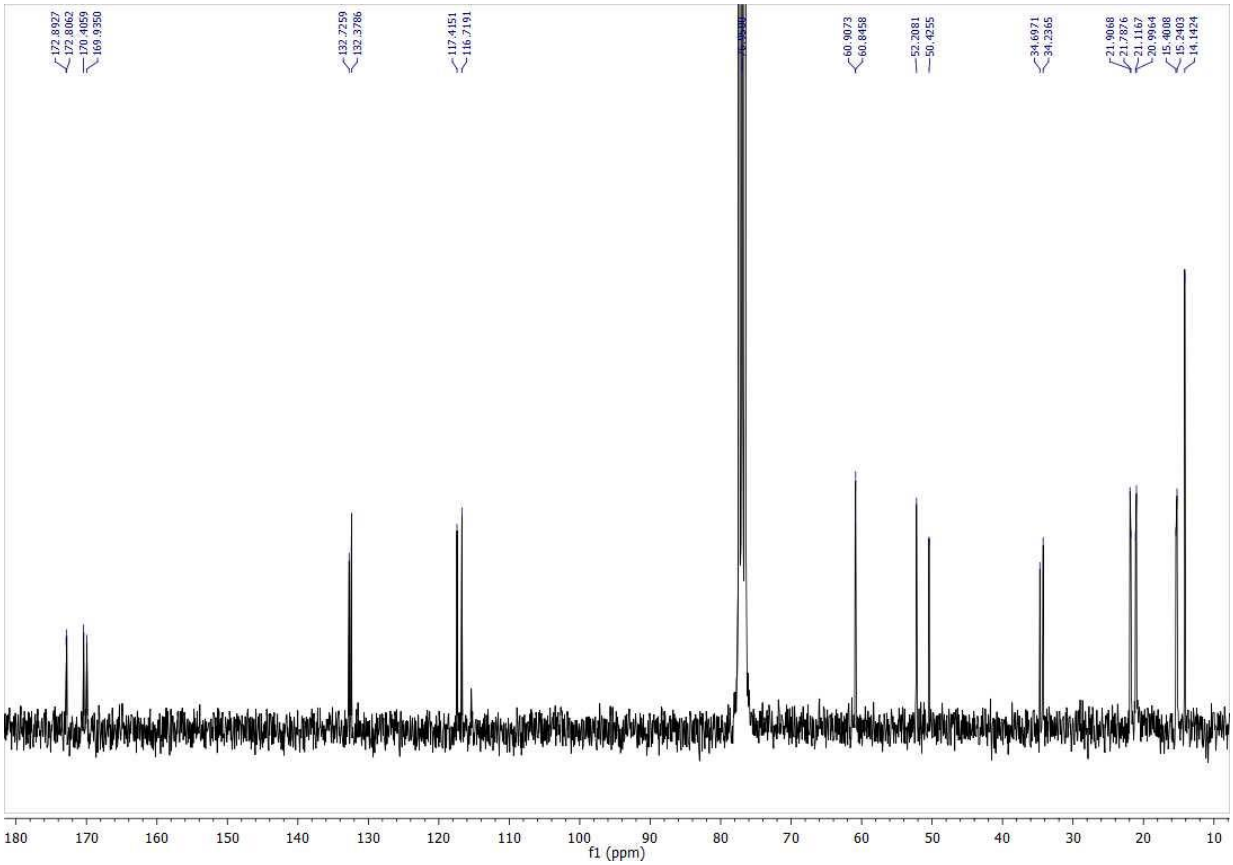
^{1}H and ^{13}C NMR spectra of **9b** in $CDCl_3$:



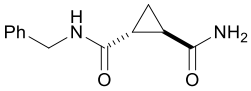
^{1}H and ^{13}C NMR spectra of **9c** in $CDCl_3$:

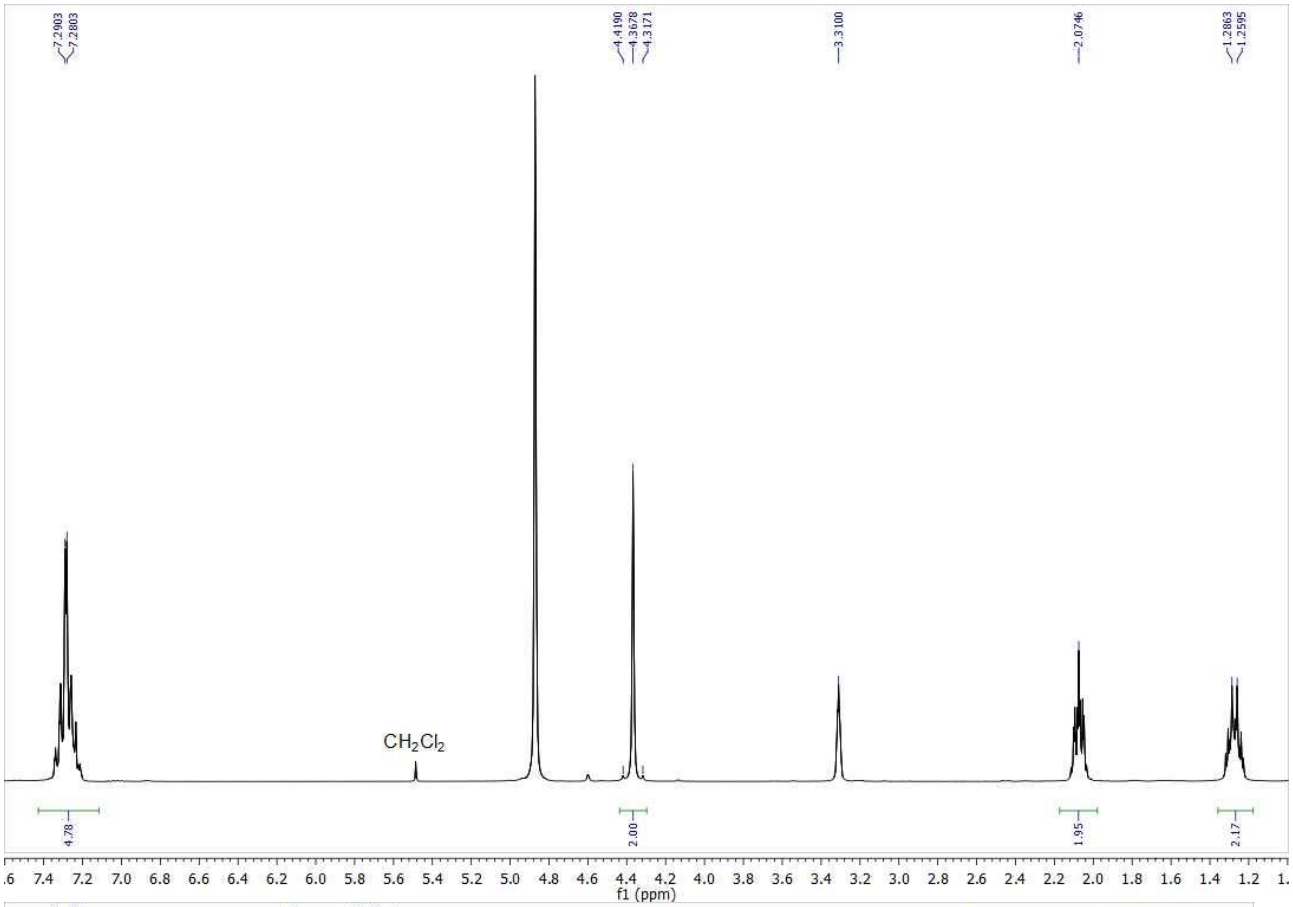


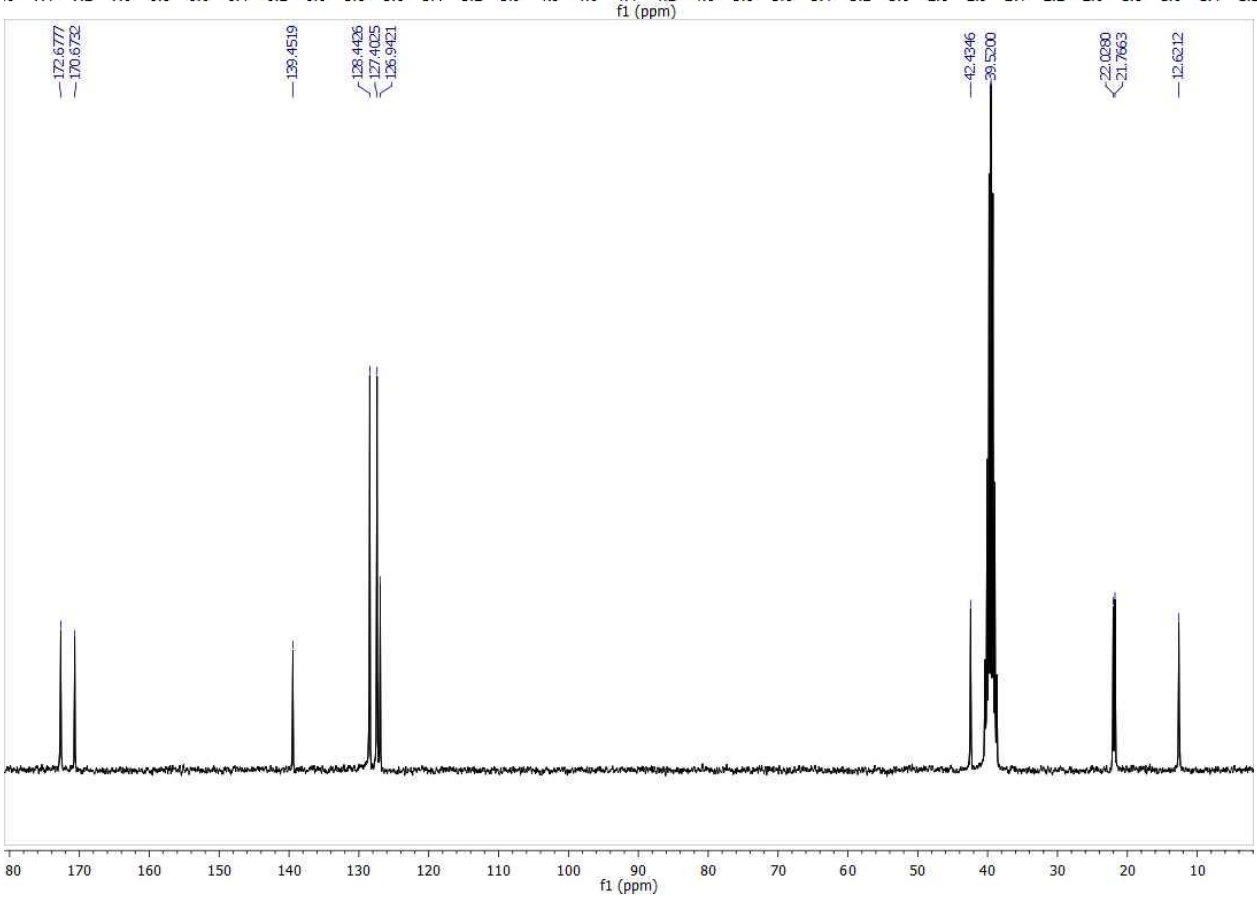




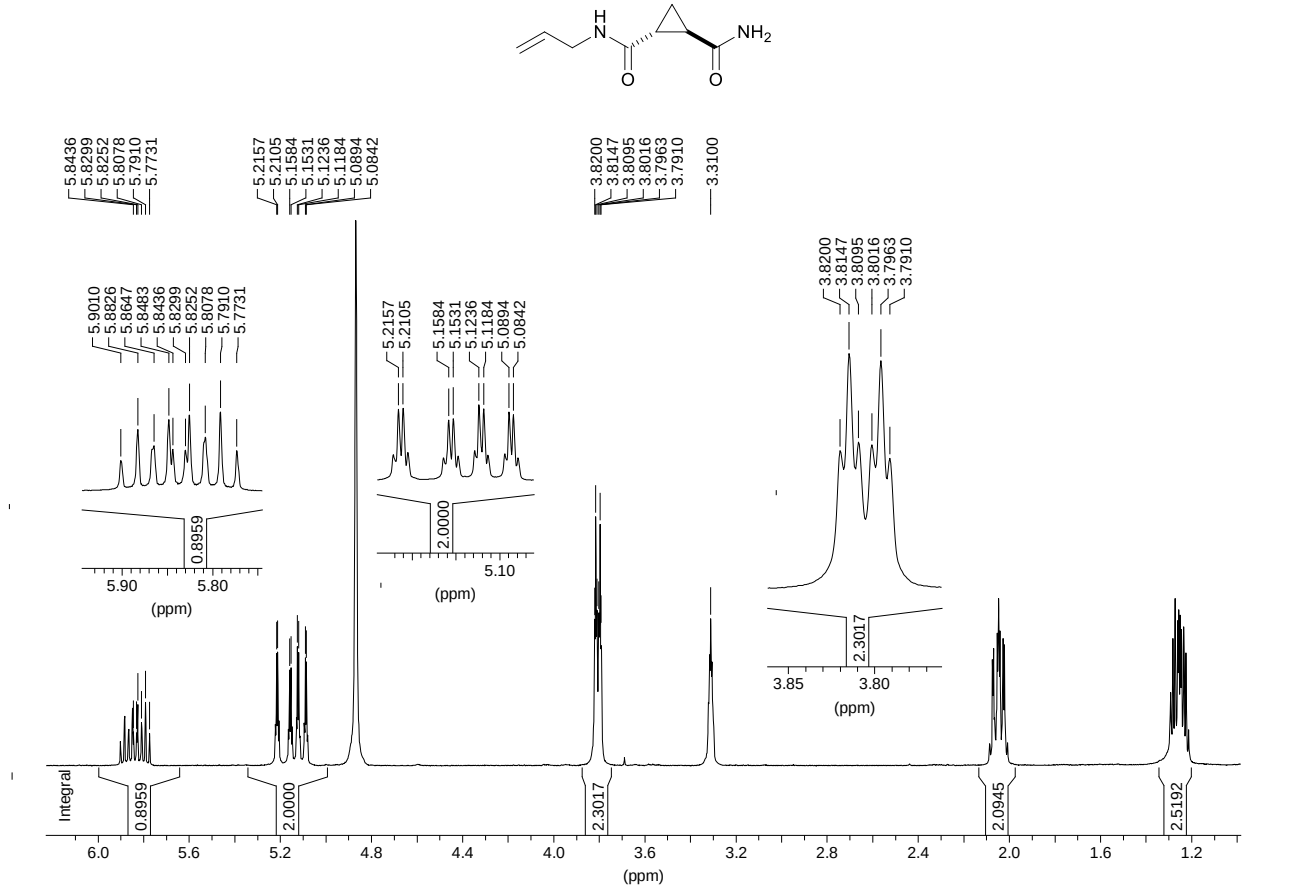
^{1}H and ^{13}C NMR spectra of **10a** (in CD_3OD and DMSO-d_6, respectively):

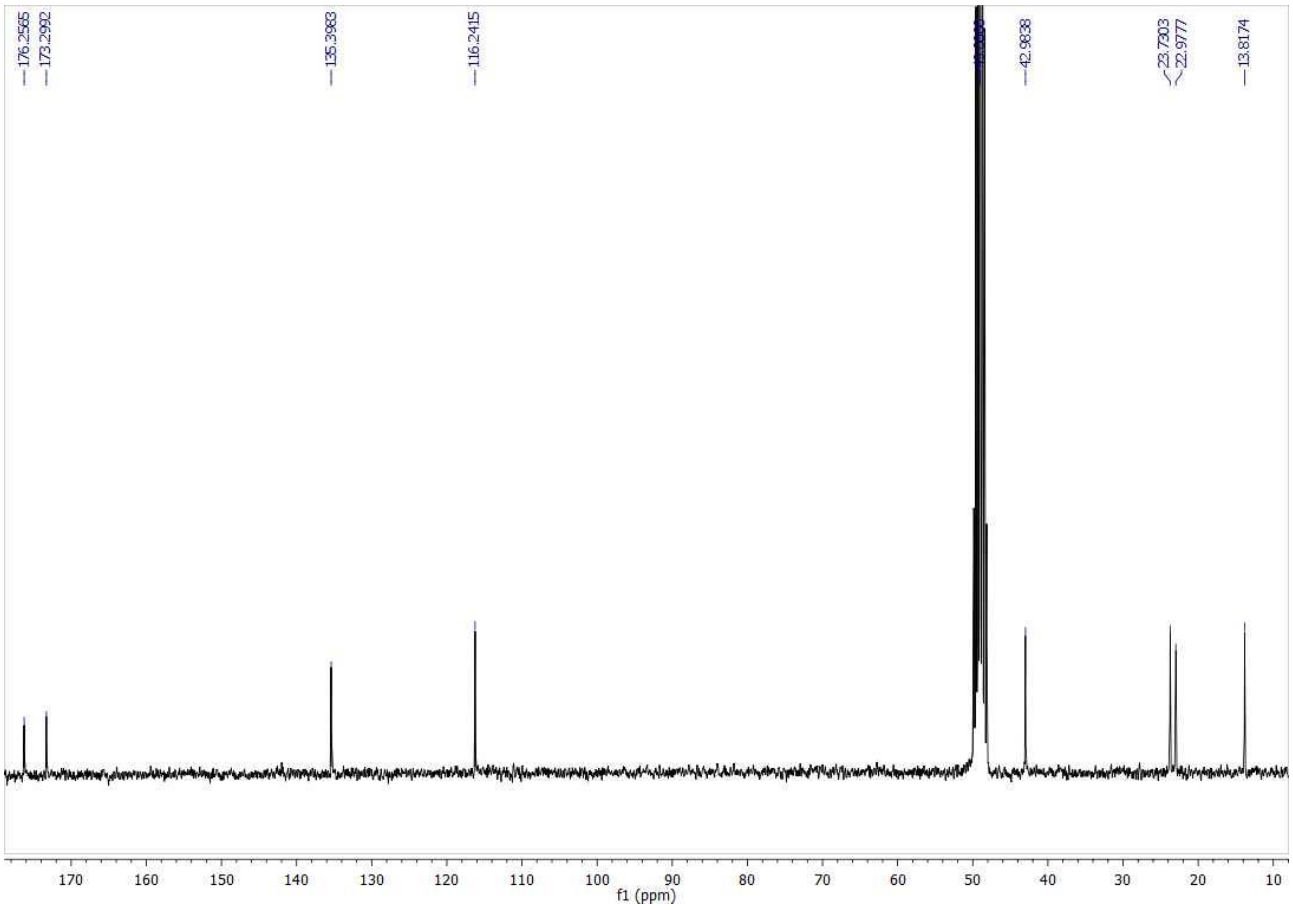




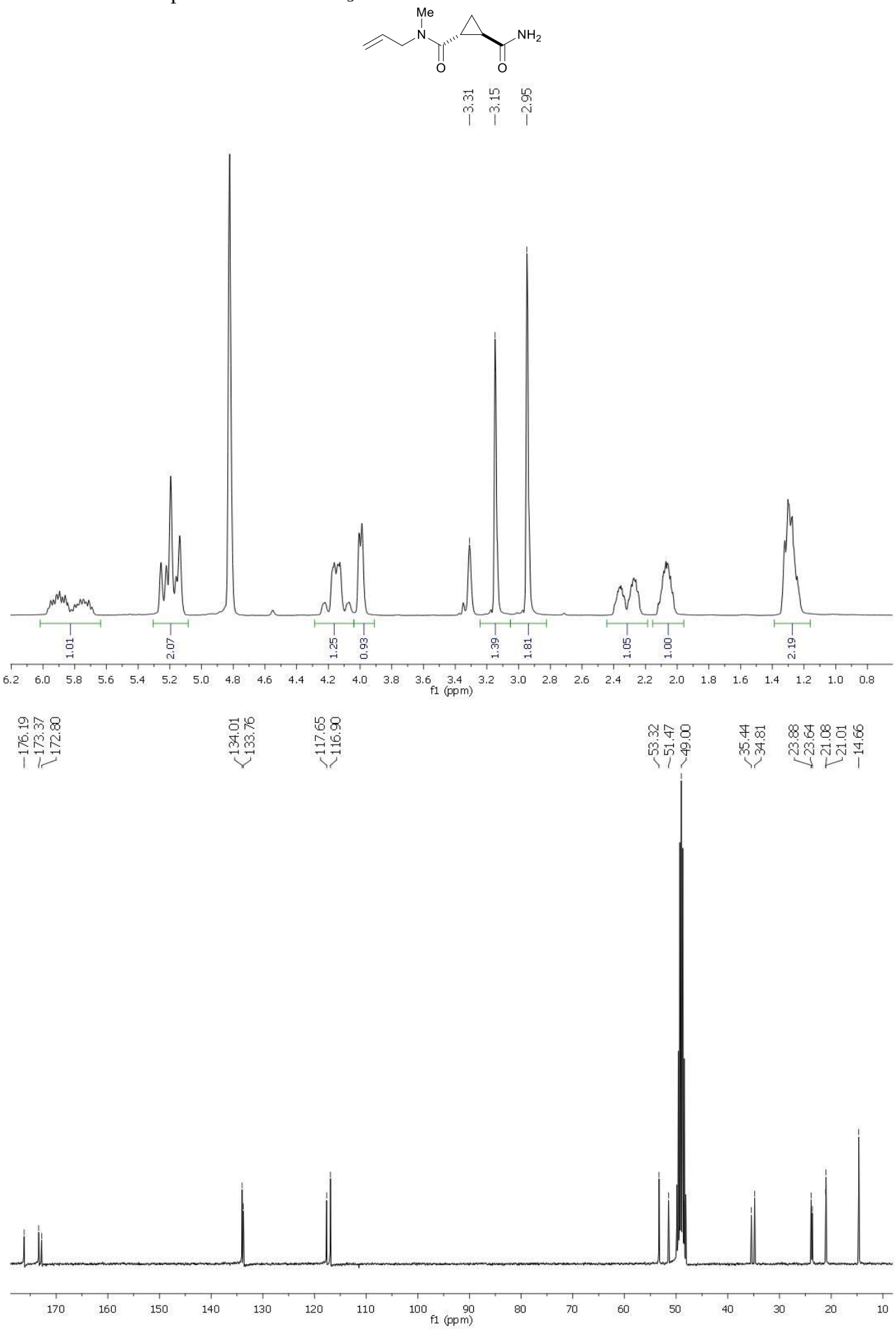


^{1}H and ^{13}C NMR spectra of **10b** in CD_3OD:

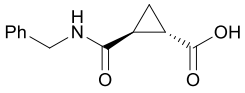


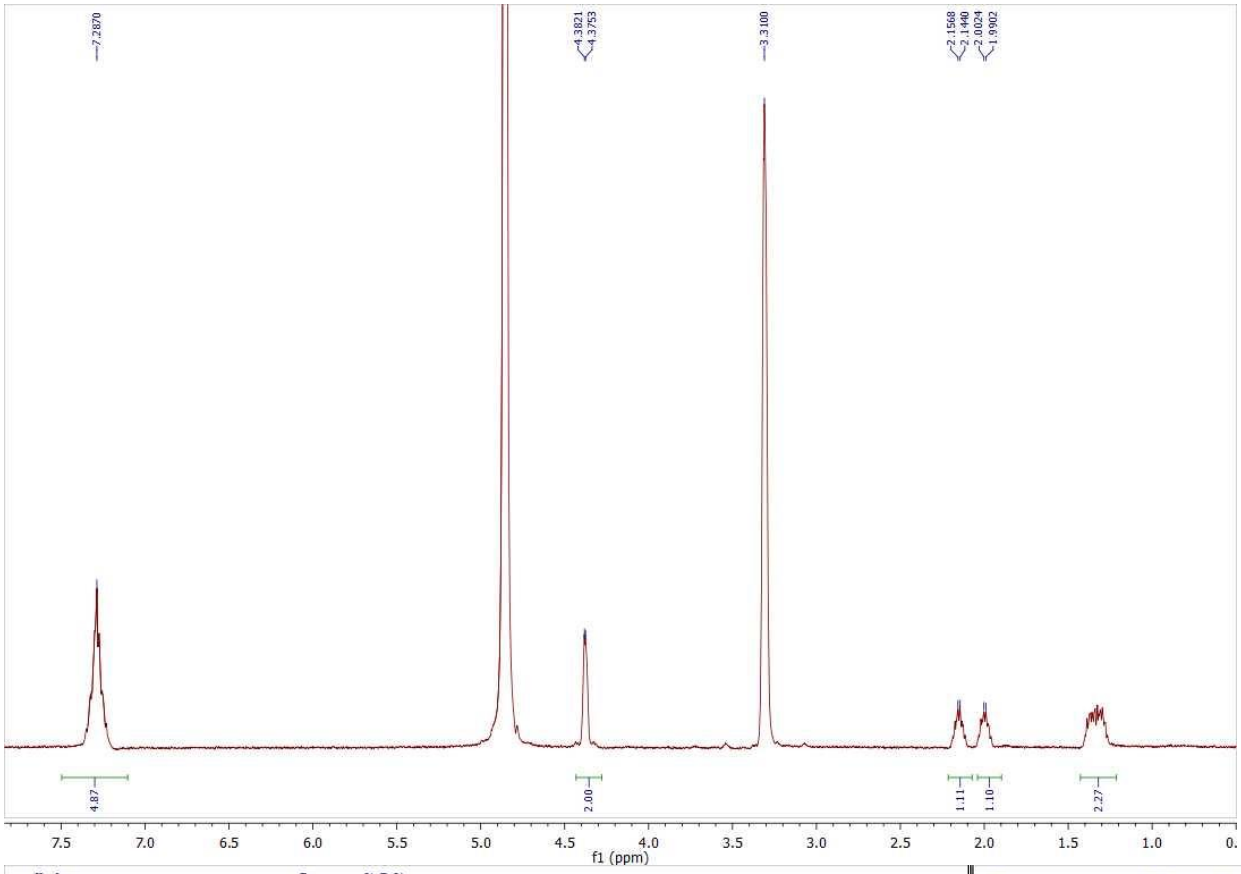


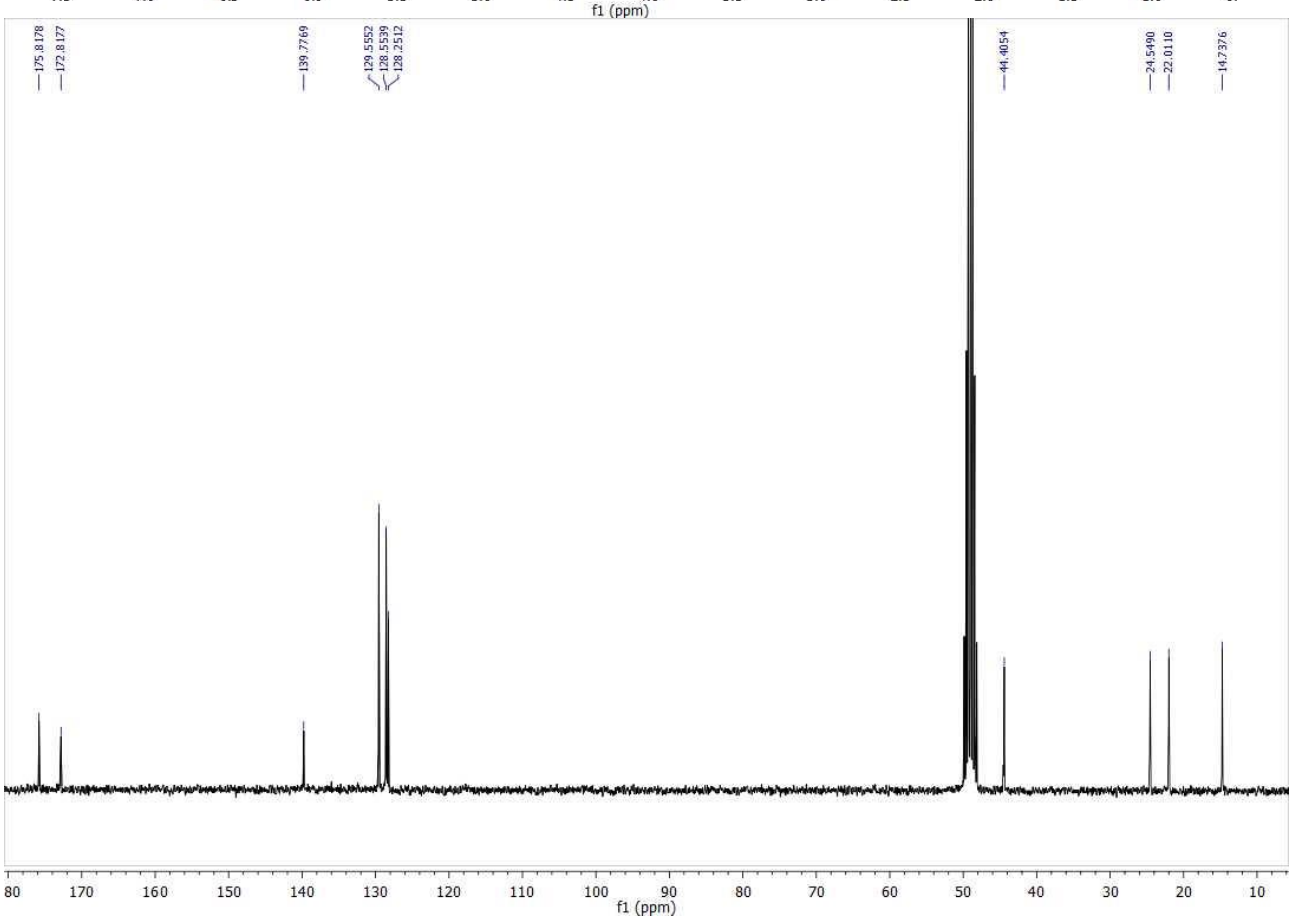
^{1}H and ^{13}C NMR spectra of **10c** in CD_3OD:



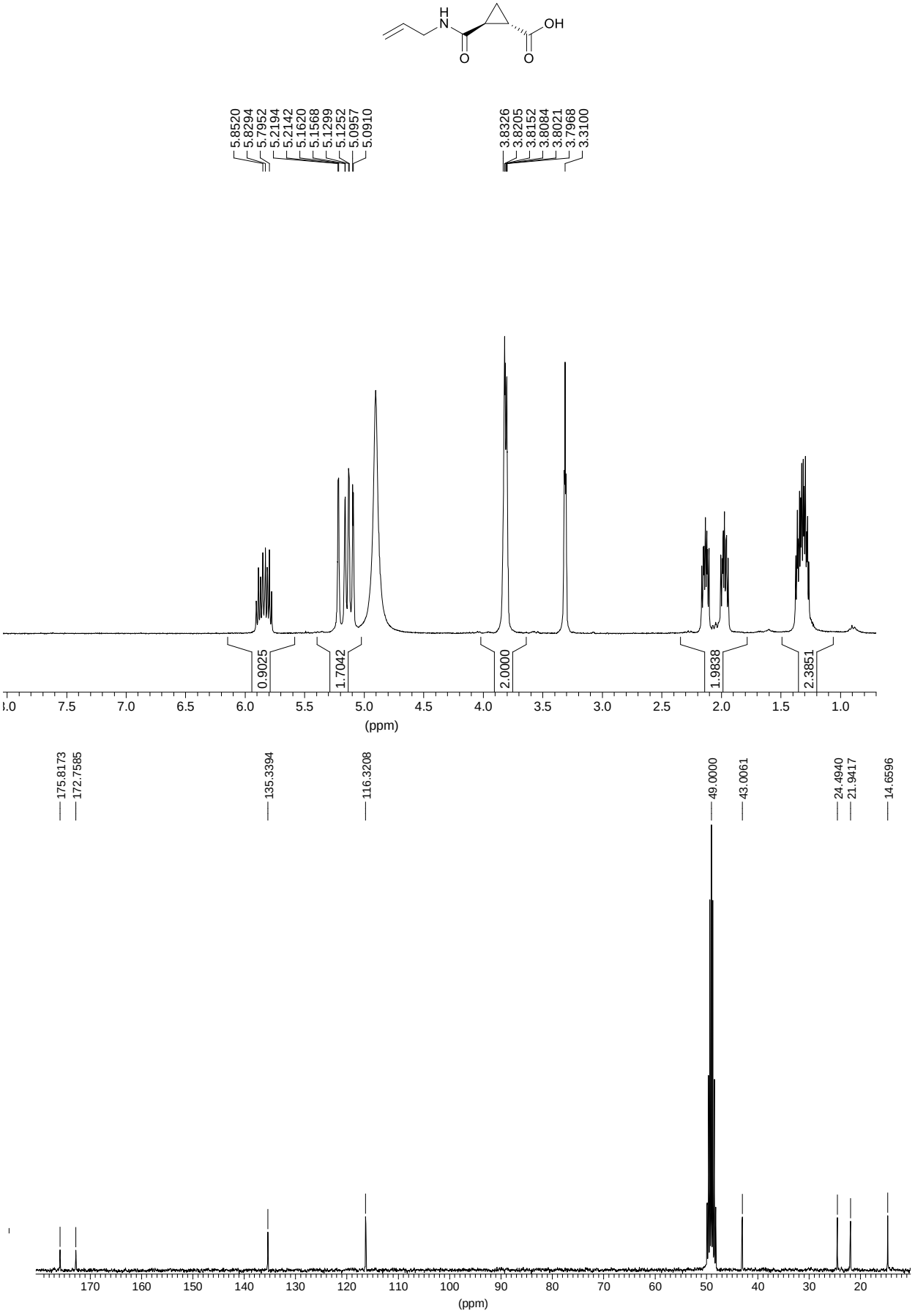
^{1}H and ^{13}C NMR spectra of **11a** in CD_3OD:



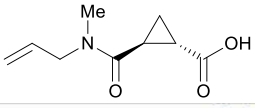


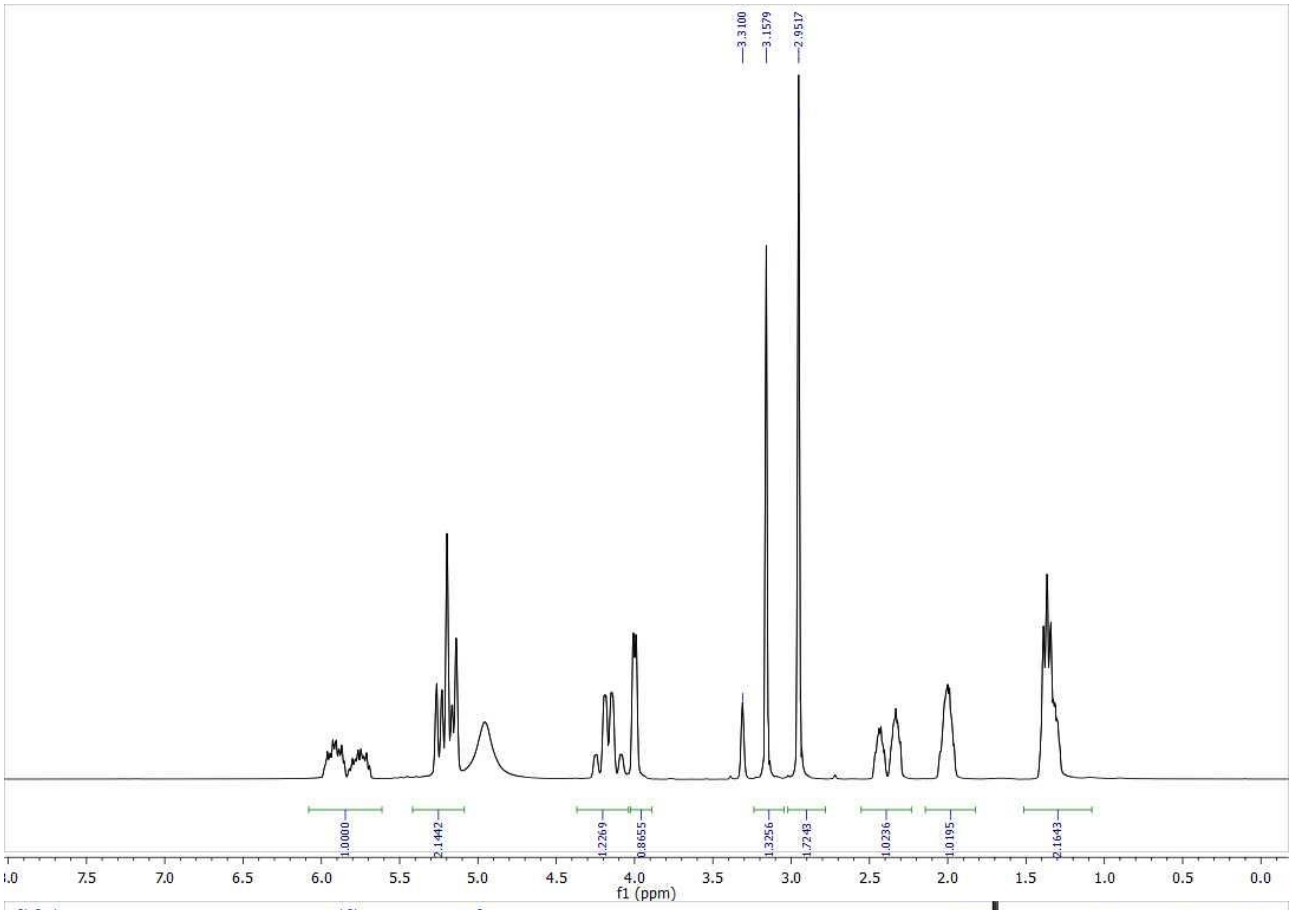


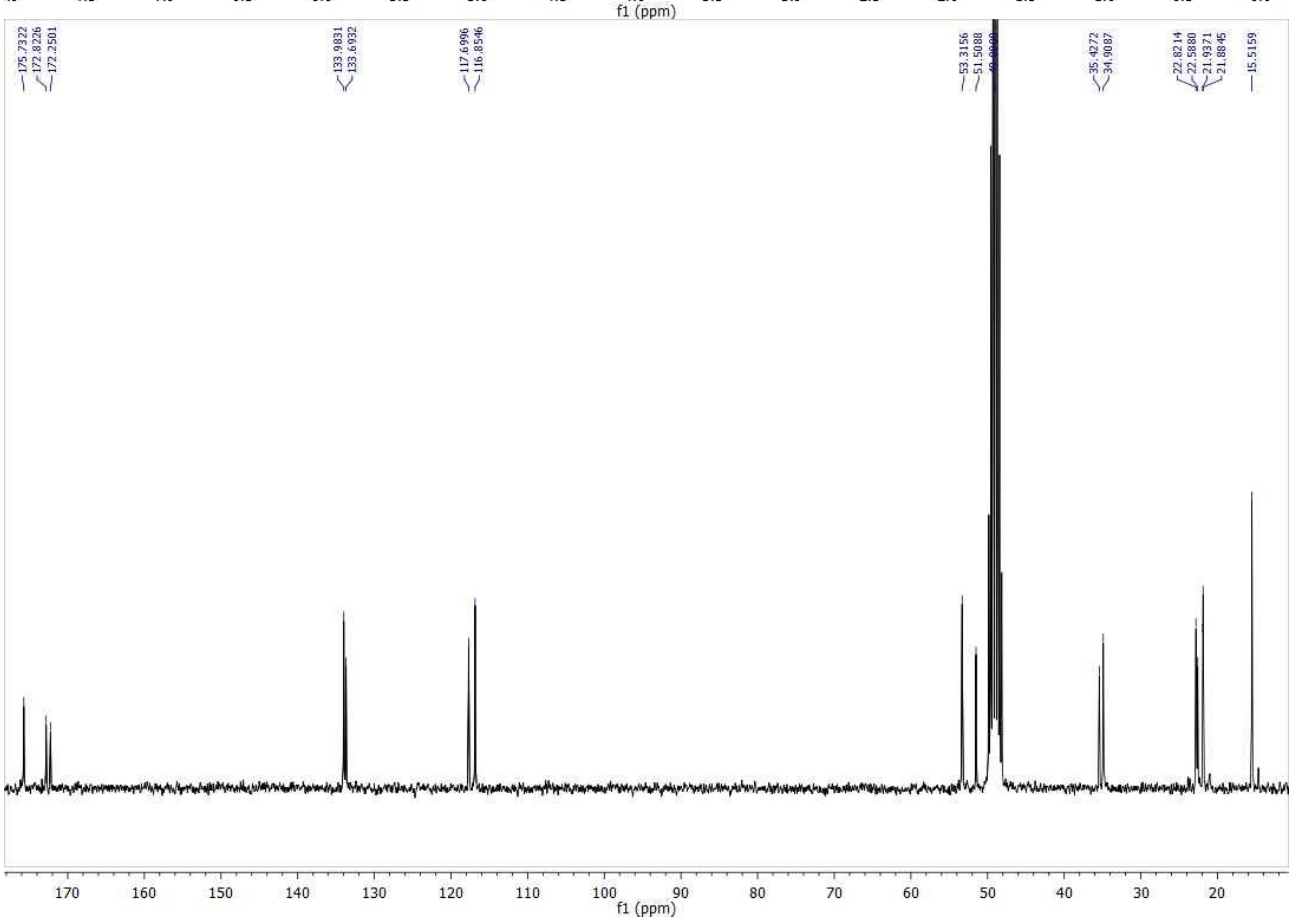
^{1}H and ^{13}C NMR spectra of **11b** in CD_3OD:



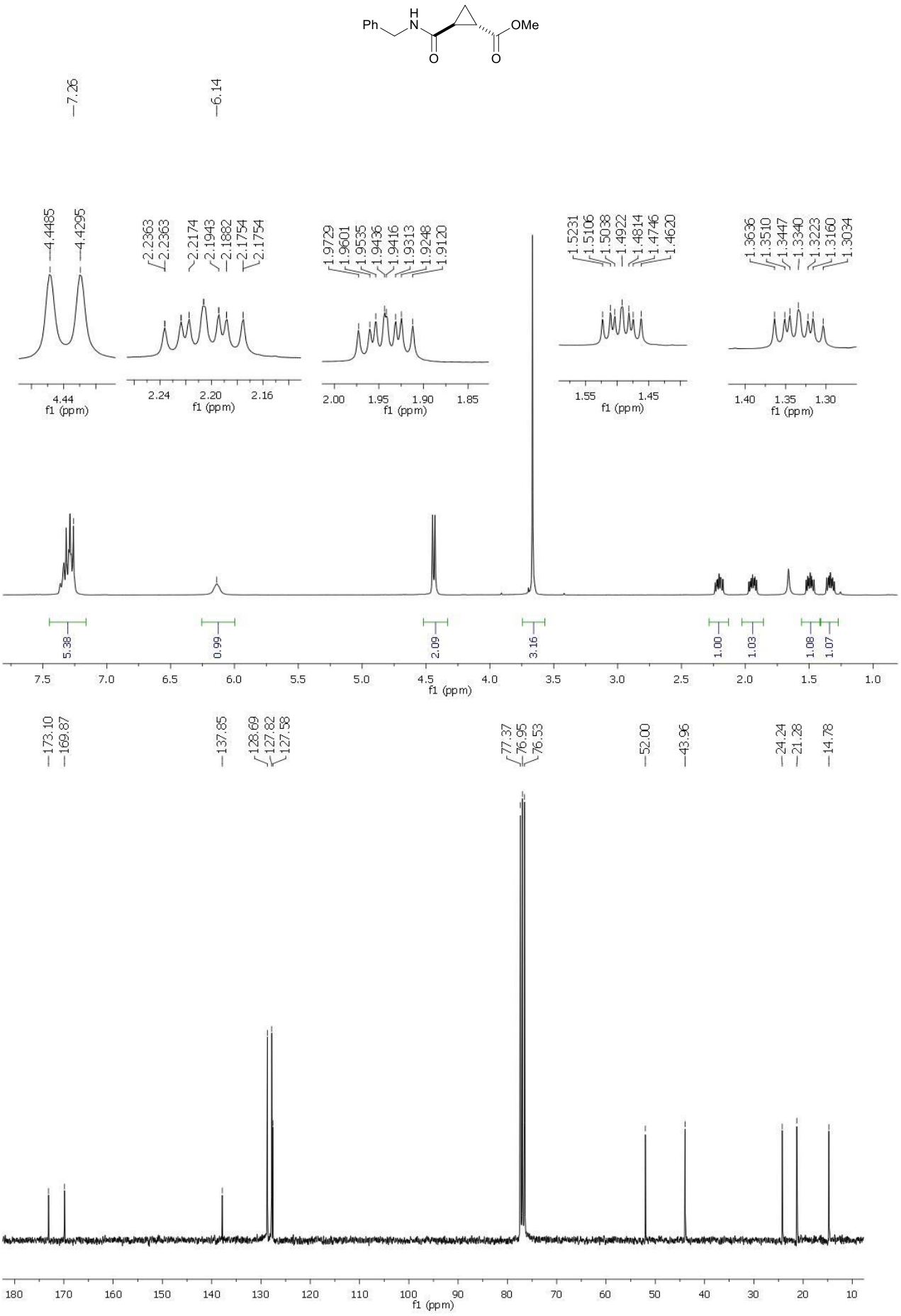
^{1}H and ^{13}C NMR spectra of **11c** in CD_3OD:



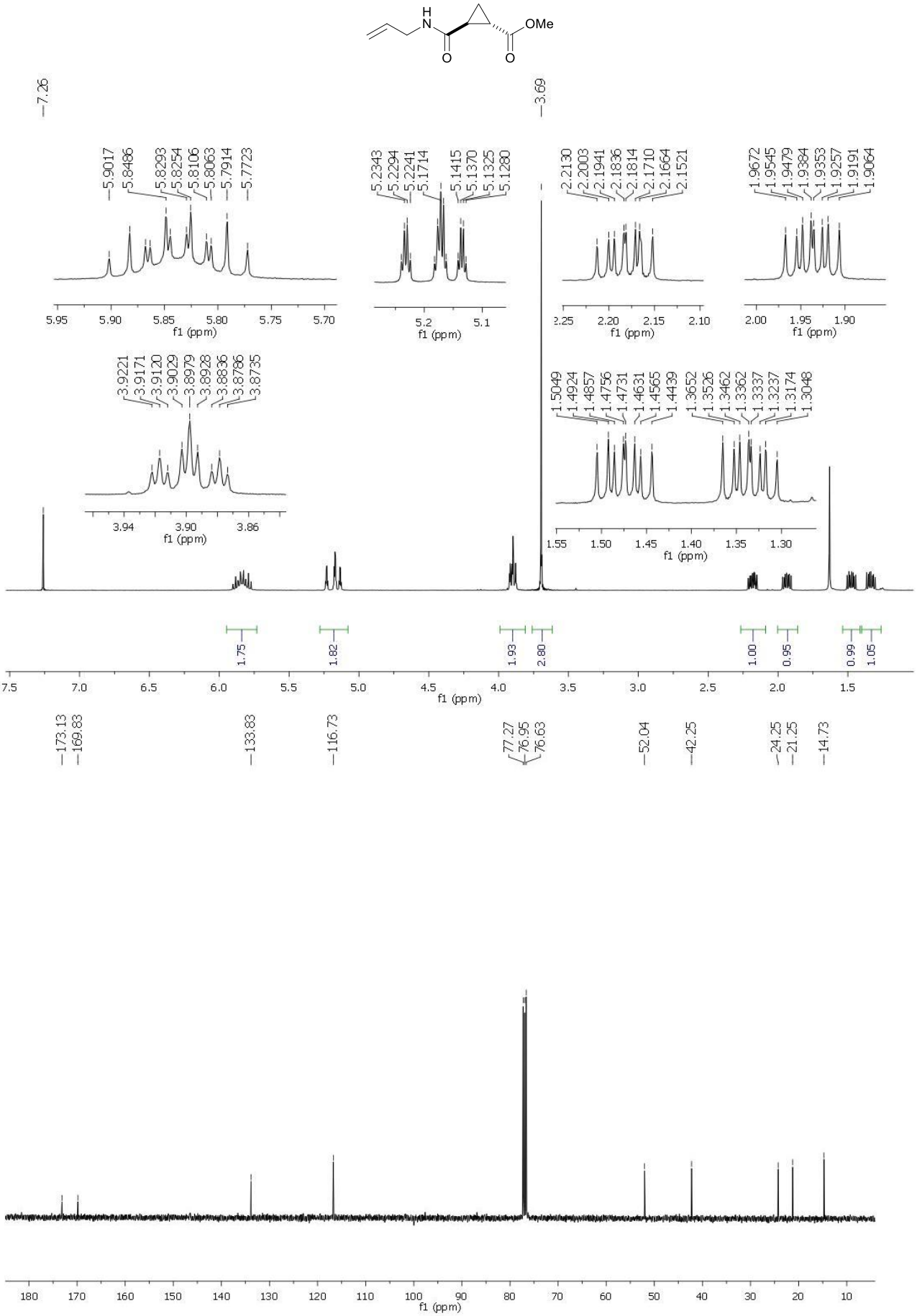




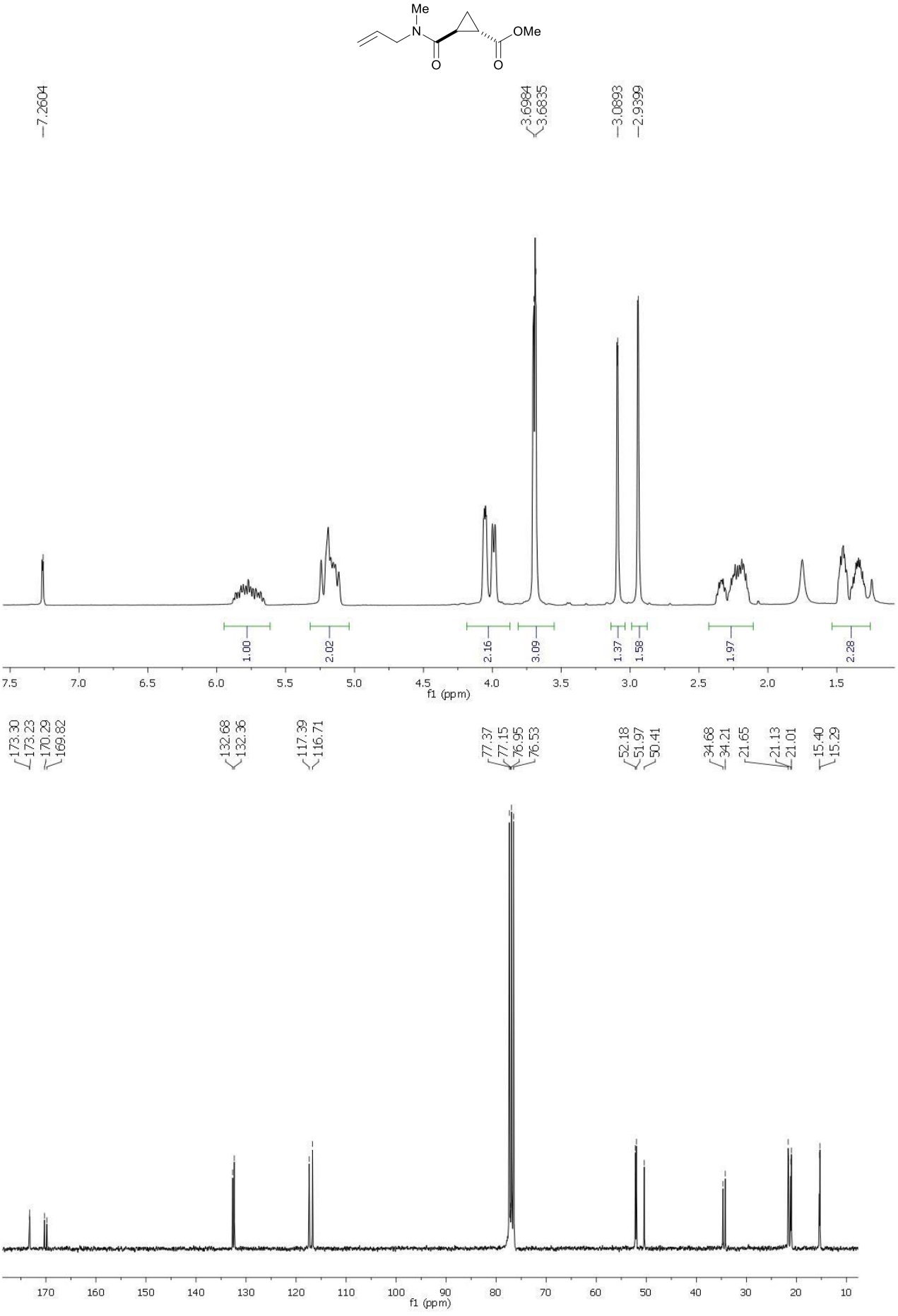
^{1}H and ^{13}C NMR spectra of (±)-**12a** in $CDCl_3$.



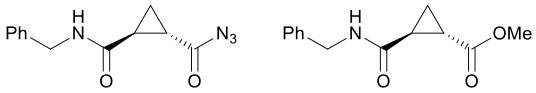
^{1}H and ^{13}C NMR spectra of (±)-**12b** in $CDCl_3$.



^{1}H and ^{13}C NMR spectra of (±)-**12c** in $CDCl_3$.

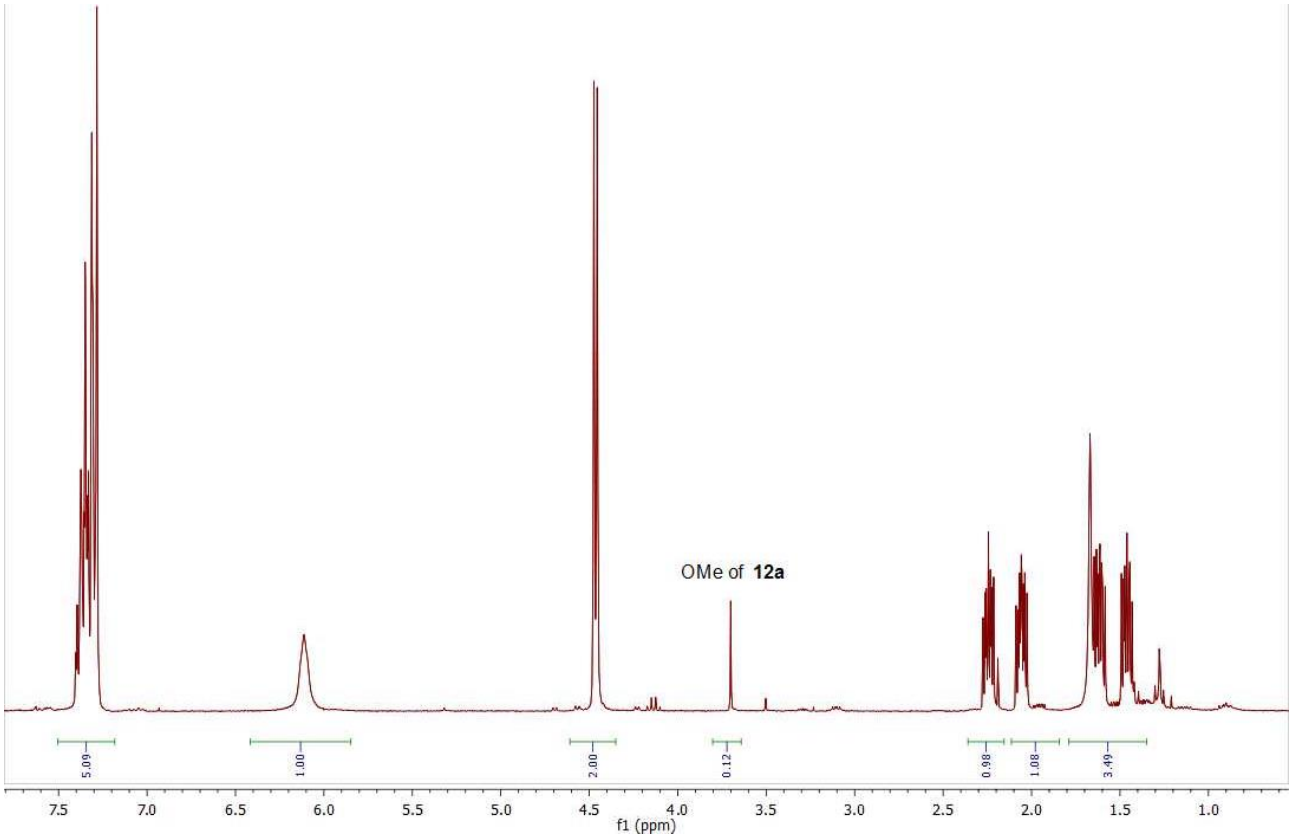


^{1}H NMR spectrum of the crude acyl azide (1*S*,2*S*)-**13a** in $CDCl_3$.

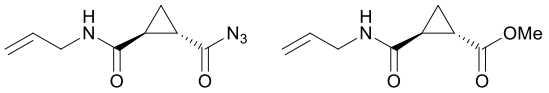


(1*S*,2*S*)-**13a** (1*S*,2*S*)-**12a**

The molar ratio **13a**:**12a** is 96:4.

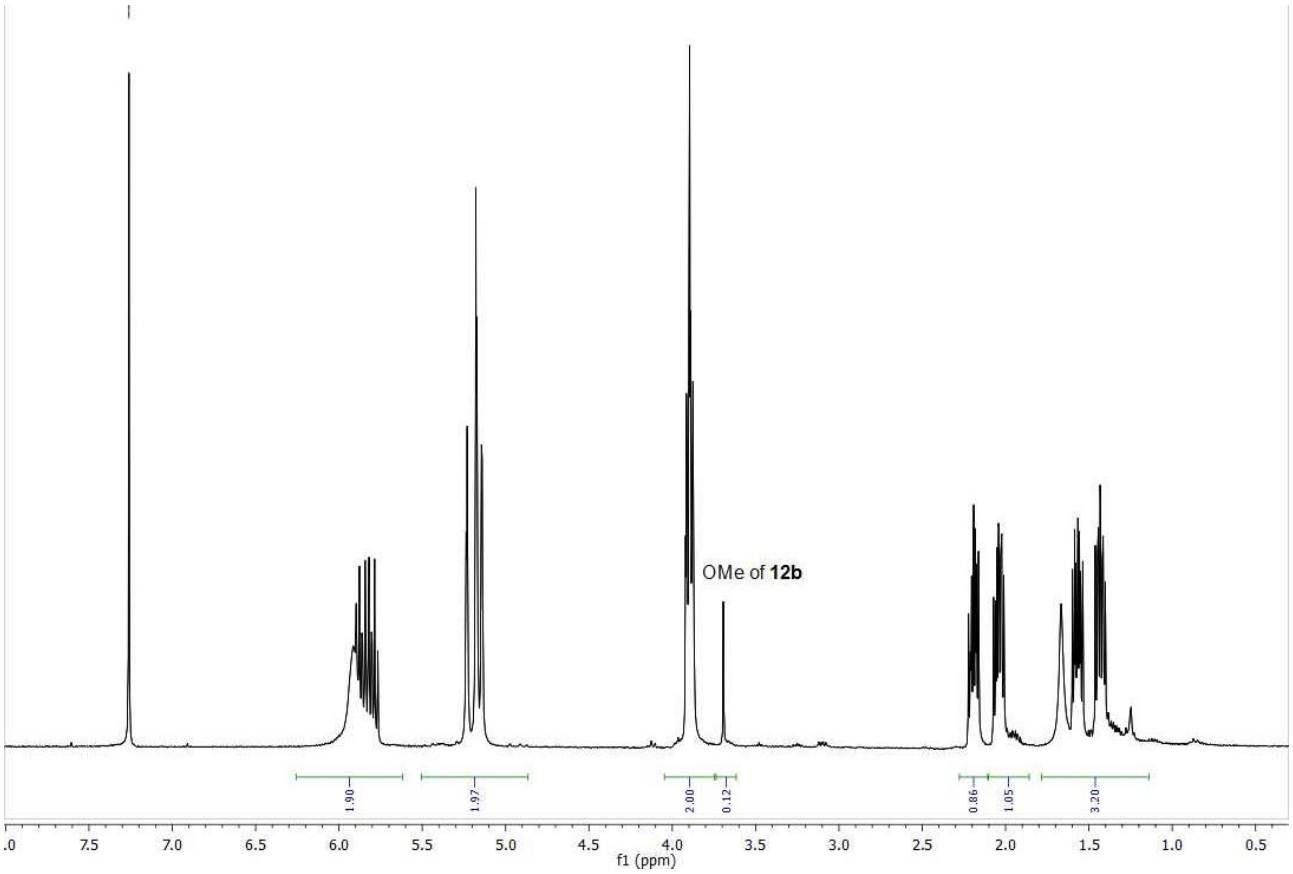


^{1}H NMR spectrum of the crude acyl azide (1*S*,2*S*)-**13b** in $CDCl_3$.

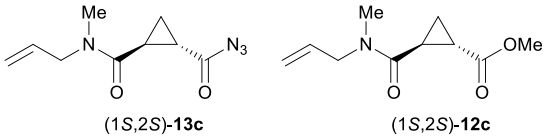


(1*S*,2*S*)-**13b** (1*S*,2*S*)-**12b**

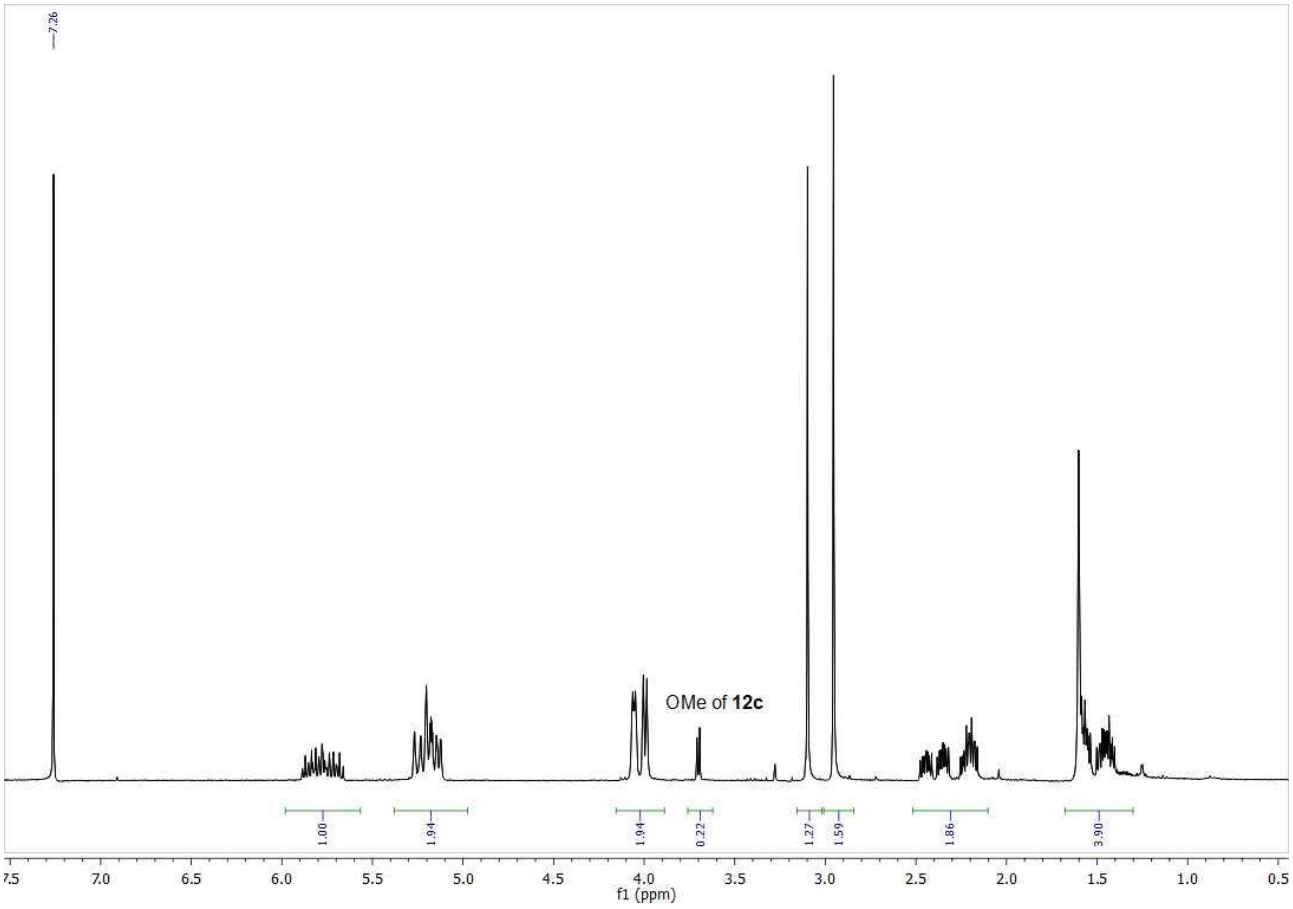
The molar ratio **13b**:**12b** is 96:4.



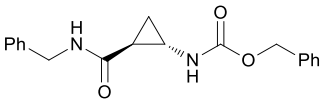
^{1}H NMR spectrum of the crude acyl azide (1*S*,2*S*)-**13c** in $CDCl_3$.

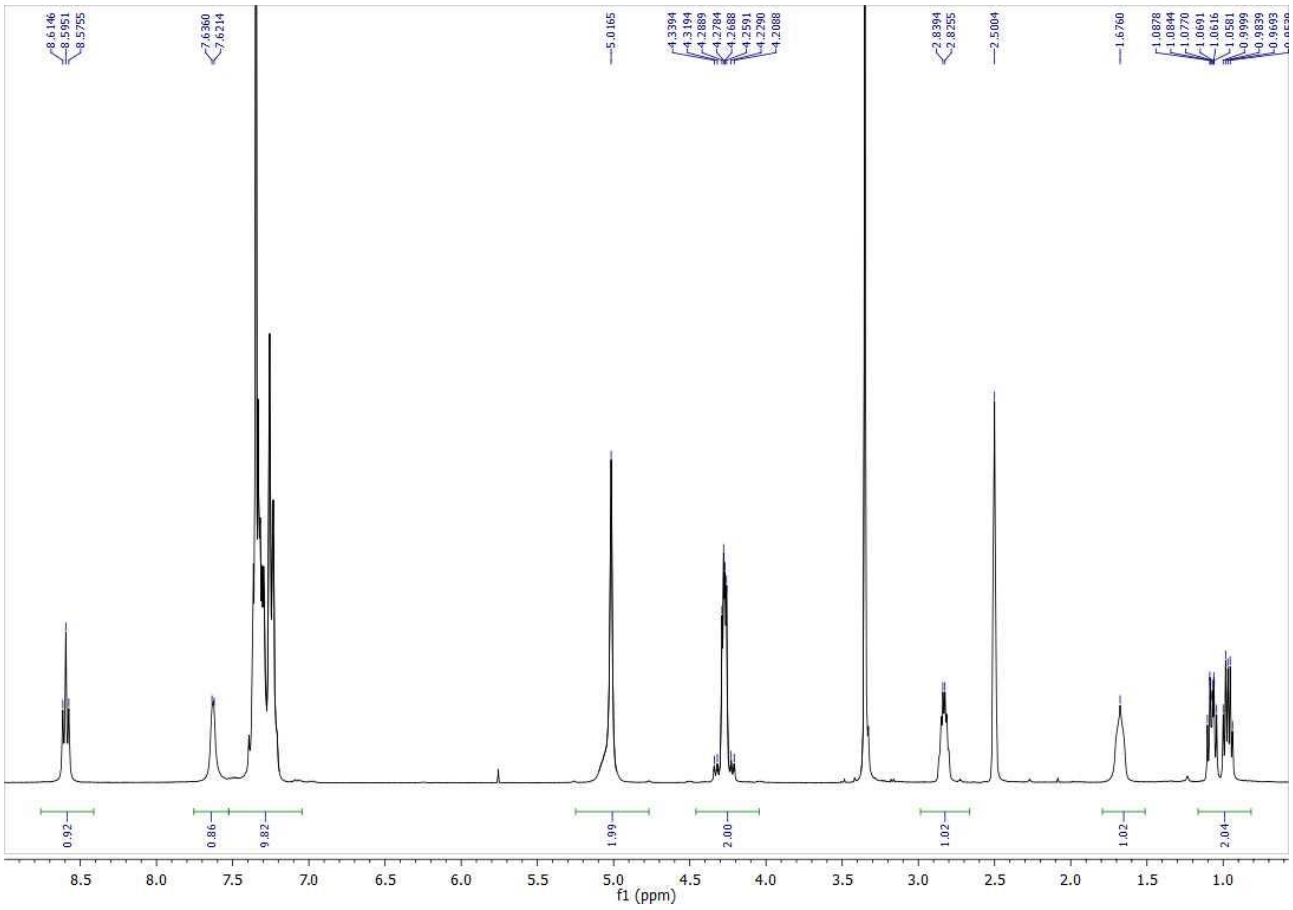


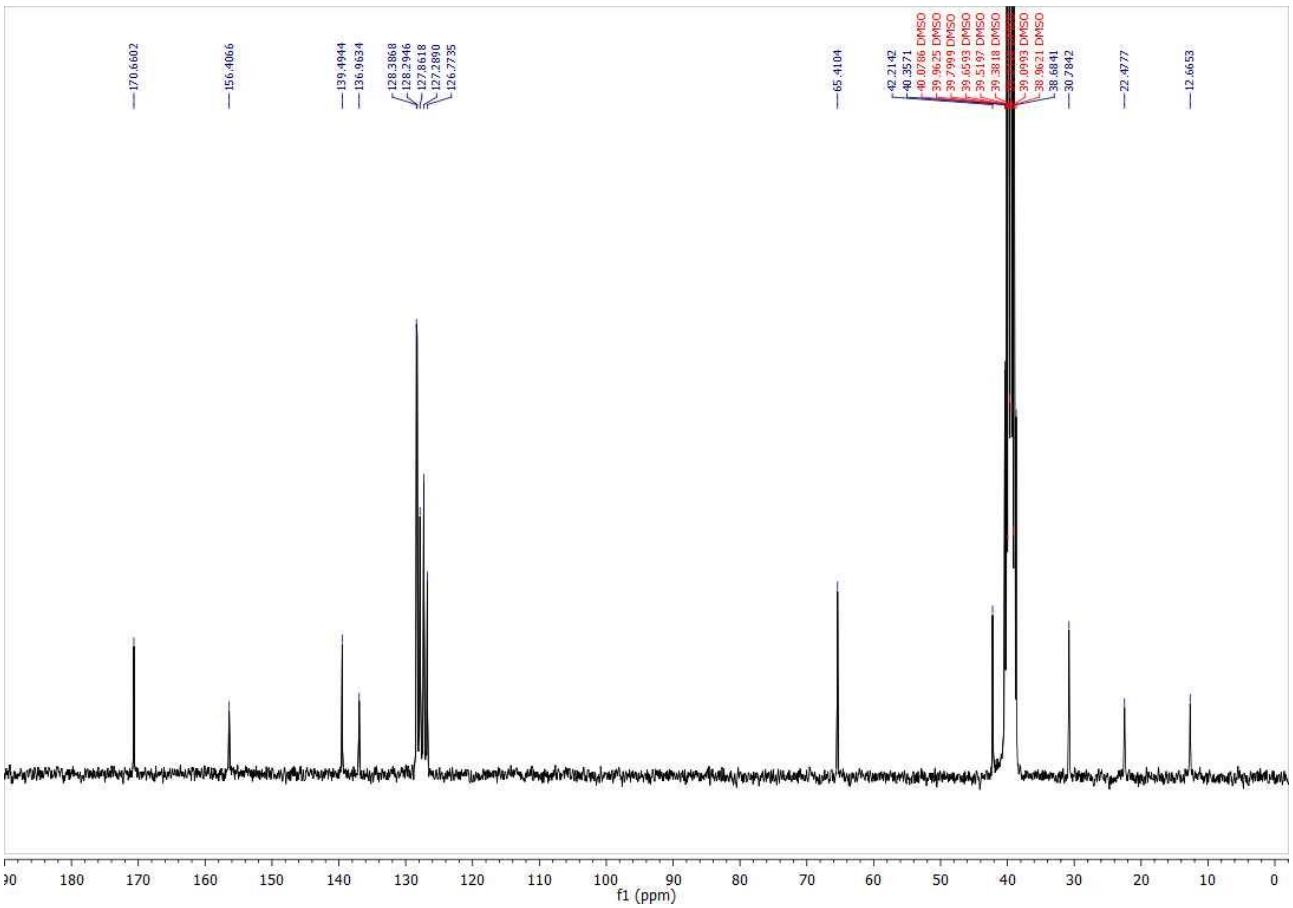
The molar ratio **13c**:**12c** is 93:7.

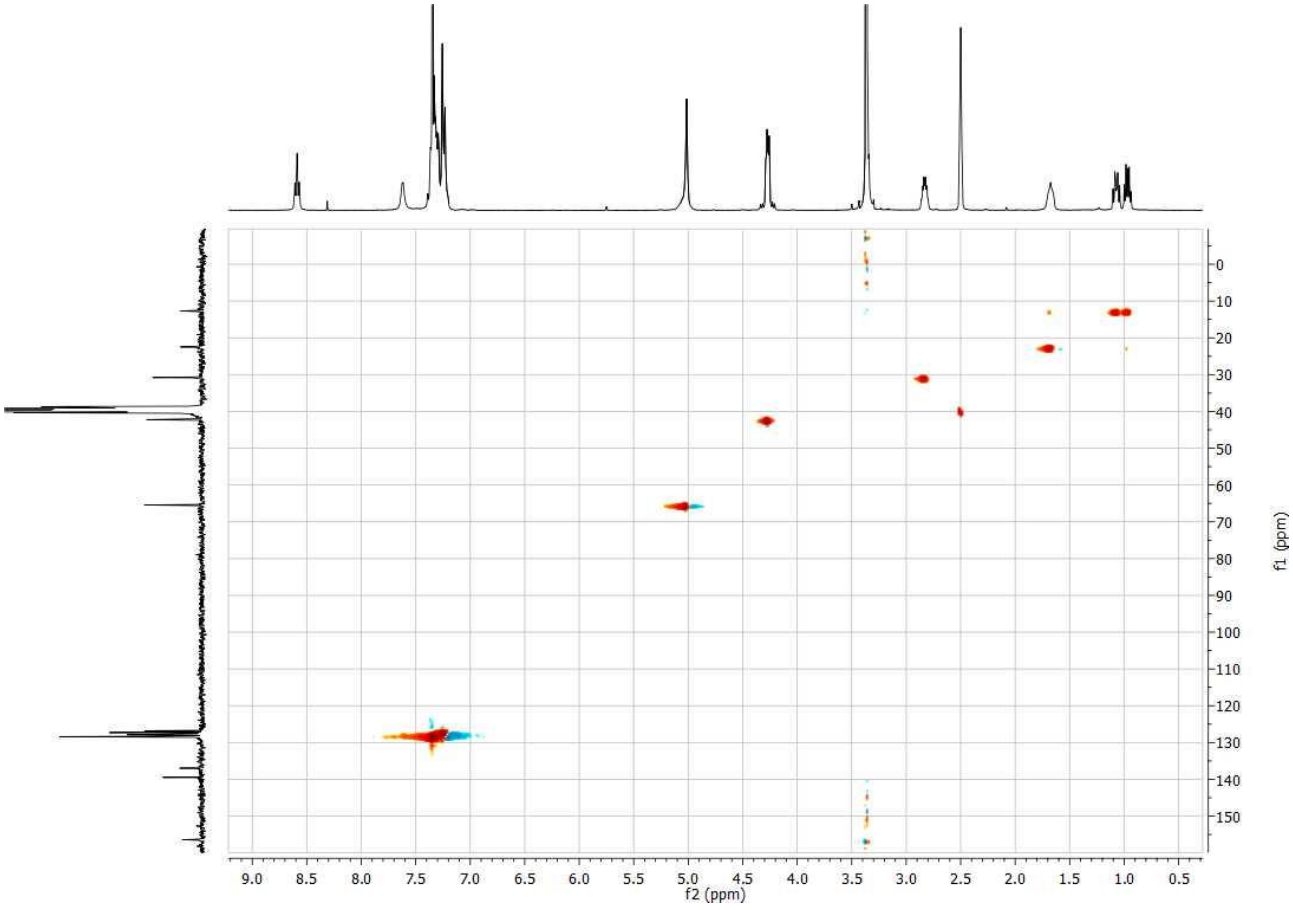


^{1}H-NMR, ^{13}C-NMR, and HSQC spectra of **14a** in DMSO-d_6:

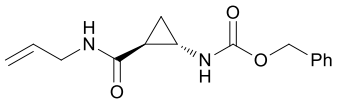


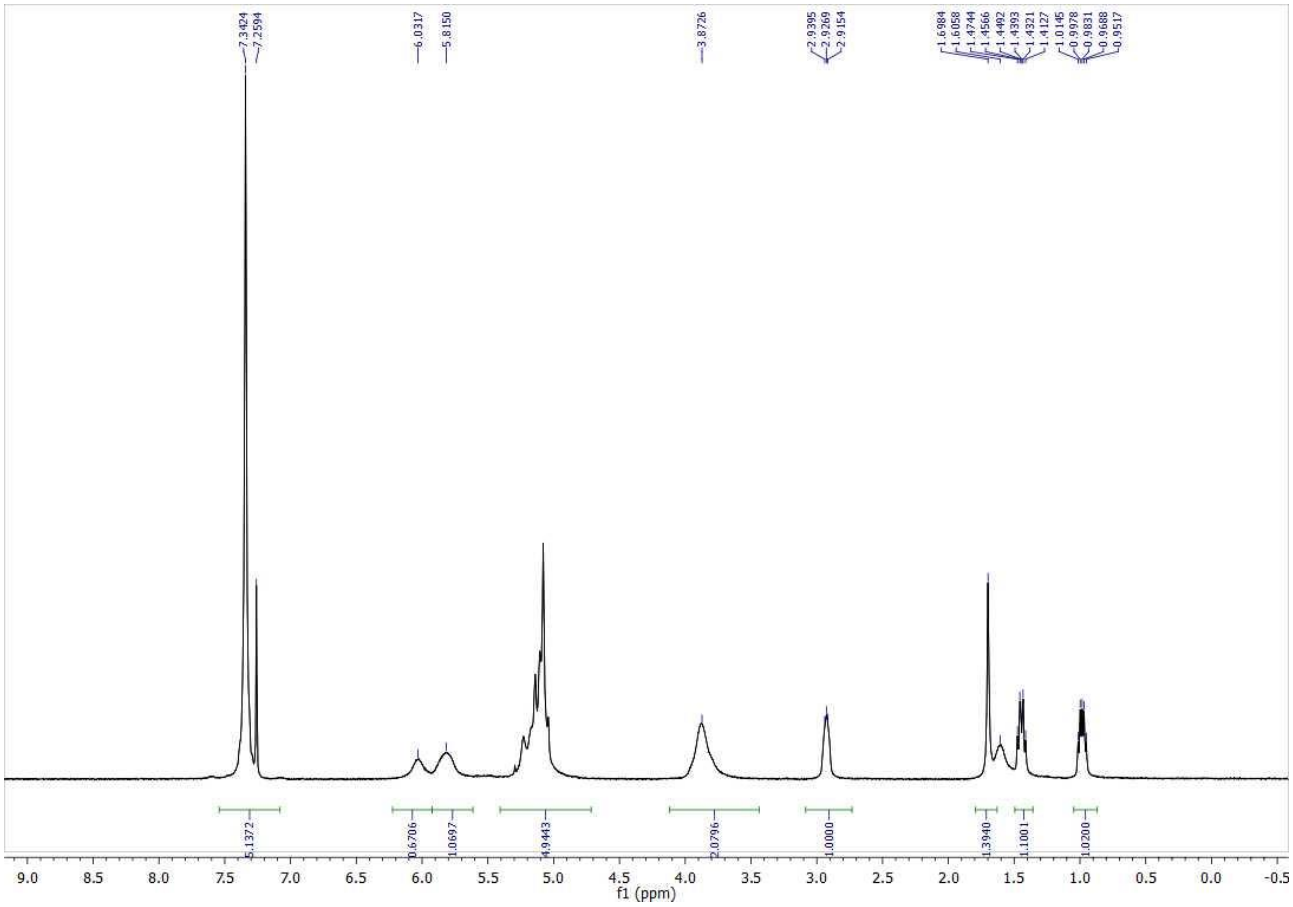


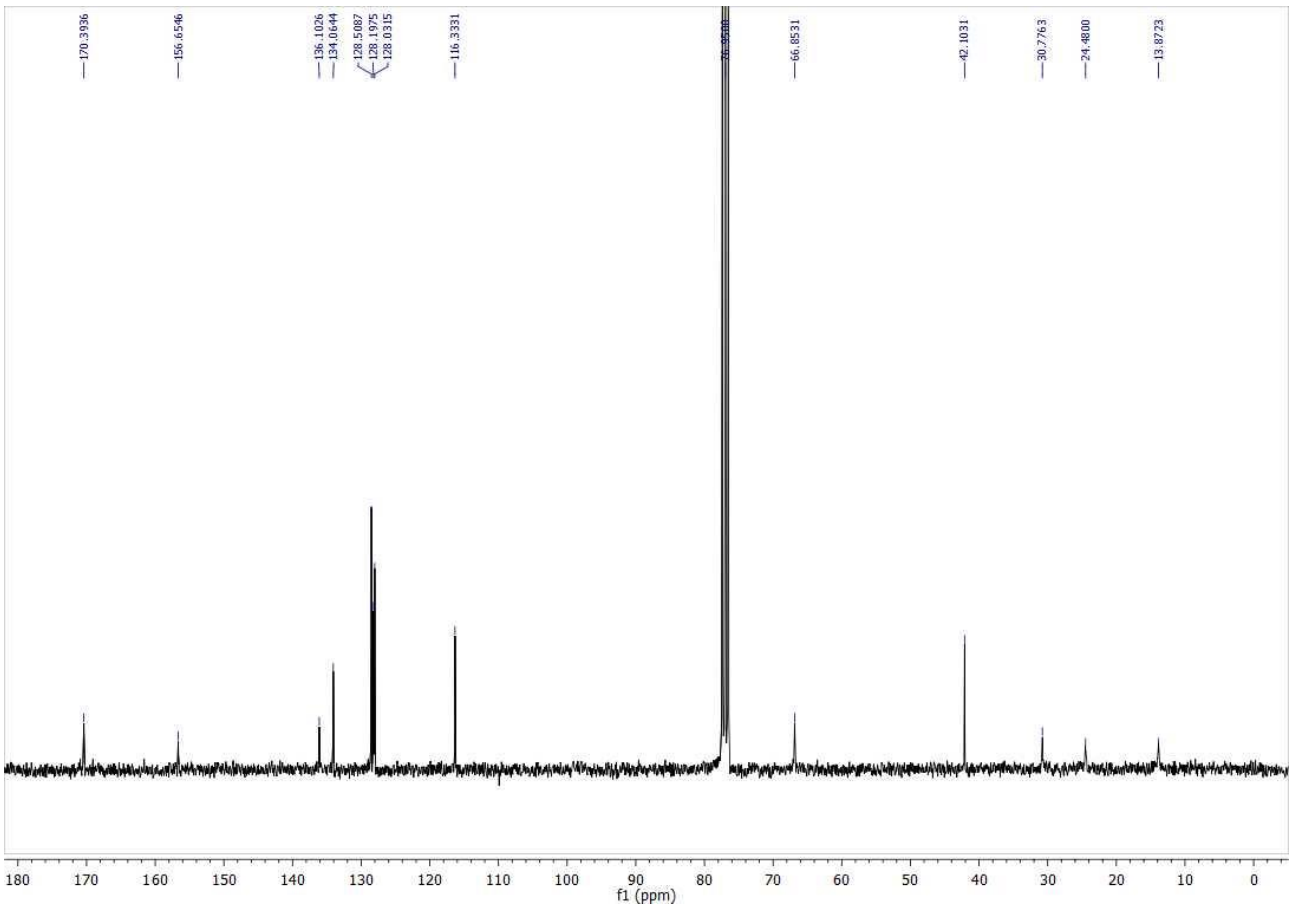

170.6602
156.4066
139.4944
136.9634
128.3868
128.2946
127.8618
127.2890
126.7735
65.4104
42.2142
40.3571
40.0786 DMSO
39.9625 DMSO
39.7999 DMSO
39.6593 DMSO
39.5197 DMSO
39.3818 DMSO
39.0993 DMSO
38.9621 DMSO
38.6841
30.7842
22.4777
12.6653
f1 (ppm)

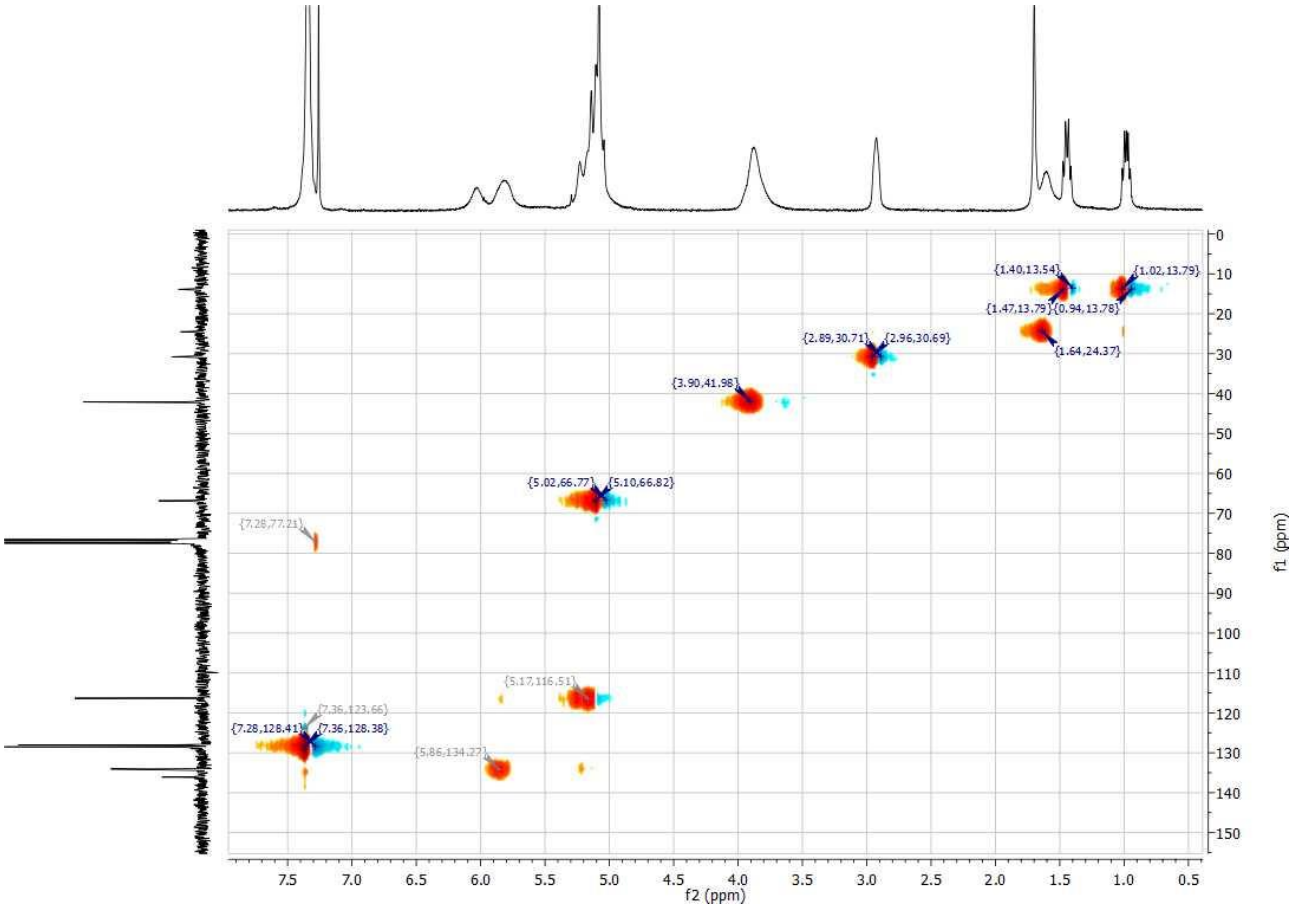

f2 (ppm)
f1 (ppm)

^{1}H-NMR, ^{13}C-NMR, and HSQC spectra of **14b** in $CDCl_3$:









^{1}H-NMR, ^{13}C-NMR, and HSQC spectra of **14c** in $CDCl_3$: