

Lewis acid mediated rearrangements of spiro[2.*n*]alkane-1,1-dicarboxylates (*n* = 2–5): an experimental evidence of stepwise 1,2-zwitter-ion formation

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1. Experimental section

1.1. General experimental details

All reagents and solvents were used of commercial grade without additional purification. All operations with Lewis acid were carried out under dry argon atmosphere. TLC analysis was performed on Merck Silica gel 60 TLC plates using aq. solution of KMnO_4 or phosphomolybdic acid in Pr^iOH as developer. For preparative chromatography, silica gel 60 (0.040–0.063 mm) was used. GC analysis was performed on Chromatec Crystal 5000.2 gas chromatographer (column J&W Scientific DB-5+, 30 m $\times$ 0.245 mm, 5%-phenyl-95%-dimethylpolysiloxane 0.25 μm , carrier gas – He, detector – FID). ^1H , ^{13}C NMR spectra were recorded on a Bruker AVANCE II 300 MHz (300.1 and 75.5 MHz respectively) in CDCl_3 , containing 0.05% Me_4Si as the internal standard. Monitoring of the reactions in NMR tube was made in CD_2Cl_2 solution containing 0.05% Me_4Si as the internal standard. Determinations of structures and stereochemistry of obtained compounds and assignments of ^1H and ^{13}C signals were made with the aid of 1D and 2D COSY, HSQC, HMBC spectra. High-resolution mass spectra were recorded on a Bruker Daltonics microTOF-Q II device (electrospray ionization).

1.2. General method for cyclopropanation of methylenecycloalkanes

Starting spiro[2.n]alkane-1,1-dicarboxylates (SADC) **1a-d** was synthesized from methylenecycloalkanes respectively. The $\text{Rh}_2(\text{esp})_2$ (0.1 mol.%) solution in dry CH_2Cl_2 (1 ml/mmol for diazo compound) was cooled to 0°C , and the corresponding methylenecycloalkane (10–15 mmol, 1.5 equiv.) was added. The mixture was stirred for 5 minutes, and then dimethyl diazomalonate (1 equiv.) was added in a single portion. After stirring the mixture for 4 hours at 0°C and overnight at room temperature, the solution was passed through SiO_2 and evaporated. The crude product was purified by vacuo distillation.

Dimethyl spiro[2.2]pentane-1,1-dicarboxylate 1a : 56%, colorless liquid, bp $107\text{--}108^\circ\text{C}/22$ Torr. ^1H NMR (300 MHz, CDCl_3) δ 0.75 – 1.13 (m, 4H, 2 CH_2), 1.92 (s, 2H, CH_2), 3.74 (s, 6H, 2 OCH_3). ^{13}C NMR (75 MHz, CDCl_3) δ 6.2 (2 CH_2), 21.3 (CH_2), 25.1 (C), 33.5 (C), 52.4 (CH_3), 169.7 (CO_2CH_3). The NMR spectra correspond to the literature data.^{S1}

Dimethyl spiro[2.3]hexane-1,1-dicarboxylate 1b : 59%, colorless liquid, bp $120\text{--}122^\circ\text{C}/15$ Torr. ^1H NMR (300 MHz, CDCl_3) δ : 1.64 (s, 2H, CH_2), 2.16 – 1.84 (m, 4H, 2 CH_2), 2.49 – 2.23 (m, 2H, CH_2), 3.69 (s, 6H, 2 OCH_3). ^{13}C NMR (75 MHz, CDCl_3) δ : 15.9 (CH_2), 27.5 (CH_2), 28.5 (2 CH_2), 36.8 (C), 37.5 (C), 52.1 (CO_2CH_3), 168.8 (2 CO_2CH_3). HRMS (ESI), m/z : 199.0969 $[\text{M}+\text{H}]^+$, (calc. for $\text{C}_{10}\text{H}_{14}\text{O}_4^+$, m/z : 199.0973).

Dimethyl spiro[2.4]heptane-1,1-dicarboxylate 1c : 65%, colorless liquid, bp $135\text{--}140^\circ\text{C}/10$ Torr. ^1H NMR (300 MHz, CDCl_3) δ : 1.58 (s, 2H, CH_2), 1.54 – 1.63 (m, 2H, CH_2), 1.67 – 1.90 (m, 6H, 3 CH_2), 3.74 (s, 6H, 2 OCH_3). ^{13}C NMR (75 MHz, CDCl_3) δ 25.7, 28.0, 32.8, 38.3, 40.1, 52.3, 169.5. The NMR spectra correspond to the literature data.^{S2}

Dimethyl spiro[2.5]octane-1,1-dicarboxylate 1d : 86%, colorless liquid, bp $52\text{--}55^\circ\text{C}/1.5 \times 10^{-2}$ Torr. ^1H NMR (300 MHz, CDCl_3) δ : 1.42 (s, 2H, CH_2), 1.39 – 1.53 (m, 5H, 2 CH_2 and H^a from CH_2), 1.54 – 1.69 (m, 5H, 2 CH_2 and H^b from CH_2), 3.73 (s, 6H, 2 OCH_3). ^{13}C NMR (75 MHz, CDCl_3) δ : 25.4 (CH_2), 25.6 (CH_2), 25.9 (CH_2), 31.5 (CH_2), 36.4, 39.6, 52.3 (CO_2CH_3), 169.1 (CO_2CH_3). The NMR spectra correspond to the literature data.^{S3}

1.3. General synthetic procedures and spectroscopic data for obtained products

All operations were performed under dry argon atmosphere. The Lewis acid (1.0–2.0 equiv.) was added in one portion to a solution of SADC **1a-d** (0.4–0.5 mmole, 1.0 equiv.) in dry CH_2Cl_2 (5–10 ml) at room temperature and the reaction mixture was stirred for 3 hours. After that, 8–12 ml of aqueous solution of HCl (10%) was added and the reaction mixture was extracted with CH_2Cl_2 (3 $\times$ 15 ml). The organic layer was dried over MgSO_4 and the solvent was removed *in vacuo*. The residue was analyzed by ^1H NMR spectroscopy using 1,4-dinitrobenzene as an internal standard and the yields are presented in Table 1 of the Main Article. For the compound characterizations, crude product mixtures were purified by column chromatography on silica gel (benzene to benzene-EtOAc (10:1)) followed by additional purification on TLC plates (20 $\times$ 20 cm) eluting with benzene. These resulted pure products **2–8**, either in isomerically pure form or as mixtures of 2–3 isomers, but however with substantial losses on a preparative TLC stage. In certain cases, lactones **S1–S3** were detected. However, their quantities were irreproducible and believed to be a result of traces of moisture evidently introduced during the reactions set up.

Dimethyl [(1-chloromethyl)cyclopropyl]malonate 2 : colorless liquid. ^1H NMR (300 MHz, CDCl_3) δ : 0.76–0.87 (m, 4H, 2 CH_2), 3.52 (s, 1H, CH), 3.70 (s, 2H, CH_2Cl), 3.75 (s, 6H, 2 CO_2CH_3). ^{13}C NMR (75 MHz, CDCl_3) δ : 12.6 (2 CH_2), 21.9 (C), 52.1 (CH_2Cl), 52.5 (2 CO_2CH_3), 53.9 (CH), 168.3 (2 CO_2CH_3). HRMS (ESI), m/z : 243.0396 [$\text{M}+\text{Na}$] $^+$, (calc. for $\text{C}_9\text{H}_{13}\text{ClO}_4\text{Na}^+$, m/z : 243.0395).

Dimethyl [(1-chlorocyclobutyl)methyl]malonate 3b : colorless liquid. ^1H NMR (300 MHz, CDCl_3) δ : 2.04–2.13 (m, 2H, CH_2), 2.27–2.50 (m, 4H, 2 CH_2), 2.58 (d, 2H, CH_2CH , 3J 6.4 Hz), 3.68 (t, 2H, CH_2CH , 3J 6.4 Hz), 3.76 (br.s, 6H, 2 CO_2CH_3). ^{13}C NMR (75 MHz, CDCl_3) δ : 15.8 (CH_2), 28.4 (2 CH_2), 40.8 (CH_2CH), 48.5 (CH_2CH), 52.1 (2 CO_2CH_3), 70.3 (C-Cl), 168.7 (2 CO_2Me). HRMS (ESI), m/z : 235.0732 [$\text{M}+\text{H}$] $^+$, (calc. for $\text{C}_{10}\text{H}_{15}\text{ClO}_4\text{H}^+$, m/z : 235.0742).

Dimethyl [(1-chlorocyclopentyl)methyl]malonate 3c : colorless liquid. ^1H NMR (300 MHz, CDCl_3) δ : 1.9–1.96 (m, 8H, 4 CH_2), 2.70 (d, 2H, CH_2CH , 3J 7.0 Hz), 3.76 (s, 6H, 2 CO_2CH_3), 3.87 (t, 1H, CH_2CH , 3J 7.0 Hz). ^{13}C NMR (75 MHz, CDCl_3) δ : 22.8 (2 CH_2), 30.4 (CH_2CH), 42.2 (2 CH_2), 49.4 (CH_2CH), 52.5 (2 CO_2CH_3), 80.9 (C-Cl), 169.9 (2 CO_2Me). HRMS (ESI), m/z : 213.1121 [$\text{M}+\text{H}$] $^+$, (calc. for $\text{C}_{11}\text{H}_{16}\text{O}_4\text{H}^+$, m/z : 213.1131).

Dimethyl [(1-chlorocyclohexyl)methyl]malonate 3d : colorless liquid. ^1H NMR (300 MHz, CDCl_3) δ : 1.18–1.32 (m, 2H, CH_2), 1.52–1.69 (m, 4H, 2 CH_2), 1.77–1.94 (m, 4H, 2 CH_2), 2.47 (d, 2H, CH_2CH , 3J 6.0 Hz), 3.75 (br.s, 6H, 2 CO_2CH_3), 3.80–3.84 (m, 1H, CH_2CH). ^{13}C NMR (75 MHz, CDCl_3) δ : 21.9 (2 CH_2), 25.0 (2 CH_2), 27.8 (CH_2), 43.6 (CH_2CH), 47.7 (CH_2CH), 52.7 (2 CO_2CH_3), 73.9 (C-Cl), 169.5 (2 CO_2Me). HRMS (ESI), m/z : 285.0845 [$\text{M}+\text{Na}$] $^+$, (calc. for $\text{C}_{12}\text{H}_{19}\text{ClO}_4\text{Na}^+$, m/z : 285.0864).

Dimethyl (cyclopentylmethylene)malonate 4c : colorless liquid. ^1H NMR (300 MHz, CDCl_3) δ : 1.33–1.45 (m, 4H, 2 CH_2), 1.56–1.78 (m, 4H, 2 CH_2), 2.76–2.85 (m, 1H, $\text{CH}=\text{CH}$ =), 3.78 (s, 3H, CO_2CH_3), 3.83 (s, 3H, CO_2CH_3), 6.94 (d, 1H, $\text{CH}=\text{CH}$ =, 3J 10.5 Hz). ^{13}C NMR (75 MHz, CDCl_3) δ : 25.7 (2 CH_2), 33.2 (2 CH_2), 40.5 ($\text{CH}=\text{CH}$ =), 52.2 (CO_2CH_3), 52.3 (CO_2CH_3), 126.3 ($\text{CH}=\text{C}$ -), 154.9 ($\text{CH}=\text{C}$ -), 164.6 (CO_2Me), 166.2 (CO_2Me). HRMS (ESI), m/z : 213.1121 [$\text{M}+\text{H}$] $^+$, (calc. for $\text{C}_{11}\text{H}_{16}\text{O}_4\text{H}^+$, m/z : 213.1131).

Dimethyl (cyclohexylmethylene)malonate 4d : colorless liquid. ^1H NMR (300 MHz, CDCl_3) δ : 1.11–1.36 (m, 4H, 2 CH_2), 1.64–1.78 (m, 6H, 3 CH_2), 2.33–2.45 (m, 1H, $\text{CH}=\text{CH}$ =), 3.77 (s, 3H, CO_2CH_3), 3.83 (s, 3H, CO_2CH_3), 6.85 (d, 1H, $\text{CH}=\text{CH}$ =, 3J 10.5 Hz). ^{13}C NMR (75 MHz, CDCl_3) δ : 25.2 (CH_2), 25.6 (2 CH_2), 31.2 (2 CH_2), 39.2 ($\text{CH}=\text{CH}$ =), 52.3 (CO_2CH_3), 52.4 (CO_2CH_3), 126.1 ($\text{CH}=\text{C}$ -), 154.7 ($\text{CH}=\text{CH}$ =), 164.7 (CO_2Me), 166.2 (CO_2Me). HRMS (ESI), m/z : 227.1276 [$\text{M}+\text{H}$] $^+$, (calc. for $\text{C}_{12}\text{H}_{18}\text{O}_4\text{H}^+$, m/z : 227.1278).

Dimethyl (cyclobutylidene)malonate 5a : colorless liquid. ^1H NMR (300 MHz, CDCl_3) δ : 2.13 (p, 2H, CH_2 , 3J 7.9 Hz), 3.15 (t, 4H, 2 CH_2 , 3J 7.9 Hz), 3.77 (s, 6H, 2 CO_2CH_3). ^{13}C NMR (75 MHz, CDCl_3) δ : 17.3 (CH_2), 33.9 (2 CH_2), 51.7 (2 CO_2CH_3), 119.4 ($\text{C}(\text{CO}_2\text{Me})_2$), 164.6 (C=C), 176.0 (2 CO_2CH_3). HRMS (ESI), m/z : 207.0630 [$\text{M}+\text{Na}$] $^+$, (calc. for $\text{C}_9\text{H}_{12}\text{O}_4\text{Na}^+$, m/z : 207.0628).

Dimethyl (cyclopentylidene)malonate 5b : colorless liquid. ^1H NMR (300 MHz, CDCl_3) δ : 1.64–1.69 (m, 4H, 2 CH_2), 2.58–2.63 (m, 4H, 2 CH_2), 3.70 (s, 6H, 2 CO_2CH_3). ^{13}C NMR (75 MHz, CDCl_3) δ : 25.9 (2 CH_2), 34.4 (2 CH_2), 51.8 (2 CO_2CH_3), 119.9 ($\text{C}(\text{CH}_2)_2$), 165.9 (C=), 170.3 (2 CO_2Me). HRMS (ESI), m/z : 199.0973 [$\text{M}+\text{H}$] $^+$, (calc. for $\text{C}_{10}\text{H}_{14}\text{O}_4\text{H}^+$, m/z : 199.0973).

Dimethyl -(3-chloro-2-methylenepropyl)malonate 6. ^1H NMR (300 MHz, CDCl_3) δ : 5.20 (s, 1H, $\text{C}=\text{CH}^a$), 5.01 (s, 1H, $\text{C}=\text{CH}^b$), 4.0 (br s, 2H, CH_2), 3.74 (s, 6H, 2 CO_2CH_3), 3.67 (t, $J=7.7$ Hz, 1H, CH), 2.80 (d, $J=7.7$ Hz, 2H, CH_2); ^{13}C NMR (75 MHz, CDCl_3) δ : 169.06 (2 CO_2CH_3), 141.39 (C=C), 116.68 (C= CH_2), 52.67 (2 CH_3), 50.14 (CH), 47.45 (CH_2), 32.03 (CH_2). The NMR spectra correspond to the literature data.^{S4}

Dimethyl (4-chloro-2-methylenebutyl)malonate 7 : colorless liquid. ^1H NMR (300 MHz, CDCl_3) δ : 2.50 (t, 2H, $\text{CH}_2\text{CH}_2\text{Cl}$, 3J 7.1 Hz), 2.66 (d, 2H, CH_2CH , 3J 7.8 Hz), 3.59–3.65 (m, 3H, $\text{CH}_2\text{CH}_2\text{Cl}$, CH_2CH), 3.74 (br.s, 6H, 2 CO_2CH_3), 4.91 (br.s, 2H, $=\text{CH}_2$). ^{13}C NMR (75 MHz, CDCl_3) δ : 34.5 (CH_2CH), 38.9 ($\text{CH}_2\text{CH}_2\text{Cl}$), 42.3 (CH_2CH), 50.3 (CH_2Cl), 52.7 (2 CO_2CH_3), 113.9 (C= CH_2), 141.7 (C= CH_2), 169.2 (2 CO_2Me). HRMS (ESI), m/z : 235.0736 [$\text{M}+\text{H}$] $^+$, (calc. for $\text{C}_{10}\text{H}_{15}\text{ClO}_4\text{H}^+$, m/z : 235.0732).

Dimethyl (cyclopent-1-en-1-ylmethyl)malonate 8c : colorless liquid. ^1H NMR (300 MHz, CDCl_3) δ : 1.80–1.90 (m, 2H, CH_2), 2.22–2.28 (m, 4H, 2 CH_2), 2.69 (d, 2H, CH_2CH , 3J 7.7 Hz), 3.61 (t, 1H, CH_2CH , 3J 7.7 Hz), 3.73 (br.s, 6H, 2 CO_2CH_3), 5.39 (br.s, 1H, $\text{CH}=\text{C}$). ^{13}C NMR (75 MHz, CDCl_3) δ : 23.34(CH_2), 30.4 (CH_2), 32.5 (CH_2), 34.9 (CH_2), 50.6 (CH_2), 52.5 (2 CO_2CH_3), 125.9 ($\text{CH}=\text{C}$ -), 140.4 ($\text{CH}=\text{C}$ -), 169.7 (2 CO_2Me). HRMS (ESI), m/z : 213.1121 $[\text{M}+\text{H}]^+$, (calc. for $\text{C}_{11}\text{H}_{16}\text{O}_4\text{H}^+$, m/z : 213.1131).

Dimethyl 2-(cyclohex-1-en-1-ylmethyl)malonate 8d : colorless liquid. ^1H NMR (300 MHz, CDCl_3) δ : 1.11–1.36 (m, 2H, CH_2), 1.90–1.94 (m, 4H, 2 CH_2), 2.33–2.45 (m, 2H, CH_2), 2.54 (d, 2H, CH_2CH , 3J 8.0 Hz), 3.58 (t, 1H, CH_2CH , 3J 8.0 Hz), 3.72 (br.s, 6H, 2 CO_2CH_3), 5.39 (br.s, 1H, $\text{CH}=\text{C}$). ^{13}C NMR (75 MHz, CDCl_3) δ : 22.3 (CH_2), 22.9 (CH_2), 25.3 (CH_2), 28.0 (CH_2), 37.1 (CH_2CH), 50.5 (CH_2CH), 52.5 (2 CO_2CH_3), 123.9 ($\text{CH}=\text{C}$ -), 133.6 ($\text{CH}=\text{C}$ -), 169.6 (2 CO_2Me). HRMS (ESI), m/z : 227.1276 $[\text{M}+\text{H}]^+$, (calc. for $\text{C}_{12}\text{H}_{18}\text{O}_4\text{H}^+$, m/z : 227.1278).

Methyl 6-oxo-5-oxaspiro[3.4]octane-7-carboxylate S1 : colorless liquid. ^1H NMR (300 MHz, CDCl_3) δ : 1.64–1.77 (m, 1H, CH_2), 1.83–1.95 (m, 1H, CH_2), 2.12–2.29 (m, 2H, 2 CH_2), 2.42–2.73 (m, 4H, 2 CH_2 , CH_2CH), 3.63 (t, 1H, CH_2CH , 3J 8.9 Hz), 3.80 (s, 3H, CO_2CH_3). ^{13}C NMR (75 MHz, CDCl_3) δ : 12.1 (CH_2), 34.6 (CH_2), 34.8 (CH_2), 37.1 (CH_2CH), 46.9 (CH_2CH), 53.1 (CO_2CH_3), 84.6 (C_{spiro}), 168.2 (CO_2Me), 171.1 ($\text{C}=\text{O}$). HRMS (ESI), m/z : 223.0373 $[\text{M}+\text{K}]^+$, (calc. for $\text{C}_9\text{H}_{12}\text{O}_4\text{K}^+$, m/z : 223.0367).

Methyl 2-oxo-1-oxaspiro[4.4]nonane-3-carboxylate S2 : colorless liquid. ^1H NMR (300 MHz, CDCl_3) δ : 1.61–2.1 (m, 8H, 4 CH_2), 2.42 (dd, 1H, CH_2CH , 2J 13.0 Hz, 3J 9.3 Hz), 2.70 (dd, 1H, CH_2CH , 2J 13.0 Hz, 3J 9.3 Hz), 3.69–3.76 (m, 1H, CH_2CH), 3.81 (s, 3H, CO_2CH_3). ^{13}C NMR (75 MHz, CDCl_3) δ : 23.6 (CH_2), 23.9 (CH_2), 36.0 (CH_2CH), 47.8 (CH_2CH), 53.1 (CO_2CH_3), 94.1 (C_{spiro}), 168.4 (CO_2Me), 171.3 ($\text{C}=\text{O}$). HRMS (ESI), m/z : 221.0782 $[\text{M}+\text{Na}]^+$, (calc. for $\text{C}_{10}\text{H}_{14}\text{O}_4\text{Na}^+$, m/z : 221.0784).

Methyl 2-oxo-1-oxaspiro[4.5]decane-3-carboxylate S3 : colorless liquid. ^1H NMR (300 MHz, CDCl_3) δ : 1.32–1.90 (m, 10H, 5 CH_2), 2.31 (dd, 1H, CH_2CH , 2J 13.1 Hz, 3J 9.9 Hz), 2.44 (dd, 1H, CH_2CH , 2J 13.1 Hz, 3J 9.9 Hz), 3.71 (t, 1H, CH_2CH , 3J 9.9 Hz), 3.81 (s, 3H, CO_2CH_3). ^{13}C NMR (75 MHz, CDCl_3) δ : 22.6 (CH_2), 24.8 (CH_2), 36.7 (CH_2CH), 36.8 (CH_2), 37.6 (CH_2), 46.8 (CH_2CH), 53.1 (CO_2CH_3), 85.6 (C_{spiro}), 168.6 (CO_2Me), 171.2 ($\text{C}=\text{O}$). HRMS (ESI), m/z : 213.1123 $[\text{M}+\text{H}]^+$, (calc. for $\text{C}_{11}\text{H}_{16}\text{O}_4\text{H}^+$, m/z : 213.1121).

2.1 GC monitoring for 1a rearrangement on TiCl₄

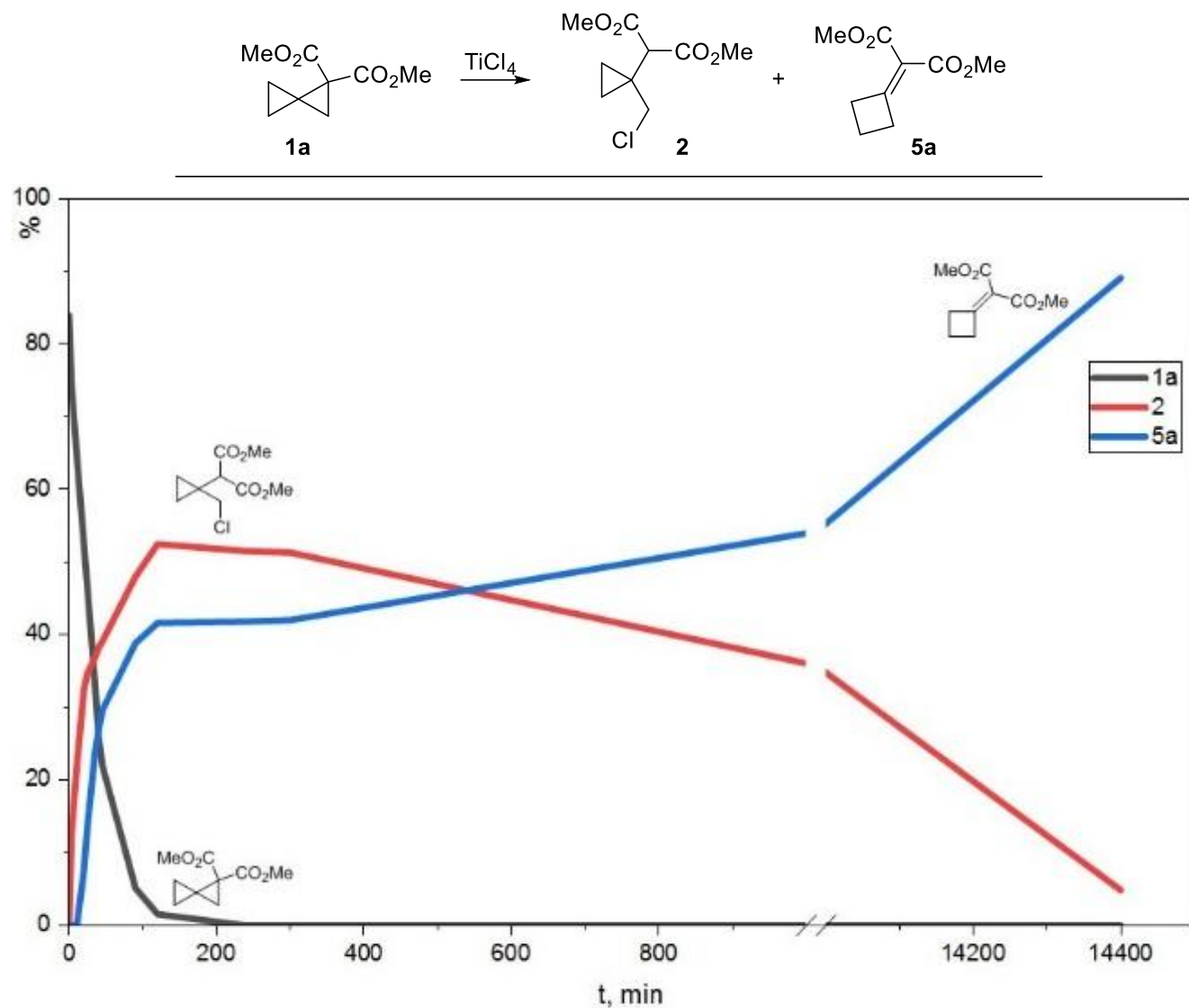
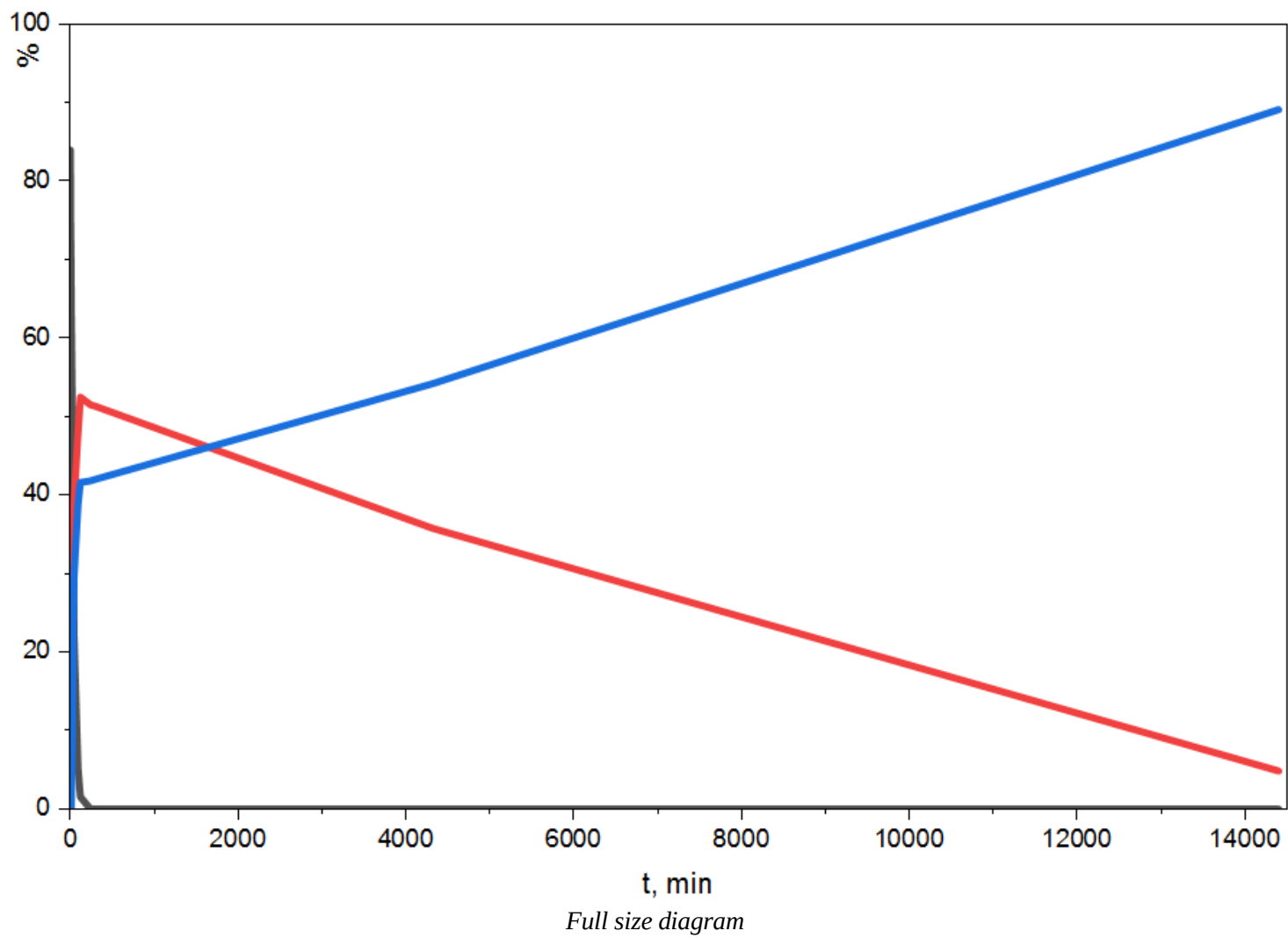
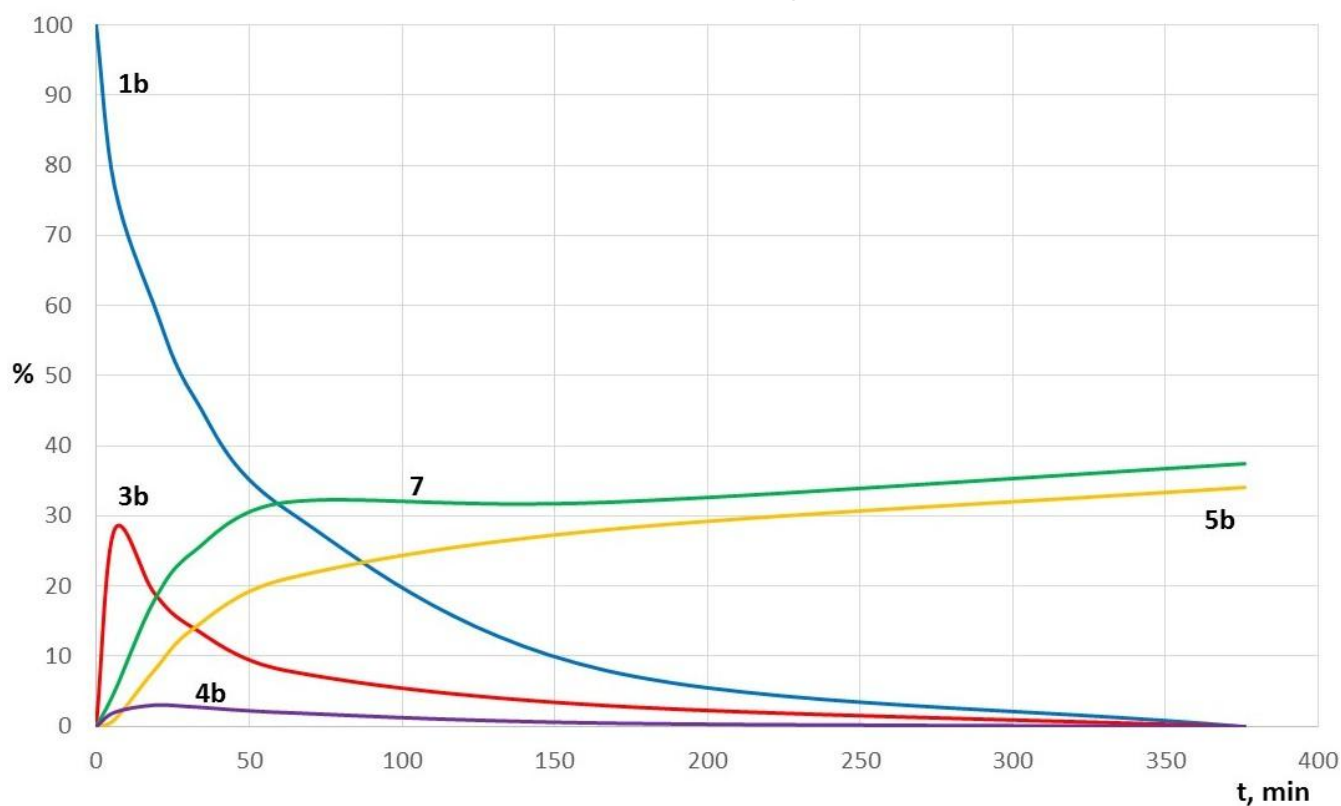
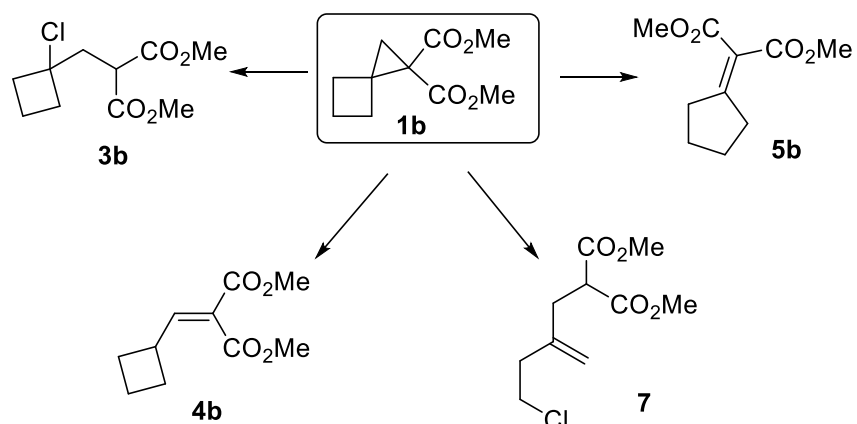


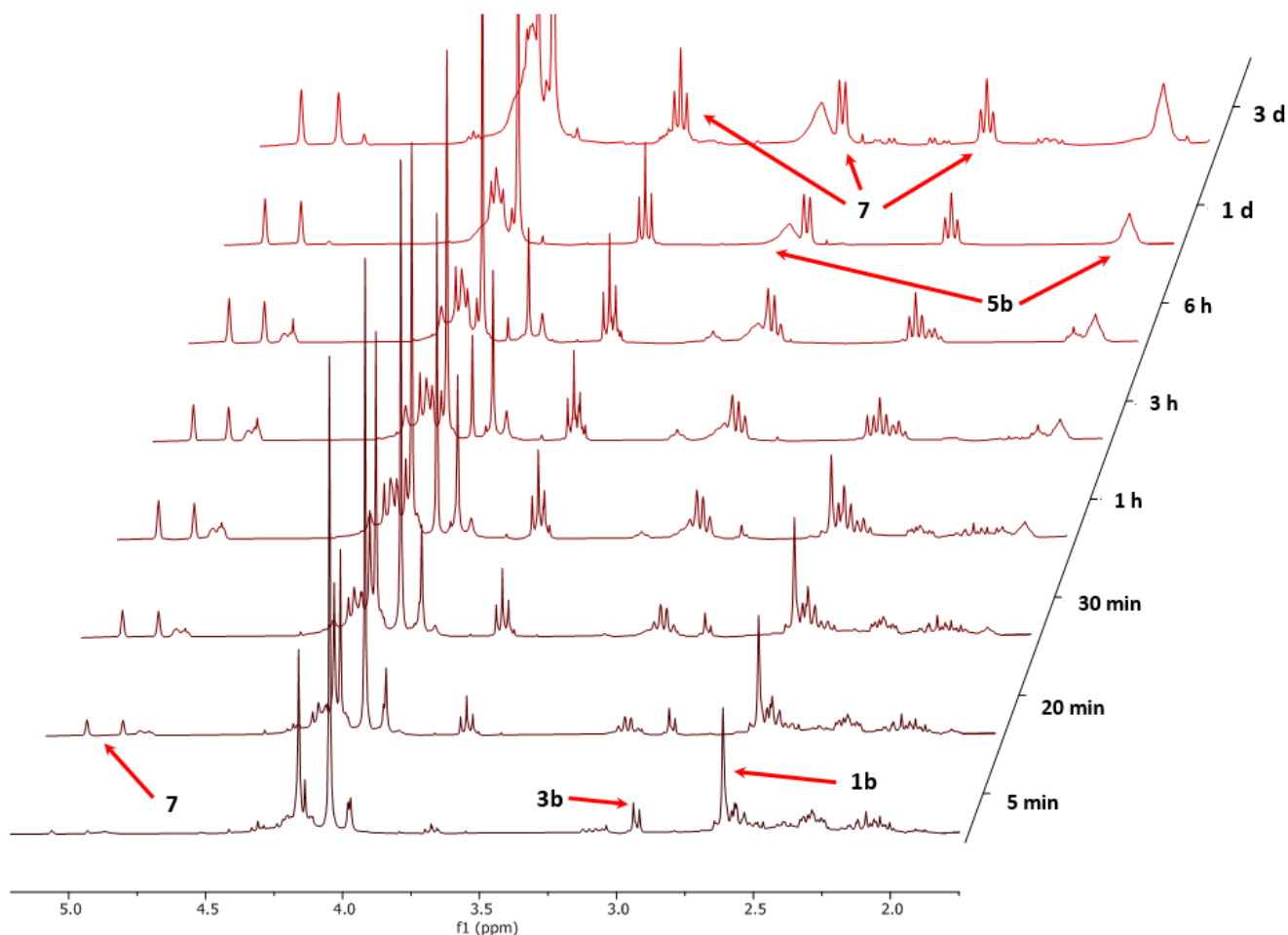
Diagram with a break along the horizontal axis (range excluded: 1000 – 14000 min)



t/min	Yields, %			t/min	Yields, %		
	1a	2	5a		1a	2	5a
0	100	0	0	30	43	37	20
1	88	12	0	35	36	39	25
2	87	13	0	40	29	42	29
3	86	14	0	45	24	43	33
7	79	21	0	60	16	46	39
9	79	21	0	90	6	52	42
11	74	26	0	120	2	55	44
13	70	29	1	240	0	56	44
15	63	34	3	300	0	55	45
20	57	35	8	4320	0	40	60
25	49	37	14	14400	0	5	95

2.2 NMR monitoring for 1b rearrangement on TiCl₄





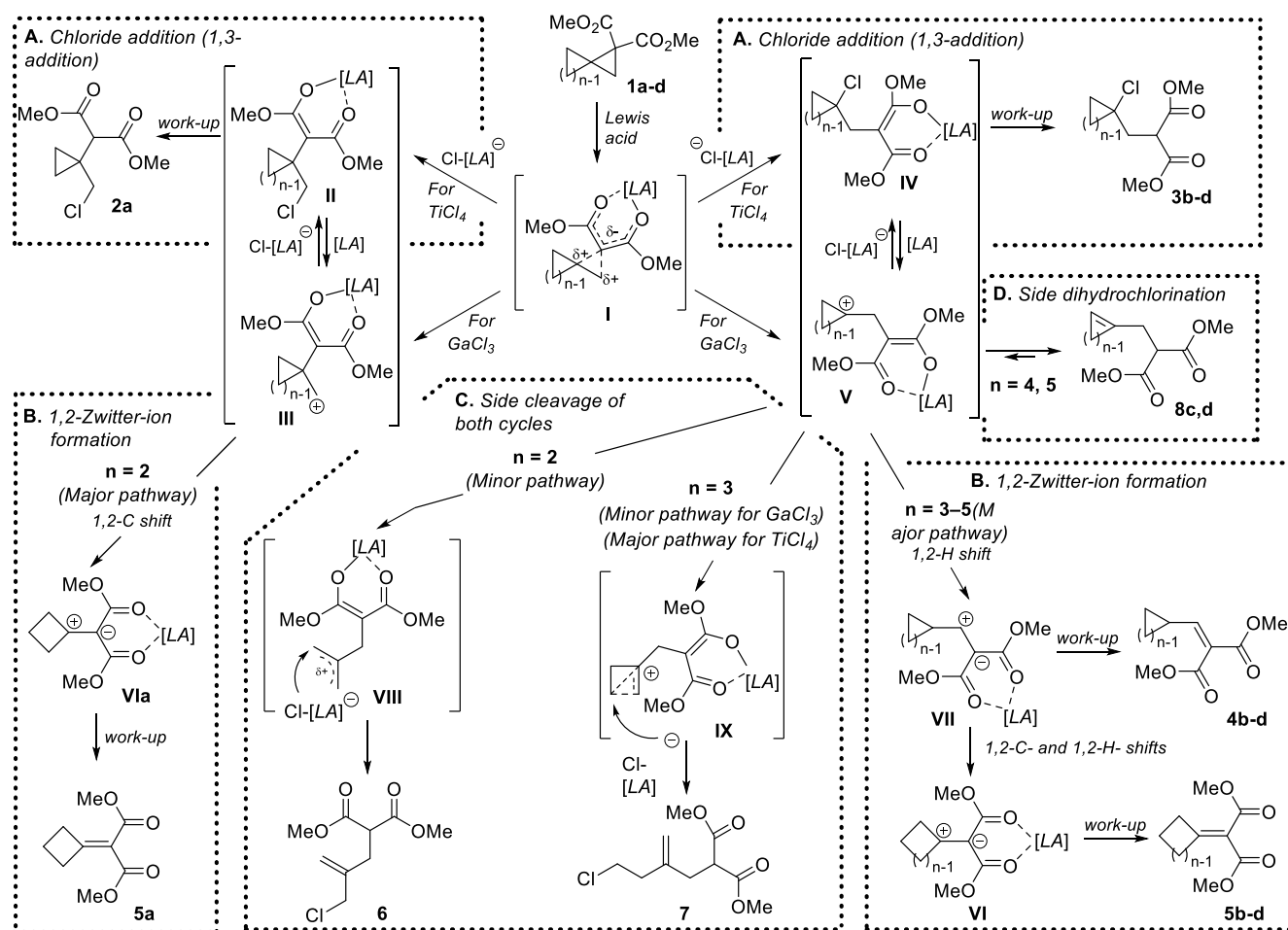
t/min	Yields, %				
	1b	3b	7	5b	4b
0	100	0	0	0	0
6	68	25	4	1	2
19	56	18	17	7	3
32	46	14	24	14	3
62	33	9	34	22	2
167	11	4	45	39	1
376	0	0	52	48	0
1654	0	0	60	40	0
4427	0	0	52	48	0

2.3 Additional mechanistic discussion

Overall proposed mechanism presented below includes ionization of DAC *via* coordination of LA on malonate fragment. Next, cleavage of C(1)-C(2) or C(1)-C(3) proceeded that involves either nucleophilic assistance by chloride source or its ionization similar to S_N1 -type processes. The ratio between these two plausible cleavage mechanism is likely determined by chloride source nucleophilicity, Lewis acidity of $TiCl_4/GaCl_3$, the ability of polychlorinated Ti/Ga-anions to donate chloride as well as by corresponding carbocation stability. Intermediates **II-III** and **IV-V** are likely existing in an equilibrium to each other *via* reversible LA mediated ionization and ion-pair return processes.^{S5} These processes are obviously governed by Lewis acidity of the reaction medium. Thus, chlorides **2** and **3** (products of aqueous work-up of intermediates **II** and **IV**) could be easily observed in $TiCl_4$ -mediated reactions, but not in $GaCl_3$ -mediated that should be attributed to well-known extremely high acidity of $GaCl_3$ and its' high chloride affinity.^{S5,S6}

Further carbocationic rearrangements *via* intermediates **II/III** and **IV/V** lead to the formation of alkylidene malonates as the final products in all the cases. This outcome is one of the most remarkable achievement in this work. Plausible mechanism should involve a set of 1,2-H- and 1,2-alkyl migrations in the formed carbocationic

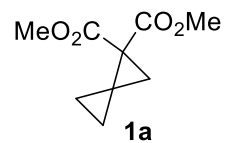
intermediates as illustrated below as rearrangements of **III** to **Vla** via 1,2-alkyl shift, of **V** to **VII** via 1,2-H shift, and of **VII** to **VI** via subsequent 1,2-alkyl and 1,2-H shifts. Intermediates **VI** and **VII** represents complexes of alkylidene malonate anions coordinated on Lewis acid that in the case of Ga(III) are known as 1,2-zwitter ions and therefor are able to react in gallium specific carbocation cascades.^{S7} However, formation of 1,2-zwitter-ions from DACs up to date were known only for most common 2-arylcyclopropane-1,1-dicarboxylates. Moreover, herein we clearly observed that 1,2-zwitter-ion formation from DACs can be stepwise via preliminary chloride-mediated ring-opening followed by subsequent carbocation rearrangements, however, at least for TiCl₄. Moreover, similarity of TiCl₄ and GaCl₃ in their ability to favor 1,2-zwitter-ion formation is also remarkable. However, the detailed comparison of a degree of C=C-bond polarization induced by GaCl₃ and TiCl₄ in these adducts to reveal their 1,2-zwitter-ionic nature and to compare their reactivity in carbocations transformations are currently undergoing and will be published separately.



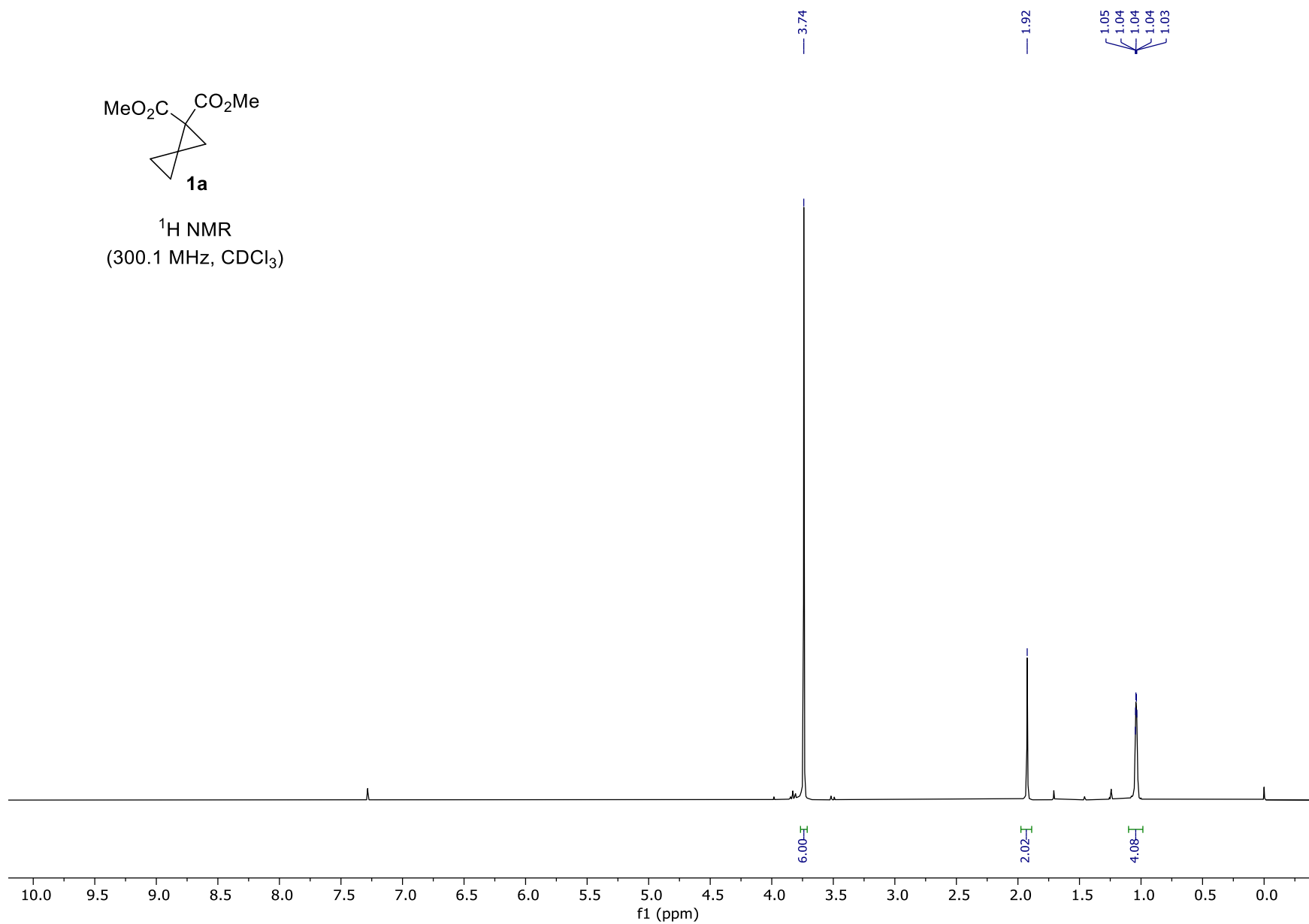
3. References

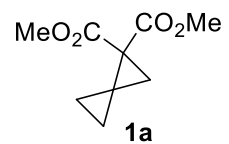
- S1. A. de Meijere, K. Ernst, B. Zuck, M. Brandl, S. I. Kozhushkov, M. Tamm, D. S. Yufit, J. A. K. Howard and T. Labahn, *Eur. J. Org. Chem.*, 1999, **11**, 3105; [https://doi.org/10.1002/\(SICI\)1099-0690\(199911\)1999:11<3105::AID-EJOC3105>3.0.CO;2-1](https://doi.org/10.1002/(SICI)1099-0690(199911)1999:11<3105::AID-EJOC3105>3.0.CO;2-1).
- S2. J. A. Campbell and A. Good, *Patent WO02060926A2*, 2002; <https://patentimages.storage.googleapis.com/63/22/d0/065c8b8780d1a8/WO2002060926A2.pdf>.
- S3. H.-H. Zhang, Y.-C. Luo, H.-P. Wang, W. C. Peng and F. Xu, *Org. Lett.*, 2014, **16**, 4896; <https://doi.org/10.1021/ol5024079>.
- S4. B. Martin-Matute, E. Bunuel, M. Mendez, C. Nieto-Oberhuber, D. J. Cardenas and A. M. Echavarren, *J. Organomet. Chem.*, 2003, **687**, 410; <https://doi.org/10.1016/j.jorganchem.2003.07.027>.
- S5. R. A. Novikov, D. O. Balakirev, V. P. Timofeev and Y. V. Tomilov, *Organometallics*, 2012, **31**, 8627; <https://doi.org/10.1021/om301072v>.
- S6. H. Friedman and H. Taube, *J. Am. Chem. Soc.*, 1950, **72**, 2236; <https://doi.org/10.1021/ja01161a100>.
- S7. R. A. Novikov, D. A. Denisov, K. V. Potapov, Y. V. Tkachev, E. V. Shulishov and Y. V. Tomilov, *J. Am. Chem. Soc.*, 2018, **140**, 14381; <https://doi.org/10.1021/jacs.8b08913>.

3. NMR spectra of obtained compounds:

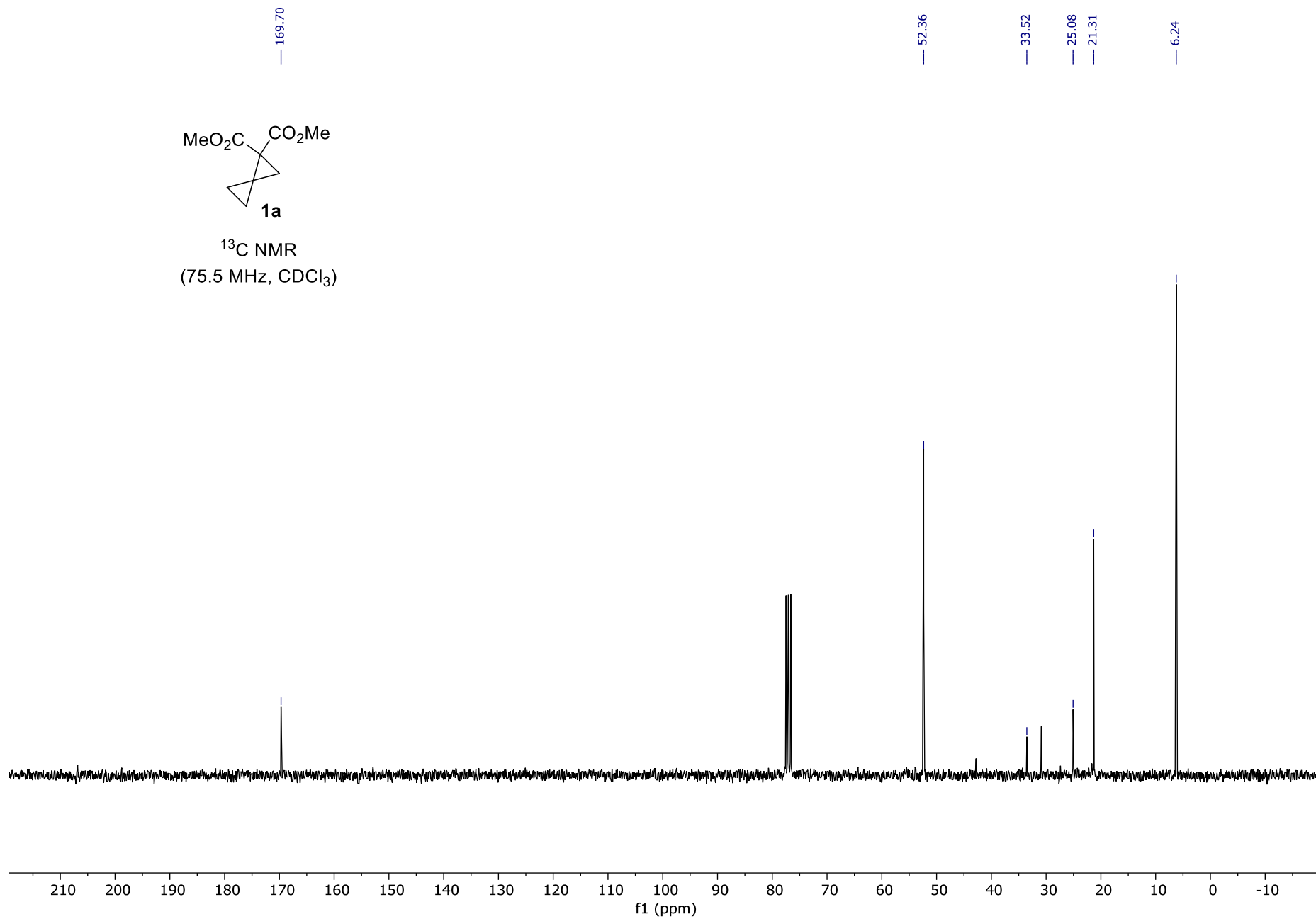


^1H NMR
(300.1 MHz, CDCl_3)

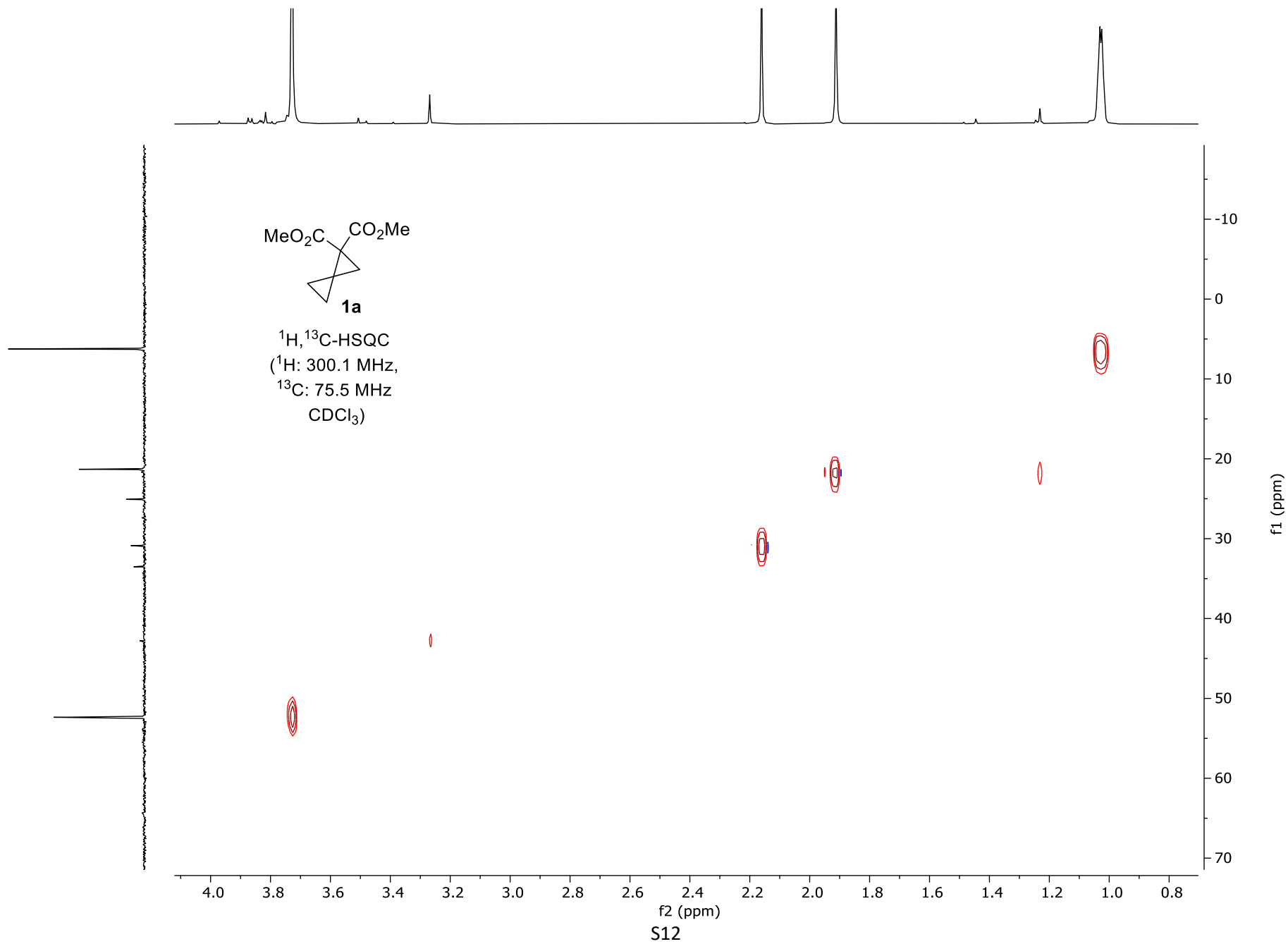


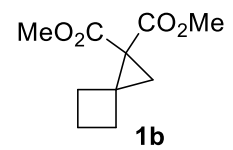


^{13}C NMR
(75.5 MHz, CDCl_3)

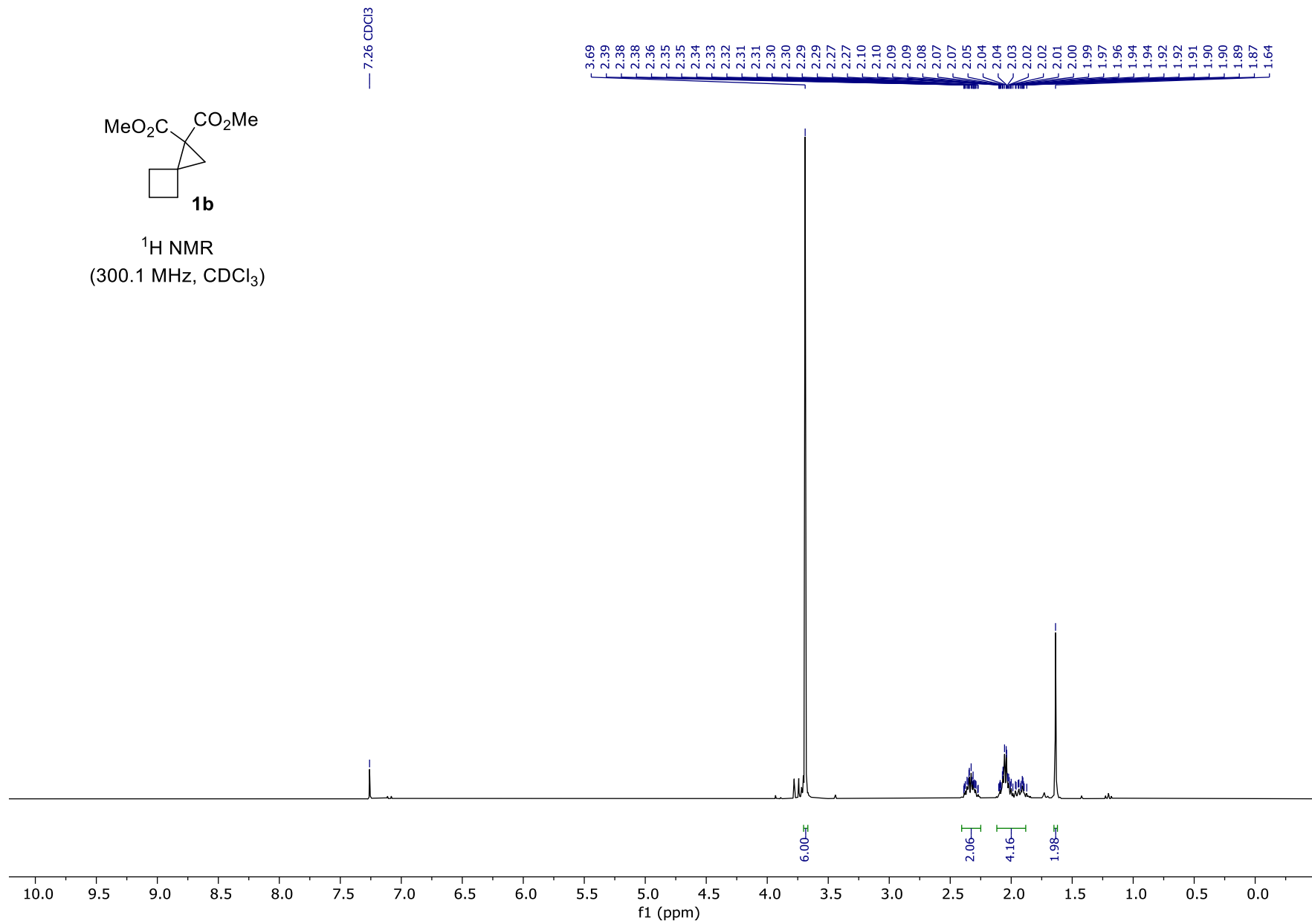


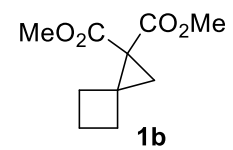
S11



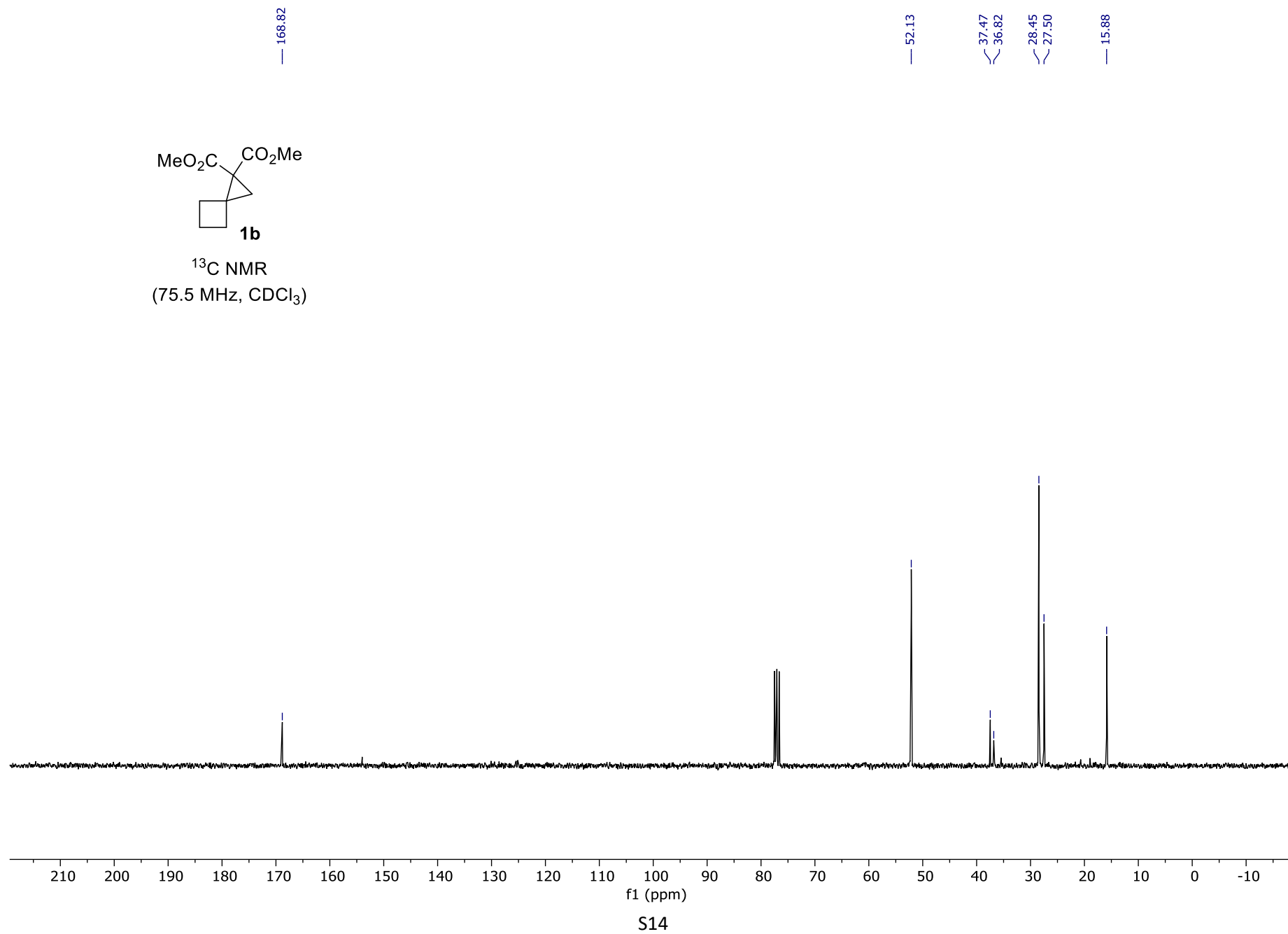


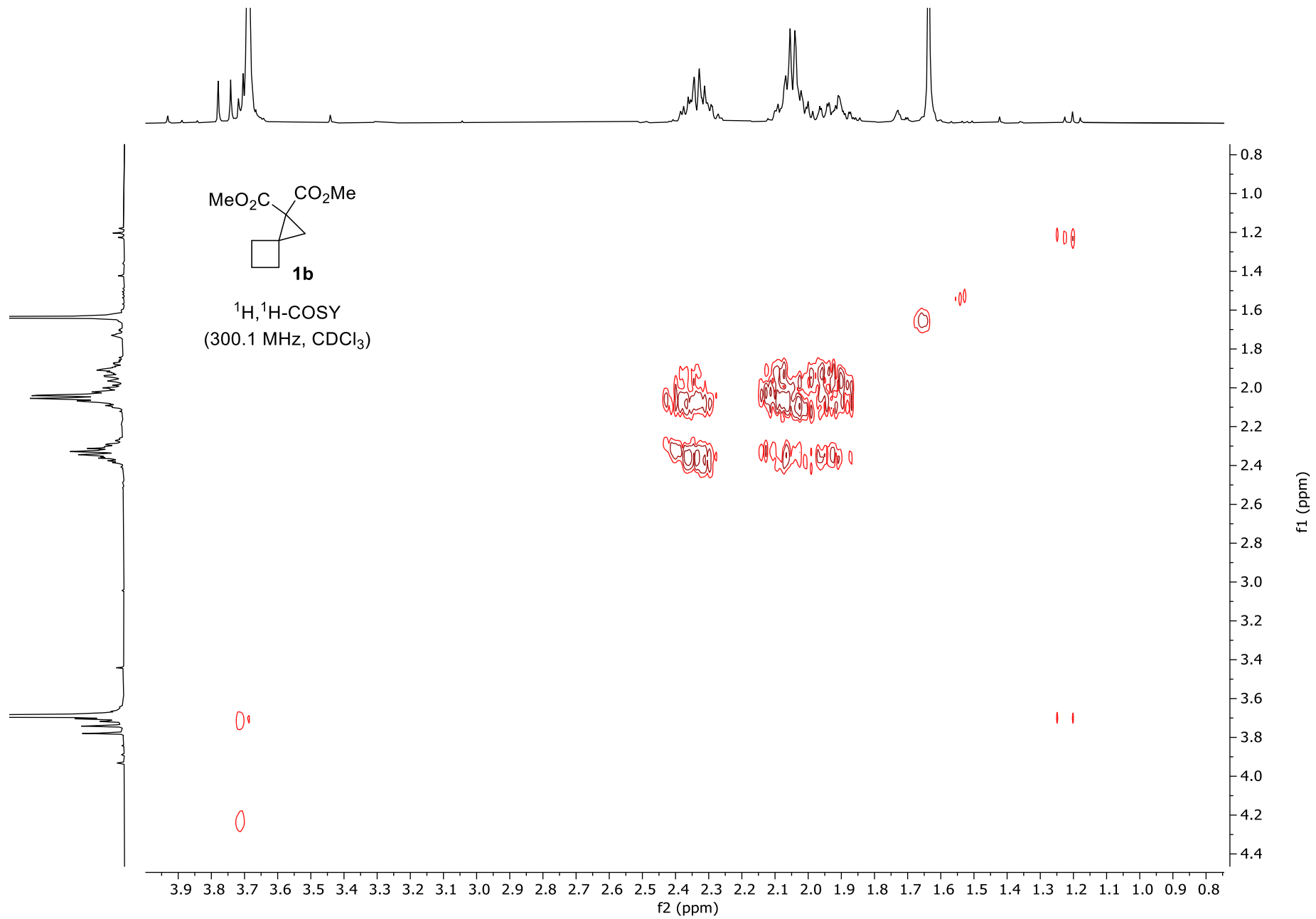
¹H NMR
 (300.1 MHz, CDCl₃)

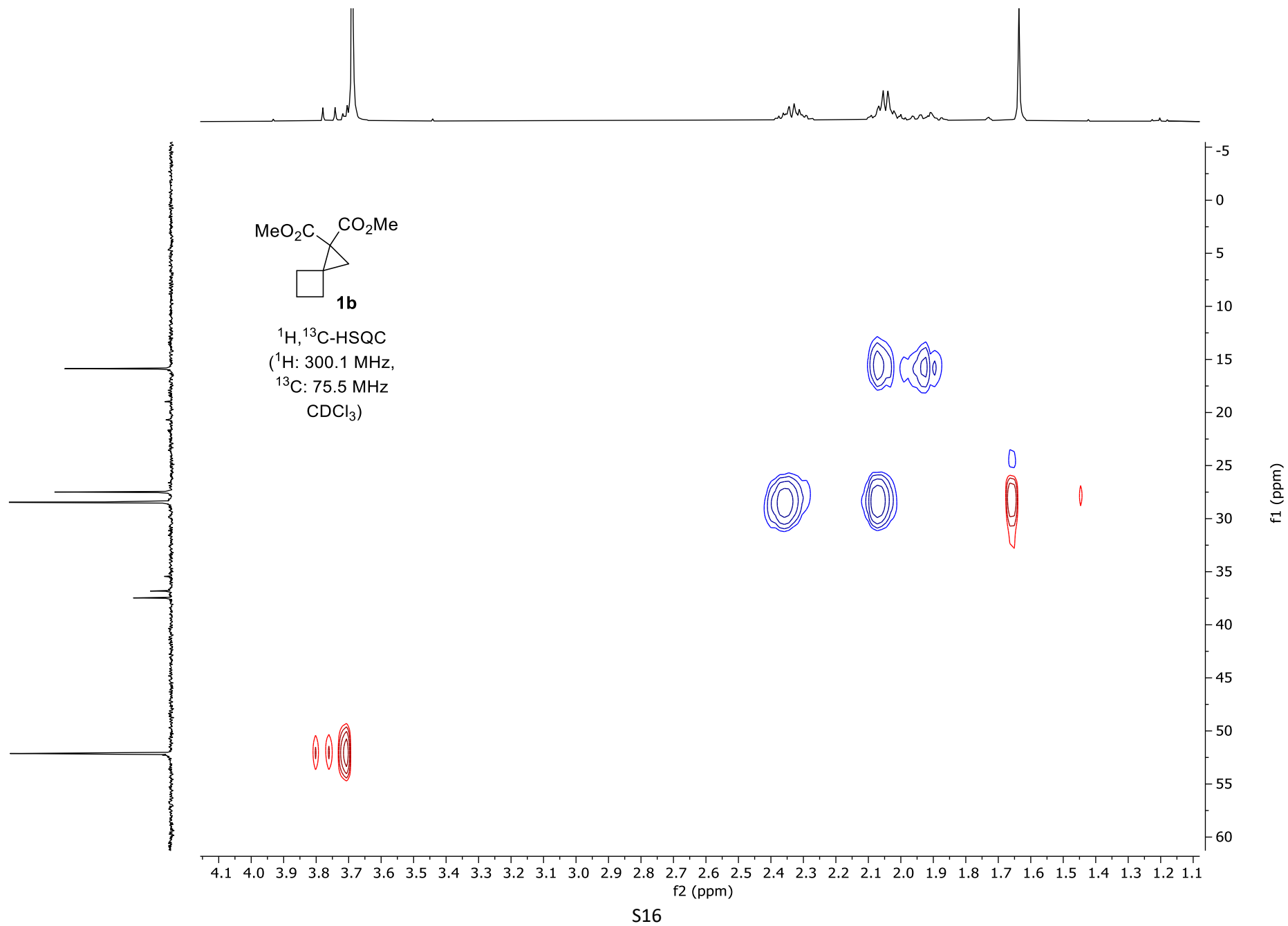


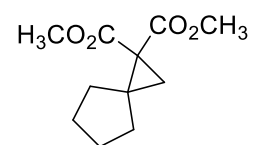


^{13}C NMR
 (75.5 MHz, CDCl_3)

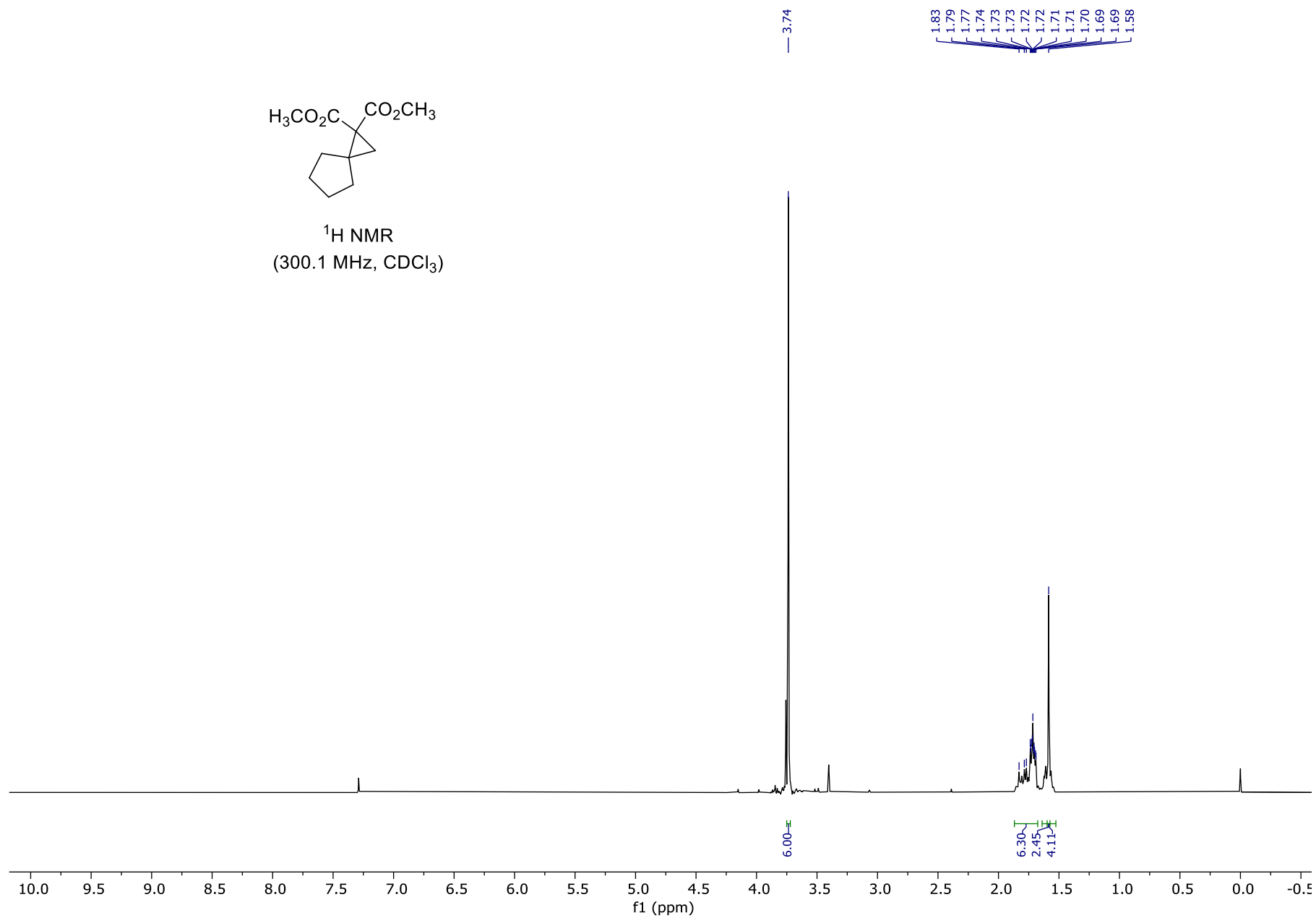


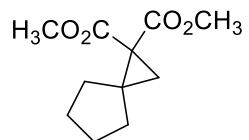




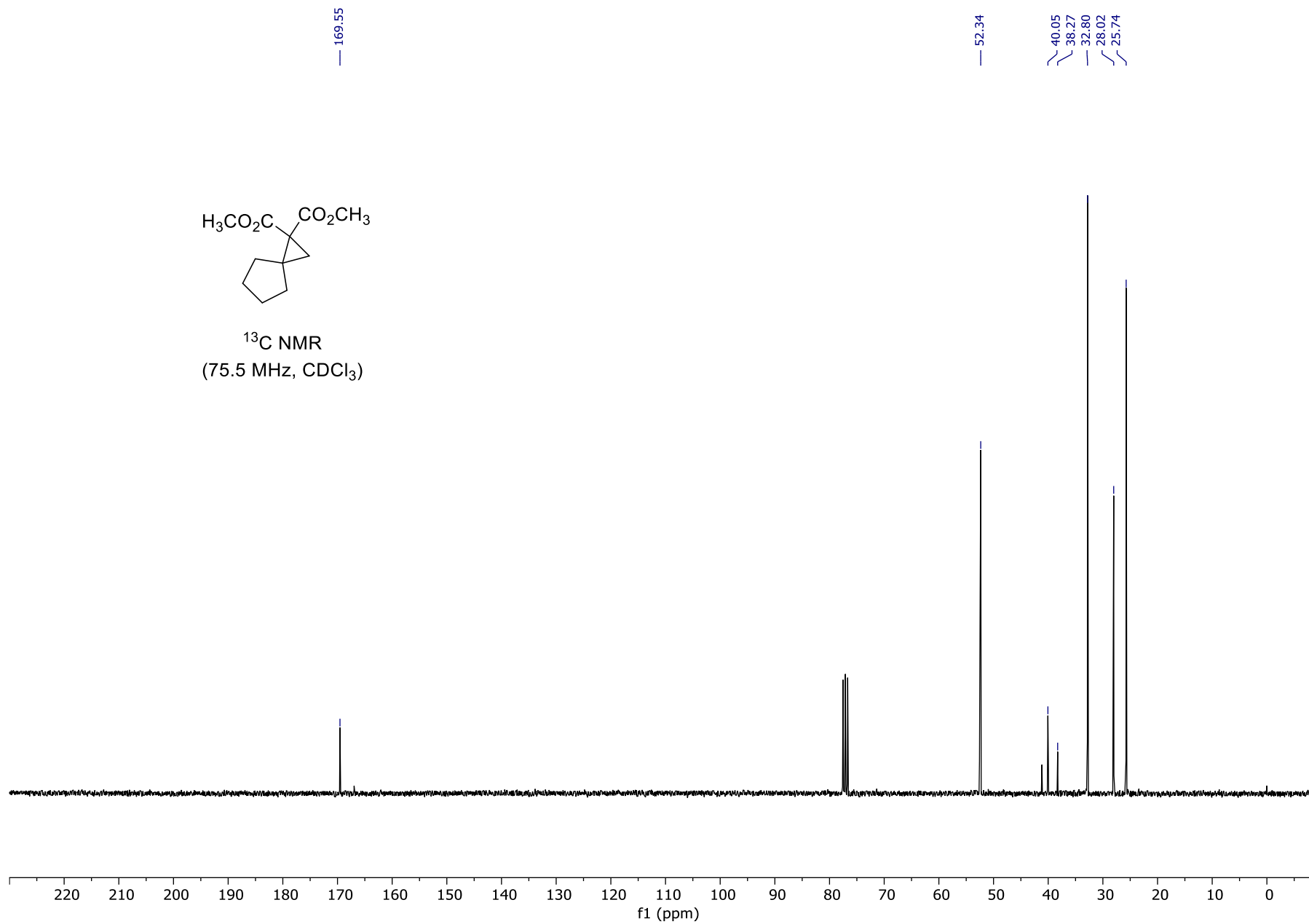


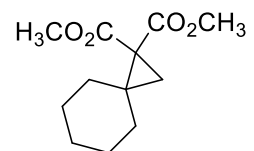
^1H NMR
(300.1 MHz, CDCl_3)



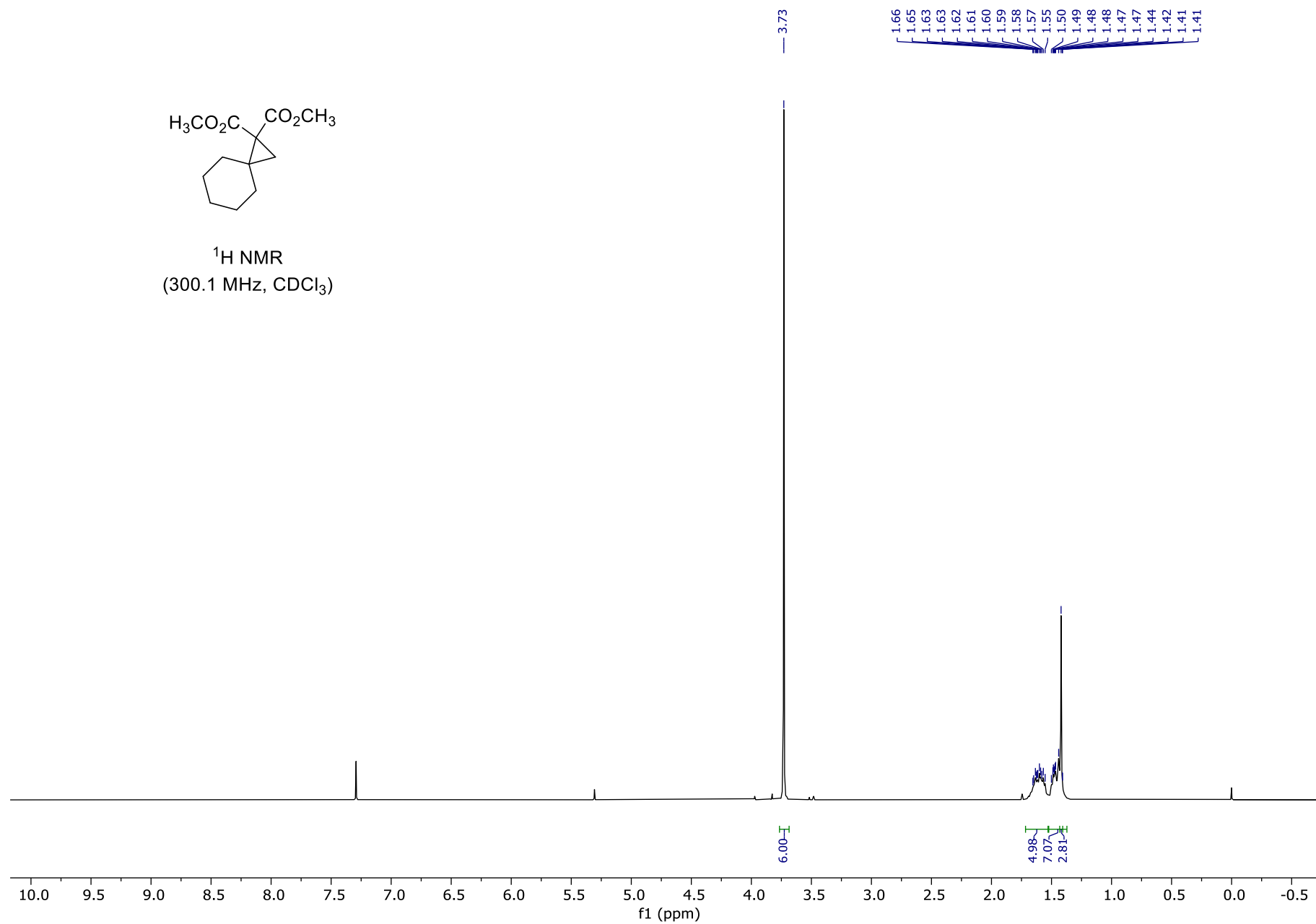


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(75.5 MHz, CDCl_3)

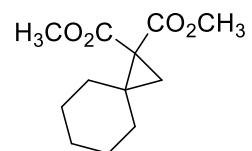




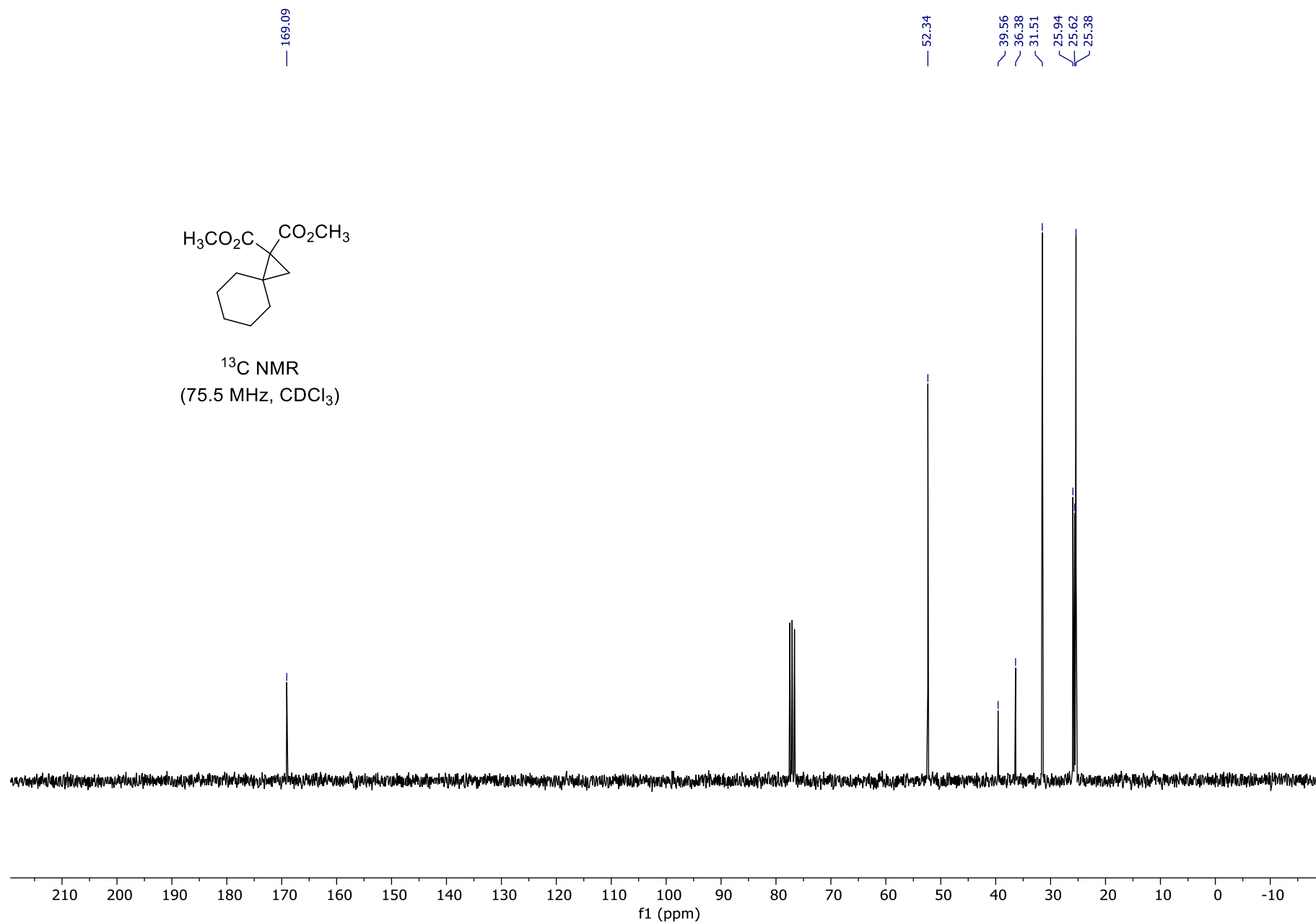
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(300.1 MHz, CDCl_3)

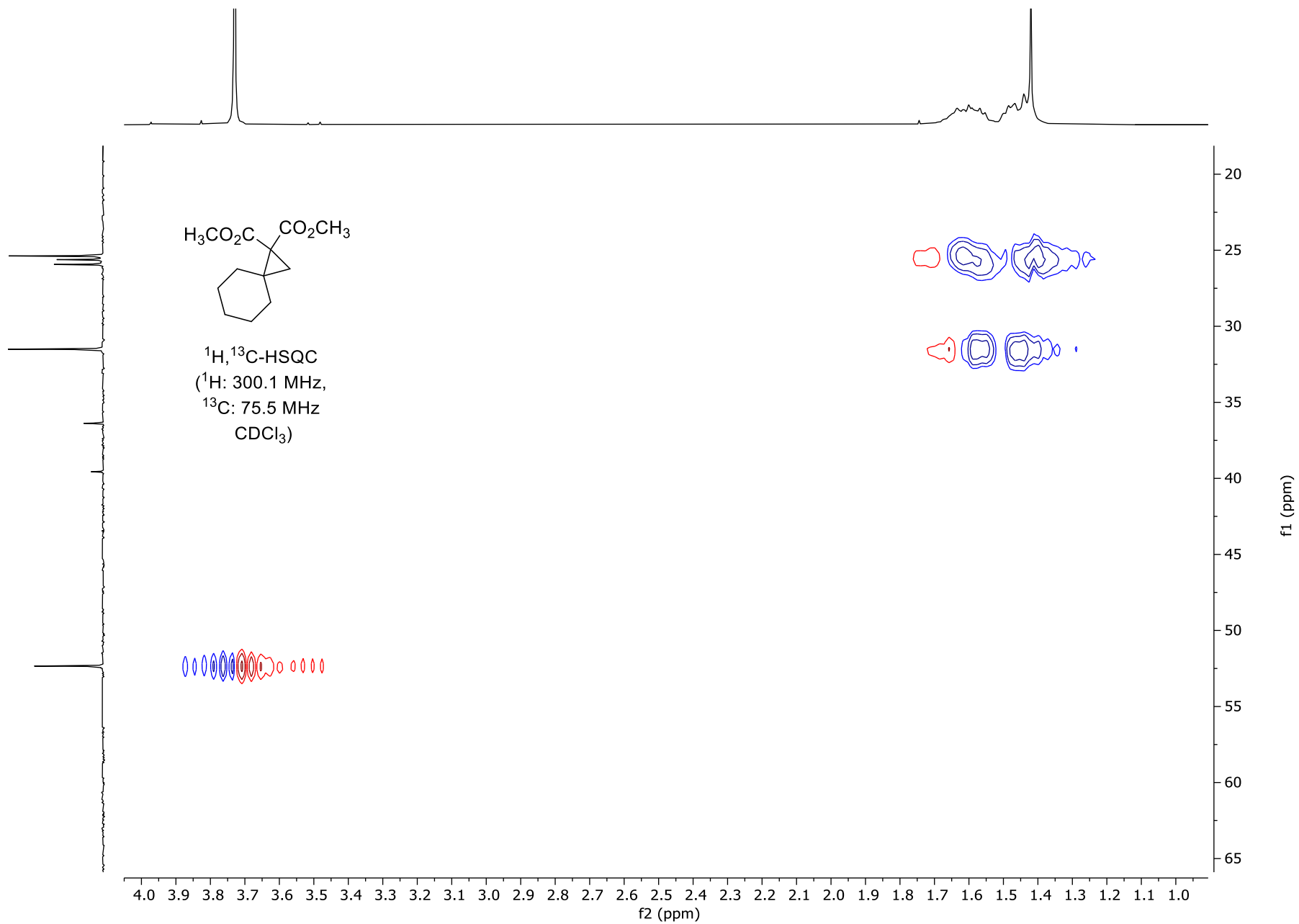


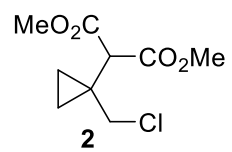
S19



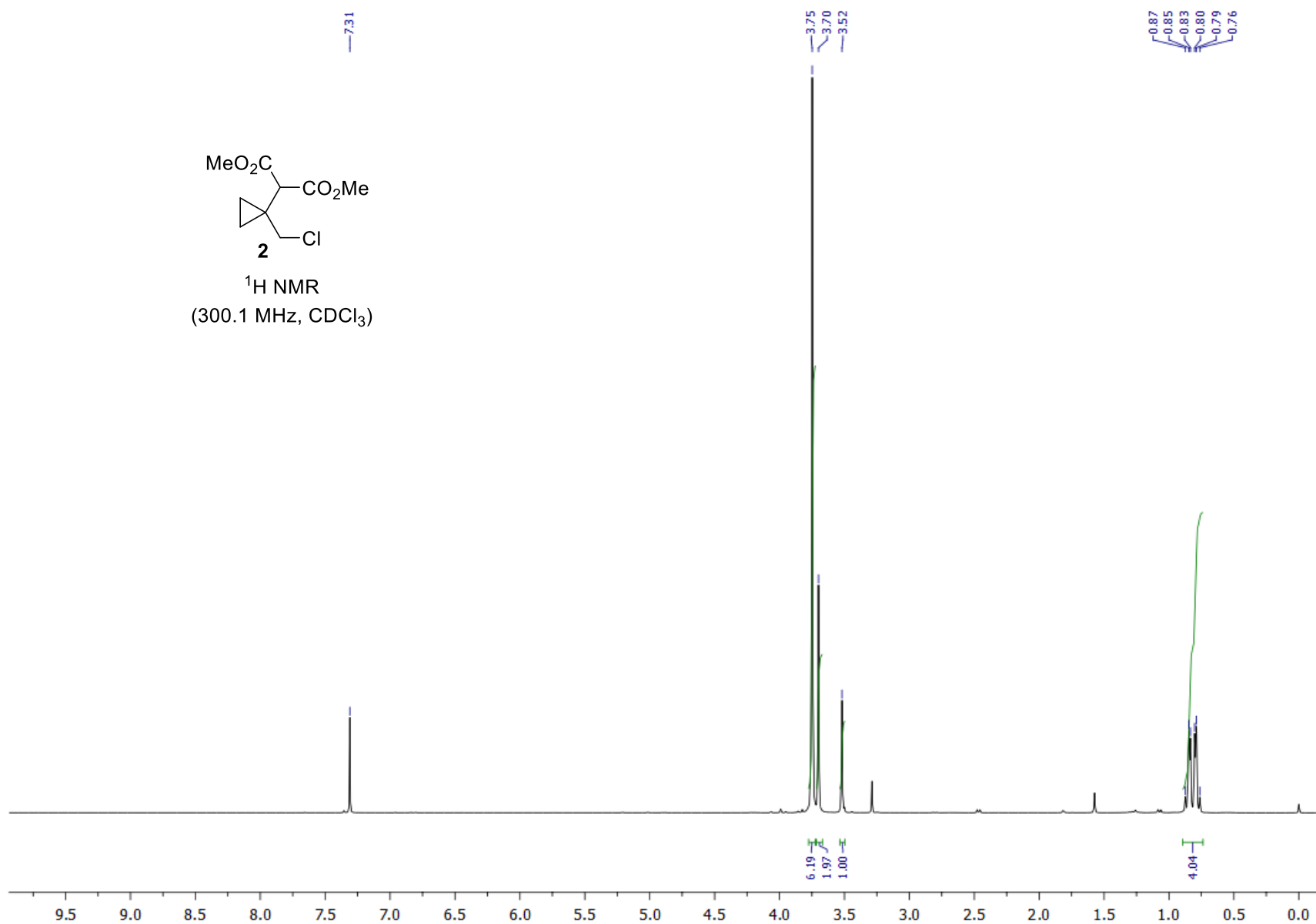
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(75.5 MHz, CDCl_3)

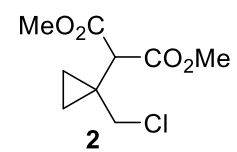




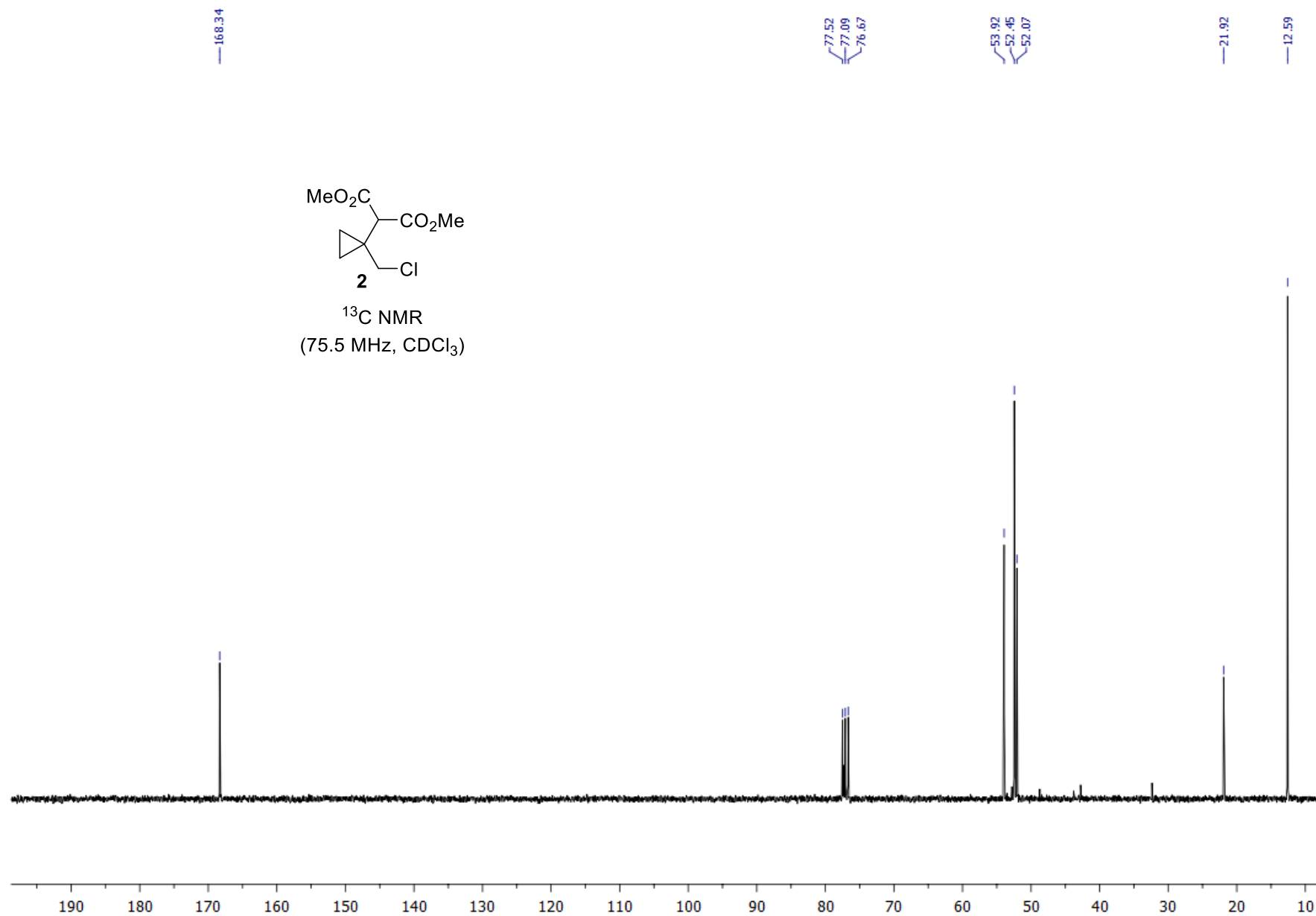


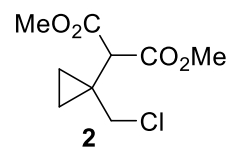
^1H NMR
(300.1 MHz, CDCl_3)



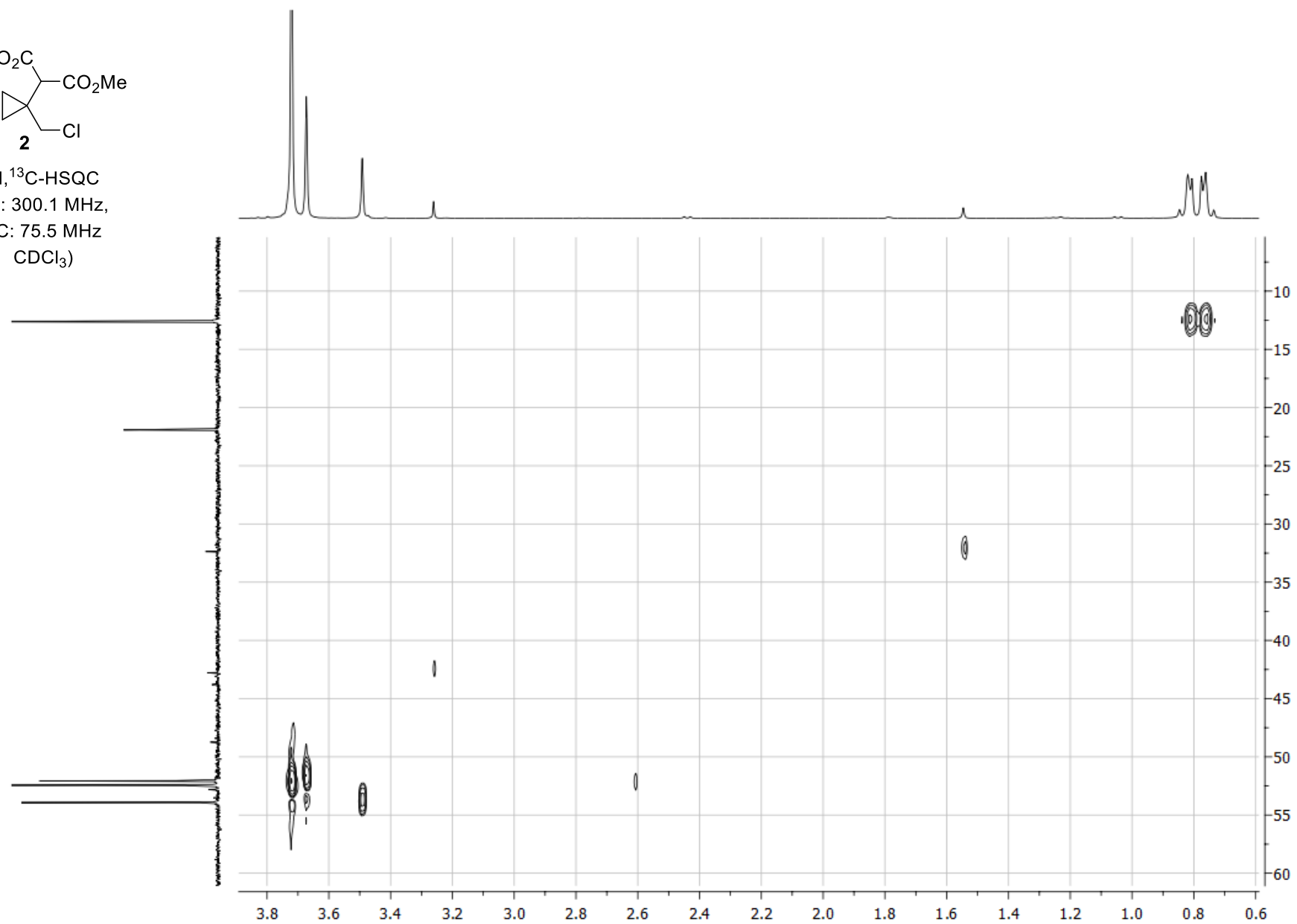


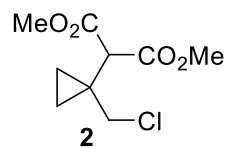
^{13}C NMR
 (75.5 MHz, CDCl_3)



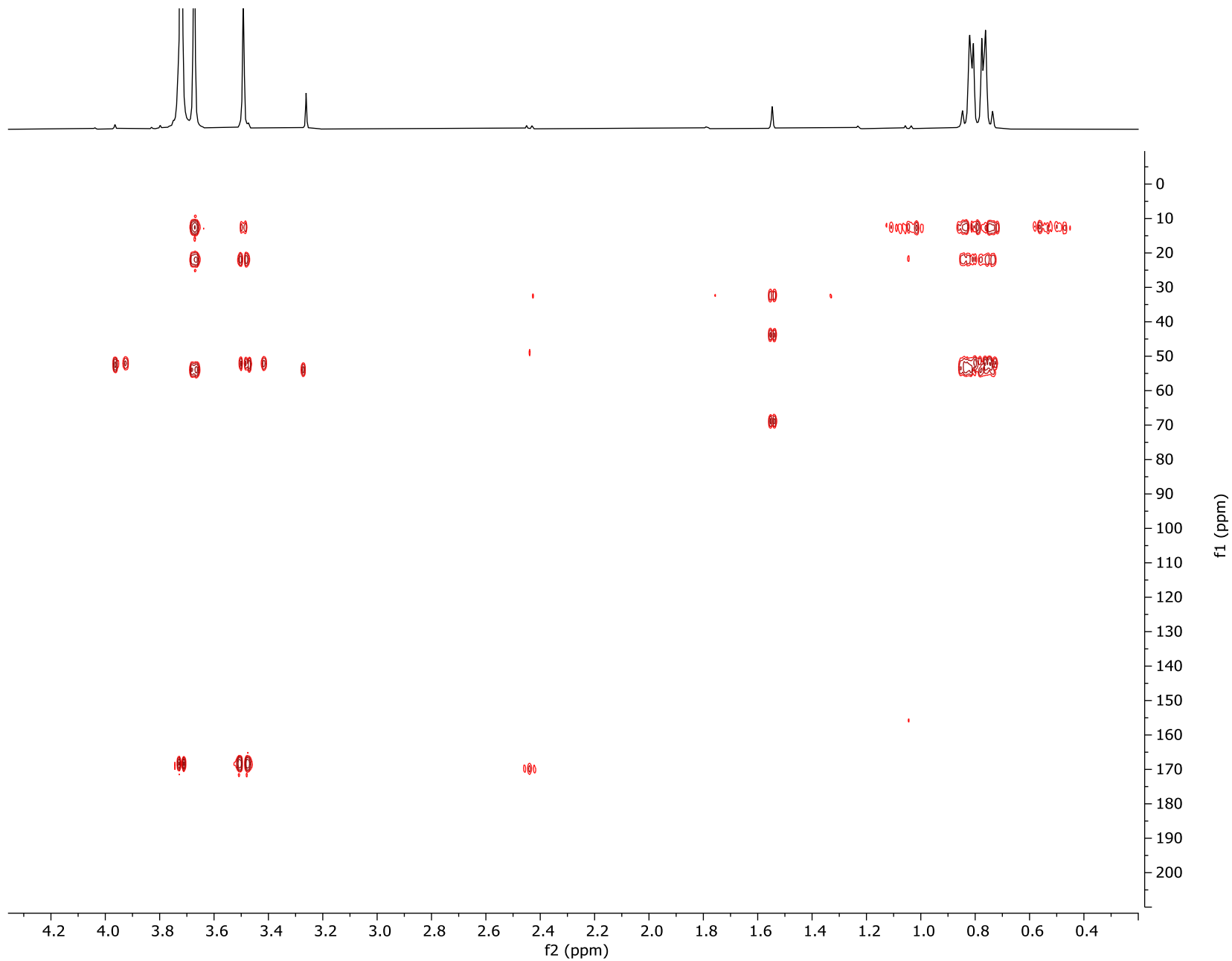


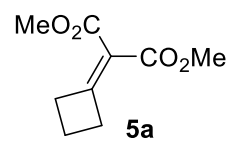
^1H , ^{13}C -HSQC
 (^1H : 300.1 MHz,
 ^{13}C : 75.5 MHz
 CDCl_3)



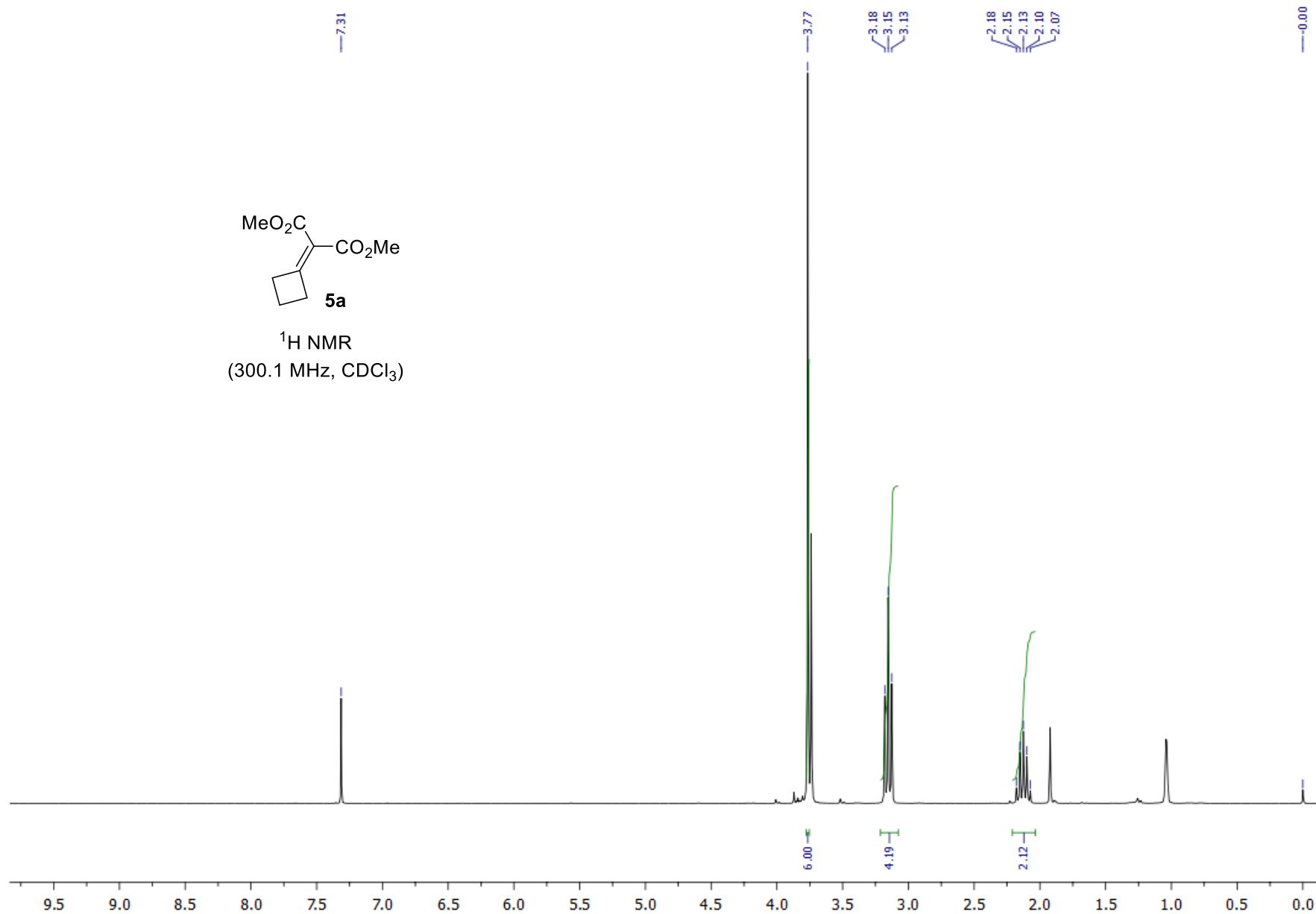


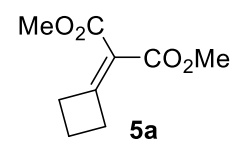
$^1\text{H}, ^{13}\text{C}$ -HMBC
 (^1H : 300.1 MHz,
 ^{13}C : 75.5 MHz
 CDCl_3)



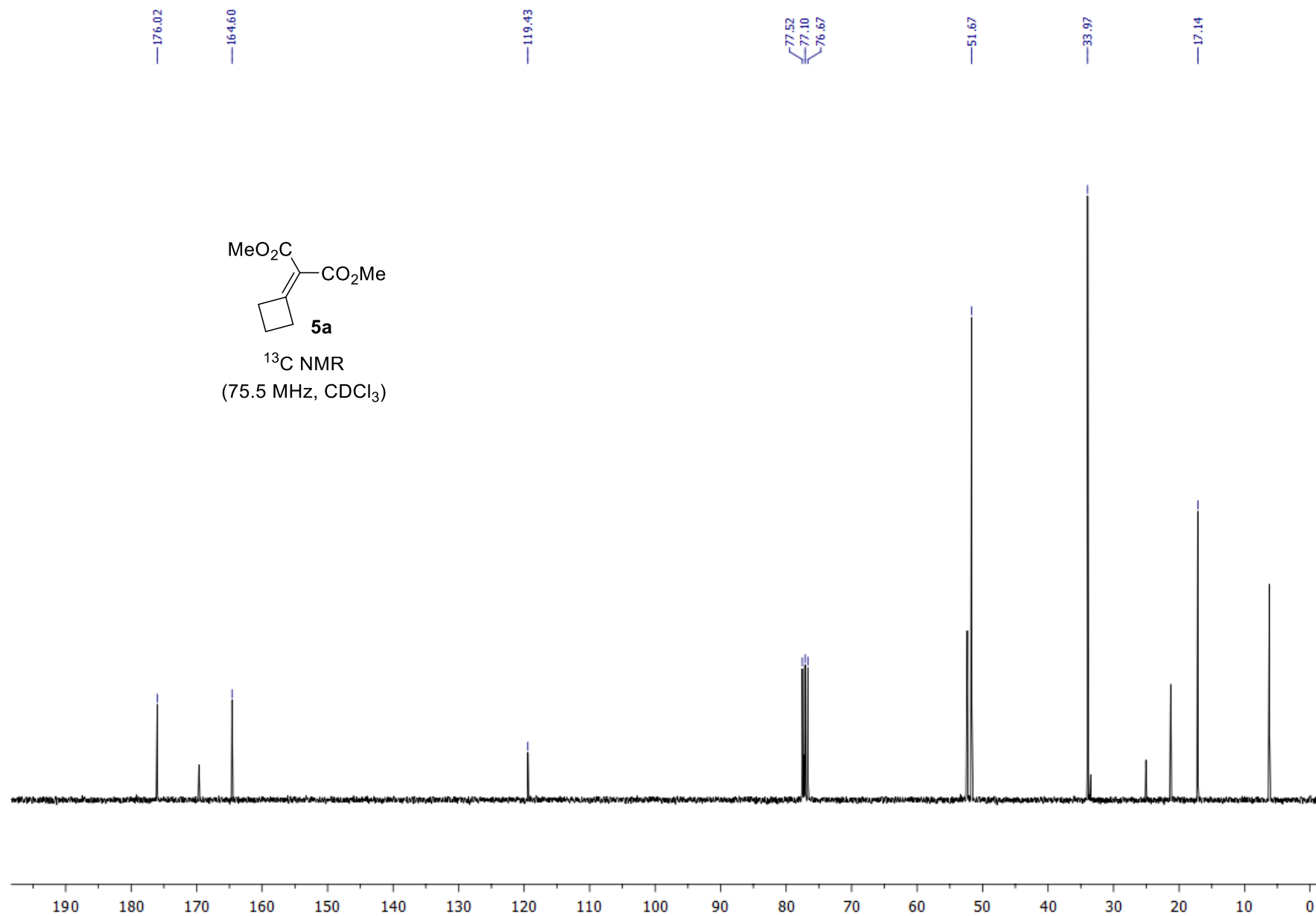


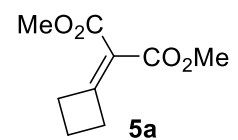
^1H NMR
 (300.1 MHz, CDCl_3)



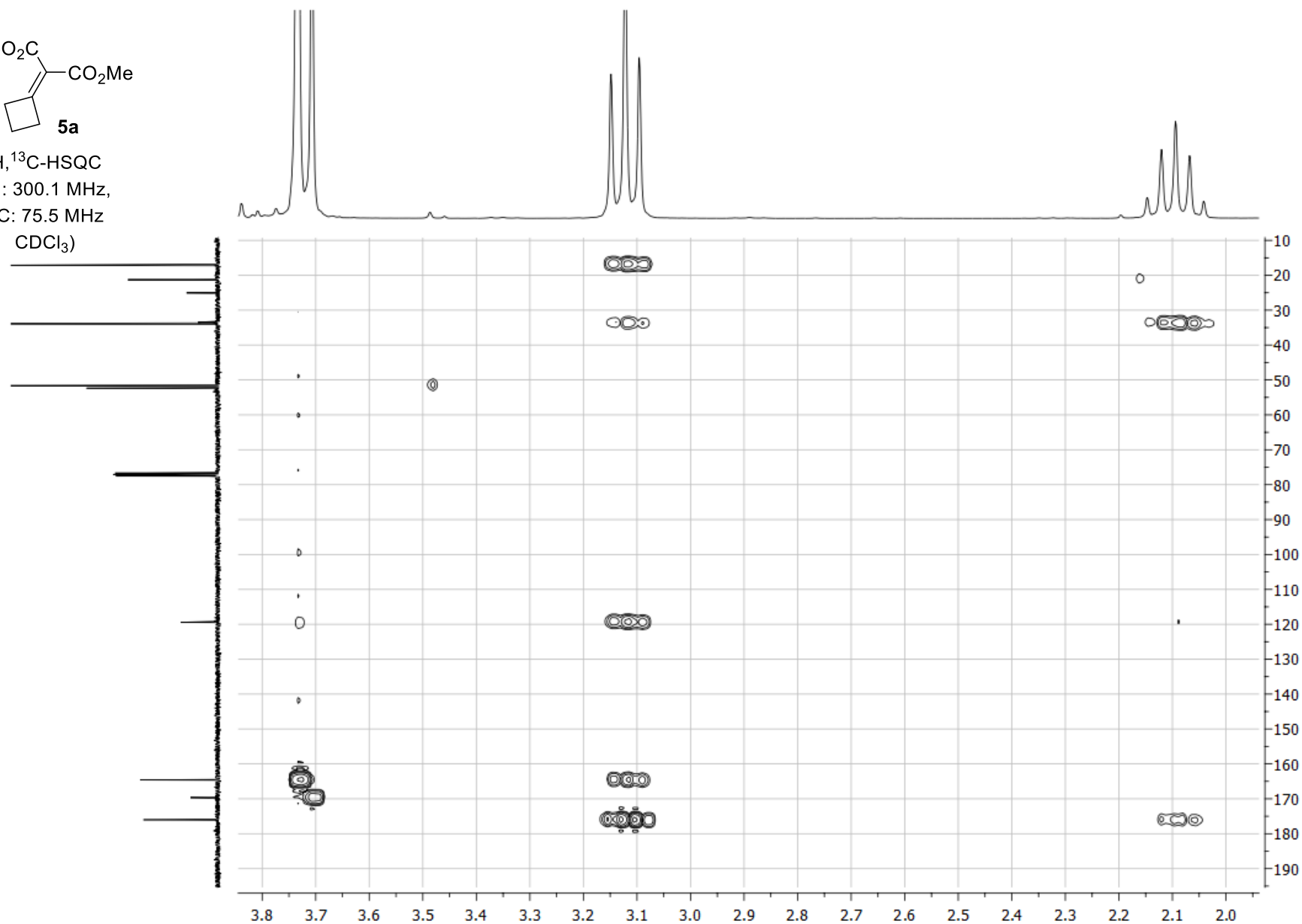


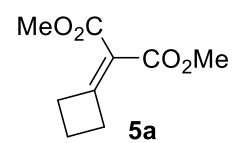
^{13}C NMR
 (75.5 MHz, CDCl_3)



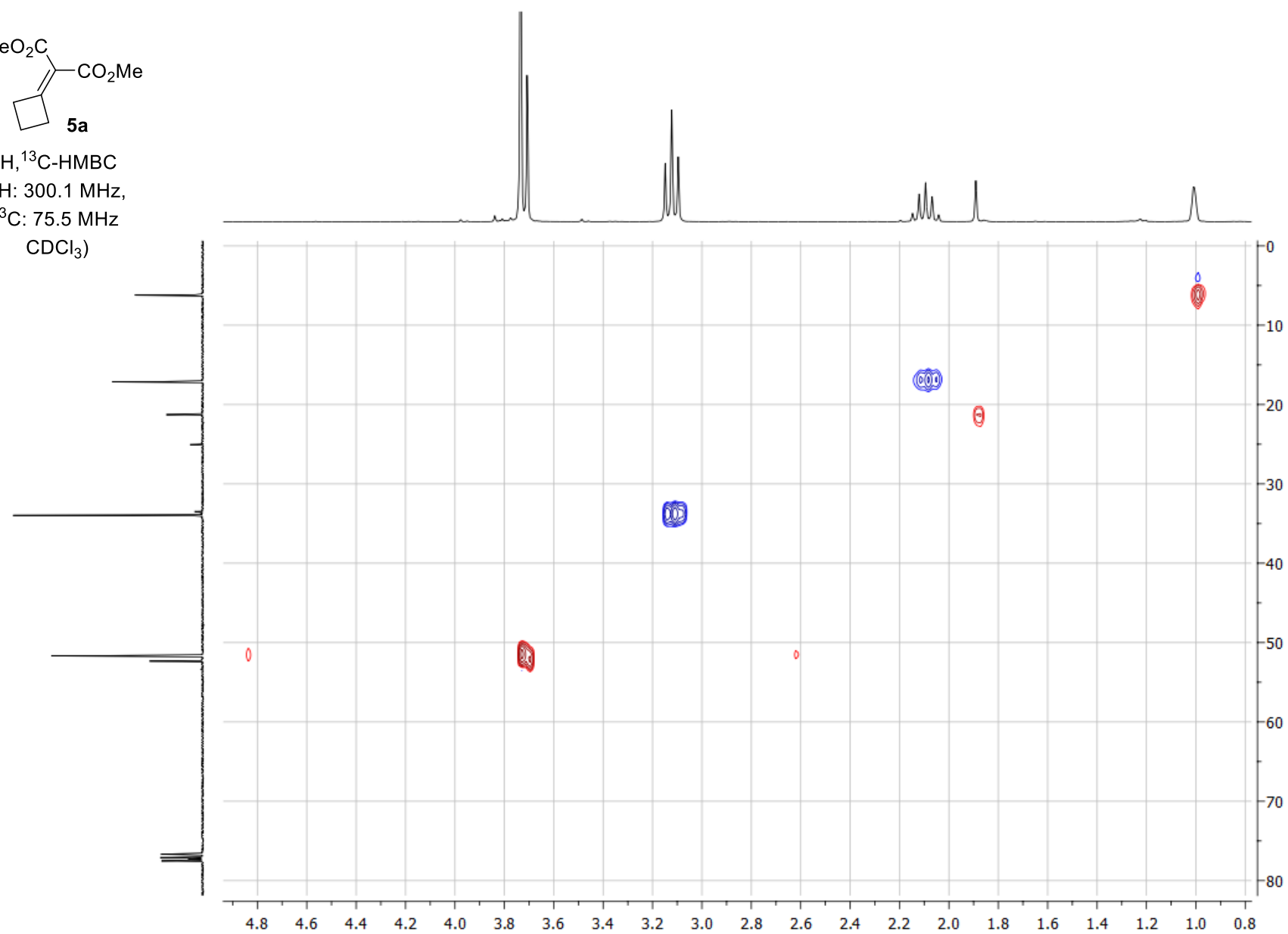


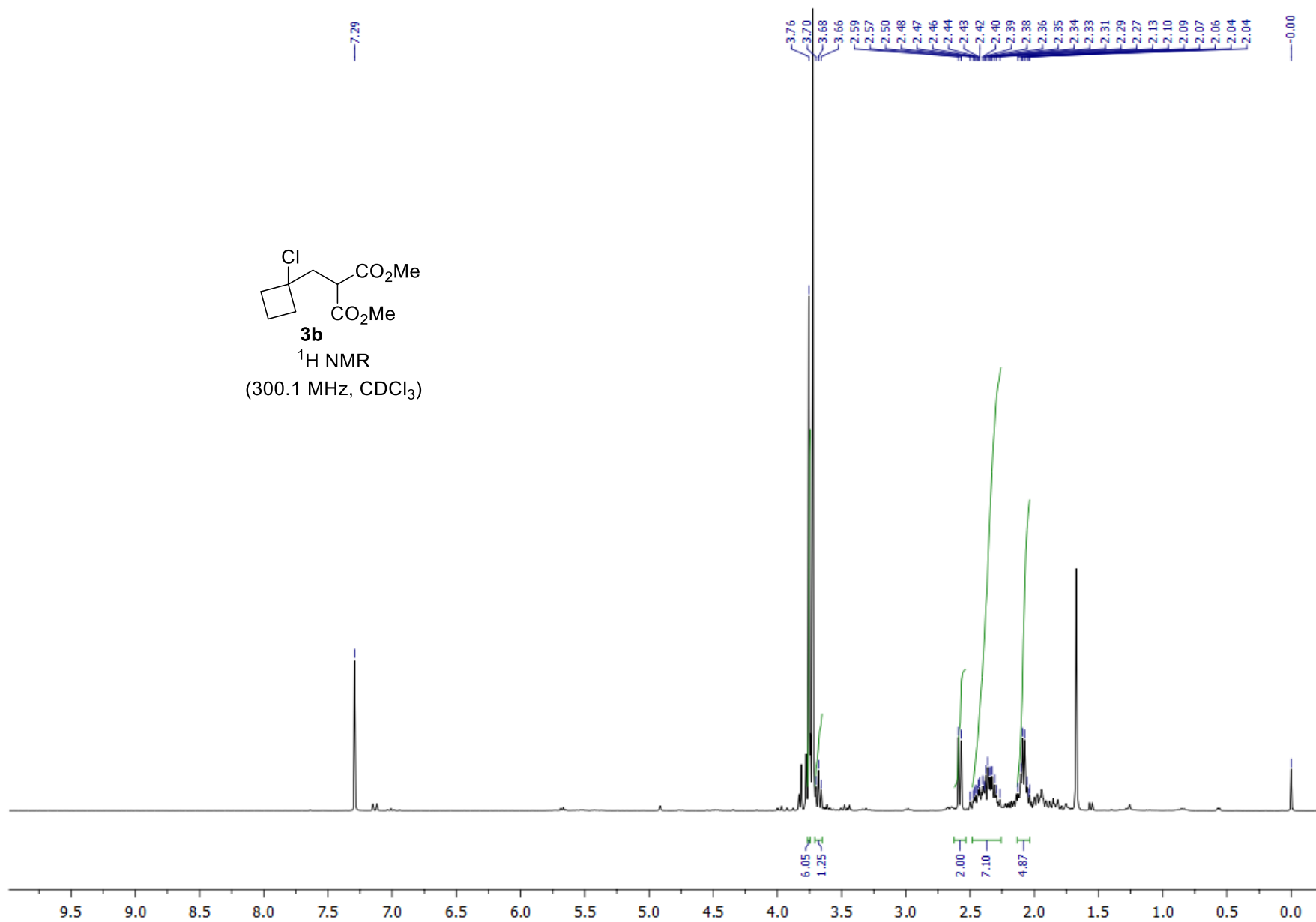
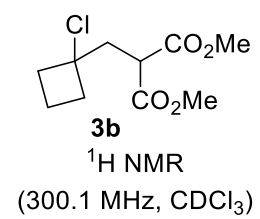
$^1\text{H}, ^{13}\text{C}$ -HSQC
 (^1H : 300.1 MHz,
 ^{13}C : 75.5 MHz
 CDCl_3)

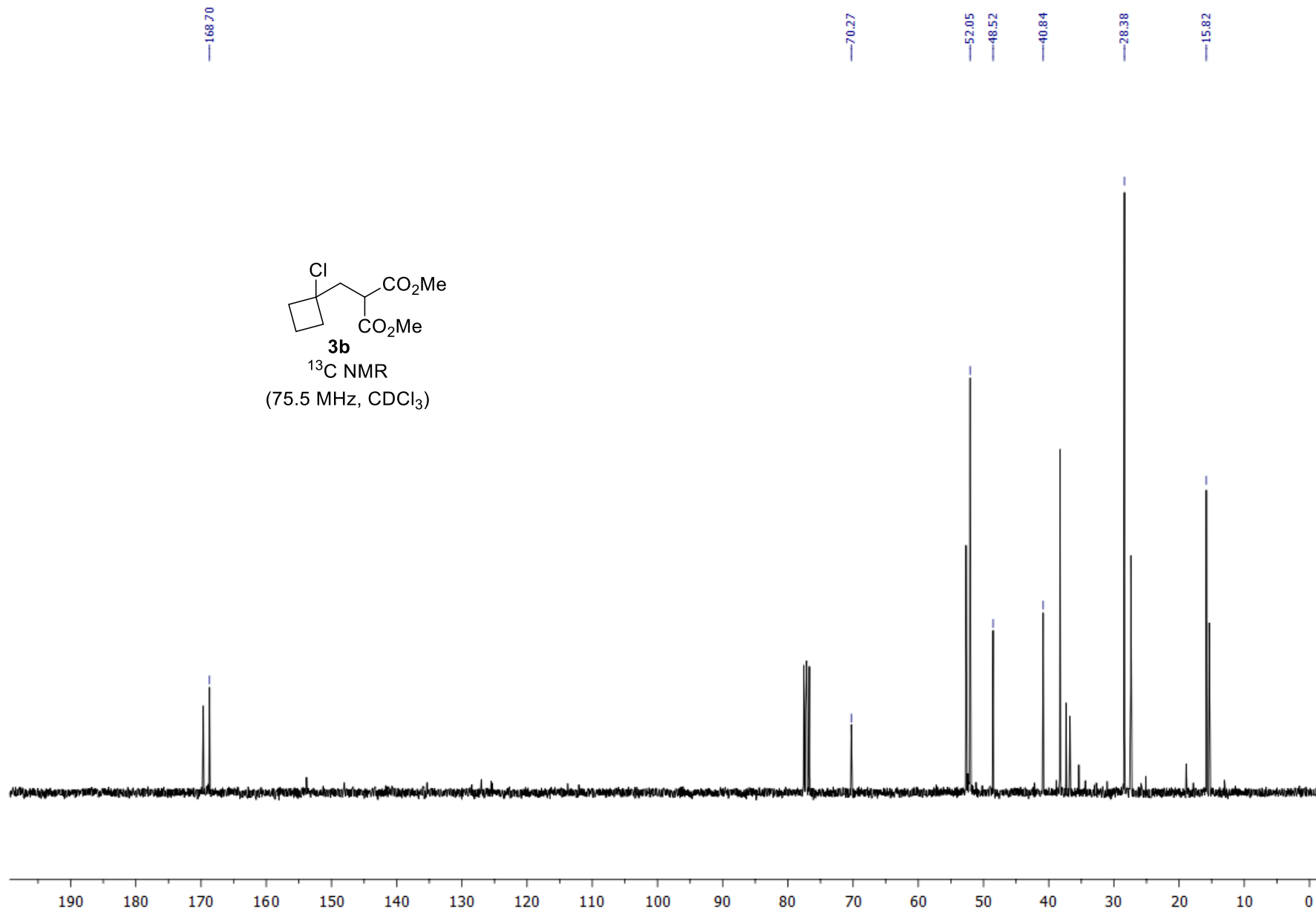
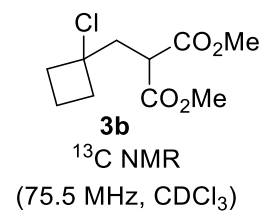


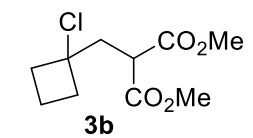


^1H , ^{13}C -HMBC
 (^1H : 300.1 MHz,
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 CDCl_3)

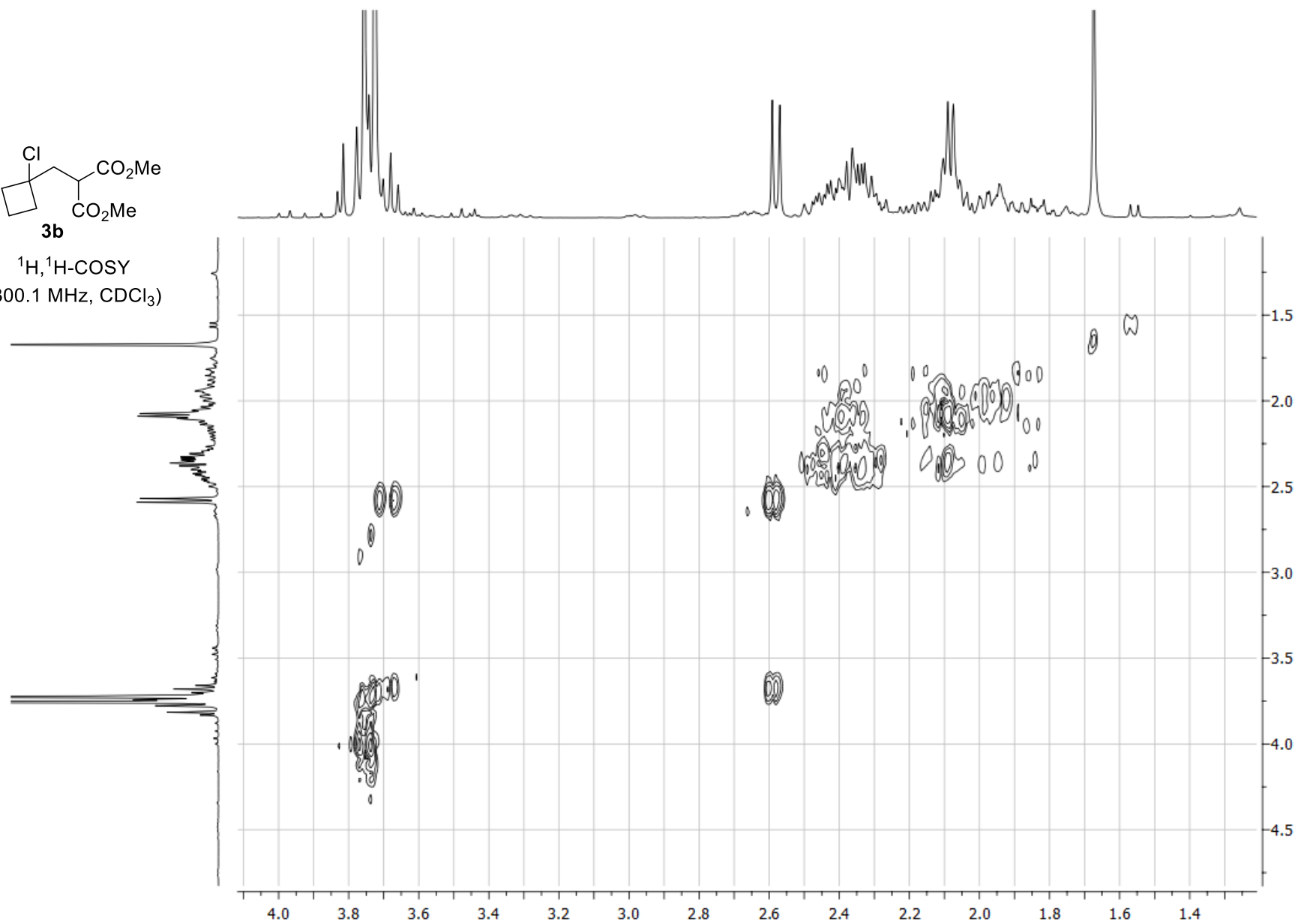


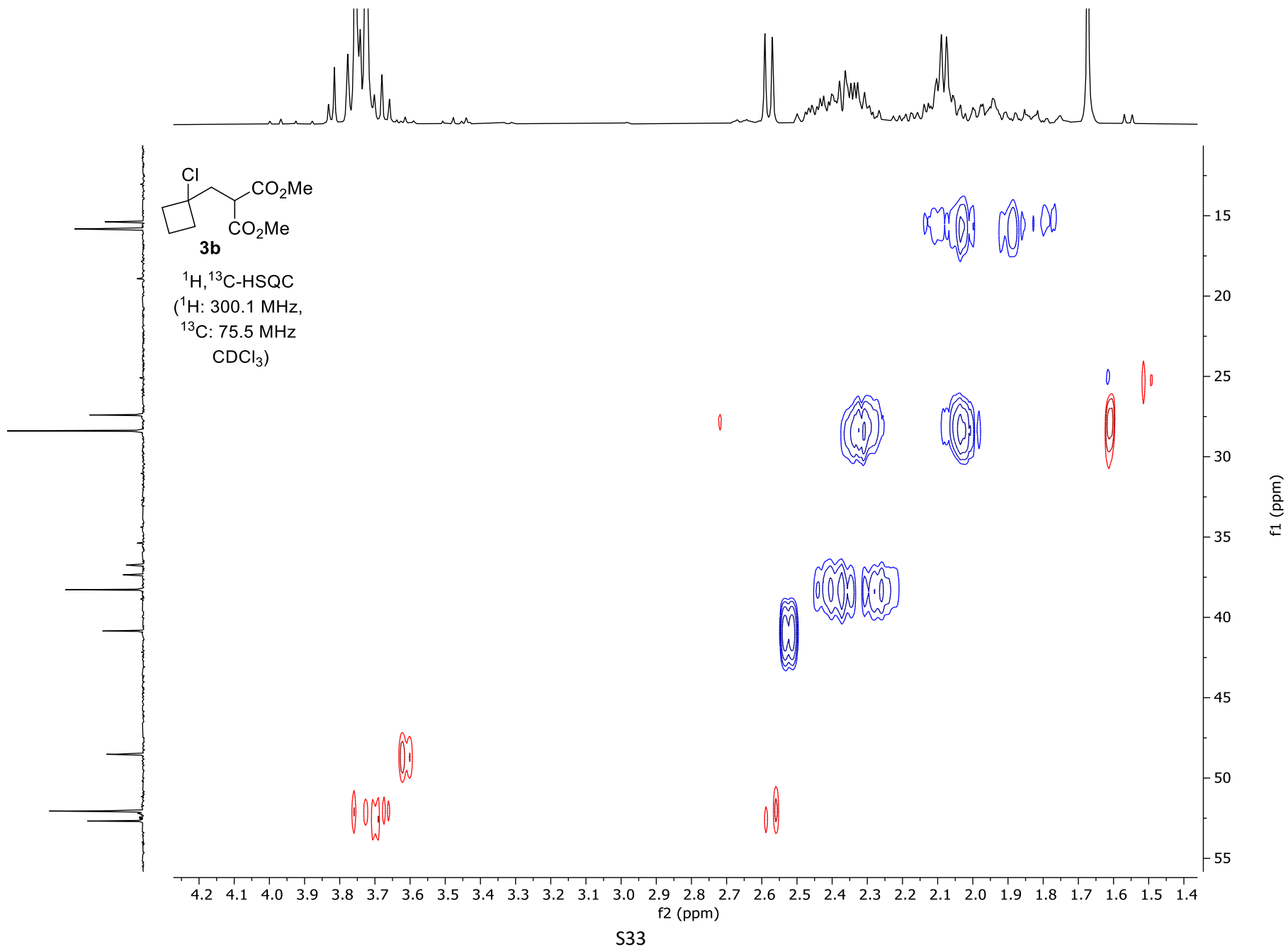


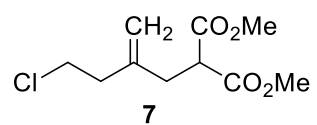




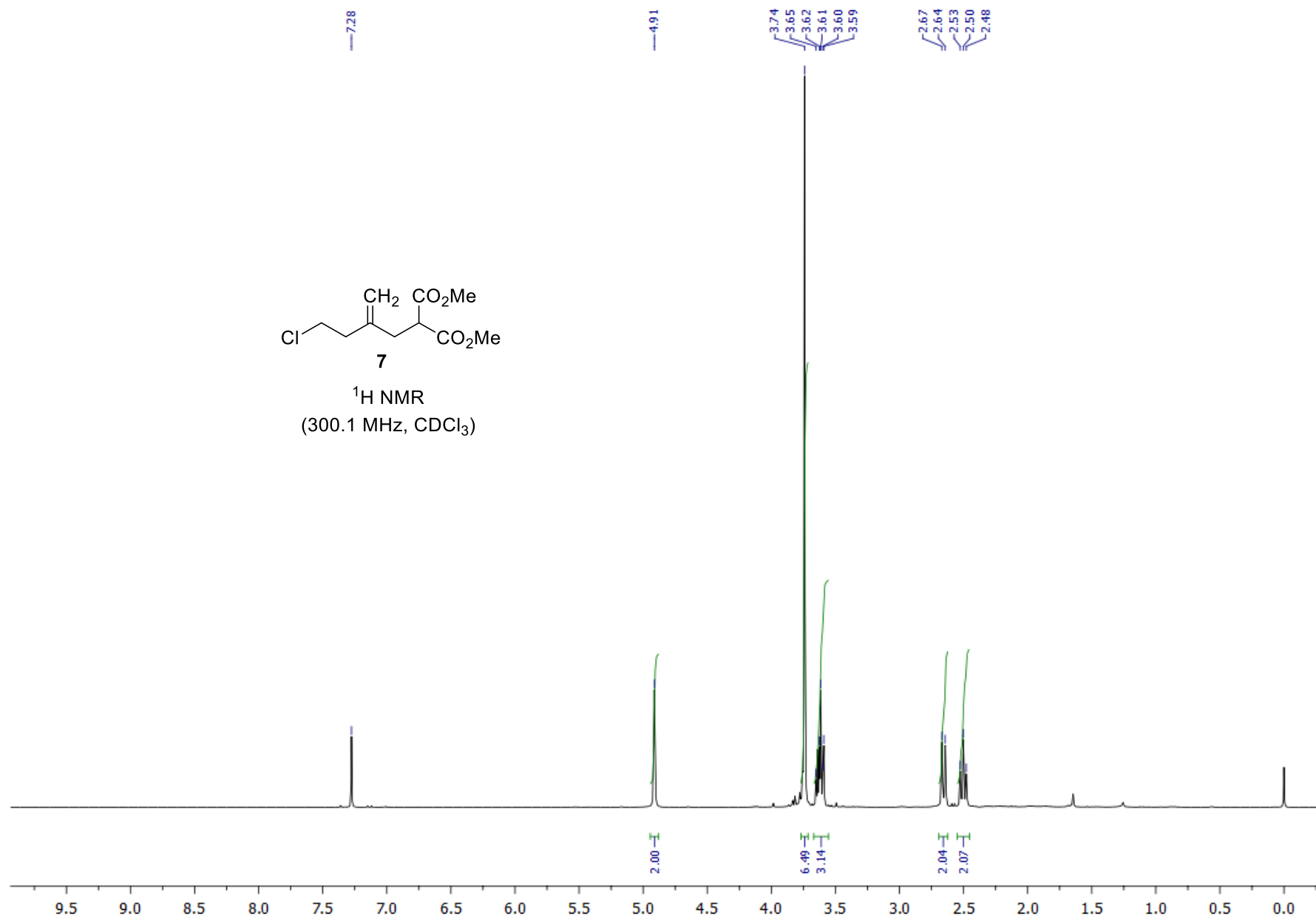
$^1\text{H}, ^1\text{H}$ -COSY
(300.1 MHz, CDCl_3)

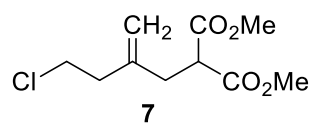




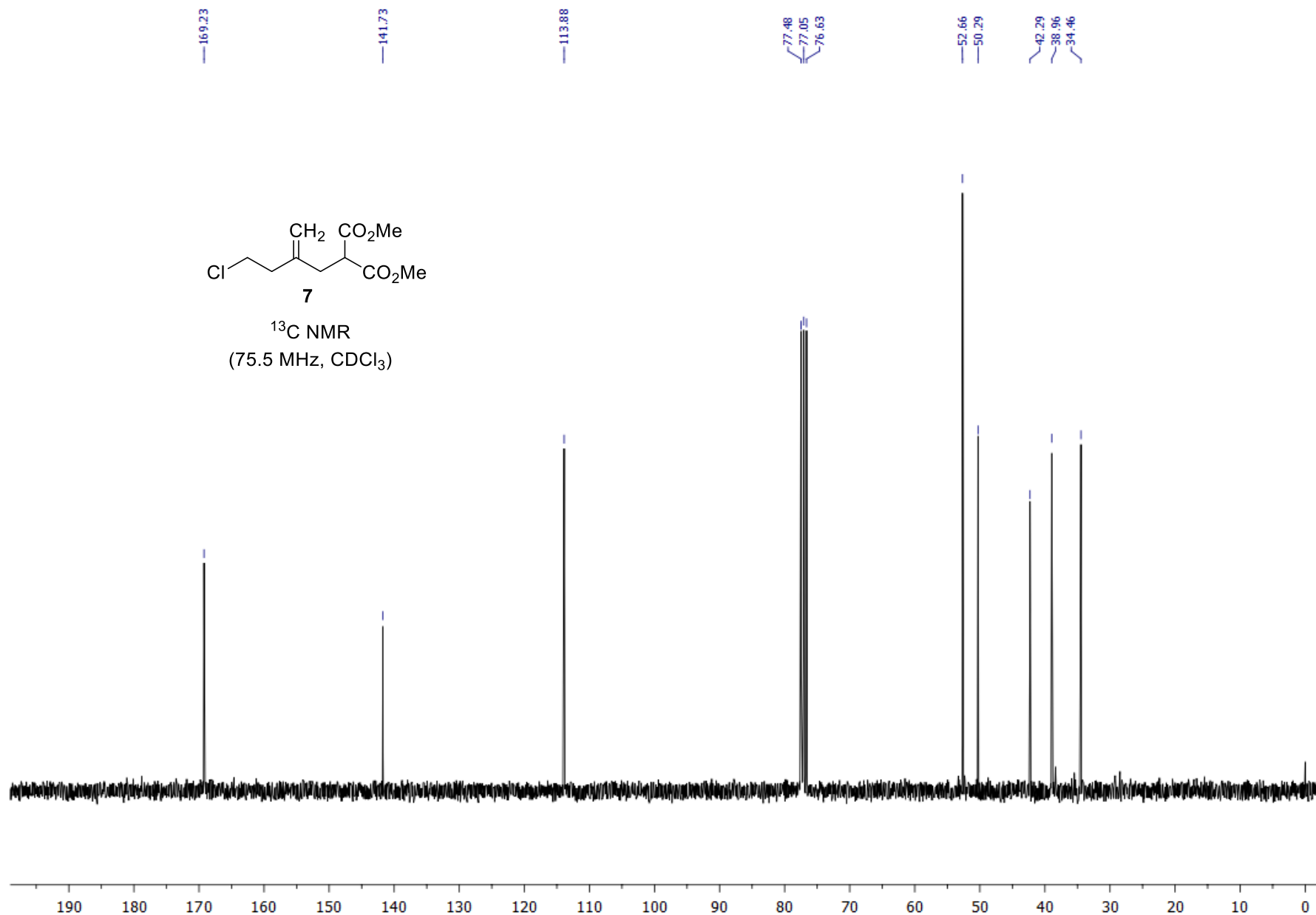


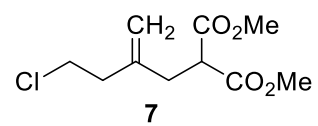
^1H NMR
(300.1 MHz, CDCl_3)



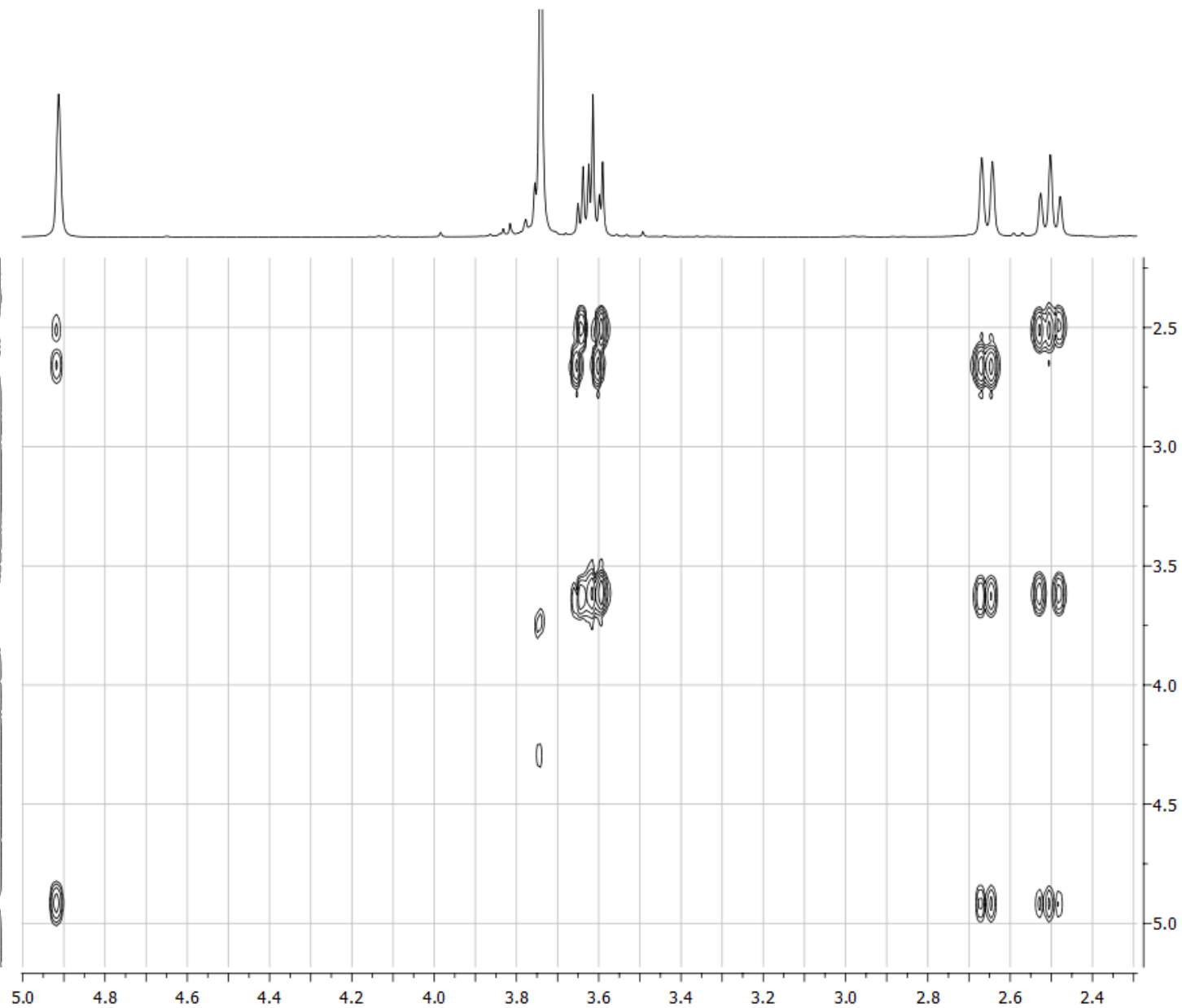


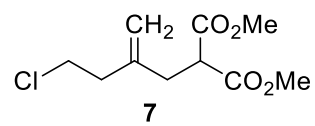
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(75.5 MHz, CDCl_3)



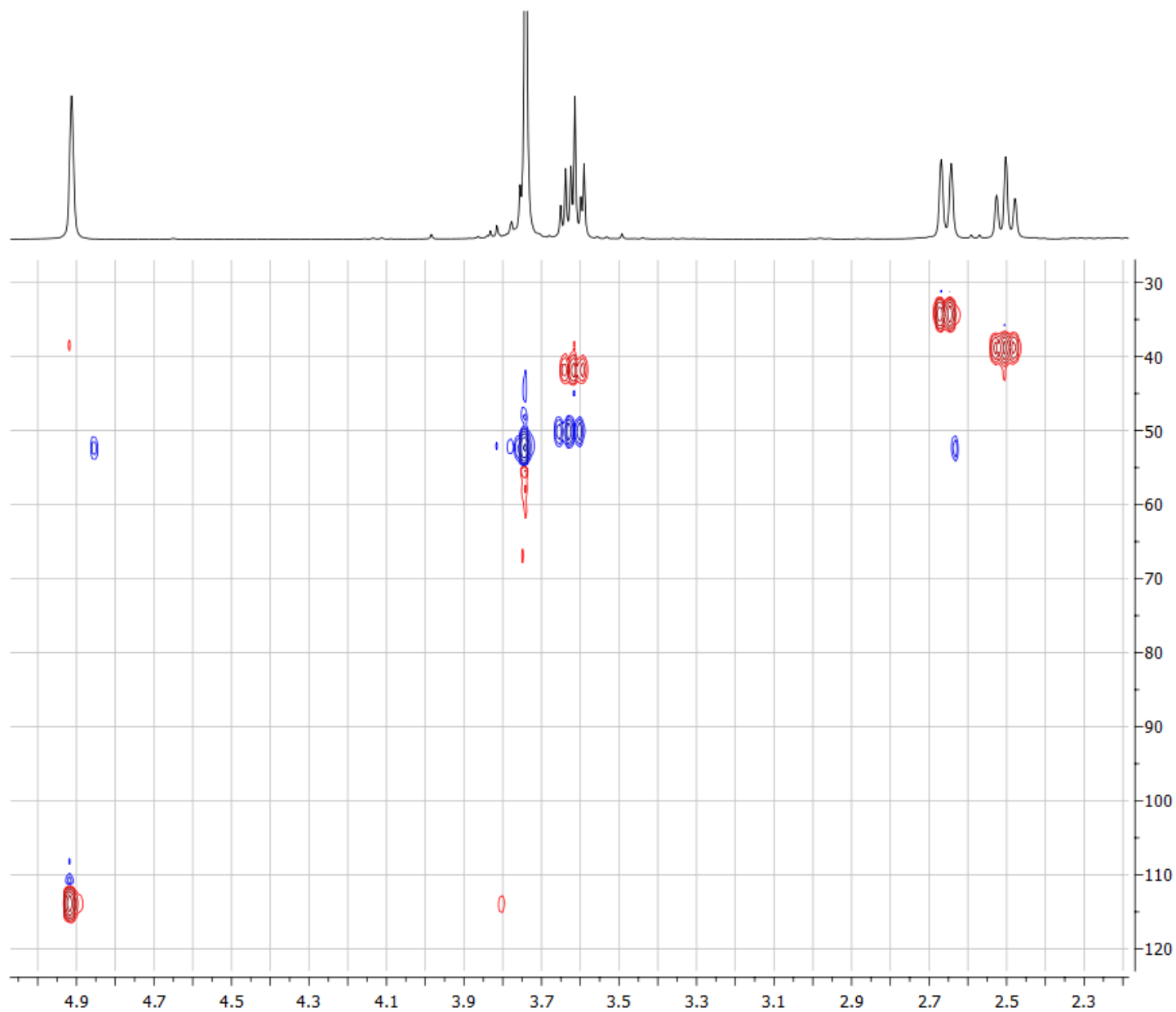


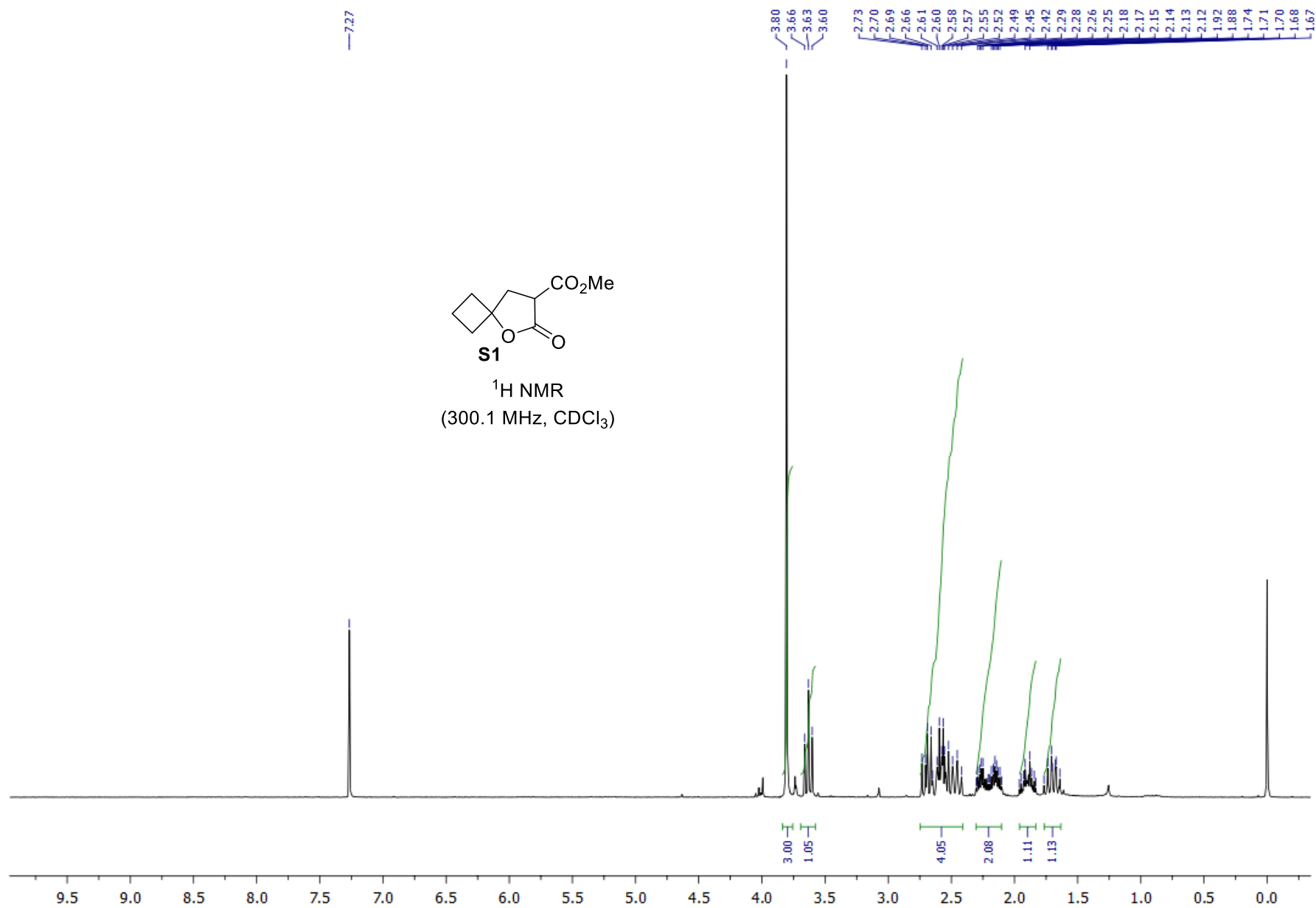
$^1\text{H}, ^1\text{H}$ -COSY
(300.1 MHz, CDCl_3)

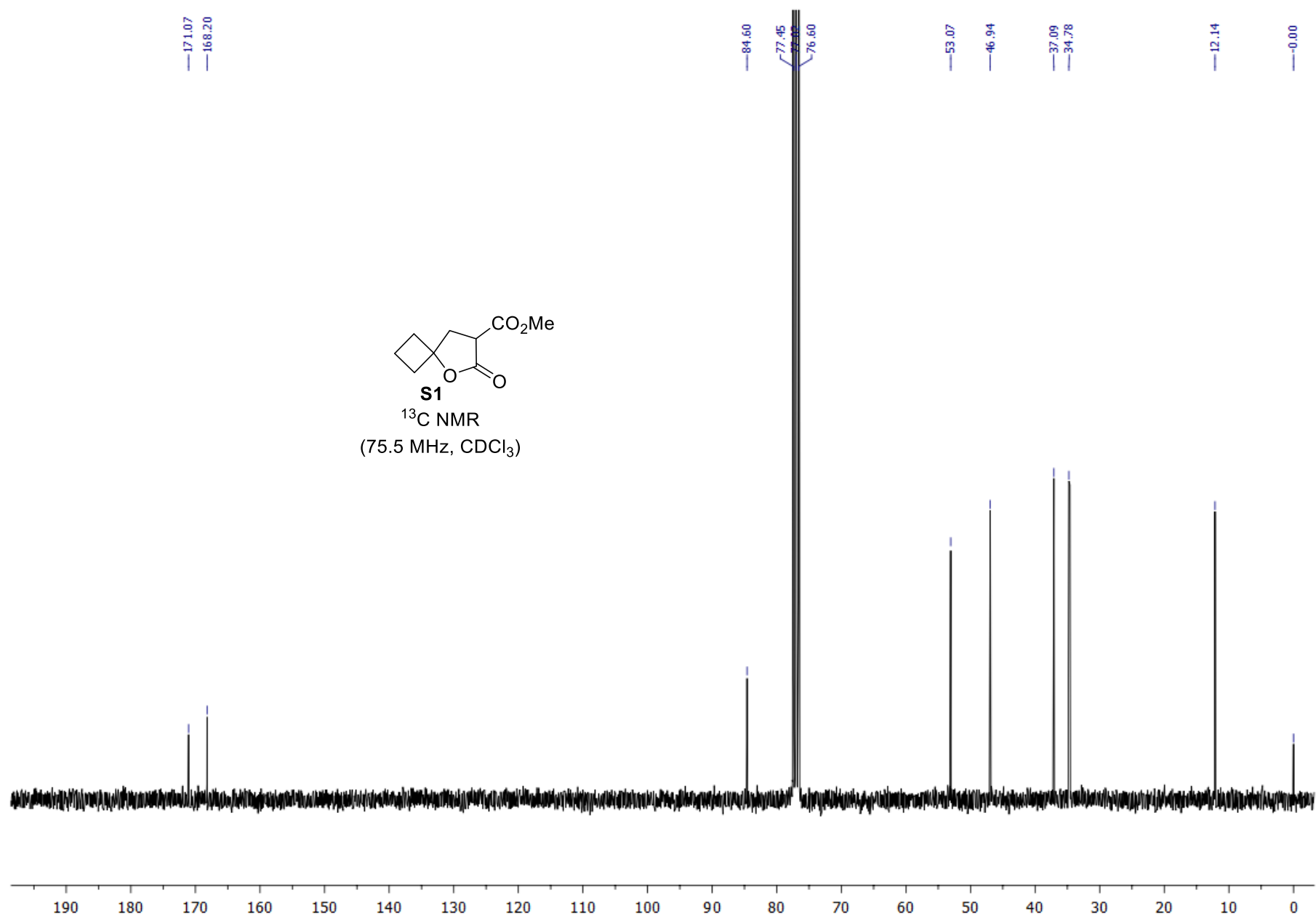


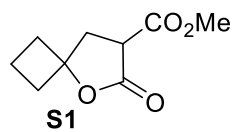


$^1\text{H}, ^{13}\text{C}$ -HSQC
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 CDCl_3)

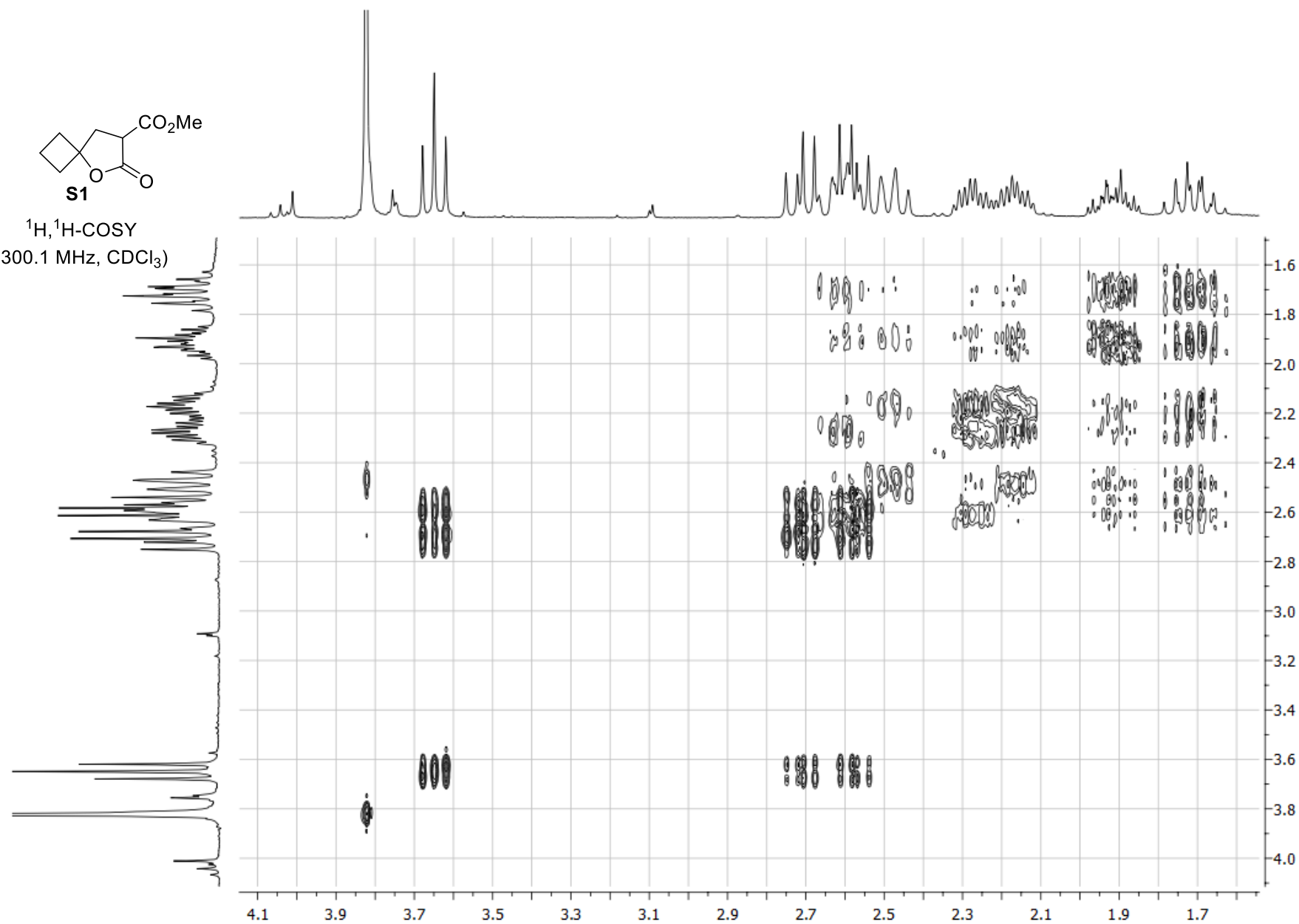


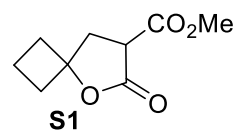




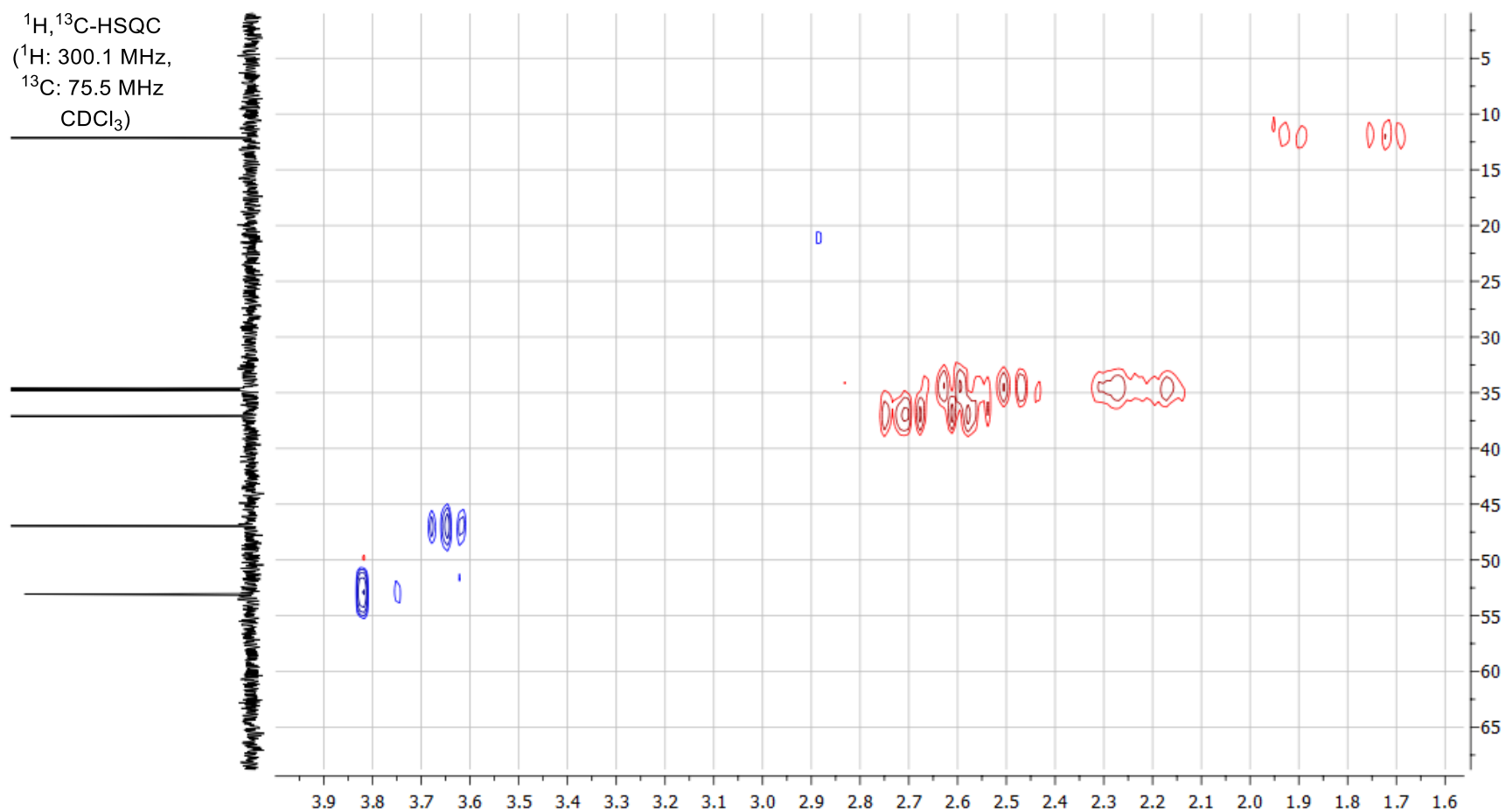


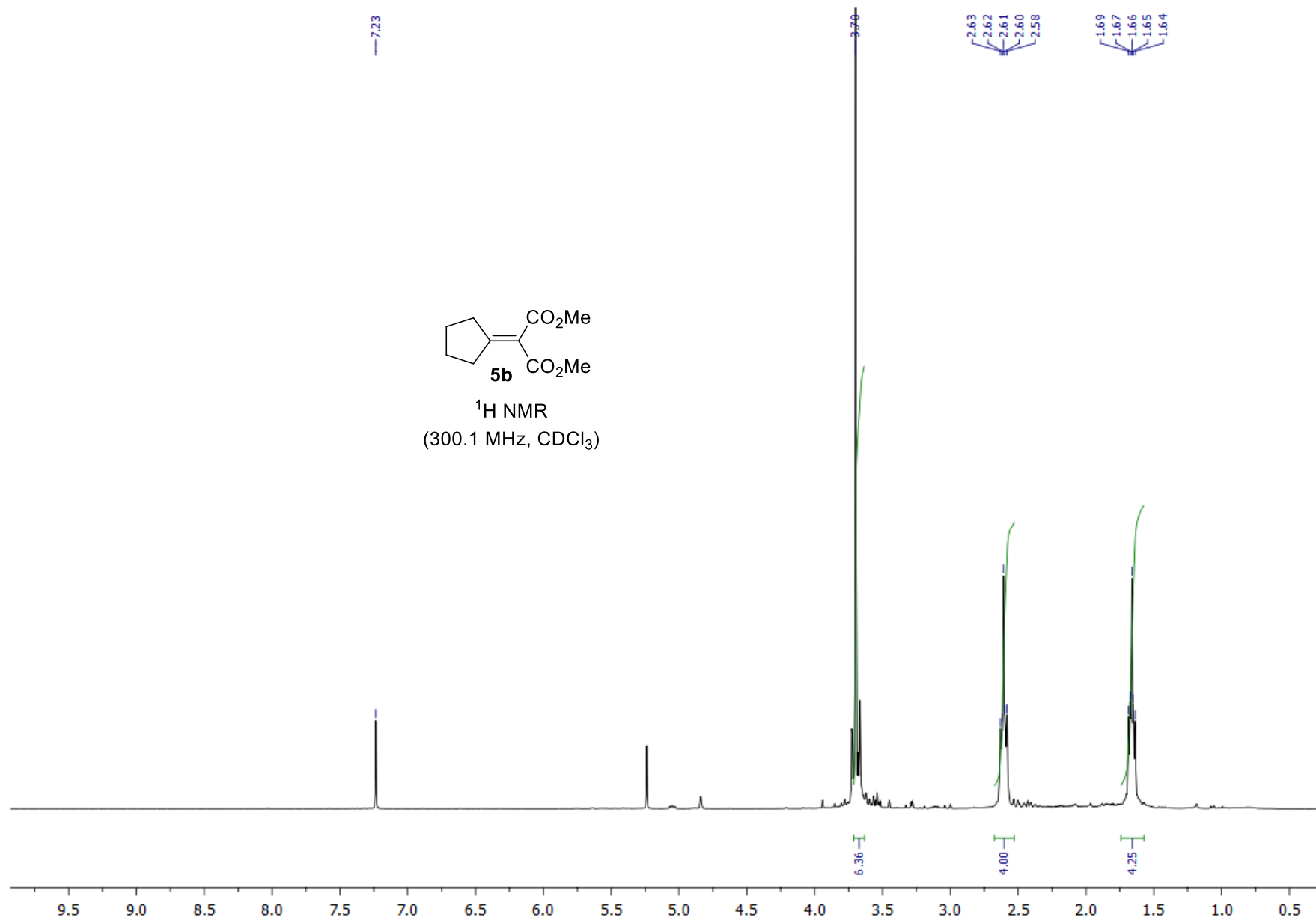
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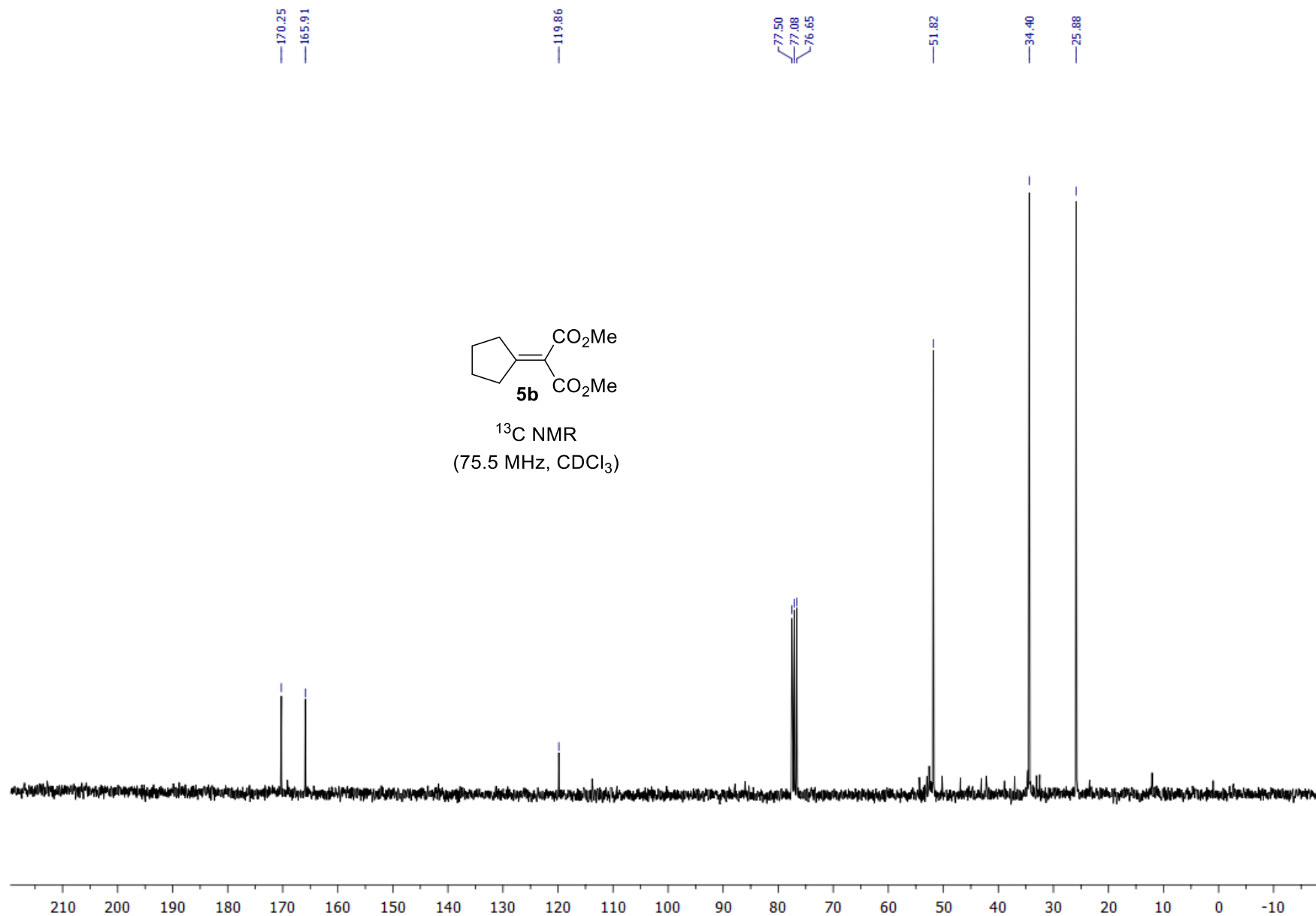


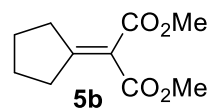


$^1\text{H}, ^{13}\text{C}$ -HSQC
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 CDCl_3)

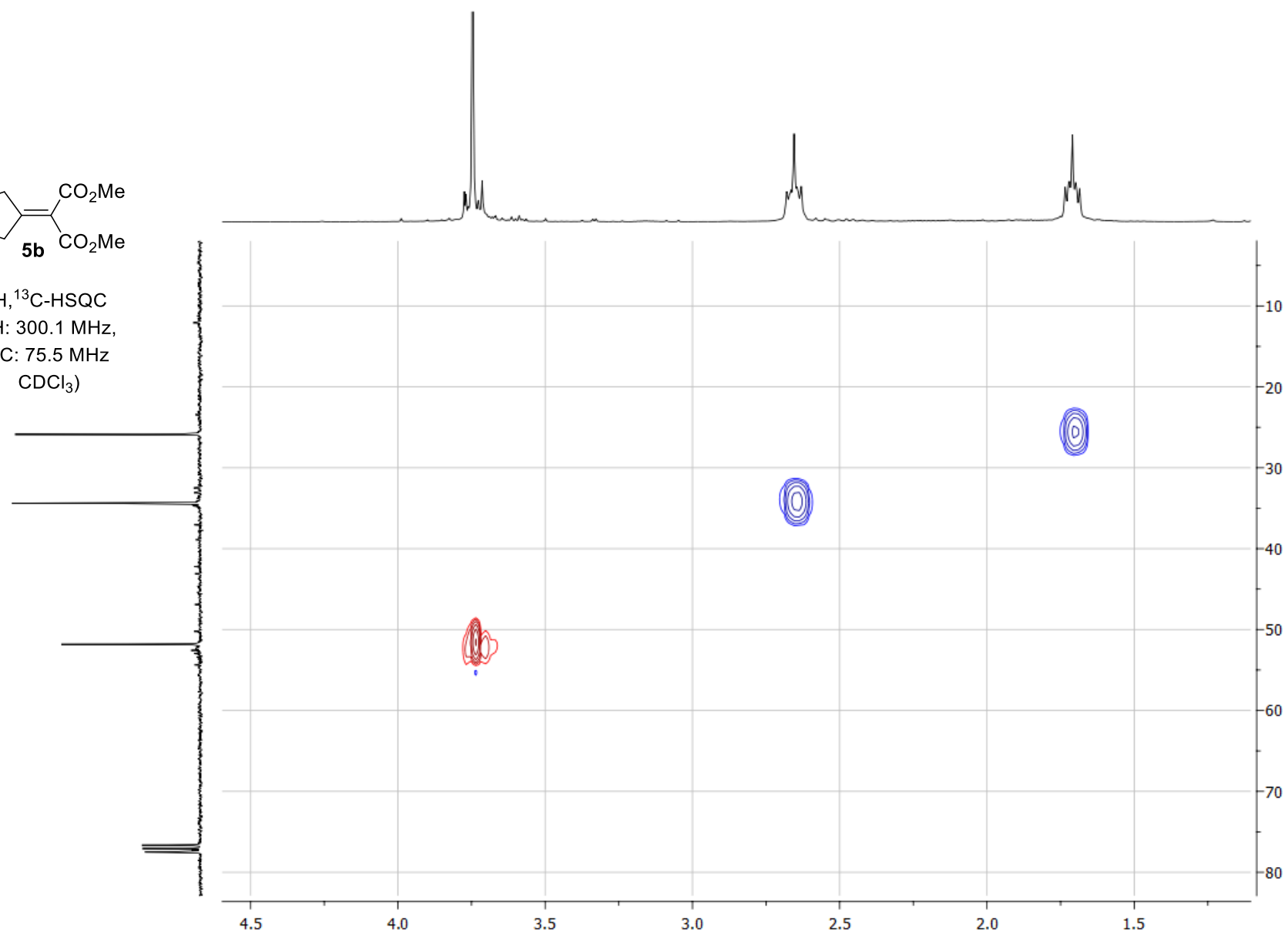


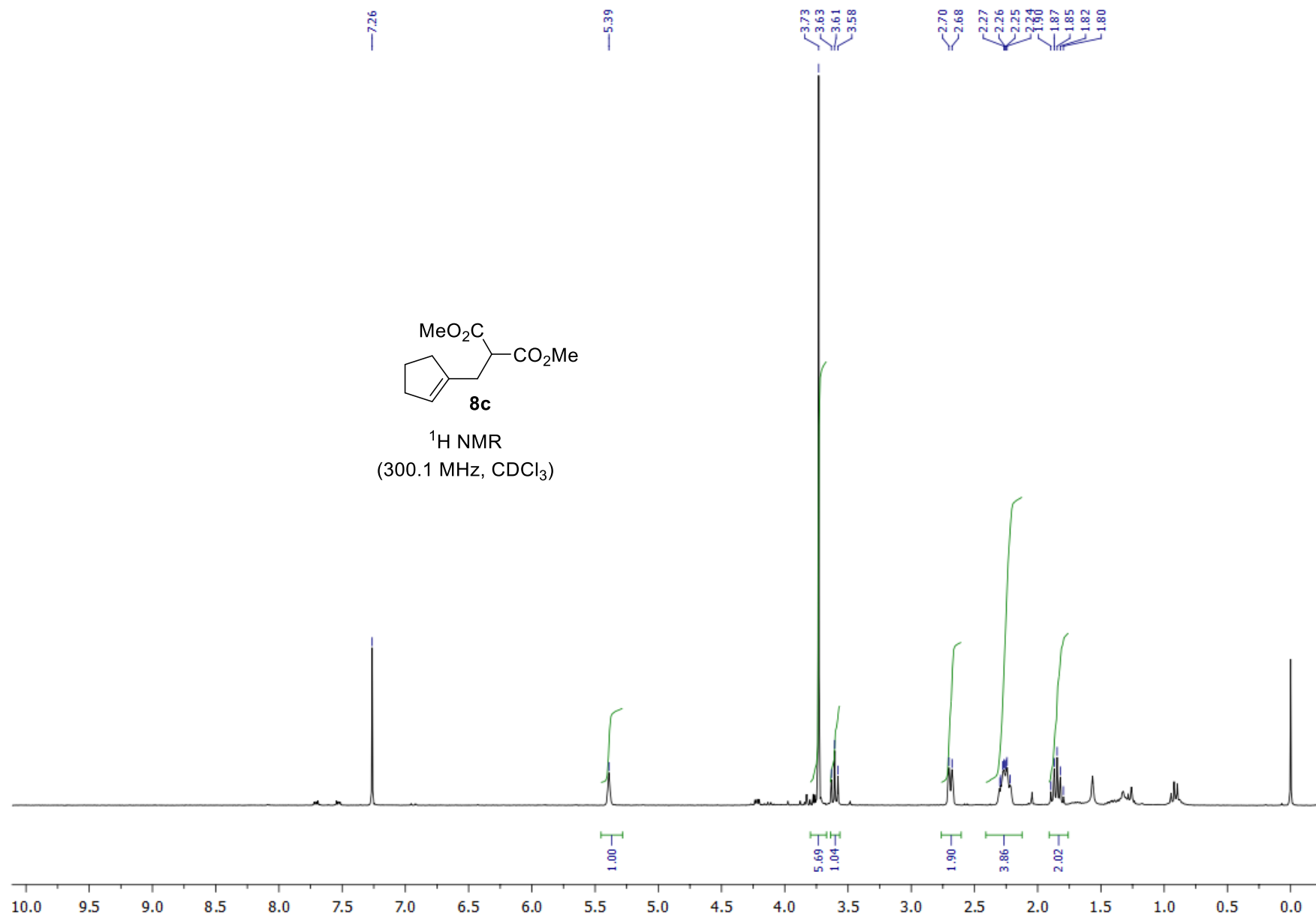


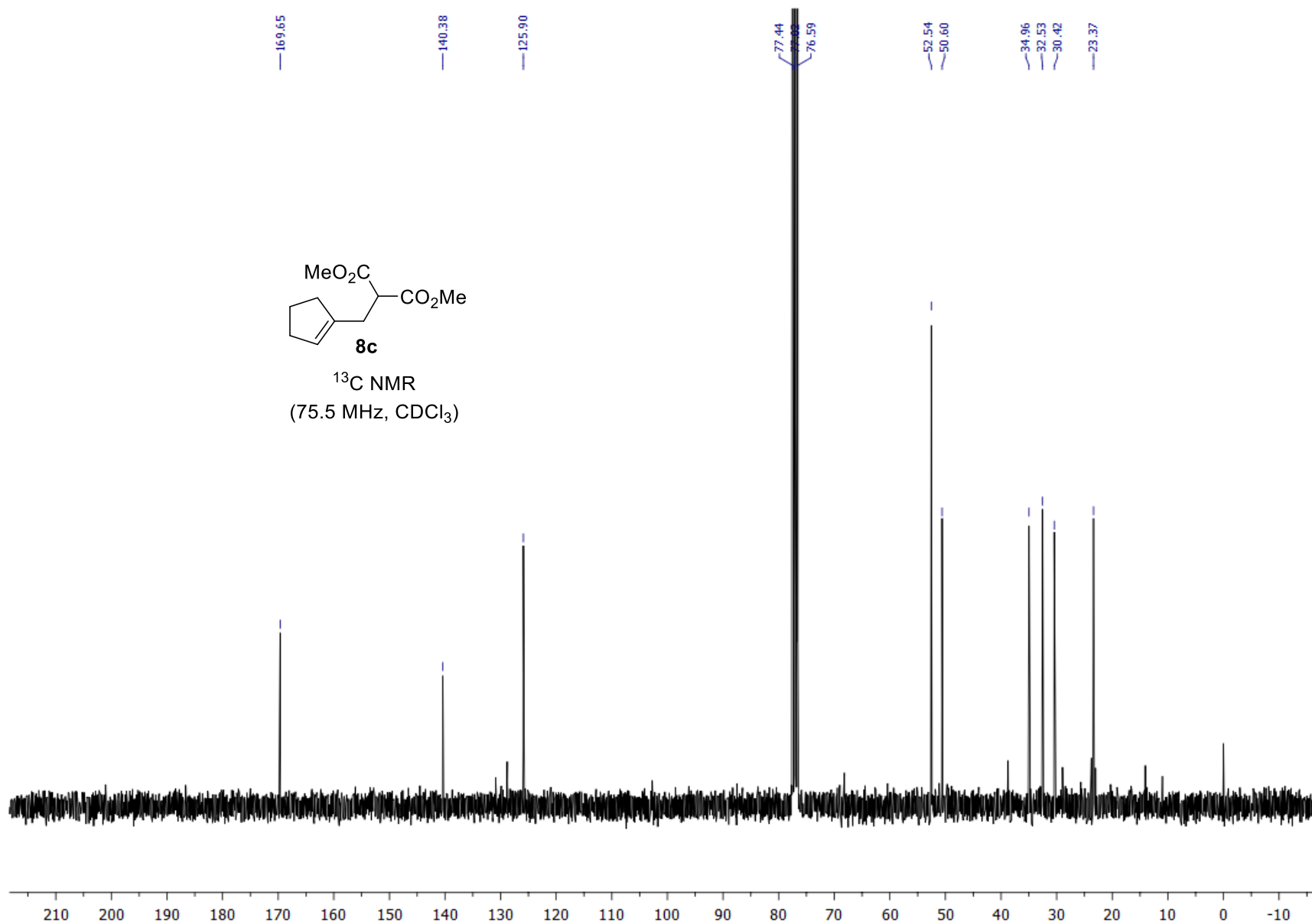


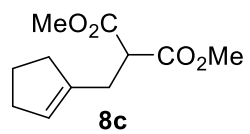


$^1\text{H}, ^{13}\text{C}$ -HSQC
 (^1H : 300.1 MHz,
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 CDCl_3)

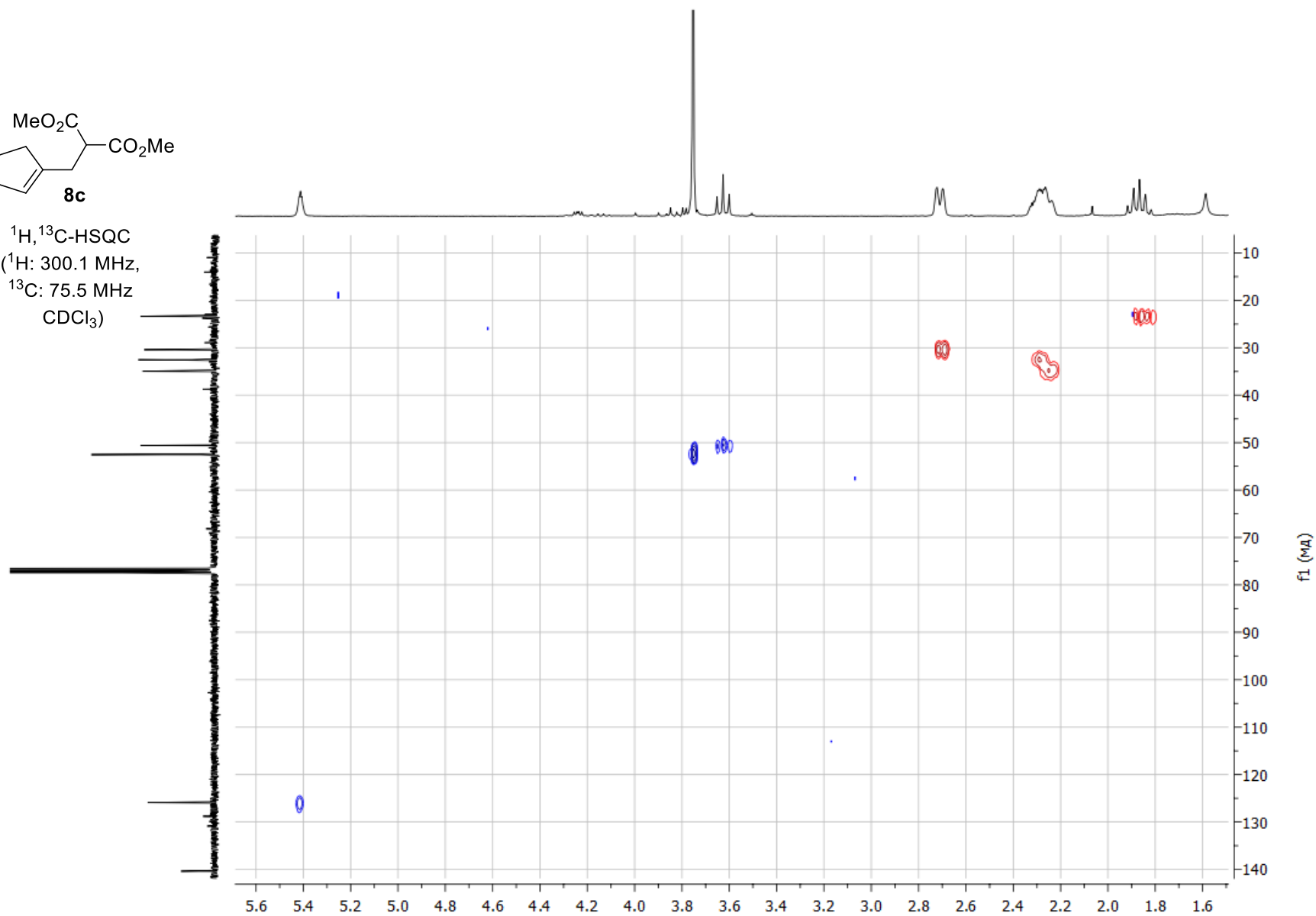


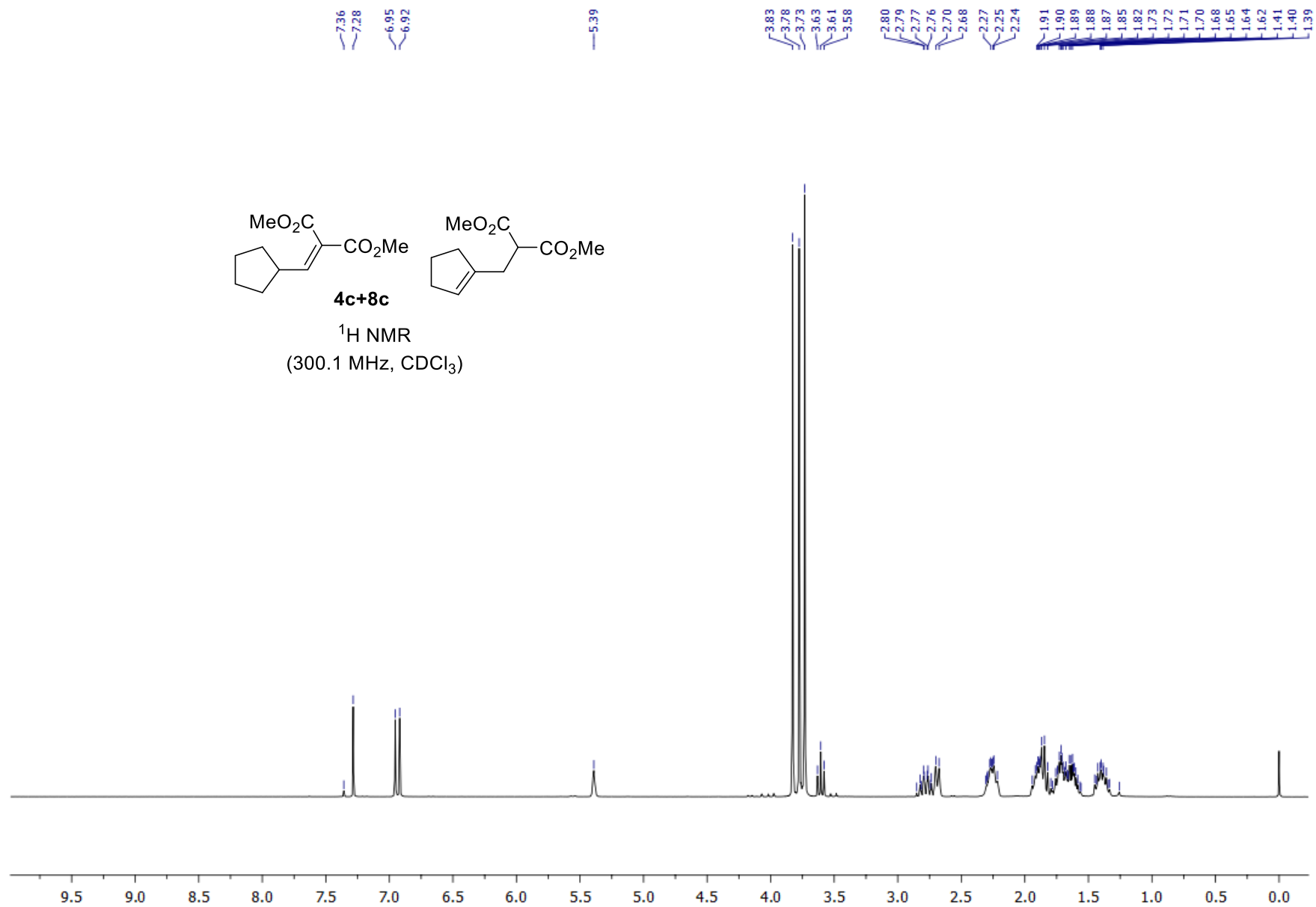






^1H , ^{13}C -HSQC
 (^1H : 300.1 MHz,
 ^{13}C : 75.5 MHz
 CDCl_3)





169.60
166.16
164.53

154.91

140.37

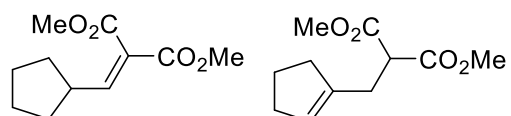
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125.87

77.47
77.05
76.52

52.50
52.26
52.22
50.57

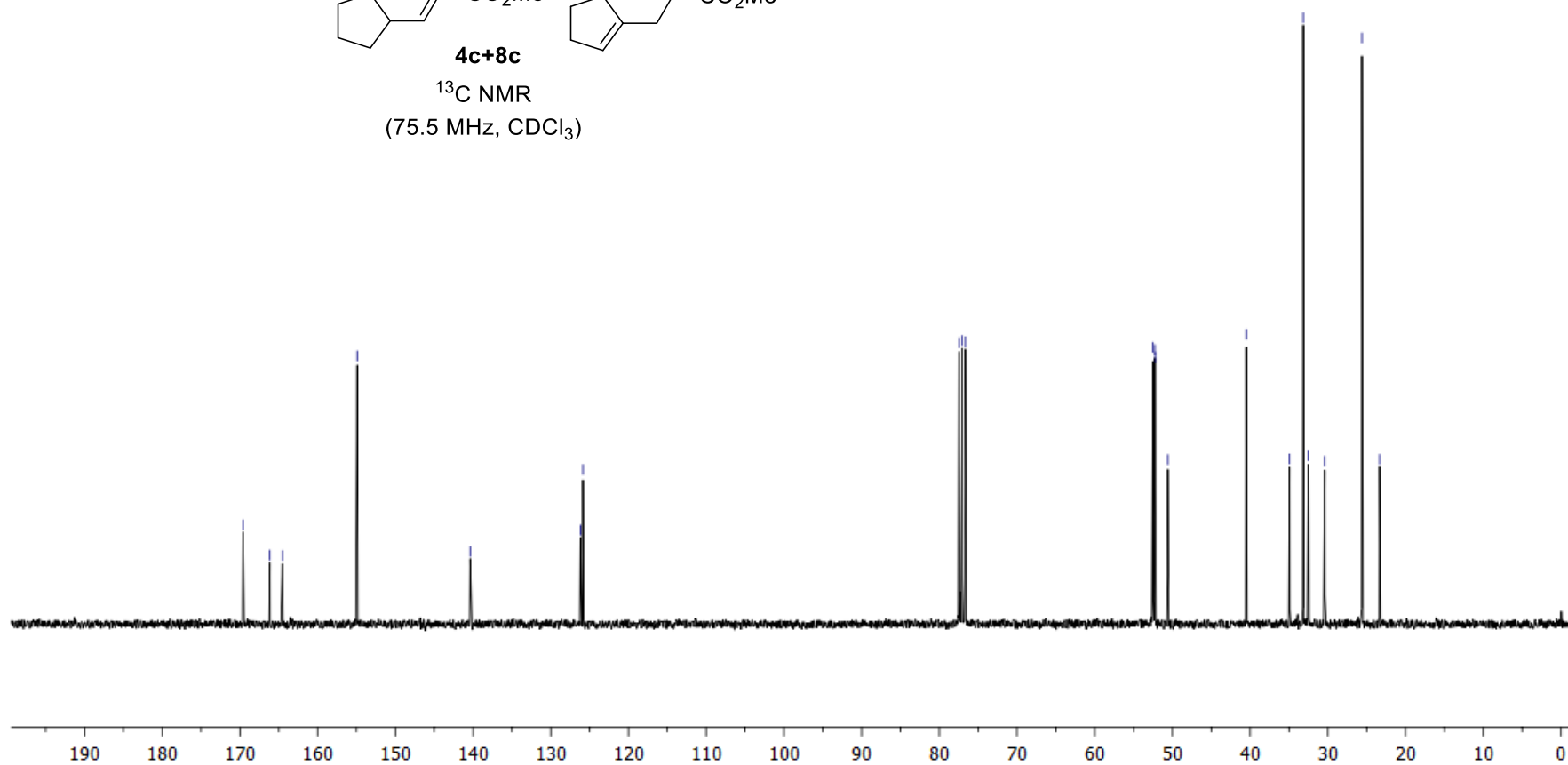
40.50

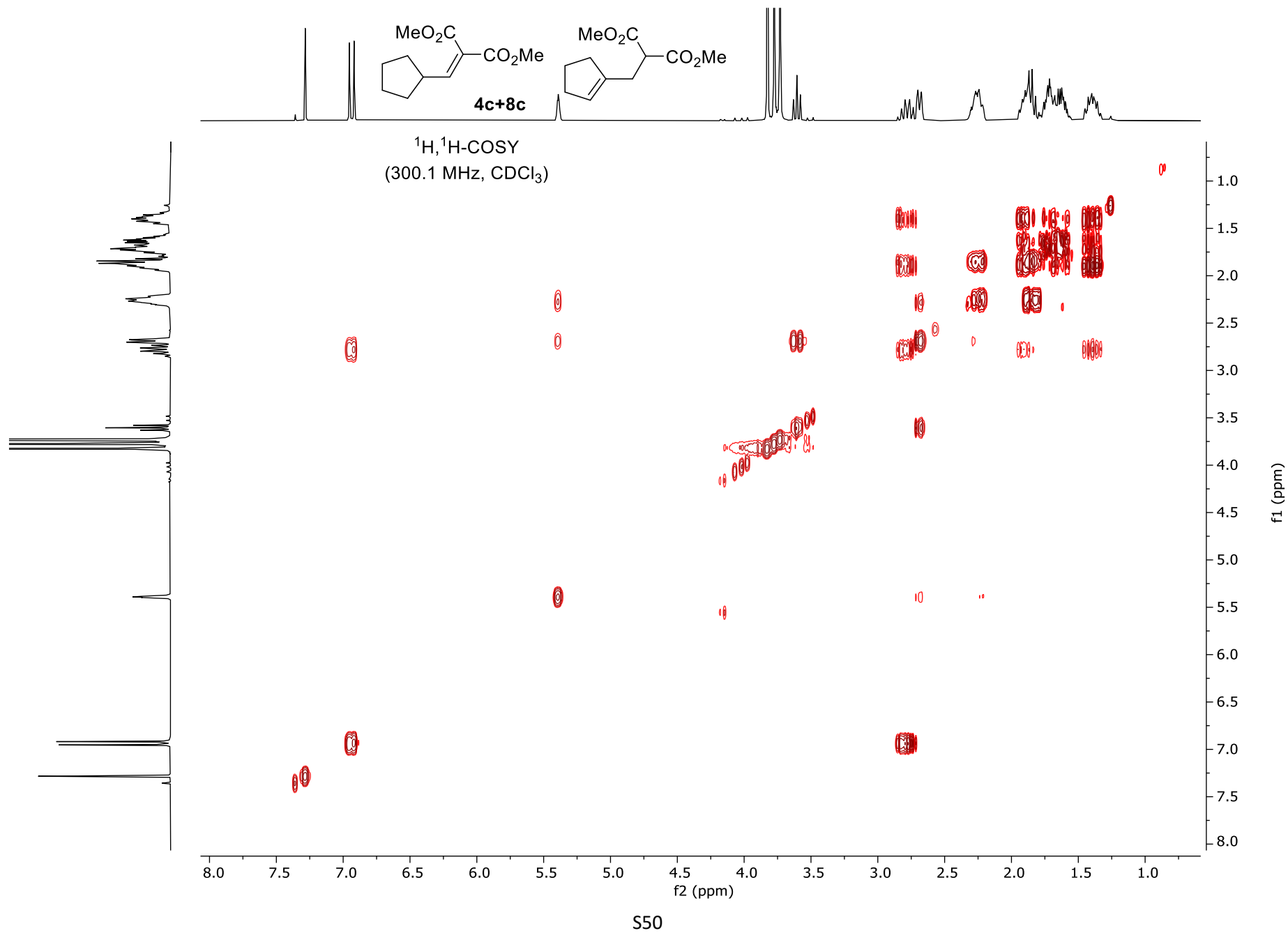
34.93
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23.34

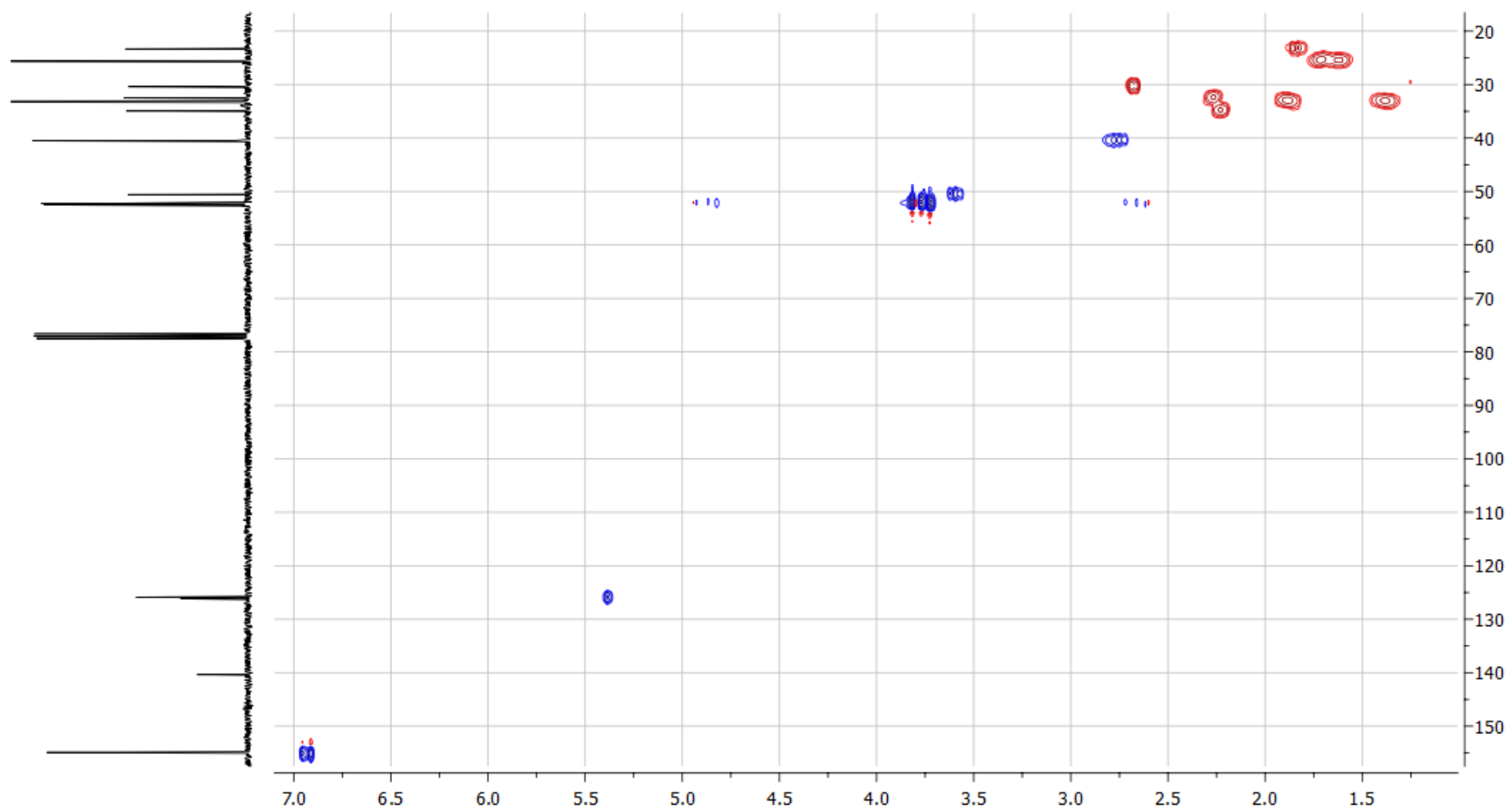
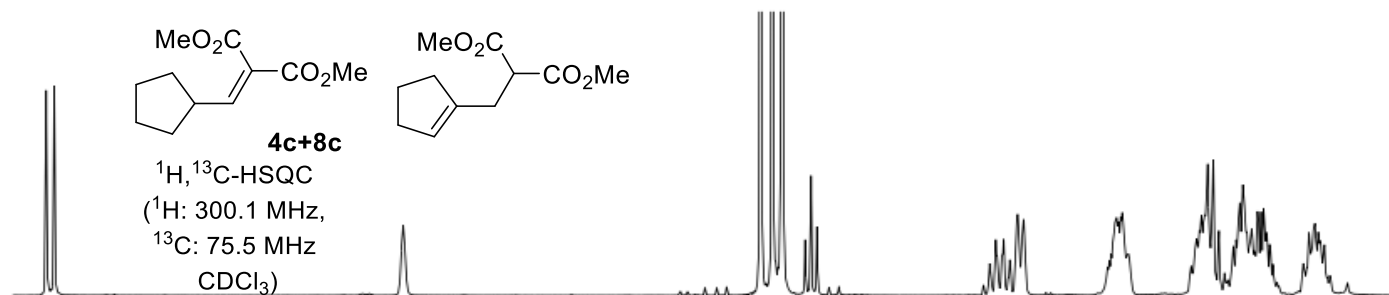


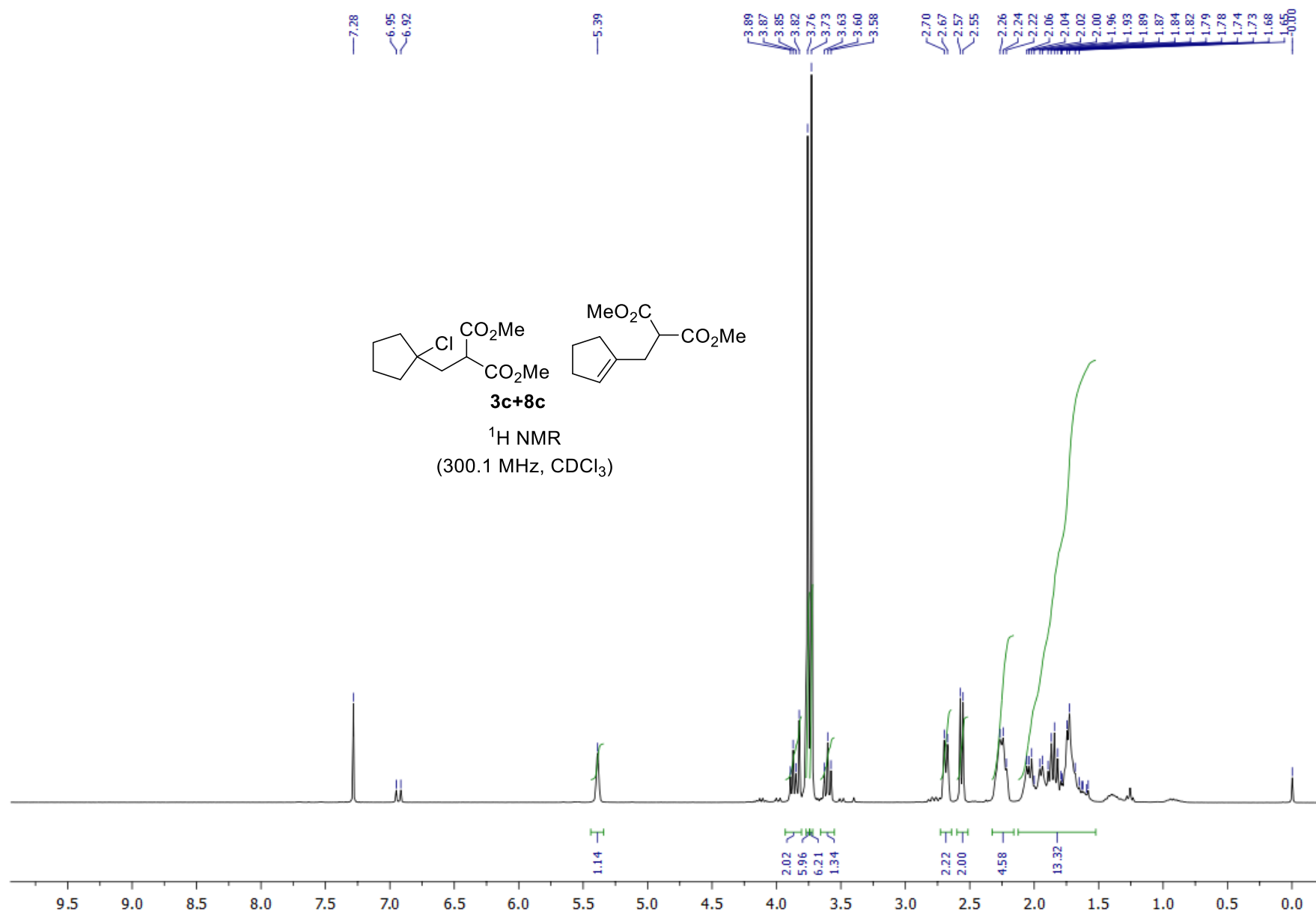
4c+8c

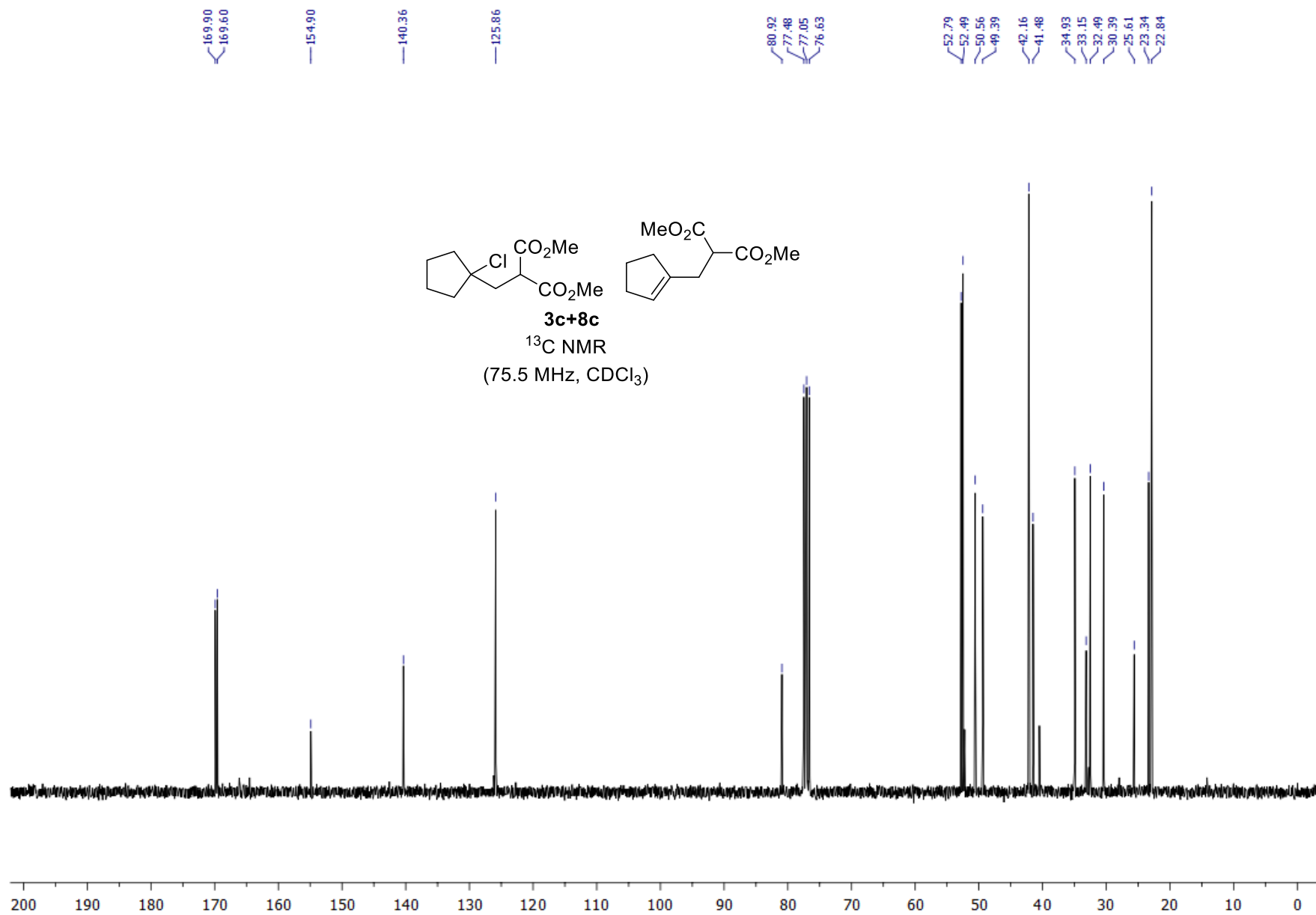
^{13}C NMR
(75.5 MHz, CDCl_3)

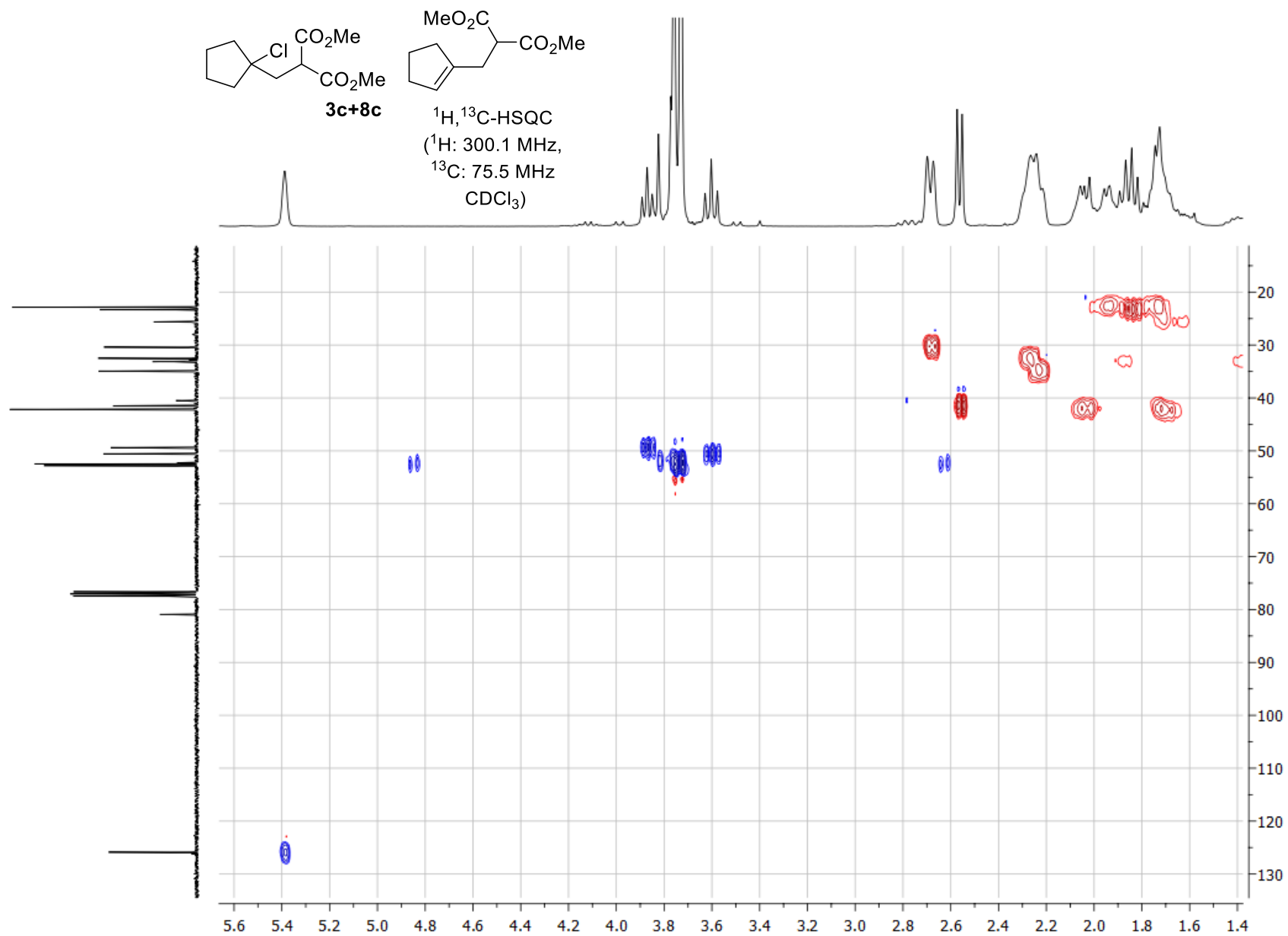


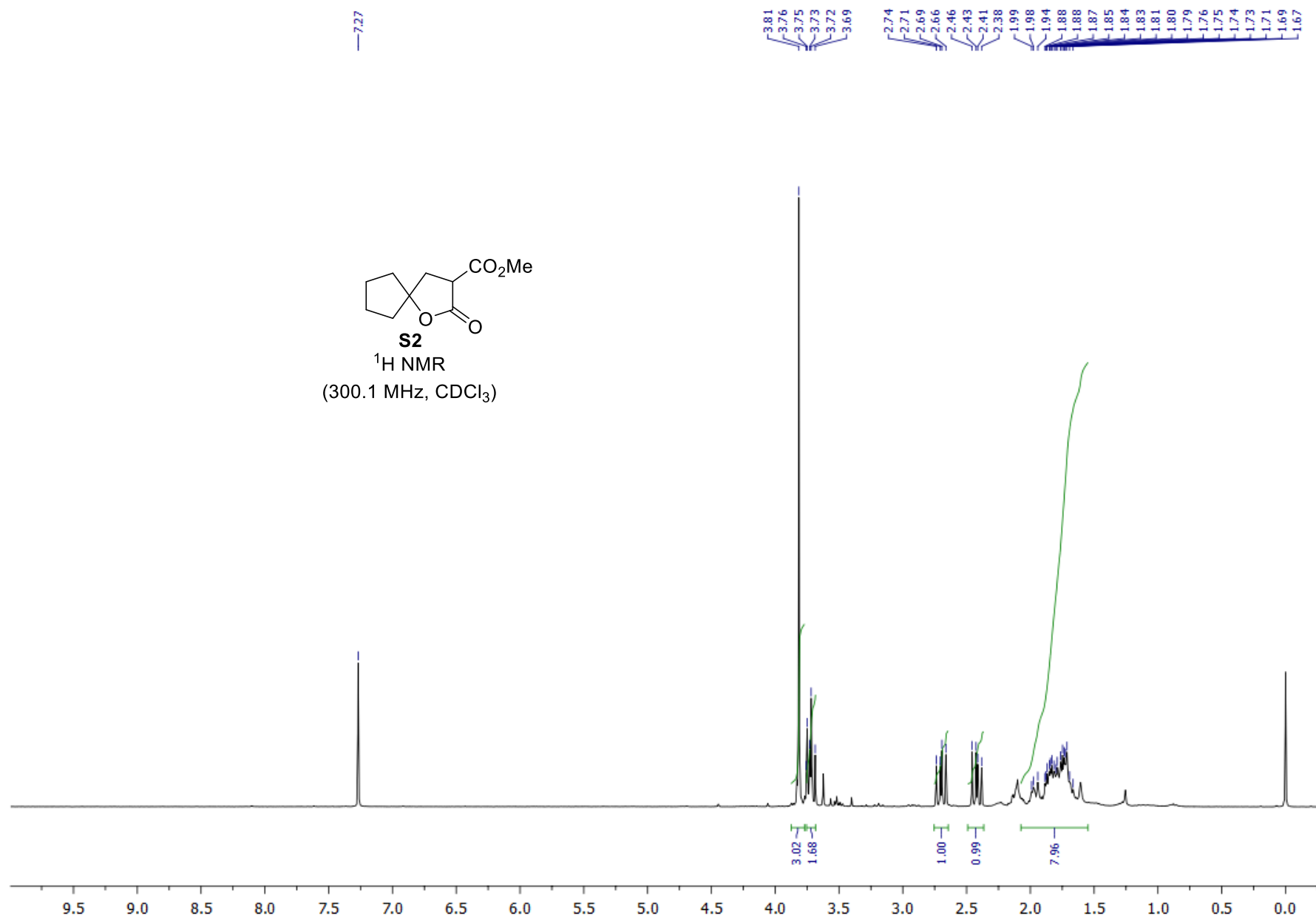
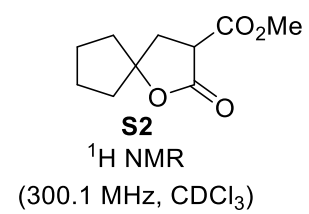


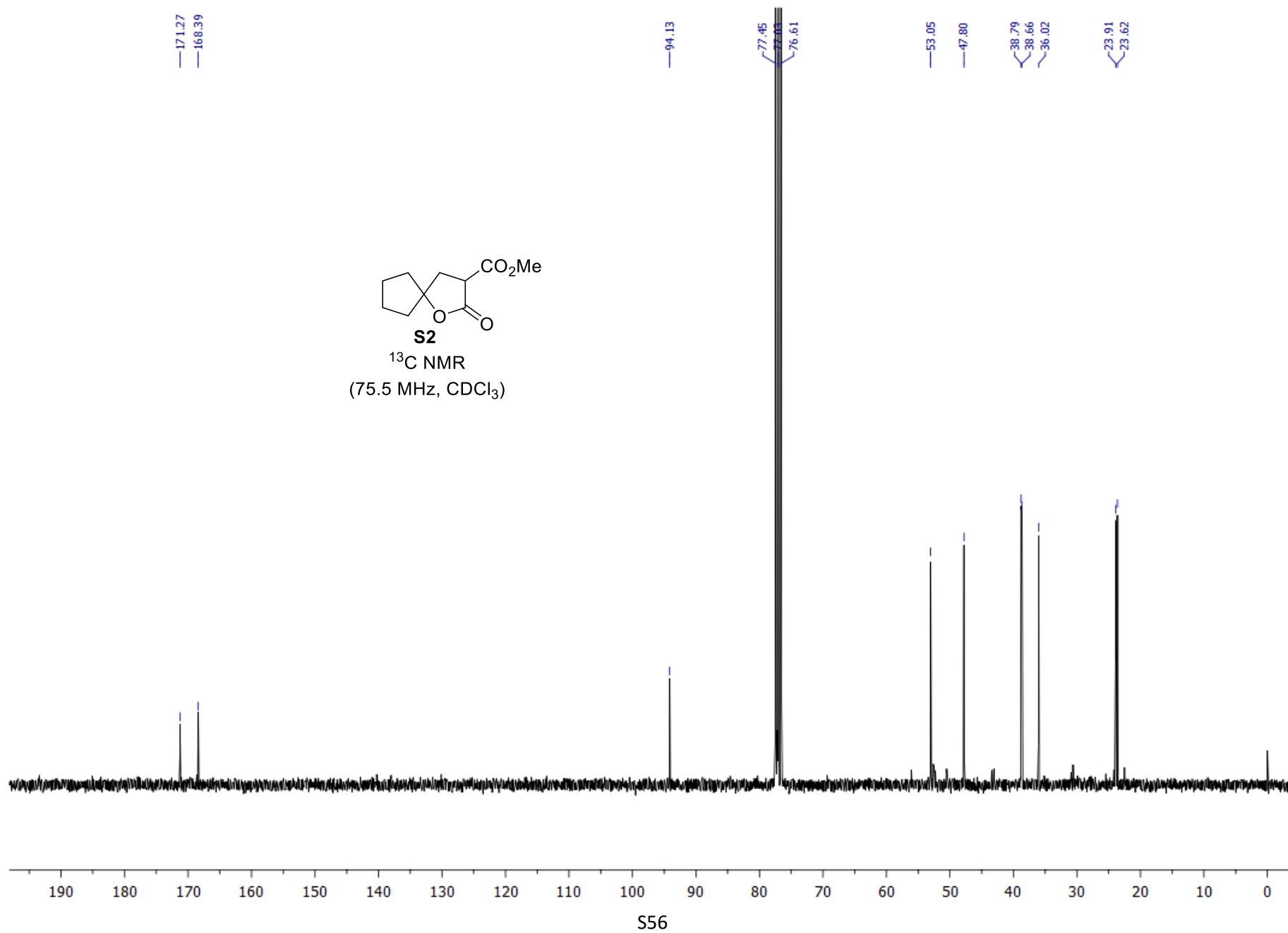
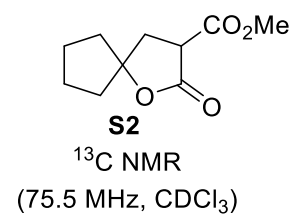


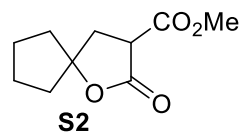




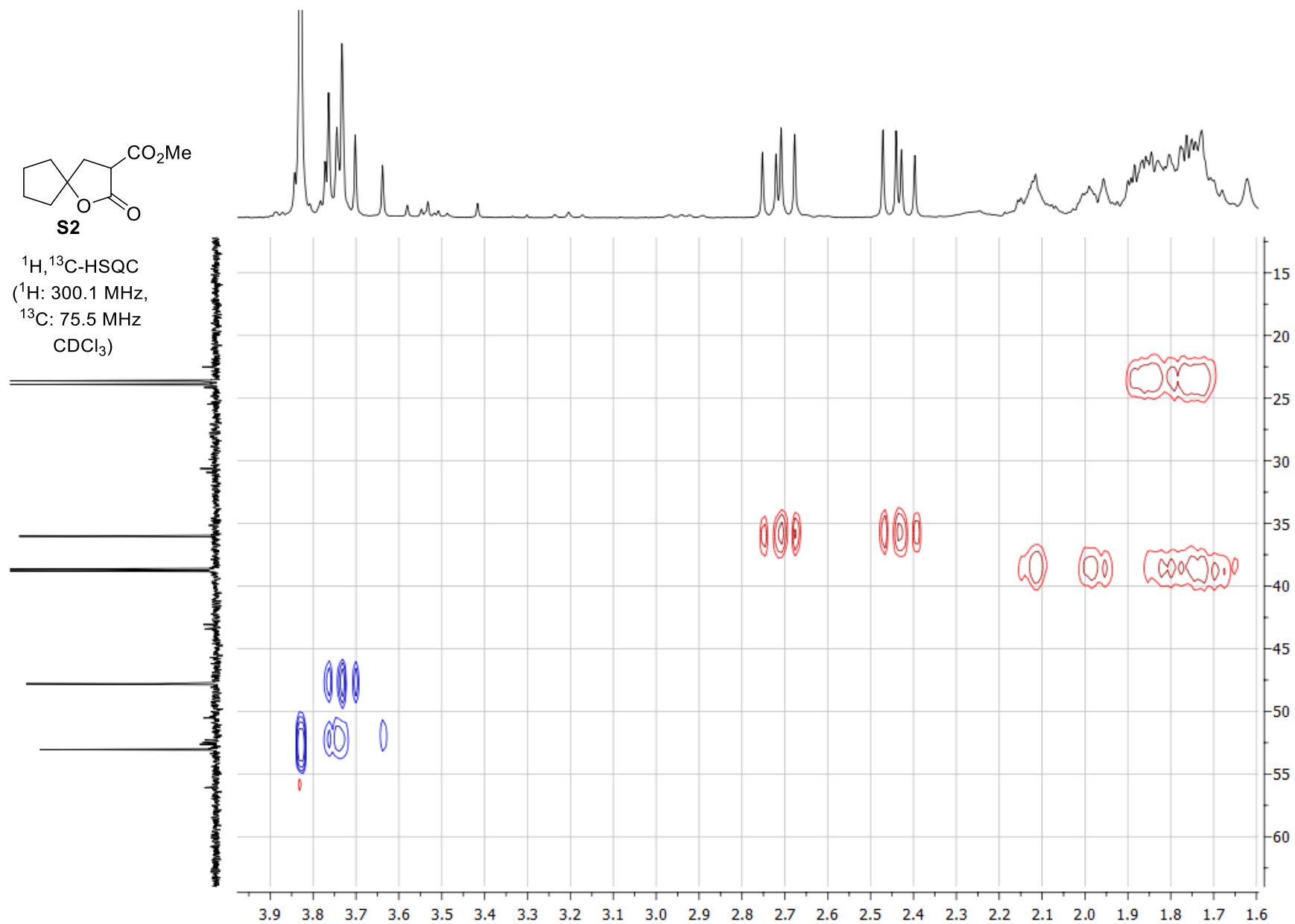


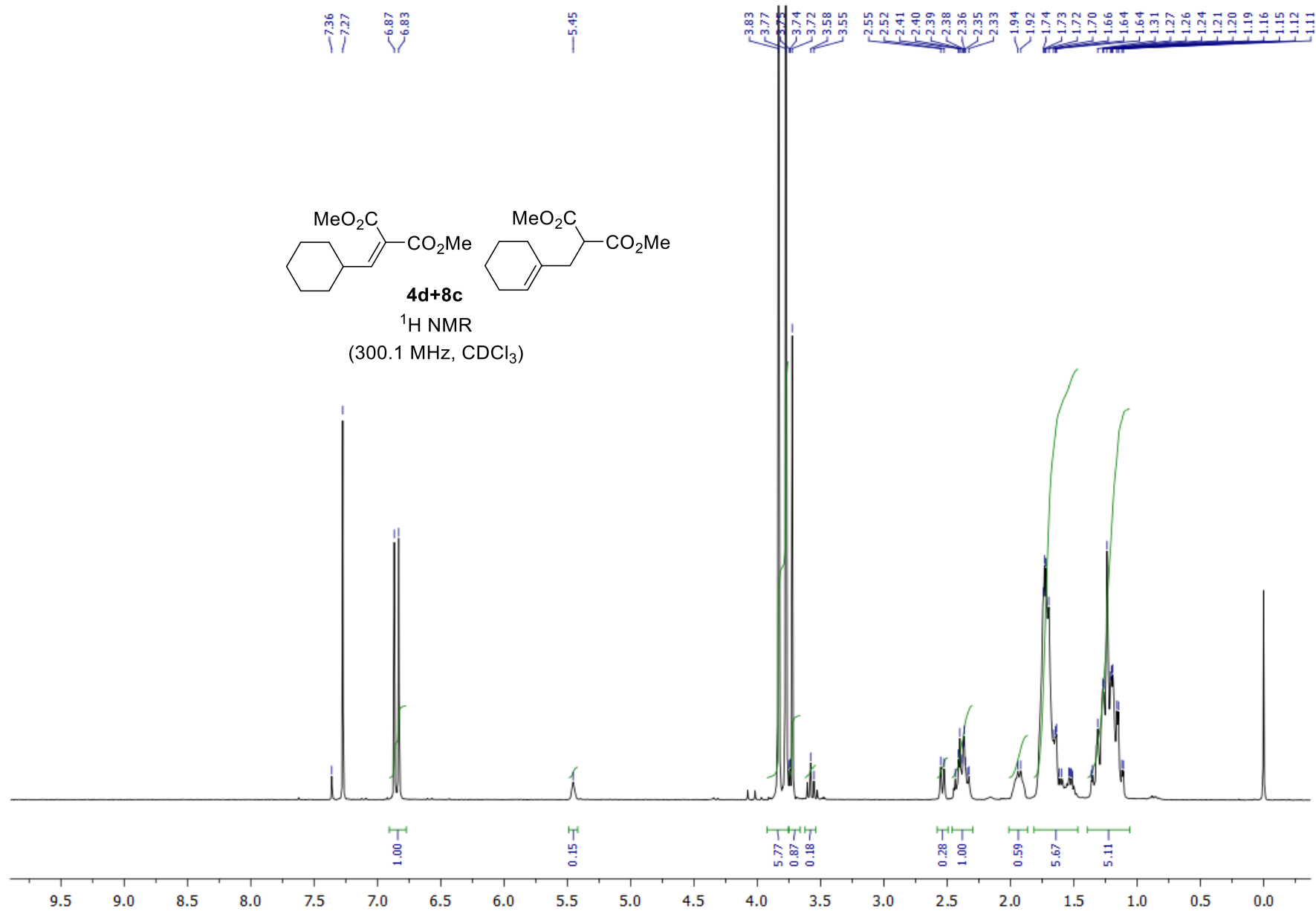


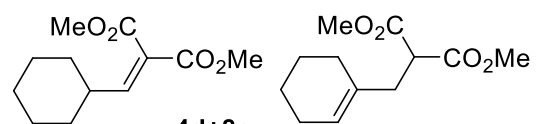




$^1\text{H}, ^{13}\text{C}$ -HSQC
 (^1H : 300.1 MHz,
 ^{13}C : 75.5 MHz
 CDCl_3)

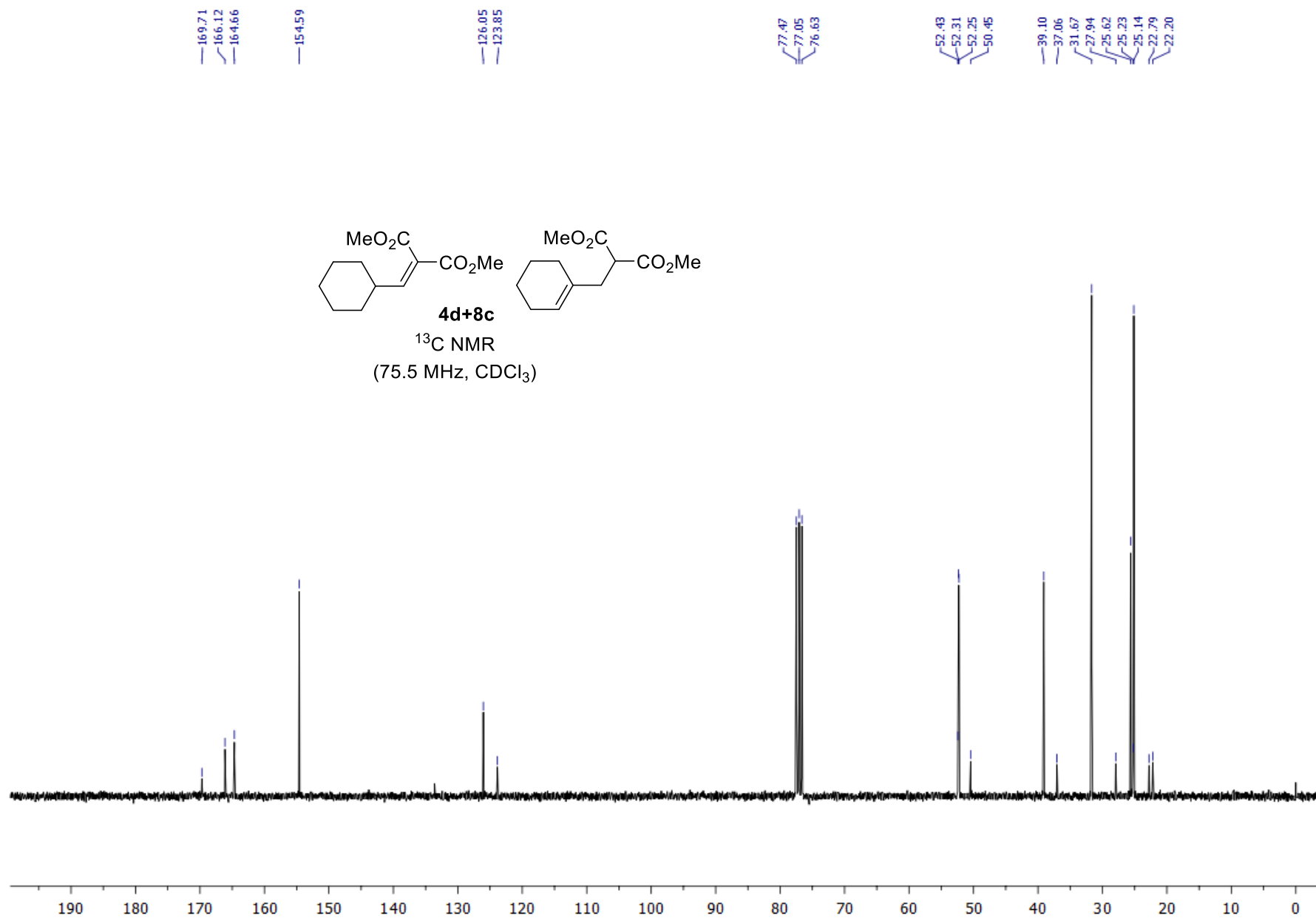


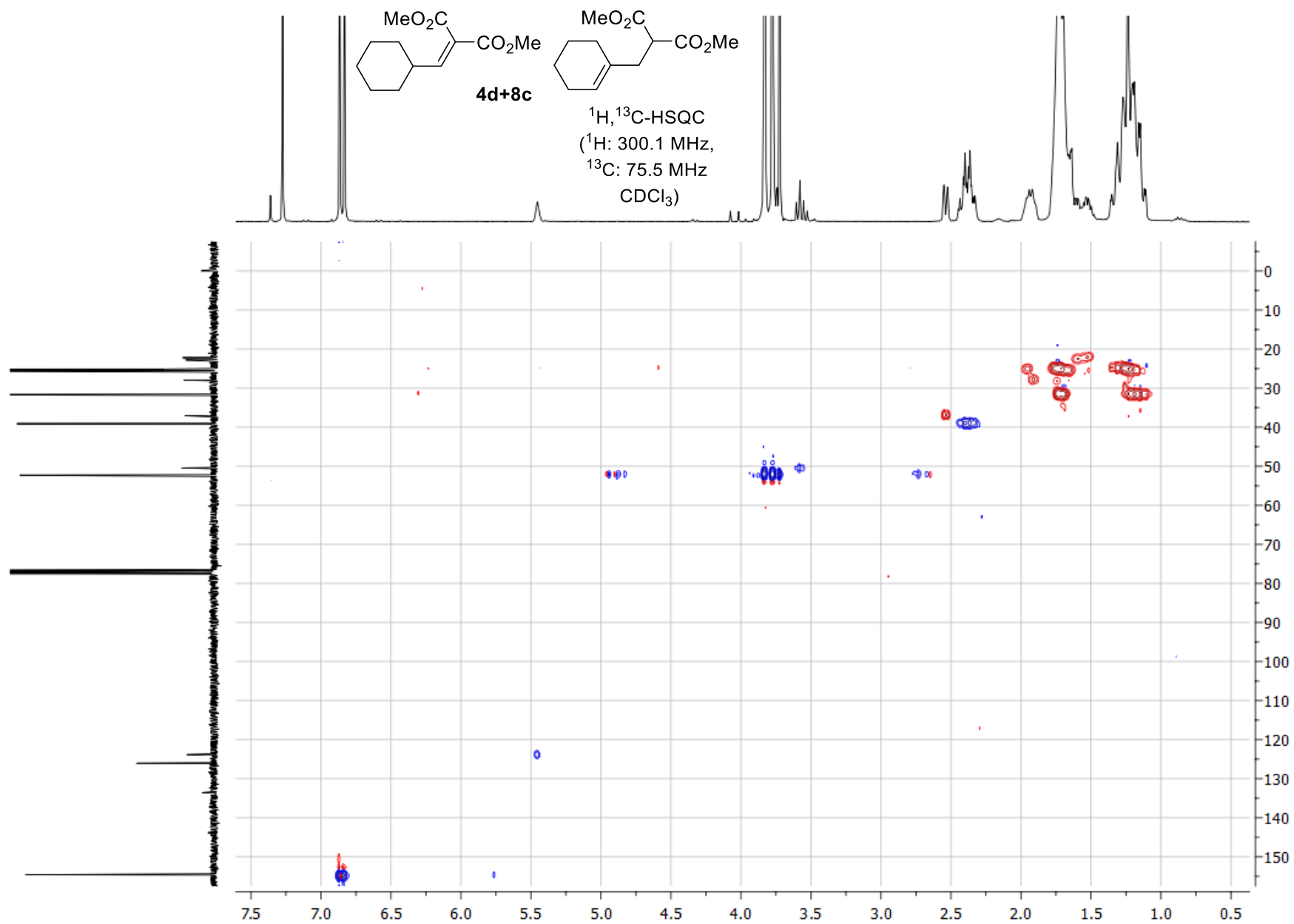


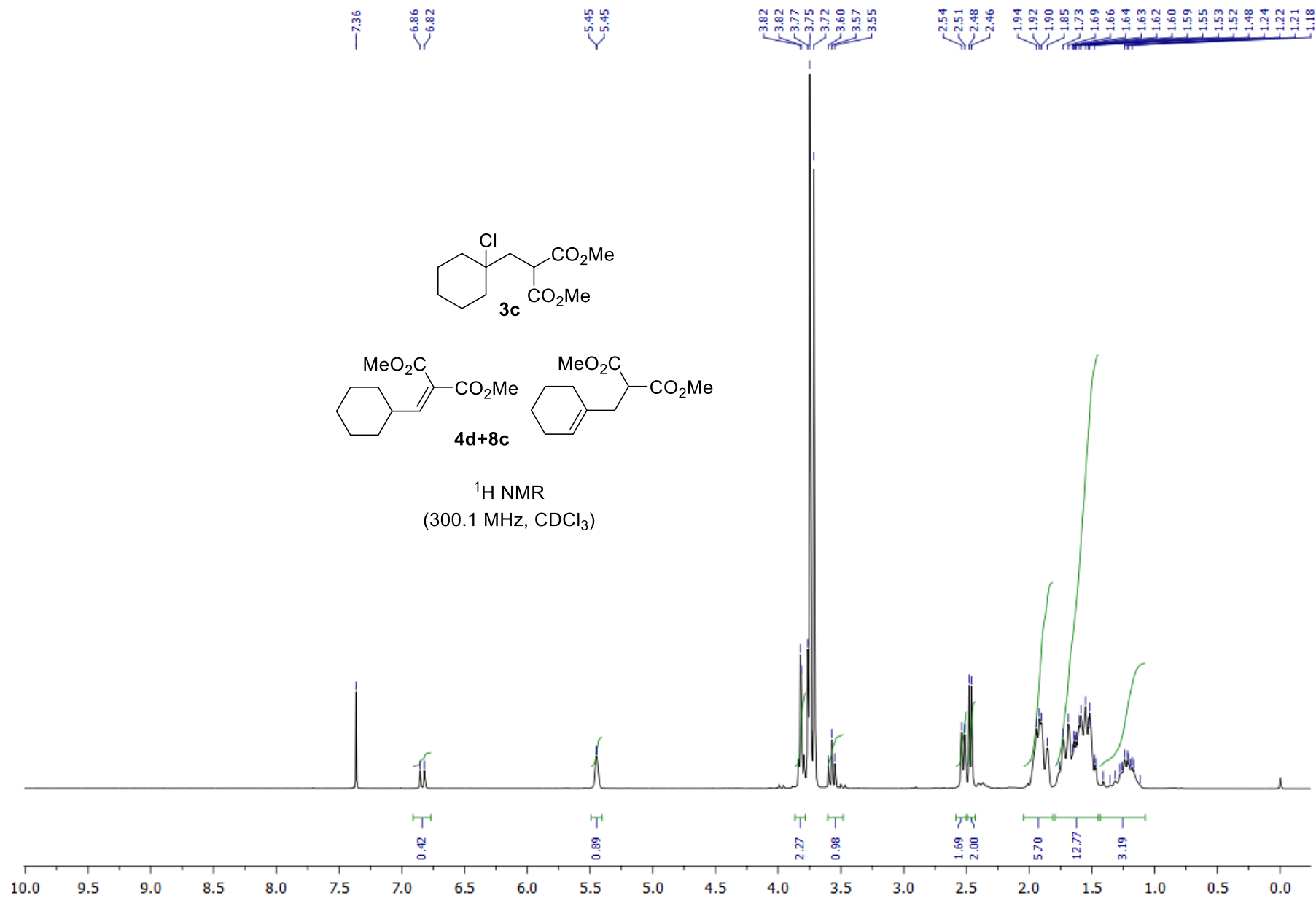


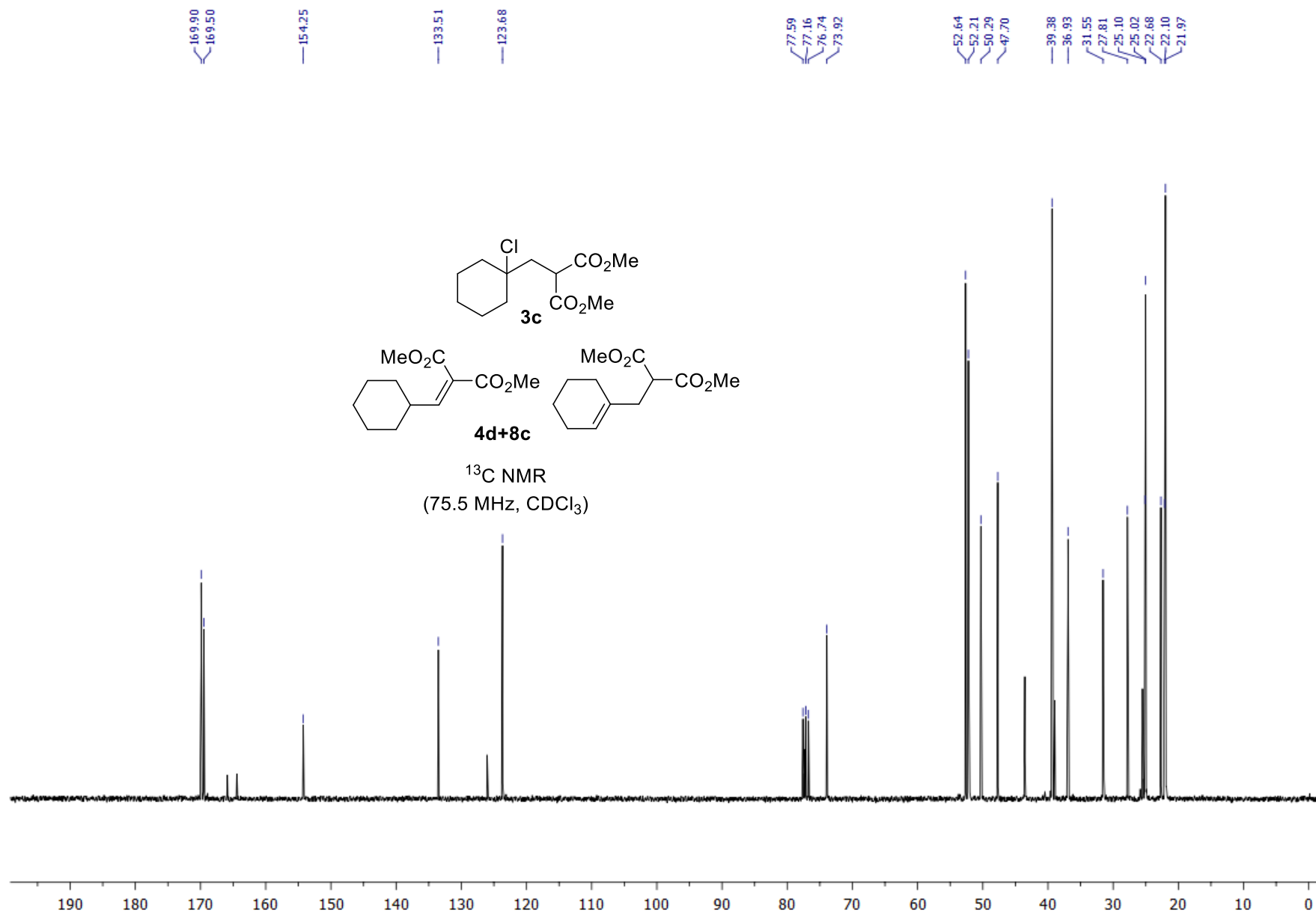
4d+8c

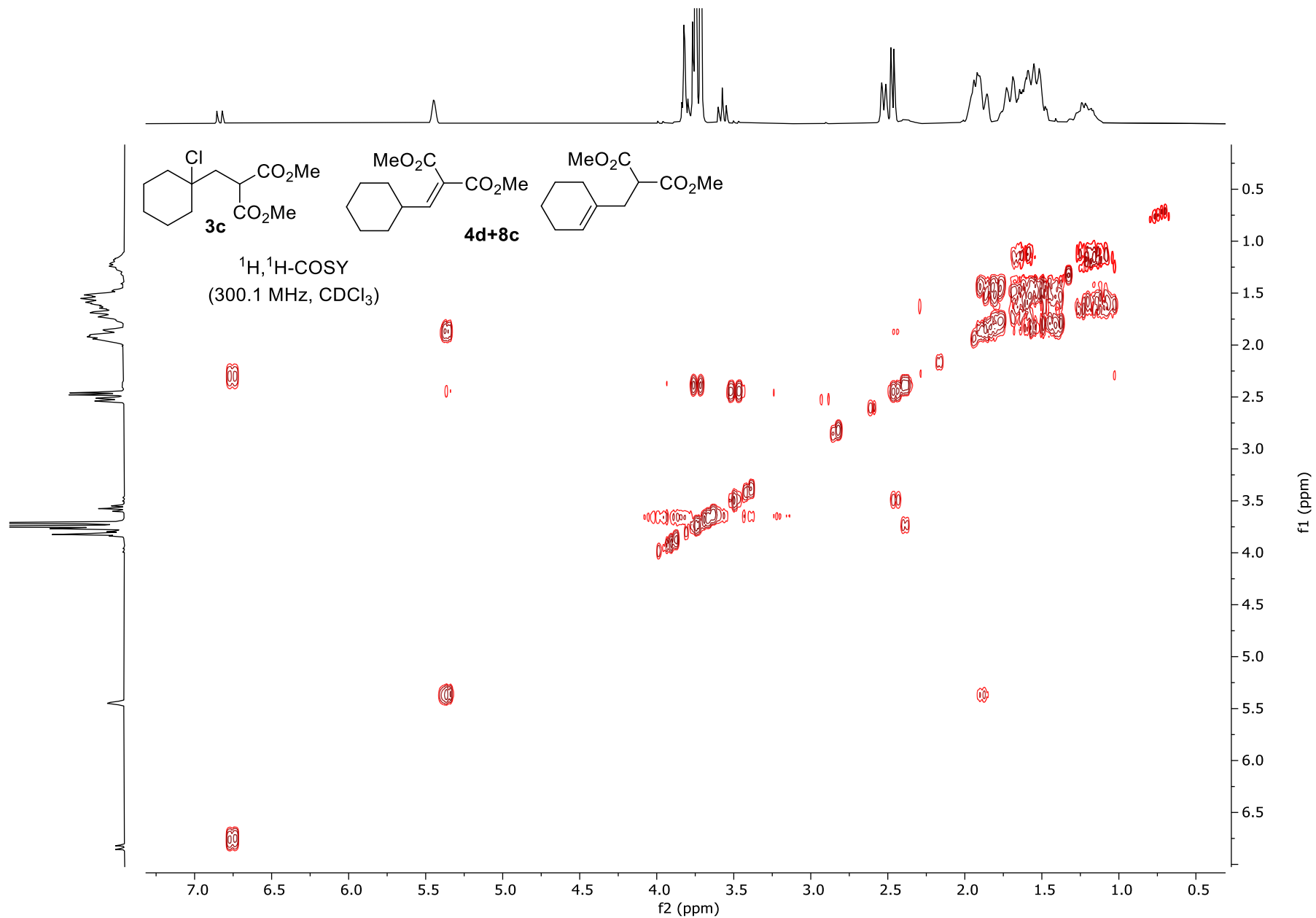
¹³C NMR
(75.5 MHz, CDCl₃)

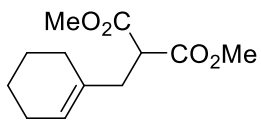
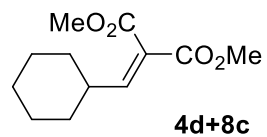
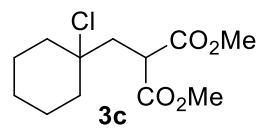




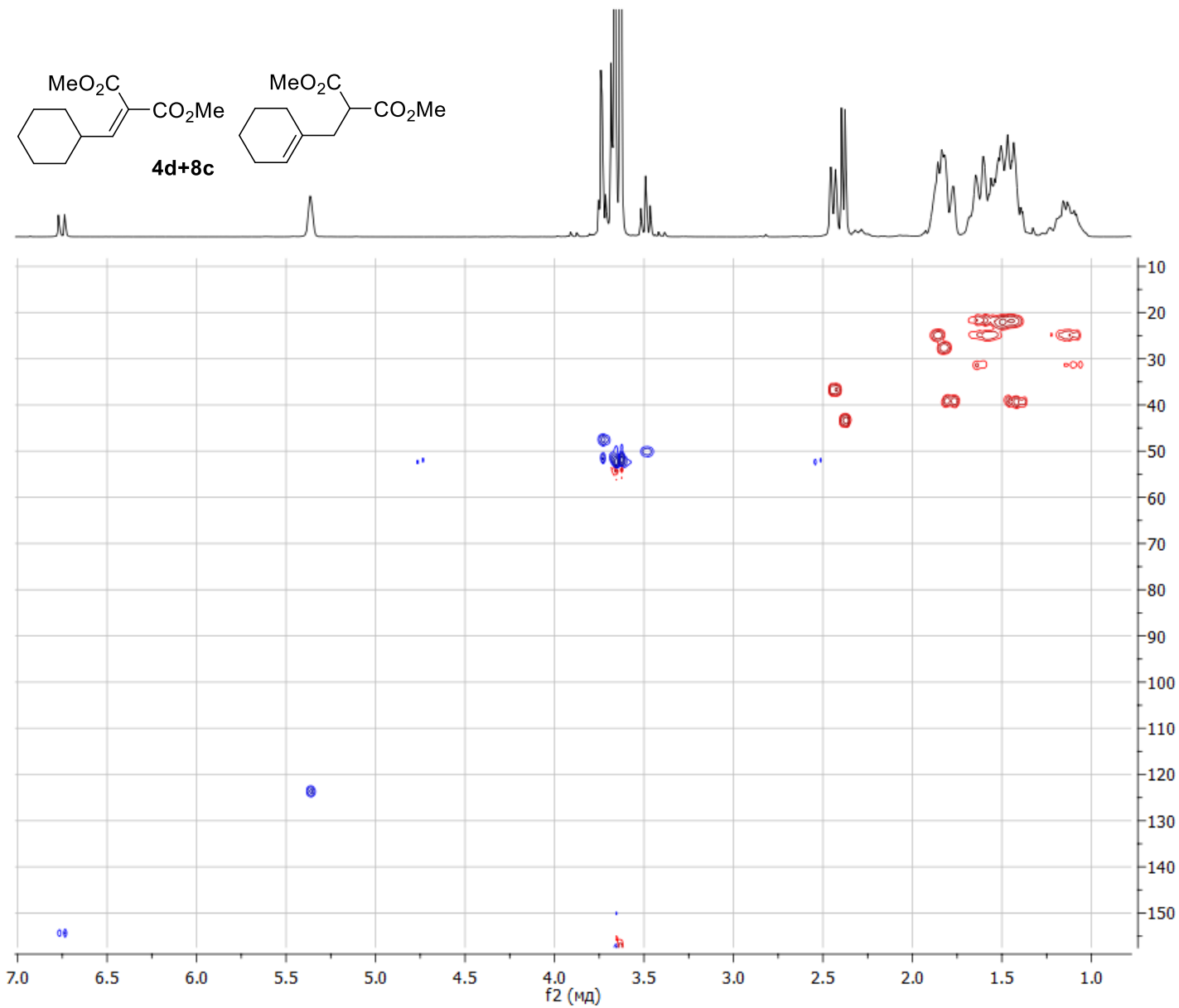


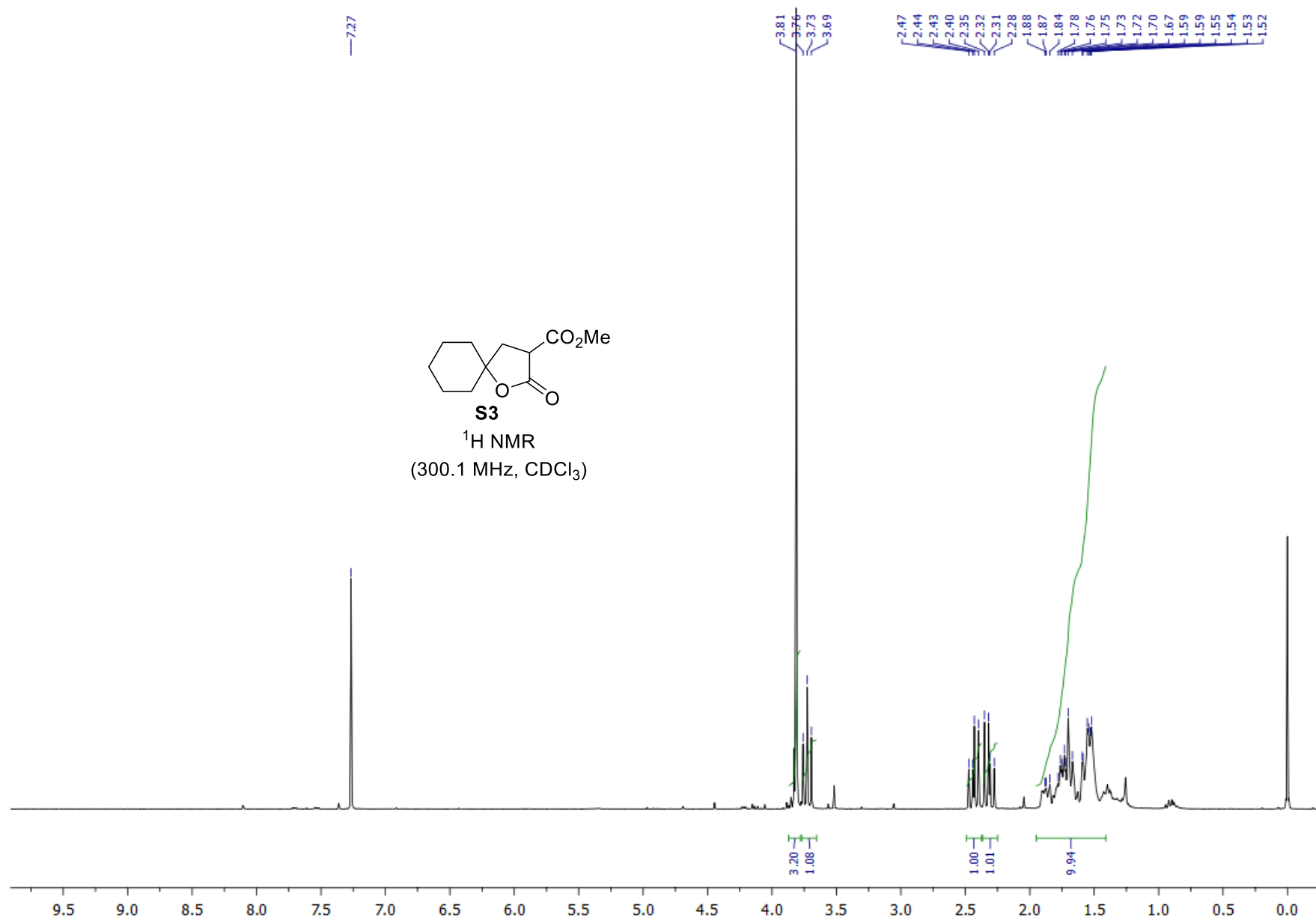


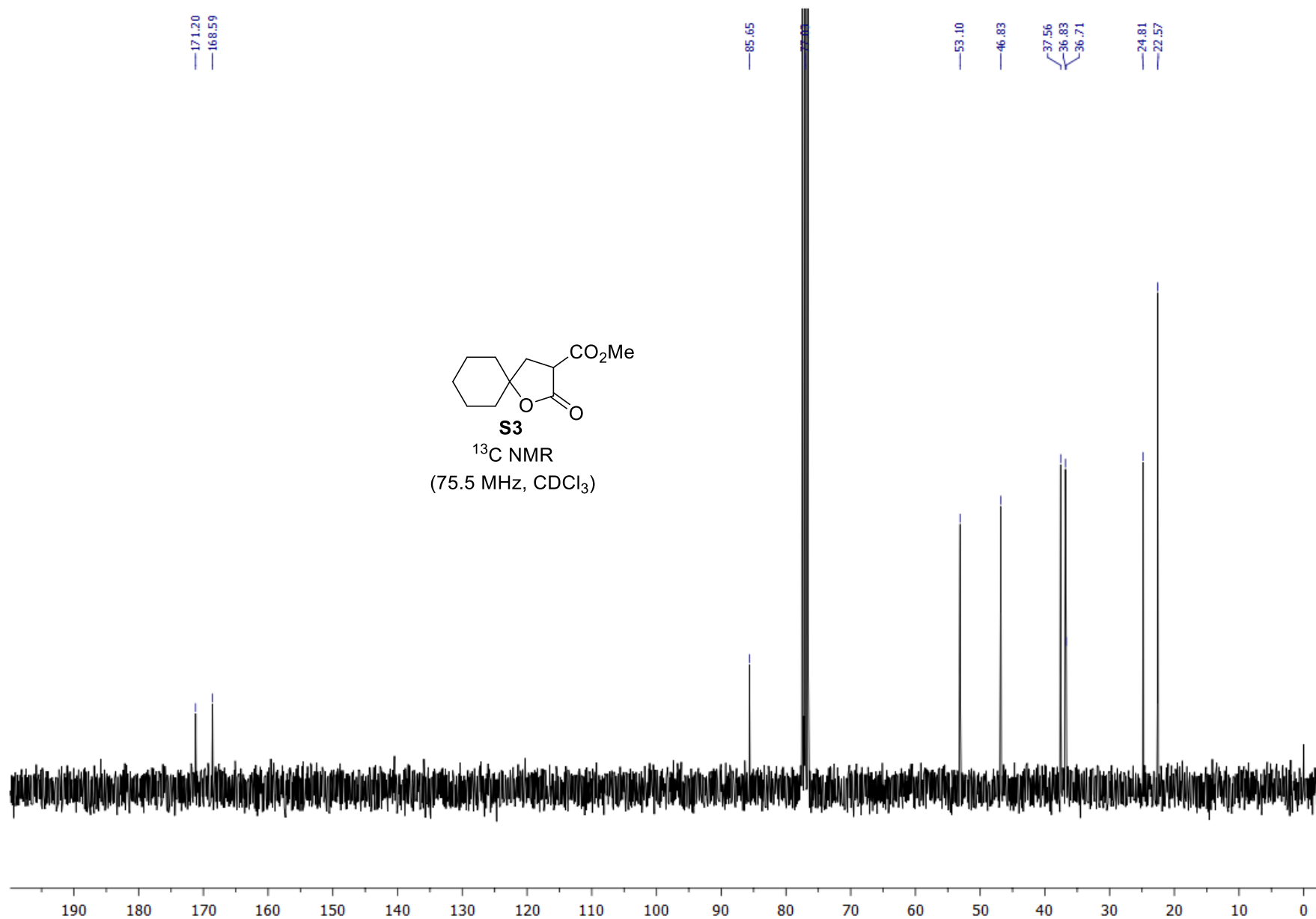


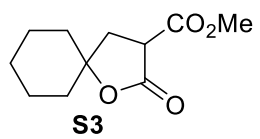


$^1\text{H}, ^{13}\text{C}$ -HSQC
 (^1H : 300.1 MHz,
 ^{13}C : 75.5 MHz
 CDCl_3)









^1H , ^{13}C -HSQC
 (^1H : 300.1 MHz,
 ^{13}C : 75.5 MHz
 CDCl_3)

