

Supporting Information

Poly(methylhydrosiloxane) as a reductant in the catalytic base-free Wittig Reaction

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1. General considerations

The employed aryl substituted maleimides **2j–m** were synthesized by a procedure from Mitchell and co-workers.^{1, 2} The spectral data of the obtained products (**2j–m**) was in agreement with the reported data. The catalyst **4a** was prepared according to a previously reported two step synthesis (more details below). Polymethylhydrosiloxane (PMHS) was purchased from *Sigma-Aldrich* (viscosity 15-40 mPa·s). The content of reductive Si-H groups was determined with ¹H-NMR spectroscopy. All other chemicals were purchased from commercial sources with purities ≥95% and used without further purification. Deuterated solvents were ordered from *Deutero GmbH* and stored over molecular sieves. NMR spectra were recorded using *Bruker* 300 Fourier, *Bruker* AV 300 and *Bruker* AV 400 spectrometers. Chemical shifts are reported in ppm relative to the deuterated solvent. Coupling constants are expressed in Hertz (Hz). The following abbreviations are used: s = singlet, d = doublet, t = triplet and m = multiplet. IR spectra were recorded on a Nicolet iS10 MIR FT-IR-spectrometer from *Thermo Fisher Scientific*. Thin layer chromatography was performed on *Merck* TLC-plates with fluorescence indication (silica type 60, F₂₅₄), spots were visualized using UV-light, potassium permanganate or Seebach's "magic" stain (composed of 2.0 g cerium(IV) sulfate, 5.0 g phosphomolybdic acid, 16 ml sulfuric acid, 190 ml water). Flash chromatography was performed using silica with a grain size of 40–63 μm from *Macherey-Nagel*.

2. Additional information on the catalyst screening and optimization experiments

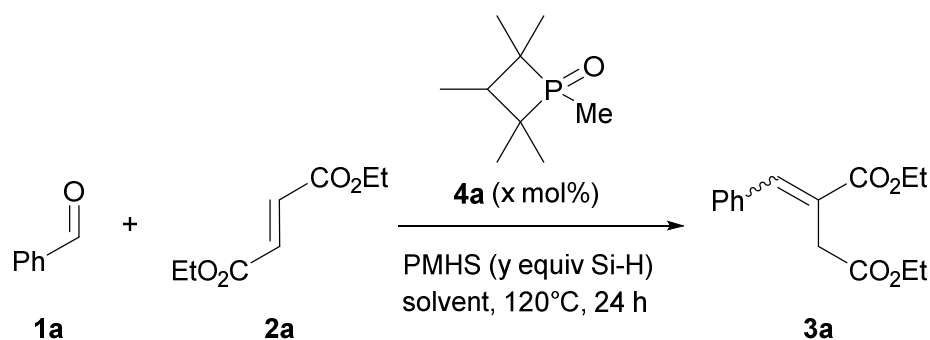
General procedure A: A 50 ml Schlenk flask under vacuum was flushed with argon. Benzaldehyde (**1a**, 53 mg, 0.50 mmol, 1.0 equiv), diethyl fumarate (**2a**, 129 mg, 0.750 mmol, 1.50 equiv) and polymethylhydrosiloxane (173 mg, 173 μ L, 5.00 equiv Si-H) were added. Subsequently, the catalyst (**4a**, 25–5.0 μ mol, 0.05–0.01 equiv) was added as a solution in the respective solvent (0.017 M, total volume is 1.5 ml). The reaction mixture was heated to 120°C in an oil bath for 24 h. Hexadecane (56 mg, 0.25 mmol, 0.50 equiv) was added and the reaction mixture was then diluted with EtOAc (5 ml). The yield and selectivity were determined using gas chromatography (GC-FID).

The base-free Wittig reaction for the model substrate was also conducted in toluene as well as under solvent free conditions. The reaction in toluene afforded a good yield of the alkene **3a** of 78% (Table S1, entry 1). The reaction without solvent was conducted multiple times under similar conditions. Here, the reaction mixtures solidified by polymerization (Figure S1), which made the work-up more demanding and might be the reason for the poor reproducibility. Decreasing the equivalents of terminal reductant under optimized conditions also resulted in lower yield (entry 8–11).



Figure S1 Solidified reaction mixture under solvent free conditions after 24 h at 120°C.

Table S1 Optimization of reaction parameters in the model reaction of benzaldehyde **1a** and diethyl fumarate **2a**.



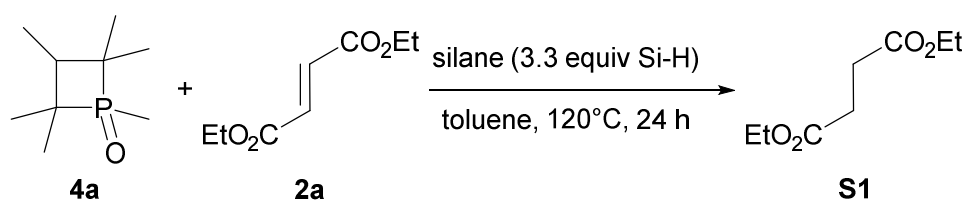
Entry	Solvent	Catalyst/mol%	PMHS/equiv Si-H	Yield 3a ^a /%	<i>E/Z</i> ^a
1	Toluene	5.0	5.0	78	97:3
2	Neat	5.0	3.0	77	98:2
3	Neat	5.0	3.0	70	97:3
4	Neat	1.0	3.0	59	97:3
5	Neat	2.0	10	59	97:3
6	Neat	1.0	10	75	96:4
7	Neat	1.0	10	58	96:4
8	BuOAc	5.0	3.0	62	97:3
9	BuOAc	5.0	2.0	42	97:3
10	BuOAc	5.0	1.5	33	97:3
11	BuOAc	5.0	1.0	17	97:3

Reaction conditions: 1.0 equiv **1a** (0.5 mmol), 1.5 equiv **2a** (0.75 mmol), x mol% catalyst **4a**, y equiv Si-H of PMHS, 1.5 ml solvent, 120°C, 24 h. ^a Yield and selectivity determined by GC-FID with hexadecane as internal standard.

3. Mechanistic studies

The formation of water by condensation of silanol was investigated by reducing the catalyst in the presence of diethyl fumarate. The reduction of the phosphane oxide leads to the formation of 1.0 equiv of silanol, which was proposed to dimerize under reaction conditions to form 0.5 equiv water. This would reduce the alkene by the previously reported mechanism under regeneration of 0.5 equiv of phosphane oxide.³ Consequently, for 1.0 equiv of catalyst 1.0 equiv alkane would be formed. The reduction of the alkene could be observed in dependence of the amount of catalyst used by using PMHS (table 1, entry 1, 2), as well as phenyl silane (entry 3, 4).

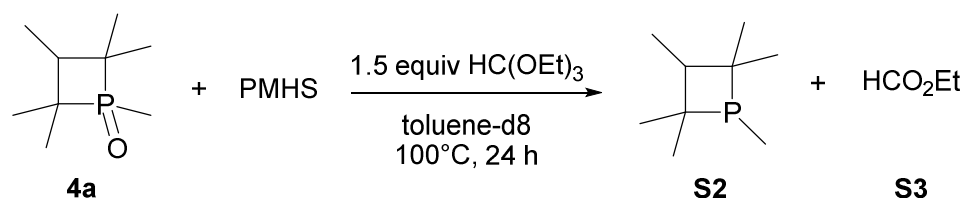
Table S2 Reduction of the phosphetane oxide **4a** in the presence of diethyl fumarate (**2a**).



Entry	Silane	Catalyst 4a /mol%	Yield S1 ^a /%
1	PMHS	3.3	10
2	PMHS	100	100
3	PhSiH ₃	3.3	9
4	PhSiH ₃	67	76

Reaction conditions: 1.0 equiv **2a** (0.75 mmol), x mol% catalyst **4a**, 3.3 equiv Si-H of silanes (2.5 mmol), 1.5 ml solvent, 120°C, 24 h. ^a Yield determined by GC with hexadecane as internal standard.

Additionally, the formation of water was investigated by using triethyl orthoformate as a water scavenger in the reduction of the phosphetane oxide **4a** with PMHS. Thus, with an excess of the catalyst, 1.0 equiv Si-H of the PMHS lead to the formation of 0.5 equiv ethyl formate (**S3**).



Scheme S1 Indirect detection of water. Reaction conditions: 1.5 equiv **4a** (86 μmol), 1.0 equiv Si-H of PMHS (57 μmol), 1.5 equiv triethyl orthoformate (86 μmol), 0.5 ml toluene-*d*₈, 100°C, 24 h. Yield determined by ¹H NMR.

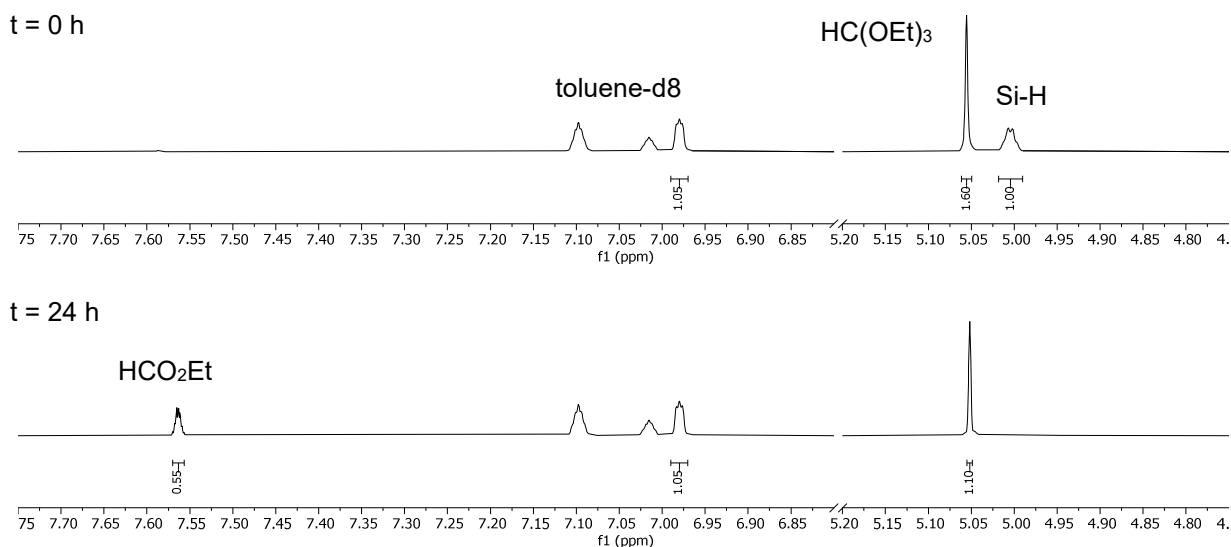
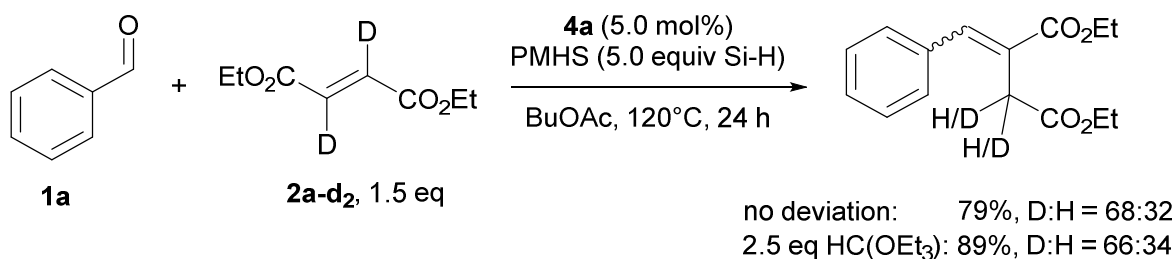


Figure S2 ^1H NMR spectra depicting the formation of water by silanol condensation by scavenging with triethyl orthoformate.

Furthermore, the reaction of ethyl fumarate-2,3- d_2 (**2a-d₂**) with benzaldehyde was investigated.



Scheme S2 Reaction ethyl fumarate-2,3- d_2 (**2a-d₂**) with benzaldehyde (**1a**) in the catalytic base-free Wittig reaction.

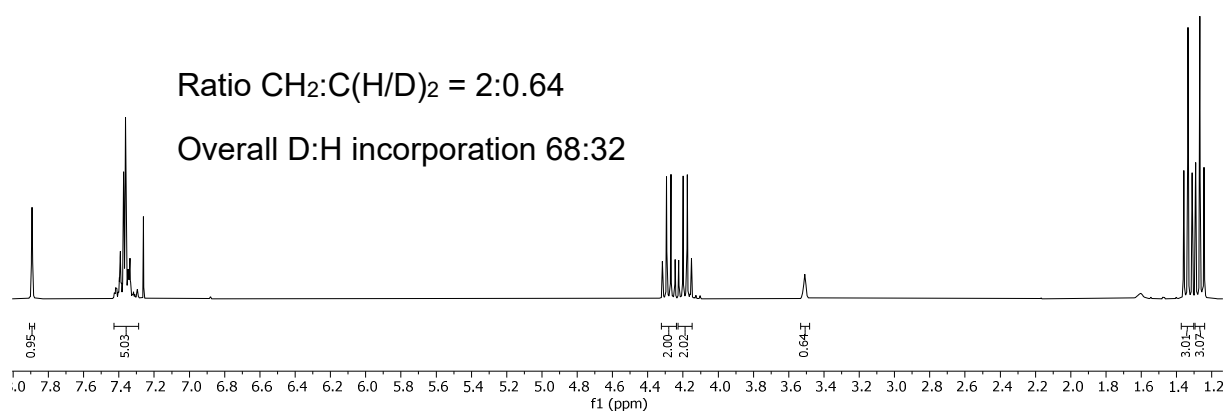
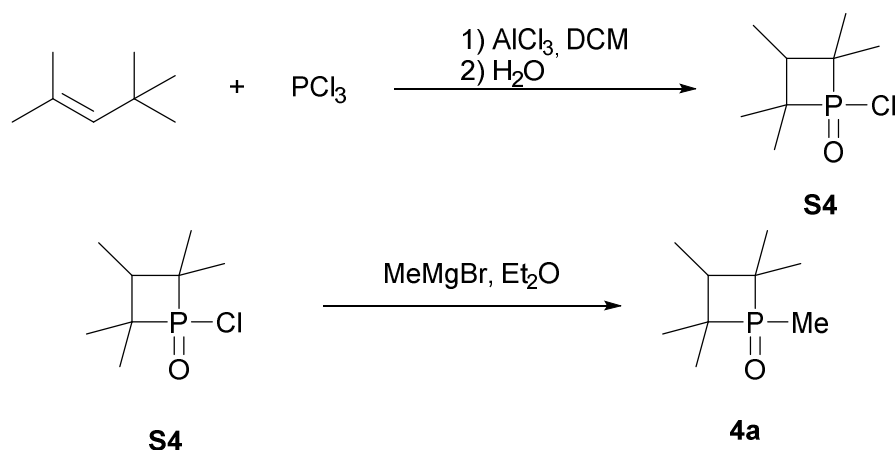


Figure S3 ^1H NMR spectrum of the product obtained by reaction of ethyl fumarate-2,3- d_2 (**2a-d₂**) in the base-free Wittig reaction.

4. Synthesis of the employed catalyst and reactants



Scheme S3 Synthesis of phosphetane oxide catalyst **4a**.

1-Chloro-2,2,3,4,4-pentamethylphosphetane 1-oxide (**4a**)⁴

Anhydrous aluminium chloride (6.7 g, 50 mmol) was added to a 250 ml Schlenk flask and the flask was purged with argon. Dry CH_2Cl_2 (30 ml) and subsequently phosphorus trichloride (6.9 g, 50 mmol, 4.4 ml) were added and the reaction mixture was cooled to 0°C . Over a period of 15 min, 2,4,4-trimethyl-2-pentene (5.6 g, 50 mmol, 7.8 ml) was added via syringe under strong stirring and the reaction mixture was kept stirring at 0°C for 2 h. The reaction was then carefully quenched with cold water (50 ml) over a period of 1 h at 0°C . The mixture was diluted with CH_2Cl_2 (100 ml) and transferred to a separatory funnel. The organic phase was separated and the aqueous phase was extracted with CH_2Cl_2 (2×50 ml). The combined organic phase was dried with Na_2SO_4 and all volatiles were removed. The crude product **S4** (8.9 g, 46 mmol, 93%) was then used without further purification.

1,2,2,3,4,4-Hexamethylphosphetane 1-oxide (**4a**)⁴

1-Chloro-2,2,3,4,4-pentamethylphosphetane 1-oxide **S4** (8.48 g, 43.6 mmol) was added to a 250 ml Schlenk flask and the flask was purged with argon. Subsequently, dry Et_2O (50 ml) was added and the solution was cooled to 0°C in an ice bath. A solution of methyl magnesium bromide (3.0 M in Et_2O , 15.2 ml, 45.7 mmol, 1.05 equiv) was added over 30 min and the mixture was allowed to warm to room temperature. The solution was then heated to reflux for 2 h, cooled to 0° and quenched with saturated ammonium chloride solution. Afterwards, 50 ml of water and 50 ml of

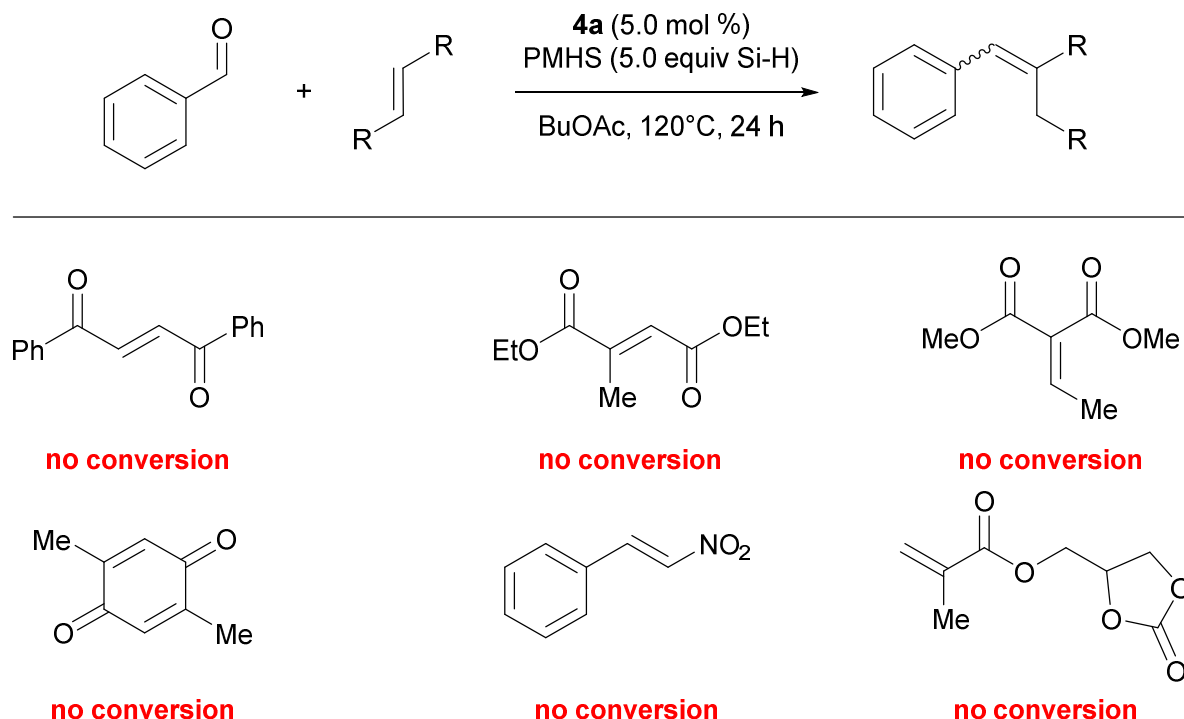
CH₂Cl₂ were added and the organic phase was separated. The aqueous phase was extracted with CH₂Cl₂ (2×50 ml) and the combined organic phase was washed with brine and dried over Na₂SO₄. All volatiles were removed in vacuo and the crude product was recrystallized from cyclohexane to obtain **4a** (9.1 g, 36.2 mmol, 83%) as a single diastereoisomer. ¹H NMR (400 MHz, CDCl₃) δ = 1.51–1.35 (m, 4H), 1.24–0.97 (m, 12H), 0.79 (dd, *J* = 7.1 Hz, 1.7 Hz, 3H) ppm; ³¹P NMR (162 MHz, CDCl₃) δ = 59.3 ppm.

Methyl (*E*)-4-(diethylamino)-4-oxobut-2-enoate (2i)

A 50 ml Schlenk flask under vacuum was flushed with argon. Mono-methylfumaric acid (651 mg, 5.00 mmol, 1.00 equiv) and oxalyl chloride (1.90 g, 15.0 mmol, 3.00 equiv) and DMF (1 drop) were stirred in DCM (15 ml) at 23°C for 2 h. The volatiles were removed in vacuo and the residue was dissolved in DCM (5 ml). The mixture was slowly added to a solution of diethylamine (731 mg, 10.0 mmol, 2.00 equiv) in DCM (15 ml) at 0°C. The reaction mixture was stirred for 18 h at 23°C, after which the volatiles were removed in vacuo and the residue was dissolved in ethyl acetate. The organic phase was washed with hydrochloric acid (1 mol l⁻¹, 15 ml), saturated, aqueous NaHCO₃ (15 ml) and water (15 ml). All volatiles were removed. Purification by column chromatography (SiO₂, cyclohexane:EtOAc = 2:1) gave alkene **2i** (657 mg, 3.55 mmol, 71%) as a colorless oil. ¹H NMR (300 MHz, CDCl₃) δ = 7.31 (d, *J* = 15.3 Hz, 1H), 6.77 (d, *J* = 15.3 Hz, 1H), 3.75 (s, 3H), 3.47–3.32 (m, 4H), 1.23–1.07 (m, 6H) ppm. ¹³C NMR (75 MHz, CDCl₃) δ = 166.3, 163.8, 134.4, 130.7, 52.1, 42.5, 41.0, 15.1, 13.0 ppm. IR (ATR): 2975 (m), 2936 (w), 2876 (w), 1725 (s), 1651 (s), 1432 (s), 1295 (s), 1169 (m), 1136 (m), 972 (m), 764 (m) cm⁻¹. MS (EI, 70 eV): *m/z* (%): 185 (6.8) [M⁺], 154 (18.3), 126 (11.8), 113 (100), 85 (22.2), 72 (69.0), 58 (31.0). HRMS (ESI⁺): *m/z* calcd for C₉H₁₅NO₄ [M+H]⁺ 186.1130, found: 186.1132.

5. Additional information on the substrate scope

Substrates with lower electrophilicity or more steric hindrance, which showed no conversion, are depicted in Scheme S4.



Scheme S4 Substrates in the catalytic, base-free Wittig reaction, which showed no conversion.

General Procedure B: A 50 ml Schlenk flask under vacuum was flushed with argon. The aldehyde (**1**, 0.500 mmol, 1.00 equiv), alkene (**2**, 0.750 mmol, 1.50 equiv) and polymethylhydrosiloxane (173 mg, 173 μ L, 5.00 equiv Si-H) were added. Subsequently, the catalyst (**4a**, 4.4 mg, 0.025 mmol, 0.05 equiv) was added as a solution in BuOAc (0.017 M, total volume of BuOAc is 1.5 ml). The reaction mixture was heated to 120°C in an oil bath for 24 h. The solution was cooled to room temperature, diluted with EtOAc and SiO₂ (40–63 μ m) was added. All volatiles were removed and the product **3** was obtained after purification with column chromatography (eluent cyclohexane:EtOAc).

Diethyl (*E*)-2-benzylidenesuccinate (**3a**)⁵

According to the GP B, benzaldehyde (**1a**, 53 mg, 0.50 mmol, 1.00 equiv) was converted with diethyl fumarate (**2a**, 129 mg, 123 μ L, 0.750 mmol, 1.50 equiv) and

PMHS (173 mg, 173 μ L, 5.00 equiv Si-H) in the presence of 1,2,2,3,4,4-hexamethylphosphetane 1-oxide (**4a**, 4.4 mg, 0.025 mmol, 0.05 equiv) in BuOAc (1.5 ml). Purification (SiO₂, cyclohexane:EtOAc= 10:1) gave alkene **3a** (114 mg, 0.435 mmol, 87%) as a colorless oil. ¹H NMR (300 MHz, CDCl₃) δ = 7.89 (s, 1H), 7.43–7.30 (m, 5H), 4.28 (q, *J* = 7.1 Hz, 2H), 4.19 (q, *J* = 7.2 Hz, 2H), 3.52 (d, *J* = 0.8 Hz, 2H), 1.37–1.30 (m, 3H), 1.27 (t, *J* = 7.1 Hz, 3H) ppm. ¹³C NMR (75 MHz, CDCl₃) δ = 171.2, 167.3, 141.7, 135.1, 129.0, 128.8, 128.6, 126.4, 61.1, 60.9, 33.7, 14.3, 14.2 ppm.

Diisopropyl (*E*)-2-benzylidenesuccinate (**3b**)⁵

According to the GP B, benzaldehyde (**1a**, 53 mg, 0.50 mmol, 1.00 equiv) was converted with diisopropyl fumarate (**2b**, 150 mg, 150 μ L, 0.750 mmol, 1.50 equiv) and PMHS (173 mg, 173 μ L, 5.00 equiv Si-H) in the presence of 1,2,2,3,4,4-hexamethylphosphetane 1-oxide (**4a**, 4.4 mg, 0.025 mmol, 0.05 equiv) in BuOAc (1.5 ml). Purification (SiO₂, cyclohexane:EtOAc= 20:1) gave alkene **3b** (125 mg, 0.429 mmol, 86%) as a colorless oil. ¹H NMR (300 MHz, CDCl₃) δ = 7.86 (s, 1H), 7.43–7.29 (m, 5H), 5.14 (hept, *J* = 6.5 Hz, 1H), 5.05 (hept, *J* = 6.3 Hz, 1H), 3.48 (d, *J* = 0.8 Hz, 2H), 1.31 (d, *J* = 6.3 Hz, 6H), 1.25 (d, *J* = 6.3 Hz, 6H) ppm. ¹³C NMR (75 MHz, CDCl₃) δ = 170.8, 167.0, 141.4, 135.4, 129.1, 128.8, 128.7, 127.0, 68.7, 68.4, 34.2, 22.0, 21.9 ppm.

Dibutyl (*E*)-2-benzylidenesuccinate (**3c**)⁶

According to the GP B, benzaldehyde (**1a**, 53 mg, 0.50 mmol, 1.00 equiv) was converted with dibutyl fumarate (**2c**, 150 mg, 150 μ L, 0.750 mmol, 1.50 equiv) and PMHS (173 mg, 173 μ L, 5.00 equiv Si-H) in the presence of 1,2,2,3,4,4-hexamethylphosphetane 1-oxide (**4a**, 4.4 mg, 0.025 mmol, 0.05 equiv) in BuOAc (1.5 ml). Purification (SiO₂, cyclohexane:EtOAc= 20:1) gave alkene **3c** (143 mg, 0.450 mmol, 90%) as a colorless oil. ¹H NMR (300 MHz, CDCl₃) δ = 7.89 (s, 1H), 7.44–7.29 (m, 5H), 4.22 (t, *J* = 6.6 Hz, 2H), 4.13 (t, *J* = 6.6 Hz, 2H), 3.53 (d, *J* = 0.8 Hz, 2H), 1.74–1.56 (m, 4H), 1.50–1.31 (m, 4H), 0.96 (t, *J* = 7.3 Hz, 3H), 0.93 (t, *J* = 7.4 Hz, 3H) ppm. ¹³C NMR (75 MHz, CDCl₃) δ = 171.3, 167.5, 141.8, 135.2, 129.1, 128.9, 128.7, 126.5, 65.1, 64.9, 33.8, 30.8, 30.7, 19.3, 19.2, 13.8, 13.8 ppm.

Diallyl (*E*)-2-benzylidenesuccinate (**3d**)

According to the GP B, benzaldehyde (**1a**, 53 mg, 0.50 mmol, 1.00 equiv) was converted with diallyl maleate (**2d**, 147 mg, 139 μ L, 0.750 mmol, 1.50 equiv) and PMHS (173 mg, 173 μ L, 5.00 equiv Si-H) in the presence of 1,2,2,3,4,4-hexamethylphosphetane 1-oxide (**4a**, 4.4 mg, 0.025 mmol, 0.05 equiv) in BuOAc (1.5 ml). Purification (SiO₂, cyclohexane:EtOAc= 20:1) gave alkene **3d** (133 mg, 0.420 mmol, 84%) as a colorless oil. ¹H NMR (300 MHz, CDCl₃) δ = 7.94 (s, 1H), 7.44–7.31 (m, 5H), 6.07–5.82 (m, 2H), 5.41–5.20 (m, 4H), 4.73 (dt, *J* = 5.6, 1.5 Hz, 2H), 4.63 (dt, *J* = 5.7, 1.4 Hz, 2H), 3.58 (d, *J* = 0.8 Hz, 2H) ppm. ¹³C NMR (75 MHz, CDCl₃) δ = 170.9, 167.1, 142.4, 135.0, 132.2, 132.1, 129.2, 129.1, 128.8, 126.0, 118.4, 118.3, 65.9, 65.7, 33.8 ppm. IR (ATR): 3083 (w), 3025 (w), 2940 (w), 1735 (s), 1707 (s), 1642 (m), 1447 (m), 1322 (m), 1265 (m), 1167 (m), 1090 (m), 956 (m), 927 (m), 833 (w), 760 (m), 695 cm⁻¹. MS (EI, 70 eV): *m/z* (%): 286 (2.7) [M⁺], 229 (20.3), 201 (10.8), 155 (22.0), 129 (22.6), 115 (100), 41 (78.0). HRMS (ESI⁺): *m/z* calcd for C₁₇H₁₈O₄ [M+Na]⁺ 309.1102, found: 309.1101.

(*E*)-3-Benzylidenepyrrolidine-2,5-dione (**3e**)⁶

According to the GP B, benzaldehyde (**1a**, 53 mg, 0.50 mmol, 1.0 equiv) was converted with maleimide (**2e**, 73 mg, 0.75 mmol, 1.5 equiv) and PMHS (173 mg, 173 μ L, 5.00 equiv Si-H) in the presence of 1,2,2,3,4,4-hexamethylphosphetane 1-oxide (**4a**, 4.4 mg, 0.025 mmol, 0.05 equiv) in BuOAc (1.5 ml). Purification (SiO₂, cyclohexane:EtOAc = 3:2) gave alkene **3e** (81 mg, 0.43 mmol, 87%) as a colorless solid. ¹H NMR (400 MHz, DMSO-*d*6) δ = 11.44 (s, 1H), 7.65–7.59 (m, 2H), 7.50–7.40 (m, 2H), 7.38 (t, *J* = 2.5 Hz, 1H), 3.65 (d, *J* = 2.4 Hz, 2H) ppm. ¹³C NMR (75 MHz, DMSO-*d*6) δ = 175.8, 172.0, 134.2, 131.5, 130.2, 129.7, 129.0, 127.0, 34.8 ppm.

(*E*)-3-Benzylidene-1-methylpyrrolidine-2,5-dione (**3f**)⁶

According to the GP B, benzaldehyde (**1a**, 53 mg, 0.50 mmol, 1.0 equiv) was converted with *N*-Methylmaleimide (**2f**, 83 mg, 0.75 mmol, 1.5 equiv) and PMHS (173 mg, 173 μ L, 5.00 equiv Si-H) in the presence of 1,2,2,3,4,4-hexamethylphosphetane 1-oxide (**4a**, 4.4 mg, 0.025 mmol, 0.05 equiv) in BuOAc (1.5 ml). Purification (SiO₂, cyclohexane:EtOAc= 5:1) gave alkene **3f** (93 mg, 0.46 mmol, 92%) as a colorless

solid. ^1H NMR (300 MHz, CDCl_3) δ = 7.63 (t, J = 2.4 Hz, 1H), 7.53–7.39 (m, 5H), 3.58 (d, J = 2.3 Hz, 2H), 3.13 (s, 3H) ppm. ^{13}C NMR (75 MHz, CDCl_3) δ = 174.4, 171.4, 134.5, 134.3, 130.4, 130.4, 129.4, 123.7, 34.3, 25.2 ppm.

Upscale experiment: According to the GP B, benzaldehyde (**1a**, 1.06 g, 10.0 mmol, 1.0 equiv) was converted with *N*-Methylmaleimide (**2f**, 1.67 g, 15 mmol, 1.5 equiv) and PMHS (3.45 g, 5.00 equiv Si-H) in the presence of 1,2,2,3,4,4-hexamethylphosphetane 1-oxide (**4a**, 87.1 mg, 0.5 mmol, 0.05 equiv) in BuOAc (15 ml). Water (30 ml) was added and the reaction mixture was extracted with EtOAc (3 x 30 ml). The combined organic phase was dried using Na_2SO_4 and all volatiles were removed. The crude product was purified by two-solvent recrystallization (EtOAc:cyclohexane) to give the alkene **3f** (1.86 g, 9.24 mmol, 92%) as an off-white solid.

(E)-3-Benzylidene-1-(tert-butyl)pyrrolidine-2,5-dione (3g)⁶

According to the GP B, Benzaldehyde (**1a**, 53 mg, 0.50 mmol, 1.00 equiv) was converted with *N*-(*tert*-butyl)maleimide (**2g**, 115 mg, 0.750 mmol, 1.50 equiv) and PMHS (173 mg, 173 μL , 5.00 equiv Si-H) in the presence of 1,2,2,3,4,4-hexamethylphosphetane 1-oxide (**4a**, 4.4 mg, 0.025 mmol, 0.05 equiv) in BuOAc (1.5 ml). Purification (SiO_2 , cyclohexane:EtOAc= 5:1) gave alkene **3g** (96 mg, 0.40 mmol, 80%) as a colorless solid. ^1H NMR (300 MHz, CDCl_3) δ = 7.53 (t, J = 2.5 Hz, 1H), 7.49–7.36 (m, 5H), 3.48 (d, J = 2.5 Hz, 2H), 1.66 (s, 9H) ppm. ^{13}C NMR (75 MHz, CDCl_3) δ = 175.2, 172.2, 134.6, 133.0, 130.1, 129.9, 129.1, 124.2, 58.8, 34.9, 28.7 ppm.

Ethyl (E)-2-benzylidene-4-oxo-4-phenylbutanoate (3h)⁶

According to the GP B, benzaldehyde (**1a**, 53 mg, 0.50 mmol, 1.00 equiv) was converted with Ethyl-3-benzoylacrylat (**2h**, 153 mg, 135 μL , 0.750 mmol, 1.50 equiv) and PMHS (173 mg, 173 μL , 5.00 equiv Si-H) in the presence of 1,2,2,3,4,4-hexamethylphosphetane 1-oxide (**4a**, 4.4 mg, 0.025 mmol, 0.05 equiv) in BuOAc (1.5 ml). Purification (SiO_2 , cyclohexane:EtOAc= 20:1) gave alkene **3h** (58 mg, 0.20 mmol, 40%) as a yellow oil. ^1H NMR (300 MHz, CDCl_3) δ = 8.04–7.98 (m, 3H), 7.62–7.56 (m, 1H), 7.52–7.44 (m, 2H), 7.39–7.27 (m, 5H), 4.24 (q, J = 7.1 Hz, 2H),

4.19 (d, $J = 0.7$ Hz, 2H), 1.27 (t, $J = 7.1$ Hz, 3H) ppm. ^{13}C NMR (75 MHz, CDCl_3) $\delta = 197.6, 167.5, 142.1, 136.8, 135.4, 133.3, 128.8, 128.8, 128.7, 128.7, 128.4, 127.5, 61.2, 38.1, 14.3$ ppm.

Methyl (*E*)-2-benzylidene-4-(diethylamino)-4-oxobutanoate (3i**)**

According to the GP B, benzaldehyde (**1a**, 53 mg, 0.50 mmol, 1.00 equiv) was converted with Methyl (*E*)-4-(diethylamino)-4-oxobut-2-enoate (**2i**, 139 mg, 0.750 mmol, 1.50 equiv) and PMHS (173 mg, 173 μL , 5.00 equiv Si-H) in the presence of 1,2,2,3,4,4-hexamethylphosphetane 1-oxide (**4a**, 4.4 mg, 0.025 mmol, 0.05 equiv) in BuOAc (1.5 ml). Purification (SiO_2 , cyclohexane:EtOAc= 2:1) gave alkene **3i** (81 mg, 0.29 mmol, 59%) as a colorless oil. ^1H NMR (400 MHz, CDCl_3) $\delta = 7.89$ (s, 1H), 7.40–7.29 (m, 5H), 3.81 (s, 3H), 3.53–3.48 (m, 2H), 3.46–3.32 (m, 4H), 1.23–1.12 (m, 6H) ppm. ^{13}C NMR (101 MHz, CDCl_3) $\delta = 169.6, 168.4, 141.3, 135.7, 129.2, 128.7, 128.6, 128.0, 52.3, 42.3, 40.7, 32.6, 14.3, 13.3$ ppm. IR (ATR): 2973 (m), 2934 (m), 1710 (s), 1636 (s), 1432 (m), 1272 (m), 1200 (m), 1092 (m), 762 (m), 696 (m) cm^{-1} . MS (EI, 70 eV): m/z (%): 275 (23.7) [M^+], 244 (11.2), 216 (16.3), 115 (52.6), 100 (100), 91 (6.8), 72 (42.9). HRMS (EI): m/z calcd for $\text{C}_{16}\text{H}_{21}\text{O}_3\text{N}$ [M] $^+$ 275.1516, found: 275.1516.

(*E*)-3-Benzylidene-1-phenylpyrrolidine-2,5-dione (3j**)**

According to the GP B, benzaldehyde (**1a**, 53 mg, 0.50 mmol, 1.00 equiv) was converted with 1-phenylpyrrolidine-2,5-dione (**2j**, 130 mg, 0.750 mmol, 1.50 equiv) and PMHS (173 mg, 173 μL , 5.00 equiv Si-H) in the presence of 1,2,2,3,4,4-hexamethylphosphetane 1-oxide (**4a**, 4.4 mg, 0.025 mmol, 0.05 equiv) in BuOAc (1.5 ml). Purification (SiO_2 , cyclohexane:EtOAc= 5:1) gave alkene **3j** (69 mg, 0.26 mmol, 52%) as a colorless solid. ^1H NMR (300 MHz, CDCl_3) $\delta = 7.76$ (t, $J = 2.4$ Hz, 1H), 7.58–7.36 (m, 10H), 3.78 (d, $J = 2.4$ Hz, 2H) ppm. ^{13}C NMR (101 MHz, CDCl_3) $\delta = 173.2, 170.2, 135.6, 134.2, 132.1, 130.5, 130.4, 129.3, 129.3, 128.8, 126.6, 123.2, 34.4$ ppm. IR (ATR): 3058 (w), 1774 (m), 1703 (s), 1656 (m), 1499 (m), 1450 (m), 1392 (m), 1251 (m), 1218 (m), 1177 (m), 904 (m), 465 (m), 739 (m), 697 (s) cm^{-1} . MS (EI, 70 eV): m/z (%): 263 (83.7) [M^+], 234 (5.5), 144 (6.0), 116 (100), 89 (6.2). HRMS (ESI $^+$): m/z calcd for $\text{C}_{17}\text{H}_{13}\text{NO}_2$ [$\text{M}+\text{H}$] $^+$ 264.1024, found: 264.1024.

(E)-3-Benzylidene-1-(4-(trifluoromethyl)phenyl)pyrrolidine-2,5-dione (3k)

According to the GP B, benzaldehyde (**1a**, 53 mg, 0.50 mmol, 1.00 equiv) was converted with 1-(4-(trifluoromethyl)phenyl)-1H-pyrrole-2,5-dione (**2k**, 181 mg, 0.750 mmol, 1.50 equiv) and PMHS (173 mg, 173 μ L, 5.00 equiv Si-H) in the presence of 1,2,2,3,4,4-hexamethylphosphetane 1-oxide (**4a**, 4.4 mg, 0.025 mmol, 0.05 equiv) in BuOAc (1.5 ml). Purification (SiO₂, cyclohexane:EtOAc= 5:1) gave alkene **3k** (80 mg, 0.24 mmol, 49%) as a colorless solid. ¹H NMR (300 MHz, CDCl₃) δ = 7.80–7.75 (m, 3H), 7.61–7.46 (m, 7H), 3.80 (d, J = 2.4 Hz, 2H). ¹³C NMR (101 MHz, CDCl₃) δ = 172.7, 169.7, 136.4, 135.2, 134.0, 130.8, 130.5, 129.4, 126.8, 126.4 (q, J = 3.7 Hz), 122.6, 34.4 ppm; Because of low solubility the signal of CF₃ and C-CF₃ could not be resolved. ¹⁹F NMR (282 MHz, CDCl₃) δ = –62.72 ppm. IR (ATR): 3067 (w), 2924 (w), 1778 (m), 1699 (s), 1655 (m), 1403 (m), 1327 (m), 1168 (m), 1111 (m), 1066 (m), 908 (m), 748 (m), 728 (s), 688 (s) cm⁻¹. MS (EI, 70 eV): m/z (%): 331 (91.6) [M⁺], 312 (8.8), 116 (100), 89 (5.7). HRMS (EI): m/z calcd for C₁₈H₁₂O₂NF₃ [M]⁺ 331.0815, found: 331.0812.

(E)-3-Benzylidene-1-(4-methoxyphenyl)pyrrolidine-2,5-dione (3l)

According to the GP B, benzaldehyde (**1a**, 53 mg, 0.50 mmol, 1.00 equiv) was converted with 1-(4-methoxyphenyl)pyrrolidine-2,5-dione (**2l**, 152 mg, 0.750 mmol, 1.50 equiv) and PMHS (173 mg, 173 μ L, 5.00 equiv Si-H) in the presence of 1,2,2,3,4,4-hexamethylphosphetane 1-oxide (**4a**, 4.4 mg, 0.025 mmol, 0.05 equiv) in BuOAc (1.5 ml). Purification (SiO₂, cyclohexane:EtOAc= 5:1) gave alkene **3l** (72 mg, 0.25 mmol, 50%) as a colorless solid. ¹H NMR (400 MHz, CDCl₃) δ = 7.74 (t, J = 2.4 Hz, 1H), 7.56–7.52 (m, 2H), 7.52–7.41 (m, 3H), 7.32–7.27 (m, 2H), 7.04–6.99 (m, 2H), 3.84 (s, 3H), 3.75 (d, J = 2.4 Hz, 2H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ = 173.5, 170.4, 159.6, 135.4, 134.2, 130.4, 130.4, 129.3, 127.8, 124.7, 123.3, 114.6, 55.7, 34.4 ppm. IR (ATR): 3053 (w), 2999 (w), 2934 (w), 2837 (w), 1763 (m), 1703 (s), 1656 (m), 1511 (m), 1379 (m), 1301 (m), 1253 (m), 1219 (m), 1168 (m), 1223 (m), 1031 (m), 822 (m), 764 (m) cm⁻¹. MS (EI, 70 eV): m/z (%): 293 (100) [M⁺], 264 (8.5), 149 (6.5), 134 (8.0), 115 (44.8). HRMS (ESI⁺): m/z calcd for C₁₈H₁₅NO₃ [M+H]⁺ 294.1130, found: 294.1128.

Diethyl (*E*)-2-(4-methoxybenzylidene)succinate (**3n**)⁵

According to the GP B, 4-methoxybenzaldehyde (**1n**, 68 mg, 0.50 mmol, 1.00 equiv) was converted with diethyl fumarate (**2a**, 129 mg, 123 μ L, 0.750 mmol, 1.50 equiv) and PMHS (173 mg, 173 μ L, 5.00 equiv Si-H) in the presence of 1,2,2,3,4,4-hexamethylphosphetane 1-oxide (**4a**, 4.4 mg, 0.025 mmol, 0.05 equiv) in BuOAc (1.5 ml). Purification (SiO₂, cyclohexane:EtOAc= 20:1) gave alkene **3n** (111 mg, 0.380 mmol, 76%) as a colorless oil. ¹H NMR (300 MHz, CDCl₃) δ = 7.91–7.71 (m, 1H), 7.39–7.28 (m, 2H), 6.98–6.82 (m, 2H), 4.26 (q, *J* = 7.1 Hz, 2H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.82 (s, 3H), 3.54 (d, *J* = 0.8 Hz, 2H), 1.32 (t, *J* = 7.1 Hz, 3H), 1.26 (t, *J* = 7.1 Hz, 3H) ppm. ¹³C NMR (75 MHz, CDCl₃) δ = 171.3, 167.6, 160.2, 141.4, 130.9, 127.5, 124.3, 114.1, 61.0, 60.9, 55.3, 33.8, 14.3, 14.2 ppm.

Diethyl (*E*)-2-(4-(methoxycarbonyl)benzylidene)succinate (**3o**)

According to the GP B, methyl 4-formylbenzoate (**1o**, 82 mg, 0.50 mmol, 1.00 equiv) was converted with diethyl fumarate (**2a**, 129 mg, 123 μ L, 0.750 mmol, 1.50 equiv) and PMHS (173 mg, 173 μ L, 5.00 equiv Si-H) in the presence of 1,2,2,3,4,4-hexamethylphosphetane 1-oxide (**4a**, 4.4 mg, 0.025 mmol, 0.05 equiv) in BuOAc (1.5 ml). Purification (SiO₂, cyclohexane:EtOAc= 50:1) gave alkene **3o** (128 mg, 0.400 mmol, 80%) as a colorless oil. ¹H NMR (300 MHz, CDCl₃) δ = 8.07–7.98 (m, 2H), 7.87 (s, 1H), 7.42–7.37 (m, 2H), 4.26 (q, *J* = 7.1 Hz, 2H), 4.16 (q, *J* = 7.1 Hz, 2H), 3.89 (s, 3H), 3.46 (d, *J* = 0.9 Hz, 2H), 1.31 (t, *J* = 7.1 Hz, 3H), 1.24 (t, *J* = 7.1 Hz, 3H) ppm. ¹³C NMR (75 MHz, CDCl₃) δ = 170.8, 166.9, 166.5, 140.5, 139.6, 130.2, 129.8, 128.9, 128.1, 61.3, 61.1, 52.2, 33.7, 14.2, 14.2 ppm. IR (ATR): 2982 (w), 2954 (m), 1710 (m), 1436 (m), 1369 (m), 1271 (m), 1177 (m), 1093 (m), 1018 (m), 769 (m), 721 (m) cm⁻¹. MS (EI, 70 eV): *m/z* (%): 320 (45.2) [M⁺], 289 (26.8), 275 (61.1), 247 (36.2), 202 (24.1), 174 (48.1), 143 (100), 129 (36.7), 115 (91.6), 59 (21.8). HRMS (ESI⁺): *m/z* calcd for C₁₇H₂₀O₆ [M+Na]⁺ 343.1157, found: 343.1155.

Diethyl (*E*)-2-(4-chlorobenzylidene)succinate (**3p**)⁵

According to the GP B, 4-chlorobenzaldehyde (**1p**, 70 mg, 0.50 mmol, 1.00 equiv) was converted with diethyl fumarate (**2a**, 129 mg, 123 μ L, 0.750 mmol, 1.50 equiv) and PMHS (173 mg, 173 μ L, 5.00 equiv Si-H) in the presence of 1,2,2,3,4,4-

hexamethylphosphetane 1-oxide (**4a**, 4.4 mg, 0.025 mmol, 0.05 equiv) in BuOAc (1.5 ml). Purification (SiO₂, cyclohexane:EtOAc= 50:1) gave alkene **3p** (110 mg, 0.370 mmol, 74%) as a colorless oil. ¹H NMR (300 MHz, CDCl₃) δ = 7.70 (s, 1H), 7.28–7.21 (m, 2H), 7.20–7.14 (m, 2H), 4.16 (q, *J* = 7.1 Hz, 2H), 4.07 (q, *J* = 7.1 Hz, 2H), 3.36 (d, *J* = 0.8 Hz, 2H), 1.21 (t, *J* = 7.1 Hz, 3H), 1.15 (t, *J* = 7.1 Hz, 3H) ppm. ¹³C NMR (75 MHz, CDCl₃) δ = 171.0, 167.0, 140.4, 134.9, 133.5, 130.4, 128.9, 127.0, 61.3, 61.1, 33.7, 14.2, 14.2 ppm.

Diethyl (*E*)-2-(3-chlorobenzylidene)succinate (**3q**)

According to the GP B, 3-chlorobenzaldehyde (**1q**, 70 mg, 0.50 mmol, 1.00 equiv) was converted with diethyl fumarate (**2a**, 129 mg, 123 μ L, 0.750 mmol, 1.50 equiv) and PMHS (173 mg, 173 μ L, 5.00 equiv Si-H) in the presence of 1,2,2,3,4,4-hexamethylphosphetane 1-oxide (**4a**, 4.4 mg, 0.025 mmol, 0.05 equiv) in BuOAc (1.5 ml). Purification (SiO₂, cyclohexane:EtOAc= 50:1) gave alkene **3q** (107 mg, 0.365 mmol, 73%) as a colorless oil. ¹H NMR (300 MHz, CDCl₃) δ = 7.80 (s, 1H), 7.36–7.27 (m, 3H), 7.25–7.17 (m, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.47 (d, *J* = 0.8 Hz, 2H), 1.32 (t, *J* = 7.1 Hz, 3H), 1.26 (t, *J* = 7.1 Hz, 3H) ppm. ¹³C NMR (75 MHz, CDCl₃) δ = 170.9, 167.0, 140.2, 136.9, 134.7, 123.0, 129.0, 128.9, 127.8, 127.1, 61.4, 61.1, 33.8, 14.3, 14.3 ppm. IR (ATR): 2981 (w), 2937 (w), 1731 (s), 1708 (s), 1368 (m), 1323 (m), 1278 (m), 1178 (m), 1091 (m), 1026 (m), 788 (m), 683 (m) cm⁻¹. MS (EI, 70 eV): *m/z* (%): 296 (32.3) [M⁺], 251 (41.3), 223 (23.5), 195 (15.9), 178 (17.8), 167 (22.0), 151 (61.4), 115 (100). HRMS (ESI⁺): *m/z* calcd for C₉H₁₈O₄ [M+Na]⁺ 219.0712, found: 319.0707.

Diethyl (*E*)-2-(2-chlorobenzylidene)succinate (**3r**)

According to the GP B, 2-chlorobenzaldehyde (**1r**, 70 mg, 0.50 mmol, 1.00 equiv) was converted with diethyl fumarate (**2a**, 129 mg, 123 μ L, 0.750 mmol, 1.50 equiv) and PMHS (173 mg, 173 μ L, 5.00 equiv Si-H) in the presence of 1,2,2,3,4,4-hexamethylphosphetane 1-oxide (**4a**, 4.4 mg, 0.025 mmol, 0.05 equiv) in BuOAc (1.5 ml). Purification (SiO₂, cyclohexane:EtOAc= 50:1) gave alkene **3r** (107 mg, 0.360 mmol, 72%) as a colorless oil. ¹H NMR (300 MHz, CDCl₃) δ = 7.92 (d, *J* = 0.8 Hz, 1H), 7.47–7.38 (m, 1H), 7.36–7.21 (m, 3H), 4.28 (q, *J* = 7.1 Hz, 2H), 4.16 (q, *J* =

7.1 Hz, 2H), 3.38 (d, $J = 0.8$ Hz, 2H), 1.32 (t, $J = 7.1$ Hz, 3H), 1.25 (t, $J = 7.1$ Hz, 3H) ppm. ^{13}C NMR (75 MHz, CDCl_3) $\delta = 171.0, 166.8, 139.0, 134.1, 133.8, 130.1, 130.0, 129.7, 128.3, 126.9, 61.3, 61.0, 34.0, 14.3, 14.2$ ppm. IR (ATR): 2981 (w), 2937 (w), 1709 (s), 1469 (m), 1369 (m), 1323 (m), 1286 (m), 1261 (m), 1178 (m), 1093 (m), 1027 (m), 758 (m), cm^{-1} . MS (EI, 70 eV): m/z (%): 296 (0.03) [M^+], 261 (100), 251 (18.8), 187 (51.9), 159 (52.2), 149 (16.4), 115 (43.5). HRMS (ESI+): m/z calcd for $\text{C}_9\text{H}_{18}\text{O}_4$ [$\text{M}+\text{Na}$] $^+$ 319.0712, found: 319.0712.

Diethyl (*E*)-2-([1,1'-biphenyl]-4-ylmethylene)succinate (**3s**)⁵

According to the GP B, [1,1'-biphenyl]-4-carbaldehyde (**1s**, 91 mg, 0.50 mmol, 1.00 equiv) was converted with diethyl fumarate (**2a**, 129 mg, 123 μL , 0.750 mmol, 1.50 equiv) and PMHS (173 mg, 173 μL , 5.00 equiv Si-H) in the presence of 1,2,2,3,4,4-hexamethylphosphetane 1-oxide (**4a**, 4.4 mg, 0.025 mmol, 0.05 equiv) in BuOAc (1.5 ml). Purification (SiO_2 , cyclohexane:EtOAc= 50:1) gave alkene **3s** (100 mg, 0.295 mmol, 59%) as a colorless oil. ^1H NMR (300 MHz, CDCl_3) $\delta = 7.93$ (s, 1H), 7.62 (m, 4H), 7.51–7.33 (m, 5H), 4.30 (q, $J = 7.1$ Hz, 2H), 4.21 (q, $J = 7.1$ Hz, 2H), 3.59 (d, $J = 0.8$ Hz, 2H), 1.35 (t, $J = 7.1$ Hz, 3H), 1.28 (t, $J = 7.1$ Hz, 3H) ppm. ^{13}C NMR (75 MHz, CDCl_3) $\delta = 171.2, 167.4, 141.7, 141.3, 140.2, 134.0, 129.7, 128.9, 127.8, 127.3, 127.1, 126.3, 61.2, 61.0, 33.9, 14.3, 14.2$ ppm.

Diethyl (*E*)-2-(naphthalen-2-ylmethylene)succinate (**3t**)⁵

According to the GP B, 2-naphthaldehyde (**1t**, 47 mg, 0.30 mmol, 1.0 equiv) was converted with diethyl fumarate (**2a**, 77 mg, 74 μL , 0.45 mmol, 1.5 equiv) and PMHS (173 mg, 173 μL , 5.00 equiv Si-H) in the presence of 1,2,2,3,4,4-hexamethylphosphetane 1-oxide (**4a**, 2.6 mg, 0.015 mmol, 0.05 equiv) in BuOAc (1.5 ml). Purification (SiO_2 , cyclohexane:EtOAc= 50:1) gave alkene **3t** (81 mg, 0.26 mmol, 86%) as a colorless oil. ^1H NMR (300 MHz, CDCl_3) $\delta = 8.05$ (d, $J = 0.7$ Hz, 1H), 7.91–7.80 (m, 4H), 7.55–7.43 (m, 3H), 4.31 (q, $J = 7.1$ Hz, 2H), 4.22 (q, $J = 7.1$ Hz, 2H), 3.61 (d, $J = 0.8$ Hz, 2H), 1.36 (t, $J = 7.1$ Hz, 3H), 1.29 (t, $J = 7.1$ Hz, 3H) ppm. ^{13}C NMR (75 MHz, CDCl_3) $\delta = 171.3, 167.5, 141.8, 133.2, 133.2, 132.6, 128.9, 128.4, 128.4, 127.8, 127.0, 126.7, 126.6, 126.4, 61.3, 61.1, 33.9, 14.3, 14.3$ ppm.

Diethyl (*E*)-2-(furan-2-ylmethylene)succinate (**3u**)⁷

According to the GP B, furan-2-carbaldehyde (**1u**, 48 mg, 0.50 mmol, 1.00 equiv) was converted with diethyl fumarate (**2a**, 129 mg, 123 μ L, 0.750 mmol, 1.50 equiv) and PMHS (173 mg, 173 μ L, 5.00 equiv Si-H) in the presence of 1,2,2,3,4,4-hexamethylphosphetane 1-oxide (**4a**, 4.4 mg, 0.025 mmol, 0.05 equiv) in BuOAc (1.5 ml). Purification (SiO₂, cyclohexane:EtOAc= 50:1) gave alkene **3u** (115 mg, 0.455 mmol, 91%) as a yellow oil. ¹H NMR (300 MHz, CDCl₃) δ = 7.54 (q, *J* = 0.4 Hz, 1H), 7.52 (dt, *J* = 1.9 Hz, 0.6 Hz, 1H), 6.64 (ddd, *J* = 3.4 Hz, 0.4 Hz, 1H), 6.48 (ddd, *J* = 3.4 Hz, 1.8 Hz, 0.3 Hz, 1H), 4.25 (q, *J* = 7.1 Hz, 2H), 4.15 (q, *J* = 7.1 Hz, 2H), 3.84 (d, *J* = 0.6 Hz, 2H), 1.32 (t, *J* = 7.1 Hz, 3H), 1.24 (t, *J* = 7.1 Hz, 3H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ = 171.2, 167.6, 151.1, 144.9, 127.5, 121.7, 116.6, 112.2, 61.1, 60.8, 33.7, 14.3, 14.2 ppm.

Diethyl (*E*)-2-(thiophene-2-ylmethylene)succinate (**3v**)⁵

According to the GP B, thiophene-2-carbaldehyde (**1v**, 56 mg, 0.50 mmol, 1.00 equiv) was converted with diethyl fumarate (**2a**, 129 mg, 123 μ L, 0.750 mmol, 1.50 equiv) and PMHS (173 mg, 173 μ L, 5.00 equiv Si-H) in the presence of 1,2,2,3,4,4-hexamethylphosphetane 1-oxide (**4a**, 4.4 mg, 0.025 mmol, 0.05 equiv) in BuOAc (1.5 ml). Purification (SiO₂, cyclohexane:EtOAc= 50:1) gave alkene **3v** (129 mg, 0.480 mmol, 96%) as a colorless oil. ¹H NMR (300 MHz, CDCl₃) δ = 7.98 (t, *J* = 0.7 Hz, 1H), 7.48 (ddd, *J* = 5.1 Hz, 1.2 Hz, 0.7 Hz, 1H), 7.30 (ddd, *J* = 3.7 Hz, 1.2 Hz, 0.7 Hz, 1H), 7.10 (dd, *J* = 5.1 Hz, 3.7 Hz, 1H), 4.27 (q, *J* = 7.1 Hz, 2H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.75 (d, *J* = 0.6 Hz, 2H), 1.33 (t, *J* = 7.1 Hz, 3H), 1.26 (t, *J* = 7.1 Hz, 3H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ = 170.4, 167.4, 137.9, 133.9, 132.5, 129.5, 127.7, 122.4, 61.2, 61.0, 34.0, 14.3, 14.2 ppm.

Diethyl (*E*)-2-(benzofuran-2-ylmethylene)succinate (**3w**)⁵

According to the GP B, benzofuran-2-carbaldehyde (**1w**, 73 mg, 0.50 mmol, 1.00 equiv) was converted with diethyl fumarate (**2a**, 129 mg, 123 μ L, 0.750 mmol, 1.50 equiv) and PMHS (173 mg, 173 μ L, 5.00 equiv Si-H) in the presence of 1,2,2,3,4,4-hexamethylphosphetane 1-oxide (**4a**, 4.4 mg, 0.025 mmol, 0.05 equiv) in BuOAc (1.5 ml). Purification (SiO₂, cyclohexane:EtOAc= 50:1) gave alkene **3w**

(135 mg, 0.445 mmol, 89%) as a colorless oil. ^1H NMR (300 MHz, CDCl_3) δ = 7.66 (q, J = 0.5 Hz, 1H), 7.59 (ddd, J = 7.7 Hz, 1.4 Hz, 0.7 Hz, 1H), 7.47 (dq, J = 8.3 Hz, 1.0 Hz, 1H), 7.39–7.31 (m, 1H), 7.29–7.22 (m, 1H), 7.00–6.97 (m, 1H), 4.29 (q, J = 7.1 Hz, 2H), 4.18 (q, J = 7.1 Hz, 2H), 4.01 (d, J = 0.6 Hz, 2H), 1.35 (t, J = 7.1 Hz, 3H), 1.26 (t, J = 7.1 Hz, 3H) ppm. ^{13}C NMR (75 MHz, CDCl_3) δ = 171.1, 167.3, 155.7, 152.6, 127.9, 127.8, 126.3, 124.9, 123.5, 121.8, 112.8, 111.5, 61.4, 60.9, 34.0, 14.3 ppm.

Diethyl (*E*)-2-heptylidenesuccinate (**3x**)

According to the GP B, heptanal (**1x**, 57 mg, 0.50 mmol, 1.00 equiv) was converted with diethyl fumarate (**2a**, 129 mg, 123 μL , 0.750 mmol, 1.50 equiv) and PMHS (173 mg, 173 μL , 5.00 equiv Si-H) in the presence of 1,2,2,3,4,4-hexamethylphosphetane 1-oxide (**4a**, 4.4 mg, 0.025 mmol, 0.05 equiv) in BuOAc (1.5 ml). Purification (SiO_2 , cyclohexane:EtOAc= 20:1) gave alkene **3x** (94 mg, 0.35 mmol, 70%) as a colorless oil. ^1H NMR (300 MHz, CDCl_3) δ = 6.95 (t, J = 7.6 Hz, 1H), 4.19 (q, J = 7.1 Hz, 2H), 4.13 (q, J = 7.1 Hz, 2H), 3.33 (s, 2H), 2.17 (q, J = 7.4 Hz, 2H), 1.50–1.39 (m, 2H), 1.34–1.21 (m, 12H), 0.93–0.82 (m, 3H) ppm. ^{13}C NMR (75 MHz, CDCl_3) δ = 170.9, 167.0, 145.6, 125.6, 60.7, 60.7, 32.4, 31.6, 29.0, 28.9, 28.5, 22.5, 14.2, 14.2, 14.0 ppm. MS (EI, 70 eV): m/z (%): 270 (0.5) [M^+], 224 (100), 196 (25.5), 167 (29.6), 139 (75.1), 123 (50.2), 111 (29.6), 98 (30.2), 81 (36.4), 67 (30.2). IR (ATR): 2957 (m), 2929 (m), 2858 (m), 1738 (s), 1709 (s), 1653 (w), 1464 (w), 1368 (m), 1281 (m), 1176 (m), 1032 (m), 768 (m) cm^{-1} . HRMS (EI): m/z calcd for $\text{C}_{15}\text{H}_{26}\text{O}_4$ [M] $^+$ 270.1826, found: 270.1825.

Diethyl (*E*)-2-(3-phenylpropylidene)succinate (**3y**)

According to the GP B, 3-phenylpropanal (**1y**, 67 mg, 0.50 mmol, 1.00 equiv) was converted with diethyl fumarate (**2a**, 129 mg, 123 μL , 0.750 mmol, 1.50 equiv) and PMHS (173 mg, 173 μL , 5.00 equiv Si-H) in the presence of 1,2,2,3,4,4-hexamethylphosphetane 1-oxide (**4a**, 4.4 mg, 0.025 mmol, 0.05 equiv) in BuOAc (1.5 ml). Purification (SiO_2 , cyclohexane:EtOAc= 10:1) gave alkene **3y** (124 mg, 0.425 mmol, 85%) as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ = 7.33–7.27 (m, 2H), 7.24–7.16 (m, 3H), 7.00 (t, J = 7.5 Hz, 1H), 4.20 (q, J = 7.1 Hz, 2H), 4.12 (q, J = 7.1 Hz, 2H), 3.28 (s, 2H), 2.80–2.75 (m, 2H), 2.51 (q, J = 7.7 Hz, 2H), 1.28 (t, J = 7.1 Hz, 3H), 1.24 (t, J = 7.1 Hz, 3H) ppm. ^{13}C NMR (101 MHz, CDCl_3) δ = 170.9, 167.0, 144.3,

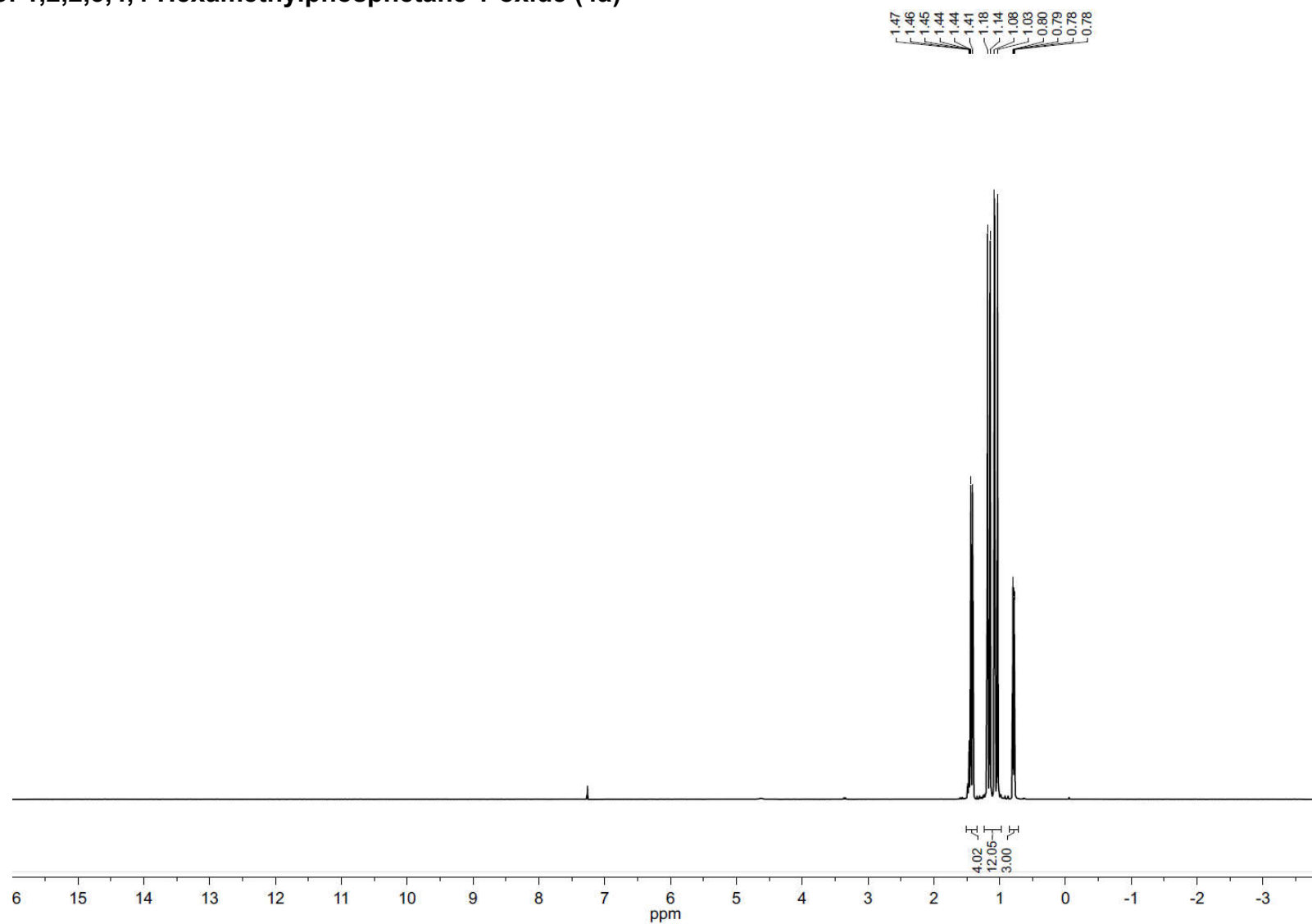
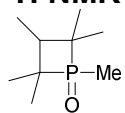
141.0, 128.6, 128.5, 126.5, 126.3, 60.9, 60.9, 34.7, 32.5, 31.0, 14.3, 14.3 ppm. IR (ATR): 3027 (w), 2981 (w), 2936 (w), 1734 (s), 1705 (s), 1653 (w), 1454 (w), 1368 (m), 1274 (m), 1172 (m), 1029 (m), 748 (m), 699 (m) cm^{-1} . MS (EI, 70 eV): m/z (%): 290 (6.0) [M^+], 244 (27.3), 216 (9.7), 199 (11.0), 170 (15.3), 153 (14.9), 128 (17.3), 91 (100). HRMS (EI): m/z calcd for $\text{C}_{17}\text{H}_{22}\text{O}_4$ [M] $^+$ 290.1513, found: 290.1517.

Diethyl (*E*)-2-(3,7-dimethyloct-6-en-1-ylidene)succinate (**3z**)

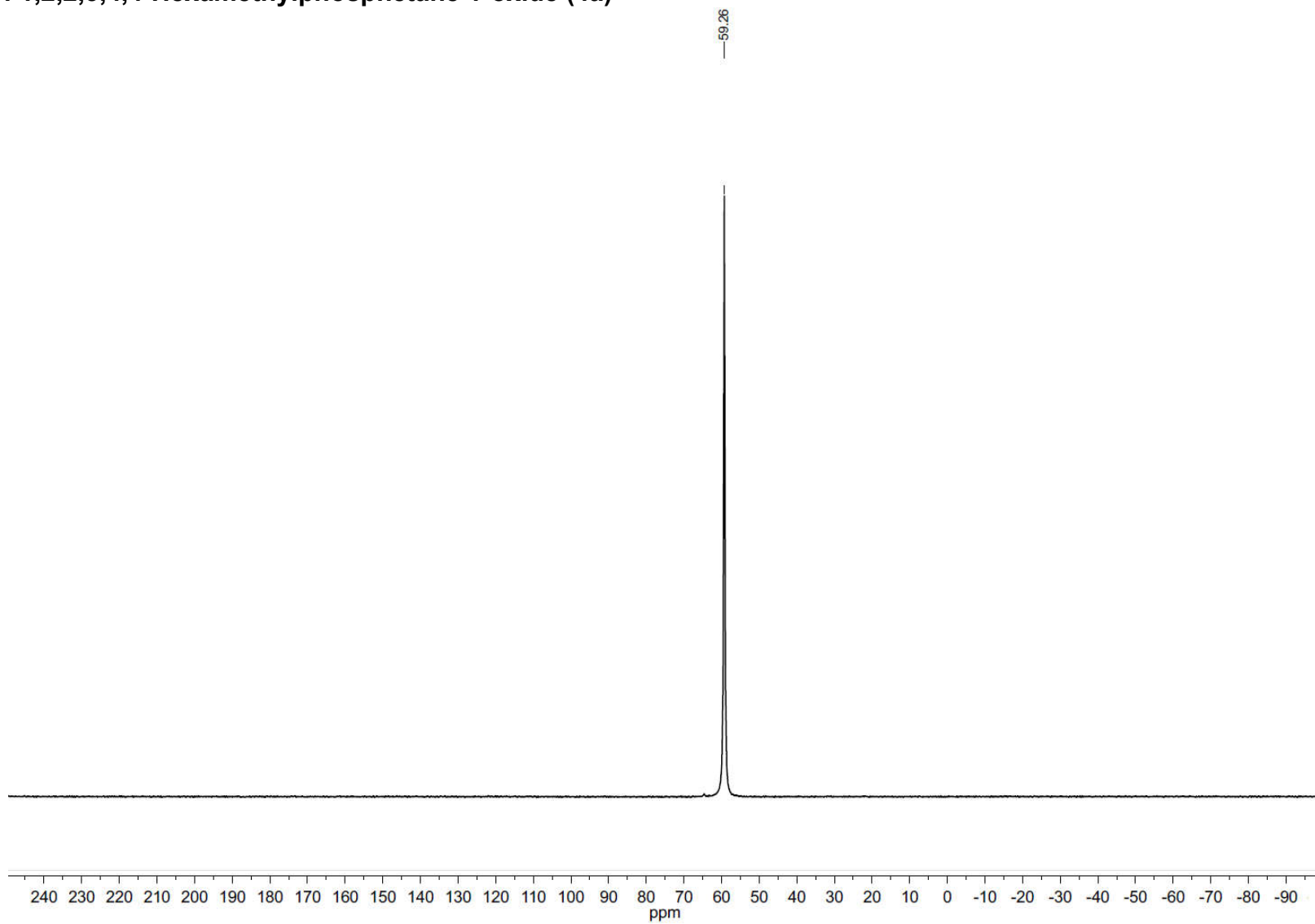
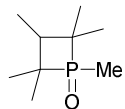
According to the GP B, citronellal (**1z**, 77 mg, 0.50 mmol, 1.00 equiv) was converted with diethyl fumarate (**2a**, 129 mg, 123 μL , 0.750 mmol, 1.50 equiv) and PMHS (173 mg, 173 μL , 5.00 equiv Si-H) in the presence of 1,2,2,3,4,4-hexamethylphosphetane 1-oxide (**4a**, 4.4 mg, 0.025 mmol, 0.05 equiv) in BuOAc (1.5 ml). Purification (SiO_2 , cyclohexane:EtOAc= 20:1) gave alkene **3z** (146 mg, 0.470 mmol, 94%) as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ = 6.97 (t, J = 7.6 Hz, 1H), 5.12–5.03 (m, 1H), 4.20 (q, J = 7.1 Hz, 2H), 4.13 (q, J = 7.1 Hz, 2H), 3.33 (s, 2H), 2.19 (ddd, J = 14.8, 7.3, 5.6 Hz, 1H), 2.07–1.90 (m, 3H), 1.68 (d, J = 1.3 Hz, 3H), 1.69–1.61 (m, 1H), 1.60 (d, J = 1.3 Hz, 3H), 1.41–1.32 (m, 1H), 1.28 (t, J = 7.1 Hz, 3H), 1.24 (t, J = 7.1 Hz, 3H), 1.23–1.14 (m, 1H), 0.91 (d, J = 6.6 Hz, 3H) ppm. ^{13}C NMR (75 MHz, CDCl_3) δ = 171.0, 167.1, 144.6, 131.6, 126.5, 124.5, 60.9, 60.9, 37.0, 36.3, 32.7, 32.7, 25.8, 25.7, 19.8, 17.8, 14.4, 14.3 ppm. IR (ATR): 2964 (m), 2913 (m), 2873 (m), 1738 (s), 1709 (s), 1653 (w), 1448 (m), 1368 (m), 1287 (m), 1178 (m), 1031 (m), 766 (m) cm^{-1} . MS (EI, 70 eV): m/z (%): 310 (4.1) [M^+], 264 (30.2), 249 (44.7), 219 (72.0), 203 (36.0), 190 (55.2), 175 (48.4), 148 (66.5), 107 (59.1), 93 (43.4), 81 (41.9), 69 (100). HRMS (EI): m/z calcd for $\text{C}_{18}\text{H}_{30}\text{O}_4$ [M] $^+$ 310.2139, found: 310.2147.

6. NMR-spectra of the synthesized compounds

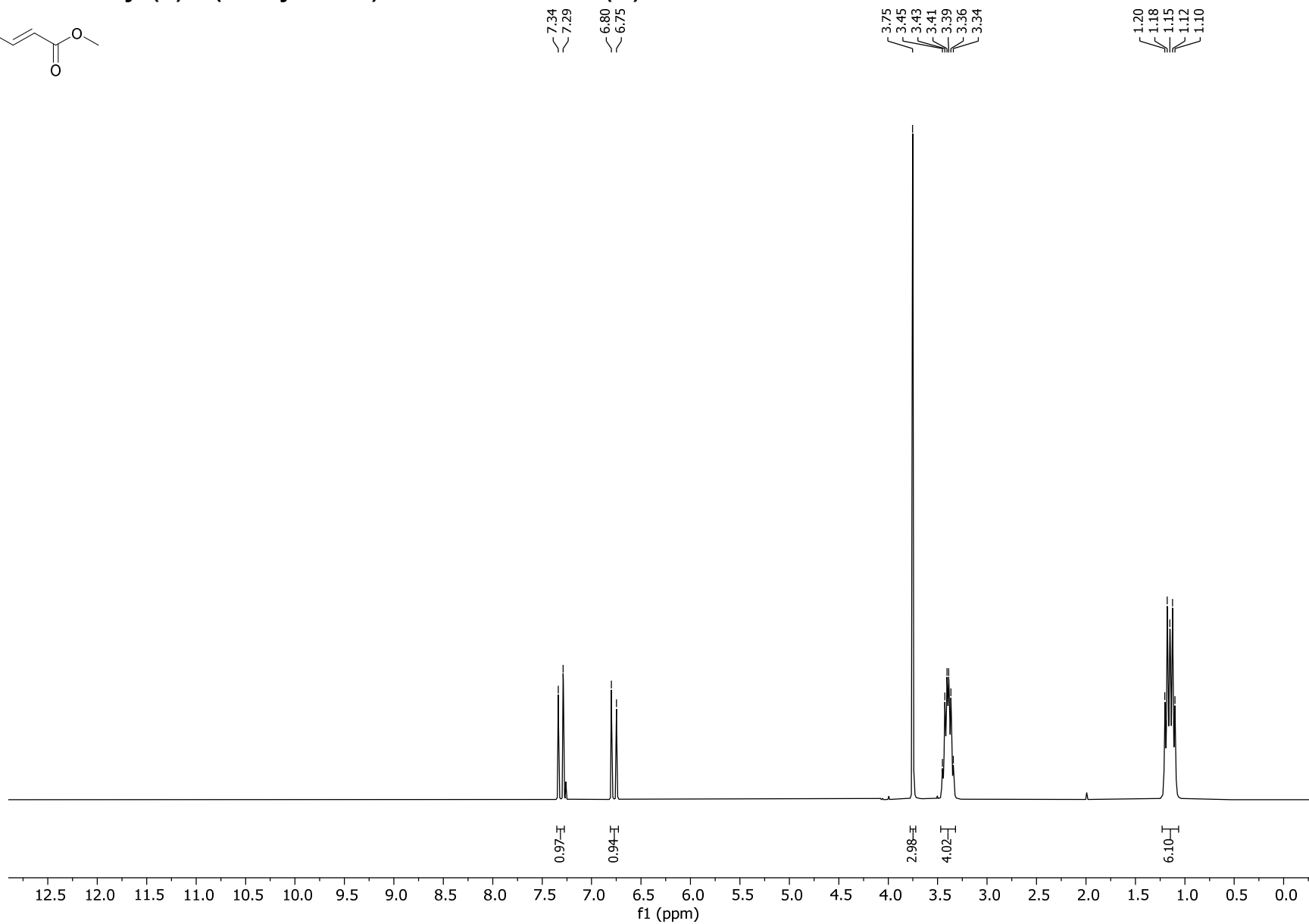
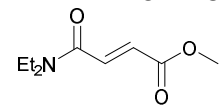
^1H NMR of 1,2,2,3,4,4-Hexamethylphosphetane 1-oxide (4a)



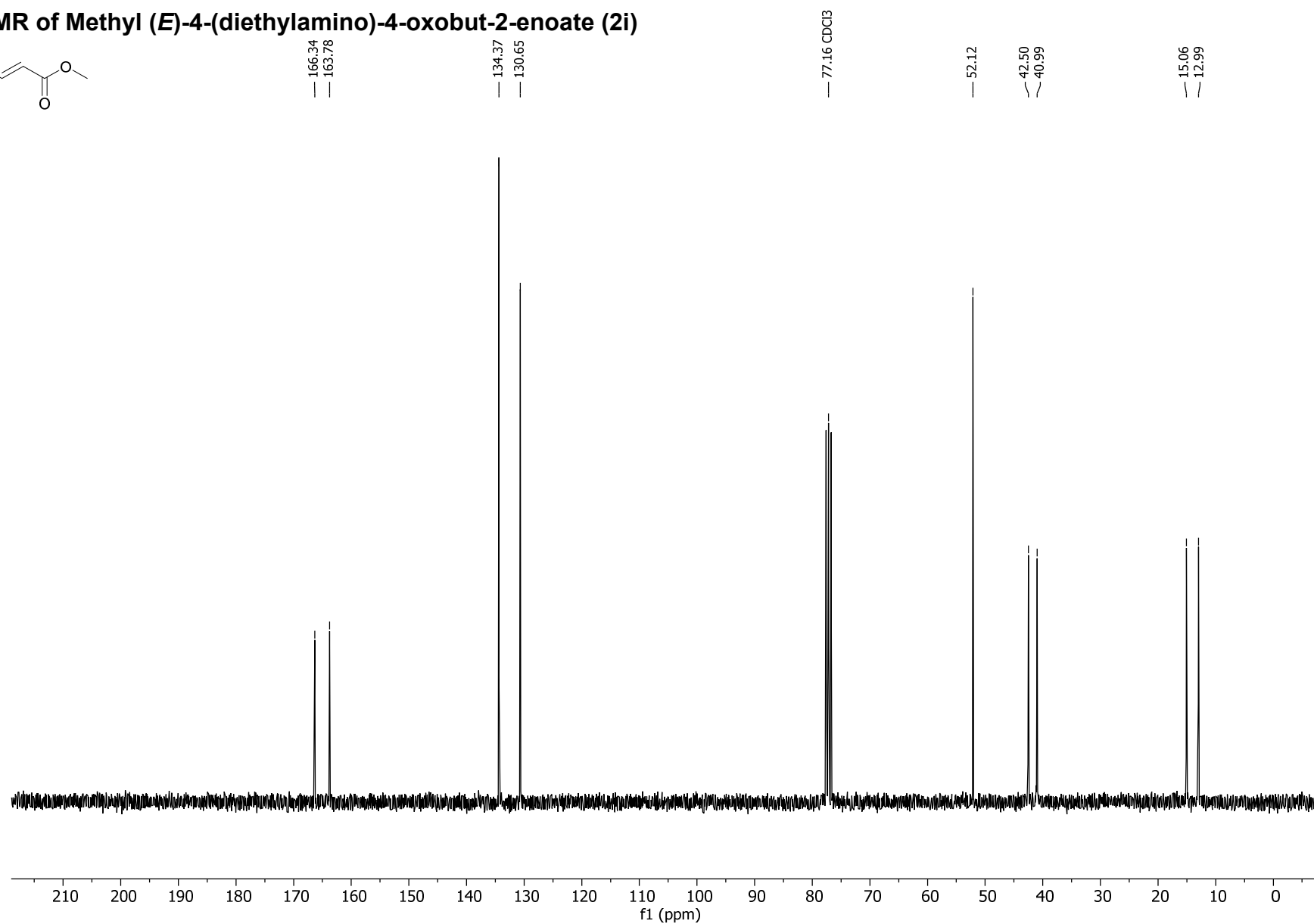
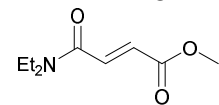
³¹P NMR of 1,2,2,3,4,4-Hexamethylphosphetane 1-oxide (4a)



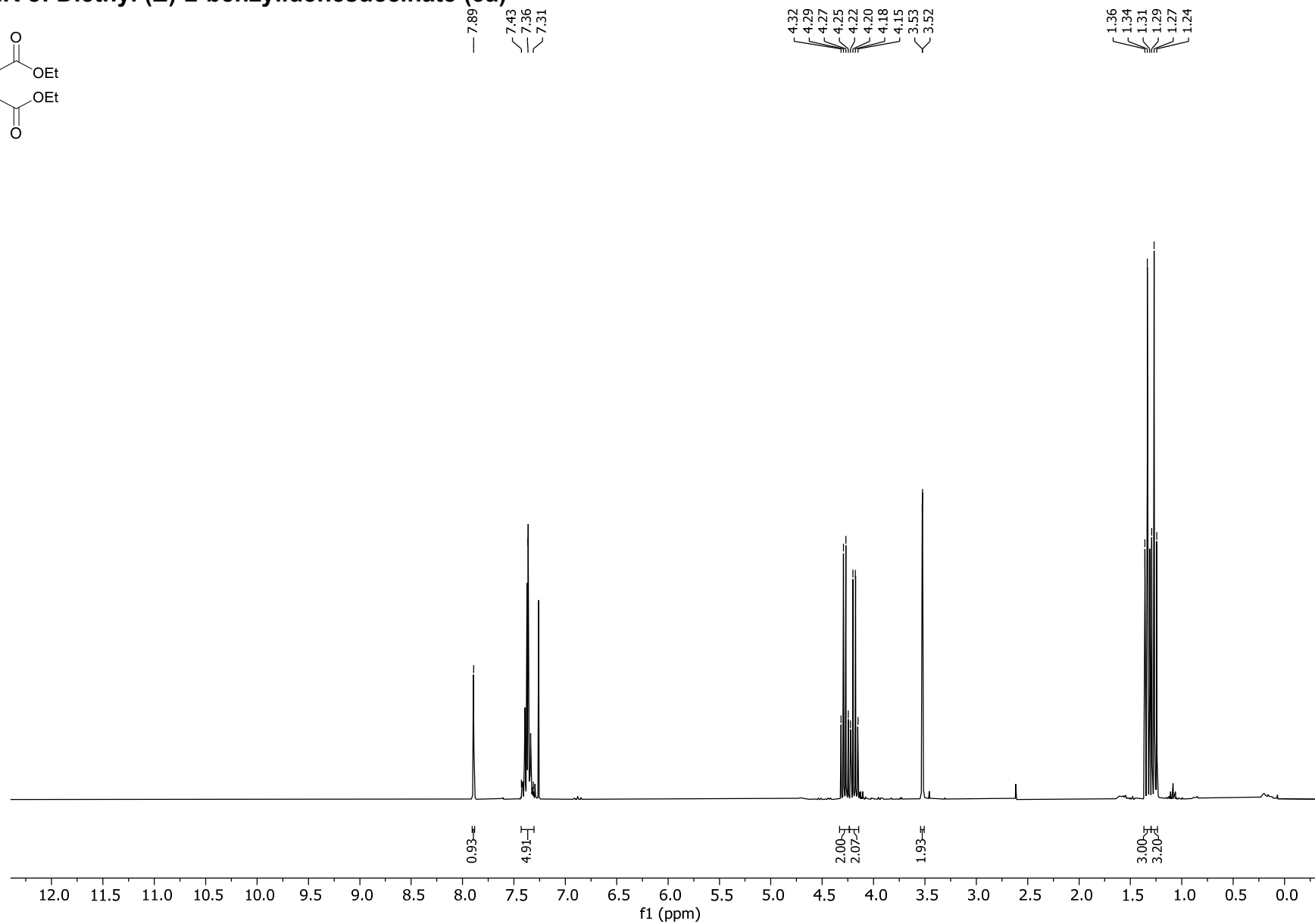
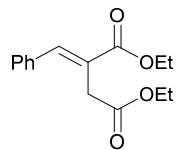
¹H NMR of Methyl (*E*)-4-(diethylamino)-4-oxobut-2-enoate (2i)



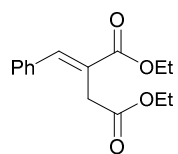
¹³C NMR of Methyl (*E*)-4-(diethylamino)-4-oxobut-2-enoate (2i)



¹H NMR of Diethyl (*E*)-2-benzylidenesuccinate (3a)



¹³C NMR of Diethyl (*E*)-2-benzylidenesuccinate (3a)



— 171.17
— 167.34

— 141.70

— 135.09

— 129.03

— 128.84

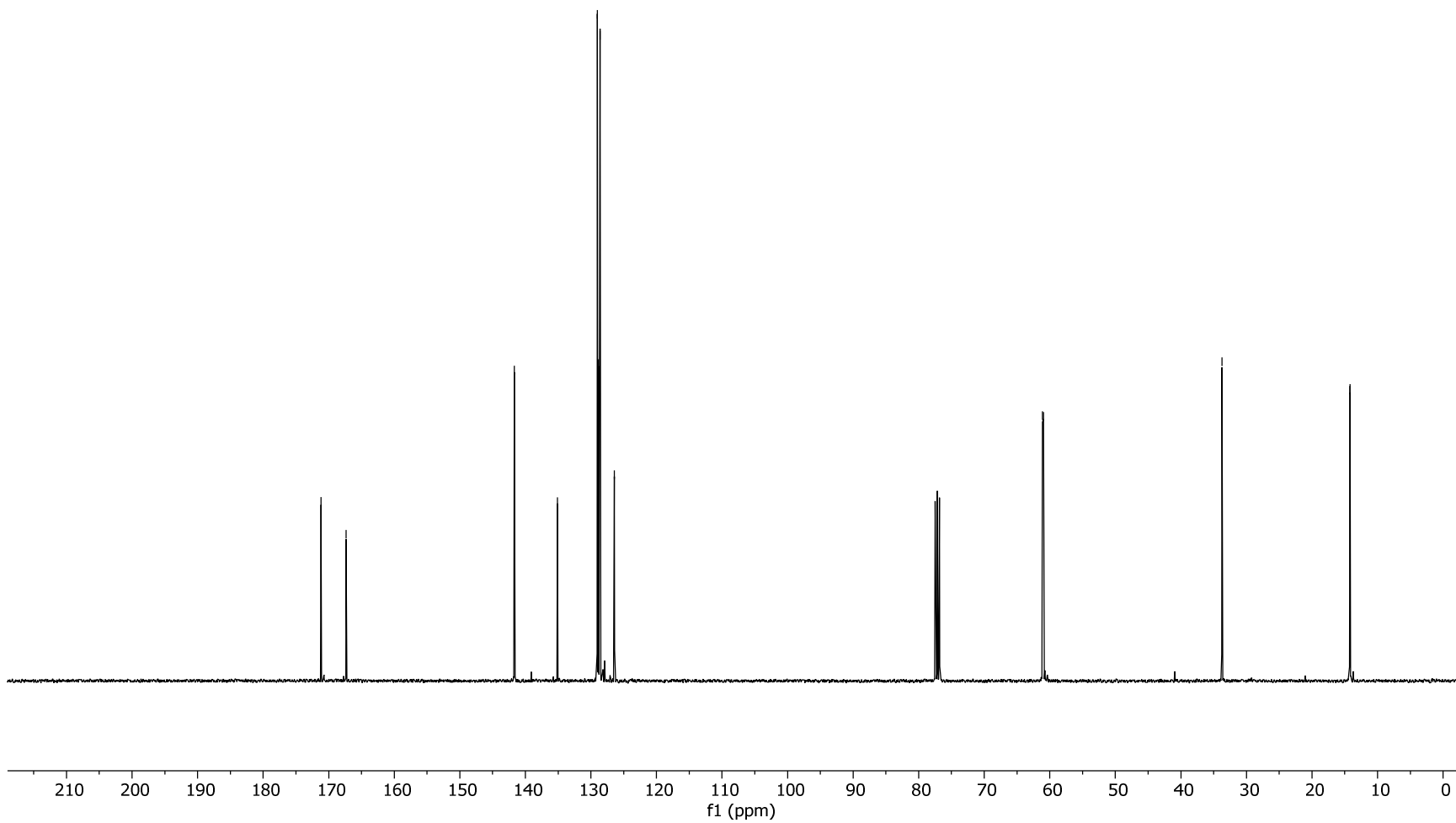
— 128.62

— 126.42

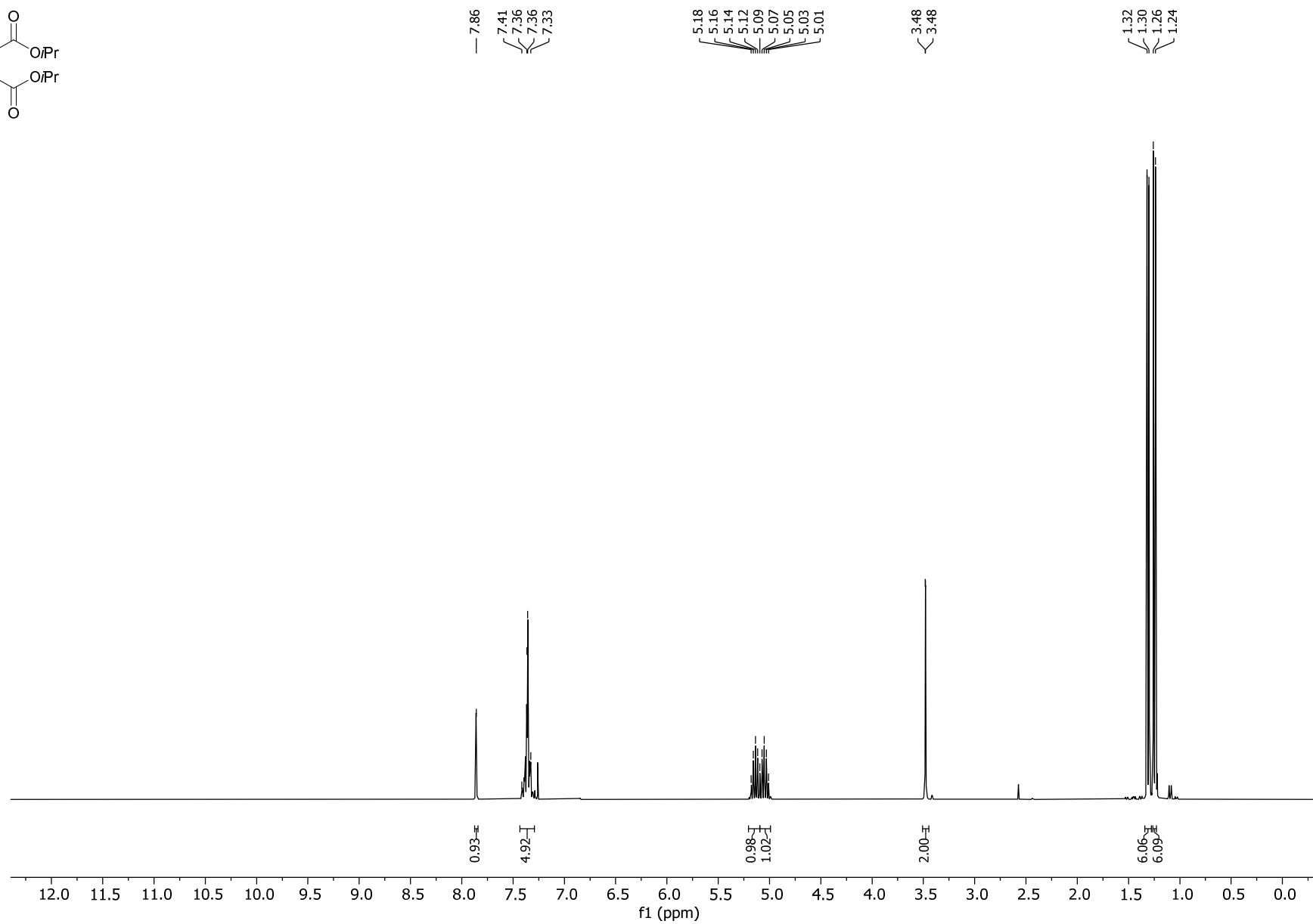
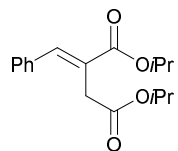
— 61.13
— 60.94

— 33.74

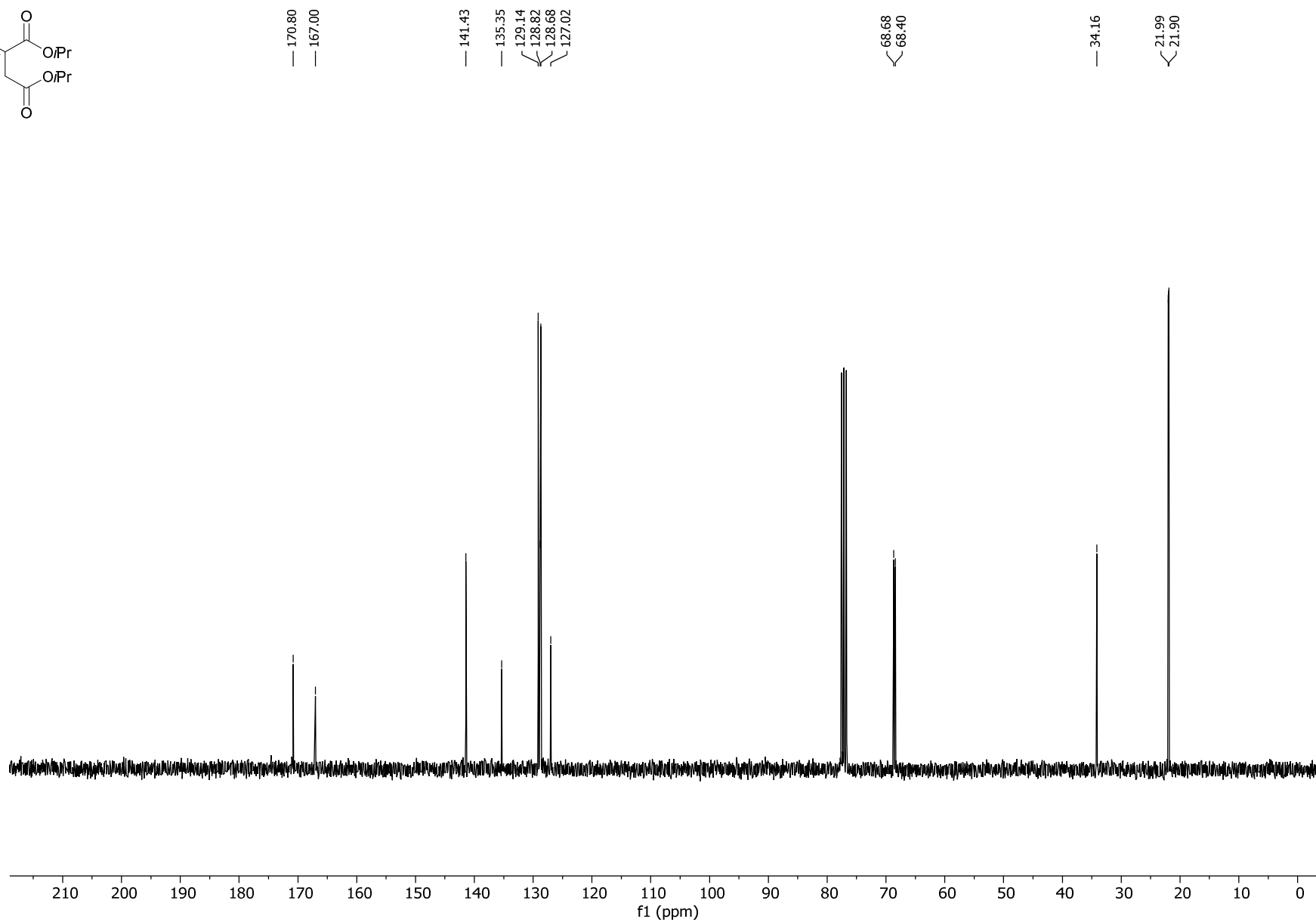
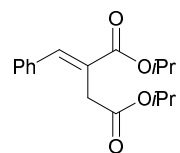
— 14.25
— 14.21



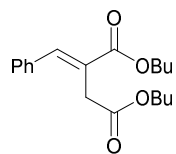
¹H NMR of Diisopropyl (*E*)-2-benzylidenesuccinate (3b)



¹³C NMR of Diisopropyl (*E*)-2-benzylidenesuccinate (3b)



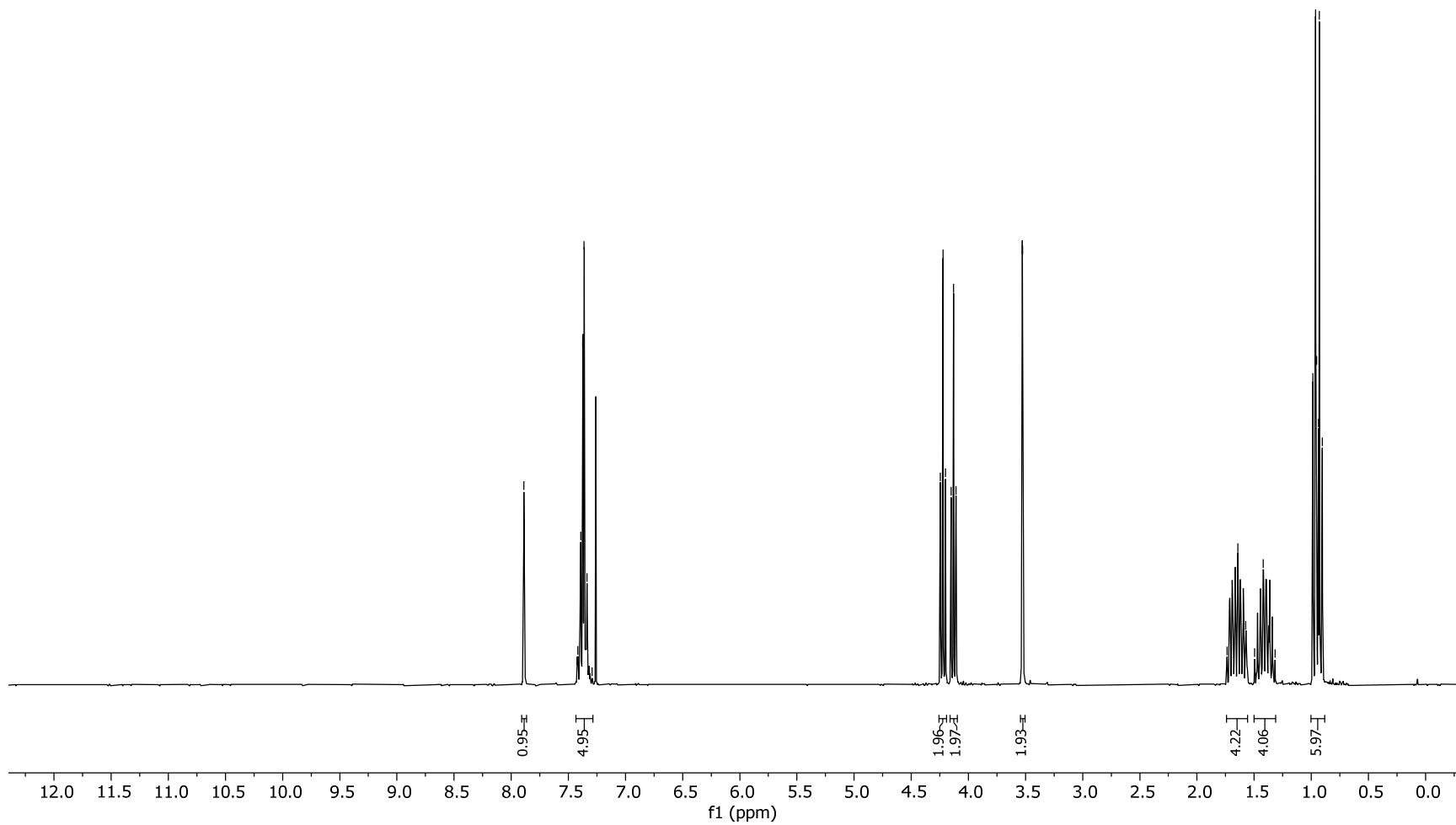
¹H NMR of Dibutyl (*E*)-2-benzylidenesuccinate (3c)



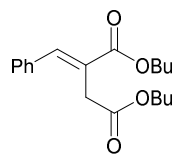
7.89
7.43
7.42
7.39
7.37
7.36
7.34
7.29

4.24
4.22
4.20
4.15
4.13
4.11
3.53
3.53

1.74
1.64
1.57
1.50
1.42
1.32
0.99
0.96
0.95
0.94
0.93
0.90



¹³C NMR of Dibutyl (*E*)-2-benzylidenesuccinate (3c)



— 171.30
— 167.51

— 141.77

— 135.18

— 129.12

— 128.91

— 128.69

— 126.49

— 65.11

— 64.94

— 33.84

— 30.80

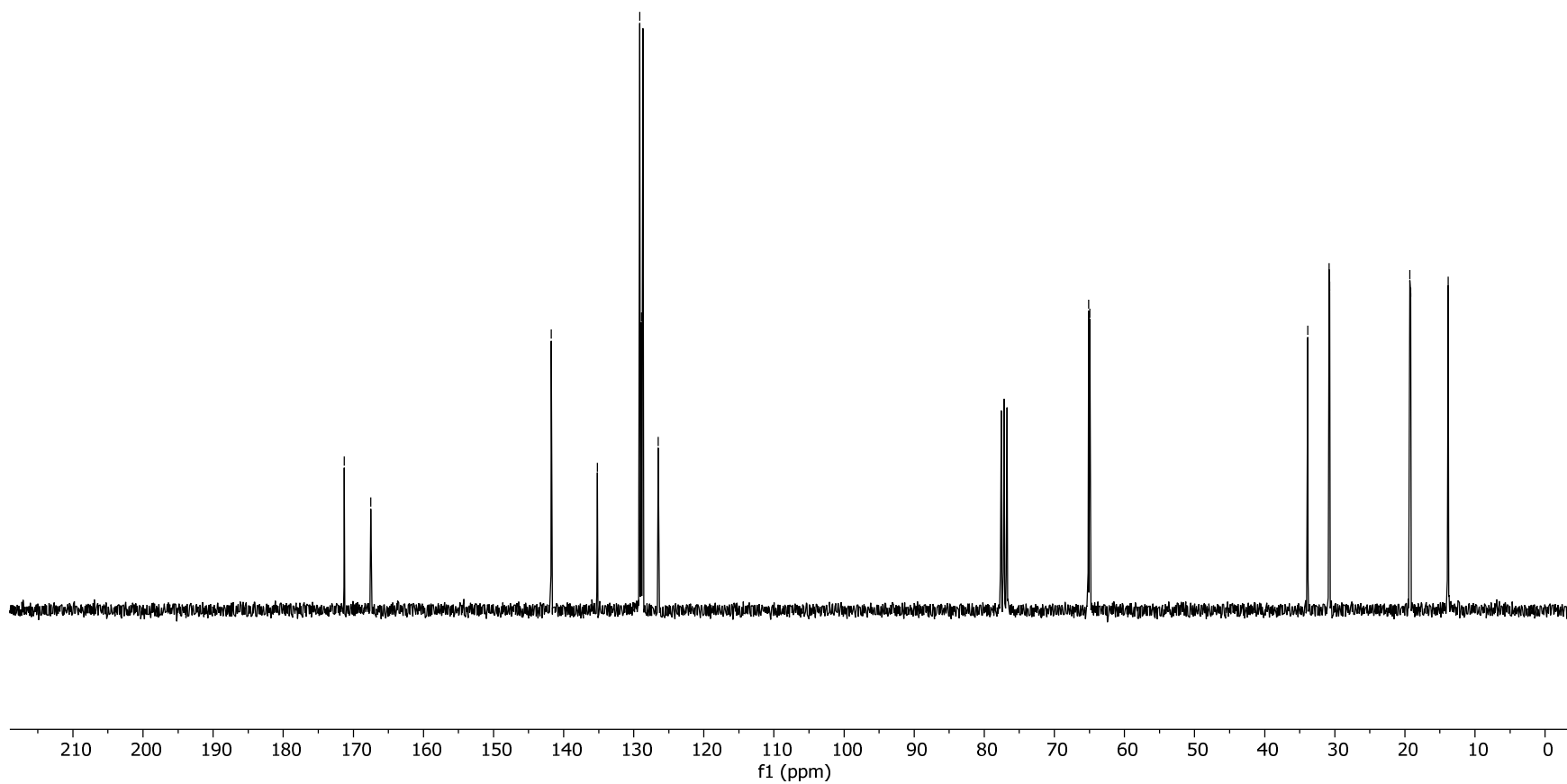
— 30.72

— 19.30

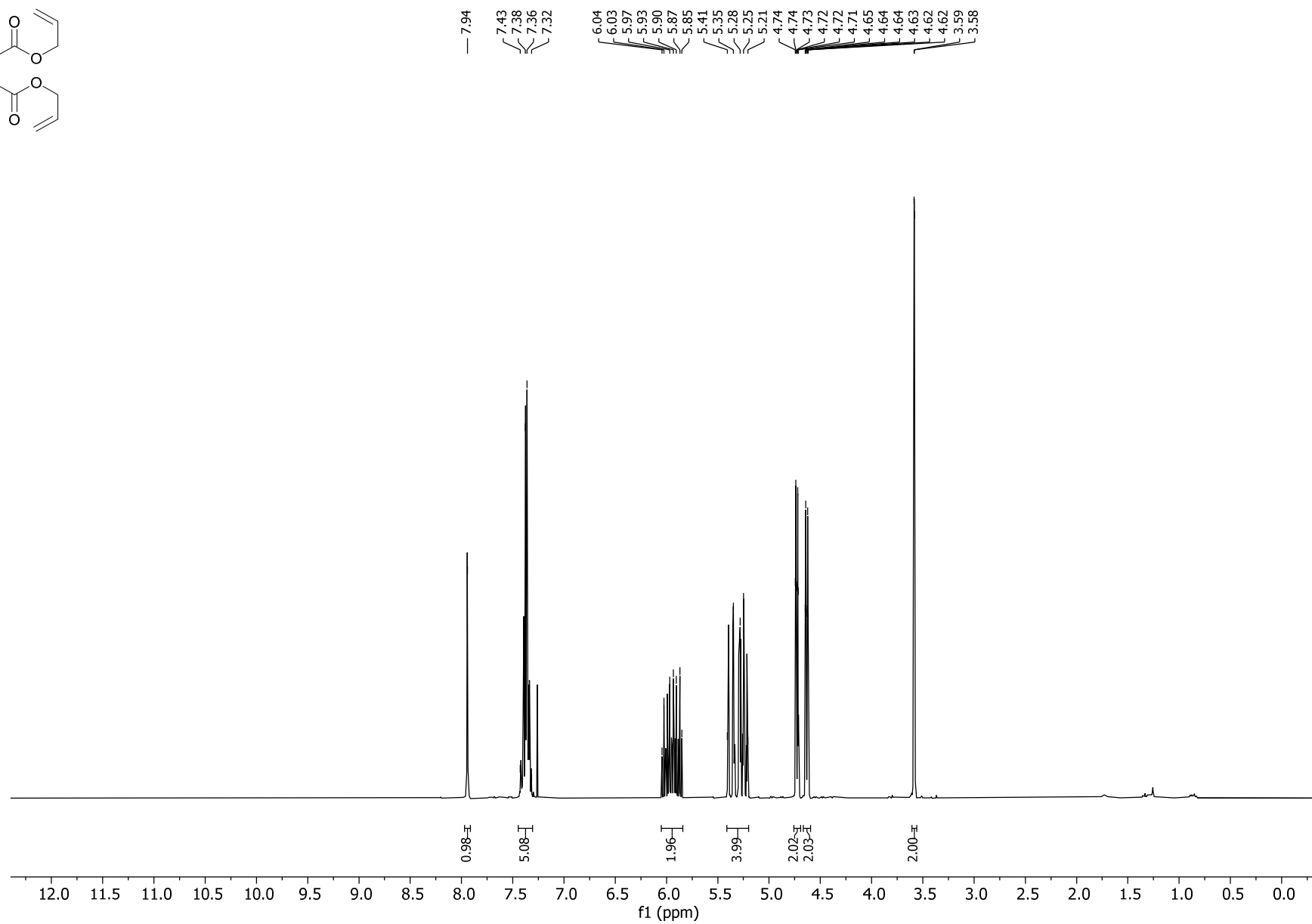
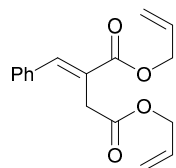
— 19.18

— 13.83

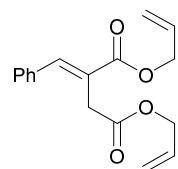
— 13.78



¹H NMR of Diallyl (*E*)-2-benzylidenesuccinate (3d)



¹³C NMR of Diallyl (*E*)-2-benzylidenesuccinate (3d)

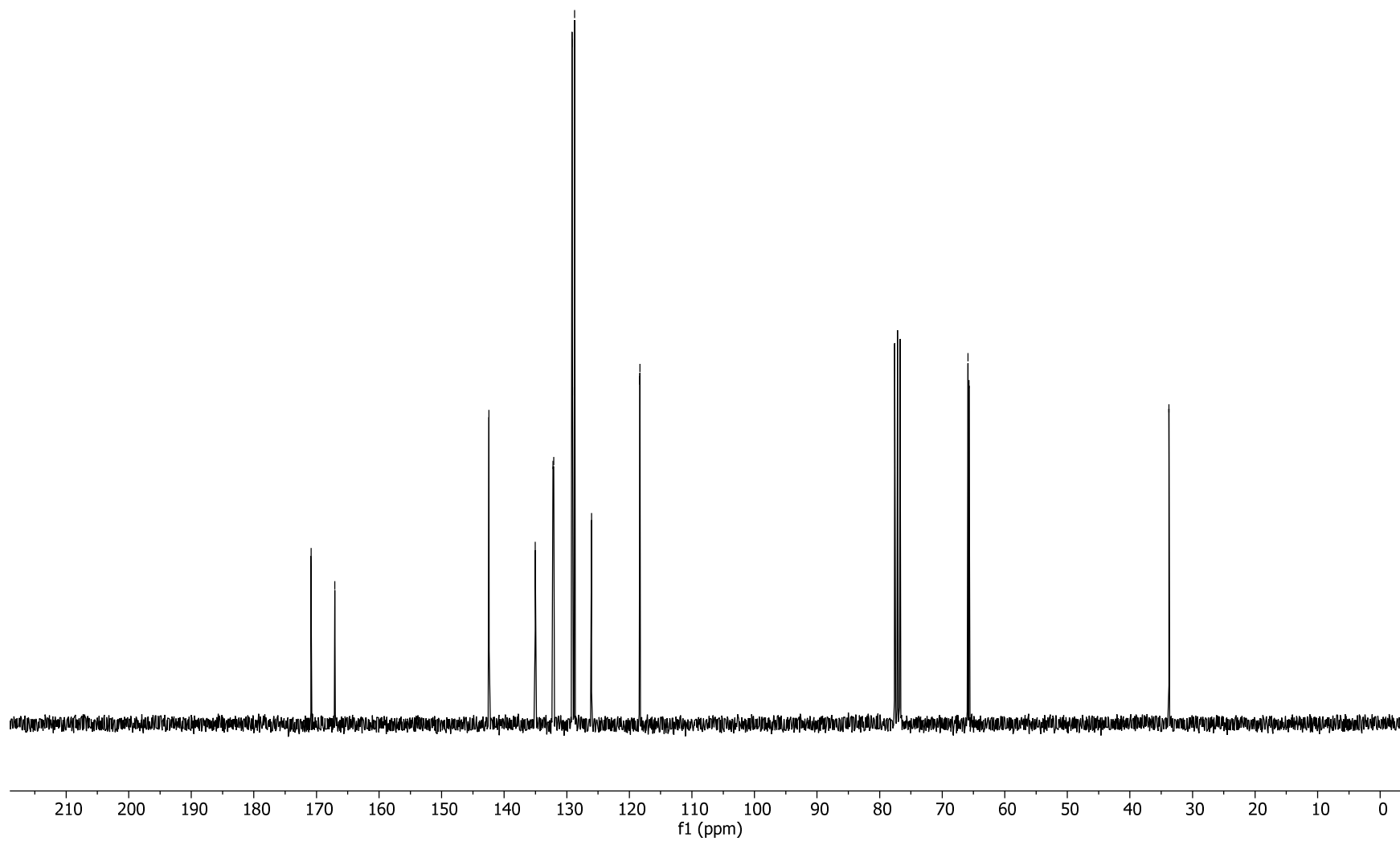


— 170.87
— 167.05

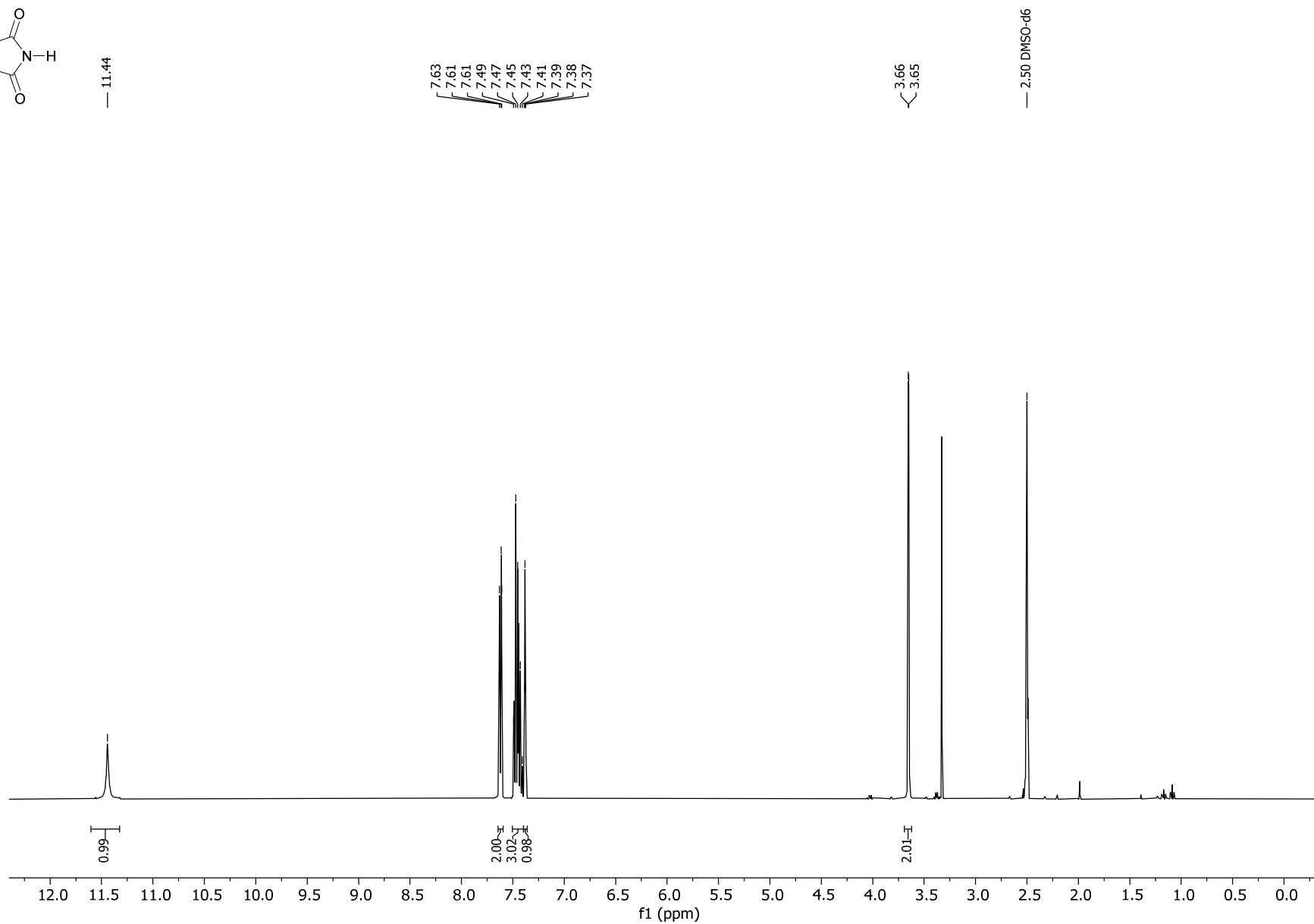
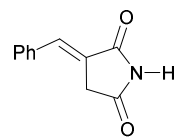
— 142.43
/ 135.03
/ 132.21
/ 132.09
/ 129.15
/ 129.07
/ 128.76
/ 126.03
/ 118.37
/ 118.31

∨ 65.89
∨ 65.70

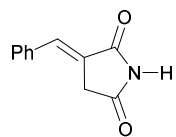
— 33.76



¹H NMR of (*E*)-3-Benzylidenepyrrolidine-2,5-dione (3e)



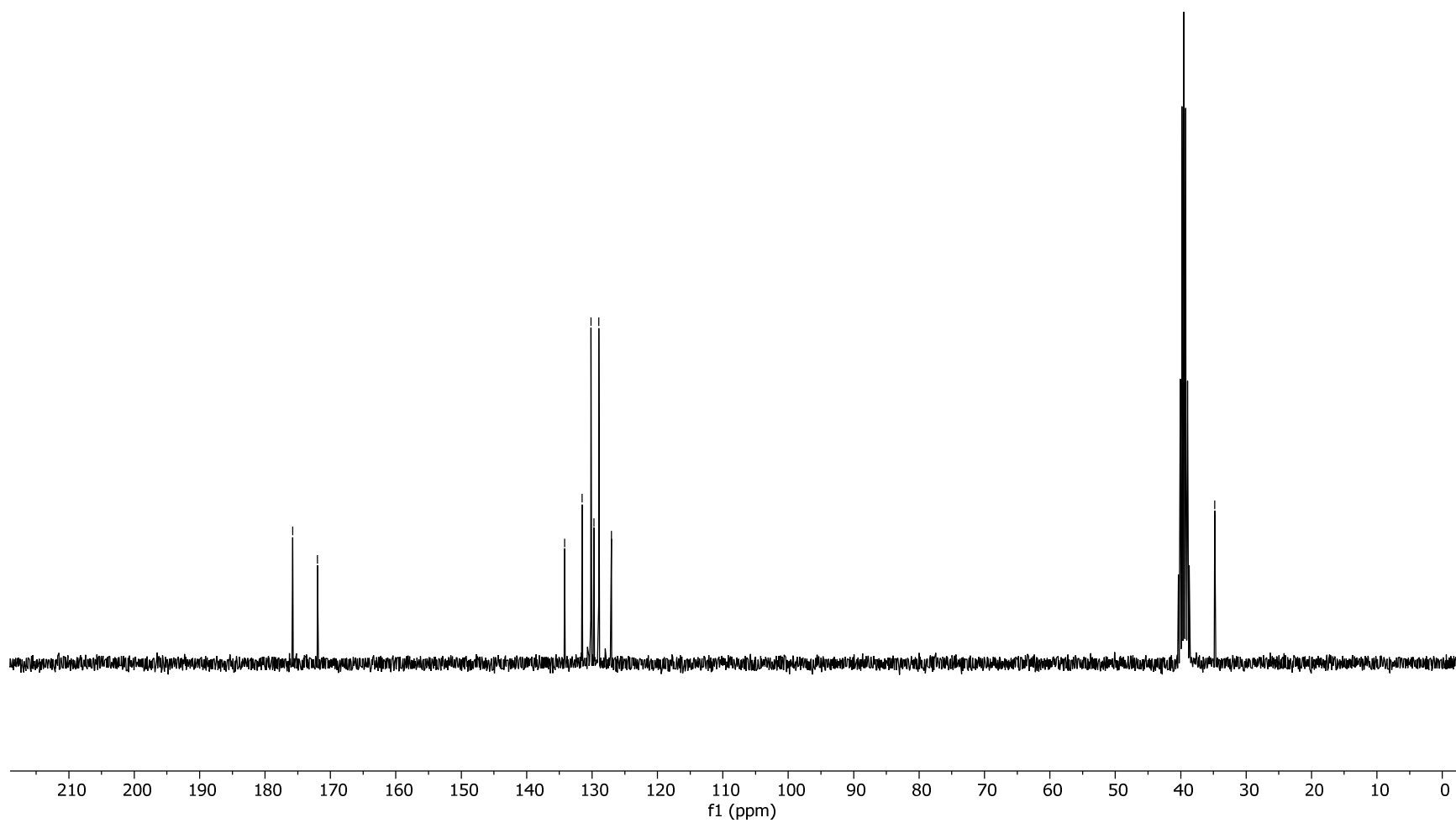
¹³C NMR of (*E*)-3-Benzylidenepyrrolidine-2,5-dione (3e)



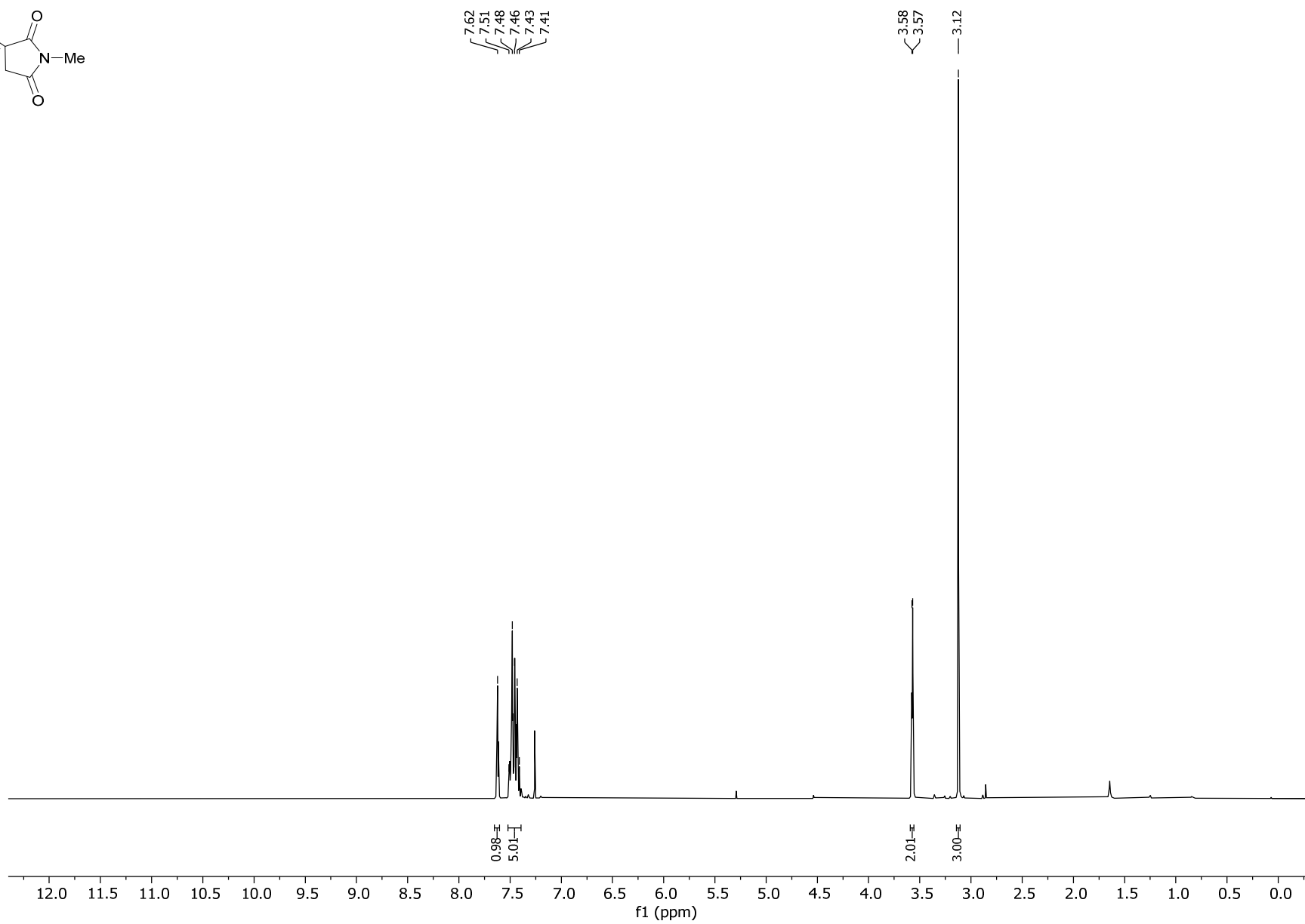
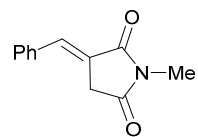
— 175.78
— 171.98

134.18
131.50
130.18
129.71
128.96
127.03

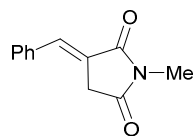
— 34.80



¹H NMR of (*E*)-3-Benzylidene-1-methylpyrrolidine-2,5-dione (3f)



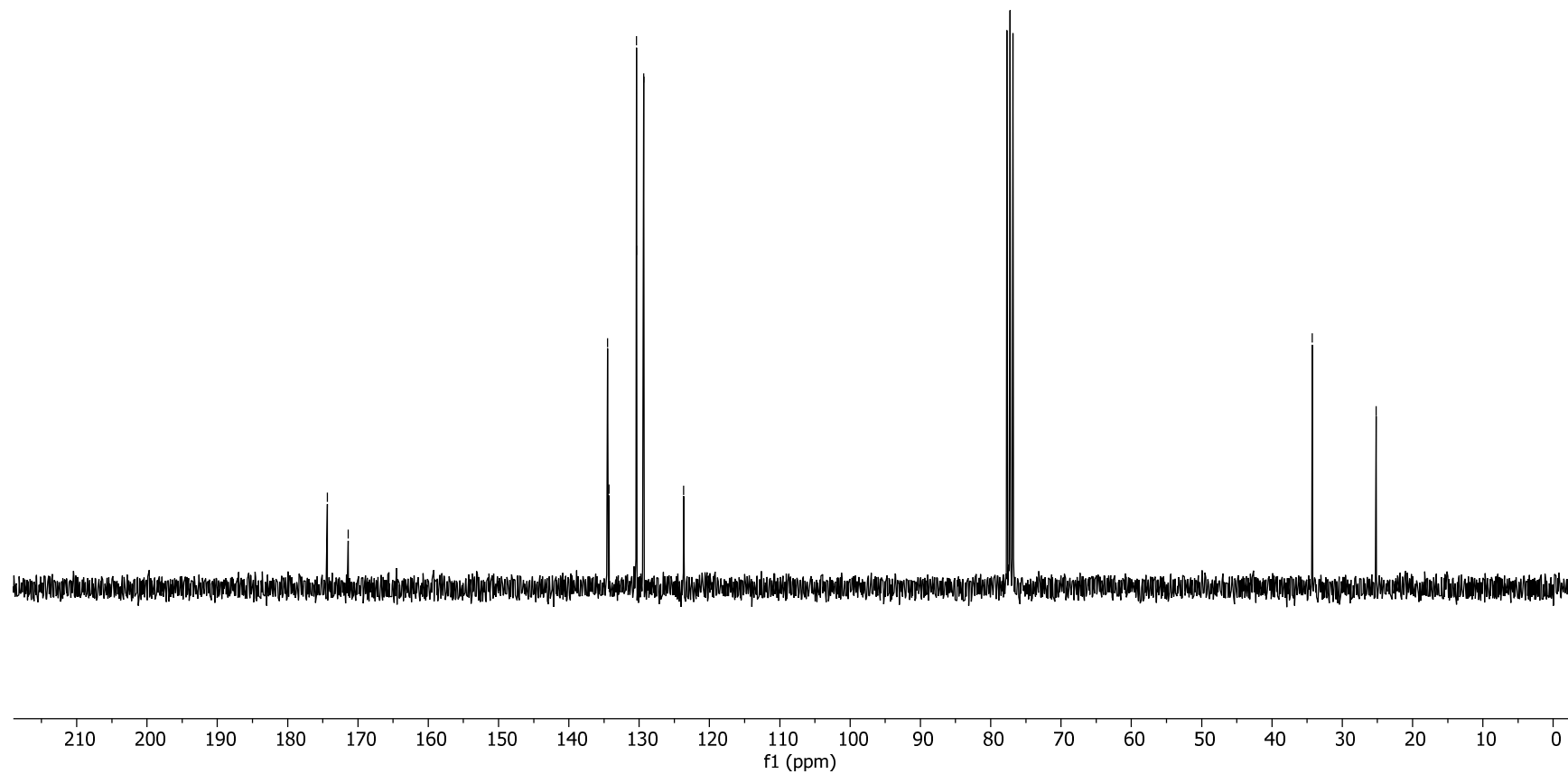
¹³C NMR of (*E*)-3-Benzylidene-1-methylpyrrolidine-2,5-dione (3f)



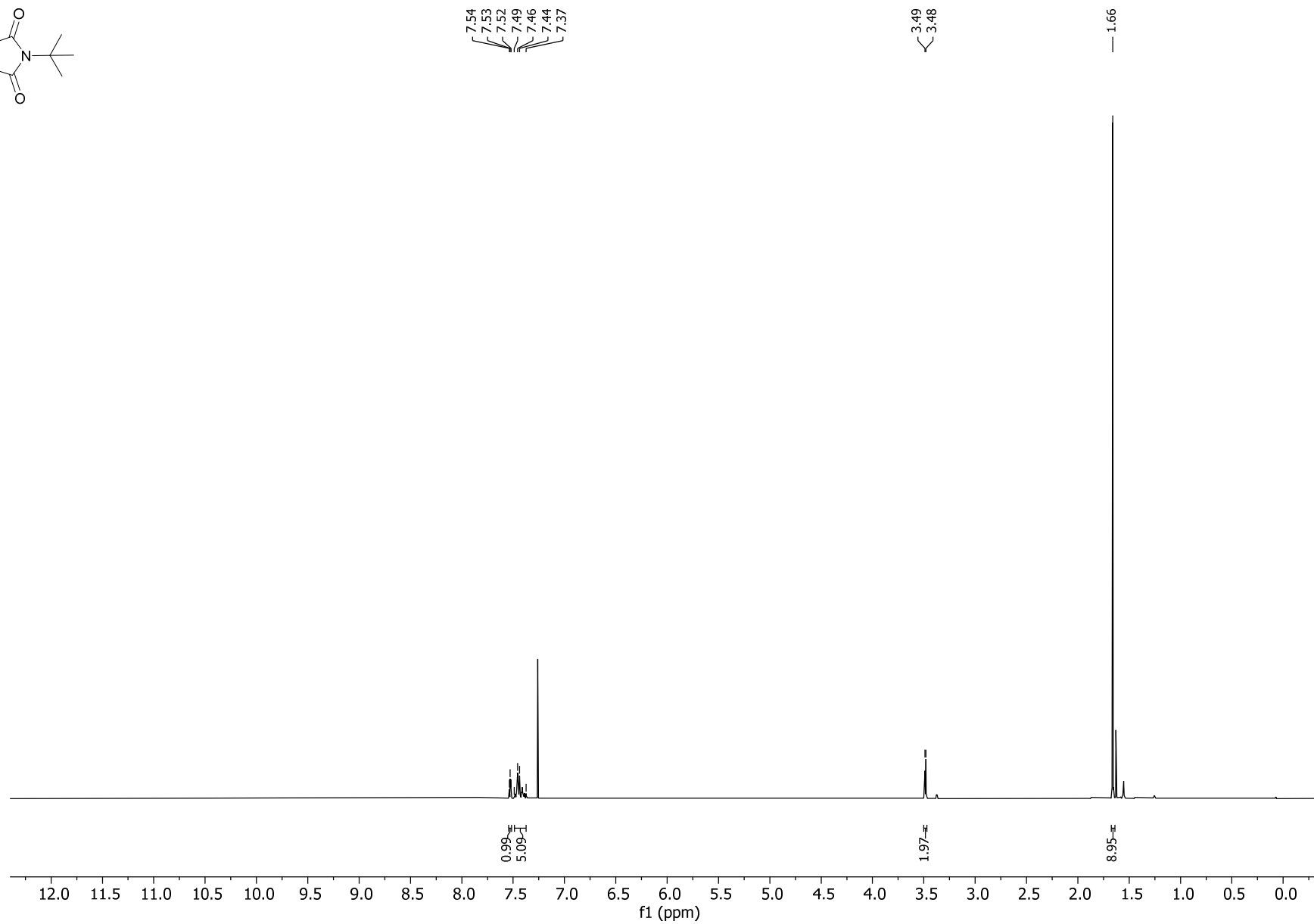
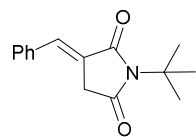
— 174.36
— 171.38

134.49
134.30
130.40
130.38
129.35
— 123.69

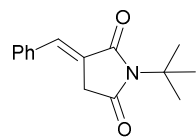
— 34.28
— 25.17



¹H NMR of (*E*)-3-Benzylidene-1-(*tert*-butyl)pyrrolidine-2,5-dione (3g)



¹³C NMR of (*E*)-3-Benzylidene-1-(*tert*-butyl)pyrrolidine-2,5-dione (3g)



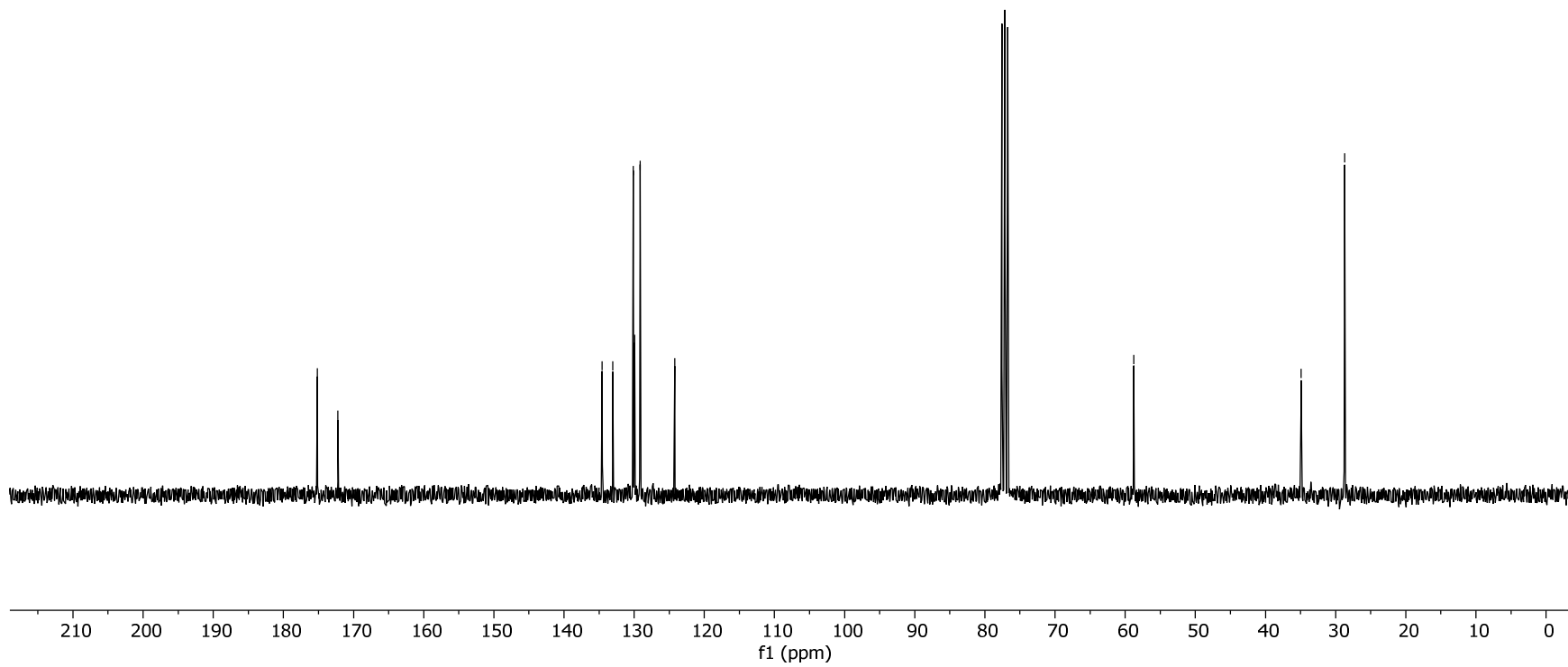
— 175.16
— 172.23

134.55
133.03
130.13
129.90
129.13
124.22

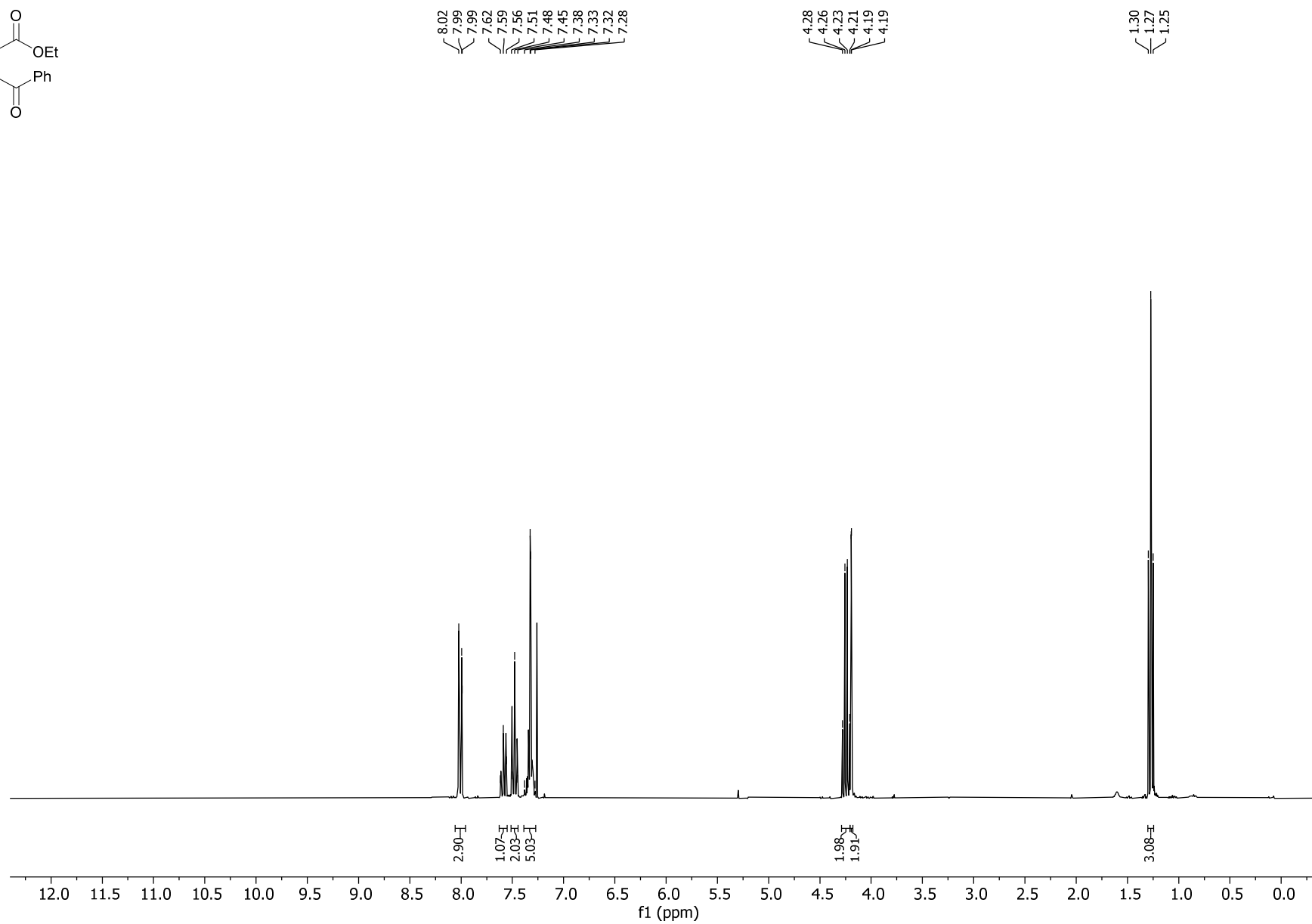
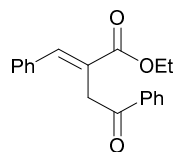
— 58.77

— 34.92

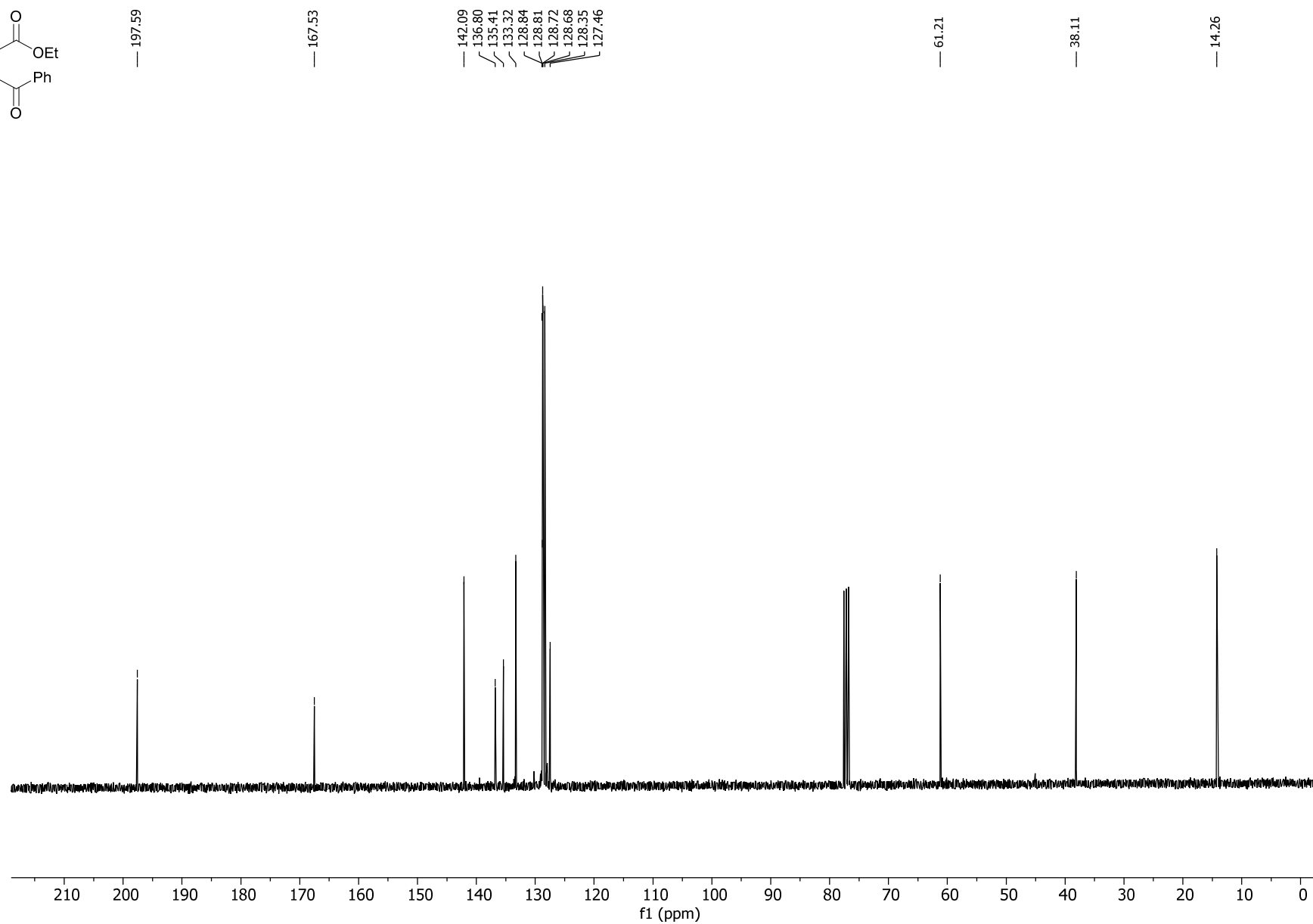
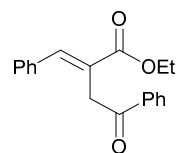
— 28.71



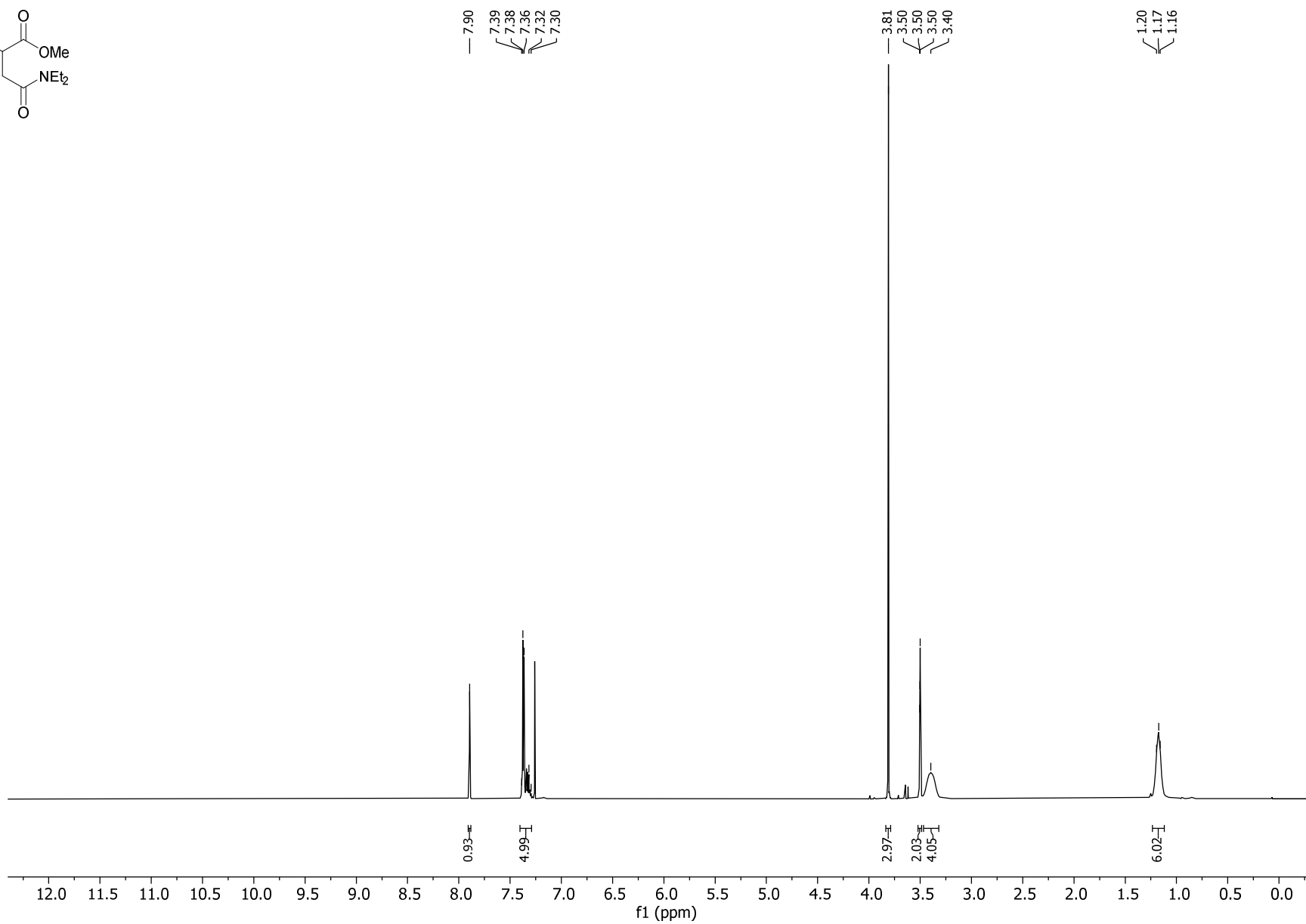
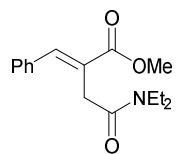
¹H NMR of Ethyl (*E*)-2-benzylidene-4-oxo-4-phenylbutanoate (3h)



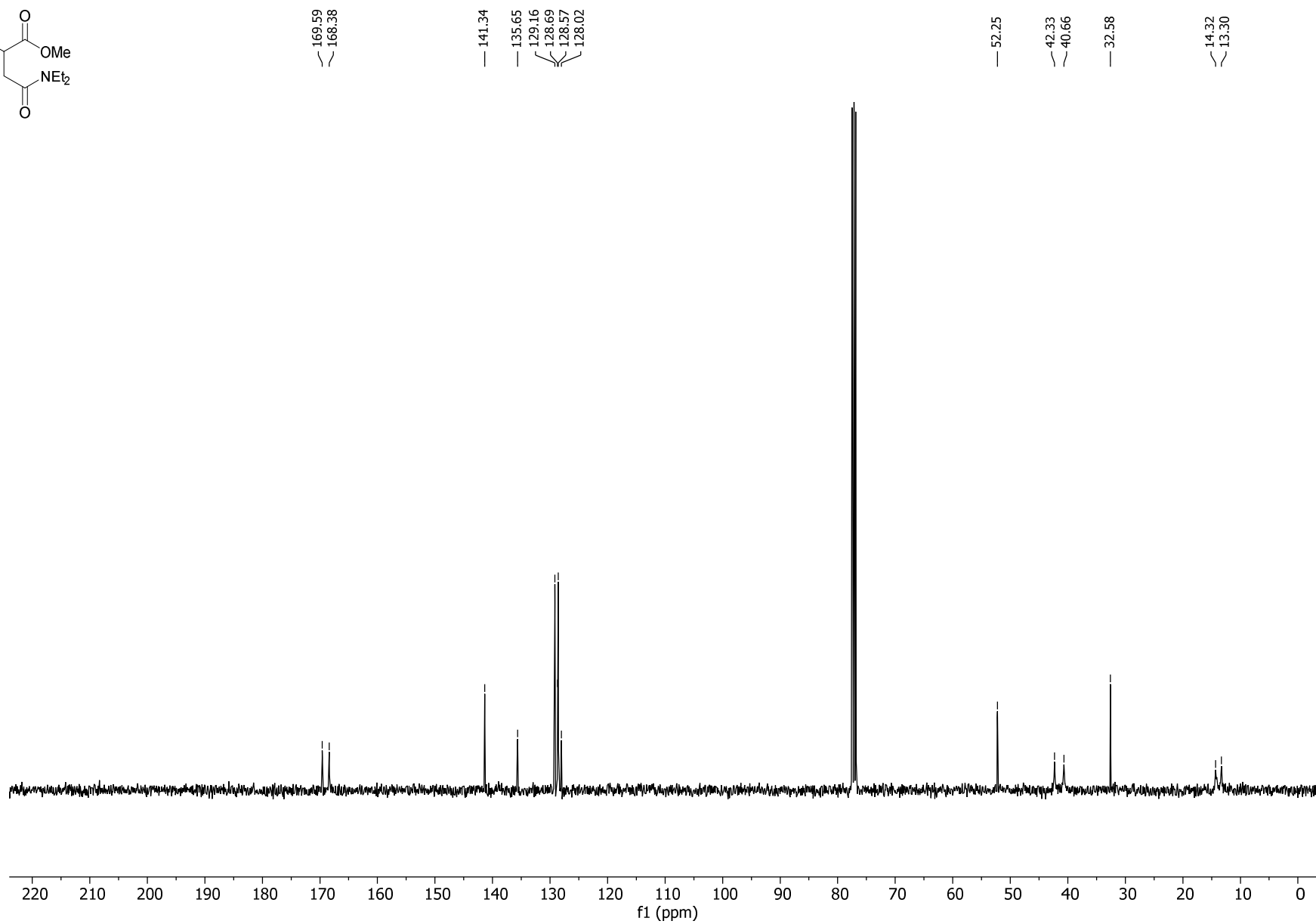
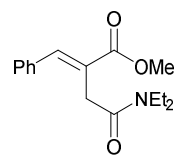
¹³C NMR of Ethyl (*E*)-2-benzylidene-4-oxo-4-phenylbutanoate (3h)



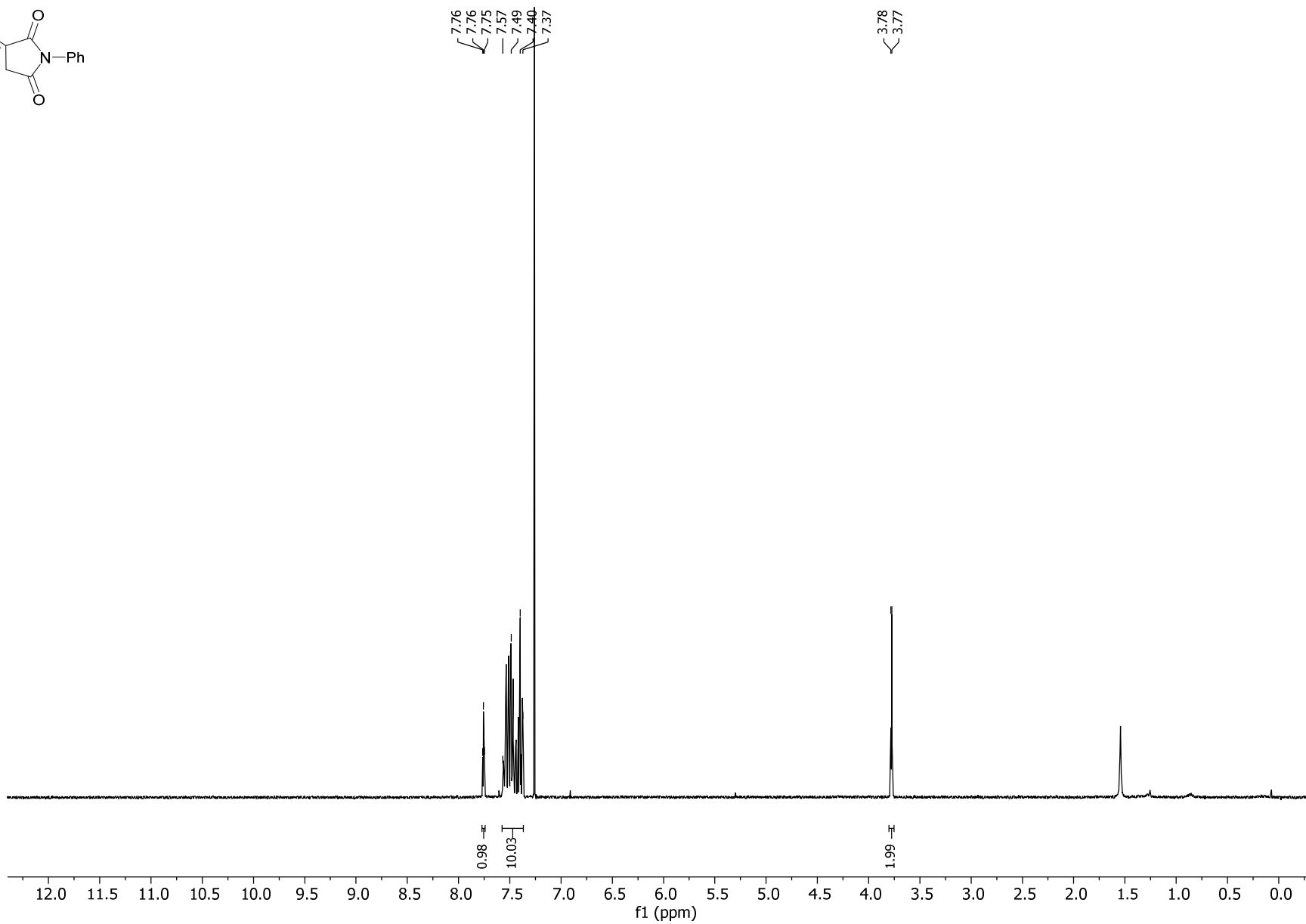
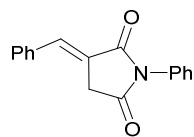
¹H NMR of Methyl (*E*)-2-benzylidene-4-(diethylamino)-4-oxobutanoate (3i)



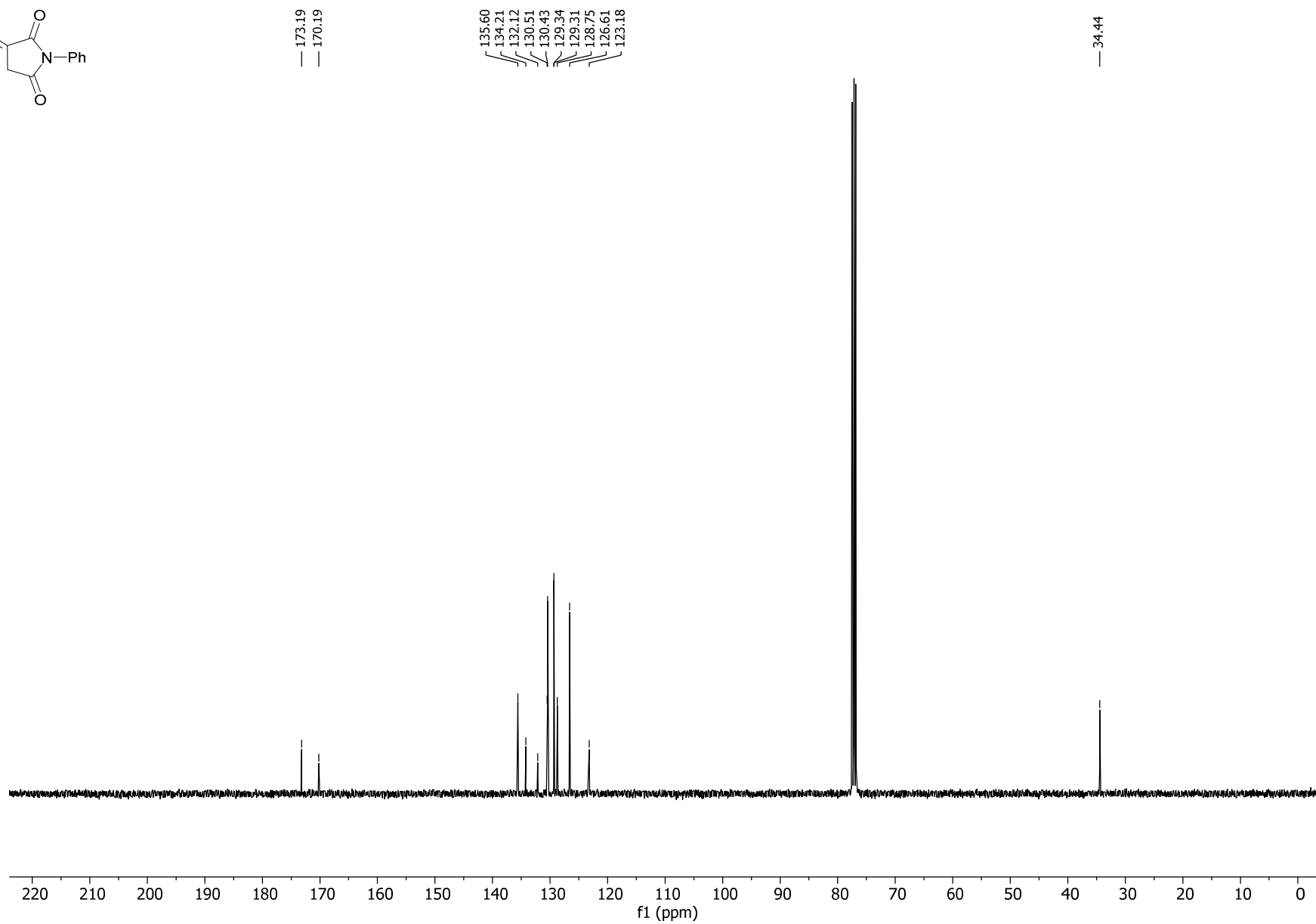
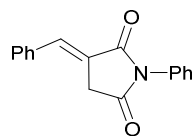
¹³C NMR of Methyl (*E*)-2-benzylidene-4-(diethylamino)-4-oxobutanoate (3i)



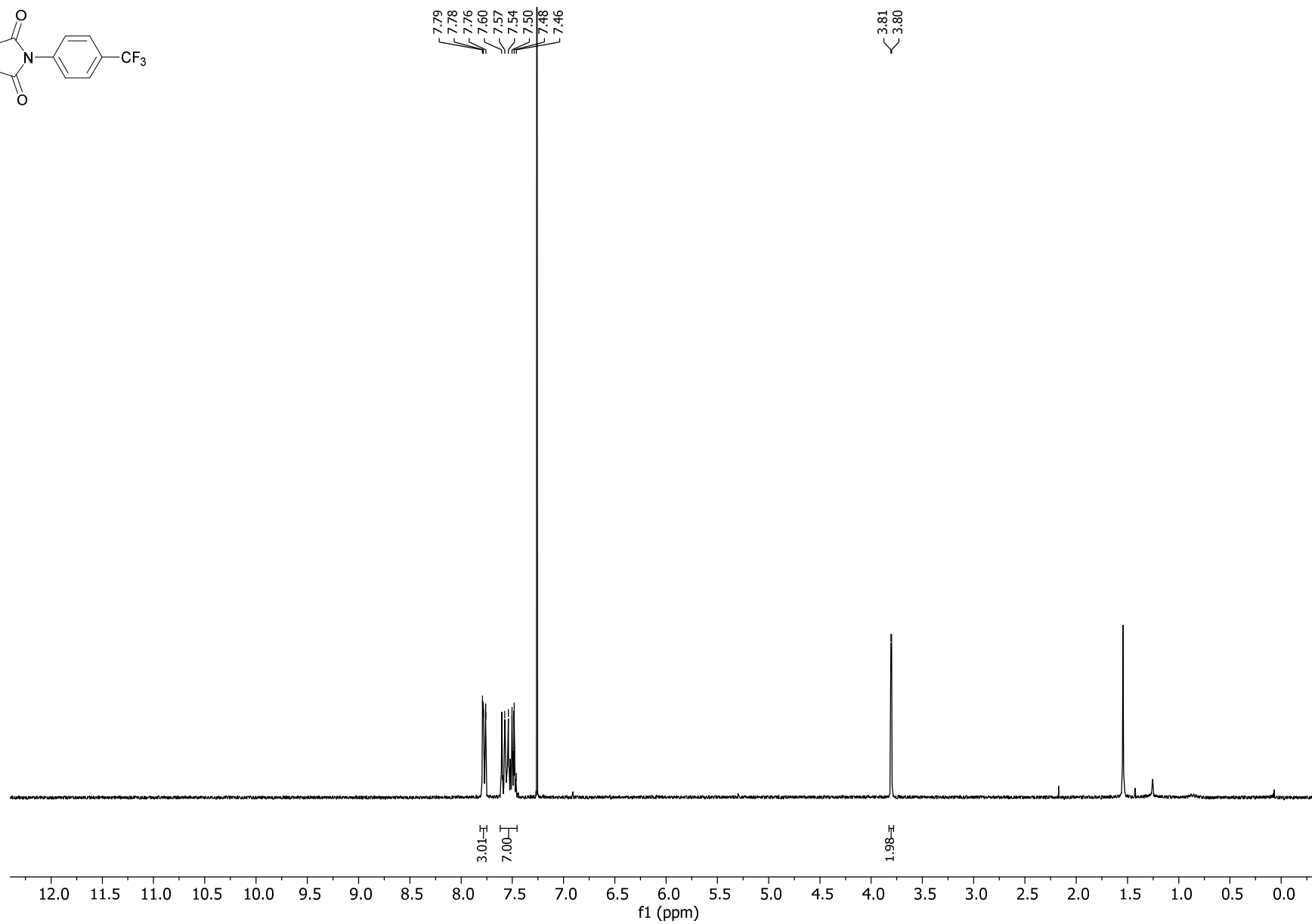
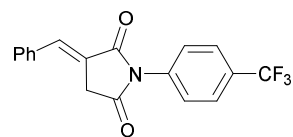
¹H NMR of (*E*)-3-Benzylidene-1-phenylpyrrolidine-2,5-dione (3j)



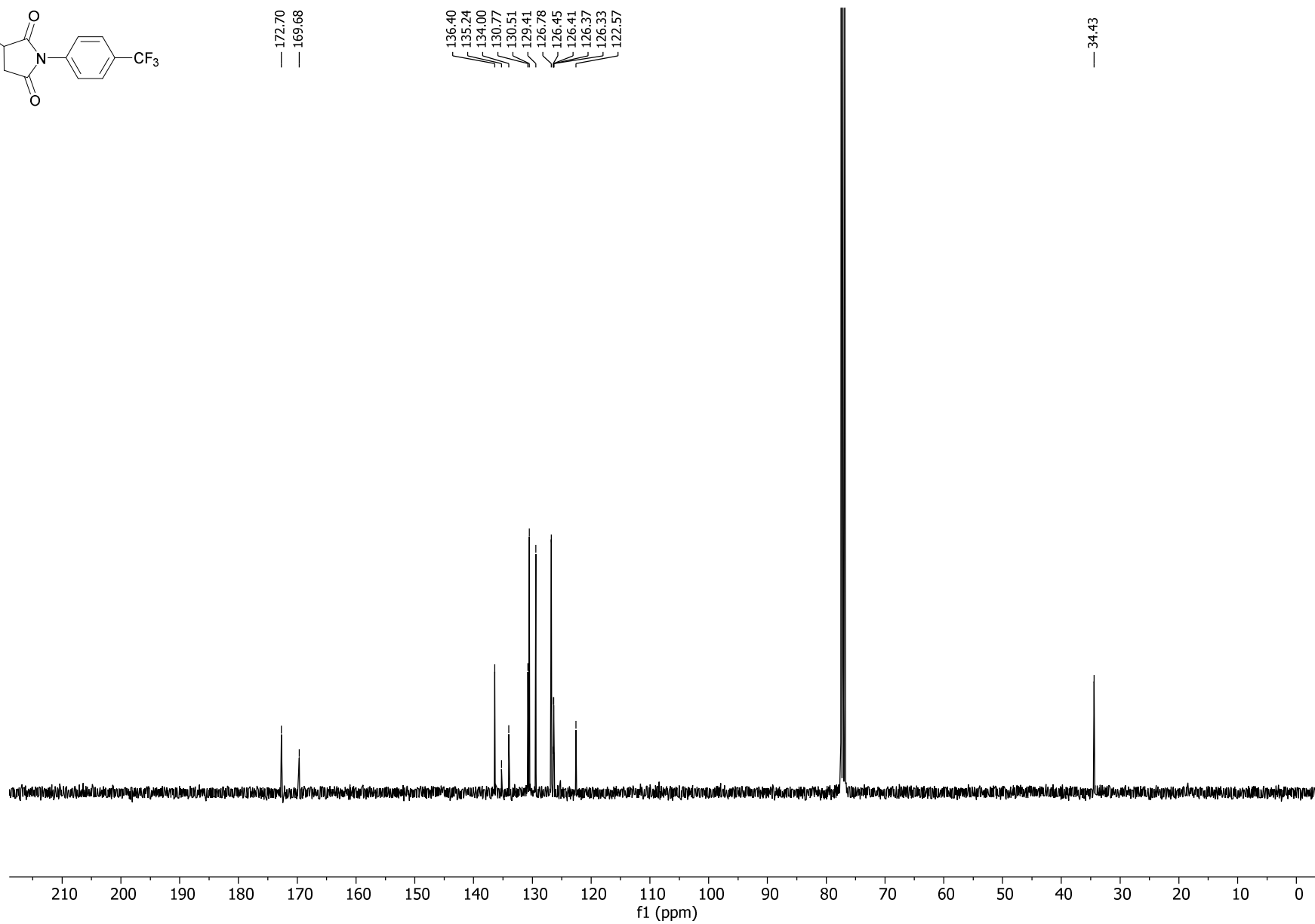
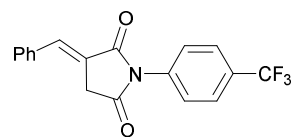
¹³C NMR of (*E*)-3-Benzylidene-1-phenylpyrrolidine-2,5-dione (3j)



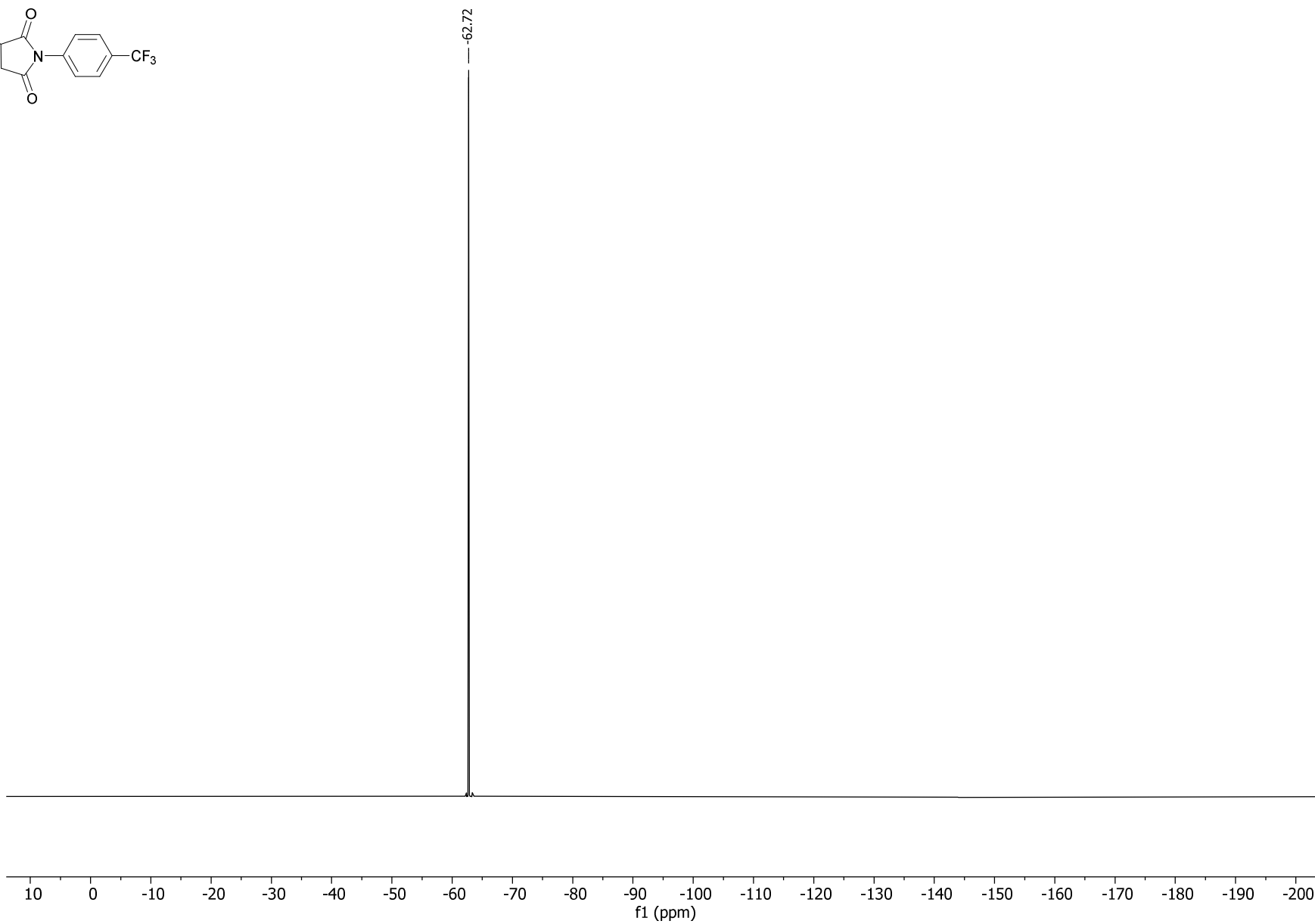
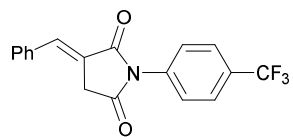
¹H NMR of (*E*)-3-Benzylidene-1-(4-(trifluoromethyl)phenyl)pyrrolidine-2,5-dione (3k)



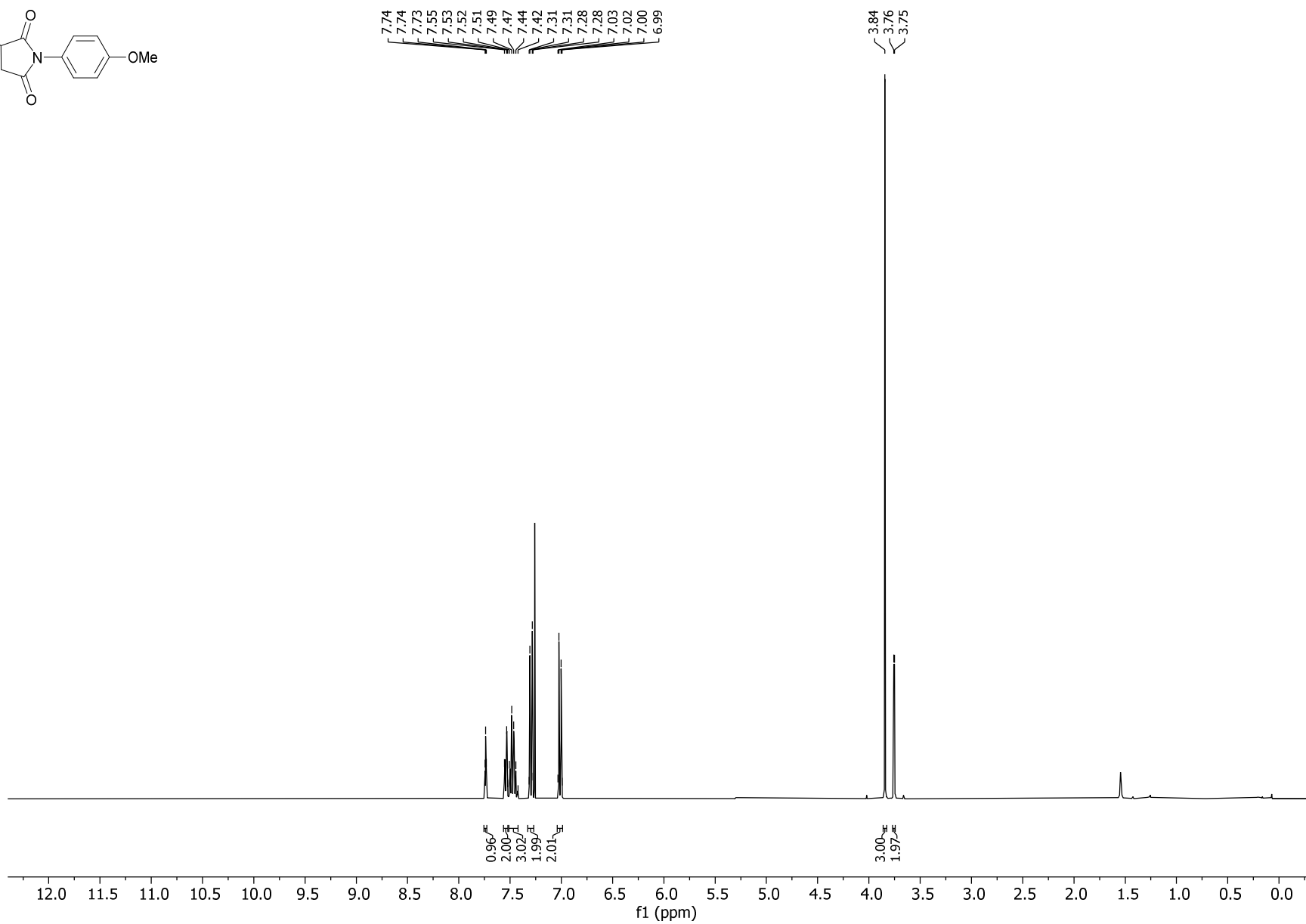
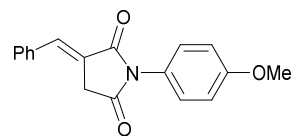
¹³C NMR of (*E*)-3-Benzylidene-1-(4-(trifluoromethyl)phenyl)pyrrolidine-2,5-dione (3k)



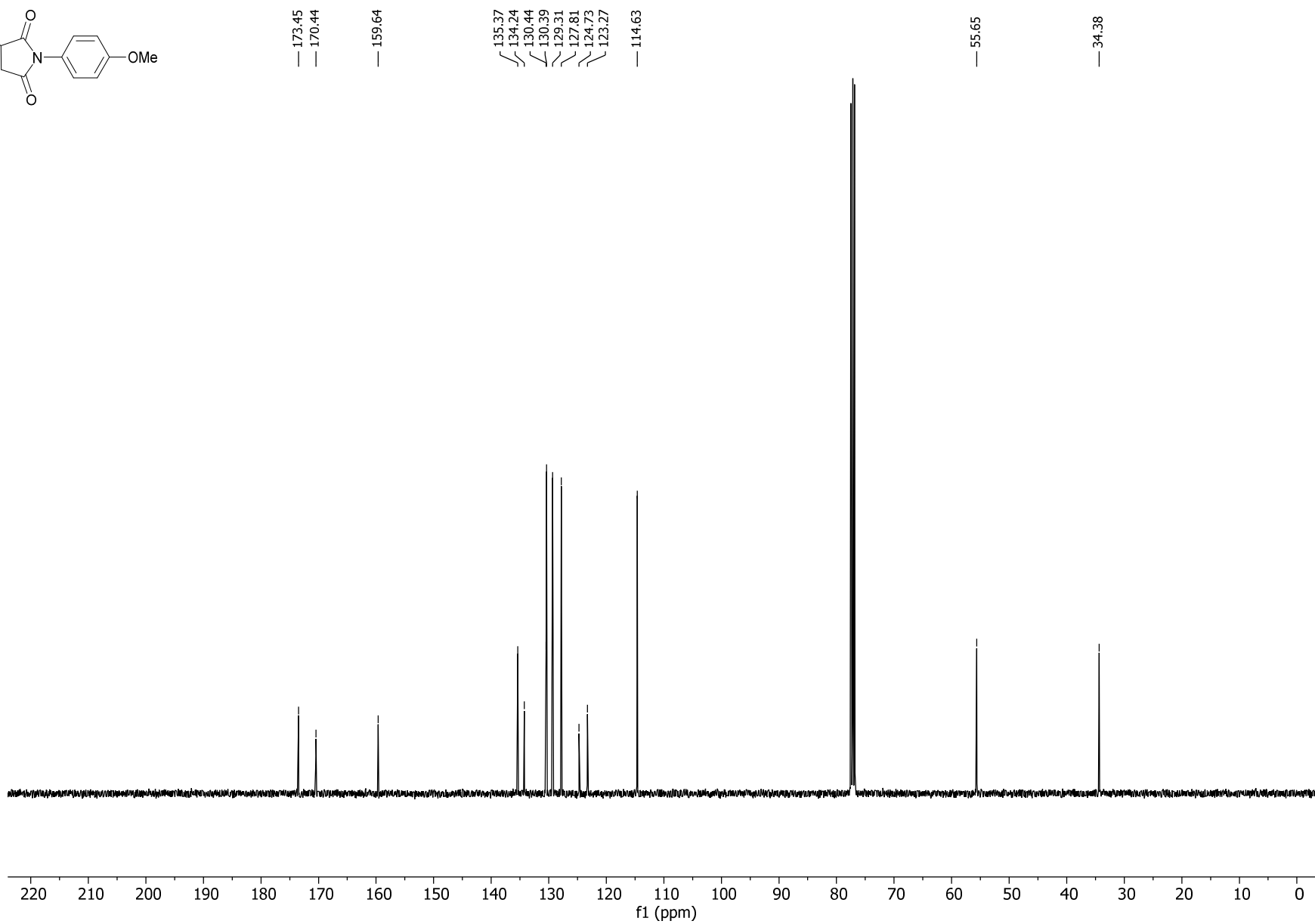
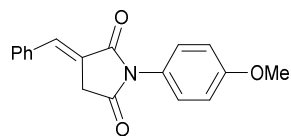
¹⁹F NMR of (*E*)-3-Benzylidene-1-(4-(trifluoromethyl)phenyl)pyrrolidine-2,5-dione (3k)



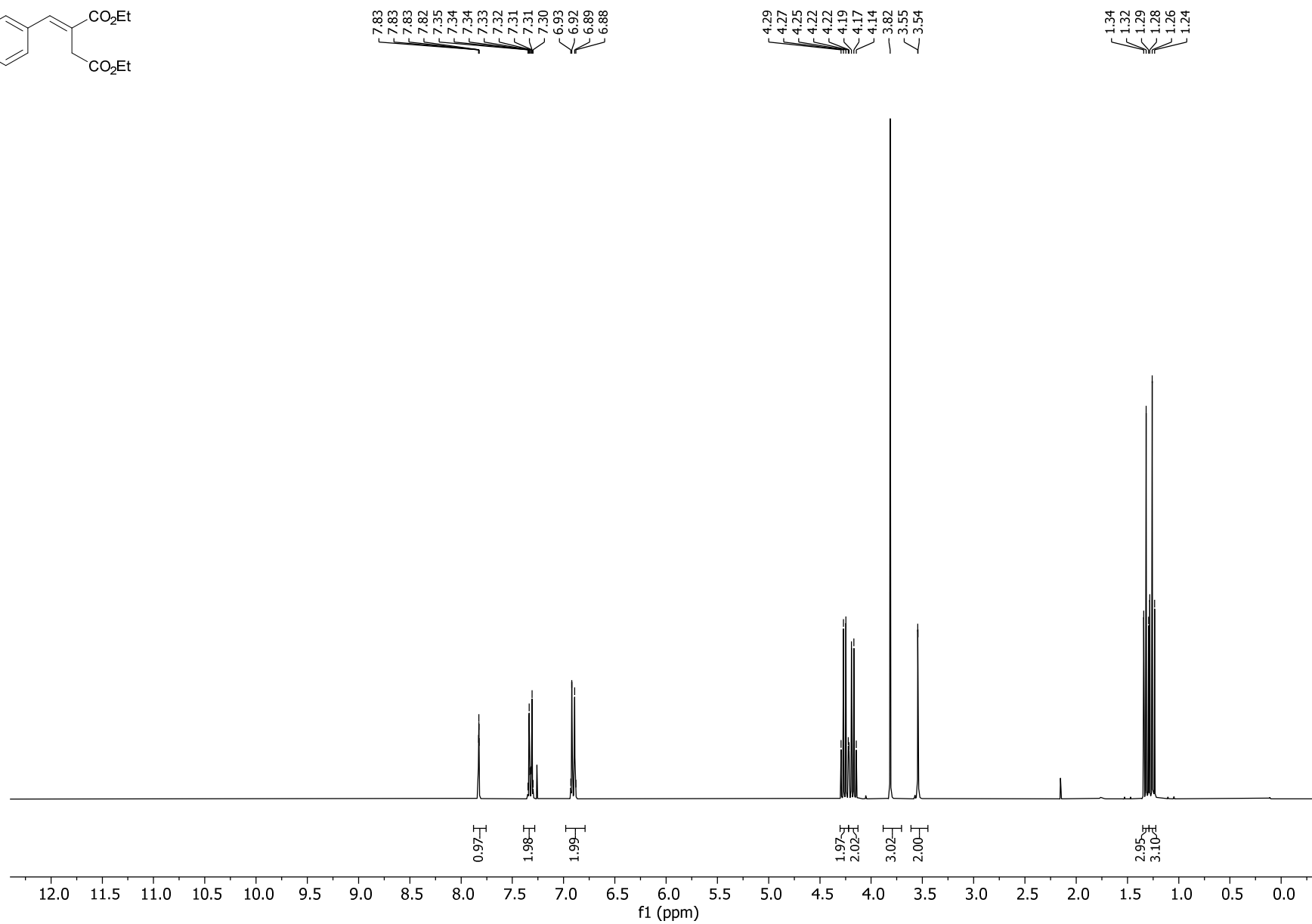
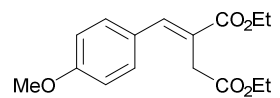
¹H NMR of (*E*)-3-Benzylidene-1-(4-methoxyphenyl)pyrrolidine-2,5-dione (3I)



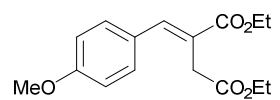
¹³C NMR of (*E*)-3-Benzylidene-1-(4-methoxyphenyl)pyrrolidine-2,5-dione (3I)



¹H NMR of Diethyl (*E*)-2-(4-methoxybenzylidene)succinate (3n)

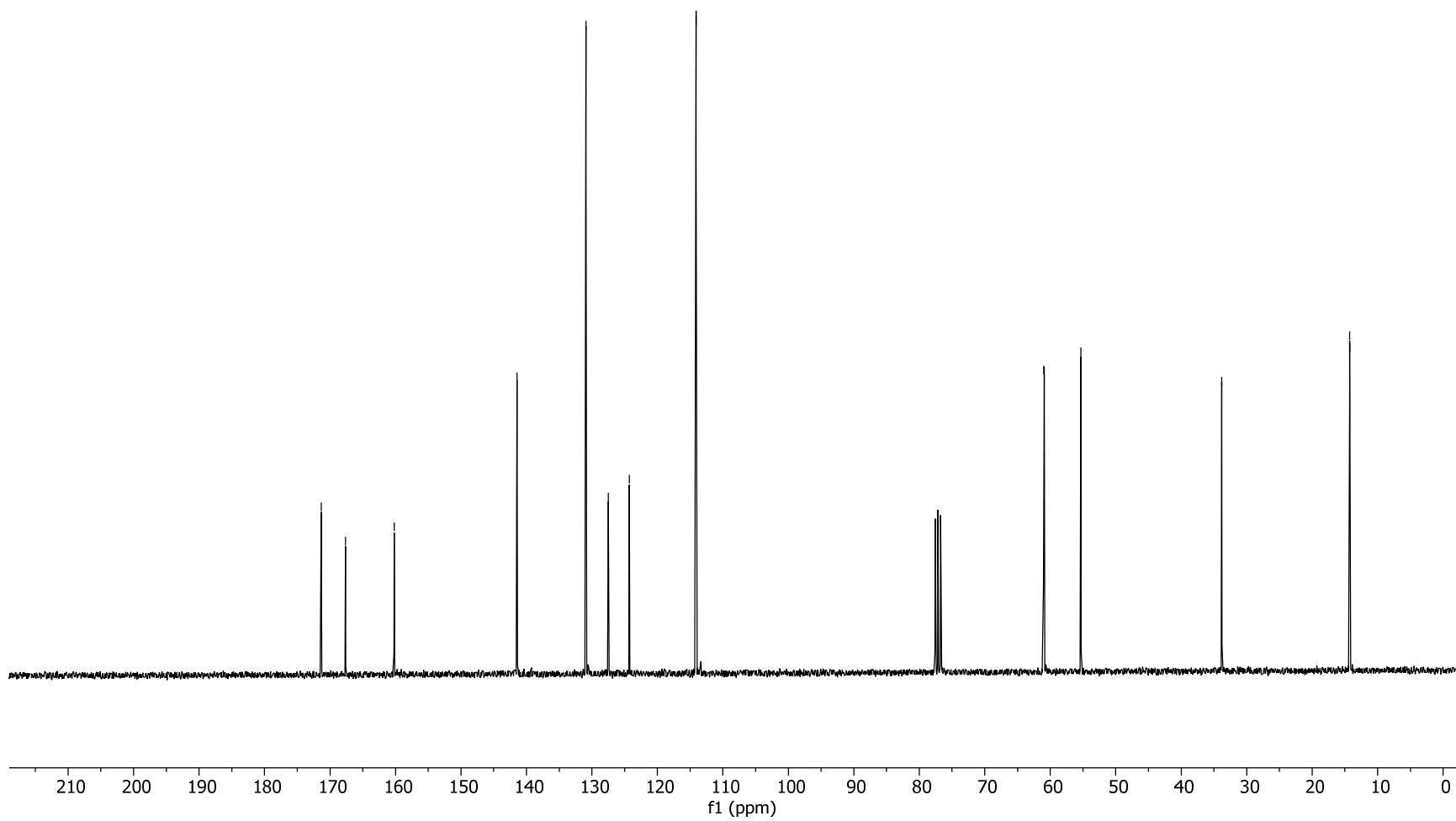


¹³C NMR of Diethyl (*E*)-2-(4-methoxybenzylidene)succinate (3n)

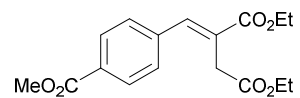


— 171.34
— 167.64
— 160.21
— 141.44
~ 130.91
— 127.51
~ 124.30
— 114.11

< 61.01
— 60.92
— 55.31
— 33.80
< 14.29
— 14.23



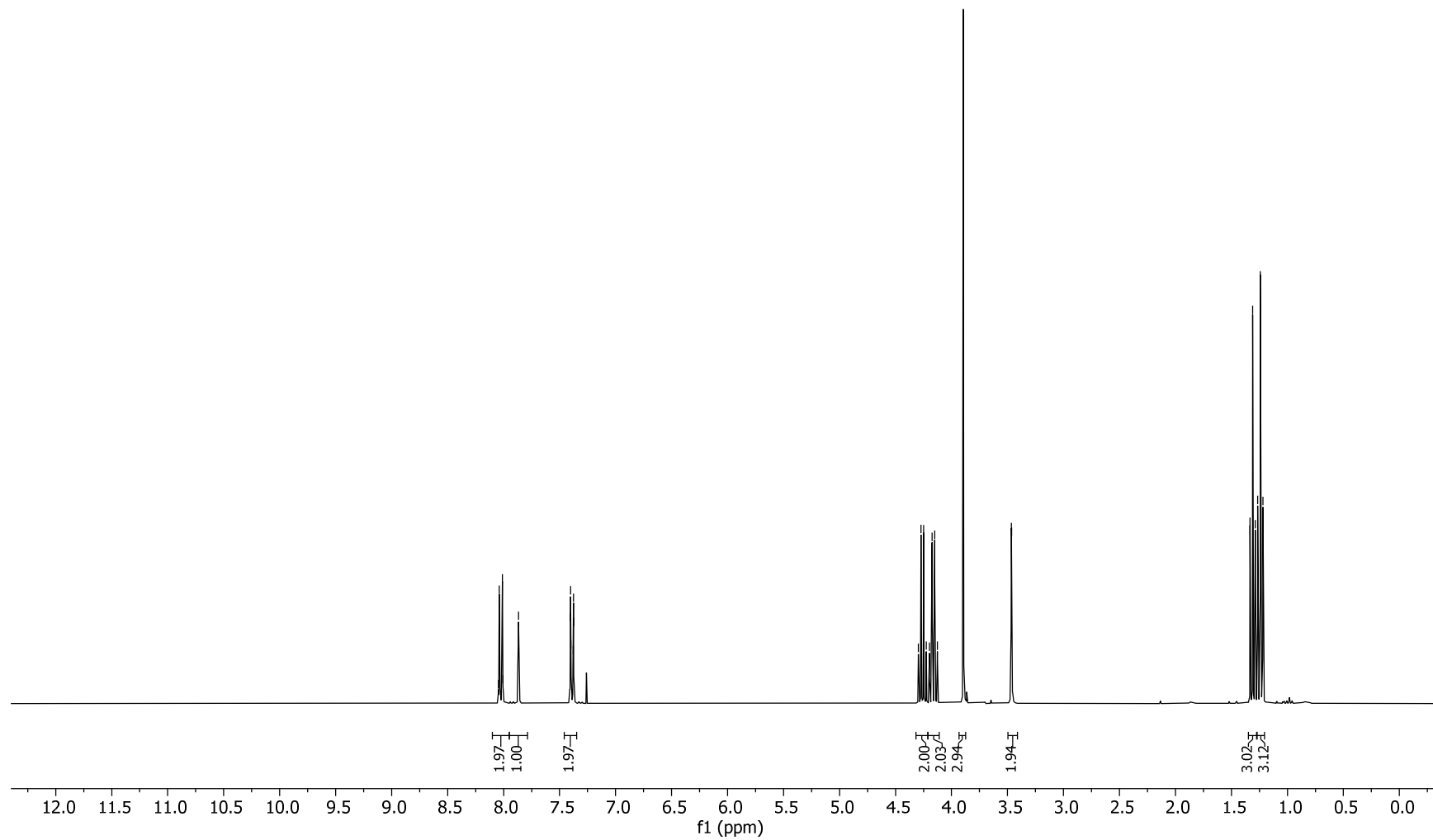
¹H NMR of Diethyl (*E*)-2-(4-(methoxycarbonyl)benzylidene)succinate (3o)



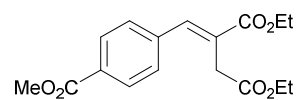
8.05
8.04
8.01
8.01
7.87
7.41
7.40
7.40
7.38
7.37

4.30
4.27
4.25
4.23
4.20
4.17
4.15
4.13
3.89
3.47
3.46

1.33
1.31
1.29
1.27
1.24
1.22



¹³C NMR of Diethyl (*E*)-2-(4-(methoxycarbonyl)benzylidene)succinate (3o)



170.80
166.90
166.48

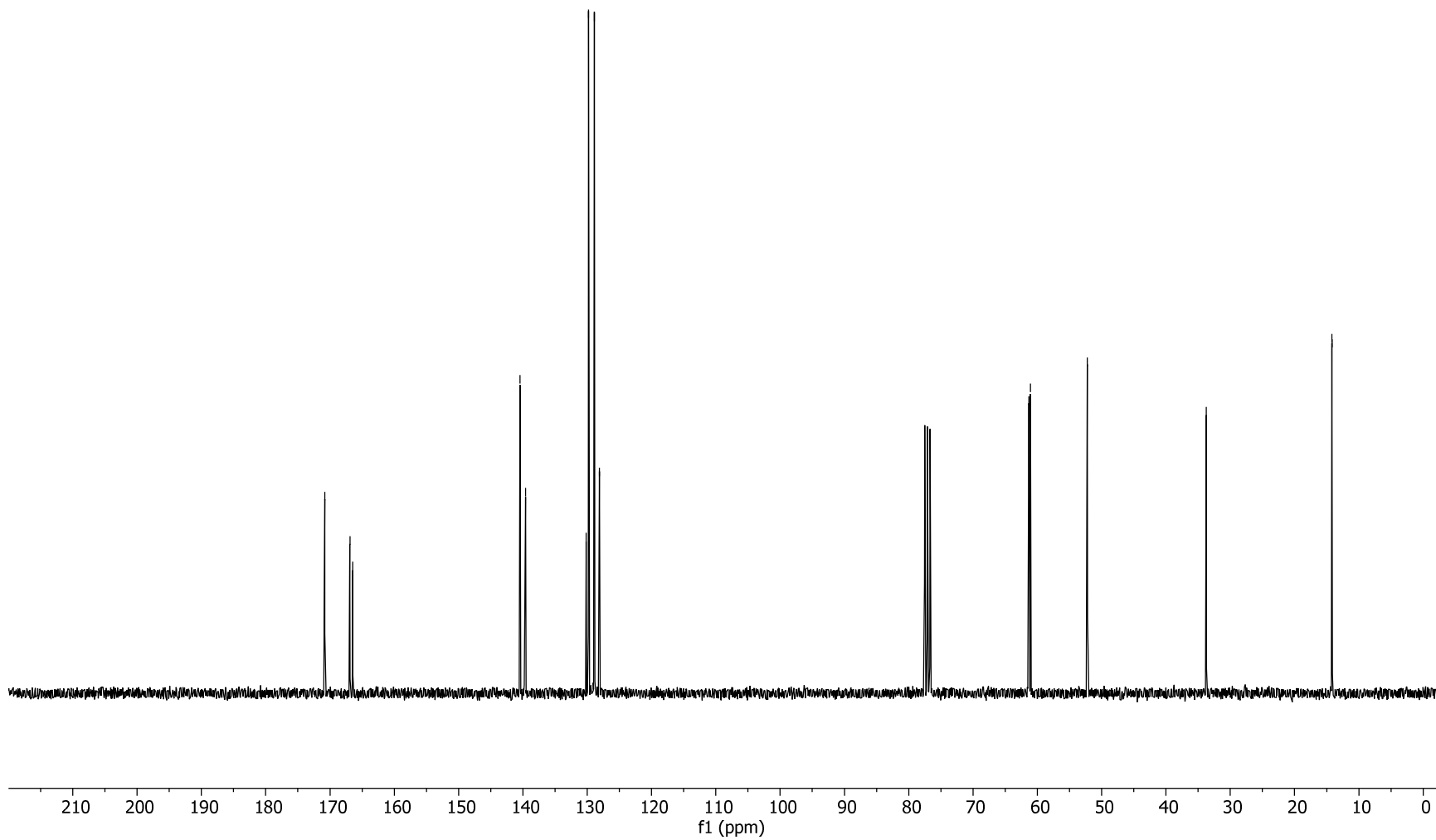
140.45
139.58
130.19
129.79
128.89
128.11

61.31
61.05

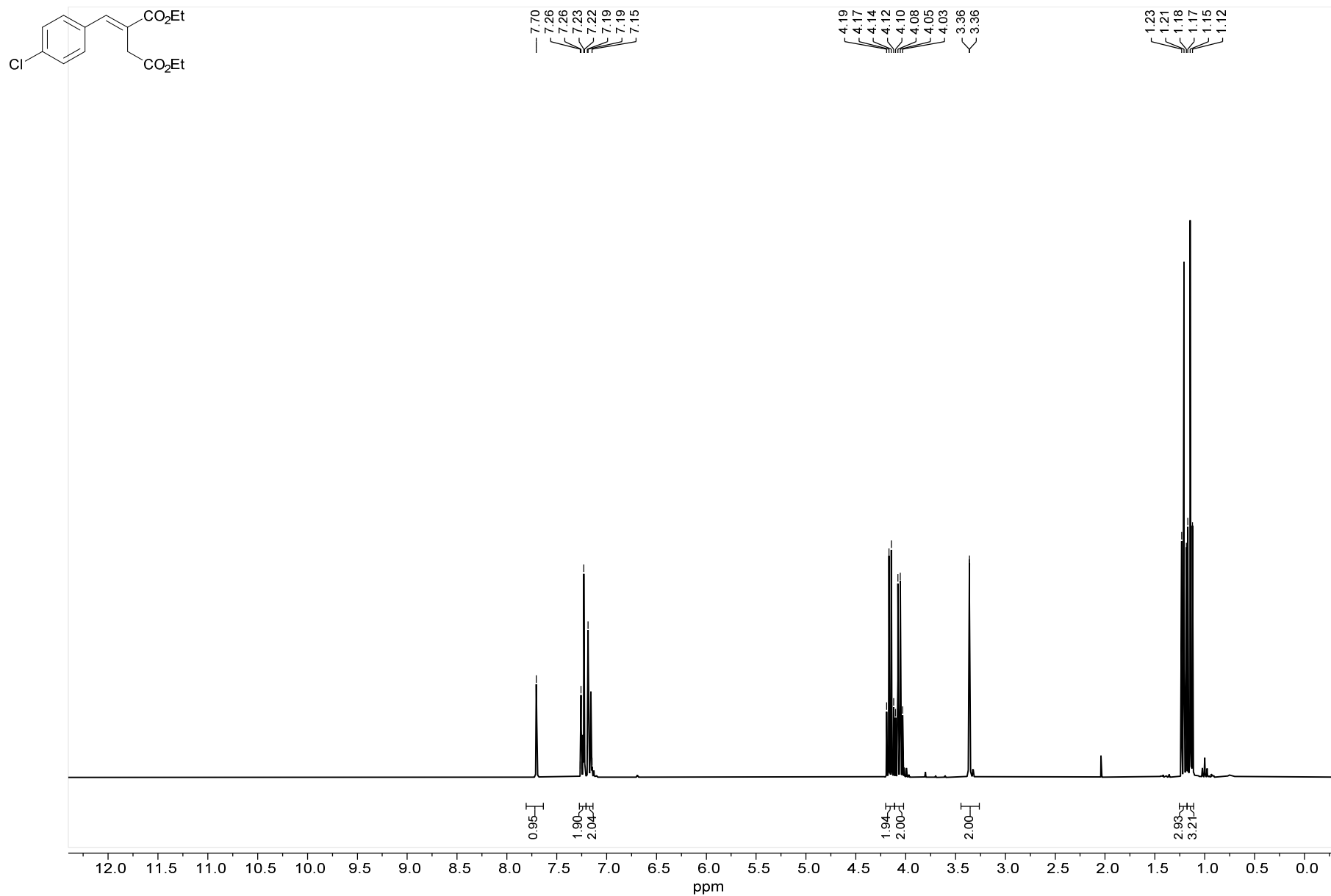
52.22

33.71

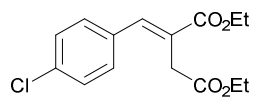
14.18
14.16



¹H NMR of Diethyl (*E*)-2-(4-chlorobenzylidene)succinate (3p)



¹³C NMR of Diethyl (*E*)-2-(4-chlorobenzylidene)succinate (3p)



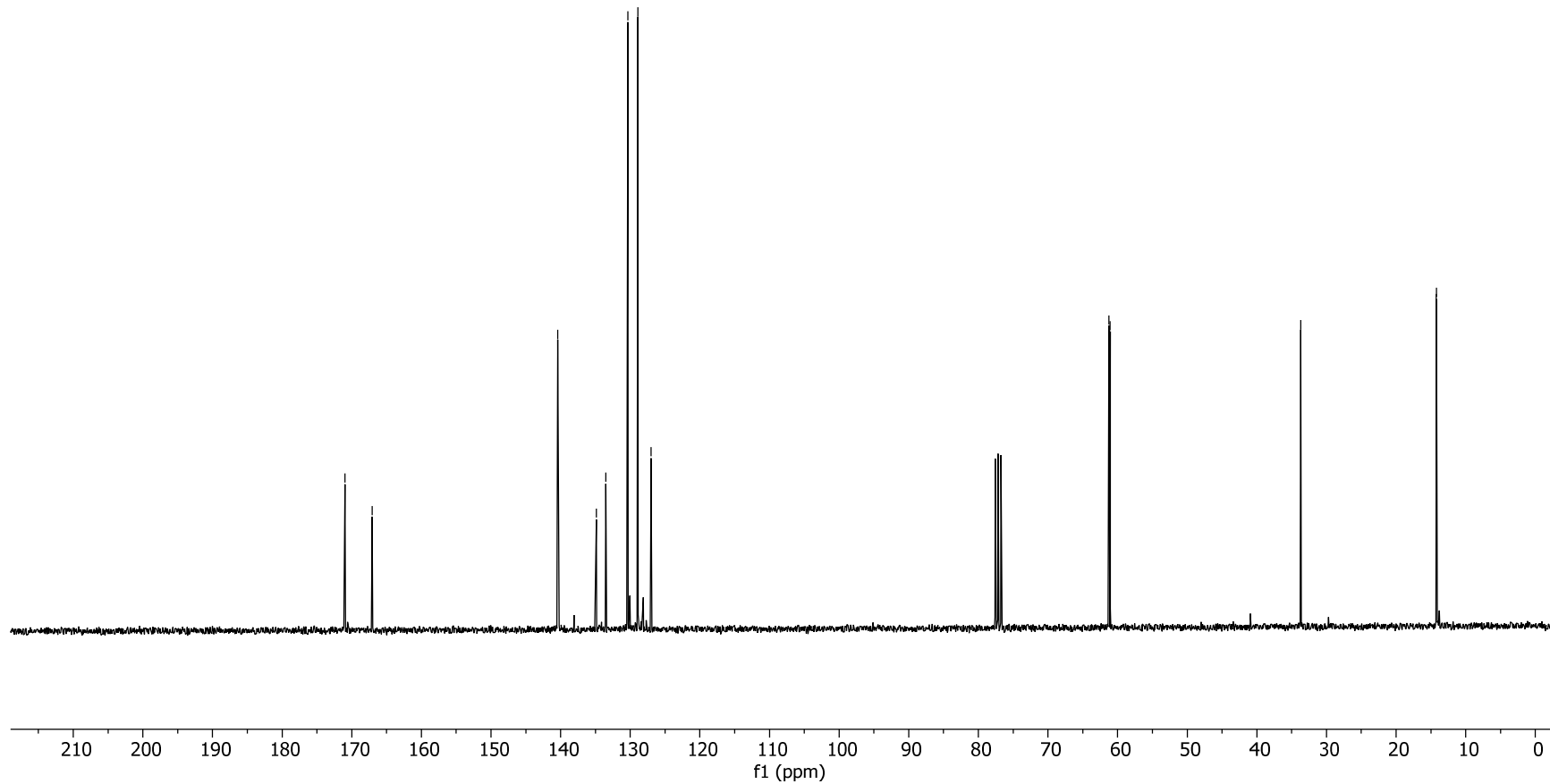
— 170.97
— 167.08

— 140.40
— 134.88
— 133.51
— 130.35
— 128.91
— 127.02

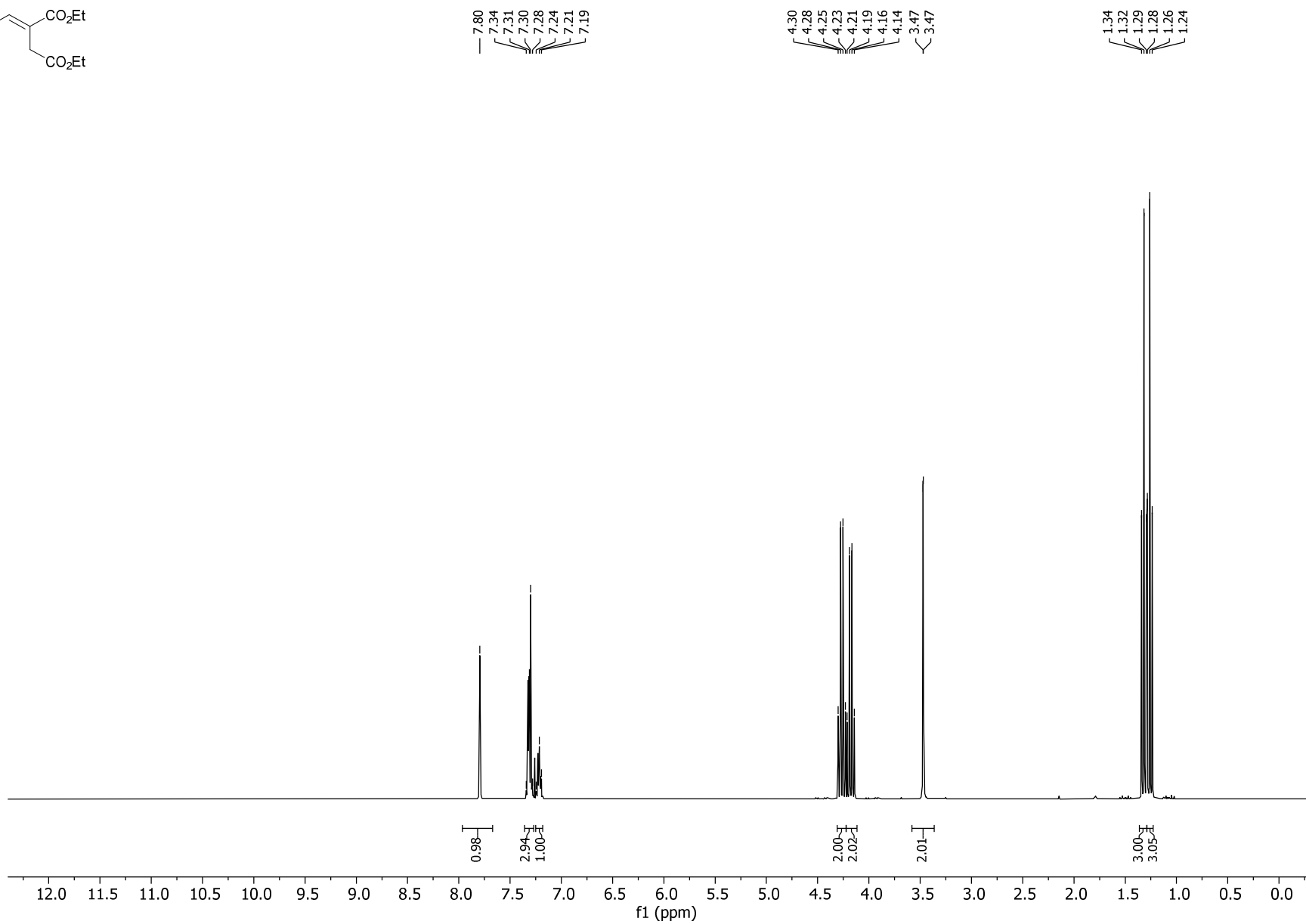
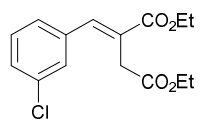
— 61.26
— 61.06

— 33.70

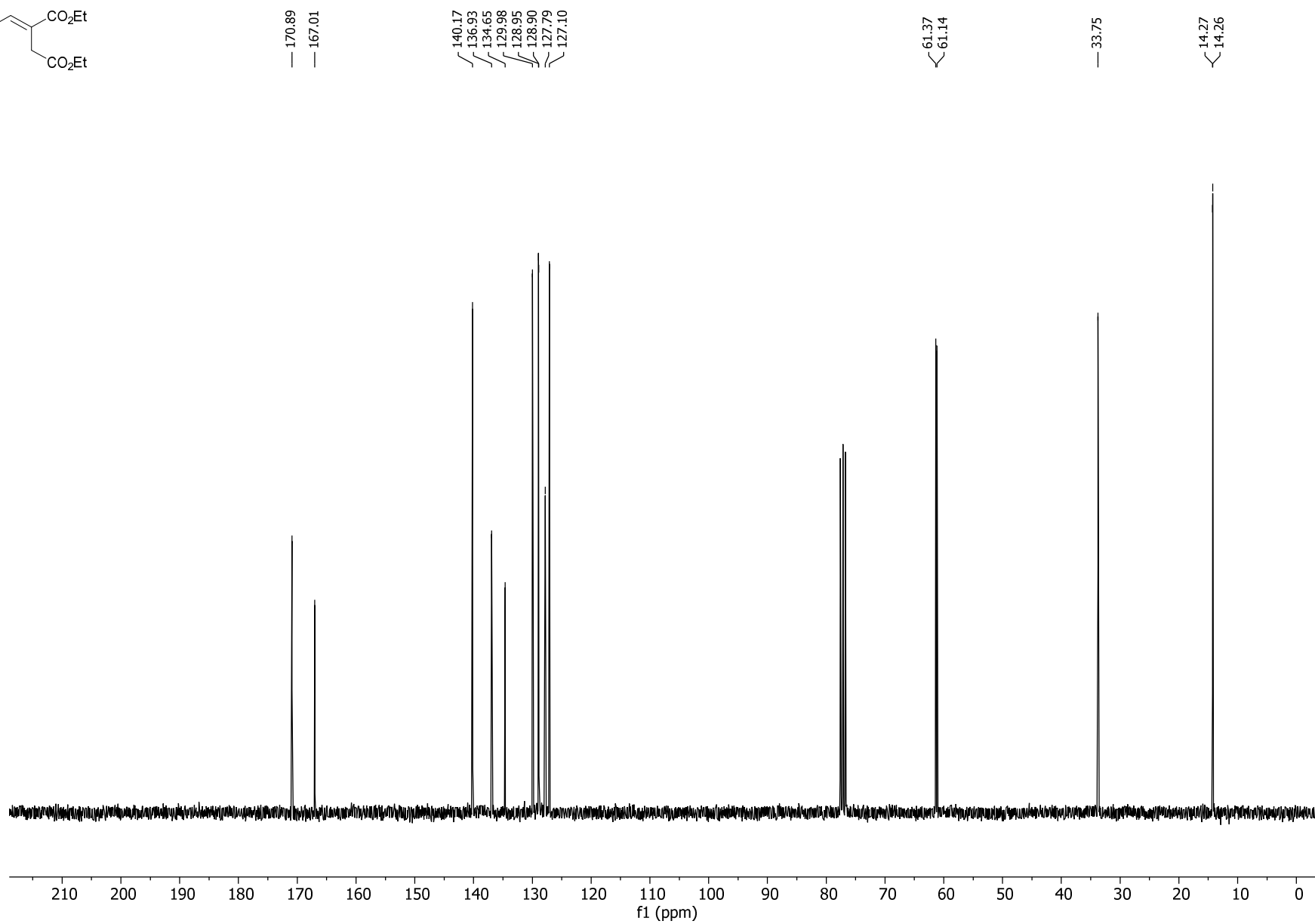
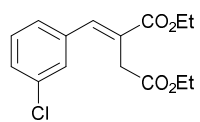
— 14.24
— 14.21



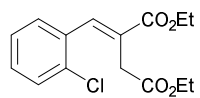
¹H NMR of Diethyl (*E*)-2-(3-chlorobenzylidene)succinate (3q)



¹³C NMR of Diethyl (*E*)-2-(3-chlorobenzylidene)succinate (3q)



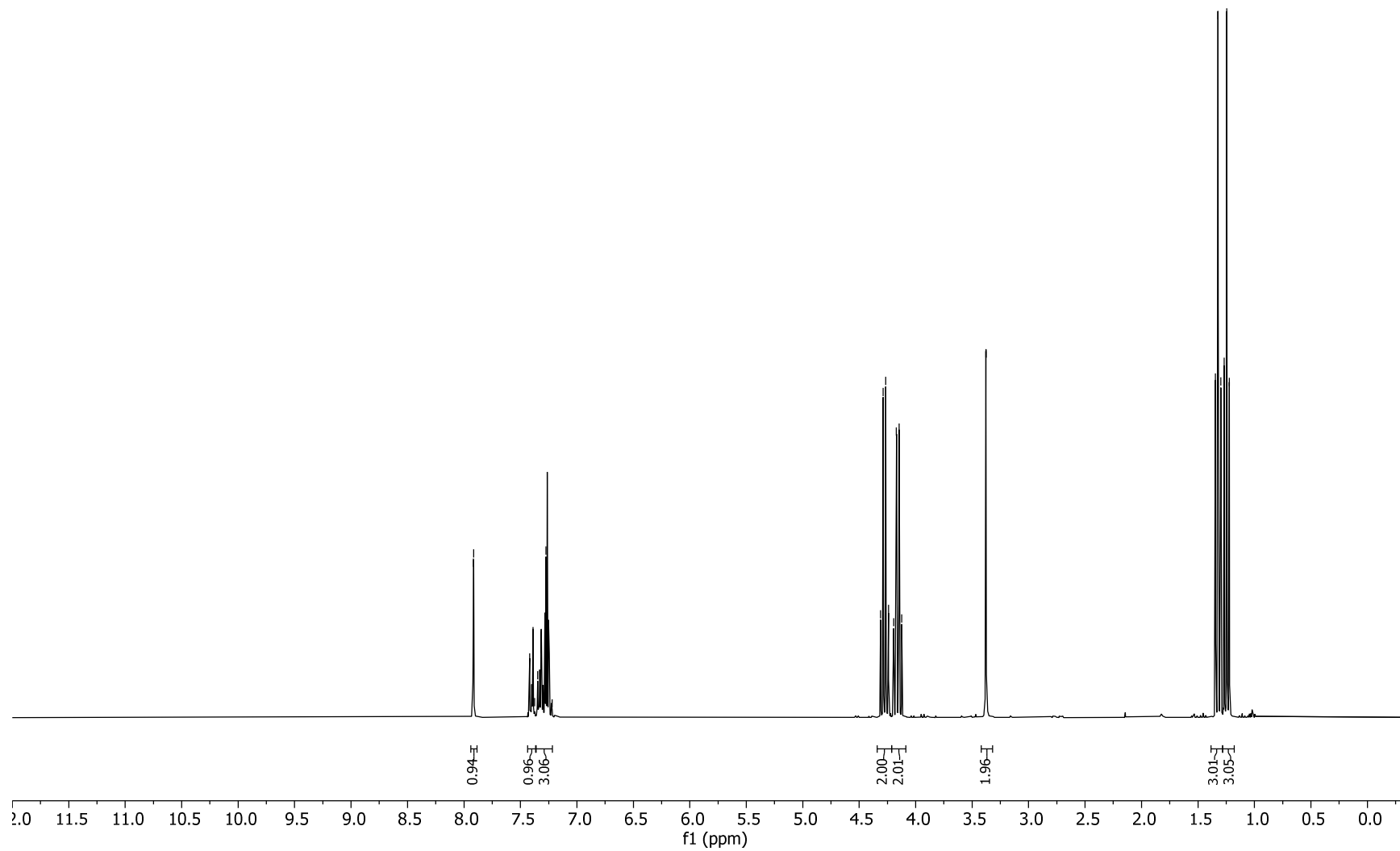
¹H NMR of Diethyl (*E*)-2-(2-chlorobenzylidene)succinate (3r)



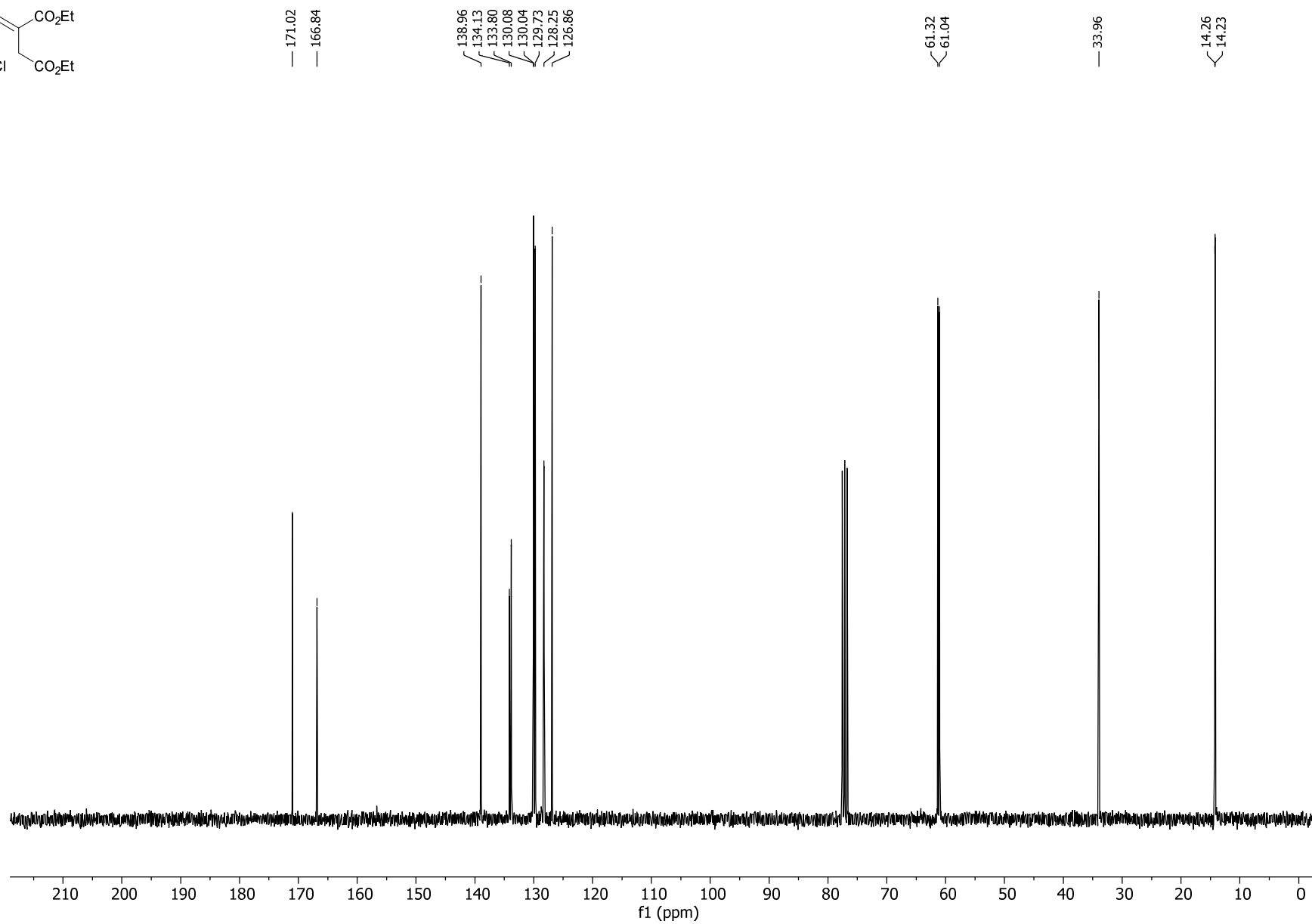
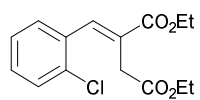
7.92
7.91
7.42
7.39
7.38
7.35
7.32
7.27
7.25
7.22

4.31
4.29
4.26
4.24
4.19
4.17
4.15
4.12
3.38
3.38

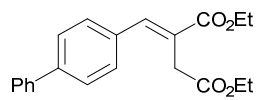
1.35
1.32
1.30
1.27
1.25
1.22



¹³C NMR of Diethyl (*E*)-2-(2-chlorobenzylidene)succinate (3r)



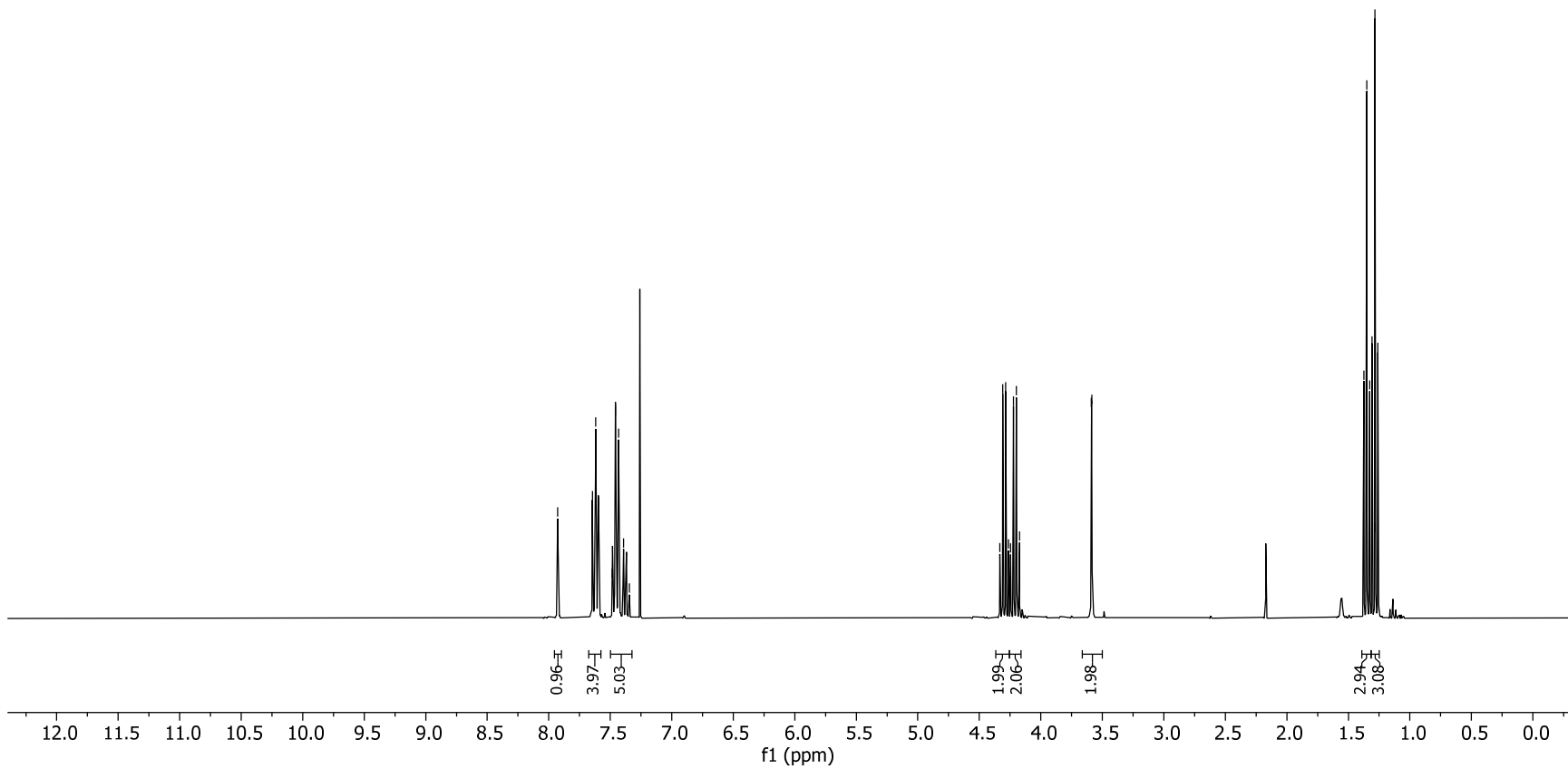
¹H NMR of Diethyl (*E*)-2-([1,1'-biphenyl]-4-ylmethylene)succinate (3s)



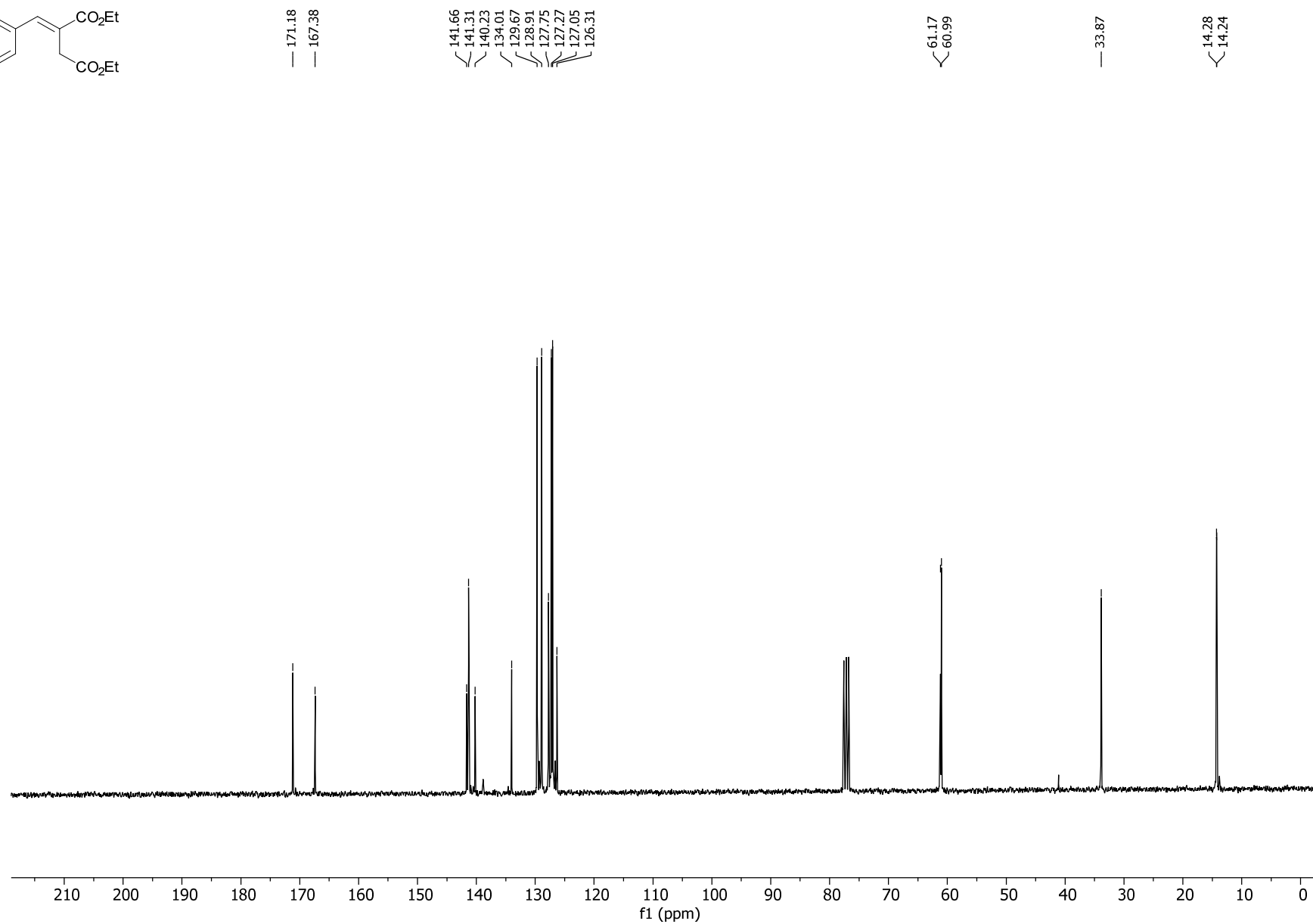
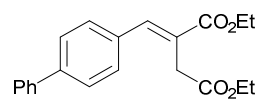
7.93
7.65
7.62
7.59
7.49
7.46
7.43
7.39
7.34

4.33
4.31
4.29
4.26
4.25
4.22
4.20
4.17
3.59
3.59

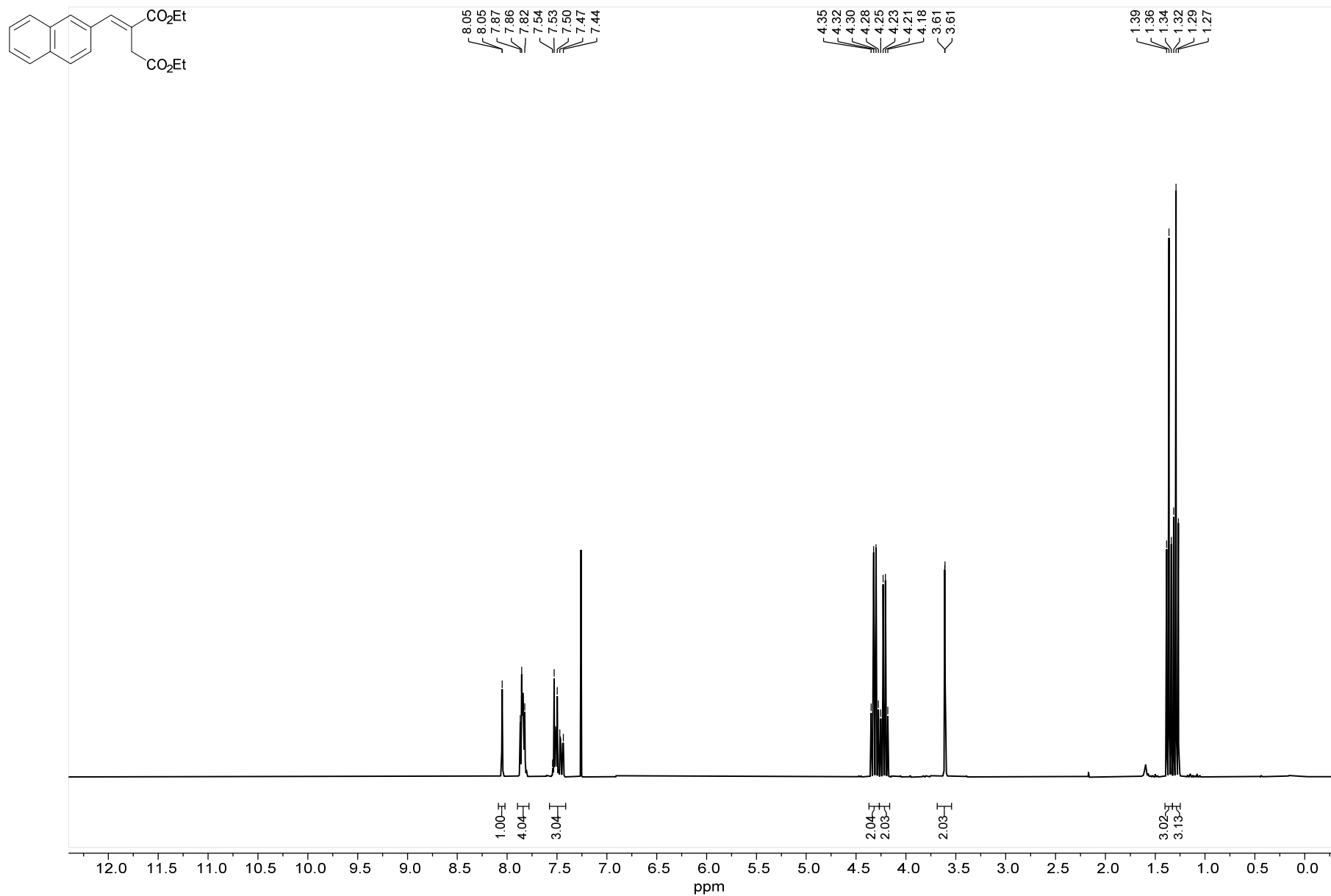
1.37
1.35
1.33
1.31
1.28
1.26



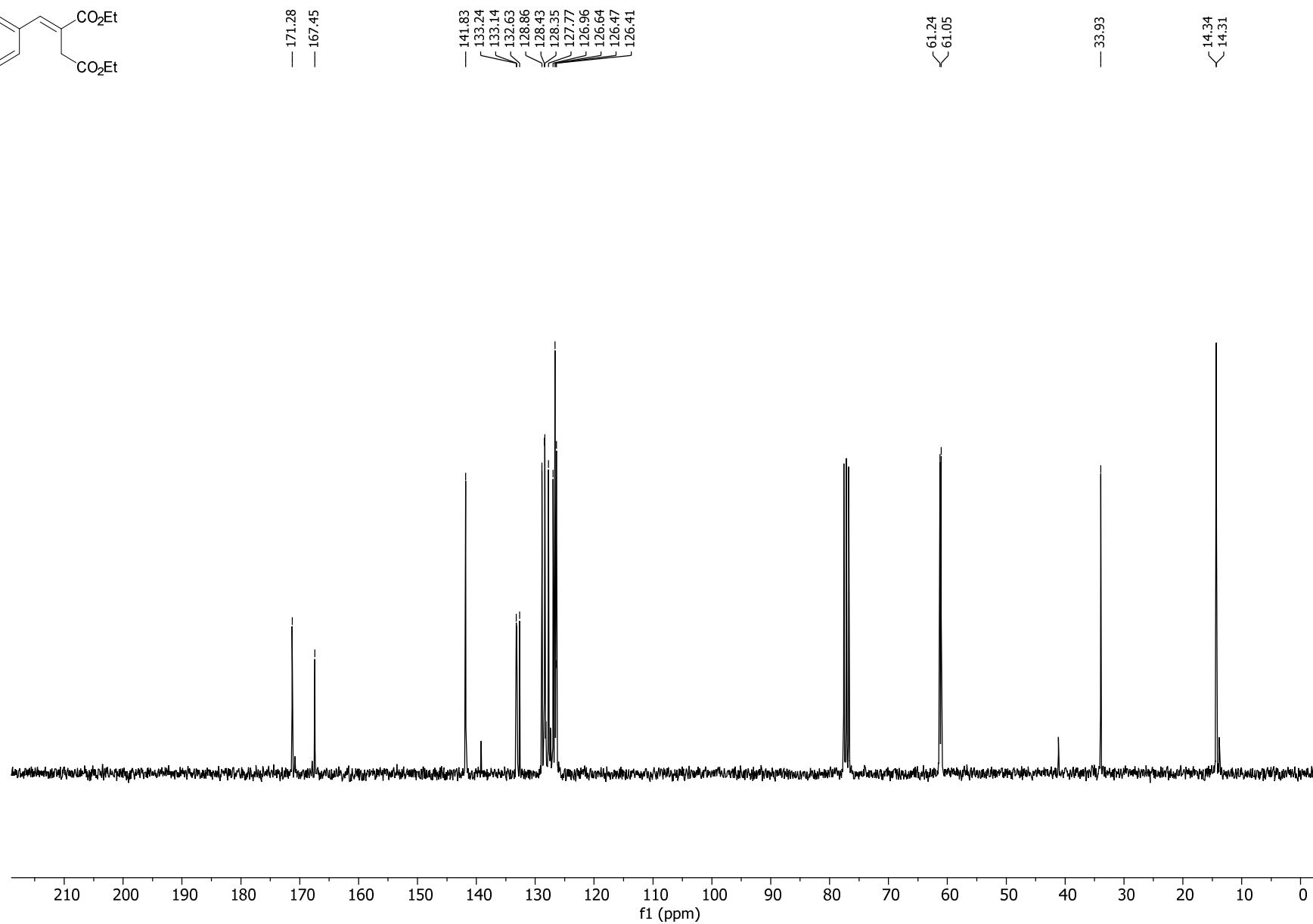
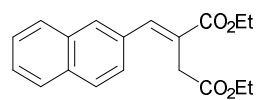
¹³C NMR of Diethyl (*E*)-2-([1,1'-biphenyl]-4-ylmethylene)succinate (3s)



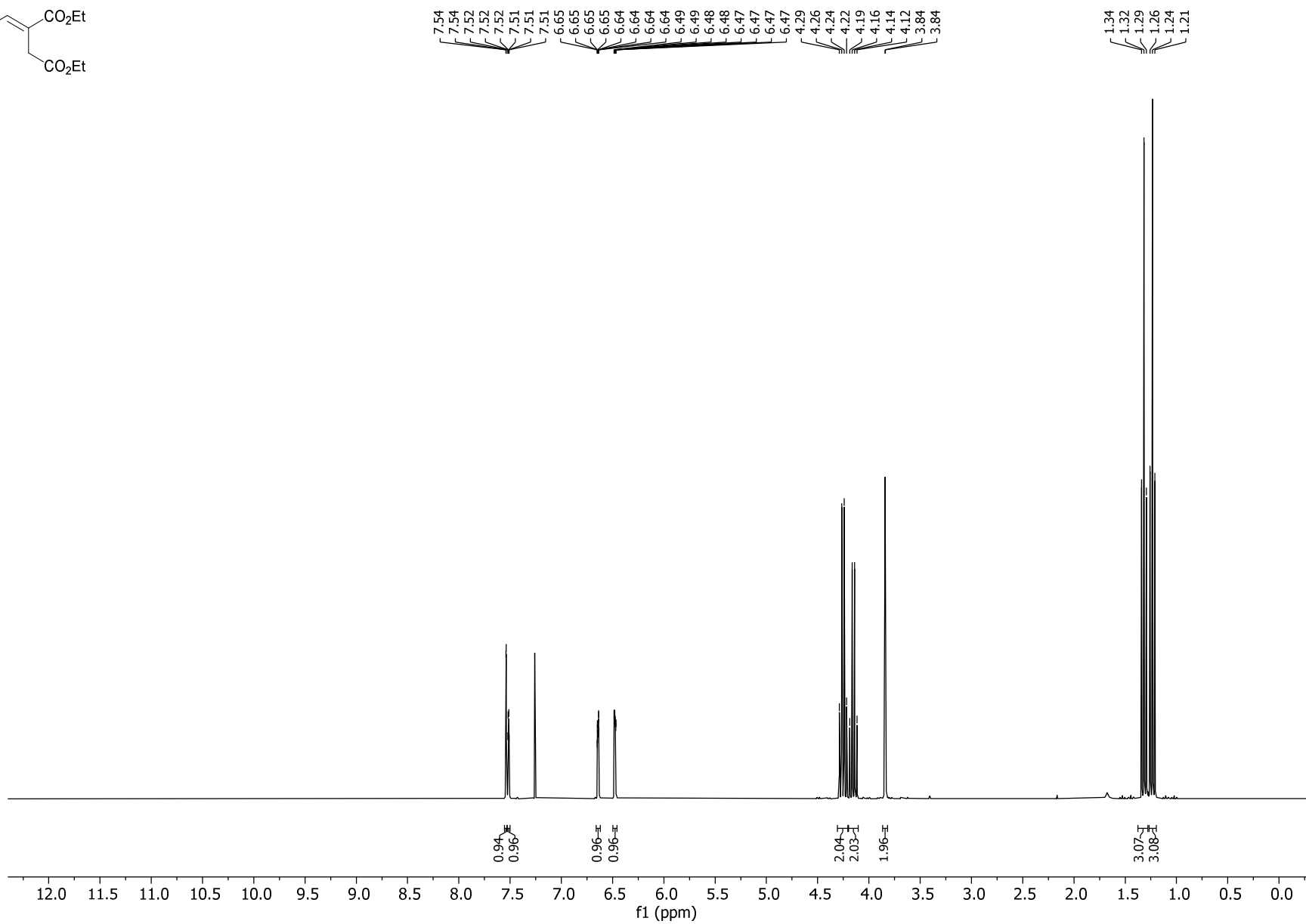
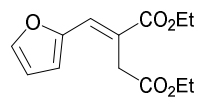
¹H NMR of Diethyl (*E*)-2-(naphthalen-2-ylmethylene)succinate (3t)



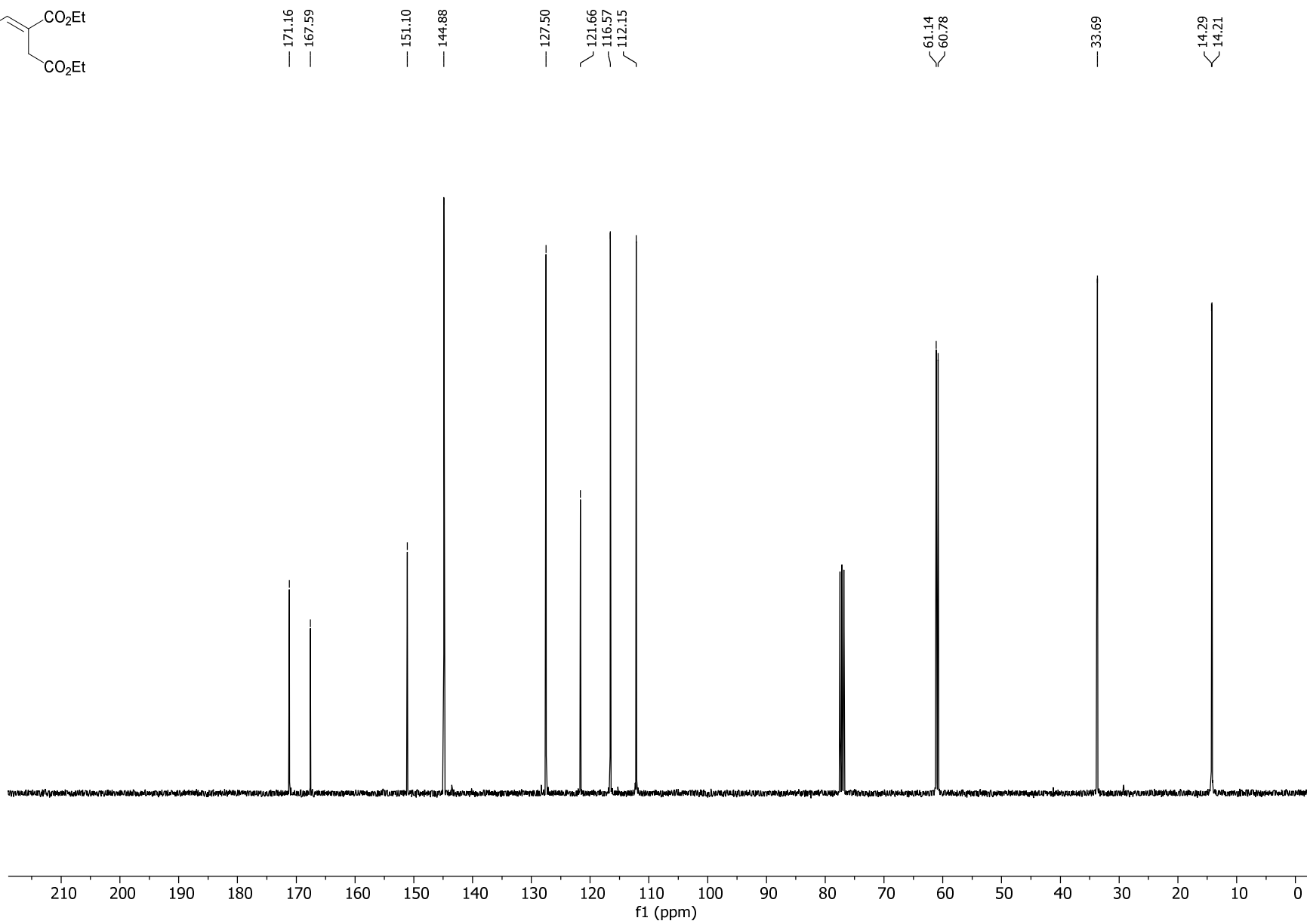
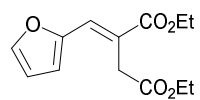
¹³C NMR of Diethyl (*E*)-2-(naphthalen-2-ylmethylene)succinate (3t)



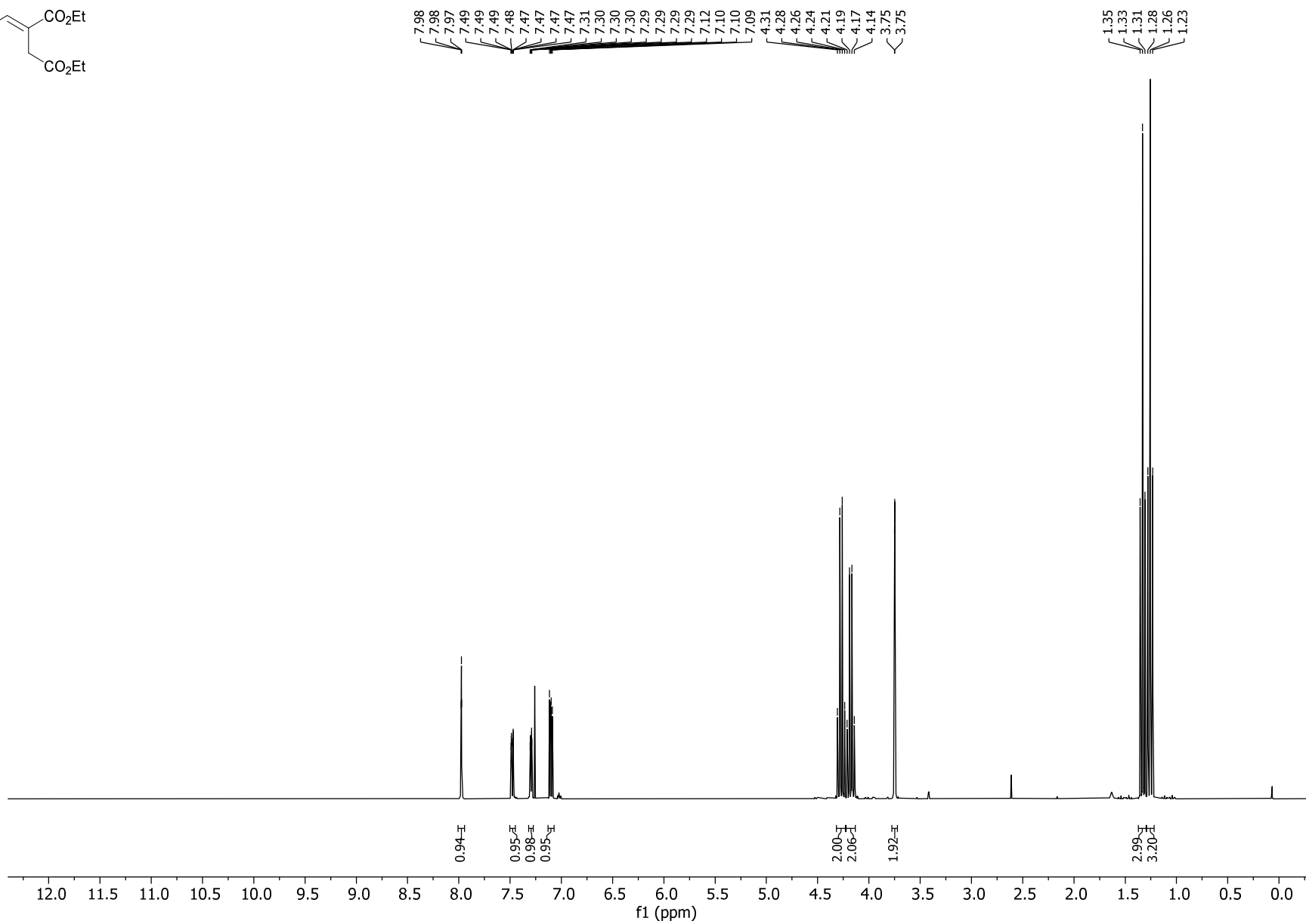
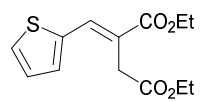
¹H NMR of Diethyl (*E*)-2-(furan-2-ylmethylene)succinate (3u)



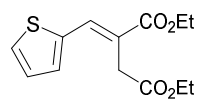
¹³C NMR of Diethyl (*E*)-2-(furan-2-ylmethylene)succinate (3u)



¹H NMR of Diethyl (*E*)-2-(thiophene-2-ylmethylene)succinate (3v)



¹³C NMR of Diethyl (*E*)-2-(thiophene-2-ylmethylene)succinate (3v)



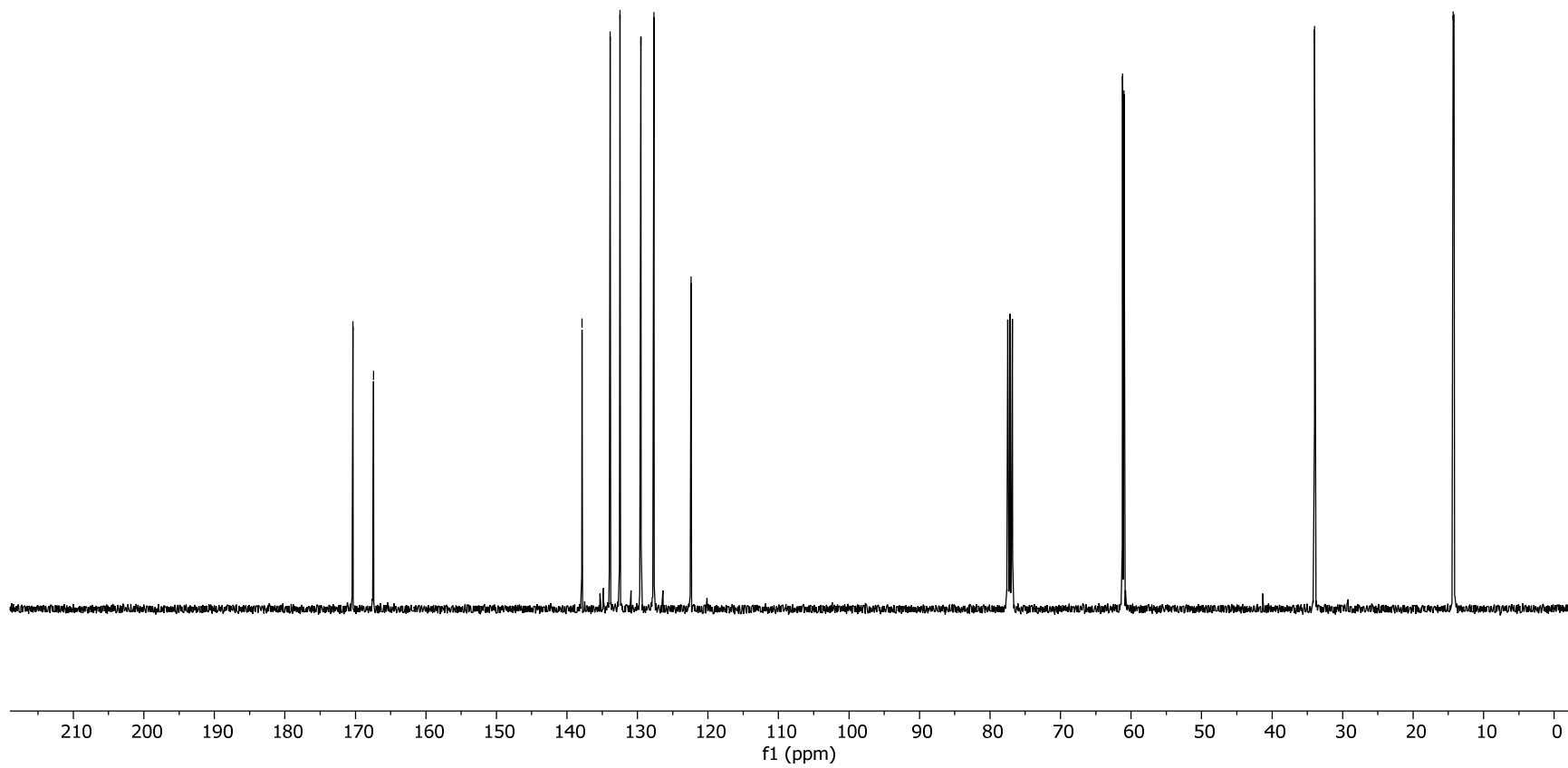
— 170.37
— 167.44

— 137.86
— 133.88
— 132.48
— 129.50
— 127.68
— 122.40

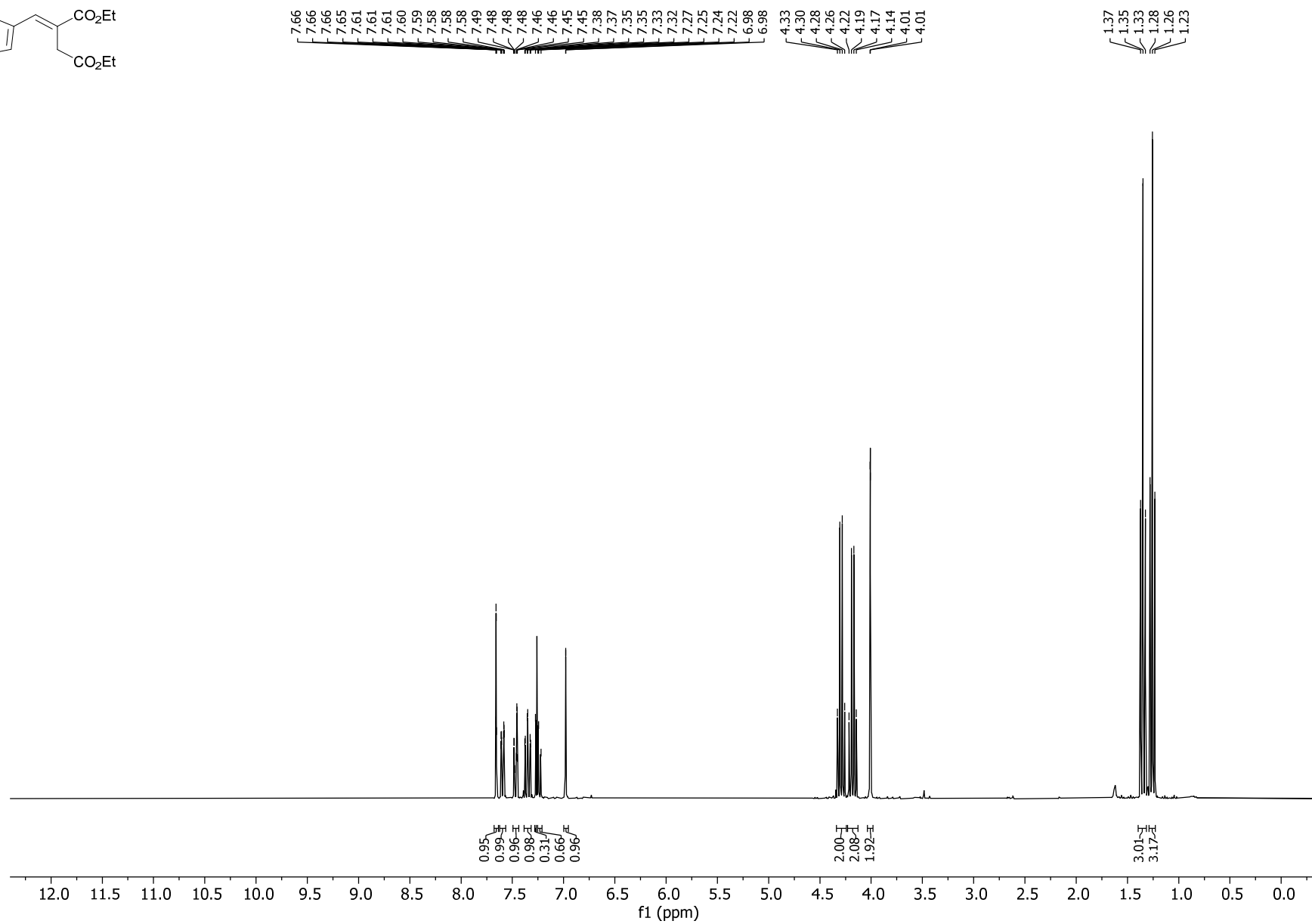
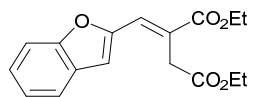
61.19
61.01

— 33.96

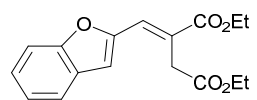
14.30
14.21



¹H NMR of Diethyl (*E*)-2-(benzofuran-2-ylmethylene)succinate (3w)



¹³C NMR of Diethyl (*E*)-2-(benzofuran-2-ylmethylene)succinate (3w)



— 171.05
— 167.30

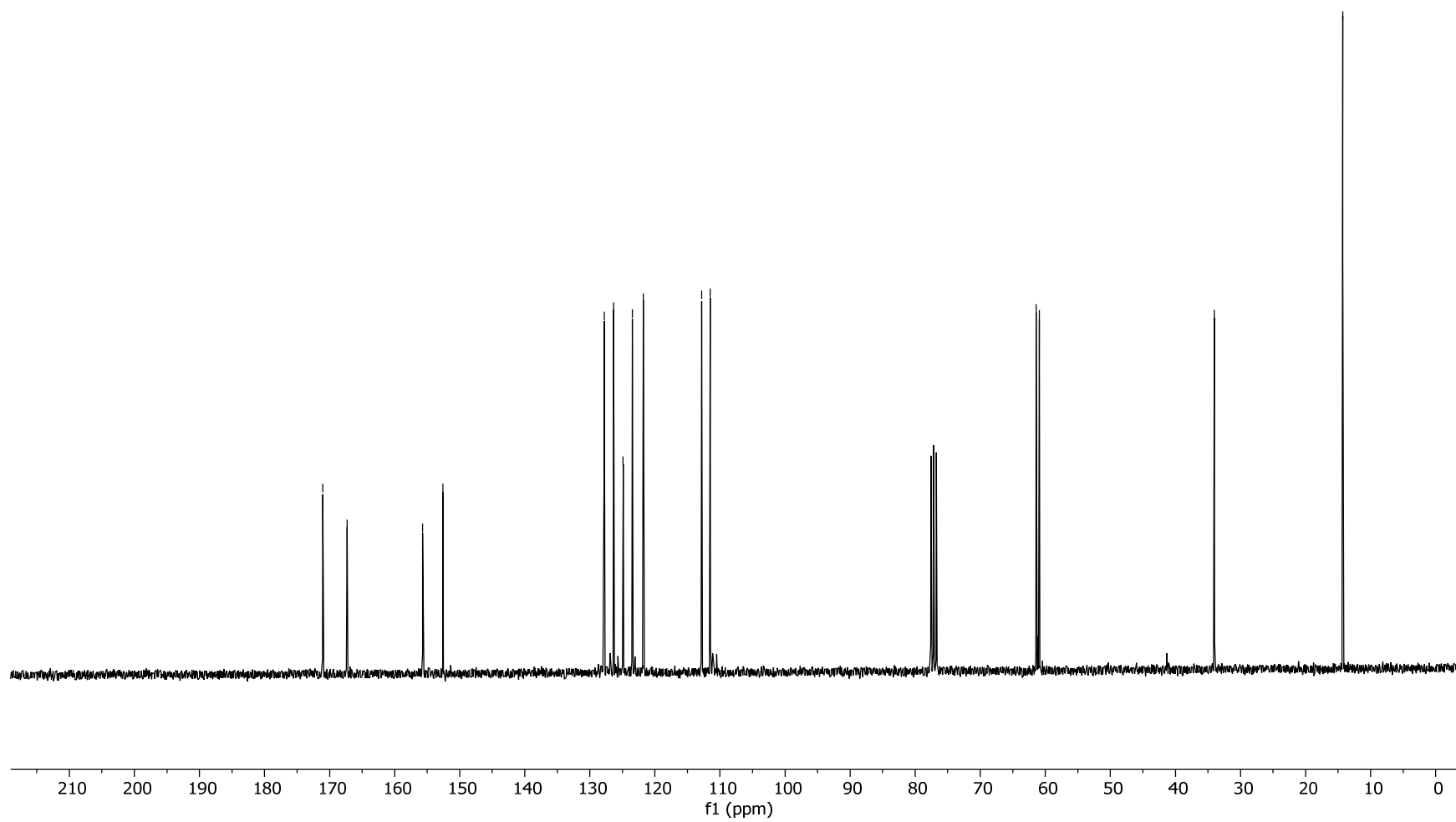
— 155.69
— 152.58

127.85
127.79
126.34
124.89
123.47
121.79
112.81
111.48

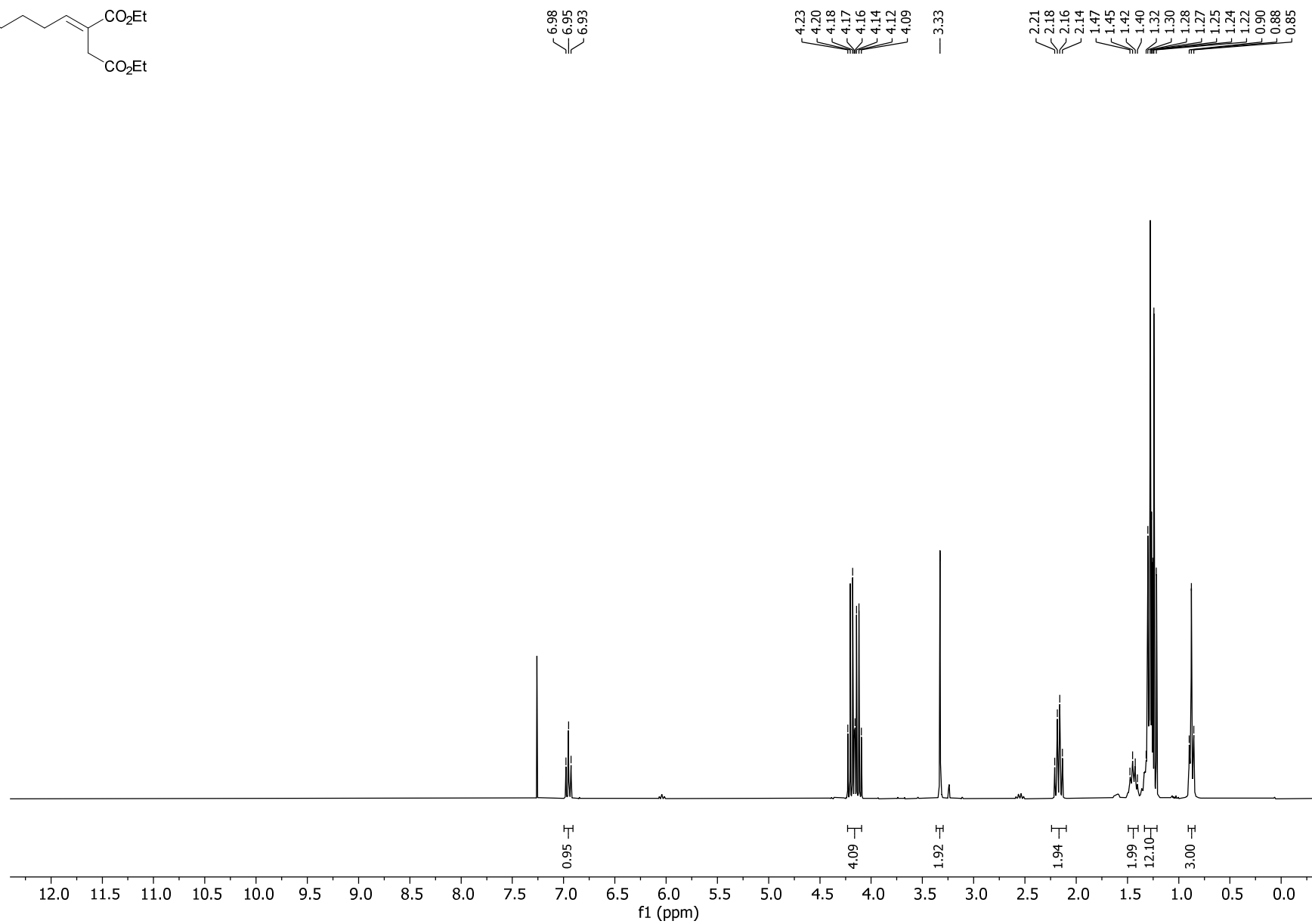
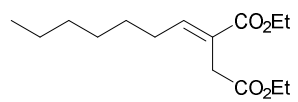
61.39
60.90

— 34.00

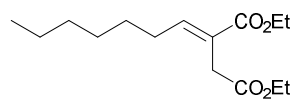
— 14.30



¹H NMR of Diethyl (*E*)-2-heptylidenesuccinate (3x)



¹³C NMR of Diethyl (*E*)-2-heptylidenesuccinate (3x)



— 170.92
— 167.04

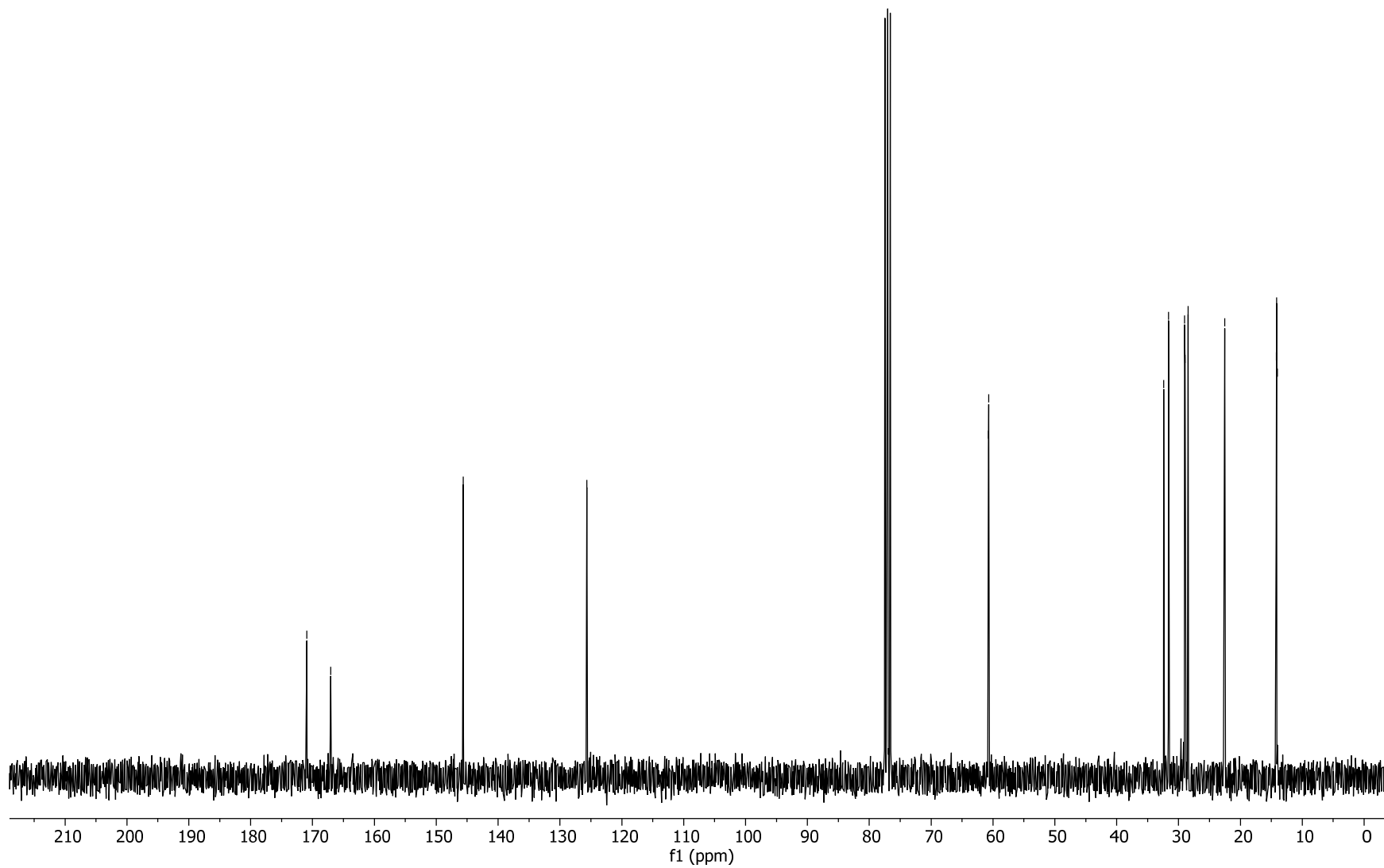
— 145.63

— 125.64

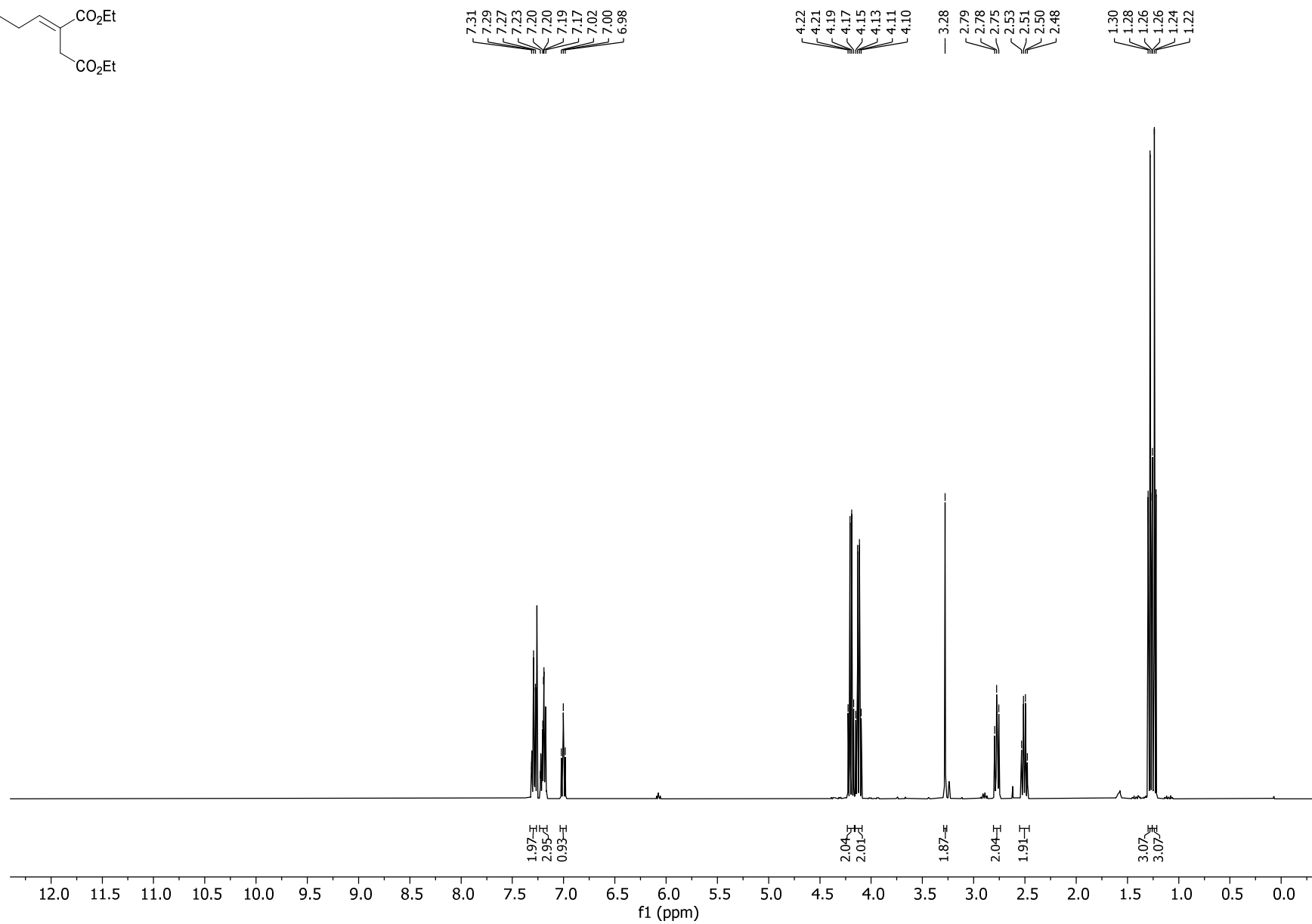
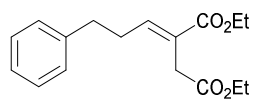
60.74
60.70

32.41
31.60
29.01
28.94
28.45
22.54

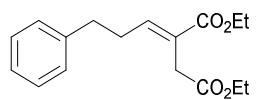
14.20
14.16
14.04



¹H NMR of Diethyl (*E*)-2-(3-phenylpropylidene)succinate (**3y**)



¹³C NMR of Diethyl (*E*)-2-(3-phenylpropylidene)succinate (3y)



— 170.89
— 167.01

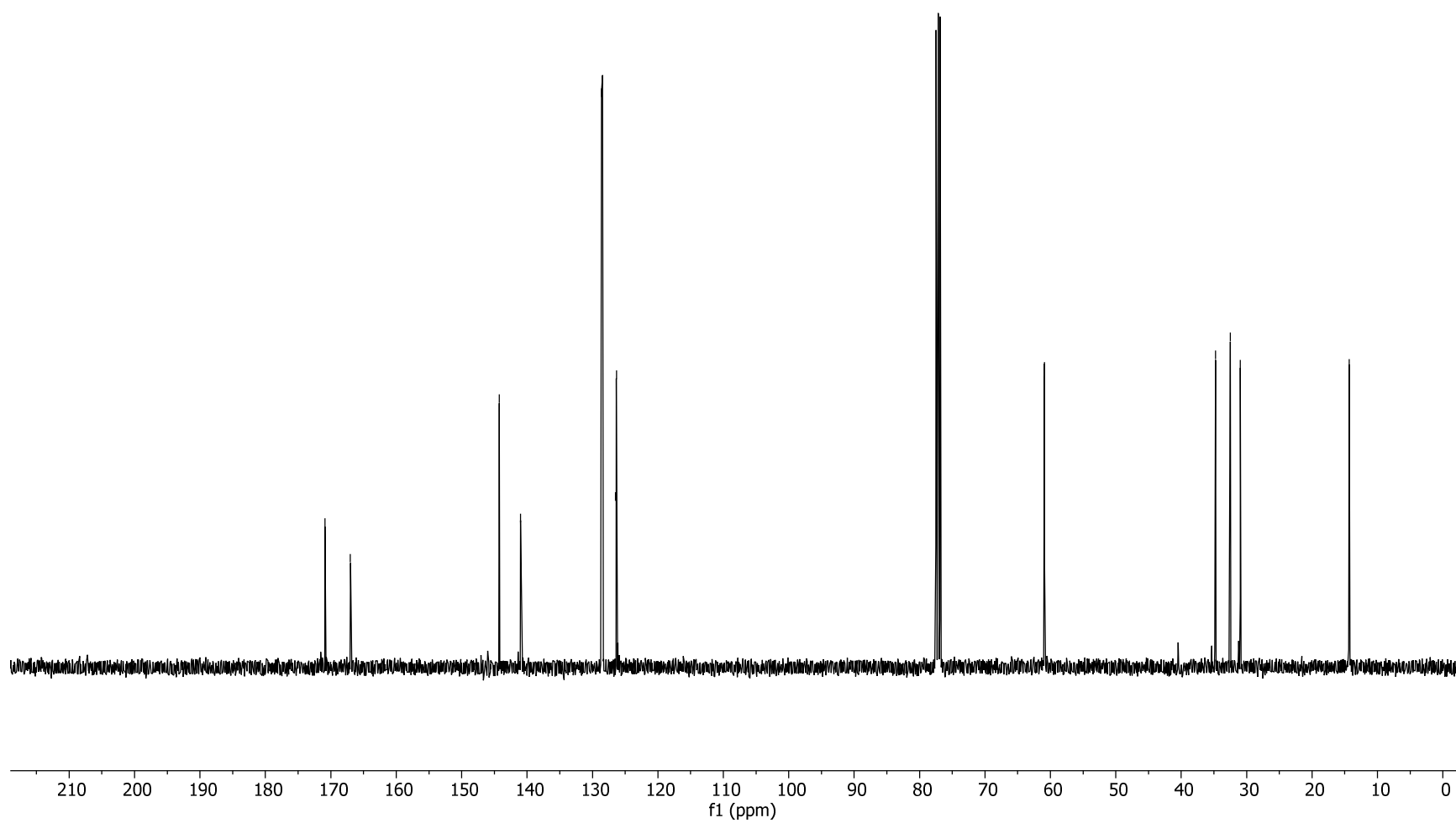
— 144.25
— 140.98

↙ 128.63
↘ 128.47
↙ 126.47
↘ 126.34

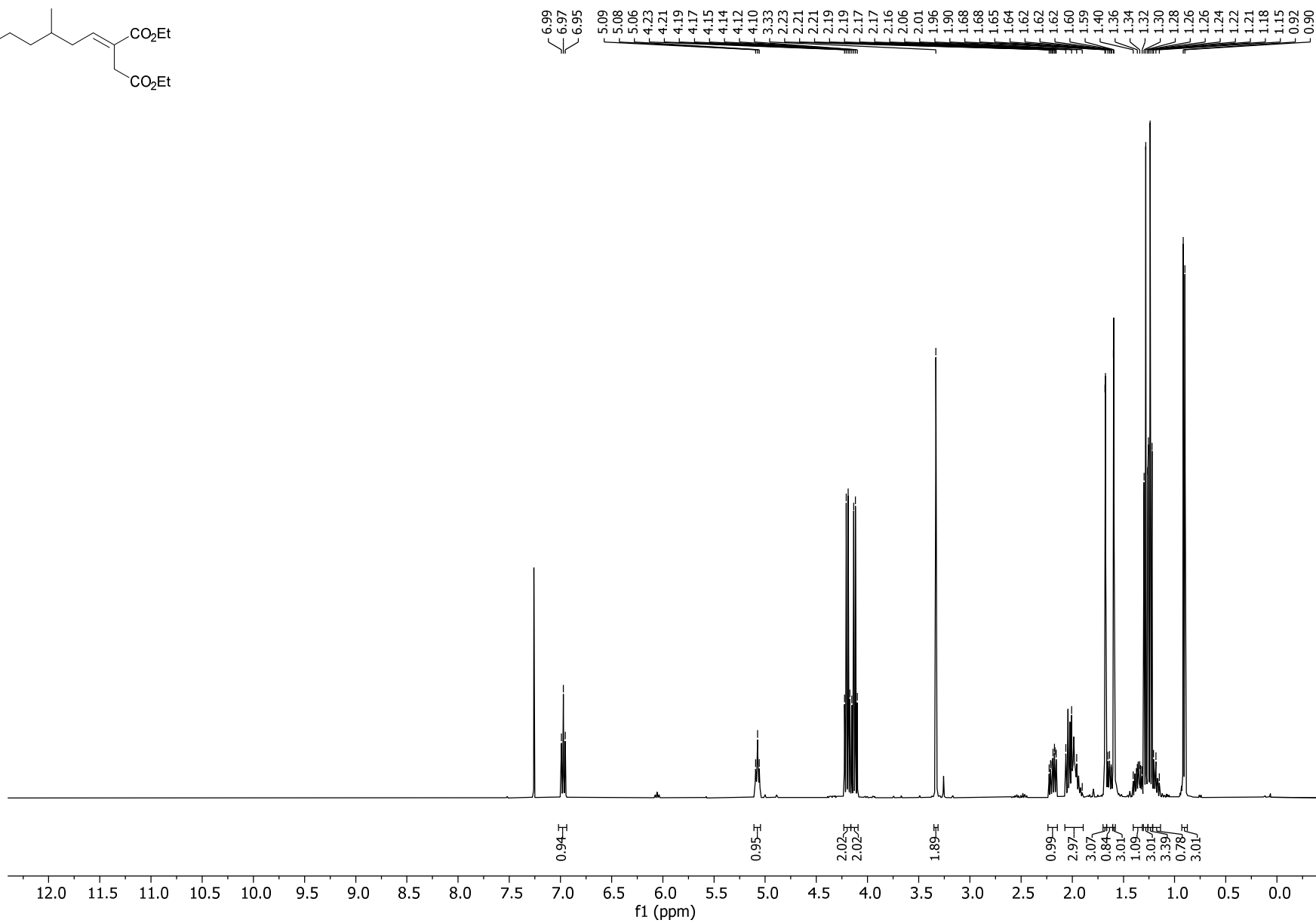
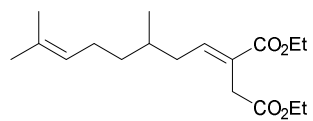
↙ 60.94
↘ 60.92

↙ 34.74
↘ 32.50
↙ 30.97

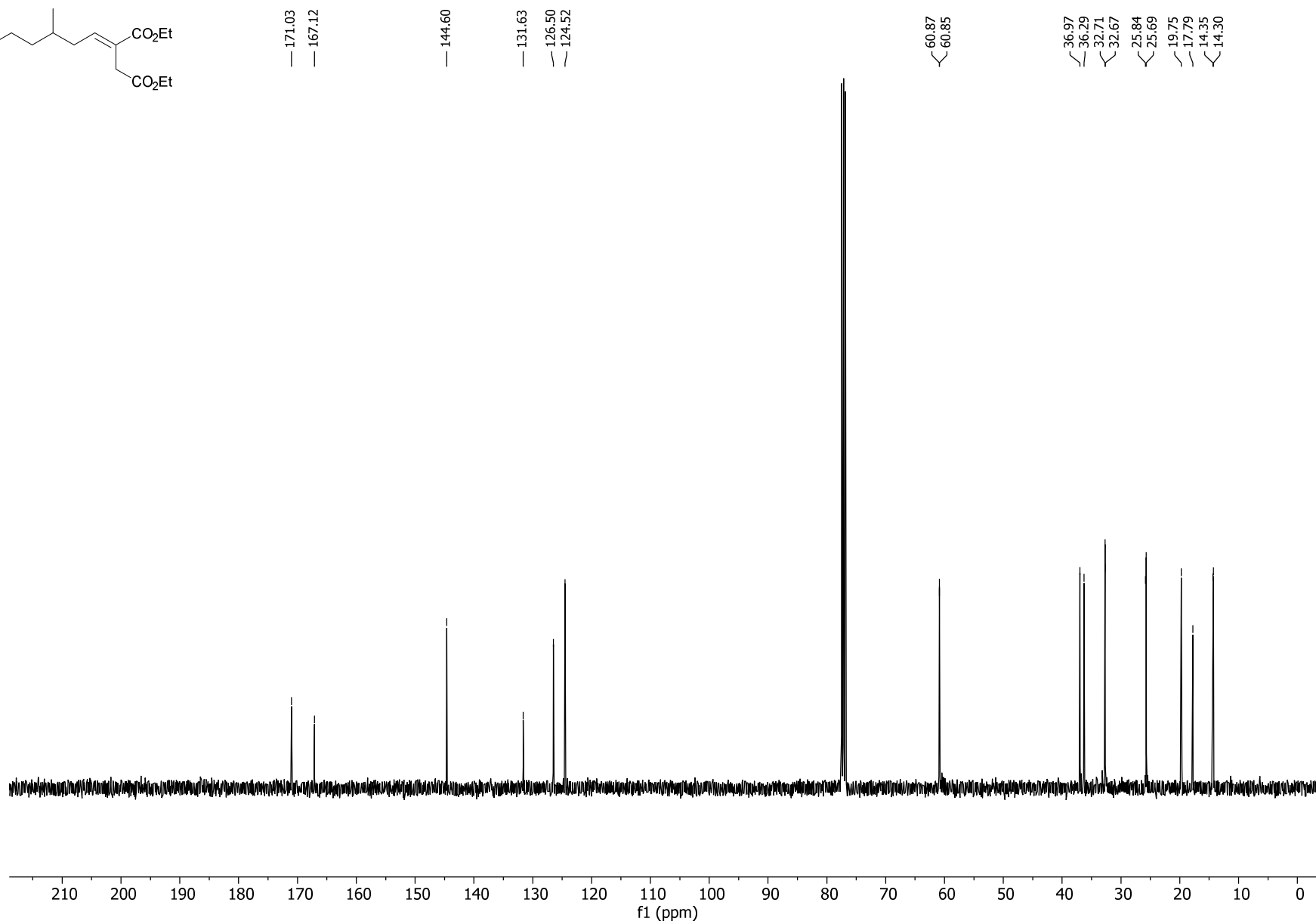
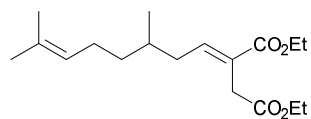
↙ 14.33
↘ 14.30



¹H NMR of Diethyl (E)-2-(3,7-dimethyloct-6-en-1-ylidene)succinate (3z)



¹³C NMR of Diethyl (*E*)-2-(3,7-dimethyloct-6-en-1-ylidene)succinate (3z)



7. References

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2. N. Matuszak, G. G. Muccioli, G. Labar and D. M. Lambert, *J. Med. Chem.*, 2009, **52**, 7410–7420.
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7. Y. Shen and Z. Zhang, *J. Chem. Res. Synop.*, 1998, 642–643.