Hydrogen peroxide-promoted Mizoroki-Heck reactions of phenyldiazenes with acrylates, acrylamides and styrenes

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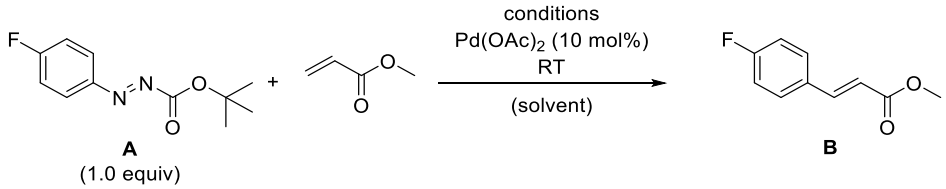
1.1 General remarks

Solvents and reagents were obtained from commercial sources and used as received. NMR spectra were recorded on *Bruker* Avance 600 (^{1}H: 600 MHz, ^{13}C: 151 MHz) and *Bruker* Avance 360 (^{1}H: 360 MHz, ^{13}C: 91 MHz). For ^{1}H-NMR $CDCl_3$ and CD_3OD, and are used as solvents referenced to TMS (δ = 0.00 ppm), $CDCl_3$ (δ = 7.26 ppm) or CD_3OD (δ = 3.31 ppm). For ^{13}C-NMR $CDCl_3$ and CD_3OD are used as solvents with $CDCl_3$ (δ = 77.0 ppm), and CD_3OD (δ = 49.0 ppm) as standards. Chemical shifts are reported in parts per million (ppm). Coupling constants are in Hertz (*J* Hz). The following abbreviations are used for the description of signals: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet) and bs (broad singlet). Mass spectra were recorded using electron impact (EI). A sector field mass was used for HRMS measurements.

Analytical TLC was carried out on *Merck* silica gel plates using short wave (254 nm) UV light, $KMnO_4$ [3.0 g $KMnO_4$, 20 g potassium carbonate, 5.0 mL aqueous sodium hydroxide (5% *w*/*w*) in 300 mL H_2O] and ninhydrin [200 mg ninhydrin in 100 mL ethanol] to visualize components. For flash column chromatography silica gel (Kieselgel 60, grain size 40 - 63 μm, *Merck*) was used. The phenylazocarboxylic esters **1a-1k** have been previously characterized[1] and were prepared according to established procedures.

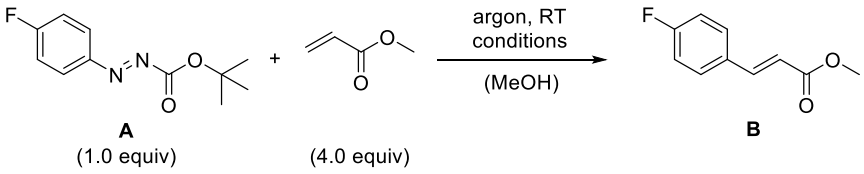
Table S1. Experiments with *tert*-butyl 2-(4-fluorophenyl)azocarboxylate: variation of solvent, base and ligand.



Entry	Conditions					Yield [%][a]	
	Atmos-phere	Solvent	Ligand	Base (1.0 equiv)	Acrylate (equiv)	**B**	**A**[b]
1	Argon	MeOH	-	-	2	6	89
2	Argon	MeOH	-	NEt_3	2	25	41
3	Air	MeOH	-	NEt_3	4	28	6
4	Air	CH_3CN	-	NEt_3	4	2	86
5	Air	MeOH	PPh_3 (10 mol%)	NEt_3	4	29	3
6	Argon	MeOH	PPh_3 (10 mol%)	K_2CO_3	4	5	-

[a] Yields determined by ^{1}H-NMR using dimethyl terephthalate (0.1 mmol, δ = 8.1 (s, 4 H)) as internal standard;
[b] recovered starting material **A**

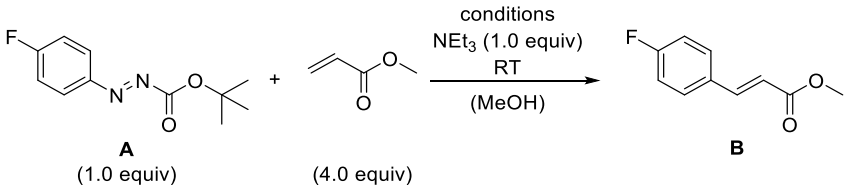
Table S2. Experiments with *tert*-butyl 2-(4-fluorophenyl)azocarboxylate: variation of Pd-source, base and additive.



Entry	Conditions			Yield [%][a]	
	Pd-salt	Ligand	Base (1.0 equiv)	**B**	**A**[b]
1	$Pd[(C_6H_5)_3P]_4$ (5 mol%)	-	NEt_3	19	-
2	$PdCl_2$ (10 mol%)	PPh_3 (10 mol%)	NEt_3	43	17
3	$PdCl_2$ (10 mol%)	PPh_3 (20 mol%)	NEt_3	42	6
4	$PdCl_2$ (10 mol%)	PPh_3 (20 mol%)	K_2CO_3	16	-

[a] Yields determined by ^{1}H-NMR using dimethyl terephthalate (0.1 mmol, δ = 8.1 (s, 4 H)) as internal standard;
[b] recovered starting material **A**

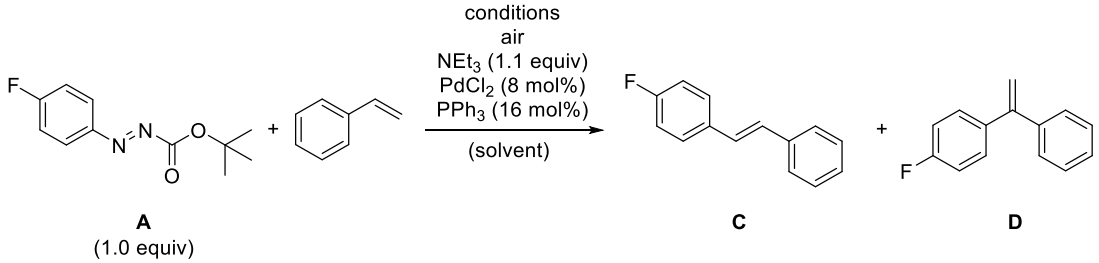
Table S3. Experiments with *tert*-butyl 2-(4-fluorophenyl)azocarboxylate: variation of catalyst loading and amount of additive.



Entry	Conditions			Yield [%][a]	
	Atmosphere	$PdCl_2$ (mol%)	PPh_3 (mol%)	**B**	**A**[b]
1	Argon	8	16	48	-
2	Argon	5	10	35	9
3	Argon	3	6	30	15
4	Argon	1	2	12	21
5	Air	1	2	12	9

[a] Yields determined by ^{1}H-NMR using dimethyl terephthalate (0.1 mmol, δ = 8.1 (s, 4 H)) as internal standard; [b] recovered starting material **A**

Table S4. Experiments with *tert*-butyl 2-(4-fluorophenyl)azocarboxylate: variation of solvent and temperature.

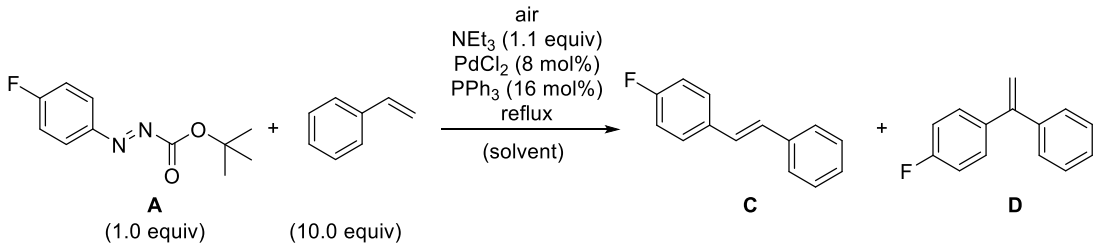


A (1.0 equiv) **C** **D**

Entry	Conditions			Yield [%][a]			Ratio **C**/**D**
	Solvent	Temperature	Styrene (equiv)	**C**	**D**	**A**[b]	
1	MeOH	RT	4	61	20	17	3/1
2	MeOH	0°C → RT	4	55	22	12	2.5/1
3	EtOH	RT	4	6	2	72	3/1
4	dioxan	RT	4	-	-	66	-
5	DMF	RT	4	-	-	86	-
6	CH_3CN	RT	4	10	-	90	1/0

[a] Yields determined by ^{1}H-NMR using dimethyl terephthalate (0.1 mmol, δ = 8.1 (s, 4 H)) as internal standard; [b] recovered starting material **A**

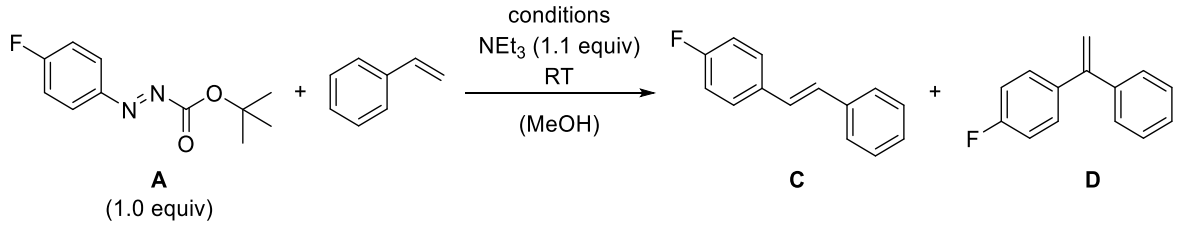
Table S5. Experiments with *tert*-butyl 2-(4-fluorophenyl)azocarboxylate: variation of solvent



Entry	Solvent	Yield [%][a]		
		C	**D**	**A**[b]
1	CH_3CN	12	-	58
2	CH_3CN / H_2O (5%)	12	1	65
3	CH_3CN / H_2O (10%)	14	1	41

[a] Yields determined by ^{1}H-NMR using dimethyl terephthalate (0.1 mmol, δ = 8.1 (s, 4 H)) as internal standard; [b] recovered starting material **A**

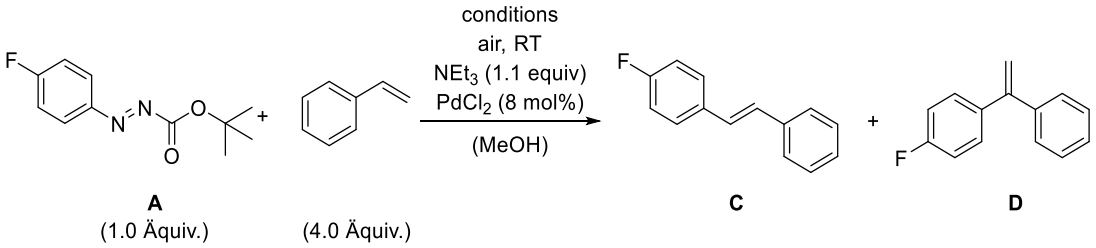
Table S6. Experiments with *tert*-butyl 2-(4-fluorophenyl)azocarboxylate: variation of catalyst loading and phosphine additive



Entry	Conditions				Yield [%][a]			Ratio **C**/D
	Atmos-phere	$PdCl_2$ [mol%]	Ligand	Styrene (equiv)	**C**	**D**	**A**[b]	
1	Argon	5.5	Dppf (5 mol%)	4	22	10	-	2.2/1
2	Argon	8	Dppp (8 mol%)	10	48	11	13	4.4/1
3	Air	8	P(*o*-tol)$_3$ (16 mol%)	4	48	8	6	6/1
4	Argon	8	P(Cy)$_3$ (16 mol%)	10	26	1	-	26/1
5	Air	8	-	4	8	-	74	1/0

[a] Yields determined by ^{1}H-NMR using dimethyl terephthalate (0.1 mmol, δ = 8.1 (s, 4 H)) as internal standard; [b] recovered starting material **A**

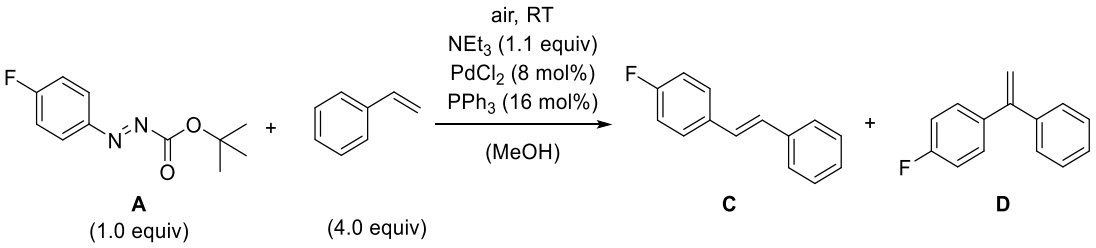
Table S7. Experiments with *tert*-butyl 2-(4-fluorophenyl)azocarboxylate: further additives



Entry	Conditions		Yield [%][a]			Ratio **C/D**
	Additive	PPh_3	**C**	**D**	**A**[b]	
1	$CuCl_2$ (8 mol%)	16 mol%	30	5	-	6/1
2	I_2 (8 mol%)	-	10	-	82	1/0
3	NaBr (0.5 eq)	16 mol%	41	12	4	3.4/1

[a] Yields determined by ^{1}H-NMR using dimethyl terephthalate (0.1 mmol, δ = 8.1 (s, 4 H)) as internal standard; [b] recovered starting material **A**

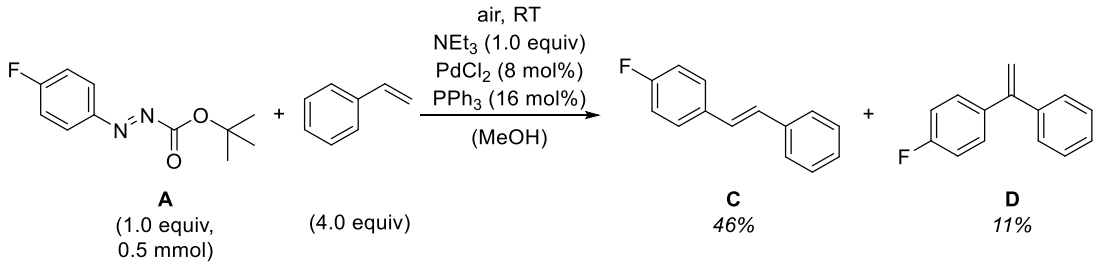
Table S8. Experiments with *tert*-butyl 2-(4-fluorophenyl)azocarboxylate: dilution of the reaction mixture



Entry	Concentration of **A** in MeOH	Yield [%][a]		
		C	**D**	**A**[b]
1	standard conc.: 0.1 mol/L	61	20	17
2	0.2 mol/L	4	1	84
3	0.03 mol/L	56	15	14

[a] Yields determined by ^{1}H-NMR using dimethyl terephthalate (0.1 mmol, δ = 8.1 (s, 4 H)) as internal standard; [b] recovered starting material **A**

Scheme S1. Experiments with *tert*-butyl 2-(4-fluorophenyl)azocarboxylate: yields after purification with column chromatography



Scheme S2. Preperation of methyl 2-(4-fluorophenyl)azocarboxylate

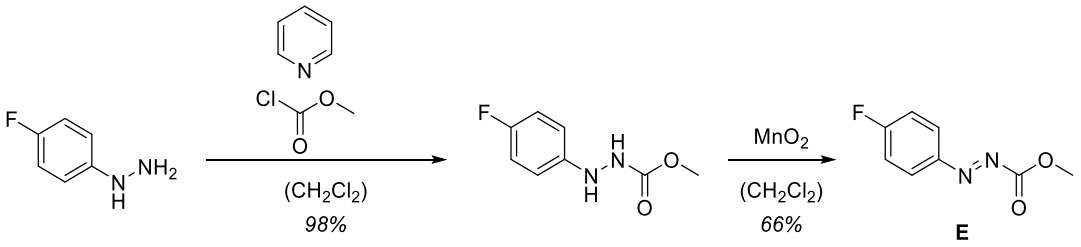
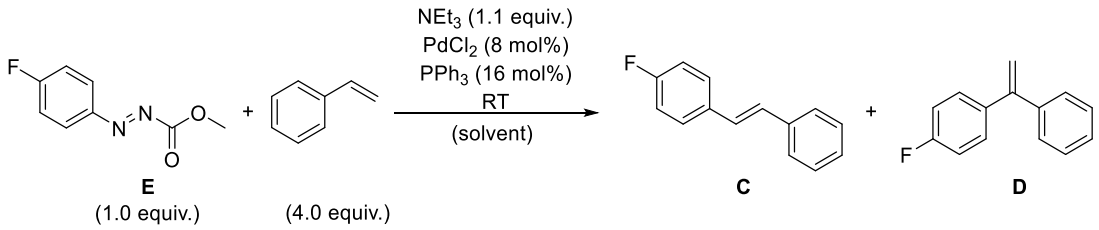


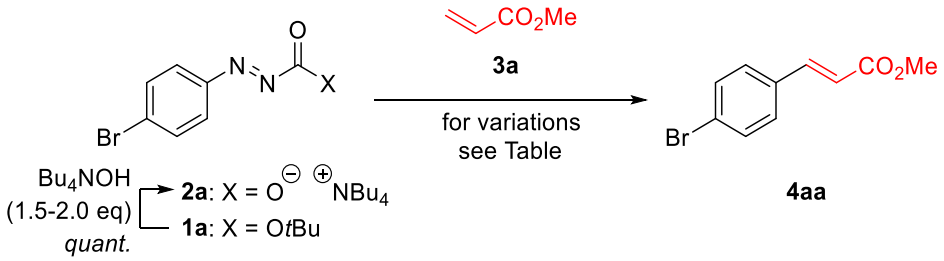
Table S9. Experiments with methyl 2-(4-fluorophenyl)azocarboxylate: variation of solvent and atmosphere.



Entry	Conditions		Yield [%][a]			Ratio **C**/**D**
	Atmosphere	Solvent	**C**	**D**	**E**[b]	
1	Argon	MeOH	26	8	-	3.3/1
2	Air	MeOH	33	5	-	6.6/1
3	Argon	CH_3CN	26	-	73	1/0

[a] Yields determined by ^{1}H-NMR using dimethyl terephthalate (0.1 mmol, δ = 8.1 (s, 4 H)) as internal standard; [b] recovered starting material **E**

Table S10. Preliminary optimization experiments with **1a** on a 175 µmol scale



Entry	Variation of conditions[a] (equiv)	Yield[b] **4aa** (%)
1	Bu_4NOH (2.0), AgOAc (2.5), $Pd(OAc)_2$ (0.38), **3a** (15), 30 min, CH_3CN/AcOH (1 mL/0.25 mL)	68%
2	Bu_4NOH (2.0), AgOAc (2.5), $Pd(OAc)_2$ (0.1), **3a** (15), 30 min, CH_3CN/AcOH (1 mL/0.25 mL)	63%
3	Bu_4NOH (2.0), AgOAc (2.5), $Pd(OAc)_2$ (0.1), **3a** (15), 30 min, CH_3CN/AcOH (0.75 mL/0.75 mL)	68%
4	Bu_4NOH (1.5), AgOAc (2.5), $Pd(OAc)_2$ (0.1), **3a** (5), 30 min, CH_3CN/AcOH (1 mL/0.2 mL)	76%
5	Bu_4NOH (1.5), AgOAc (2.5), $Pd(OAc)_2$ (0.05), **3a** (5), 45 min, CH_3CN/AcOH (1 mL/0.2 mL)	61%
6	Bu_4NOH (1.5) AgOAc (2.5), **3a** (5), 45 min, CH_3CN/AcOH (1 mL/0.2 mL)	0%
7	Bu_4NOH (1.5), AgOAc (3.0), $Pd(OAc)_2$ (0.1), **3a** (5), 45 min, CH_3CN/AcOH (1 mL/0.1 mL)	66%
8	Bu_4NOH (1.5), AgOAc (2.0), $Pd(OAc)_2$ (0.1), **3a** (5), 45 min, CH_3CN/AcOH (1 mL/0.2 mL)	73%
9	Bu_4NOH (1.5), AgOAc (0.1), $Pd(OAc)_2$ (0.1), **3a** (5), 45 min, CH_3CN/AcOH (1 mL/0.2 mL)	25%
10	Bu_4NOH (1.5), $Pd(OAc)_2$ (0.1), **3a** (5), 45 min, CH_3CN/AcOH (1 mL/0.2 mL)	51%
11	Bu_4NOH (1.5), $Pd(OAc)_2$ (0.1), **3a** (20), 60 min, CH_3CN/AcOH (1 mL/0.2 mL)	23%
12	Bu_4NOH (1.5), AgOAc (2.0), $Pd(OAc)_2$ (0.1), **3a** (5), 45 min, AcOH (1.2 mL)	75%
13	Bu_4NOH (1.5), AgOAc (2.5), $Pd(OAc)_2$ (0.1), **3a** (5), 45 min, MeOH/AcOH (1 mL/0.2 mL)	60%

[a]Reaction conditions: Tetrabutylammonium hydroxide (262-300 µmol) and **1a** (175 µmol) in CH_3CN (1.0 mL) 5 min; then slow addition of **2a** (over 30-60 min, see table) to **3a** (0.875-3.5 mmol), AgOAc (17.5-525 µmol), $Pd(OAc)_2$ (0-67 µmol), solvent (see table), rt. [b]Yields determined by ^{1}H-NMR using 1,3,5-trimethoxybenzene as internal standard.

Table S11. Preliminary optimization experiments with **1a** on a 0.5 mmol scale

Entry	Variation of conditions[a] (equiv)	Yield[b] **4aa** (%)
1	Bu_4NOH (1.5), AgOAc (2.0), $Pd(OAc)_2$ (0.1), **3a** (20), 120 min, CH_3CN/AcOH (3 mL/0.6 mL)	61%
2	Bu_4NOH (1.5), AgOAc (2.0), $Pd(OAc)_2$ (0.1), **3a** (5), 45 min, CH_3CN/AcOH (3 mL/0.6 mL)	57%
3	Bu_4NOH (1.5), AgOAc (2.0), $Pd(OAc)_2$ (0.1), **3a** (5), 45 min, CH_3CN/AcOH/H_2O (1 mL/1 mL/1 mL)	55%
4	Bu_4NOH (1.5), AgOAc (2.0), $Pd(OAc)_2$ (0.1), **3a** (5), 45 min, AcOH (3 mL)	72%
5	Bu_4NOH (1.5), AgOAc (2.0), $Pd(OAc)_2$ (0.1), 3a (5), 45 min, AcOH (3 mL), reaction at 60°C	53%
6	Bu_4NOH (1.5), AgOAc (2.0), $Pd(OAc)_2$ (0.1), PPh_3 (0.1), **3a** (5), 45 min, AcOH (3 mL)	75%
7	Bu_4NOH (1.5), H_2O_2 (2.0) instead of AgOAc, $Pd(OAc)_2$ (0.1), **3a** (5), 45 min, AcOH (3 mL)	83%

[a]Reaction conditions: Tetrabutylammonium hydroxide (0.75 mmol) and **1a** (0.5 mmol) in CH_3CN (1.4 mL), 5 min; then slow addition of **2a** (over 45-120 min, see table) to **3a** (2.5-10 mmol), AgOAc (1.0 mmol), $Pd(OAc)_2$ (0.05 mmol), solvent (see table), rt (if not otherwise mentioned in table). [b]Yields determined by ^{1}H-NMR using 1,3,5-trimethoxybenzene as internal standard.

Table S12. Qualitative screening for suitable oxidants

Entry	Variation of conditions[a] (equiv)	Qualitative TLC analysis referenced to **4aa**
1	Bu_4NOH (1.5), MnO_2 (2.0), $Pd(OAc)_2$ (0.1), **3a** (5), 30 min, AcOH (0.5 mL)	**4aa** as major product, few side products
2	Bu_4NOH (1.5), $KMnO_4$ (2.0), $Pd(OAc)_2$ (0.1), **3a** (5), 30 min, AcOH (0.5 mL)	traces of **4aa**, many side products
3	Bu_4NOH (1.5), $Cu(OTf)_2$ (2.0), $Pd(OAc)_2$ (0.1), **3a** (5), 30 min, AcOH (0.5 mL)	traces of **4aa**, many side products
4	Bu_4NOH (1.5), H_2O_2 (2.0), $Pd(OAc)_2$ (0.1), **3a** (5), 30 min, AcOH (0.5 mL)	**4aa** as major product, no side products

[a]Reaction conditions: Tetrabutylammonium hydroxide (188 µmol) and **1a** (125 µmol) in CH_3CN (0.5 mL) 5 min; then slow addition of **2a** (over 30min) to **3a** (0.625 mmol), oxidant (0.25 mmol, see table), $Pd(OAc)_2$ (12.5 µmol), AcOH (0.5 mL), rt.

1.2 General procedures

General procedure for method A (GP A)

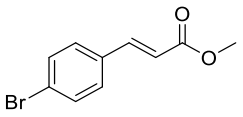
Tetrabutylammonium hydroxide solution (1.5 M in H_2O, 0.75 mmol, 0.5 mL) is added to a solution of *tert*-butyl phenylazocarboxylate (0.5 mmol) in CH_3CN (1.4 mL) and stirred for 5 min. This mixture is added to a suspension of palladium(II) acetate (50.0 µmol), silver(I) acetate (1.0 mmol), triphenylphosphane (50.0 µmol) and the acrylate or acrylamide (2.5 mmol) in acetic acid (3.0 mL) over 45 min with a syringe pump. The reaction mixture is stirred for additional 10 min and CH_2Cl_2 (25 mL) is added. The organic phase is washed with water (5 mL), a saturated aqueous solution of sodium chloride (5 mL) and dried over sodium sulfate. The solvent is removed under reduced pressure and the residue is subjected to column chromatography on silica gel.

General procedure for method B (GP B)

Tetrabutylammonium hydroxide solution (1.5 M in H_2O, 750 µmol, 0.5 mL) is added to a solution of *tert*-butyl phenylazocarboxylate (0.5 mmol) in CH_3CN (1.4 mL) and stirred for 5 min. This mixture is added to a suspension of palladium(II) acetate (50.0 µmol), hydrogen peroxide solution (1.0 mmol, 30% in H_2O) and the acrylate, acrylamide or styrene (2.5 mmol) in acetic acid (3.0 mL) over 45 min with a syringe pump. The reaction mixture is stirred for additional 10 min and CH_2Cl_2 (25 mL) is added. The organic phase is washed with water (5 mL), a saturated aqueous solution of sodium chloride (5 mL) and dried over sodium sulfate. The solvent is removed under reduced pressure and the residue is subjected to column chromatography on silica gel.

1.3 Synthesis of cinnamic esters and amides

1.3.1 Methyl 4-bromocinnamate (**4aa**)



$C_{10}H_9BrO_2$
241.08 g/mol

Compound **4aa** is prepared from *tert*-butyl 2-(4-bromophenyl)azocarboxylate (**1a**) (500 µmol, 142 mg) and methyl acrylate (**3a**) (2.50 mmol, 223 µL) according to general procedure GP A and GP B. The crude product is subjected to column chromatography (silica gel, hexane / ethyl acetate = 9:1) to give the title compound **4aa** (375 µmol, 90.4 mg, 75%, GP A), (402 µmol, 96.9 mg, 80%, GP B) as a white solid.

In a modified version tetrabutylammonium hydroxide solution (1.5 M in H_2O, 263 µmol, 175 µL) is added to a solution of *tert*-butyl 2-(4-bromophenyl)azocarboxylate (**1a**) (175 µmol, 50.0 mg) in CH_3CN (0.8 mL) and stirred for 5 min. This mixture is added to a solution of palladium(II) acetate (17.5 µmol, 4.00 mg), methyl acrylate **3a** (875 µmol, 78.0 µL) and hydrogen peroxide solution (350 µmol, 30% in H_2O) in acetic acid (1.4 mL). The reaction mixture is stirred for one hour and concentrated under reduced pressure. The yield of **4aa** (112 µmol, 64%) is determined with an internal standard of 1,3,5-trimethoxybenzene

Experiment on 3 mmol scale:

Compound **4aa** is prepared from *tert*-butyl 2-(4-bromophenyl)azocarboxylate (**1a**) (3.00 µmol, 855 mg) and methyl acrylate (**3a**) (15.0 mmol, 1.35 mL) according to general procedure GP B. The crude product is subjected to column chromatography (silica gel, hexane / ethyl acetate = 10:1) to give the title compound **4aa** (2.58 mmol, 622 mg, 86%) as a white solid.

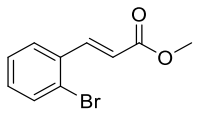
***R*f** 0.4 (hexane / ethyl acetate = 9:1) [UV].

^{1}H-NMR (600 MHz, $CDCl_3$): δ (ppm) = 3.81 (3 H), 6.42 (d, J = 16.0 Hz, 1 H), 7.38 (d, J = 8.4 Hz, 2 H), 7.52 (d, J = 8.4 Hz, 2 H), 7.62 (d, J = 16.0 Hz, 1 H).

^{13}C-NMR (91 MHz, $CDCl_3$): δ (ppm) = 51.7 (CH_3), 118.5 (CH), 124.5 (C_q), 129.4 (2 × CH), 132.1 (2 × CH), 133.3 (C_q), 143.4 (CH), 167.1 (C_q).

Analytical data is in agreement with those reported in literature[2].

1.3.2 Methyl 2-bromocinnamate (**4ba**)



$C_{10}H_9BrO_2$
241.08 g/mol

Compound **4ba** is prepared from *tert*-butyl 2-(2-bromophenyl)azocarboxylate (**1b**) (500 µmol, 142 mg) and methyl acrylate (**3a**) (2.50 mmol, 223 µL) according to general procedure GP B. The crude product is subjected to column chromatography (silica gel, hexane / ethyl acetate = 10:1) to give the title compound **4ba** (299 µmol, 72.0 mg, 60%) as a white solid.

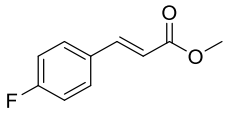
***R*f** 0.5 (hexane / ethyl acetate = 9:1) [UV].

^{1}H-NMR (600 MHz, $CDCl_3$): δ (ppm) = 3.82 (3 H), 6.39 (d, *J* = 16.0 Hz, 1 H), 7.20-7.25 (m, 1 H), 7.30-7.35 (m, 1 H), 7.61 (dt, *J* = 1.4 Hz, *J* = 8.1 Hz, 2 H), 8.06 (d, *J* = 16.0 Hz, 1 H).

^{13}C-NMR (91 MHz, $CDCl_3$): δ (ppm) = 51.8 (CH_3), 120.7 (CH), 125.3 (C_q), 127.7 (CH), 127.7 (CH), 131.2 (CH), 133.4 (CH), 134.5 (C_q), 143.1 (CH), 166.7 (C_q).

Analytical data is in agreement with those reported in literature[3].

1.3.3 Methyl 4-fluorocinnamate (**4ca**)



$C_{10}H_9FO_2$
180.18 g/mol

Compound **4ca** is prepared from *tert*-butyl 2-(4-fluorophenyl)azocarboxylate (**1c**) (500 µmol, 112 mg) and methyl acrylate (**3a**) (2.50 mmol, 223 µL) according to general procedure GP A and GP B. The crude product is subjected to column chromatography (silica gel, hexane / ethyl acetate = 9:1) to give the title compound **4ca** (381 µmol, 68.7 mg, 76%, GP A), (365 µmol, 65.8 mg, 73%, GP B) as a white solid.

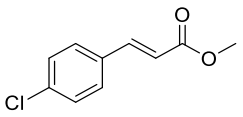
***R*f** 0.4 (hexane / ethyl acetate = 9:1) [UV].

^{1}H-NMR (600 MHz, $CDCl_3$): δ (ppm) = 3.81 (3 H), 6.37 (d, J = 16.0 Hz, 1 H), 7.10 (t, J = 8.6 Hz, 2 H), 7.51 (dd, J_{HF} = 5.4 Hz, J = 8.6 Hz, 2 H), 7.66 (d, J = 16.0 Hz, 1 H).

^{13}C-NMR (91 MHz, $CDCl_3$): δ (ppm) = 51.7 (CH_3), 116.0 (d, J_{CF} = 22.0 Hz, 2 × CH), 117.6 (d, J_{CF} = 2.4 Hz, CH), 129.9 (d, J_{CF} = 8.5 Hz, 2 × CH), 130.7 (d, J_{CF} = 3.4 Hz, C_q), 143.5 (d, J_{CF} = 0.8 Hz, CH), 163.9 (d, J_{CF} = 251.4 Hz, C_q), 167.3 (C_q).

Analytical data is in agreement with those reported in literature[4]

1.3.4 Methyl 4-chlorocinnamate (**4da**)



$C_{10}H_9ClO_2$
196.63 g/mol

Compound **4da** is prepared from *tert*-butyl 2-(4-chlorophenyl)azocarboxylate (**1d**) (500 µmol, 120 mg) and methyl acrylate (**3a**) (2.50 mmol, 223 µL) according to general procedure GP A and GP B. The crude product is subjected to column chromatography (silica gel, hexane / ethyl acetate = 10:1) to give the title compound **4da** (375 µmol, 73.7 mg, 75%, GP A), (390 µmol, 76.7 mg, 78%, GP B) as a white solid.

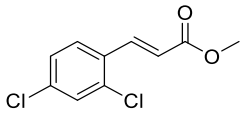
***R*f** 0.4 (hexane / ethyl acetate = 9:1) [UV].

^{1}H-NMR (600 MHz, $CDCl_3$): δ (ppm) = 3.81 (3 H), 6.41 (d, *J* = 16.0 Hz, 1 H), 7.36 (d, *J* = 8.4 Hz, 2 H), 7.45 (d, *J* = 8.4 Hz, 2 H), 7.64 (d, *J* = 16.0 Hz, 1 H).

^{13}C-NMR (91 MHz, $CDCl_3$): δ (ppm) = 52.8 (CH_3), 118.4 (CH), 129.2 (2 × CH), 129.2 (2 × CH), 132.9 (C_q), 136.2 (C_q), 143.4 (CH), 167.1 (C_q).

Analytical data is in agreement with those reported in literature[4]

1.3.5 Methyl 2,4-dichlorocinnamate (**4ea**)



$C_{10}H_8Cl_2O_2$
231.07 g/mol

Compound **4ea** is prepared from *tert*-butyl 2-(2,4-dichlorophenyl)azocarboxylate (**1e**) (500 µmol, 138 mg) and methyl acrylate (**3a**) (2.50 mmol, 223 µL) according to general procedure GP B. The crude product is subjected to column chromatography (silica gel, hexane / ethyl acetate = 12:1) to give the title compound **4ea** (304 µmol, 72.2 mg, 61%) as a white solid.

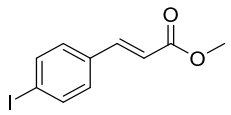
***R*f** 0.5 (hexane / ethyl acetate = 9:1) [UV].

^{1}H-NMR (600 MHz, $CDCl_3$): δ (ppm) = 3.82 (3 H), 6.39 (d, *J* = 16.0 Hz, 1 H), 7.20-7.25 (m, 1 H), 7.30-7.35 (m, 1 H), 7.61 (dt, *J* = 1.4 Hz, *J* = 8.1 Hz, 2 H), 8.06 (d, *J* = 16.0 Hz, 1 H).

^{13}C-NMR (91 MHz, $CDCl_3$): δ (ppm) = 51.9 (CH_3), 120.9 (CH), 127.6 (CH), 128.3 (CH), 130.0 (CH), 131.3 (C_q), 135.5 (C_q), 136.4 (C_q), 139.4 (CH), 166.6 (C_q).

Analytical data is in agreement with those reported in literature[5]

1.3.6 Methyl 4-iodocinnamate (**4fa**)



$C_{10}H_9IO_2$
288.08 g/mol

Compound **4fa** is prepared from *tert*-butyl 2-(4-iodophenyl)azocarboxylate (**1f**) (500 µmol, 166 mg) and methyl acrylate (**3a**) (2.50 mmol, 223 µL) according to general procedure GP A and GP B. The crude product is subjected to column chromatography (silica gel, hexane / ethyl acetate = 9:1) to give the title compound **4fa** (239 µmol, 68.8 mg, 48%, GP A), (158 µmol, 45.5 mg, 32%, GP B) as a white solid.

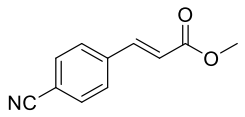
***R*f** 0.4 (hexane / ethyl acetate = 9:1) [UV].

^{1}H-NMR (600 MHz, $CDCl_3$): δ (ppm) = 3.81 (3 H), 6.43 (d, *J* = 16.0 Hz, 1 H), 7.24 (d, *J* = 8.4 Hz, 2 H), 7.60 (d, *J* = 16.0 Hz, 1 H), 7.72 (d, *J* = 8.4 Hz, 2 H).

^{13}C-NMR (91 MHz, $CDCl_3$): δ (ppm) = 51.7 (CH_3), 96.5 (C_q), 118.6 (CH), 129.5 (2 × CH), 133.9 (C_q), 138.1 (2 × CH), 143.6 (CH), 167.1 (C_q).

Analytical data is in agreement with those reported in literature[6]

1.3.7 Methyl 4-cyanocinnamate (**4ga**)



$C_{11}H_9NO_2$
187.28 g/mol

Compound **4ga** is prepared from *tert*-butyl 2-(4-cyanophenyl)azocarboxylate (**1g**) (500 µmol, 166 mg) and methyl acrylate (**3a**) (2.50 mmol, 223 µL) according to general procedure GP B. The crude product is subjected to column chromatography (silica gel, hexane / ethyl acetate = 5:1) to give the title compound **4ga** (278 µmol, 52.0 mg, 56%) as a white solid.

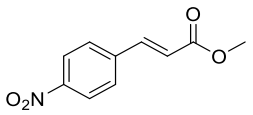
***R*f** 0.3 (hexane / ethyl acetate = 6:1) [UV].

^{1}H-NMR (600 MHz, $CDCl_3$): δ (ppm) = 3.83 (3 H), 6.52 (d, *J* = 16.0 Hz, 1 H), 7.61 (d, *J* = 8.3 Hz, 2 H), 7.67 (d, *J* = 16.0 Hz, 1 H), 7.68 (d, *J* = 8.3 Hz, 2 H).

^{13}C-NMR (91 MHz, $CDCl_3$): δ (ppm) = 52.0 (CH_3), 113.4 (C_q), 118.3 (C_q), 121.4 (CH), 128.4 (2 × CH), 132.6 (2 × CH), 138.6 (C_q), 142.4 (CH), 166.5 (C_q).

Analytical data is in agreement with those reported in literature[7]

1.3.8 Methyl 4-nitrocinnamate (**4ha**)



$C_{10}H_9NO_4$
207.19 g/mol

Compound **4ha** is prepared from *tert*-butyl 2-(4-nitrophenyl)azocarboxylate (**1h**) (500 µmol, 126 mg) and methyl acrylate (**3a**) (2.50 mmol, 223 µL) according to general procedure GP B. The crude product is subjected to column chromatography (silica gel, hexane / ethyl acetate = 4:1) to give the title compound **4ha** (243 µmol, 50.4 mg, 49%) as a white solid.

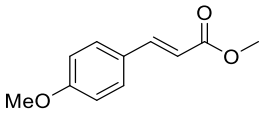
***R*f** 0.1 (hexane / ethyl acetate = 3:1) [UV].

^{1}H-NMR (600 MHz, $CDCl_3$): δ (ppm) = 3.84 (3 H), 6.56 (d, *J* = 16.1 Hz, 1 H), 7.67 (d, *J* = 8.6 Hz, 2 H), 7.72 (d, *J* = 16.1 Hz, 1 H), 8.25 (d, *J* = 8.6 Hz, 2 H).

^{13}C-NMR (91 MHz, $CDCl_3$): δ (ppm) = 52.0 (CH_3), 122.1 (CH), 124.2 (2 × CH), 128.6 (2 × CH), 140.5 (C_q), 141.9 (CH), 148.5 (C_q), 166.4 (C_q).

Analytical data is in agreement with those reported in literature[3].

1.3.9 Methyl 4-methoxycinnamate (**4ia**)



$C_{11}H_{12}O_3$
192.21 g/mol

Compound **4ia** is prepared from *tert*-butyl 2-(4-methoxyphenyl)azocarboxylate (**1i**) (500 µmol, 118 mg) and methyl acrylate (**3a**) (2.50 mmol, 223 µL) according to general procedure GP B. The crude product is subjected to column chromatography (silica gel, hexane / ethyl acetate = 12:1) to give the title compound **4ia** (278 µmol, 53.4 mg, 56%) as a white solid.

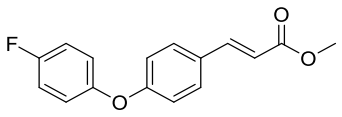
***R*f** 0.x (hexane / ethyl acetate = 9:1) [UV].

^{1}H-NMR (600 MHz, $CDCl_3$): δ (ppm) = 3.79 (3 H), 3.84 (3 H), 6.31 (d, *J* = 16.0 Hz, 1 H), 6.91 (d, *J* = 8.6 Hz, 2 H), 7.47 (d, *J* = 8.6 Hz, 2 H), 7.65 (d, *J* = 16.0 Hz, 1 H).

^{13}C-NMR (91 MHz, $CDCl_3$): δ (ppm) = 51.5 (CH_3), 55.4 (CH_3), 114.3 (2 × CH), 115.3 (CH), 127.2 (C_q), 129.7 (2 × CH), 144.5 (CH), 161.4 (C_q), 167.7 (C_q).

Analytical data is in agreement with those reported in literature[4]

1.3.10 Methyl 4-(4-fluorophenoxy)cinnamate (**4ja**)



$C_{16}H_{13}FO_3$
272.28 g/mol

Compound **4ja** is prepared from *tert*-butyl 2-(4-fluorophenoxyphenyl)azocarboxylate (**1j**) (500 µmol, 158 mg) and methyl acrylate (**3a**) (2.50 mmol, 223 µL) according to general procedure GP B. The crude product is subjected to column chromatography (silica gel, hexane / ethyl acetate = 10:1) to give the title compound **4ja** (439 µmol, 119 mg, 88%) as a white solid.

***R*f** 0.5 (hexane / ethyl acetate = 9:1) [UV].

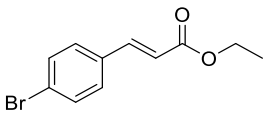
^{1}H-NMR (600 MHz, $CDCl_3$): δ (ppm) = 3.80 (3 H), 6.34 (d, J = 16.0 Hz, 1 H), 6.94 (d, J = 8.6 Hz, 2 H), 7.00-7.08 (m, 4 H), 7.48 (d, J = 8.6 Hz, 2 H), 7.66 (d, J = 16.0 Hz, 1 H).

^{13}C-NMR (91 MHz, $CDCl_3$): δ (ppm) = 51.6 (CH_3), 116.5 (d, J_{CF} = 23.0 Hz, 2 × CH), 116.5 (CH), 117.9 (2 × CH), 121.3 (d, J_{CF} = 8.3 Hz, 2 × CH), 129.2 (C_q), 129.8 (2 × CH), 144.0 (CH), 151.8 (d, J_{CF} = 2.7 Hz, C_q), 159.3 (d, J_{CF} = 242.8 Hz, C_q), 159.8 (d, J_{CF} = 0.7 Hz, C_q), 167.5 (C_q).

MS (EI) *m/z* (%): 272.1 [M^+].

HRMS (ESI) calcd. for $C_{16}H_{13}FO_3$ [$M^+ + Na^+$]: 295.0741, found: 295.0743.

1.3.11 Ethyl 4-bromocinnamate (**4ab**)



$C_{11}H_{11}BrO_2$
255.11 g/mol

Compound **4ab** is prepared from *tert*-butyl 2-(4-bromophenyl)azocarboxylate (**1a**) (500 µmol, 138 mg) and ethyl acrylate (**3b**) (2.50 mmol, 270 µL) according to general procedure GP A. The crude product is subjected to column chromatography (silica gel, hexane / ethyl acetate = 20:1) to give the title compound **4ab** (388 µmol, 99.1 mg, 78%) as a white solid.

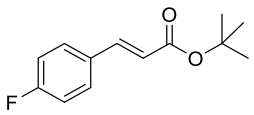
***R*f** 0.3 (hexane / ethyl acetate = 20:1) [UV].

^{1}H-NMR (600 MHz, $CDCl_3$): δ (ppm) = 1.34 (t, *J* = 7.1 Hz, 3 H), 4.27 (q, *J* = 7.1 Hz, 2 H), 6.42 (d, *J* = 16.0 Hz, 1 H), 7.38 (d, *J* = 8.3 Hz, 2 H), 7.52 (d, *J* = 8.3 Hz, 2 H), 7.61 (d, *J* = 16.0 Hz, 1 H).

^{13}C-NMR (91 MHz, $CDCl_3$): δ (ppm) = 14.3 (CH_3), 60.6 (CH_2), 119.0 (CH), 124.4 (C_q), 129.4 (2 × CH), 132.1 (2 × CH), 133.4 (C_q), 143.2 (CH), 166.7 (C_q).

Analytical data is in agreement with those reported in literature[8]

1.3.12 *tert*-Butyl 4-fluorocinnamate (**4cc**)



$C_{13}H_{15}FO_2$
222.26 g/mol

Compound **4cc** is prepared from *tert*-butyl 2-(4-fluorophenyl)azocarboxylate (**1c**) (500 µmol, 112 mg) and *tert*-butyl acrylate (**3c**) (2.50 mmol, 366 µL) according to general procedure GP A. The crude product is subjected to column chromatography (silica gel, hexane / ethyl acetate = 10:1) to give the title compound **4cc** (386 µmol, 85.7 mg, 77%) as a white solid.

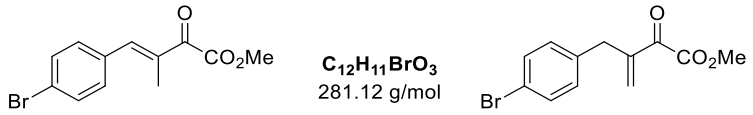
***R*f** 0.6 (hexane / ethyl acetate = 9:1) [UV].

^{1}H-NMR (600 MHz, $CDCl_3$): δ (ppm) = 1.53 (s, 9 H), 6.29 (dd, J_{HF} = 0.5 Hz, J = 16.0 Hz, 1 H), 7.06 (d, J = 8.6 Hz, 2 H), 7.49 (dd, J_{HF} = 5.4 Hz, J = 8.6 Hz, 2 H), 7.54 (d, J = 16.0 Hz, 1 H).

^{13}C-NMR (91 MHz, $CDCl_3$): δ (ppm) = 28.2 (3 × CH_3), 80.6 (C_q), 115.9 (d, J_{CF} = 21.9 Hz, 2 × CH), 120.0 (d, J_{CF} = 2.4 Hz, CH), 129.7 (d, J_{CF} = 8.4 Hz, 2 × CH), 130.9 (d, J_{CF} = 3.4 Hz, C_q), 142.2 (d, J_{CF} = 0.7 Hz, CH), 163.7 (d, J_{CF} = 250.7 Hz, C_q), 166.1 (C_q).

Analytical data is in agreement with those reported in literature[9]

1.3.13 Methyl (*E*)-3-(4-bromophenyl)-3-methylacrylate (**4ad**) and methyl 2-(4-bromobenzyl)acrylate (**4ad‘**)



Compounds **4ad** and **4ad’** are prepared from *tert*-butyl 2-(4-bromophenyl)azocarboxylate (**1a**) (500 µmol, 142 mg) and methyl methacrylate (**3d**) (2.50 mmol, 270 µL) according to general procedure GP A and GP B. The yield of the isomers **4ad** (13%) and **4ad’** (42%) from GP A is determined with an internal standard of 1,3,5-trimethoxybenzene. The crude product from GP B is subjected to column chromatography (silica gel, hexane / ethyl acetate = 10:1) to give the title compounds **4ad** (75.6 µmol, 21.3 mg, 15%, GP B) and **4ad’** (248 µmol, 68.8 mg, 50%, GP B) as colorless oils.

Methyl (*E*)-3-(4-bromophenyl)-3-methylacrylate (4ad)

***R*f** 0.6 (hexane / ethyl acetate = 9:1) [UV].

^{1}H-NMR (600 MHz, $CDCl_3$): δ (ppm) = 2.09 (d, *J* = 1.5 Hz, 3 H), 3.82 (s, 3 H), 7.26 (d, *J* = 8.2 Hz, 2 H), 7.52 (d, *J* = 8.2 Hz, 2 H), 7.61 (s, 1 H).

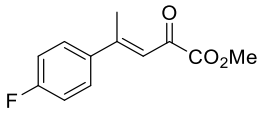
Methyl 2-(4-bromobenzyl)acrylate (4ad‘)

***R*f** 0.6 (hexane / ethyl acetate = 9:1) [UV].

^{1}H-NMR (600 MHz, $CDCl_3$): δ (ppm) = 3.58 (bs, 2 H), 3.73 (s, 3 H), 5.48 (q, *J* = 1.4 Hz, 1 H), 6.24 (mc, 1 H), 7.08 (d, *J* = 8.5 Hz, 2 H), 7.41 (d, *J* = 8.5 Hz, 2 H).

Analytical data is in agreement with those reported in literature[10]

1.3.14 Methyl (*E*)-3-(4-fluorophenyl)-3-methylacrylate (**4ce**)



$C_{12}H_{11}FO_3$
222.22 g/mol

Compound **4ce** is prepared from *tert*-butyl 2-(4-fluorophenyl)azocarboxylate (**1c**) (500 µmol, 112 mg) and methyl crotonate (**3e**) (2.50 mmol, 270 µL) according to general procedure GP B. The crude product is subjected to column chromatography (silica gel, hexane / ethyl acetate = 14:1) to give the title compound **4ce** (318 µmol, 61.8 mg, 64%) as a colorless oil.

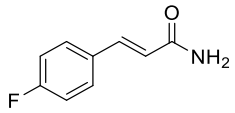
***R*f** 0.6 (hexane / ethyl acetate = 9:1) [UV].

^{1}H-NMR (360 MHz, $CDCl_3$): δ (ppm) = 2.56 (d, J = 1.3 Hz, 3 H), 3.75 (s, 3 H), 6.09 (q, J = 1.3 Hz, 1 H), 7.06 (t, J = 8.6 Hz, 2 H), 7.45 (dd, J_{HF} = 5.4 Hz, J = 8.6 Hz, 2 H).

^{13}C-NMR (91 MHz, $CDCl_3$): δ (ppm) = 18.0 (CH_3), 51.1 (CH_3), 115.5 (d, J_{CF} = 21.5 Hz, 2 × CH), 116.6 (d, J_{CF} = 1.3 Hz, C_q), 128.1 (d, J_{CF} = 8.3 Hz, 2 × CH), 138.2 (d, J_{CF} = 3.4 Hz, C_q), 154.6 (CH), 163.2 (d, J_{CF} = 249.1 Hz, C_q), 167.1 (C_q).

Analytical data is in agreement with those reported in literature[11]

1.3.15 4-Fluorocinnamide (**4cf**)



C_9H_8FNO
165.17 g/mol

Compound **4cf** is prepared from *tert*-butyl 2-(4-fluorophenyl)azocarboxylate (**1c**) (500 µmol, 112 mg) and acrylamide (**3f**) (2.50 mmol, 178 mg) according to general procedure GP A and GP B. The crude product is subjected to column chromatography (silica gel, chloroform / methanol = 20:1) to give the title compound **4cf** (435 µmol, 71.8 mg, 87%, GP A), (416 µmol, 68.7 mg, 83%, GP B) as a white solid.

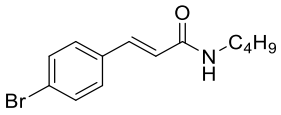
***R*f** 0.1 (chloroform / methanol = 20:1) [UV].

^{1}H-NMR (600 MHz, CD_3OD): δ (ppm) = 6.58 (d, J = 15.8 Hz, 1 H), 7.13 (d, J = 8.6 Hz, 2 H), 7.53 (d, J = 15.8 Hz, 1 H), 7.61 (dd, J_{HF} = 5.5 Hz, J = 8.6 Hz, 2 H).

^{13}C-NMR (91 MHz, CD_3OD): δ (ppm) = 116.0 (d, J_{CF} = 21.9 Hz, 2 × CH), 119.3 (CH), 129.6 (d, J_{CF} = 8.5 Hz, 2 × CH), 130.7 (d, J_{CF} = 3.4 Hz, C_q), 141.0 (CH), 163.6 (d, J_{CF} = 250.6 Hz, C_q), 168.5 (C_q).

Analytical data is in agreement with those reported in literature[12]

1.3.16 *N*-Butyl 4-bromocinnamide (**4ag**)



$C_{13}H_{16}BrNO$
282.18 g/mol

Compound **4ag** is prepared from *tert*-butyl 2-(4-bromophenyl)azocarboxylate (**1a**) (500 µmol, 142 mg) and *n*-butylacrylamide (**3g**) (2.50 mmol, 318 mg) according to general procedure GP B. The crude product is subjected to column chromatography (silica gel, hexane / ethyl acetate = 3:1) to give the title compound **4ag** (460 µmol, 85.7 mg, 92%) as a white solid.

***R*f** 0.2 (hexane / ethyl acetate = 3:1) [UV].

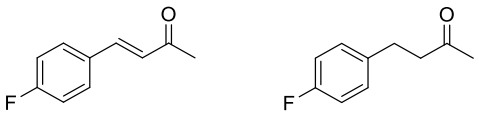
^{1}H-NMR (600 MHz, $CDCl_3$): δ (ppm) = 0.94 (t, *J* = 7.4 Hz, 3 H), 1.39 (qd, *J* = 7.4 Hz, *J* = 14.7 Hz, 2 H), 1.59 (mc, 2 H), 3.45-3.42 (m, 2 H), 5.87 (bs, NH), 6.40 (d, *J* = 16.0 Hz, 1 H), 7.35 (d, *J* = 8.4 Hz, 2 H), 7.48 (d, *J* = 8.4 Hz, 2 H), 7.56 (d, *J* = 16.0 Hz, 1 H).

^{13}C-NMR (91 MHz, $CDCl_3$): δ (ppm) = 13.7 (CH_3), 20.1 (CH_2), 31.7 (CH_2), 39.6 (CH_2), 121.4 (CH), 123.7 (C_q), 129.1 (2 × CH), 132.0 (2 × CH), 133.8 (C_q), 139.6 (CH), 165.6 (C_q).

MS (EI) *m/z* (%): 282.0 [MH^+].

HRMS (ESI) calcd. for $C_{13}H_{16}BrNO$ [$M^+ + Na^+$]: 304.0307, found: 304.0303.

1.3.17 (*E*)-4-(4-Fluorophenyl)but-3-en-2-one (**4ah**) and 4-(4-fluorophenyl)butan-2-one (**4ah'**)



$C_{10}H_9FO$
164.18 g/mol

$C_{10}H_{11}FO$
166.20 g/mol

Compounds **4ah** and **4ah'** are prepared from *tert*-butyl 2-(4-fluorophenyl)azocarboxylate (**1c**) (500 µmol, 112 mg) and methyl vinyl ketone (**3h**) (2.50 mmol, 211 µL) according to general procedure GP B. The crude product is subjected to column chromatography (silica gel, hexane / ethyl acetate = 6:1) to give the title compounds **4ah** (171 µmol, 28.1 mg, 34%) and **4ah'** (239 µmol, 39.7 mg, 48%) as colorless oils.

In a modified version tetrabutylammonium hydroxide solution (1.5 M in H_2O, 263 µmol, 175 µmol) is added to a solution of *tert*-butyl 2-(4-fluorophenyl)azocarboxylate (**1c**) (175 µmol, 39.2 mg) in CH_3CN (0.8 mL) and stirred for 5 min. This mixture is added to a solution of palladium(II) acetate (17.5 µmol, 4.00 mg) and methyl vinyl ketone (875 µmol, 94.0 µL) in formic acid (1.4 mL) over 45 min with a syringe pump. The reaction mixture is stirred for additional 10 min and concentrated under reduced pressure. The yield of **4ah'** (136 µmol, 22.4 mg, 78%) is determined with an internal standard of 1,3,5-trimethoxybenzene.

(*E*)-4-(4-Fluorophenyl)but-3-en-2-one (4ah)

***R*f** 0.4 (hexane / ethyl acetate = 6:1) [UV].

^{1}H-NMR (360 MHz, $CDCl_3$): δ (ppm) = 2.38 (s, 3 H), 6.65 (d, J = 16.3 Hz, 1 H), 7.10 (t, J = 8.6 Hz, 2 H), 7.48 (d, J = 16.3 Hz, 1 H), 7.54 (dd, J_{HF} = 5.4 Hz, J = 8.6 Hz, 2 H).

^{13}C-NMR (91 MHz, $CDCl_3$): δ (ppm) = 27.6 (CH_3), 116.2 (d, J_{CF} = 22.0 Hz, 2 × CH), 126.9 (d, J_{CF} = 2.4 Hz, CH), 130.1 (d, J_{CF} = 8.6 Hz, 2 × CH), 130.7 115.2 (d, J_{CF} = 3.5 Hz, C_q), 142.0 (CH), 164.0 (d, J_{CF} = 251.8 Hz, C_q), 198.0 (C_q).

4-(4-Fluorophenyl)butan-2-one (4ah')

***R*f** 0.4 (hexane / ethyl acetate = 6:1) [UV].

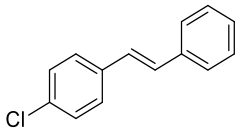
^{1}H-NMR (600 MHz, $CDCl_3$): δ (ppm) = 2.13 (s, 3 H), 2.74 (t, J = 7.6 Hz, 2 H), 2.87 (t, J = 7.6 Hz, 2 H), 6.96 (t, J = 8.7 Hz, 2 H), 7.13 (dd, J_{HF} = 5.4 Hz, J = 8.7 Hz, 2 H).

^{13}C-NMR (91 MHz, $CDCl_3$): δ (ppm) = 28.9 (CH_2), 30.1 (CH_3), 45.2 (CH_2), 115.2 (d, J_{CF} = 21.2 Hz, 2 × CH), 129.7 (d, J_{CF} = 7.8 Hz, 2 × CH), 136.6 (d, J_{CF} = 3.2 Hz, C_q), 161.4 (d, J_{CF} = 243.9 Hz, C_q), 207.6 (C_q).

Analytical data is in agreement with those reported in literature[13]

1.4 Synthesis of stilbenes

1.4.1 (*E*)-4-Chlorostilbene (**4di**)



$C_{14}H_{11}Cl$
214.69 g/mol

Compound **4di** is prepared from *tert*-butyl 2-(4-chlorophenyl)azocarboxylate (**1d**) (500 µmol, 120 mg) and styrene (**3i**) (2.50 mmol, 280 µL) according to general procedure GP B. The crude product is subjected to column chromatography (silica gel, hexane / ethyl acetate = 9:1) to give the title compound **4di** (352 µmol, 75.7 mg, 71%) as a pale yellow solid.

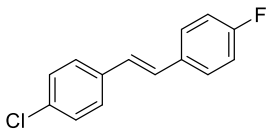
***R*f** 0.8 (hexane / ethyl acetate = 9:1) [UV].

^{1}H-NMR (600 MHz, $CDCl_3$): δ (ppm) = 7.05 (d, *J* = 16.3 Hz, 1 H), 7.08 (d, *J* = 16.3 Hz, 1 H), 7.26-7.29 (m, 1 H), 7.32 (d, *J* = 8.5 Hz, 2 H), 7.36 (t, *J* = 7.7 Hz, 2 H), 7.44 (d, *J* = 8.5 Hz, 2 H), 7.50-7.51 (m, 2 H).

^{13}C-NMR (91 MHz, $CDCl_3$): δ (ppm) = 126.5 (2 × CH), 127.4 (CH), 127.6 (2 × CH), 127.9 (CH), 128.7 (2 × CH), 128.7 (2 × CH), 129.3 (CH), 133.2 (C_q), 135.8 (C_q), 137.0 (C_q).

Analytical data is in agreement with those reported in literature[14]

1.4.2 (*E*)-4-Chloro-4‘-fluorostilbene (**4dj**)



$C_{14}H_{10}ClF$
232.68 g/mol

Compound **xx** is prepared from *tert*-butyl 2-(4-chlorophenyl)azocarboxylate (**1d**) (500 µmol, 120 mg) and 4-fluorostyrene (**3j**) (2.50 mmol, 298 µL) according to general procedure GP B. The crude product is subjected to column chromatography (silica gel, hexane / ethyl acetate = 10:1) to give the title compound **4dj** (350 µmol, 81.4 mg, 70%) as a pale yellow solid.

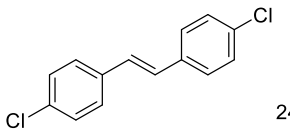
***R*f** 0.7 (hexane / ethyl acetate = 9:1) [UV].

^{1}H-NMR (600 MHz, $CDCl_3$): δ (ppm) = 6.95 (d, J = 16.3 Hz, 1 H), 7.01-7.07 (m, 3 H), 7.32 (d, J = 8.5 Hz, 2 H), 7.42 (d, J = 8.5 Hz, 2 H), 7.46 (dd, J_{HF} = 5.4 Hz, J = 8.5 Hz, 2 H).

^{13}C-NMR (151 MHz, $CDCl_3$): δ (ppm) = 115.7 (d, J_{CF} = 21.8 Hz, 2 × CH), 127.2 (d, J_{CF} = 2.5 Hz, CH), 127.5 (2 × CH), 128.1 (d, J_{CF} = 7.9 Hz, 2 × CH), 128.1 (C_q), 128.9 (2 × CH), 133.2 (d, J_{CF} = 3.4 Hz, C_q), 133.2 (C_q), 135.7 (CH), 162.4 (d, J_{CF} = 247.7 Hz, C_q).

Analytical data is in agreement with those reported in literature[15]

1.4.3 (*E*)-4,4'-Dichlorostilbene (**4dk**)



$C_{14}H_{10}Cl_2$
249.13 g/mol

Compound **xx** is prepared from *tert*-butyl 2-(4-chlorophenyl)azocarboxylate (**1d**) (500 µmol, 120 mg) and 4-chlorostyrene (**3k**) (2.50 mmol, 320 µL) according to general procedure GP B. The crude product is subjected to column chromatography (silica gel, hexane / ethyl acetate = 14:1) to give the title compound **4dk** (399 µmol, 99.4 mg, 80%) as a pale yellow solid.

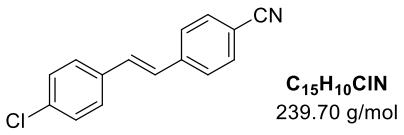
***R*f** 0.7 (hexane / ethyl acetate = 9:1) [UV].

^{1}H-NMR (600 MHz, $CDCl_3$): δ (ppm) = 7.01 (s, 2 H), 7.32 (d, *J* = 8.7 Hz, 4 H), 7.42 (d, *J* = 8.7 Hz, 4 H).

^{13}C-NMR (91 MHz, $CDCl_3$): δ (ppm) = 127.7 (4 × CH), 127.9 (2 × CH), 128.9 (4 × CH), 133.4 (2 × C_q), 135.5 (2 × CH).

Analytical data is in agreement with those reported in literature[16]

1.4.4 (*E*)-4-chloro-4’-cyanostilbene (**4dl**)



Compound **xx** is prepared from *tert*-butyl 2-(4-chlorophenyl)azocarboxylate (**1d**) (500 µmol, 120 mg) and 4-cyanostyrene (**3l**) (2.50 mmol, 322 µL) according to general procedure GP B. The crude product is subjected to column chromatography (silica gel, hexane / ethyl acetate = 14:1) to give the title compound **4dl** (305 µmol, 72.6 mg, 61%) as a pale yellow solid.

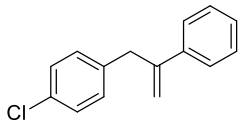
***R*f** 0.5 (hexane / ethyl acetate = 9:1) [UV].

^{1}H-NMR (600 MHz, $CDCl_3$): δ (ppm) = 7.06 (d, *J* = 16.3 Hz, 1 H), 7.16 (d, *J* = 16.3 Hz, 1 H), 7.36 (d, *J* = 8.5 Hz, 2 H), 7.46 (d, *J* = 8.3 Hz, 2 H), 7.58 (d, *J* = 8.3 Hz, 2 H), 7.64 (d, *J* = 8.5 Hz, 2 H).

^{13}C-NMR (91 MHz, $CDCl_3$): δ (ppm) = 110.9 (C_q), 118.9 (C_q), 126.9 (2 × CH), 127.3 (CH), 128.0 (2 × CH), 129.1 (2 × CH), 131.0 (CH), 132.5 (2 × CH), 134.3 (C_q), 134.7 (C_q), 141.5 (C_q).

Analytical data is in agreement with those reported in literature[17]

1.4.5 1-Chloro-4-(2-phenylallyl)benzene (**4dm'**)



$C_{15}H_{13}Cl$
228.72 g/mol

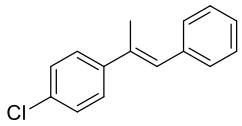
Compound **xx** is prepared from *tert*-butyl 2-(4-chlorophenyl)azocarboxylate (**1d**) (500 µmol, 120 mg) and α-methylstyrene **3m** (2.50 mmol, 325 µL) according to general procedure GP B. The crude product is subjected to column chromatography (silica gel, hexane / ethyl acetate = 25:1) to give the title compound **4dm'** (71.2 µmol, 16.3 mg, 14%) as a highly viscous brown oil.

***R*f** 0.5 (hexane / ethyl acetate = 9:1) [UV].

^{1}H-NMR (600 MHz, $CDCl_3$): δ (ppm) = 3.80 (bs, 2 H), 5.03 (q, *J* = 1.3 Hz, 1 H), 5.49 (td, *J* = 0.5 Hz, *J* = 1.3 Hz, 1 H), 7.15 (d, *J* = 8.8 Hz, 2 H), 7.21-7.33 (m, 5 H), 7.40 (d, *J* = 8.8 Hz, 2 H).

Analytical data is in agreement with those reported in literature[18]

1.4.6 (*E*)-1-Chloro-4-(1-phenylprop-1-en-2-yl)benzene (**4dn**)



$C_{15}H_{13}Cl$
228.72 g/mol

Compound **xx** is prepared from *tert*-butyl 2-(4-chlorophenyl)azocarboxylate (**1d**) (500 µmol, 120 mg) and β-methylstyrene (**3n**) (2.50 mmol, 325 µL) according to general procedure GP B. The crude product is subjected to column chromatography (silica gel, hexane / ethyl acetate = 10:1) to give the title compound **4dn** (280 µmol, 64.0 mg, 49%) as a colorless oil.

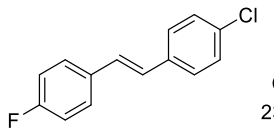
***R*f** 0.5 (hexane / ethyl acetate = 9:1) [UV].

^{1}H-NMR (600 MHz, $CDCl_3$): δ (ppm) = 2.26 (d, *J* = 1.4 Hz, 3 H), 6.82 (s, 1 H), 7.24-7.28 (m, 1 H), 7.34 (d, *J* = 8.8 Hz, 2 H), 7.35-7.40 (m, 4 H), 7.46 (d, *J* = 8.8 Hz, 2 H).

^{13}C-NMR (91 MHz, $CDCl_3$): δ (ppm) = 17.4 (CH_3), 126.7 (CH), 127.3 (2 × CH), 128.1 (CH), 128.2 (2 × CH), 128.4 (2 × CH), 129.1 (2 × CH), 132.9 (C_q), 136.2 (C_q), 138.0 (C_q), 142.4 (C_q).

Analytical data is in agreement with those reported in literature[19]

1.4.7 (*E*)-4-Fluoro-4‘-chlorostilbene (**4ck**)



$C_{14}H_{10}ClF$
232.68 g/mol

Compound **xx** is prepared from *tert*-butyl 2-(4-fluorophenyl)azocarboxylate (**1c**) (500 µmol, 112 mg) and 4-chlorostyrene (**3k**) (2.50 mmol, 320 µL) according to general procedure GP B. The crude product is subjected to column chromatography (silica gel, hexane / ethyl acetate = 9:1) to give the title compound **4ck** (367 µmol, 85.4 mg, 73%) as a pale yellow solid.

***R*f** 0.7 (hexane / ethyl acetate = 9:1) [UV].

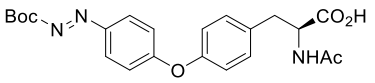
^{1}H-NMR (600 MHz, $CDCl_3$): δ (ppm) = 6.96 (d, J = 16.3 Hz, 1 H), 7.02-7.07 (m, 3 H), 7.32 (d, J = 8.5 Hz, 2 H), 7.42 (d, J = 8.5 Hz, 2 H), 7.46 (dd, J_{HF} = 5.4 Hz, J = 8.6 Hz, 2 H).

^{13}C-NMR (91 MHz, $CDCl_3$): δ (ppm) = 115.7 (d, J_{CF} = 21.7 Hz, 2 × CH), 127.2 (d, J_{CF} = 2.5 Hz, CH), 127.6 (2 × CH), 128.0 (d, J_{CF} = 8.0 Hz, 2 × CH), 128.1 (d, J_{CF} = 1.0 Hz, C_q), 128.9 (2 × CH), 133.2 (d, J_{CF} = 3.3 Hz, C_q), 133.2 (C_q), 135.7 (CH), 162.4 (d, J_{CF} = 247.7 Hz, C_q).

Analytical data is in agreement with those reported in literature[15]

1.5 Two-step functionalization of *N*-acetyl tyrosine:

1.5.1 (*S*,*E*)-2-Acetamido-3-(4-(4-((*tert*-butoxycarbonyl)diazenyl)phenoxy)-phenyl)propanoic acid (**6**)



$C_{22}H_{25}N_3O_6$
427.46 g/mol

A mixture of K_2CO_3 (5.00 mmol, 691 mg) and 18-crown-6 (5.00 mmol, 1.32 g) in dry DMF (15 mL) is stirred under argon for 15 min. *N*-Acetyl-*L*-tyrosine (**5**) (1.20 mmol, 268 mg) is added and stirred for 30 min. After the addition of *tert*-butyl 2-(4-nitrophenyl)azocarboxylate (**1h**) (1.00 mmol, 251 mg) the mixture is stirred for 3 h. Under cooling with ice, the reaction is quenched with water and an aqueous solution of hydrogen chloride (1 M, 15 mL) is added. The resulting mixture is extracted with ethyl acetate (2 × 25 mL). The combined organic phases are washed with a saturated aqueous sodium chloride solution and dried over sodium sulphate. The crude product is purified by column chromatography (chloroform / methanol = 20:1) to give the title compound **6** (0.82 mmol, 352 mg, 82%) as an orange solid.

***R*f** 0.2 (chloroform / methanol = 9:1) [UV].

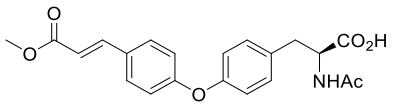
^{1}H-NMR (300 MHz, $CDCl_3$): δ (ppm) = 1.65 (s, 9 H), 2.02 (s, 3 H), 3.12 (dd, *J* = 5.9 Hz, *J* = 14.1 Hz, 1 H), 3.25 (dd, *J* = 5.5 Hz, *J* = 14.1 Hz, 1 H), 4.87 (dd, *J* = 5.8 Hz, *J* = 13.2 Hz, 1 H), 6.34 (d, *J* = 7.5 Hz, NH), 7.00 (d, *J* = 8.5 Hz, 2 H), 7.02 (d, *J* = 8.5 Hz, 2 H), 7.20 (d, *J* = 8.5 Hz, 2 H), 7.90 (d, *J* = 8.9 Hz, 2 H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ (ppm) = 22.9 (CH_3), 27.8 (3 × CH_3), 36.7 (CH_2), 53.4 (CH), 84.8 (C_q), 117.8 (2 × CH), 120.4 (2 × CH), 125.9 (2 × CH), 131.0 (2 × CH), 132.4 (C_q), 146.9 (C_q), 154.4 (C_q), 161.1 (C_q), 162.4 (C_q), 170.9 (C_q), 173.6 (C_q).

MS (ESI) *m/z* (%): 426 [M-H$^-$].

HRMS (ESI) calcd. for $C_{22}H_{25}N_3O_6$ [$M^+ + Na^+$]: 450.1636, found: 450.1636.

1.5.2 (*S*,*E*)-2-Acetamido-3-(4-(4-(3-methoxy-3-oxoprop-1-en-1-yl)phenoxy)phenyl)propanoic acid (**7**)



Tetrabutylammonium hydroxide solution (1.5 M in H_2O, 1.05 mmol, 0.7 mL) is added to a solution of (*E*)-2-acetamido-3-(4-(4-((*tert*-butoxycarbonyl)-diazenyl)phenoxy)phenyl)-propanoic acid (**6**) (351 µmol, 150 mg) in CH_3CN (1.4 mL) and stirred for 5 min. This mixture is added to a suspension of palladium(II) acetate (35.0 µmol, 7.80 mg), hydrogen peroxide solution (0.7 mmol, 30% in H_2O) and methyl acrylate (**3a**) (1.75 mmol, 160 µL) in acetic acid (3.0 mL) over 45 min with a syringe pump. The reaction mixture is stirred for additional 10 min and ethyl acetate (25 mL) is added. The organic phase is washed with water (5 mL), a saturated aqueous solution of sodium chloride (5 mL) and dried over sodium sulfate. The solvent is removed under reduced pressure and the residue is subjected to column chromatography (silica gel, chloroform / methanol = 20:1) to give the title compound **7** (228 µmol, 87.4 mg, 65%) as a viscous brown oil.

***R*f** 0.1 (chloroform / methanol = 9:1) [UV].

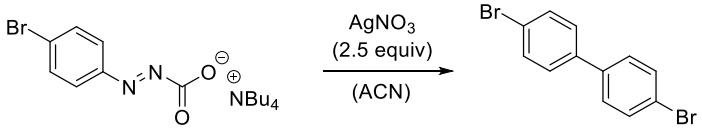
^{1}H-NMR (300 MHz, $CDCl_3$): δ (ppm) = 2.02 (s, 3 H), 3.04-3.31 (m, 2 H), 3.80 (s, 3 H), 4.87 (bs, 1 H), 6.15 (bs, 1 H), 6.34 (d, *J* = 16.0 Hz, 1 H), 6.90-7.04 (m, 4 H), 7.16 (d, *J* = 8.3 Hz, 2 H), 7.47 (d, *J* = 8.7 Hz, 2 H), 7.65 (d, *J* = 16.0 Hz, 1 H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ (ppm) = 23.0 (CH_3), 36.6 (CH_2), 51.7 (CH_3), 53.4 (CH), 116.5 (CH), 118.5 (2 × CH), 119.6 (2 × CH), 129.4 (C_q), 129.8 (2 × CH), 130.8 (2 × CH), 131.4 (C_q), 144.1 (C_q), 155.3 (C_q), 159.2 (C_q), 167.7 (C_q), 170.9 (C_q). One signal missing.

MS (ESI) *m/z* (%): 384 [MH^+].

HRMS (ESI) calcd. for $C_{21}H_{21}NO_6$ [$M^+ + Na^+$]: 406.1261, found: 406.1262.

Scheme S3. Silver(I)-induced fragmentation of phenylazocarboxylate salts



To a solution of solution of silver(I) nitrate (438 µmol, 74.4 mg) in CH_3CN (1.0 mL) a prestirred mixture of tetrabutylammonium hydroxide solution (1.5 M in H_2O, 350 µmol, 233 µL) and *tert*-butyl 2-(4-bromophenyl)azocarboxylate (**1a**) (175 µmol, 50.0 mg) in CH_3CN (0.5 mL) is added over 15 min with a syringe pump. The solvent is removed under reduced pressure. The yield of 4,4'-dibromobiphenyl (52.5 µmol, 30%) is determined with an internal standard of 1,3,5-trimethoxybenzene and verified by GC-MS analysis.

^{1}H-NMR (360 MHz, $CDCl_3$): δ (ppm) = 7.41 (d, *J* = 8.7 Hz, 4 H), 7.56 (d, *J* = 8.7 Hz, 4 H).

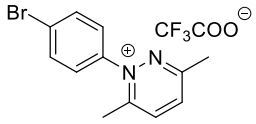
MS (EI) *m/z* (%): .312.0 [M^+].

Competition experiment with acrylonitrile:

Tetrabutylammonium hydroxide solution (1.5 M in H_2O, 750 µmol, 0.5 mL) is added to a solution of *tert*-butyl 2-(4-fluorophenyl)azocarboxylate (**1c**) (500 µmol, 112 mg) in CH_3CN (1.4 mL) and stirred for 5 min. This mixture is added to a solution of palladium(II) acetate (50.0 µmol, 11.3 mg), methyl acrylate (2.50 mmol, 223 µL), acrylonitrile (2.50 mmol, 165 µL) and hydrogen peroxide solution (1.00 mmol, 30% in H_2O) in acetic acid (3.0 mL) over 45 min with a syringe pump. The reaction mixture is stirred for additional 10 min and concentrated under reduced pressure. The yield of **4ca** (235 µmol, 47%) is determined with an internal standard of 1,3,5-trimethoxybenzene. (*E*)-3-(4-Fluorophenyl)acrylonitrile cannot be detected.

Competition experiment with 2,5-dimethylfuran – trapping of phenyldiazene:

A solution of tetrabutylammonium hydroxide (1.5 M in H_2O, 263 µmol), *tert*-butyl 2-(4-bromophenyl)azocarboxylate (**1a**) (175 µmol, 50.0 mg) and palladium(II) acetate (17.5 µmol, 4.00 mg) in CH_3CN (2.0 mL) is stirred for 5 min. To this mixture a solution of methyl acrylate (700 µmol, 190 µL), 2,5-dimethylfuran (700 µmol, 74.0 µL) and trifluoroacetic acid (100 µL) in CH_3CN (0.5 mL) is added and stirred for 10 minutes. The solvent is removed under reduced pressure. 1-(4-Bromophenyl)-3,6-dimethylpyridazinium trifluoroacetate is obtained in quantitative yield. Trace amounts of **4aa** can be identified in ^{1}H-NMR and GC-MS analysis.



^{1}H-NMR (600 MHz, $CDCl_3$): δ (ppm) = 2.77 (s, 3 H), 2.81 (s, 3 H), 7.42 (d, *J* = 8.9 Hz, 2 H), 7.82 (d, *J* = 8.9 Hz, 2 H), 8.22 (d, *J* = 8.7 Hz, 1 H), 8.36 (d, *J* = 8.7 Hz, 2 H).

Analytical data is in agreement with those reported in literature[1]

Experiment with excess of benzene:

Tetrabutylammonium hydroxide solution (1.5 M in H_2O, 263 µmol) is added to a solution of *tert*-butyl 2-(4-bromophenyl)azocarboxylate (**1a**) (175 µmol, 50.0 mg) in CH_3CN (0.8 mL) and stirred for 5 min. This mixture is added to a solution of silver(I) acetate (350 µmol, 58.0 mg), palladium(II) acetate (17.5 µmol, 4.00 mg) and benzene (1.0 mL) in CH_3CN/acetic acid (0.2 mL/1.0 mL) over 45 min with a syringe pump. The solvent is removed under reduced pressure. 4-Bromobiphenyl could not be detected via GC-MS and NMR analysis.

1.6 References

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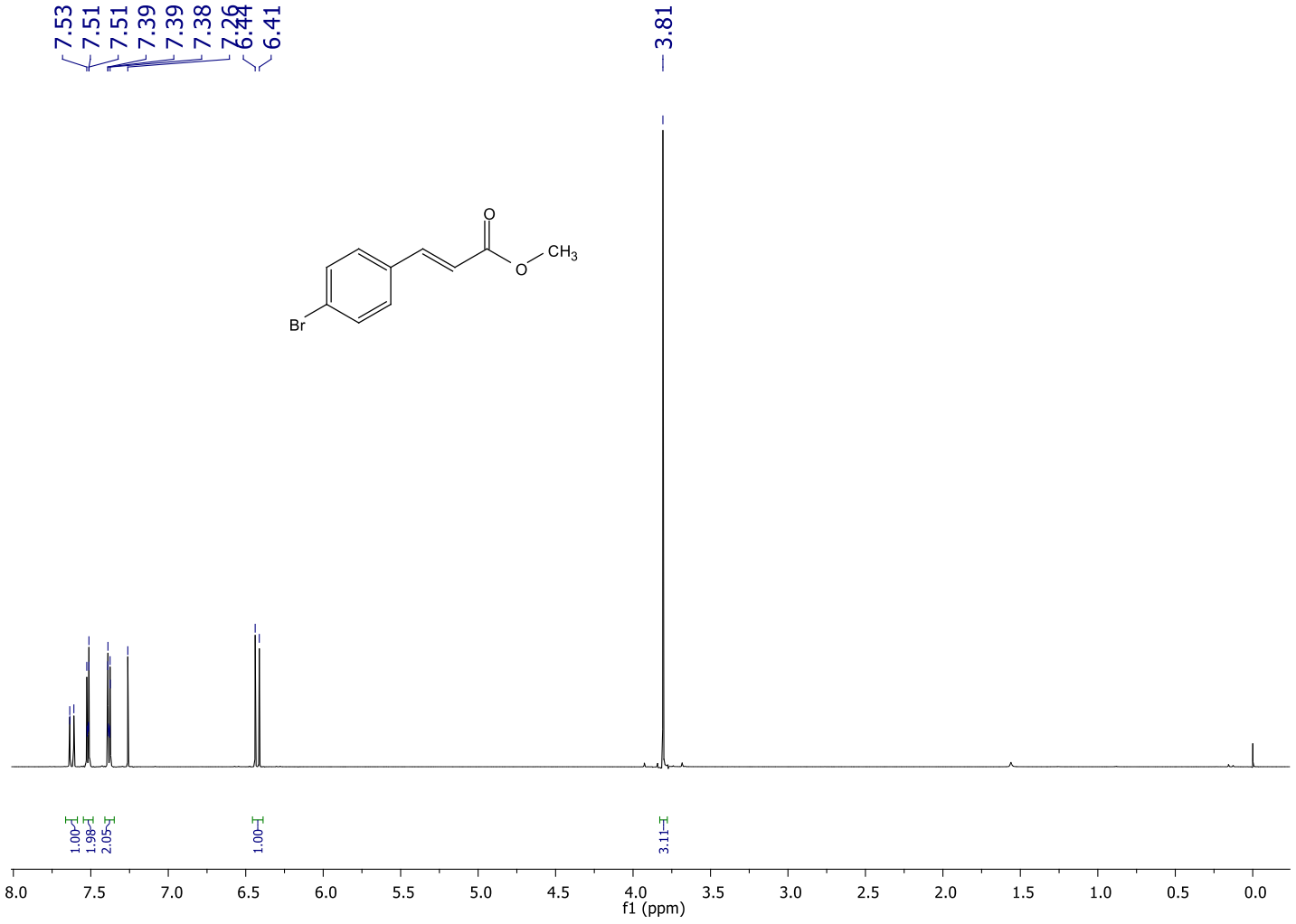
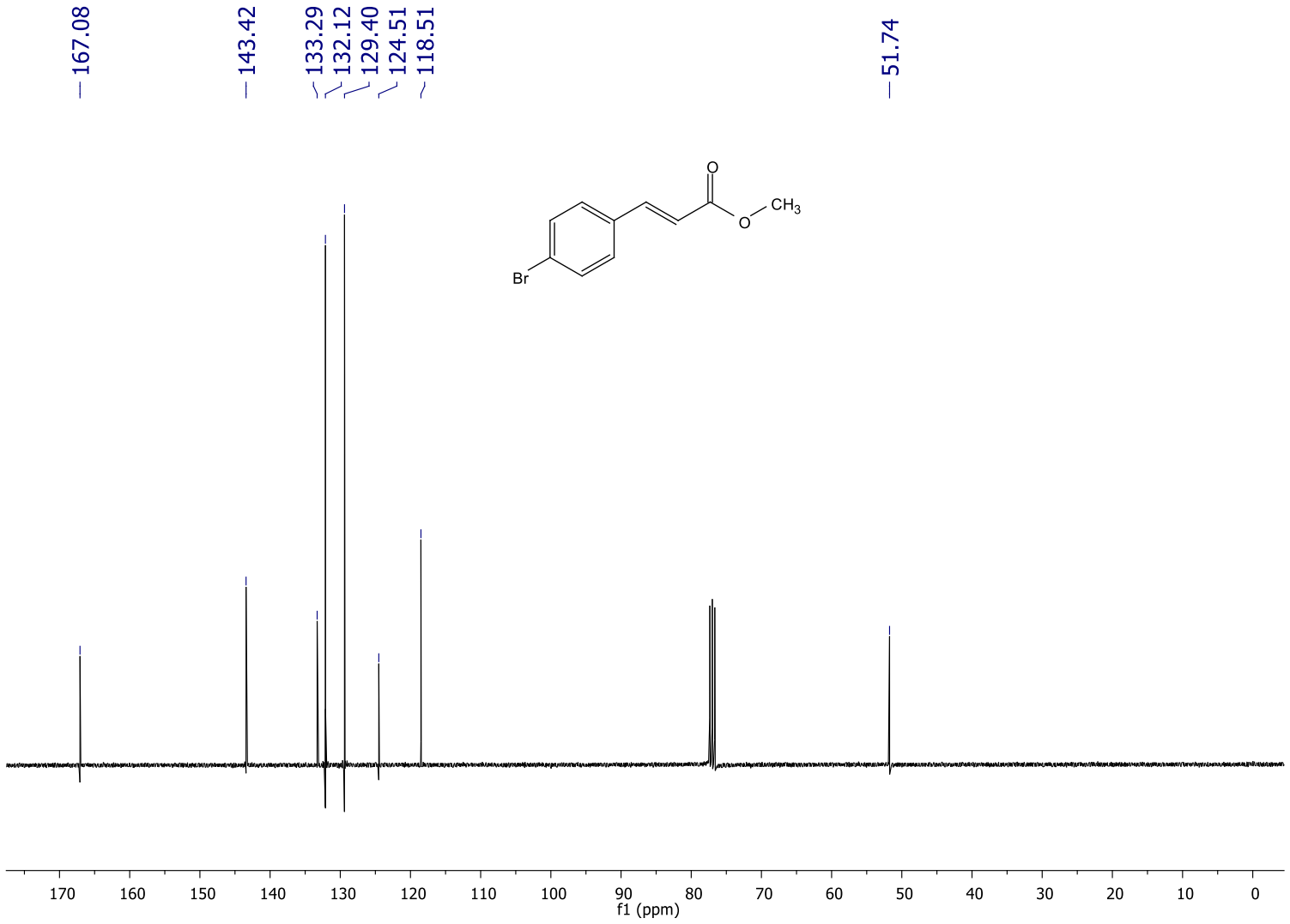
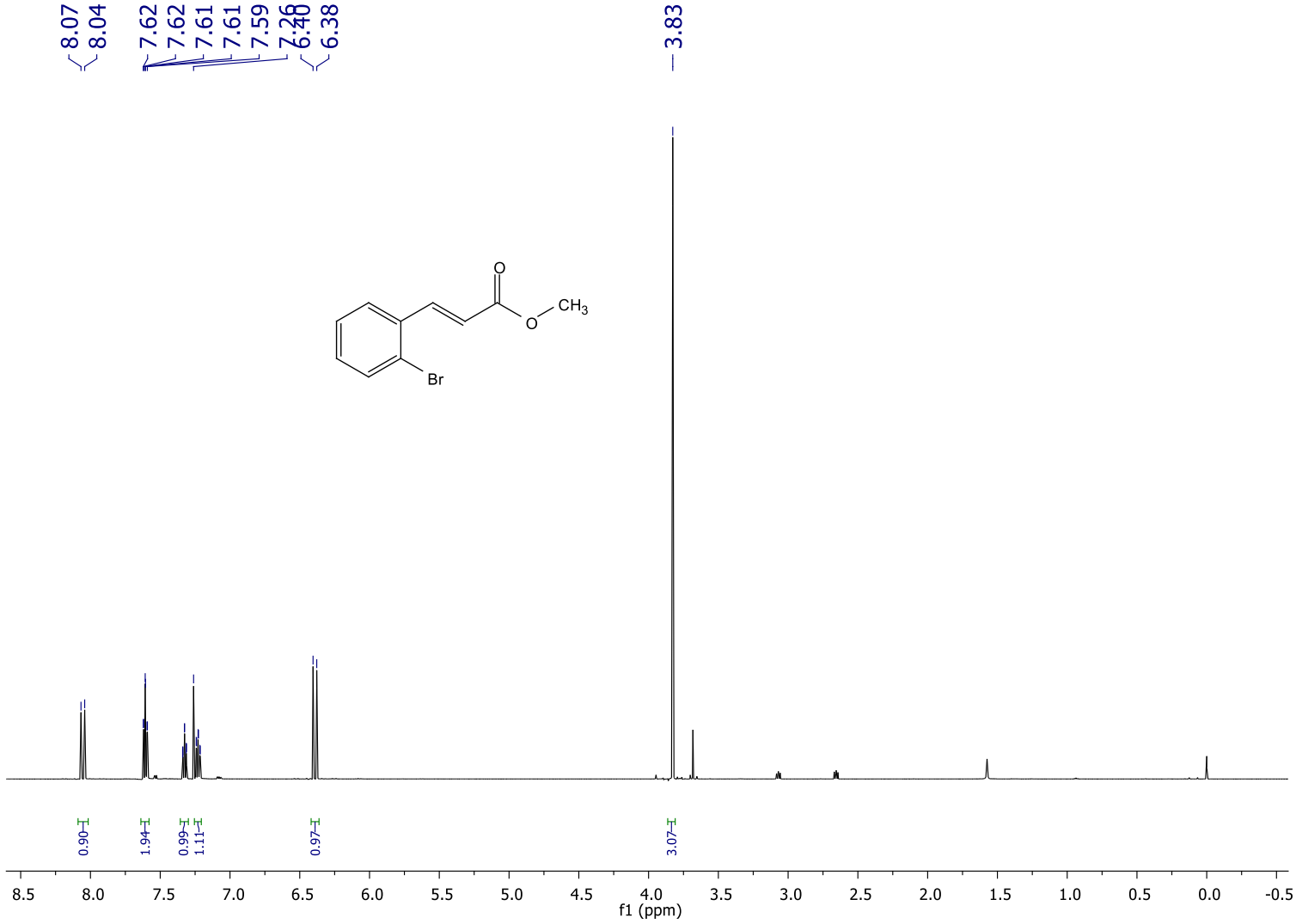
1.7 Copies of ^{1}H and ^{13}C spectra

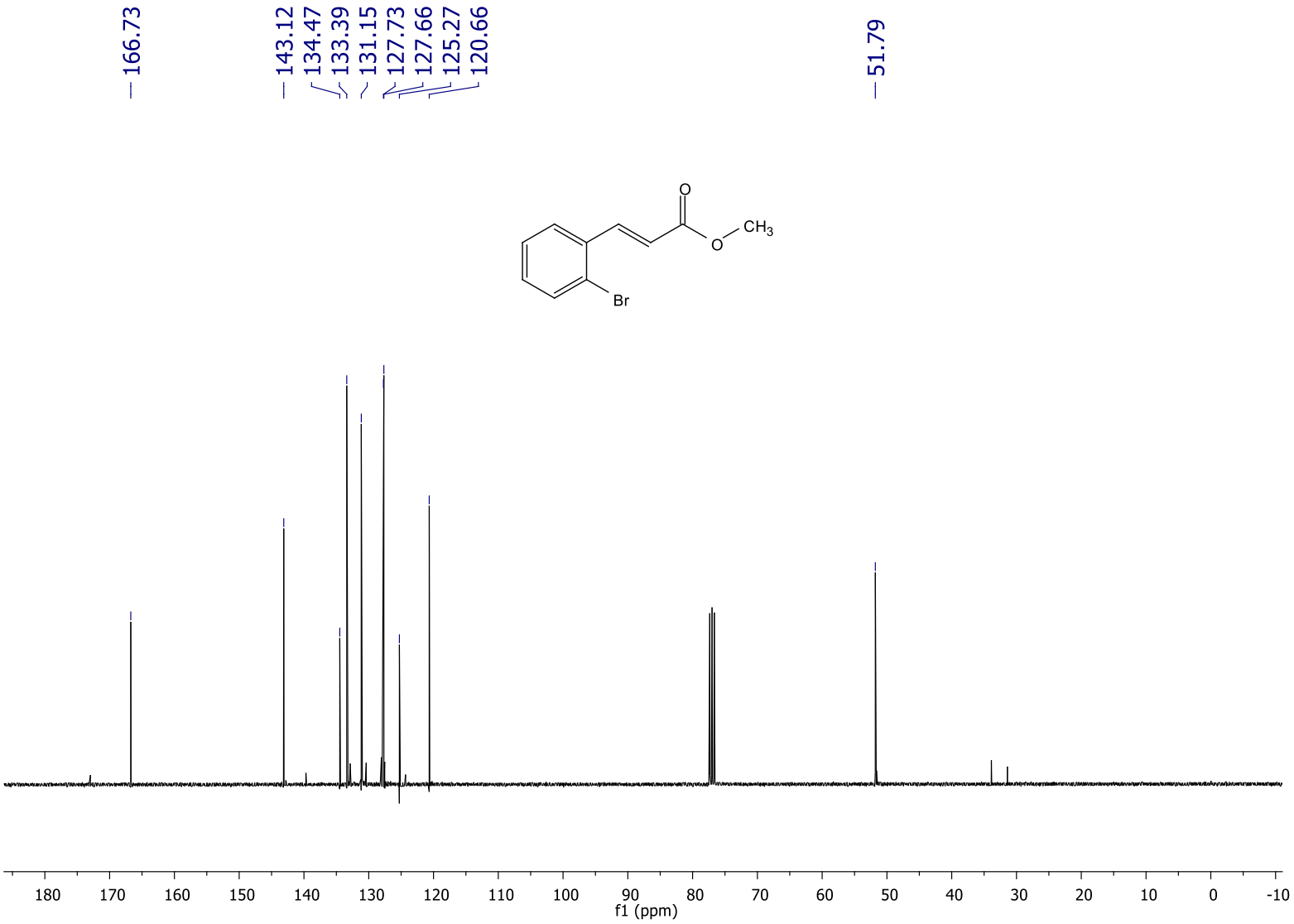
Methyl 4-bromocinnamate (**4aa**)



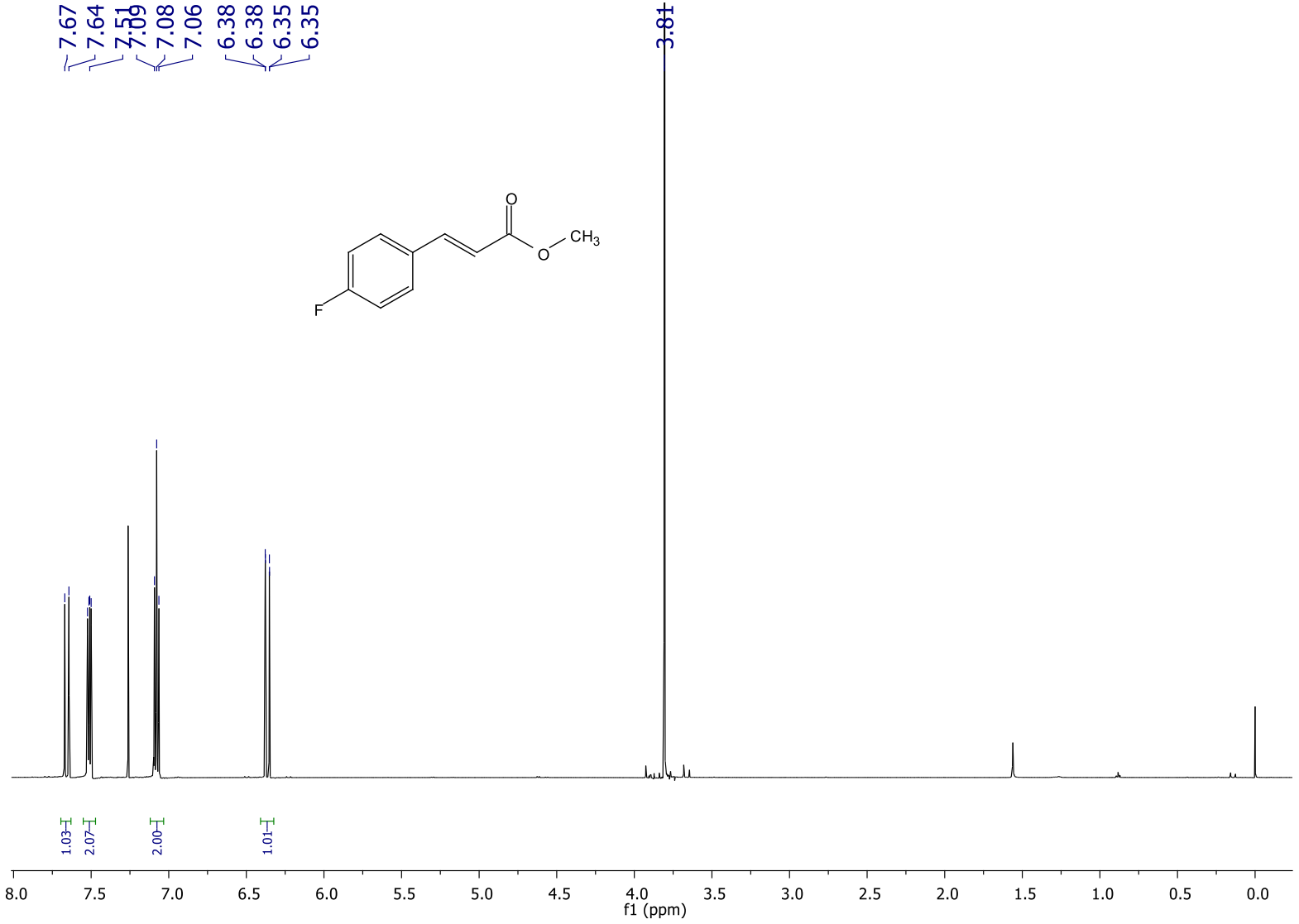

167.08
143.42
133.29
132.12
129.40
124.51
118.51
51.74
O
O
CH3
Br
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

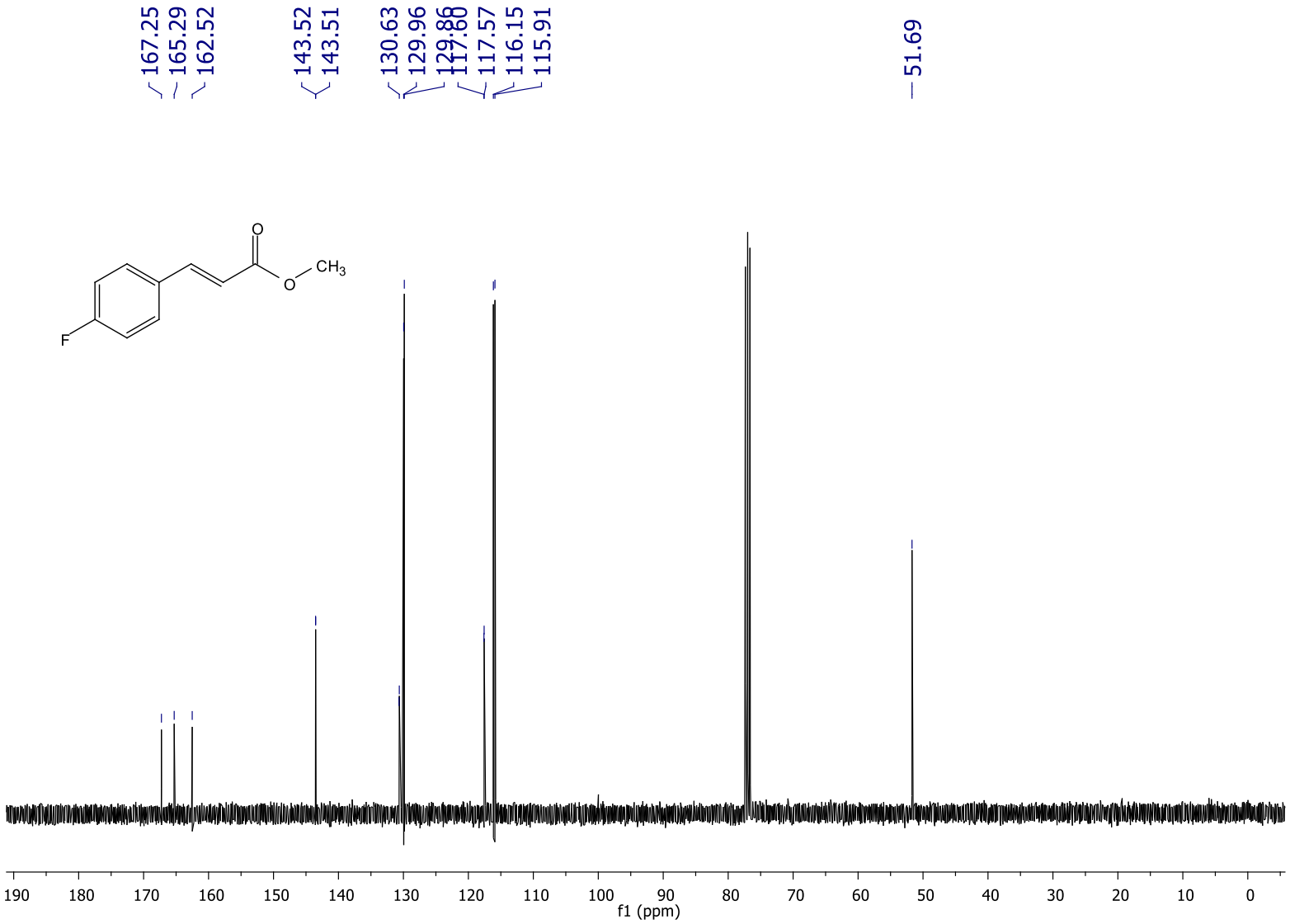
Methyl 2-bromocinnamate (**4ba**)



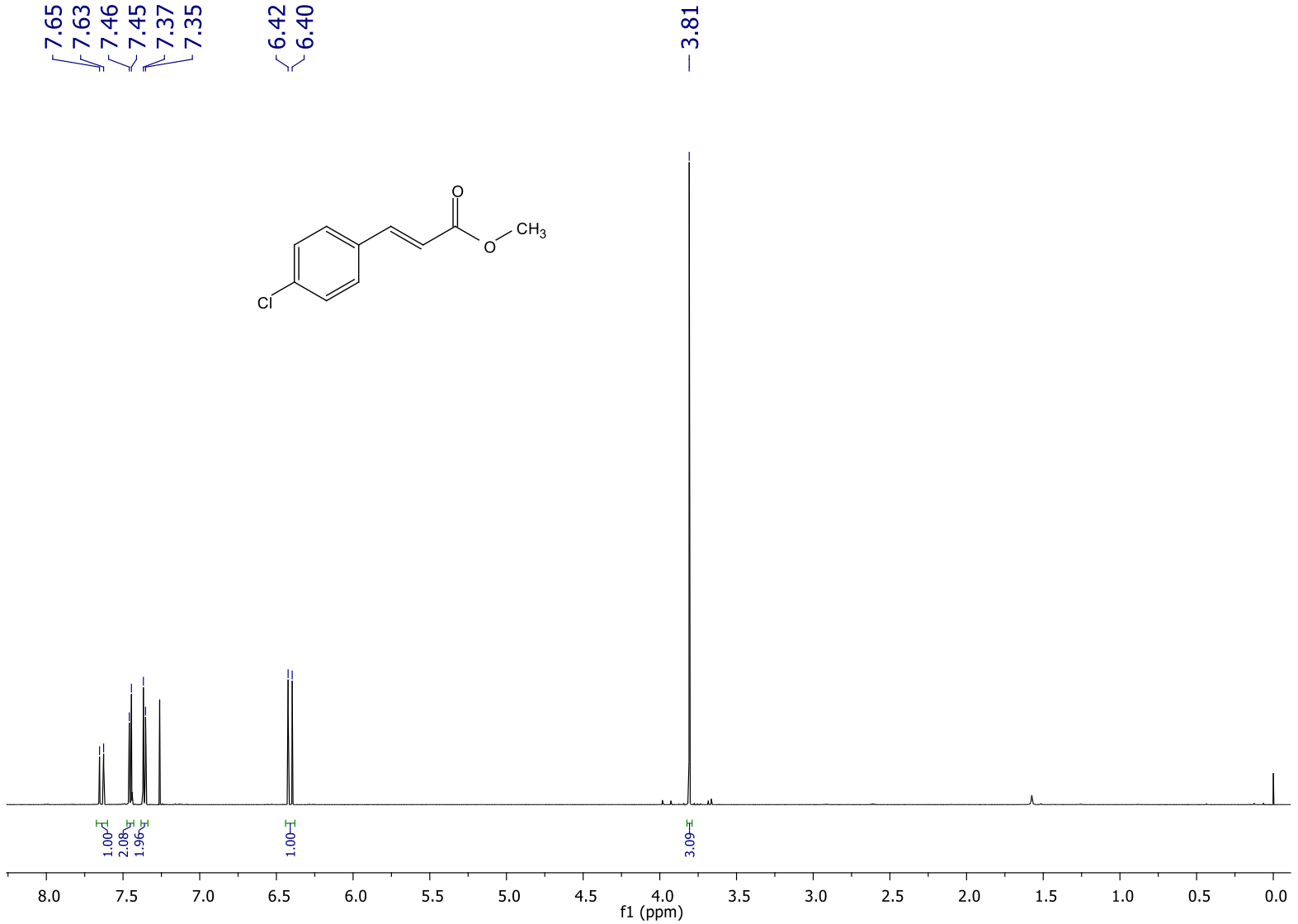

166.73
143.12
134.47
133.39
131.15
127.73
127.66
125.27
120.66
51.79
O
O
CH3
Br
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

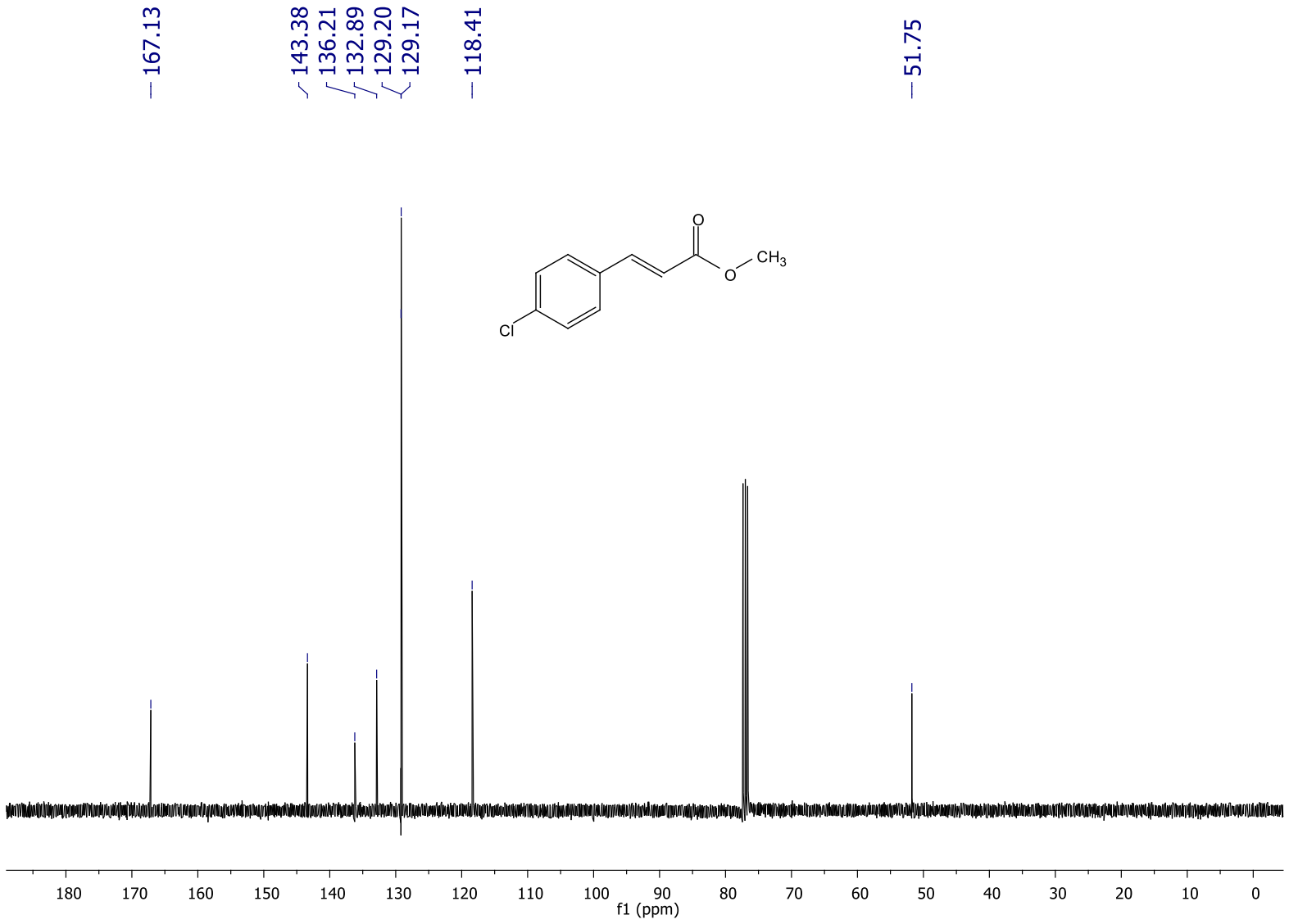
Methyl 4-fluorocinnamate (**4ca**)



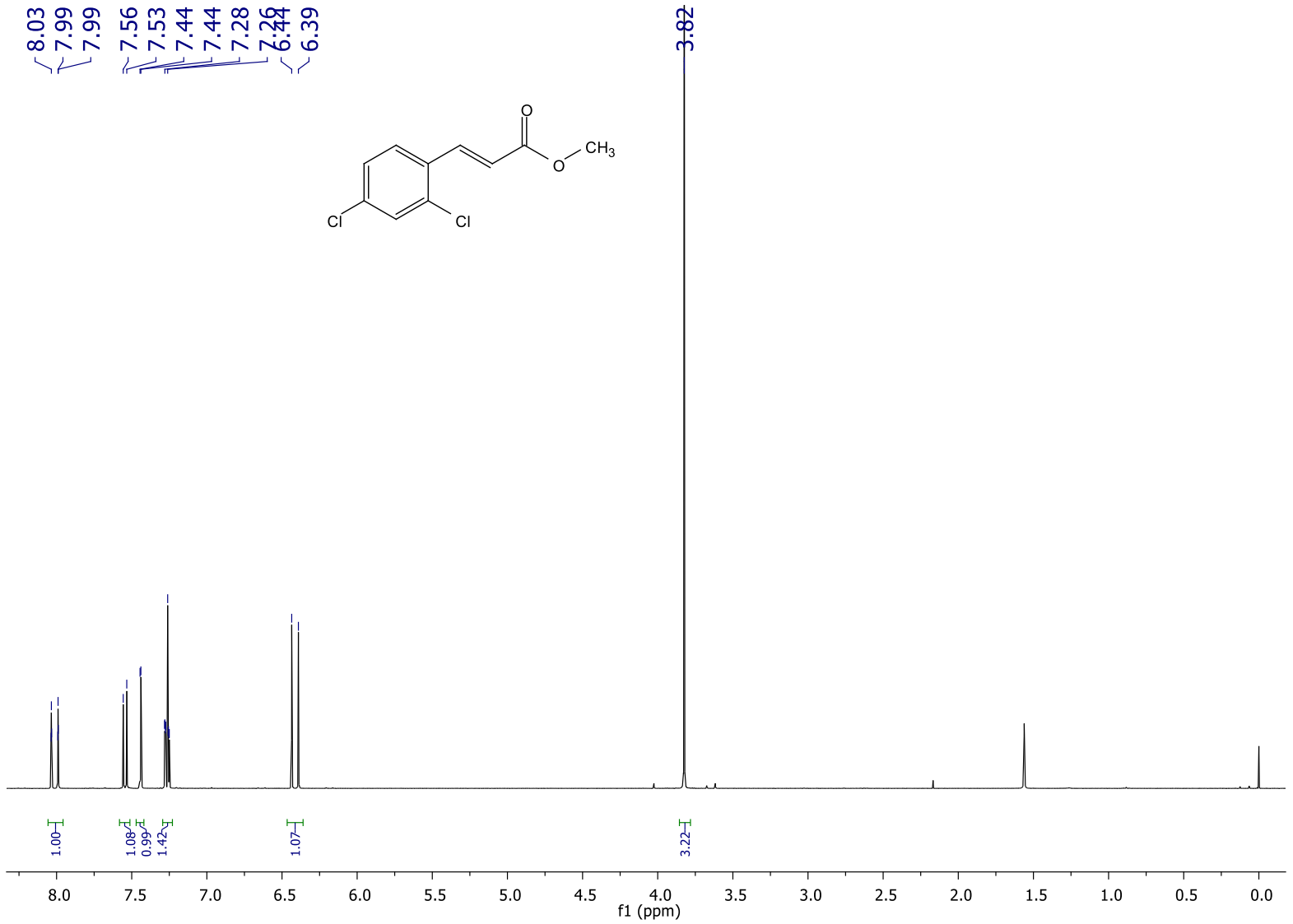

167.25
165.29
162.52
143.52
143.51
130.63
129.96
129.86
117.80
117.57
116.15
115.91
51.69
O
O
CH3
F
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

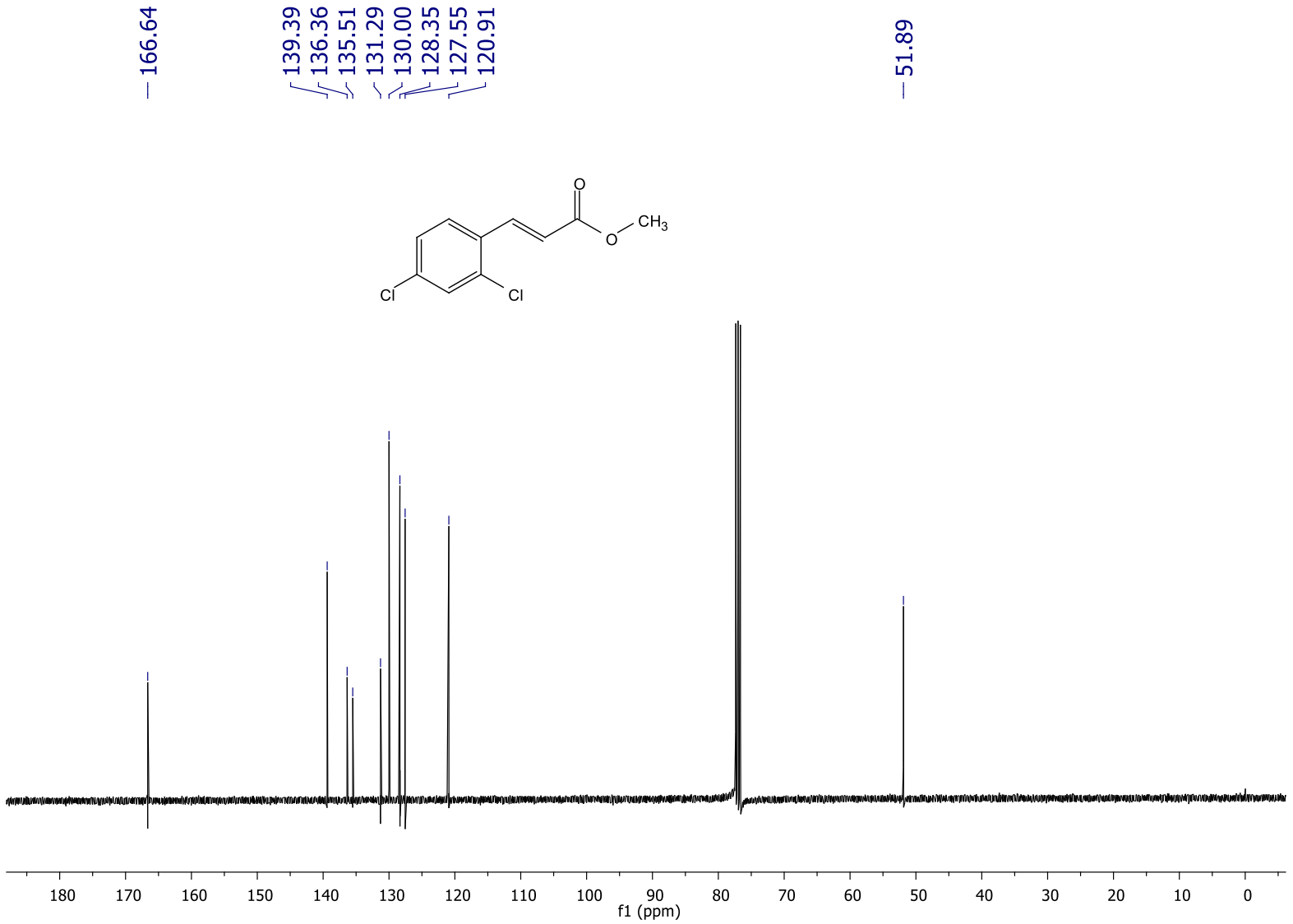
Methyl 4-chlorocinnamate (**4da**)



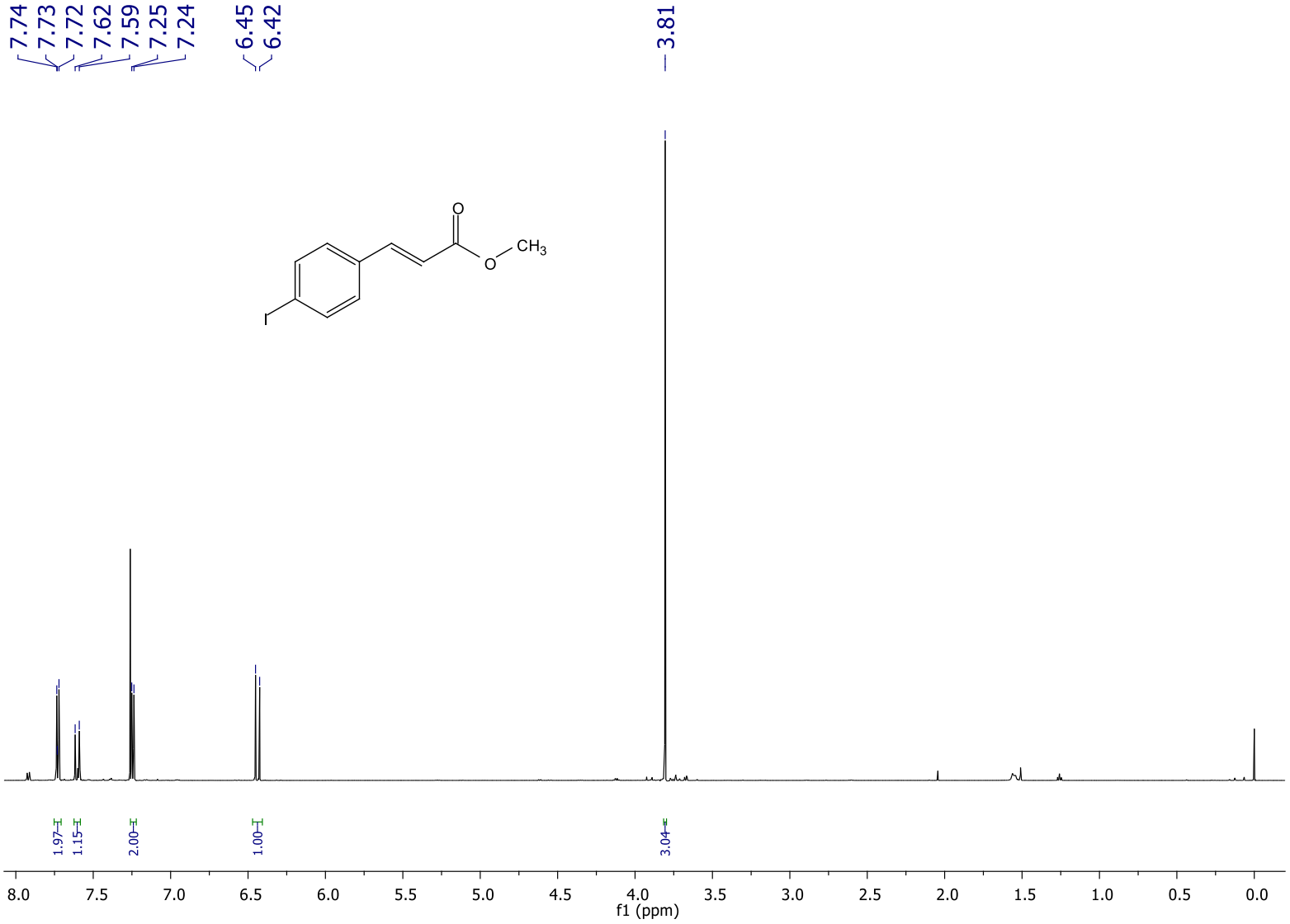

167.13
143.38
136.21
132.89
129.20
129.17
118.41
51.75
O
O
CH3
Cl
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

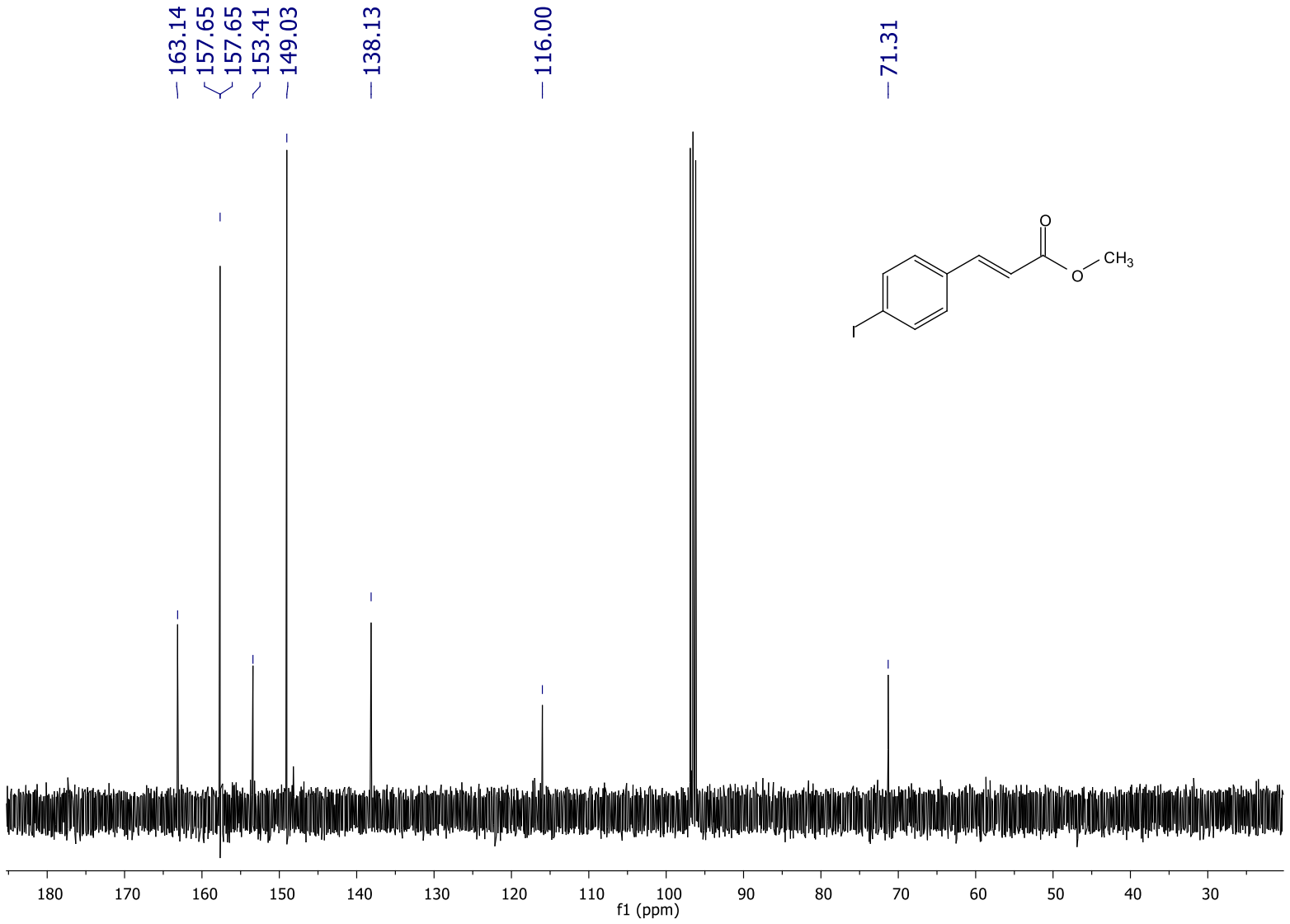
Methyl 2,4-dichlorocinnamate (**4ea**)



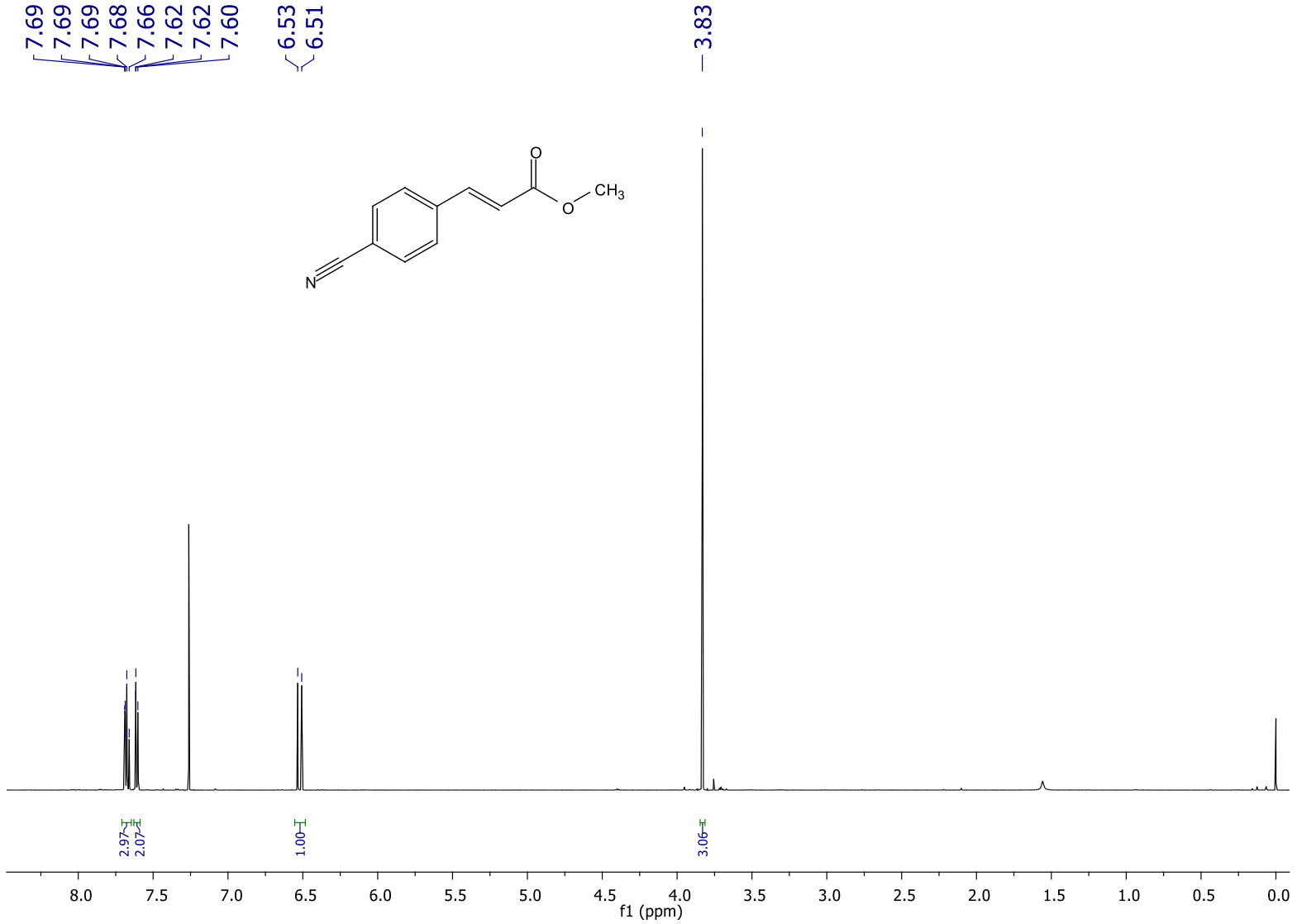

166.64
139.39
136.36
135.51
131.29
130.00
128.35
127.55
120.91
51.89
O
O
CH3
Cl
Cl
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

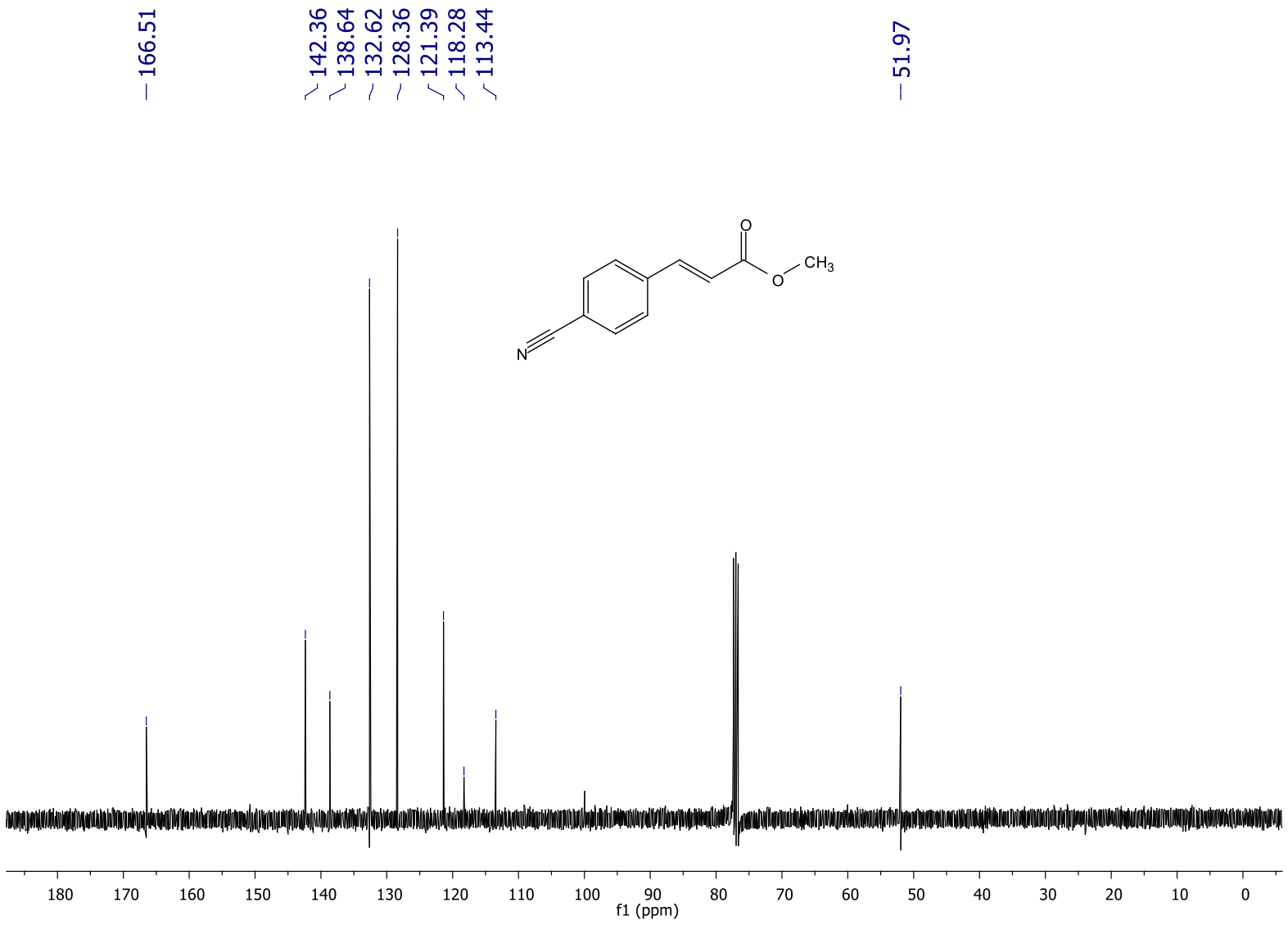
Methyl 4-iodocinnamate (**4fa**)



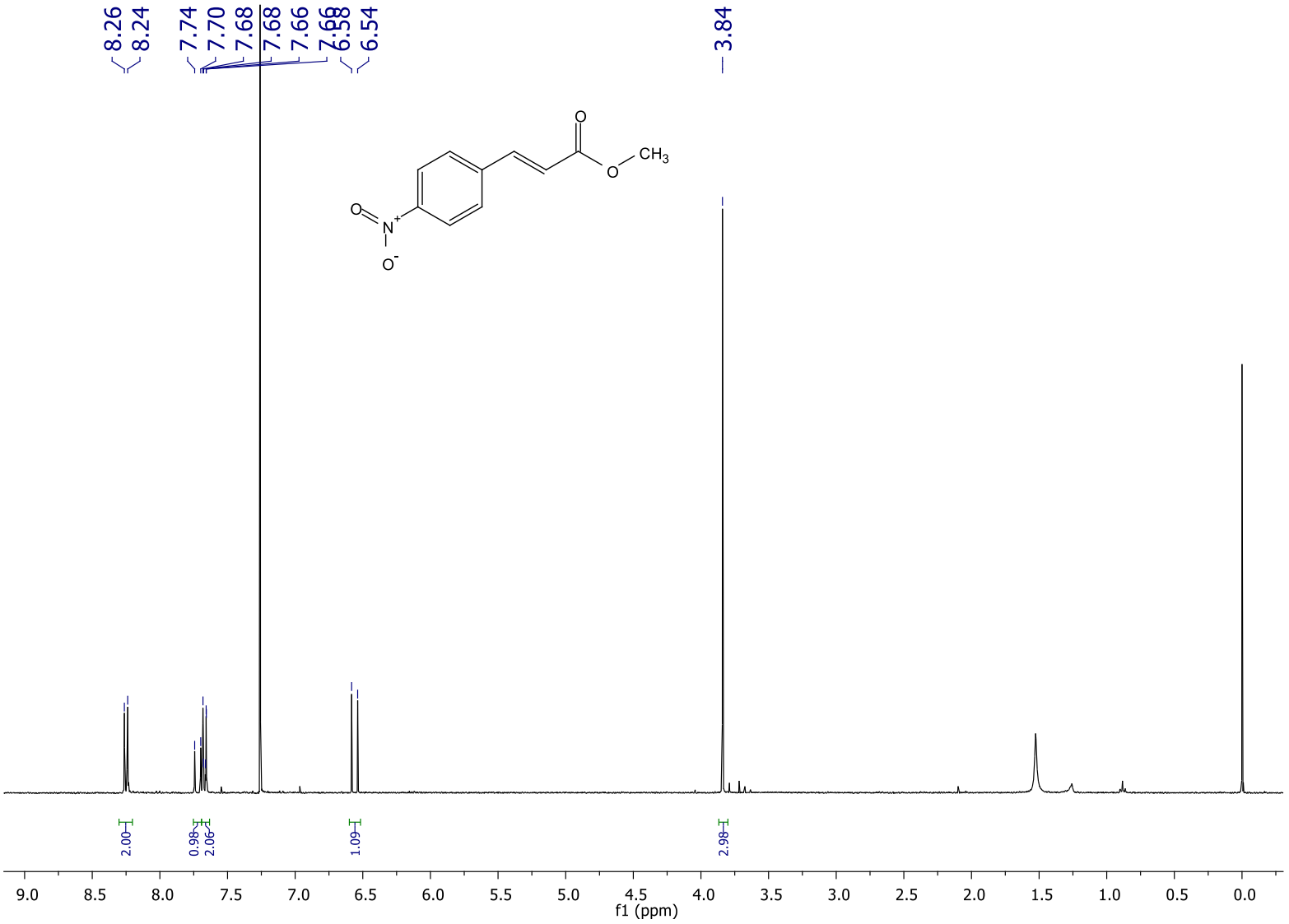

163.14
157.65
157.65
153.41
149.03
138.13
116.00
71.31
O
O
CH3
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
f1 (ppm)

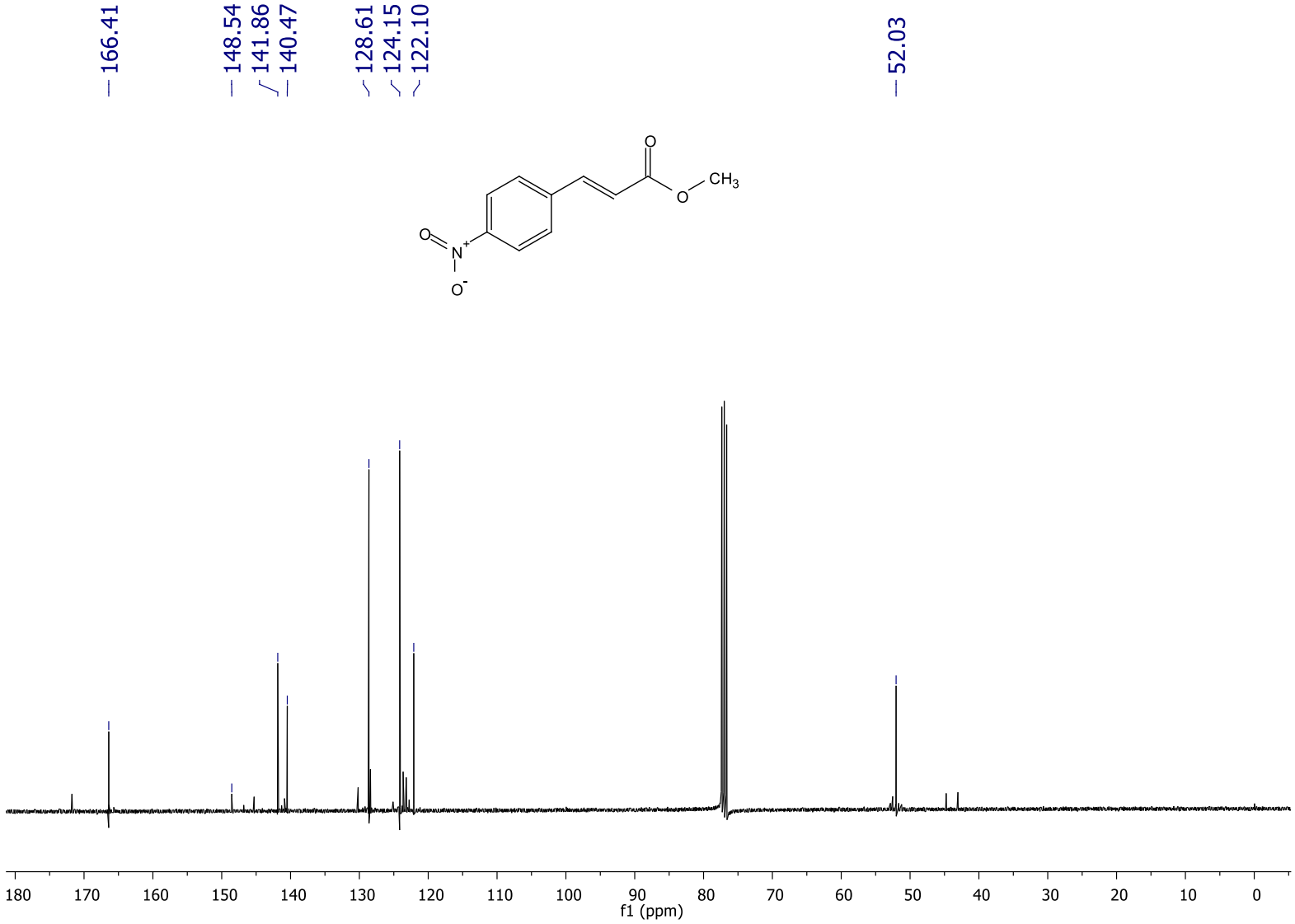
Methyl 4-cyanocinnamate (**4ga**)



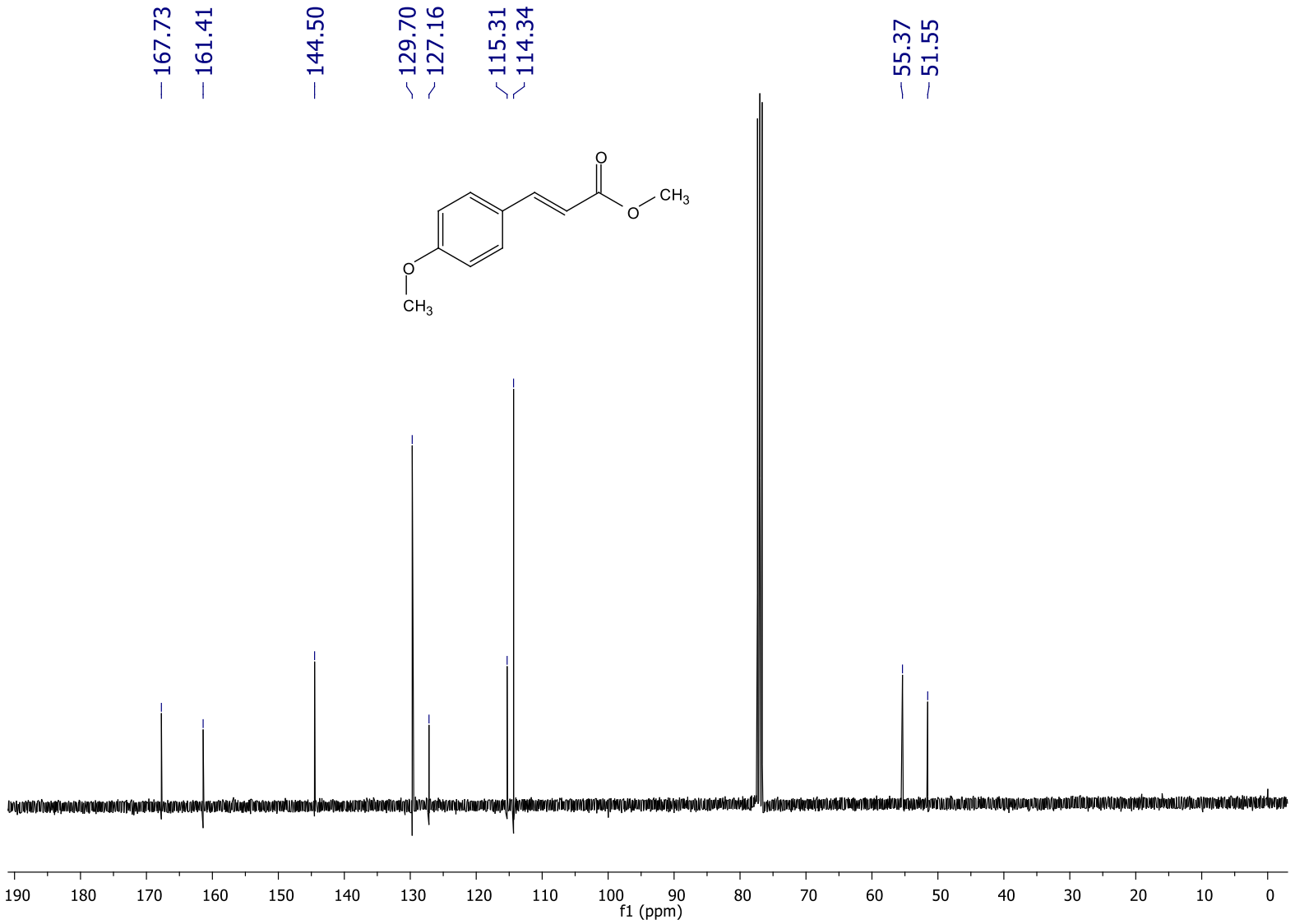

166.51
142.36
138.64
132.62
128.36
121.39
118.28
113.44
51.97
O
O
CH3
N
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

Methyl 4-nitrocinnamate (**4ha**)

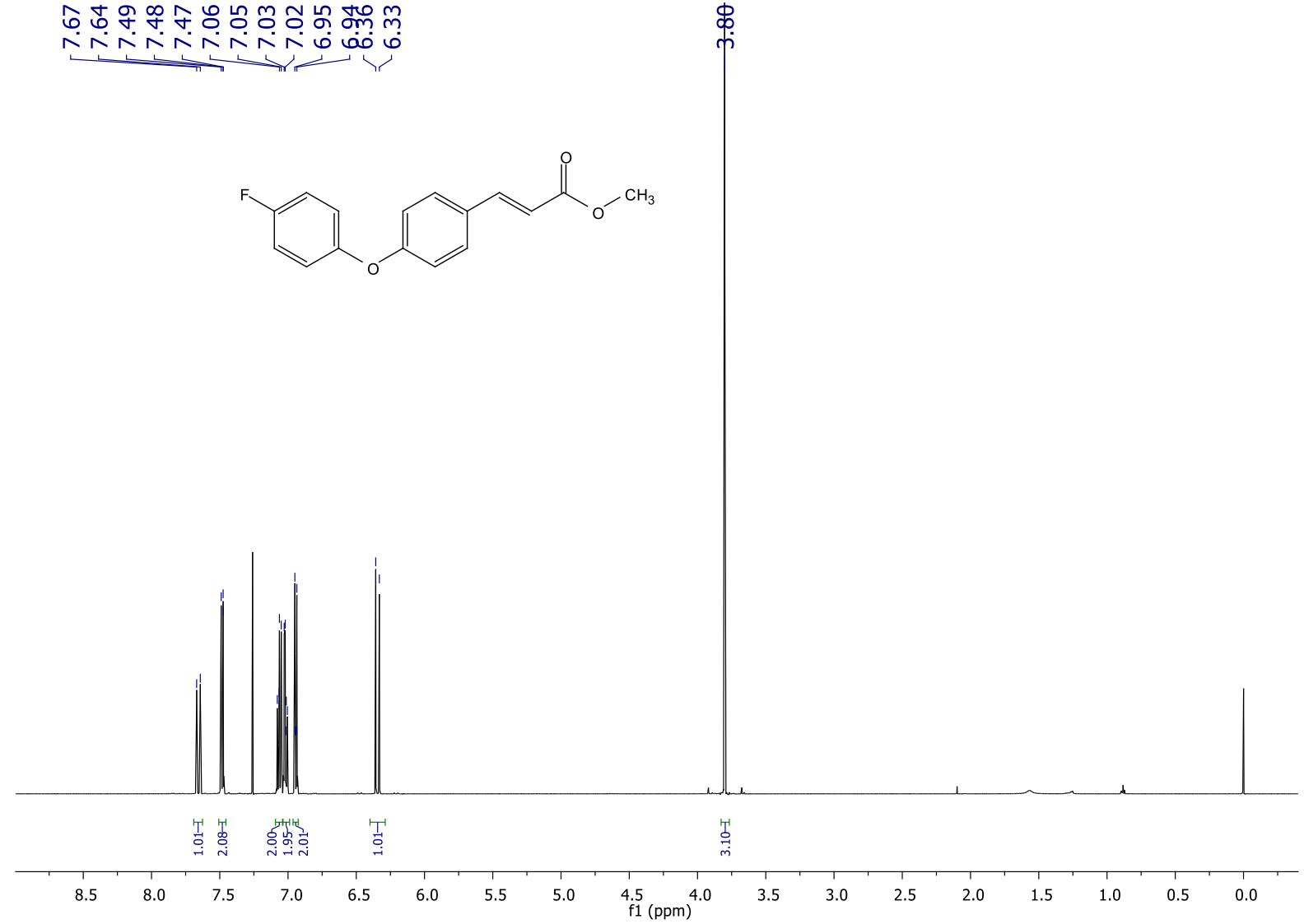


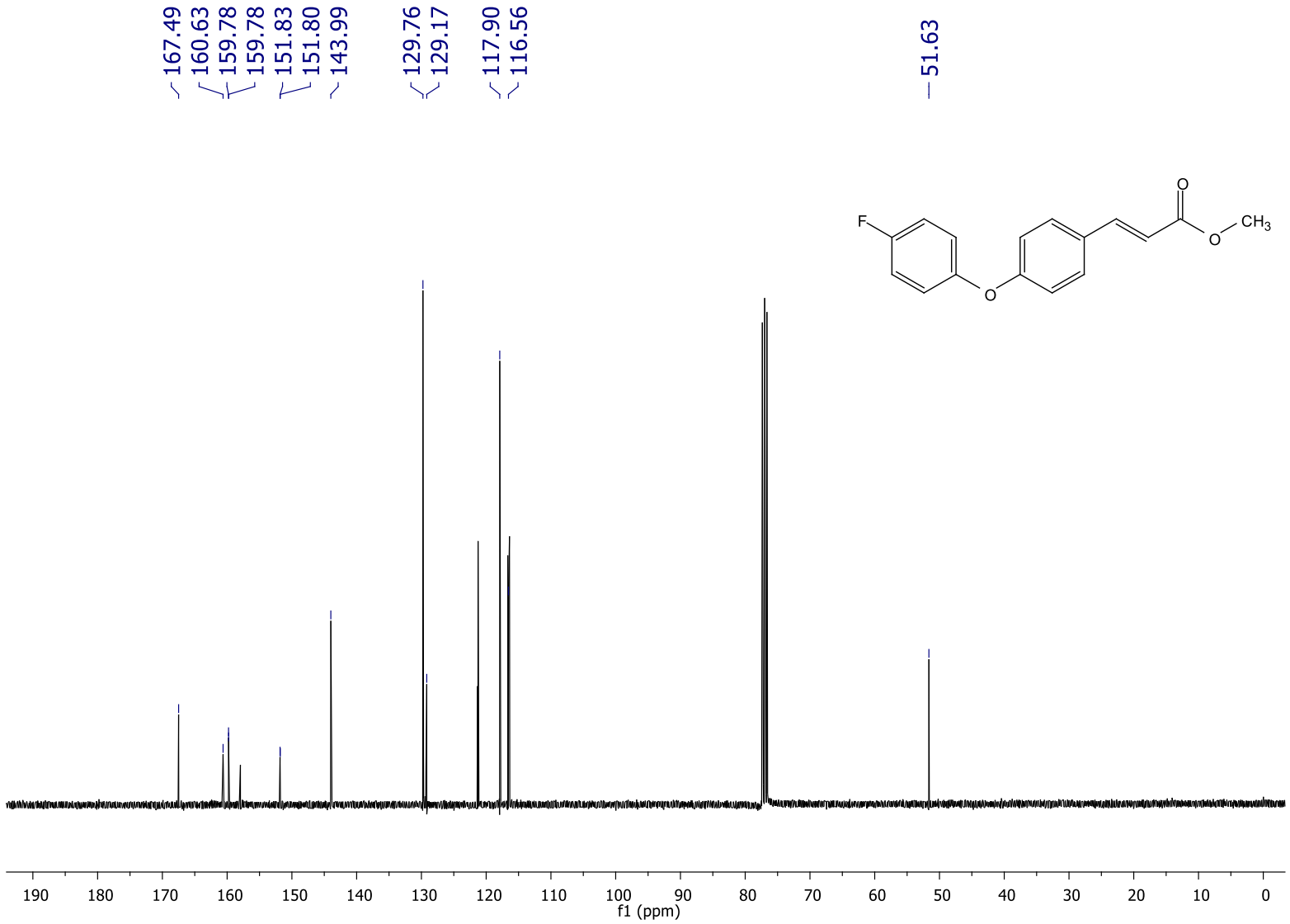

166.41
148.54
141.86
140.47
128.61
124.15
122.10
52.03
O
O
CH3
O
N+
O-
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

Methyl 4-methoxycinnamate (**4ia**)

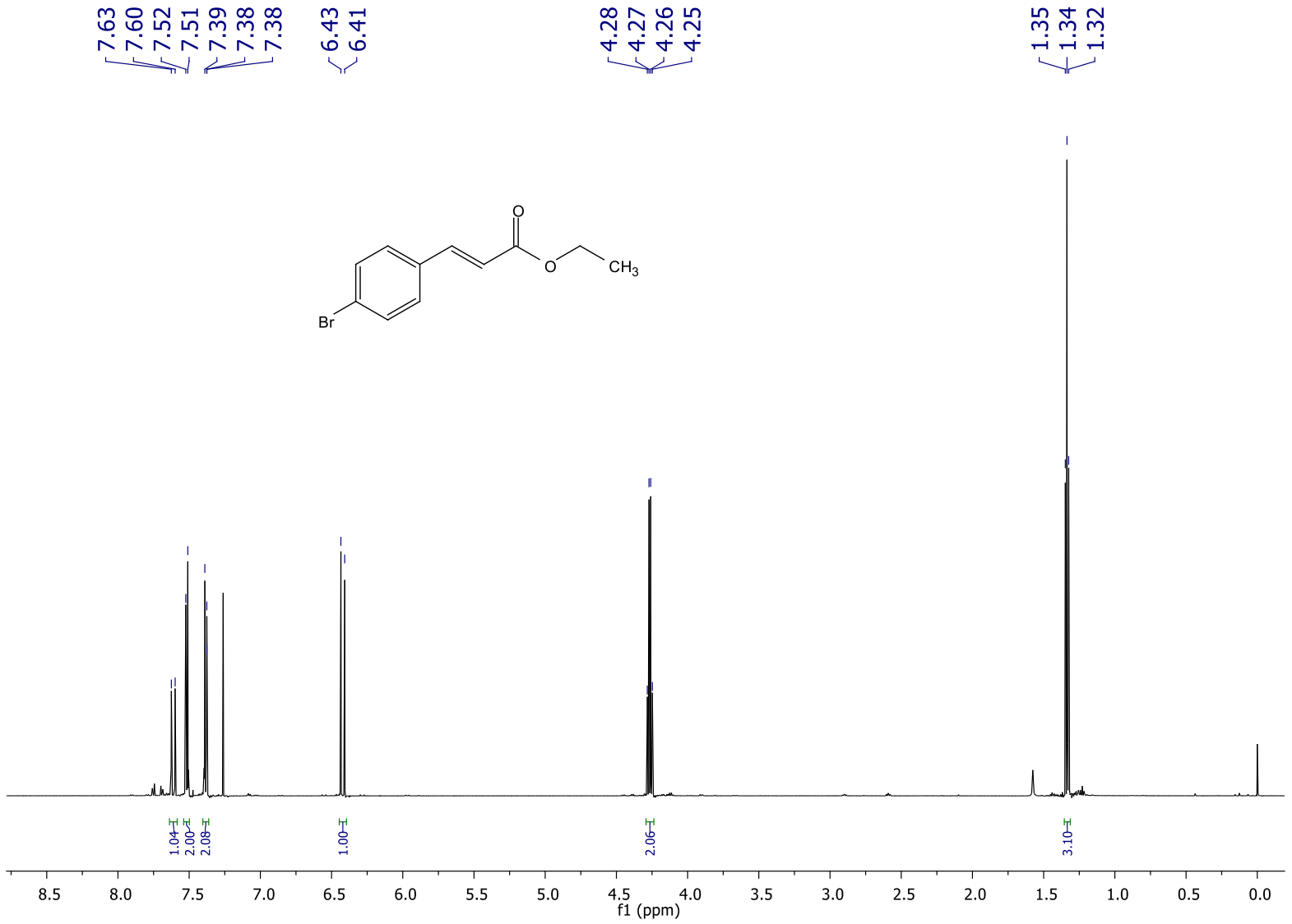

167.73
161.41
144.50
129.70
127.16
115.31
114.34
55.37
51.55
O
O
CH3
O
CH3
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

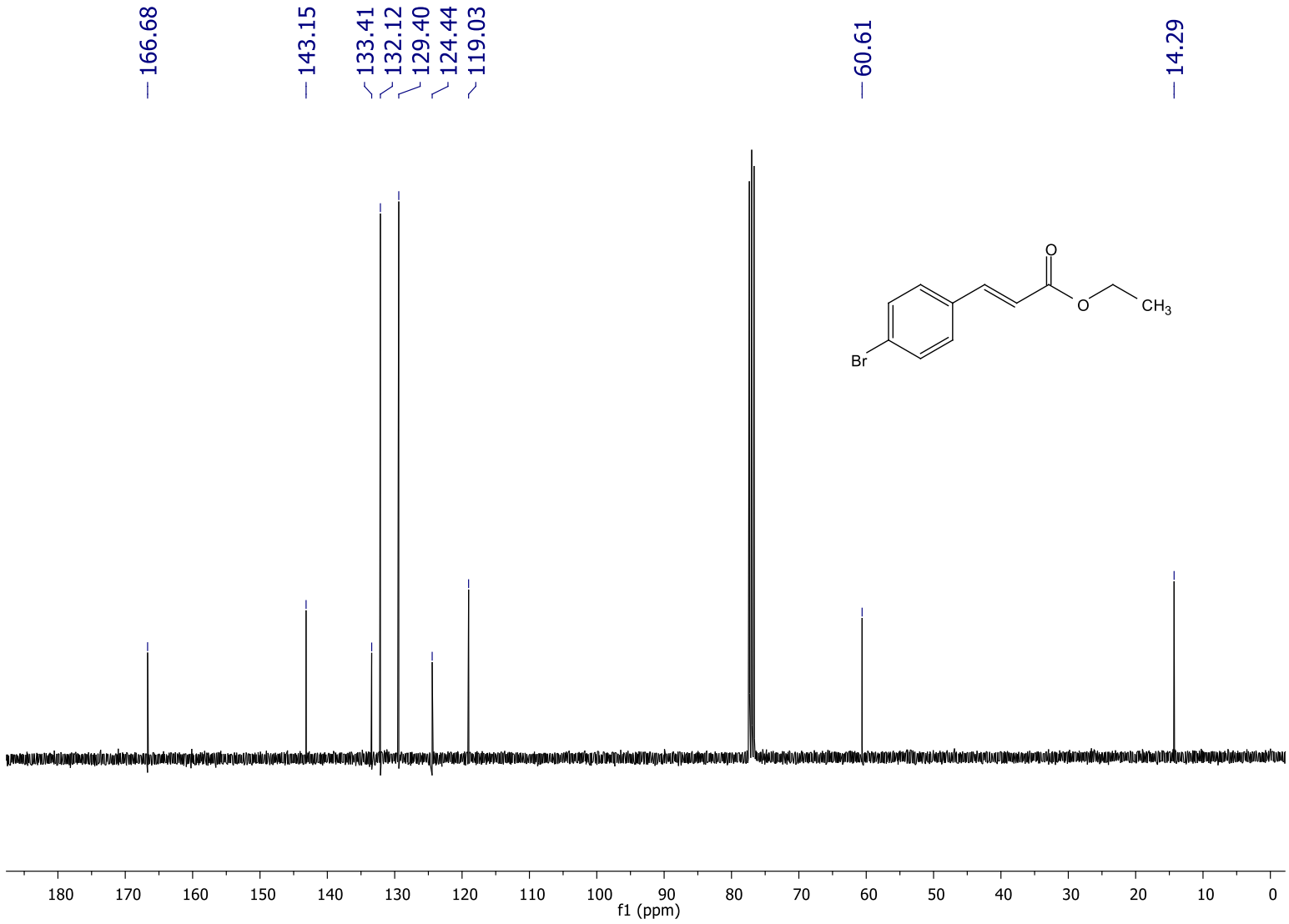
Methyl 4-(4-fluorophenoxy)cinnamate (**4ja**)



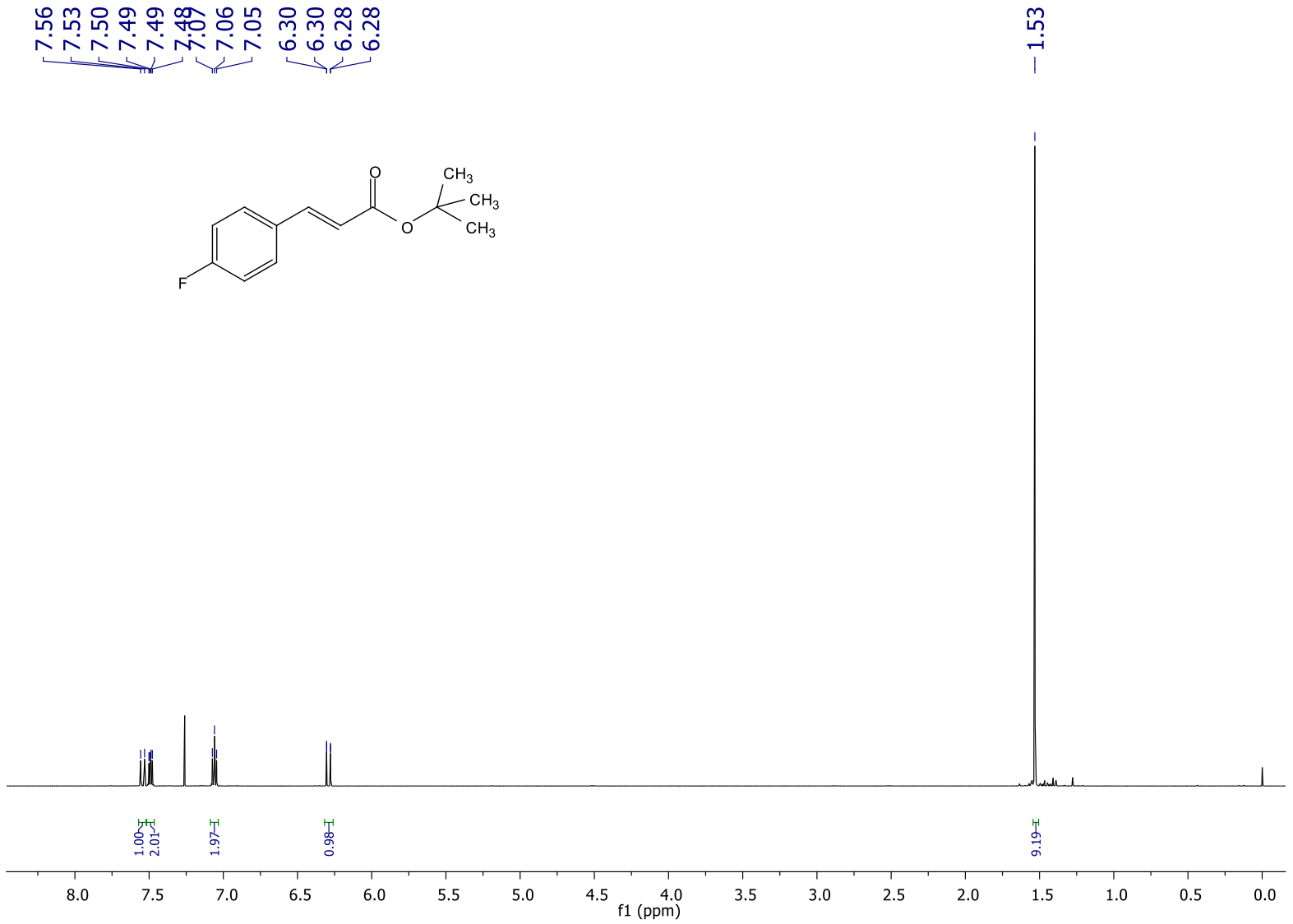

167.49
160.63
159.78
159.78
151.83
151.80
143.99
129.76
129.17
117.90
116.56
51.63
F
O
O
O
CH3
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

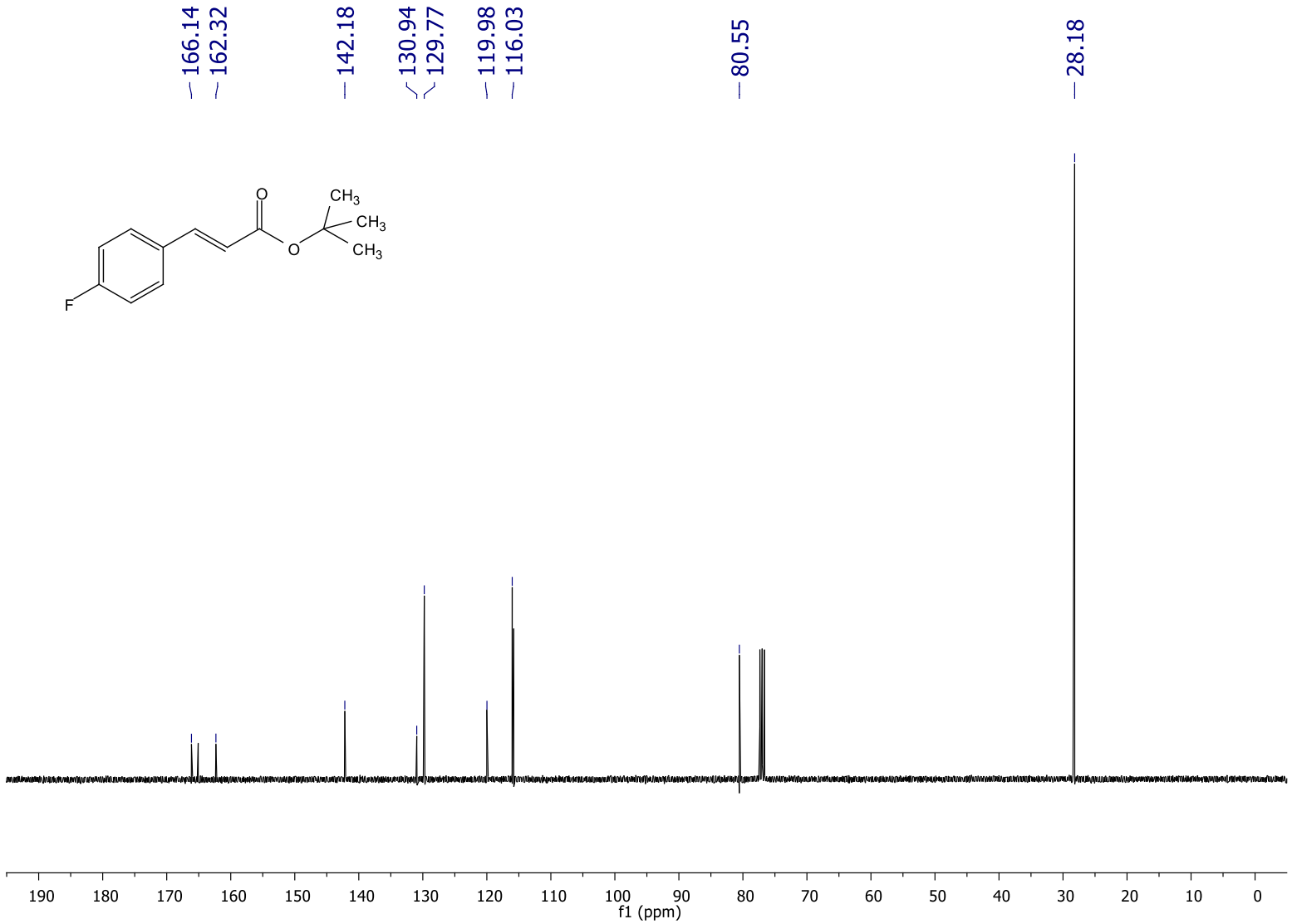
Ethyl 4-bromocinnamate (**4ab**)



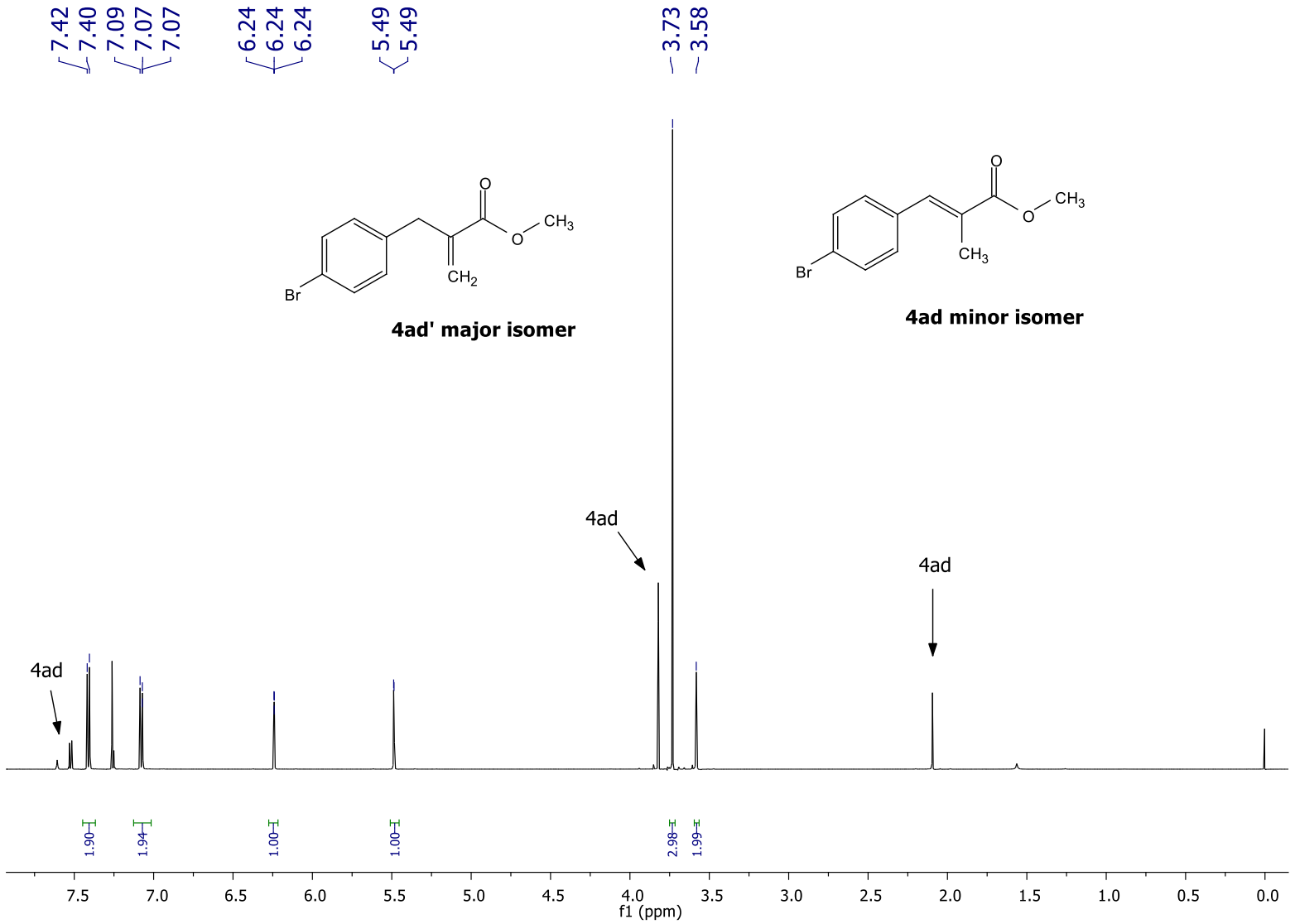

166.68
143.15
133.41
132.12
129.40
124.44
119.03
60.61
14.29
O
O
CH3
Br
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

tert-Butyl 4-fluorocinnamate (**4cc**)

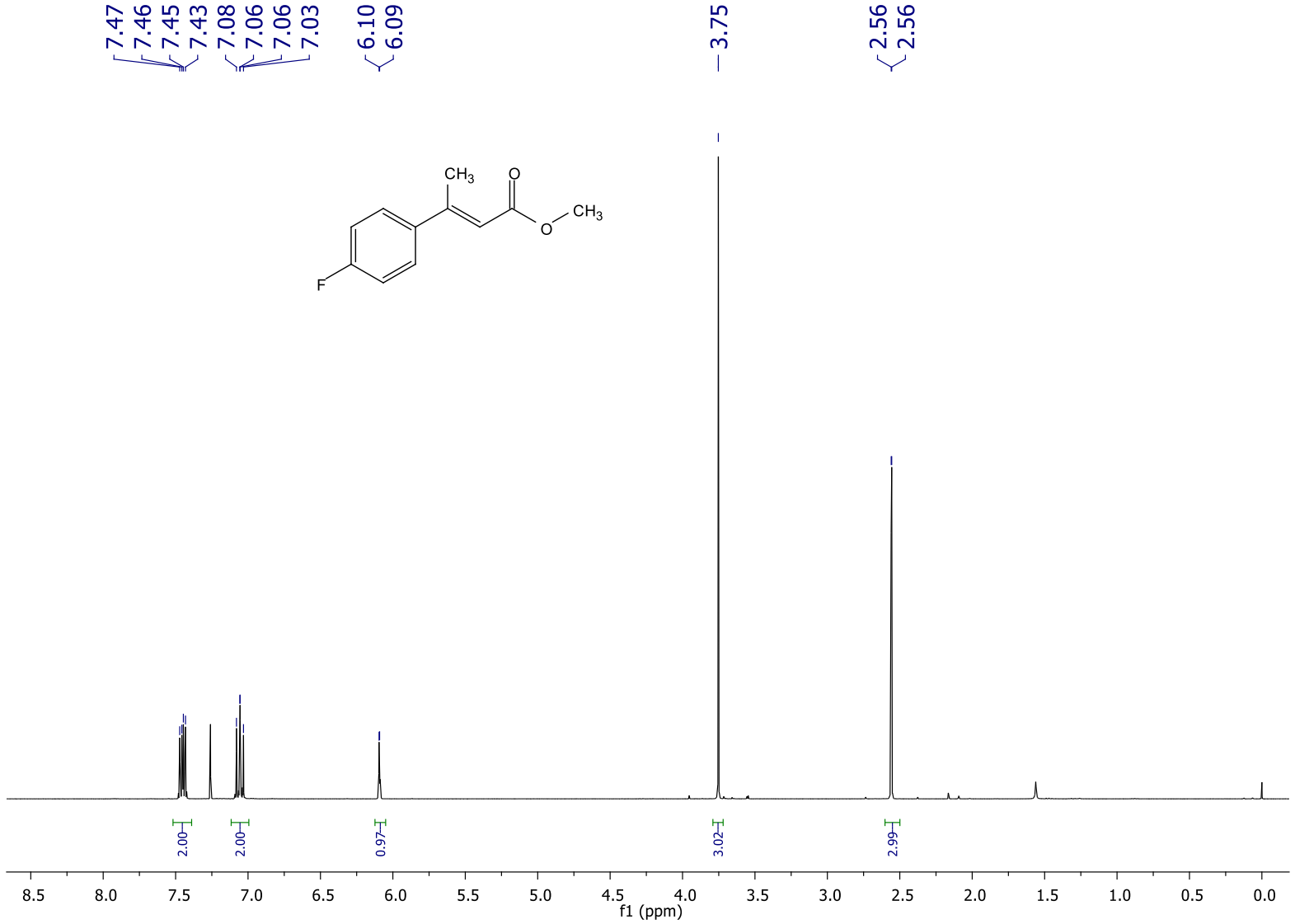


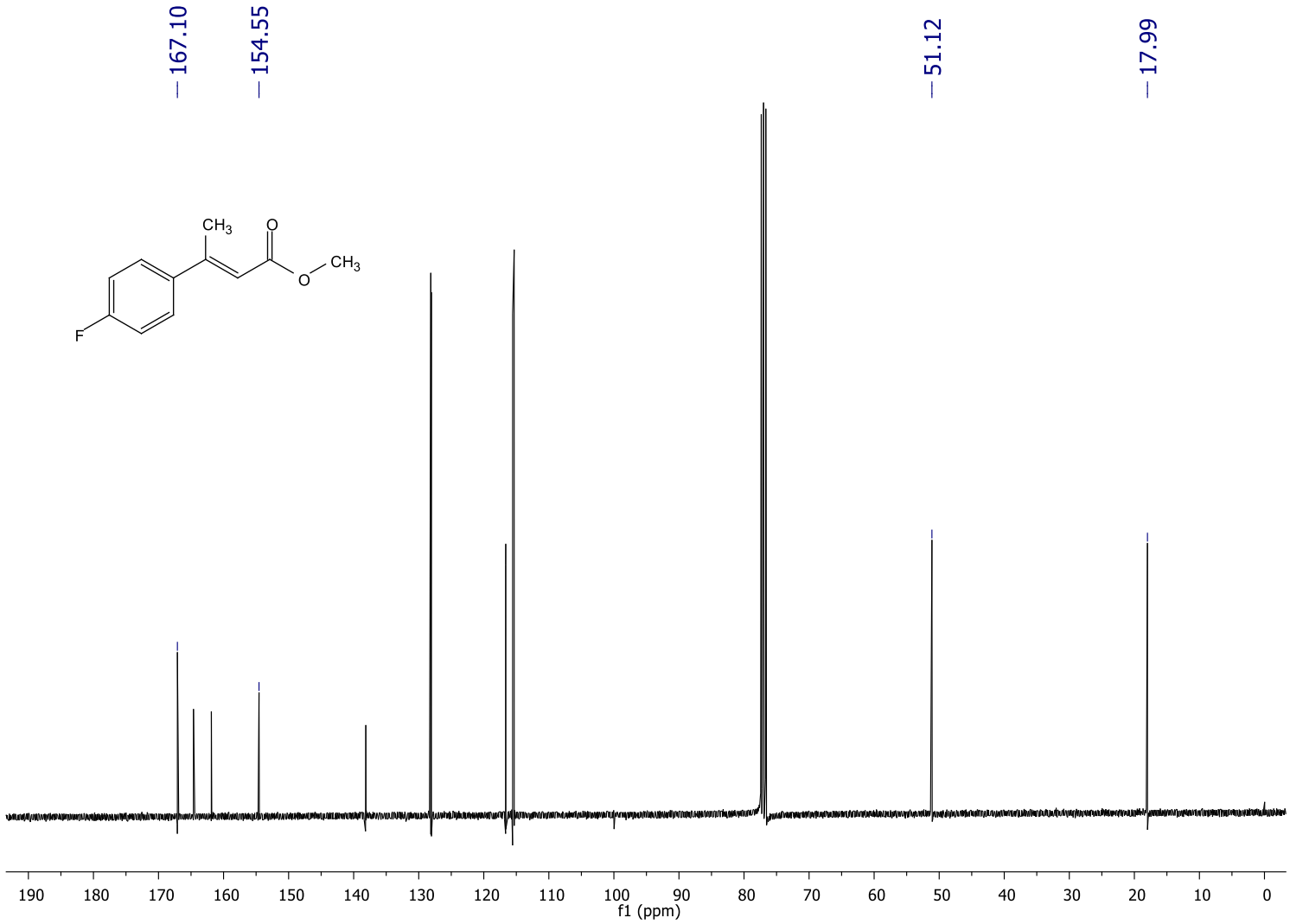

166.14
162.32
142.18
130.94
129.77
119.98
116.03
80.55
28.18
O
CH3
CH3
CH3
O
F
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

Methyl 2-(4-bromobenzyl)acrylate (**4ad'**) and methyl (*E*)-3-(4-bromophenyl)-3-methylacrylate (**4ad**)

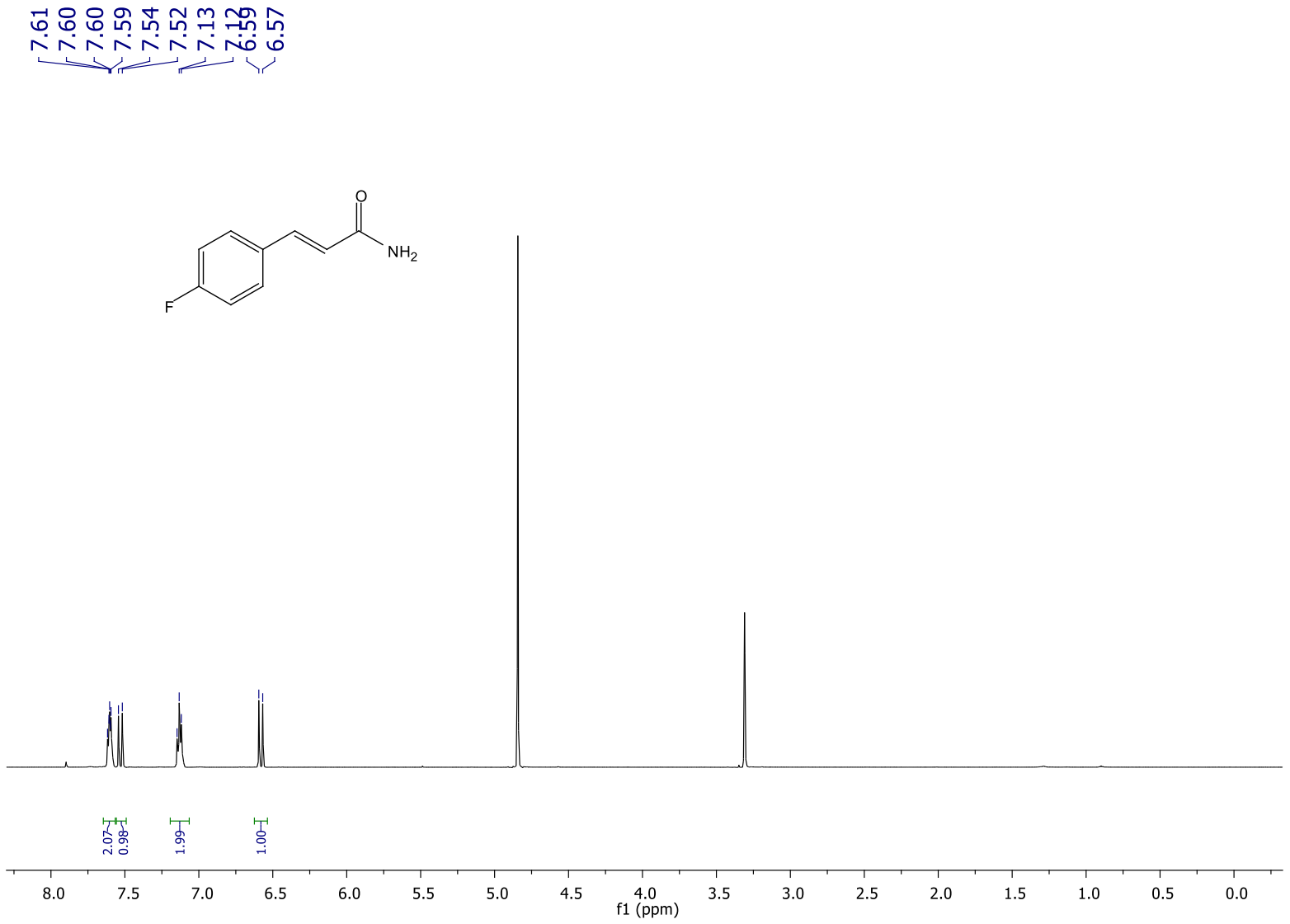


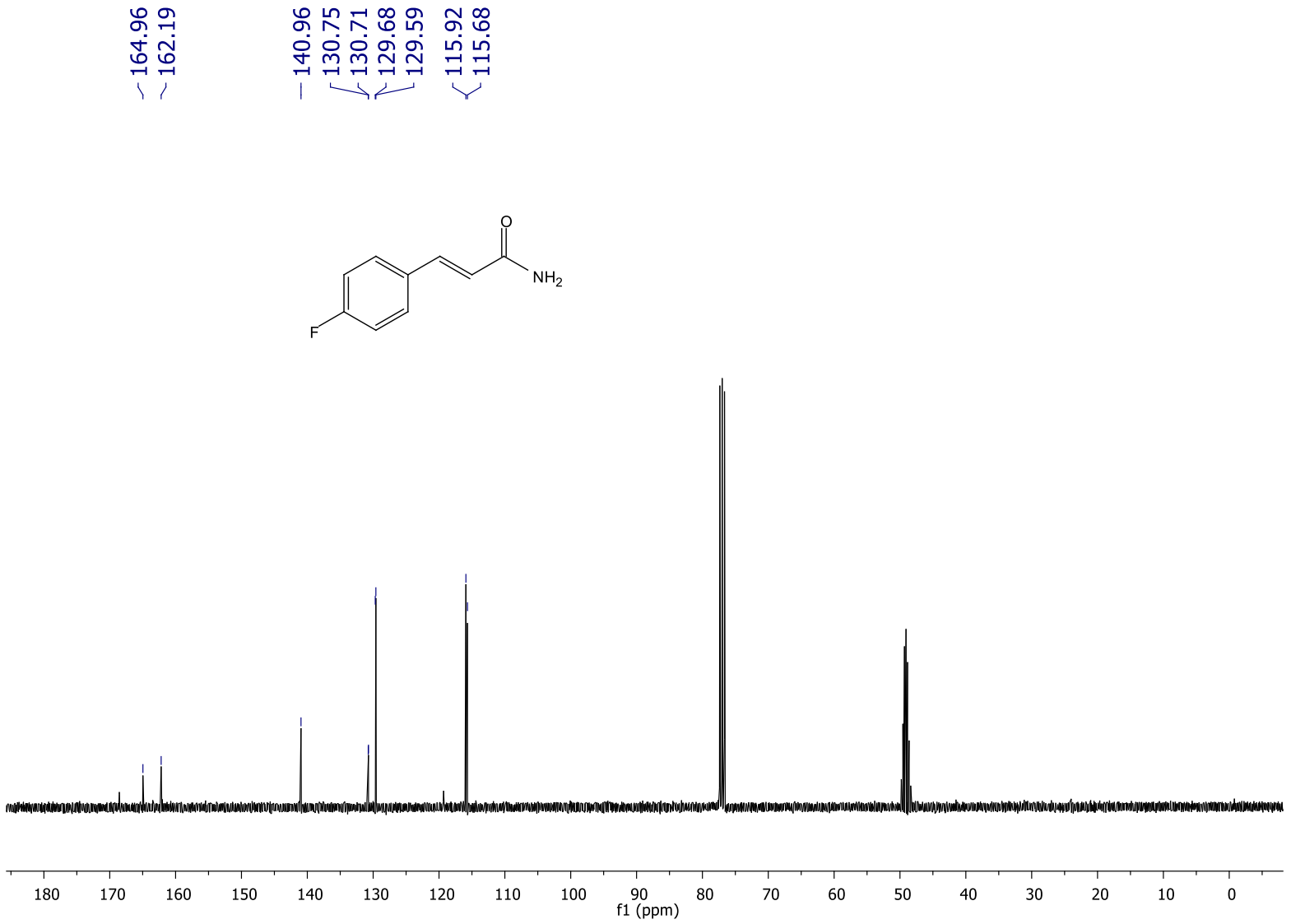
Methyl (*E*)-3-(4-fluorophenyl)-3-methylacrylate (**4ce**)



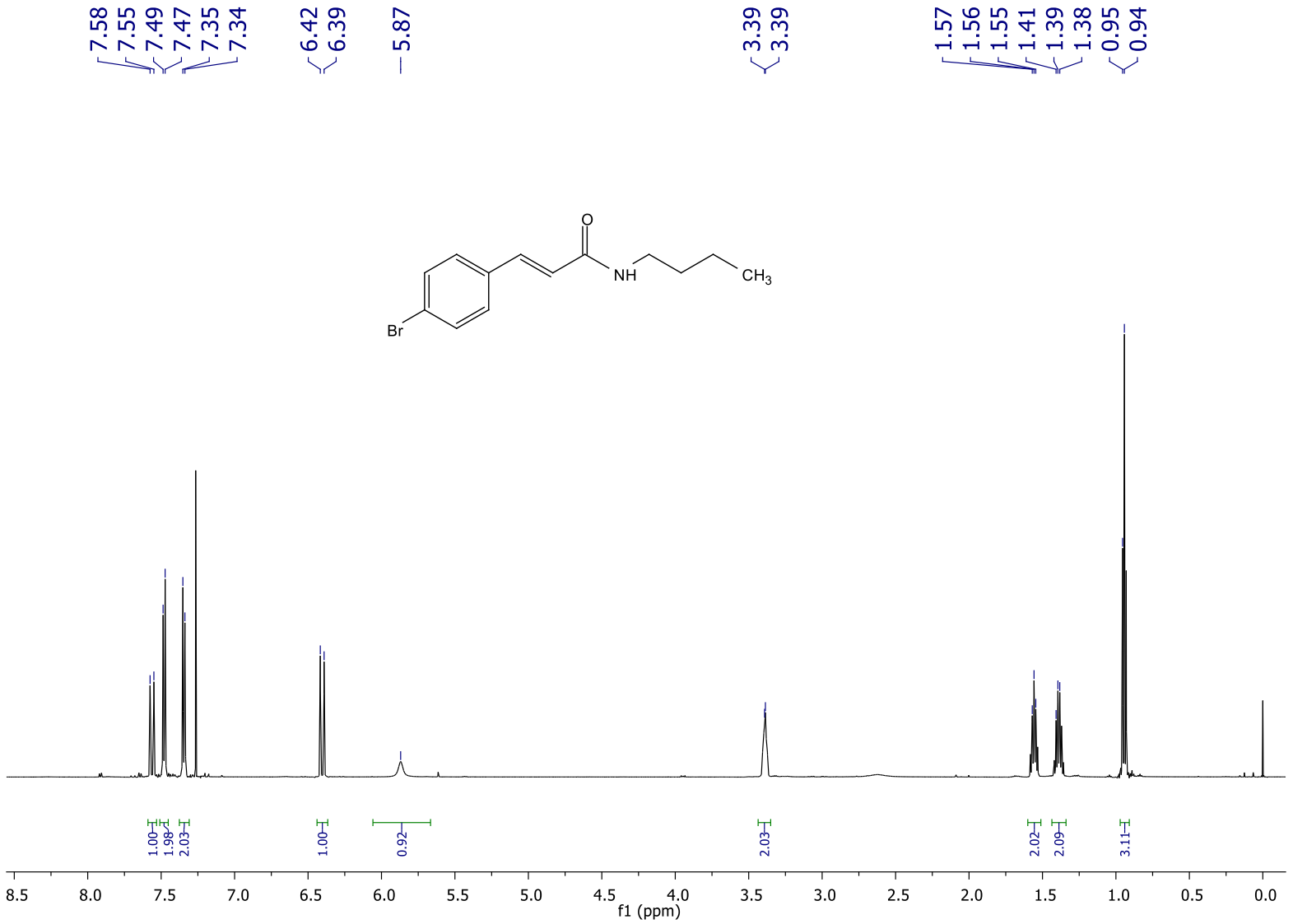

167.10
154.55
51.12
17.99
CH3
O
CH3
O
F
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

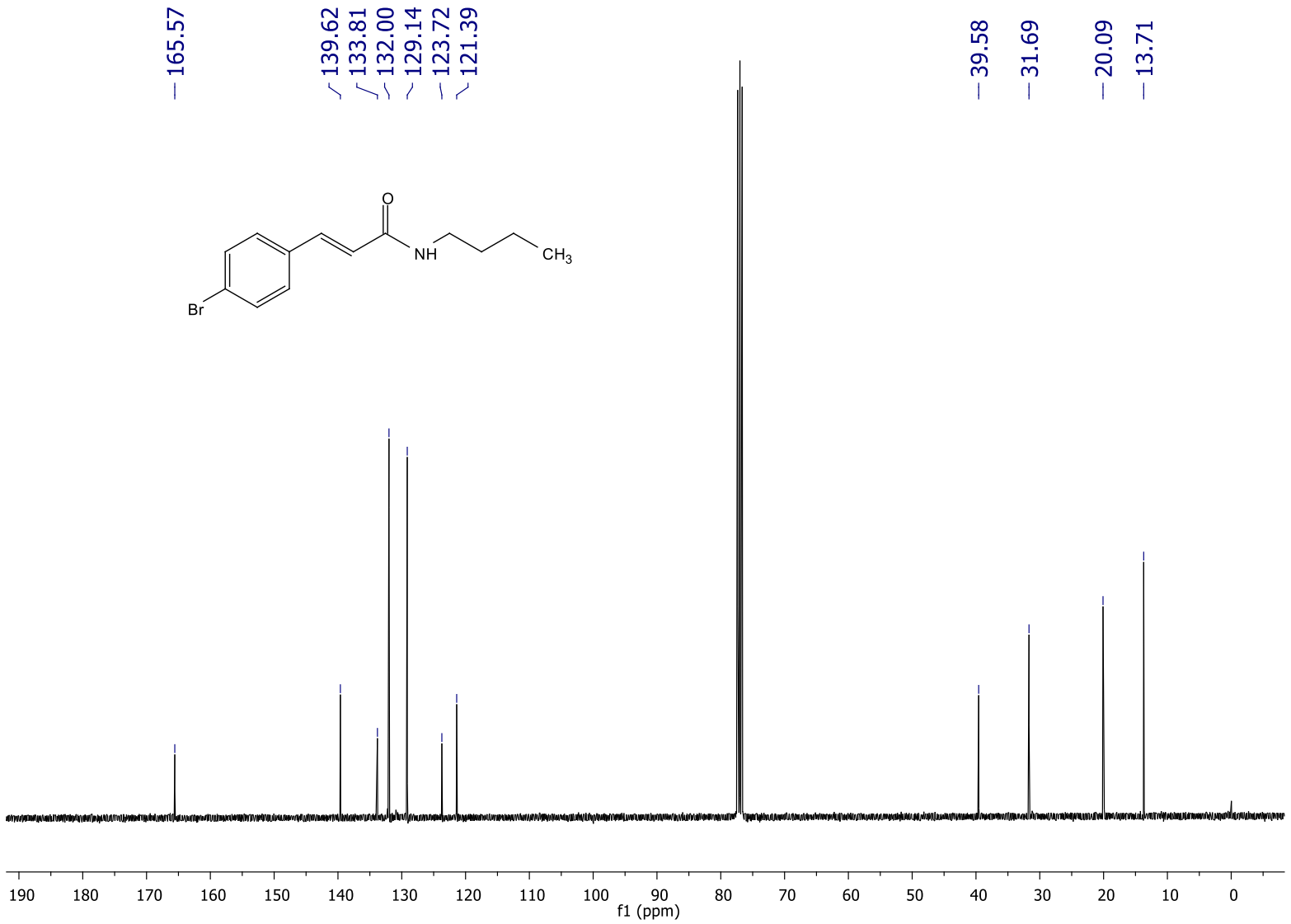
4-Fluorocinnamide (**4cf**)



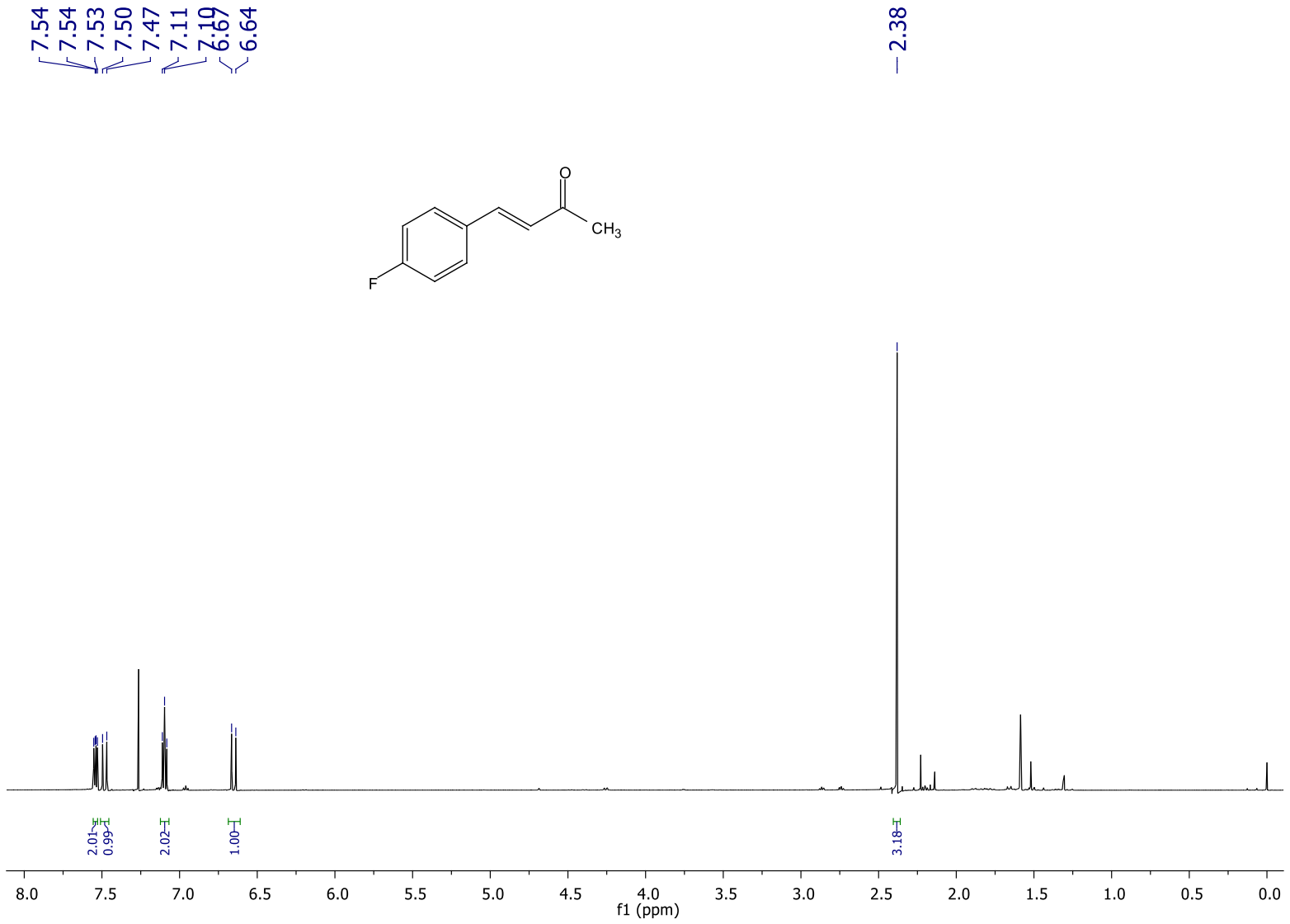

164.96
162.19
140.96
130.75
130.71
129.68
129.59
115.92
115.68
O
NH2
F
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

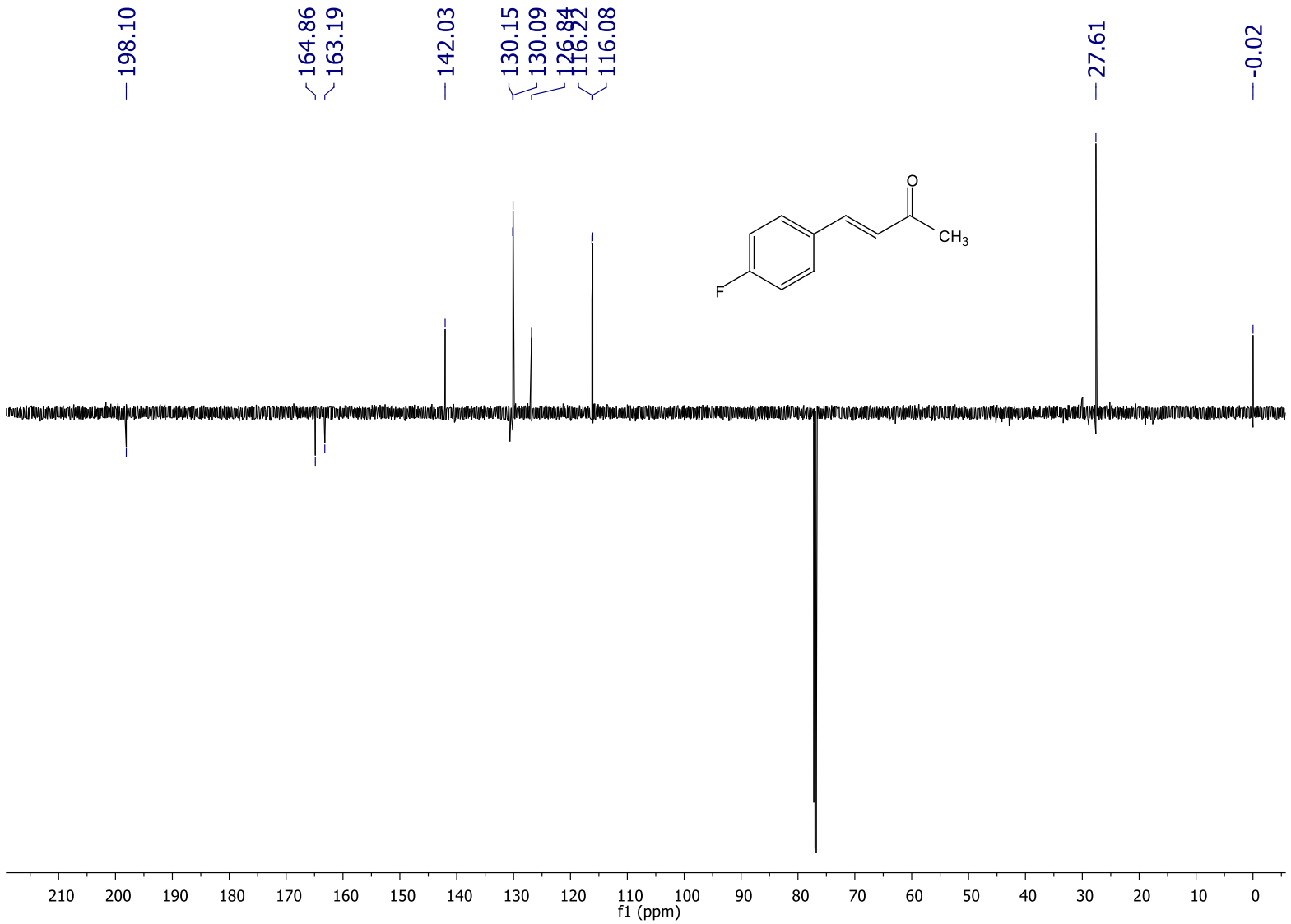
N-Butyl 4-bromocinnamide (**4ag**)



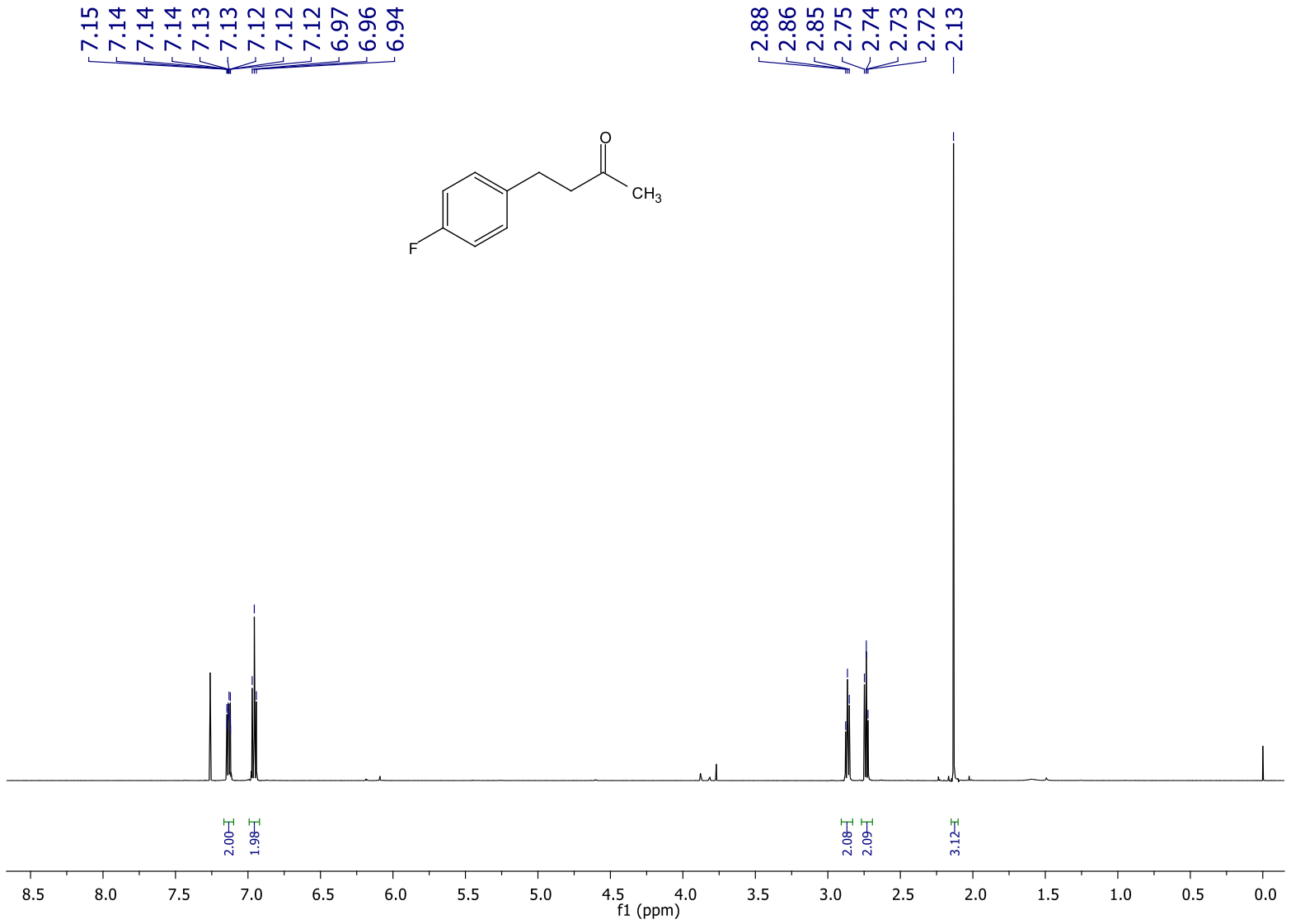

165.57
139.62
133.81
132.00
129.14
123.72
121.39
39.58
31.69
20.09
13.71
O
NH
CH3
Br
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

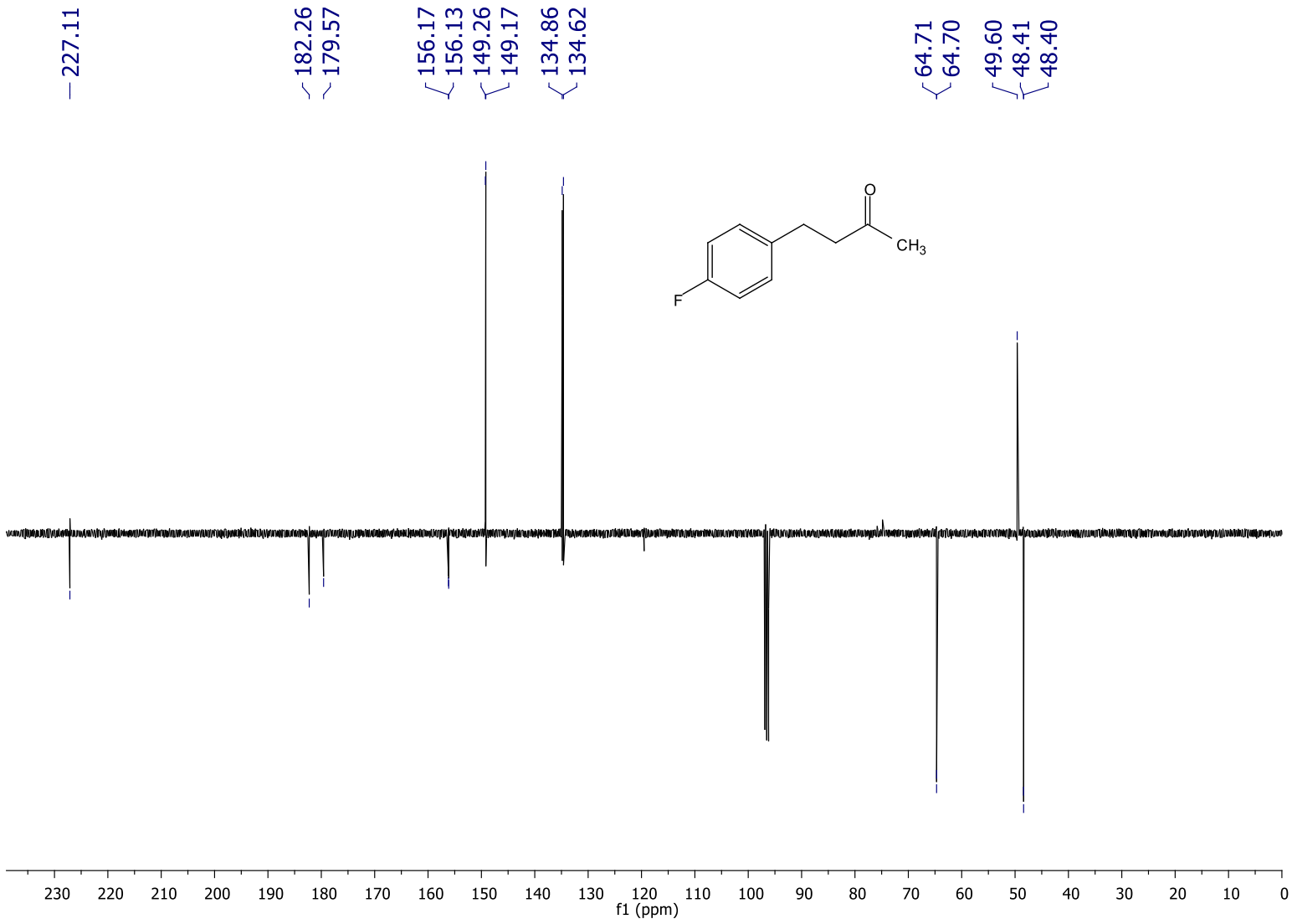
(*E*)-4-(4-Fluorophenyl)but-3-en-2-one (**4ah**)



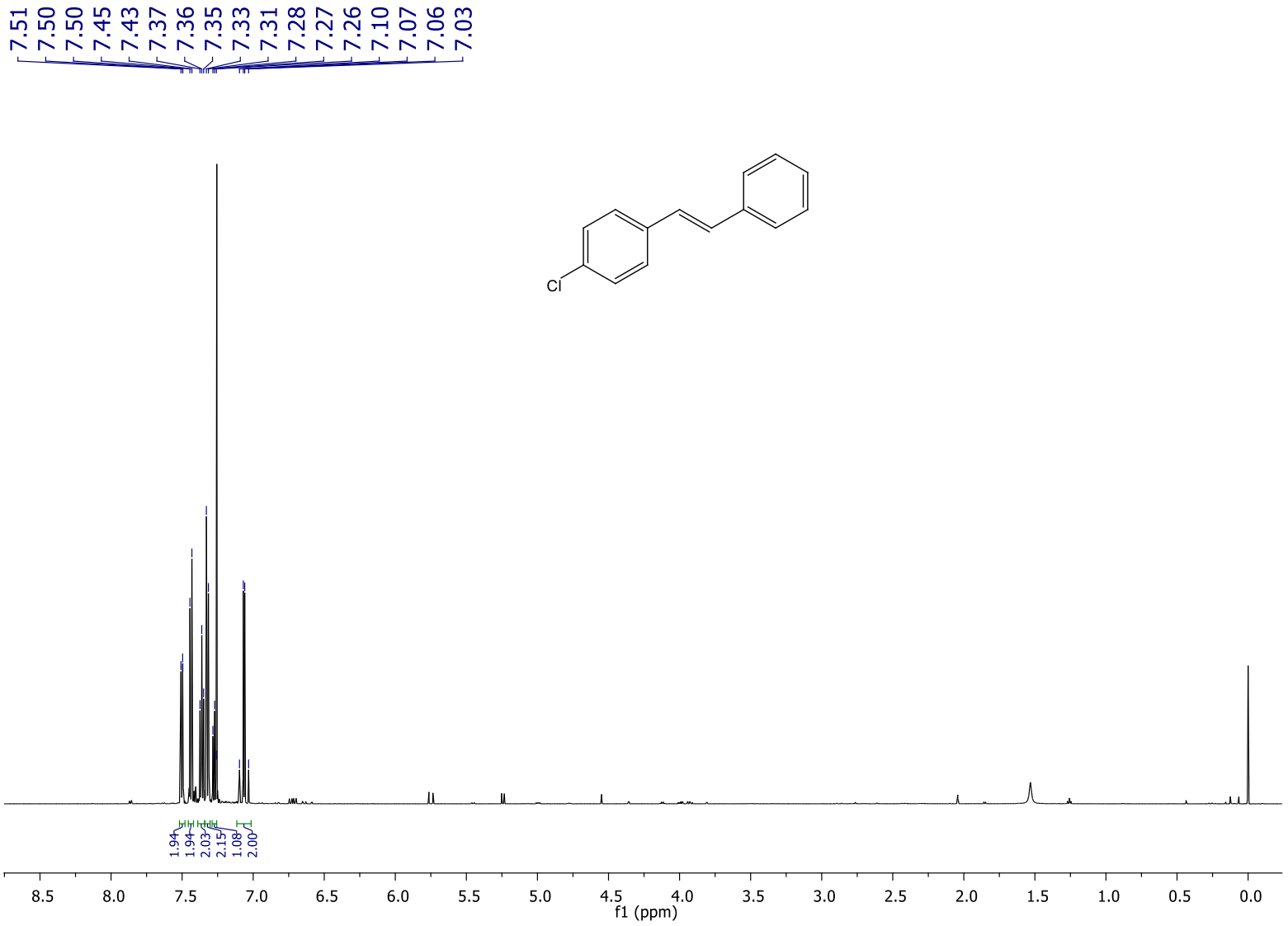

198.10
164.86
163.19
142.03
130.15
130.09
126.84
116.22
116.08
27.61
-0.02
O
CH3
F
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

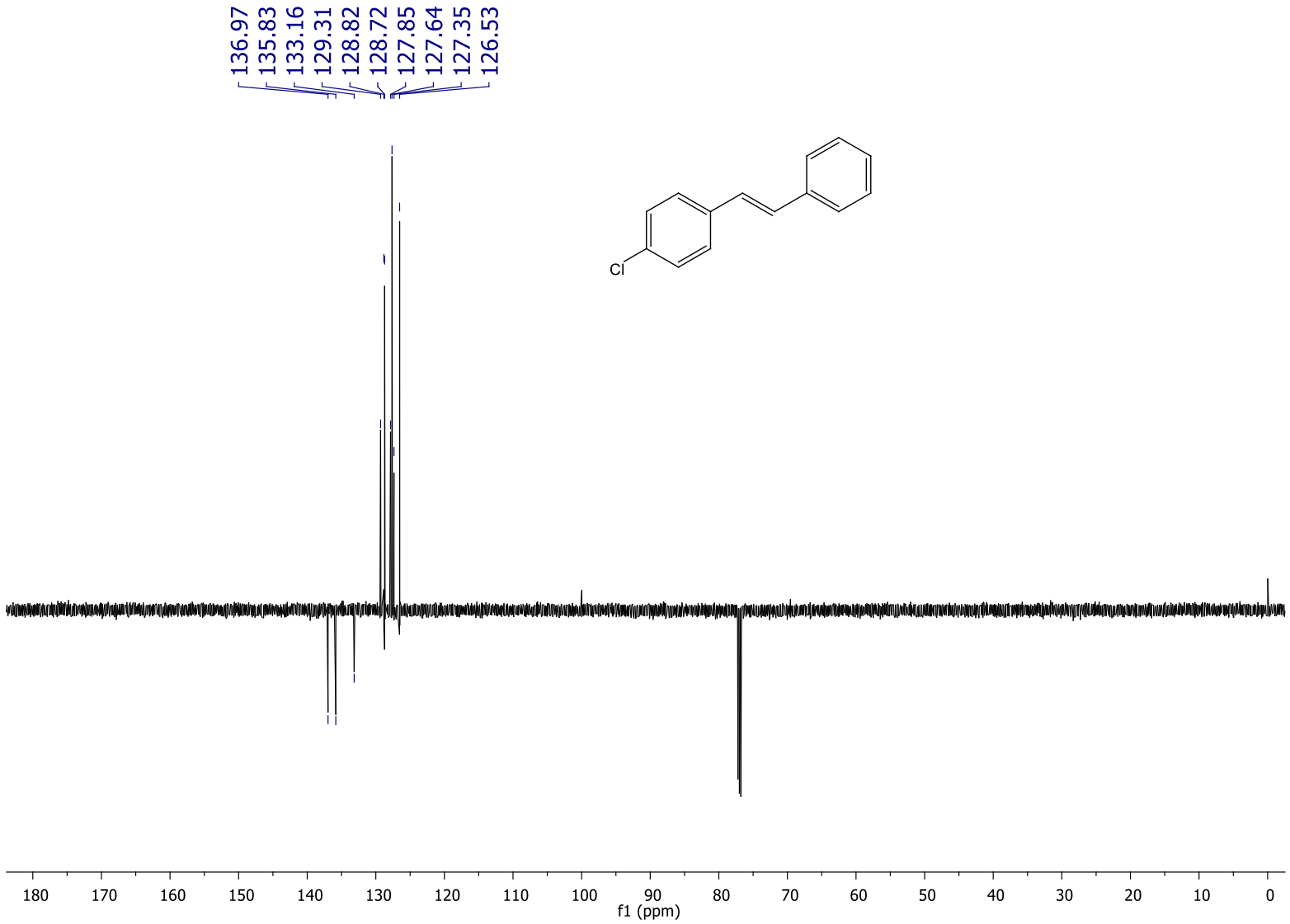
4-(4-Fluorophenyl)butan-2-one (**4ah'**)



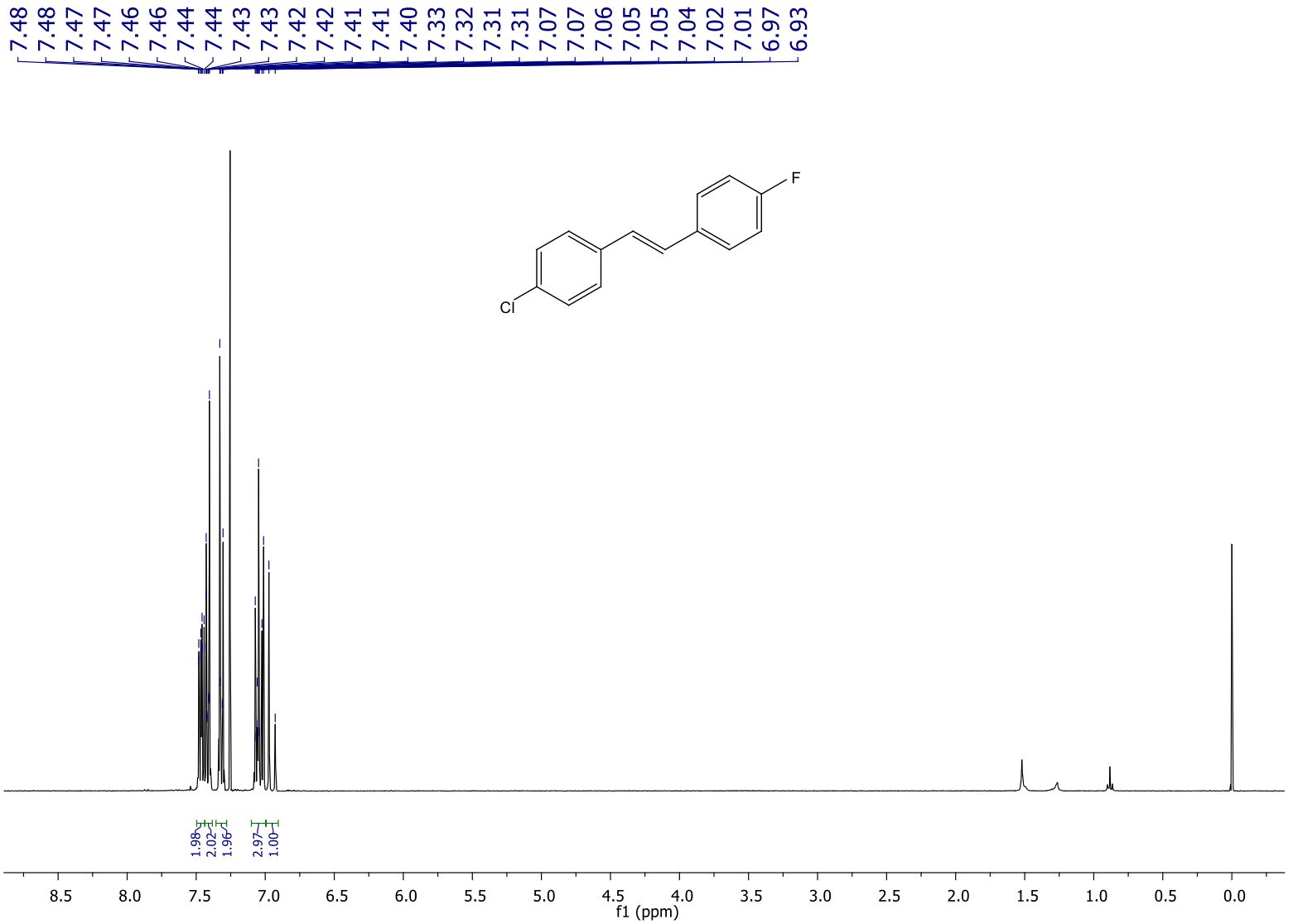

227.11
182.26
179.57
156.17
156.13
149.26
149.17
134.86
134.62
64.71
64.70
49.60
48.41
48.40
O
CH3
F
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

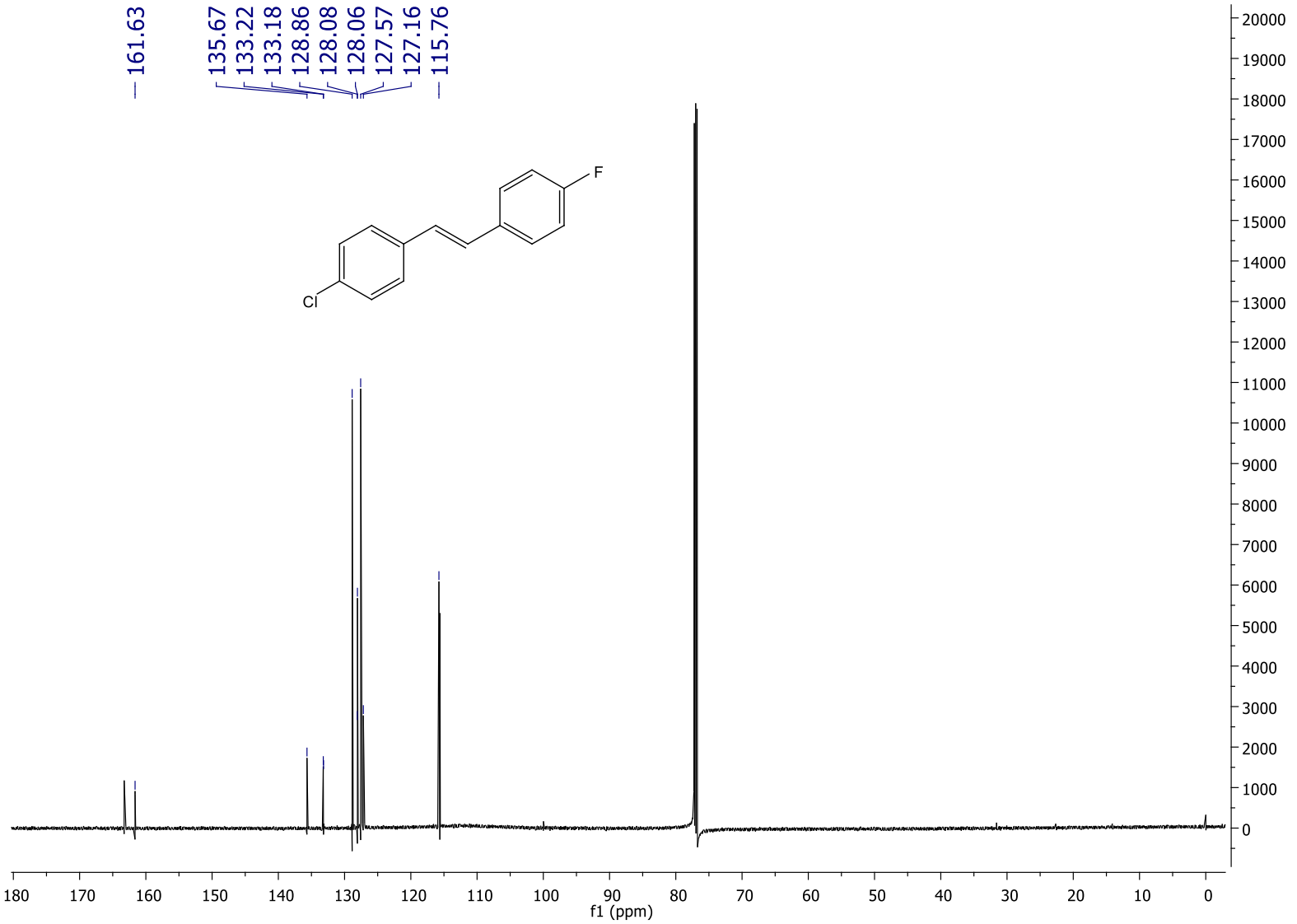
(*E*)-4-Chlorostilbene (**4di**)



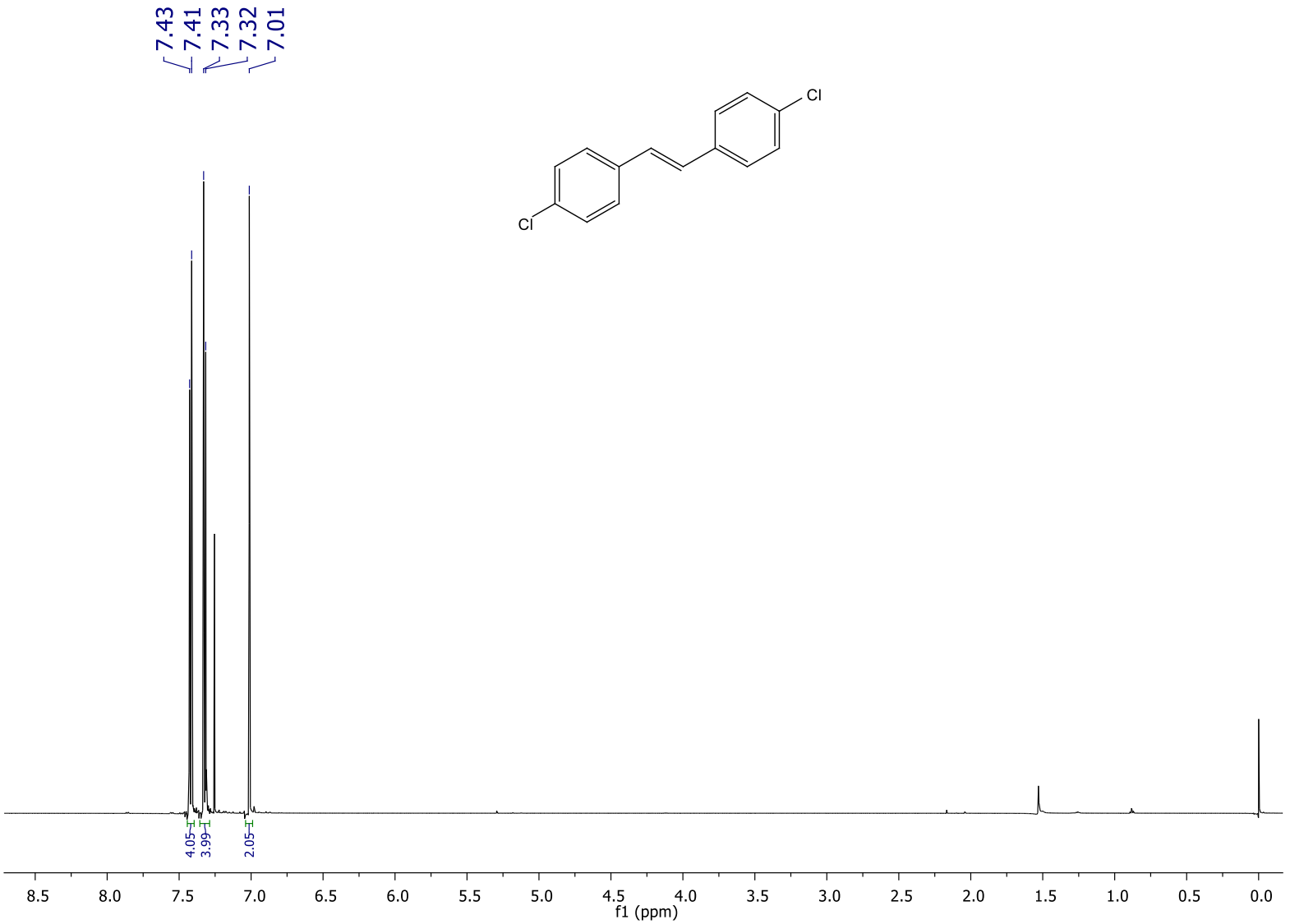

136.97
135.83
133.16
129.31
128.82
128.72
127.85
127.64
127.35
126.53
Cl
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

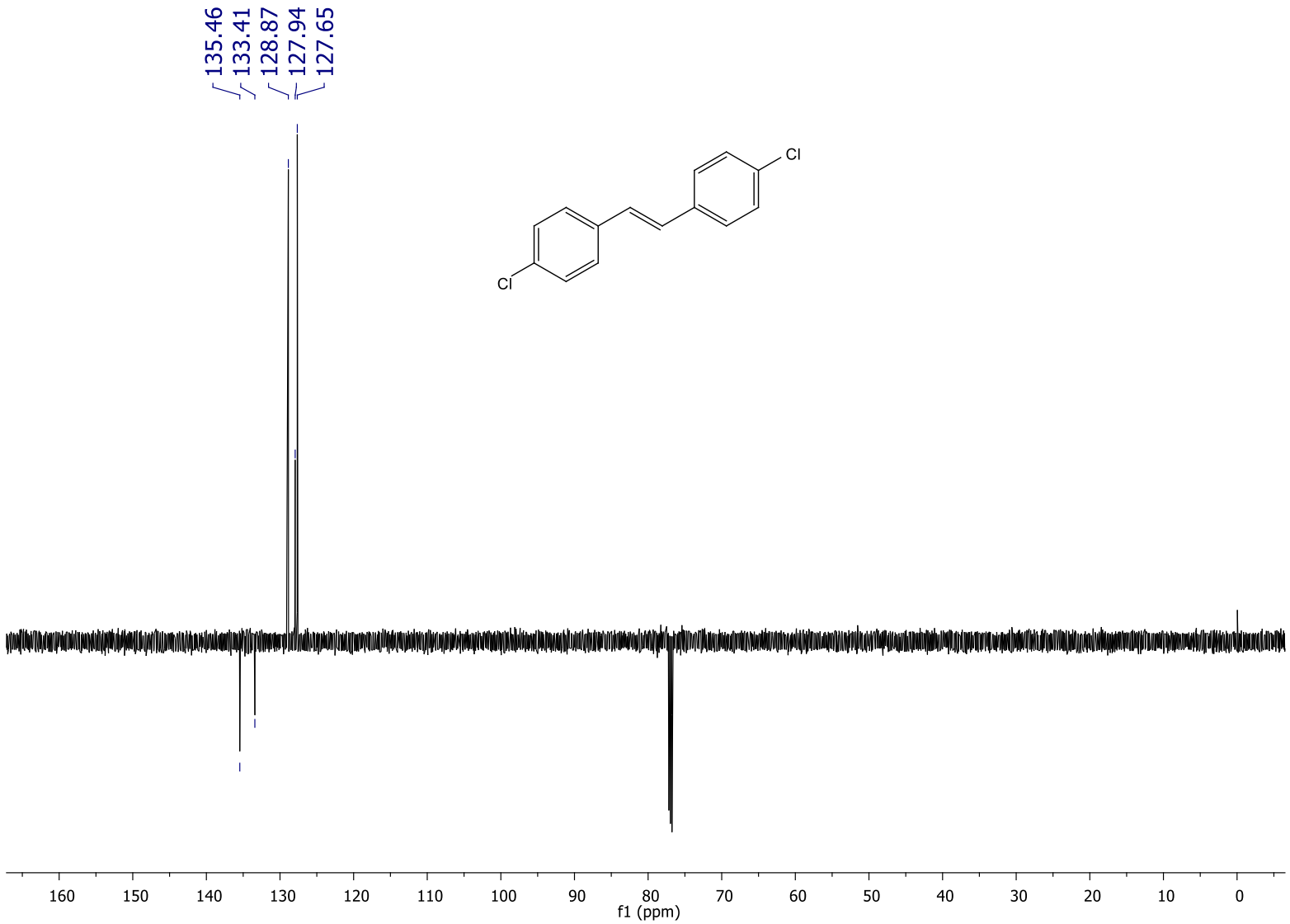
(*E*)-4-Chloro-4’-fluorostilbene (**4dj**)



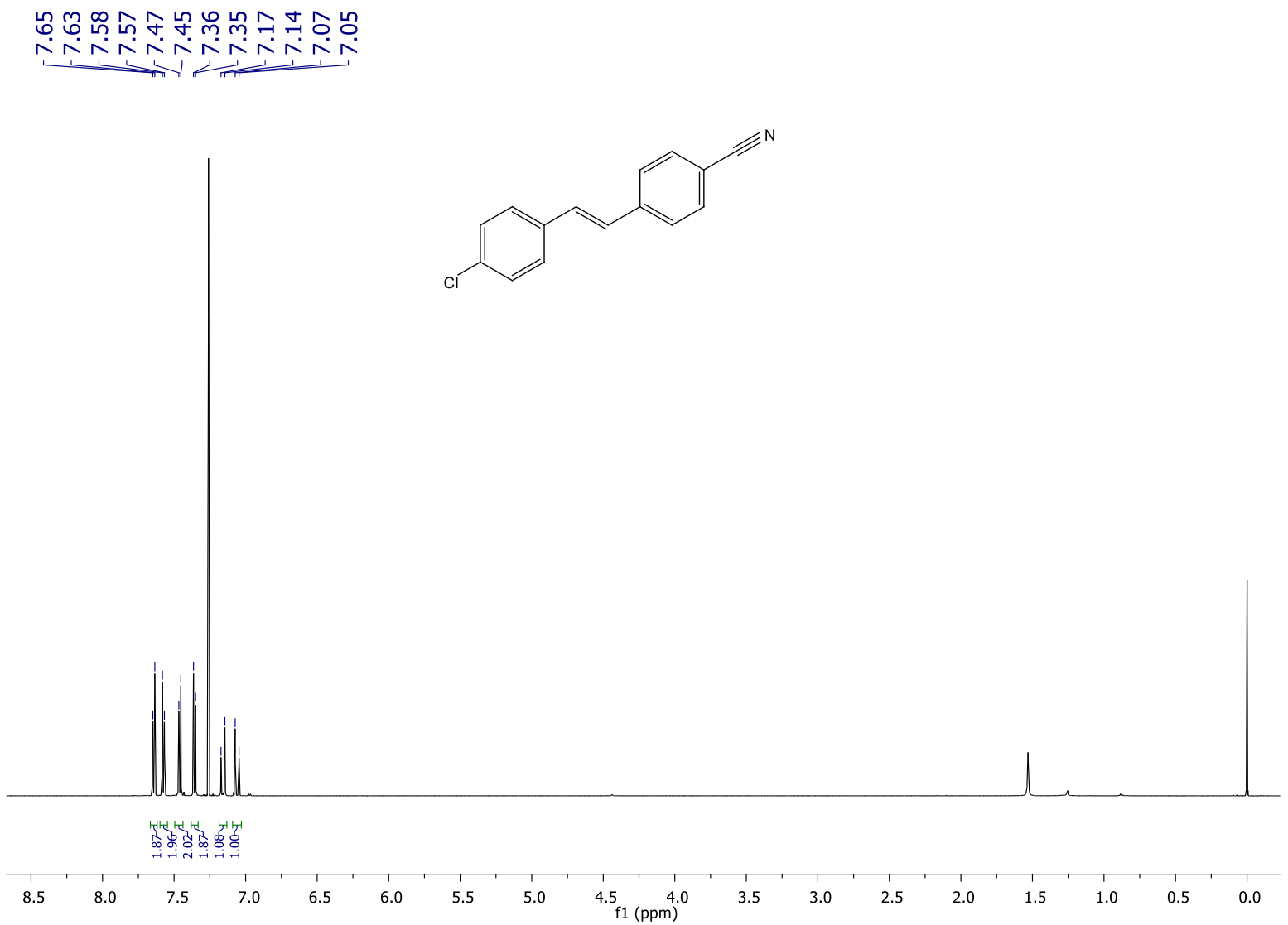

161.63
135.67
133.22
133.18
128.86
128.08
128.06
127.57
127.16
115.76
F
Cl
f1 (ppm)

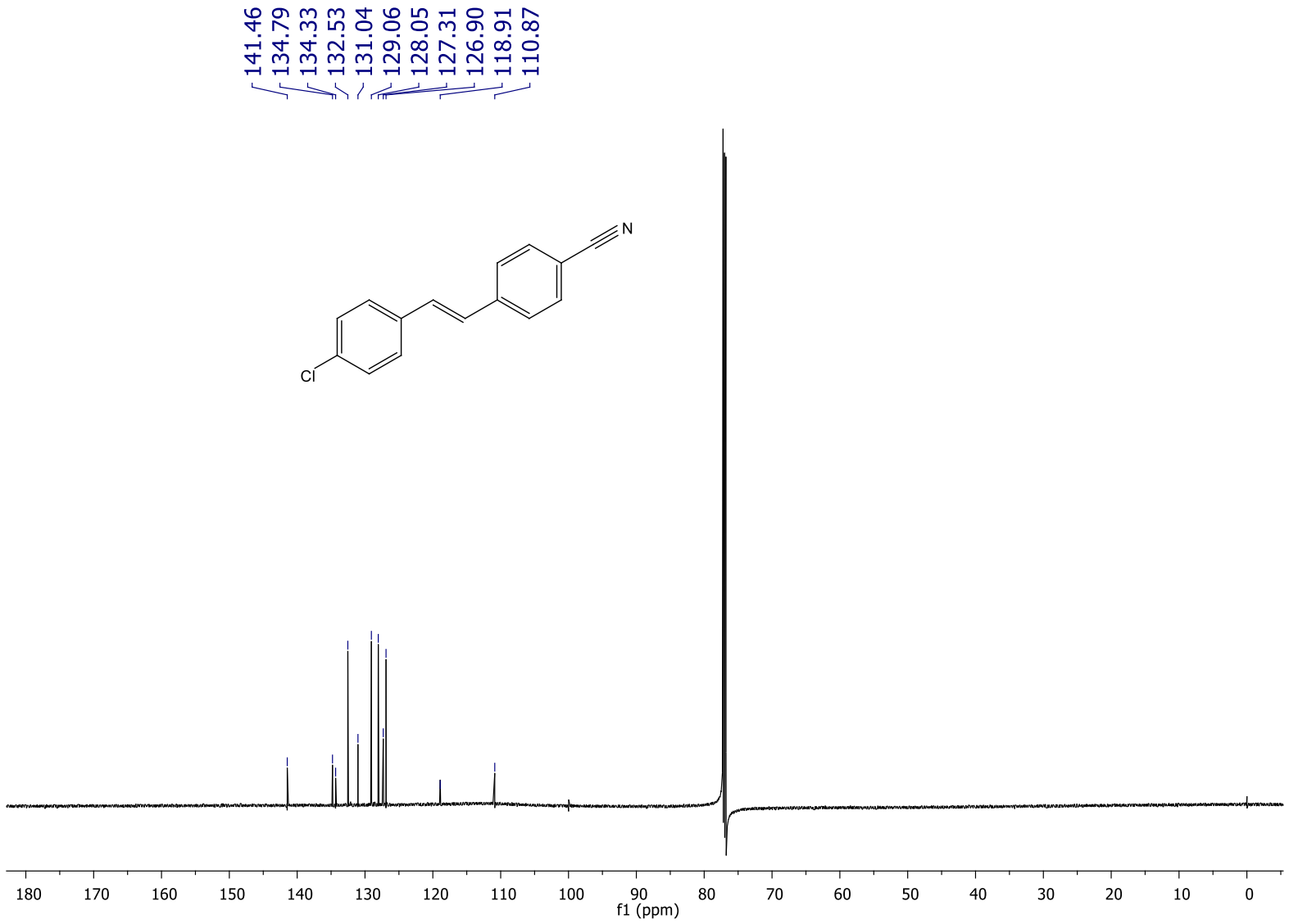
(*E*)-4,4‘-Dichlorostilbene (**4dk**)



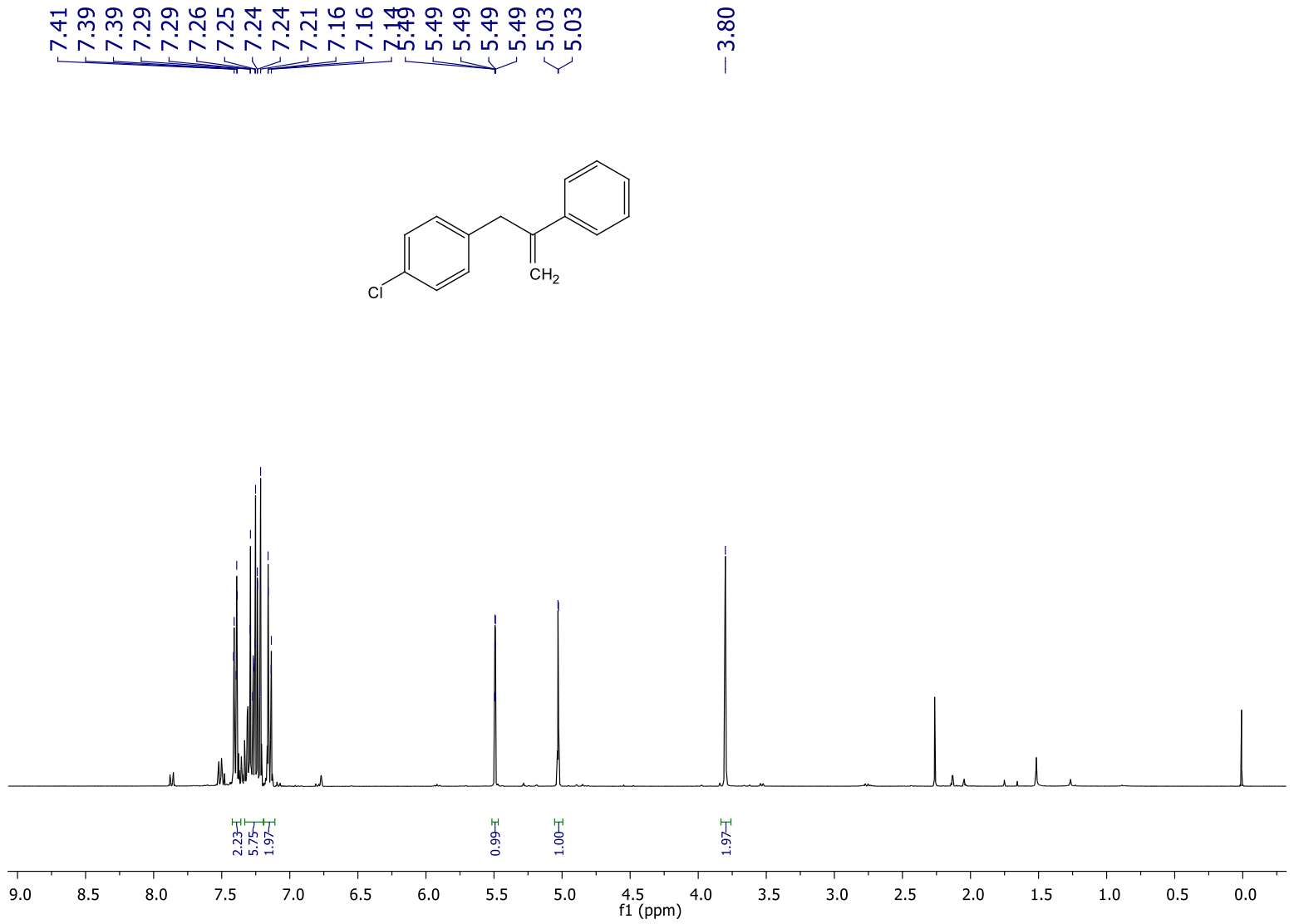

135.46
133.41
128.87
127.94
127.65
Cl
Cl
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

(*E*)-4-Chloro-4’-cyanostilbene (**4dl**)

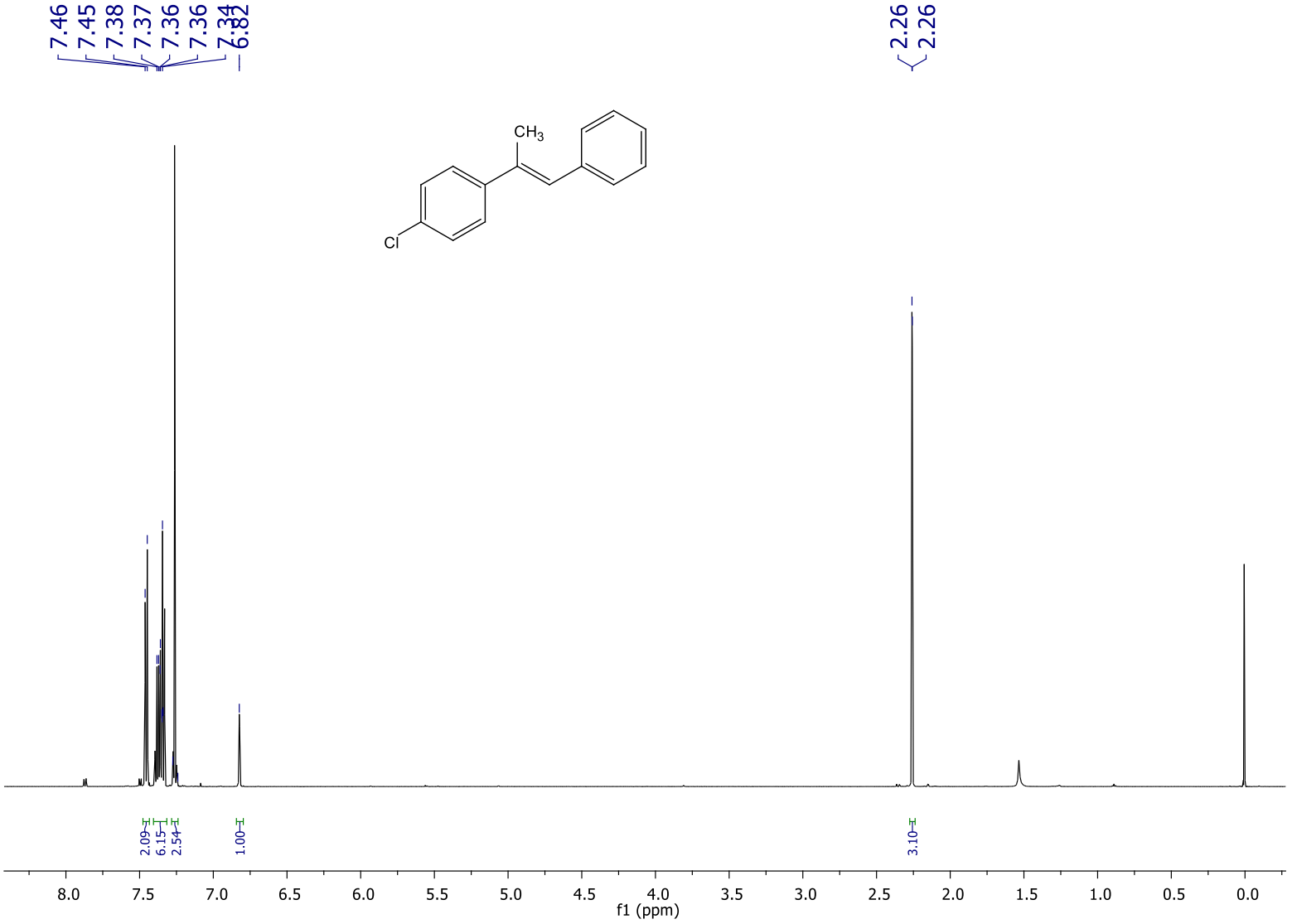


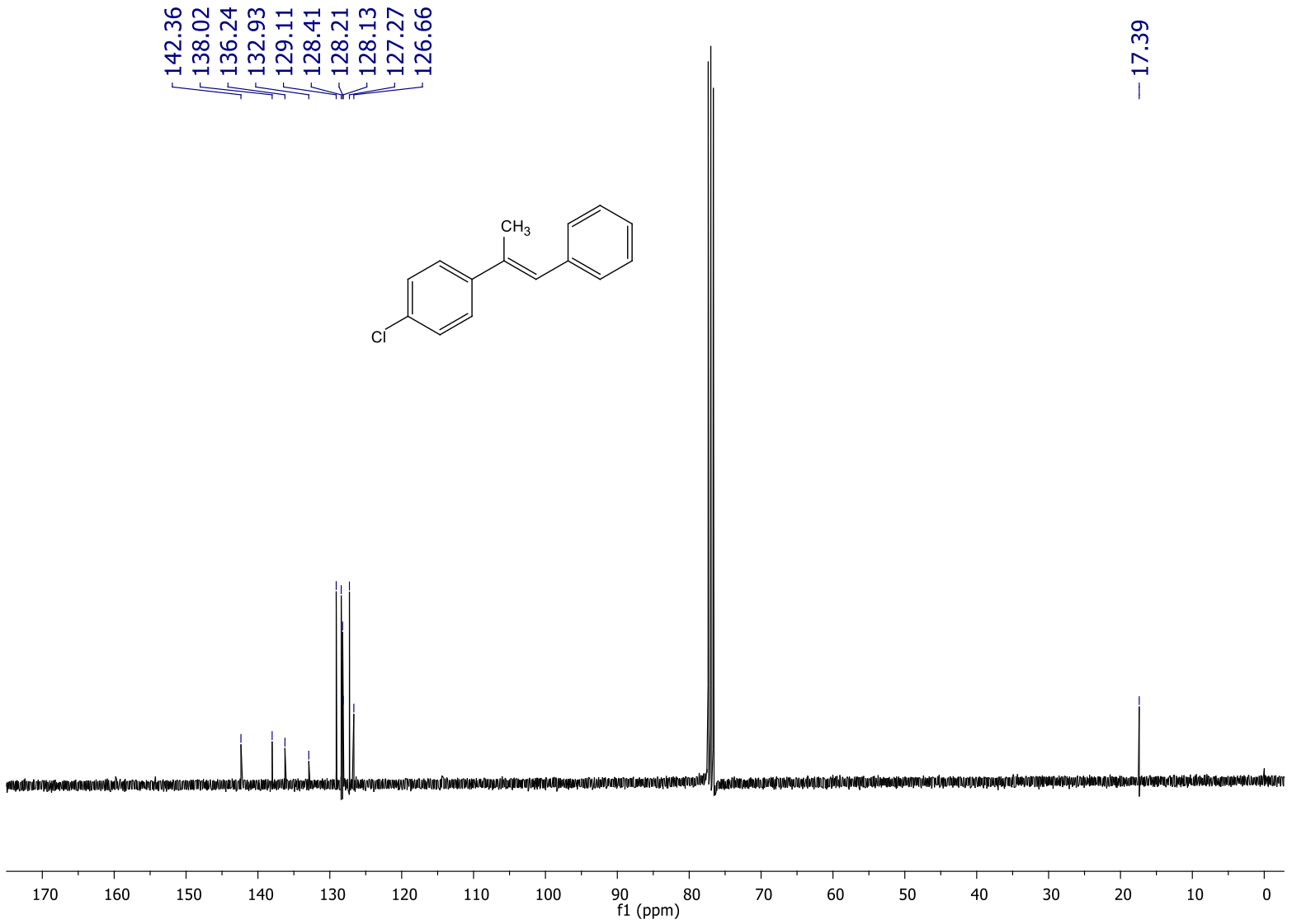

141.46
134.79
134.33
132.53
131.04
129.06
128.05
127.31
126.90
118.91
110.87
N
Cl
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

1-Chloro-4-(2-phenylallyl)benzene (**4dm'**)

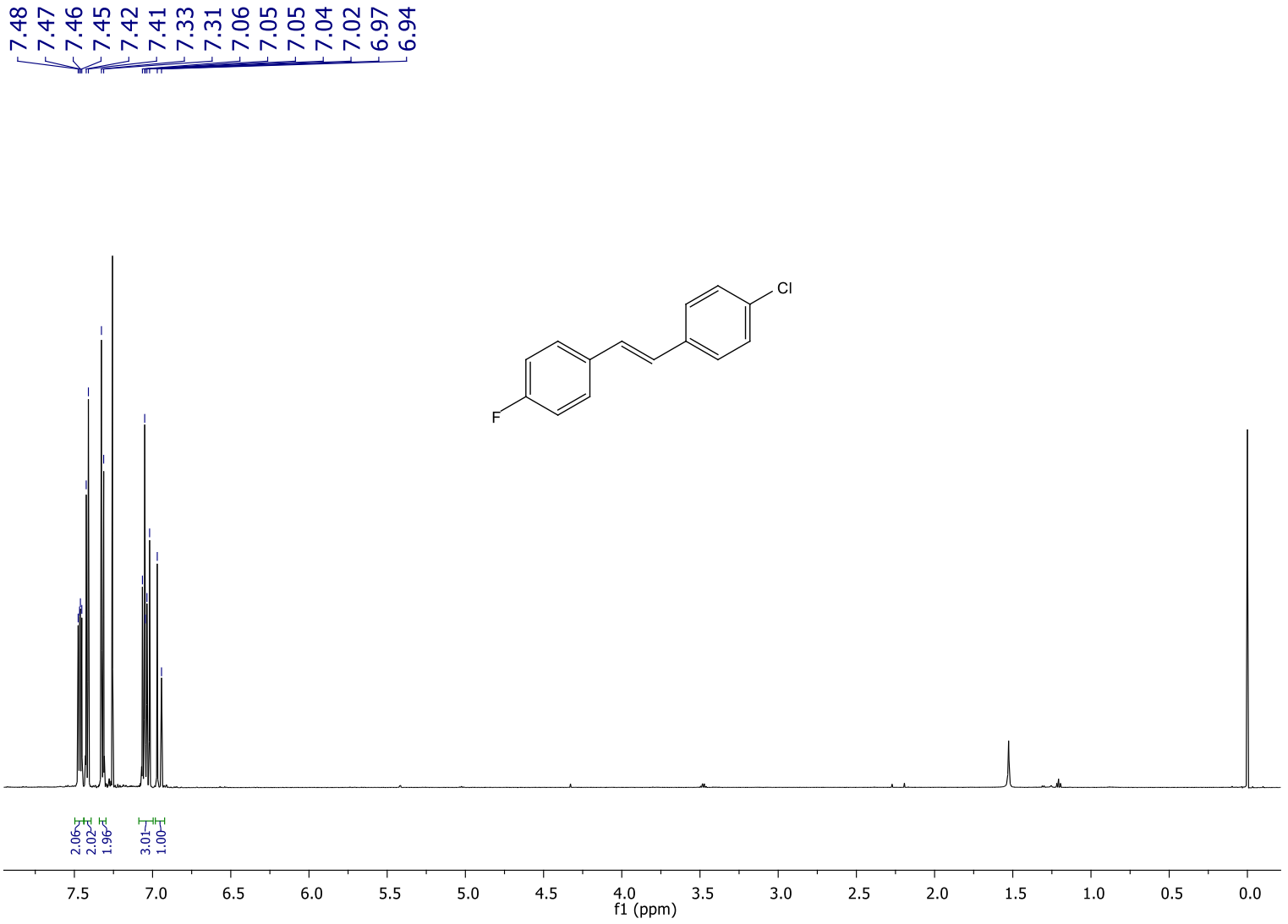


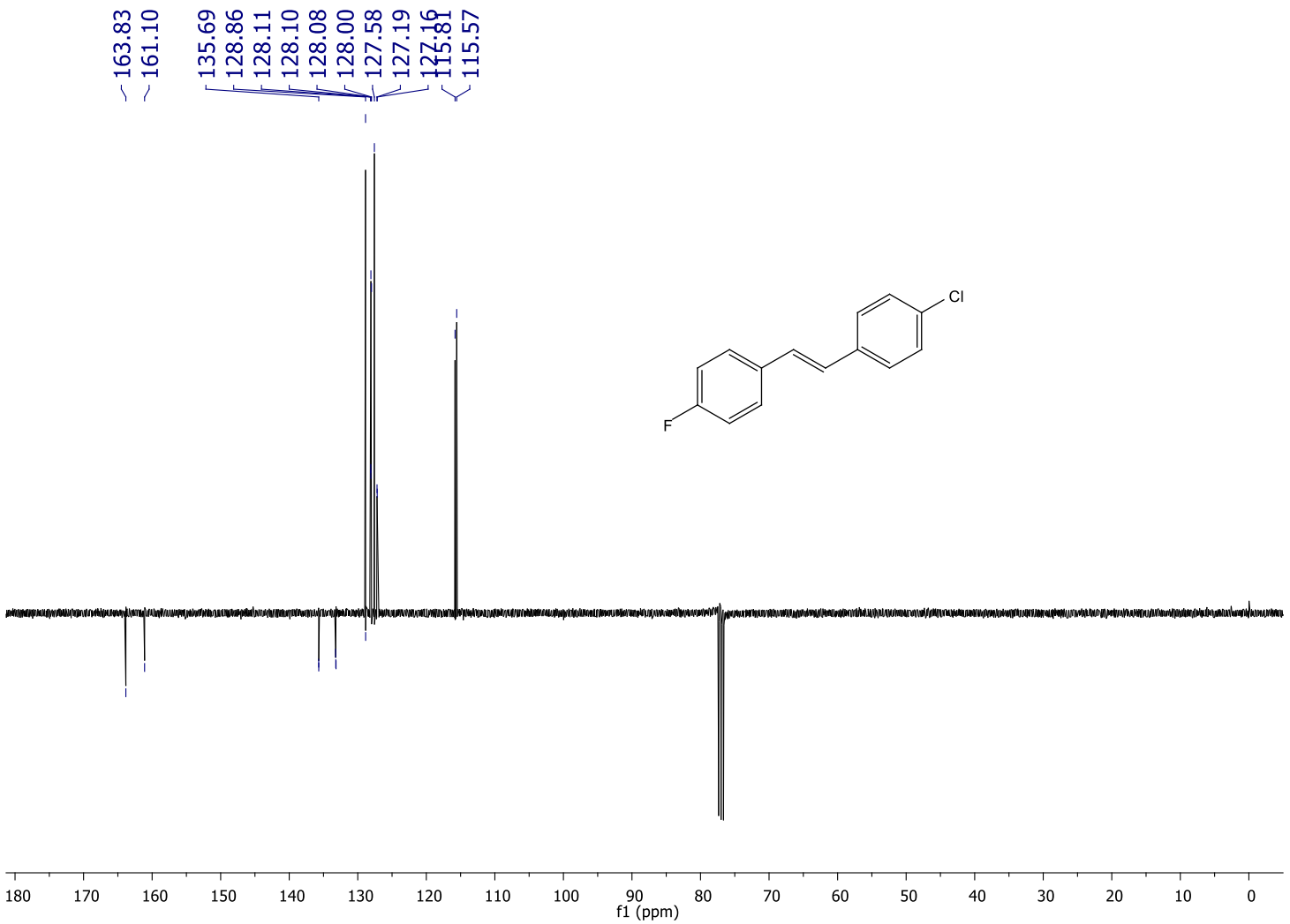
(*E*)-1-Chloro-4-(1-phenylprop-1-en-2-yl)benzene (**4dn**)



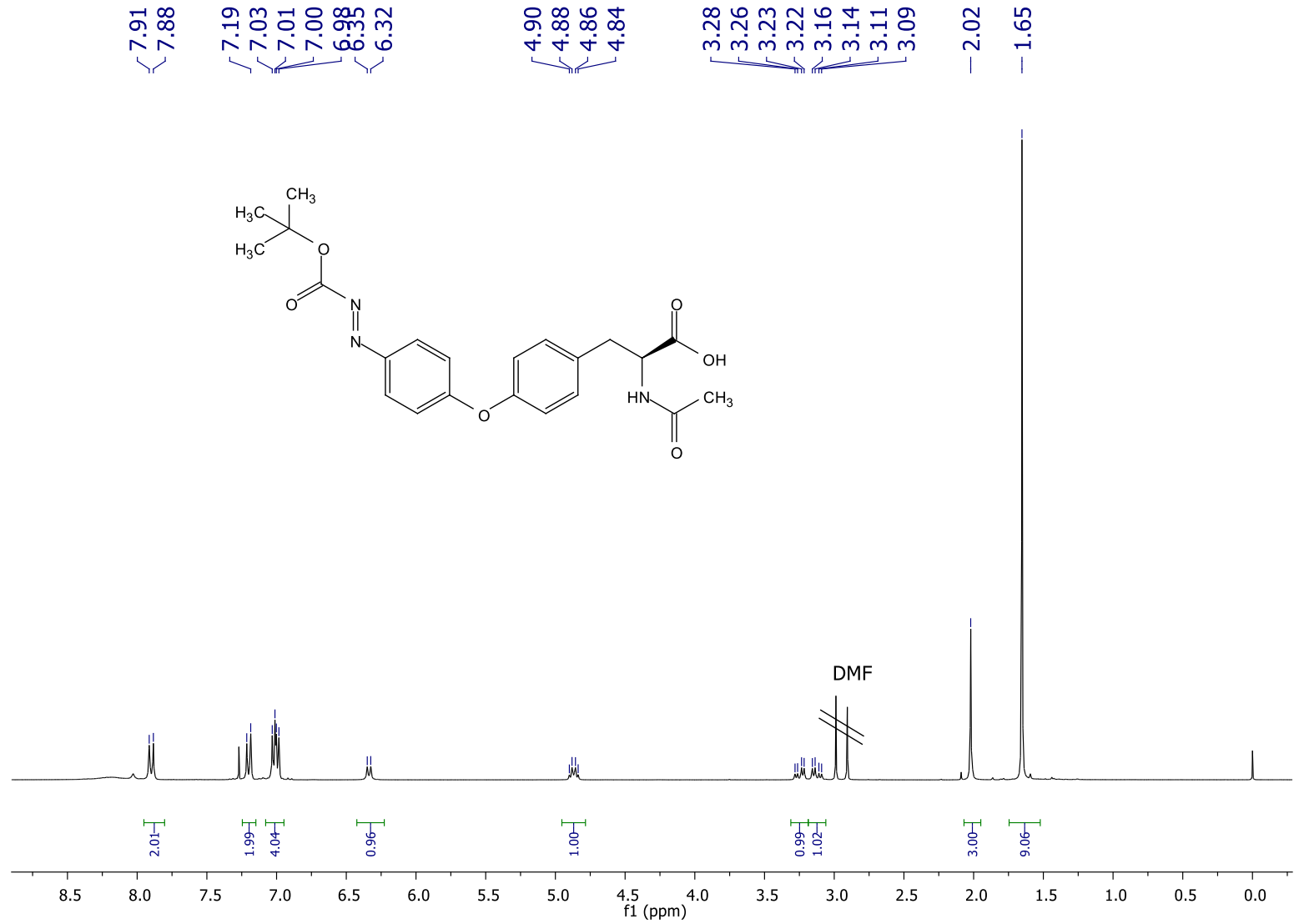

142.36
138.02
136.24
132.93
129.11
128.41
128.21
128.13
127.27
126.66
17.39
CH3
Cl
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

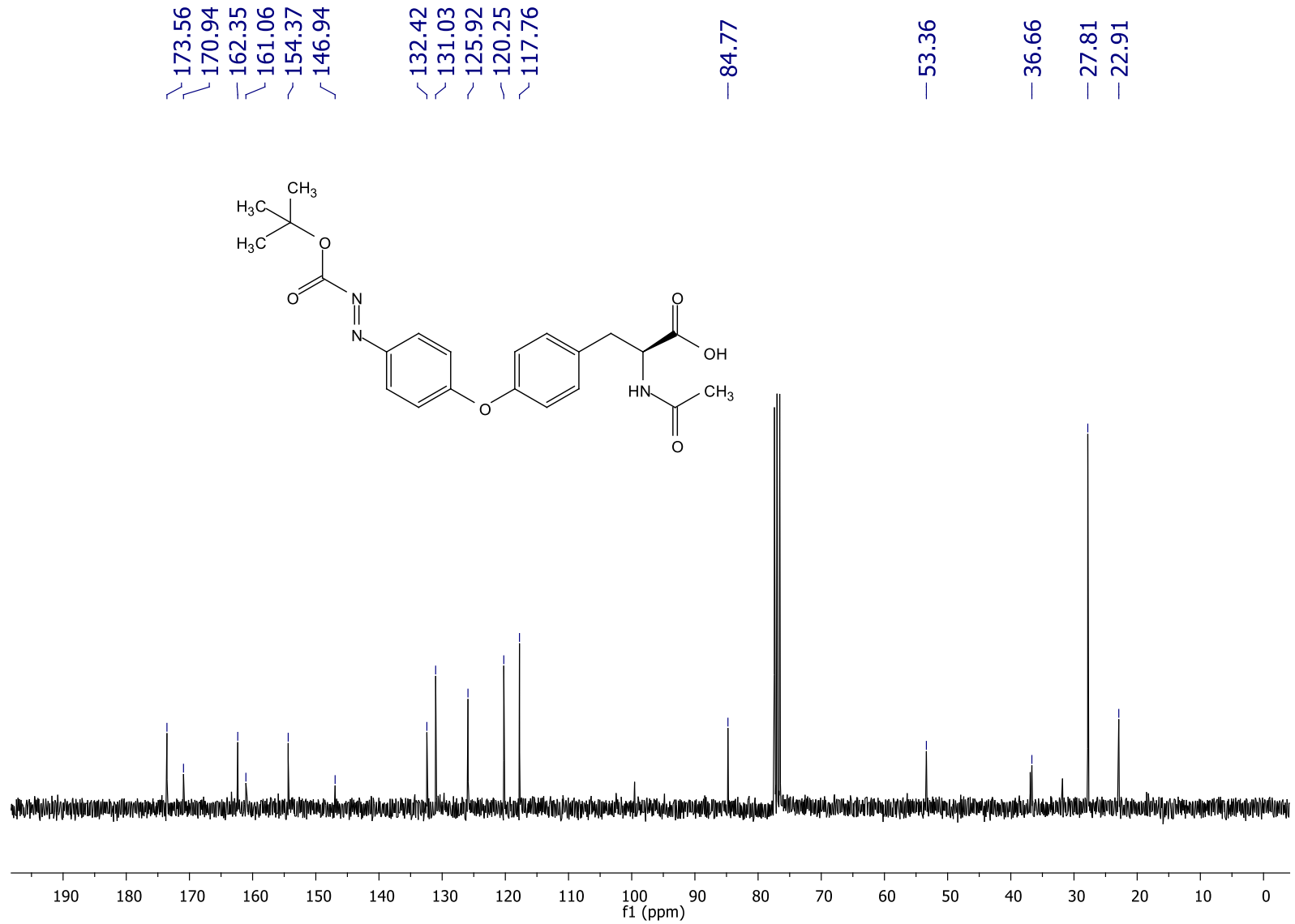
(*E*)-4-Chloro-4’-fluorostilbene (**4dj**)



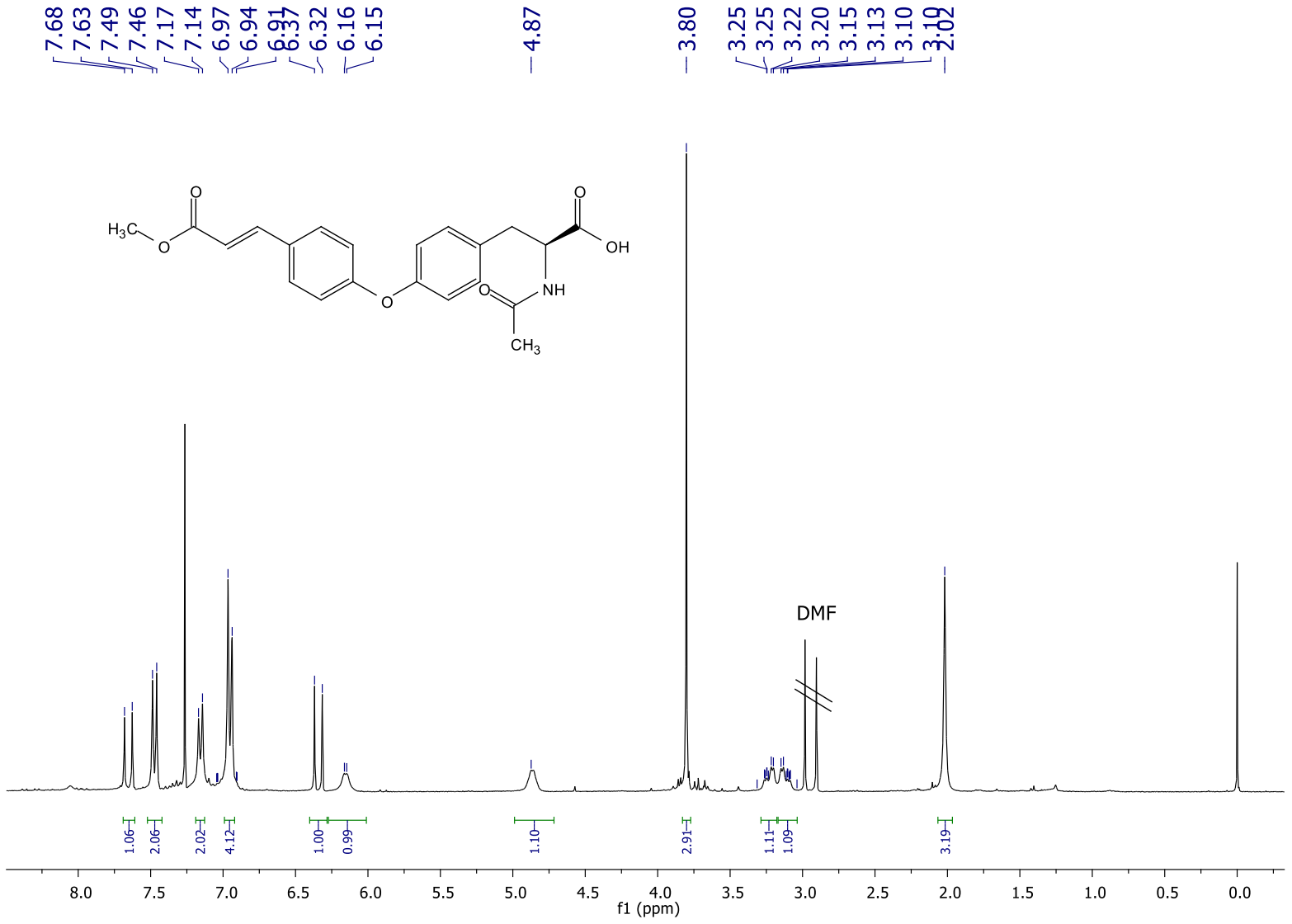

163.83
161.10
135.69
128.86
128.11
128.10
128.08
128.00
127.58
127.19
127.16
115.81
115.57
Cl
F
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

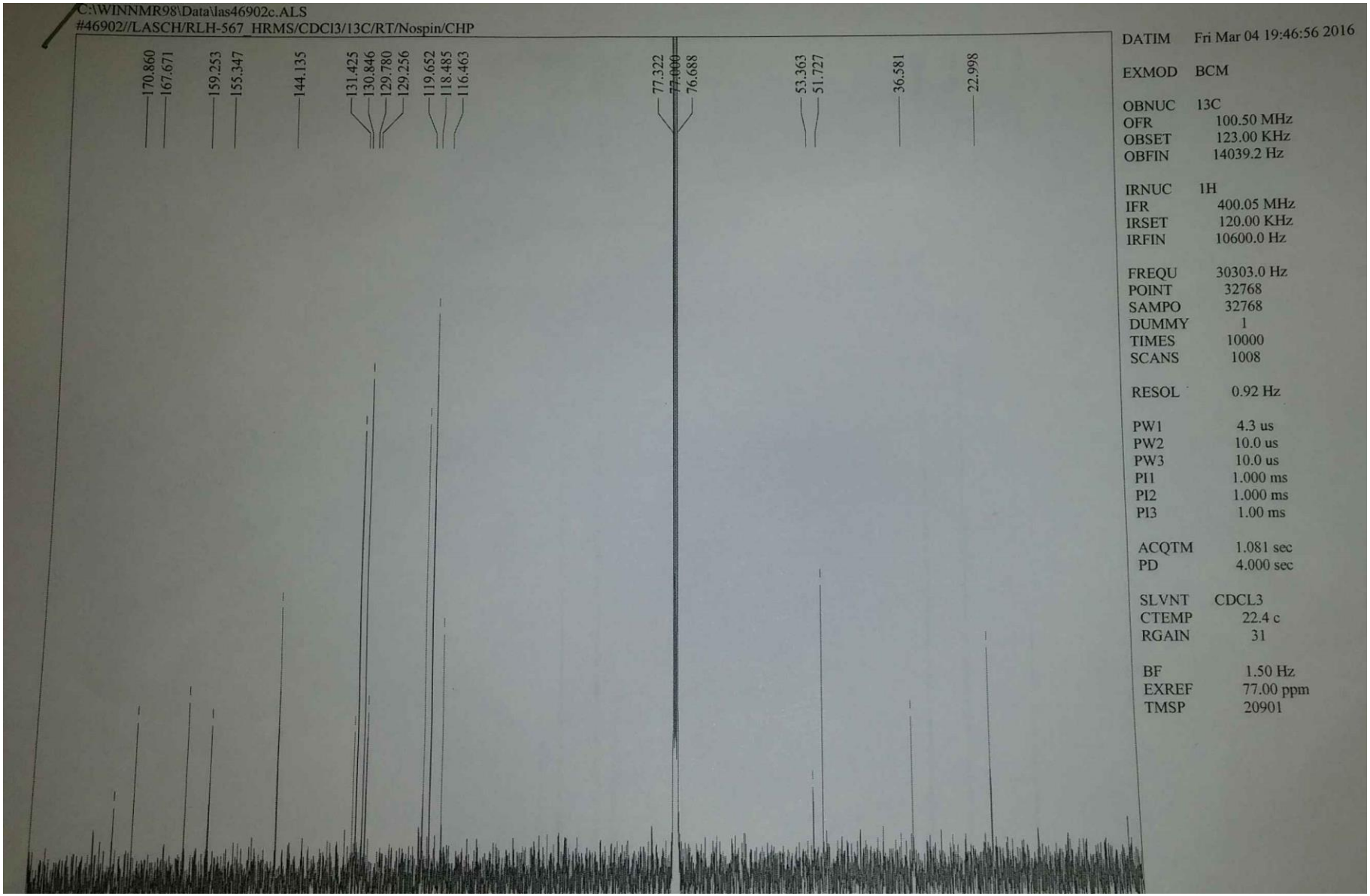
(S,*E*)-2-Acetamido-3-(4-(4-((*tert*-butoxycarbonyl)diazenyl)phenoxy)-phenyl)propanoic acid (**6**)




173.56
170.94
162.35
161.06
154.37
146.94
132.42
131.03
125.92
120.25
117.76
84.77
53.36
36.66
27.81
22.91
CH3
H3C
H3C
O
O
N
N
O
O
OH
HN
CH3
O
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

(*S*,*E*)-2-acetamido-3-(4-(4-(3-methoxy-3-oxoprop-1-en-1-yl)phenoxy)phenyl)propanoic acid (**7**)




C:\WINNMR98\Data\las46902c.ALS
#46902//LASCH/RLH-567_HRMS/CDCl3/13C/RT/Nospin/CHP
170.860
167.671
159.253
155.347
144.135
131.425
130.846
129.780
129.256
119.652
118.485
116.463
77.322
77.000
76.688
53.363
51.727
36.581
22.998
DATIM Fri Mar 04 19:46:56 2016
EXMOD BCM
OBNUC 13C
OFR 100.50 MHz
OBSET 123.00 KHz
OBFIN 14039.2 Hz
IRNUC 1H
IFR 400.05 MHz
IRSET 120.00 KHz
IRFIN 10600.0 Hz
FREQU 30303.0 Hz
POINT 32768
SAMPO 32768
DUMMY 1
TIMES 10000
SCANS 1008
RESOL 0.92 Hz
PW1 4.3 us
PW2 10.0 us
PW3 10.0 us
PI1 1.000 ms
PI2 1.000 ms
PI3 1.00 ms
ACQTM 1.081 sec
PD 4.000 sec
SLVNT CDCL3
CTEMP 22.4 c
RGAIN 31
BF 1.50 Hz
EXREF 77.00 ppm
TMSP 20901