Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

An Enhanced Stereoselective Synthesis of α,β-Unsaturated Esters Through the Horner-Wadsworth-Emmons reaction in Deep Eutectic Solvents

Andrea Nicola Paparella, Margherita Stallone, Mara Pulpito, Filippo Maria Perna*, Vito Capriati* and Paola Vitale*

EXPERIMENTAL SECTION

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General Methods

Deep Eutectic Solvents [choline chloride ChCl/urea (1:2), choline acetate (ChOAc)/urea (1:2), choline chloride ChCl/H_2O (1:2),] were prepared by heating under stirring at 60–80 °C for 10–30 min the corresponding individual components until a clear solution was obtained. Reactions were quenched with deionized water (pH = 6.1, determined by the pH meter 507 Crison). For ^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz), $CDCl_3$ was used as the solvent; chemical shifts are reported in parts per million (δ). FT-IR spectra were recorded on a Perkin–Elmer 681 spectrometer.

GC analyses were performed on a HP 6890 model, Series II by using a HP1 column (methyl siloxane; 30 m × 0.32 mm × 0.25 µm film thickness). Analytical thin-layer chromatography (TLC) was carried out on pre-coated 0.25 mm thick plates of Kieselgel 60 F_{254}; visualization was accomplished by UV light (254 nm) or by spraying a solution of 5 % (w/v) ammonium molybdate and 0.2 % (w/v) cerium(III) sulfate in 100 mL 17.6 % (w/v) aq. sulphuric acid and heating to 473 K until blue spots appeared.

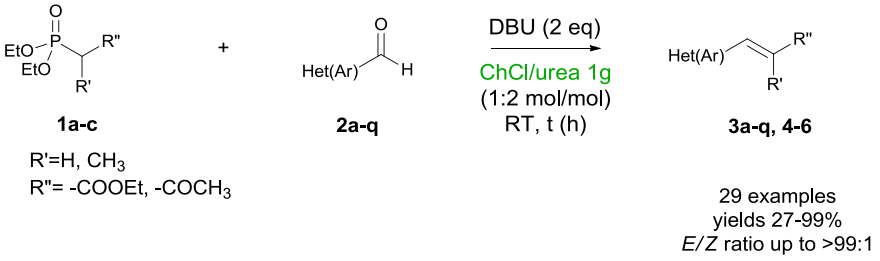
Chromatography was run by using silica gel 60 with a particle size distribution 40–63 µm and 230–

400 ASTM. GC-MS analyses were performed on a HP 5995C model. High-resolution mass spectrometry (HRMS) analyses were performed using a Bruker microTOF QII mass spectrometer equipped with an electrospray ion source (ESI).

Other reagents and solvents, unless otherwise specified, were purchased from Sigma-Aldrich (SigmaAldrich, St. Louis, MO, USA) and were used without any further purification.

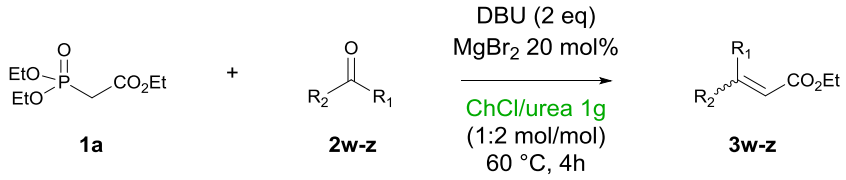
Full characterization data, including copies of ^{1} H and ^{13}C NMR spectra, have been reported for both the newly synthesized and the known compounds. The following abbreviations have been used to explain the multiplicities: s = singlet; br s = broad singlet; d = doublet; t = triplet; q = quartet; m = multiplet; dd = double of doublets; td = triplet of doublets.

General procedure for the Horner-Wadsworth-Emmons reaction of aldehydes (2a-q) in Deep Eutectic Solvents



In a 10 mL round bottom flask, aldehydes (**2a-q**, 1mmol), phosphonate (**1a-c**, 1mmol), DBU (2mmol, 298 µL) and ChCl/Urea DES (1 g) were sequentially added. The reaction was stirred at 25°C for 4 h. After this time, water (3 mL) and some drops of HCl 10% v/v were added until pH reached 4 [Except for compounds **2p**,**q**]. The mixture was then extracted with AcOEt (5 mL x 3) and the reunited organic phases were washed with brine, dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The crude was purified by flash column chromatography (silica gel, hexane/EtOAc 70:30–90:10) to provide the desired α,β-unsaturated compounds **3a-q, 4-6.**

General procedure for the Horner-Wadsworth-Emmons reaction of ketones (2w-z) with 1a in Deep Eutectic Solvents

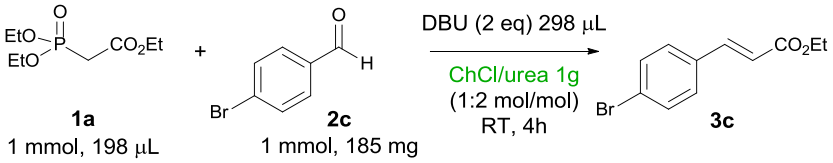


In a 10 mL round bottom flask, ketone (**2w-z**, 1 mmol), phosphonate (**1a**, 1 mmol), DBU (2 mmol, 298 µL), $MgBr_2$ (20 mol%, 36 mg) and ChCl/Urea DES (1 g) were sequentially added. The reaction was stirred at 60 °C for 16 h. After this time, the reaction was stopped and 3 mL of water and some drops of HCl 10% v/v until pH 4 were added. After this time, reaction was stopped and 3 mL of water and some drops of HCl 10% v/v until pH 4 were added. The mixture was then extracted with AcOEt (5 mL x 3) and the reunited organic phases were washed with brine, dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The crude was purified by flash column chromatography (silica gel, hexane/EtOAc 70:30–90:10) to provide the desired α,β-unsaturated esters **(3w-z).**

Reuse of DES. Low yields were obtained by attempting to reuse the solvent together with the DBU for two consecutive cycles (yields of 81% and 32% respectively), carrying out the reaction on a gram-scale, and isolating the final liquid product by decantation without a solvent extraction. A previous work by A. N. Paparella and others, employing DBU as a base in DESs,[1] revealed the presence of the ammonium salt of DBU in DES at the conclusion of the reaction. Consequently, irrespective of using EtOAc for the extraction of products and starting materials, it has been suggested to include DBU with fresh reagents **2c** and **1a** in the same solvent (1ChCl/2urea) in each reaction cycle.

Procedure for the DES reuse for the synthesis of Ethyl (*E*)-3-(4-bromophenyl)acrylate (3c)

In a 10 mL round bottom flask, 4-bromobenzaldehyde (**2c**, 1 mmol, 185 mg), triethylphosphonoacetate (**1a**, 1 mmol, 198 µL), DBU (2 mmol, 298 µL) and ChCl/Urea DES (1 g) were sequentially added. The reaction was stirred at RT for 4 h, and after this time, the mixture was extracted with AcOEt (3 mL x 5). The combined organic phases were washed with brine, HCl 1 M, dried over anhydrous Na_2SO_4 and concentrated *in vacuo* to afford the crude product. The latter was then analyzed by using CH_2Br_2 as an internal standard to determine the yield of ethyl (*E*)-3-(4-bromophenyl)acrylate (**3c**). Upon adding new, fresh reagents [4-bromobenzaldehyde (**2c**), triethylphosphonoacetate (**1a**), and DBU] the reaction medium could be easily re-used for additional reaction cycles.



1st run: 93% (0.93 mmol, 236 mg)
2nd run: 70% (0.70 mmol, 178 mg)
3rd run: 25% (0.25 mmol, 63 mg)

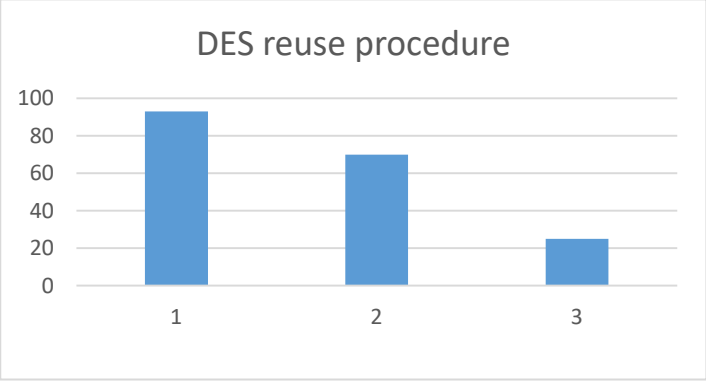


Figure S1. Reuse of DES ChCl/Urea (1:2) in the HWE reaction of 4-bromobenzaldheyde (**2c**) with **1a** to afford α,β-unsaturated ester (**3c**).

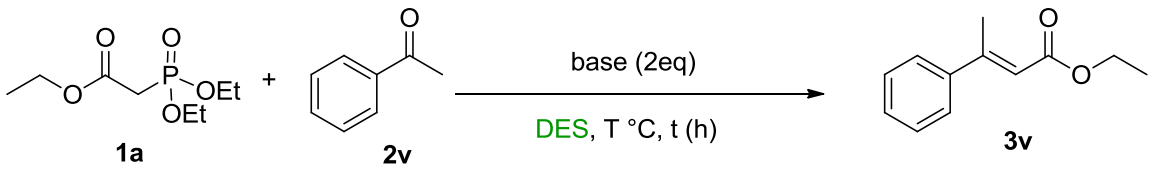
Eco Scale Analysis for the synthesis of Ethyl (*E*)-3-(4-bromophenyl)acrylate (3c)

EcoScale calculation is a post-synthesis analysis tool which estimates sustainability of the organic preparation based on six parameters (Table 5): (1) yield, (2) price of reaction components to obtain 10 mmol of end-product, (3) safety of the reactants based on the hazard warning symbols, (4) technical setup of the processes, (5) temperature and time, and (6) ease of workup/purification processes. An ideal reaction has the EcoScale value of 100. The EcoScale value for the synthesis of a product is calculated by lowering the maximum value of 100 by any applicable penalty points, according to the following equation:[3]

$$EcoScale = 100 - \sum penalty\ points = 100 - 29 = \mathbf{71}$$

EcoScale Parameters	Penalty points
Yield (100-%yield)/2	
90%	**5**
Price of reaction components to obtain 10 mmol of end-product:[a]	
4-Br-benzaldehyde (0.011 mol, 2.053 g)	**0**
Triethylphosphonoacetate (0.011 mol, 2.475 g)	**0**
DBU (0.02 mol, 3.33 g)	**0**
DES component: ChCl (5.91 g)	**0**
DES component: urea (5.02 g)	**0**
Safety of the reactants	
Triethylphosphonoacetate (N)	**5**
DBU (T)	**5**
Technical setup	
common setup	**0**
Temperature/time:	
Room temperature, 4 h	**1**
Workup/purification processes	
dilution with H_2O and HCl 10% v/v	**0**
extraction with AcOEt and washing with brine	**3**
drying over anhydrous Na_2SO_4	**0**
filtration over celite pad	**0**
evaporation of AcOEt	**0**
flash column chromatography	**10**
Penalty points total	**29**
[a]prices listed on the Sigma Aldrich catalogue. N = dangerous for environment, T = toxic	

Table S1. Study of the Horner-Wadsworth-Emmons reaction in DES between phosphonate **1a** and acetophenone **2v**.

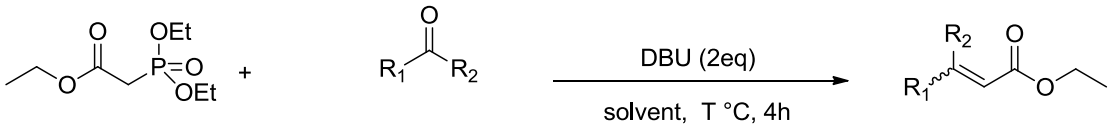


1a **2v** **3v**

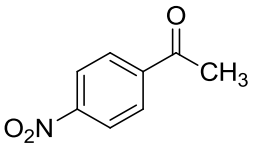
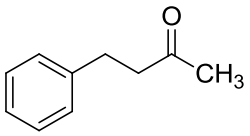
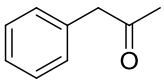
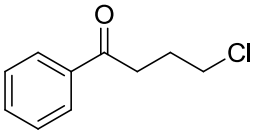
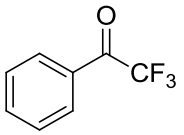
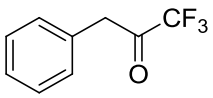
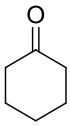
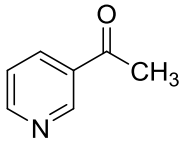
Entry	Base	Addictive	Solvent	T (°C)	Time (h)	Yield[a] (%)
1	LiOH	/	ChCl/urea (1:2)	25	12	NR[b]
2	DBU	/	ChCl/urea (1:2)	25	15	trace
3	DBU	/	ChCl/urea (1:2)	60	4	10
4	DBU	$ZnCl_2$ 20mol%	ChCl/urea (1:2)	60	4	NR[b]
5	DBU	/	ChCl/urea (1:2)	100	4	NR[b]
6	DBU	/	ChCl/EG (1:2)	60	4	NR[b]
7	DBU	/	$Me(Ph)_3PBr$/EG (1:5)	60	4	NR[b]
8	DBU	$MgBr_2$ 10mol%	ChCl/urea (1:2)	25	16	NR[b]
9	DBU	$MgBr_2$ 10mol%	H_2O	40	4	NR[b]
10	DBU	$MgBr_2$ 10mol% +TBAB 10mol%	H_2O	40	4	NR[b]
11	DBU	$MgBr_2$10mol%	ChCl/Gly (1:2)	40	4	NR[b]
12	DBU	$MgBr_2$ 10mol%	Gly/Pro (3:1)	40	4	NR[b]
13	DBU	/	ZnCl/Acetamide (1:2)	40	4	NR[b]
14	DBU	$MgBr_2$ 20mol%	2Me-THF	40	4	NR[b]
15	DBU	$Ba(OAc)_2$	ChCl/urea (1:2)	80	4	10
16	DBU	$MgBr_2$ 20mol%	ChCl/Lactic Acid (1:2)	40	4	NR[b]
17	DBU	$Mg(ClO_4)_2$	ChCl/urea (1:2)	40	4	NR[b]
18	DBU /TEPA	$MgBr_2$ 40mol%	ChCl/urea (1:2)	120	1) 0.5 2) 3.5	NR[b]
19	DBU	$BaTiO_3$	ChCl/urea (1:2)	40	4	NR[b]
20	LDA	/	ChCl/urea (1:2)	40	4	NR[b]
21	DBU	Al_2O_3	ChCl/urea (1:2)	40	4	15
22	DBU	$MgBr_2$ 10mol%	neet	60	15	15
23	DBU	$Cu(CH_3COO)_2$	ChCl/urea (1:2)	60	4	NR[b]
24	DBU	Ti(OiPr)	ChCl/urea (1:2)	60	6	NR[b]
25	DBU	TFE	ChCl/urea (1:2)	60	4	25
26	DBU	/	ChCl/TFA (1:2)	60	15	NR[b]
27	DBU	Et_2OBF_3	ChCl/urea (1:2)	90	24	NR[b]
28	DBU (0,5 eq) + K_2CO_3 (1,5 eq)	/	ChCl/urea (1:2)	60	72	16
29	DBU	$CeCl_3x7H_2O$ 20mol%	ChCl/urea (1:2)	60	4	NR[b]
30	DBU	$Sc(OTf)_3$ 10mol%	ChCl/urea (1:2)	60	4	NR[b]
31	DBU	$ZnBr_2$ 10mol%	ChCl/urea (1:2)	60	4	NR[b]
32	DBU	$ZnBr_2$ 50mol%	ChCl/urea (1:2)	60	15	NR[b]
33	DBU	Ce^{4+} MOF	ChCl/U (1:2) (0,5 mL)	hv	5	NR[b]
34	DBU	Ce^{4+} MOF	ChCl/urea (1:2)	60	5	NR[b]
35	DBU	$SmCl_3$ 10mol%	ChCl/urea (1:2)	60	15	NR[b]
36	DBU	$FeCl_3$ 10mol%	ChCl/urea (1:2)	60	15	NR[b]
37	[TEPA (0.5 mmol) + NaH (2 mmol)] in 2-MeTHF	/	ChCl/urea (1:2)	60	15	NR[b]
38	1-(TEPA + NaH)	/	ChCl/urea (1:2)	60	1-60 min 2-15	NR[b]

Table S2

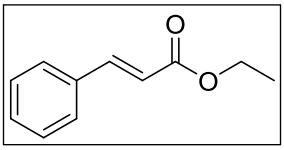
Horner-Wadsworth-Emmons reaction in DES between phosphonate **1a** and various aliphatic and aromatic ketones **2.**



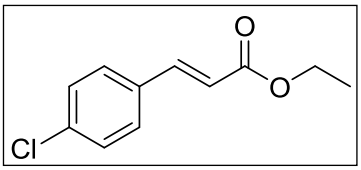
1 **2** **3**

Entry	Ketone	Solvent	Additive.	T (°C)	t (h)	Yield (%)
1		1ChCl/2urea	/			30
2		1ChCl/2urea	$MgBr_2$ 20mol%			70 (E/Z 97:3)
3		1ChCl/2urea	"			70
4		1ChCl/2urea	"			32
5		PBr_2/Eg (1:5 $_{mol/mol}$) 1ChCl/2urea	"			<10
6			/	60	16	<10
7		1ChCl/2urea	$MgBr_2$ 20mol%	40	5	20
8		1ChCl/2urea	$MgBr_2$ 20mol%	60	15	NR
9		1ChCl/2urea	$MgBr_2$ 20mol%	40	4	5
10		1ChCl/2urea	$MgBr_2$ 20mol%	60	15	NR
11		1ChCl/2urea	$MgBr_2$ 20mol%	40	4	5
12		1ChCl/2urea	$MgBr_2$ 20mol%	60	15	60
13		1ChCl/2urea	$MgBr_2$ 20mol%	40	4	10
14		1ChCl/2urea	$MgBr_2$ 20mol%	40	15	54
15		1ChCl/2urea	$MgBr_2$ 20mol%	60	15	80
16		1ChCl/2urea	$MgBr_2$ 20mol%	40	6	20
17		1ChCl/2urea	$MgBr_2$ 20mol%	60	15	18
18		1ChCl/2urea	/	40	4	25
19		1ChCl/2urea	$MgBr_2$ 20mol%	60	15	20

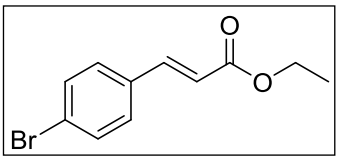
Characterization data for compounds (3a-z, 4-6)



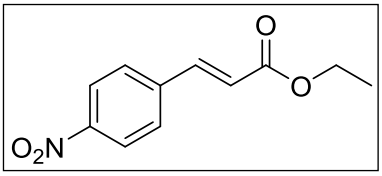
Ethyl cinnamate (3a):[4] colourless oil, 80% yield from the reaction with DBU (2 eq) in DES (*E*/*Z* 98:2). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.68 (d, *J* = 16.0 Hz, 1H), 7.53 – 7.51 (m, 2H), 7.38 – 7.37 (m, 3H), 6.44 (d, *J* = 16.0 Hz, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 1.34 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 166.9, 144.5, 134.5, 130.1, 128.8, 128.0, 118.4, 60.4, 14.3; FT-IR (Film, cm^{-1}): 2962, 1712, 1640, 1310, 1188, 1204, 808; GC/MS (70 eV) *m/z* (%): 176 (M^+, 32), 147 (22), 131 (100), 103 (58), 77 (42), 51 (19); HRMS (ESI) *m/z* calc. for $[C_{11}H_{12}O_2 + Na]^+$: 199.0730; found: 199.0726. Purified by flash column chromatography (Hex/AcOEt 10:1).



Ethyl *(E)*-3-(4-chlorophenyl)acrylate (3b):[5] white waxy solid, 99% yield from the reaction with DBU (2 eq) in DES (*E*/*Z* 99:1). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.63 (d, *J* = 16.0 Hz, 1H), 7.46 – 7.45 (m, 2H), 7.37 – 7.35 (m, 2H), 6.41 (d, *J* = 16.0 Hz, 1H), 4.27 (q, *J* = 7.1 Hz, 2H), 1.34 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 166.7, 143.1, 136.1, 133.0, 129.2, 129.1, 118.9, 60.6, 14.3; FT-IR (Film, cm^{-1}): 2982, 1713, 1639, 1491, 1310, 1174, 1089, 821; GC/MS (70 eV) *m/z* (%): 212 (M^++2, 10), 210 (M^+, 43), 167 (34), 165 (100), 139 (11), 137 (30), 101 (35), 75 (22), 51 (11); HRMS (ESI) *m/z* calc. for $[C_{11}H_{11}ClO_2 + Na]^+$: 233.0340; found: 233.0339.

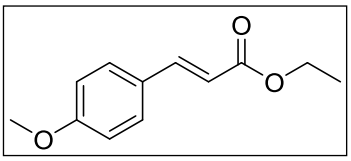


Ethyl *(E)*-3-(4-bromophenyl)acrylate (3c):[6] colourless oil, 88% yield from the reaction with DBU (2 eq) in DES (*E*/*Z* 96:4). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.60 (d, *J* = 16.0 Hz, 1H), 7.51 – 7.50 (m, 2H), 7.38 – 7.37 (m, 2H), 6.41 (d, *J* = 16.0 Hz, 1H), 4.25 (q, *J* = 7.1 Hz, 2H), 1.33 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 166.7, 143.1, 133.4, 132.1, 129.4, 124.4, 119.0, 60.6, 14.3; FT-IR (Film, cm^{-1}): 2981, 1714, 1636, 1488, 1310, 1174, 1038, 818; GC/MS (70 eV) *m/z* (%): 256 (M^++2, 38), 254 (M^+, 40), 226 (23), 209 (86), 183 (20), 130 (16), 102 (100), 75 (30), 51 (19); HRMS (ESI) *m/z* calc. for $[C_{11}H_{11}BrO_2 + H]^+$: 255.0015; found: 255.0020. Purified by flash column chromatography (Hex/AcOEt 10:1).

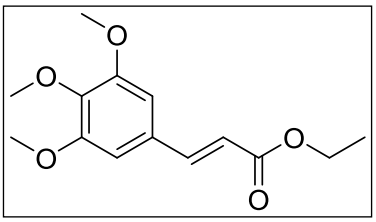


Ethyl *(E)*-3-(4-nitrophenyl)acrylate (3d):[7] pale yellow solid, m.p. 115-117 °C, 90% yield from the reaction with DBU (2 eq) in DES (*E*/*Z*

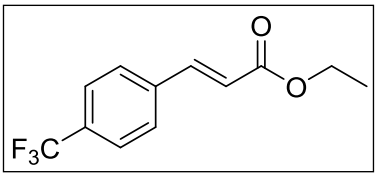
99:1). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.26 – 8.25 (m, 2H), 7.73 – 7.67 (m, 3H), 6.56 (d, *J* = 16.0 Hz, 1H), 4.30 (q, *J* = 7.1 Hz, 2H), 1.36 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 166.0, 141.6, 140.6, 128.6, 124.2, 122.6, 61.0, 14.3; FT-IR (KBr, cm^{-1}): 3045, 2935, 1712, 1643, 1518, 1342; GC/MS (70 eV) *m/z* (%): 221 (M^+, 25), 193 (50), 176 (100), 160 (11), 146 (25), 130 (43), 102 (52), 91 (32), 76 (35), 51 (8); HRMS (ESI) *m/z* calc. for $[C_{11}H_{11}NO_4 + Na]^+$: 244.0580; found: 244.0588. Crystalized from methanol hot/cold.



Ethyl *(E)*-3-(4-methoxyphenyl)acrylate (3e):[8] colourless oil, 75% yield from the reaction with DBU (2 eq) in DES (*E*/*Z* 98:2). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.63 (d, *J* = 15.9 Hz, 1H), 7.47 – 7.46 (m, 2H), 6.90 – 6.88 (m, 2H), 6.30 (d, *J* = 15.9 Hz, 1H), 4.24 (q, *J* = 7.1 Hz, 2H), 3.80 (s, 3H), 1.32 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 167.5, 161.6, 144.4, 129.8, 127.4, 115.9, 114.5, 60.5, 14.4 ; FT-IR (Film, cm^{-1}): 2982, 2936, 2840, 1713, 1605, 1514, 1253, 1172, 1034, 829; GC/MS (70 eV) *m/z* (%): 206 (M^+, 68), 178 (15), 161 (100), 134 (44), 89 (20), 77 (18), 51 (19); HRMS (ESI) *m/z* calc. for $[C_{12}H_{14}O_3 + Na]^+$: 229.0835; found: 229.0838. Purified by flash column chromatography (Hex/AcOEt 10:1).

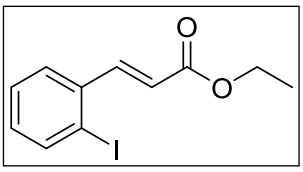


Ethyl *(E)*-3-(3,4,5-trimethoxyphenyl)acrylate (3f):[9] white solid, m.p. 65-67 °C, 90% (*E*/*Z* 99:1). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.61 (d, *J* = 15.9 Hz, 1H), 6.76 (s, 2H), 6.35 (d, *J* = 15.9 Hz, 1H), 4.27 (q, *J* = 7.1 Hz, 2H), 3.89 (s, 6H), 3.88 (s, 3H), 1.35 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 167.0, 153.4, 144.6, 140.1, 130.0, 117.5, 105.2, 61.0, 60.5, 56.2, 14.3; FT-IR (Film, cm^{-1}): 3062, 2972, 2835, 1714, 1695, 1584, 1423, 1248, 1125, 1008, 819; GC/MS (70 eV) *m/z* (%): 266 (M^+, 100), 251 (55), 221 (21), 177 (15), 163 (18), 135 (12), 77 (10); HRMS (ESI) *m/z* calc. for $[C_{14}H_{18}O_5 + Na^+]$: 289.1046; found: 289.1051. Purified by flash column chromatography (Hex/AcOEt 8:2).

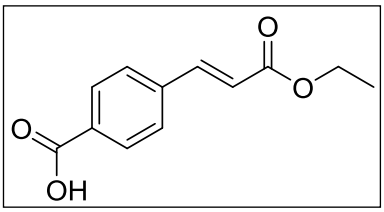


Ethyl *(E)*-3-(4-(trifluoromethyl)phenyl)acrylate (3i):[10] white waxy solid, 77% yield from the reaction with DBU (2 eq) in DES (*E*/*Z* 98:2). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.70 (d, *J* = 16.1 Hz, 1H), 7.65 – 7.62 (m, 4H), 6.51 (d, *J* = 16.1 Hz, 1H), 4.29 (q, *J* = 7.1 Hz, 2H), 1.35 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (150 MHz,

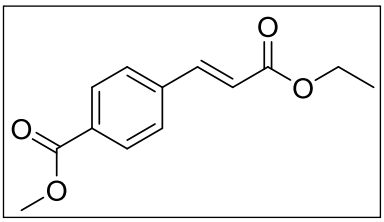
$CDCl_3$): δ 166.4, 142.7, 137.8, 131.7 (q, ^2J = 33 Hz), 128.2, 125.8 (q, ^3J = 4 Hz), 123.8 (q, ^1J = 272 Hz), 120.9, 60.8, 14.3; FT-IR (Film, cm^{-1}): 3372, 2985, 2933, 1715, 1642, 1325, 1169, 1067, 833; GC/MS (70 eV) *m/z* (%): 244 (M^+, 22), 225 (12), 216 (25), 199 (100), 171 (41), 151 (50), 102 (15); HRMS (ESI) *m/z* calc. for $[C_{12}H_{11}F_3O_2 + H]^+$: 245.0784; found: 245.0809. Purified by flash column chromatography (Hex/AcOEt 10:1).



Ethyl *(E)*-3-(2-iodophenyl)acrylate (3j):[11] colourless oil, 78% (*E*/*Z* 98:2). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.93 – 7.90 (m, 2H), 7.58 – 7.56 (m, 1H), 7.38 – 7.36 (m, 1H), 7.08 – 7.05 (m, 1H), 6.33 (d, *J* = 15.8 Hz, 1H), 4.30 (q, *J* = 7.1 Hz, 2H), 1.37 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 166.3, 147.7, 140.0, 137.9, 131.2, 128.5, 127.4, 121.3, 101.1, 60.7, 14.3 ; FT-IR (Film, cm^{-1}): 3060, 2980, 2932, 1714, 1634, 1461, 1313, 1262, 1204, 1178, 1037, 1013, 759; GC/MS (70 eV) *m/z* (%): 302 (M^+, 4), 257 (11), 175 (44), 147 (100), 130 (40), 102 (48), 91 (26), 76 (14); HRMS (ESI) *m/z* calc. for $[C_{11}H_{12}IO_2 + H]^+$: 302.9876; found: 302.9866. Purified by flash column chromatography (Hex/AcOEt 10:1).

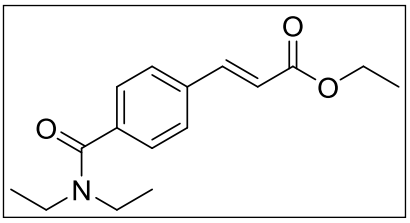


Ethyl (*E*)-3-(4-carboxyphenyl)acrylate (3k):[12] white solid, m.p. 190-192 °C, 68% (*E*/*Z* = 99:1). ^{1}H NMR (600 MHz, Methanol-d_4): δ 8.03 – 8.02 (m, 2H), 7.70 – 7.66 (m, 3H), 6.59 (d, *J* = 16.0 Hz, 1H), 4.24 (q, *J* = 7.1 Hz, 2H), 1.32 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (150 MHz, Methanol-d_4): δ 167.8, 166.8, 143.2, 138.6, 132.1, 129.9, 127.7, 120.1, 60.4, 13.2; FT-IR (Film, cm^{-1}): 3377, 2986, 1681, 1293,1016; GC/MS (70 eV) *m/z* (%): 220 (M^+, 38), 192 (30), 175 (100), 147 (27), 131 (38), 103 (65), 77 (43); HRMS (ESI) *m/z* calc. for $[C_{12}H_{12}O_4 - H]^+$: 219.0663; found: 219.0398. Purified by flash column chromatography DCM/Methanol 9:1.

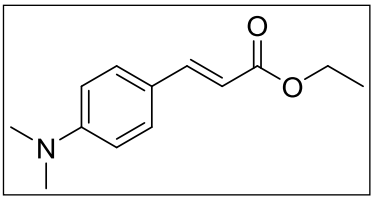


Ethyl (*E*)-3-(4-methoxycarbonylphenyl)acrylate (3l):[13] white waxy solid, 40% (*E*/*Z* = 99:1). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.08 – 8.07 (m, 2H), 7.72 (d, *J* = 16.1 Hz, 1H), 7.61 – 7.60 (m, 2H), 6.54 (d, *J* = 16.1 Hz, 1H), 4.30 (q, *J* = 7.1 Hz, 2H), 3.96 (s, 3H), 1.37 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 166.4_2, 166.4_0, 143.1, 138.8, 131.4, 130.1, 127.8, 120.8, 60.6, 52.1, 14.2; FT-IR (Film, cm^{-1}): 2920, 2840, 1714, 1636, 1275, 1174, 1105; GC/MS (70 eV) *m/z* (%): 234

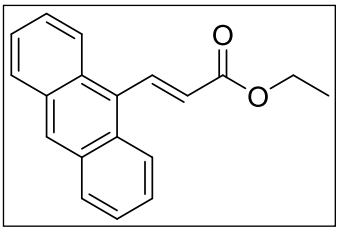
(M^+, 67), 205 (30), 203 (53), 189 (100), 175 (62), 145 (49), 131 (38), 115 (33), 102 (69), 77 (15); HRMS (ESI) *m/z* calc. for $[C_{13}H_{14}O_4 + H]^+$: 235.0965; found: 235.1414. Purified by flash column chromatography Hex/AcOEt 9:1.



Ethyl (E)-3-[4-(*N,N*-diethylcarbamoyl)phenyl]acrylate (3m): pale yellow oil, 43% (*E*/*Z* > 99:1). ^{1}H NMR (600 MHz, Methanol-d_4): δ 7.74 – 7.72 (m, 3H), 7.45 – 7.43 (m, 2H), 6.62 (d, *J* = 16.1 Hz, 1H), 4.28 (q, *J* = 7.1 Hz, 2H), 3.59 – 3.57 (m, 2H), 3.34 – 3.31 (m, 2H) 1.35 (t, *J* = 7.1 Hz, 3H), 1.28 (t, *J* = 7.2 Hz, 3H), 1.15 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (150 MHz, Methanol-d_4): δ 171.4, 166.9, 143.4, 138.3, 135.6, 128.0, 126.6, 119.2, 60.4, 43.5, 39.5, 13.2, 13.0, 11.7; FT-IR (Film, cm^{-1}): 2918, 1712, 1633, 1427, 1311, 1286, 1175, 1094; GC/MS (70 eV) *m/z* (%): 275 (M^+, 54), 246 (20), 203 (100), 175 (15), 102 (19); HRMS (ESI) *m/z* calc. for $[C_{16}H_{21}NO_3 + Na]^+$: 298.1414; found: 298.1418. Purified by flash column chromatography Hex/AcOEt 1:1.

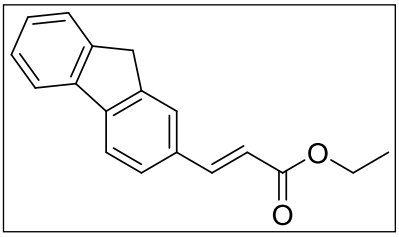


Ethyl (E)-3-[4-(dimethylamino)phenyl]acrylate (3n):[14] white solid, m.p. 74-76 °C, 65% (*E*/*Z* > 99:1). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.65 (d, *J* = 15.8 Hz, 1H), 7.45 – 7.43 (m, 2H), 6.69 – 6.68 (m, 2H), 6.25 (d, *J* = 15.8 Hz, 1H), 4.27 (q, *J* = 7.2 Hz, 2H), 3.03 (s, 6H), 1.35 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 167.8, 151.8, 145.0, 126.9, 122.5, 112.8, 111.9, 59.9, 40.1, 14.4; FT-IR (Film, cm^{-1}): 2902, 2817, 1886, 1701, 1601, 1526, 1446, 1306, 1154, 1094, 815; GC/MS (70 eV) *m/z* (%): 219 (M^+, 100), 190 (32), 174 (74), 147 (69), 146 (50), 130 (15); HRMS (ESI) *m/z* calc. for $[C_{13}H_{17}NO_2 + Na]^+$: 242.1151; found: 242.1179. Purified by flash column chromatography Hex/AcOEt 9:1.

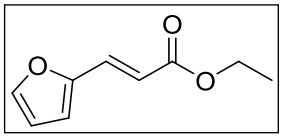


Ethyl *(E)*-3-(anthracen-9-yl)acrylate (3o):[15] yellow solid, m.p. 80 - 82 °C, 83% (*E*/*Z* 99:1). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.66 (d, *J* = 16.3 Hz, 1H), 8.41 (s, 1H), 8.27 – 8.25 (m, 2H), 8.00 – 7.99 (m, 2H), 7.53 – 7.48 (m, 4H), 6.45 (d, *J* = 16.3 Hz, 1H), 4.43 (q, *J* = 7.1 Hz, 2H), 1.45 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 166.4, 141.9, 131.3, 129.4, 129.3, 128.8, 128.2, 127.3, 126.3, 125.3, 125.2, 60.8, 14.4.; FT-IR (Film, cm^{-1}): 3051, 2980, 2835, 1712, 1203, 1162, 1043, 855, 706;

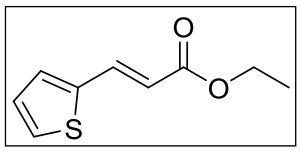
GC/MS (70 eV) *m/z* (%): 276 (M^+, 28), 203 (100), 101 (20); HRMS (ESI) *m/z* calc. for [$C_{19}H_{16}O_2$ + Na^+]: 299.1043; found: 299.1036. Purified by flash column chromatography (Hex/Et_2O 9:1).



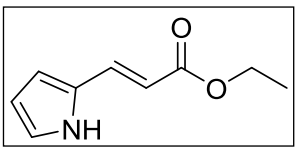
Ethyl *(E)*-3-(9H-fluoren-2-yl)acrylate (3p):[16] pale yellow solid, m.p. 100 - 102 °C, 50% yield from the reaction with DBU (2 eq) in DES at 40 °C (*E/Z* 98:2). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.82 – 7.77 (m, 3H), 7.72 (s, 1H), 7.58 – 7.56 (m, 2H), 7.42 – 7.39 (m, 1H), 7.36 – 7.34 (m, 1H), 6.49 (d, *J* = 16.0 Hz, 1H), 4.29 (q, *J* = 7.1 Hz, 2H), 3.93 (s, 2H), 1.36 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 167.2, 145.0, 144.0, 143.9, 143.8, 140.9, 133.1, 127.5, 127.4, 127.0, 125.2, 124.5, 120.3, 120.2, 117.4, 60.4, 36.8, 14.4.; FT-IR (Film, cm^{-1}): 2981, 2922, 1708, 1634, 1322, 1174, 1033, 978, 830, 774, 743; GC/MS (70 eV) *m/z* (%): 264 (M^+, 100), 235 (15), 218 (159), 189 (69), 165 (26), 95 (25), 83 (11); HRMS (ESI) *m/z* calc. for [$C_{18}H_{16}O_2$ – H^-]: 263.1078; found: 263.1077. Purified by flash column chromatography (Hex/AcOEt 11:1).



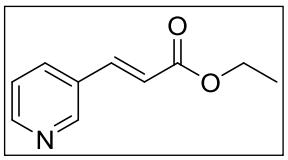
Ethyl *(E)*-3-(furan-2-yl)acrylate (3q):[17] yellow oil, 93% (*E/Z* 99:1). ^{1}H-NMR (600 MHz, acetone-d6): δ 7.71 (d, *J* = 1.8 Hz, 1H), 7.46 (d, *J* = 15.8 Hz, 1H), 6.87 – 6.86 (m, 1H), 6.60 – 6.59 (m, 1H), 6.25 (d, *J* = 15.8 Hz, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 1.27 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 167.04, 150.96, 144.58, 130.78 (d, *J* = 57.7 Hz), 116.05, 114.47, 112.28, 60.22 (d, *J* = 64.4 Hz), 14.26; FT-IR (Film, cm^{-1}): 2983, 1700, 1638, 1210, 1017, 751; GC/MS (70 eV) *m/z* (%): 166 (M^+, 47), 138 (32), 121 (100), 110 (14), 94 (38), 82 (6), 65 (51), 55 (7); HRMS (ESI) *m/z* calc. for [$C_9H_{10}O_3$ + Na] $^+$: 189.0552; found: 189.0663.



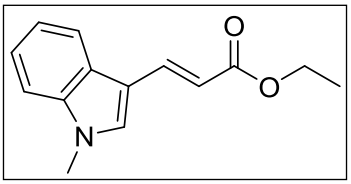
Ethyl *(E)*-3-(thiophen-2-yl)acrylate (3r):[18] pale yellow oil, 80% (*E/Z* 94:6). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.80 (d, *J* = 15.7 Hz, 1H), 7.40 – 7.38 (m, 1H), 7.28 – 7.27 (m, 1H), 7.08 – 7.06 (m, 1H), 6.26 (d, *J* = 15.7 Hz, 1H), 4.27 (q, *J* = 7.1 Hz, 2H), 1.35 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 166.8, 139.6, 137.0, 130.7, 128.3, 128.0, 117.1, 60.4, 14.3; FT-IR (Film, cm^{-1}): 2980, 2932, 1708, 1627, 1305, 1263, 1204, 1163, 1042, 706; GC/MS (70 eV) *m/z* (%): 182 (M^+, 35), 154 (62), 137 (100), 121 (21), 109 (58), 97 (15), 65 (38); HRMS (ESI) *m/z* calc. for [$C_9H_{10}O_2S$+ Na] $^+$: 205.0294; found: 205.0298. Purified by flash column chromatography (Hex/AcOEt 9:1).



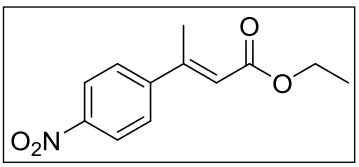
Ethyl *(E)*-3-(pyrrol-2-yl)acrylate (3s):[19] pale yellow oil, 50% (*E*/*Z* 99:1). ^{1}H-NMR (600 MHz, $CDCl_3$): δ 9.21 (br s, 1H), 7.57 (d, *J* = 15.9 Hz, 1H), 6.93 – 6.92 (m, 1H), 6.56 – 6.55 (m, 1H), 6.28 – 6.26 (m, 1H), 6.05 (d, *J* = 15.9 Hz, 1H), 4.24 (q, *J* = 7.1 Hz, 2H), 1.32 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 167.7, 134.3, 128.5, 122.4, 114.3, 111.3, 110.8, 60.2, 14.4; FT-IR (Film, cm^{-1}): 3332, 2981, 2937, 2904, 2872, 1682, 1621, 1349, 1417, 1367, 1323, 1297, 1267, 1228, 1181, 1127, 1097, 1035, 974, 851, 736; GC/MS (70 eV) *m/z* (%): 165 (M^+, 78), 120 (81), 119 (100), 92 (50), 91 (42), 65 (38); HRMS (ESI) *m/z* calc. for $[C_9H_{11}O_2N+ Na]^+$: 188.0682; found: 188.0678.Purified by flash column chromatography (Hex/AcOEt 7:3).



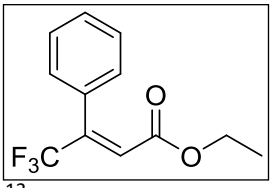
Ethyl *(E)*-3-(pyridine-3-yl)acrylate (3t):[20] colorless oil, 98% yield from the reaction with DBU (2 eq) in DES (*E*/*Z* 98:2). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.72 (s, 1H), 8.58 (dd, *J* = 4.8, 1.6 Hz, 1H), 7.84 – 7.81 (m, 1H), 7.65 (d, *J* = 16.1 Hz, 1H), 7.33 – 7.31 (m, 1H), 6.49 (d, *J* = 16.1 Hz, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 1.33 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 166.3, 150.9, 149.6, 140.8, 134.2, 130.3, 123.7, 120.5, 60.8, 14.3; FT-IR (Film, cm^{-1}): 2982, 1714, 1643, 1312, 1265, 1188, 982, 806, 698; GC/MS (70 eV) *m/z* (%): 177 (M^+, 10), 148 (18), 132 (100), 120 (13), 104 (39), 77 (19), 51 (31); HRMS (ESI) *m/z* calc. for $[C_{10}H_{11}NO_2 + H]^+$: 178.0863; found: 178.0883. Purified by flash column chromatography (Hex/AcOEt 6:4).



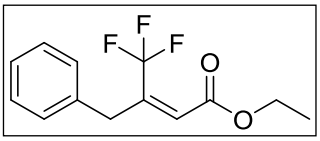
Ethyl *(E)*-3-(1-methyl-1H-indol-3-yl)acrylate (3u):[21] pale yellow solid, m.p. 95 – 96°C, 73% yield from the reaction with DBU (2 eq) in DES (*E*/*Z* 99:1). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.94 – 7.89 (m, 2H), 7.36 – 7.26 (m, 4H), 6.43 (d, *J* = 16.0 Hz, 1H), 4.29 (q, *J* = 7.1 Hz, 2H), 3.80 (s, 3H), 1.37 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 168.3, 137.9, 133.0, 126.1, 122.9, 121.2, 120.6, 112.7, 112.2, 109.9, 60.0, 33.1, 14.5; FT-IR (Film, cm^{-1}): 3105, 2987, 2924, 1698, 1614, 1531, 1377, 1189, 1176, 840; GC/MS (70 eV) *m/z* (%): 229 (M^+, 95), 201 (14), 184 (100), 157 (90), 115 (38), 77 (152); HRMS (ESI) *m/z* calc. for $[C_{14}H_{15}NO_2 + Na]^+$: 252.0995; found: 252.1002. Purified by flash column chromatography (Hex/Et_2O 3:7).



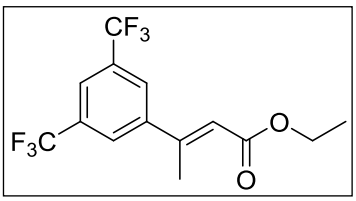
Ethyl *(E)*-3-(4-nitrophenyl)but-2-enoate (3w):[22] white solid, m.p. 70-72 °C, 70% (*E*/*Z* 97:3). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.25 – 8.24 (m, 2H), 7.63 – 7.62 (m, 2H), 6.20 (s, 1H), 4.25 (q, *J* = 7.1 Hz, 2H), 2.60 (s, 3H), 1.34 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 166.1, 152.6, 148.6, 148.0, 127.2, 123.8, 120.2, 60.3, 17.9, 14.3; FT-IR (KBr, cm^{-1}): 3085, 2988, 2959, 1716, 1597, 1518, 1277, 1184, 848; GC/MS (70 eV) *m/z* (%): 235 (M^+, 21), 218 (25), 190 (100), 160 (31), 144 (15), 115 (88), 77 (10), 51 (8); HRMS (ESI) *m/z* calc. for $[C_{12}H_{13}NO_4 + H]^+$: 236.0917; found: 236.0924. Crystalized from methanol hot/cold.



Ethyl *(E)*-4,4,4-trifluoro-3-phenylbut-2-enoate (3x):[23] pale yellow oil, 60% (*E*/*Z* 60:40). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.46 – 7.43 (m, 3H), 7.32 – 7.31 (m, 2H), 6.64 (q, *J* = 1.5 Hz, 1H), 4.07 (q, *J* = 7.1 Hz, 2H), 1.09 (t, *J* = 7.1 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 164.1, 142.2 (q, ^{2}J = 31 Hz), 131.1, 129.2, 128.7, 128.1, 124.6 (q, ^{3}J = 6 Hz), 122.5 (q, ^{1}J = 275Hz), 61.0, 13.6; FT-IR (KBr, cm^{-1}): 2919, 2850, 1738, 1657, 1446, 1284, 1257, 1179, 1135, 1028, 698; GC/MS (70 eV) *m/z* (%): 244 (M^+, 65), 215 (70), 199 (100), 171 (22), 151 (82), 102 (33), 77 (10), 51 (12); HRMS (ESI) *m/z* calc. for $[C_{12}H_{11}F_3O_2 + Na]^+$: 267.0603; found: 267.0610. Purified by flash column chromatography (Hex/Et_2O 20:1).

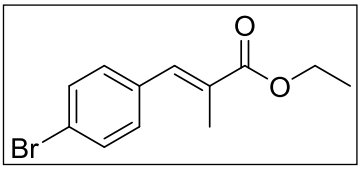


Ethyl (*Z*)-3-benzyl-4,4,4-trifluorobut-2-enoate (3y):[24] colourless oil, 90% (*E*/*Z* 8:92). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.41 – 7.34 (m, 6H), 4.22 (q, *J* = 7.1 Hz, 2H), 3.39 (s, 2H), 1.29 (t, *J* = 7.1 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 169.6, 144.5, 136.0 (q, ^{3}J = 6 Hz), 133.8, 128.9, 128.6, 124.1 (q, ^{1}J = 273 Hz), 124.06 (q, ^{2}J = 30 Hz), 61.3, 32.4, 14.0; FT-IR (KBr, cm^{-1}): 3030, 2985, 2939, 1732, 1668, 1449, 1325, 1305, 1224, 1163, 896; GC/MS (70 eV) *m/z* (%): 258 (M^+, 35), 213 (14), 185 (100), 165 (72), 145 (15), 115 (65), 77 (5), 51 (11); HRMS (ESI) *m/z* calc. for $[C_{13}H_{13}F_3O_2 + Na]^+$: 281.0760; found: 281.0762. Purified by flash column chromatography (Hex/AcOEt 20:1).

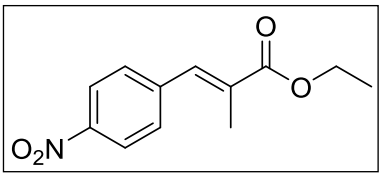


Ethyl *(E)*-3-(3,5-bis(trifluoromethyl)phenyl)but-2-enoate (3z): pale yellow oil, 70% (*E*/*Z* 88:12). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.91 – 7.89 (m, 3H), 6.21 (s, 1H), 4.27 (q, *J* = 7.2 Hz, 2H), 2.63 (s, 3H), 1.36 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 165.8, 151.6, 144.4, 132.1

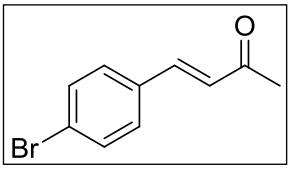
(q, ^{2}J = 33 Hz), 126.3, 123.1 (q, ^{1}J = 273 Hz), 122.3 (m), 120.2, 60.3, 17.8, 14.2; FT-IR (KBr, cm^{-1}): 3090, 2960, 1710, 1645, 1274, 1111; GC/MS (70 eV) *m/z* (%): 326 (M^{+}, 48), 307 (23), 281 (100), 278 (90), 233 (30), 213 (22), 183 (29), 164 (35), 15 (20); HRMS (ESI) *m/z* calc. for [$C_{14}H_{12}F_6O_2$ - H]: 325.0669; found: 325.0666. Purified by flash column chromatography (Hex/AcOEt 20:1).



Ethyl *(E)*-3-(4-bromophenyl)-2-methylacrylate (4):[25] yellow oil, 71% (*E*/*Z* 80:20). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.61 (s, 1H), 7.53 – 7-52 (m, 2H), 7.28 – 7.26 (m, 2H), 4.28 (q, *J* = 7.1 Hz, 2H), 2.09 (d, *J* = 1.6 Hz, 1H), 1.36 (t, *J* = 7.1 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 168.4, 137.3, 134.8, 131.6, 131.1, 129.4, 122.4, 61.0, 14.3, 14.0; FT-IR (Film, cm^{-1}): 2920, 1707, 1637, 1477, 1163, 1123, 748; GC/MS (70 eV) *m/z* (%): 270 (M^{+}+2, 42), 268 (M^{+}, 45), 223 (28), 194 (40), 160 (22), 115 (100), 89 (19), 75 (15); HRMS (ESI) *m/z* calc. for [$C_{12}H_{13}BrO_2$ + Na] $^{+}$: 290.9991; found: 290.9998. Purified by flash column chromatography (Hex/AcOEt 10:1).



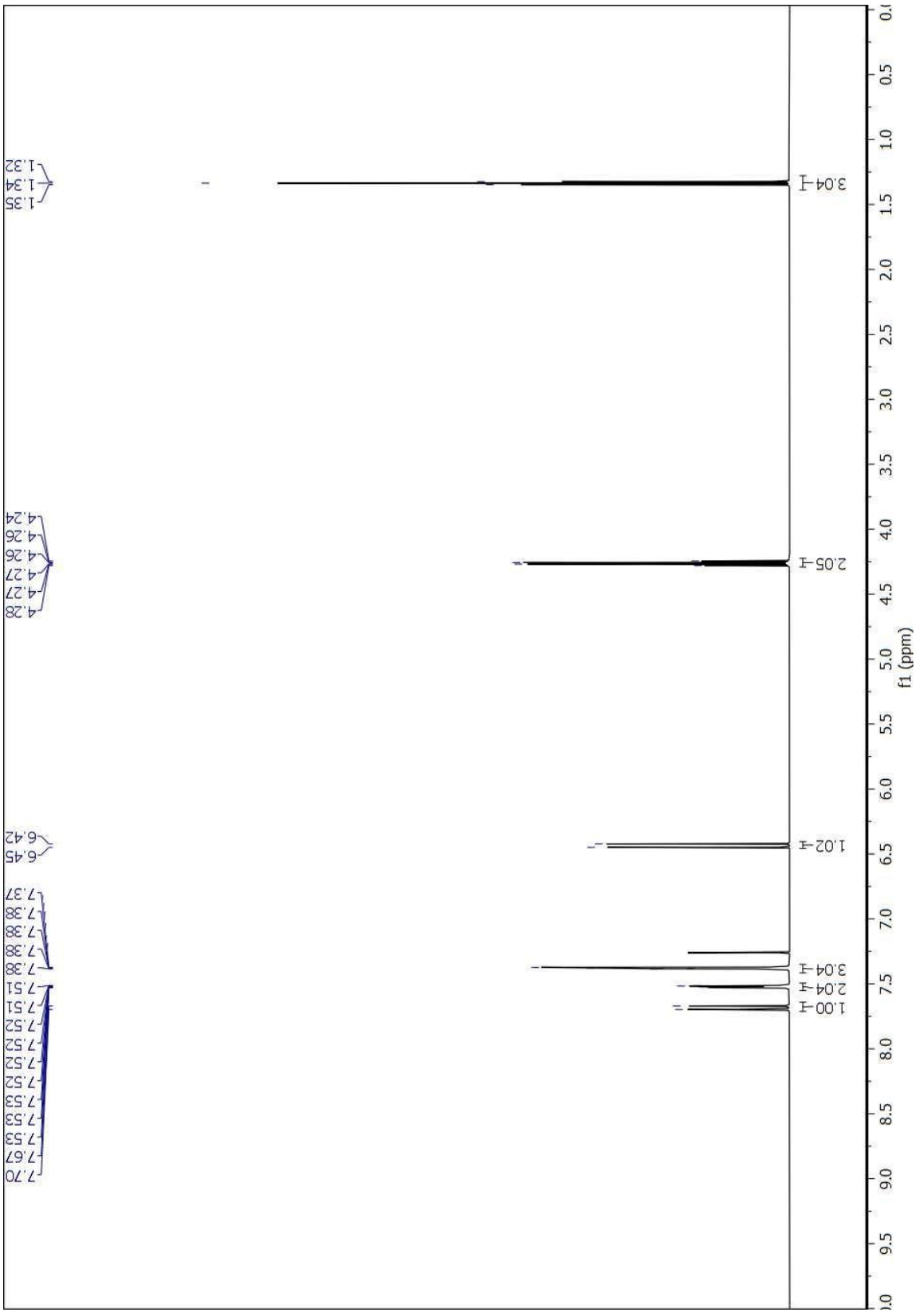
Ethyl *(E)*-2-methyl-3-(4-nitrophenyl)acrylate (5):[26] orange solid, m.p. 78-79 °C, 80% (*E*/*Z* 80:20). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.26 – 8.25 (m, 2H), 7.69 (bs, 1H), 7.54 – 7.53 (m, 2H), 4.30 (q, *J* = 7.1 Hz, 1H), 2.12 (s, 3H), 1.37 (t, *J* = 7.1 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 167.8, 147.2, 142.5, 136.0, 132.3, 130.2, 123.6, 61.3, 14.3, 14.2; FT-IR (KBr, cm^{-1}): 2921, 2851, 1702, 1516, 1324, 1264, 1168, 1129, 1067, 849; GC/MS (70 eV) *m/z* (%): 235 (M^{+}, 30), 218 (35), 190 (100), 160 (48), 144 (24), 115 (68), 77 (20); HRMS (ESI) *m/z* calc. for [$C_{12}H_{13}NO_4$ + H] $^{+}$: 236.0917; found: 236.0922. Crystallized from hot/cold methanol.



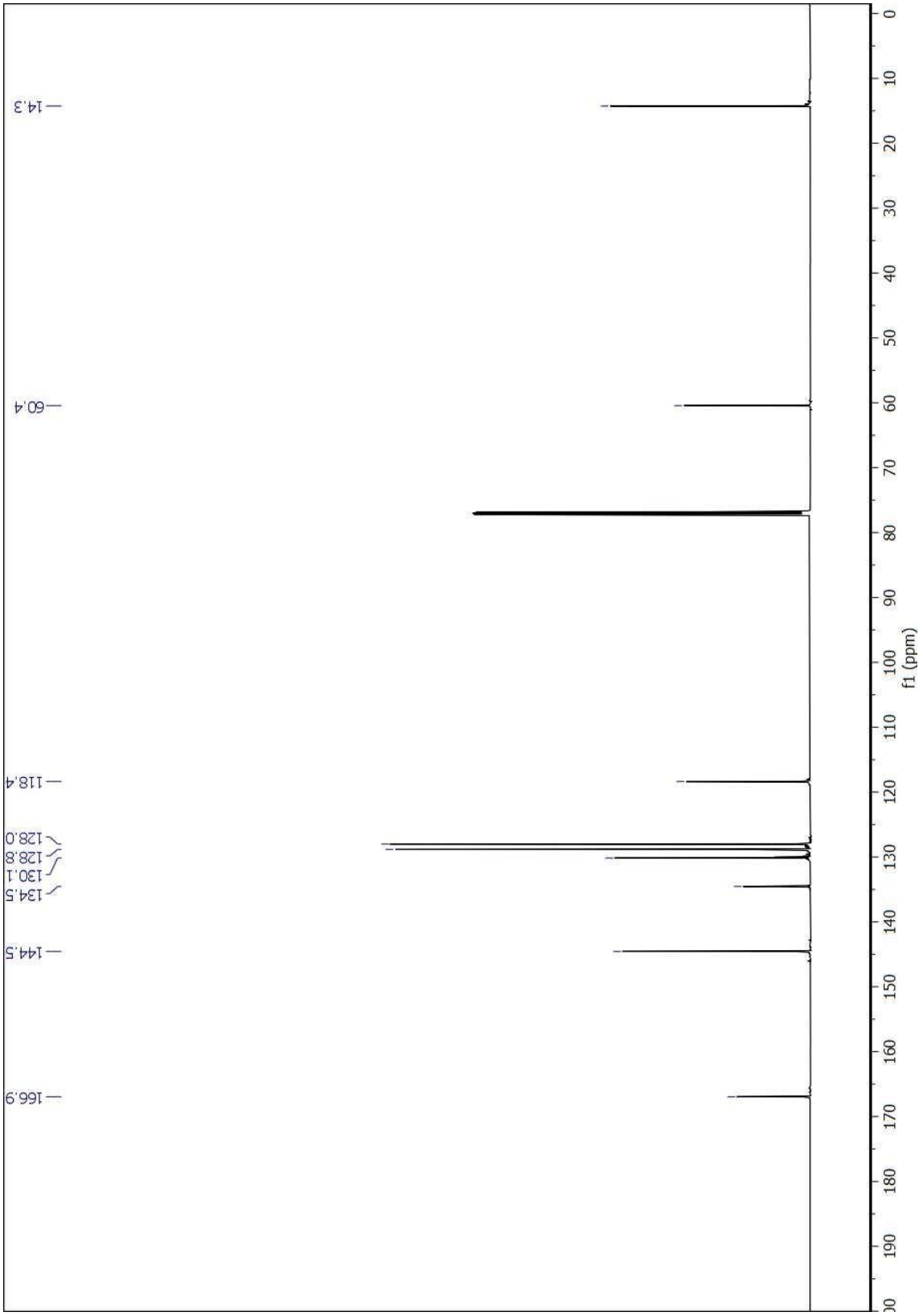
(*E*)-4-(4-bromophenyl)but-3-en-2-one (6):[27] white solid, m.p. 76-78 °C, 70% (*E*/*Z* > 99:1). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.68 (d, *J* = 16.0 Hz, 1H), 7.53 – 7.51 (m, 2H), 7.44 (d, *J* = 16.3 Hz, 1H), 7.41 – 7.39 (m, 2H), 6.69 (d, *J* = 16.3 Hz, 1H), 2.37 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 197.8, 141.8, 133.5, 132.2, 129.5, 127.6, 124.7, 27.6; FT-IR (Film, cm^{-1}): 3055, 2917, 2850, 1651, 1594, 1582, 1625, 1487, 1360, 1255, 1074, 982; GC/MS (70 eV) *m/z* (%): 226 (M^{+} + 2, 23), 224 (M^{+}, 24), 209 (73), 181 (24), 145 (61), 102 (100), 75 (24); HRMS (ESI) *m/z* calc. for [$C_{10}H_9O_2Br$ +H] $^{+}$: 224.9910; found: 224.9735. Purified by crystallization from hot/cold methanol.

NMR Spectra

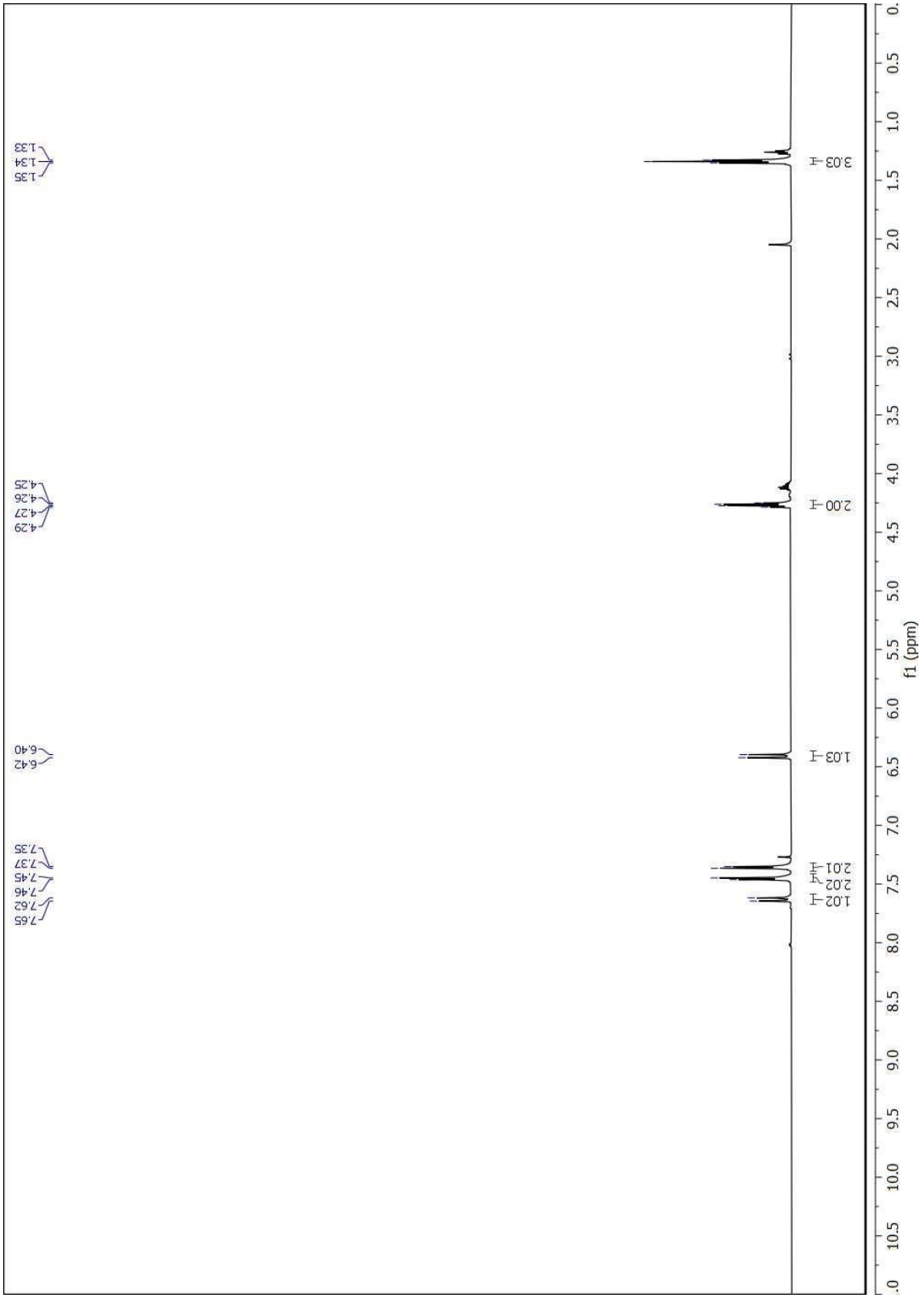
(*E)*-Ethyl cinnamate (3a)



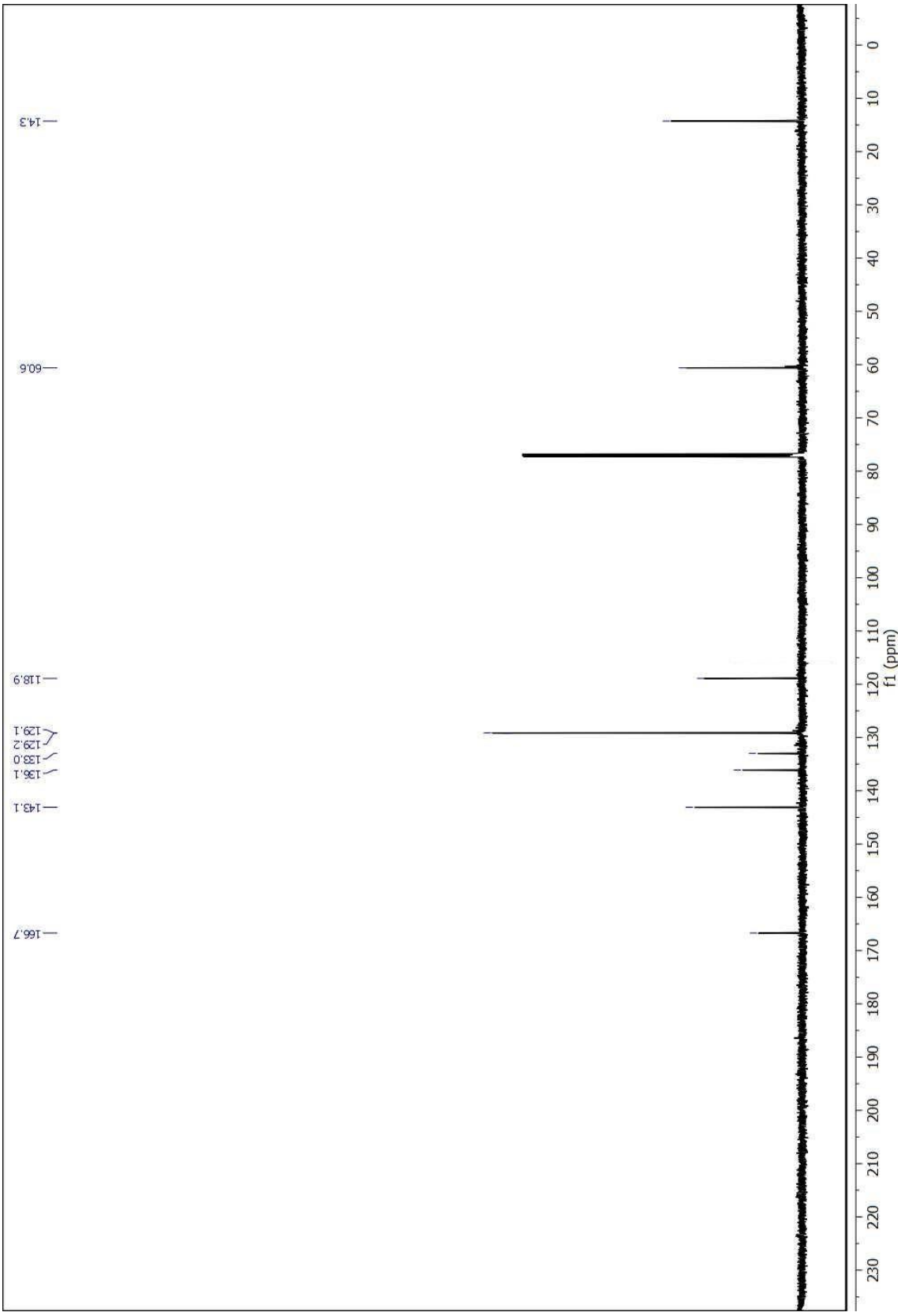
(*E*)-Ethyl cinnamate (3a)



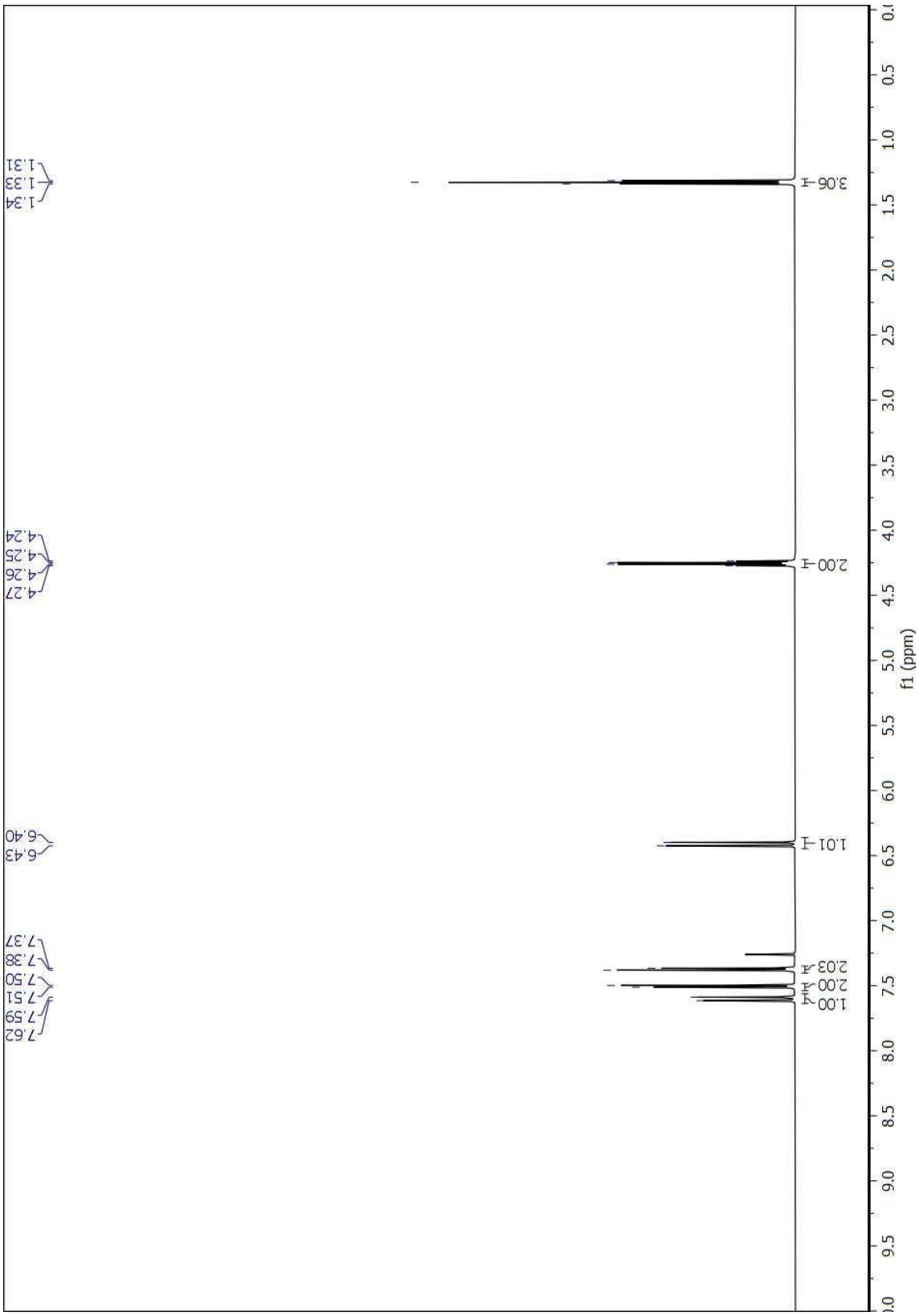
Ethyl *(E)*-3-(4-chlorophenyl)acrylate (3b)



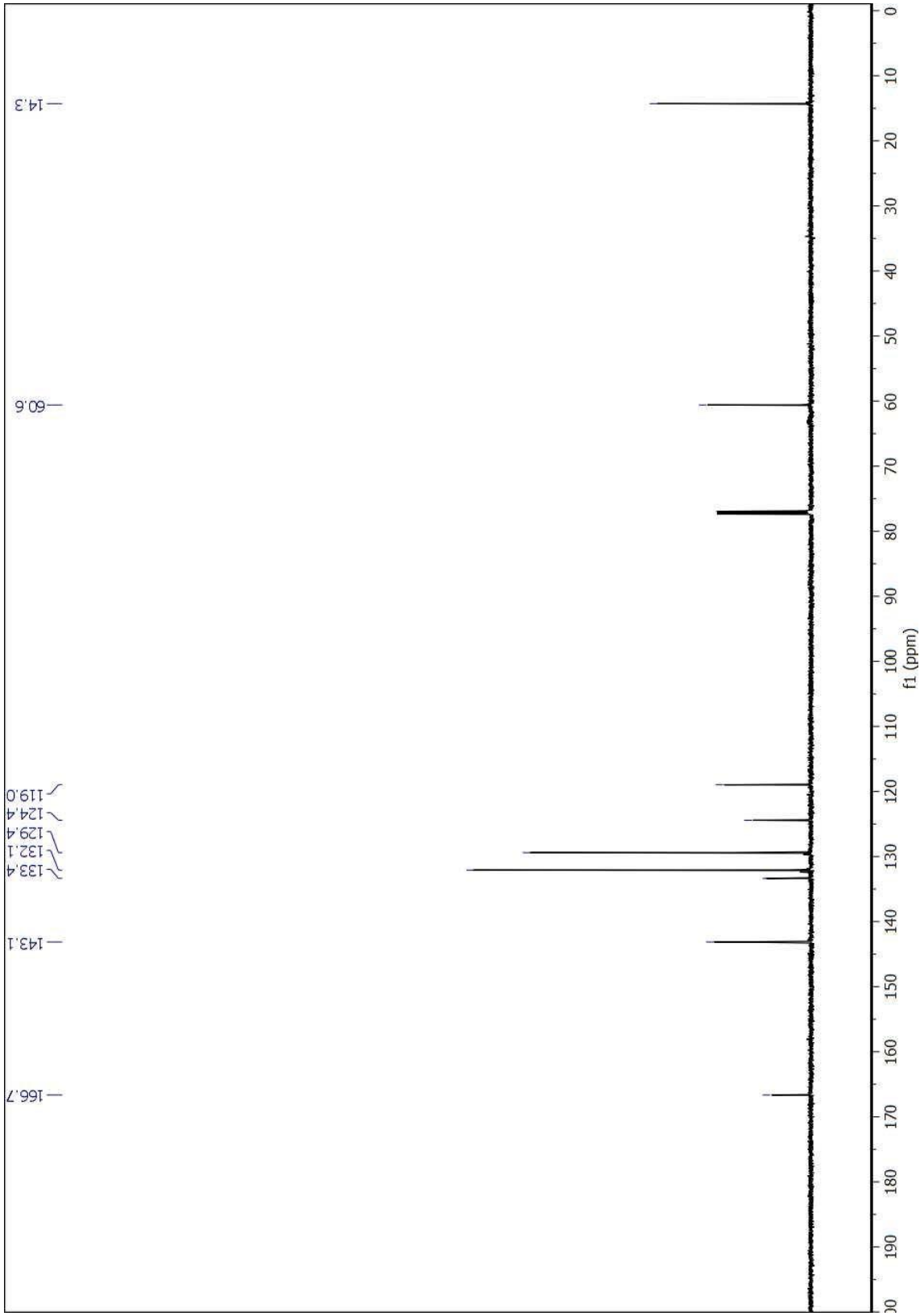
Ethyl *(E)*-3-(4-chlorophenyl)acrylate (3b)



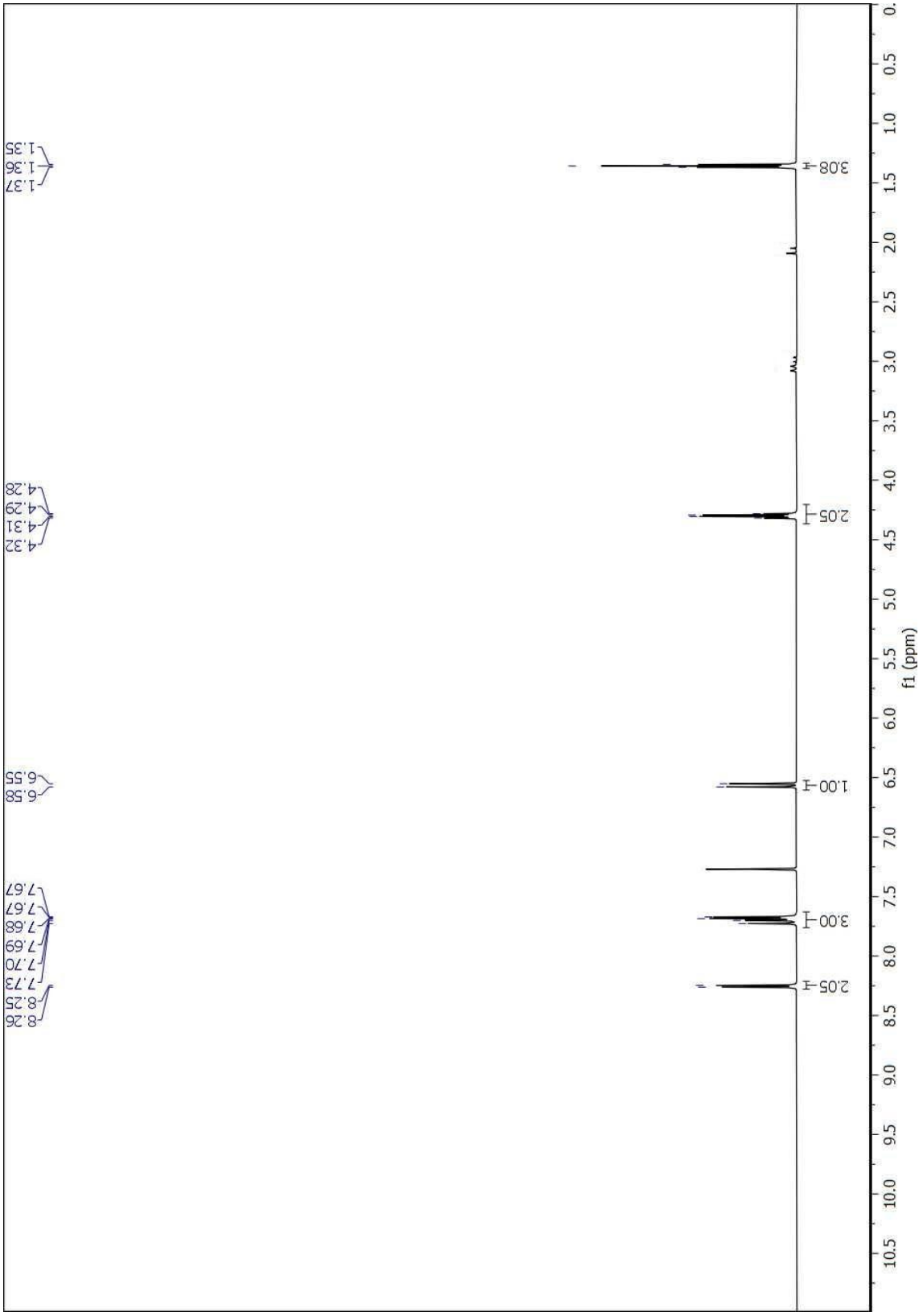
Ethyl *(E)*-3-(4-bromophenyl)acrylate (3c)



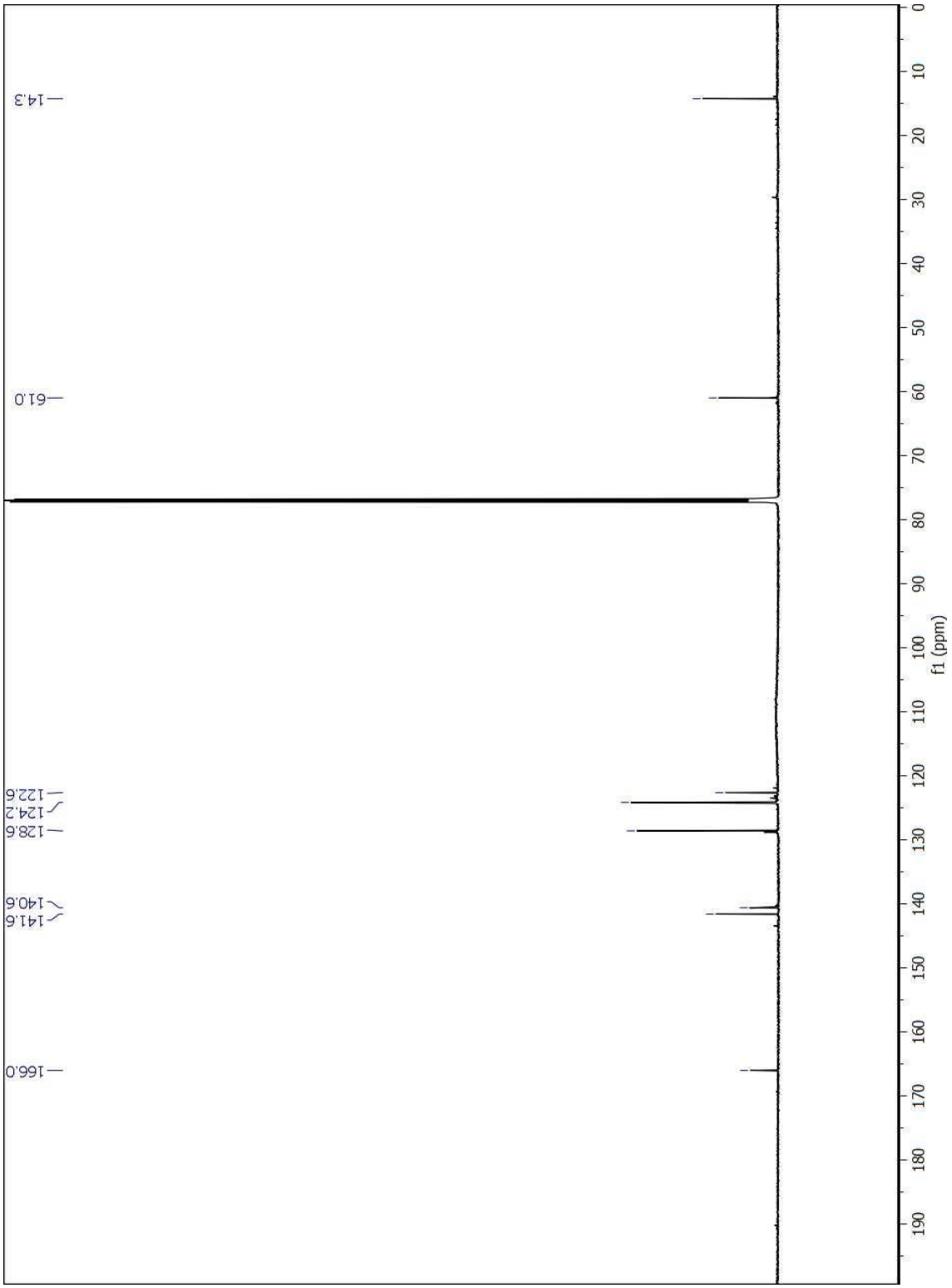
Ethyl *(E)*-3-(4-bromophenyl)acrylate (3c)



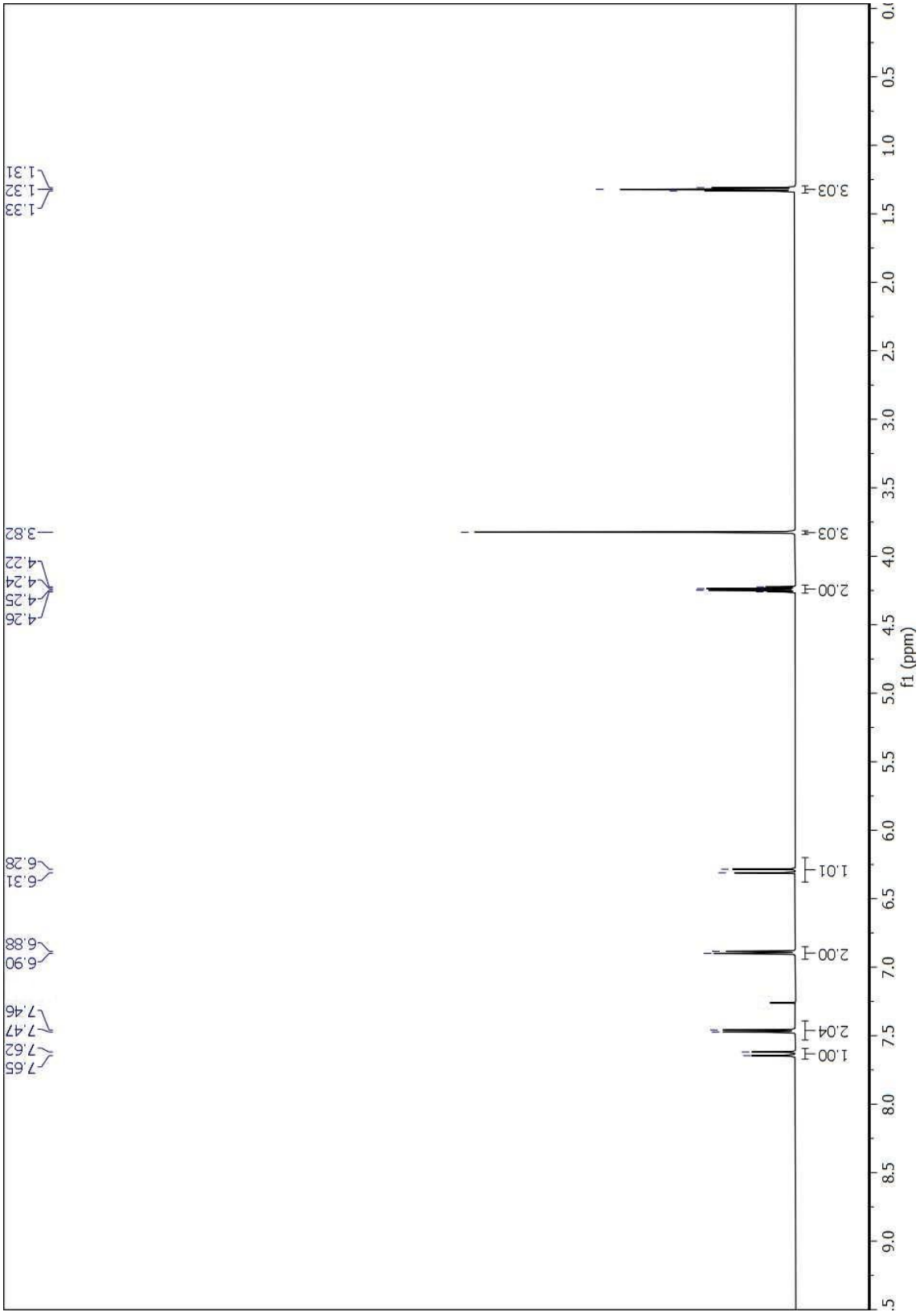
Ethyl *(E)*-3-(4-nitrophenyl)acrylate (3d)



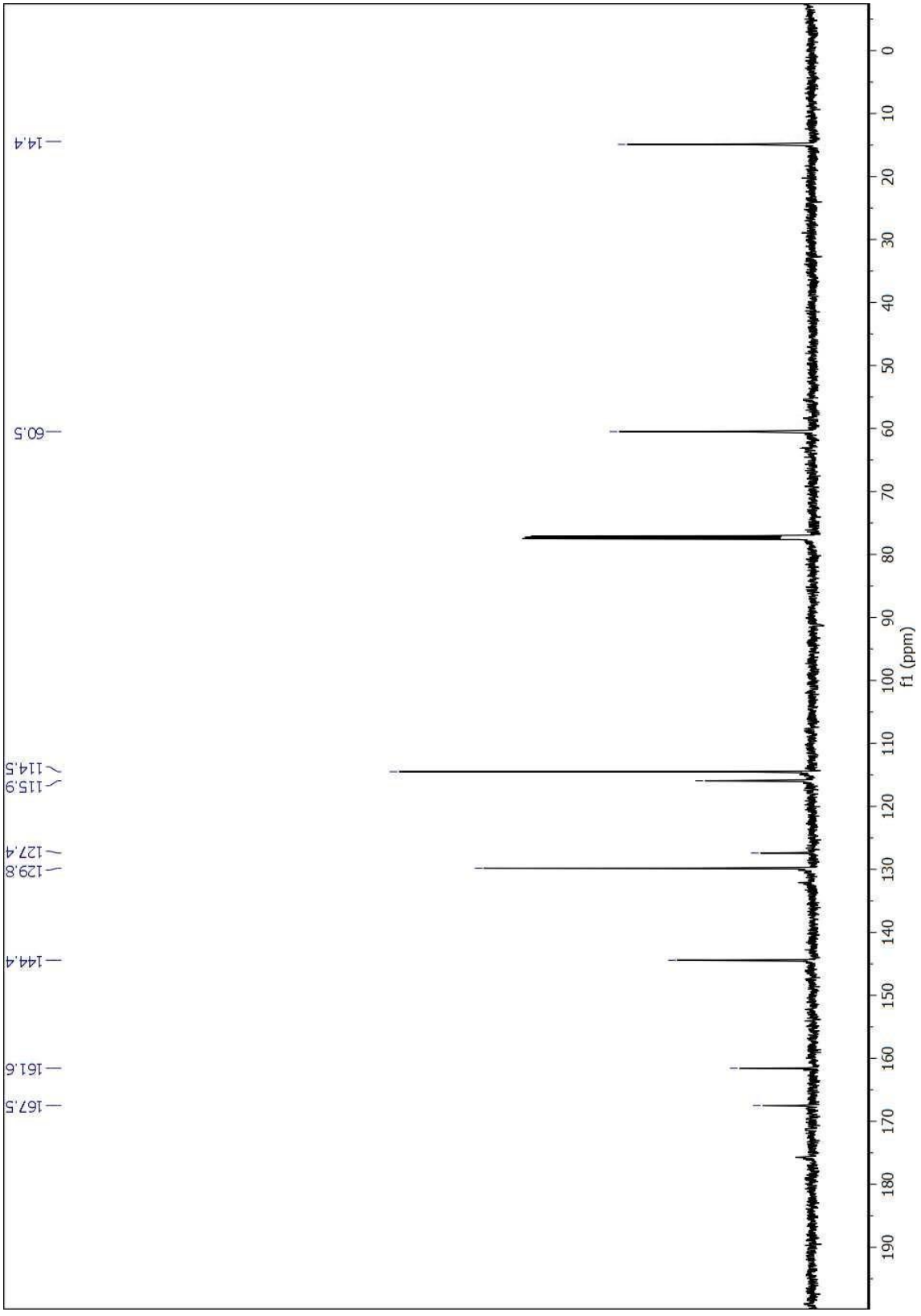
Ethyl *(E)*-3-(4-nitrophenyl)acrylate (3d)



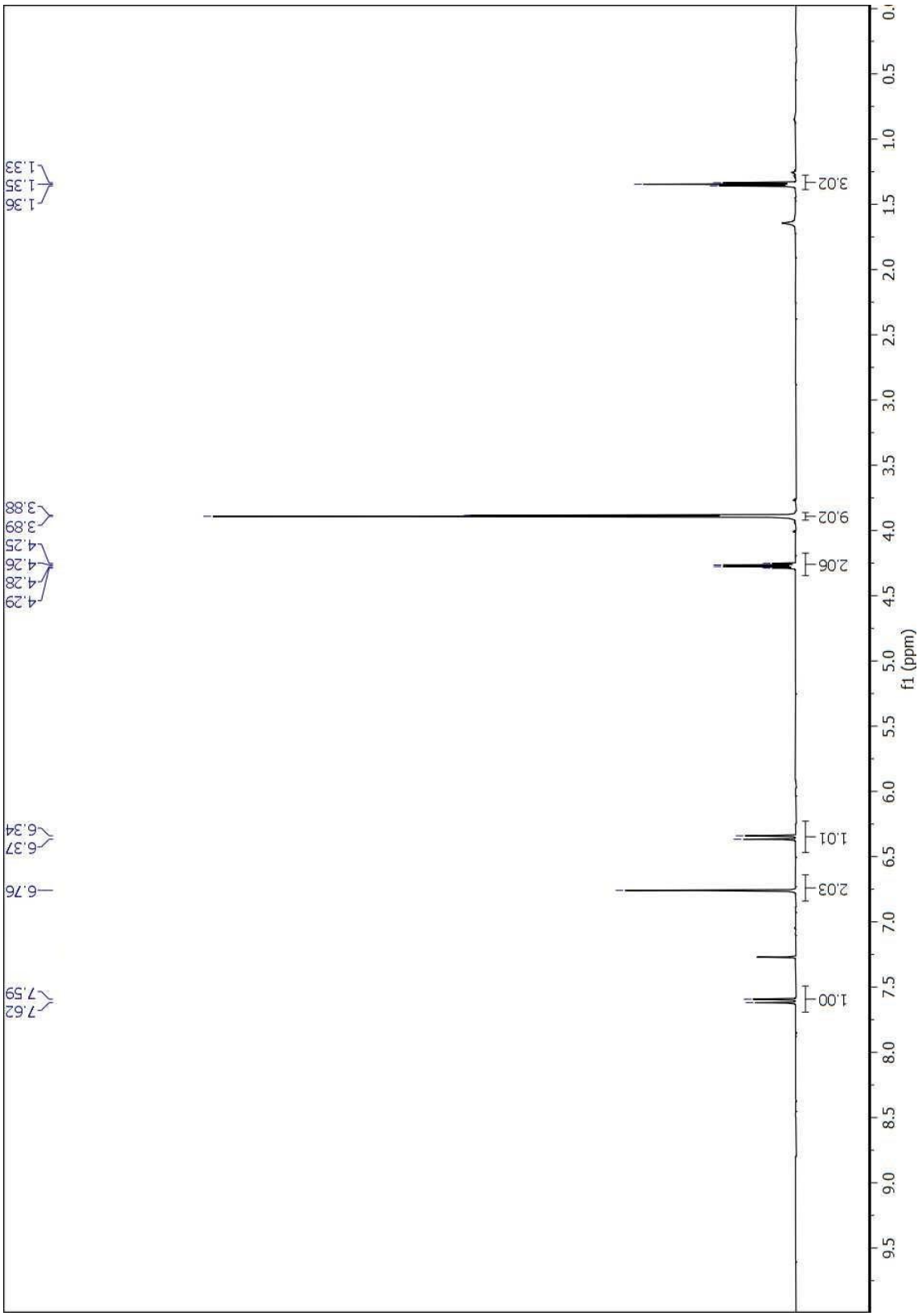
Ethyl *(E)*-3-(4-methoxyphenyl)acrylate (3e)



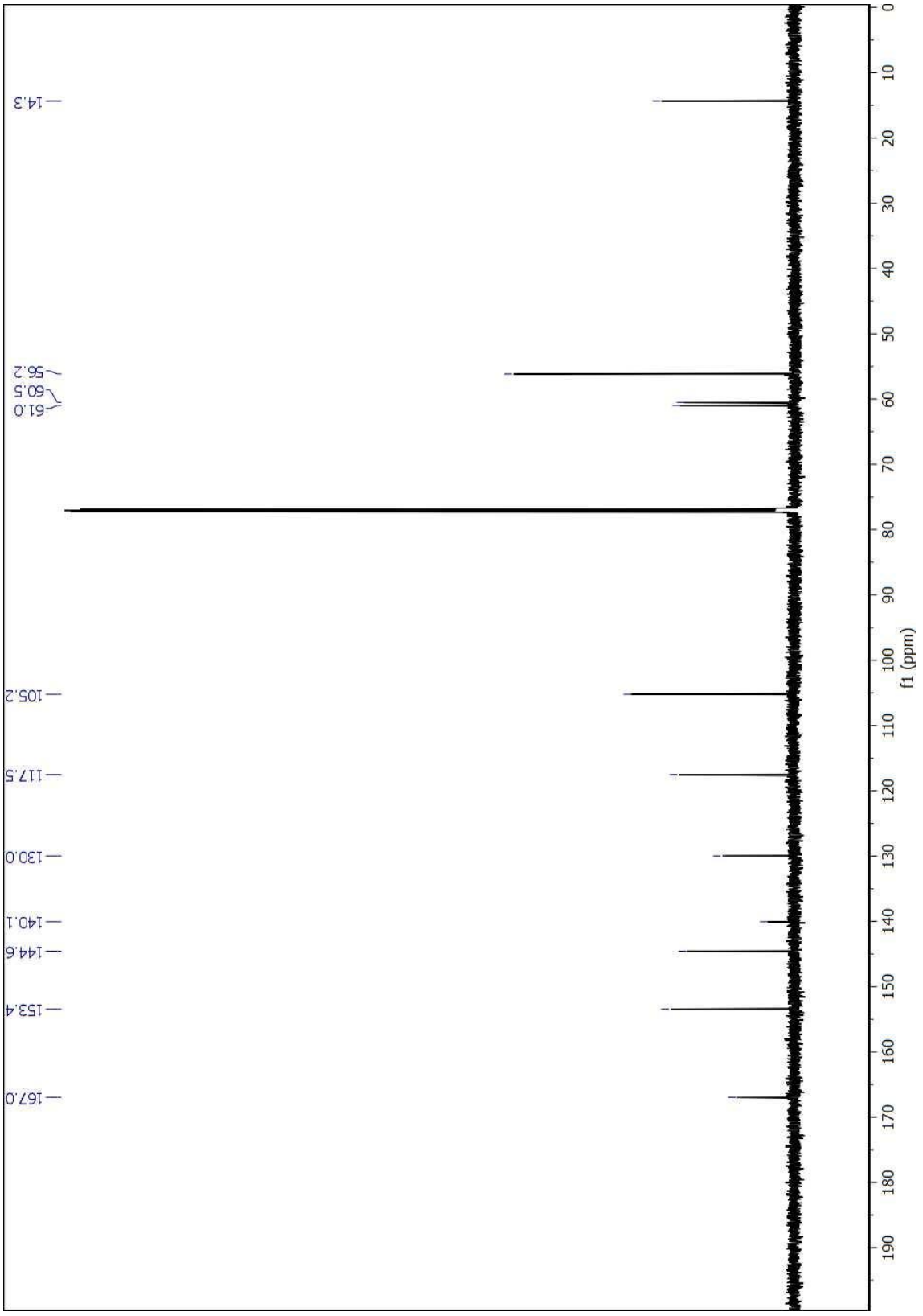
Ethyl *(E)*-3-(4-methoxyphenyl)acrylate (3e)



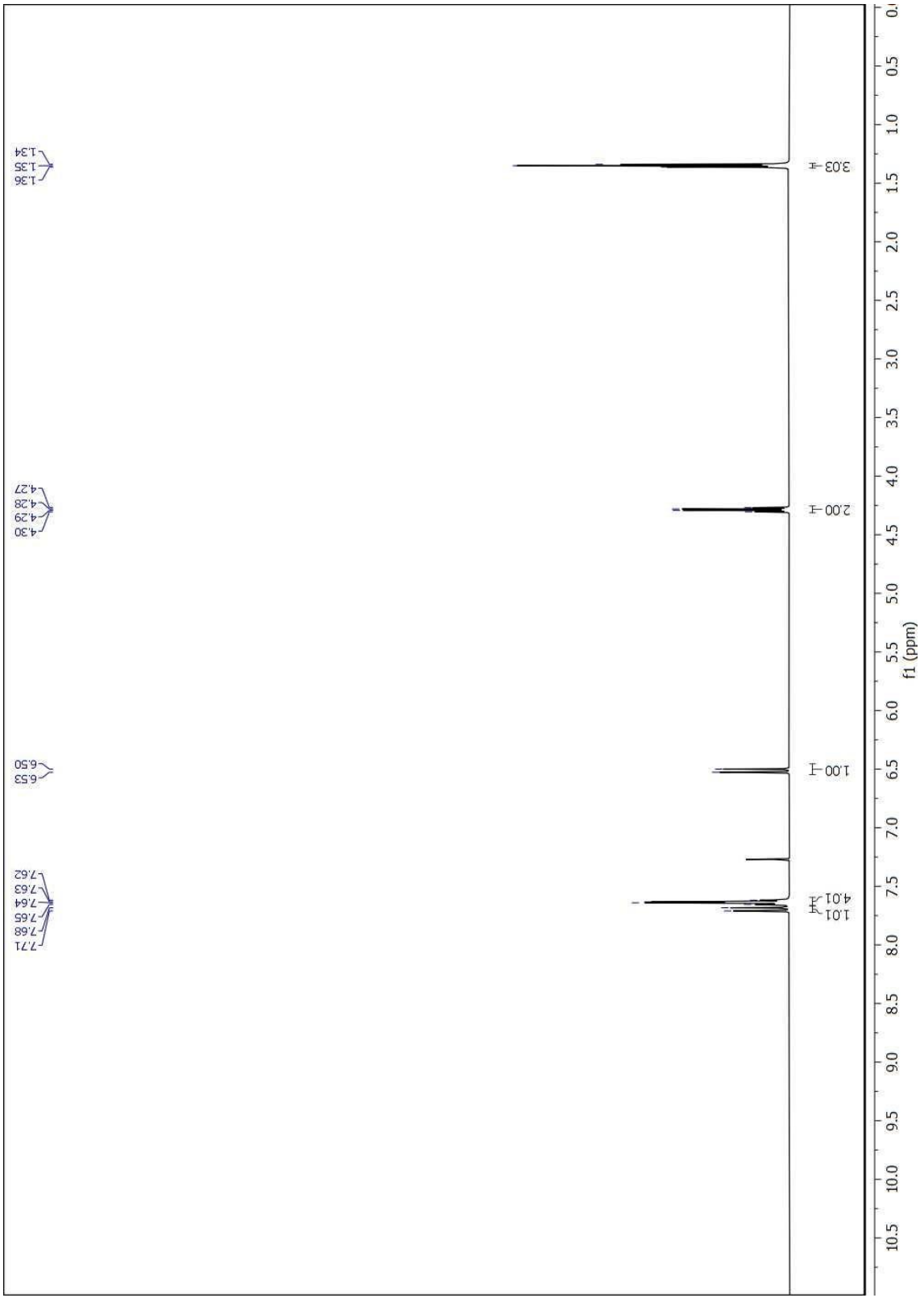
Ethyl *(E)*-3-(3,4,5-trimethoxyphenyl)acrylate (3f)



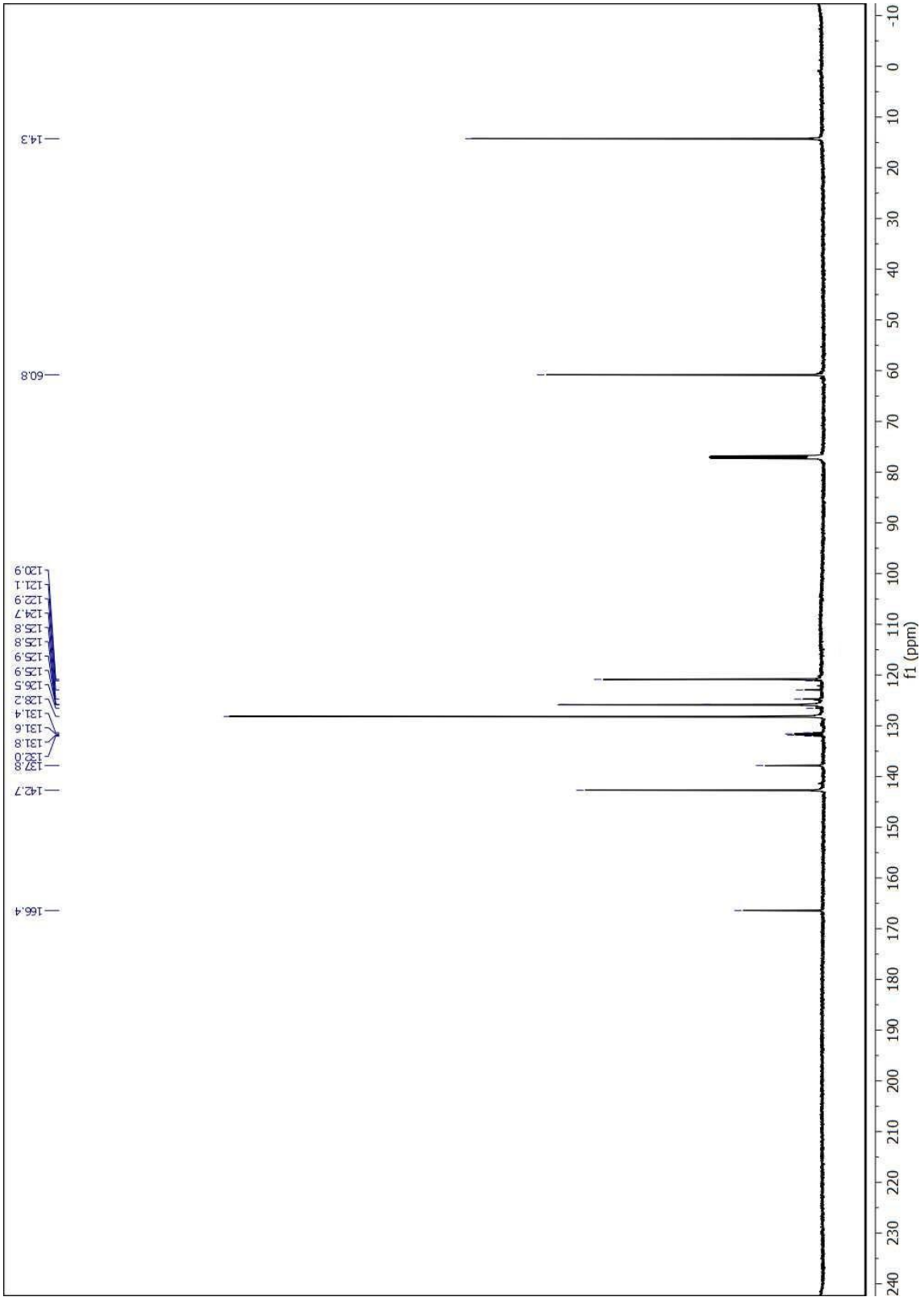
Ethyl *(E)*-3-(3,4,5-trimethoxyphenyl)acrylate (3f)



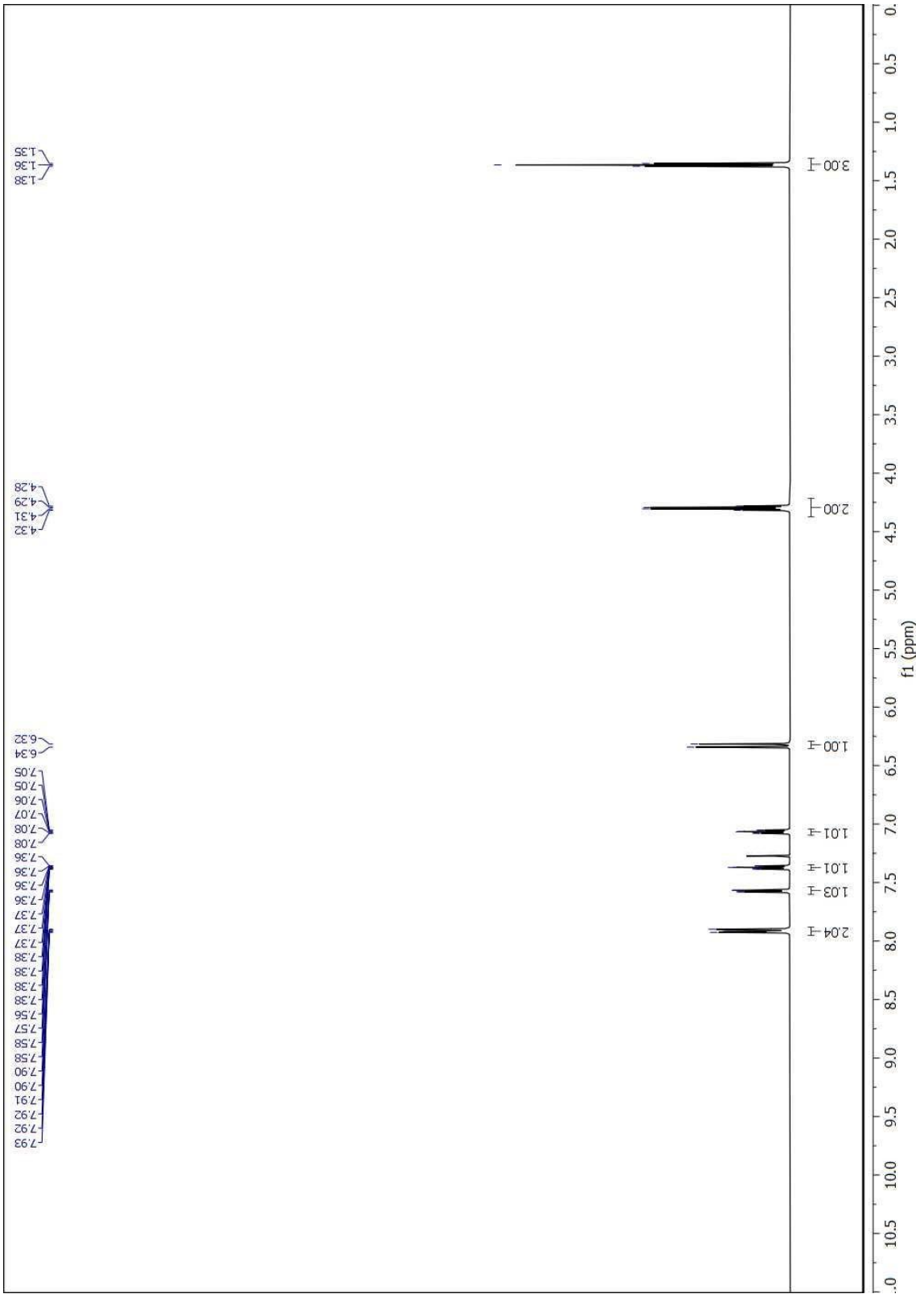
Ethyl *(E)*-3-(4-(trifluoromethyl)phenyl)acrylate (3i)



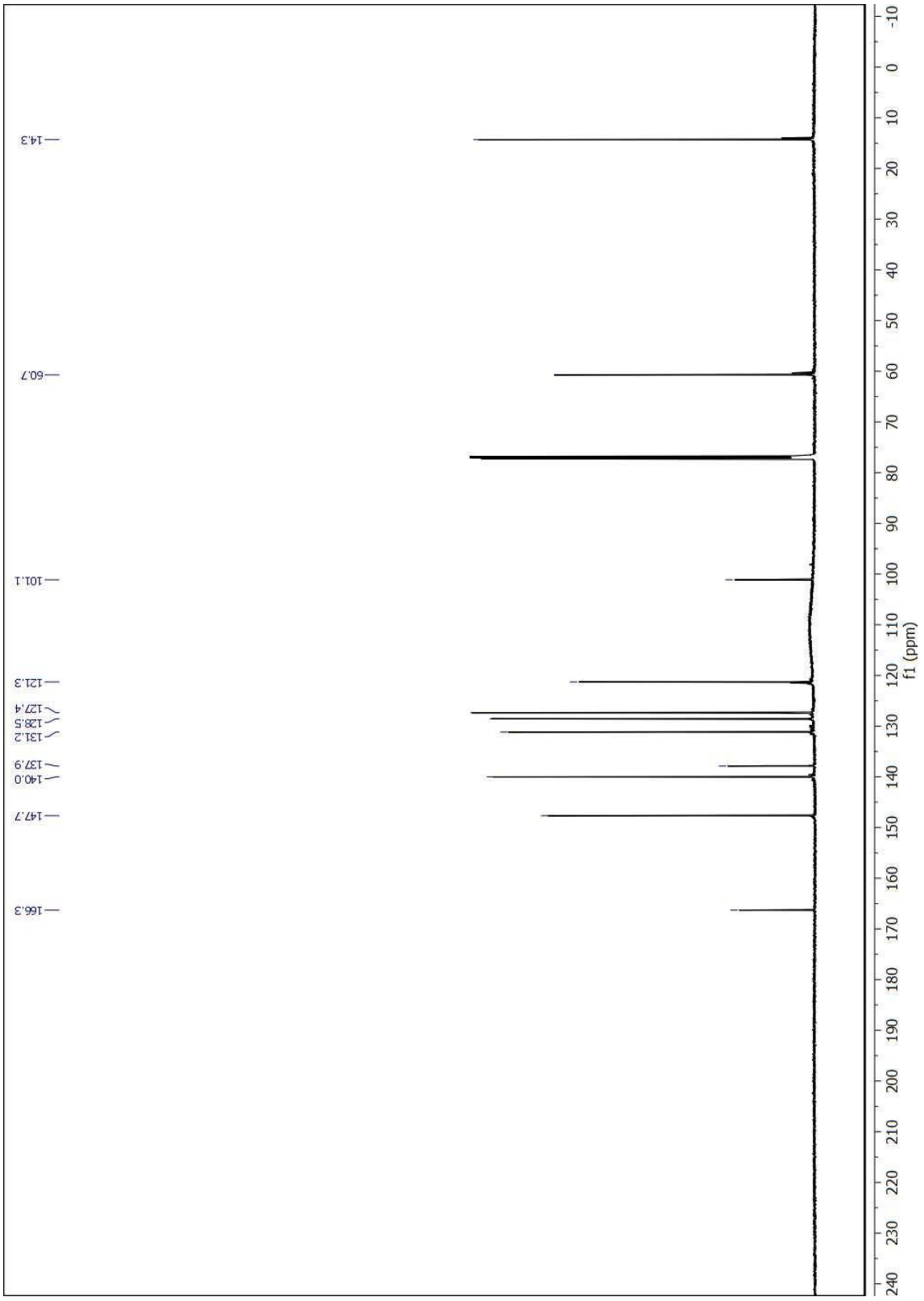
Ethyl *(E)*-3-(4-(trifluoromethyl)phenyl)acrylate (3i)



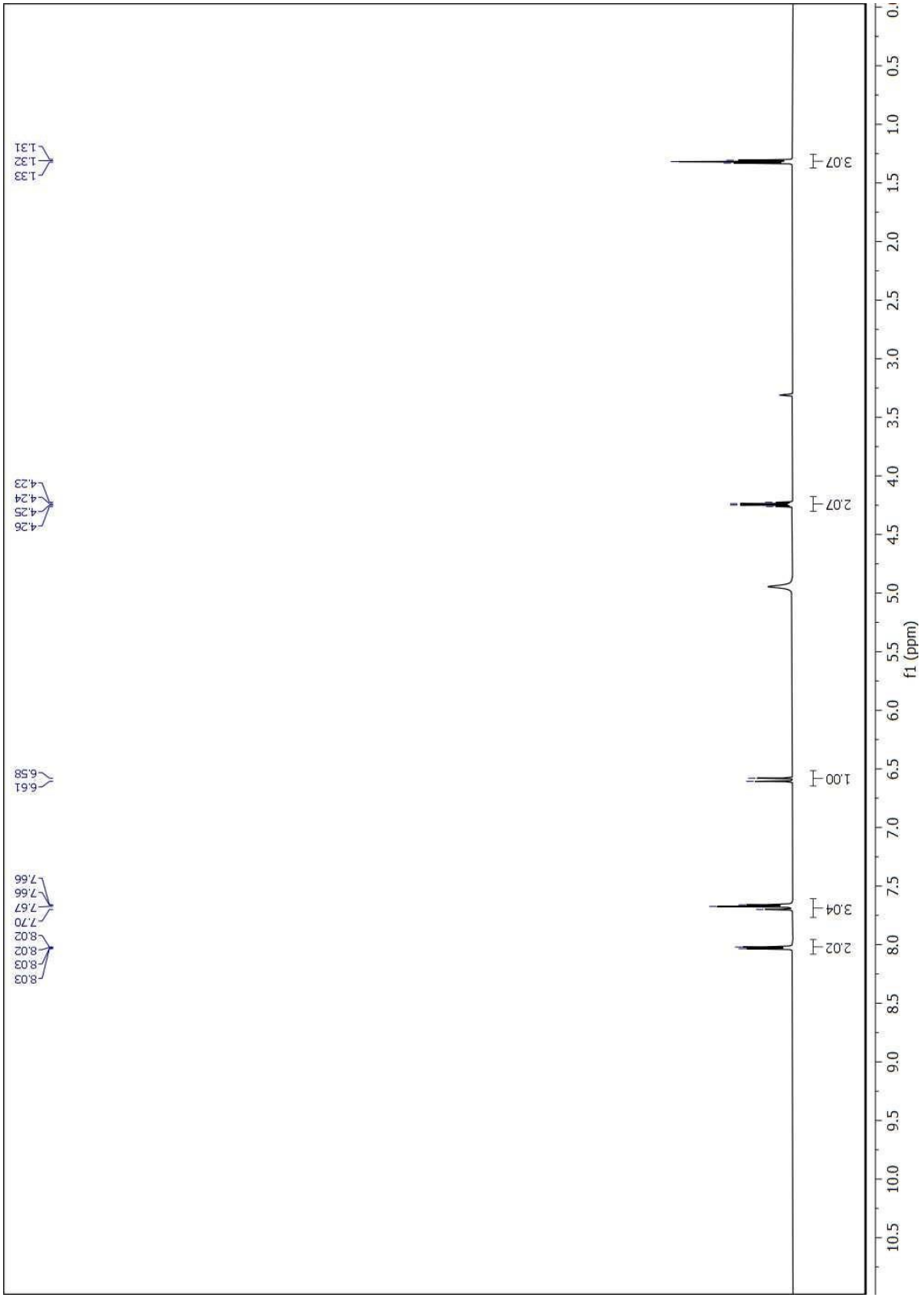
Ethyl *(E)*-3-(2-iodophenyl)acrylate (3j)



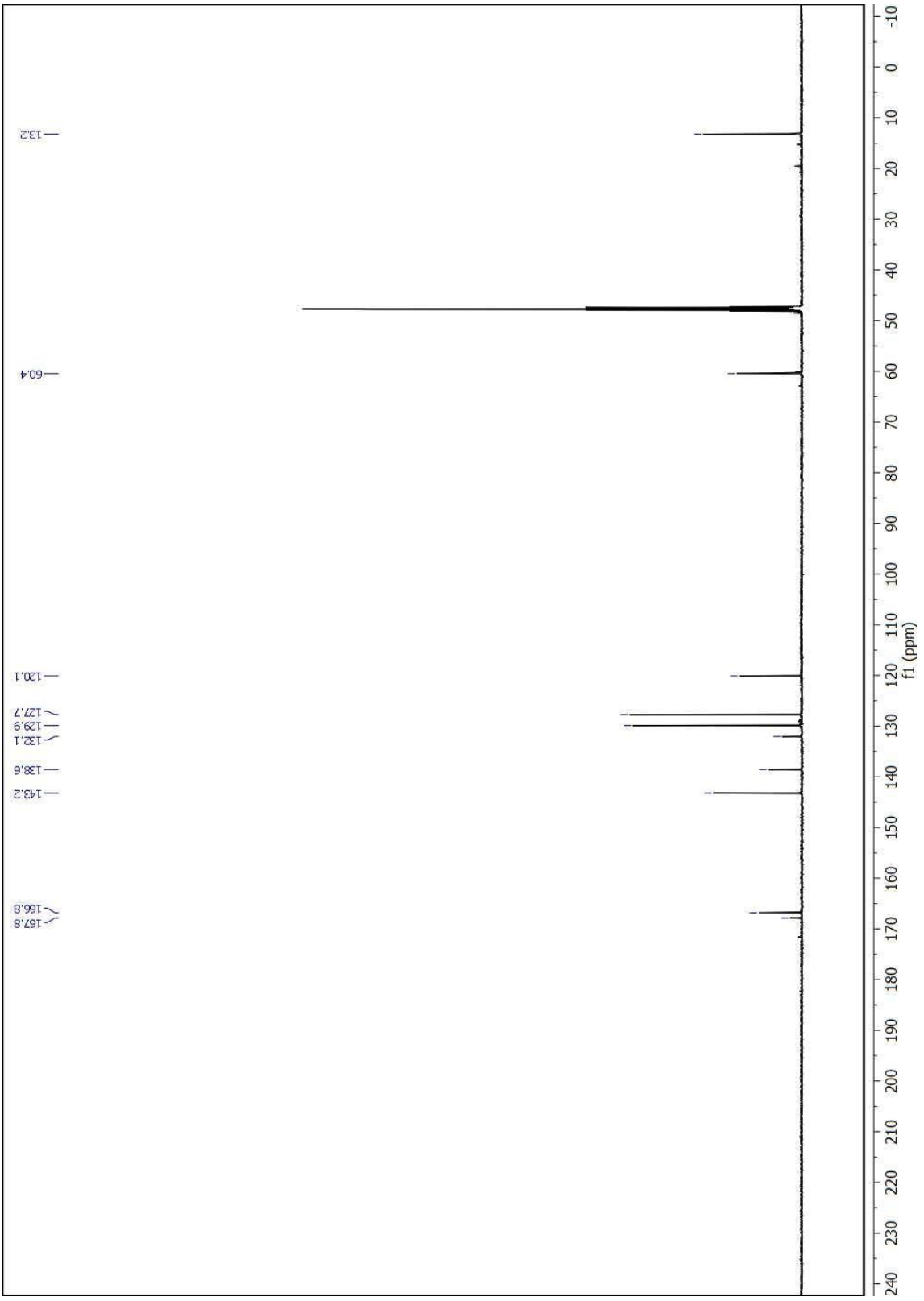
Ethyl *(E)*-3-(2-iodophenyl)acrylate (3j)



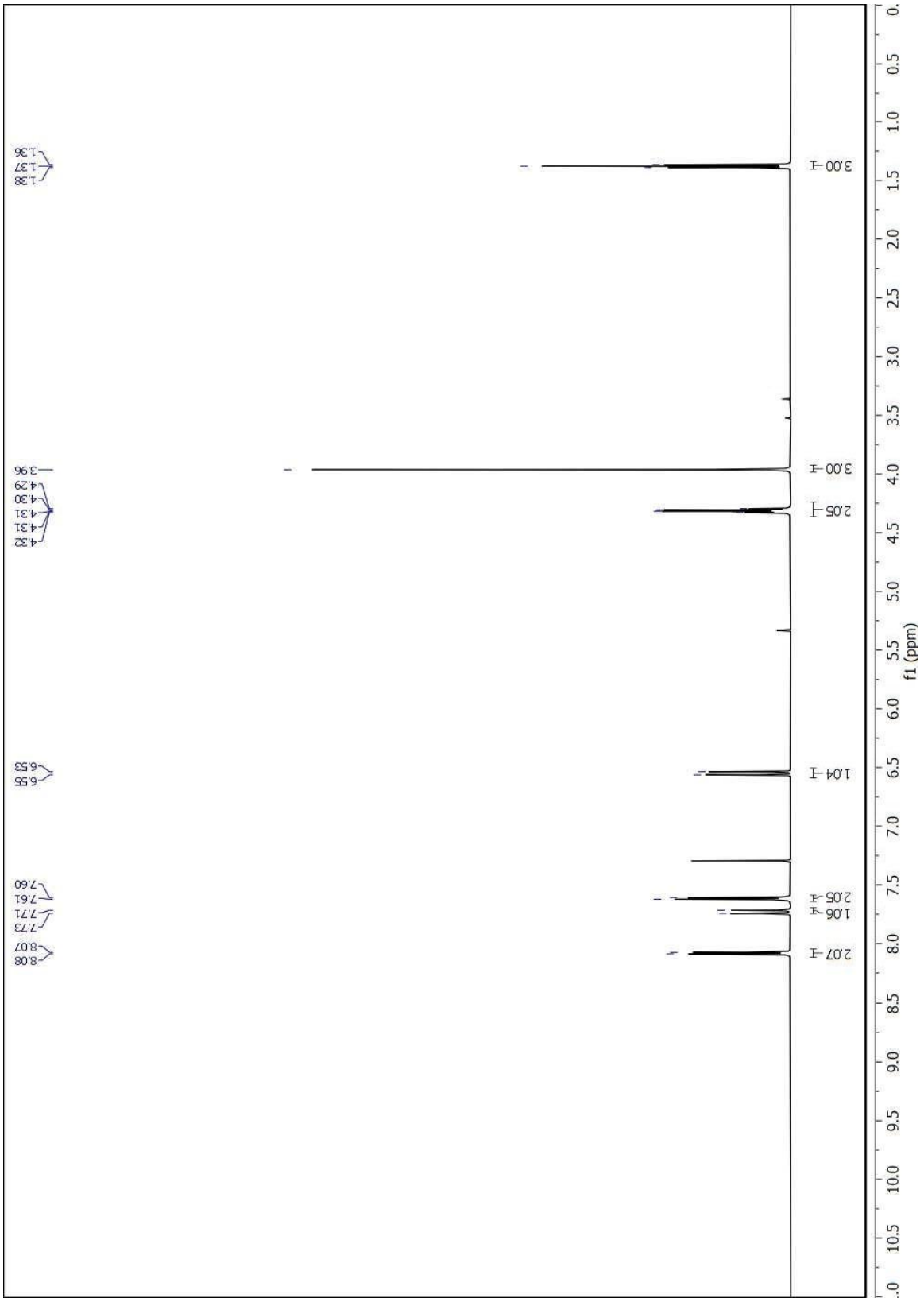
Ethyl (E)-3-(4-carboxyphenyl)acrylate (3k)



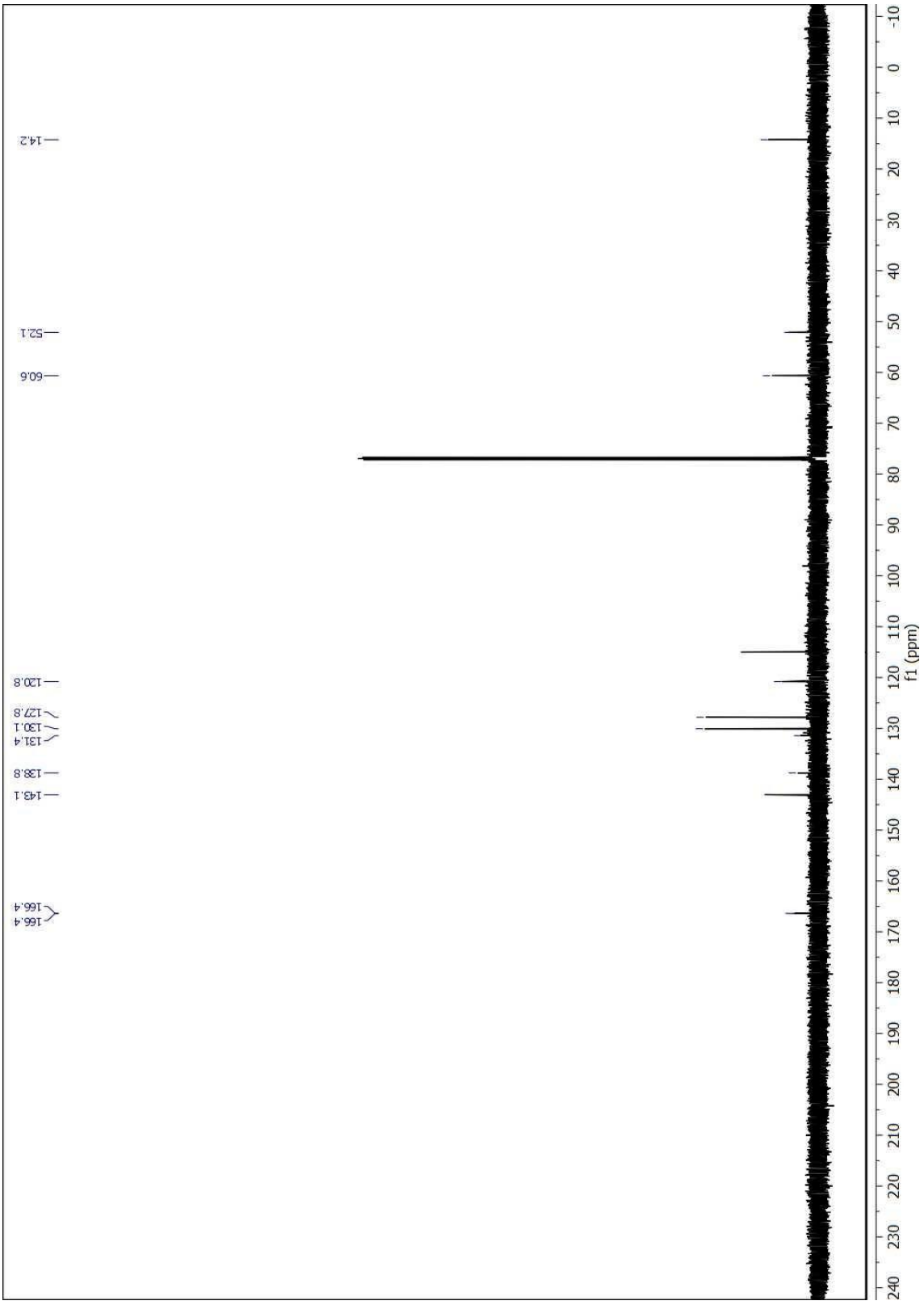
Ethyl (E)-3-(4-carboxyphenyl)acrylate (3k)



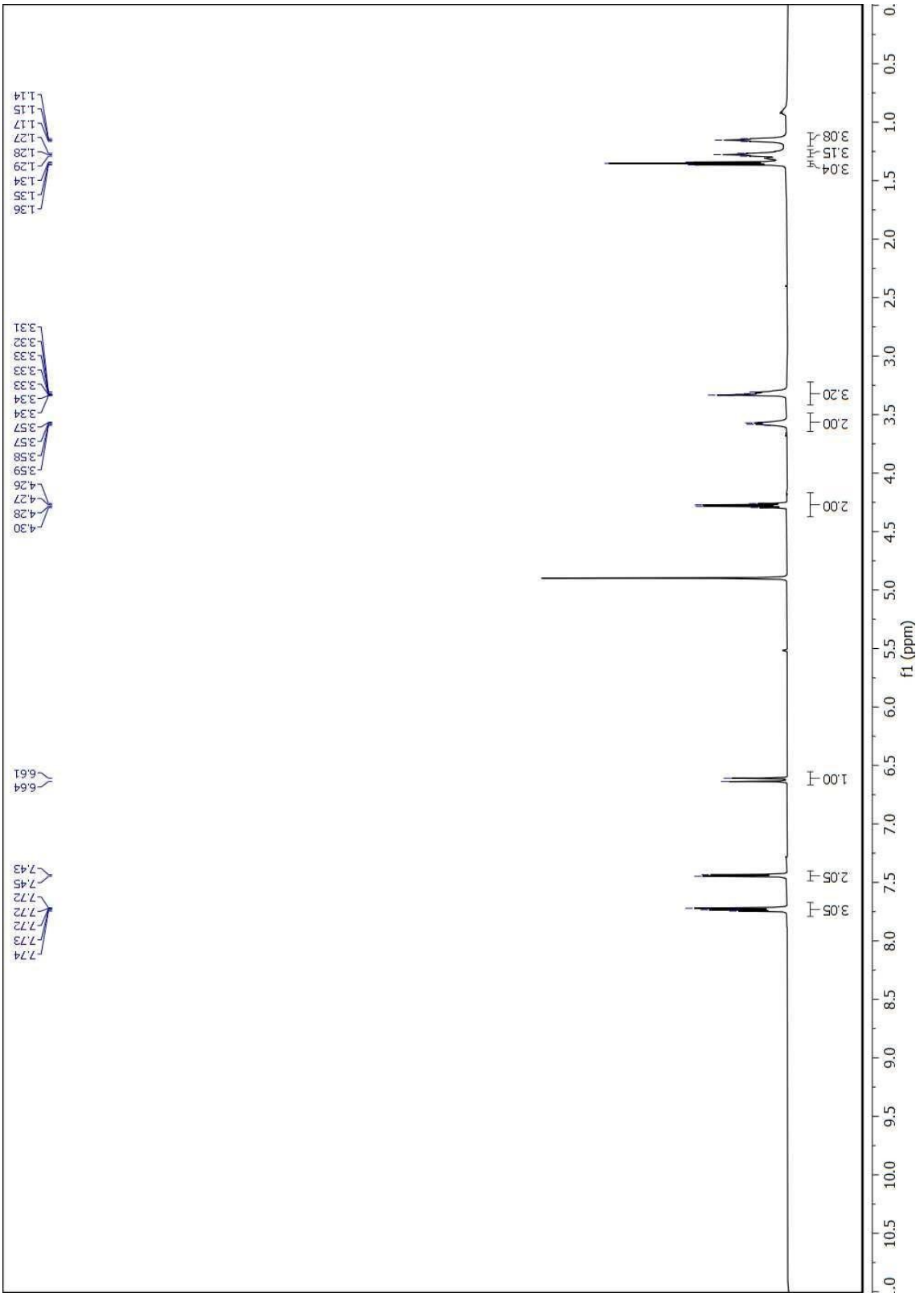
Ethyl (E)-3-(4-methoxycarbonylphenyl)acrylate (3l)



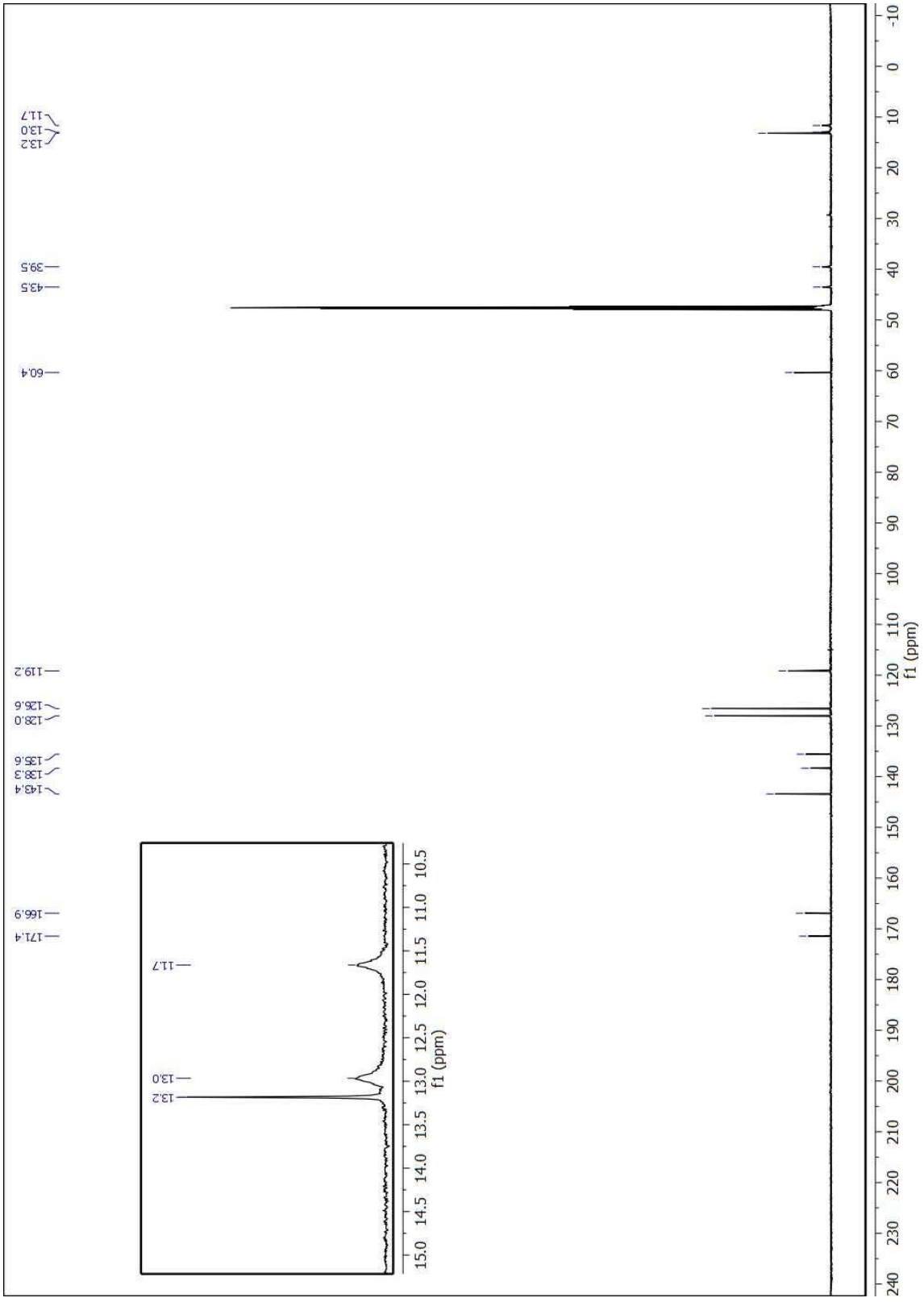
Ethyl (E)-3-(4-methoxycarbonylphenyl)acrylate (3l)



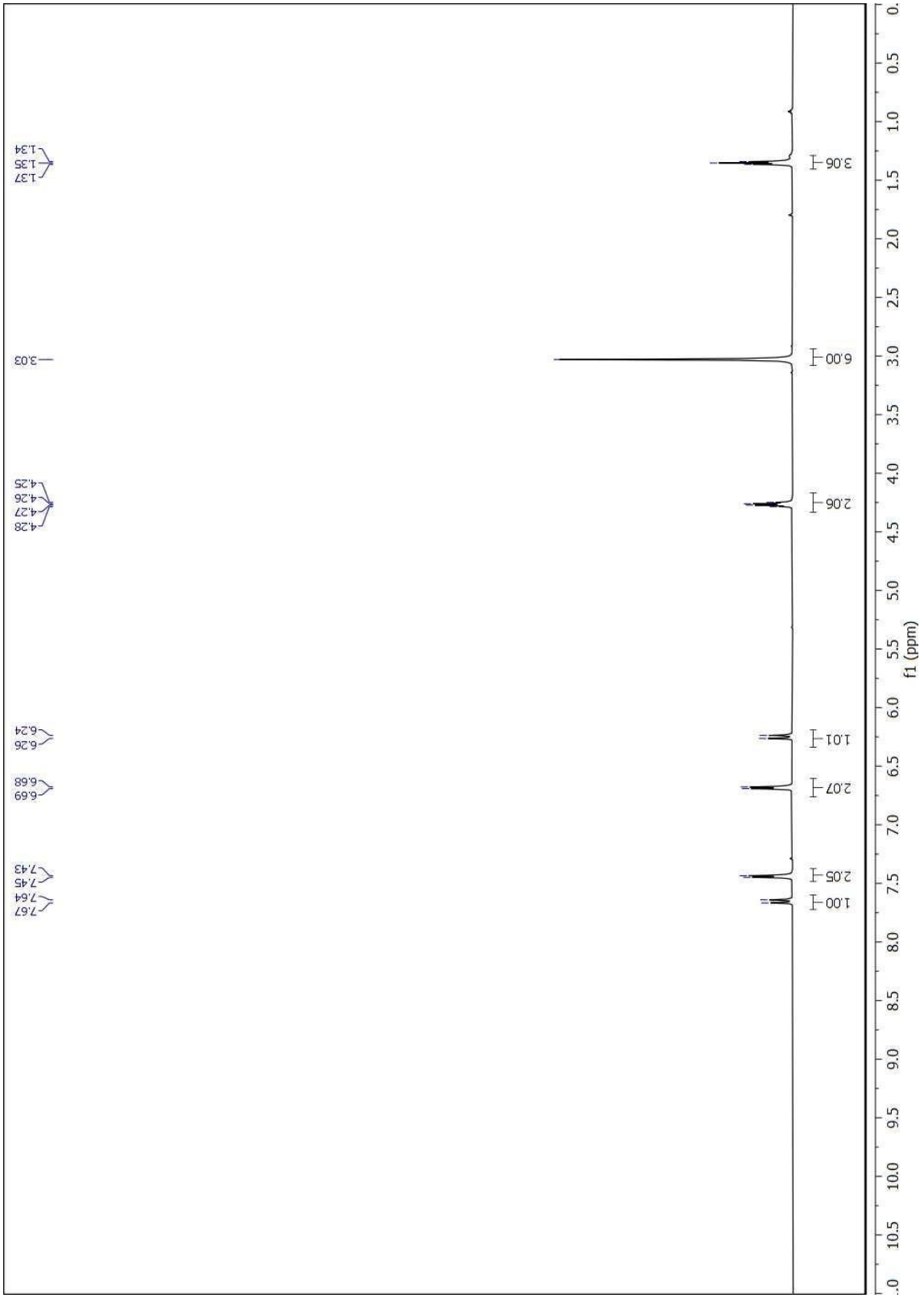
Ethyl (E)-3-[4-(*N,N*-diethylcarbamoyl)phenyl]acrylate (3m)



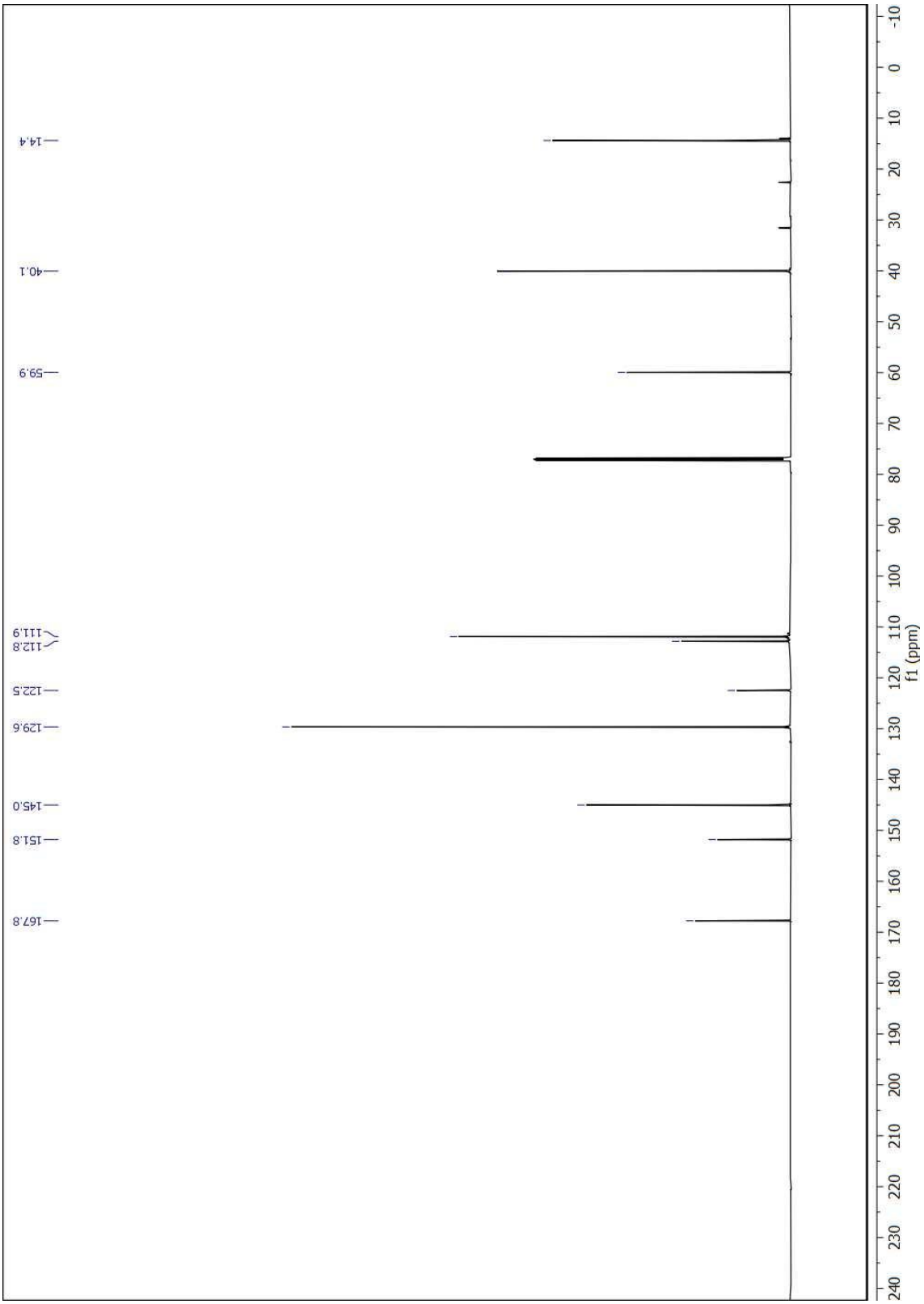
Ethyl (E)-3-[4-(*N,N*-diethylcarbamoyl)phenyl]acrylate (3m)



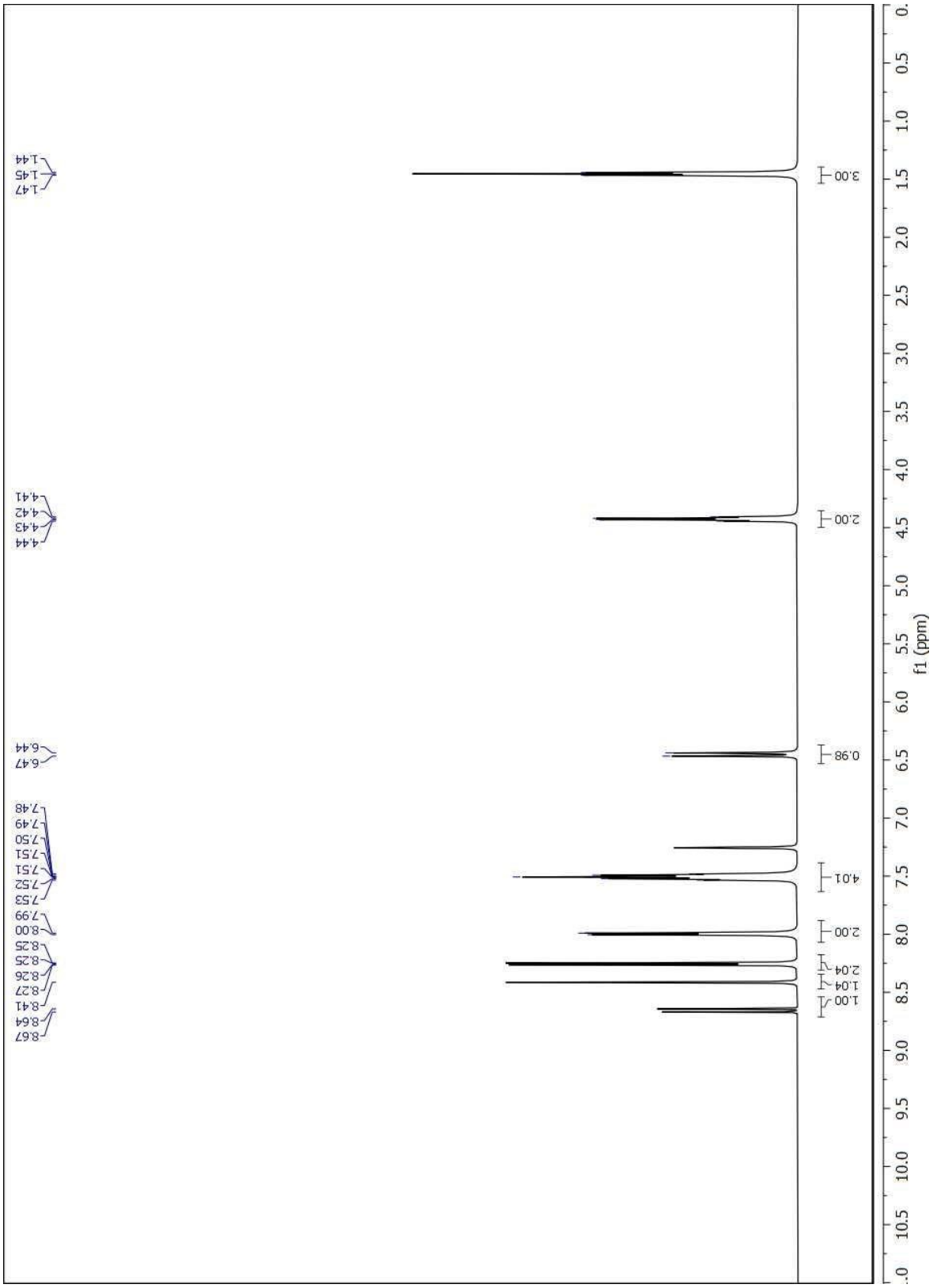
Ethyl (E)-3-[4-(dimethylamino)phenyl]acrylate (3n)



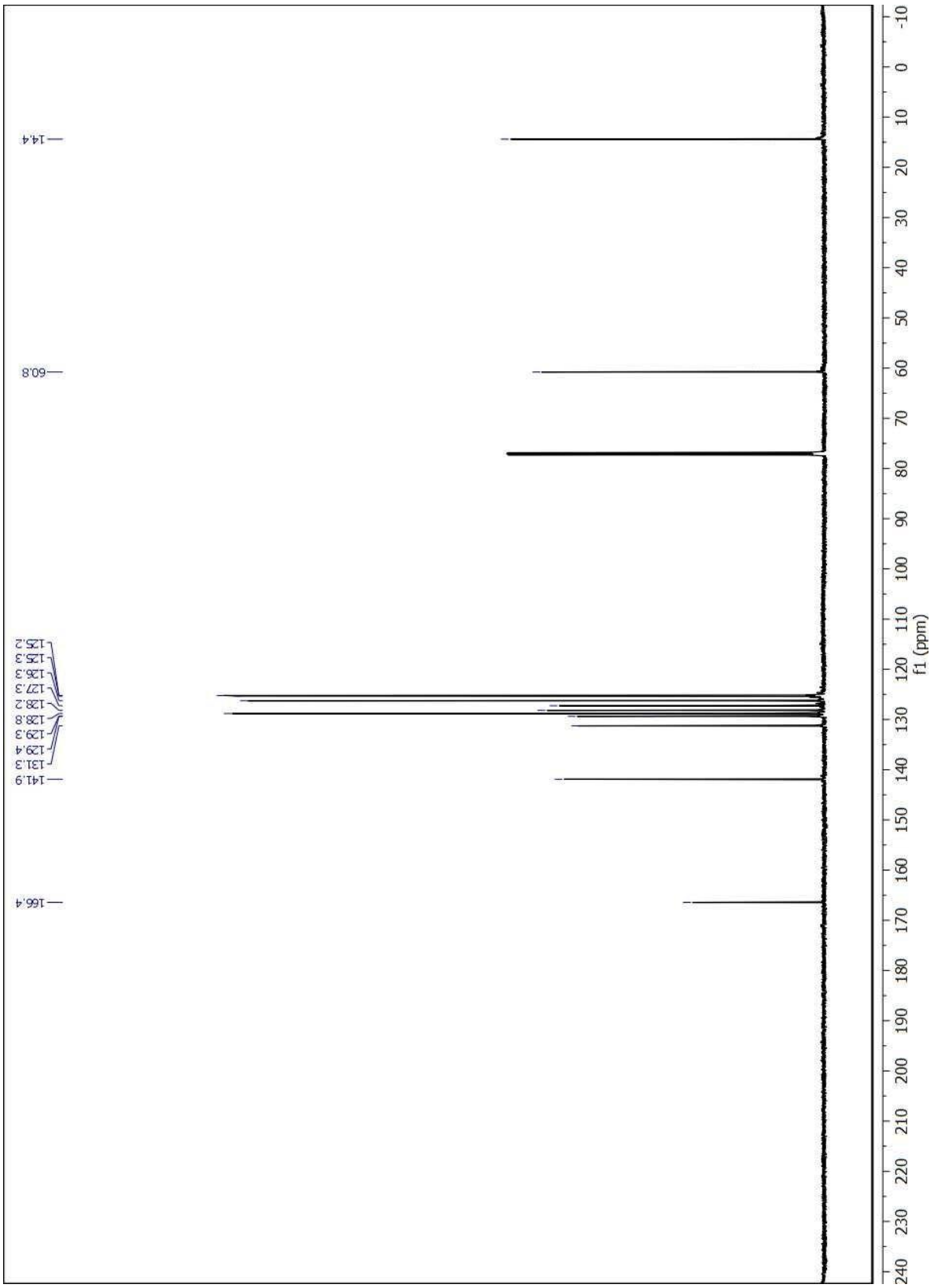
Ethyl (E)-3-[4-(dimethylamino)phenyl]acrylate (3n)



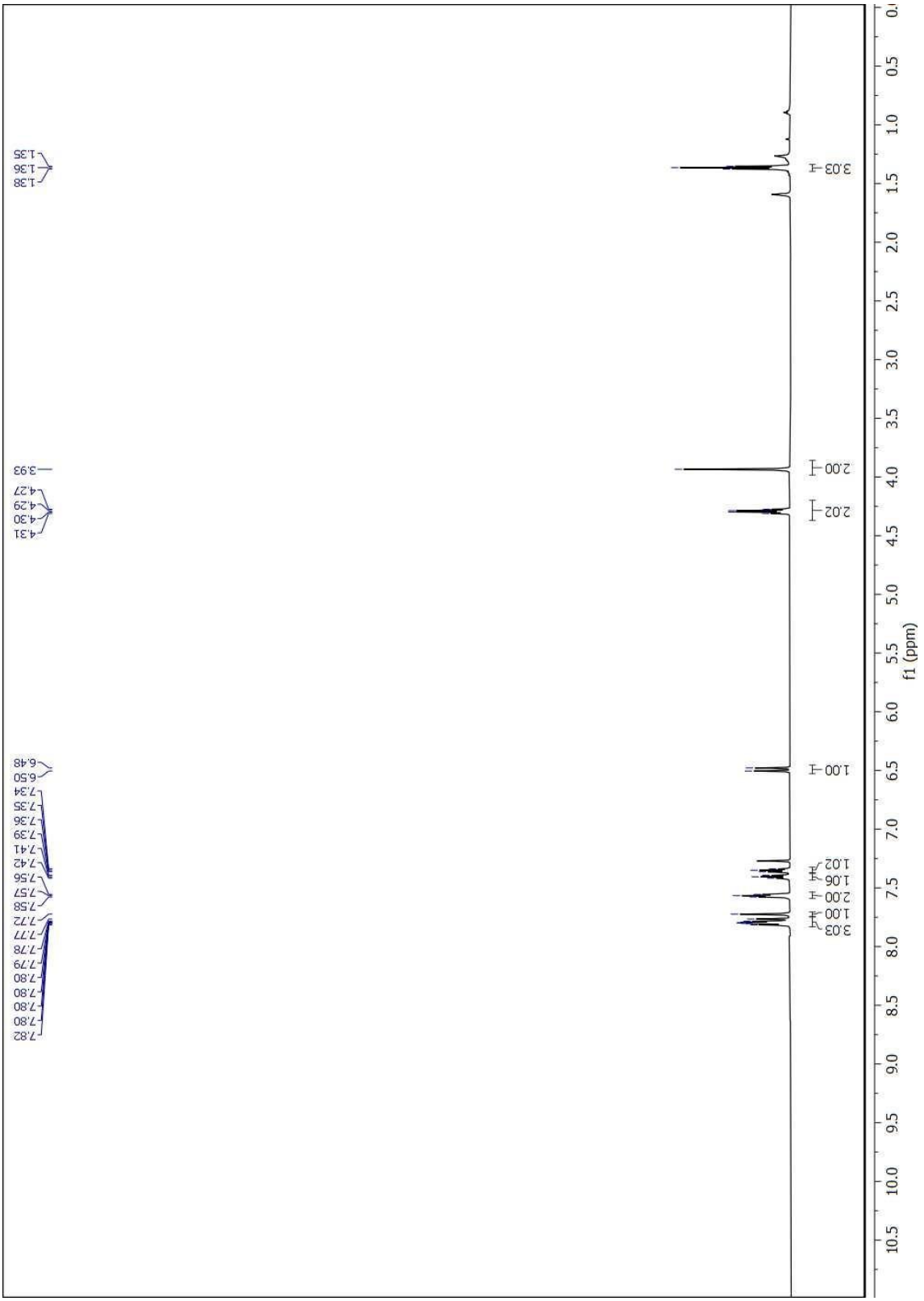
Ethyl *(E)*-3-(anthracen-9-yl)acrylate (3o)



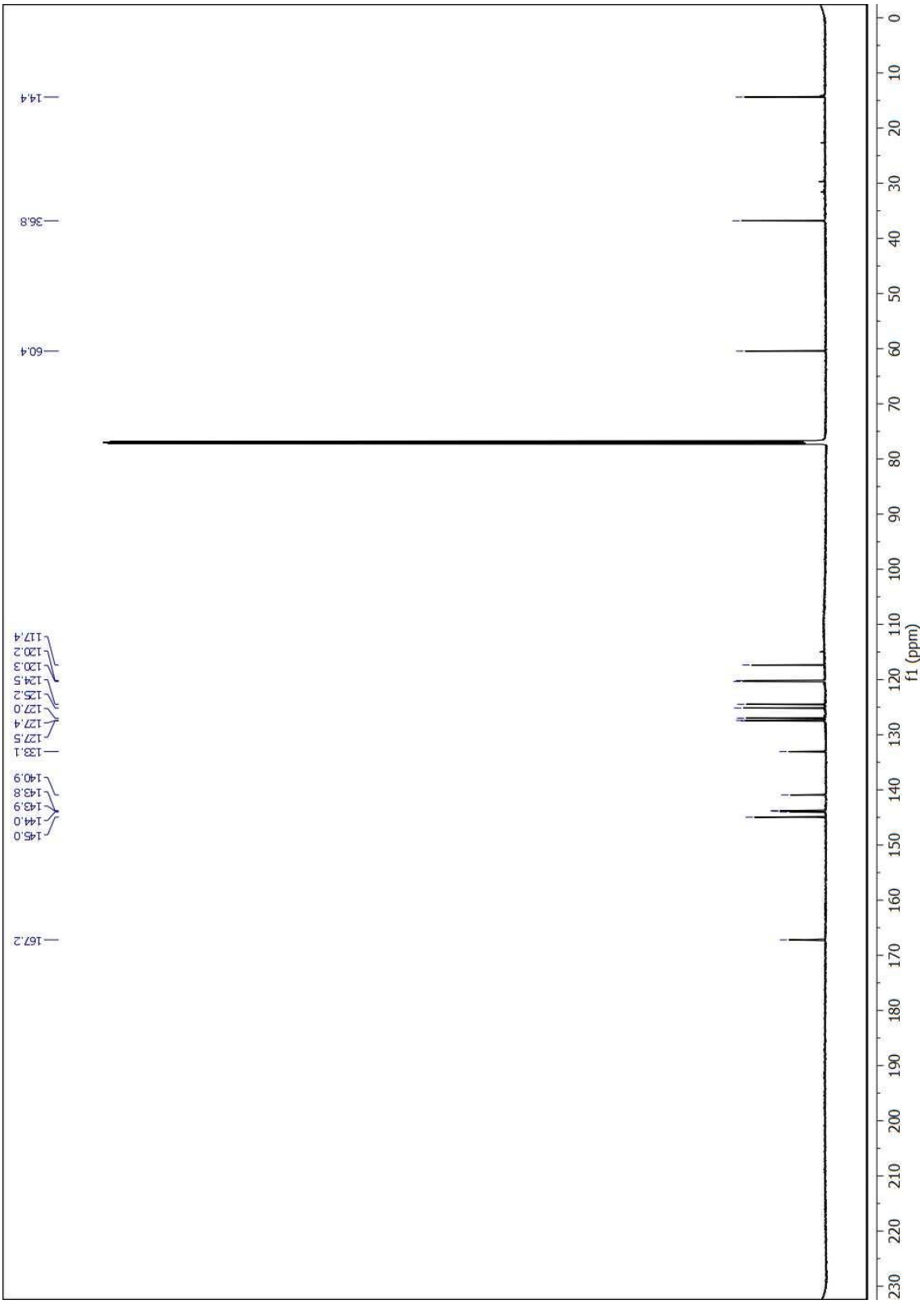
Ethyl *(E)*-3-(anthracen-9-yl)acrylate (3o)



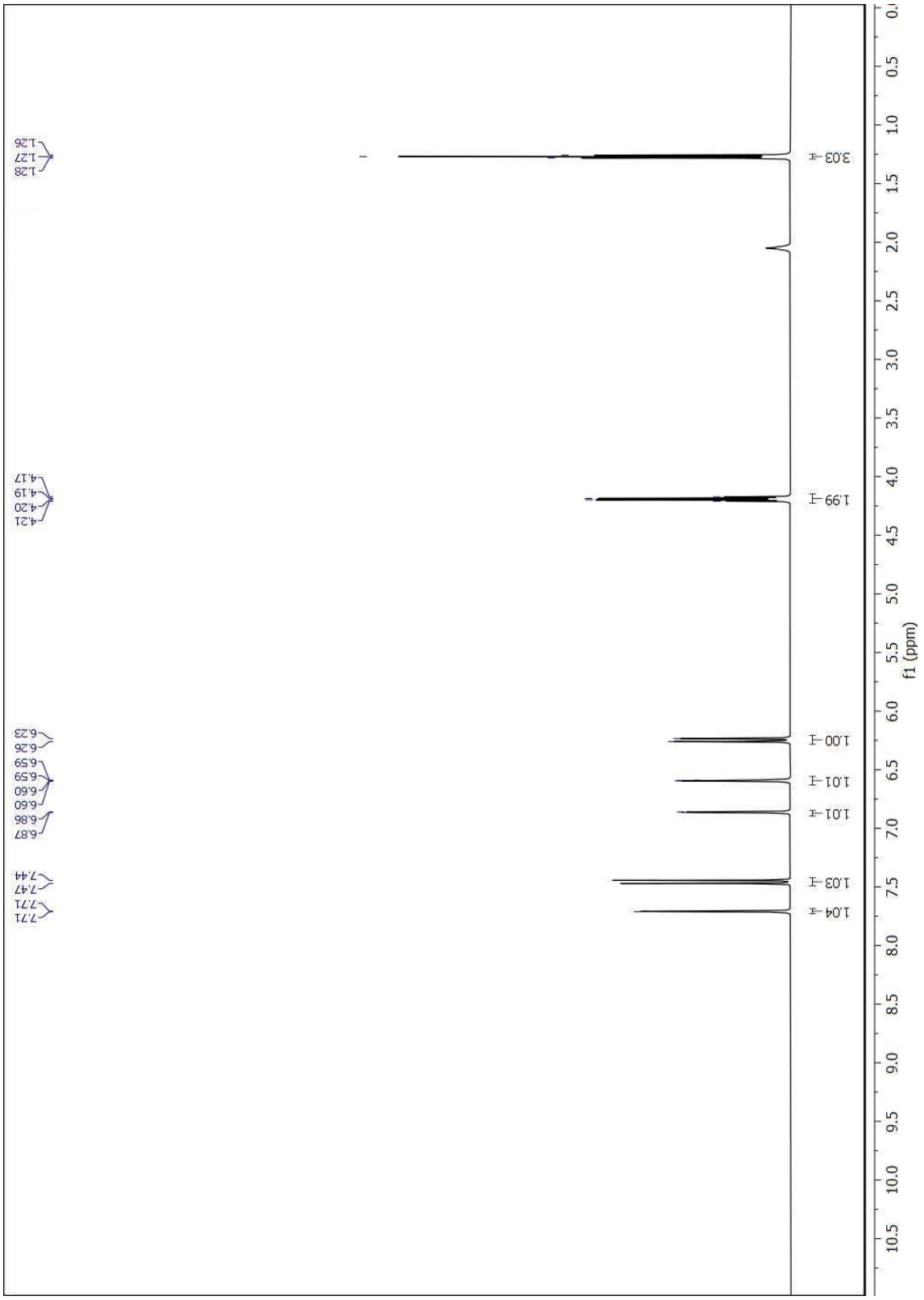
Ethyl *(E)*-3-(9H-fluoren-2-yl)acrylate (3p)



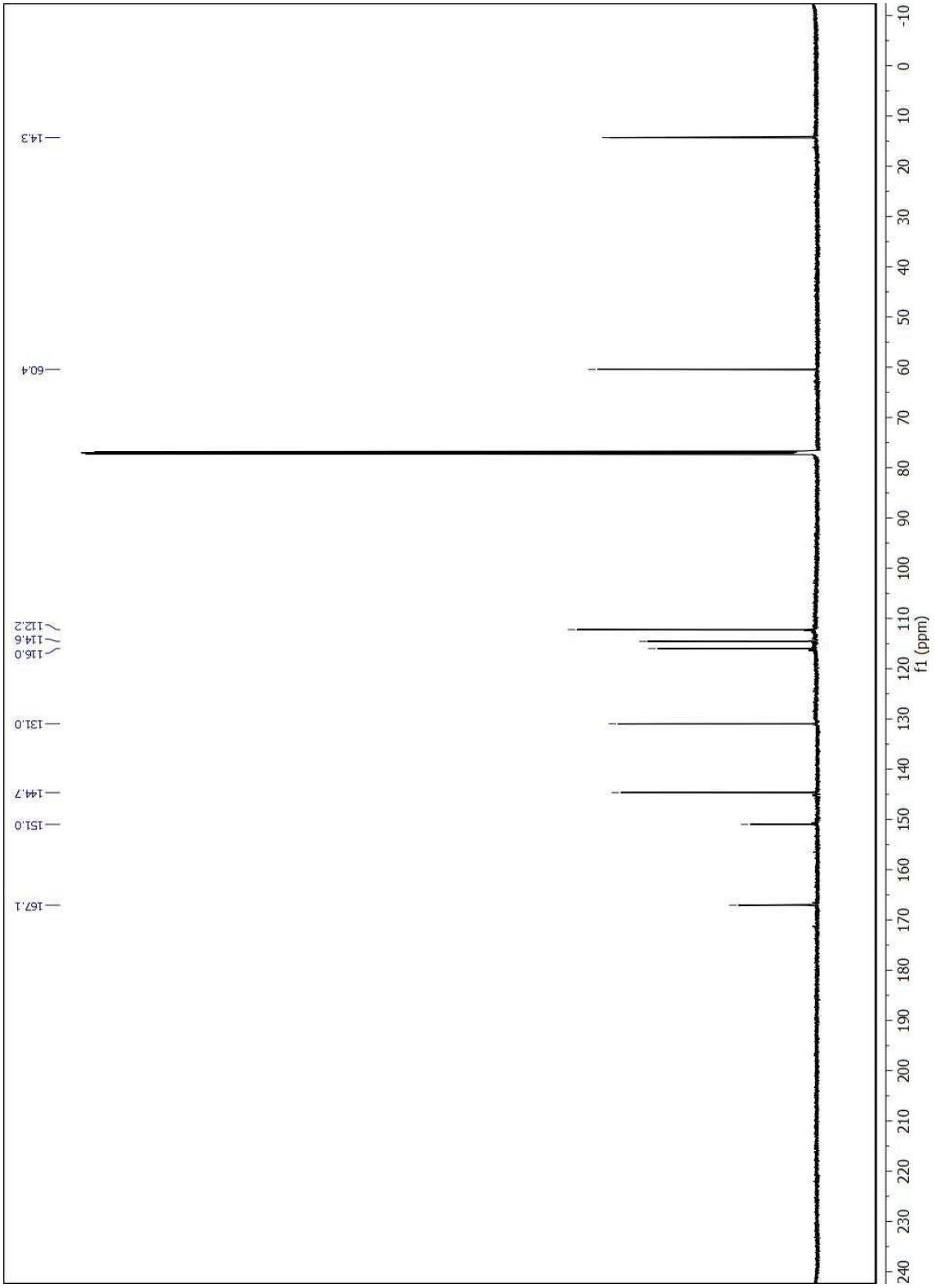
Ethyl *(E)*-3-(9H-fluoren-2-yl)acrylate (3p)



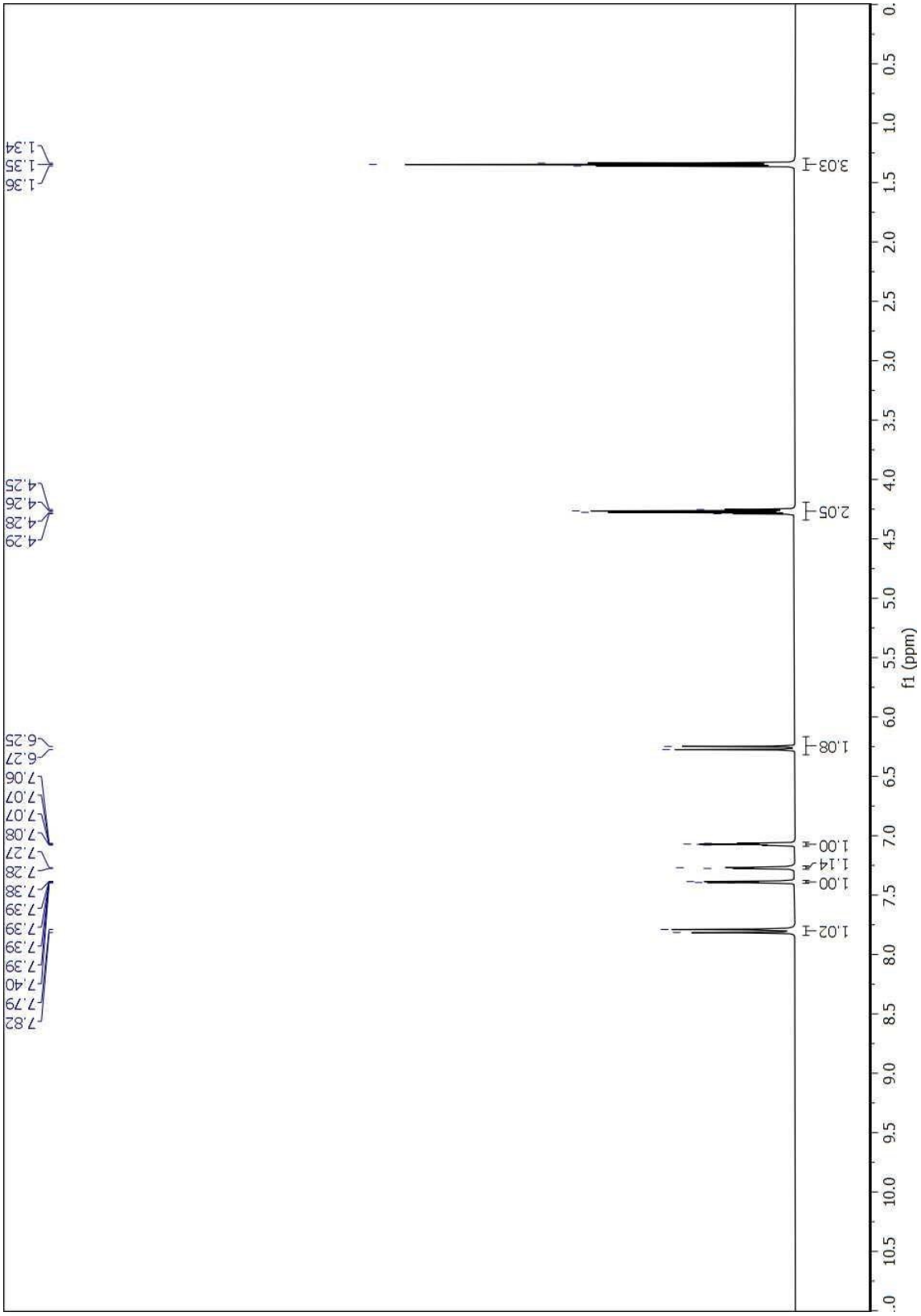
Ethyl *(E)*-3-(furan-2-yl)acrylate (3q)



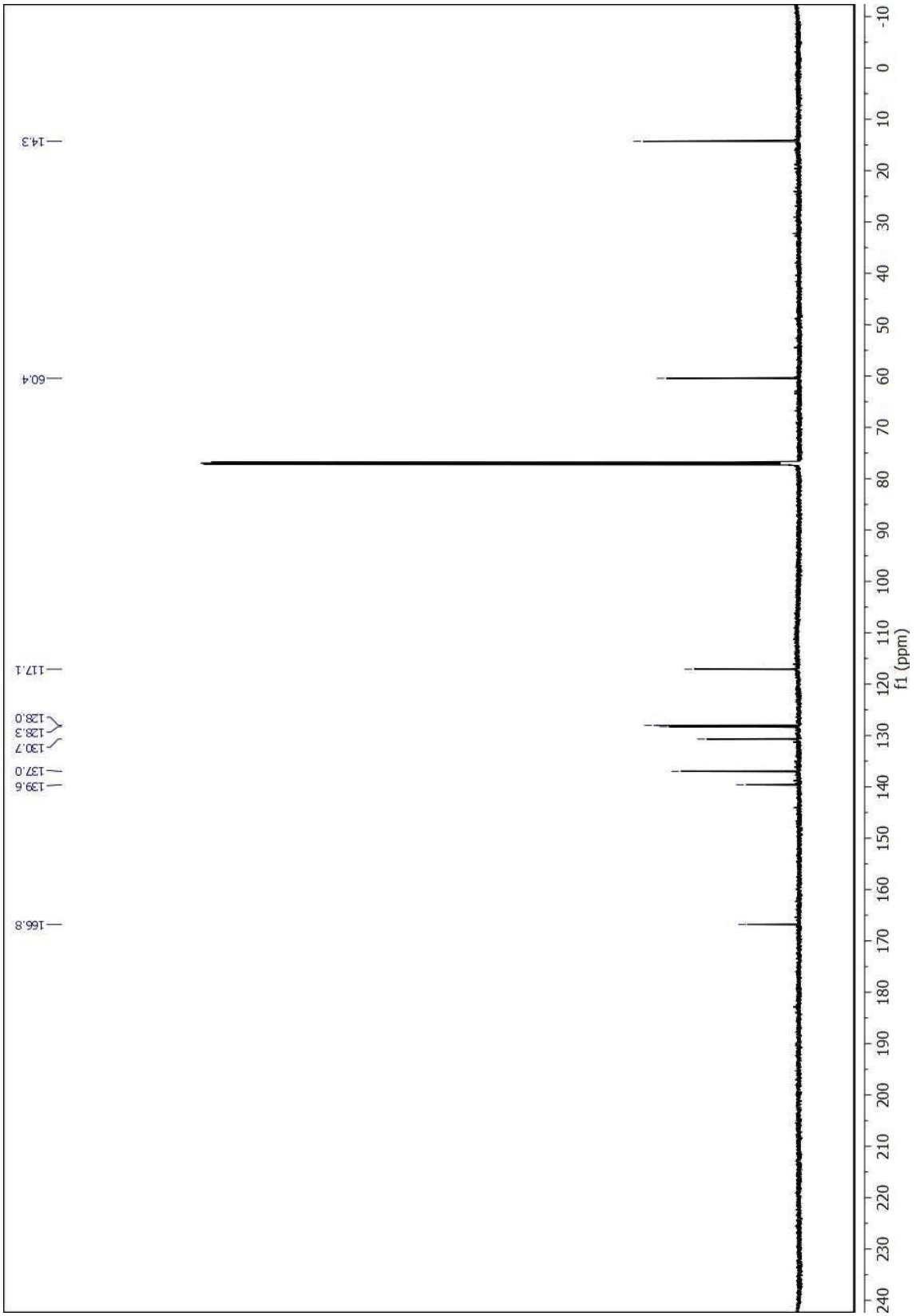
Ethyl *(E)*-3-(furan-2-yl)acrylate (3q)



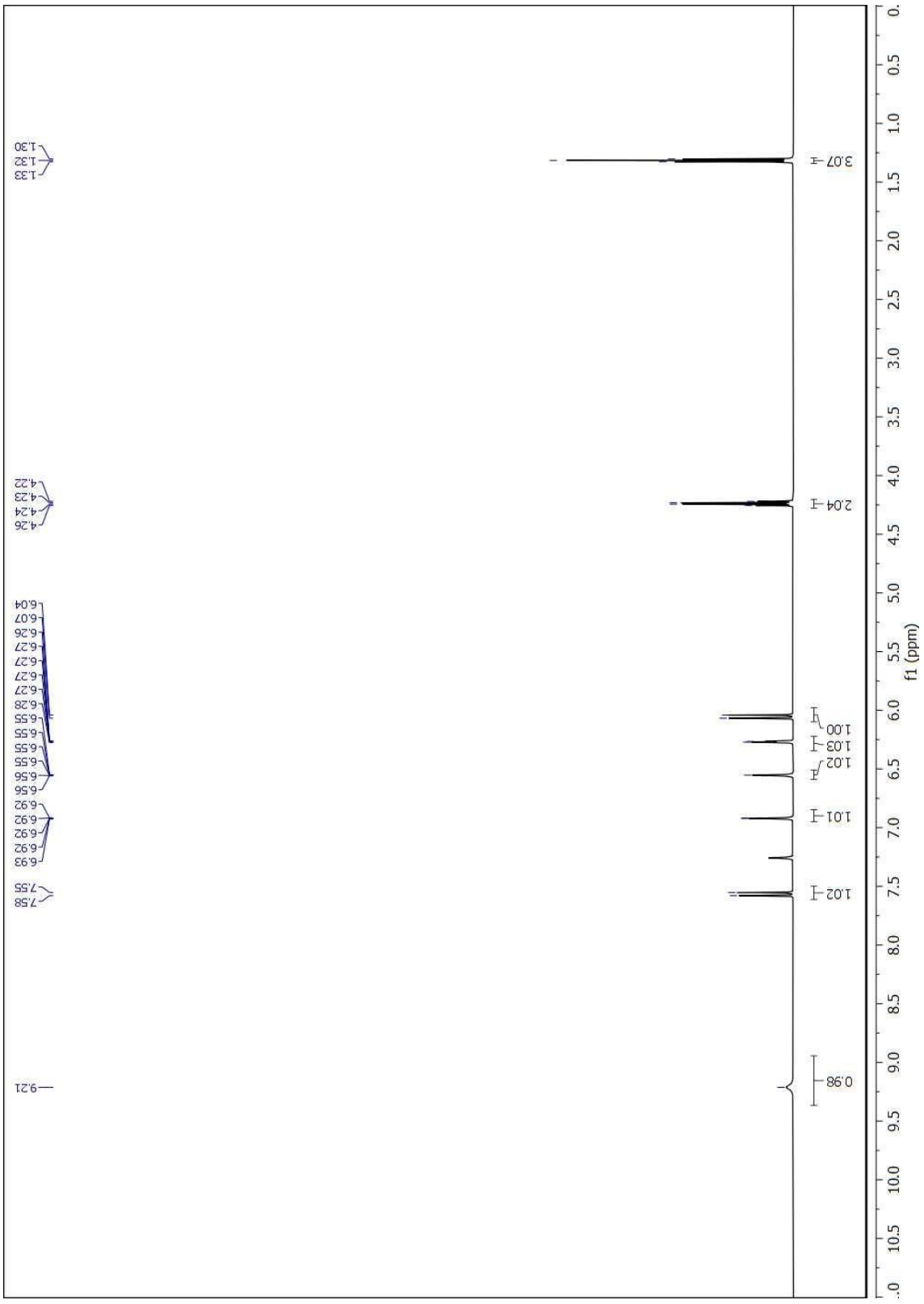
Ethyl *(E)*-3-(thiophen-2-yl)acrylate (3r)



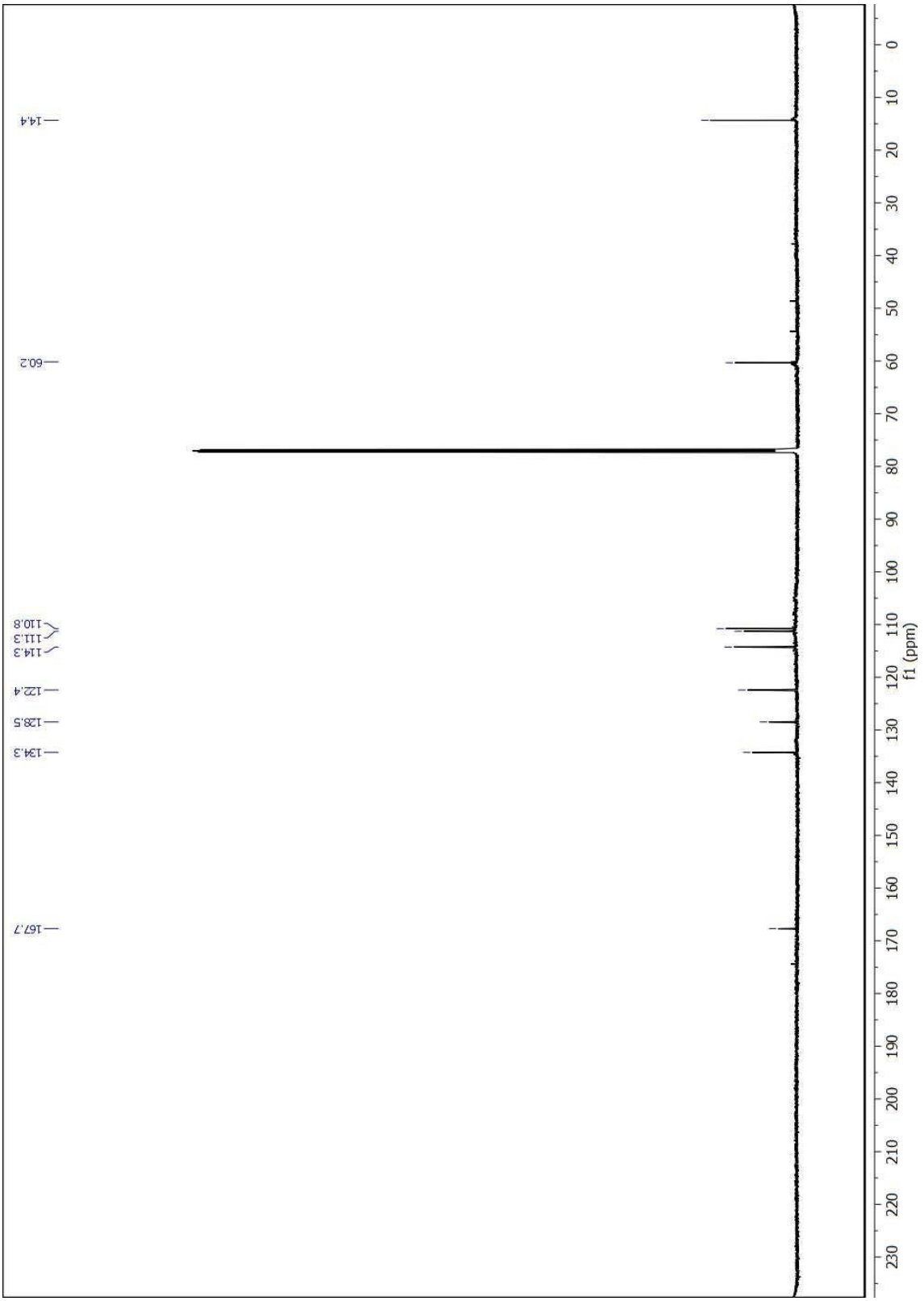
Ethyl *(E)*-3-(thiophen-2-yl)acrylate (3r)



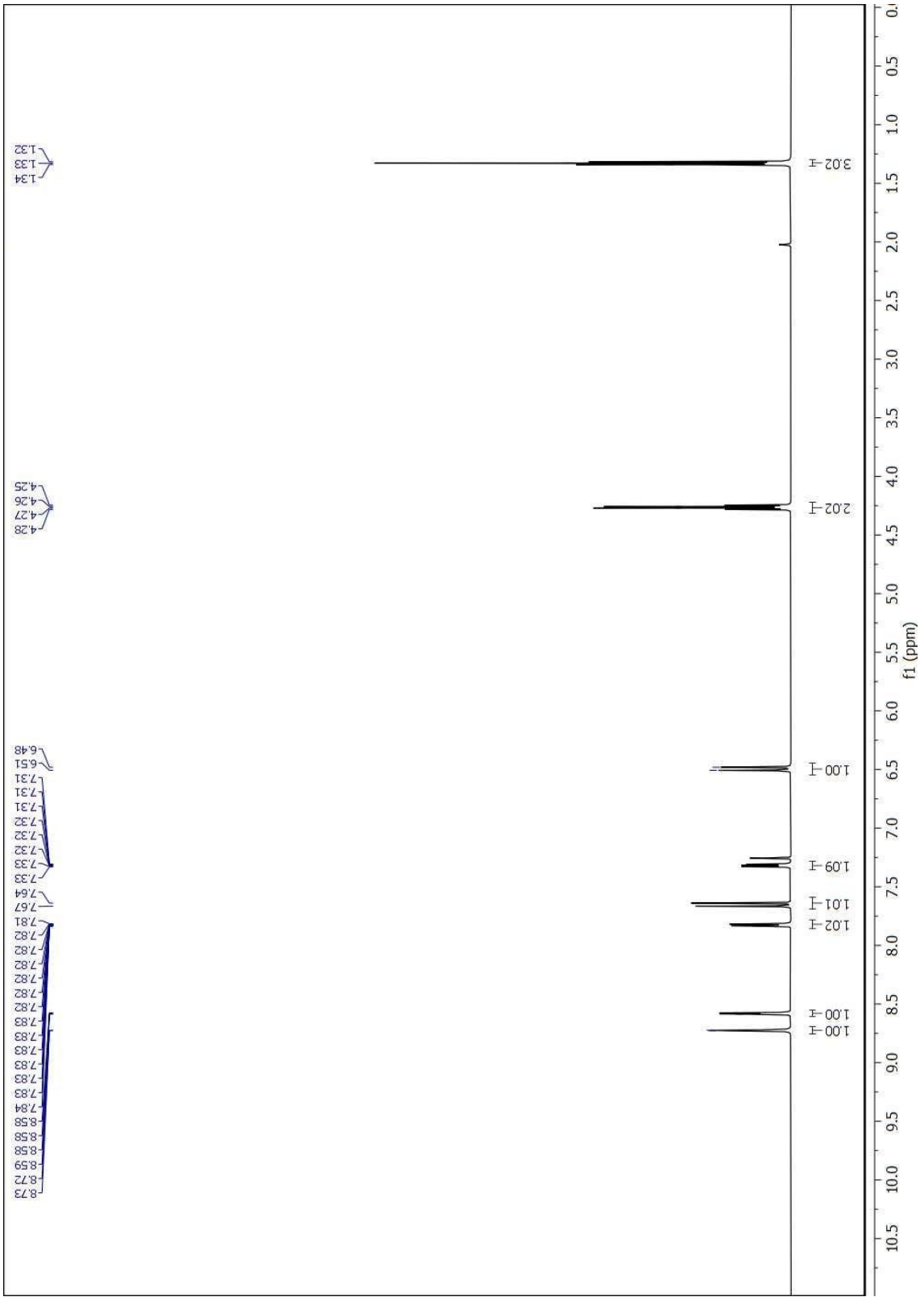
Ethyl *(E)*-3-(pyrrol-2-yl)acrylate (3s)



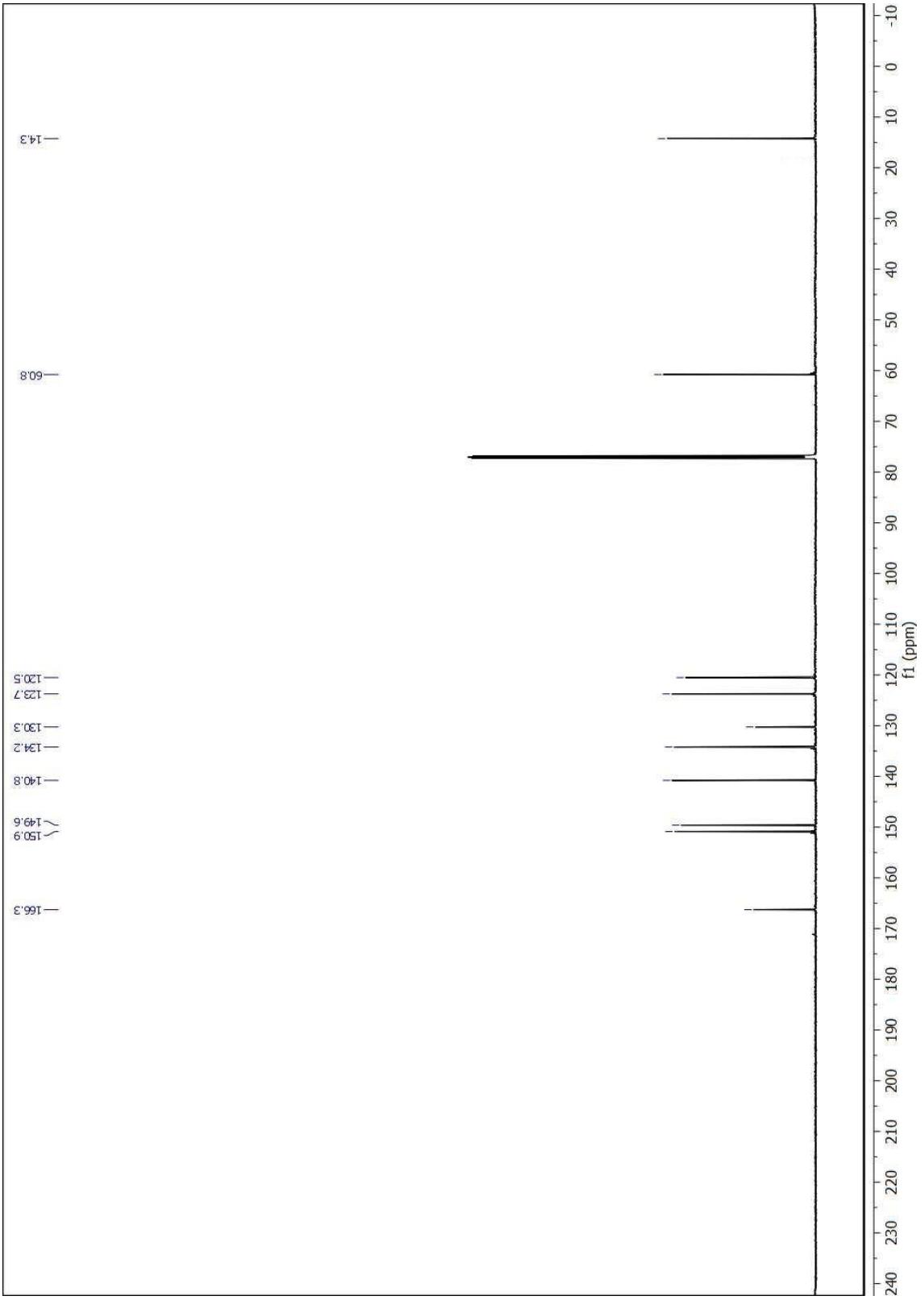
Ethyl *(E)*-3-(pyrrol-2-yl)acrylate (3s)



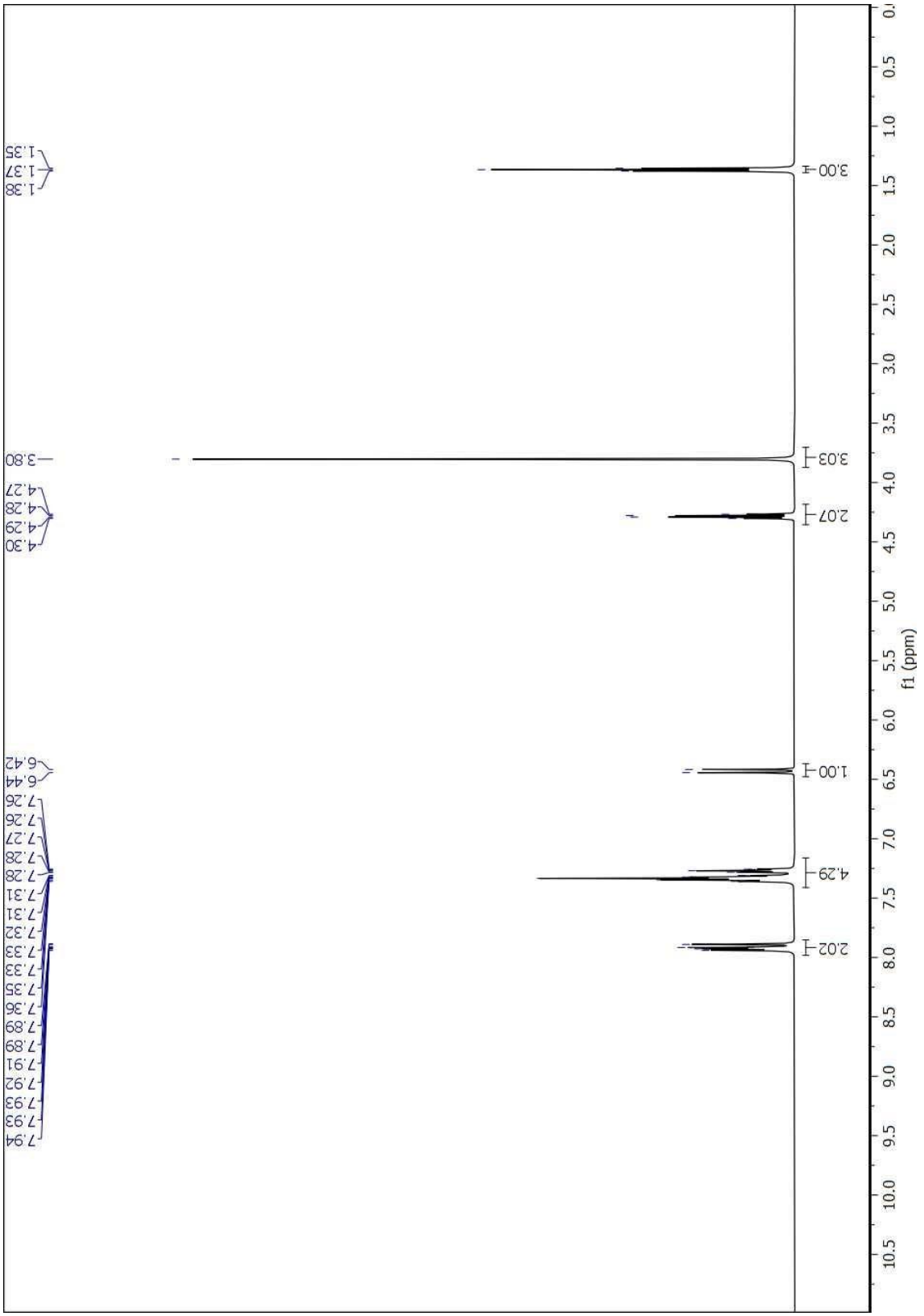
Ethyl *(E)*-3-(pyridine-3-yl)acrylate (3t)



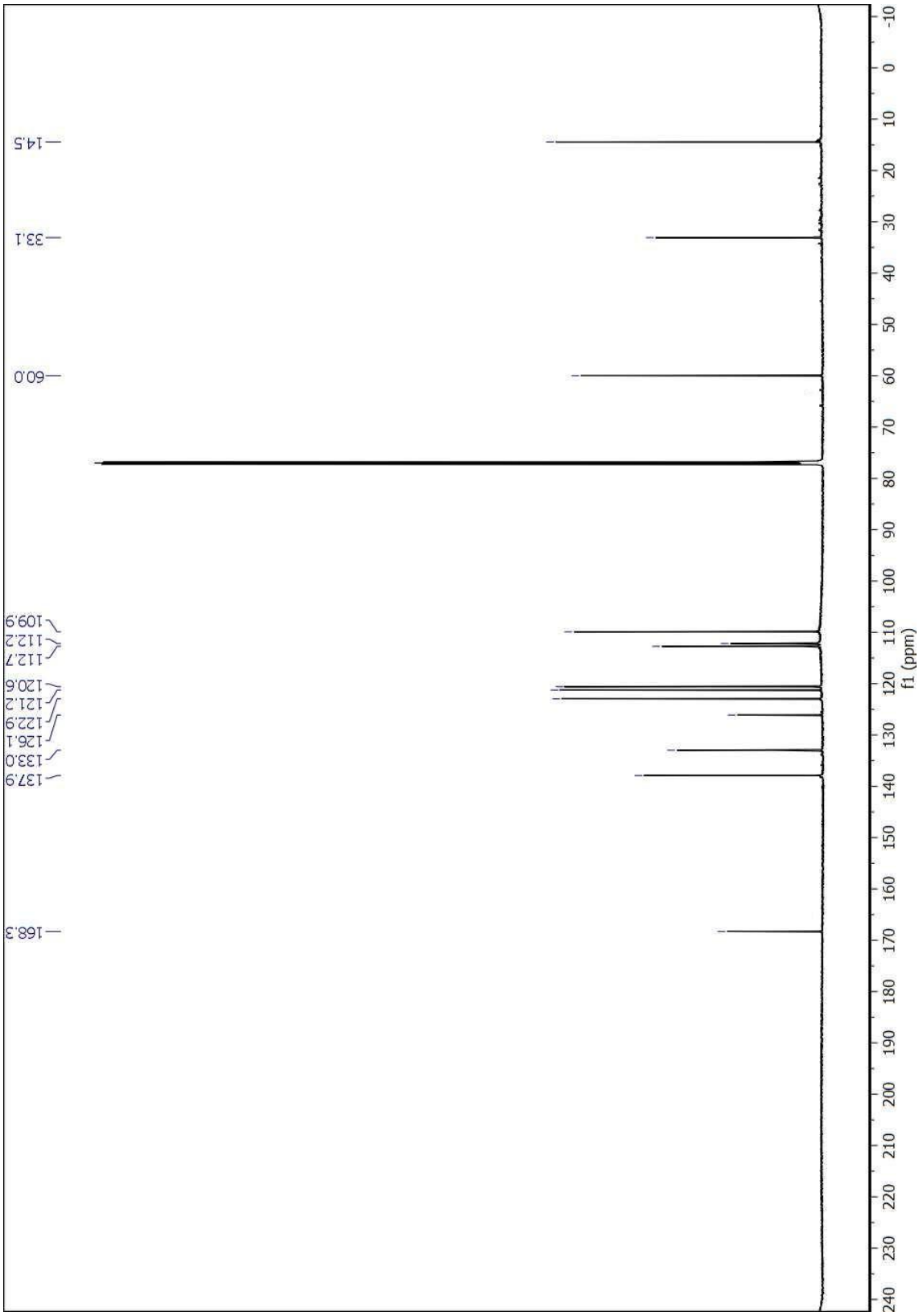
Ethyl *(E)*-3-(pyridine-3-yl)acrylate (3t)



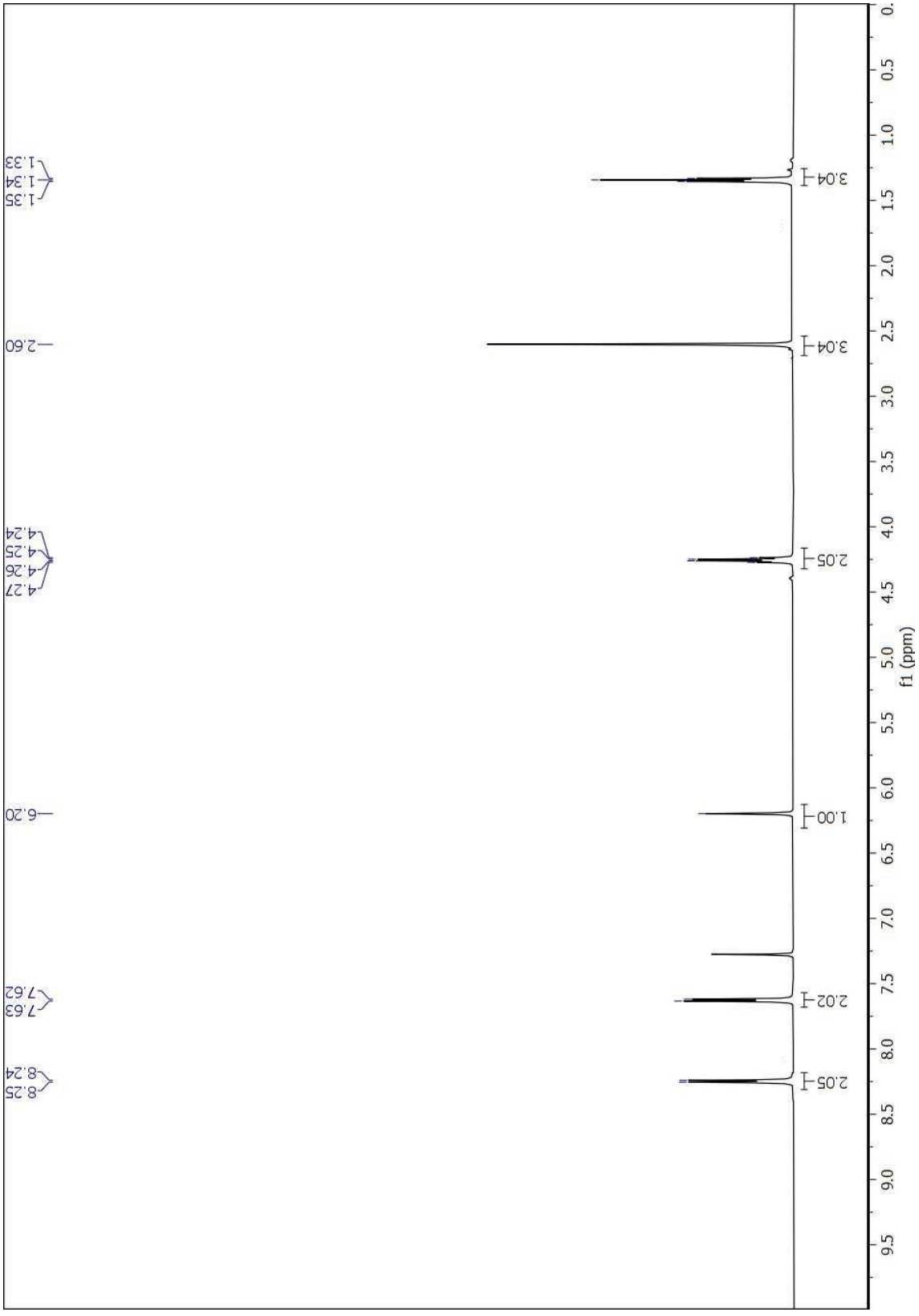
Ethyl *(E)*-3-(1-methyl-1H-indol-3-yl)acrylate (3u)



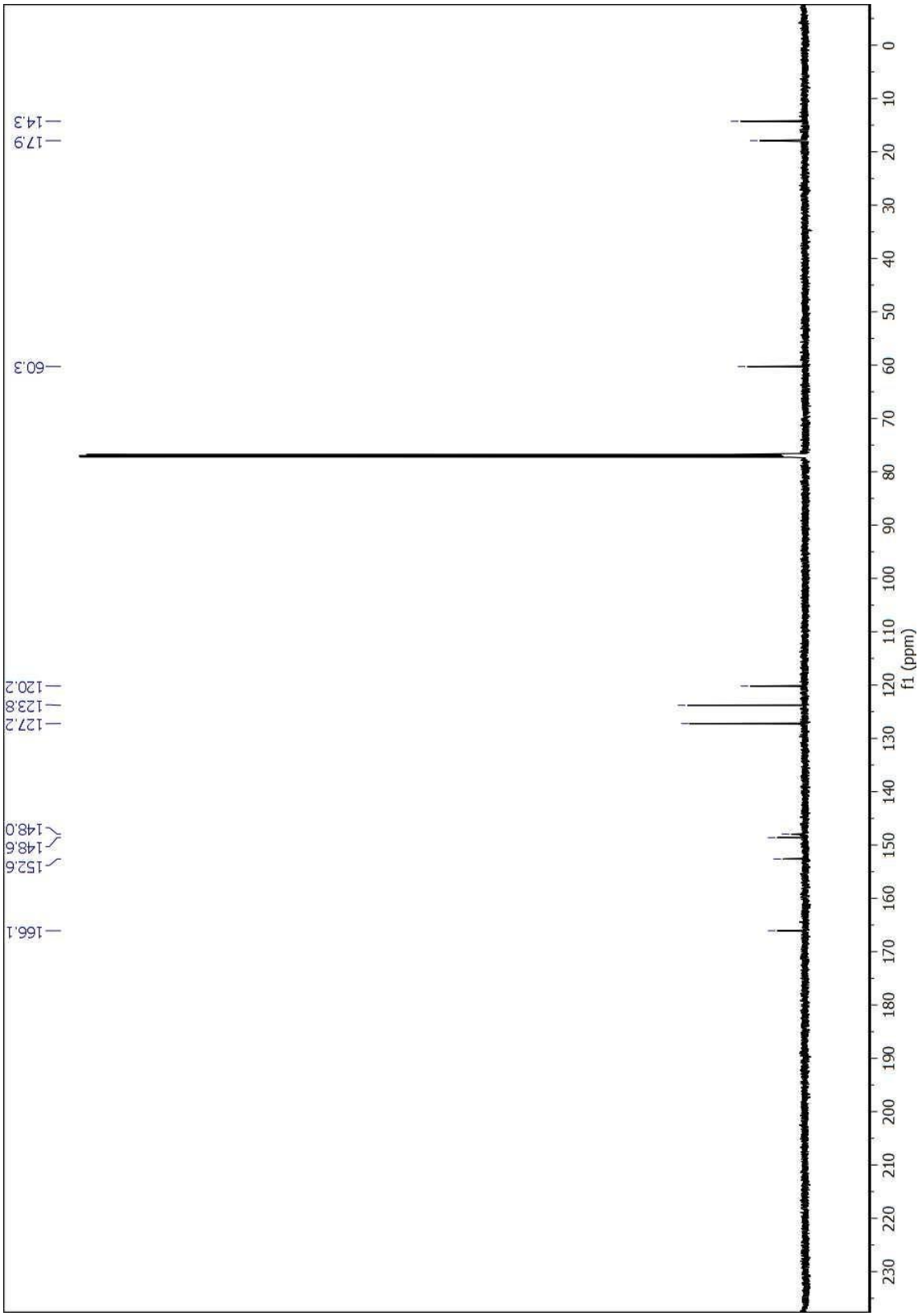
Ethyl *(E)*-3-(1-methyl-1H-indol-3-yl)acrylate (3u)



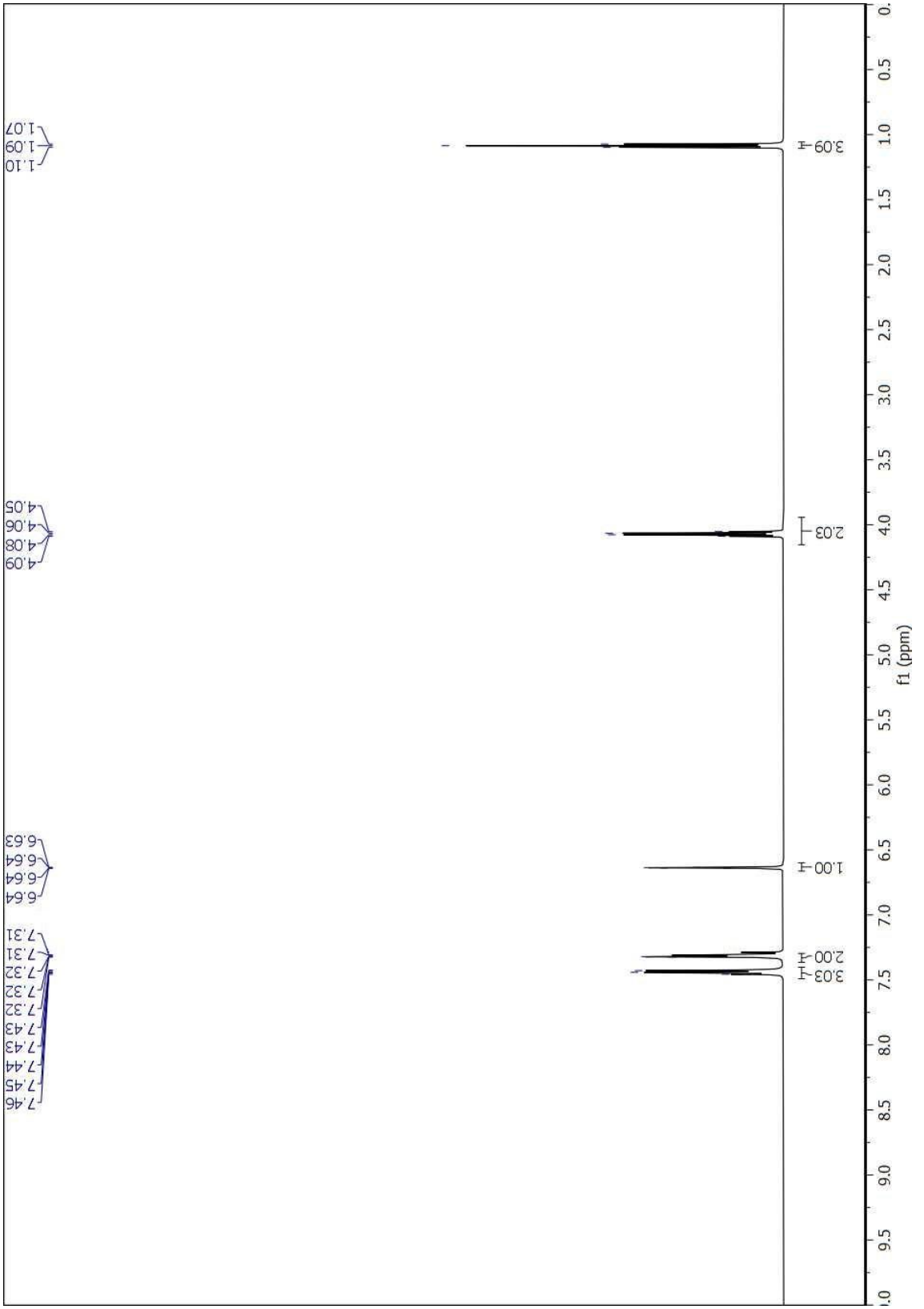
Ethyl *(E)*-3-(4-nitrophenyl)but-2-enoate (3w)



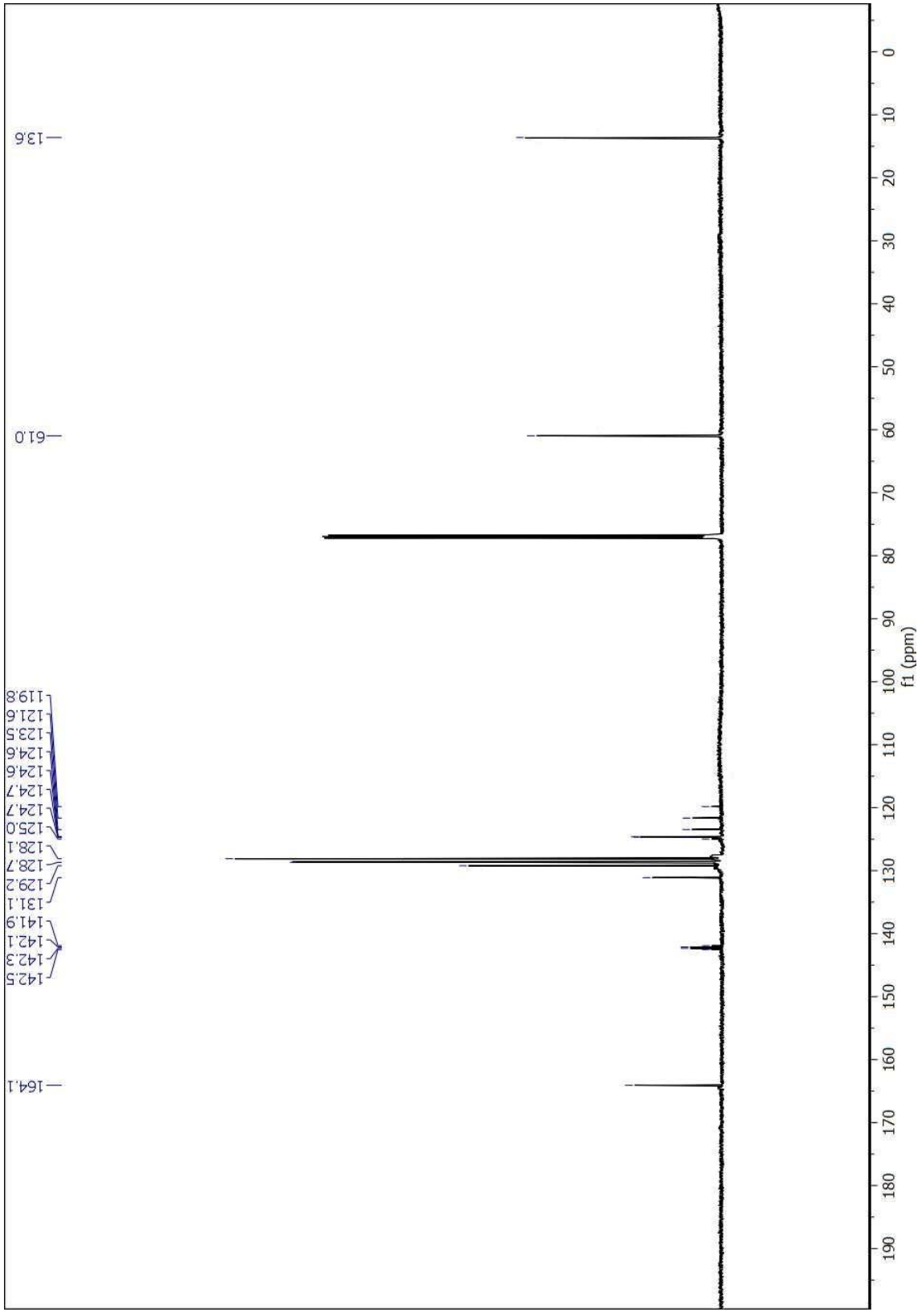
Ethyl *(E)*-3-(4-nitrophenyl)but-2-enoate (3w)



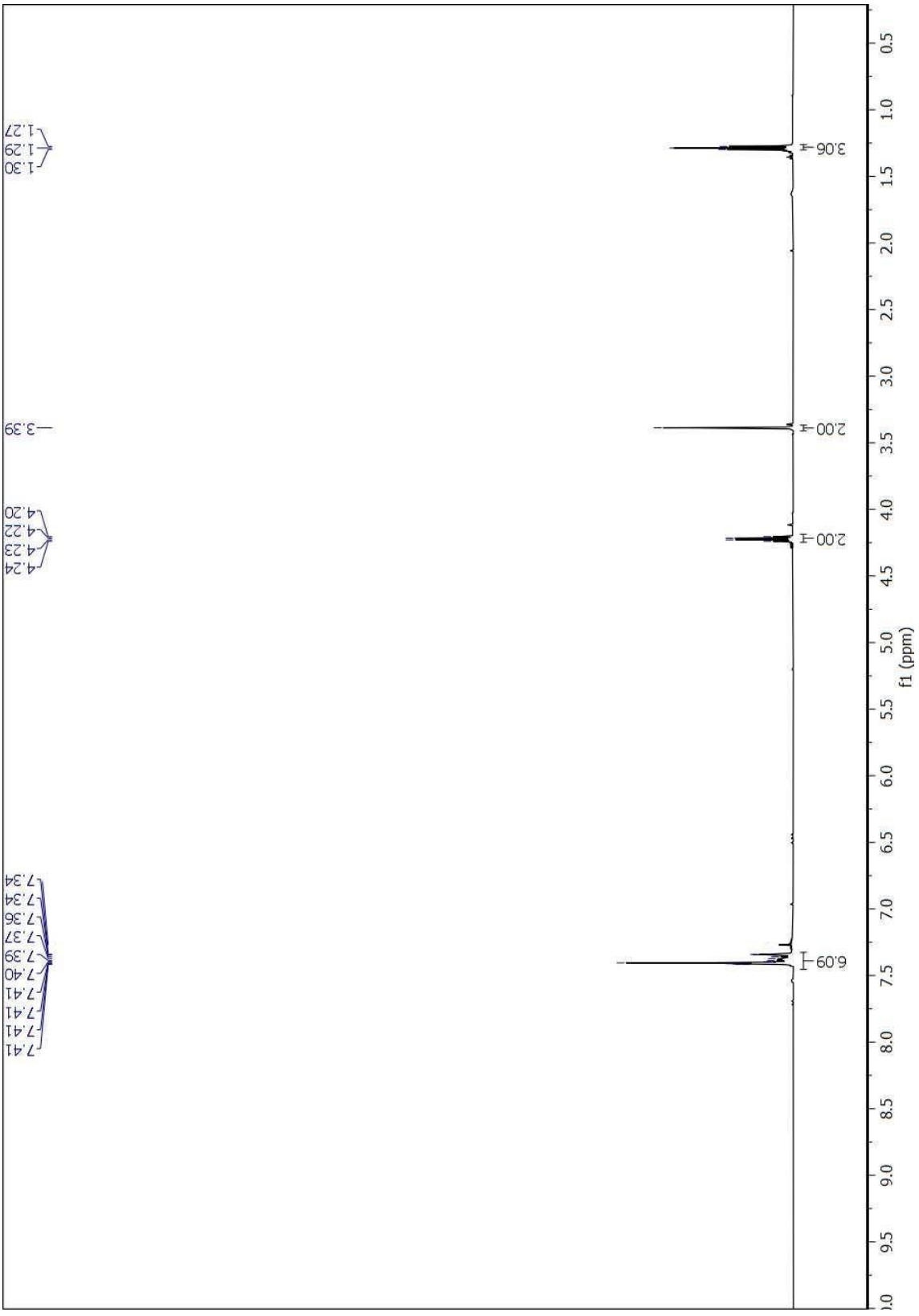
Ethyl *(E)*-4,4,4-trifluoro-3-phenylbut-2-enoate (3x)



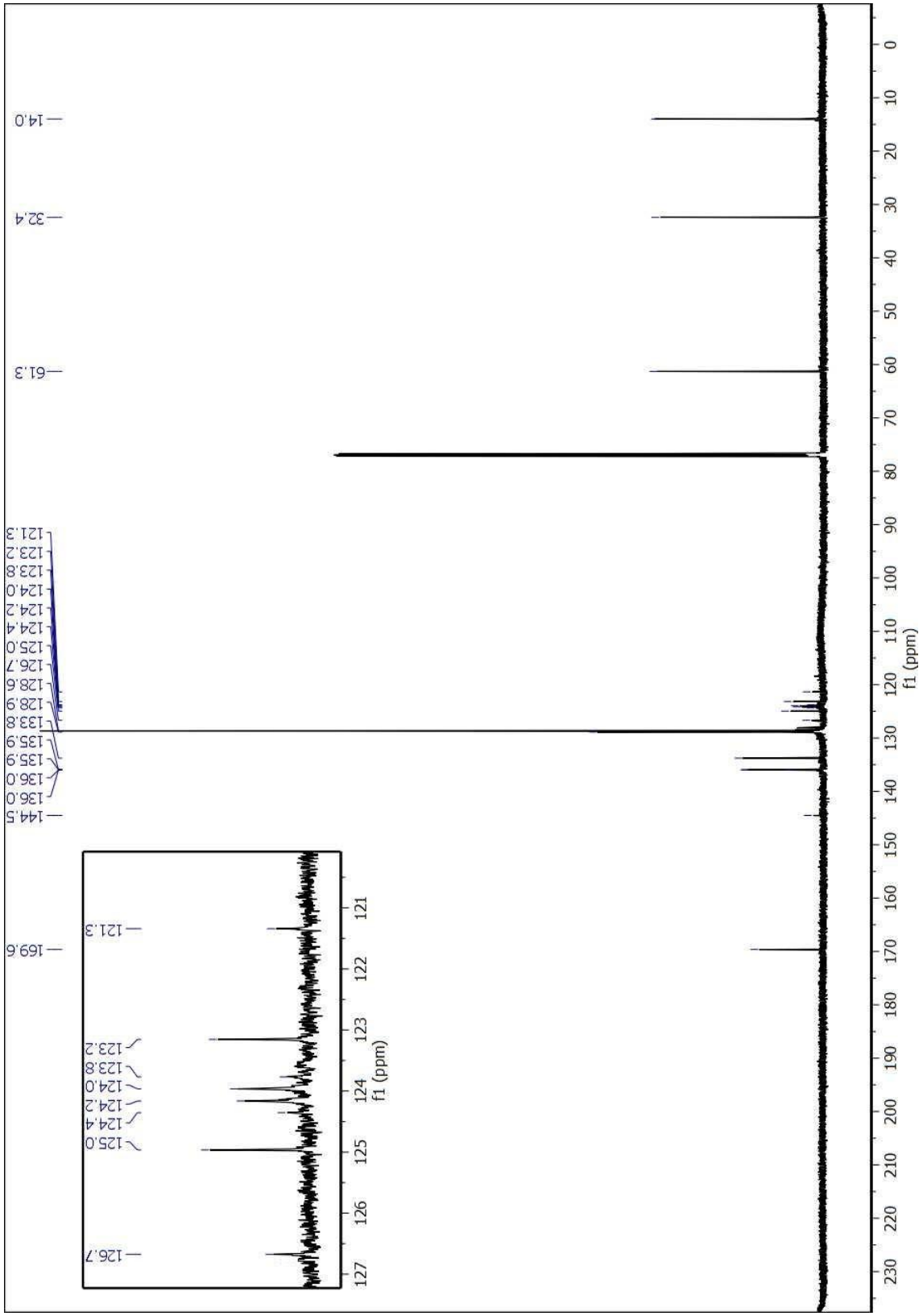
Ethyl *(E)*-4,4,4-trifluoro-3-phenylbut-2-enoate (3x)



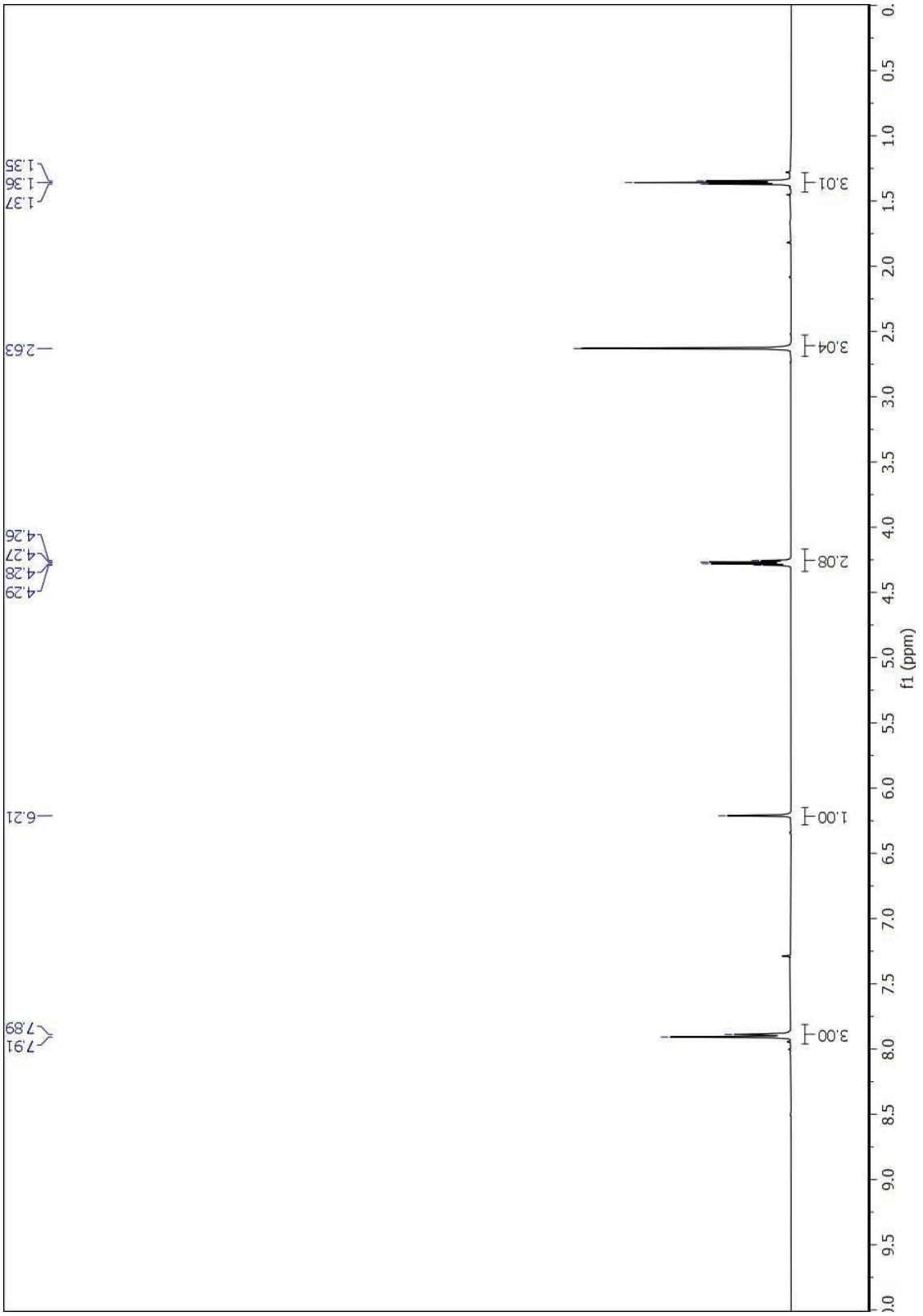
Ethyl (*Z*)-3-benzyl-4,4,4-trifluorobut-2-enoate (3y)



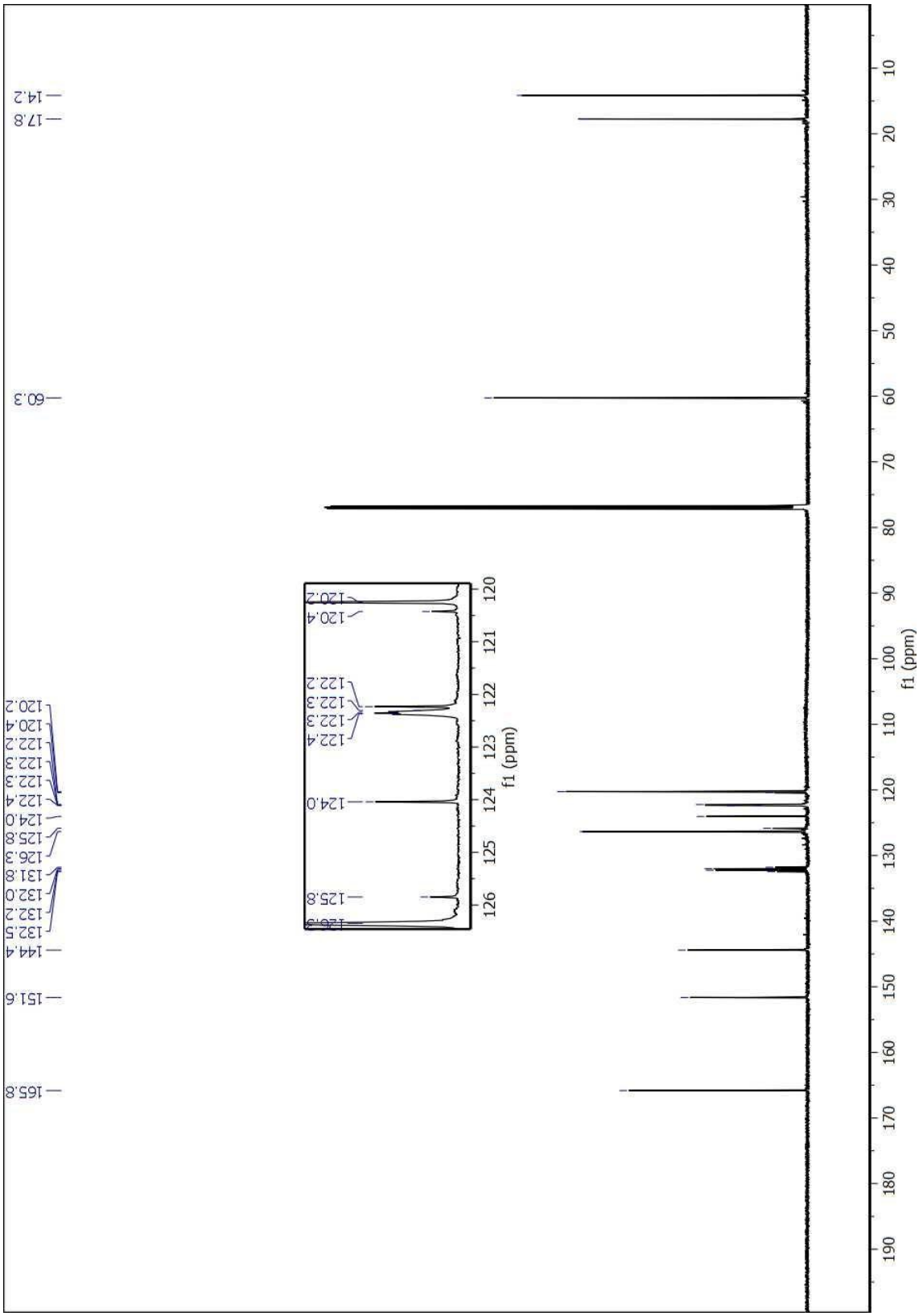
Ethyl (*Z*)-3-benzyl-4,4,4-trifluorobut-2-enoate (3y)



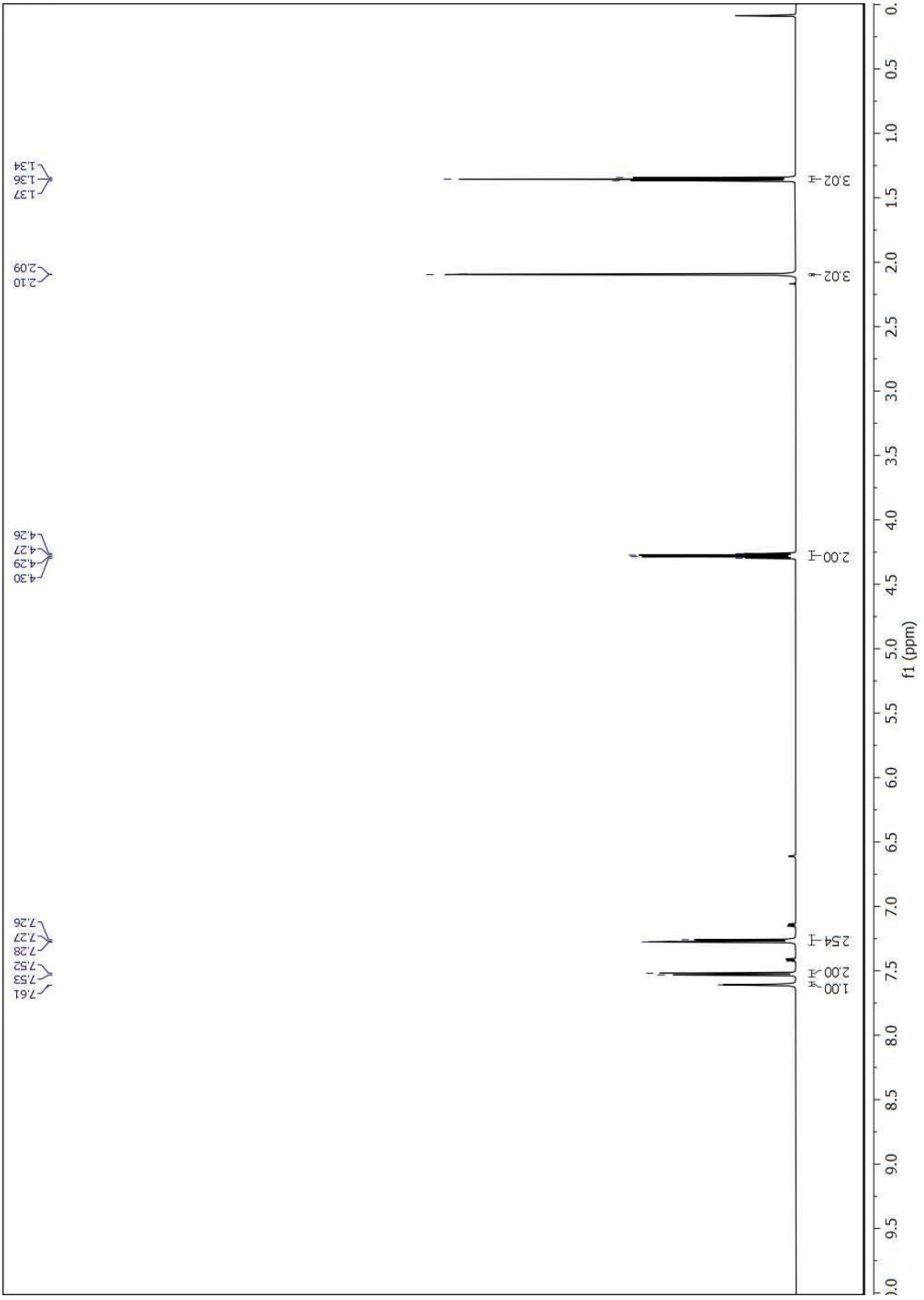
Ethyl *(E)*-3-(3,5-bis(trifluoromethyl)phenyl)but-2-enoate (3z)



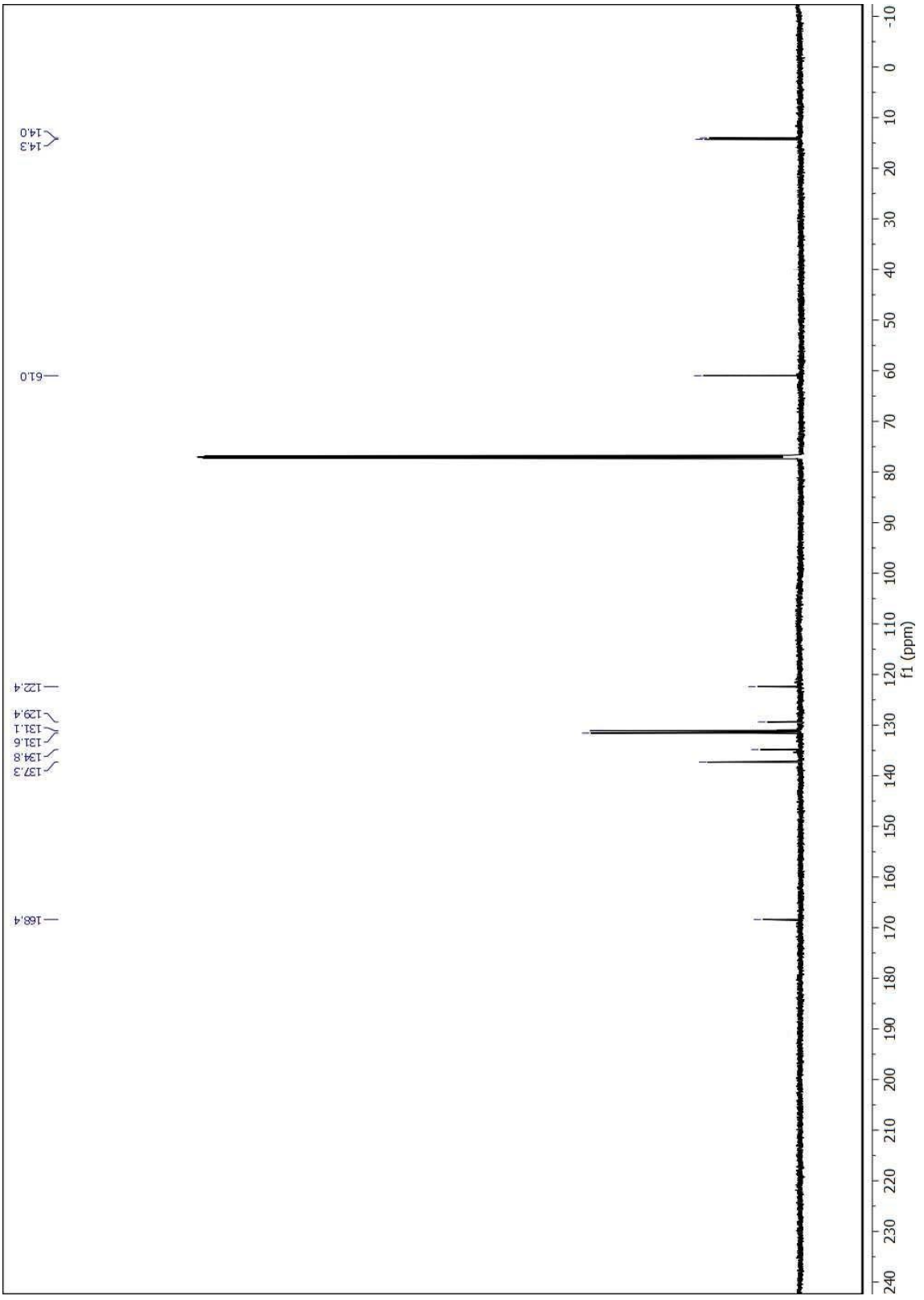
Ethyl *(E)*-3-(3,5-bis(trifluoromethyl)phenyl)but-2-enoate (3z)



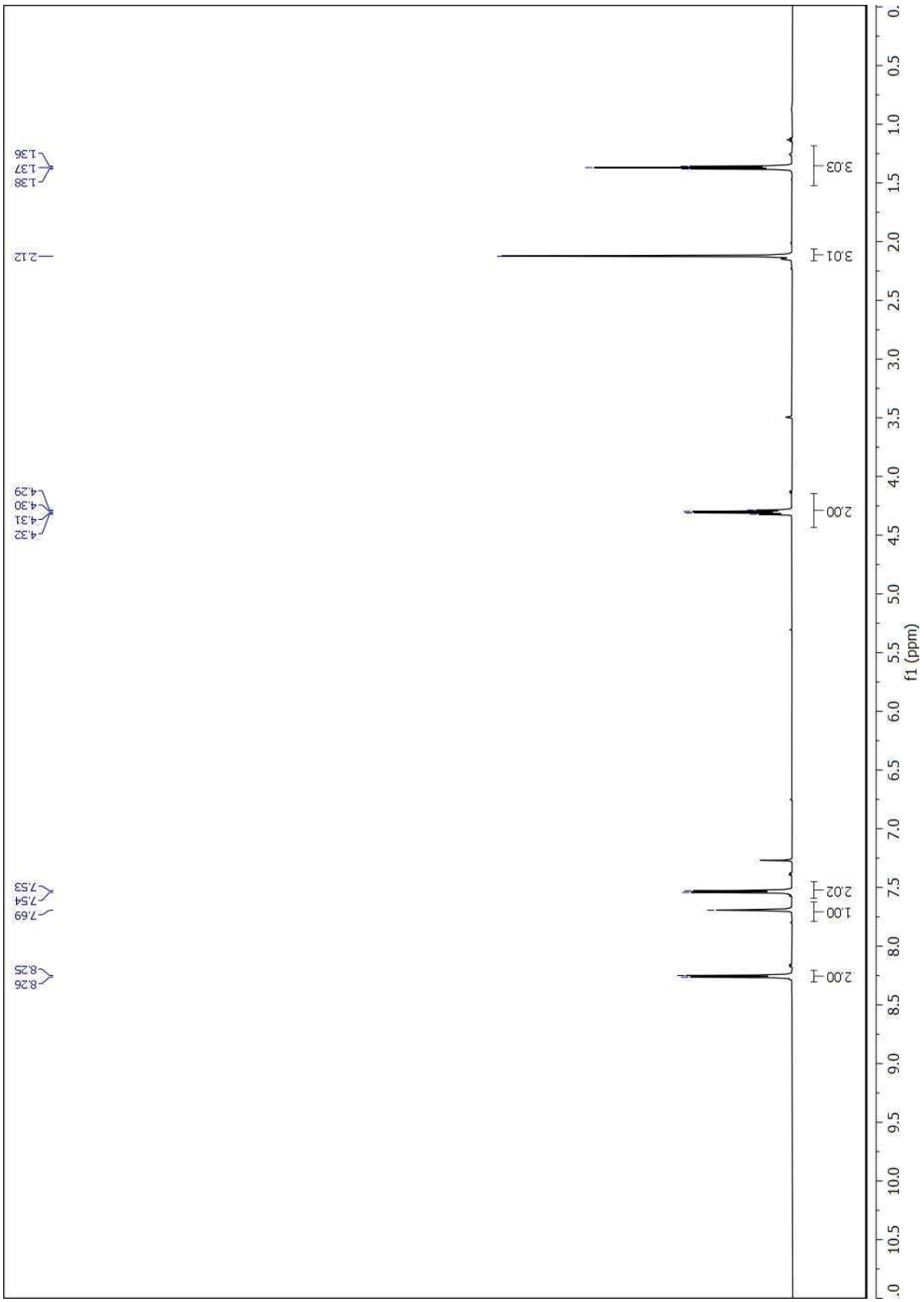
Ethyl *(E)*-3-(4-bromophenyl)-2-methylacrylate (4)



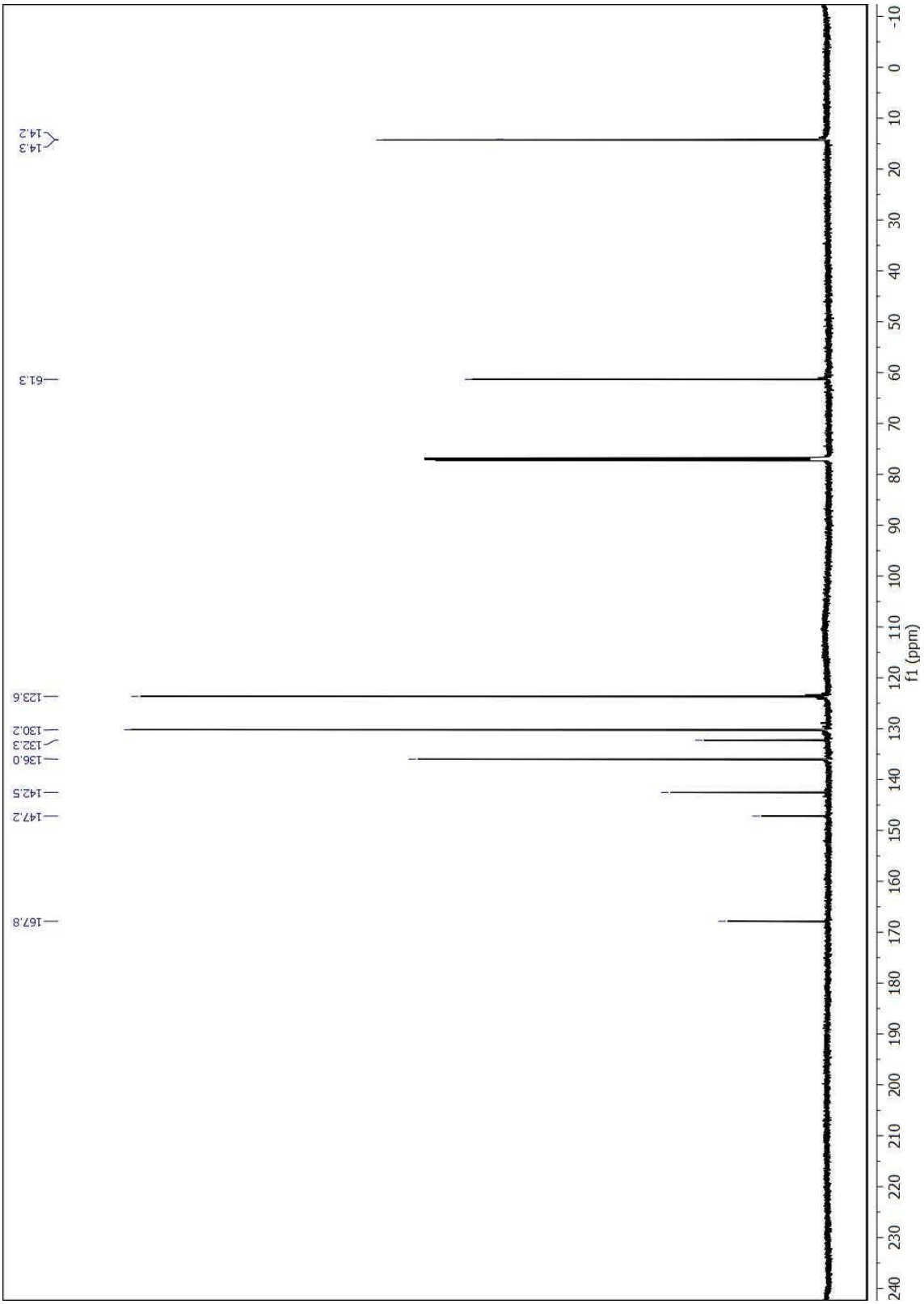
Ethyl *(E)*-3-(4-bromophenyl)-2-methylacrylate (4)



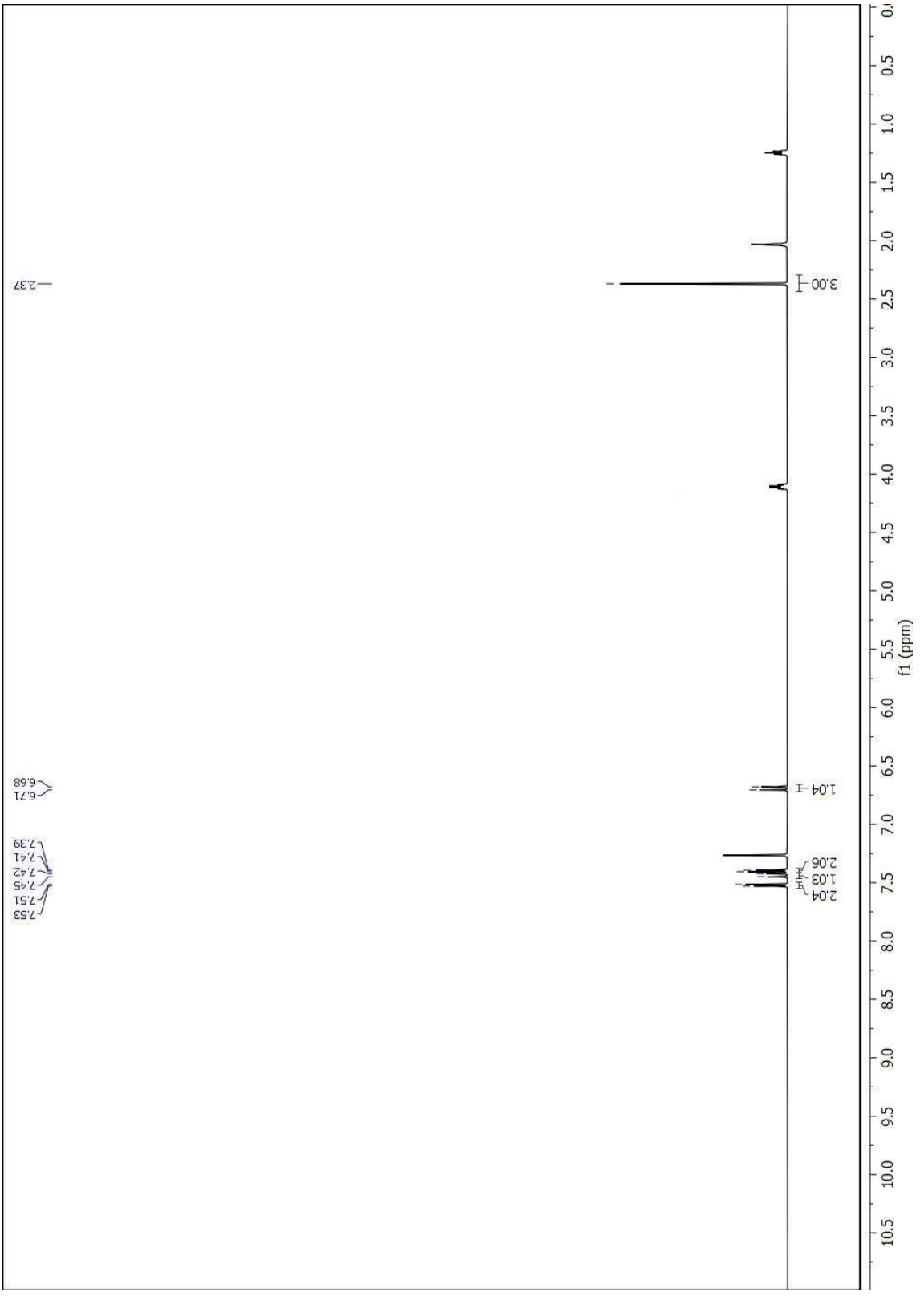
Ethyl *(E)*-2-methyl-3-(4-nitrophenyl)acrylate (5)



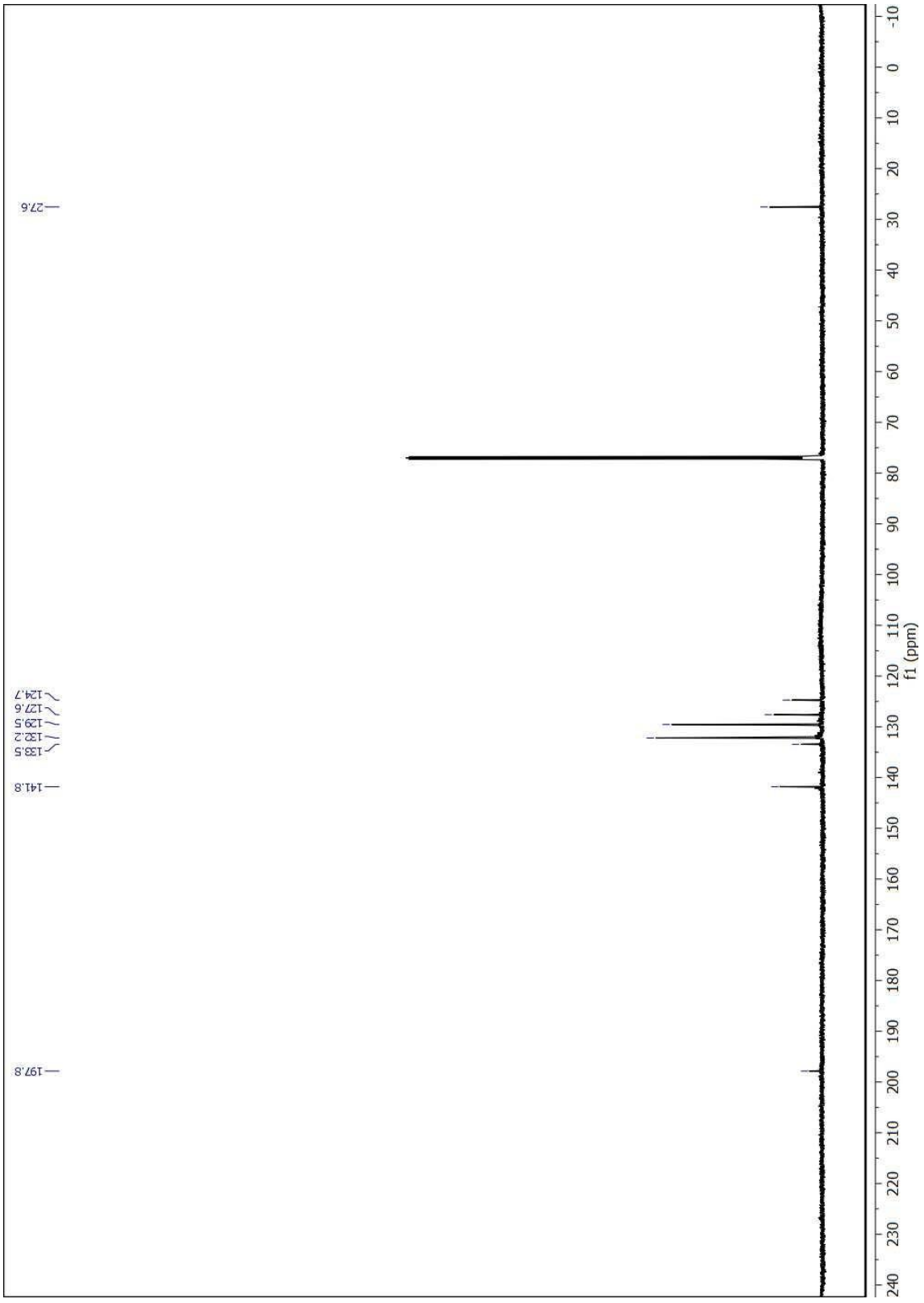
Ethyl *(E)*-2-methyl-3-(4-nitrophenyl)acrylate (5)



(*E*)-4-(4-bromophenyl)but-3-en-2-one (6)



(*E*)-4-(4-bromophenyl)but-3-en-2-one (6)



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