

SUPPORTING INFORMATION

Tailored polymeric cationic tag-anionic Pd(II) complex as catalyst for the low-leaching Heck-Mizoroki coupling in flow and in biomass-derived GVL

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Experimental Section

General remarks. All chemicals were used as obtained from commercial sources without any further purification unless otherwise noted. 4-Vinylbenzylchloride (VBC) and styrene were extracted three times with a 5% w/w NaOH solution to remove the polymerization inhibitor (tert-butyl catechol). Dibenzoylperoxide was re-crystallized from methanol. GLC analyses were performed by using Hewlett-Packard HP 5890 SERIES II equipped with a capillary column DB-5MS (30 m, 0.32 mm), a FID detector and helium as gas carrier. GC-EIMS analyses were carried out by using a Hewlett-Packard HP 6890N Network GC system/5975 Mass Selective Detector equipped with an electron impact ionizer at 70 eV. NMR spectra in solution were recorded on a Bruker DRX-ADVANCE 400 MHz (^1H at 400 MHz and ^{13}C at 100.6 MHz). Chemical shifts are reported in ppm and coupling constants in Hertz. Solid-state ^{13}C CP-MAS NMR spectra of support were recorded on a Bruker 500 MHz spectrometer with samples packed in zirconia rotors spinning at different kHz. CHN analyses (EA) were conducted on Fisons EA 1108 elemental analyzer. Elemental analysis of palladium content was carried out using an Agilent 4210 MP-AES instrument. Melting points were measured on a Büchi 510 apparatus.

Flow procedures were performed using a Jasco PU-4180 pump, an Omnifit Glass Column as reservoir and Supelco HPLC Column Blank as base/catalyst column.

Characterization data and copies of the ^1H and ^{13}C NMR are reported below.

Synthesis of catalyst 1

Preparation of SP-Cl support 2.¹ A three-neck cylinder-shaped glass vessel, equipped with a mechanical stirrer, a condenser, and a nitrogen inlet was charged with an aqueous NaCl (2 wt%, 2.4 g) solution containing acacia gum (4 wt%, 4.8g) (120 mL). After deoxygenation by purging with nitrogen, a mixture of styrene (5.62 g, 53.95 mmol), vinylbenzylchloride (1.48 g, 9.75 mmol), 1,4-bis (4-vinylphenoxy)benzene¹ (0.409 g, 1.3 mmol), chlorobenzene (8 mL), and dibenzoylperoxide (150 mg, 0.62 mmol, 2% wt/wt) was rapidly added to the solution. Next, this reaction mixture was kept under stirring at room temperature for an additional 30 min, then heated at 85 °C for 24 h. Subsequently, the reaction mixture was cooled at room temperature, and the polymer beads were isolated by filtration, washed with water (50 mL), then extracted by using water (100 mL), THF (100 mL), and n-hexane (100 mL) in a Soxhlet apparatus. Finally, the resin (1) was dried under vacuum for 15 h at room temperature (6.18 g, 1.96 mmol Cl/g – theoretical, 80% yield).

Post polymerization functionalization of SP-Cl 2 with 3,3-bis(1H-imidazol-1-yl)propan-1-ol (3).² A 25 mL three-neck round bottom flask equipped with a magnetic stirrer was charged with 3,3-bis(1H-imidazol-1-yl)propan-1-ol (3) (0.370 g, 2.5 mmol, 1.6 eq) in 10 mL of dry DMF under nitrogen. Then, 3.75 mmol of NaH (60% in mineral oil; 3eq, 0.23 g) were added. This mixture was left under stirring at r.t. for 30 min, then resin 2 (0.770 mg) was added and the mixture was heated to 60 °C. After 24h, the resulting resin 4 was filtered and washed with water and acetone and dried under vacuum (pale yellow solid). The bis-imidazole unit loading was determined to be 0.76 mmol/g by elemental analysis C: 78.11; H: 6.88, N: 4.27.

Preparation of SP-supported imidazolium salt 5.³ In a 10 mL stainless steel vessel, resin 4 (0.9 g) was added to iodomethane (5 mL, 79.5 mol) and the reaction mixture was then kept under stirring at 90 °C. After 20 h, the mixture was filtered, and the residual solid was washed with methanol and acetone, then dried under vacuum. The SP-supported imidazolium salt 5 was obtained as a yellow solid. The bis-imidazolium moiety loading was determined to be 0.51 mmol/g by elemental analysis C: 71.47; H: 6.47, N: 2.83.

Immobilization of [PdCl₄]²⁻.⁴ A 50 mL round-bottom flask equipped with a magnetic stirrer was charged with PdCl₂ (0.074 g, 0.42 mmol) and NaCl (0.54 g, 9.24 mmol), in water (15 mL). The mixture was then heated at 80 °C under stirring for ~30 min, i.e. until the formation of Na₂PdCl₄. Next, the solution was cooled at r.t. and added dropwise to a suspension of 5 (0.6 g) in water (10 mL) under stirring. The suspension was kept under stirring at r.t. for 2 h, then filtered under reduced pressure, washed with water and methanol and dried under vacuum. The product (1) was obtained as a black powder. The loading of Pd was determined to be 3 wt% by MP-AES analysis.

Typical procedure for Heck-Mizoroki reaction in GVL under batch conditions (extraction work up).

In a 4 mL screw-capped vial equipped with a magnetic stirrer, the aryl iodide 6 (1mmol), the alkene 7 or 9 (1.2 mmol), GVL (0.8 M, 1.25 mL), diethylaminomethyl-polystyrene (1.5 equiv, 0.47 g) and catalyst 1 (0.1 mol%, 4.6 mg) and were consecutively added, and the resulting mixture was left under stirring at 130 °C for the time required to complete conversion of the aryl iodide 6, monitored by GLC. After 2 h, the heterogeneous base and catalyst were filtered off, 3 mL of n-heptane were added and the organic phase was washed with water (3x2 mL). Then the organic phase was dried under vacuum, and compound 8 or 10 were isolated.

Typical procedure for Heck-Mizoroki reaction in GVL under batch conditions (precipitation work up).

In a 4 mL screw-capped vial equipped with a magnetic stirrer, the aryl iodide **6** (1mmol), the alkene **9** (1.2 mmol), GVL (0.8 M, 1.25 mL), diethylaminomethyl-polystyrene (1.5 equiv, 0.47 g) and catalyst **1** (0.1 mol%, 4.6 mg) and were consecutively added, and the resulting mixture was left under stirring at 130 °C for the time required to complete conversion of the aryl iodide **6**, monitored by GLC. After 2 h, the heterogeneous base and catalyst were filtered off and washed with ethylacetate (1mL), then this latter was distilled off and the residue was cooled down to 0°C and added with water (1 mL). The precipitate was filtered off and washed with 1 mL of cold water, then dried under vacuum to afford compound **10**.

Regeneration procedure for PS-TEA (batch reaction).

The catalyst-base system (474.6 mg) filtered from the reaction mixture was charged into a screw-capped vial equipped with a magnetic stirrer, and TEA (1.5 eq, 2.25 mmol, 314 µL) in 1 mL GVL was added. The mixture was kept under stirring for 30 min, at r.t. Next, the catalyst-base system was filtered off, washed with 1 mL of GVL, and dried under vacuum.

Typical procedure for Heck-Mizoroki reaction in GVL under flow conditions

A pre-mixed mixture of aryl iodide (1 mmol) and acrylate or styrene derivative (1.2 mmol) in GVL (0.8 M, 1.2 mL) was charged into a glass column functioning as a reservoir. Diethylaminomethyl-polystyrene (~3.2 mmol/g, 469 mg) and catalyst **1** (3 wt%, 4.6 mg, 0.1 mol%) were mixed and dispersed in 1 mm diameter solid glass beads and charged in a stainless steel HPLC column (15cm, 4mm I.D.); the equipment was connected, by using the appropriate valves, to a pump and installed into a thermostatted box. The reaction mixture was continuously pumped (flow rate 1.0 mLmin⁻¹) through the base - catalyst column at 130 °C until complete conversion of reactants to product was achieved (the reaction was monitored by GLC). At this stage, the pump was left to run in order to recover the reaction mixture into the reservoir. To completely recover the product and clean the reactor, GVL (3 x 1.2 mL at a 1 mLmin⁻¹) was cyclically pumped through the base - catalyst column for 15 min (each fraction) and then collected into the reservoir to isolate the product, after removal and recovery of the solvent (ca 98% of which was recovered) via distillation. A solution of TEA (0.2 mL in 2 mL of GVL) was cyclically pumped through the base/catalyst column (1 mLmin⁻¹, 30 min) to regenerate the diethylaminomethyl-polystyrene. Finally, GVL (5 mL) was cyclically pumped through the base/catalyst column in two portions to remove residual TEA. After removal of TEA via vacuum distillation, GVL was distilled and recovered (98 %) as pure solvent, as confirmed by ¹HNMR analysis.

Preparation of the samples for MP-AES analyses.

The crude reaction mixture from Heck coupling, after separation of heterogeneous catalyst-base systems and evaporation under vacuum was dissolved in aqua regia and stirred for 1h at room temperature. Water was added to reach a final volume of 10 mL. If present, residual solid was filtered off and the sample was analyzed by MP-AES 4210 instrument.

References.

1. (a) A. Marrocchi, P. Adriaensens, E. Bartollini, B. Barkakaty, R. Carleer, J. Chen, D. K. Hensley, C. Petrucci, M. Tassi and L. Vaccaro, *Eur. Polym. J.*, **2015**, 73, 391-401, (b) M. Tassi,

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Representative E-factor calculation.

Batch reaction of iodobenzene (6a) with methylacrylate (7a):

E-factor = [0.208 g (6a) + 0.104 g (7a) + 1.312 g (GVL) + 0.469 g (PS-TEA) + 0.0046 g (catalyst 1) + 2.052 g (n-heptane) + 6.000 g (water) – 0.148 g (product)]/0.148 g (product) = **67.58**.

or (batch protocol envisaging GVL recovery):

E-factor = [0.208 g (6a) + 0.104 g (7a) + 1.312 g (GVL) + 0.228 g (TEA wash) + 1.05 g (GVL for PS-TEA regeneration) + 1.05 g (GVL wash) + 0.897 g (ethyl acetate) + 2.000 g (water) – 0.148 g (product) – 3.41 g (97% GVL recovered, regeneration/wash steps)]/0.148 g (product) = **22.24**.

PS-TEA and catalyst 1 were not considered due to their complete recovery

Batch reaction of iodobenzene (6a) with butylacrylate (7b):

E-factor = [0.208 g (6a) + 0.157 g (7b) + 1.312 g (GVL) + 0.469 g (PS-TEA) + 0.0046 g (catalyst 1) + 2.052 g (n-Heptane) + 6.000 g (water) – 0.176 g (product)]/0.176 g (product) = **56.97**.

Batch reaction of 4-methyl-iodobenzene (6b) with methylacrylate (7a):

E-factor = [0.220 g (6b) + 0.104 g (7a) + 1.312 g (GVL) + 0.469 g (PS-TEA) + 0.0046 g (catalyst 1) + 0.897 g (ethyl acetate) + 2.000 g (water) – 0.148 g (product)]/0.148 g (product) = **32.83**.

Batch reaction of 4-methyl-iodobenzene (6b) with butylacrylate (7b):

E-factor = [0.220 g (6b) + 0.157 g (7b) + 1.312 g (GVL) + 0.469 g (PS-TEA) + 0.0046 g (catalyst 1) + 2.052 g (n-heptane) + 6.000 g (water) – 0.192 g (product)]/0.192 g (product) = **52.20**.

Batch reaction of 4-methoxy-iodobenzene (6c) with methylacrylate (7a):

E-factor = [0.239 g (6c) + 0.104 g (7a) + 1.312 g (GVL) + 0.469 g (PS-TEA) + 0.0046 g (catalyst 1) + 0.897 g (ethyl acetate) + 2.000 g (water) – 0.170 g (product)]/0.170 g (product) = **28.56**.

Batch reaction of 4-methoxy-iodobenzene (6c) with butylacrylate (7b):

E-factor = [0.239 g (6c) + 0.157 g (7b) + 1.312 g (GVL) + 0.469 g (PS-TEA) + 0.0046 g (catalyst 1) + 2.052 g (n-heptane) + 6.000 g (water) – 0.211 g (product)]/0.211 g (product) = **47.50**.

Batch reaction of 4-iodoacetophenone (6d) with methylacrylate (7a):

E-factor = [0.251 g (6d) + 0.104 g (7a) + 1.312 g (GVL) + 0.469 g (PS-TEA) + 0.0046 g (catalyst 1) + 0.897 g (ethyl acetate) + 2.000 g (water) – 0.182 g (product)]/0.182 g (product) = **26.68**.

Batch reaction of 4-iodoacetophenone (6d) with butylacrylate (7b):

E-factor = [0.251 g (6d) + 0.157 g (7b) + 1.312 g (GVL) + 0.469 g (PS-TEA) + 0.0046 g (catalyst 1) + 2.052 g (n-heptane) + 6.000 g (water) – 0.230 g (product)]/0.230 g (product) = **43.55**.

Batch reaction of 2-iodothiophene (6e) with methylacrylate (7a):

E-factor = [0.214 g (**6e**) + 0.104 g (**7a**) + 1.312 g (GVL) + 0.469 g (PS-TEA) + 0.0046 g (catalyst 1) + 2.052 (n-heptane) + 6.000 g (water) – 0.133 g (**product**)]/0.133 g (**product**) = **75.36**.

or (**batch protocol envisaging GVL recovery**):

E-factor = [0.214 g (**6e**) + 0.104 g (**7a**) + 1.312 g (GVL) + 2.052 g (n-heptane) + 0.228 g (TEA wash) + 1.05 g (GVL for PS-TEA regeneration) + 1.05g (GVL wash) + 6.000g (water) – 0.133 g (**product**) – 3.41 g (97% GVL recovered, regeneration/wash steps)]/0.133 g (**product**) = **63.66**.

PS-TEA and catalyst 1 were not considered due to their complete recovery.

Batch reaction of 2-iodothiophene (6e) with butylmetacrylate (7b):

E-factor = [0.214 g (**6e**) + 0.157 g (**7b**) + 1.312 g (GVL) + 0.469 g (PS-TEA) + 0.0046 g (catalyst 1) + 2.052 (n-heptane) + 6.000 g (water) – 0.183 g (**product**)]/0.183 g (**product**) = **54.78**.

Batch reaction of iodobenzene (6a) with styrene (9a):

E-factor = [0.208 g (**6a**) + 0.128 g (**9a**) + 1.312 g (GVL) + 0.469 g (PS-TEA) + 0.0046 g (catalyst 1) + 0.897 g (Ethyl acetate) + 2.000 g (water) – 0.153 g (**product**)]/0.153 g (**product**) = **31.80**.

Batch reaction of iodobenzene (6a) with 4-chlorostyrene (9b):

E-factor = [0.208 g (**6a**) + 0.171 g (**9b**) + 1.312 g (GVL) + 0.469 g (PS-TEA) + 0.0046 g (catalyst 1) + 0.897 g (ethyl acetate) + 2.000 g (water) – 0.186 g (**product**)]/0.186 g (**product**) = **26.21**.

Batch reaction of 4-methyl-iodobenzene (6b) with styrene (9a):

E-factor = [0.220 g (**6b**) + 0.128 g (**9a**) + 1.312 g (GVL) + 0.469 g (PS-TEA) + 0.0046 g (catalyst 1) + 0.897 g (ethyl acetate) + 2.000 g (water) – 0.168 g (**product**)]/0.168 g (**product**) = **28.94**.

Batch reaction of 4-methyl-iodobenzene (6b) with 4-chlorostyrene (9b):

E-factor = [0.220 g (**6b**) + 0.171 g (**9b**) + 1.312 g (GVL) + 0.469 g (PS-TEA) + 0.0046 g (catalyst 1) + 0.897 g (ethyl acetate) + 2.000 g (water) – 0.188 g (**product**)]/0.188 g (**product**) = **25.99**.

Batch reaction of 4-methoxy-iodobenzene (6c) with styrene (9a):

E-factor = [0.239 g (**6c**) + 0.128 g (**9a**) + 1.312 g (GVL) + 0.469 g (PS-TEA) + 0.0046 g (catalyst 1) + 0.897 g (ethyl acetate) + 2.000 g (water) – 0.187 g (**product**)]/0.187 g (**product**) = **26.00**.

Batch reaction of 4-methoxy-iodobenzene (6c) with 4-chlorostyrene (9b):

E-factor = [0.239 g (**6c**) + 0.171 g (**9b**) + 1.312 g (GVL) + 0.469 g (PS-TEA) + 0.0046 g (catalyst 1) + 0.897 g (ethyl acetate) + 2.000 g (water) – 0.221 g (**product**)]/0.221 g (**product**) = **22.04**.

Batch reaction of 4-iodo-acetophenone (6d) with styrene (9a):

E-factor = [0.251 g (**6d**) + 0.128 g (**9a**) + 1.312 g (GVL) + 0.469 g (PS-TEA) + 0.0046 g (catalyst **1**) + 0.897 g (ethyl acetate) + 2.000 g (water) – 0.207 g (**product**)]/0.207 g (**product**) = **23.45**.

Batch reaction of 4-iodo-acetophenone (6d) with 4-chlorostyrene (9b):

E-factor = [0.251 g (**6d**) + 0.171 g (**9b**) + 1.312 g (GVL) + 0.469 g (PS-TEA) + 0.0046 g (catalyst **1**) + 0.897 g (ethyl acetate) + 2.000 g (water) – 0.229 g (**product**)]/0.229 g (**product**) = **21.29**.

or (batch protocol envisaging GVL recovery):

E-factor = [0.251 g (**6d**) + 0.171 g (**9b**) + 1.312 g (GVL) + 0.897 g (ethyl acetate) + 0.228 g (TEA wash) + 1.05 g (GVL for PS-TEA regeneration) + 1.05g (GVL wash) + 2.000g (water) – 0.229 g (**product**) – 3.41 g (97% GVL recovered, regeneration/wash steps)]/0.229 g (**product**) = **14.5**.

PS-TEA and catalyst 1 were not considered due to their complete recovery

Batch reaction of 2-iodothiophene (6e) with styrene (9a):

E-factor = [0.214 g (**6e**) + 0.128 g (**9a**) + 1.312 g (GVL) + 0.469 g (PS-TEA) + 0.0046 g (catalyst **1**) + 0.897 g (ethyl acetate) + 2.000 g (water) – 0.142 g (**product**)]/0.142 g (**product**) = **34.38**.

Batch reaction of 2-iodothiophene (6e) with 4-chlorostyrene (9b):

E-factor = [0.214 g (**6e**) + 0.171 g (**9b**) + 1.312 g (GVL) + 0.469 g (PS-TEA) + 0.0046 g (catalyst **1**) + 0.897 g (ethyl acetate) + 2.000 g (water) – 0.176 g (**product**)]/0.176 g (**product**) = **27.79**.

Flow reaction of iodobenzene (6a) with methylacrylate (7a):

E-factor = [0.204 g (**6a**) + 0.103 g (**7a**) + 11.8 g (GVL) + 0.151 g (TEA)] – [0.193 g (**product**) + 11.1 g (94% recovered medium)]/0.193 g (**product**) = **5**

Diethylaminomethyl-polystyrene (PS-TEA) and catalyst were not considered due to their complete recovery.

Flow reaction of 4-iodoacetophenone (6d) with styrene (9a):

E-factor = [0.246 g (**6d**) + 0.125 g (**9a**) + 11.8 g (GVL) + 0.151 g (TEA)] – [0.210 g (**product**) + 11.6 g (98% recovered medium)]/0.210 g (**product**) = **2.4**

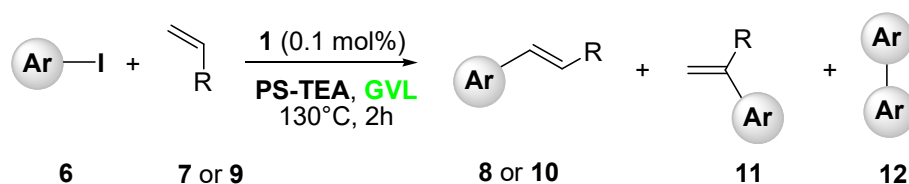
Diethylaminomethyl-polystyrene (PS-TEA) and catalyst were not considered due to their complete recovery.

Flow reaction to 2-iodothiophene (6e) with 4-chlorostyrene (9b):

E-factor = [0.210 g (**6e**) + 0.166 g (**9b**) + 11.8 g (GVL) + 0.151 g (TEA)] – [0.146 g (**product**) + 11.6 g (98% recovered medium)]/0.146 g (**product**) = **3.9**

Diethylaminomethyl-polystyrene (PS-TEA) and catalyst were not considered due to their complete recovery.

Table S1. Heck reaction between aryl iodides **6a-e** and methyl acrylates **7a-b** or styrenes **9a-b** catalyzed by **1** in GVL at 130 °C^a



entry	Ar	R	product	C(%) ^b	8(or10):11:12 ^b	E-factor ^c
1	C ₆ H ₅	CO ₂ Me	8aa	>99	100:0:0 (100:0:0) ^c	67.58 (22.24)
2		CO ₂ Bu	8ab	>99	100:0:0	56.97
3		C ₆ H ₅	10aa	97	93:7:0	31.80
4		4-Cl-C ₆ H ₅	10ab	97	94:6:0	26.21
5	4-CH ₃ -C ₆ H ₅	CO ₂ Me	8ba	96	100:0:0	32.83
6		CO ₂ Bu	8bb	>99	100:0:0	52.20
7		C ₆ H ₅	10ba	97	92:8:0	28.94
8		4-Cl-C ₆ H ₅	10bb	97	94:6:0	25.99
9	4-OCH ₃ -C ₆ H ₅	CO ₂ Me	8ca	96	100:0:0	28.56
10		CO ₂ Bu	8cb	>99	100:0:0	47.50
11		C ₆ H ₅	10ca	>99	90:10:0	26.00
12		4-Cl-C ₆ H ₅	10cb	>99	93:7:0	22.04
13	4-COCH ₃ -C ₆ H ₅	CO ₂ Me	8da	>99	100:0:0	26.68
14		CO ₂ Bu	8db	99	100:0:0	43.55
15		C ₆ H ₅	10da	>99	94:6:0 (100:0:0) ^c	23.45
16		4-Cl-C ₆ H ₅	10db	>99	95:5:0	21.29 (14.50)
17	2-iodothiophene	CO ₂ Me	8ea	>99	96:0:4	75.36 (63.66)
18		CO ₂ Bu	8eb	>99	97:0:3	54.78
19		C ₆ H ₅	10ea	93	87:9:4	34.38
20		4-Cl-C ₆ H ₅	10eb	98	94:4:2 (93:4:3) ^c	27.79

^aReaction conditions: aryl iodides **6** (1 mmol), acrylates **7** or styrenes **9** (1.2 mmol), base (1.5 mmol), GVL (1.25 mL), 130 °C, 2 h; ^bConversion of **6** to **8** or **10** and **8** (or **10**)/**11**/**12** ratio are measured by GLC analyses; ^cValues for batch protocols envisaging GVL recovery in parenthesis.

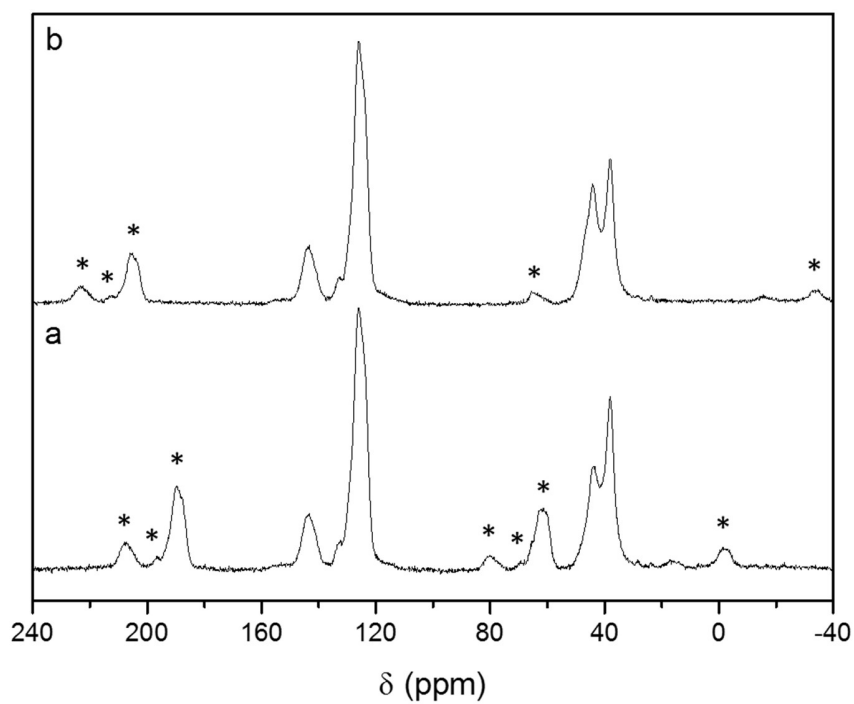


Figure S1 (a) ^{13}C CP-MAS of **2** at 8KHz (b) ^{13}C CP_MAS of **2** at 10 KHz (*) sidebands

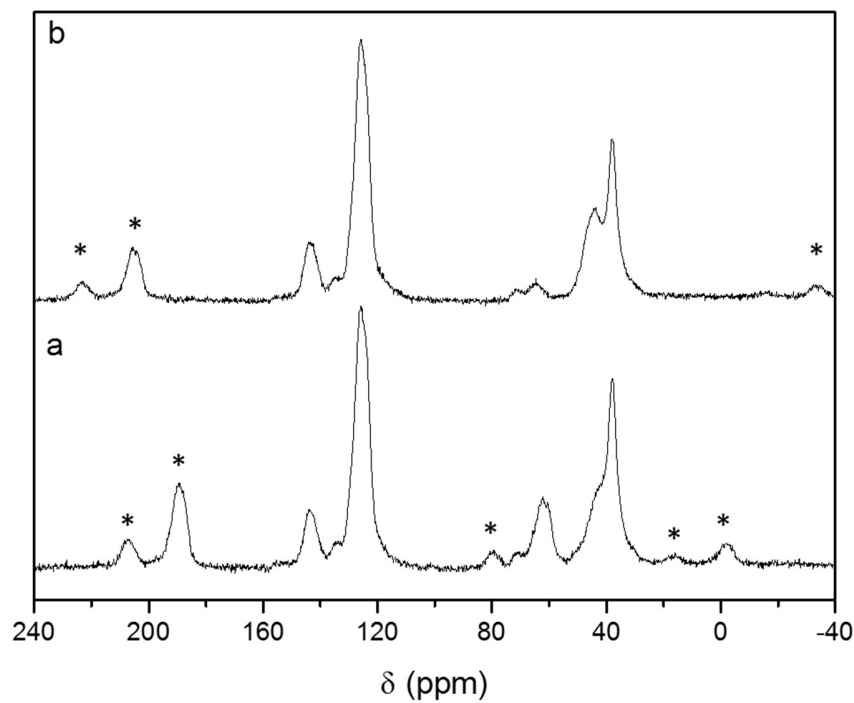


Figure S2: (a) ^{13}C CP-MAS of **5** at 8KHz (b) ^{13}C CP-MAS of **5** at 10KHz (*) sidebands

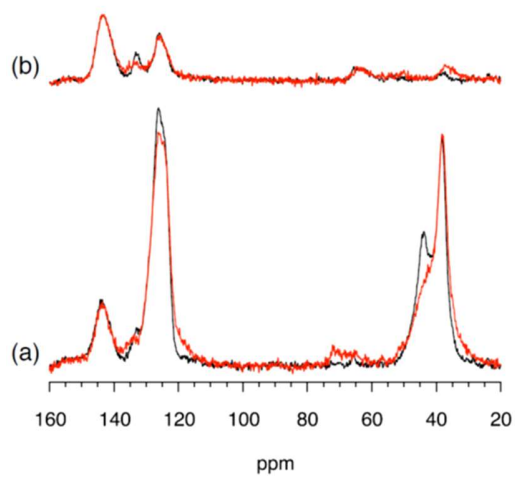
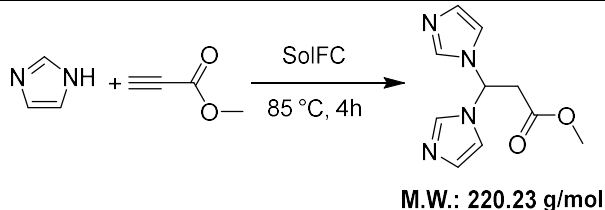
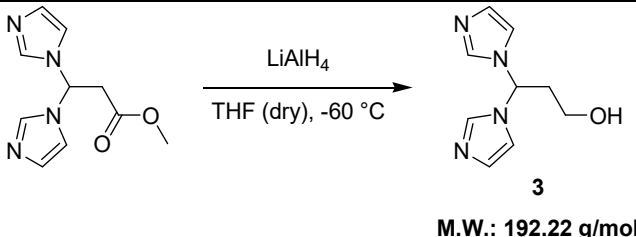


Figure S3: (a) ^{13}C CP-TOSS of 2 (black line) and 5 (red line). (b) ^{13}C CP-NQS of 2 (black line) and 5 (red line).

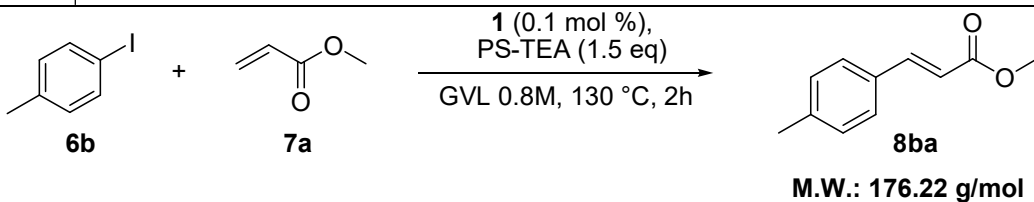
Characterization data

Chem. Name	Methyl 3,3-bis(1H-imidazol-1-yl)propanoate			
Lit. Ref.	V. Kozell, F. Rahmani, O. Piermatti, D. Lanari, L. Vaccaro, <i>Mol. Cat.</i> 2018 , 455,188–191			
<div></div> <p style="text-align: center;">M.W.: 220.23 g/mol</p>				
METHOD:				
To a 12 mL screw-capped vial equipped with a magnetic stirrer, 1H-imidazole (110.2 mmol, 7.5 g) and methyl propiolate (28.1 mmol, 2.5mL) were consequently added. The mixture was left under stirring at 85°C. After 2.5 h, the mixture was washed several times with diethyl ether and acetone to afford pure methyl 3,3-bis(1H-imidazol-1-yl)propanoate as a white solid (5.13 g, 23.3 mmol, 83% yield).				
Mol Formula	C ₁₀ H ₁₂ N ₄ O ₂		m.p.	138-140 °C
Elemental Analysis: Calc.: C: 54.54; H: 5.49; N: 25.44 found: C: 54.49; H: 5.51; N:25.47.				
¹ H NMR 400 MHz CDCl ₃	δ value	No. H	Mult.	j value/Hz
	7.68	2	s	
	7.11	2	s	
	6.99	2	s	
	6.70	1	t	7.2
	3.70	3	s	
	3.43	2	d	7.2
¹³ C NMR (100.6 MHz, CDCl ₃) δ : 168.0, 135.8, 131.2, 116.6, 64.6, 53.0, 40.2.				
GC-EIMS (m/z, %): 220 (M ⁺ , 27), 153 (100), 147 (18), 111 (81) 67 (17) 59 (24).				

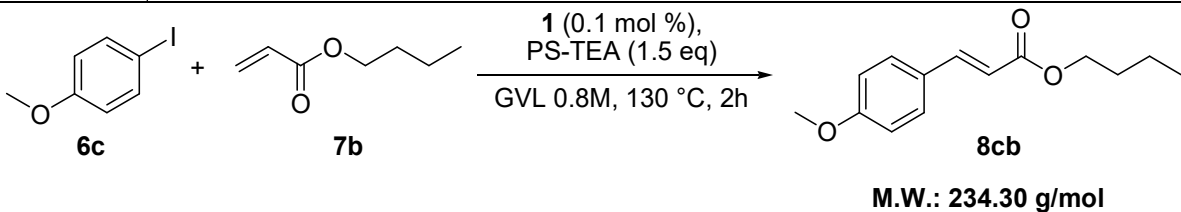
Chem. Name	3,3-bis(1H-imidazol-1-yl)propan-1-ol (3)			
Lit. Ref.	E. Díez-Barra, J. Guerra, V. Hornillos, S. Merino, J. Rodríguez-López, P. Sánchez-Verdú, J. Tejeda and J. Tolosa, <i>Arkivoc</i> , 2005 , 2005, 159-164.			
<div></div>				
METHOD:				
A 250 mL three-neck round bottom flask equipped with a magnetic stirrer was charged with LiAlH ₄ (13.6 mmol, 0.534 g) in 20 mL of dry THF under nitrogen atmosphere. The mixture was cooled down to 0°C and methyl 3,3-bis(1H-imidazol-1-yl)propanoate (4.5 mmol, 1.0 g) in 100 mL of dry THF was added dropwise over 15 min. The mixture was left under stirring at room temperature for 3 h and the excess of LiAlH ₄ was neutralized by the dropwise addition of 1 mL water. The mixture was filtrated and the remaining solid washed with warm THF (3 x 50 mL). The solvent was removed under vacuum and the residue was washed with acetone, affording 3,3-bis(1H-imidazol-1-yl)propan-1-ol (3) as a white solid (0.623 g, 3.2 mmol, 71.4% yield).				
Mol Formula	C ₉ H ₁₂ N ₄ O	m.p.	148-150 °C	
Elemental Analysis: Calc.: C: 56.24; H: 6.29; N: 29.15 found: C: 56.28; H: 6.28; N:29.21.				
¹ H NMR 400 MHz CDCl ₃	δ value	No. H	Mult.	j value/Hz
	7.68	2	s	
	7.12	2	s	
	7.01	2	s	
	6.52	1	t	7.4
	3.60	2	t	5.6
	2.60	2	m	
	1.25	1	s	
¹³ C NMR (100.6 MHz, CDCl ₃) δ : 136.0, 130.9, 116.6, 64.9, 57.0, 36.9.				
GC-EIMS (m/z, %): 192 (M ⁺ , 10) , 125 (64), 95 (100), 68 (16).				

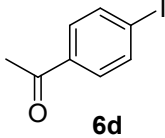
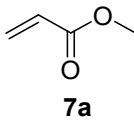
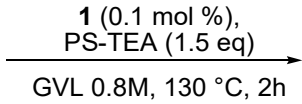
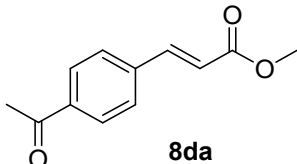
Chem. Name	Methyl cinnamate (8aa)			
Lit. Ref.	Z. Zhang, Z. Zha, C. Gan, C. Pan, Y. Zhou, Z. Wang, M-M. Zhou, <i>J. Org. Chem.</i> , 2006 , 71, 4339-4342.			
<div><div><div><p>6a 7a 8aa</p><p>M.W.: 162.19 g/mol</p></div></div></div>				
METHOD:				
In a 4 mL screw-capped vial equipped with a magnetic stirrer, catalyst 1 (2.3 wt%, 0.0046 g, 0.1 mol%), PS-TEA (~3.2 mmol/g, 0.469 g, 1.5 eq.), GVL (0.8 M, 1.25 mL), iodobenzene (6a) (0.208 g, 114 μ L, 1 mmol), and methyl acrylate (7a) (0.104 g, 110 μ L, 1.2 mmol) were consecutively added and the resulting mixture was left under stirring at 130 °C. After 2 hours the catalyst and base were filtered off. The GVL was removed by using extraction work up method. Methyl cinnamate (8aa) was obtained as a white solid (0.148 g, 91% isolated yield).				
Mol Formula	C ₁₀ H ₁₀ O ₂	m.p.	36-38°C	
Elemental Analysis: Calc.: C: 74.06; H: 6.22; found: C: 74.08; H: 6.23.				
¹ H NMR 400 MHz CDCl ₃	δ value	No. H	Mult.	j value/Hz
	7.70	1	<i>d</i>	16.0
	7.51 – 7.54	2	<i>m</i>	
	7.37 – 7.40	3	<i>m</i>	
	6.45	1	<i>d</i>	16.0
	3.81	3	<i>s</i>	
¹³ C NMR (100.6 MHz, CDCl ₃) δ : 167.6, 145.0, 134.5, 130.4, 129.0, 128.2, 117.9, 51.8.				
GC-EIMS (m/z, %): 162 (M ⁺ , 50), 161 (25), 131 (100), 103 (71), 102 (25), 77(39), 51 (22).				

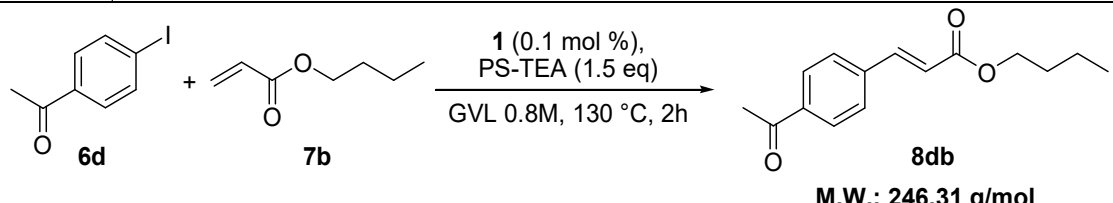
Chem. Name	Butyl cinnamate (8ab)			
Lit. Ref.	N. Iranpoor, H. Firouzabadi, R. Azadi, <i>Eur. J. Org. Chem.</i> 2007 , 13, 2197-2201.			
<div><div><div><p>6a + 7b $\xrightarrow[\text{GVL 0.8M, 130 } ^\circ\text{C, 2h}]{\text{1 (0.1 mol \%), PS-TEA (1.5 eq)}}$ 8ab</p><p>M.W.: 204.27 g/mol</p></div></div></div>				
METHOD:				
In a 4 mL screw-capped vial equipped with a magnetic stirrer, catalyst 1 (2.3 wt%, 0.0046 g, 0.1 mol%), PS-TEA (~3.2 mmol/g, 0.469 g, 1.5 equiv), GVL (0.8 M, 1.25 mL), iodobenzene (6a) (0.208 g, 114 μL , 1 mmol), and butyl acrylate (7b) (0.157 g, 174 μL , 1.2 mmol) were consecutively added and the resulting mixture was left under stirring at 130 $^\circ\text{C}$. After 2 hours the catalyst and base were filtered off. The GVL was removed by using extraction work up method. Butyl cinnamate (8ab) was obtained as a pale yellow oil (0.176 g, 86% isolated yield).				
Mol Formula	C ₁₃ H ₁₆ O ₂	m.p.		
Elemental Analysis: Calc.: C: 76.44; H: 7.90; found: C: 76.45; H: 7.92.				
¹ H NMR 400 MHz CDCl ₃	δ value	No. H	Mult.	j value/Hz
	7.68	1	<i>d</i>	16.0
	7.51 – 7.55	2	<i>m</i>	
	7.37 – 7.40	3	<i>m</i>	
	6.44	1	<i>d</i>	16.0
	4.21	2	<i>t</i>	6.8
	1.65 – 1.73	2	<i>m</i>	
	1.41 – 1.49	2	<i>m</i>	
	0.97	3	<i>t</i>	8
¹³ C NMR (100.6 MHz, CDCl ₃) δ : 167.3, 144.7, 134.6, 130.3, 129.0, 128.2, 118.4, 64.6, 30.9, 19.4, 13.9.				
GC-EIMS (m/z, %): 204 (M ⁺ , 35), 148 (87), 147 (80), 132 (17), 131 (100), 104 (16), 103 (81), 102 (20), 77 (64), 51 (20).				

Chem. Name	Methyl (E)-3-(p-tolyl)acrylate (8ba)			
Lit. Ref.	K. Mori, <i>Tetrahedron: Asymmetry</i> 2005 , 16, 685-692.			
<div><div><div></div><div><p>6b + 7a $\xrightarrow[\text{GVL 0.8M, 130 } ^\circ\text{C, 2h}]{\text{1 (0.1 mol \%), PS-TEA (1.5 eq)}}$ 8ba</p><p>M.W.: 176.22 g/mol</p></div></div></div>				
METHOD:				
In a 4 mL screw-capped vial equipped with a magnetic stirrer, catalyst 1 (2.3 wt%, 0.0046 g, 0.1 mol%), diethylaminomethyl-polystyrene (~3.2 mmol/g, 0.469 g, 1.5 equiv), GVL (0.8 M, 1.25 mL), 4-iodotoluene (6b) (0.220 gr, 1 mmol), and methyl acrylate (7a) (0.104 g, 110 μ L, 1.2 mmol) were consecutively added and the resulting mixture was left under stirring at 130 $^\circ$ C. After 2 hours the catalyst and base were filtered off and the product was precipitated by precipitation method. Methyl (E)-3-(p-tolyl)acrylate (8ba) was obtained as a white solid (0.148 g, 84% isolated yield).				
Mol Formula	C ₁₁ H ₁₂ O ₂	m.p.	54-56 $^\circ$ C	
Elemental Analysis: Calc.: C: 74.98; H: 6.86; found: C: 75.01; H: 6.89.				
¹ H NMR 400 MHz CDCl ₃	δ value	No. H	Mult.	j value/Hz
	7.67	1	<i>d</i>	16.0
	7.42	2	<i>d</i>	8.0
	7.19	2	<i>d</i>	8.0
	6.40	1	<i>d</i>	16.0
	3.80	3	<i>s</i>	
	2.37	3	<i>s</i>	
¹³ C NMR (100.6 MHz, CDCl ₃) δ : 167.8, 145.0, 140.9, 131.8, 129.8, 128.2, 116.8, 51.8, 21.6.				
GC-EIMS (m/z, %): 176 (M ⁺ , 100), 175 (56), 161 (22), 146 (40), 145 (100), 131 (16), 118 (25), 117 (100), 116 (56), 115 (100), 102 (17), 91 (67), 89 (25), 65 (32), 63 (26), 57 (16), 51 (16).				

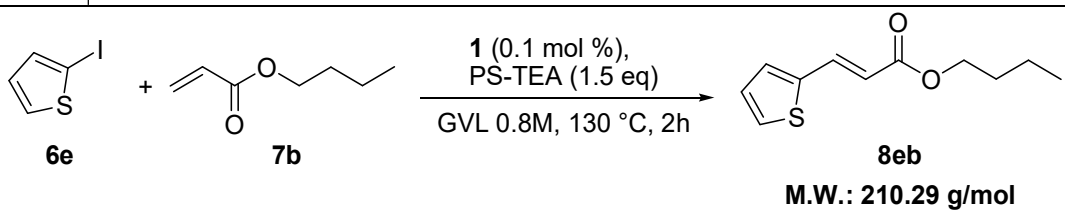
Chem. Name	Butyl (E)-3-(p-tolyl)acrylate (8bb)			
Lit. Ref.	N. Iranpoor, H. Firouzabadi, R. Azadi, <i>Eur. J. Org. Chem.</i> 2007 , 13, 2197-2201.			
<div><div><div><p>6b + 7b $\xrightarrow[\text{GVL 0.8M, 130 }^{\circ}\text{C, 2h}]{\text{1 (0.1 mol \%), PS-TEA (1.5 eq)}}$ 8bb</p><p>M.W.: 218.30 g/mol</p></div></div></div>				
METHOD:				
In a 4 mL screw-capped vial equipped with a magnetic stirrer, catalyst 1 (2.3 wt%, 0.0046 g, 0.1 mol%), diethylaminomethyl-polystyrene (~3.2 mmol/g, 0.469 g, 1.5 equiv), GVL (0.8 M, 1.25 mL), 4-iodotoluene (6d) (0.220 gr, 1 mmol), and butyl acrylate (7b) (0.157 g, 174 μ L, 1.2 mmol) were consecutively added and the resulting mixture was left under stirring at 130 $^{\circ}$ C. After 2 hours the catalyst and base were filtered off. The GVL was removed by using extraction work up method. Butyl (E)-3-(p-tolyl)acrylate (8bb) was obtained as a pale yellow oil (0.192 g, 88% isolated yield).				
Mol Formula	C ₁₄ H ₁₈ O ₂	m.p.		
Elemental Analysis: Calc.: C: 77.03; H: 8.31; found: C:77.01; H: 8.30.				
¹ H NMR 400 MHz CDCl ₃	δ value	No. H	Mult.	j value/Hz
	7.66	1	d	16.0
	7.42	2	d	8.0
	7.19	2	d	8.0
	6.40	1	d	16.0
	4.20	2	t	6.8
	2.37	3	s	
	1.65-1.73	2	m	
	1.39-1.49	2	m	
	0.97	3	t	7.4
¹³ C NMR (100.6 MHz, CDCl ₃) δ : 167.4, 144.7, 140.7, 131.9, 129.7, 128.2, 117.3, 64.5, 30.9, 21.6, 19.4, 13.9.				
GC-EIMS (m/z, %): 219 (26), 218 (M ⁺ , 100), 161 (100), 147 (100), 146 (57), 145 (100), 131 (25), 119 (18), 118 (71), 117 (100), 116 (72), 115 (100), 105 (38), 102 (23), 91 (100), 89 (25), 65 (41), 63 (21).				

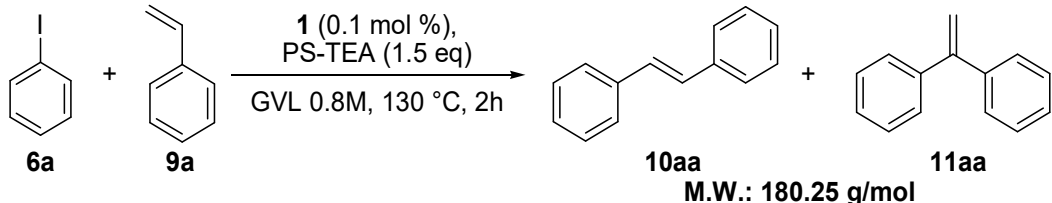
Chem.	Butyl (E)-3-(4-methoxyphenyl)acrylate (8cb)		
Lit. Ref.	N. Iranpoor, H. Firouzabadi, R. Azadi, <i>Eur. J. Org. Chem.</i> 2007 , 13, 2197-2201.		
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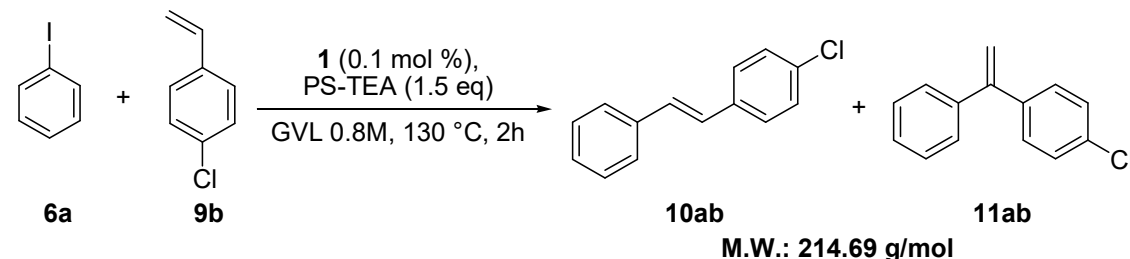
Chem. Name	Methyl (E)-3-(4-acetylphenyl)acrylate (8da)			
Lit. Ref.	J. D. Senra, L. F. B. Malta, A. L. F. Souza, L. C. S. Aguiar, O. A. C. Antunes, <i>Adv. Synth. Catal.</i> , 2008 , 350, 2551-2558.			
<div><div><div><div><p>6d</p></div><div>+</div><div><div><p>7a</p></div></div><div><div><div><div></div><div><div><p>8da</p><p>M.W.: 204.23 g/mol</p></div></div></div></div></div></div></div></div>				
METHOD:				
In a 4 mL screw-capped vial equipped with a magnetic stirrer, catalyst 1 (2.3 wt%, 0.0046 g, 0.1 mol%), diethylaminomethyl-polystyrene (~3.2 mmol/g, 0.469 g, 1.5 equiv), GVL (0.8 M, 1.25 mL), 4'-iodoacetophenone (6d) (0.251 gr, 1 mmol), and methyl acrylate (7a) (0.104 g, 110 μL, 1.2 mmol) were consecutively added and the resulting mixture was left under stirring at 130 °C. After 2 hours the catalyst and base were filtered off and the product was isolated by precipitation work up method. Methyl (E)-3-(4-acetylphenyl)acrylate 8da) was obtained as a pale yellow solid (0.182 g, 89% isolated yield).				
Mol Formula	C ₁₂ H ₁₂ O ₃	m.p.	104-106°C	
Elemental Analysis: Calc.: C: 70.58; H: 5.92; found: C: 70.61; H: 5.93.				
¹ H NMR 400 MHz CDCl ₃	δ value	No. H	Mult.	j value/Hz
	7.97	2	<i>d</i>	8.0
	7.71	1	<i>d</i>	16.0
	7.61	2	<i>d</i>	8.0
	6.53	1	<i>d</i>	16.0
	3.82	3	<i>s</i>	
	2.62	3	<i>s</i>	
¹³ C NMR (100.6 MHz, CDCl ₃) δ : 197.3, 166.9, 143.3, 138.7, 138.1, 128.9, 128.2, 120.3, 51.9, 26.7.				
GC-EIMS (m/z, %): 205 (22), 204 (M ⁺ , 100), 190 (34), 189 (81), 188 (24), 173 (24), 161 (62), 131 (37), 130 (16), 129 (27), 118 (26), 103 (20), 102 (72), 101 (18), 76 (31), 75 (24), 74 (16), 51 (26), 50 (19).				

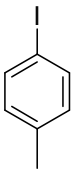
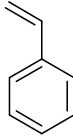
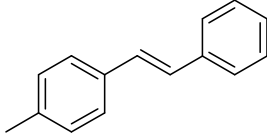
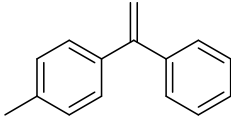
Chem. Name	Butyl (E)-3-(4-acetylphenyl)acrylate (8db)			
Lit. Ref.	N. Iranpoor, H. Firouzabadi, R. Azadi, <i>Eur. J. Org. Chem.</i> 2007 , 13, 2197-2201.			
<div></div> <p style="text-align: center;">8db M.W.: 246.31 g/mol</p>				
METHOD:				
In a 4 mL screw-capped vial equipped with a magnetic stirrer, catalyst 1 (2.3 wt%, 0.0046 g, 0.1 mol%), diethylaminomethyl-polystyrene (~3.2 mmol/g, 0.469 g, 1.5 equiv), GVL (0.8 M, 1.25 mL), 4'-iodoacetophenone (6d) (0.251 gr, 1 mmol), and butyl acrylate (7b) (0.157 g, 174 μ L, 1.2 mmol) were consecutively added and the resulting mixture was left under stirring at 130 °C. After 2 hours the catalyst and base were filtered off. The GVL was removed by using extraction work up method. Butyl (E)-3-(4-acetylphenyl)acrylate (8g) was obtained as a yellow oil (0.230 g, 93% isolated yield).				
Mol Formula	C ₁₅ H ₁₈ O ₃	m.p.		
Elemental Analysis: Calc.: C: 73.15; H: 7.37; found: C: 73.12; H: 7.36.				
¹ H NMR 400 MHz CDCl ₃	δ value	No. H	Mult.	j value/Hz
	7.94	2	<i>d</i>	8.0
	7.66	1	<i>d</i>	16.0
	7.58	2	<i>d</i>	8.0
	6.50	1	<i>d</i>	16.0
	4.20	2	<i>t</i>	6.6
	2.59	3	<i>s</i>	
	1.65-1.70	2	<i>m</i>	
	1.37-1.47	2	<i>m</i>	
	0.94	3	<i>t</i>	7.4
¹³ C NMR (100.6 MHz, CDCl ₃) δ : 197.4, 166.6, 143.0, 138.9, 138.0, 128.9, 128.2, 120.9, 64.7, 30.8, 26.8, 19.3, 13.8.				
GC-EIMS (m/z, %): 246 (M ⁺ , 65), 232 (28), 231 (92), 191 (20), 190 (51), 176 (34), 175 (100), 173 (39), 147 (24), 131 (71), 130 (19), 129 (16).				

Chem. Name	Methyl (E)-3-(thiophen-2-yl)acrylate (8ea)			
Lit. Ref.	A. El-Batta, C. Jiang, W. Zhao, R. Anness, A. L. Cooksy, M. Bergdahl, <i>J. Org. Chem.</i> 2007 , 72, 5244-5259.			
<div><div><div><p>6e + 7a $\xrightarrow[\text{GVL 0.8M, 130 } ^\circ\text{C, 2h}]{\text{1 (0.1 mol \%), PS-TEA (1.5 eq)}}$ 8ea</p><p>M.W.: 168.21 g/mol</p></div></div></div>				
METHOD:				
In a 4 mL screw-capped vial equipped with a magnetic stirrer, catalyst 1 (2.3 wt%, 0.0046 g, 0.1 mol%), diethylaminomethyl-polystyrene (~3.2 mmol/g, 0.469 g, 1.5 equiv), GVL (0.8 M, 1.25 mL), 2-iodothiophene (6e) (0.214 g, 113 μ L, 1 mmol), and methyl acrylate (7a) (0.104 g, 110 μ L, 1.2 mmol) were consecutively added and the resulting mixture was left under stirring at 130 $^\circ$ C. After 2 hours the catalyst and base were filtered off. The GVL was removed by using extraction work up method. Finally, methyl (E)-3-(thiophen-2-yl)acrylate (11a) was obtained as a pale yellow solid after purification by SiO ₂ scavenging (0.133 g, 79% isolated yield).				
Mol Formula	C ₈ H ₈ O ₂ S	m.p.	44-46 $^\circ$ C	
Elemental Analysis: Calc.: C: 57.12; H: 4.79; S: 19.06; found: C: 57.11; H: 4.79; S: 19.03.				
¹ H NMR 400 MHz CDCl ₃	δ value	No. H	Mult.	j value/Hz
	7.78	1	<i>d</i>	15.6
	7.36	1	<i>d</i>	4.8
	7.23-7.25	1	<i>m</i>	
	7.03-7.05	1	<i>m</i>	
	6.23	1	<i>d</i>	15.6
	3.78	3	<i>s</i>	
¹³ C NMR (100.6 MHz, CDCl ₃) δ : 167.4, 139.6, 137.4, 131.1, 128.6, 128.2, 116.7, 51.8.				
GC-EIMS (m/z, %): 170 (24), 169 (46), 168 (M ⁺ , 100), 166 (37), 139 (36), 138 (63), 137 (100), 123 (17), 111 (21), 110 (75), 109 (100), 108 (74), 97 (22), 82 (20), 69 (60), 65 (100), 63 (33), 58 (22), 57 (17), 51 (27), 50 (21).				

Chem. Name	Butyl (E)-3-(thiophen-2-yl)acrylate (8eb)			
Lit. Ref.	M. Oberholzera, C. M. Frech, <i>Green Chem.</i> 2013 , 15, 1678–1686.			
<div><div><div></div><div><p>6e + 7b $\xrightarrow[\text{GVL 0.8M, 130 } ^\circ\text{C, 2h}]{\text{1 (0.1 mol \%), PS-TEA (1.5 eq)}}$ 8eb</p><p>M.W.: 210.29 g/mol</p></div></div></div>				
METHOD:				
In a 4 mL screw-capped vial equipped with a magnetic stirrer, catalyst 1 (2.3 wt%, 0.0046 g, 0.1 mol%), diethylaminomethyl-polystyrene (~3.2 mmol/g, 0.469 g, 1.5 equiv), GVL (0.8 M, 1.25 mL), 2-iodothiophene (6e) (0.214 g, 113 μL , 1 mmol), and butyl acrylate (7b) (0.157 g, 174 μL , 1.2 mmol) were consecutively added and the resulting mixture was left under stirring at 130 $^\circ\text{C}$. After 2 hours the catalyst and base were filtered off. The GVL was removed by using extraction work up method. Finally, butyl (E)-3-(thiophen-2-yl)acrylate (8eb) was obtained as a pale yellow oil (0.183 g, 87% isolated yield).				
Mol Formula	C ₁₁ H ₁₄ O ₂ S	m.p.		
Elemental Analysis: Calc.: C: 62.83; H: 6.71; S: 15.25; found: C: 62.84; H: 6.72; S: 15.24.				
¹ H NMR 400 MHz CDCl ₃	δ value	No. H	Mult.	j value/Hz
	7.77	1	d	16
	7.37	1	d	5.2
	7.25-7.26	1	m	
	7.03-7.06	1	m	
	6.24	1	d	15.6
	4.19	2	t	6.6
	1.64-1.72	2	m	
	1.38-1.48	2	m	
	0.96	3	t	7.4
¹³ C NMR (100.6 MHz, CDCl ₃) δ : 167.1, 139.7, 137.1, 130.9, 128.5, 128.2, 117.2, 64.6, 30.9, 19.3, 13.9.				
GC-EIMS (m/z, %): 210 (M ⁺ , 40), 154 (93), 137 (100), 121 (30), 110 (34), 109 (61), 108 (16), 65 (36).				

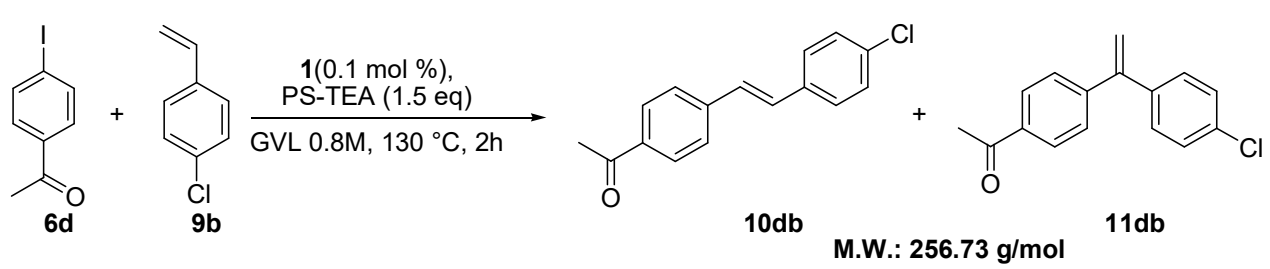
Chem. Name	(E)-stylbene (10aa)			
Lit. Ref.	Z. Zhang, Z. Zha, C. Gan, C. Pan, Y. Zhou, Z. Wang, M-M. Zhou, <i>J. Org. Chem.</i>			
<div></div>				
METHOD:				
In a 4 mL screw-capped vial equipped with a magnetic stirrer, catalyst 1 (2.3 wt%, 0.0046 g, 0.1 mol%), diethylaminomethyl-polystyrene (~3.2 mmol/g, 0.469 g, 1.5 equiv), GVL (0.8 M, 1.25 mL), iodobenzene (6a) (0.208 g, 114 μL , 1 mmol), and styrene (9a) (0.128 g, 141 μL , 1.2 mmol) were consecutively added and the resulting mixture was left under stirring at 130 $^{\circ}\text{C}$. After 2 hours the catalyst and base were filtered off and the product was isolated by precipitation work up method. A 93:7 mixture of 10aa and 11aa was obtained (0.153 g, 85% isolated yield).				
Mol Formula	C ₁₄ H ₁₂	m.p.	126-128 $^{\circ}\text{C}$	
Elemental Analysis: Calc.: C: 93.29; H: 6.71; found: C: 93.32; H: 6.72.				
¹ H NMR 400 MHz CDCl ₃	δ value	No. H	Mult.	j value/Hz
	7.53	4	<i>m</i>	
	7.38	4	<i>m</i>	
	7.28	2	<i>m</i>	
	7.13	2	<i>s</i>	
¹³ C NMR (100.6 MHz, CDCl ₃) δ : 137.5, 128.8, 127.8, 126.7.				
GC-EIMS (m/z, %): 181 (40), 180 (M ⁺ , 100), 179 (100), 178 (91), 177 (24), 176 (27), 166 (19), 165 (86), 152 (35), 151 (17), 102 (23), 89 (46), 77 (19), 76 (33), 63 (18), 51 (23).				

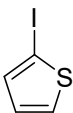
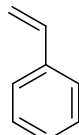
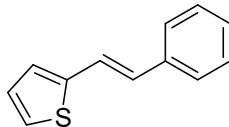
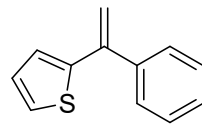
Chem. Name	(E)-1-chloro-4-styrylbenzene (10ab)			
Lit. Ref.	N. Iranpoor, H. Firouzabadi, R. Azadi, <i>Eur. J. Org. Chem.</i> 2007 , 13, 2197-2201.			
<div></div>				
METHOD: In a 4 mL screw-capped vial equipped with a magnetic stirrer, catalyst 1 (2.3 wt%, 0.0046 g, 0.1 mol%), diethylaminomethyl-polystyrene (~3.2 mmol/g, 0.469 g, 1.5 equiv), GVL (0.8 M, 1.25 mL), iodobenzene (6a) (0.208 g, 114 μ L, 1 mmol), and 4-chlorostyrene (9b) (0.171 g, 148 μ L, 1.2 mmol) were consecutively added and the resulting mixture was left under stirring at 130 $^{\circ}$ C. After 2 hours the catalyst and base were filtered off and the product was isolated by precipitation work up method. A 94:6 mixture of 10ab and 11ab was obtained (0.186 g, 87% isolated yield).				
Mol Formula	C ₁₄ H ₁₁ Cl	m.p.	128-130 $^{\circ}$ C	
Elemental Analysis: Calc.: C: 78.32; H: 5.16; found: C: 78.31; H: 5.16.				
¹H NMR 400 MHz CDCl₃	δ value	No. H	Mult.	j value/Hz
	7.51	2	<i>d</i>	7.6
	7.44	2	<i>d</i>	8.4
	7.38	2	<i>d</i>	7.6
	7.34	2	<i>m</i>	
	7.27-7.31	1	<i>m</i>	
	7.01-7.11	2	<i>m</i>	
¹³C NMR (100.6 MHz, CDCl₃) δ : 137.1, 136.0, 133.3, 129.5, 129.0, 129.0, 128.0, 127.8, 127.5, 126.7.				
GC-EIMS (m/z, %): 216 (76), 215 (45), 214 (M ⁺ , 97), 199 (18), 180 (41), 179 (55), 178 (100), 177 (53), 176 (53), 152 (32), 151 (26), 102 (16), 89 (61), 88 (30), 76 (55), 75 (23), 63 (18), 51 (19).				

Chem. Name	(E)-1-methyl-4-styrylbenzene (10ba)			
Lit. Ref.	N. Iranpoor, H. Firouzabadi, R. Azadi, <i>Eur. J. Org. Chem.</i> 2007 , 13, 2197-2201.			
<div><div><div><div></div><div>6b</div></div><div>+</div><div><div><div></div><div>9a</div></div><div><div><div>1 (0.1 mol %), PS-TEA (1.5 eq)</div><div>→</div></div><div><div>GVL 0.8M, 130 °C, 2h</div></div></div><div><div><div></div><div>10ba</div></div><div>+</div><div><div><div></div><div>11ba</div></div></div><div>M.W.: 194.28 g/mol</div></div></div></div></div>				
METHOD:				
In a 4 mL screw-capped vial equipped with a magnetic stirrer, catalyst 1 (2.3 wt%, 0.0046 g, 0.1 mol%), diethylaminomethyl-polystyrene (~3.2 mmol/g, 0.469 g, 1.5 equiv), GVL (0.8 M, 1.25 mL), 4-iodotoluene (6b) (0.220 gr, 1 mmol), and styrene (9a) (0.128 g, 141 μL, 1.2 mmol) were consecutively added and the resulting mixture was left under stirring at 130 °C. After 2 hours the catalyst and base were filtered off and the product was isolated by precipitation work up method. A 92:8 mixture of 10ba and 11ba was obtained (0.168 g, 86% isolated yield).				
Mol Formula	C ₁₅ H ₁₄	m.p.	120-122 °C	
Elemental Analysis: Calc.: C: 92.74; H: 7.26; found: C: 92.69; H: 7.24.				
¹ H NMR 400 MHz CDCl ₃	δ value	No. H	Mult.	j value/Hz
	7.52	2	<i>d</i>	7.6
	7.43	2	<i>d</i>	8
	7.37	2	<i>m</i>	
	7.24-7.28	1	<i>m</i>	
	7.18	2	<i>d</i>	8
	7.04-7.14	2	<i>m</i>	
	2.38	3	<i>s</i>	
¹³ C NMR (100.6 MHz, CDCl ₃) δ : 137.7, 137.7, 134.7, 129.5, 128.8, 128.8, 127.8, 127.5, 126.6, 126.5, 21.4.				
GC-EIMS (m/z, %): 195 (31), 194 (M ⁺ , 97), 193 (46), 180 (29), 179 (100), 178 (94), 165 (27), 152 (19), 115 (26), 89 (17).				

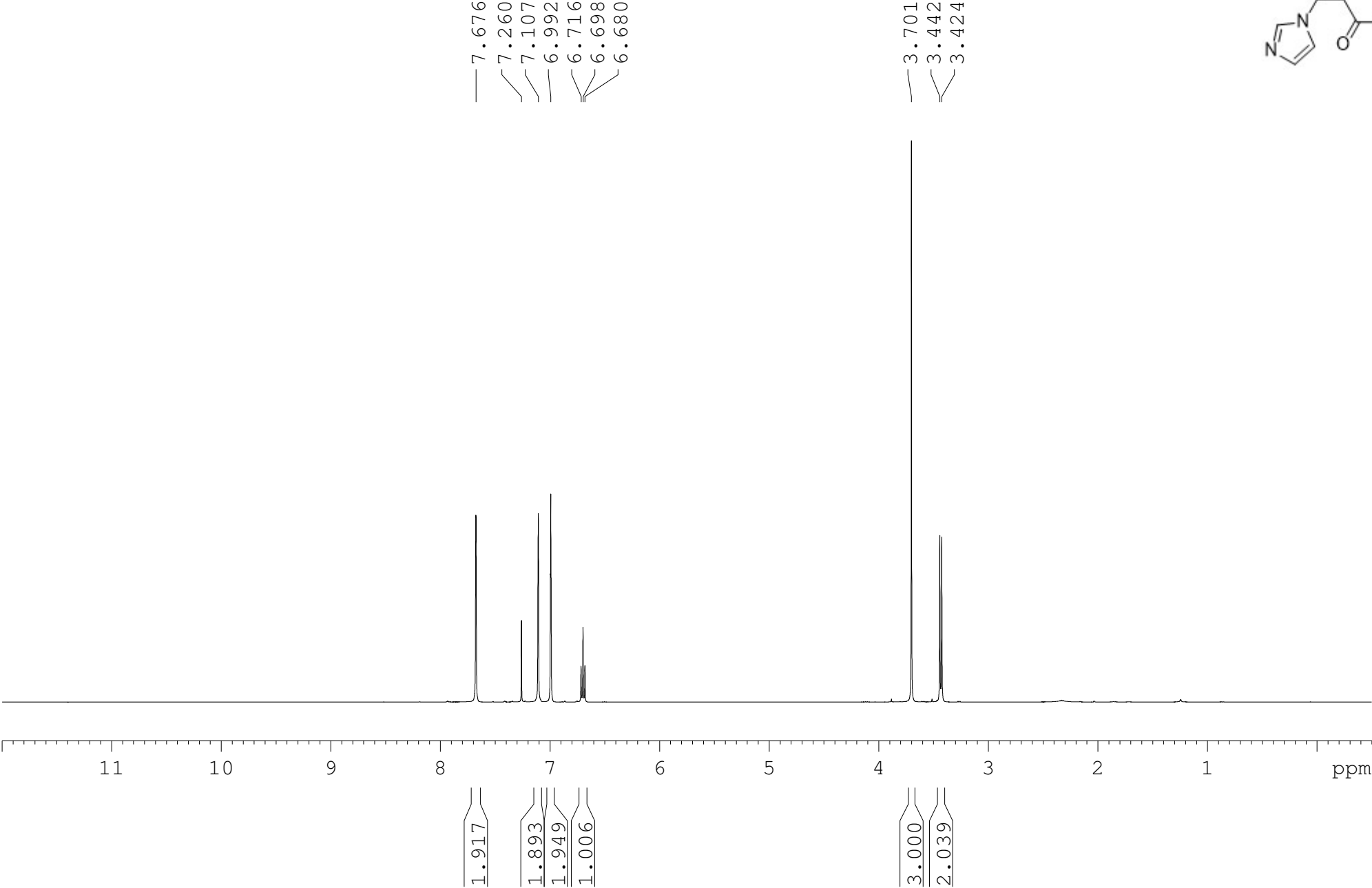
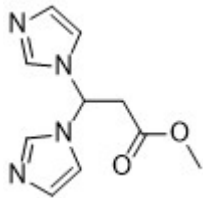
Chem. Name	(E)-1-methoxy-4-styrylbenzene (10ca)			
Lit. Ref.	J. D. Senra, L. F. B. Malta, A. L. F. Souza, L. C. S. Aguiar, O. A. C. Antunes, <i>Adv.</i>			
<p>Reaction scheme showing the synthesis of (E)-1-methoxy-4-styrylbenzene (10ca) and (E)-1-methoxy-4-phenylstyrene (11ca) from 4-iodoanisole (6c) and styrene (9a). The reaction conditions are: catalyst 1 (0.1 mol %), PS-TEA (1.5 eq), GVL 0.8M, 130 °C, 2h. The molecular weight of 10ca is 210.28 g/mol.</p>				
METHOD:				
<p>In a 4 mL screw-capped vial equipped with a magnetic stirrer, catalyst 1 (2.3 wt%, 0.0046 g, 0.1 mol%), diethylaminomethyl-polystyrene (~3.2 mmol/g, 0.469 g, 1.5 equiv), GVL (0.8 M, 1.25 mL), 4-iodoanisole (6c) (0.239 gr, 1 mmol), and styrene (9a) (0.128 g, 141 μL, 1.2 mmol) were consecutively added and the resulting mixture was left under stirring at 130 °C. After 2 hours the catalyst and base were filtered off and the product was isolated by precipitation work up method. A 90:10 mixture of 10ca and 11ca was obtained (0.187 g, 89% isolated yield).</p>				
Mol Formula	C ₁₅ H ₁₄ O	m.p.	136-138°C	
Elemental Analysis: Calc.: C: 85.68; H: 6.71; found: C: 85.67; H: 6.70.				
¹ H NMR 400 MHz CDCl ₃	δ value	No. H	Mult.	j value/Hz
	7.51-7.45	4	<i>m</i>	
	7.35	2	<i>t</i>	7.6
	7.23	1	<i>m</i>	
	7.03	2	<i>m</i>	
	6.91	2	<i>d</i>	8.8
	3.84	3	<i>s</i>	
¹³ C NMR (100.6 MHz, CDCl ₃) δ : 159.4, 137.8, 130.3, 128.8, 128.4, 127.9, 127.4, 126.8, 126.4, 114.3, 55.5.				
GC-EIMS (m/z, %): 211 (56), 210 (M ⁺ , 100), 209 (56), 195 (62), 194 (22), 179 (36), 178 (26), 177 (17), 167 (77), 166 (43), 165 (87), 152 (62), 115 (20), 89 (22).				

Chem. Name	(E)-1-(4-styrylphenyl)ethan-1-one (10da)			
Lit. Ref.	N. Iranpoor, H. Firouzabadi, R. Azadi, <i>Eur. J. Org. Chem.</i> 2007 , 13, 2197-2201.			
<div><p style="text-align: center;">10da 11da M.W.: 222.29 g/mol</p></div>				
METHOD:				
In a 4 mL screw-capped vial equipped with a magnetic stirrer, catalyst 1 (2.3 wt%, 0.0046 g, 0.1 mol%), diethylaminomethyl-polystyrene (~3.2 mmol/g, 0.469 g, 1.5 equiv), GVL (0.8 M, 1.25 mL), 4'-iodoacetophenone (6d) (0.251 gr, 1 mmol), and styrene (9a) (0.128 g, 141 μ L, 1.2 mmol) were consecutively added and the resulting mixture was left under stirring at 130 °C. After 2 hours the catalyst and base were filtered off and the product was isolated by precipitation work up method. A 94:6 mixture of 10da and 11da was obtained (0.207 g, 93% isolated yield).				
Mol Formula	C ₁₆ H ₁₄ O	m.p.	140-142°C	
Elemental Analysis: Calc.: C: 86.45; H: 6.35; found: C: 86.42; H: 6.34.				
¹ H NMR 400 MHz CDCl ₃	δ value	No. H	Mult.	j value/Hz
	7.96	2	<i>d</i>	8.4
	7.59	2	<i>d</i>	8
	7.54	2	<i>d</i>	7.6
	7.39	2	<i>m</i>	
	7.30-7.32	1	<i>m</i>	
	7.21-7.28	1	<i>m</i>	
	7.11-7.16	1	<i>m</i>	
	2.61	3	<i>s</i>	
¹³ C NMR (100.6 MHz, CDCl ₃) δ : 197.5, 142.2, 136.8, 136.1, 131.6, 129.0, 129.0, 128.5, 127.6, 127.0, 126.7, 26.7.				
GC-EIMS (m/z, %): 223 (27), 222 (M ⁺ , 89), 208 (38), 207 (100), 179 (52), 178 (89), 177 (25), 176 (26), 152 (23), 89 (21).				

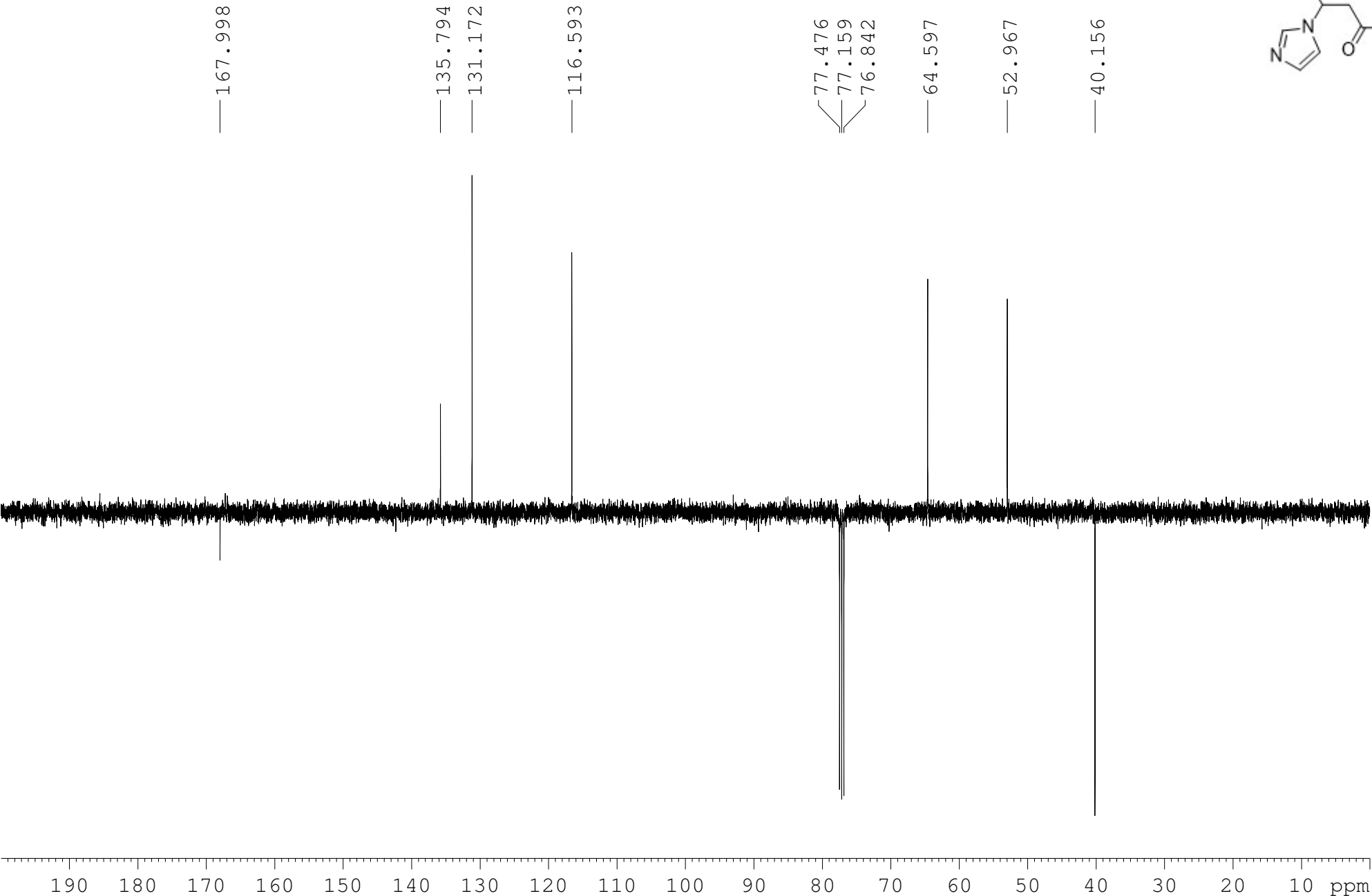
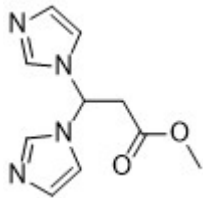
Chem. Name	(E)-1-(4-(4-chlorostyryl)phenyl)ethan-1-one (10db)			
Lit. Ref.	P. K. Suganthi, R. N. Prabhu, V. S. Sridevi, <i>Tetrahed. Lett.</i> 2013 , 54, 5695-5698.			
<div></div> <p style="text-align: center;">M.W.: 256.73 g/mol</p>				
METHOD:				
In a 4 mL screw-capped vial equipped with a magnetic stirrer, catalyst 1 (2.3 wt%, 0.0046 g, 0.1 mol%), diethylaminomethyl-polystyrene (~3.2 mmol/g, 0.469 g, 1.5 equiv), GVL (0.8 M, 1.25 mL), 4'-iodoacetophenone (6d) (0.251 gr, 1 mmol), and 4-chlorostyrene (9b) (0.171 g, 1.2 mmol) were consecutively added and the resulting mixture was left under stirring at 130 °C. After 2 hours the catalyst and base were filtered off and the product was isolated by precipitation work up method. A 95:5 mixture of 10db and 11db was obtained (0.229 g, 89% isolated yield).				
Mol Formula	C ₁₆ H ₁₃ ClO		m.p.	138-140°C
Elemental Analysis: Calc.: C: 74.86; H: 5.10; found: C: 74.88; H: 5.07.				
¹ H NMR 400 MHz CDCl ₃	δ value	No. H	Mult.	j value/Hz
	7.95	2	<i>d</i>	8.4
	7.57	2	<i>d</i>	8.4
	7.46	2	<i>d</i>	8.4
	7.35	2	<i>d</i>	8.4
	7.07-7.19	2	<i>m</i>	
	2.61	3	<i>s</i>	
¹³ C NMR (100.6 MHz, CDCl ₃) δ : 197.7, 141.9, 136.4, 135.5, 134.2, 130.3, 129.2, 129.1, 128.3, 128.2, 126.8, 26.8.				
GC-EIMS (m/z, %): 258 (35), 257 (31), 256 (M ⁺ , 91), 243 (75), 242 (45), 241 (100), 179 (23), 178 (88), 177 (40), 176 (55), 152 (24), 151 (22), 89 (20), 88 (29).				

Chem. Name	(E)-2-(2-phenylethenyl)thiophene (10ea)			
Lit. Ref.	S. Fu, N.-Y. Chen, X. Liu, Z. Shao, S.-P. Luo, Q. Liu, <i>J. Am. Chem. Soc.</i> 2016 , 138, 8588-8594.			
<div><div><div><div><div></div><div>6e</div></div><div><div></div><div>9a</div></div></div><div><div><div>1 (0.1 mol %), PS-TEA (1.5 eq)</div><div>→</div><div>GVL 0.8M, 130 °C, 2h</div></div><div><div><div><div></div><div>10ea</div></div><div><div></div><div>11ea</div></div></div><div>M.W.: 186.27 g/mol</div></div></div></div></div>				
METHOD:				
In a 4 mL screw-capped vial equipped with a magnetic stirrer, catalyst 1 (2.3 wt%, 0.0046 g, 0.1 mol%), diethylaminomethyl-polystyrene (~3.2 mmol/g, 0.469 g, 1.5 equiv), GVL (0.8 M, 1.25 mL), 2-iodothiophene (6e) (0.214 g, 113 μL, 1 mmol), and styrene (9a) (0.128 g, 141 μL, 1.2 mmol) were consecutively added and the resulting mixture was left under stirring at 130 °C. After 2 hours the catalyst and base were filtered off and the product was isolated by precipitation work up method. A 97:3 mixture of 10ea and 11ea was obtained (0.142 g, 76% isolated yield).				
Mol Formula	C ₁₂ H ₁₀ S	m.p.	110-112°C	
Elemental Analysis: Calc.: C: 77.38; H: 5.41;S: 17.21; found: C: 77.41; H: 5.41; S:17.19.				
¹ H NMR 400 MHz CDCl ₃	δ value	No. H	Mult.	j value/Hz
	7.47	2	<i>d</i>	7.6
	7.35	2	<i>t</i>	7.6
	7.19-7.27	3	<i>m</i>	
	7.07	1	<i>d</i>	3.2
	6.99-7.02	1	<i>m</i>	
	6.93	1	<i>d</i>	16.0
¹³ C NMR (100.6 MHz, CDCl ₃) δ : 143.0, 137.0, 128.9, 128.5, 127.7, 126.4, 126.2, 124.5, 121.9.				
GC-EIMS (m/z, %): 187 (19), 186 (M ⁺ , 100), 185 (89), 184 (41), 171 (21), 153 (29), 152 (31), 141 (23), 115 (20).				

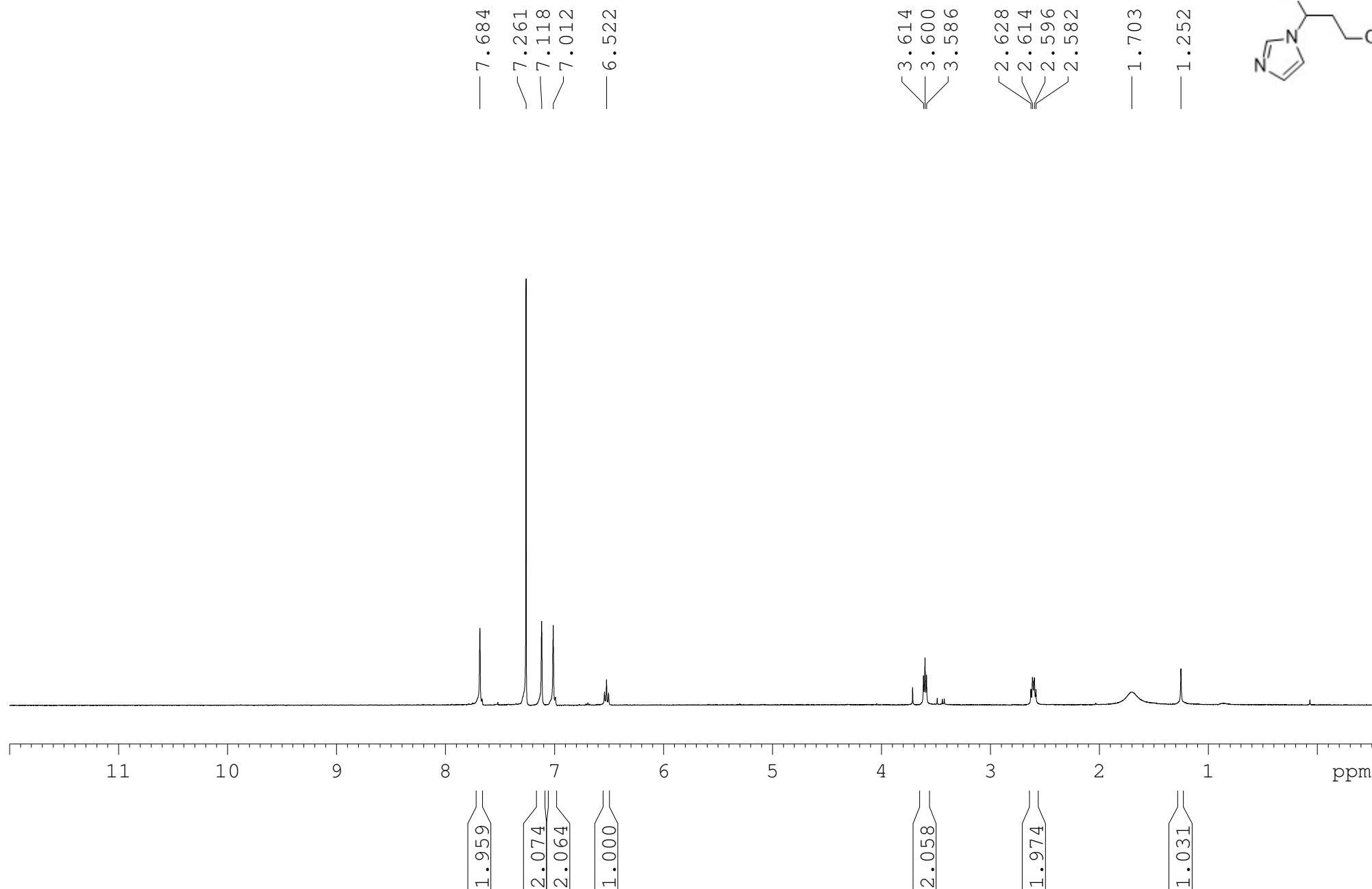
Methyl 3,3-bis(1H-imidazol-1-yl)propanoate



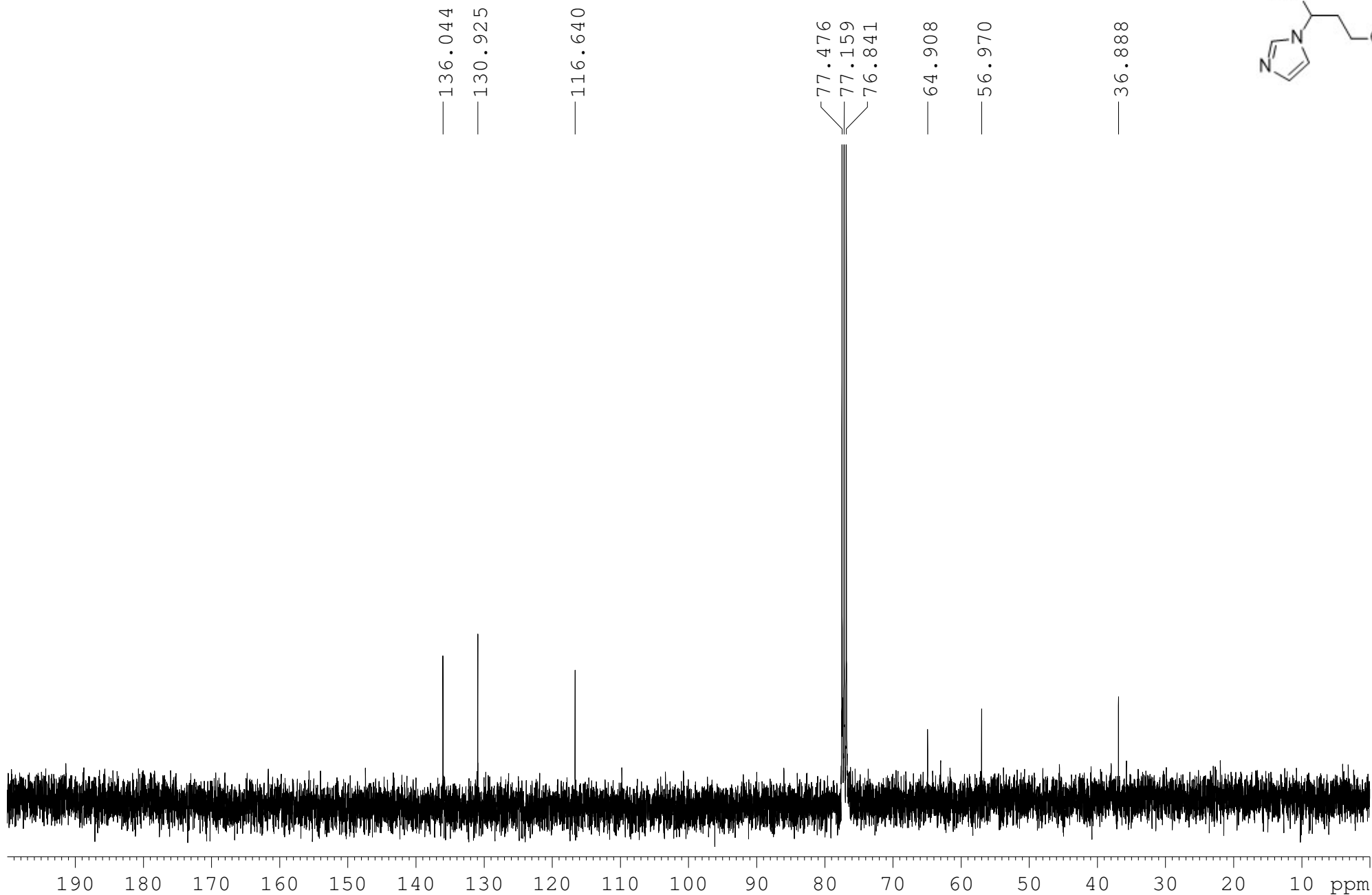
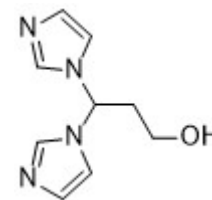
Methyl 3,3-bis(1H-imidazol-1-yl)propanoate



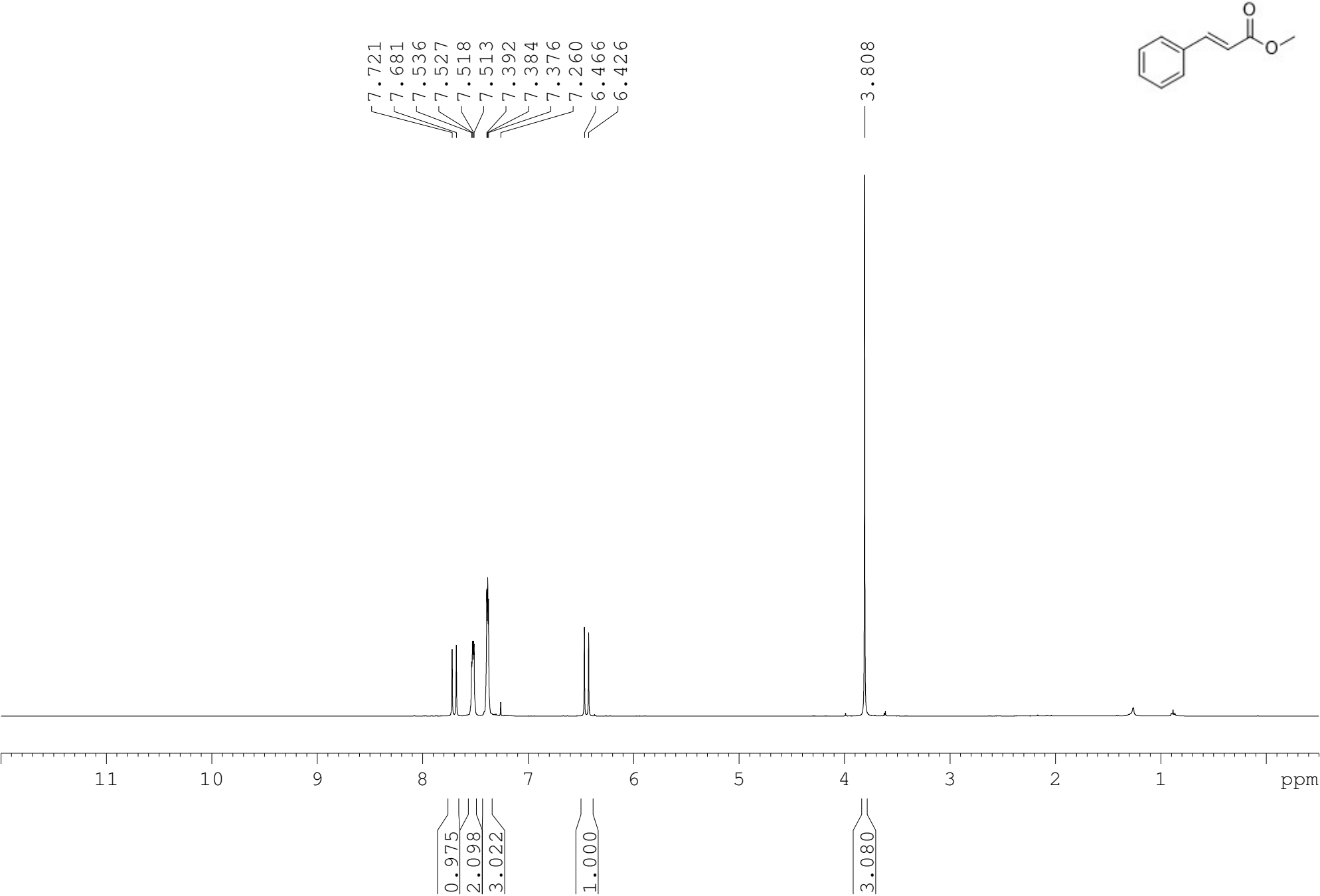
3,3-bis(1H-imidazol-1-yl)propan-1-ol (**3**)



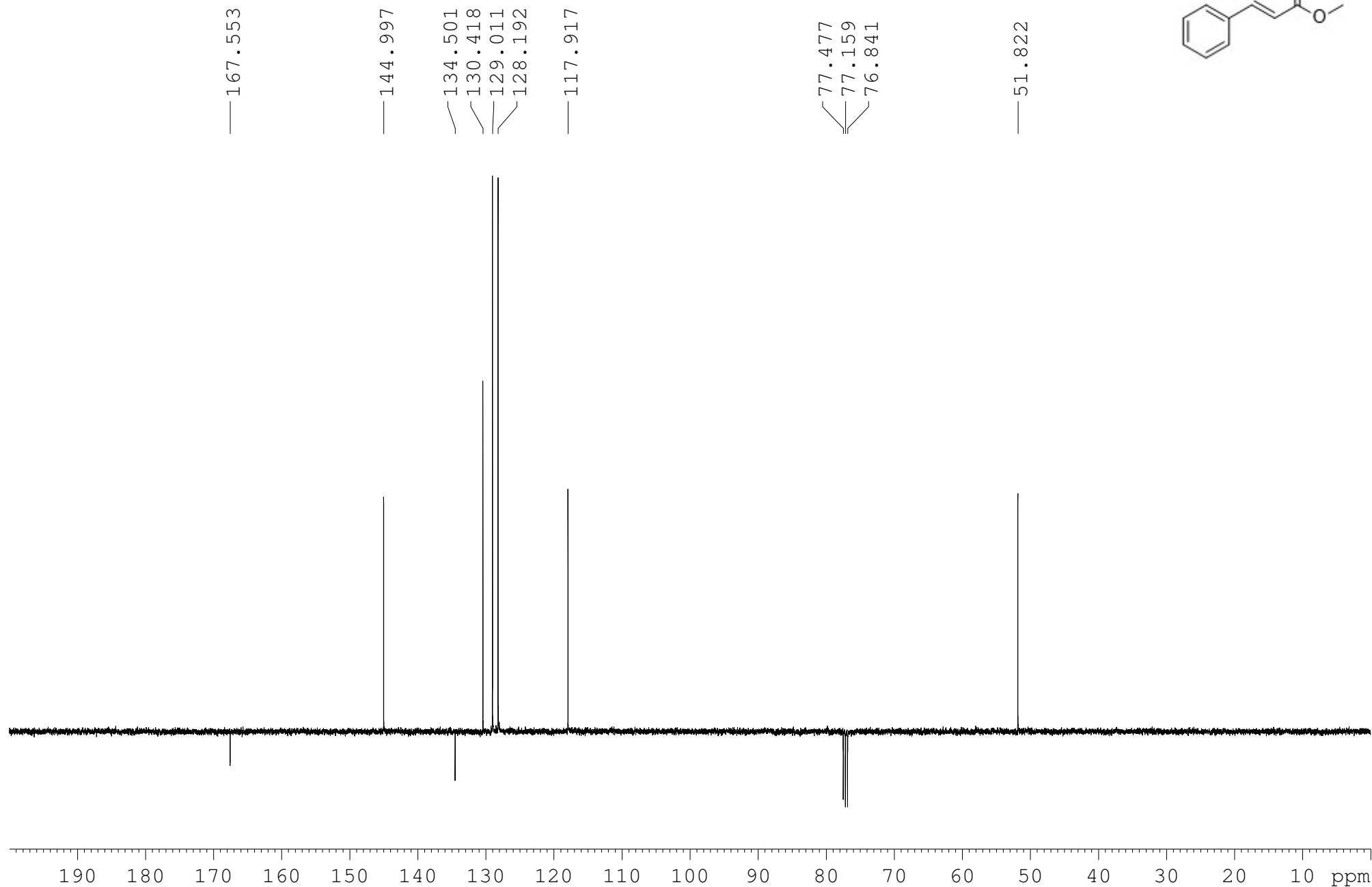
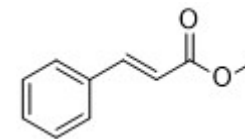
3,3-bis(1H-imidazol-1-yl)propan-1-ol (**3**)



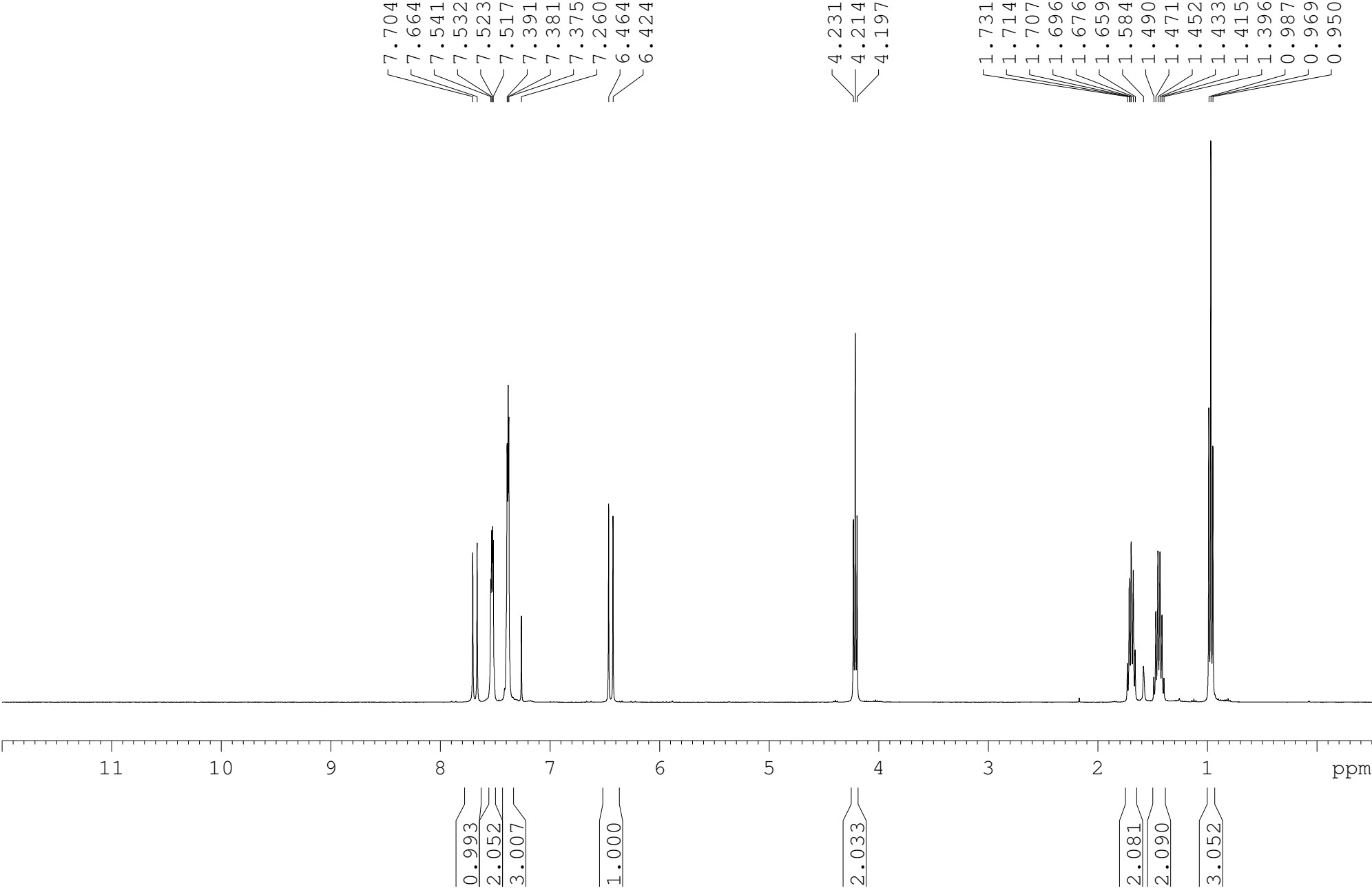
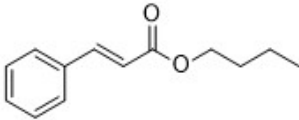
Methyl cinnamate (8aa)



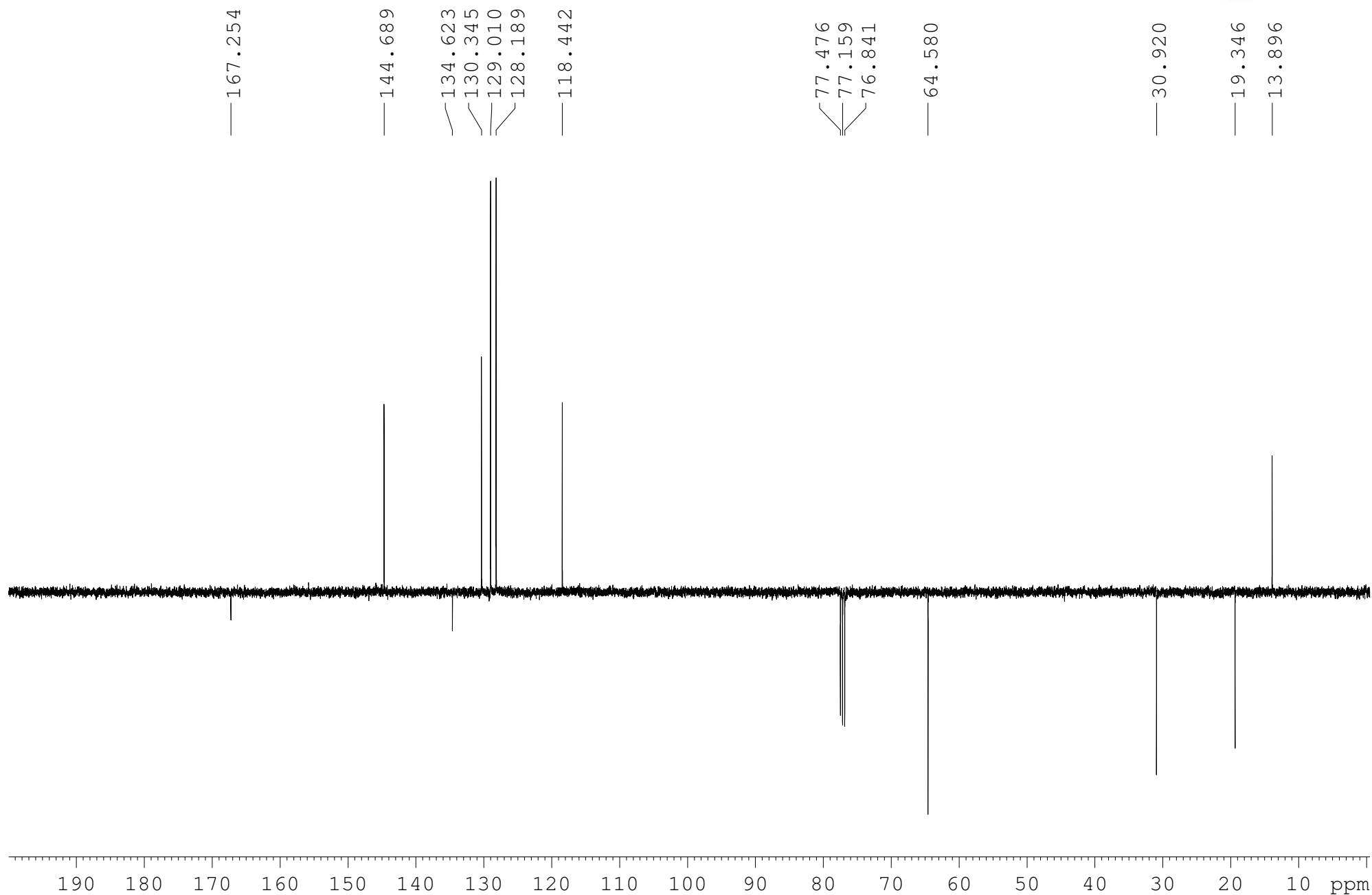
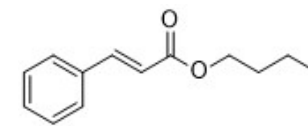
Methyl cinnamate (8aa)



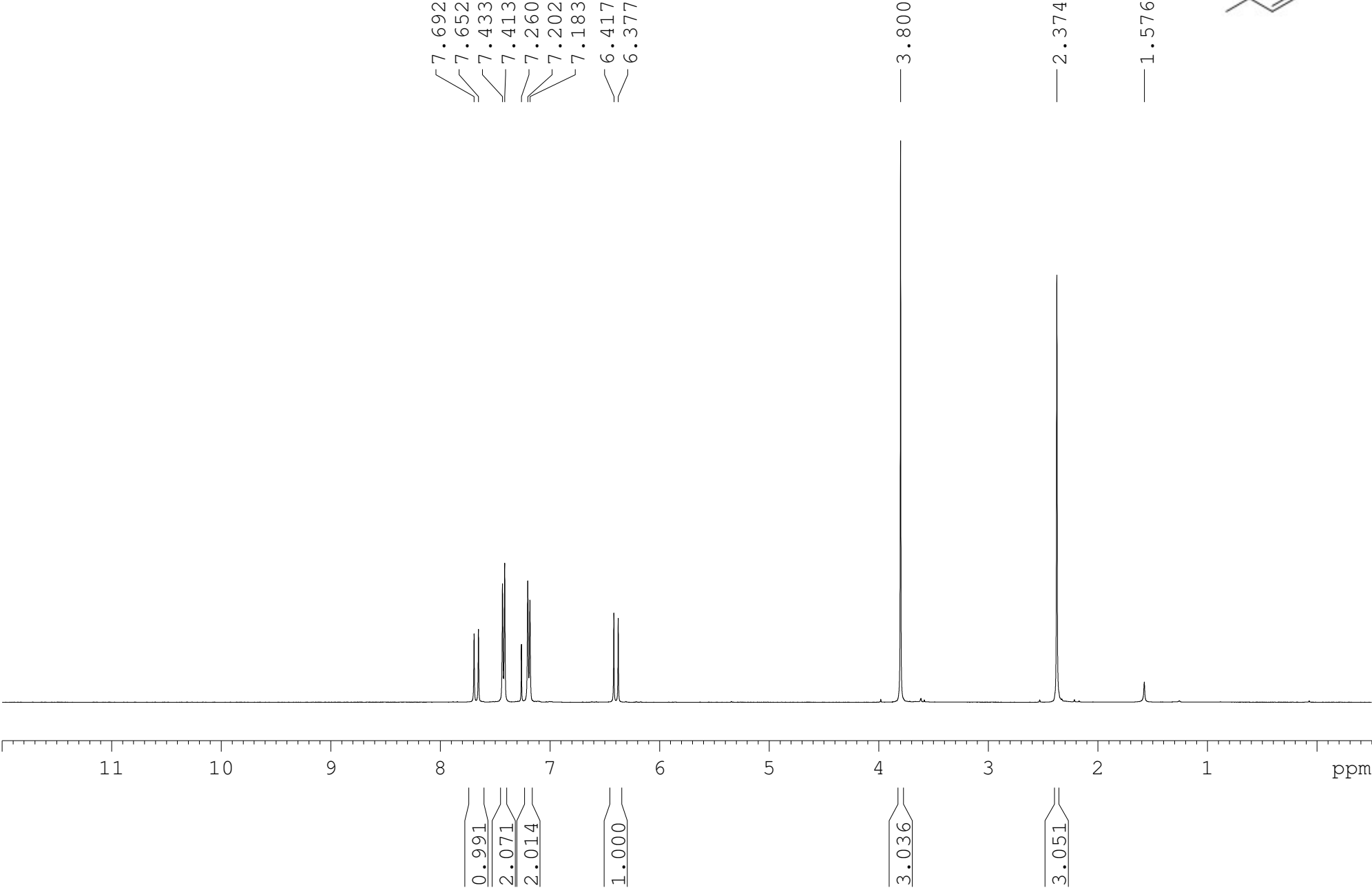
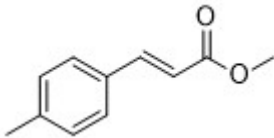
Butyl cinnamate (8ab)



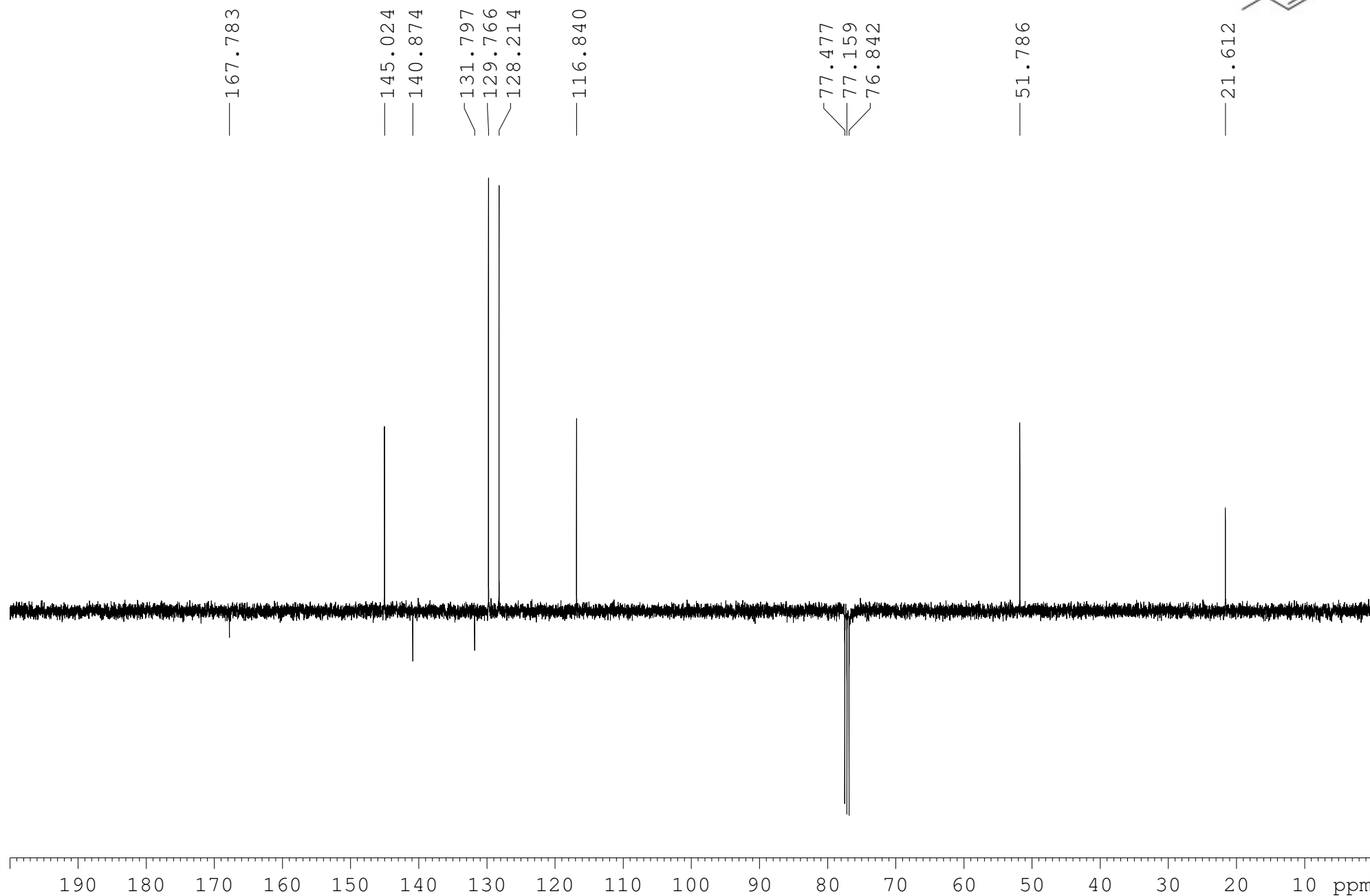
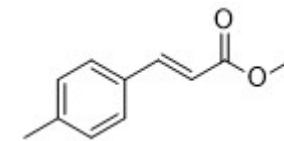
Butyl cinnamate (**8ab**)



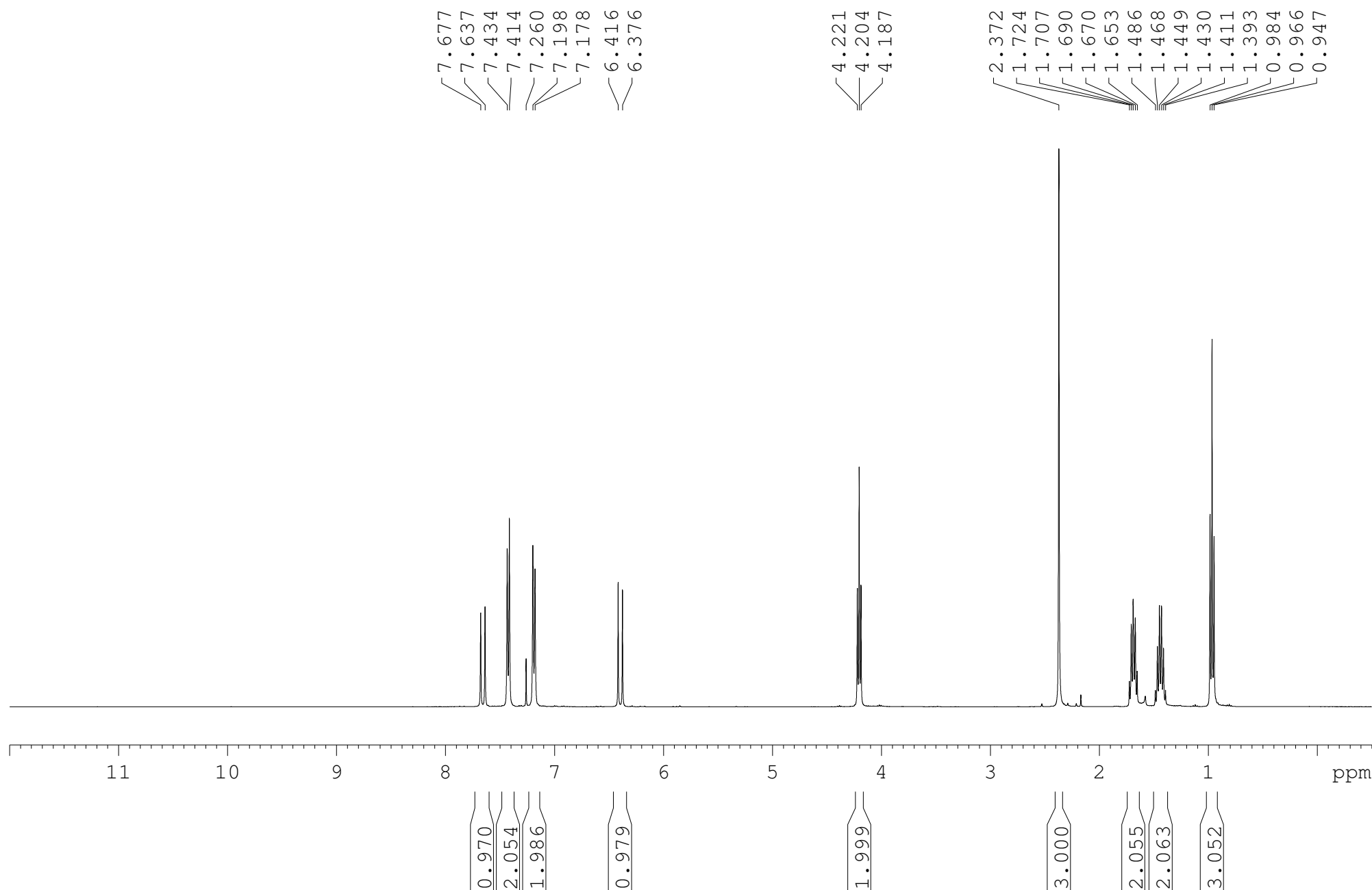
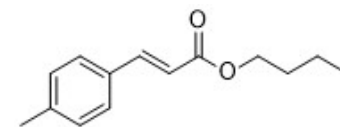
Methyl (E)-3-(p-tolyl)acrylate (**8ba**)



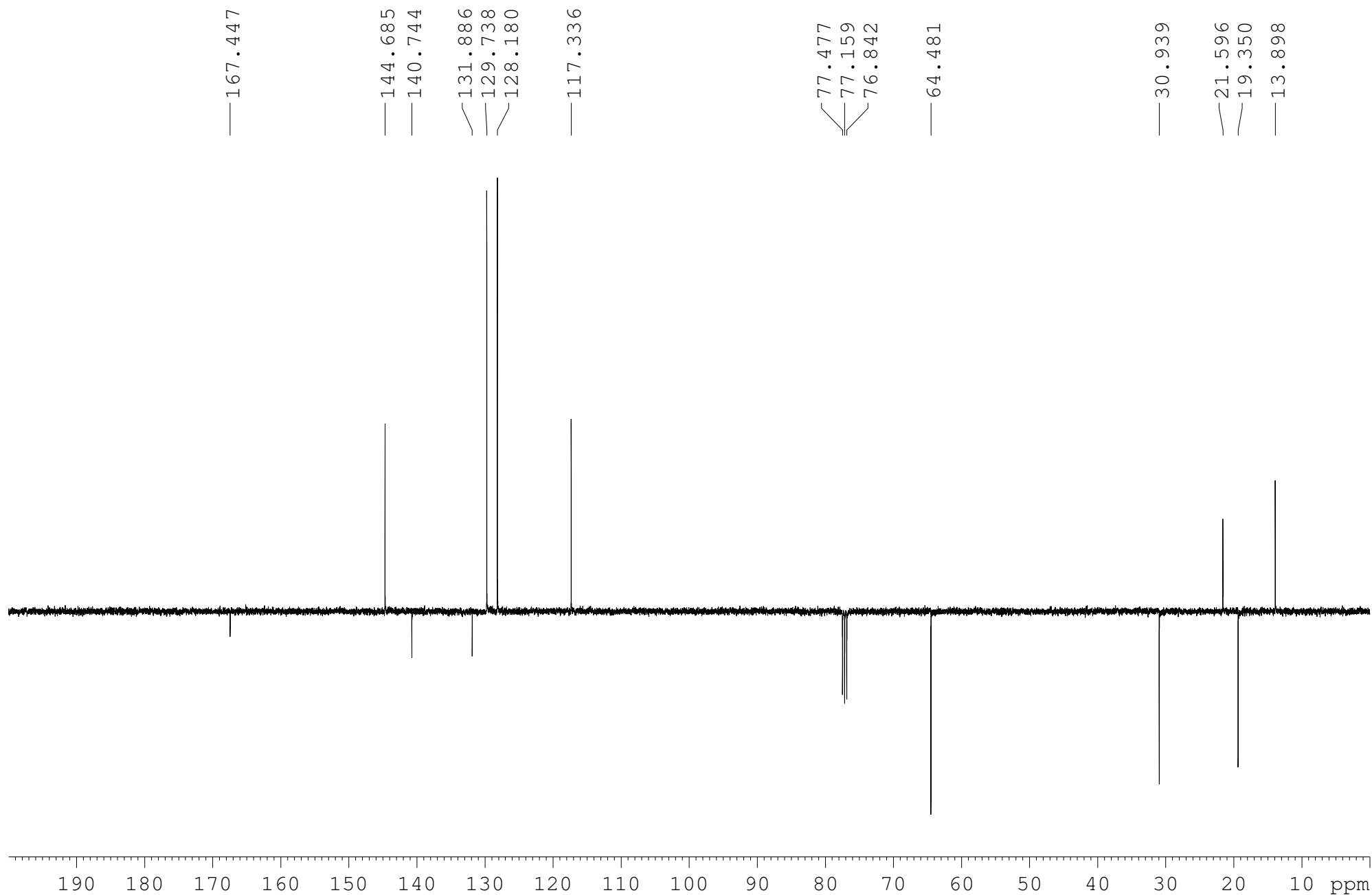
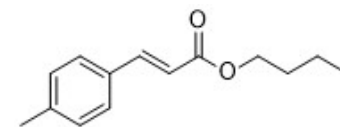
Methyl (E)-3-(p-tolyl)acrylate (**8ba**)



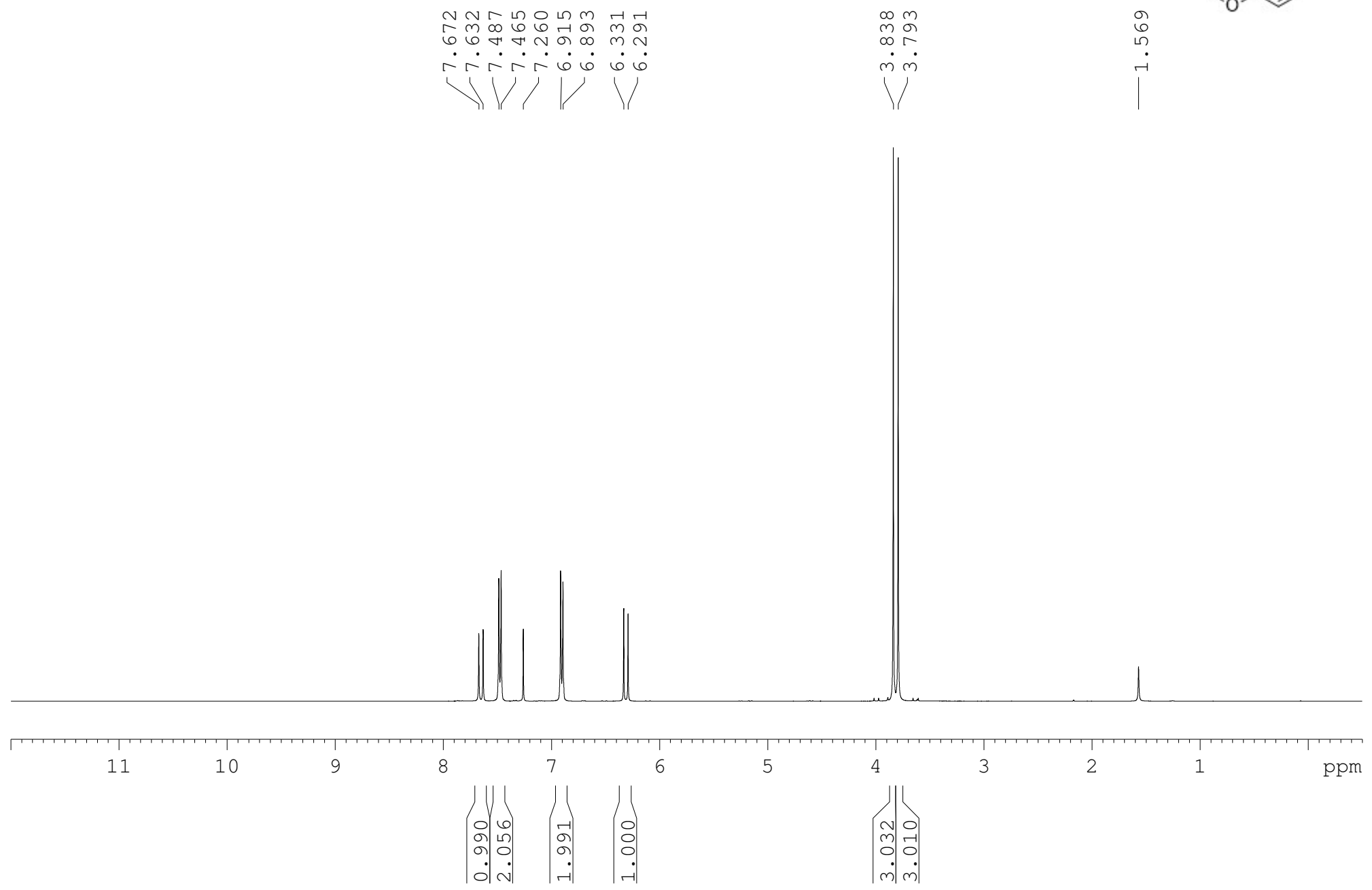
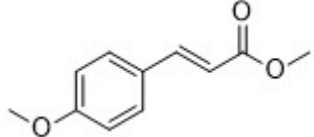
Butyl (E)-3-(p-tolyl)acrylate (**8bb**)



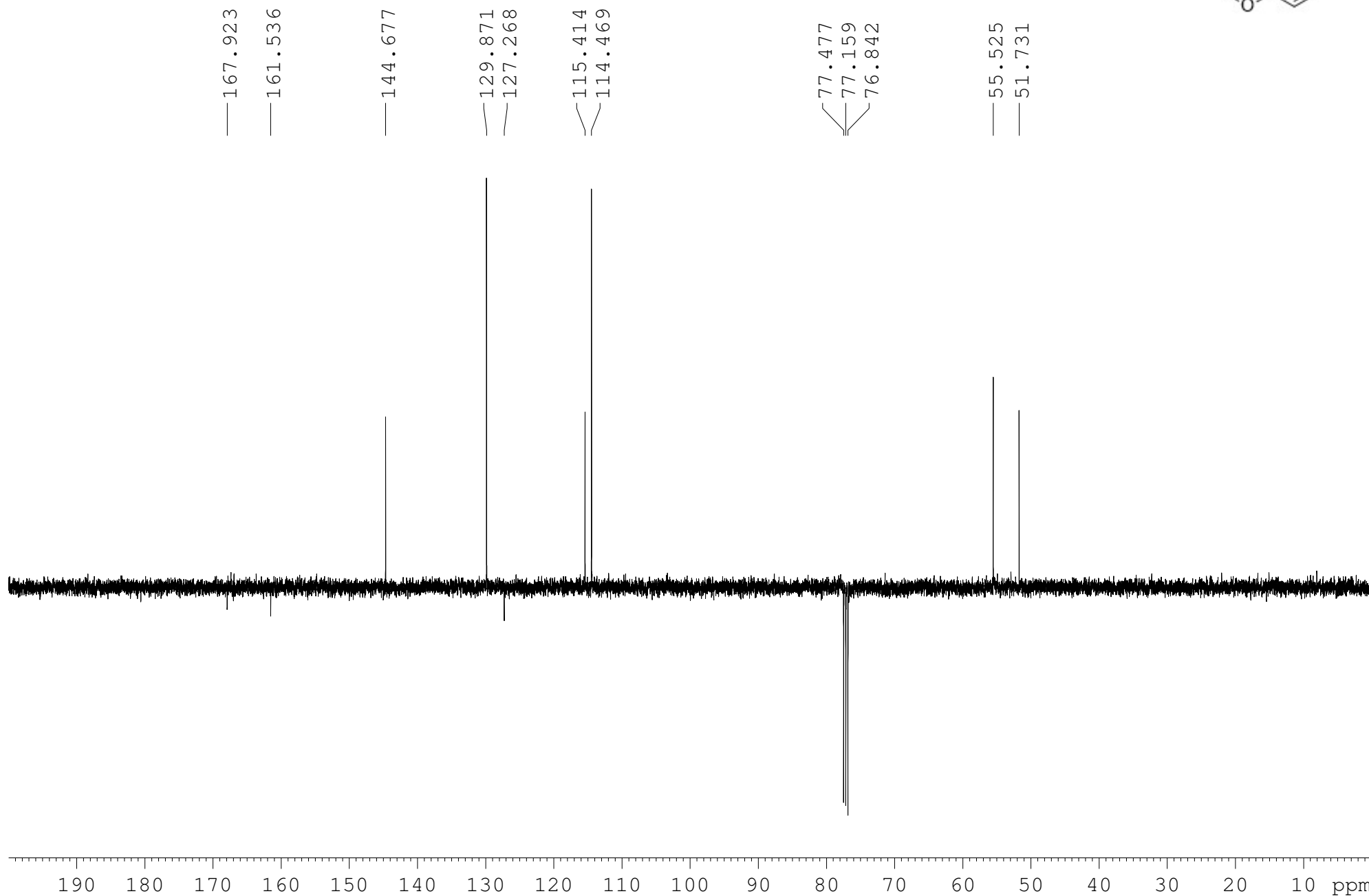
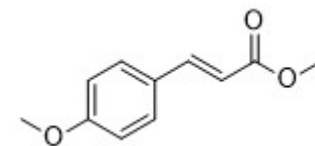
Butyl (E)-3-(p-tolyl)acrylate (**8bb**)



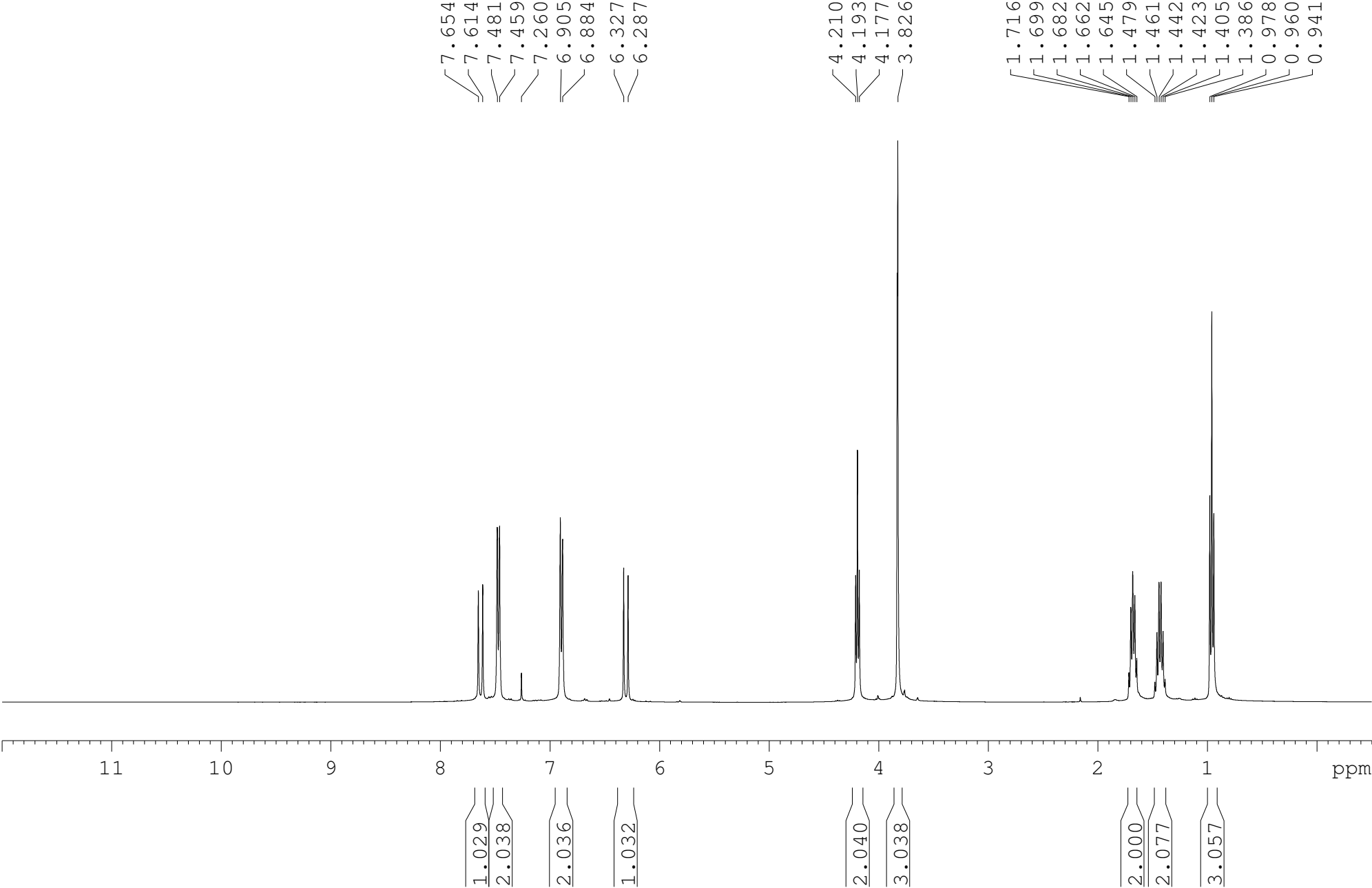
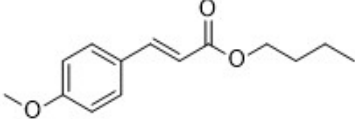
Methyl (E)-3-(4-methoxyphenyl)acrylate (**8ca**)



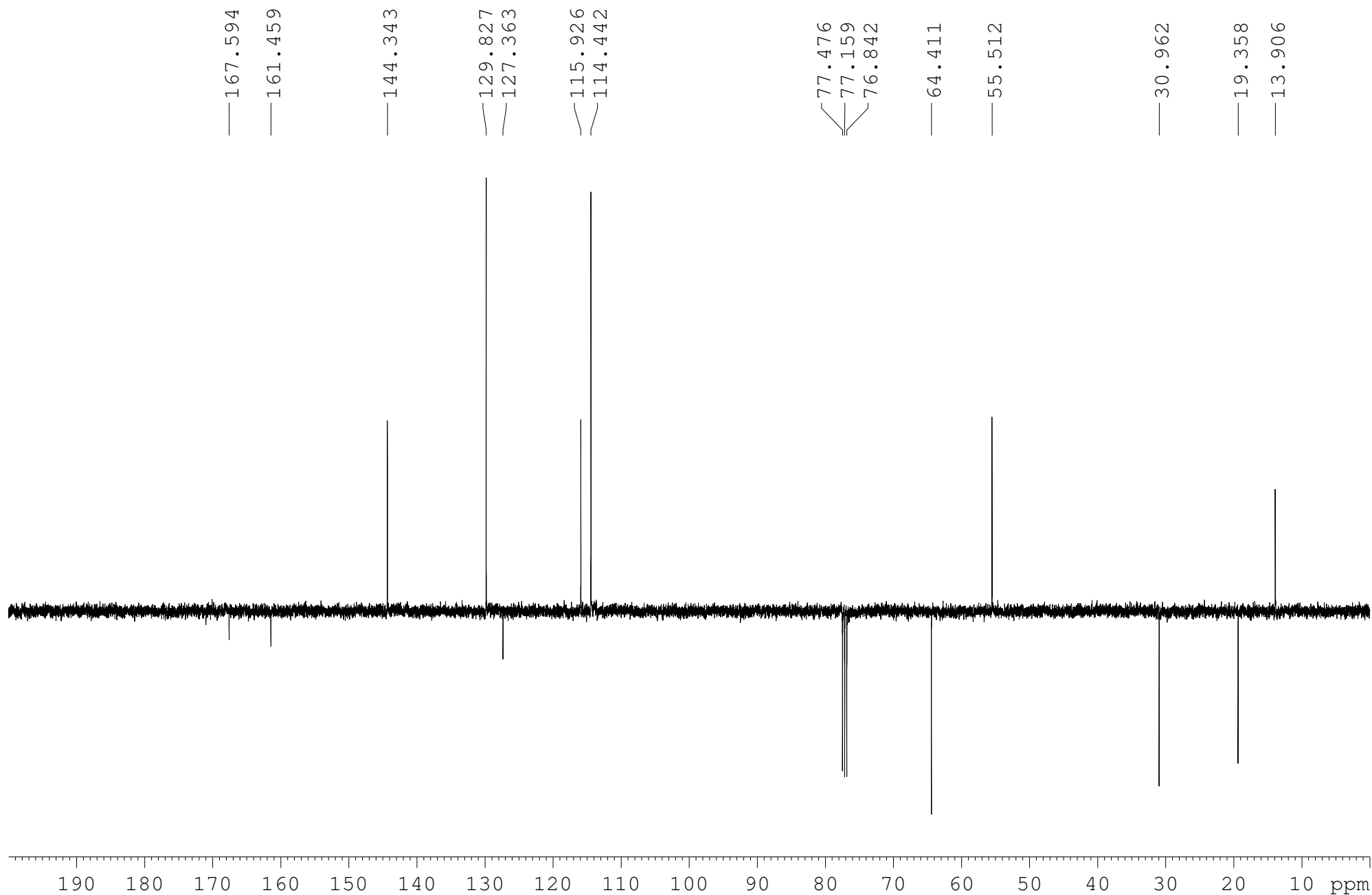
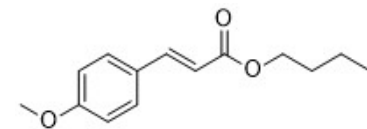
Methyl (E)-3-(4-methoxyphenyl)acrylate (**8ca**)



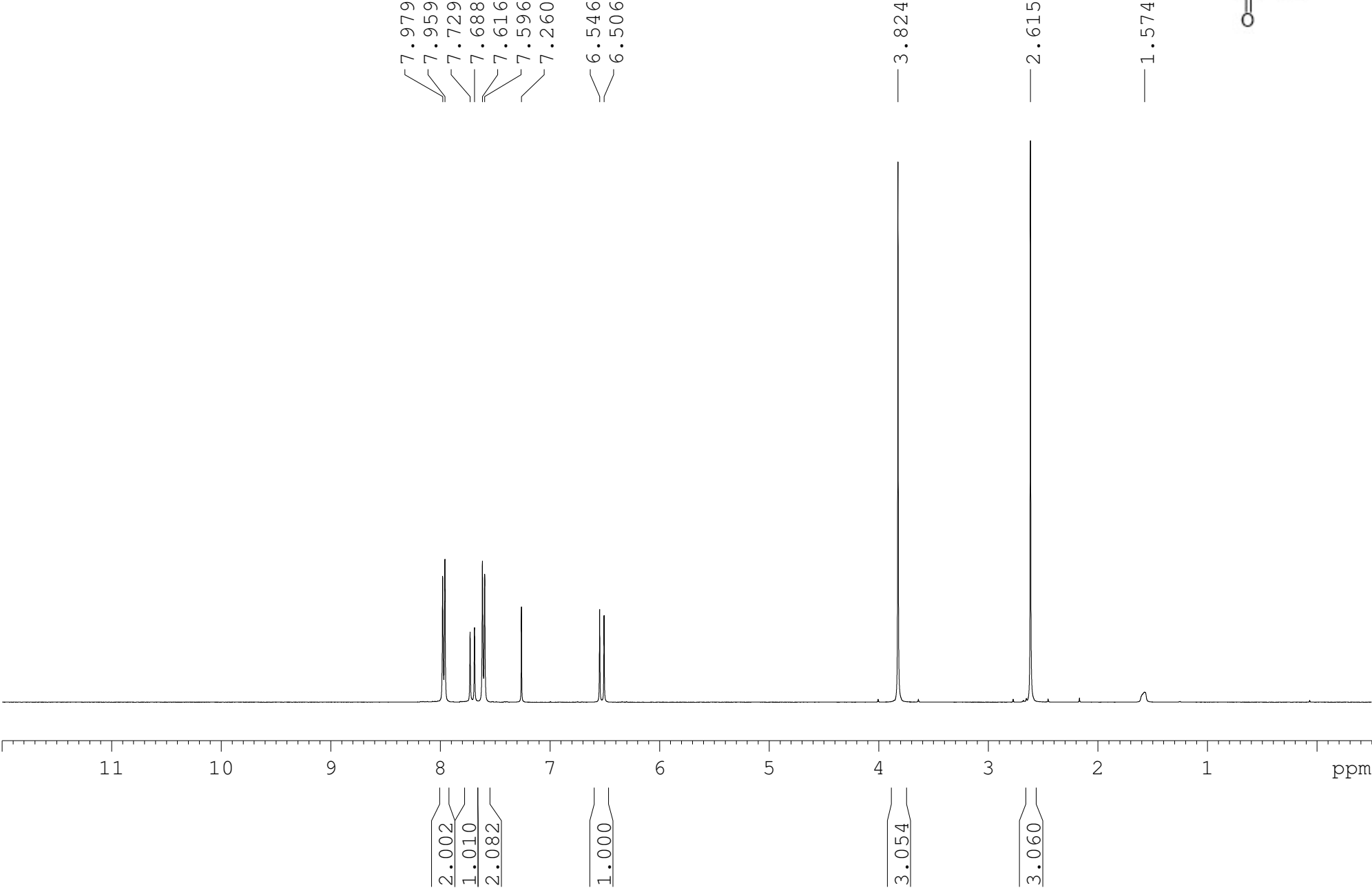
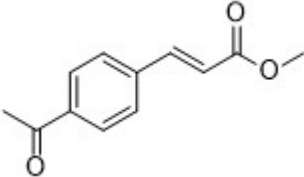
Butyl (E)-3-(4-methoxyphenyl)acrylate (**8cb**)



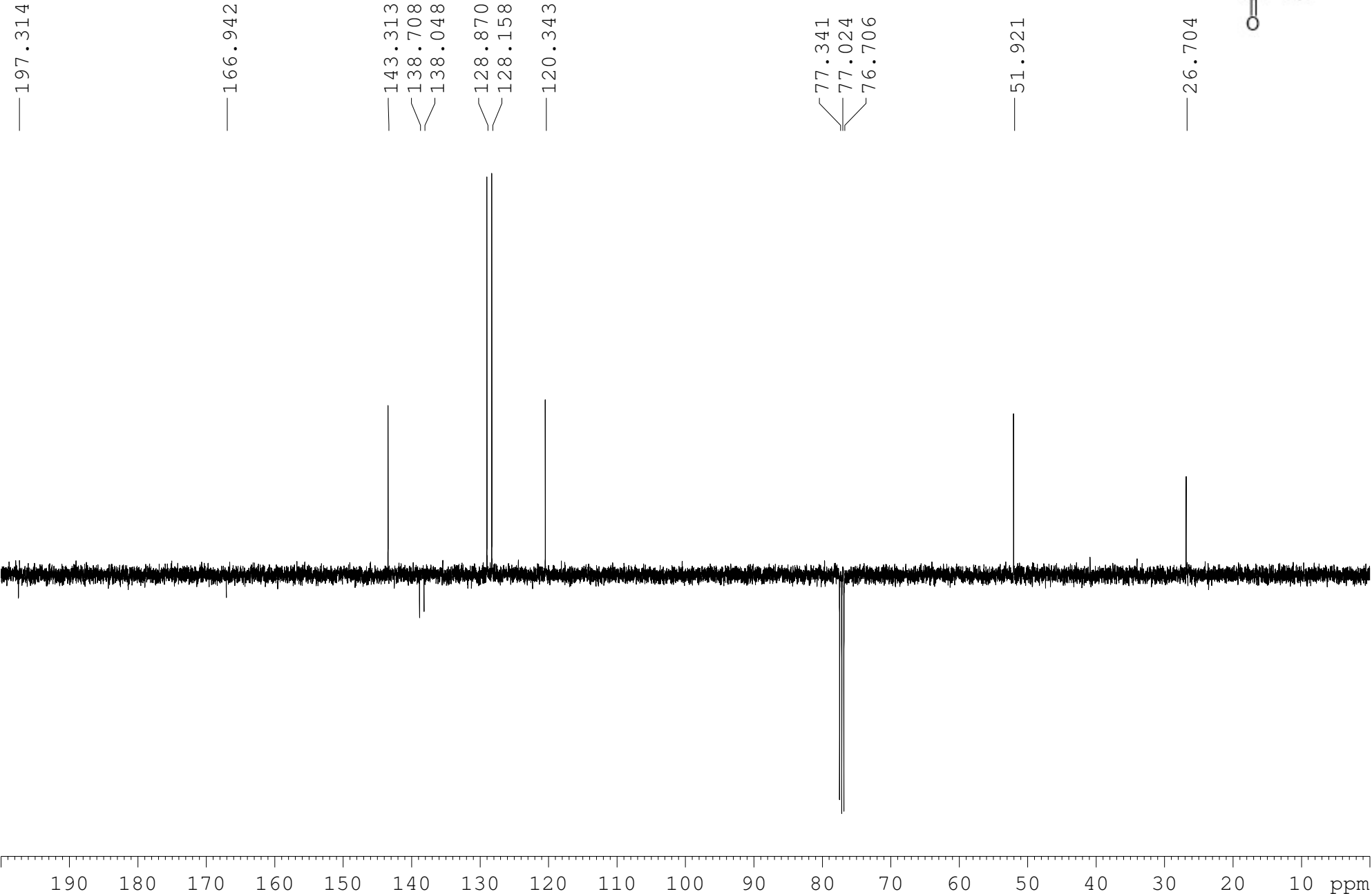
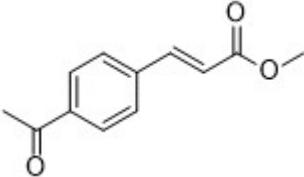
Butyl (E)-3-(4-methoxyphenyl)acrylate (**8cb**)



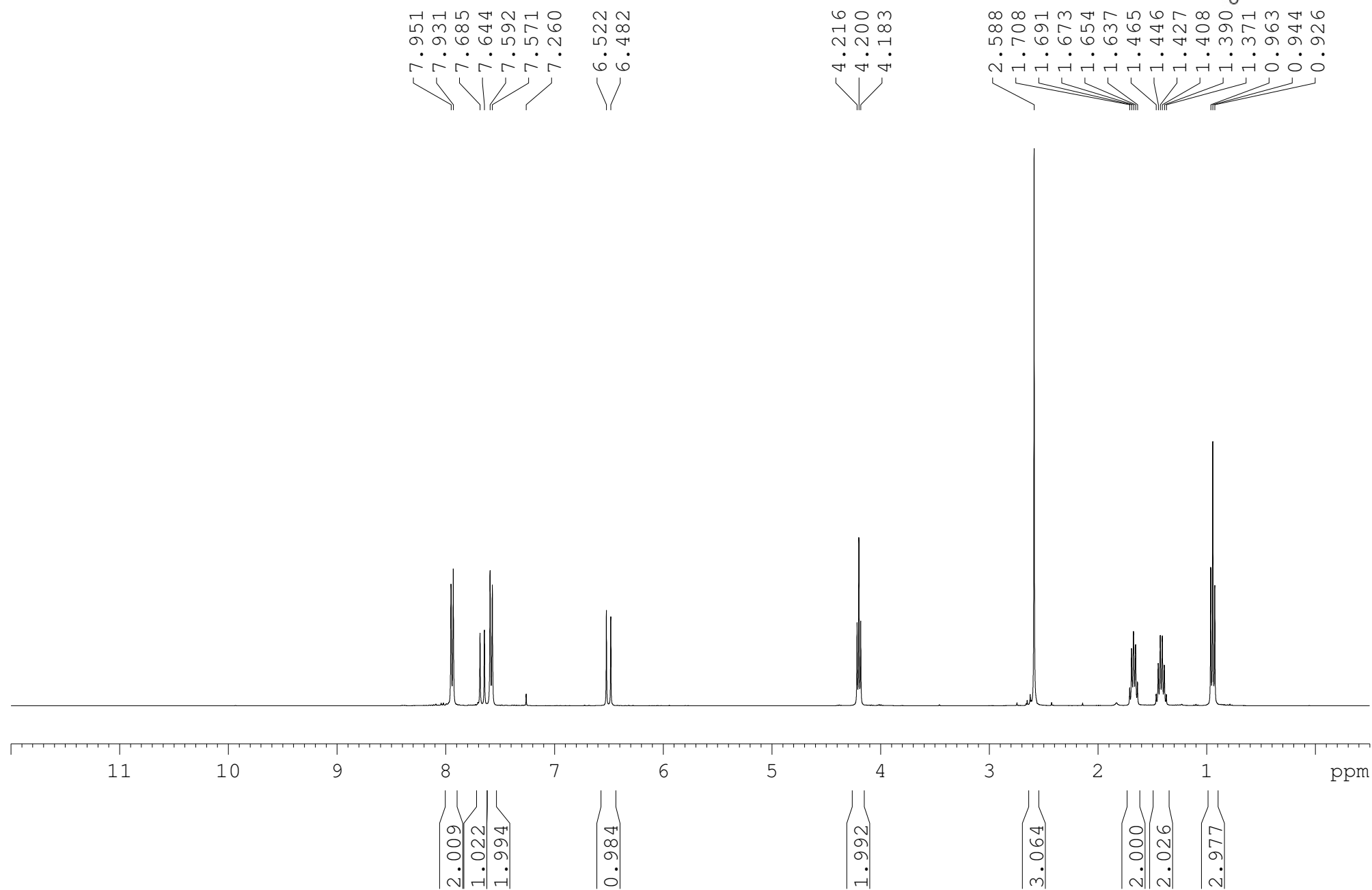
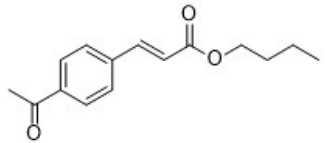
Methyl (E)-3-(4-acetylphenyl)acrylate (**8da**)



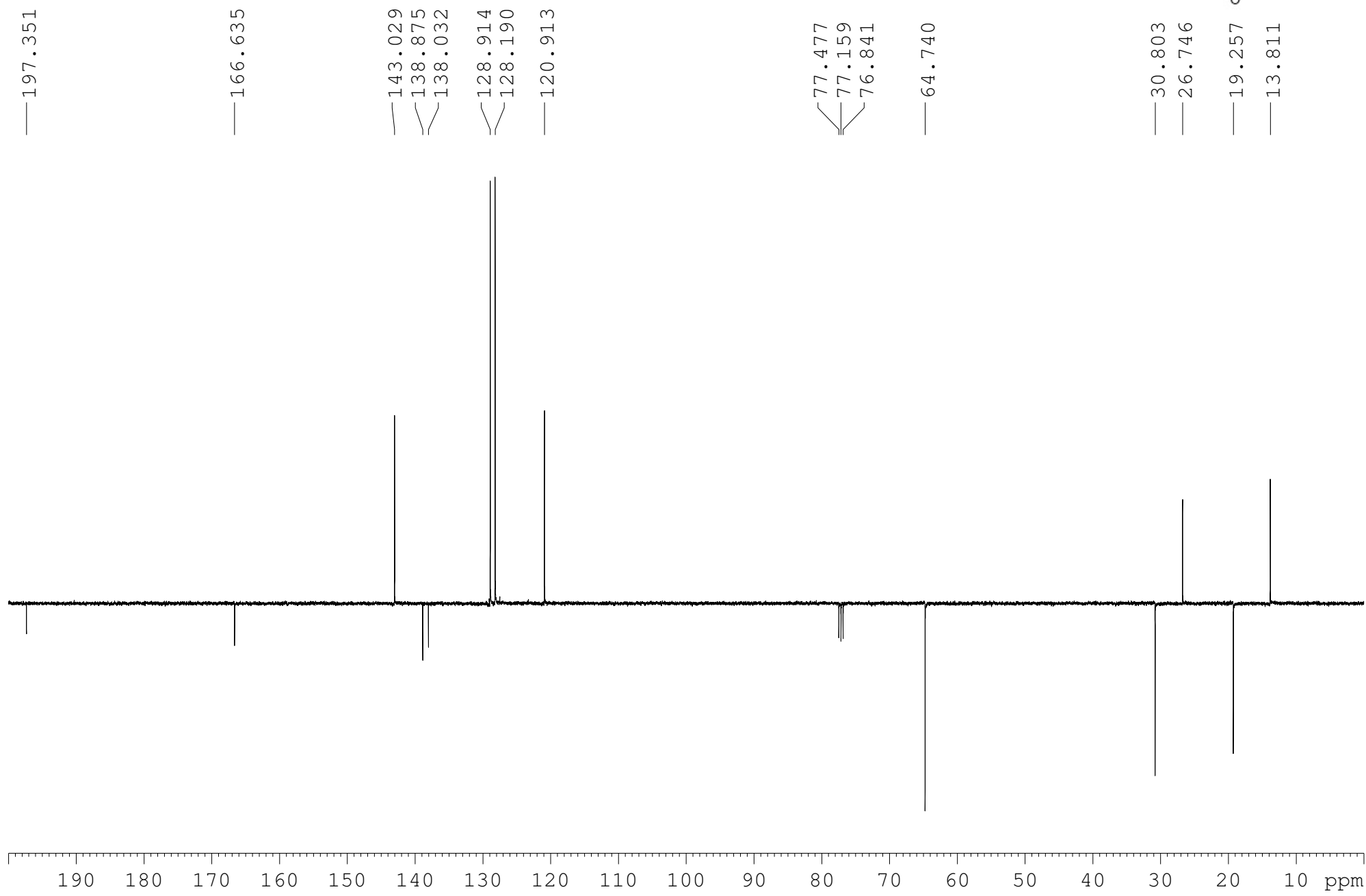
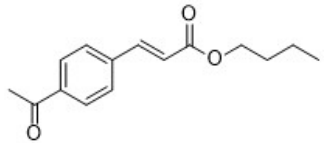
Methyl (E)-3-(4-acetylphenyl)acrylate (**8da**)



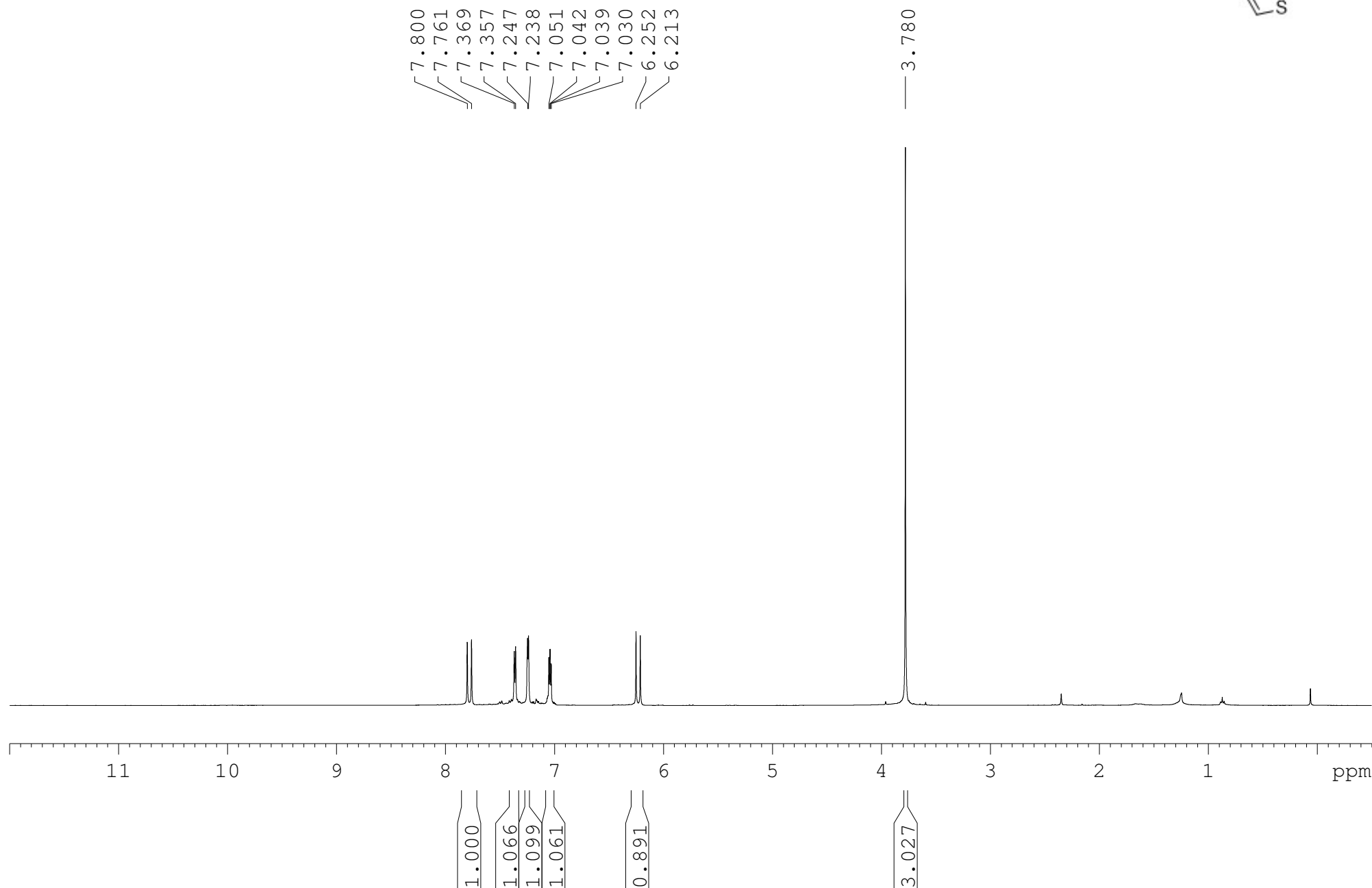
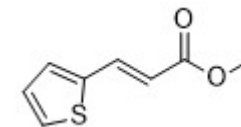
Butyl (E)-3-(4-acetylphenyl)acrylate (**8db**)



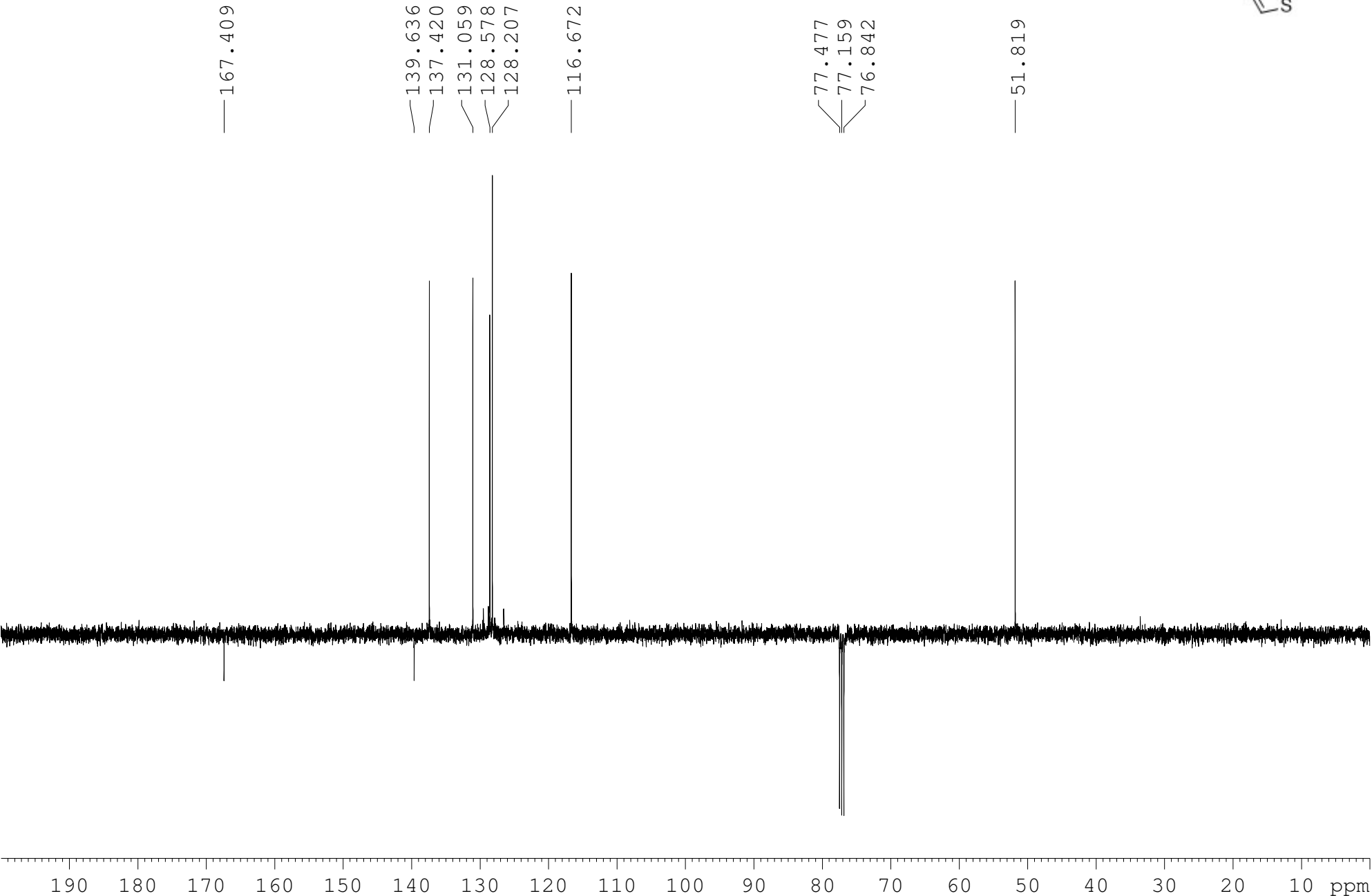
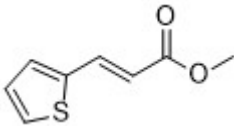
Butyl (E)-3-(4-acetylphenyl)acrylate (**8db**)



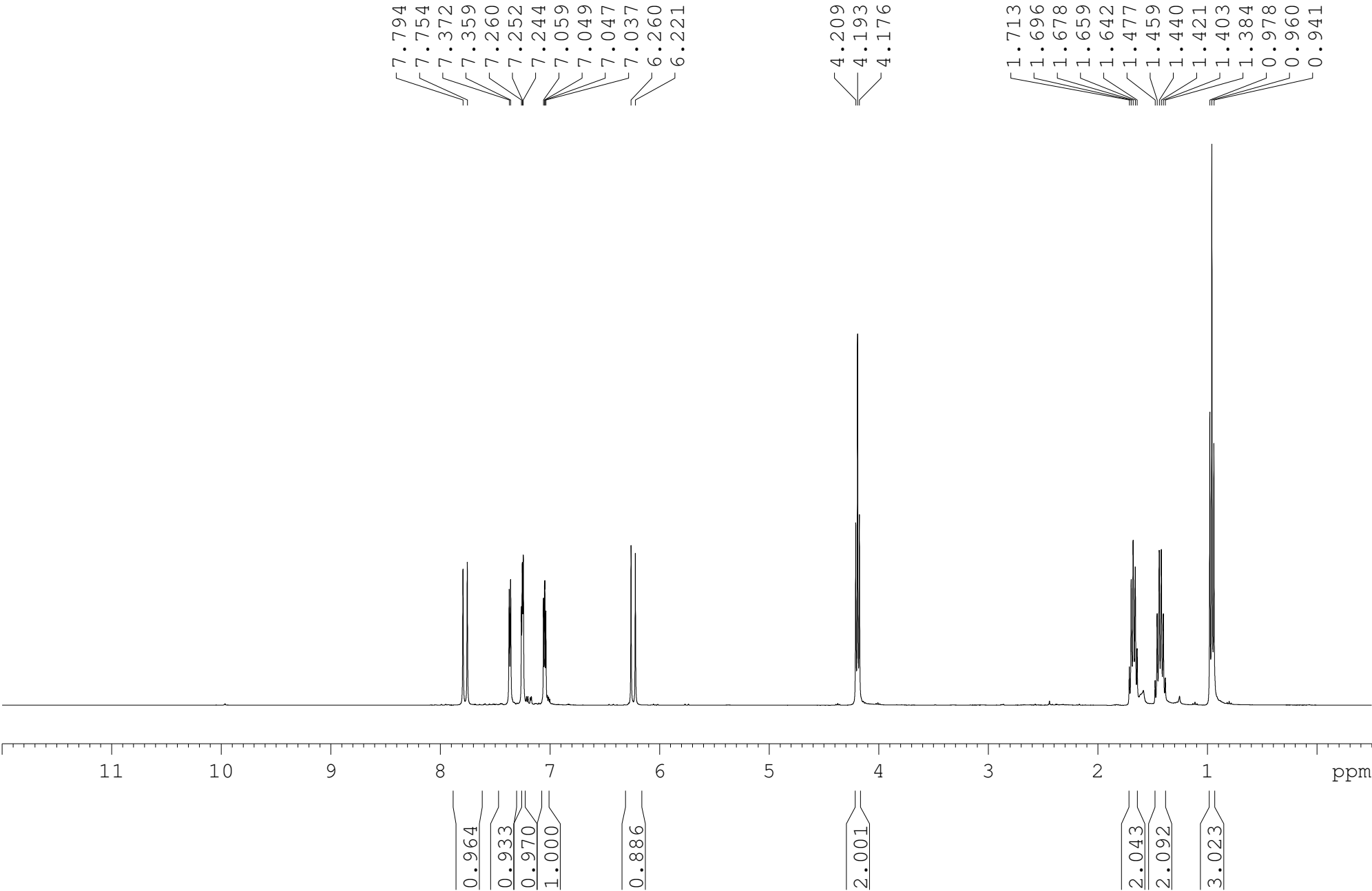
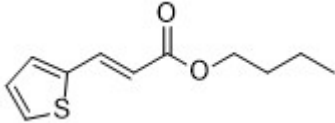
Methyl (E)-3-(thiophen-2-yl)acrylate (**8ca**)



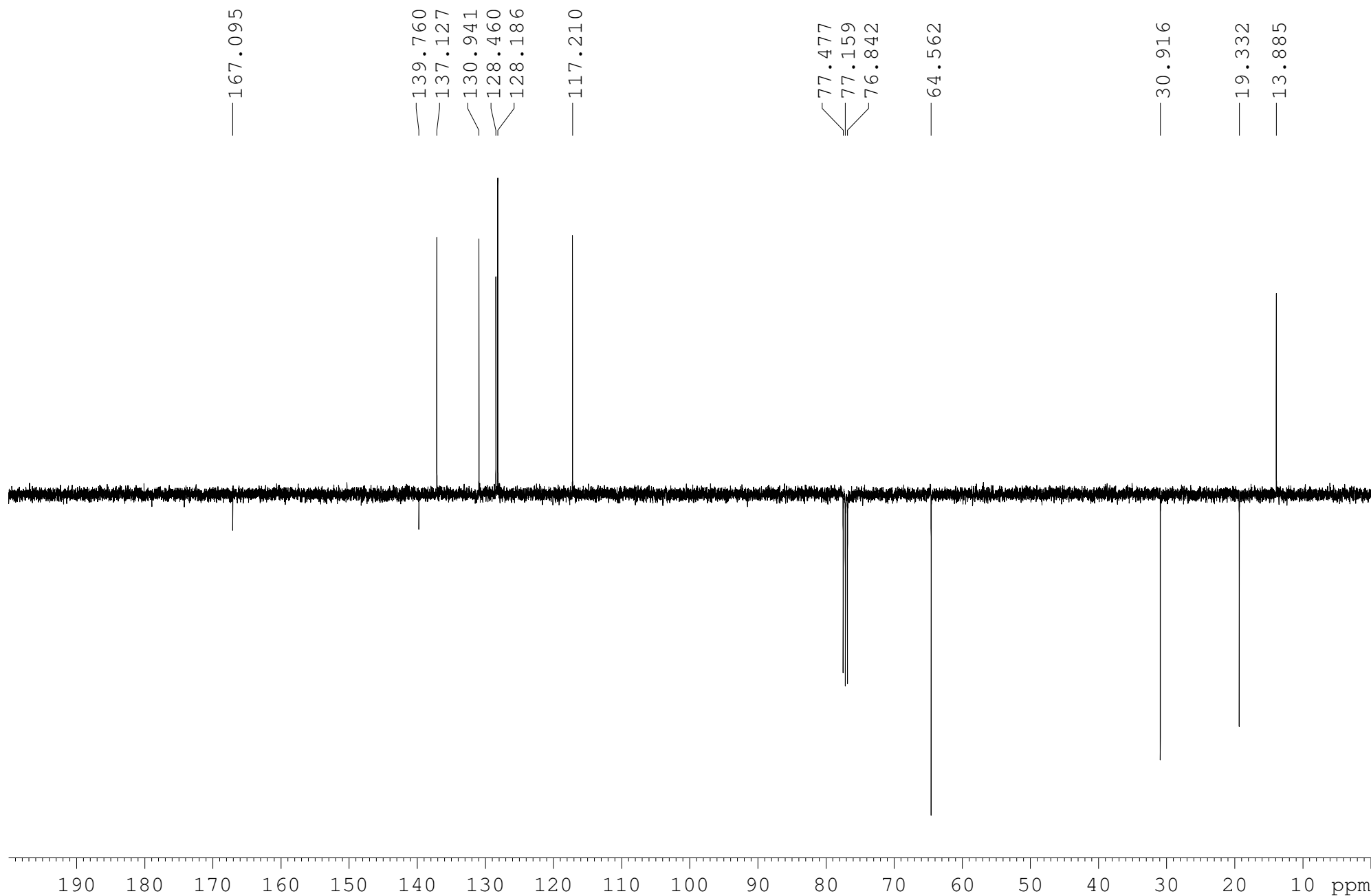
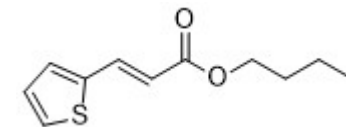
Methyl (E)-3-(thiophen-2-yl)acrylate (**8ca**)



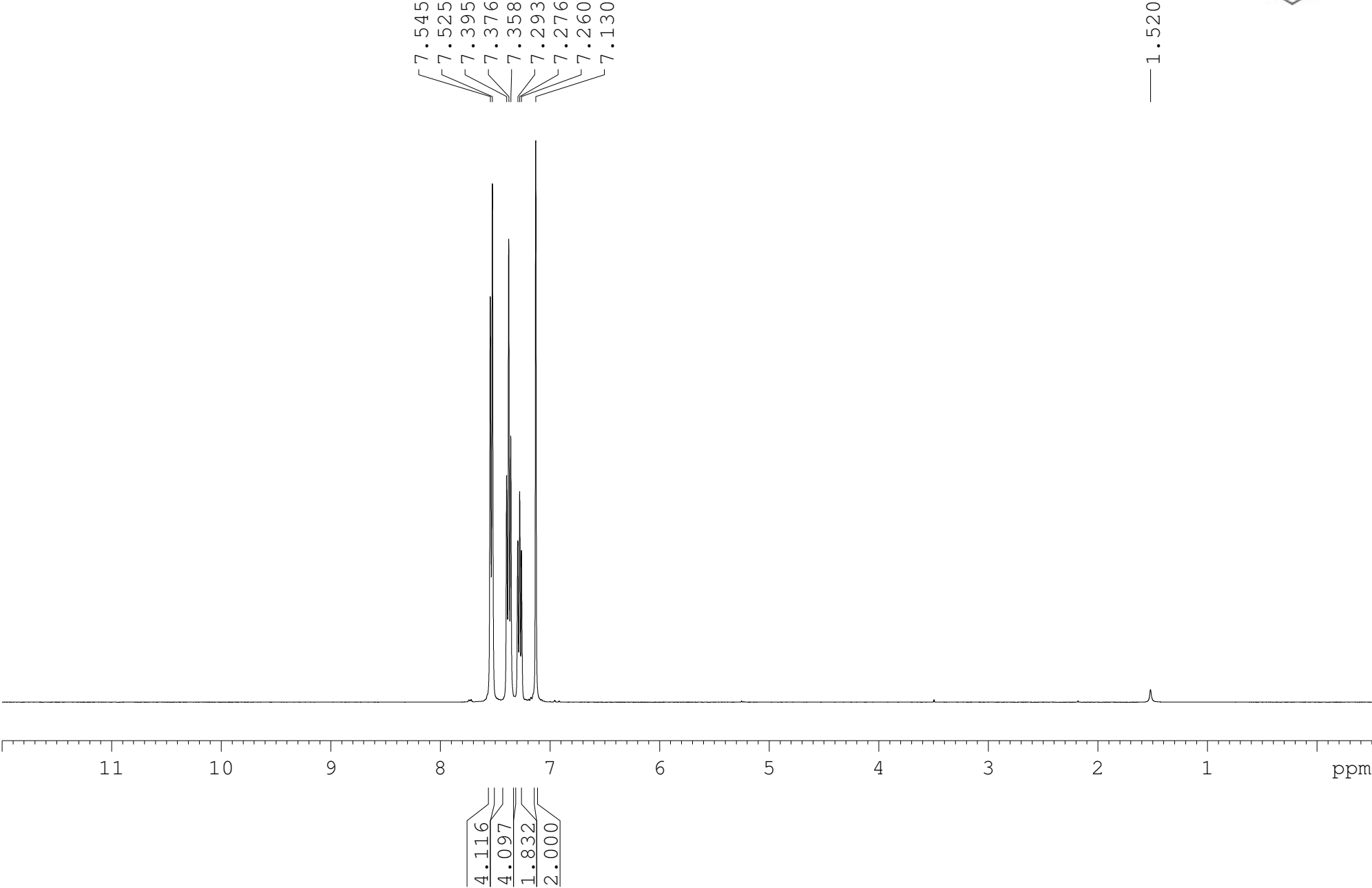
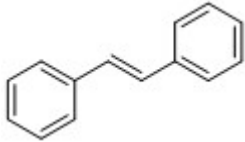
Butyl (E)-3-(thiophen-2-yl)acrylate (**8eb**)



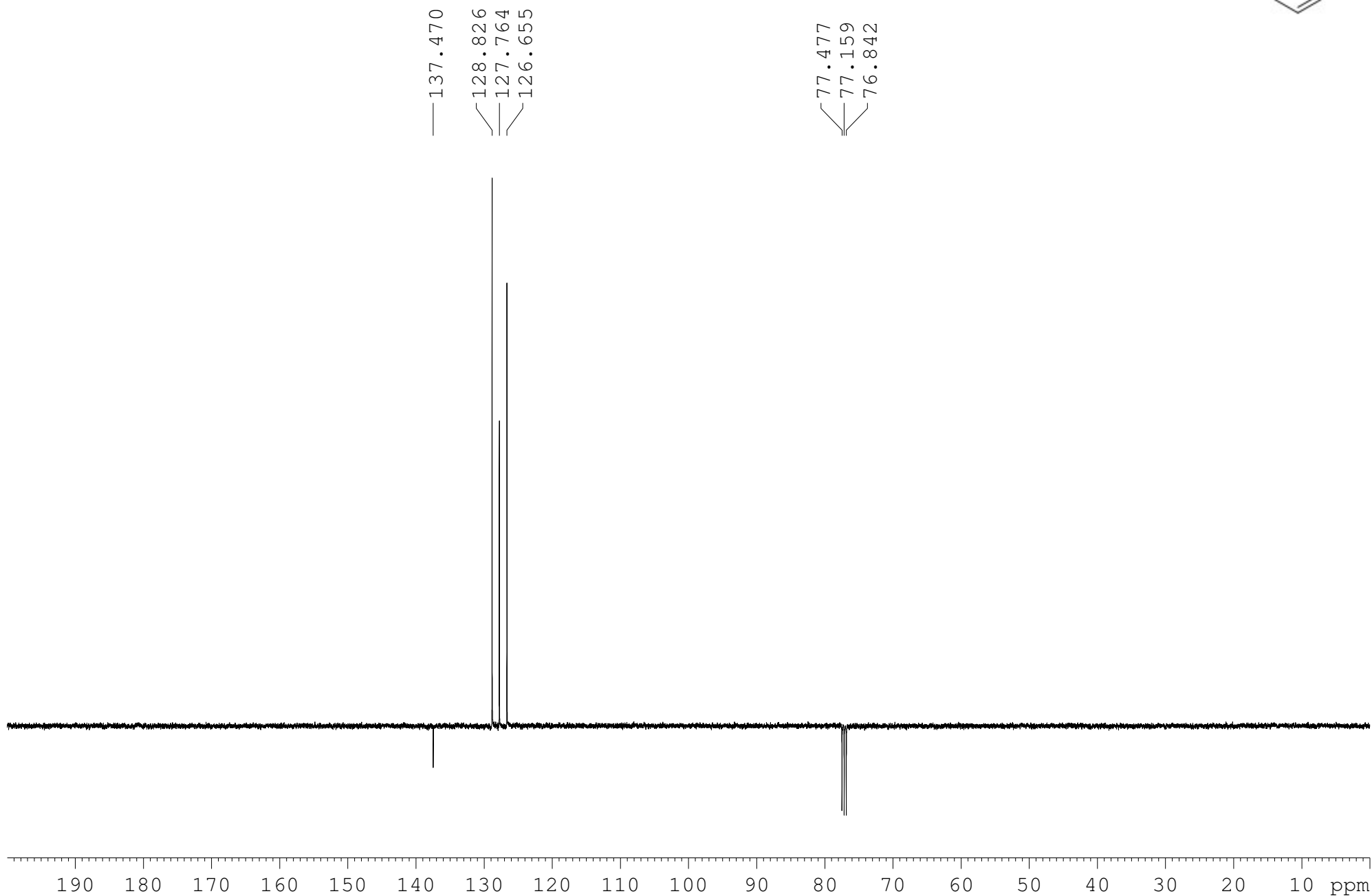
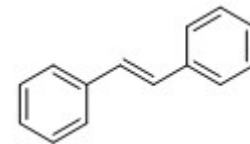
Butyl (E)-3-(thiophen-2-yl)acrylate (**8eb**)



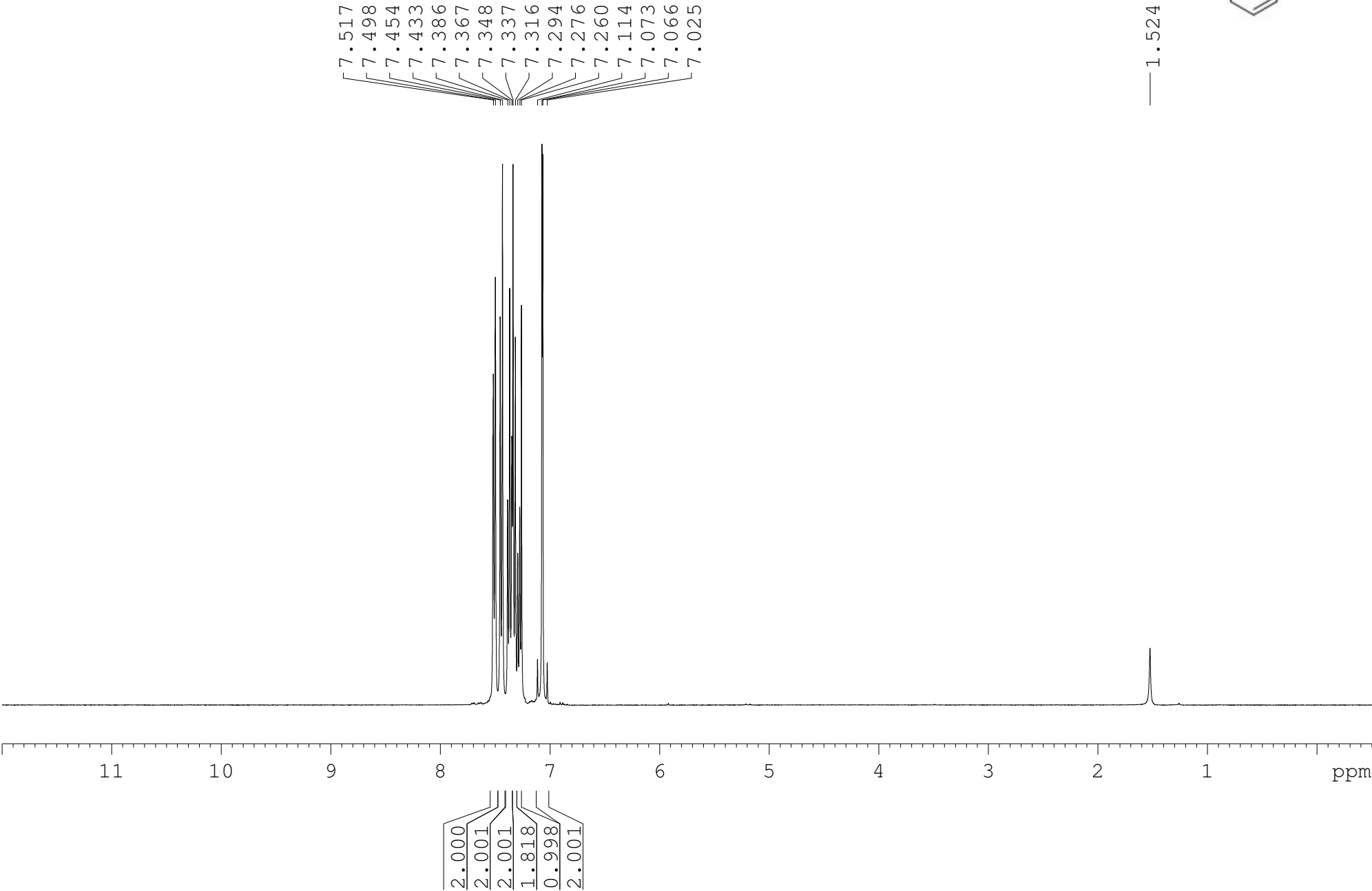
(E)-stylbene (**10aa**)



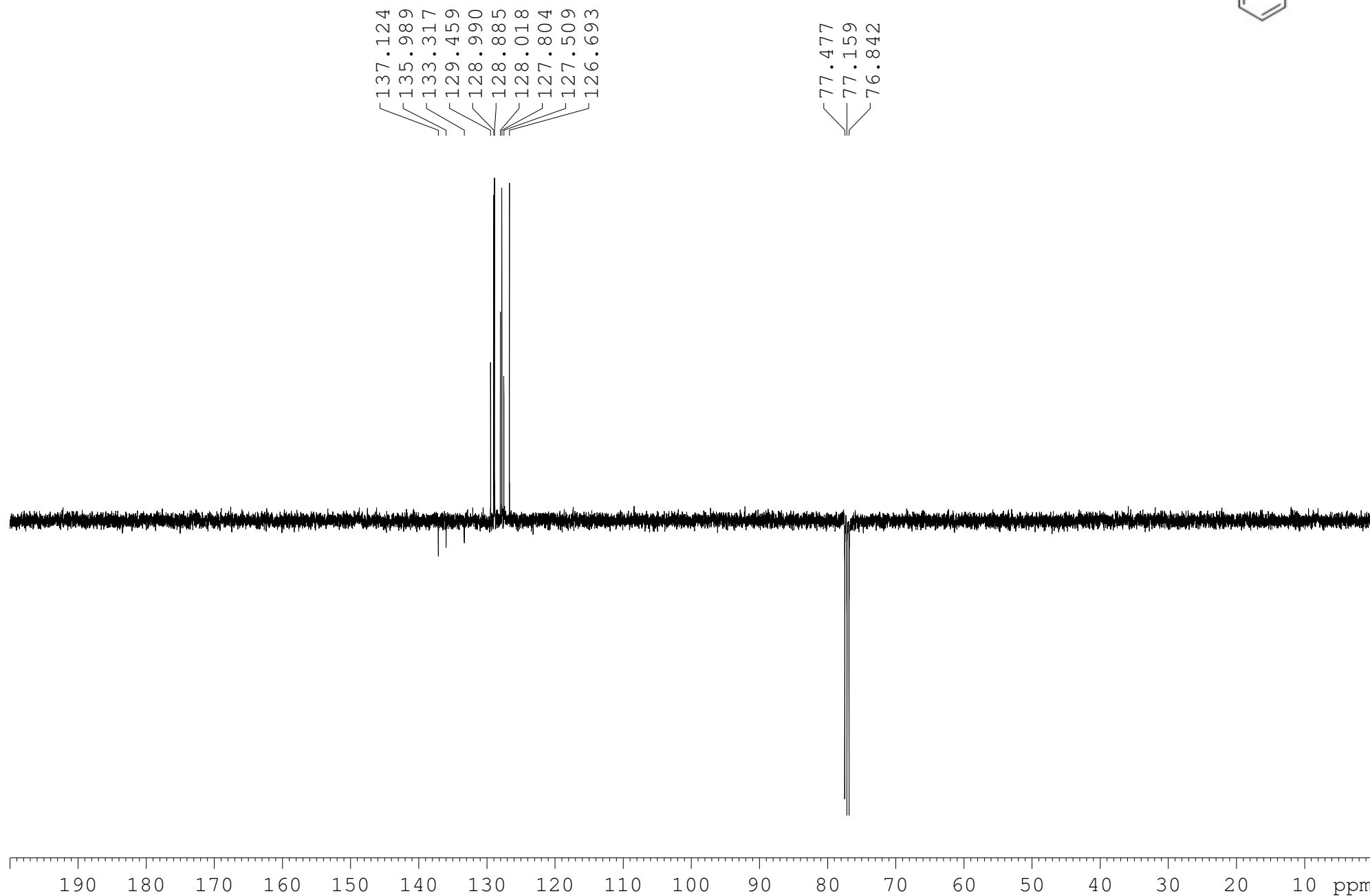
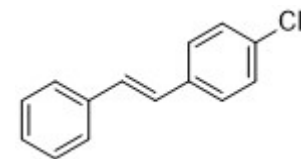
(E)-stylbene (**10aa**)



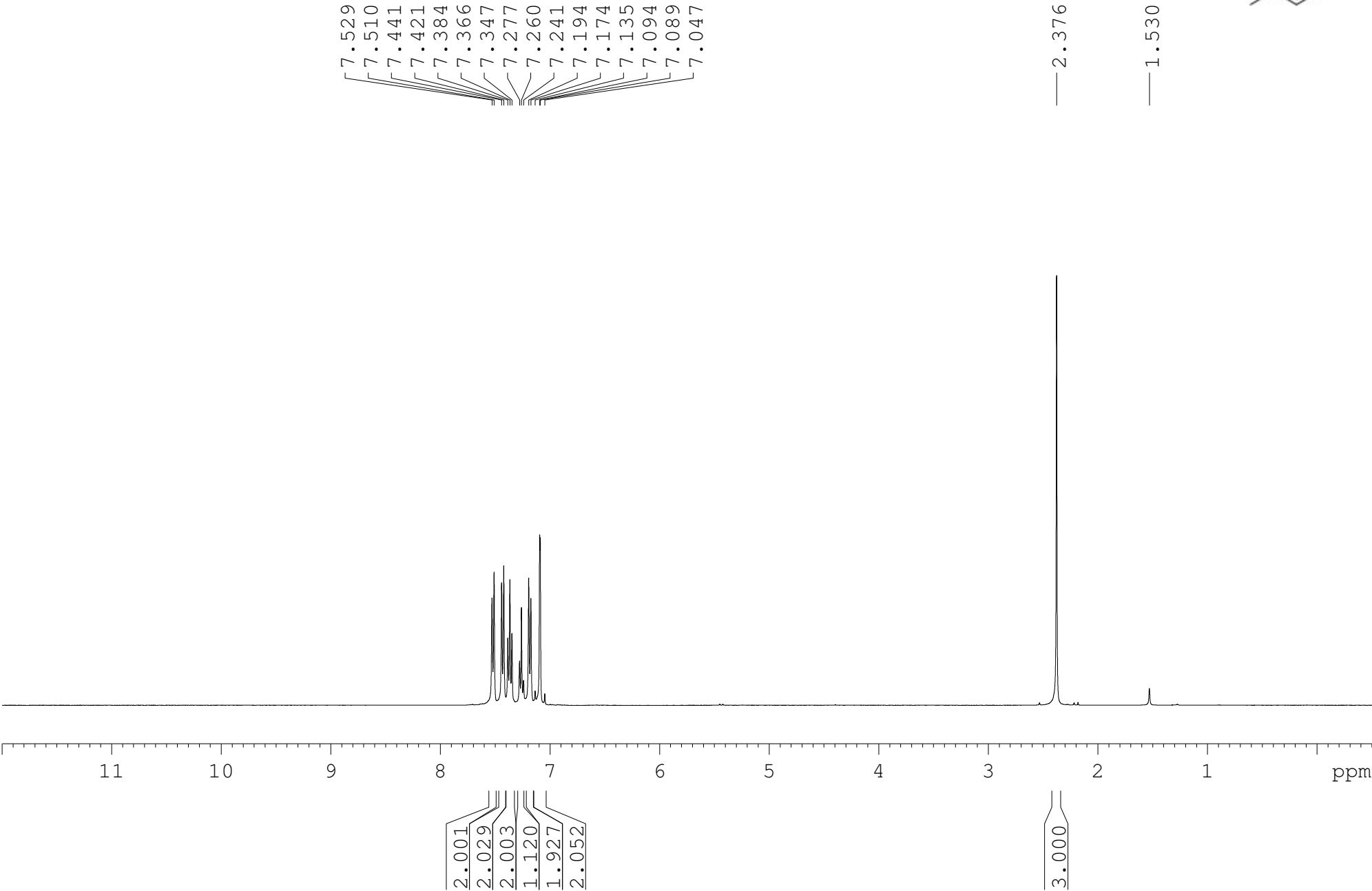
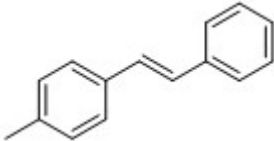
(E)-1-chloro-4-styrylbenzene (**10ab**)



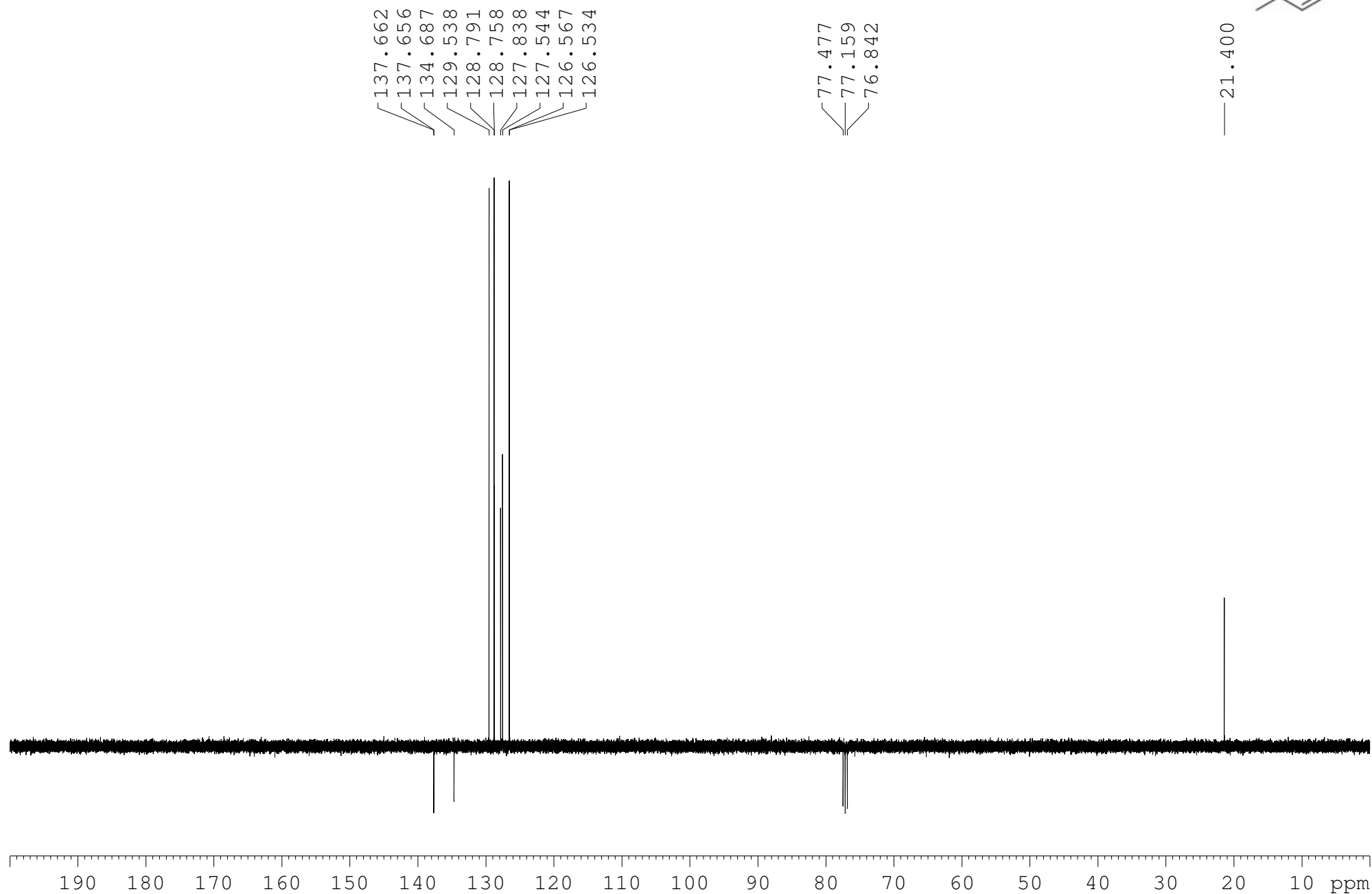
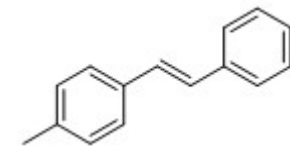
(E)-1-chloro-4-styrylbenzene (**10ab**)



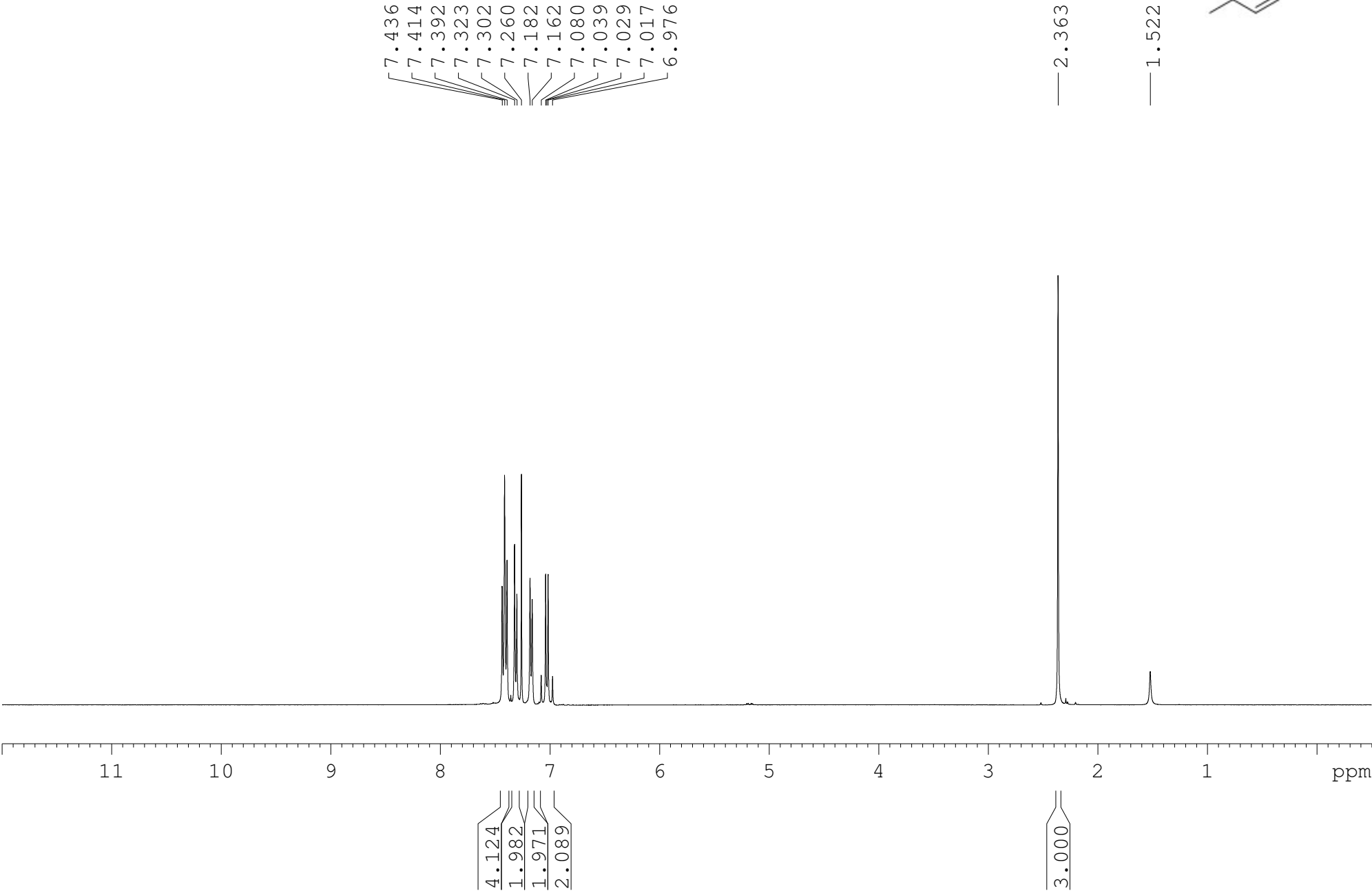
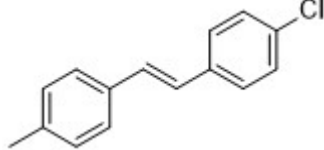
(E)-1-methyl-4-styrylbenzene (**10ba**)



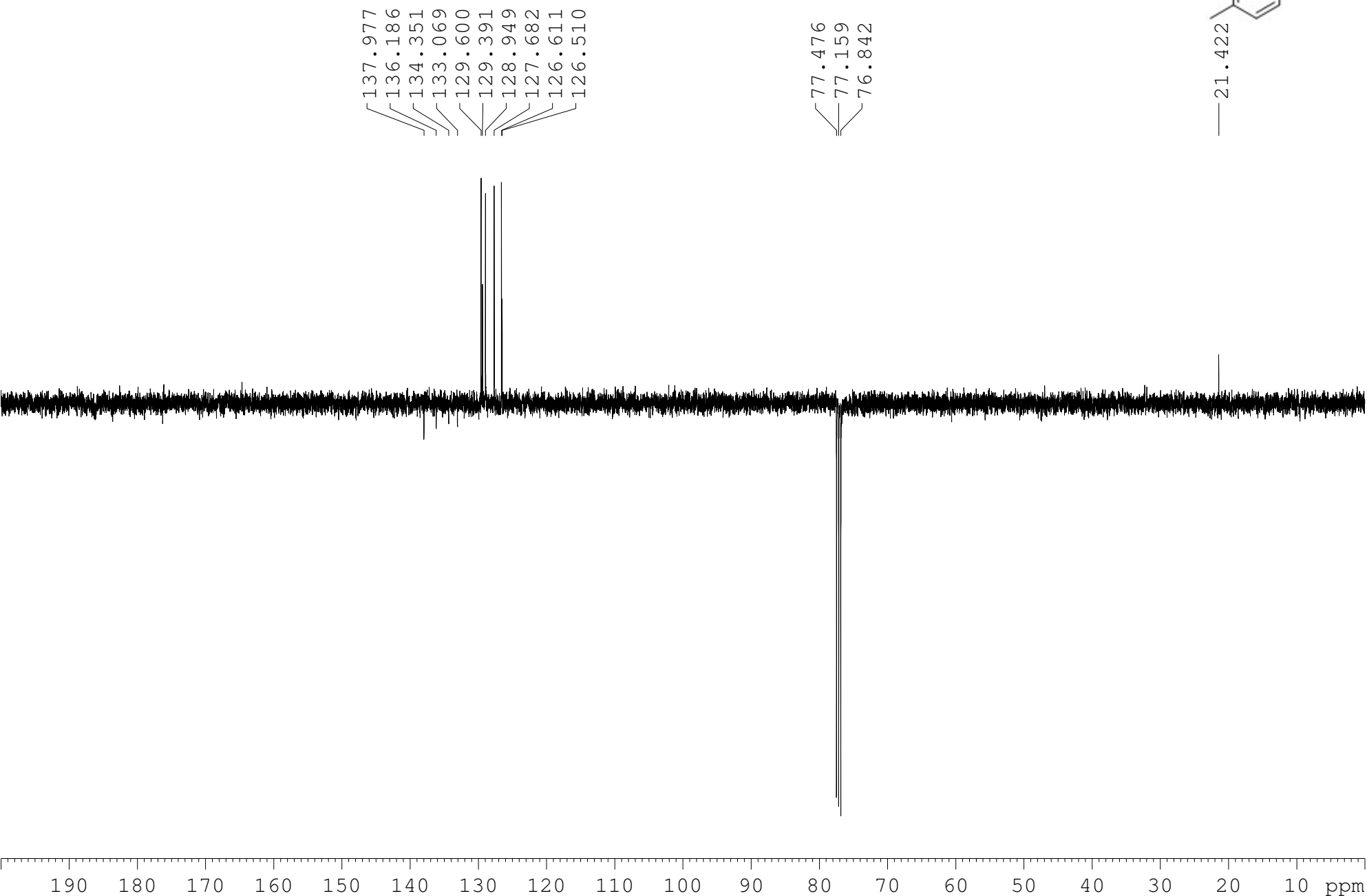
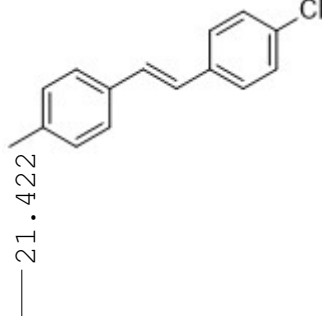
(E)-1-methyl-4-styrylbenzene (**10ba**)



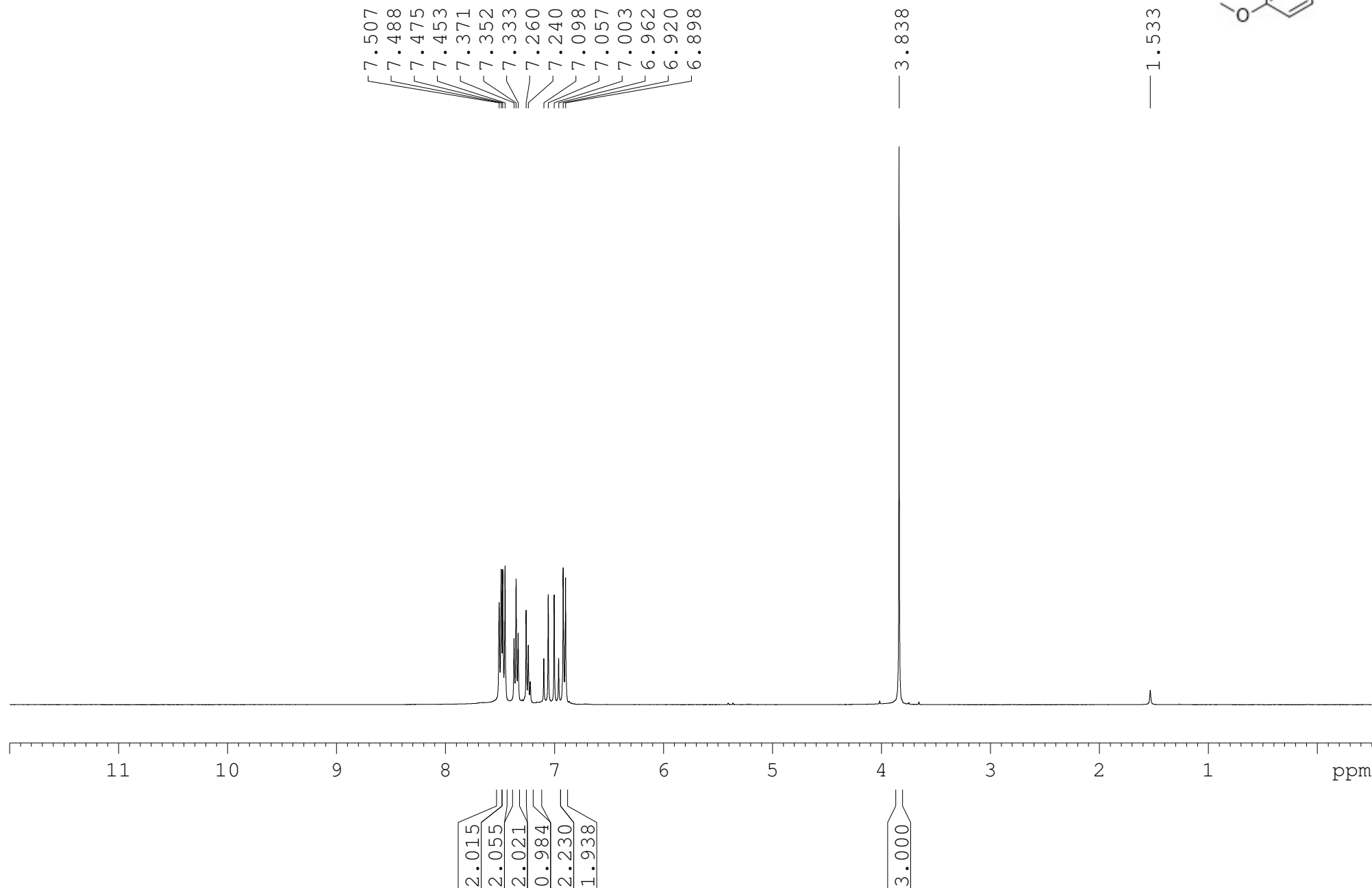
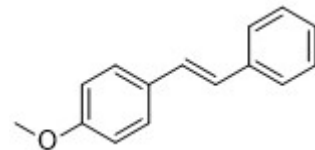
(E)-1-chloro-4-(4-methylstyryl)benzene (**10bb**)



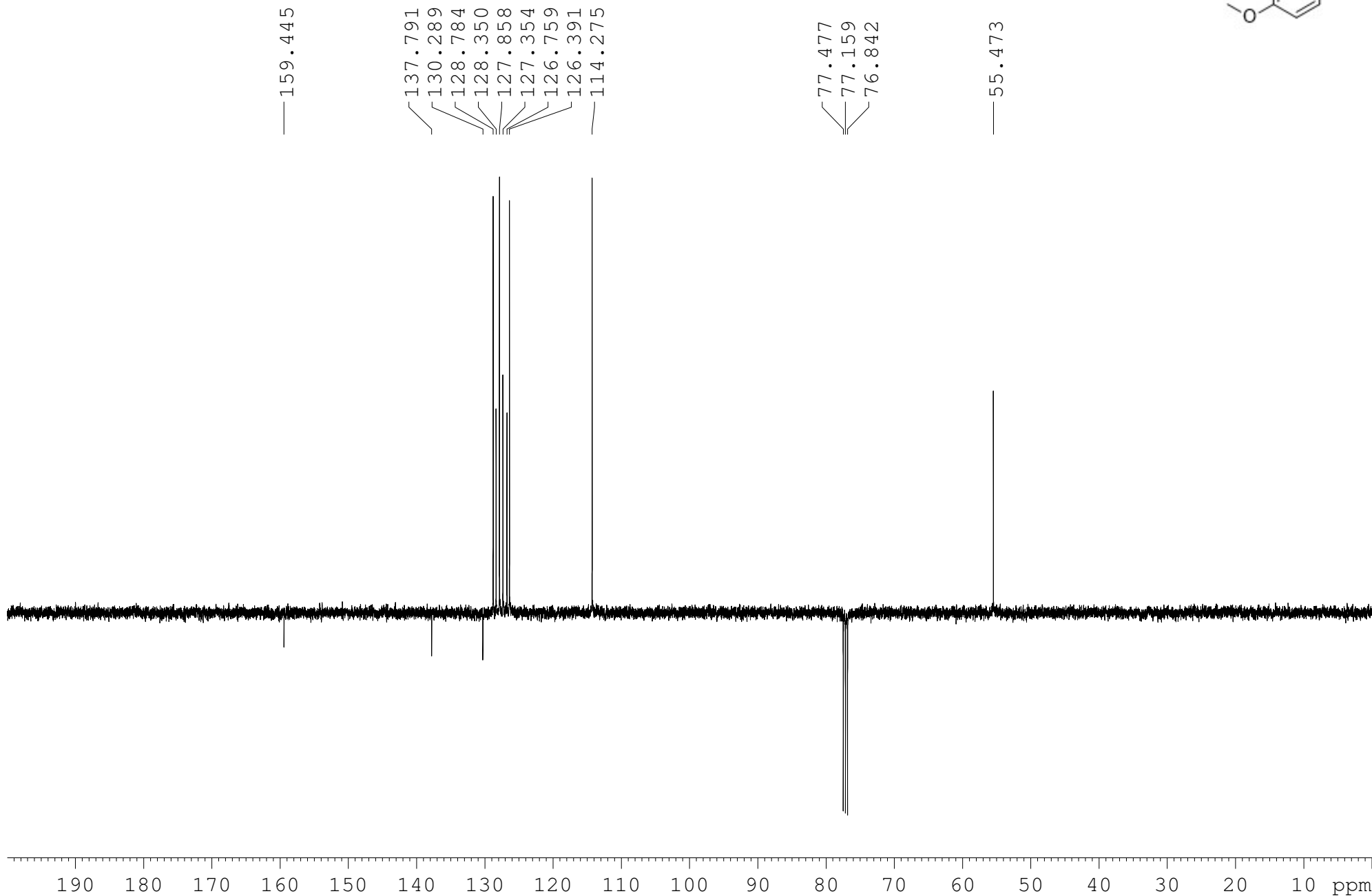
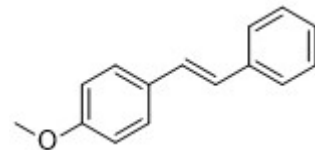
(E)-1-chloro-4-(4-methylstyryl)benzene (**10bb**)



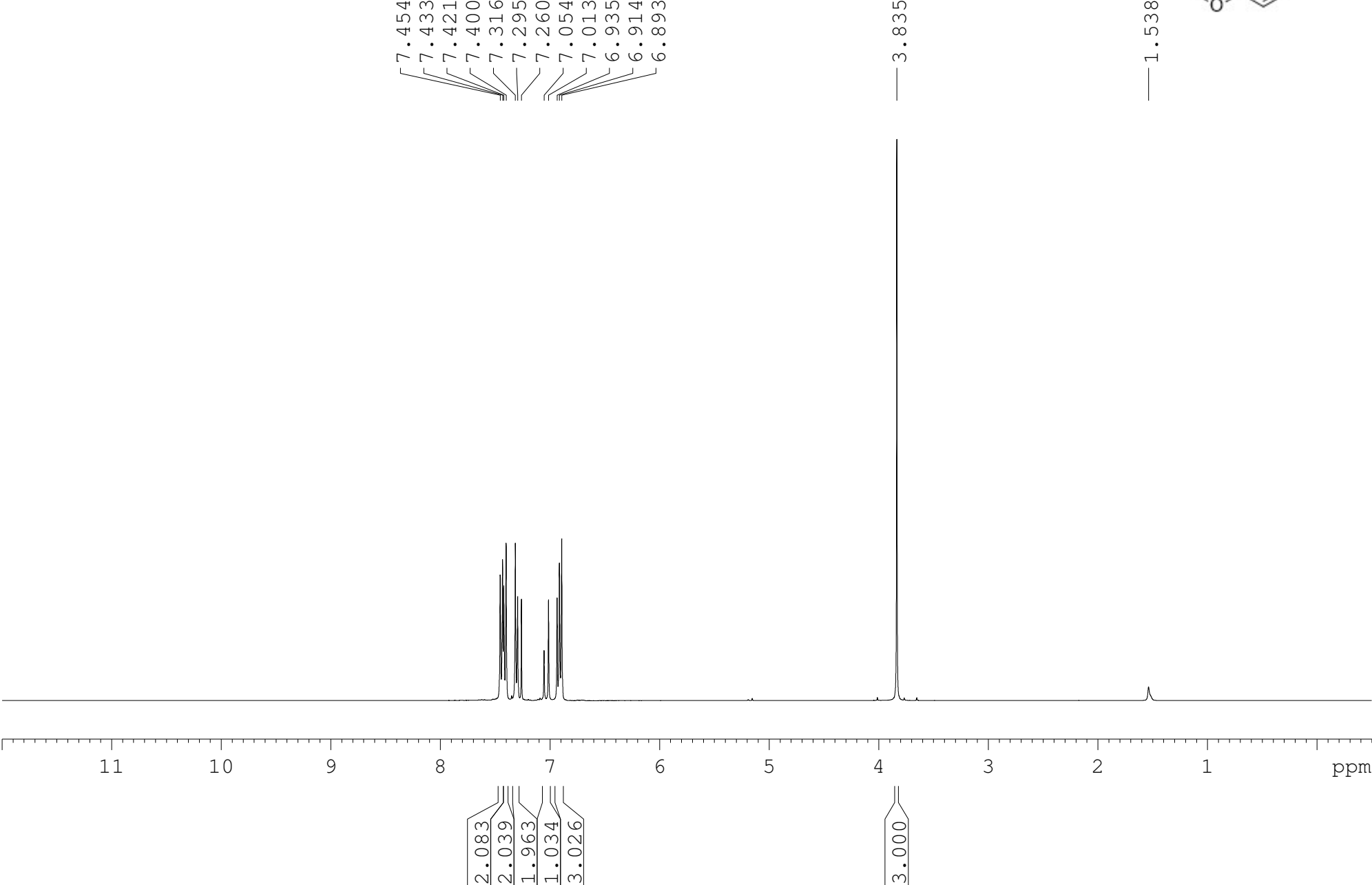
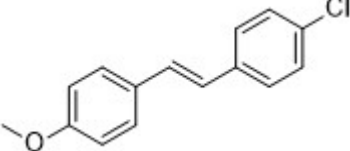
(E)-1-methoxy-4-styrylbenzene (**10ca**)



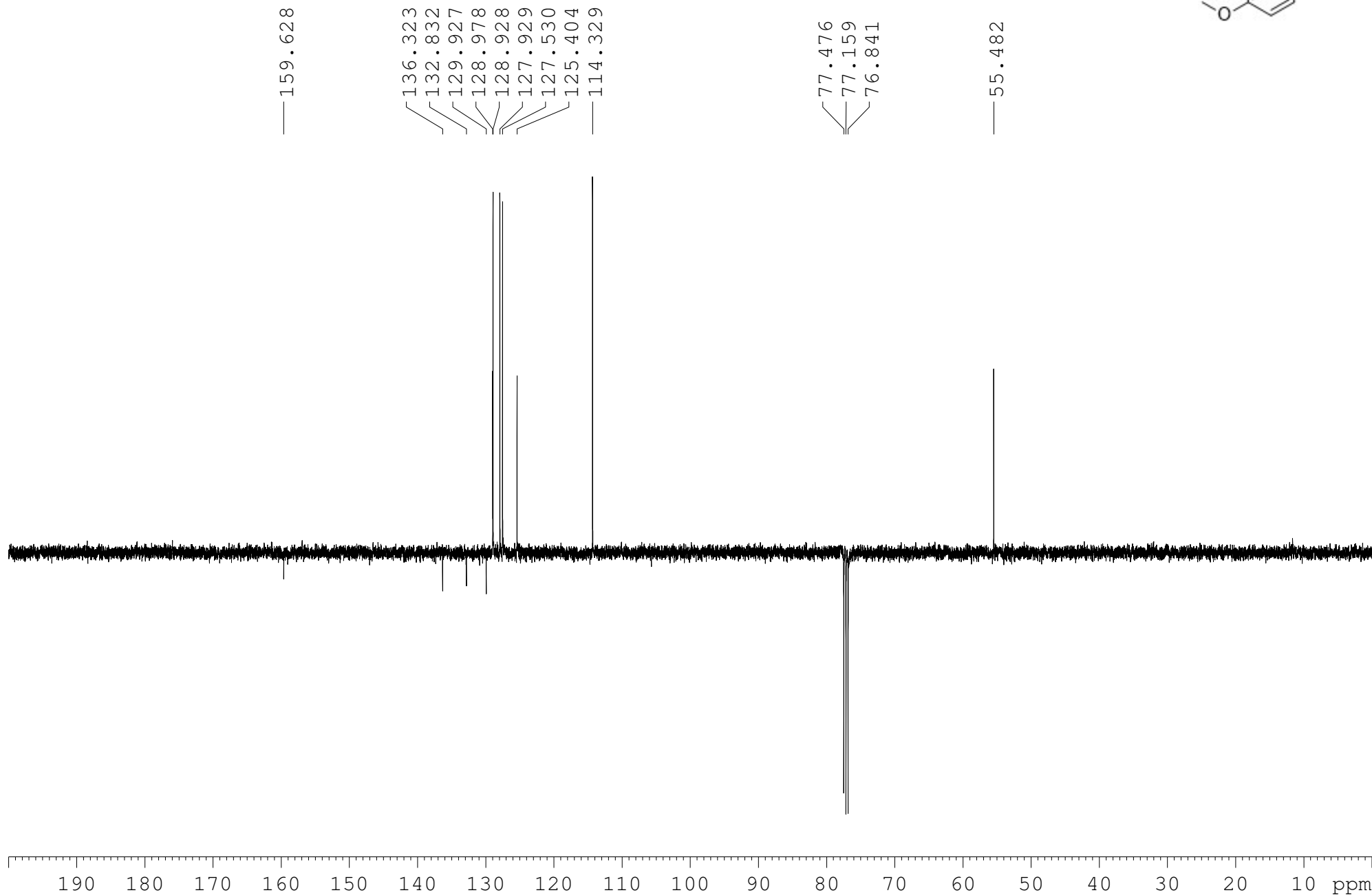
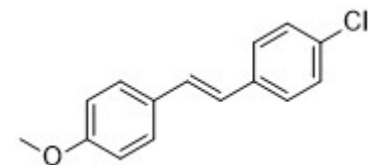
(E)-1-methoxy-4-styrylbenzene (**10ca**)



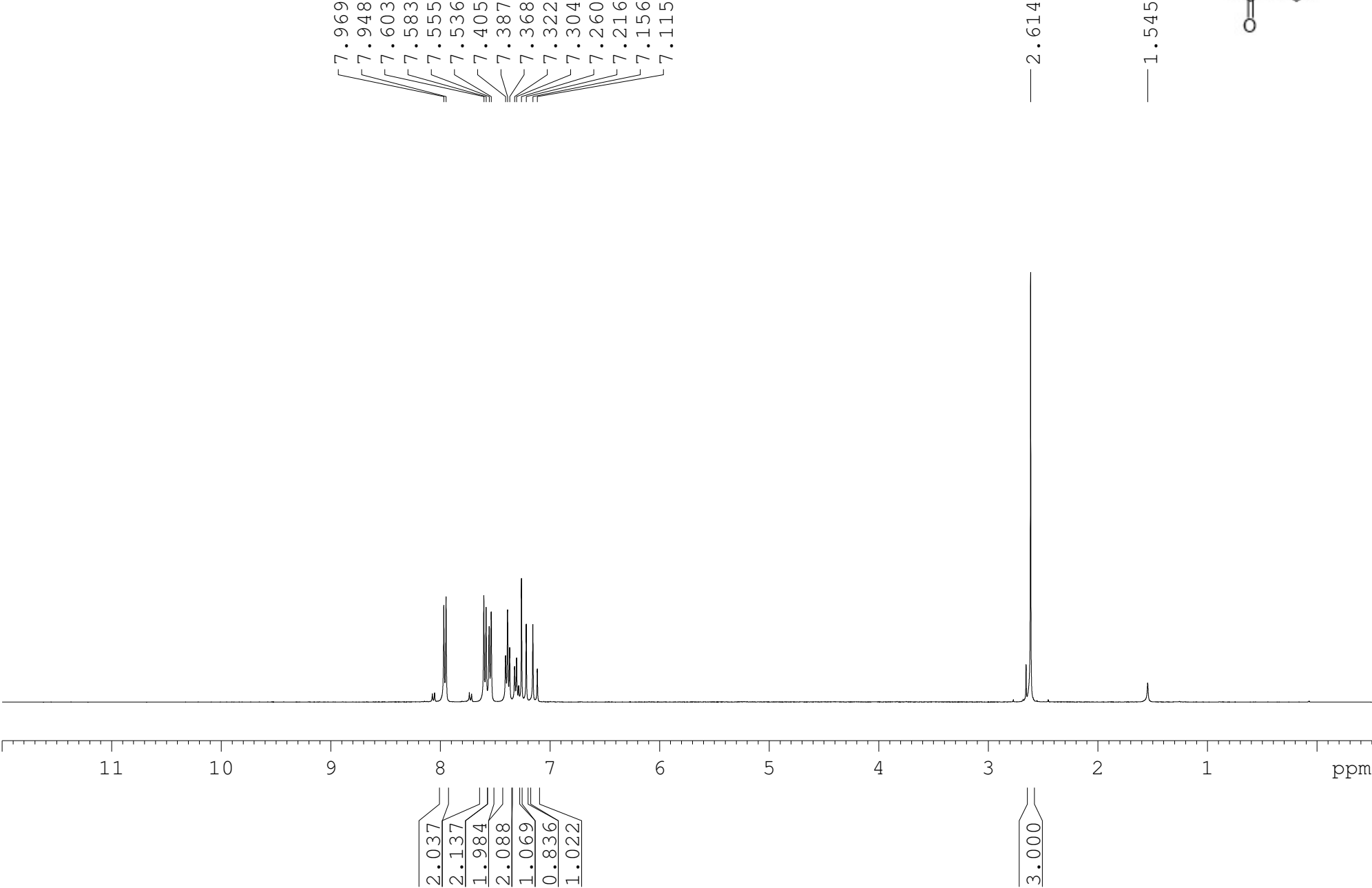
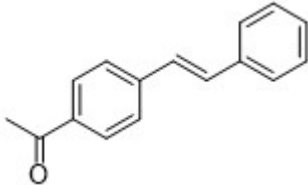
(E)-1-chloro-4-(4-methoxystyryl)benzene (**10cb**)



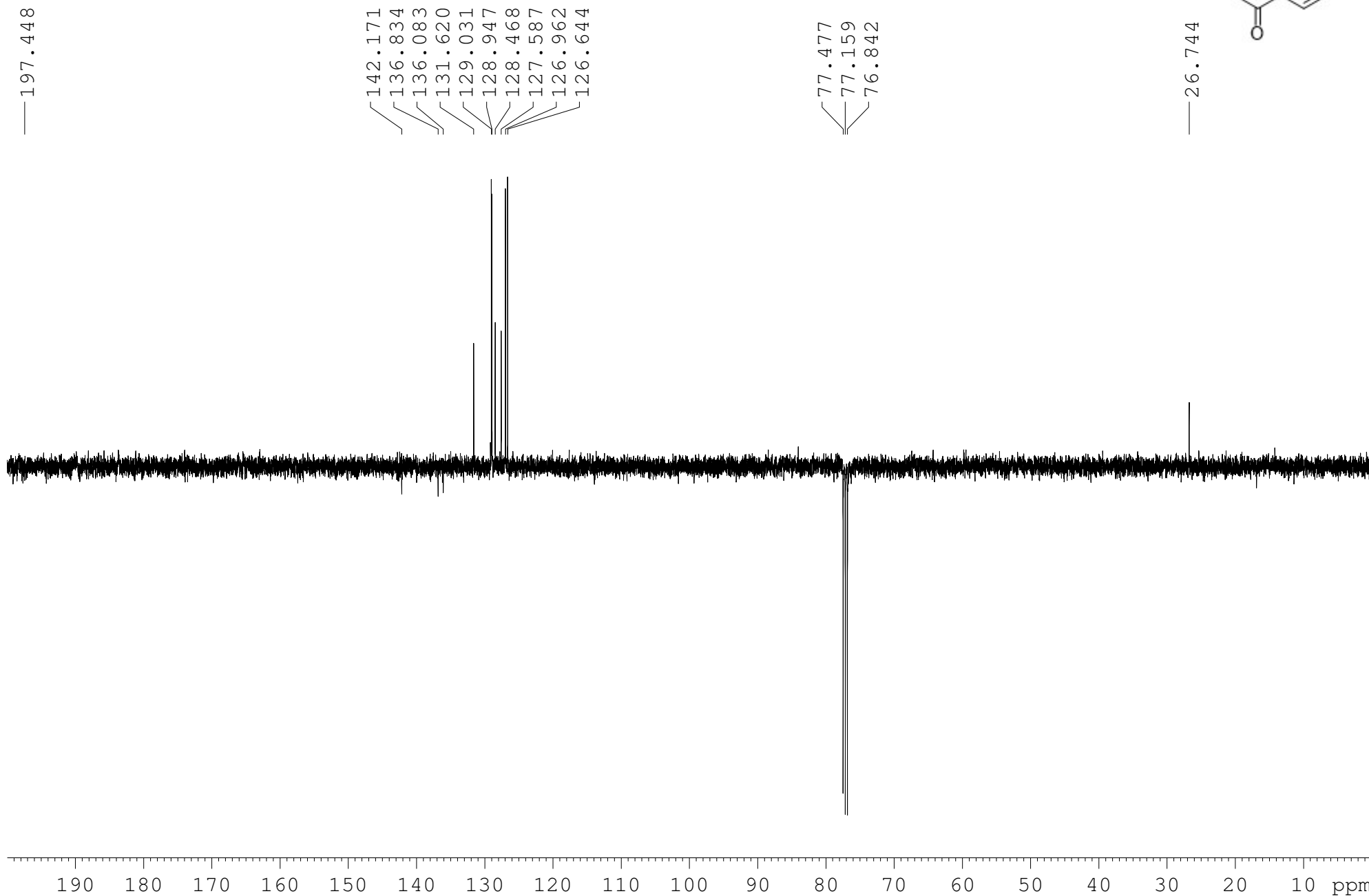
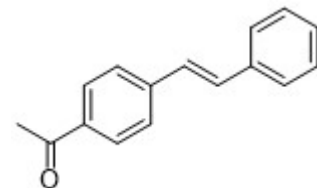
(E)-1-chloro-4-(4-methoxystyryl)benzene (**10cb**)



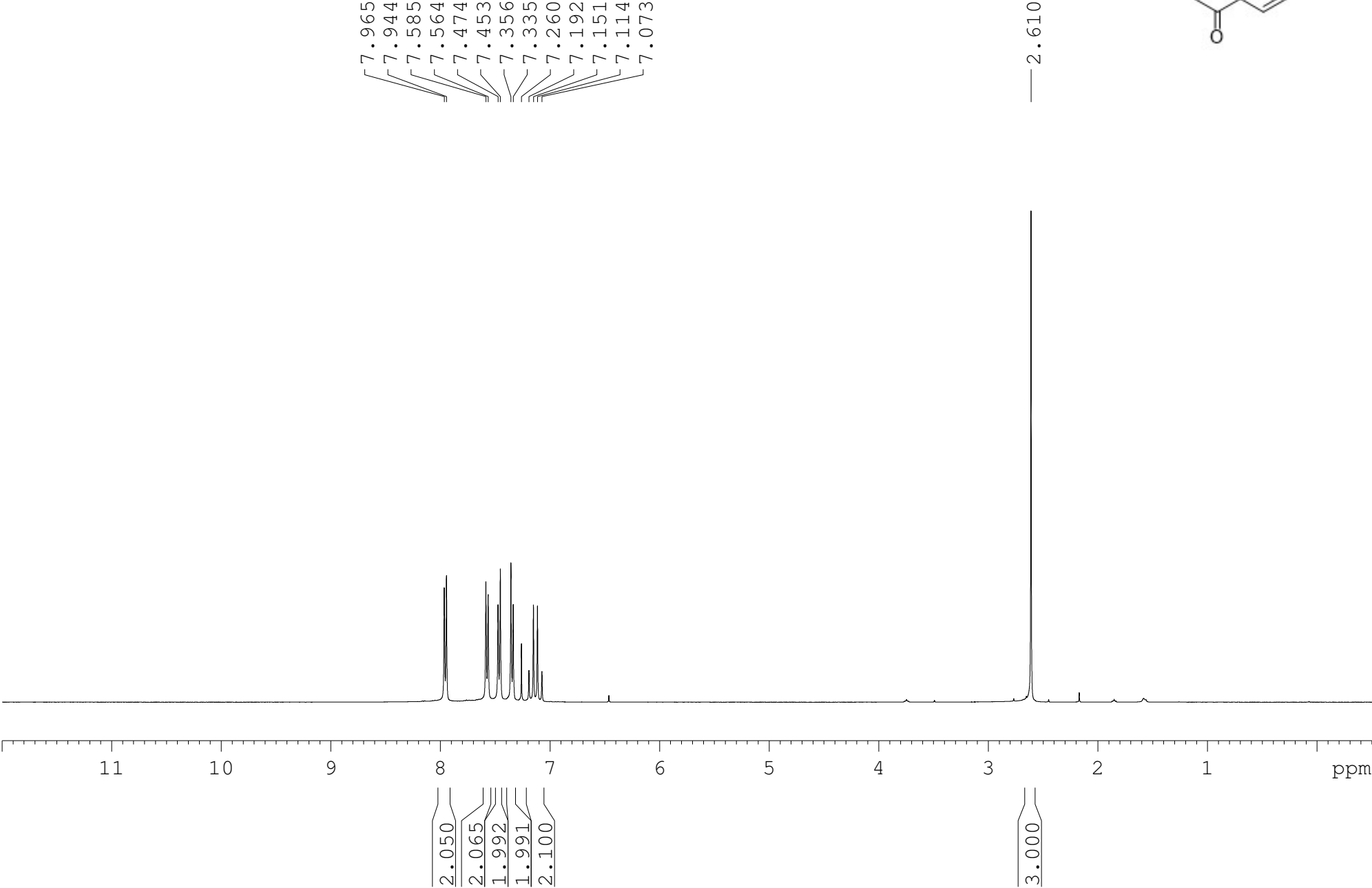
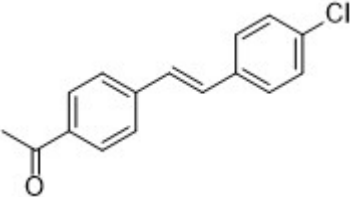
(E)-1-(4-styrylphenyl)ethan-1-one (**10da**)



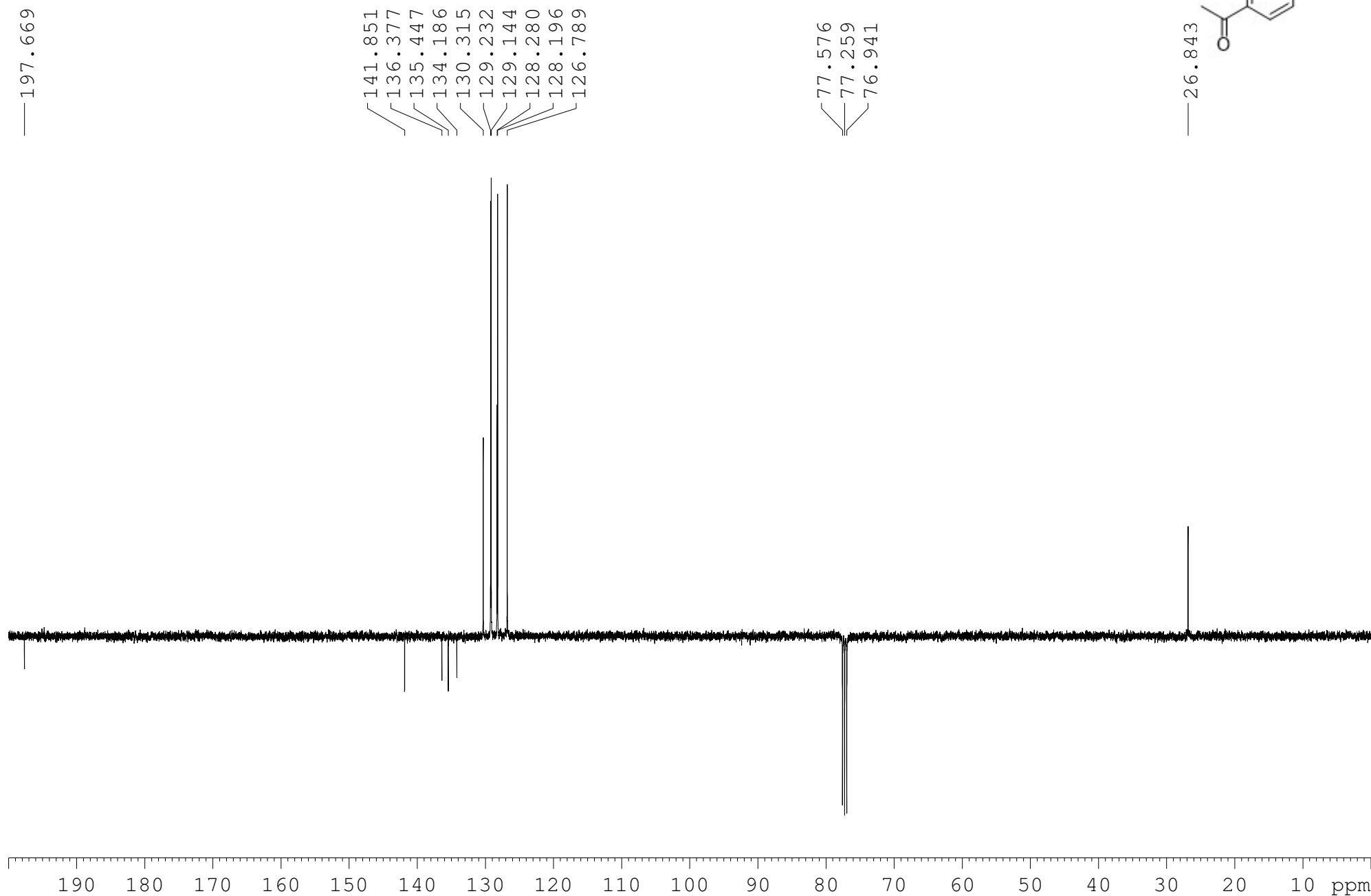
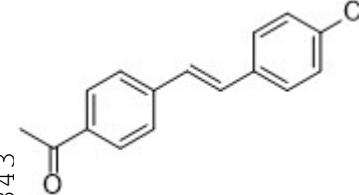
(E)-1-(4-styrylphenyl)ethan-1-one (**10da**)



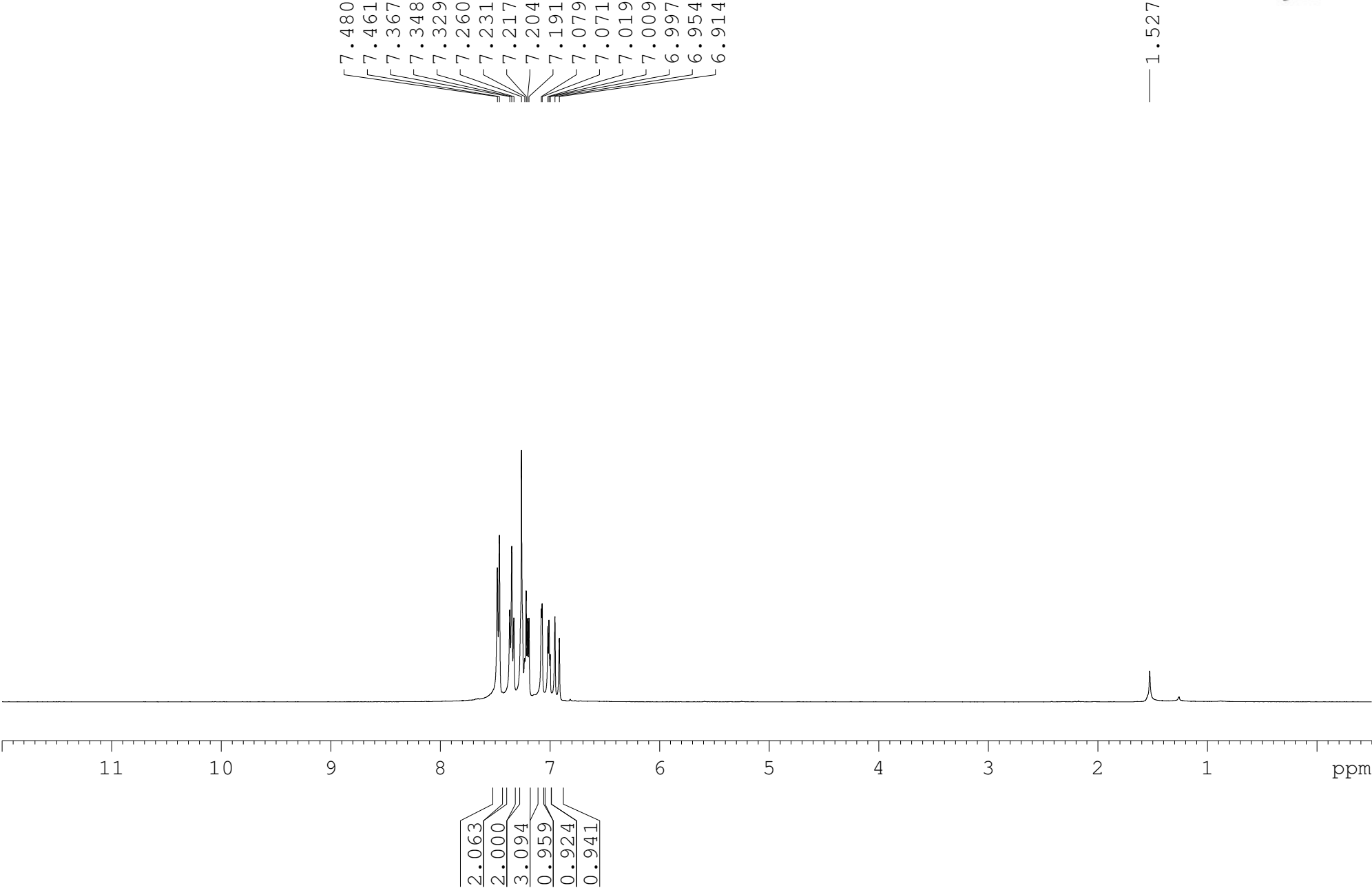
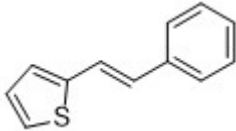
(E)-1-(4-(4-chlorostyryl)phenyl)ethan-1-one (**10db**)



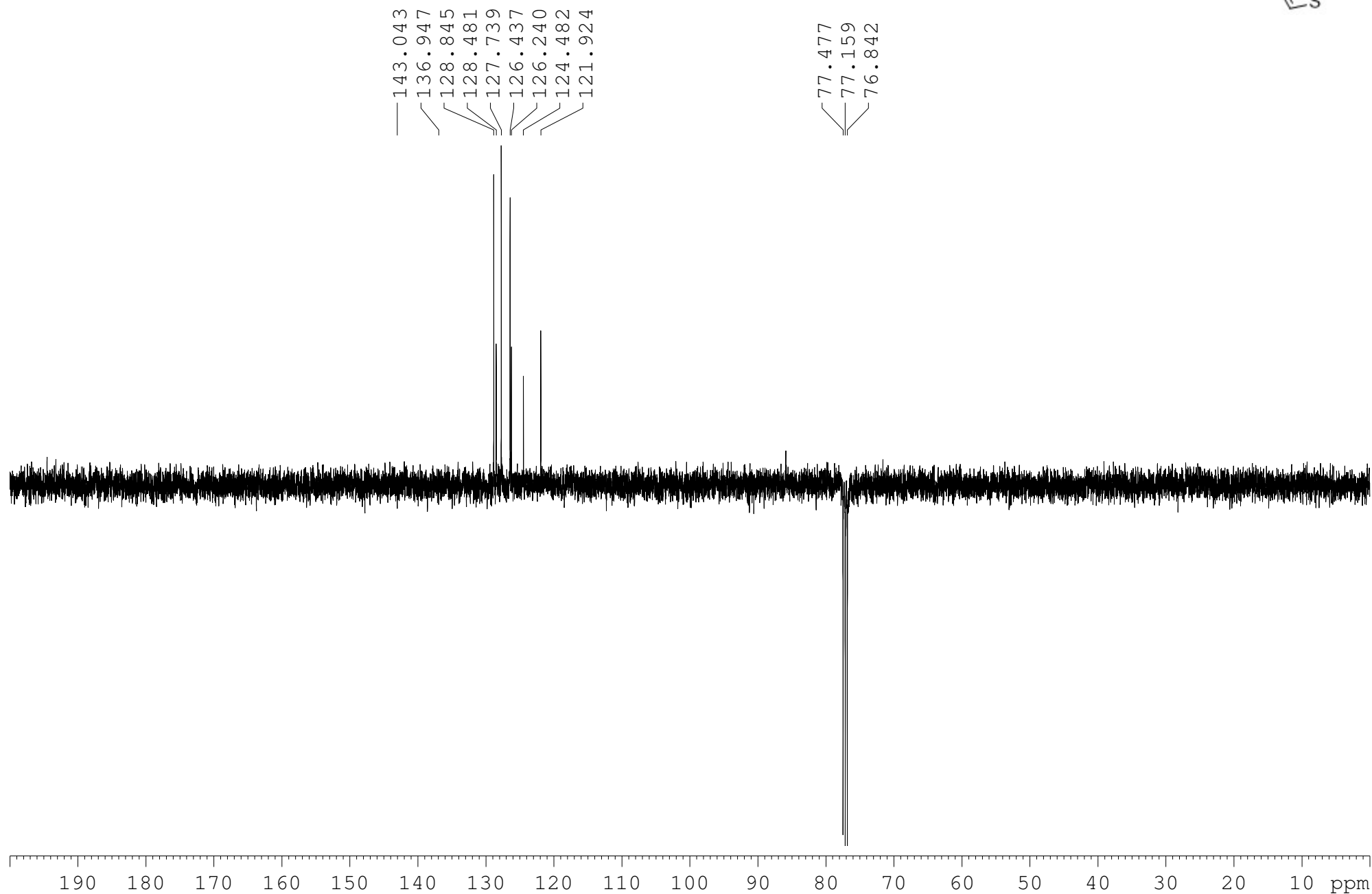
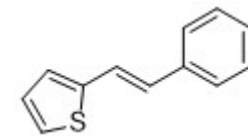
(E)-1-(4-(4-chlorostyryl)phenyl)ethan-1-one (**10db**)



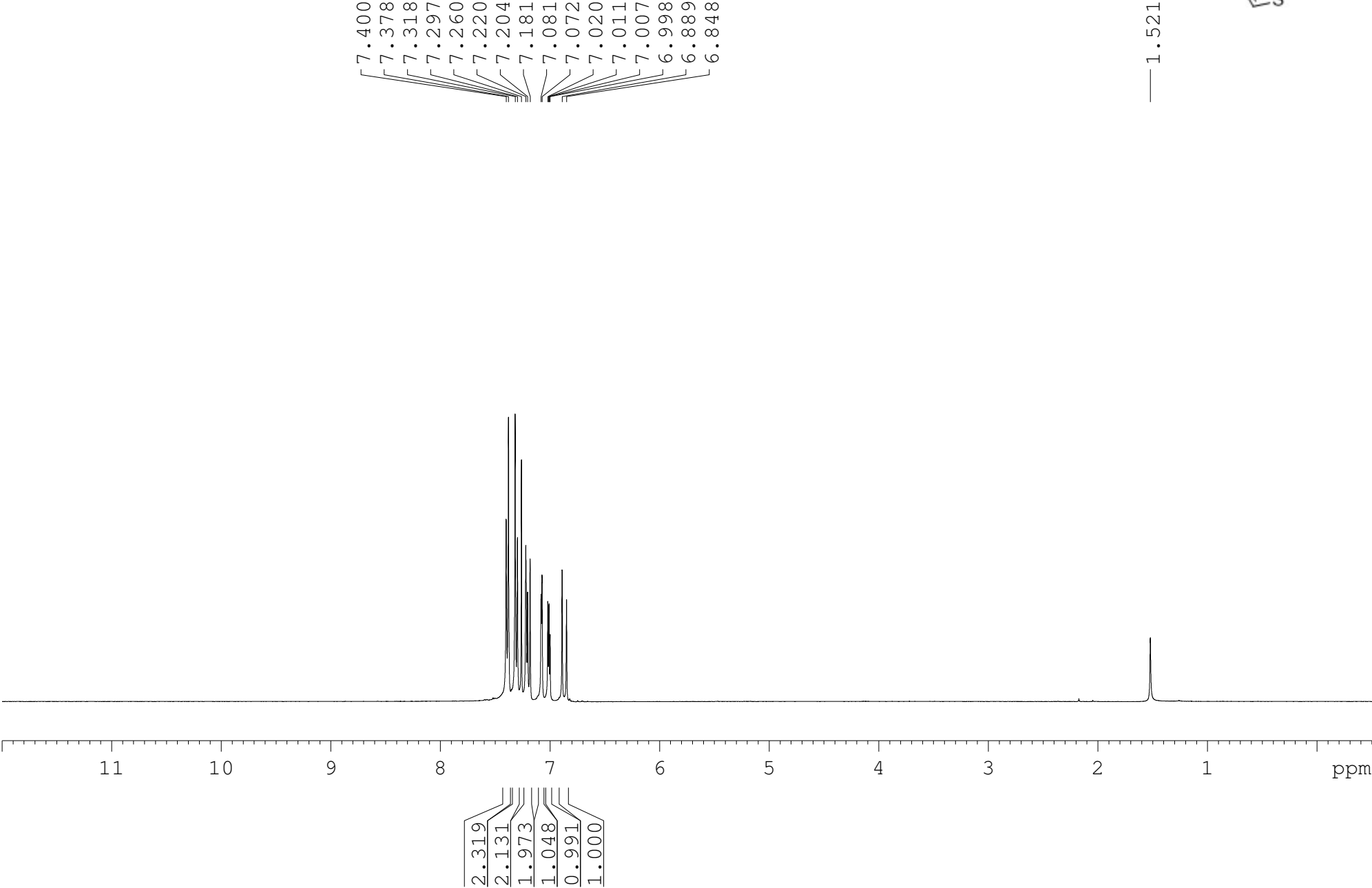
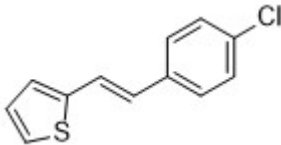
(E)-2-(2-phenylethenyl)thiophene (**10ea**)



(E)-2-(2-phenylethenyl)thiophene (**10ea**)



2-(4-chlorophenylethenyl-E)-thiophene (**10eb**)



2-(4-chlorophenylethenyl-E)-thiophene (**10eb**)

