Palladium-Catalyzed Heck-Type Arylation of Acrylate with Diaryliodonium Salts

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SUPPORTING INFORMATION

Contents

General Remarks.

All reactions were carried out under an air atmosphere condition. Various iodine reagents and various acrylate were purchased from Aldrich, Acros or Alfa. Flash column chromatography was performed using silica gel (200–300 mesh). Analytical thin-layer chromatography was performed using glass plates pre-coated with 200–300 mesh silica gel impregnated with a fluorescent indicator (254 nm). NMR spectra were recorded in $CDCl_3$ on a Bruker NMR-400 (400MHz) and Bruker NMR-500 (500MHz) with TMS as an internal reference. Products were characterized by comparison of ^{1}H NMR, ^{13}C NMR and TOF-MS data in the literatures.

General Procedure for preparation of diaryliodonium salts

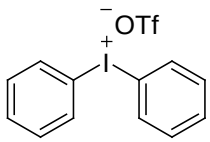
A . Preparation of Aryl (mesityl) iodonium trifluoromethane sulfonates [1, 2]

To a solution of the appropriate iodoarene (45.0 mmol) and m-CPBA (dried under vacuum at room temperature for 1 hour, assume 75%) (1.10 equiv) in dichloromethane at 0 ˚C was added mesitylene (1.10 equiv) was added dropwise over 2 minutes, followed by trifluoromethanesulfonic acid (2.00 equiv) dropwise over 2 minutes. The mixture was stirred for 30 mininutes and the ice bath was then removed and the reaction stirred for 2 hours at room temperature. The reaction was allowed to warm to room temperature and stirred overnight. The solvent was removed in vacuum and diethyl ether added. The resulting solid was filtered and washed on the filter with diethyl ether to give the iodonium triflate as a solid that was dried at 100 ˚C under vacuum for 1 hour.

B. General procedure for diaryliodonium trifluoromethanesulfonates via tetrafluoroborates [1, 2]

To an oven-dried round-bottom flask was added m-CPBA (1.10 equiv) and CH_2Cl_2 (0.25 M). The appropriate iodoarene (1.00 equiv) was then added, followed by BF_3•OEt_2 (3.00 equiv). The mixture was stirred for 1 hour at room temperature. After cooling to 0 ºC, the boronic acid (1.10 equiv) was added in one portion. The reaction was stirred at 0 ºC for 10 minutes then room temperature for 30 minutes. The mixture was cooled back down to 0 ºC and trifluoromethanesulfonic acid (1.10 equiv) was added slowly. The mixture was warmed to room temperature and stirred an additional 15 minutes. The solvent was removed in vacuum and Et_2O was added to the residual solids. The heterogeneous mixture was cooled to –20 ºC for at least 30 minutes and the diaryliodonium trifluoromethanesulfonate was collected via filtration, washed with Et_2O, and dried under vacuum.

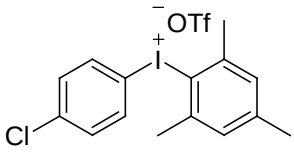
Characterization Data for Compounds 1a–1j



1a

Diphenyliodonium trifluoromethanesulfonate (1a) [3,4]

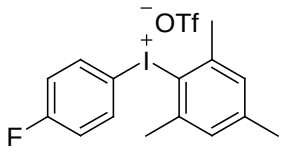
Prepared according to General Procedure A from iodobenzene. Product obtained as a white solid; ^{1}H NMR(400MHz, CD_3OD) δ 7.99 (d, *J* = 8.0 Hz, 4H), 7.66 (t, *J* = 8.0 Hz, 2H), 7.50 (t, *J* = 8.0 Hz, 4H); ^{13}C NMR (100MHz, CD_3OD) δ 137.1, 133.6, 133.2, 121.8, 117.1. HRMS (ESI) m/z calculated for $C_{12}H_{10}I$ $[M\text{-}OTf]^+$ 280.9827, found 280.9825.



1b

4-Chlorophenyl(mesityl)iodonium trifluoromethanesulfonate (1b) [1]

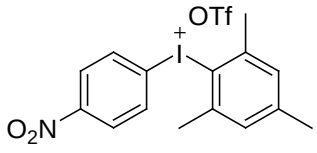
Prepared according to General Procedure A from 4-chloroiodobenzene. Product obtained as an white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61–7.69 (m, 2H), 7.34–7.38 (m, 2H), 7.10 (s, 2H), 2.62 (s, 6H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.5, 142.4, 134.3, 132.2, 130.2, 27.0, 21.1; HRMS (ESI) m/z calculated for $C_{15}H_{15}ClI$ $[M\text{-}OTf]^+$ 356.9907, found 356.9910.



1c

4-Fluorophenyl(mesityl)iodonium trifluoromethanesulfonate (1c) [2]

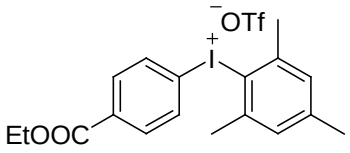
Prepared according to the general procedure A from 4-fluoroiodobenzene. Product obtained as an off-white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (dd, *J* = 4.8, 9.1 Hz, 2H), 7.29 (t, 2H, *J* = 8.8 Hz), 7.25 (s, 2H), 2.68 (s, 6H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.2, 145.9, 143.4, 138.1, 131.3, 122.7, 120.6, 107.8, 27.0, 21.0; HRMS (ESI) m/z calculated for $C_{15}H_{15}FI$ $[M\text{-}OTf]^+$ 341.0197, found 341.0195.



1d

4-Nitrophenyl(mesityl)iodonium trifluoromethanesulfonate (1d) [2]

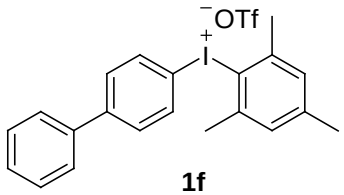
Prepared according to the general procedure A from 4-nitroiodobenzene. Product obtained as a light yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.32 (d, *J* = 9.1 Hz, 2H), 8.15 (d, *J* = 9.1 Hz, 2H), 7.28 (s, 2H), 2.61 (s, 6H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.1, 145.9, 143.7, 136.2, 131.6, 127.5, 121.7, 119.8, 27.1, 21.0; HRMS (ESI) m/z calculated for $C_{15}H_{15}INO_2$ $[M\text{-}OTf]^+$ 368.0142, found 368.0140.



1e

(4-(Ethoxycarbonyl)phenyl)(mesityl)iodonium trifluoromethanesulfonate (1e) [2]

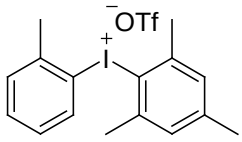
Prepared according to the general procedure A from ethyl 4-iodobenzoate. Product obtained as a white solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (d, *J* = 8.2 Hz, 2H), 7.73 (d, *J* = 8.8 Hz , 2H), 7.14 (s, 2H), 4.39 (q, *J* = 7.2 Hz, 2H), 2.61 (s, 6H), 2.38 (s, 3H), 1.39 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.7, 144.5, 142.5, 133.4, 132.7, 132.6, 130.3, 120.6, 116.3, 61.7, 27.0, 21.1, 14.1; HRMS (ESI) m/z calculated for $C_{18}H_{20}IO_2$ $[M\text{-}OTf]^+$ 395.0503, found 395.0501.



1f

(Biphenyl-4-yl)(mesityl)iodonium trifluoromethanesulfonate (1f) [1]

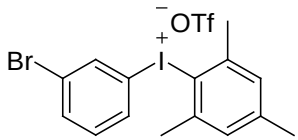
Prepared according to the general procedure A from ethyl 4-iodobenzoate.product was obtained as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.4 Hz, 2H), 7.62 (d, *J* = 8.4 Hz, 2H), 7.52-7.40 (m, 5H), 7.14 (s, 2H), 2.75 (s, 6H), 2.36 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.7, 145.3, 143.4, 139.3, 135.9, 131.3, 131.1, 130.0, 129.6, 128.0, 121.9, 111.6, 27.1, 21.0; HRMS (ESI) m/z calculated for $C_{12}H_{20}I$ $[M\text{-}OTf]^+$ 399.0609, found 399.0608.



1g

2-methylphenyl(mesityl)iodonium trifluoromethanesulfonate (1g) [2]

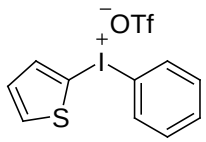
Prepared according to the general procedure A from 2-iodotoluene. Product obtained as a white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50-7.37 (m, 3H), 7.20 (m, 1H), 7.13 (s, 2H), 2.60 (s, 9H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.4, 142.3, 140.1, 133.7, 132.4, 132.4, 130.6, 129.7, 119.4, 115.6, 26.8, 24.7, 20.9; HRMS (ESI) m/z calculated for $C_{16}H_{18}I$ $[M\text{-}OTf]^+$ 337.0447, found 337.0445.



1h

3-Bromophenyl(mesityl)iodonium trifluoromethanesulfonate (1h) [2]

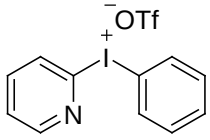
Prepared according to the general procedure A from 3-bromoiodobenzene. Product obtained as a white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (t, *J* = 1.6 Hz, 1H), 7.69 (d, *J* = 8.2 Hz, 1H), 7.63 (d, *J* = 8.1 Hz, 1H), 7.27 (t, *J* = 8.1 Hz, 1H), 7.11 (s, 2H), 2.62 (s, 6H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.5, 142.4, 134.9, 134.8, 132.9, 131.6, 130.3, 124.9, 120.7, 111.8, 27.0, 21.1; $C_{15}H_{15}BrI$ $[M\text{-}OTf]^+$ 400.9396, found 400.9391.



1i

(2-Thienyl)iodonium trifluoromethanesulfonate (1i) [2,5]

Prepared according to the general procedure B from 2-boronic acid-thiophen. Product obtained as a yellow solid. ^{1}H NMR (400MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.5 Hz, 2H), 7.87 (m, 1H), 7.72 (m, 1H), 7.61 (t, *J* = 8.5 Hz, 1H), 7.47 (t, *J* = 8.5 Hz, 2H), 7.14 (m, 1H). ^{13}C NMR(100MHz, $CDCl_3$) δ 141.6, 137.7, 133.9, 132.6, 132.4, 130.3, 120.2, 117.7, 95.1. HRMS (ESI) m/z calculated for $C_{10}H_8IS$ $[M\text{-}TfO]^+$ 286.9391, found 286.9392.



1j

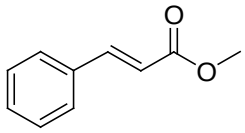
(2- pyridin)iodonium trifluoromethanesulfonate (1i)

Prepared according to the general procedure B from 2-boronic acid-pyridine. Product obtained as a yellow solid. ^{1}H NMR (400MHz, $CDCl_3$) δ 8.02 (m, 2H), 7.94 (m, 1H), 7.75 (m, 3H), 7.60 (m, 1H), 7.44 (m, 2H). ^{13}C NMR(100MHz, $CDCl_3$) δ 141.1, 136.6, 135.4, 132.6, 132.3, 113.7, 112.8, 99.9. HRMS (ESI) m/z calculated for $C_{11}H_9IN$ $[M\text{-}TfO]^+$ 281.9774, found 281.9769.

General procedure for Arylation of Acrylate with Diaryliodonium Salts

A mixture of Diaryliodonium Salts (0.4 mmol), acrylate (0.8 mmol), $Pd(OAc)_2$ (2 mol %), and DMF (1 mL) in a Schlenk tube was stirred under air atmosphere at 130 °C for the 1 hour, the consumption of starting material was monitored by TLC. After the mixture was poured into ether, then washed with water, extracted with ethyl acetate, dried by anhydrous Na_2SO_4, then filtered and evaporated under vacuum, the residue was purified by flash column chromatography (petroleum ether/ethyl acetate) to afford the corresponding coupling products.

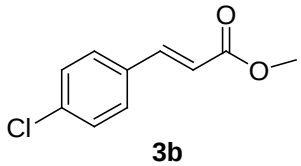
Characterization Data for Compounds 3a–3ah



3a

Methyl cinnamate (3a) [7-10]

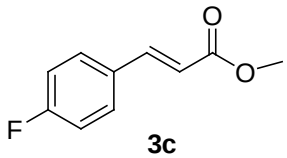
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 16.0 Hz, 1H), 7.54 (m, 2H), 7.39 (m, 3H), 6.46 (d, *J* = 16.0 Hz, 1H), 3.81 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.4, 144.8, 134.3, 130.3, 128.9, 128.0, 117.8, 51.7.



3b

(*E*)-Methyl 4-chlorocinnamate (3b) [11-13]

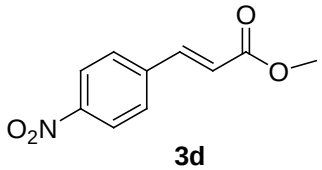
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 16.0 Hz, 1H), 7.45(d, *J* = 8.4 Hz, 1H), 7.35 (d, *J* = 8.40 Hz, 1H), 6.42 (d, *J* = 16.0 Hz, 1H), 3.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$,) δ 167.4, 143.5, 136.8, 136.2, 133.1, 132.9, 129.2, 118.4, 51.7.



3c

(*E*)-methyl 3-(4-fluorophenyl)acrylate (3c) [9,11,12]

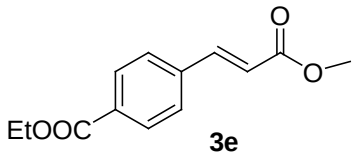
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67(d, *J* = 16.0 Hz, 1H), 7.49-7.53 (m, 2H), 7.05-7.10 (m, 2H), 6.38 (d, *J* = 16.0 Hz, 1H), 6.37 (d, *J* = 16.0 Hz, 1H), 3.80 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.3, 164.9, 162.9, 143.5, 129.9, 117.5, 116.1, 115.9, 51.7.



3d

(*E*)-methyl 3-(4-nitrophenyl)acrylate (3d) [14]

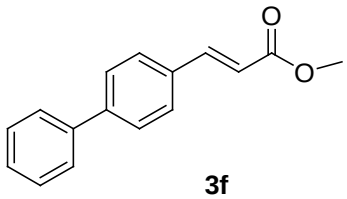
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.37 (d, *J* = 9.0 Hz, 1H), 8.02 (d, *J* = 8.5 Hz, 1H), 7.69 (d, *J* = 9.0 Hz, 1H), 7.12 (d, *J* = 8.5 Hz, 1H), 6.58 (d, *J* = 16.0 Hz, 1H), 3.84 (s, 3H).^{13}C NMR (125 MHz, $CDCl_3$) δ 166.4, 148.5, 141.9, 140.4, 128.6, 124.1, 123.6, 52.1.



3e

(*E*)-ethyl 4-(3-methoxy-3-oxoprop-1-enyl)benzoate (3e) [11,14]

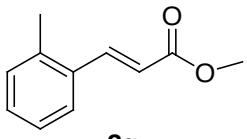
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04-8.06 (d, *J* = 8.5 Hz, 2H), 7.69-7.72 (d, *J* = 16.0 Hz, 1H), 7.57-7.59 (d, *J* = 8.5 Hz, 2H), 6.50-6.53 (d, *J* = 16.0 Hz, 1H), 4.37-4.41 (q, 2H), 3.82 (s, 3H), 1.41 (t, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.0, 165.9, 143.5, 138.4, 131.7, 130.1, 127.8, 120.1, 61.2, 51.9, 29.1, 14.3**.**



3f

(*E*)-methyl 3-(biphenyl-4-yl)acrylate (3f) [11]

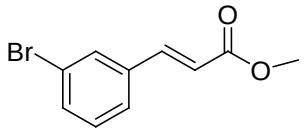
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 16.0 Hz, 1H), 7.59-7.61 (m, 5H), 7.44-7.47 (m, 2H), 7.37-7.39 (m, 2H), 6.50 (d, *J* = 16.0 Hz, 1H), 3.82 (s, 3H).



3g

(*E*)-methyl 3-o-tolylacrylate (3g) [15]

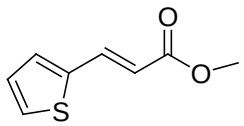
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (d, *J* = 16.0 Hz, 1H), 7.55 (d, *J* = 7.5 Hz, 1H), 7.19-7.29 (m, 3H), 6.38 (d, *J* = 16.0 Hz, 1H), 3.81 (s, 3H), 2.32 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.5, 142.5, 136.8, 133.3, 130.9, 129.1, 126.3, 122.7, 118.8, 51.7, 21.0.



3h

(*E*)-methyl 3-(3-bromophenyl)acrylate (3h) [16]

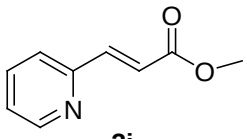
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (t, *J* = 1.5 Hz, 1H), 7.62 (d, *J* = 16.0 Hz, 1H), 7.51 (m, 1H), 7.44 (d, *J* = 7.5 Hz, 1H), 7.27 (m, 1H), 6.44 (d, *J* = 16.0 Hz, 1H), 3.81 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.9, 143.1, 136.6, 133.0, 130.8, 129.1, 126.6, 122.7, 119.2, 51.8.



3i

(*E*)-methyl 3-(thiophen-2-yl)acrylate (3i) [8]

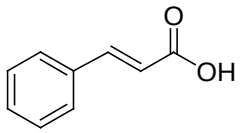
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (d, *J* = 15.8 Hz, 1H), 7.37 (d, *J* = 5.4 Hz, 1H), 7.25 (d, *J* = 3.0 Hz, 1H), 7.04 (d, *J* = 5.4 Hz, 1H), 6.23 (d, *J* = 15.8 Hz, 1H), 3.78 (s, 3H).



3j

(*E*)-methyl 3-(pyridin-2-yl)acrylate (3j) [13]

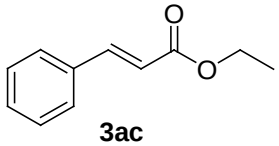
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56-8.57 (m, 1H), 7.59-7.66 (m, 2H), 7.33 (d, *J* = 7.8 Hz, 1H), 7.16-7.21 (m, 1H), 6.84 (d, *J* = 15.6 Hz, 1H), 3.74 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.3, 153, 150.3, 143.7, 136.9, 124.4, 124.4, 122.1, 52.



3ab

Cinnamic acid (3ab) [17]

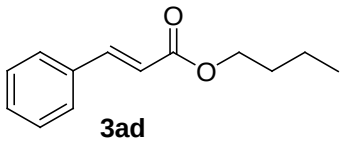
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (d, *J* = 16.0 Hz, 1H), 7.54-7.56 (m, 2H), 7.37-7.41 (m, 3H), 6.44 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.9, 146.9, 134.1, 130.7, 128.9, 128.3, 117.3.



3ac

Ethyl cinnamate (3ac) [10,13,18]

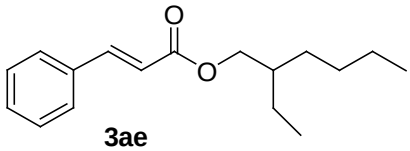
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (d, *J* =16.0 Hz, 1H), 7.51-7.53 (m, 2H), 7.36-7.38 (m, 3H), 6.45 (d, *J* =16.0 Hz, 1H), 4.28 (q, *J* =7.0 Hz, 2H), 1.35 (t, *J* =7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.0, 144.5, 134.5, 130.2, 128.9, 128.1, 118.3, 60.5, 14.3.



3ad

Butyl cinnamate (3ad) [10,19]

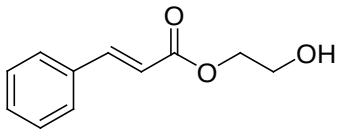
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66-7.69 (d, *J* = 16.0 Hz, 1H), 7.50-7.53 (m, 2H), 7.36-7.40 (m, 3H), 6.45 (d, *J* = 16.0 Hz, 1H), 4.19-4.22 (t, *J* = 6.5 Hz, 2H), 1.66-1.72 (m, 2H), 1.40-1.47 (m, 2H), 0.95-0.98 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.1, 144.5, 134.4, 130.2, 128.9, 128.1, 118.3, 64.4, 30.7, 19.2, 13.7.



3ae

2-Ethylhexylcinnamate (3ae) [10]

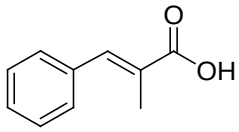
^{1}H NMR (500MHz, $CDCl_3$) δ 7.69 (d, *J* = 16.0 Hz, 1H), 7.52-7.54 (m, 2H), 7.36-7.40 (m, 3H), 6.46 (d, *J* = 16.0 Hz, 1H), 4.10-4.15 (m, 2H), 1.63-1.66 (m, 1H), 1.41-1.46 (m, 2H), 1.31-1.39 (m, 6H), 0.89-0.94 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.2, 144.5, 134.5, 130.3, 128.8, 128.0, 118.3, 67.0, 38.9, 30.5, 28.9, 23.8, 23.0, 14.0, 11.0.



3af

2-Hydroxyethyl 3-(phenyl)-2-propenoate (3af) [10]

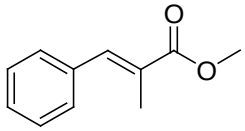
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (d, *J* = *16.0* Hz, 1H), 7.54 (m, 2H), 7.40 (m, 3H), 6.47 (d, *J* = 16.0 Hz, 1H), 4.37 (m, 2H), 3.66 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) 166.6, 145.7, 134.2, 130.5, 128.9, 128.1, 117.5, 64.1, 41.8.



3ag

(*E*)-2-methyl-3-phenylacrylic acid (3ag) [17]

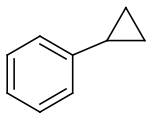
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 (s, 1H), 7.36-7.44 (m, 4H), 7.29-7.34 (m, 1H) 7.21-7.25 (m, 1H), 2.14 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.2, 143.1, 135.5, 129.8, 128.7, 127.5, 37.5, 13.7.



3ah

(*E*)-Methyl2-methyl-3-phenylacrylate (3ah) [19]

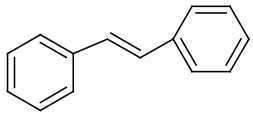
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (s, 1H), 7.39-7.40 (d, *J* = 4.5 Hz, 2H), 7.27-7.36 (m, 2H), 7.18-7.21 (m, 1H), 3.81 (s, 3H), 2.14(s, 3H); ^{13}C NMR(125 MHz, $CDCl_3$): δ 169.1, 138.9, 135.3, 129.6, 129.0, 128.5, 126.3, 52.0, 14.0.



3ai

Phenylcyclopropane (3ai) [20]

^{1}H NMR (500MHz, $CDCl_3$) δ 7.05-7.28 (m, 5H), 1.89 (m, 1H), 0.95 (m, 2H), 0.70 (m, 2H); ^{13}C NMR (125MHz, $CDCl_3$) δ 144.2, 128.4, 125.9, 125.6, 15.6, 9.3.

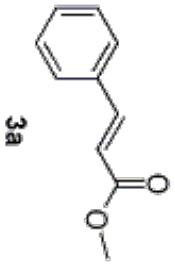


3aj

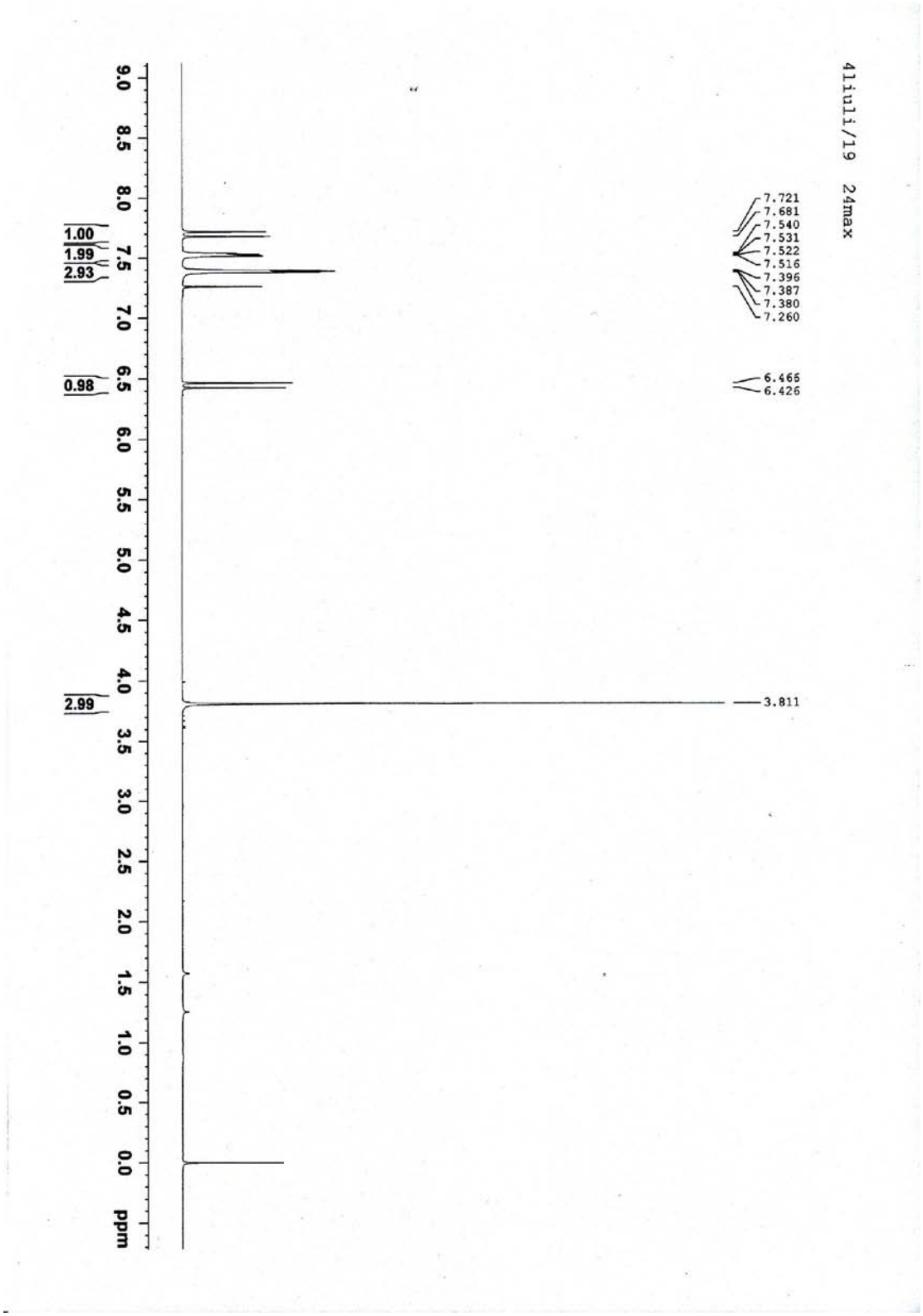
(*E*)-1,2-diphenylethene (3aj) [18]

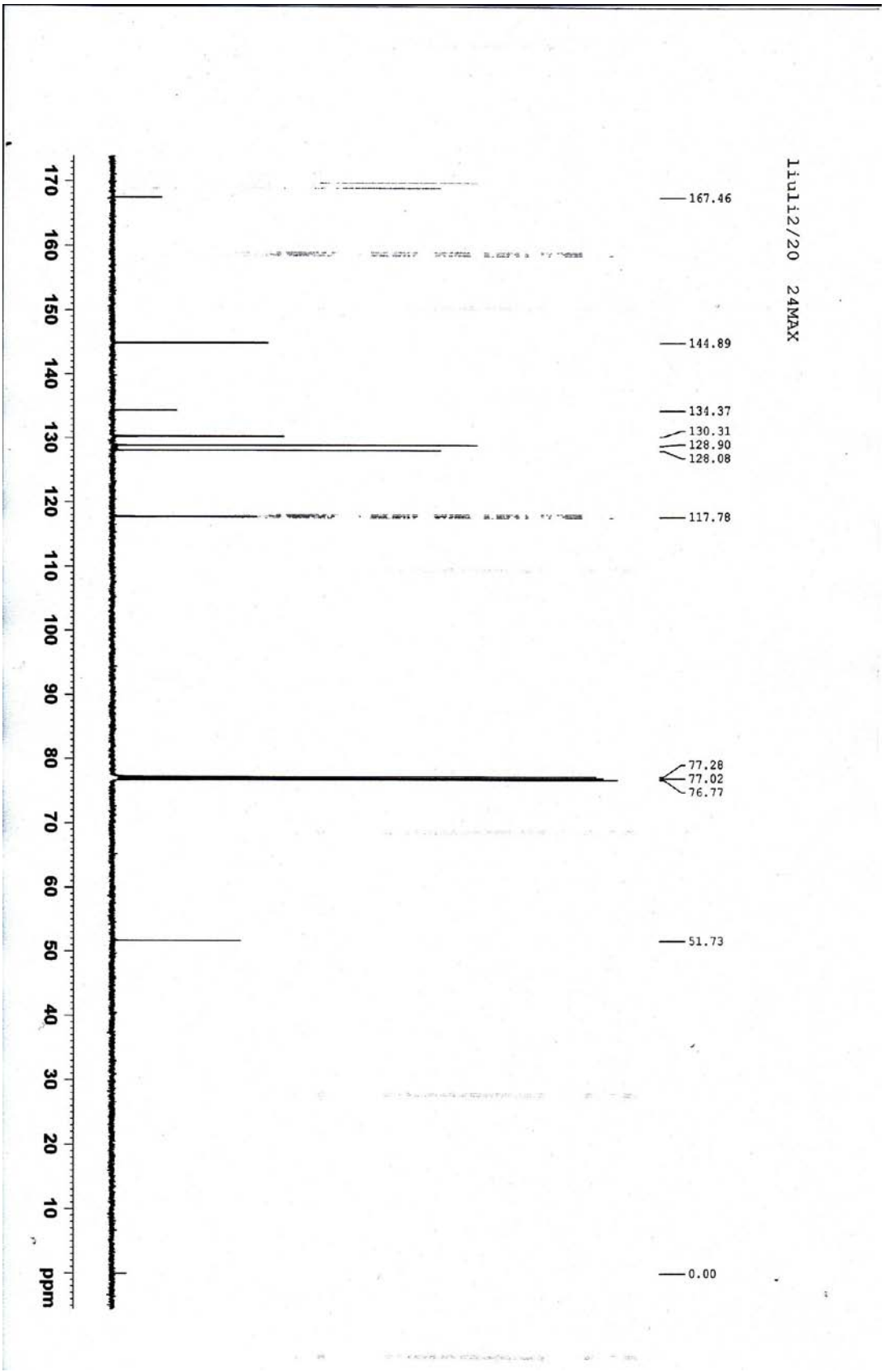
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51-7.53 (d, *J* = 8.0 Hz, 4H), 7.34-7.37 (t, *J* = 7.6 Hz, 4H), 7.24-7.28 (t, *J* = 8.0 Hz, 2H), 7.11 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.5, 128.7, 127.6, 126.5.

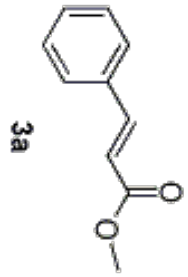
^{1}H- and ^{13}C-NMR spectra for compounds 3

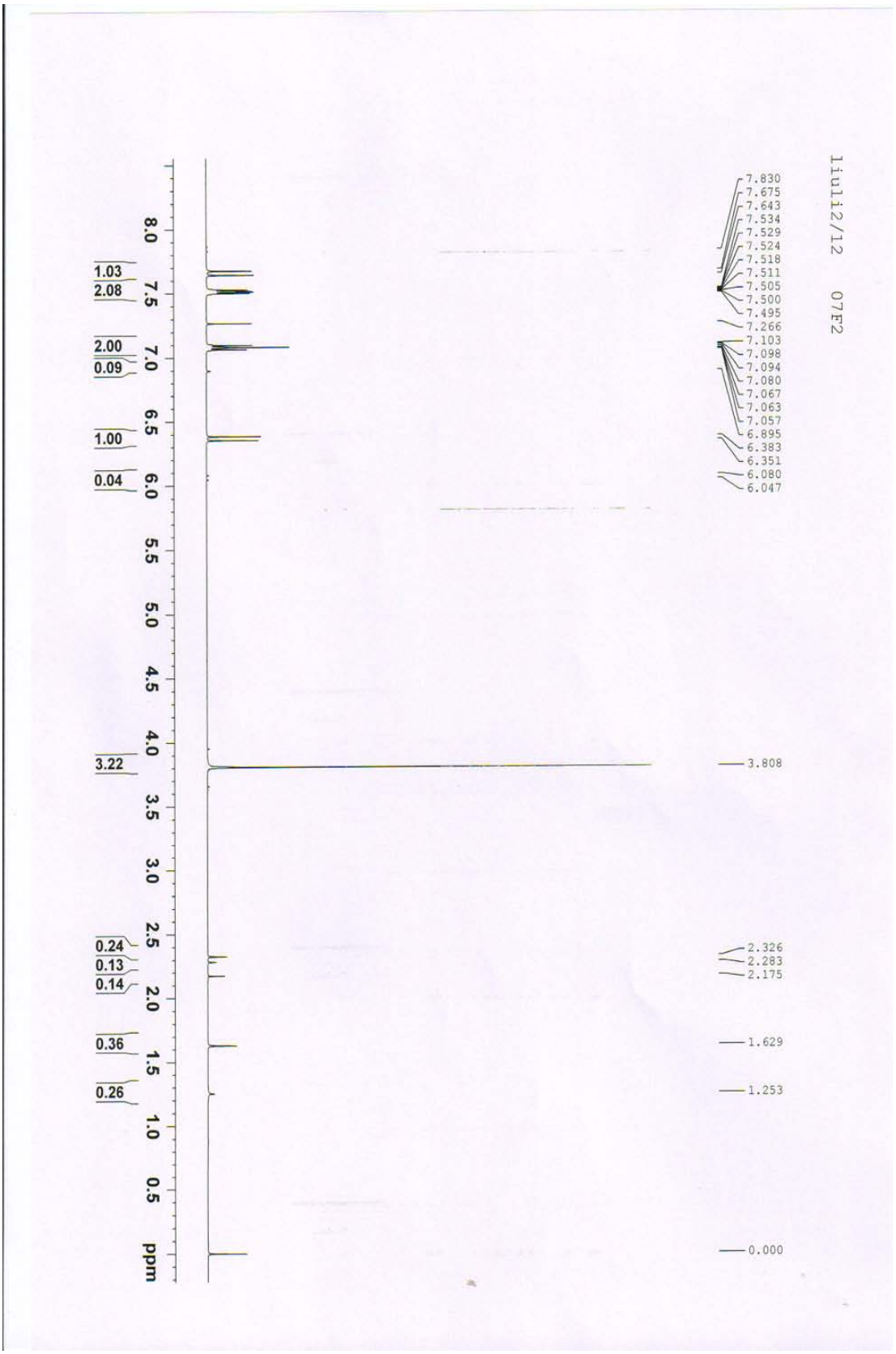


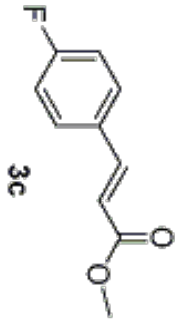
3a











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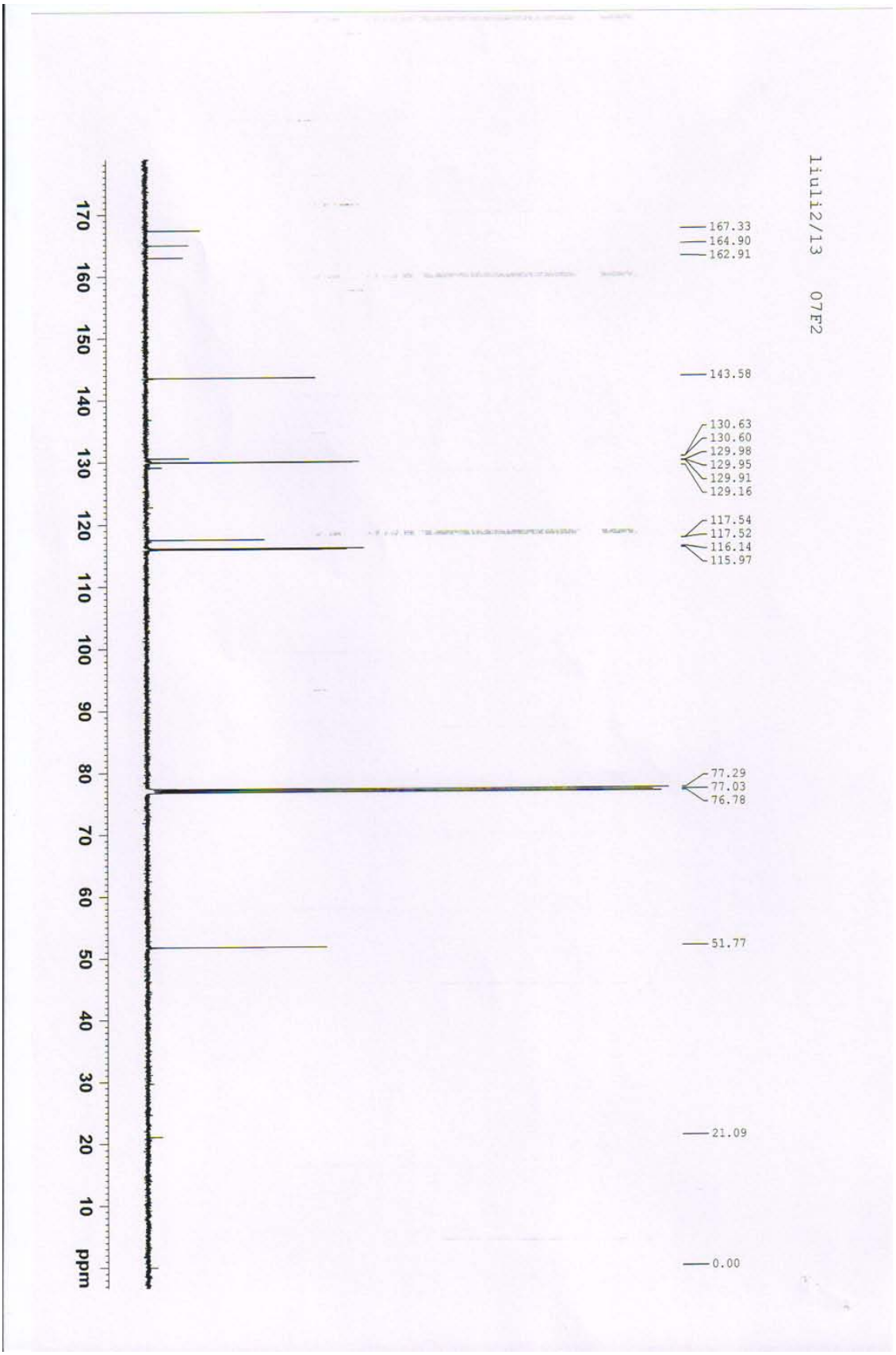

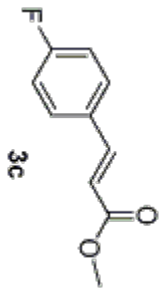

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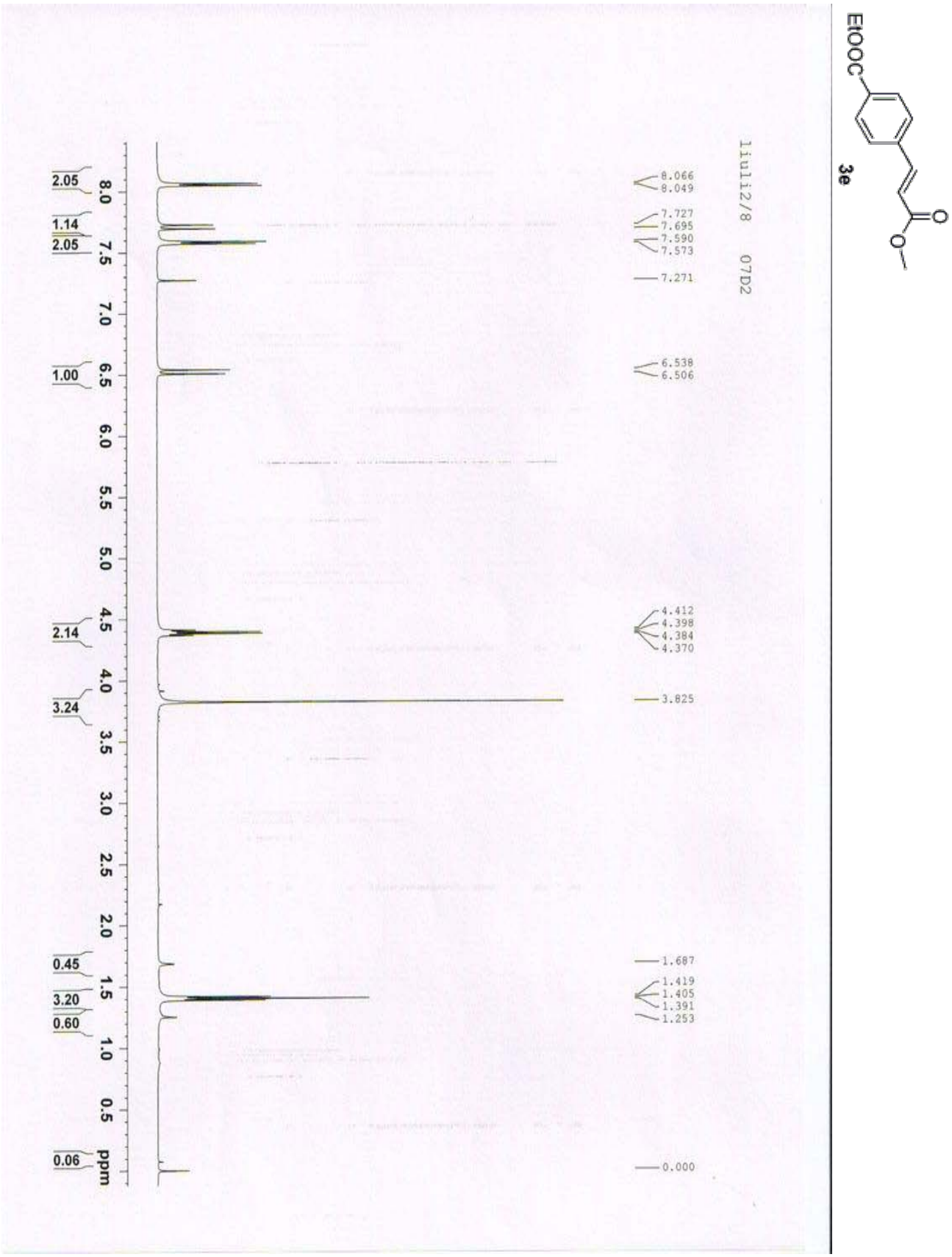

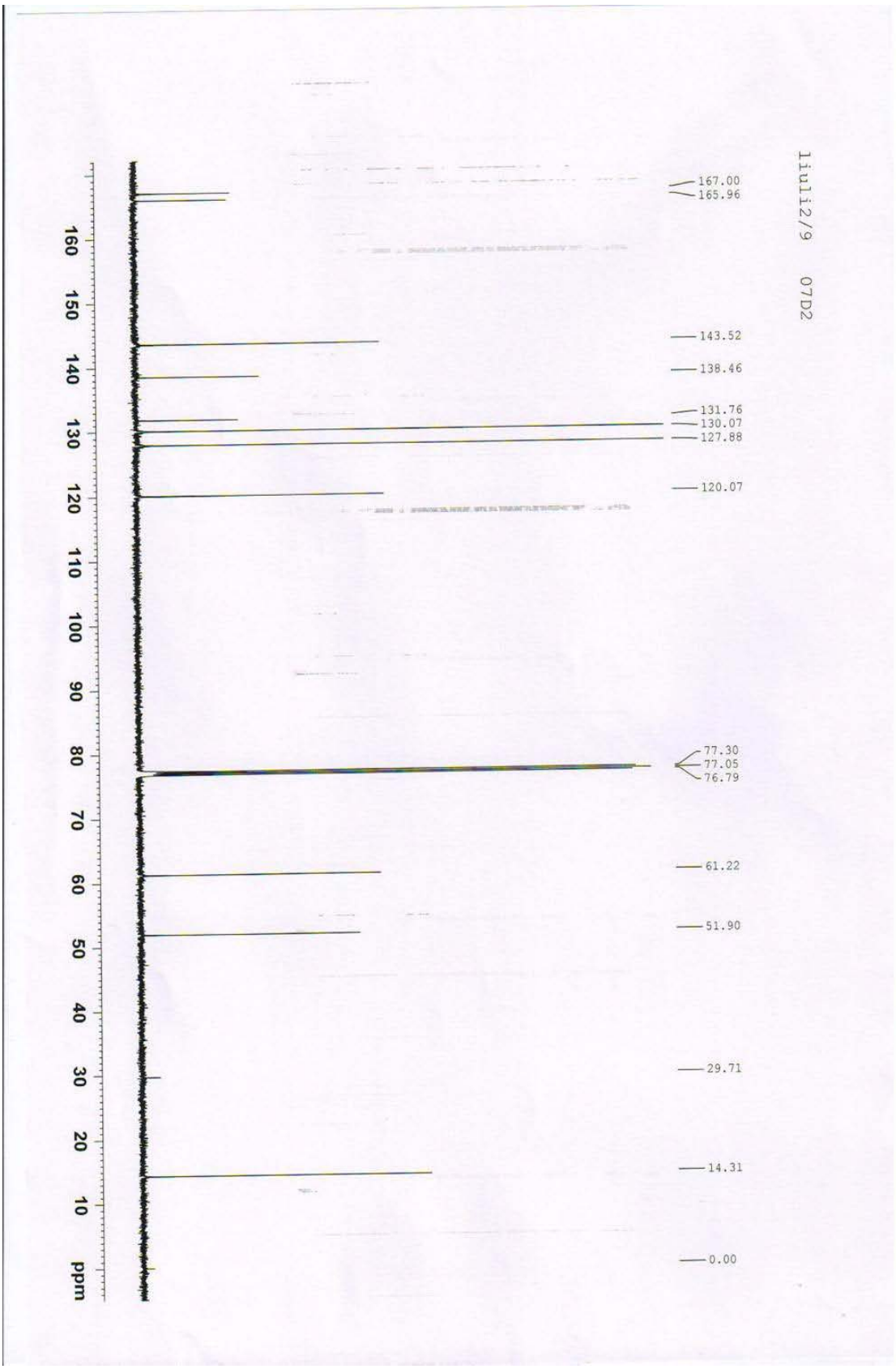

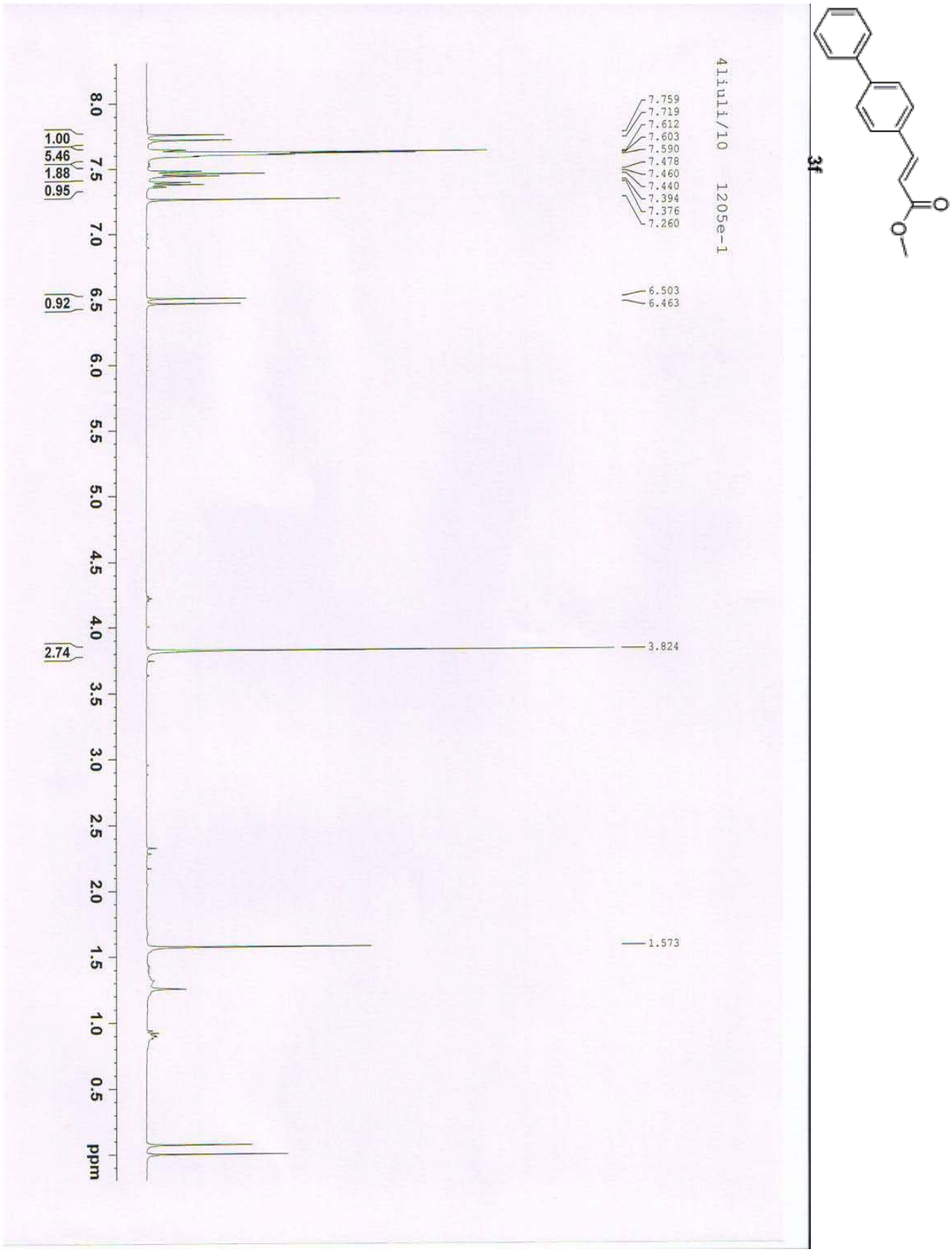

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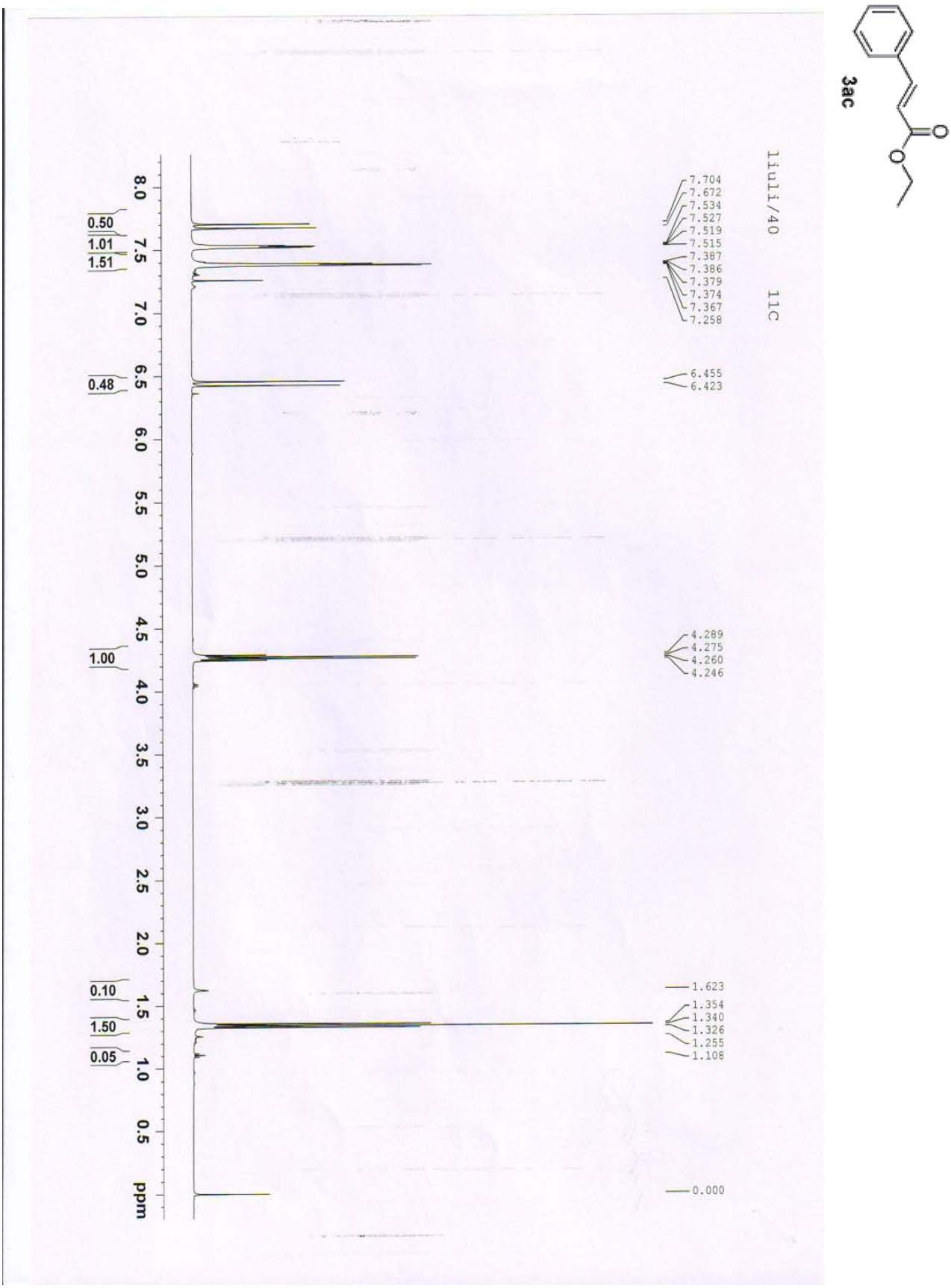

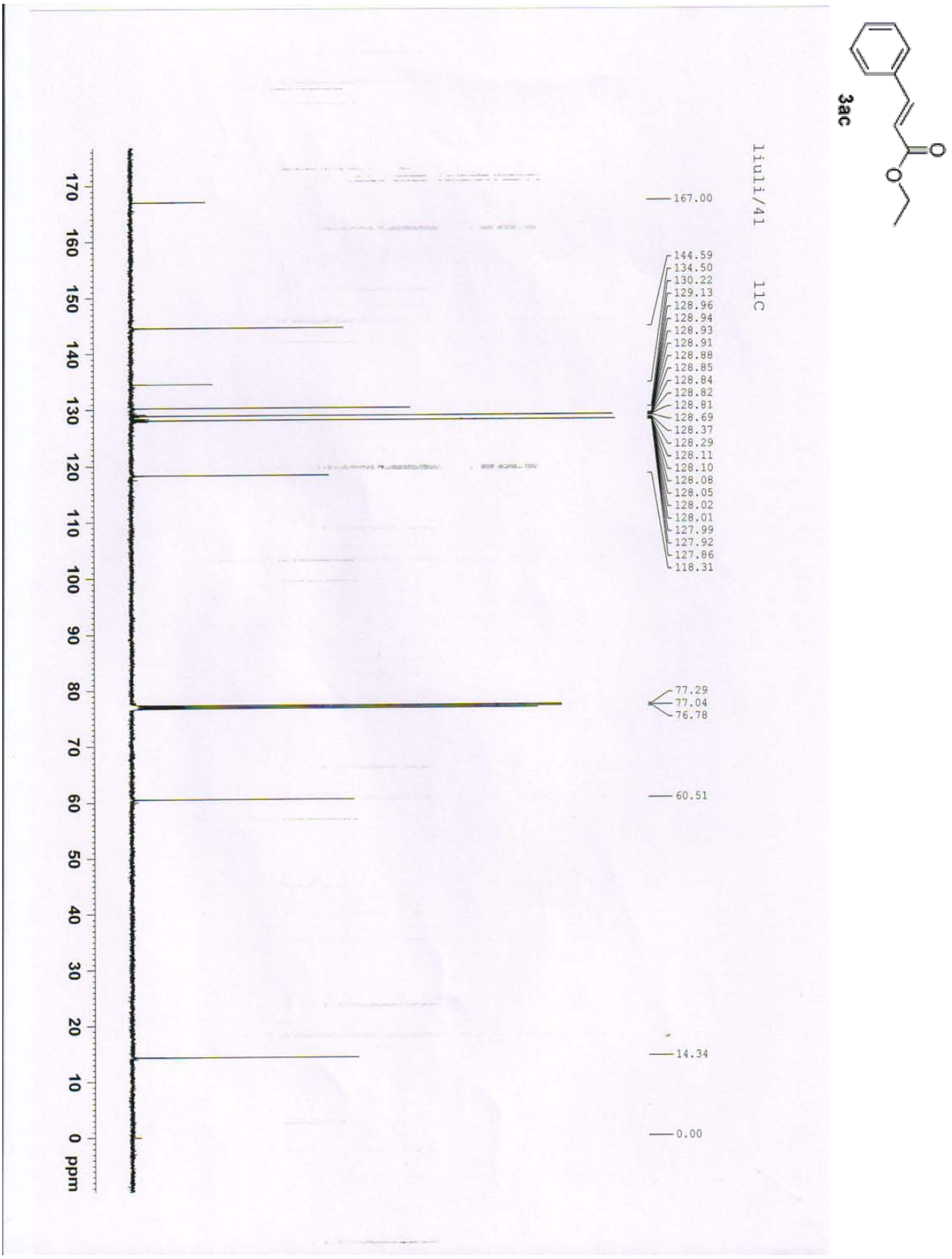

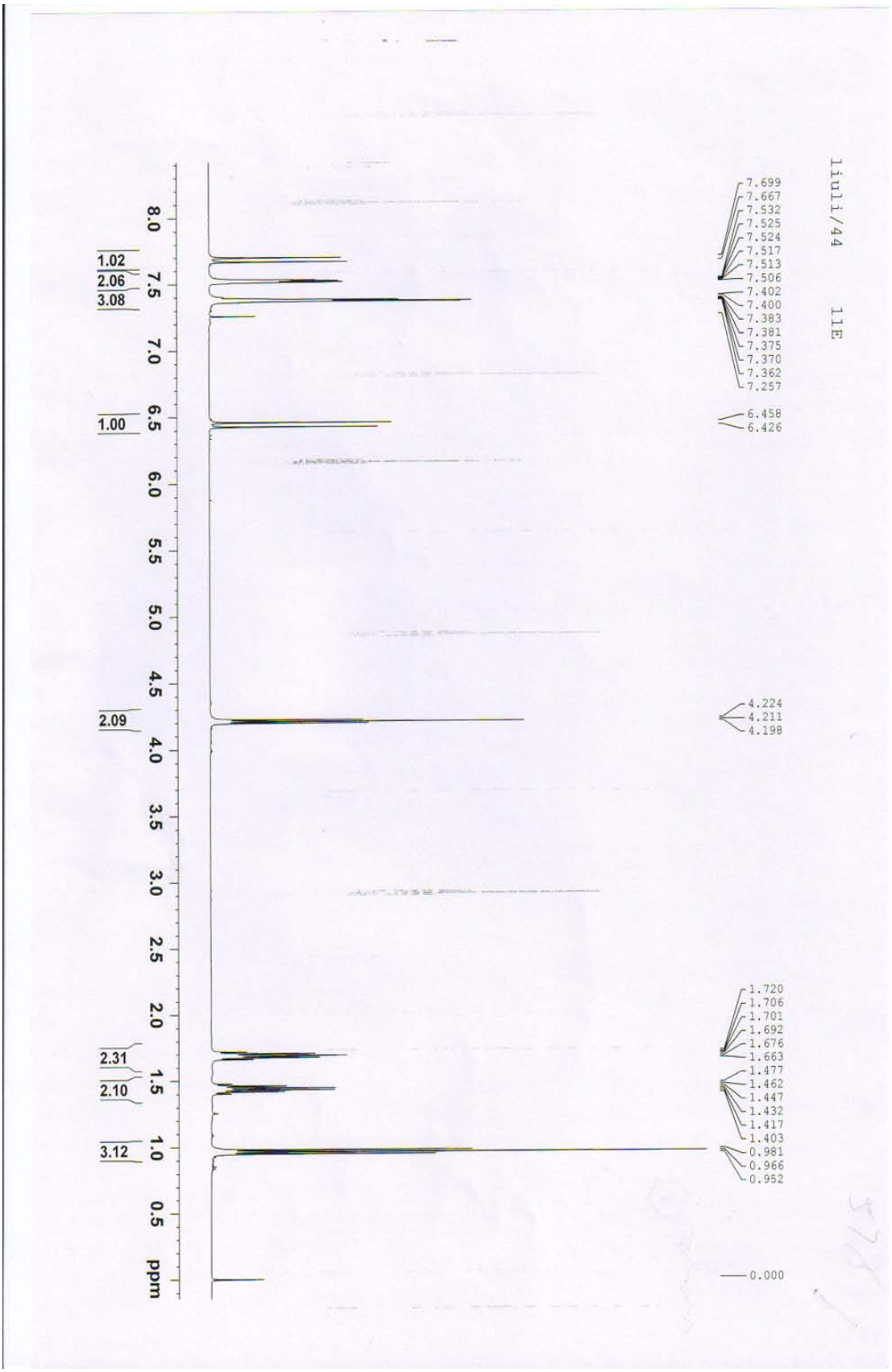

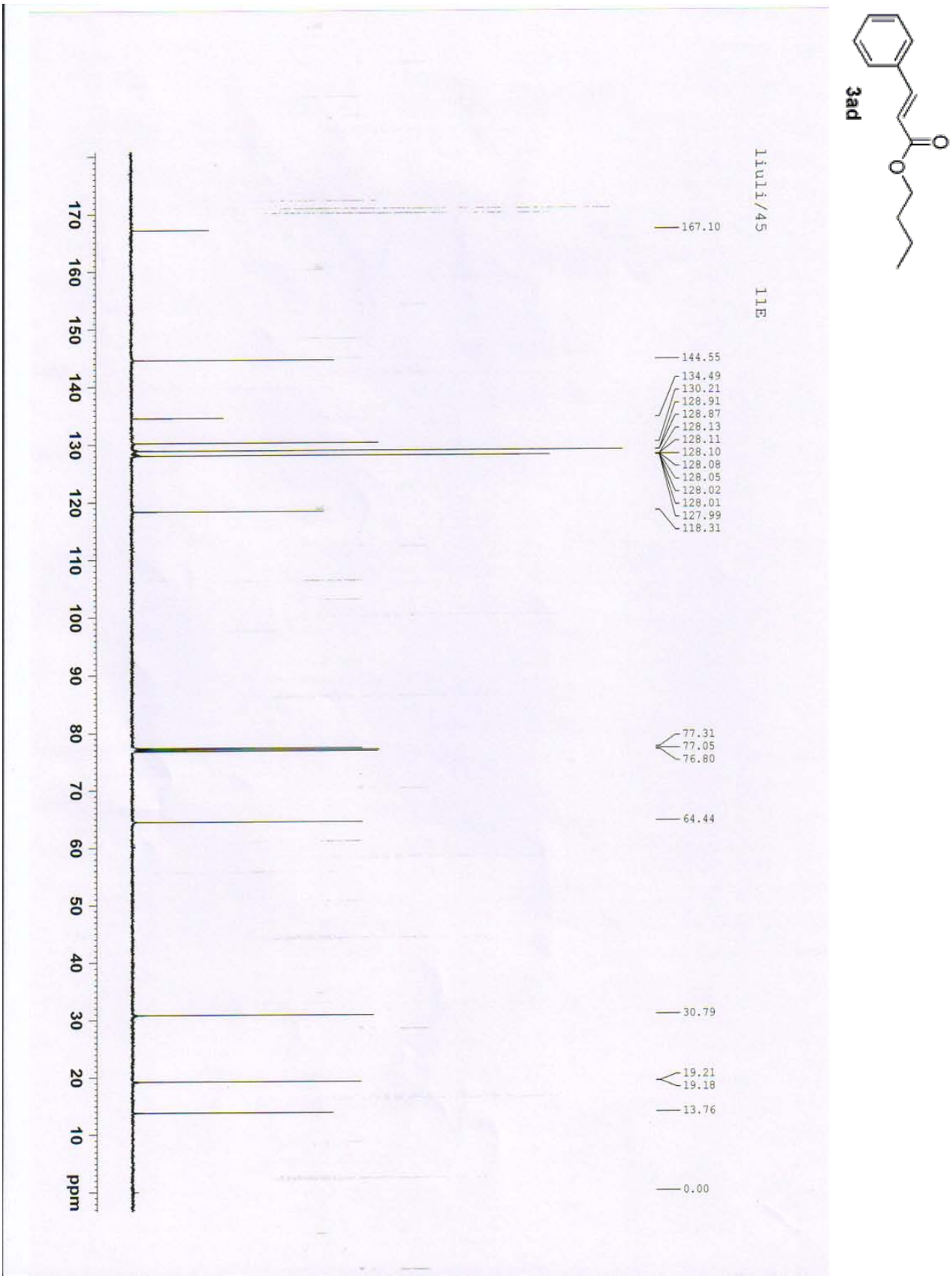

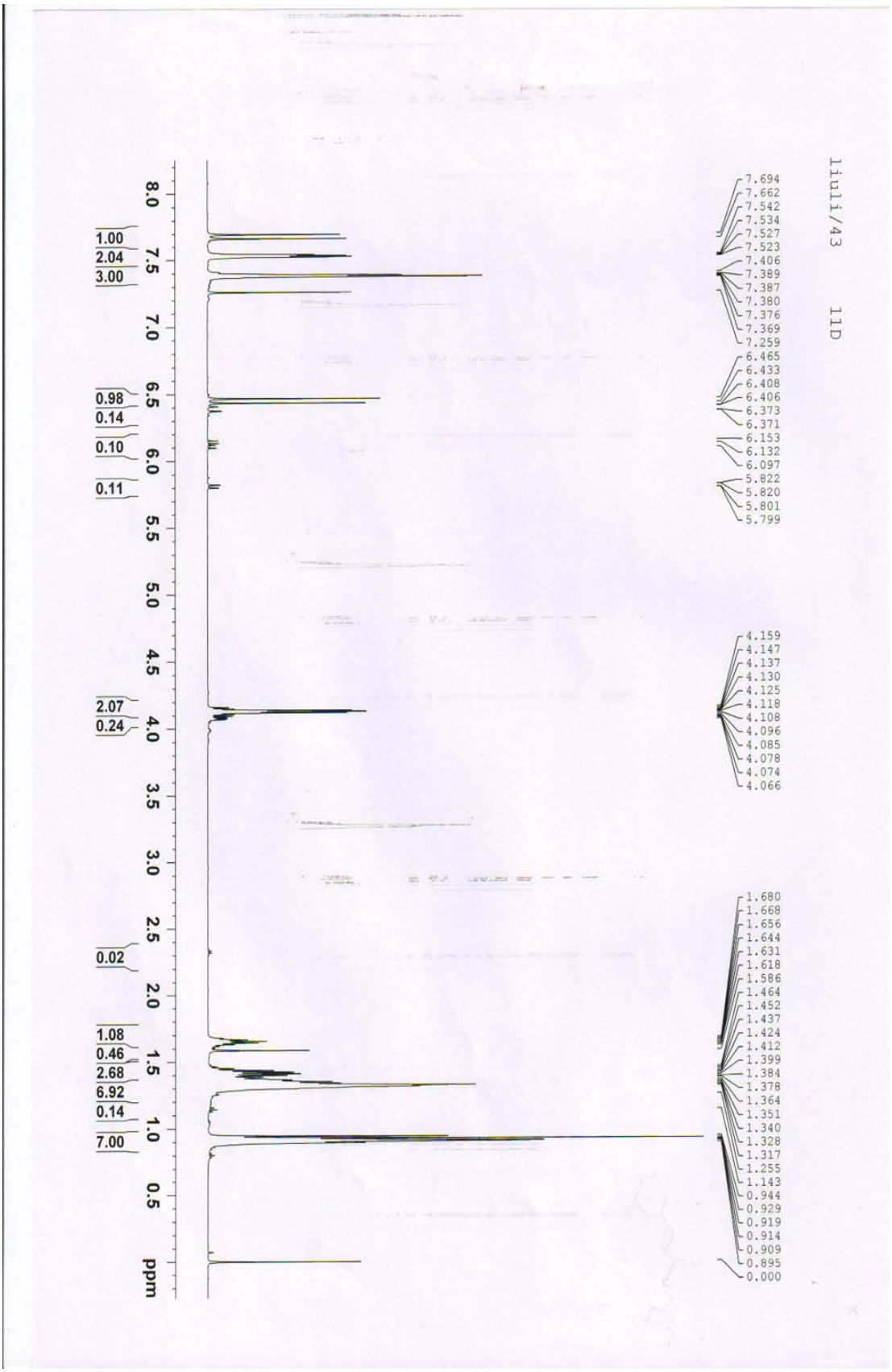

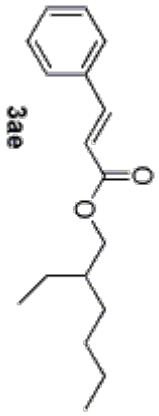

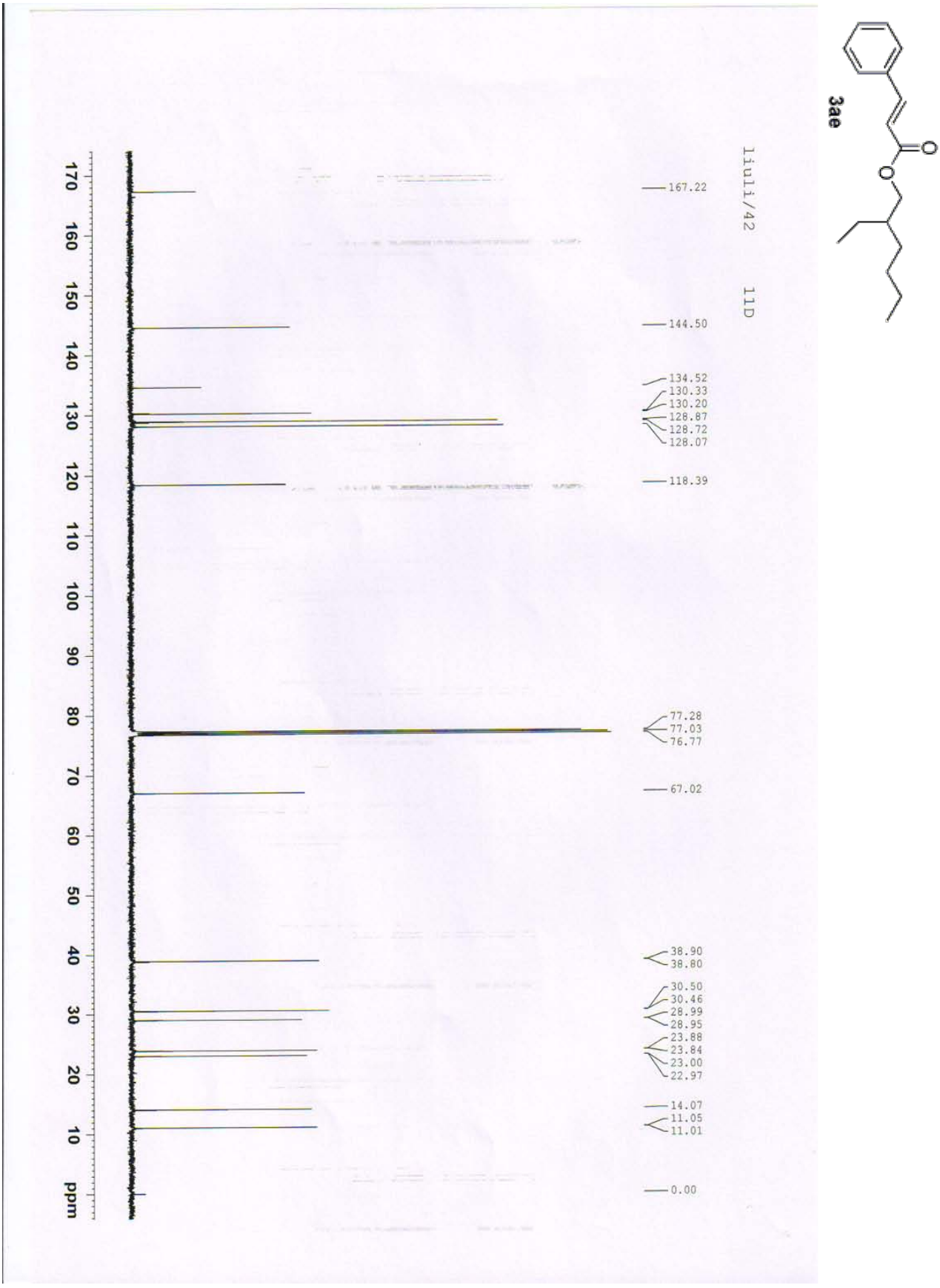
3ae
liuli/42 11D
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144.50
134.52
130.33
130.20
128.87
128.72
128.07
118.39
77.28
77.03
76.77
67.02
38.90
38.80
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28.95
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11.01
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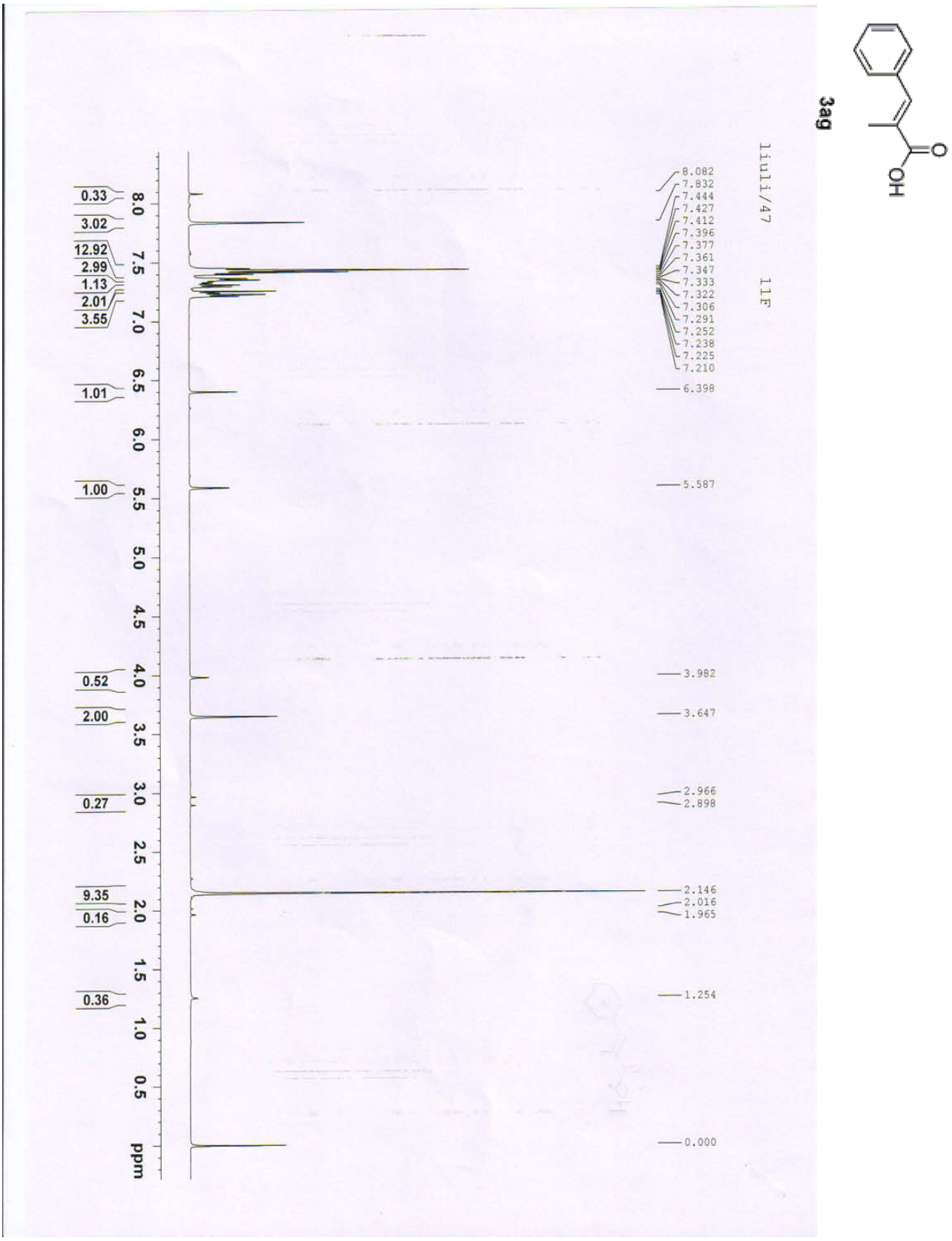

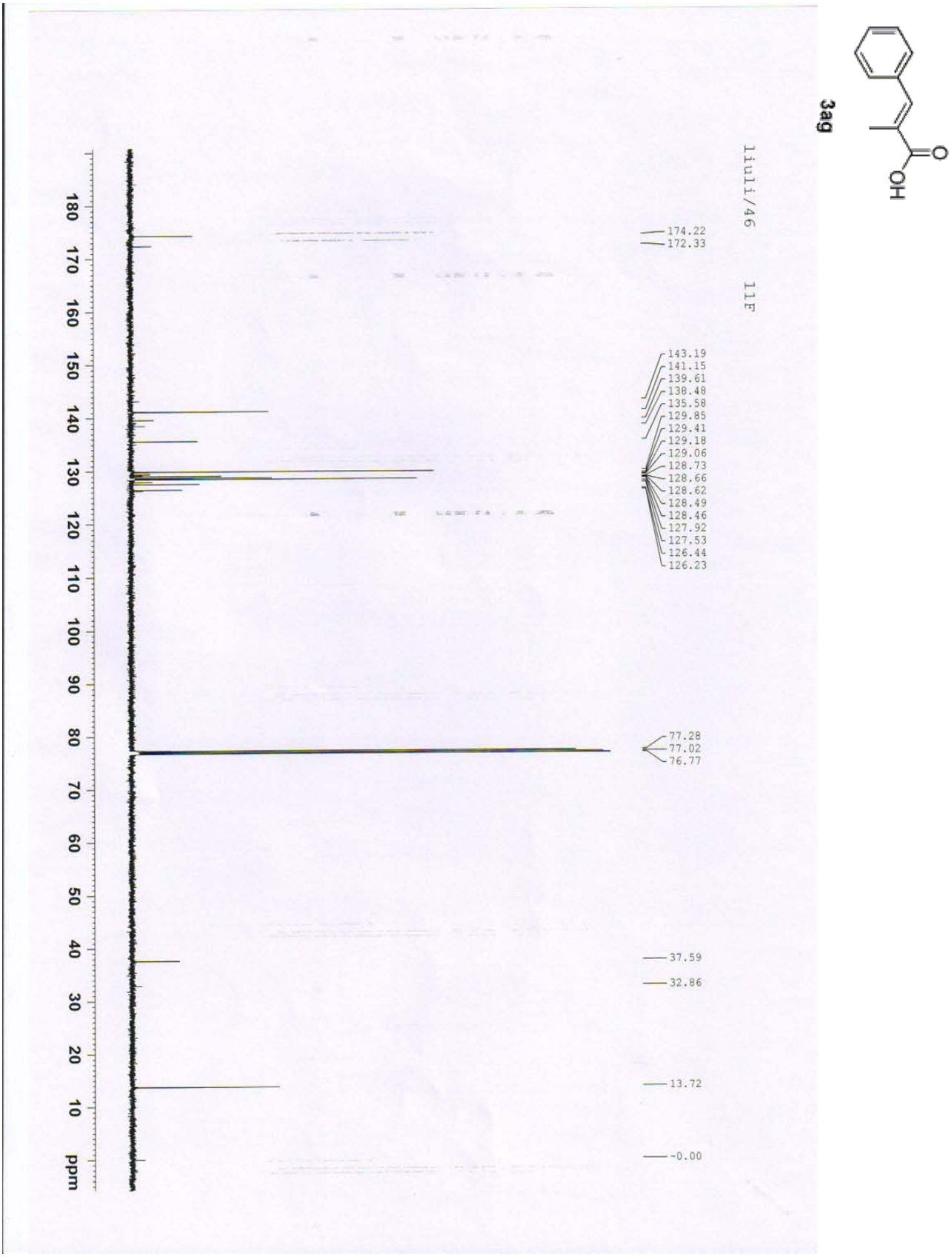

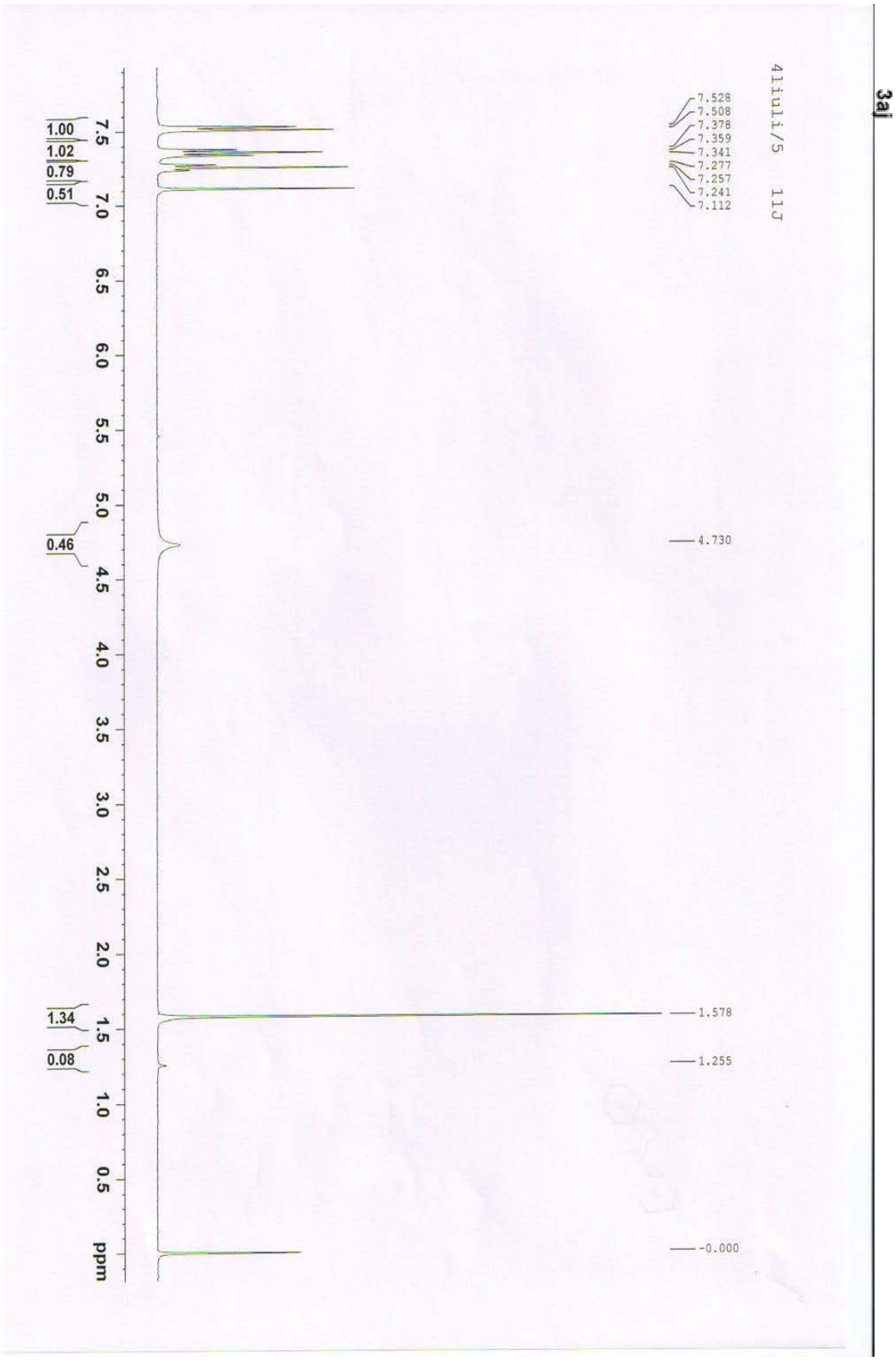
3aj
4liuli/5 11J
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7.378
7.359
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7.257
7.241
7.112
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1.255
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1.00
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0.51
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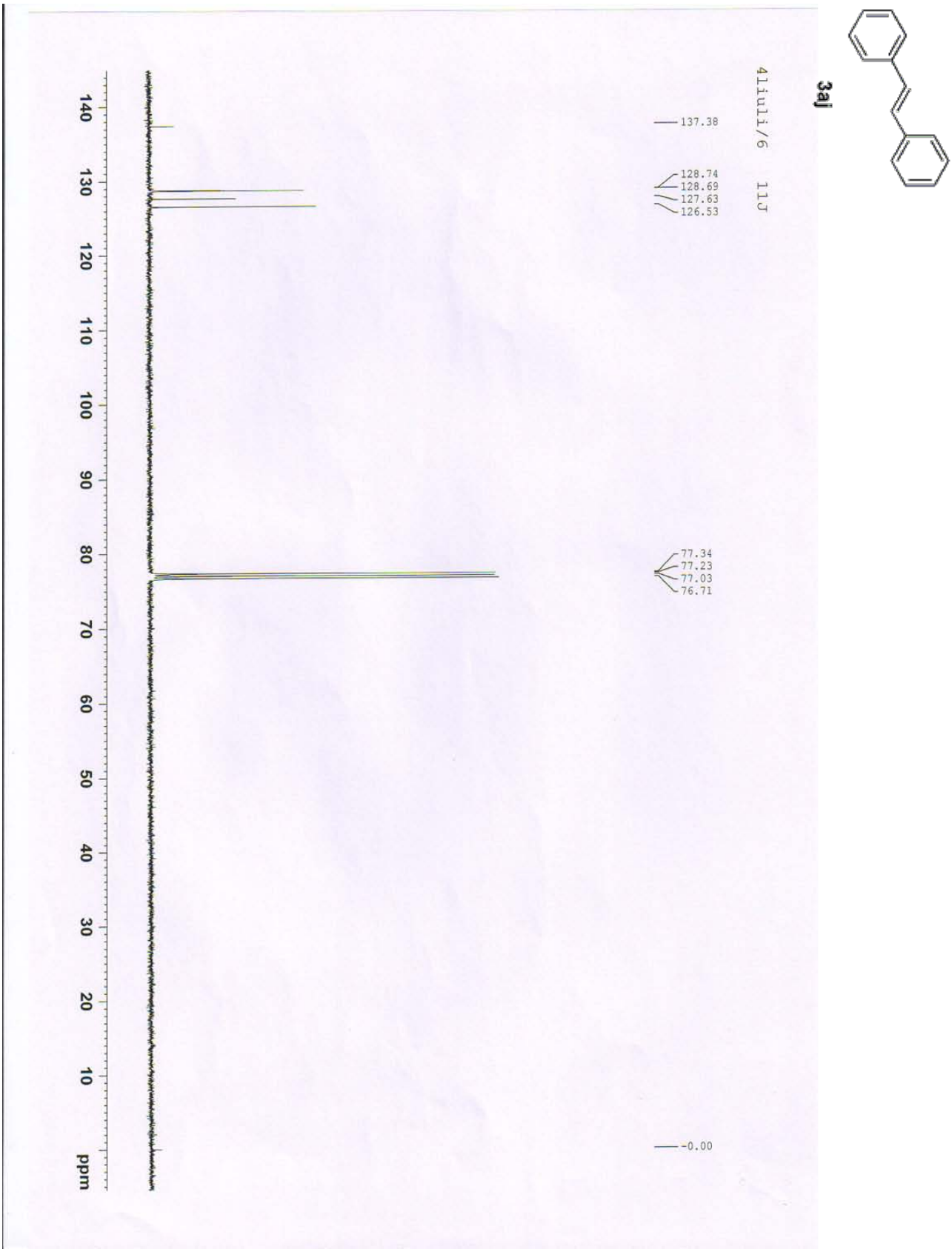
1.34
0.08
ppm


3aj
4liuli/6 11J
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128.69
127.63
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77.03
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140
130
120
110
100
90
80
70
60
50
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30
20
10
ppm

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