Supporting Information for

A mild synthetic strategy of removing acetic acid from fast pyrolysis bio-oils utilizing Friedel-Crafts acylation reactions

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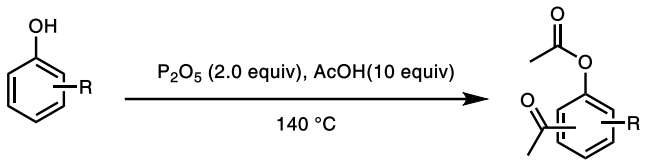
1. General information

Unless otherwise noted, commercially available reagents were purchased from Sigma-Aldrich, Acros Organics, Combi-Blocks, TCI or Alfa Aesar and used as received unless otherwise stated. Reaction temperatures were controlled by an IKAmag or DLAB temperature modulator unless otherwise indicated. Purified water was obtained using a Barnstead NANOpure Infinity UV/UF system. Brine solutions are saturated aqueous solutions of sodium chloride. Reaction progress was monitored by thin-layer chromatography (TLC). Analytical thin-layer chormatography (TLC) was performed with TLC Silica gel 60 F_{254} (Merck) and visualized by UV fluorescence quenching and $KMnO_4$ stain. Silicycle Silia*Flash* P60 Academic Silica gel (particle size 0.040-0.064 mm) was used for flash column chromatography. All NMR spectra were recorded on Bruker 400 MHz. Data for ^1H NMR are reported as follows: s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, sept = septuplet, m = multiplet, br s = broad singlet, br d= broad doublet, app = apparent. Data for ^{13}C are reported in terms of chemical shifts (δ ppm). High resolution mass spectra (HRMS) were obtained from Bruker ESI Q-TOF Mass Spectrometer with electrospray ionization (ESI+), atmospheric pressure chemical ionization (APCI+), or mixed ionization mode (MM: ESI-APCI+).

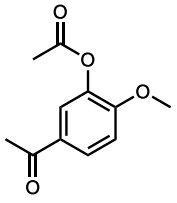
2. Experimental procedures and spectroscopic data

General procedure 1 for the Friedel-Crafts acylations



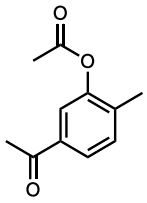
1 *3*

To a stirred solution of phenol **1** in acetic acid (10.0 equiv), phosphorus pentoxide (2.00 equiv) was added in one portion and the reaction mixture was allowed to stir at 140 ºC for 12 h. Upon completion, the reaction mixture was cooled to room temperature and quenched with saturated $NaHCO_3$ solution. The solution was extracted with CH_2Cl_2 and the aqueous layer was washed with CH_2Cl_2 twice. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4 and evaporated under reduced pressure and purified by flash column chromatography to generate acetylated compound **3**.



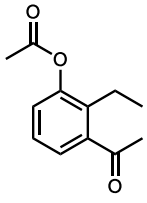
3a

5-acetyl-2-methoxyphenyl acetate (3a). The title compound was synthesized according to the general procedure 1 from 2-methoxyphenol (30 mg, 0.242 mmol), acetic acid (0.100 mL, 1.75 mmol) and phosphorous pentoxide (68 mg, 0.479 mmol). The product was purified by preparative thin-layer chromatography (1:4 EtOAc/hexanes): 27.0 mg (61%); R_f= 0.30 (1:2 EtOAc:hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (dd, *J* = 8.6, 2.2 Hz, 1H), 7.66 (d, *J* = 2.2 Hz, 1H), 7.00 (d, *J* = 8.6 Hz, 1H), 3.90 (s, 3H), 2.54 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.96, 168.80, 155.23, 139.57, 130.46, 128.10, 123.20, 111.57, 56.13, 26.30, 20.59; HRMS(ESI) *m/z* ($[M+Na]^+$) calcd for $C_{11}H_{12}NaO_4$: 231.0633, found: 231.0630.



3b

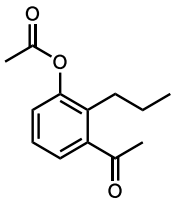
5-acetyl-2-methylphenyl acetate (3b). The title compound was synthesized according to the general procedure 1 from *o*-cresol (30.0 mg, 0.277 mmol), acetic acid (0.160 mL, 2.80 mmol) and phosphorous pentoxide (78.0 mg, 0.550 mmol). The product was purified by column chromatography on silica gel (1:9 EtOAc/hexanes): 26.0 mg (60%); R_f= 0.43 (1:6 EtOAc/hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 2.3 Hz, 1H), 7.81 (dd, *J* = 8.3, 2.3 Hz, 1H), 7.11 (d, *J* = 8.3 Hz, 1H), 2.58 (s, 3H), 2.35 (s, 3H), 2.24 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.17, 168.71, 153.11, 134.99, 131.43, 130.68, 127.50, 122.22, 26.62, 20.83, 16.27; HRMS(ESI) *m/z* ($[M+Na]^+$) calcd for $C_{11}H_{12}NaO_3$: 215.0684 , found: 215.0682.



3c

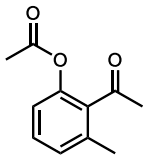
3-acetyl-2-ethylphenyl acetate (3c). The title compound was synthesized according to the general procedure 1 from 2-ethylphenol (30.0 mg, 0.246 mmol), acetic acid (0.140 mL, 2.25 mmol) and phosphorous pentoxide (69.0 mg, 0.486 mmol). The product was purified by preparative Thin-layer chromatography (1:4 EtOAc/hexanes): 26.0 mg (38%); R_f= 0.45 (1:4 EtOAc/hexanes twice)**;** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 2.2 Hz, 1H), 7.81 (dd, *J* = 8.4, 2.3 Hz, 1H), 7.12 (d, *J* = 8.4 Hz, 1H), 2.60 (d, *J* = 8.8 Hz, 5H), 2.34 (s, 3H), 1.22 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.26, 168.99, 152.63, 136.33, 135.13, 129.76, 127.45, 122.49, 26.61, 23.25, 20.89; HRMS(ESI) *m/z*

([M+Na]$^+$) calcd for $C_{12}H_{14}NaO_3$: 229.0840, found: 229.837.



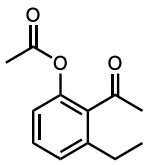
3d

3-acetyl-2-propylphenyl acetate (3d). The title compound was synthesized according to the general procedure 1 from 2-propylphenol (30.0 mg, 0.220 mmol), acetic acid (0.126 mL, 2.20 mmol) and phosphorous pentoxide (62.0 mg, 0.437 mmol). The product was purified by preparative thin-layer chromatography (1:4 EtOAc/hexanes): 26.0 mg (57%); R_f= 0.62 (1:3 EtOAc/hexanes twice); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 2.2 Hz, 1H), 7.81 (dd, *J* = 8.4, 2.3 Hz, 1H), 7.12 (d, *J* = 8.4 Hz, 1H), 2.59 (s, 3H), 2.57 – 2.52 (m, 2H), 2.34 (s, 3H), 1.68 – 1.57 (m, 2H), 0.95 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.23, 168.98, 152.75, 134.96, 134.86, 130.55, 127.45, 122.54, 32.21, 26.62, 23.01, 20.93, 13.93; HRMS(ESI) *m/z* ([M+Na]$^+$) calcd for $C_{13}H_{16}NaO_3$: 243.0997, found: 243.0950.



3e

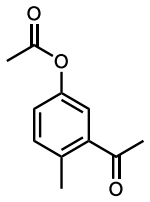
2-acetyl-3-methylphenyl acetate (3e). The title compound was synthesized according to the general procedure 1 from *m*-cresol (30.0 mg, 0.277 mmol), acetic acid (0.800 mL, 14.0 mmol) and phosphorous pentoxide (78.0 mg, 0.550 mmol). The product was purified by column chromatography on silica gel (1:9 EtOAc/hexanes): 30.0 mg (62%); R_f= 0.45 (1:2 EtOAc/hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.4 Hz, 1H), 7.01 (dd, *J* = 8.4, 2.5 Hz, 1H), 6.98 (d, *J* = 2.6 Hz, 1H), 2.57 (s, 3H), 2.54 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.34, 169.04, 152.67, 141.14, 135.09, 131.09, 124.98, 118.79, 29.47, 21.82, 21.13; HRMS(ESI) *m/z* ([M+Na]$^+$) calcd for $C_{11}H_{12}NaO_3$: 215.0684, found: 215.0682.



3f

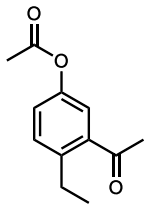
2-acetyl-3-ethylphenyl acetate (3f). The title compound was synthesized according to the general procedure 1 from 3-ethylphenol (30.0 mg, 0.246 mmol), acetic acid (0.140 mL, 0.245 mmol) and

phosphorous pentoxide (69.0 mg, 0.486 mmol). The product was purified by preparative thin-layer chromatography (1:4 EtOAc/hexanes): 17.0 mg (34%); R_f= 0.17 (1:4 EtOAc/hexanes)**;** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 9.2 Hz, 1H), 7.01 (dq, *J* = 4.0, 2.3 Hz, 2H), 2.89 (d, *J* = 7.5 Hz, 2H), 2.57 (s, 3H), 2.31 (s, 3H), 1.26 – 1.18 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.91, 169.09, 152.78, 146.92, 135.23, 130.77, 123.27, 118.75, 29.86, 27.15, 21.17, 15.45; HRMS(ESI) *m/z* ([M+Na]$^+$) calcd for $C_{12}H_{14}NaO_3$: 229.0840, found: 229.0834.



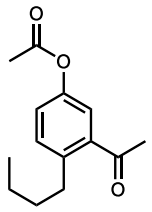
3g

3-acetyl-4-methylphenyl acetate (3g). The title compound was synthesized according to the general procedure 1 from *p*-cresol (30.0 mg, 0.277 mmol), acetic acid (0.800 mL, 14.0 mmol) and phosphorous pentoxide (78.0 mg, 0.550 mmol). The product was purified by column chromatography on silica gel (1:4 EtOAc/hexanes): 26.0 mg (56%); R_f= 0.61 (1:3 EtOAc/hexanes)'; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 2.4 Hz, 1H), 7.33 (dd, *J* = 8.2, 2.3 Hz, 1H), 7.00 (d, *J* = 8.2 Hz, 1H), 2.54 (s, 3H), 2.39 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.72, 169.74, 146.90, 135.87, 134.05, 130.71, 130.37, 123.56, 29.41, 21.18, 20.86; HRMS(ESI) *m/z* ([M+Na]$^+$) calcd for $C_{11}H_{12}NaO_3$: 215.0684, found: 215.0683.



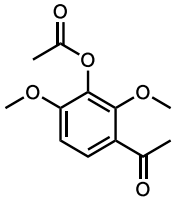
3h

3-acetyl-4-ethylphenyl acetate (3h). The title compound was synthesized according to the general procedure 1 from 4-ethylphenol (30.0 mg, 0.246 mmol), acetic acid (0.140 mL, 2.45 mmol) and phosphorous pentoxide (69.0 mg, 0.486 mmol). The product was purified by preparative thin-layer chromatography (1:8 EtOAc/hexanes): 20.0 mg (40%); R_f= 0.62 (1:8 EtOAc/hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 2.3 Hz, 1H), 7.36 (dd, *J* = 8.3, 2.3 Hz, 1H), 7.02 (d, *J* = 8.2 Hz, 1H), 2.69 (q, *J* = 7.6 Hz, 2H), 2.55 (s, 3H), 2.34 (s, 3H), 1.26 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.81, 169.73, 147.04, 142.11, 132.88, 130.47, 129.57, 123.61, 29.45, 28.24, 21.20, 15.41; HRMS(ESI) *m/z* ([M+Na]$^+$) calcd for $C_{12}H_{14}NaO_3$: 229.0840, found: 229.0837.



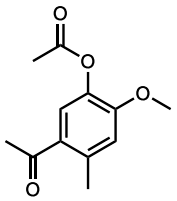
3i

3-acetyl-4-butylphenyl acetate (3i). The title compound was synthesized according to the general procedure 1 from 4-butylphenol (30.0 mg, 0.200 mmol), acetic acid (0.110 mL, 1.92 mmol) and phosphorous pentoxide (56.0 mg, 0.395 mmol). The product was purified by preparative thin-layer chromatography (1:4 EtOAc/hexanes): 28.0 mg (48%); R_f= 0.50 (1:4 EtOAc/hexanes twice); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 2.2 Hz, 1H), 7.34 (dd, *J* = 8.3, 2.3 Hz, 1H), 7.01 (d, *J* = 8.2 Hz, 1H), 2.67 – 2.61 (m, 2H), 2.55 (s, 3H), 2.33 (s, 3H), 1.65 – 1.52 (m, 2H), 1.43 – 1.31 (m, 2H), 0.94 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.81, 169.70, 147.03, 140.85, 130.41, 130.05, 123.52, 34.99, 33.45, 29.46, 22.31, 21.20, 13.90; HRMS(ESI) *m/z* ([M+Na]$^+$) calcd for $C_{14}H_{18}NaO_3$: 257.1153, found: 257.1149.



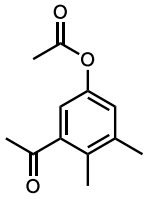
3j

3-acetyl-2,6-dimethoxyphenyl acetate (3j). The title compound was synthesized according to the general procedure 1 from 2,6-dimethoxyphenol (154 mg, 0.100 mmol), acetic acid (0.572 mL, 10.0 mmol) and phosphorous pentoxide (284 mg, 2.00 mmol). But the reaction time was changed for 1 hour. The product was purified by column chromatography on silica gel (1:3→1:2 EtOAc/hexanes): 37.9 mg (16%) And then left mixture was purified by preparative Thin-layer chromatography (1:8 EtOAc/hexanes): 14.4 mg (6%). The uncompleted compound that was purified by column chromatography was reacted according to the general procedure 1, but reaction time was 1 h. The product was purified by column chromatography on silica gel (1:3→1:2 EtOAc/hexanes): 7.8 mg (3%). The product from 2,6-dimethoxyphenol was 25% yield; R_f= 0.27 (1:2 EtOAc/hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.9 Hz, 1H), 6.77 (d, *J* = 8.9 Hz, 1H), 3.87 (s, 6H), 2.59 (s, 3H), 2.37 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.39, 168.37, 155.97, 153.36, 133.08, 128.40, 125.66, 107.15, 61.93, 56.31, 30.63, 20.50; HRMS(ESI) *m/z* ([M+Na]$^+$) calcd for $C_{12}H_{14}NaO_5$: 261.0738, found: 261.0735.



3k

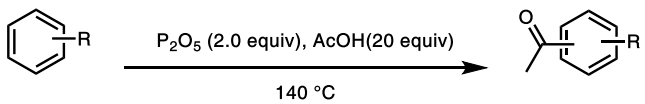
5-acetyl-2-methoxy-4-methylphenyl acetate (3k). The title compound was synthesized according to the general procedure 1 from 2-methoxy-4-methylphenol (30.0 mg, 0.217 mmol), acetic acid (0.180 mL, 3.15 mmol) and phosphorous pentoxide (61.0 mg, 0.430 mmol). The product was purified by preparative thin-layer chromatography (1:4 EtOAc/hexanes): 27.0 mg (57%); R_f= 0.53 (1:3 EtOAc/hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (s, 1H), 6.79 (s, 1H), 3.87 (s, 3H), 2.57 (s, 3H), 2.52 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.63, 169.02, 153.42, 139.90, 136.77, 129.26, 125.02, 115.59, 55.96, 29.08, 22.41, 20.60; HRMS(ESI) *m/z* ([M+Na]$^+$) calcd for $C_{12}H_{14}NaO_4$: 245.0789, found: 245.0786.



3l

3-acetyl-4,5-dimethylphenyl acetate (3l). The title compound was synthesized according to the general procedure 1 from 3,4-dimethoxyphenol (30.0 mg, 0.246 mmol), acetic acid (0.140 mL, 2.45 mmol) and phosphorous pentoxide (69.0 mg, 0.486 mmol). The product was purified by preparative thin-layer chromatography (1:4 EtOAc/hexanes): 26.0 mg (53%); R_f= 0.44 (1:3 EtOAc/hexanes twice); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (s, 1H), 6.88 (s, 1H), 2.53 (s, 3H), 2.34 (s, 3H), 2.29 (d, *J* = 1.1 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.10, 169.89, 147.24, 143.40, 134.54, 131.52, 127.74, 124.75, 29.31, 21.20, 19.98, 19.20; HRMS(ESI) *m/z* ([M+Na]$^+$) calcd for $C_{12}H_{14}NaO_3$: 229.0840, found: .229.0838

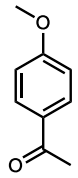
General procedure 2 for the Friedel-Crafts acylations



4 *5*

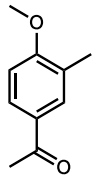
To a stirred solution of compound **3** in acetic acid (20.0 equiv), phosphorus pentoxide (2.00 equiv) was added in one portion and the reaction mixture was allowed to stir at 140 °C for 12 h. Upon completion,

the reaction mixture was cooled to room temperature and quenched with saturated $NaHCO_3$ solution. It was extracted with CH_2Cl_2 and the aqueous layer was washed with CH_2Cl_2 twice. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4 and evaporated under reduced pressure and purified by flash column chromatography to generate acetylated compound **5**.



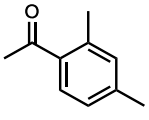
5a

1-(4-methoxyphenyl)ethan-1-one (5a). The title compound was synthesized according to the general procedure 2 from 1-(4-methoxyphenyl)ethan-1-one (1.05 mL, 9.25 mmol), acetic acid (10.6 mL, 18.5 mmol) and phosphorous pentoxide (2.26 g, 18.5 mmol). But the reaction time was changed for 1 h. The product was purified by column chromatography on silica gel (1:4→1:3→1:2 EtOAc/hexanes): 966 mg (70%); R_f= 0.32 (1:8 EtOAc:hexanes)**;** ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 – 7.92 (m, 2H), 6.96 – 6.89 (m, 2H), 3.87 (s, 3H), 2.56 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.80, 163.50, 130.60, 130.37, 113.70, 55.48, 26.35; HRMS(ESI) *m/z* ([M+Na]$^+$) calcd for $C_9H_{10}NaO_2$: 173.0578, found: 173.0576.



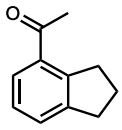
5b

1-(4-methoxy-3-methylphenyl)ethan-1-one (5b). The title compound was synthesized according to the general procedure 2 from 1-methoxy-2-methylbenzene (0.100mL, 0.806 mmol), acetic acid (0.140 mL, 2.45 mmol) and phosphorous pentoxide (116 mg, 0.817 mmol). The product was purified by column chromatography on silica gel (1:8 EtOAc/hexanes): 84.0 mg (53%); R_f= 0.30 (1:8 EtOAc/hexanes)**;** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (dd, *J* = 8.6, 2.4 Hz, 1H), 7.77 (d, *J* = 2.8 Hz, 1H), 6.84 (d, *J* = 8.6 Hz, 1H), 3.89 (s, 3H), 2.54 (s, 3H), 2.24 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.12, 161.78, 130.91, 129.86, 128.49, 126.76, 109.16, 55.53, 26.32, 16.25; HRMS(ESI) *m/z* ([M+Na]$^+$) calcd for $C_{10}H_{12}NaO_2$: 187.0735, found: 187.0737.



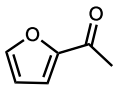
5c

1-(2,4-dimethylphenyl)ethan-1-one (5c). The title compound was synthesized according to the general procedure 2 from *m*-xylene (30.0 mg, 0.283 mmol), acetic acid (0.160 mL, 1.75 mmol) and phosphorous pentoxide (80.0 mg, 0.564 mmol). The product was purified by column chromatography on silica gel (1:13 EtOAc/hexanes): 17.0 mg (42%); R_f= 0.45 (1:8 EtOAc/hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 – 7.59 (m, 1H), 7.07 (d, *J* = 7.1 Hz, 2H), 2.56 (s, 3H), 2.52 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.04, 142.17, 138.96, 134.71, 132.95, 130.00, 126.31, 29.36, 21.82, 21.37; HRMS(ESI) *m/z* ([M+Na]$^+$) calcd for $C_{10}H_{12}NaO$: 171.0785, found: 171.0782.



5d

1-(2,3-dihydro-1H-inden-4-yl)ethan-1-one (5d). The title compound was synthesized according to the general procedure 2 from 2,3-dihydro-1-1H-indene (30.0 mg, 0.258 mmol), acetic acid (0.700 mL, 12.2 mmol) and phosphorous pentoxide (73.2 mg, 0.516 mmol). The product was purified by column chromatography on silica gel (1:9 EtOAc/hexanes): 18.0 mg (45%); R_f= 0.34 (1:7 EtOAc/hexanes twice)**;** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 1.3 Hz, 1H), 7.75 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.29 (d, *J* = 7.7 Hz, 1H), 2.95 (t, *J* = 7.5 Hz, 4H), 2.58 (s, 3H), 2.12 (p, *J* = 7.5 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.27, 150.27, 144.79, 135.74, 126.90, 124.32, 124.25, 33.03, 32.57, 26.73, 25.40; HRMS(ESI) *m/z* ([M+Na]$^+$) calcd for $C_{11}H_{12}NaO$: 183.0785, found: 183.0782.



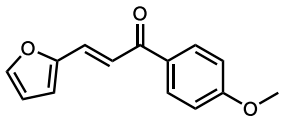
5e

1-(furan-3-yl)ethan-1-one (5e). The title compound was synthesized according to the general procedure 2 from furan (0.100 mL, 1.38 mmol), acetic acid (0.250 mL, 4.37 mmol) and phosphorous pentoxide (208 mg, 1.47 mmol). The product was purified by column chromatography (1:4 EtOAc/hexanes): 63.0 mg (59%); R_f= 0.39 (1:9 EtOAc/Petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (s, 1H), 7.17 (dd, *J* = 3.5, 0.6 Hz, 1H), 6.52 (dd, *J* = 3.6, 1.8 Hz, 1H), 2.47 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 186.93, 152.87, 146.47, 117.31, 112.28, 26.02; HRMS(ESI) *m/z* ([M+Na]$^+$) calcd for $C_6H_6NaO_2$: 133.0265, found: 133.0262.

General procedure 3 for the Claisen-Schmidt condensation

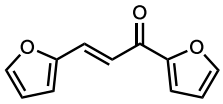
To a solution of furfural **6** in methanol (0.5 M) at 0 °C was added slowly aqueous NaOH 10 wt% solution (0.50 M), followed by slow addition of acetylated compounds from the Friedel-Crafts acylation reactions. The reaction mixture was warmed to room temperature and stirred for 12 h. The aqueous

phase was extracted with CH_2Cl_2 and then the combined organic layer was washed with brine and dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography.



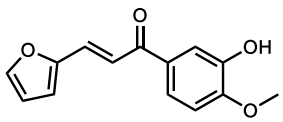
7

(*E*)-3-(furan-2-yl)-1-(4-methoxyphenyl)prop-2-en-1-one (7). The title compound was synthesized according to the general procedure 3 from 1-(4-methoxyphenyl)ethan-1-one (50.0 mg, 0.333 mmol), furfural **6** (0.270 mL, 3.33 mmol), NaOH 10 wt% (0.670 mL, 0.50 M) and methanol (0.670 mL, 0.50 M). The product was purified by column chromatography on silica gel (1:8 EtOAc/hexanes): 49.0mg (64%); R_f= 0.29 (1:4 EtOAc/hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, J = 8.9 Hz, 2H), 7.59 (d, J = 15.3 Hz, 1H), 7.52 (d, J = 1.8 Hz, 1H), 7.47 (d, J = 15.4 Hz, 1H), 6.98 (d, J = 8.9 Hz, 2H), 6.70 (d, J = 3.4 Hz, 1H), 6.51 (dd, J = 3.4, 1.8 Hz, 1H), 3.89 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.15, 163.52, 151.94, 144.78, 131.19, 130.82, 130.06, 119.33, 115.84, 113.93, 112.69, 55.56; HRMS(ESI) *m/z* ([M+Na]$^+$) calcd for $C_{14}H_{12}NaO_3$: 251.0684, found: 251.0682



8

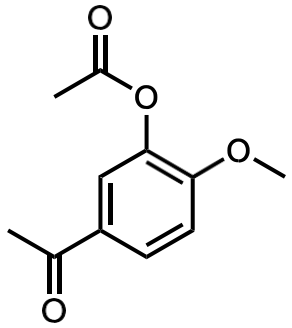
(*E*)-1,3-di(furan-2-yl)prop-2-en-1-one (8). The title compound was synthesized according to the general procedure 3 from 2-acetylfuran (1.00 g, 9.08 mmol), furfural **6** (0.790 mL, 9.08 mmol), NaOH 10 wt% (18.2 mL, 0.50 M) and methanol (18.2 mL, 0.50 M). The product was purified by column chromatography on silica gel (1:8 EtOAc/hexanes): 1.26 g (74%); R_f= 0.16 (1:8 EtOAc/hexanes); ^{1}H NMR (400 MHz, $CDCl_3$δ 7.51 (dd, *J* = 1.8, 0.8 Hz, 1H), 7.47 (d, *J* = 15.5 Hz, 1H), 7.37 (d, *J* = 1.8 Hz, 1H), 7.17 (dd, *J* = 3.6, 0.8 Hz, 1H), 7.17 (d, *J* = 15.5 Hz, 1H), 6.57 (d, *J* = 3.4 Hz, 1H), 6.42 (dd, *J* = 3.5, 1.7 Hz, 1H), 6.34 (dd, *J* = 3.4, 1.8 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.17, 153.33, 151.14, 146.34, 144.81, 129.39, 118.52, 117.17, 116.07, 112.43, 112.21; HRMS(ESI) *m/z* ([M+Na]$^+$) calcd for $C_{11}H_8NaO_3$: 211.0371, found: 211.0368.



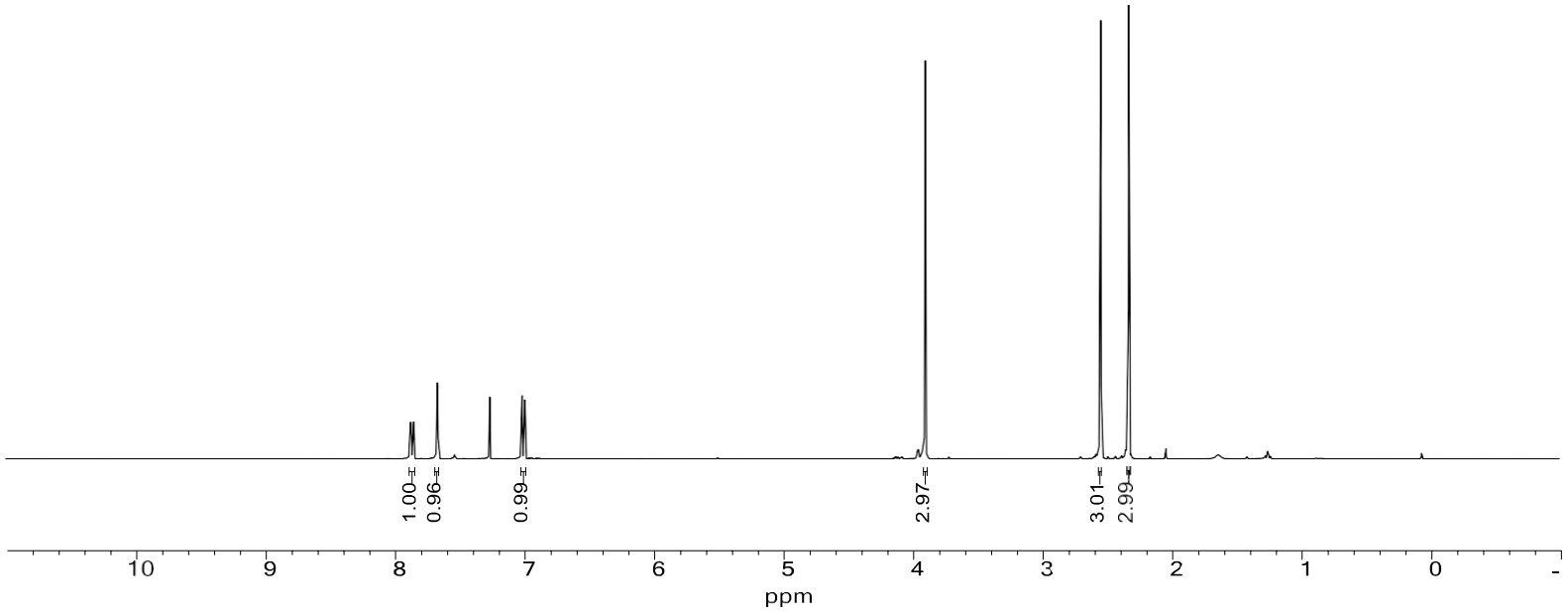
9

(*E*)-3-(furan-2-yl)-1-(3-hydroxy-4-methoxyphenyl)prop-2-en-1-one (9). The title compound was

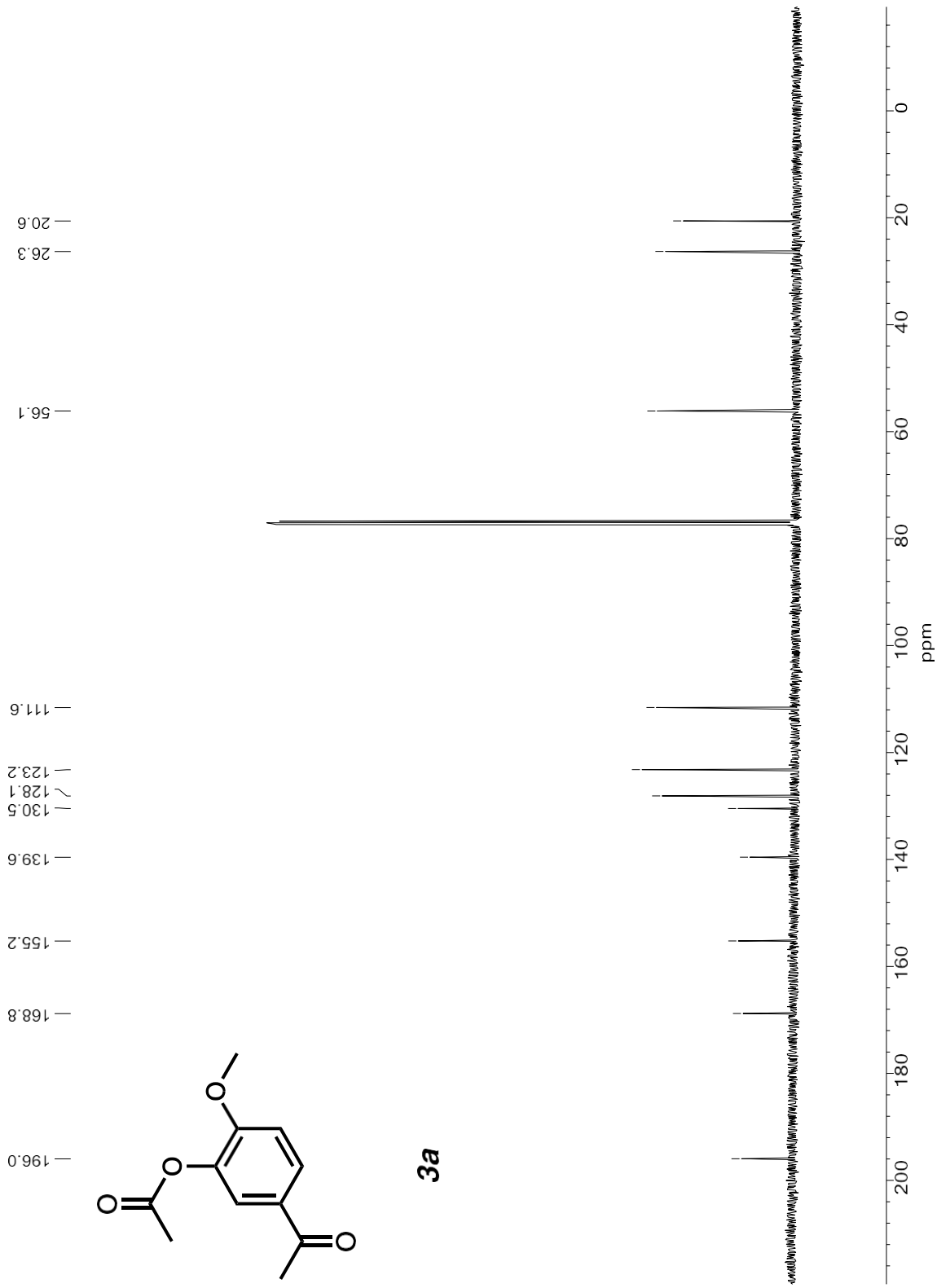
synthesized according to the general procedure 3 from 5-acetyl-2-methoxyphenyl acetate (48.4 mg, 0.23 mmol), furfural **6** (0.020 mL, 0.241 mmol), NaOH 10 wt% (0.480 mL, 0.50 M) and methanol (0.480 mL, 0.50 M). The product was purified by column chromatography on silica gel (1:4→1:2 EtOAc/hexanes): 30.2 mg (50%); R_f= 0.09 (1:4 EtOAc/hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 – 7.62 (m, 2H), 7.57 (d, *J* = 15.4 Hz, 1H), 7.51 (d, *J* = 1.8 Hz, 1H), 7.44 (d, *J* = 15.3 Hz, 1H), 6.92 (d, *J* = 8.1 Hz, 1H), 6.69 (d, *J* = 3.4 Hz, 1H), 6.50 (dd, *J* = 3.4, 1.8 Hz, 1H), 5.80 (s, 1H), 3.96 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.37, 151.97, 150.73, 145.73, 144.85, 132.03, 130.21, 122.11, 119.34, 115.93, 114.77, 112.72, 110.12, 56.22; HRMS(ESI) *m/z* ($[M+Na]^+$) calcd for $C_{14}H_{12}NaO_4$: 267.0633, found: 267.0632.



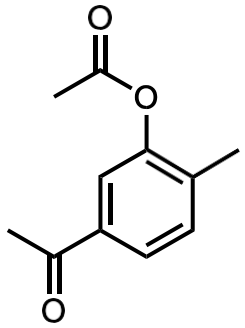
3a



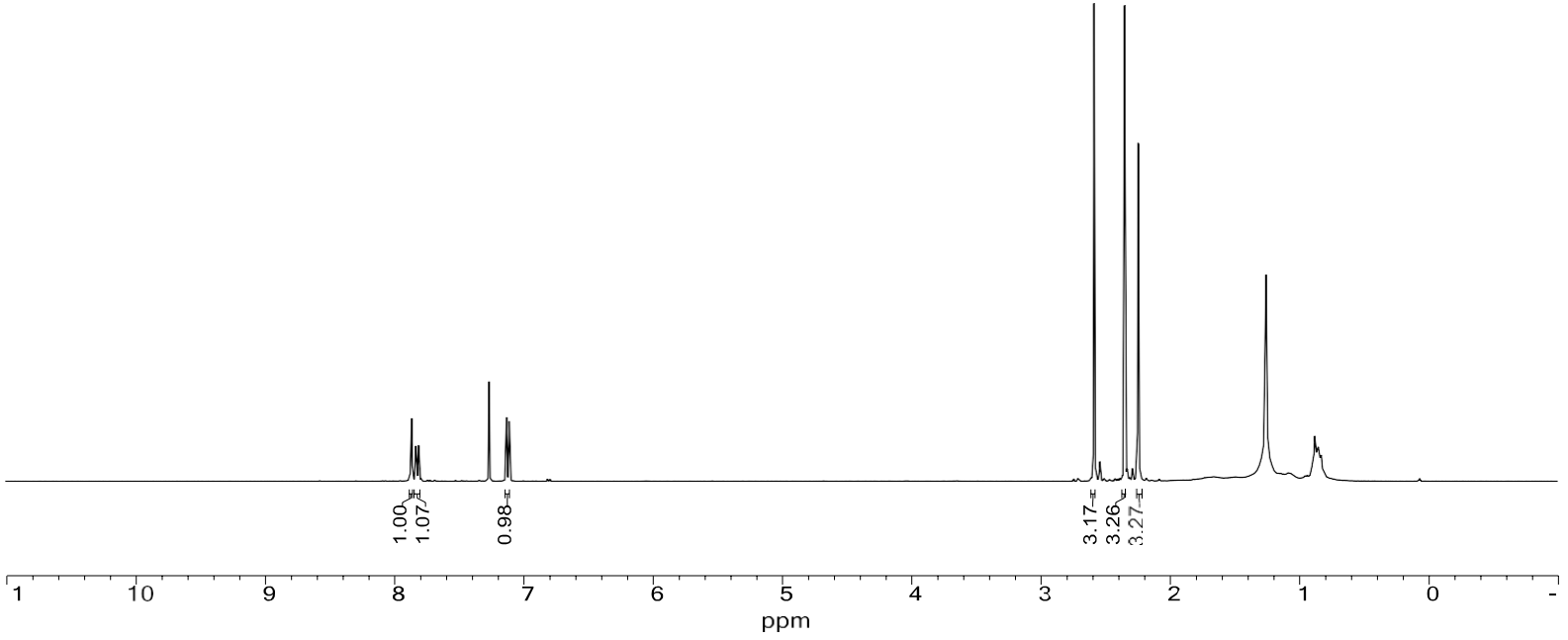
^{1}H NMR (400MHz, $CDCl_3$) of compound **3a**.



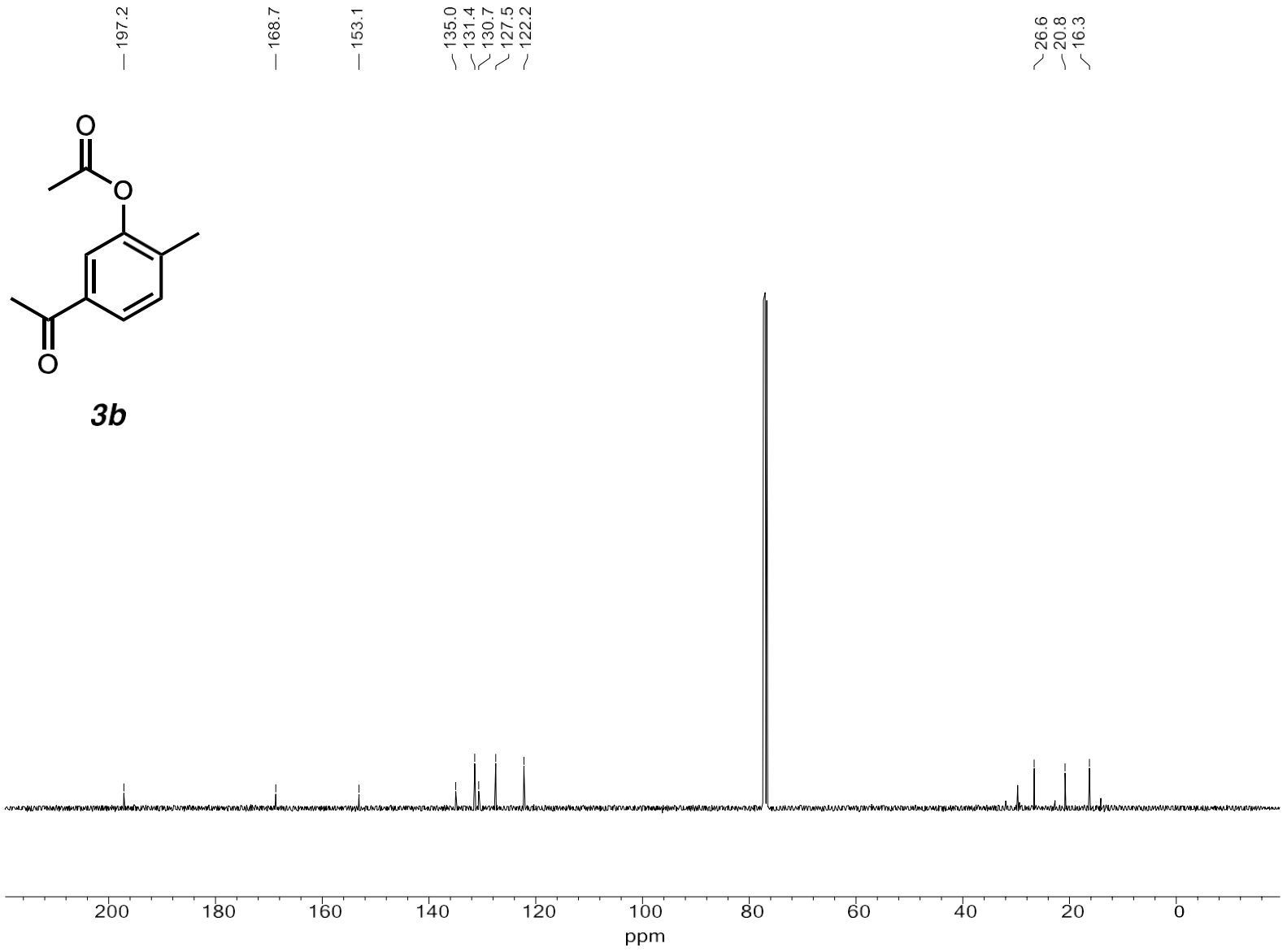
^{13}C NMR (101MHz, $CDCl_3$) of compound **3a.**



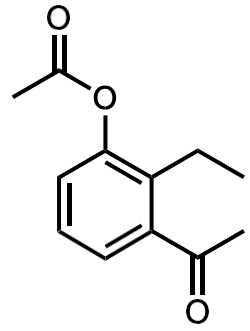
3b



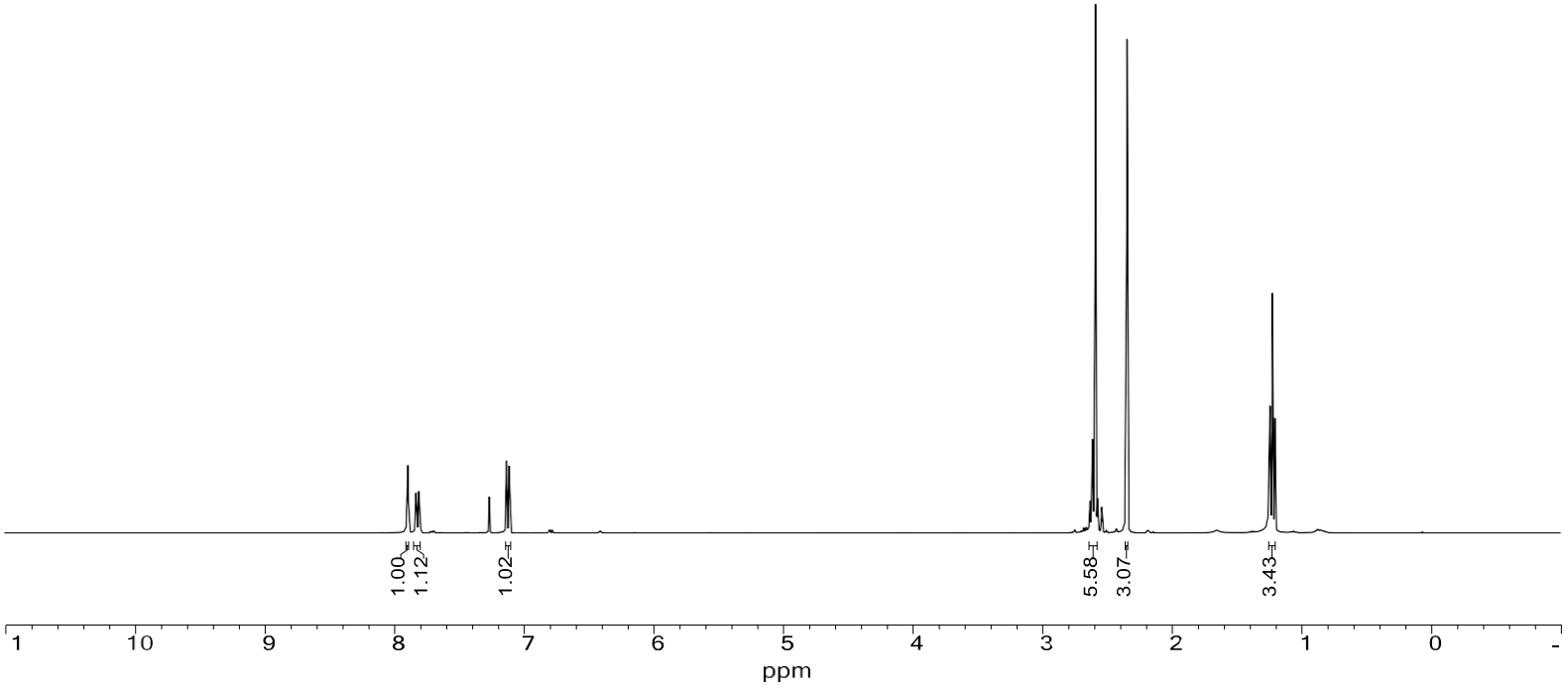
^{1}H NMR (400MHz, $CDCl_3$) of compound **3b**.



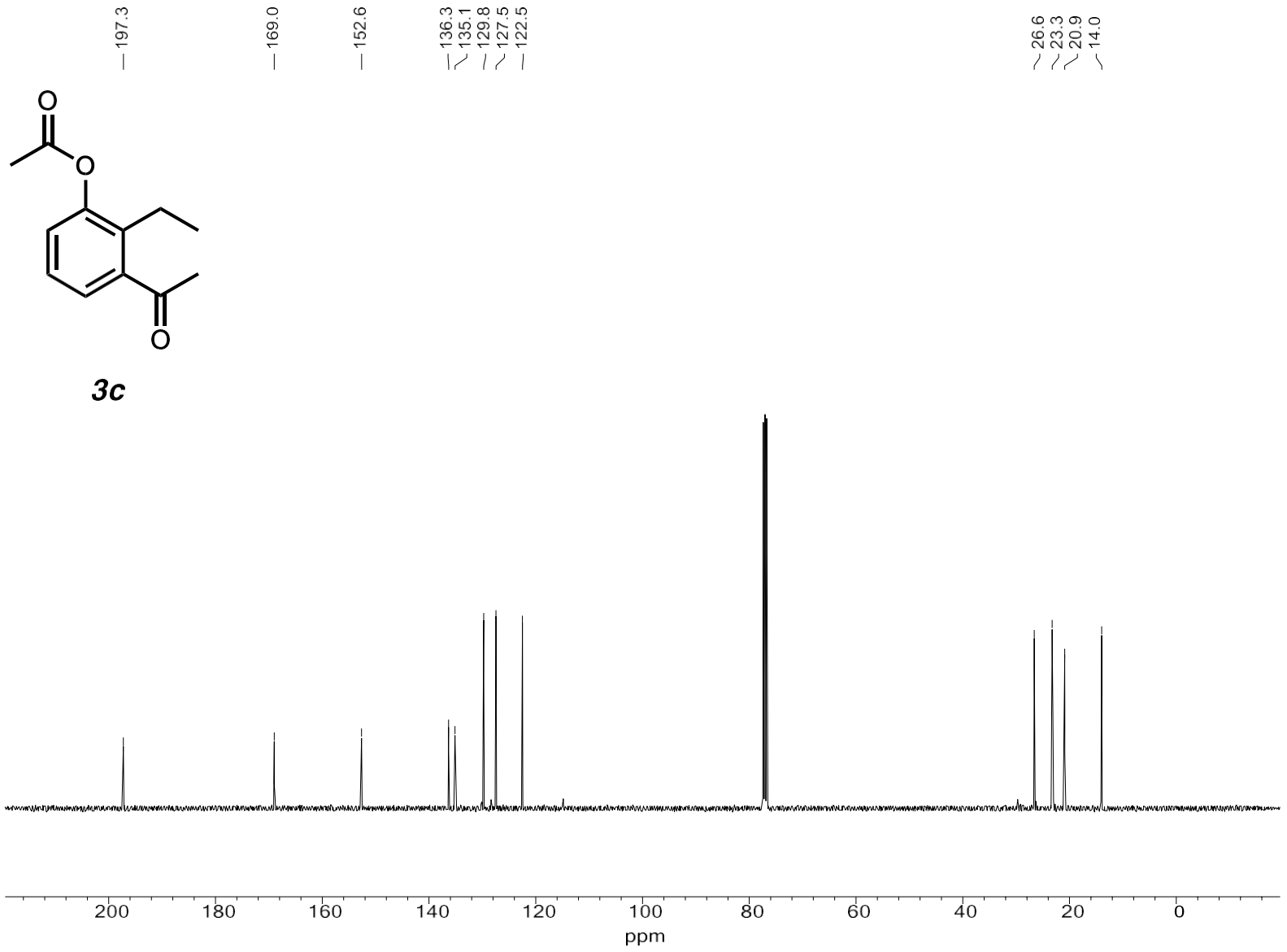
^{13}C NMR (101MHz, $CDCl_3$) of compound **3b**.



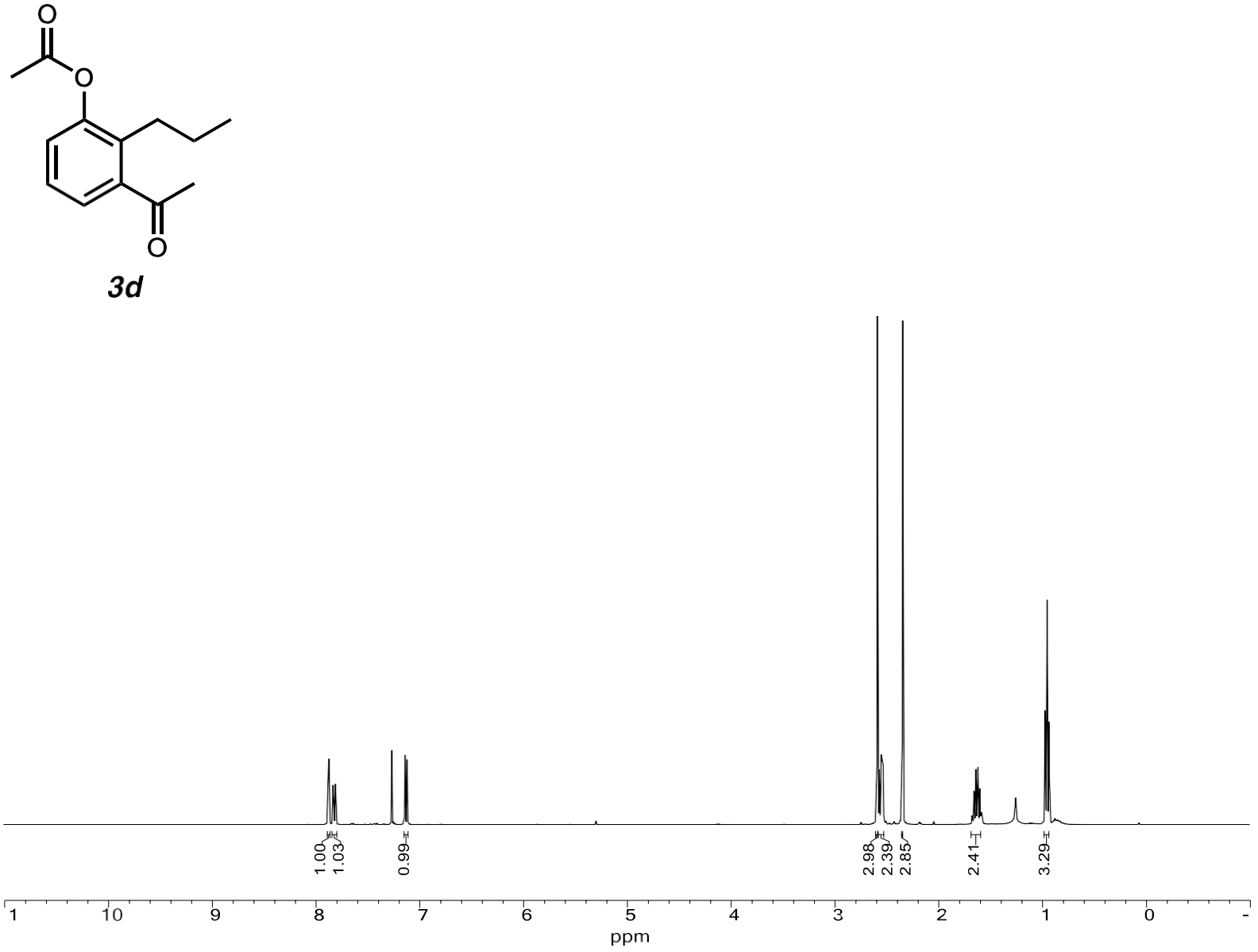
3c



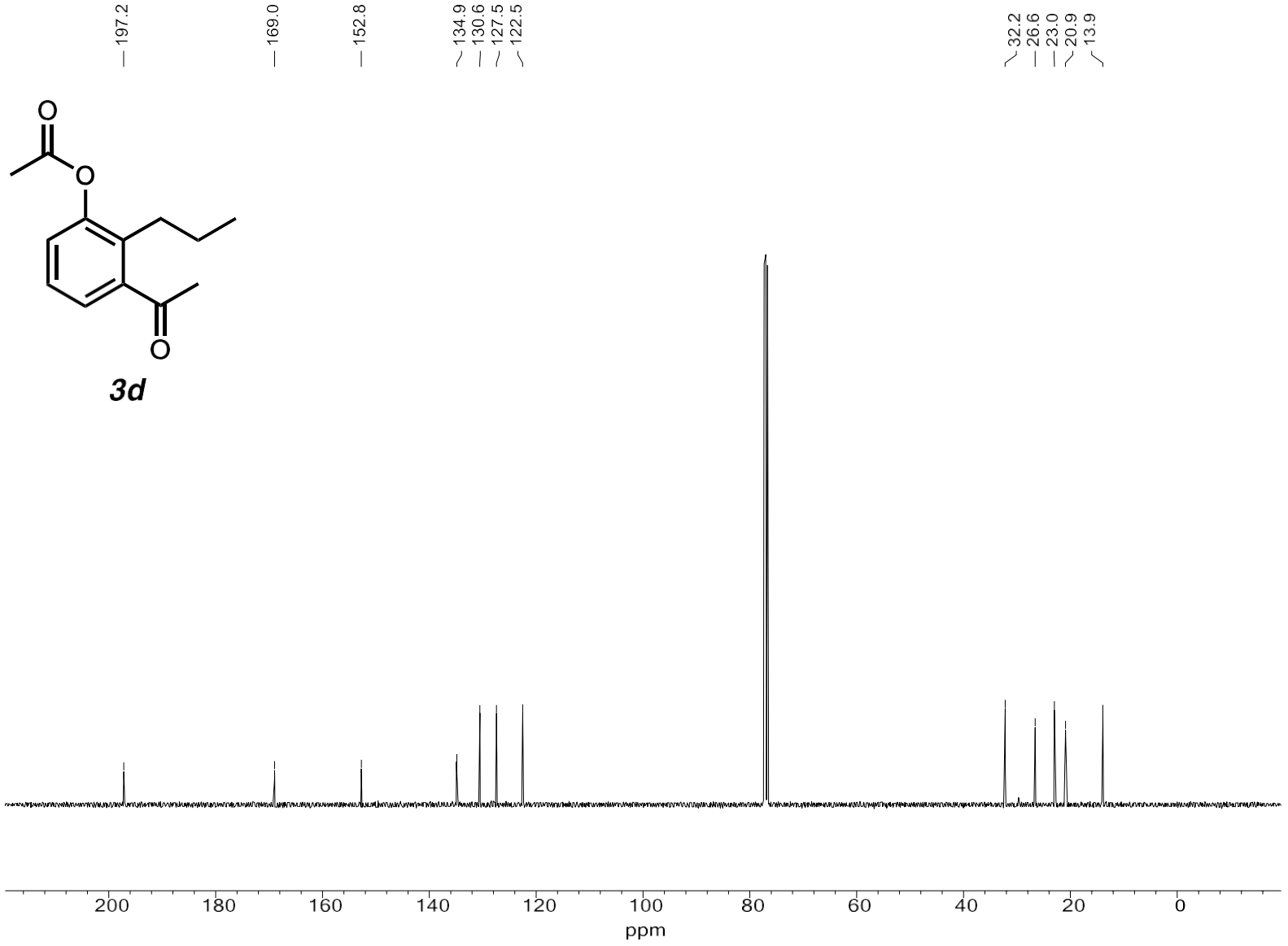
^{1}H NMR (400MHz, $CDCl_3$) of compound **3c**.



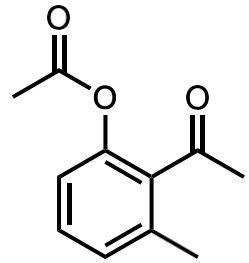
^{13}C NMR (101MHz, $CDCl_3$) of compound **3c**.



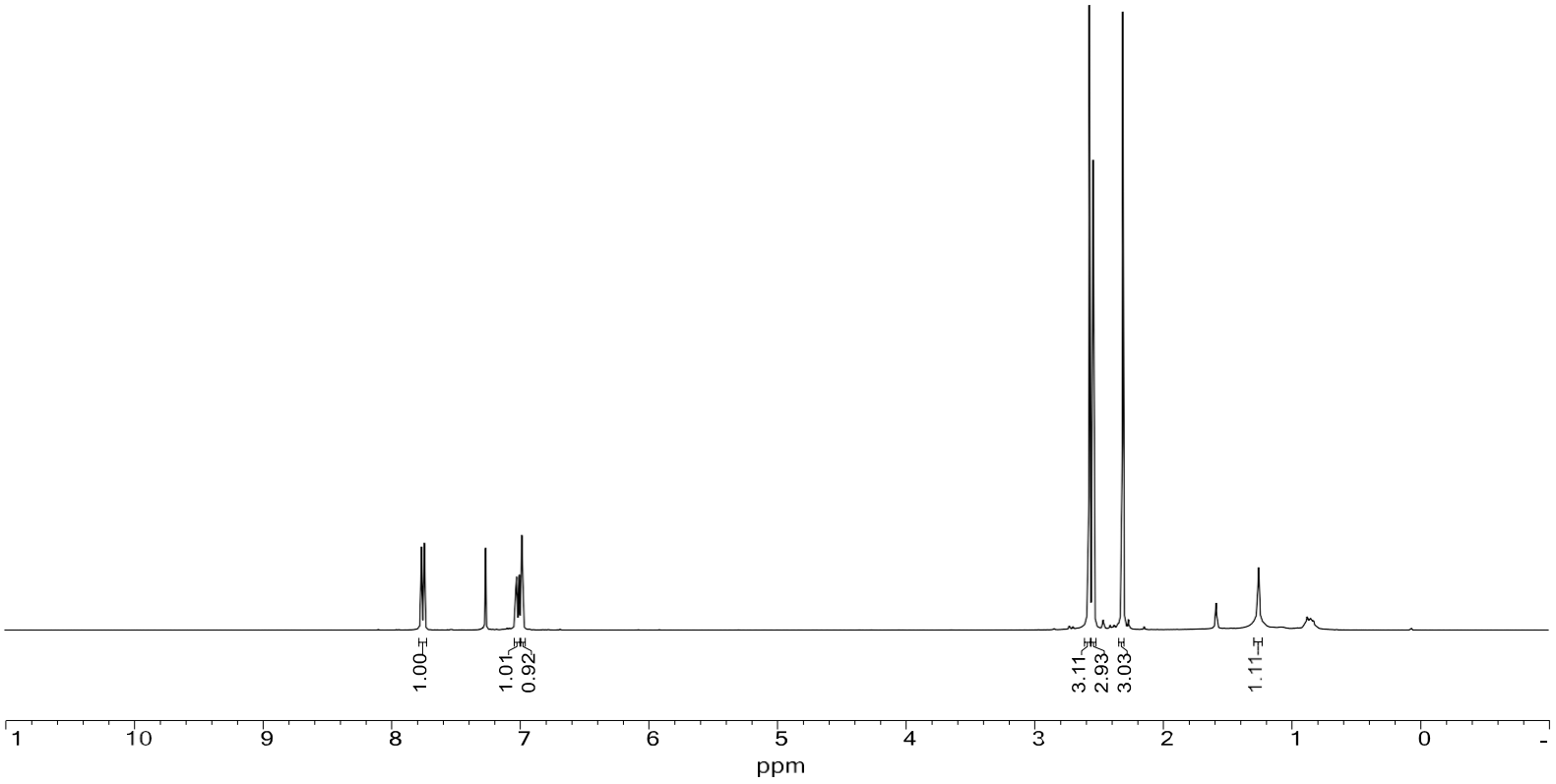
^{1}H NMR (400MHz, $CDCl_3$) of compound **3d**.



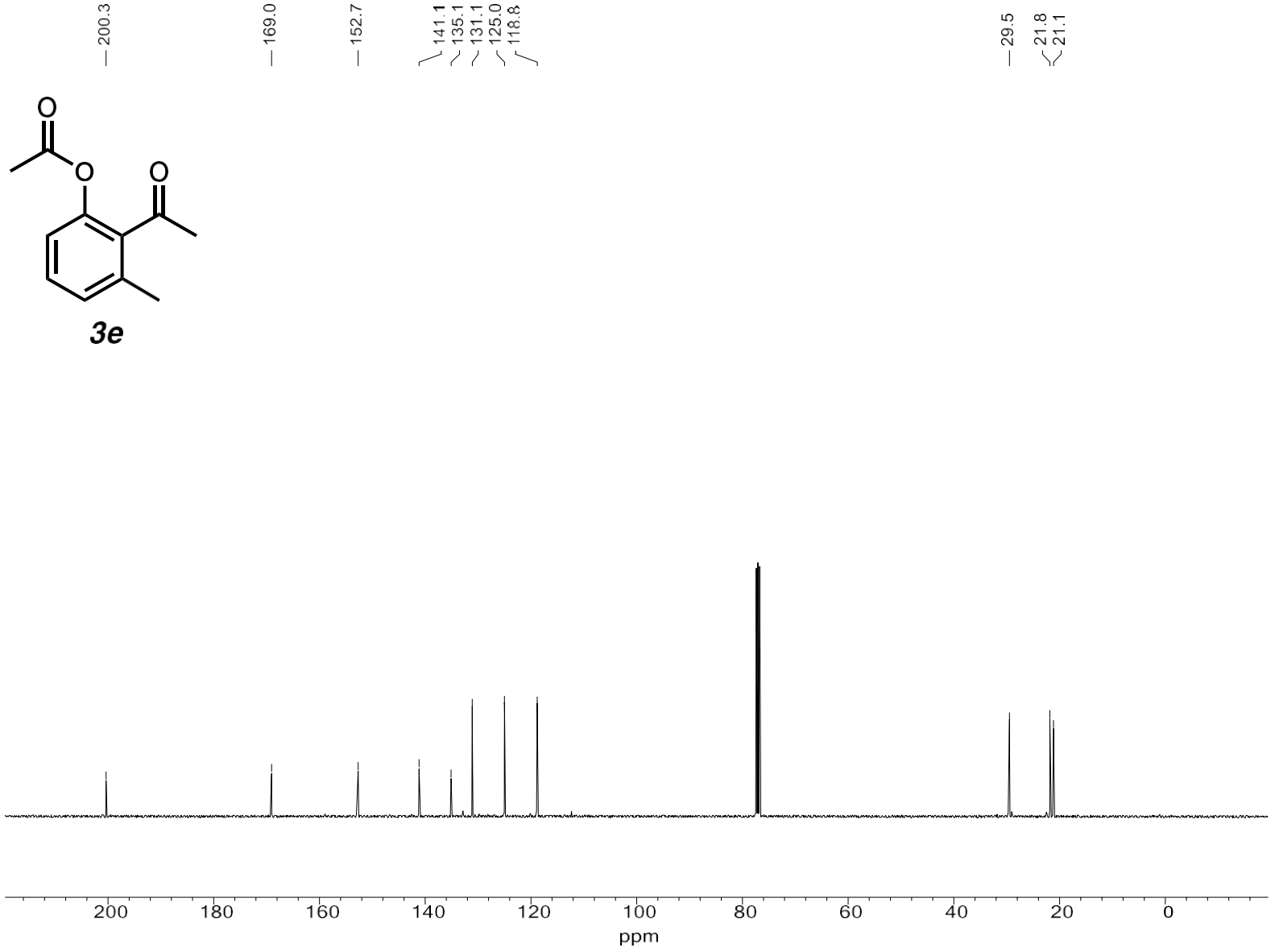
^{13}C NMR (101MHz, $CDCl_3$) of compound **3d**.



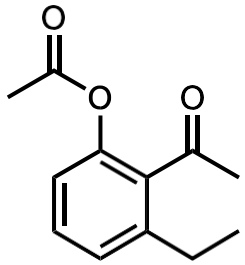
3e



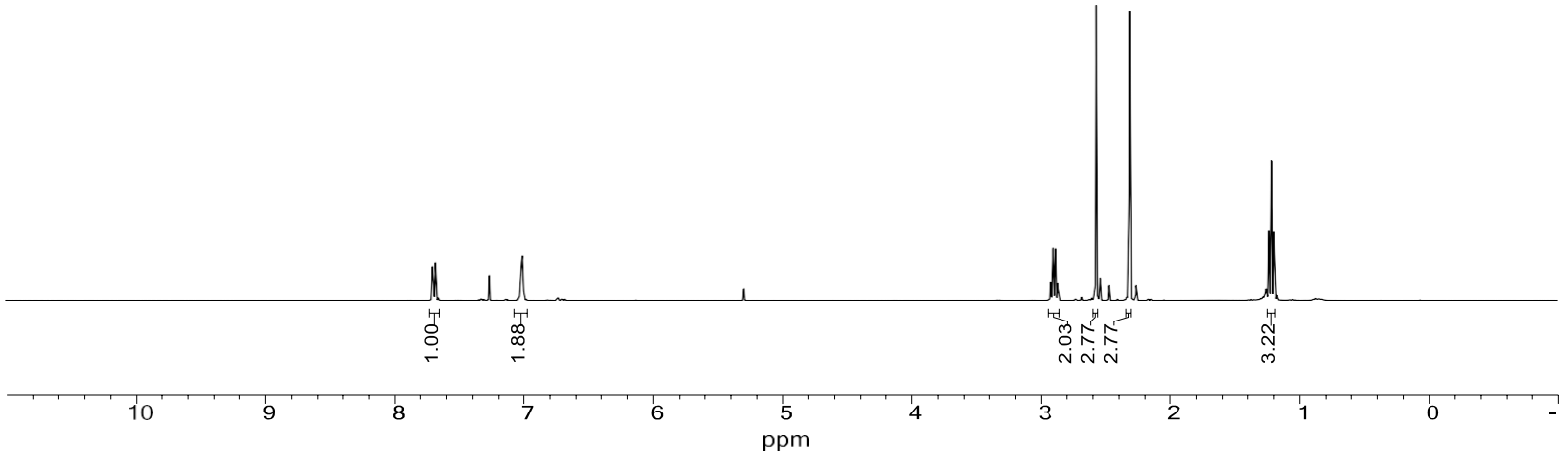
^{1}H NMR (400MHz, $CDCl_3$) of compound **3e**.



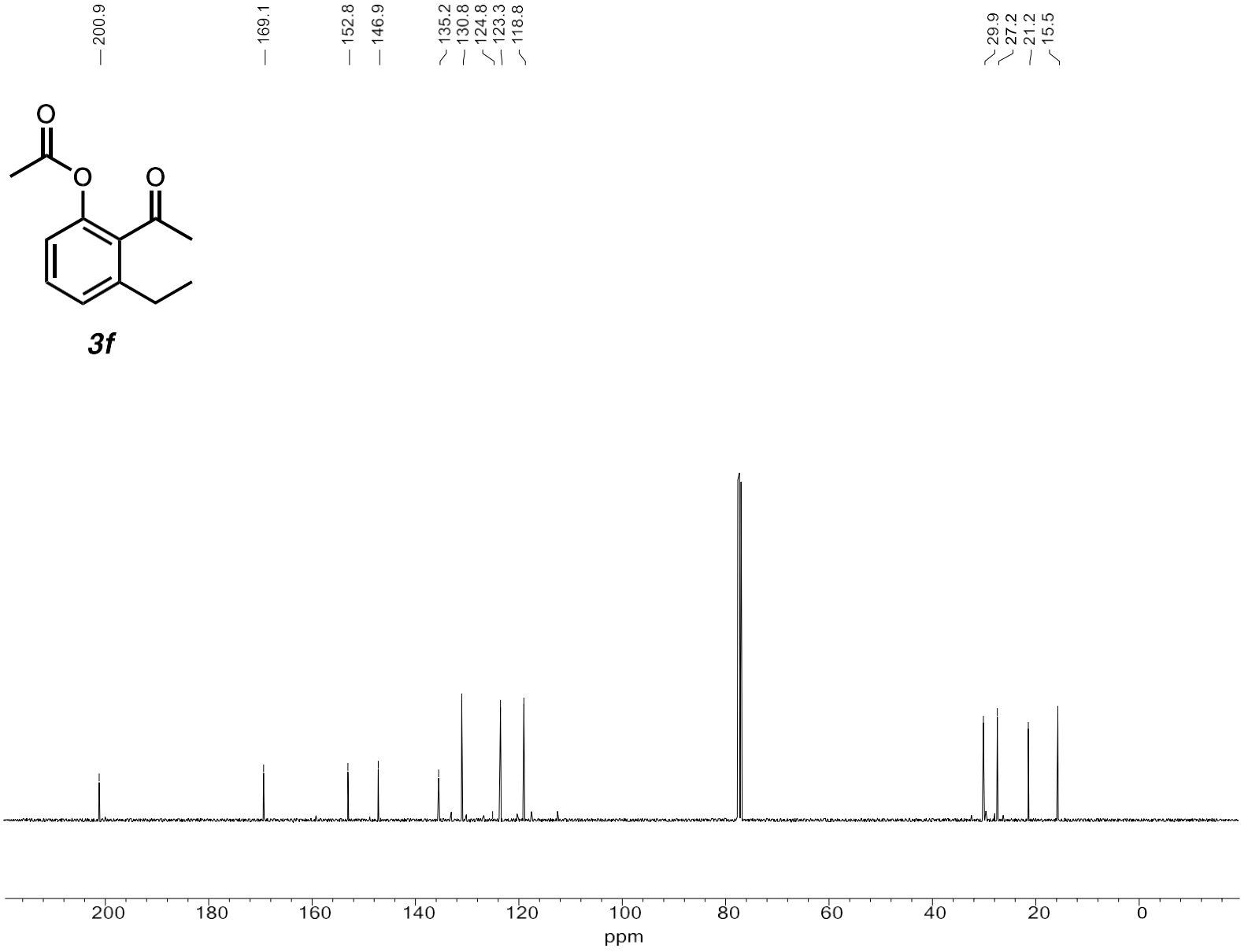
^{13}C NMR (101MHz, $CDCl_3$) of compound **3e**.



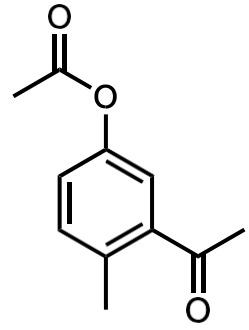
3f



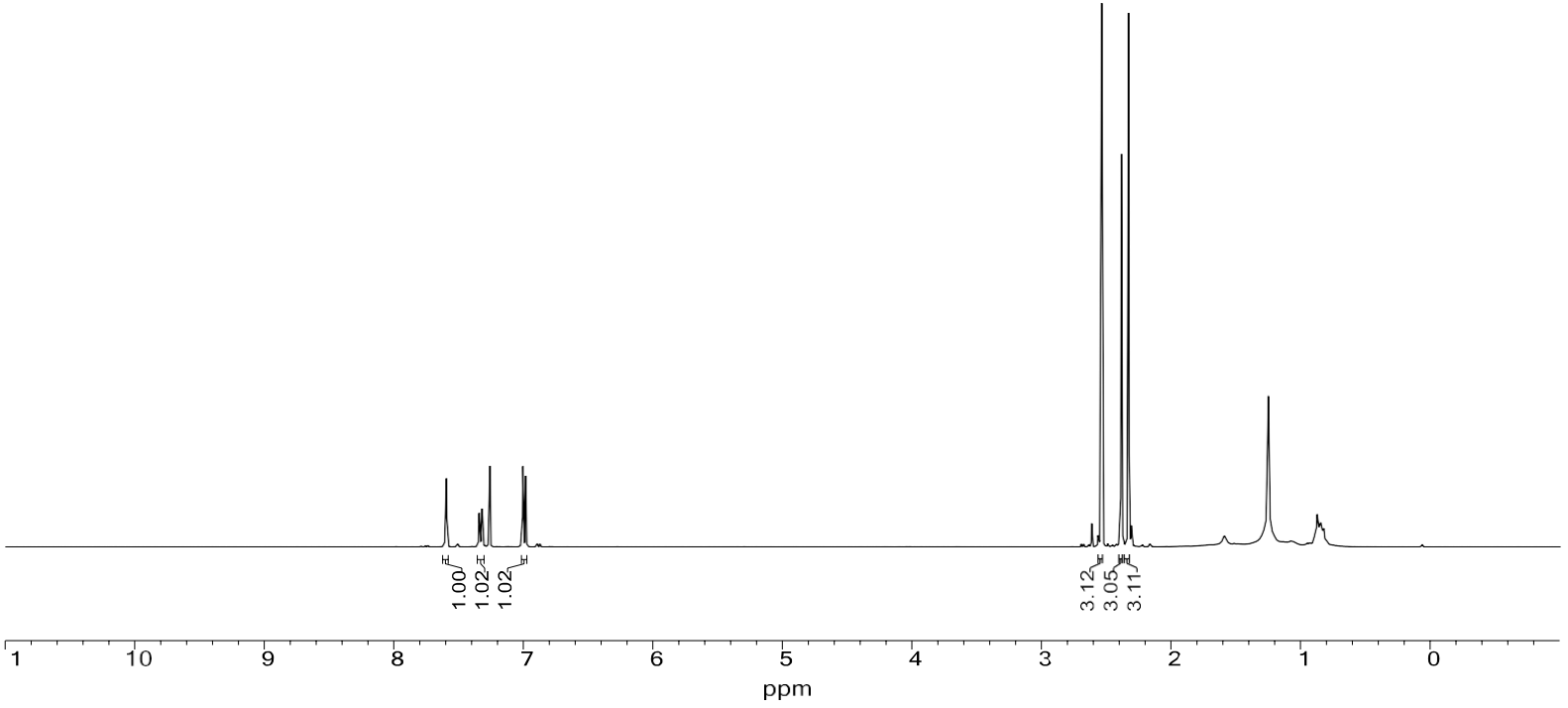
^{1}H NMR (400MHz, $CDCl_3$) of compound **3f**.



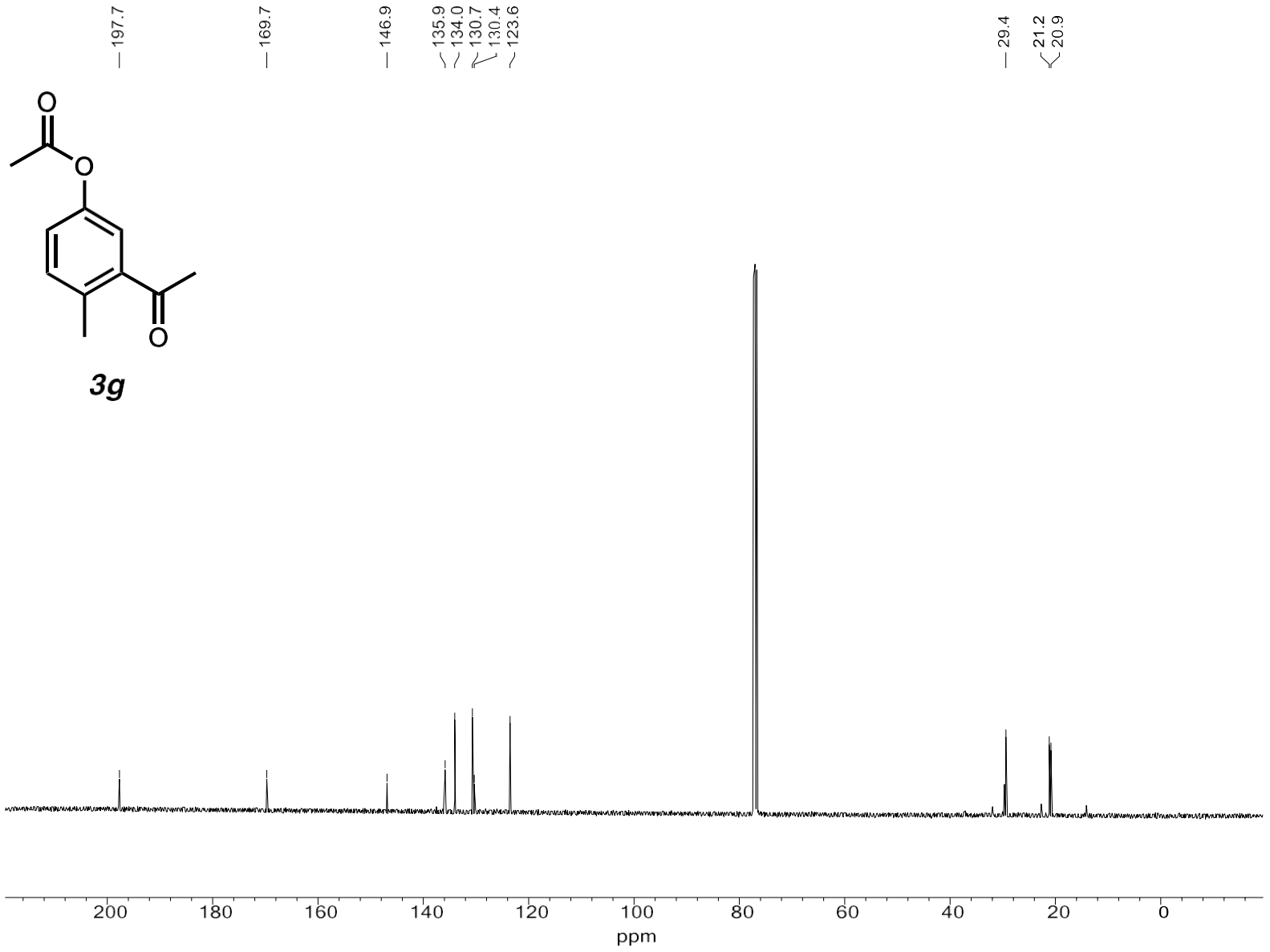
^{13}C NMR (101MHz, $CDCl_3$) of compound **3f**.



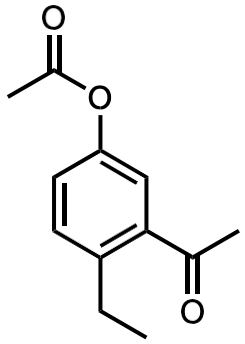
3g



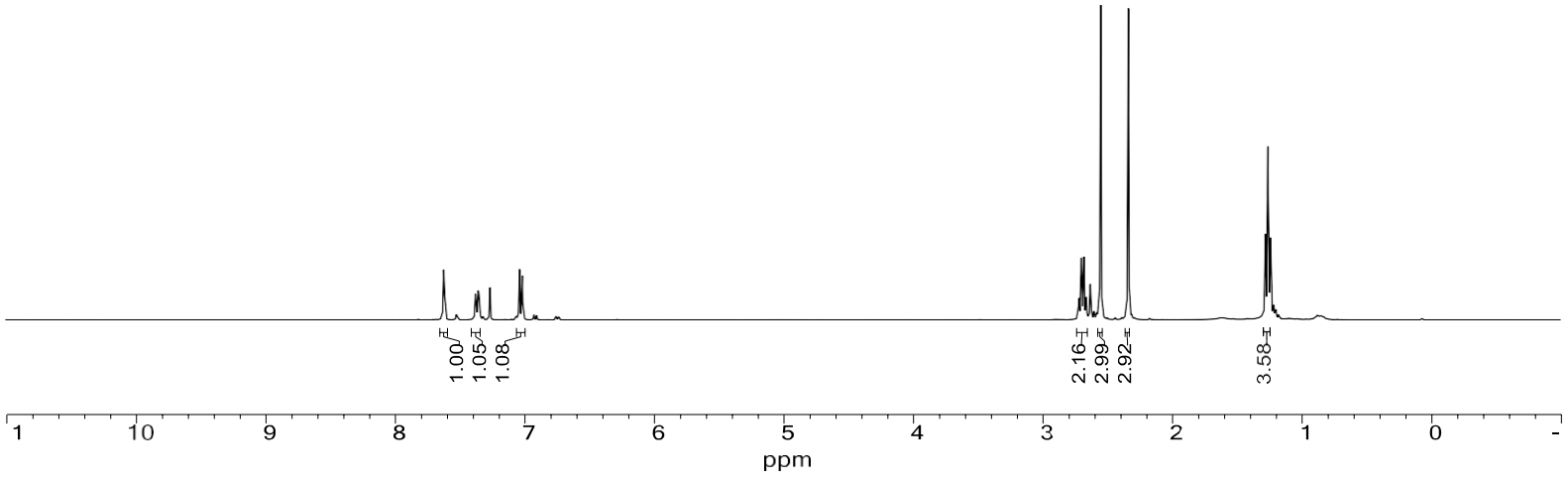
^{1}H NMR (400MHz, $CDCl_3$) of compound **3g**.



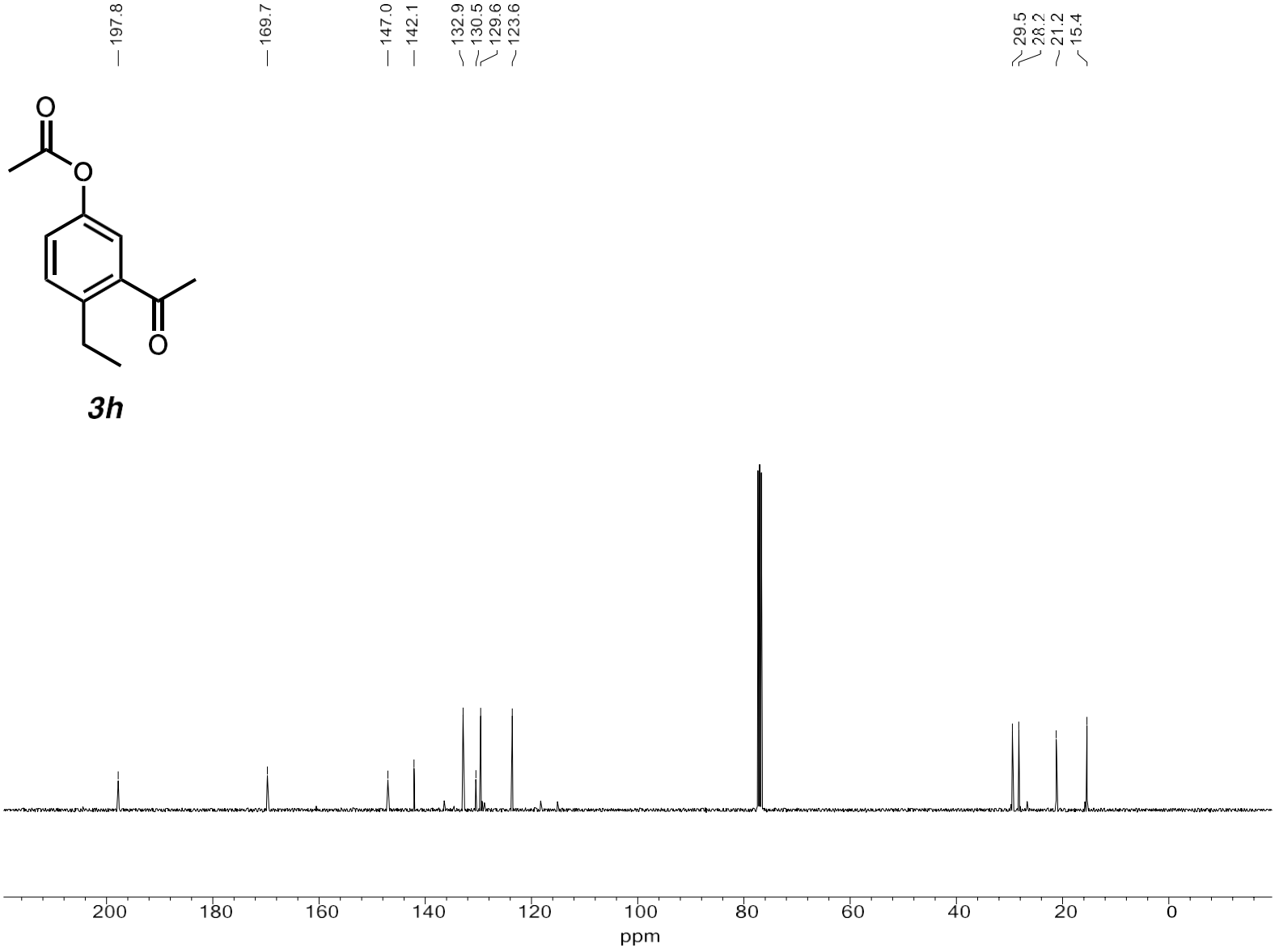
^{13}C NMR (101MHz, $CDCl_3$) of compound **3g**.



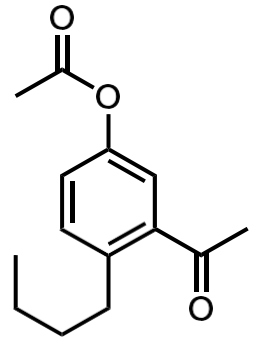
3h



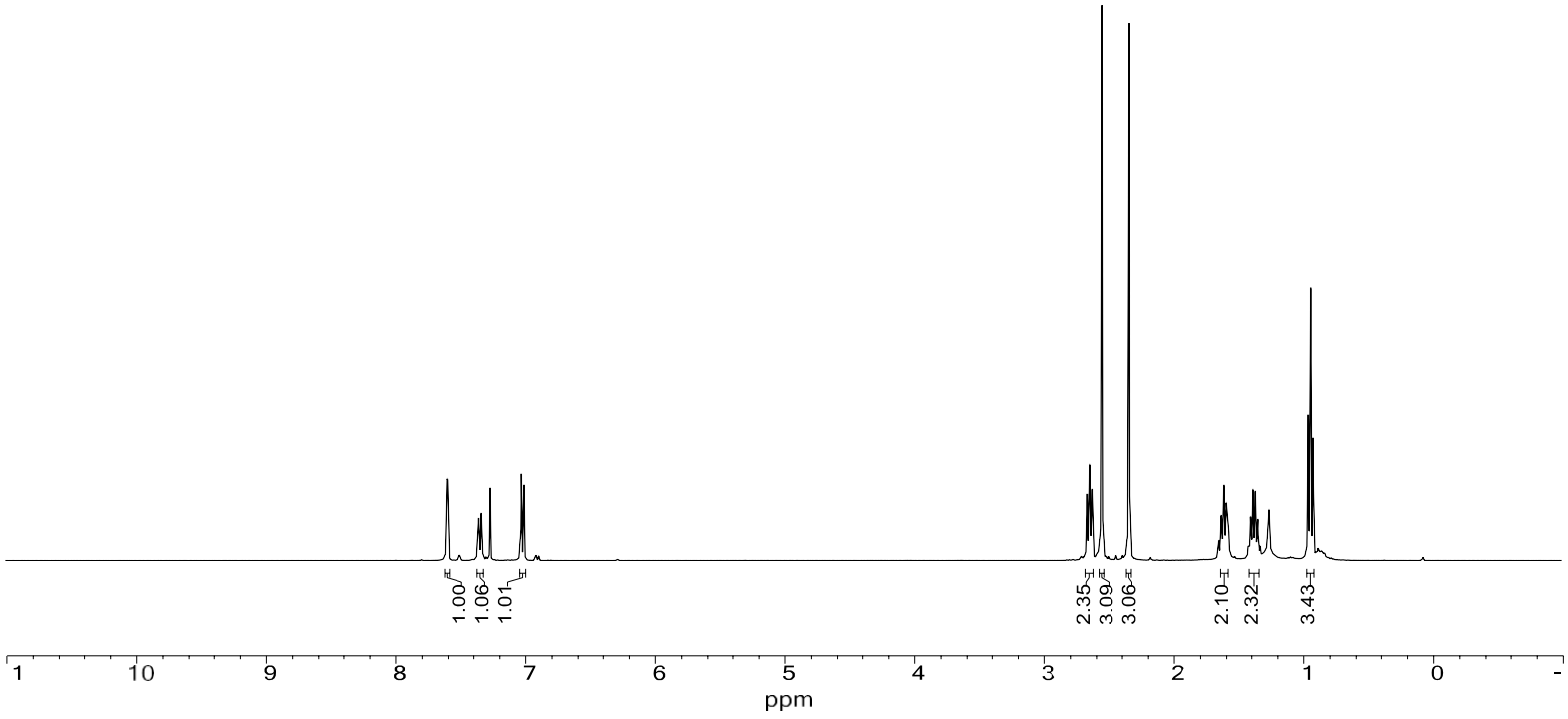
^{1}H NMR (400MHz, $CDCl_3$) of compound **3h**.



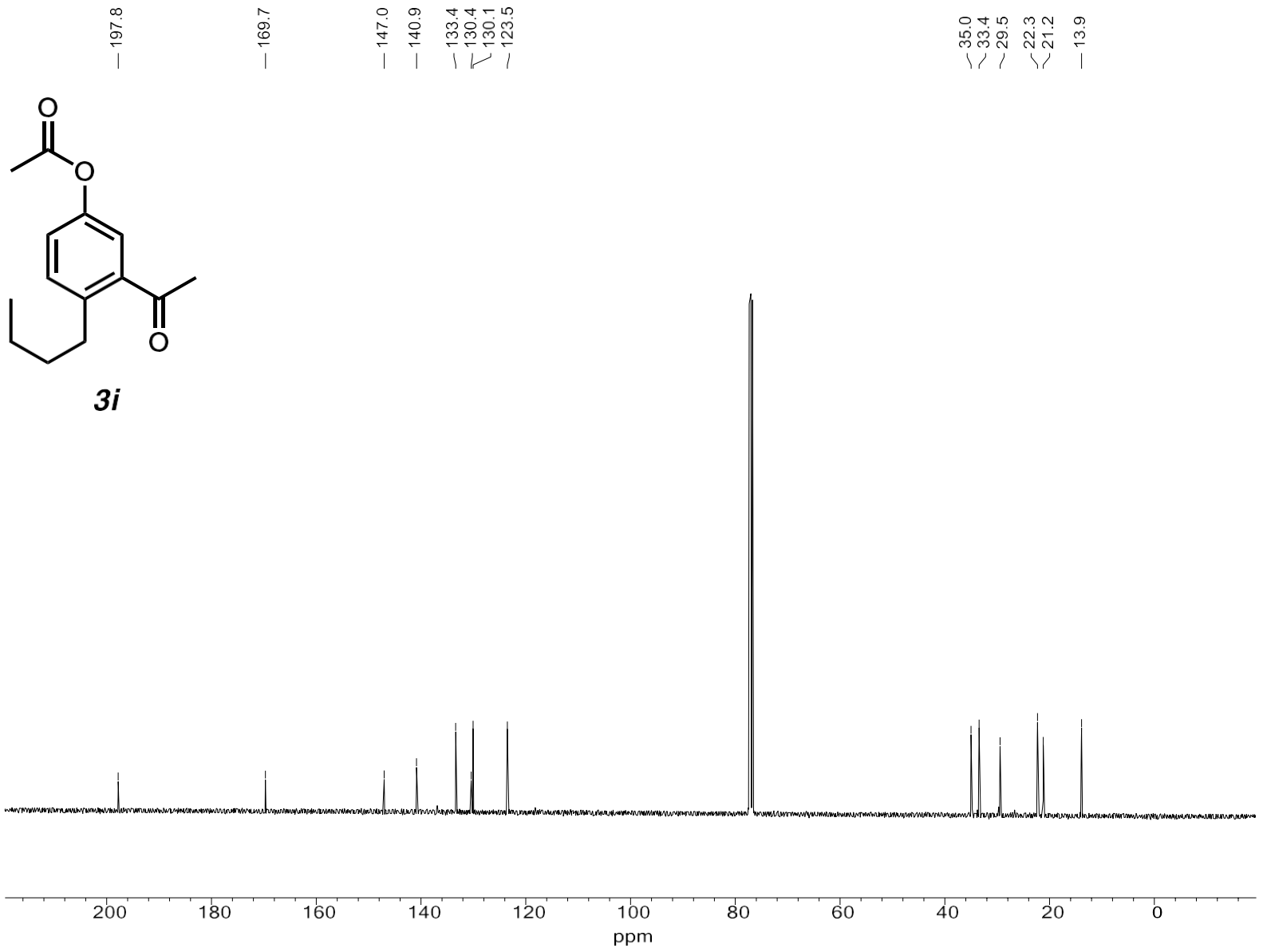
^{13}C NMR (101MHz, $CDCl_3$) of compound **3h**.



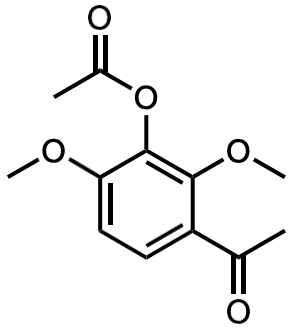
3i



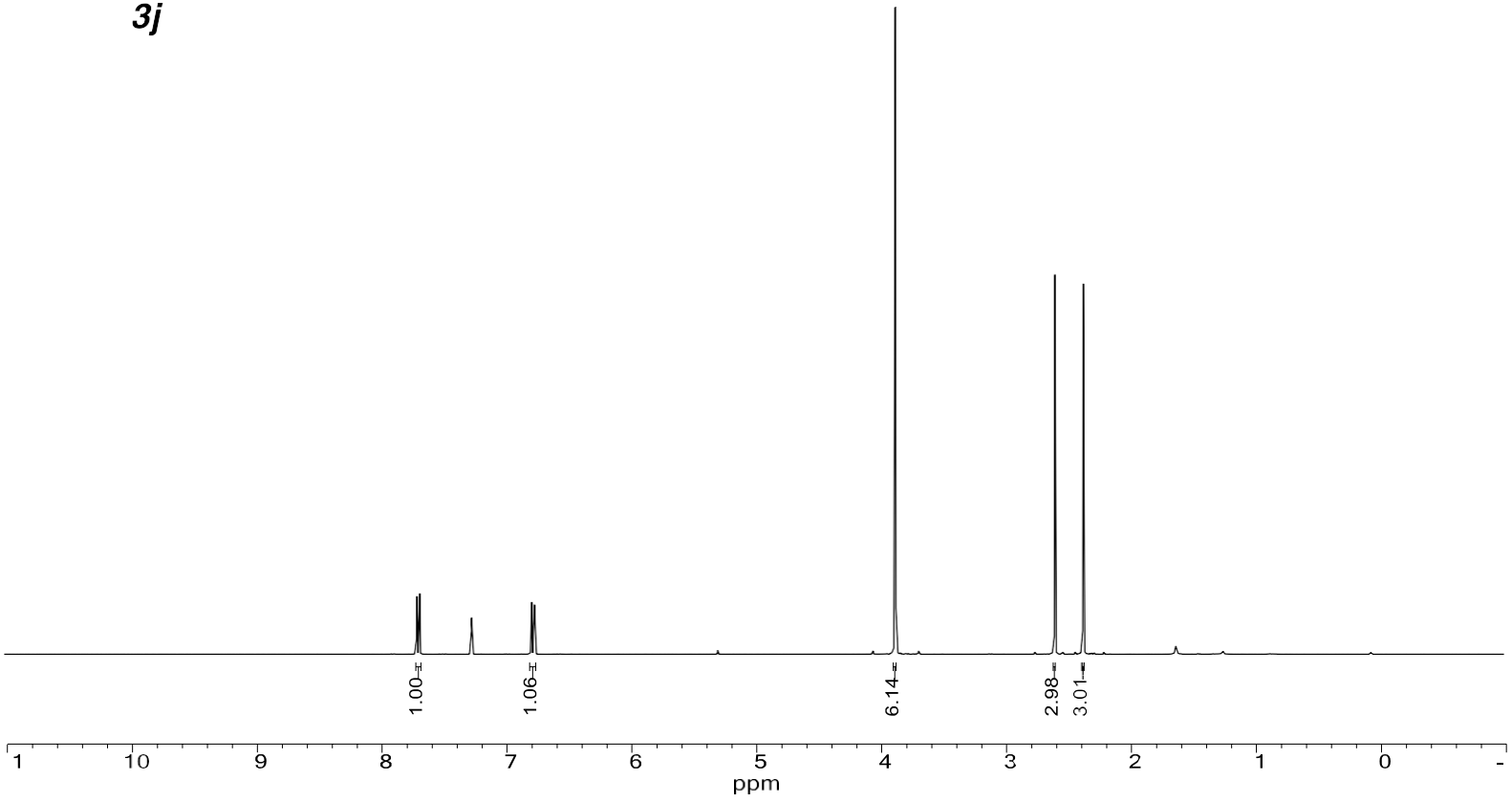
^{1}H NMR (400MHz, $CDCl_3$) of compound **3i**.



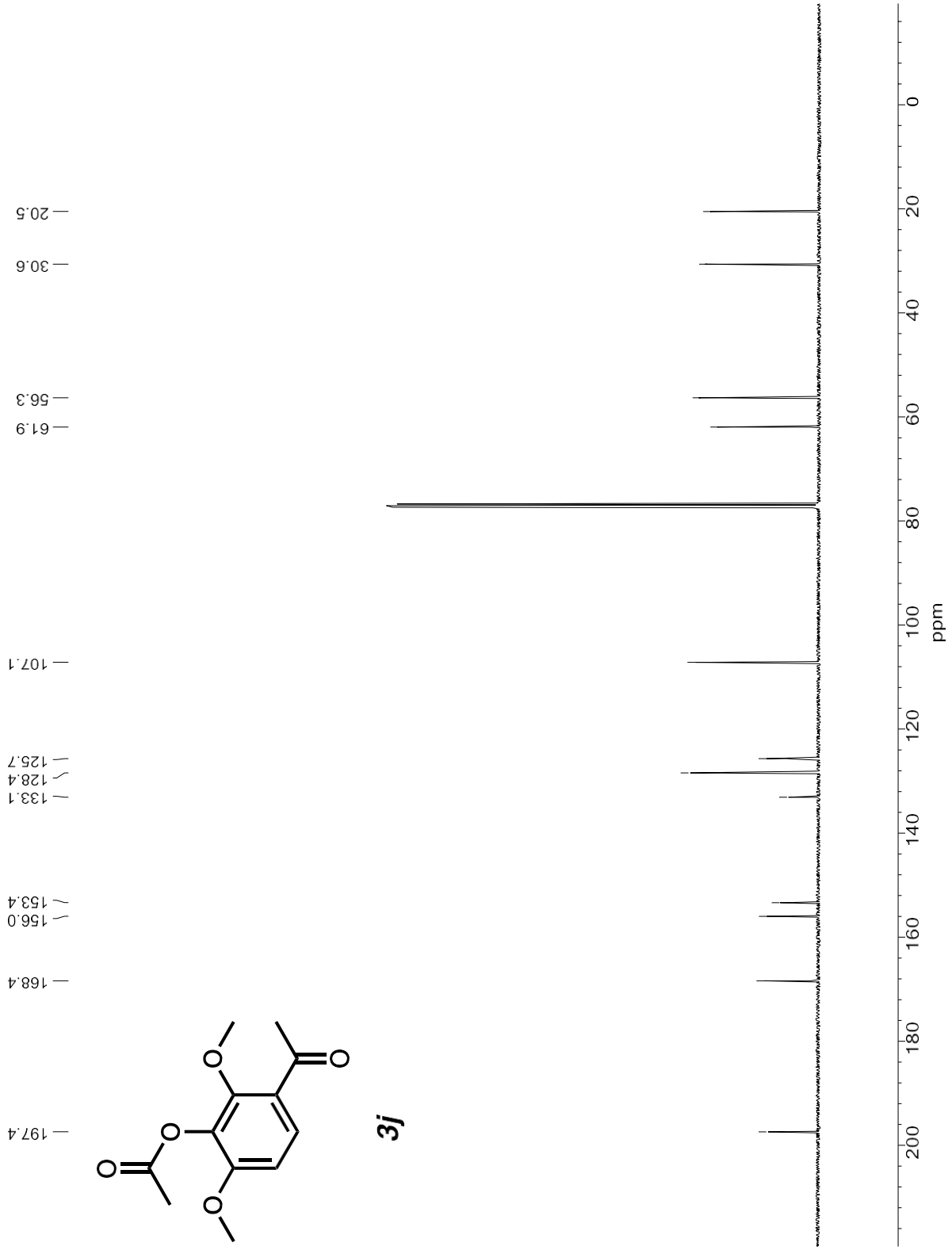
^{13}C NMR (101MHz, $CDCl_3$) of compound **3i**.



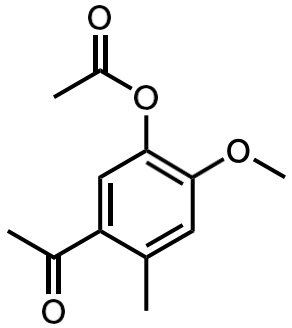
3j



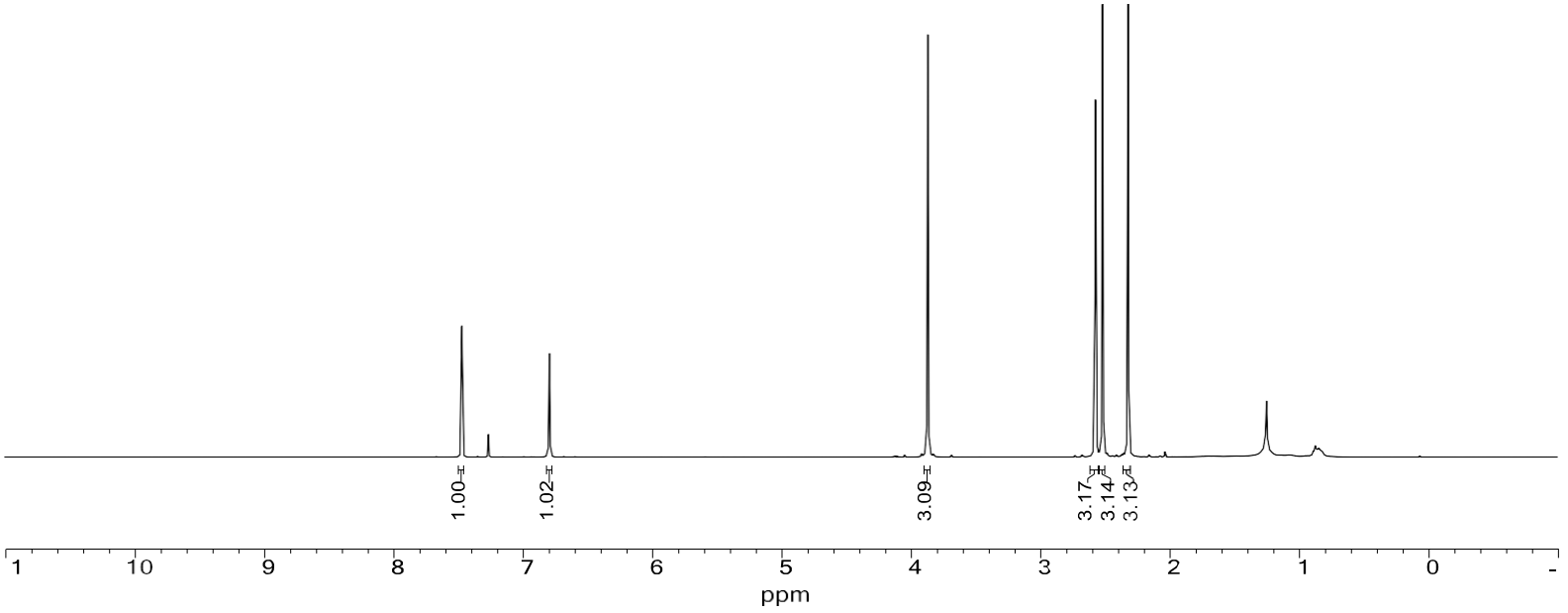
^{1}H NMR (400MHz, $CDCl_3$) of compound **3j**.



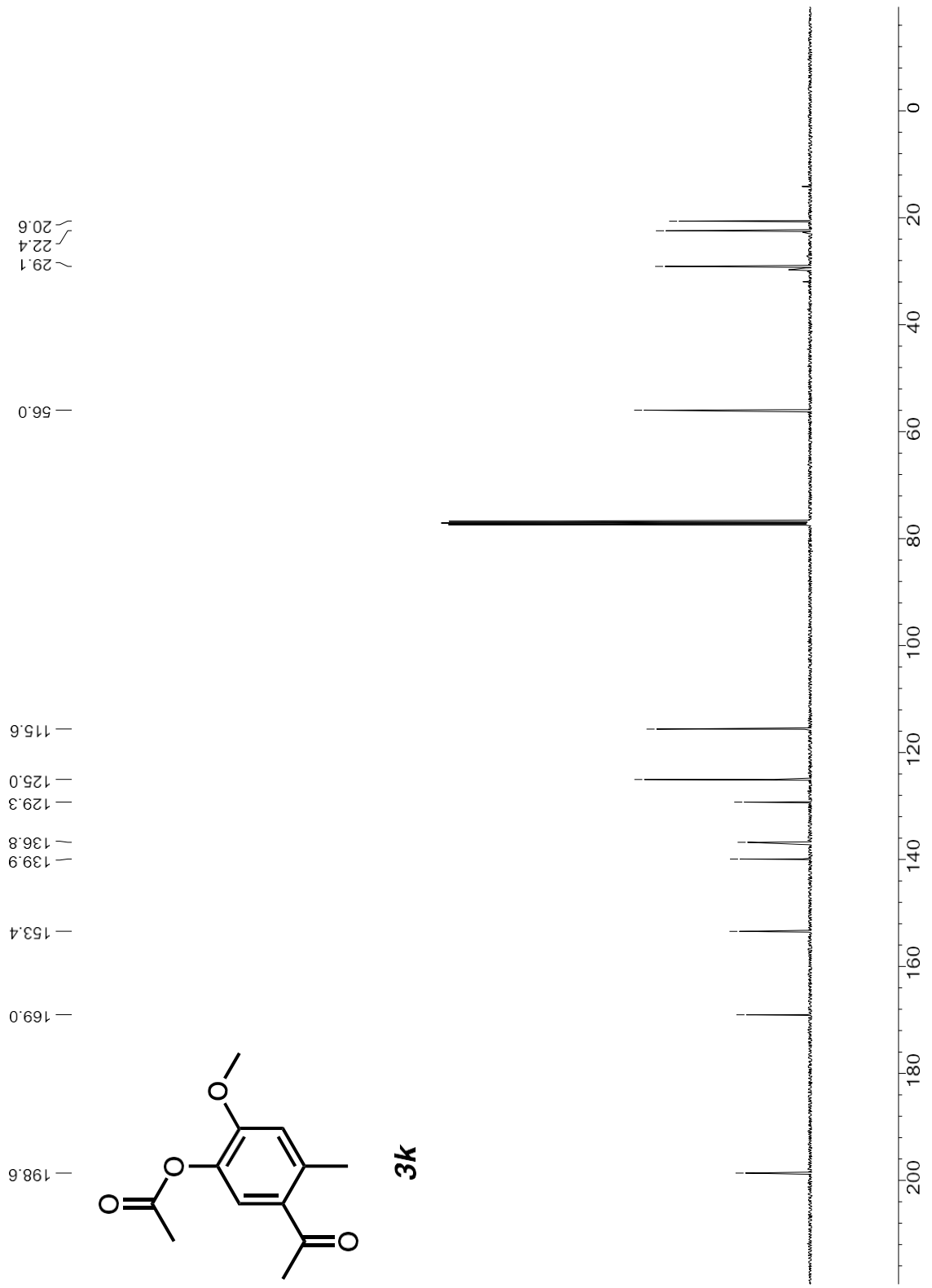
^{13}C NMR (101MHz, $CDCl_3$) of compound **3j**.



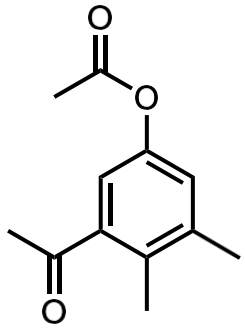
3k



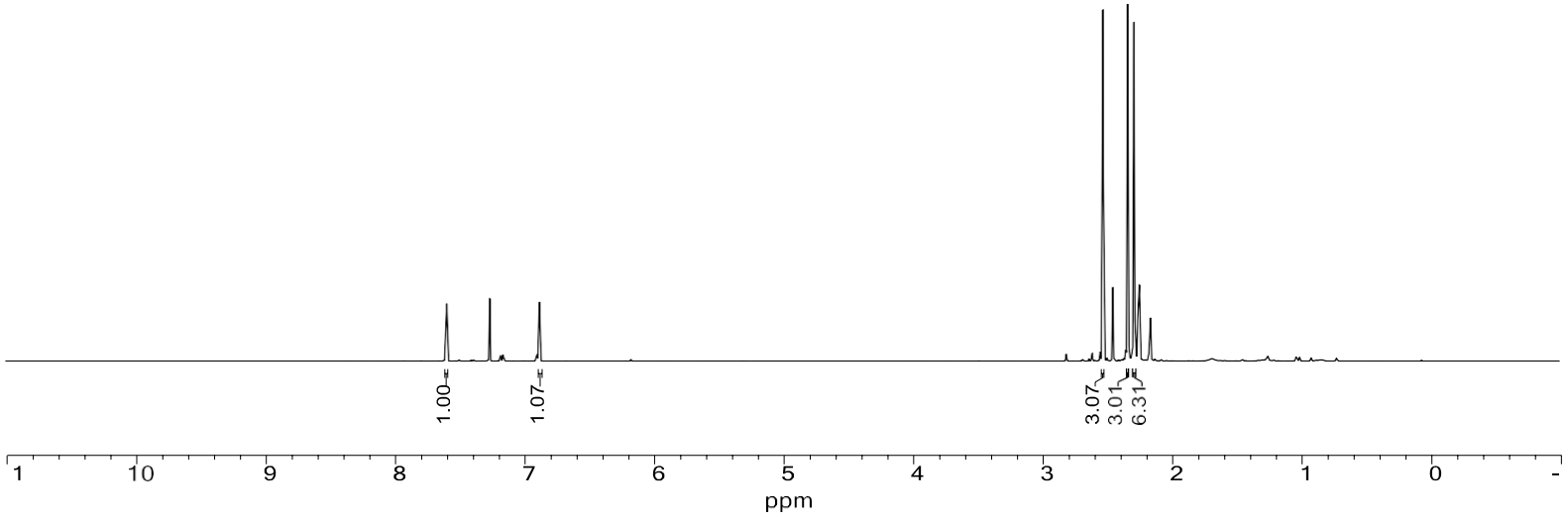
^{1}H NMR (400MHz, $CDCl_3$) of compound **3k**.



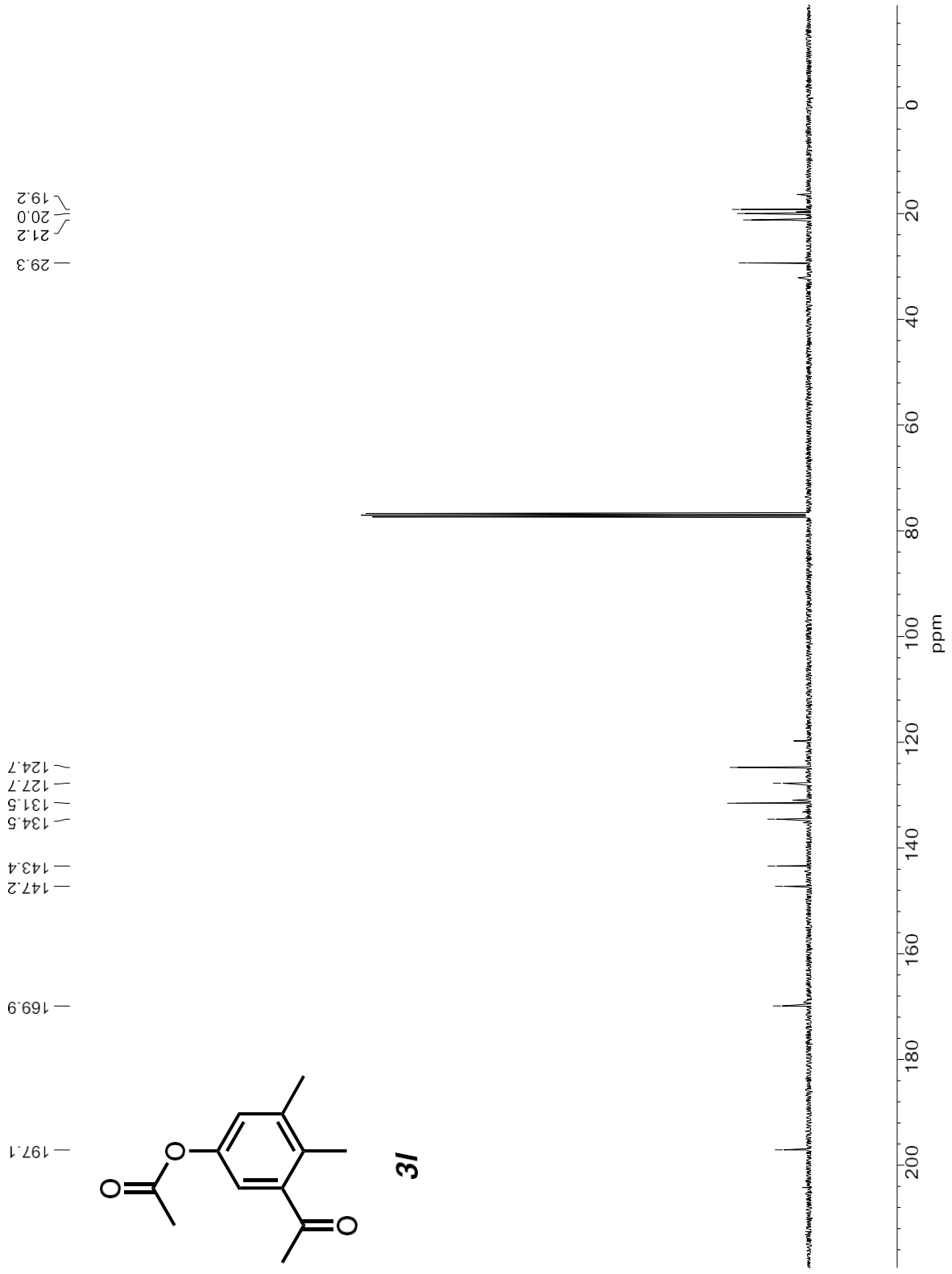
^{13}C NMR (101MHz, $CDCl_3$) of compound **3k.**



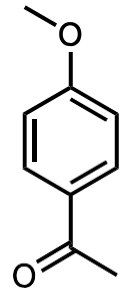
3l



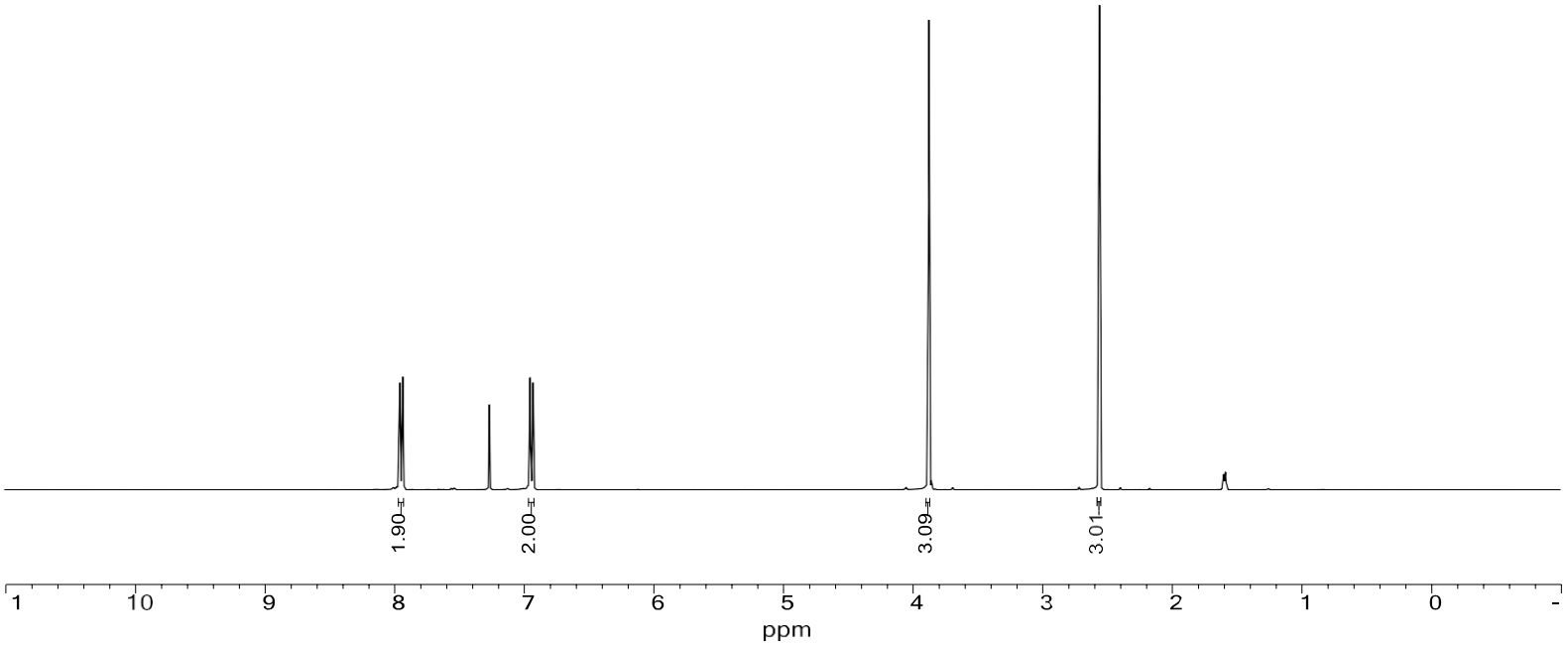
^{1}H NMR (400MHz, $CDCl_3$) of compound **3l**.



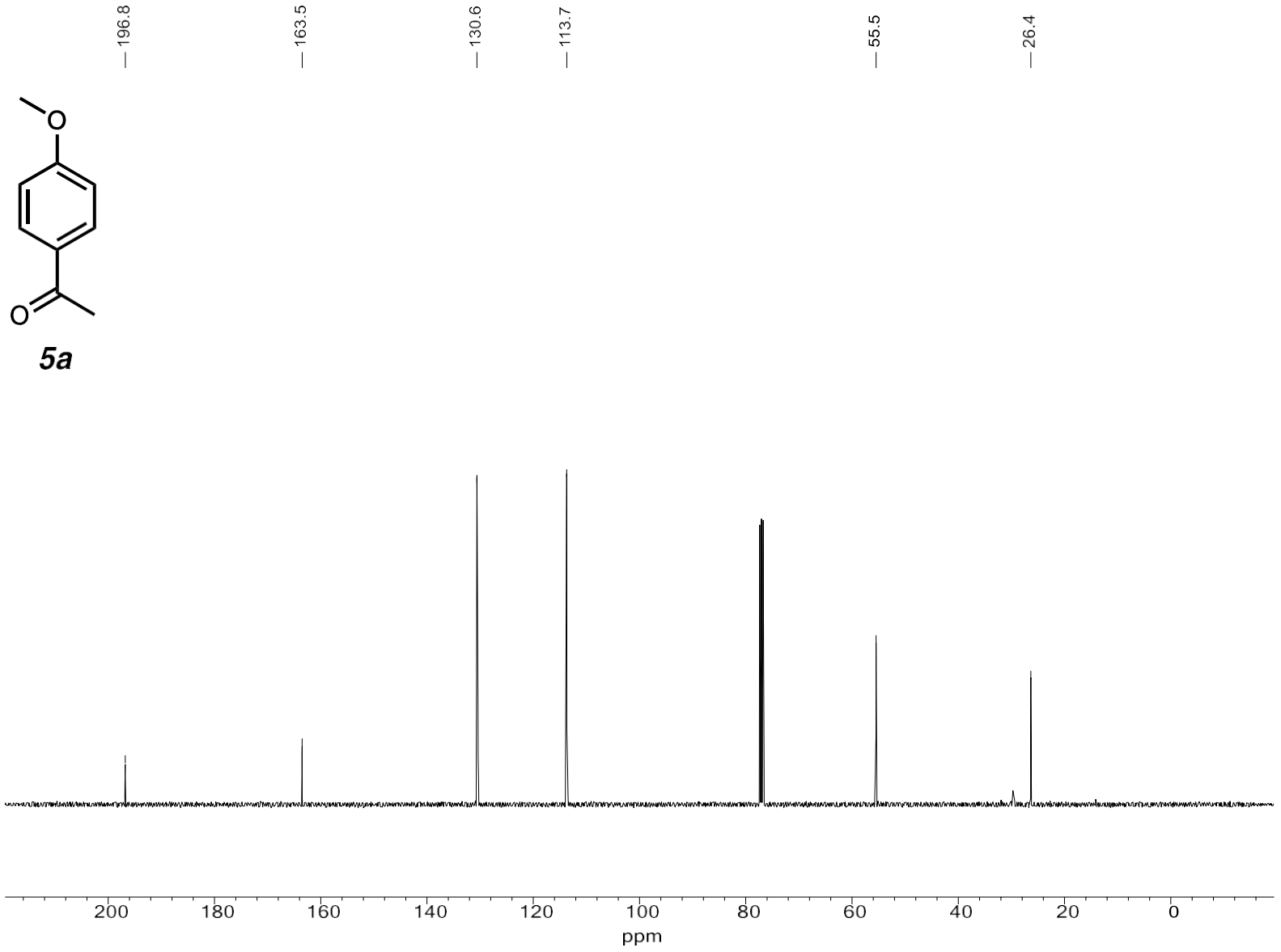
^{13}C NMR (101MHz, $CDCl_3$) of compound **3l.**



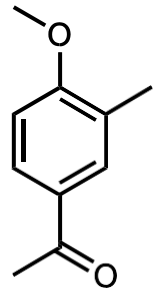
5a



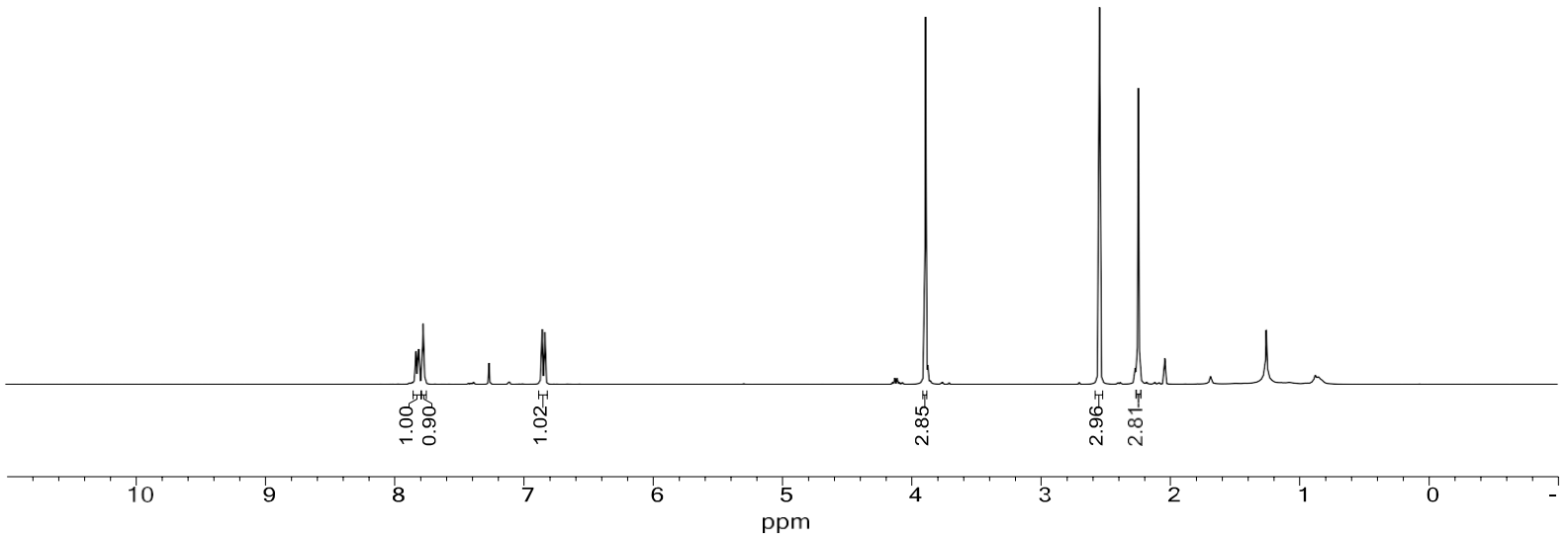
^{1}H NMR (400MHz, $CDCl_3$) of compound **5a.**



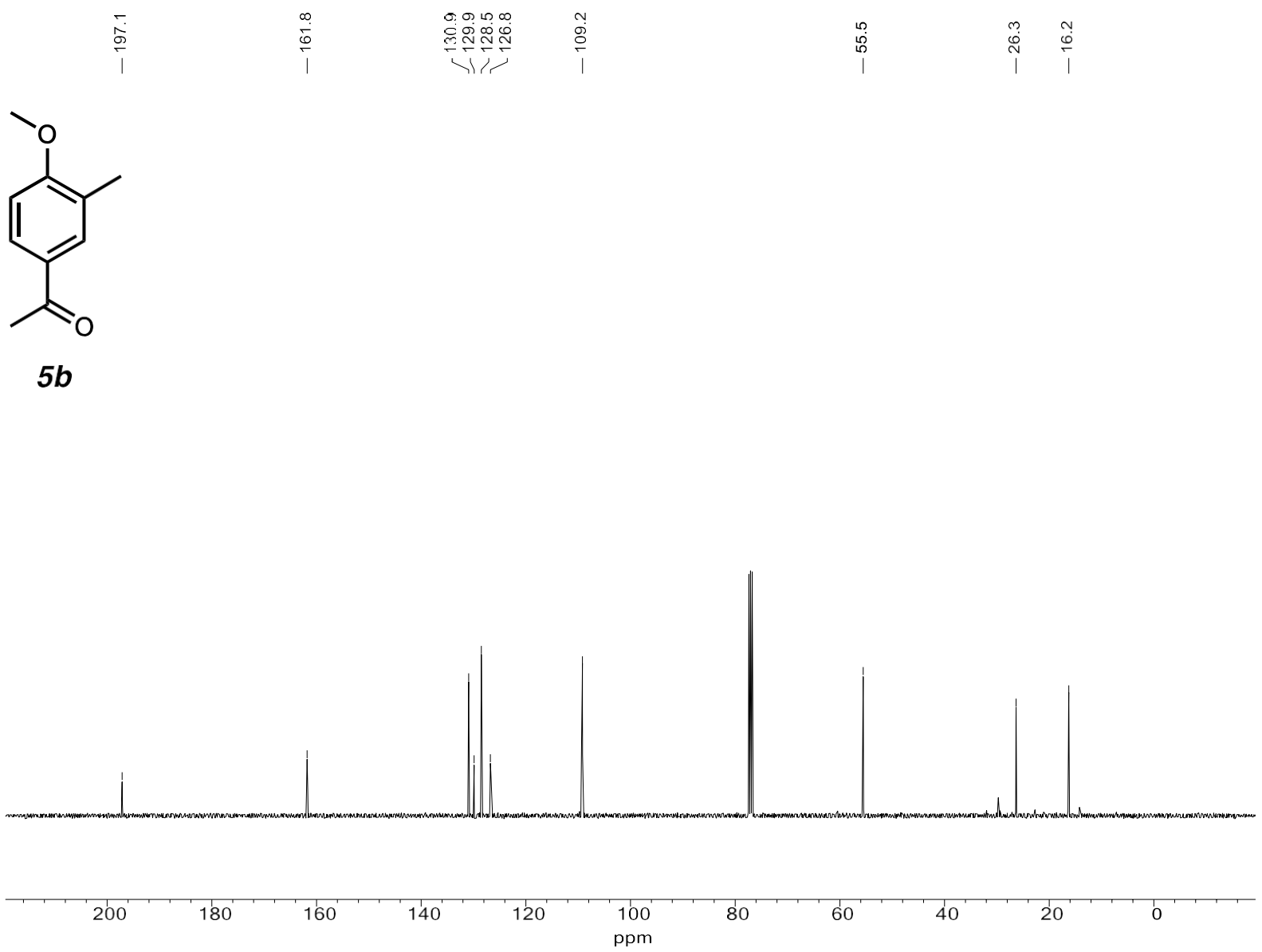
^{13}C NMR (101MHz, $CDCl_3$) of compound **5a**.



5b

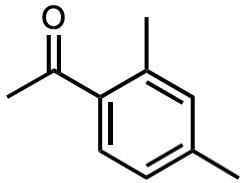


^{1}H NMR (400MHz, $CDCl_3$) of compound **5b.**

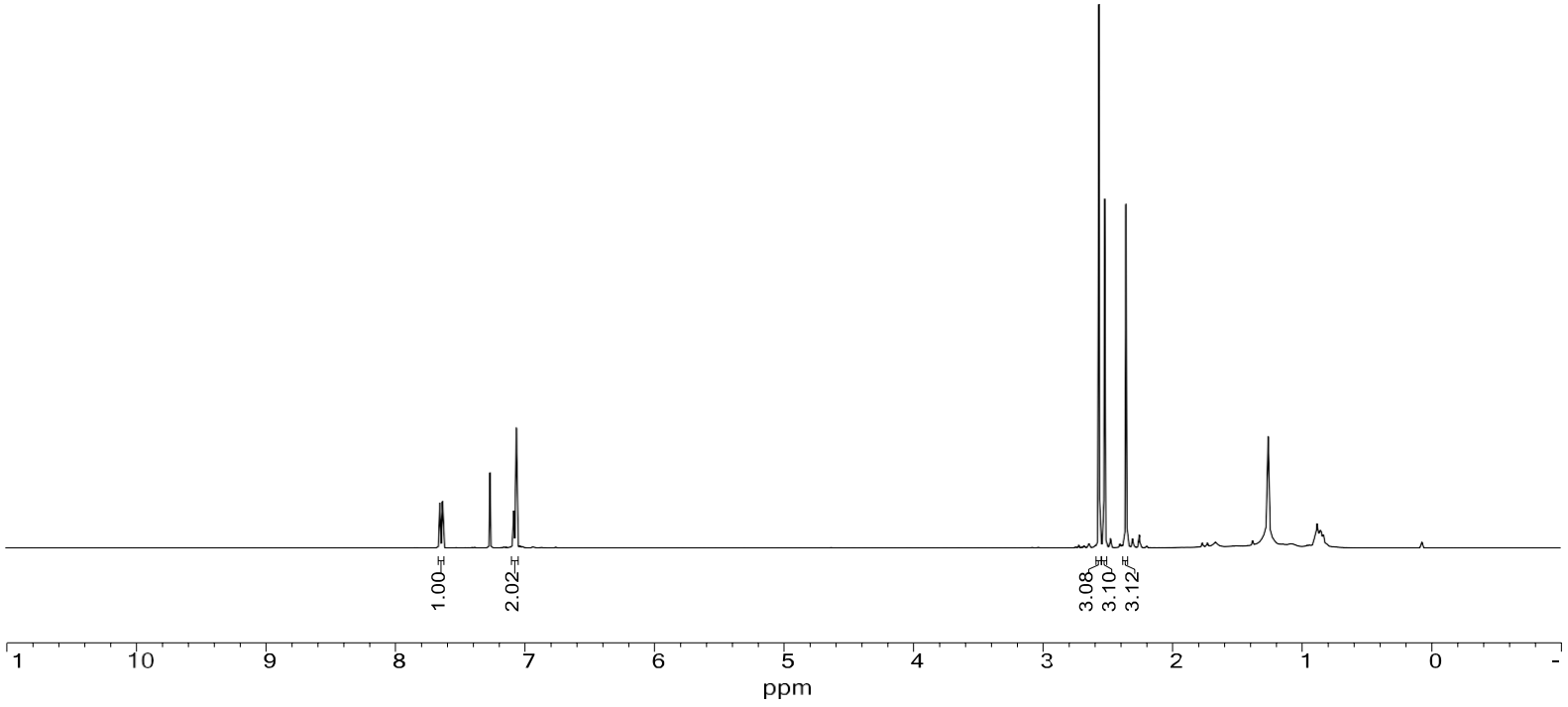


5b

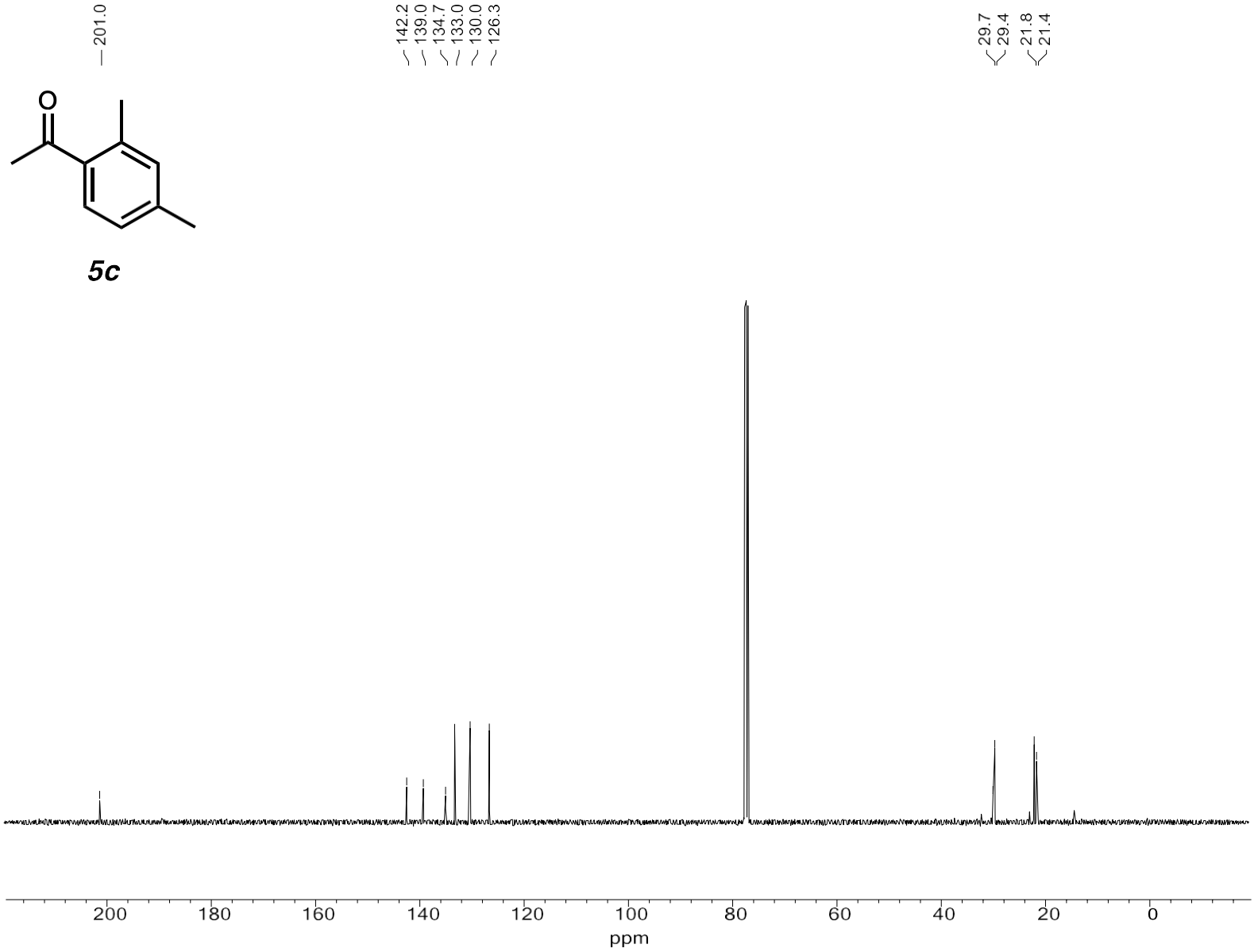
^{13}C NMR (101MHz, $CDCl_3$) of compound **5b**.



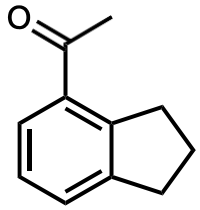
5c



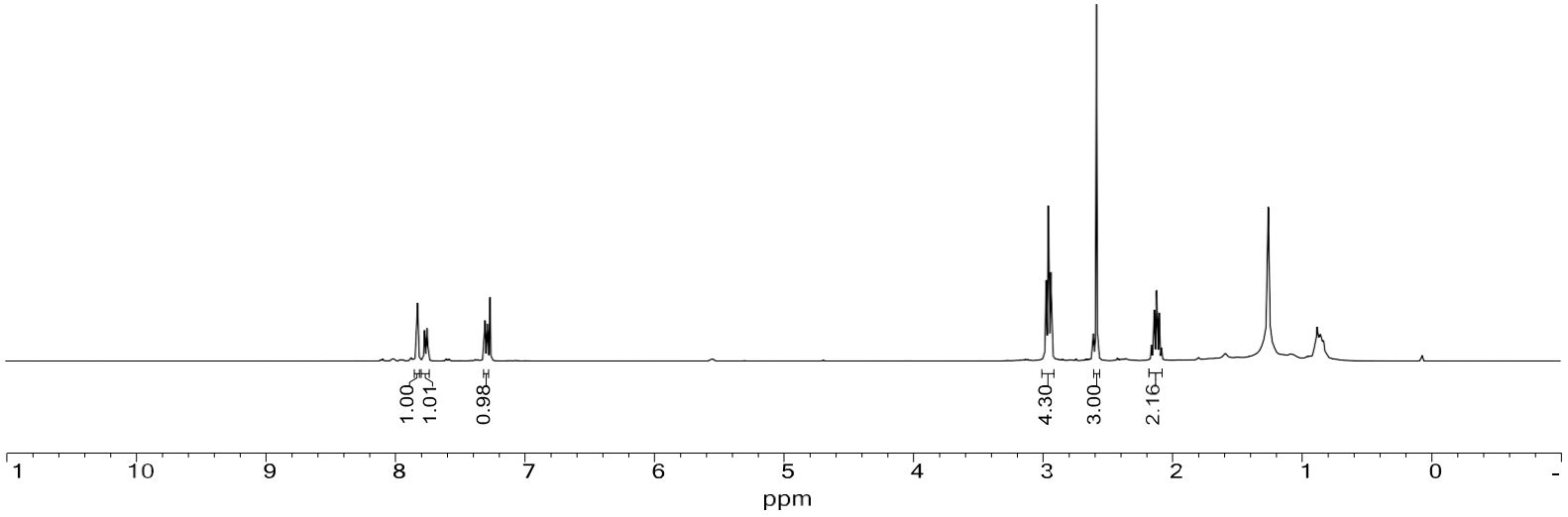
^{1}H NMR (400MHz, $CDCl_3$) of compound **5c.**



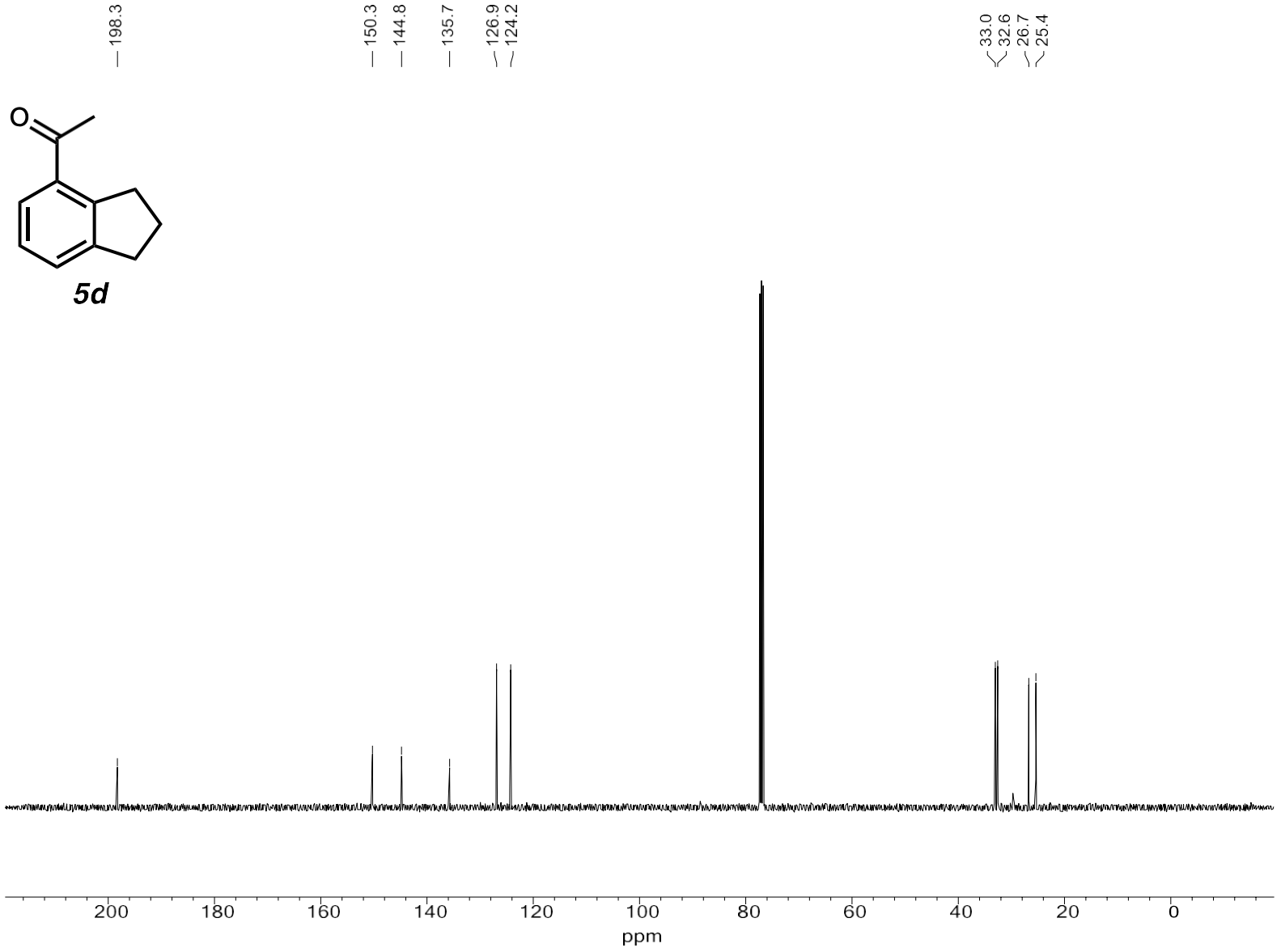
^{13}C NMR (101MHz, $CDCl_3$) of compound **5c**.



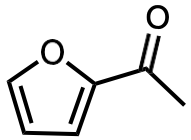
5d



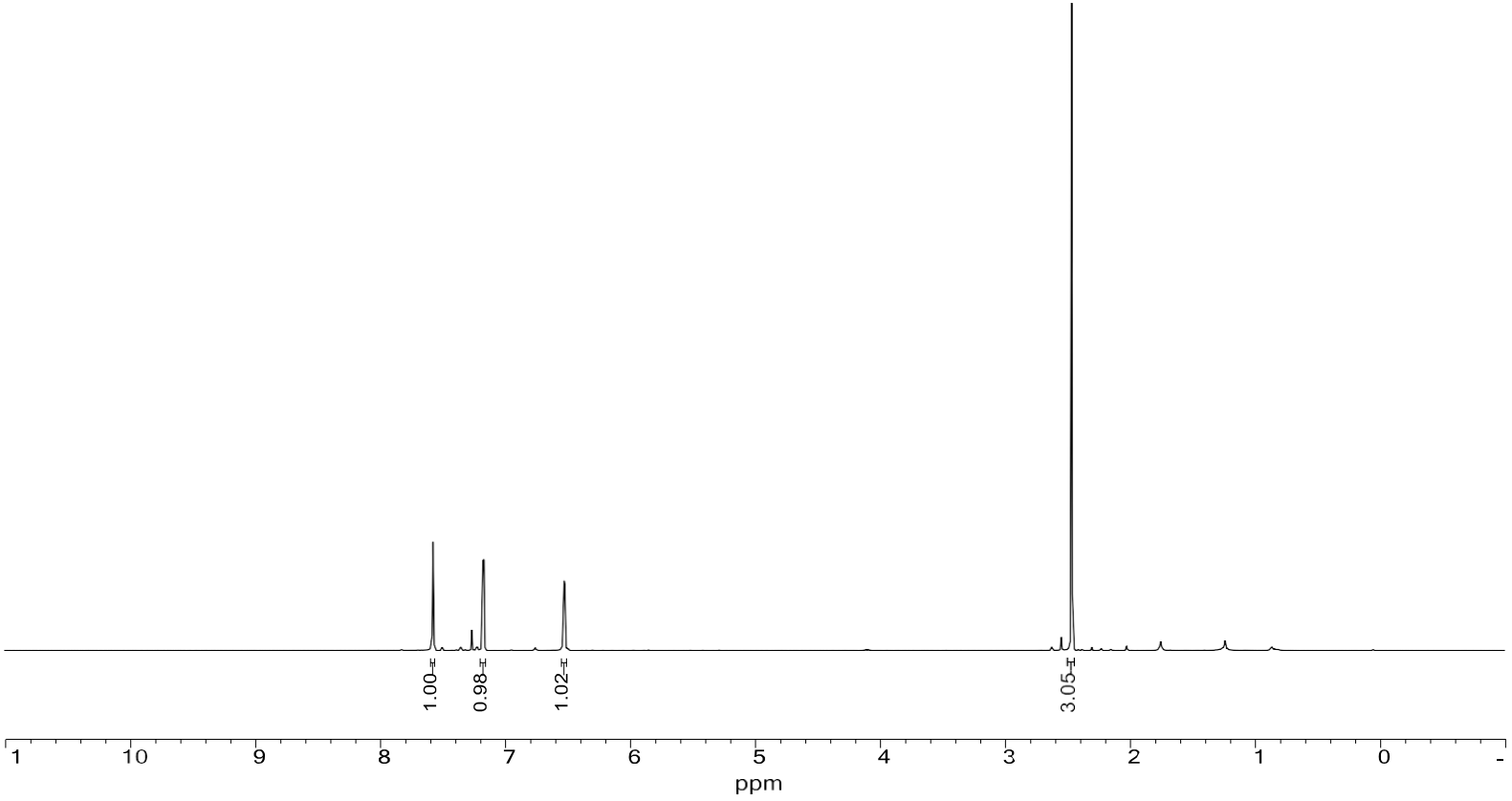
^{1}H NMR (400MHz, $CDCl_3$) of compound **5d.**



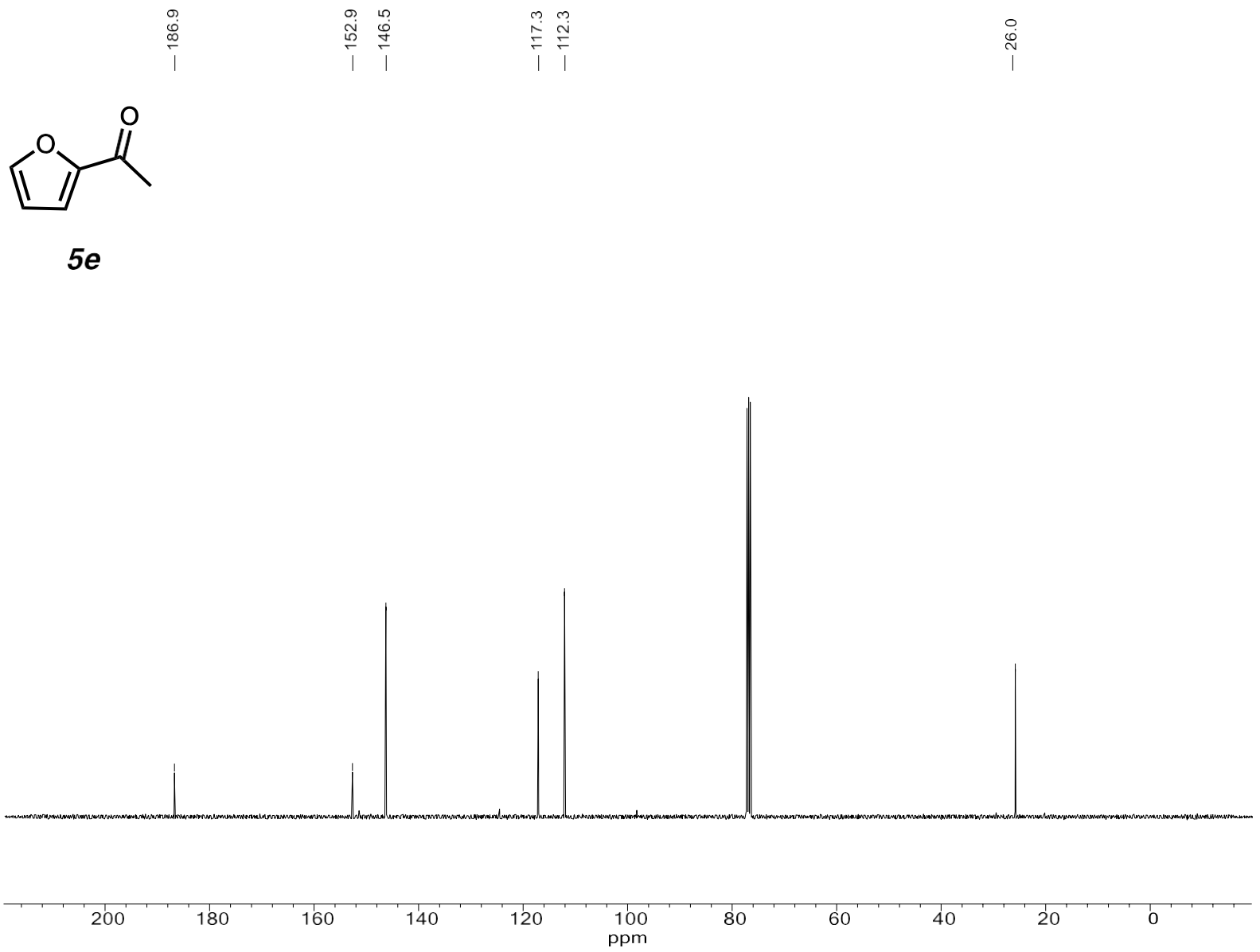
^{13}C NMR (101MHz, $CDCl_3$) of compound **5d**.



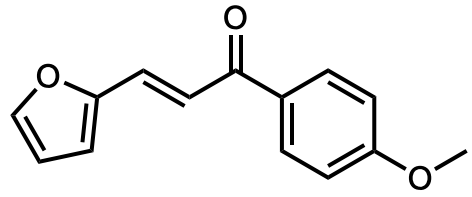
5e



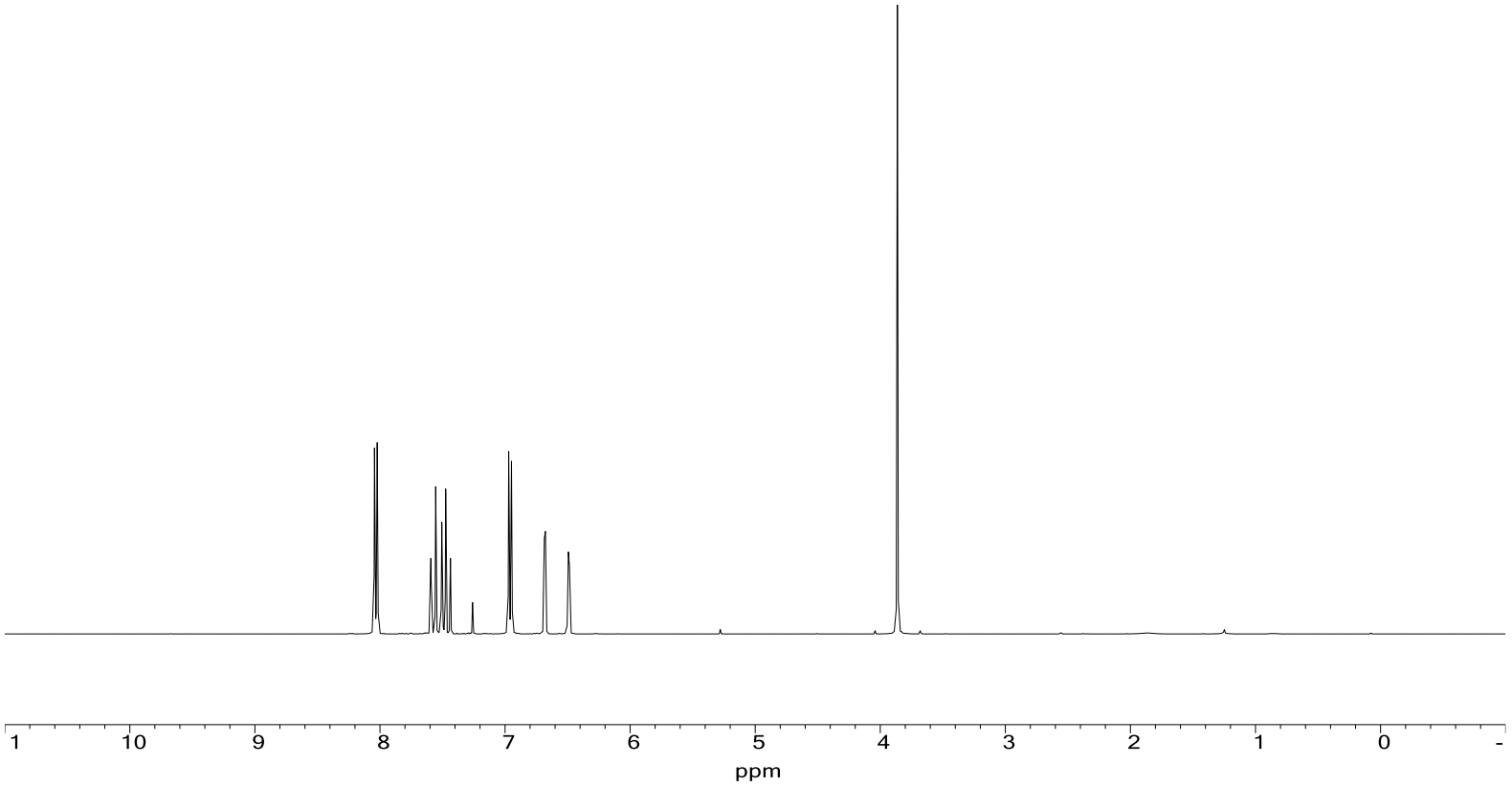
^{1}H NMR (400MHz, $CDCl_3$) of compound **5e.**



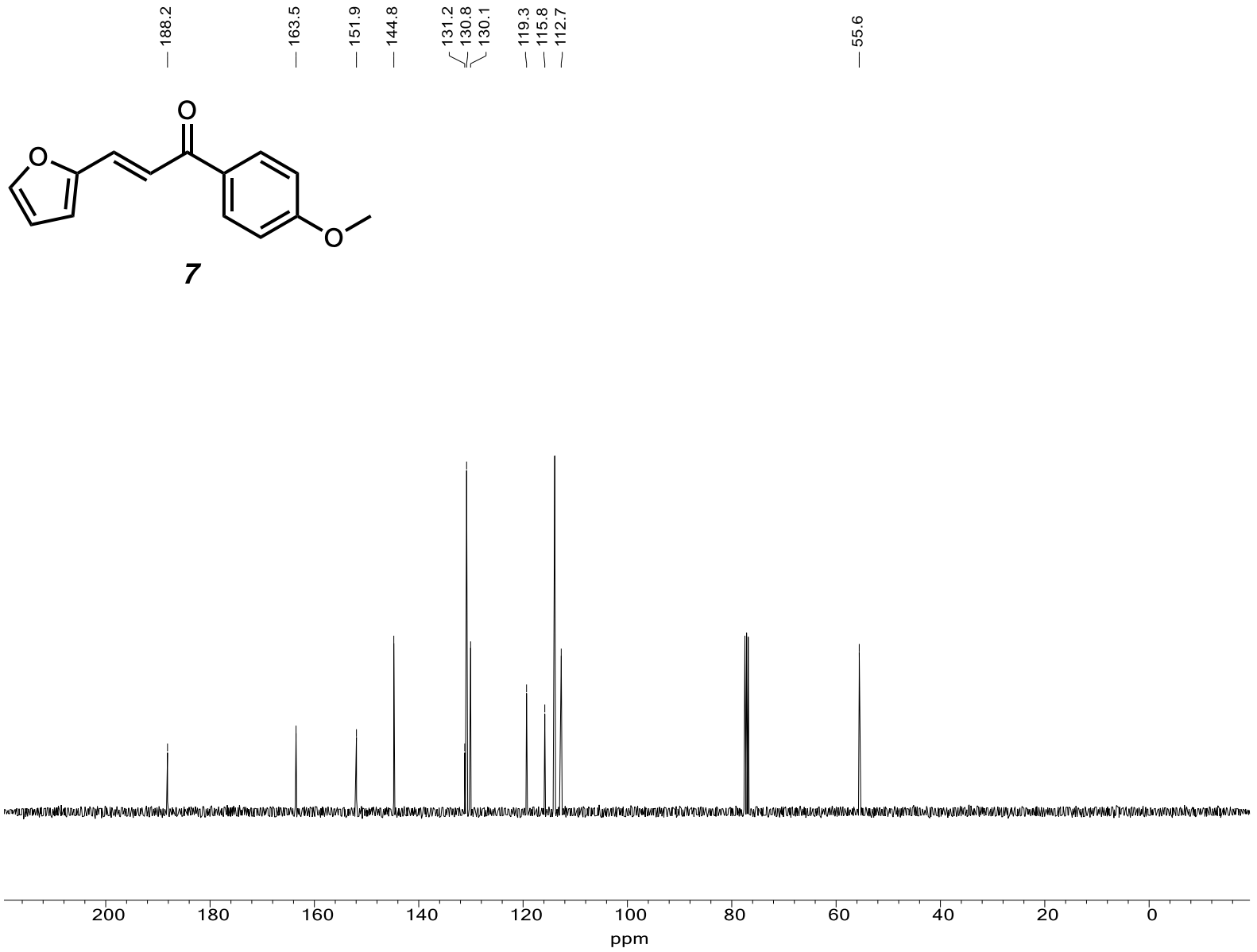
^{13}C NMR (101MHz, $CDCl_3$) of compound **5e**.



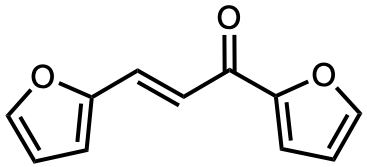
7



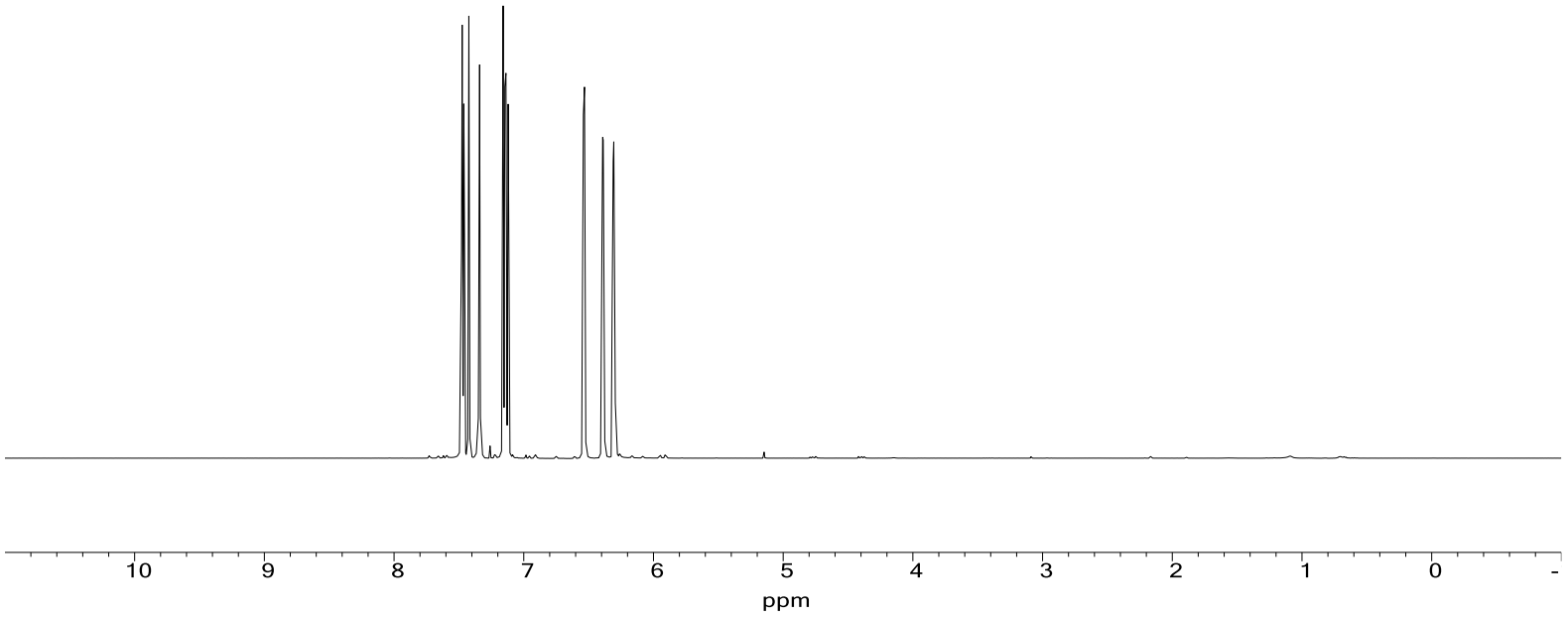
^{1}H NMR (400MHz, $CDCl_3$) of compound **7**.



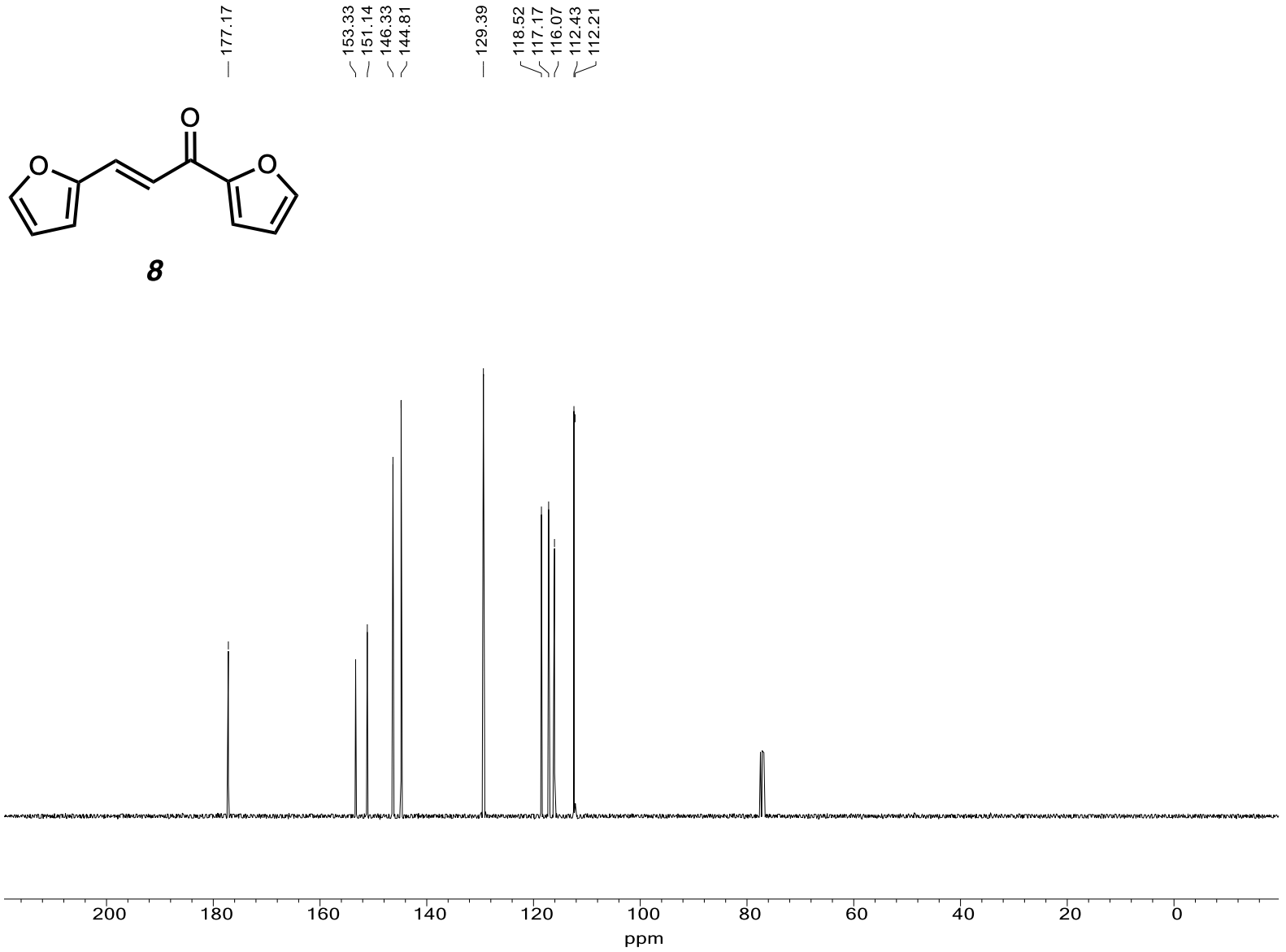
^{13}C NMR (101MHz, $CDCl_3$) of compound **7**.



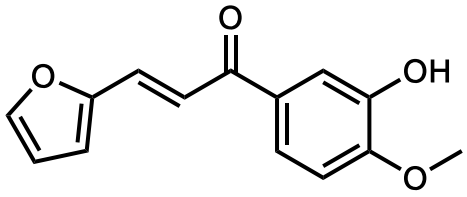
8



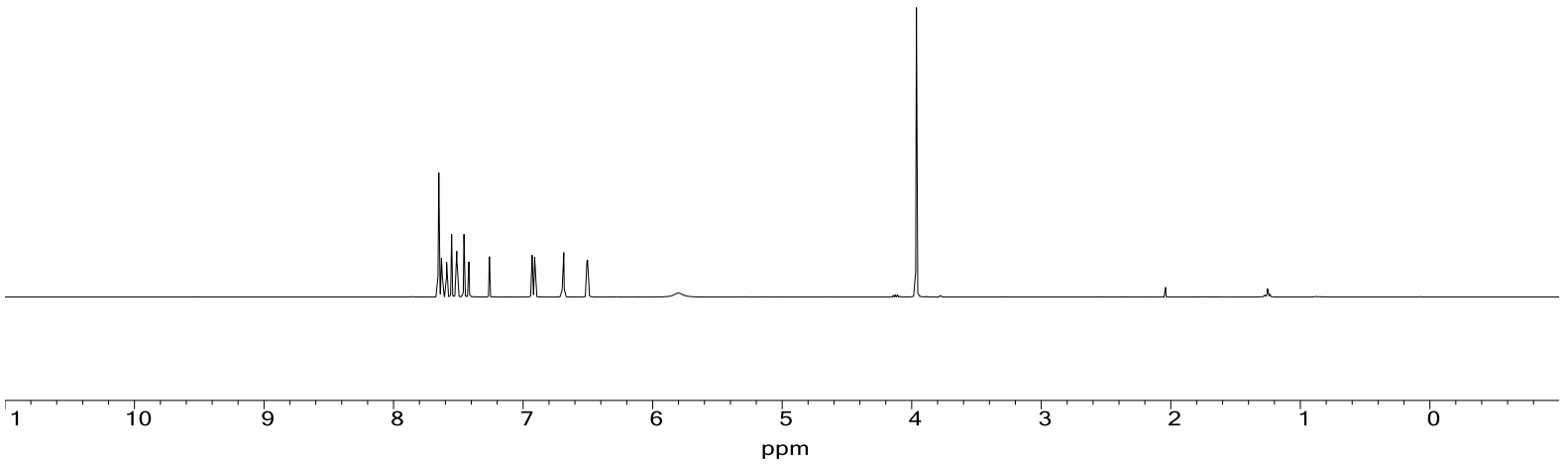
^{1}H NMR (400MHz, $CDCl_3$) of compound **8**.



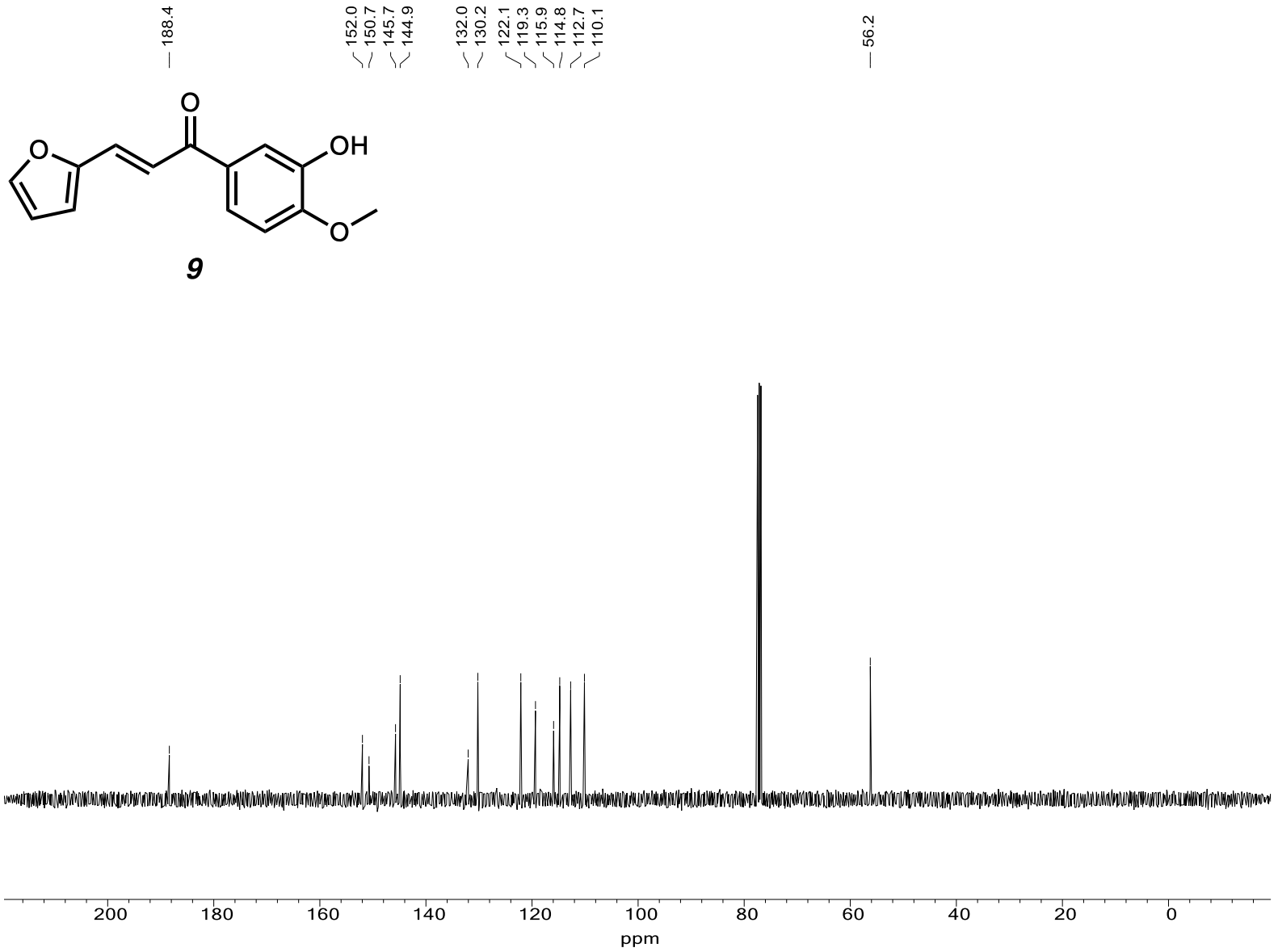
^{13}C NMR (101MHz, $CDCl_3$) of compound **8**.



9



^{1}H NMR (400MHz, $CDCl_3$) of compound **9**.



^{13}C NMR (101MHz, $CDCl_3$) of compound **9**.