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

Supporting Information

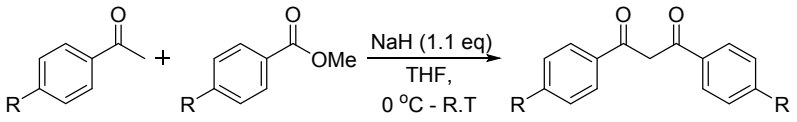
Direct synthesis of 2,3,5-trisubstituted pyrroles via copper-mediated one-pot multicomponent reaction

1. General experimental details

All reagents and solvents were purchased from commercial sources (Energy Chemical, Adamas, TCI, and Macklin) and used without further purification unless otherwise stated. All reported reaction temperatures correspond to oil bath temperatures. ^{1}H-NMR spectra were recorded at 400 MHz. Chemical shifts (in ppm) were referenced to $CDCl_3$ (δ = 7.26 ppm) in as an internal standard. ^{13}C-NMR spectra were obtained at 100 MHz and were calibrated with $CDCl_3$ (δ = 77.0 ppm). The NMR data are reported as follows: chemical shift (ppm), integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quad, m = multiplicity, br = wide state) and coupling constant (Hz). The highresolution mass spectra (HRMS) were recorded on an FT-ICR mass spectrometer using electrospray ionization (ESI). Thin layer chromatography (TLC) was performed on a glass plate coated with GF254 silica gel and observed under 254nm UV light, while column chromatography was performed using silica gel HG/T2354-2010.

2. Synthetic Methods

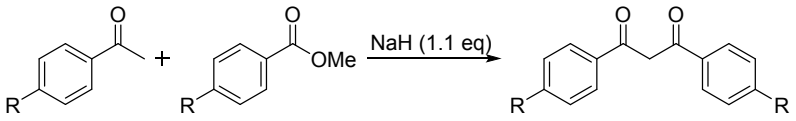
2.1 General procedure for the synthesis of 1,3-dicarbonyl compounds 1a and 1d



Following a modified literature procedure,[1] to a suspension of ketone (10 mmol) in THF (40 mL) was added NaH (0.8g, 20 mmol, 60%). After the reaction mixture was stirred at 0^{o}C for about 1 h, the ester was added dropwise at the same temperature. Then the mixture was stirred at room temperature until TLC indicated the total consumption of the ketone. The reaction mixture was poured into ice-water (100 mL), acidified with aqueous HCl (3 M) to pH 2~3 and extracted with EtOAc (100 mL × 3). The combined organic layer was dried over sodium sulfate and evaporated under reduced pressure to yield the crude product. This was further purified by recrystallization from EtOH to

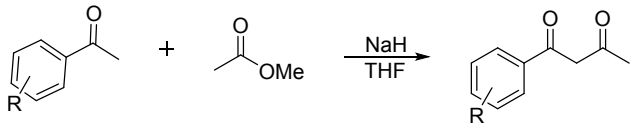
give the clean product **1a** and **1d**.

2.2 General procedure for the synthesis of 1,3-dicarbonyl compounds 1b and 1c



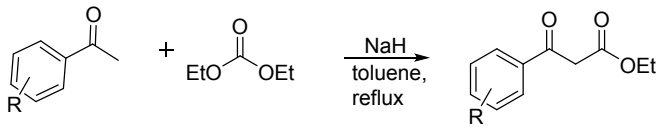
Following a modified literature procedure,[2] the corresponding ester (20 mmol, 2 equiv.) and NaH (1.2 g, 28 mmol, 2.8 equiv., 60% in mineral oil) were dissolved in dry THF (20 mL) in oven-dried glassware under N_2. A solution of the corresponding ketone (10 mmol) in dry THF (20 mL) was added slowly and the reaction mixture, heated to reflux and stirred overnight. The reaction mixture was quenched with aqueous HCl (25 mL, 1 M) and dichloromethane (50 mL). The aqueous layer was extracted with dichloromethane (2 × 20 mL) and the combined organic phase washed with brine (20 mL). The organic layer was dried ($MgSO_4$) and the solvent removed under reduced pressure to yield the crude product. This was further purified by recrystallization from EtOH to give the clean product **1b** and **1c**.

2.3 General procedure for the synthesis of 1,3-dicarbonyl compounds 1e-1n



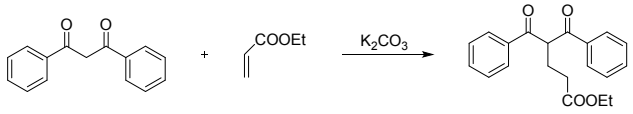
Following a modified literature procedure,[3] to a suspension of ketone (10 mmol) in THF (40 mL) was added NaH (20 mmol, 60%). After the reaction mixture was stirred at 0 ^oC for about 1 h, the ester was added dropwise at the same temperature. Then the mixture was stirred at room temperature until TLC indicated the total consumption of the ketone. The reaction mixture was poured into ice water (100 mL), acidified with aqueous HCl (3 M) to pH 2~3 and extracted with EtOAc (100 mL x 3). The combined organic layer was dried over sodium sulfate and evaporated under reduced pressure. The residues were purified by column chromatography to give the desired product **1e-1n**.

2.4 General Procedure for the Preparation of β-keto esters 1o-1q



Following a modified literature procedure,[4] to a dried three-necked flask equipped with a dropping funnel, a condenser, and a magnetic stirrer was added NaH (28 mmol), diethyl carbonate (20 mmol), and toluene (10 mL). The mixture was heated to reflux. A solution of ketone (10 mmol) in toluene (5 mL) was added dropwise from the dropping funnel over 1-2 h. After the addition, the mixture was heated to reflux until the evolution of hydrogen ceased (15-20 min). When the reaction was cooled to room temperature, glacial acetic acid (3mL) was added dropwise and a heavy, pasty solid appeared. Ice-water was added until the solid was dissolved completely. The toluene layer was separated, and the water layer was extracted with EtOAc (3×10 mL). The combined organic solution was washed with water (10 mL) and brine (10 mL), then dried over Na_2SO_4. After evaporation of the solvent, the mixture was distilled under reduced pressure or subjected chromatography to give the desired ß-keto esters **1o-1q**.

2.5 General Procedure for the Preparation of ethyl 4-benzoyl-5-oxo-5-phenylpentanoate 1a'



A mixture of 1,3-diphenyl-1,3-propanedione (5 mmol), ethyl acrylate (1.5 equiv.), and K_2CO_3 (0.1 equiv.) in MECN was heated to reflux and stirred overnight. Then the mixture was stirred at room temperature until TLC indicated the total consumption of 1,3-diphenyl-1,3-propanedione. The reaction mixture was filtered through a Celite pad washing with 10 ml of EtOAc. The filtrate was evaporated to afford the crude product. Finally, the crude product was purified by column chromatography to afford the desired product **1a'** as a colorless liquid (86%). 1H NMR (300 MHz, CDCl3) δ 8.08 – 7.96 (m,

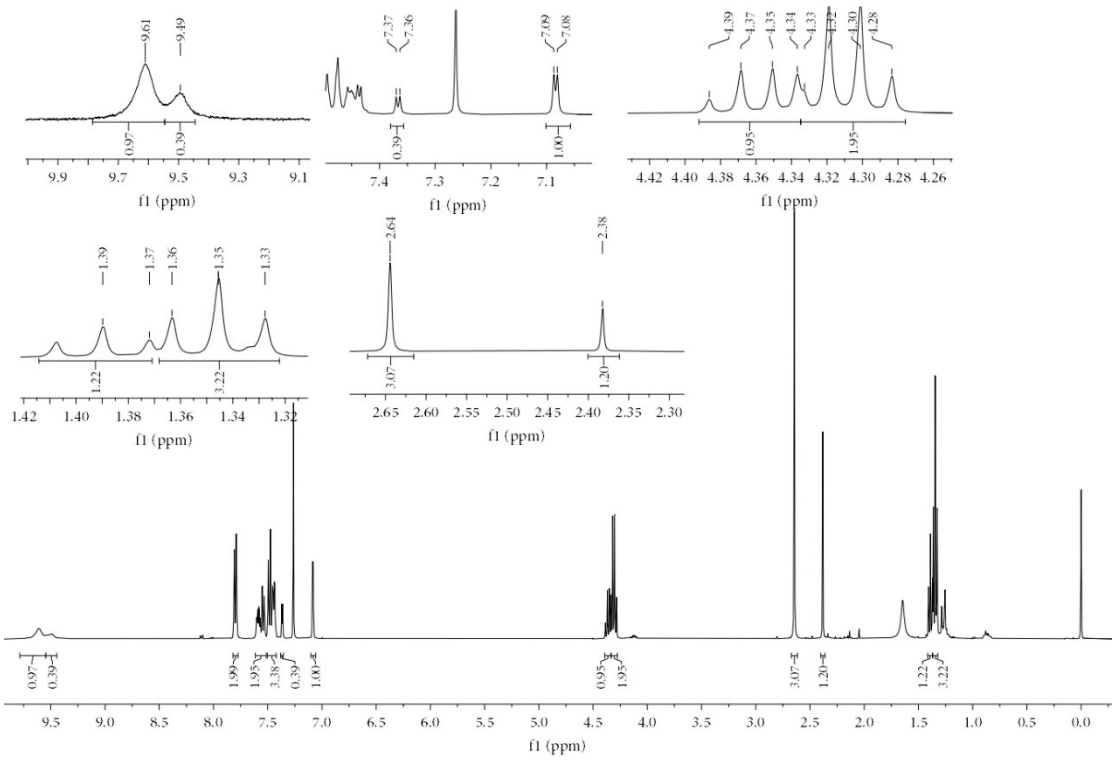
4H), 7.62 – 7.52 (m, 2H), 7.50 – 7.39 (m, 4H), 5.54 (t, J = 6.7 Hz, 1H), 4.14 (q, J = 7.2 Hz, 2H), 2.53 (t, J = 6.3 Hz, 2H), 2.43 – 2.34 (m, 2H), 1.24 (t, J = 7.1 Hz, 3H).

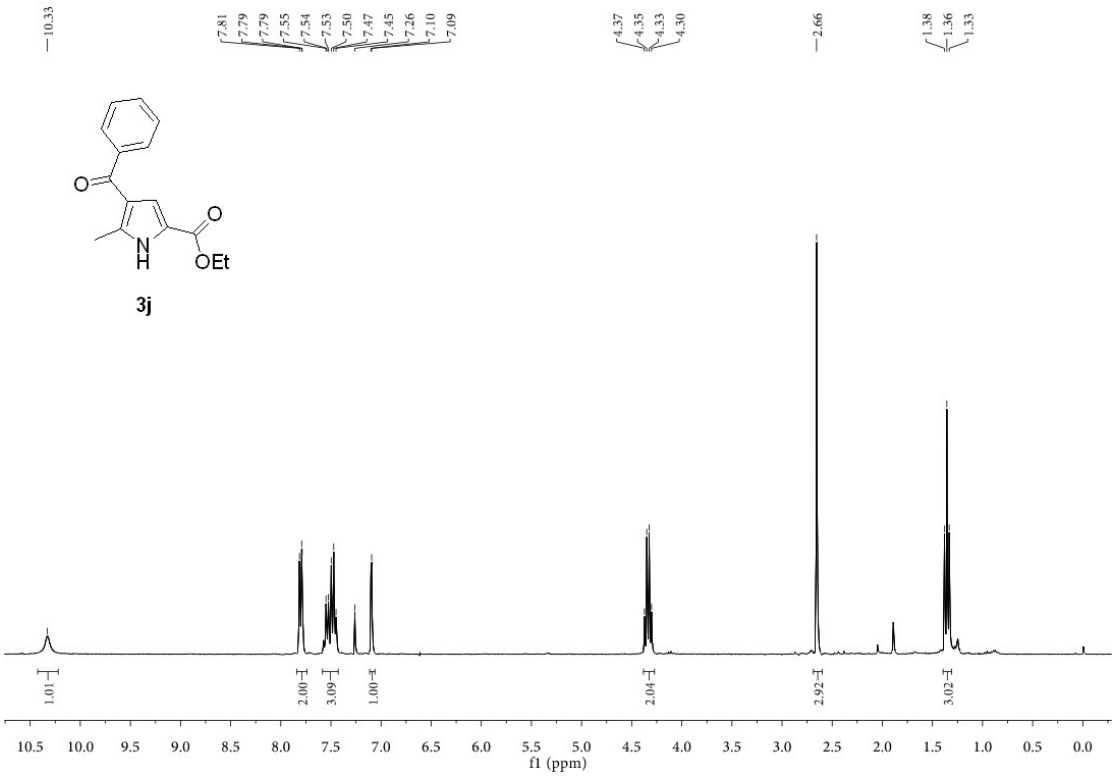
2.6 General Procedure for the Preparation of 2,3,5-trisubstituted pyrroles

In a pressure tube equipped with a stir bar, the 1,3-dicarbonyl compounds (1.0 equiv., 0.15 mmol), acrylate (2.0 equiv.), $Cu(OAc)_2$•H2O (2 equiv.), and NH_4OAc (5 equiv.) was dissolved in HFIP (2.0 mL). The tube was fitted with a Teflon screw cap and the reaction mixture was heated to 110°C and allowed to stir for 24 h. Upon cooling to room temperature, the reaction mixture was diluted with ethyl acetate and filtered through a pad of Celite. The filtrate was washed with saturated solution of $NaHCO_3$ and brine. The organic extract was dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by silica gel flash column chromatography to result in the desired product.

3. The separation of two isomers (3j and 3j')

(1) ^{1}H NMR of 3j and 3j'





According to ^{1}H NMR of two isomers, we found that the ratio of **3j** to **3j'** is 1:0.4. After separating two isomers which had very similar polarity, the desired product **3j** was obtained.

(2) X-ray data of compound 3j

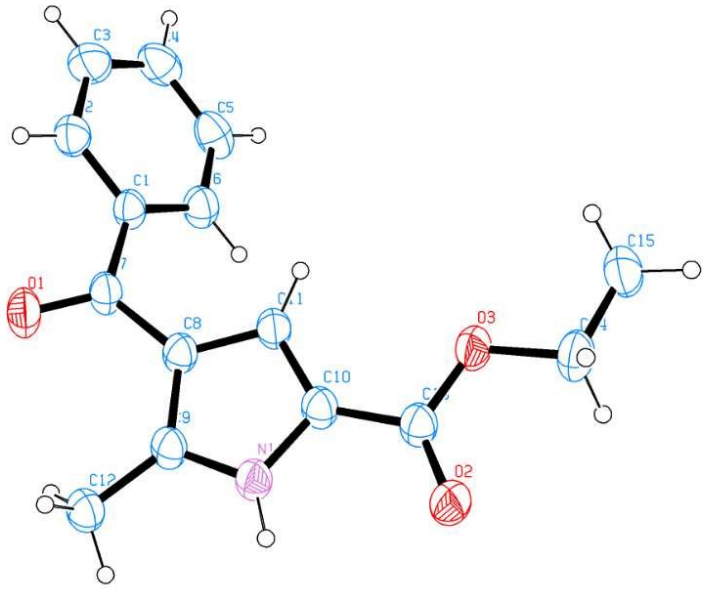
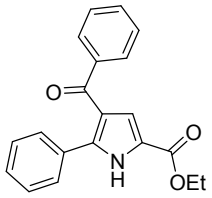


Table S1. Crystal data and structure refinement for 3j

Identification code	CCDC 2039332
Empirical formula	$C_{15}H_{15}NO_3$
Formula weight	257.28
Temperature/K	291.1(6)
Crystal system	monoclinic
Space group	C2/c
a/Å	22.7345(17)
b/Å	4.4106(5)
c/Å	28.580(3)
α/°	90
β/°	109.958(10)
γ/°	90
Volume/Å^3	2693.7(5)
Z	8
ρ_{calc}g/cm^3	1.269
μ/mm^{-1}	0.726
F (000)	1088.0
Crystal size/mm^3	0.14 × 0.05 × 0.04
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	19.83 to 133.192
Index ranges	-26 ≤ h ≤ 24, -3 ≤ k ≤ 5, -31 ≤ l ≤ 33
Reflections collected	3962
Independent reflections	2341 [R_{int} = 0.0307, R_{sigma} = 0.0452]
Data/restraints/parameters	2341/0/175
Goodness-of-fit on F^2	1.085
Final R indexes [I>=2σ (I)]	R_1 = 0.0551, wR_2 = 0.1656
Final R indexes [all data]	R_1 = 0.0847, wR_2 = 0.2440
Largest diff. peak/hole / e Å^{-3}	0.28/-0.27

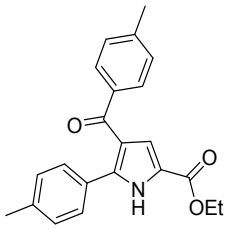
4. Analytical data for products

Ethyl 4-benzoyl-5-phenyl-1H-pyrrole-2-carboxylate (3a):[5]



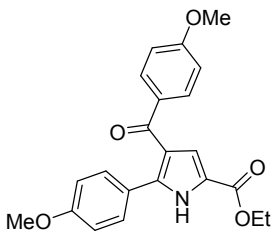
White solid. Yield: 65%. MP: 181-184 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.83 (s, 1H), 7.82 – 7.77 (m, 2H), 7.55 – 7.51 (m, 2H), 7.48 (dd, *J* = 10.5, 4.3 Hz, 1H), 7.37 (t, *J* = 7.6 Hz, 2H), 7.35 – 7.31 (m, 3H), 7.22 (d, *J* = 2.6 Hz, 1H), 4.28 (q, *J* = 7.1 Hz, 2H), 1.33 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.67, 161.10, 140.53, 138.88, 132.13, 130.78, 129.64, 128.97, 128.69, 128.48, 128.12, 122.25, 121.90, 119.29, 60.99, 14.38; HRMS calcd for $C_{20}H_{18}NO_3$ 320.1281 $[M+H]^+$, found 320.1291. This is a known structure. These data are similar to the reported one.

Ethyl 4-(4-methylbenzoyl)-5-(p-tolyl)-1H-pyrrole-2-carboxylate (3b):



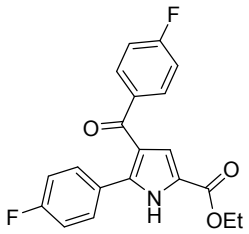
Yellow liquid. Yield: 62%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.87 (s, 1H), 7.73 (d, *J* = 8.1 Hz, 2H), 7.43 (d, *J* = 8.1 Hz, 2H), 7.22 – 7.12 (m, 5H), 4.26 (q, *J* = 7.1 Hz, 2H), 2.39 (s, 3H), 2.34 (s, 3H), 1.31 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.36, 161.09, 142.78, 140.43, 138.96, 136.26, 129.82, 129.17, 128.80, 128.39, 127.89, 121.77, 121.74, 119.27, 60.83, 21.57, 21.28, 14.35; HRMS calcd for $C_{22}H_{22}NO_3$ 348.1594 $[M+H]^+$, found 348.1603.

Ethyl 4-(4-methoxybenzoyl)-5-(4-methoxyphenyl)-1H-pyrrole-2-carboxylate (3c):



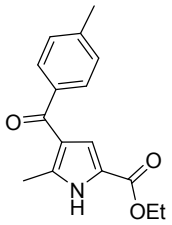
Yellow solid. Yield: 60%. MP: 160-162 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.53 (s, 1H), 7.83 (d, *J* = 8.7 Hz, 2H), 7.48 (d, *J* = 8.7 Hz, 2H), 7.17 (d, *J* = 2.5 Hz, 1H), 6.92 – 6.83 (m, 4H), 4.32 (q, *J* = 7.1 Hz, 2H), 3.83 (d, *J* = 18.6 Hz, 6H), 1.35 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.49, 162.91, 161.07, 160.10, 139.89, 132.00, 131.60, 129.84, 123.27, 121.60, 121.58, 119.13, 114.00, 113.36, 60.81, 55.41, 55.31, 14.39; HRMS calcd for $C_{22}H_{22}NO_5$ 380.1493 $[M+H]^+$, found 380.1503.

Ethyl 4-(4-fluorobenzoyl)-5-(4-fluorophenyl)-1H-pyrrole-2-carboxylate (3d):



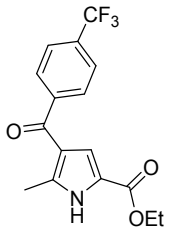
Yellow solid. Yield: 50%. MP: 168-170 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.15 (s, 1H), 7.86 – 7.78 (m, 2H), 7.56 – 7.48 (m, 2H), 7.17 (d, *J* = 2.6 Hz, 1H), 7.10 – 6.99 (m, 4H), 4.24 (q, *J* = 7.1 Hz, 2H), 1.31 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.00, 165.19 (d, *J* = 253.7 Hz), 163.05 (d, *J* = 249.8 Hz), 161.13, 139.62, 135.03 (d, *J* = 3.0 Hz), 132.08 (d, *J* = 9.1 Hz), 130.76 (d, *J* = 8.4 Hz), 126.81 (d, *J* = 3.4 Hz), 122.29, 121.59, 115.49 (d, *J* = 22.0 Hz), 115.27 (d, *J* = 22.8 Hz), 115.16, 61.06, 14.29; HRMS calcd for $C_{20}H_{16}F_2NO_3$ 356.1093 $[M+H]^+$, found 356.1102.

Ethyl 5-methyl-4-(4-methylbenzoyl)-1H-pyrrole-2-carboxylate (3e):



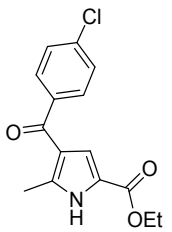
White solid. Yield: 62%. MP: 150-152 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.77 (s, 1H), 7.72 (d, *J* = 8.1 Hz, 2H), 7.28 (d, *J* = 8.8 Hz, 2H), 7.10 (d, *J* = 2.5 Hz, 1H), 4.33 (q, *J* = 7.1 Hz, 2H), 2.63 (s, 3H), 2.43 (s, 3H), 1.35 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.66, 142.23, 136.98, 129.25, 128.90, 121.54, 120.23, 118.74, 60.72, 21.56, 14.37, 13.83; HRMS calcd for $C_{16}H_{18}NO_3$ 272.1281 $[M+H]^+$, found 272.1292.

Ethyl 5-methyl-4-(4-(trifluoromethyl) benzoyl)-1H-pyrrole-2-carboxylate (3f):



Yellow solid. Yield: 51%. MP: 153-155 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.10 (s, 1H), 7.88 (d, *J* = 8.1 Hz, 2H), 7.75 (d, *J* = 8.1 Hz, 2H), 7.03 (d, *J* = 2.4 Hz, 1H), 4.34 (q, *J* = 7.1 Hz, 2H), 2.67 (s, 3H), 1.37 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.64, 161.24, 142.83, 141.49, 133.01 (q, *J* = 32.5 Hz), 129.13, 125.30 (q, *J* = 3.7 Hz), 123.77 (q, *J* = 272.5 Hz), 120.82, 120.68, 118.55, 60.96, 14.35, 13.95; HRMS calcd for $C_{16}H_{15}F_3NO_3$ 326.0999 $[M+H]^+$, found 326.1007.

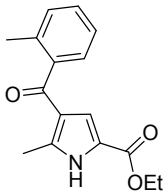
Ethyl 4-(4-chlorobenzoyl)-5-methyl-1H-pyrrole-2-carboxylate (3g):



Yellow solid. Yield: 65%. MP: 164-166 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.11 (s, 1H), 7.77 - 7.72 (m, 2H), 7.47 – 7.42 (m, 2H), 7.04 (d, *J* = 2.5 Hz, 1H), 4.34 (q, *J* = 7.1 Hz, 2H), 2.64 (s, 3H), 1.36 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.55, 161.28, 141.10, 138.00,

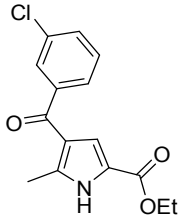
137.90, 130.43, 128.53, 121.01, 120.48, 118.52, 60.88, 14.35, 13.83; HRMS calcd for $C_{15}H_{15}ClNO_3$ 292.0735 $[M+H]^+$, found 292.0743.

Ethyl 5-methyl-4-(2-methylbenzoyl)-1H-pyrrole-2-carboxylate (3h):



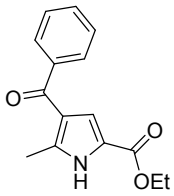
White solid. Yield: 58%. MP: 123-125 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.27 (s, 1H), 7.38 – 7.32 (m, 2H), 7.29 – 7.22 (m, 2H), 6.87 (d, *J* = 2.5 Hz, 1H), 4.31 (q, *J* = 7.1 Hz, 2H), 2.62 (s, 3H), 2.36 (s, 3H), 1.33 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.34, 161.37, 140.79, 140.48, 135.72, 130.88, 129.59, 127.60, 125.23, 122.71, 120.51, 119.06, 60.82, 19.65, 14.36, 13.94; HRMS calcd for $C_{16}H_{18}NO_3$ 272.1281 $[M+H]^+$, found 272.1290.

Ethyl 4-(3-chlorobenzoyl)-5-methyl-1H-pyrrole-2-carboxylate (3i):



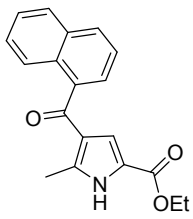
Yellow solid. Yield: 60%. MP: 150-152 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.90 (s, 1H), 7.75 (d, *J* = 1.7 Hz, 1H), 7.66 (d, *J* = 7.6 Hz, 1H), 7.54 – 7.49 (m, 1H), 7.41 (t, *J* = 7.8 Hz, 1H), 7.05 (d, *J* = 2.5 Hz, 1H), 4.34 (q, *J* = 7.1 Hz, 2H), 2.64 (s, 3H), 1.36 (t, *J* = 7.1 Hz, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 190.37, 161.32, 141.42, 141.28, 134.46, 131.58, 129.60, 128.94, 127.10, 120.94, 120.59, 118.59, 60.97, 14.40, 13.94; HRMS calcd for $C_{15}H_{15}ClNO_3$ 292.0735 $[M+H]^+$, found 292.0744.

Ethyl 4-benzoyl-5-methyl-1H-pyrrole-2-carboxylate (3j)



White solid. Yield: 48%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.33 (s, 1H), 7.88 – 7.73 (m, 1H), 7.60 – 7.40 (m, 1H), 7.10 (d, *J* = 2.4 Hz, 1H), 4.34 (q, *J* = 7.1 Hz, 1H), 2.66 (s, 1H), 1.36 (t, *J* = 7.1 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.94, 161.32, 140.92, 139.70, 131.60, 129.01, 128.21, 121.33, 120.28, 118.85, 60.79, 14.36, 13.87; HRMS calcd for $C_{15}H_{15}NO_3$ 258.1125 $[M+H]^+$, found 258.1134.

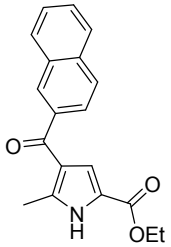
Ethyl 4-(1-naphthoyl)-5-methyl-1H-pyrrole-2-carboxylate (3k):



Yellow liquid. Yield: 57%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.35 (s, 1H), 8.17 – 8.10 (m, 1H), 7.96 (d, *J* = 8.2 Hz, 1H), 7.90 (dd, *J* = 6.7, 2.7 Hz, 1H), 7.61 (dd, *J* = 7.0, 1.1 Hz, 1H), 7.55 – 7.48 (m, 3H), 6.90 (d, *J* = 2.5 Hz, 1H), 4.27 (q, *J* = 7.1 Hz, 2H), 2.65 (s, 3H), 1.29 (t, *J* =

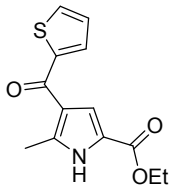
7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.54, 161.41, 141.21, 138.20, 133.68, 130.37, 130.33, 128.22, 126.86, 126.23, 126.12, 125.54, 124.49, 123.13, 120.46, 119.21, 60.78, 14.26, 14.02; HRMS calcd for $C_{19}H_{18}NO_3$ 308.1281 $[M+H]^+$, found 308.1289.

Ethyl 4-(2-naphthoyl)-5-methyl-1H-pyrrole-2-carboxylate (3l):



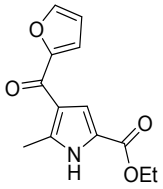
Yellow solid. Yield: 65%. MP: 181-183 °C.^{1}H NMR (400 MHz, $CDCl_3$) δ 9.88 (s, 1H), 8.28 (s, 1H), 7.94 (d, *J* = 9.3 Hz, 1H), 7.92 – 7.86 (m, 3H), 7.61 – 7.50 (m, 2H), 7.14 (d, *J* = 2.3 Hz, 1H), 4.32 (q, *J* = 7.1 Hz, 2H), 2.66 (s, 3H), 1.33 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.93, 161.27, 140.73, 137.03, 134.96, 132.44, 130.13, 129.30, 128.19, 127.84, 127.81, 126.62, 125.44, 121.65, 120.47, 118.85, 60.82, 14.40, 13.93; HRMS calcd for $C_{19}H_{18}NO_3$ 308.1281 $[M+H]^+$, found 308.1290.

Ethyl 5-methyl-4-(thiophene-2-carbonyl)-1H-pyrrole-2-carboxylate (3m):



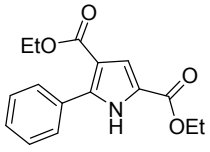
White solid. Yield: 61%. MP: 158-160 °C.^{1}H NMR (400 MHz, $CDCl_3$) δ 10.05 (s, 1H), 7.76 (dd, *J* = 3.7, 1.1 Hz, 1H), 7.63 (dd, *J* = 5.0, 1.0 Hz, 1H), 7.35 (d, *J* = 2.5 Hz, 1H), 7.15 (dd, *J* = 4.9, 3.8 Hz, 1H), 4.36 (q, *J* = 7.1 Hz, 2H), 2.63 (s, 3H), 1.38 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.63, 161.30, 145.21, 140.73, 132.49, 127.75, 121.16, 120.59, 117.56, 117.54, 60.85, 14.41, 13.69; HRMS calcd for $C_{13}H_{14}NO_3S$ 264.0689 $[M+H]^+$, found 264.0697.

Ethyl 4-(furan-2-carbonyl)-5-methyl-1H-pyrrole-2-carboxylate (3n):



White solid. Yield: 59 %. MP: 147-149 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.69 (s, 1H), 7.65 (d, *J* = 0.8 Hz, 1H), 7.61 (d, *J* = 2.5 Hz, 1H), 7.28 (d, *J* = 3.5 Hz, 1H), 6.56 (dd, *J* = 3.5, 1.7 Hz, 1H), 4.36 (q, *J* = 7.1 Hz, 2H), 2.66 (s, 3H), 1.39 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.39, 161.28, 153.83, 145.69, 141.52, 120.73, 120.17, 117.72, 117.64, 111.99, 60.79, 14.42, 14.14; HRMS calcd for $C_{13}H_{14}NO_4$ 248.0918 $[M+H]^+$, found 248.0928.

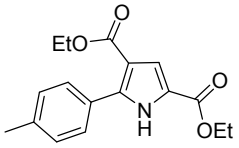
Diethyl 3-phenyl-1H-pyrrole-2,5-dicarboxylate (3o):[6]



White solid. Yield: 57%. MP: 140-143 °C. ^{1}H NMR (400 MHz,

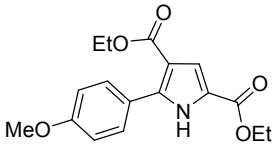
$CDCl_3$) δ 9.61 (s, 1H), 7.65 – 7.60 (m, 2H), 7.44 – 7.38 (m, 4H), 4.25 (dq, *J* = 14.3, 7.1 Hz, 4H), 1.34 (t, *J* = 7.1 Hz, 3H), 1.27 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.98, 161.02, 140.64, 130.84, 129.20, 129.05, 128.12, 122.22, 118.29, 114.12, 60.86, 60.00, 14.33, 14.21; HRMS calcd for $C_{16}H_{18}NO_4$ 288.1231 $[M+H]^+$, found 288.1240.

Diethyl 3-(p-tolyl)-1H-pyrrole-2,5-dicarboxylate (3p):



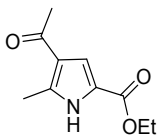
White solid. Yield: 50%. MP: 125-128 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.54 (s, 1H), 7.52 (d, *J* = 8.1 Hz, 2H), 7.38 (d, *J* = 2.8 Hz, 1H), 7.23 (d, *J* = 8.0 Hz, 2H), 4.25 (dq, *J* = 17.0, 7.1 Hz, 4H), 2.39 (s, 3H), 1.34 (t, *J* = 7.1 Hz, 3H), 1.28 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.02, 161.02, 140.84, 139.14, 129.02, 128.85, 127.91, 121.98, 118.28, 113.88, 60.79, 59.94, 21.33, 14.34, 14.25; HRMS calcd for $C_{17}H_{20}NO_4$ 302.1387 $[M+H]^+$, found 302.1395.

Diethyl 3-(4-methoxyphenyl)-1H-pyrrole-2,5-dicarboxylate (3q):



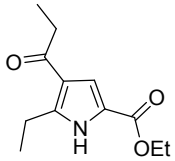
White solid. Yield: 52%. MP: 148-150 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.49 (s, 1H), 7.60 – 7.55 (m, 2H), 7.38 (d, *J* = 2.8 Hz, 1H), 6.97 – 6.93 (m, 2H), 4.31 – 4.25 (m, 2H), 4.25 – 4.20 (m, 2H), 3.84 (s, 3H), 1.34 (t, *J* = 7.1 Hz, 3H), 1.28 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.12, 161.10, 160.28, 140.78, 130.57, 123.19, 121.83, 118.39, 113.62, 113.60, 60.83, 59.97, 55.35, 14.38, 14.31; HRMS calcd for $C_{17}H_{20}NO_5$ 318.1336 $[M+H]^+$, found 318.1345.

Ethyl 4-acetyl-5-methyl-1H-pyrrole-2-carboxylate (3r):



White solid. Yield: 70%. MP: 113-115 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.13 (s, 1H), 7.21 (d, *J* = 2.5 Hz, 1H), 4.34 (q, *J* = 7.1 Hz, 2H), 2.59 (s, 3H), 2.42 (s, 3H), 1.37 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.79, 161.30, 139.58, 122.39, 120.26, 117.32, 60.76, 28.18, 14.35, 13.95; HRMS calcd for $C_{10}H_{14}NO_3$ 196.0968 $[M+H]^+$, found 196.0976.

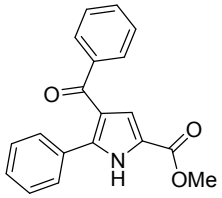
Ethyl 5-ethyl-4-propionyl-1H-pyrrole-2-carboxylate (3s):



White solid. Yield: 75%. MP: 104-106 °C. ^{1}H NMR (400 MHz, $CDCl_3$)

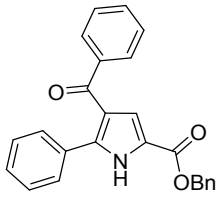
δ 9.96 (s, 1H), 7.22 (d, *J* = 2.5 Hz, 1H), 4.33 (q, *J* = 7.1 Hz, 2H), 3.04 (q, *J* = 7.5 Hz, 2H), 2.80 (q, *J* = 7.3 Hz, 2H), 1.36 (t, *J* = 7.1 Hz, 3H), 1.25 (t, *J* = 7.5 Hz, 3H), 1.15 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.54, 161.28, 145.26, 121.05, 120.22, 116.79, 60.68, 33.28, 21.19, 14.37, 12.88, 8.24; HRMS calcd for $C_{12}H_{18}NO_3$ 224.1281 $[M+H]^+$, found 224.1291.

Methyl 4-benzoyl-5-phenyl-1H-pyrrole-2-carboxylate (3t):[5]



Yellow liquid. Yield: 59%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.95 (s, 1H), 7.82 – 7.77 (m, 2H), 7.55 – 7.51 (m, 2H), 7.51 – 7.46 (m, 1H), 7.37 (t, *J* = 7.6 Hz, 2H), 7.34 – 7.31 (m, 3H), 7.21 (d, *J* = 2.6 Hz, 1H), 3.81 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.59, 161.50, 140.71, 138.78, 132.12, 130.64, 129.59, 128.96, 128.67, 128.41, 128.08, 121.87, 121.80, 119.51, 51.90; HRMS calcd for $C_{19}H_{16}NO_3$ 306.1125 $[M+H]^+$, found 306.1134.

Benzyl 4-benzoyl-5-phenyl-1H-pyrrole-2-carboxylate (3u):[7]



Yellow liquid. Yield: 69%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.03 (s, 1H), 7.80 – 7.75 (m, 2H), 7.53 – 7.44 (m, 3H), 7.39 – 7.32 (m, 7H), 7.32 – 7.28 (m, 3H), 7.25 (d, *J* = 2.6 Hz, 1H), 5.22 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.59, 160.89, 140.84, 138.72, 135.56, 132.13, 130.63, 129.59, 128.98, 128.69, 128.60, 128.43, 128.39, 128.26, 128.09, 121.98, 121.81, 119.68, 66.55; HRMS calcd for $C_{25}H_{20}NO_3$ 382.1438 $[M+H]^+$, found 382.1447.

References

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5. Z. Huang, J. Hu and Y. Gong, *Org. Biomol. Chem.*, 2015, **13**, 8561-8566.
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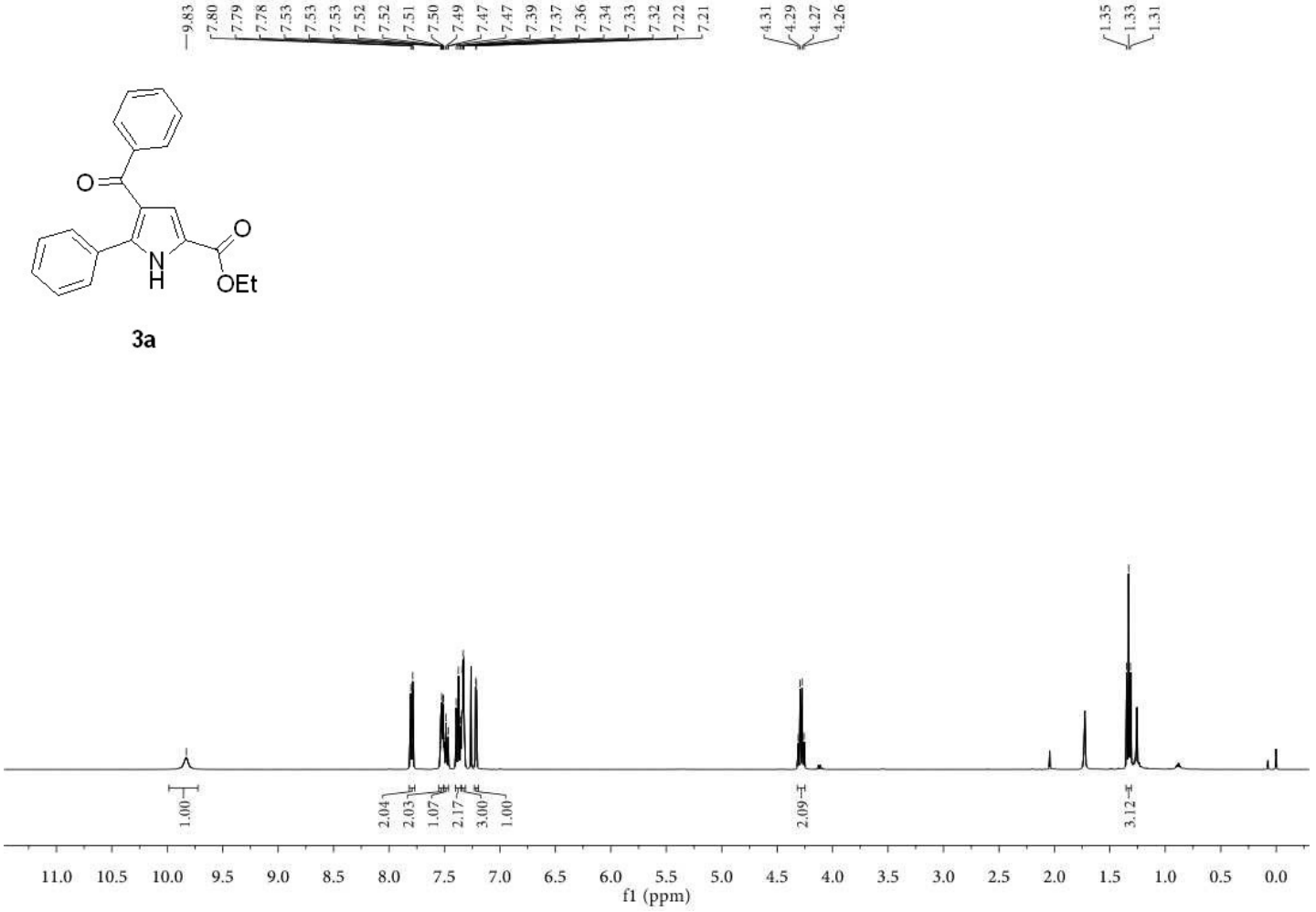
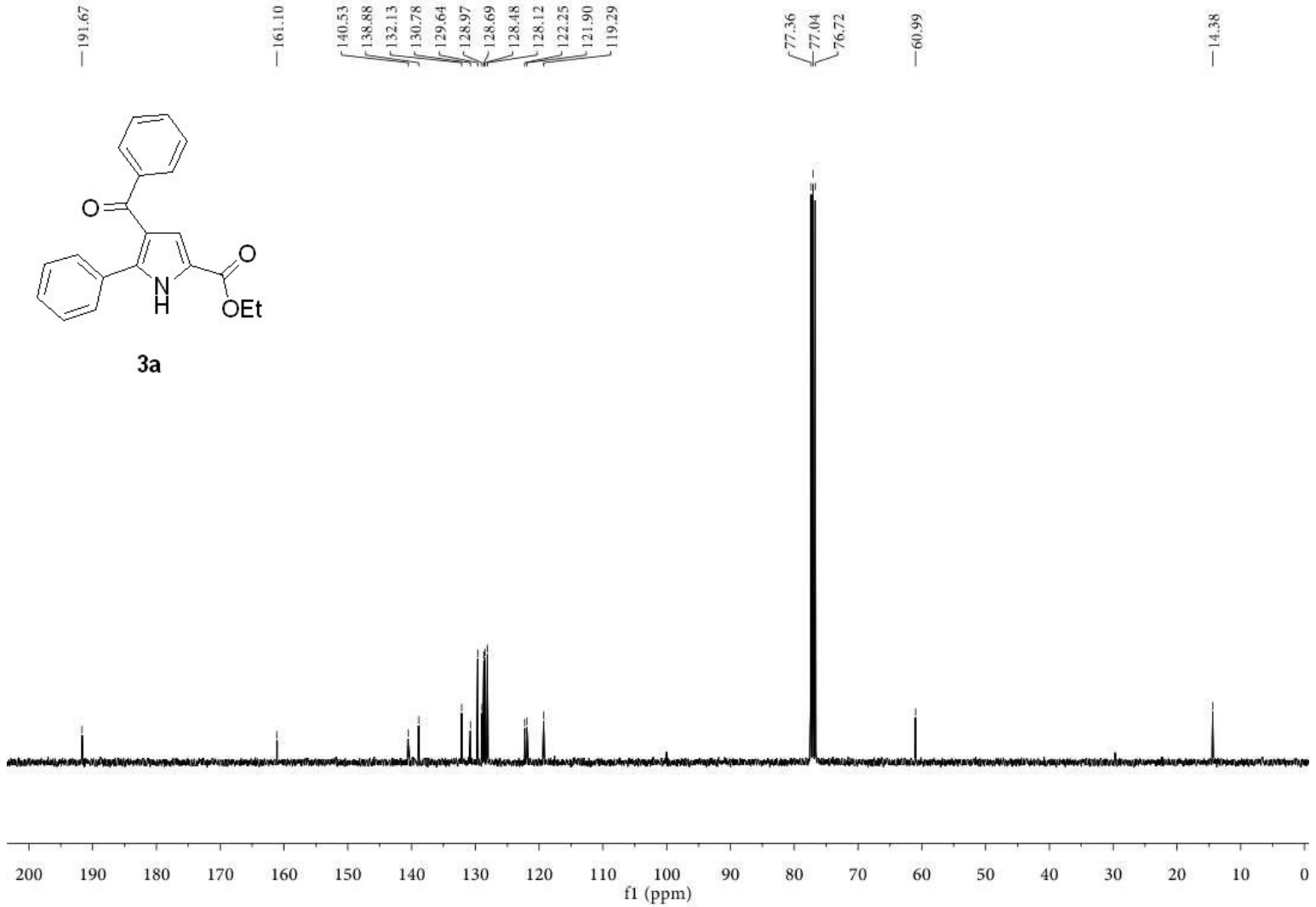
7. P. Kumar and M. Kapur, *Org. Lett.*, 2019, **21**, 2134-2138.

5. NMR spectra of all compounds

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128.97
128.69
128.48
128.12
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121.90
119.29
77.36
77.04
76.72
60.99
14.38
O
O
N
H
OEt
3a
200
190
180
170
160
150
140
130
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100
90
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70
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50
40
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10
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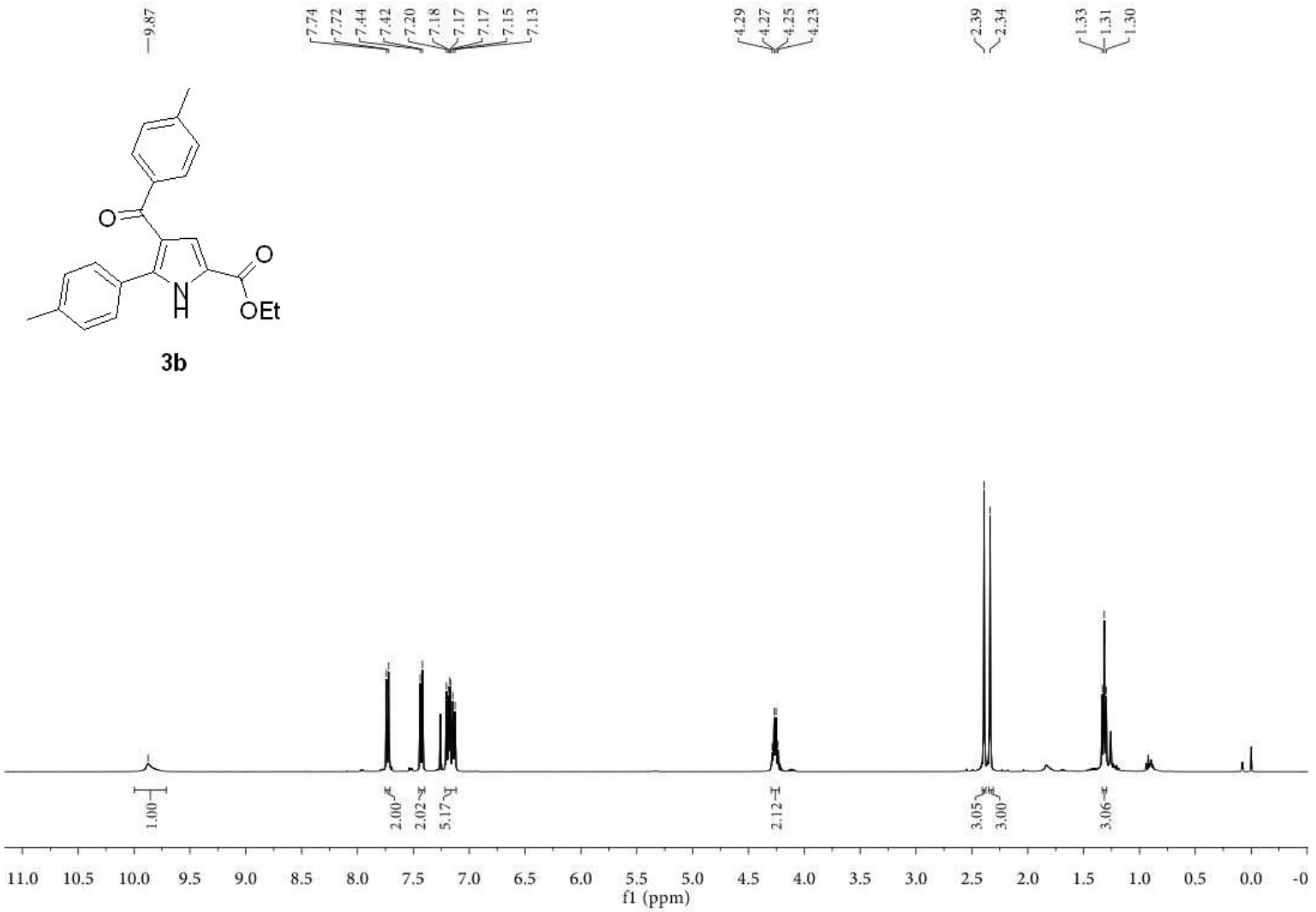
f1 (ppm)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7.13
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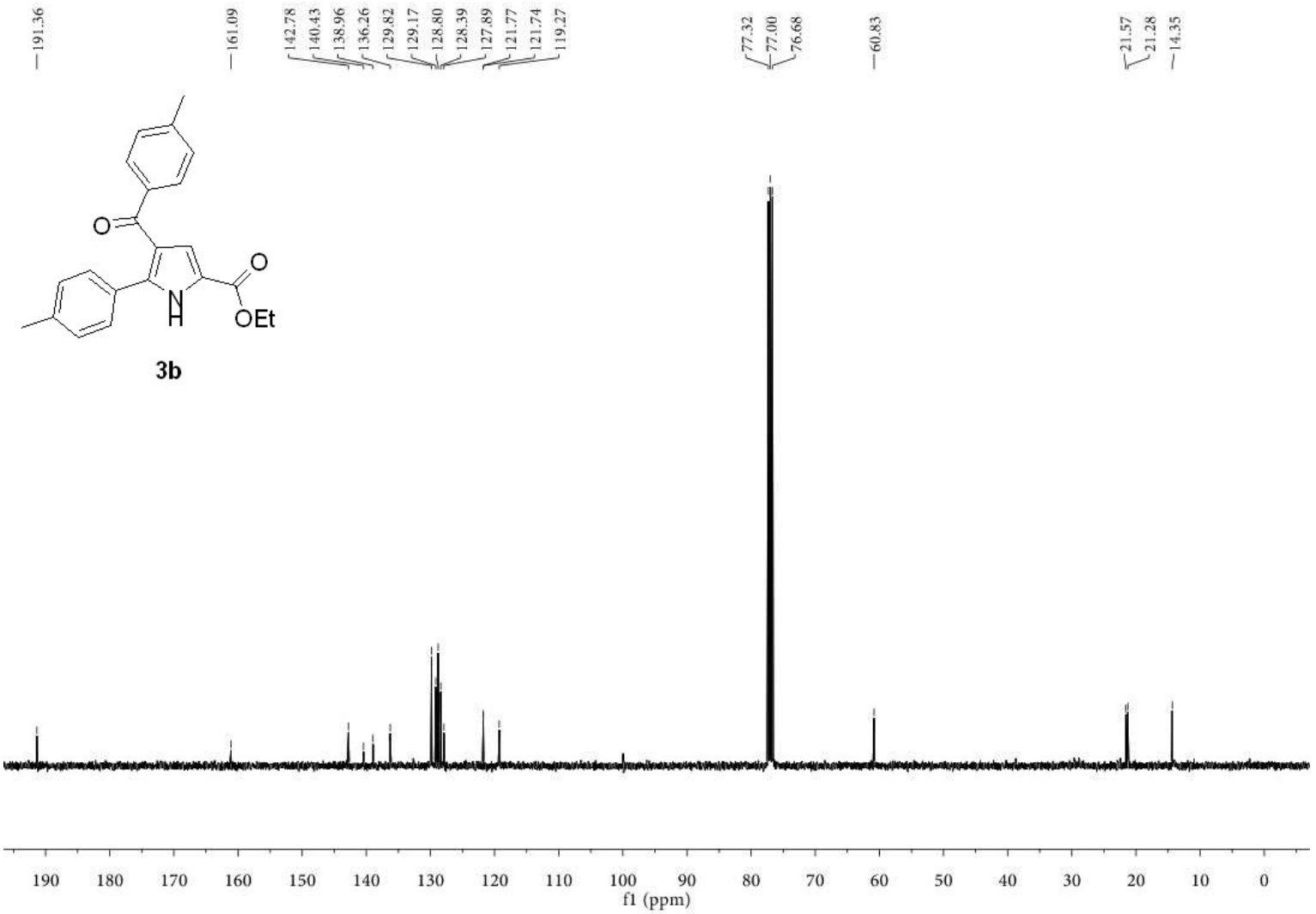
4.27
4.25
4.23
2.39
2.34
1.33
1.31
1.30
O
O
N
H
OEt
1.00
2.00
2.02
5.17
2.12
3.05
3.00
3.06
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)

3b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3b
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50
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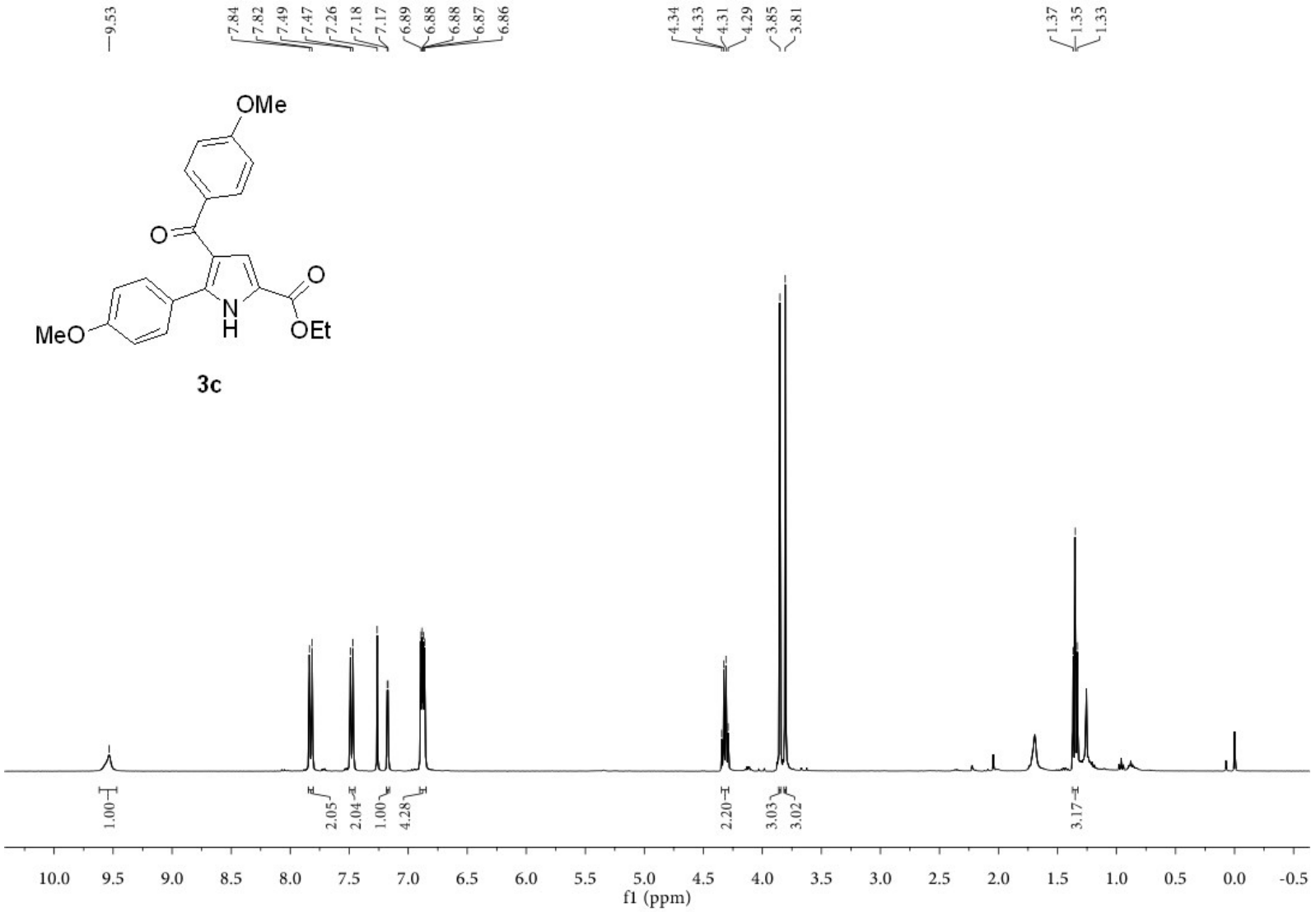
f1 (ppm)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4.33
4.31
4.29
3.85
3.81
1.37
1.35
1.33
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MeO
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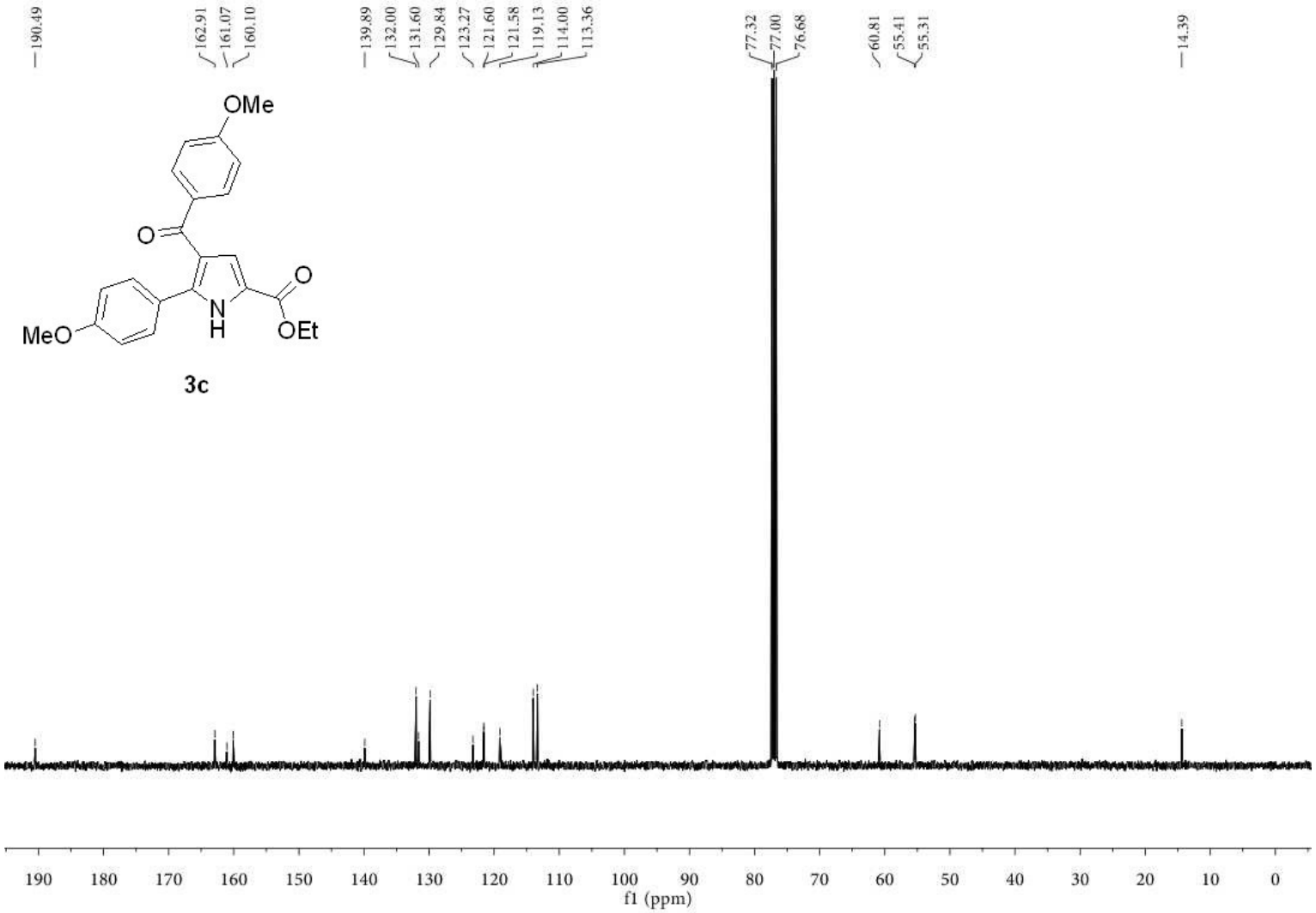
f1 (ppm)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113.36
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77.00
76.68
60.81
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55.31
14.39
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O
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N
H
O
OEt
MeO
3c
190
180
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50
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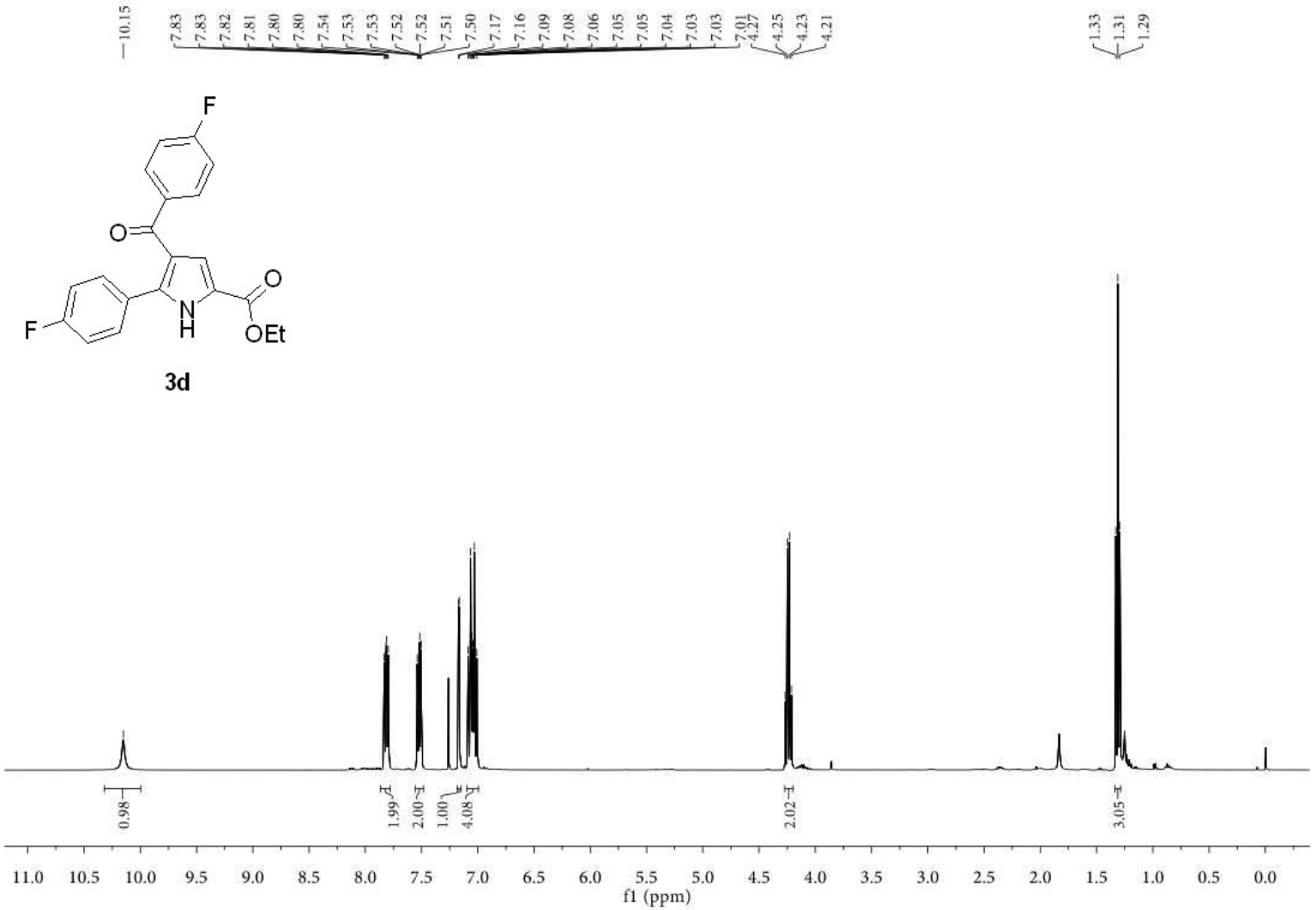
0
f1 (ppm)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1.31
1.29
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8.0
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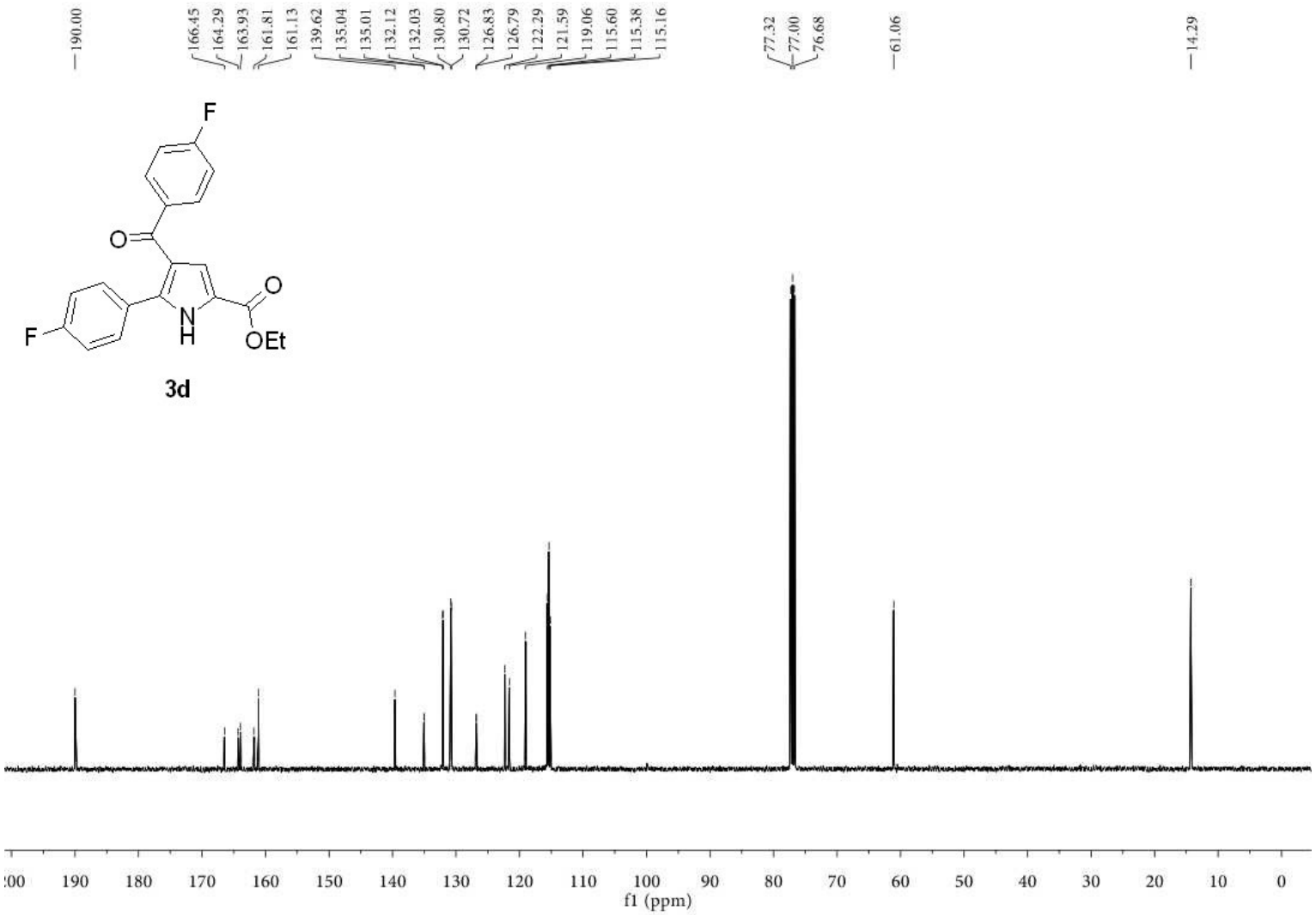
1.0
0.5
0.0
f1 (ppm)

3d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126.79
122.29
121.59
119.06
115.60
115.38
115.16
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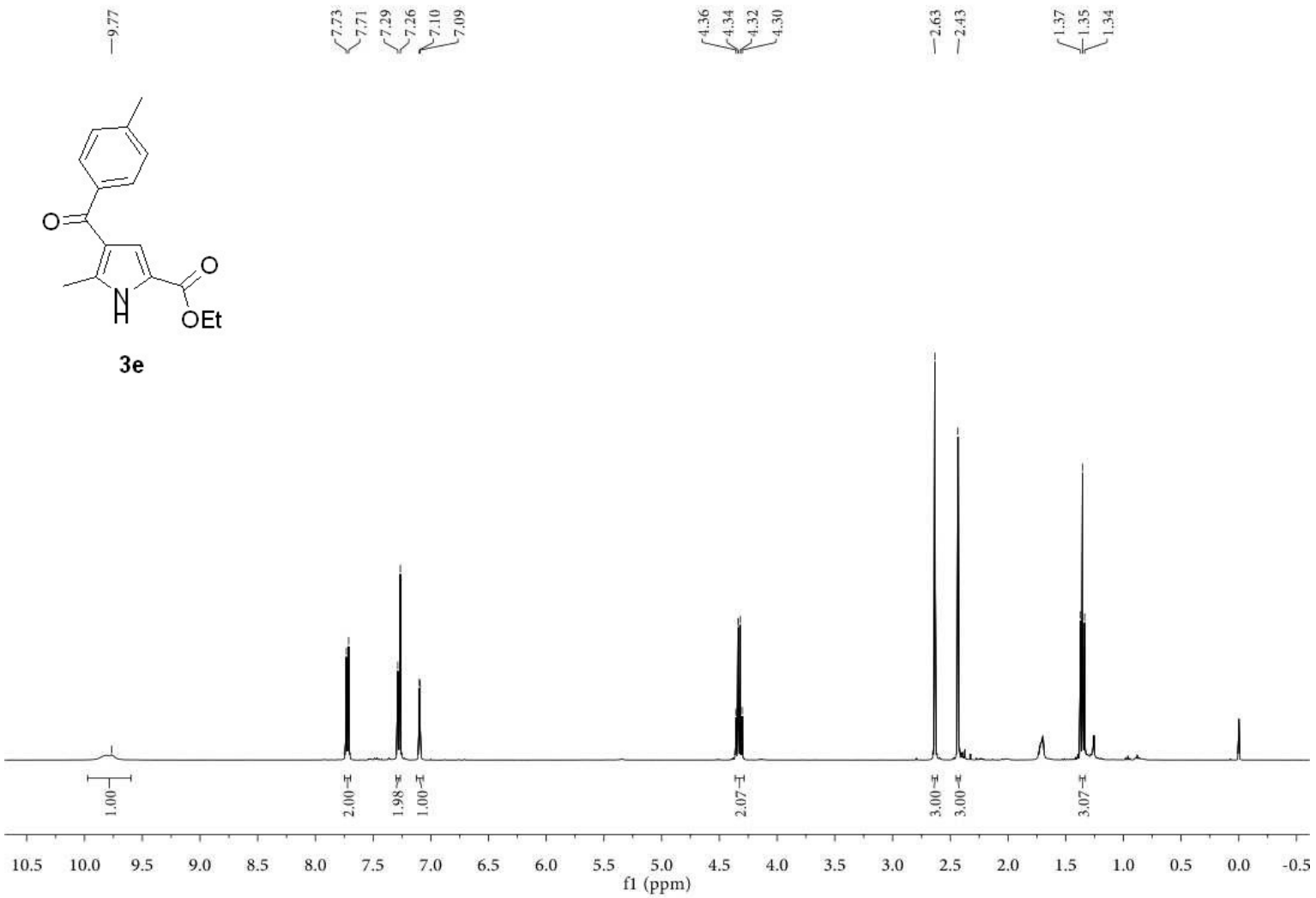
f1 (ppm)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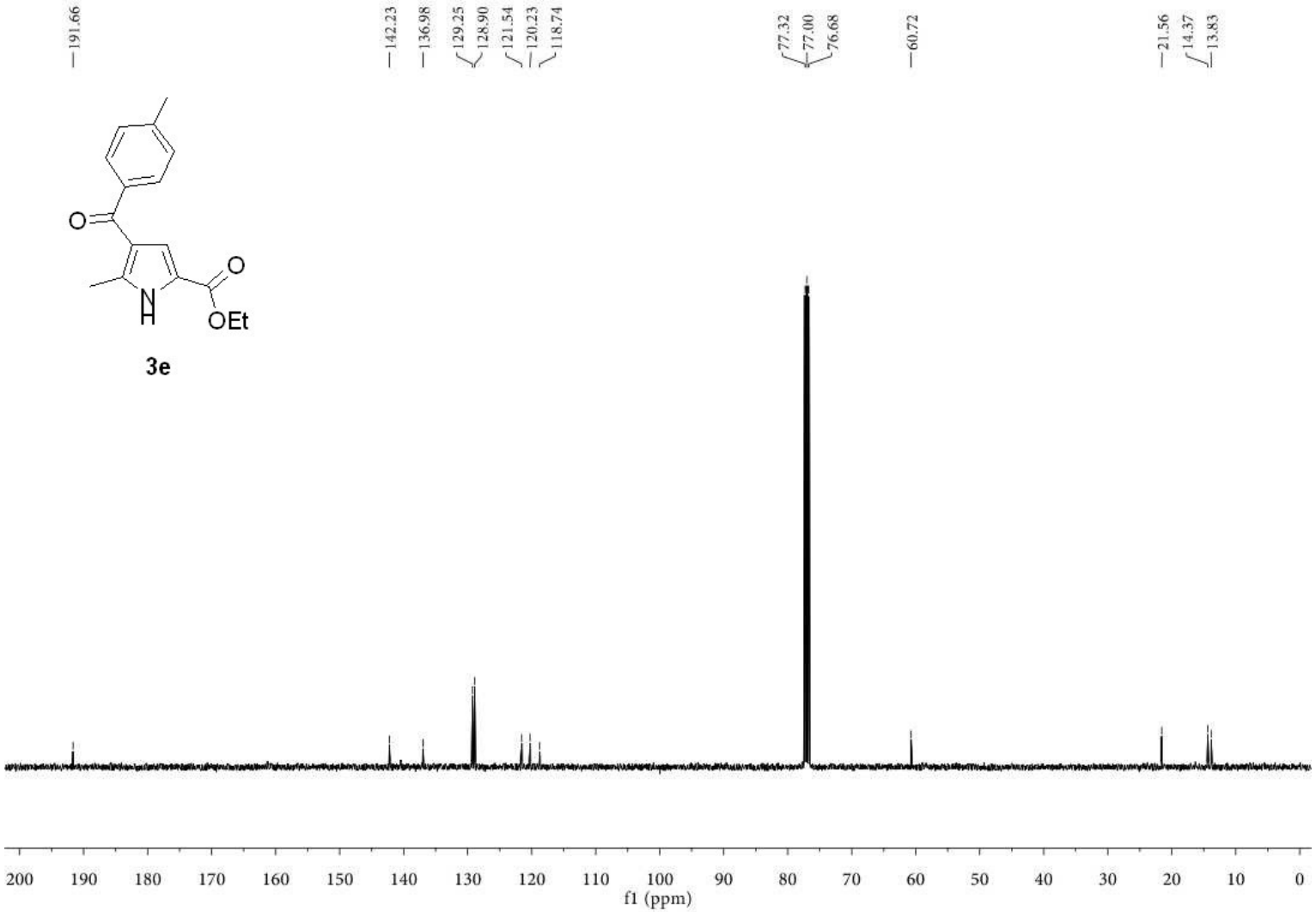
f1 (ppm)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50
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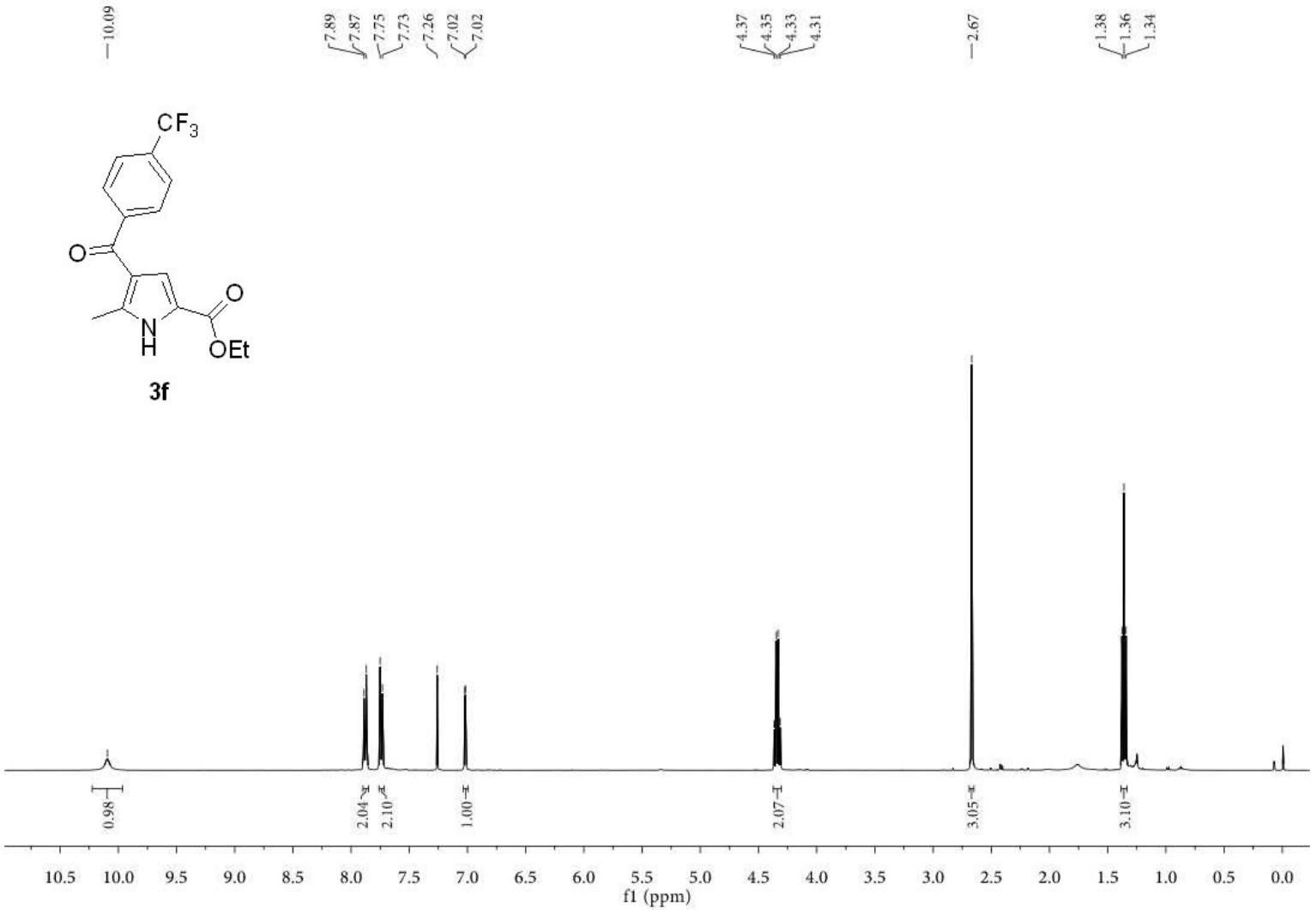
30
20
10
0
f1 (ppm)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7.75
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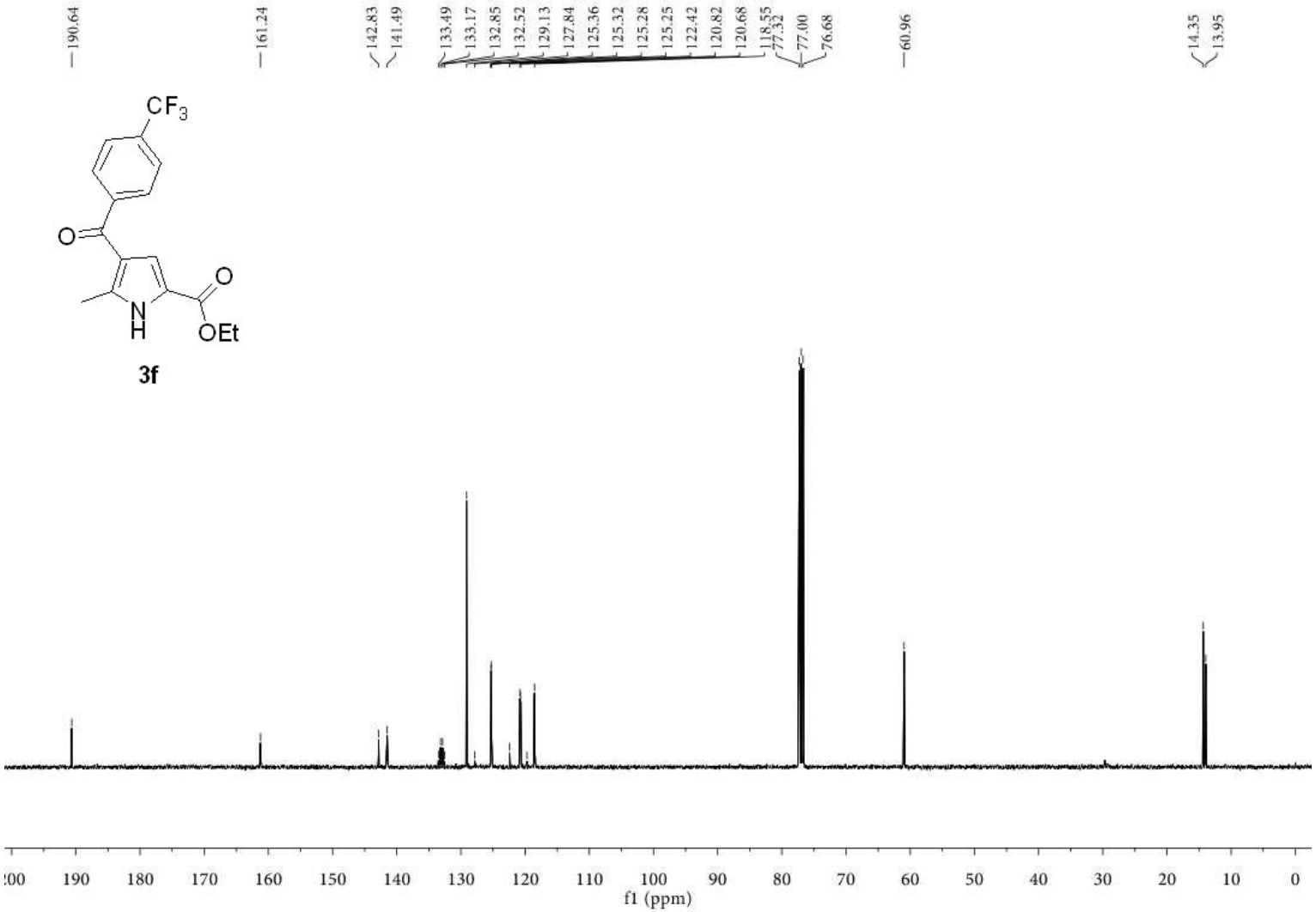
7.26
7.02
7.02
4.37
4.35
4.33
4.31
2.67
1.38
1.36
1.34
CF3
O
O
N
H
OEt
3f
0.98
2.04
2.10
1.00
2.07
3.05
3.10
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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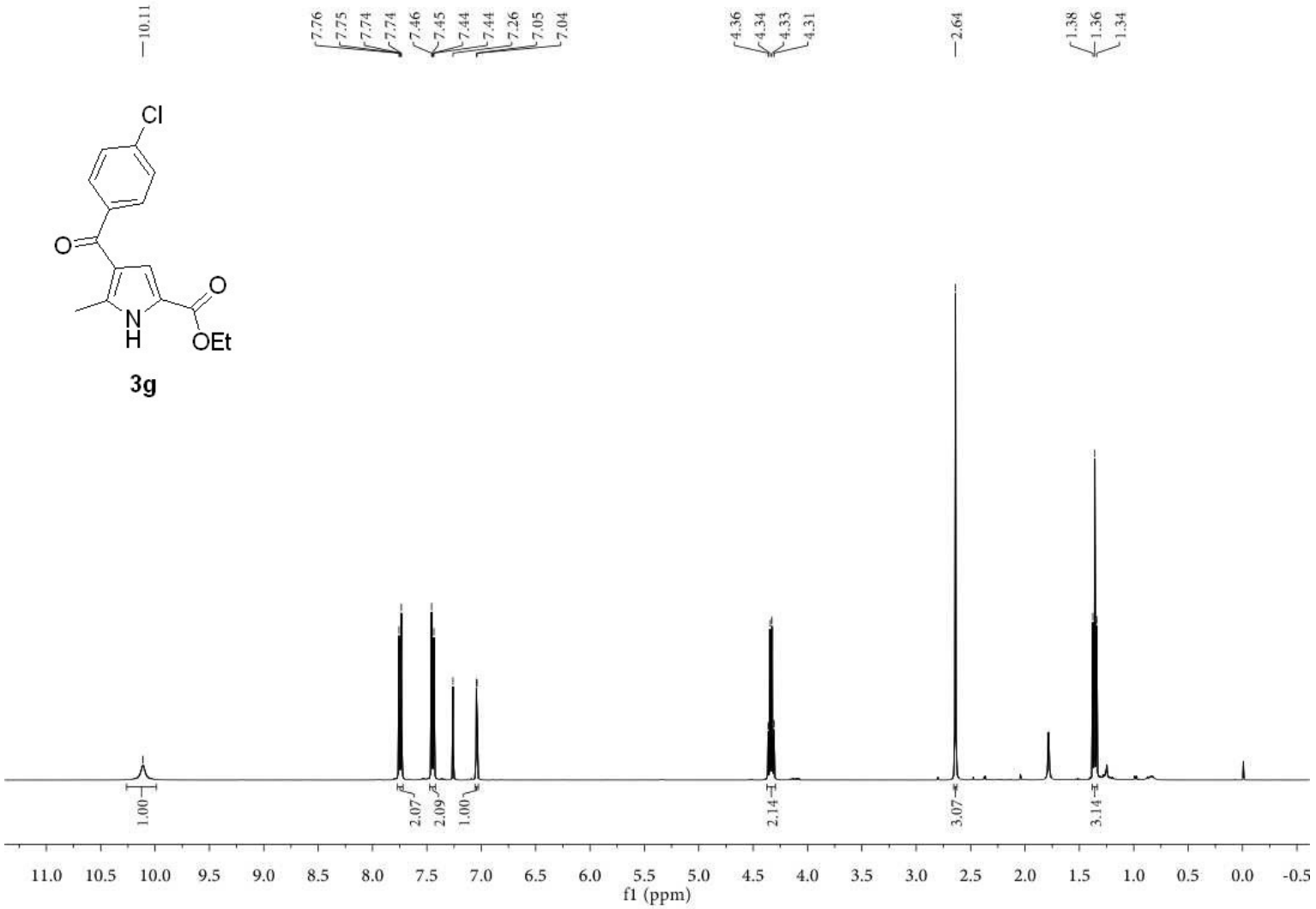
133.17
132.85
132.52
129.13
127.84
125.36
125.32
125.28
125.25
122.42
120.82
120.68
118.55
77.32
77.00
76.68
60.96
14.35
13.95
CF3
O
O
N
H
OEt
3f
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.75
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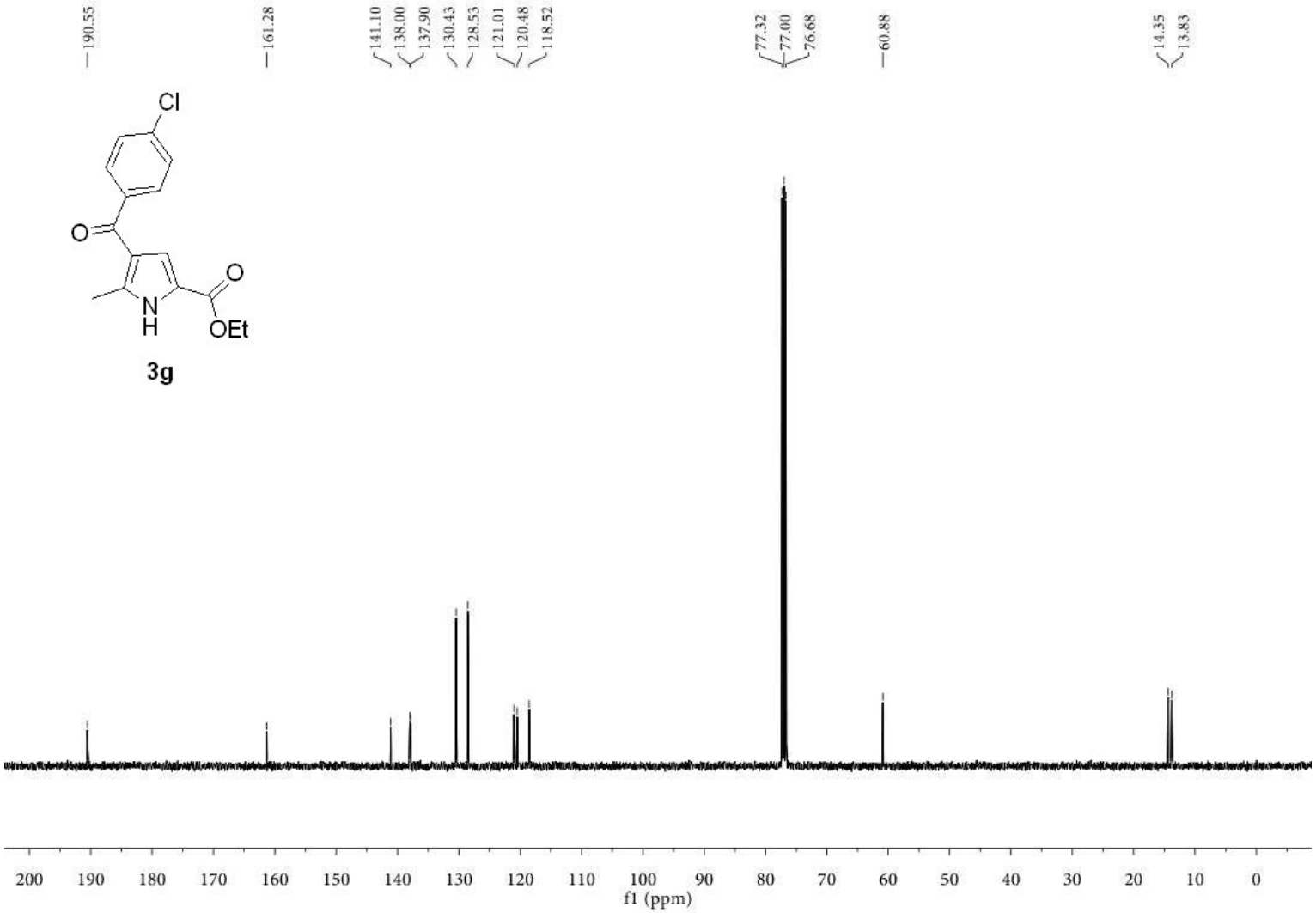
7.45
7.44
7.44
7.26
7.05
7.04
4.36
4.34
4.33
4.31
2.64
1.38
1.36
1.34
Cl
O
O
N
H
OEt
3g
1.00
2.07
2.09
1.00
2.14
3.07
3.14
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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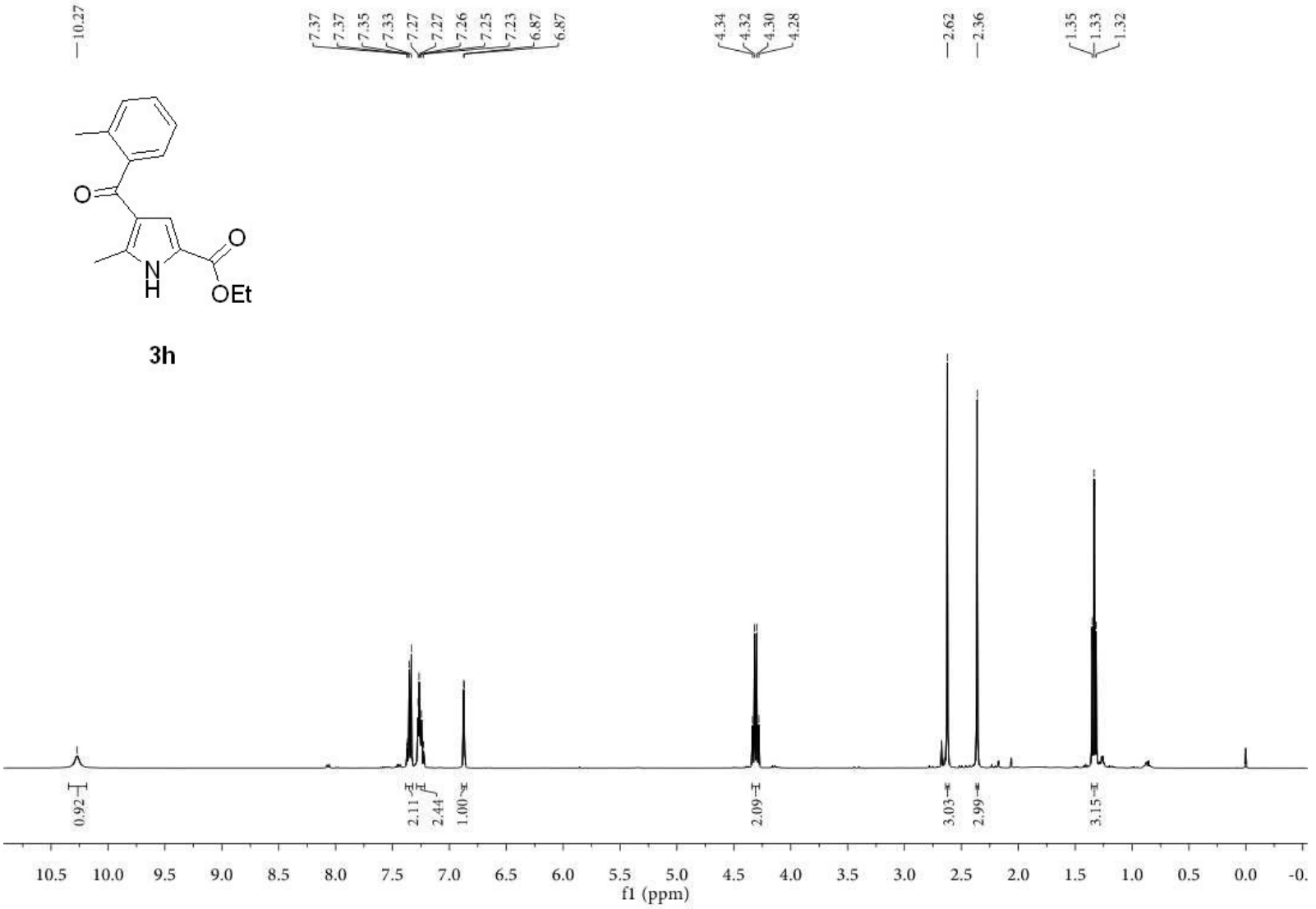
130.43
128.53
121.01
120.48
118.52
77.32
77.00
76.68
60.88
14.35
13.83
Cl
O
O
N
H
OEt
3g
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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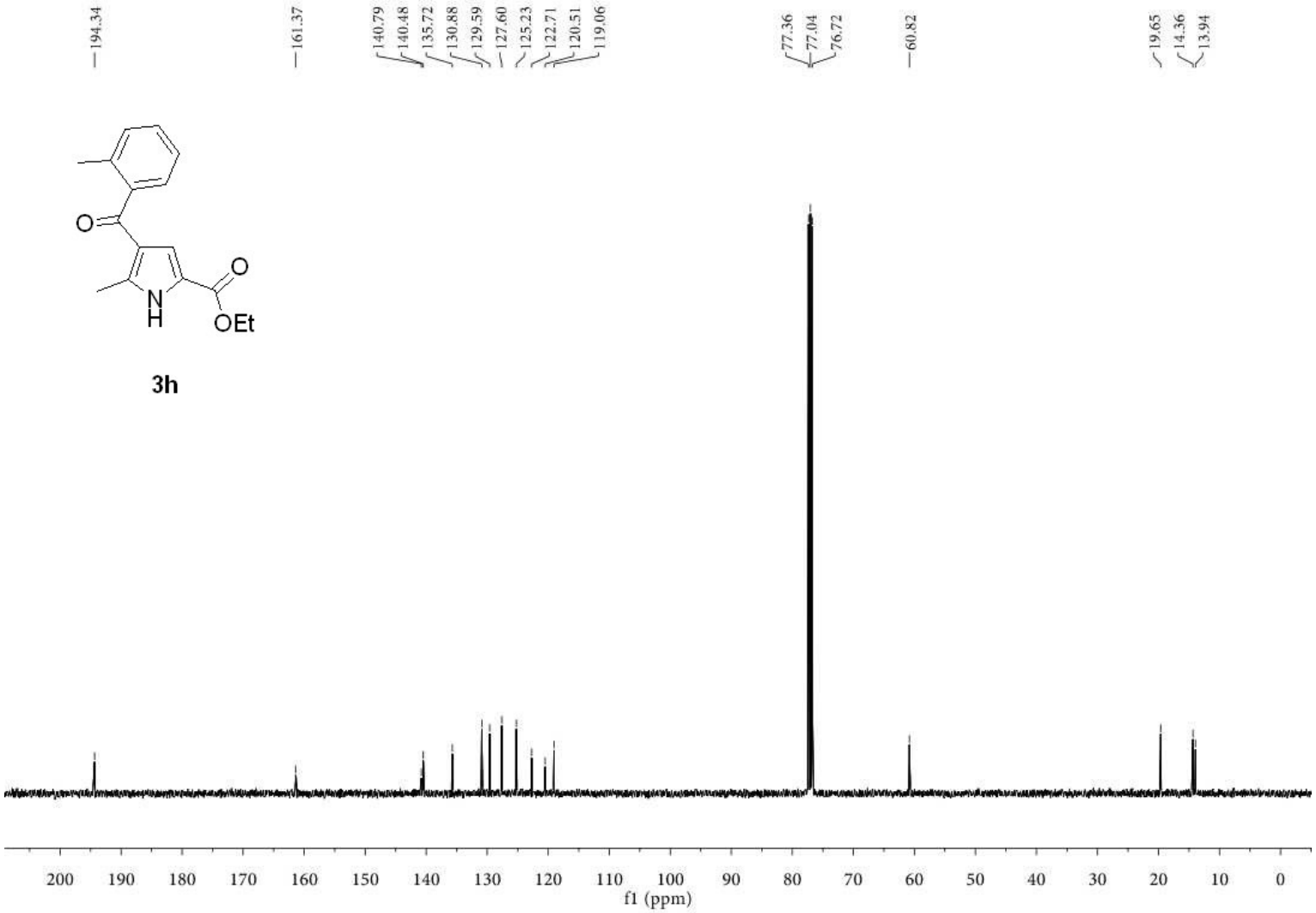
7.35
7.33
7.27
7.27
7.26
7.25
7.23
6.87
6.87
4.34
4.32
4.30
4.28
2.62
2.36
1.35
1.33
1.32
O
O
N
H
OEt
0.92
2.11
2.44
1.00
2.09
3.03
2.99
3.15
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
f1 (ppm)

3h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161.37
140.79
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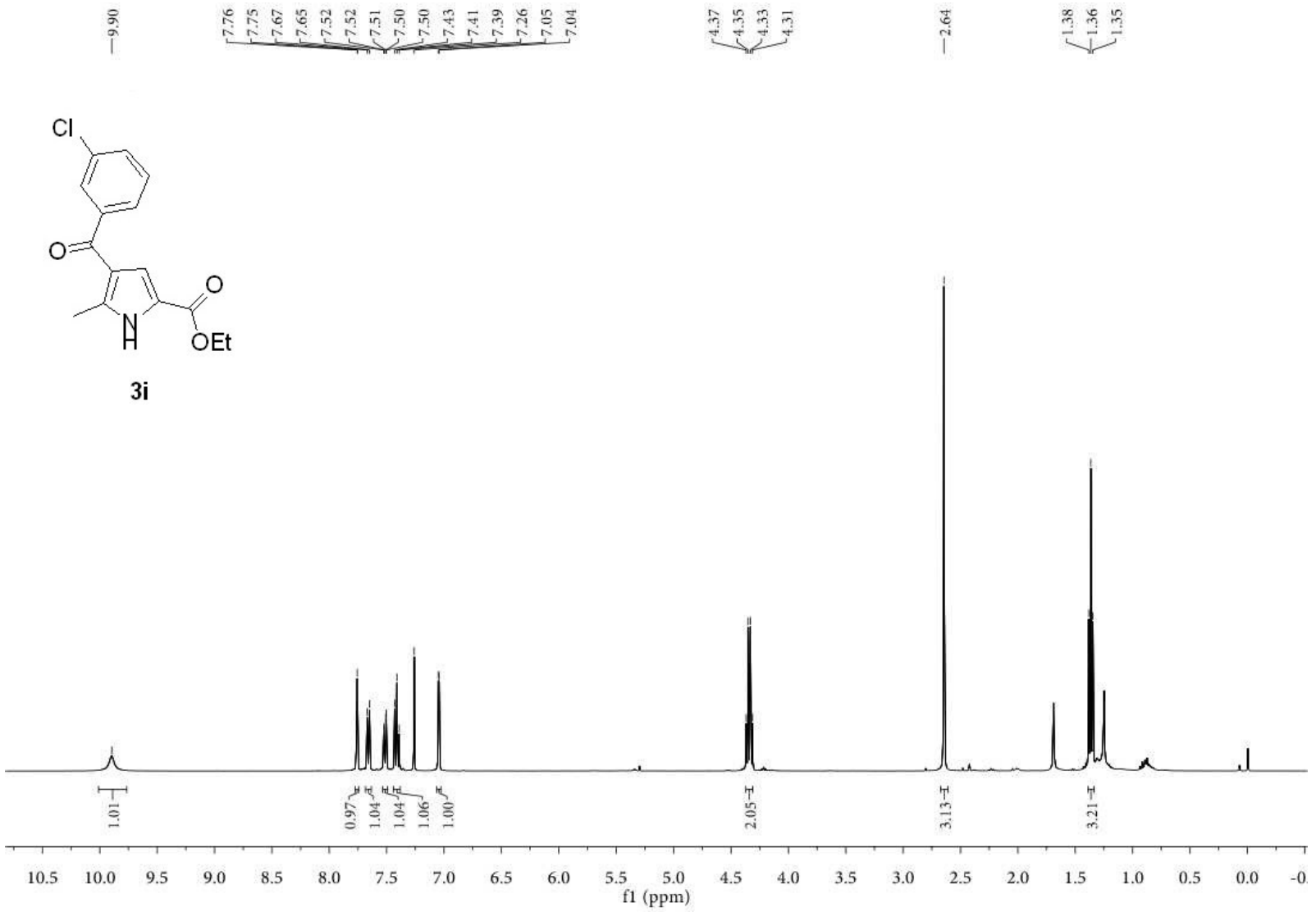
130.88
129.59
127.60
125.23
122.71
120.51
119.06
77.36
77.04
76.72
60.82
19.65
14.36
13.94
O
O
N
H
OEt
3h
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.76
7.75
7.67
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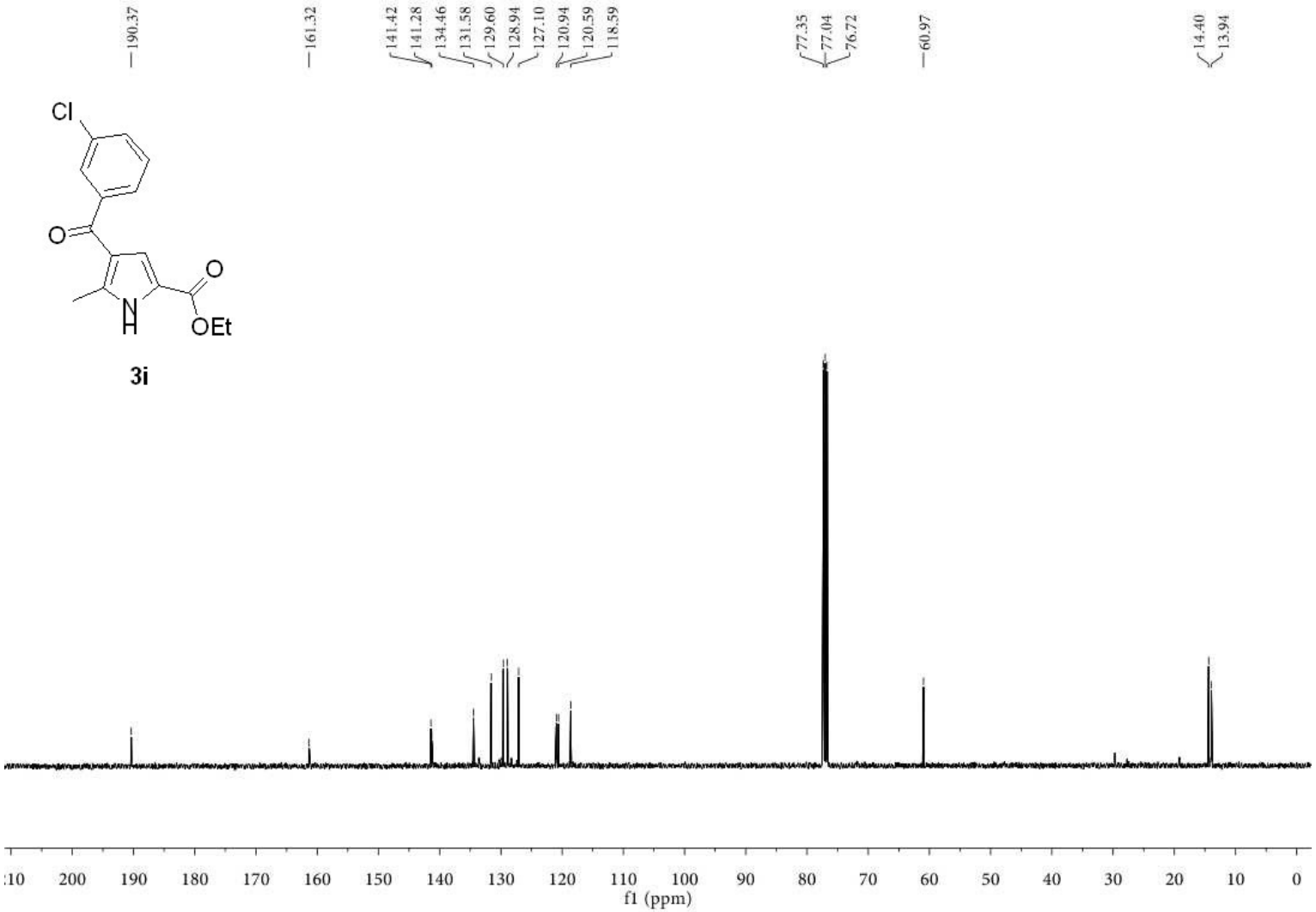
7.52
7.52
7.51
7.50
7.50
7.43
7.41
7.39
7.26
7.05
7.04
4.37
4.35
4.33
4.31
2.64
1.38
1.36
1.35
Cl
O
O
N
H
OEt
1.01
0.97
1.04
1.04
1.06
1.00
2.05
3.13
3.21
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

3i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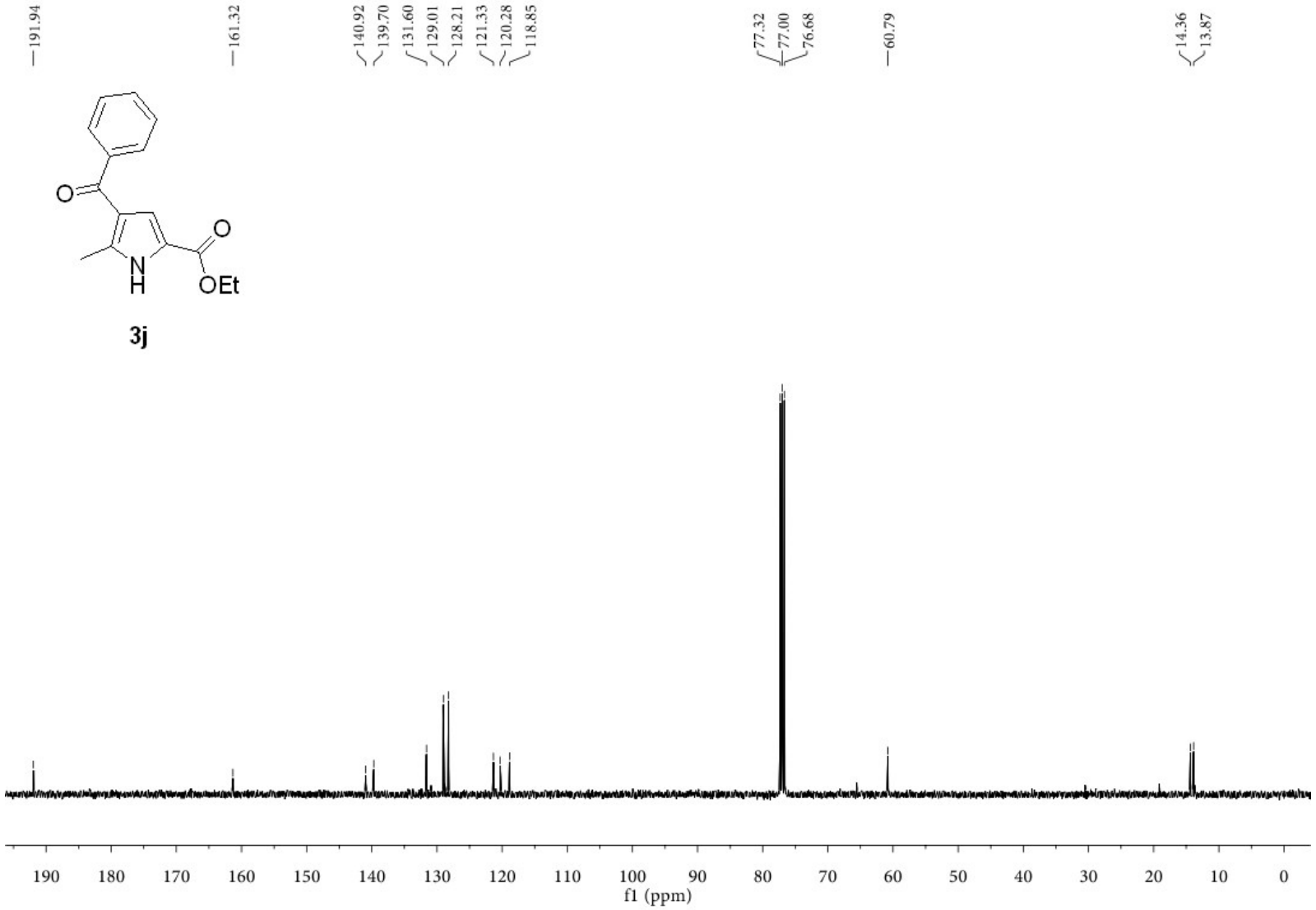
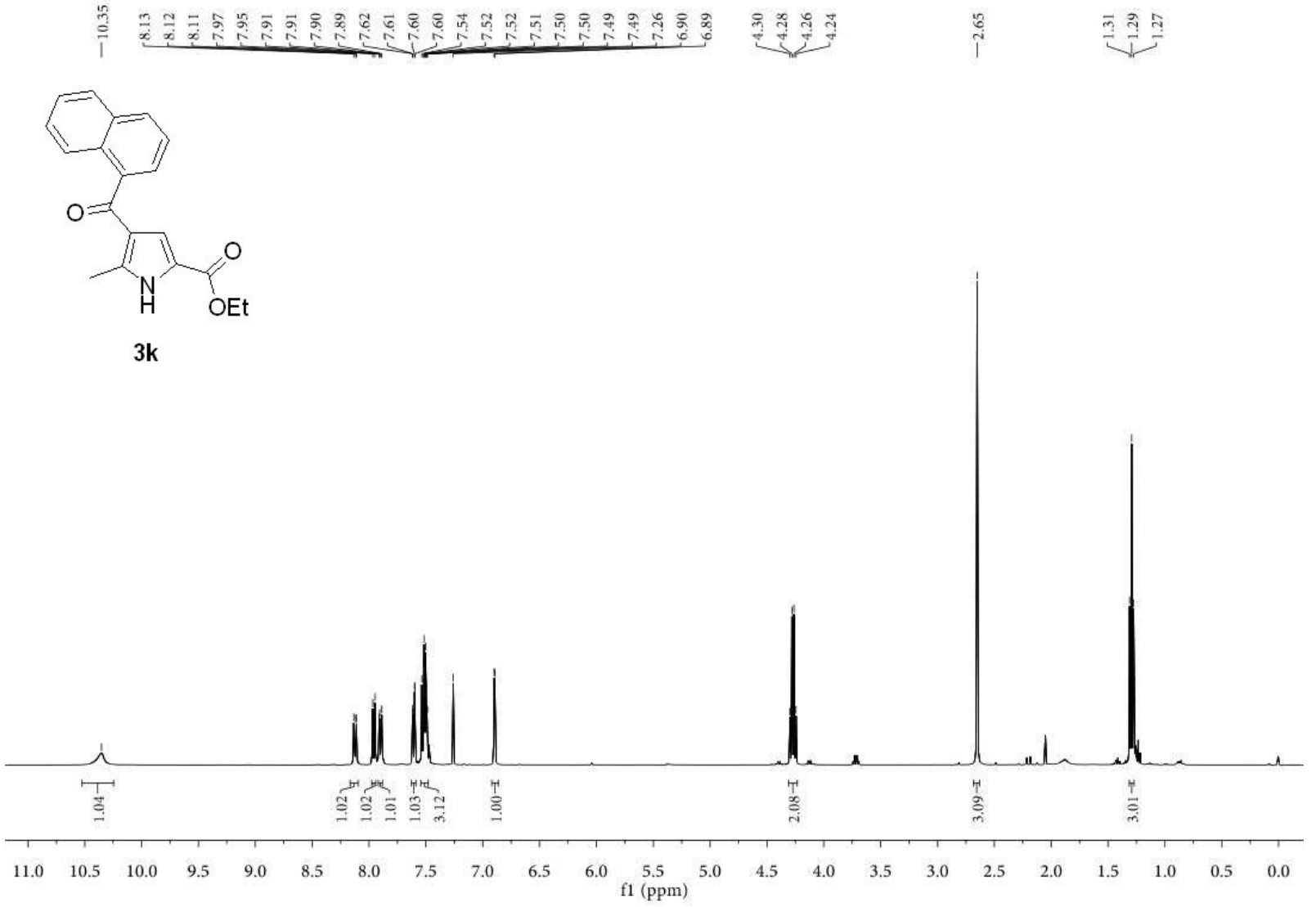
161.32
141.42
141.28
134.46
131.58
129.60
128.94
127.10
120.94
120.59
118.59
77.35
77.04
76.72
60.97
14.40
13.94
Cl
O
O
N
H
OEt
3i
f1 (ppm)


191.94
161.32
140.92
139.70
131.60
129.01
128.21
121.33
120.28
118.85
77.32
77.00
76.68
60.79
14.36
13.87
O
O
N
H
OEt
3j
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.95
7.91
7.91
7.90
7.89
7.62
7.61
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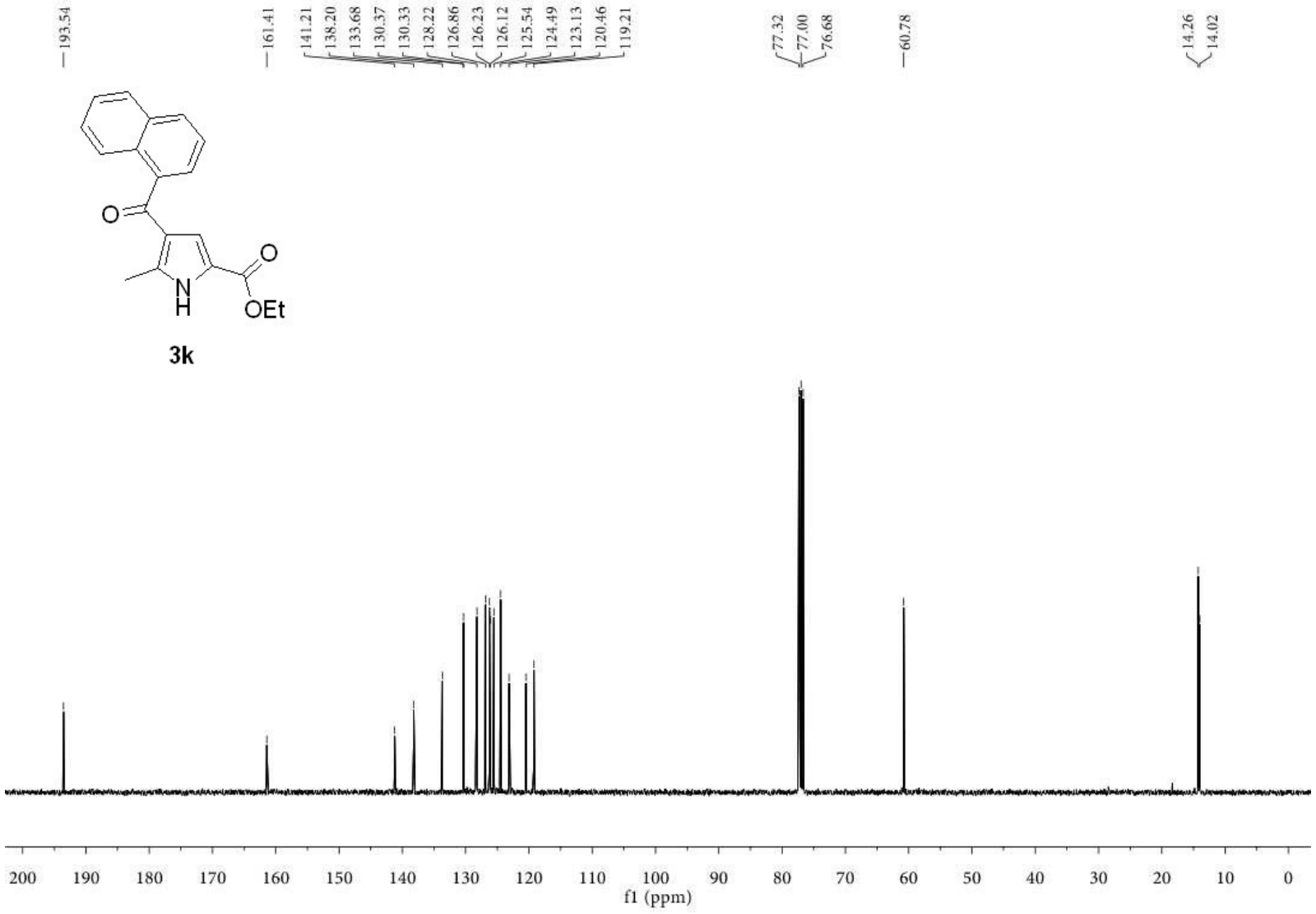
7.60
7.54
7.52
7.52
7.51
7.50
7.50
7.49
7.49
7.26
6.90
6.89
4.30
4.28
4.26
4.24
2.65
1.31
1.29
1.27
O
O
N
H
OEt
3k
1.04
1.02
1.02
1.01
1.03
3.12
1.00
2.08
3.09
3.01
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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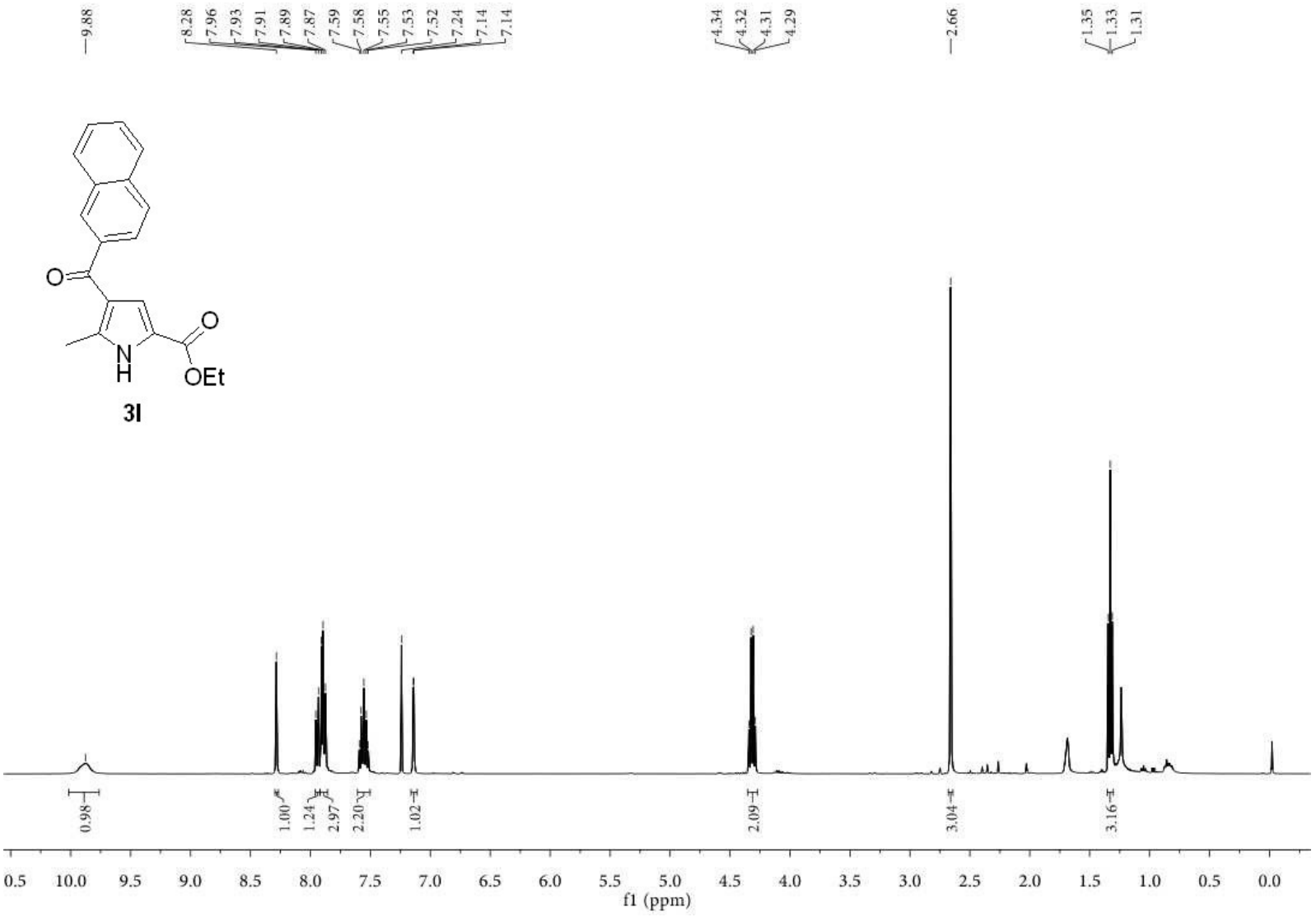
130.37
130.33
128.22
126.86
126.23
126.12
125.54
124.49
123.13
120.46
119.21
77.32
77.00
76.68
60.78
14.26
14.02
O
O
N
H
OEt
3k
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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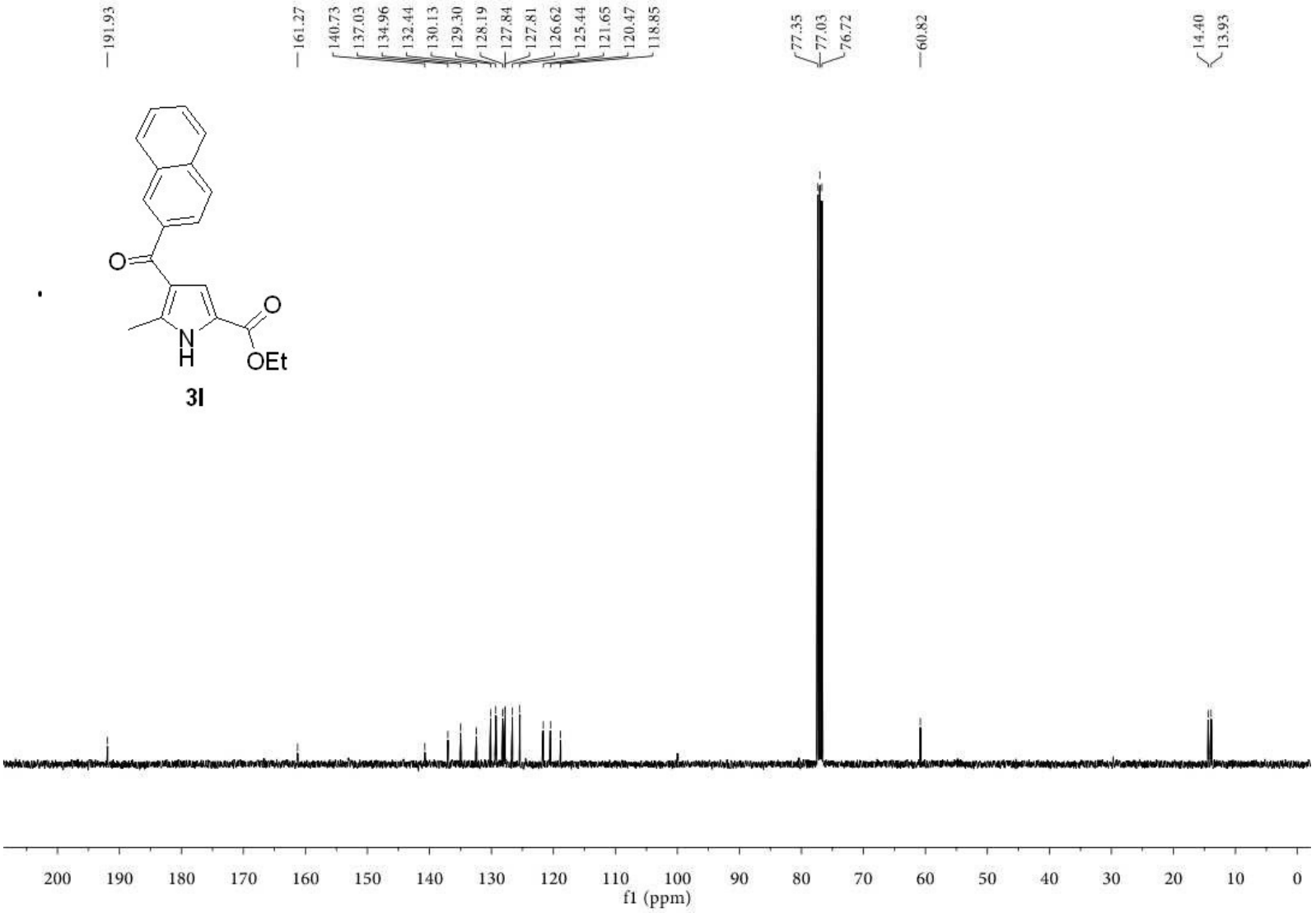
7.89
7.87
7.59
7.58
7.55
7.53
7.52
7.24
7.14
7.14
4.34
4.32
4.31
4.29
2.66
1.35
1.33
1.31
O
O
N
H
O
OEt
3l
0.98
1.00
1.24
2.97
2.20
1.02
2.09
3.04
3.16
0.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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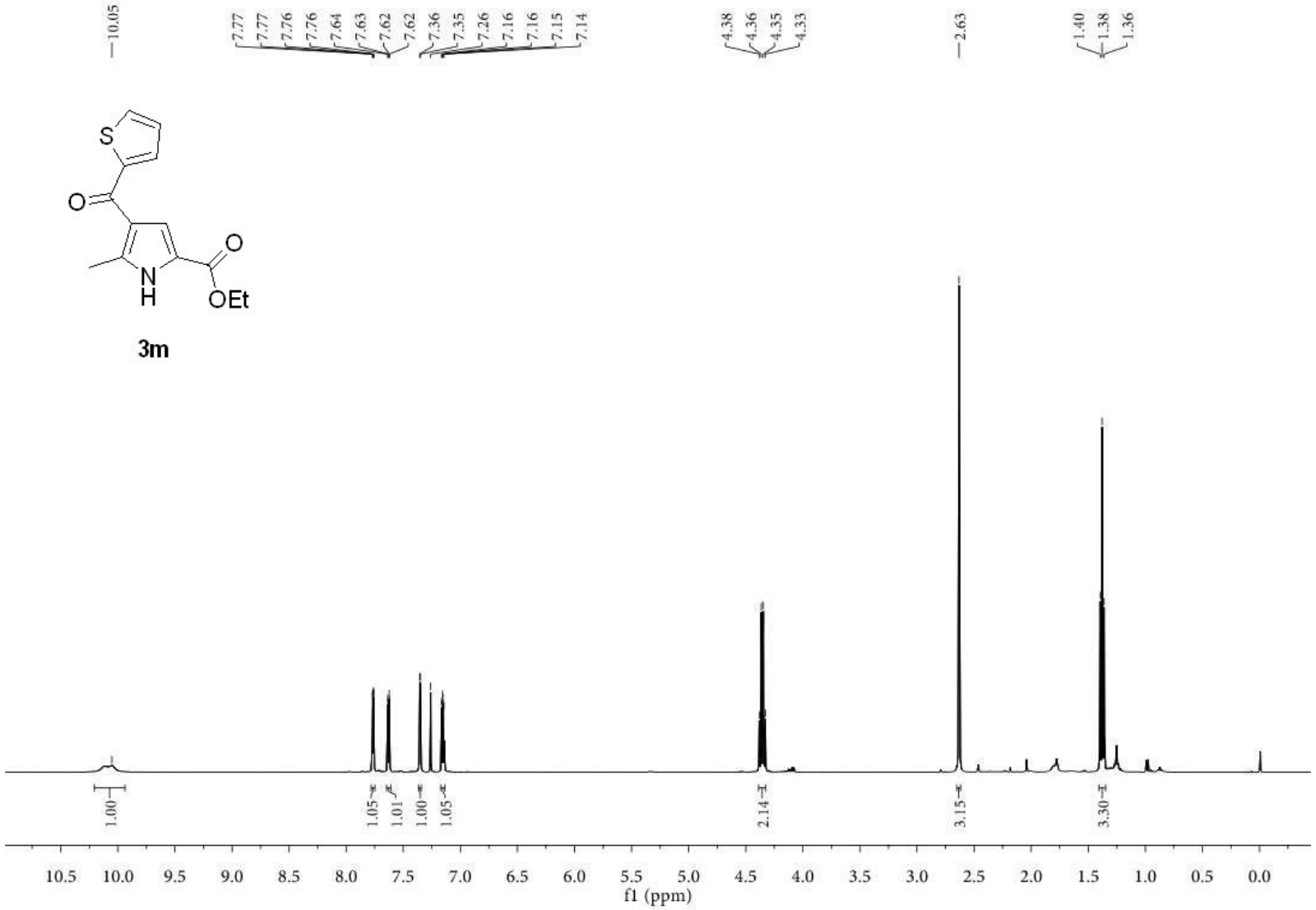
130.13
129.30
128.19
127.84
127.81
126.62
125.44
121.65
120.47
118.85
77.35
77.03
76.72
60.82
14.40
13.93
O
O
N
H
OEt
3l
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.77
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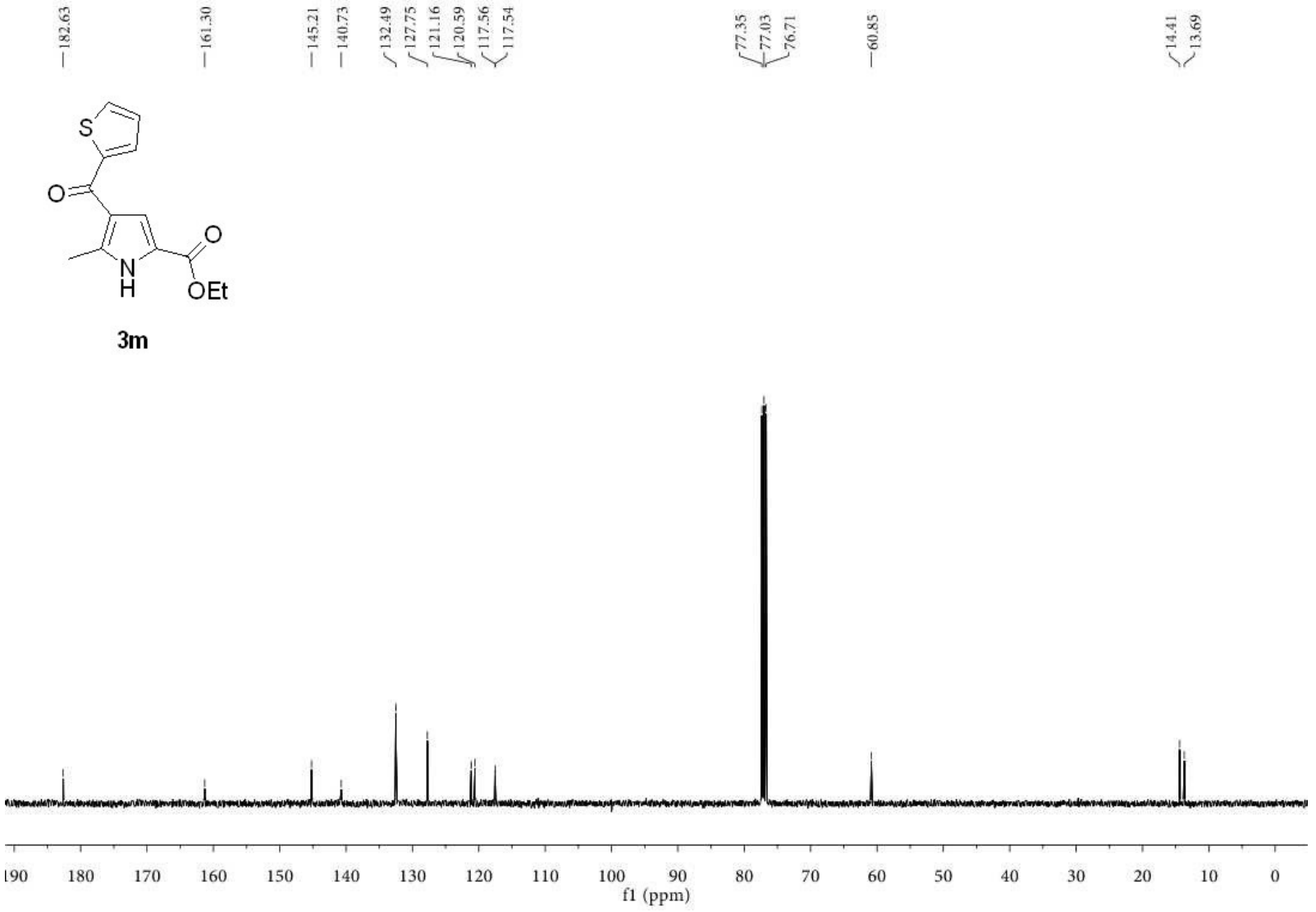
7.63
7.62
7.62
7.36
7.35
7.26
7.16
7.16
7.15
7.14
4.38
4.36
4.35
4.33
2.63
1.40
1.38
1.36
S
O
O
N
H
OEt
3m
1.00
1.05
1.01
1.00
1.05
2.14
3.15
3.30
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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127.75
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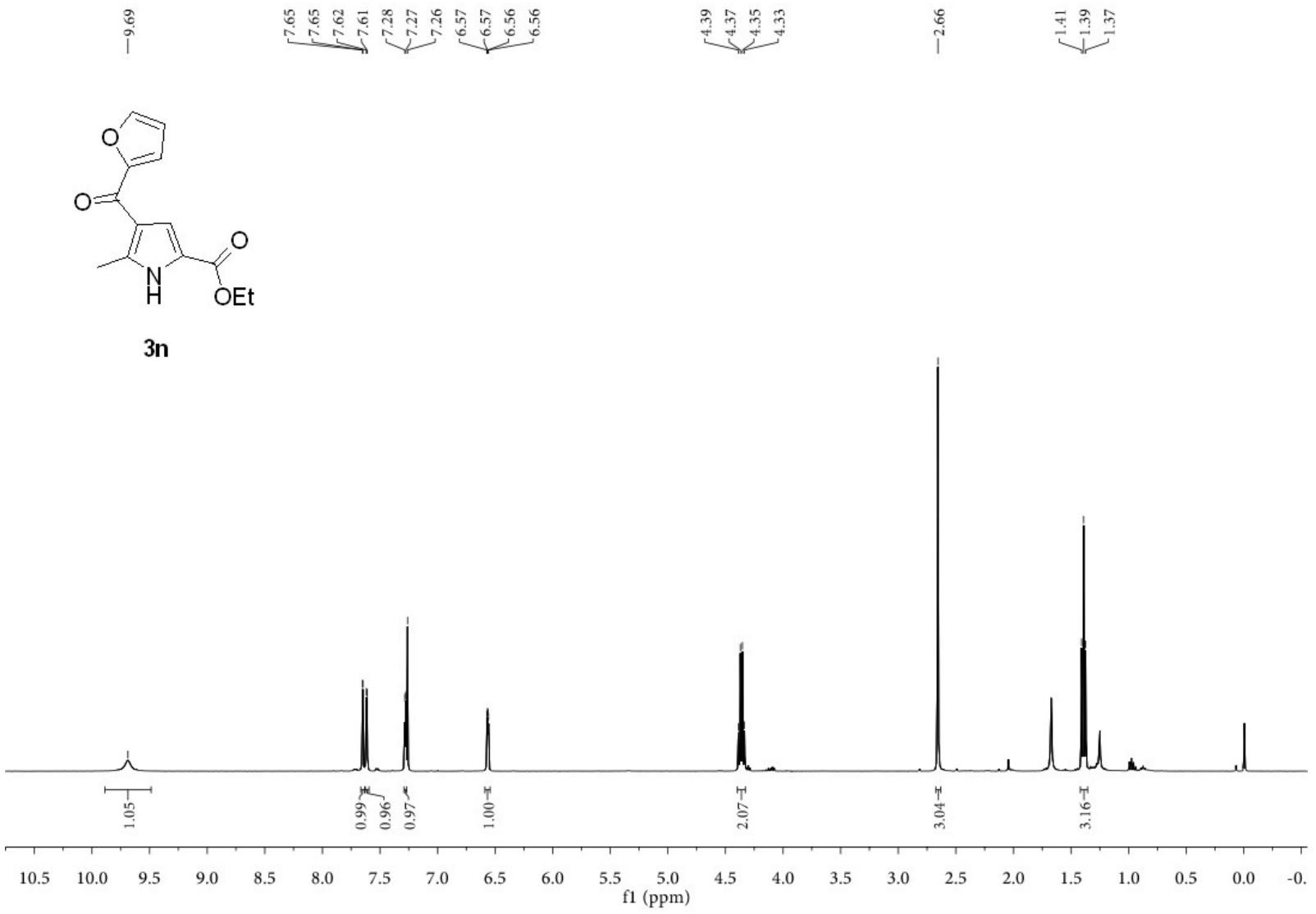
120.59
117.56
117.54
77.35
77.03
76.71
60.85
14.41
13.69
S
O
N
H
O
OEt
3m
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.26
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6.57
6.56
6.56
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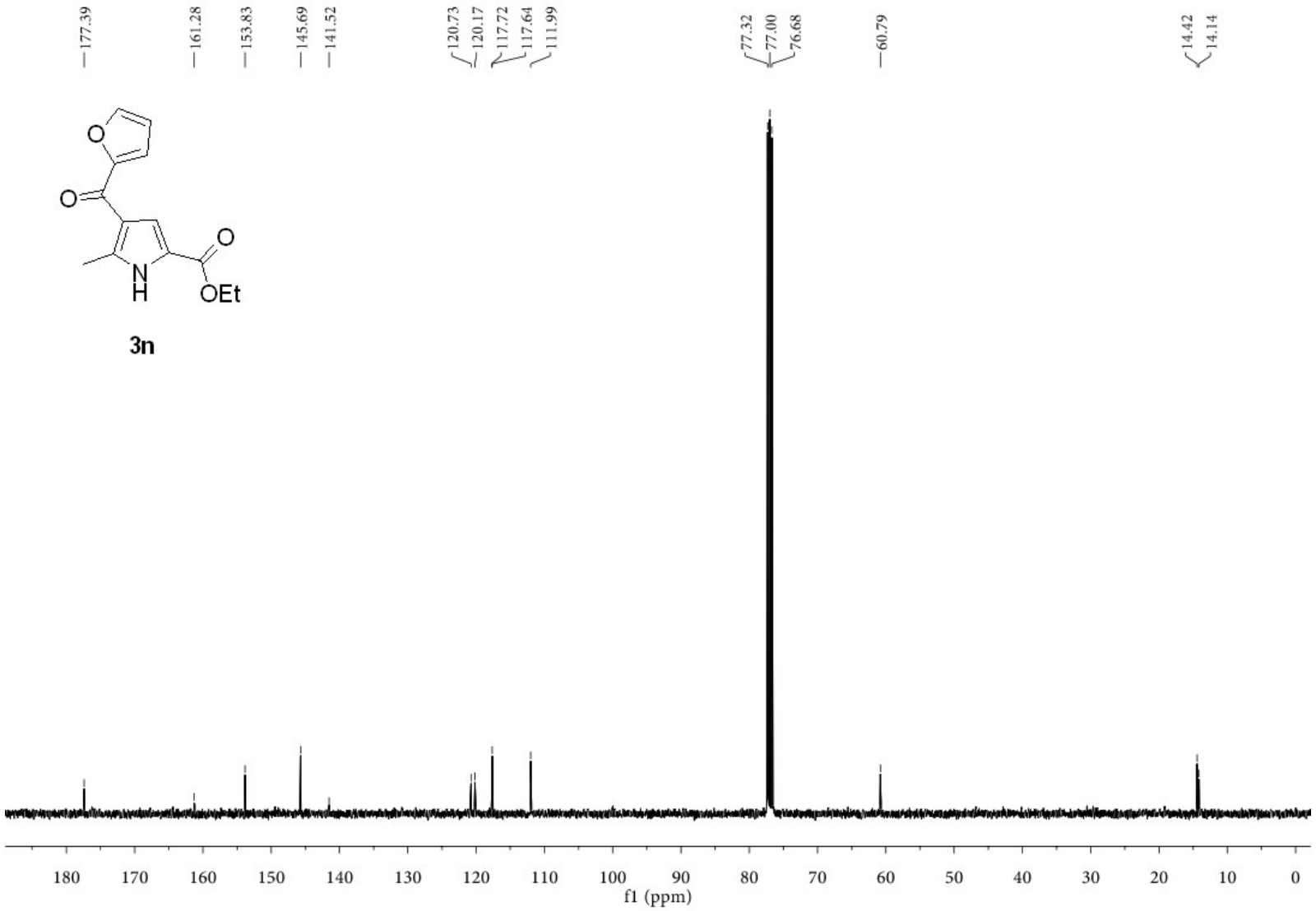
4.37
4.35
4.33
2.66
1.41
1.39
1.37
O
O
O
N
H
OEt
3n
1.05
0.99
0.96
0.97
1.00
2.07
3.04
3.16
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
f1 (ppm)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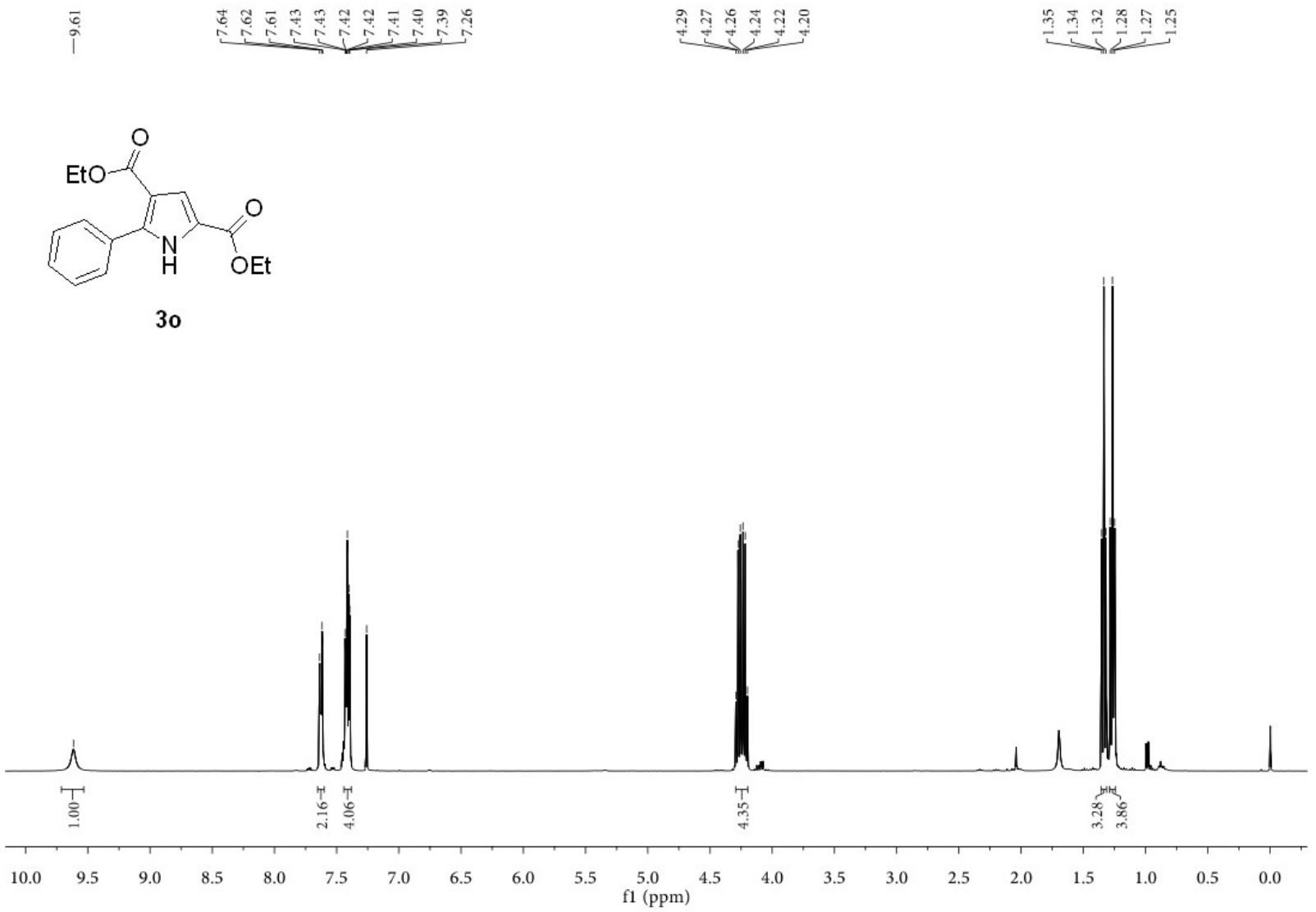
120.17
117.72
117.64
111.99
77.32
77.00
76.68
60.79
14.42
14.14
O
O
N
H
O
OEt
3n
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.42
7.41
7.40
7.39
7.26
4.29
4.27
4.26
4.24
4.22
4.20
1.35
1.34
1.32
1.28
1.27
1.25
EtO
O
O
N
H
OEt
3o
1.00
2.16
4.06
4.35
3.28
3.86
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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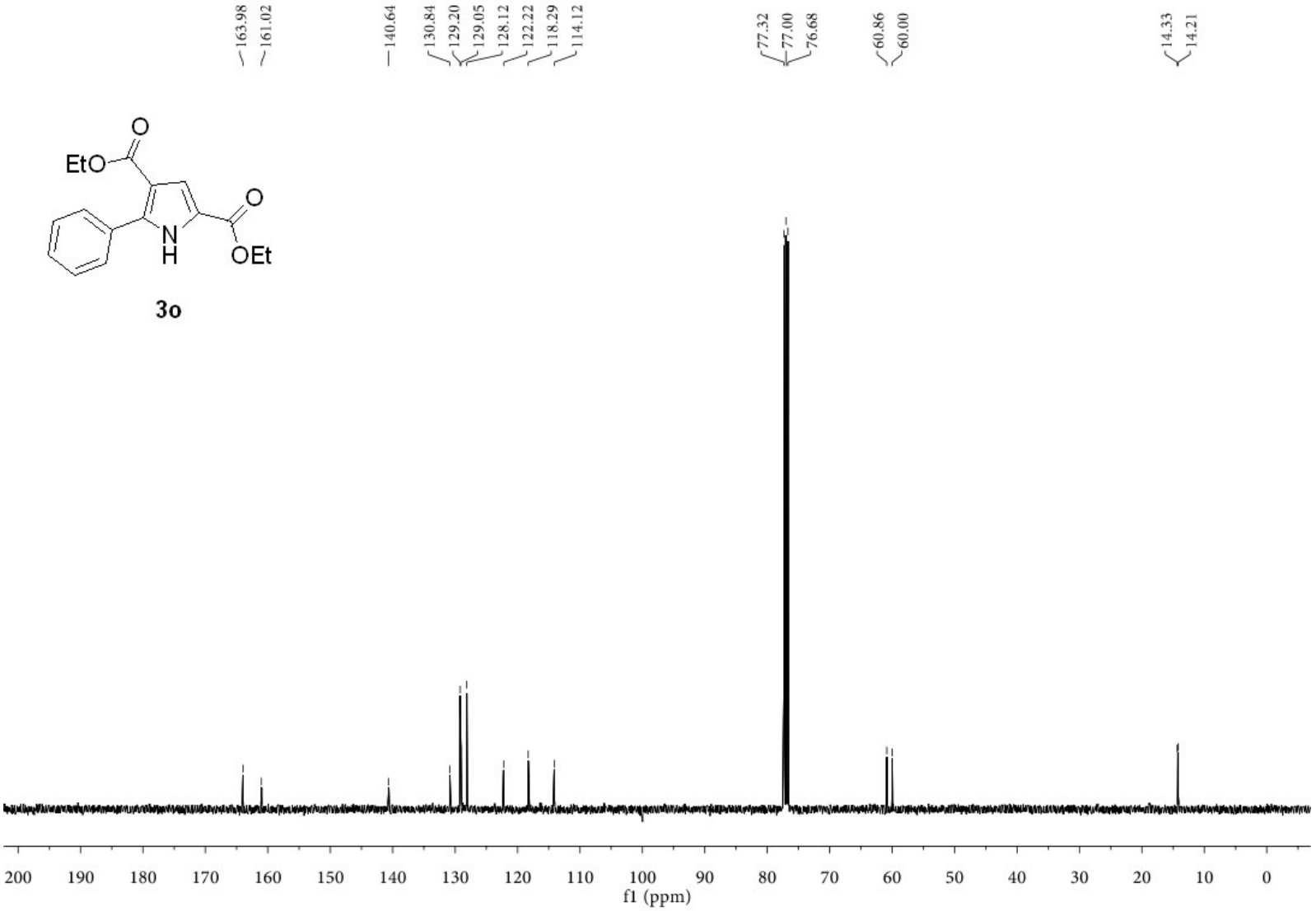
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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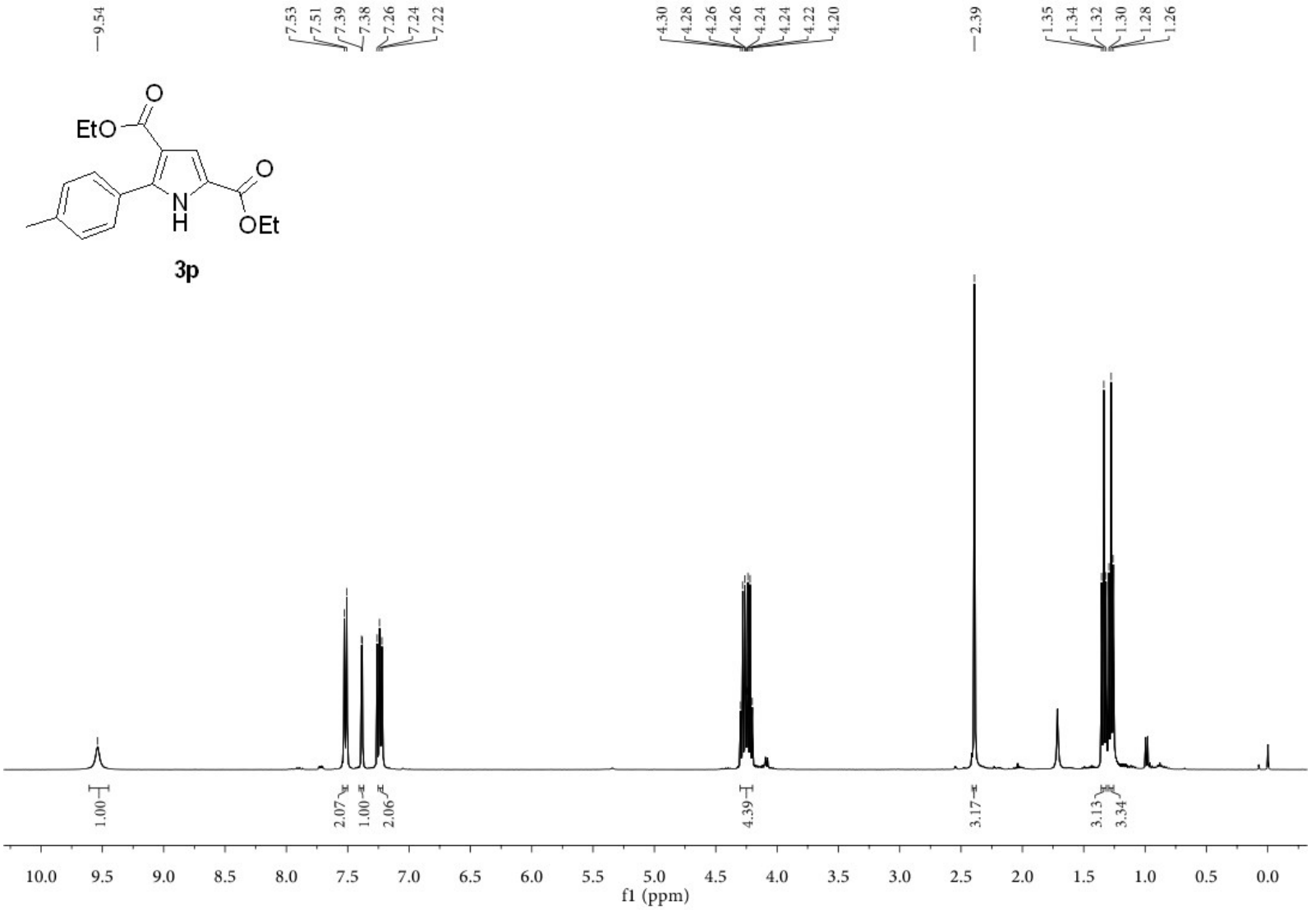
128.12
122.22
118.29
114.12
77.32
77.00
76.68
60.86
60.00
14.33
14.21
EtO
O
O
N
H
OEt
3o
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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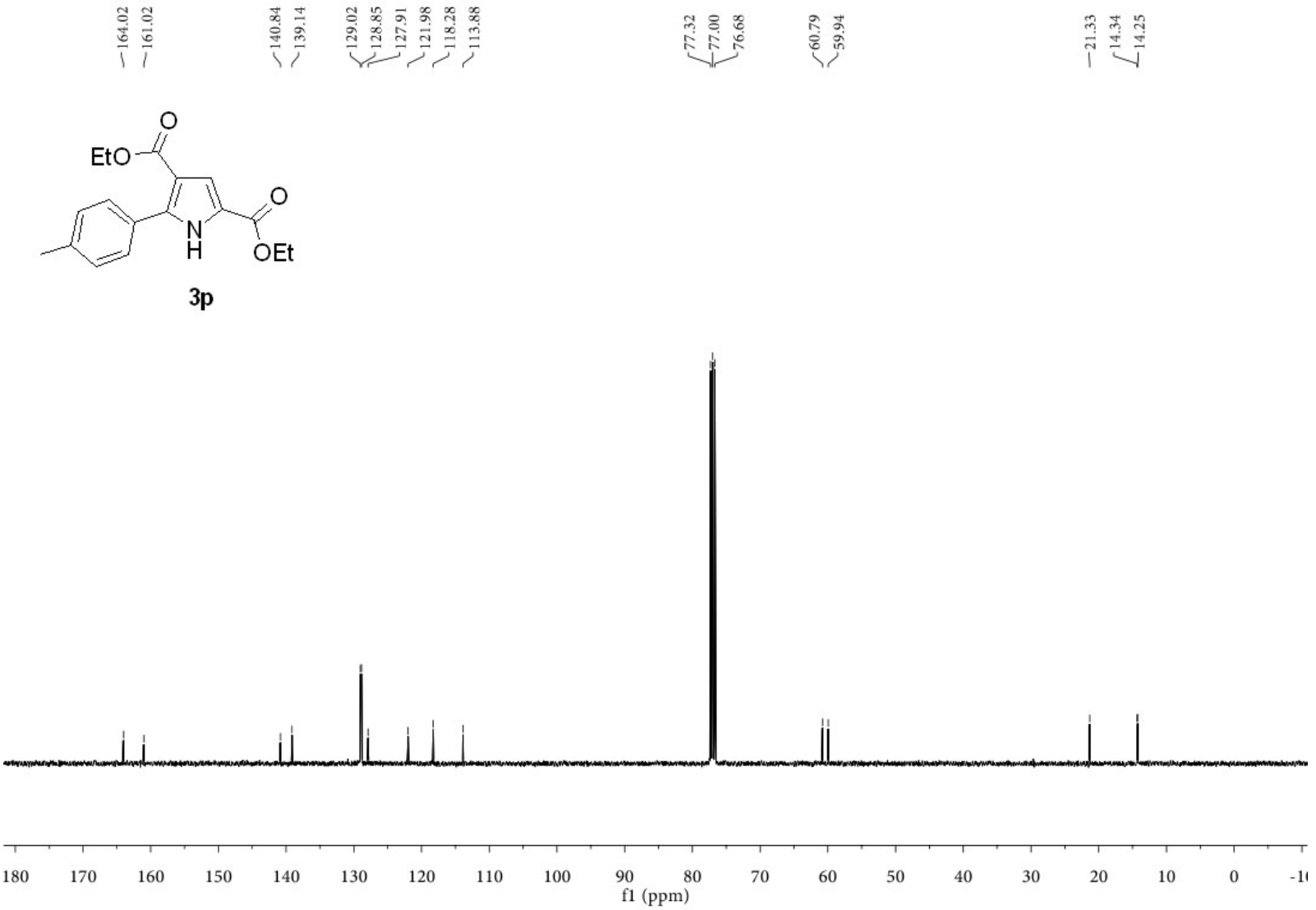
7.24
7.22
4.30
4.28
4.26
4.26
4.24
4.24
4.22
4.20
2.39
1.35
1.34
1.32
1.30
1.28
1.26
EtO
O
O
N
H
OEt
3p
1.00
2.07
1.00
2.06
4.39
3.17
3.13
3.34
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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161.02
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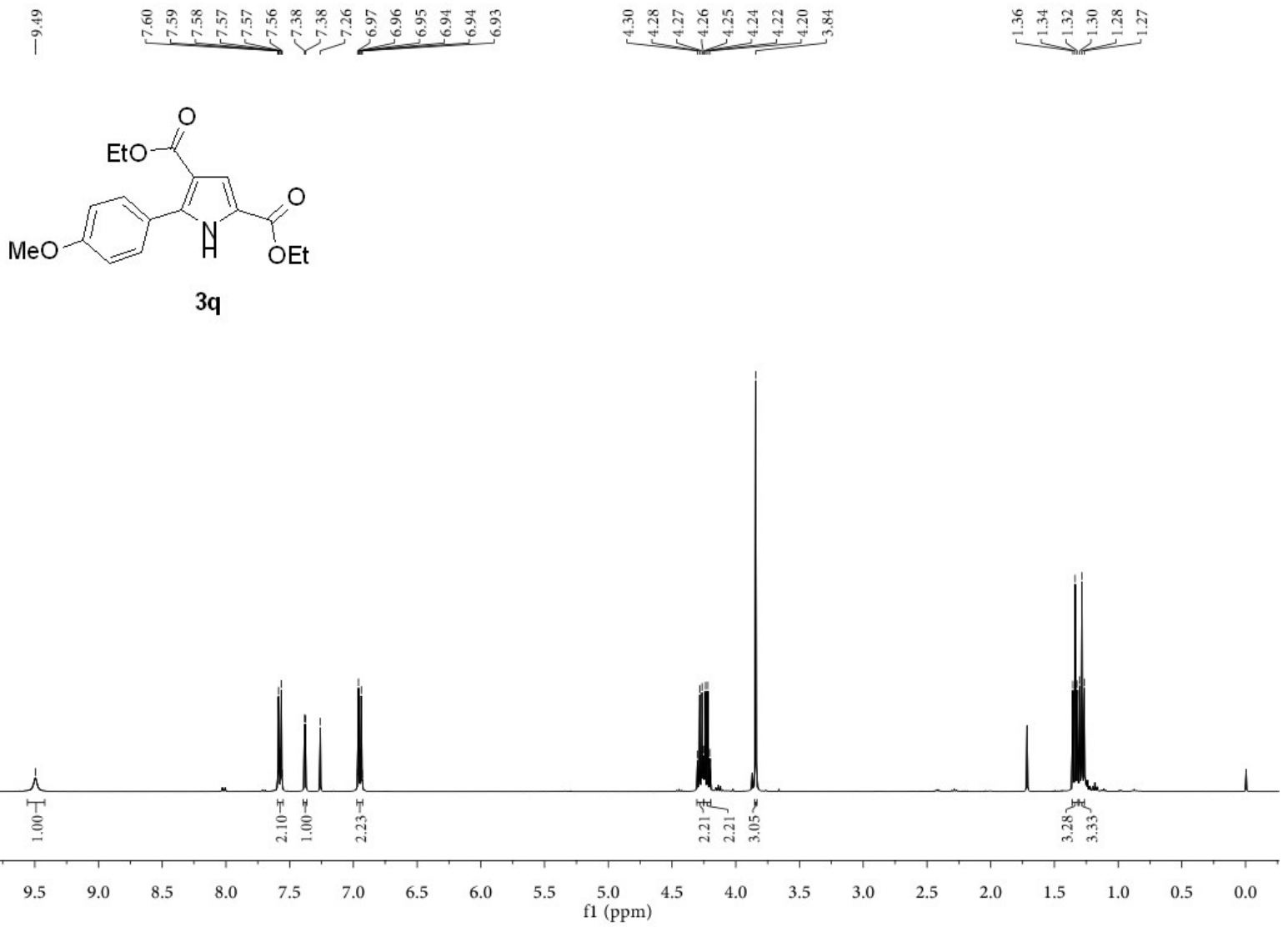
129.02
128.85
127.91
121.98
118.28
113.88
77.32
77.00
76.68
60.79
59.94
21.33
14.34
14.25
EtO
O
O
N
H
OEt
3p
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.56
7.38
7.38
7.26
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6.96
6.95
6.94
6.94
6.93
4.30
4.28
4.27
4.26
4.25
4.24
4.22
4.20
3.84
1.36
1.34
1.32
1.30
1.28
1.27
EtO
O
O
N
H
MeO
OEt
1.00
2.10
1.00
2.23
2.21
2.21
3.05
3.28
3.33
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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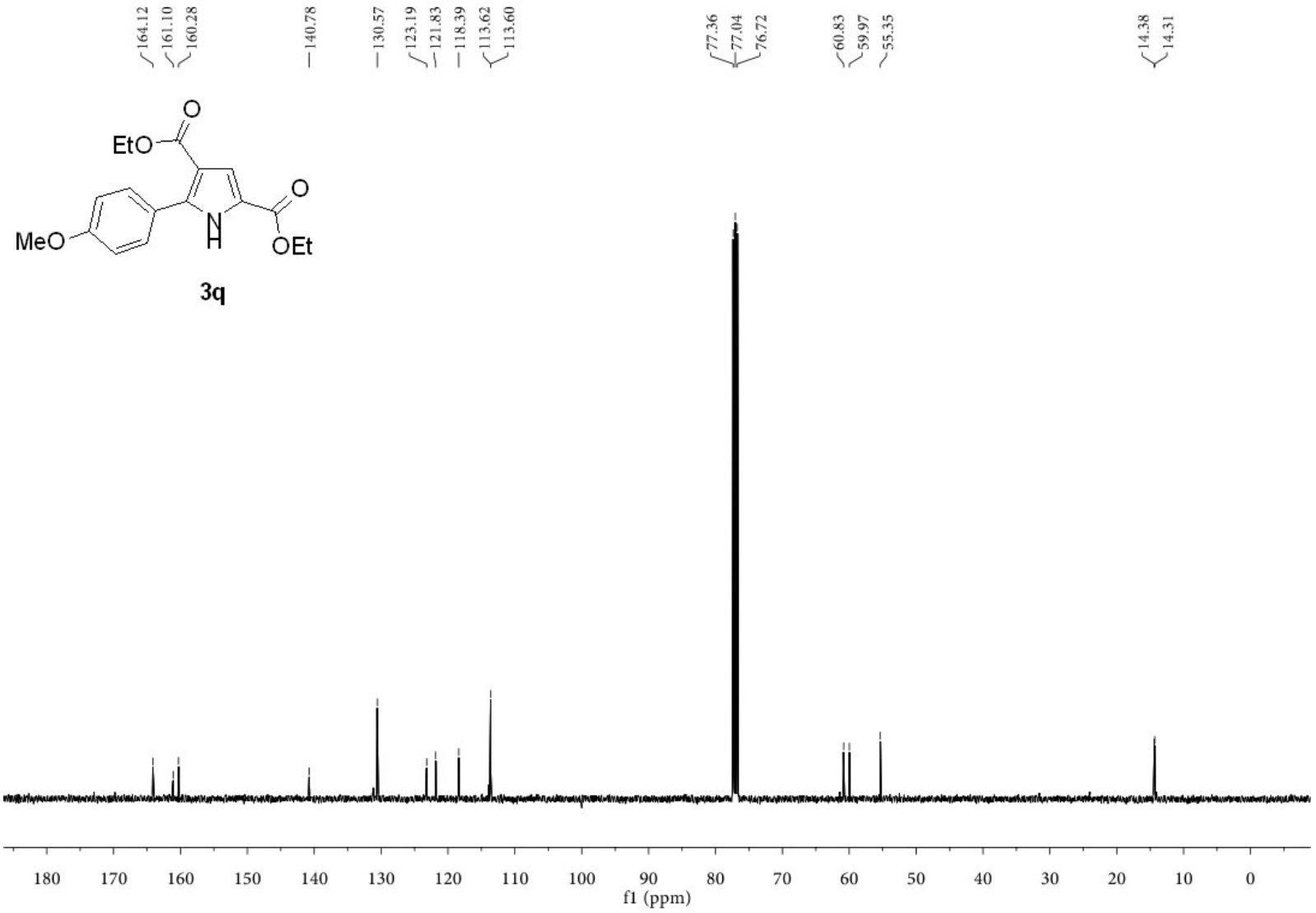
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

3q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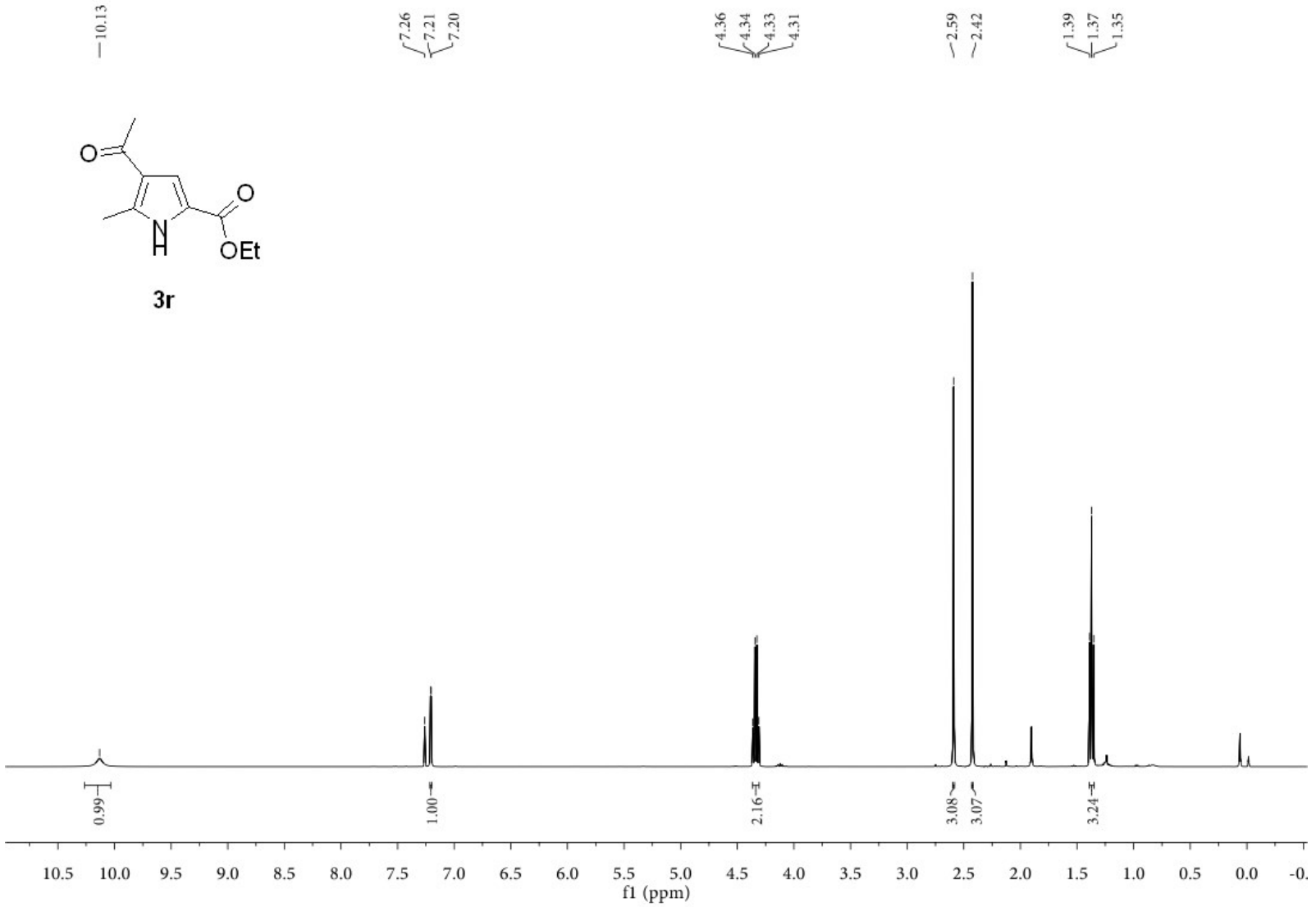
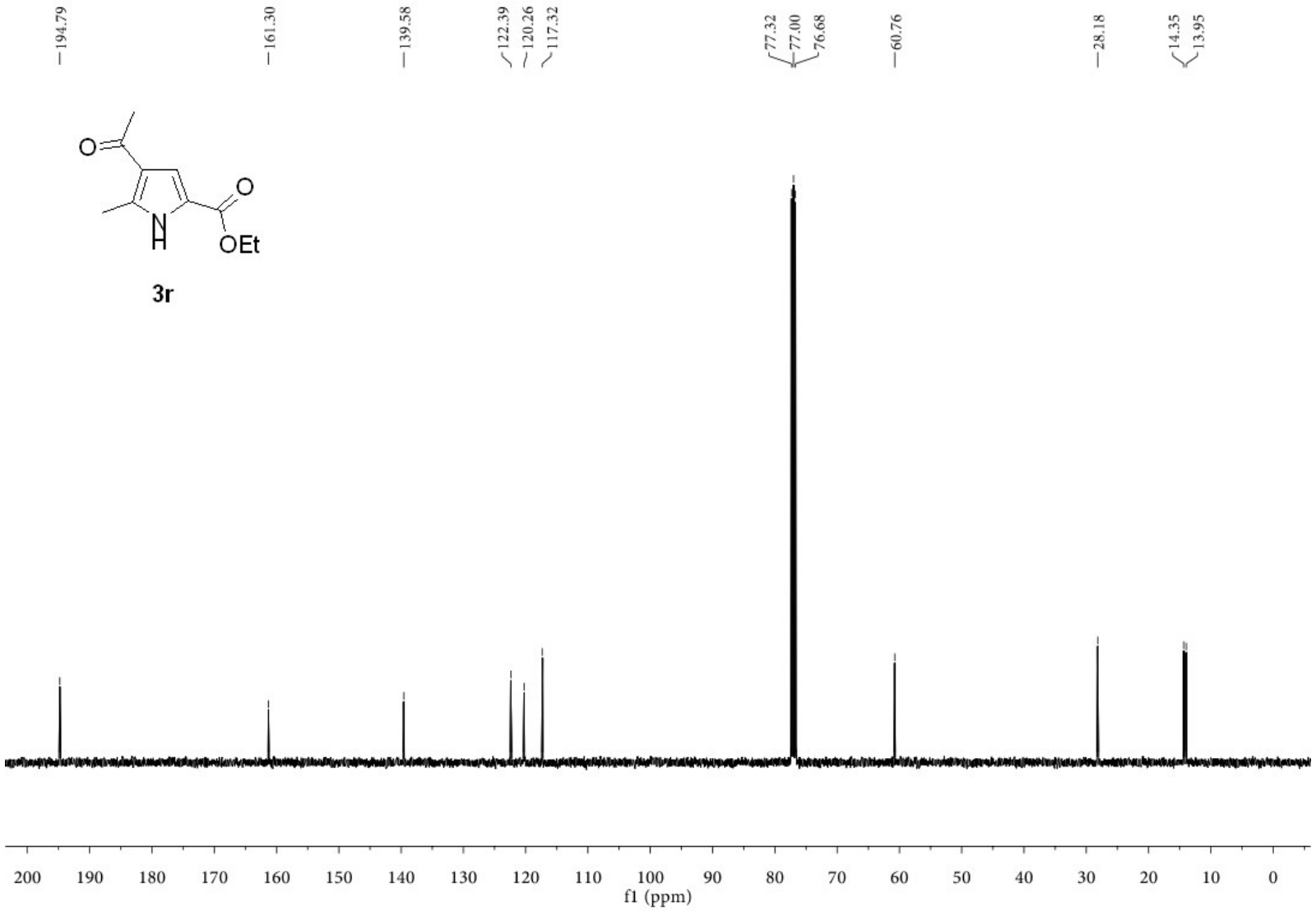
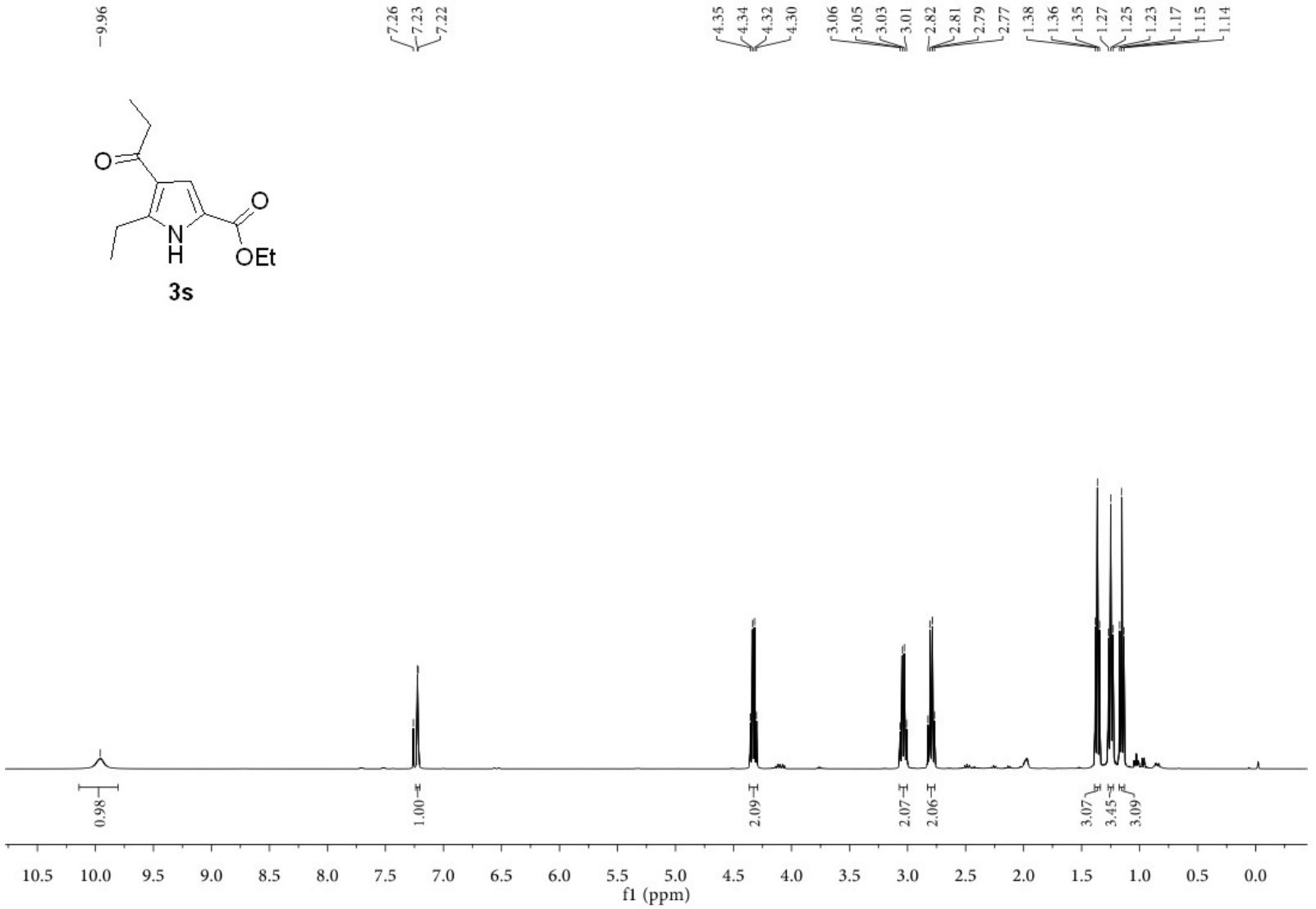
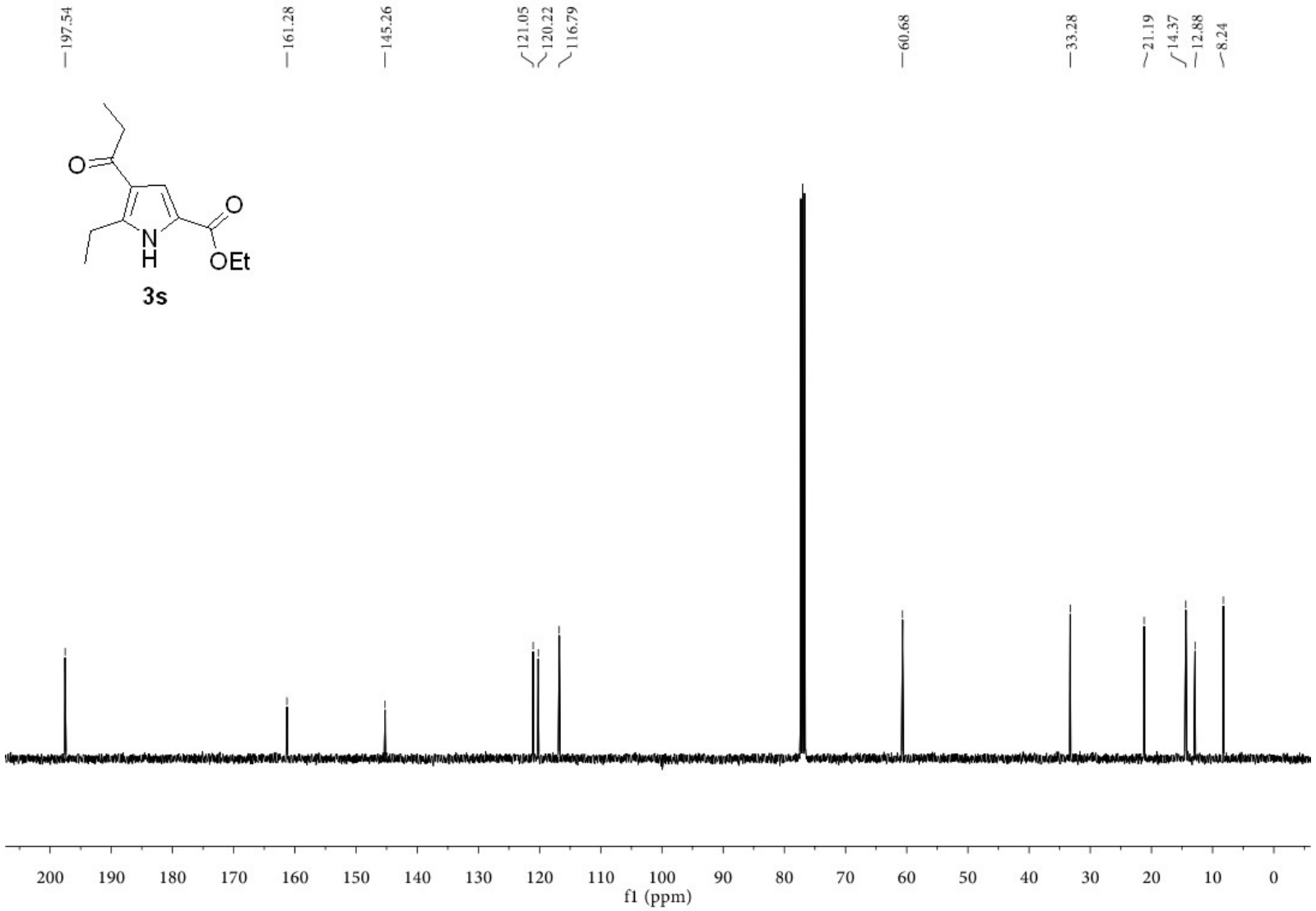
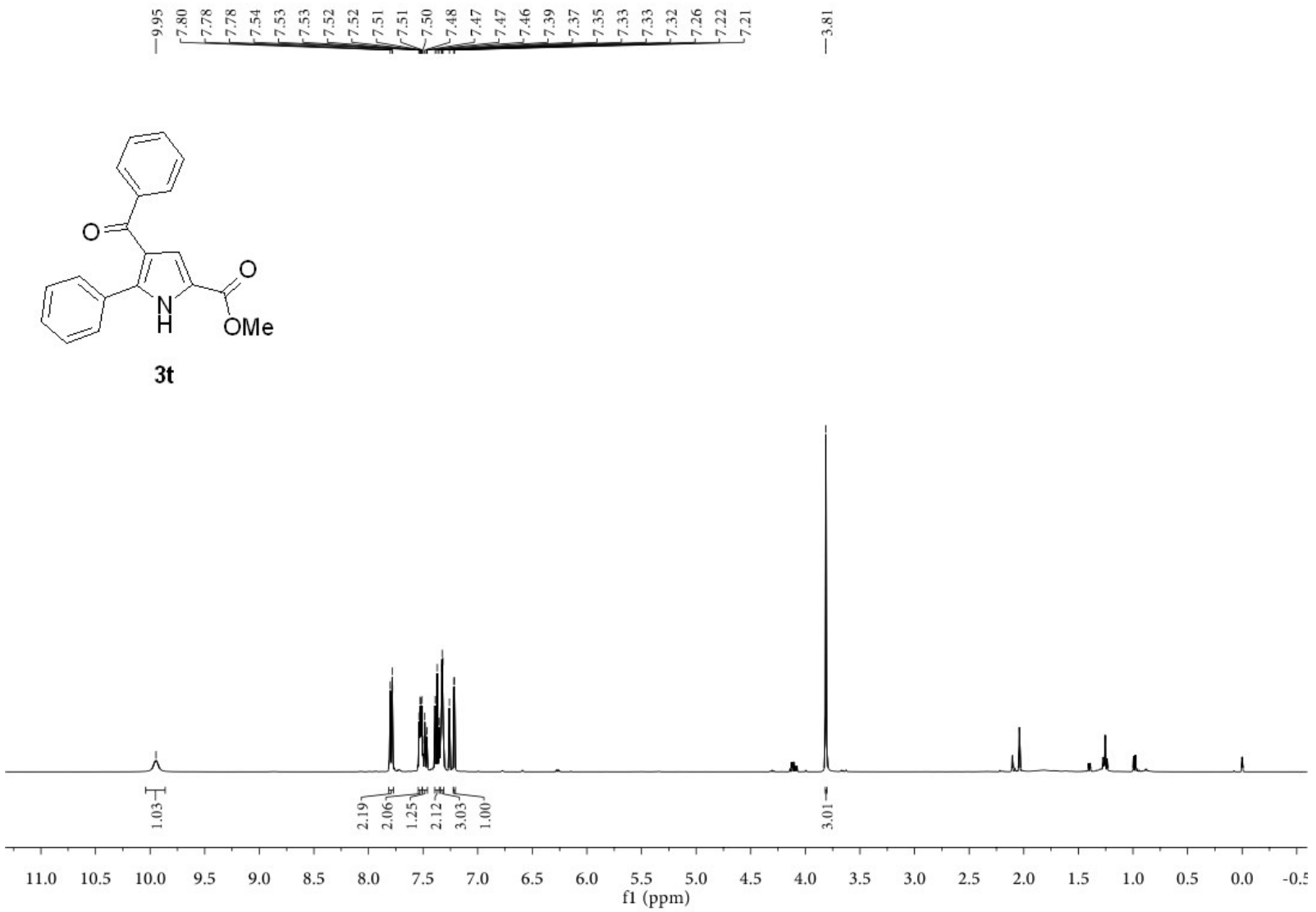
123.19
121.83
118.39
113.62
113.60
77.36
77.04
76.72
60.83
59.97
55.35
14.38
14.31
EtO
O
O
MeO
OEt
3q
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


10.13
7.26
7.21
7.20
4.36
4.34
4.33
4.31
2.59
2.42
1.39
1.37
1.35
O
O
N
H
OEt
3r
0.99
1.00
2.16
3.08
3.07
3.24
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
f1 (ppm)

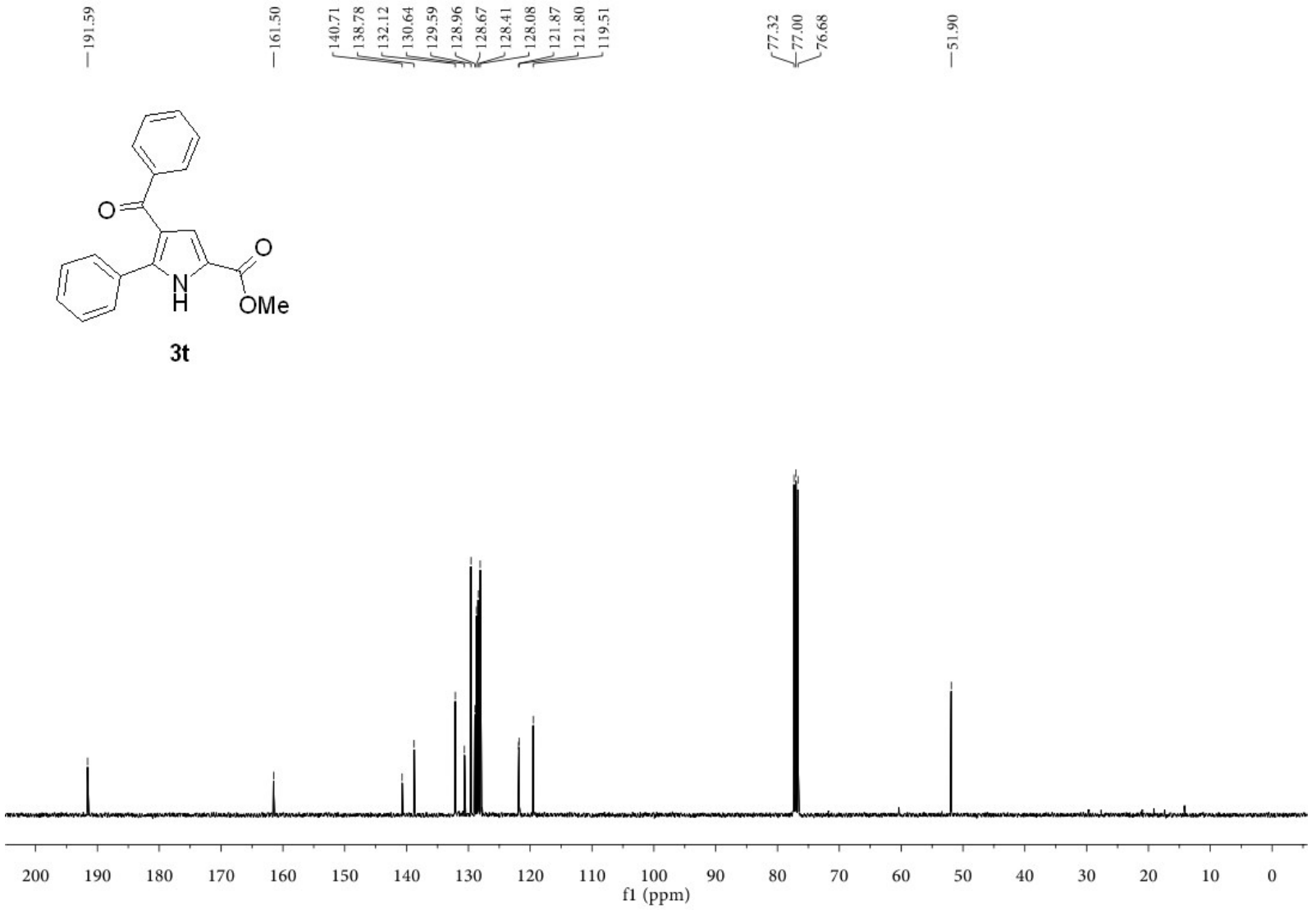

194.79
161.30
139.58
122.39
120.26
117.32
77.32
77.00
76.68
60.76
28.18
14.35
13.95
O
O
N
H
OEt
3r
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

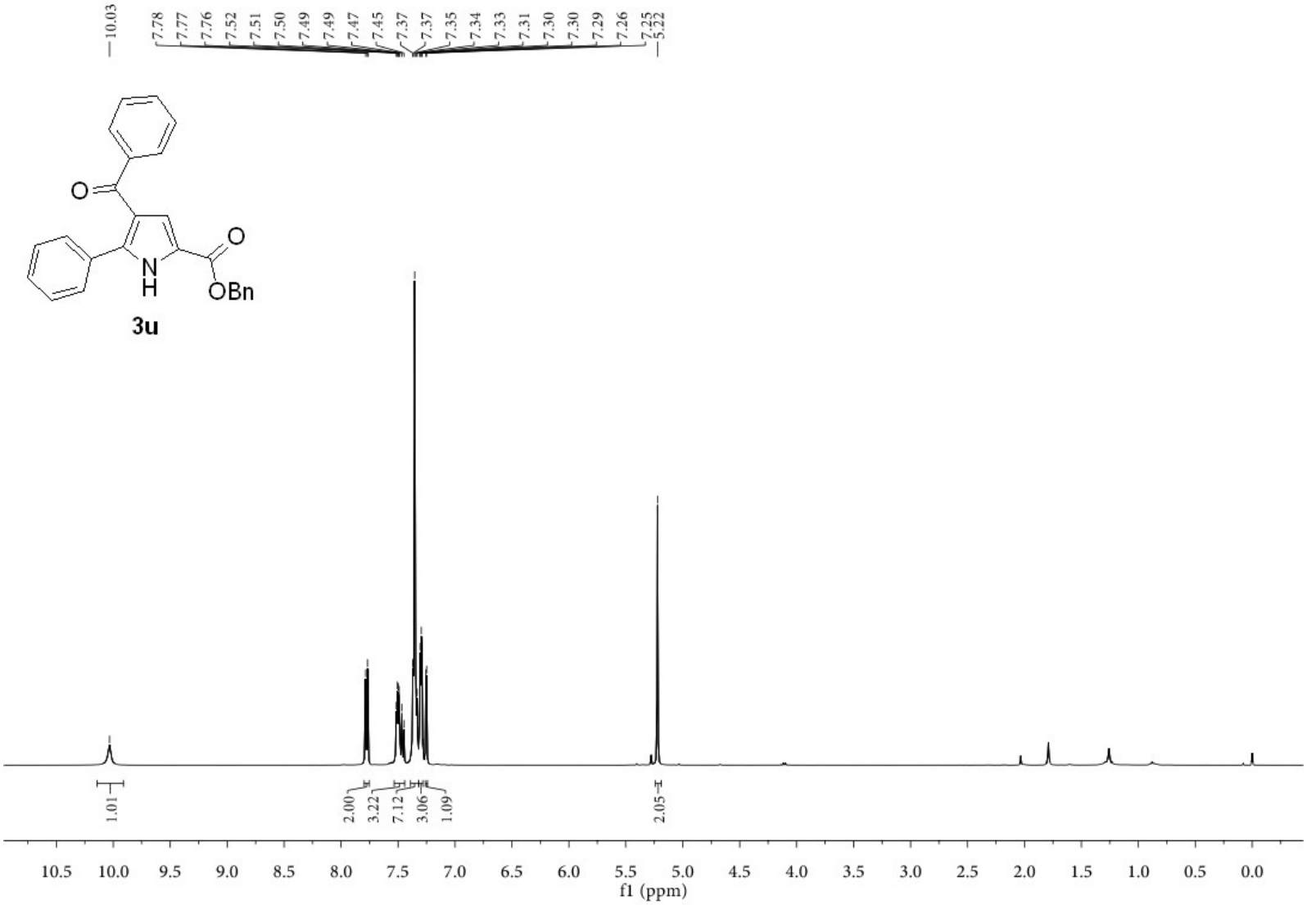

9.96
7.26
7.23
7.22
4.35
4.34
4.32
4.30
3.06
3.05
3.03
3.01
2.82
2.81
2.79
2.77
1.38
1.36
1.35
1.27
1.25
1.23
1.17
1.15
1.14
O
O
N
H
OEt
3s
0.98
1.00
2.09
2.07
2.06
3.07
3.45
3.09
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

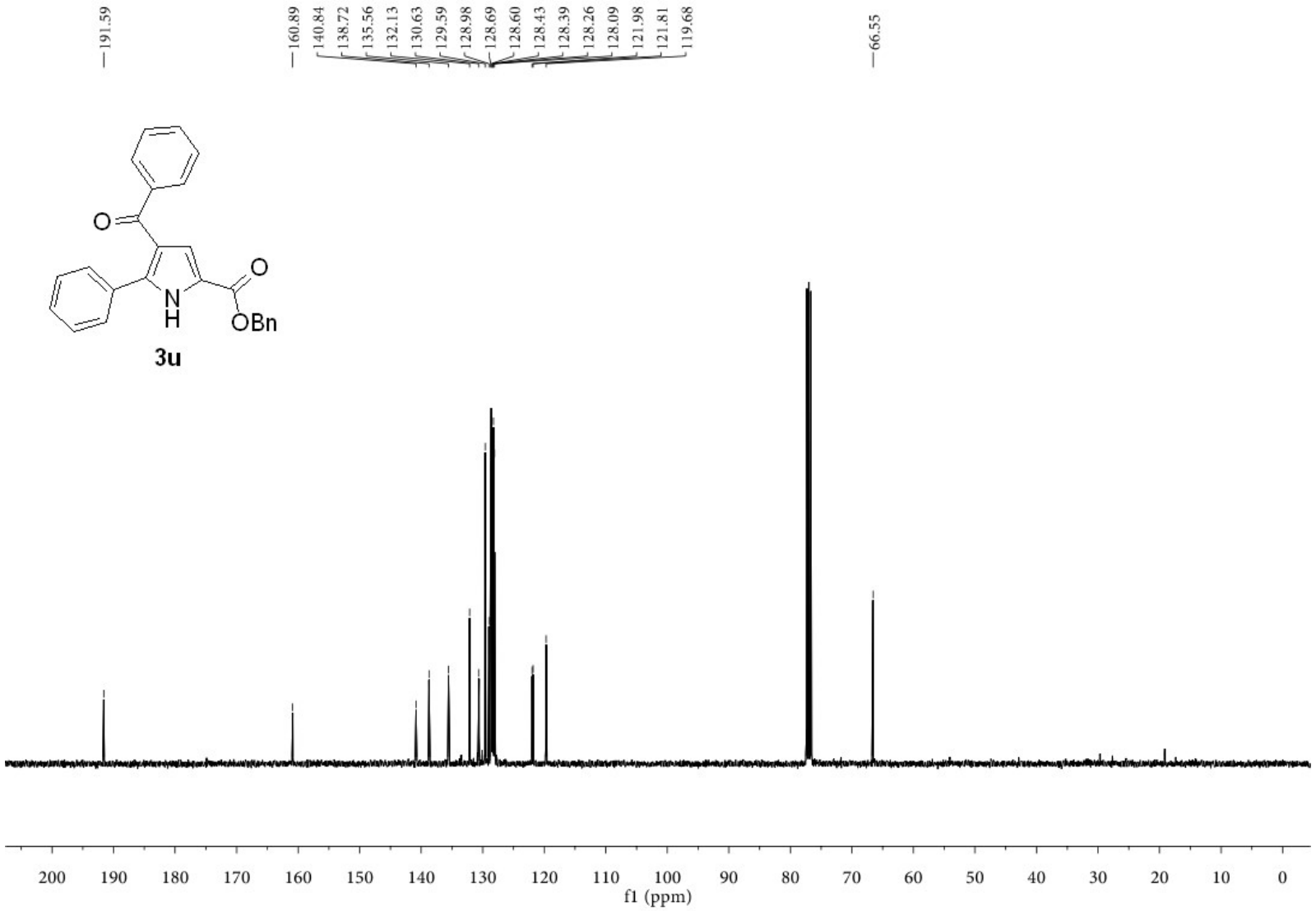

197.54
161.28
145.26
121.05
120.22
116.79
60.68
33.28
21.19
14.37
12.88
8.24
O
O
N
H
OEt
3s
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


9.95
7.80
7.78
7.78
7.54
7.53
7.53
7.52
7.52
7.51
7.51
7.50
7.48
7.47
7.47
7.46
7.39
7.37
7.35
7.33
7.33
7.32
7.26
7.22
7.21
3.81
O
O
N
H
OMe
1.03
2.19
2.06
1.25
2.12
3.03
1.00
3.01
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

3t

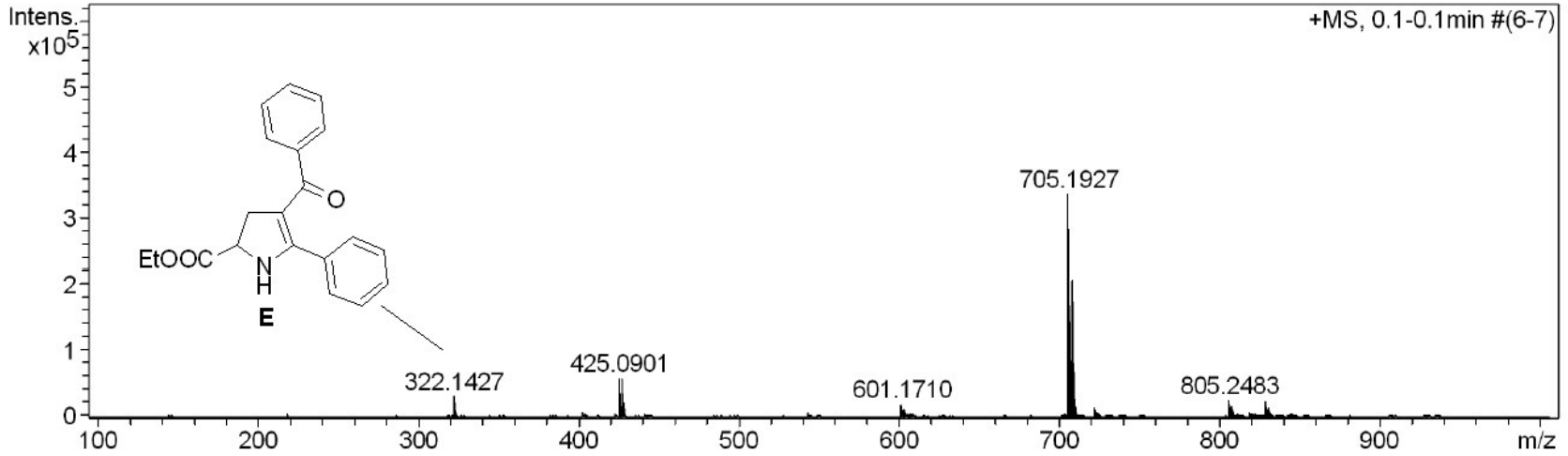

191.59
161.50
140.71
138.78
132.12
130.64
129.59
128.96
128.67
128.41
128.08
121.87
121.80
119.51
77.32
77.00
76.68
51.90
O
O
N
H
OMe
3t
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


10.03
7.78
7.77
7.76
7.52
7.51
7.50
7.49
7.49
7.47
7.45
7.37
7.37
7.35
7.34
7.33
7.31
7.30
7.30
7.29
7.26
7.25
5.22
O
O
N
H
OBn
3u
1.01
2.00
3.22
7.12
3.06
1.09
2.05
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


191.59
160.89
140.84
138.72
135.56
132.13
130.63
129.59
128.98
128.69
128.60
128.43
128.39
128.26
128.09
121.98
121.81
119.68
66.55
O
O
N
H
OBn
3u
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	180 ¡ãC
Scan Begin	100 m/z	Set End Plate Offset	-500 V	Set Dry Gas	3.0 l/min
Scan End	1000 m/z	Set Collision Cell RF	300.0 Vpp	Set Divert Valve	Waste



Meas. m/z	#	Formula	m/z	err [ppm]	Mean err [ppm]	rdb	N-Rule	e¡¥ Conf	mSigma	Std I	Std Mean m/z	Std I Var Norm	Std m/z Diff	Std Comb Dev
322.1427	1	C 20 H 20 N O 3	322.1438	3.3	3.0	11.5	ok	even	37.0	60.8	1.2	25.4	1.0	842.7