Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Remote Asymmetric Conjugate Addition Catalyzed by Bifunctional Spiro-Pyrrolidine-Derived Thiourea Catalyst

Ming-Hui Xu, [a] Yong-Hai Yuan, [a] Dong-Dong Liang, [a] Xiao-Ming Zhang,*[a] Fu-Min Zhang, [a] Yong-Qiang Tu,*[ab] Ai-Jun Ma, [c] Kun Zhang, [c] Jin-Bao Peng [c]

[a]*State Key Laboratory of Applied Organic Chemistry and College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou 730000, P. R. China*
[b]*School of Chemistry and Chemical Engineering, Frontiers Science Center for Transformative Molecules, Shanghai Jiao Tong University, Shanghai 200240, P. R. China*
[c]*School of Biotechnology and Health Science, Wuyi University, Jiangmen 529020, P. R. China*

*E-mail: tuyq@lzu.edu.cn, tuyq@sjtu.edu.cn

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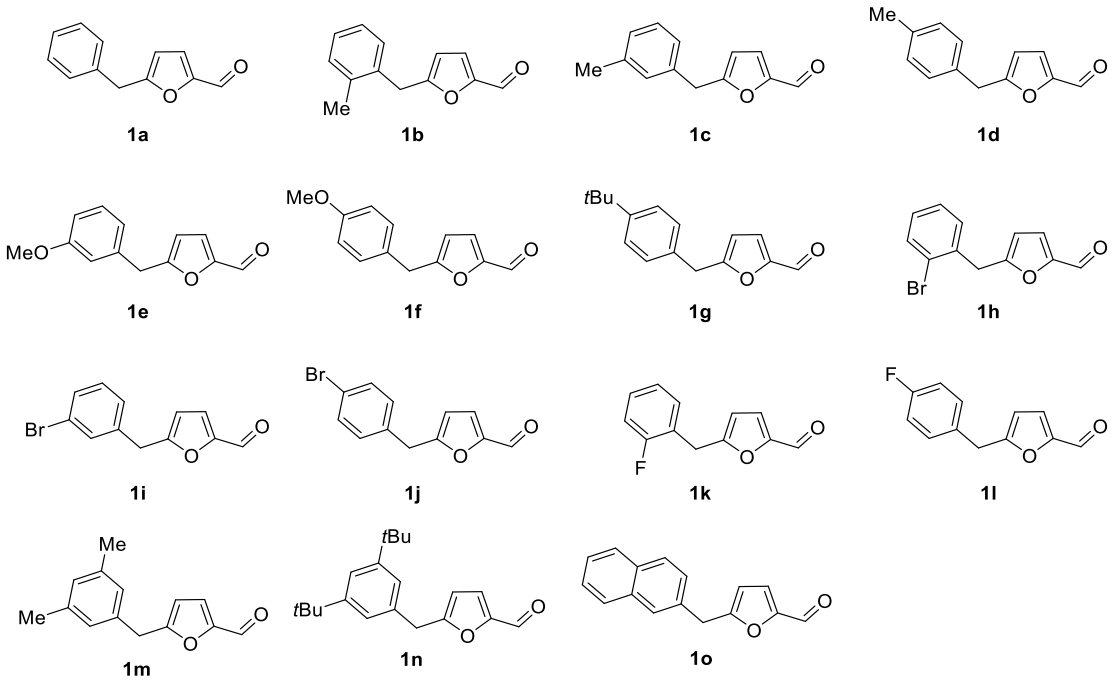
1. General information

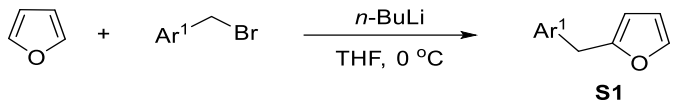
All reactions requiring anhydrous conditions were carried out under argon atmosphere using oven-dried glassware (120 ℃), which was cooled under argon. All solvents were purified and dried by standard techniques, and distilled prior to use. All reactions under standard conditions were monitored by thin-layer chromatography (TLC) on gel F_{254} plates. Silica gel (200-300 mesh) and petroleum ether (b.p. 60-90 ℃), ethyl acetate are used for product purification by flash column chromatography. **^{1}H NMR** spectra were acquired on a Bruker 400 or 600 MHz; **^{13}C NMR** spectra were acquired at 100 or 150 MHz and **^{19}F NMR** spectra were acquired at 376 MHz. Chemical shifts (δ) were reported in ppm relative to residual solvent signals (**$CDCl_3$**: 7.26 ppm for **^{1}H NMR**; 77.0 ppm for **^{13}C NMR**. **$(CD_3)_2SO$**: 2.50 ppm for **^{1}H NMR**; 39.5 ppm for **^{13}C NMR**.) The following abbreviations are used to indicate the multiplicity in **NMR** spectra: s, singlet; d, doublet; t, triplet; q, quartet; dd, double of doublets; td, triplet of doublets; m, multiplet. High-resolution mass spectral analysis (**HRMS**) data were determined on an APEXII 47e FT-ICR spectrometer by means of the ESI technique. **IR** spectra were recorded on a fourier transform infrared spectrometer. Enantioselectivities were recorded on Waters HPLC using Chiralpak columns or Waters UPC[2]. Optical rotations were detected on RUDOLPH A21202-J APTV/GW. Melting points were recorded on a melting point apparatus and uncorrected.

2. The preparation of substrates and catalysts

2.1 The substrates of 5-benzylfurfurals.



The substrates **1a-1o** were prepared according to the reported literature procedure[1]. Analytical data (**^{1}H NMR**、**^{13}C NMR**) matches with the literature. Substrates **1a-1g** and **1m-1o** were prepared according procedure A, and **1h-1l** were prepared according to procedure B.

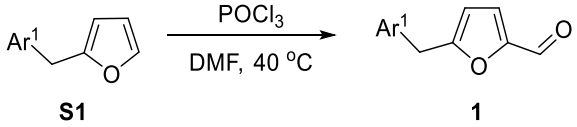


Procedure A:

To a solution of furan (20 mmol, 2.0 equiv) in dry THF (15 mL) was added *n*-BuLi (15 mmol, 1.5 equiv, 2.5 M in hexane) dropwise at 0 ℃ under argon atmosphere. After the addition was completed, the mixture was allowed to warm to room temperature and stirred for 30 min. The mixture was then cooled down to 0 ℃ and the solution of benzyl bromide (10 mmol, 1.0 equiv) in dry THF (10 mL) was added dropwise. After full addition, the reaction mixture was warmed up to room temperature and stirred overnight. The reaction was quenched with water (10 mL), and the resulting mixture was extracted with AcOEt (15 mL×3). The organic layers were combined, washed with brine (20 mL), dried over Na_2SO_4 and evaporated under reduced pressure. The crude product was purified by flash column chromatography using hexane to give the desired product **S1**.

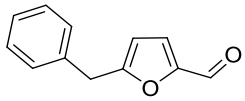
Procedure B:

To a solution of furan (20 mmol, 2.0 equiv) in dry THF (15 mL) was added *n*-BuLi (15 mmol, 1.5 equiv, 2.5 M in hexane) dropwise at 0 ℃ under argon atmosphere. After the addition was complete, the mixture was allowed to warm to room temperature and stirred for 30 min. The mixture was then cooled down to 0 ℃ and the solution of benzyl bromide (10 mmol, 1.0 equiv) and TEMPO (15 mmol, 1.5 equiv) in dry THF (10 mL) was added dropwise. After full addition, the reaction mixture was warmed up to room temperature and stirred overnight. The reaction was quenched with water (10 mL), and the resulting mixture was extracted with AcOEt (15 mL×3). The organic layers were combined, washed with brine (20 mL), dried over Na_2SO_4 and evaporated under reduced pressure. The crude product was purified by flash column chromatography using hexane to give the desired product **S1**.



To a dry DMF (13 mmol, 1.3 equiv) was added $POCl_3$ (11 mmol, 1.1 equiv) dropwise at 0 ℃ under argon atmosphere and the mixture was stirred at 40 ℃ for 1 h. Then the solution of 2-benzylfuran (10 mmol, 1.0 equiv) in anhydrous DMF (1.5 mL) was added dropwise and the reaction mixture was stirred until 2-benzylfuran disappeared via TLC detection. The reaction was quenched with water (10 mL). CH_2Cl_2 was added and the resulting mixture was washed with 1M NaOH. The organic layer was washed with brine, dried over Na_2SO_4 and evaporated under reduced pressure. The residue was purified by flash column chromatography using ethyl acetate/hexane to afford compound **1**.

5-benzylfuran-2-carbaldehyde (**1a**)

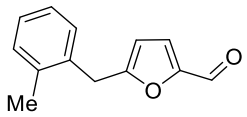


1a

The compound **1a** was prepared using the general procedure A[1a]. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.51 (s, 1H), 7.35–7.28 (m, 2H), 7.27–7.23 (m, 3H), 7.14 (d, *J* = 3.5 Hz, 1H), 6.17 (d, *J* = 3.5

Hz, 1H), 4.04 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 177.0, 161.9, 152.0, 136.0, 128.7, 128.6, 126.9, 123.1, 109.6, 34.7.

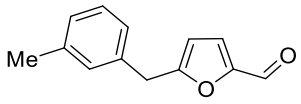
5-(2-methylbenzyl)furan-2-carbaldehyde (**1b**)



1b

The compound **1b** was prepared using the general procedure A. Analytical data matches with the literature[1b]. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.50 (s, 1H), 7.18–7.12 (m, 5H), 6.04 (d, *J* = 3.5 Hz, 1H), 4.02 (s, 2H), 2.27 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 176.9, 161.6, 151.9, 136.3, 134.2, 130.3, 129.6, 127.2, 126.2, 123.1, 109.6, 32.4, 19.2.

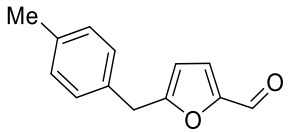
5-(3-methylbenzyl)furan-2-carbaldehyde (**1c**)



1c

The compound **1c** was prepared using the general procedure A[1c]. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.50 (s, 1H), 7.23–7.16 (m, 1H), 7.14 (d, *J* = 3.5 Hz, 1H), 7.09–7.00 (m, 3H), 6.17 (d, *J* = 3.5 Hz, 1H), 3.99 (s, 2H), 2.32 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 177.0, 162.0, 152.0, 138.2, 135.9, 129.5, 128.5, 127.6, 125.7, 123.1, 109.6, 34.6, 21.2.

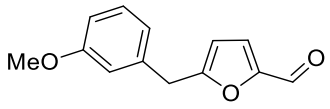
5-(4-methylbenzyl)furan-2-carbaldehyde (**1d**)



1d

The compound **1d** was prepared using the general procedure A[1c]. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.48 (s, 1H), 7.12 (d, *J* = 5.0 Hz, 5H), 6.15 (d, *J* = 3.5 Hz, 1H), 3.97 (s, 2H), 2.30 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 176.9, 162.1, 151.9, 136.4, 132.8, 129.2, 128.5, 123.1, 109.4, 34.1, 20.8.

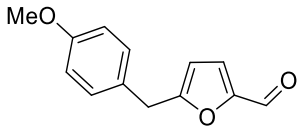
5-(3-methoxybenzyl)furan-2-carbaldehyde (**1e**)



1e

The compound **1e** was prepared using the general procedure A[1c]. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.51 (s, 1H), 7.23 (td, *J* = 7.5, 1.3 Hz, 1H), 7.15 (d, *J* = 3.5 Hz, 1H), 6.87–6.74 (m, 3H), 6.20 (d, *J* = 3.5 Hz, 1H), 4.01 (s, 2H), 3.77 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 177.0, 161.6, 159.7, 152.0, 137.4, 129.6, 123.1, 121.0, 114.5, 112.1, 109.7, 55.0, 34.6.

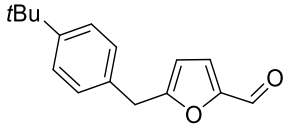
5-(4-methoxybenzyl)furan-2-carbaldehyde (**1f**)



1f

The compound **1f** was prepared using the general procedure A[1c]. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.48 (s, 1H), 7.14 (t, *J* = 6.3 Hz, 3H), 6.91–6.75 (m, 2H), 6.14 (d, *J* = 2.9 Hz, 1H), 3.96 (s, 2H), 3.75 (d, *J* = 1.8 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 176.9, 162.3, 158.4, 151.9, 129.7, 127.9, 123.1, 113.9, 109.3, 55.0, 33.7.

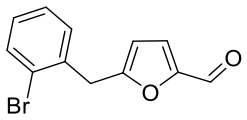
5-(4-(tert-butyl)benzyl)furan-2-carbaldehyde (**1g**)



1g

The compound **1g** was prepared using the general procedure A[1c]. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.51 (s, 1H), 7.39–7.31 (m, 2H), 7.18 (d, *J* = 8.3 Hz, 2H), 7.14 (d, *J* = 3.5 Hz, 1H), 6.19 (d, *J* = 3.5 Hz, 1H), 4.01 (s, 2H), 1.30 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 177.0, 162.1, 152.0, 149.8, 132.9, 128.4, 125.5, 123.1, 109.6, 34.3, 34.2, 31.2.

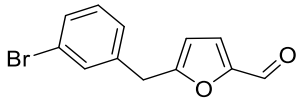
5-(2-bromobenzyl)furan-2-carbaldehyde (**1h**)



1h

The compound **1h** was prepared using the general procedure B[1a]. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.52 (s, 1H), 7.56 (d, *J* = 7.8 Hz, 1H), 7.31–7.21 (m, 2H), 7.21–7.07 (m, 2H), 6.19 (d, *J* = 3.5 Hz, 1H), 4.18 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 177.0, 160.0, 152.0, 135.5, 132.8, 130.8, 128.7, 127.7, 124.3, 123.1, 110.2, 35.0.

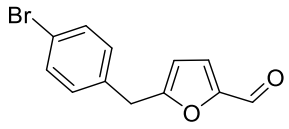
5-(3-bromobenzyl)furan-2-carbaldehyde (**1i**)



1i

The compound **1i** was prepared using the general procedure B[1a]. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.54 (s, 1H), 7.46–7.33 (m, 2H), 7.25–7.11 (m, 3H), 6.22 (d, *J* = 3.5 Hz, 1H), 4.02 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 177.1, 160.7, 152.2, 138.3, 131.8, 130.3, 130.2, 127.5, 123.0, 122.6, 110.0, 34.3.

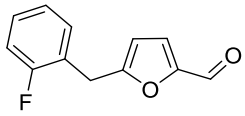
5-(4-bromobenzyl)furan-2-carbaldehyde (**1j**)



1j

The compound **1j** was prepared using the general procedure B[1a]. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.52 (s, 1H), 7.48–7.39 (m, 2H), 7.17 (d, *J* = 3.5 Hz, 1H), 7.12 (d, *J* = 8.3 Hz, 2H), 6.20 (d, *J* = 3.5 Hz, 1H), 4.00 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 177.01, 160.9, 152.1, 135.0, 131.7, 130.4, 123.1, 120.8, 109.8, 34.1.

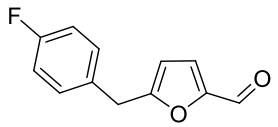
5-(2-fluorobenzyl)furan-2-carbaldehyde (**1k**)



1k

The compound **1k** was prepared using the general procedure A[1c]. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.54 (s, 1H), 7.31–7.22 (m, 2H), 7.17 (d, *J* = 3.6 Hz, 1H), 7.15–7.04 (m, 2H), 6.22 (d, *J* = 3.5 Hz, 1H), 4.10 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 177.2, 162.4, 160.5, 159.6, 152.2, 131.0 (d, *J* = 3.9 Hz), 129.1 (d, *J* = 8.1 Hz), 124.4 (d, *J* = 3.7 Hz), 123.2 (d, *J* = 15.6 Hz), 115.7, 115.4, 109.8, 28.0. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -117.8.

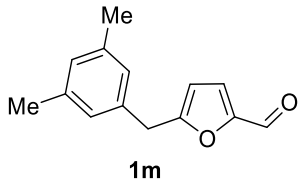
5-(4-fluorobenzyl)furan-2-carbaldehyde (**1l**)



1l

The compound **1l** was prepared using the general procedure A[1c]. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.55 (s, 1H), 7.22 (dd, *J* = 8.6, 5.3 Hz, 2H), 7.17 (d, *J* = 3.5 Hz, 1H), 7.02 (t, *J* = 8.7 Hz, 2H), 6.18 (d, *J* = 3.5 Hz, 1H), 4.04 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 177.1, 163.0, 161.6, 160.6, 152.2, 131.8, 130.3 (d, *J* = 8.0 Hz), 123.1, 115.5 (d, *J* = 18.5 Hz), 109.7, 34.0. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -115.7.

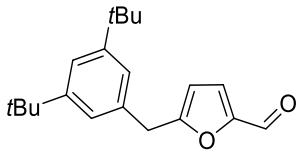
5-(3,5-dimethylbenzyl)furan-2-carbaldehyde (**1m**)



1m

The compound **1m** was prepared using the general procedure A. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.54 (s, 1H), 7.17 (d, *J* = 3.5 Hz, 1H), 6.91 (s, 1H), 6.88 (s, 2H), 6.21 (d, *J* = 3.5 Hz, 1H), 3.99 (s, 2H), 2.31 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 177.0, 162.2, 152.0, 138.1, 135.8, 128.5, 126.5, 123.0, 109.6, 34.5, 21.1.

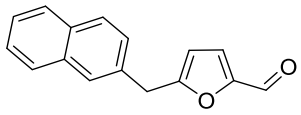
5-(3,5-di-tert-butylbenzyl)furan-2-carbaldehyde (**1n**)



1n

The compound **1n** was prepared using the general procedure A. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.55 (s, 1H), 7.33 (s, 1H), 7.16 (d, *J* = 3.4 Hz, 1H), 7.09 (d, *J* = 0.9 Hz, 2H), 6.18 (d, *J* = 3.4 Hz, 1H), 4.05 (s, 2H), 1.31 (s, 18H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 177.2, 162.7, 152.1, 151.2, 135.1, 123.1, 121.0, 109.7, 35.3, 34.8, 31.4.

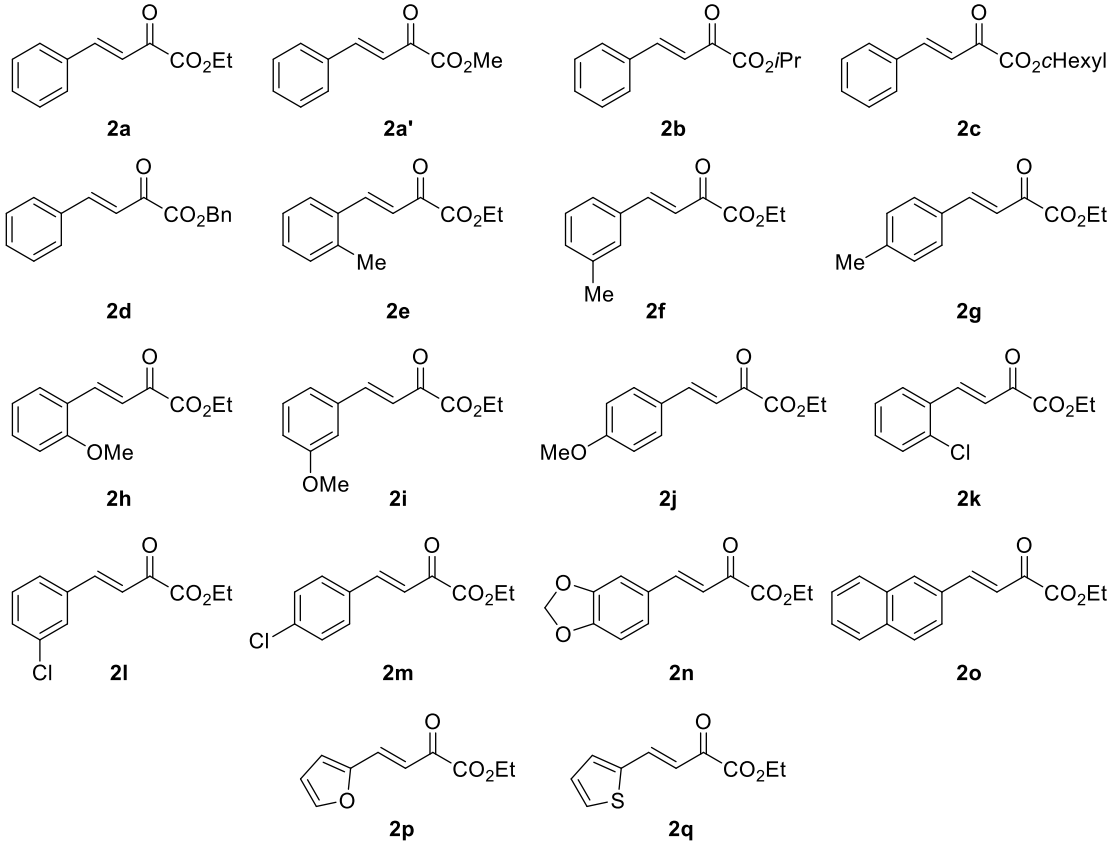
5-(naphthalen-2-ylmethyl)furan-2-carbaldehyde (**1o**)



1o

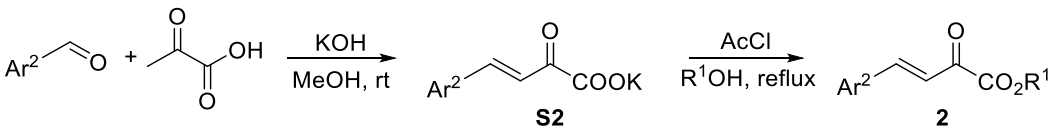
The compound **1o** was prepared using the general procedure A[1c]. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.50 (s, 1H), 7.84–7.72 (m, 3H), 7.66 (s, 1H), 7.49–7.40 (m, 2H), 7.33 (dd, *J* = 8.4, 1.7 Hz, 1H), 7.11 (d, *J* = 3.5 Hz, 1H), 6.16 (d, *J* = 3.5 Hz, 1H), 4.17 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 177.1, 161.8, 152.1, 133.4, 133.4, 132.3, 128.4, 127.6, 127.5, 127.4, 126.9, 126.2, 125.8, 123.0, 109.8, 34.9.

2.2 General procedure for the preparation of *β,γ*-unsaturated *α*-ketoesters.



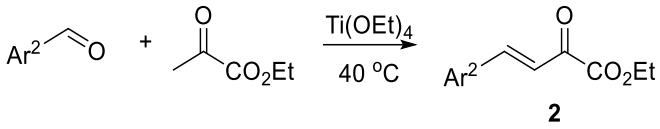
The substrates **2a**-**2q** were prepared according to the reported literature procedure. Analytical data (**^{1}H NMR**、**^{13}C NMR**) matches with the literature[2].

Procedure A:



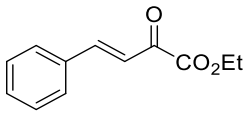
A mixture of benzaldehyde (10 mmol, 1.0 equiv), and pyruvic acid (10 mol, 1.0 equiv) in MeOH (1 mL) was added KOH (1.5 equiv, 15 mol in 5 mL MeOH) dropwise at 0 °C under argon atmosphere. The solution was stirred at room temperature overnight. The yellow suspension was filtered and then washed with ice MeOH and ethyl ether giving **S2** as yellow solid. **S2** was added to the solution of AcCl (12 mmol, 1.2 equiv) in EtOH (6 mL) at 0 °C. The solution was stirred for 6 hours at reflux temperature, and then cooled to room temperature. The solution was quenched with $NaHCO_3$ (10 mL), extracted by DCM (10 mL×3). The combined organic layer was washed with brine (20 mL), dried over anhydrous Na_2SO_4, and evaporated under reduced pressure. The residue was purified by flash chromatography on silica gel to give the product **2**.

Procedure B:



A mixture of benzaldehyde (5 mmol, 1.0 equiv), and ethyl pyruvate (6 mmol, 1.2 equiv) in toluene (25 mL) was added $Ti(OEt)_4$ (6 mmol, 1.2 equiv) dropwise at rt under argon atmosphere. The solution was stirred at 40 ℃ until benzaldehyde disappeared via TLC detection. The solution was quenched with water (1 mL) and stirred for 30 min. The mixture was dried over anhydrous Na_2SO_4, filtrated with celite, and evaporated under reduced pressure. The residue was purified by flash chromatography on silica gel (petroleum ether:EtOAc = 20:1) to give **2**.

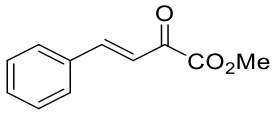
ethyl (*E*)-2-oxo-4-phenylbut-3-enoate (**2a**)



2a

The compound **2a** was prepared using the general procedure B[2b]. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 16.1 Hz, 1H), 7.61 (dd, *J* = 7.7, 1.7 Hz, 2H), 7.47–7.38 (m, 3H), 7.36 (t, *J* = 8.9 Hz, 1H), 4.38 (q, *J* = 7.1 Hz, 2H), 1.39 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 182.7, 162.1, 148.3, 133.9, 131.5, 129.0, 128.9, 120.4, 62.4, 14.0.

methyl (*E*)-2-oxo-4-phenylbut-3-enoate (**2a'**)

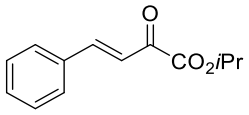


2a'

The compound **2a′** was prepared using the general procedure A[2a]. **^{1}H NMR** (400 MHz,

$CDCl_3$) δ 7.83 (d, *J* = 16.1 Hz, 1H), 7.60 (dd, *J* = 7.7, 1.3 Hz, 2H), 7.47–7.31 (m, 4H), 3.91 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 182.1, 162.2, 148.2, 133.6, 131.4, 128.8, 128.8, 120.1, 52.7.

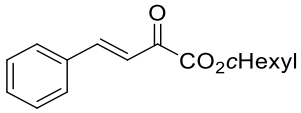
isopropyl (*E*)-2-oxo-4-phenylbut-3-enoate (**2b**)



2b

The compound **2b** was prepared using the general procedure B[2b]. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 16.2 Hz, 1H), 7.62 (dd, *J* = 7.7, 1.6 Hz, 2H), 7.49–7.31 (m, 4H), 5.26–5.19 (m, 1H), 1.39 (d, *J* = 6.3 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 183.1, 161.7, 148.0, 133.8, 131.4, 128.9, 128.8, 120.5, 70.5, 21.5.

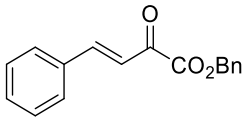
cyclohexyl (*E*)-2-oxo-4-phenylbut-3-enoate (**2c**)



2c

The compound **2c** was prepared using the general procedure A. Analytical data matches with the literature[2c]. **^{1}H NMR** (400 MHz, $(CD_3)_2SO$) δ 7.81 (dd, *J* = 7.7, 1.5 Hz, 2H), 7.76 (d, *J* = 16.3 Hz, 1H), 7.54–7.43 (m, 3H), 7.34–7.26 (m, 1H), 4.99–4.86 (m, 1H), 2.00–1.83 (m, 2H), 1.74 – 1.67 (m, 2H), 1.57 – 1.47 (m, 3H), 1.43 – 1.33 (m, 2H), 1.33–1.14 (m, 2H). **^{13}C NMR** (100 MHz, $(CD_3)_2SO$) δ 184.4, 161.9, 148.0, 133.7, 131.7, 129.1, 129.1, 121.4, 74.5, 30.8, 24.7, 23.1.

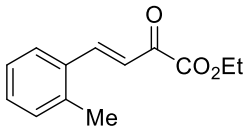
benzyl (*E*)-2-oxo-4-phenylbut-3-enoate (**2d**)



2d

The compound **2d** was prepared using the general procedure A. Analytical data matches with the literature[2c]. **^{1}H NMR** (400 MHz, $(CD_3)_2SO$) δ 7.85–7.74 (m, 3H), 7.54–7.44 (m, 5H), 7.43–7.37 (m, 3H), 7.34 (d, *J* = 16.3 Hz, 1H), 5.36 (s, 2H). **^{13}C NMR** (100 MHz, $(CD_3)_2SO$) δ 183.7, 162.2, 148.2, 135.0, 133.7, 131.7, 129.2, 129.1, 128.6, 128.5, 128.5, 121.3, 67.3.

ethyl (*E*)-2-oxo-4-(o-tolyl)but-3-enoate (**2e**)

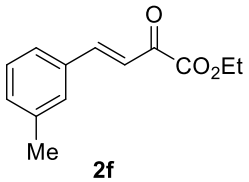


2e

The compound **2e** was prepared using the general procedure B[2b]. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.17 (d, *J* = 16.0 Hz, 1H), 7.68 (d, *J* = 7.8 Hz, 1H), 7.33 (t, *J* = 7.5 Hz, 1H), 7.29 (d, *J* = 16.0 Hz, 1H), 7.26–7.21 (m, 2H), 4.40 (q, *J* = 7.1 Hz, 2H), 2.47 (s, 3H), 1.41 (t, *J* = 7.1 Hz, 3H). **^{13}C**

NMR (150 MHz, $CDCl_3$) δ 182.8, 162.2, 145.7, 139.0, 132.8, 131.3, 131.0, 126.7, 126.4, 121.4, 62.4, 19.7, 14.0.

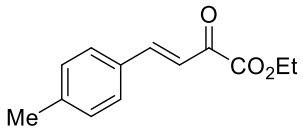
ethyl (*E*)-2-oxo-4-(m-tolyl)but-3-enoate (**2f**)



2f

The compound **2f** was prepared using the general procedure B[2b]. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 16.1 Hz, 1H), 7.44 (d, *J* = 7.4 Hz, 2H), 7.35 (d, *J* = 16.1 Hz, 1H), 7.32–7.24 (m, 2H), 4.39 (q, *J* = 7.1 Hz, 2H), 2.38 (s, 3H), 1.41 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 182.9, 162.3, 148.7, 138.8, 134.0, 132.5, 129.6, 129.0, 126.3, 120.3, 62.5, 21.3, 14.1.

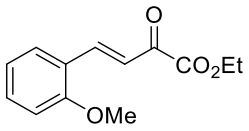
ethyl (*E*)-2-oxo-4-(p-tolyl)but-3-enoate (**2g**)



2g

The compound **2g** was prepared using the general procedure B[2b]. **^{1}H NMR** (400 MHz, $(CD_3)_2SO$) δ 7.75 (d, *J* = 16.3 Hz, 1H), 7.69 (d, *J* = 8.0 Hz, 2H), 7.33–7.23 (m, 3H), 4.33 (q, *J* = 7.1 Hz, 2H), 2.34 (s, 3H), 1.32 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $(CD_3)_2SO$) δ 183.9, 162.5, 148.1, 142.0, 131.0, 129.7, 129.2, 120.2, 61.9, 21.1, 13.8.

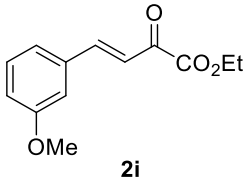
ethyl (*E*)-4-(2-methoxyphenyl)-2-oxobut-3-enoate (**2h**)



2h

The compound **2h** was prepared using the general procedure A. Analytical data matches with the literature[2d]. **^{1}H NMR** (600 MHz, $(CD_3)_2SO$) δ 7.99 (d, *J* = 16.4 Hz, 1H), 7.80 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.52–7.48 (m, 1H), 7.35 (d, *J* = 16.4 Hz, 1H), 7.14 (d, *J* = 8.0 Hz, 1H), 7.03 (t, *J* = 7.4 Hz, 1H), 4.32 (q, *J* = 7.1 Hz, 2H), 3.90 (s, 3H), 1.31 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (150 MHz, $(CD_3)_2SO$) δ 184.0, 162.5, 158.7, 142.7, 133.6, 129.4, 121.9, 121.3, 120.9, 112.0, 61.9, 55.8, 13.9.

ethyl (*E*)-4-(3-methoxyphenyl)-2-oxobut-3-enoate (**2i**)

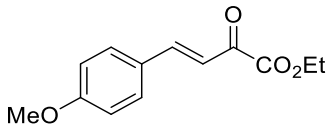


2i

The compound **2i** was prepared using the general procedure A. Analytical data matches with the literature[2d]. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80 (dd, *J* = 16.1, 6.1 Hz, 1H), 7.37-7.29 (m,

1H), 7.21 (d, *J* = 5.9 Hz, 1H), 7.12 (s, 1H), 6.99 (dd, *J* = 5.7, 2.4 Hz, 1H), 4.39 (dd, *J* = 7.1, 4.7 Hz, 2H), 3.83 (d, *J* = 5.5 Hz, 3H), 1.43–1.38 (m, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 182.6, 162.0, 159.8, 148.2, 135.1, 129.9, 121.7, 120.5, 117.5, 113.3, 62.3, 55.2, 13.9.

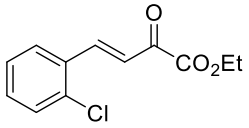
ethyl (E)-4-(4-methoxyphenyl)-2-oxobut-3-enoate (**2j**)



2j

The compound **2j** was prepared using the general procedure B[2b]. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 16.0 Hz, 1H), 7.54 (d, *J* = 8.8 Hz, 2H), 7.20 (d, *J* = 16.0 Hz, 1H), 6.90 (d, *J* = 8.8 Hz, 2H), 4.37 (q, *J* = 7.1 Hz, 2H), 3.81 (s, 3H), 1.39 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 182.2, 162.1, 162.0, 147.7, 130.6, 126.3, 117.7, 114.1, 61.8, 54.9, 13.6.

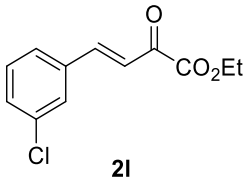
ethyl (*E*)-4-(2-chlorophenyl)-2-oxobut-3-enoate (**2k**)



2k

The compound **2k** was prepared using the general procedure B[2b]. **^{1}H NMR** (600 MHz, $(CD_3)_2SO$) δ 8.08–8.01 (m, 2H), 7.58 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.53 (td, *J* = 7.7, 1.6 Hz, 1H), 7.48–7.40 (m, 2H), 4.36 (q, *J* = 7.1 Hz, 2H), 1.36 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (150 MHz, $(CD_3)_2SO$) δ 183.2, 161.8, 141.9, 134.8, 132.9, 131.4, 130.2, 128.6, 127.9, 123.9, 62.1, 13.9.

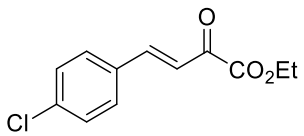
ethyl (*E*)-4-(3-chlorophenyl)-2-oxobut-3-enoate (**2l**)



2l

The compound **2l** was prepared using the general procedure B[2b]. **^{1}H NMR** (400 MHz, $(CD_3)_2SO$) δ 7.91 (s, 1H), 7.80–7.71 (m, 2H), 7.55–7.44 (m, 2H), 7.39 (d, *J* = 16.3 Hz, 1H), 4.32 (q, *J* = 7.1 Hz, 2H), 1.31 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $(CD_3)_2SO$) δ 183.9, 162.2, 146.1, 136.0, 134.0, 131.1, 130.9, 128.7, 127.7, 122.8, 62.1, 13.9.

ethyl (*E*)-4-(4-chlorophenyl)-2-oxobut-3-enoate (**2m**)

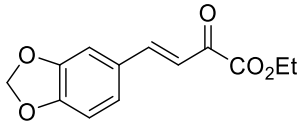


2m

The compound **2m** was prepared using the general procedure A[2a]. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 16.1 Hz, 1H), 7.56 (d, *J* = 8.5 Hz, 2H), 7.36 (dd, *J* = 16.0, 12.3 Hz, 3H), 4.39 (q, *J* = 7.1 Hz, 2H), 1.41 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 182.2, 161.7,

146.4, 137.3, 132.3, 129.9, 129.1, 120.6, 62.4, 13.8.

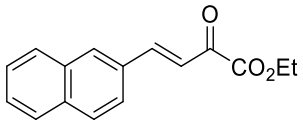
ethyl (*E*)-4-(benzo[*d*][1,3]dioxol-5-yl)-2-oxobut-3-enoate (**2n**)



2n

The compound **2n** was prepared using the general procedure A[2e]. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 16.0 Hz, 1H), 7.16 (dd, *J* = 23.6, 11.6 Hz, 3H), 6.85 (d, *J* = 8.5 Hz, 1H), 6.04 (s, 2H), 4.39 (q, *J* = 7.1 Hz, 2H), 1.41 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 182.5, 162.3, 150.9, 148.5, 148.2, 128.6, 126.5, 118.5, 108.7, 106.9, 101.8, 62.4, 14.0.

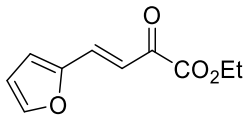
ethyl (*E*)-4-(naphthalen-2-yl)-2-oxobut-3-enoate (**2o**)



2o

The compound **2o** was prepared using the general procedure B[2b]. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.02 (d, *J* = 16.5 Hz, 2H), 7.90–7.82 (m, 3H), 7.75 (dd, *J* = 8.6, 1.4 Hz, 1H), 7.59–7.51 (m, 2H), 7.47 (d, *J* = 16.0 Hz, 1H), 4.42 (q, *J* = 7.1 Hz, 2H), 1.43 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 182.8, 162.3, 148.5, 134.8, 133.2, 131.9, 131.6, 128.9, 128.9, 128.0, 127.8, 126.9, 123.6, 120.6, 62.5, 14.1.

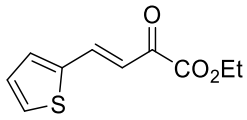
ethyl (*E*)-4-(furan-2-yl)-2-oxobut-3-enoate (**2p**)



2p

The compound **2p** was prepared using the general procedure B[2b]. **^{1}H NMR** (600 MHz, $(CD_3)_2SO$) δ 7.98–7.94 (m, 1H), 7.61 (d, *J* = 15.9 Hz, 1H), 7.18 (d, *J* = 3.5 Hz, 1H), 7.01 (d, *J* = 15.9 Hz, 1H), 6.71 (dd, *J* = 3.5, 1.8 Hz, 1H), 4.29 (q, *J* = 7.1 Hz, 2H), 1.29 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (150 MHz, $(CD_3)_2SO$) δ 182.5, 161.9, 150.4, 147.6, 133.3, 119.7, 117.6, 113.6, 61.9, 13.8.

ethyl (*E*)-2-oxo-4-(thiophen-2-yl)but-3-enoate (**2q**)

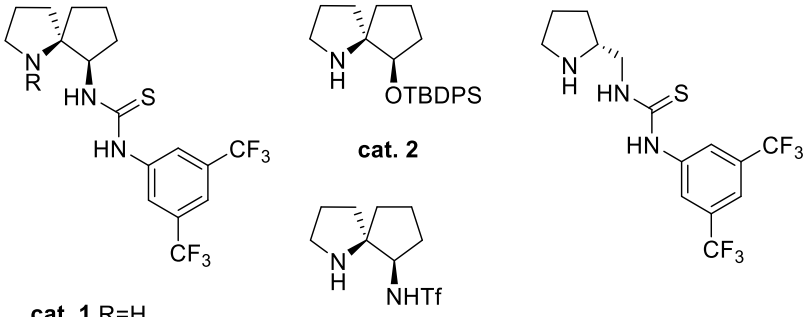


2q

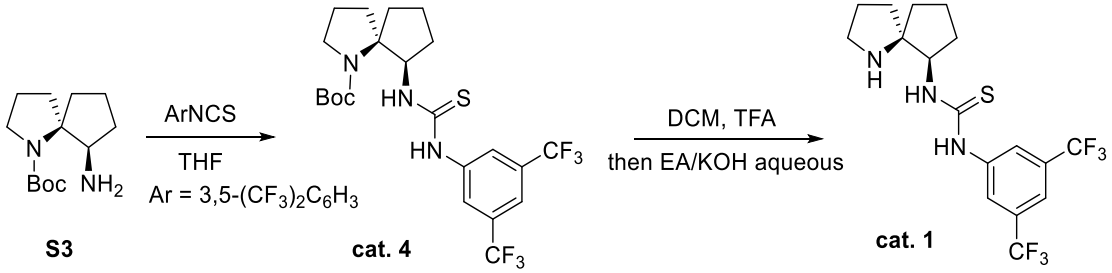
The compound **2q** was prepared using the general procedure B[2b]. **^{1}H NMR** (400 MHz, $(CD_3)_2SO$) δ 7.98 (d, *J* = 15.9 Hz, 1H), 7.87 (d, *J* = 5.0 Hz, 1H), 7.72 (d, *J* = 3.6 Hz, 1H), 7.21 (dd, *J* = 5.0, 3.7 Hz, 1H), 7.00 (d, *J* = 15.9 Hz, 1H), 4.30 (q, *J* = 7.1 Hz, 2H), 1.30 (t, *J* = 7.1

Hz, 3H). **^{13}C NMR** (100 MHz, $(CD_3)_2SO$) δ 182.8, 162.2, 140.4, 139.1, 134.9, 132.4, 129.2, 119.4, 62.0, 40.2, 40.0, 39.8, 39.6, 39.4, 39.2, 39.0, 13.9.

2.3 General procedure for the preparation of catalysts.



The catalysts **cat. 2**[3], **cat. 3**[4], and **cat. 5**[5] are known compounds and the analytical data (**^{1}H NMR**) matches with the literature.

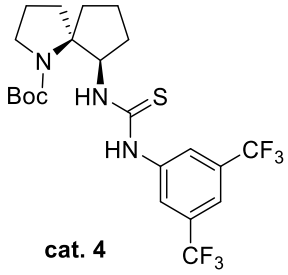


To a solution of **S3** (1.7 g, 1.0 equiv) in dry THF (30 mL), 3,5-bis(trifluoromethyl)phenyl isocyanate (2.2 g, 1.1 equiv) was added dropwise under argon atmosphere. The solution was stirred at room temperature until **S3** disappeared by TLC detection. The solution was quenched with H_2O (20 mL), and then the mixture was extracted by AcOEt (50 mL×3). The combined organic layer was washed with brine (50 mL), dried over anhydrous Na_2SO_4, and evaporated under reduced pressure. The residue was purified by flash chromatography on silica gel (petroleum ether:EtOAc = 50:1 to 10:1) to give **cat. 4** in 80% yield. (**cat. 4** was further purified by Et_2O recrystallization)

TFA (10 equiv) was added dropwise to a solution of **cat. 4** (1.0 g, 1.0 equiv) in dry DCM. The solution was stirred at room temperature until **cat. 4** disappeared by TLC detection. Then the resulting solution was concentrated in vacuo to remove most of TFA, and the residue was diluted with EtOAc (20 mL), then KOH aqueous solution (5 mL, 10 g KOH in 50 mL H_2O) was added to ensure that the pH of the mixture was 10~12, the mixture was extracted by AcOEt (20 mL×3), The combined organic layer was dried over anhydrous Na_2SO_4, and evaporated under reduced pressure. The crude residue was purified through column chromatography on silica gel (PE:EA = 5:1 to EA) to give **cat. 1** in 86% yield. (note: **cat. 1** was easily converted to **cat. 7** in DCM. Therefore, the use of DCM should be avoided after the system was alkalized. After purification and concentration, the residue was dissolved in Et_2O, and concentrated in vacuo to obtain **cat. 1** as a white solid. **Cat. 1** was stored in a frozen environment, and the purity of the catalyst had a great impact on the reaction.)

tert-butyl(5*R*,6*R*)-6-(3-(3,5-bis(trifluoromethyl)phenyl)thioureido)-1-azaspiro[4.4]nonane-1-

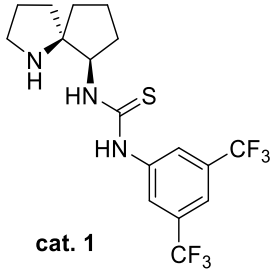
carboxylate (**cat. 4**)



cat. 4

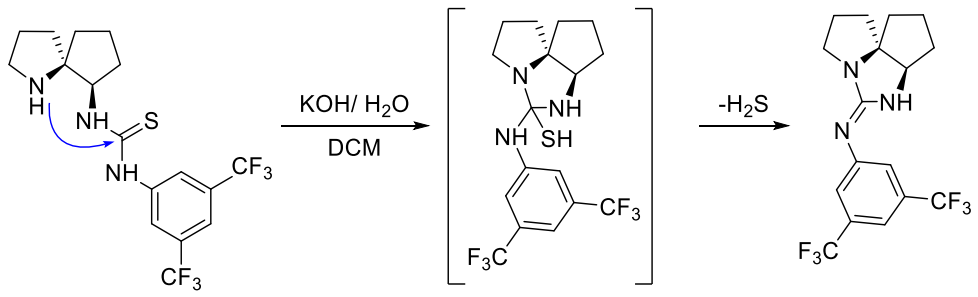
Cat. 4 was isolated as a white solid (m.p. = 193 – 195 ℃) in 80% yield. $[\alpha]_D^{19}$ = + 103.0 (c 1.0, AcOEt). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.95 (s, 1H), 8.56 (d, *J* = 7.1 Hz, 1H), 7.77 (s, 2H), 7.59 (s, 1H), 4.71 (q, *J* = 13.0, 6.2 Hz, 1H), 3.35 (d, *J* = 5.3 Hz, 2H), 2.68–2.45 (m, 1H), 2.30 – 2.15 (m, 1H), 214 – 2.03 (m, 1H), 2.02 – 1.90 (m, 2H), 1.89–1.66 (m, 3H), 1.66–1.46 (m, 2H), 1.11 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 179.2, 155.8, 139.3, 132.7, 132.4, 124.3, 132.1, 122.8, 121.6, 118.1, 107.2, 79.8, 71.3, 64.5, 48.9, 42.0, 35.0, 32.3, 28.0, 22.5, 21.9. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -63.19. **HRMS**(ESI) m/z $(M+Na)^+$: calculated for $C_{22}H_{27}F_6N_3O_2SNa$: 534.1620, found: 534.1628. **IR** (neat) cm^{-1}: 3309, 3171, 2972, 1675, 1385, 1279, 1126, 883, 725.

1-(3,5-bis(trifluoromethyl)phenyl)-3-((5*R*,6*R*)-1-azaspiro[4.4]nonan-6-yl)thiourea (**cat. 1**)



cat. 1

Cat. 1 was isolated as a white solid (m.p. = 49 – 51 ℃) in 86% yield. $[\alpha]_D^{19}$ = + 70.0 (c 1.0, AcOEt). **^{1}H NMR** (400 MHz, $(CD_3)_2SO$) δ 10.95 (s, 1H), 8.81 (s, 1H), 8.38 (s, 2H), 7.69 (s, 1H), 4.55 (s, 1H), 3.19–2.95 (m, 2H), 2.18–2.03 (m, 1H), 1.89 (s, 3H), 1.86 (s, 1H), 1.84–1.68 (m, 5H), 1.65 – 1.50 (m, 2H). **^{13}C NMR** (100 MHz, $(CD_3)_2SO$) δ 180.4, 173.1, 130.2, 129.9, 124.6, 121.9, 121.4, 115.8, 71.9, 59.7, 45.3, 35.5, 34.9, 29.8, 24.0, 21.7, 19.7. **^{19}F NMR** (376 MHz, $(CD_3)_2SO$) δ -61.67, -61.68, -61.69. **HRMS**(ESI) m/z $(M+H)^+$: calculated for $C_{17}H_{20}F_6N_3S$: 412.1277, found: 412.1280. **IR** (neat) cm^{-1}: 3443, 2960, 1596, 1384, 1276, 1128, 681.

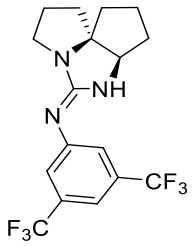


cat. 1 **7**

To the stirred solution of the (*R*,*R*)-**cat. 1** (10 mg) in DCM (0.5 mL) were added two drops of aqueous KOH (5g KOH dissolved in 50 mL H_2O) solution at room temperature, the reaction

was stirred 24 hours, and the mixture was extracted by DCM. The combined organic layer was dried over anhydrous Na_2SO_4, and evaporated under reduced pressure. The crude residue was purified through column chromatography on silica gel (PE:EA = 3:1) to give **7** (7.6 mg) as a colorless solid in 82% yield.

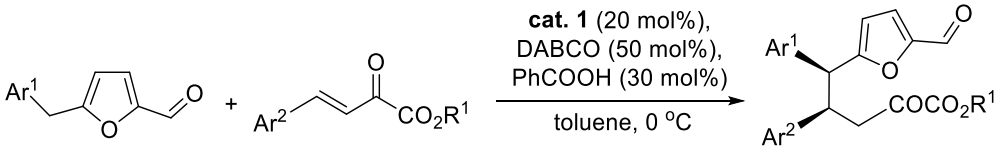
(3a*R*,9a*R*,*E*)-N-(3,5-bis(trifluoromethyl)phenyl)hexahydro-7H-cyclopenta[d]pyrrolo[1,2-c]imidazol-5(1H)-imine (**7**)



7

7 was isolated as a colorless solid (m.p. = 123 – 124 ℃) in 82% yield. $[\alpha]_D^{20}$ = + 62.0 (c 1.0, AcOEt). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.31 (d, *J* = 8.9 Hz, 3H), 6.11 (s, 1H), 3.94 (d, *J* = 4.5 Hz, 1H), 3.27 (s, 1H), 3.13–2.90 (m, 1H), 2.03–1.84 (m, 5H), 1.84–1.74 (m, 1H), 1.74–1.59 (m, 3H), 1.40 (td, *J* = 12.3, 5.7 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 160.0, 151.9, 132.3, 132.0, 131.7, 131.4, 127.7, 125.0, 122.6, 122.3, 119.6, 113.4, 79.3, 62.4, 47.4, 39.5, 36.0, 35.4, 26.2, 23.9. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.90. **HRMS**(ESI) m/z $(M+H)^+$: calculated for $C_{17}H_{18}F_6N_3$: 378.1399, found: 378.1402. **IR** (neat) cm^{-1}: 3380, 2962, 1386, 1595, 1376, 1277, 1127, 956, 703.

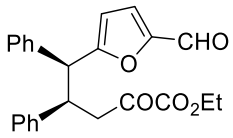
3. General procedure for the remote asymmetric conjugate addition of 5-benzylfurfurals with *β,γ*-unsaturated *α*-ketoesters



1 **2** **3**

To a solution of 5-benzylfurfurals **1** (0.225 mmol, 1.5 equiv), **cat. 1** (0.03 mmol, 0.2 equiv), DABCO (0.075 mmol, 0.5 equiv) and PhCOOH (0.045 mmol, 0.3 equiv) in toluene (1.8 mL) at 0 °C, *β,γ*-unsaturated *α*-ketoesters **2** (0.15 mmol, 1.0 equiv) was added, and the reaction mixture was stirred at the same temperature until **2** disappeared by TLC detection. The solution was then quenched with H_2O (2 mL), extracted by AcOEt (10 mL×3). The combined organic layer was washed with brine (10 mL), dried over anhydrous Na_2SO_4, and evaporated under reduced pressure. The residue was purified by flash chromatography on silica gel (petroleum ether:EtOAc = 10:1 to 3:1) to afford compound **3**.

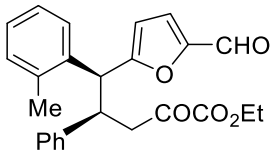
ethyl (4*R*,5*S*)-5-(5-formylfuran-2-yl)-2-oxo-4,5-diphenylpentanoate (**3a**)



3a

The reaction was carried out following the general procedure to give two diastereoisomers with 81% yield and 81:19 dr. The major isomer **3a** was isolated as a white solid (m.p. = 117 – 119 ℃; The minor isomer **3a′** was isolated as a white solid (m.p. = 123 – 124 ℃). Enantiomeric excess was determined by UPC^2 using Chiralpak IG-3 column, CO_2/MeOH 95:5, flow rate 2mL/min, **3a**: 96%, t_{minor} = 3.449 min, t_{major} = 3.821 min; **3a′**: 91%, t_{minor} = 3.329 min, t_{major} = 3.654 min. $[\alpha]_D^{27}$ = -5.0 (c 1.0, AcOEt, **3a**); $[\alpha]_D^{27}$ = -160.0 (c 0.1, AcOEt, **3a′**). **^{1}H NMR** (400 MHz, $CDCl_3$) **3a**: δ 9.41 (s, 1H), 7.51–7.42 (m, 2H), 7.36 (t, *J* = 7.4 Hz, 2H), 7.31–7.25 (m, 1H), 7.23–7.15 (m, 4H), 7.14 – 7.08 (m, 1H), 6.91 (d, *J* = 3.6 Hz, 1H), 6.08 (d, *J* = 3.6 Hz, 1H), 4.31 (d, *J* = 11.6 Hz, 1H), 4.22–4.04 (m, 3H), 3.27 (dd, *J* = 17.5, 9.9 Hz, 1H), 2.92 (dd, *J* = 17.5, 4.1 Hz, 1H), 1.23 (t, *J* = 7.1 Hz, 3H); **3a′**: δ 9.58 (s, 1H), 7.16 (d, *J* = 3.6 Hz, 1H), 7.15–7.11 (m, 5H), 7.11–7.01 (m, 5H), 6.42 (d, *J* = 3.6 Hz, 1H), 4.34 (d, *J* = 10.8 Hz, 1H), 4.23–4.16 (m, 2H), 4.15 – 4.08 (m, 1H), 3.40 (dd, *J* = 17.6, 9.0 Hz, 1H), 3.16 (dd, *J* = 17.6, 4.9 Hz, 1H), 1.27 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) **3a** : δ 192.1, 177.0, 162.1, 160.3, 151.8, 140.9, 138.5, 129.1, 128.5, 128.5, 127.8, 127.0, 109.9, 62.4, 52.0, 44.9, 43.7, 13.8; **3a′** δ 192.0, 177.2, 162.4, 160.4, 152.2, 140.3, 138.3, 128.5, 128.4, 128.3, 128.1, 127.1, 126.9, 110.4, 62.5, 51.7, 45.1, 44.0, 13.8. **HRMS**(ESI) m/z $(M+Na)^+$: calculated for $C_{24}H_{22}O_5Na$: 413.1359, found: 413.1364 (**3a**); 413.1359 (**3a′**). **IR** (neat) cm^{-1}: **3a** 2925, 1724, 1671, 1512, 1260, 1069, 1022, 760, 700; **3a′** 2963, 1670, 1384, 1260, 1087, 798.

ethyl (4*R*,5*S*)-5-(5-formylfuran-2-yl)-2-oxo-4-phenyl-5-(o-tolyl)pentanoate (**3b**)

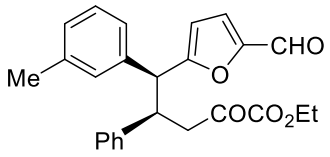


3b

The reaction was carried out following the general procedure to give two diastereoisomers with 66% yield and 75:25 dr as a colorless oil. Enantiomeric excess was determined by UPC^2 using Chiralpak IG-3 column, CO_2/MeOH 95:5, flow rate 2mL/min, the major isomer **3b**: 95%, t_{major} = 2.656 min, t_{minor} = 2.996 min; the minor isomer **3b′**: 90%, t_{minor} = 2.888 min, t_{major} = 3.104 min. $[\alpha]_D^{27}$ = -18.0 (c 1.0, AcOEt, **3b**); $[\alpha]_D^{27}$ = -36.0 (c 0.5, AcOEt, **3b′**). **^{1}H NMR** (600 MHz, $(CD_3)_2SO$) **3b** δ 9.33 (s, 1H), 7.58 (d, *J* = 7.4 Hz, 1H), 7.37 (d, *J* = 7.2 Hz, 2H), 7.29–7.15 (m, 6H), 7.11 (t, *J* = 7.3 Hz, 1H), 6.46 (d, *J* = 3.6 Hz, 1H), 4.70 (d, *J* = 11.7 Hz, 1H), 4.13 (td, *J* = 11.2, 3.5 Hz, 1H), 4.07 (q, *J* = 7.1 Hz, 2H), 3.34–3.29 (m, 1H), 2.85 (dd, *J* = 17.3, 3.6 Hz, 1H), 1.16 (t, *J* = 7.1 Hz, 3H); **3b′** δ 9.49 (s, 1H), 7.56 (d, *J* = 7.5 Hz, 1H), 7.46 (d, *J* = 3.5 Hz, 1H), 7.26–7.22 (m, 2H), 7.11–7.06 (m, 3H), 7.03 – 6.97 (m, 1H), 6.94 -6.86 (m, 2H), 6.75 (d, *J* = 3.6 Hz, 1H), 4.86 (d, *J* = 11.5 Hz, 1H), 4.11 (q, *J* = 7.1 Hz, 3H), 3.43 (dd, *J* = 17.6, 9.6 Hz, 1H), 3.11 (dd, *J* = 17.5, 4.4 Hz, 1H), 2.16 (s, 3H), 1.18 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (150 MHz, $(CD_3)_2SO$) **3b** δ 192.3, 177.3, 162.3, 160.0, 151.0, 141.6, 137.4, 136.4, 130.7, 128.1, 128.1, 127.2, 127.1, 126.8, 126.7, 110.2, 61.7, 45.9, 44.1, 42.8, 19.7, 13.7; **3b′** δ 191.8, 177.6, 162.4, 160.0, 151.8, 141.4, 137.3, 135.6, 130.0, 128.2, 127.9, 127.8, 126.4, 126.0, 110.6, 61.7, 45.0,

44.0, 43.8, 19.4, 13.7. **HRMS**(ESI) m/z $(M+Na)^+$: calculated for $C_{25}H_{24}O_5Na$: 427.1516, found: 427.1521 (**3b**); 427.1516 (**3b′**). **IR** (neat) cm^{-1}: **3b** 2962, 1725, 1675, 1260, 1020, 798, 755, 700; **3b′** 2922, 1724, 1675, 1261, 1024, 799.

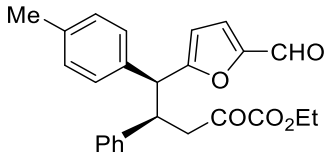
ethyl (4*R*,5*S*)-5-(5-formylfuran-2-yl)-2-oxo-4-phenyl-5-(m-tolyl)pentanoate (**3c**)



3c

The reaction was carried out following the general procedure to give two diastereoisomers with 80% yield and 76:24 dr. The major isomer **3c** was isolated as a light yellow solid (m.p. = 81 – 83 ℃; The minor isomer **3c′** was isolated as a light yellow solid (m.p. = 121 – 122 ℃). Enantiomeric excess of the major isomer **3c** was determined by UPC^2 using Trefoil™ CEL1 column, CO_2/MeOH 90:10, flow rate 2mL/min, 93%, t_{minor} = 1.005 min, t_{major} = 1.186 min; Enantiomeric excess of the minor isomer **3c′** was determined by UPC^2 using Chiralpak IG-3 column, CO_2/MeOH 95:5, flow rate 2mL/min, 89%, t_{minor} = 2.757 min, t_{major} = 3.045 min. $[\alpha]_D^{26}$ = -1.0 (c 1.0, AcOEt, **3c**); $[\alpha]_D^{26}$ = -88.0 (c 0.5, AcOEt, **3c′**). **^{1}H NMR** (400 MHz, $CDCl_3$) **3c** δ 9.42 (s, 1H), 7.34–7.16 (m, 8H), 7.15 – 7.06 (m, 2H), 6.91 (d, *J* = 3.5 Hz, 1H), 6.08 (d, *J* = 3.5 Hz, 1H), 4.26 (d, *J* = 11.7 Hz, 1H), 4.20–4.03 (m, 3H), 3.27 (dd, *J* = 17.6, 9.9 Hz, 1H), 2.92 (dd, *J* = 17.5, 3.9 Hz, 1H), 2.36 (s, 3H), 1.24 (t, *J* = 7.1 Hz, 3H); **3c′** δ 9.59 (s, 1H), 7.20–7.09 (m, 3H), 7.08 – 6.98 (m, 4H), 6.97 -6.88 (m, 3H), 6.40 (d, *J* = 3.4 Hz, 1H), 4.30 (d, *J* = 10.7 Hz, 1H), 4.20 (q, *J* = 7.0 Hz, 2H), 4.16–4.05 (m, 1H), 3.39 (dd, *J* = 17.6, 9.0 Hz, 1H), 3.15 (dd, *J* = 17.6, 4.8 Hz, 1H), 2.20 (s, 3H), 1.28 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) **3c** δ 192.2, 177.1, 162.4, 160.3, 151.8, 141.1, 138.9, 138.5, 129.2, 129.1, 128.6, 128.5, 127.8, 127.1, 125.5, 109.9, 62.4, 52.0, 44.8, 43.9, 21.5, 13.8; **3c′** δ 192.1, 177.3, 162.7, 160.5, 152.2, 140.4, 138.1, 138.0, 129.3, 128.3, 128.2, 127.9, 126.9, 125.5, 110.4, 62.5, 51.6, 45.0, 44.0, 21.3, 13.9. **HRMS**(ESI) m/z $(M+Na)^+$: calculated for $C_{25}H_{24}O_5Na$: 427.1516, found: 427.1521 (**3c**); 427.1516 (**3c′**). **IR** (neat) cm^{-1}: **3c** 2962, 1725, 1674, 1260, 1069, 1022, 799, 751, 700; **3c′** 2963, 2924, 1725, 1676, 1384, 1260, 1092, 1020, 798.

ethyl (4*R*,5*S*)-5-(5-formylfuran-2-yl)-2-oxo-4-phenyl-5-(p-tolyl)pentanoate (**3d**)

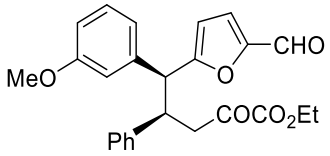


3d

The reaction was carried out following the general procedure to give two diastereoisomers with 80% yield and 82:18 dr as a colorless oil. Enantiomeric excess of the major isomer **3d** was determined by UPC^2 using Chiralpak IG-3 column, CO_2/MeOH 95:5, flow rate 2mL/min, 97%, t_{minor} = 3.296 min, t_{major} = 4.126 min; Enantiomeric excess of the minor isomer **3d′** was determined by UPC^2 using Chiralpak AD-3 column, CO_2/MeOH 95:5, flow rate 2mL/min, 91%, t_{minor} = 1.816 min, t_{major} = 2.143 min. $[\alpha]_D^{27}$ = -10.0 (c 1.0, AcOEt, **3d**); $[\alpha]_D^{27}$ = -60.0 (c 0.5, AcOEt, **3d′**). **^{1}H NMR** (400 MHz, $CDCl_3$) **3d** δ 9.41 (s, 1H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.24–7.15 (m, 6H), 7.14–7.07 (m, 1H), 6.90 (d, *J* = 3.6 Hz, 1H), 6.06 (d, *J* = 3.6 Hz, 1H), 4.27 (d, *J* = 11.6 Hz, 1H), 4.19–4.07 (m, 3H), 3.25 (dd, *J* = 17.5, 9.9 Hz, 1H), 2.94 (dd, *J* = 17.5, 4.1 Hz,

1H), 2.33 (s, 3H), 1.23 (t, *J* = 7.1 Hz, 3H); **3d′** δ 9.57 (s, 1H), 7.17–7.10 (m, 3H), 7.10–6.99 (m, 5H), 6.94 (d, *J* = 8.0 Hz, 2H), 6.39 (d, *J* = 3.6 Hz, 1H), 4.32 (d, *J* = 10.7 Hz, 1H), 4.25–4.16 (m, 2H), 4.15 – 4.05 (m, 1H), 3.37 (dd, *J* = 17.6, 8.9 Hz, 1H), 3.14 (dd, *J* = 17.6, 4.9 Hz, 1H), 2.20 (s, 3H), 1.27 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) **3d** δ 192.2, 177.0, 162.5, 160.3, 151.7, 141.1, 137.6, 135.5, 129.8, 128.5, 128.4, 127.8, 127.0, 109.8, 62.3, 51.7, 44.9, 43.8, 21.0, 13.8; **3d′** δ 192.1, 177.2, 162.8, 160.5, 152.2, 140.5, 136.7, 135.2, 129.1, 128.3, 128.3, 128.2, 126.8, 110.3, 62.5, 51.2, 45.0, 44.1, 20.9, 13.8. **HRMS**(ESI) m/z $(M+Na)^+$: calculated for $C_{25}H_{24}O_5Na$: 427.1516, found: 427.1520 (**3d**); 427.1516 (**3d′**). **IR** (neat) cm^{-1}: **3d** 2925, 1725, 1672, 1511, 1260, 1069, 1020, 793, 755, 700; **3d′** 2922, 1726, 1674, 1384, 1261, 1021, 800.

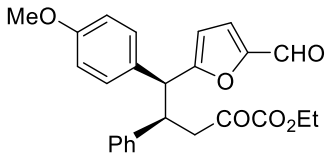
ethyl (4*R*,5*S*)-5-(5-formylfuran-2-yl)-5-(3-methoxyphenyl)-2-oxo-4-phenylpentanoate (**3e**)



3e

The reaction was carried out following the general procedure to give two diastereoisomers with 65% yield and 78:22 dr. The major isomer **3e** was isolated as a light yellow oil; The minor isomer **3e′** was isolated as a light yellow solid (m.p. = 138 – 140 ℃). Enantiomeric excess was determined by UPC[2] using Chiralpak AD-3 column, CO_2/MeOH 95:5, flow rate 2mL/min, **3e**: 94%, t_{minor} = 1.899 min, t_{major} = 2.611 min; **3e′**: 88%, t_{minor} = 2.007 min, t_{major} = 2.262 min. $[\alpha]_D^{27}$ = -4.0 (c 1.0, AcOEt, **3e**); $[\alpha]_D^{27}$ = -76.0 (c 0.5, AcOEt, **3e′**). **^{1}H NMR** (400 MHz, $(CD_3)_2SO$) **3e** δ 9.33 (s, 1H), 7.35 (d, *J* = 7.2 Hz, 2H), 7.29 (t, *J* = 7.9 Hz, 1H), 7.24–7.15 (m, 3H), 7.13 – 7.05 (m, 3H), 6.85 (dd, *J* = 8.1, 2.0 Hz, 1H), 6.51 (d, *J* = 3.6 Hz, 1H), 4.57 (d, *J* = 11.8 Hz, 1H), 4.09–3.95 (m, 3H), 3.76 (s, 3H), 3.26 (dd, *J* = 17.3, 10.4 Hz, 1H), 2.85 (dd, *J* = 17.3, 3.9 Hz, 1H), 1.14 (t, *J* = 7.1 Hz, 3H); **3e′** δ 9.51 (s, 1H), 7.48 (d, *J* = 3.5 Hz, 1H), 7.19 (d, *J* = 7.3 Hz, 2H), 7.11 (t, *J* = 7.5 Hz, 2H), 7.07–6.99 (m, 2H), 6.81 – 6.71 (m, 3H), 6.60 (dd, *J* = 8.1, 2.2 Hz, 1H), 4.62 (d, *J* = 11.3 Hz, 1H), 4.10 (q, *J* = 7.1 Hz, 2H), 4.06–3.96 (m, 1H), 3.61 (s, 3H), 3.38 (d, *J* = 10.0 Hz, 1H), 3.32 (s, 1H), 3.05 (dd, *J* = 17.4, 4.2 Hz, 1H), 1.18 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $(CD_3)_2SO$) **3e** δ 192.1, 177.4, 162.6, 159.9, 159.5, 151.0, 141.8, 141.0, 129.9, 128.0, 126.6, 120.5, 114.5, 112.5, 110.0, 61.7, 55.0, 50.4, 44.2, 43.4, 13.6; **3e′** δ 191.9, 177.7, 162.5, 160.0, 158.9, 151.8, 141.1, 140.6, 129.2, 128.3, 127.9, 126.4 120.7, 114.4, 111.9, 110.5, 61.7, 54.8, 49.9, 44.2, 44.0, 13.7. **HRMS**(ESI) m/z $(M+Na)^+$: calculated for $C_{25}H_{24}O_6Na$: 443.1465, found: 443.1470 (**3e**); 443.1465 (**3e′**). **IR** (neat) cm^{-1}: **3e** 2925, 1720, 1668, 1384, 1259, 1068, 748, 697; **3e′** 2923, 1723, 1670, 1384, 1260, 1020, 799, 696.

ethyl (4*R*,5*S*)-5-(5-formylfuran-2-yl)-5-(4-methoxyphenyl)-2-oxo-4-phenylpentanoate (**3f**)

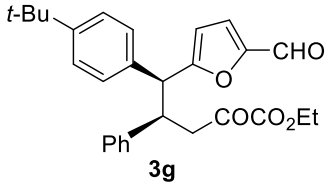


3f

The reaction was carried out following the general procedure to give two diastereoisomers with 73% yield and 81:19 dr as a light yellow oil. Enantiomeric excess of the major isomer **3f** was determined by UPC[2] using Chiralpak IG-3 column, CO_2/MeOH 95:5, flow rate 2mL/min,

97%, t_{minor} = 1.971 min, t_{major} = 2.499 min; Enantiomeric excess of the minor isomer **3f′** was determined by UPC^2 using Chiralpak AD-3 column, CO_2/MeOH 95:5, flow rate 2mL/min, 94%, t_{minor} = 2.511 min, t_{major} = 3.017 min. $[\alpha]_D^{27}$ = -4.0 (c 1.0, AcOEt, **3f**). $[\alpha]_D^{27}$ = -120.0 (c 0.5, AcOEt, **3f′**). **^{1}H NMR** (600 MHz, $(CD_3)_2SO$) **3f** δ 9.33 (s, 1H), 7.43 (t, *J* = 5.7 Hz, 2H), 7.34 (d, *J* = 7.2 Hz, 2H), 7.23–7.15 (m, 3H), 7.08 (t, *J* = 7.3 Hz, 1H), 6.94 (d, *J* = 8.7 Hz, 2H), 6.45 (d, *J* = 3.6 Hz, 1H), 4.54 (d, *J* = 11.8 Hz, 1H), 4.06 (q, *J* = 7.1 Hz, 2H), 3.96 (td, *J* = 11.1, 3.9 Hz, 1H), 3.73 (s, 3H), 3.24 (dd, *J* = 17.3, 10.3 Hz, 1H), 2.85 (dd, *J* = 17.3, 4.0 Hz, 1H), 1.14 (t, *J* = 7.1 Hz, 3H); **3f′** δ 9.50 (s, 1H), 7.47 (d, *J* = 3.5 Hz, 1H), 7.17 (d, *J* = 7.2 Hz, 2H), 7.14–7.09 (m, 4H), 7.02 (t, *J* = 7.3 Hz, 1H), 6.69 (dd, *J* = 14.9, 6.1 Hz, 3H), 4.58 (d, *J* = 11.3 Hz, 1H), 4.10 (q, *J* = 7.1 Hz, 2H), 4.02–3.95 (m, 1H), 3.61 (s, 3H), 3.37 – 3.31 (m, 1H), 3.31 (s, 1H), 3.04 (dd, *J* = 17.4, 4.3 Hz, 1H), 1.18 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (150 MHz, $(CD_3)_2SO$) **3f** δ 192.3, 177.3, 163.1, 160.0, 158.5, 151.0, 141.9, 131.4, 129.5, 128.1, 128.0, 126.5, 114.2, 109.7, 61.7, 55.0, 49.6, 44.5, 43.5, 13.7; **3f′** δ 191.9, 177.6, 163.1, 160.0, 157.7, 151.7, 141.3, 131.0, 129.5, 128.3, 127.9, 126.3, 113.5, 110.2, 61.7, 54.8, 49.1, 44.3, 44.0, 13.7. **HRMS**(ESI) m/z $(M+Na)^+$: calculated for $C_{25}H_{24}O_6Na$: 443.1465, found: 443.1469 (**3f**); 443.1465 (**3f′**). **IR** (neat) cm^{-1}: **3f** 2961, 1725, 1674, 1511, 1249, 1069, 1026, 799, 754, 701; **3f′** 2924, 1725, 1671, 1511, 1260, 1024, 800, 699.

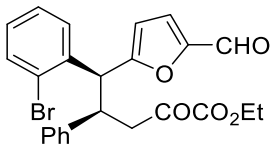
ethyl (4*R*,5*S*)-5-(4-(tert-butyl)phenyl)-5-(5-formylfuran-2-yl)-2-oxo-4-phenylpentanoate (**3g**)



3g

The reaction was carried out following the general procedure to give two diastereoisomers with 89% yield and 78:22 dr. The major isomer **3g** was isolated as a light yellow solid (m.p. = 128 – 129 ℃); The minor isomer **3g′** was isolated as a white solid (m.p. = 138 – 139 ℃). Enantiomeric excess was determined by UPC^2 using Chiralpak IG-3 column, CO_2/MeOH 95:5, flow rate 2mL/min, **3g**: 97%, t_{minor} = 2.651 min, t_{major} = 3.104 min; **3g′**: 91%, t_{major} = 2.616 min, t_{minor} = 3.051 min. $[\alpha]_D^{26}$ = -8.0 (c 1.0, AcOEt, **3g**). $[\alpha]_D^{26}$ = -100.0 (c 0.5, AcOEt, **3g′**). **^{1}H NMR** (400 MHz, $CDCl_3$) **3g** δ 9.41 (s, 1H), 7.37 (s, 4H), 7.25–7.15 (m, 4H), 7.14 – 7.08 (m, 1H), 6.90 (d, *J* = 3.6 Hz, 1H), 6.06 (d, *J* = 3.6 Hz, 1H), 4.27 (d, *J* = 11.7 Hz, 1H), 4.18–4.07 (m, 3H), 3.29 (dd, *J* = 17.5, 10.2 Hz, 1H), 2.91 (dd, *J* = 17.5, 3.9 Hz, 1H), 1.30 (s, 9H), 1.23 (t, *J* = 7.1 Hz, 3H); **3g′** δ 9.59 (s, 1H), 7.18–7.13 (m, 3H), 7.13 – 7.07 (m, 2H), 7.06 – 6.98 (m, 5H), 6.38 (d, *J* = 3.6 Hz, 1H), 4.31 (d, *J* = 10.3 Hz, 1H), 4.26–4.15 (m, 2H), 4.14 – 4.04 (m, 1H), 3.40 (dd, *J* = 17.6, 9.1 Hz, 1H), 3.14 (dd, *J* = 17.6, 4.9 Hz, 1H), 1.27 (t, *J* = 7.1 Hz, 3H), 1.21 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) **3g** δ 192.3, 177.0, 162.5, 160.4, 151.7, 150.7, 141.0, 135.4, 128.5, 128.1, 127.8, 127.0, 126.0, 109.8, 62.4, 51.7, 44.9, 43.8, 34.5, 31.3, 13.8; **3g′** δ 192.2, 177.3, 162.7, 160.5, 152.2, 149.9, 140.5 135.1, 128.2, 128.1, 128.1, 126.8, 125.2, 110.5, 62.5, 51.2, 45.2, 43.7, 34.3, 31.2, 13.9. **HRMS**(ESI) m/z $(M+Na)^+$: calculated for $C_{28}H_{30}O_5Na$: 469.1985, found: 469.1989 (**3g**); 469.1987 (**3g′**). **IR** (neat) cm^{-1}: **3g** 2963, 1726, 1675, 1510, 1260, 1069, 1022, 800, 760, 700; **3g′** 2962, 1727, 1678, 1509, 1384, 1261, 1069, 1022, 800, 759, 700.

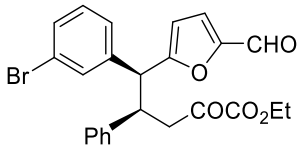
ethyl (4*R*,5*S*)-5-(2-bromophenyl)-5-(5-formylfuran-2-yl)-2-oxo-4-phenylpentanoate (**3h**)



3h

The reaction was carried out following the general procedure to give two diastereoisomers with 67% yield and 80:20 dr as a colorless oil. Enantiomeric excess of the major isomer **3h** was determined by UPC^2 using Chiralpak IG-3 column, CO_2/MeOH 95:5, flow rate 2mL/min, 96%, t_{minor} = 3.141 min, t_{major} = 3.419 min; Enantiomeric excess of the minor isomer **3h′** was determined by UPC^2 using Chiralpak OD-3 column, CO_2/MeOH 95:5, flow rate 2mL/min, 96%, t_{minor} = 3.134 min, t_{major} = 3.440 min. $[\alpha]_D^{24}$ = + 43.0 (c 1.0, AcOEt, **3h**); $[\alpha]_D^{24}$ = -28.0 (c 1.0, AcOEt, **3h′**). **^{1}H NMR** (600 MHz, $(CD_3)_2SO$) **3h** δ 9.35 (s, 1H), 7.69 (ddd, *J* = 12.0, 7.9, 1.3 Hz, 2H), 7.46 (td, *J* = 7.7, 1.2 Hz, 1H), 7.30 (d, *J* = 7.2 Hz, 2H), 7.27–7.20 (m, 4H), 7.14–7.09 (m, 1H), 6.56 (d, *J* = 3.6 Hz, 1H), 4.97 (d, *J* = 11.7 Hz, 1H), 4.12 (td, *J* = 11.3, 3.6 Hz, 1H), 4.09–4.04 (m, 2H), 3.31 (s, 1H), 2.83 (dd, *J* = 17.4, 3.8 Hz, 1H), 1.15 (t, *J* = 7.1 Hz, 3H); **^{1}H NMR** (400 MHz, $(CD_3)_2SO$) **3h′** δ 9.51 (s, 1H), 7.73 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.48 (d, *J* = 3.5 Hz, 1H), 7.36 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.30–7.22 (m, 3H), 7.11 (t, *J* = 7.5 Hz, 2H), 7.06–6.95 (m, 2H), 6.78 (d, *J* = 3.6 Hz, 1H), 5.08 (d, *J* = 11.4 Hz, 1H), 4.21–4.07 (m, 3H), 3.42 (dd, *J* = 17.7, 9.3 Hz, 1H), 3.15 (dd, *J* = 17.7, 4.4 Hz, 1H), 1.18 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (150 MHz, $(CD_3)_2SO$) **3h** δ 191.7, 177.6, 160.8, 159.8, 151.2, 141.2, 137.9, 133.1, 129.6, 128.7, 128.3, 127.9, 126.9, 124.7, 110.8, 61.7, 49.3, 44.1, 42.4, 13.7; **^{13}C NMR** (100 MHz, $(CD_3)_2SO$) **3h′** δ 191.6, 177.8, 160.6, 159.9, 152.0, 140.7, 137.8, 132.5, 130.2, 128.8, 128.2, 128.0, 127.9 126.6, 124.1, 111.2, 61.8, 48.3, 43.7, 43.5, 13.7. **HRMS**(ESI) m/z $(M+Na)^+$: calculated for $C_{24}H_{21}BrO_5Na$: 491.0465, found: 491.0469 (**3h**); 491.0466 (**3h′**). **IR** (neat) cm^{-1}: **3h** 2925, 1726, 1677, 1261, 1084, 1022, 759, 701; **3h′** 2961, 2923, 1724, 1384, 1003, 798.

ethyl (4*R*,5*S*)-5-(3-bromophenyl)-5-(5-formylfuran-2-yl)-2-oxo-4-phenylpentanoate (**3i**)

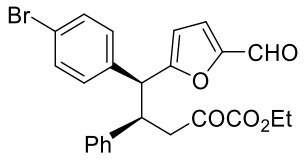


3i

The reaction was carried out following the general procedure to give two diastereoisomers with 77% yield and 73:27 dr. The major isomer **3i** was isolated as a light yellow oil; The minor isomer **3i′** was isolated as a light yellow solid (m.p. = 118 – 119 ℃). Enantiomeric excess of **3i** was determined by HPLC using Chiralpak IC-3 column, Hexane/*i*PrOH 80:20, flow rate 1mL/min, 89%, t_{minor} = 15.272 min, t_{major} = 17.082 min; Enantiomeric excess of **3i′** was determined by HPLC using Chiralpak ID-3 column, Hexane/*i*PrOH 80:20, flow rate 1mL/min, 89%, t_{minor} = 9.793 min, t_{major} = 11.908 min. $[\alpha]_D^{25}$ = + 16.0 (c 1.0, AcOEt, **3i**); $[\alpha]_D^{25}$ = -42.0 (c 0.5, AcOEt, **3i′**). ^{1}H NMR (400 MHz, $(CD_3)_2SO$) **3i** δ 9.33 (s, 1H), 7.78 (s, 1H), 7.56 (d, *J* = 7.7 Hz, 1H), 7.51–7.45 (m, 1H), 7.35 (t, *J* = 7.8 Hz, 3H), 7.24–7.15 (m, 3H), 7.08 (t, *J* = 7.3 Hz, 1H), 6.56 (d, *J* = 3.6 Hz, 1H), 4.67 (d, *J* = 11.9 Hz, 1H), 4.11–3.98 (m, 3H), 3.29 (dd, *J* = 17.3, 10.3 Hz, 1H), 2.83 (dd, *J* = 17.3, 4.0 Hz, 1H), 1.15 (t, *J* = 7.1 Hz, 3H); **3i′** δ 9.52 (s, 1H), 7.50 (d, *J* = 3.5 Hz, 1H), 7.38 (s, 1H), 7.28 – 7.18 (m, 4H), 7.17 – 7.08 (m, 3H), 7.07 – 7.00 (m, 1H), 6.80 (d, *J* = 3.6 Hz, 1H), 4.71 (d, *J* = 11.5 Hz, 1H), 4.10 (q, *J* = 7.1 Hz, 2H), 4.02 (td, *J* =

10.1, 4.1 Hz, 1H), 3.42–3.36 (m, 1H), 3.07 (dd, *J* = 17.5, 4.1 Hz, 1H), 1.18 (d, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $(CD_3)_2SO$) **3i** δ 191.9, 177.5, 162.0, 159.8, 151.1, 142.3, 141.6, 131.3, 131.1, 130.4, 128.1, 127.5, 126.6, 122.1, 110.3, 61.7, 49.8, 44.1, 43.3, 13.7; **3i′** δ 191.7, 177.8, 161.8, 159.9, 151.9, 141.9, 140.8, 131.2, 130.3, 129.6, 128.3, 128.0, 127.5, 126.5, 121.3, 110.7, 61.8, 49.3, 44.0, 43.9, 13.7. **HRMS**(ESI) m/z $(M+Na)^+$: calculated for $C_{24}H_{21}BrO_5Na$: 491.0465, found: 491.0470 (**3i**); 491.0467 (**3i′**). **IR** (neat) cm^{-1}: **3i** 2962, 2926, 1726, 1675, 1260, 1070, 1022, 798, 701; **3i′** 2962, 2924, 1724, 1675, 1384, 1260, 1019, 798.

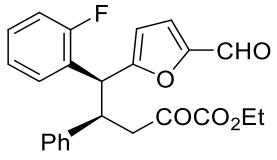
ethyl (4*R*,5*S*)-5-(4-bromophenyl)-5-(5-formylfuran-2-yl)-2-oxo-4-phenylpentanoate (**3j**)



3j

The reaction was carried out following the general procedure to give two diastereoisomers with 68% yield and 82:18 dr. The major isomer **3j** was isolated as a light yellow oil; The minor isomer **3j′** was isolated as a light yellow solid (m.p. = 138 – 139 ℃). Enantiomeric excess was determined by UPC[2] using Chiralpak AD-3 column, CO_2/MeOH 95:5, flow rate 2mL/min, **3j**: 96%, t_{minor} = 3.267 min, t_{major} = 3.713 min; **3j′**: 89%, t_{minor} = 3.462 min, t_{major} = 4.088 min. $[\alpha]_D^{24}$ = -6.0 (c 1.0, AcOEt, **3j**); $[\alpha]_D^{24}$ = -92.0 (c 0.5, AcOEt, **3j′**). **^{1}H NMR** (400 MHz, $(CD_3)_2SO$) **3j** δ 9.33 (s, 1H), 7.58 (d, *J* = 8.3 Hz, 2H), 7.49 (d, *J* = 8.4 Hz, 2H), 7.35 (d, *J* = 7.5 Hz, 2H), 7.24–7.16 (m, 3H), 7.08 (t, *J* = 7.3 Hz, 1H), 6.51 (d, *J* = 3.6 Hz, 1H), 4.65 (d, *J* = 11.8 Hz, 1H), 4.06 (q, *J* = 7.0 Hz, 2H), 4.03–3.93 (m, 1H), 3.28 (dd, *J* = 17.4, 10.3 Hz, 1H), 2.83 (dd, *J* = 17.4, 3.9 Hz, 1H), 1.15 (t, *J* = 7.1 Hz, 3H); **3j′** δ 9.51 (s, 1H), 7.49 (d, *J* = 3.5 Hz, 1H), 7.31 (d, *J* = 8.4 Hz, 2H), 7.18 (dd, *J* = 10.6, 8.0 Hz, 4H), 7.11 (t, *J* = 7.5 Hz, 2H), 7.02 (t, *J* = 7.3 Hz, 1H), 6.76 (d, *J* = 3.6 Hz, 1H), 4.69 (d, *J* = 11.5 Hz, 1H), 4.10 (q, *J* = 7.1 Hz, 2H), 4.05–3.96 (m, 1H), 3.42–3.35 (m, 1H), 3.07 (dd, *J* = 17.5, 4.2 Hz, 1H), 1.17 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $(CD_3)_2SO$) **3j** δ 192.0, 177.4, 162.1, 159.9, 151.1, 141.7, 139.0, 131.8, 130.7, 128.1, 126.6, 120.7, 110.2, 61.7, 49.6, 44.1, 43.3, 13.7; **^{13}C NMR** (150 MHz, $(CD_3)_2SO$) **3j′** δ 191.7, 177.7, 162.0, 159.9, 151.9, 140.9, 138.7, 131.0, 130.7, 128.3, 128.0, 126.5, 119.8, 110.6, 61.7, 49.2, 44.1, 43.9, 13.7. **HRMS**(ESI) m/z $(M+Na)^+$: calculated for $C_{24}H_{21}BrO_5Na$: 491.0465, found: 491.0469 (**3j**); 491.0465 (**3j′**). **IR** (neat) cm^{-1}: **3j** 2961, 2926, 1726, 1675, 1489, 1277, 1071, 799, 759, 701; **3j′** 2922, 2851, 1724, 1674, 1384, 1069, 1004, 799.

ethyl (4*R*,5*S*)-5-(2-fluorophenyl)-5-(5-formylfuran-2-yl)-2-oxo-4-phenylpentanoate (**3k**)

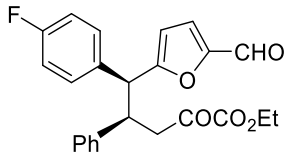


3k

The reaction was carried out following the general procedure to give two diastereoisomers with 63% yield and 79:21 dr as a light yellow oil. Enantiomeric excess of the major isomer **3k** was determined by HPLC using Chiralpak IC-3 column, Hexane/*i*PrOH 80:20, flow rate 1mL/min, 96%, t_{minor} = 15.145 min, t_{major} = 17.011 min; Enantiomeric excess of the minor isomer **3k′** was determined by UPC[2] using Chiralpak IG-3 column, CO_2/MeOH 95:5, flow rate

2mL/min, 90%, t_{minor} = 2.366 min, t_{major} = 2.560 min. $[\alpha]_D^{24}$ = -20.0 (c 1.0, AcOEt, **3k**); $[\alpha]_D^{24}$ = -50.0 (c 0.5, AcOEt, **3k′**). **^{1}H NMR** (400 MHz, $(CD_3)_2SO$) **3k** δ 9.34 (s, 1H), 7.64 (td, *J* = 7.9, 1.8 Hz, 1H), 7.41–7.31 (m, 3H), 7.28–7.17 (m, 5H), 7.13–7.07 (m, 1H), 6.49 (d, *J* = 3.6 Hz, 1H), 4.80 (d, *J* = 11.8 Hz, 1H), 4.15–4.02 (m, 3H), 3.34–3.25 (m, 1H), 2.89 (dd, *J* = 17.3, 3.9 Hz, 1H), 1.15 (t, *J* = 7.1 Hz, 3H); **3k′** δ 9.51 (s, 1H), 7.54 – 7.46 (m, 2H), 7.21 (d, *J* = 7.3 Hz, 2H), 7.14–7.06 (m, 3H), 7.06–6.99 (m, 2H), 6.93 – 6.81 (m, 1H), 6.79 (d, *J* = 3.6 Hz, 1H), 4.92 (d, *J* = 11.6 Hz, 1H), 4.11 (q, *J* = 7.1 Hz, 3H), 3.46–3.38 (m, 1H), 3.13 (dd, *J* = 17.6, 4.2 Hz, 1H), 1.18 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $(CD_3)_2SO$) **3k** δ 191.8, 177.5, 161.1, 159.8, 158.9, 151.1, 141.3, 130.1 (d, *J* = 3.4 Hz), 129.7 (d, *J* = 8.4 Hz), 128.1 (d, *J* = 10.6 Hz), 126.8, 125.9 (d, *J* = 14.0 Hz), 125.1 (d, *J* = 3.3 Hz), 116.0, 115.8, 110.6, 61.7, 43.5, 43.1 (d, *J* = 12.1 Hz), 13.7; **3k′** δ 191.8, 177.8, 161.2, 160.7, 160.0, 158.3, 151.9, 140.9, 130.2 (d, *J* = 3.8 Hz), 128.9 (d, *J* = 8.2 Hz), 128.0 (d, *J* = 14.0 Hz), 126.6, 126.0 (d, *J* = 14.3 Hz), 124.4, 115.3, 115.1, 110.8, 61.8, 44.0, 43.3, 42.7, 13.7. **^{19}F NMR** (376 MHz, $(CD_3)_2SO$) **3k** δ -116.78. **3k′** δ -117.16. **HRMS**(ESI) m/z $(M+Na)^+$: calculated for $C_{24}H_{21}FO_5Na$: 431.1265, found: 431.1268 (**3k**); 431.1266 (**3k′**). **IR** (neat) cm^{-1}: **3k** 2962, 1725, 1675, 1260, 1069, 1021, 799, 756; **3k′** 2924, 2852, 1726, 1677, 1384, 1261, 1070, 1023, 802, 758, 700.

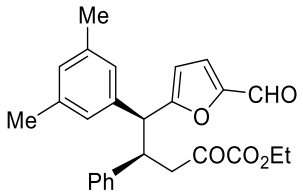
ethyl (4*R*,5*S*)-5-(4-fluorophenyl)-5-(5-formylfuran-2-yl)-2-oxo-4-phenylpentanoate (**3l**)



3l

The reaction was carried out following the general procedure to give two diastereoisomers with 73% yield and 82:18 dr as a light yellow oil. Enantiomeric excess was determined by UPC^2 using Chiralpak IG-3 column, CO_2/MeOH 95:5, flow rate 2mL/min, the major isomer **3l**: 96%, t_{minor} = 2.462 min, t_{major} = 2.964 min; the minor isomer **3l′**: 89%, t_{minor} = 2.570 min, t_{major} = 2.783 min. $[\alpha]_D^{24}$ = -8.0 (c 1.0, AcOEt, **3l**); $[\alpha]_D^{24}$ = -58.0 (c 0.5, AcOEt, **3l′**). **^{1}H NMR** (400 MHz, $(CD_3)_2SO$) δ **3l** 9.33 (s, 1H), 7.60–7.55 (m, 2H), 7.37–7.32 (m, 2H), 7.25–7.16 (m, 6H), 7.08 (t, *J* = 7.3 Hz, 1H), 6.49 (d, *J* = 3.6 Hz, 1H), 4.65 (d, *J* = 11.8 Hz, 1H), 4.06 (q, *J* = 7.0 Hz, 2H), 4.02 – 3.94 (m, 1H), 3.26 (dd, *J* = 17.4, 10.2 Hz, 1H), 2.83 (dd, *J* = 17.3, 4.1 Hz, 1H), 1.14 (t, *J* = 7.1 Hz, 3H); **3l′** δ 9.52 (s, 1H), 7.49 (d, *J* = 3.5 Hz, 1H), 7.26–7.20 (m, 2H), 7.17 (d, *J* = 7.2 Hz, 2H), 7.11 (t, *J* = 7.5 Hz, 2H), 7.02 (t, *J* = 7.2 Hz, 1H), 6.93 (t, *J* = 8.9 Hz, 2H), 6.76 (d, *J* = 3.6 Hz, 1H), 4.68 (d, *J* = 11.4 Hz, 1H), 4.10 (q, *J* = 7.1 Hz, 2H), 4.04–3.93 (m, 1H), 3.43–3.35 (m, 1H), 3.06 (dd, *J* = 17.5, 4.2 Hz, 1H), 1.18 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $(CD_3)_2SO$) **3l** δ 192.1, 177.41, 162.5, 160.2, 159.9, 151.1, 141.7, 135.7, 130.5 (d, *J* = 8.2 Hz), 128.1 (d, *J* = 3.5 Hz), 126.6, 115.5, 115.6, 110.1, 61.7, 49.5, 44.4, 43.4, 13.7; **^{13}C NMR** (150 MHz, $CDCl_3$) **3l′** δ 191.8, 177.7, 162.4, 161.5, 159.9, 151.9, 141.0, 135.4 (d, *J* = 2.9 Hz), 130.3 (d, *J* = 8.0 Hz), 128.3, 128.0, 126.4, 115.0, 114.8, 110.5, 61.7, 49.1, 44.4, 43.9, 13.7. **^{19}F NMR** (376 MHz, $(CD_3)_2SO$) **3l** δ -115.08. **3l′** δ -115.96. **HRMS**(ESI) m/z $(M+Na)^+$: calculated for $C_{24}H_{21}FO_5Na$: 431.1265, found: 431.1267 (**3l**); 431.1265 (**3l′**). **IR** (neat) cm^{-1}**: 3l** 3117, 2962, 1726, 1508, 1226, 1069, 800, 756, 701; **3l′** 2962, 2925, 1726, 1676, 1508, 1260, 1069, 1019, 799.

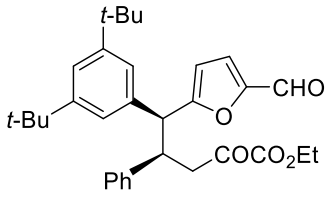
ethyl (4*R*,5*S*)-5-(3,5-dimethylphenyl)-5-(5-formylfuran-2-yl)-2-oxo-4-phenylpentanoate (**3m**)



3m

The reaction was carried out following the general procedure to give two diastereoisomers with 79% yield and 64:36 dr as a light yellow oil. Enantiomeric excess was determined by UPC[2] using Chiralpak IG-3 column, CO_2/MeOH 95:5, flow rate 2mL/min, the major isomer **3m**: 90%, t_{minor} = 1.636 min, t_{major} = 1.963 min; the minor isomer **3m′**: 88%, t_{minor} = 2.174 min, t_{major} = 2.487 min. $[\alpha]_D^{27}$ = + 1.0 (c 1.0, AcOEt, **3m**); $[\alpha]_D^{27}$ = -90.0 (c 0.5, AcOEt, **3m′**). **^{1}H NMR** (400 MHz, $(CD_3)_2SO$) **3m** δ 9.32 (s, 1H), 7.35 (d, *J* = 7.2 Hz, 2H), 7.23–7.15 (m, 3H), 7.12 (s, 2H), 7.07 (t, *J* = 7.3 Hz, 1H), 6.90 (s, 1H), 6.50 (d, *J* = 3.6 Hz, 1H), 4.49 (d, *J* = 11.9 Hz, 1H), 4.05 (q, *J* = 7.1 Hz, 2H), 4.02–3.94 (m, 1H), 3.24 (dd, *J* = 17.2, 10.4 Hz, 1H), 2.83 (dd, *J* = 17.2, 4.0 Hz, 1H), 2.26 (s, 6H), 1.14 (t, *J* = 7.1 Hz, 3H); **3m′** δ 9.50 (s, 1H), 7.47 (d, *J* = 3.5 Hz, 1H), 7.19 (d, *J* = 7.2 Hz, 2H), 7.11 (t, *J* = 7.5 Hz, 2H), 7.02 (t, *J* = 7.3 Hz, 1H), 6.81 (s, 2H), 6.71 (d, *J* = 3.6 Hz, 1H), 6.65 (s, 1H), 4.54 (d, *J* = 11.3 Hz, 1H), 4.10 (q, *J* = 7.1 Hz, 2H), 4.07–3.98 (m, 1H), 3.37 (d, *J* = 9.8 Hz, 1H), 3.31 (s, 1H), 3.04 (dd, *J* = 17.4, 4.2 Hz, 1H), 2.09 (s, 6H), 1.18 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $(CD_3)_2SO$) **3m** δ 192.2, 177.3, 163.0, 159.9, 150.9, 141.9, 139.4, 137.9, 128.8, 128.1, 126.5, 126.1, 109.9, 61.7, 50.4, 44.2, 43.6, 21.0, 13.7; **3m′** δ 191.9, 177.6, 162.9, 160.0, 151.7, 141.2, 138.9, 136.9, 128.3, 128.1, 127.9, 126.3, 126.2, 110.3, 61.7, 49.8, 43.9, 20.8, 13.7. **HRMS**(ESI) m/z $(M+Na)^+$: calculated for $C_{26}H_{26}O_5Na$: 441.1672, found: 441.1677 (**3m**); 441.1674 (**3m′**). **IR** (neat) cm^{-1}: **3m** 2963, 1726, 1675, 1511, 1260, 1023, 799; **3m′** 2921, 1726, 1675, 1509, 1384, 1260, 1022, 801, 698.

ethyl(4*R*,5*S*)-5-(3,5-di-tert-butylphenyl)-5-(5-formylfuran-2-yl)-2-oxo-4-phenylpentanoate (**3n**)

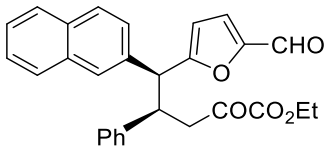


3n

The reaction was carried out following the general procedure to give two diastereoisomers with 92% yield and 43:57 dr. The minor isomer **3n** as white solid (m.p. = 162 – 163 ℃); The major isomer **3n′** as a white solid (m.p. = 159 – 160 ℃). Enantiomeric excess of **3n** was determined by UPC[2] using Trefoil™ CEL1 column, CO_2/MeOH 95:5, flow rate 2mL/min, 81%, t_{minor} = 1.110 min, t_{major} = 1.225 min; Enantiomeric excess of **3n′** was determined by HPLC using Chiralpak ID-3 column, Hexane/*i*PrOH 90:10, flow rate 1mL/min, 90%, t_{minor} = 6.621 min, t_{major} = 7.372 min. $[\alpha]_D^{28}$ = + 1.0 (c 1.0, AcOEt, **3n**); $[\alpha]_D^{28}$ = -88.0 (c 1.0, AcOEt, **3n′**). **^{1}H NMR** (400 MHz, $CDCl_3$) **3n** δ 9.44 (s, 1H), 7.33 (t, *J* = 1.7 Hz, 1H), 7.24 (d, *J* = 1.7 Hz, 2H), 7.19 (d, *J* = 4.3 Hz, 4H), 7.16 – 7.08 (m, 1H), 6.94 (d, *J* = 3.6 Hz, 1H), 6.11 (d, *J* = 3.6 Hz, 1H), 4.29 (d, *J* = 11.1 Hz, 1H), 4.18–4.04 (m, 3H), 3.22 (dd, *J* = 17.5, 9.5 Hz, 1H), 2.99 (dd, *J* = 17.5, 4.4 Hz, 1H), 1.33 (s, 18H), 1.23 (t, *J* = 7.1 Hz, 3H); **3n′** δ 9.60 (s, 1H), 7.18 (d, *J* = 3.6 Hz, 1H), 7.11 (t, *J* = 1.7 Hz, 1H), 7.10 – 7.02 (m, 3H), 6.95–6.90 (m, 2H), 6.86 (d, *J* = 1.7 Hz, 2H), 6.43

(d, *J* = 3.6 Hz, 1H), 4.28 (d, *J* = 10.3 Hz, 1H), 4.21 (q, *J* = 7.2 Hz, 2H), 4.04 (td, *J* = 9.5, 5.1 Hz, 1H), 3.42 (dd, *J* = 17.6, 9.0 Hz, 1H), 3.16 (dd, *J* = 17.6, 5.1 Hz, 1H), 1.28 (t, *J* = 7.1 Hz, 3H), 1.18 (s, 18H). **^{13}C NMR** (100 MHz, $CDCl_3$) **3n** δ 192.3, 162.7, 160.4, 151.7, 151.4, 141.2, 137.3, 128.4, 127.9, 127.0, 122.9, 121.6, 110.0, 62.3, 52.6, 45.1, 43.7, 34.9, 31.4, 13.8; **3n′** δ 192.3, 177.3, 162.9, 160.6, 152.1, 150.5, 140.3, 136.9, 128.3, 128.1, 126.7, 123.1, 120.6, 110.4, 62.5, 52.2, 45.6, 43.7, 34.6, 31.3, 13.9. **HRMS**(ESI) m/z $(M+Na)^+$: calculated for $C_{32}H_{38}O_5Na$: 525.2611, found: 525.2615 (**3n**); 525.2611 (**3n′**). **IR** (neat) cm^{-1}: **3n** 2961, 2866, 1723, 1675, 1384, 1260, 1070, 1022, 800, 759, 701; **3n′** 2962, 2866, 1725, 1677, 1384, 1260, 1068, 1021, 802, 698.

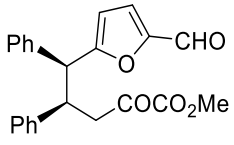
ethyl (4*R*,5*S*)-5-(5-formylfuran-2-yl)-5-(naphthalen-2-yl)-2-oxo-4-phenylpentanoate (**3o**)



3o

The reaction was carried out following the general procedure to give two diastereoisomers with 71% yield and 80:20 dr. The major isomer **3o** was isolated as a white solid (m.p. = 72 – 74 ℃); The minor isomer **3o′** was isolated as a white solid (m.p. = 152 – 154 ℃). Enantiomeric excess of **3o** was determined by HPLC using Chiralpak ID-3 column, Hexane/*i*PrOH 80:20, flow rate 1 mL/min, 96%, t_{minor} = 14.678 min, t_{major} = 16.231 min; Enantiomeric excess of **3o′** was determined by UPC^2 using Chiralpak IG-3 column, CO_2/MeOH 95:5, flow rate 2mL/min, **3o′**: 81%, t_{minor} = 2.669 min, t_{major} = 3.098 min. $[\alpha]_D^{27}$ = + 34.0 (c 1.0, AcOEt, **3o**); $[\alpha]_D^{27}$ = - 58.0 (c 1.0, AcOEt, **3o′**). **^{1}H NMR** (400 MHz, $CDCl_3$) **3o** δ 9.42 (s, 1H), 7.90–7.80 (m, 4H), 7.60 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.55–7.45 (m, 2H), 7.30–7.27 (m, 2H), 7.25 – 7.19 (m, 2H), 7.19–7.12 (m, 1H), 6.93 (d, *J* = 3.6 Hz, 1H), 6.14 (d, *J* = 3.6 Hz, 1H), 4.49 (d, *J* = 11.7 Hz, 1H), 4.26 (ddd, *J* = 11.7, 9.6, 4.4 Hz, 1H), 4.09–3.92 (m, 2H), 3.27 (dd, *J* = 17.6, 9.6 Hz, 1H), 3.00 (dd, *J* = 17.6, 4.4 Hz, 1H), 1.14 (t, *J* = 7.1 Hz, 3H); **3o′** δ 9.59 (s, 1H), 7.74–7.62 (m, 3H), 7.56 (s, 1H), 7.45–7.36 (m, 2H), 7.33 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.17 (d, *J* = 3.6 Hz, 1H), 7.08 (d, *J* = 4.3 Hz, 4H), 7.04 – 6.98 (m, 1H), 6.45 (d, *J* = 3.6 Hz, 1H), 4.54 (d, *J* = 10.8 Hz, 1H), 4.33–4.24 (m, 1H), 4.21 (qd, *J* = 7.5, 5.5 Hz, 2H), 3.43 (dd, *J* = 17.6, 8.9 Hz, 1H), 3.22 (dd, *J* = 17.6, 4.9 Hz, 1H), 1.28 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) **3o** δ 192.0, 177.1, 162.1, 160.2, 151.8, 141.1, 135.9, 133.4, 132.8, 129.2, 128.6, 127.9, 127.9, 127.7, 127.1, 126.5, 126.3, 125.8, 110.1, 62.4, 52.2, 44.8, 43.9, 13.7; **3o′** δ 192.0, 177.2, 162.5, 160.4, 152.2, 140.3, 135.7, 133.1, 132.3, 128.4, 128.2, 128.1, 127.7, 127.7, 127.5, 126.9, 126.1, 126.1, 125.9, 110.5, 62.6, 51.6, 44.8, 44.2, 13.9. **HRMS**(ESI) m/z $(M+Na)^+$: calculated for $C_{28}H_{24}O_5Na$: 463.1516, found: 463.1521 (**3o**); 463.1517 (**3o′**). **IR** (neat) cm^{-1}: **3o** 3059, 2925, 1724, 1671, 1385, 1261, 1068, 1018, 799, 749, 701; **3o′** 2962, 2924, 1725, 1674, 1507, 1384, 1261, 1069, 1021, 800.

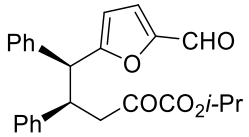
methyl (4*R*,5*S*)-5-(5-formylfuran-2-yl)-2-oxo-4,5-diphenylpentanoate (**4a**)



4a

The reaction was carried out following the general procedure to give two diastereoisomers with 74% yield and 83:17 dr. The major isomer **4a** was isolated as a white solid (m.p. = 126 – 127 ℃); The minor isomer **4a′** was isolated as a colorless oil. Enantiomeric excess of **4a** was determined by UPC^2 using Chiralpak IG-3 column, CO_2/MeOH 95:5, flow rate 2mL/min, 96%, t_{minor} = 3.858 min, t_{major} = 4.265 min; Enantiomeric excess of **4a′** was determined by UPC^2 using Chiralpak OD-3 column, CO_2/MeOH 95:5, flow rate 2mL/min, 89%, t_{minor} = 3.343 min, t_{major} = 3.700 min. $[\alpha]_D^{26}$ = -8.0 (c 1.0, AcOEt, **4a**); $[\alpha]_D^{26}$ = -51.61 (c 0.31, AcOEt, **4a′**). **^{1}H NMR** (400 MHz, $(CD_3)_2SO$) **4a** δ 9.33 (s, 1H), 7.57–7.50 (m, 2H), 7.41–7.34 (m, 4H), 7.27 (t, *J* = 7.3 Hz, 1H), 7.23–7.16 (m, 3H), 7.08 (t, *J* = 7.3 Hz, 1H), 6.50 (d, *J* = 3.6 Hz, 1H), 4.60 (d, *J* = 11.8 Hz, 1H), 4.08–3.95 (m, 1H), 3.60 (s, 3H), 3.31 (dd, *J* = 17.7, 10.6 Hz, 1H), 2.82 (dd, *J* = 17.6, 3.7 Hz, 1H); **4a′** δ 9.51 (s, 1H), 7.48 (d, *J* = 3.5 Hz, 1H), 7.24–7.15 (m, 4H), 7.10 (q, *J* = 7.7 Hz, 4H), 7.05–6.96 (m, 2H), 6.75 (d, *J* = 3.6 Hz, 1H), 4.64 (d, *J* = 11.4 Hz, 1H), 4.02 (td, *J* = 9.8, 4.1 Hz, 1H), 3.66 (s, 3H), 3.39 (dd, *J* = 17.8, 9.9 Hz, 1H), 3.08 (dd, *J* = 17.7, 4.1 Hz, 1H). **^{13}C NMR** (100 MHz, $(CD_3)_2SO$) **4a** δ 191.7, 177.4, 162.7, 160.3, 151.0, 141.8, 139.5, 128.9, 128.5, 128.1, 128.03, 127.4, 126.6, 110.0, 52.5, 50.4, 44.1, 43.5; **4a′** δ 191.4, 177.7, 162.7, 160.4, 151.8, 141.2, 139.2, 128.4, 128.3, 128.1, 127.9, 126.6, 126.3, 110.4, 52.5, 50.0, 44.1, 44.1. **HRMS**(ESI) m/z $(M+Na)^+$: calculated for $C_{23}H_{20}O_5Na$: 399.1203, found: 399.1209 (**4a**); 399.1203 (**4a′**). **IR** (neat) cm^{-1}: **4a** 2960, 1727, 1671, 1384, 1260, 1021, 798, 760, 700; **4a′** 2924, 1727, 1672, 1384, 1260, 1088, 1021, 799.

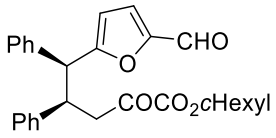
isopropyl (4*R*,5*S*)-5-(5-formylfuran-2-yl)-2-oxo-4,5-diphenylpentanoate (**4b**)



4b

The reaction was carried out following the general procedure to give two diastereoisomers with 47% yield and 67:33 dr. The major isomer **4b** was isolated as a white solid (m.p. = 139 – 140 ℃); The minor isomer **4b′** was isolated as a white solid (m.p. = 124 – 125 ℃). Enantiomeric excess was determined by UPC^2 using Chiralpak IG-3 column, CO_2/MeOH 95:5, flow rate 2mL/min, **4b**: 95%, t_{minor} = 2.849 min, t_{major} = 3.218 min; **4b′**: 88%, t_{minor} = 2.596 min, t_{major} = 3.006 min. $[\alpha]_D^{26}$ = -5.0 (c 1.0, AcOEt, **4b**); $[\alpha]_D^{26}$ = -90.0 (c 0.5, AcOEt, **4b′**). ^{1}H NMR (600 MHz, $(CD_3)_2SO$) **4b** δ 9.34 (d, *J* = 6.5 Hz, 1H), 7.54 (d, *J* = 7.3 Hz, 2H), 7.40–7.34 (m, 4H), 7.28 (t, *J* = 7.4 Hz, 1H), 7.22–7.17 (m, 3H), 7.09 (t, *J* = 7.3 Hz, 1H), 6.49 (d, *J* = 3.6 Hz, 1H), 4.87 – 4.77 (m, 1H), 4.61 (d, *J* = 11.8 Hz, 1H), 4.01 (td, *J* = 11.1, 3.9 Hz, 1H), 3.26 (dd, *J* = 17.1, 10.5 Hz, 1H), 2.80 (dd, *J* = 17.1, 3.9 Hz, 1H), 1.13 (dd, *J* = 6.2, 1.3 Hz, 6H); **4b′** δ 9.52 (s, 1H), 7.48 (d, *J* = 3.5 Hz, 1H), 7.21 (d, *J* = 7.3 Hz, 2H), 7.18 (d, *J* = 7.3 Hz, 2H), 7.13 – 7.07 (m, 4H), 7.05 – 6.98 (m, 2H), 6.75 (d, *J* = 3.5 Hz, 1H), 4.92 – 4.85 (m, 1H), 4.65 (d, *J* = 11.4 Hz, 1H), 4.03 (td, *J* = 10.6, 4.2 Hz, 1H), 3.40–3.33 (m, 1H), 3.06 (dd, *J* = 17.2, 4.2 Hz, 1H), 1.18 (dd, *J* = 6.2, 3.5 Hz, 6H). **^{13}C NMR** (150 MHz, $(CD_3)_2SO$) **4b** δ 192.6, 177.3, 162.7, 159.5, 151.1, 141.7, 139.5, 128.9, 128.5, 128.1, 128.1, 127.4, 126.6, 110.0, 69.8, 50.5, 44.5, 43.4, 21.2, 21.2; **4b′** δ 192.2, 177.6, 162.6, 159.5, 151.8, 141.0, 139.1, 128.4, 128.3, 128.2, 127.9, 126.6, 126.4, 110.4, 69.9, 50.0, 44.4, 43.9, 21.2. **HRMS**(ESI) m/z $(M+Na)^+$: calculated for $C_{25}H_{24}O_5Na$: 427.1516, found: 427.1519 (**4b**); 427.1516 (**4b′**). **IR** (neat) cm^{-1}: **4b** 2925, 1716, 1670, 1280, 1068, 1023, 759, 700; **4b′** 2963, 1720, 1673, 1384, 1261, 1022, 800, 762, 698.

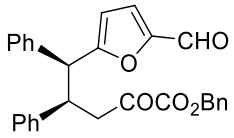
cyclohexyl (4*R*,5*S*)-5-(5-formylfuran-2-yl)-2-oxo-4,5-diphenylpentanoate (**4c**)



4c

The reaction was carried out following the general procedure to give two diastereoisomers with 50% yield and 71:29 dr. The major isomer **4c** was isolated as a white solid (m.p. = 143 – 144 ℃); The minor isomer **4c′** was isolated as a white solid (m.p. = 108 – 110 ℃). Enantiomeric excess was determined by UPC^2 using Chiralpak IG-3 column, CO_2/MeOH 90:10, flow rate 2mL/min, **4c**: 94%, t_{minor} = 3.112 min, t_{major} = 3.481 min,; **4c′**: 87%, t_{minor} = 2.482 min, t_{major} = 2.878 min. $[\alpha]_D^{23}$ = -9.0 (c 1.0, AcOEt, **4c**); $[\alpha]_D^{24}$ = -45.0 (c 1.0, AcOEt, **4c′**). **^{1}H NMR** (400 MHz, $(CD_3)_2SO$) **4c** δ 9.33 (s, 1H), 7.53 (d, *J* = 7.3 Hz, 2H), 7.41–7.31 (m, 4H), 7.28 (t, *J* = 7.3 Hz, 1H), 7.24–7.15 (m, 3H), 7.08 (t, *J* = 7.3 Hz, 1H), 6.48 (d, *J* = 3.6 Hz, 1H), 4.71–4.55 (m, 2H), 4.00 (td, *J* = 11.1, 3.9 Hz, 1H), 3.24 (dd, *J* = 17.0, 10.5 Hz, 1H), 2.80 (dd, *J* = 17.0, 3.9 Hz, 1H), 1.69 (s, 2H), 1.59 (d, *J* = 6.3 Hz, 2H), 1.49 – 1.40 (m, 1H), 1.39 – 1.20 (m, 1H); **4c′** δ 9.51 (s, 1H), 7.48 (d, *J* = 3.5 Hz, 1H), 7.23–7.15 (m, 4H), 7.10 (dd, *J* = 15.9, 7.7 Hz, 4H), 7.05 – 6.97 (m, 2H), 6.75 (d, *J* = 3.6 Hz, 1H), 4.74–4.60 (m, 2H), 4.08–3.94 (m, 1H), 3.41 – 3.29 (m, 1H), 3.05 (dd, *J* = 17.1, 4.3 Hz, 1H), 1.81 – 1.69 (m, 2H), 1.67–1.57 (m, 2H), 1.50–1.42 (m, 1H), 1.41–1.32 (m, 3H), 1.31–1.22 (m, 2H). **^{13}C NMR** (100 MHz, $(CD_3)_2SO$) **4c** δ 192.6, 177.4, 162.7, 159.3, 151.1, 141.7, 139.5, 128.9, 128.5, 128.10, 128.0, 127.4, 126.6, 110.0, 74.1, 50.5, 44.5, 43.5, 30.6, 30.5, 24.6, 22.9; **4c′** δ 192.3, 177.7, 162.6, 159.4, 151.8, 141.0, 139.1, 128.5, 128.3, 128.2, 127.9, 126.6, 126.4, 110.5, 74.2, 50.0, 44.5, 44.0, 30.6, 30.6, 24.7, 22.9. **HRMS**(ESI) m/z $(M+Na)^+$: calculated for $C_{28}H_{28}O_5Na$: 467.1829, found: 467.1834 (**4c**); 467.1830 (**4c′**). **IR** (neat) cm^{-1}: **4c** 2925, 2853, 1717, 1672, 2384, 1258, 1068, 1024, 799, 758, 699; **4c′** 2932, 2857, 1720, 1676, 1511, 1384, 1260, 1021, 799, 698.

benzyl (4*R*,5*S*)-5-(5-formylfuran-2-yl)-2-oxo-4,5-diphenylpentanoate (**4d**)

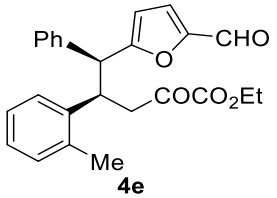


4d

The reaction was carried out following the general procedure to give two diastereoisomers with 74% yield and 81:19 dr. The major isomer **4d** was isolated as a white solid (m.p. = 120 – 122 ℃); The minor isomer **4d′** was isolated as a white solid (m.p. = 121 – 122 ℃). Enantiomeric excess was determined by UPC^2 using Chiralpak IG-3 column, CO_2/MeOH 90:10, flow rate 2mL/min, **4d**: 97%, t_{minor} = 3.800 min, t_{major} = 4.323 min,; **4d′**: 91%, t_{minor} = 3.701 min, t_{major} = 4.316 min. $[\alpha]_D^{27}$ = -3.0 (c 1.0, AcOEt, **4d**); $[\alpha]_D^{27}$ = -75.0 (c 0.2, AcOEt, **4d′**). **^{1}H NMR** (400 MHz, $(CD_3)_2SO$) **4d** δ 9.33 (s, 1H), 7.50 (d, *J* = 7.2 Hz, 2H), 7.42–7.30 (m, 9H), 7.27 (d, *J* = 7.3 Hz, 1H), 7.22 (d, *J* = 3.6 Hz, 1H), 7.17 (t, *J* = 7.5 Hz, 2H), 7.08 (t, *J* = 7.3 Hz, 1H), 6.47 (d, *J* = 3.6 Hz, 1H), 5.09 (s, 2H), 4.60 (d, *J* = 11.8 Hz, 1H), 4.09–3.95 (m, 1H), 3.28 (dd, *J* = 17.2, 10.5 Hz, 1H), 2.85 (dd, *J* = 17.2, 3.9 Hz, 1H); **4d′** δ 9.50 (s, 1H), 7.44 (d, *J* = 3.5 Hz, 1H), 7.42–7.34 (m, 5H), 7.21–6.96 (m, 11H), 6.72 (d, *J* = 3.6 Hz, 1H), 5.15 (s, 2H), 4.64 (d, *J* = 11.4 Hz, 1H), 4.08 – 3.95 (m, 1H), 3.44–3.35 (m, 1H), 3.11 (dd, *J* = 17.3, 4.2 Hz, 1H). ^{13}C NMR

(100 MHz, $(CD_3)_2SO$) **4d** δ 191.8, 177.4, 162.7, 159.6, 151.1, 141.7, 139.5, 134.9, 128.9, 128.5, 128.5, 128.4, 128.4, 128.1, 128.1, 127.4, 126.6, 110.0, 67.0, 50.5, 44.3, 43.7; **4d′** δ 191.5, 177.7, 162.6, 159.6, 151.8, 141.0, 139.1, 134.9, 128.5, 128.5, 128.3, 128.2, 127.9, 126.6, 126.4, 110.4, 67.1, 50.0, 44.3, 44.2. **HRMS**(ESI) m/z $(M+Na)^+$: calculated for $C_{29}H_{24}O_5Na$: 475.1516, found: 475.1522 (**4d**); 475.1516 (**4d′**). **IR** (neat) cm^{-1}: **4d** 3029, 2961, 1724, 1669, 1260, 1060, 798, 754, 697; **4d′** 2922, 2851, 1726, 1675, 1384, 1087, 1003, 698.

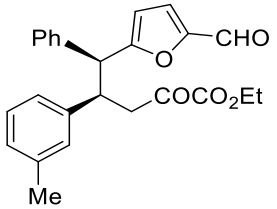
ethyl (4*R*,5*S*)-5-(5-formylfuran-2-yl)-4-(2-methoxyphenyl)-2-oxo-5-phenylpentanoate (**4e**)



4e

The reaction was carried out following the general procedure to give two diastereoisomers with 69% yield and 88:12 dr as a colorless oil. Enantiomeric excess of the major isomer **4e** was determined by UPC^2 using Chiralpak OD-3 column, CO_2/MeOH 95:5, flow rate 2mL/min, 95%, t_{minor} = 2.142 min, t_{major} = 2.327 min; Enantiomeric excess of the minor isomer **4e′** was determined by UPC^2 using Chiralpak IG-3 column, CO_2/MeOH 95:5, flow rate 2mL/min, 93%, t_{minor} = 2.552 min, t_{major} = 2.857 min. $[\alpha]_D^{27}$ = -6.0 (c 1.0, AcOEt, **4e**); $[\alpha]_D^{27}$ = -250.0 (c 0.2, AcOEt, **4e′**). **^{1}H NMR** (600 MHz, $(CD_3)_2SO$) **4e** δ 9.34 (s, 1H), 7.57 (d, *J* = 7.5 Hz, 2H), 7.49 (m, 1H), 7.39 (t, *J* = 7.5 Hz, 2H), 7.29 (t, *J* = 7.3 Hz, 1H), 7.17 (d, *J* = 3.4 Hz, 1H), 7.14 – 7.06 (d, *J* = 3.5 Hz, 1H), 6.96 (d, *J* = 4.0 Hz, 2H), 6.23 (d, *J* = 2.8 Hz, 1H), 4.63 (d, *J* = 11.5 Hz, 1H), 4.26 (td, *J* = 10.9, 3.7 Hz, 1H), 4.04 (q, *J* = 7.1 Hz, 2H), 3.27 (dd, *J* = 17.4, 10.1 Hz, 1H), 2.89 (dd, *J* = 17.4, 3.8 Hz, 1H), 2.36 (s, 3H), 1.13 (t, *J* = 7.1 Hz, 3H); **4e′** δ 9.53 (s, 1H), 7.50 (d, *J* = 3.5 Hz, 1H), 7.46 (d, *J* = 7.7 Hz, 1H), 7.15 (d, *J* = 7.3 Hz, 2H), 7.14 – 7.06 (m, 1H), 7.03 (t, *J* = 7.2 Hz, 1H), 6.91 (t, *J* = 7.3 Hz, 1H), 6.85 (d, *J* = 7.4 Hz, 1H), 6.80 (d, *J* = 3.5 Hz, 1H), 4.63 (d, *J* = 11.3 Hz, 1H), 4.26–4.18 (m, 1H), 4.09 (q, *J* = 7.1 Hz, 2H), 3.37 (dd, *J* = 17.5, 9.5 Hz, 1H), 3.08 (dd, *J* = 17.5, 4.4 Hz, 1H), 2.14 (s, 3H), 1.17 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (150 MHz, $(CD_3)_2SO$) **4e** δ 192.2, 177.2, 162.5, 159.9, 151.2, 140.0, 139.4, 135.9, 129.9, 128.9, 128.5, 127.4, 126.4, 126.2, 126.0, 109.6, 61.7, 59.7, 50.5, 44.0, 20.7, 19.0, 13.6; **4e′** δ 191.8, 177.7, 162.5, 159.9, 151.9, 139.8, 139.1, 135.9, 129.8, 128.2, 128.0, 126.7, 126.1, 125.9, 110.8, 61.7, 50.2, 44.4, 19.4, 13.7. **HRMS**(ESI) m/z $(M+Na)^+$: calculated for $C_{25}H_{24}O_5Na$: 427.1516, found: 427.1520 (**4e**); 427.1516 (**4e′**). **IR** (neat) cm^{-1}: **4e** 2963, 2924, 1725, 1674, 1384, 1261, 1071, 1020, 799, 756, 702; **4e′** 2962, 2922, 1725, 1675, 1384, 1262, 1068, 1020.

ethyl (4*R*,5*S*)-5-(5-formylfuran-2-yl)-2-oxo-5-phenyl-4-(m-tolyl)pentanoate (**4f**)

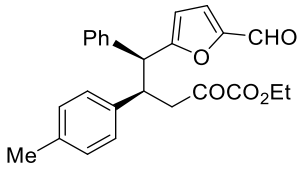


4f

The reaction was carried out following the general procedure to give two diastereoisomers with 76% yield and 83:17 dr. The major isomer **4f** was isolated as a light yellow oil; The minor isomer **4f′** was isolated as a light yellow solid (m.p. = 118 – 119 ℃). Enantiomeric excess was

determined by UPC[2] using Chiralpak IG-3 column, CO_2/MeOH 95:5, flow rate 2mL/min, **4f**: 97%, t_{minor} = 2.593 min, t_{major} = 2.871 min,; **4f′**: 87%, t_{minor} = 2.552 min, t_{major} = 2.943 min. $[\alpha]_D^{27}$ = -10.0 (c 1.0, AcOEt, **4f**); $[\alpha]_D^{27}$ = -155.0 (c 0.2, AcOEt, **4f′**). **^{1}H NMR** (400 MHz, $CDCl_3$) **4f** δ 9.42 (s, 1H), 7.48–7.41 (m, 2H), 7.38 – 7.33 (m, 2H), 7.30–7.26 (m, 1H), 7.07 (t, *J* = 7.5 Hz, 1H), 7.01 (d, *J* = 8.3 Hz, 2H), 6.95–6.91 (m, 2H), 6.09 (d, *J* = 3.6 Hz, 1H), 4.30 (d, *J* = 11.6 Hz, 1H), 4.18–4.05 (m, 3H), 3.24 (dd, *J* = 17.5, 9.8 Hz, 1H), 2.91 (dd, *J* = 17.5, 4.2 Hz, 1H), 2.25 (s, 3H), 1.23 (t, *J* = 7.1 Hz, 3H); **4f′** δ 9.58 (s, 1H), 7.18–7.11 (m, 5H), 7.11–7.07 (m, 1H), 7.00 (t, *J* = 7.9 Hz, 1H), 6.86 (d, *J* = 7.4 Hz, 1H), 6.82 (d, *J* = 6.4 Hz, 2H), 6.41 (d, *J* = 3.6 Hz, 1H), 4.33 (d, *J* = 10.7 Hz, 1H), 4.24–4.16 (m, 2H), 4.12 – 4.03 (m, 1H), 3.37 (dd, *J* = 17.6, 8.9 Hz, 1H), 3.15 (dd, *J* = 17.6, 5.0 Hz, 1H), 2.19 (s, 3H), 1.28 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) **4f** δ 192.1, 177.0, 162.3, 160.3, 151.8, 140.9, 138.6, 138.0, 129.1, 128.6, 128.5, 128.3, 127.8, 127.8, 124.8, 109.9, 62.3, 52.0, 44.8, 43.8, 21.3, 13.8; **4f′** δ 192.1, 177.2, 162.6, 160.5, 152.2, 140.3, 138.3, 137.8, 129.0, 128.5, 128.3, 128.1, 127.6, 127.1, 125.1, 110.5, 62.5, 51.6, 45.0, 44.0, 21.3, 13.8. **HRMS**(ESI) m/z $(M+Na)^+$: calculated for $C_{25}H_{24}O_5Na$: 427.1516, found: 427.1521 (**4f**); 427.1516 (**4f′**). **IR** (neat) cm^{-1}: **4f** 3028, 2962, 1725, 1674, 1511, 1260, 1023, 796, 764, 703; **4f′** 2962, 2923, 1726, 1676, 1384, 1260, 1092, 1020, 799.

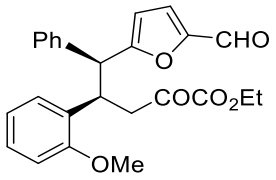
ethyl (4*R*,5*S*)-5-(5-formylfuran-2-yl)-2-oxo-5-phenyl-4-(p-tolyl)pentanoate (**4g**)



4g

The reaction was carried out following the general procedure to give two diastereoisomers with 72% yield and 84:16 dr. as a light yellow oil. Enantiomeric excess was determined by UPC[2] using Chiralpak IG-3 column, CO_2/MeOH 95:5, flow rate 2mL/min, the major isomer **4g**: 97%, t_{minor} = 4.002 min, t_{major} = 4.426 min; the minor isomer **4g′**: 87%, t_{minor} = 3.646 min, t_{major} = 4.050 min. $[\alpha]_D^{27}$ = -12.0 (c 1.0, AcOEt, **4g**); $[\alpha]_D^{27}$ = -60.0 (c 0.5, AcOEt, **4g′**). **^{1}H NMR** (400 MHz, $(CD_3)_2SO$) **4g** δ 9.33 (s, 1H), 7.55–7.48 (m, 2H), 7.37 (t, *J* = 7.6 Hz, 2H), 7.28 (d, *J* = 7.4 Hz, 1H), 7.25 – 7.18 (m, 3H), 6.99 (d, *J* = 7.8 Hz, 2H), 6.50 (d, *J* = 3.6 Hz, 1H), 4.58 (d, *J* = 11.8 Hz, 1H), 4.11–4.02 (m, 2H), 3.97 (td, *J* = 11.1, 3.8 Hz, 1H), 3.22 (dd, *J* = 17.1, 10.6 Hz, 1H), 2.76 (dd, *J* = 17.1, 3.9 Hz, 1H), 2.17 (s, 3H), 1.14 (t, *J* = 7.1 Hz, 3H); **4g′** δ 9.51 (s, 1H), 7.47 (d, *J* = 3.5 Hz, 1H), 7.25–7.18 (m, 2H), 7.12 (t, *J* = 7.5 Hz, 2H), 7.09–7.00 (m, 3H), 6.90 (d, *J* = 7.9 Hz, 2H), 6.73 (d, *J* = 3.6 Hz, 1H), 4.62 (d, *J* = 11.4 Hz, 1H), 4.10 (q, *J* = 7.1 Hz, 2H), 4.00 (ddd, *J* = 12.3, 9.1, 4.9 Hz, 1H), 3.30 (d, *J* = 9.9 Hz, 1H), 3.02 (dd, *J* = 17.3, 4.2 Hz, 1H), 2.12 (s, 3H), 1.18 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $(CD_3)_2SO$) **4g** δ 192.3, 177.4, 162.8, 160.0, 151.0, 139.6, 138.6, 135.5, 128.9, 128.7, 128.4, 127.9, 127.4, 110.0, 61.7, 50.5, 43.9, 43.6, 20.5, 13.7; **4g′** δ 191.9, 177.7, 162.8, 160.0, 151.8, 139.2, 138.0, 135.2, 128.5, 128.5, 128.2, 128.2, 126.6, 110.4, 61.7, 50.0, 44.1, 43.8, 20.5, 13.7. **HRMS**(ESI) m/z $(M+Na)^+$: calculated for $C_{25}H_{24}O_5Na$: 427.1516, found: 427.1520 (**4g**); 427.1517 (**4g′**). **IR** (neat) cm^{-1}: **4g** 2922, 1724, 1673, 1513, 1260, 1072, 764, 701; **4g′** 29236, 1724, 1654, 1630, 1384, 1260, 1094, 1003, 798.

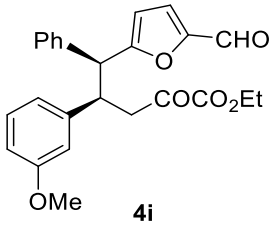
ethyl (4*R*,5*S*)-5-(5-formylfuran-2-yl)-4-(2-methoxyphenyl)-2-oxo-5-phenylpentanoate (**4h**)



4h

The reaction was carried out following the general procedure to give two diastereoisomers with 59% yield and 89:11 dr as a light yellow oil. Enantiomeric excess was determined by UPC^2 using Chiralpak IG-3 column, CO_2/MeOH 95:5, flow rate 2mL/min, the major isomer **4h**: 96%, t_{minor} = 3.134 min, t_{major} = 3.559 min; the minor isomer **4h′**: 92%, t_{minor} = 3.109 min, t_{major} = 3.510 min. $[\alpha]_D^{27}$ = -1.0 (c 1.0, AcOEt, **4h**); $[\alpha]_D^{27}$ = -38.41 (c 0.13, AcOEt, **4h′**). **^{1}H NMR** (400 MHz, $(CD_3)_2SO$) **4h** δ 9.32 (s, 1H), 7.49 (d, *J* = 7.2 Hz, 2H), 7.42–7.32 (m, 3H), 7.28 (t, *J* = 7.3 Hz, 1H), 7.22 (d, *J* = 3.6 Hz, 1H), 7.13–7.07 (m, 1H), 6.88–6.78 (m, 2H), 6.39 (d, *J* = 3.6 Hz, 1H), 4.70 (d, *J* = 11.7 Hz, 1H), 4.37 (td, *J* = 11.1, 4.1 Hz, 1H), 4.14–3.98 (m, 2H), 3.75 (s, 3H), 3.06 – 2.93 (m, 1H), 2.87 (dd, *J* = 15.5, 4.3 Hz, 1H), 1.17 (dd, *J* = 7.8, 6.4 Hz, 3H); **^{1}H NMR** (600 MHz, $(CD_3)_2SO$) **4h′** δ 9.51 (s, 1H), 7.48 (d, *J* = 3.5 Hz, 1H), 7.22–7.16 (m, 3H), 7.10 (t, *J* = 7.7 Hz, 2H), 7.04–6.98 (m, 2H), 6.77–6.73 (m, 2H), 6.71 (td, *J* = 7.4, 0.6 Hz, 1H), 4.72 (d, *J* = 11.5 Hz, 1H), 4.40 (td, *J* = 11.2, 4.4 Hz, 1H), 4.19 – 4.08 (m, 2H), 3.68 (s, 3H), 3.17 (dd, *J* = 16.0, 9.7 Hz, 1H), 3.08 (dd, *J* = 16.0, 4.4 Hz, 1H), 1.21 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $(CD_3)_2SO$) **4h** δ 191.9, 177.3, 163.0, 159.7, 156.7, 151.2, 139.5, 128.9, 128.8, 128.6, 127.92, 127.4, 120.3, 111.0, 109.3, 61.6, 55.4, 49.1, 43.0, 20.7, 13.7; **^{13}C NMR** (150 MHz, $(CD_3)_2SO$) **4h′** δ 192.2, 178.2, 163.3, 160.4, 157.2, 152.3, 139.8, 129.4, 128.9, 128.6, 128.5, 128.2, 127.1, 120.6, 111.3, 110.9, 62.2, 55.7, 49.3, 43.8, 14.2. **HRMS**(ESI) m/z $(M+Na)^+$: calculated for $C_{25}H_{24}O_6Na$: 443.1465, found: 443.1470 (**4h**); 443.1465 (**4h′**). **IR** (neat) cm^{-1}: **4h** 2961, 1726, 1675, 1494, 1244, 1074, 1025, 799, 755, 702; **4h′** 2961, 2852, 1630, 1384, 1094, 1004, 799.

ethyl (4*R*,5*S*)-5-(5-formylfuran-2-yl)-4-(3-methoxyphenyl)-2-oxo-5-phenylpentanoate (**4i**)

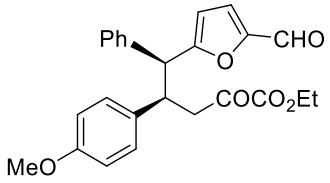


4i

The reaction was carried out following the general procedure to give two diastereoisomers with 65% yield and 80:20 dr. The major isomer **4i** was isolated as a light yellow solid (m.p. = 101 – 102 ℃); The minor isomer **4i′** was isolated as a light yellow solid (m.p. = 88 – 89 ℃). Enantiomeric excess of **4i** was determined by UPC^2 using Chiralpak OD-3 column, CO_2/MeOH 95:5, flow rate 2mL/min, 97%, t_{minor} = 2.545 min, t_{major} = 2.964 min; Enantiomeric excess of **4i′** was determined by UPC^2 using Chiralpak AD-3 column, CO_2/MeOH 95:5, flow rate 2mL/min, 82%, t_{minor} = 2.141 min, t_{major} = 2.436 min. $[\alpha]_D^{24}$ = -9.0 (c 1.0, AcOEt, **4i**); $[\alpha]_D^{24}$ = -67.65 (c 0.34, AcOEt, **4i′**). **^{1}H NMR** (400 MHz, $(CD_3)_2SO$) **4i** δ 9.35 (s, 1H), 7.53 (d, *J* = 7.2 Hz, 2H), 7.37 (t, *J* = 7.6 Hz, 2H), 7.31–7.22 (m, 2H), 7.10 (t, *J* = 7.9 Hz, 1H), 6.97 – 6.88 (m, 2H), 6.65 (dd, *J* = 8.1, 2.0 Hz, 1H), 6.53 (d, *J* = 3.6 Hz, 1H), 4.62 (d, *J* = 11.8 Hz, 1H), 4.06 (q, *J* = 7.1 Hz, 2H), 4.03–3.95 (m, 1H), 3.68 (s, 3H), 3.27 (dd, *J* = 17.2, 10.4 Hz, 1H), 2.79 (dd, *J* = 17.2,

3.9 Hz, 1H), 1.14 (t, *J* = 7.1 Hz, 3H); **4i′** δ 9.51 (s, 1H), 7.47 (d, *J* = 3.5 Hz, 1H), 7.24 (d, *J* = 7.4 Hz, 2H), 7.13 (t, *J* = 7.6 Hz, 2H), 7.02 (dt, *J* = 24.5, 7.6 Hz, 2H), 6.79 (s, 1H), 6.77–6.73 (m, 2H), 6.57 (dd, *J* = 8.1, 2.0 Hz, 1H), 4.66 (d, *J* = 11.3 Hz, 1H), 4.11 (q, *J* = 7.1 Hz, 2H), 4.03 (dt, *J* = 3.6 Hz, 1H), 3.62 (s, 3H), 3.41–3.34 (m, 2H), 3.06 (dd, *J* = 17.3, 4.2 Hz, 1H), 1.18 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $(CD_3)_2SO$) **4i** δ 192.2, 177.4, 162.8, 160.0, 159.0, 151.1, 143.4, 139.6, 129.1, 128.9, 128.5, 127.4, 120.3, 113.9, 111.9, 110.0, 61.7, 54.9, 50.3, 44.3, 43.4, 13.7; **4i′** δ 191.8, 177.6, 162.7, 160.0, 158.8, 151.8, 142.7, 139.2, 128.9, 128.5, 128.2, 126.6, 120.6, 114.1, 111.7, 110.4, 61.7, 54.8, 49.9, 44.3, 43.9, 13.7. **HRMS**(ESI) m/z $(M+Na)^+$: calculated for $C_{25}H_{24}O_6Na$: 443.1465, found: 443.1469 (**4i**); 443.1465 (**4i′**). **IR** (neat) cm^{-1}: **4i** 2926, 2836, 1726, 1674, 1259, 1025, 792, 764, 701; **4i′** 2962, 2922, 1724, 1384, 1260, 1020, 798.

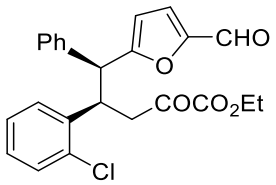
ethyl (4*R*,5*S*)-5-(5-formylfuran-2-yl)-4-(4-methoxyphenyl)-2-oxo-5-phenylpentanoate (**4j**)



4j

The reaction was carried out following the general procedure to give two diastereoisomers with 69% yield and 81:19 dr as colorless oil. Enantiomeric excess of the major isomer **4j** was determined by UPC^2 using Chiralpak IG-3 column, CO_2/MeOH 95:5, flow rate 2mL/min, 91%, t_{major} = 5.429 min, t_{minor} = 5.958 min; Enantiomeric excess of the minor isomer **4j′** was determined by UPC^2 using Chiralpak AD-3 column, CO_2/MeOH 95:5, flow rate 2mL/min, 75%, t_{minor} = 2.550 min, t_{major} = 3.337 min. $[\alpha]_D^{26}$ = -15.0 (c 1.0, AcOEt, **4j**); $[\alpha]_D^{26}$ = -200.0 (c 0.1, AcOEt, **4j′**). **^{1}H NMR** (400 MHz, $(CD_3)_2SO$) **4j** δ 9.34 (s, 1H), 7.52 (d, *J* = 7.2 Hz, 2H), 7.37 (t, *J* = 7.6 Hz, 2H), 7.30–7.23 (m, 4H), 6.75 (t, *J* = 5.8 Hz, 2H), 6.50 (d, *J* = 3.6 Hz, 1H), 4.56 (d, *J* = 11.8 Hz, 1H), 4.05 (q, *J* = 7.1 Hz, 2H), 3.96 (td, *J* = 11.1, 3.8 Hz, 1H), 3.65 (s, 3H), 3.22 (dd, *J* = 17.0, 10.6 Hz, 1H), 2.75 (dd, *J* = 17.0, 3.8 Hz, 1H), 1.14 (t, *J* = 7.1 Hz, 3H); **4j′** δ 9.51 (s, 1H), 7.47 (d, *J* = 3.5 Hz, 1H), 7.24–7.18 (m, 2H), 7.16–7.02 (m, 5H), 6.73 (d, *J* = 3.5 Hz, 1H), 6.65 (d, *J* = 8.7 Hz, 2H), 4.60 (d, *J* = 11.3 Hz, 1H), 4.11 (q, *J* = 7.1 Hz, 2H), 4.05 – 3.92 (m, 1H), 3.61 (s, 3H), 3.35 (s, 1H), 3.37 – 3.25 (m, 1H), 3.01 (dd, *J* = 17.1, 4.2 Hz, 1H), 1.18 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $(CD_3)_2SO$) **4j** δ 192.4, 177.4, 162.9, 160.0, 157.7, 151.0, 139.7, 133.4, 129.1, 128.9, 128.4, 127.4, 113.4, 110.0, 61.7, 54.8, 50.6, 43.6, 43.5, 13.7; **4j′** δ 192.0, 177.6, 162.8, 160.0, 157.5, 151.8, 139.3, 132.8, 129.3, 128.4, 128.1, 126.6, 113.2, 110.3, 61.7, 54.7, 50.1, 44.1, 43.5, 13.7. **HRMS**(ESI) m/z $(M+Na)^+$: calculated for $C_{25}H_{24}O_6Na$: 443.1465, found: 443.1470 (**4j**); 443.1465 (**4j′**). **IR** (neat) cm^{-1}: **4j** 2961, 2837, 1725, 1674, 1513, 1249, 1179, 1027, 798, 764, 702; **4j′** 2924, 1723, 1670, 1384, 1023, 798.

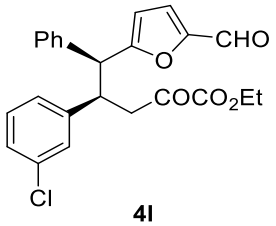
ethyl (4*R*,5*S*)-4-(2-chlorophenyl)-5-(5-formylfuran-2-yl)-2-oxo-5-phenylpentanoate (**4k**)



4k

The reaction was carried out following the general procedure to give two diastereoisomers with 62% yield and 88:12 dr. The major isomer **4k** was isolated as a light yellow oil; The minor isomer **4k′** was isolated as a colorless oil. Enantiomeric excess was determined by UPC^2 using Chiralpak IG-3 column, CO_2/MeOH 95:5, flow rate 2mL/min, **4k**: 83%, t_{minor} = 3.320 min, t_{major} = 4.433 min,; **4k′**: 88%, t_{minor} = 3.295 min, t_{major} = 3.815 min. $[\alpha]_D^{27}$ = + 7.0 (c 1.0, AcOEt, **4k**); $[\alpha]_D^{28}$ = -75.0 (c 0.2, AcOEt, **4k′**). **^{1}H NMR** (600 MHz, $(CD_3)_2SO$) **4k** δ 9.35 (s, 1H), 7.66 (d, *J* = 6.0 Hz, 1H), 7.53 (d, *J* = 7.2 Hz, 2H), 7.40 (t, *J* = 7.7 Hz, 2H), 7.32–7.25 (m, 3H), 7.22 (d, *J* = 3.6 Hz, 1H), 7.13 (td, *J* = 7.7, 1.5 Hz, 1H), 6.35 (d, *J* = 2.7 Hz, 1H), 4.70 (d, *J* = 10.5 Hz, 1H), 4.52 (s, 1H), 4.07 (q, *J* = 7.1 Hz, 2H), 3.14 (s, 1H), 3.02 (dd, *J* = 16.7, 4.1 Hz, 1H), 1.16 (t, *J* = 7.1 Hz, 3H); **4k′** δ 9.53 (s, 1H), 7.57 (d, *J* = 7.6 Hz, 1H), 7.49 (d, *J* = 3.5 Hz, 1H), 7.23 – 7.18 (m, 3H), 7.16 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.12 (t, *J* = 7.6 Hz, 2H), 7.08–7.02 (m, 2H), 6.76 (d, *J* = 3.6 Hz, 1H), 4.75 (d, *J* = 11.3 Hz, 1H), 4.62–4.50 (m, 1H), 4.13 (q, *J* = 7.1 Hz, 2H), 3.31–3.18 (m, 2H), 1.20 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (150 MHz, $(CD_3)_2SO$) **4k** δ 191.3, 177.4, 162.0, 159.6, 151.3, 138.8, 133.3, 129.1, 128.9, 128.7, 128.6, 128.3, 127.6, 127.3, 109.5, 61.7, 59.7, 49.9, 43.3, 20.7, 13.7; **4k′** δ 191.1, 177.8, 161.9, 159.7, 152.0, 138.6, 138.5, 133.4, 129.0, 128.2, 128.1, 128.1, 128.0, 127.1, 126.8, 110.7, 61.7, 49.4, 43.7, 13.7. **HRMS**(ESI) m/z $(M+Na)^+$: calculated for $C_{24}H_{21}ClO_5Na$: 447.0970, found: 447.0975 (**4k**); 447.0970 (**4k′**). **IR** (neat) cm^{-1}: **4k** 2962, 2925, 1725, 1674, 1384, 1260, 1076, 1022, 799, 756, 702; **4k′** 2962, 2923, 1724, 1672, 1384, 1260, 1086, 1020, 799.

ethyl (4*R*,5*S*)-4-(3-chlorophenyl)-5-(5-formylfuran-2-yl)-2-oxo-5-phenylpentanoate (**4l**)

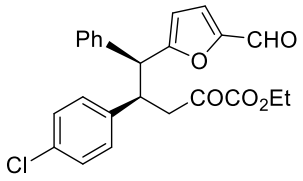


4l

The reaction was carried out following the general procedure to give two diastereoisomers with 82% yield and 74:26 dr. The major isomer **4l** was isolated as a white solid (m.p. = 100 – 101 ℃); The minor isomer **4l′** was isolated as a white solid (m.p. = 125 – 126 ℃). Enantiomeric excess was determined by UPC^2 using Chiralpak IG-3 column, CO_2/MeOH 95:5, flow rate 2mL/min, **4l**: 95%, t_{minor} = 2.951 min, t_{major} = 3.167 min; **4l′**: 87%, t_{minor} = 2.948 min, t_{major} = 3.273 min. $[\alpha]_D^{26}$ = -16.0 (c 1.0, AcOEt, **4l**); $[\alpha]_D^{26}$ = -66.0 (c 0.5, AcOEt, **4l′**). **^{1}H NMR** (600 MHz, $(CD_3)_2SO$) **4l** δ 9.34 (s, 1H), 7.55 – 7.50 (m, 3H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.33 (d, *J* = 7.7 Hz, 1H), 7.30 – 7.26 (m, 1H), 7.25 (d, *J* = 3.6 Hz, 1H), 7.21 (t, *J* = 7.8 Hz, 1H), 7.17–7.13 (m, 1H), 6.57 (d, *J* = 3.6 Hz, 1H), 4.65 (d, *J* = 11.9 Hz, 1H), 4.06 (q, *J* = 7.1 Hz, 2H), 4.03–3.99 (m, 1H), 3.34–3.27 (m, 1H), 2.82 (dd, *J* = 17.7, 3.7 Hz, 1H), 1.14 (t, *J* = 7.1 Hz, 3H); **4l′** δ 9.51 (s, 1H), 7.50 (d, *J* = 3.5 Hz, 1H), 7.33 (s, 1H), 7.23 (d, *J* = 7.2 Hz, 2H), 7.19–7.09 (m, 4H), 7.08–7.02 (m, 2H), 6.76 (d, *J* = 3.6 Hz, 1H), 4.69 (d, *J* = 11.5 Hz, 1H), 4.11 (q, *J* = 7.1 Hz, 2H),

4.03 (td, *J* = 11.2, 10.6, 4.0 Hz, 1H), 3.41 (dd, *J* = 17.9, 10.0 Hz, 1H), 3.09 (dd, *J* = 17.9, 4.0 Hz, 1H), 1.19 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (150 MHz, $(CD_3)_2SO$) **4l** δ 192.5, 177.9, 163.0, 160.3, 151.6, 145.0, 139.8, 133.2, 130.3, 129.4, 128.9, 128.5, 128.0, 127.6, 127.1, 110.6, 62.2, 50.5, 44.4, 43.6, 14.1; **4l′** δ 191.7, 177.7, 162.4, 159.9, 151.8, 143.8, 138.9, 132.5, 129.6, 128.4, 128.3, 127.3, 126.7, 126.3, 110.4, 61.8, 49.6, 43.8, 43.7, 13.7. **HRMS**(ESI) m/z $(M+Na)^+$: calculated for $C_{24}H_{21}ClO_5Na$: 447.0970, found: 447.0976 (**4l**); 447.0972 (**4l′**). **IR** (neat) cm^{-1}: **4l** 2962, 2924, 1723, 1670, 1384, 1071, 1020, 796, 696; **4l′** 2962, 2924, 1723, 1671, 1384, 1260, 1091, 1019, 799.

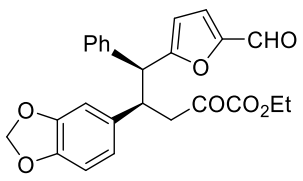
ethyl (4*R*,5*S*)-4-(4-chlorophenyl)-5-(5-formylfuran-2-yl)-2-oxo-5-phenylpentanoate (**4m**)



4m

The reaction was carried out following the general procedure to give two diastereoisomers with 85% yield and 79:21 dr. The major isomer **4m** was isolated as a yellow oil; The minor isomer **4m′** was isolated as a white solid (m.p. = 122–123 ℃). Enantiomeric excess was determined by UPC^2 using Chiralpak IG-3 column, CO_2/MeOH 95:5, flow rate 2mL/min, **4m**: 93%, t_{minor} = 4.313 min, t_{major} = 4.848 min; **4m′**: 84%, t_{minor} = 4.053 min, t_{major} = 4.450 min. $[\alpha]_D^{26}$ = -22.0 (c 1.0, AcOEt, **4m**); $[\alpha]_D^{26}$ = -74.0 (c 0.5, AcOEt, **4m′**). **^{1}H NMR** (400 MHz, $(CD_3)_2SO$) **4m** δ 9.34 (s, 1H), 7.53 (d, *J* = 7.2 Hz, 2H), 7.43–7.34 (m, 4H), 7.31–7.22 (m, 4H), 6.53 (d, *J* = 3.6 Hz, 1H), 4.61 (d, *J* = 11.9 Hz, 1H), 4.13–4.04 (m, 2H), 4.04–3.94 (m, 1H), 3.29 (dd, *J* = 17.6, 10.6 Hz, 1H), 2.81 (dd, *J* = 17.6, 3.7 Hz, 1H), 1.14 (t, *J* = 7.1 Hz, 3H); **4m′** δ 9.51 (s, 1H), 7.48 (d, *J* = 3.6 Hz, 1H), 7.25–7.18 (m, 4H), 7.17–7.11 (m, 4H), 7.07–7.01 (m, 1H), 6.76 (d, *J* = 3.6 Hz, 1H), 4.65 (d, *J* = 11.5 Hz, 1H), 4.11 (q, *J* = 7.1 Hz, 2H), 4.07–3.99 (m, 1H), 3.46–3.36 (m, 1H), 3.08 (dd, *J* = 17.7, 4.0 Hz, 1H), 1.18 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $(CD_3)_2SO$) **4m** δ 192.0, 177.4, 162.5, 159.9, 151.1, 140.9, 139.3, 131.1, 130.0, 128.9, 128.4, 128.0, 127.5, 110.1, 61.7, 50.2, 43.6, 43.2; **4m′** δ 191.7, 177.7, 162.4, 159.9, 151.8, 140.3, 139.0, 130.8, 130.3, 128.4, 128.3, 127.8, 126.7, 110.4, 61.8, 49.8, 43.8, 43.6, 13.7. **HRMS**(ESI) m/z $(M+Na)^+$: calculated for $C_{24}H_{21}ClO_5Na$: 447.0970, found: 447.0976 (**4m**); 447.0970 (**4m′**). **IR** (neat) cm^{-1}: **4m** 2962, 1725, 1674, 1491, 1260, 1072, 1014, 798, 763, 702; **4m′** 2962, 2924, 1724, 1671, 1384, 1260, 1091, 1014, 799.

ethyl (4*R*,5*S*)-4-(benzo[*d*][1,3]dioxol-5-yl)-5-(5-formylfuran-2-yl)-2-oxo-5-phenylpentanoate (**4n**)

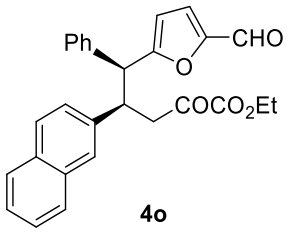


4n

The reaction was carried out following the general procedure to give two diastereoisomers with 56% yield and 67:33 dr. The major isomer **4n** was isolated as a light yellow solid (m.p. =

150 – 151 ℃); The minor isomer **4n′** was isolated as a colorless oil. Enantiomeric excess of **4n** was determined by UPC^2 using Chiralpak IG-3 column, CO_2/MeOH 95:5, flow rate 2mL/min, 99%, t_{major} = 5.152 min, t_{minor} = 5.704 min; Enantiomeric excess of **4n′** was determined by UPC^2 using Chiralpak AD-3 column, CO_2/MeOH 95:5, flow rate 2mL/min, 69%, t_{minor} = 2.848 min, t_{major} = 3.227 min. $[\alpha]_D^{27}$ = -19.0 (c 1.0, AcOEt, **4n**); $[\alpha]_D^{27}$ = -85.0 (c 0.2, AcOEt, **4n′**). **^{1}H NMR** (400 MHz, $CDCl_3$) **4n** δ 9.44 (s, 1H), 7.46–7.41 (m, 2H), 7.39 – 7.32 (m, 2H), 7.30–7.26 (m, 1H), 6.96 (d, *J* = 3.6 Hz, 1H), 6.71 (d, *J* = 1.6 Hz, 1H), 6.67 (dd, *J* = 8.0, 1.7 Hz, 1H), 6.61 (d, *J* = 8.0 Hz, 1H), 6.13 (d, *J* = 3.6 Hz, 1H), 5.87 (s, 2H), 4.23 (d, *J* = 11.6 Hz, 1H), 4.20–4.13 (m, 2H), 4.12–4.04 (m, 1H), 3.19 (dd, *J* = 17.4, 10.1 Hz, 1H), 2.87 (dd, *J* = 17.4, 4.0 Hz, 1H), 1.26 (t, *J* = 7.1 Hz, 3H); **^{1}H NMR** (600 MHz, $CDCl_3$) **4n′** δ 9.57 (s, 1H),7.20–7.14 (m, 5H), 7.15 (s, 1H), 7.14–7.09 (m, 1H), 6.53 (d, *J* = 8.1 Hz, 2H), 6.48 (dd, *J* = 8.0, 1.6 Hz, 1H), 6.41 (d, *J* = 3.6 Hz, 1H), 5.83 (dd, *J* = 6.5, 1.4 Hz, 2H), 4.26 (d, *J* = 10.8 Hz, 1H), 4.24–4.18 (m, 2H), 4.08–4.01 (m, 1H), 3.32 (dd, *J* = 17.5, 9.3 Hz, 1H), 3.09 (dd, *J* = 17.5, 4.7 Hz, 1H), 1.29 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) **4n** δ 192.1, 177.0, 162.1, 160.3, 151.8, 147.7, 146.4, 138.5, 134.7, 129.1, 128.5, 127.8, 121.3, 110.0, 108.2, 107.9, 100.9, 62.4, 52.2, 44.6, 43.9, 13.8; **^{13}C NMR** (150 MHz, $CDCl_3$) **4n′** δ 192.0, 177.2, 162.4, 160.4, 152.2, 147.5, 146.2, 138.3, 134.1, 128.4, 127.1, 121.6, 110.4, 108.2, 108.0, 100.8, 62.5, 51.8, 44.8, 44.2, 13.9. **HRMS**(ESI) m/z $(M+Na)^+$: calculated for $C_{25}H_{22}O_7Na$: 457.1258, found: 457.1261 (**4n**); 457.1258 (**4n′**). **IR** (neat) cm^{-1}: **4n** 2962, 2920, 1725, 1674, 1488, 1247, 1036, 933, 801, 763, 702; **4n′** 2922, 1725, 1675, 1489, 1384, 1244, 1033, 931, 802.

ethyl (4*R*,5*S*)-5-(5-formylfuran-2-yl)-4-(naphthalen-2-yl)-2-oxo-5-phenylpentanoate (**4o**)

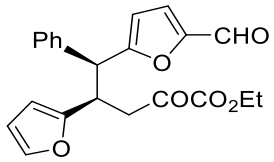


4o

The reaction was carried out following the general procedure to give two diastereoisomers with 71% yield and 82:18 dr. The major isomer **4o** was isolated as a light yellow solid (m.p. = 108 – 109 ℃); The minor isomer **4o′** was isolated as a white solid (m.p. = 143 – 144 ℃). Enantiomeric excess was determined by UPC^2 using Chiralpak AD-3 column, CO_2/MeOH 95:5, flow rate 2mL/min, **4o**: 96%, t_{minor} = 4.121 min, t_{major} = 5.056 min,; **4o′**: 74%, t_{minor} = 4.075 min, t_{major} = 5.351 min. $[\alpha]_D^{26}$ = -32.0 (c 1.0, AcOEt, **4o**); $[\alpha]_D^{26}$ = -80.0 (c 0.2, AcOEt, **4o′**). **^{1}H NMR** (400 MHz, $CDCl_3$) **4o** δ 9.37 (s, 1H), 7.76–7.67 (m, 4H), 7.54–7.47 (m, 2H), 7.44–7.36 (m, 5H), 7.32 – 7.27 (m, 1H), 6.83 (d, *J* = 3.6 Hz, 1H), 6.09 (d, *J* = 3.6 Hz, 1H), 4.46 (d, *J* = 11.6 Hz, 1H), 4.40–4.28 (m, 1H), 4.14–4.03 (m, 2H), 3.38 (dd, *J* = 17.5, 9.8 Hz, 1H), 3.00 (dd, *J* = 17.5, 4.0 Hz, 1H), 1.16 (t, *J* = 7.1 Hz, 3H); **4o′** δ 9.60 (s, 1H), 7.72–7.61 (m, 3H), 7.50 (s, 1H), 7.43–7.35 (m, 2H), 7.25–7.15 (m, 4H), 7.14 – 7.07 (m, 2H), 7.06–6.99 (m, 1H), 6.44 (d, *J* = 3.6 Hz, 1H), 4.49 (d, *J* = 10.7 Hz, 1H), 4.40–4.28 (m, 1H), 4.20–4.09 (m, 2H), 3.58–3.44 (m, 1H), 3.23 (dd, *J* = 17.6, 4.8 Hz, 1H), 1.20 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) **4o** δ 192.1, 176.9, 162.0, 160.3, 151.8, 138.5, 138.4, 133.2, 132.4, 129.2, 128.5, 128.3, 127.9, 127.7, 127.5, 127.0, 126.1, 125.8, 125.6, 110.0, 62.4, 51.9, 45.0, 43.8, 13.7; **4o′** δ 192.0, 177.2, 162.4, 160.4, 152.3, 138.2, 137.9, 133.1, 132.3, 128.5, 128.4, 128.1, 127.7, 127.4, 127.4, 127.1, 125.9, 125.8, 125.7, 110.5, 62.5, 51.5, 45.2, 44.1, 13.7. **HRMS**(ESI) m/z $(M+Na)^+$: calculated for

$C_{28}H_{24}O_5Na$: 463.1516, found: 463.1521 (**4o**); 463.1516 (**4o′**). **IR** (neat) cm^{-1}: **4o** 3057, 2961, 1725, 1673, 1510, 1259, 1072, 798, 748, 701; **4o′** 2962, 2921, 1725, 1673, 1510, 1260, 1072, 1024, 802, 749, 702.

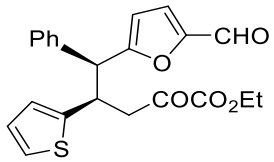
ethyl (4*R*,5*S*)-5-(5-formylfuran-2-yl)-4-(furan-2-yl)-2-oxo-5-phenylpentanoate (**4p**)



4p

The reaction was carried out following the general procedure to give two diastereoisomers with 68% yield and 74:26 dr. The major isomer **4p** was isolated as a light yellow oil; The minor isomer **4p′** was isolated as a light yellow solid (m.p. = 81 – 82 ℃). Enantiomeric excess was determined by UPC^2 using Chiralpak IG-3 column, CO_2/MeOH 95:5, flow rate 2mL/min, **4p**: 93%, t_{major} = 2.821 min, t_{minor} = 3.060 min; **4p′**: 88%, t_{minor} = 2.430 min, t_{major} = 2.690 min. $[\alpha]_D^{25}$ = -6.0 (c 1.0, AcOEt, **4p**); $[\alpha]_D^{25}$ = -48.0 (c 0.5, AcOEt, **4p′**). **^{1}H NMR** (600 MHz, $(CD_3)_2SO$) **4p** δ 9.41 (s, 1H), 7.43 (d, *J* = 7.8 Hz, 3H), 7.38–7.33 (m, 3H), 7.28 (t, *J* = 7.3 Hz, 1H), 6.56 (d, *J* = 3.6 Hz, 1H), 6.23 (dd, *J* = 3.1, 1.8 Hz, 1H), 6.07 (d, *J* = 3.1 Hz, 1H), 4.54 (d, *J* = 11.1 Hz, 1H), 4.18–4.13 (m, 1H), 4.11 (q, *J* = 7.1 Hz, 2H), 3.19 (dd, *J* = 17.3, 10.1 Hz, 1H), 2.84 (dd, *J* = 17.3, 4.0 Hz, 1H), 1.18 (t, *J* = 7.1 Hz, 3H); **4p′** δ 9.51 (s, 1H), 7.47 (d, *J* = 3.6 Hz, 1H), 7.36 (d, *J* = 1.1 Hz, 1H), 7.24–7.19 (m, 2H), 7.19 – 7.14 (m, 3H), 6.68 (d, *J* = 3.6 Hz, 1H), 6.14 (dd, *J* = 3.1, 1.8 Hz, 1H), 5.90 (d, *J* = 3.1 Hz, 1H), 4.55 (d, *J* = 9.9 Hz, 1H), 4.19 – 4.12 (m, 3H), 3.29 (dd, *J* = 17.6, 9.6 Hz, 2H), 3.06 (dd, *J* = 17.6, 4.3 Hz, 1H), 1.22 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (150 MHz, $(CD_3)_2SO$) **4p** δ 191.5, 177.5, 162.2, 159.7, 154.1, 151.4, 141.8, 138.6, 128.9, 128.4, 127.5, 110.2, 109.8, 106.8, 61.8, 48.8, 41.0, 37.8, 13.70; **4p′** δ 191.8, 178.2, 162.2, 160.2, 153.9, 152.3, 142.0, 139.0, 128.7, 127.5, 111.1, 110.5, 107.6, 62.2, 49.2, 41.6, 38.2, 14.1. **HRMS**(ESI) m/z $(M+Na)^+$: calculated for $C_{22}H_{20}O_6Na$: 403.1152, found: 403.1156 (**4p**); 403.1153(**4p′**). **IR** (neat) cm^{-1}: **4p** 2962, 2925, 1727, 1674, 1384, 1260, 1091, 1019, 799; **4p′** 2962, 2924, 1727, 1676, 1384, 1261, 1095, 1021, 799.

ethyl (4*R*,5*S*)-5-(5-formylfuran-2-yl)-2-oxo-5-phenyl-4-(thiophen-2-yl)pentanoate (**4q**)

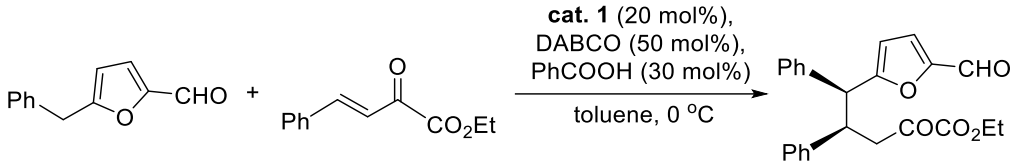


4q

The reaction was carried out following the general procedure to give two diastereoisomers with 61% yield and 73:27 dr. The major isomer **4q** was isolated as a light yellow solid (m.p. = 97 – 98 ℃); The minor isomer **4q′** was isolated as a yellow solid (m.p. = 95 – 96 ℃). Enantiomeric excess was determined by UPC^2 using Chiralpak IG-3 column, CO_2/MeOH 90:10, flow rate 2mL/min, **4q**: 83%, t_{minor} = 1.924 min, t_{major} = 2.152 min; **4q′**: 88%, t_{minor} = 1.778 min, t_{major} = 1.993 min. $[\alpha]_D^{26}$ = -9.0 (c 1.0, AcOEt, **4q**); $[\alpha]_D^{26}$ = -85.0 (c 1.0, AcOEt, **4q′**). **^{1}H NMR** (600 MHz, $(CD_3)_2SO$) **4q** δ 9.40 (s, 1H), 7.50 (d, *J* = 7.2 Hz, 2H), 7.37 (t, *J* = 7.7 Hz, 2H), 7.31 – 7.26 (m, 2H), 7.24 (dd, *J* = 5.0, 0.9 Hz, 1H), 6.94 (dd, *J* = 3.4, 0.8 Hz, 1H), 6.83 (dd, *J* = 5.0, 3.5 Hz, 1H), 6.55 (d, *J* = 3.6 Hz, 1H), 4.54 (d, *J* = 11.5 Hz, 1H), 4.35 (td, *J* = 10.8, 3.8

Hz, 1H), 4.09 (q, *J* = 7.1 Hz, 2H), 3.27 (dd, *J* = 17.5, 10.3 Hz, 1H), 2.87 (dd, *J* = 17.5, 3.8 Hz, 1H), 1.17 (t, *J* = 7.1 Hz, 3H); **4q′** δ 9.52 (s, 1H), 7.47 (d, *J* = 2.4 Hz, 1H), 7.23 (d, *J* = 7.7 Hz, 2H), 7.18 (dd, *J* = 14.6, 6.2 Hz, 3H), 7.12 (t, *J* = 7.1 Hz, 1H), 6.80–6.73 (m, 2H), 6.71 (d, *J* = 2.3 Hz, 1H), 4.56 (d, *J* = 10.5 Hz, 1H), 4.35 (td, *J* = 9.9, 3.7 Hz, 1H), 4.14 (q, *J* = 7.0 Hz, 2H), 3.41–3.35 (m, 1H), 3.11 (dd, *J* = 17.6, 3.2 Hz, 1H), 1.23–1.18 (m, 3H). **^{13}C NMR** (150 MHz, $(CD_3)_2SO$) **4q** δ 192.1, 177.9, 162.7, 160.2, 151.6, 145.1, 139.5, 129.4, 128.8, 127.9, 127.0, 125.8, 124.7, 110.6, 62.2, 52.0, 44.5, 14.1; **4q′** δ 191.7, 178.2, 162.3, 160.3, 152.2, 144.4, 139.1, 128.9, 128.7, 127.4, 126.8, 126.0, 124.7, 111.2, 62.2, 51.4, 44.8, 14.1. **HRMS**(ESI) m/z $(M+Na)^+$: calculated for $C_{22}H_{20}O_5SNa$: 419.0924, found: 419.0928 (**4q**); 419.0925 (**4q′**). **IR** (neat) cm^{-1}: **4q** 2962, 2924, 1725, 1673, 1259, 1068, 1022, 799, 764, 701; **4q′** 2962, 2925, 1724, 1673, 1509, 1384, 1260, 1068, 1020, 798, 696.

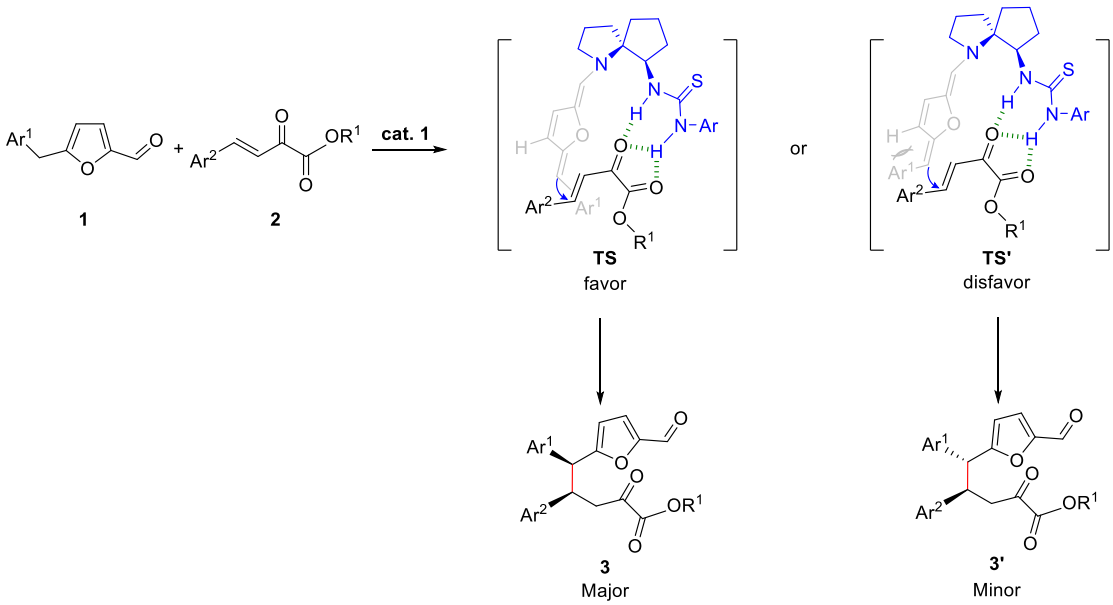
4. Gram-scale reaction of 3a



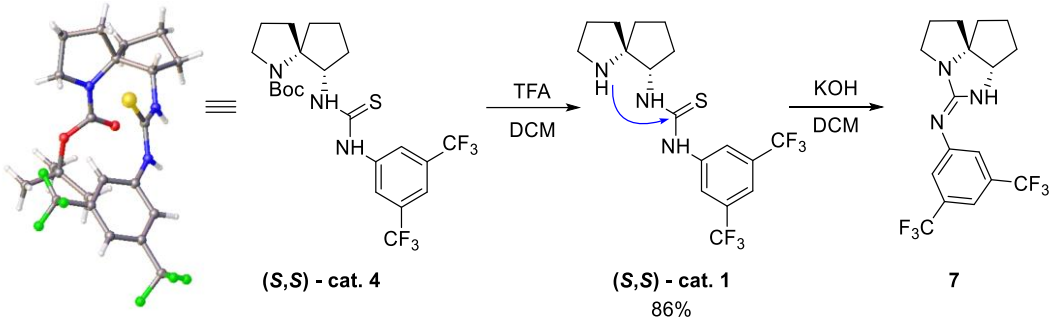
1a **2a** **3a**

To a solution of 5-benzylfurfurals **1a** (1.4 g, 7.5 mmol, 1.5 equiv), **cat. 1** (1 mmol, 0.2 equiv), DABCO (2.5 mmol, 0.5 equiv) and PhCOOH (1.5 mmol, 0.3 equiv) in toluene (60 mL) at 0 °C, *β,γ*-unsaturated *α*-ketoesters **2a** (1.0 g, 5 mmol, 1.0 equiv) was added and the reaction mixture was stirred at the same temperature until **2a** disappeared by TLC detection. The solution was quenched with H_2O (20 mL), extracted by AcOEt (20 mL ×3). The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, and evaporated under reduced pressure. The residue was purified by flash chromatography on silica gel (petroleum ether:EtOAc = 15:1 or 3:1) to afford compound **3a** (1.4g, 74% yield, 81:19 dr, 97/87% ee).

5. Plausible reaction mechanism



A trienamine intermediate would be formed by reaction of the secondary amine of the catalyst with the furfural. **3** was obtained by intermediate **TS**, and **3′** was obtained by intermediate **TS′**. Due to the steric hindrance of **TS′**, **3** was easier to obtain as the major product than **3′**. In addition, PhCOOH was required to activate the carbonyl group for the attack by an amine catalyst, and DABCO might act as a base to help remove the benzylic proton of the resulting iminium ion intermediate, which could generate the active dearomative trienamine species.



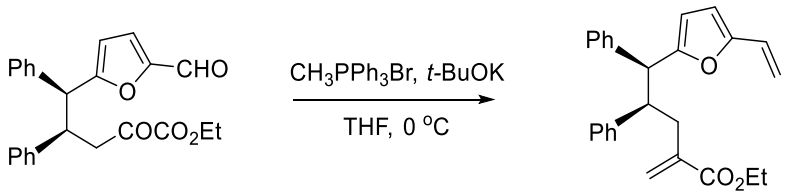
(*S*,*S*) - cat. 4 **(*S*,*S*) - cat. 1** **7**

86%

The structure of the novel SPD-bifunctional thiourea **cat. 1** was then determined by X-ray analysis of the single crystal of **cat. 4**. Interestingly, after deprotection of the Boc group, an intramolecular condensation could take place in DCM in the presence of a strong base to produce guanidine **7** with the loss of H_2S, which also demonstrates the proximity of the secondary amine moiety with the thiourea that might exert additional benefit for a highly enantioselective reaction process.

6. Product derivatization

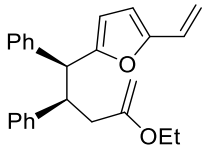
6.1 product derivatization



3a **5**

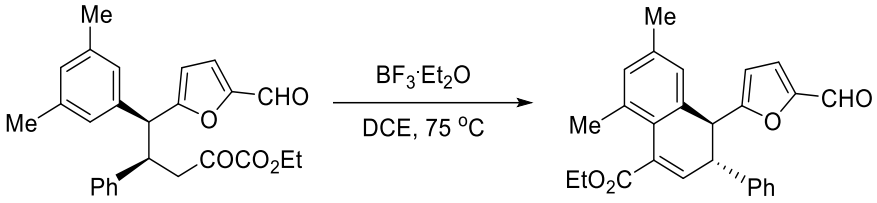
To a solution of CH_3PPh_3Br (201.5 mg, 2.2 equiv) in THF (5 mL) was added *t*-BuOK (63.0 mg, 2.2 equiv) at 0 ºC, and the reaction mixture was stirred for 30 minutes at the room temperature. Then the reaction mixture was cooled to 0 ℃, the reaction mixture was added drop by drop to a solution of **3a** (100.0 mg, 1.0 equiv) in THF (5 mL), and **3a** disappeared via TLC detection after 5 minutes. The solution was quenched with icy H_2O (10 mL), extracted by AcOEt (15 mL×3). The combined organic layer was washed with brine (20 mL), dried over anhydrous Na_2SO_4, and evaporated under reduced pressure. The residue was purified by flash chromatography on silica gel (petroleum ether:EtOAc = 20:1) to afford compound **5** as a colorless oil (79.5 mg, 80% yield, 95% ee).

2-((1*S*,2*R*)-4-ethoxy-1,2-diphenylpent-4-en-1-yl)-5-vinylfuran (**5**)



5

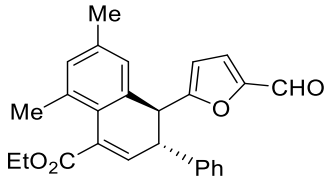
Enantiomeric excess of **5** was determined by UPC^2 using Trefoil^{TM} CEL2 column, CO_2/MeOH 98:2, flow rate 2mL/min, 95%, t_{major} = 2.051 min, t_{minor} = 2.446 min. $[\alpha]_D^{20}$ = + 28.0 (c 1.0, AcOEt). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.47–7.42 (m, 2H), 7.38 – 7.31 (m, 2H), 7.18 (t, *J* = 7.3 Hz, 2H), 7.12–7.05 (m, 3H), 6.30 (dd, *J* = 17.5, 11.2 Hz, 1H), 5.88 (dd, *J* = 11.3, 2.2 Hz, 2H), 5.76 (d, *J* = 3.2 Hz, 1H), 5.46 (dd, *J* = 17.5, 1.3 Hz, 1H), 5.09 (s, 1H), 5.00 (dd, *J* = 11.2, 1.4 Hz, 1H), 4.17–4.05 (m, 3H), 3.70 (td, *J* = 11.2, 3.8 Hz, 1H), 2.63 (dd, *J* = 13.9, 3.3 Hz, 1H), 2.39 (dd, *J* = 13.9, 11.6 Hz, 1H), 1.23 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.9, 155.6, 151.6, 142.0, 140.7, 138.3, 128.6, 128.5, 128.3, 127.9, 126.8, 126.8, 126.2, 125.0, 110.7, 108.6, 108.0, 60.4, 52.4, 49.0, 36.9, 14.1. **HRMS**(ESI) m/z $(M+Na)^+$: calculated for $C_{26}H_{26}O_3Na$: 409.1774, found: 409.1780; **IR** (neat) cm^{-1}: 3028, 2926, 1712, 1384, 1187, 1024, 700.



3m **6**

To a solution of **3m** (37.4 mg, 1.0 equiv) in DCE (2 mL) was added $BF_3{\cdot}Et_2O$ (22 μL, 2.0 equiv) at 0 °C, then the reaction mixture was stirred at 75 °C until the substrate disappeared via TLC detection. The solution was cooled to room temperature and quenched with H_2O (5 mL), extracted by DCM (10 mL×3). The combined organic layer was washed with brine (10 mL), dried over anhydrous Na_2SO_4, and evaporated under reduced pressure. The residue was purified by flash chromatography on silica gel (petroleum ether:EtOAc = 10:1) to afford compound **6** as a colorless oil (28 mg, 79% yield, 90% ee).

ethyl(3*R*,4*S*)-4-(5-formylfuran-2-yl)-6,8-dimethyl-3-phenyl-3,4-dihydronaphthalene-1-carboxylate (**6**)

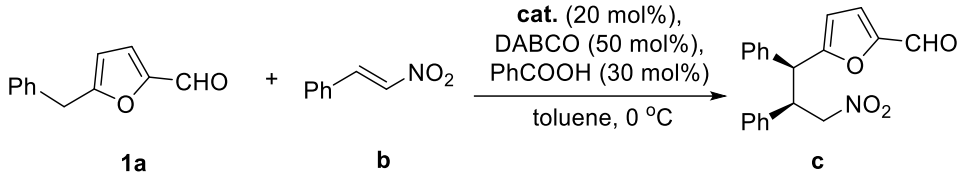


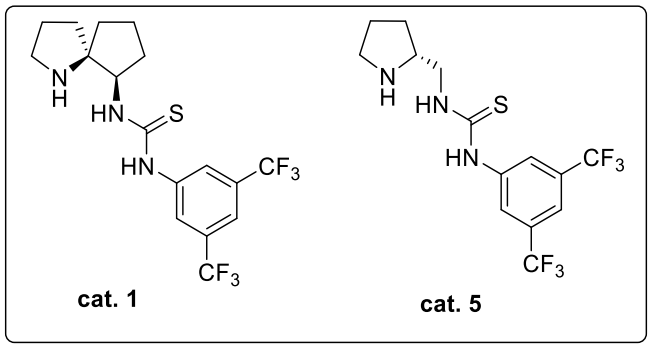
6

Enantiomeric excess of **6** was determined by UPC^2 using Chiralpak IG-3 column, CO_2/MeOH 90:10, flow rate 2mL/min, 90%, t_{major} = 1.642 min, t_{minor} = 2.364 min. $[\alpha]_D^{20}$ = -160.0 (c 1.0, AcOEt). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.54 (s, 1H), 7.24–7.16 (m, 3H), 7.15–7.10 (m, 2H), 7.08 (d, *J* = 3.6 Hz, 1H), 6.96 (s, 1H), 6.74 (d, *J* = 5.5 Hz, 1H), 6.54 (s, 1H), 6.06 (d, *J* = 3.5 Hz, 1H), 4.34 – 4.27 (m, 3H), 4.17 (t, *J* = 6.0 Hz, 1H), 2.28 (s, 3H), 2.21 (s, 3H),

1.34 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δδ 177.2, 168.5, 162.7, 152.1, 139.5, 138.3, 136.8, 134.6, 134.5, 134.22, 131.7, 128.5, 127.8, 127.6, 127.1, 126.7, 111.4, 61.1, 47.5, 44.3, 21.1, 21.0, 14.1. **^{13}C DEPT^{135} NMR** (100 MHz, $CDCl_3$) δ 177.2, 136.8, 131.7, 128.5, 127.8, 127.1, 126.7, 111.4, 61.1, 47.5, 44.3, 21.1, 21.0, 14.1. **HRMS**(ESI) m/z $(M+H)^+$: calculated for $C_{26}H_{25}O_4$: 401.1747, found: 401.1737; **IR** (neat) cm^{-1}: 2980, 1720, 1679, 1510, 1240, 1193, 1049, 804, 700.

6.2 Reaction expansion

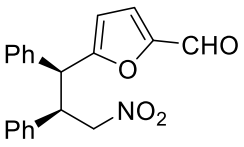




entry	solvent	**cat.**	additive	temp (°C)	yield (%)	dr	ee(%)
1	toluene	**cat. 1**	DABCO/ PhCOOH	0	98	53:47	major: 96 minor: 74
2	toluene	**cat. 5**	DABCO/ PhCOOH	0	96	78:22	major: 96 minor: 73

To a solution of 5-benzylfurfural **1a** (0.225 mmol, 1.5 equiv), **cat.** (0.03 mmol, 0.2 equiv), DABCO (0.075 mmol, 0.5 equiv) and PhCOOH (0.045 mmol, 0.3 equiv) in toluene (1.8 mL) at 0 °C, nitroalkene **b** (0.15 mmol, 1.0 equiv) was added, and the reaction mixture was stirred at the same temperature until **b** disappeared by TLC detection. The solution was then quenched with H_2O (2 mL), extracted by AcOEt (10 mL×3). The combined organic layer was washed with brine (10 mL), dried over anhydrous Na_2SO_4, and evaporated under reduced pressure. The residue was purified by flash chromatography on silica gel (petroleum ether:EtOAc = 10:1 to 3:1) to afford compound **c**.

Asymmetric conjugate addition of 5-benzylfurfurals with nitroalkene has been investigated by using **cat.1** and **cat.5**. Under our optimal conditions, the reaction catalysed by **cat. 1** can produce **c** in 98% yield with lower diastereoselectivities (dr = 53:47) and similar enantioselectivities (96%/74%).

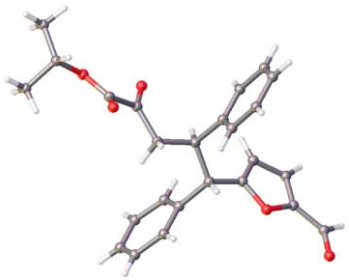


c

The reaction was carried out following the general procedure to give two diastereoisomers with 98% yield and 53:47 dr. Enantiomeric excess of major isomer **c** was determined by UPC^2 using Chiralpak AD-3 column, CO_2/MeOH 95:5, flow rate 2mL/min, 96%, t_{minor} = 2.799 min, t_{major} = 3.236 min; Enantiomeric excess of minor isomer **c′** was determined by UPC^2 using Chiralpak IG-3 column, CO_2/MeOH 95:5, flow rate 2mL/min, 74%, t_{minor} = 3.777 min, t_{major} = 4.136 min. **^{1}H NMR** (400 MHz, $CDCl_3$) **c** δ 9.62 (s, 1H), 7.23–7.10 (m, 9H), 7.02 (d, *J* = 7.0 Hz, 2H), 6.45 (d, *J* = 3.6 Hz, 1H), 4.78 (dd, *J* = 12.9, 9.5 Hz, 1H), 4.63 (dd, *J* = 12.9, 4.7 Hz, 1H), 4.48 – 4.30 (m, 2H); **c′** δ 9.44 (s, 1H), 7.49 (d, *J* = 7.3 Hz, 2H), 7.41 (t, *J* = 7.4 Hz, 2H), 7.34 (t, *J* = 7.3 Hz, 1H), 7.29–7.15 (m, 5H), 6.93 (d, *J* = 3.6 Hz, 1H), 6.11 (d, *J* = 3.6 Hz, 1H), 4.67–4.49 (m, 1H), 4.46–4.26 (m, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) **c** δ 177.2, 160.8, 152.5, 137.1, 136.5, 128.7, 128.4, 127.9, 127.9, 127.6, 110.9, 78.6, 49.2, 48.3; **c′** δ 177.0, 160.7, 152.0, 137.3, 137.1, 129.5, 128.9, 128.4, 128.1, 128.1, 127.6, 110.2, 78.9, 49.7, 48.0.

7. Single crystal X-ray diffraction data for 4b, cat. 4, and 7

7.1 X-Ray of 4b



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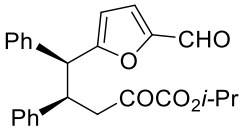


4b

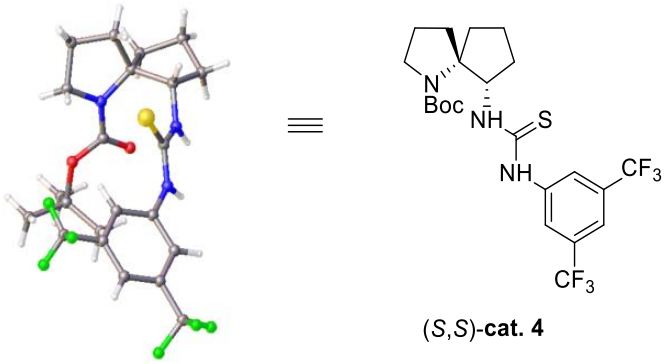
Table S1. Crystal data and structure refinement for 4b (CCDC 2048401)

dentification code	4b
Empirical formula	$C_{25}H_{24}O_5$
Formula weight	404.44
Temperature/K	293(2)
Crystal system	orthorhombic
Space group	P212121
a/Å	6.1221(4)
b/Å	16.6749(15)
c/Å	21.0774(18)
α/°	90
β/°	90
γ/°	90

Volume/Å3	2151.7(3)
Z	4
ρcalcg/cm3	1.248
μ/mm-1	0.703
F(000)	856.0
Crystal size/mm3	0.15 × 0.06 × 0.04
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/ °	8.39 to 133.196
Index ranges	-5 ≤ h ≤ 7, -19 ≤ k ≤ 19, -25 ≤ l ≤ 24
Reflections collected	11429
Independent reflections	3799 [Rint = 0.0296, Rsigma = 0.0353]
Data/restraints/parameters	3799/0/273
Goodness-of-fit on F2	1.024
Final R indexes [I>=2σ (I)]	R1 = 0.0438, wR2 = 0.1028
Final R indexes [all data]	R1 = 0.0577, wR2 = 0.1157
Largest diff. peak/hole / e Å-3	0.13/-0.16
Flack parameter	0.06(13)

7.2 X-Ray of cat. 4

Cat. 4 was determined by X-ray analysis of the single crystal of (*S*,*S*)-**cat.4** which was synthesized from (*S*,*S*)-**S3** material.



(*S*,*S*)-**cat. 4**

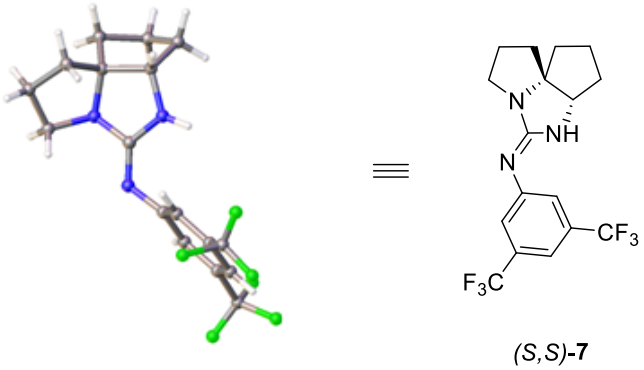
Table S2. Crystal data and structure refinement for cat. 4 (CCDC 2048402)

Identification code	xumh_0110
Empirical formula	$C_{22}H_{27}F_6N_3O_2S$
Formula weight	511.52
Temperature/K	293.58(10)
Crystal system	orthorhombic
Space group	P212121
a/Å	8.8909(2)

b/Å	12.4974(3)
c/Å	22.9357(6)
α/°	90
β/°	90
γ/°	90
Volume/Å3	2548.46(11)
Z	4
ρcalcg/cm3	1.333
μ/mm-1	1.739
F(000)	1064.0
Crystal size/mm3	0.14 × 0.07 × 0.05
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	8.056 to 133.176
Index ranges	-10 ≤ h ≤ 7, -14 ≤ k ≤ 14, -21 ≤ l ≤ 27
Reflections collected	8895
Independent reflections	4515 [Rint = 0.0245, Rsigma = 0.0357]
Data/restraints/parameters	4515/0/364
Goodness-of-fit on F2	1.027
Final R indexes [I>=2σ (I)]	R1 = 0.0389, wR2 = 0.0915
Final R indexes [all data]	R1 = 0.0489, wR2 = 0.0998
Largest diff. peak/hole / e Å-3	0.11/-0.13
Flack parameter	0.002(11)

7.3 X-Ray of 7

7 was determined by X-ray analysis of the single crystal of (*S*,*S*)-**7** which was synthesized from (*S*,*S*)-**S3** material.



(S,S)-**7**

Table S3. Crystal data and structure refinement for (*S*,*S*)-7 (CCDC 2048404)

Identification code	7

Empirical formula	$C_{17}H_{17}F_6N_3$
Formula weight	377.33
Temperature/K	294.03(15)
Crystal system	hexagonal
Space group	P61
a/Å	12.0427(3)
b/Å	12.0427(3)
c/Å	22.0973(6)
α/°	90
β/°	90
γ/°	120
Volume/Å3	2775.36(17)
Z	6
ρcalcg/cm3	1.358
μ/mm-1	1.091
F(000)	1170.0
Crystal size/mm3	0.18 × 0.15 × 0.12
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	8.478 to 139.658
Index ranges	-11 ≤ h ≤ 14, -8 ≤ k ≤ 11, -26 ≤ l ≤ 26
Reflections collected	6679
Independent reflections	3199 [Rint = 0.0297, Rsigma = 0.0345]
Data/restraints/parameters	3199/85/325
Goodness-of-fit on F2	1.058
Final R indexes [I>=2σ (I)]	R1 = 0.0471, wR2 = 0.1121
Final R indexes [all data]	R1 = 0.0621, wR2 = 0.1292
Largest diff. peak/hole / e Å-3	0.12/-0.18
Flack parameter	0.28(12)

8. References

1 (a) A. Skrzyńska, A. Przydacz and Ł. Albrecht, *Org. Lett.*, 2015, **17**, 5682-5685; (b) D. S. Ryabukhin, D. N. Zakusilo, M. O. Kompanets, A. A. Tarakanov, I. A. Boyarskaya, T. O. Artamonova, M. A. Khohodorkovskiy, I. O. Opeida and A. V. Vasilyev, *Beilstein J. Org. Chem.*, 2016, **12**, 2125-2135; (c) Y.-L. Su, Z.-Y. Han, Y.-H. Li and L.-Z. Gong, *ACS Catal.*, 2017, **7**, 7917-7922.

2 (a) Y.-C. Wu, L. Liu, H.-J. Li, D. Wang and Y.-J. Chen, *J. Org. Chem.*, 2006, **71**, 6592-

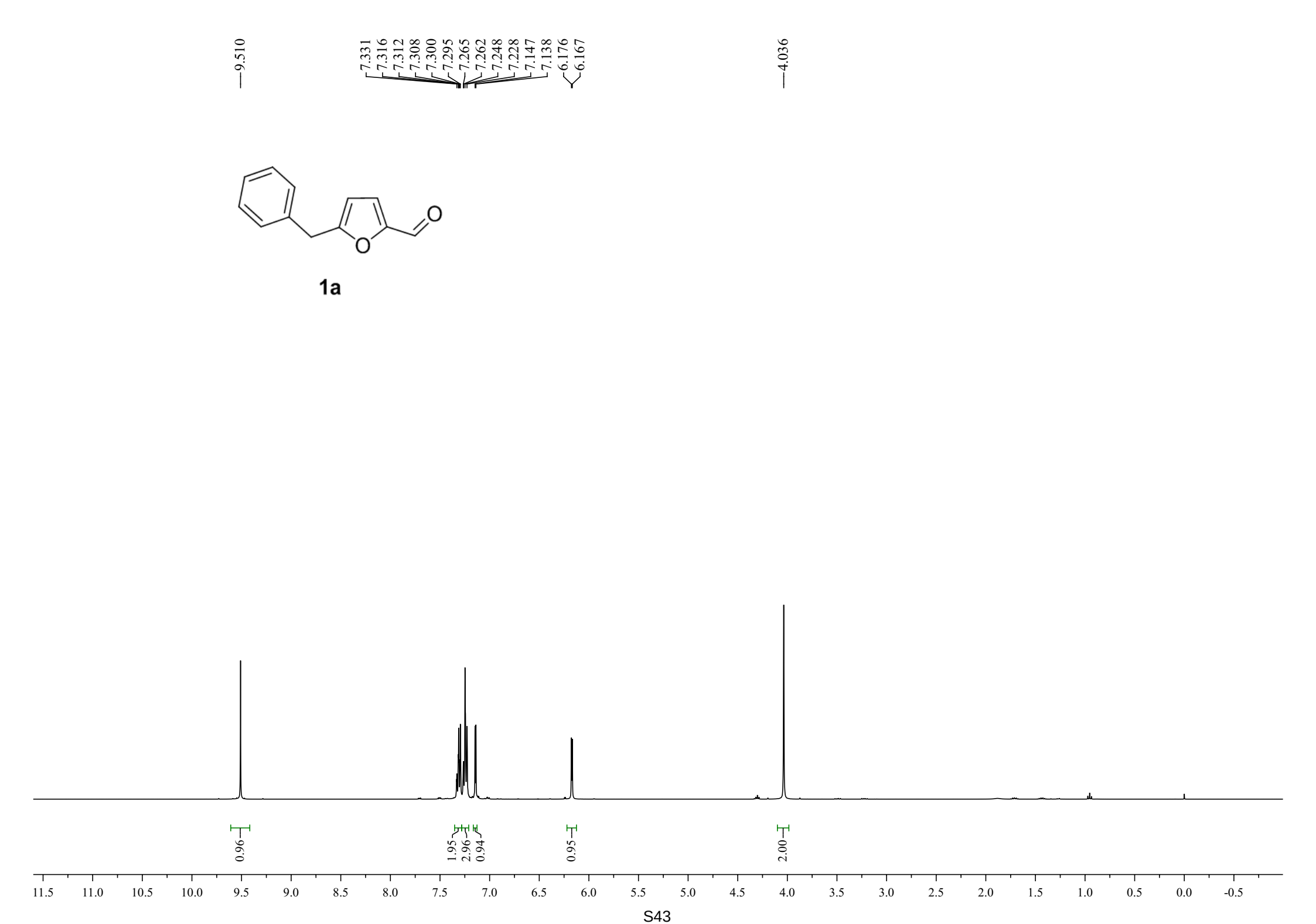
6595; (b) P. Xing, W. Zang, Z.-G. Huang, Y.-X. Zhan, C.-J. Zhu and B. Jiang, *Synlett*, 2012, **23**, 2269-2273; (c) M. Dajek , A. Pruszczyńska, K. A. Konieczny and R. Kowalczyk, *Adv. Synth. Catal.*, 2020, **362**, 3613-3620; (d) M. Espinosa, A. Garc á-Ortiz, G. Blay, L. Cardona, M. C. Muñoz and J. R. Pedro, *RSC Adv.*, 2016, **6**, 15655; (e) Q. Meng, L. Zhu and Z. Zhang, *J. Org. Chem.*, 2008, **73**, 7209-7212.

3 J.-M. Tian, Y.-H. Yuan, Y.-Q. Tu, F.-M. Zhang, X.-B. Zhang, S.-H. Zhang, S.-H. Wang and X.-M. Zhang, *Chem. Commun.*, 2015, **51**, 9979-9982.

4 Y.-H. Yuan, X. Han, F.-P. Zhu, J.-M. Tian, F.-M. Zhang, X.-M. Zhang, Y.-Q. Tu, S.-H. Wang and X. Guo, *Nat. Commun.*, 2019, **10**, 3394.

5 C.-L. Cao, M.-C. Ye, X.-L. Sun and Y. Tang, *Org. Lett.*, 2006, **8**, 2901-2904.

9. Copies of NMR spectra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7.138
6.176
6.167
4.036
O
O
1a
0.96
1.95
2.96
0.94
0.95
2.00
11.5
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
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3.5
3.0
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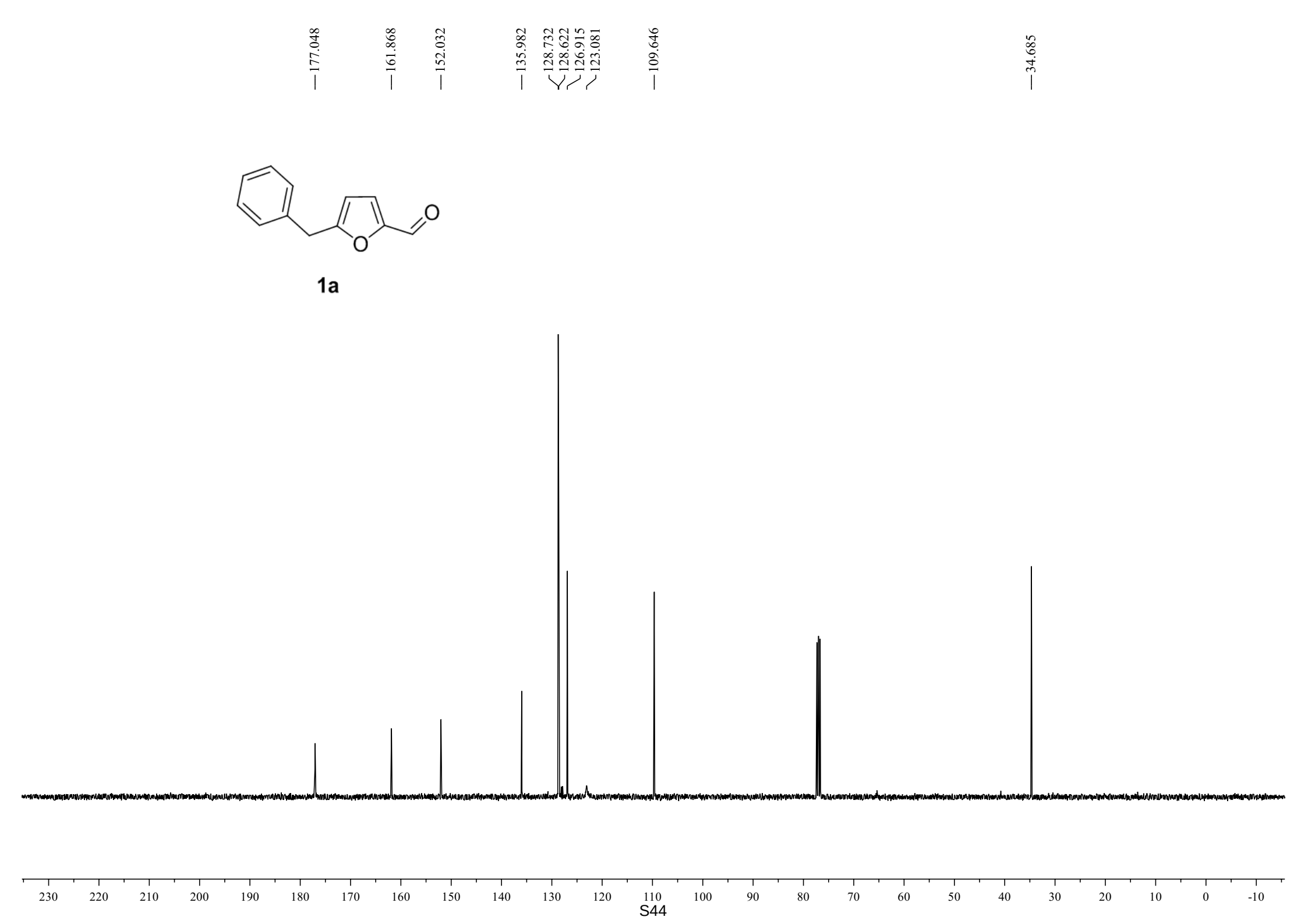
2.0
1.5
1.0
0.5
0.0
-0.5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1a
230
220
210
200
190
180
170
160
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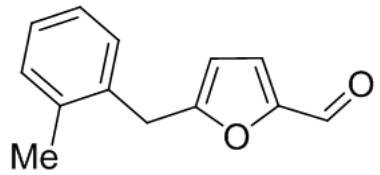
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10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O
O

1b

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6.040
4.019
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0.95
4.89
0.96
2.00
2.98
12.0
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11.0
10.5
10.0
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8.0
7.5
7.0
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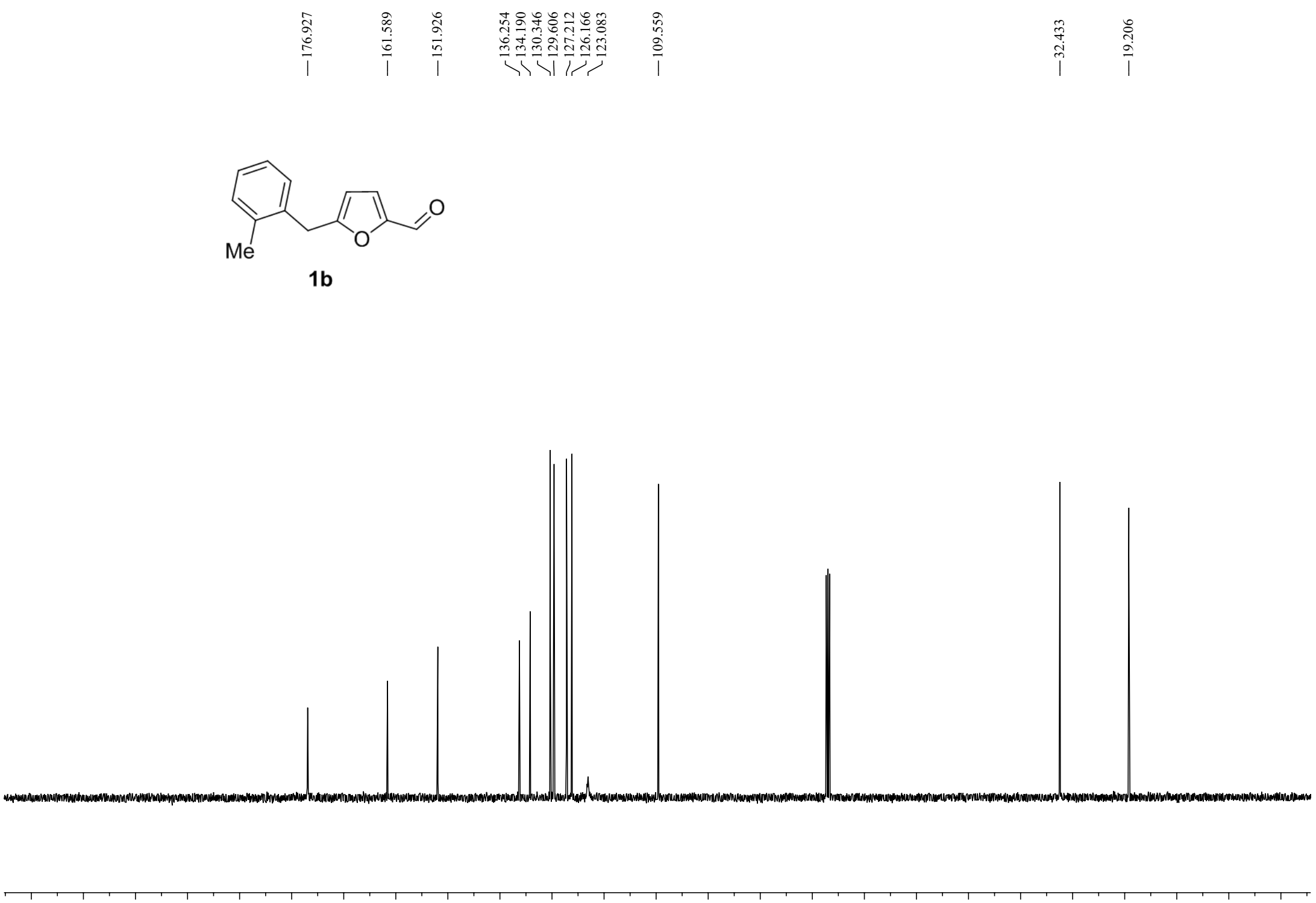
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200
190
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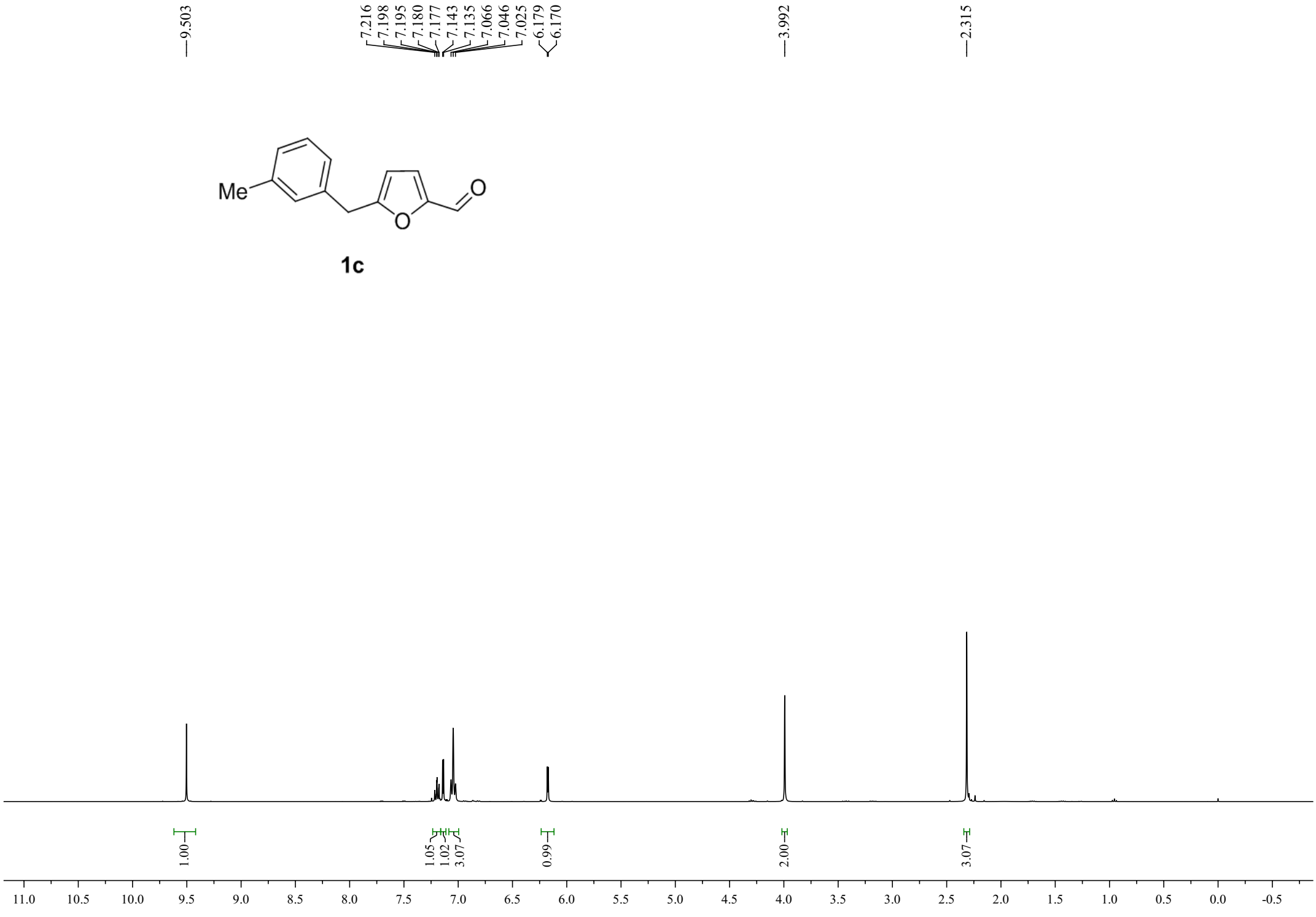
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2.315
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O
1c
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1.05
1.02
3.07
0.99
2.00
3.07
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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1.5
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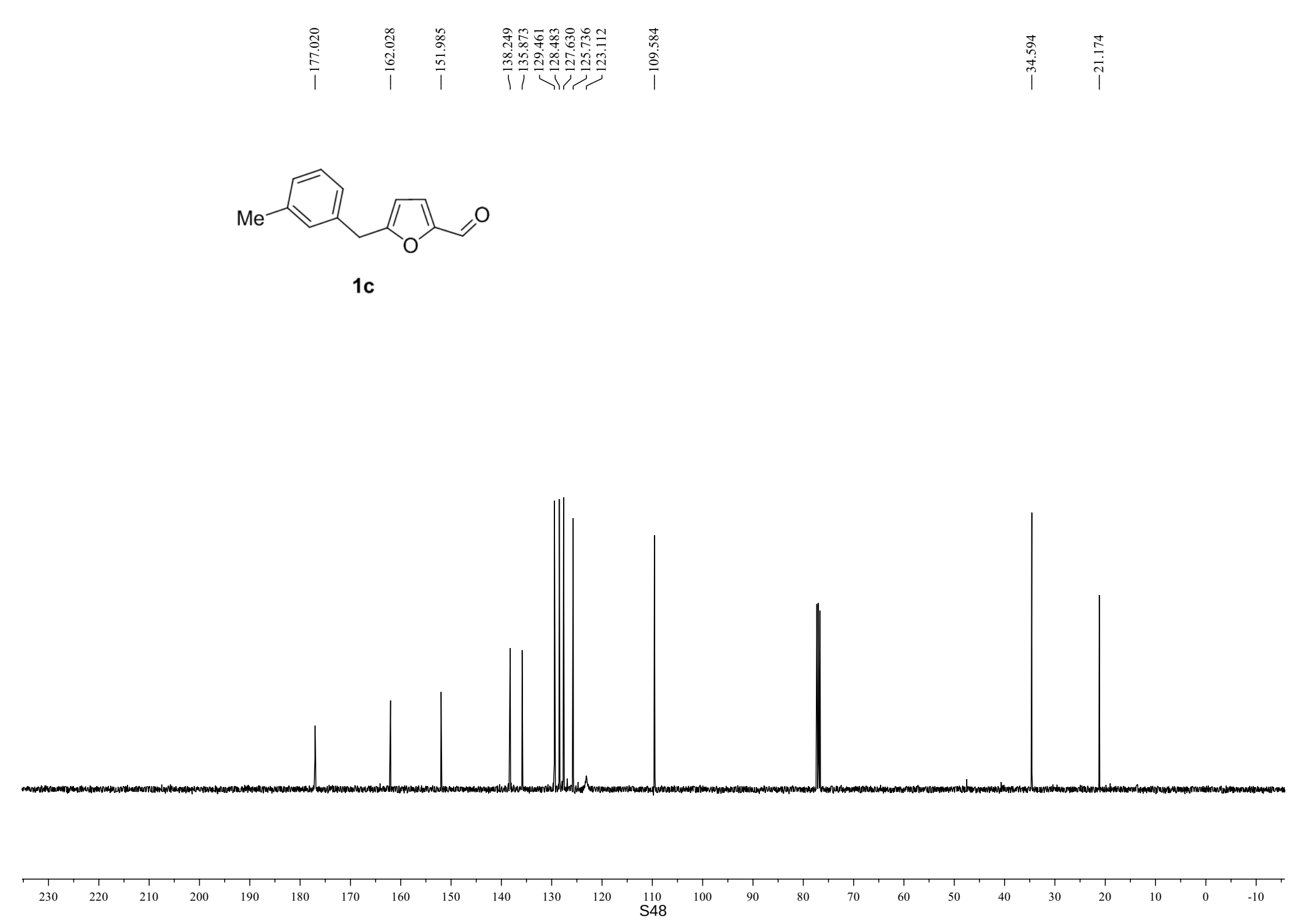
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230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
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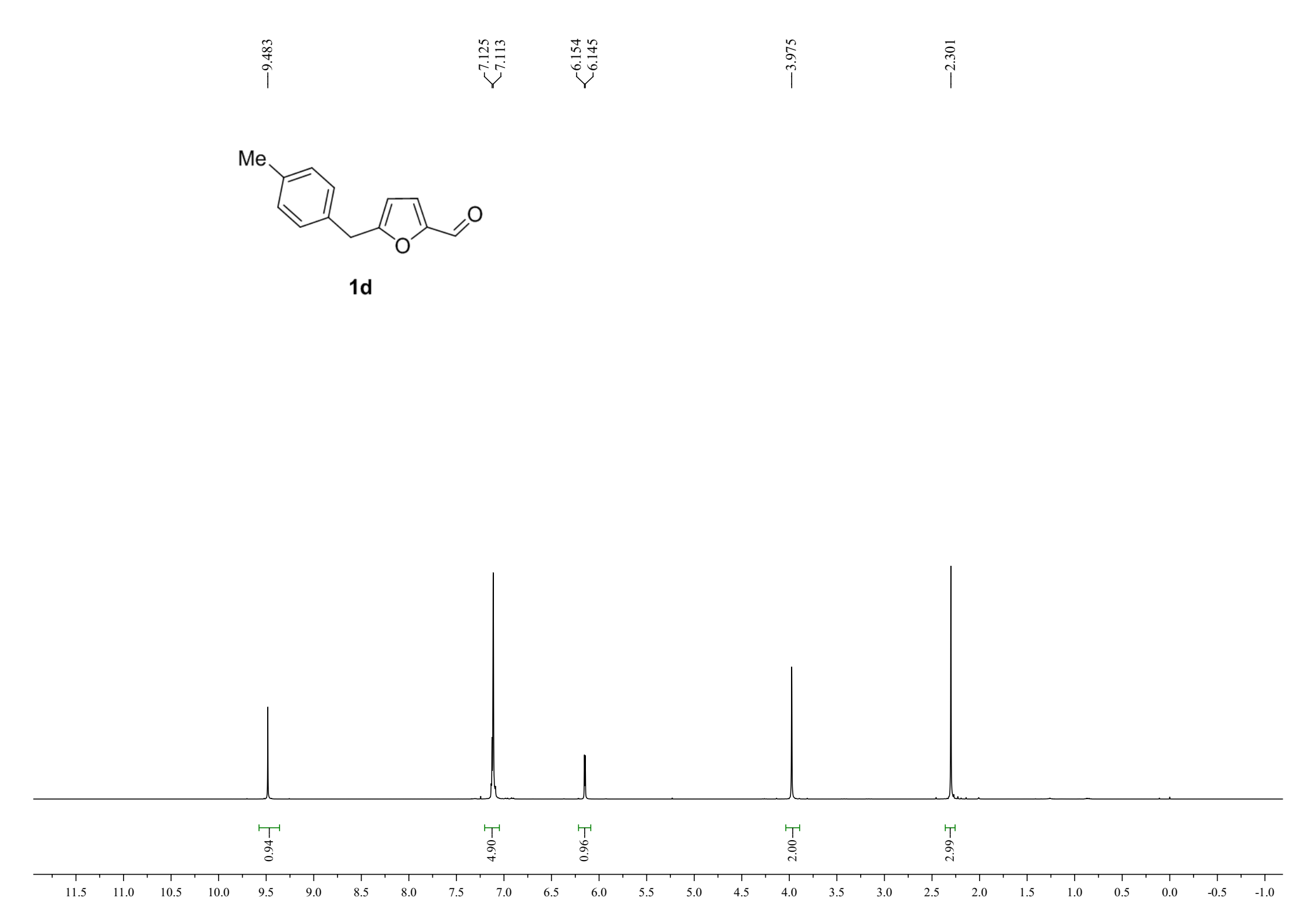
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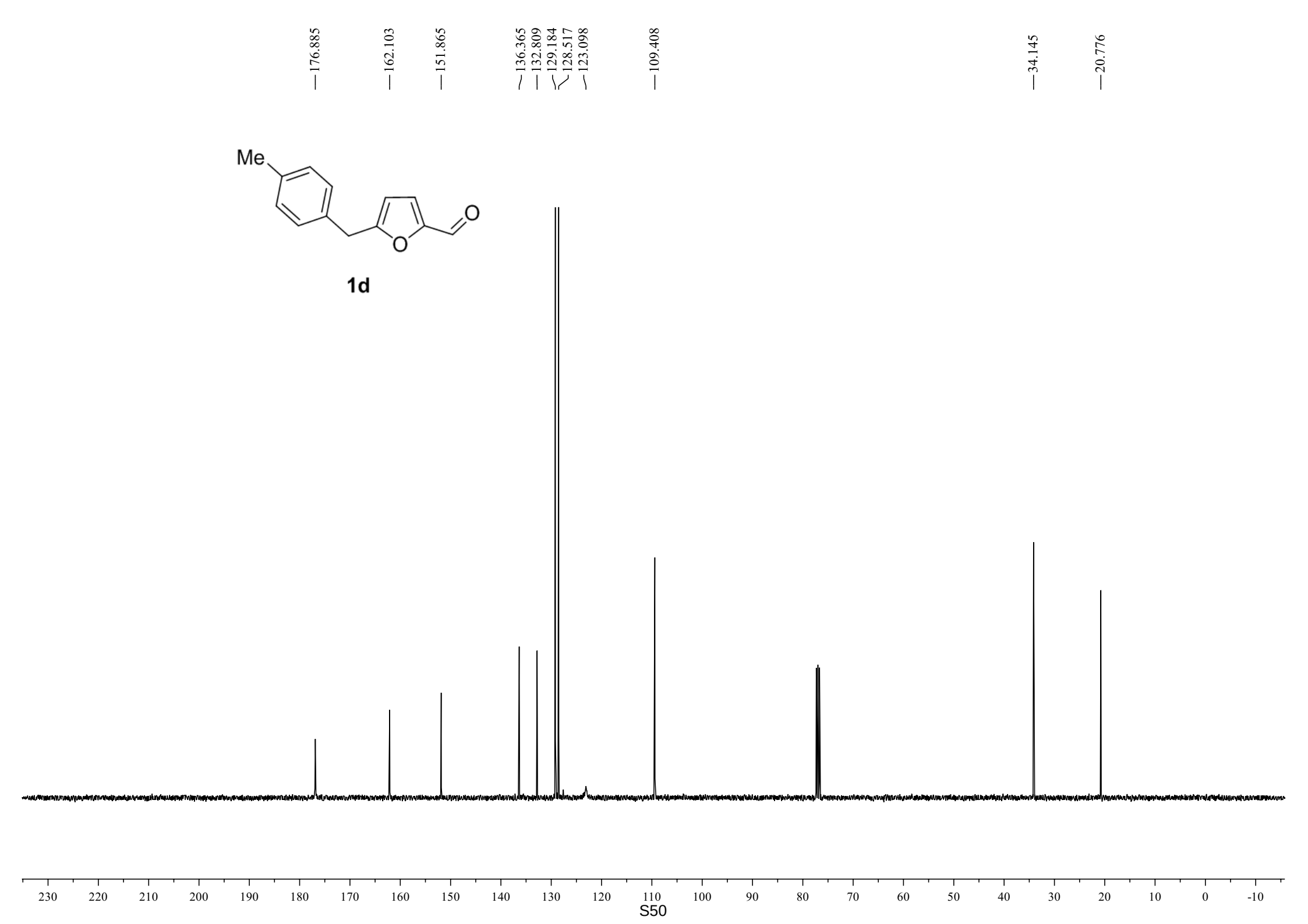
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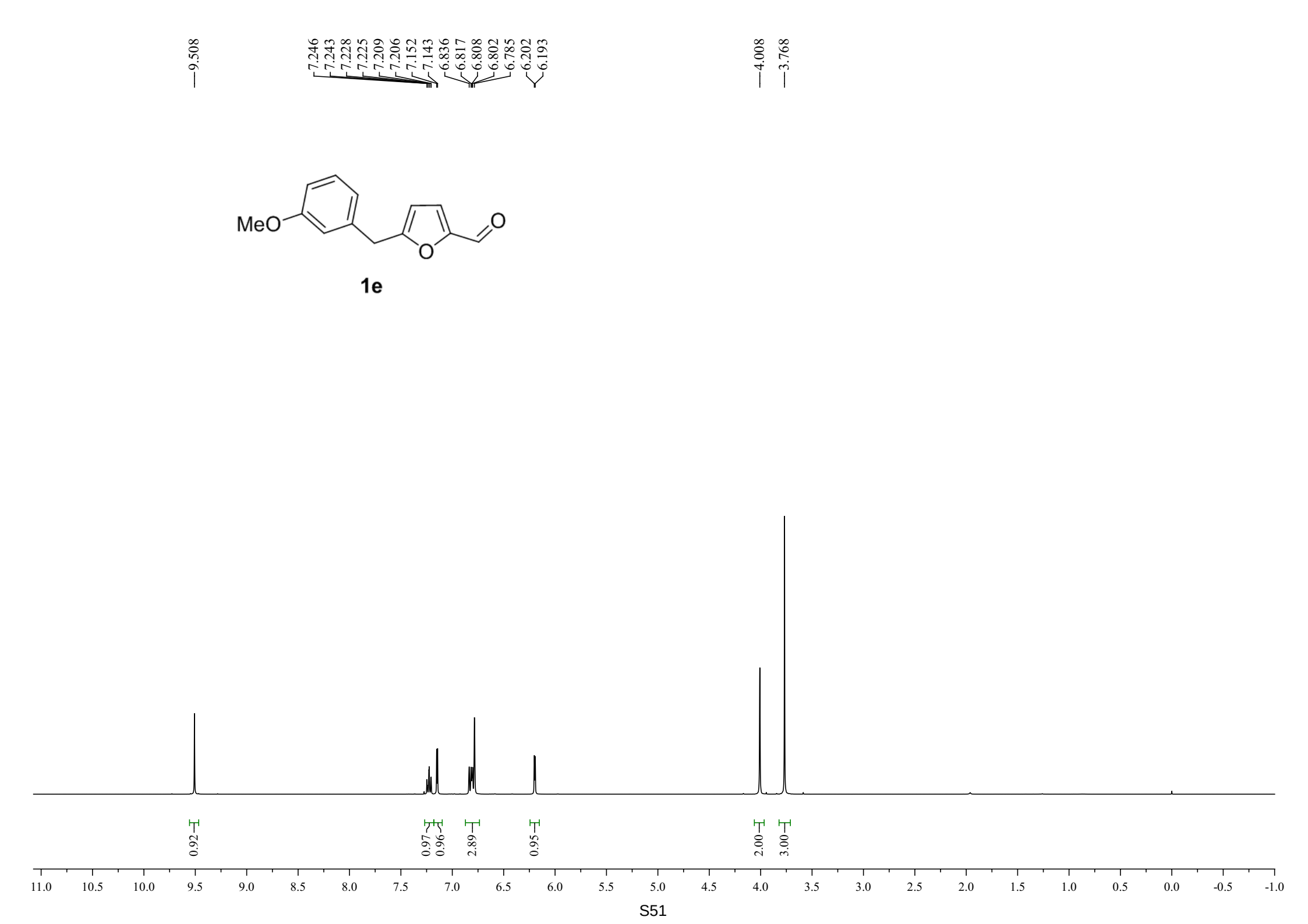
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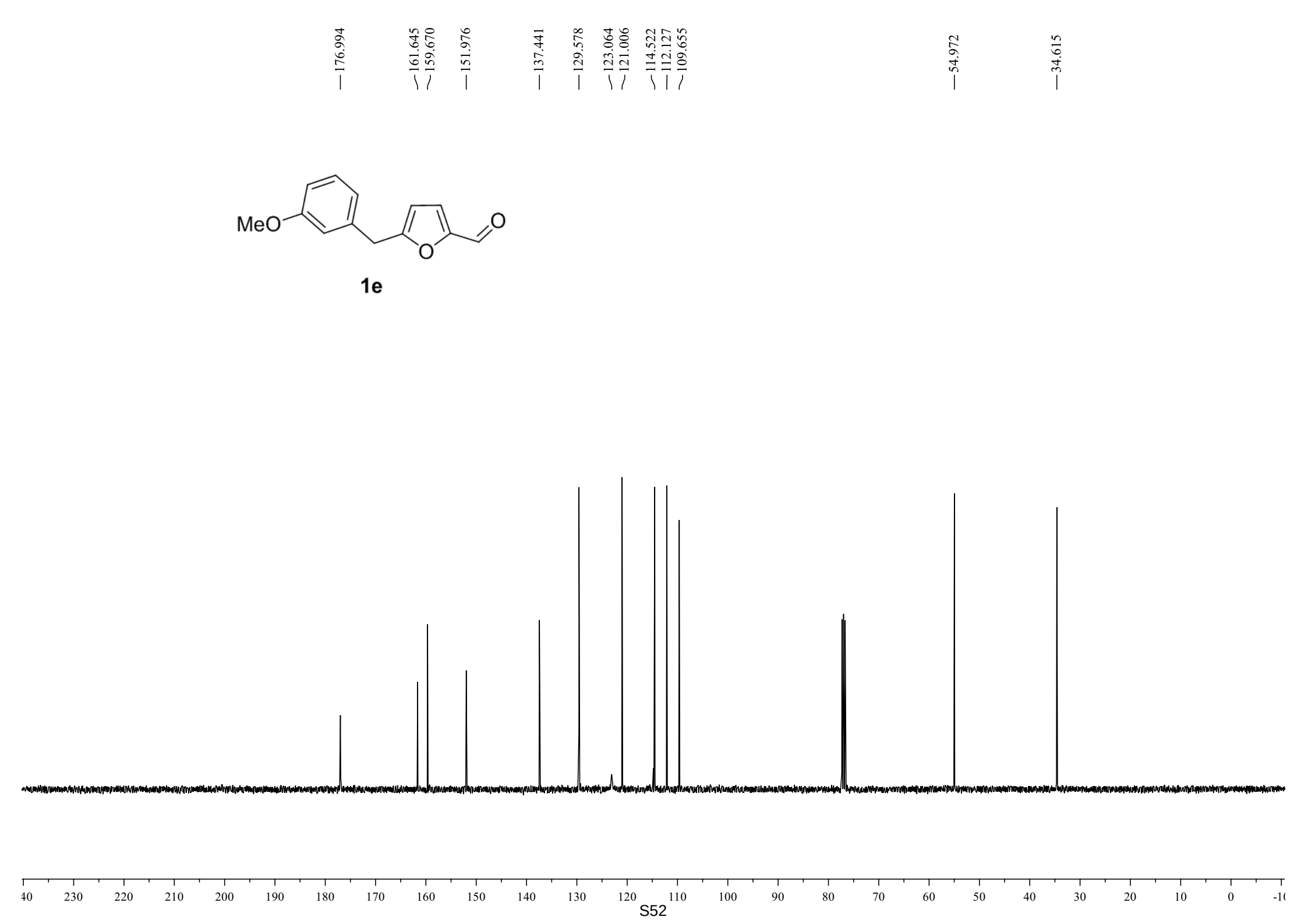
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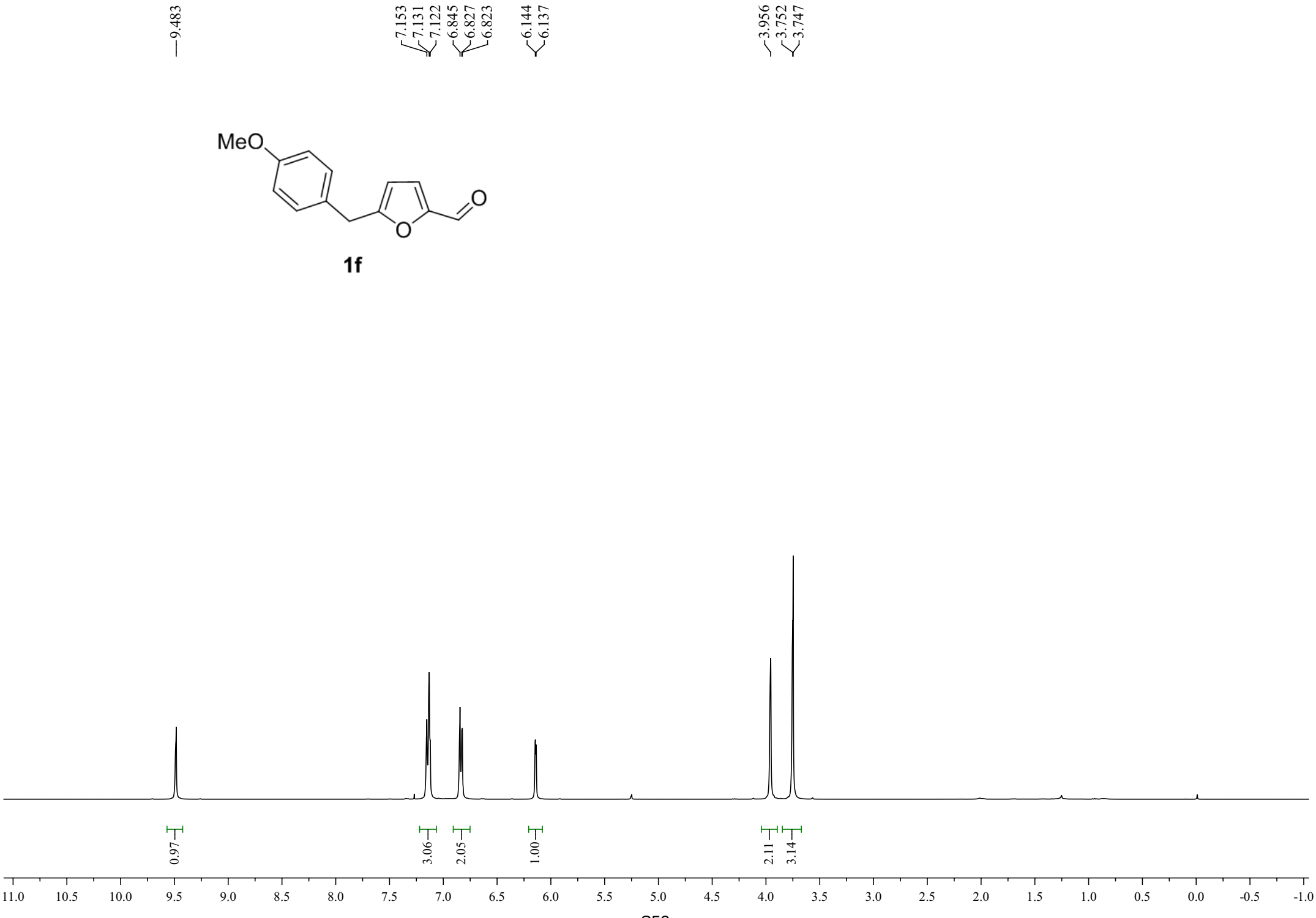
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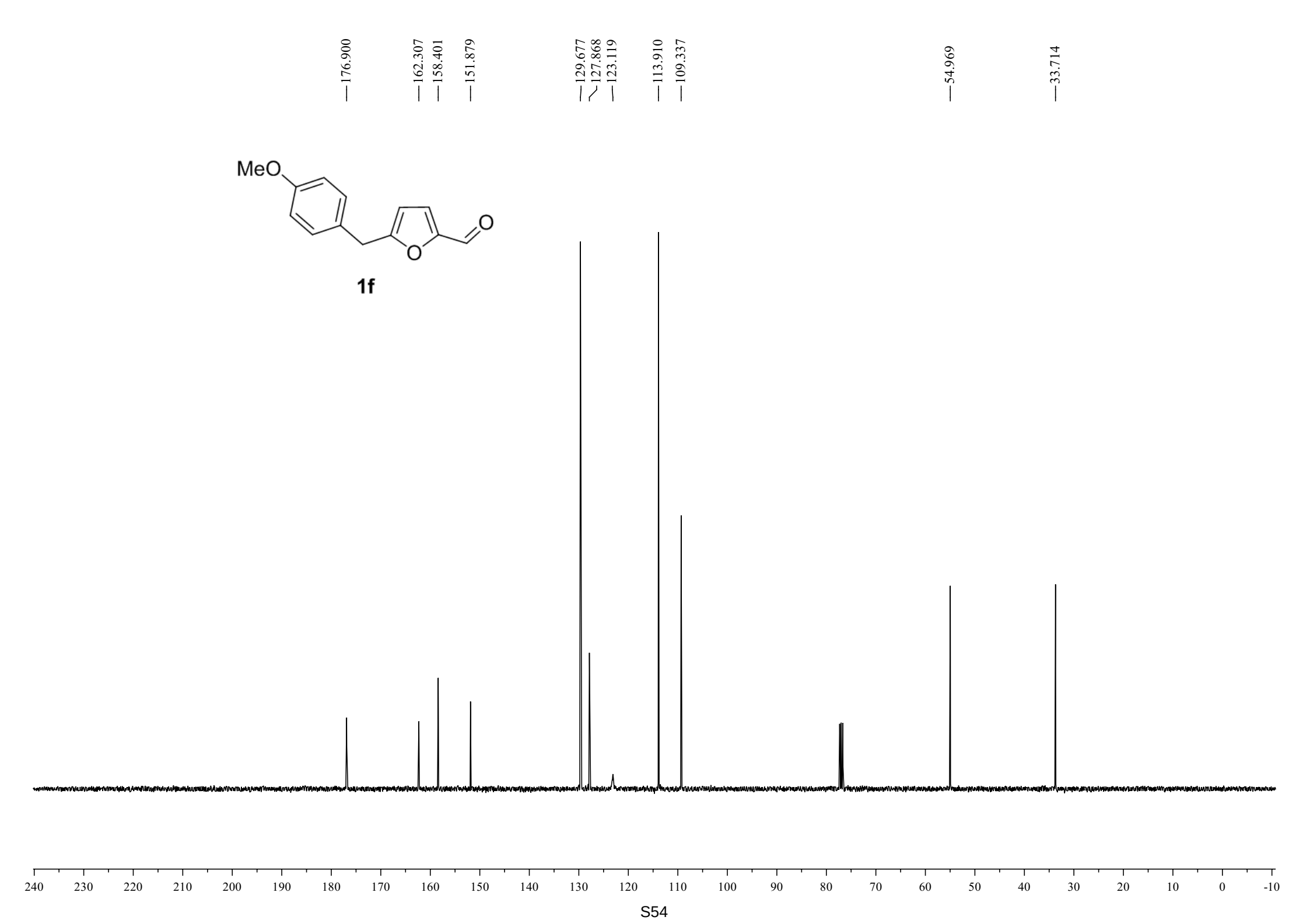
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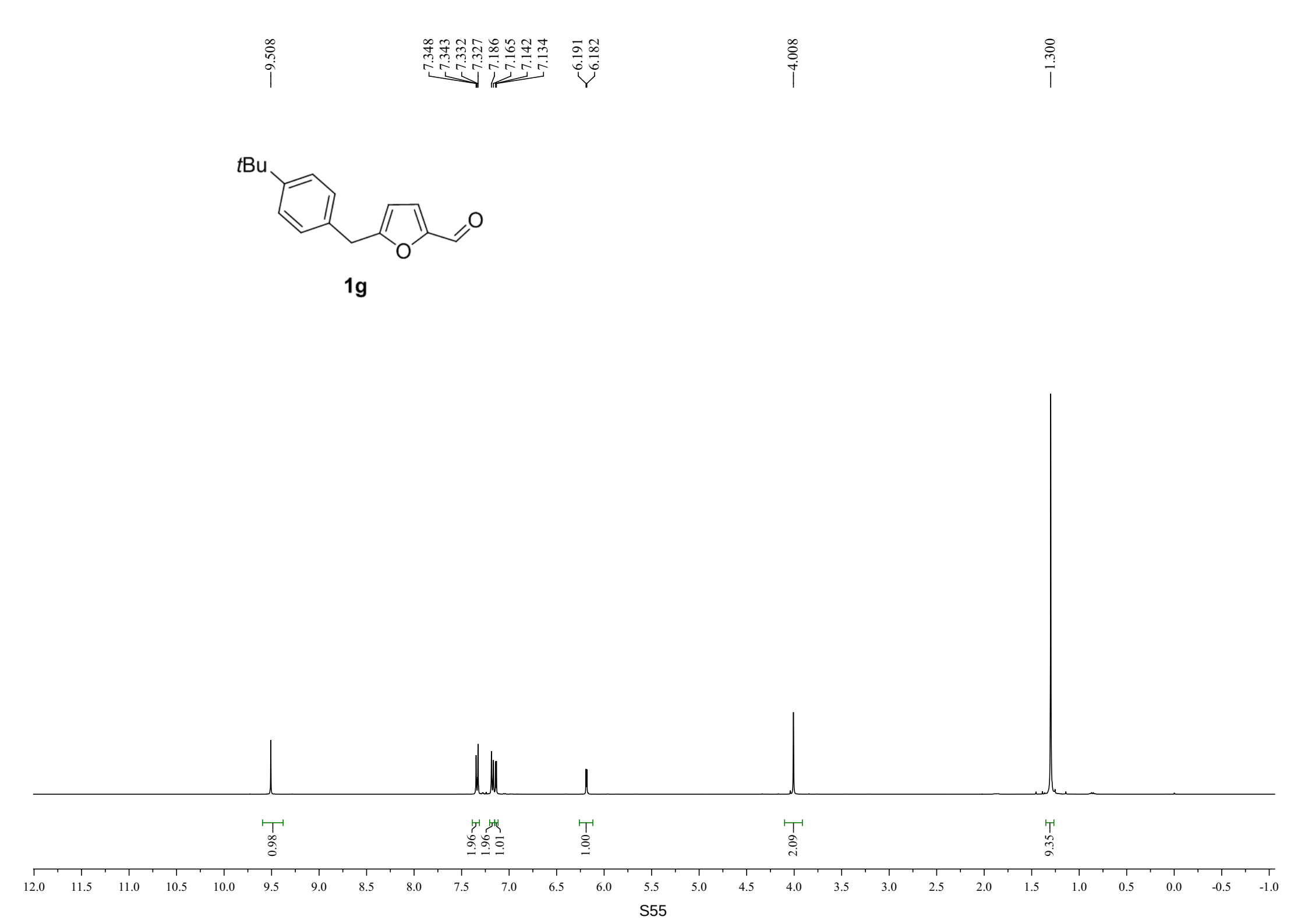
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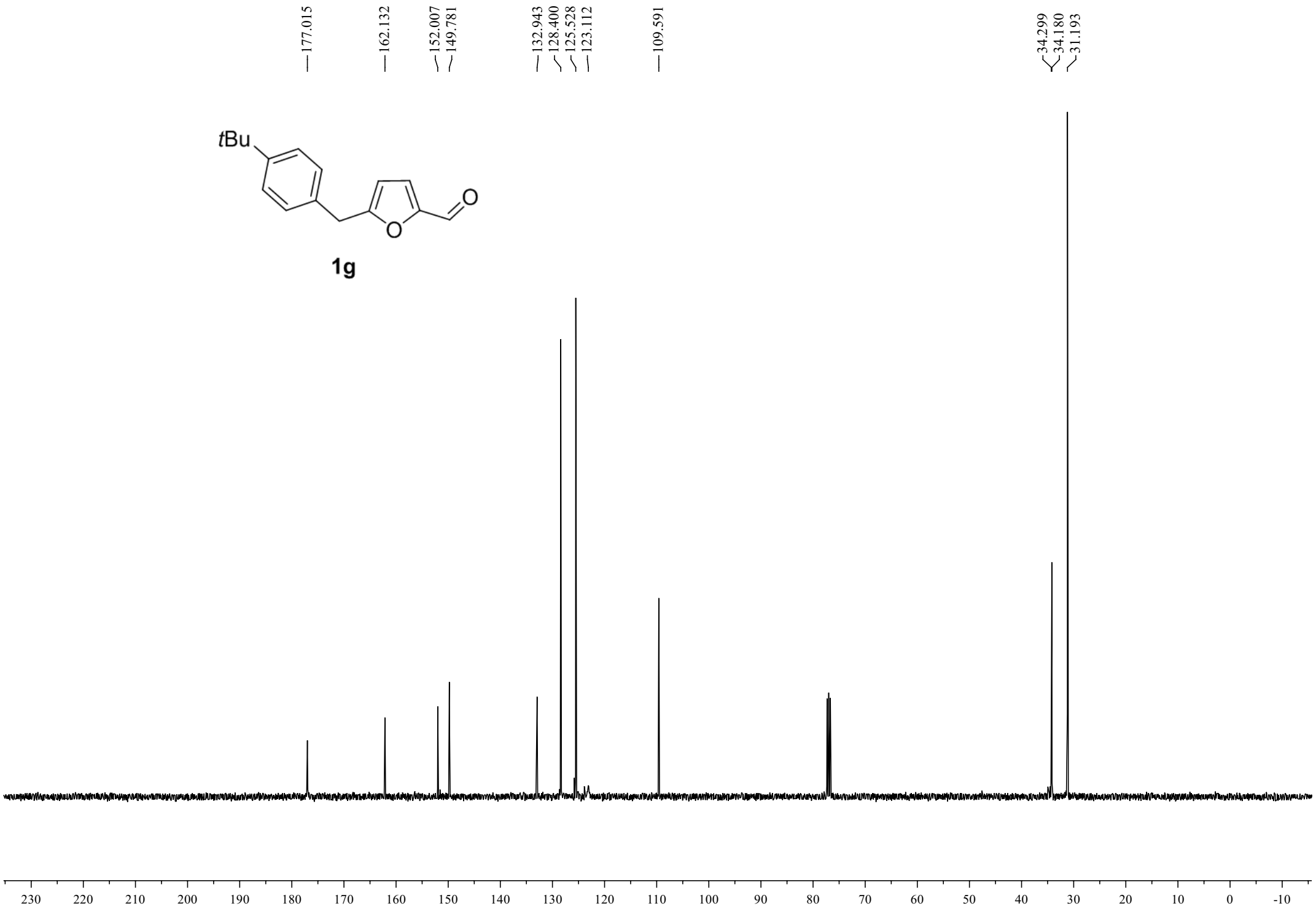
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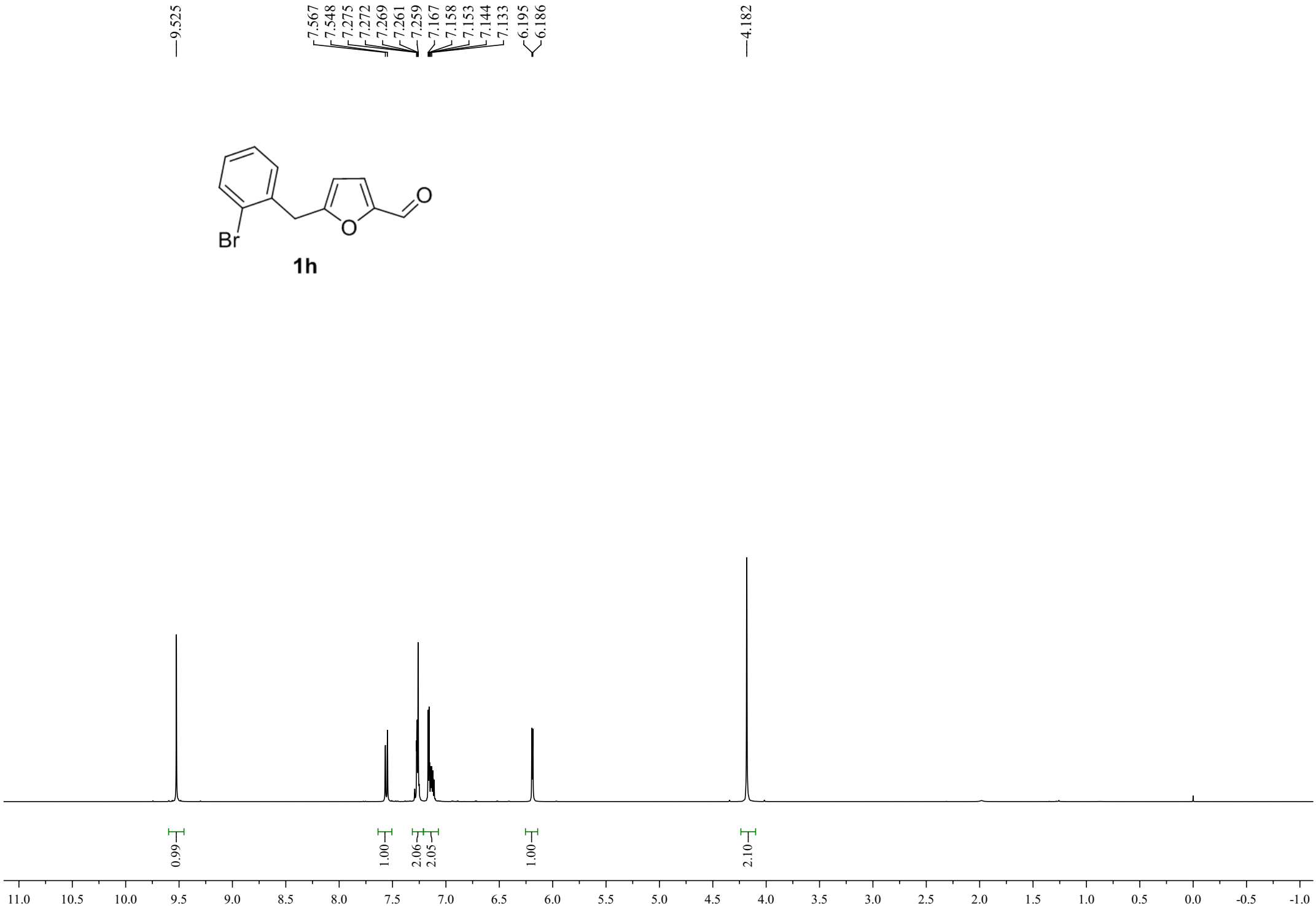
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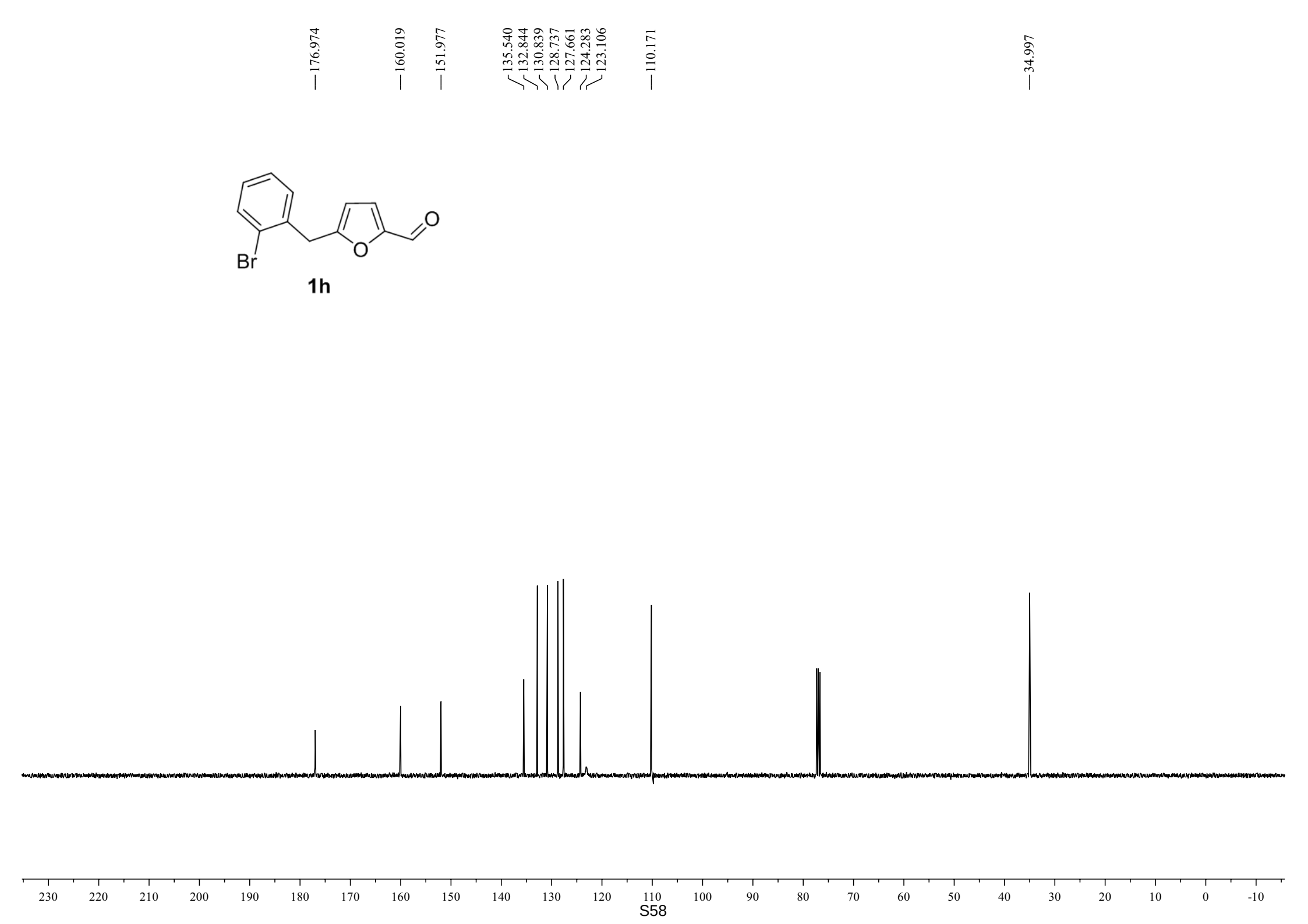
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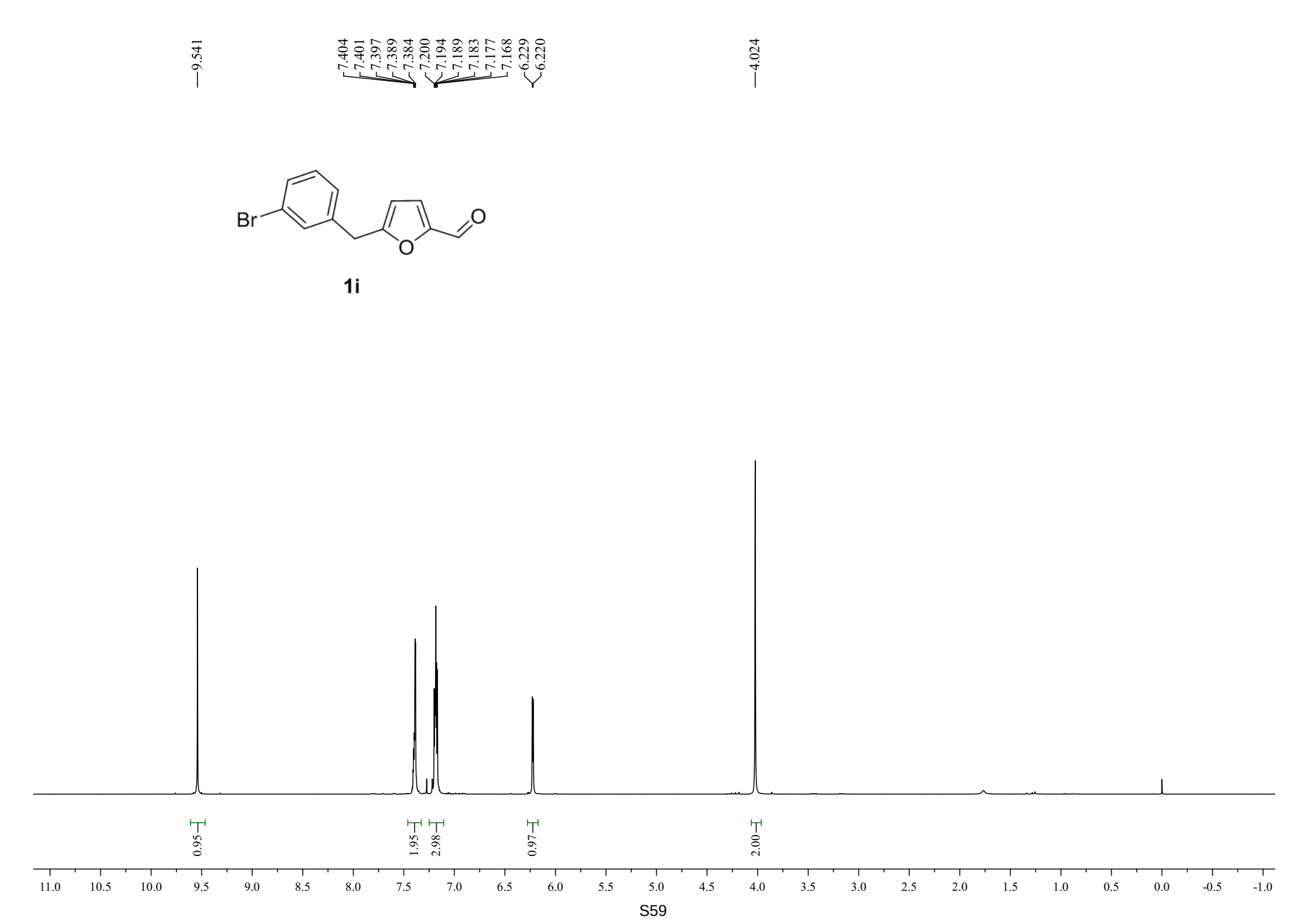
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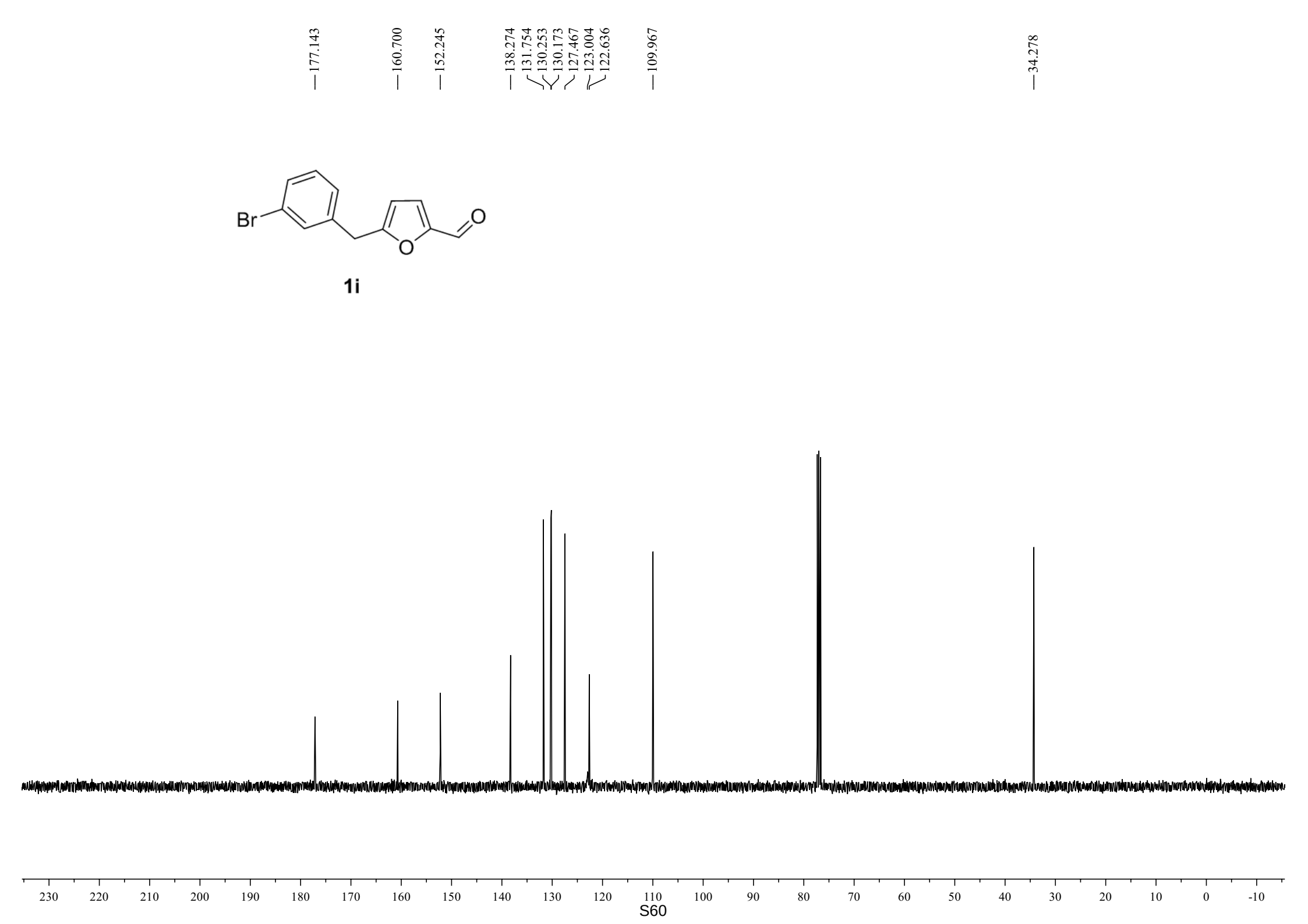
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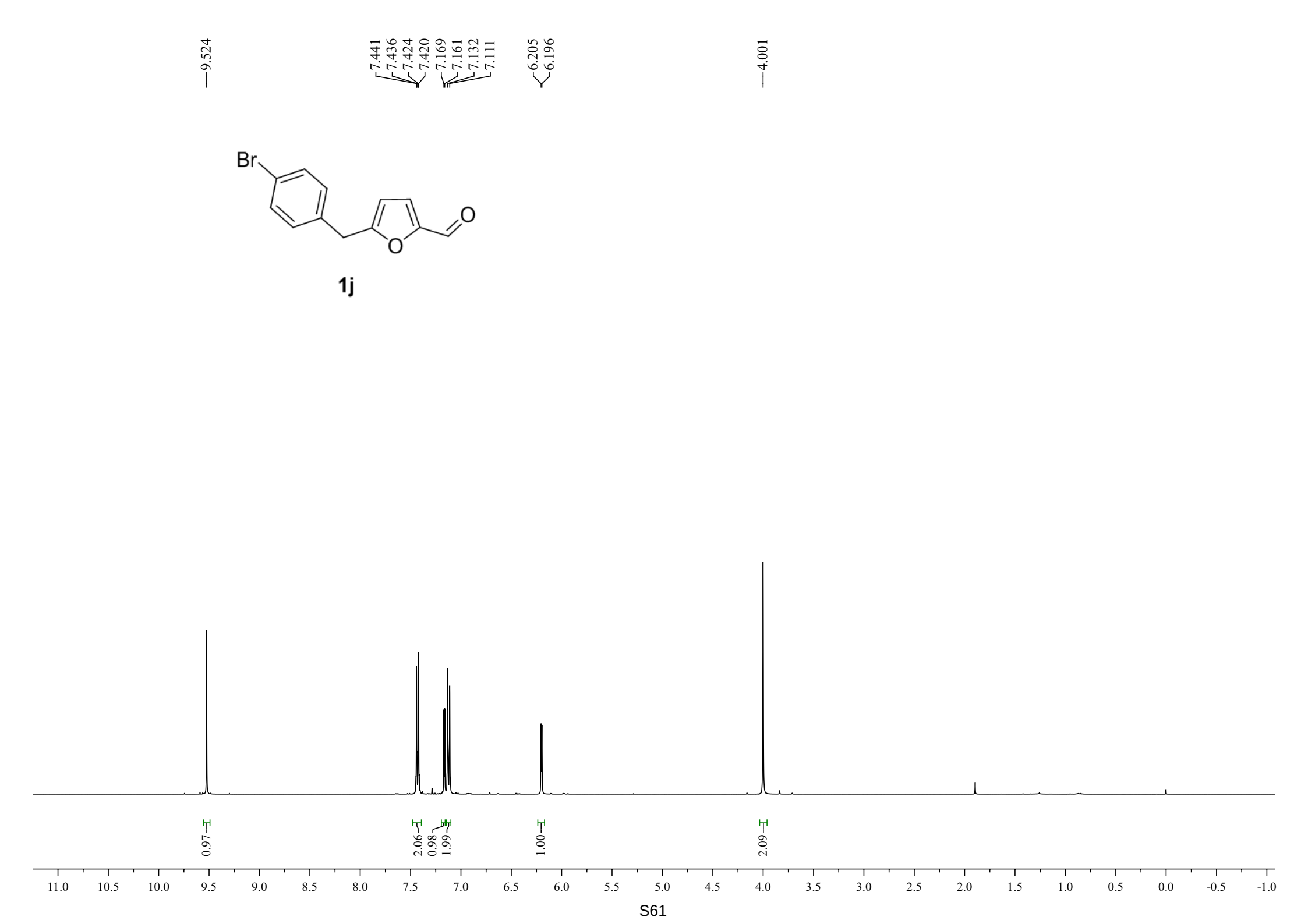
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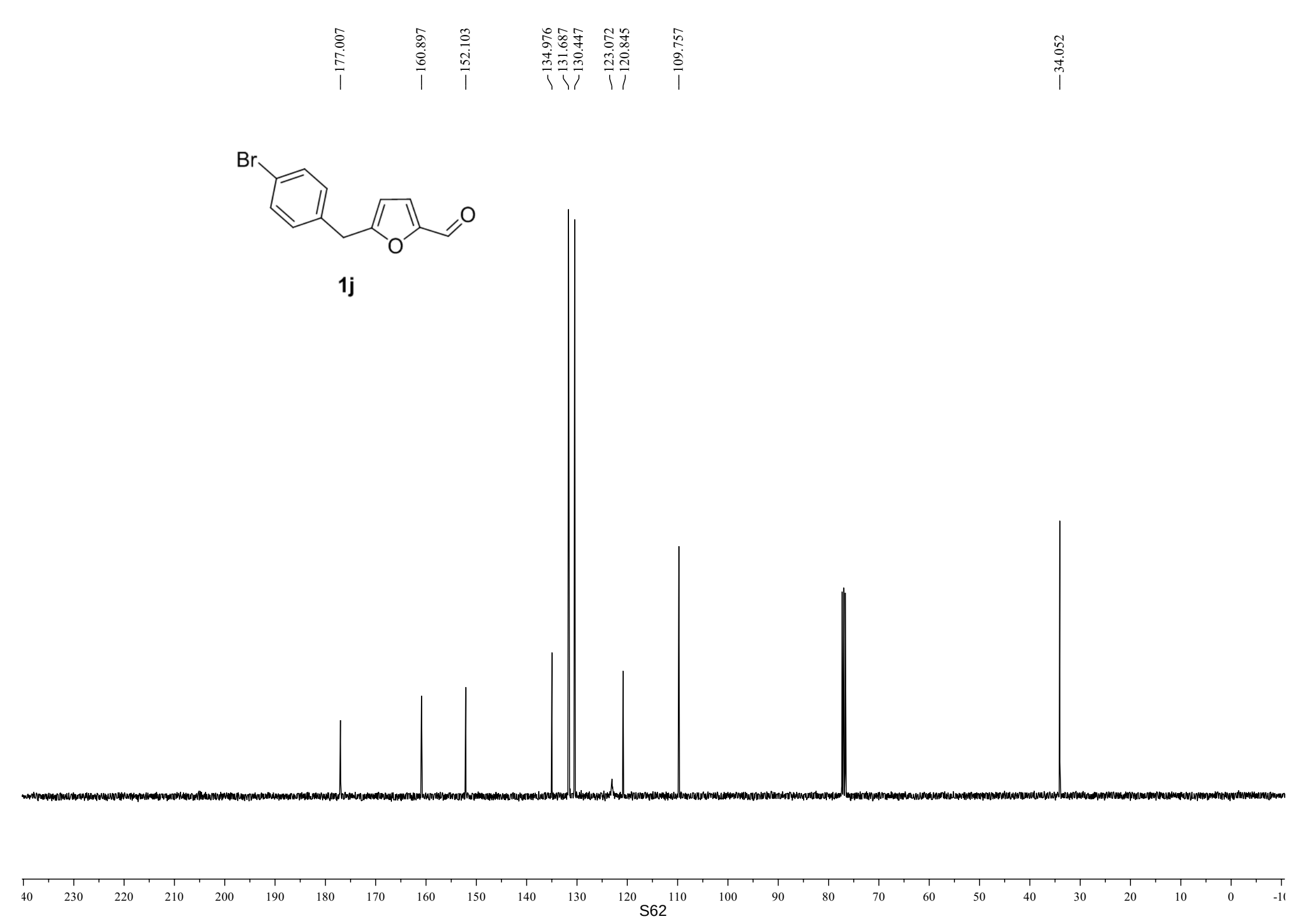
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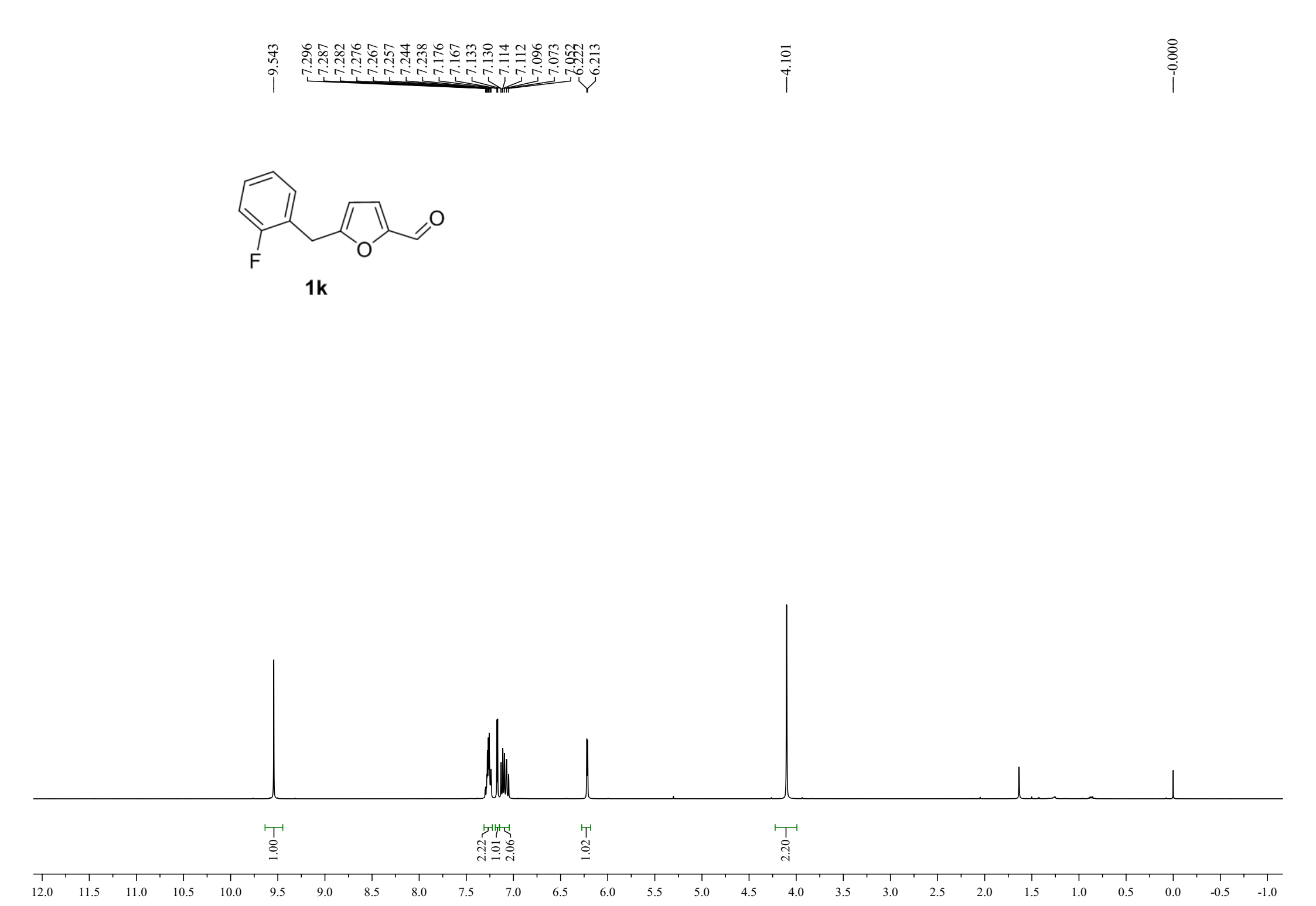
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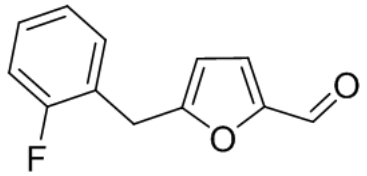

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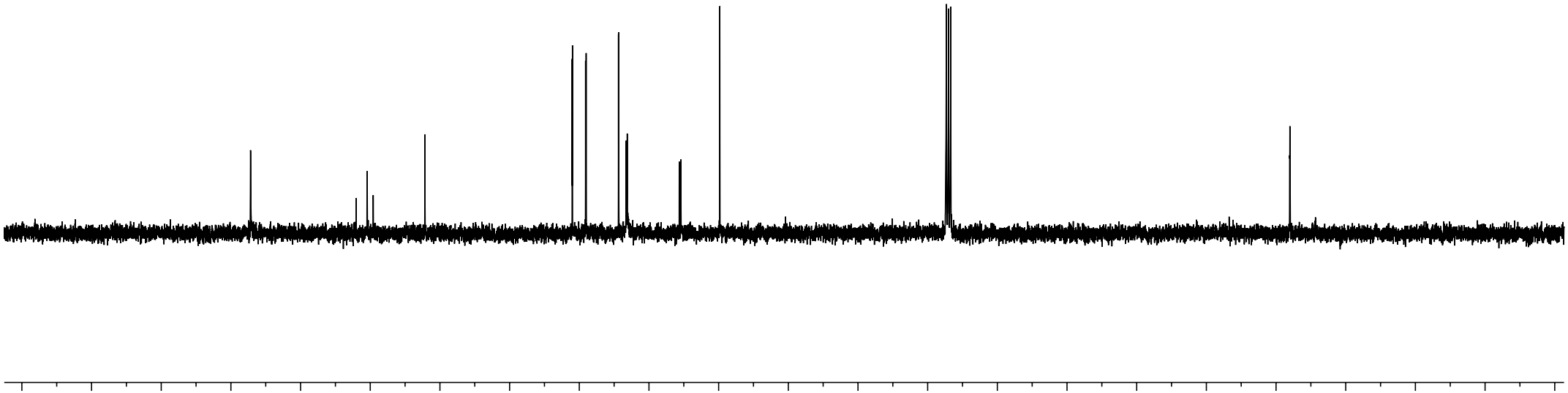

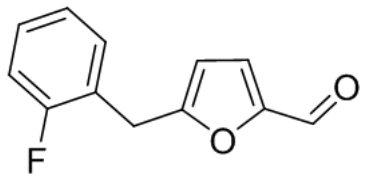

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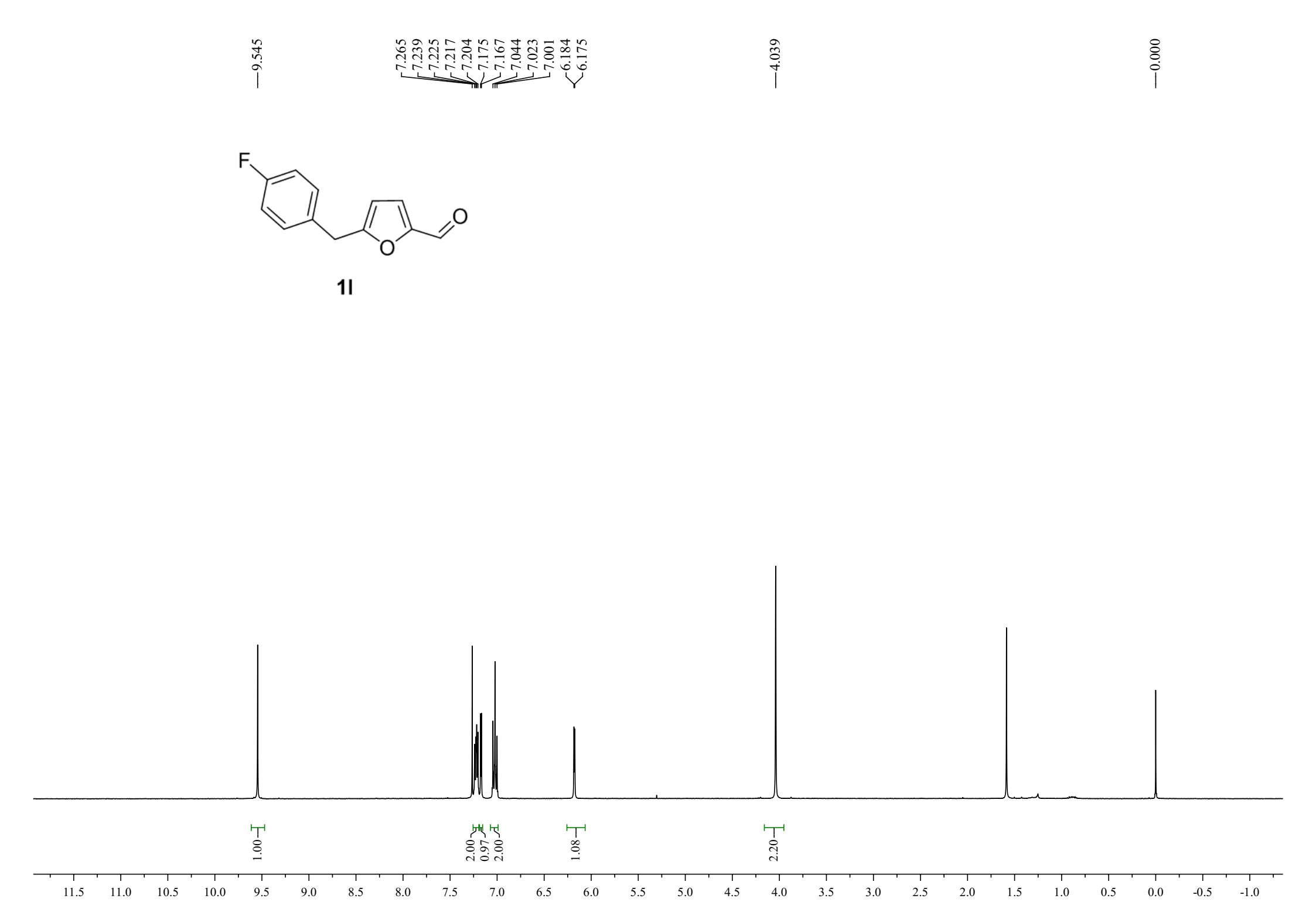
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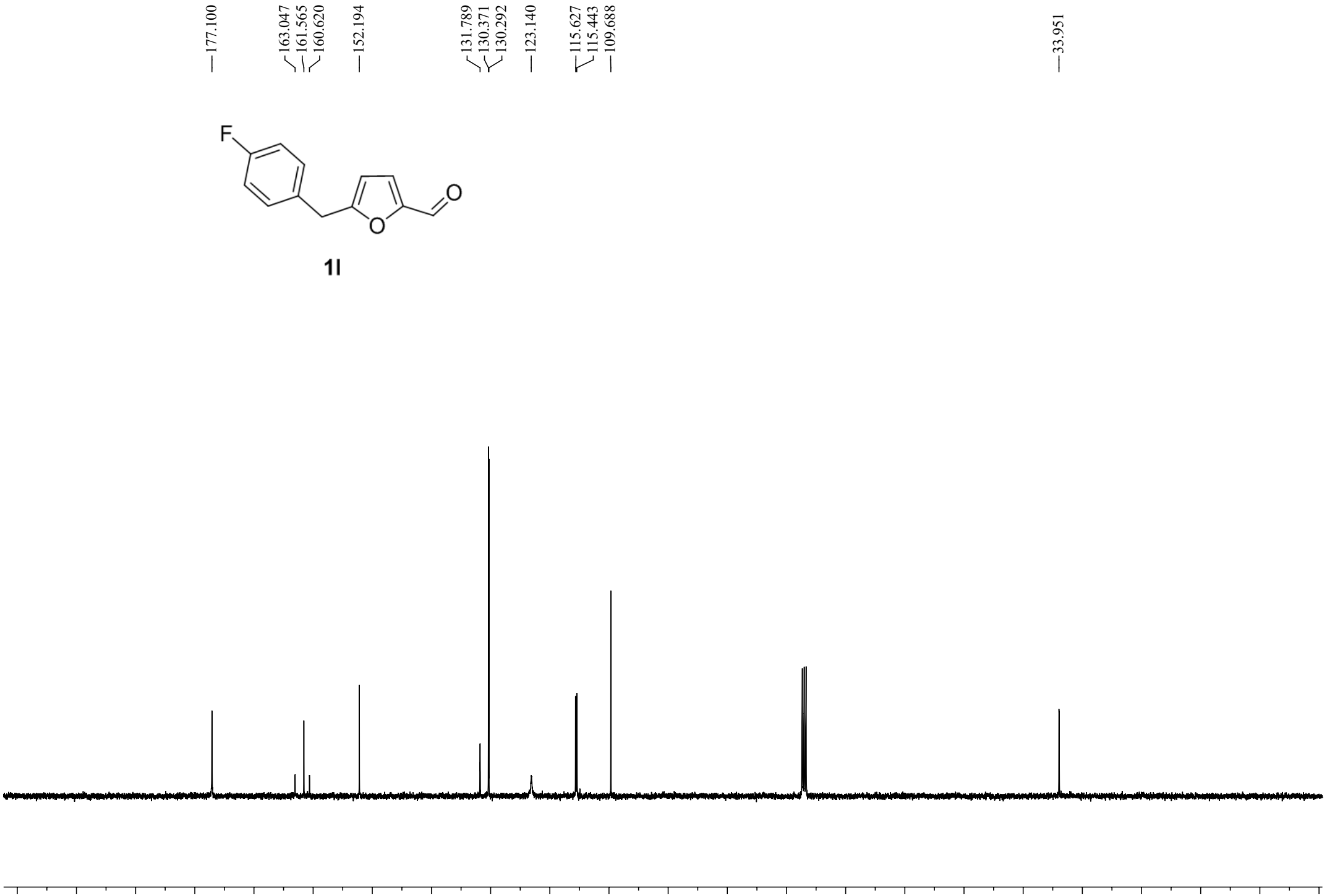
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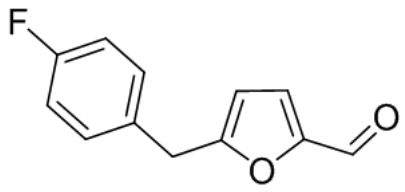
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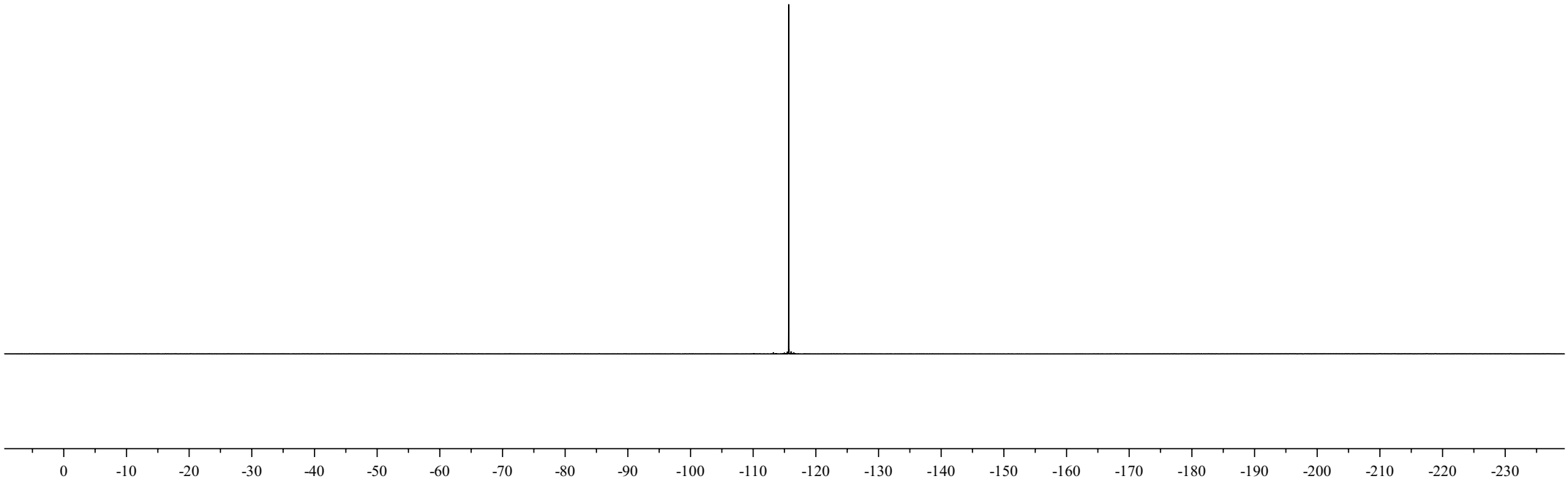
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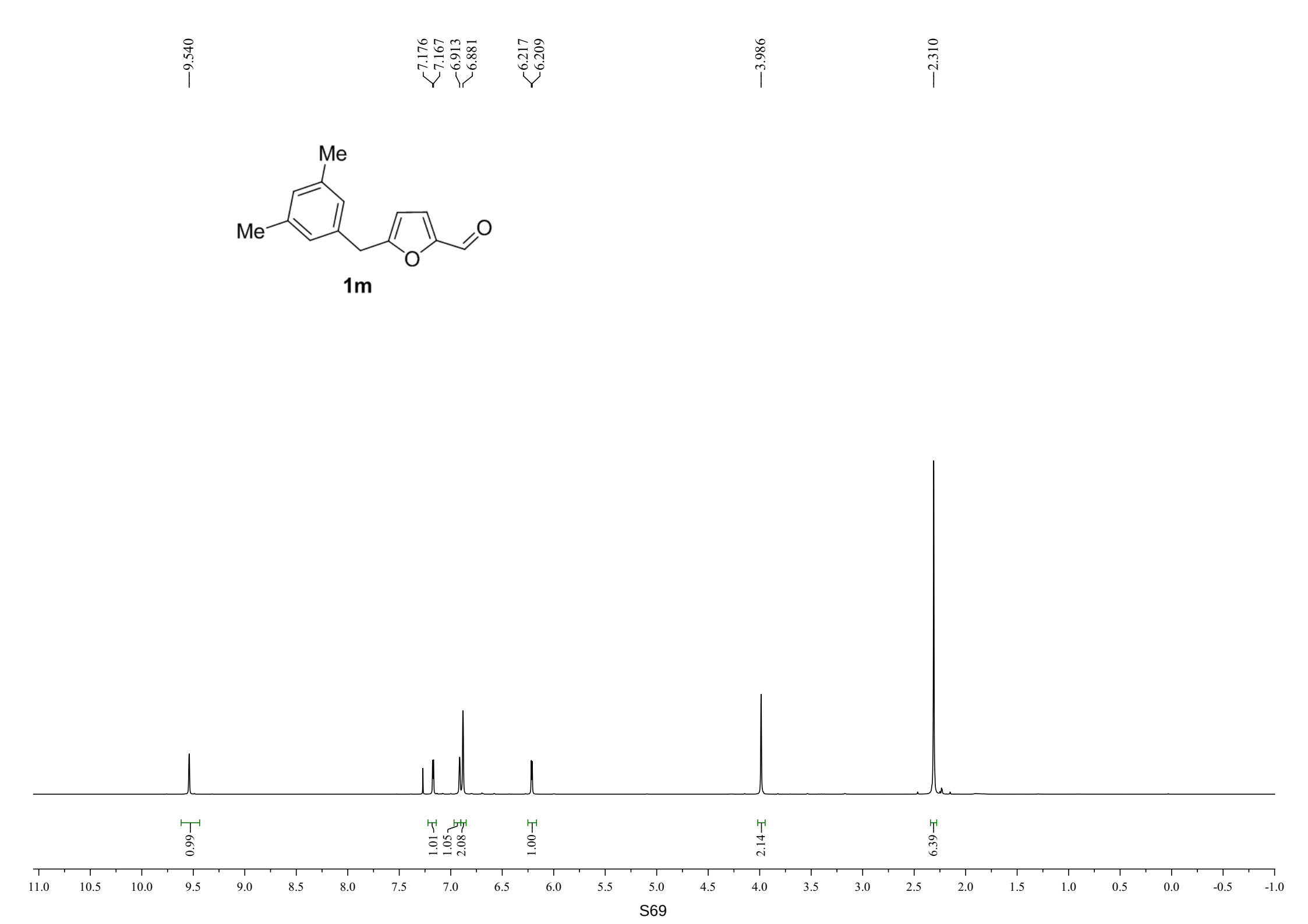
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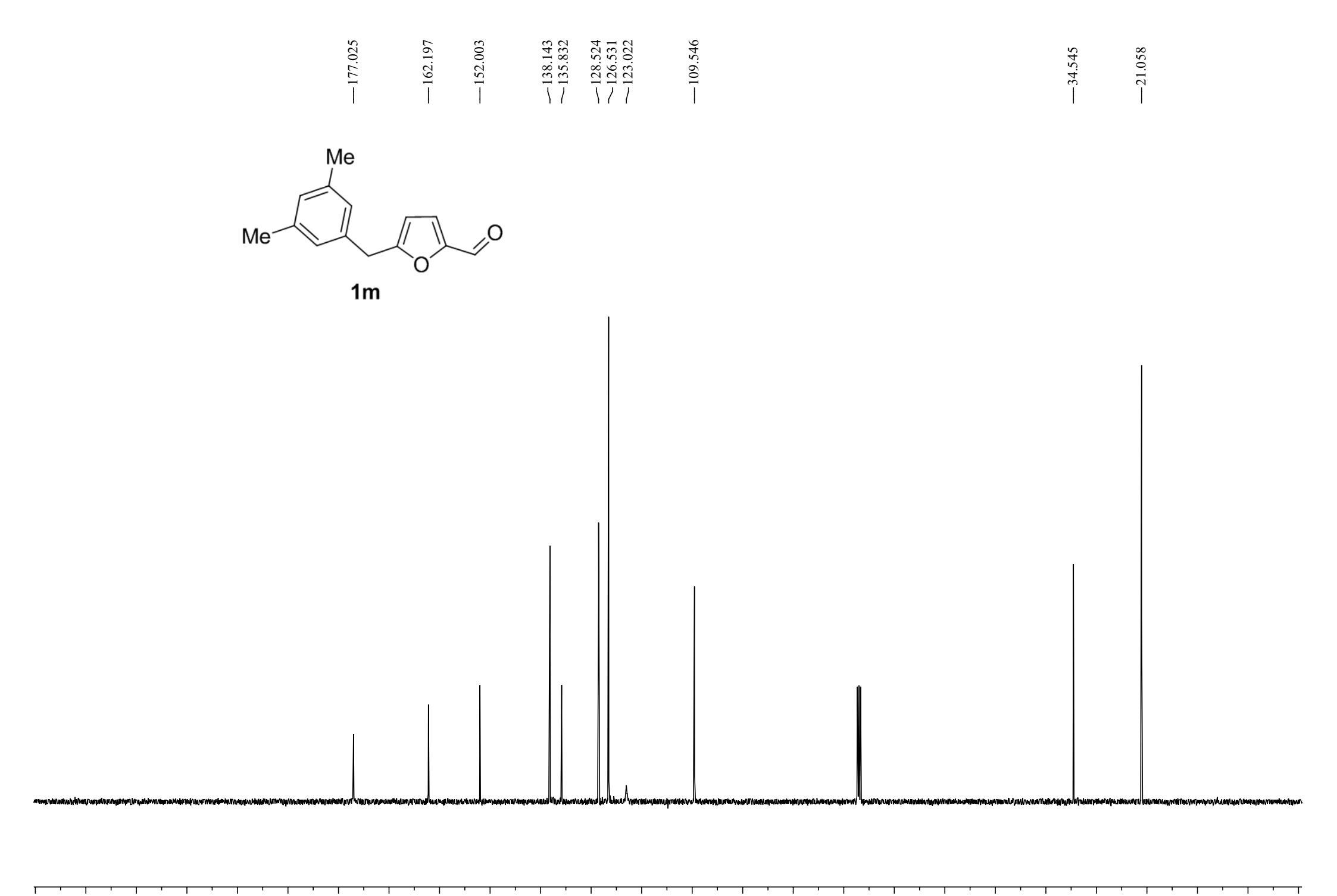
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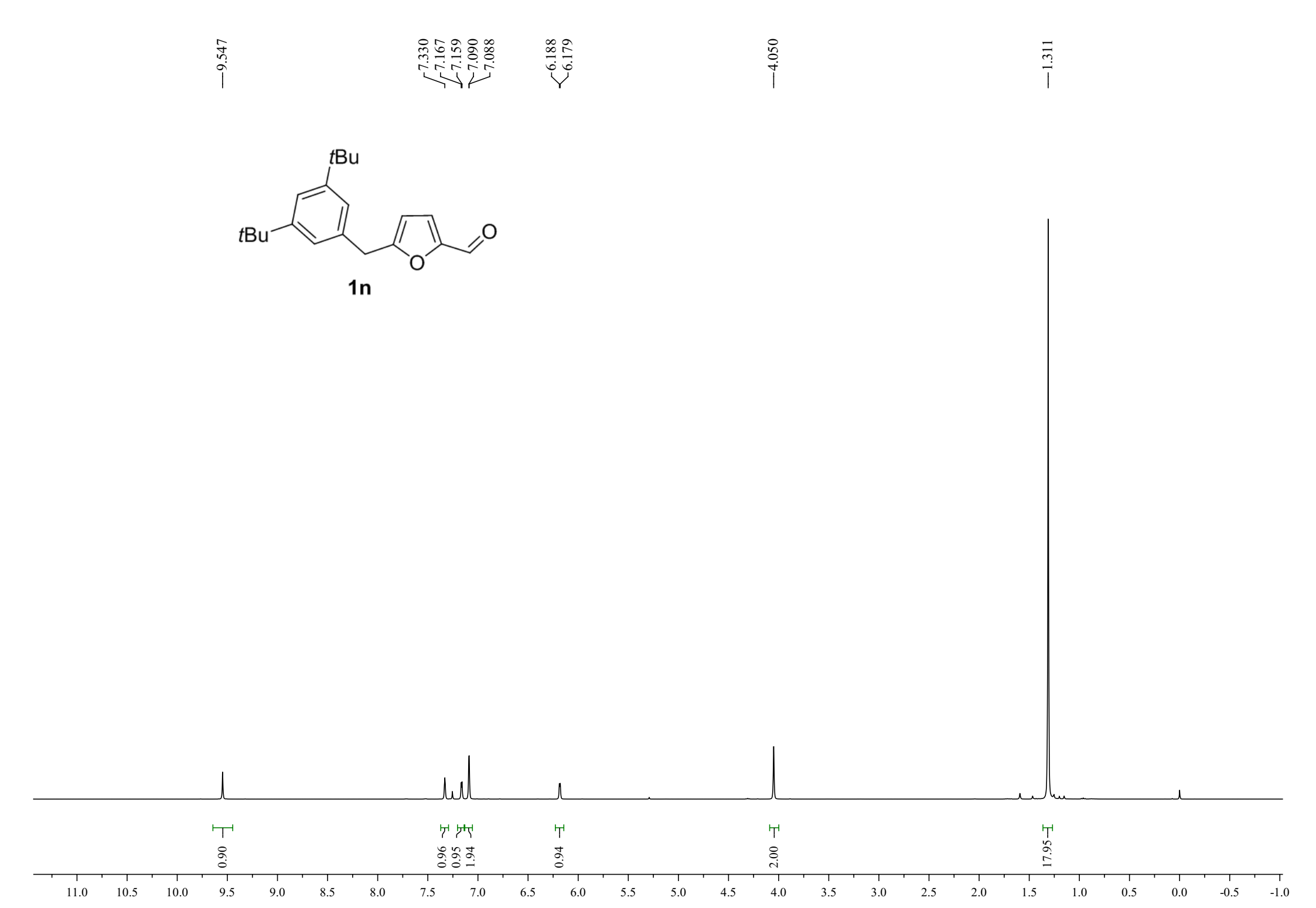
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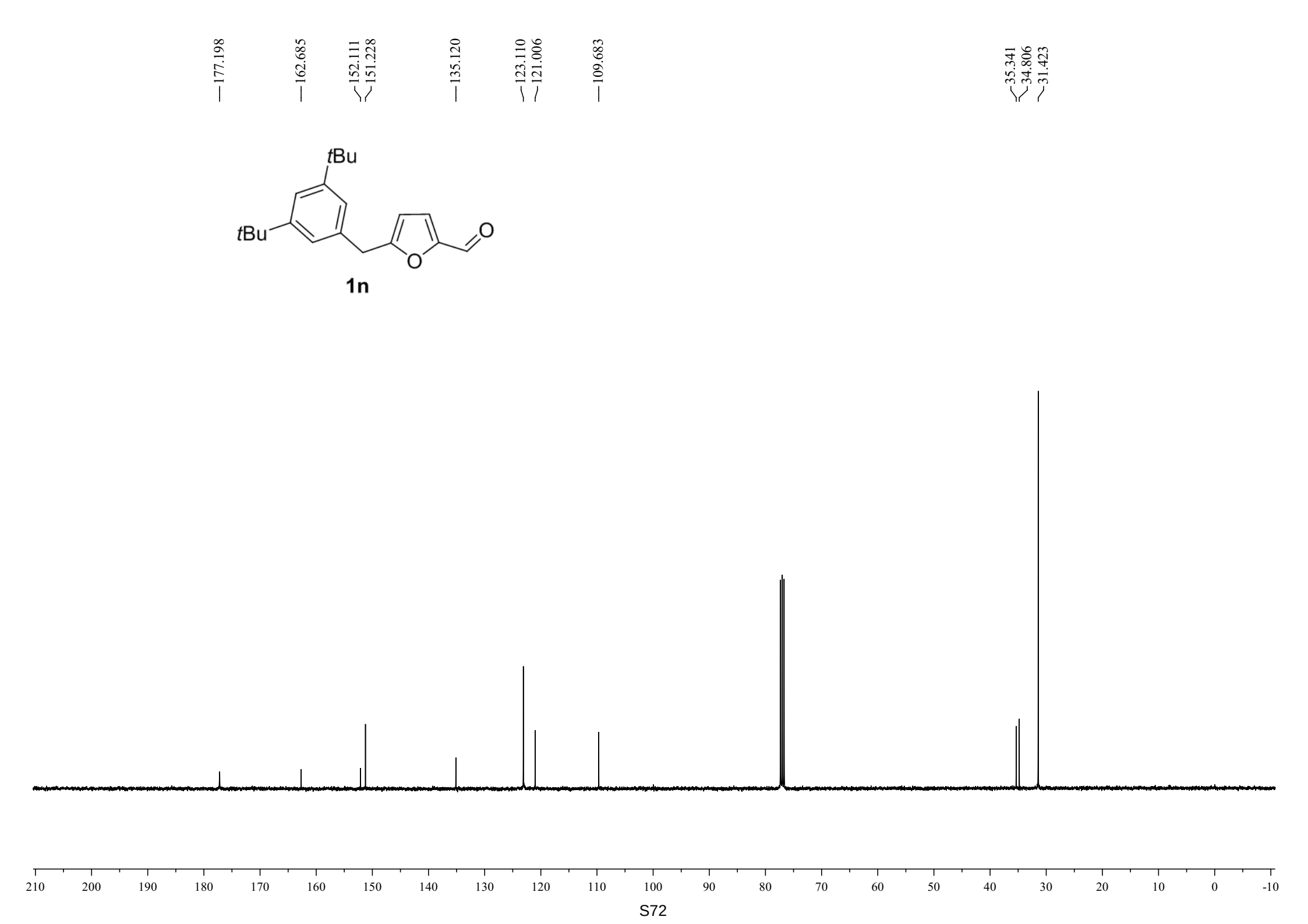
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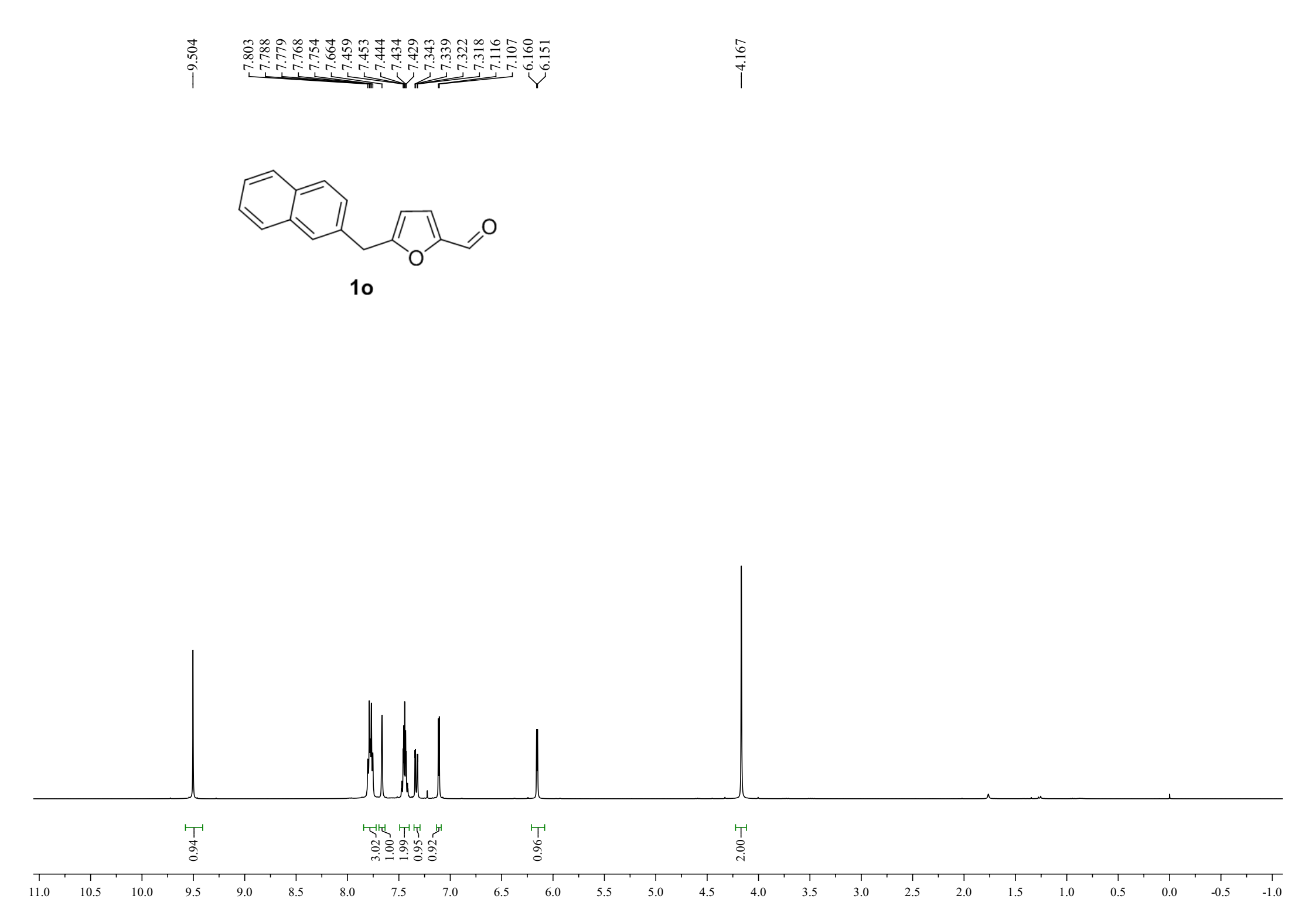
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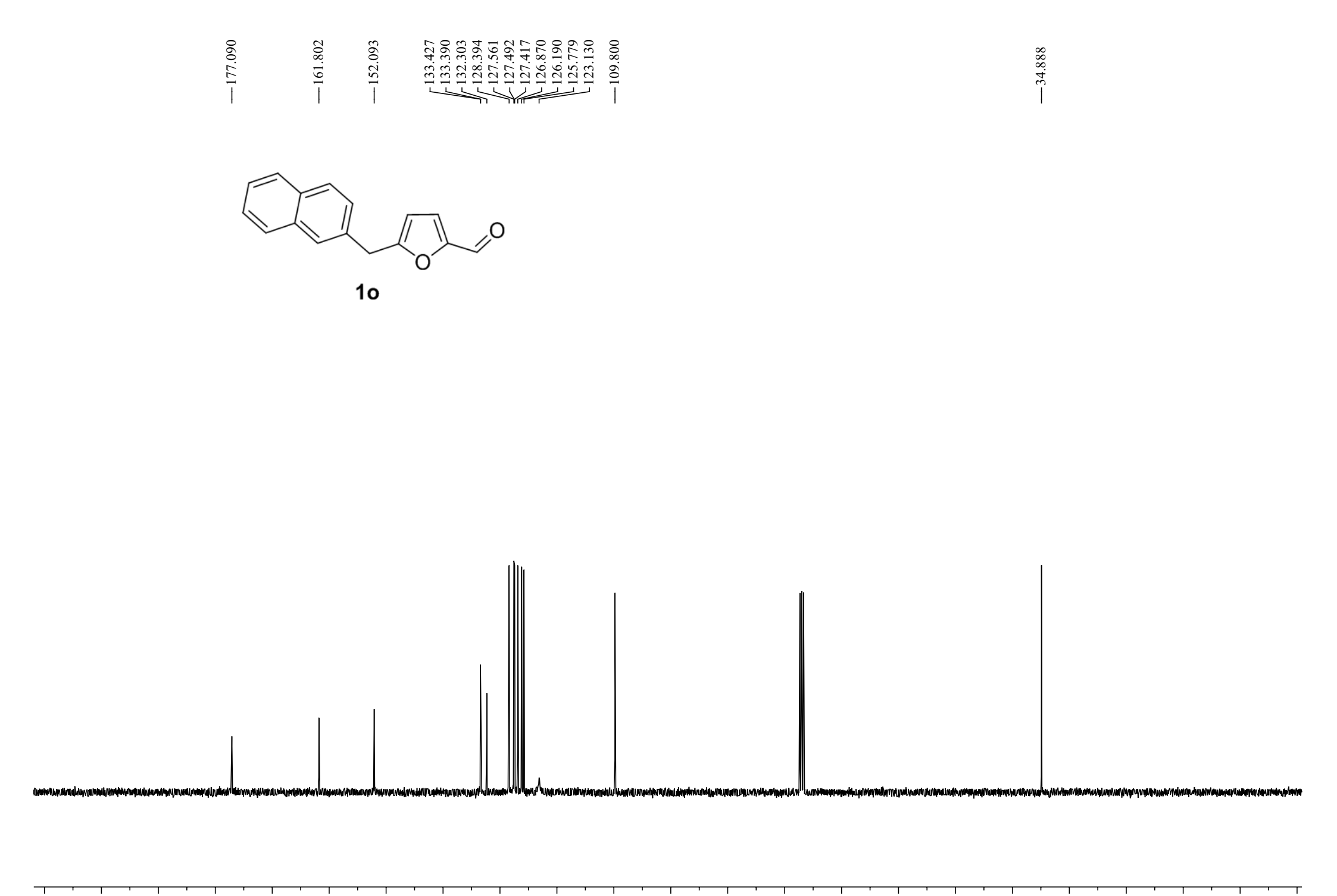
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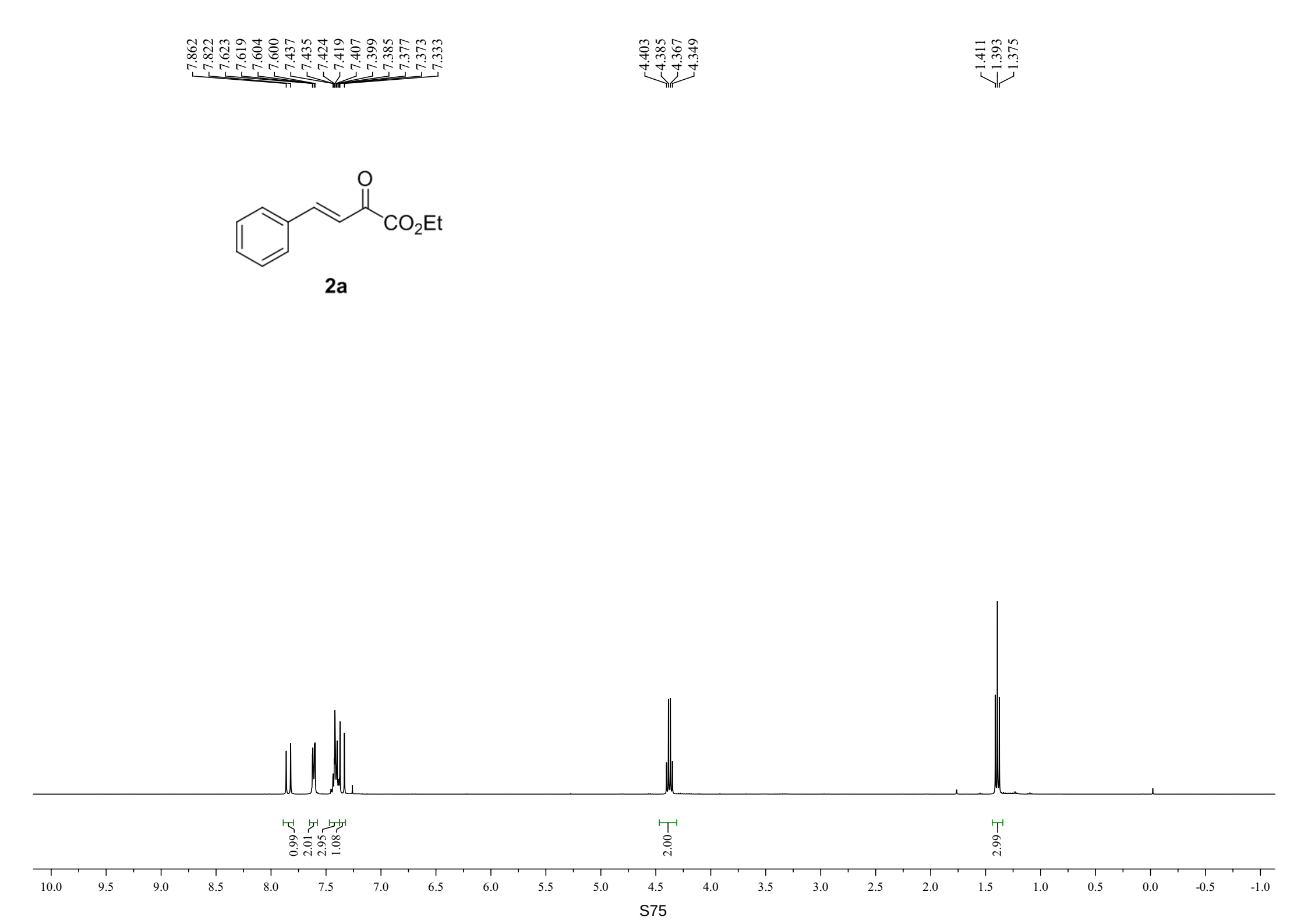
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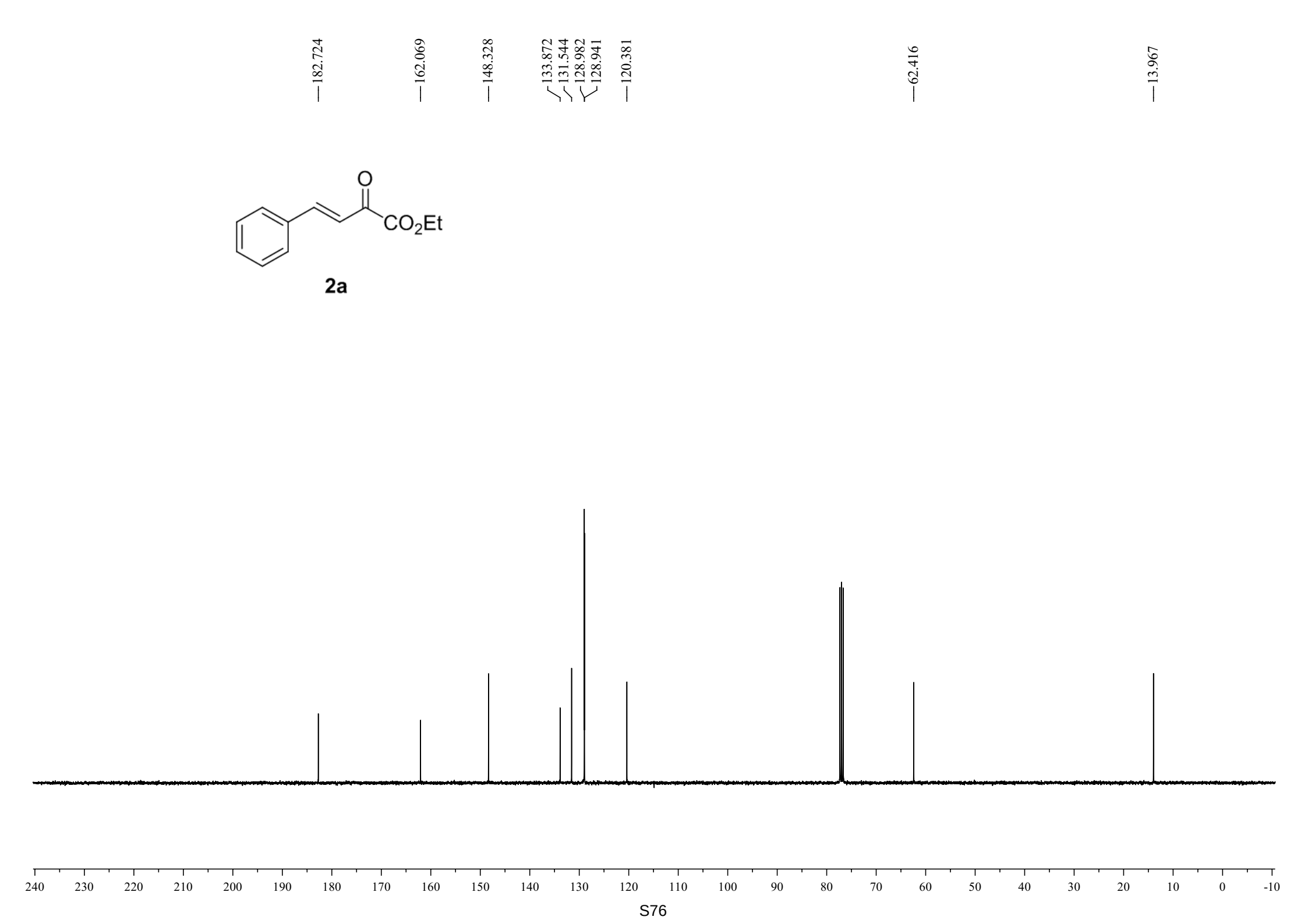
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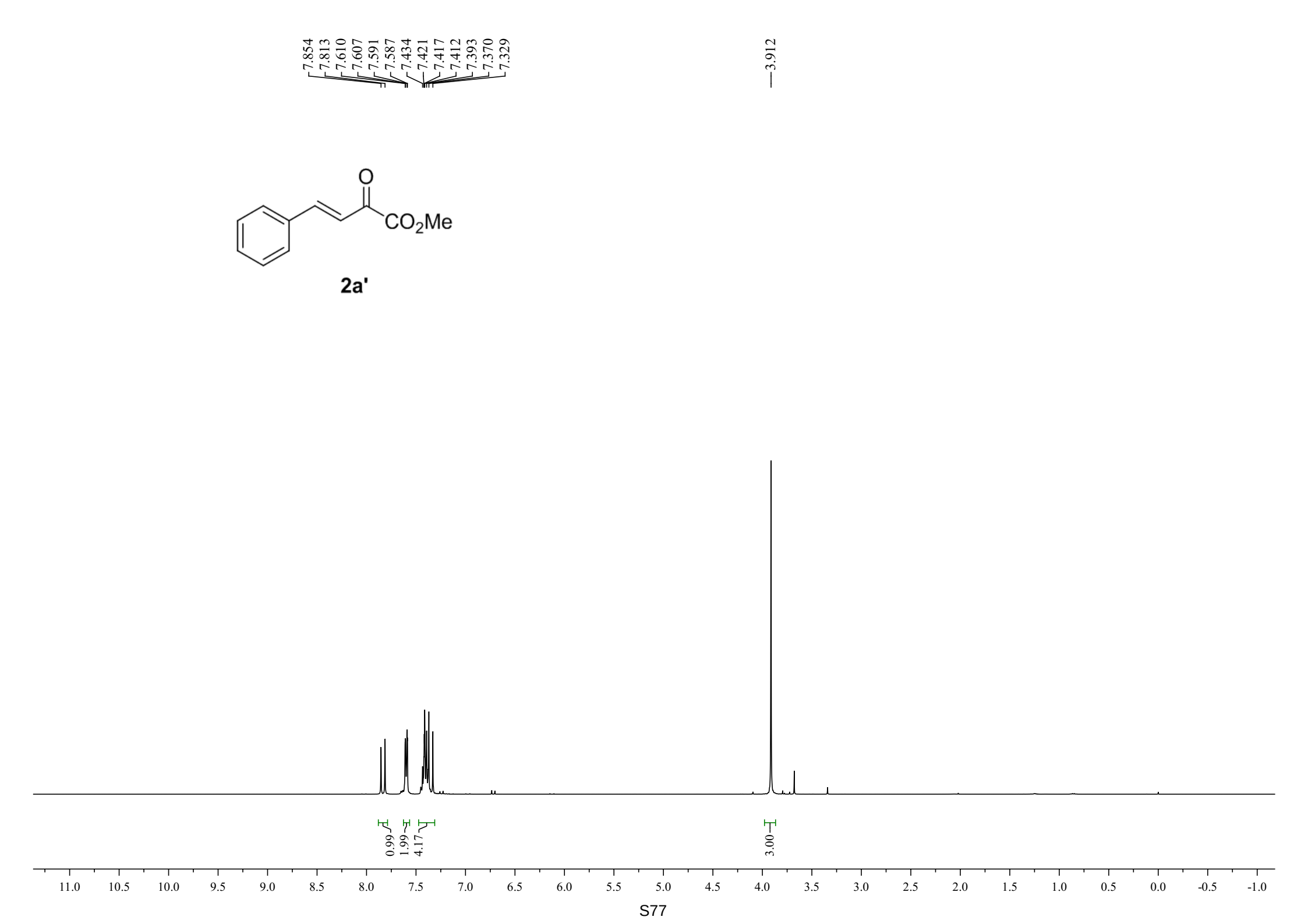
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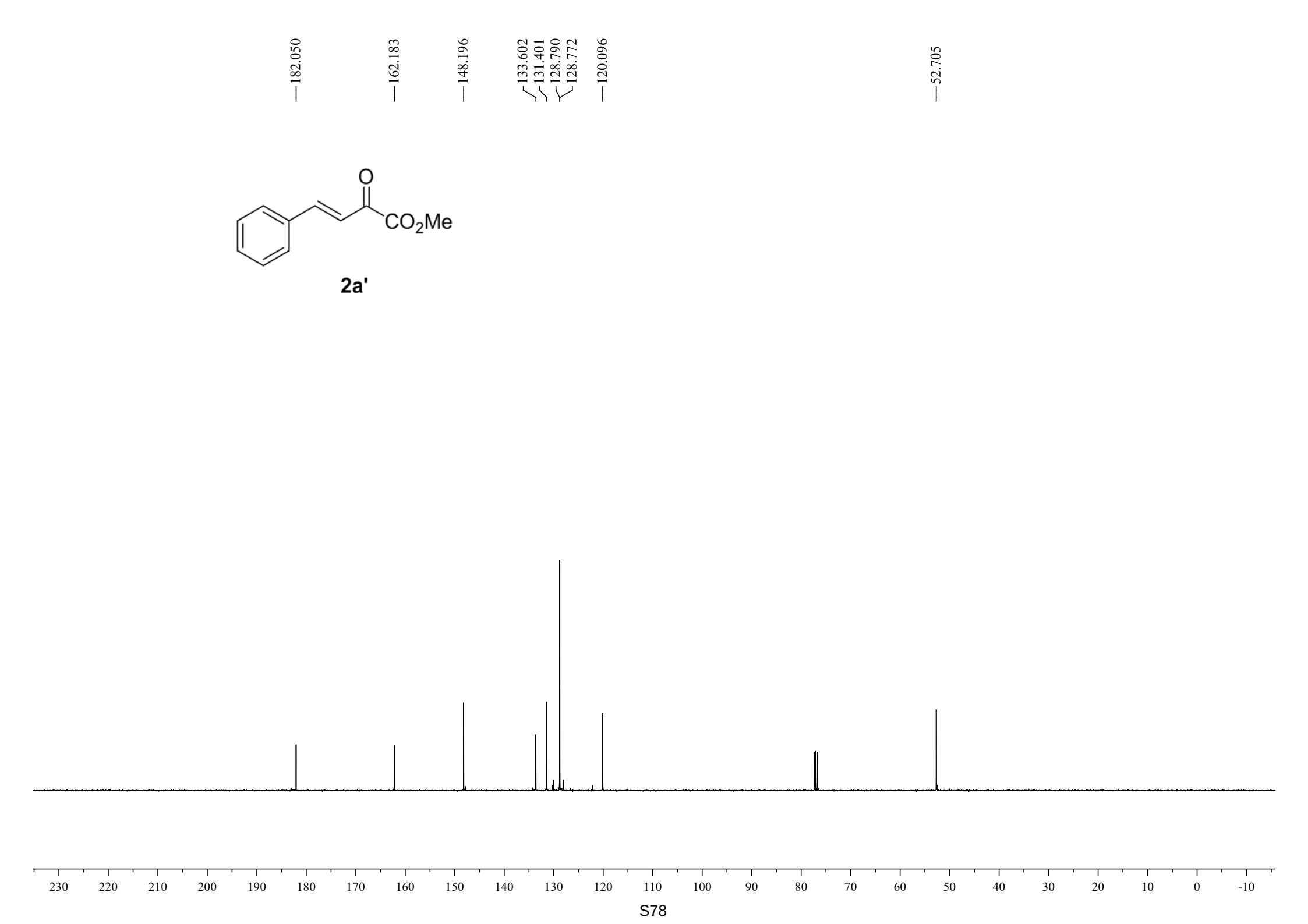
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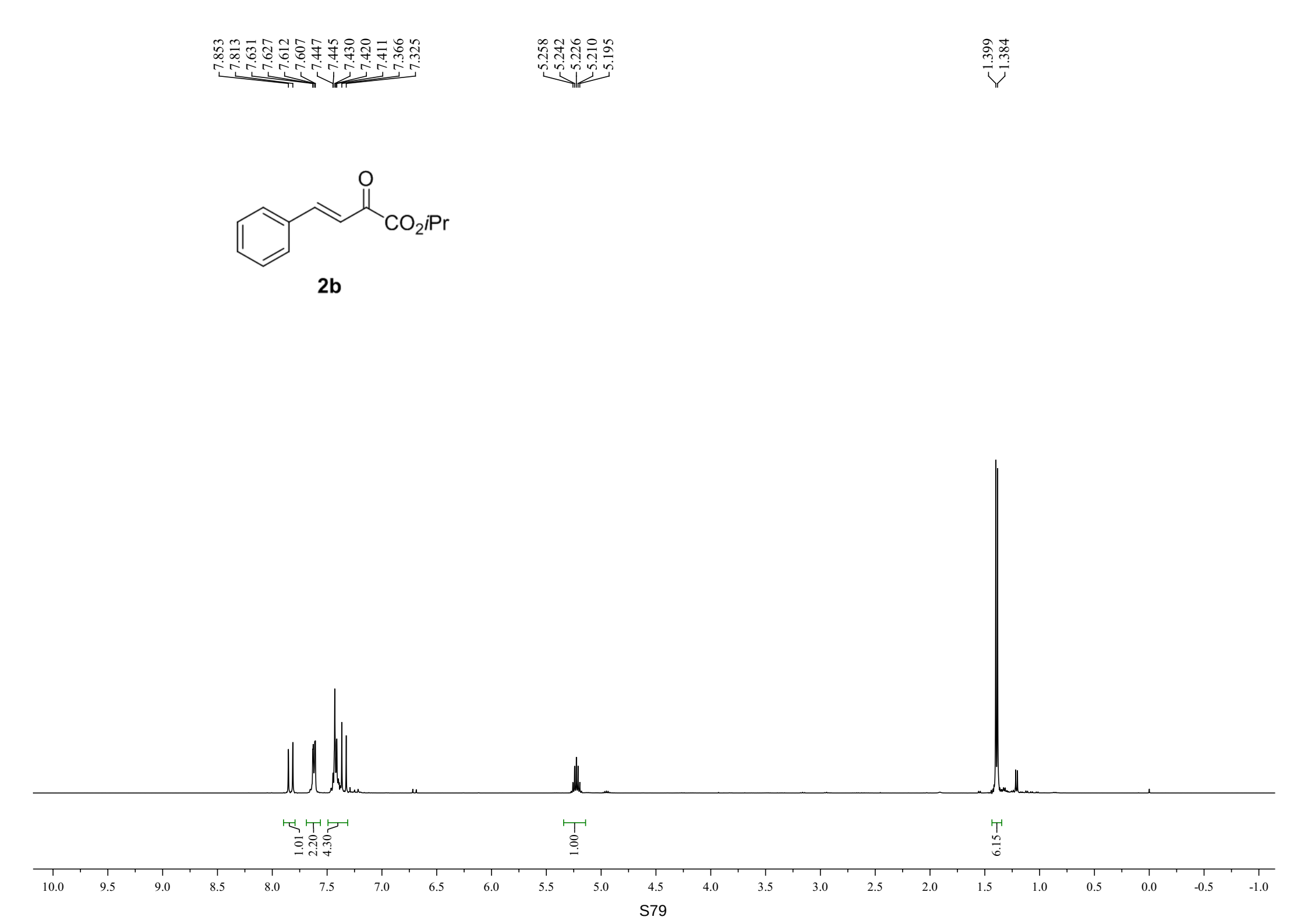
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7.325
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5.242
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2b
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2.20
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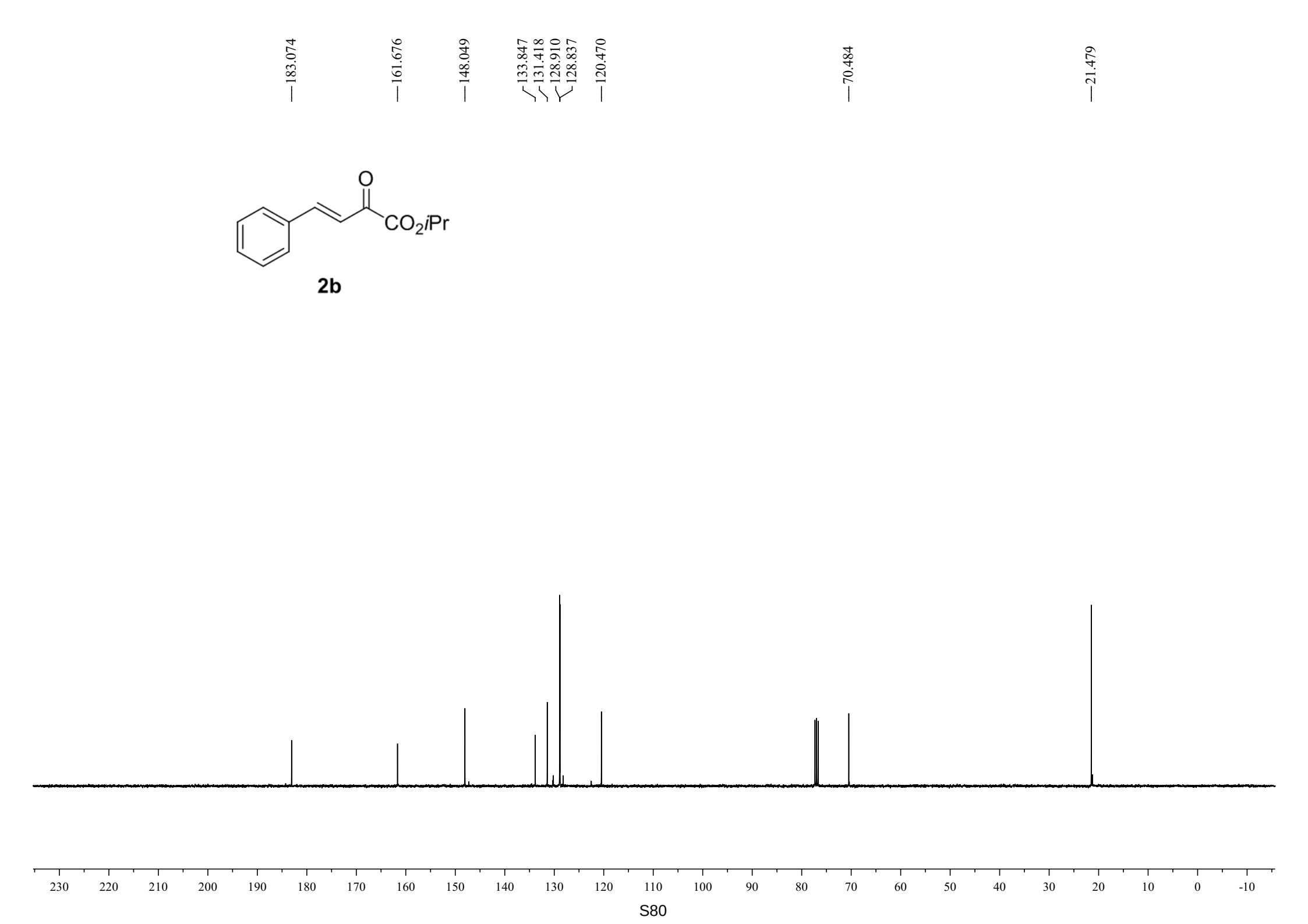
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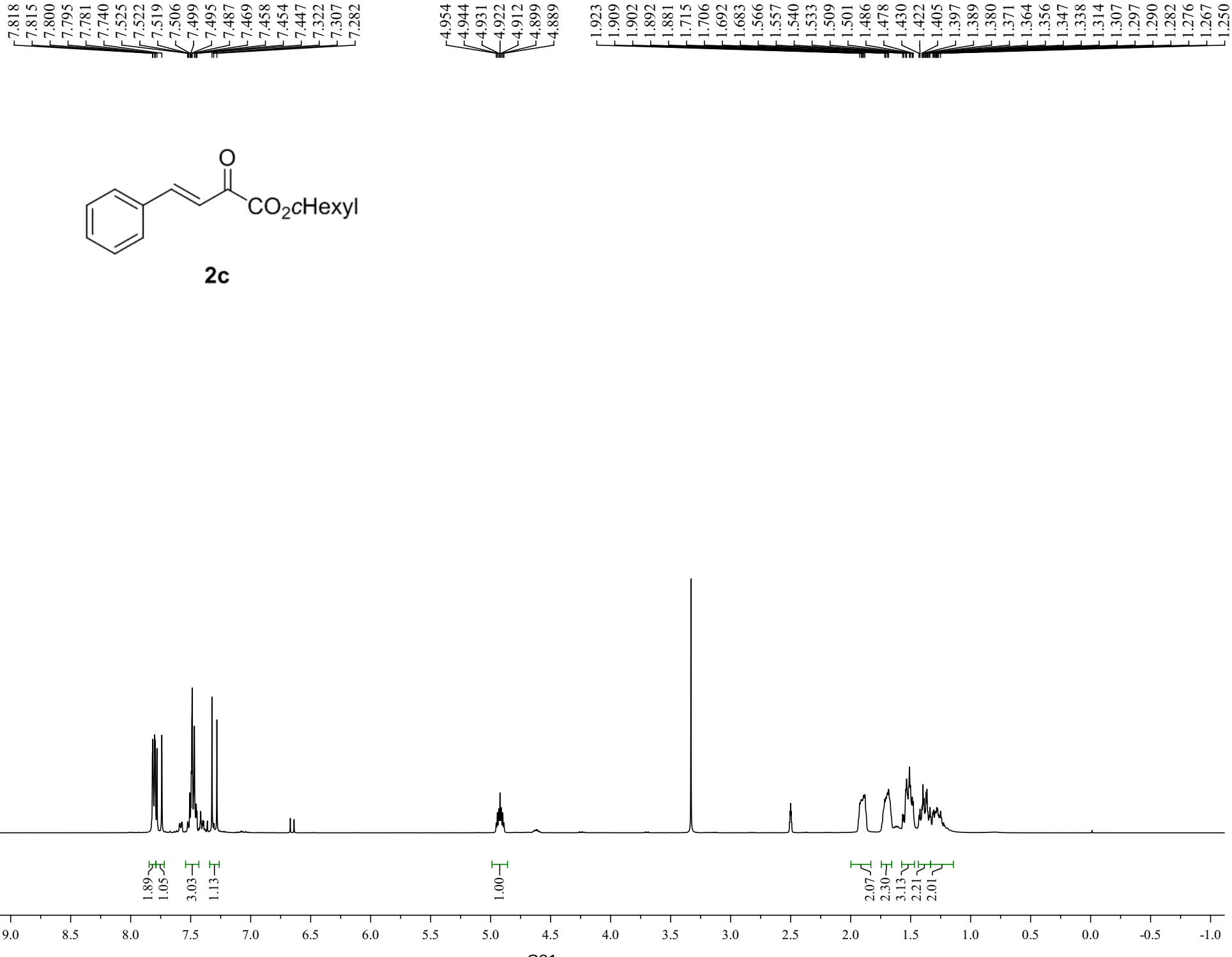
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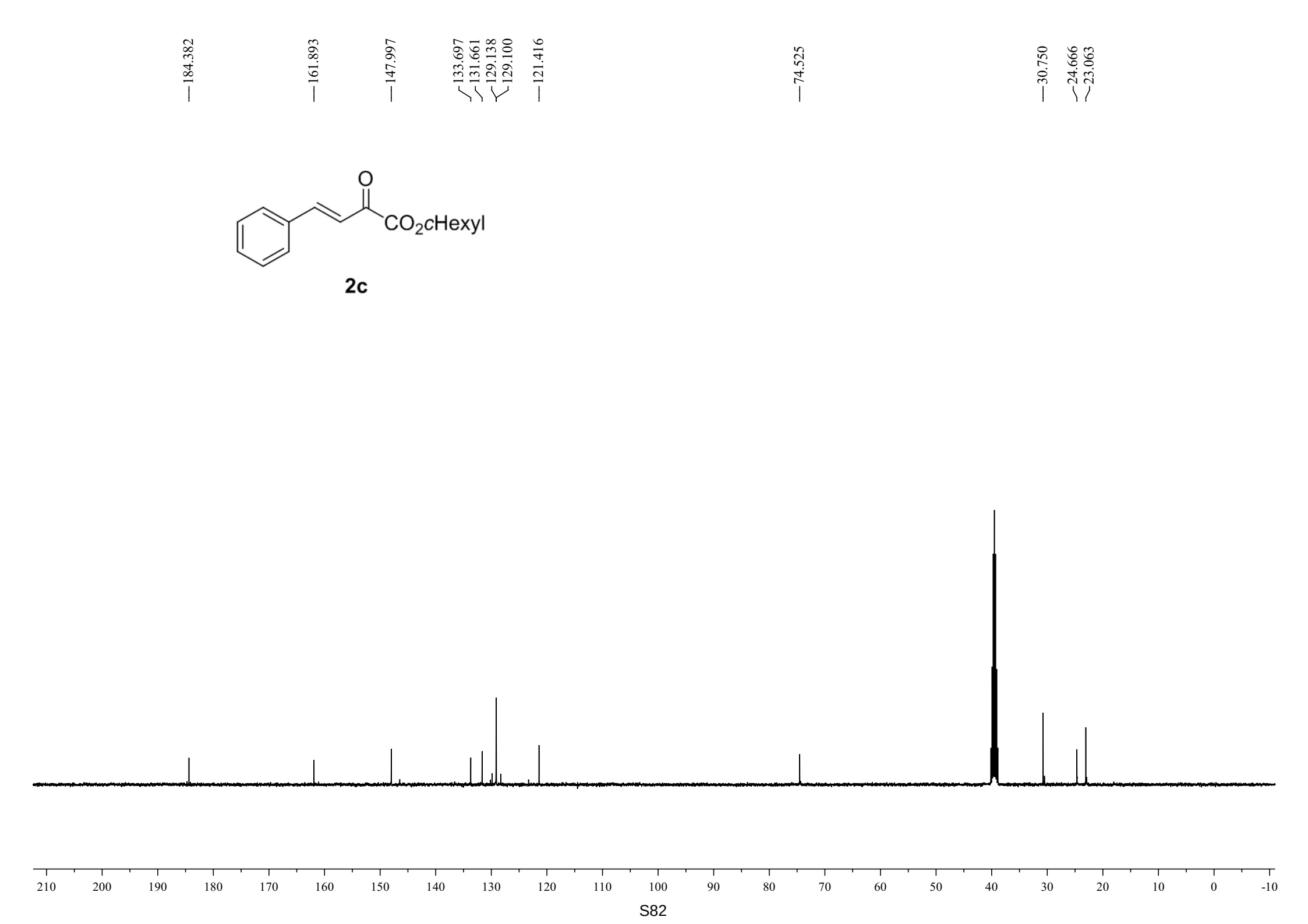
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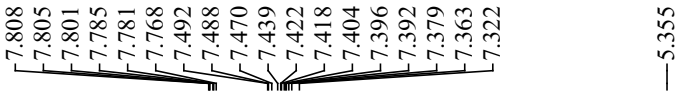
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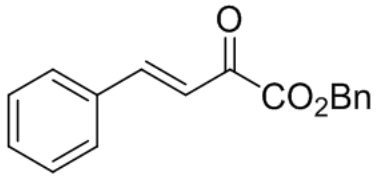
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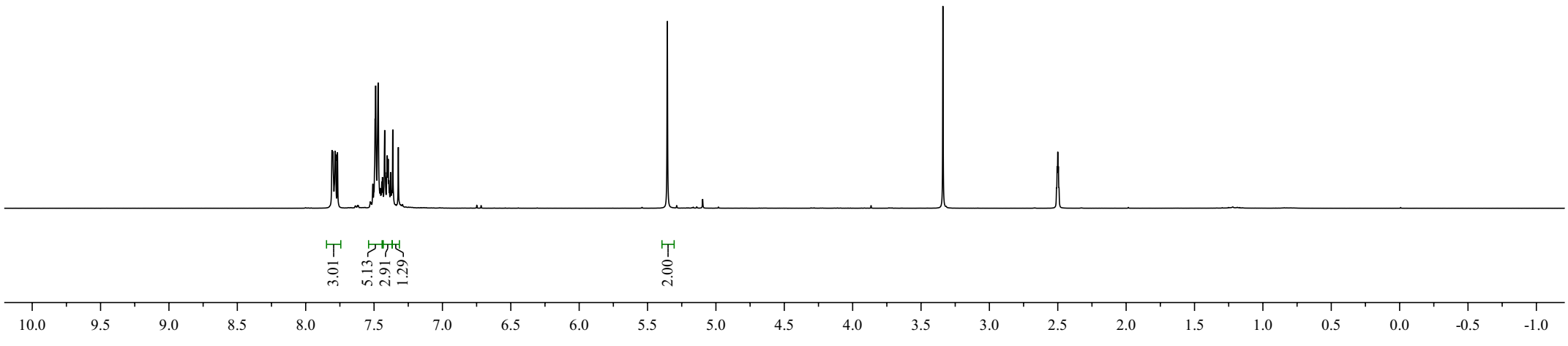
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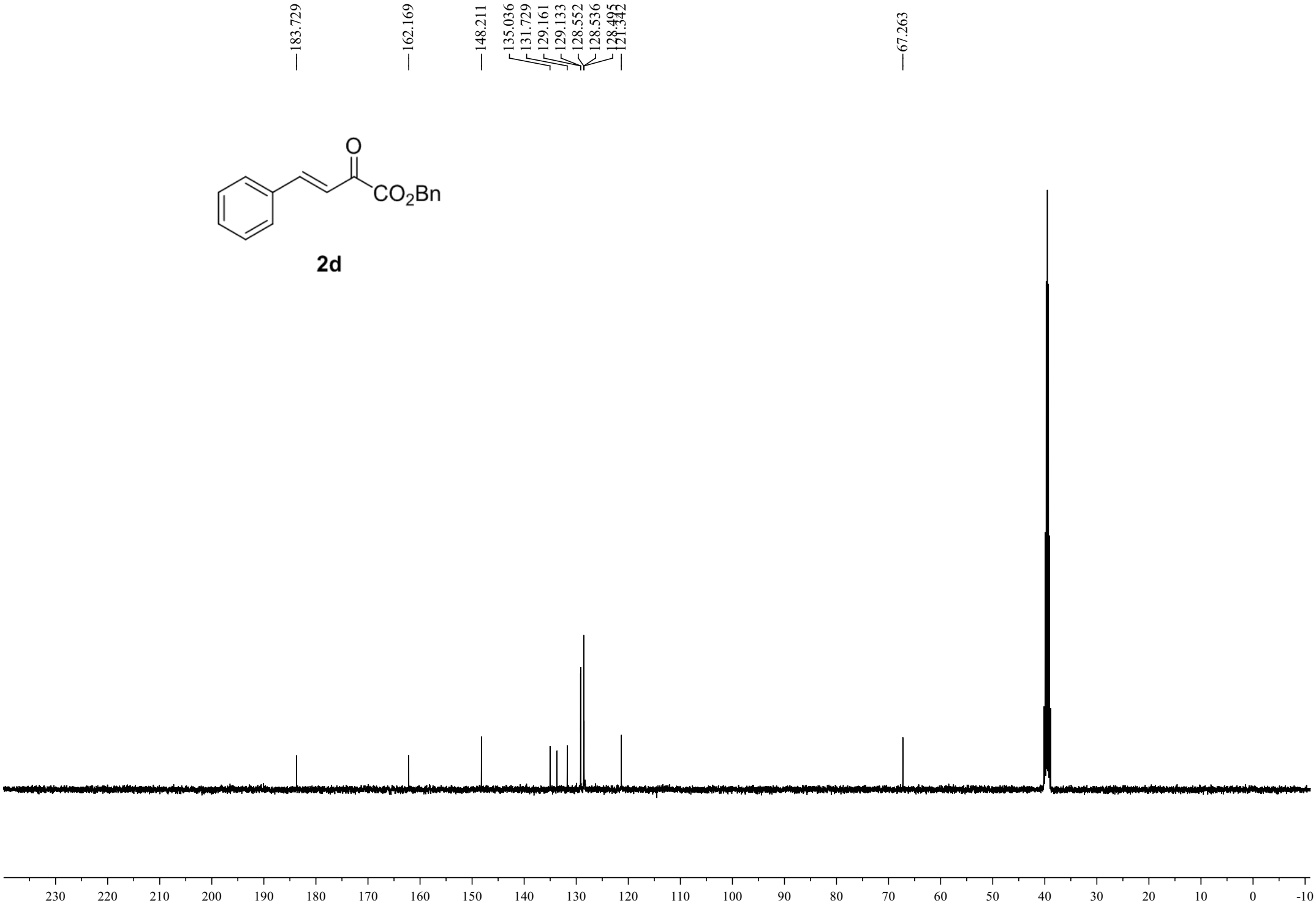
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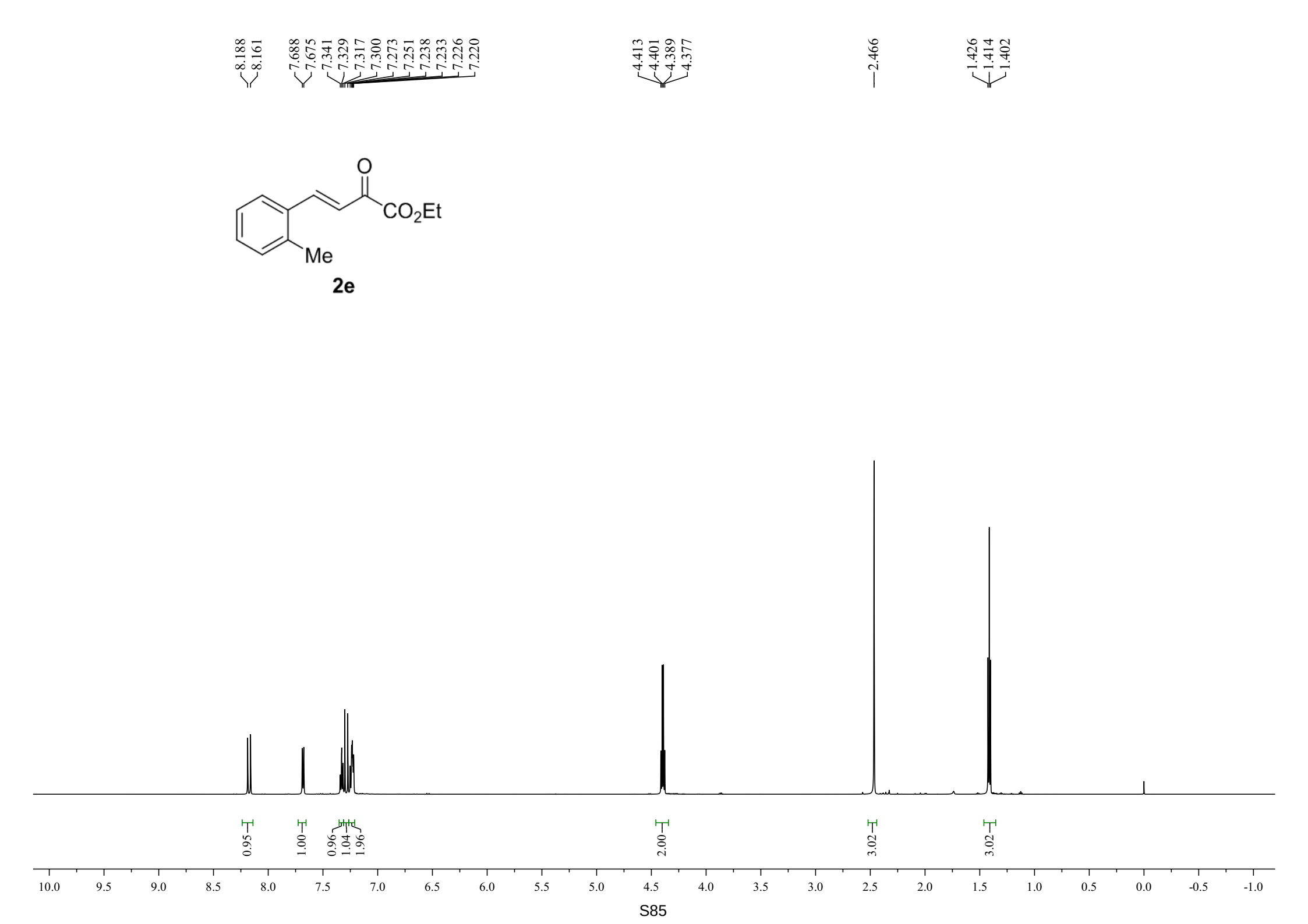
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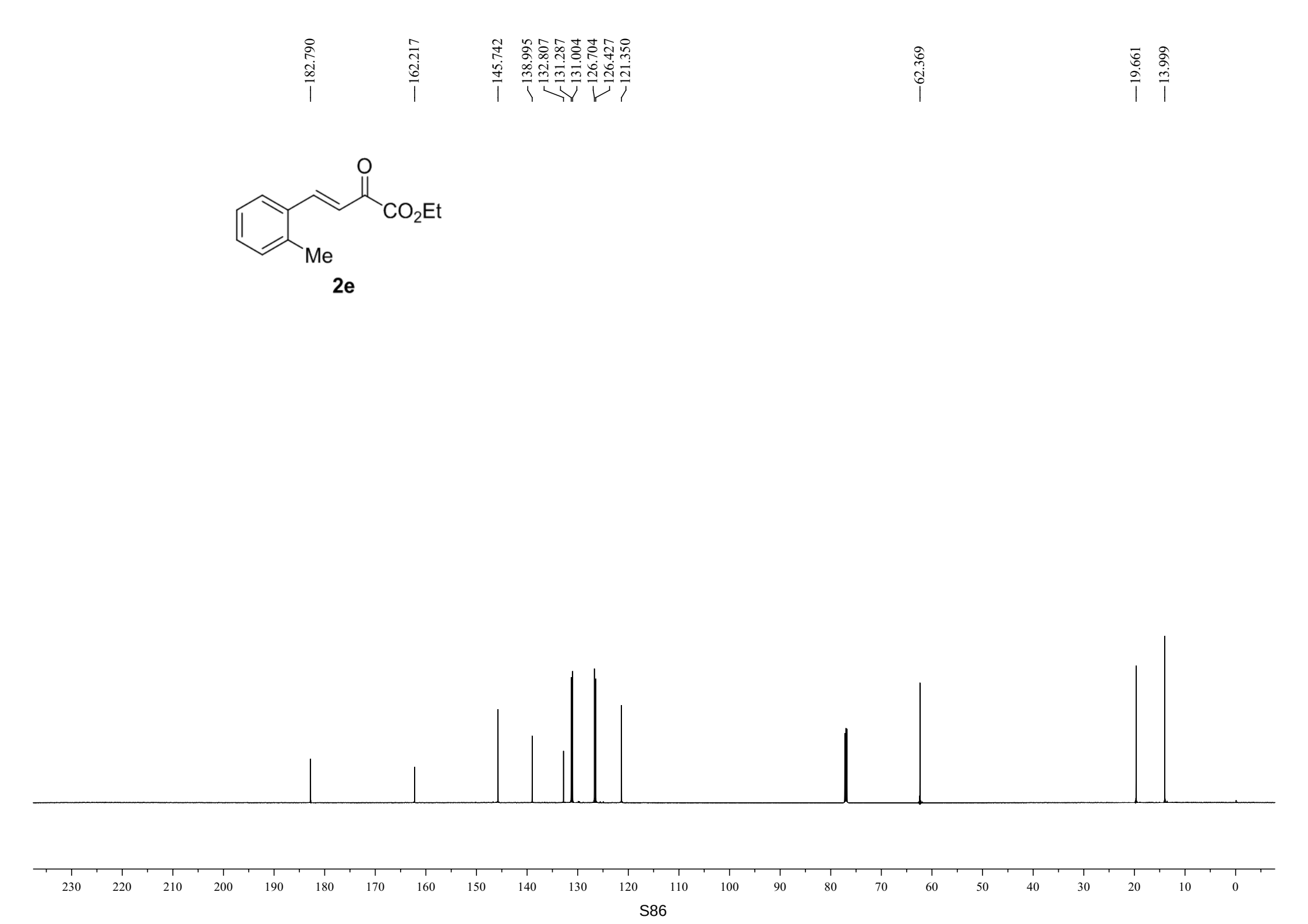
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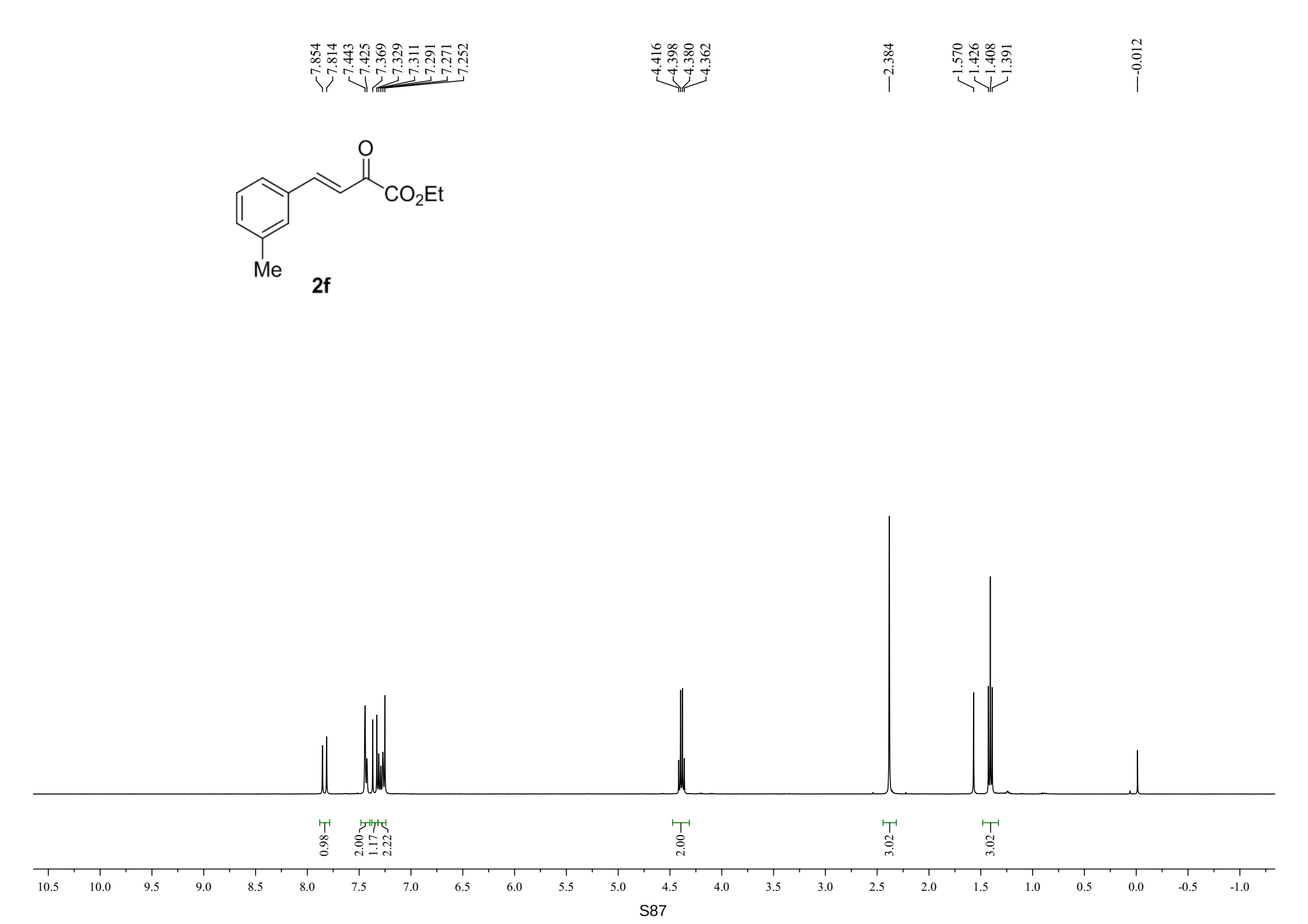
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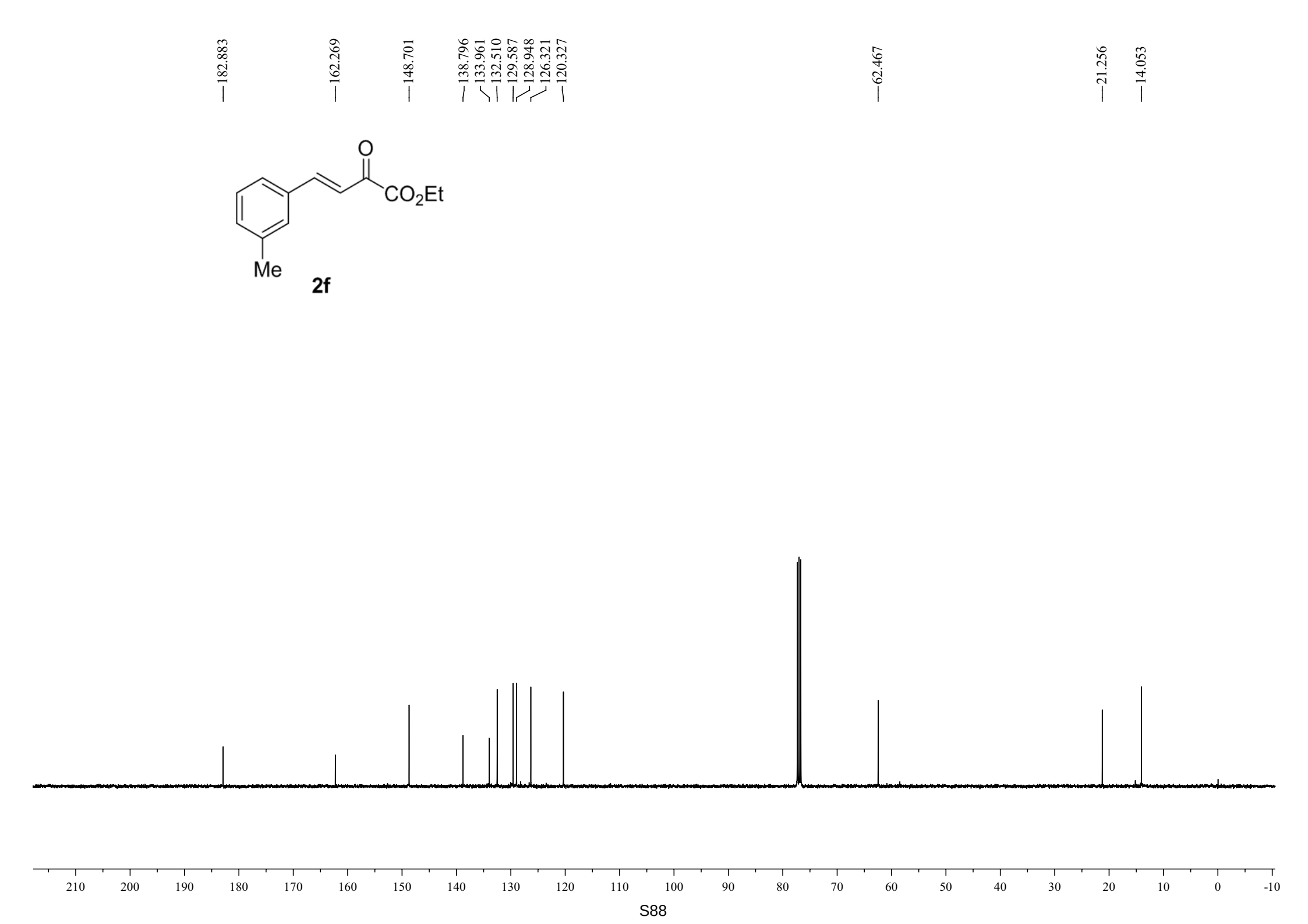
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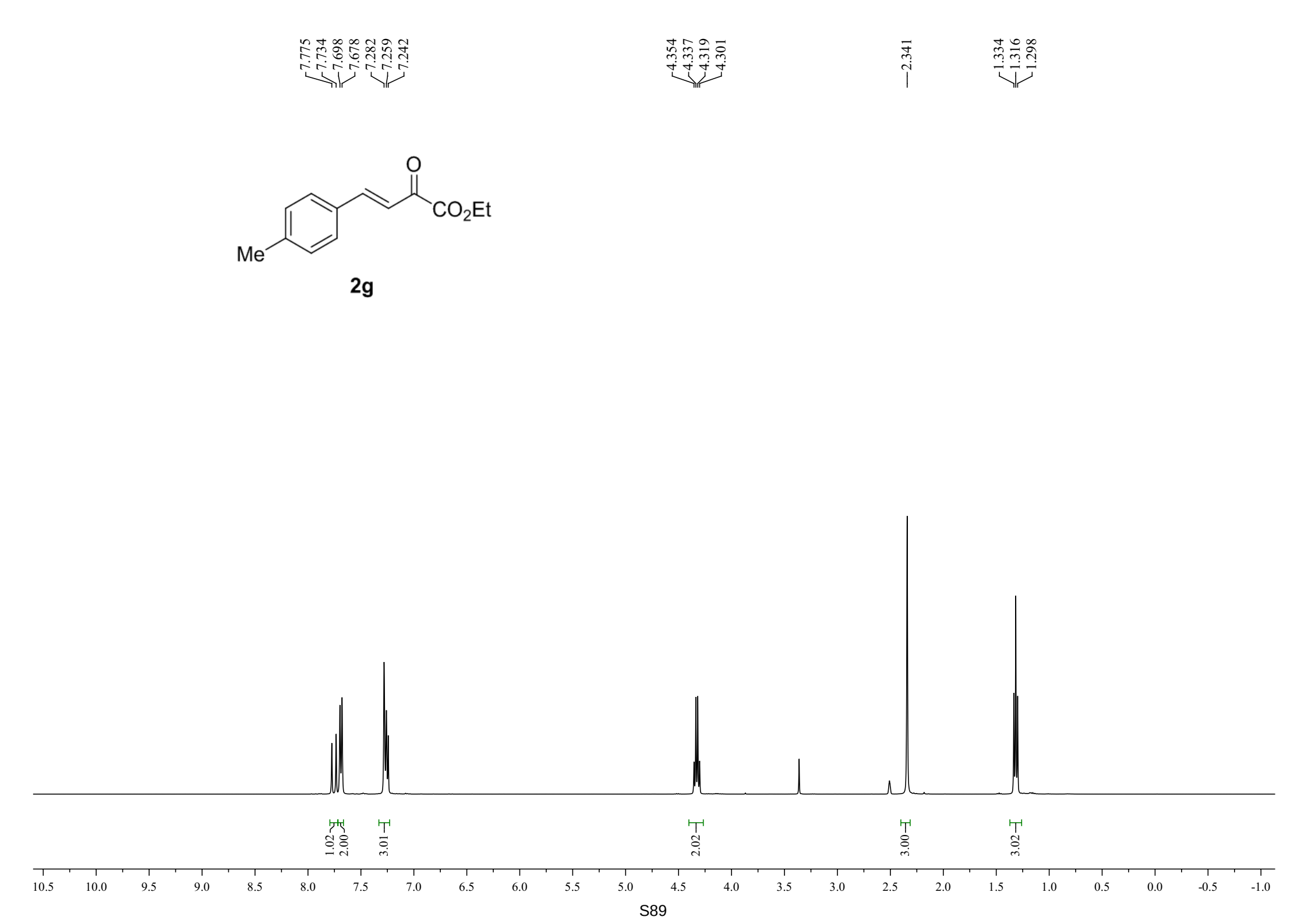
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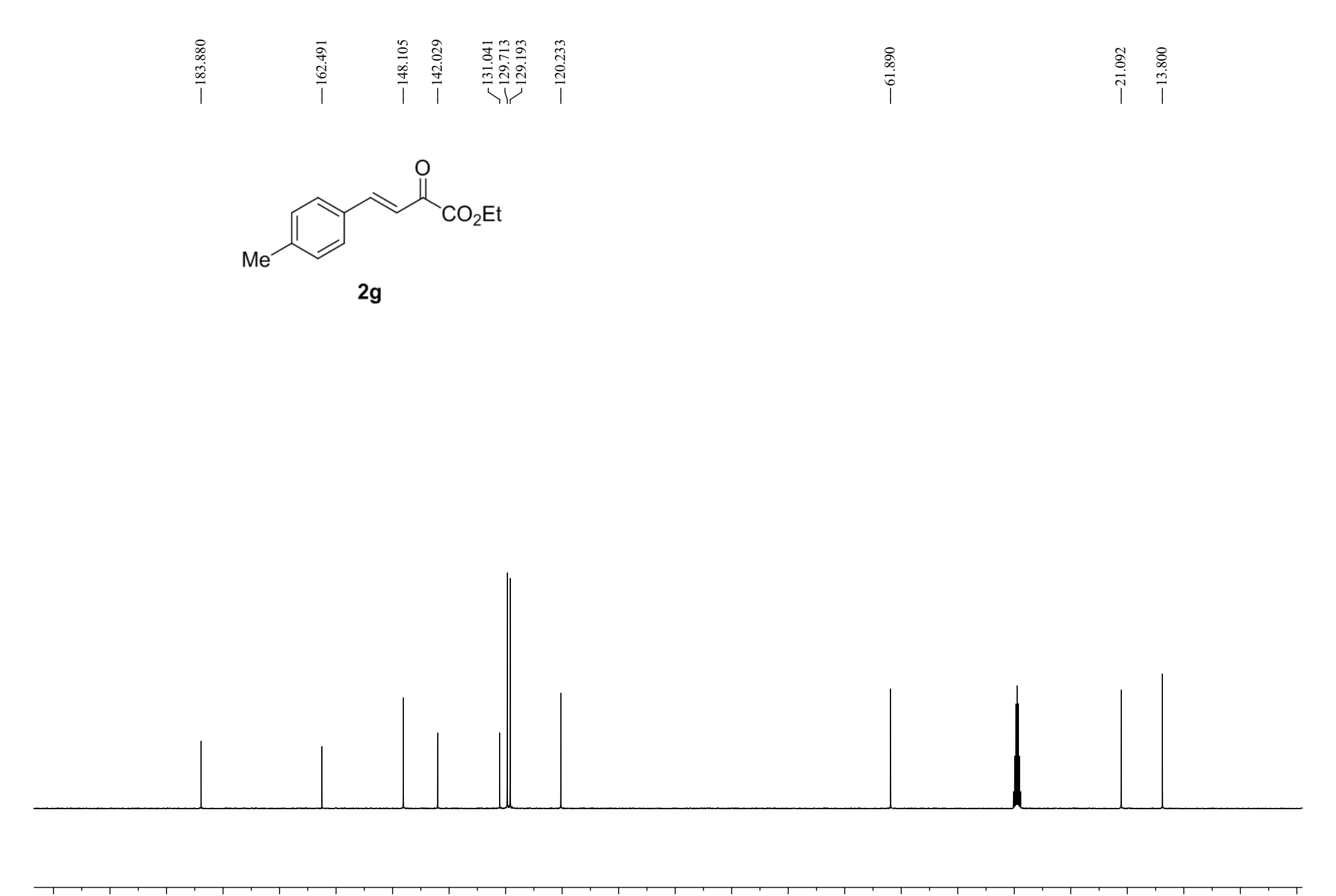
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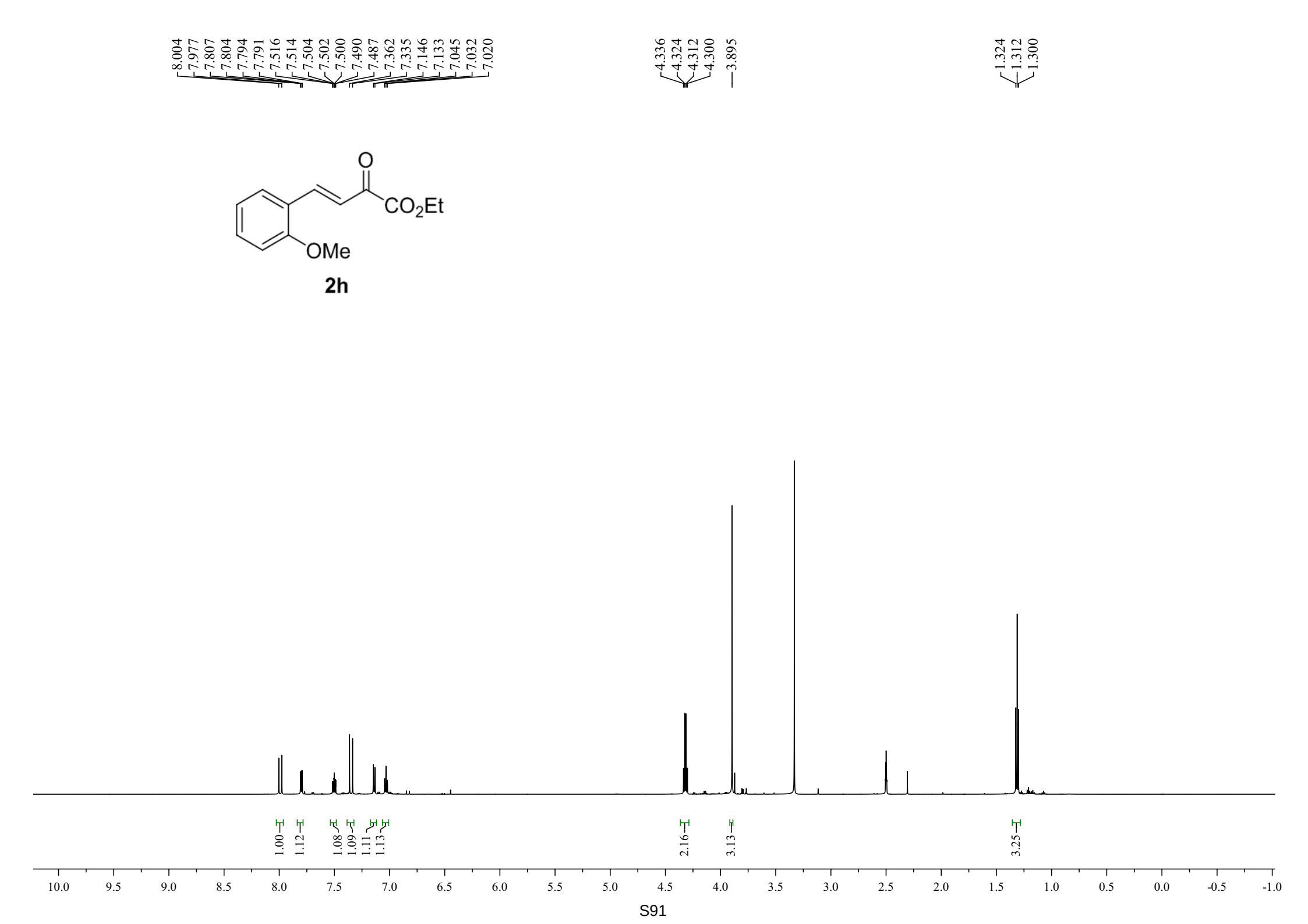
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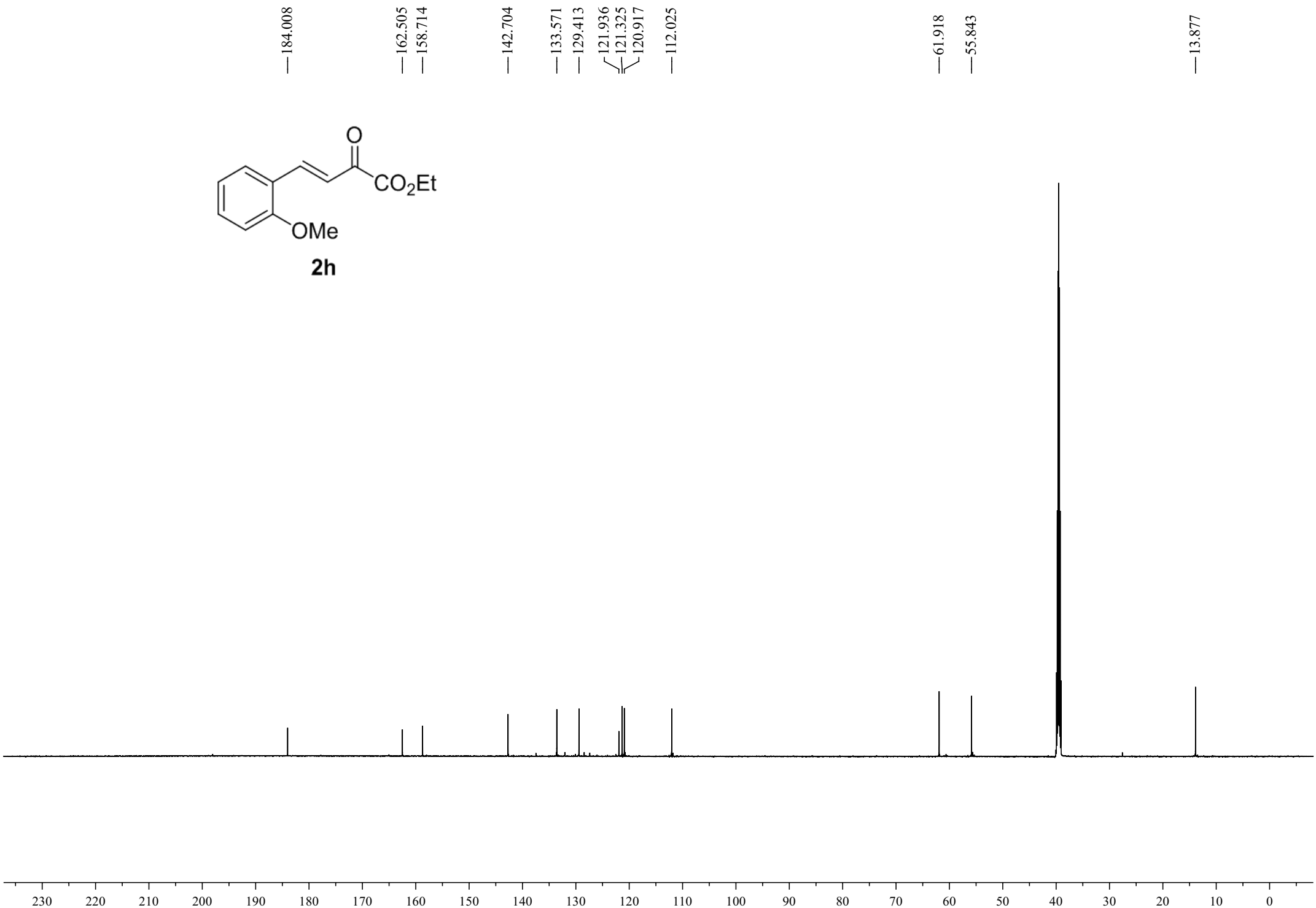
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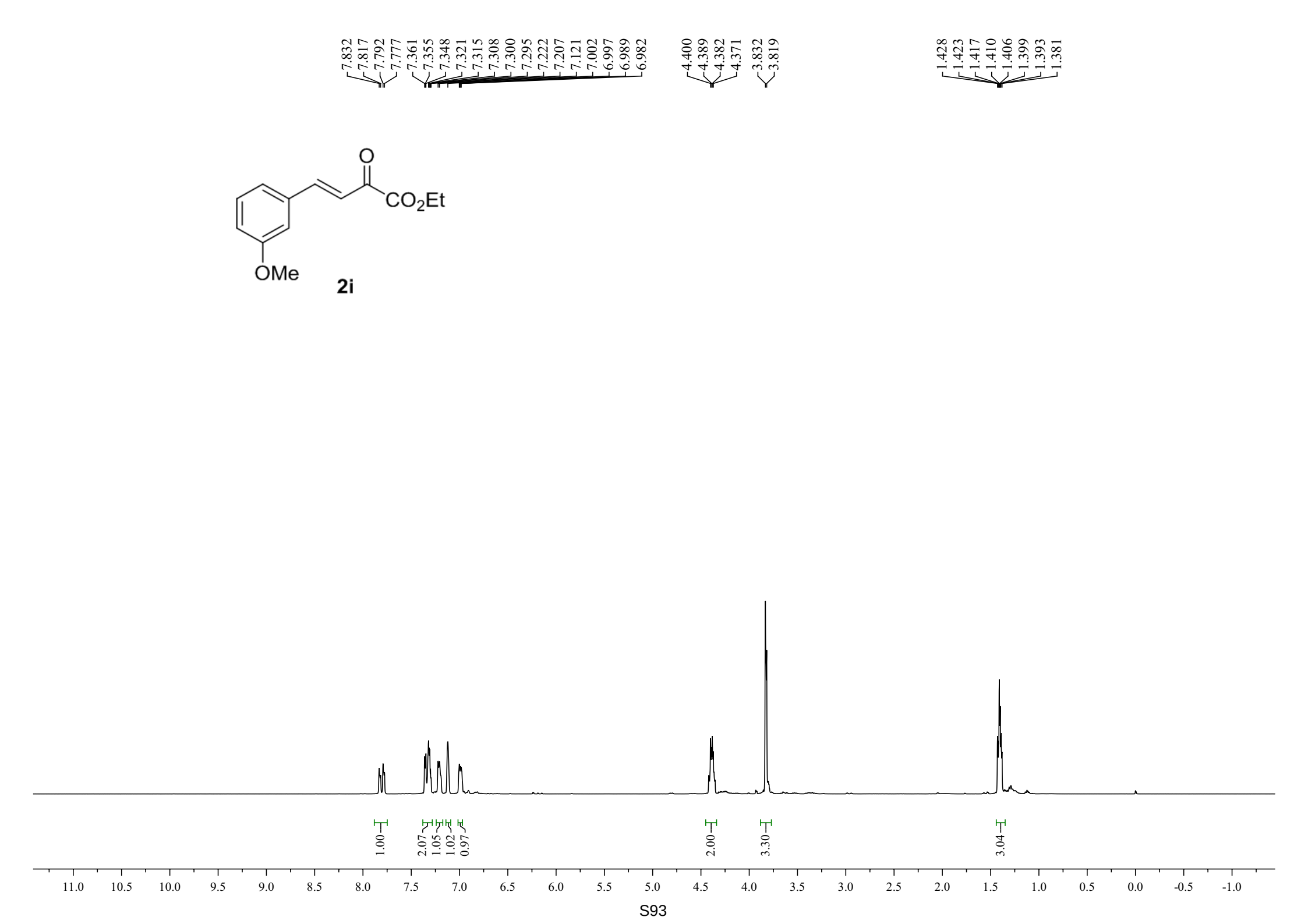
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OMe
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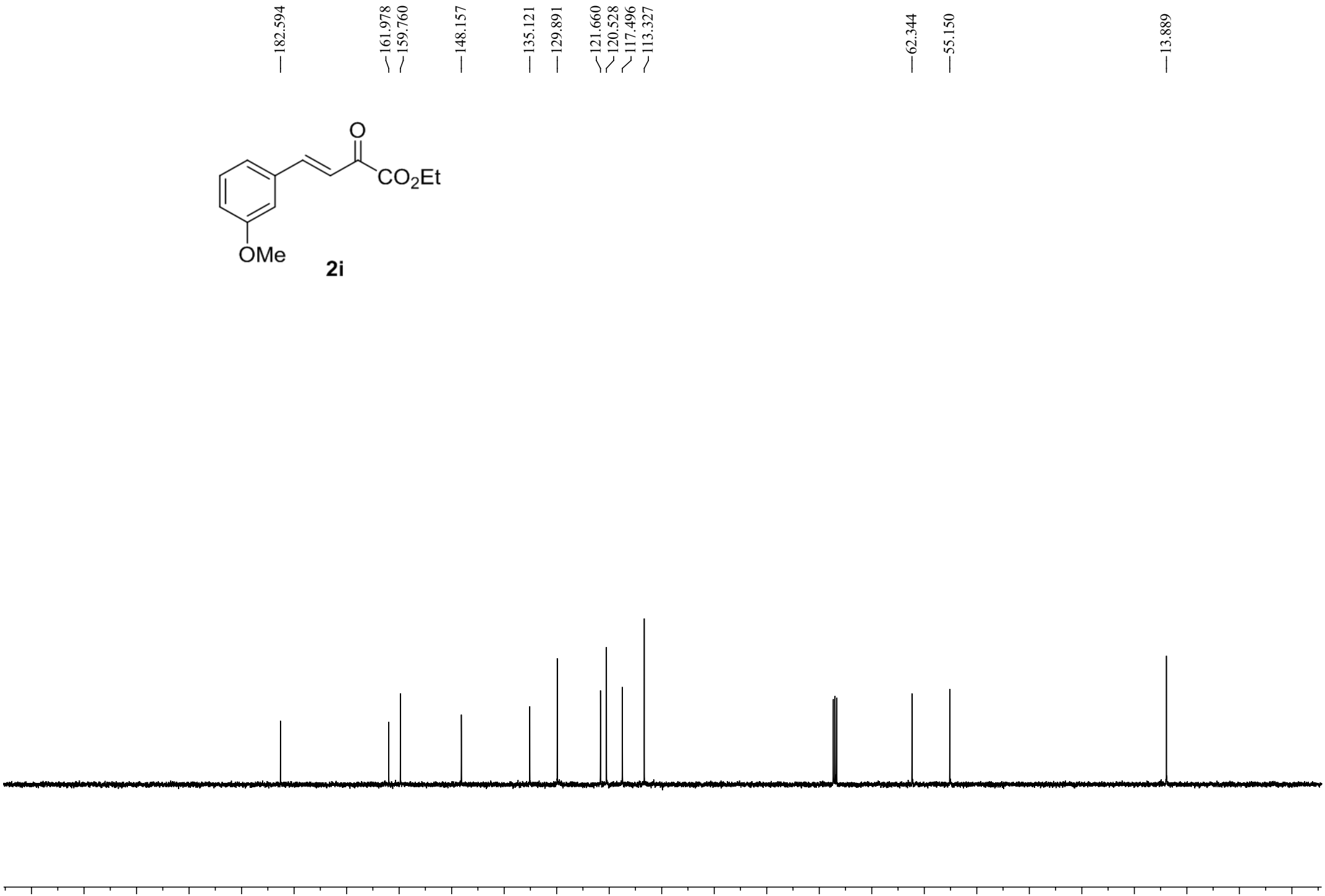
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2i
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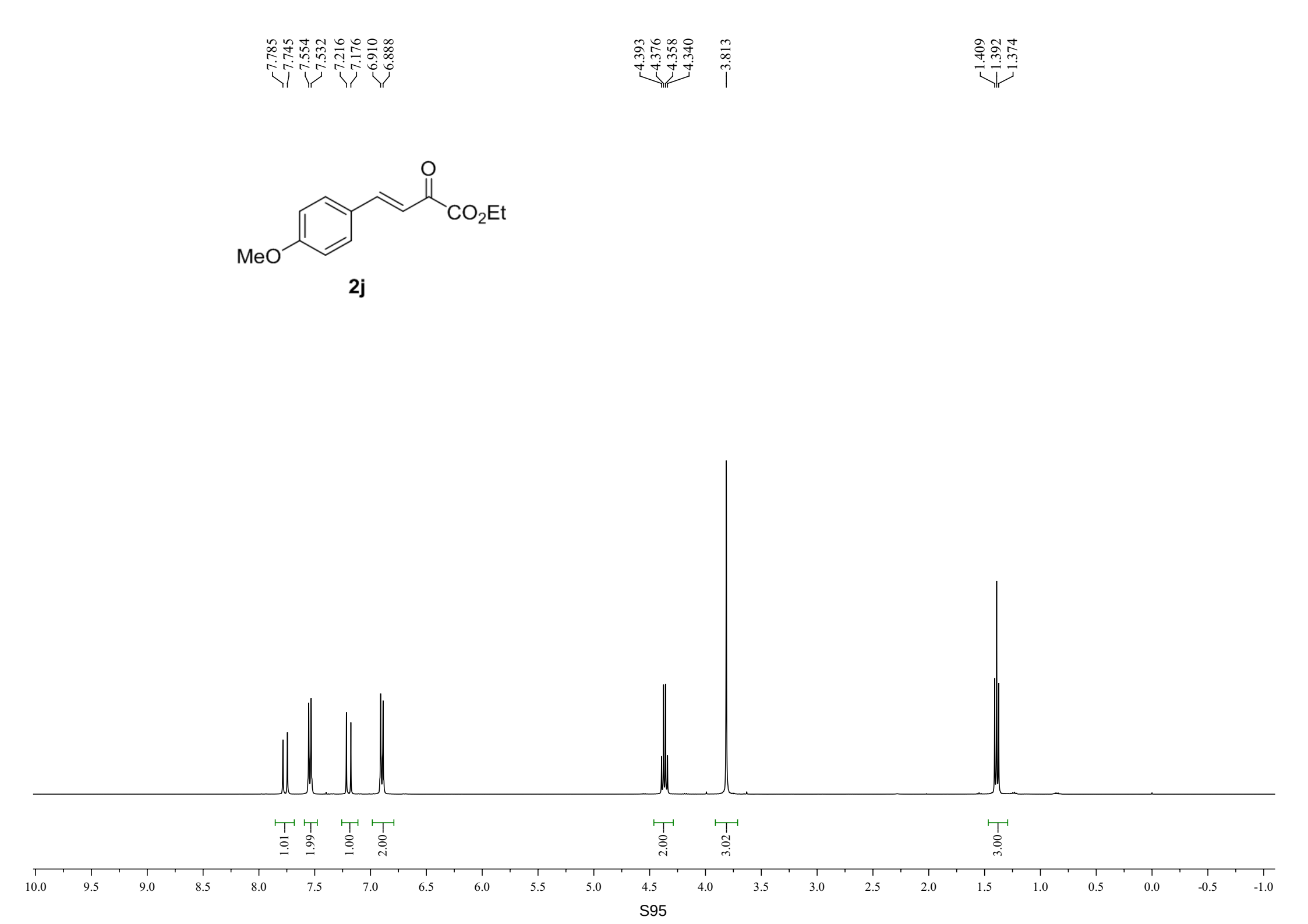
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MeO
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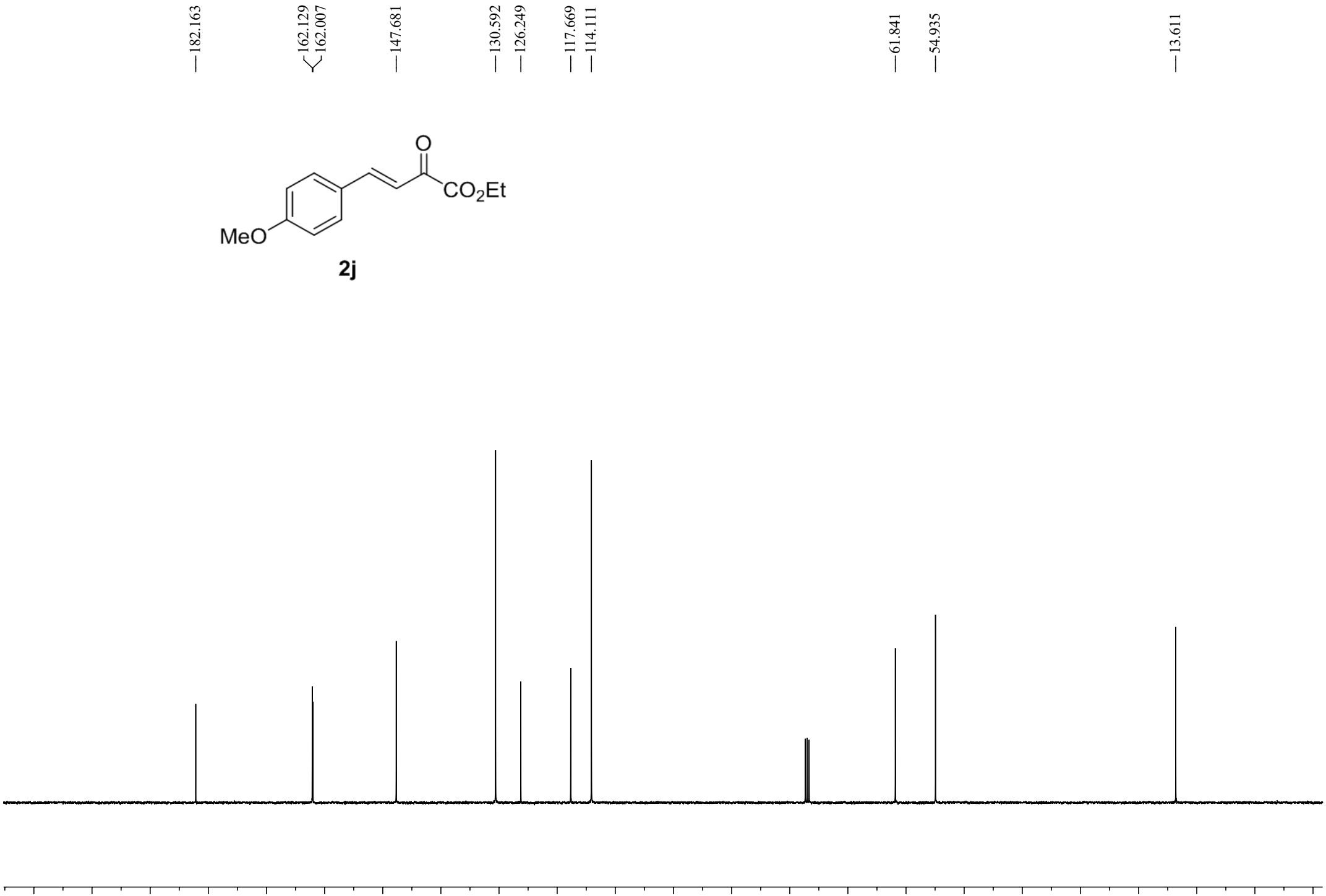
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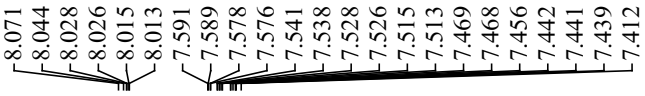
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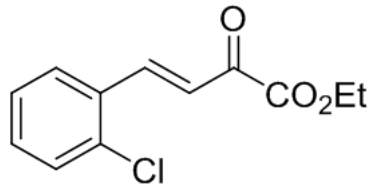
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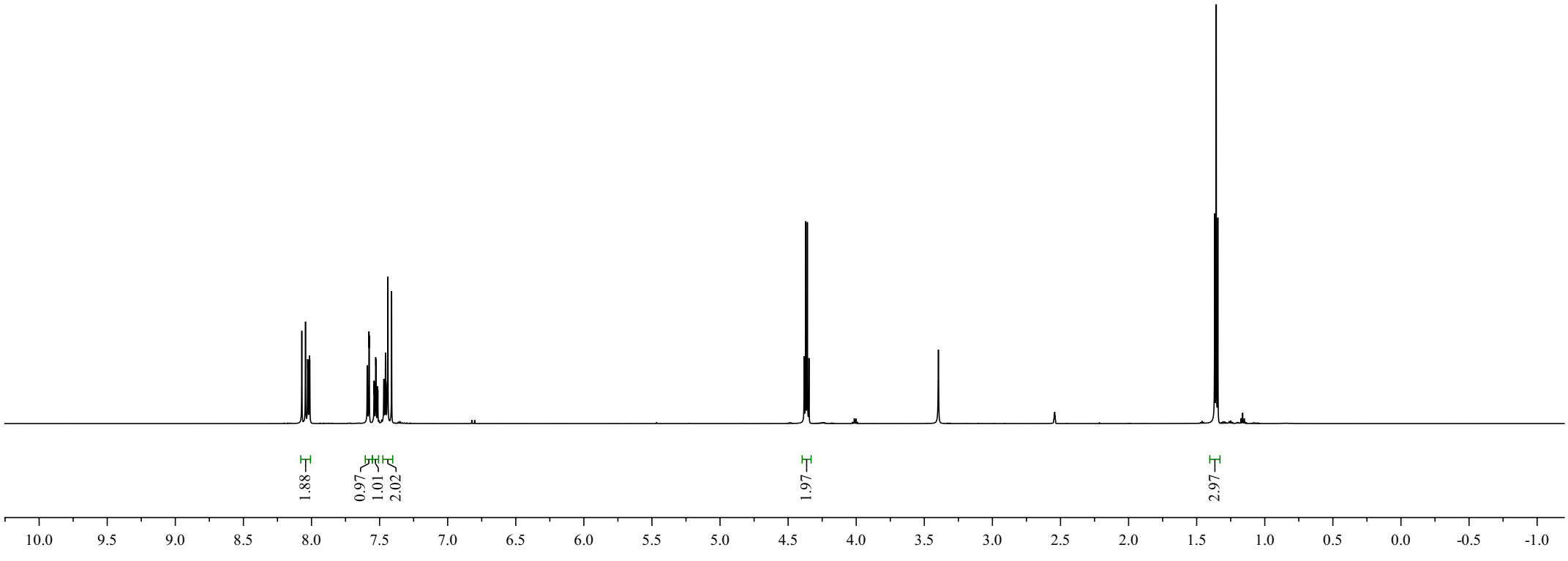
2k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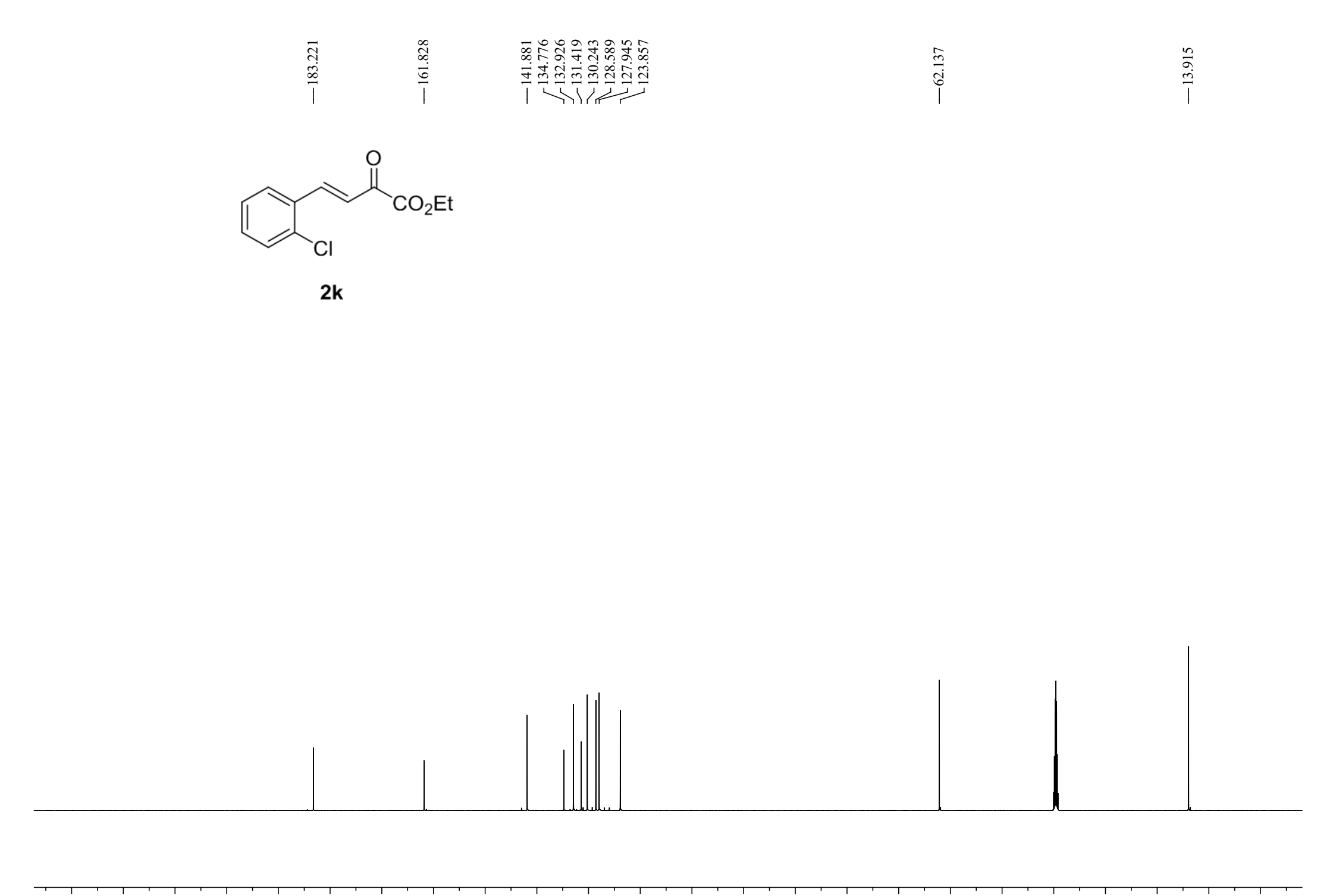
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Cl
2k
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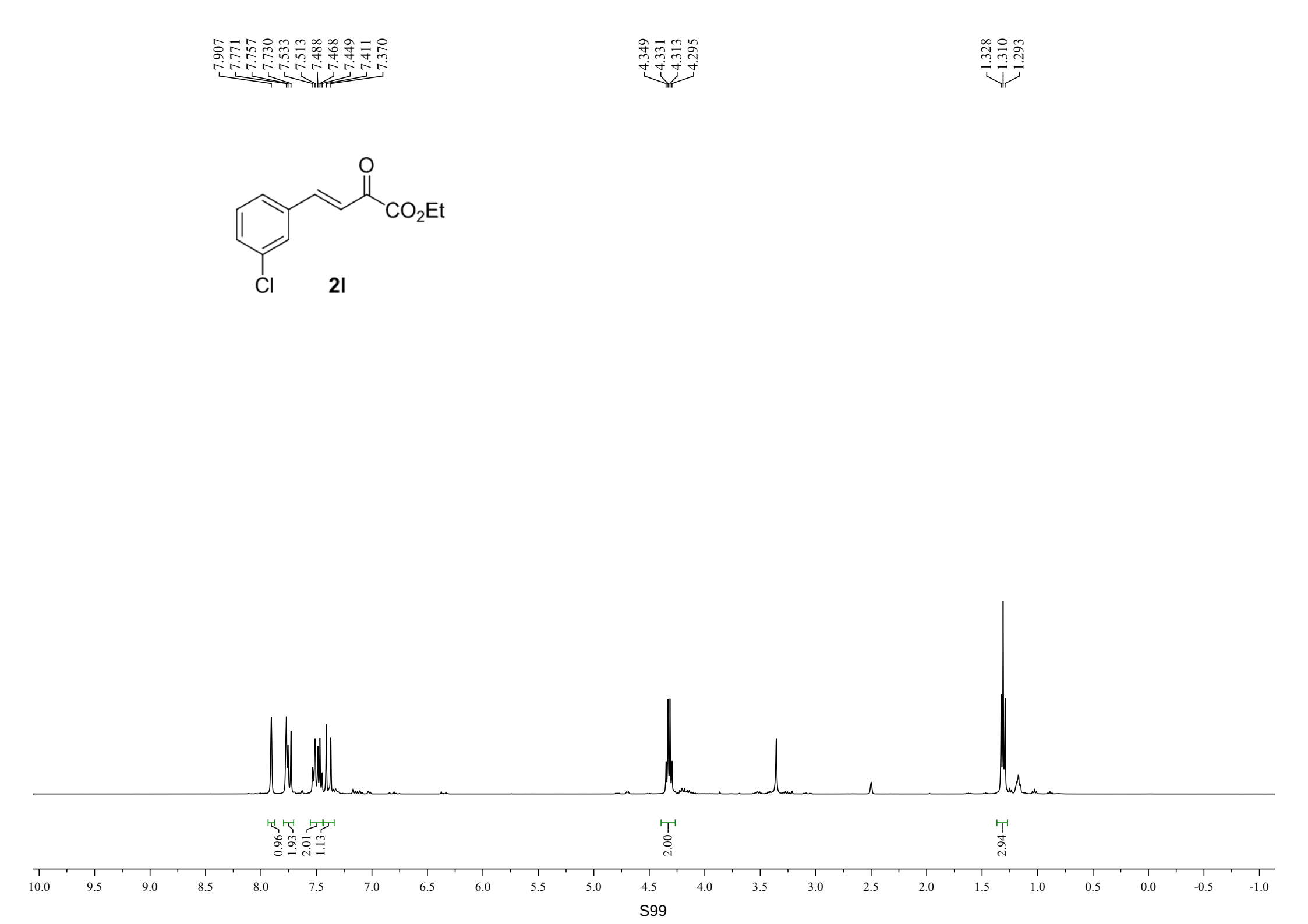
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1.310
1.293
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Cl
2l
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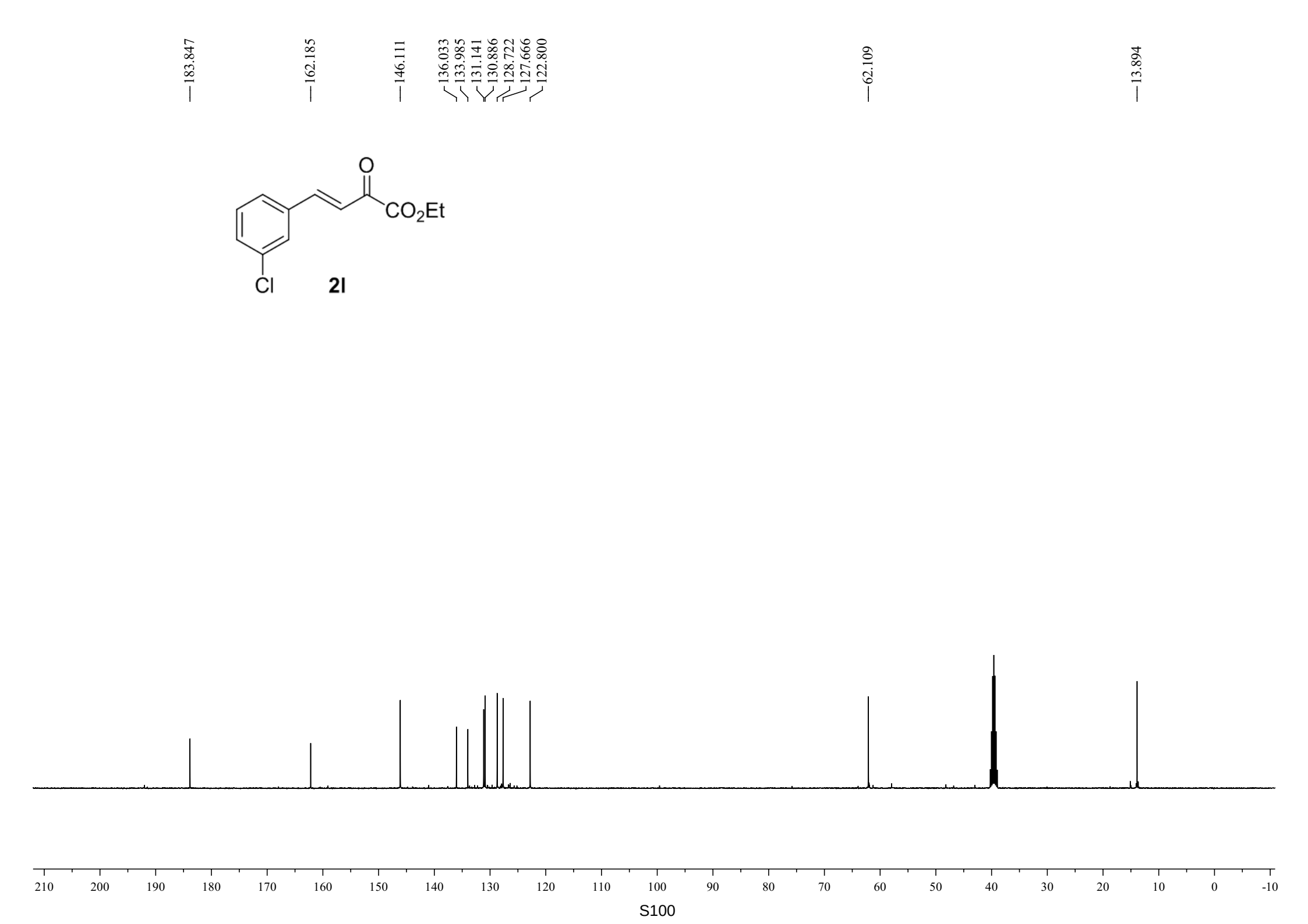
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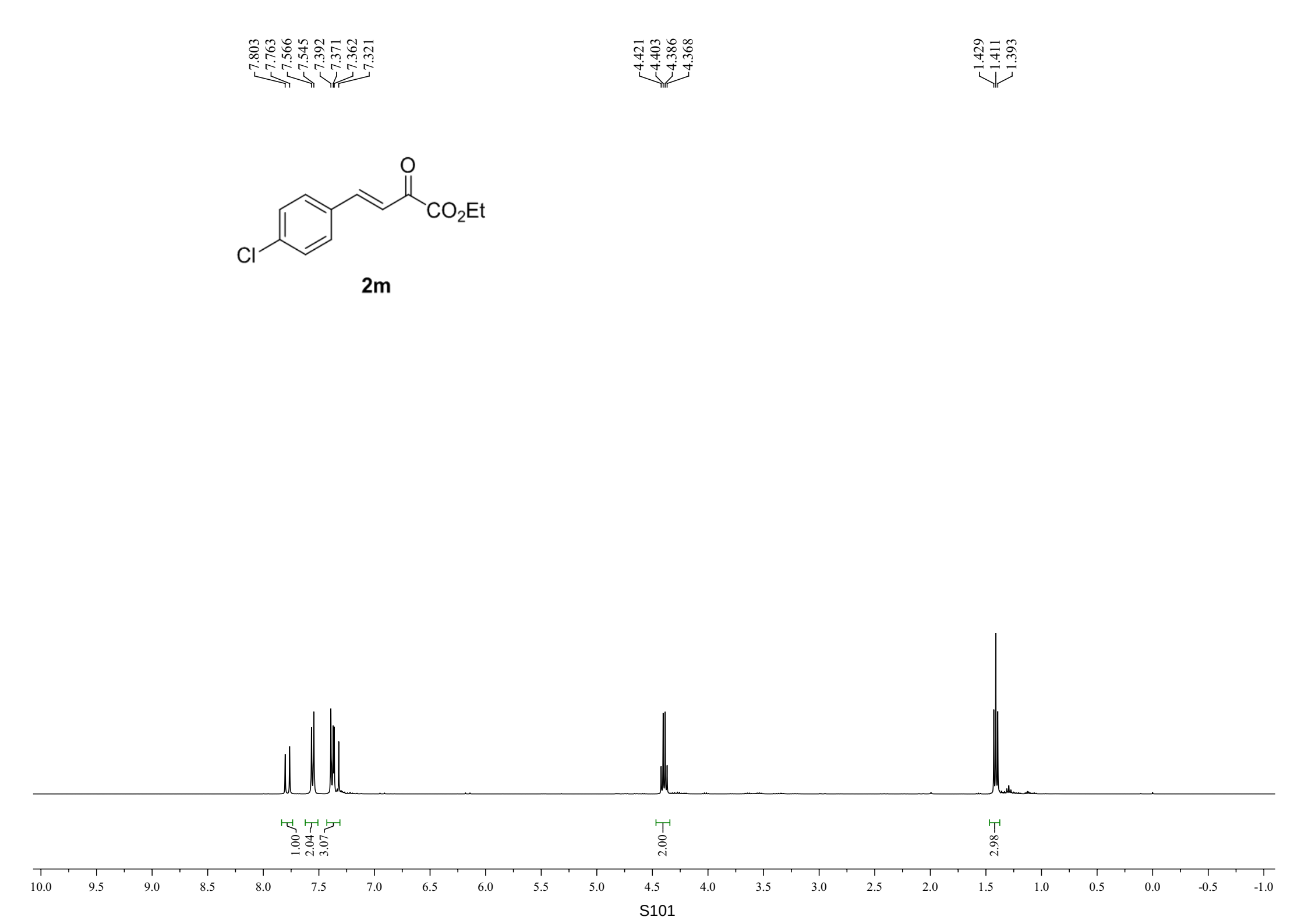
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O
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Cl
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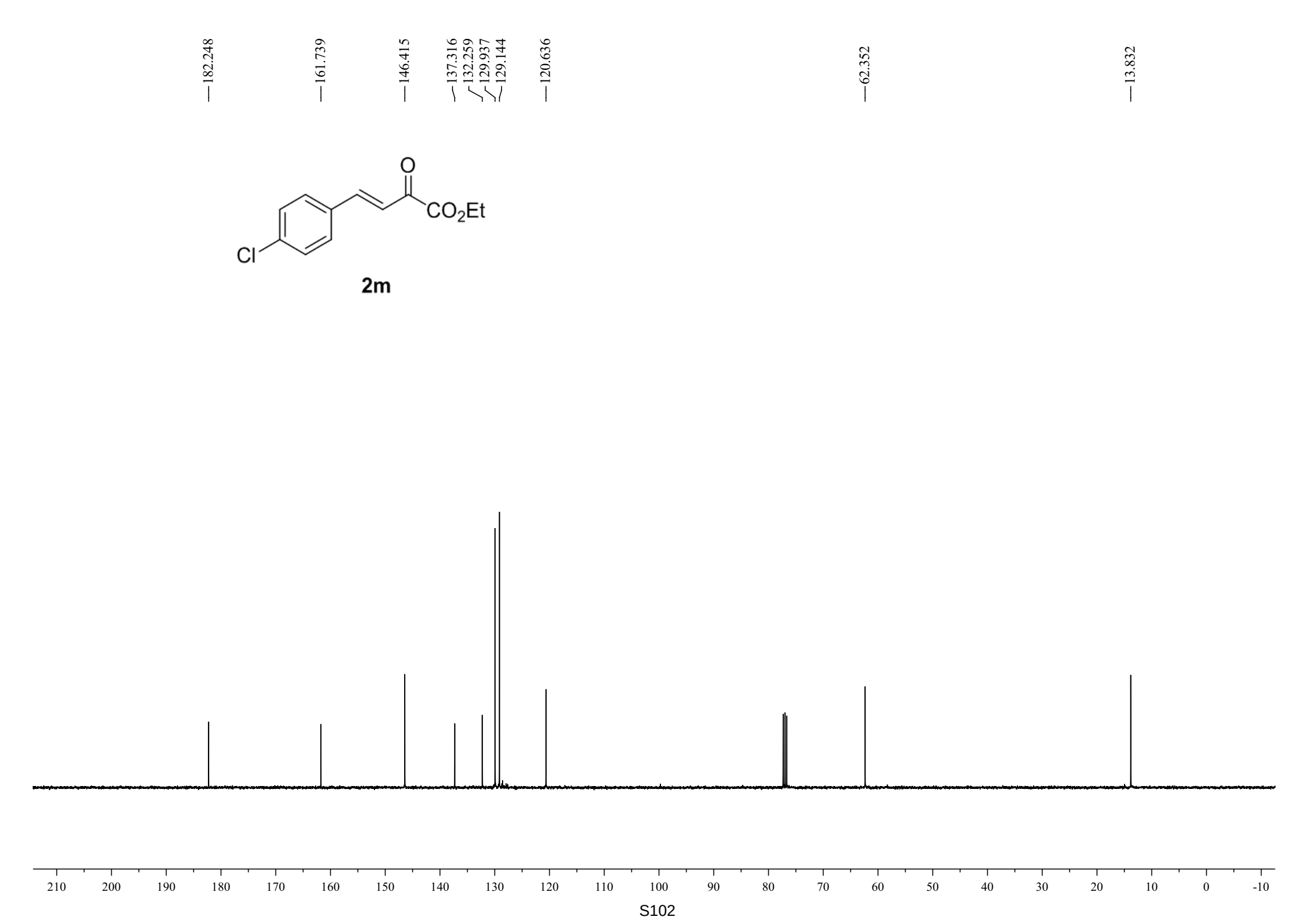
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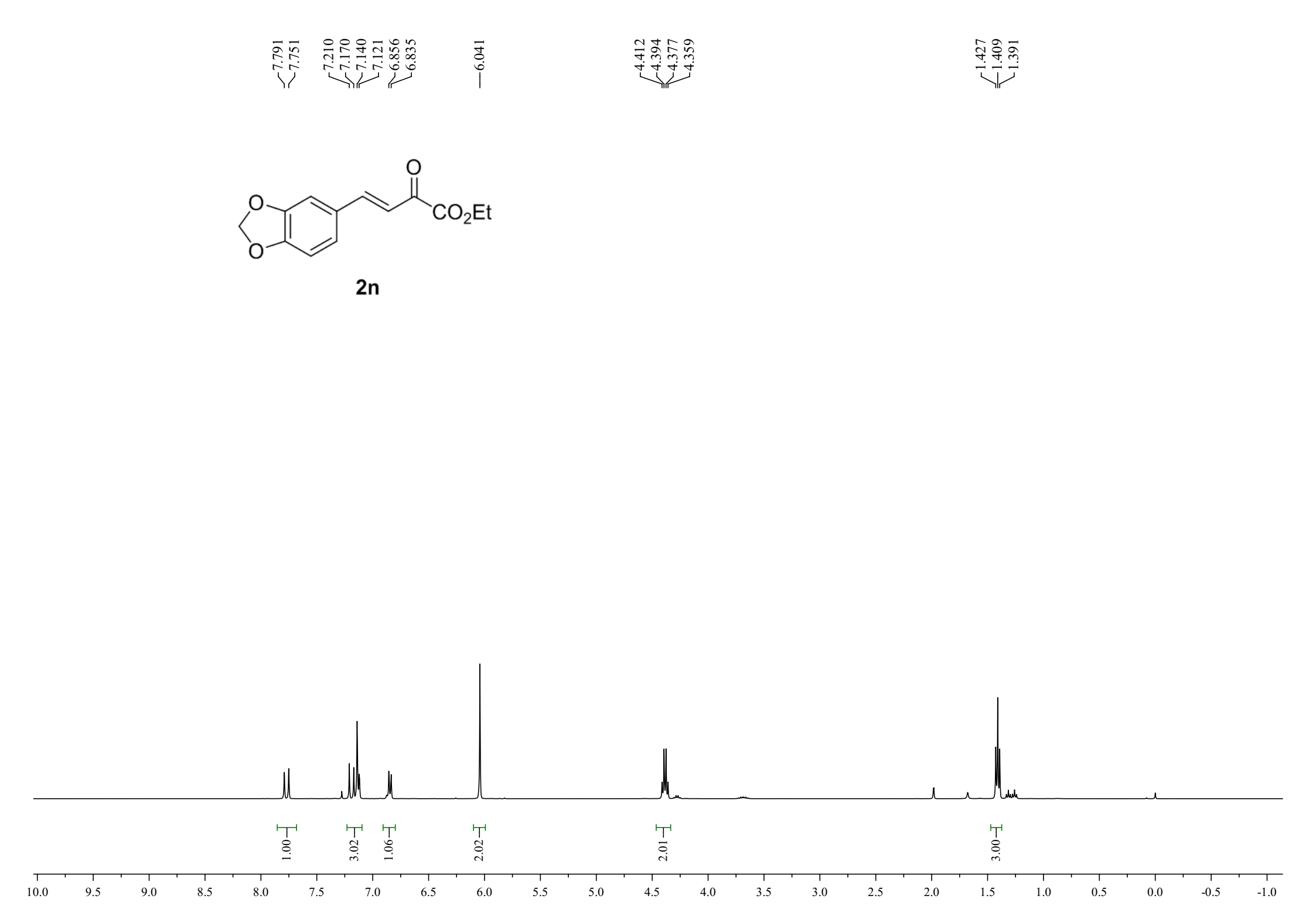
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O
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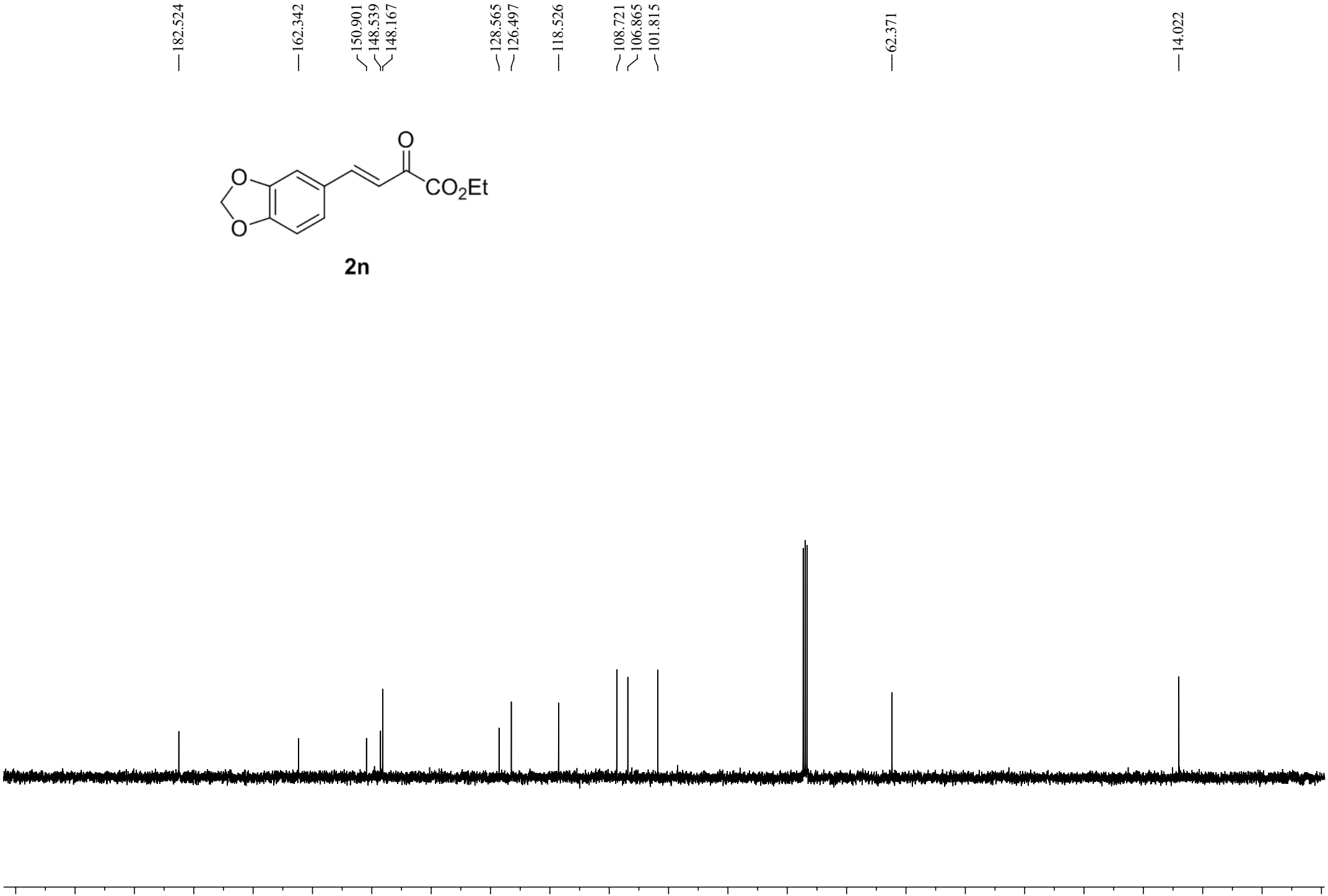
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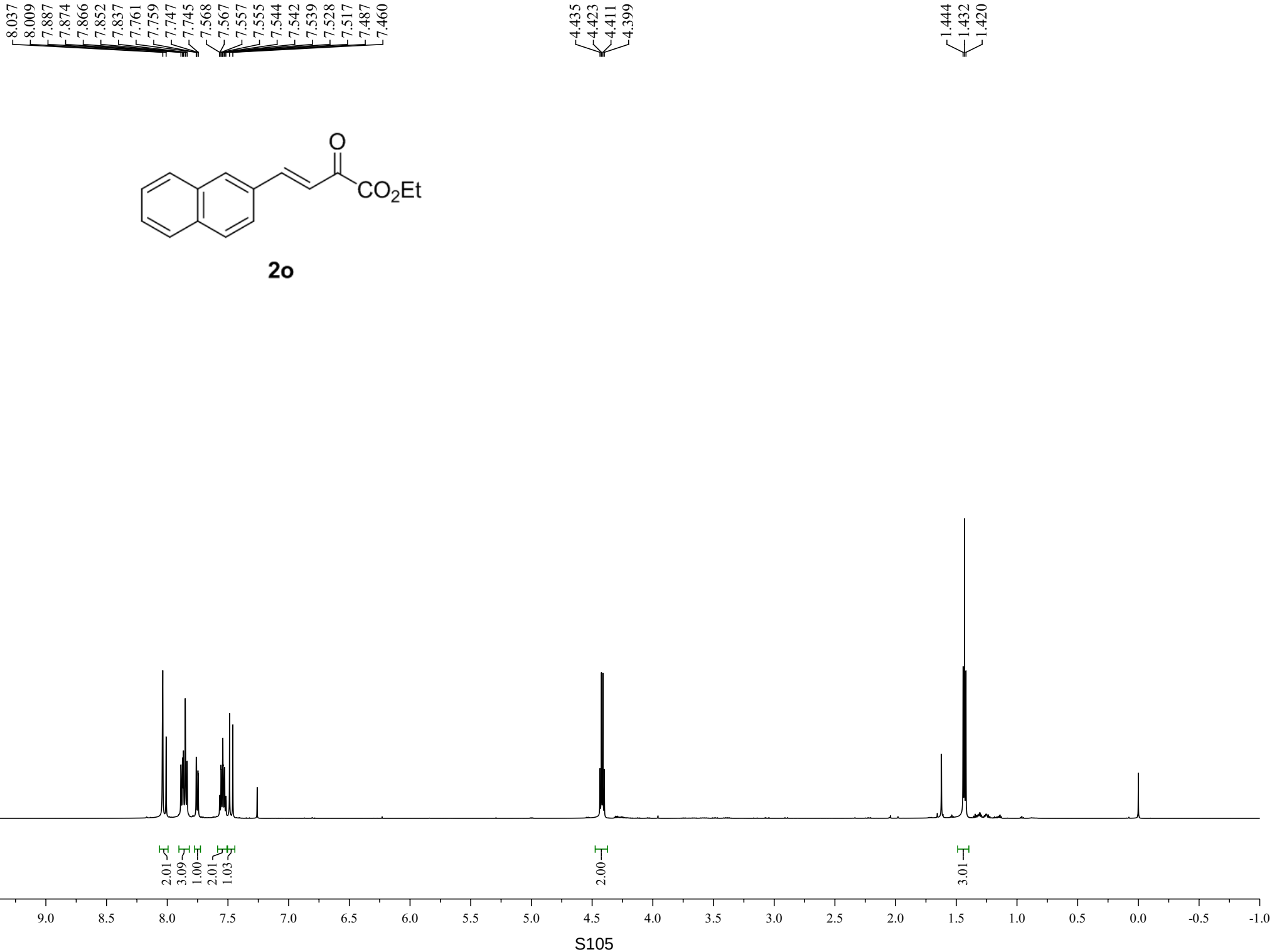
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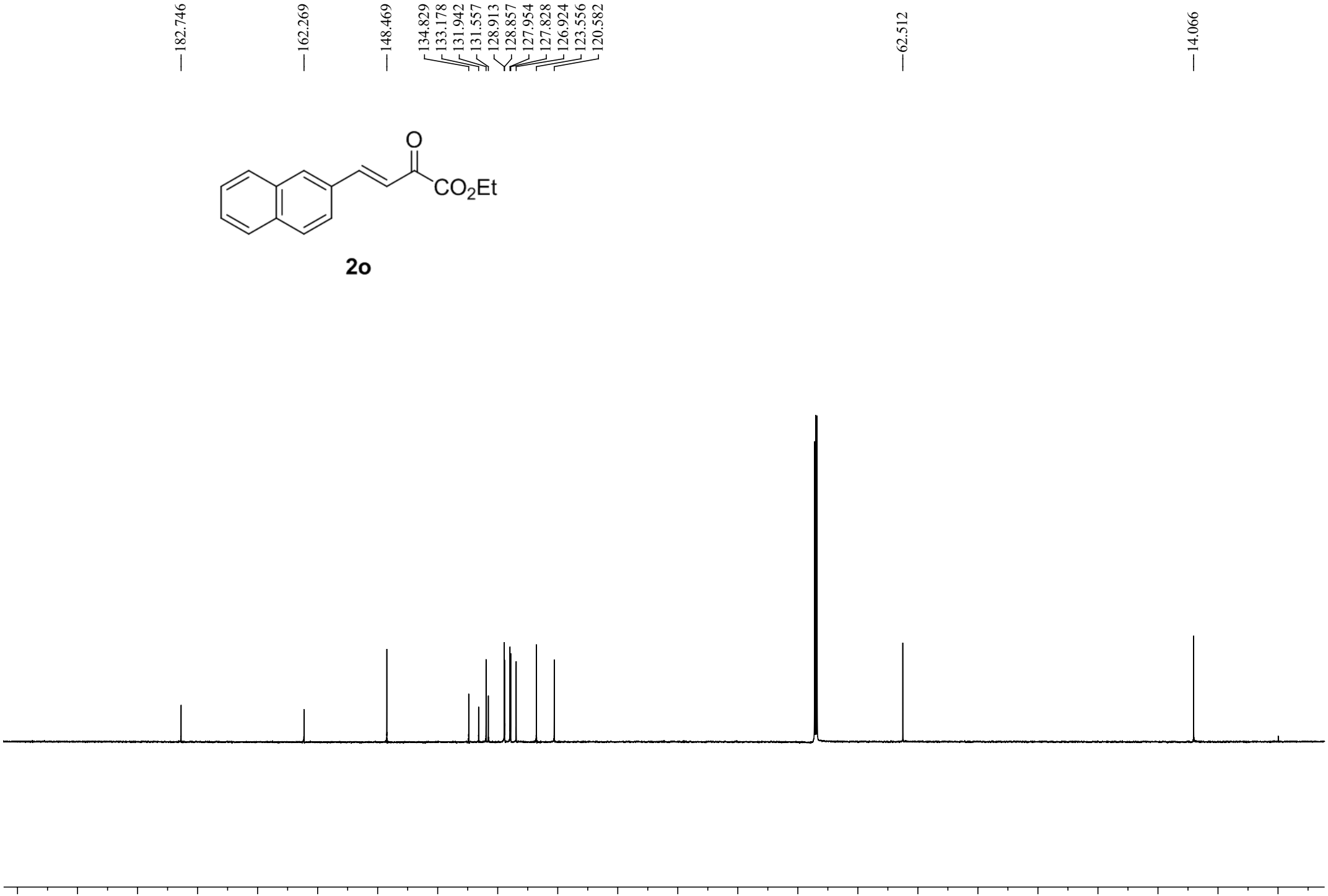
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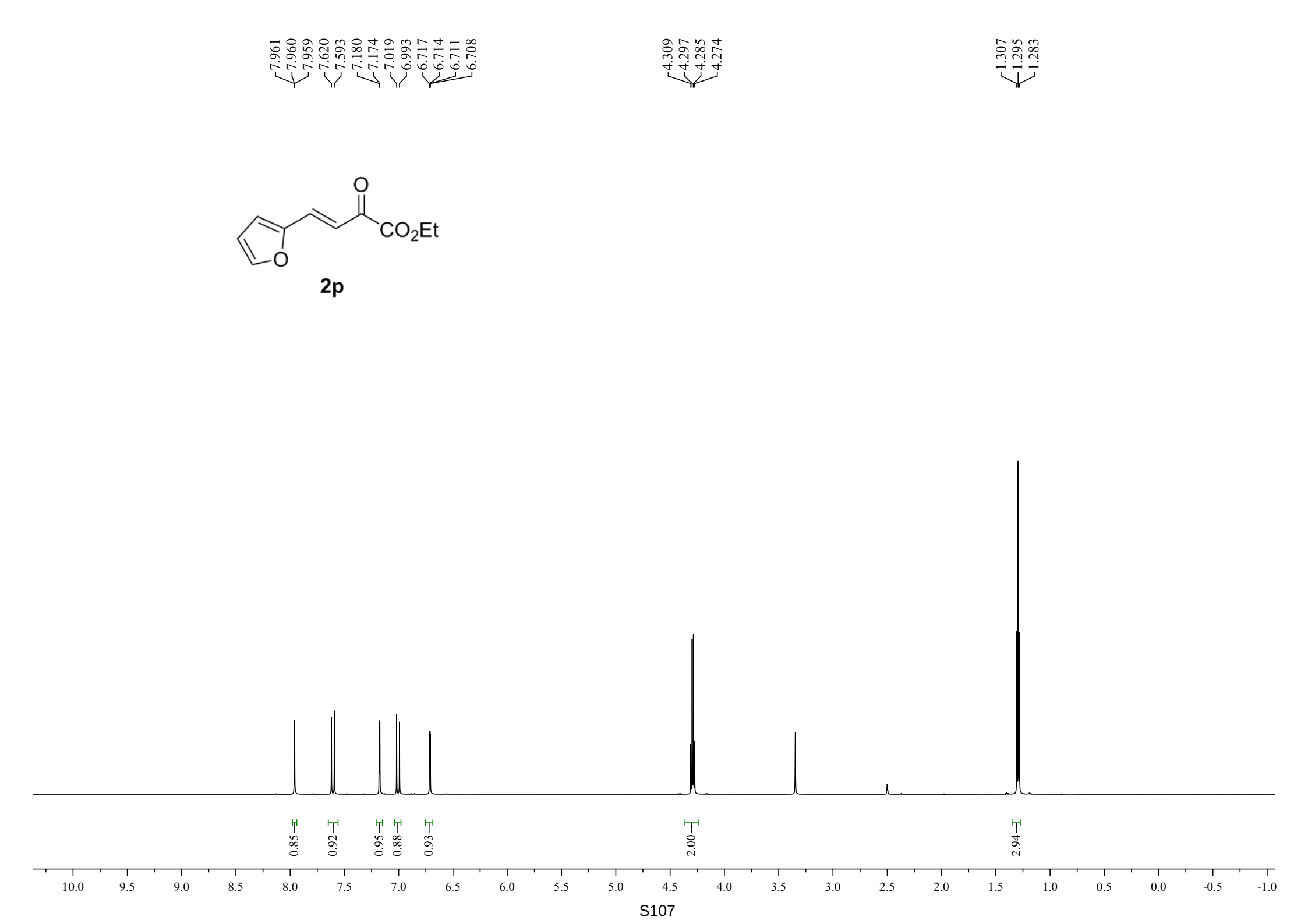
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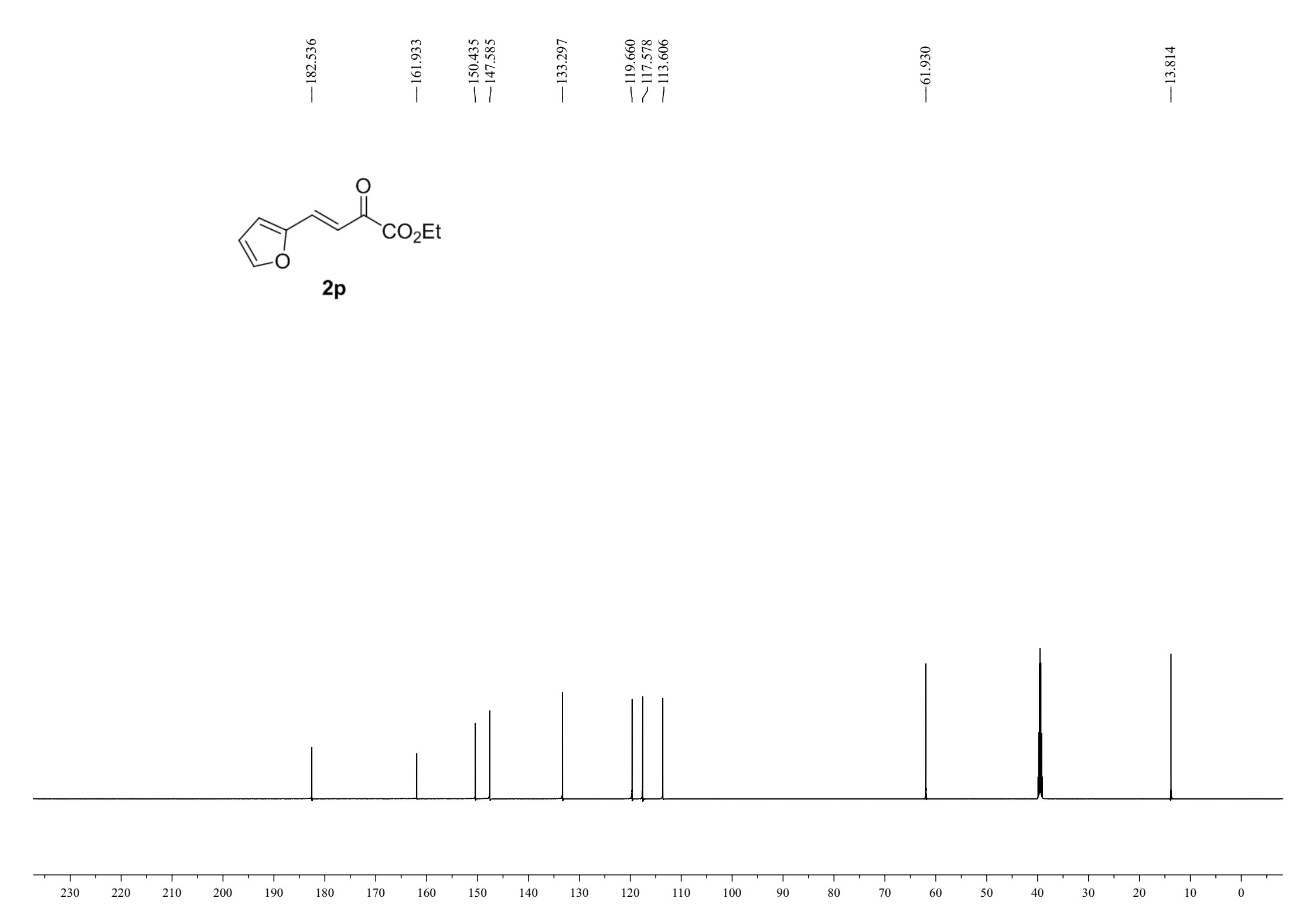
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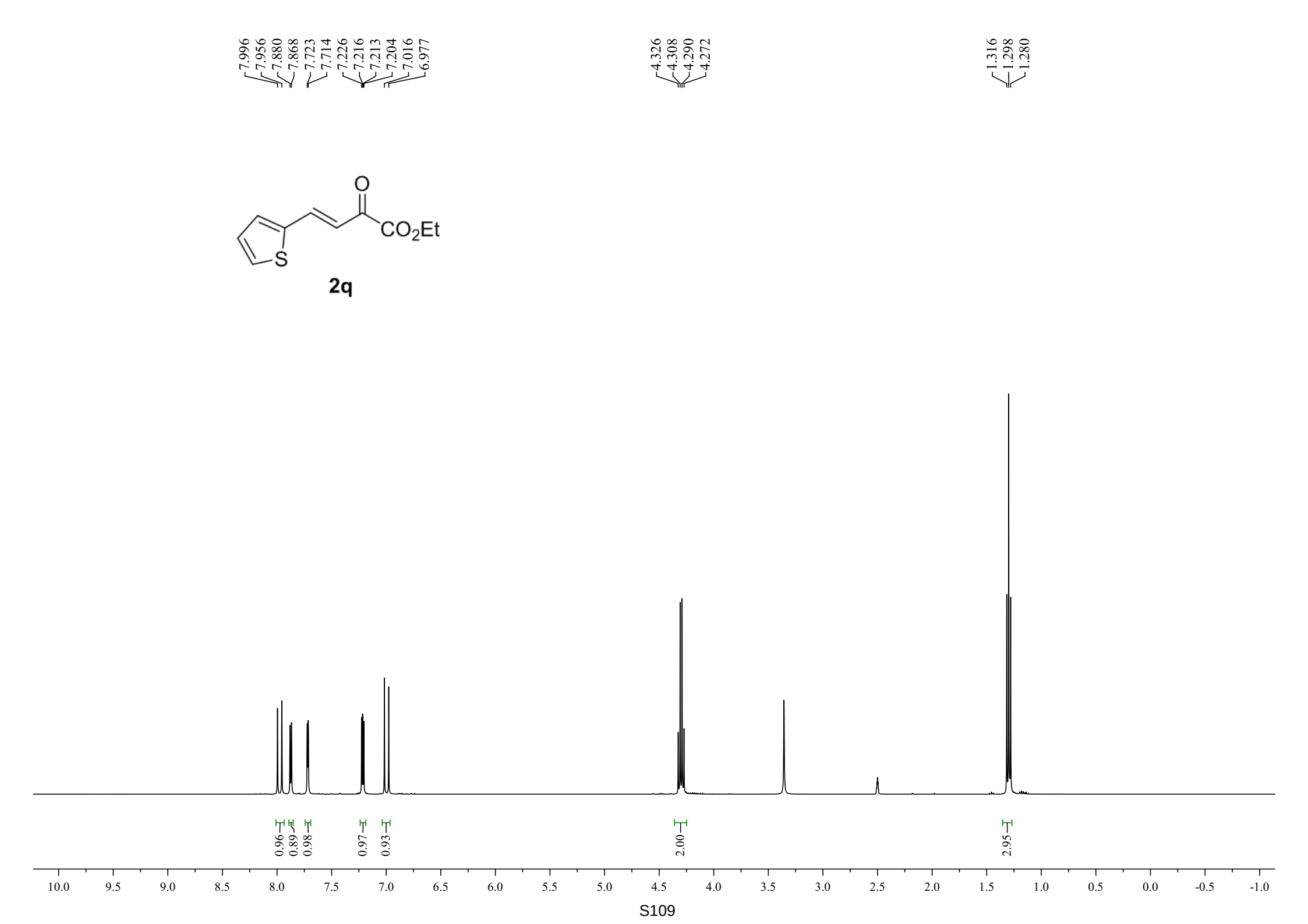
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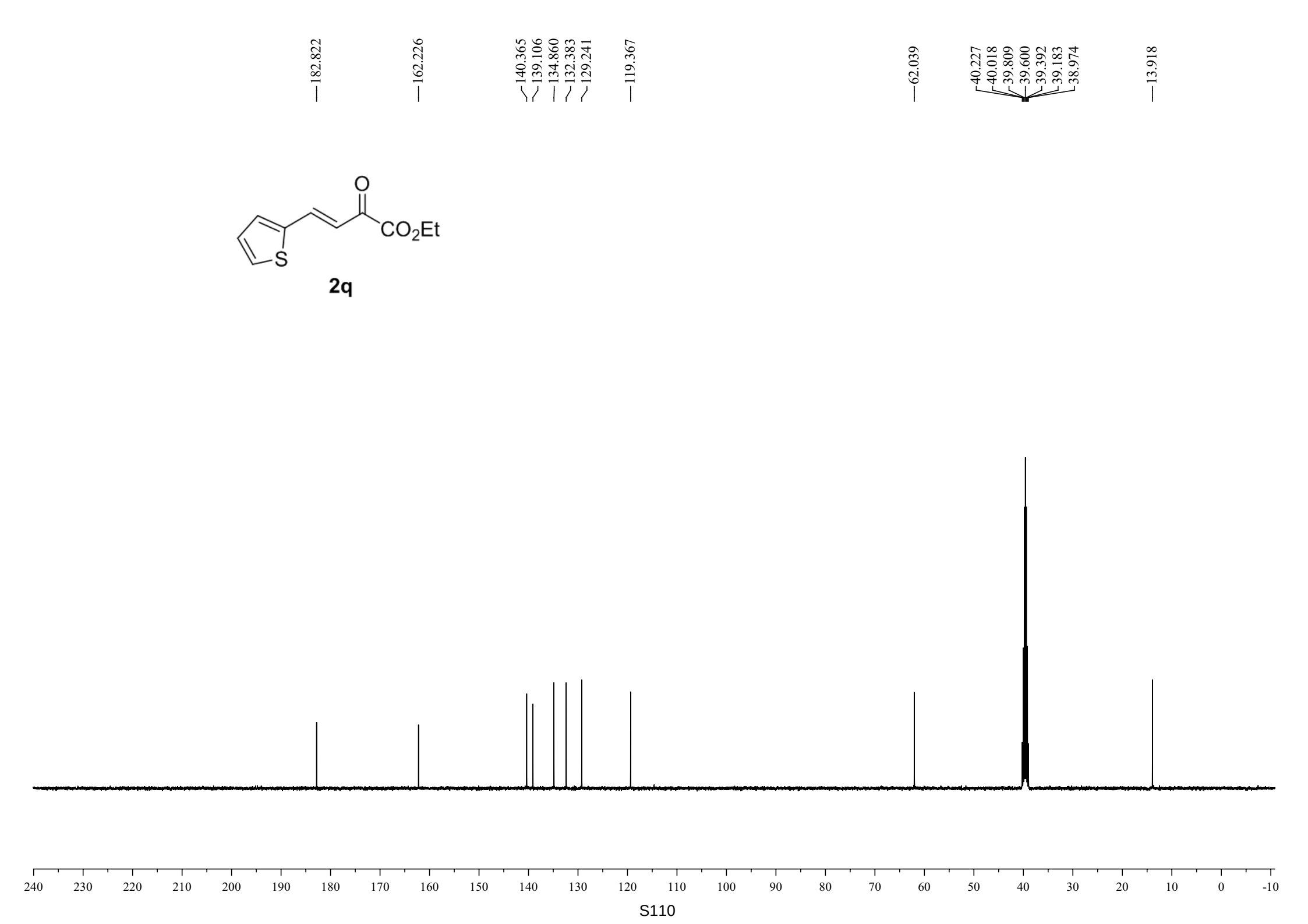
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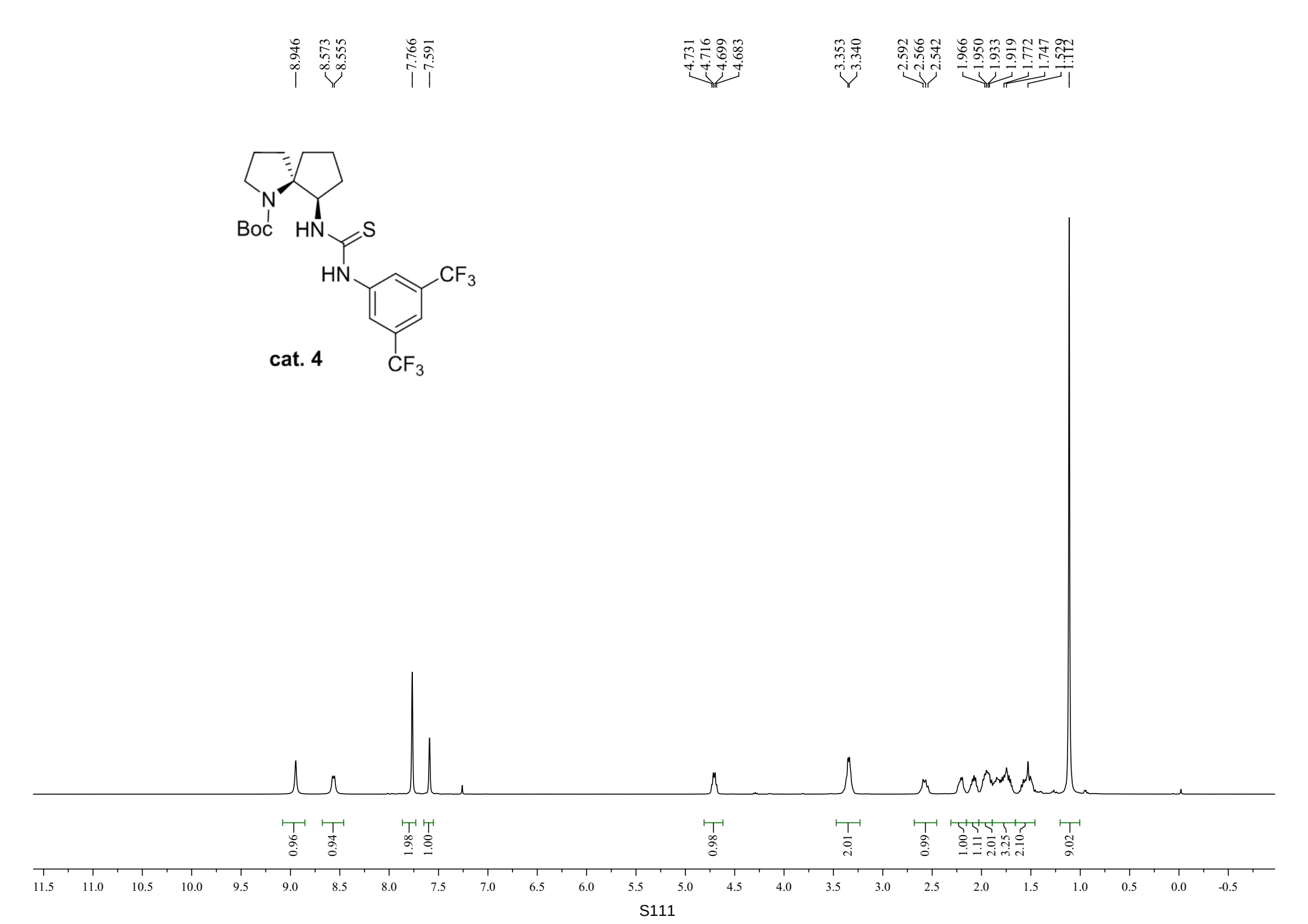
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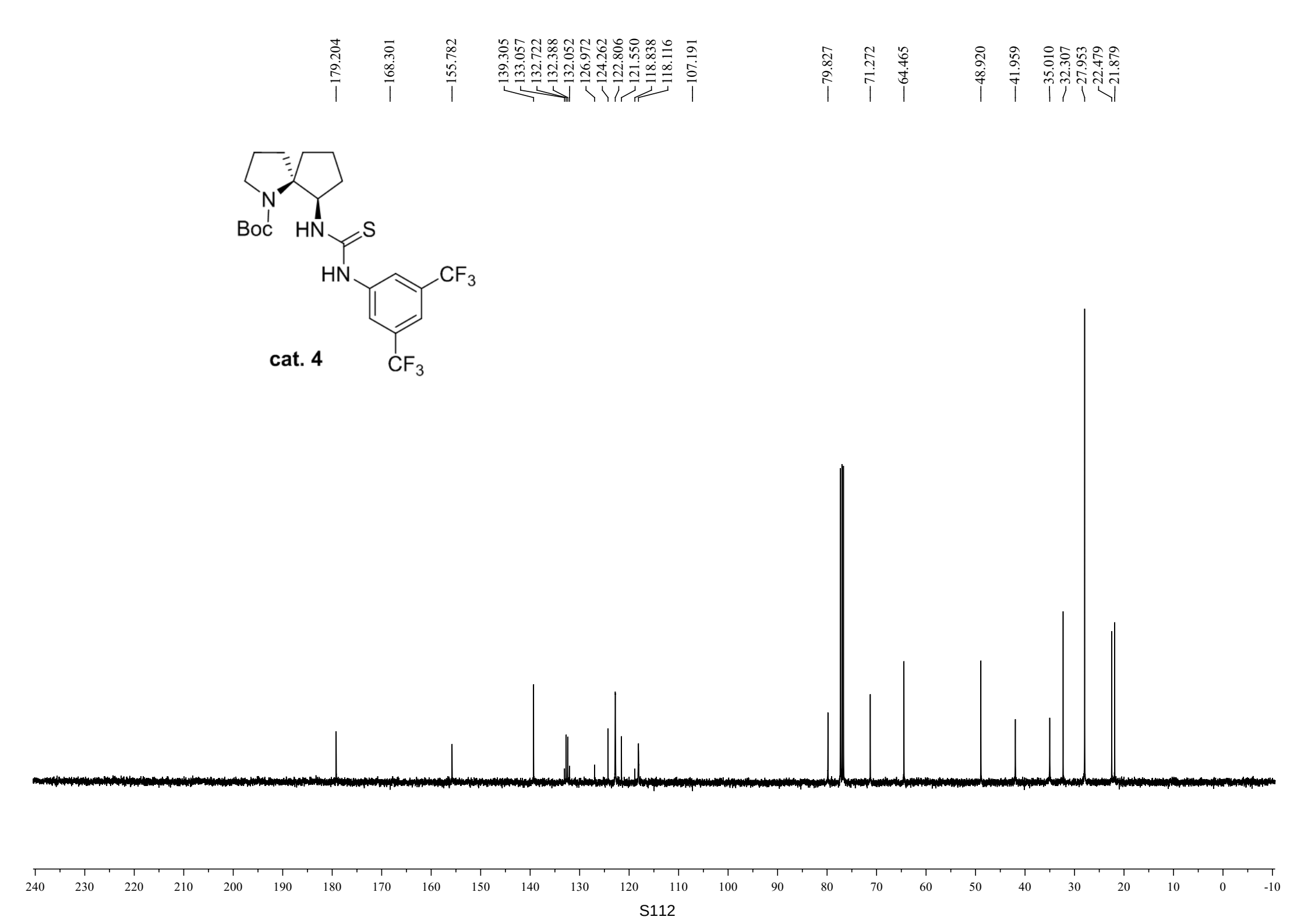
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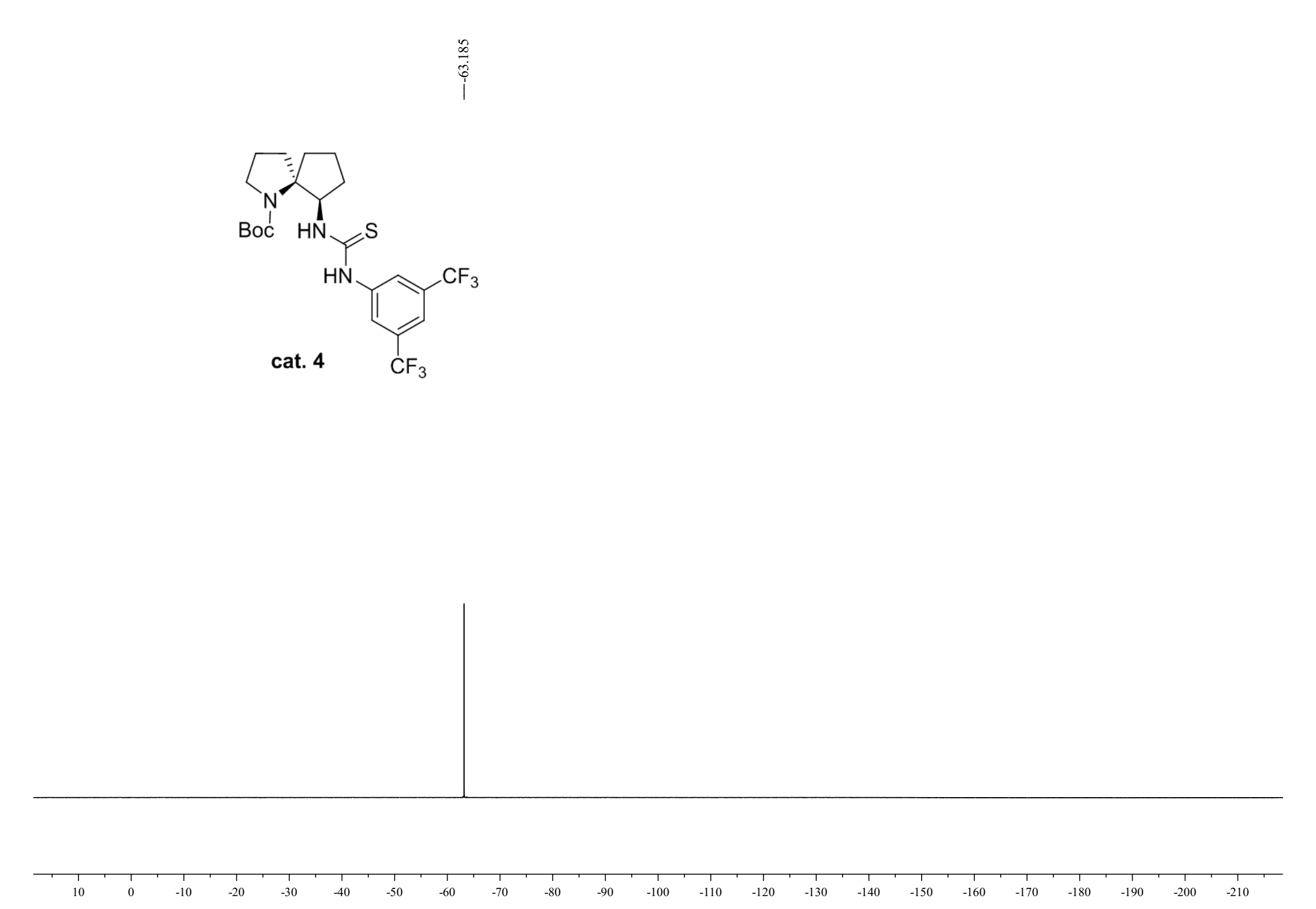
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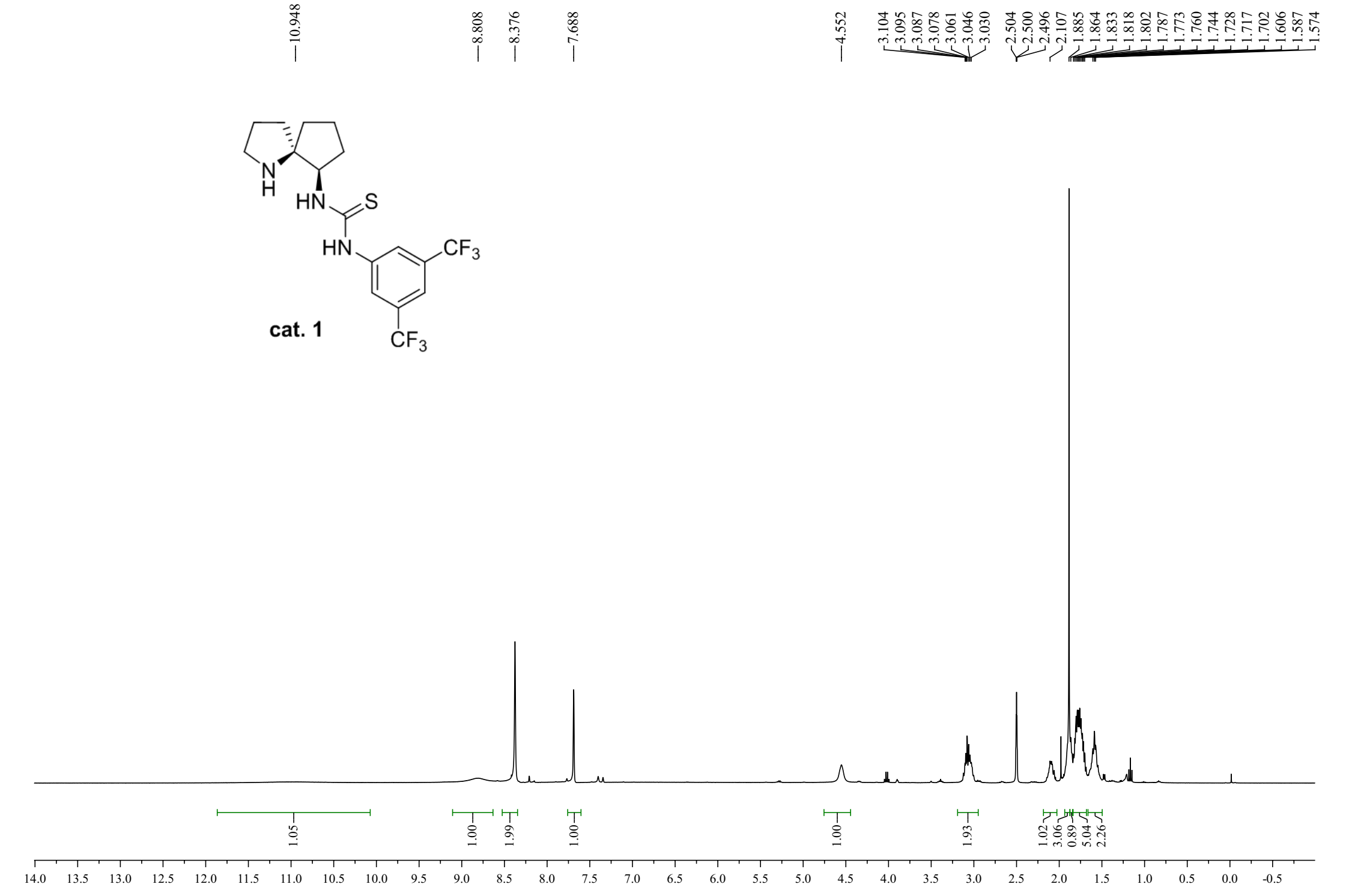
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CF3
CF3
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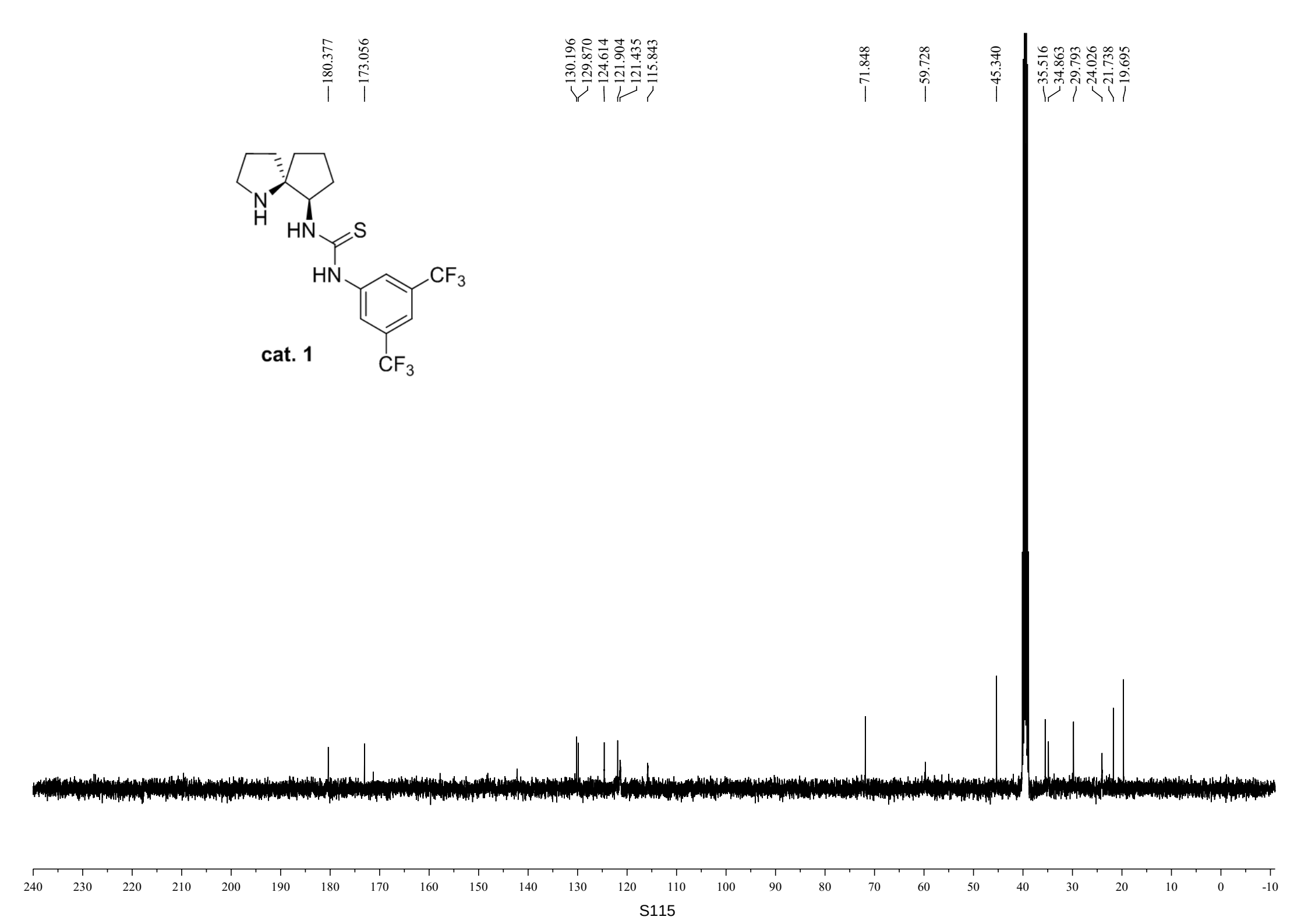
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CF3
CF3
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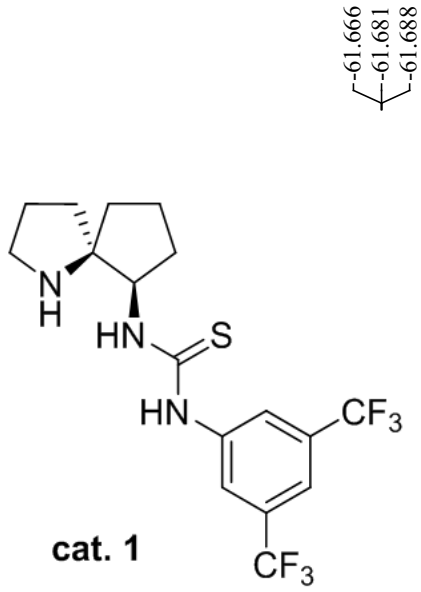
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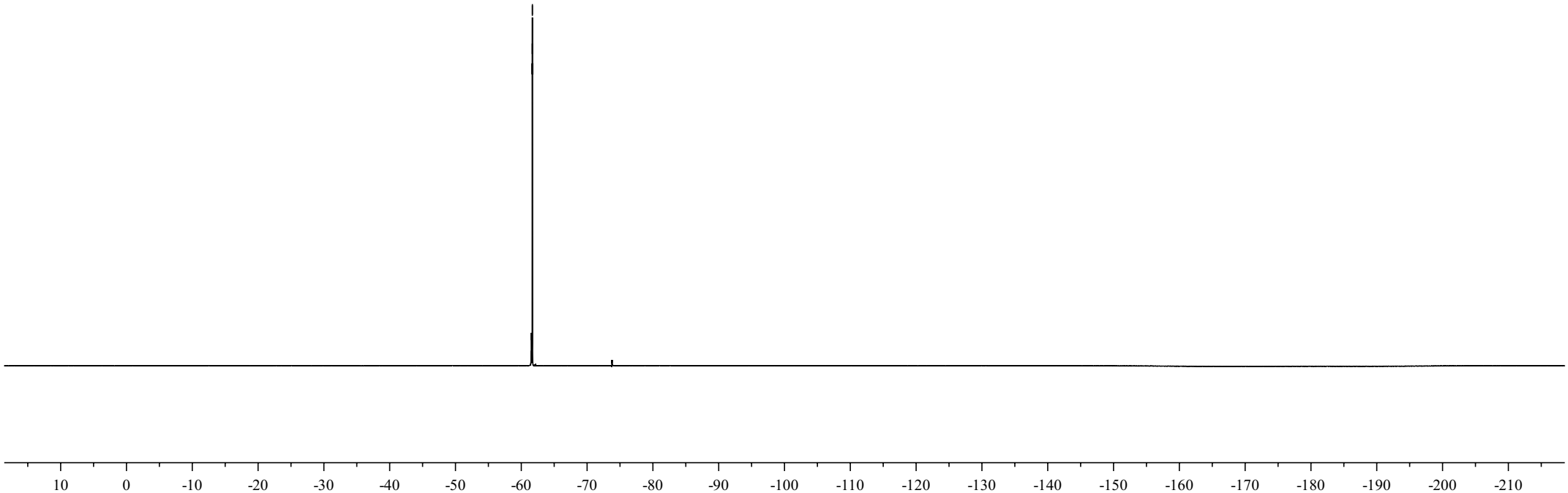
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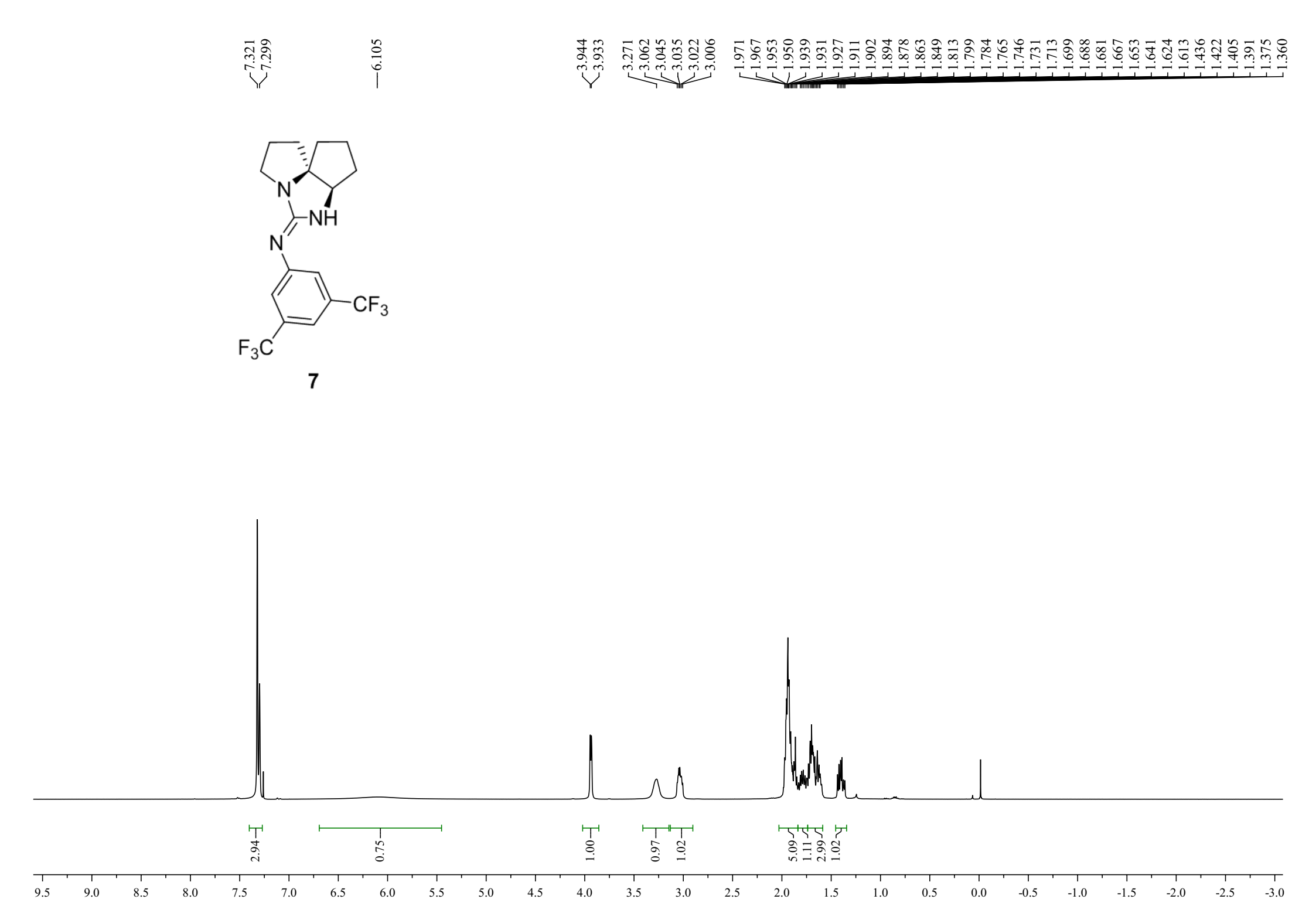
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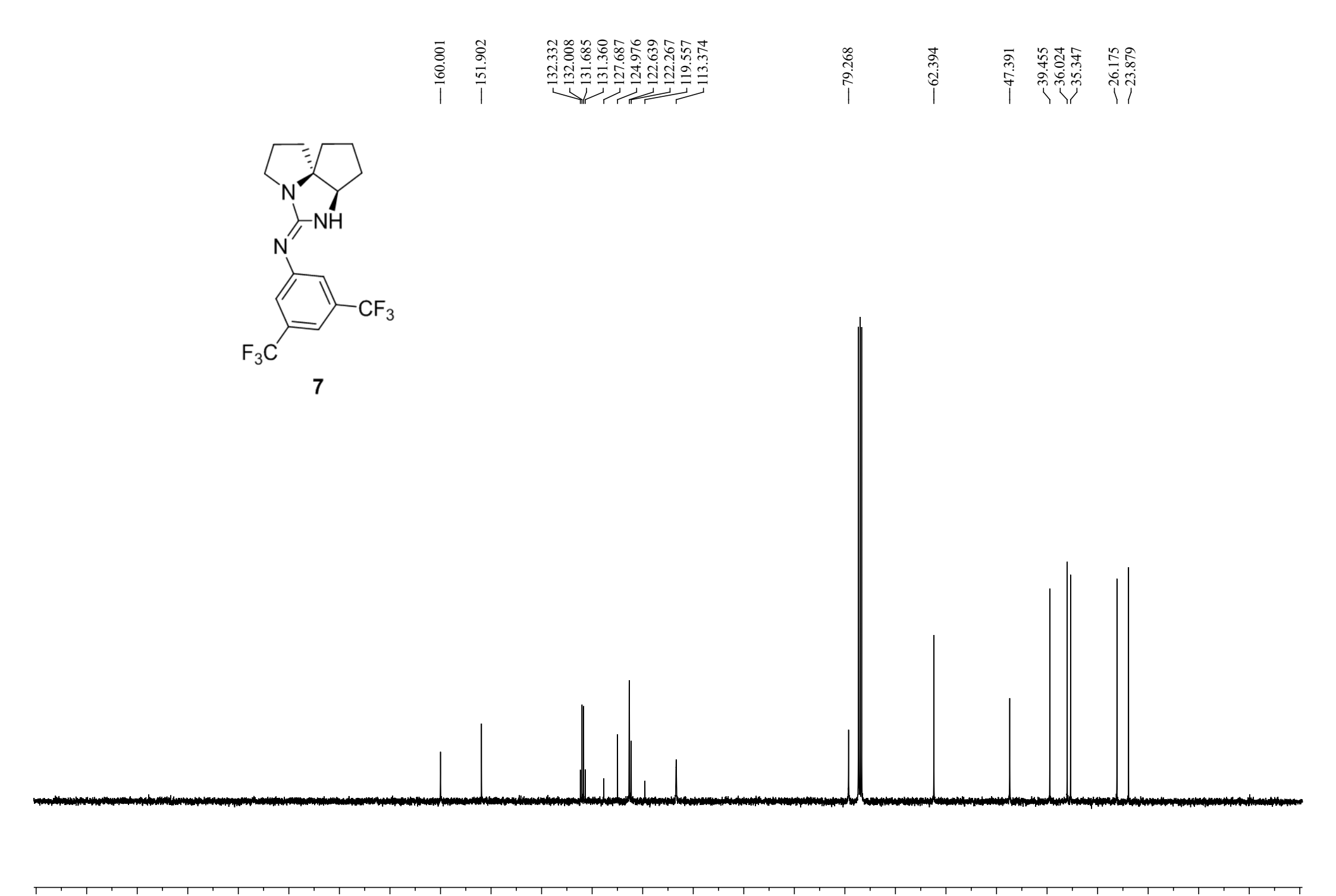
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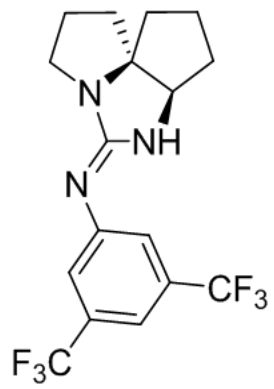
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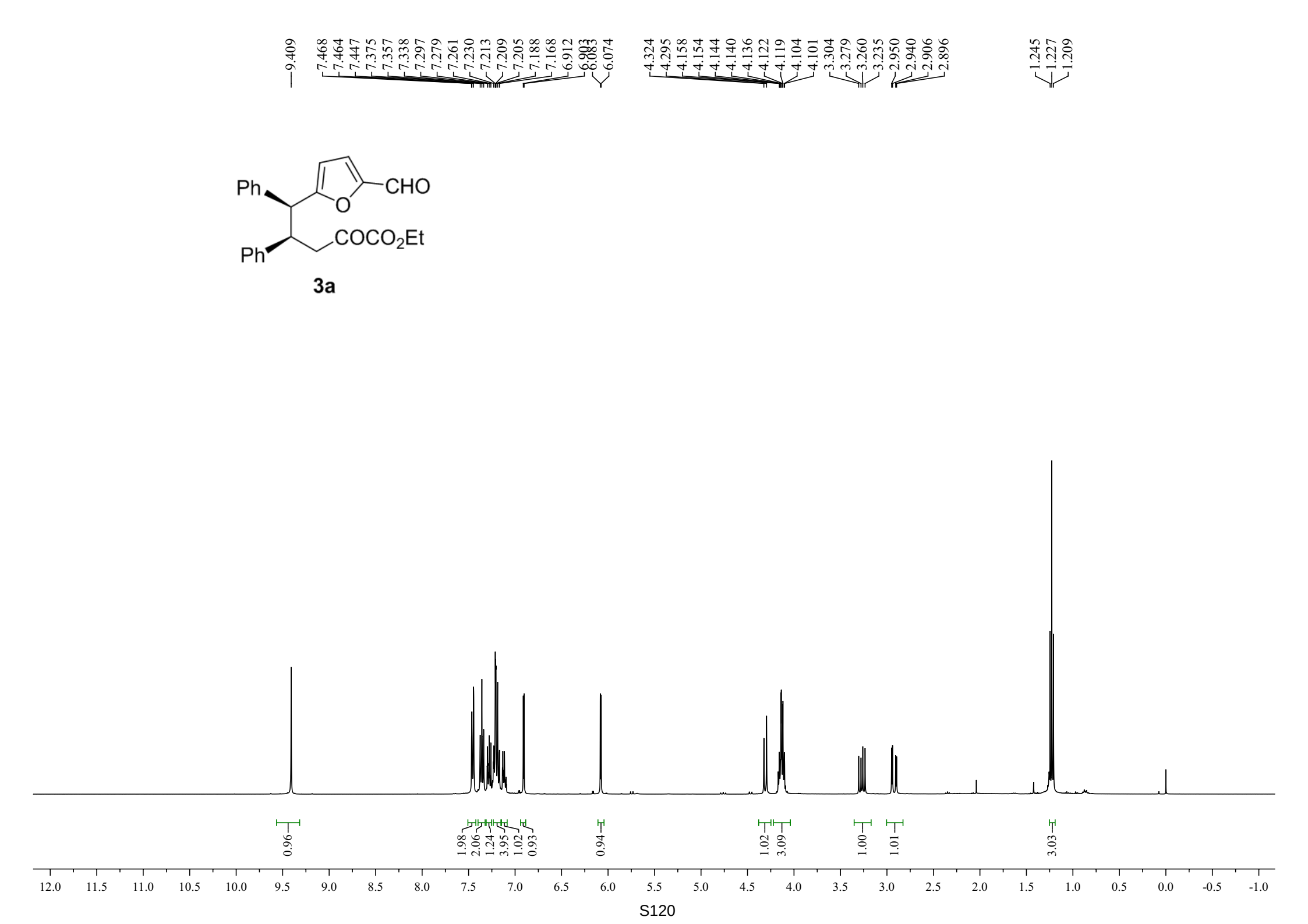
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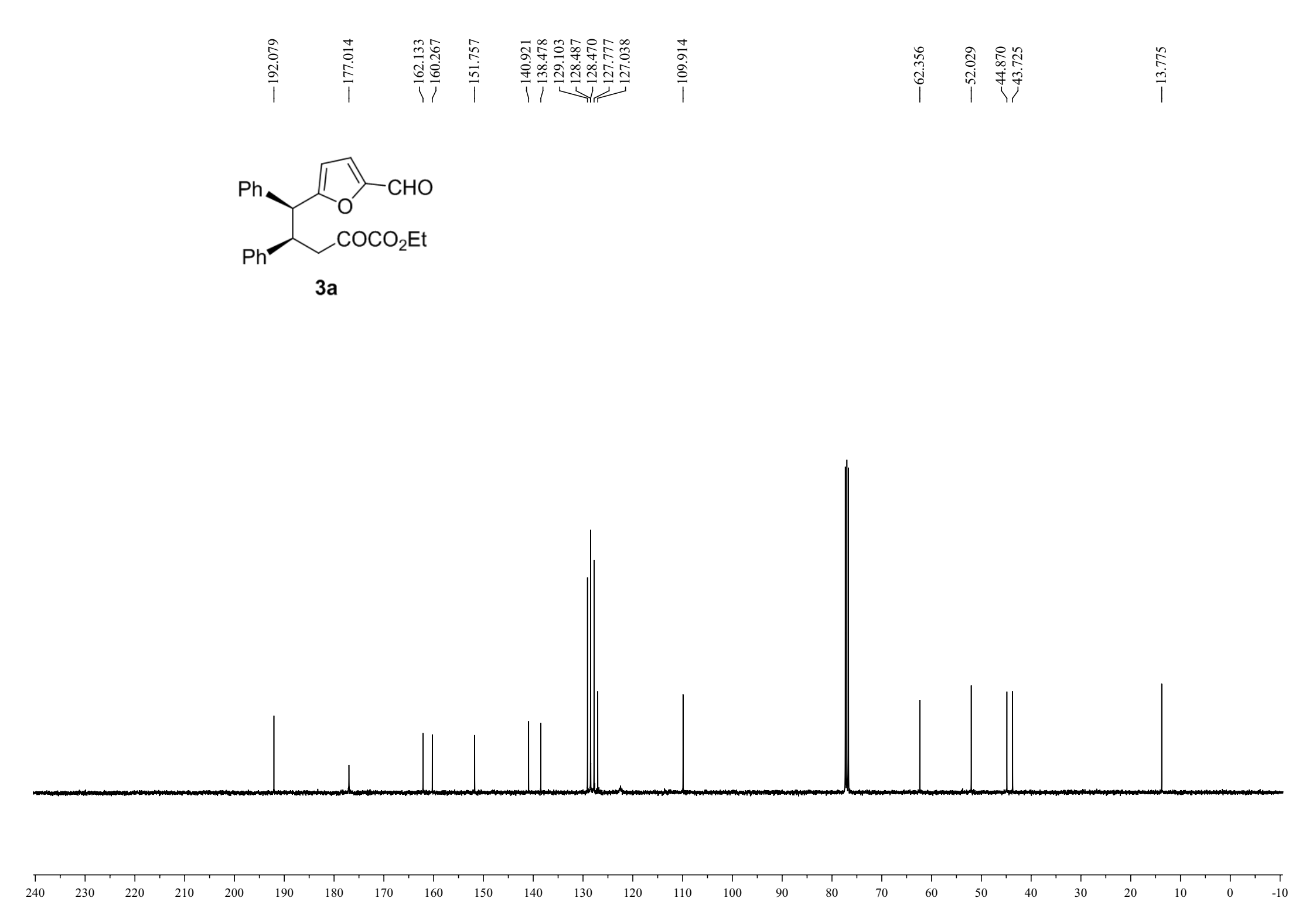
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COCO2Et
Ph
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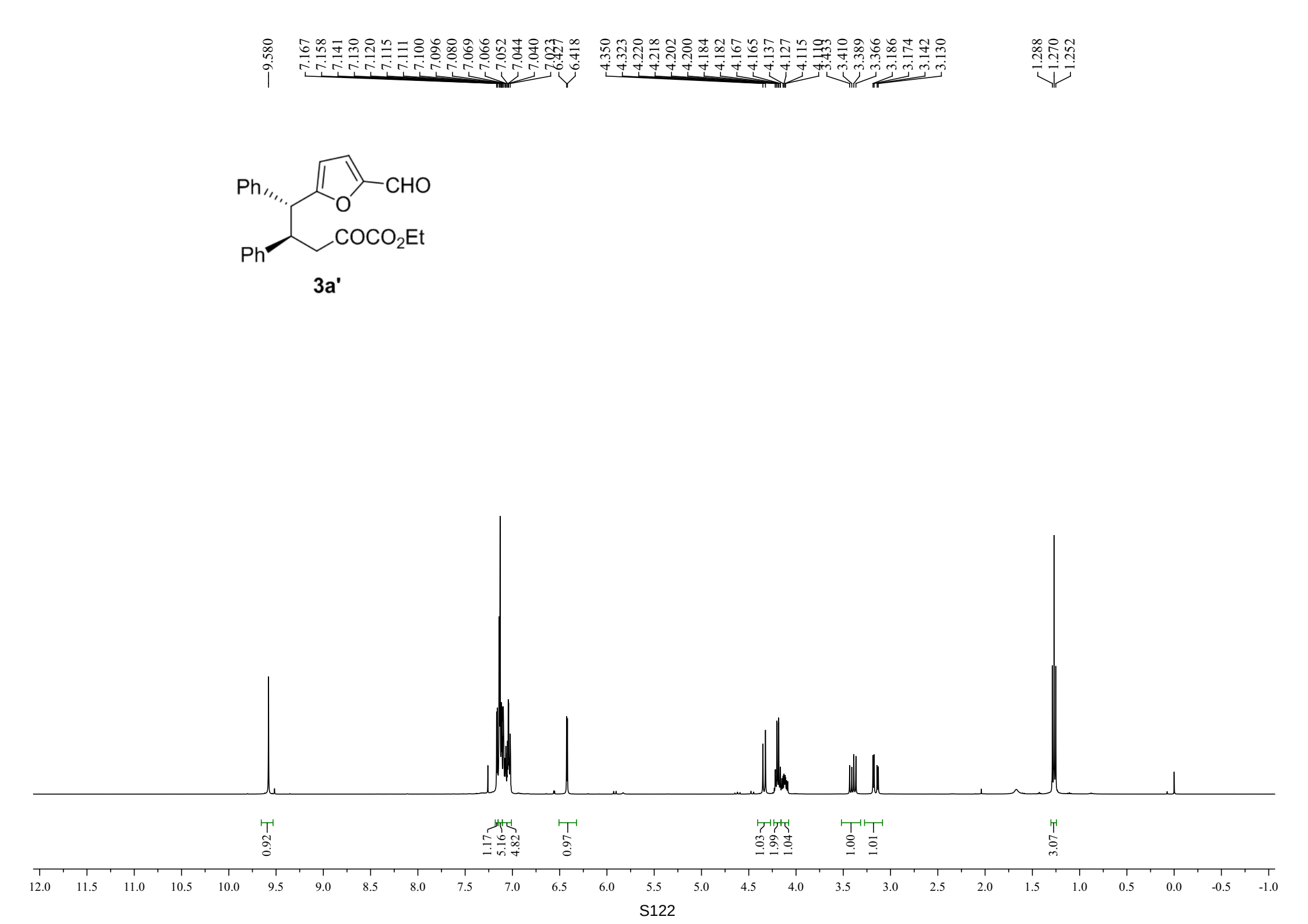
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Ph
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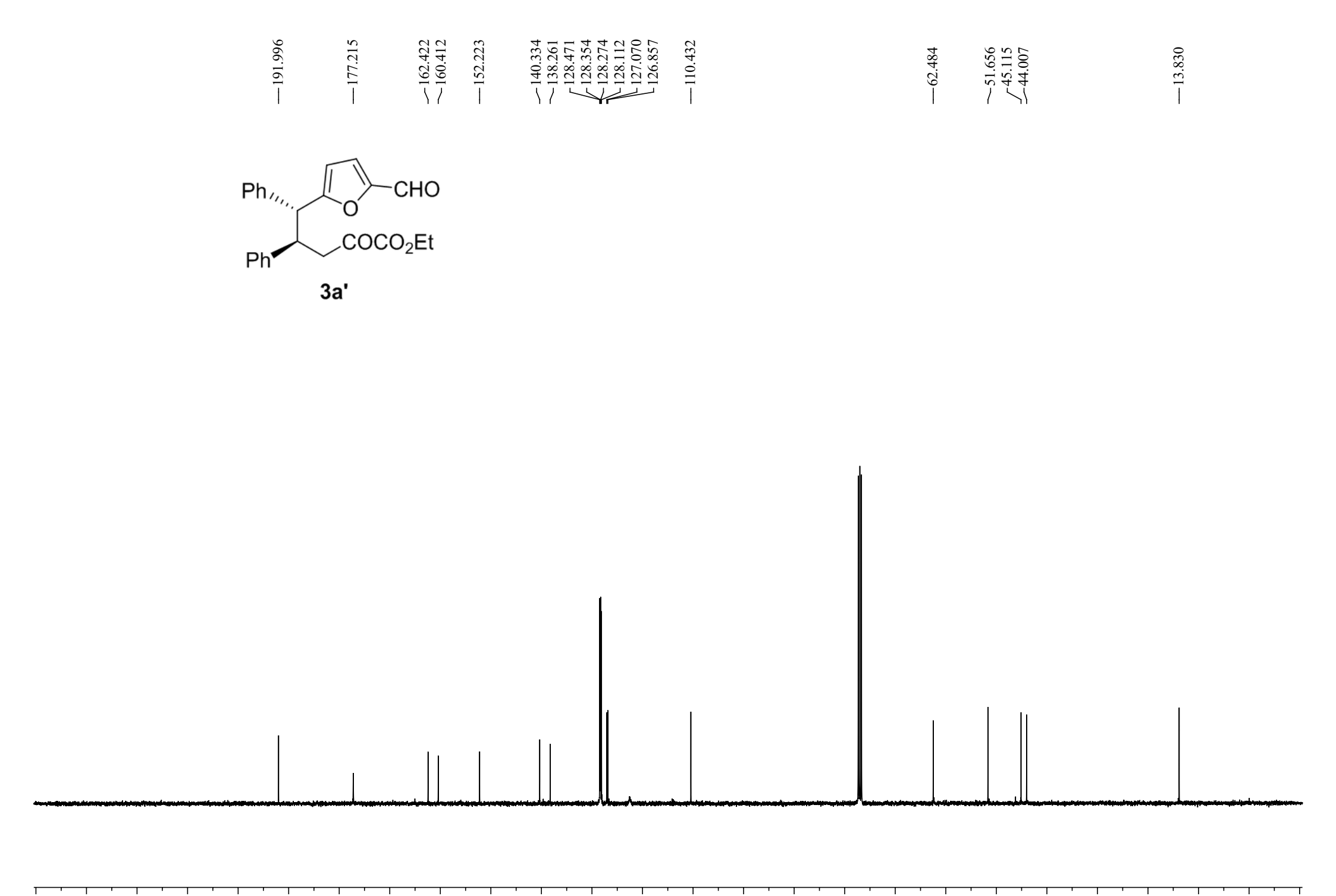
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CHO
COCO2Et
Ph
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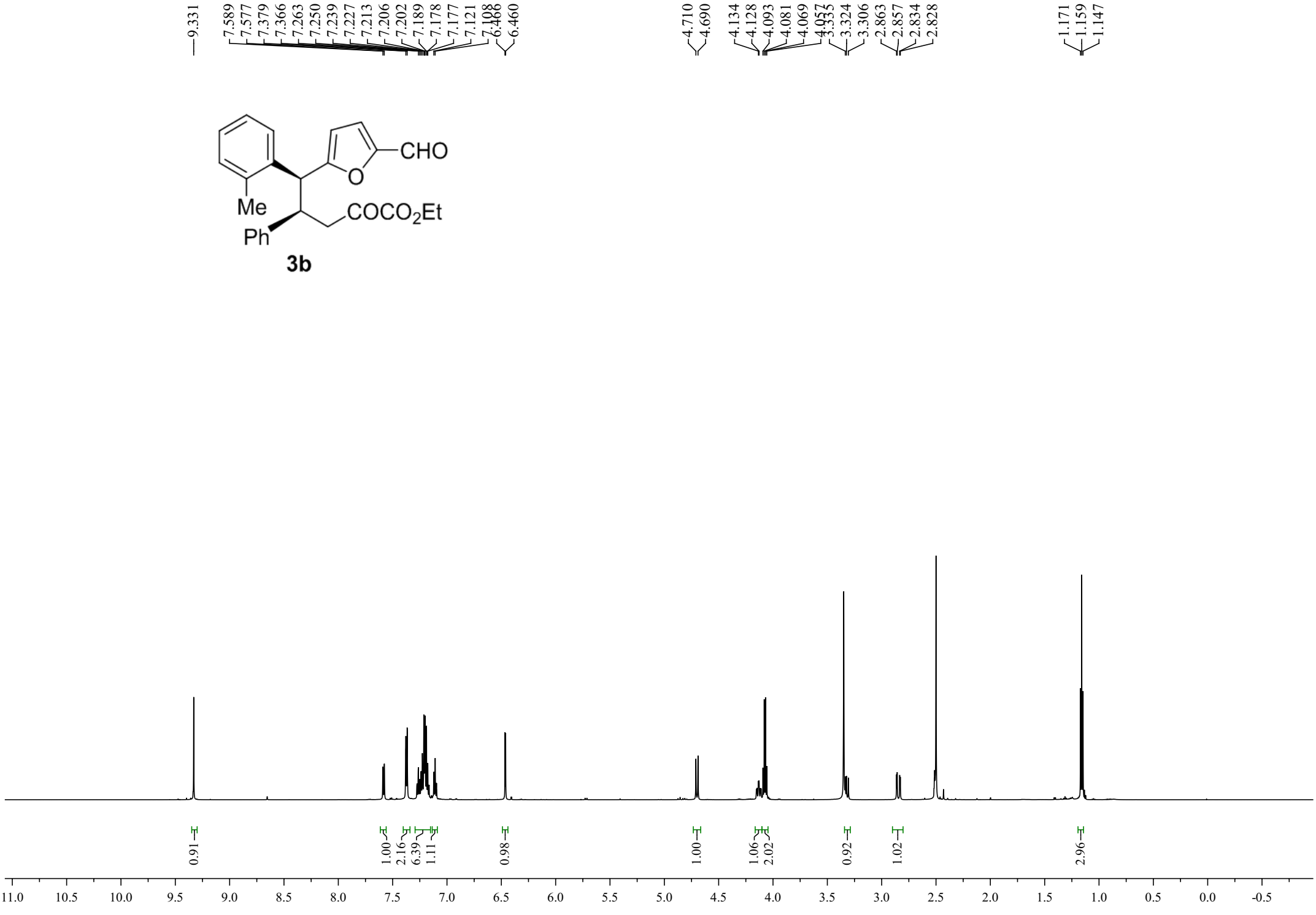
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Ph
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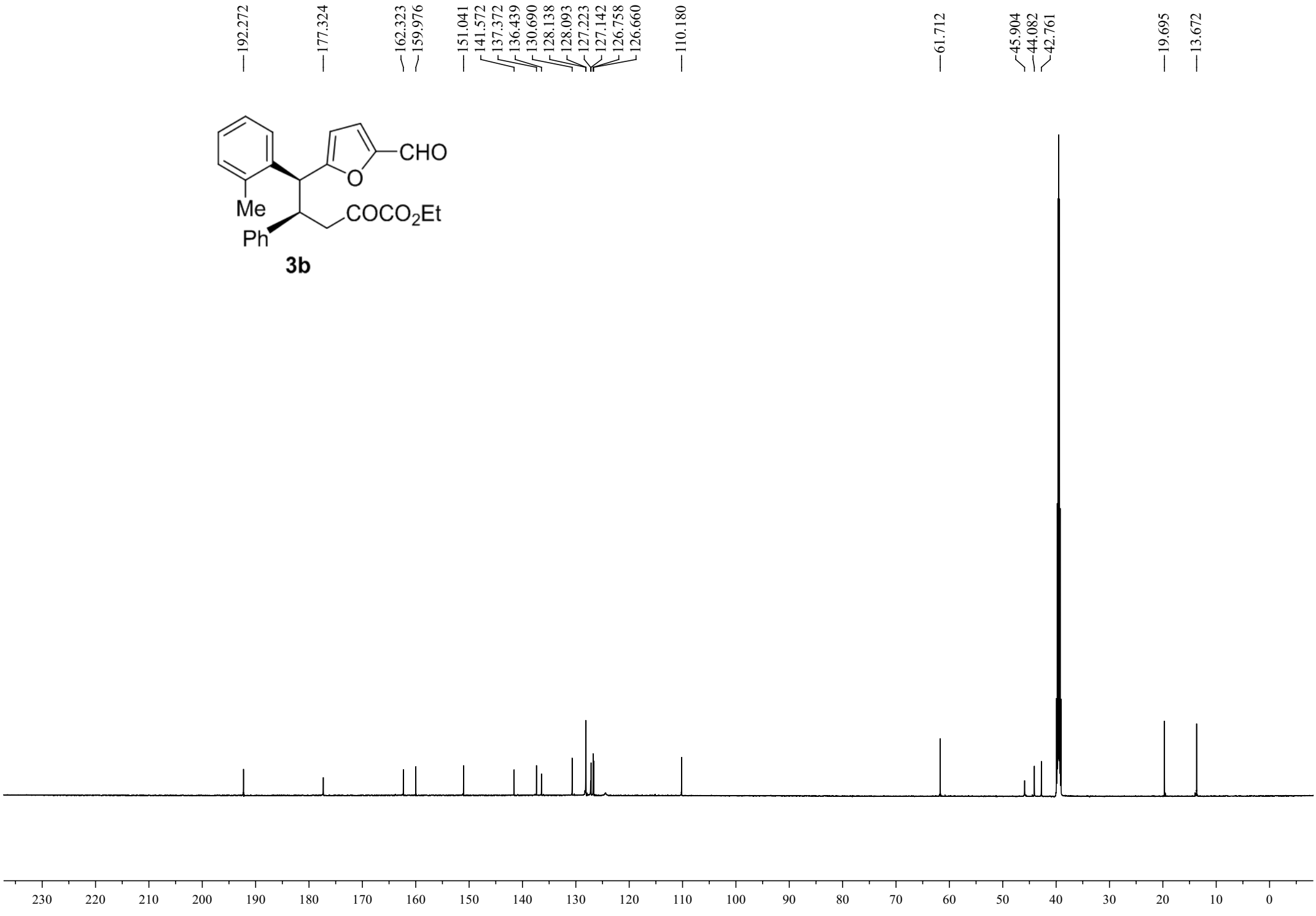
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COCO2Et
Ph
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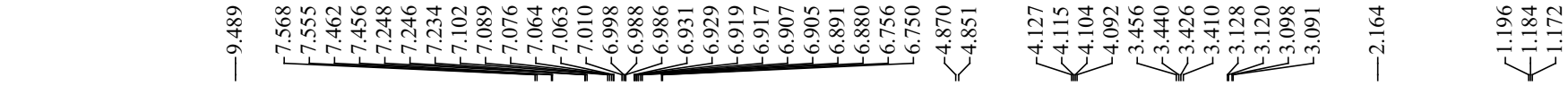
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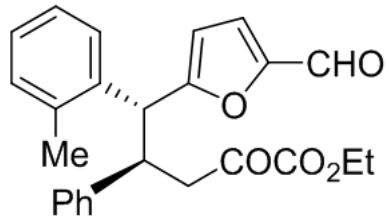
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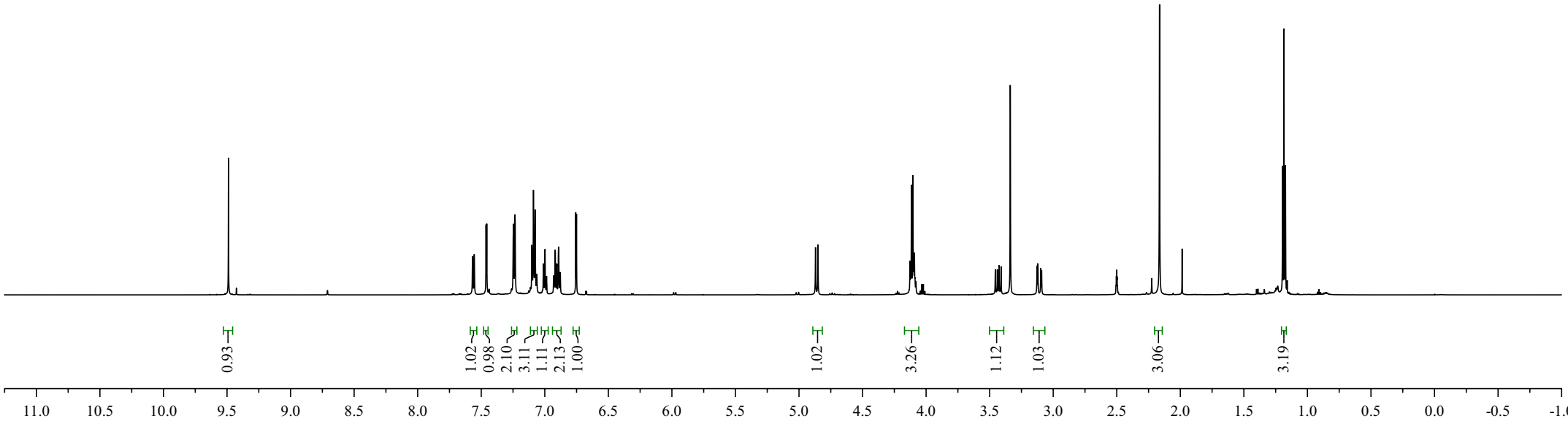
Ph

3b'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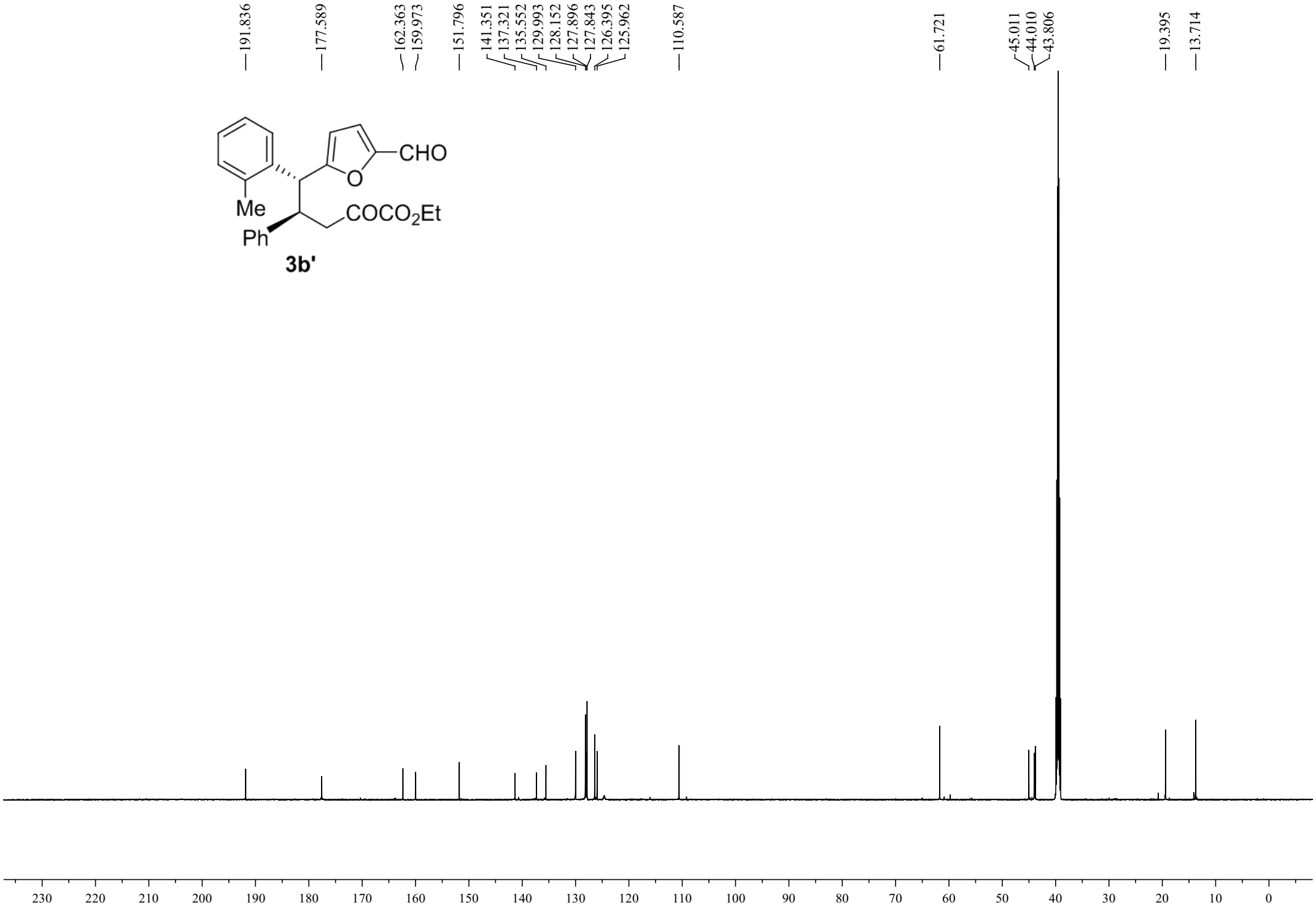
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CHO
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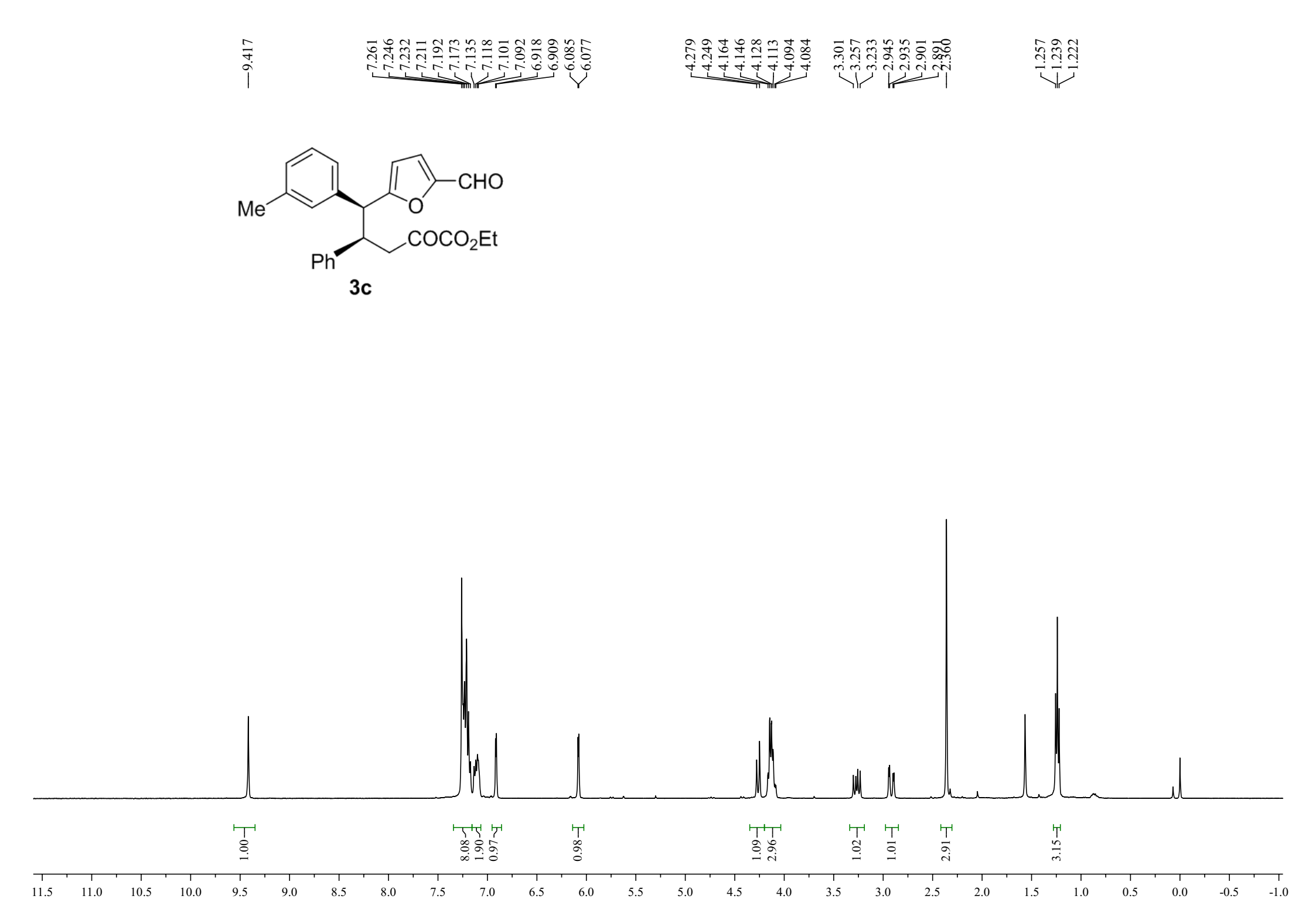
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Ph
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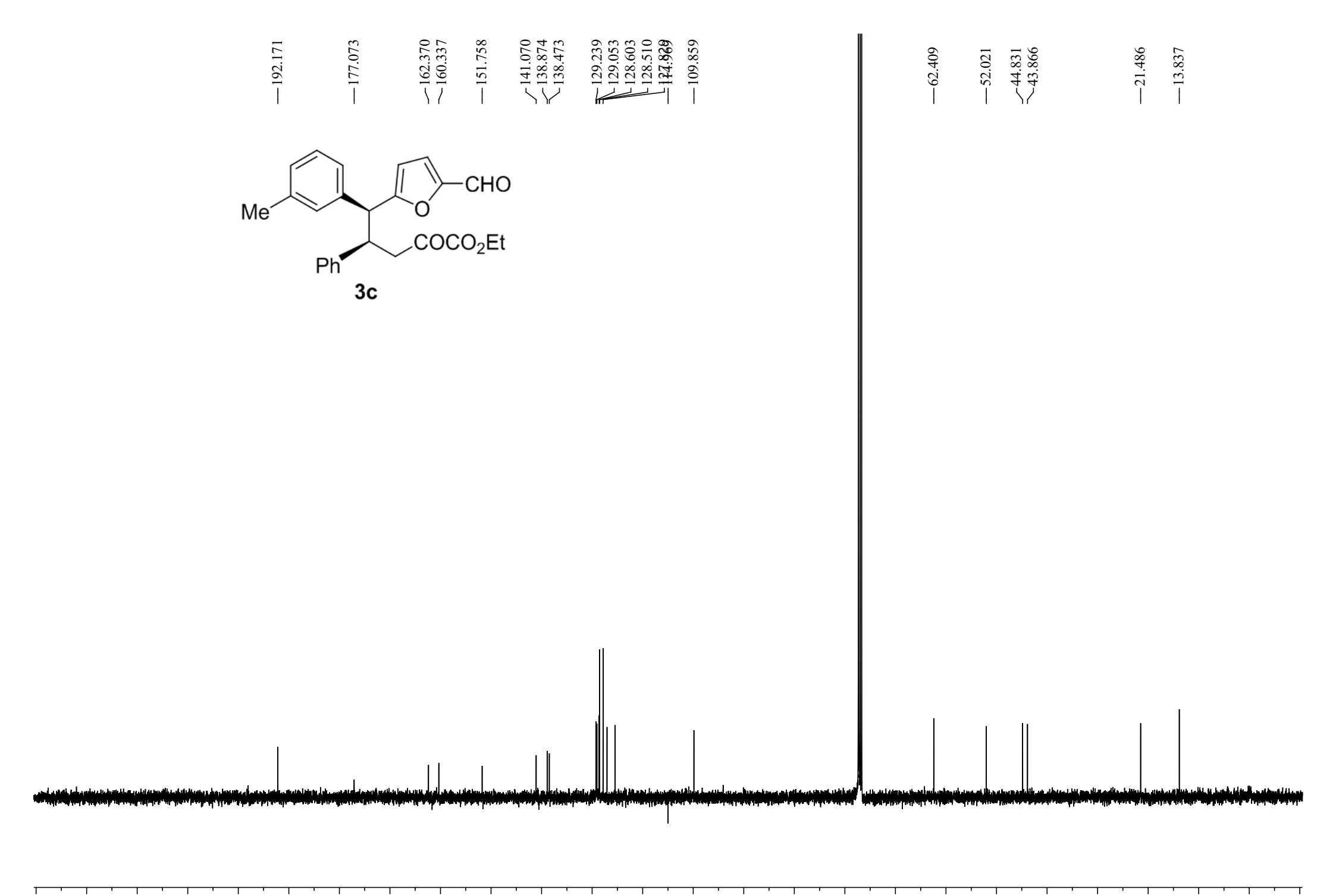
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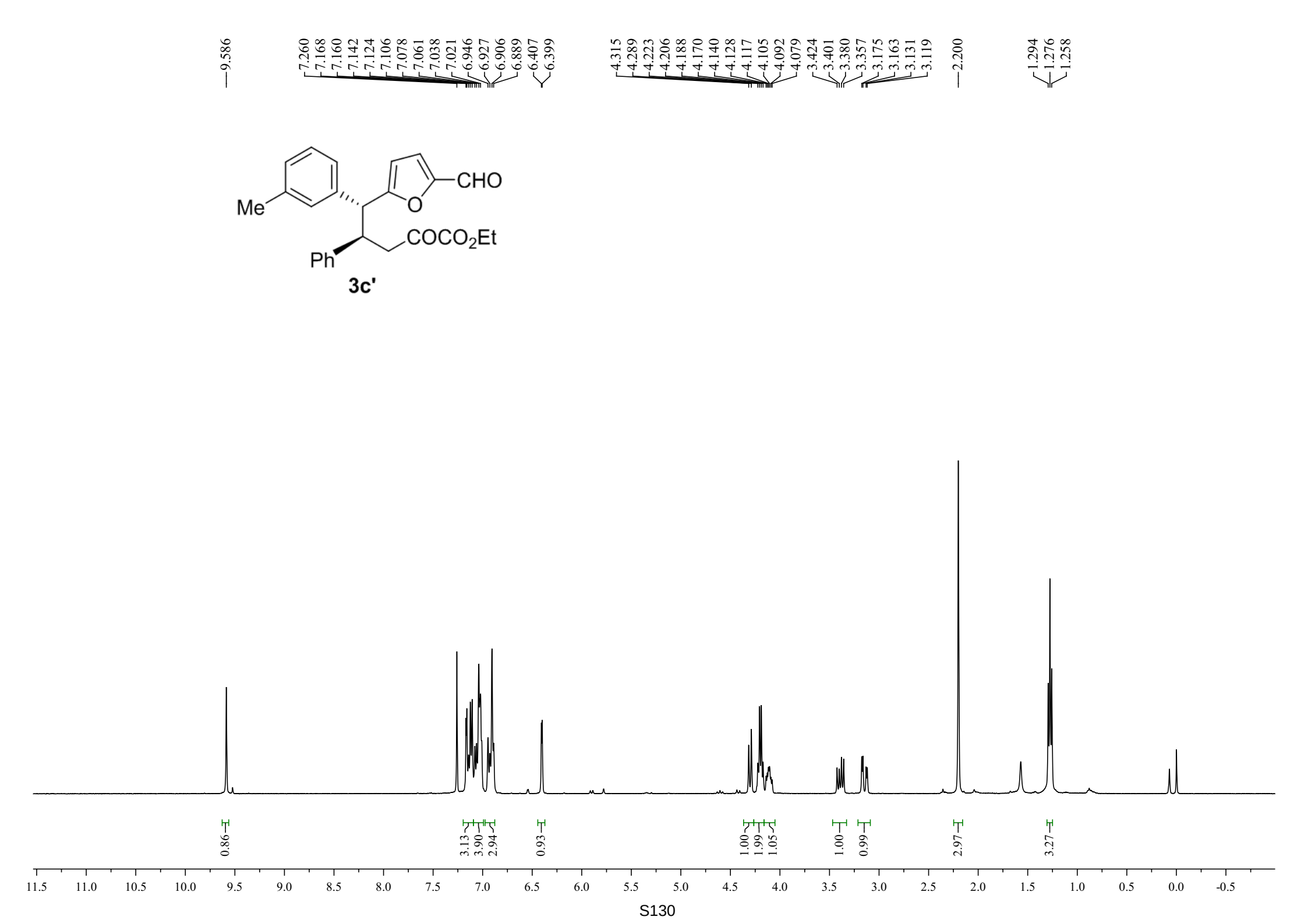
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Ph
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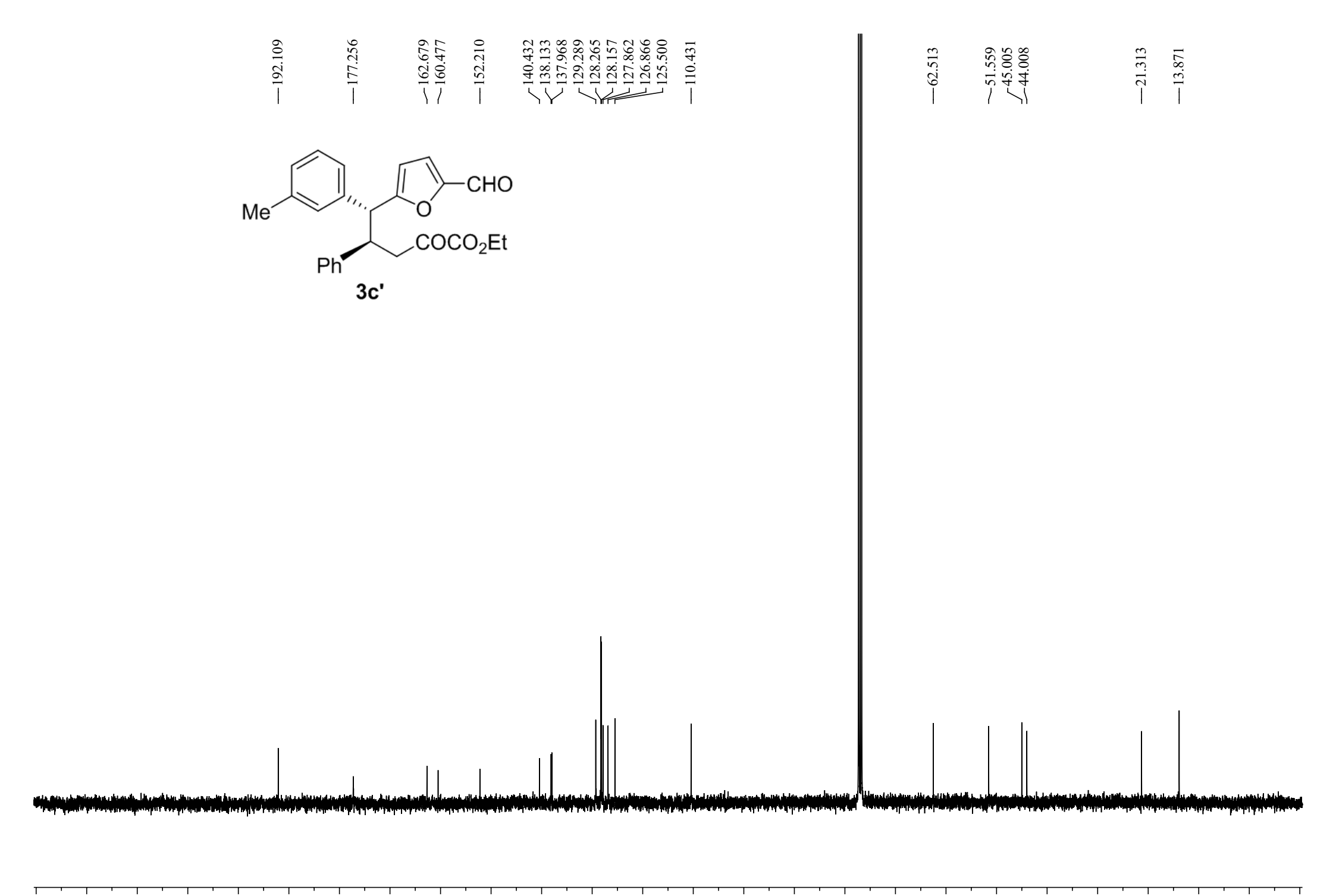
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Ph
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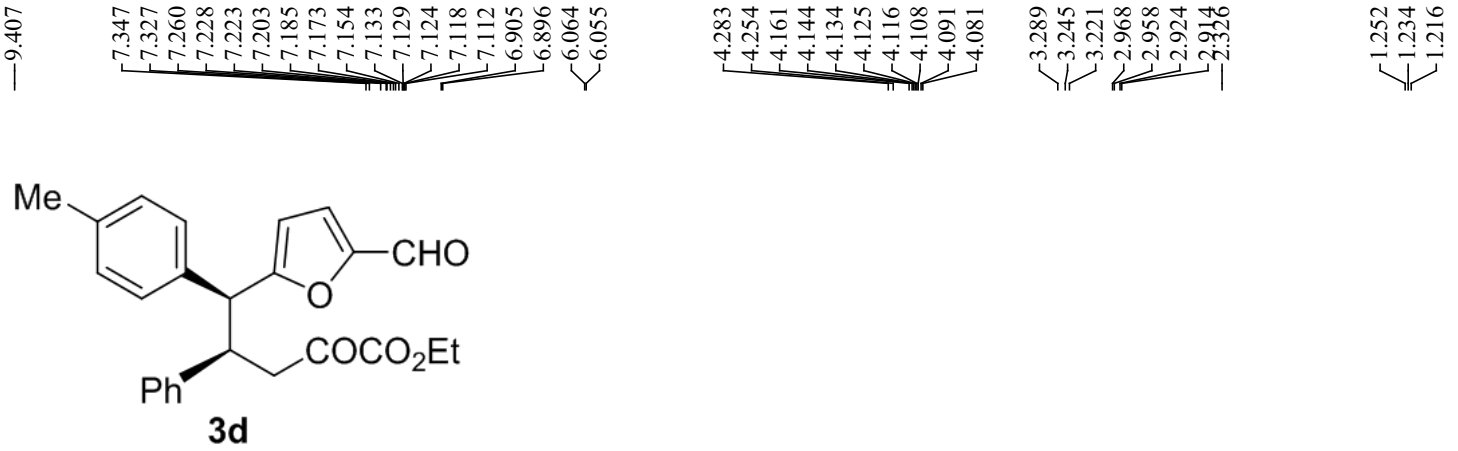
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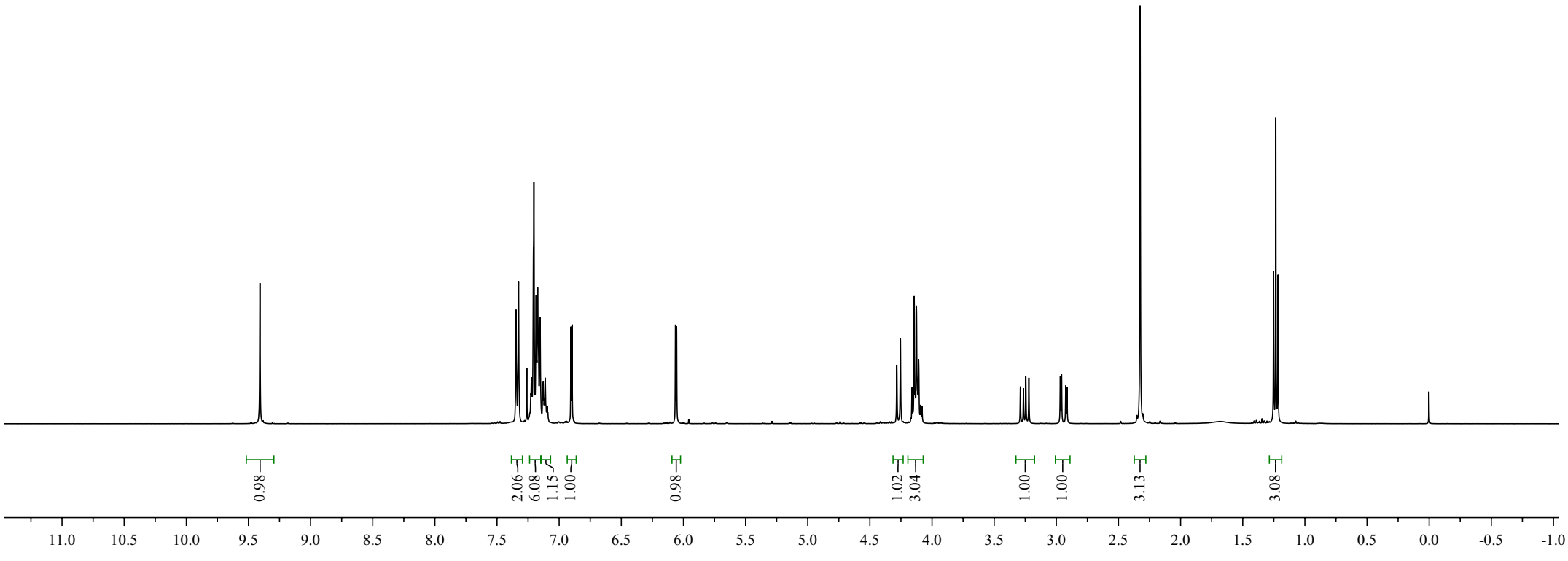
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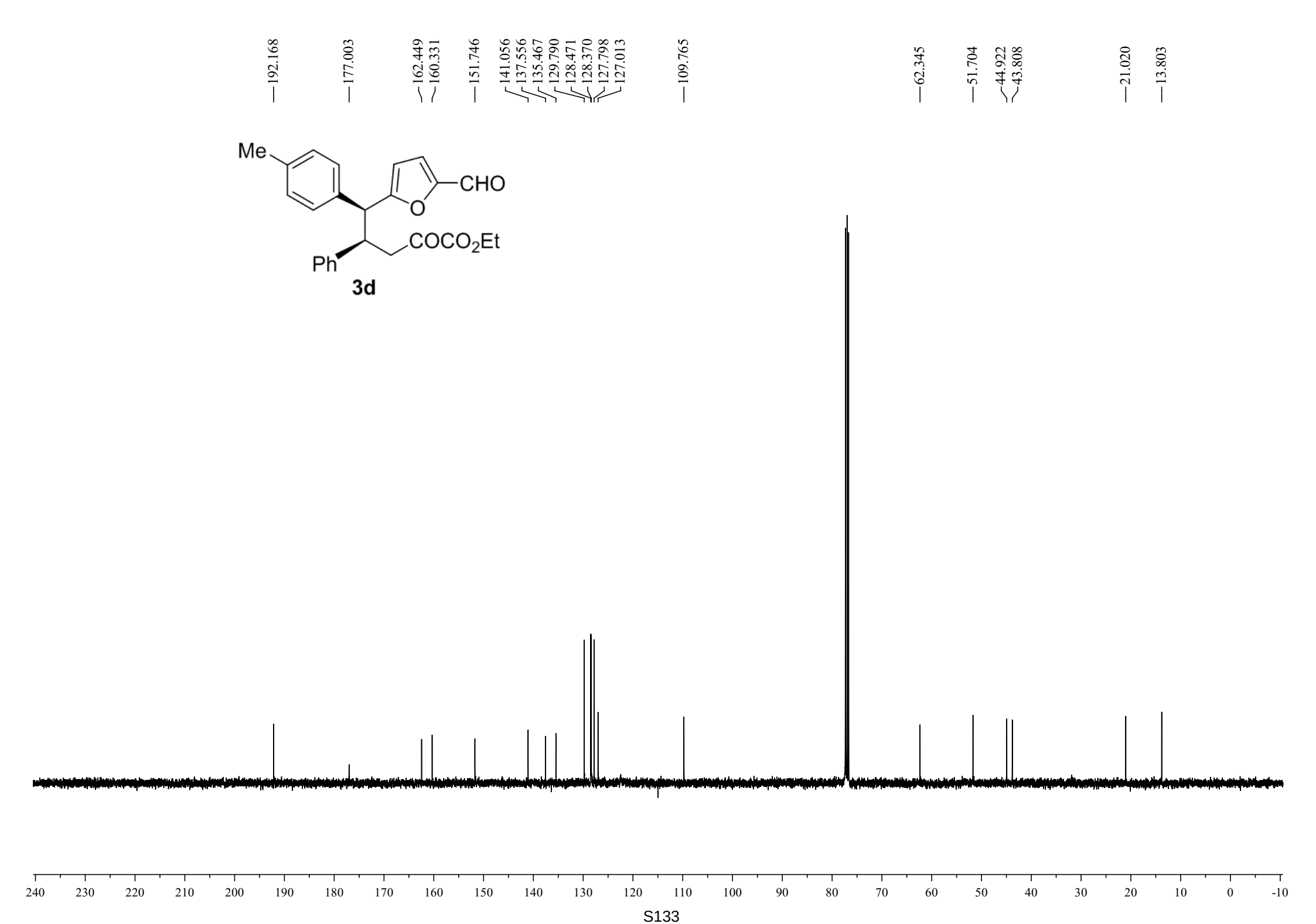
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CHO
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COCO2Et
Ph
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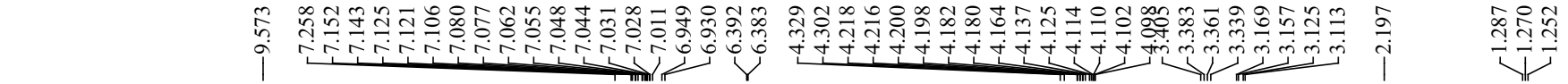
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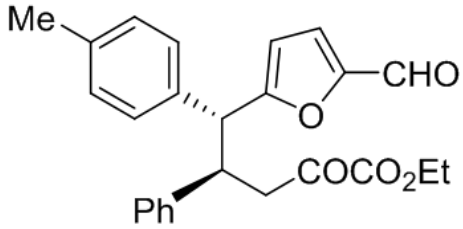
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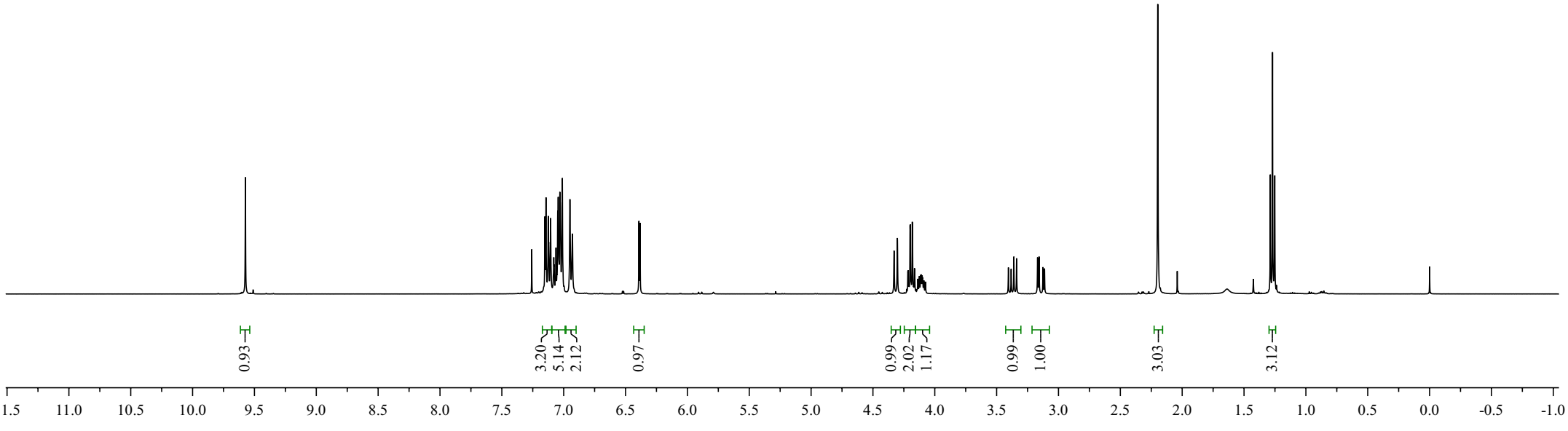
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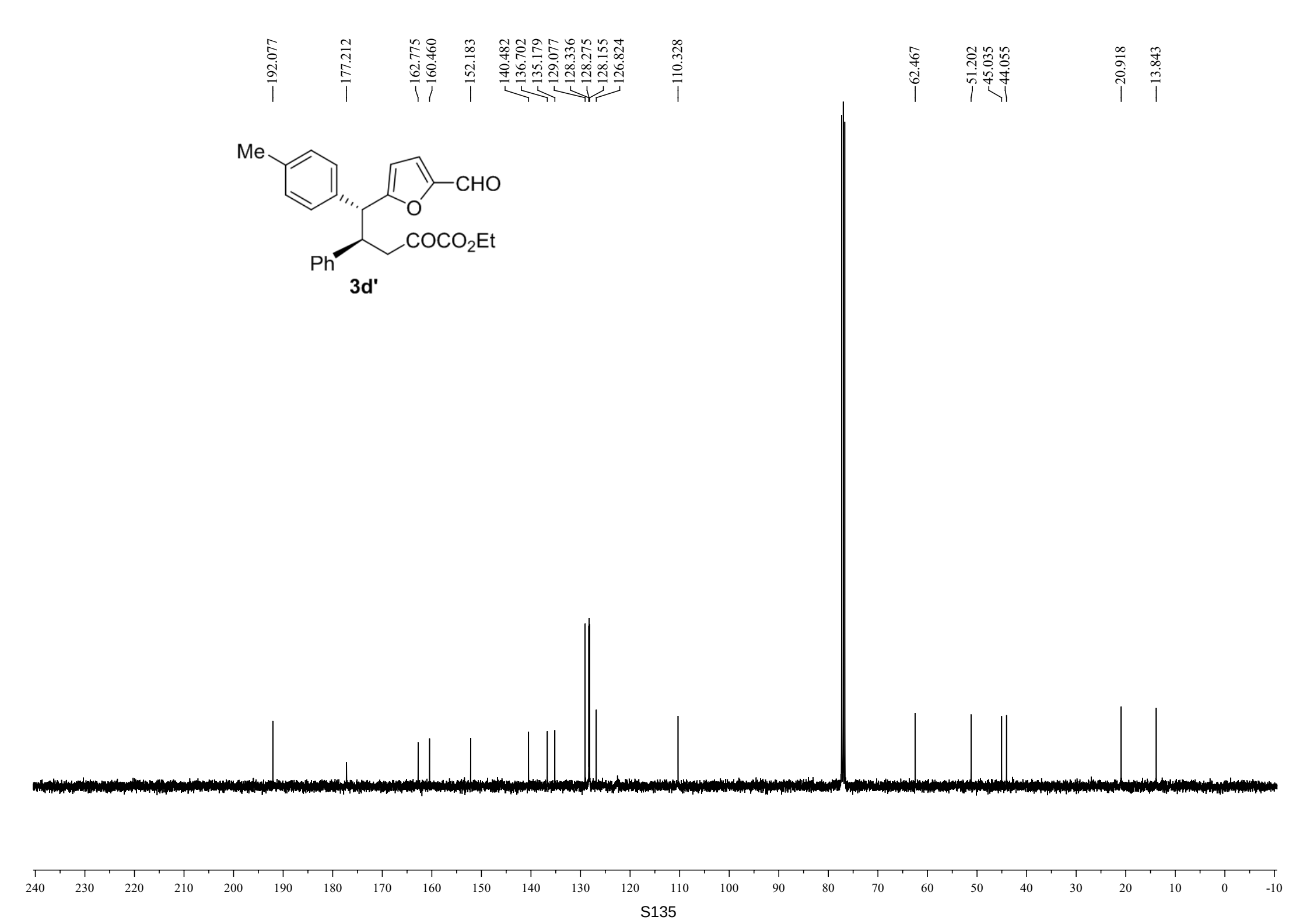
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COCO2Et
Ph
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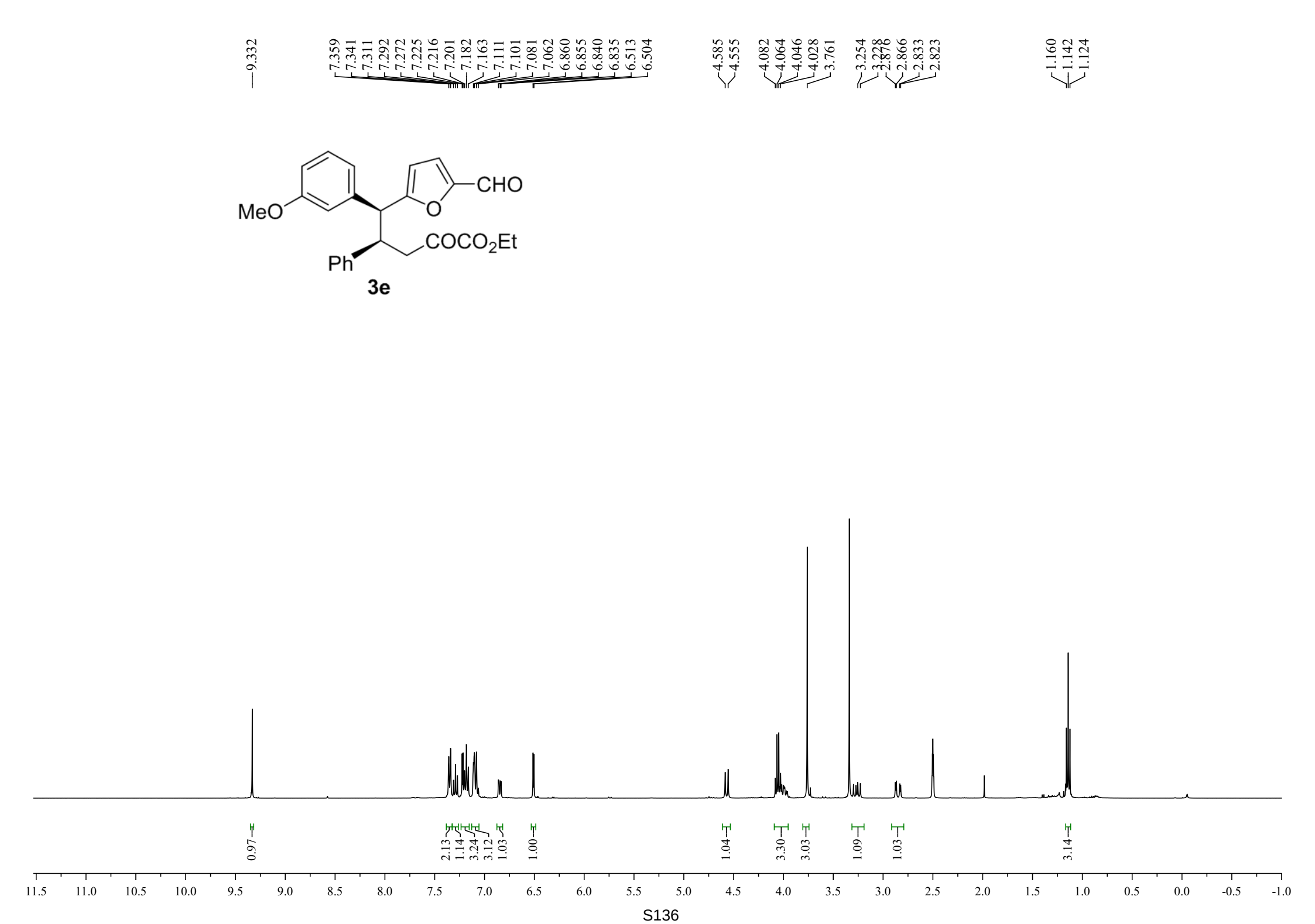
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Ph
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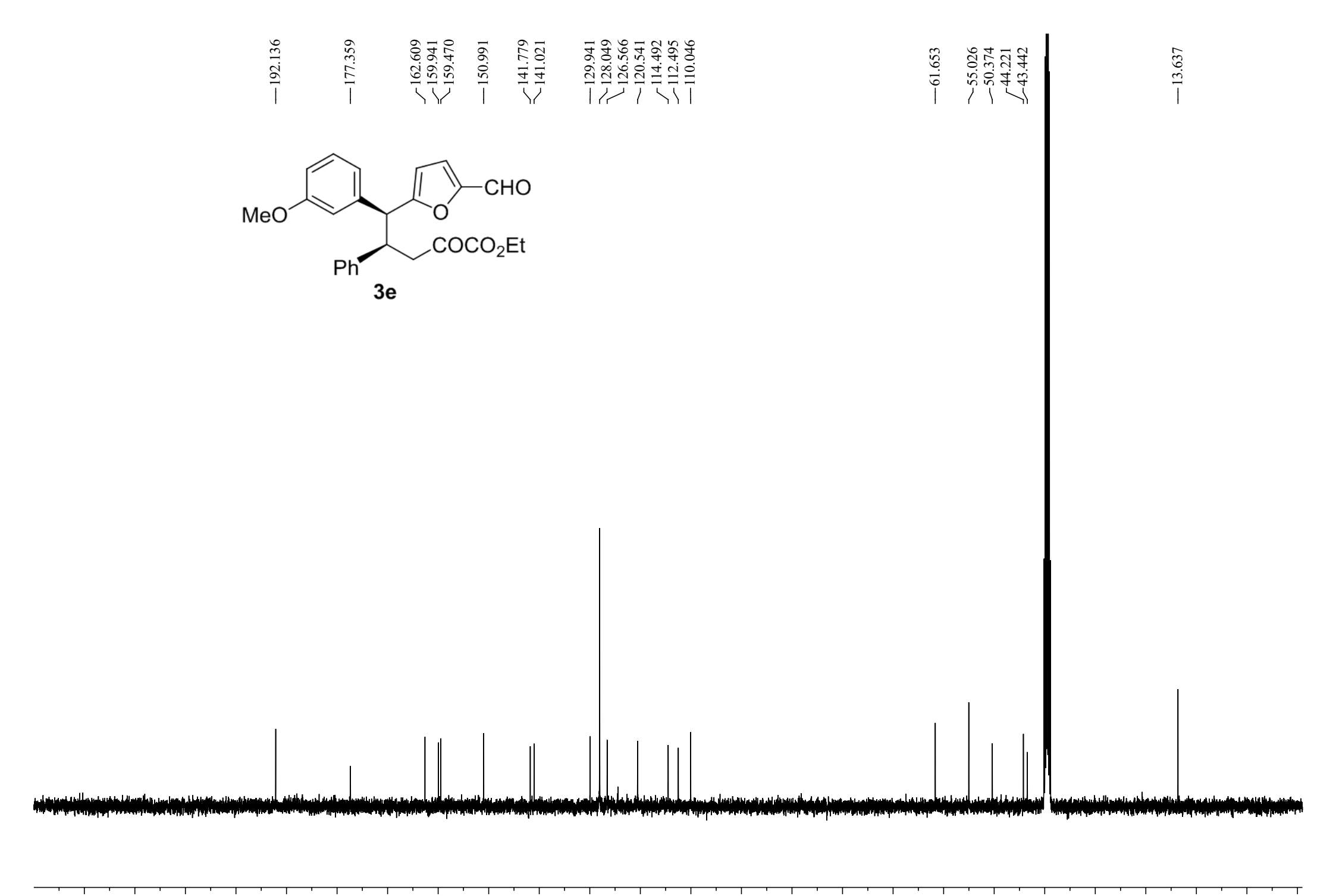
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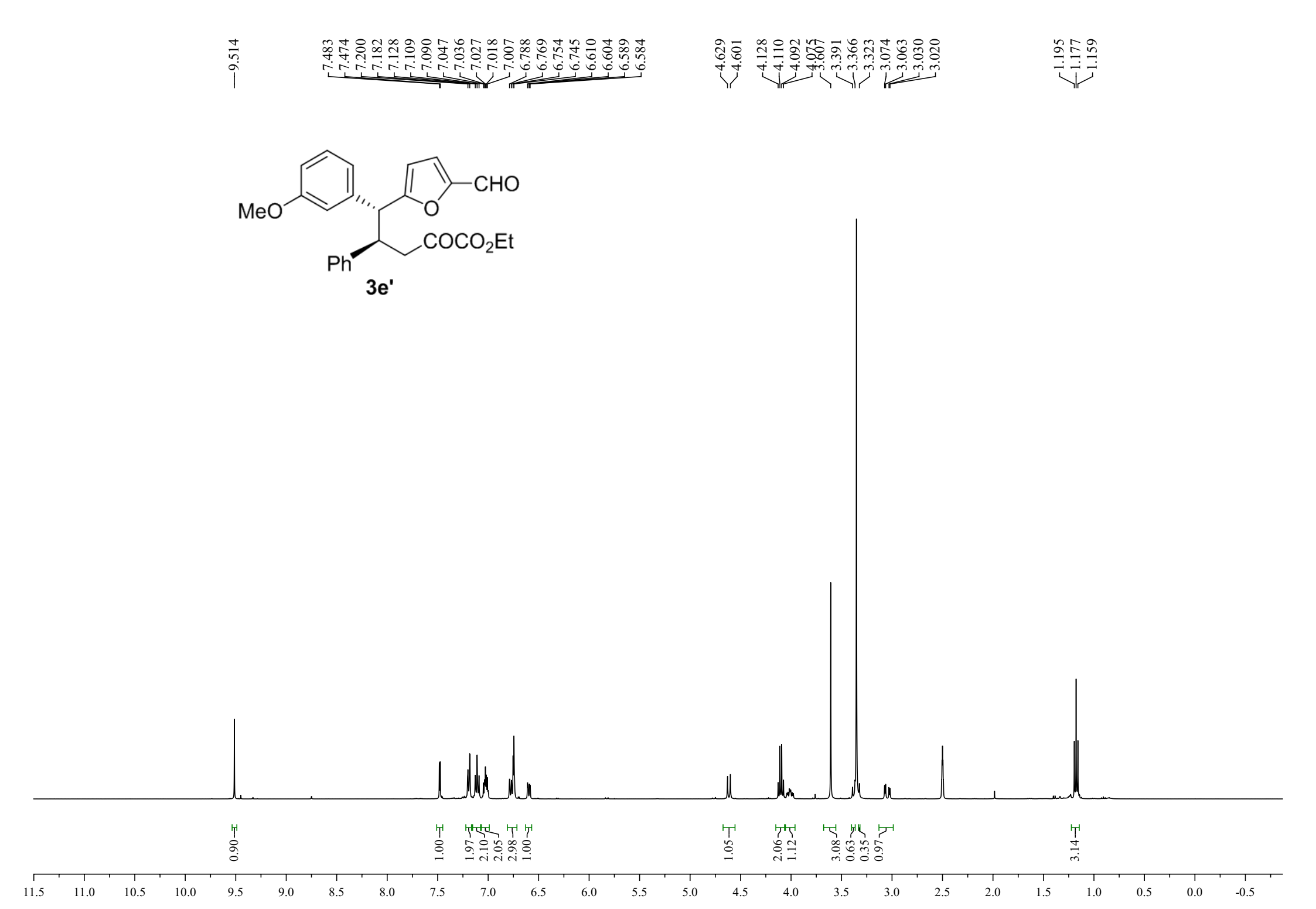
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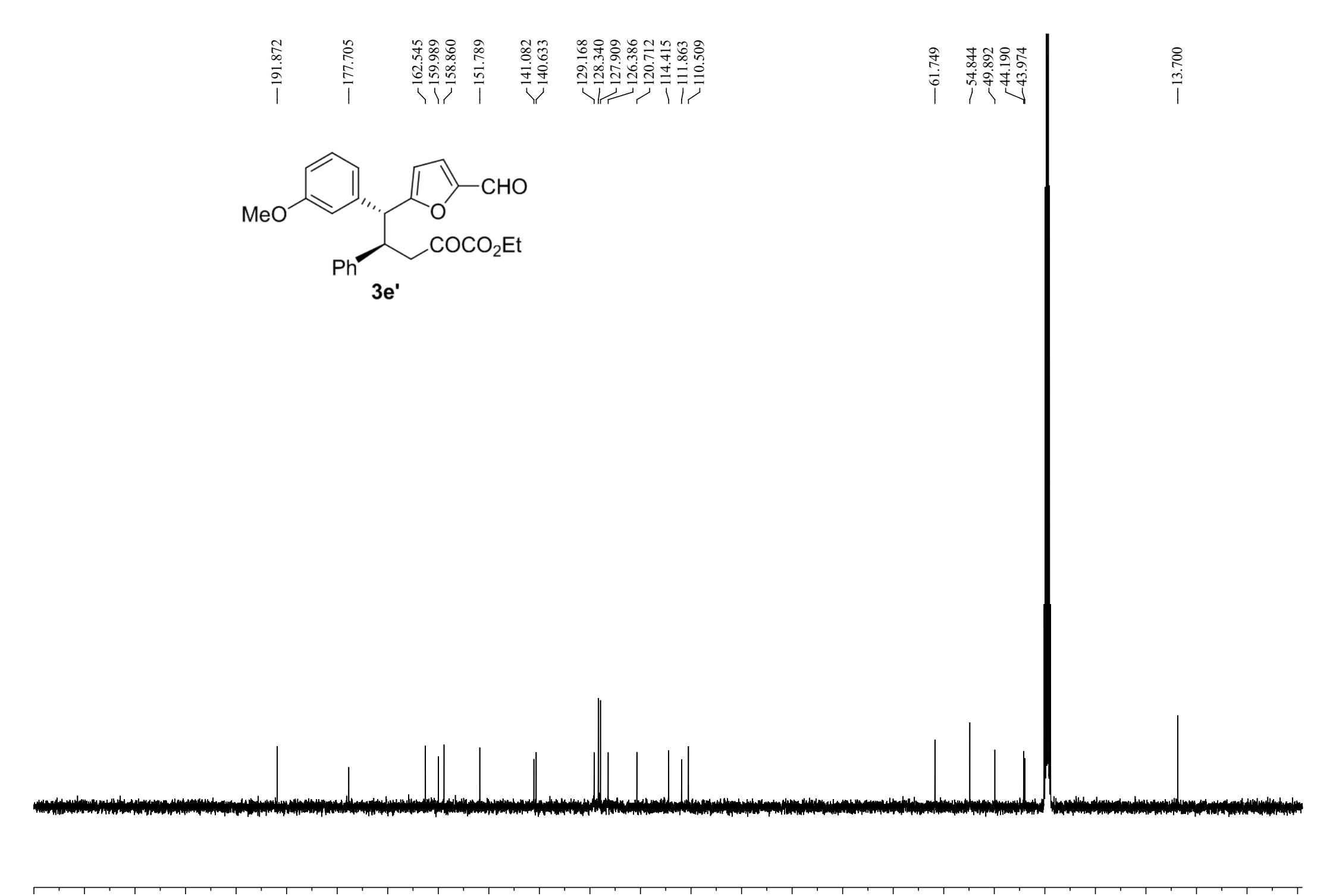
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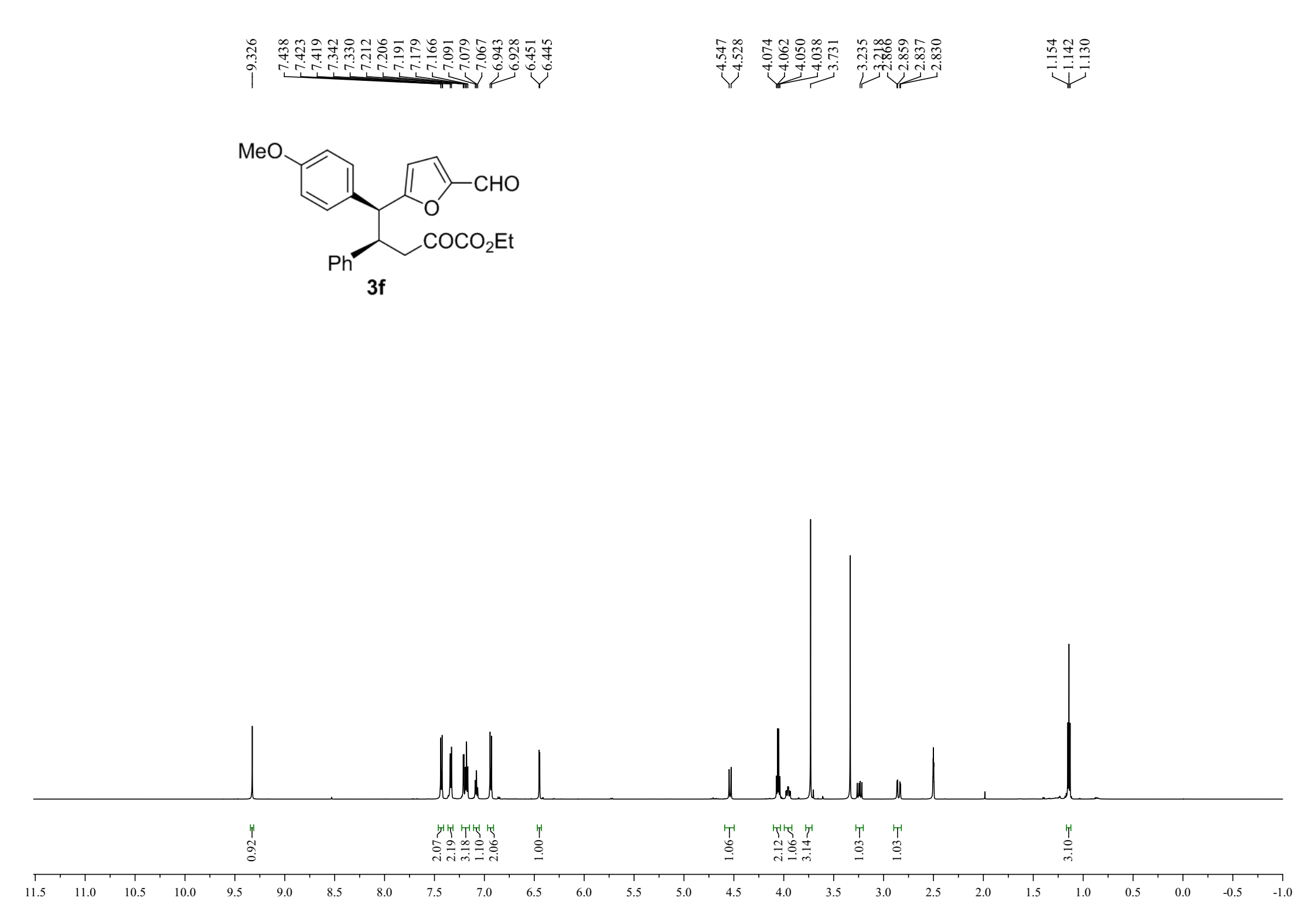
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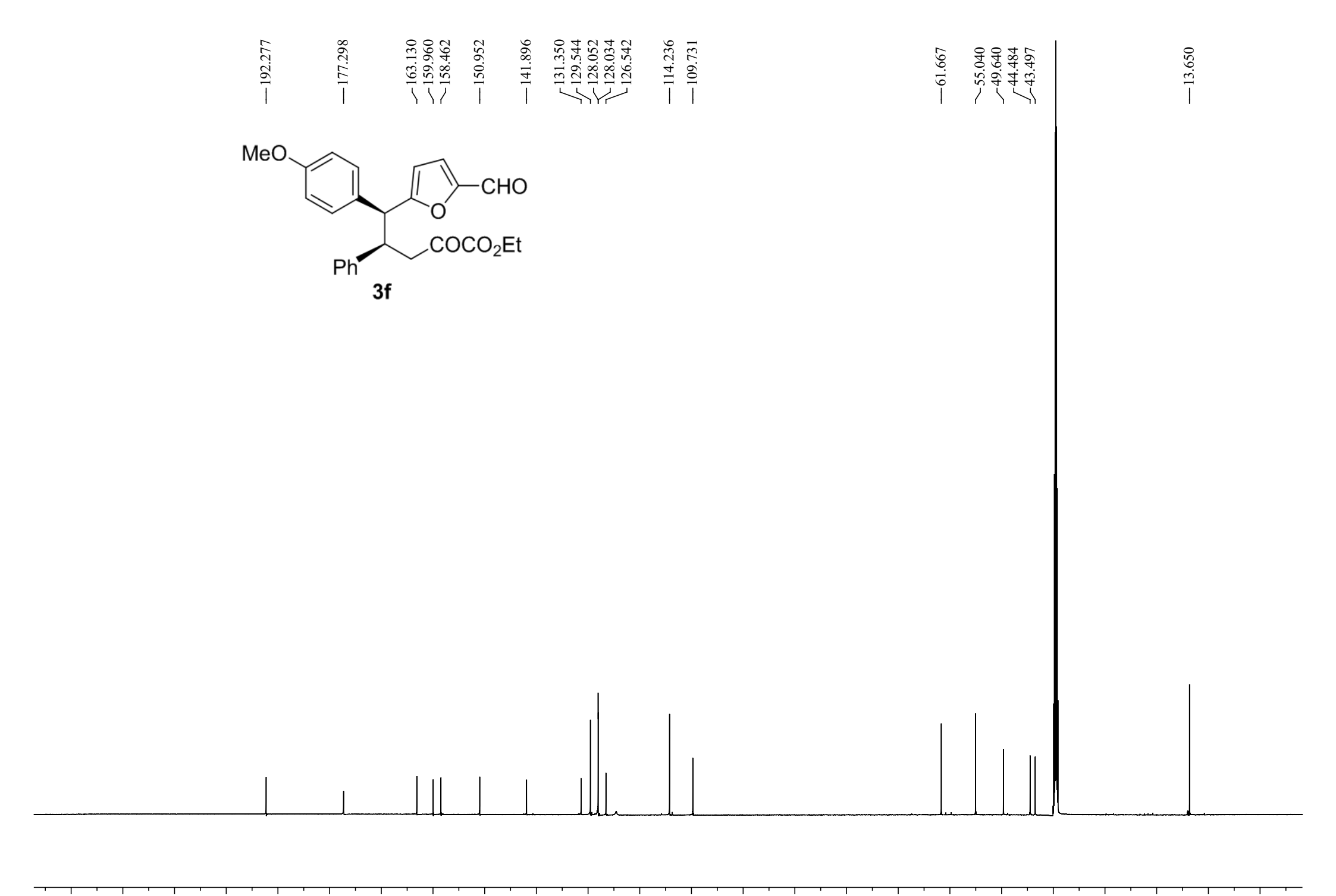
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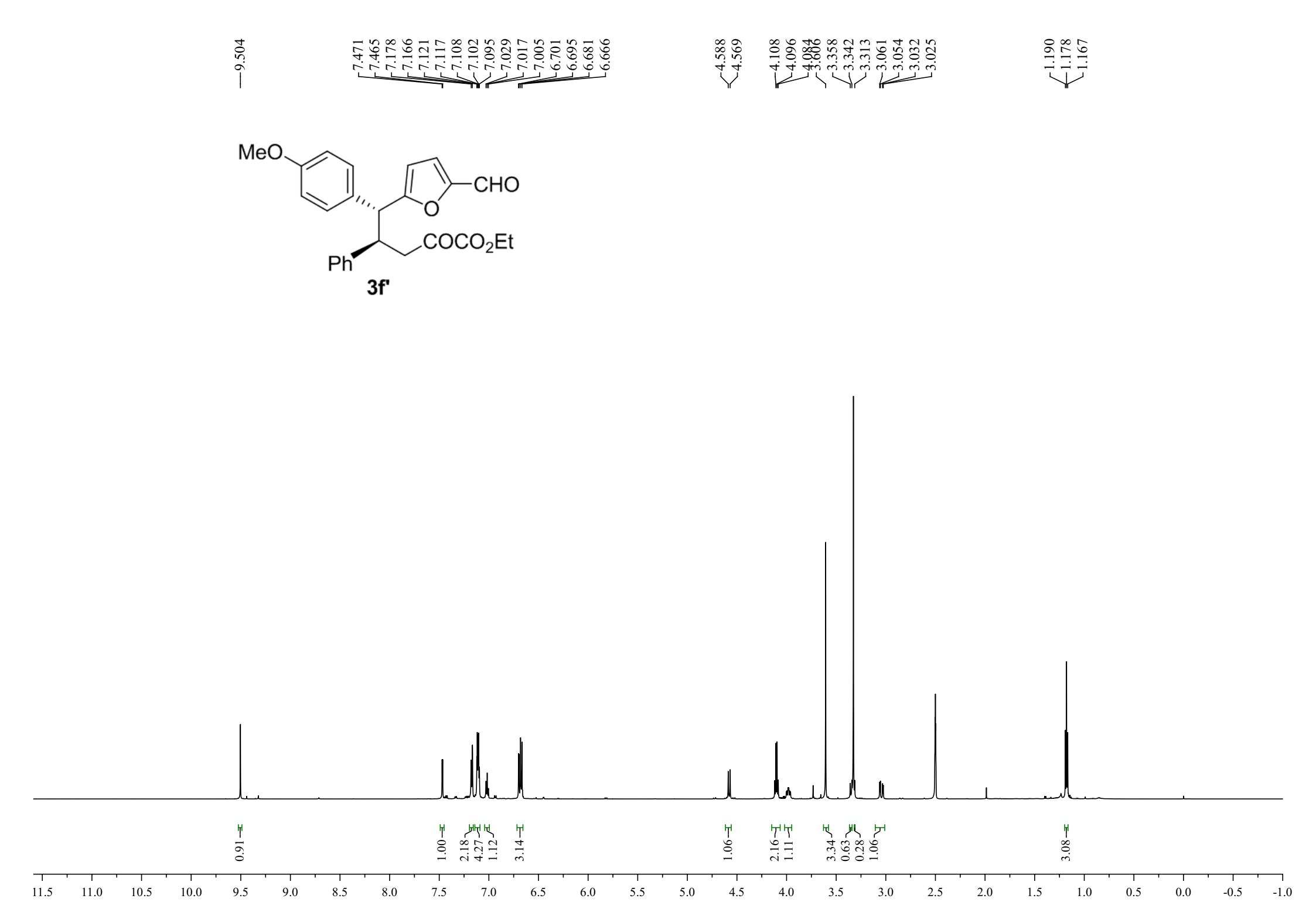
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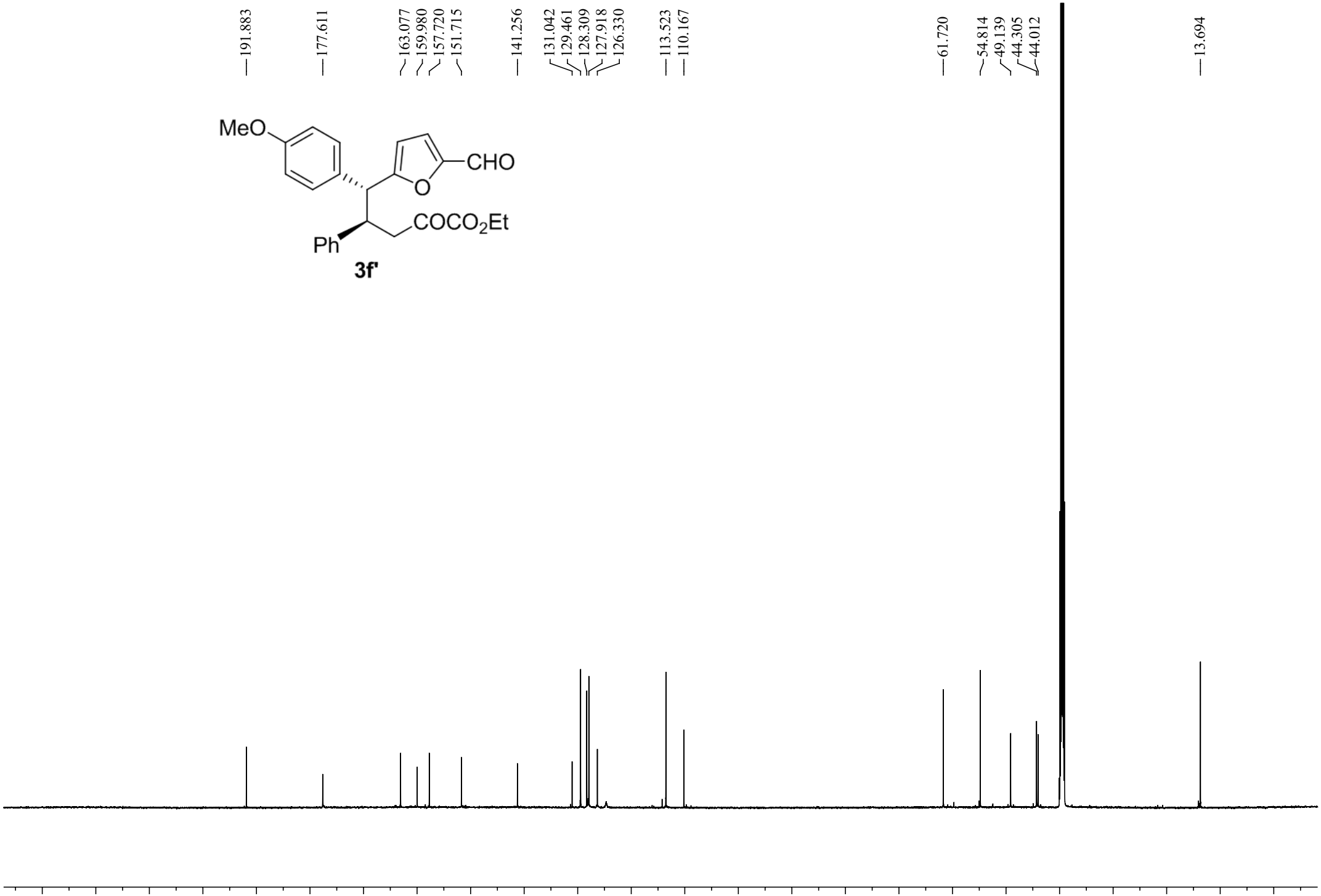
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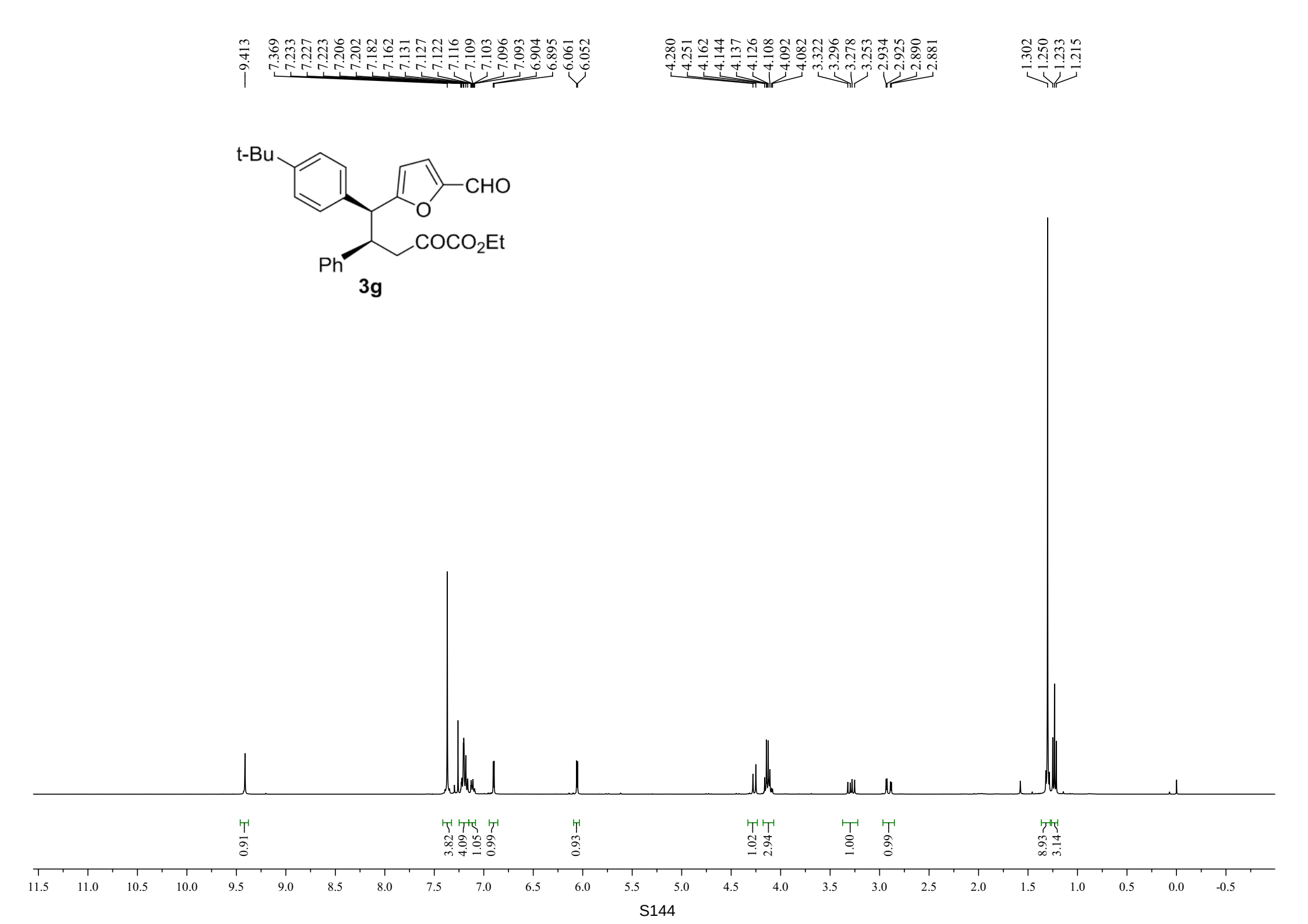
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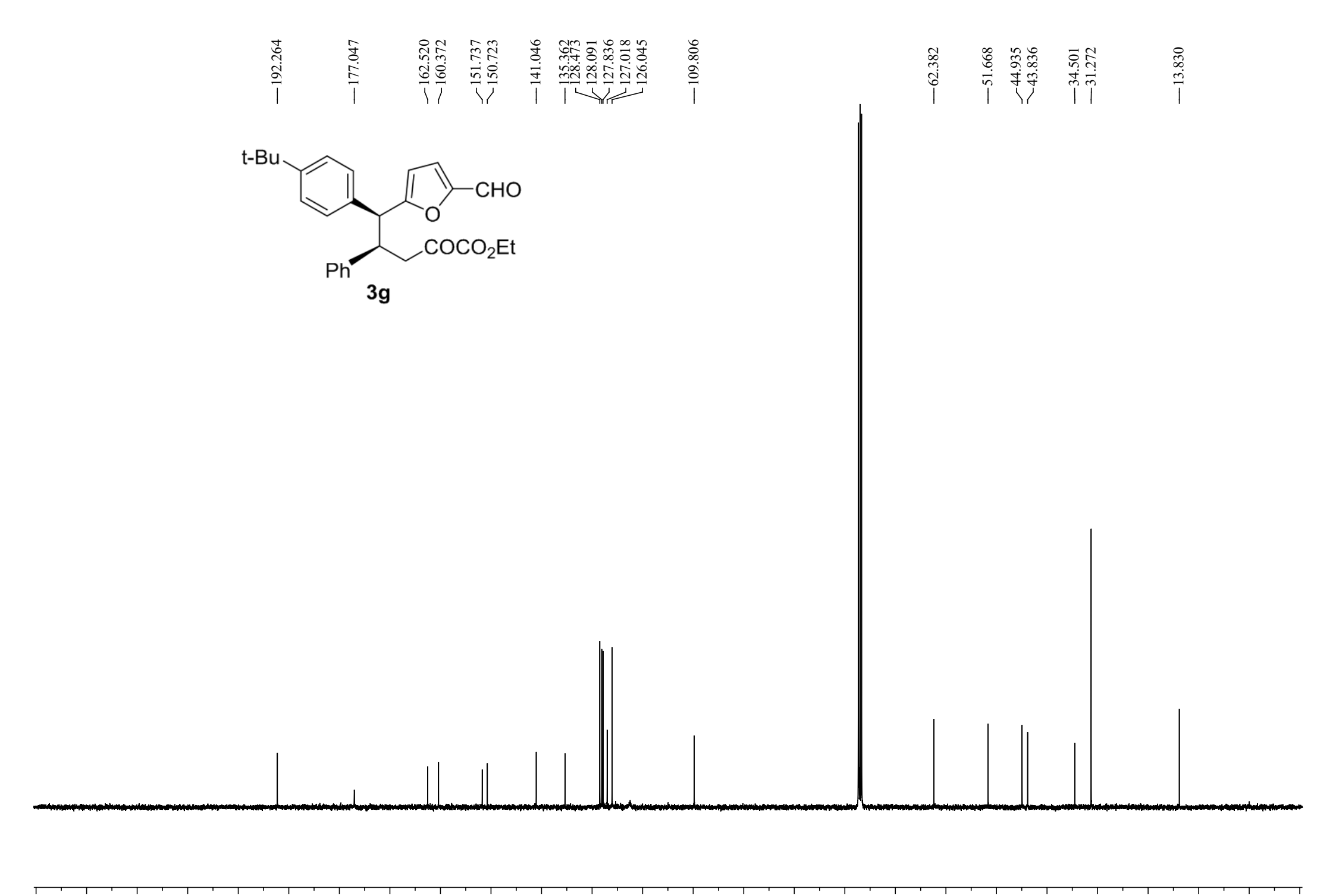
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COCO2Et
Ph
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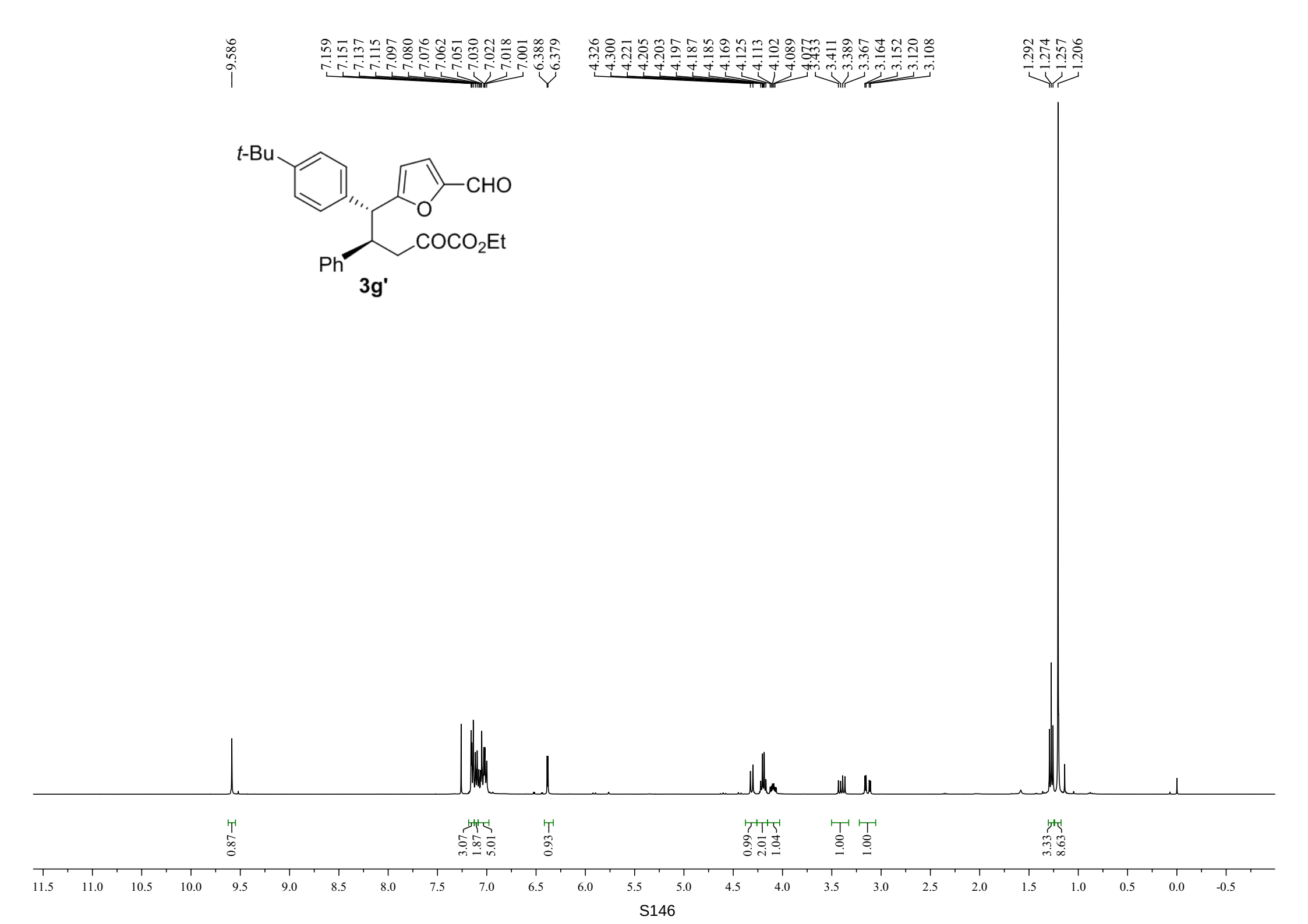
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CHO
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COCO2Et
Ph
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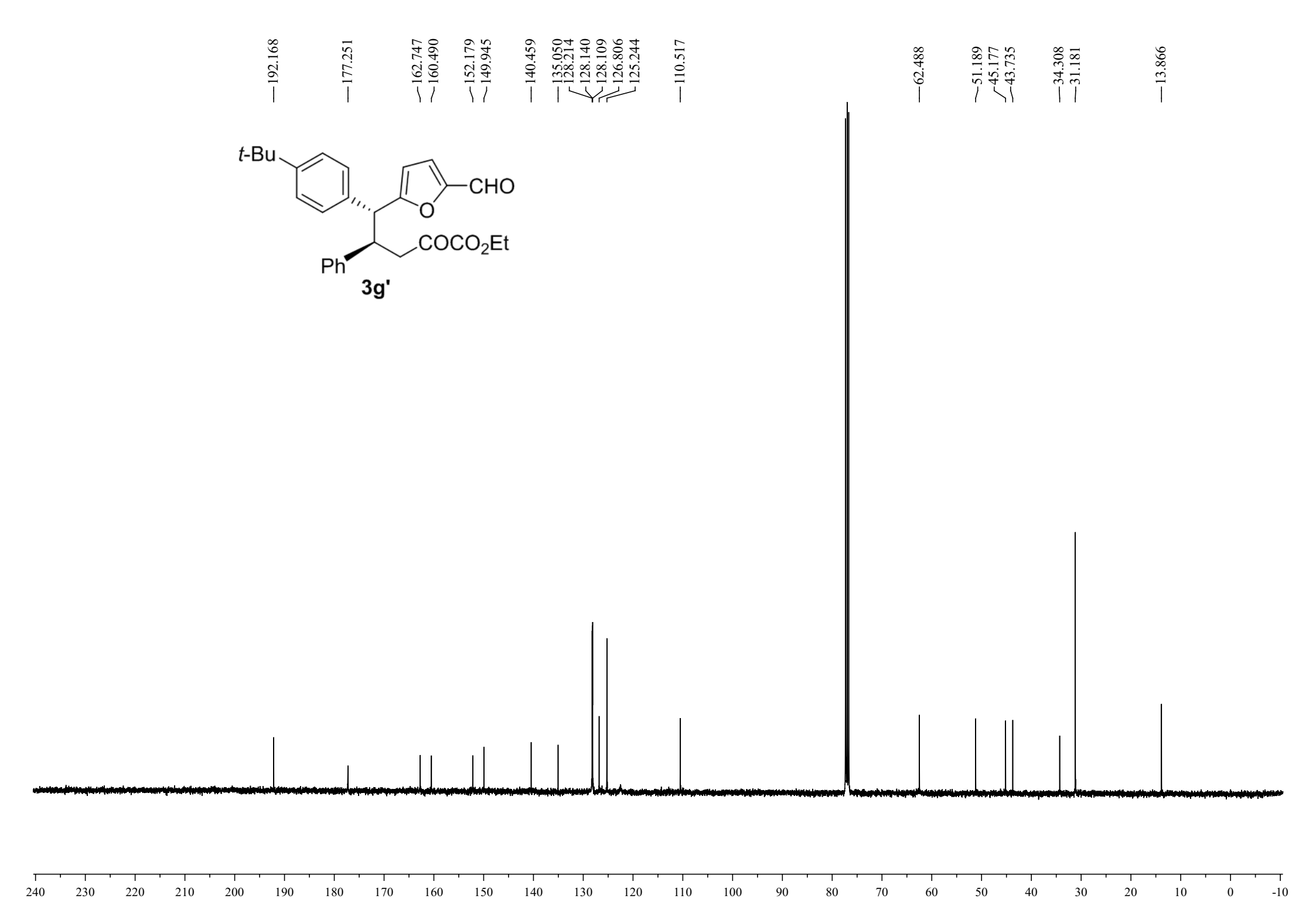
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COCO2Et
Ph
3g'
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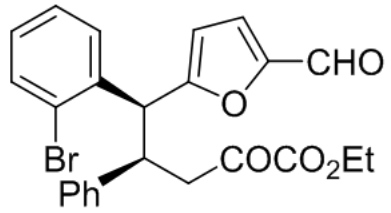
CHO
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Br
Ph
COCO2Et

3h

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1.02
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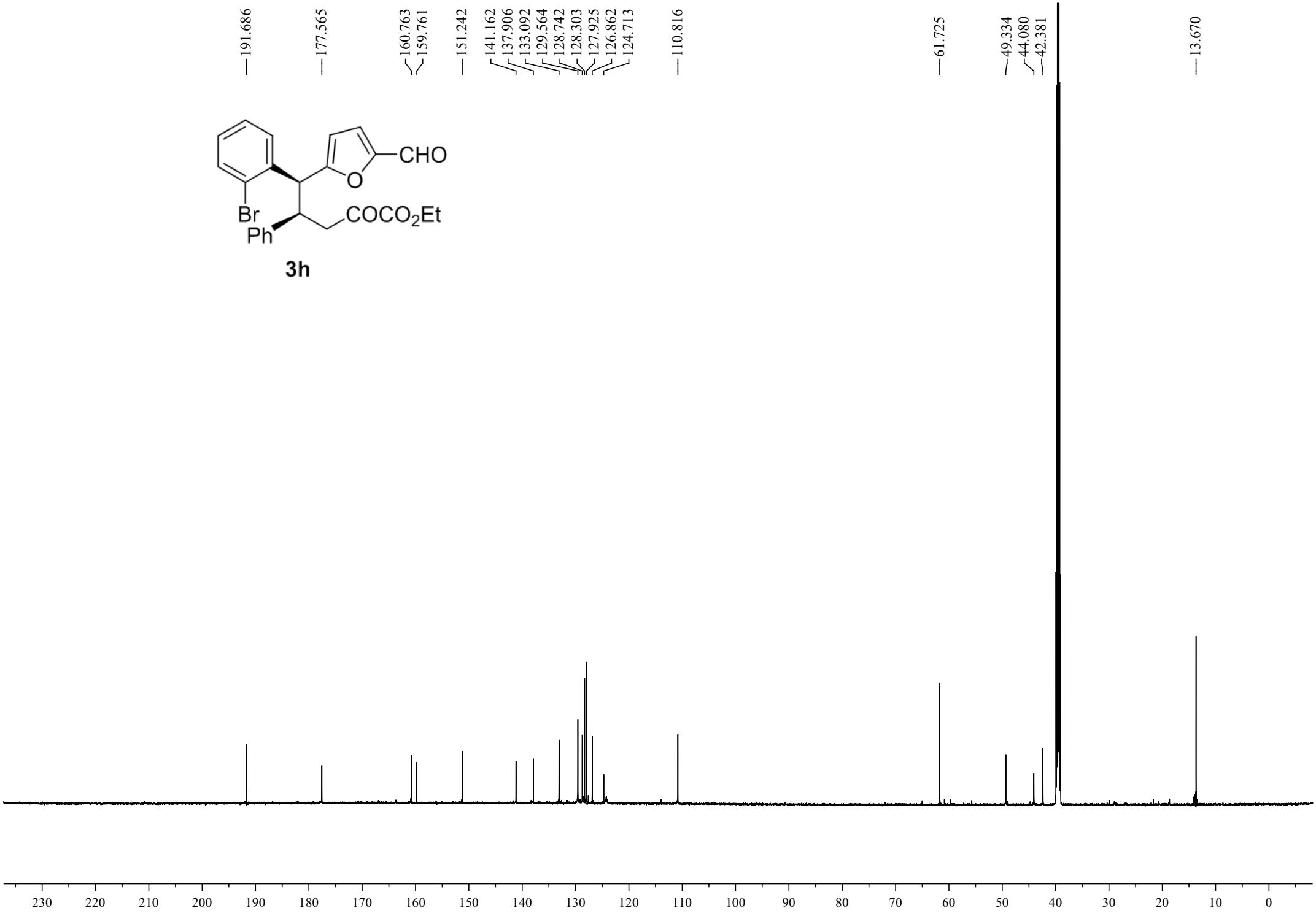
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13.670
CHO
O
Br
Ph
COCO2Et
3h
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220
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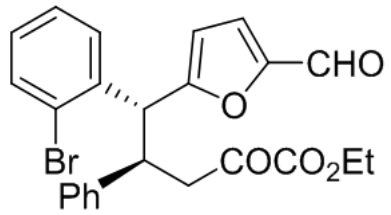

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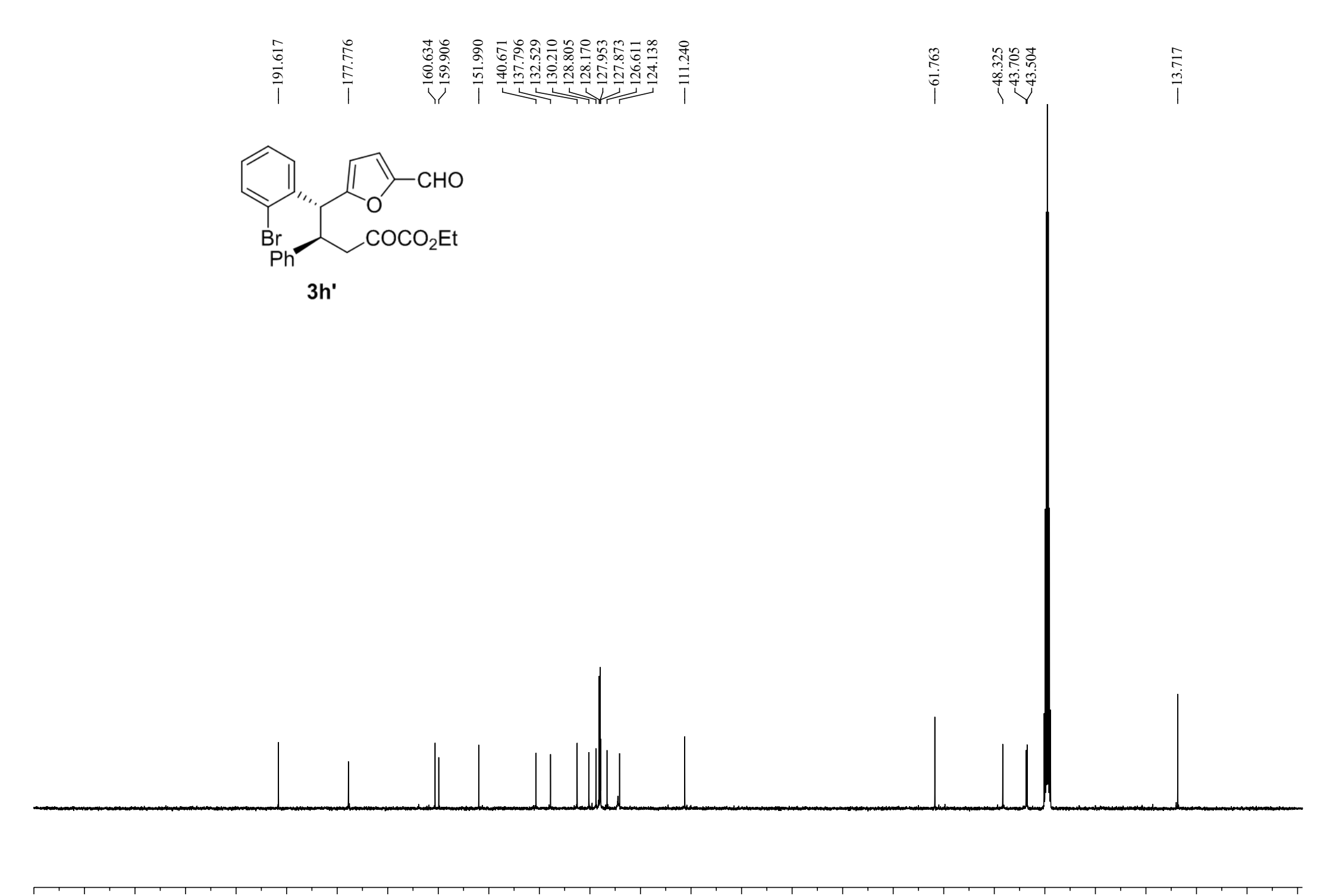
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43.504
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CHO
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Br
Ph
COCO2Et
3h'
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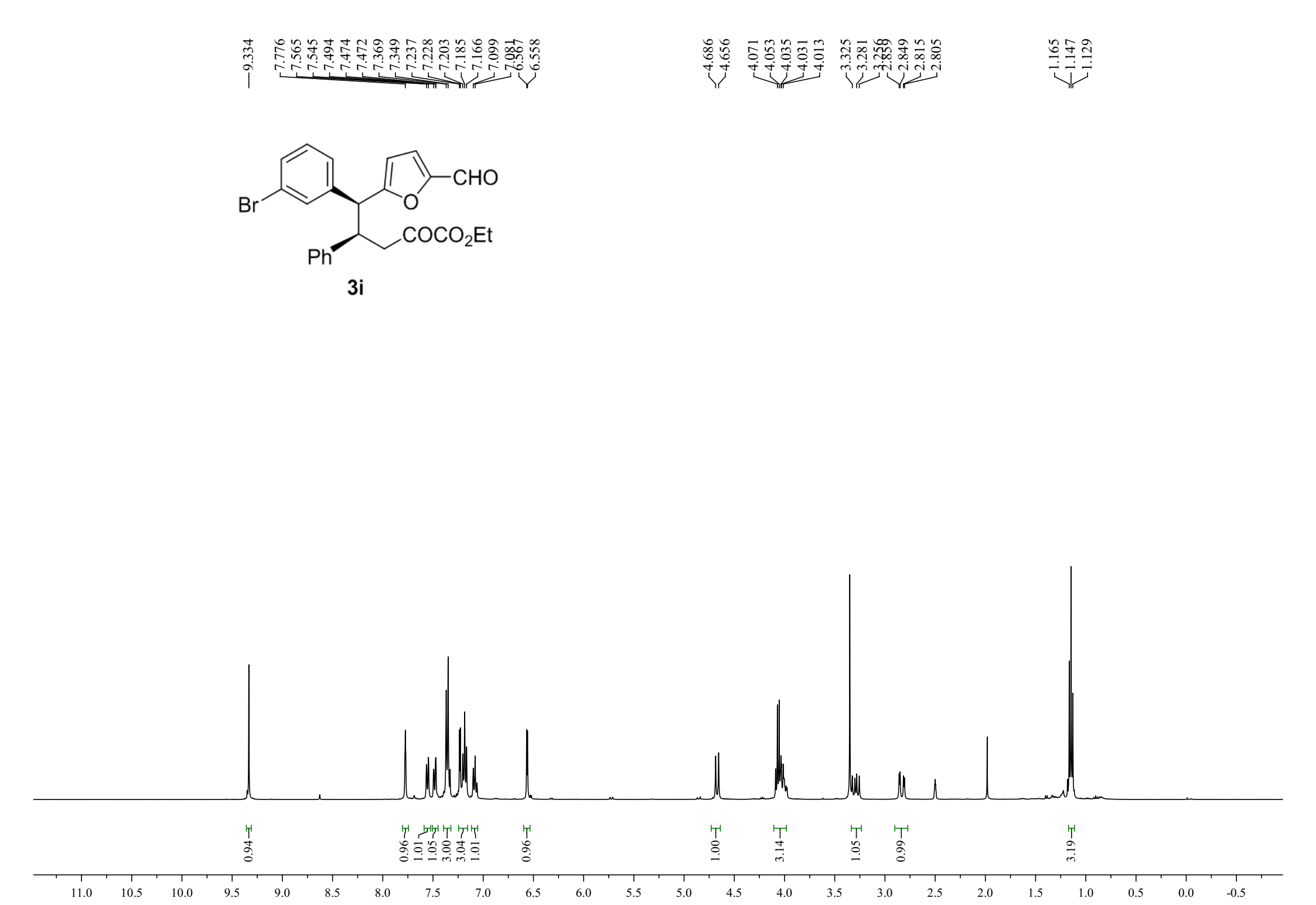
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4.053
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4.031
4.013
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3.256
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CHO
Br
O
COCO2Et
Ph
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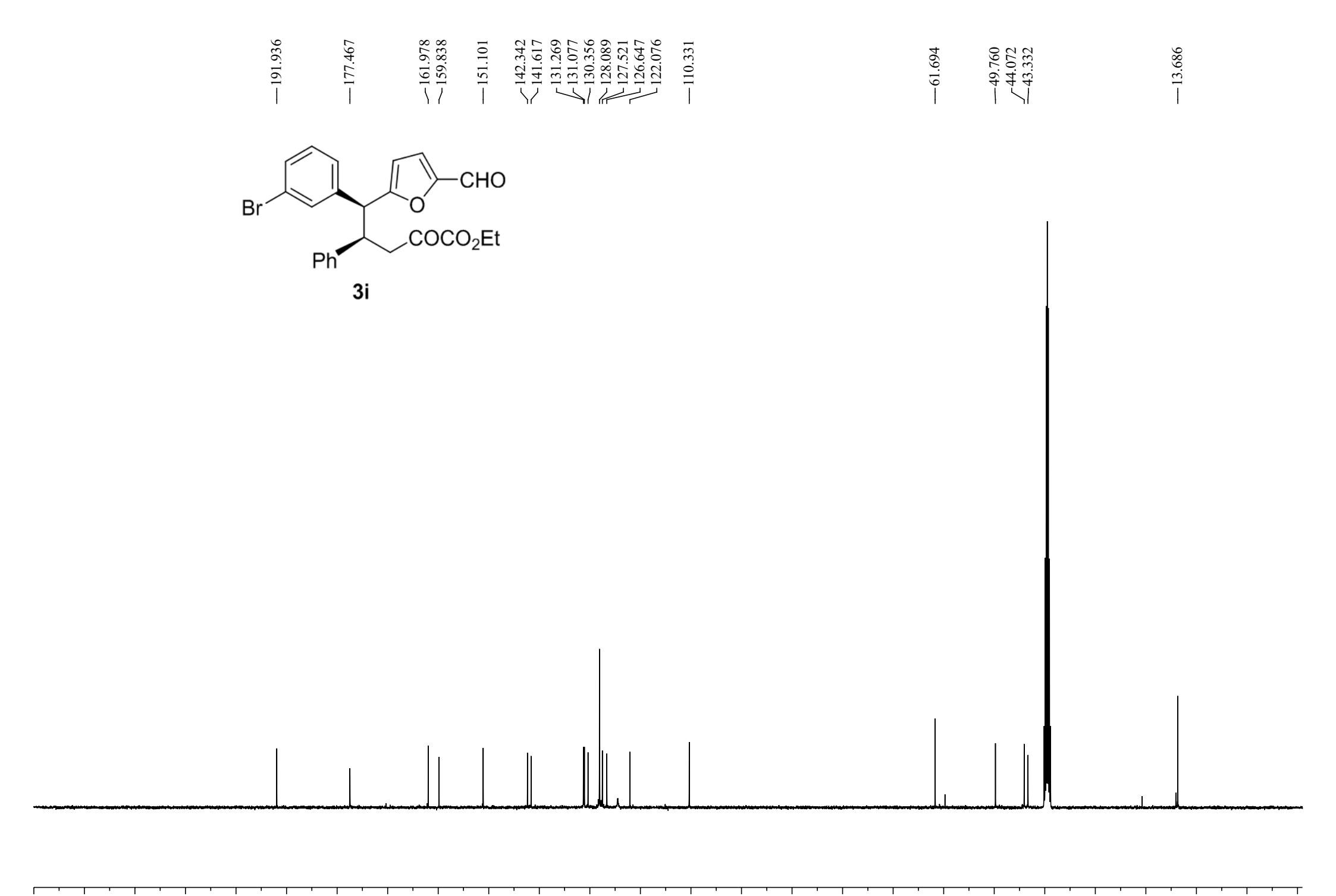
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CHO
COCO2Et
Ph
3i
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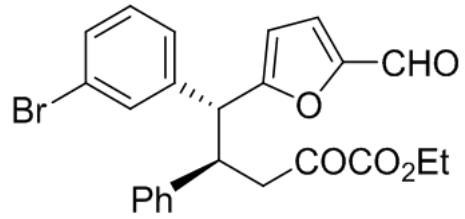
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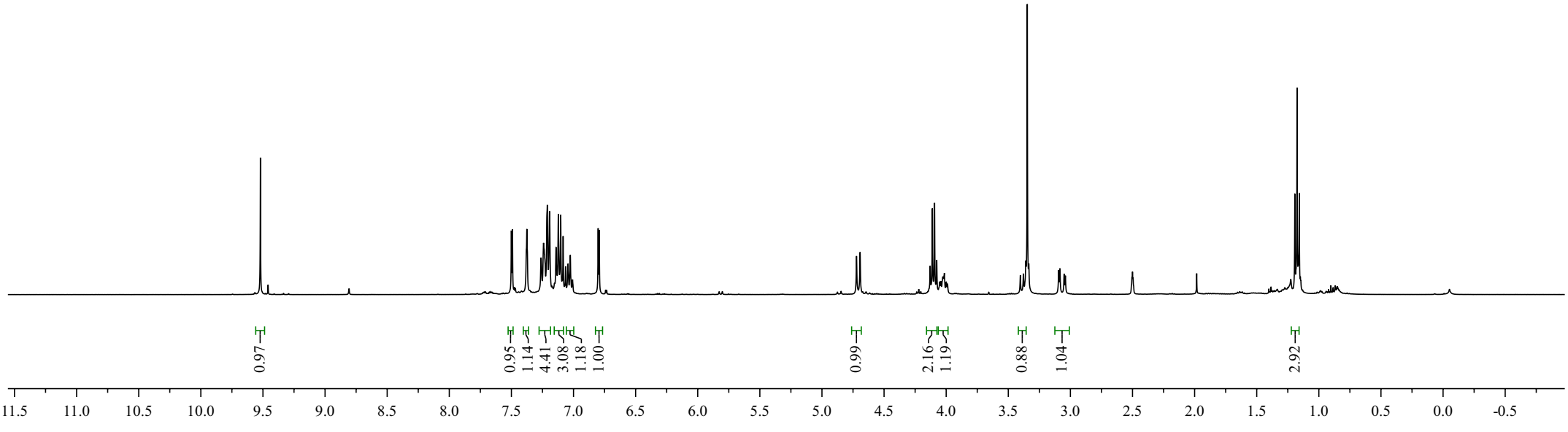
CHO
COCO2Et
Ph

3i'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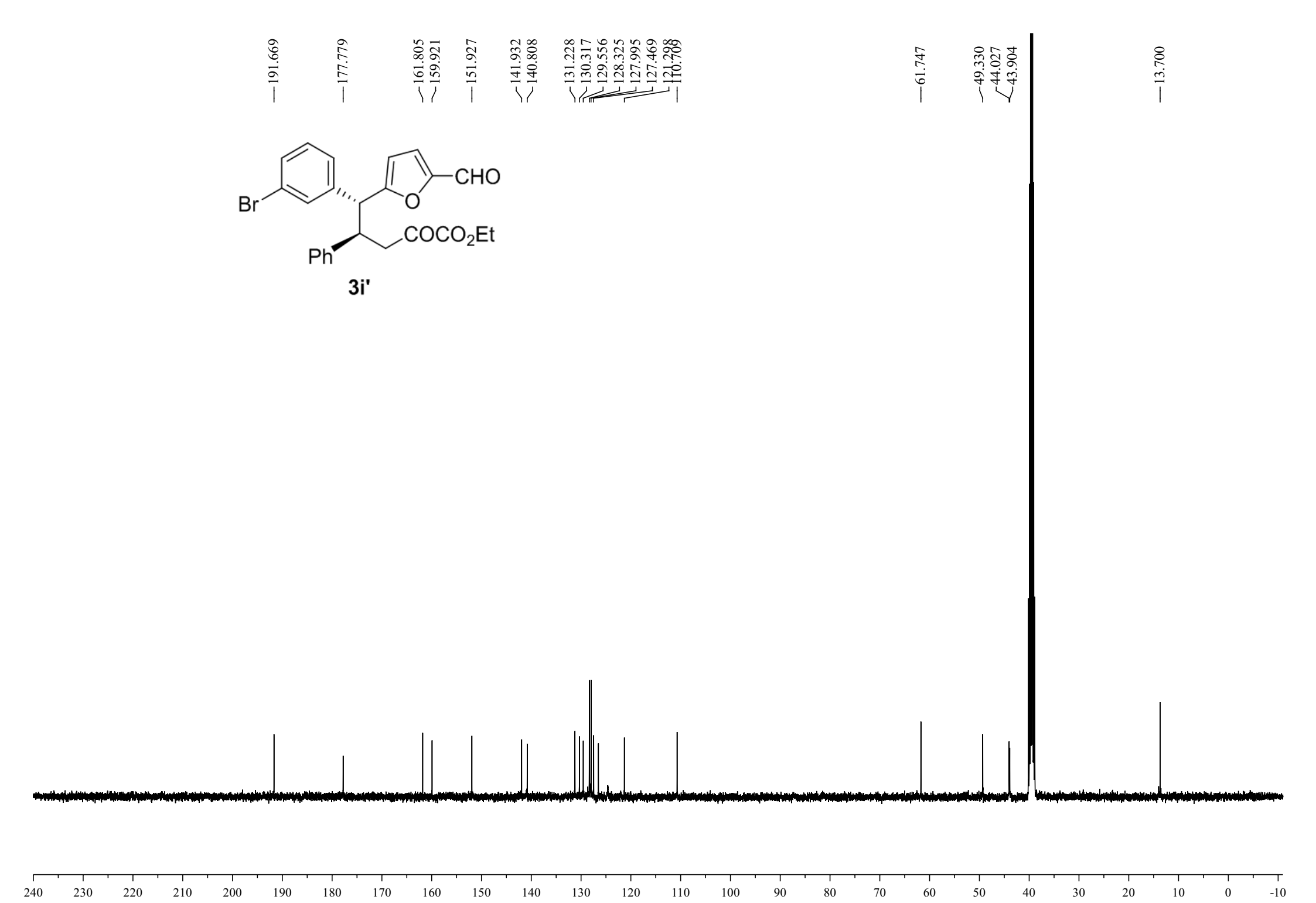
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CHO
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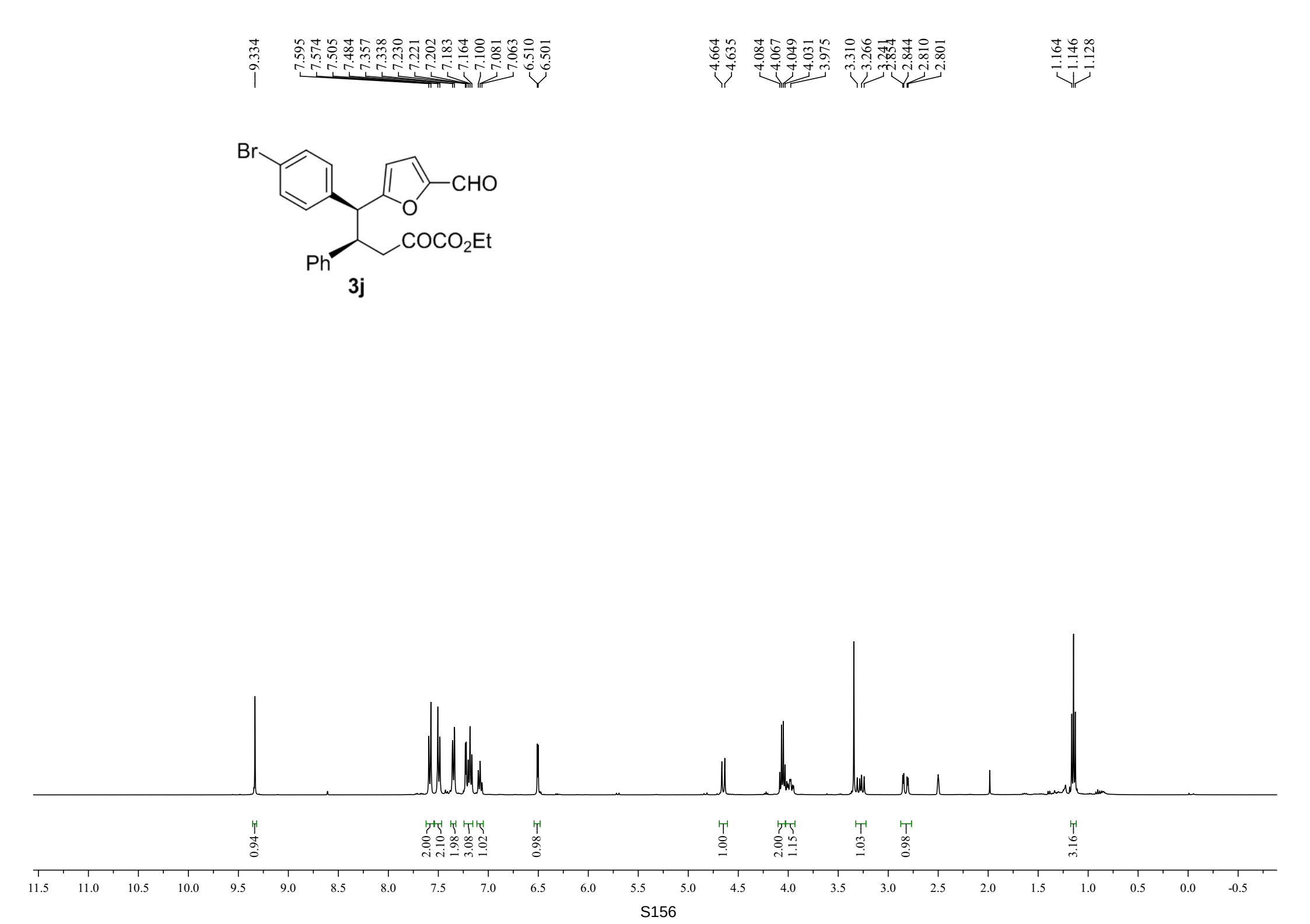
O
COCO2Et
Ph
3i'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CHO
O
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Ph
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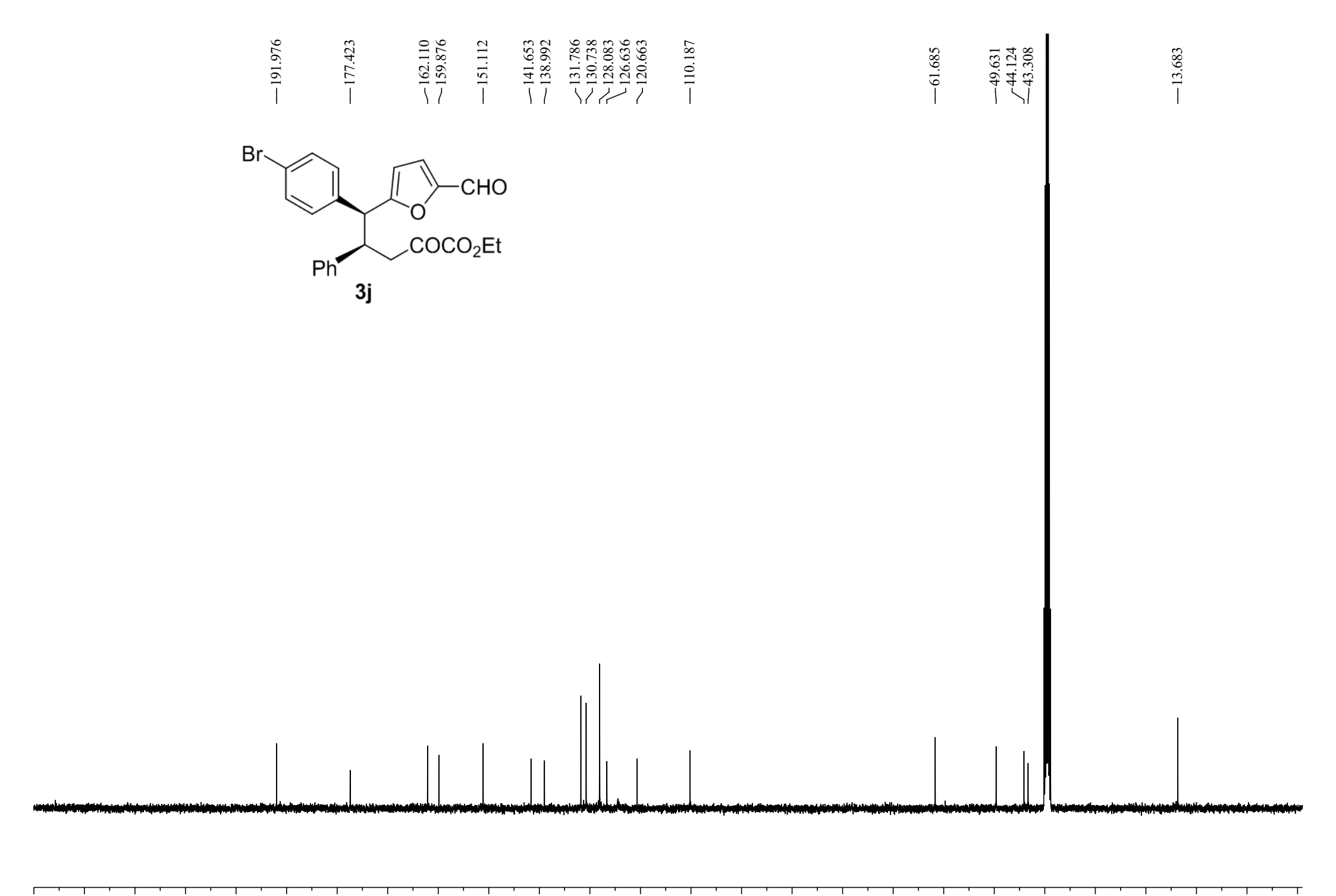
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COCO2Et
Ph
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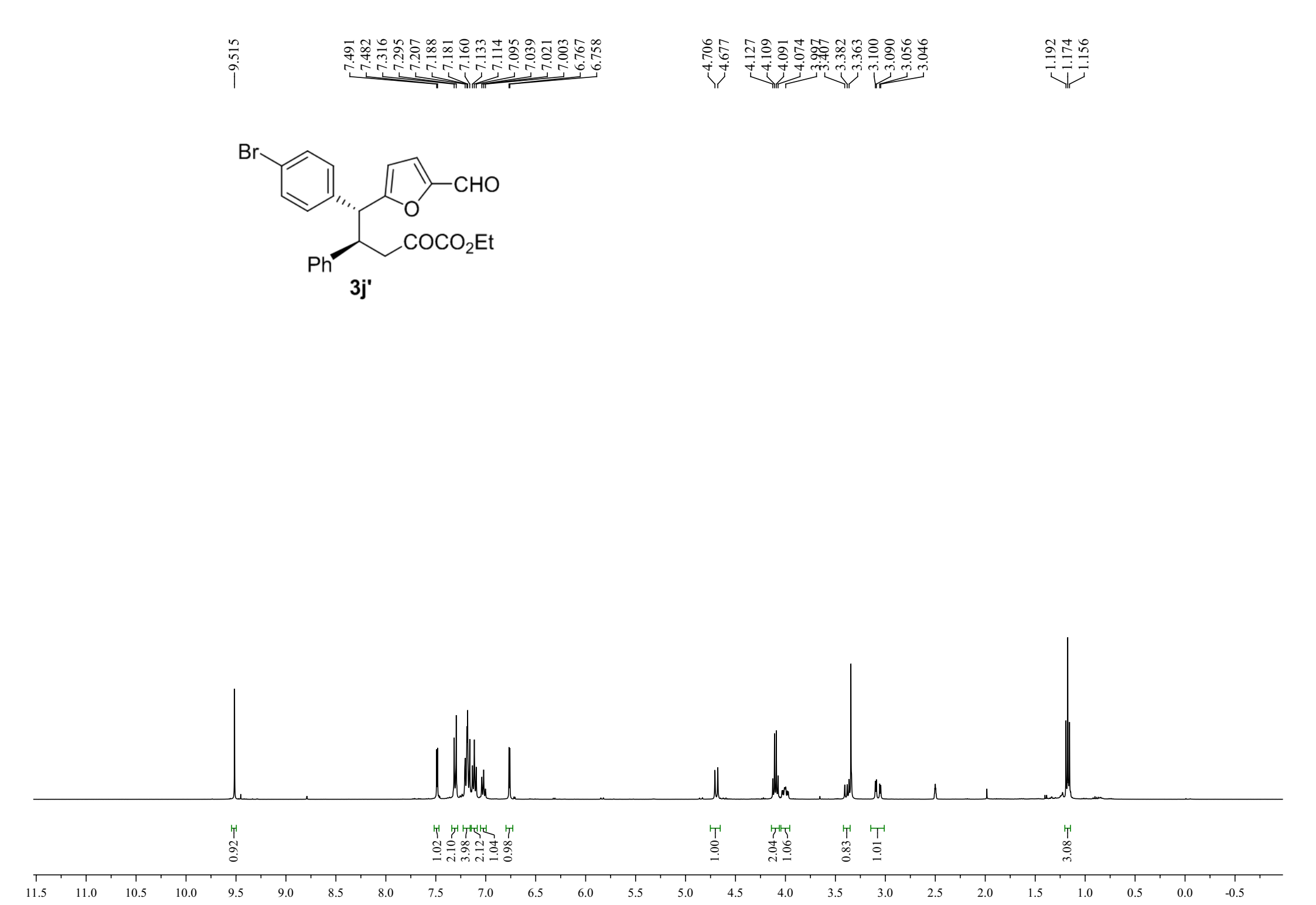
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Br
CHO
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Ph
3j'
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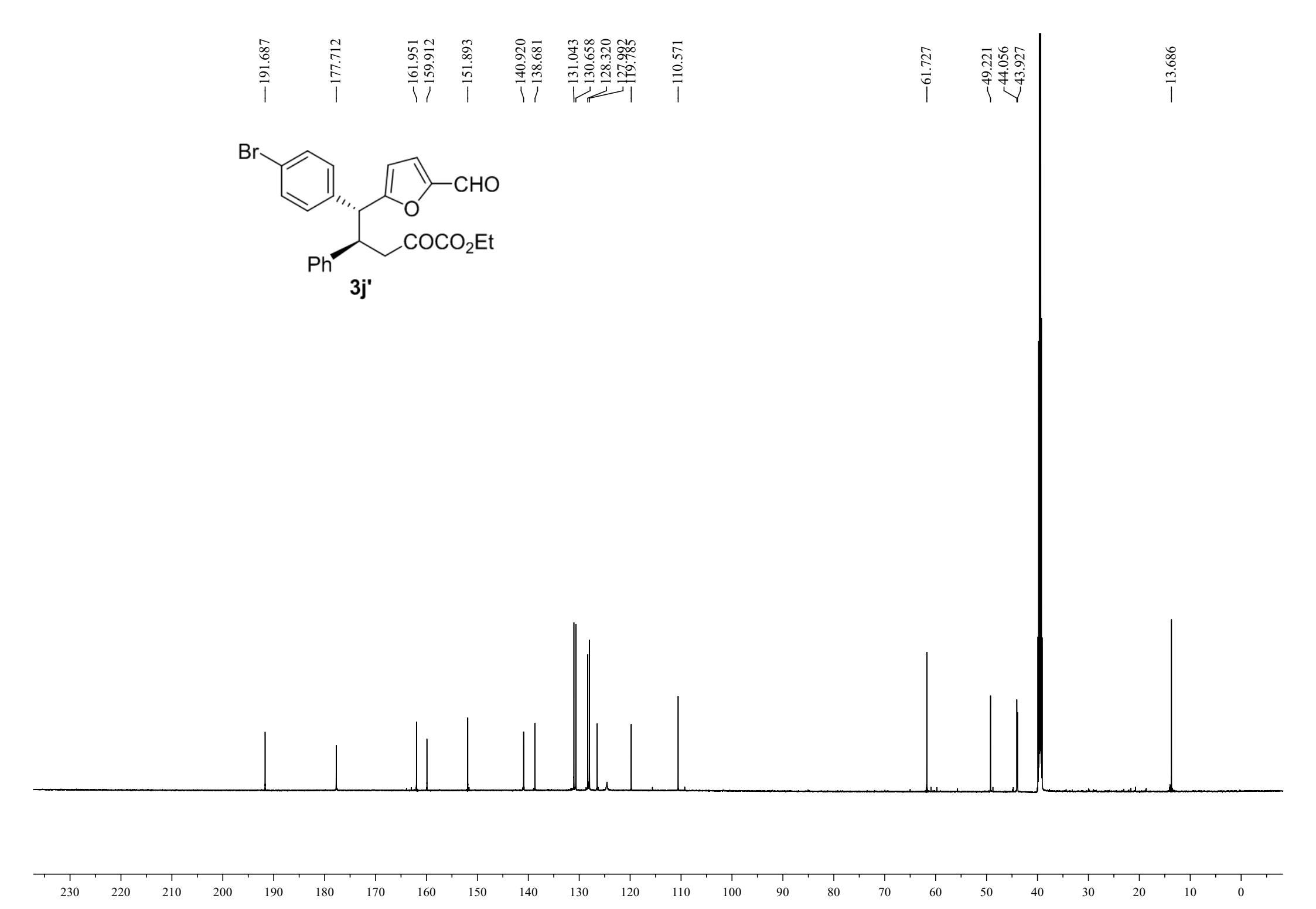
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COCO2Et
Ph
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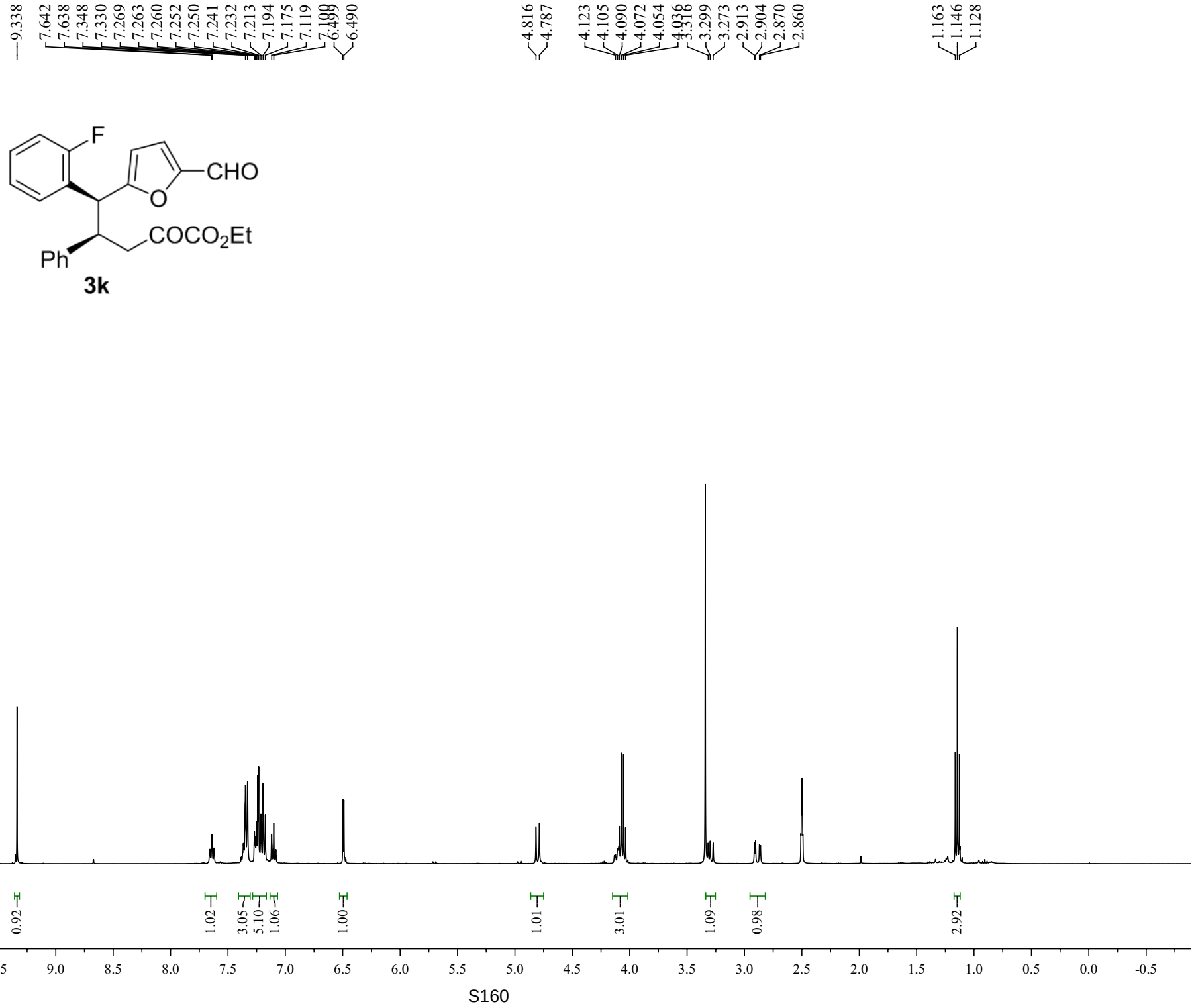
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Ph
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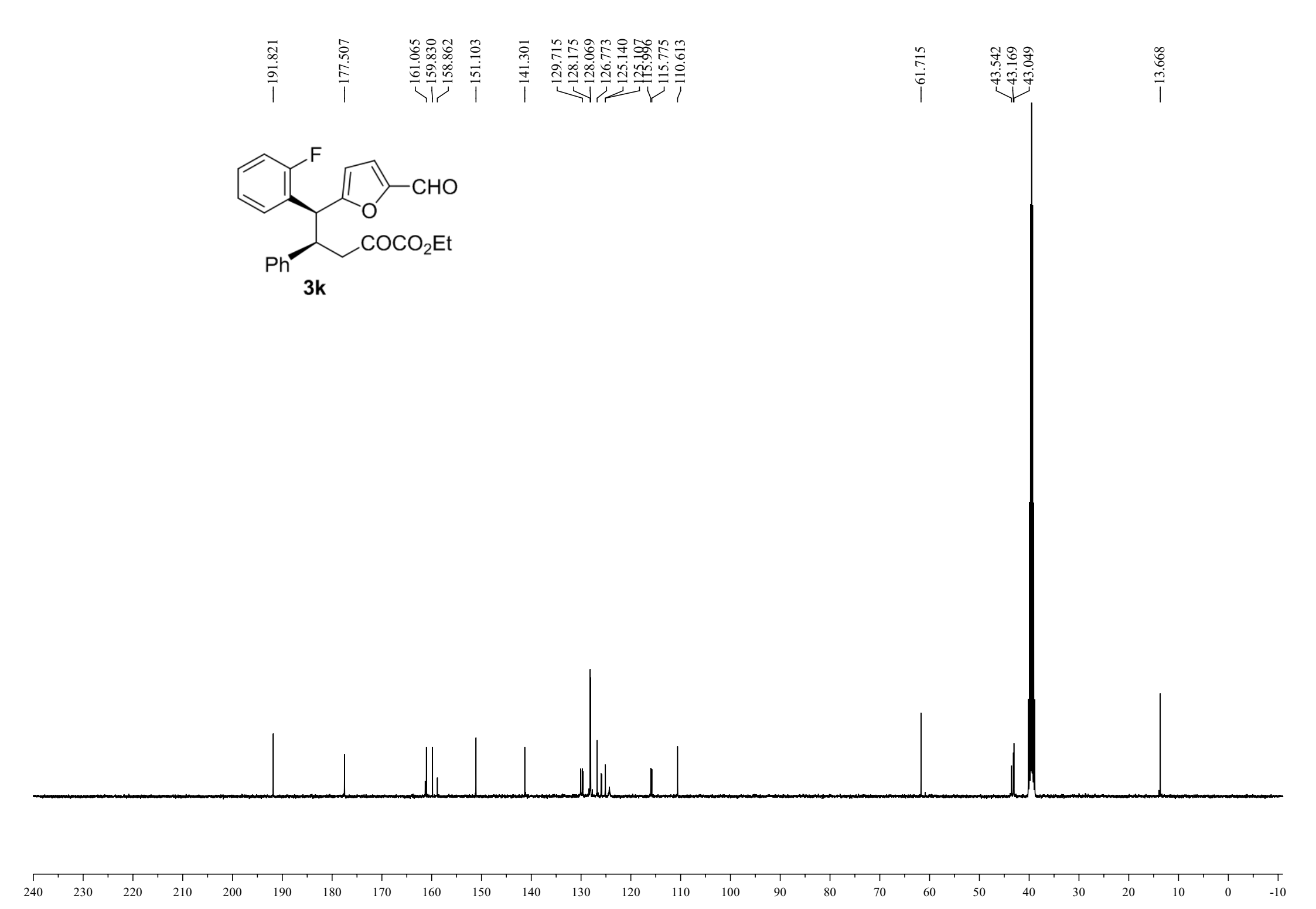
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13.668
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O
COCO2Et
Ph
3k
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200
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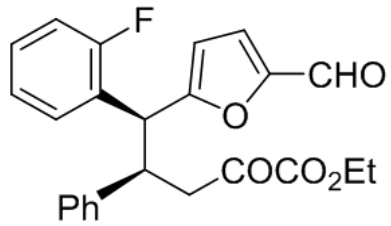
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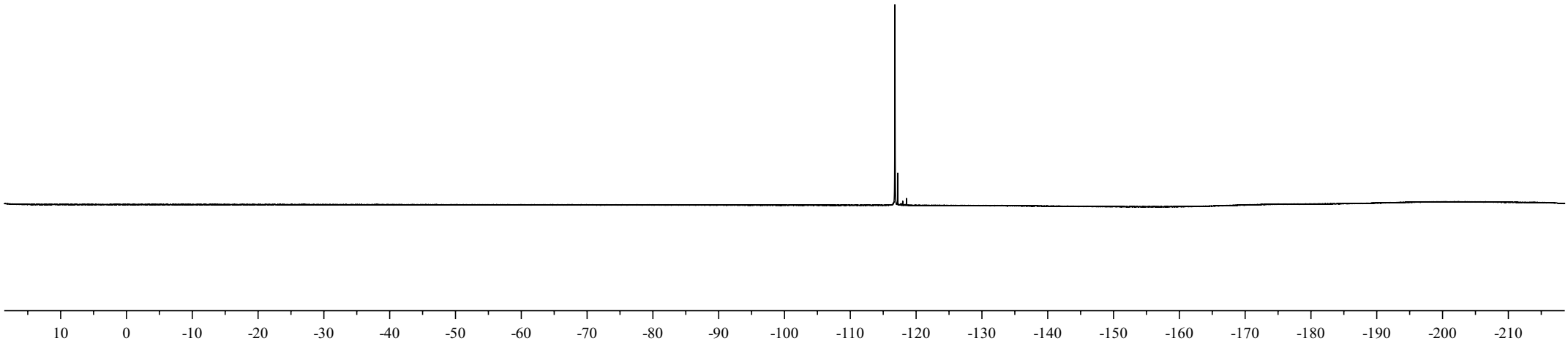
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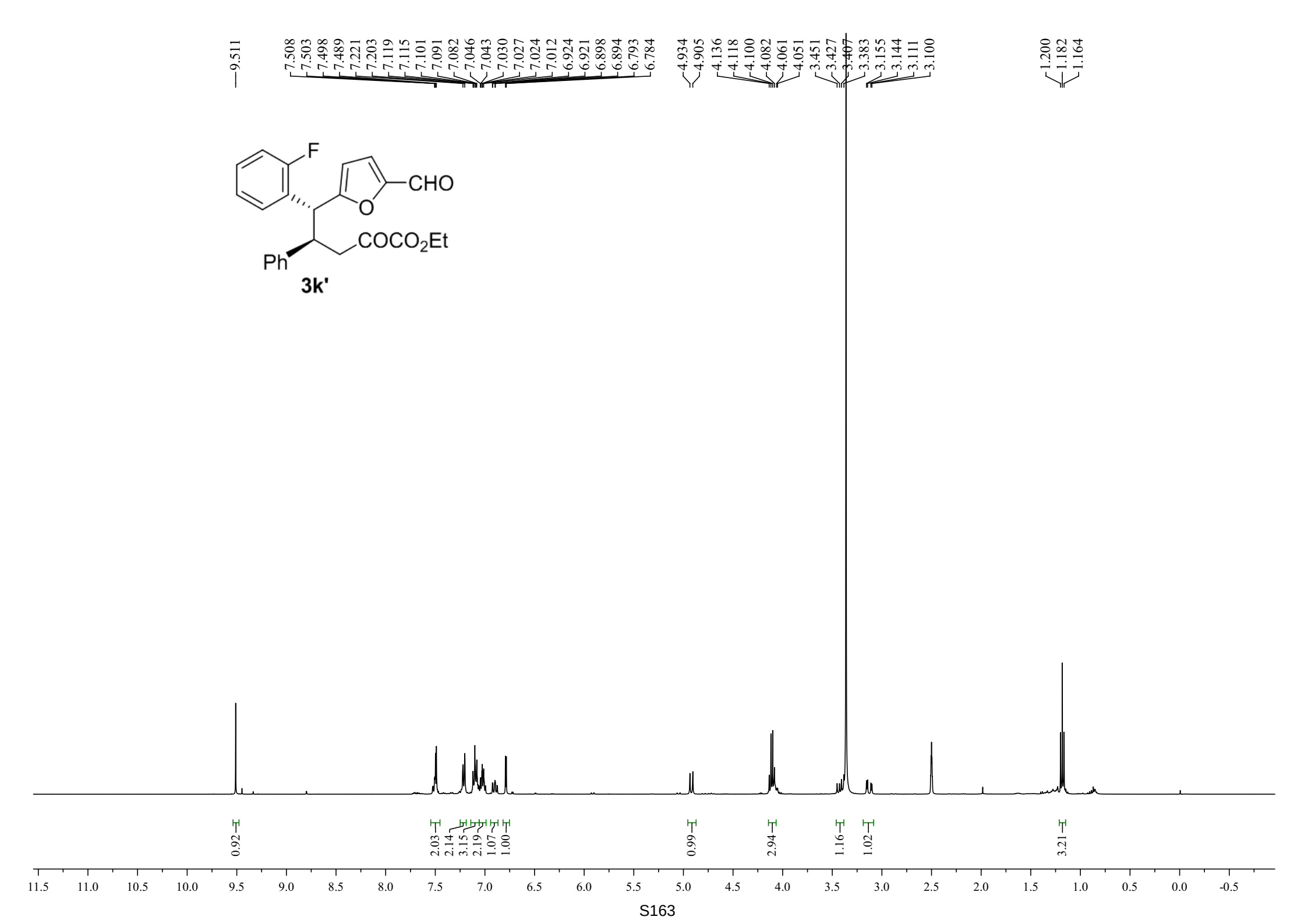
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Ph
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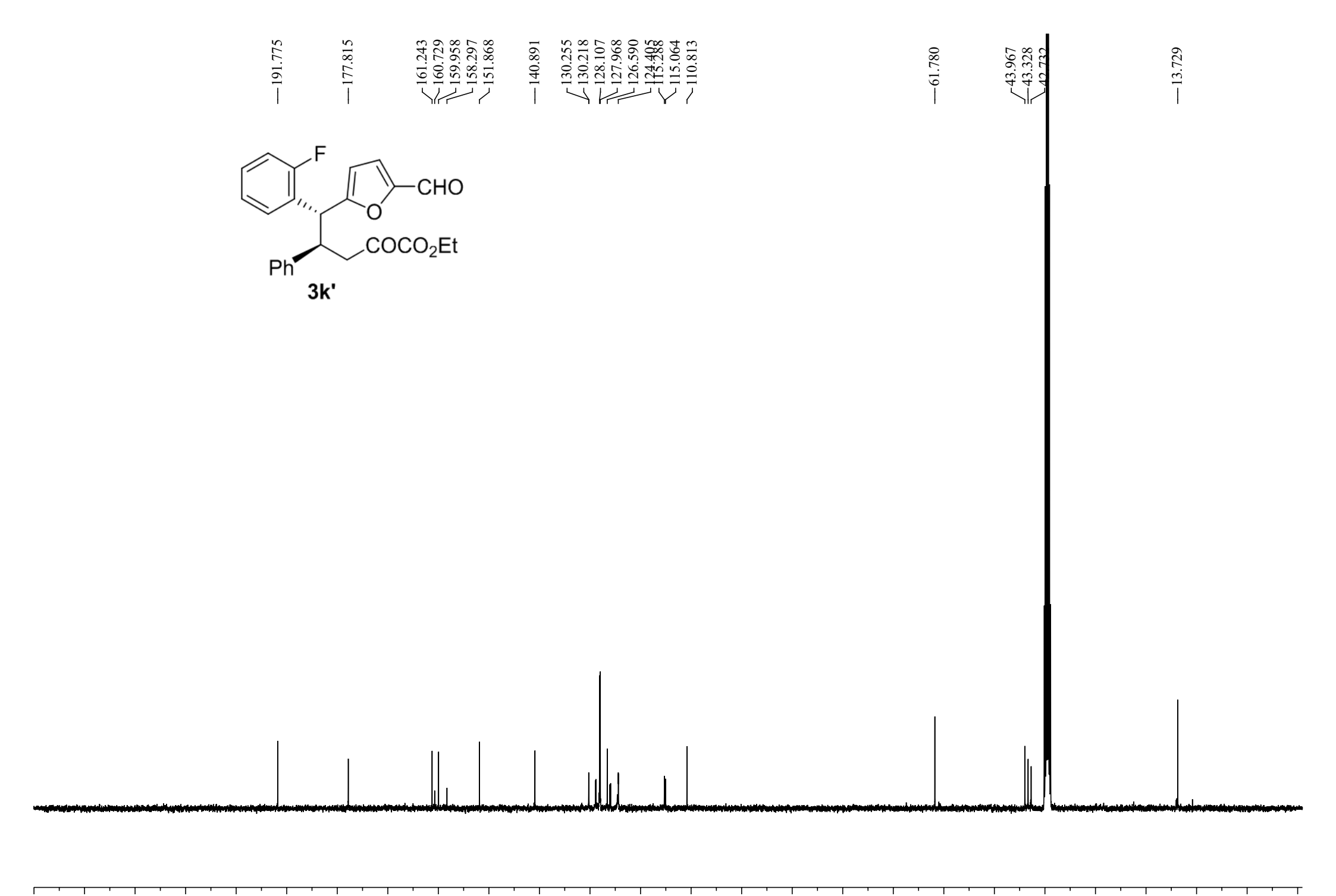
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42.732
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F
CHO
O
COCO2Et
Ph
3k'
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230
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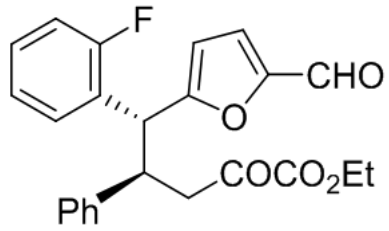
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3k'

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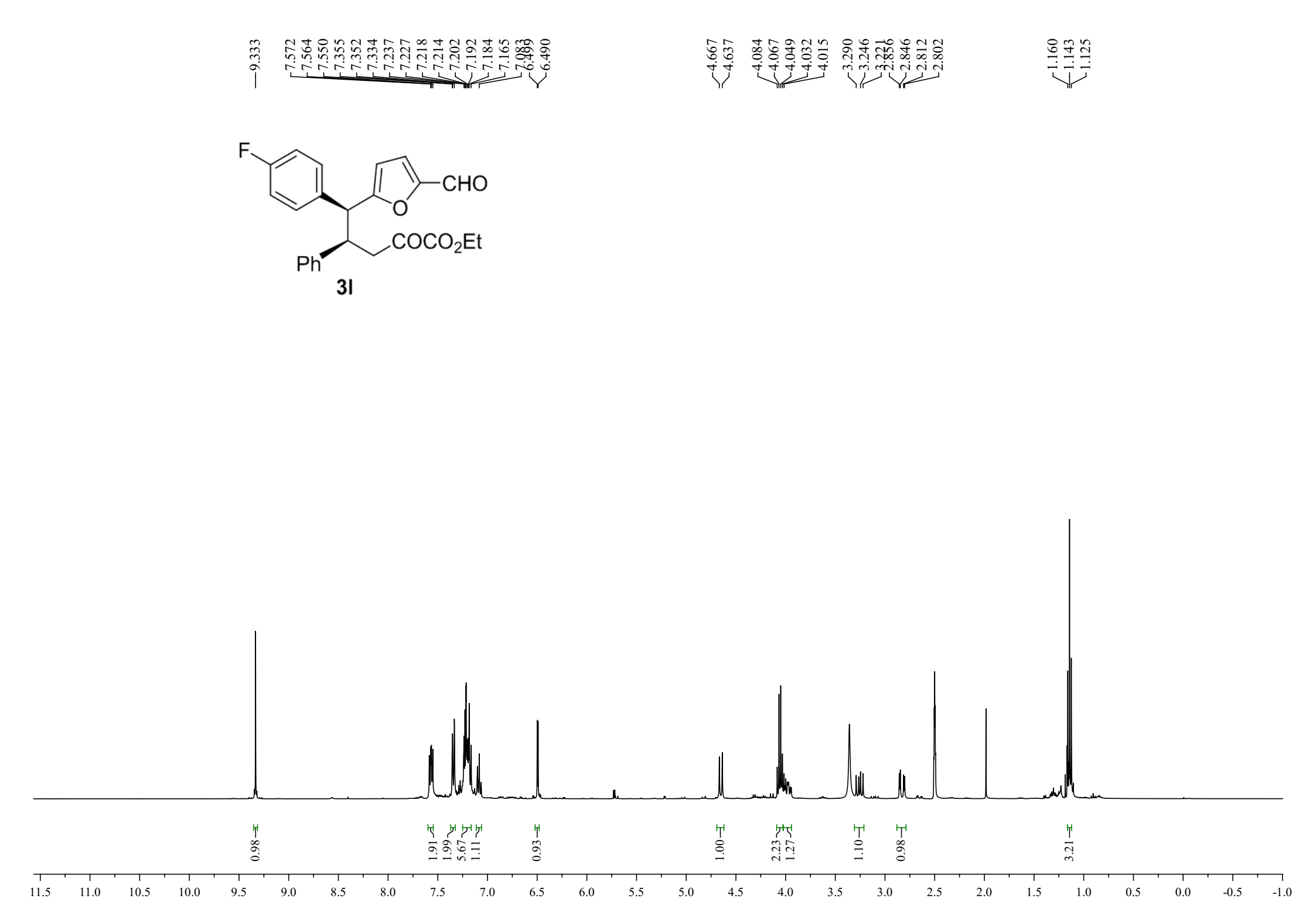
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CHO
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COCO2Et
Ph
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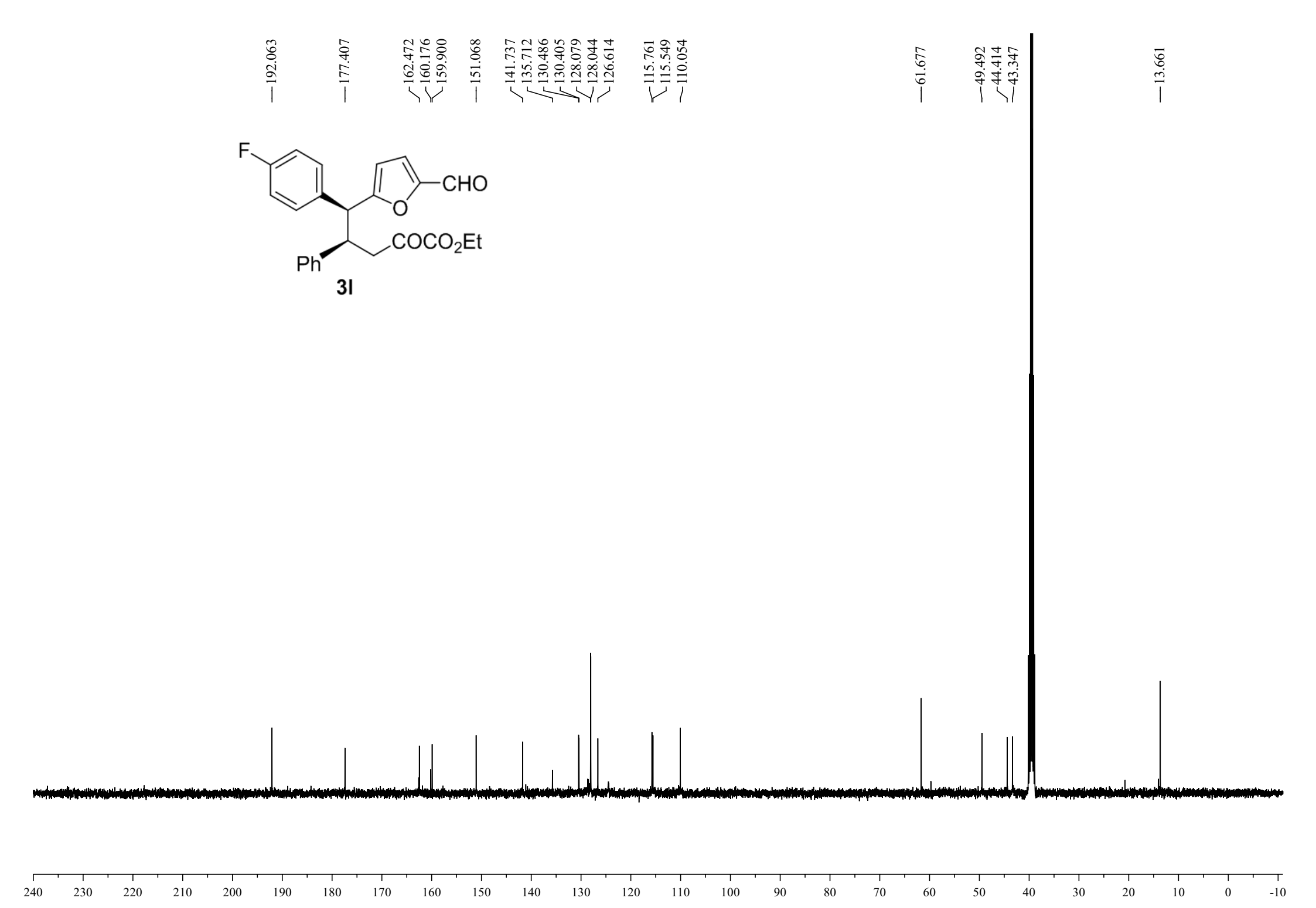
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Ph
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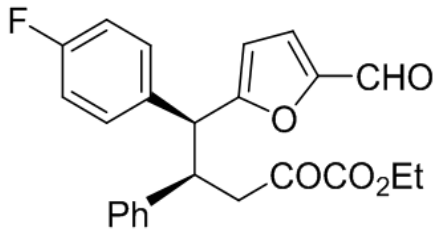
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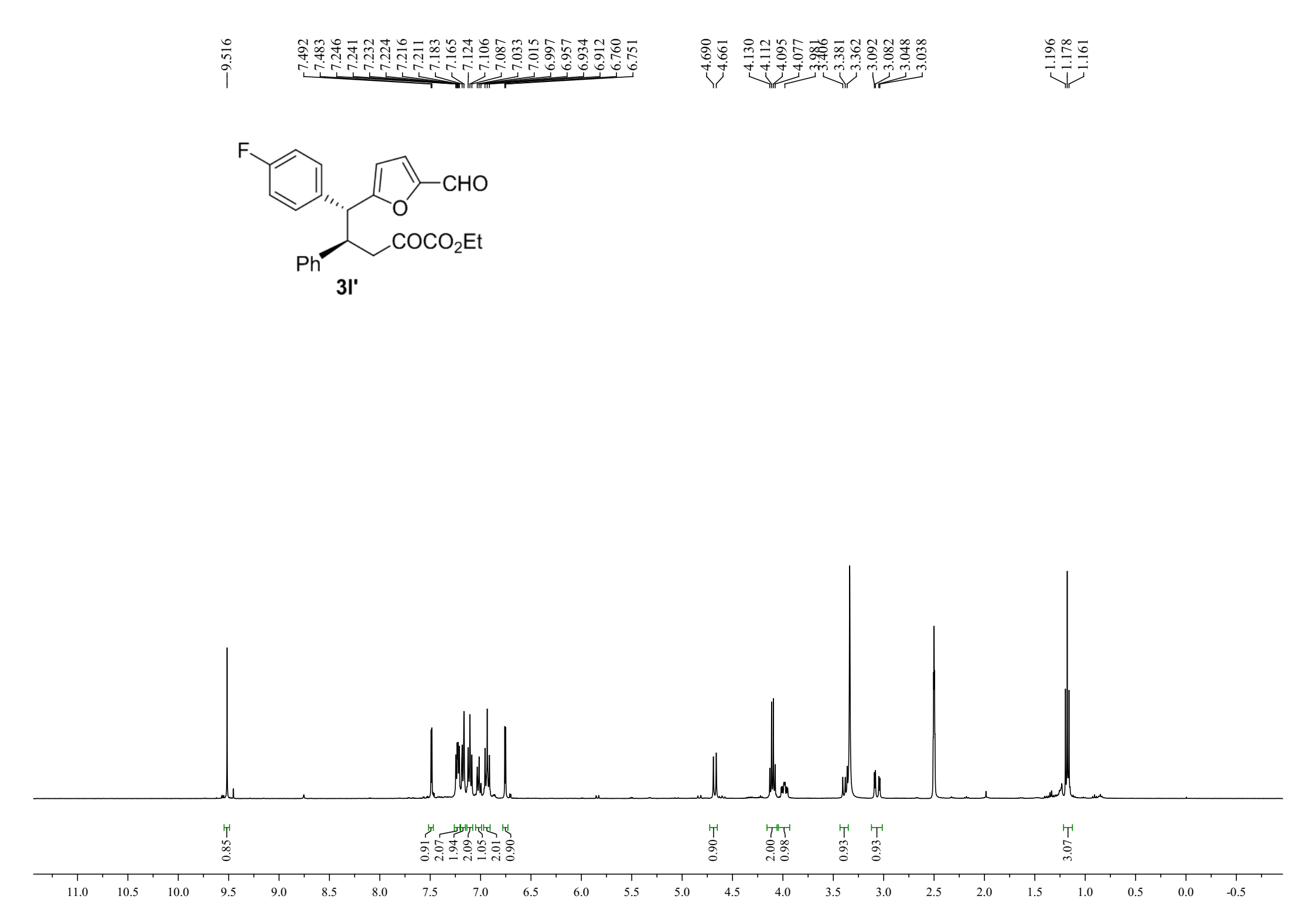
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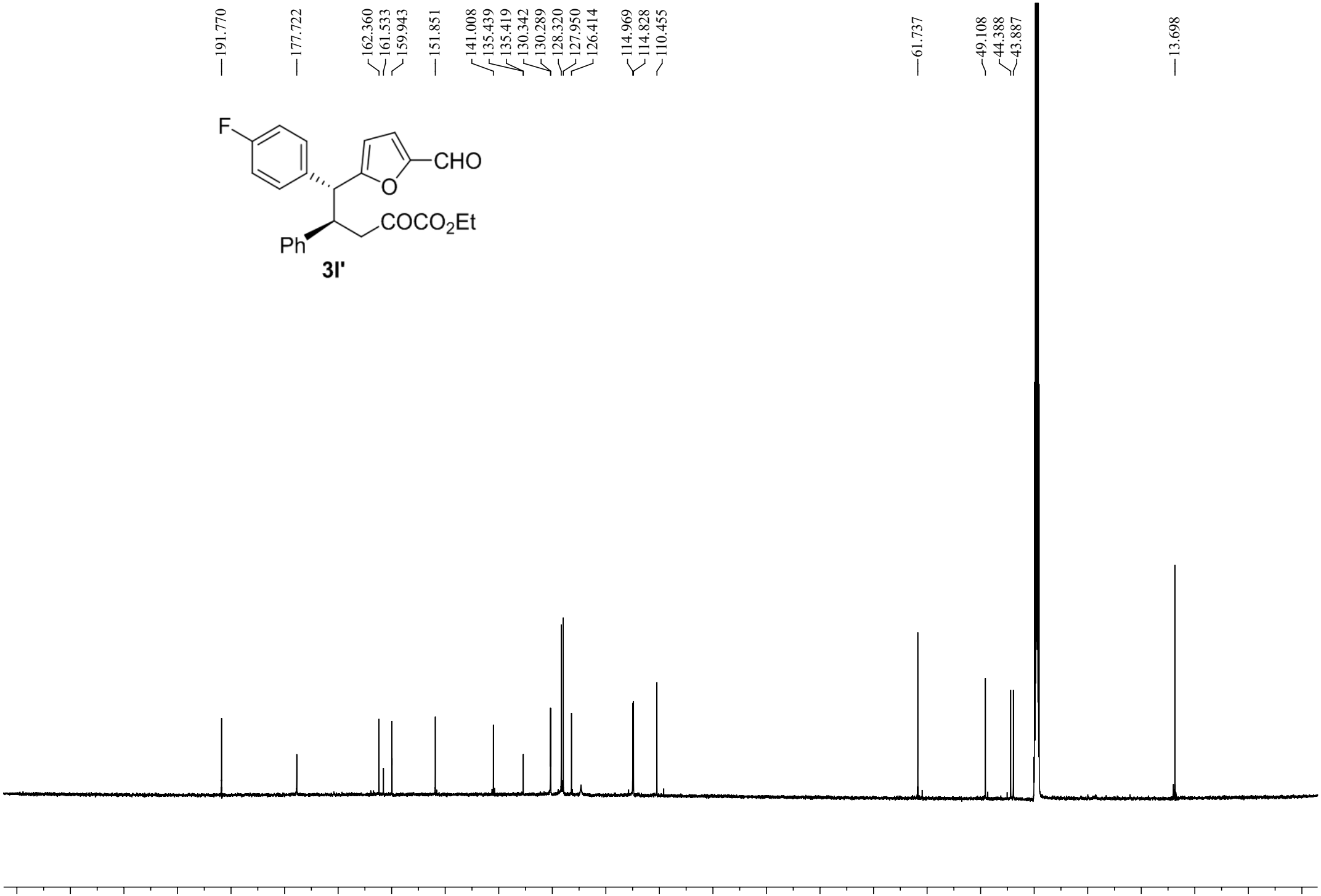
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COCO2Et
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3l'
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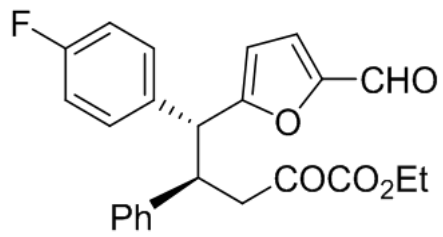
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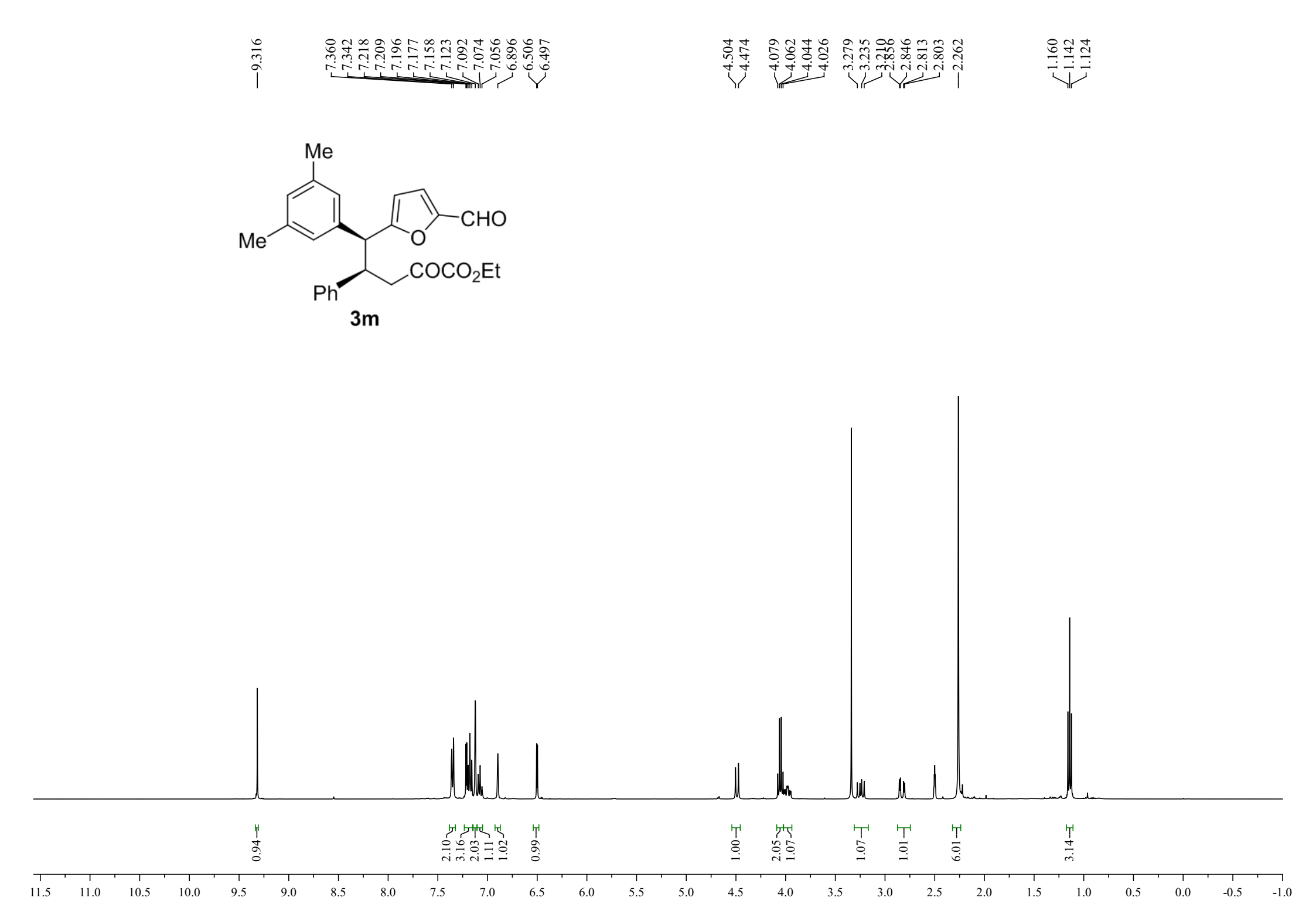
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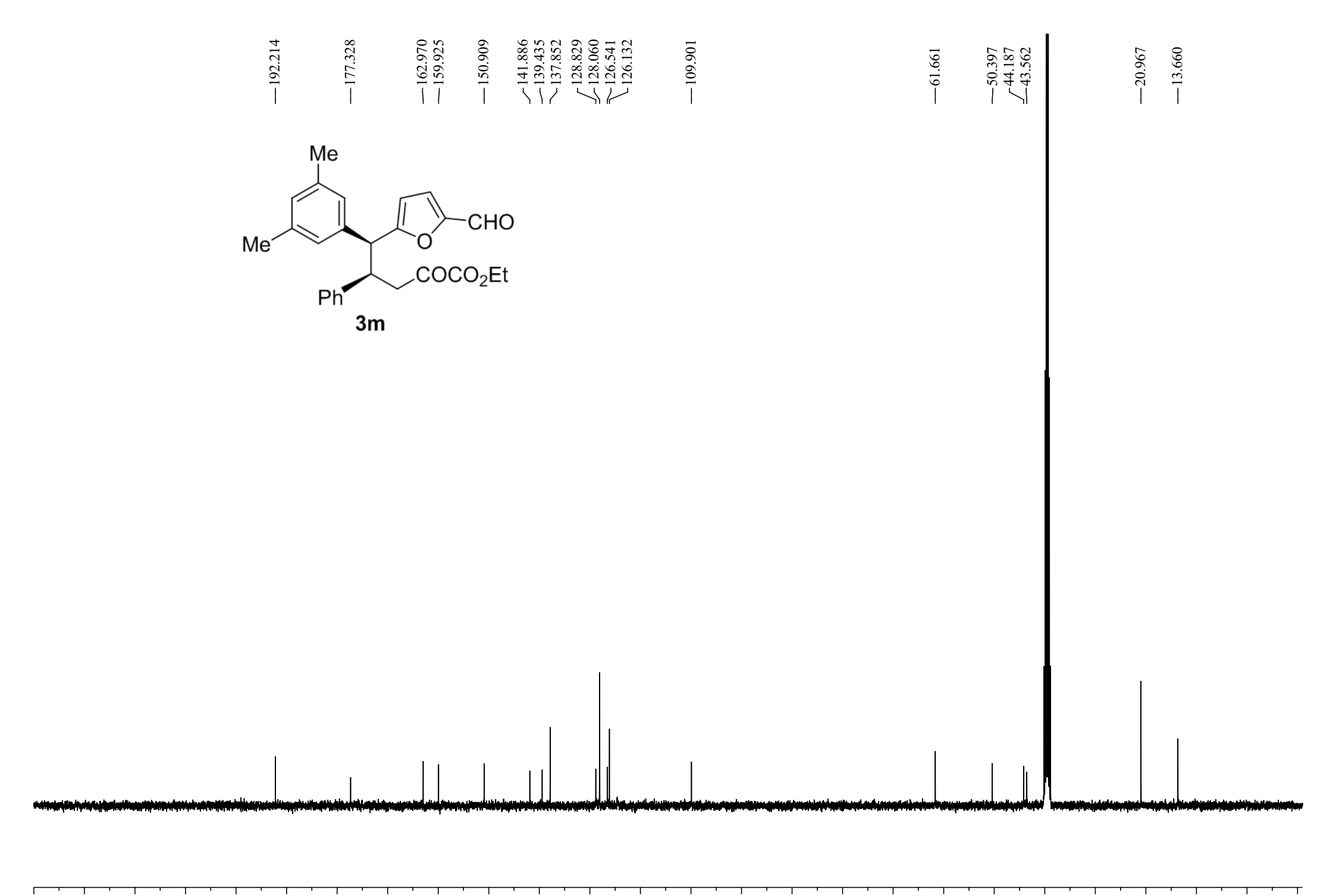
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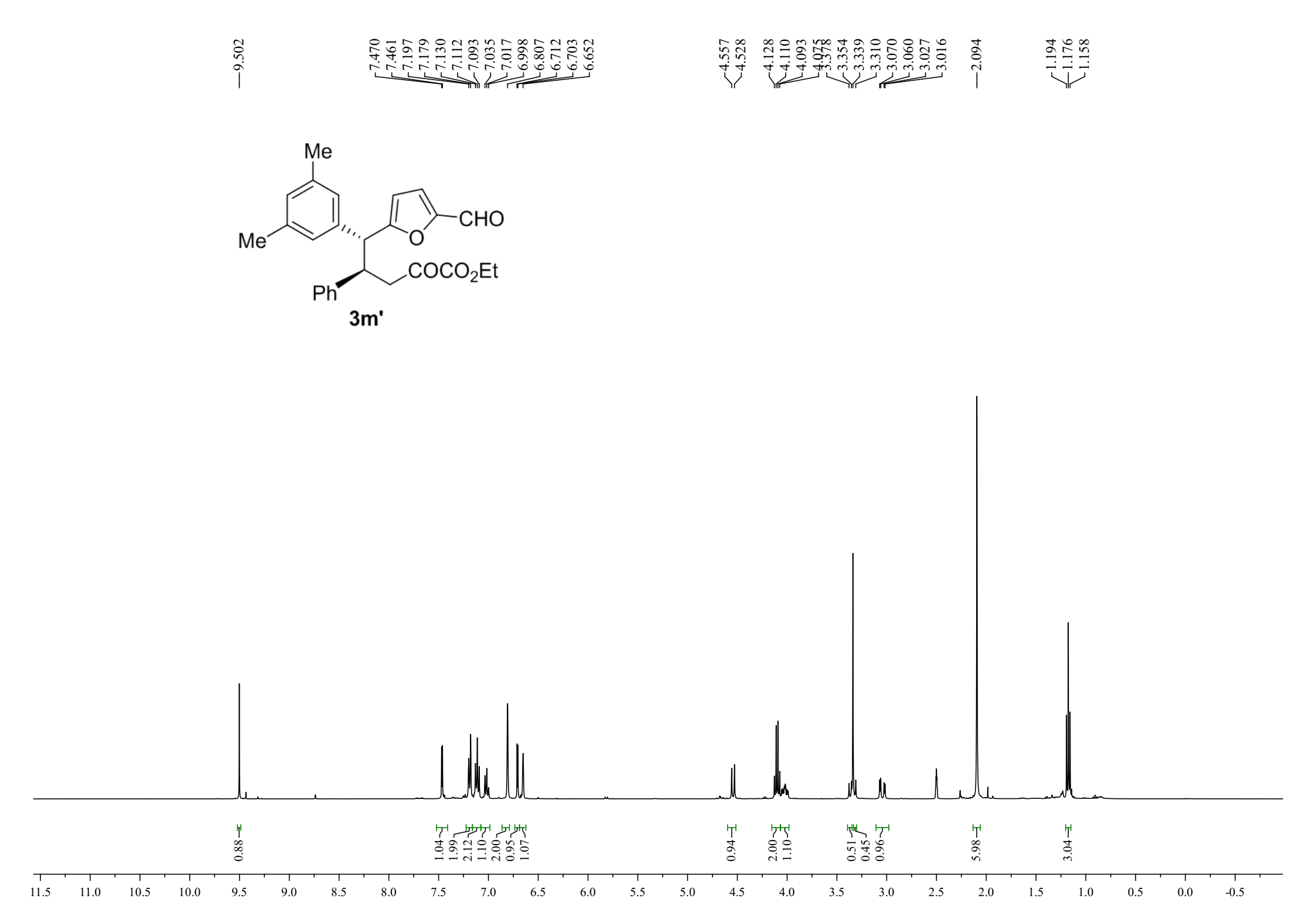
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Me
CHO
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Ph
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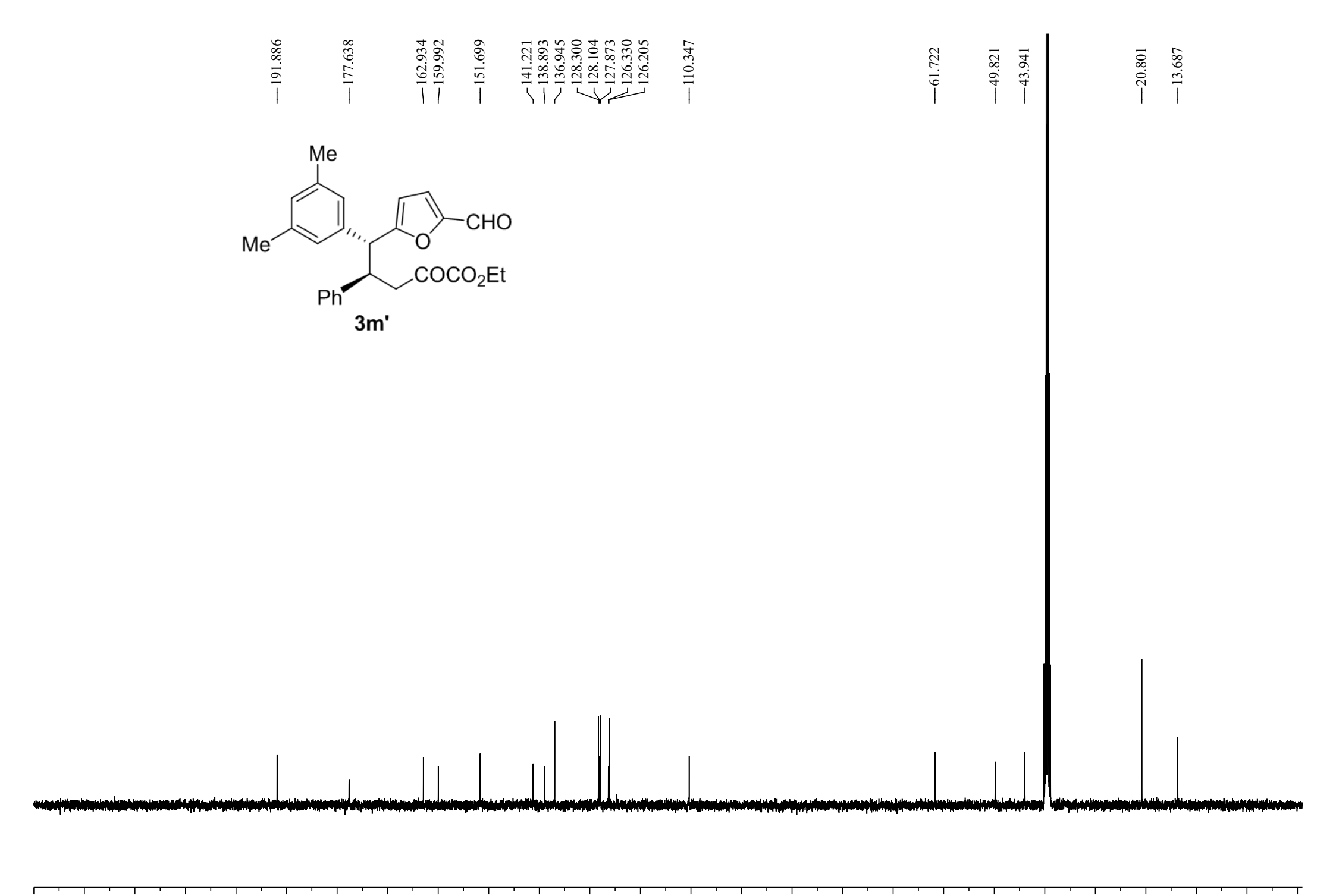
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Me
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COCO2Et
Ph
3m'
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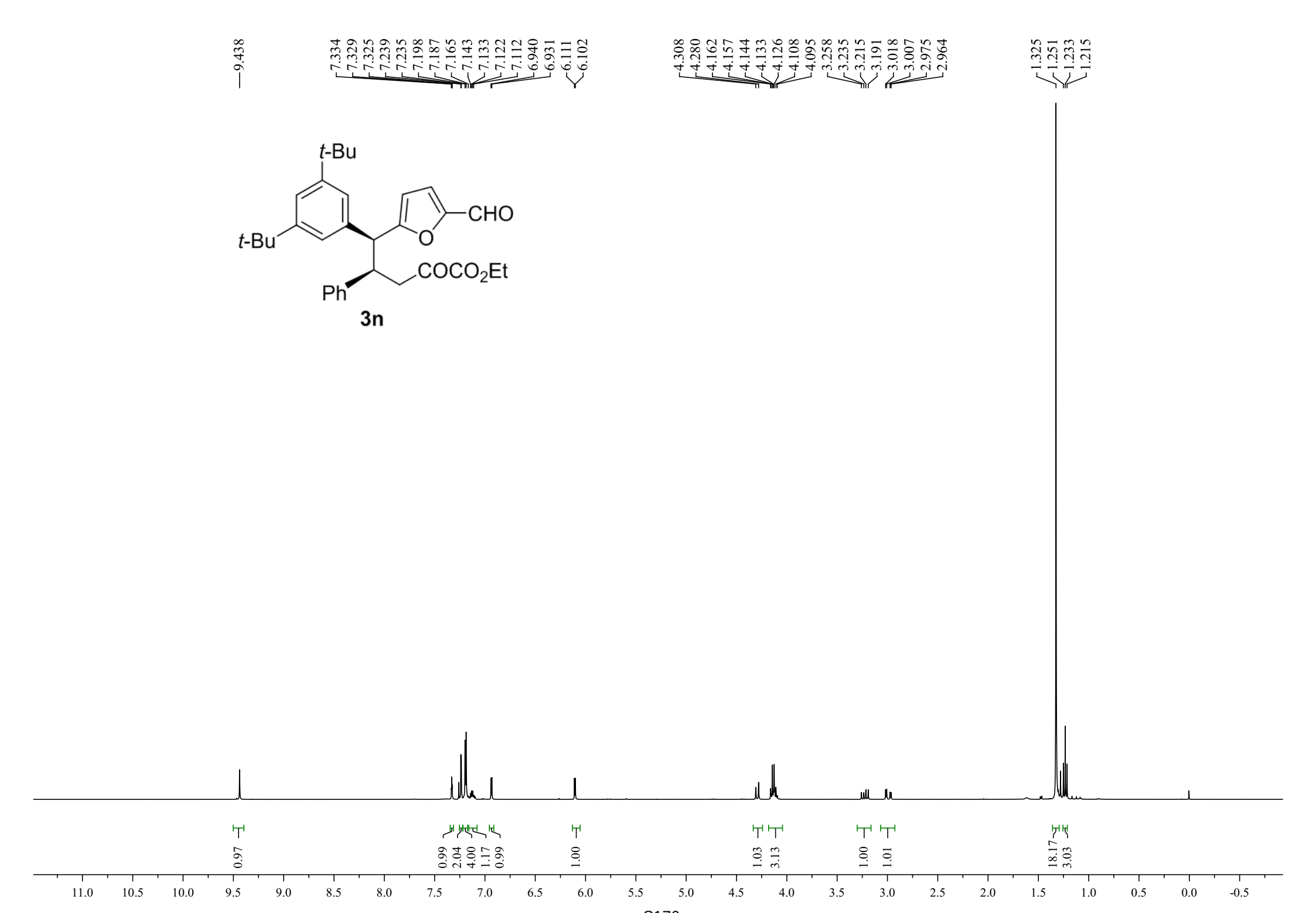
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t-Bu
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O
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Ph
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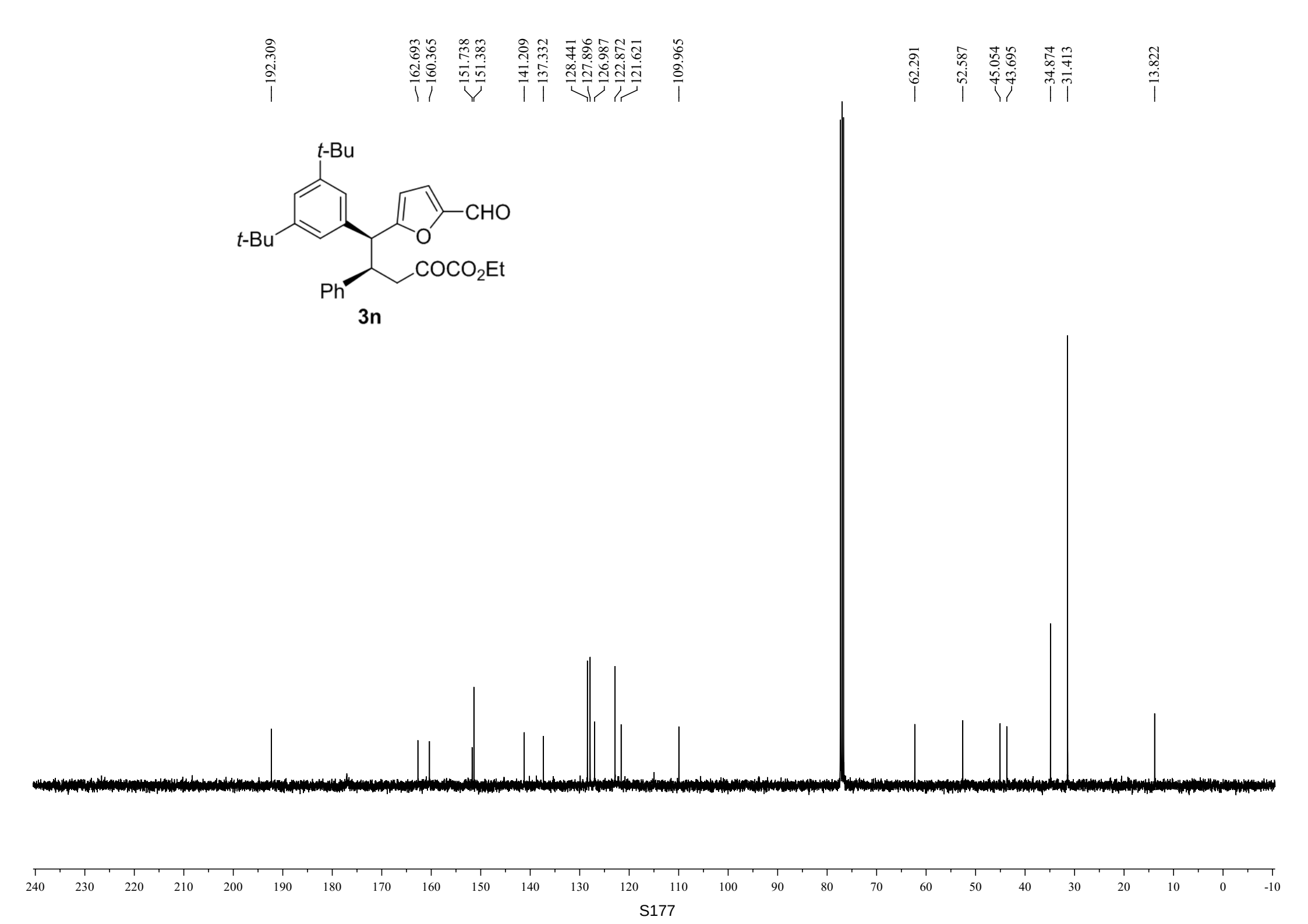
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t-Bu
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O
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Ph
3n
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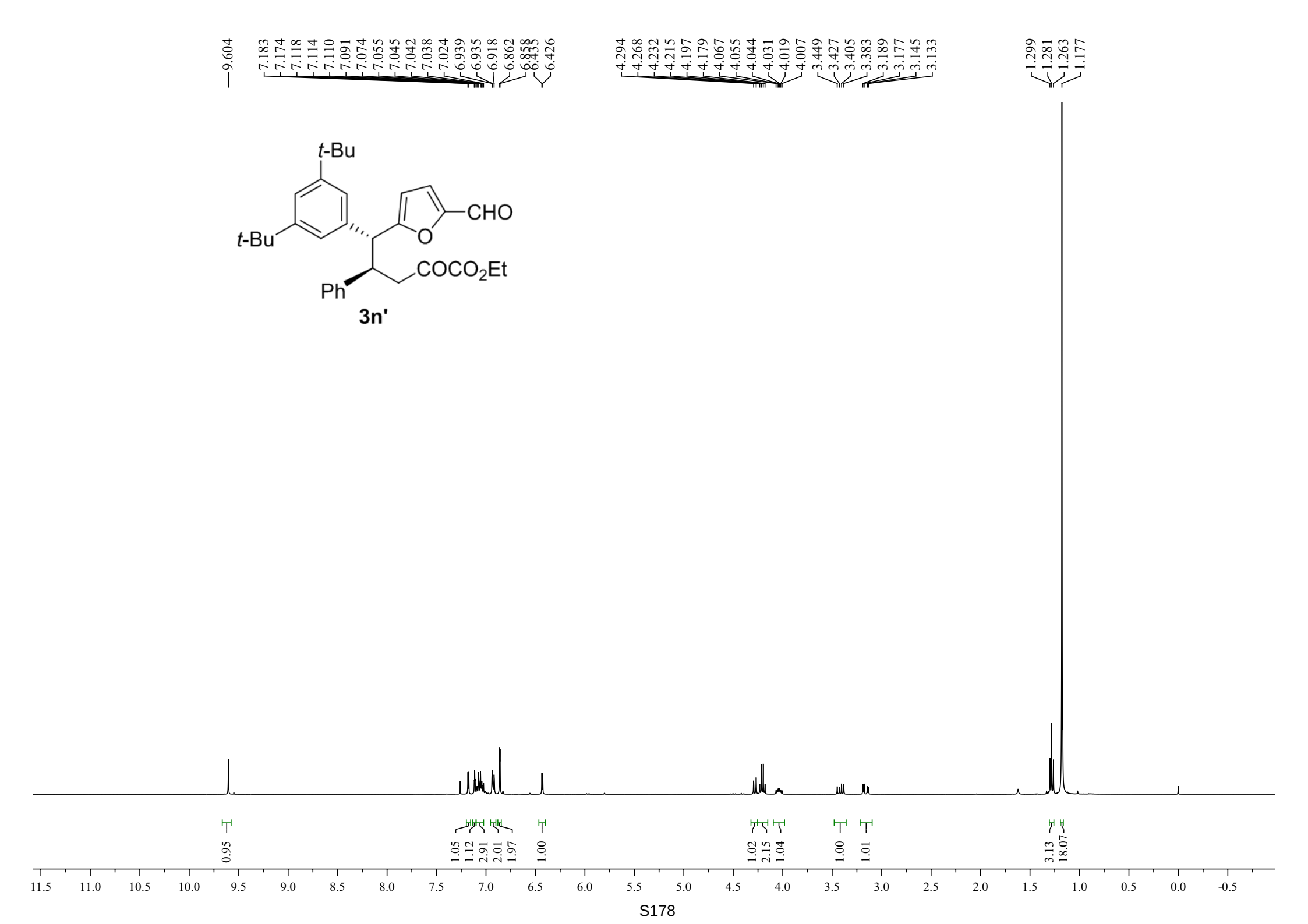
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Ph
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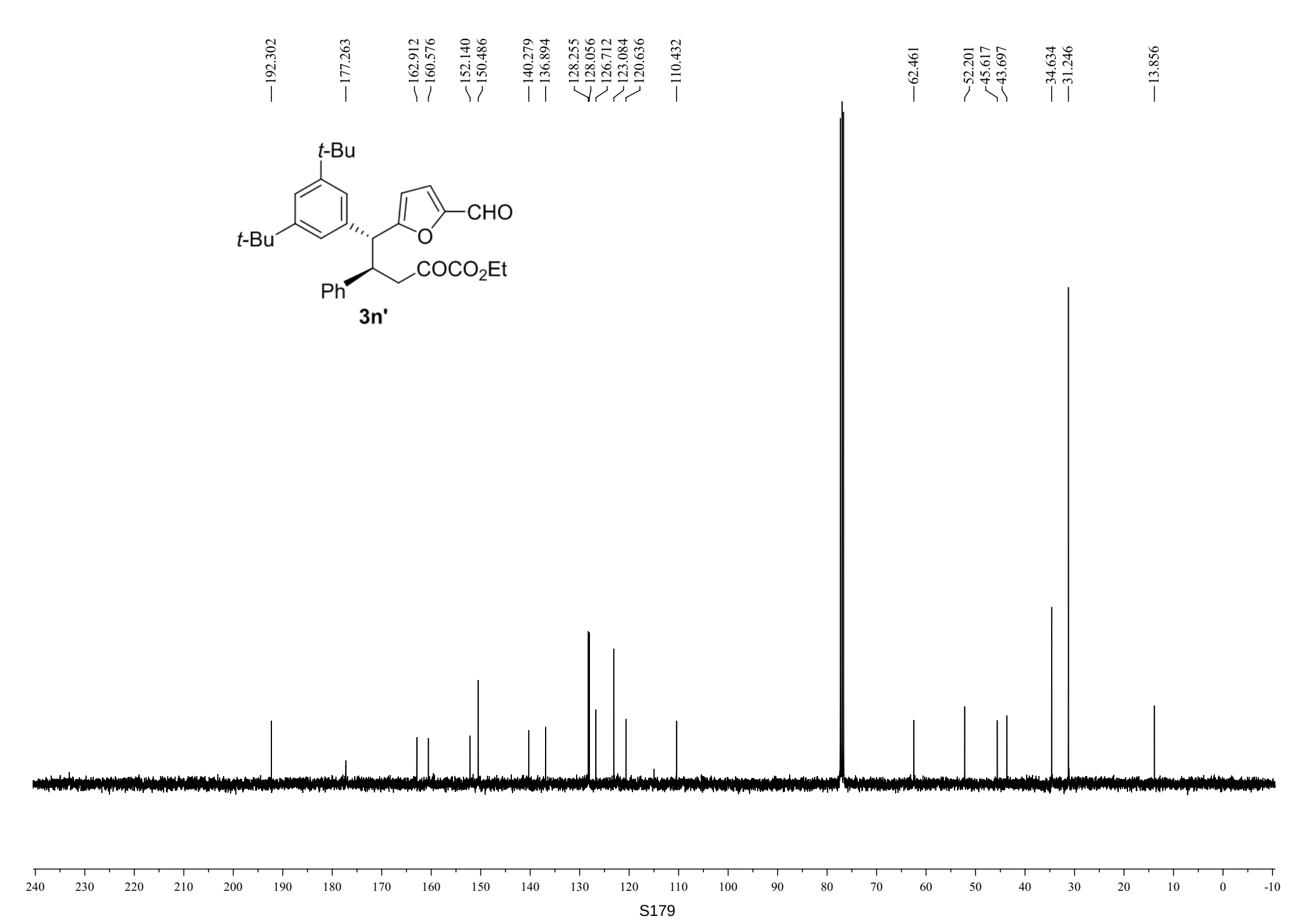
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t-Bu
t-Bu
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COCO2Et
Ph
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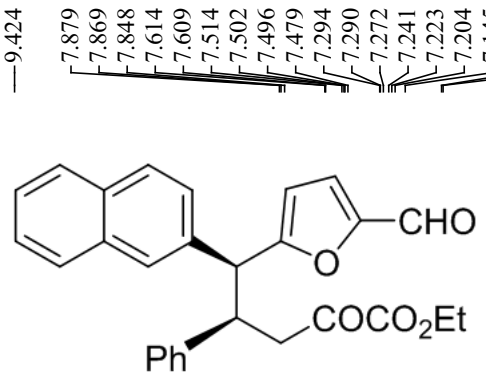

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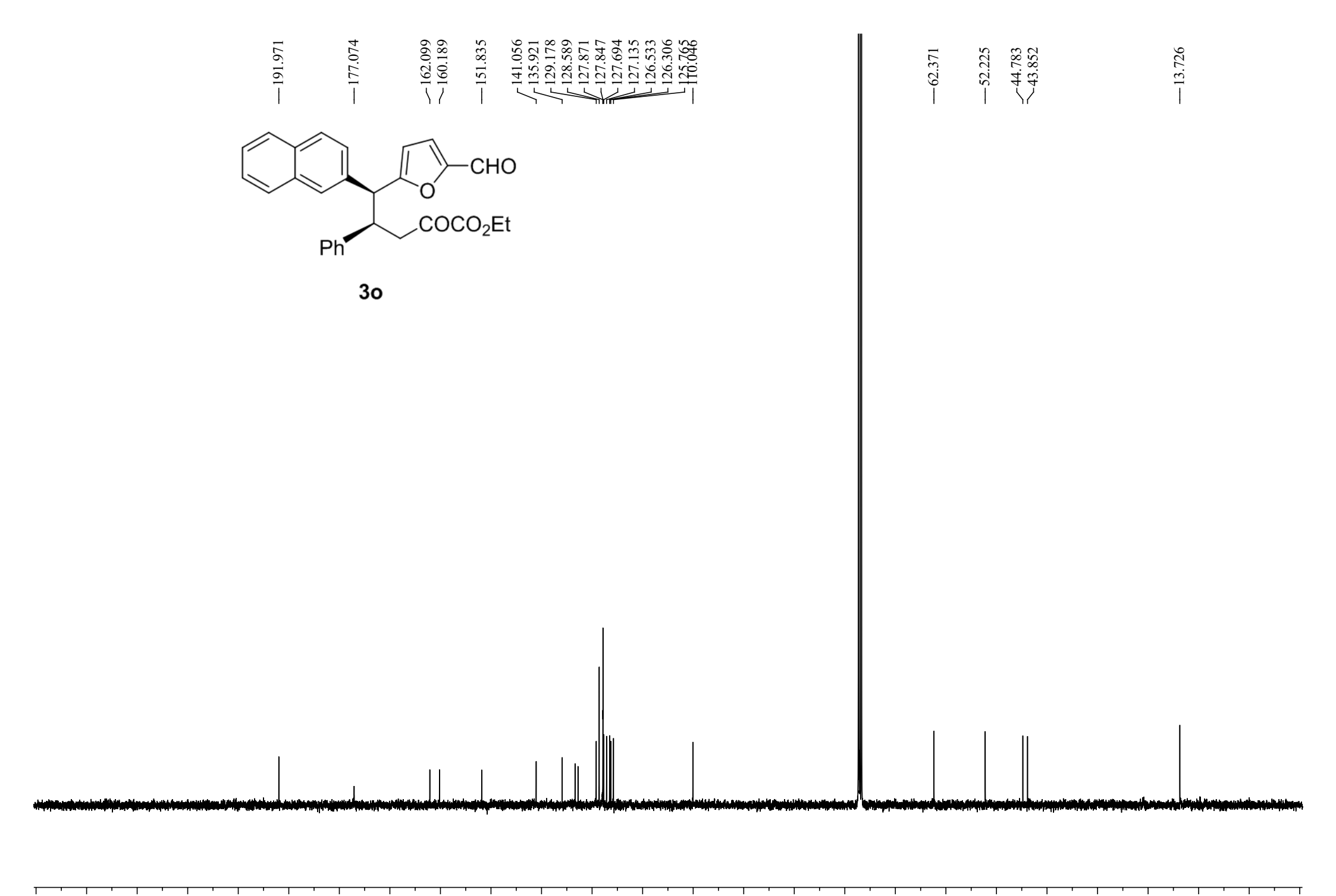
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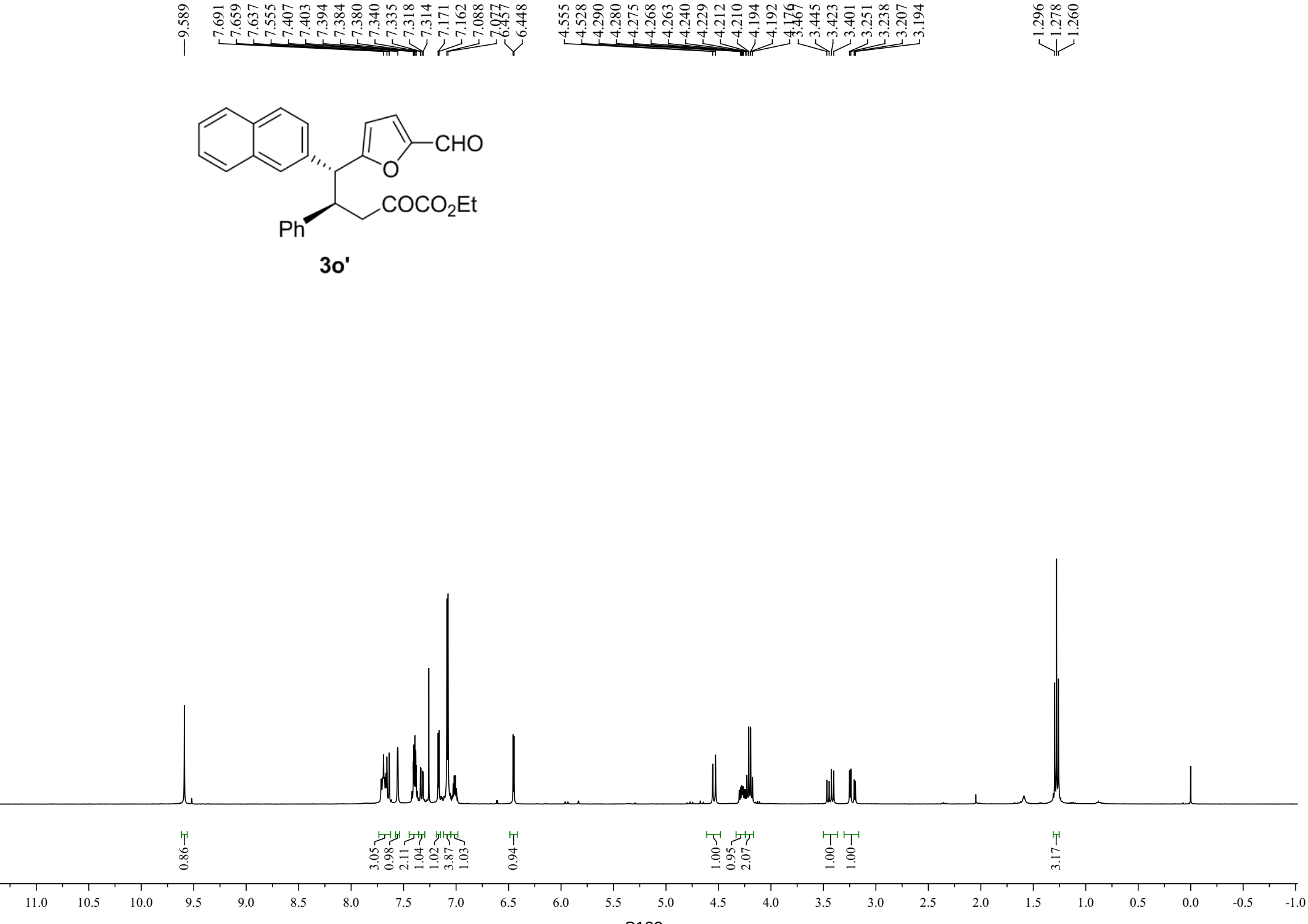
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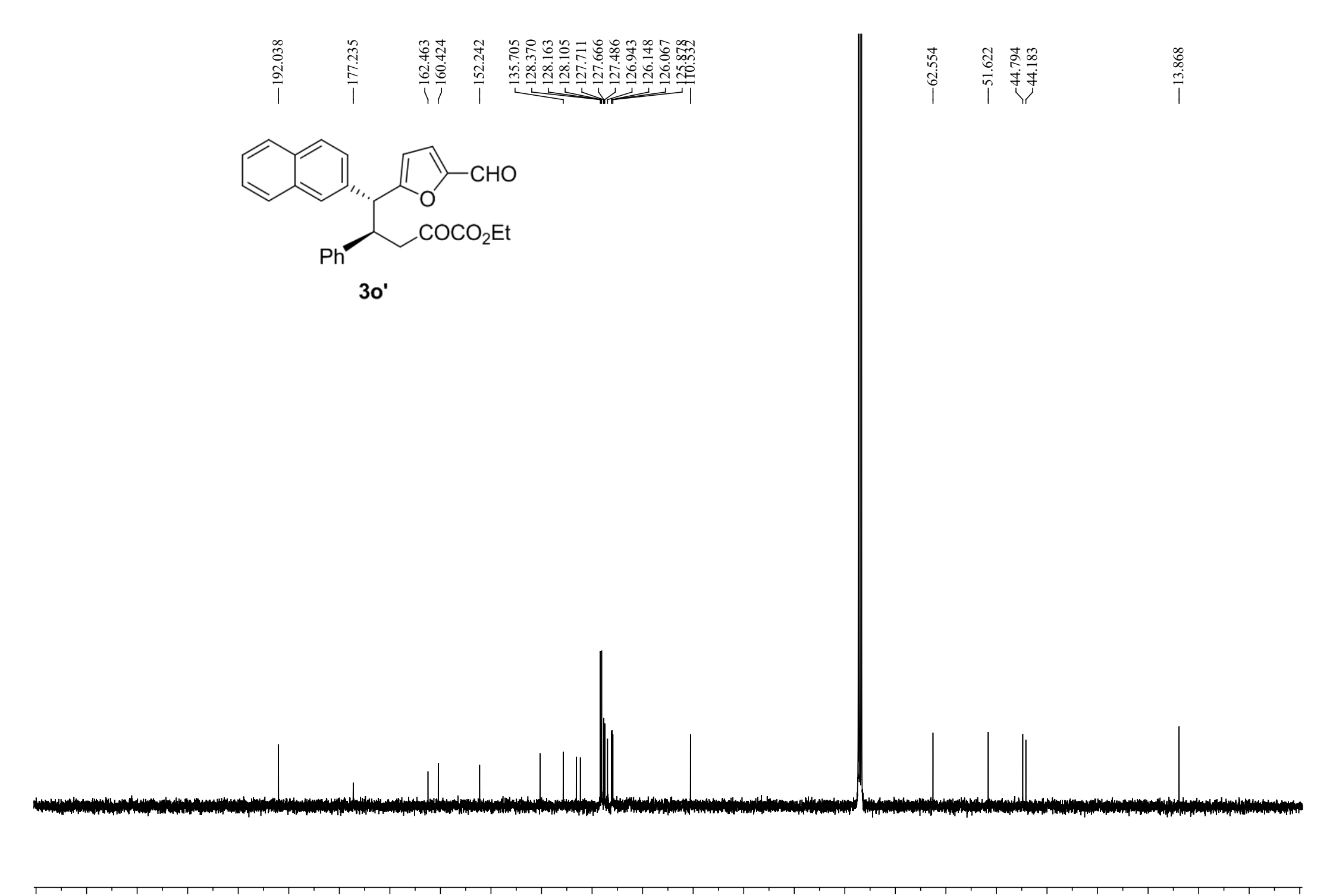
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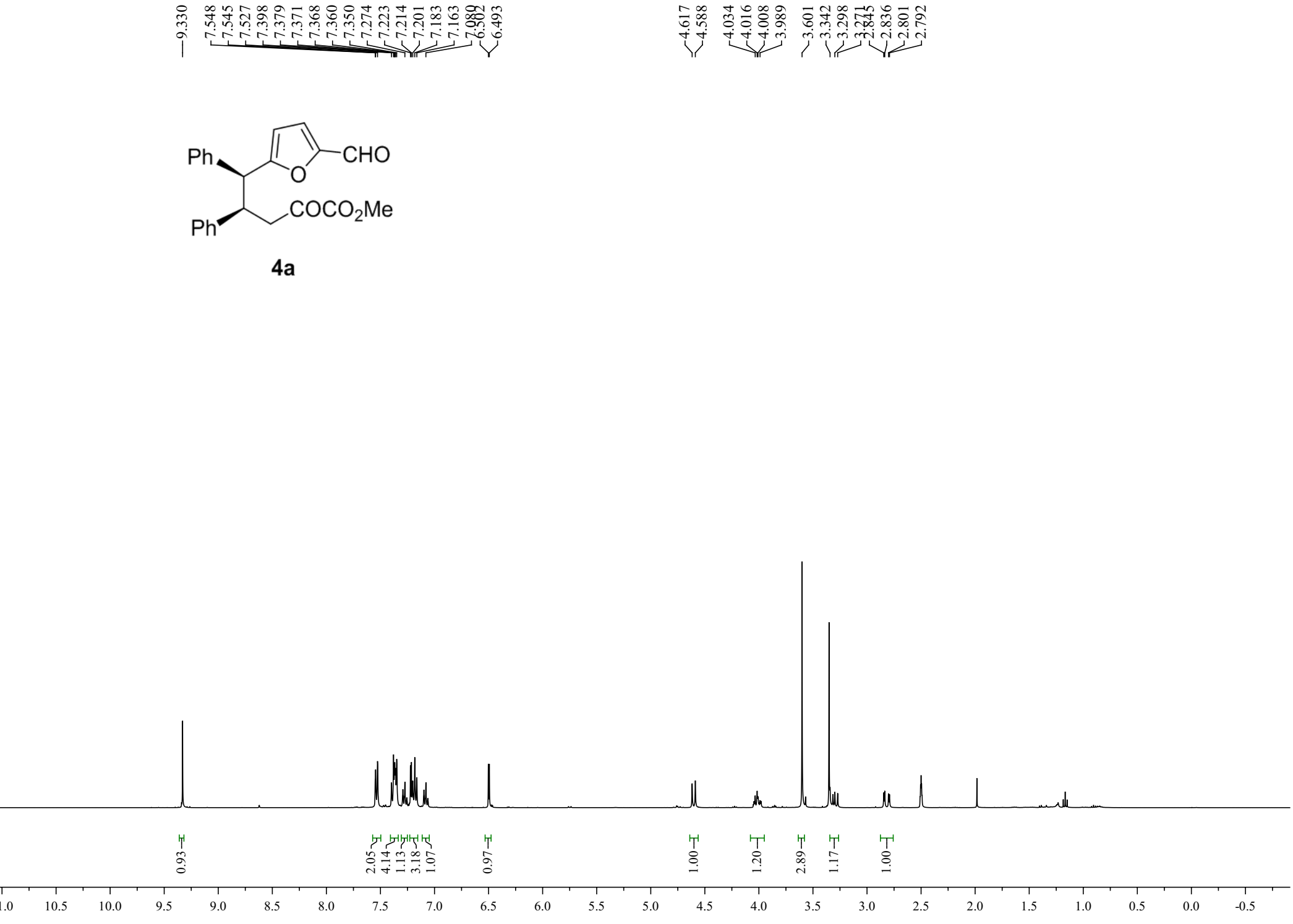
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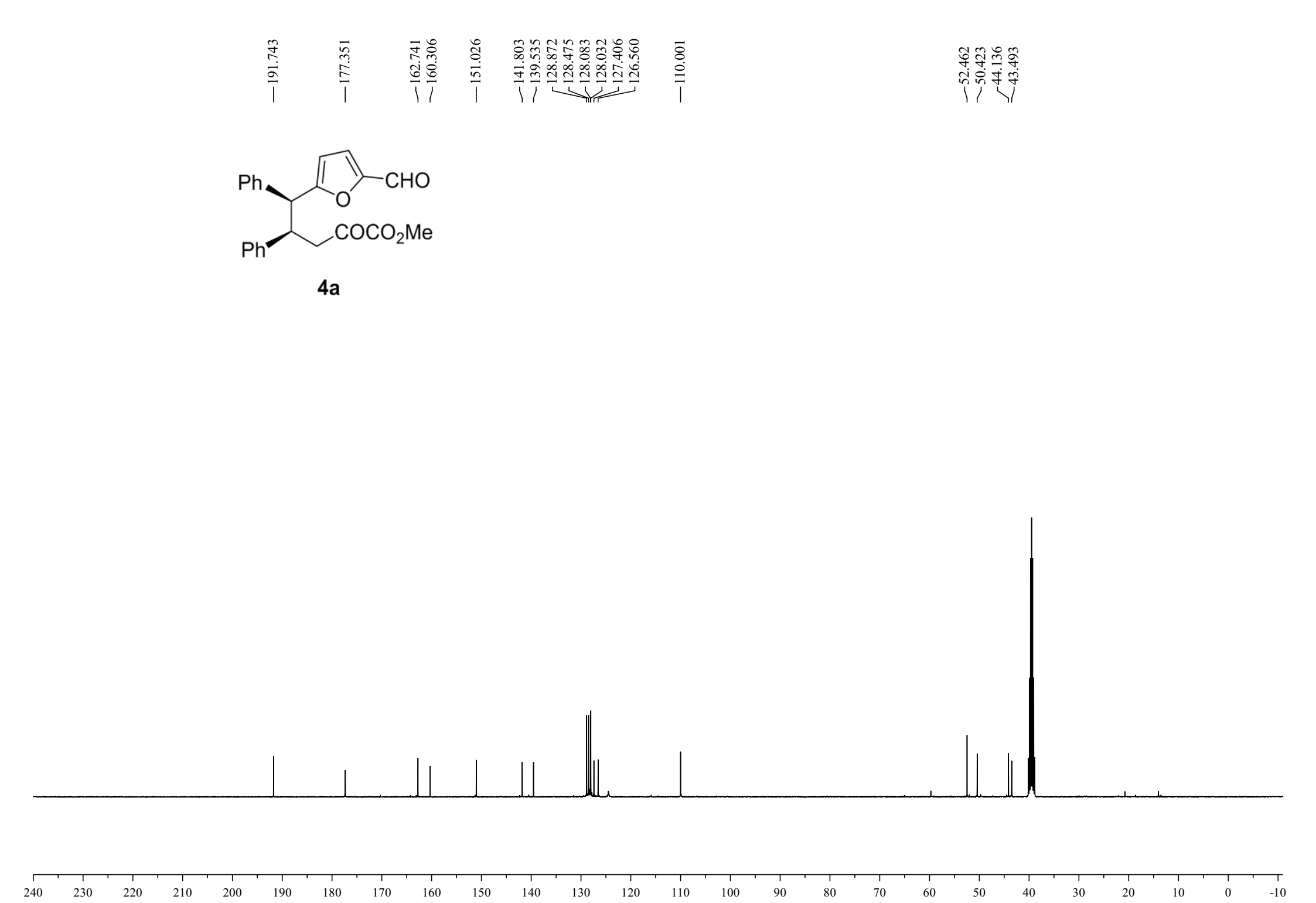
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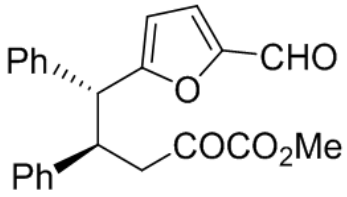
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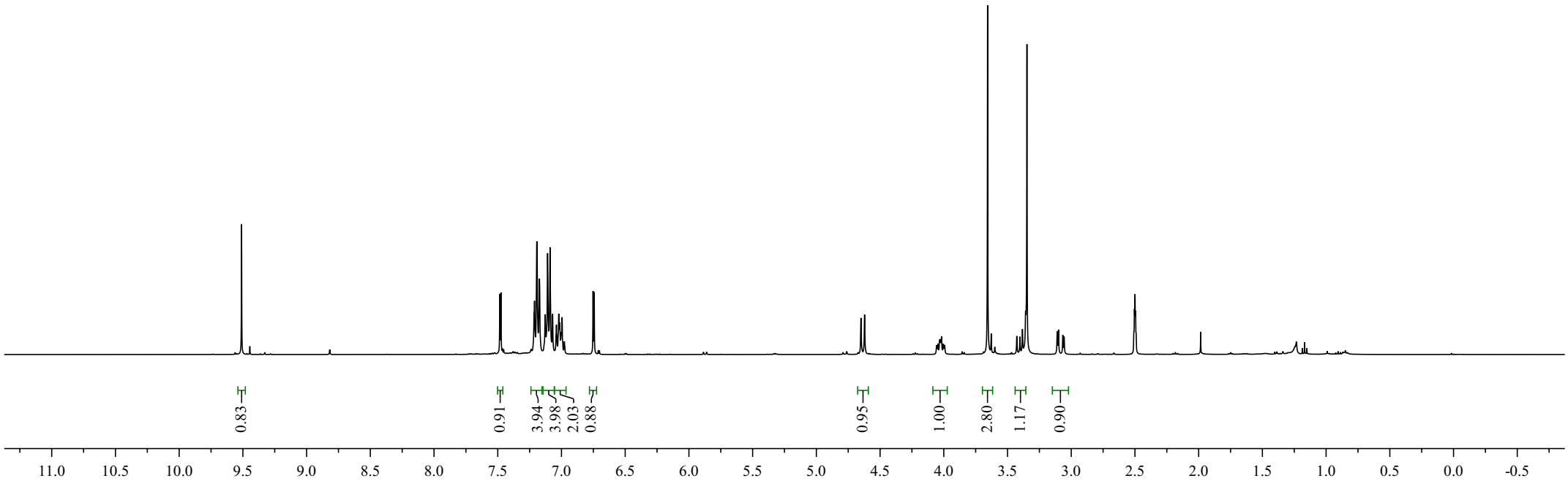
CHO
O
COCO2Me
Ph

4a'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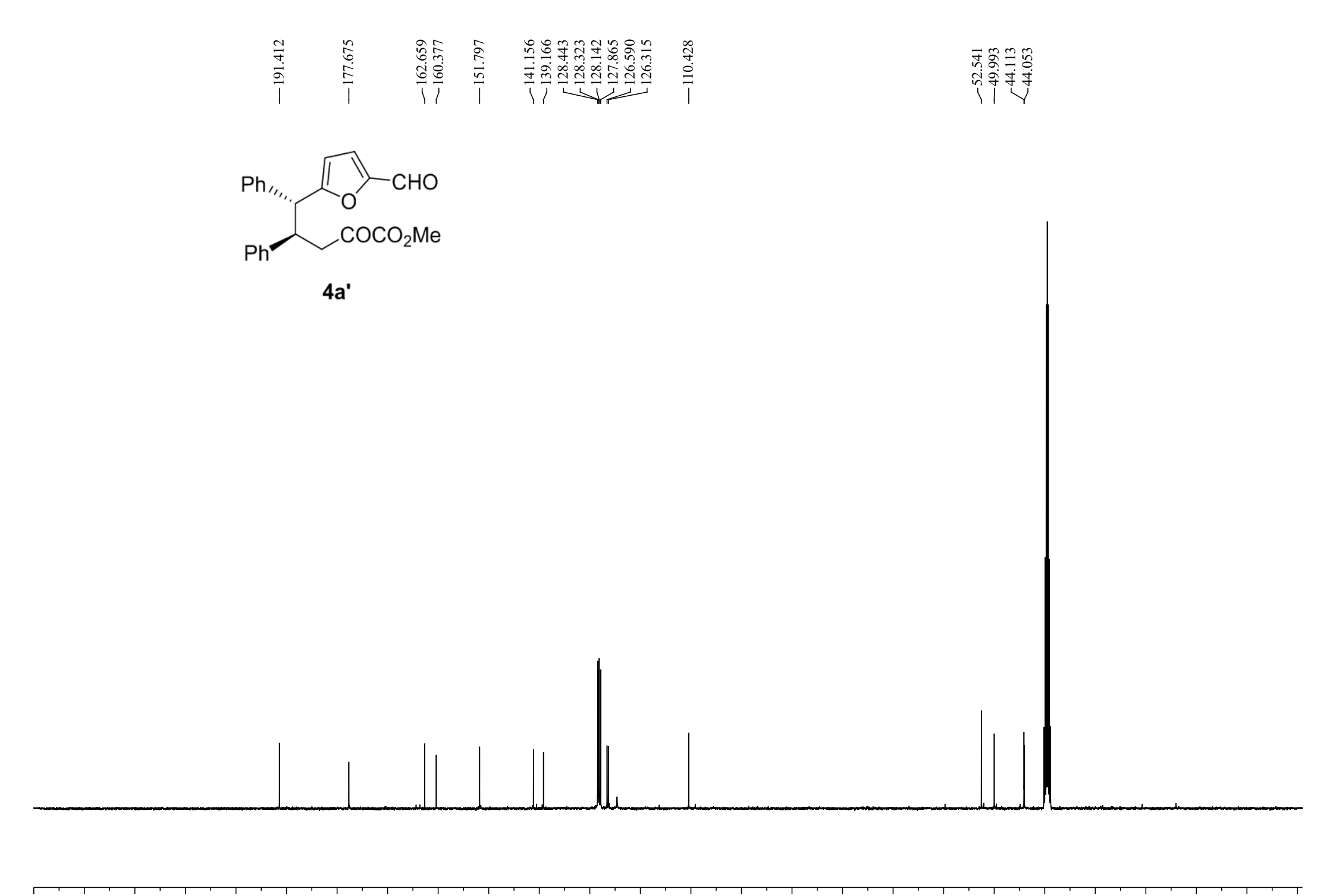
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126.315
110.428
52.541
49.993
44.113
44.053
Ph
O
CHO
COCO2Me
Ph
4a'
240
230
220
210
200
190
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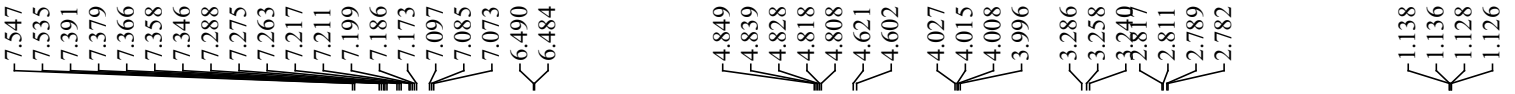
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4.808
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4.027
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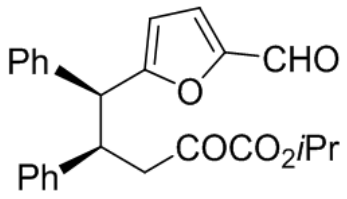
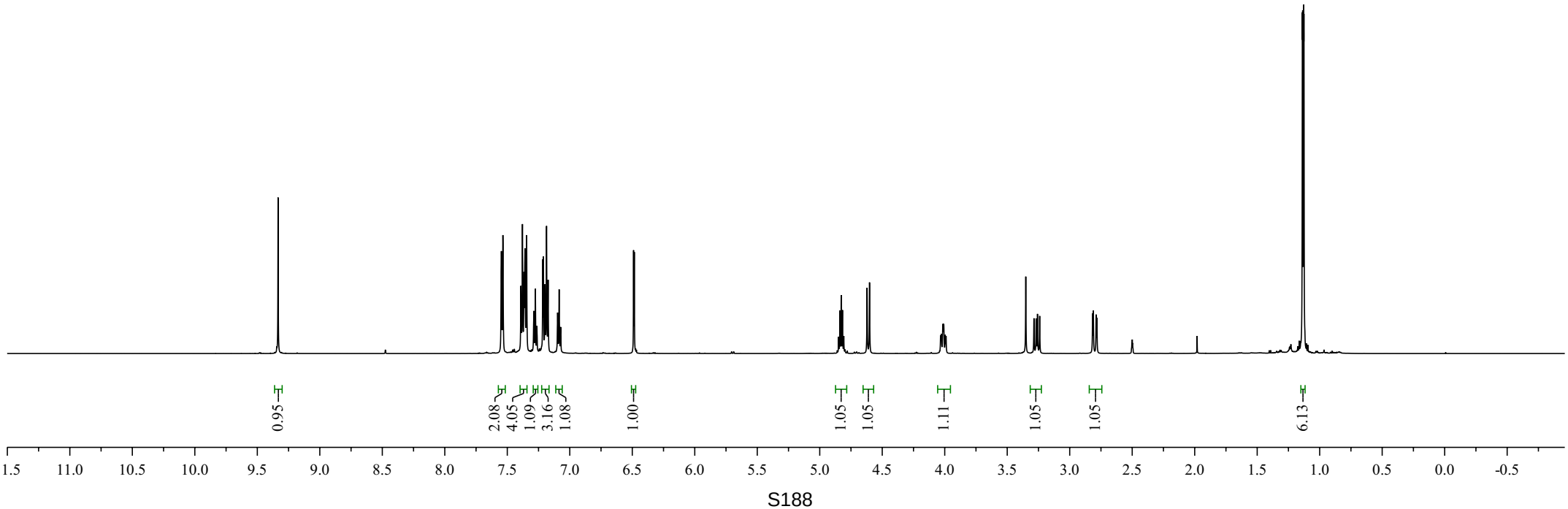

Ph
CHO
O
COCO2iPr
Ph

4b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11.5
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10.0
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8.5
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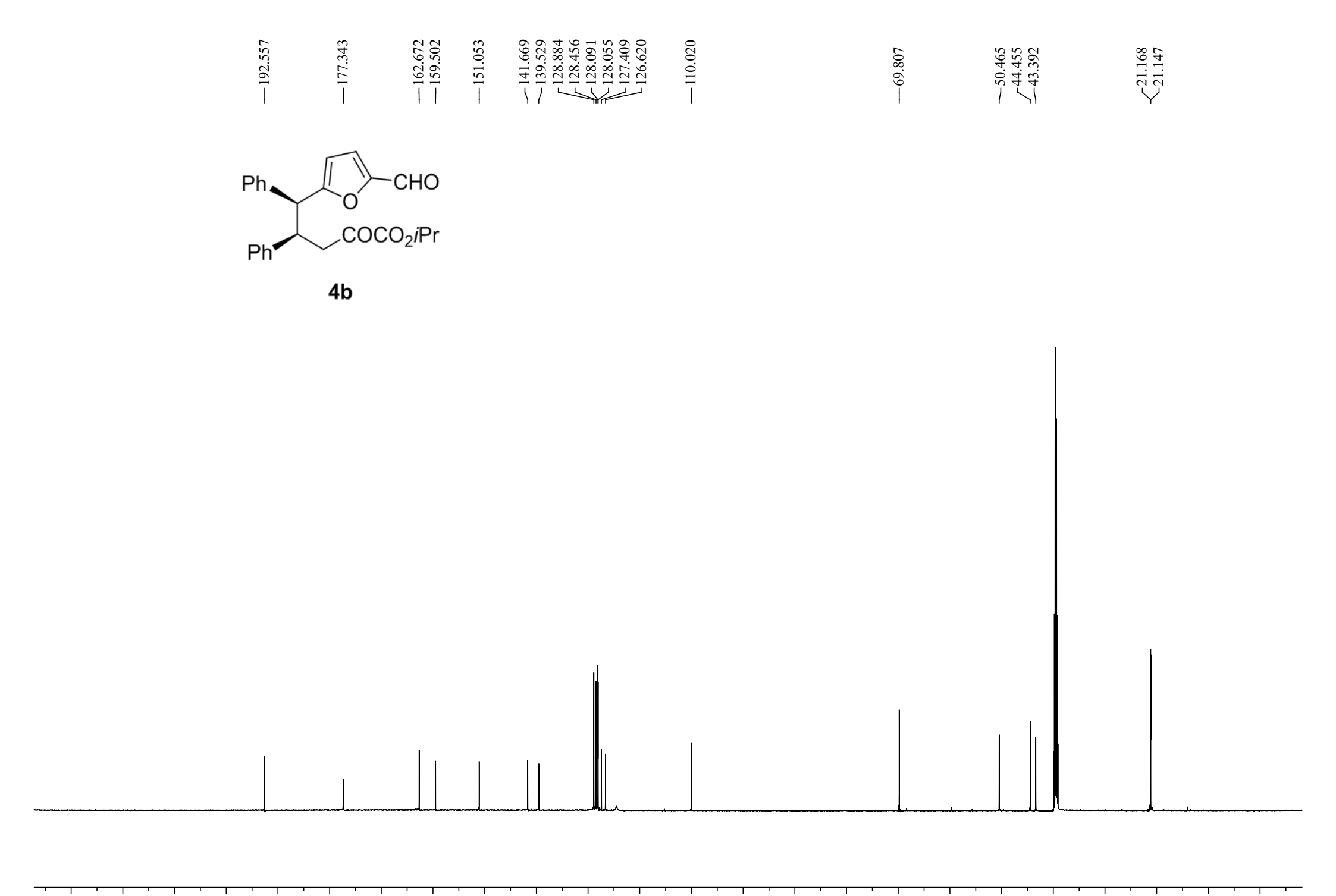
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127.409
126.620
110.020
69.807
50.465
44.455
43.392
21.168
21.147
Ph
O
CHO
COCO2iPr
Ph
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

4b


9.518
7.483
7.477
7.217
7.205
7.184
7.172
7.124
7.111
7.106
7.098
7.093
7.081
7.035
7.023
7.013
7.001
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6.756
6.750
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4.892
4.882
4.871
4.861
4.659
4.640
4.032
4.025
4.014
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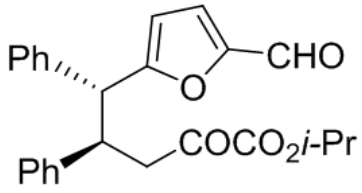
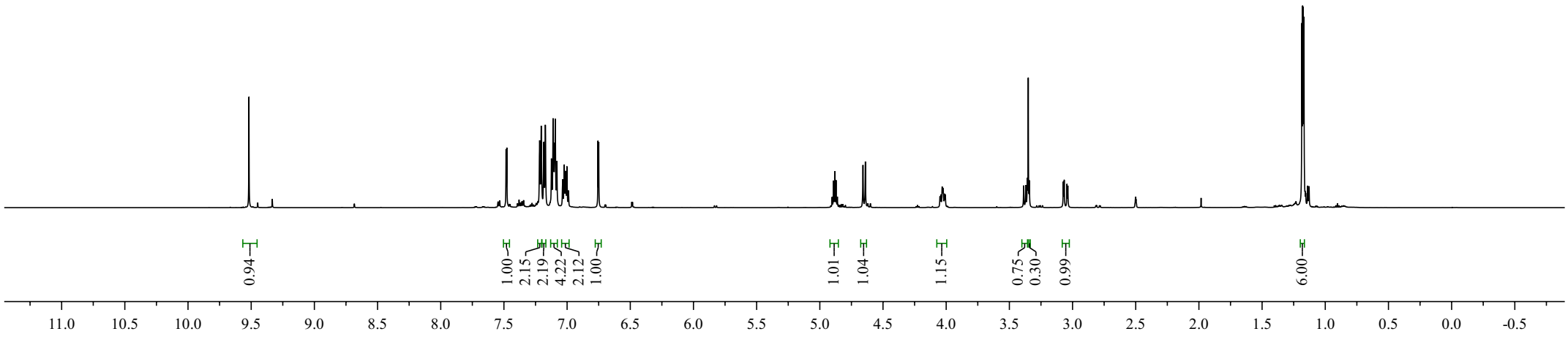
1.175
1.169


Ph
CHO
O
COCO2i-Pr
Ph

4b'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6.00
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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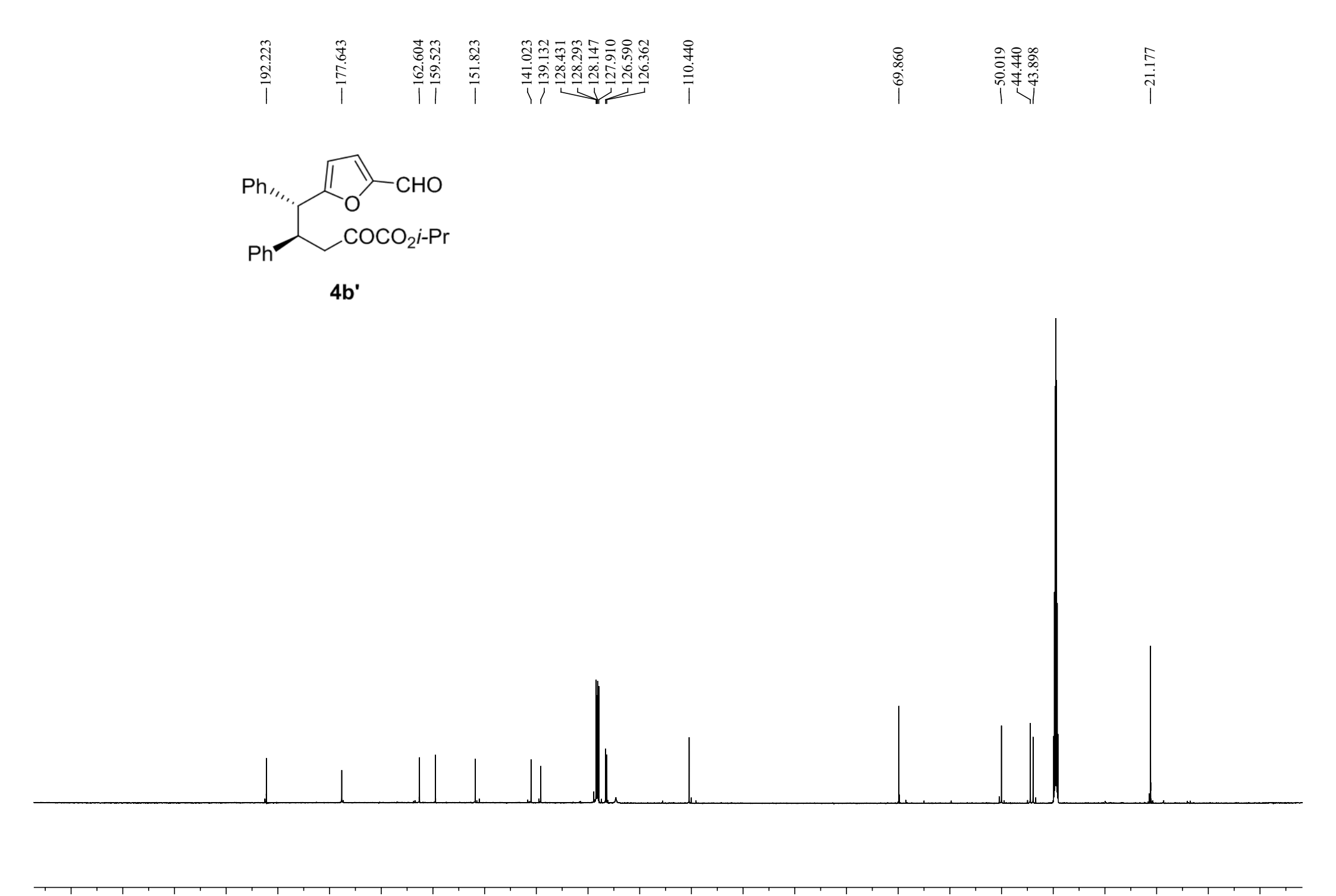
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126.362
110.440
69.860
50.019
44.440
43.898
21.177
Ph
O
CHO
COCO2i-Pr
Ph
4b'
230
220
210
200
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150
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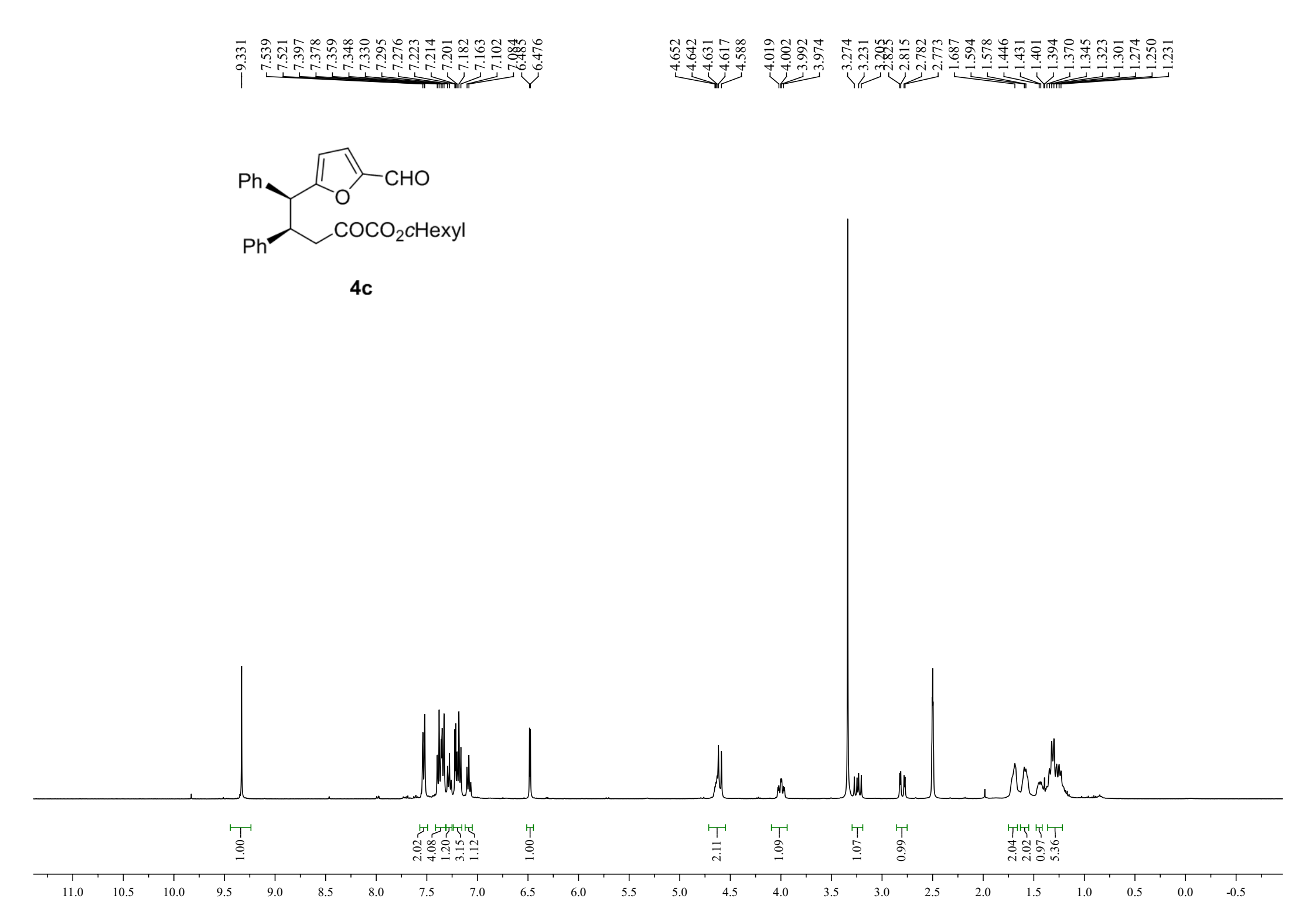
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7.163
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7.084
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6.476
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3.195
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1.446
1.431
1.401
1.394
1.370
1.345
1.323
1.301
1.274
1.250
1.231
Ph
O
CHO
COCO2cHexyl
Ph
4c
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4.08
1.20
3.15
1.12
1.00
2.11
1.09
1.07
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2.04
2.02
0.97
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8.0
7.5
7.0
6.5
6.0
5.5
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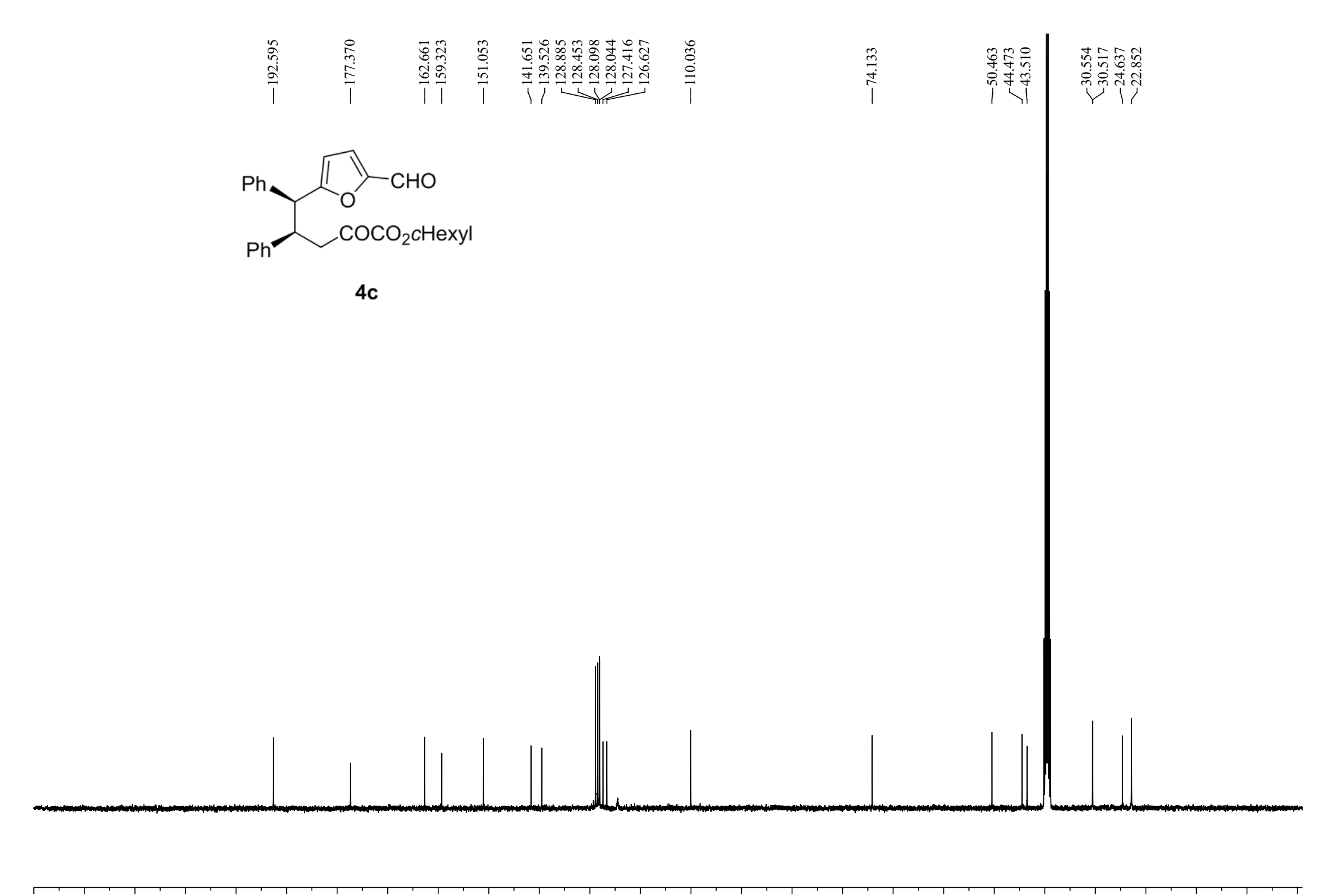
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74.133
50.463
44.473
43.510
30.554
30.517
24.637
22.852
Ph
O
CHO
COCO2cHexyl
Ph
240
230
220
210
200
190
180
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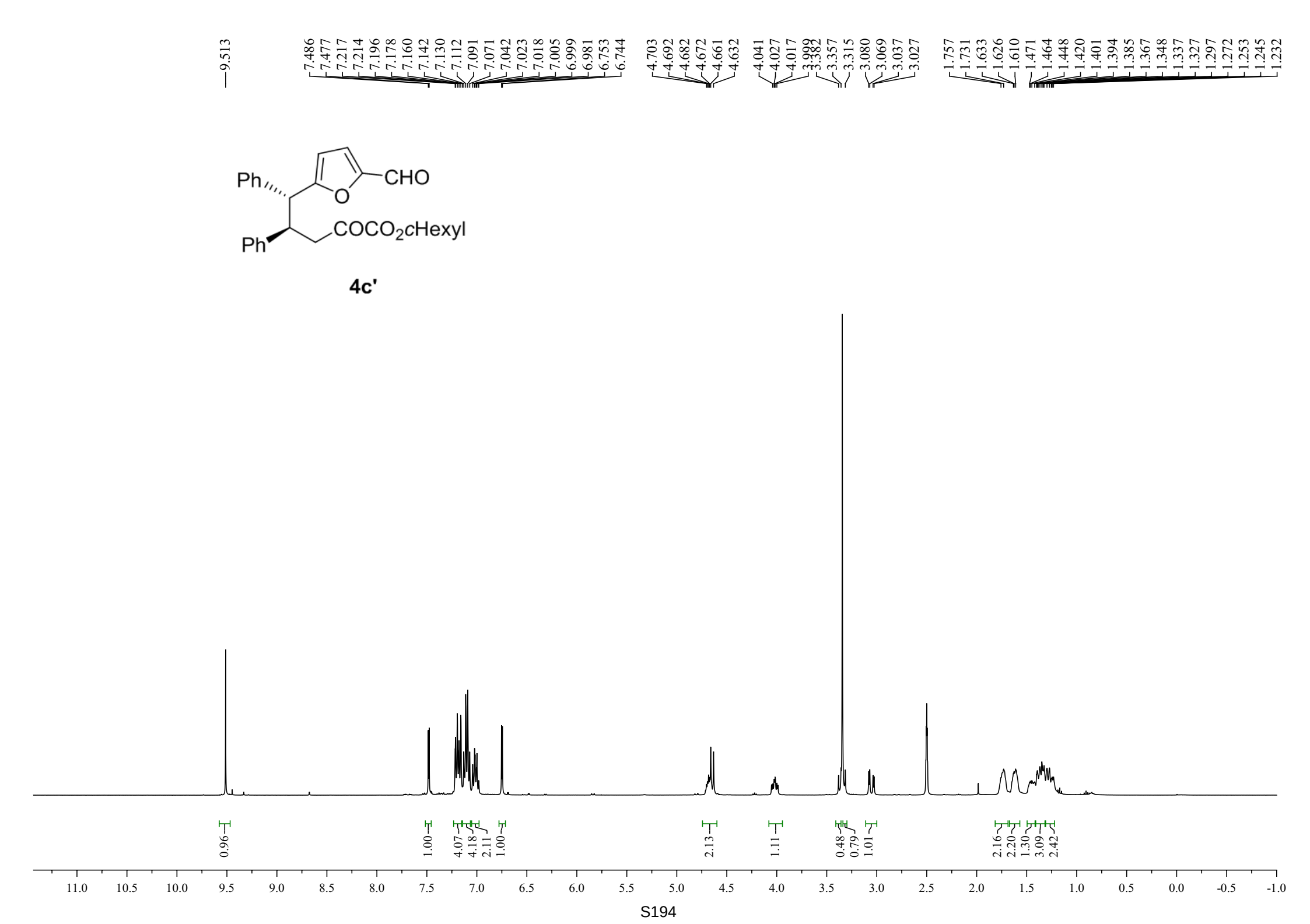
-10

4c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7.160
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7.071
7.042
7.023
7.018
7.005
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6.753
6.744
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3.357
3.315
3.080
3.069
3.037
3.027
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1.731
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1.626
1.610
1.471
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1.420
1.401
1.394
1.385
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1.337
1.327
1.297
1.272
1.253
1.245
1.232
Ph
O
CHO
COCO2cHexyl
Ph
4c'
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4.07
4.18
2.11
1.00
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5.0
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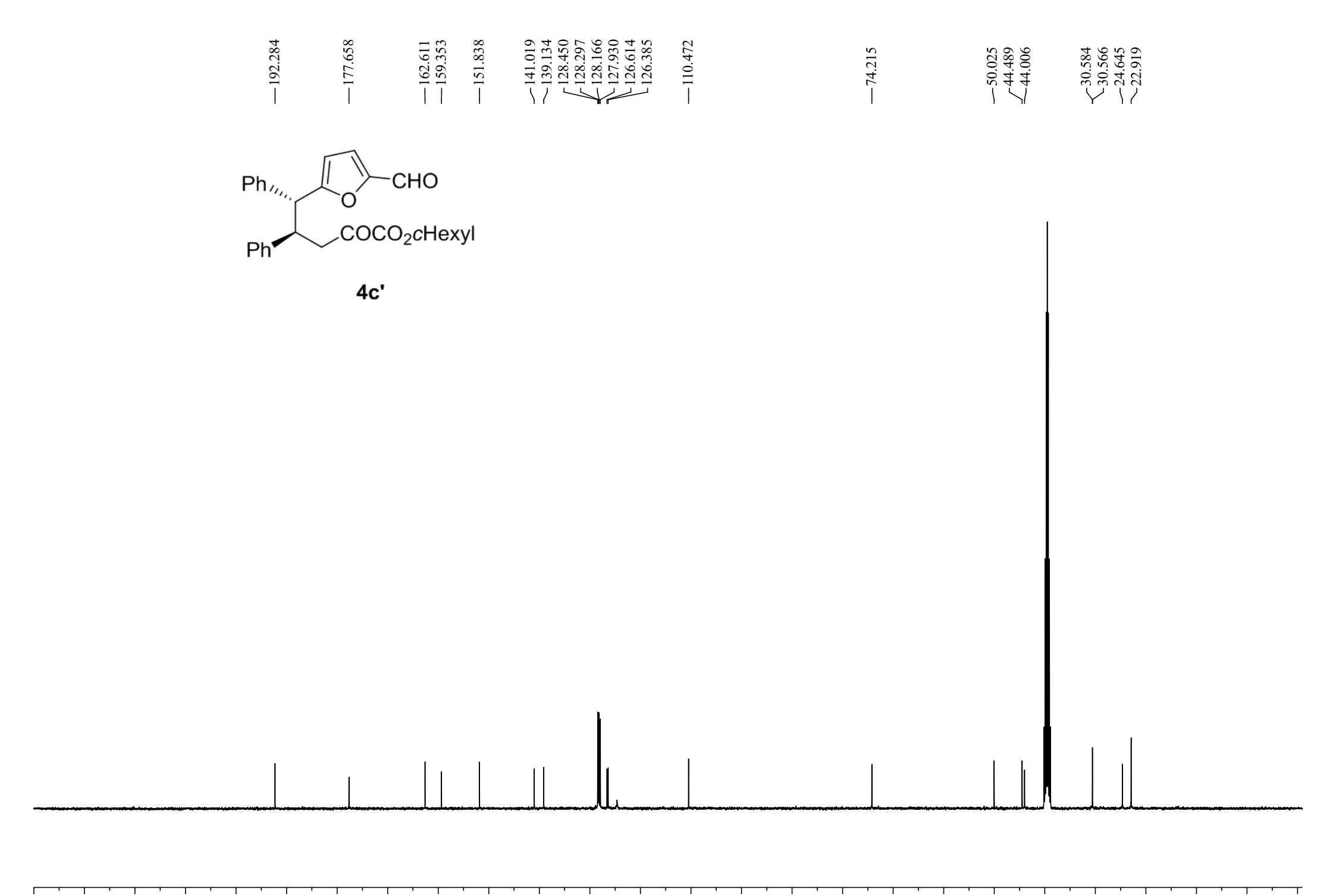
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74.215
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44.489
44.006
30.584
30.566
24.645
22.919
Ph
O
CHO
COCO2cHexyl
Ph
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

4c'


9.331
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7.327
7.308
7.258
7.220
7.211
7.188
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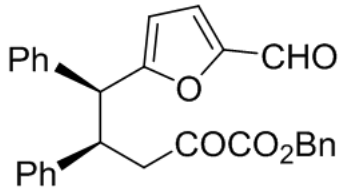
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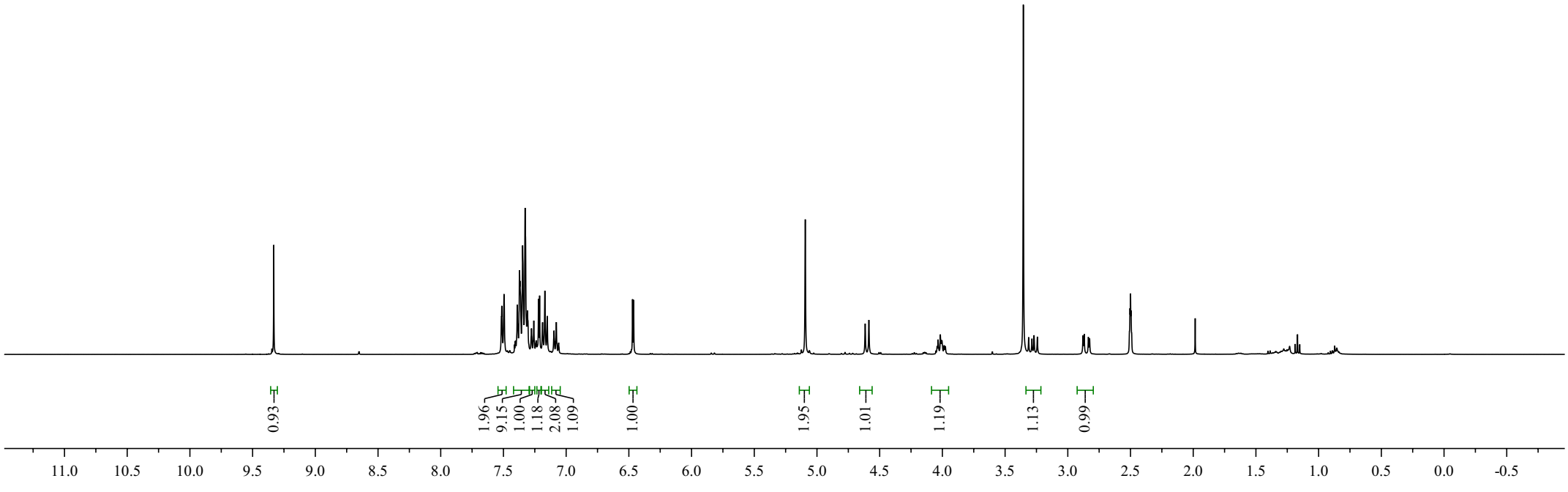
O
COCO2Bn
Ph

4d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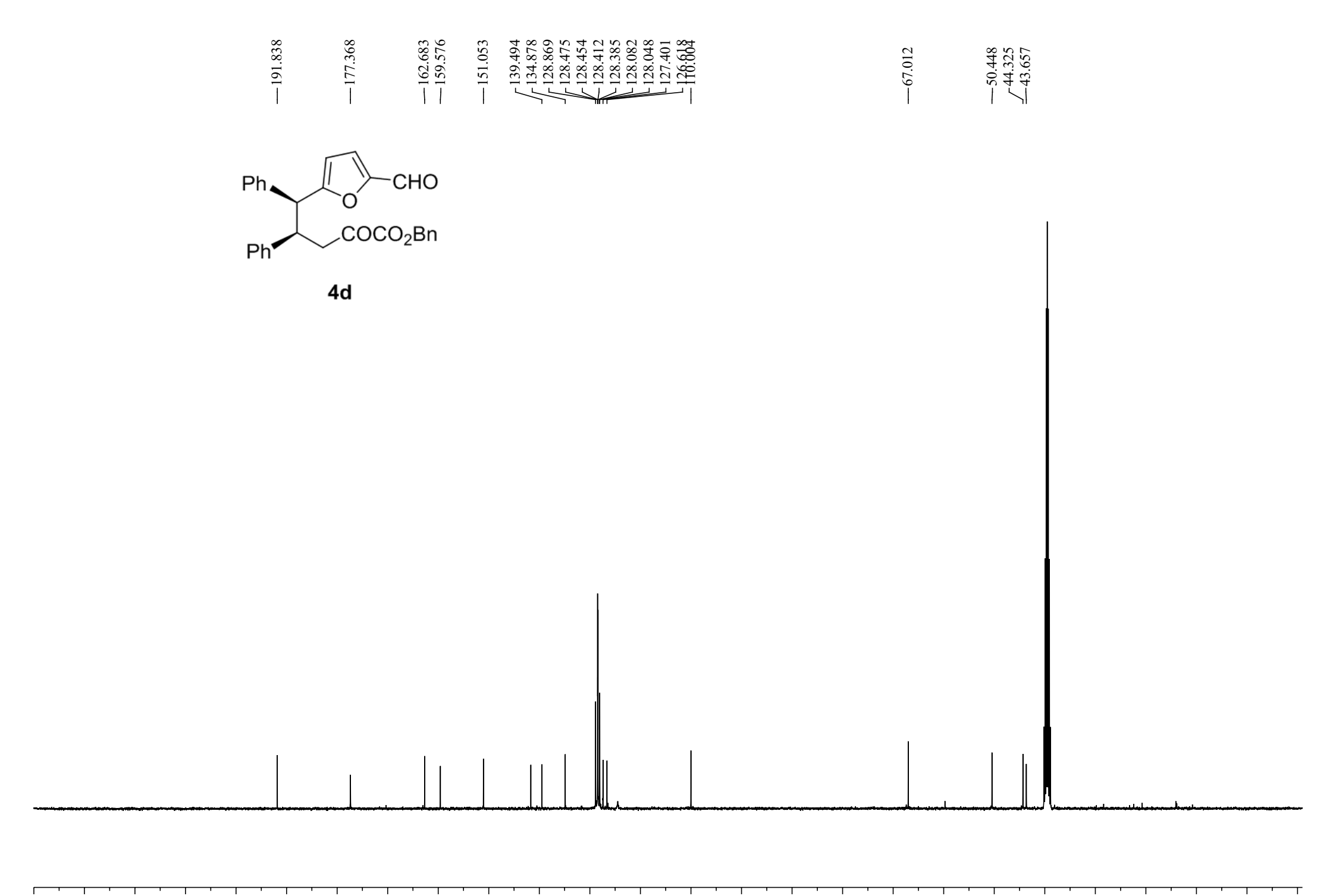
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128.048
127.401
126.618
110.004
67.012
50.448
44.325
43.657
Ph
CHO
O
COCO2Bn
Ph
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
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80
70
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4d


9.501
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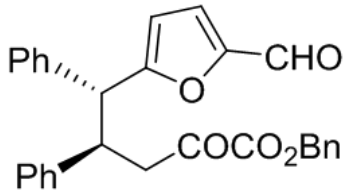
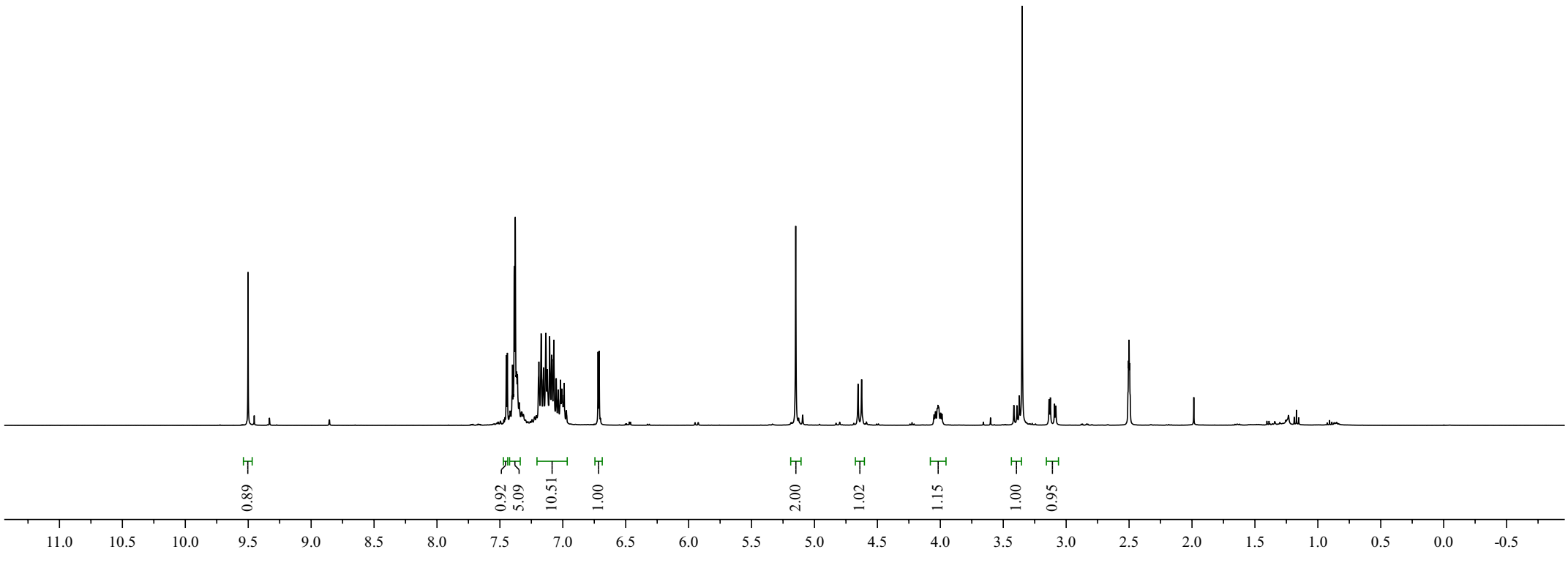

Ph
CHO
O
COCO2Bn
Ph

4d'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5.5
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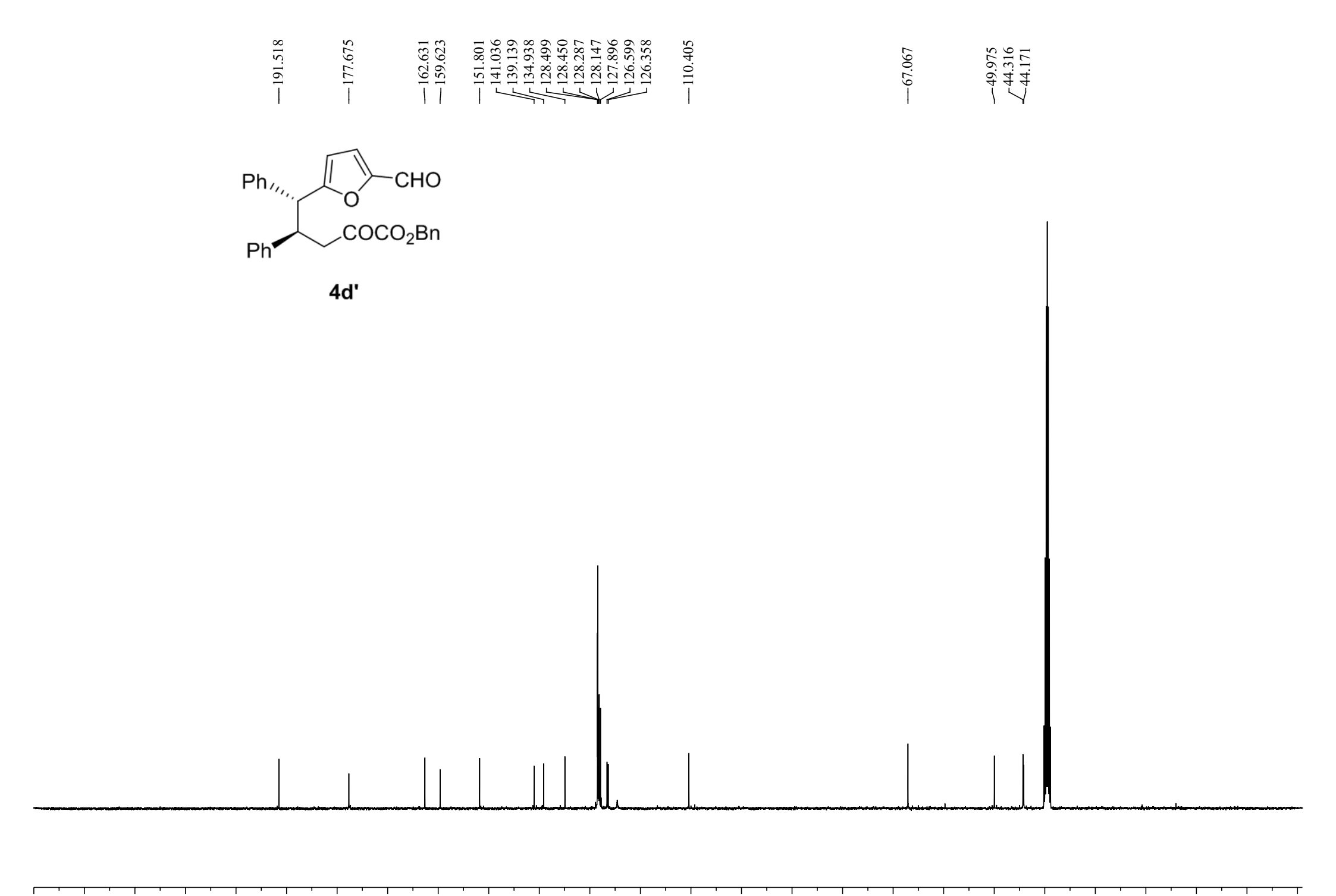
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128.287
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127.896
126.599
126.358
110.405
67.067
49.975
44.316
44.171
Ph
O
CHO
COCO2Bn
Ph
4d'
240
230
220
210
200
190
180
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100
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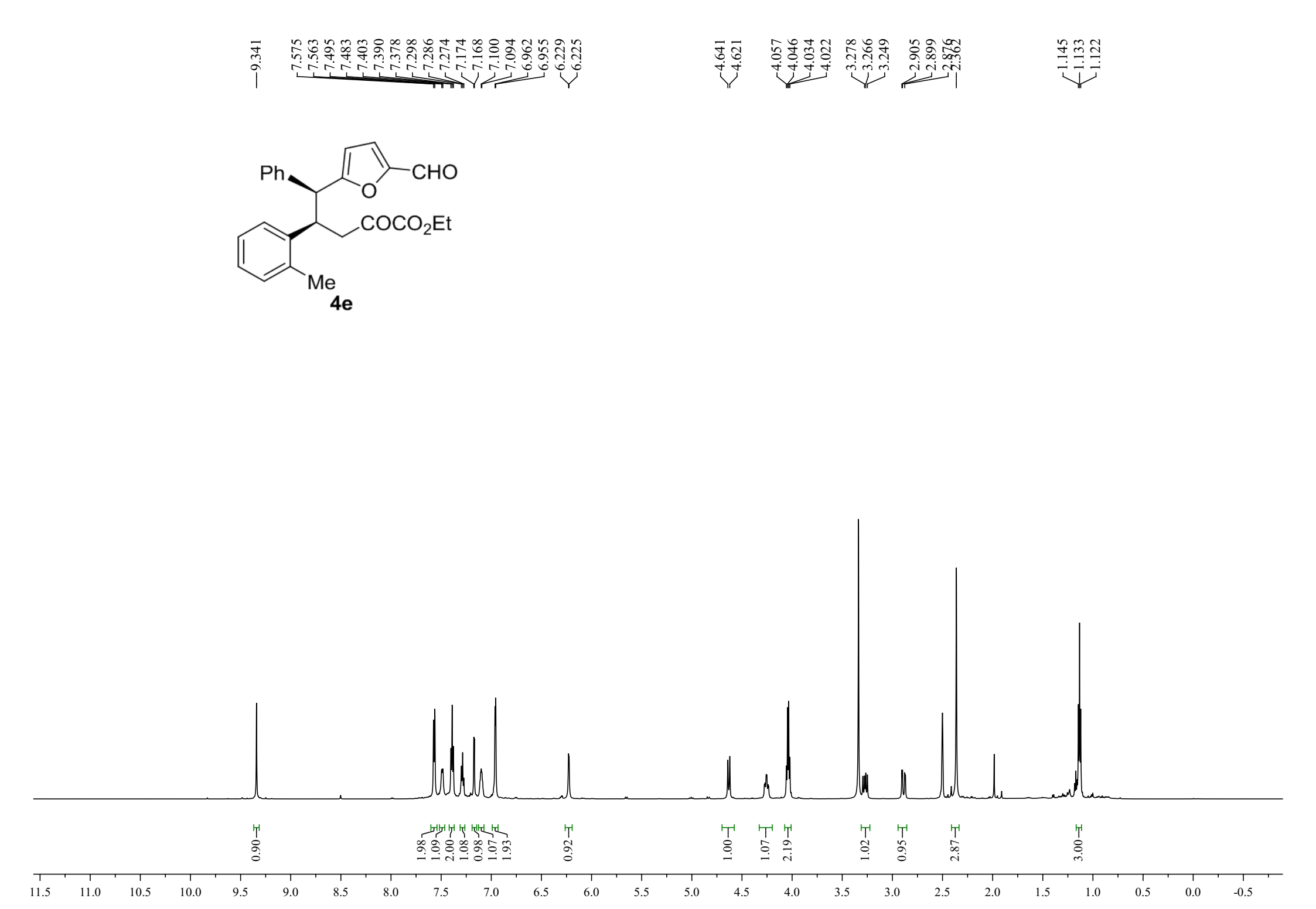
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1.133
1.122
Ph
CHO
O
COCO2Et
Me
4e
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1.09
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0.98
1.07
1.93
0.92
1.00
1.07
2.19
1.02
0.95
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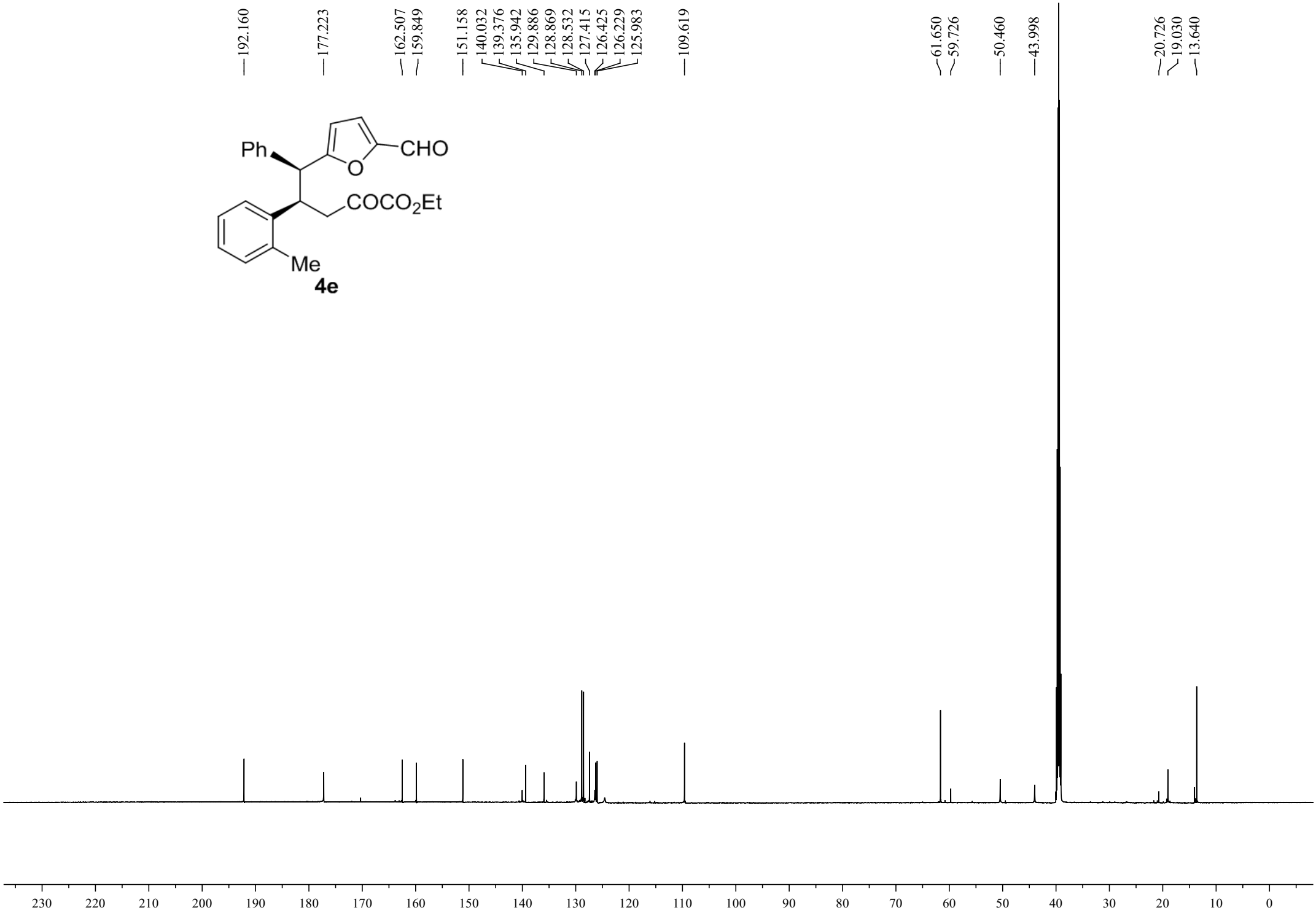
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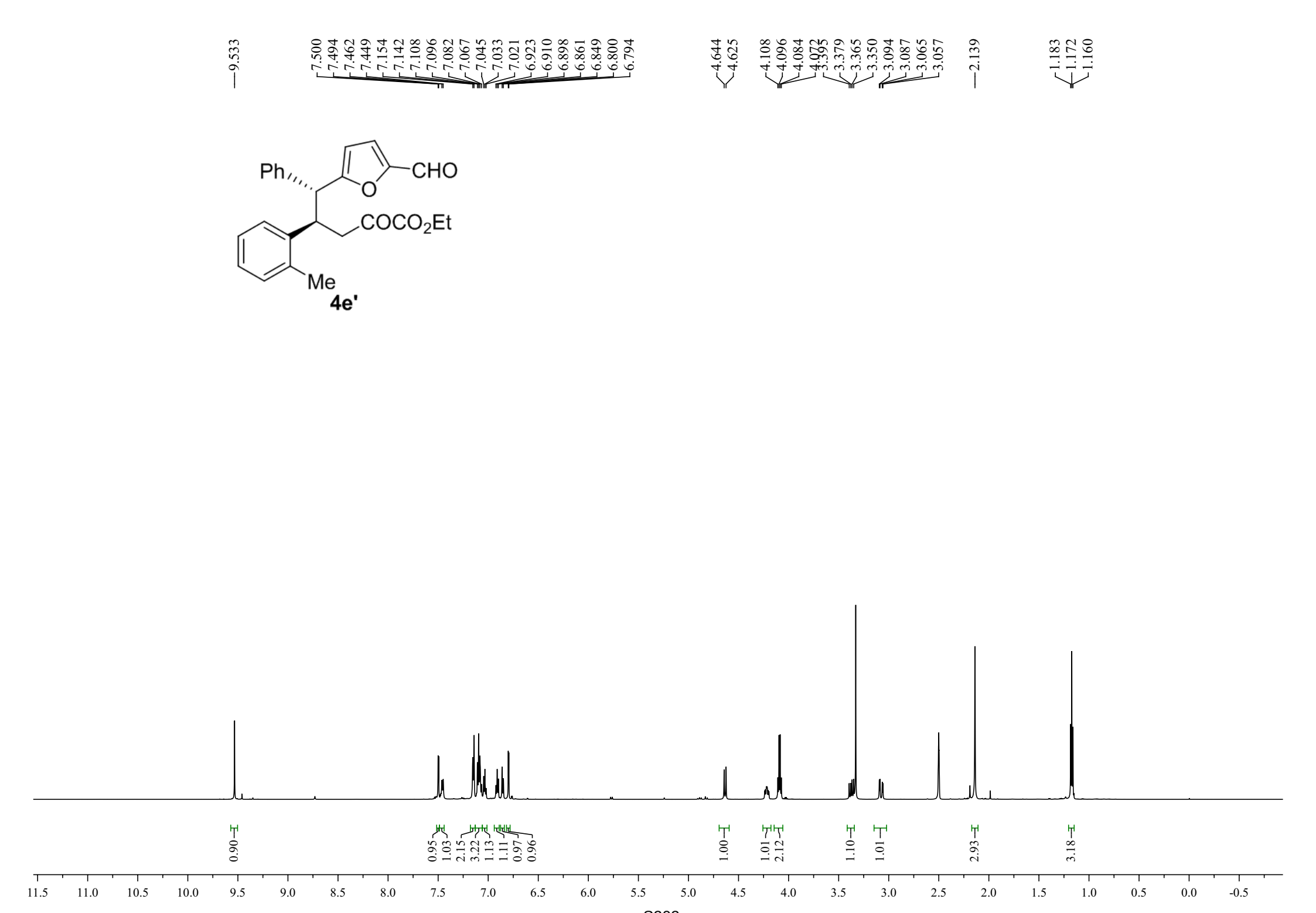
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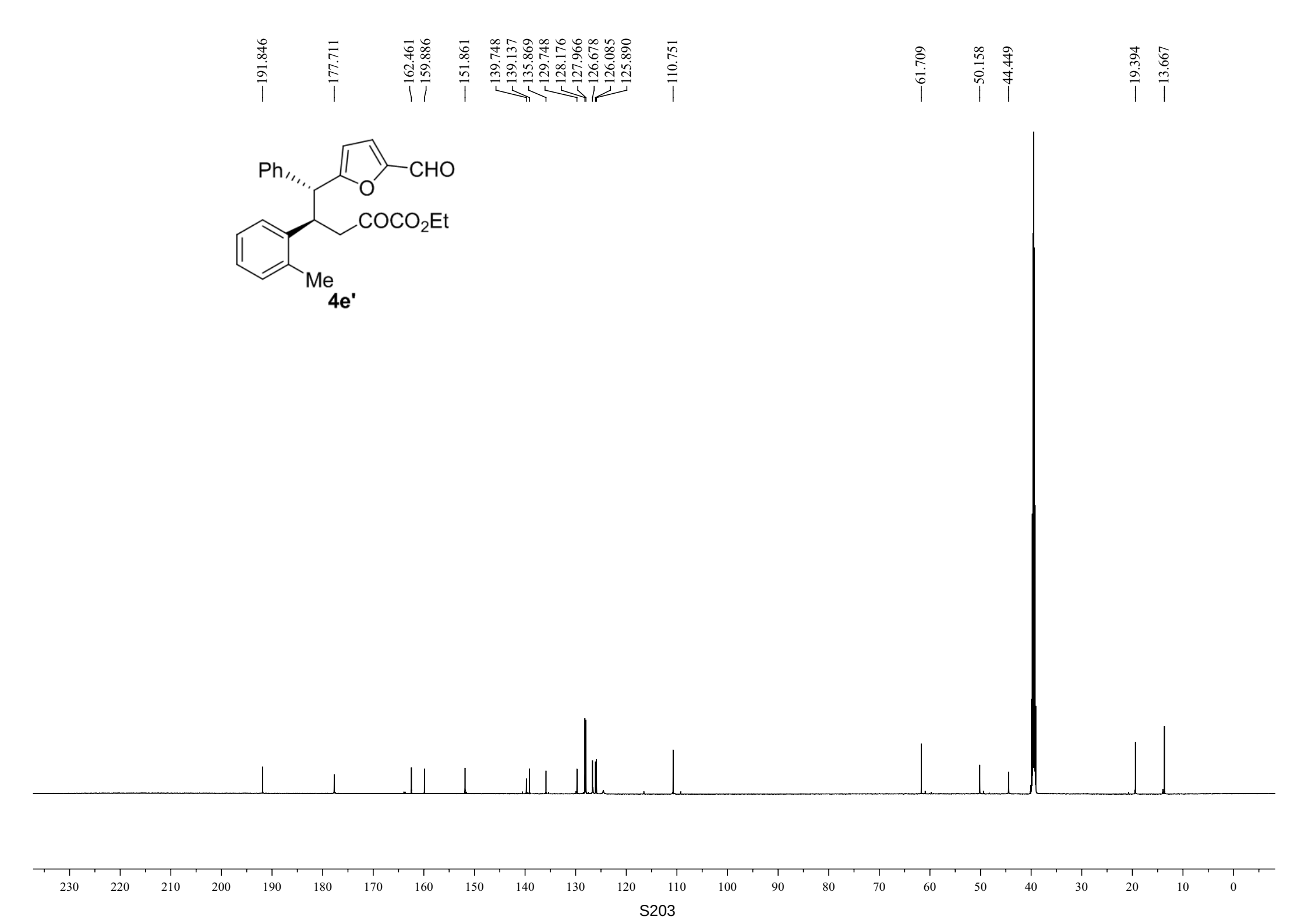
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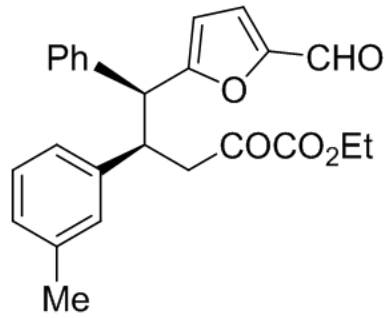
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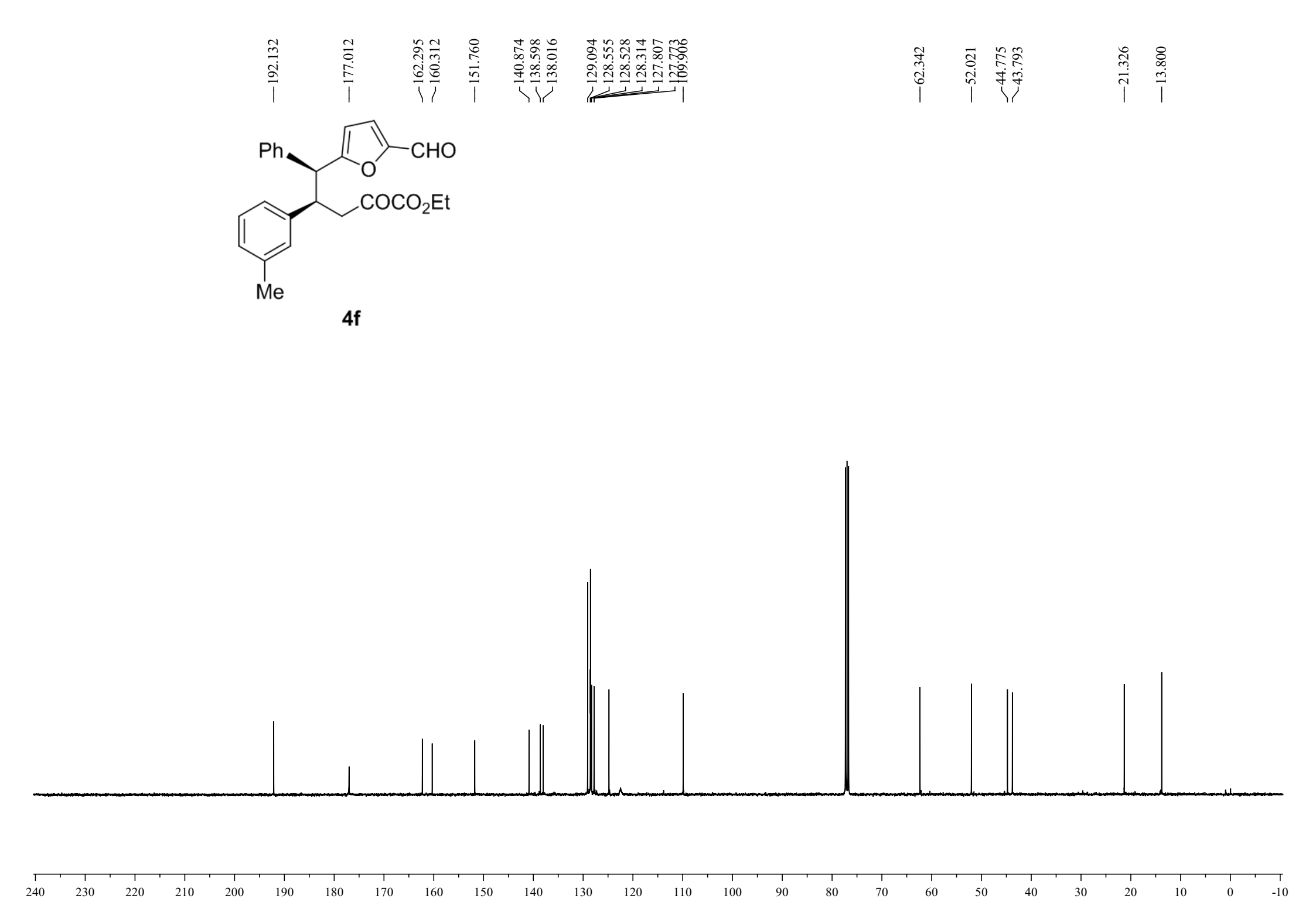
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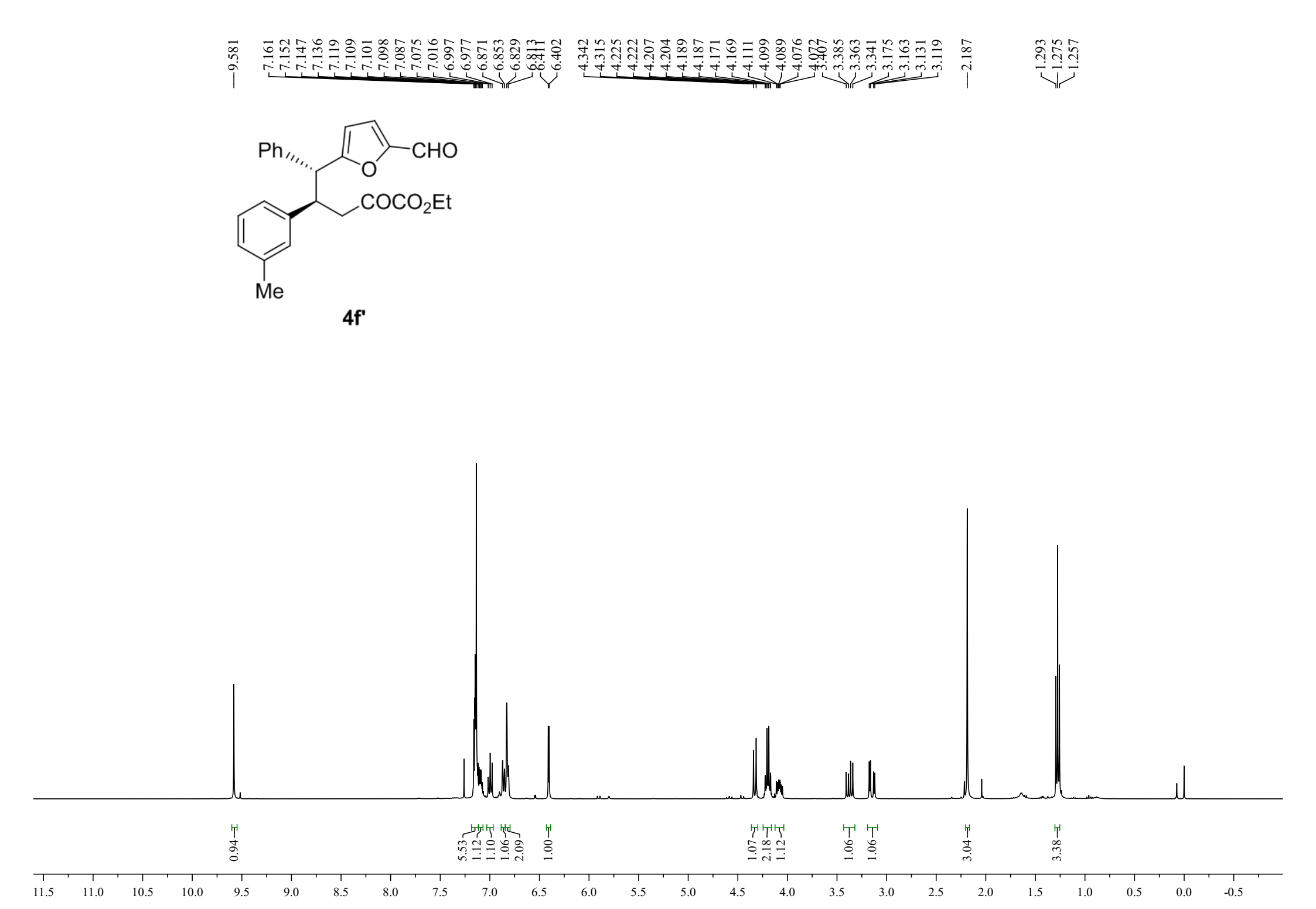
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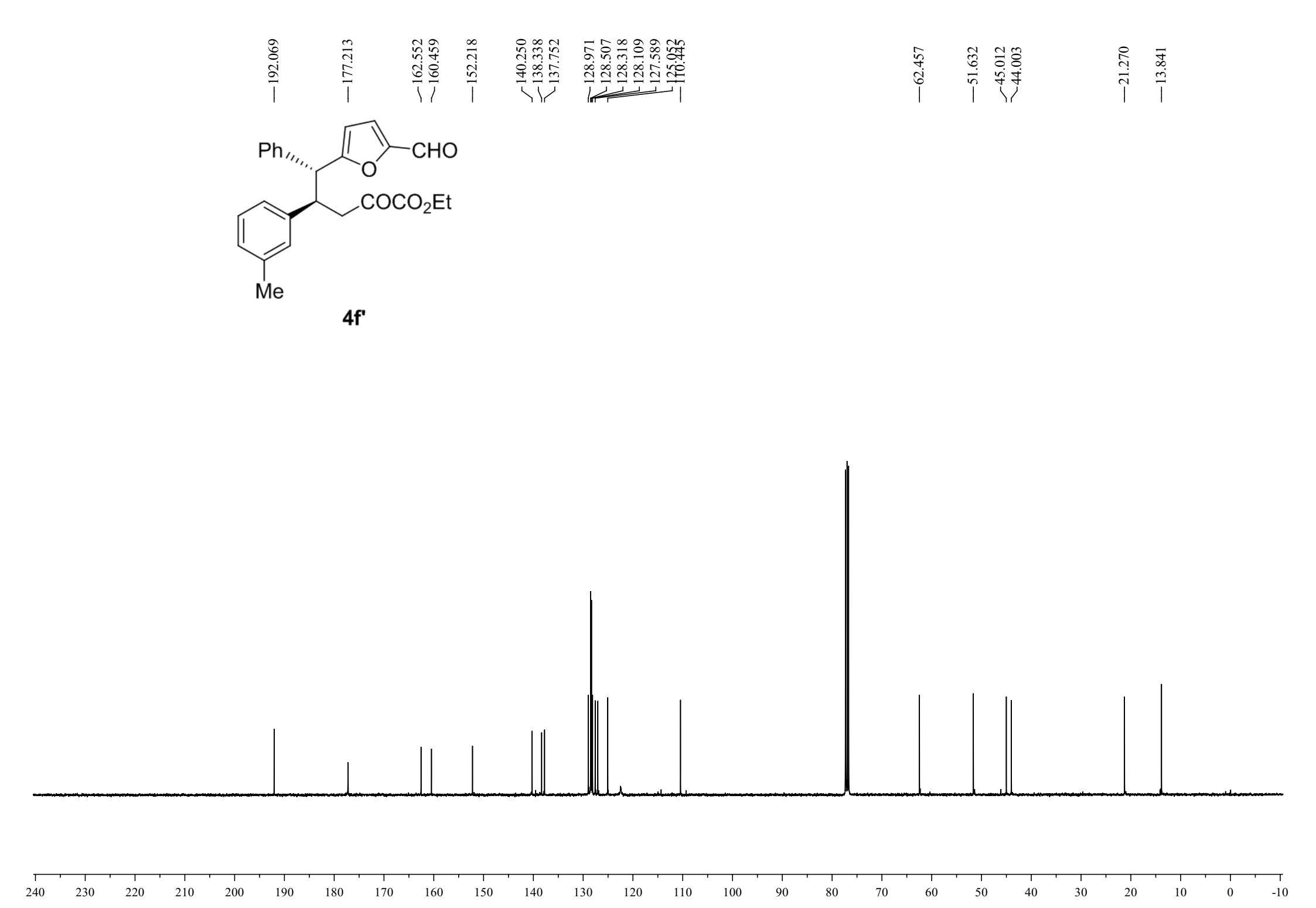
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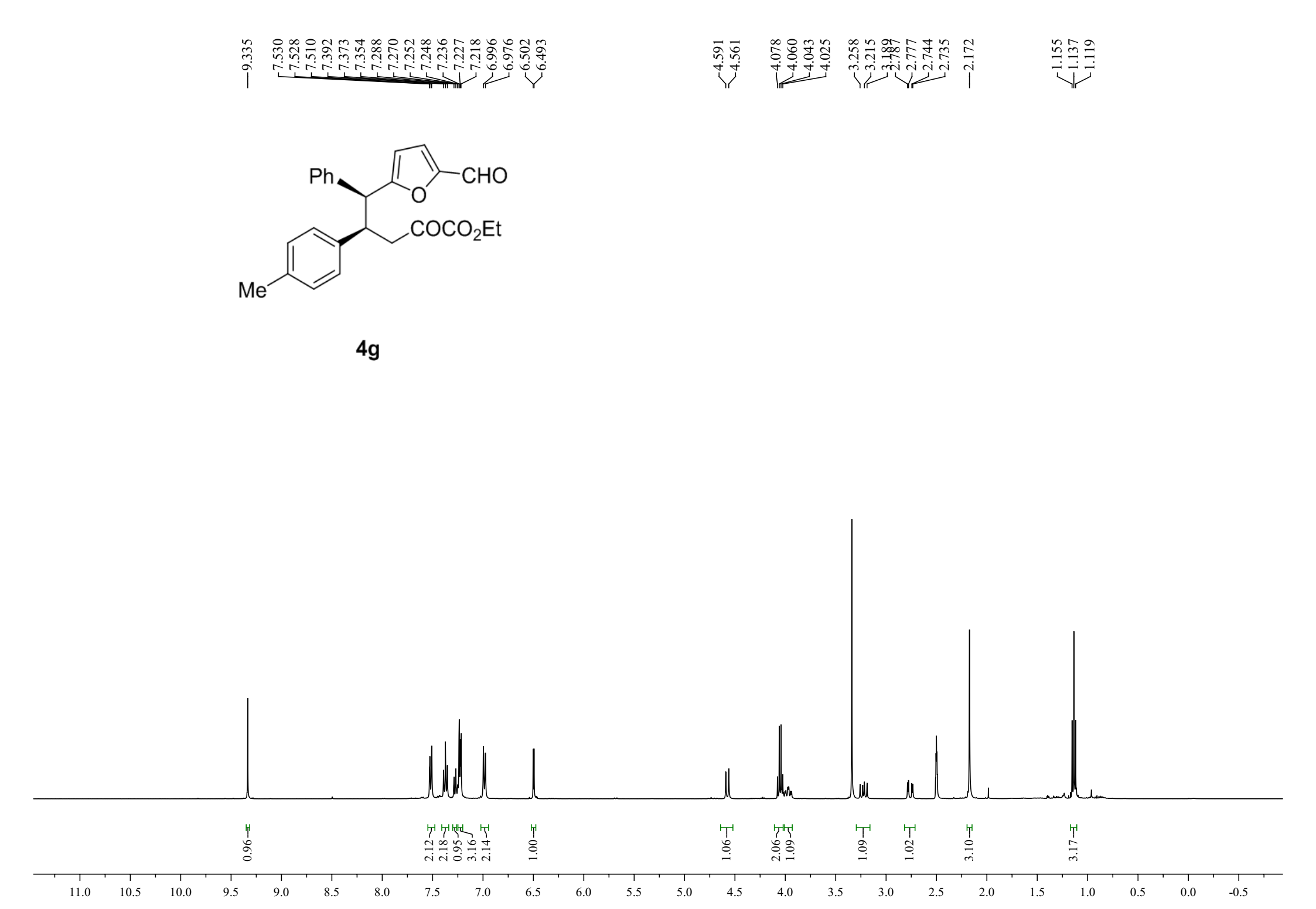
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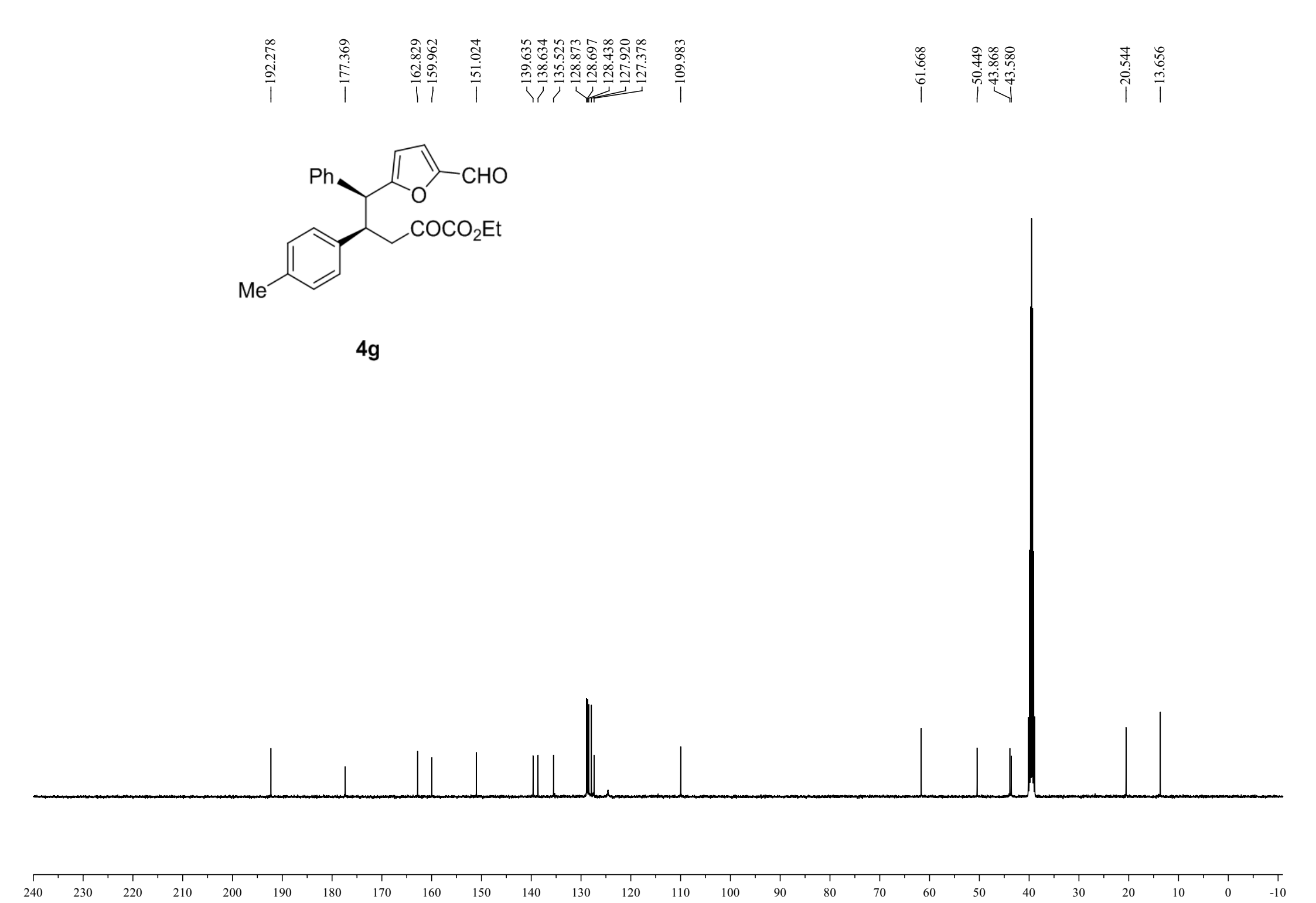
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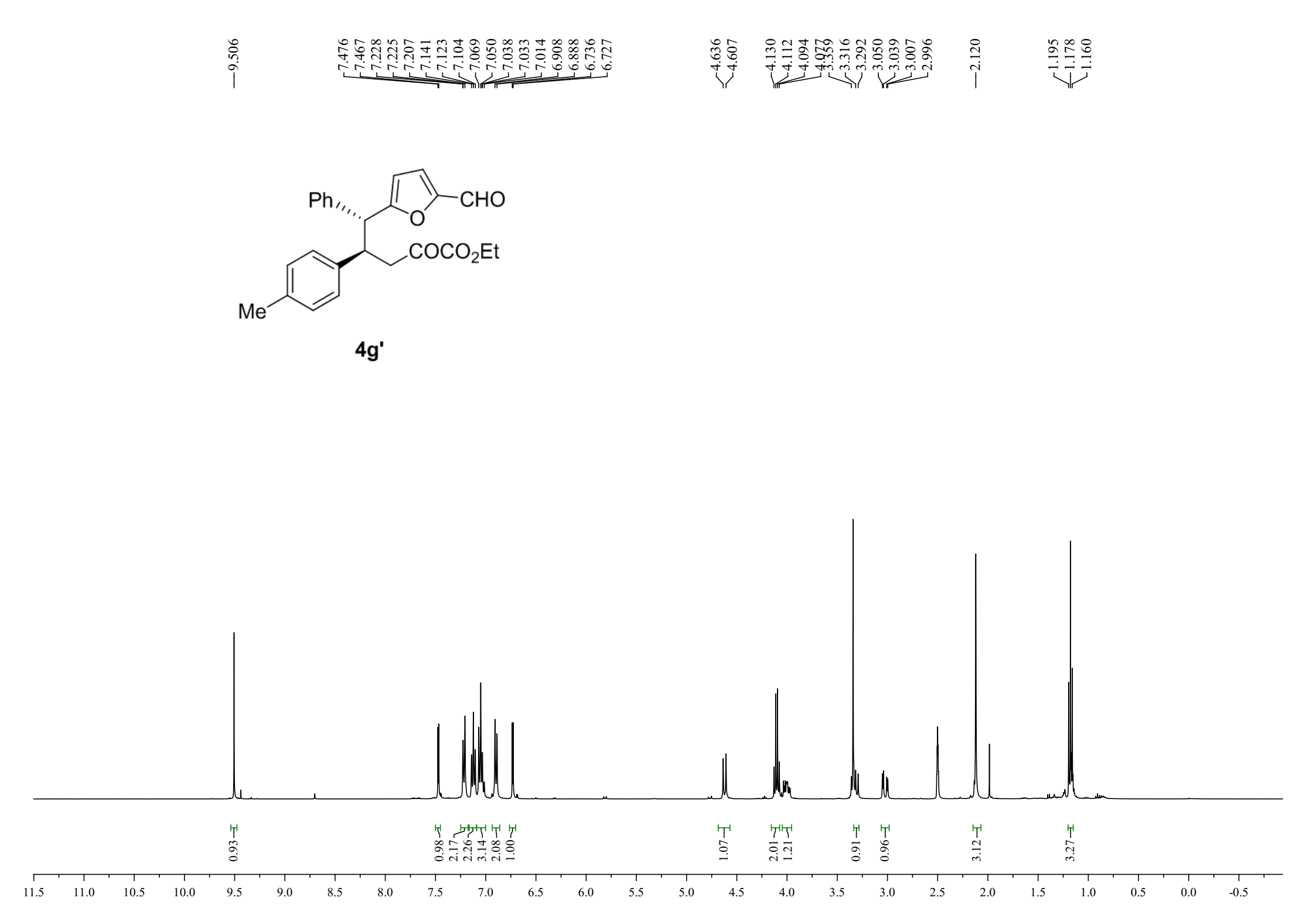
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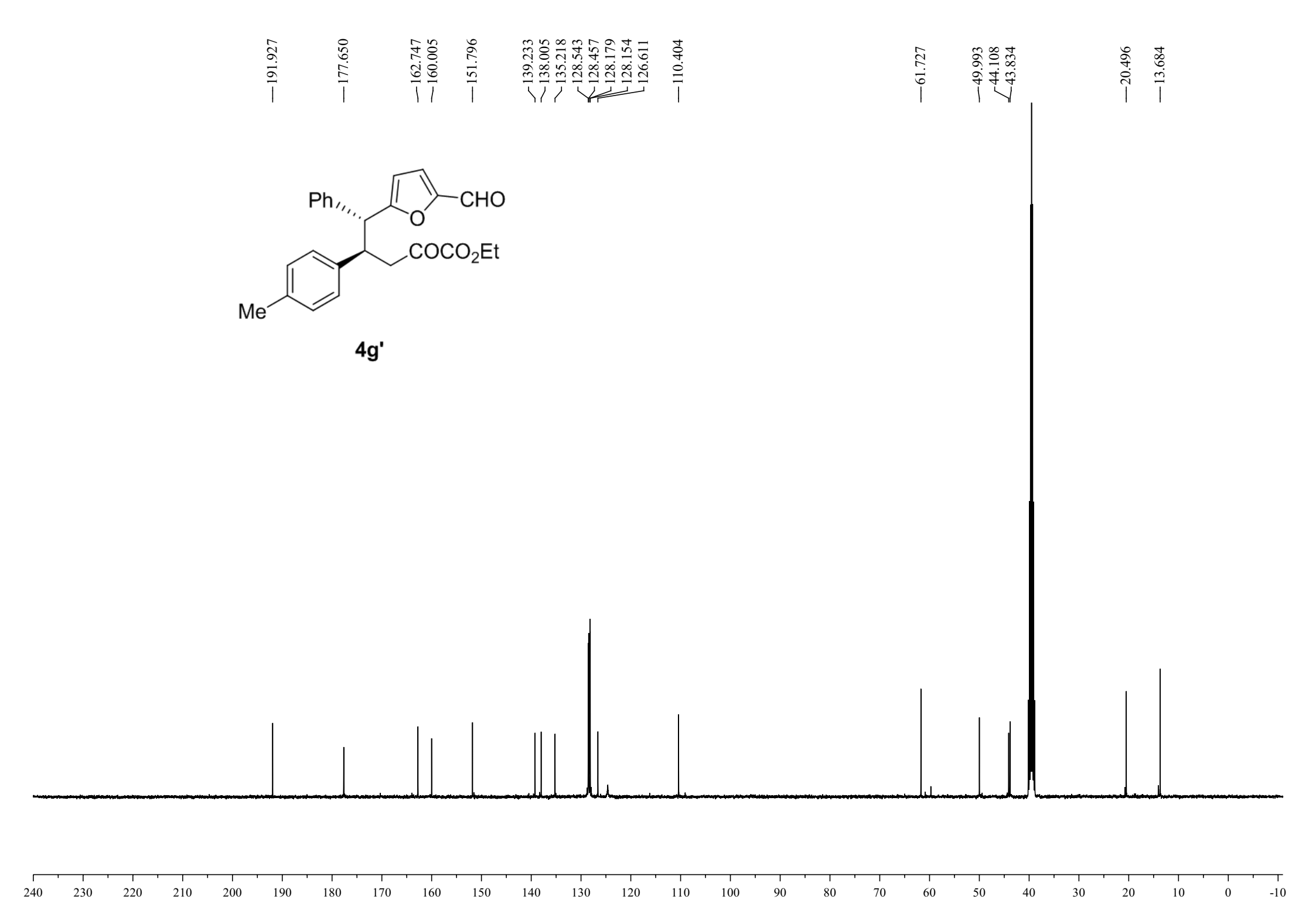
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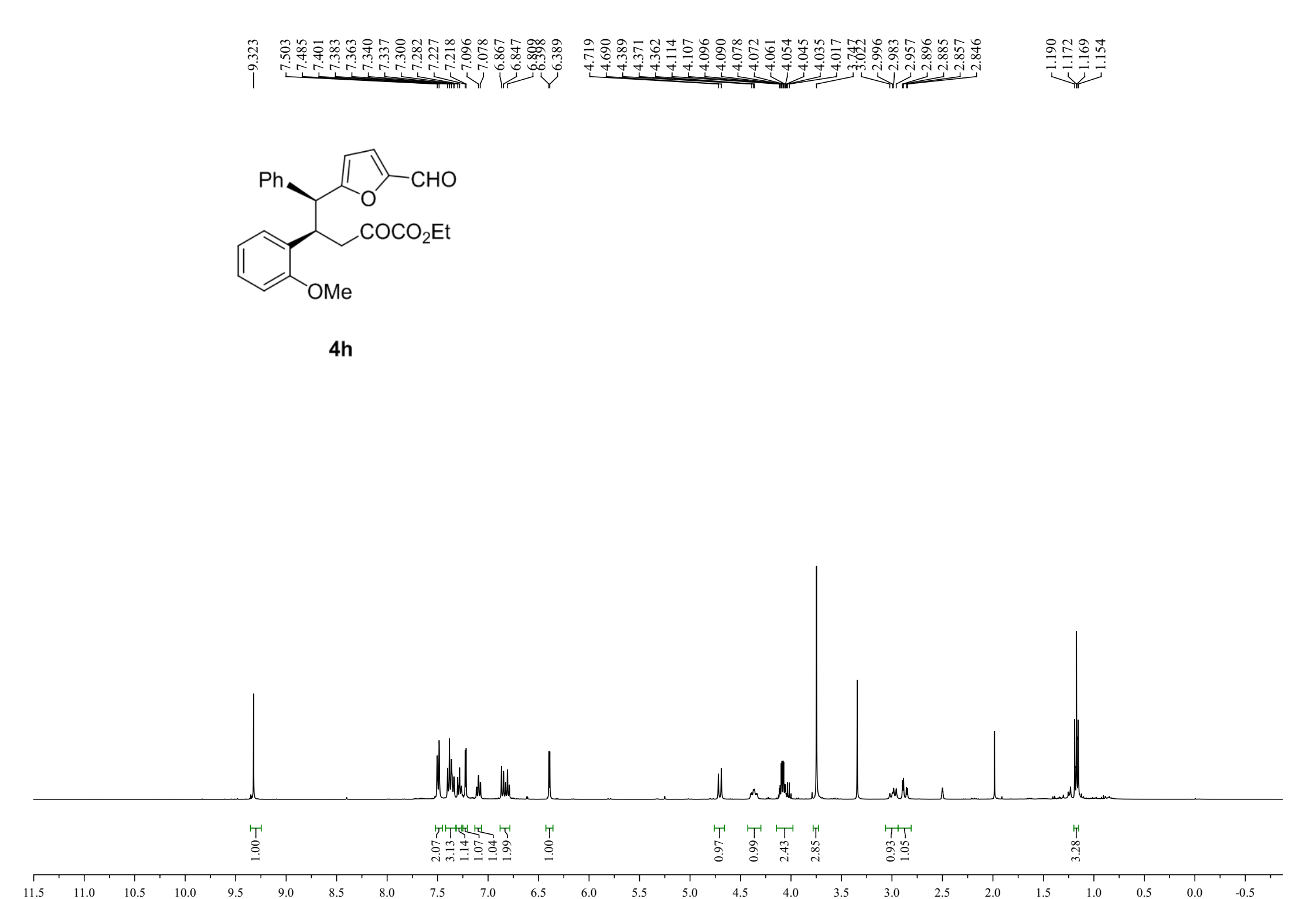
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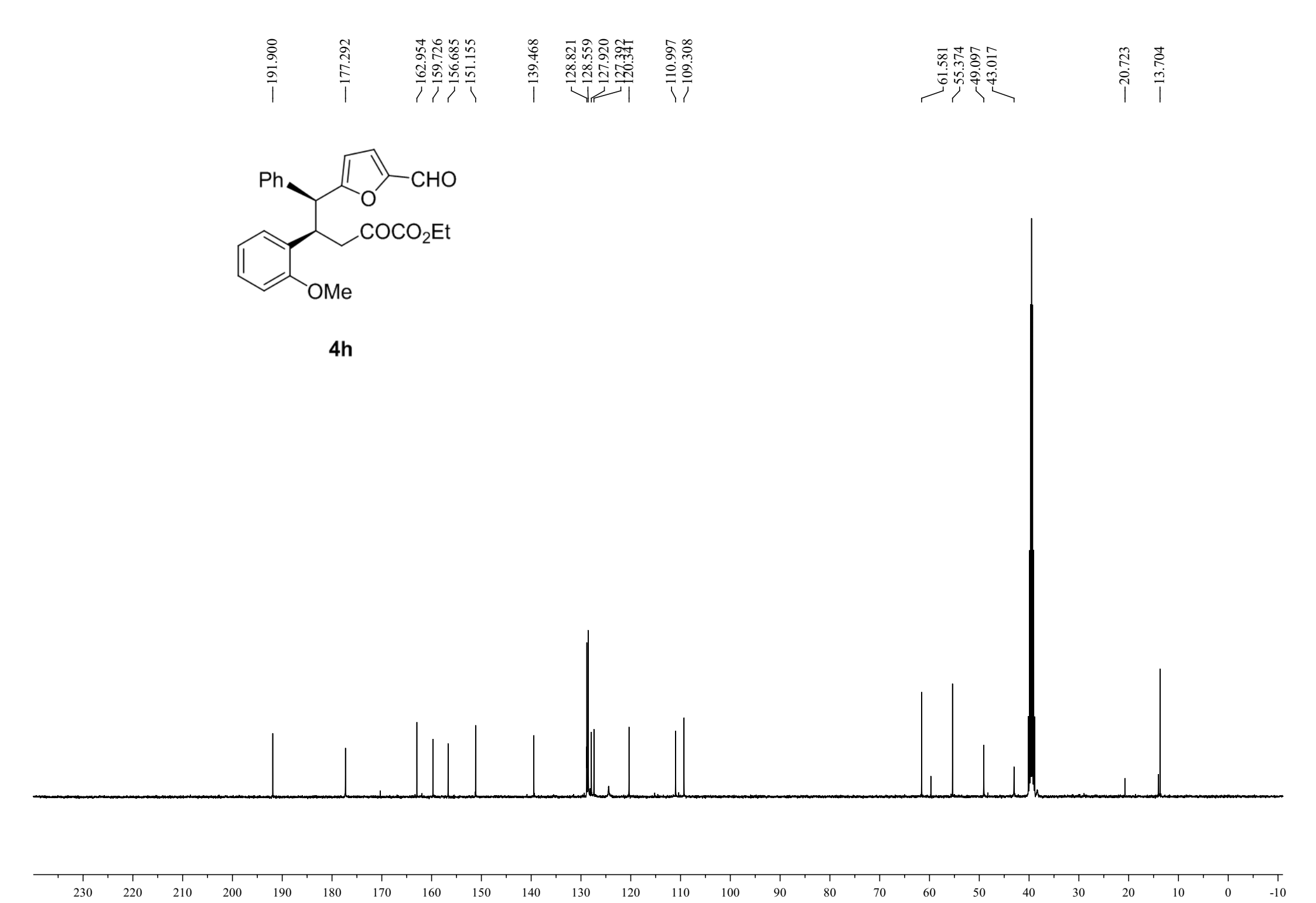
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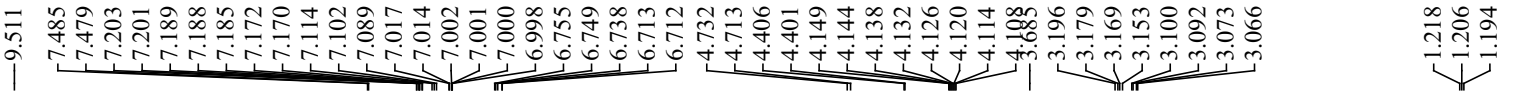
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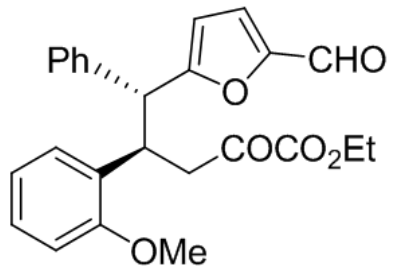
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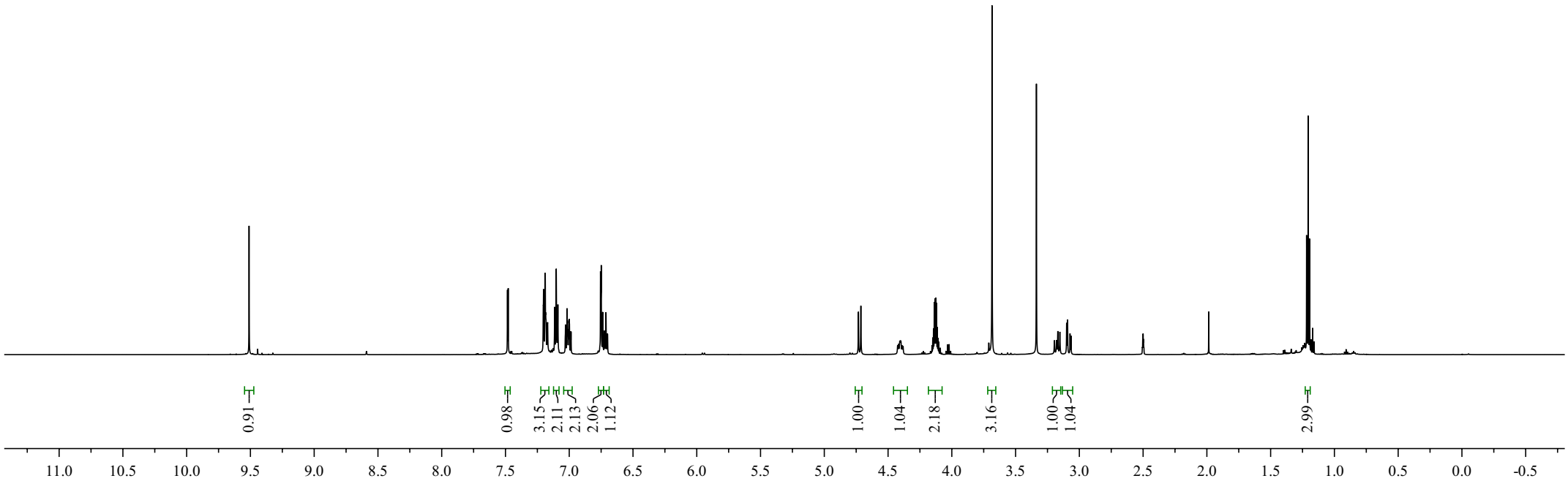
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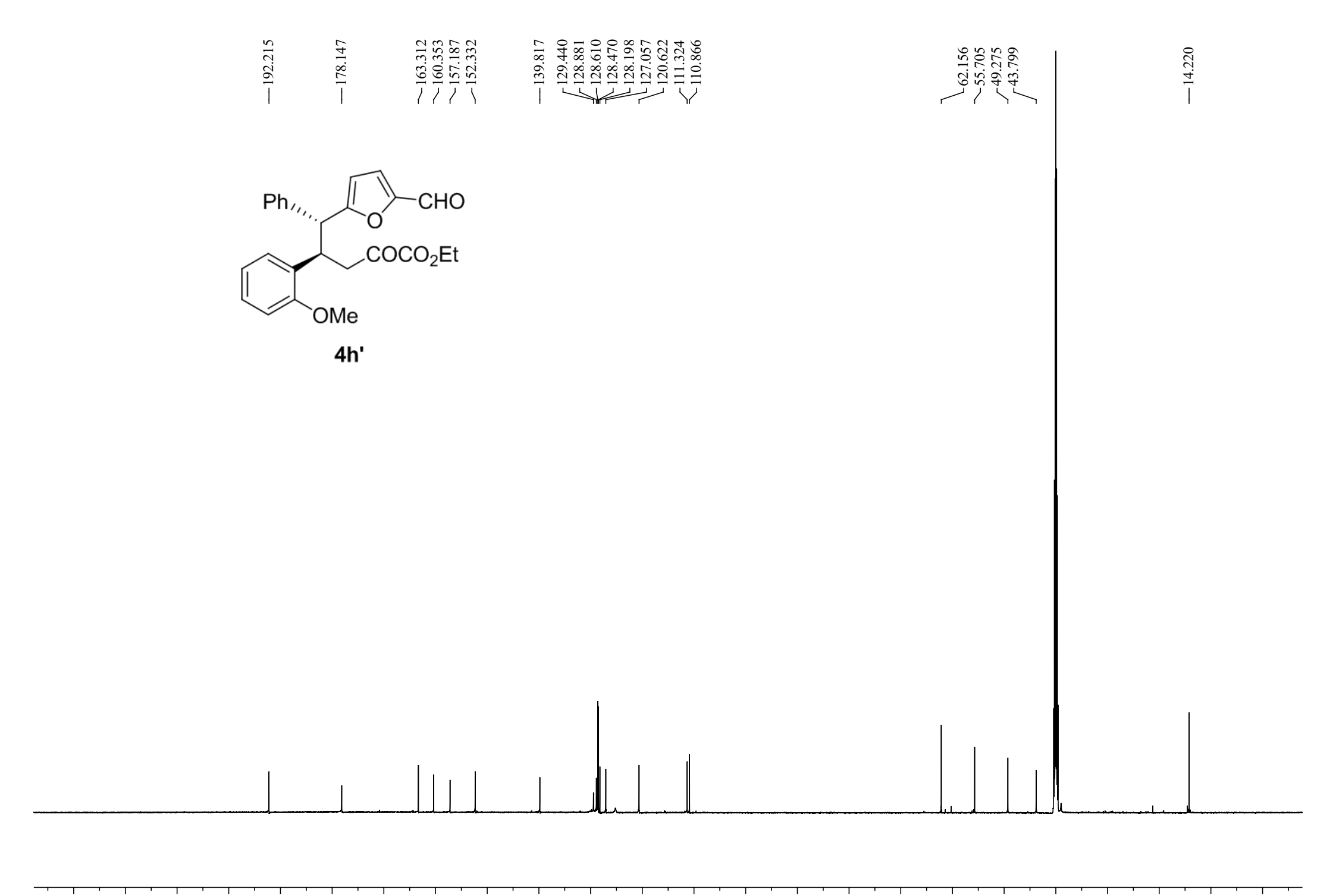
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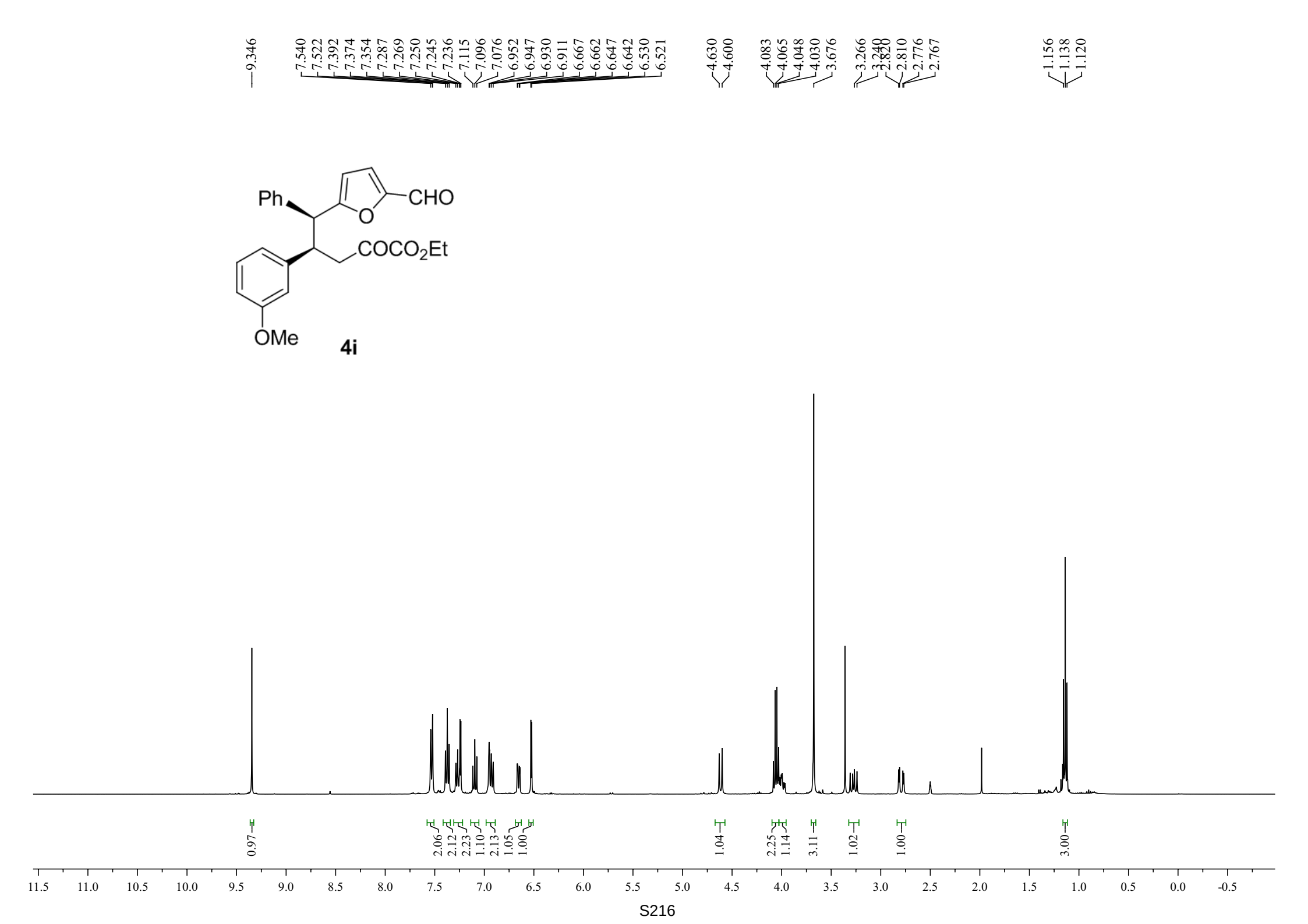
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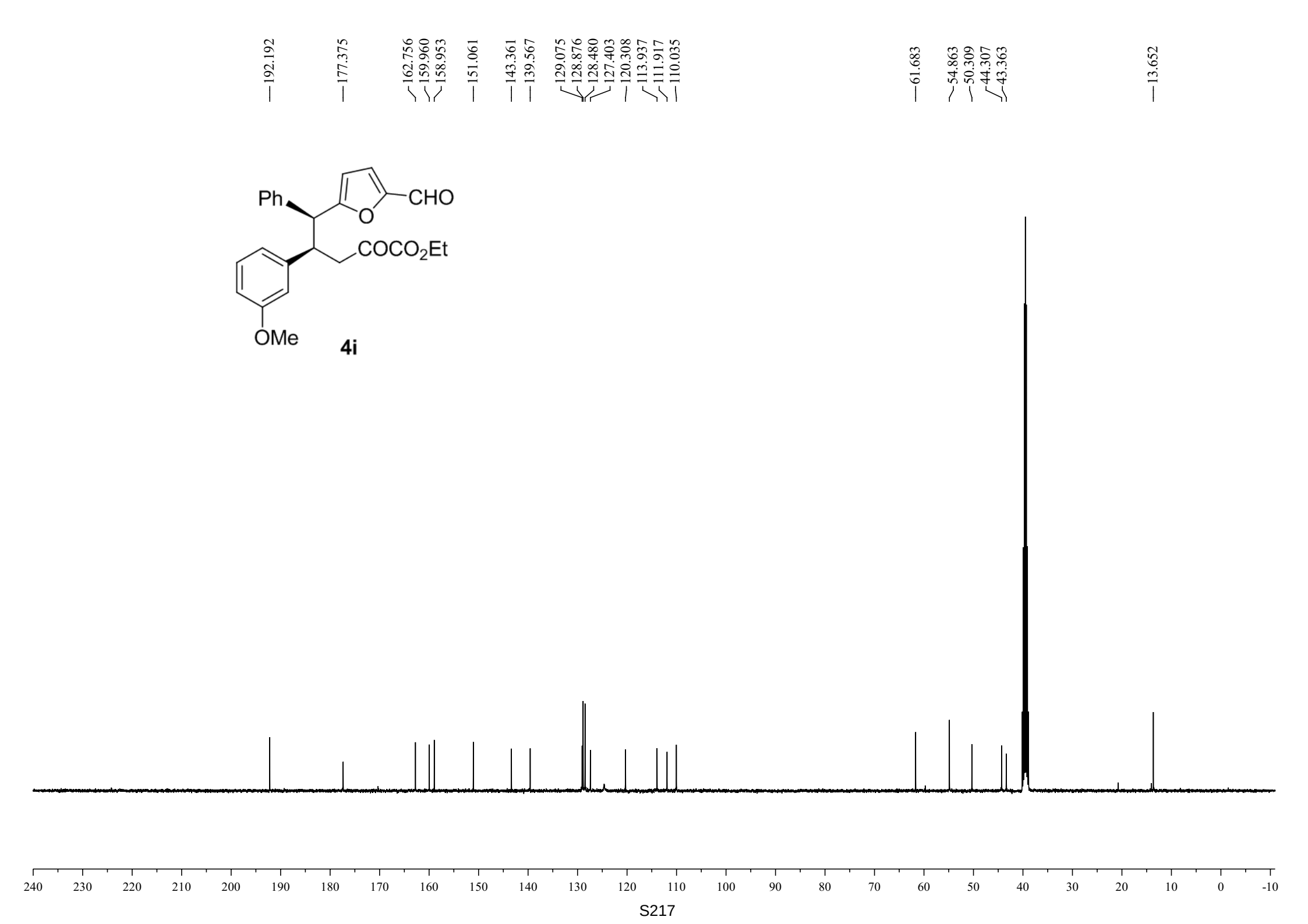
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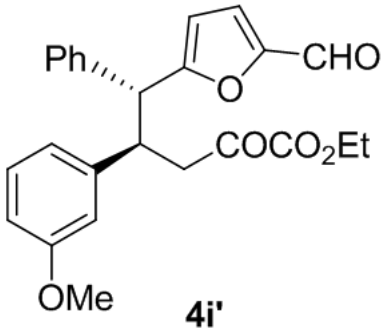

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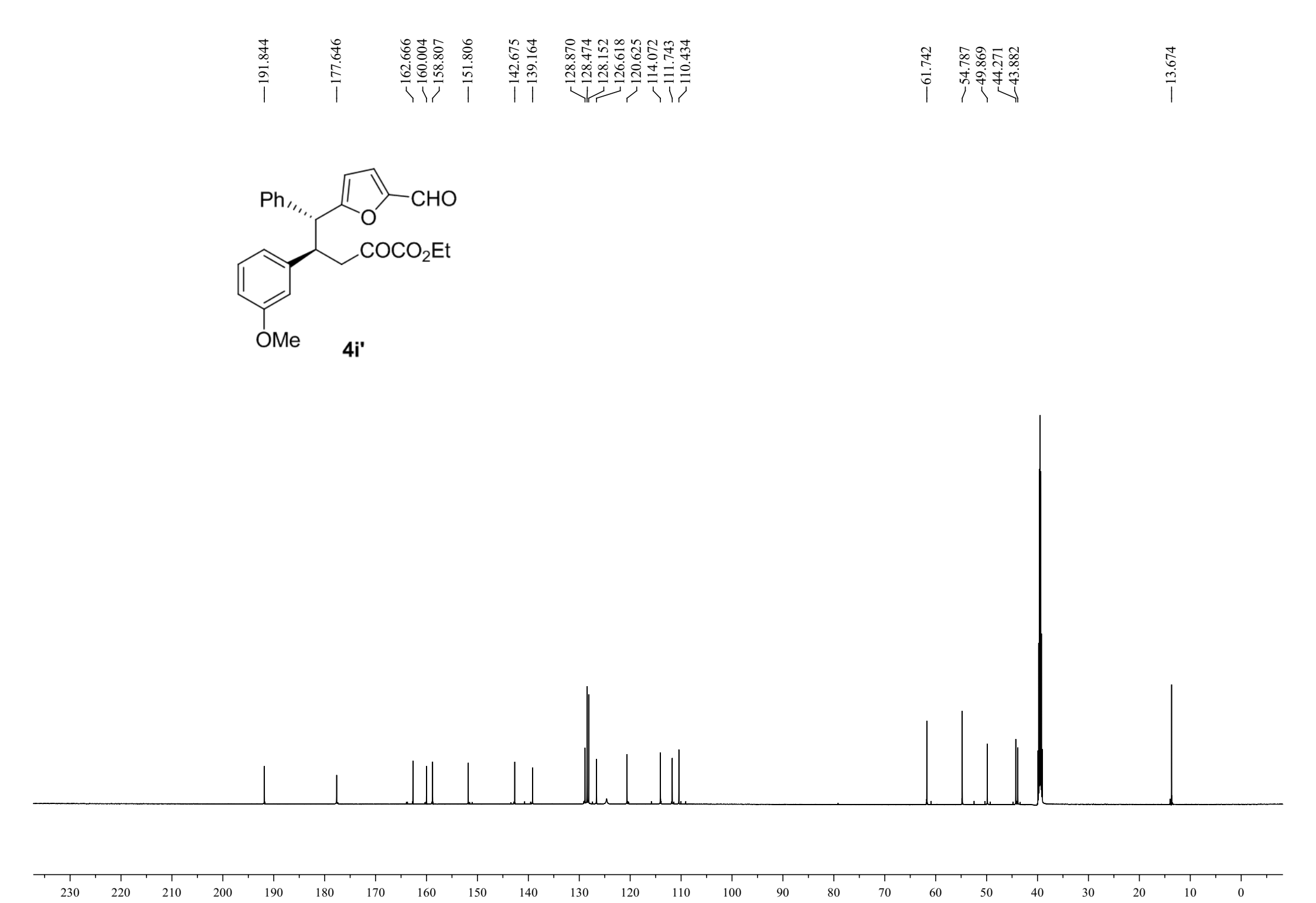
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CHO
O
COCO2Et
OMe
4i'
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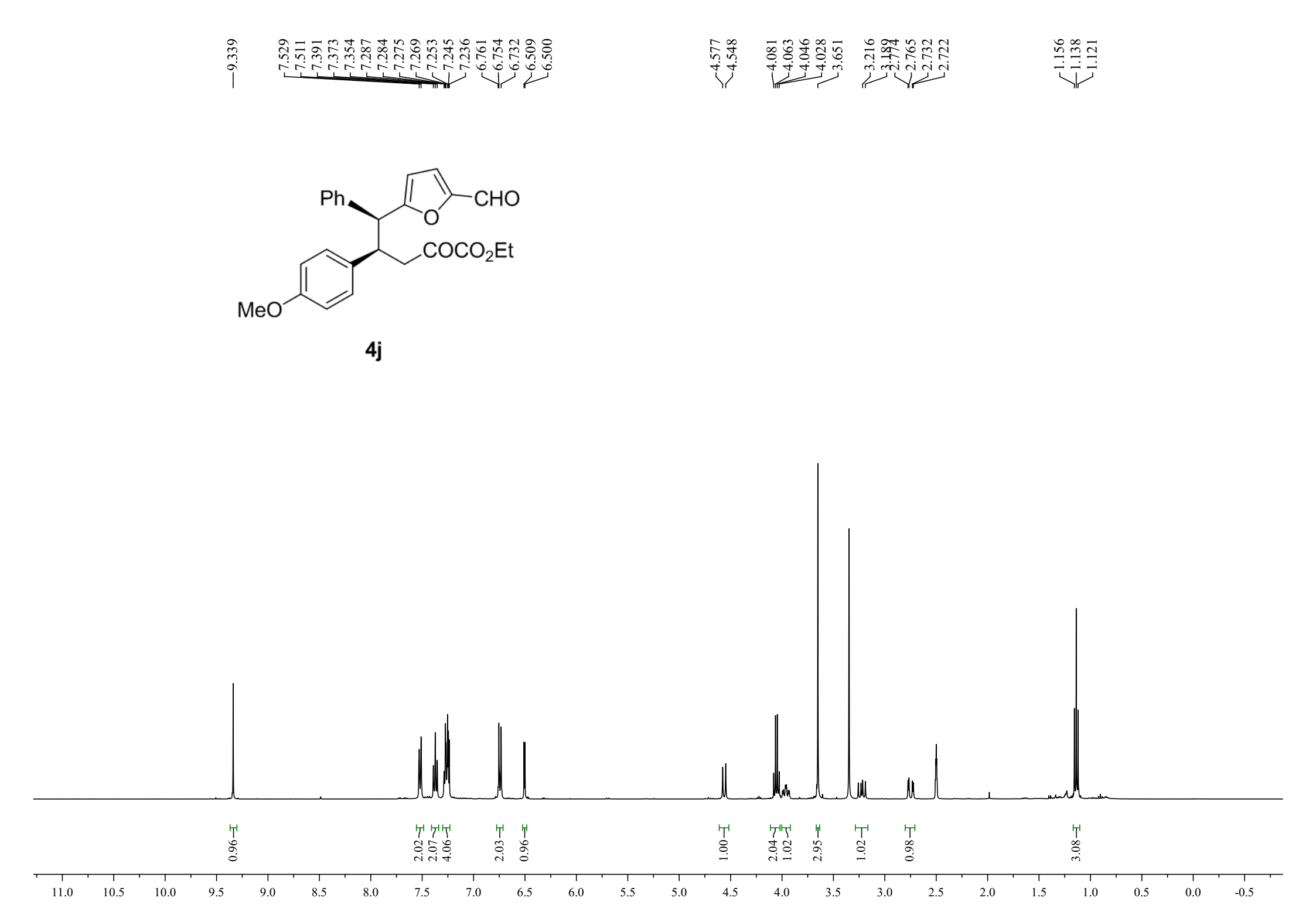
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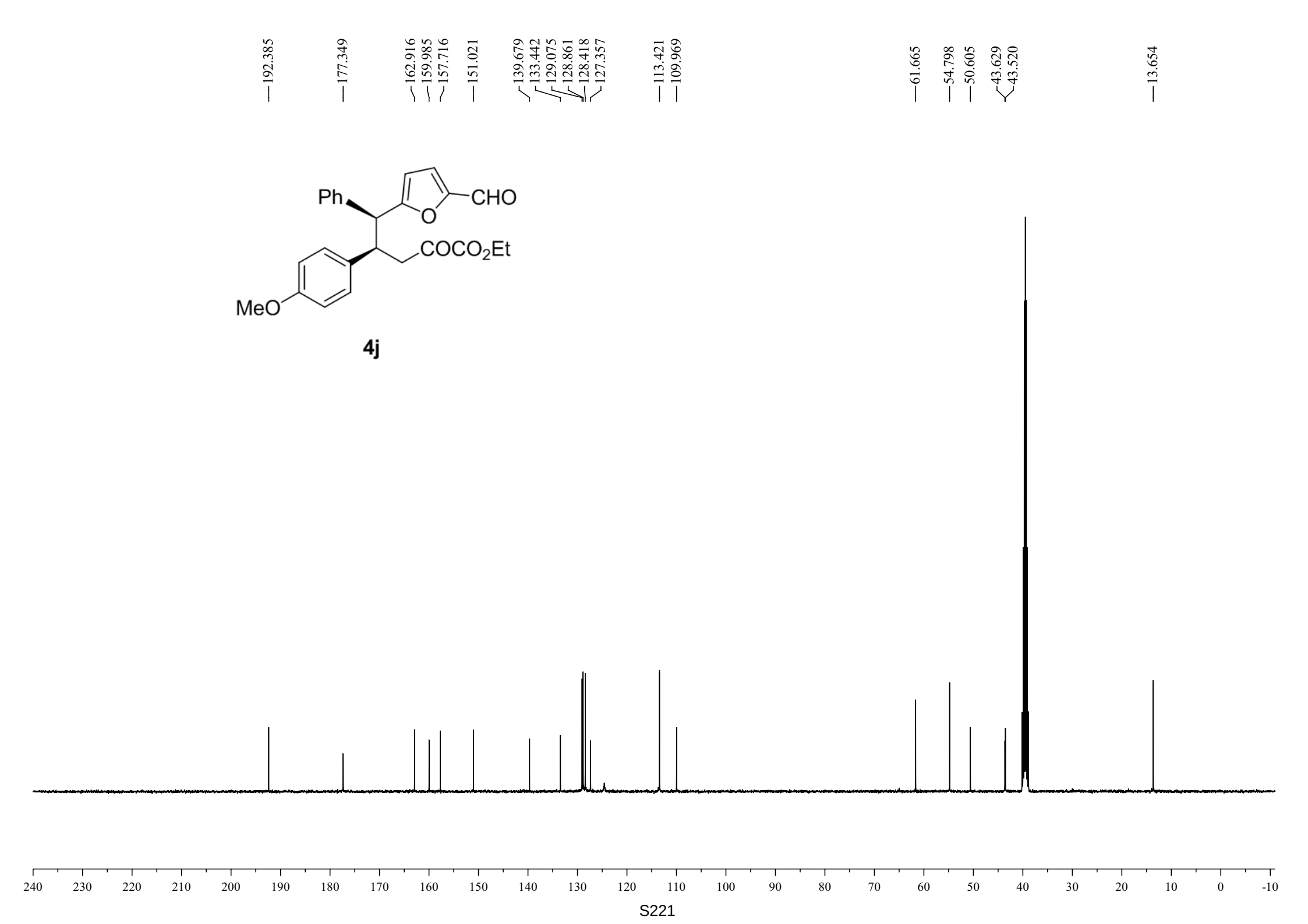
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Ph
CHO
O
COCO2Et
MeO
4j
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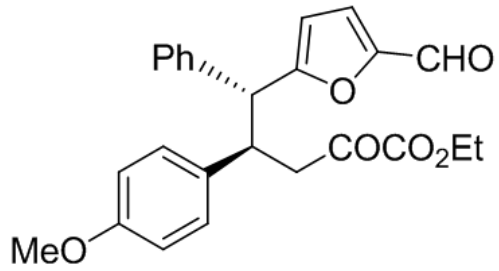

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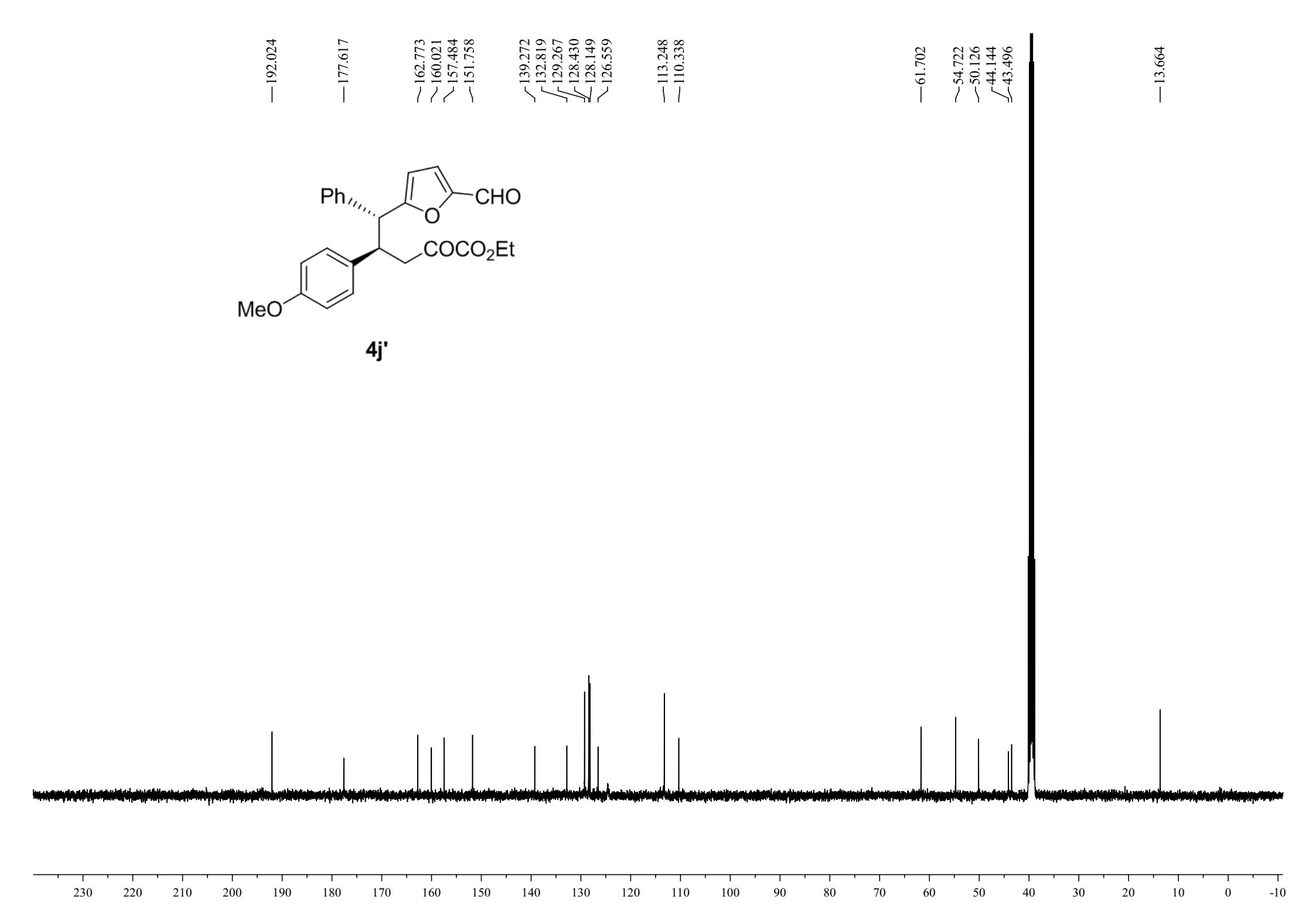
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O
CHO
COCO2Et
MeO
4j'
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200
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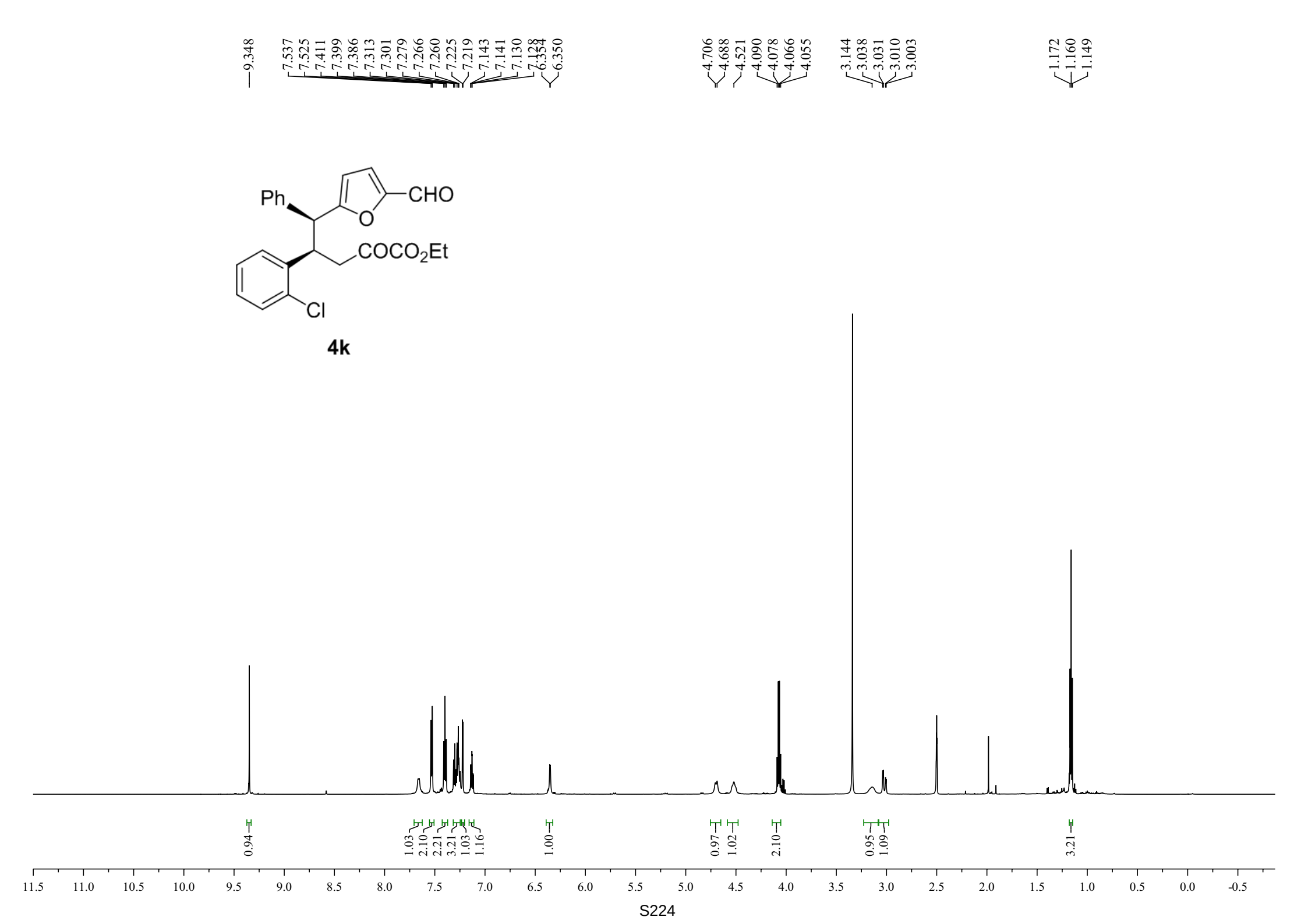
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4.055
3.144
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COCO2Et
Cl
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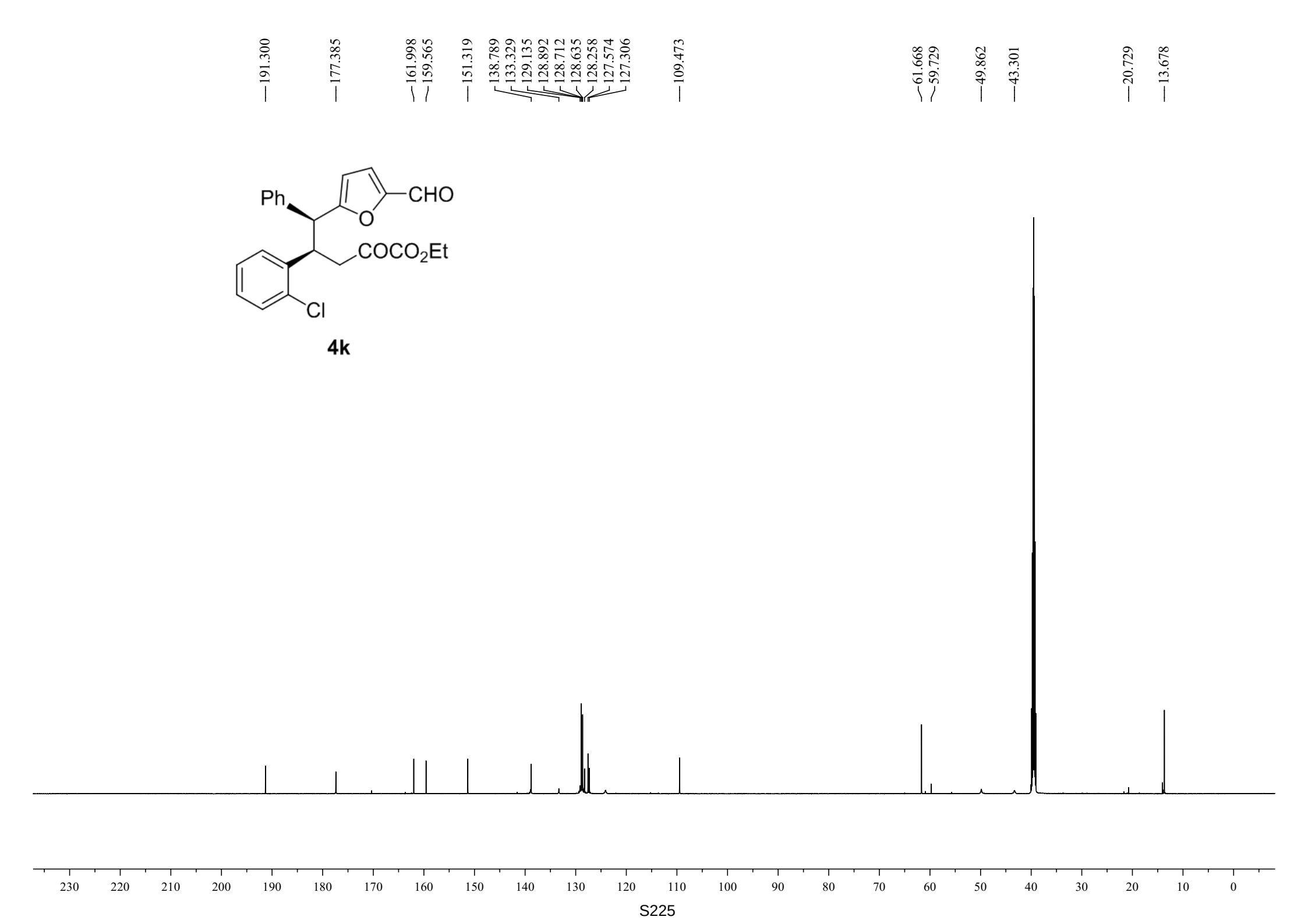
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Cl
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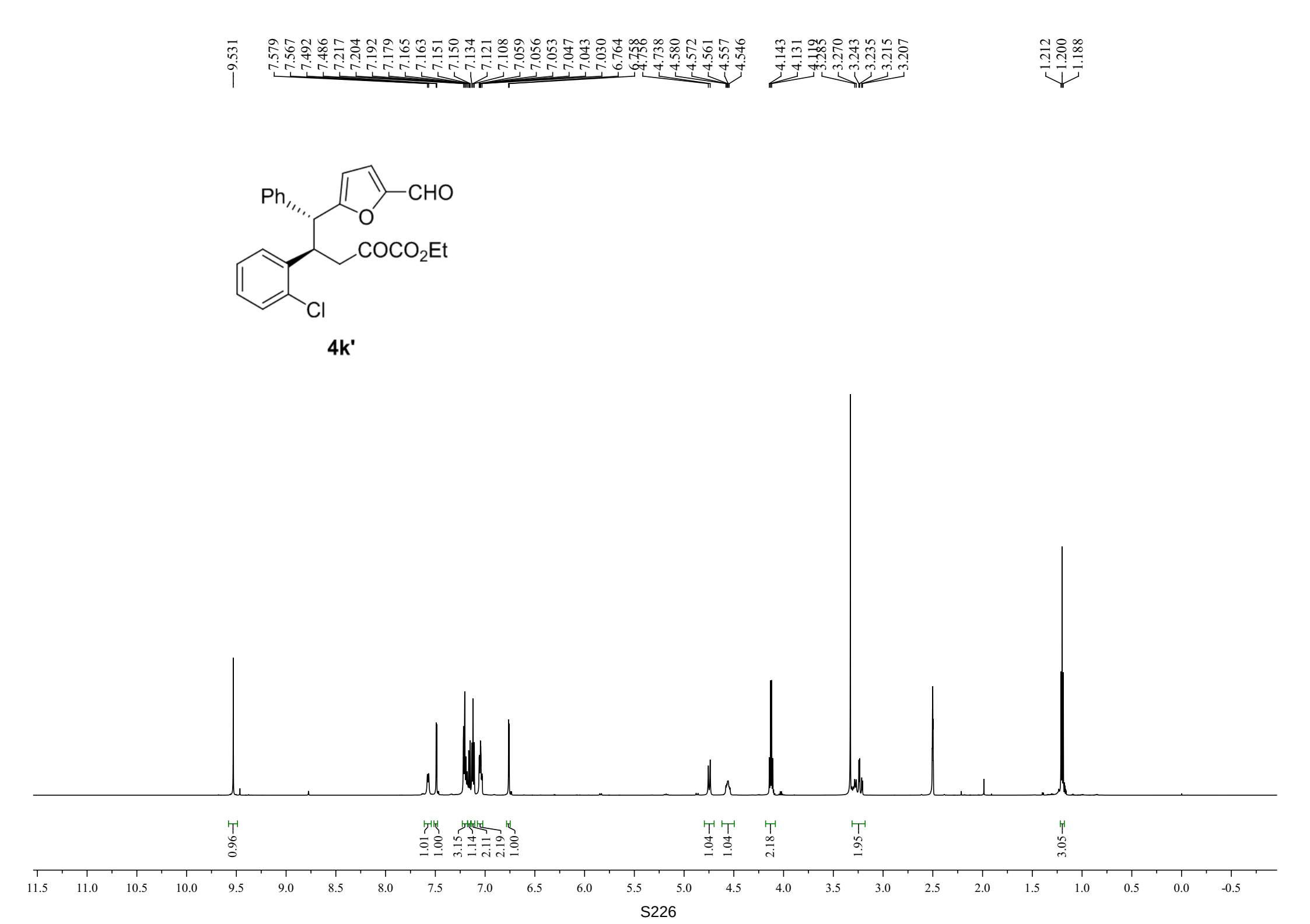
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Cl
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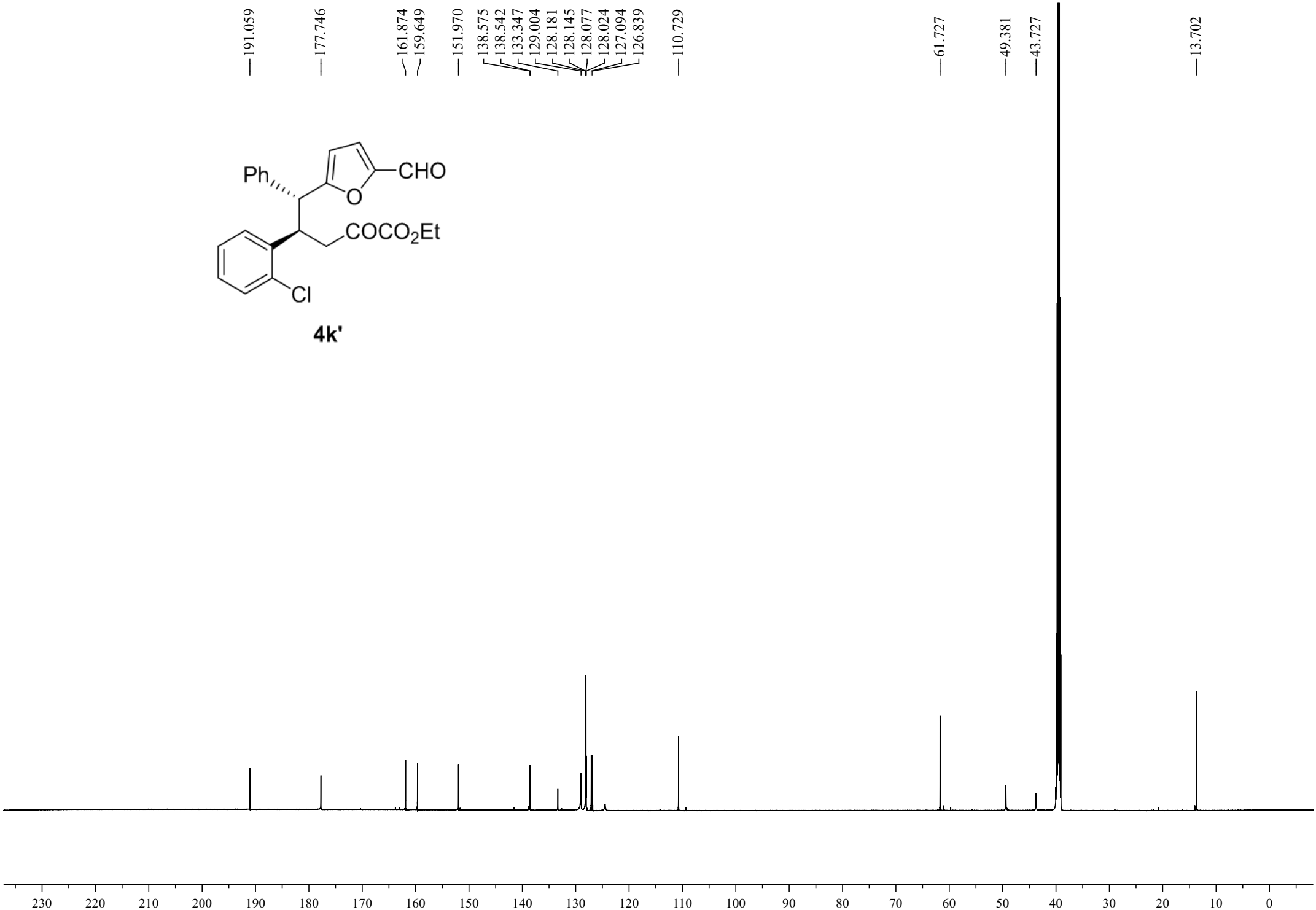
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Cl
4k'
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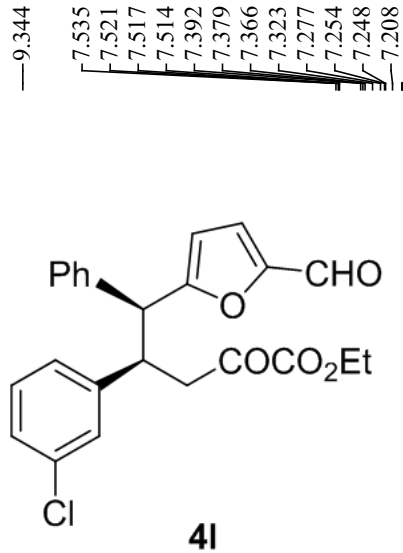

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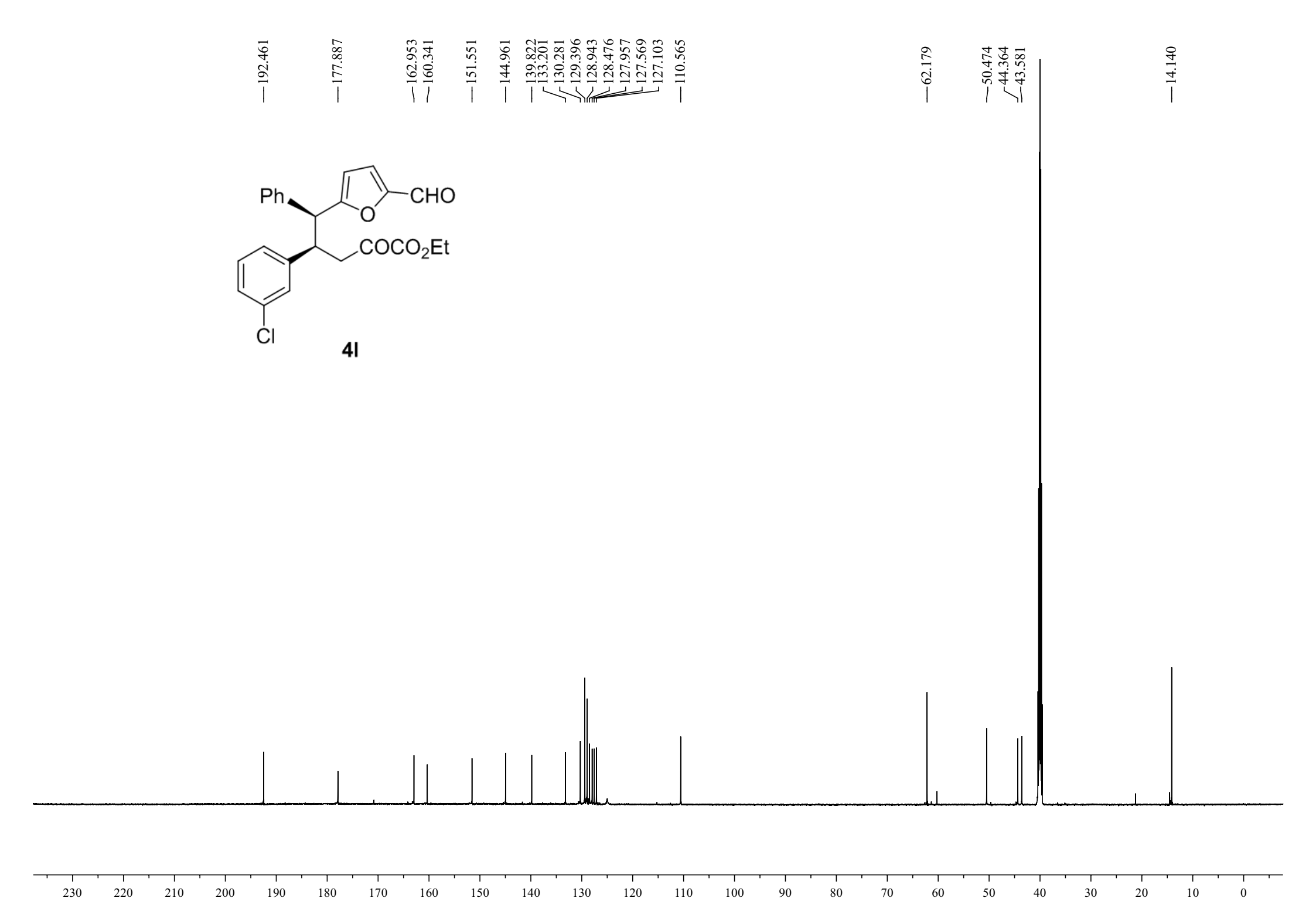
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CHO
O
COCO2Et
Cl
4l
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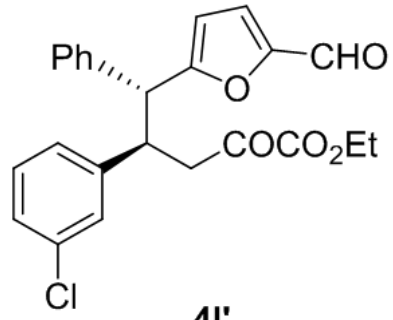

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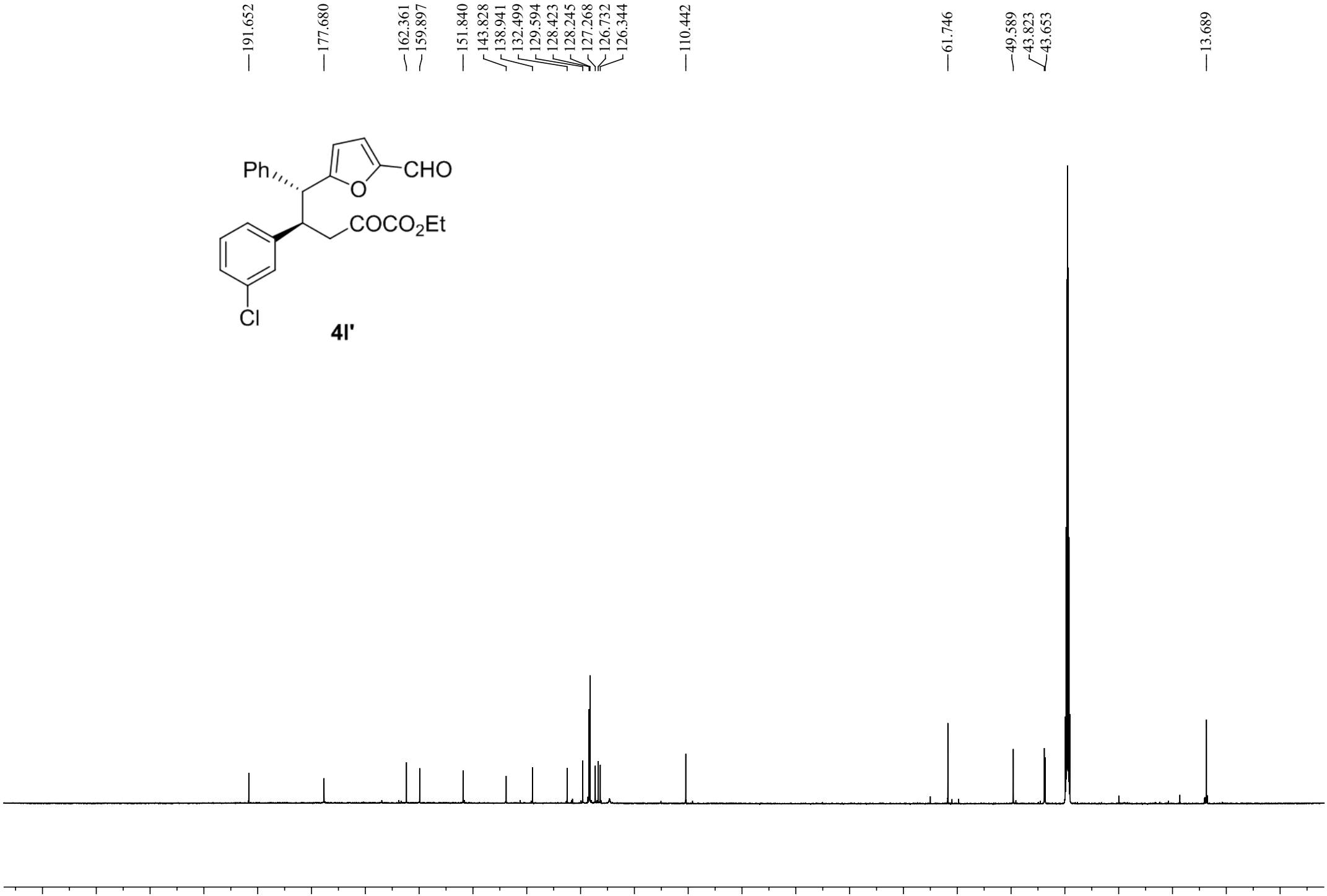
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CHO
COCO2Et
Cl
4l'
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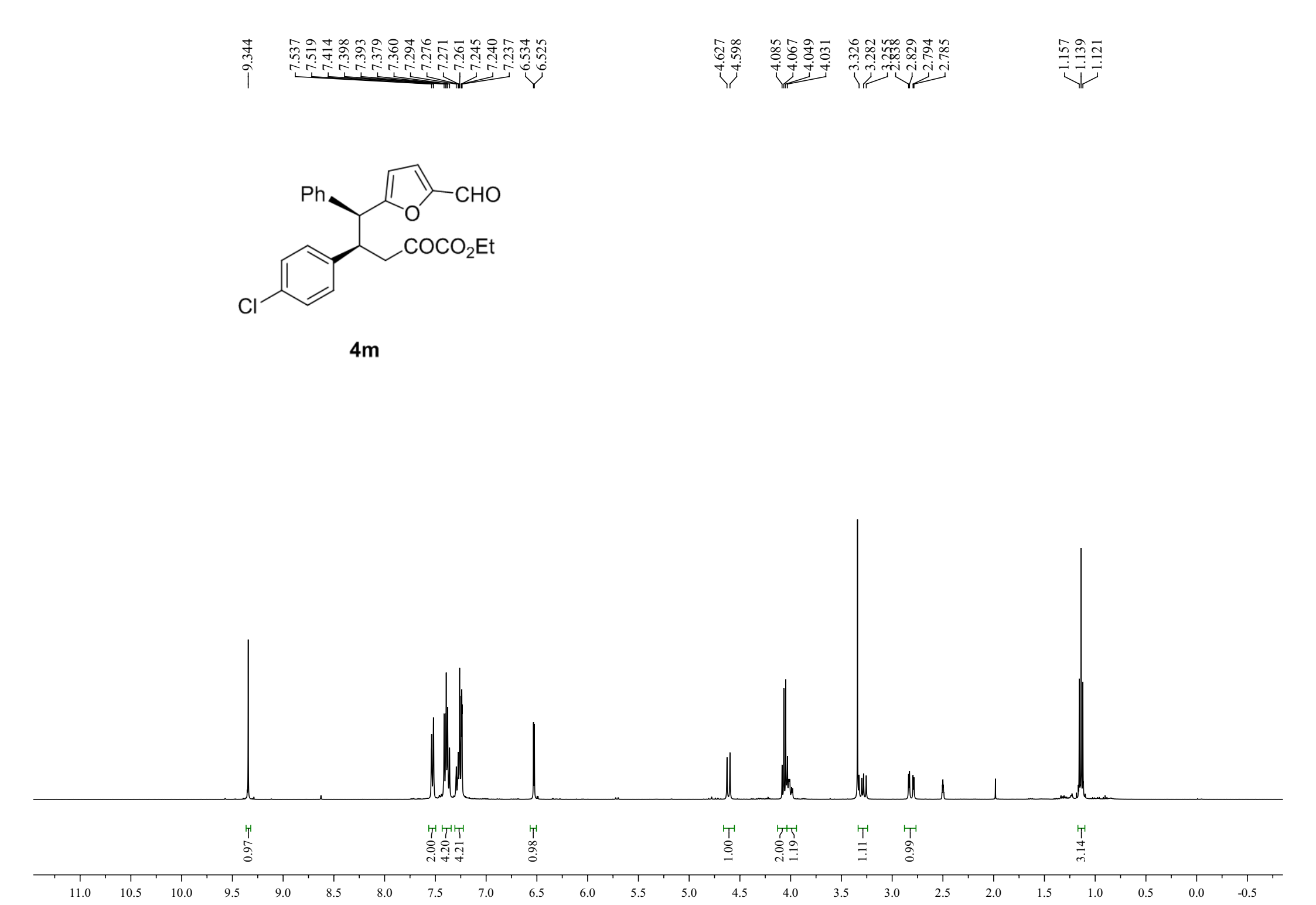
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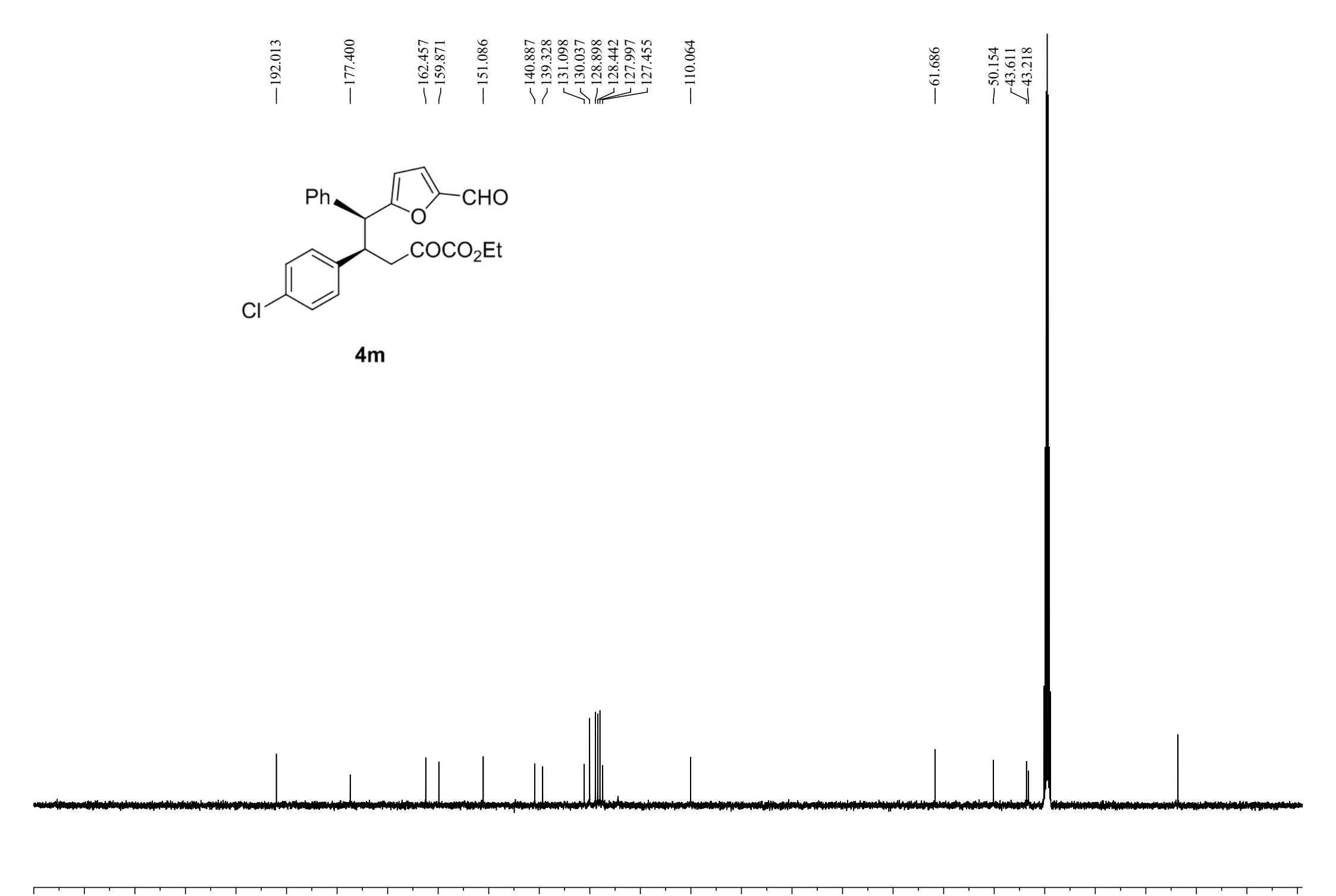
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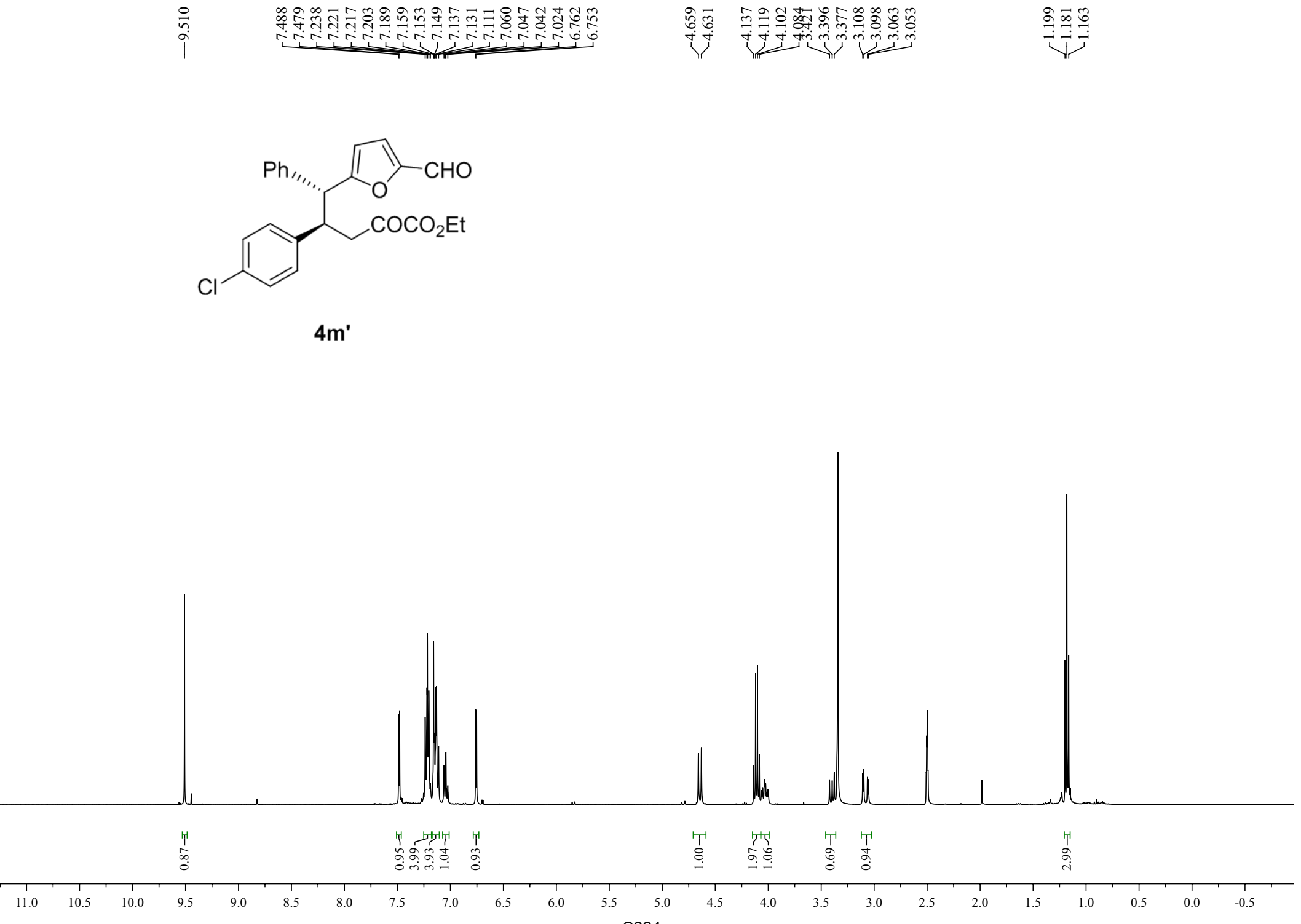
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Cl
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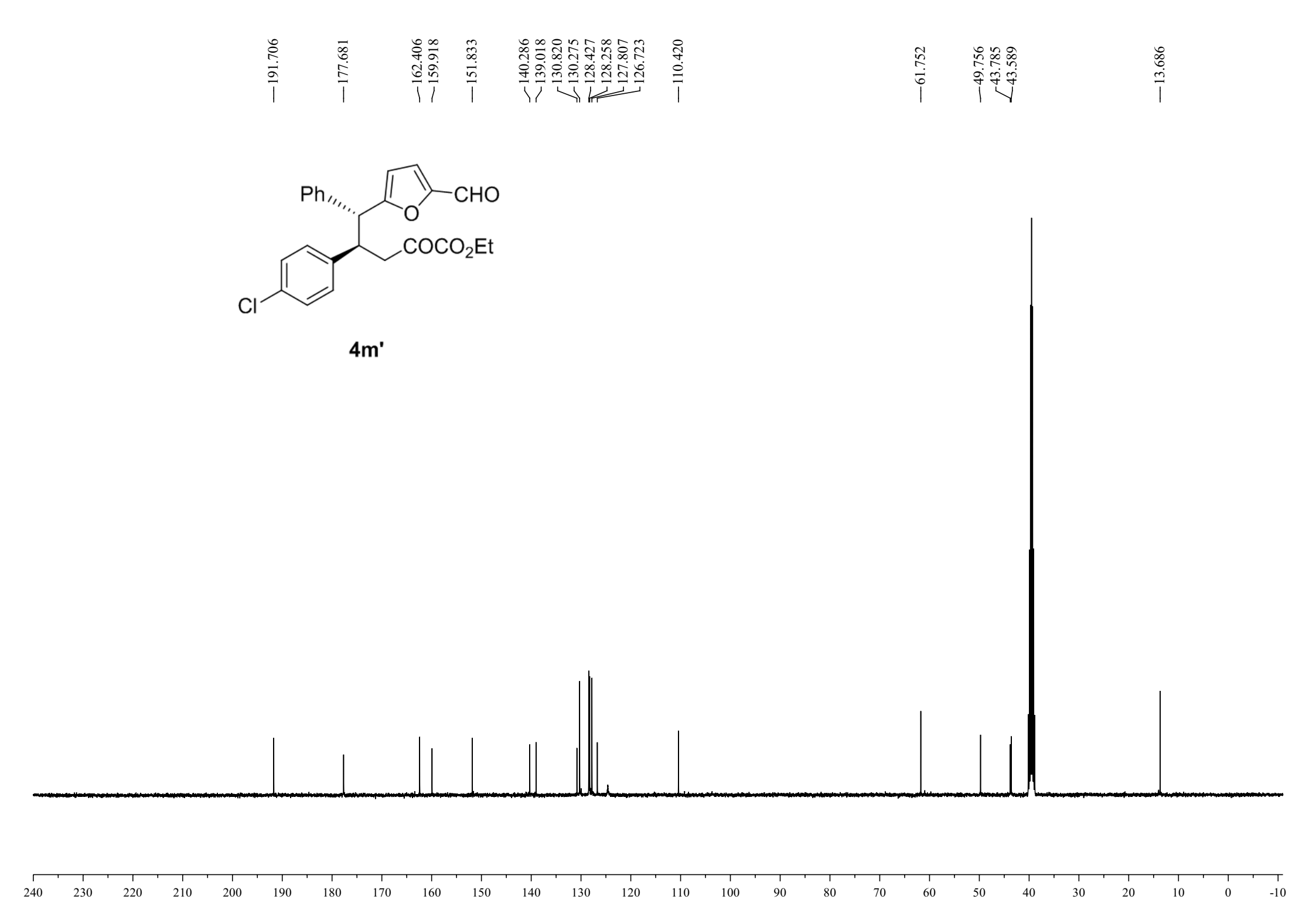
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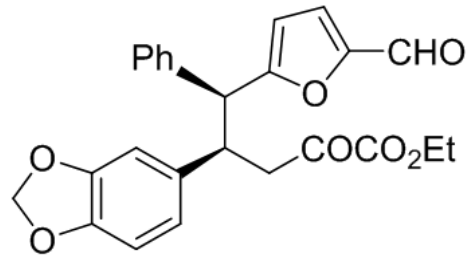
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4n

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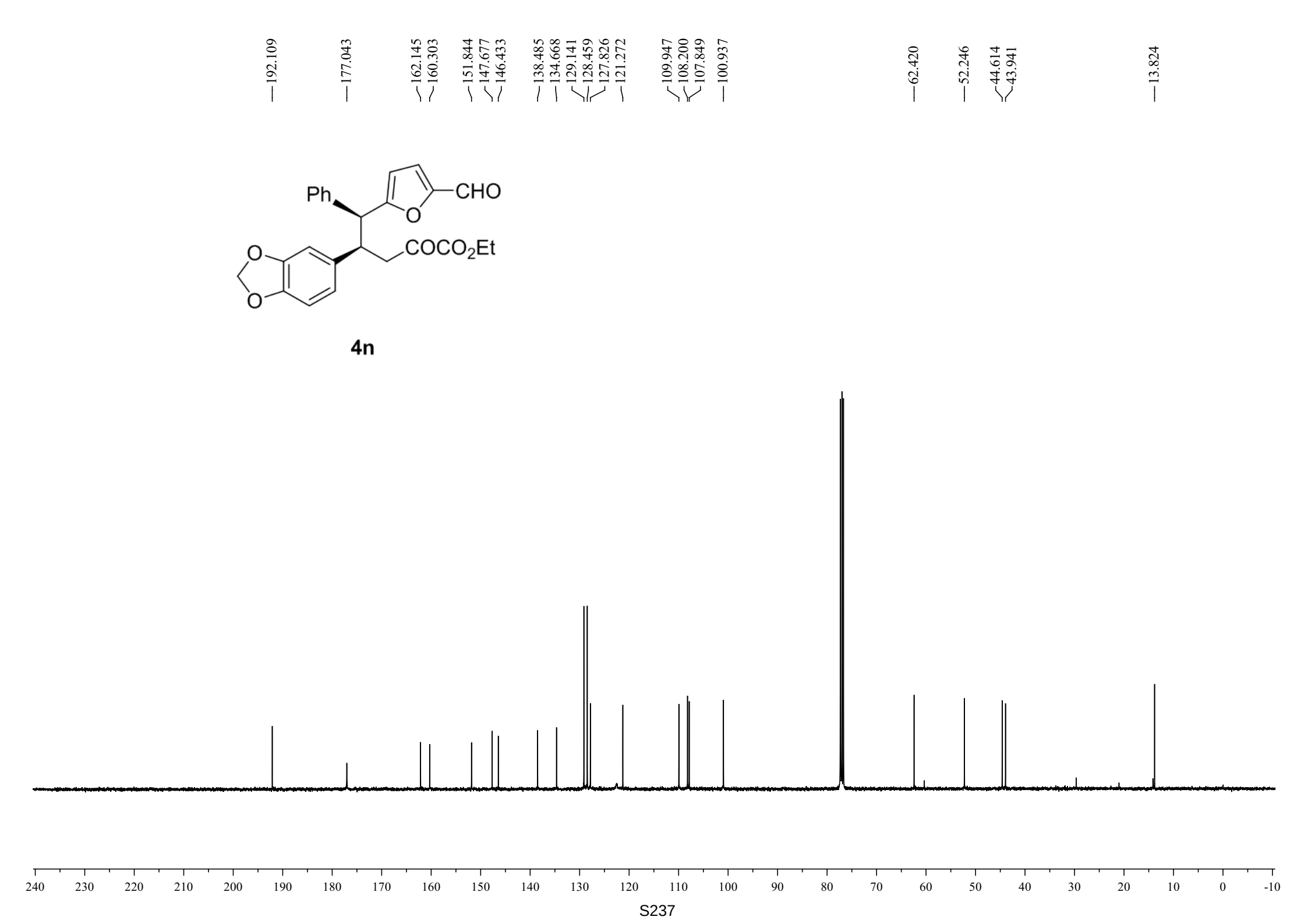
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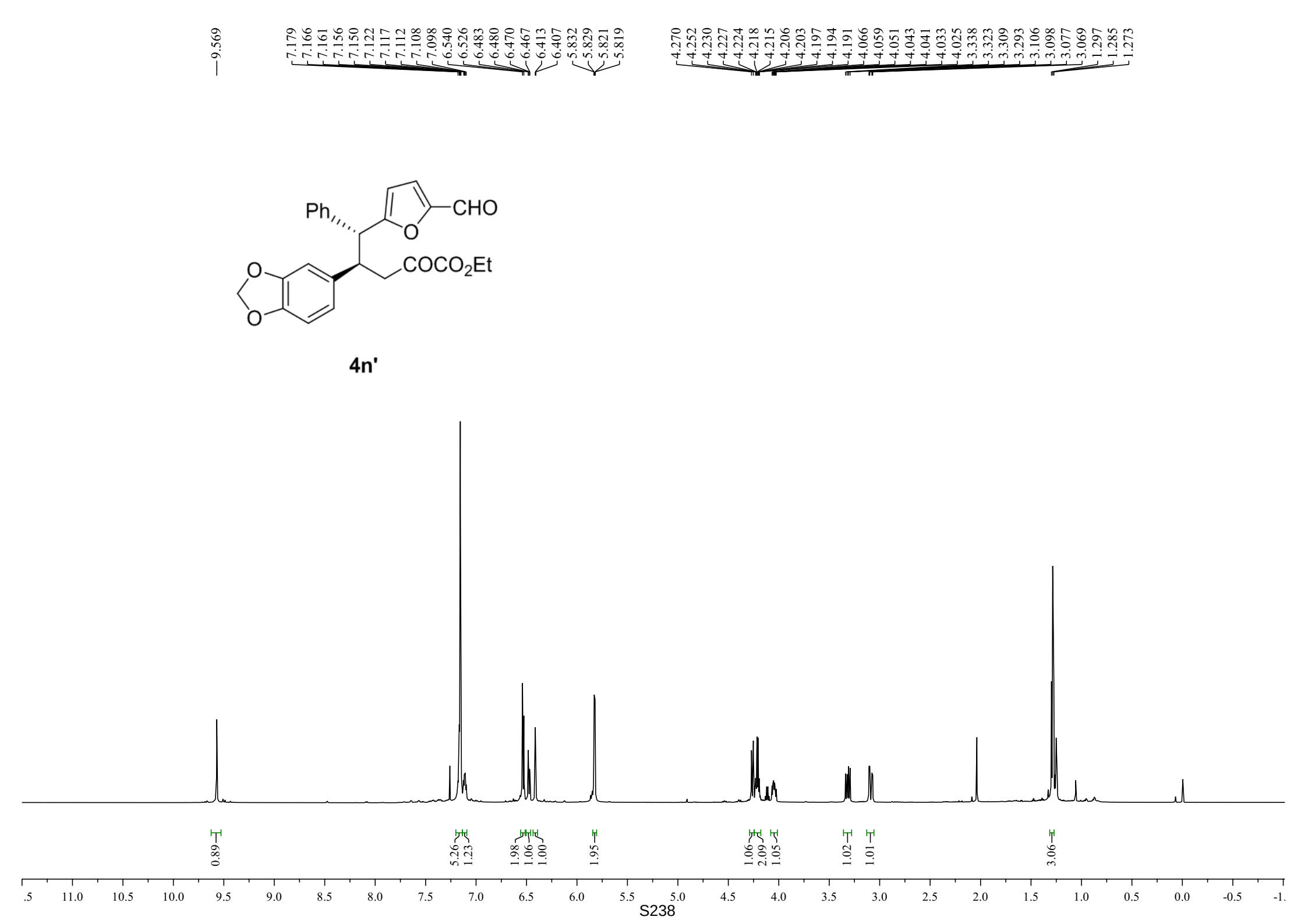
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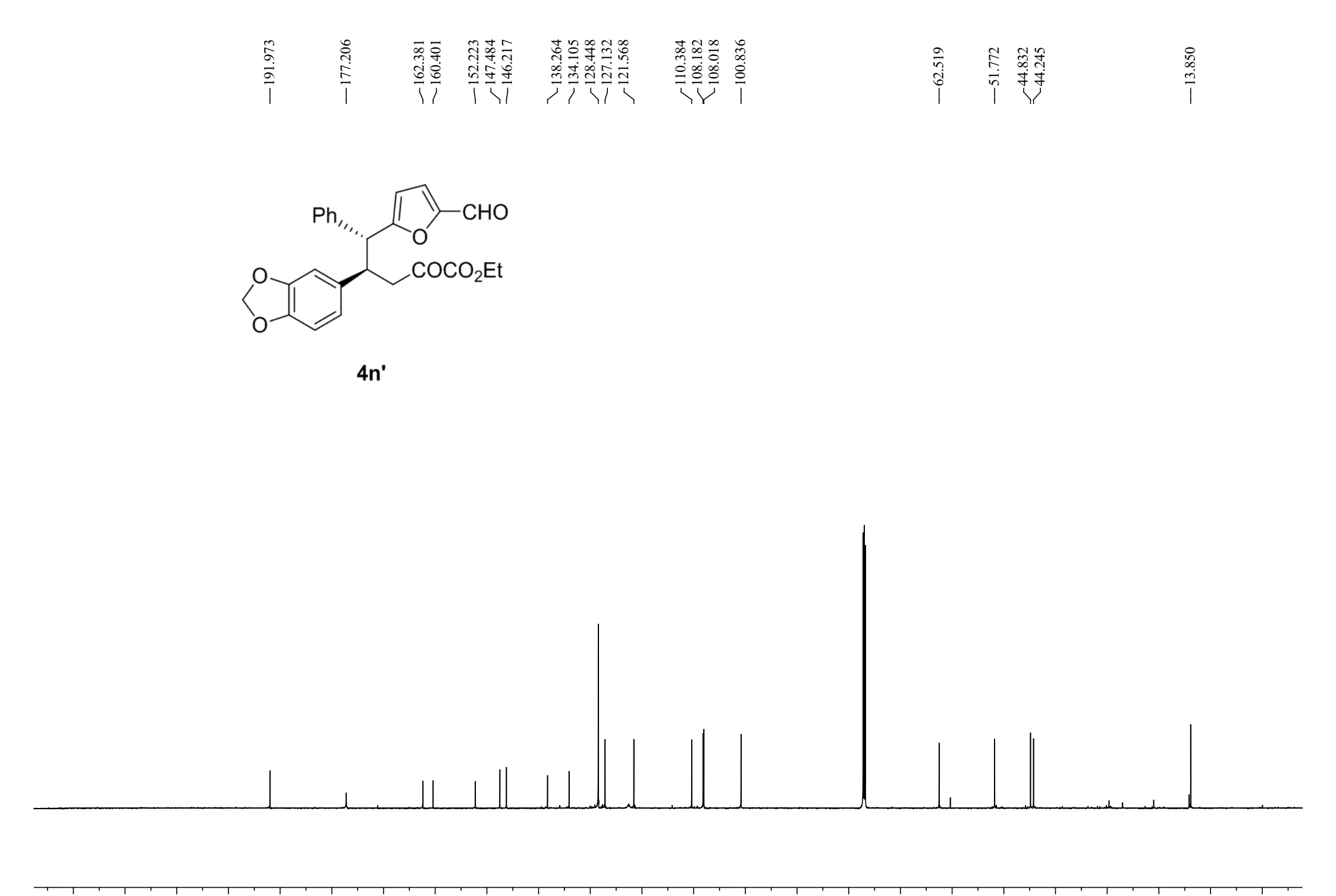
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CHO
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COCO2Et
O
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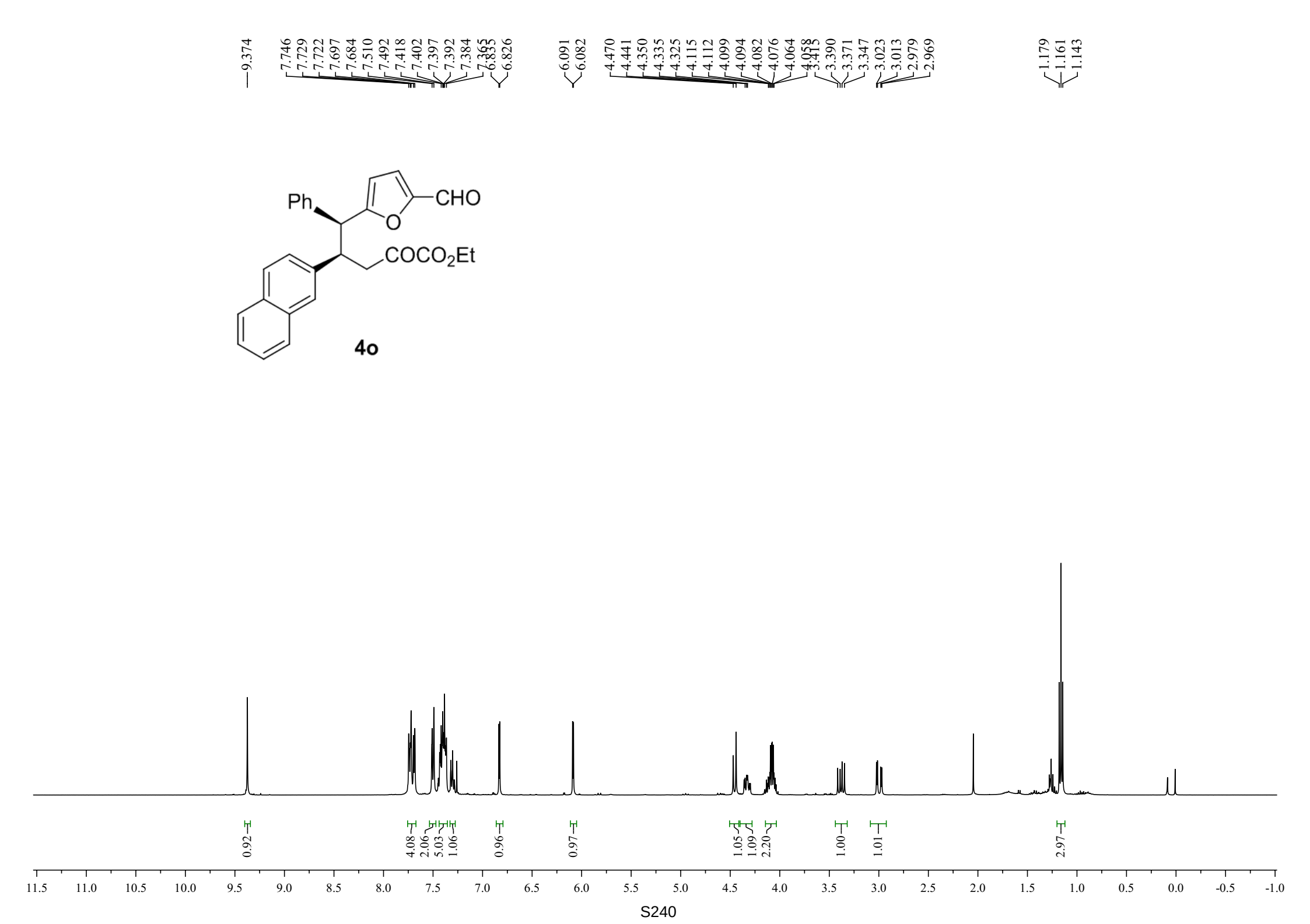
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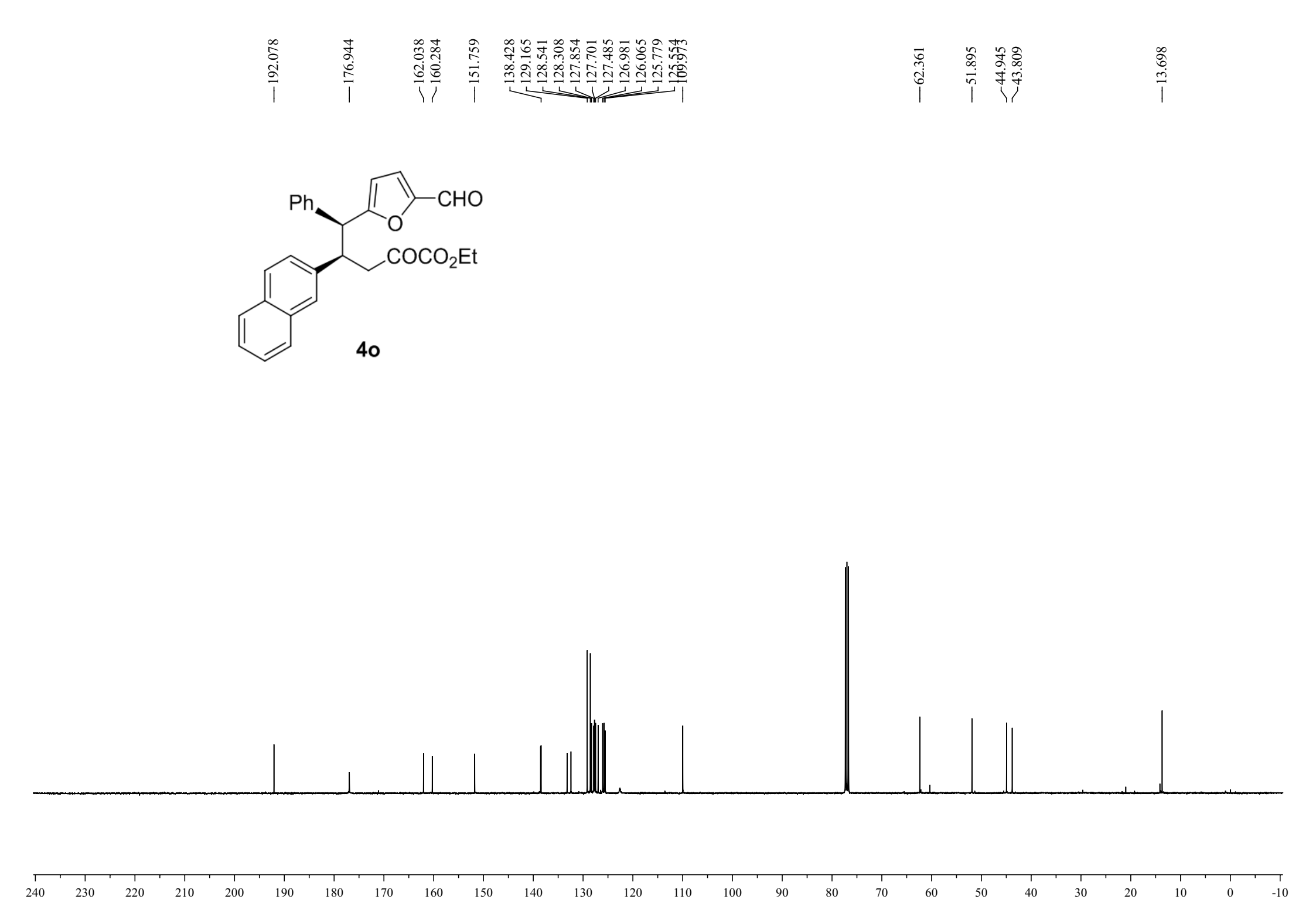
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CHO
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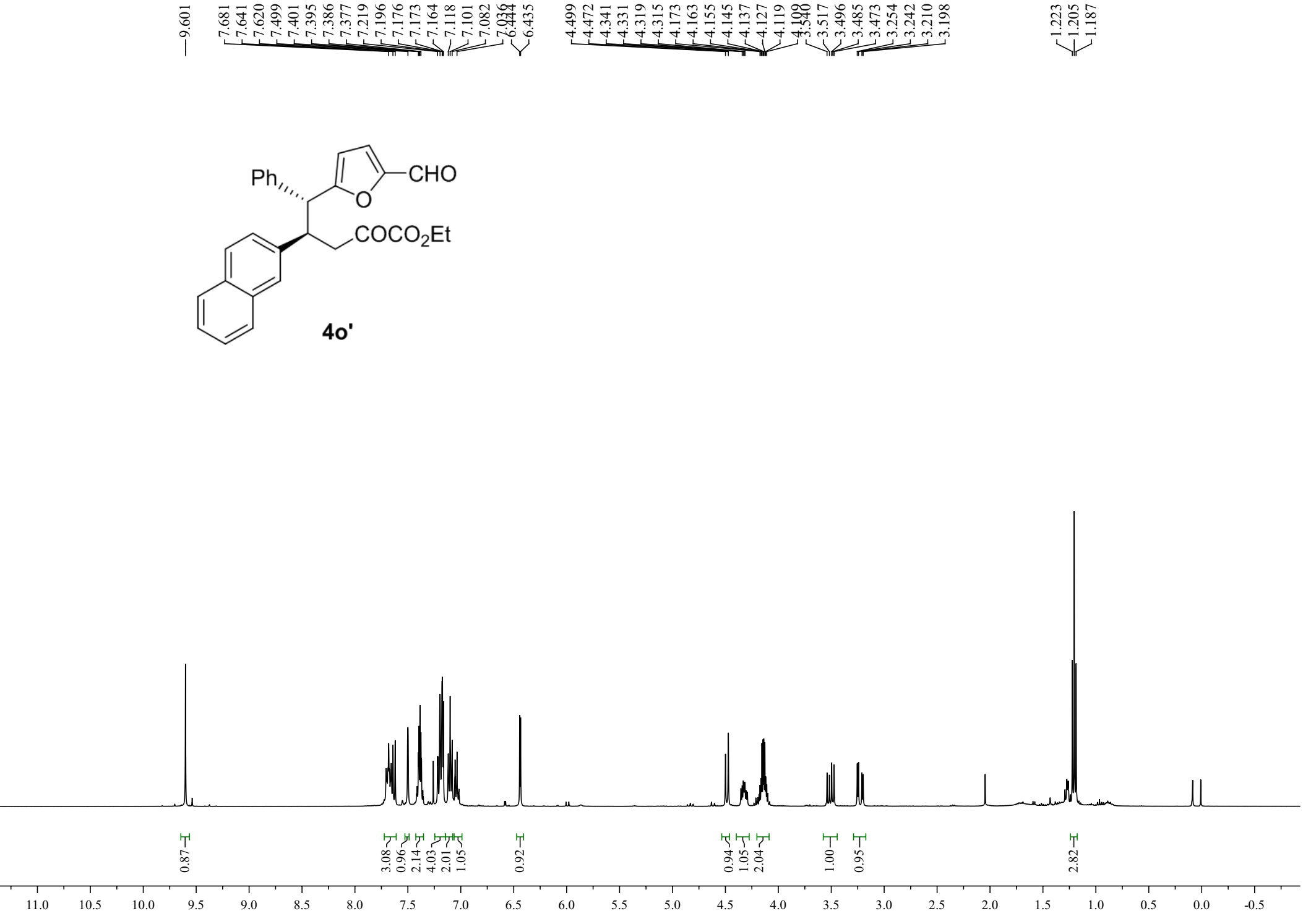
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1.187
Ph
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COCO2Et
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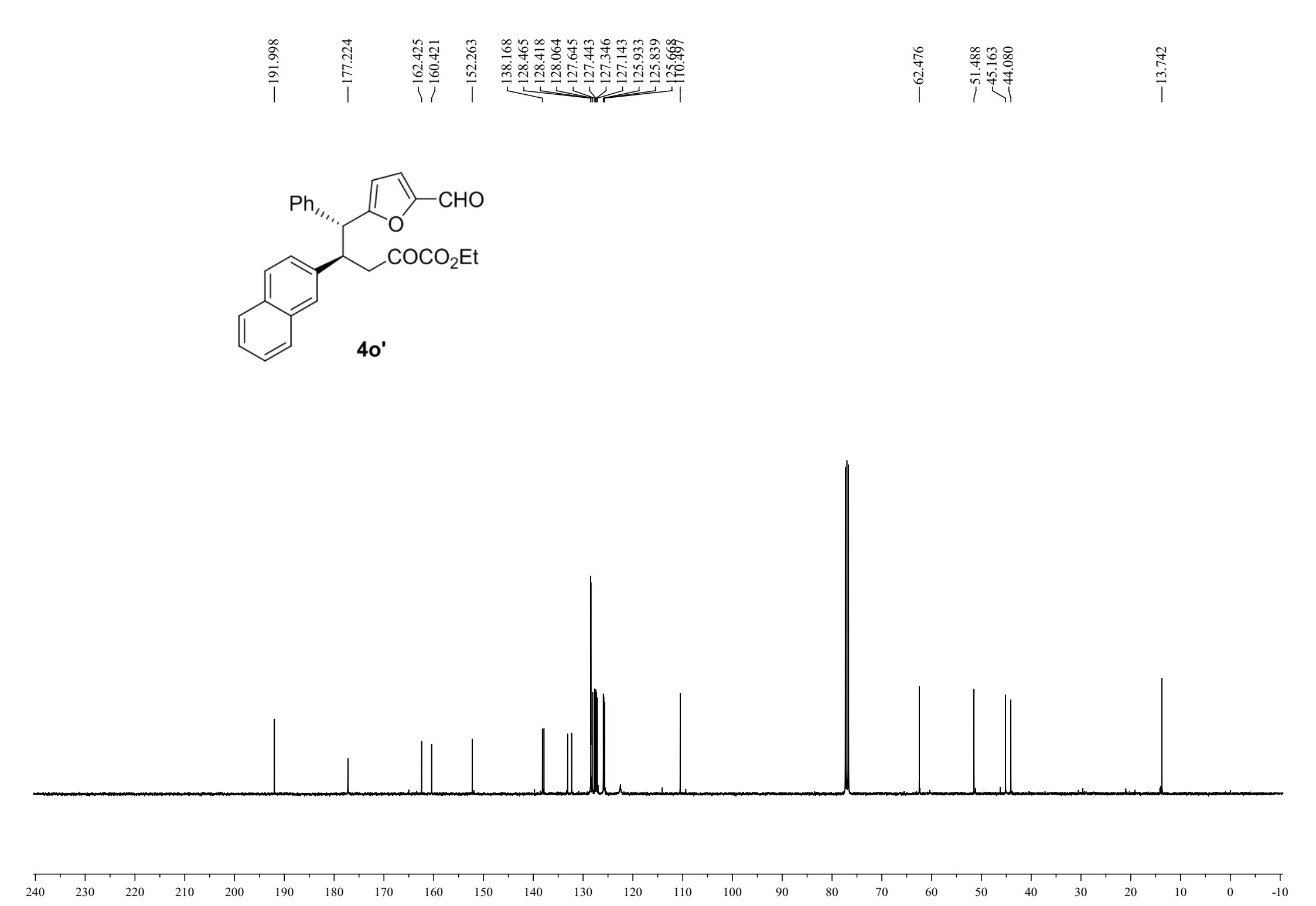
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CHO
COCO2Et
4o'
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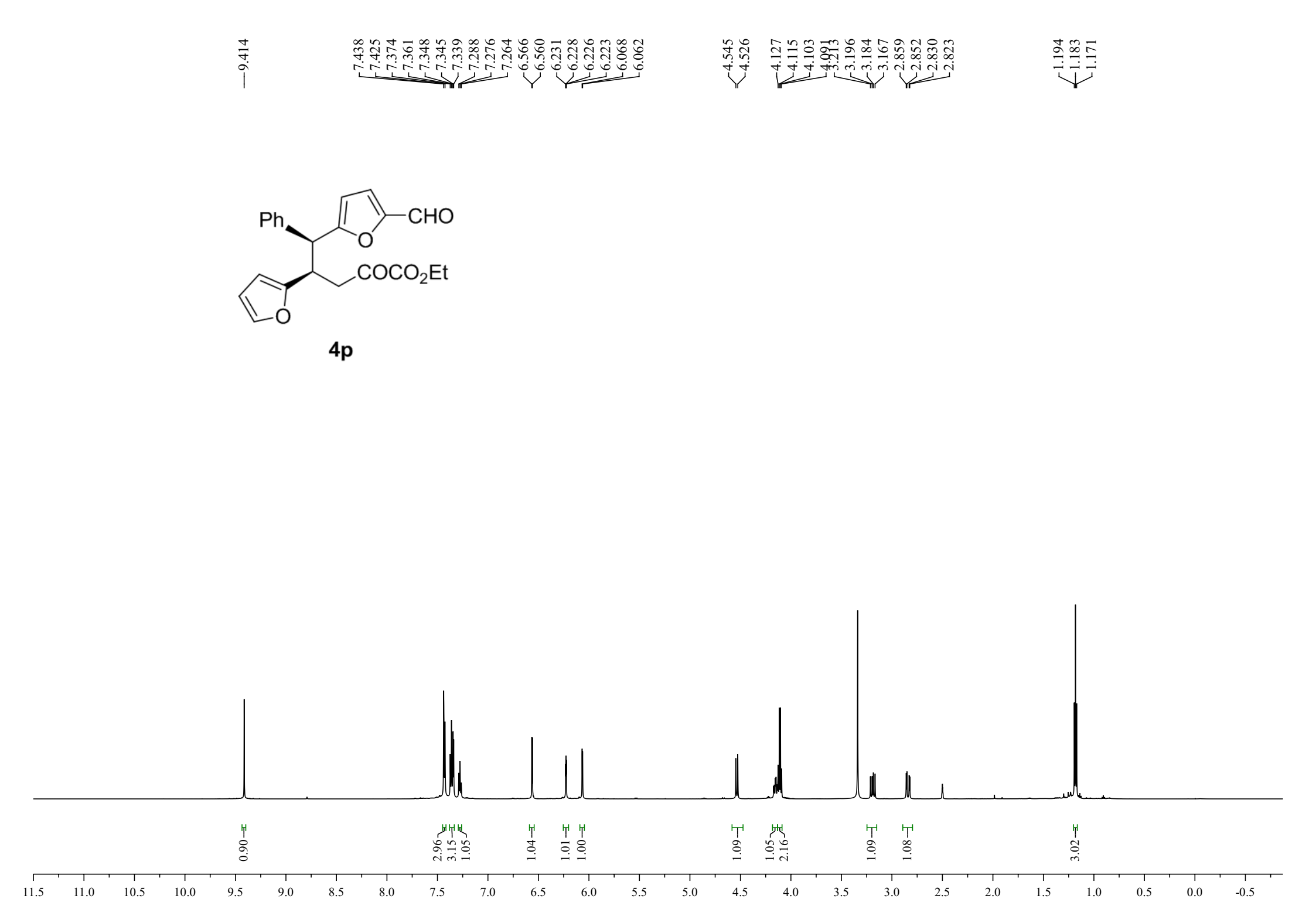
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O
4p
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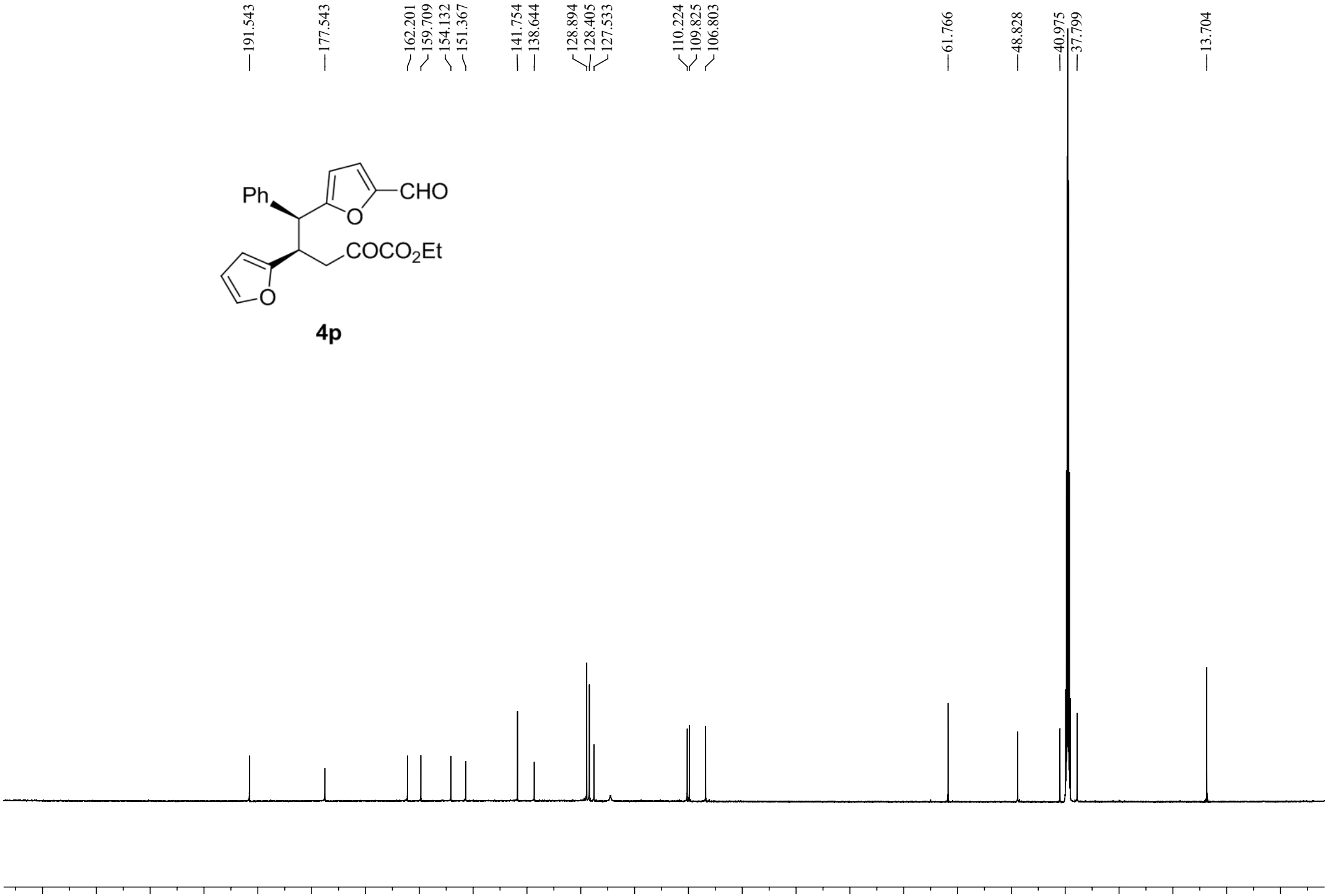
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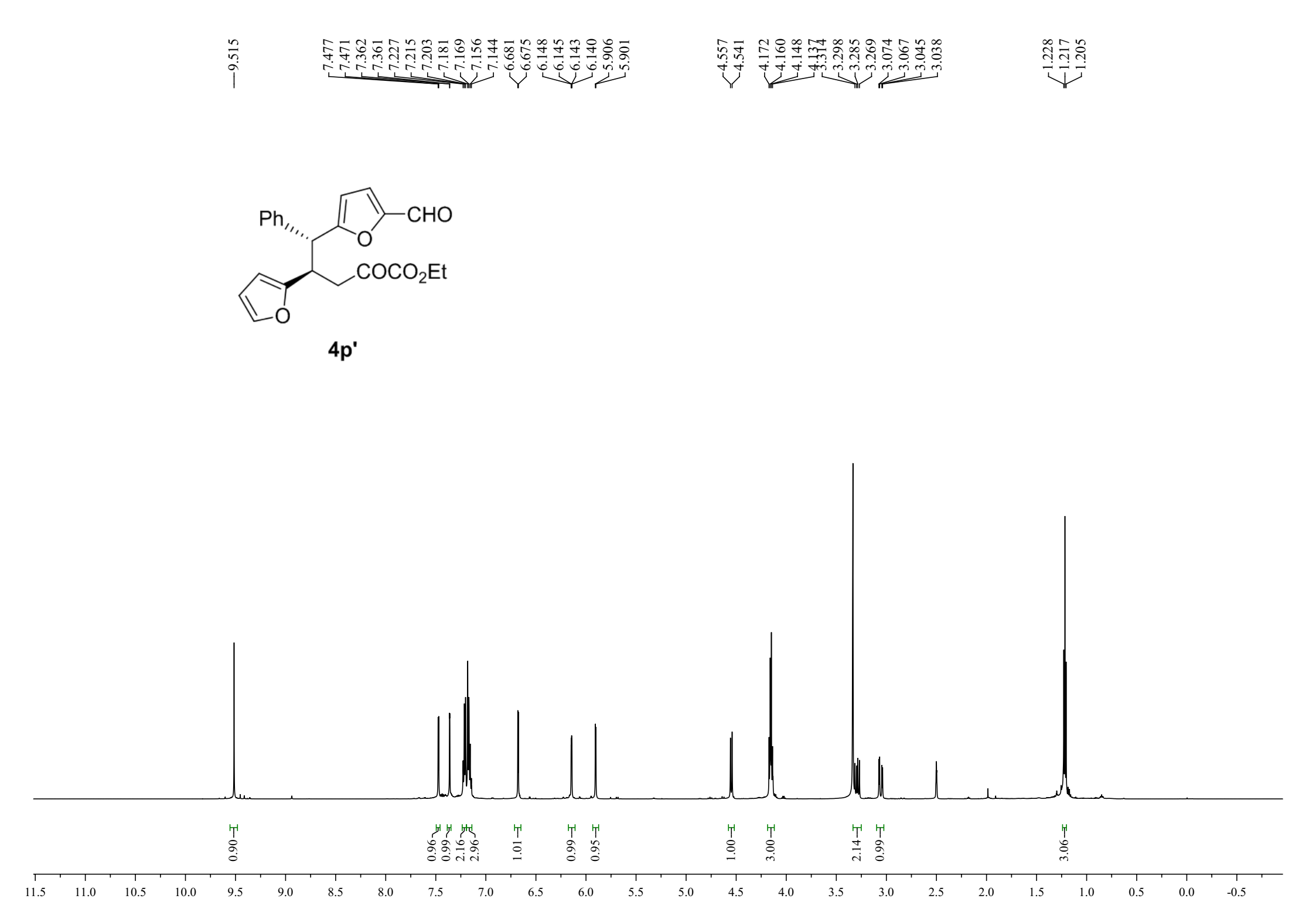
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COCO2Et
O
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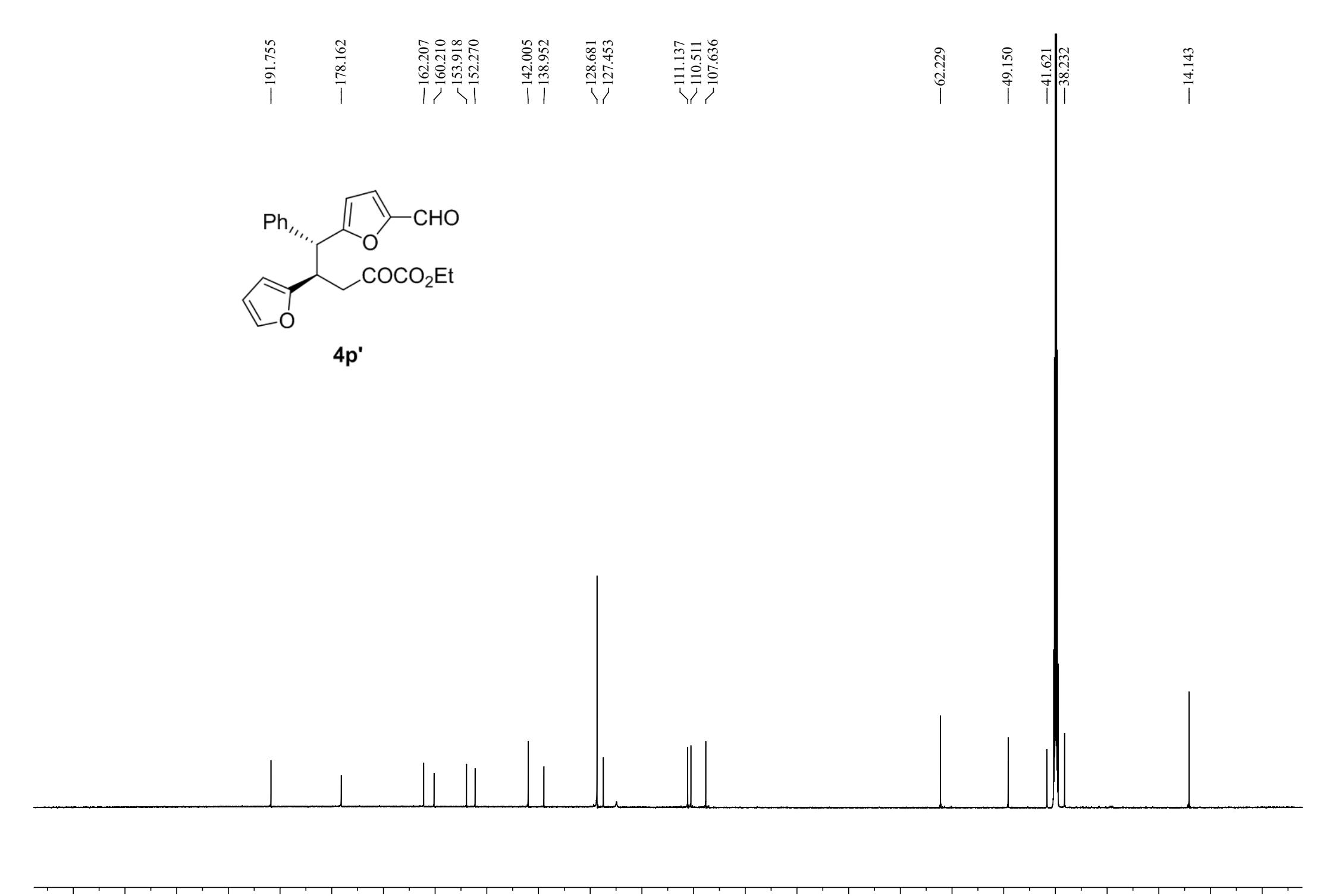
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COCO2Et
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4p'
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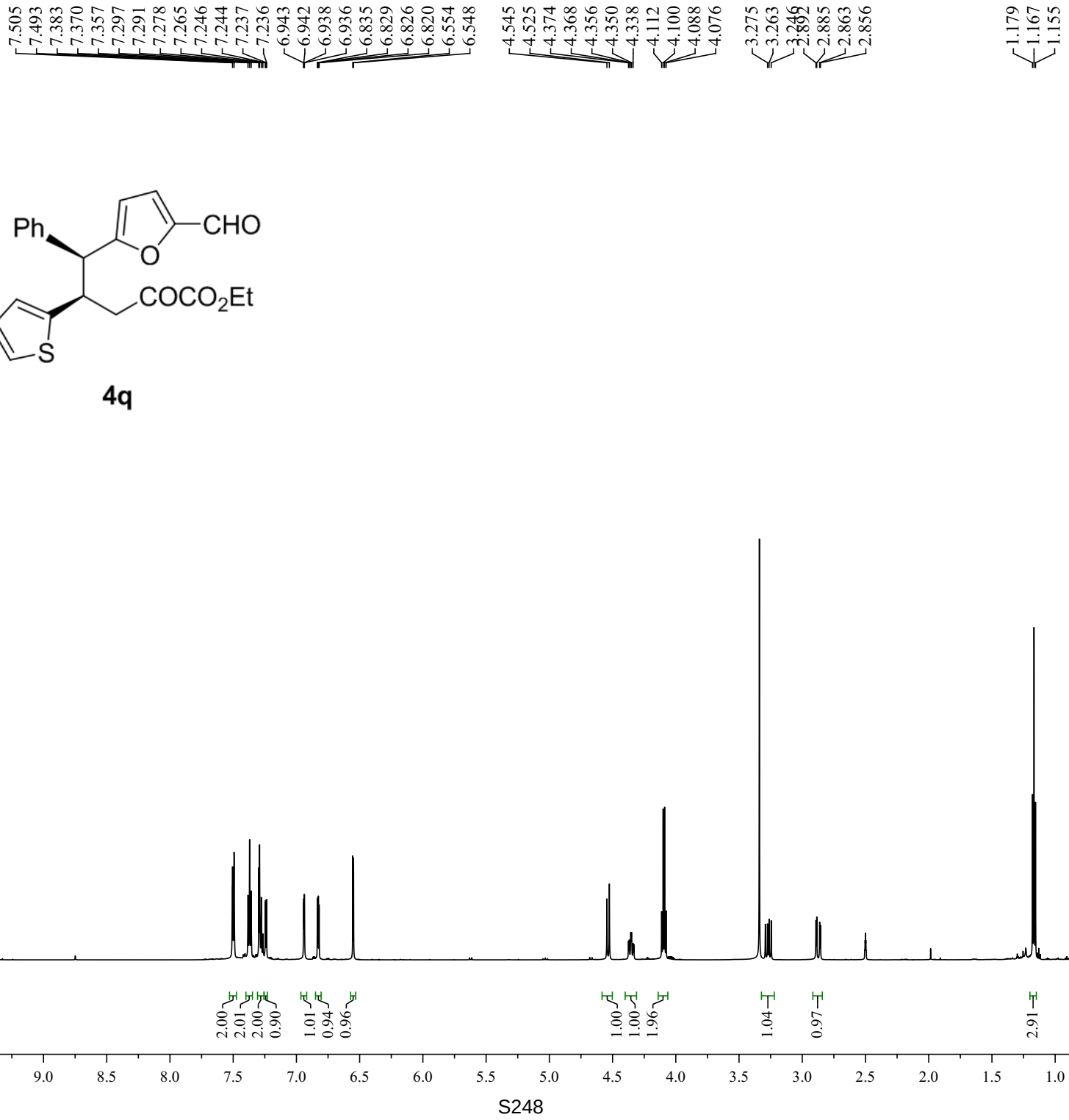
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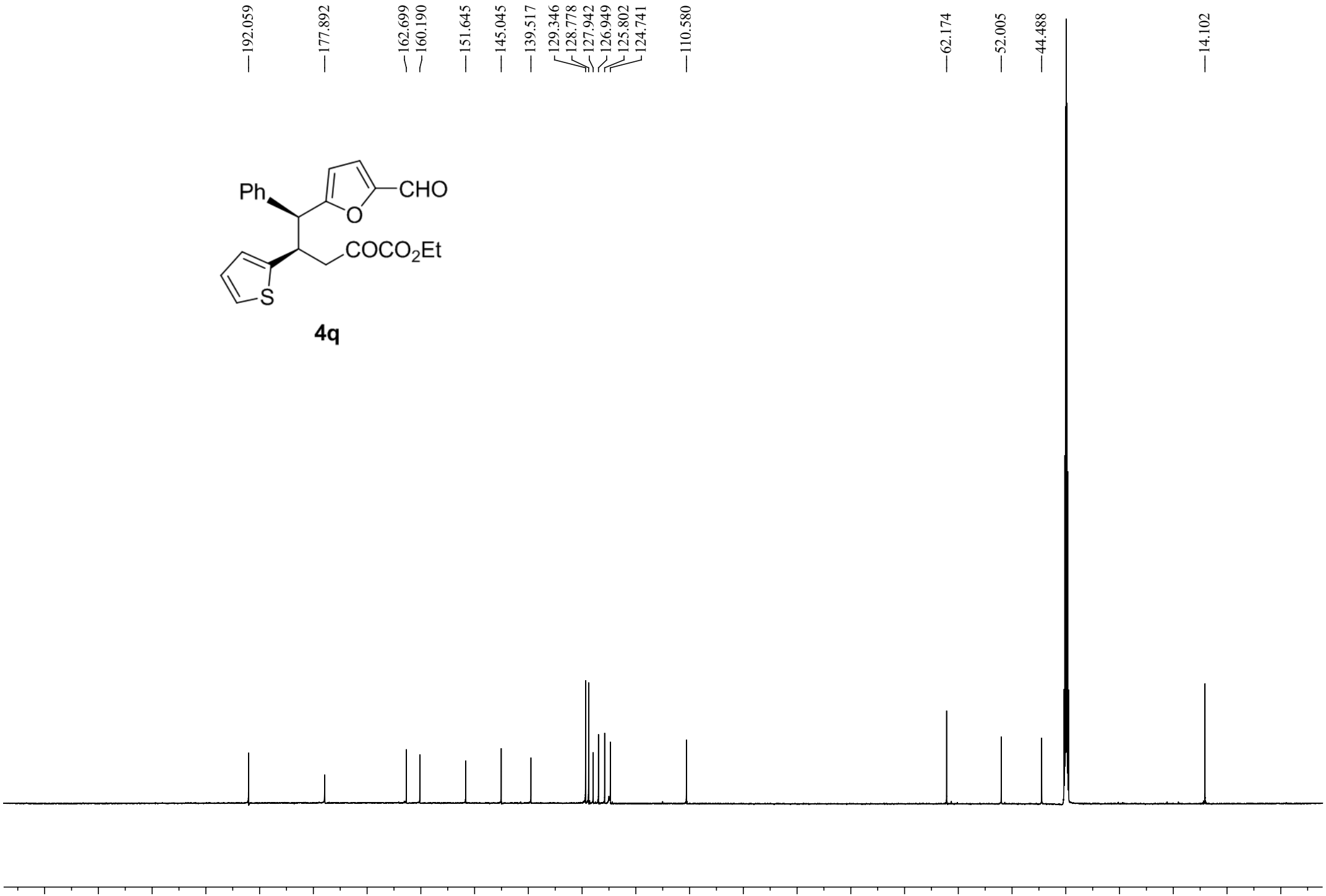
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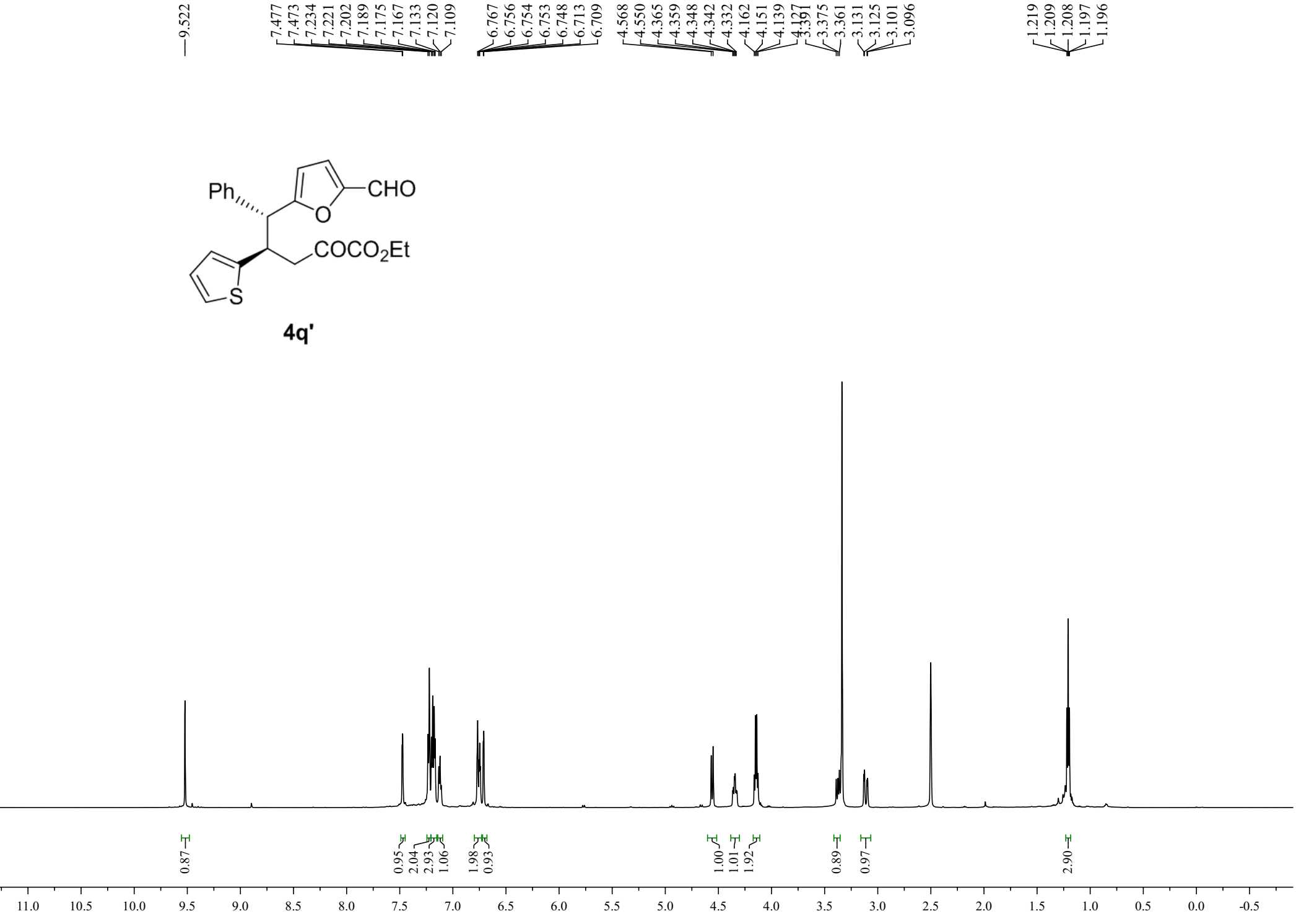
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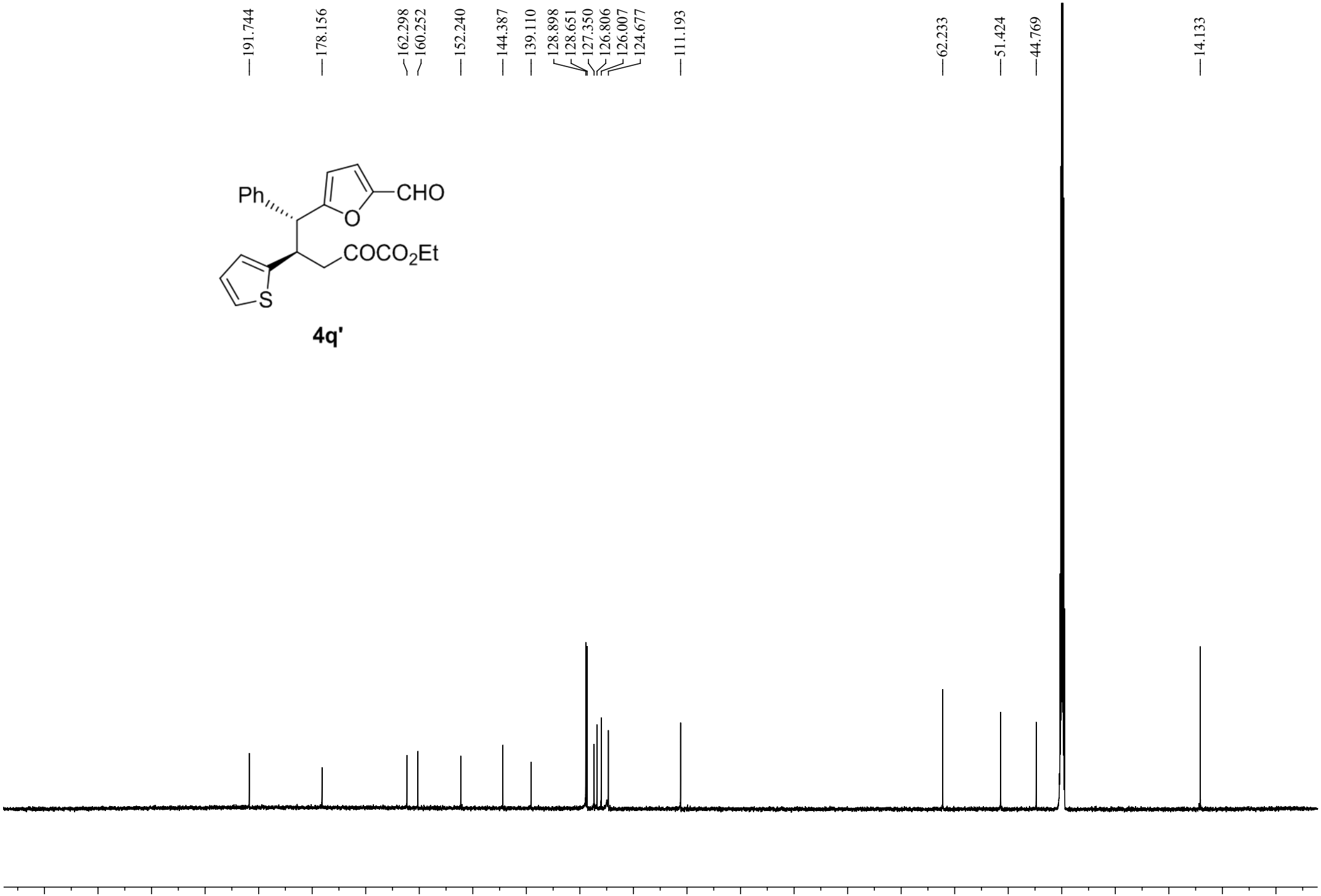
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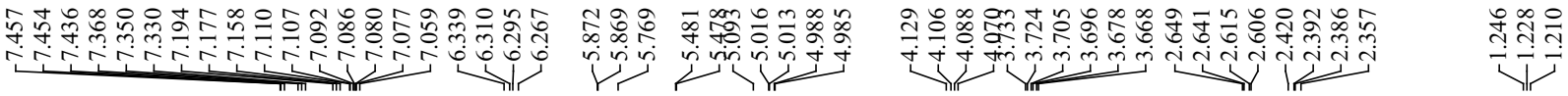
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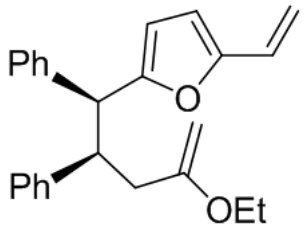
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Ph
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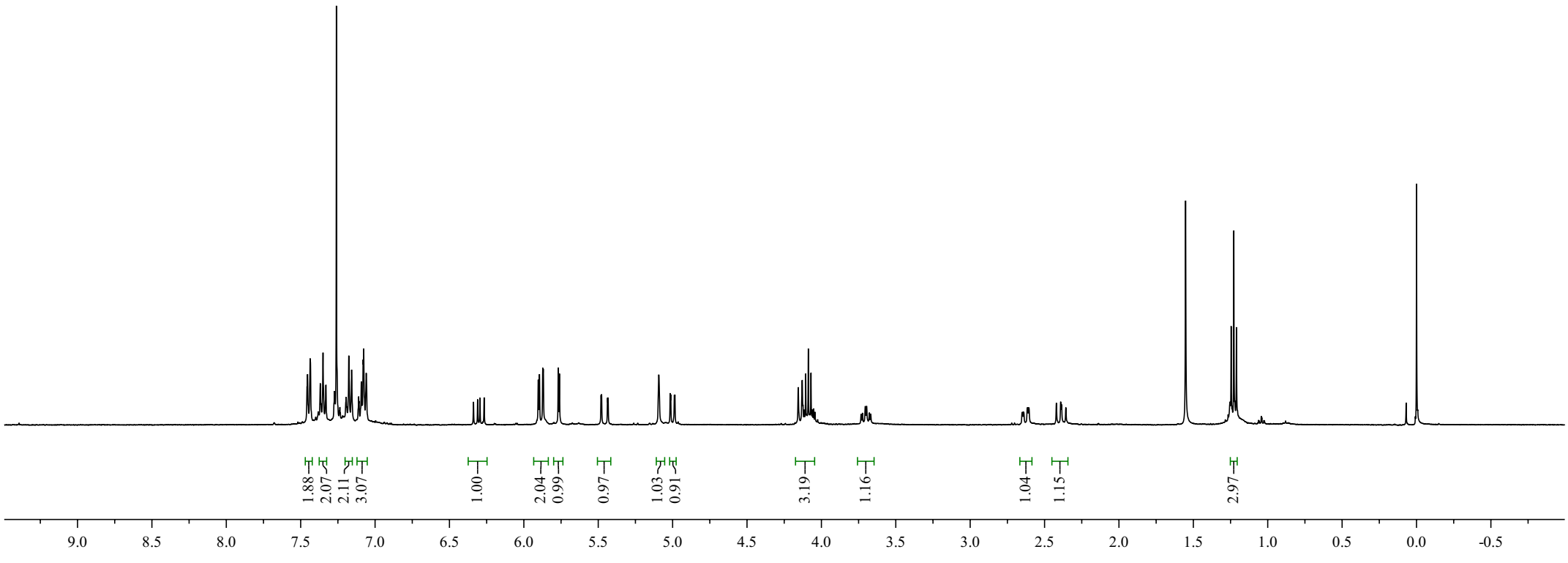
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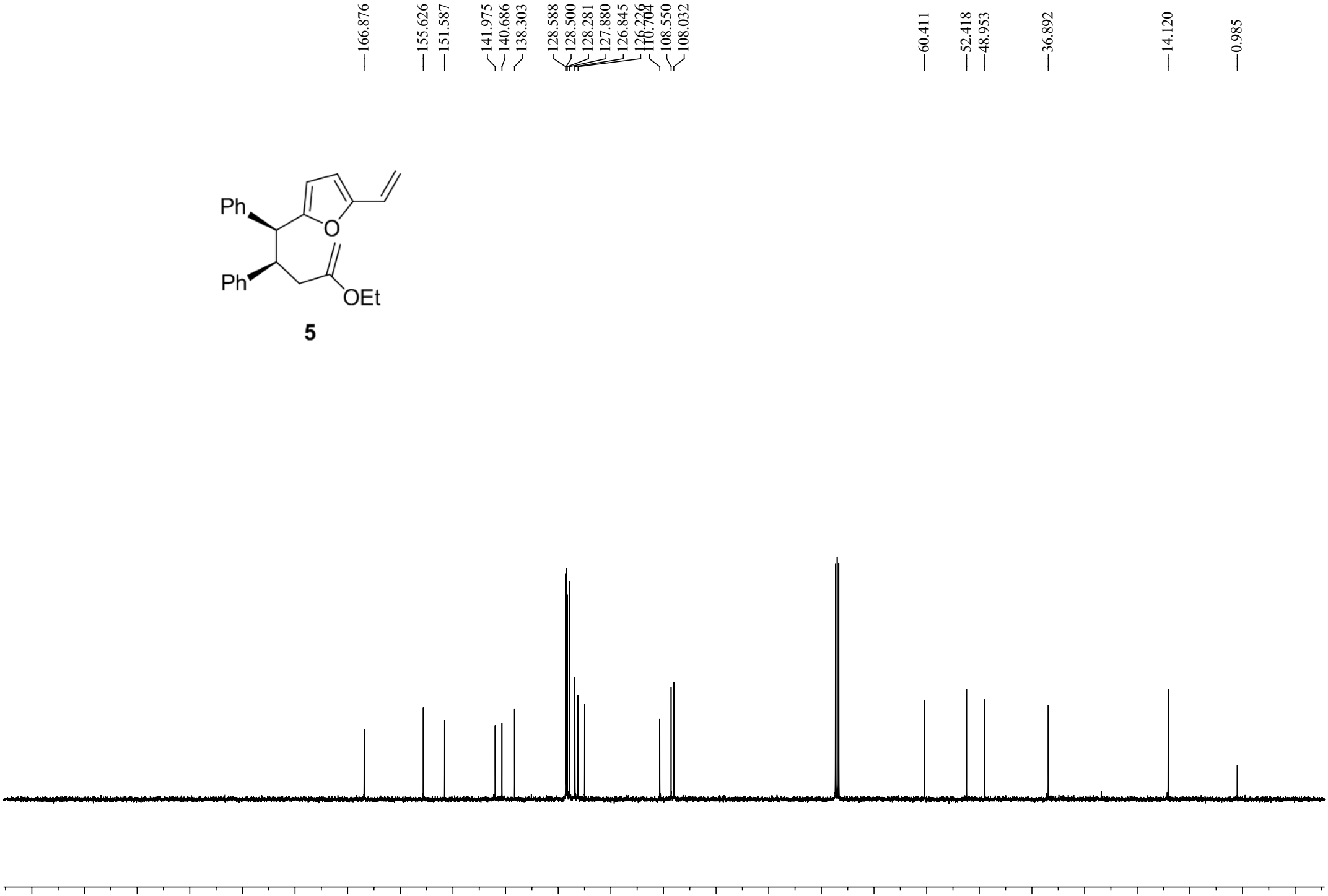
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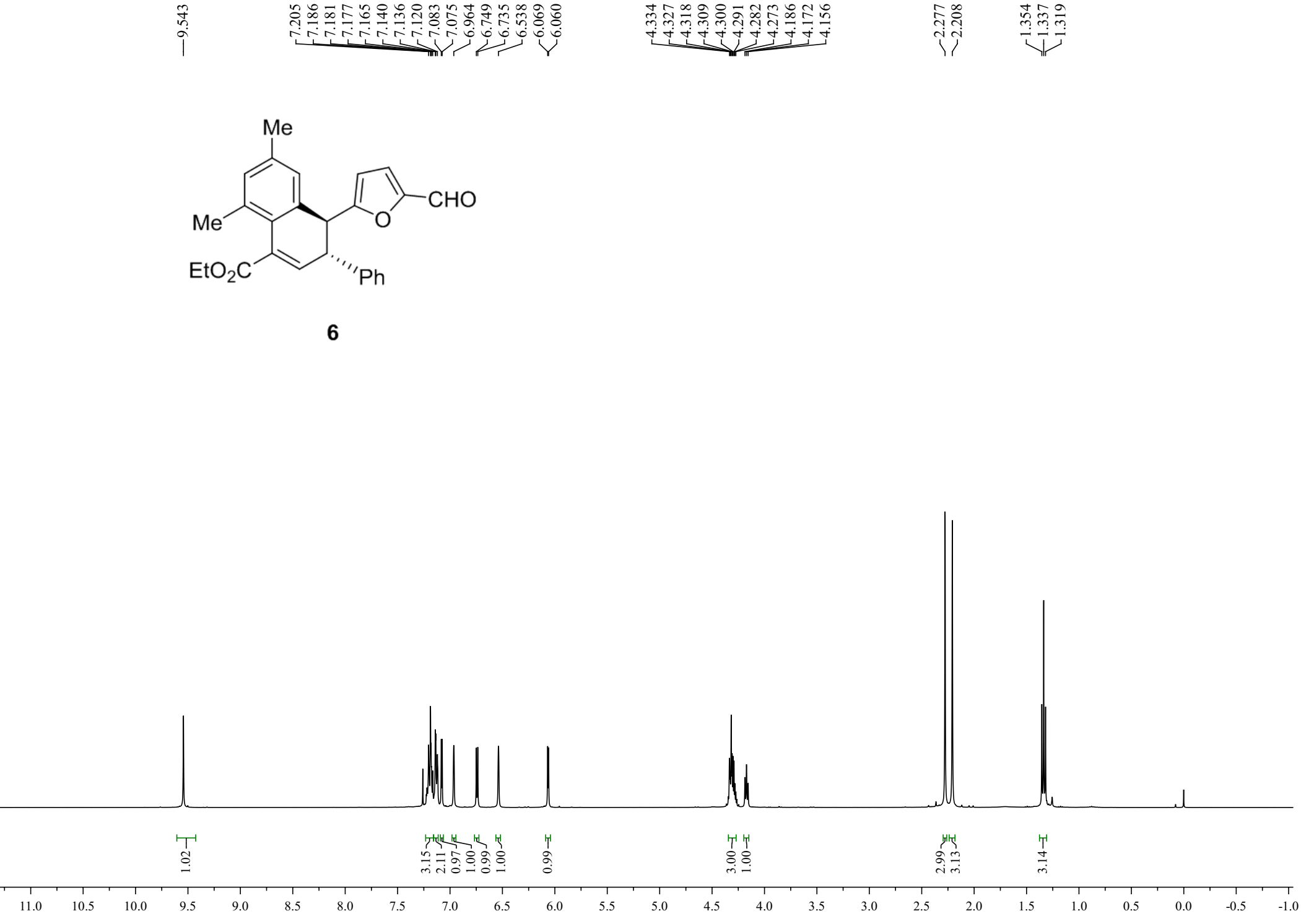
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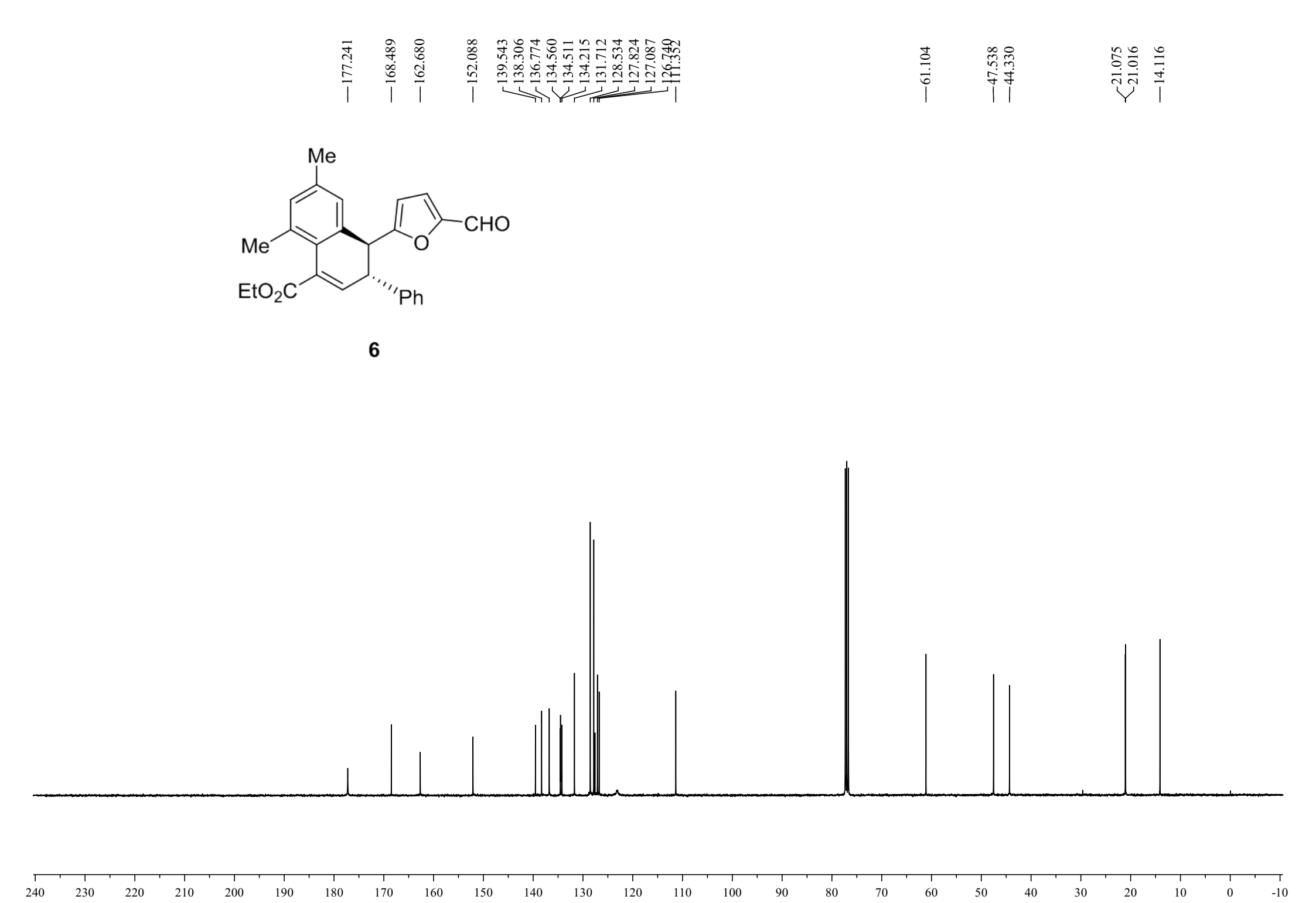
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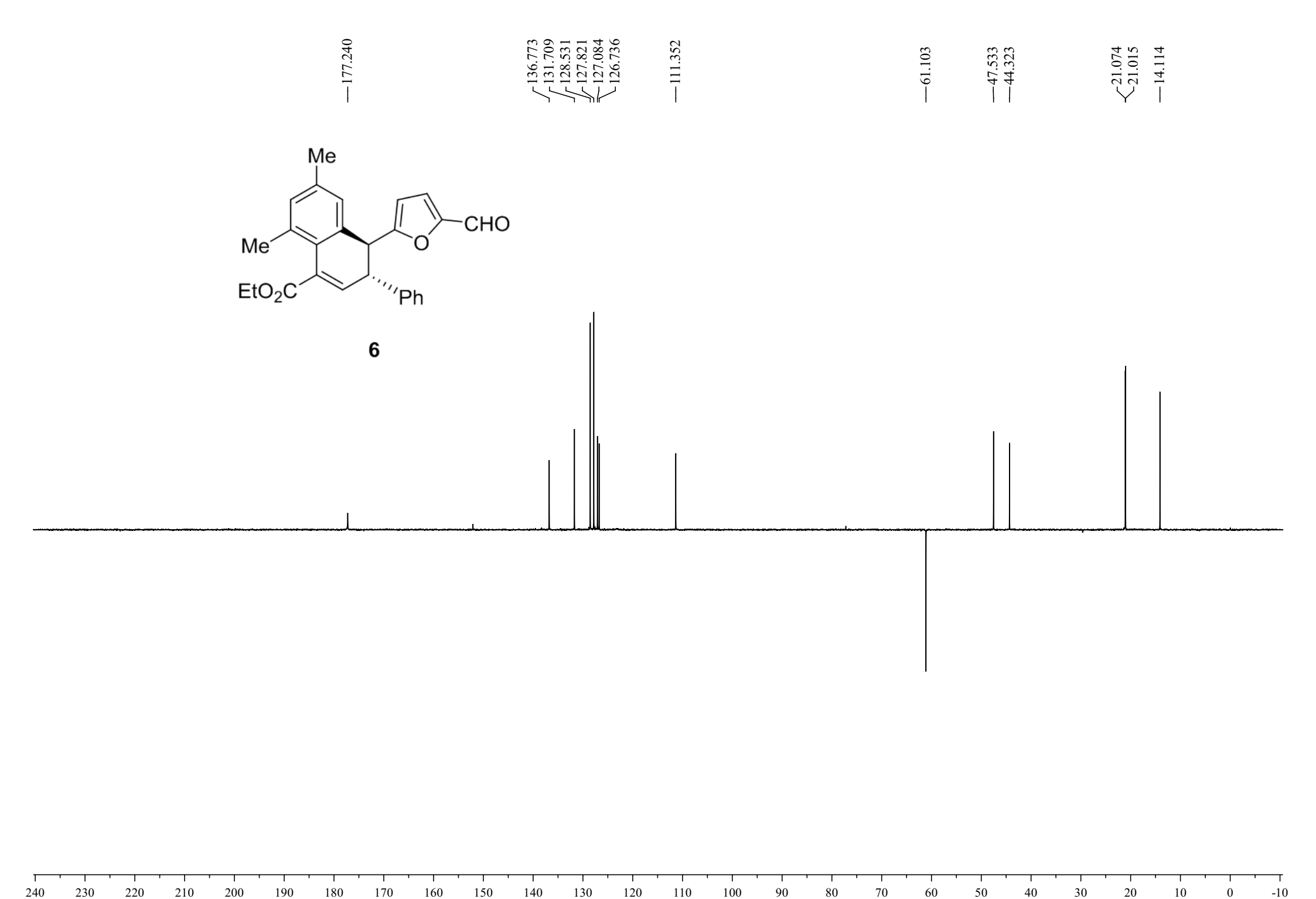
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61.103
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21.015
14.114
Me
Me
CHO
O
EtO2C
Ph
6
240
230
220
210
200
190
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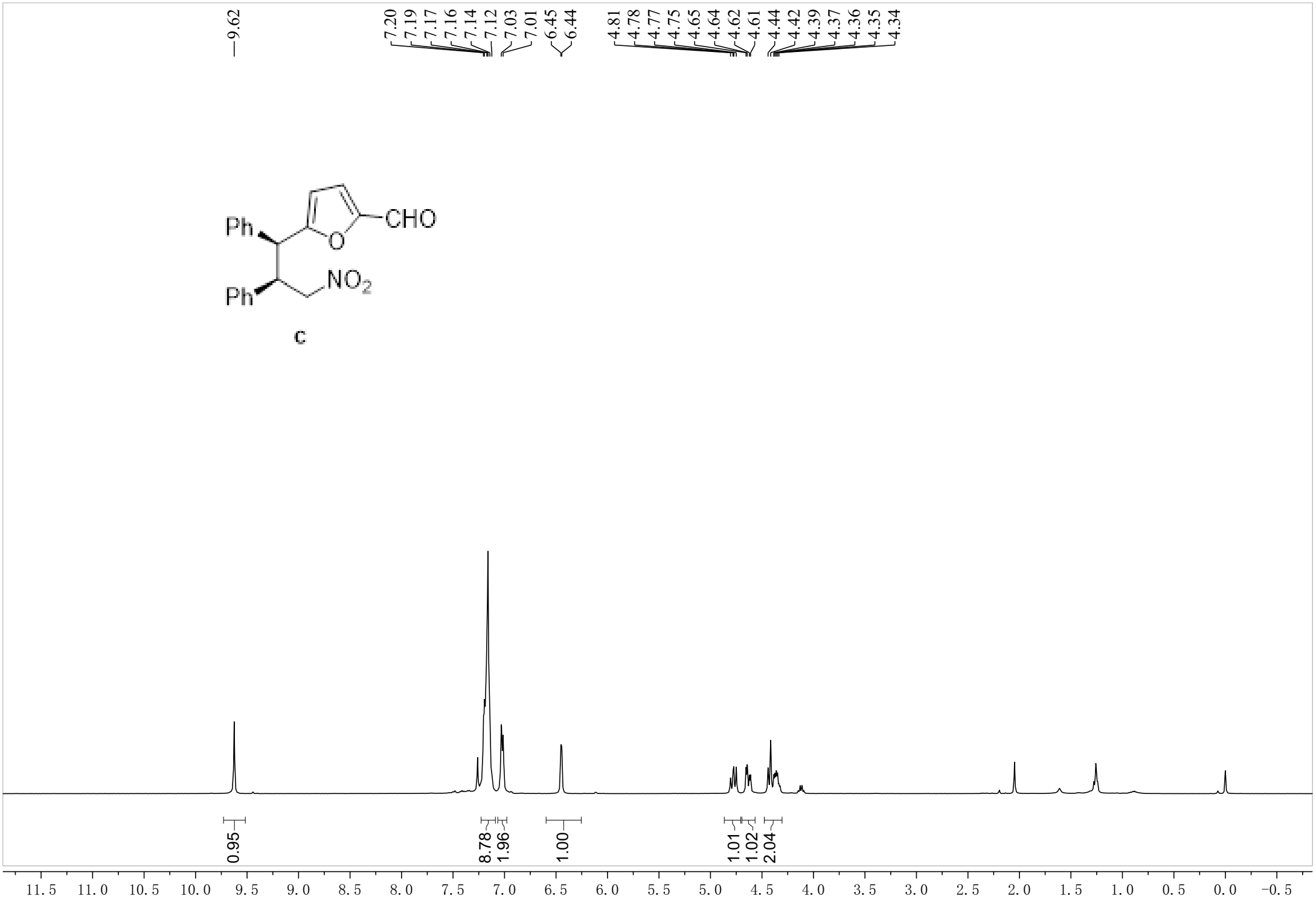
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7.14
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7.03
7.01
6.45
6.44
4.81
4.78
4.77
4.75
4.65
4.64
4.62
4.61
4.44
4.42
4.39
4.37
4.36
4.35
4.34
Ph
CHO
O
NO2
Ph
c
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8.78
1.96
1.00
1.01
1.02
2.04
11.5
11.0
10.5
10.0
9.5
9.0
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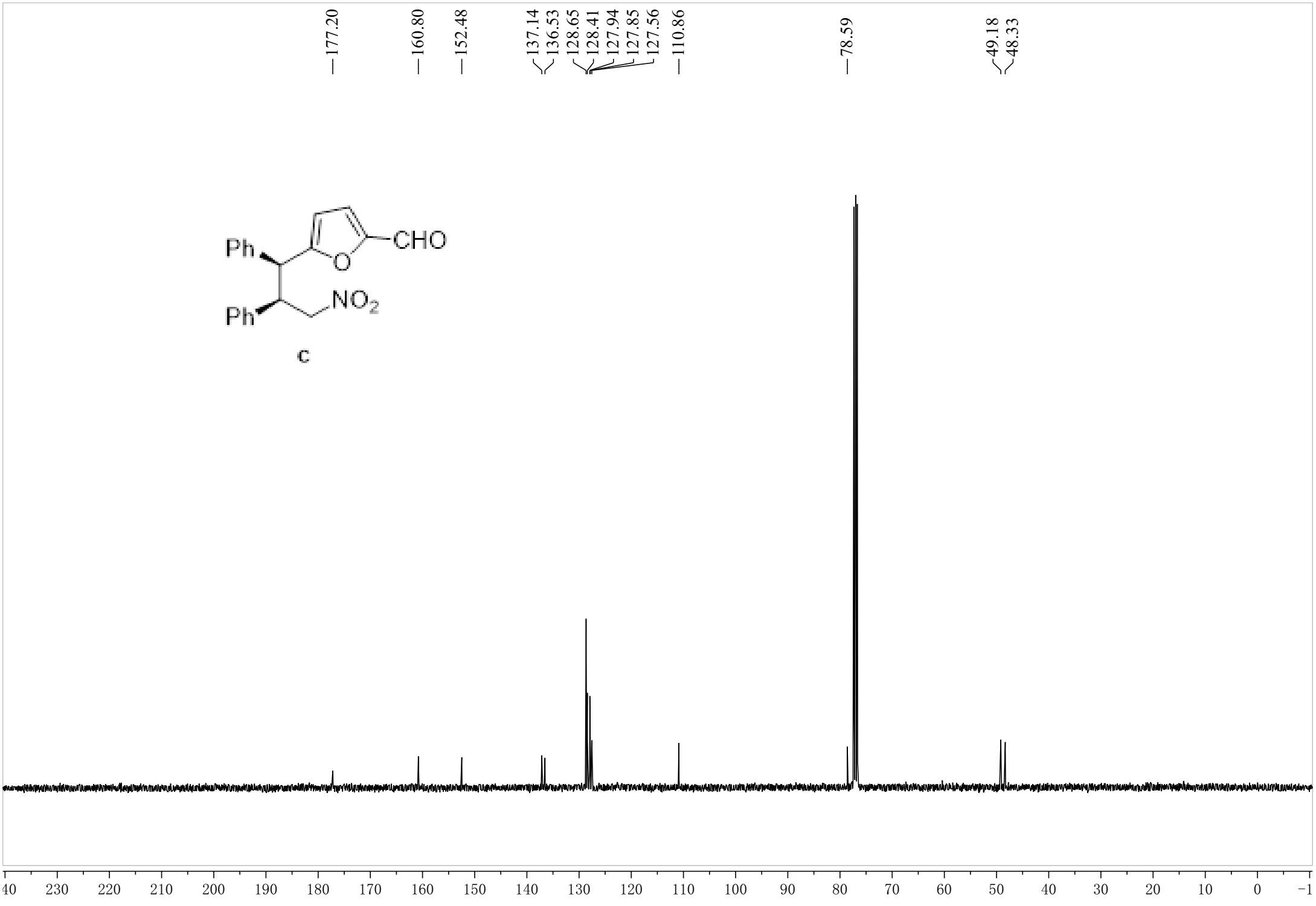
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c
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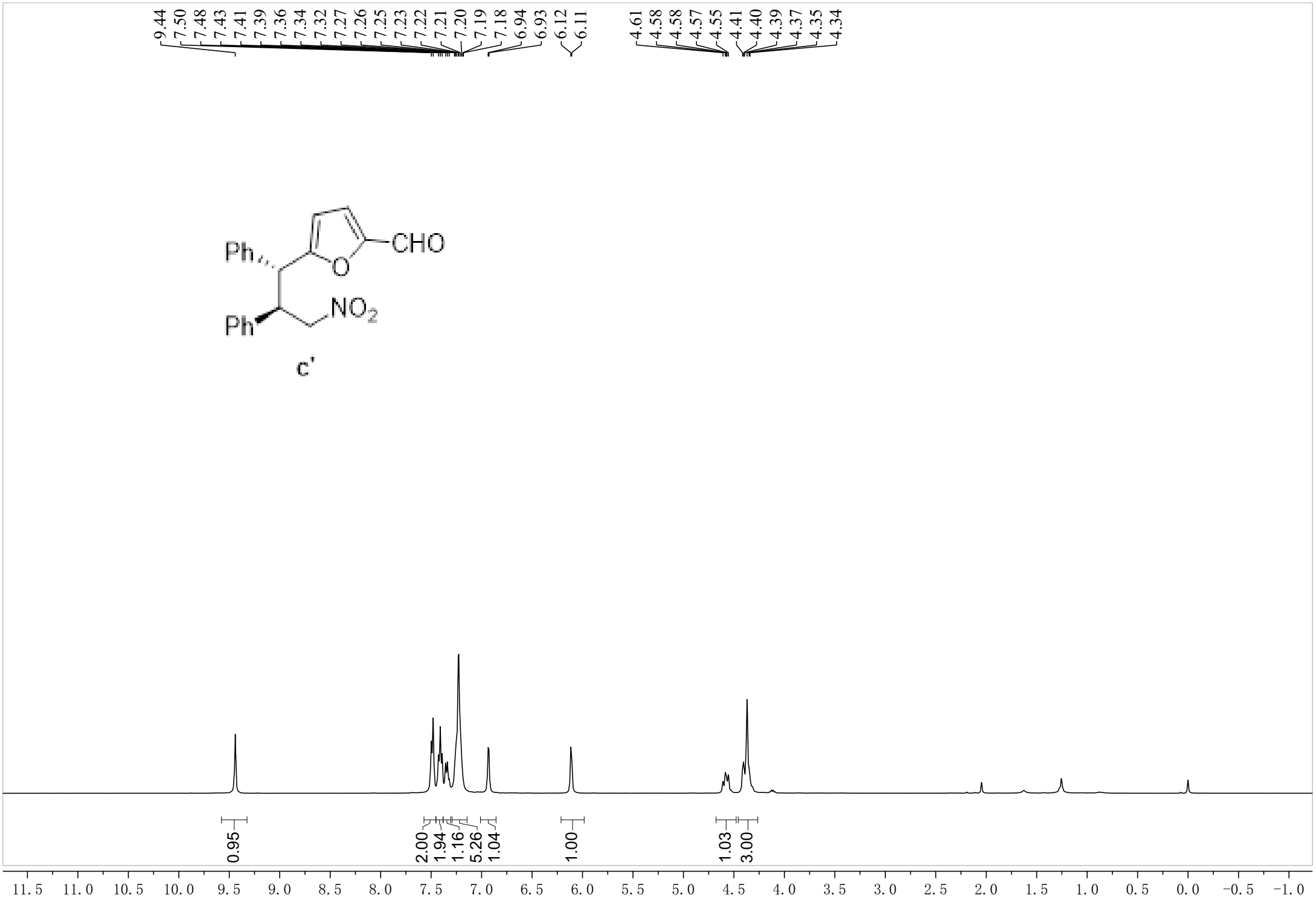
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7.21
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7.19
7.18
6.94
6.93
6.12
6.11
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4.58
4.58
4.57
4.55
4.41
4.40
4.39
4.37
4.35
4.34
Ph
O
CHO
NO2
Ph
c'
0.95
2.00
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1.04
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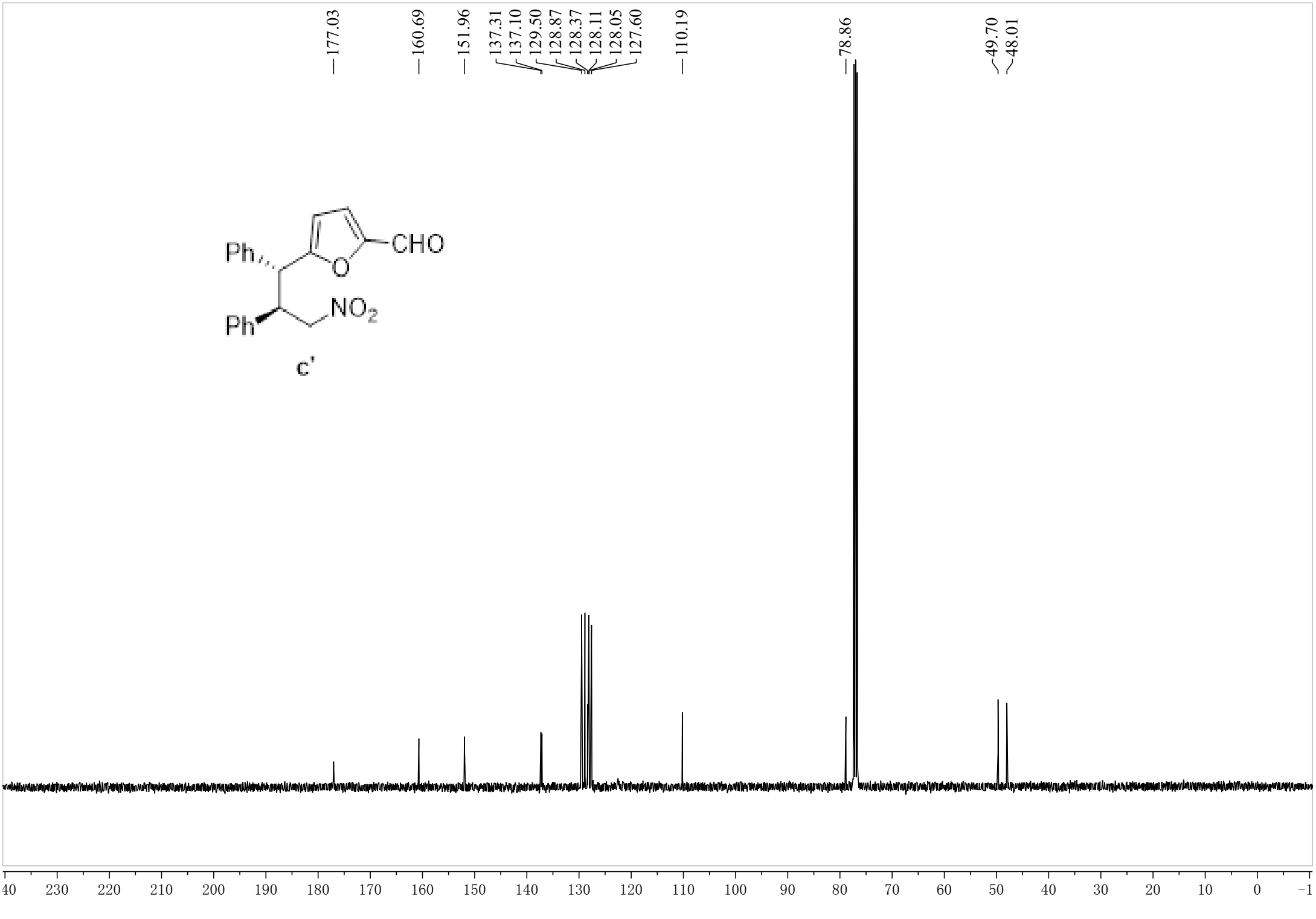
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CHO
O
Ph
NO2
Ph
c'
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220
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180
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160
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100
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50
40
30
20
10
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−1

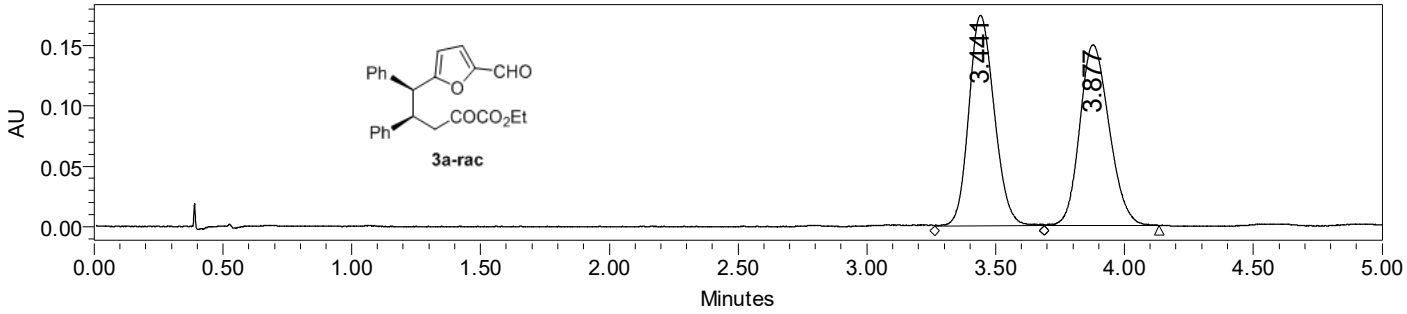
10. HPLC or UPC2 spectra copies of compounds

Empower™ 3 SOFTWARE

Sample Information

Sample Name: 3a-rac Wave Length: 283.0nm

Column: Chiralpak IG-3 95:5



peak information:

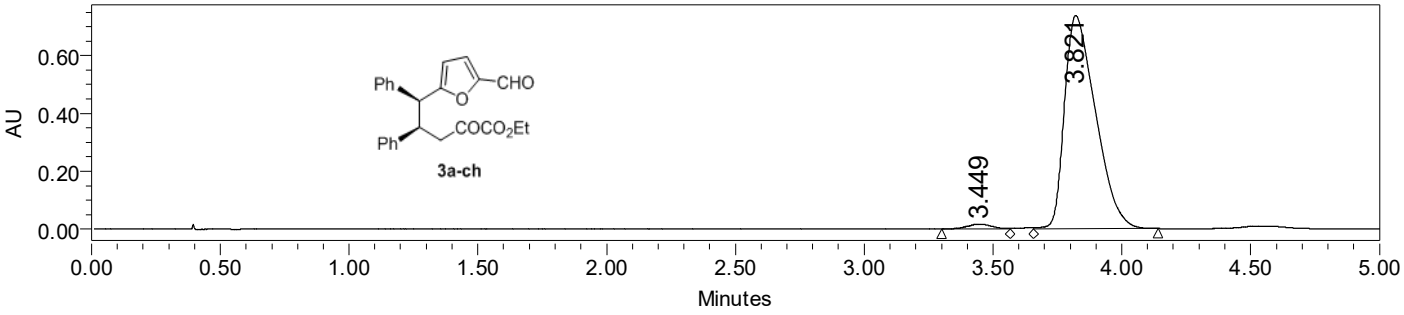
	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	3.441	1205909	50.15	174374
2	3.877	1198703	49.85	149876

Empower™ 3 SOFTWARE

Sample Information

Sample Name: 3a-ch Wave Length: 283.0nm

Column: Chiralpak IG-3 95:5



peak information:

	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	3.449	113649	1.80	16735
2	3.821	6209201	98.20	737964

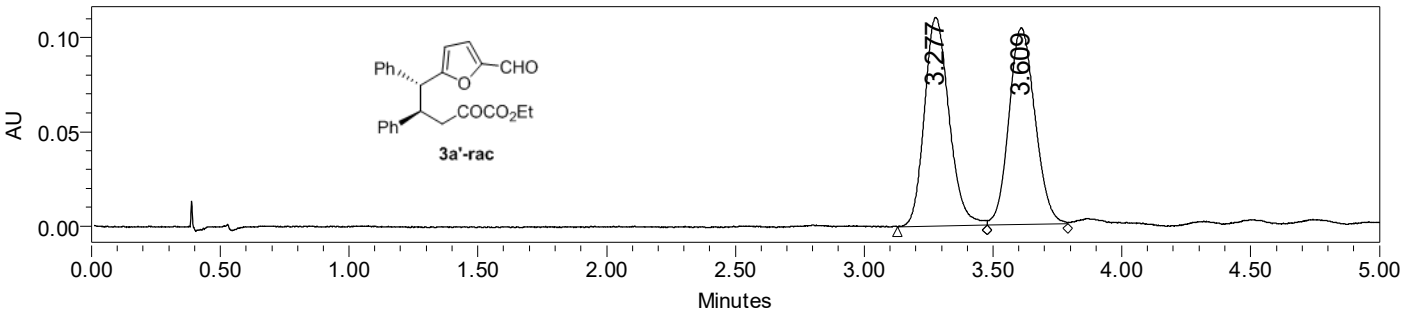
Empower™ 3 SOFTWARE

Sample Information

Sample Name: 3a'-rac

Wave Length: 283.0nm

Column: Chiralpak IG-3 95:5



peak information:

	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	3.277	736874	50.19	110503
2	3.609	731366	49.81	104172

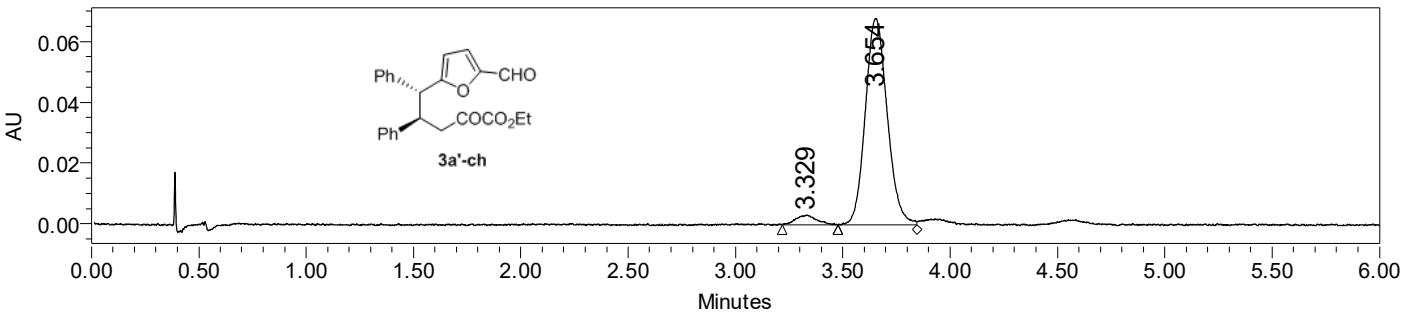
Empower™ 3 SOFTWARE

Sample Information

Sample Name: 3a'-ch

Wave Length: 283.0nm

Column: Chiralpak IG-3 95:5



peak information:

	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	3.329	22048	4.35	3252
2	3.654	484936	95.65	67903

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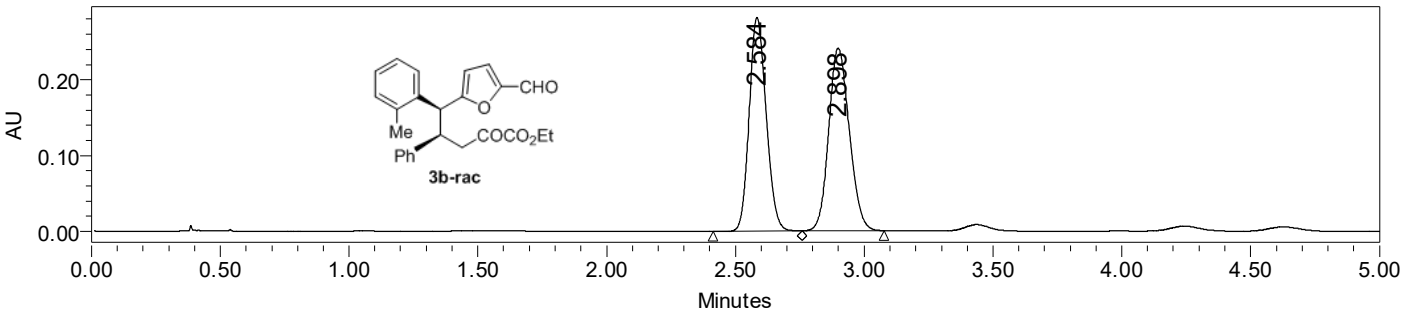
Sample Information

Sample Name: 3b-rac

Wave Length: 284.0nm

Column: Chiralpak IG-3 95:5



peak information:

	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	2.584	1302254	49.23	282076
2	2.898	1342774	50.77	241103

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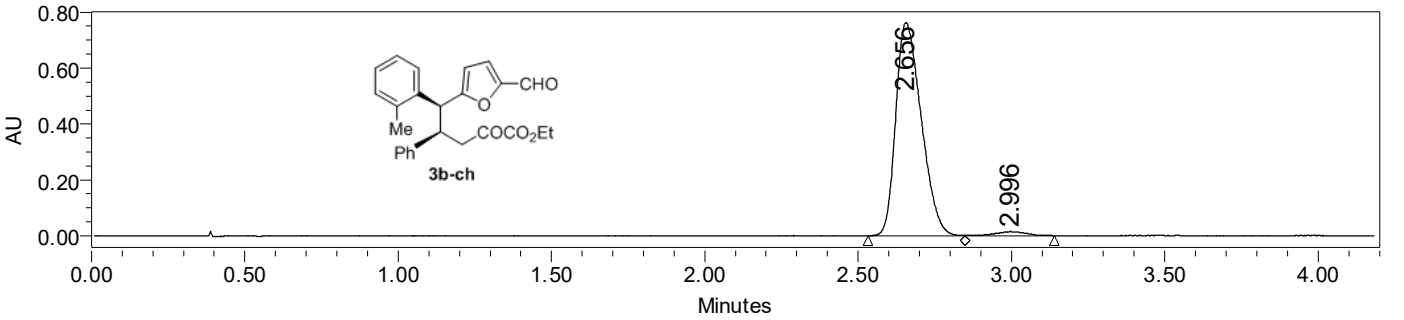
Sample Information

Sample Name: 3b-ch

Wave Length: 284.0nm

Column: Chiralpak IG-3 95:5



peak information:

	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	2.656	4408144	97.69	762644
2	2.996	104062	2.31	14244

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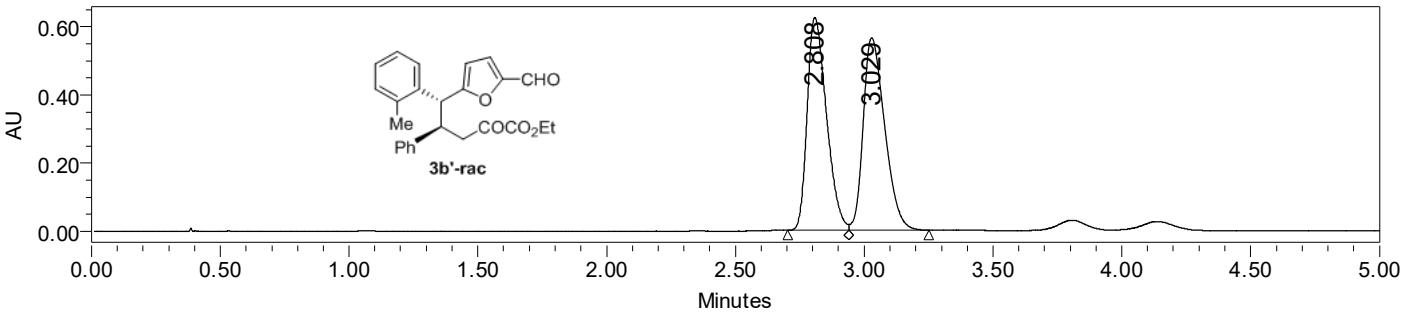
Sample Information

Sample Name: 3b'-rac

Wave Length: 284.0nm

Column: Chiralpak IG-3 95:5



peak information:

	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	2.808	3260063	49.75	624174
2	3.029	3293377	50.25	564707

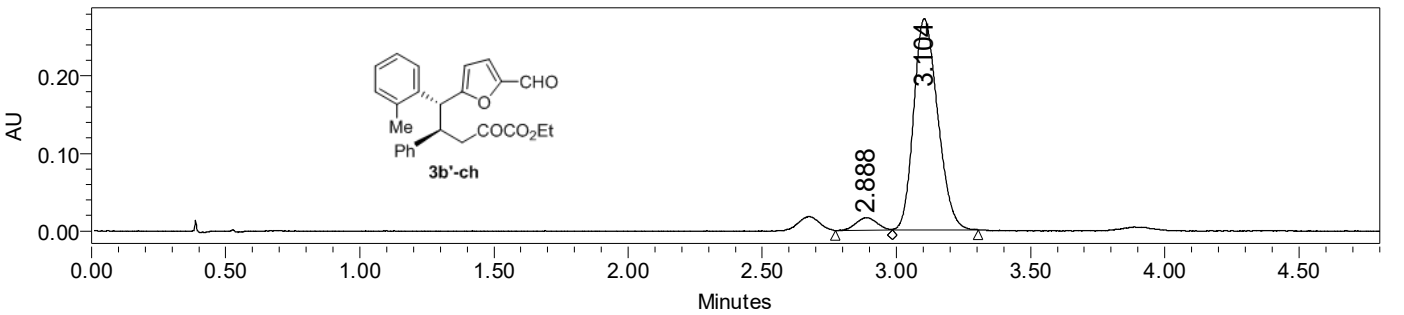
Empower™ 3 SOFTWARE

Sample Information

Sample Name: 3b'-ch

Wave Length: 284.0nm

Column: Chiralpak IG-3 95:5



peak information:

	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	2.888	90253	5.05	16442
2	3.104	1697738	94.95	272919

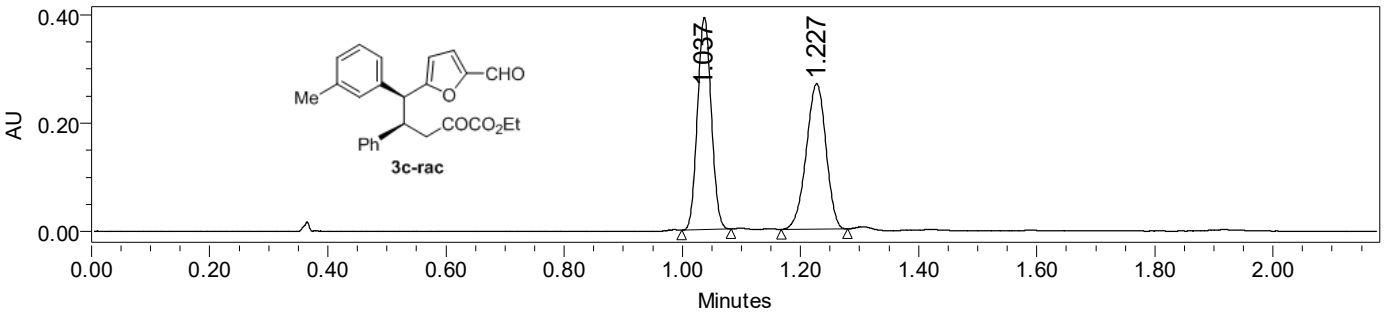
Empower™ 3 SOFTWARE

Sample Information

Sample Name: 3c-rac

Wave Length: 285.0nm

Column: Trefoil TM CEL1 90:10



peak information:

	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	1.037	633979	50.36	392251
2	1.227	624879	49.64	269220

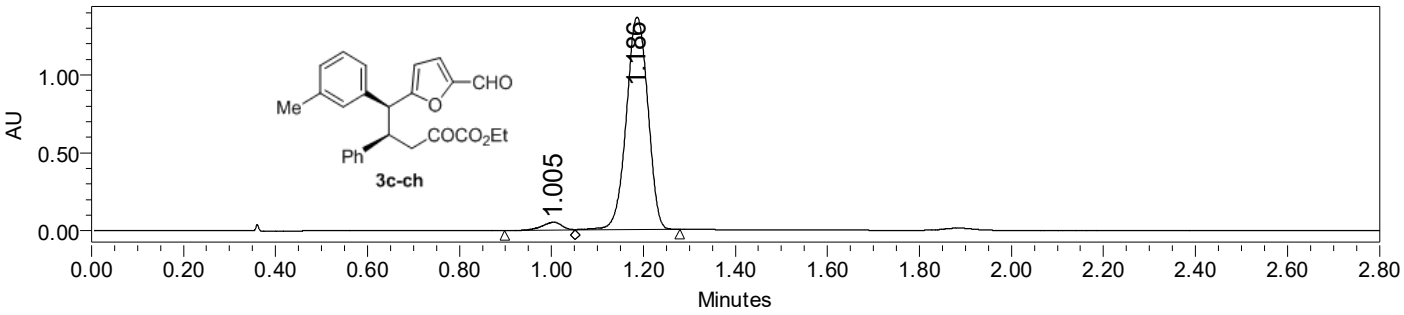
Empower™ 3 SOFTWARE

Sample Information

Sample Name: 3c-ch

Wave Length: 285.0nm

Column: Trefoil TM CEL1 90:10



peak information:

	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	1.005	157694	3.40	51085
2	1.186	4475333	96.60	1363951

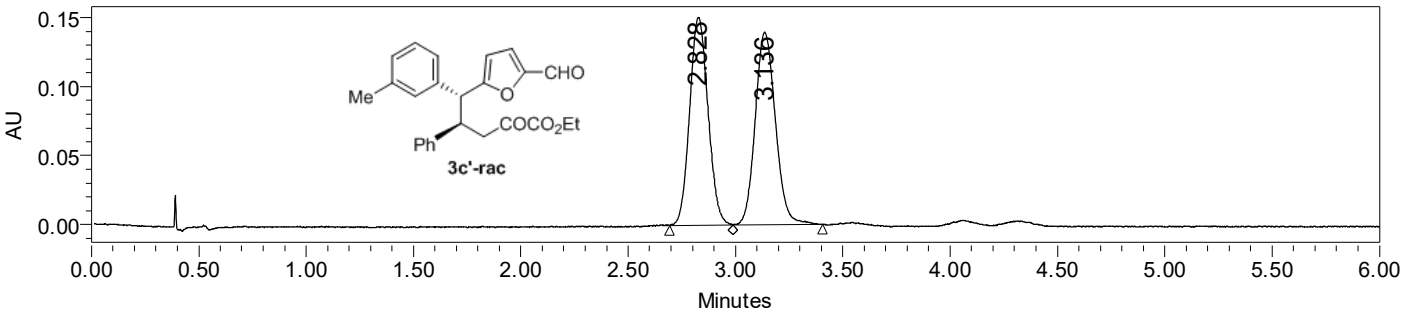
Empower™ 3 SOFTWARE

Sample Information

Sample Name: 3c'-rac

Wave Length: 283.0nm

Column: Chiralpak IG-3 95:5



peak information:

	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	2.828	900565	49.44	150700
2	3.136	921105	50.56	139746

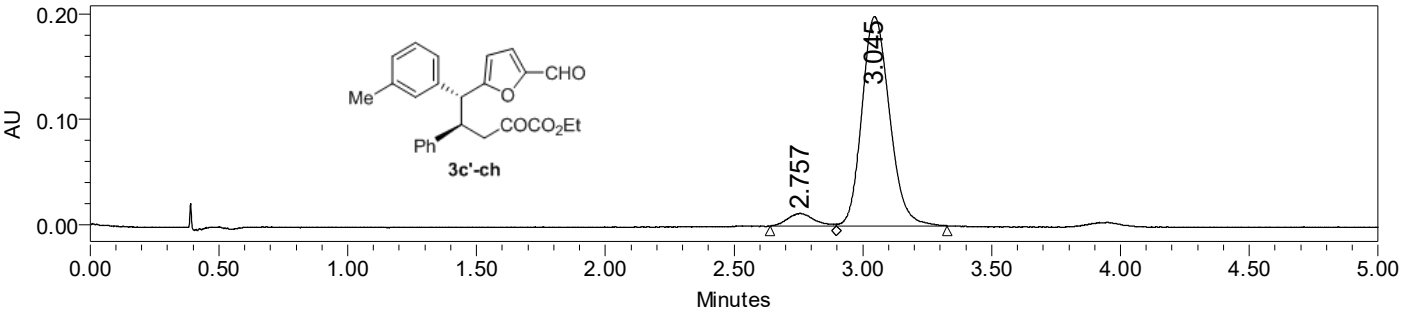
Empower™ 3 SOFTWARE

Sample Information

Sample Name: 3c'-ch

Wave Length: 283.0nm

Column: Chiralpak IG-3 95:5



peak information:

	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	2.757	85168	5.41	12012
2	3.045	1487815	94.59	198845

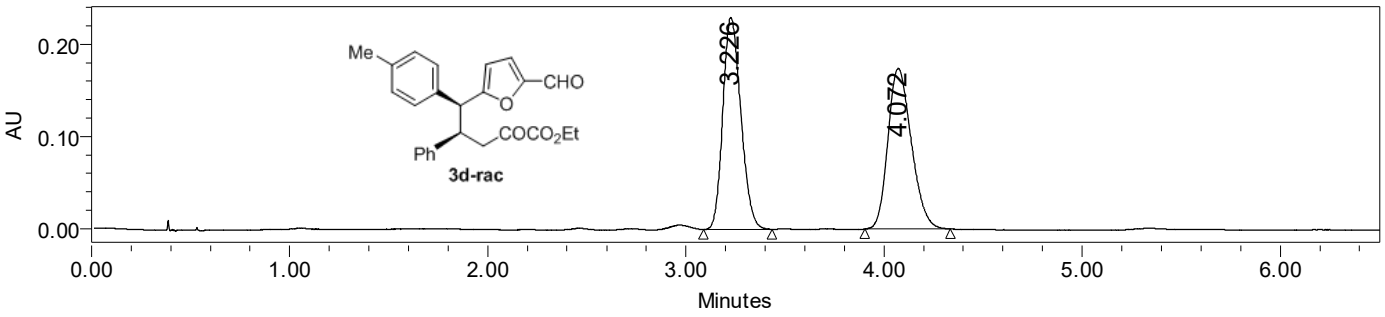
Empower™ 3 SOFTWARE

Sample Information

Sample Name: 3d-rac

Wave Length: 284.0nm

Column: Chiralpak IG-3 95:5



peak information:

	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	3.226	1444143	50.21	229788
2	4.072	1431998	49.79	174153

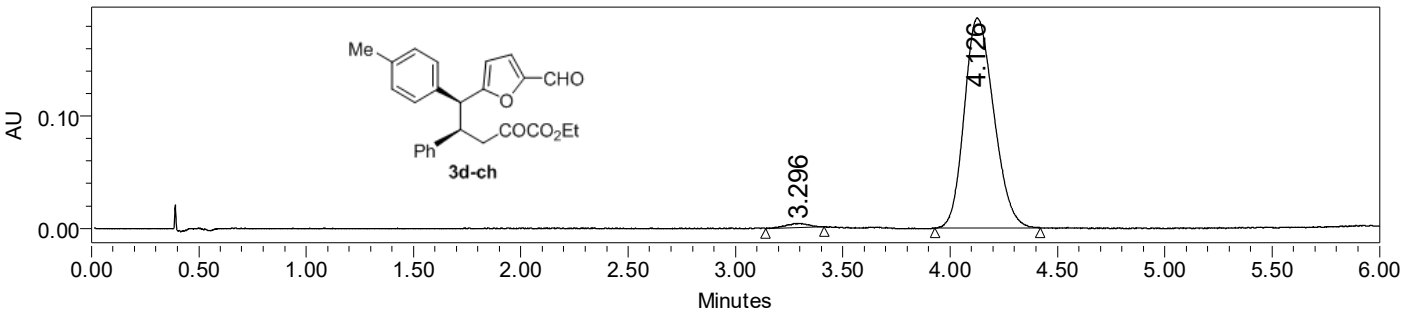
Empower™ 3 SOFTWARE

Sample Information

Sample Name: 3d-ch

Wave Length: 284.0nm

Column: Chiralpak IG-3 95:5



peak information:

	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	3.296	26744	1.46	3620
2	4.126	1799278	98.54	186900

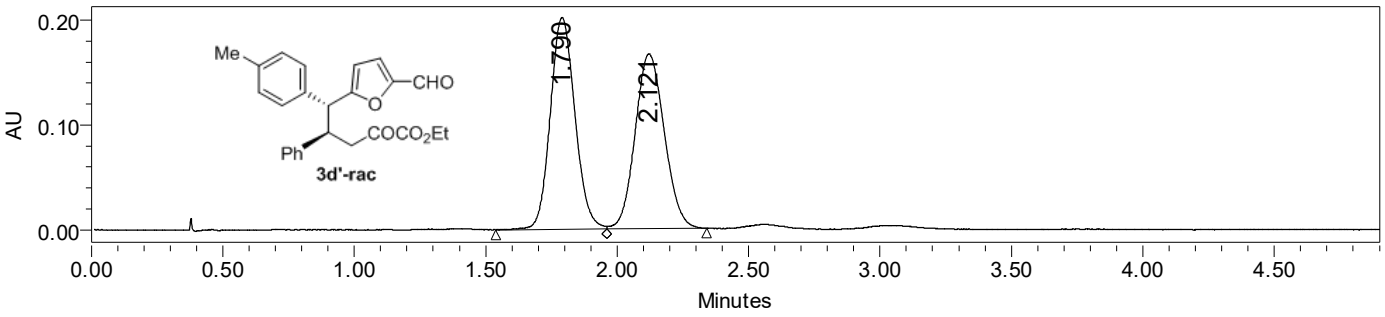
Empower™ 3 SOFTWARE

Sample Information

Sample Name: 3d'-rac

Wave Length: 284.0nm

Column: Chiralpak AD-3 95:5



peak information:

	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	1.790	1322367	50.60	202137
2	2.121	1290812	49.40	166755

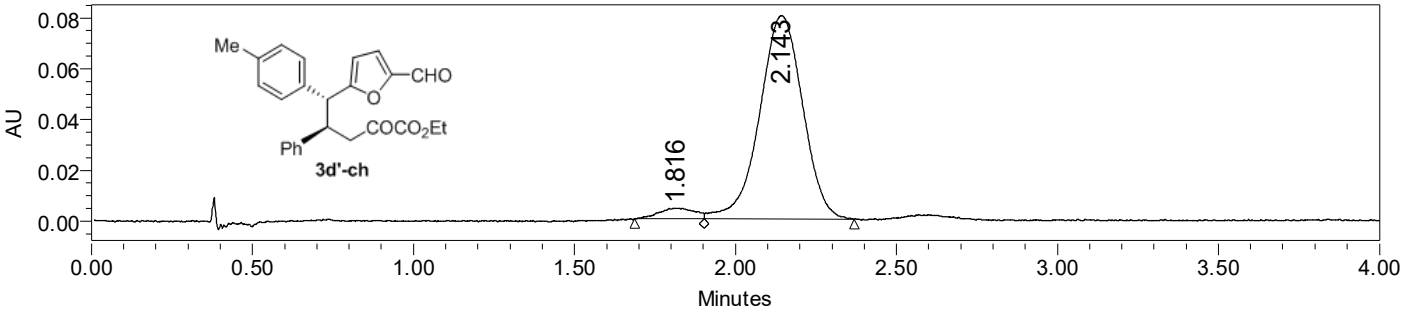
Empower™ 3 SOFTWARE

Sample Information

Sample Name: 3d'-ch

Wave Length: 284.0nm

Column: Chiralpak AD-3 95:5



peak information:

	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	1.816	33772	4.32	4244
2	2.143	747674	95.68	80150

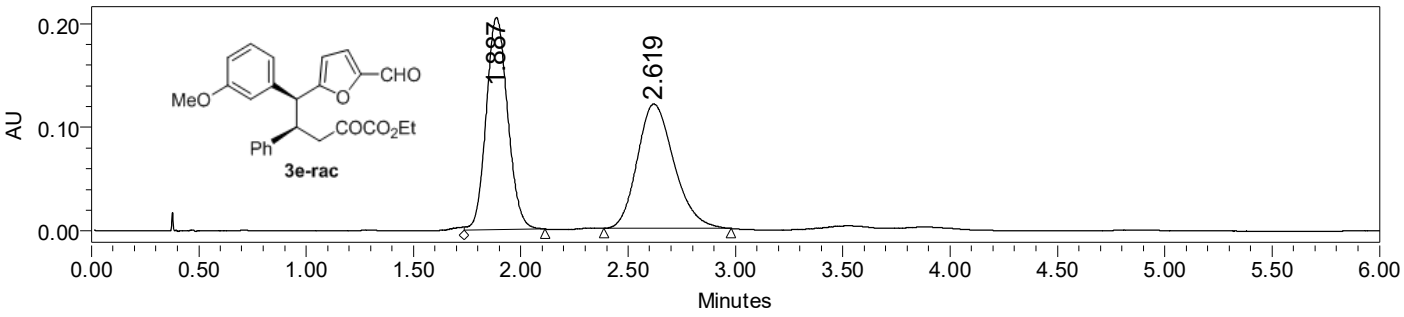
Empower™ 3 SOFTWARE

Sample Information

Sample Name: 3e-rac

Wave Length: 283.0nm

Column: Chiralpak AD-3 95:5



peak information:

	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	1.887	1432573	50.00	204907
2	2.619	1432714	50.00	120103

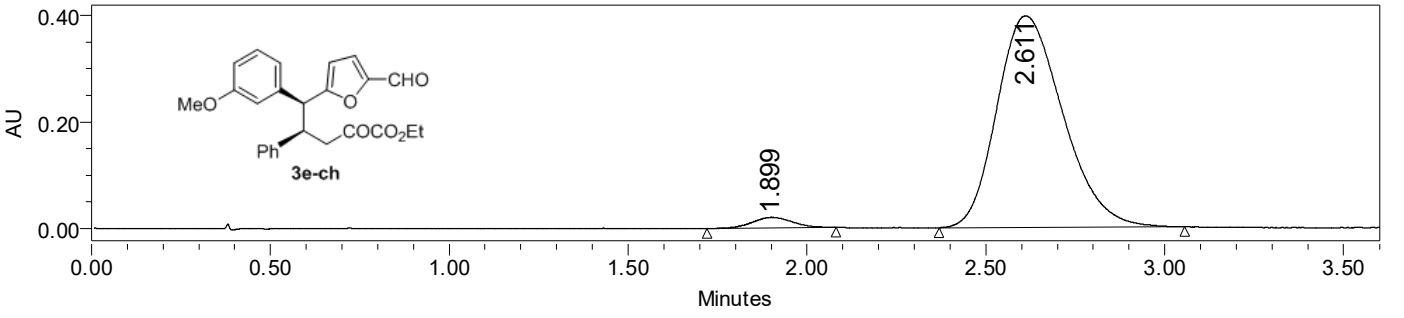
Empower™ 3 SOFTWARE

Sample Information

Sample Name: 3e-ch

Wave Length: 283.0nm

Column: Chiralpak AD-3 95:5



peak information:

	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	1.899	154191	2.94	19728
2	2.611	5095032	97.06	397515

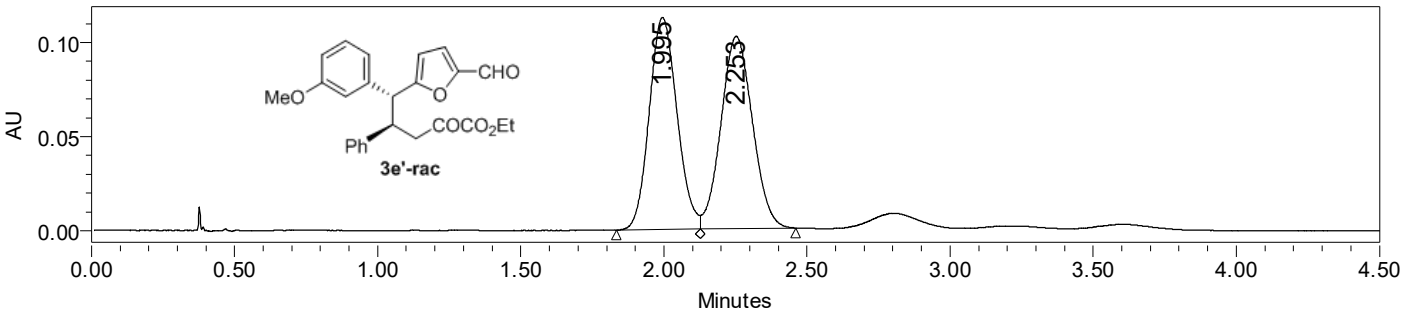
Empower™ 3 SOFTWARE

Sample Information

Sample Name: 3e'-rac

Column: Chiralpak AD-3 95:5

Wave Length: 283.0nm



peak information:

	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	1.995	763287	49.40	112693
2	2.253	781712	50.60	102128

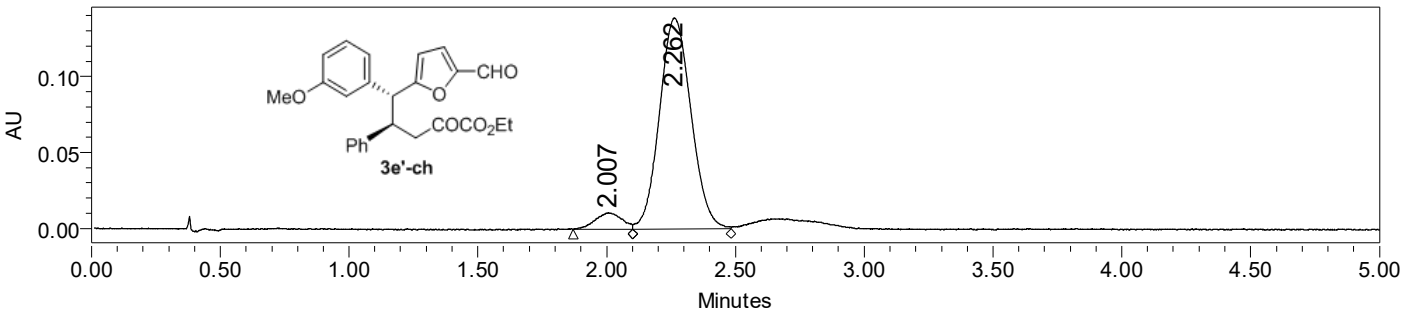
Empower™ 3 SOFTWARE

Sample Information

Sample Name: 3e'-ch

Column: Chiralpak AD-3 95:5

Wave Length: 283.0nm



peak information:

	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	2.007	78171	6.16	10898
2	2.262	1190904	93.84	139051

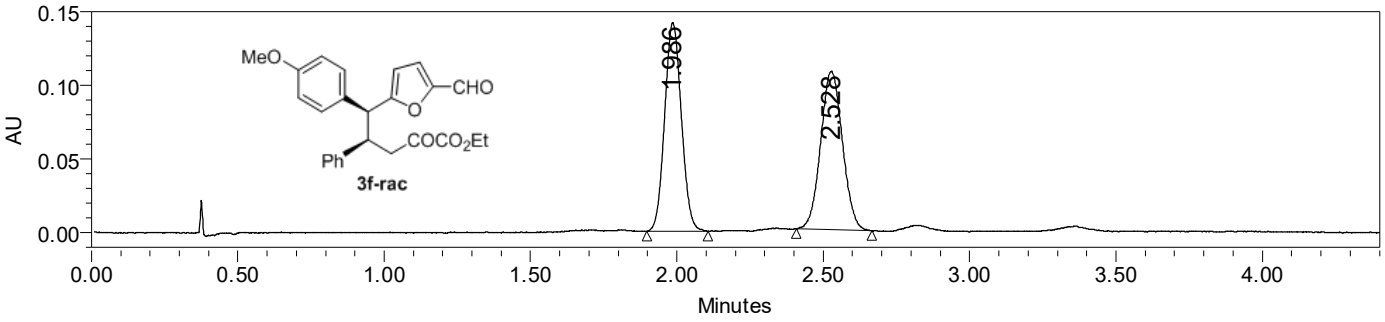
Empower™ 3 SOFTWARE

Sample Information

Sample Name: 3f-rac

Column: Chiralpak IG-3 95:5

Wave Length: 285.0nm



peak information:

	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	1.986	565680	50.35	141912
2	2.528	557765	49.65	107644

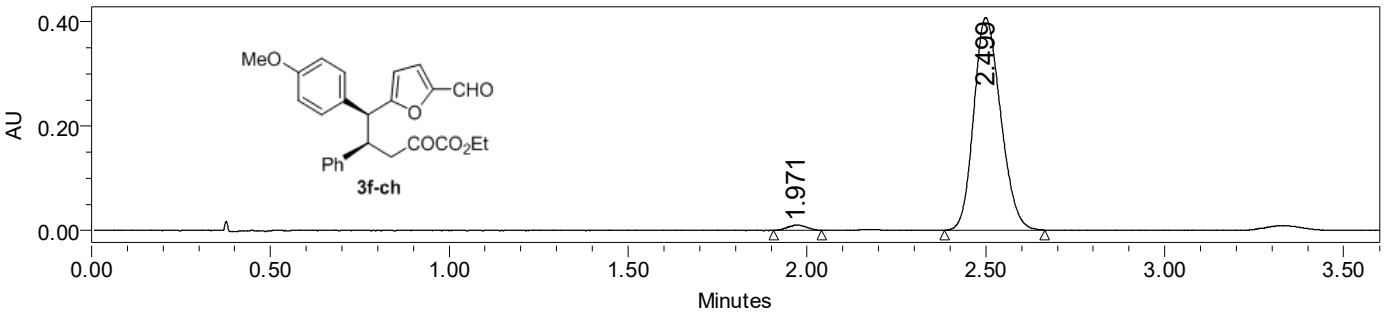
Empower™ 3 SOFTWARE

Sample Information

Sample Name: 3f-ch

Column: Chiralpak IG-3 95:5

Wave Length: 285.0nm



peak information:

	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	1.971	36814	1.70	9950
2	2.499	2129477	98.30	407582

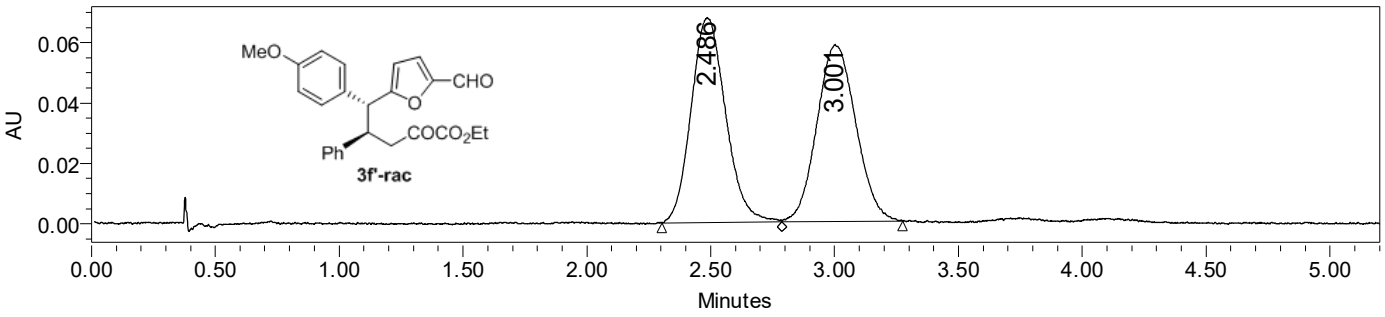
Empower™ 3 SOFTWARE

Sample Information

Sample Name: 3f'-rac

Wave Length: 283.0nm

Column: Chiralpak AD-3 95:5



peak information:

	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	2.486	656646	50.64	67981
2	3.001	640165	49.36	58617

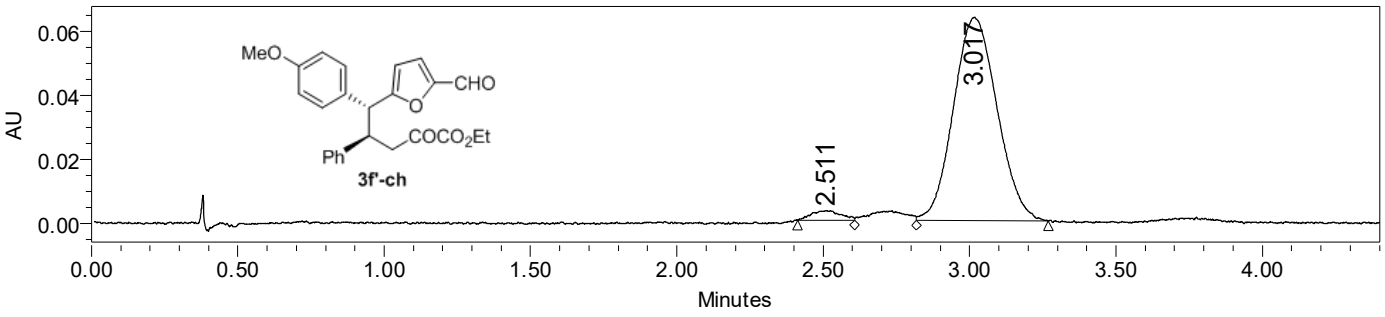
Empower™ 3 SOFTWARE

Sample Information

Sample Name: 3f'-ch

Wave Length: 283.0nm

Column: Chiralpak AD-3 95:5



peak information:

	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	2.511	20865	3.06	3062
2	3.017	661146	96.94	63614

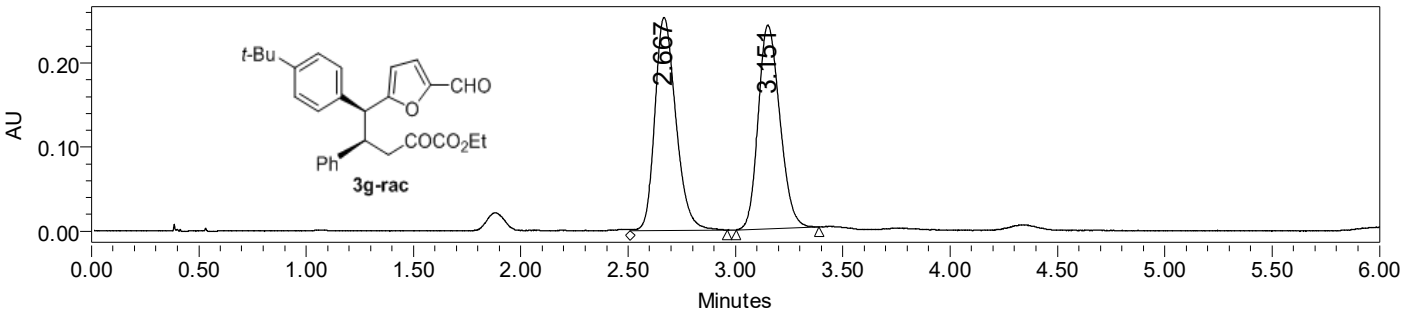
Empower™ 3 SOFTWARE

Sample Information

Sample Name: 3g-rac

Wave Length: 285.0nm

Column: Chiralpak IG-3 95:5



peak information:

	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	2.667	1730739	50.40	253357
2	3.151	1703197	49.60	242197

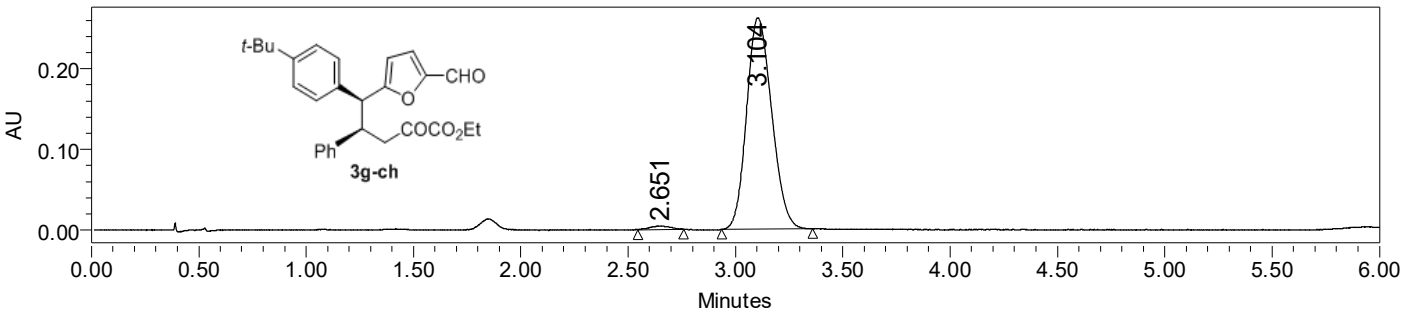
Empower™ 3 SOFTWARE

Sample Information

Sample Name: 3g-ch

Wave Length: 285.0nm

Column: Chiralpak IG-3 95:5



peak information:

	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	2.651	30440	1.40	4553
2	3.104	2141579	98.60	262049

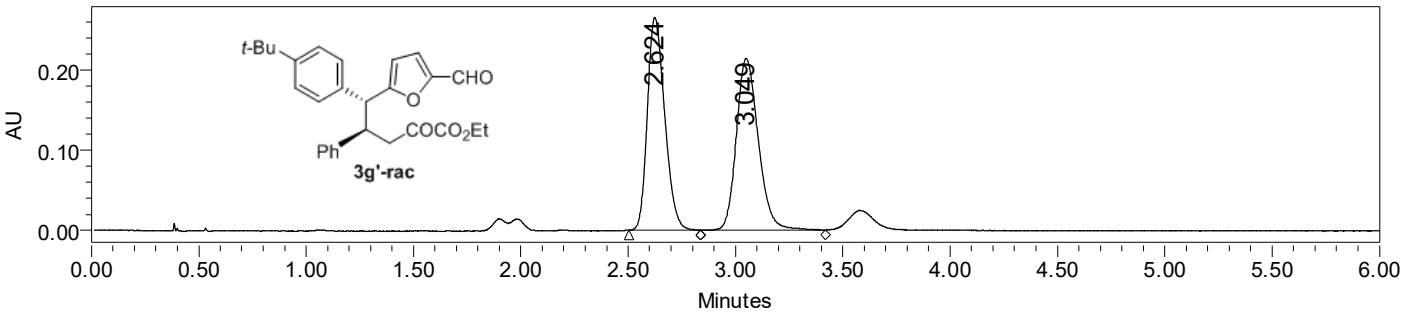
Empower™ 3 SOFTWARE

Sample Information

Sample Name: 3g'-rac

Wave Length: 284.0nm

Column: Chiralpak IG-3 95:5



peak information:

	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	2.624	1503733	49.59	265727
2	3.049	1528653	50.41	214594

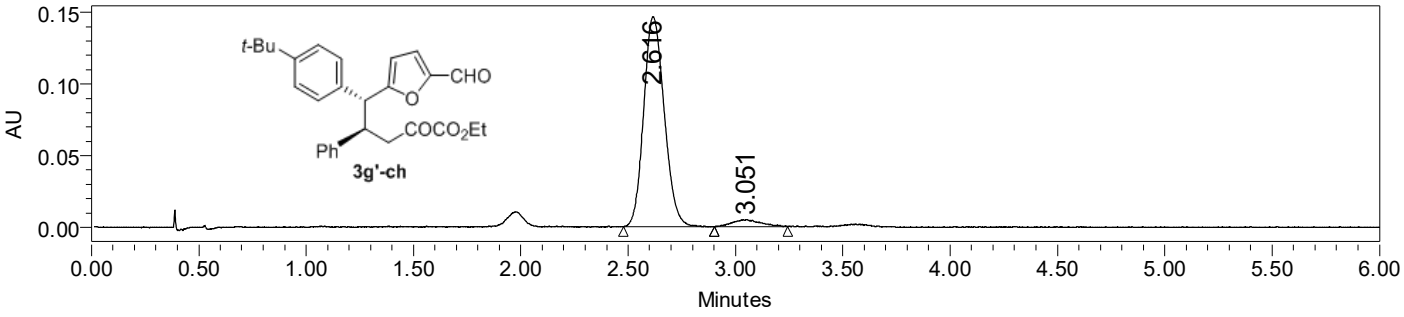
Empower™ 3 SOFTWARE

Sample Information

Sample Name: 3g'-ch

Wave Length: 284.0nm

Column: Chiralpak IG-3 95:5



peak information:

	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	2.616	980905	95.41	146636
2	3.051	47203	4.59	4953

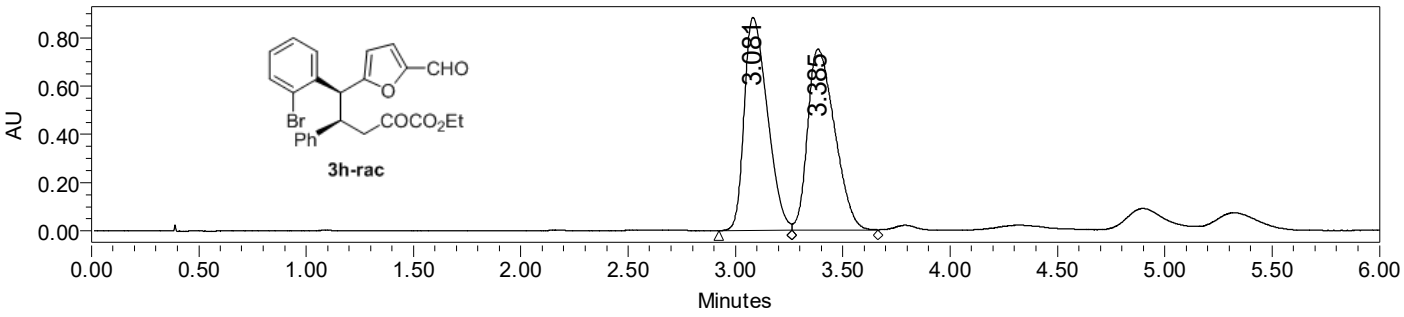
Empower™ 3 SOFTWARE

Sample Information

Sample Name: 3h-rac

Wave Length: 283.0nm

Column: Chiralpak IG-3 95:5



peak information:

	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	3.081	6633118	50.21	882600
2	3.385	6578058	49.79	750360

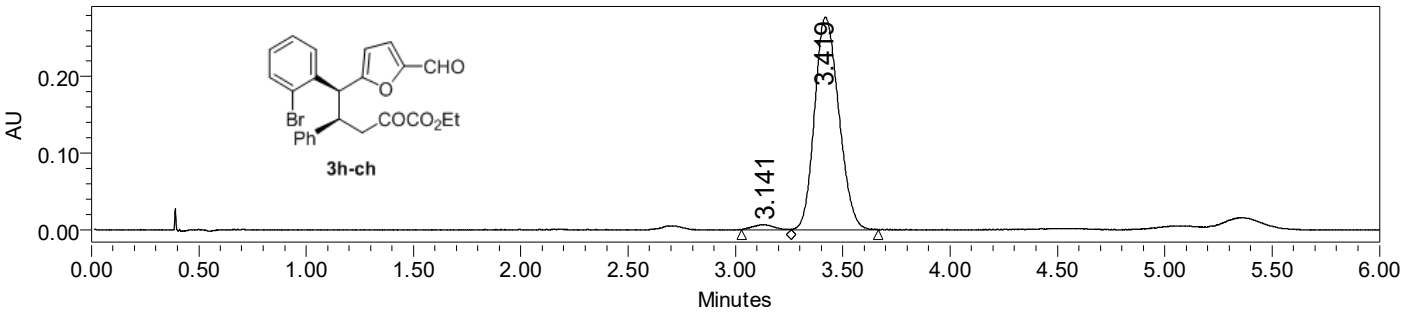
Empower™ 3 SOFTWARE

Sample Information

Sample Name: 3h-ch

Wave Length: 283.0nm

Column: Chiralpak IG-3 95:5



peak information:

	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	3.141	41770	1.89	6268
2	3.419	2166041	98.11	276962

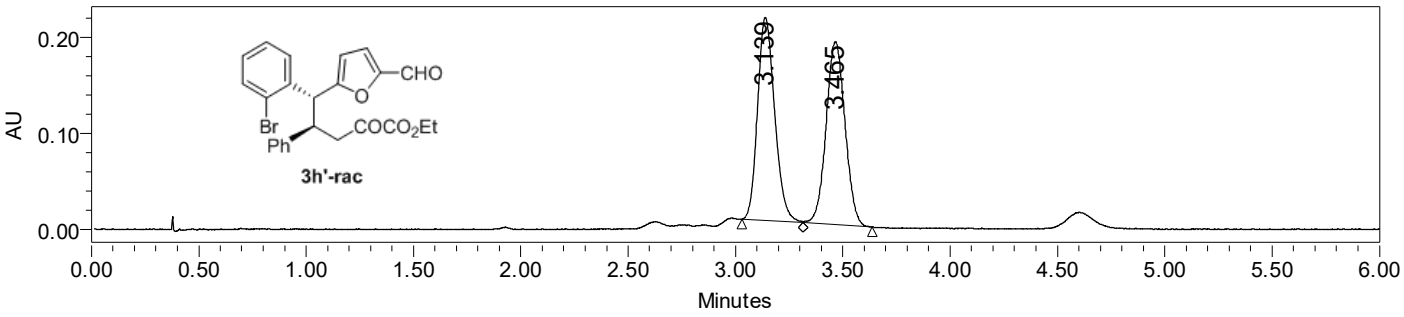
Empower™ 3 SOFTWARE

Sample Information

Sample Name: 3h'-rac

Wave Length: 282.0nm

Column: Chiralpak OD-3 95:5



peak information:

	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	3.139	1176648	50.18	211429
2	3.465	1168384	49.82	190788

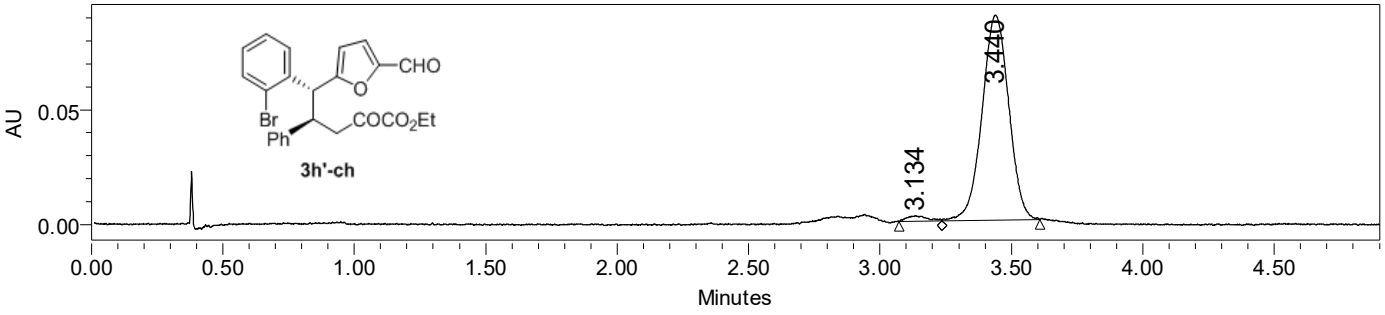
Empower™ 3 SOFTWARE

Sample Information

Sample Name: 3h'-ch

Wave Length: 282.0nm

Column: Chiralpak OD-3 95:5

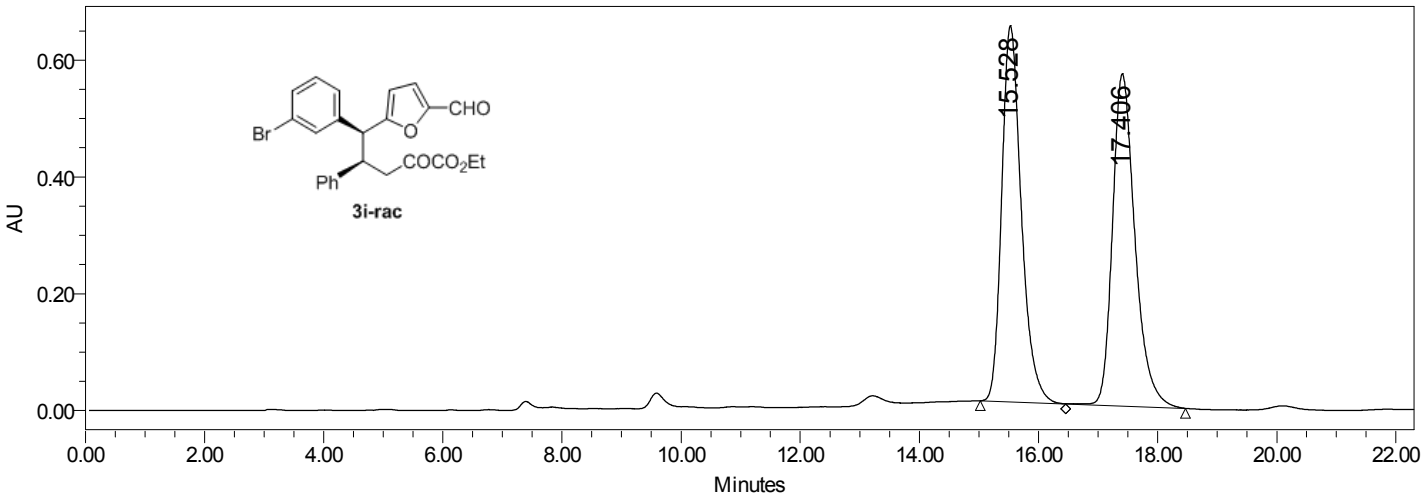


peak information:

	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	3.134	12632	1.96	2458
2	3.440	630838	98.04	89221

Sample Name: 3i-rac Wave Length: 285.0 纳米

Column: Chiralpak IC-3 80:20



peak information

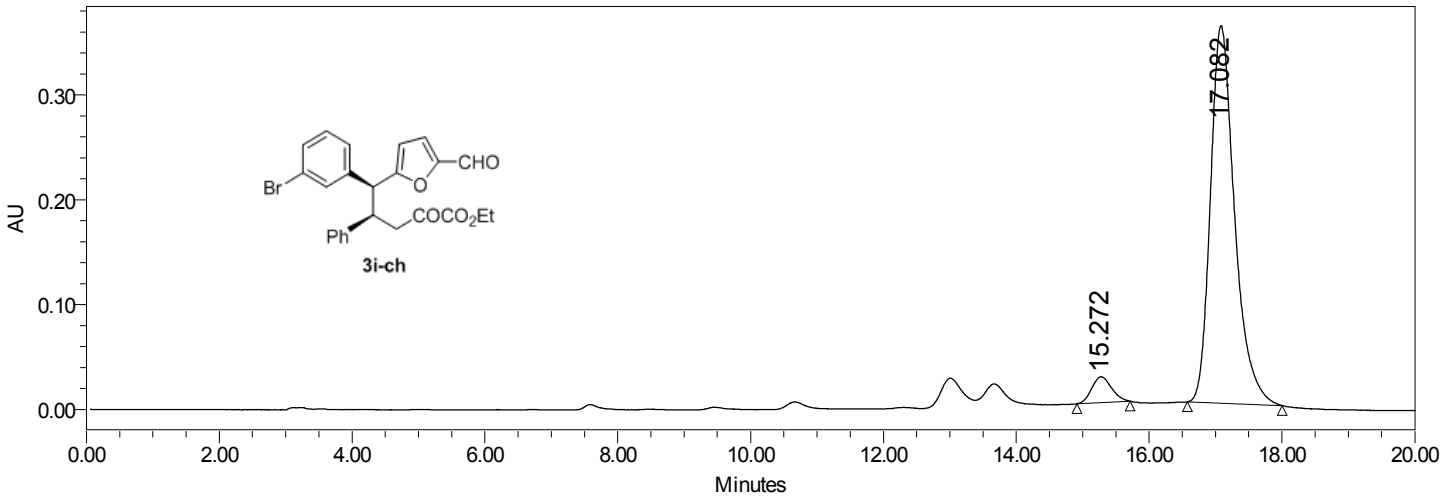
	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	15.528	14697392	49.68	644269
2	17.406	14889057	50.32	568963

Empower™ 3 SOFTWARE

Sample Information

Sample Name: 3i-ch Wave Length: 285.0 纳米

Column: Chiralpak IC-3 80:20

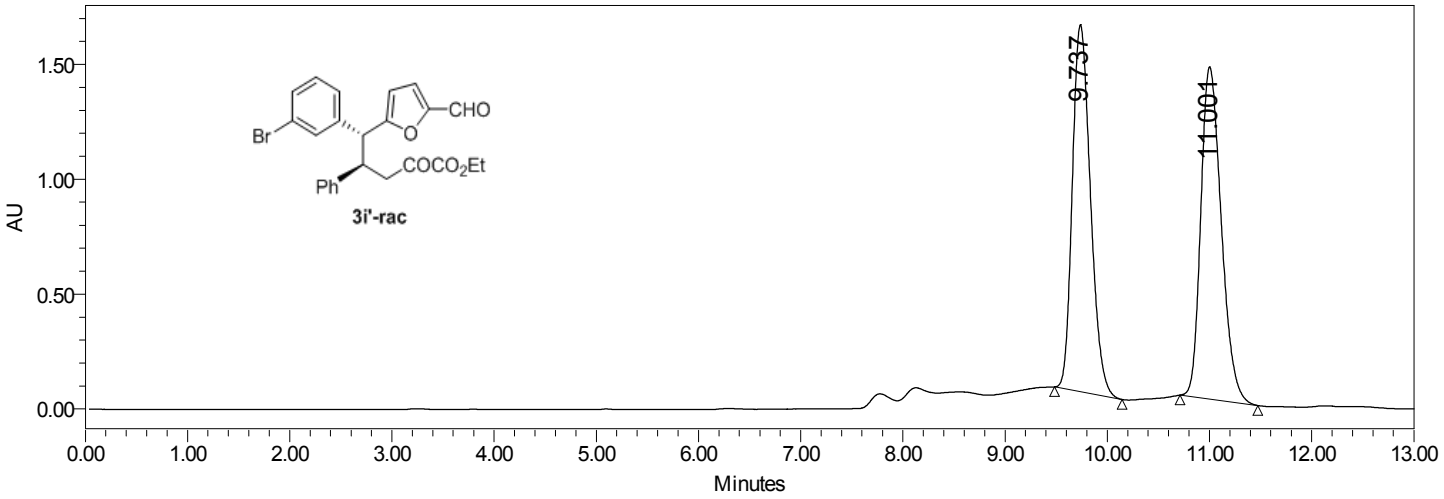


peak information

	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	15.272	511894	5.32	24653
2	17.082	9106027	94.68	359852

Sample Name: 3i'-rac Wave Length: 284.0 纳米

Column: Chiralpak ID-3 80:20

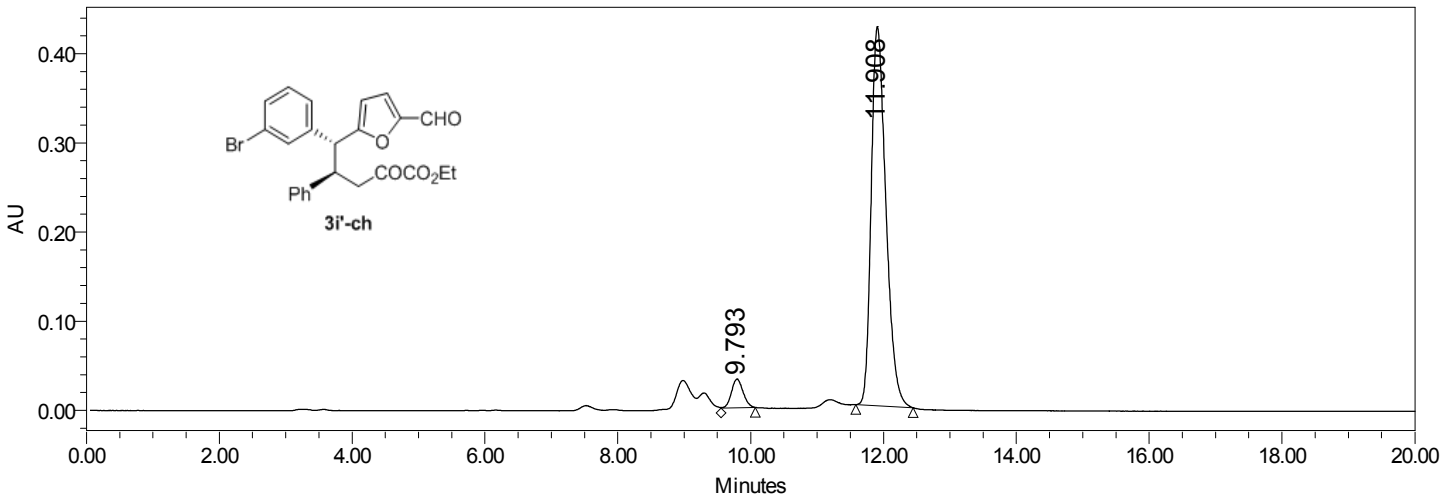


peak information

	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	9.737	19670926	49.46	1597467
2	11.001	20096503	50.54	1445622

Sample Name: 3i'-ch Wave Length: 284.0 纳米

Column: Chiralpak ID-3 80:20



peak information

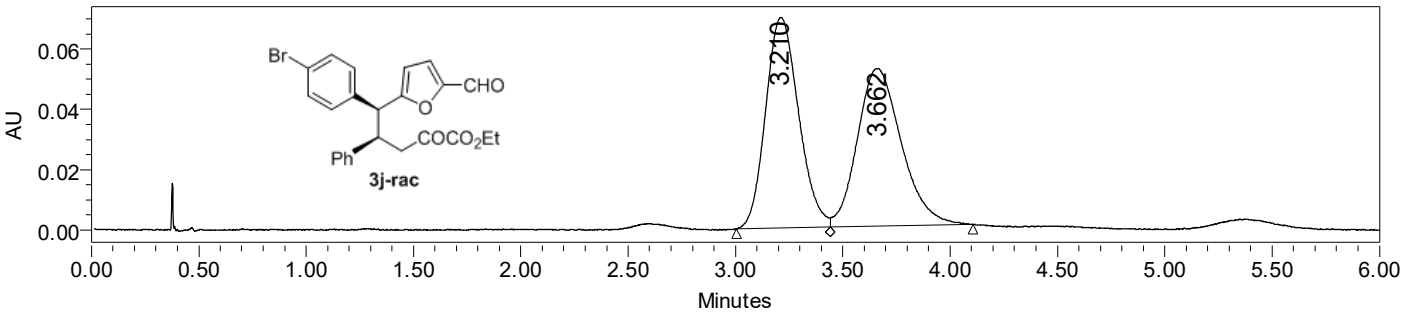
	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	9.793	390019	5.64	32124
2	11.908	6526220	94.36	425289

Empower™ 3 SOFTWARE

Sample Information

Sample Name: 3j-rac Wave Length: 283.0nm

Column: Chiralpak AD-3 95:5



peak information:

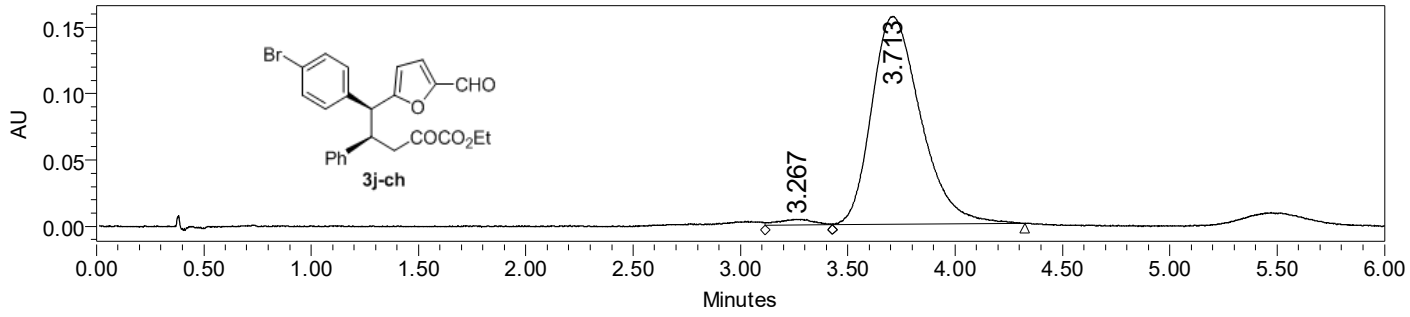
	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	3.210	749875	49.99	69842
2	3.662	750233	50.01	52344

Empower™ 3 SOFTWARE

Sample Information

Sample Name: 3j-ch Wave Length: 283.0nm

Column: Chiralpak AD-3 95:5



peak information:

	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	3.267	48085	1.89	4298
2	3.713	2496268	98.11	156710

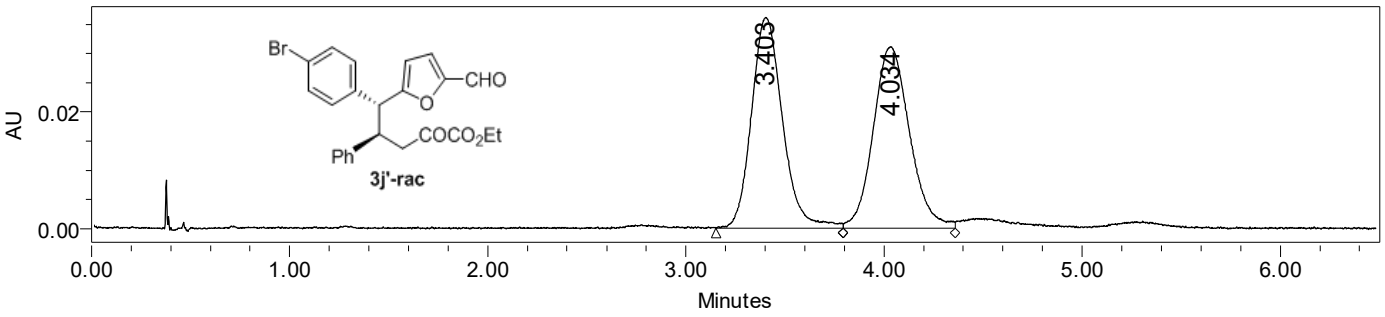
Empower™ 3 SOFTWARE

Sample Information

Sample Name: 3j'-rac

Wave Length: 282.0nm

Column: Chiralpak AD-3 95:5



peak information:

	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	3.403	394686	49.90	36135
2	4.034	396269	50.10	31052

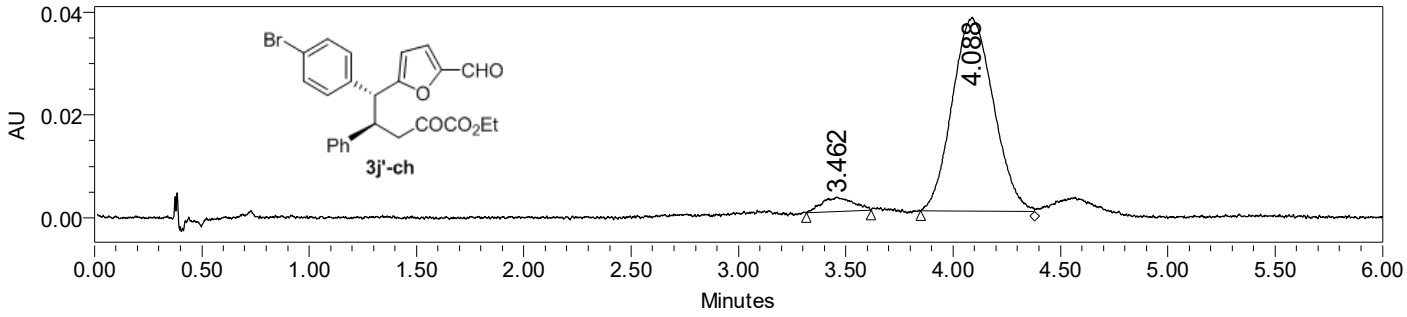
Empower™ 3 SOFTWARE

Sample Information

Sample Name: 3j'-ch

Wave Length: 282.0nm

Column: Chiralpak AD-3 95:5

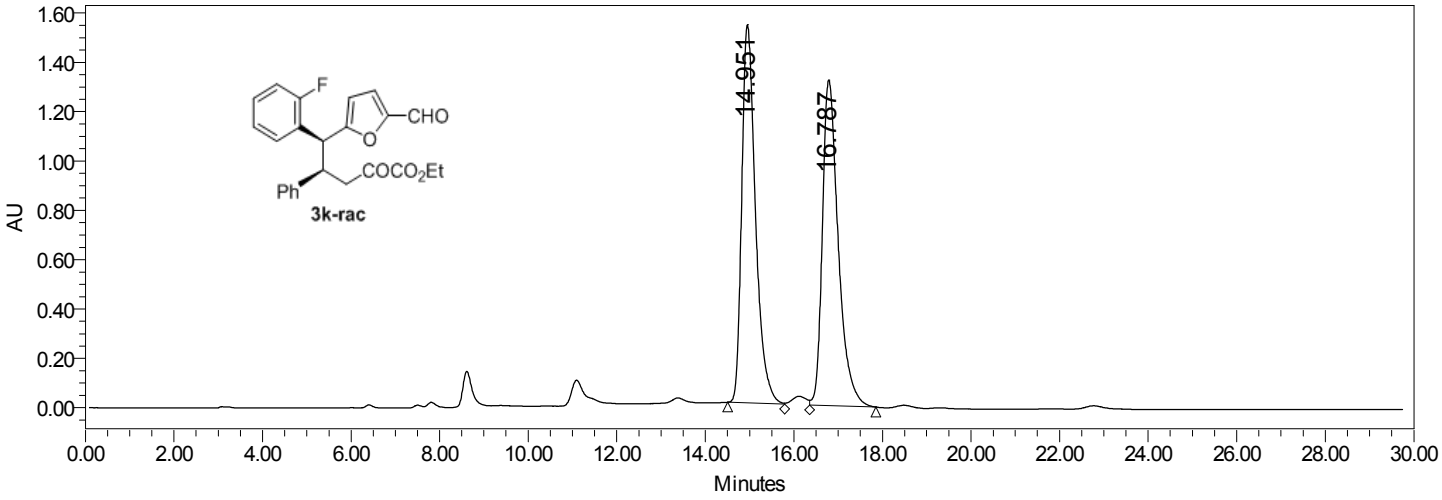


peak information:

	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	3.462	28923	5.43	2778
2	4.088	503276	94.57	37680

Sample Name: 3k-rac Wave Length: 284.0 纳米

Column: Chiralpak IC-3 80:20

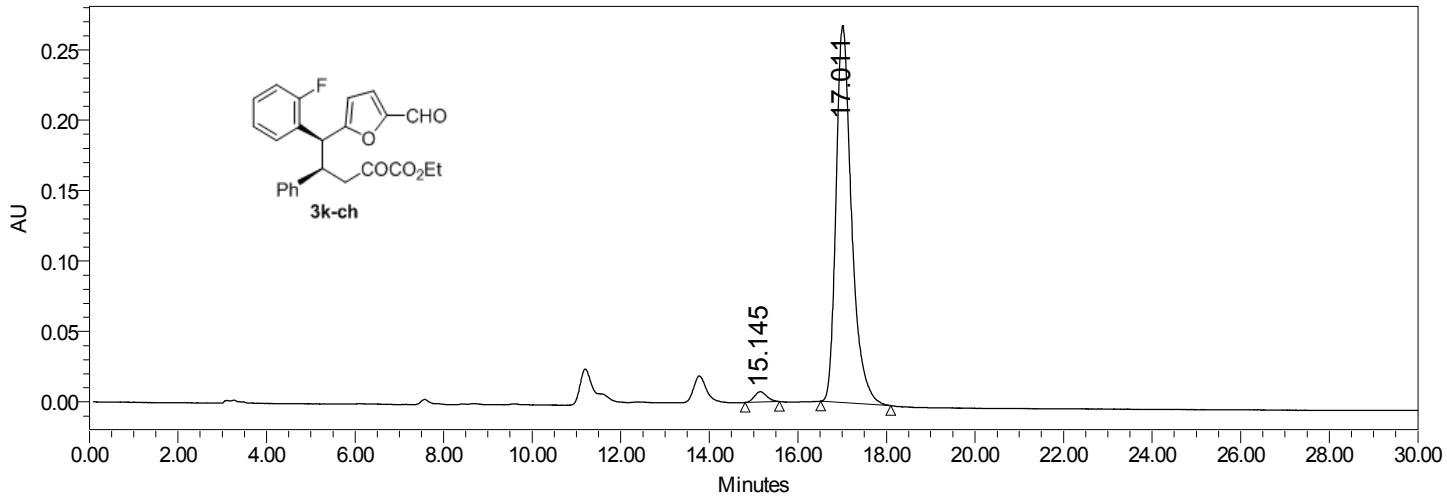


peak information

	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	14.951	33026976	50.16	1532899
2	16.787	32811129	49.84	1319526

Sample Name: 3k-ch Wave Length: 284.0 纳米

Column: Chiralpak IC-3 80:20



peak information

	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	15.145	142301	2.13	7369
2	17.011	6551224	97.87	267679

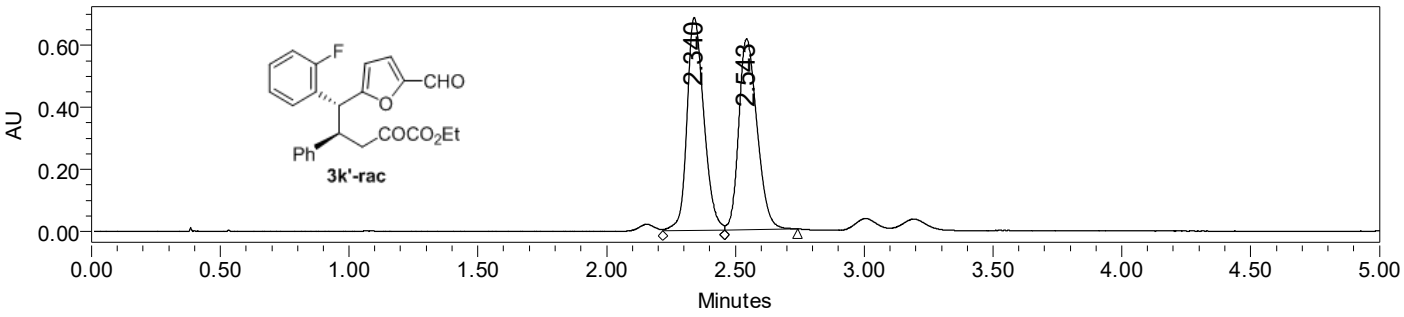
Empower™ 3 SOFTWARE

Sample Information

Sample Name: 3k'-rac

Wave Length: 280.0nm

Column: Chiralpak IG-3 95:5



peak information:

	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	2.340	3134770	50.82	686011
2	2.543	3033733	49.18	614450

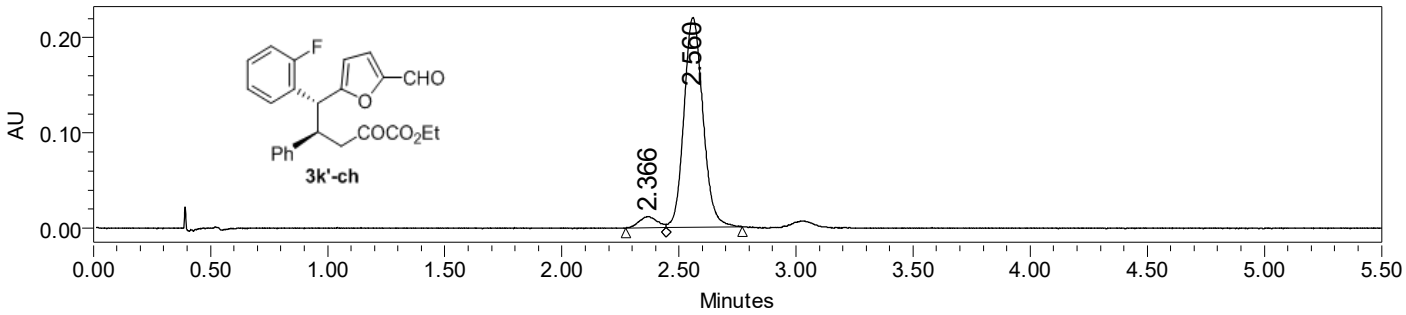
Empower™ 3 SOFTWARE

Sample Information

Sample Name: 3k'-ch

Wave Length: 280.0nm

Column: Chiralpak IG-3 95:5



peak information:

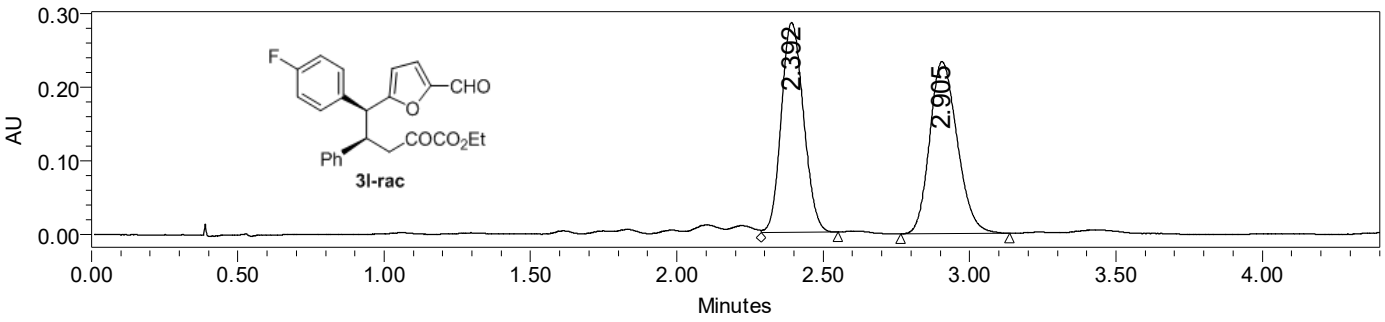
	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	2.366	62725	4.80	11799
2	2.560	1242873	95.20	219963

Empower™ 3 SOFTWARE

Sample Information

Sample Name: 3l-rac Wave Length: 283.0nm

Column: Chiralpak IG-3 95:5



peak information:

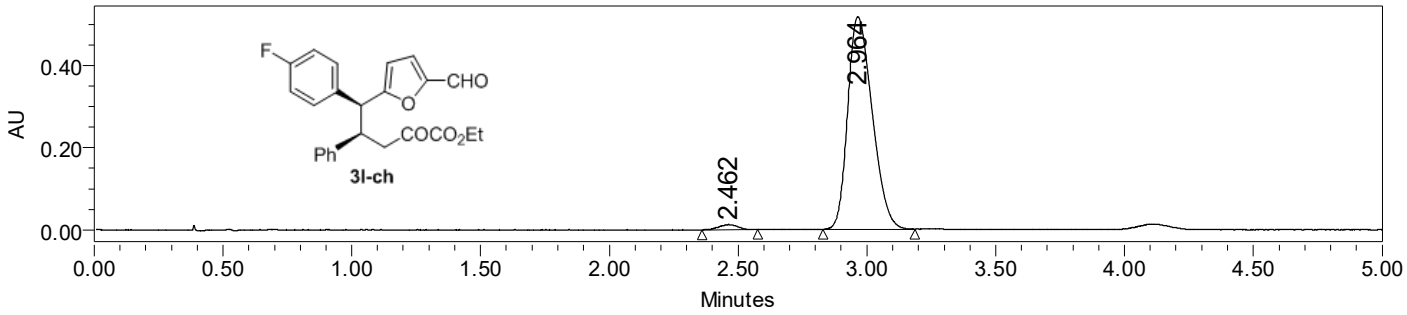
	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	2.392	1509973	49.61	285359
2	2.905	1533433	50.39	234279

Empower™ 3 SOFTWARE

Sample Information

Sample Name: 3l-ch Wave Length: 283.0nm

Column: Chiralpak IG-3 95:5



peak information:

	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	2.462	67737	1.94	12758
2	2.964	3419417	98.06	516761

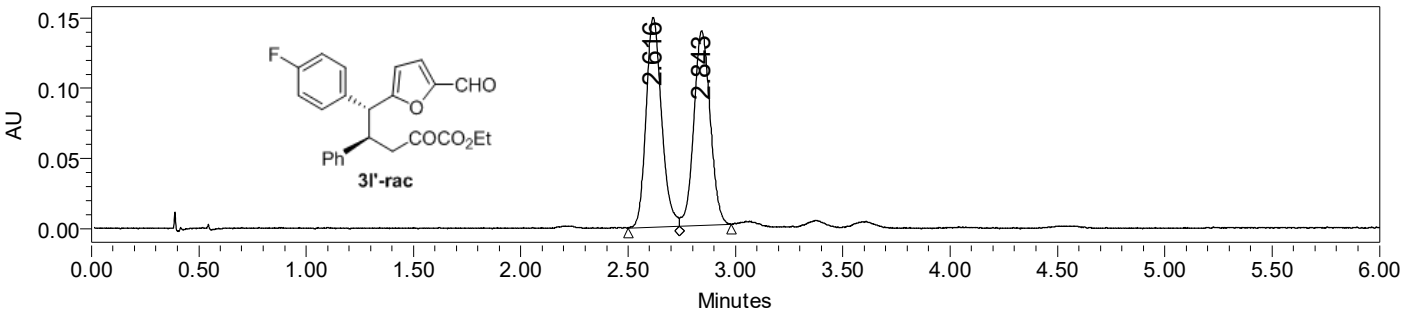
Empower™ 3 SOFTWARE

Sample Information

Sample Name: 3l'-rac

Wave Length: 282.0nm

Column: Chiralpak IG-3 95:5



peak information:

	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	2.616	751167	50.62	149228
2	2.843	732698	49.38	138539

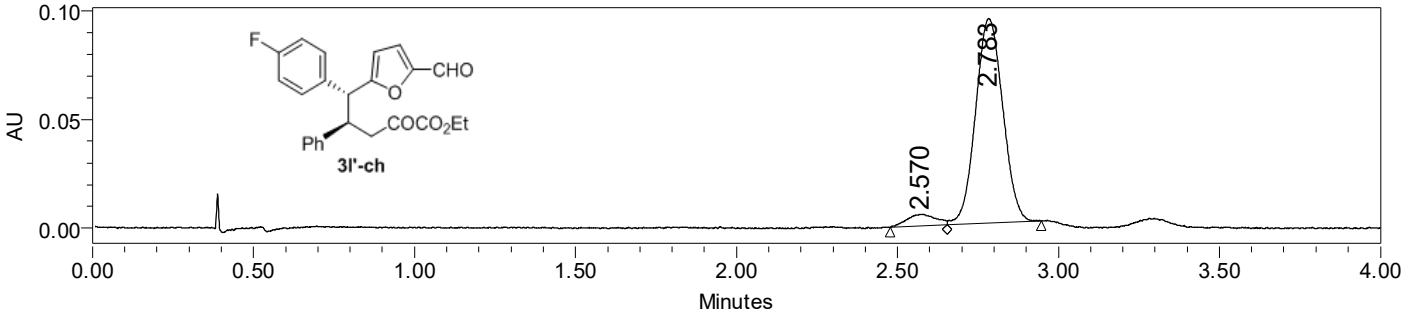
Empower™ 3 SOFTWARE

Sample Information

Sample Name: 3l'-ch

Wave Length: 282.0nm

Column: Chiralpak IG-3 95:5



peak information:

	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	2.570	33249	5.66	5253
2	2.783	554377	94.34	94124

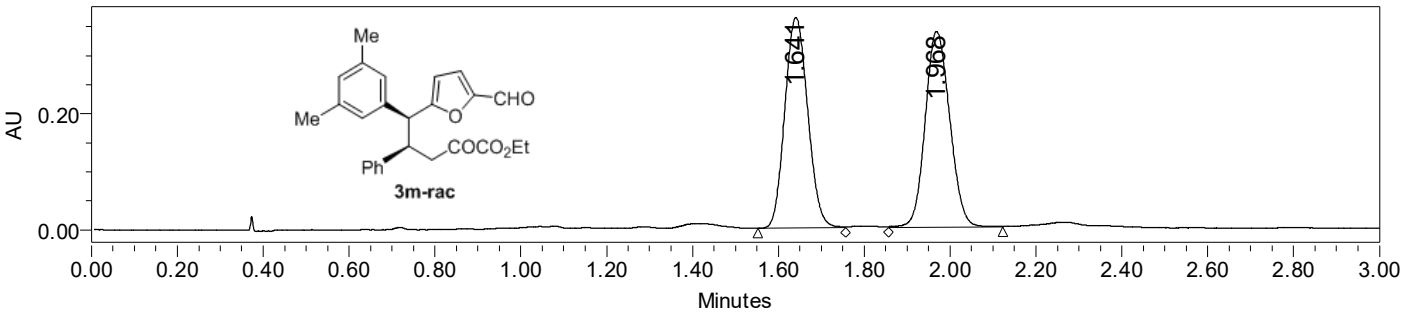
Empower™ 3 SOFTWARE

Sample Information

Sample Name: 3m-rac

Column: Chiralpak IG-3 95:5

Wave Length: 285.0nm



peak information:

	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	1.641	1346175	50.20	362828
2	1.968	1335657	49.80	337102

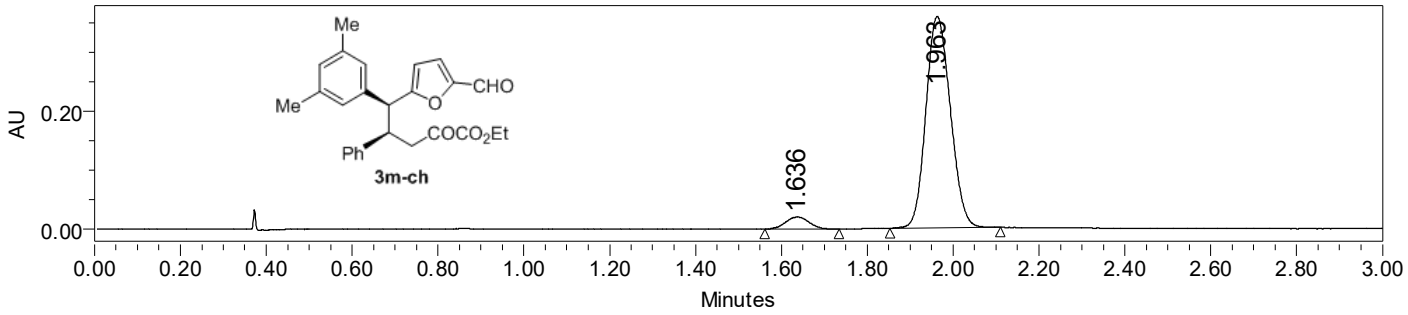
Empower™ 3 SOFTWARE

Sample Information

Sample Name: 3m-ch

Column: Chiralpak IG-3 95:5

Wave Length: 285.0nm



peak information:

	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	1.636	76450	5.09	20288
2	1.963	1424075	94.91	359235

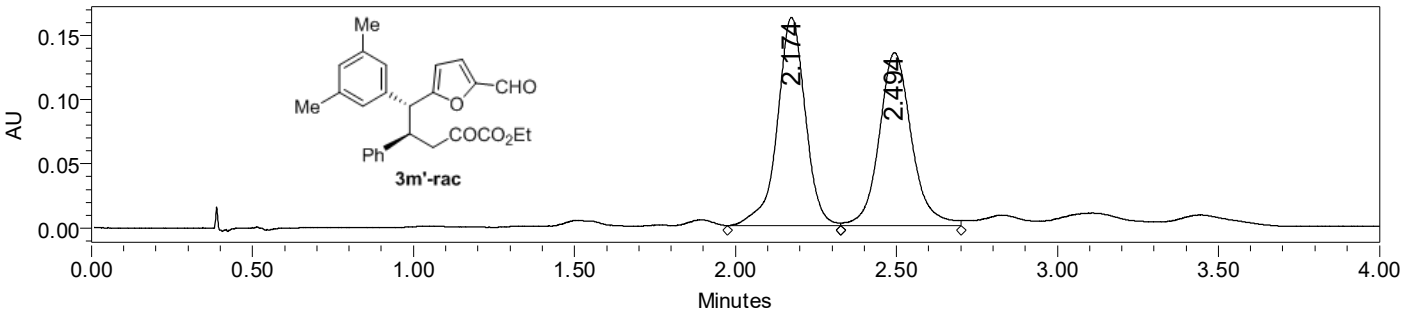
Empower™ 3 SOFTWARE

Sample Information

Sample Name: 3m'-rac

Wave Length: 284.0nm

Column: Chiralpak IG-3 95:5



peak information:

	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	2.174	979280	51.00	162052
2	2.494	940706	49.00	134781

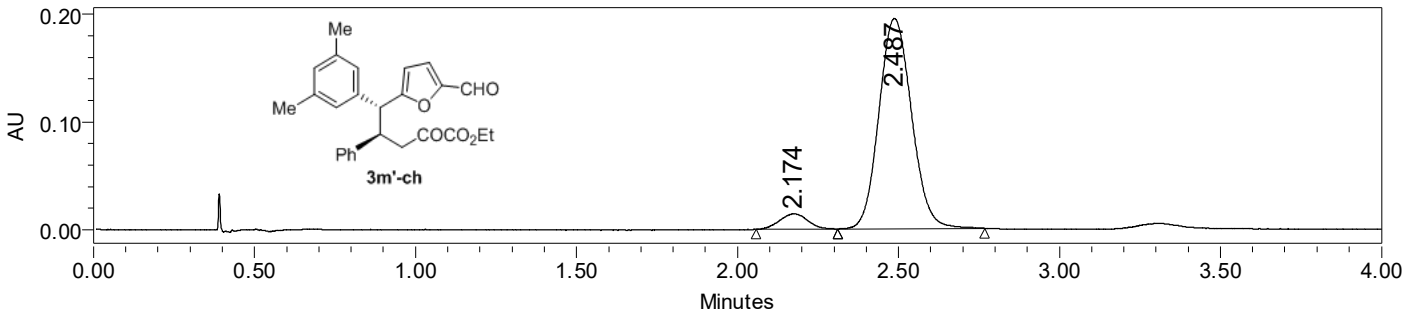
Empower™ 3 SOFTWARE

Sample Information

Sample Name: 3m'-ch

Wave Length: 284.0nm

Column: Chiralpak IG-3 95:5



peak information:

	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	2.174	85702	5.87	14144
2	2.487	1374064	94.13	195190

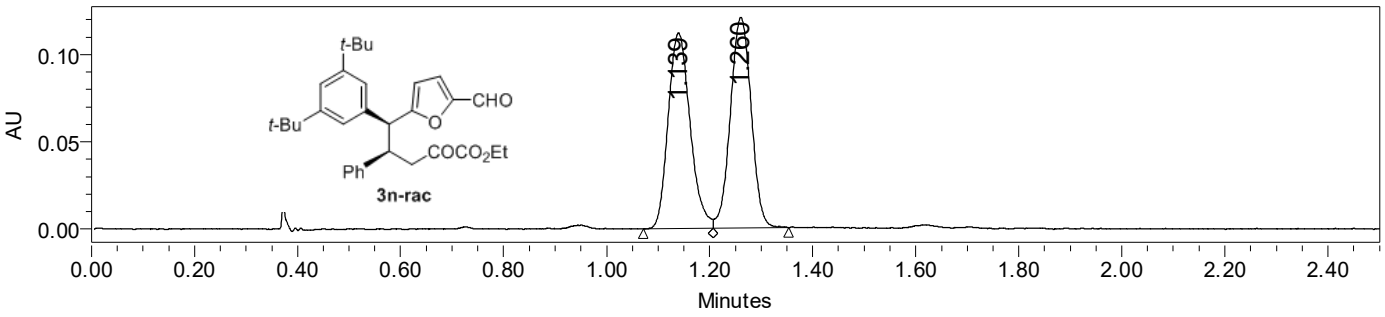
Empower™ 3 SOFTWARE

Sample Information

Sample Name: 3n-rac

Wave Length: 285.0nm

Column: Trefoil TM CEL1 95:5



peak information:

	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	1.139	332273	49.60	112138
2	1.260	337620	50.40	120604

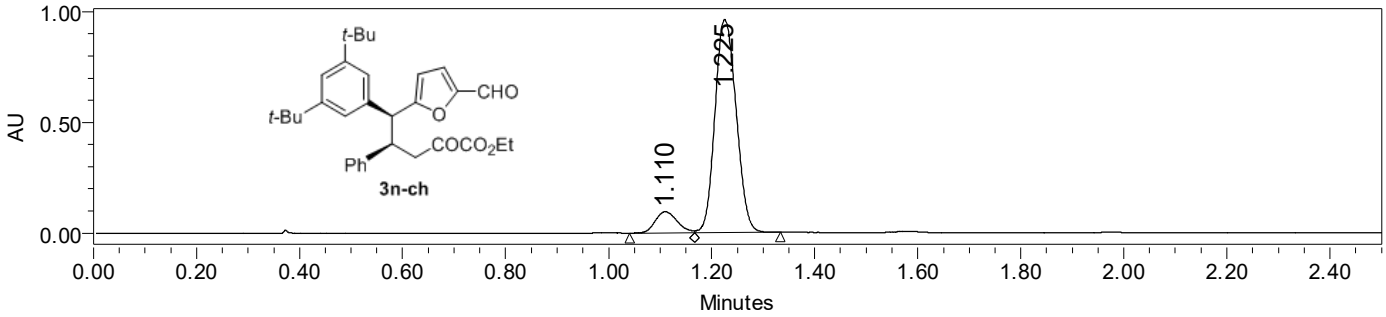
Empower™ 3 SOFTWARE

Sample Information

Sample Name: 3n-ch

Wave Length: 285.0nm

Column: Trefoil TM CEL1 95:5

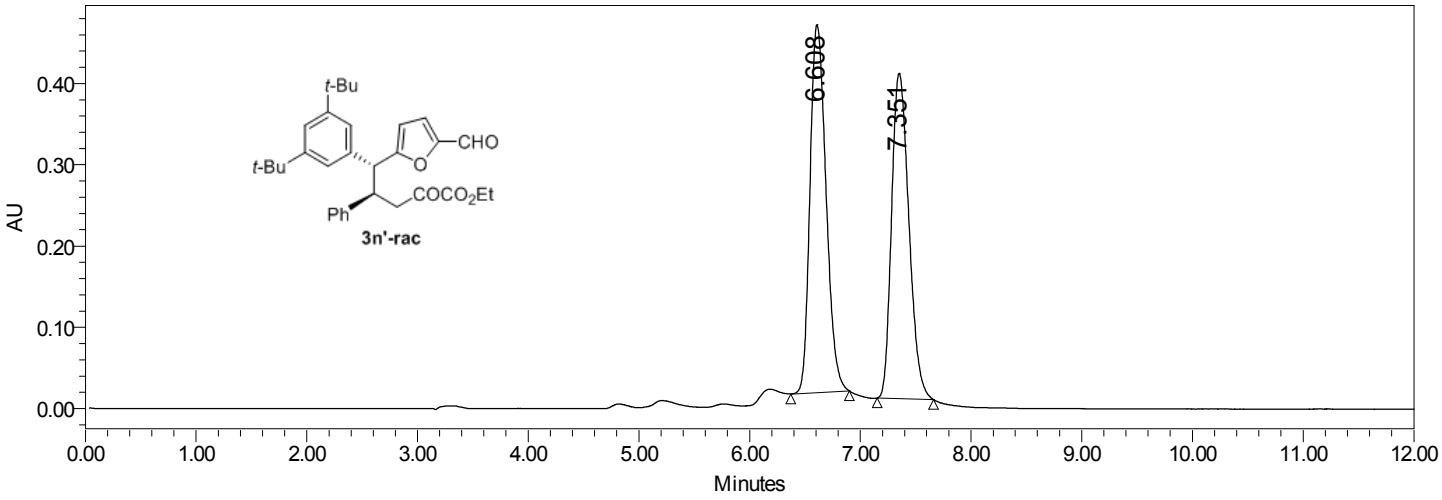


peak information:

	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	1.110	284099	9.34	95734
2	1.225	2757435	90.66	962465

Sample Name: 3n'-rac Wave Length: 285.0 纳米

Column: Chiralpak ID-3 90:10

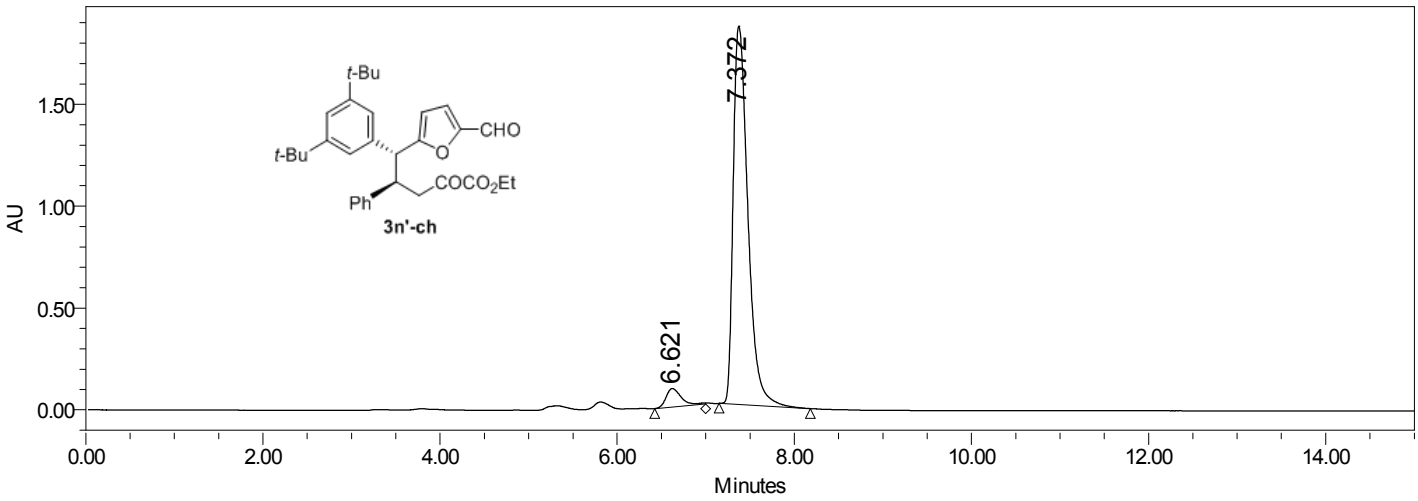


peak information

	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	6.608	4554928	51.18	452779
2	7.351	4344870	48.82	400305

Sample Name: 3n'-ch Wave Length: 285.0 纳米

Column: Chiralpak ID-3 90:10

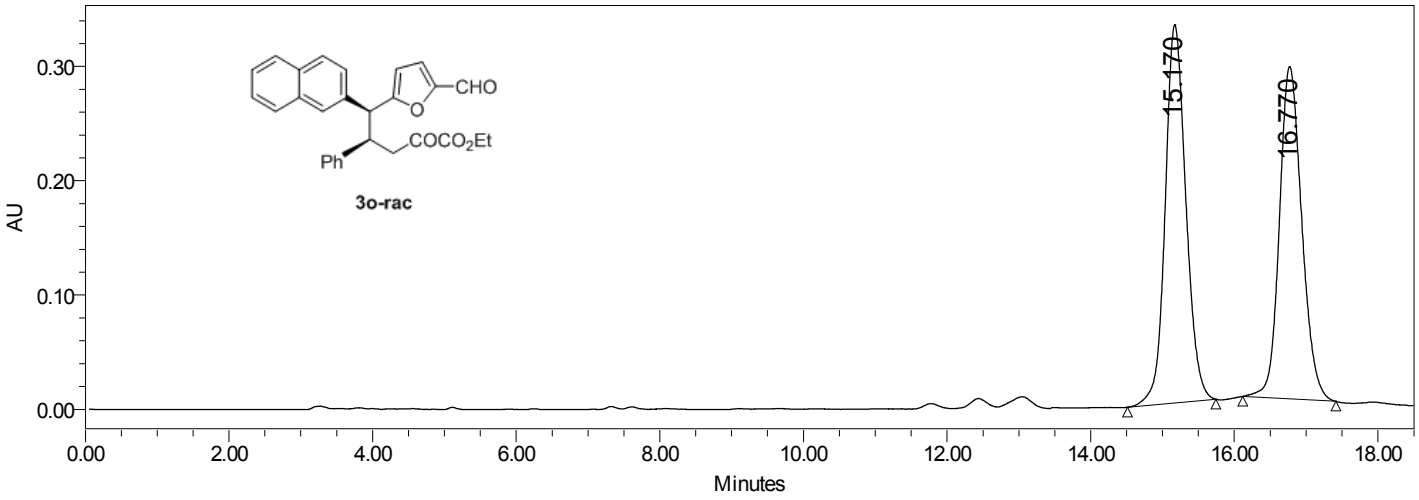


peak information

	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	6.621	1079850	4.82	90799
2	7.372	21315536	95.18	1857845

Sample Name: 3o-rac Wave Length: 285.0 纳米

Column: Chiralpak ID-3 80:20

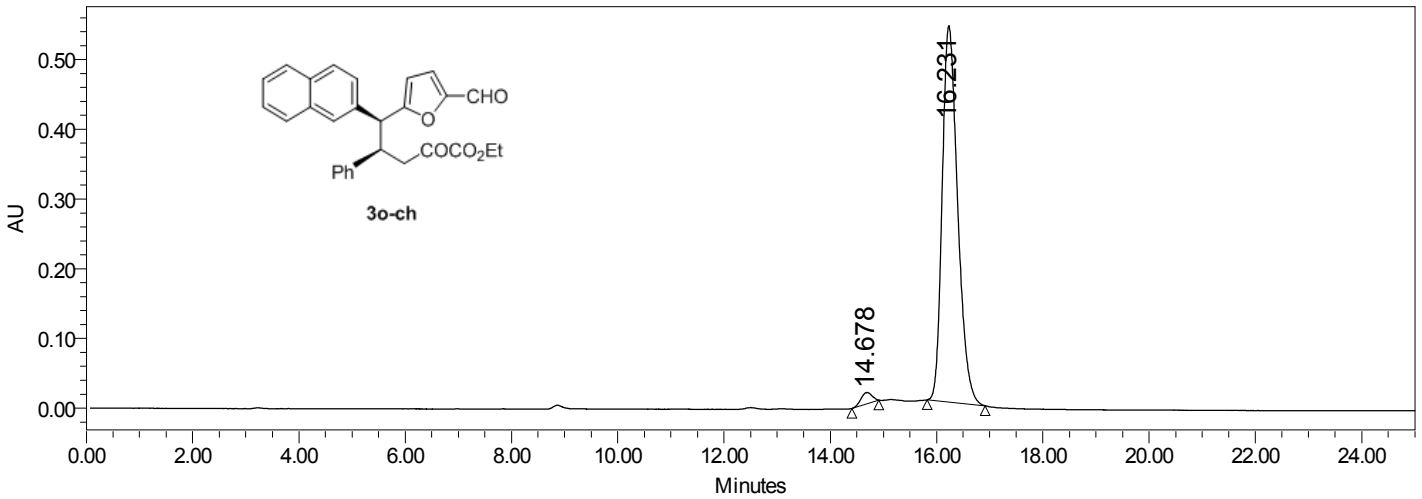


peak information

	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	15.170	6601442	51.18	330915
2	16.770	6295998	48.82	290734

Sample Name: 3o-ch Wave Length: 285.0 纳米

Column: Chiralpak ID-3 80:20



peak information

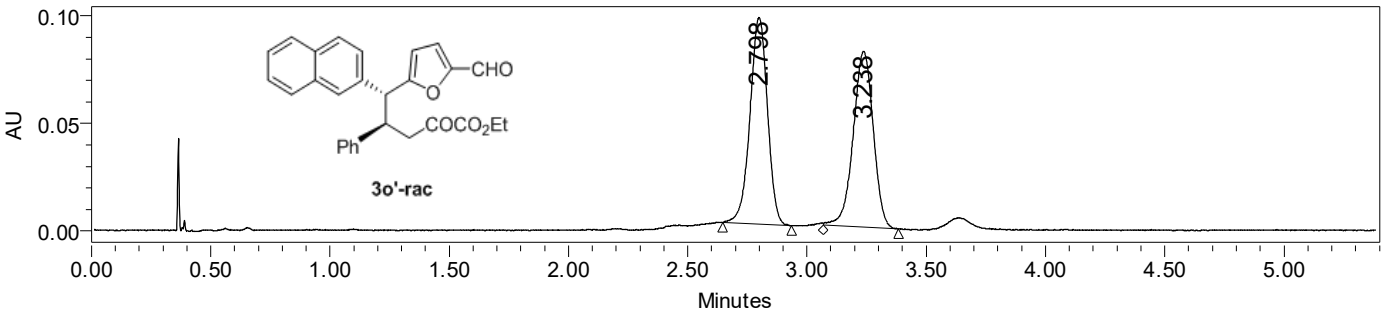
	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	14.678	237186	2.13	16415
2	16.231	10899402	97.87	539483

Empower™ 3 SOFTWARE

Sample Information

Sample Name: 3o'-rac Wave Length: 284.0nm

Column: Chiralpak IG-3 90:10



peak information:

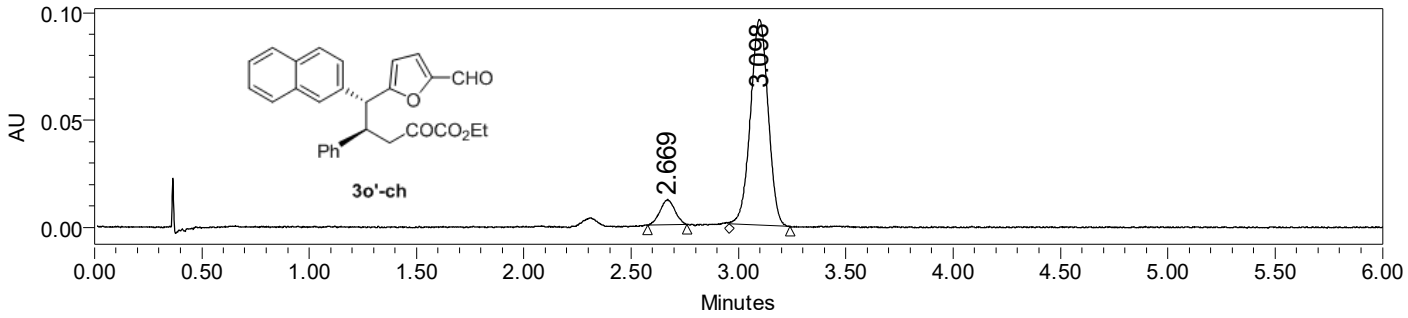
	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	2.798	491290	50.53	96043
2	3.238	480895	49.47	81860

Empower™ 3 SOFTWARE

Sample Information

Sample Name: 3o'-ch Wave Length: 284.0nm

Column: Chiralpak IG-3 90:10



peak information:

	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	2.669	57770	9.52	11764
2	3.098	549306	90.48	95873

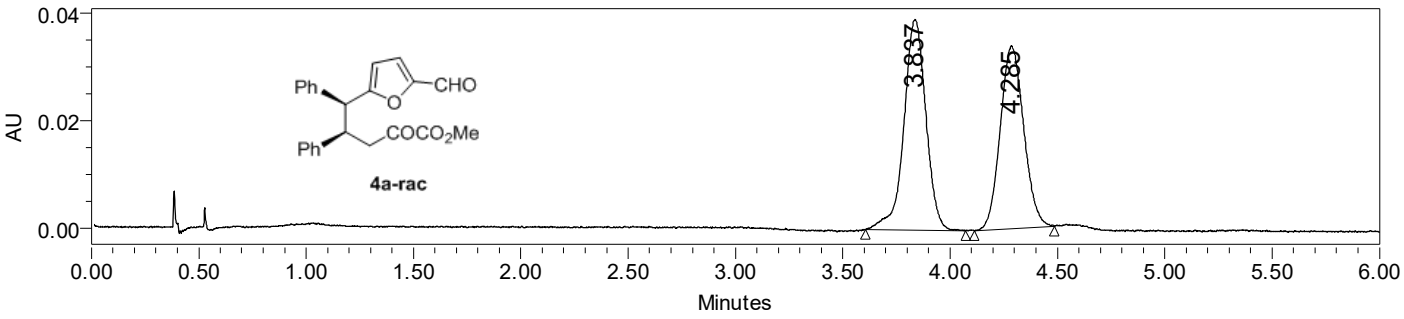
Empower™ 3 SOFTWARE

Sample Information

Sample Name: 4a-rac

Wave Length: 284.0nm

Column: Chiralpak IG-3 95:5



peak information:

	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	3.837	277914	51.85	39138
2	4.285	258115	48.15	34008

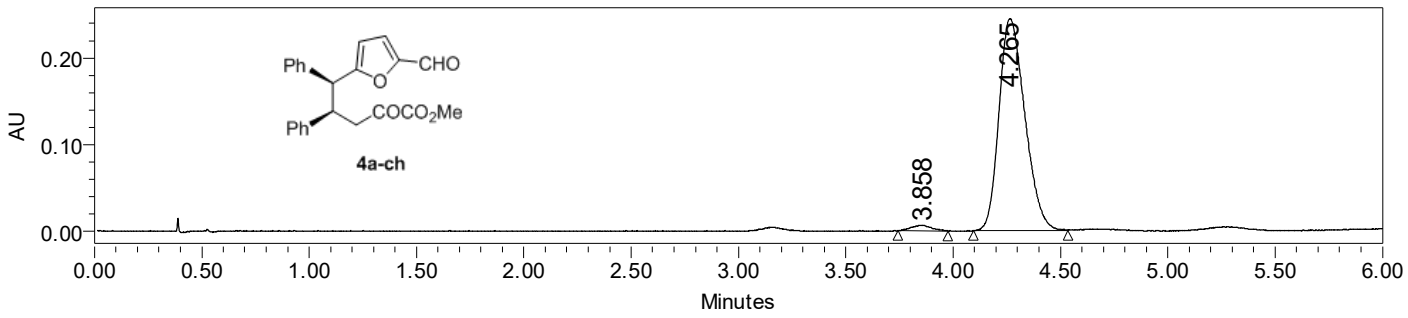
Empower™ 3 SOFTWARE

Sample Information

Sample Name: 4a-ch

Wave Length: 283.0nm

Column: Chiralpak IG-3 95:5



peak information:

	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	3.858	40998	1.96	6011
2	4.265	2049068	98.04	244811

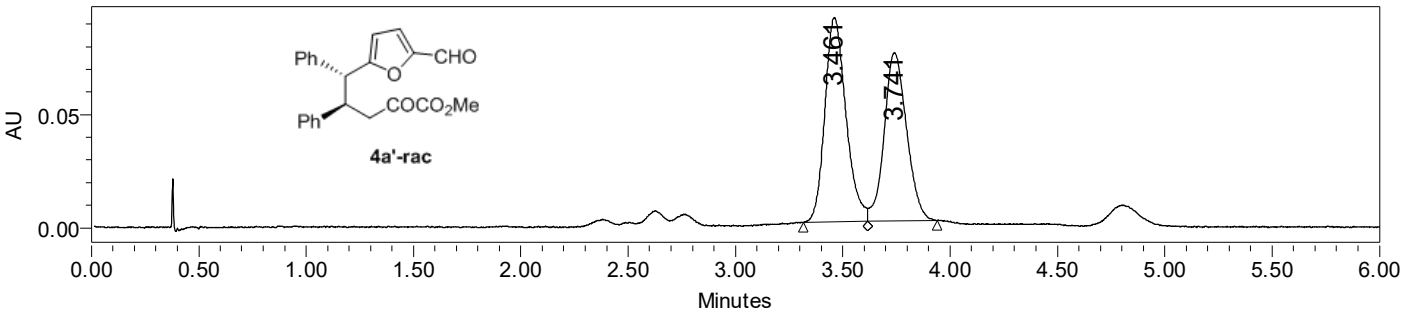
Empower™ 3 SOFTWARE

Sample Information

Sample Name: 4a'-rac

Wave Length: 283.0nm

Column: Chiralpak OD-3 95:5



peak information:

	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	3.461	616427	53.23	90257
2	3.741	541510	46.77	74406

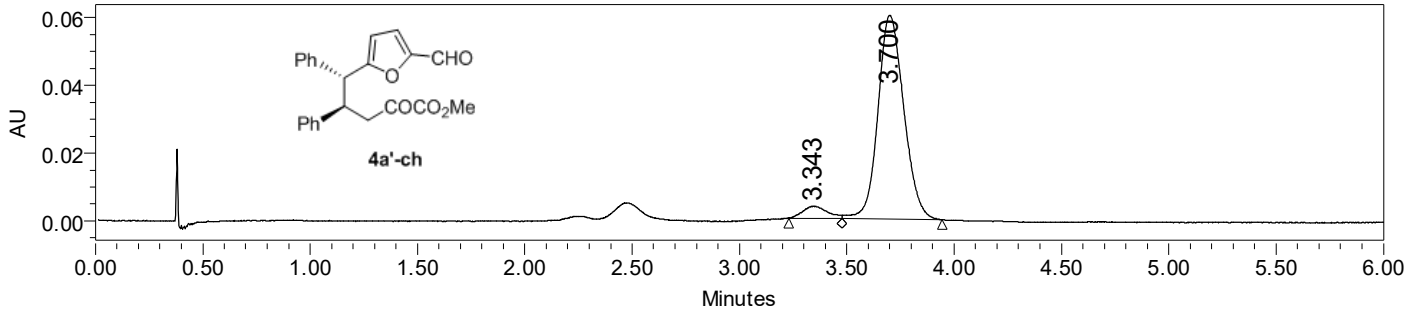
Empower™ 3 SOFTWARE

Sample Information

Sample Name: 4a'-ch

Wave Length: 283.0nm

Column: Chiralpak OD-3 95:5



peak information:

	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	3.343	28905	5.40	3573
2	3.700	506027	94.60	60151

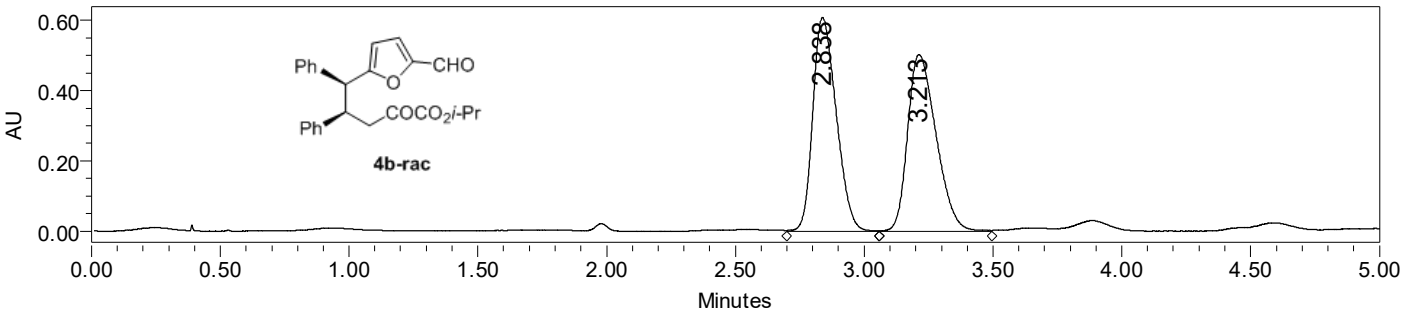
Empower™ 3 SOFTWARE

Sample Information

Sample Name: 4b-rac

Wave Length: 283.0nm

Column: Chiralpak IG-3 95:5



peak information:

	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	2.838	3853201	50.04	608869
2	3.213	3847806	49.96	503109

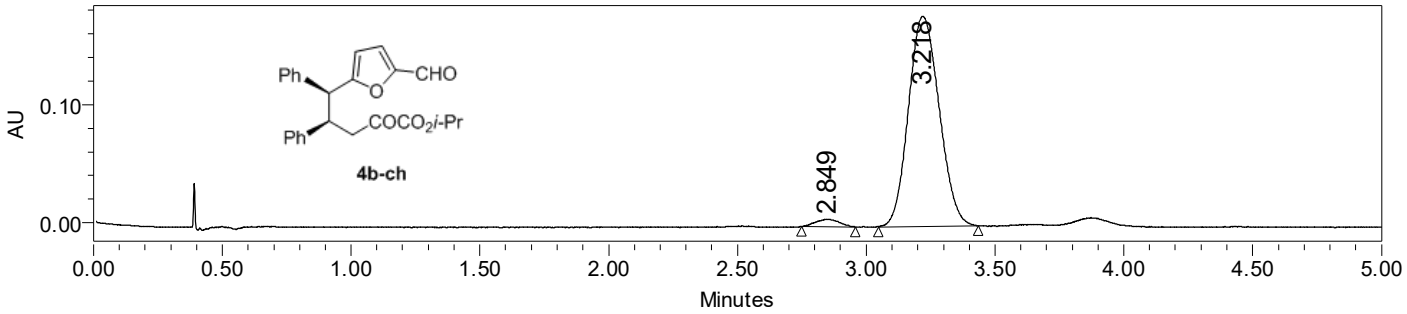
Empower™ 3 SOFTWARE

Sample Information

Sample Name: 4b-ch

Wave Length: 283.0nm

Column: Chiralpak IG-3 95:5



peak information:

	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	2.849	40150	2.65	6188
2	3.218	1473793	97.35	177948

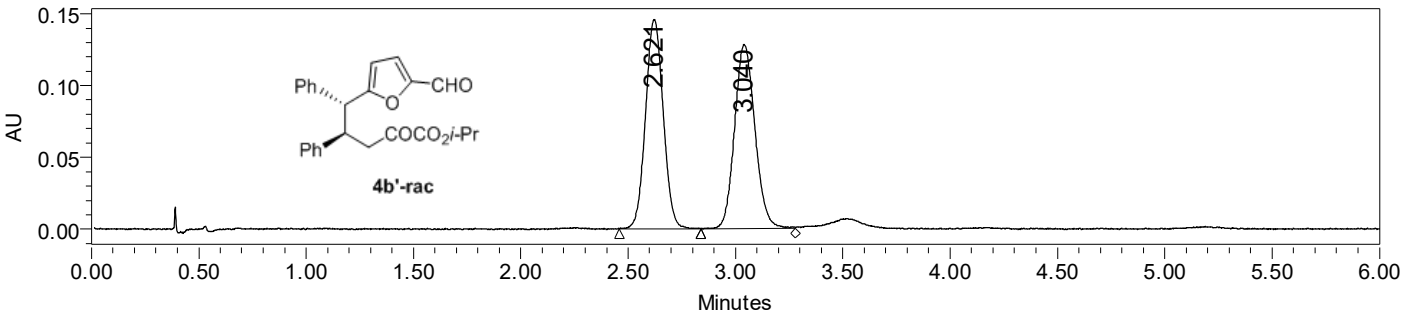
Empower™ 3 SOFTWARE

Sample Information

Sample Name: 4b'-rac

Wave Length: 283.0nm

Column: Chiralpak IG-3 95:5



peak information:

	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	2.621	840921	49.76	145818
2	3.040	848926	50.24	128296

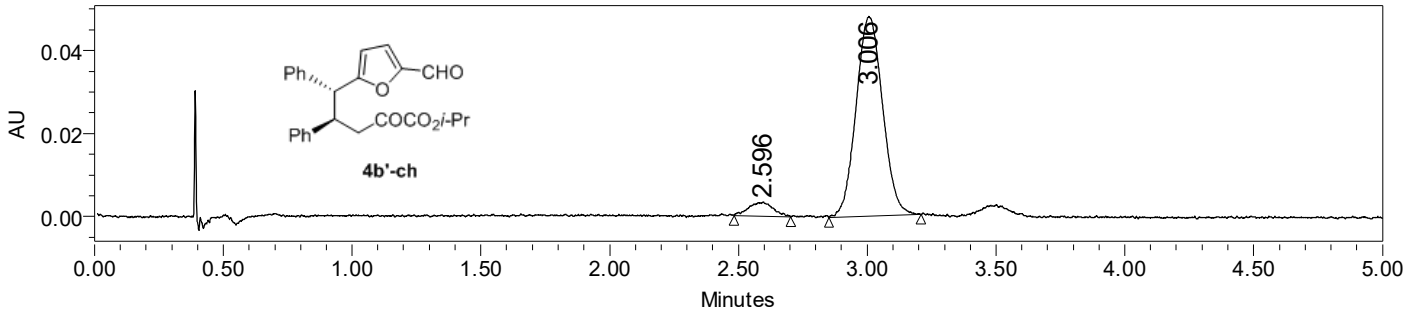
Empower™ 3 SOFTWARE

Sample Information

Sample Name: 4b'-ch

Wave Length: 283.0nm

Column: Chiralpak IG-3 95:5



peak information:

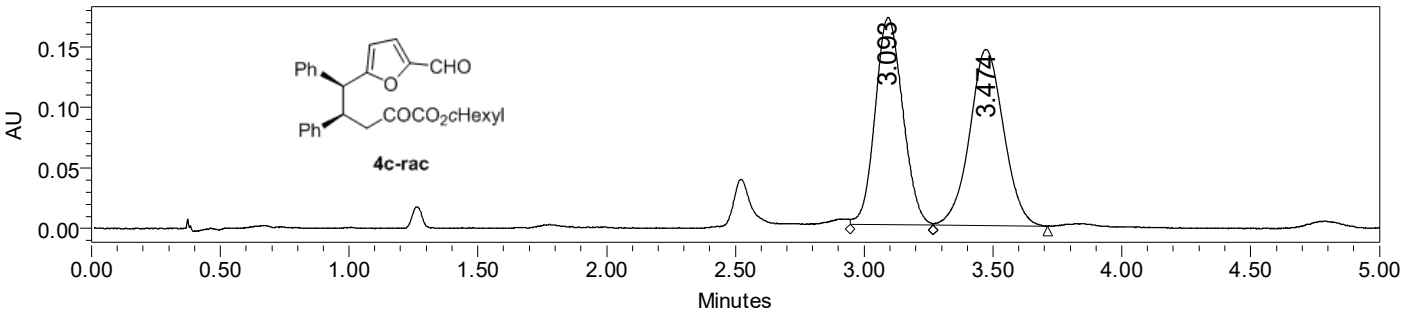
	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	2.596	21612	5.90	3313
2	3.006	344427	94.10	48133

Empower™ 3 SOFTWARE

Sample Information

Sample Name: 4c-rac Wave Length: 285.0nm

Column: Chiralpak IG-3 90:10



peak information:

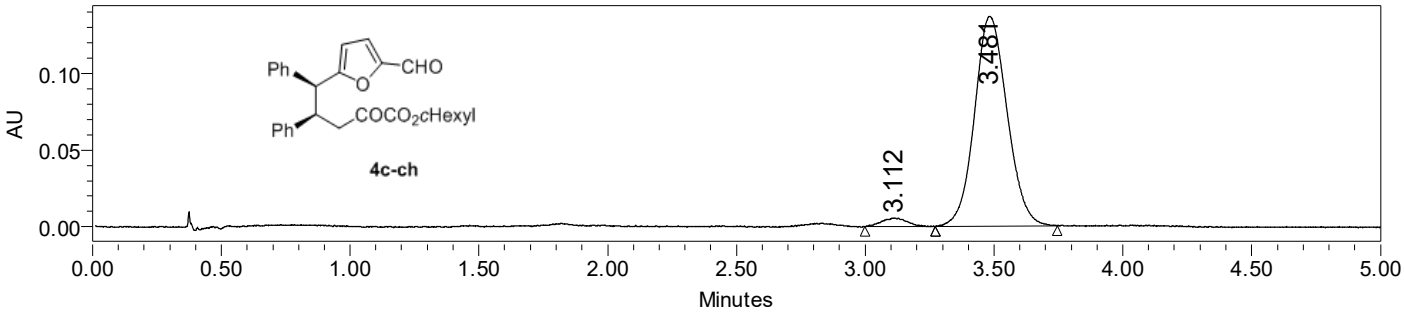
	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	3.093	1271100	48.74	170732
2	3.474	1336611	51.26	145197

Empower™ 3 SOFTWARE

Sample Information

Sample Name: 4c-ch Wave Length: 285.0nm

Column: Chiralpak IG-3 90:10



peak information:

	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	3.112	38242	3.05	5567
2	3.481	1213567	96.95	137105

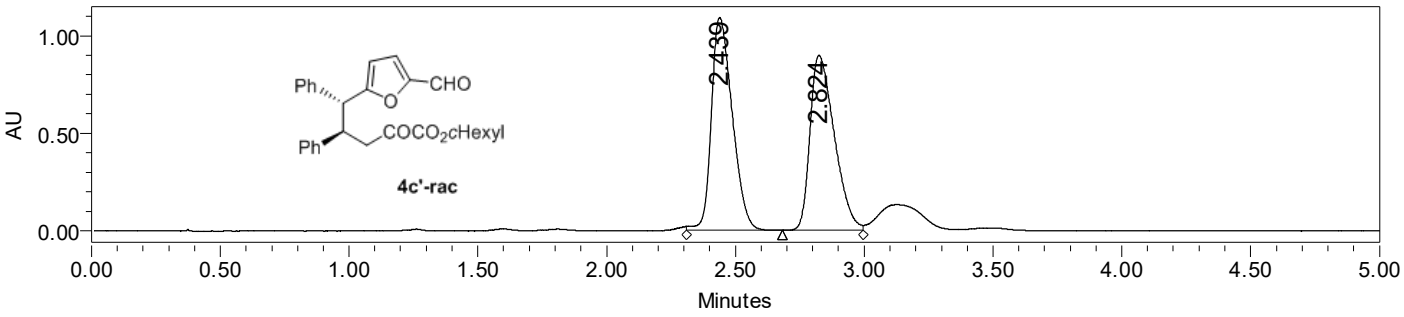
Empower™ 3 SOFTWARE

Sample Information

Sample Name: 4c'-rac

Wave Length: 284.0nm

Column: Chiralpak IG-3 90:10



peak information:

	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	2.439	6138144	51.10	1091247
2	2.824	5874972	48.90	896460

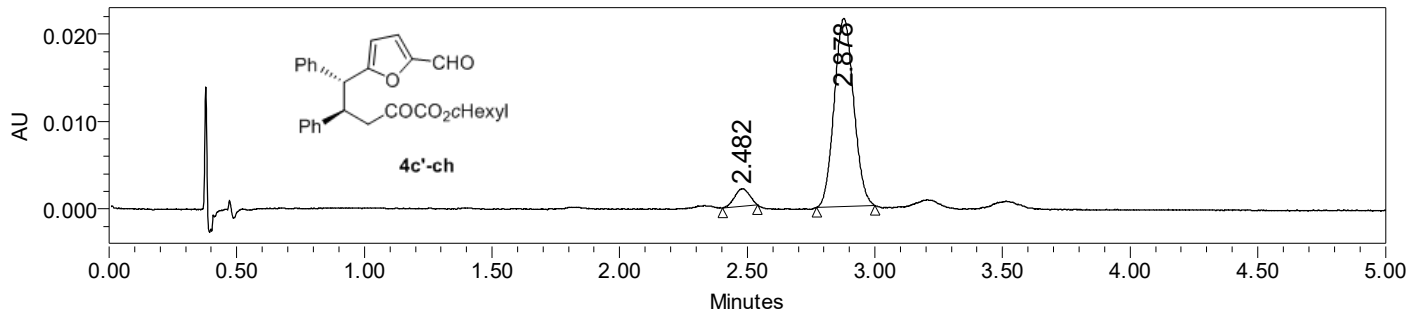
Empower™ 3 SOFTWARE

Sample Information

Sample Name: 4c'-ch

Wave Length: 284.0nm

Column: Chiralpak IG-3 90:10



peak information:

	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	2.482	8141	6.63	2010
2	2.878	114560	93.37	21535

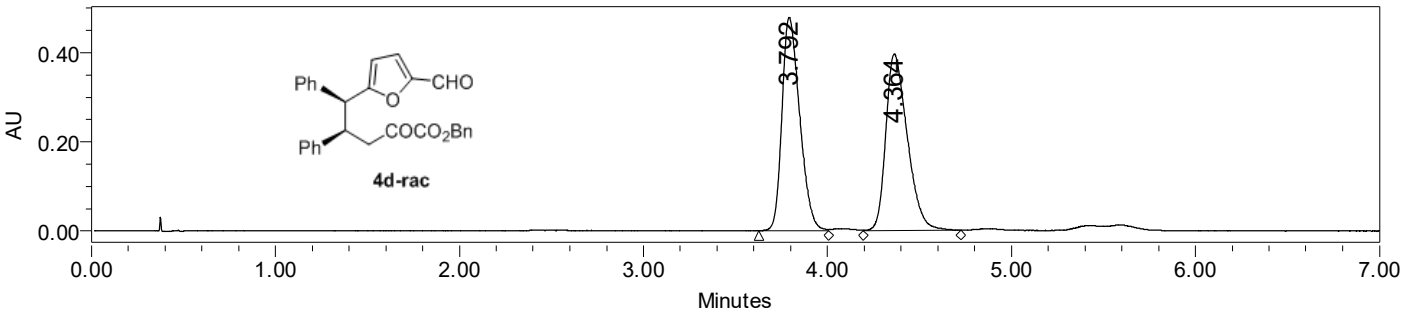
Empower™ 3 SOFTWARE

Sample Information

Sample Name: 4d-rac

Wave Length: 285.0nm

Column: Chiralpak IG-3 90:10



peak information:

	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	3.792	3213183	49.86	478290
2	4.364	3231159	50.14	395544

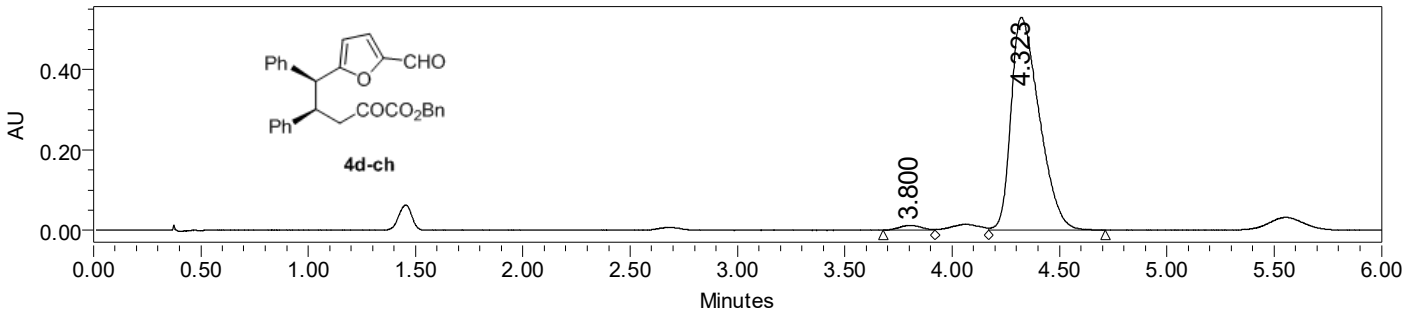
Empower™ 3 SOFTWARE

Sample Information

Sample Name: 4d-ch

Wave Length: 285.0nm

Column: Chiralpak IG-3 90:10



peak information:

	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	3.800	86467	1.76	12171
2	4.323	4816443	98.24	528966

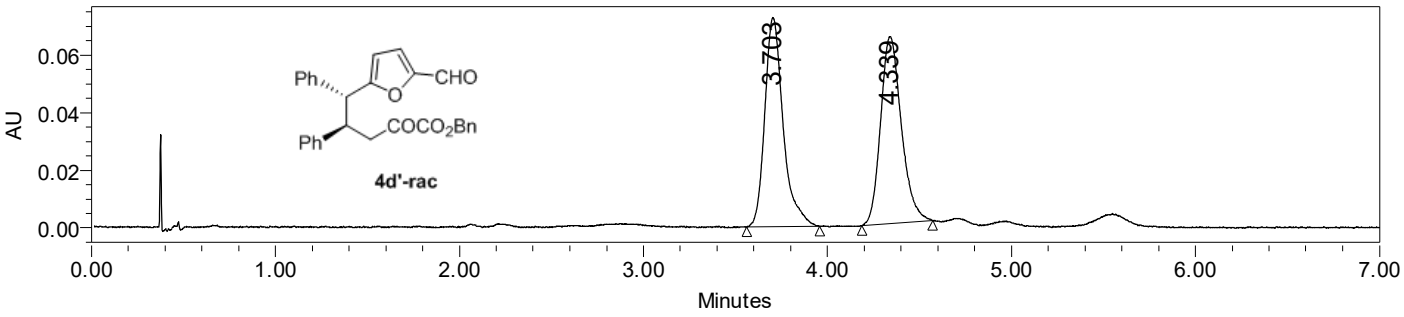
Empower™ 3 SOFTWARE

Sample Information

Sample Name: 4d'-rac

Wave Length: 284.0nm

Column: Chiralpak IG-3 90:10



peak information:

	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	3.703	509114	49.89	72799
2	4.339	511386	50.11	64988

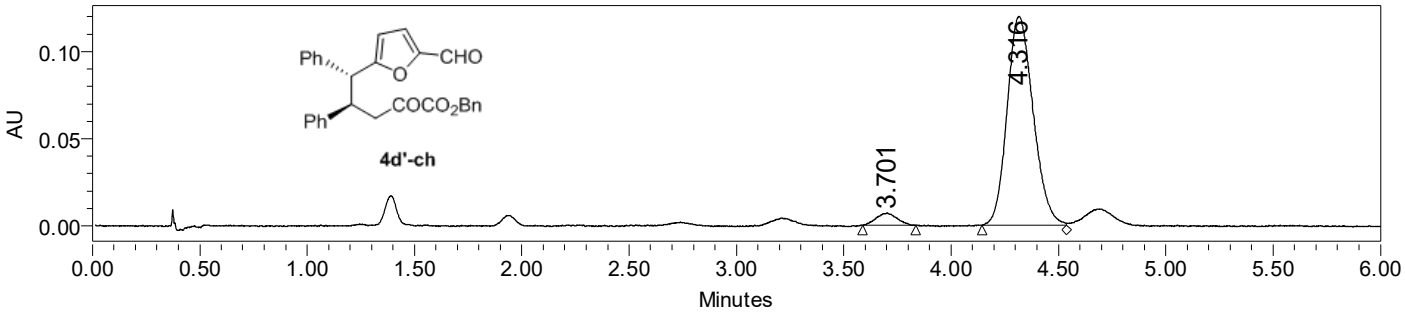
Empower™ 3 SOFTWARE

Sample Information

Sample Name: 4d'-ch

Wave Length: 284.0nm

Column: Chiralpak IG-3 90:10



peak information:

	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	3.701	47216	4.47	6937
2	4.316	1008437	95.53	119808

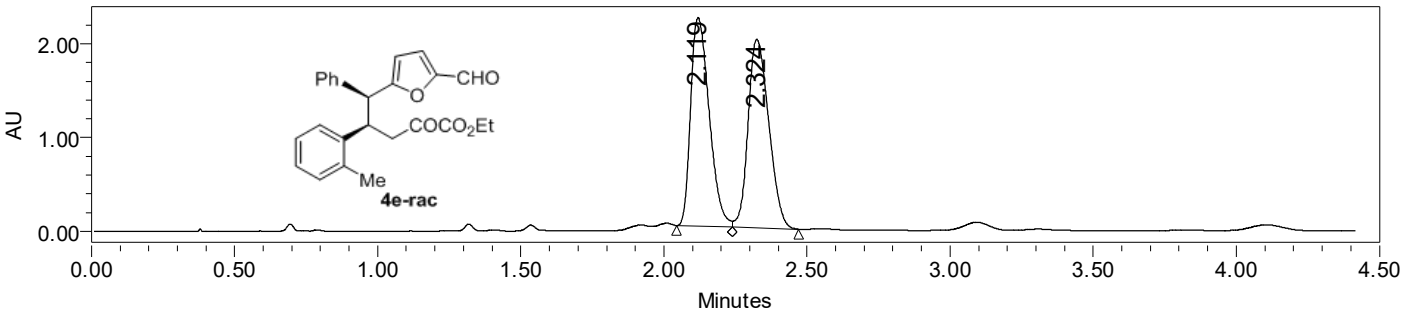
Empower™ 3 SOFTWARE

Sample Information

Sample Name: 4e-rac

Wave Length: 284.0nm

Column: Chiralpak OD-3 95:5



peak information:

	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	2.119	10052839	49.79	2227188
2	2.324	10135980	50.21	2012180

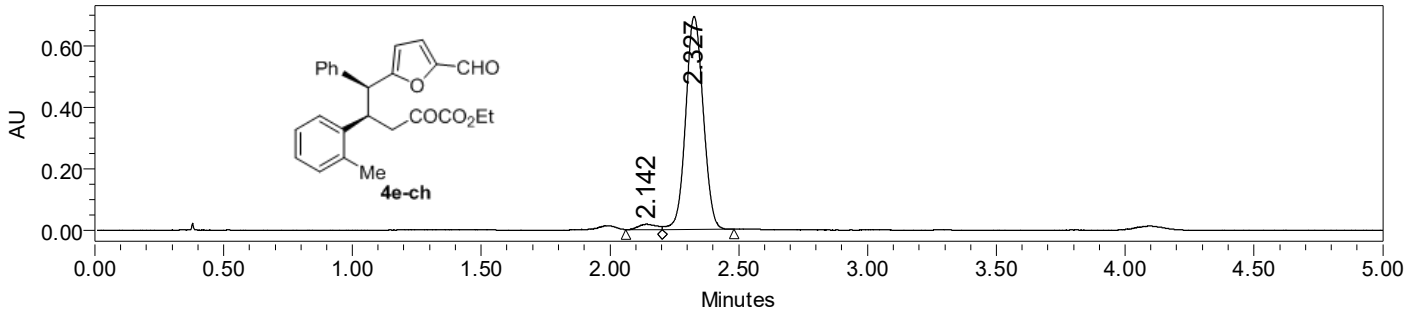
Empower™ 3 SOFTWARE

Sample Information

Sample Name: 4e-ch

Wave Length: 284.0nm

Column: Chiralpak OD-3 95:5



peak information:

	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	2.142	86312	2.55	17719
2	2.327	3295869	97.45	693512

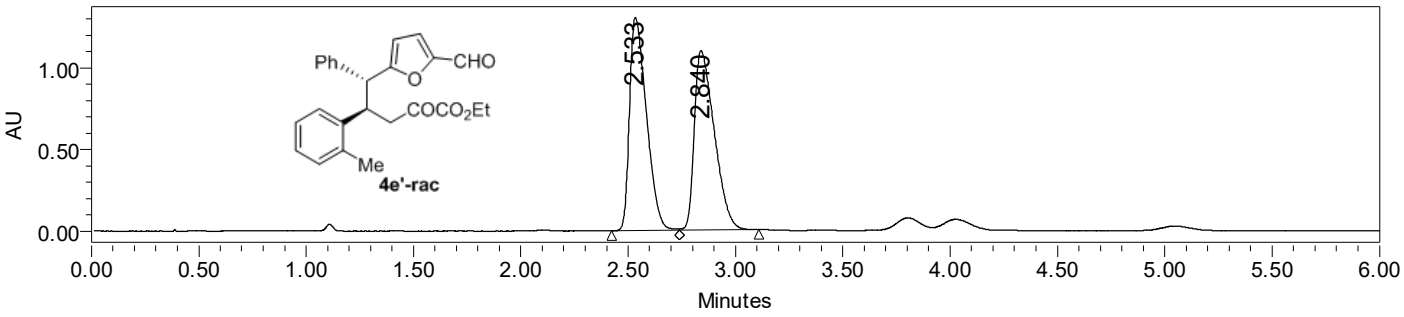
Empower™ 3 SOFTWARE

Sample Information

Sample Name: 4e'-rac

Wave Length: 282.0nm

Column: Chiralpak IG-3 95:5



peak information:

	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	2.533	7156913	50.18	1306561
2	2.840	7104452	49.82	1099547

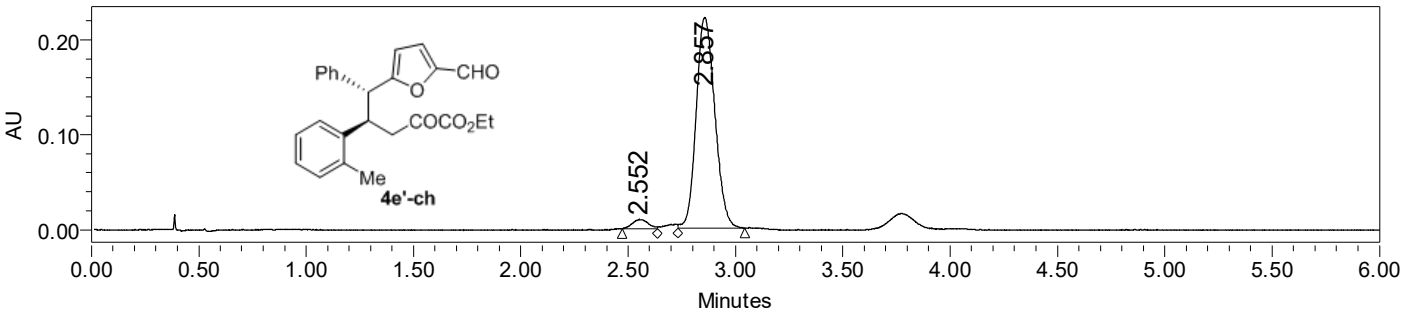
Empower™ 3 SOFTWARE

Sample Information

Sample Name: 4e'-ch

Wave Length: 282.0nm

Column: Chiralpak IG-3 95:5



peak information:

	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	2.552	49542	3.57	9636
2	2.857	1339007	96.43	222180

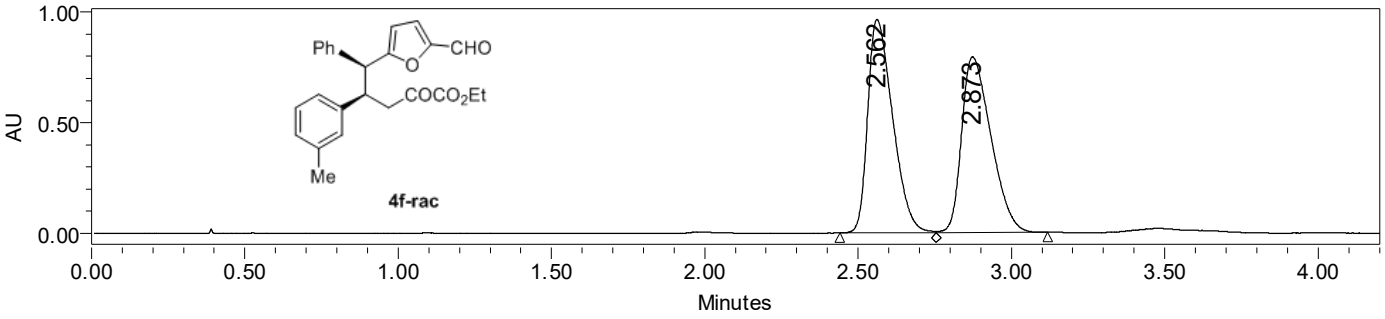
Empower™ 3 SOFTWARE

Sample Information

Sample Name: 4f-rac

Wave Length: 284.0nm

Column: Chiralpak IG-3 95:5



peak information:

	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	2.562	5466939	50.74	964598
2	2.873	5306572	49.26	794728

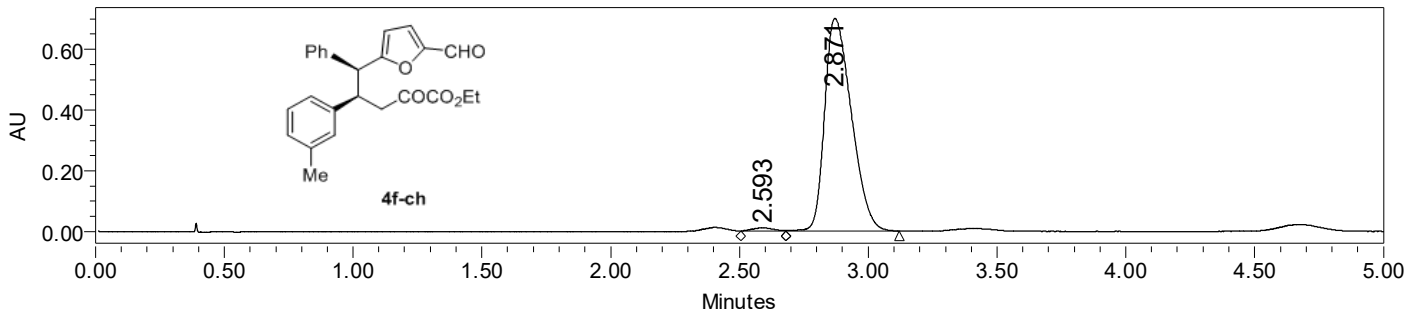
Empower™ 3 SOFTWARE

Sample Information

Sample Name: 4f-ch

Wave Length: 284.0nm

Column: Chiralpak IG-3 95:5



peak information:

	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	2.593	65755	1.28	10910
2	2.871	5059283	98.72	700014

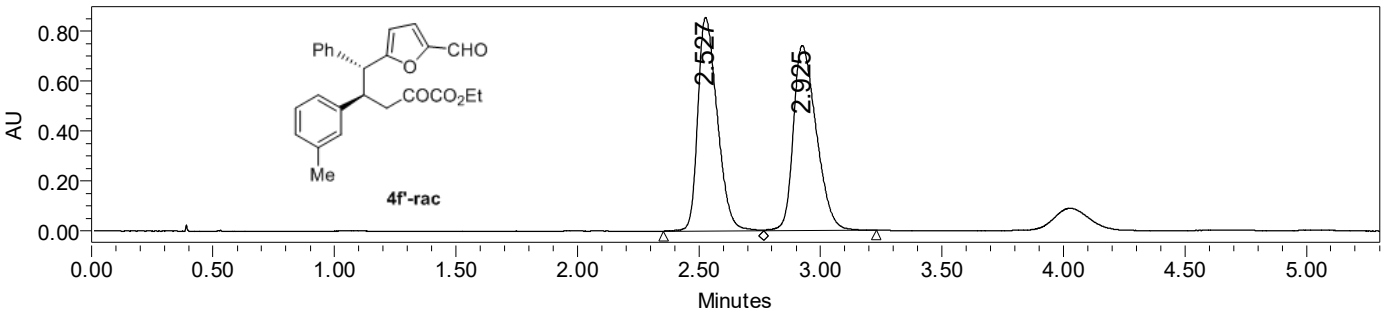
Empower™ 3 SOFTWARE

Sample Information

Sample Name: 4f'-rac

Wave Length: 283.0nm

Column: Chiralpak IG-3 95:5



peak information:

	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	2.527	4737246	49.39	854272
2	2.925	4854196	50.61	740350

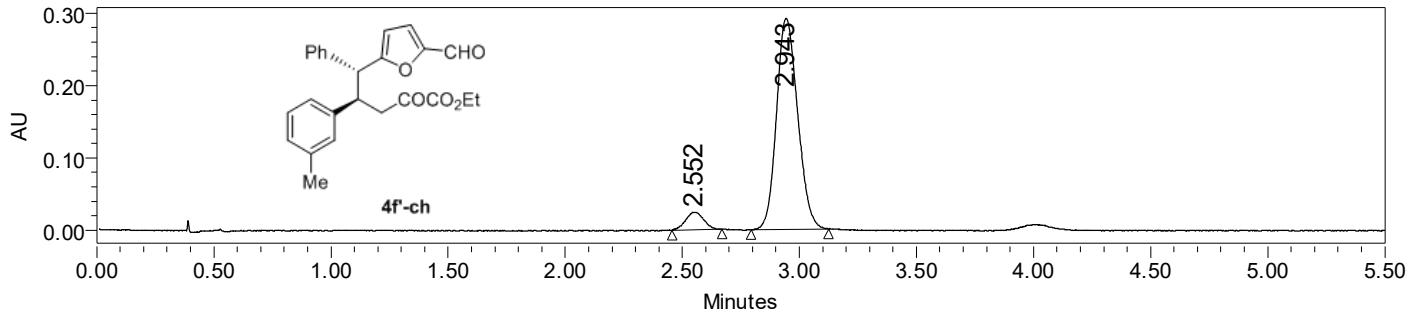
Empower™ 3 SOFTWARE

Sample Information

Sample Name: 4f'-ch

Wave Length: 283.0nm

Column: Chiralpak IG-3 95:5



peak information:

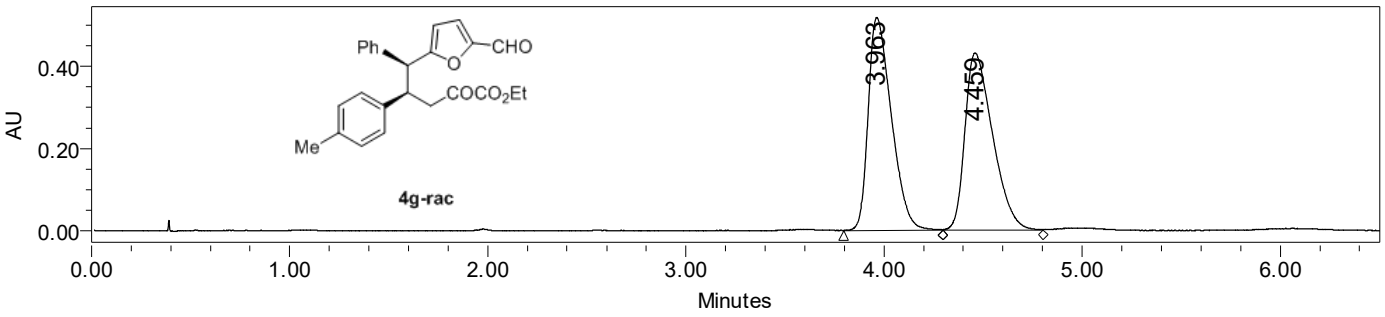
	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	2.552	131516	6.67	24298
2	2.943	1839725	93.33	291921

Empower™ 3 SOFTWARE

Sample Information

Sample Name: 4g-rac Wave Length: 284.0nm

Column: Chiralpak IG-3 95:5



peak information:

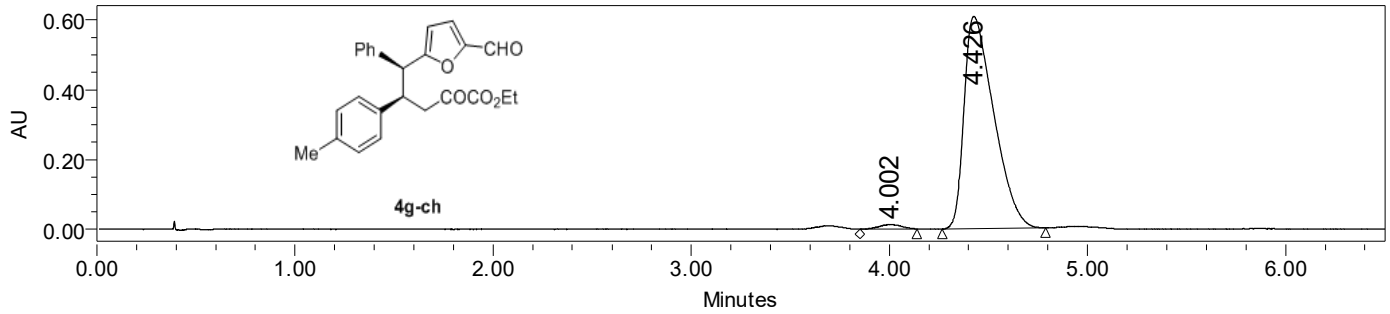
	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	3.963	4227206	50.15	517934
2	4.459	4201546	49.85	430694

Empower™ 3 SOFTWARE

Sample Information

Sample Name: 4g-ch Wave Length: 284.0nm

Column: Chiralpak IG-3 95:5



peak information:

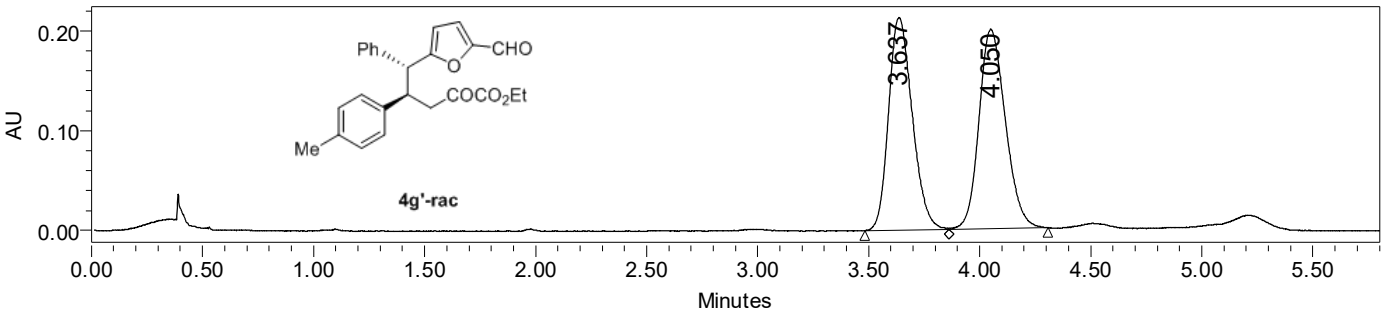
	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	4.002	102141	1.58	12894
2	4.426	6379807	98.42	608696

Empower™ 3 SOFTWARE

Sample Information

Sample Name: 4g'-rac Wave Length: 283.0nm

Column: Chiralpak IG-3 95:5



peak information:

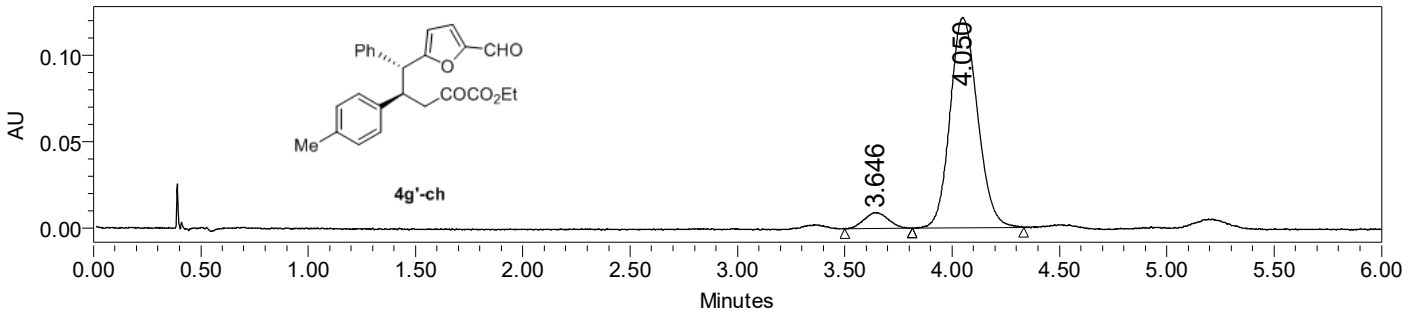
	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	3.637	1582112	48.85	213153
2	4.050	1656827	51.15	199739

Empower™ 3 SOFTWARE

Sample Information

Sample Name: 4g'-ch Wave Length: 283.0nm

Column: Chiralpak IG-3 95:5



peak information:

	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	3.646	74400	6.40	9292
2	4.050	1087914	93.60	122082

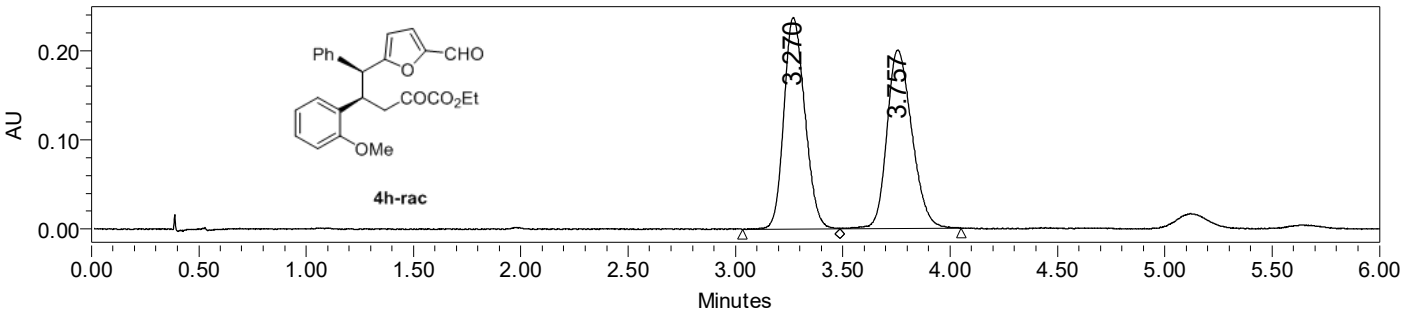
Empower™ 3 SOFTWARE

Sample Information

Sample Name: 4h-rac

Wave Length: 283.0nm

Column: Chiralpak IG-3 95:5



peak information:

	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	3.270	1620692	49.95	237378
2	3.757	1623989	50.05	200028

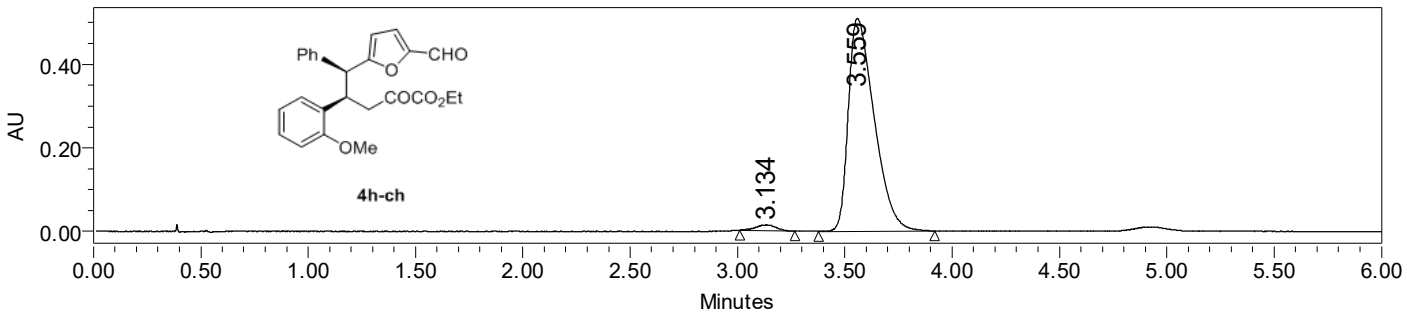
Empower™ 3 SOFTWARE

Sample Information

Sample Name: 4h-ch

Wave Length: 283.0nm

Column: Chiralpak IG-3 95:5



peak information:

	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	3.134	92481	2.11	13929
2	3.559	4282171	97.89	509870

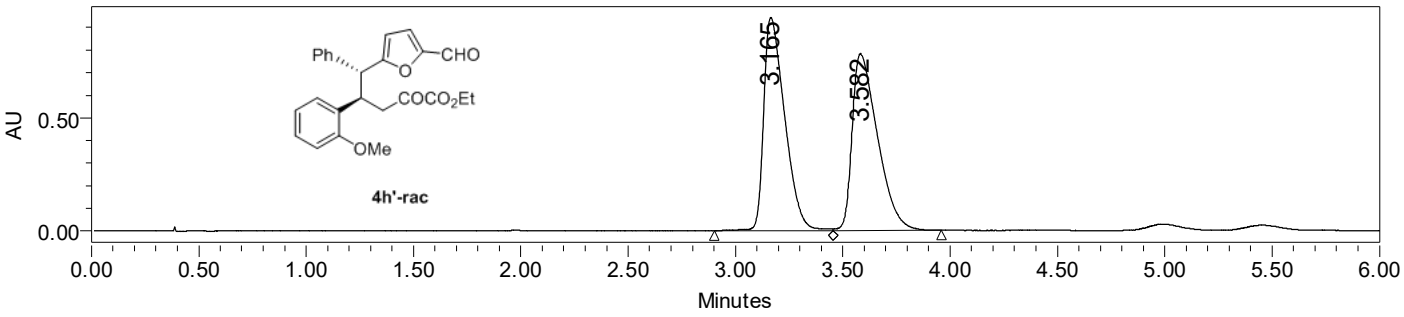
Empower™ 3 SOFTWARE

Sample Information

Sample Name: 4h'-rac

Column: Chiralpak IG-3 95:5

Wave Length: 283.0nm



peak information:

	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	3.165	6451695	50.08	943056
2	3.582	6431394	49.92	781589

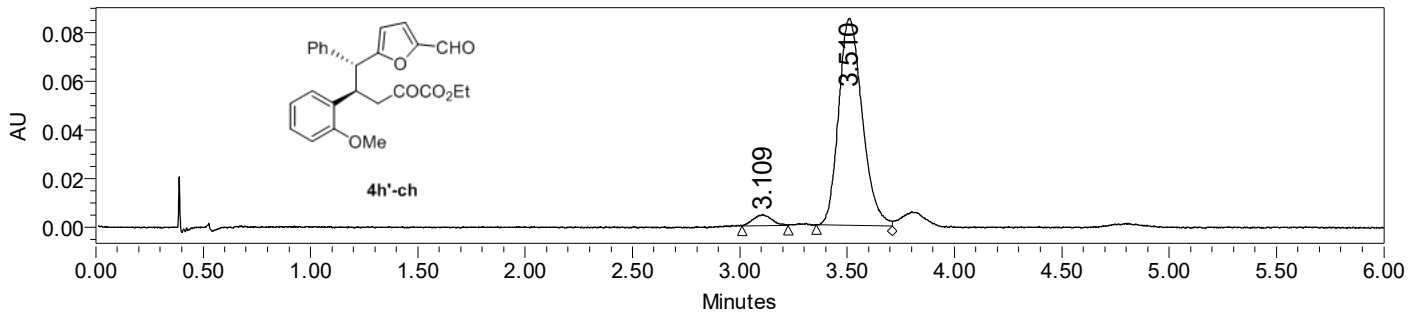
Empower™ 3 SOFTWARE

Sample Information

Sample Name: 4h'-ch

Column: Chiralpak IG-3 95:5

Wave Length: 280.0nm



peak information:

	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	3.109	26653	3.94	4470
2	3.510	649630	96.06	85127

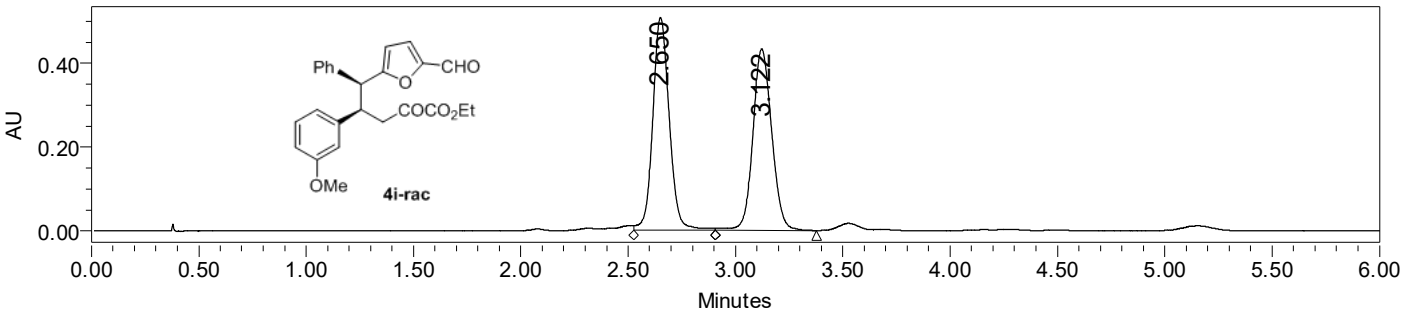
Empower™ 3 SOFTWARE

Sample Information

Sample Name: 4i-rac

Wave Length: 282.0nm

Column: Chiralpak OD-3 95:5



peak information:

	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	2.650	2740845	50.64	508475
2	3.122	2671303	49.36	433646

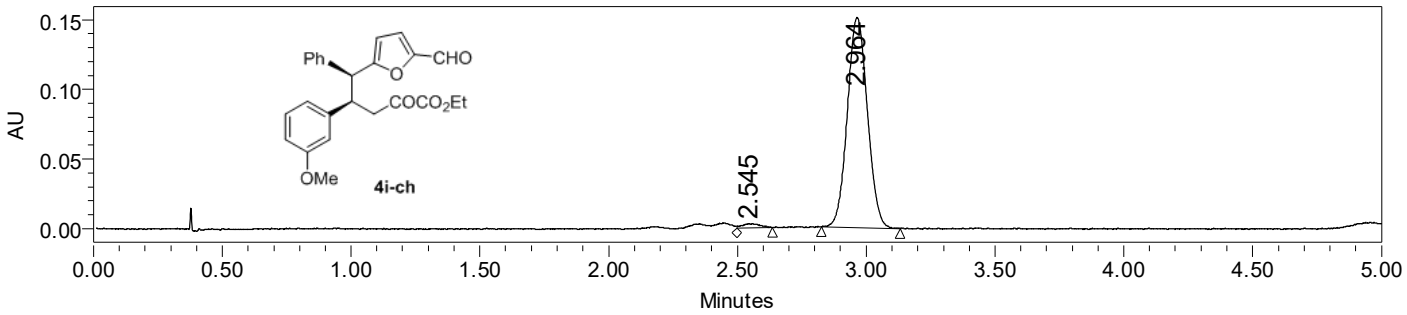
Empower™ 3 SOFTWARE

Sample Information

Sample Name: 4i-ch

Wave Length: 282.0nm

Column: Chiralpak OD-3 95:5



peak information:

	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	2.545	13768	1.65	2940
2	2.964	819305	98.35	151020

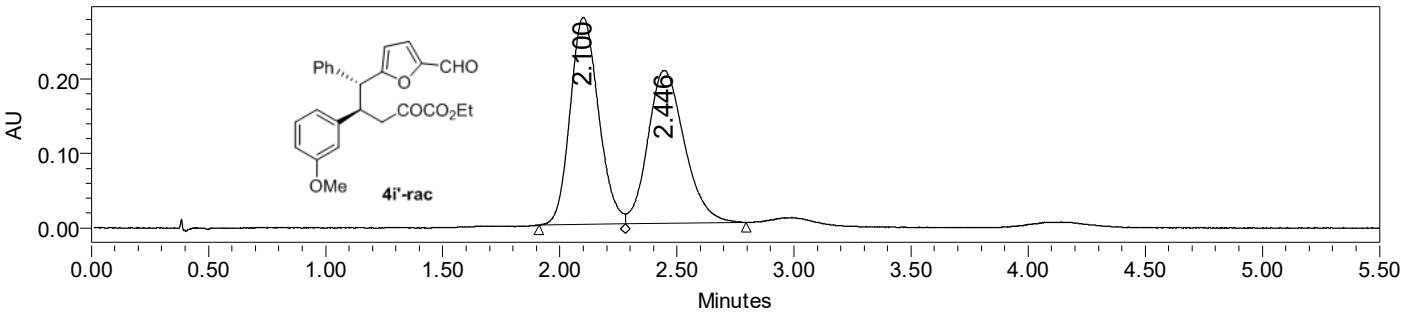
Empower™ 3 SOFTWARE

Sample Information

Sample Name: 4i'-rac

Wave Length: 282.0nm

Column: Chiralpak AD-3 95:5



peak information:

	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	2.100	2351388	51.37	277895
2	2.446	2225812	48.63	205435

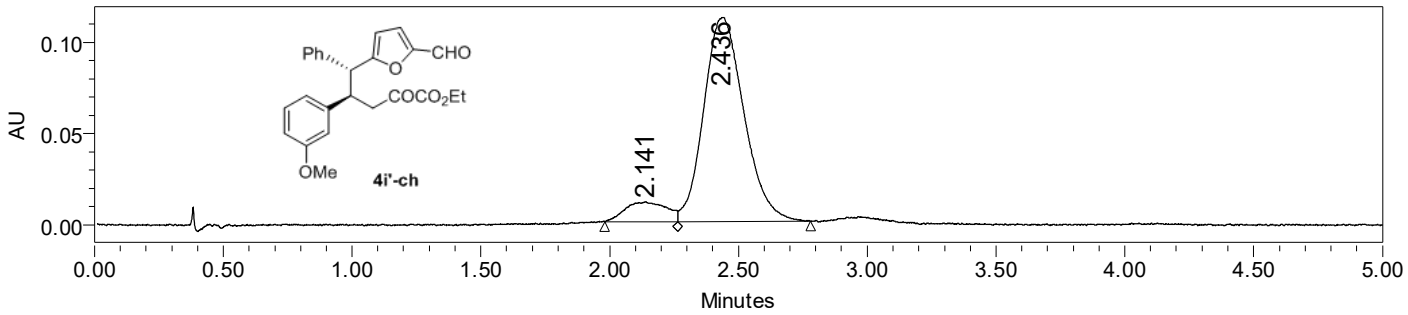
Empower™ 3 SOFTWARE

Sample Information

Sample Name: 4i'-ch

Wave Length: 282.0nm

Column: Chiralpak AD-3 95:5



peak information:

	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	2.141	122867	9.20	10727
2	2.436	1212954	90.80	111831

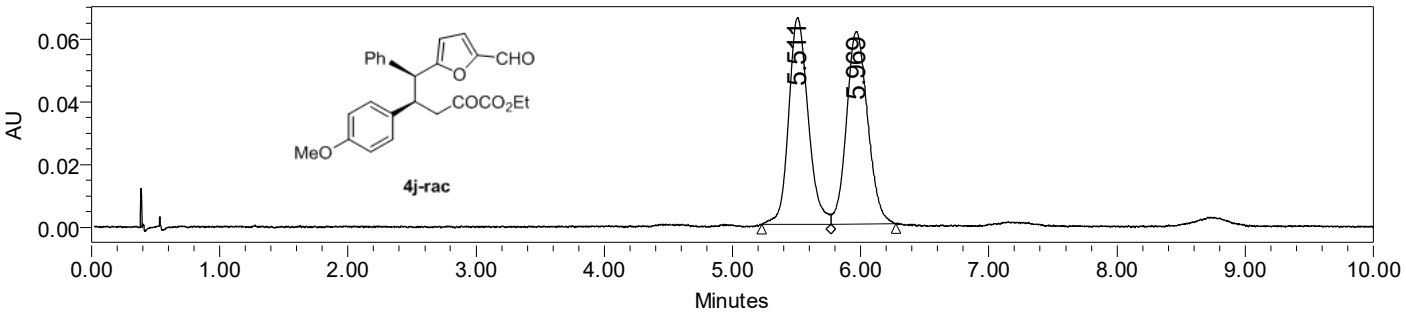
Empower™ 3 SOFTWARE

Sample Information

Sample Name: 4j-rac

Wave Length: 283.0nm

Column: Chiralpak IG-3 95:5



peak information:

	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	5.511	697983	49.87	65867
2	5.969	701744	50.13	61236

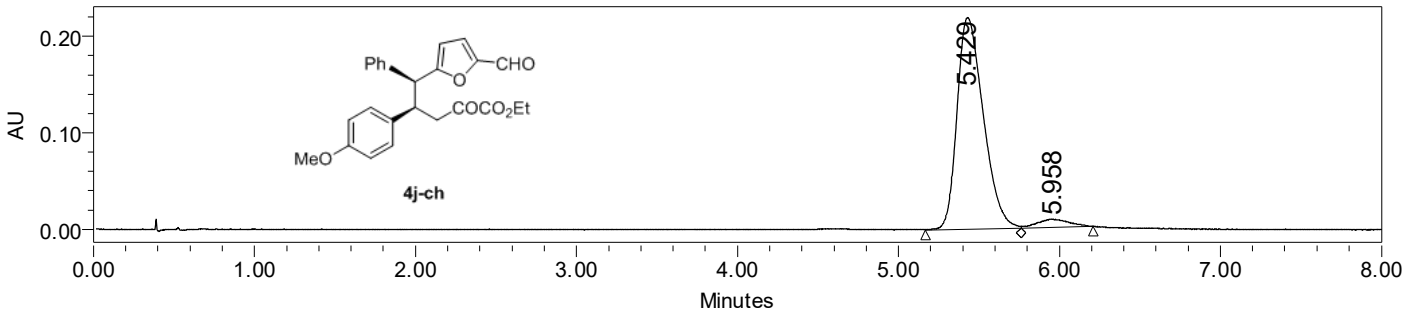
Empower™ 3 SOFTWARE

Sample Information

Sample Name: 4j-ch

Wave Length: 283.0nm

Column: Chiralpak IG-3 95:5



peak information:

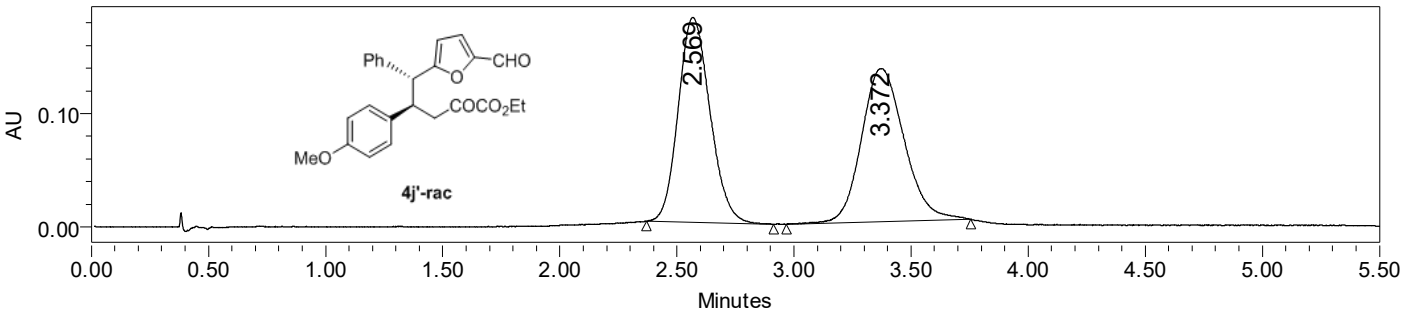
	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	5.429	2487978	95.64	219237
2	5.958	113412	4.36	8150

Empower™ 3 SOFTWARE

Sample Information

Sample Name: 4j'-rac Wave Length: 283.0nm

Column: Chiralpak AD-3 95:5



peak information:

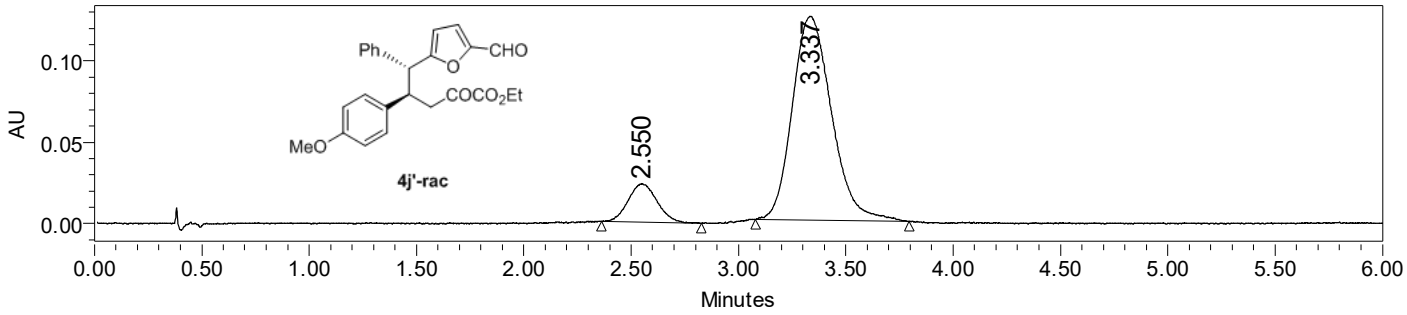
	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	2.569	1703948	49.88	180451
2	3.372	1712409	50.12	134985

Empower™ 3 SOFTWARE

Sample Information

Sample Name: 4j'-ch Wave Length: 283.0nm

Column: Chiralpak AD-3 95:5



peak information:

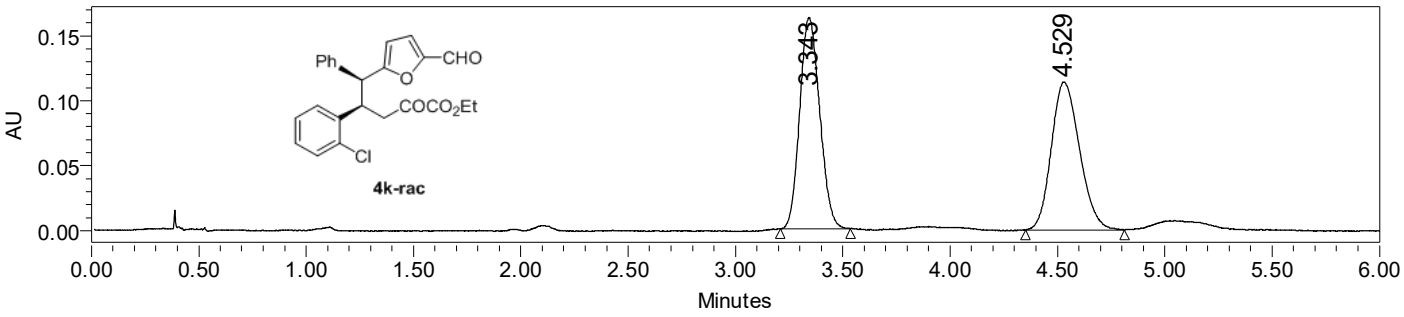
	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	2.550	224098	12.34	23649
2	3.337	1591843	87.66	125237

Empower™ 3 SOFTWARE

Sample Information

Sample Name: 4k-rac Wave Length: 283.0nm

Column: Chiralpak IG-3 95:5



peak information:

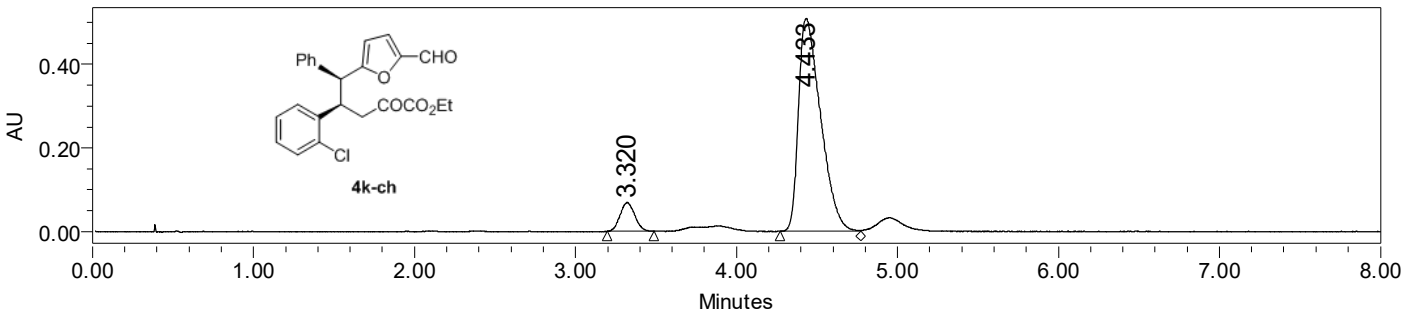
	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	3.343	1053773	50.26	162765
2	4.529	1042786	49.74	113824

Empower™ 3 SOFTWARE

Sample Information

Sample Name: 4k-ch Wave Length: 283.0nm

Column: Chiralpak IG-3 95:5



peak information:

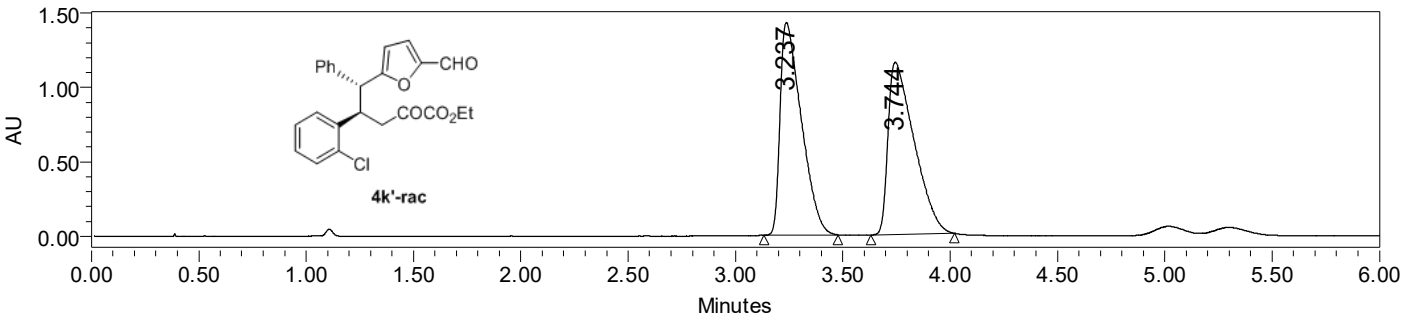
	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	3.320	438734	8.29	68672
2	4.433	4852130	91.71	508943

Empower™ 3 SOFTWARE

Sample Information

Sample Name: 4k'-rac Wave Length: 282.0nm

Column: Chiralpak IG-3 95:5



peak information:

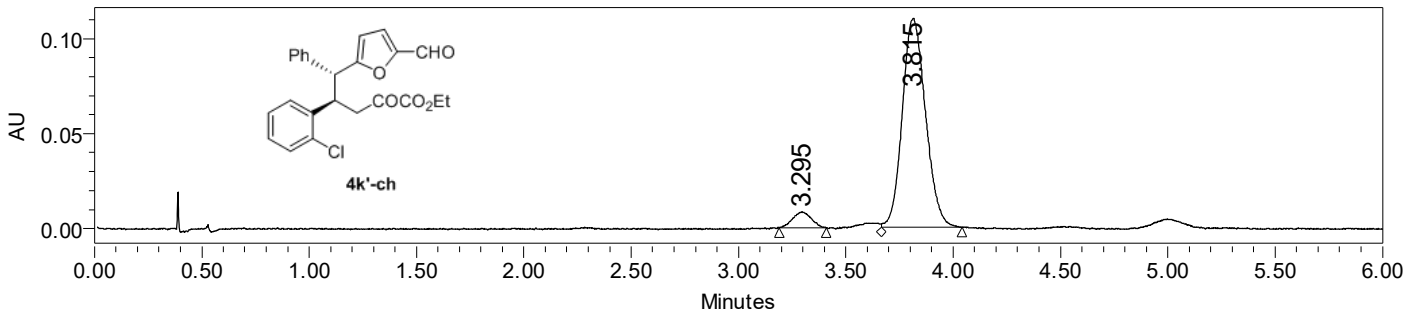
	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	3.237	9854563	50.22	1430712
2	3.744	9769861	49.78	1157208

Empower™ 3 SOFTWARE

Sample Information

Sample Name: 4k'-ch Wave Length: 282.0nm

Column: Chiralpak IG-3 95:5



peak information:

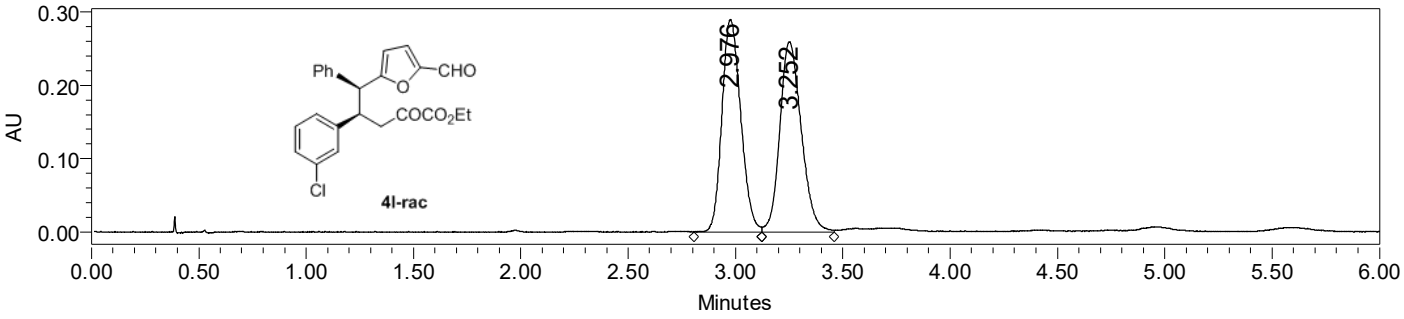
	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	3.295	51103	5.83	8325
2	3.815	824897	94.17	109968

Empower™ 3 SOFTWARE

Sample Information

Sample Name: 4l-rac Wave Length: 283.0nm

Column: Chiralpak IG-3 95:5



peak information:

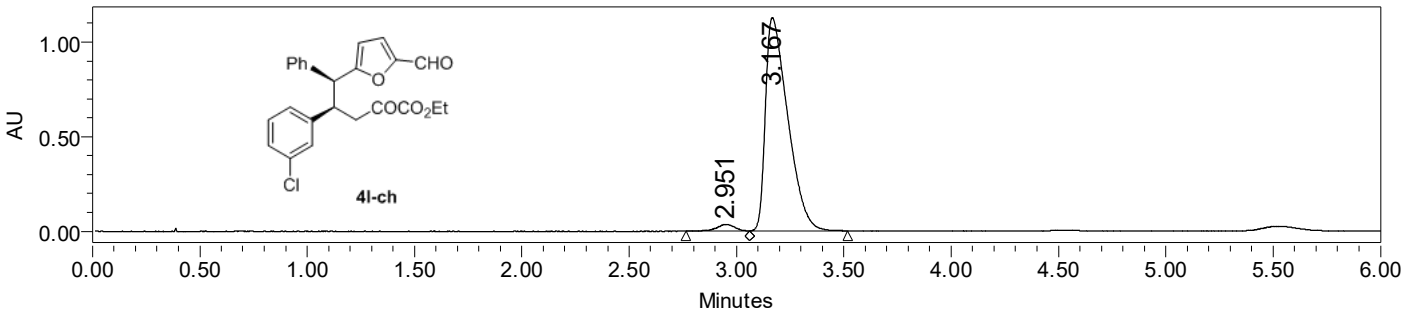
	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	2.976	1758171	49.34	290022
2	3.252	1805331	50.66	259409

Empower™ 3 SOFTWARE

Sample Information

Sample Name: 4l-ch Wave Length: 283.0nm

Column: Chiralpak IG-3 95:5



peak information:

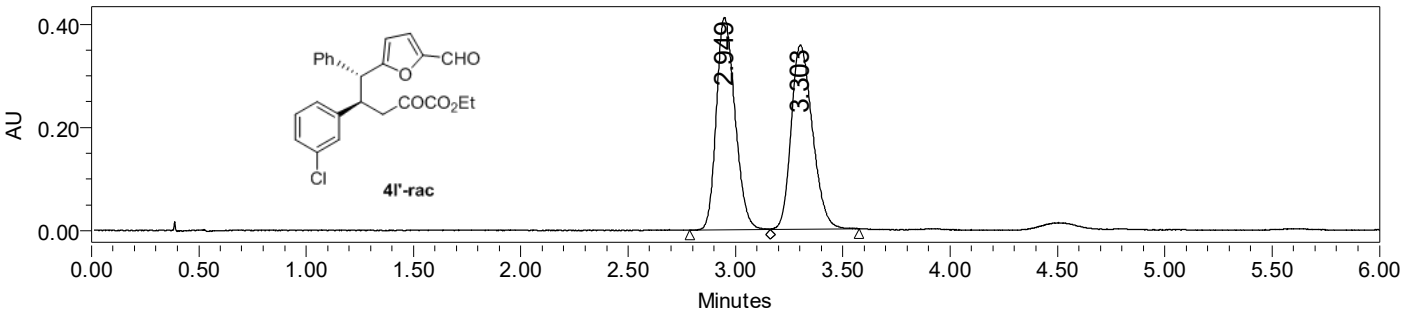
	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	2.951	210273	2.50	34804
2	3.167	8188978	97.50	1127457

Empower™ 3 SOFTWARE

Sample Information

Sample Name: 4l'-rac Wave Length: 282.0nm

Column: Chiralpak IG-3 95:5



peak information:

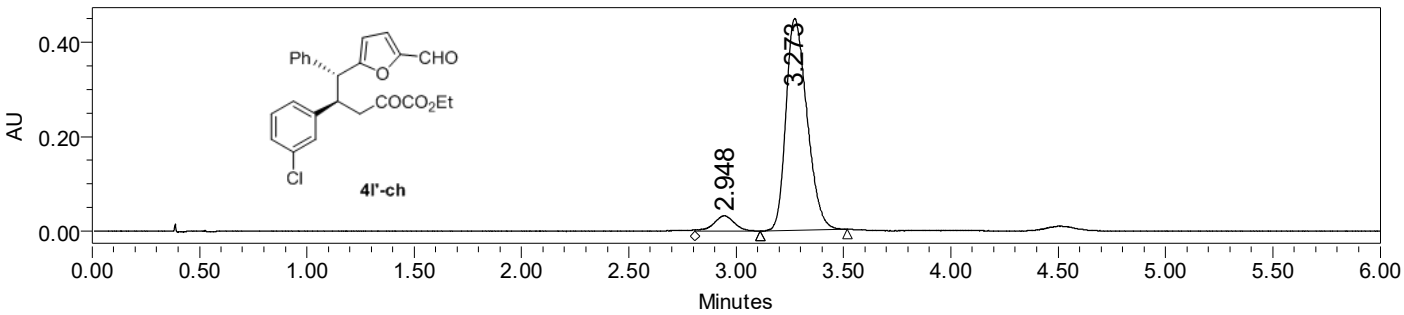
	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	2.949	2481771	50.19	412092
2	3.303	2462555	49.81	357424

Empower™ 3 SOFTWARE

Sample Information

Sample Name: 4l'-ch Wave Length: 282.0nm

Column: Chiralpak IG-3 95:5



peak information:

	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	2.948	218763	6.67	32207
2	3.273	3062844	93.33	448347

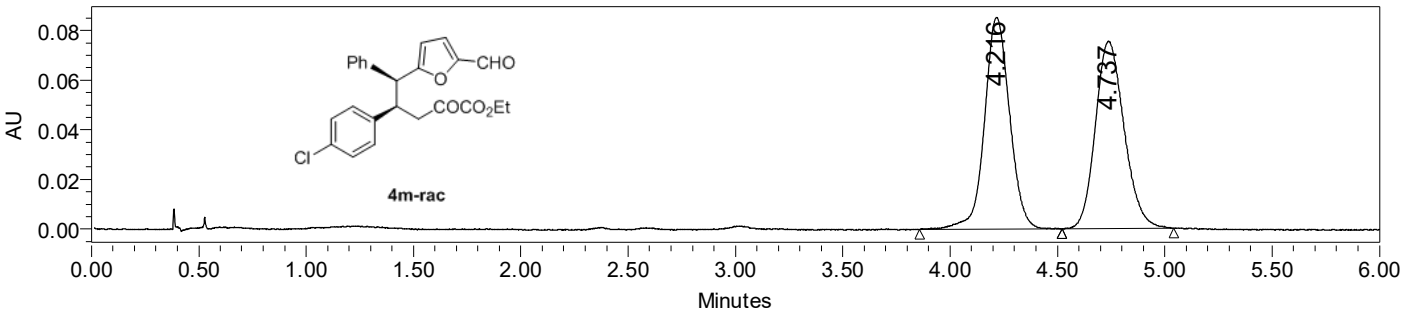
Empower™ 3 SOFTWARE

Sample Information

Sample Name: 4m-rac

Wave Length: 283.0nm

Column: Chiralpak IG-3 95:5



peak information:

	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	4.216	697579	49.84	85275
2	4.737	702069	50.16	75439

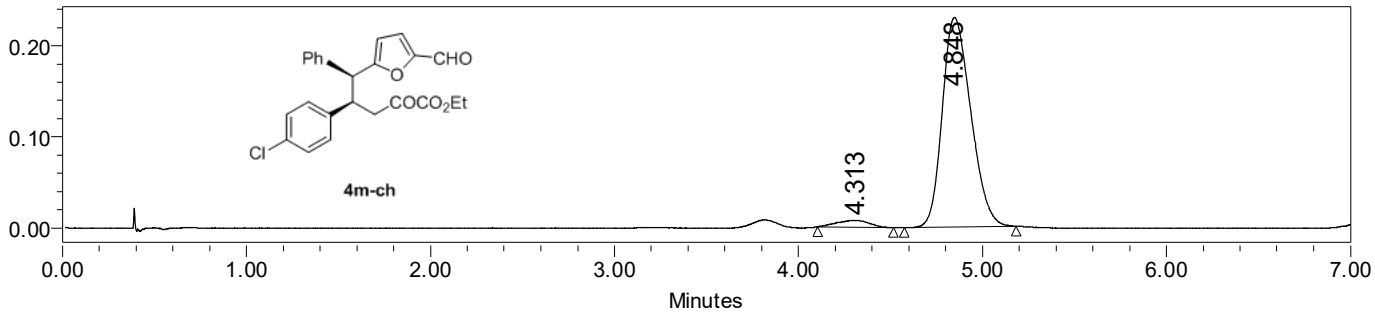
Empower™ 3 SOFTWARE

Sample Information

Sample Name: 4m-ch

Wave Length: 283.0nm

Column: Chiralpak IG-3 95:5



peak information:

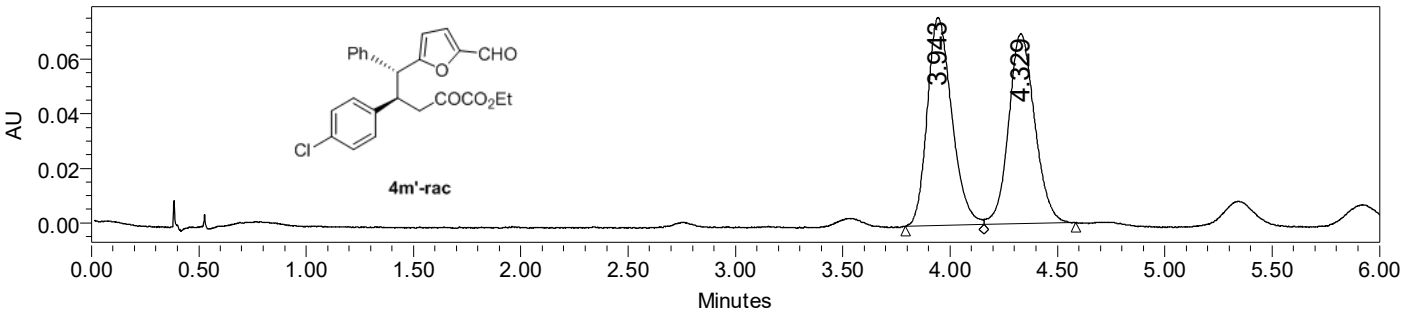
	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	4.313	94804	3.67	7564
2	4.848	2488402	96.33	230219

Empower™ 3 SOFTWARE

Sample Information

Sample Name: 4m'-rac Wave Length: 282.0nm

Column: Chiralpak IG-3 95:5



peak information:

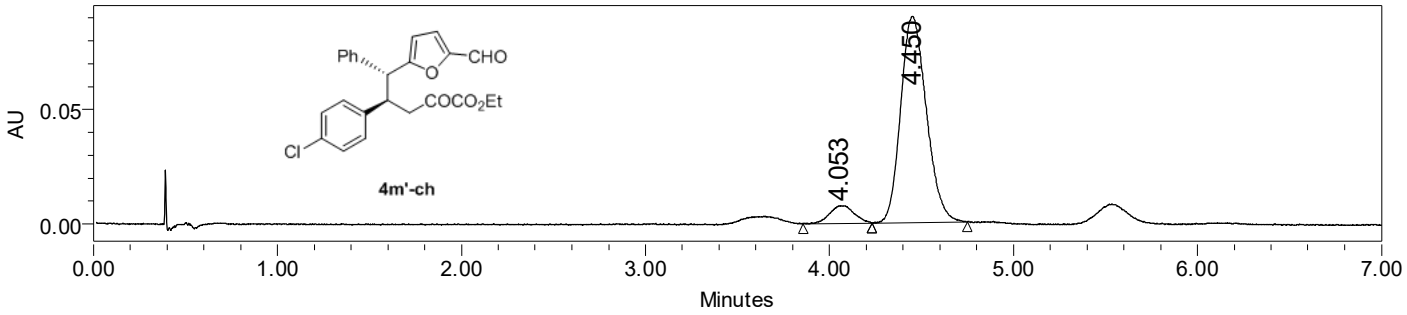
	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	3.943	607001	50.85	76410
2	4.329	586634	49.15	69757

Empower™ 3 SOFTWARE

Sample Information

Sample Name: 4m'-ch Wave Length: 282.0nm

Column: Chiralpak IG-3 95:5



peak information:

	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	4.053	74648	7.87	7871
2	4.450	874347	92.13	90103

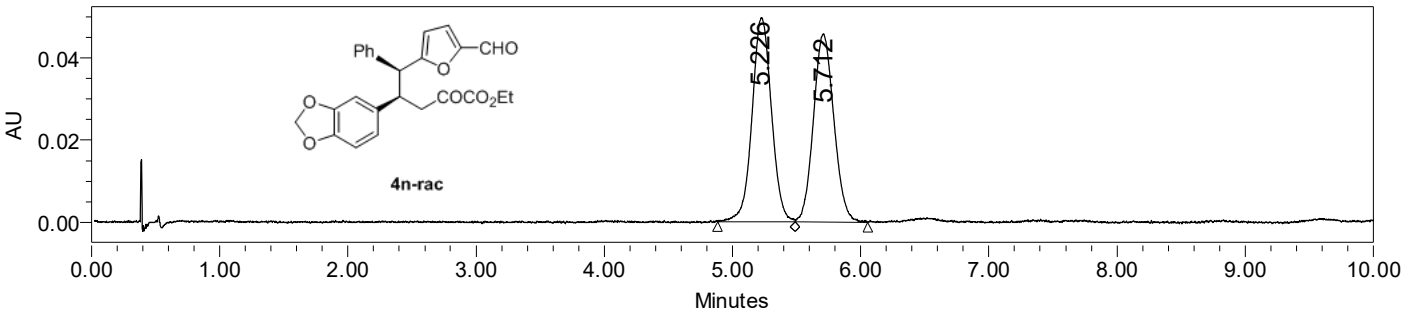
Empower™ 3 SOFTWARE

Sample Information

Sample Name: 4n-rac

Wave Length: 283.0nm

Column: Chiralpak IG-3 95:5



peak information:

	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	5.226	524475	50.74	49784
2	5.712	509128	49.26	45811

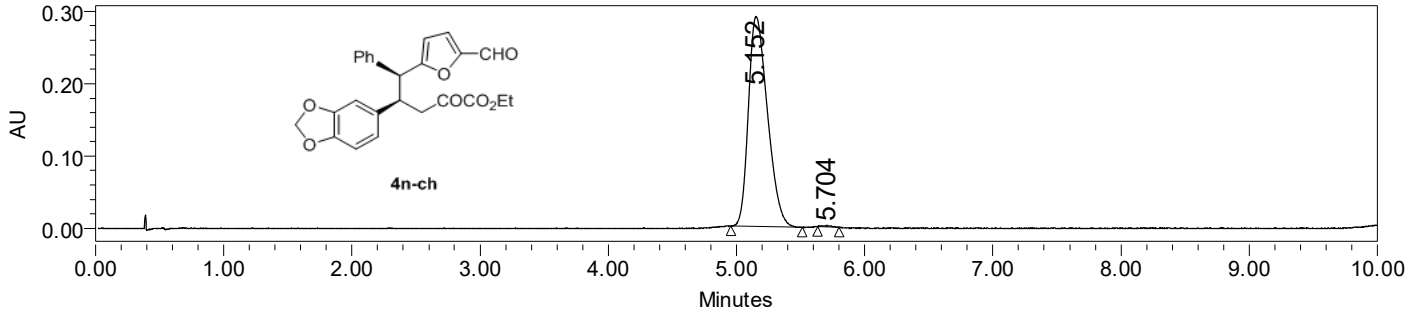
Empower™ 3 SOFTWARE

Sample Information

Sample Name: 4n-ch

Wave Length: 283.0nm

Column: Chiralpak IG-3 95:5



peak information:

	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	5.152	3011138	99.69	290823
2	5.704	9273	0.31	1711

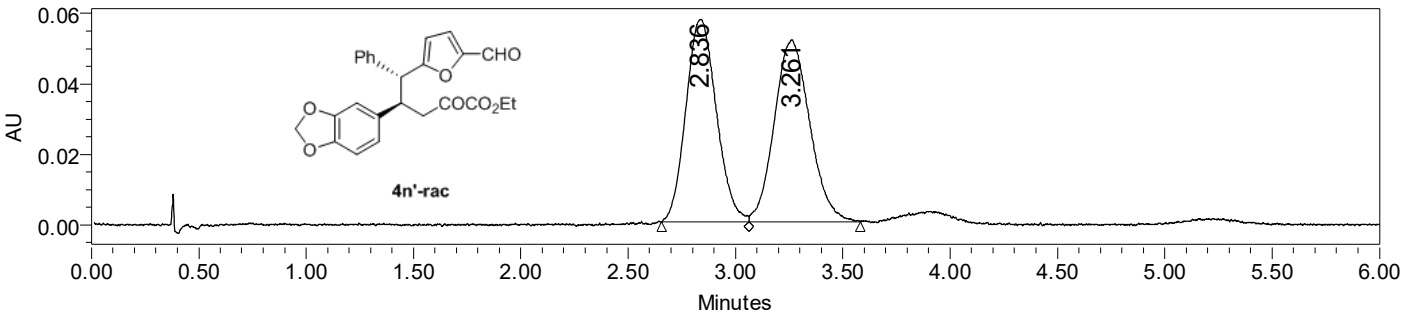
Empower™ 3 SOFTWARE

Sample Information

Sample Name: 4n'-rac

Wave Length: 283.7nm

Column: Chiralpak AD-3 95:5



peak information:

	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	2.836	568627	48.94	57476
2	3.261	593359	51.06	51654

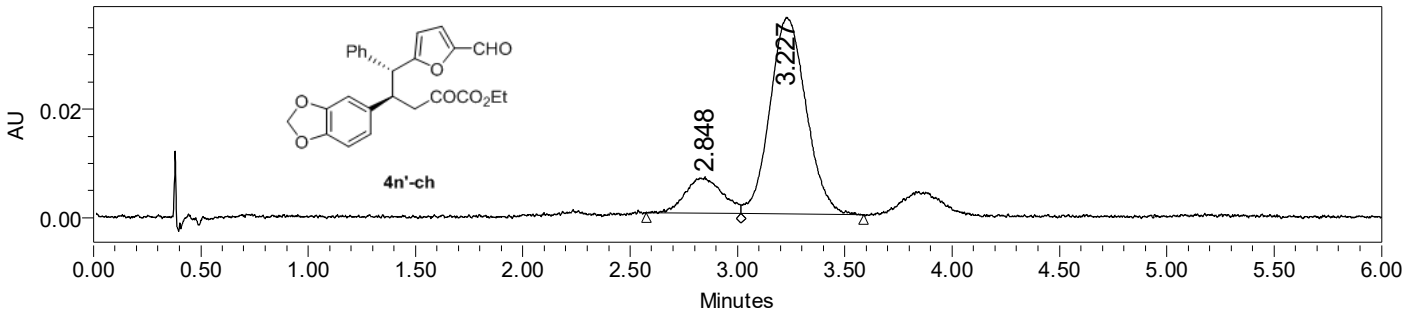
Empower™ 3 SOFTWARE

Sample Information

Sample Name: 4n'-ch

Wave Length: 285.0nm

Column: Chiralpak AD-3 95:5



peak information:

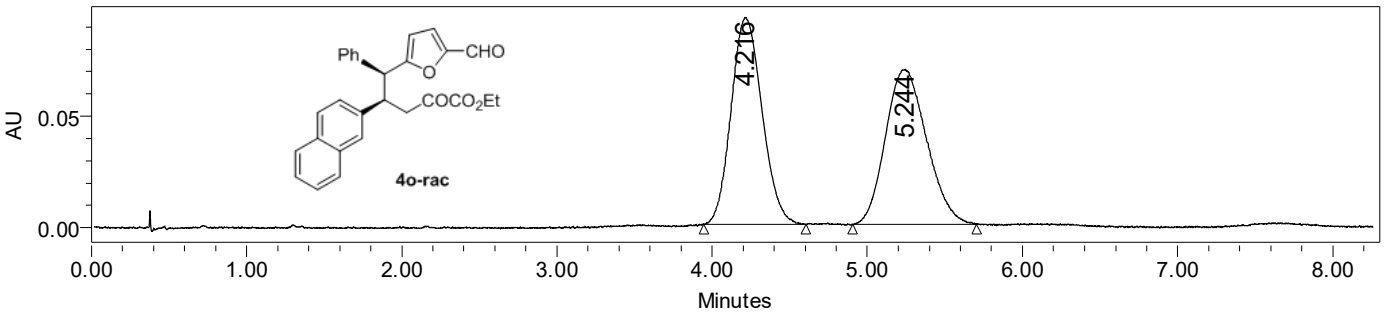
	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	2.848	78705	15.64	6640
2	3.227	424679	84.36	36167

Empower™ 3 SOFTWARE

Sample Information

Sample Name: 4o-rac Wave Length: 283.0nm

Column: Chiralpak AD-3 95:5



peak information:

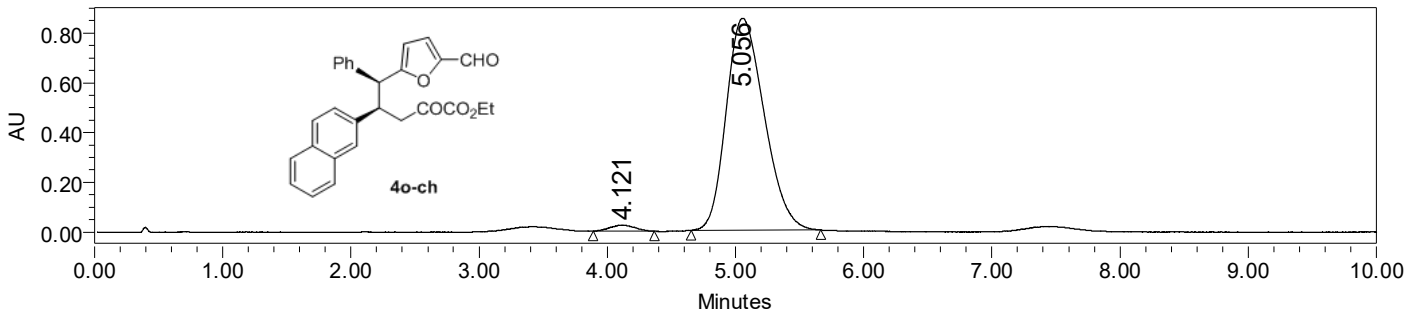
	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	4.216	1285904	50.09	92853
2	5.244	1281116	49.91	69440

Empower™ 3 SOFTWARE

Sample Information

Sample Name: 4o-ch Wave Length: 222.0nm

Column: Chiralpak AD-3 95:5



peak information:

	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	4.121	328906	1.84	23834
2	5.056	17557647	98.16	851667

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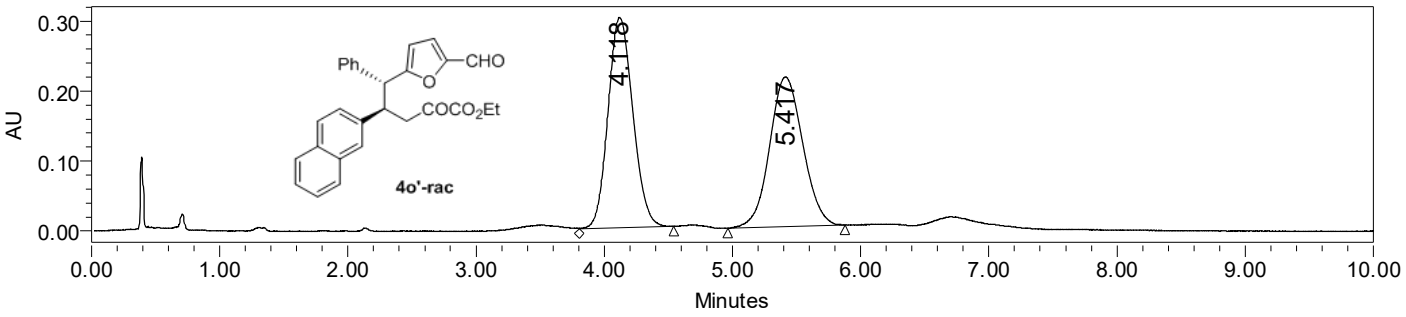
Sample Information

Sample Name: 4o'-rac

Wave Length: 222.0nm

Column: Chiralpak AD-3 95:5



peak information:

	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	4.118	4040379	51.15	300614
2	5.417	3857978	48.85	213998

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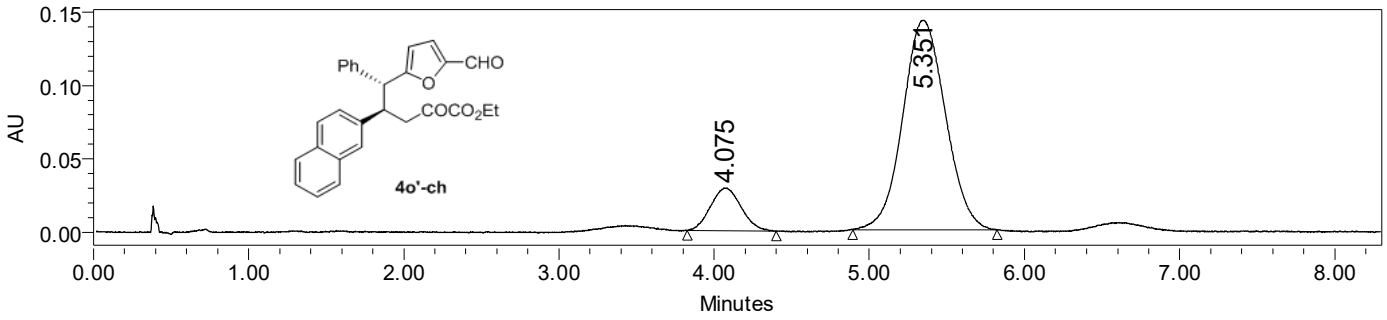
Sample Information

Sample Name: 4o'-ch

Wave Length: 222.0nm

Column: Chiralpak AD-3 95:5



peak information:

	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	4.075	404589	12.92	29336
2	5.351	2727439	87.08	142928

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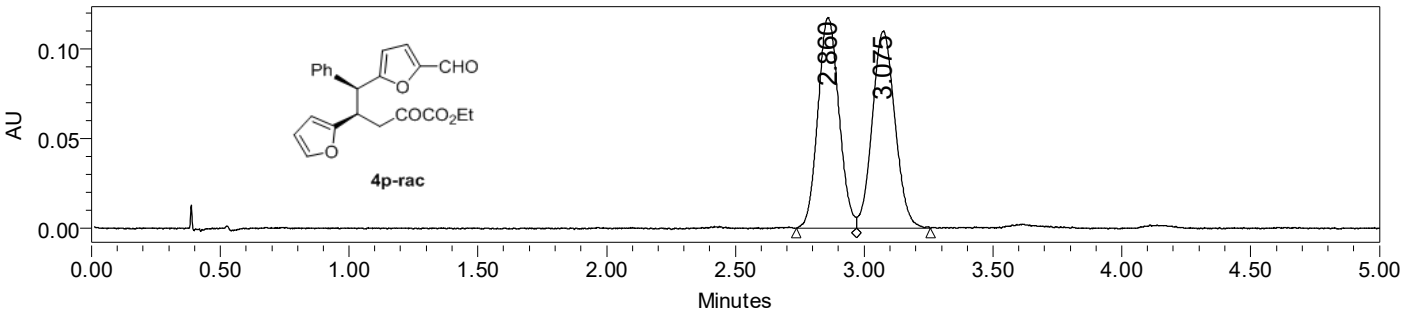
Sample Information

Sample Name: 4p-rac Wave Length: 283.0nm

Column: Chiralpak IG-3 95:5



peak information:

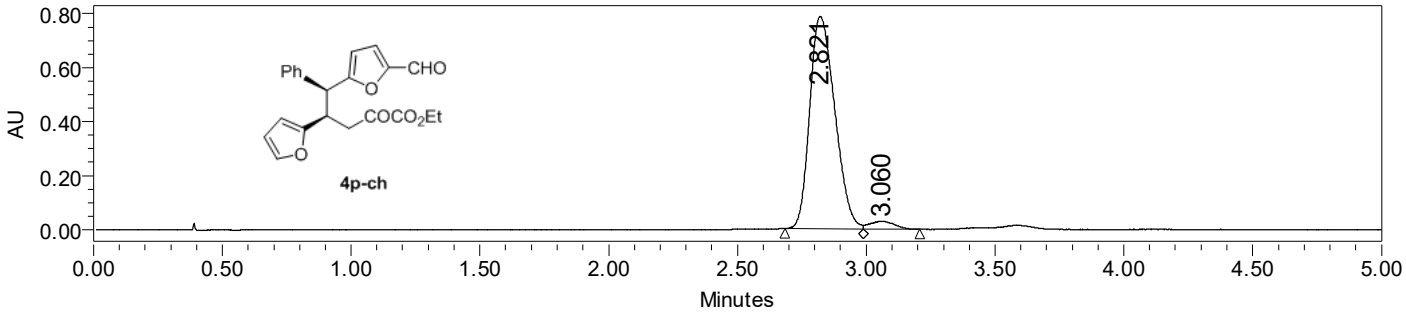
	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	2.860	666853	49.72	117460
2	3.075	674260	50.28	109856

Empower™ 3 SOFTWARE

Sample Information

Sample Name: 4p-ch Wave Length: 283.0nm

Column: Chiralpak IG-3 95:5



peak information:

	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	2.821	5329055	96.44	785563
2	3.060	196579	3.56	28445

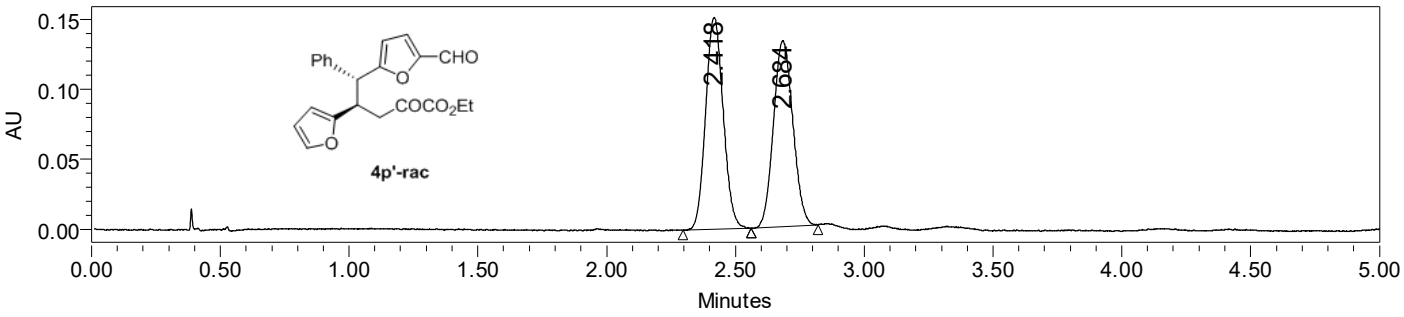
Empower™ 3 SOFTWARE

Sample Information

Sample Name: 4p'-rac

Wave Length: 282.0nm

Column: Chiralpak IG-3 95:5



peak information:

	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	2.418	717482	50.85	151240
2	2.684	693553	49.15	132675

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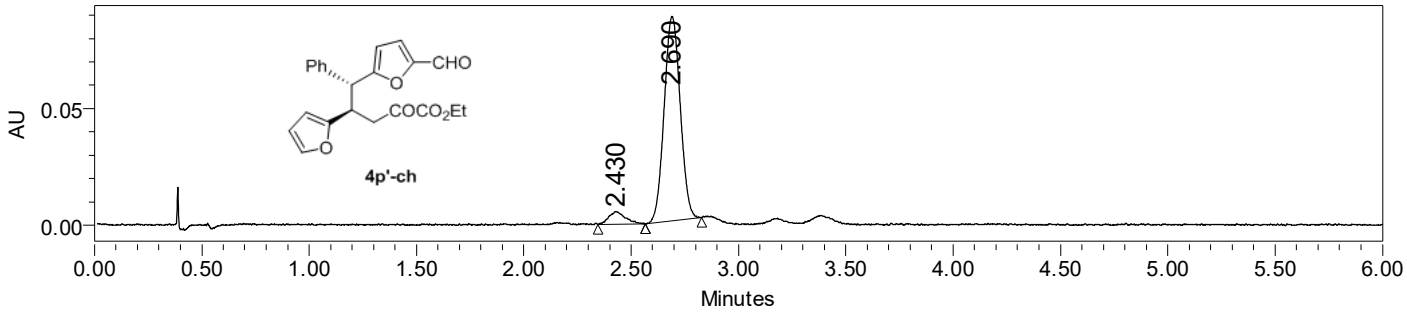
Sample Information

Sample Name: 4p'-ch

Wave Length: 282.0nm

Column: Chiralpak IG-3 95:5



peak information:

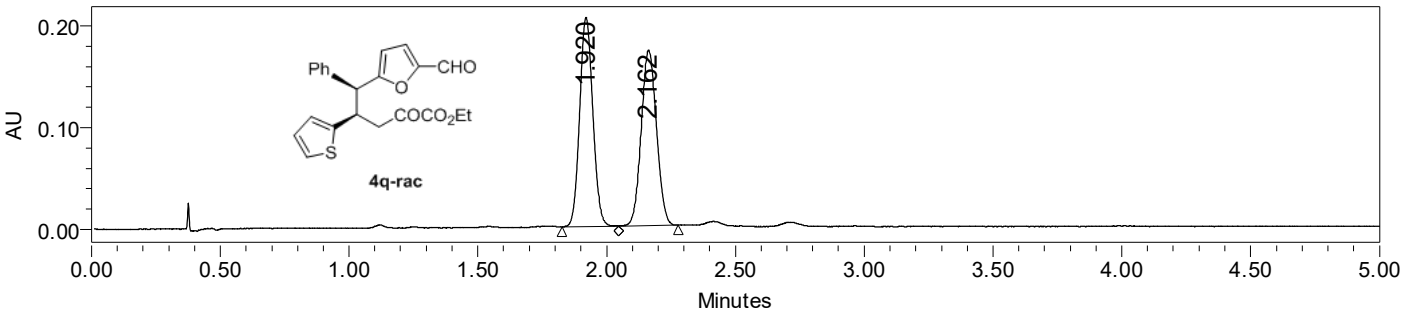
	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	2.430	29608	6.05	5409
2	2.690	459936	93.95	87701

Empower™ 3 SOFTWARE

Sample Information

Sample Name: 4q-rac Wave Length: 284.0nm

Column: Chiralpak IG-3 90:10



peak information:

	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	1.920	733716	50.76	205626
2	2.162	711766	49.24	172498

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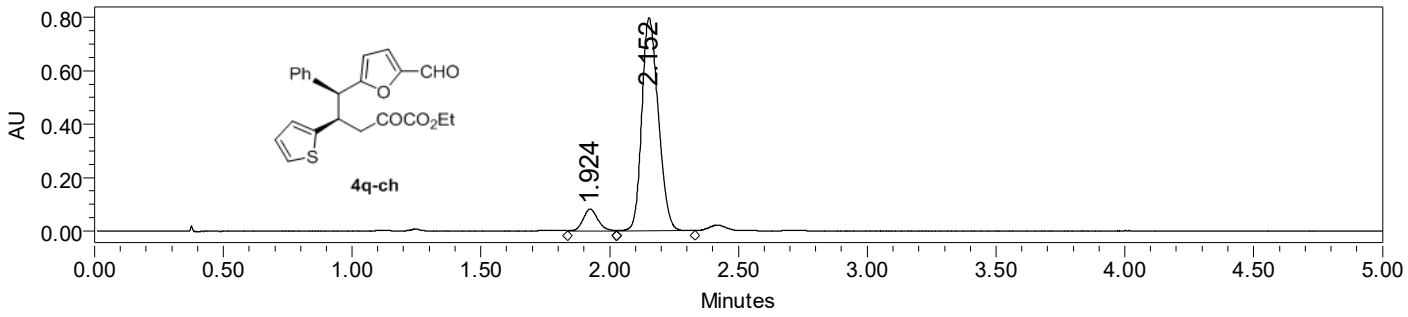
Sample Information

Sample Name: 4q-ch Wave Length: 284.0nm

Column: Chiralpak IG-3 90:10



peak information:

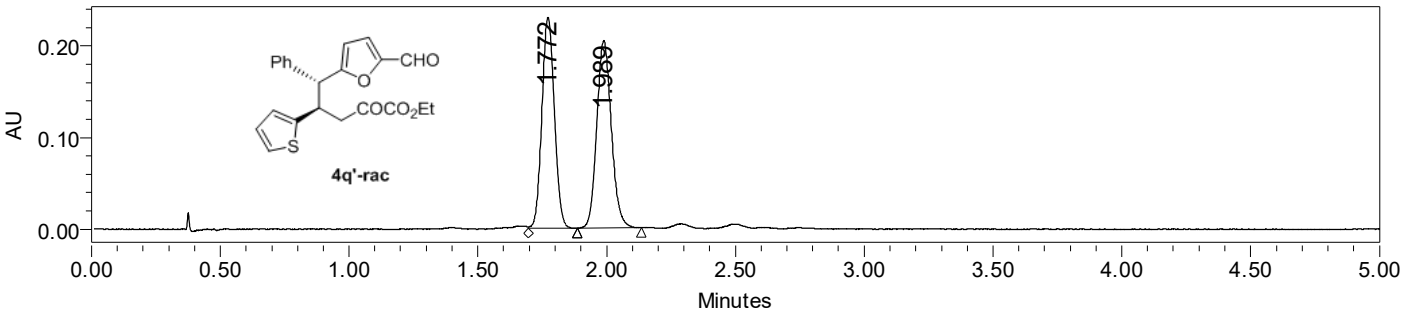
	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	1.924	320559	8.30	81408
2	2.152	3539937	91.70	797484

Empower™ 3 SOFTWARE

Sample Information

Sample Name: 4q'-rac Wave Length: 283.0nm

Column: Chiralpak IG-3 90:10



peak information:

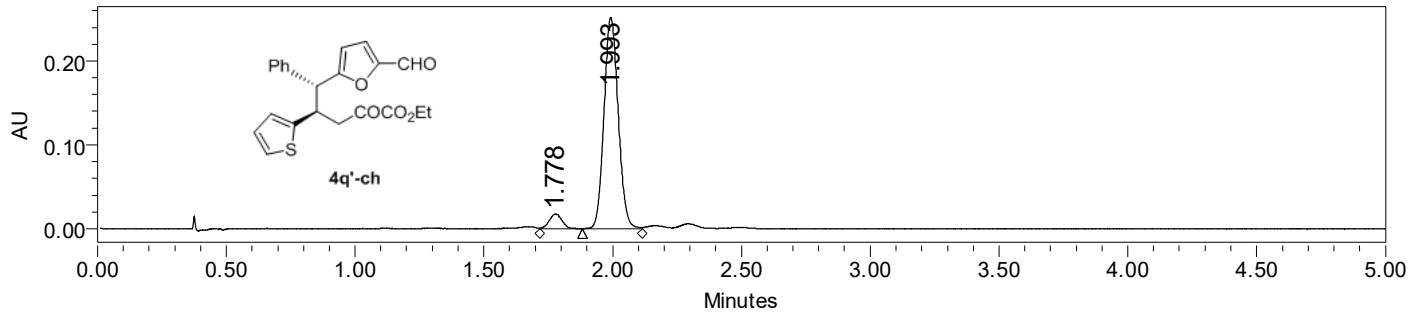
	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	1.772	774565	49.12	230355
2	1.989	802358	50.88	204655

Empower™ 3 SOFTWARE

Sample Information

Sample Name: 4q'-ch Wave Length: 283.0nm

Column: Chiralpak IG-3 90:10



peak information:

	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	1.778	59669	5.84	17643
2	1.993	961352	94.16	251955

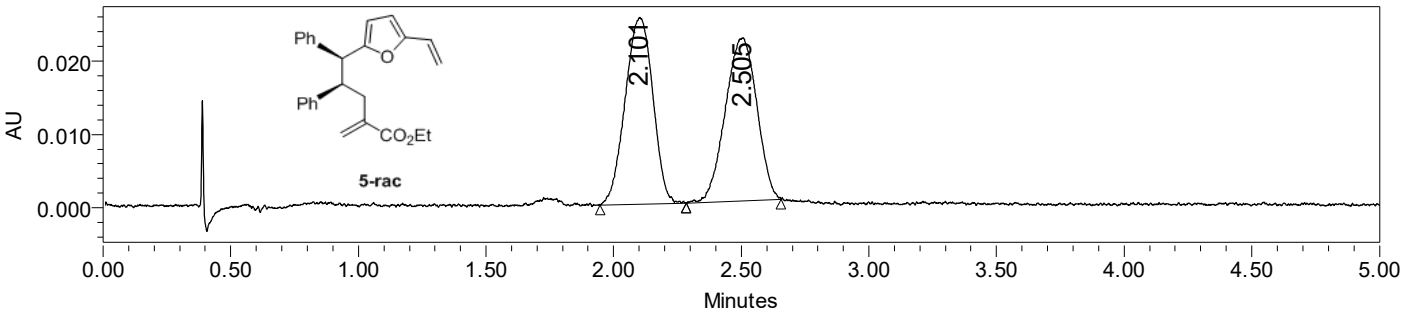
Empower™ 3 SOFTWARE

Sample Information

Sample Name: 5-rac

Wave Length: 282.0nm

Column: Trefoil TM CEL2 98:2



peak information:

	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	2.101	191760	50.20	25448
2	2.505	190201	49.80	22179

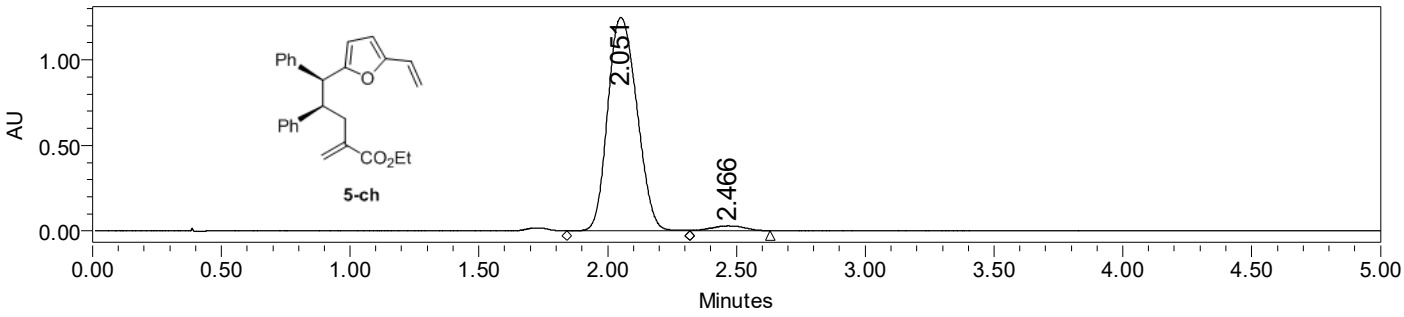
Empower™ 3 SOFTWARE

Sample Information

Sample Name: 5-ch

Wave Length: 273.0nm

Column: Trefoil TM CEL2 98:2



peak information:

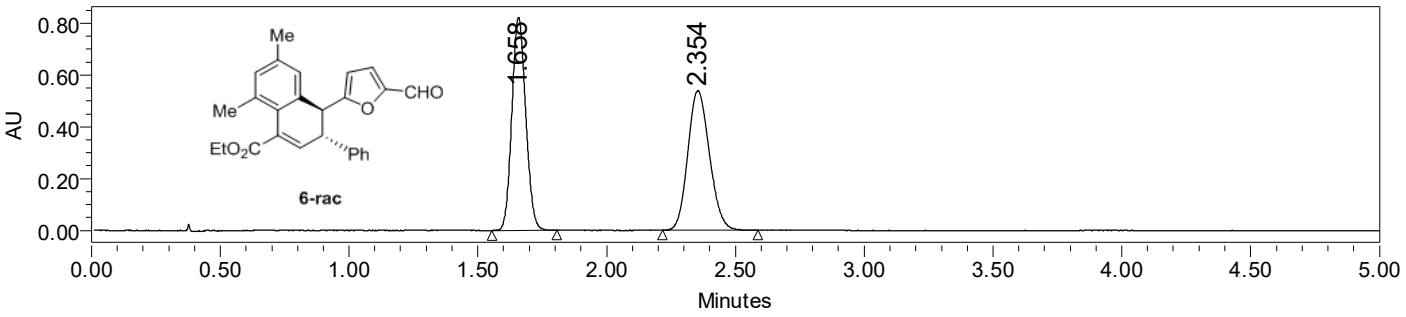
	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	2.051	9807075	97.38	1248744
2	2.466	264341	2.62	29050

Empower™ 3 SOFTWARE

Sample Information

Sample Name: 6-rac Wave Length: 280.0nm

Column: Chiralpak IG-3 90:10



peak information:

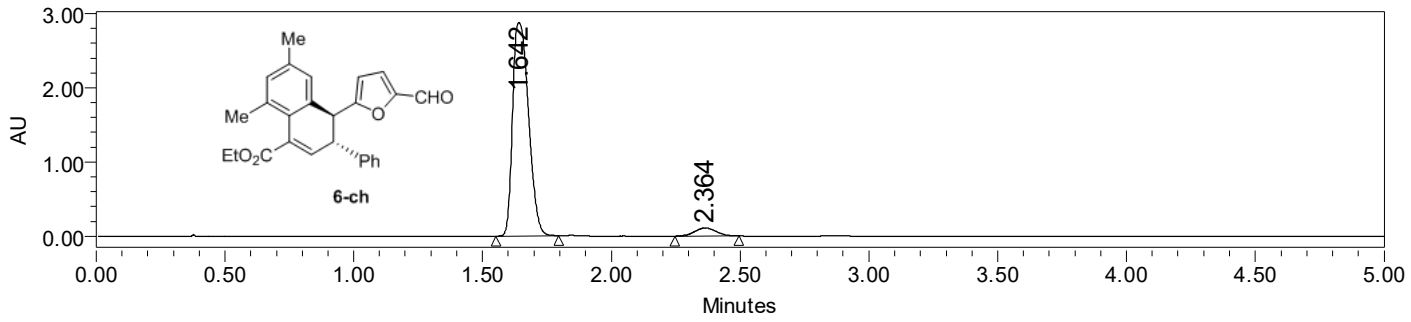
	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	1.658	3072353	49.27	821620
2	2.354	3163181	50.73	538987

Empower™ 3 SOFTWARE

Sample Information

Sample Name: 6-ch Wave Length: 280.0nm

Column: Chiralpak IG-3 90:10



peak information:

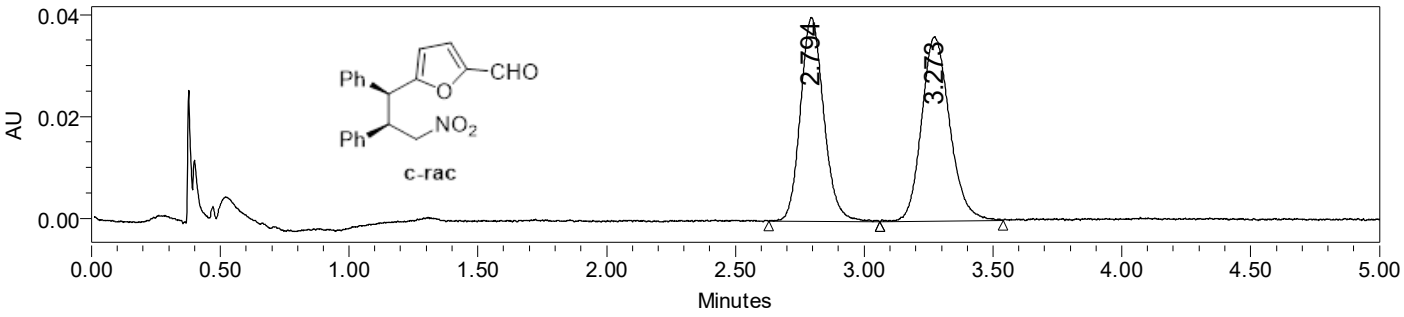
	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	1.642	12317296	95.11	2878313
2	2.364	633407	4.89	109975

Empower™ 3 SOFTWARE

Sample Information

Sample Name: c-rac Wave Length: 212.0nm

Column: Chiralpak AD-3 95:5



peak information:

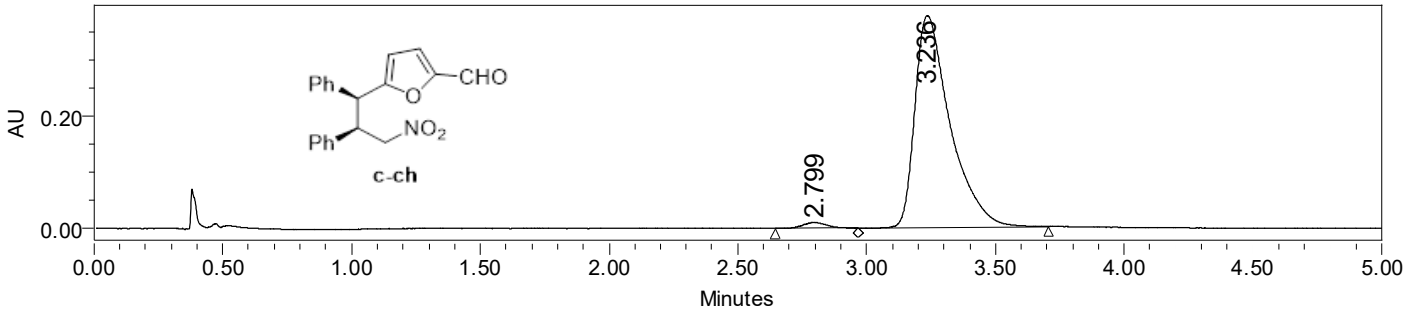
	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	2.794	252035	47.89	40015
2	3.273	274210	52.11	36175

Empower™ 3 SOFTWARE

Sample Information

Sample Name: c-ch Wave Length: 212.0nm

Column: Chiralpak AD-3 95:5



peak information:

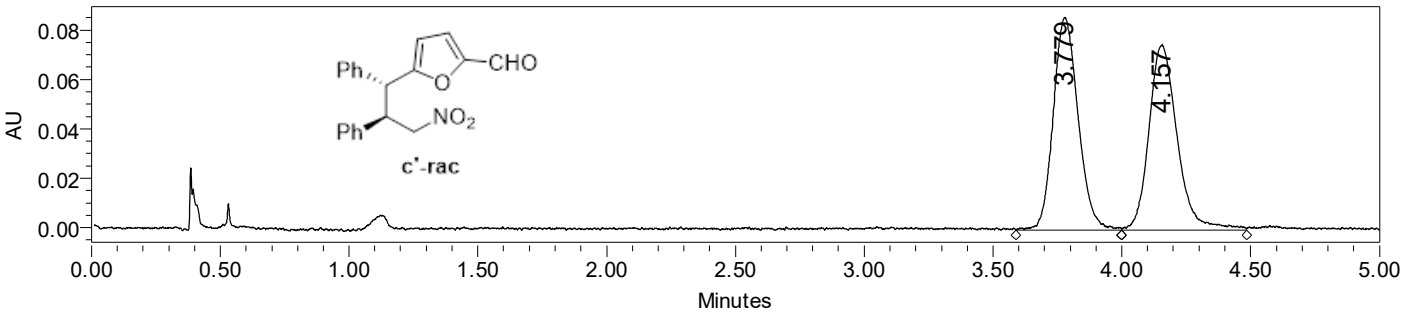
	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	2.799	63533	1.76	10075
2	3.236	3556140	98.24	375589

Empower™ 3 SOFTWARE

Sample Information

Sample Name: c'-rac Wave Length: 219.4nm

Column: Chiralpak IG-3 95:5



peak information:

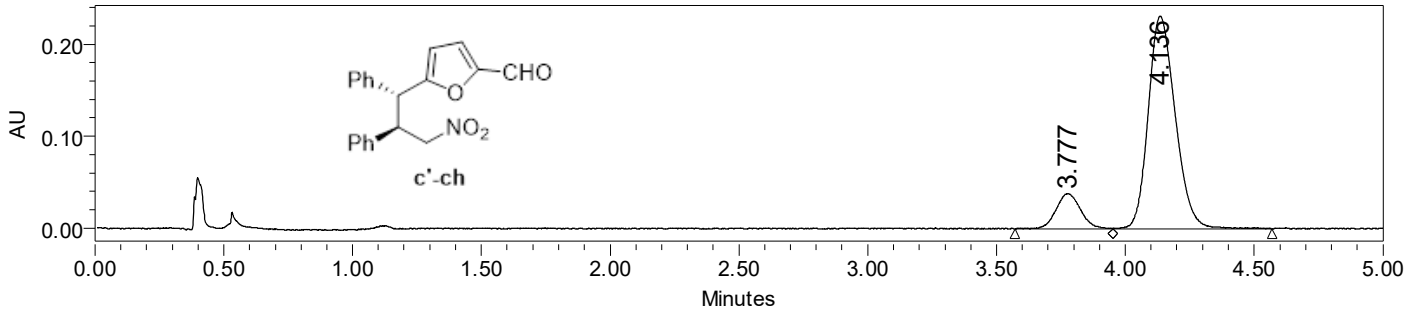
	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	3.779	581636	50.12	86303
2	4.157	578821	49.88	75236

Empower™ 3 SOFTWARE

Sample Information

Sample Name: c'-ch Wave Length: 212.0nm

Column: Chiralpak IG-3 95:5



peak information:

	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	3.777	255312	13.04	38277
2	4.136	1702002	86.96	231069