[3+3] Annulation of Donor-Acceptor Cyclopropanes with Mercaptoacetaldehyde: Application to the Synthesis of Tetrasubstituted Thiophenes

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ELECTRONIC SUPPLEMENTARY INFORMATION

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EXPERIMENTAL SECTION

General remarks. Melting points were determined by open capillary tube method and are uncorrected. The ^{1}H and ^{13}C NMR spectra were recorded on a 400 MHz NMR spectrometer. HRMS (ESI) were recorded on a Q-Tof mass spectrometer. X-ray crystallographic data were collected on a CCD diffractometer using graphite-monochromated Mo-Kα radiation. Thin layer chromatography (TLC) was performed on pre-coated alumina sheets and detected under UV light. Silica gel (100-200 mesh) was used for column chromatography.

General procedure for the synthesis of thiophenes 4a-n:

To a stirred suspension of 1,4-dithiane-2,5-diol **2** (2.5 mmol) in DCM (5 mL) was added *trans*-2-aroyl-3-aryl-cyclopropane-1,1-dicarboxylates **1** (0.5 mmol) followed by $AlCl_3$ (0.5 mmol) at room temperature. After the reaction was complete (24 h), the reaction mixture was filtered through Celite. The filtrate was washed with water and concentrated to obtain crude diastereomeric mixture of tetrahydrothiopyranols **3** and **3′** (in some cases, the mixture was crystallized from EtOAc/hexane (1:9) to obtain single diastereomer). The crude product was dissolved in DCM (5 mL), DBU (1 mmol) was added and stirred at room temperature. After the completion of the reaction (12 h), water was added and extracted with dichloromethane. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4 and evaporated in vacuum. The crude product was purified by flash chromatography on silica gel using EtOAc/hexane (1:9) as eluent to obtain pure thiophene **4**.

Ethyl (5-formyl-2,4-diphenyl-thiophen-3-yl)acetate (4a):

Colourless solid. Yield: 0.126 g (72%). M.p. 98-100 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.59 (s, 1H), 7.53-7.45 (m, 8H), 7.39-7.37 (m, 2H), 4.01 (q, J = 7.2 Hz, 2H), 3.49 (s, 2H), 1.11 (t, J = 7.2 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 184.3, 171.2, 152.8, 150.7, 138.6, 133.5, 133.2, 131.7, 130.1, 129.4, 129.1, 128.9, 128.7, 61.1, 33.4, 14.2 ppm. HRMS calcd for $C_{21}H_{18}O_3S$: 351.1055 [M + H^+], found: 351.1057.

Ethyl [2-(4-methylphenyl)-5-formyl-4-phenyl-thiophen-3-yl]acetate (4b):

Colourless solid. Yield: 0.135 g (74%). M.p. 118-120 ºC.^{1}H NMR (400 MHz, $CDCl_3$): δ 9.57 (s, 1H), 7.48-7.45 (m, 3H), 7.41-7.36 (m, 4H), 2.27-2.25 (m, 2H), 4.01 (q, *J* = 7.2 Hz, 2H), 3.48 (s, 2H), 2.41 (s, 3H), 1.12 (t, *J* = 7.2 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 184.3, 171.3, 152.9, 151.0, 139.5, 138.3, 133.6, 131.5, 130.3, 130.1, 129.8, 129.2, 128.9, 128.7, 61.1, 33.4, 21.5, 14.2 ppm. HRMS calcd for $C_{22}H_{20}O_3S$: 365.1211 [M + H^+], found: 365.1214.

Ethyl [2-(4-chlorophenyl)-5-formyl-4-phenyl-thiophen-3-yl]acetate (4c):

Colourless solid. Yield: 0.148 g (77%). M.p. 88-90 ºC.^{1}H NMR (400 MHz, $CDCl_3$): δ 9.61 (s, 1H), 7.52-7.45 (m, 7H), 7.40-7.29 (m, 2H), 4.04 (q, *J* = 7.2 Hz, 2H), 3.48 (s, 2H), 1.15 (t, *J* = 7.2 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 184.2, 171.0, 152.7, 149.1, 139.0, 135.7, 133.4, 132.1, 132.1, 131.8, 130.1, 129.4, 129.0, 128.7, 61.2, 33.4, 14.2 ppm. HRMS calcd for $C_{21}H_{17}ClO_3S$: 385.0665 [M + H^+], found: 385.0657.

Ethyl [2-(3-fluorophenyl)-5-formyl-4-phenyl-thiophen-3-yl]acetate (4d):

Colourless solid. Yield: 0.116 g (63%). M.p. 110-112 ºC.^{1}H NMR (400 MHz, $CDCl_3$): δ 9.59 (s, 1H), 7.48-7.47 (m, 3H), 7.44-7.41 (m, 1H), 7.38-7.36 (m, 2H), 7.31-7.23(m, 2H), 7.17-7.13 (m, 1H), 4.03 (q, *J* = 7.2 Hz, 2H), 3.48 (s, 2H), 1.13 (t, *J* = 7.2 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 184.3, 171.0, 164.1, 161.6, 152.7, 148.8, 139.0, 135.2, 133.3, 132.2, 130.8, 130.1, 129.0, 128.8, 125.3, 125.2, 116.5, 116.3, 61.3, 33.4, 14.2 ppm. HRMS calcd for $C_{21}H_{17}FO_3S$: 391.0780 [M + Na^+], found: 391.0784.

Ethyl [2-phenyl-5-formyl-4-(4-methylphenyl)-thiophen-3-yl]acetate (4e):

Yellow oil. Yield: 0.124 g (68%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.59 (s, 1H), 7.52-7.50 (m, 2H), 7.46-7.44 (m, 2H), 7.26 (br s, 5H), 4.02 (q, *J* = 7.2 Hz, 2H), 3.48 (s, 2H), 2.43 (s, 3H), 1.12 (t, *J* = 7.2 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 184.5, 171.2, 153.0, 150.6, 138.9, 138.6, 133.4, 131.8, 130.6, 130.0, 129.4, 129.3, 129.0, 61.1, 33.4, 21.4, 14.2 ppm. HRMS calcd for $C_{22}H_{20}O_3S$: 365.1211 [M + H^+], found: 365.1206.

Ethyl [2-phenyl -5-formyl-4-(4-methoxylphenyl)-thiophen-3-yl]acetate (4f):

Yellow solid. Yield: 0.142 g (75%). M.p. 77-79 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.60 (s,1H), 7.49-7.44 (m, 5H), 7.30 (d, *J* = 8.4 Hz, 2H), 6.99 (d, *J* = 8.8 Hz, 2H), 4.03 (q, *J* = 7.2 Hz, 2H), 3.87 (s, 3H), 3.49 (s, 2H), 1.13 (t, *J* = 7.2 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 184.4, 171.2, 160.2, 152.7, 150.6, 138.7, 133.4, 132.0, 131.4, 129.4, 129.3, 129.0, 125.8, 114.2, 61.1, 55.5, 33.5, 14.2 ppm. HRMS calcd for $C_{22}H_{20}O_4S$: 381.1161 [M + H^+], found: 381.1161.

Ethyl [2-phenyl -5-formyl-4-(4-chlorophenyl)-thiophen-3-yl]acetate (4g):

White solid. Yield: 0.140 g (73%). M.p. 83-85 ºC.^{1}H NMR (400 MHz, $CDCl_3$): δ 9.58 (s,1H), 7.50-7.45 (m, 7H), 7.34-7.32 (m, 2H), 4.02 (q, *J* = 7.2 Hz, 2H), 3.46 (s, 2H), 1.14 (t, *J* = 7.2 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 183.7, 171.0, 151.2, 151.0, 138.9, 135.3, 133.1, 132.0, 131.6, 131.5, 129.5, 129.4, 129.1, 129.0, 61.3, 33.3, 14.2 ppm. HRMS calcd for $C_{21}H_{17}ClO_3S$: 385.0665 [M + H^+], found: 385.0667.

Ethyl [2-(4-chlorophenyl)-5-formyl-4-(4-methylphenyl)-thiophen-3-yl]acetate (4h):

Yellow oil. Yield: 0.143 g (72%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.56 (s, 1H), 7.45 (d, *J* = 8.4 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 7.27 (d, *J* = 6.0 Hz, 2H), 4.03 (q, *J* = 7.2 Hz, 2H), 3.45 (s, 2H), 2.41 (s, 3H), 1.14 (t, *J* = 7.2 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 183.8, 171.2, 151.29, 151.28, 139.7, 138.5, 135.2, 132.1, 131.4, 131.3, 130.1, 129.8, 129.2, 129.0, 61.2, 33.3, 21.5, 14.2 ppm. HRMS calcd for $C_{22}H_{19}ClO_3S$: 399.0822 [M + H^+], found: 399.0822.

Ethyl [2-(4-methoxyphenyl)-5-formyl-4-(4-methoxyphenyl)-thiophen-3-yl]acetate (4i):

Colourless oil. Yield: 0.146 g (71%). M.p.^{1}H NMR (400 MHz, $CDCl_3$): δ 9.58 (s, 1H), 7.44 (d, *J* = 8.8 Hz, 2H), 7.29 (d, *J* = 8.8 Hz, 2H), 7.00-6.96 (m, 4H), 4.04 (q, *J* = 7.2 Hz, 2H), 3.87 (s, 3H), 3.86 (s, 3H), 3.47 (s, 2H), 1.15 (t, *J* = 7.2 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 184.4, 171.4, 160.6, 160.2, 152.9, 150.8, 138.1, 131.4, 130.7, 125.9, 125.7, 114.5, 114.1, 61.1, 55.55, 55.51, 33.5, 14.3 ppm. HRMS calcd for $C_{23}H_{22}O_5S$: 411.1266 [M + H^+], found: 411.1266.

Ethyl (2'-formyl-5'-phenyl-[2, 3']bithiophenyl-4'-yl)acetate (4j):

White solid. Yield: 0.139 g (78%). M.p. 79-81 ºC.^{1}H NMR (400 MHz, $CDCl_3$): δ 9.78 (s, 1H), 7.51-7.45 (m, 6H), 7.17-7.14 (m, 2H), 4.09 (q, *J* = 7.2 Hz, 2H), 3.58 (s, 2H), 1.17 (t, *J* = 7.2 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 184.1, 171.1, 150.5, 144.3, 140.1, 133.13, 133.09, 132.3, 130.2, 129.5, 129.4, 129.1, 128.2, 127.6, 61.3, 33.6, 14.3 ppm. HRMS calcd for $C_{19}H_{16}O_3S_2$: 379.0439 [M + Na^+], found: 379.0439.

Ethyl [5'-(4-chloro-phenyl)-2'-formyl-[2, 3']bithiophenyl-4'-yl]acetate (4k):

White solid. Yield: 0.160 g (82%). M.p. 97-99 ºC.^{1}H NMR (400 MHz, $CDCl_3$): δ 9.78 (s, 1H), 7.51 (d, *J* = 5.2 Hz, 1H), 7.46-7.41 (m, 4H), 7.18-7.14 (m, 2H), 4.10 (q, *J* = 7.2 Hz, 2H), 3.55 (s, 2H), 1.19 (t, *J* = 7.2 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 184.1, 171.0, 149.0, 144.3, 140.3, 135.8, 132.8, 132.6, 131.5, 130.6, 130.3, 129.4, 128.3, 127.7, 61.4, 33.6, 14.3 ppm. HRMS calcd for $C_{19}H_{15}ClO_3S_2$: 391.0229 [M + H^+], found: 391.0232.

Ethyl [2'-formyl-5'-(4-nitro-phenyl)-[2, 3']bithiophenyl-4'-yl]acetate (4l):

Yellow solid. Yield: 0.110 g (55%). M.p.118-120 ºC.^{1}H NMR (400 MHz, $CDCl_3$): δ 9.80 (s, 1H), 8.33 (d, *J* = 8.8 Hz, 2H), 7.70 (d, *J* = 8.8 Hz, 2H) 7.55-7.53 (m, 1H), 7.20-7.15 (m, 2H), 4.12 (q, *J* = 7.2 Hz, 2H), 3.57 (s, 2H), 1.20 (t, *J* = 7.2 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 184.0, 170.7, 148.4, 147.0, 144.3, 141.4, 139.6, 133.7, 132.4, 130.5, 130.3, 128.6, 127.8, 124.3, 61.6, 33.6, 14.3 ppm. HRMS calcd for $C_{19}H_{15}NO_5S_2$: 424.0289 [M + Na^+], found: 424.0269.

Methyl (5-formyl-2, 4-diphenyl-thiophen-3-yl)acetate (4m):

Colourless solid. Yield: 0.117g (70%). M.p 85-87 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.58 (s, 1H), 7.50-7.45 (m, 8H), 7.38-7.35 (m, 2H), 3.54 (s, 3H), 3.50 (s, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 184.3, 171.6, 152.8, 150.7, 138.7, 133.5, 133.2, 131.6, 130.0, 129.4, 129.1, 129.0, 128.7, 52.2, 33.1 ppm. HRMS calcd for $C_{20}H_{16}O_3S$: 337.0898 [M + H^+], found: 337.0898.

Methyl (2'-formyl-5'-phenyl-[2,3']bithiophenyl-4'-yl)acetate (4n):

Yellow oil. Yield: 0.135 g (79%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.78 (s, 1H), 7.51-7.46 (m, 6H), 7.17-7.13 (m, 2H), 3.63 (s, 3H), 3.59 (s, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 184.1, 171.5, 150.5, 144.3, 140.1, 133.0, 132.9, 132.1, 130.2, 129.5, 129.3, 129.1, 128.2, 127.7, 52.4, 33.4 ppm. HRMS calcd for $C_{18}H_{14}O_3S_2$: 343.0463 [M + H^+], found: 343.0462.

The tetrahydrothiopyranols **3a**, **3k** and **3m** were obtained as single diastereomers by crystallization from EtOAc/hexane (1:9) and their characterization data are given below.

Diethyl 3-benzoyl-5-hydroxy-2-phenyl-tetrahydro-thiopyran-4,4-dicarboxylate (3a):

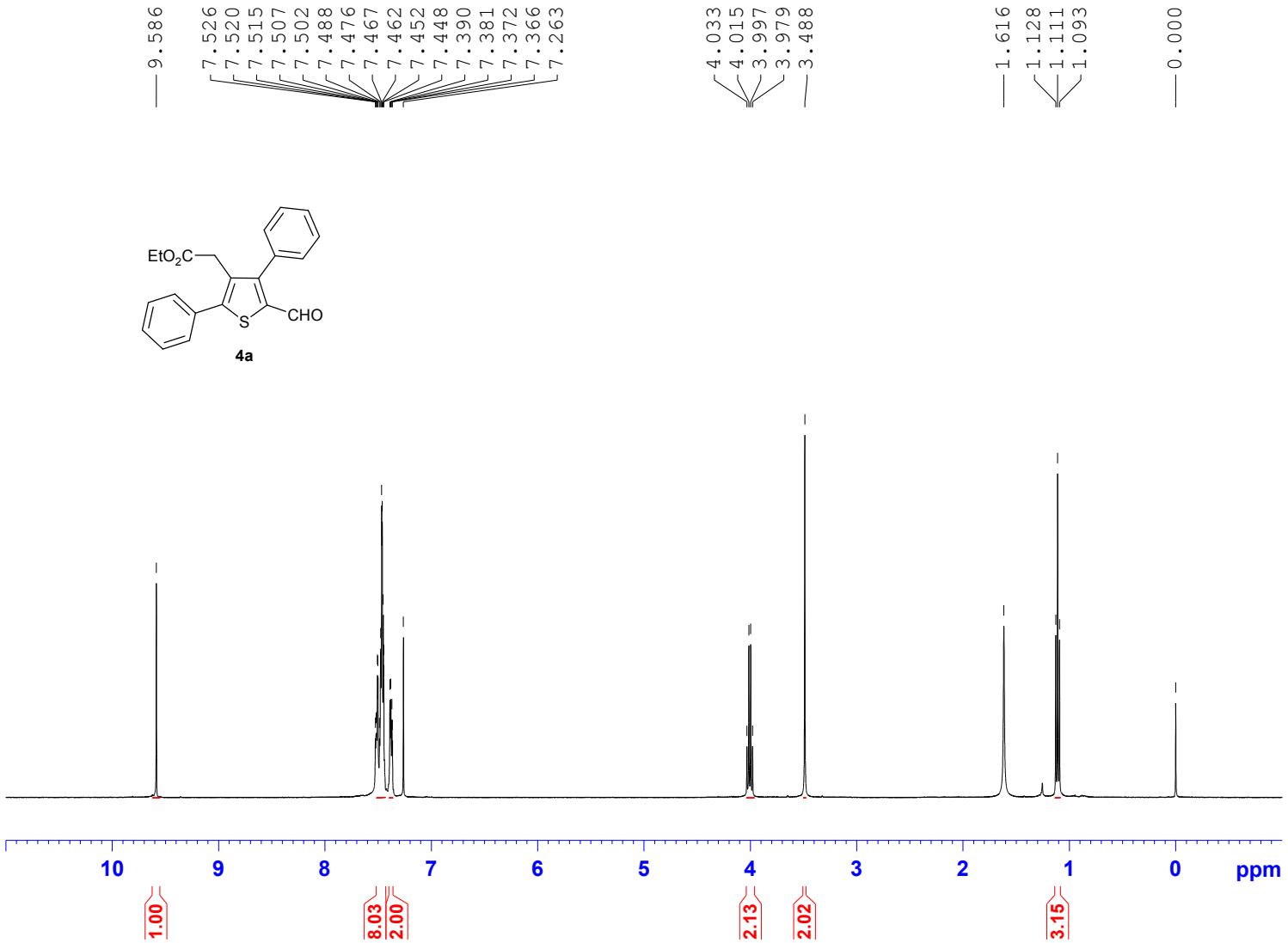
Colourless oil. Yield: 0.132 g (60%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 (d, *J* = 7.6 Hz, 2H), 7.23 (d, *J* = 7.6 Hz, 1H), 7.07-7.04 (m, 4H), 6.95-6.92 (3H), 5.51 (d, *J* = 4.4 Hz, 1H), 5.39 (dd, *J* = 11.6, 4.4 Hz, 1H), 4.87 (d, *J* = 4.4 Hz, 1H), 4.37-4.29 (m, 2H), 4.01-3.93 (m, 2H), 3.85-3.77 (m, 1H), 3.31 (dd, *J* = 13.2, 11.6 Hz, 1H), 2.89 (dd, *J* = 13.6, 4.8 Hz, 1H), 1.34 (t, *J* = 7.2 Hz, 3H), 0.77 (t, *J* = 7.2 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.4, 171.5, 169.3, 138.2, 137.8, 132.2, 128.3, 128.2, 127.9, 127.8, 68.6, 62.3, 62.0, 61.6, 52.8, 45.8, 30.6, 14.2, 13.3 ppm. HRMS calcd for $C_{24}H_{26}O_6S$: 465.1348 [M + Na^+], found: 465.1326.

Diethyl 2-(4-chloro-phenyl)-5-hydroxy-3-(thiophene-2-carbonyl)-tetrahydro-thiopyran-4,4-dicarboxylate (3k):

Colourless solid. Yield: 0.182 g (75%). M.p. 138-140 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41 (d, *J* = 4.2 Hz, 1H), 7.07 (d, *J* = 8.4 Hz, 2H), 7.00 (d, *J* = 8.4 Hz, 2H), 6.85 (d, *J* = 4.0 Hz, 1H), 6.73 (t, *J* = 4.4 Hz, 1H), 5.48 (d, *J* = 4.0 Hz, 1H), 5.32 (dd, *J* = 11.2, 4.0 Hz, 1H), 4.51 (d, *J* = 4.0 Hz, 1H), 4.36-4.28 (m, 2H), 4.01-3.90 (m, 3H), 3.28 (dd, *J* = 11.6, 1.6 Hz, 1H), 2.87 (dd, *J* = 13.2, 4.4 Hz, 1H), 1.32 (t, *J* = 7.2 Hz, 3H), 0.82 (t, *J* = 7.2 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.1, 171.1, 169.2, 145.8, 137.0, 134.0, 133.9, 132.3, 129.5, 128.5, 127.8, 68.6, 62.4, 62.2, 61.5, 55.1, 45.3, 30.6, 14.2, 13.3 ppm. HRMS calcd for $C_{22}H_{23}ClO_6S_2$: 505.0522 [M + Na^+], found: 505.0522.

Dimethyl 3-benzoyl-5-hydroxy-2-phenyl-tetrahydro-thiopyran-4,4-dicarboxylate (3m):

Colourless solid. Yield: 0.138 g (67%). M.p. 152-154 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54 (d, *J* = 8.0 Hz, 2H), 7.28 (t, *J* = 6.8 Hz, 1H), 7.12 (t, *J* = 7.6 Hz, 2H), 7.03-6.87 (m, 5H), 5.11 (d, *J* = 3.6 Hz, 1H), 4.80 (dd, *J* = 12.0, 2.4 Hz, 1H), 4.21 (d, *J* = 3.6 Hz, 1H), 3.95 (s, 3H), 3.67 (s, 3H), 3.58 (d, *J* = 14.0 Hz, 1H), 3.02 (dd, *J* = 14.4, 3.2 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 200.1, 169.0, 168.9, 138.7, 137.3, 132.4, 128.6, 128.5, 128.1, 127.8, 127.7, 64.6, 63.8, 54.0, 53.6, 48.9, 47.9, 36.2 ppm. HRMS calcd for $C_{22}H_{22}O_6S$: 437.1035 [M + Na^+], found: 437.1032.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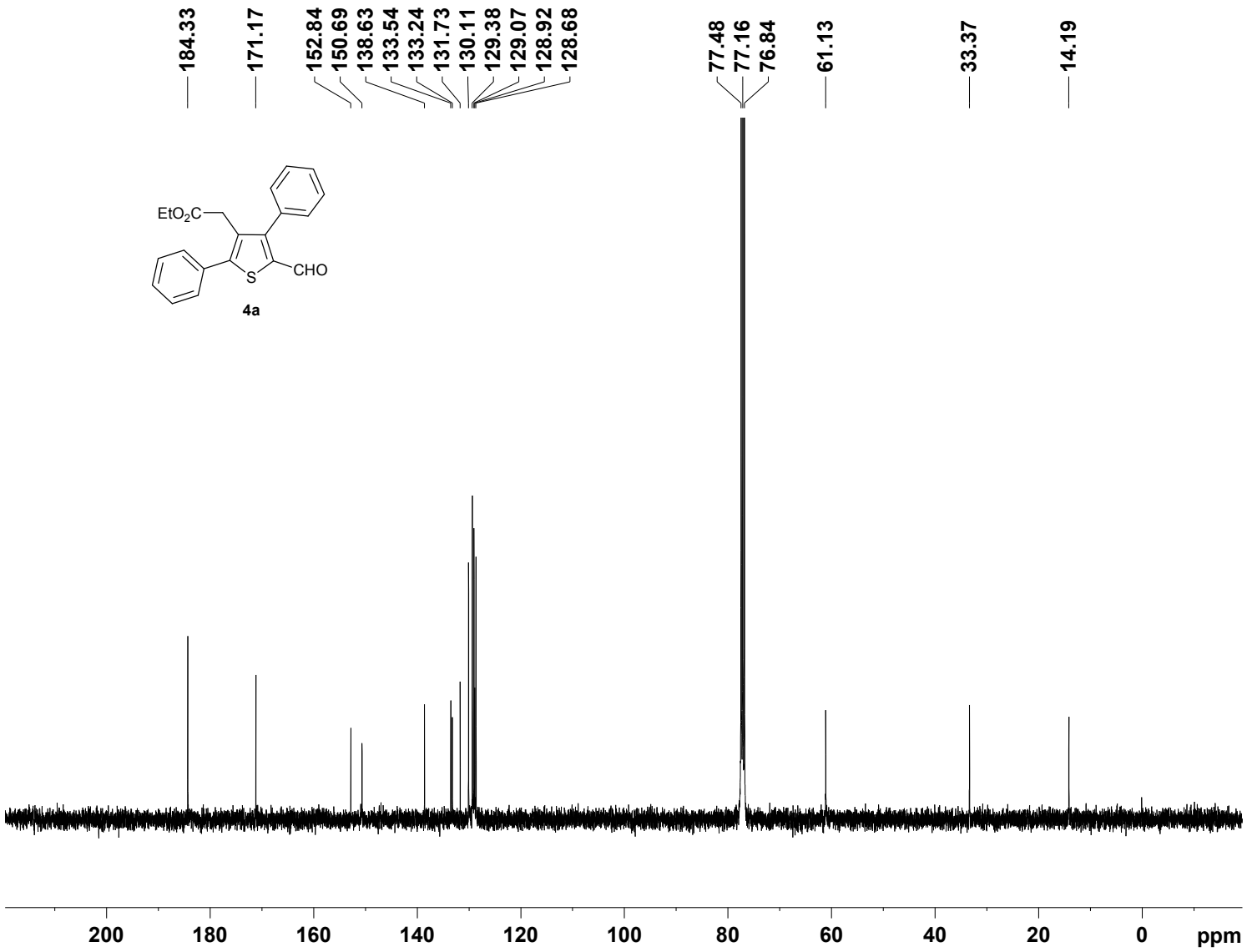
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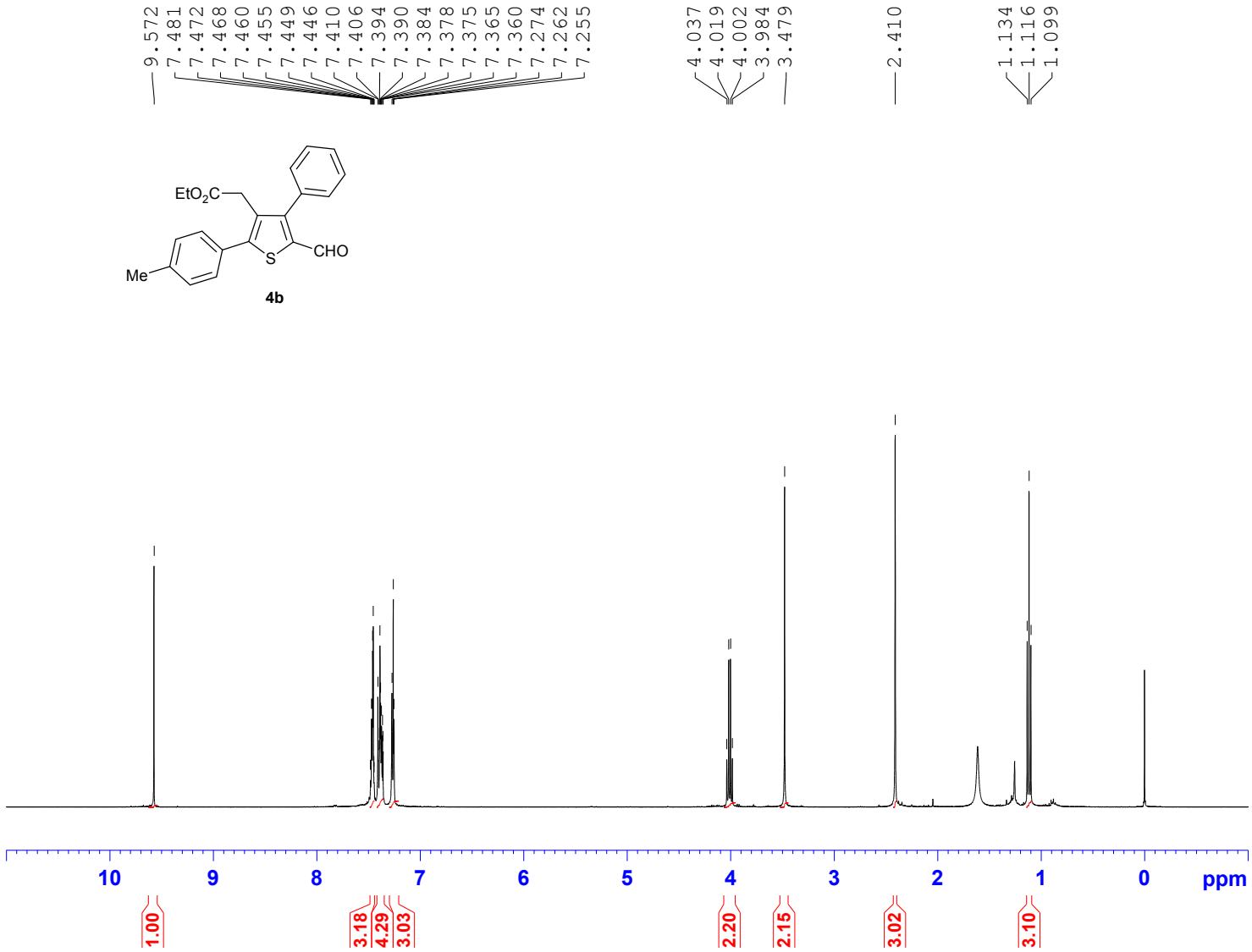
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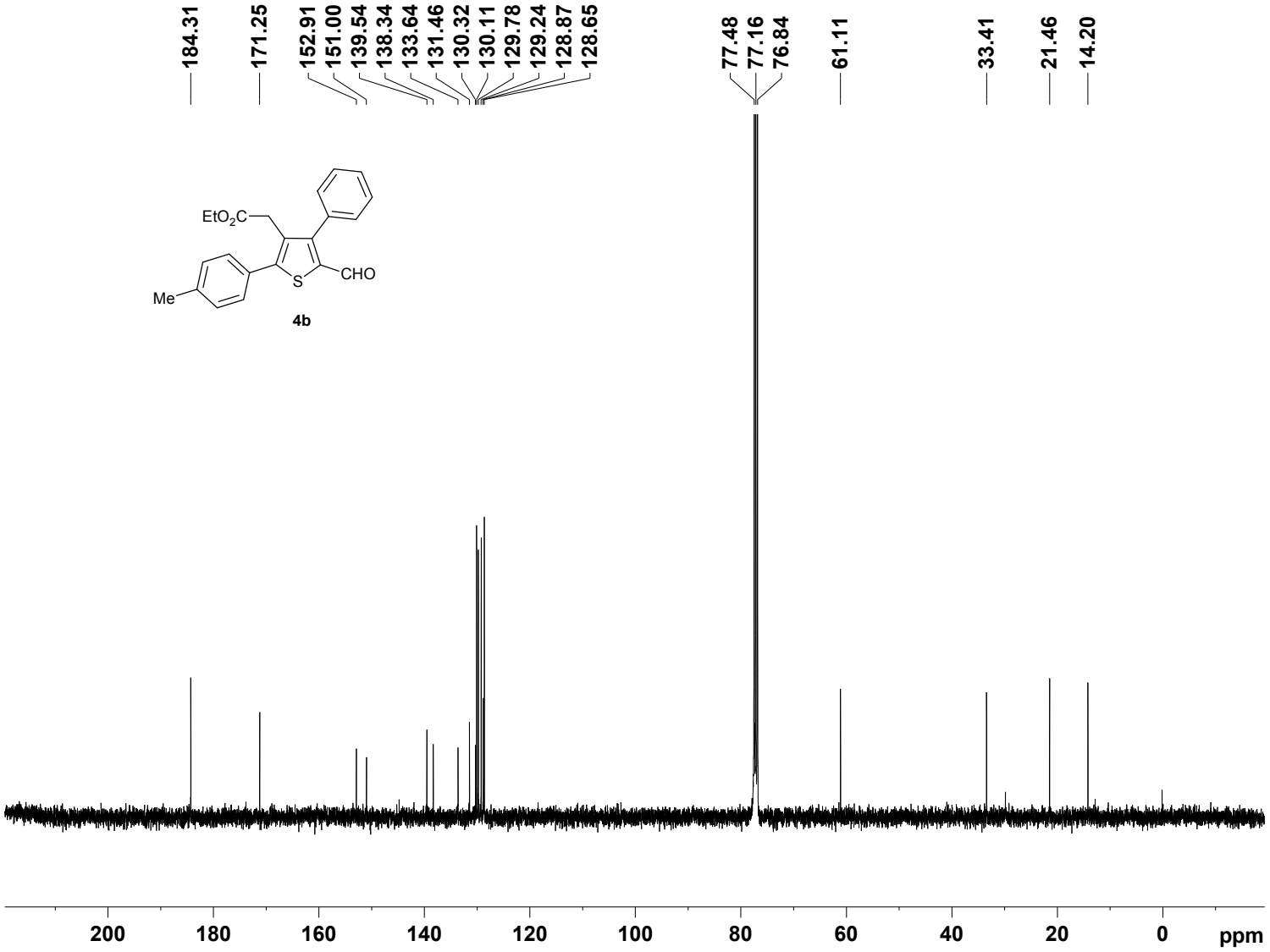
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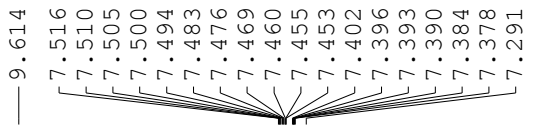
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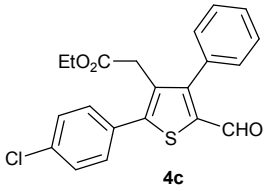
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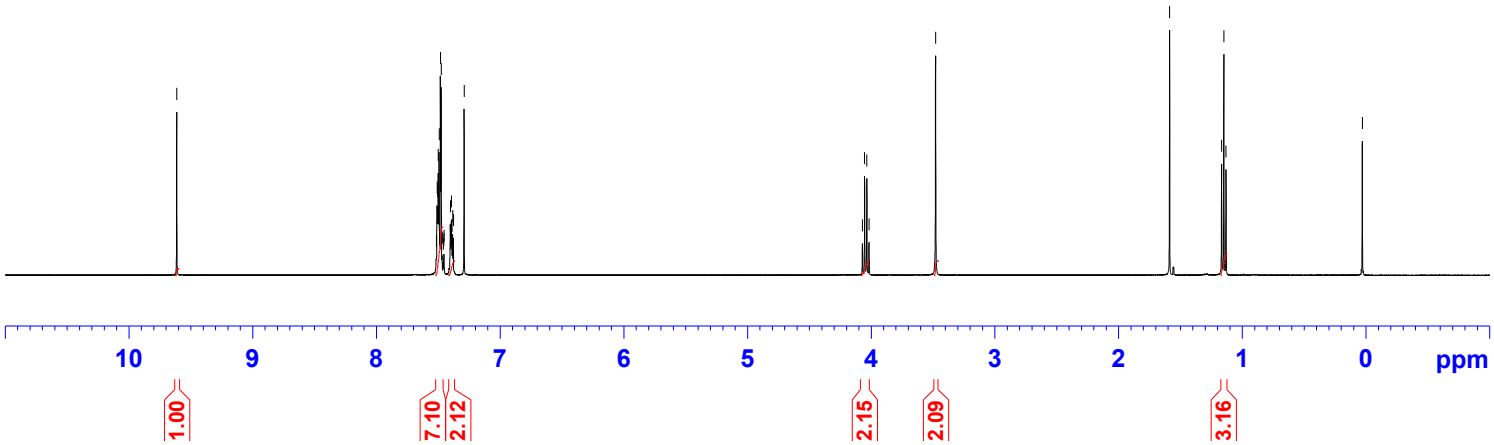
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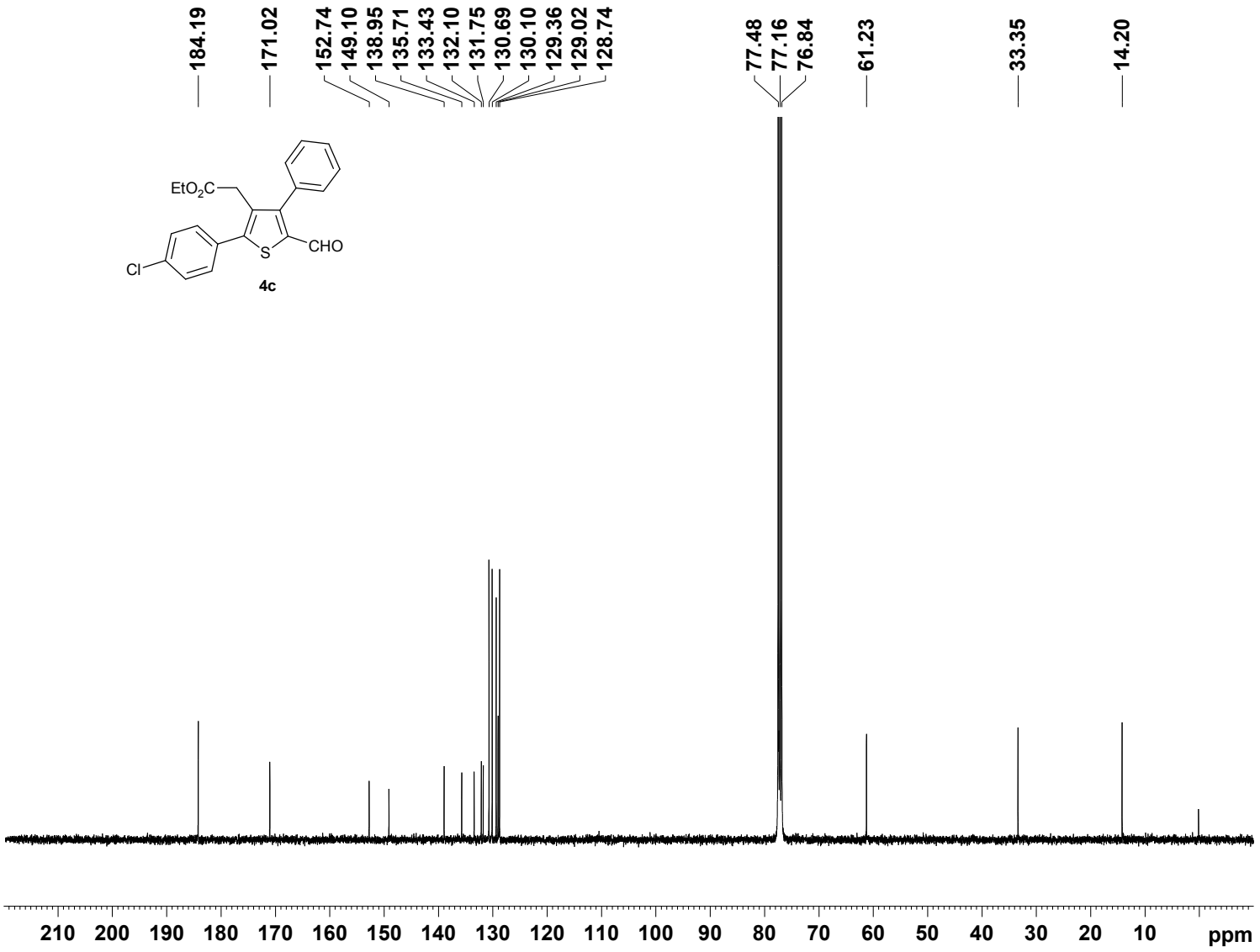
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128.74
77.48
77.16
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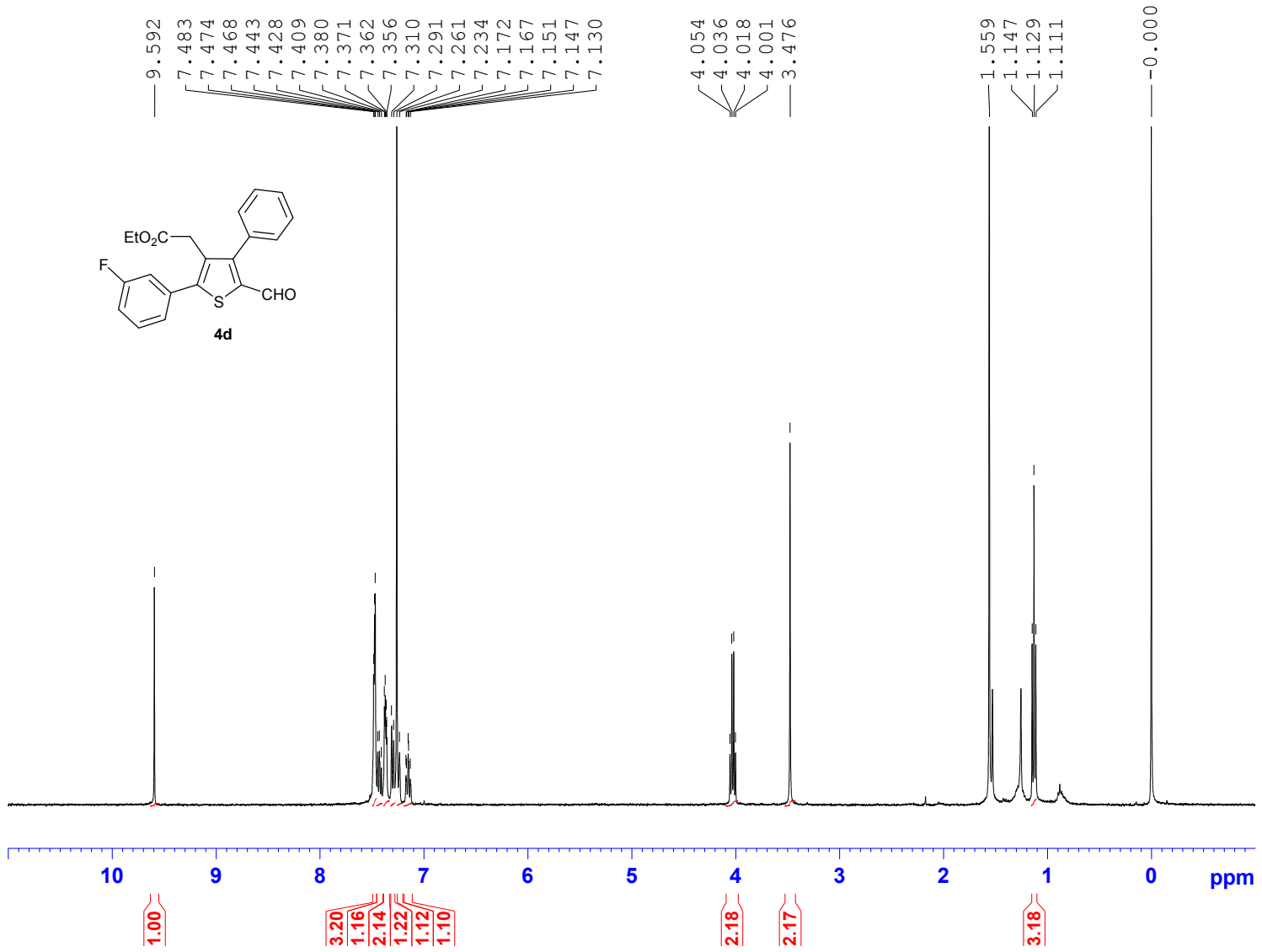
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7.234
7.172
7.167
7.151
7.147
7.130
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4.036
4.018
4.001
3.476
1.559
1.147
1.129
1.111
-0.000
EtO2C
F
S
CHO
4d
10
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8
7
6
5
4
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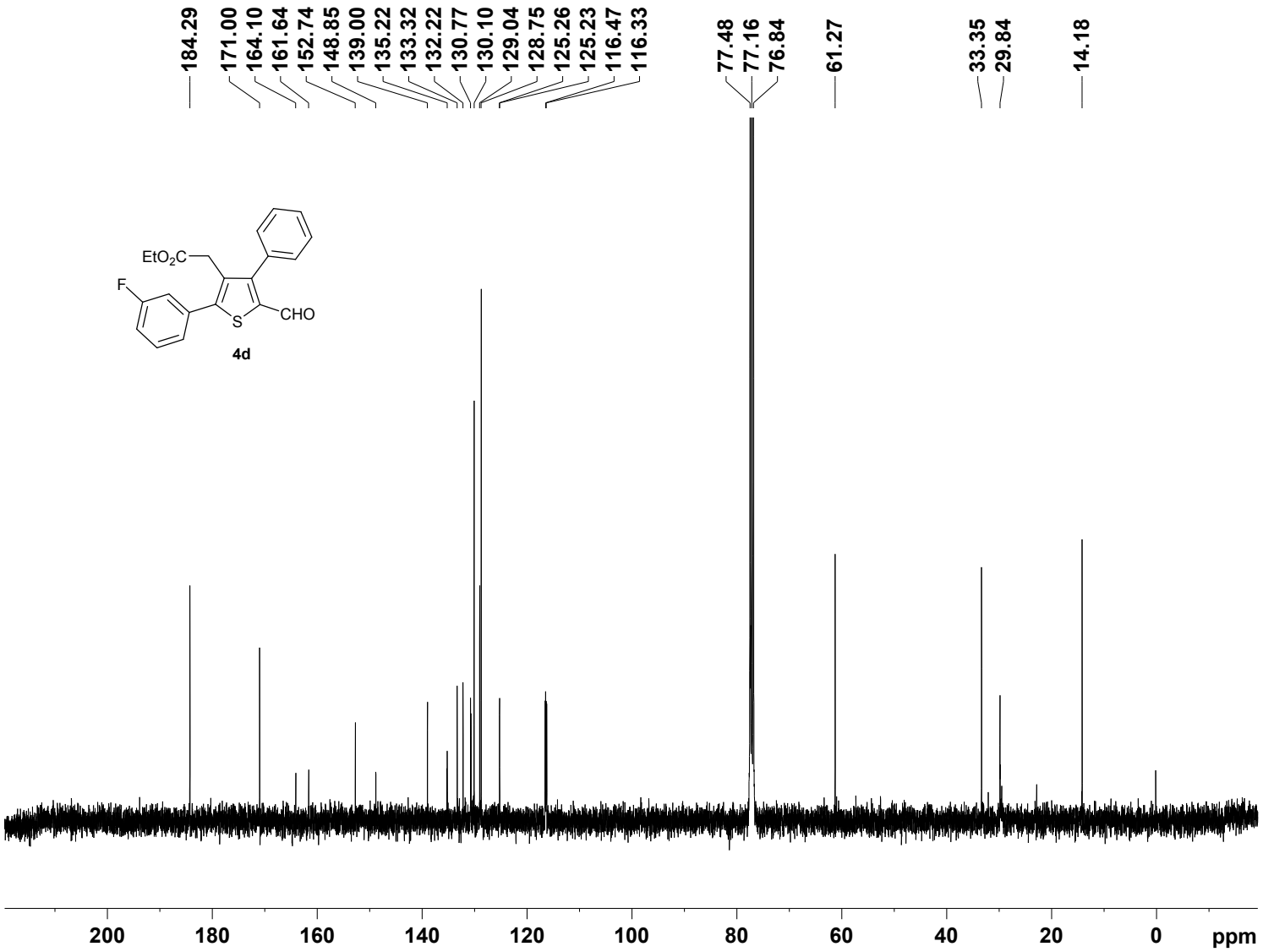
3.18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125.26
125.23
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77.16
76.84
61.27
33.35
29.84
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S
CHO
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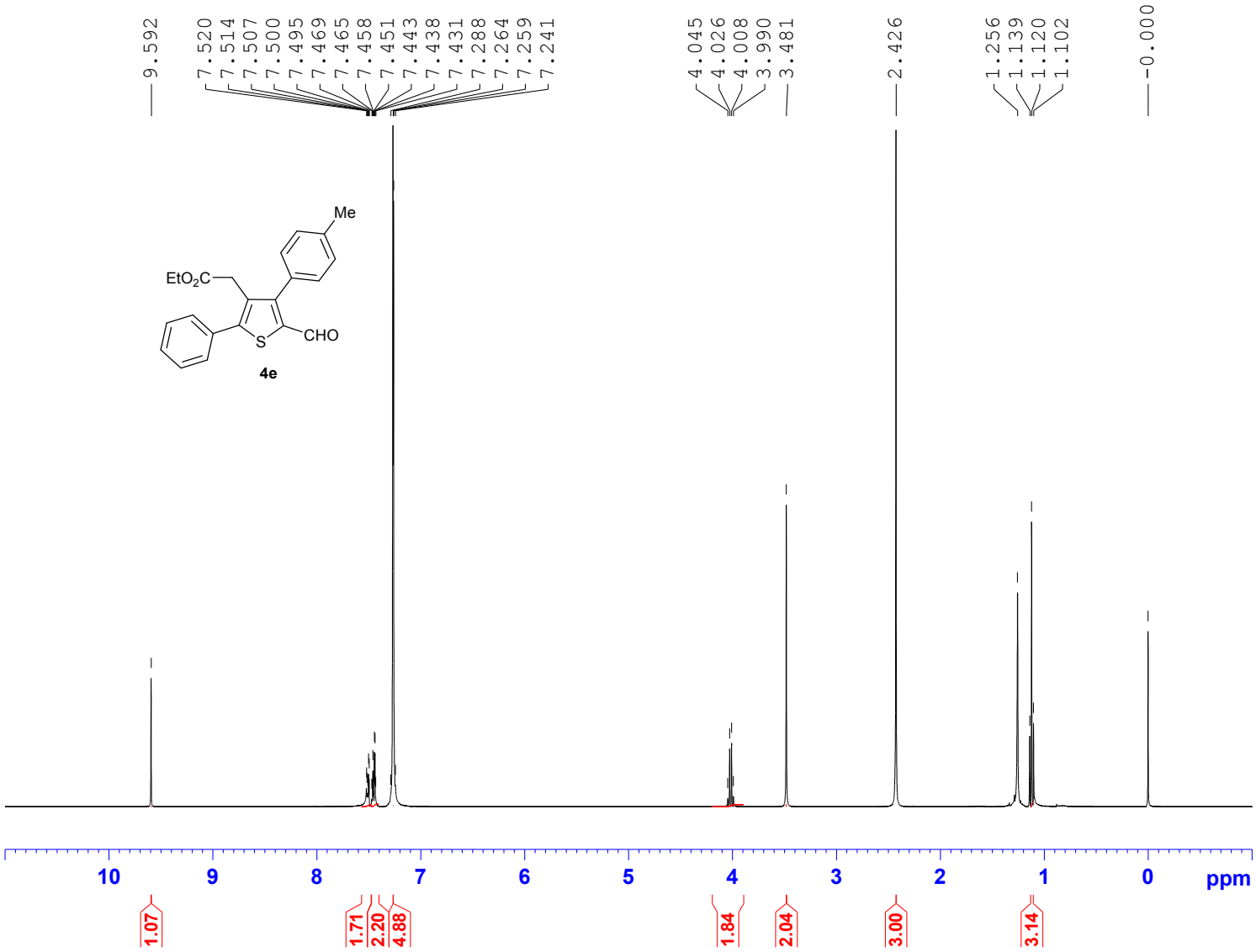
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7.438
7.431
7.288
7.264
7.259
7.241
4.045
4.026
4.008
3.990
3.481
2.426
1.256
1.139
1.120
1.102
-0.000
Me
EtO2C
S
CHO
4e
10
9
8
7
6
5
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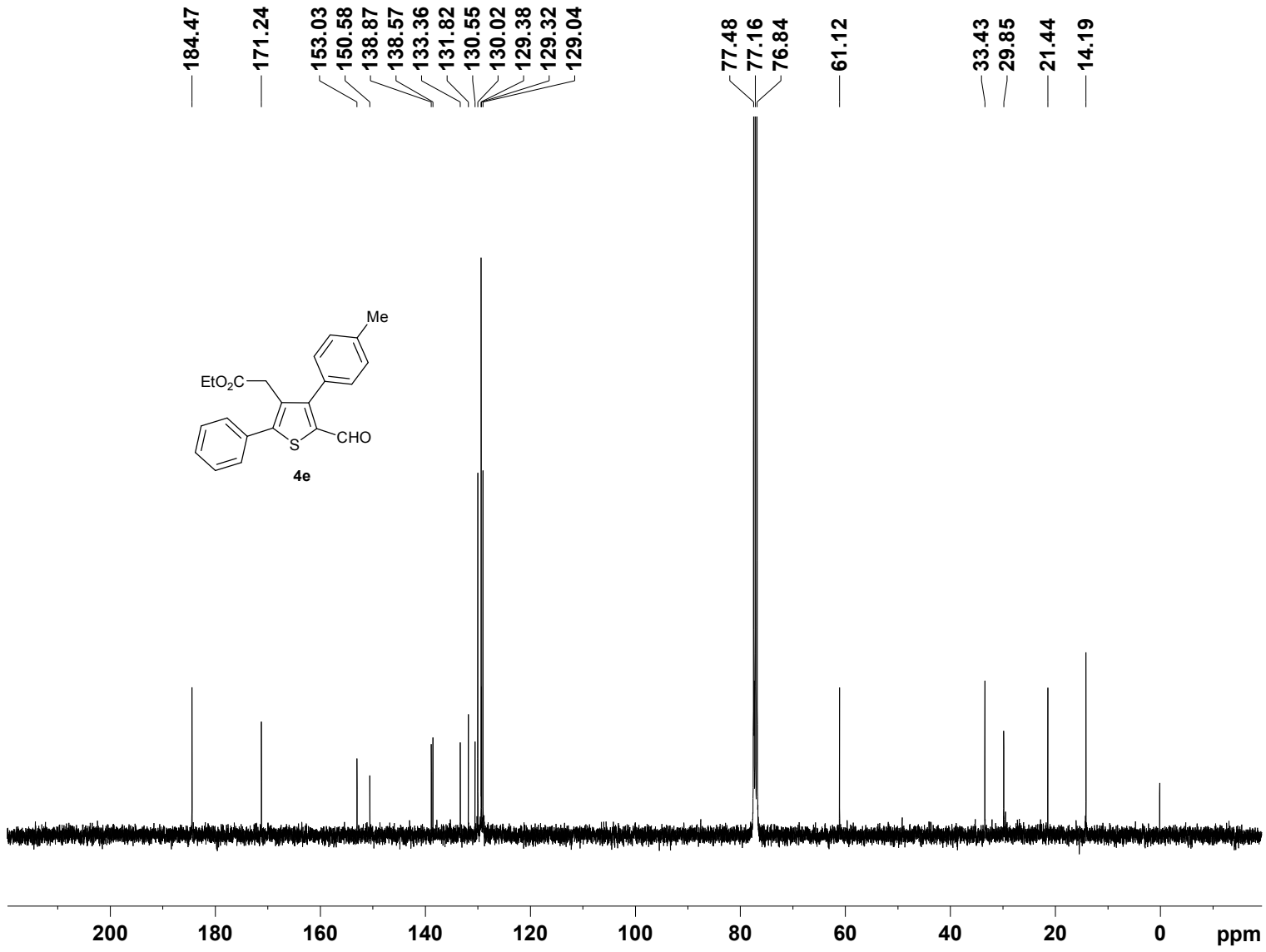
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77.16
76.84
61.12
33.43
29.85
21.44
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120
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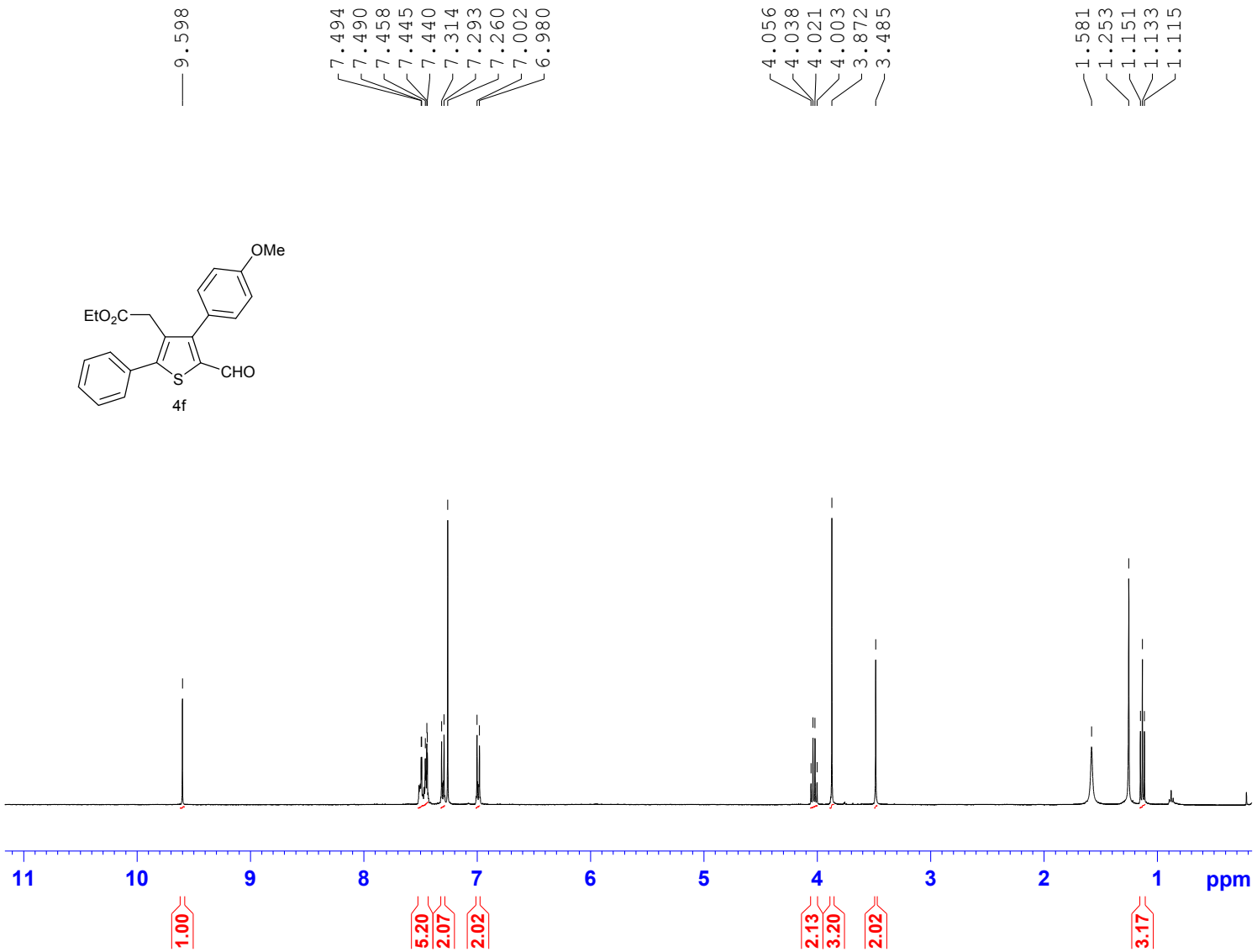
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7.293
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7.002
6.980
4.056
4.038
4.021
4.003
3.872
3.485
1.581
1.253
1.151
1.133
1.115
OMe
EtO2C
CHO
S
4f
11
10
9
8
7
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ppm
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2.02
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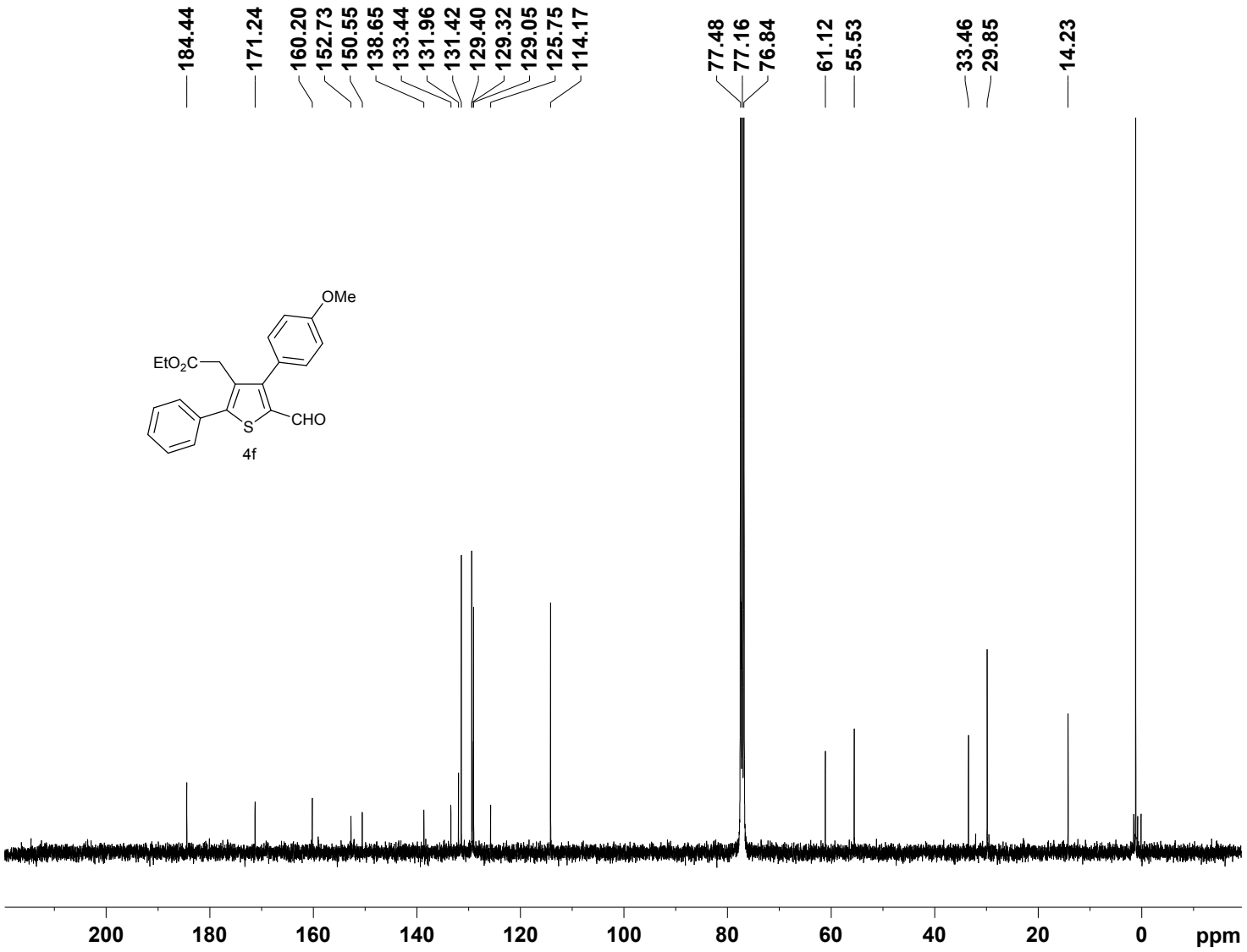
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114.17
77.48
77.16
76.84
61.12
55.53
33.46
29.85
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CHO
S
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120
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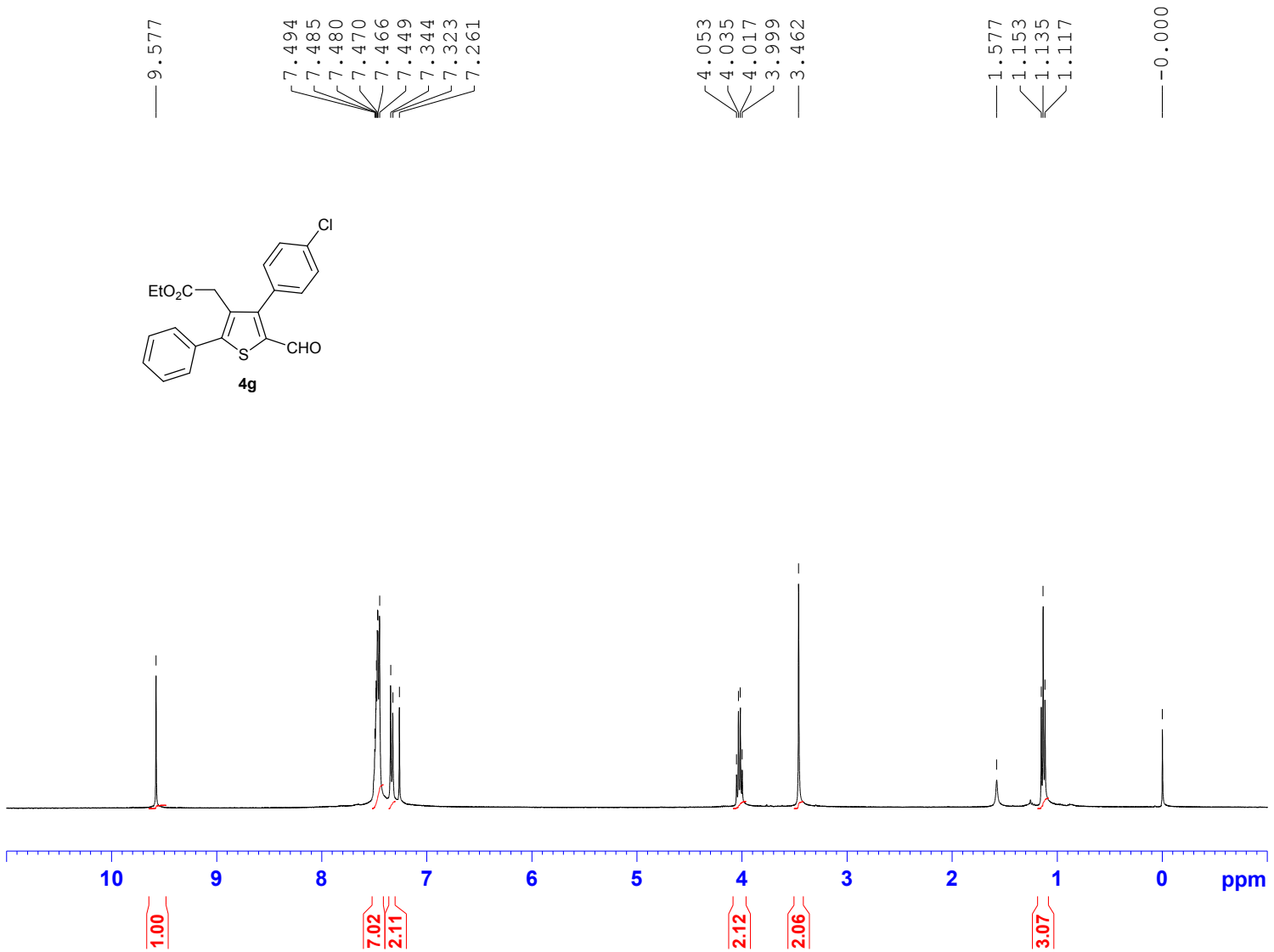
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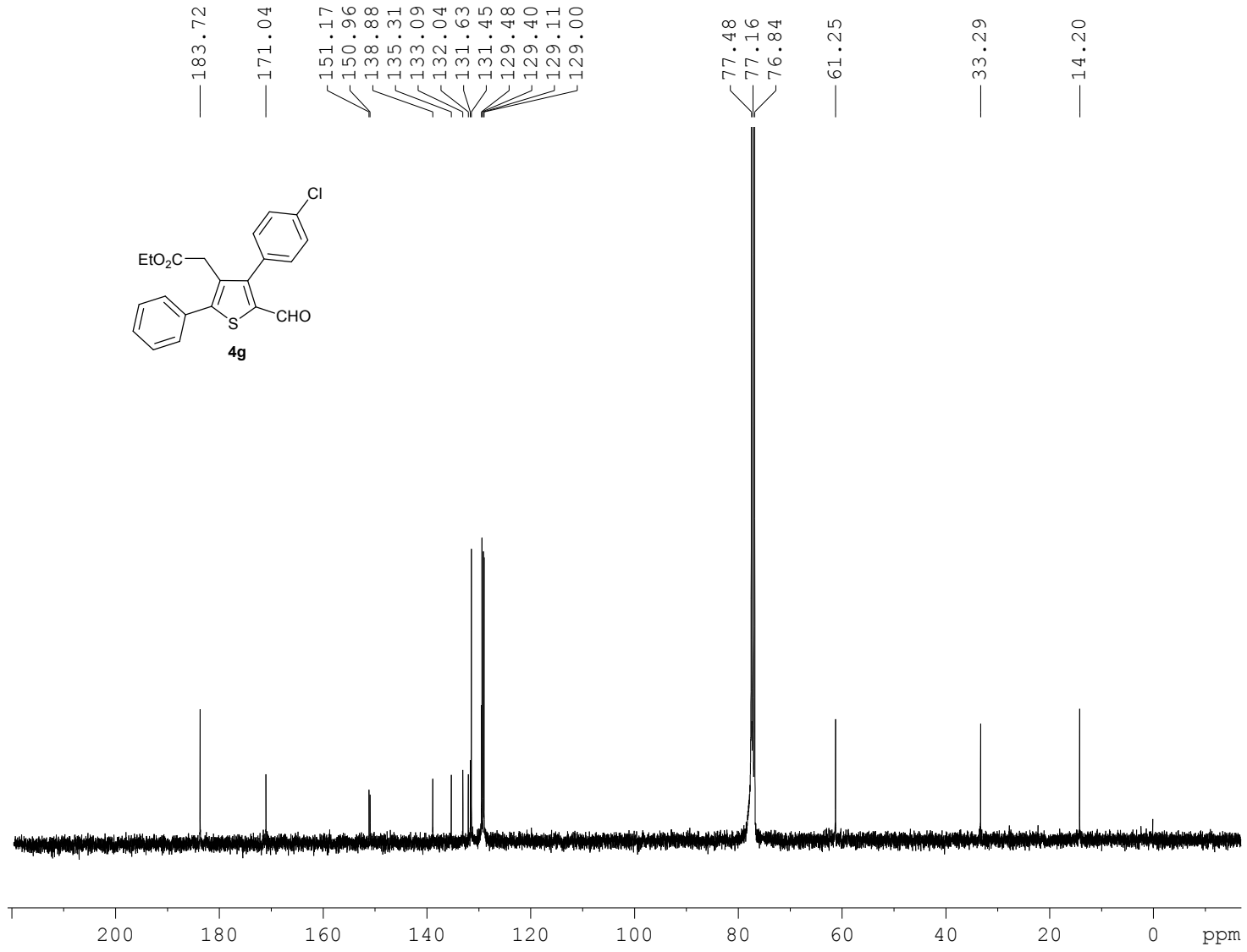
7.449
7.344
7.323
7.261
4.053
4.035
4.017
3.999
3.462
1.577
1.153
1.135
1.117
0.000
Cl
EtO2C
S
CHO
4g
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
7.02
2.11
2.12
2.06
3.07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129.40
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129.00
77.48
77.16
76.84
61.25
33.29
14.20
Cl
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S
CHO
4g
200
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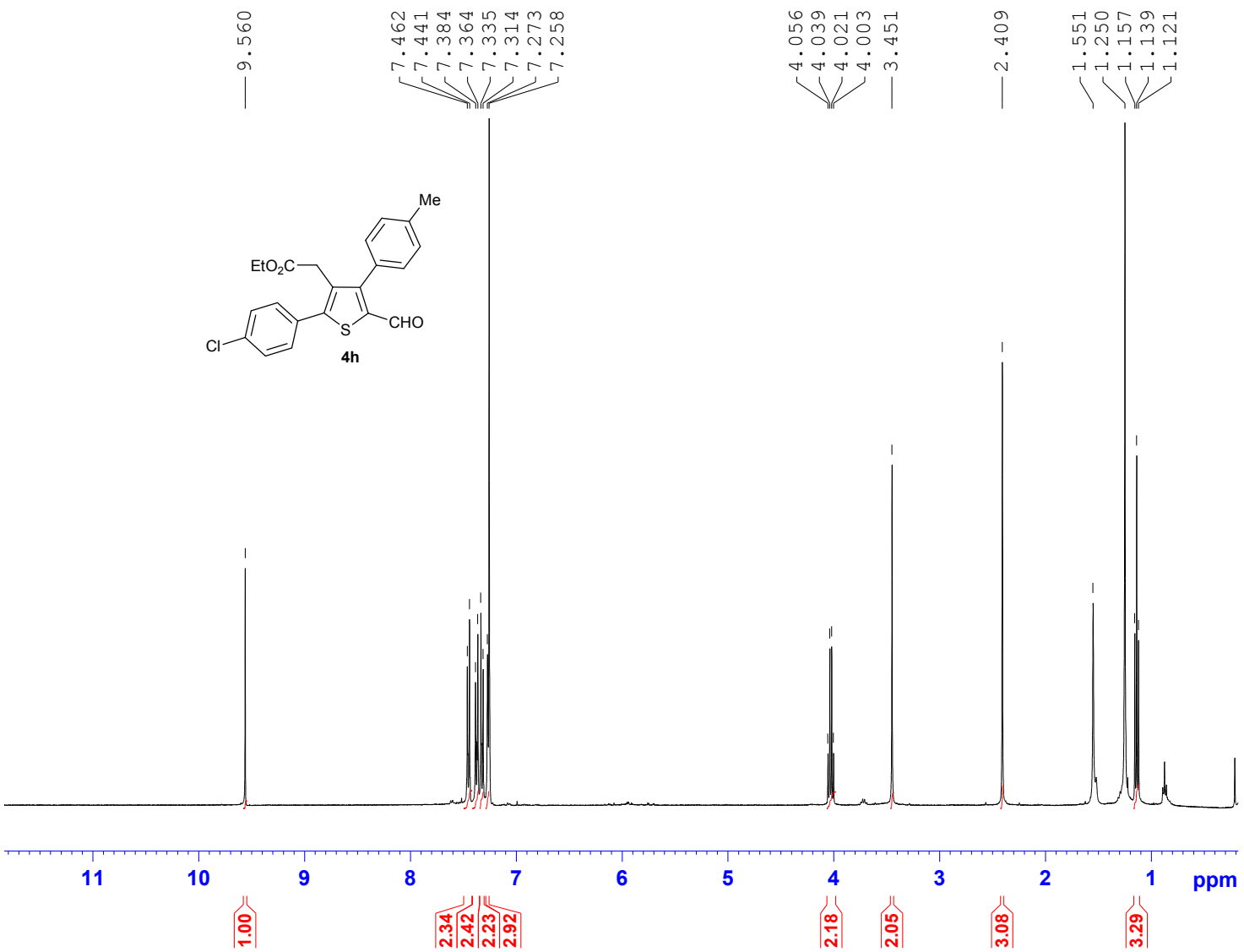
160
140
120
100
80
60
40
20
0
ppm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4.021
4.003
3.451
2.409
1.551
1.250
1.157
1.139
1.121
Me
EtO2C
CHO
S
Cl
4h
11
10
9
8
7
6
5
4
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ppm
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2.92
2.18
2.05
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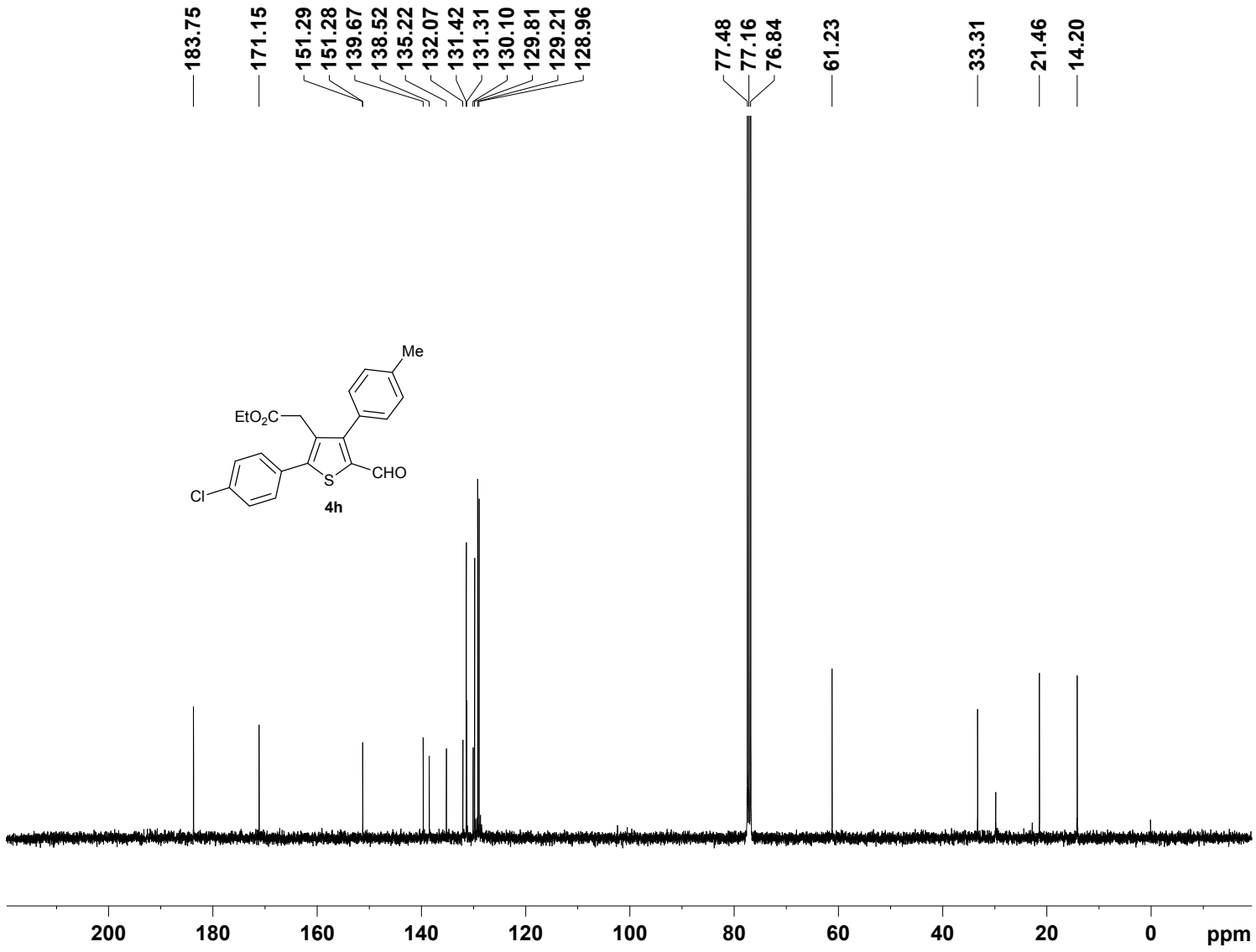
3.29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132.07
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130.10
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129.21
128.96
77.48
77.16
76.84
61.23
33.31
21.46
14.20
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EtO2C
CHO
S
Cl
4h
200
180
160
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100
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60
40
20
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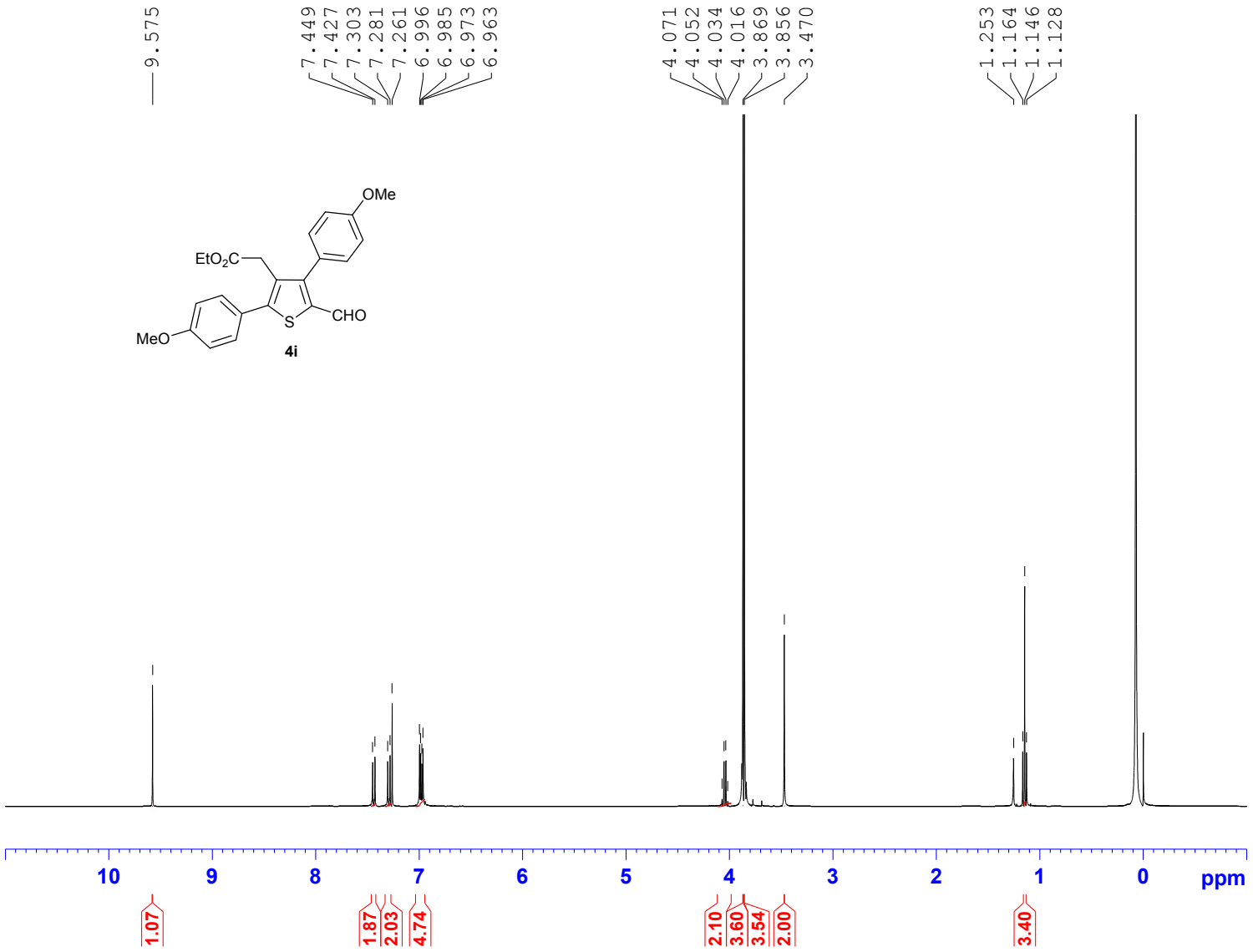
ppm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4.034
4.016
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3.856
3.470
1.253
1.164
1.146
1.128
OMe
EtO2C
CHO
S
MeO
4i
10
9
8
7
6
5
4
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ppm
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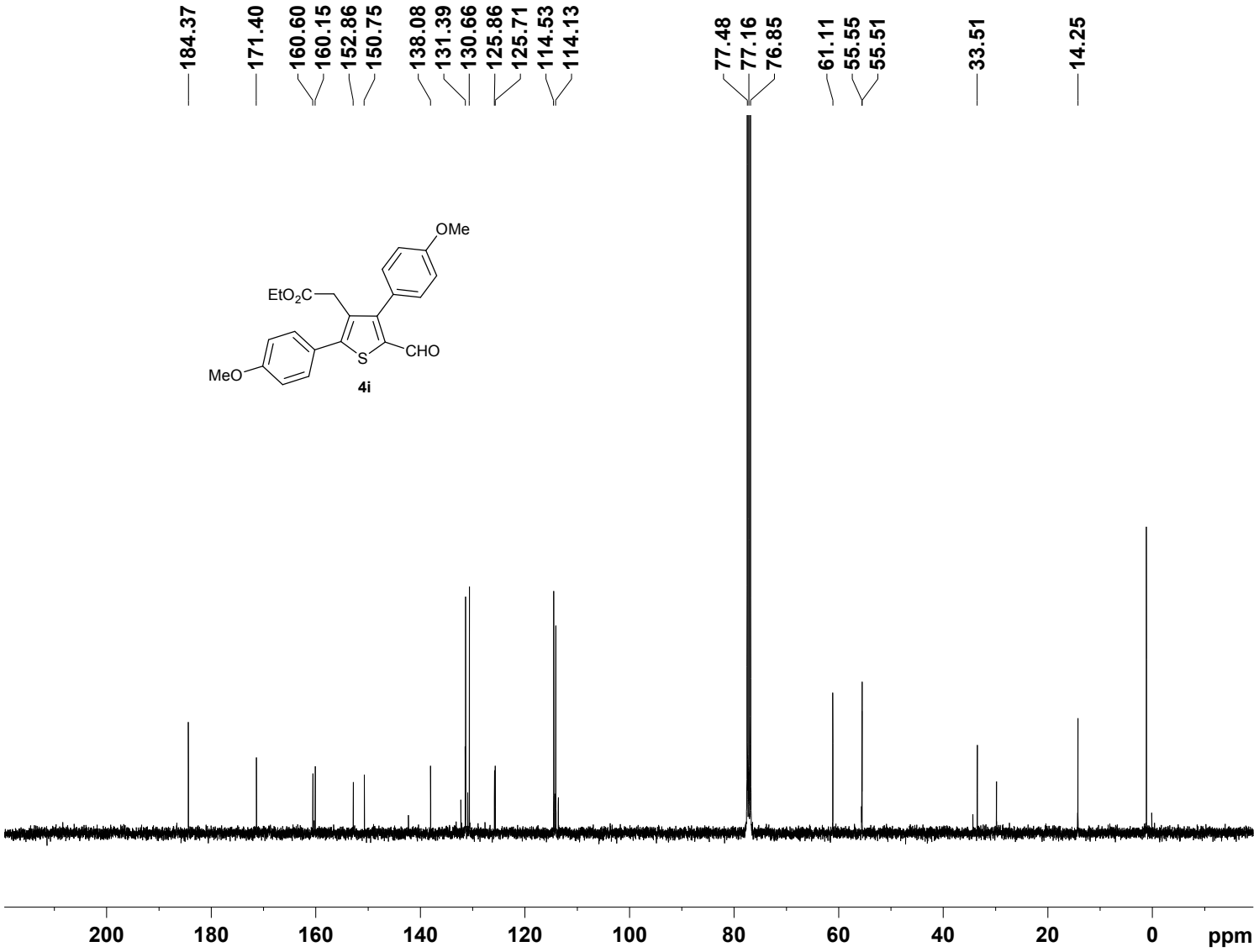
3.40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114.53
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77.48
77.16
76.85
61.11
55.55
55.51
33.51
14.25
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EtO2C
S
CHO
MeO
4i
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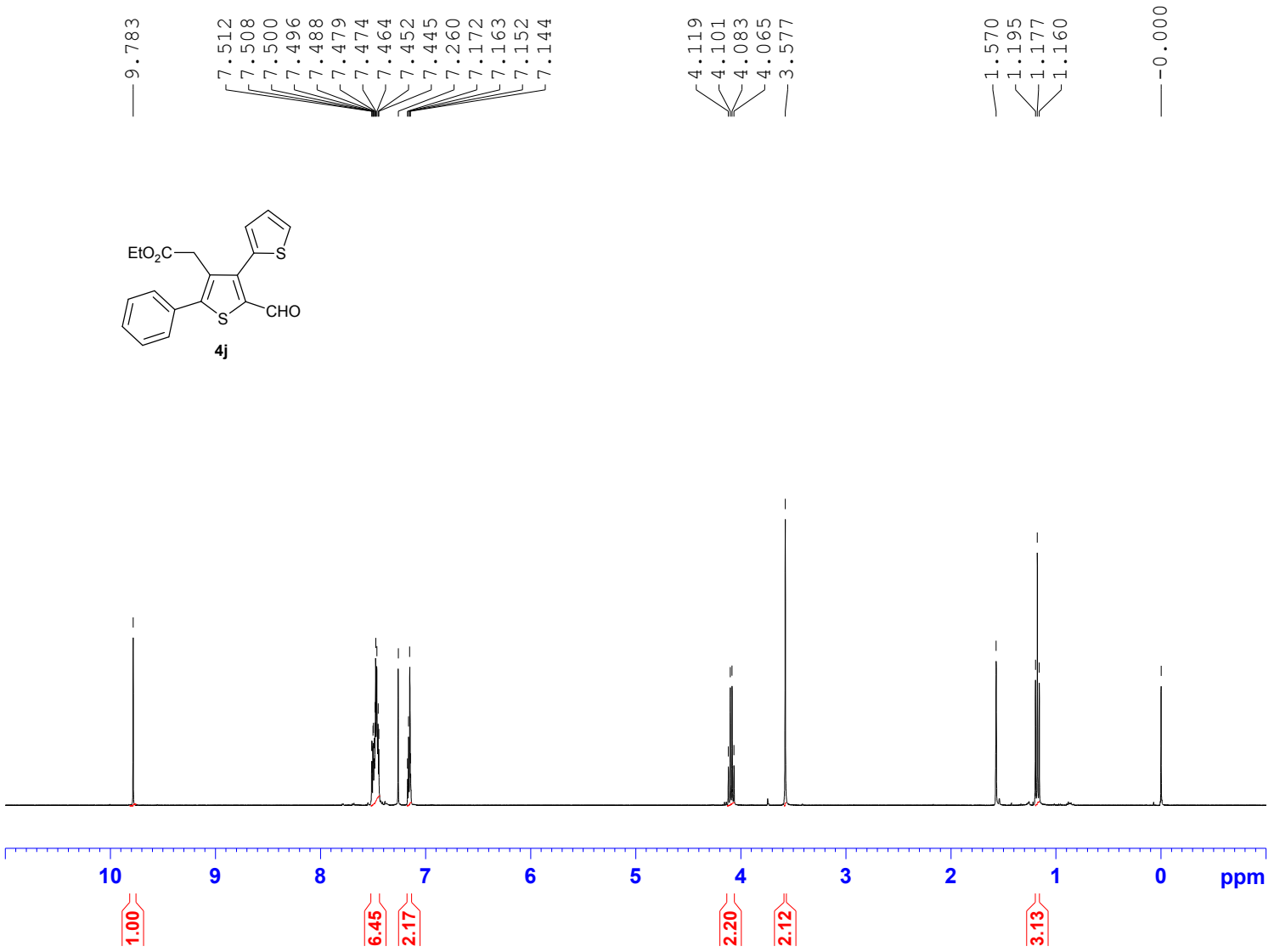
180
160
140
120
100
80
60
40
20
0
ppm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7.452
7.445
7.260
7.172
7.163
7.152
7.144
4.119
4.101
4.083
4.065
3.577
1.570
1.195
1.177
1.160
0.000
EtO2C
S
S
CHO
4j
10
9
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4
3
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6.45
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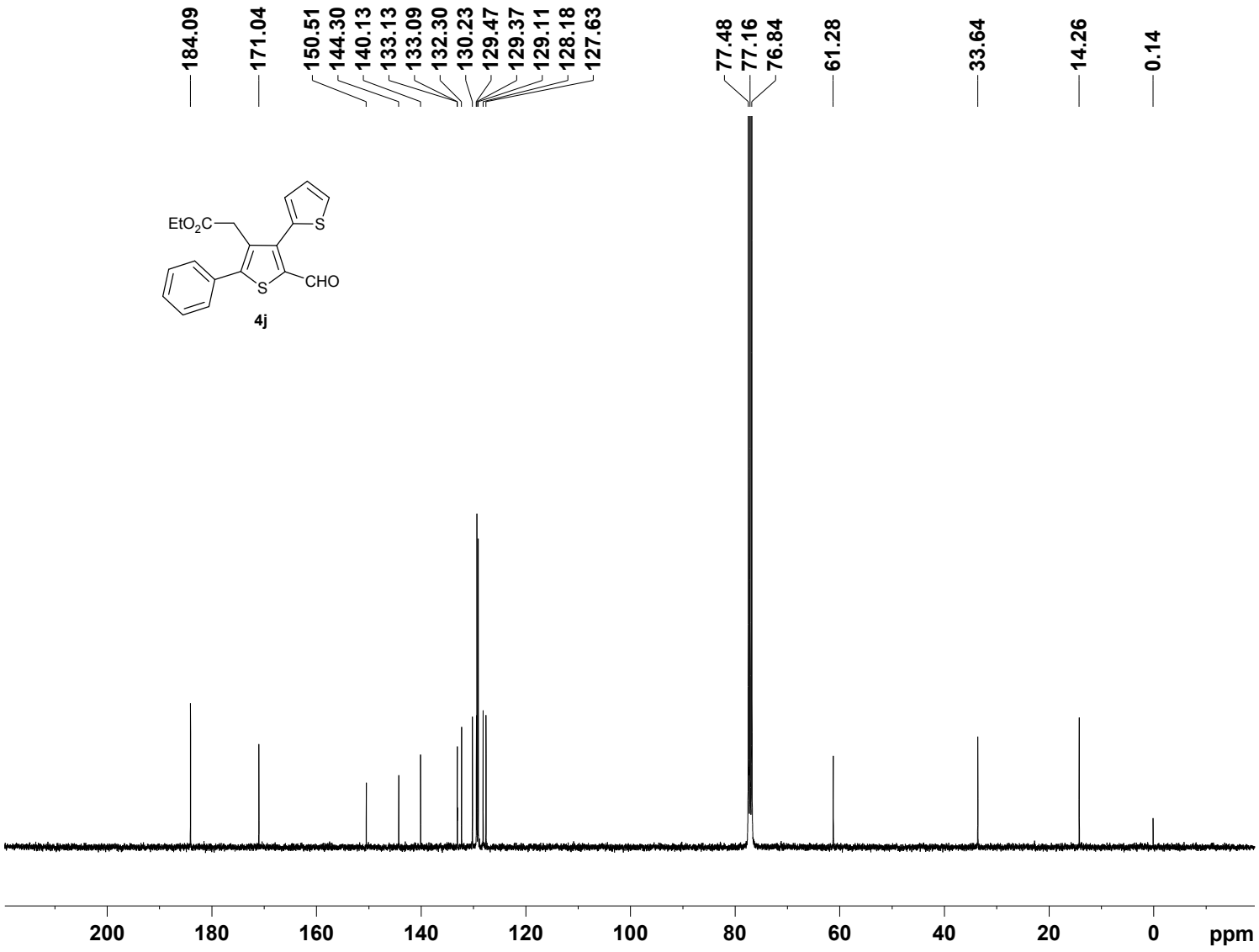
2.20
2.12
3.13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128.18
127.63
77.48
77.16
76.84
61.28
33.64
14.26
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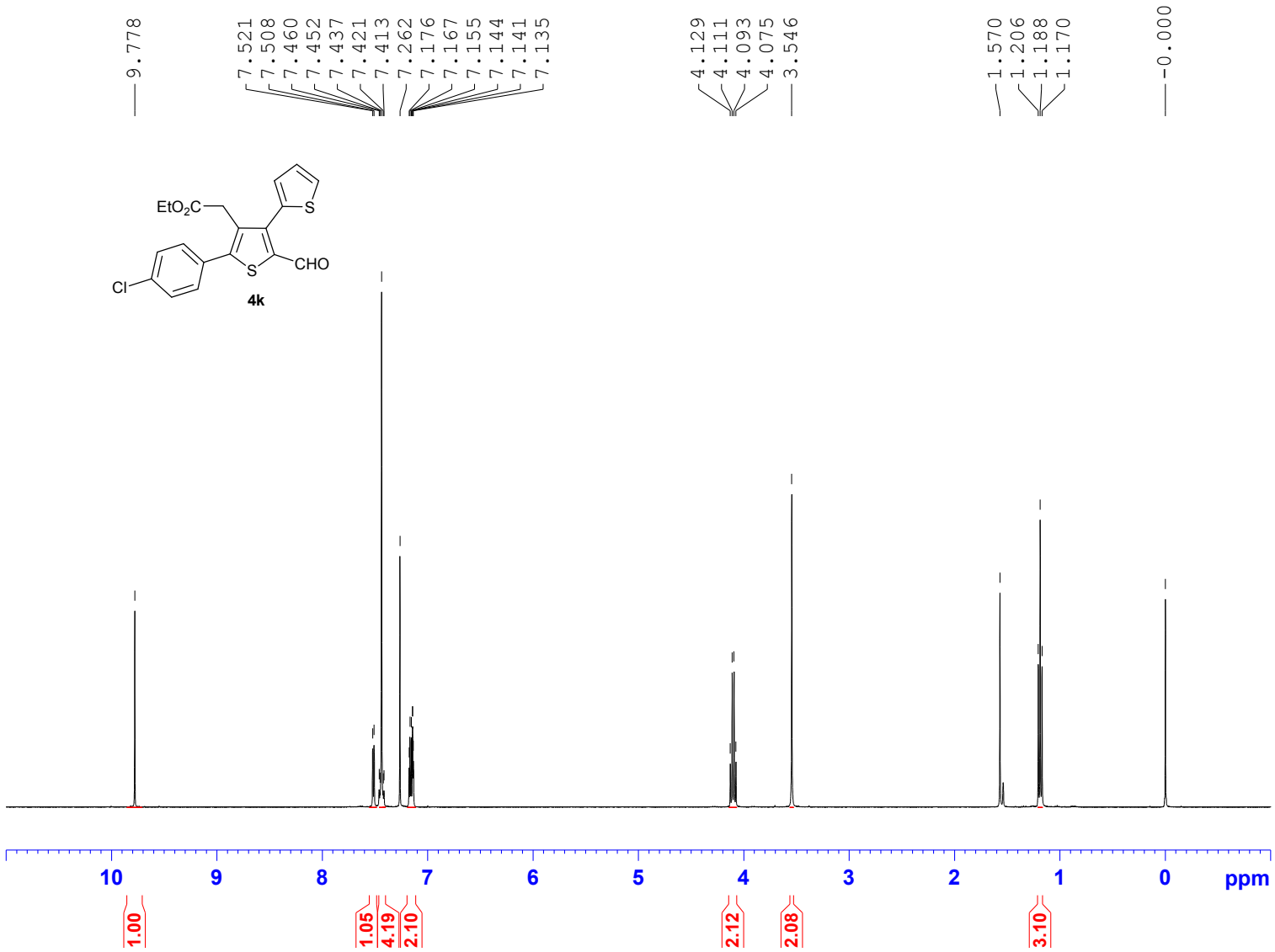
S
S
CHO
4j
200
180
160
140
120
100
80
60
40
20
0
ppm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7.167
7.155
7.144
7.141
7.135
4.129
4.111
4.093
4.075
3.546
1.570
1.206
1.188
1.170
0.000
EtO2C
S
S
CHO
Cl
4k
10
9
8
7
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4
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2
1
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ppm
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4.19
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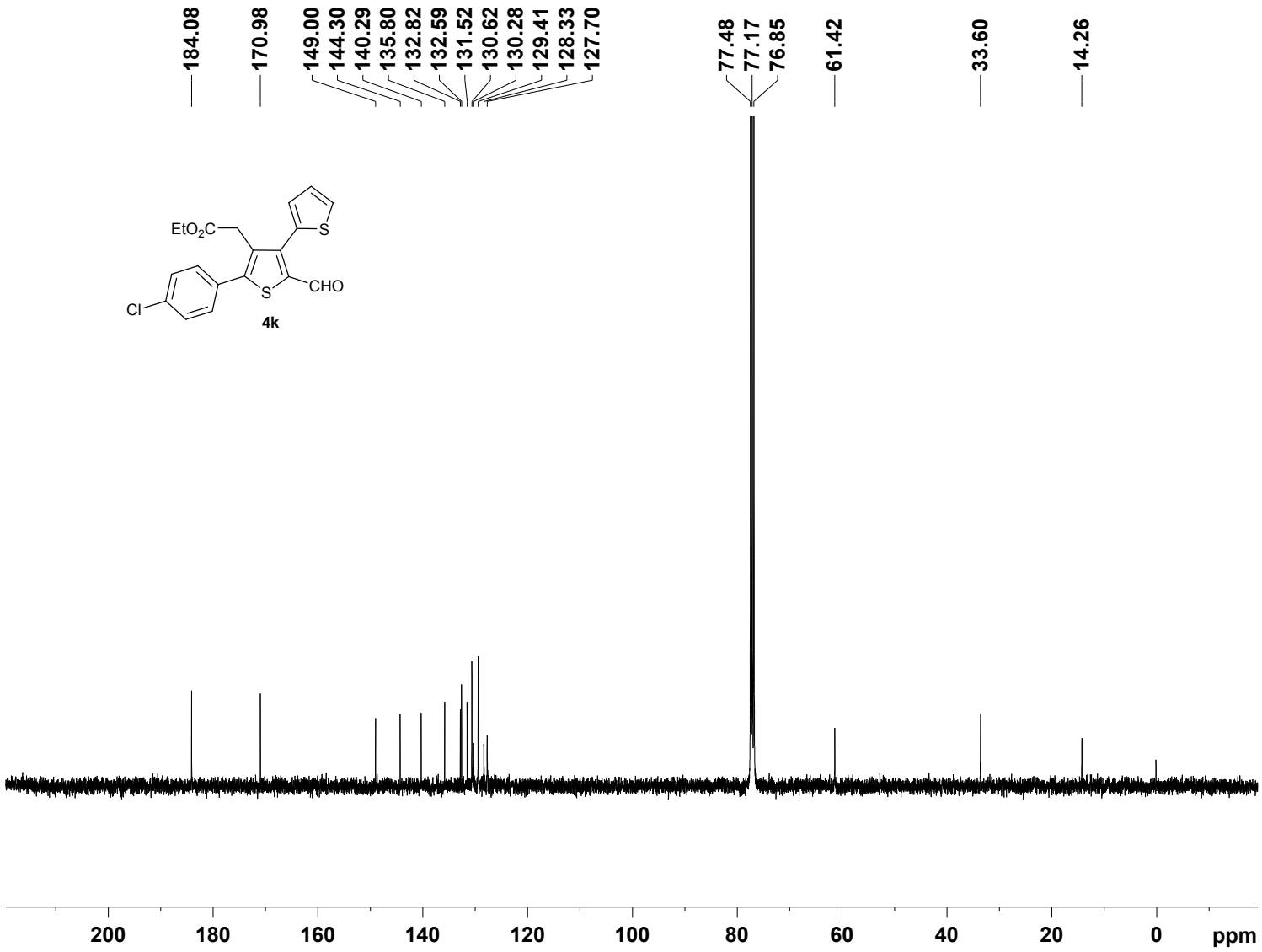
3.10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77.48
77.17
76.85
61.42
33.60
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EtO2C
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S
CHO
Cl
4k
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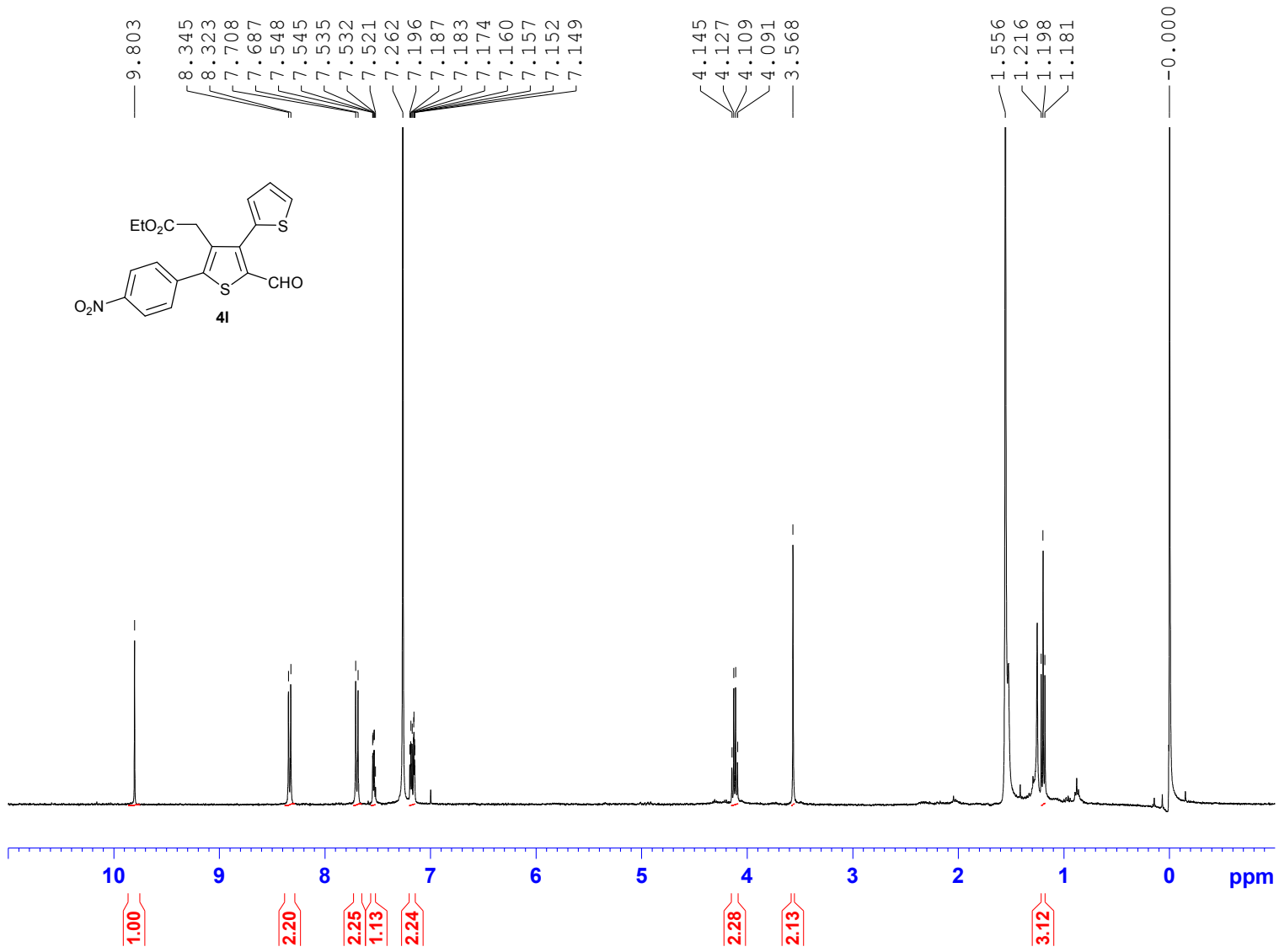
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7.183
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7.160
7.157
7.152
7.149
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4.091
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1.198
1.181
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S
S
CHO
O2N
4l
10
9
8
7
6
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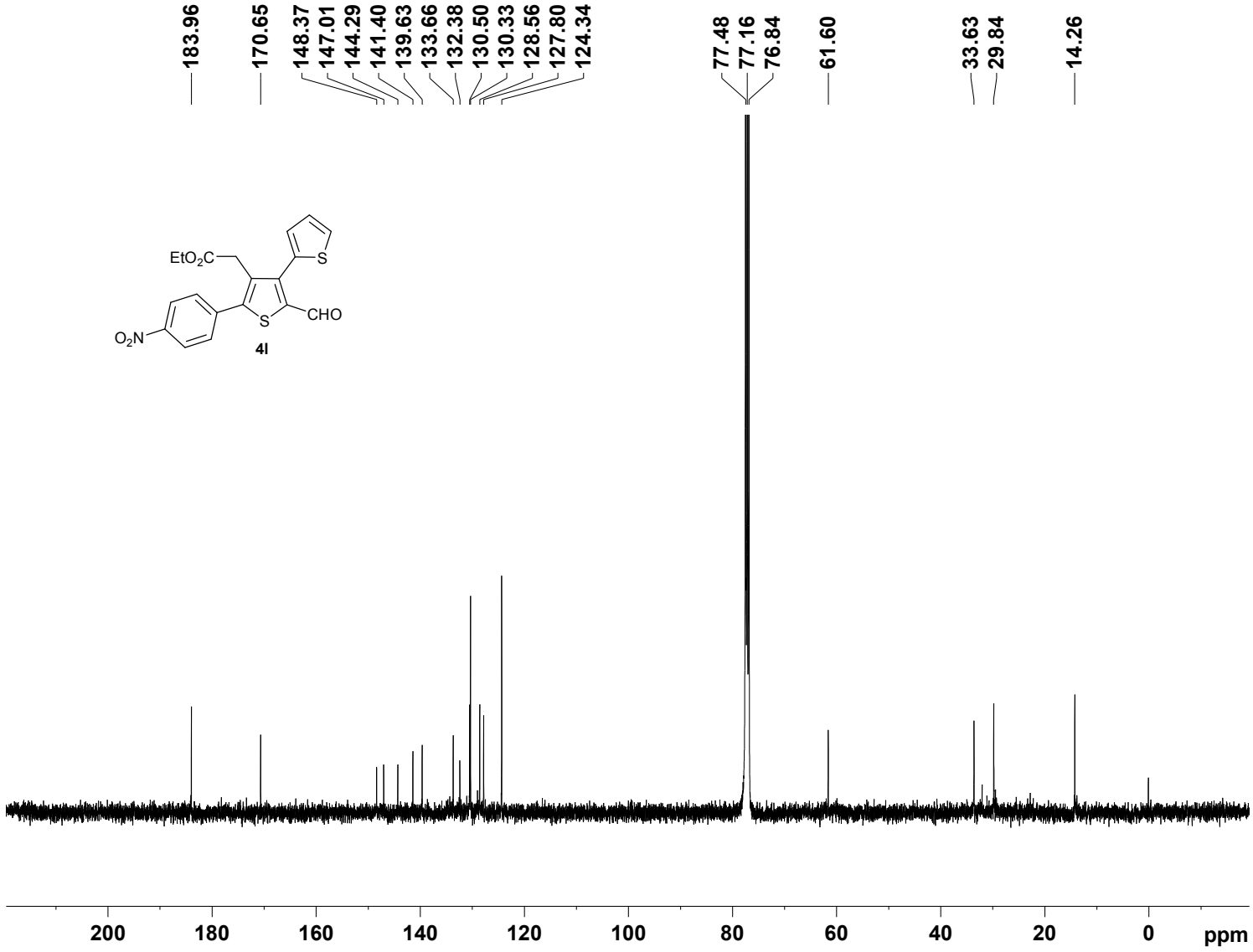
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124.34
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77.16
76.84
61.60
33.63
29.84
14.26
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S
CHO
O2N
4l
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120
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0
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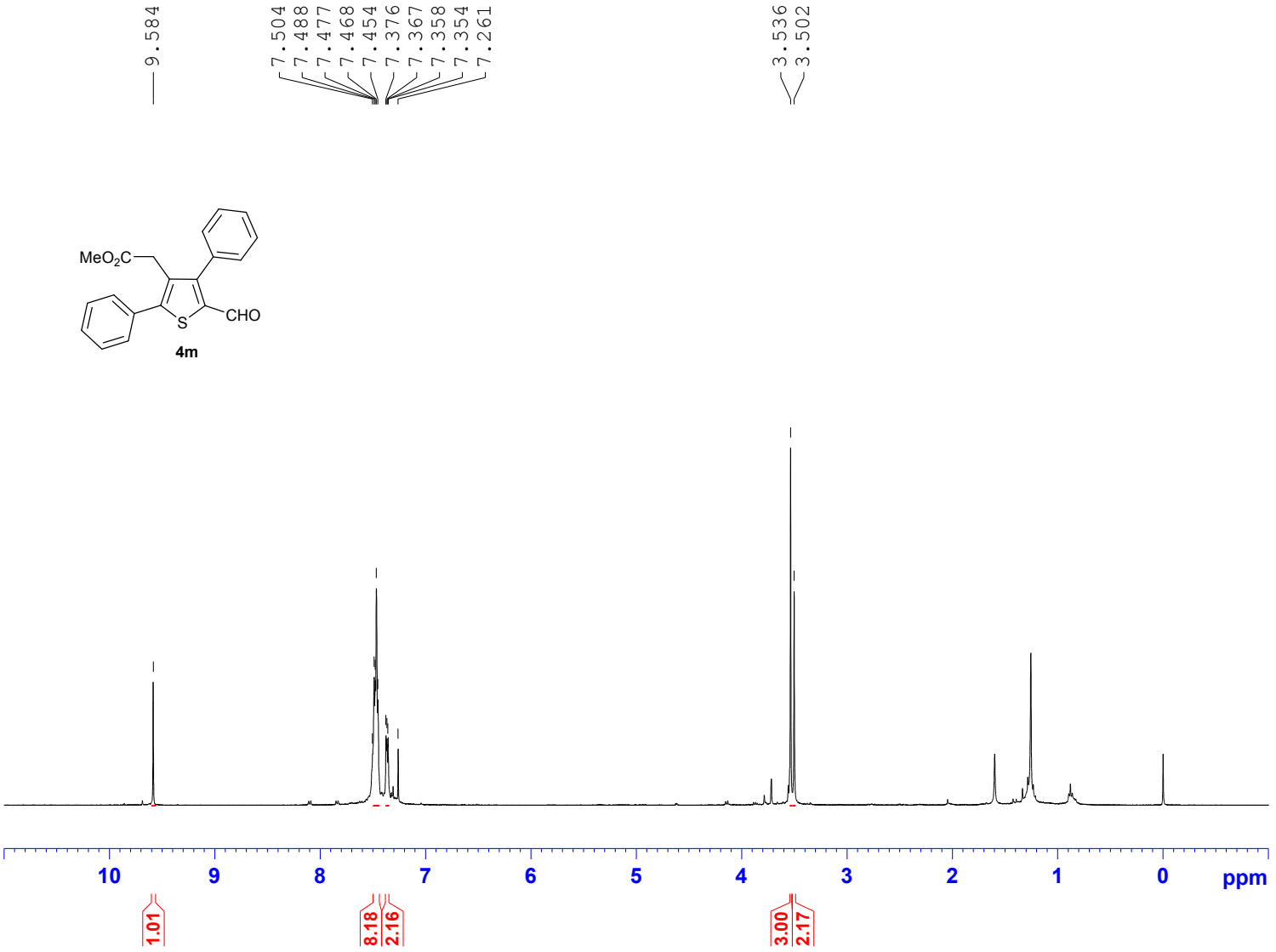
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S
CHO
4m
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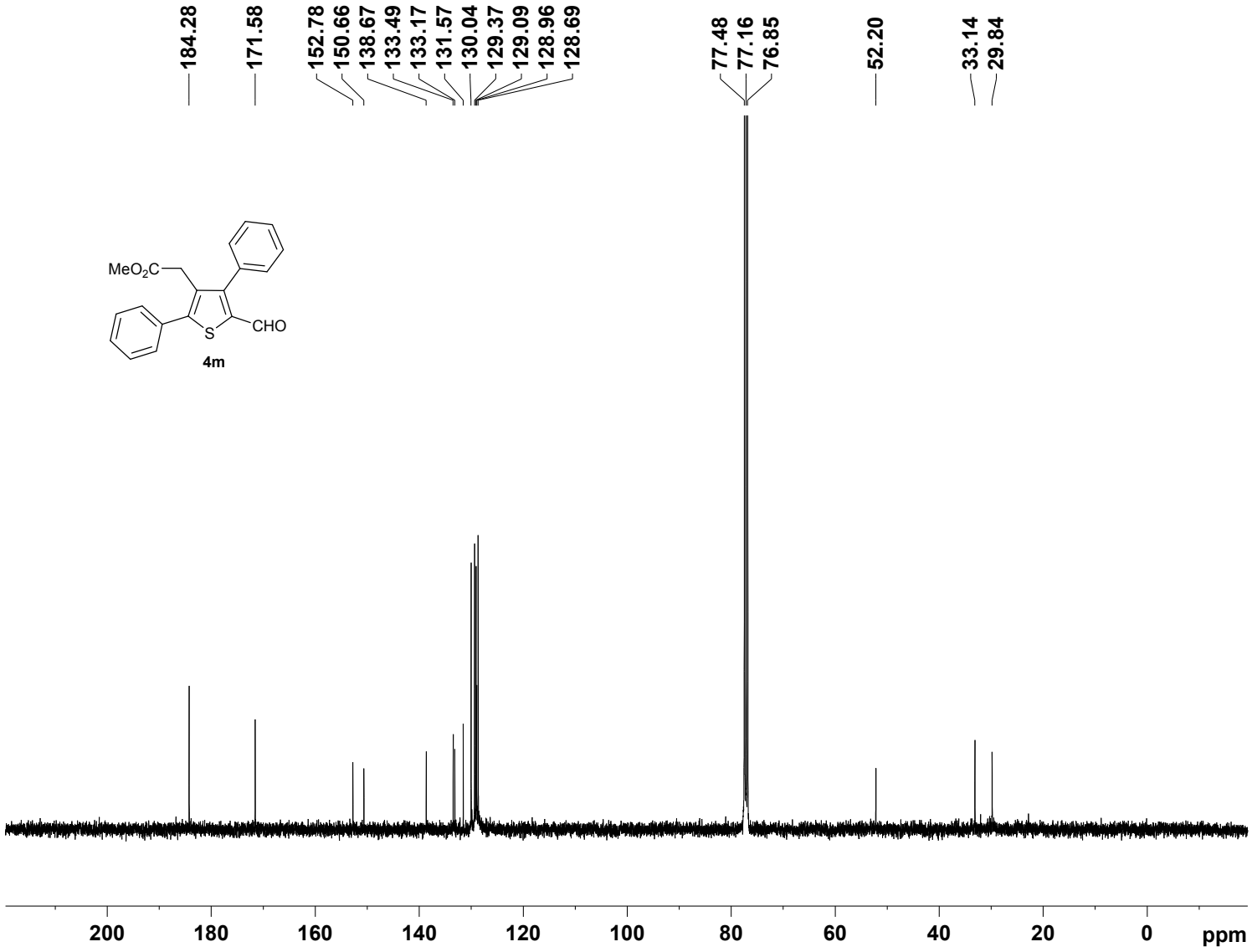
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128.69
77.48
77.16
76.85
52.20
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S
CHO
4m
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120
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20
0
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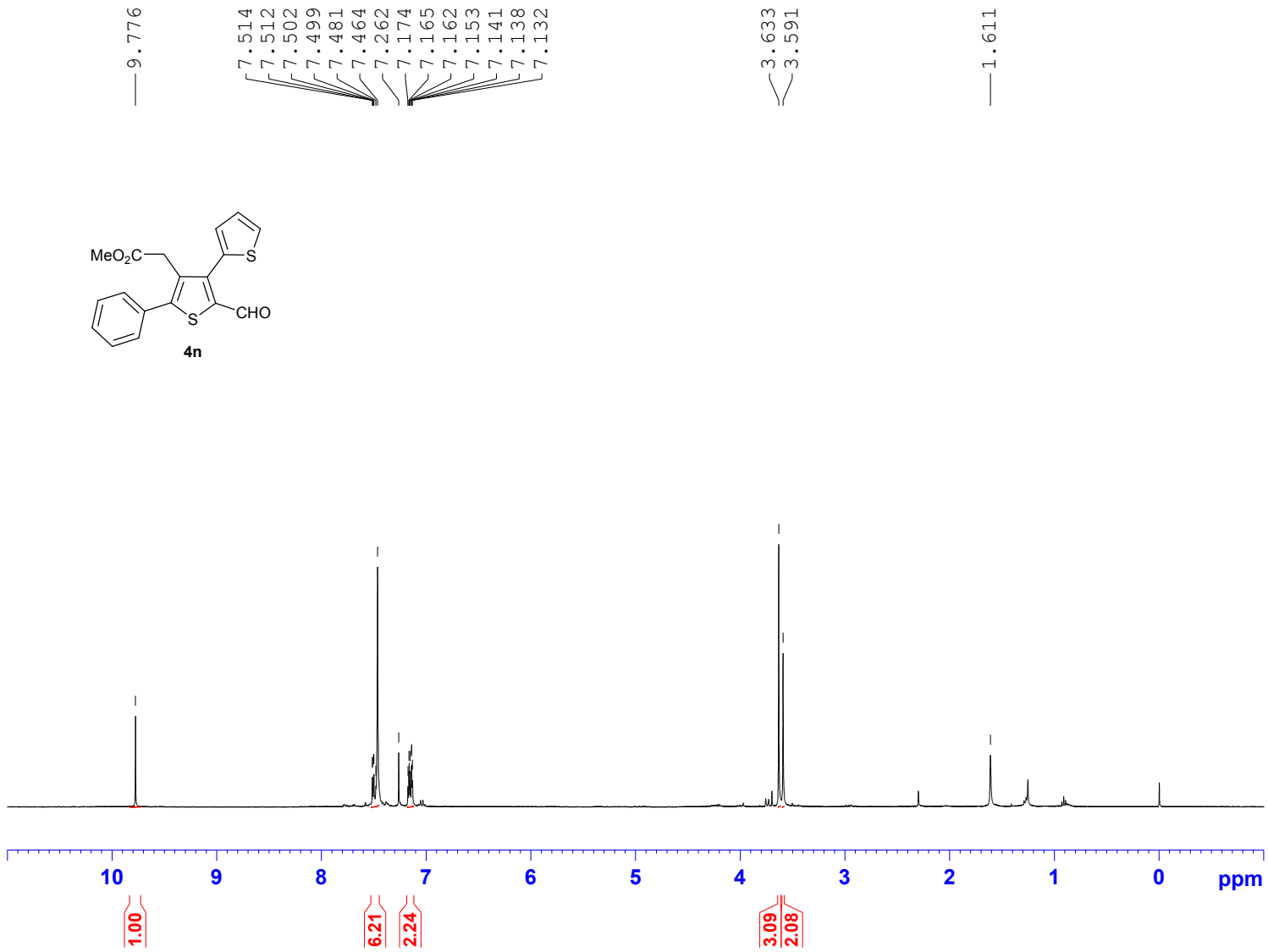
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7.132
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3.591
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MeO2C
S
S
CHO
4n
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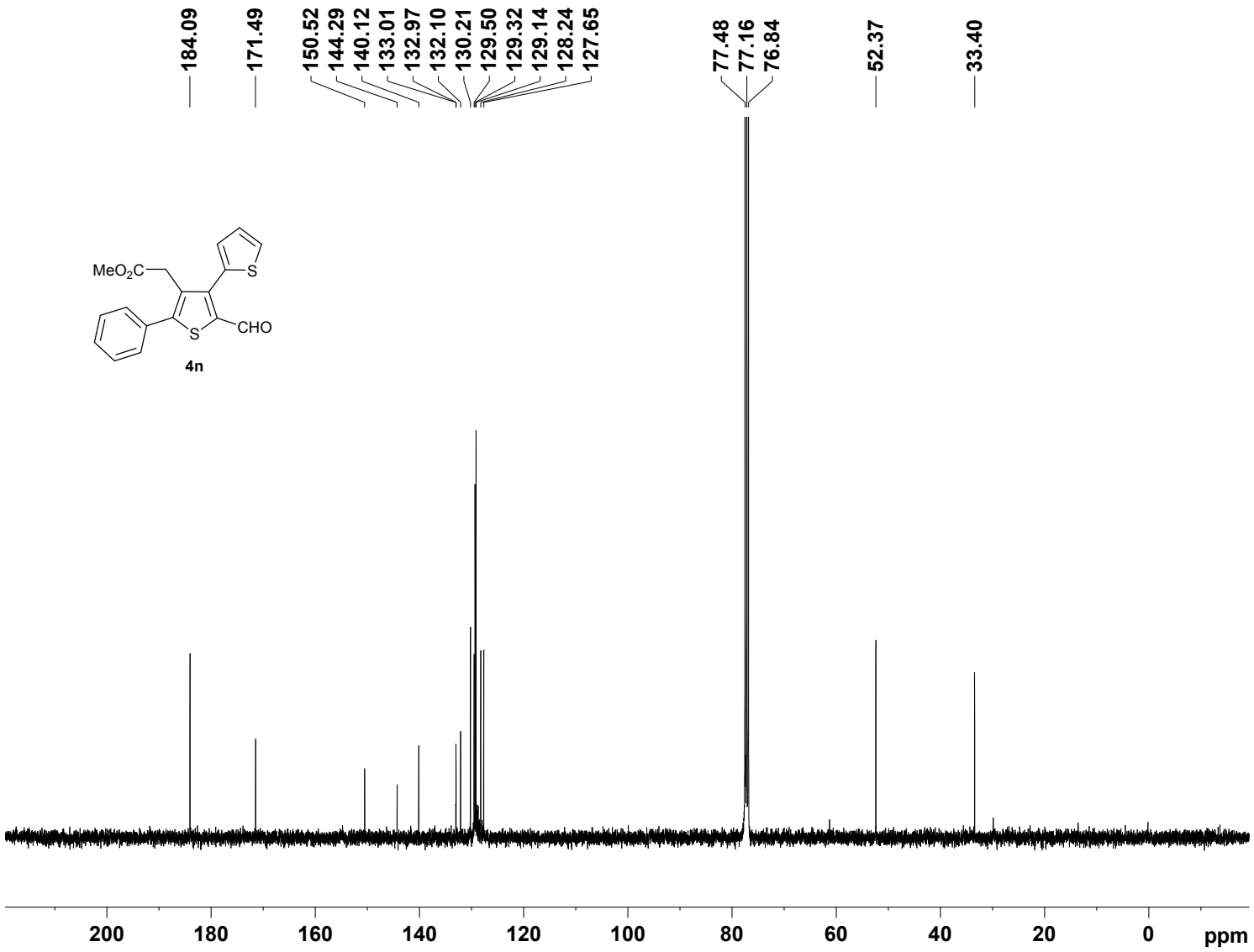
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129.14
128.24
127.65
77.48
77.16
76.84
52.37
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S
CHO
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200
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120
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0
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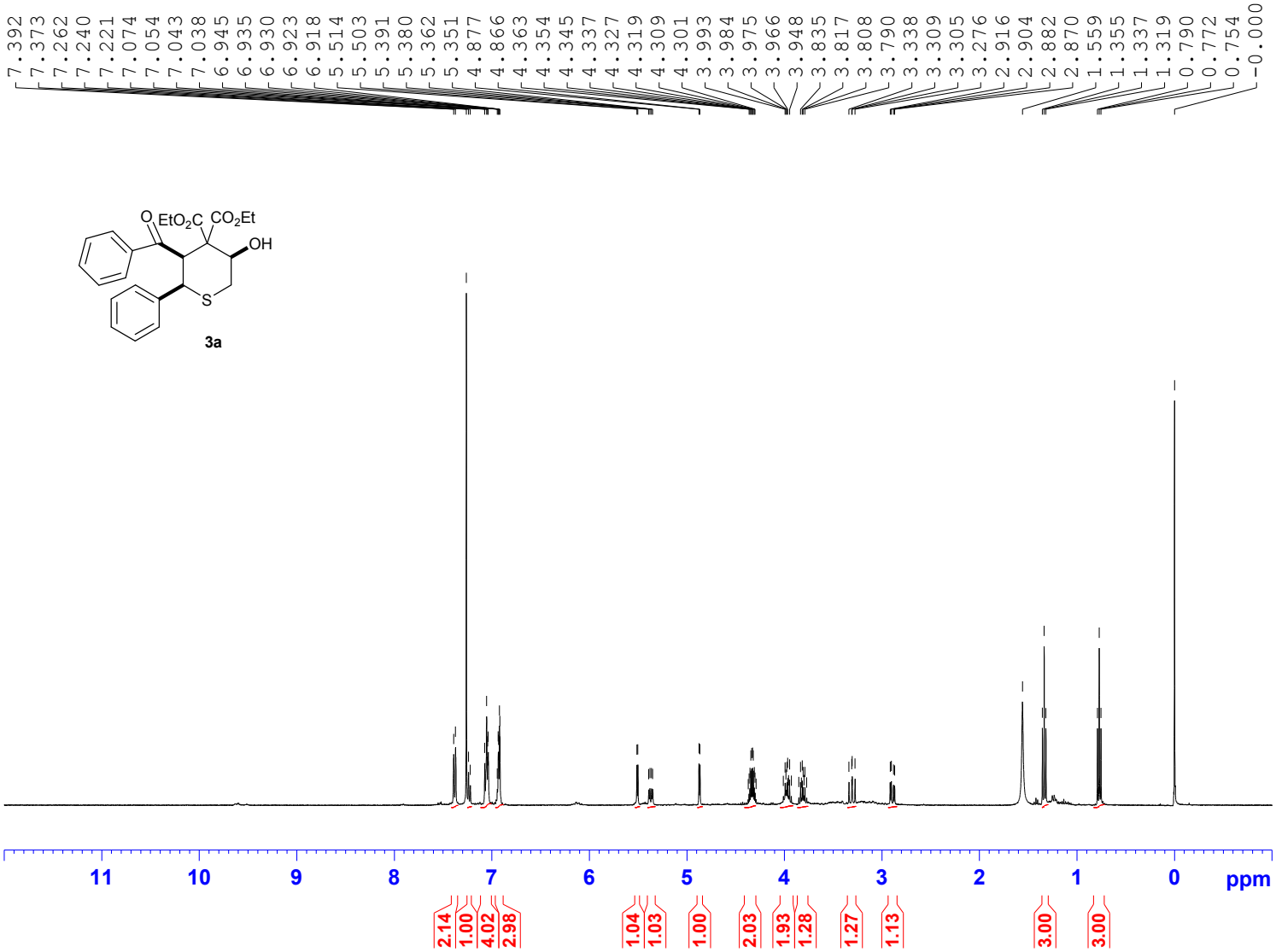
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4.327
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4.309
4.301
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3.975
3.966
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3.835
3.817
3.808
3.790
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3.309
3.305
3.276
2.916
2.904
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2.870
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1.337
1.319
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0.772
0.754
-0.000
O
EtO2C
CO2Et
OH
S
3a
11
10
9
8
7
6
5
4
3
2
1
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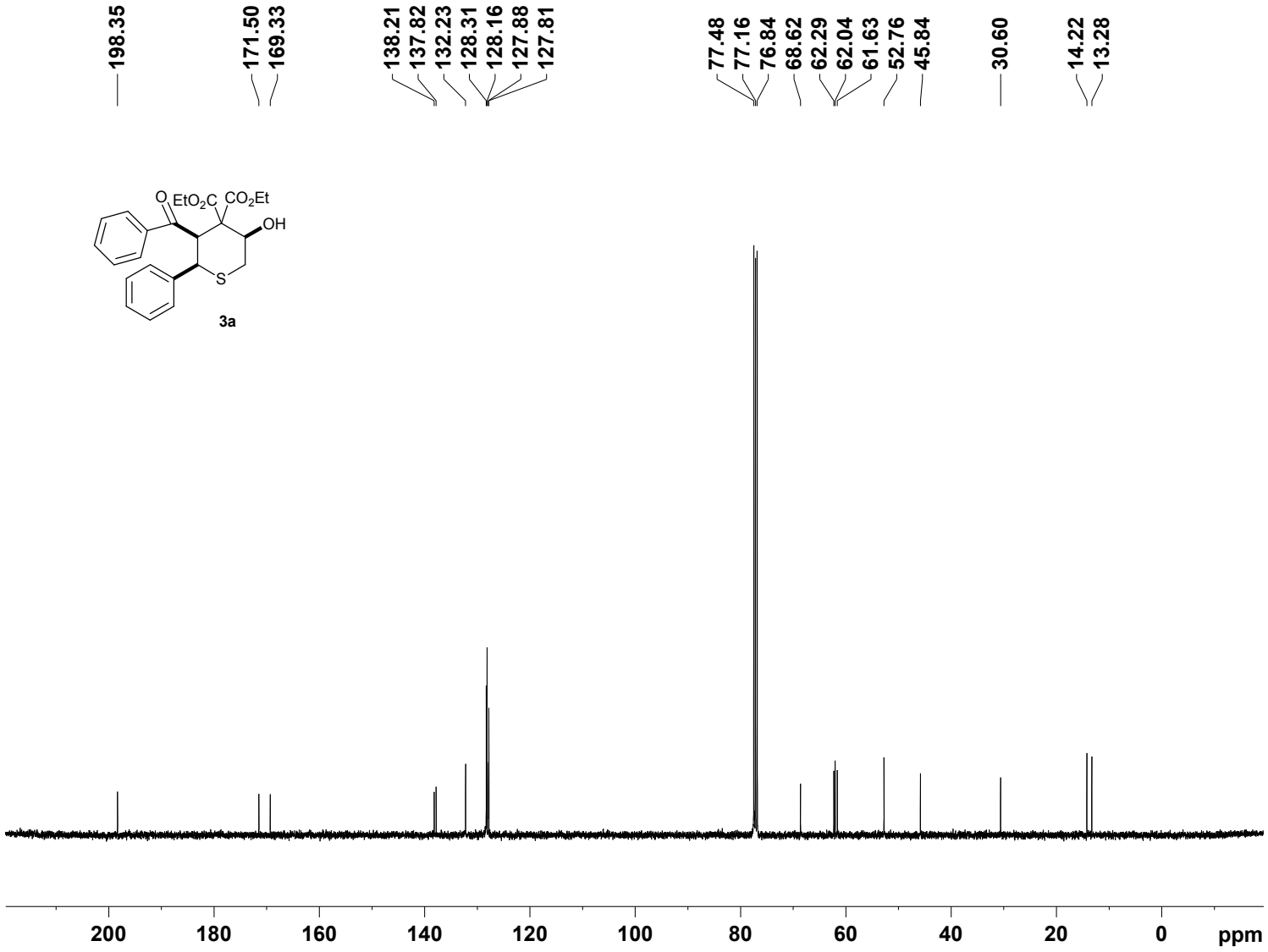
3.00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68.62
62.29
62.04
61.63
52.76
45.84
30.60
14.22
13.28
O
EtO2C
CO2Et
OH
S
3a
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120
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0
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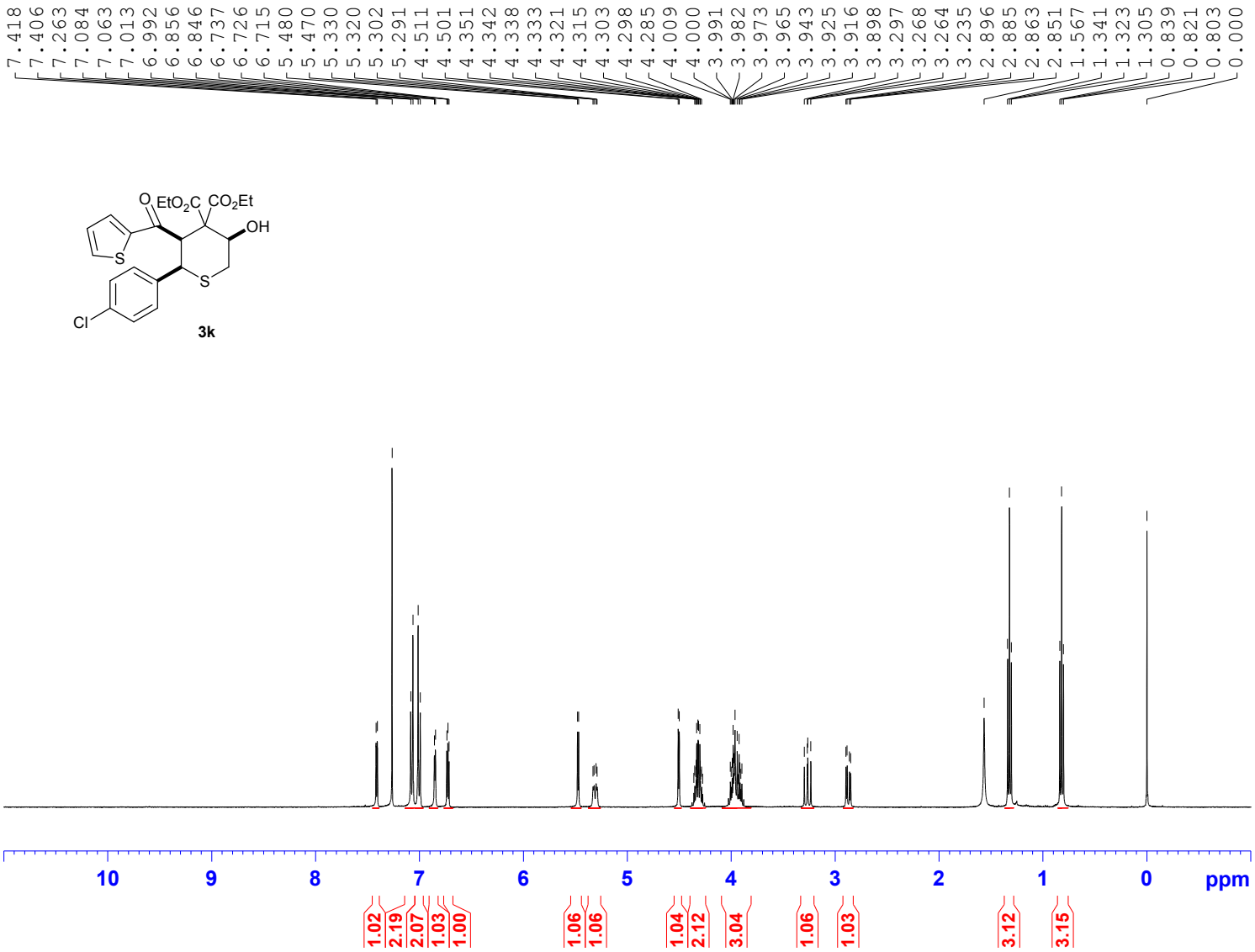
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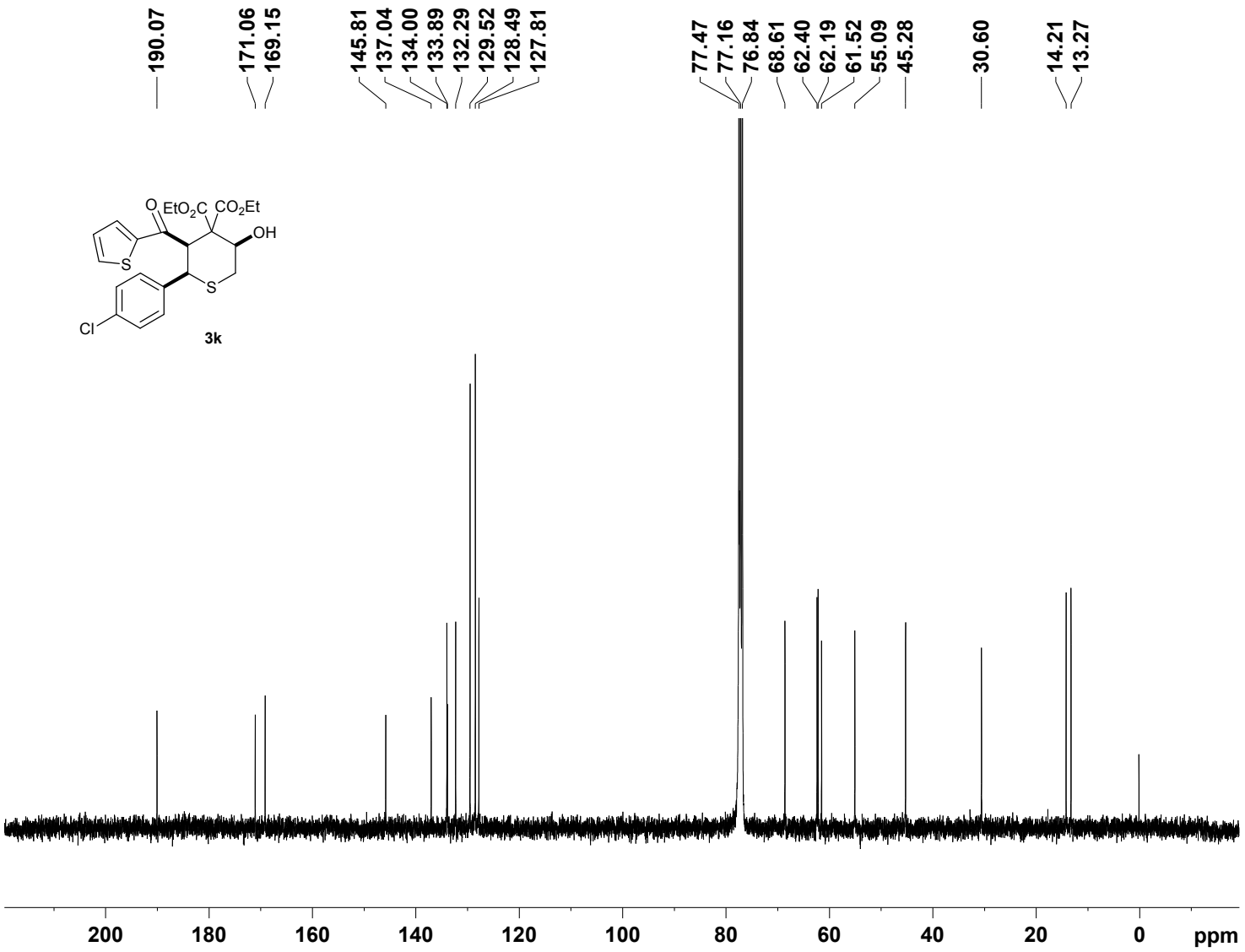
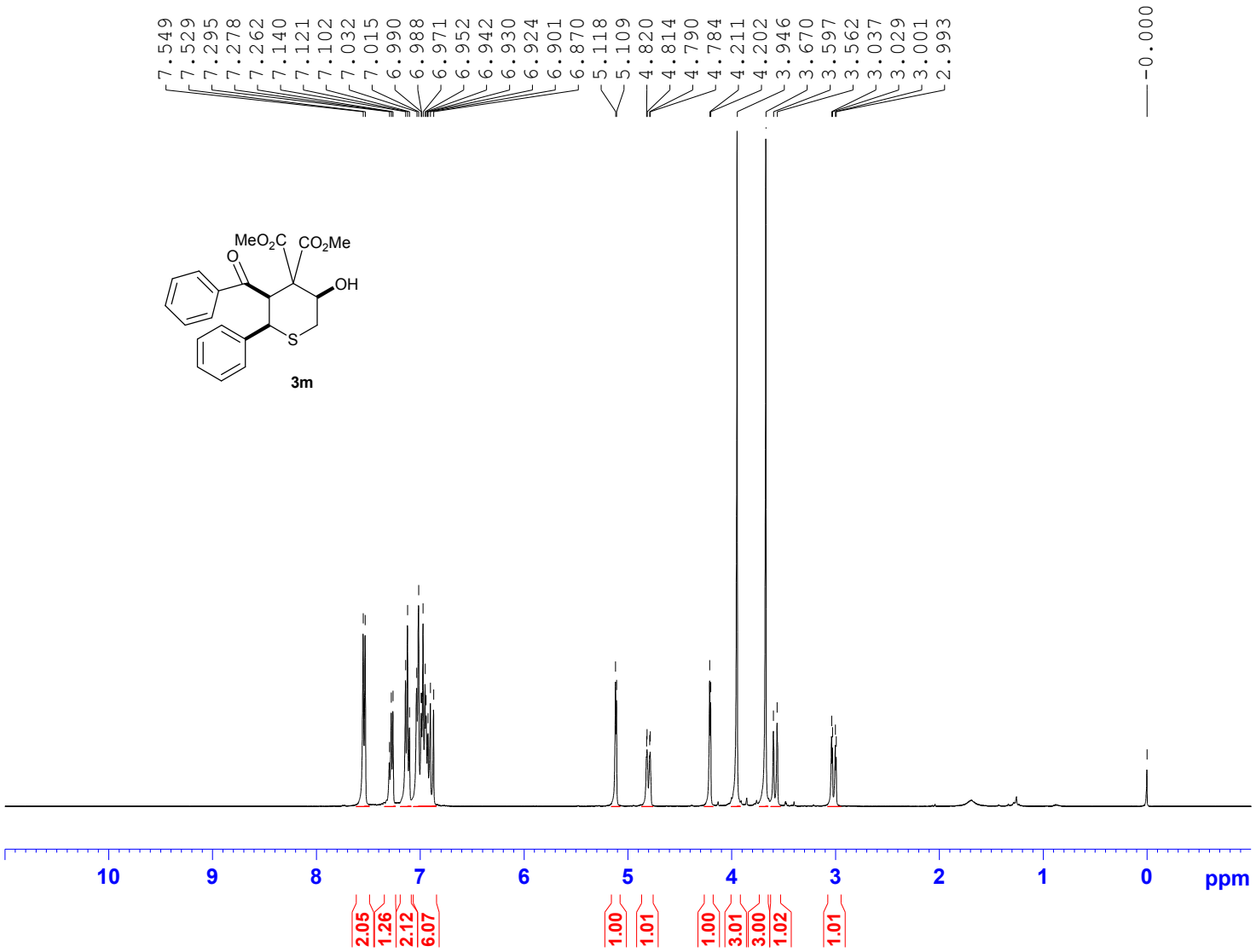
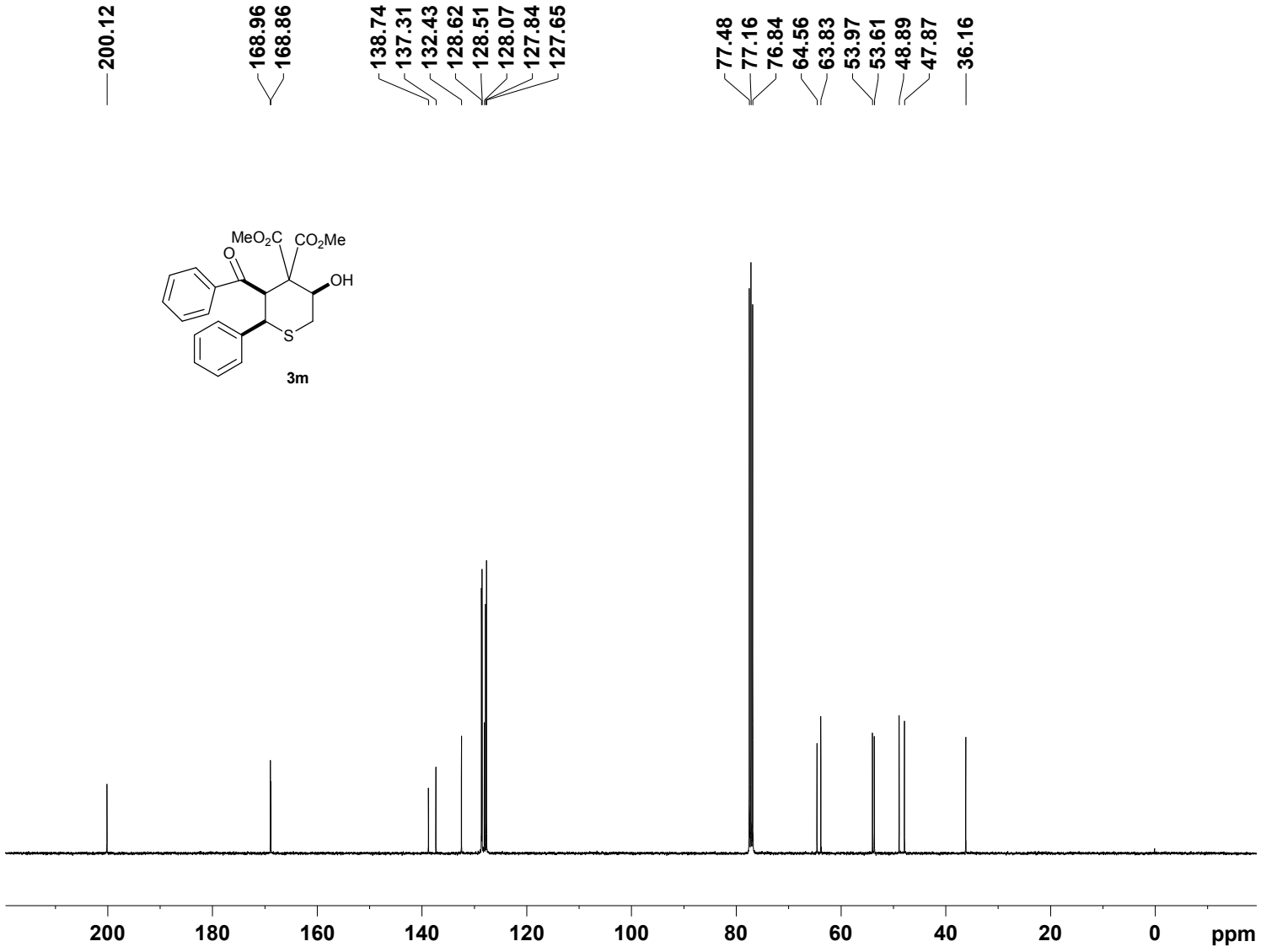
3.235
2.896
2.885
2.863
2.851
1.567
1.341
1.323
1.305
0.839
0.821
0.803
0.000
O
EtO2C
CO2Et
OH
S
S
Cl
3k
10
9
8
7
6
5
4
3
2
1
0
ppm
1.02
2.19
2.07
1.03
1.00
1.06
1.06
1.04
2.12
3.04
1.06
1.03
3.12
3.15


190.07
171.06
169.15
145.81
137.04
134.00
133.89
132.29
129.52
128.49
127.81
77.47
77.16
76.84
68.61
62.40
62.19
61.52
55.09
45.28
30.60
14.21
13.27
O
EtO2C
CO2Et
OH
S
S
Cl
3k
200
180
160
140
120
100
80
60
40
20
0
ppm


7.549
7.529
7.295
7.278
7.262
7.140
7.121
7.102
7.032
7.015
6.990
6.988
6.971
6.952
6.942
6.930
6.924
6.901
6.870
5.118
5.109
4.820
4.814
4.790
4.784
4.211
4.202
3.946
3.670
3.597
3.562
3.037
3.029
3.001
2.993
-0.000
MeO2C
CO2Me
O
OH
S
3m
10
9
8
7
6
5
4
3
2
1
0
ppm
2.05
1.26
2.12
6.07
1.00
1.01
1.00
3.01
3.00
1.02
1.01


200.12
168.96
168.86
138.74
137.31
132.43
128.62
128.51
128.07
127.84
127.65
77.48
77.16
76.84
64.56
63.83
53.97
53.61
48.89
47.87
36.16
MeO2C
CO2Me
O
OH
S
3m
200
180
160
140
120
100
80
60
40
20
0
ppm

^{1}H NMR spectrum of diastereomeric mixture of 3a and 3a′ (*dr* 9:1)