Supporting Information

Sequential Carboxylation/Intramolecular Cyclization Reaction of *o*-Alkynyl Acetophenone Using CO_2

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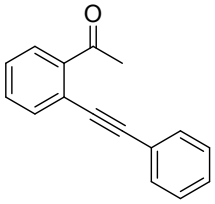
1. General Information

NMR spectra were recorded on a Bruker AvanceII 400M type (^{1}H NMR, 400 MHz; ^{13}C NMR, 100 MHz) spectrometer. Their peak freguencies were referenced versus an internal standard (TMS) shifts at 0 ppm for ^{1}H NMR and against the solvent ($CDCl_3$, 77.0 ppm) for ^{13}C NMR, respectively. Multiplicity abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. High resolution mass spectra (HRMS) were recorded on a Q-TOF mass spectrometry (Micromass, Wythenshawe, UK) equipped with Z-spray ionization source. Infrared spectra (IR) were measured using a Nicolet NEXUS FT-IR spectrophotometer.

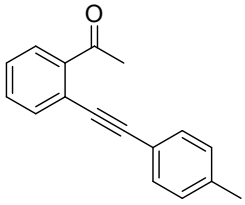
2. Synthesis of *o*-Alkynyl Ketone Substrates

Alkynyl ketones were synthesized through Sonogashira reaction of corresponding 2-bromoketones with terminal alkynes using the following protocol:[1,2] Under a nitrogen atmosphere, to a solution 2-bromoketone (5.00 mmol) in triethylamine (20 mL), the appropriate terminal alkyne (6.00 mmol) and $Pd(PPh_3)_2Cl_2$ (0.10 mmol) were added. The reaction was stirred at room temperature for 15 min, then CuI (0.05 mmol) was added. The reaction mixture was then stirred at 80 °C until all starting materials was consumed (TLC analysis). The solvent was evaporated under reduced pressure and the crude was purified by flash chromatography over a silica gel column to yield corresponding alkynyl ketone.



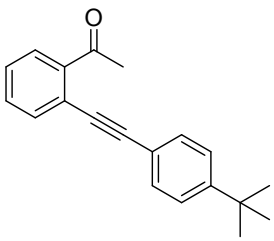
2-(Phenylethynyl)phenylethanone (1a)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.76-7.35 (m, 9H), 2.79 (s, 3H).



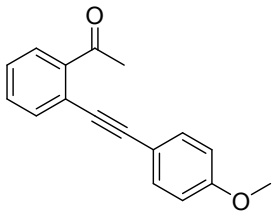
2-(4-Methylphenylethynyl)phenylethanone (1b)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.75 (d, J = 7.7 Hz, 1H), 7.62 (d, J = 7.6 Hz, 1H), 7.49-7.37 (m, 4H), 7.18 (d, J = 7.8 Hz, 2H), 2.80 (s, 3H), 2.38 (s, 3H).



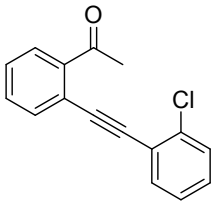
2-(4-*tert*-Butylphenylethynyl)phenylethanone (1c)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.75 (d, J = 7.7 Hz, 1H), 7.62 (d, J = 7.6 Hz, 1H), 7.53-7.35 (m, 6H), 2.81 (s, 3H), 1.33 (s, 9H).



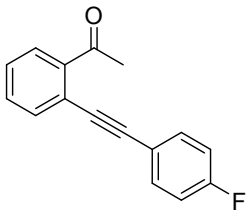
2-(4-Methoxyphenylethynyl)phenylethanone (1d)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.75 (d, J = 7.1 Hz, 1H), 7.61 (d, J = 7.2 Hz, 1H), 7.55-7.43 (m, 3H), 7.38 (t, J = 7.6 Hz, 1H), 6.90 (d, J = 8.7 Hz, 2H), 3.84 (s, 3H), 2.80 (s, 3H).



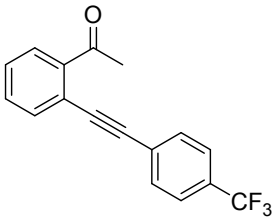
2-(2-Chlorophenylethynyl)phenylethanone (1e)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.76 (d, J = 7.7 Hz, 1H), 7.68 (d, J = 7.6 Hz, 1H), 7.58 (dd, J = 7.1, 1.9 Hz, 1H), 7.49 (t, J = 7.5 Hz, 1H), 7.42 (t, J = 7.6 Hz, 2H), 7.34-7.21 (m, 2H), 2.82 (s, 3H).



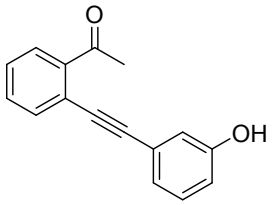
2-(4-Fluoroxyphenylethynyl)phenylethanone (1f)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.76 (d, J = 7.8 Hz, 1H), 7.62 (d, J = 7.6 Hz, 1H), 7.58-7.45 (m, 3H), 7.41 (t, J = 7.6 Hz, 1H), 7.07 (t, J = 8.7 Hz, 2H), 2.77 (s, 3H).



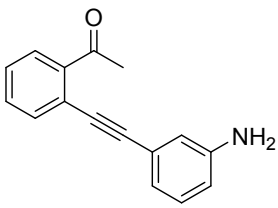
2-(4-Trifluoromethylphenylethynyl)phenylethanone (1g)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.78 (dd, J = 7.7, 1.1 Hz, 1H), 7.69-7.60 (m, 5H), 7.53-7.43 (m, 2H), 2.76 (s, 3H).



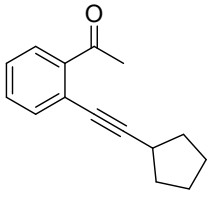
2-(3-Hydroxyphenylethynyl)phenylethanone (1h)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.77 (d, J = 7.6 Hz, 1H), 7.62 (d, J = 7.6 Hz, 1H), 7.48 (t, J = 7.4 Hz, 1H), 7.40 (t, J = 7.7 Hz, 1H), 7.29-6.99 (m, 3H), 6.93-6.84 (m, 1H), 6.07 (s, 1H), 2.80 (s, 3H).



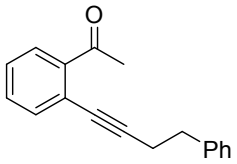
2-(3-Aminophenylethynyl)phenylethanone (1i)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.75 (d, J = 6.1 Hz, 1H), 7.61 (s, 1H), 7.47-7.40 (m, 2H), 7.15 (s, 1H), 6.96-6.87 (m, 2H), 6.70 (s, 1H), 3.74 (s, 2H), 2.80 (s, 3H).



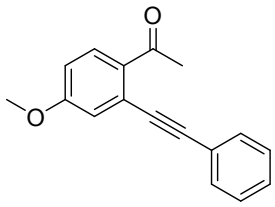
2-(Cyclopentylethynyl)phenylethanone (1j)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.66 (dd, J = 7.8, 1.1 Hz, 1H), 7.47 (dd, J = 7.7, 1.0 Hz, 1H), 7.39 (td, J = 7.5, 1.4 Hz, 1H), 7.32 (td, J = 7.6, 1.4 Hz, 1H), 2.92-2.85 (m, 1H), 2.73 (s, 3H), 2.09-1.94 (m, 2H), 1.84-1.53 (m, 6H).



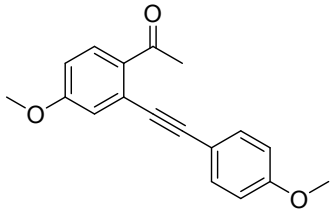
2-(4-Phenyl-1-butynyl)phenylethanone (1k)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.64 (d, J = 7.7 Hz, 1H), 7.45 (d, J = 7.6 Hz, 1H), 7.41-7.35 (m, 1H), 7.35-7.20 (m, 6H), 2.94 (t, J = 7.4 Hz, 2H), 2.76 (t, J = 7.4 Hz, 2H), 2.59 (s, 3H).



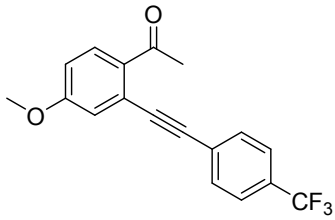
2-(Phenylethynyl)-4-methoxyphenylethanone (1l)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.84 (d, J = 8.8 Hz, 1H), 7.60-7.53 (m, 2H), 7.42-7.34 (m, 3H), 7.11 (d, J = 2.6 Hz, 1H), 6.92 (dd, J = 8.8, 2.7 Hz, 1H), 3.88 (s, 3H), 2.77 (s, 3H).



2-(4-Methoxyphenylethynyl)-4-methoxyphenylethanone (1m)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.83 (d, J = 8.8 Hz, 1H), 7.55-7.47 (m, 2H), 7.09 (d, J = 2.6 Hz, 1H), 6.93-6.87 (m, 3H), 3.88 (s, 3H), 3.84 (s, 3H), 2.77 (s, 3H).

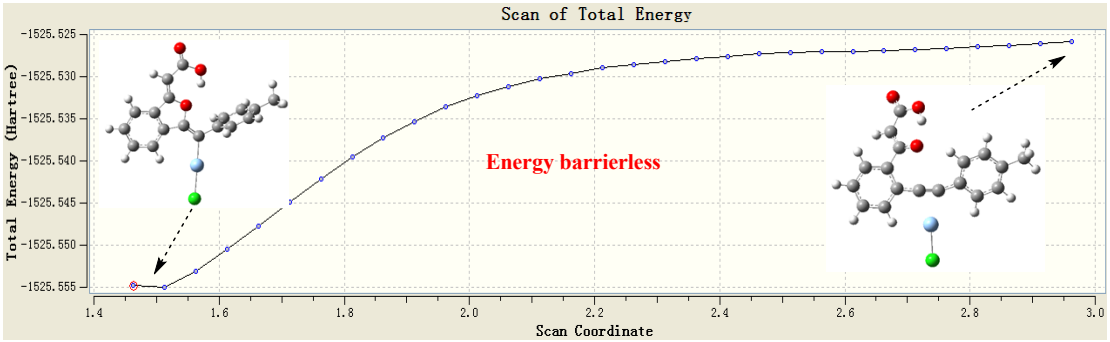


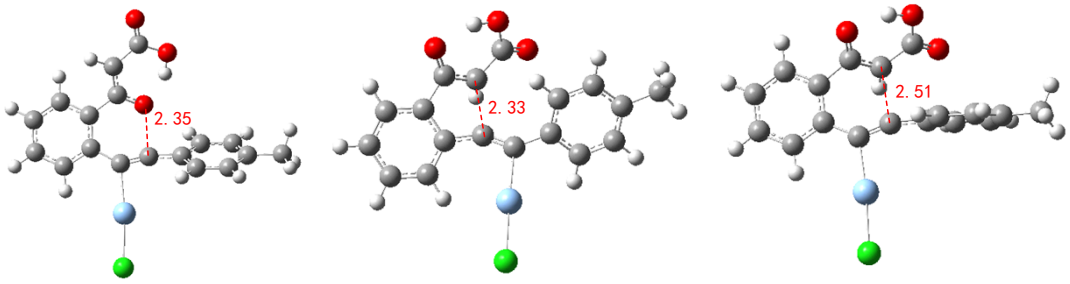
2-(4-Trifluoromethylphenylethynyl)-4-methoxyphenylethanone (1n)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.83 (d, J = 8.8 Hz, 1H), 7.67 (d, J = 8.3 Hz, 2H), 7.61 (d, J = 8.3 Hz, 2H), 7.12 (d, J = 2.6 Hz, 1H), 6.93 (dd, J = 8.8, 2.6 Hz, 1H), 3.87 (s, 3H), 2.72 (s, 3H).

3. Computational Study

DFT calculations were performed using the Gaussian 09 package.[3] Firstly, many DFT methods such as B3LYP, B3PW91, TPSSh were used to find the TS which leads to 5-*exo* oxygen cyclization, but all those methods failed to find the TS. So a flexible scan of the petential energy surface (PES) of the formed C-O bond was carried out (Figure S1).





14.1 kcal/mol　　13.8 kcal/mol　　9.4 kcal/mol

Figure S1. Top: scan curve for the 5-*exo* oxygen cyclization. Below: the other three transition state structures and the solvation free energy computed by the B3LYP method.

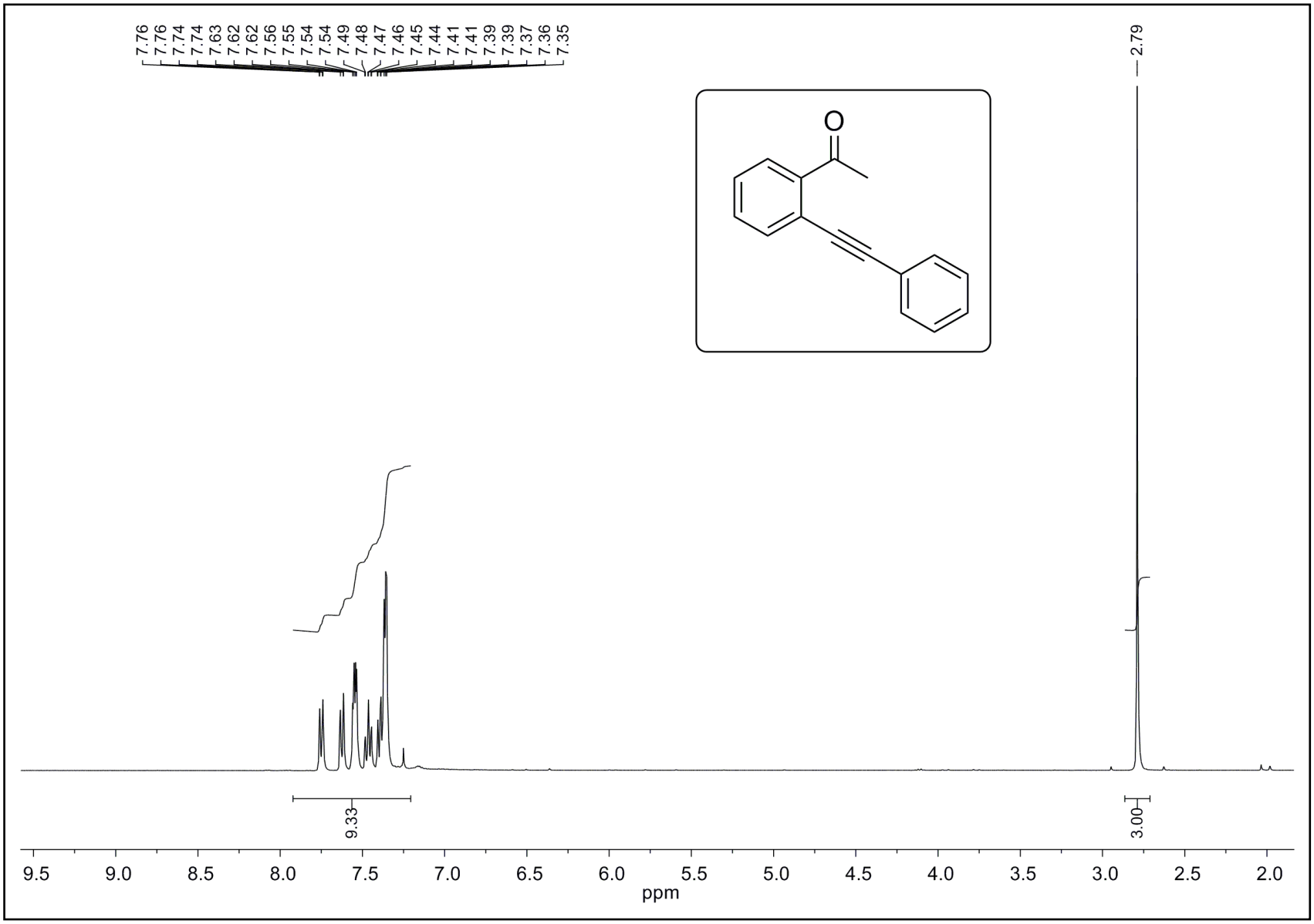
4. References

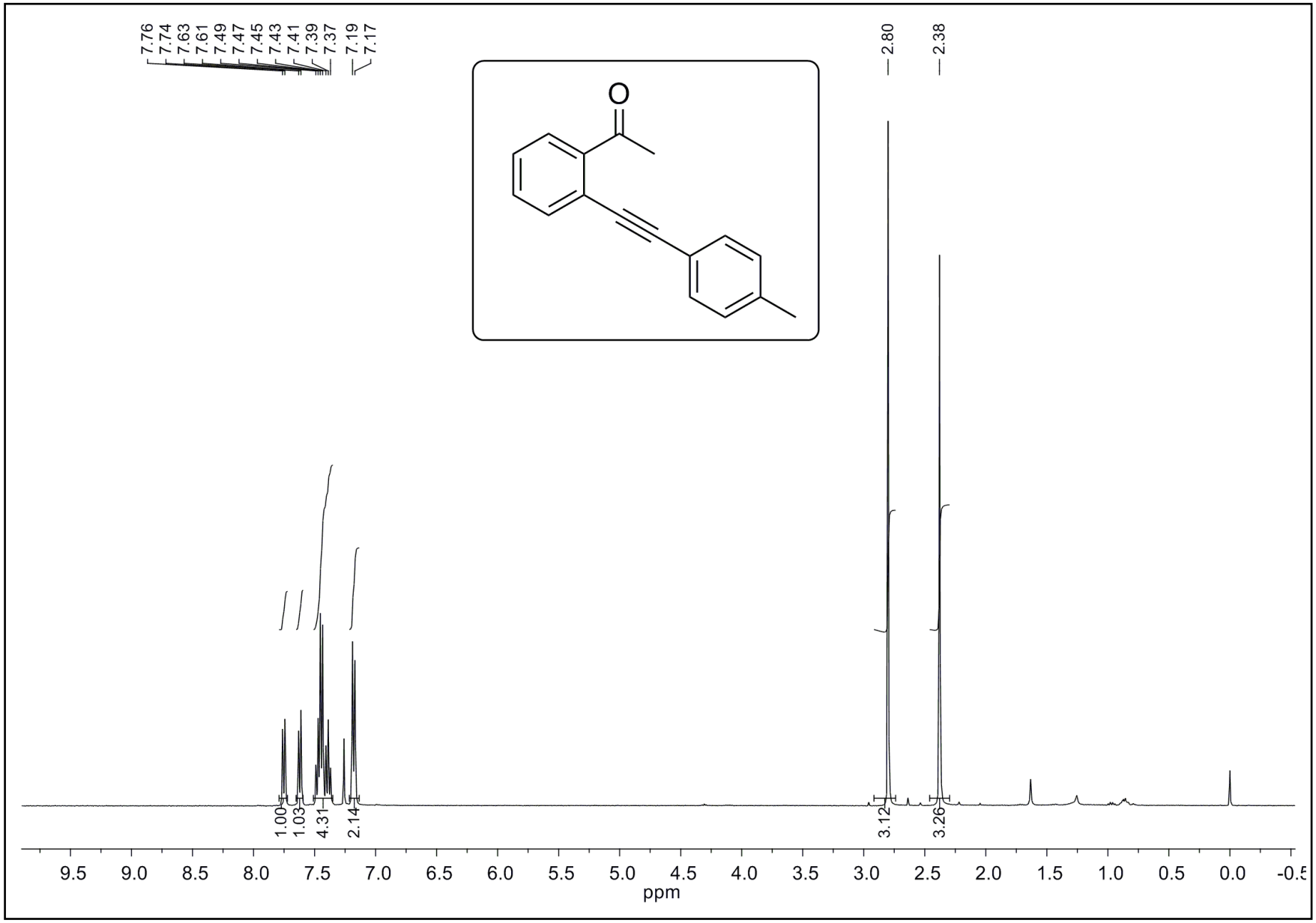
[1] M. Dell'Acqua, G. Abbiati, A. Arcadi, E. Rossi, *Org. Biomol. Chem.* **2011**, *9*, 7836.

[2] N. Chernyak, S. I. Gorelsky, V. Gevorgyan, *Angew. Chem. Int. Ed.* **2011**, *50*, 2342.

[3] Gaussian 09, Revision B.01. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian Inc., Wallingford CT, 2009.

5. Copies of ^{1}H NMR and ^{13}C NMR Spectra of Substrates and Products

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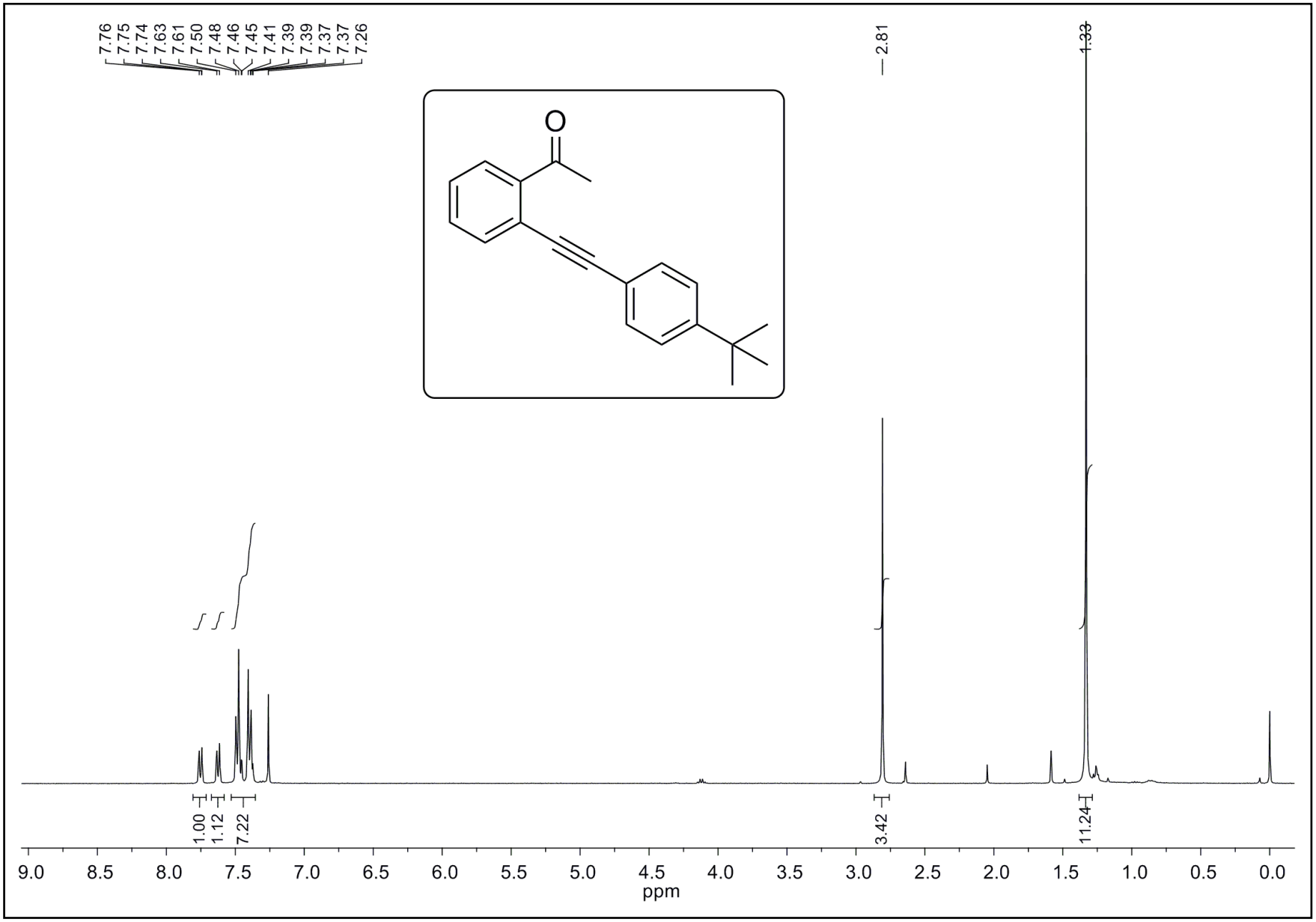
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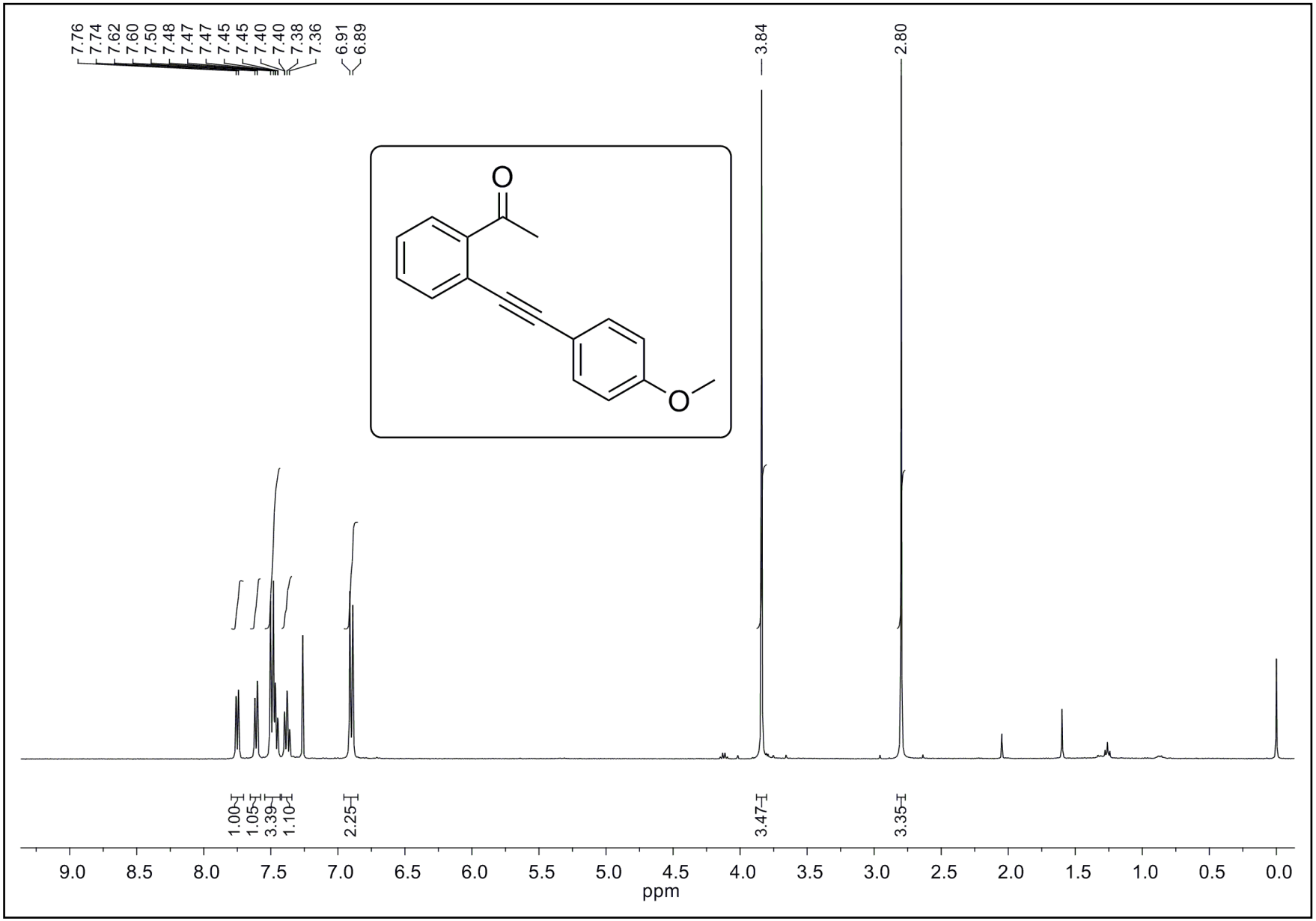
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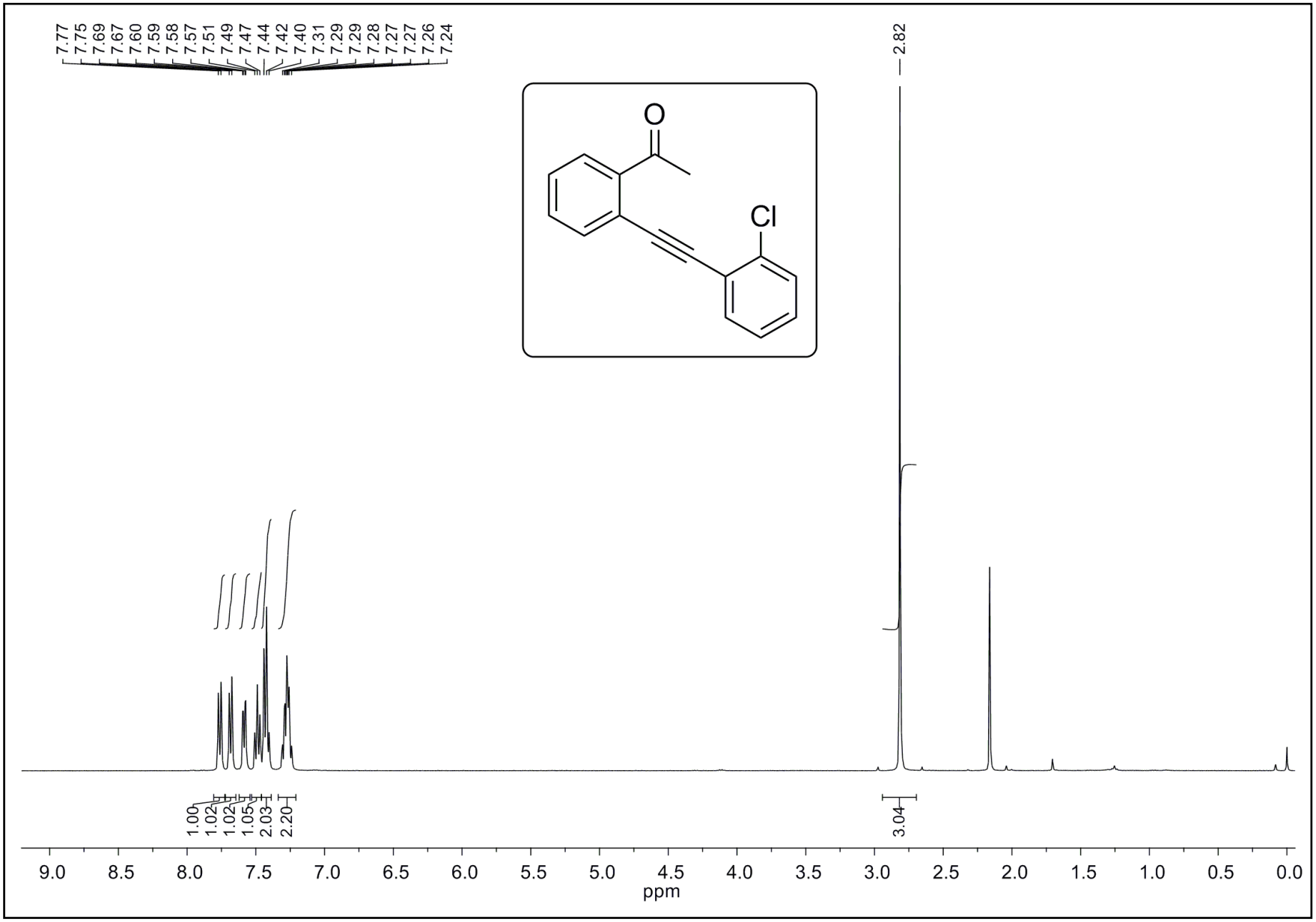
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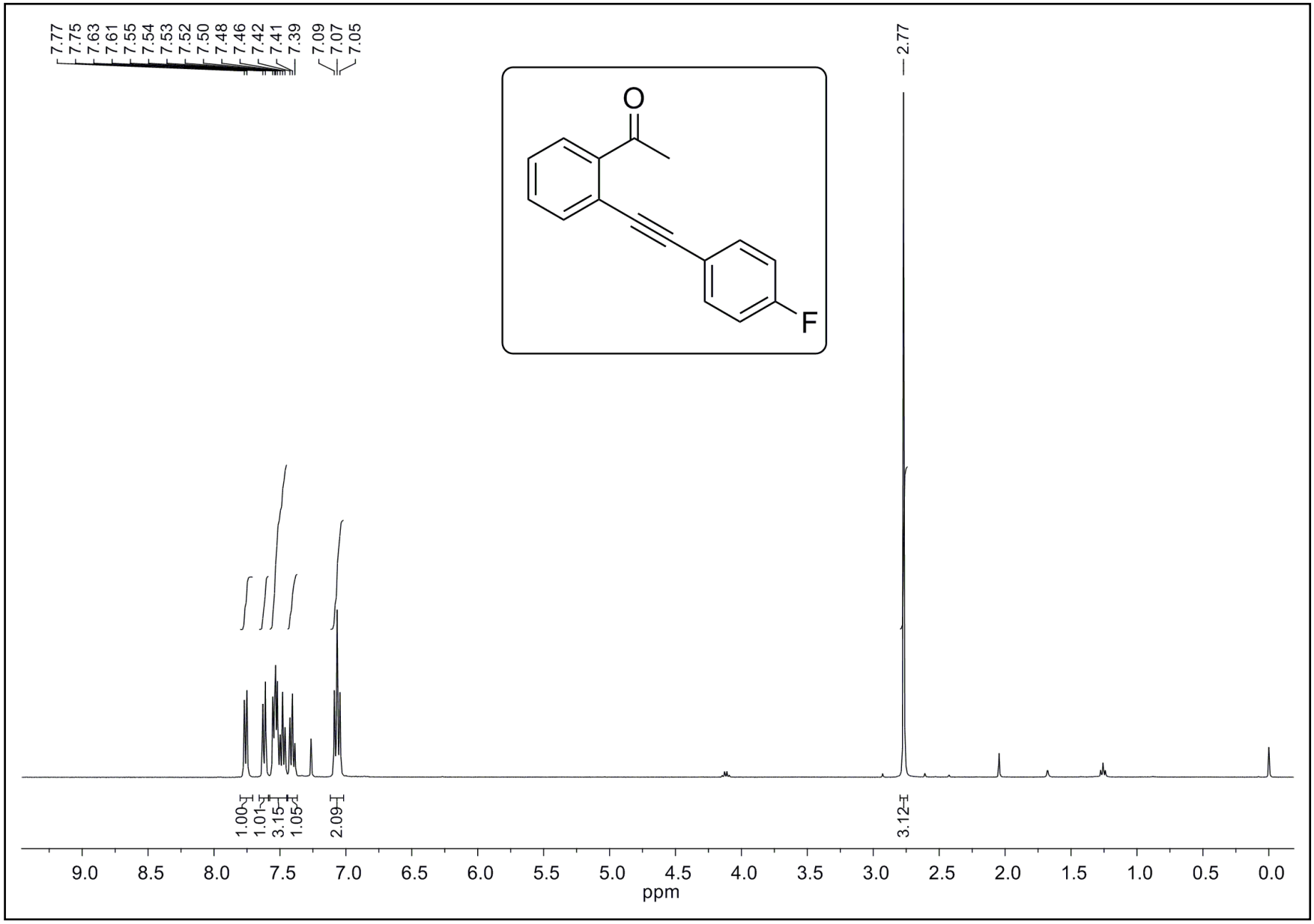
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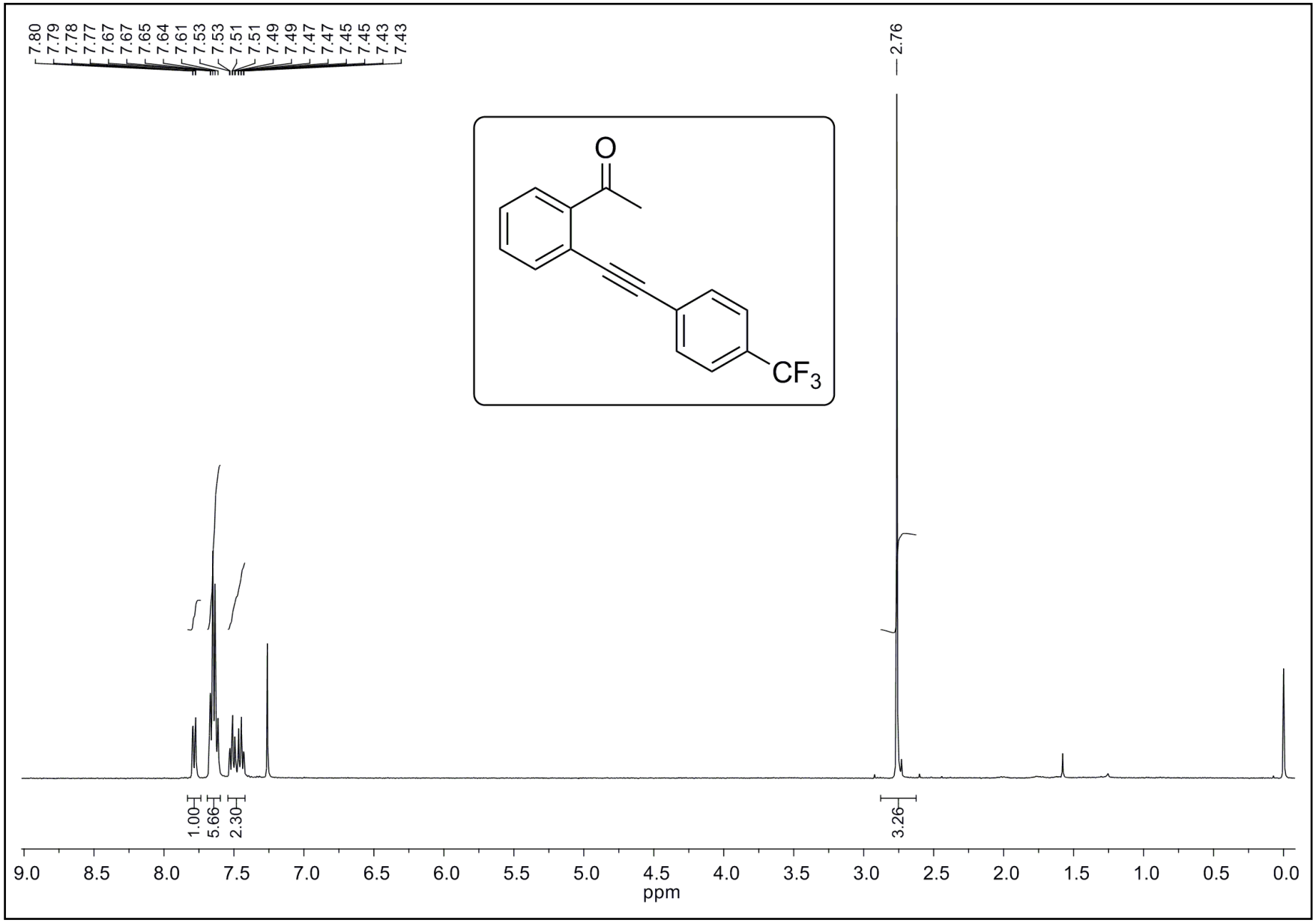
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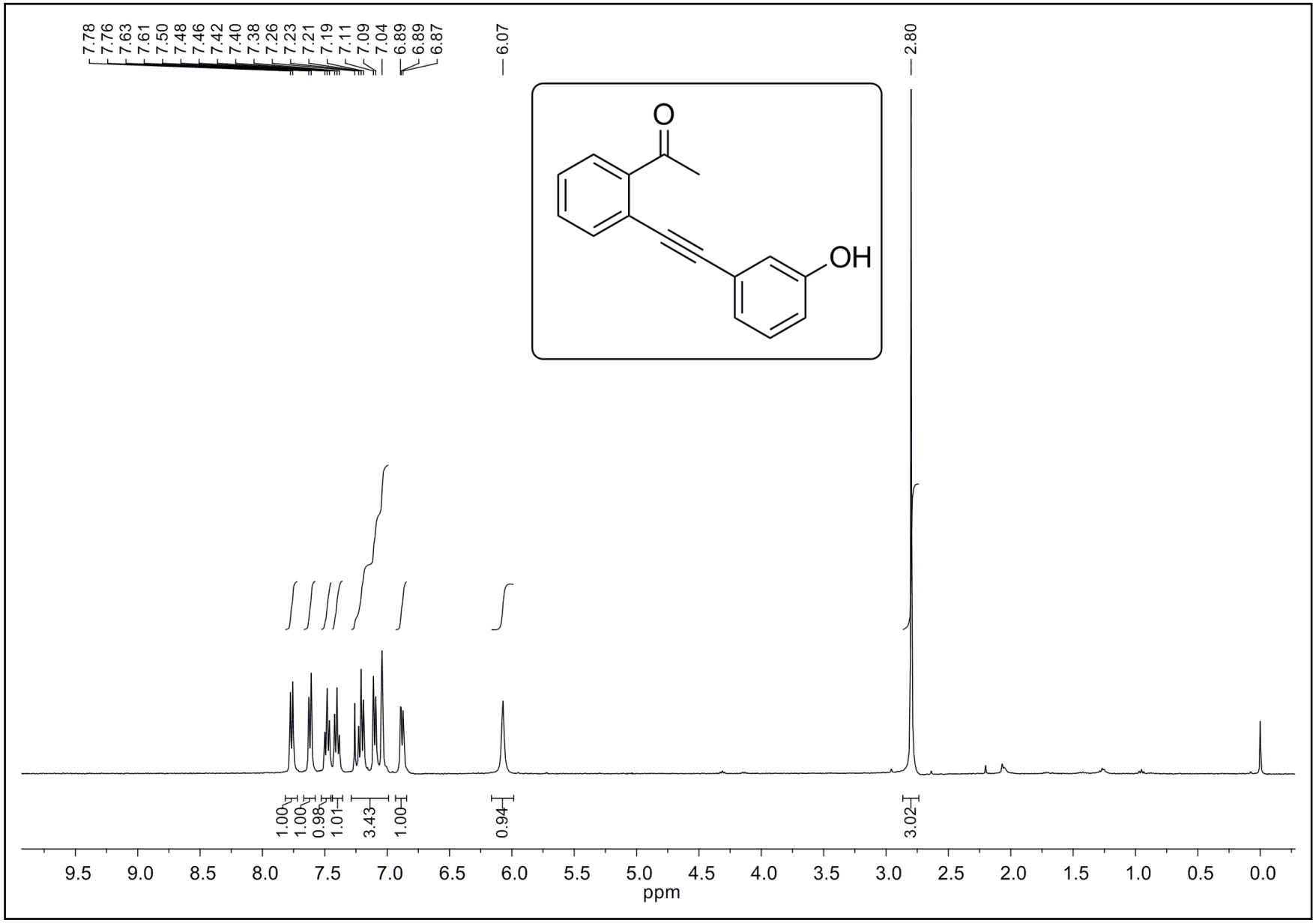
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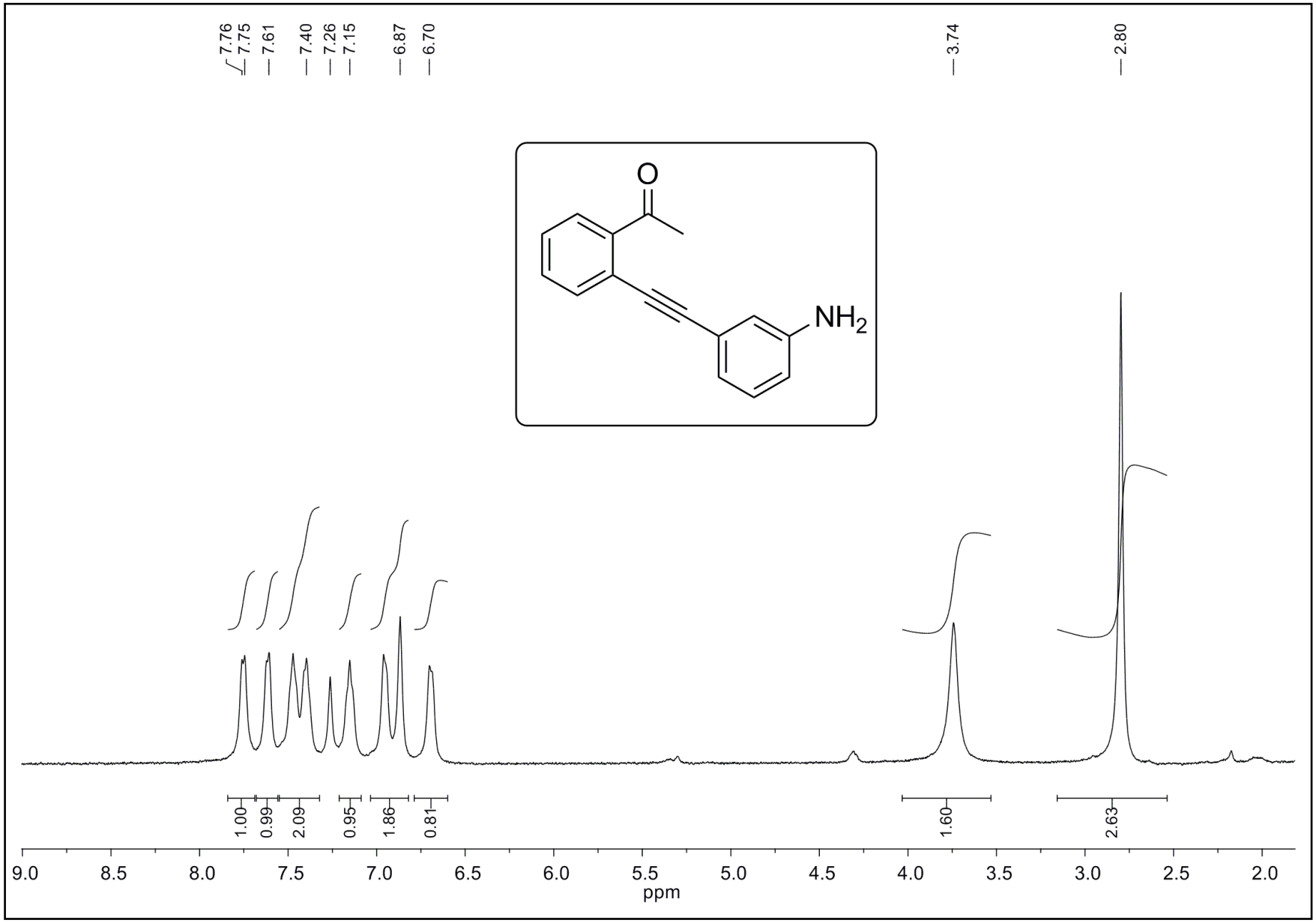
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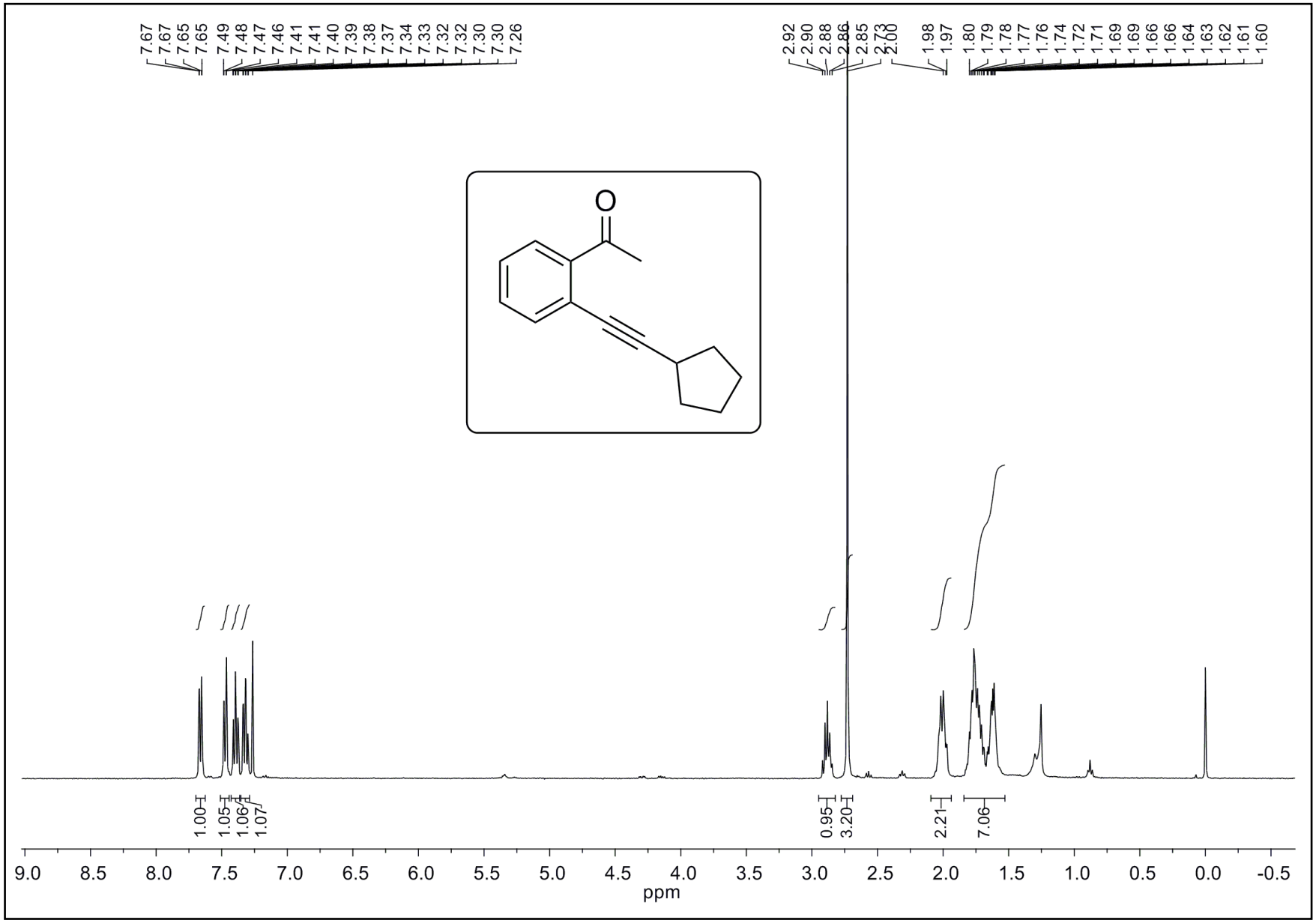
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2.85
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1.62
1.61
1.60
O
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1.06
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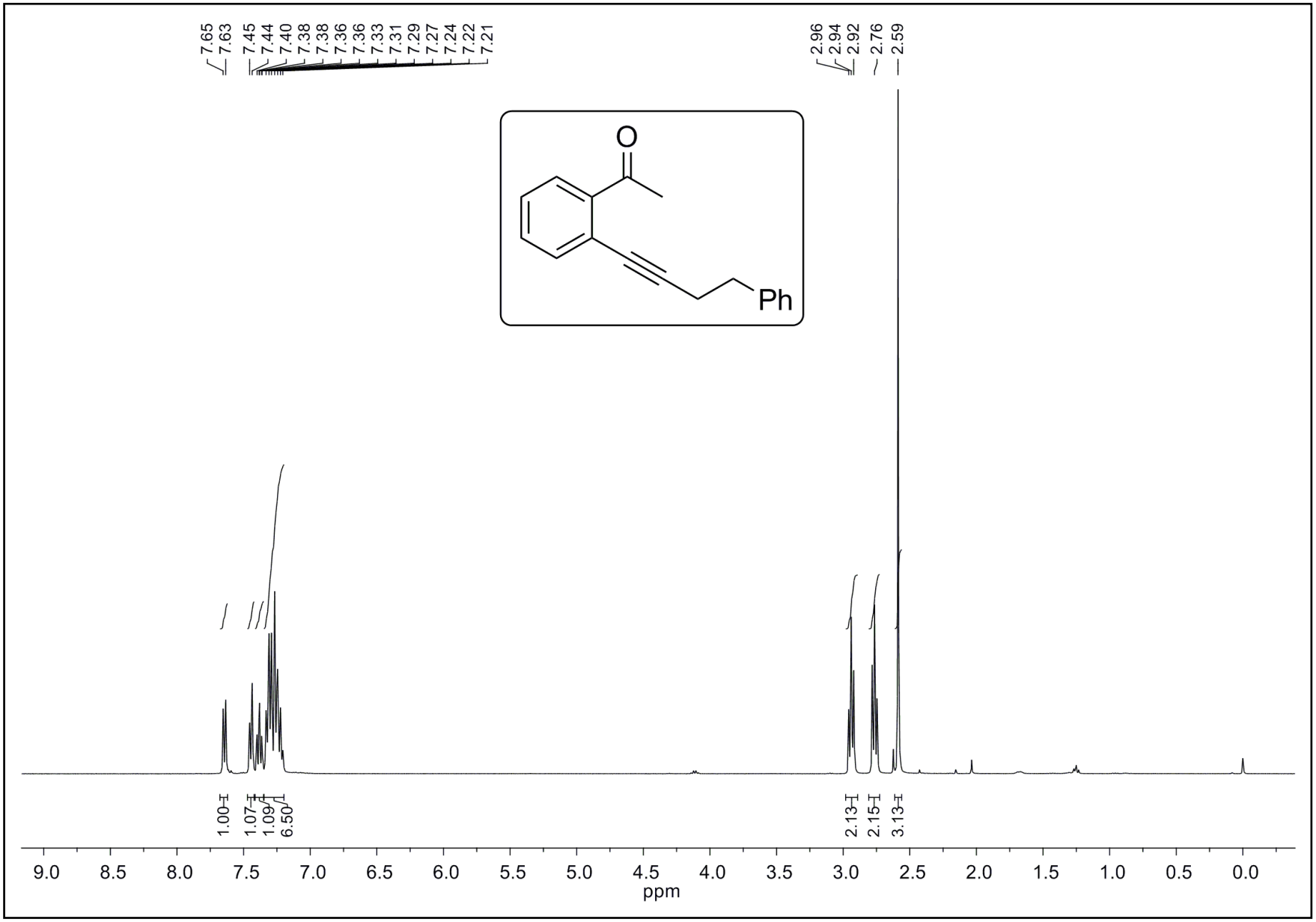
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2.92
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2.59
O
Ph
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1.07
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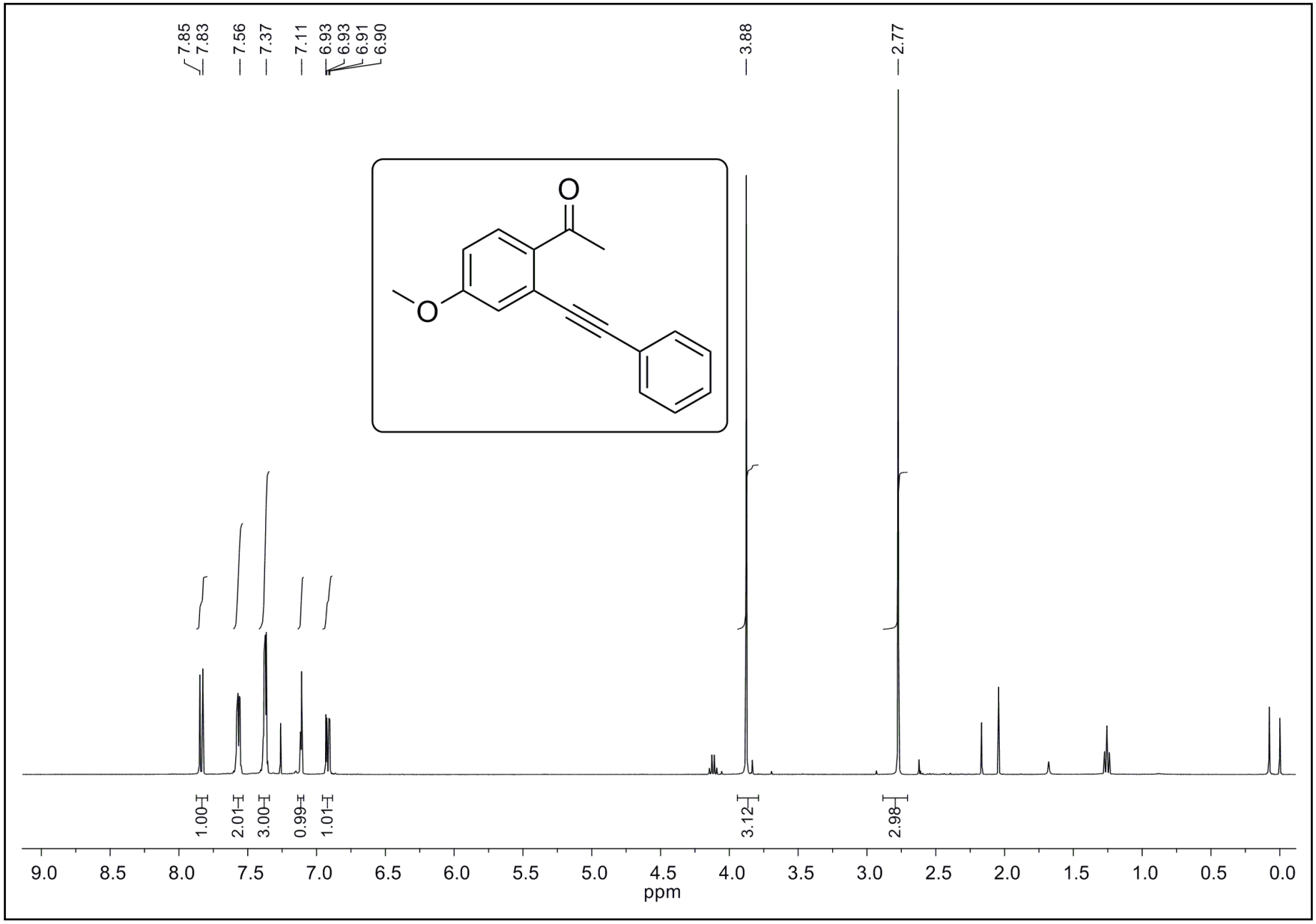
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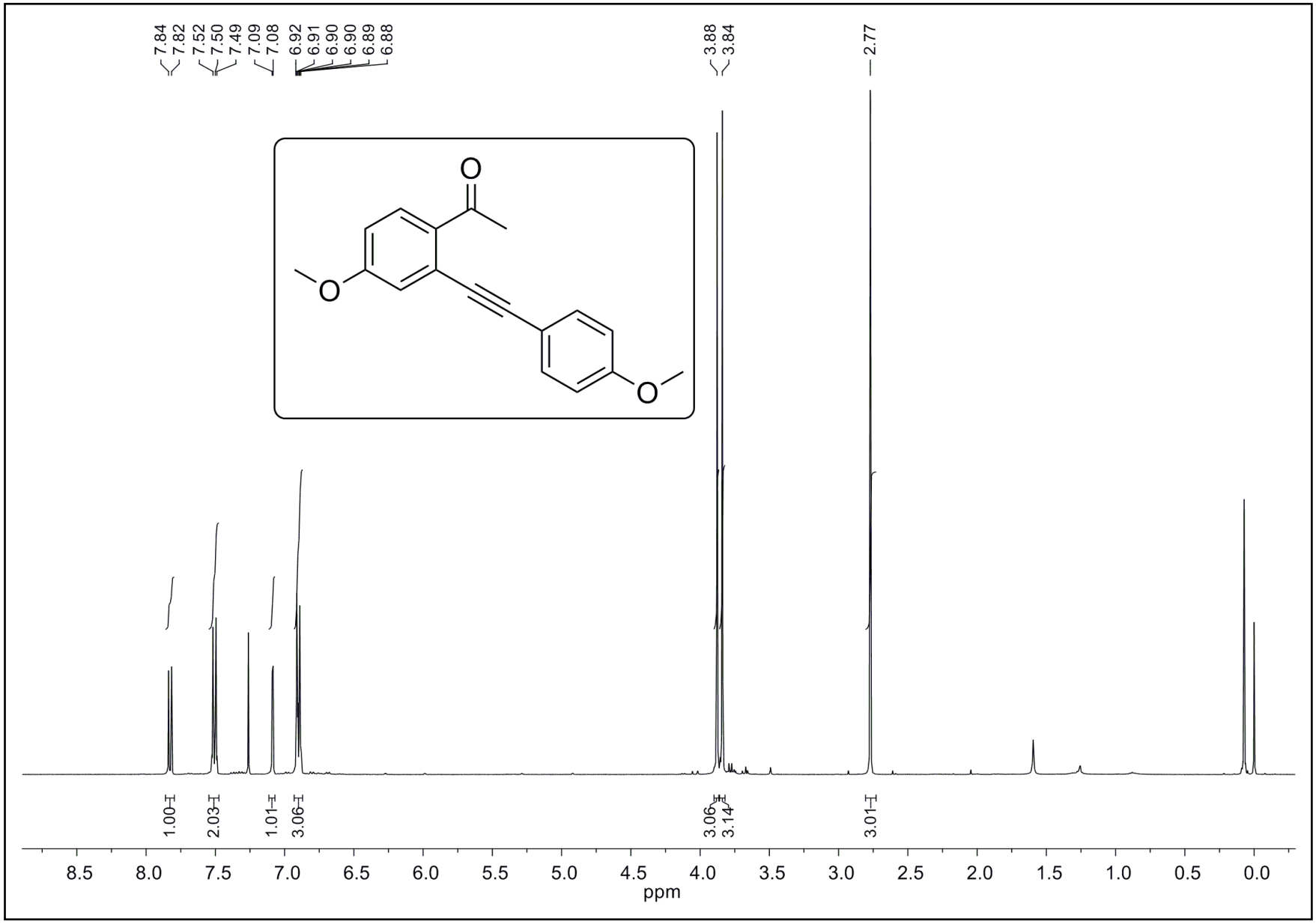
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O
O
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1.01
3.06
3.06
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3.01
8.5
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7.0
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4.0
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3.0
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ppm


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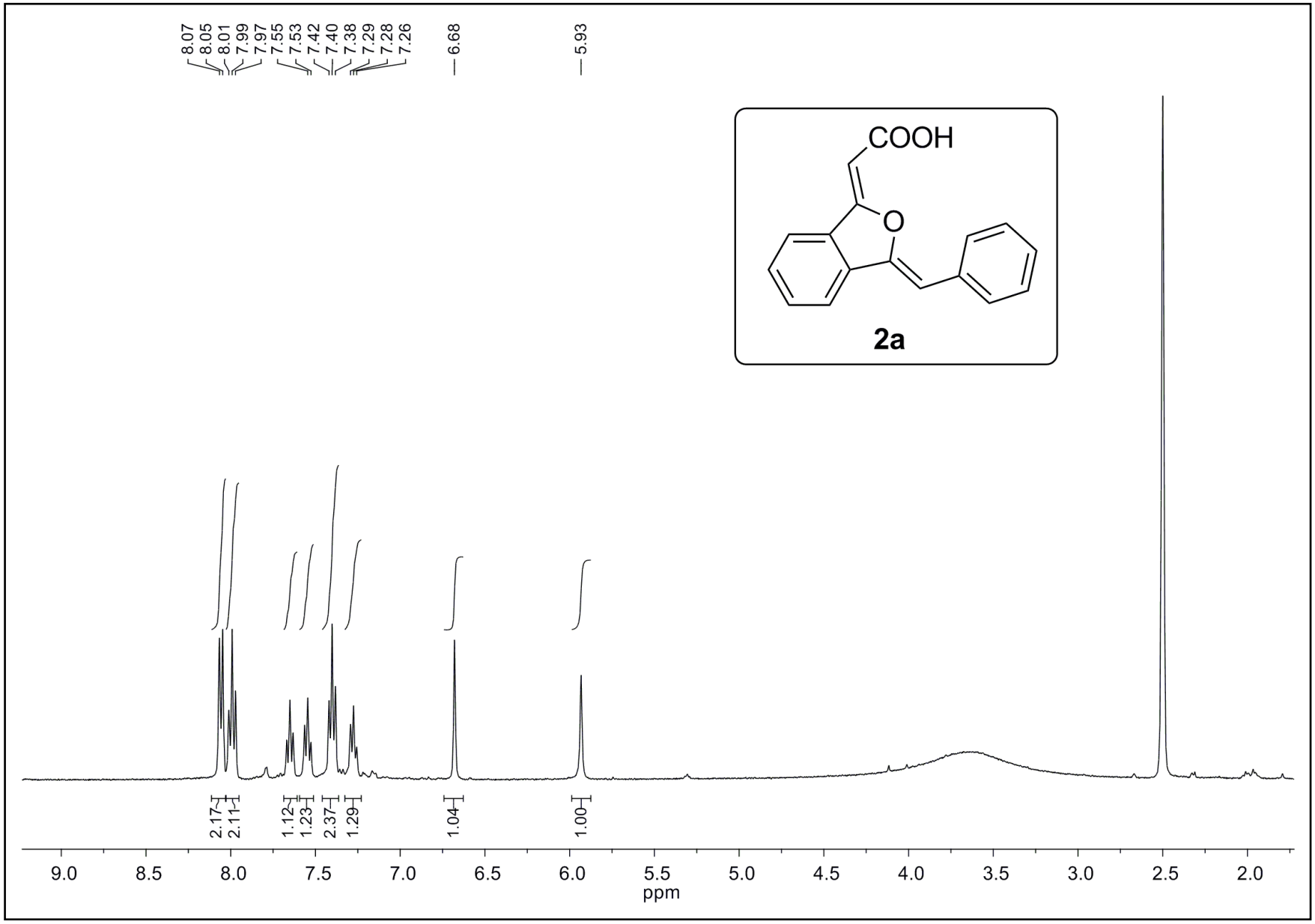
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5.93
COOH
O
2a
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2.11
1.12
1.23
2.37
1.29
1.04
1.00
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8.0
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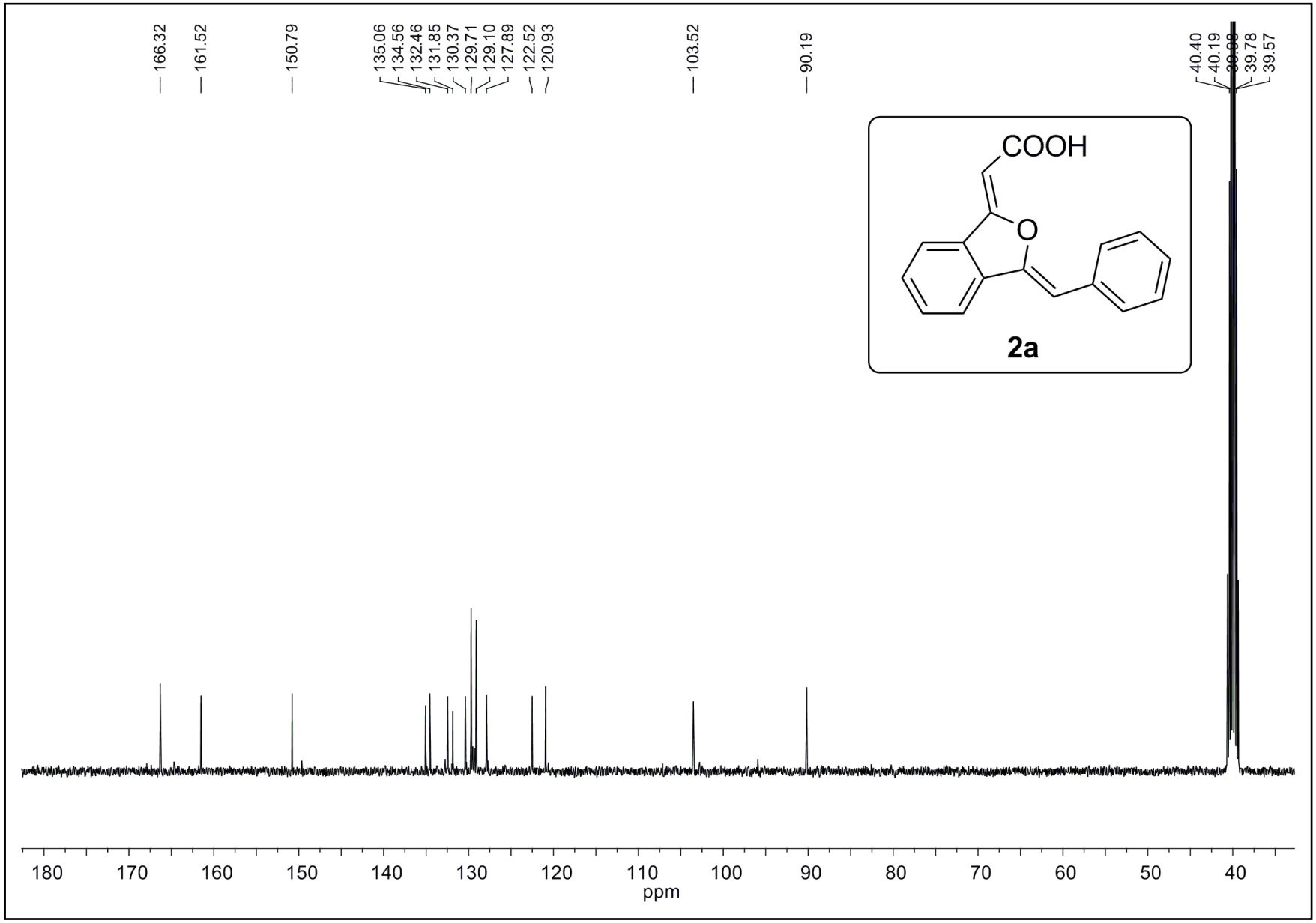
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122.52
120.93
103.52
90.19
40.40
40.19
39.78
39.57
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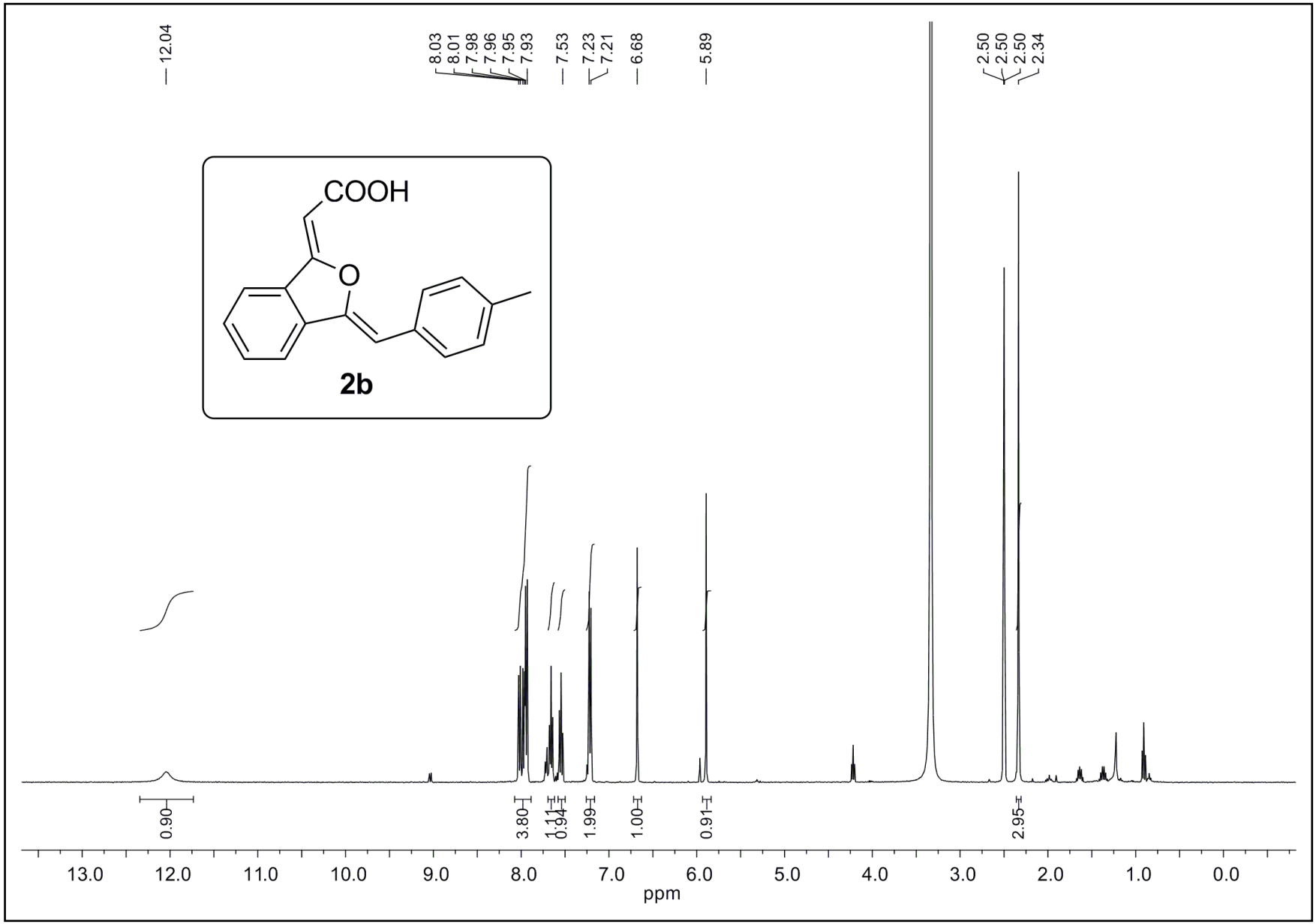
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2.50
2.50
2.34
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O
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3.80
1.11
0.94
1.99
1.00
0.91
2.95
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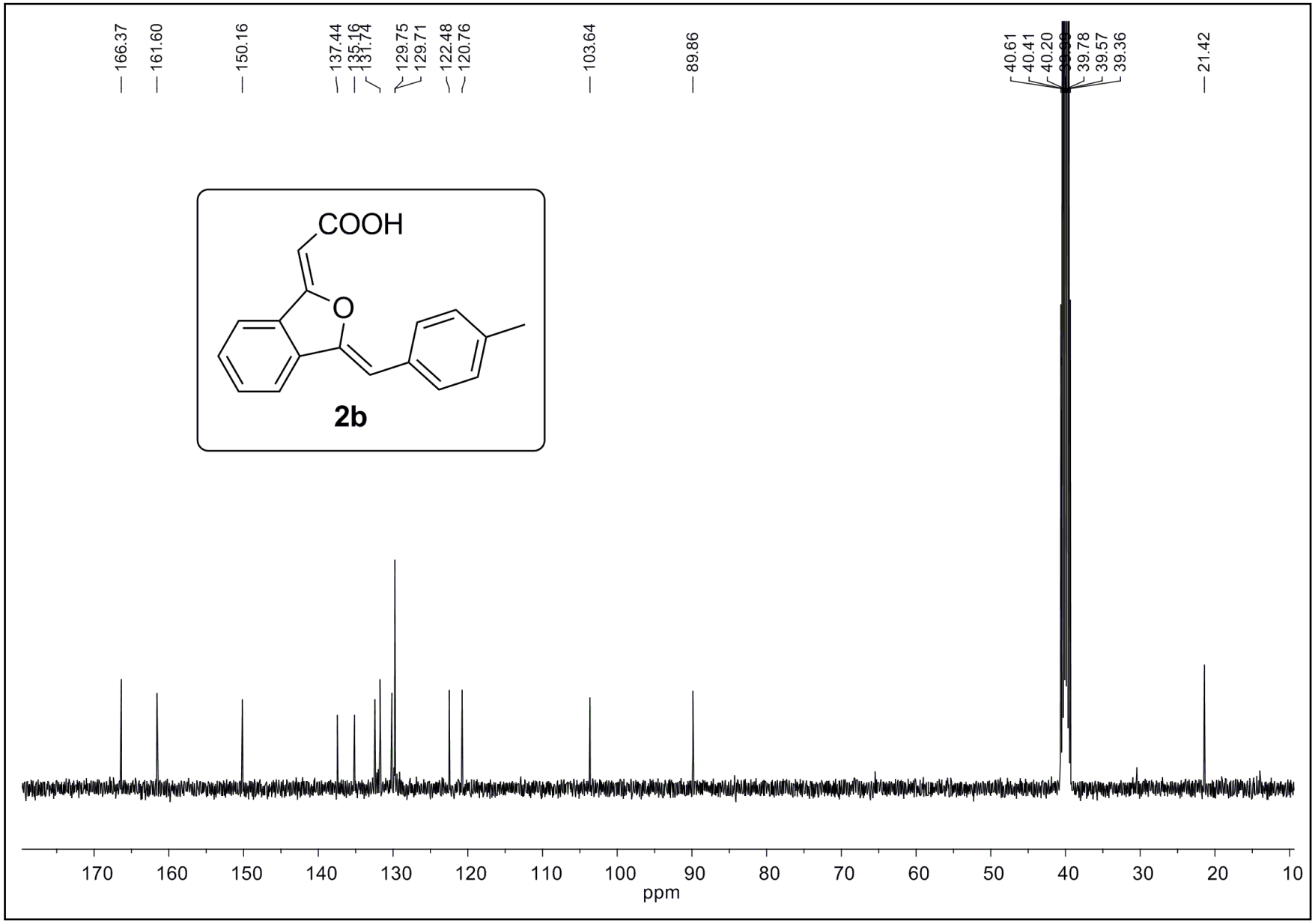
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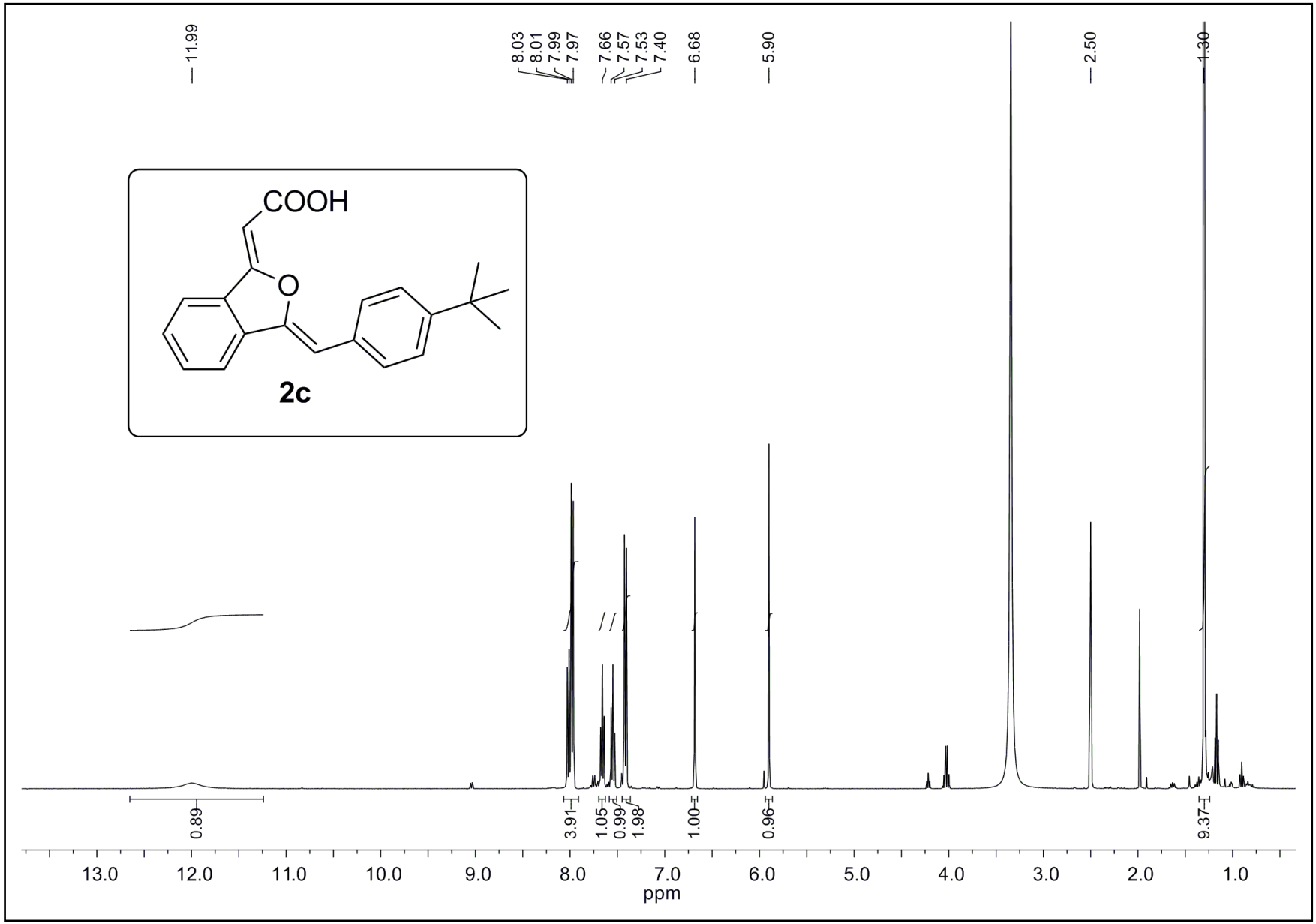
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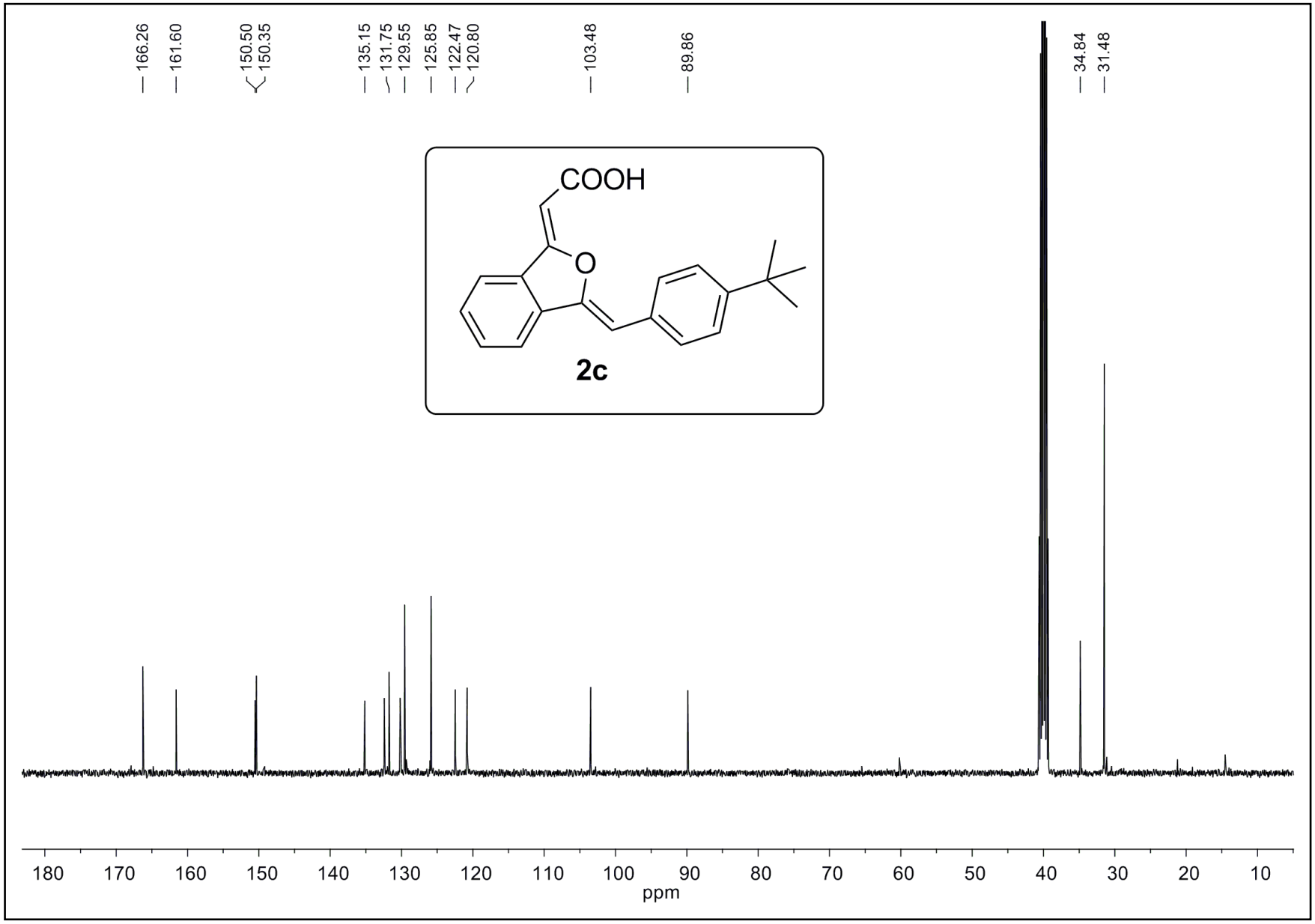
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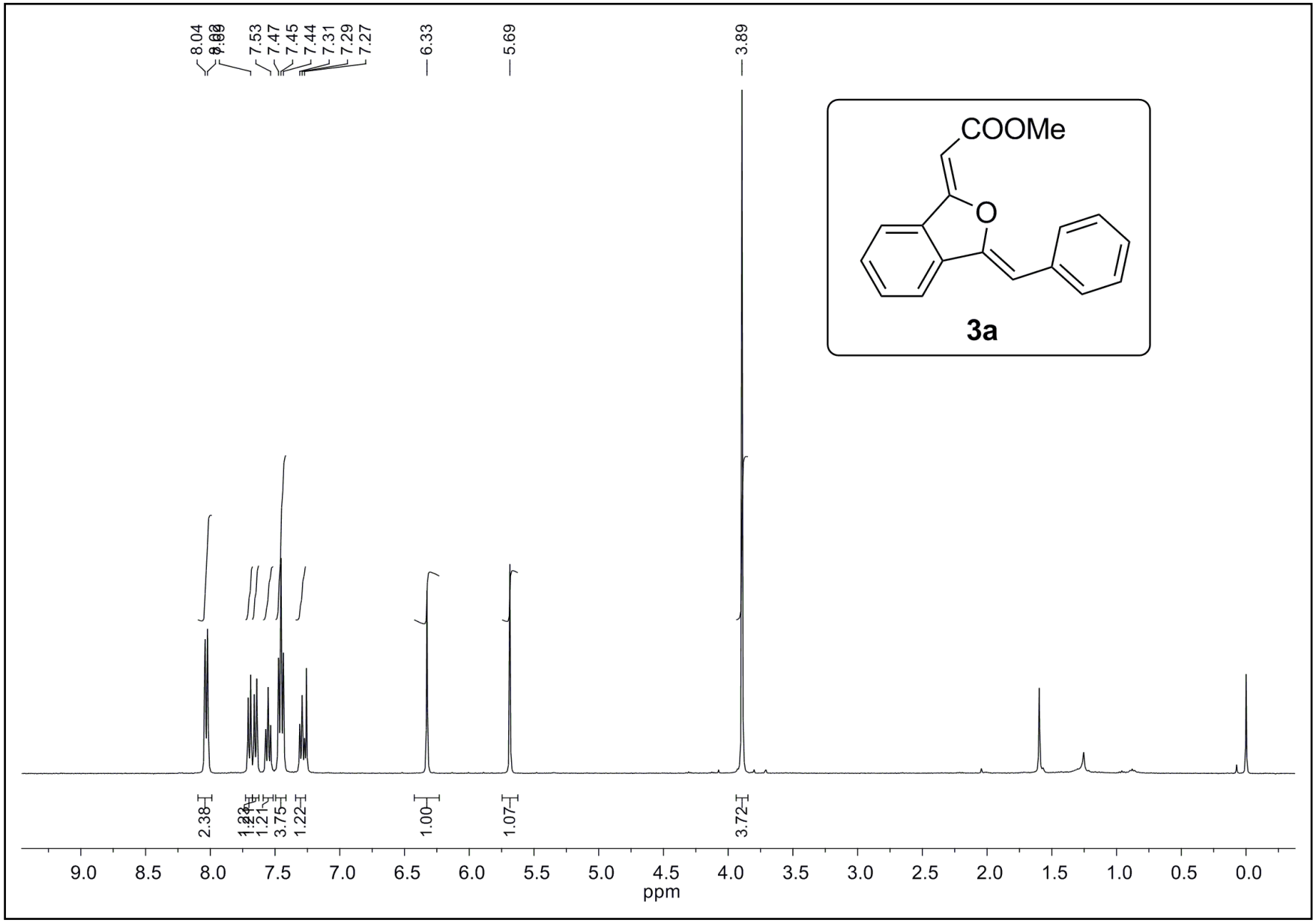
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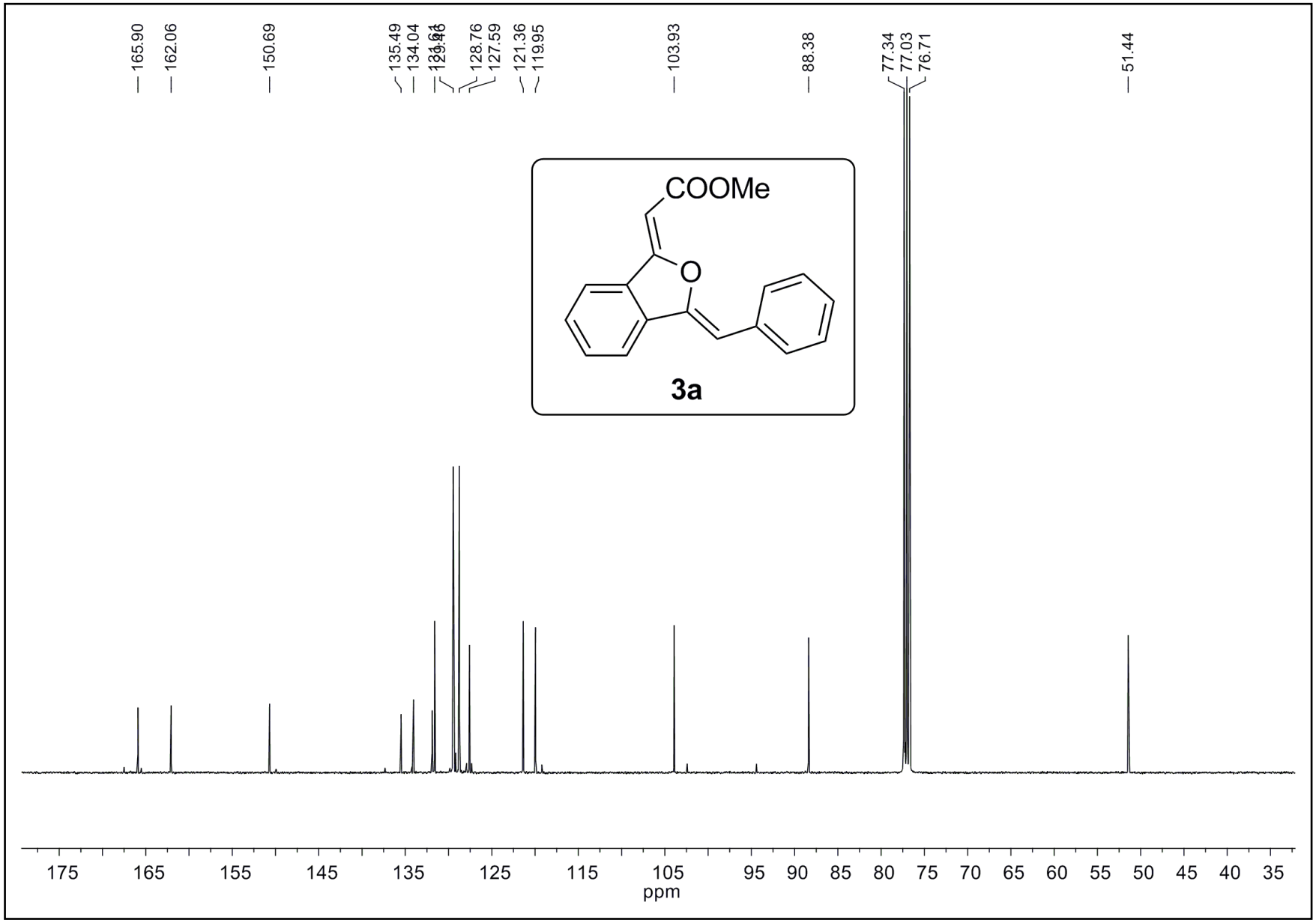
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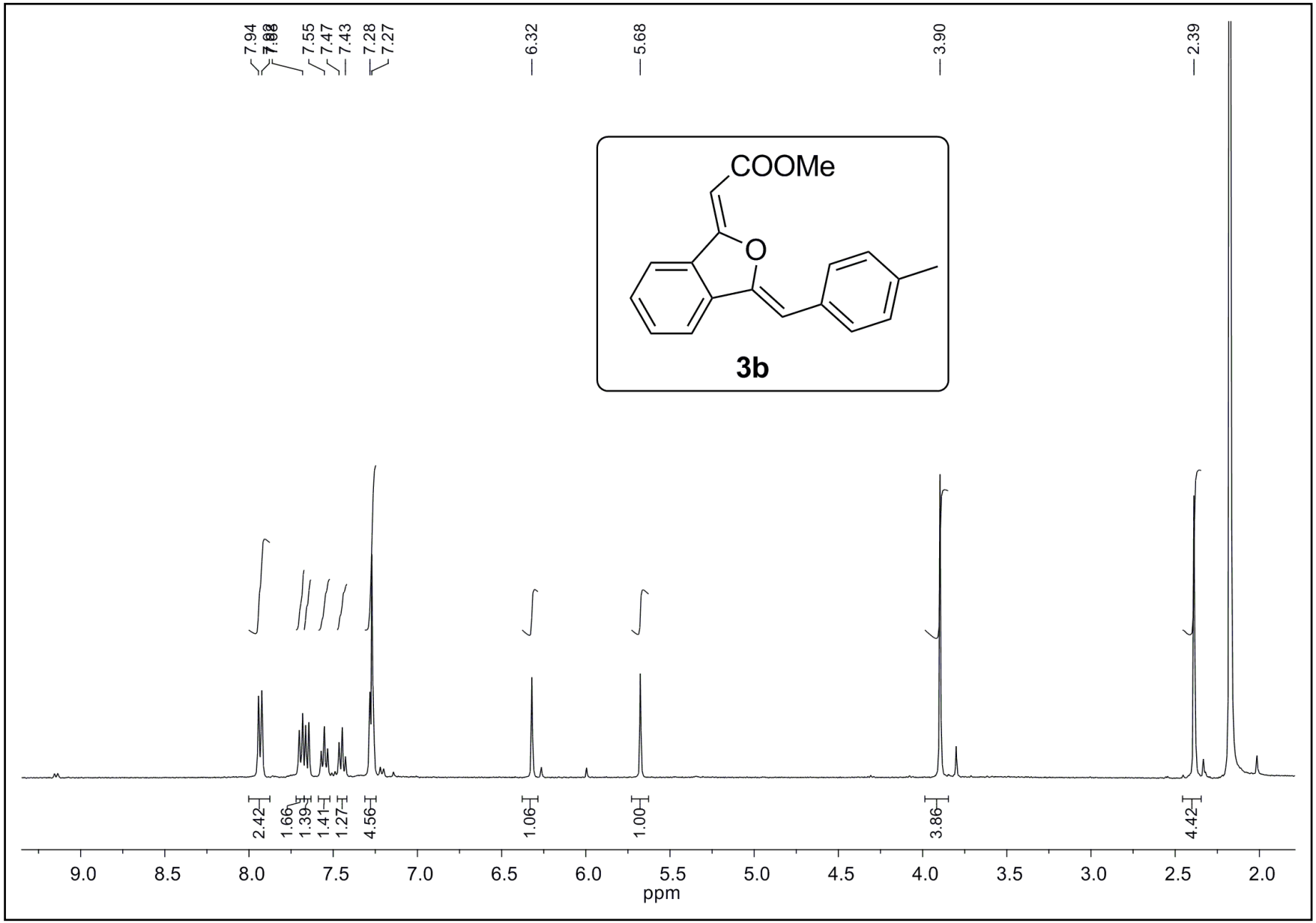
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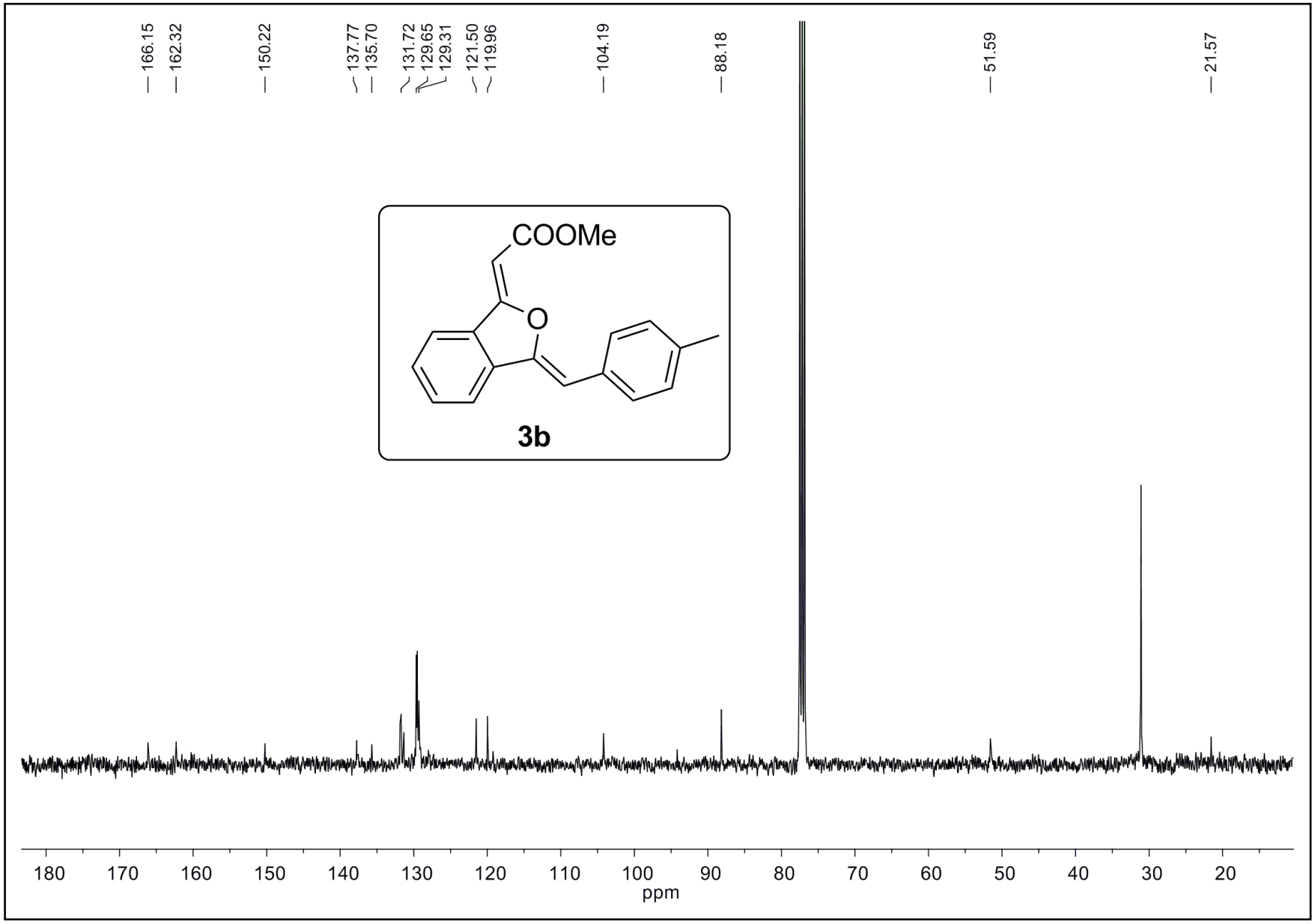
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COOMe
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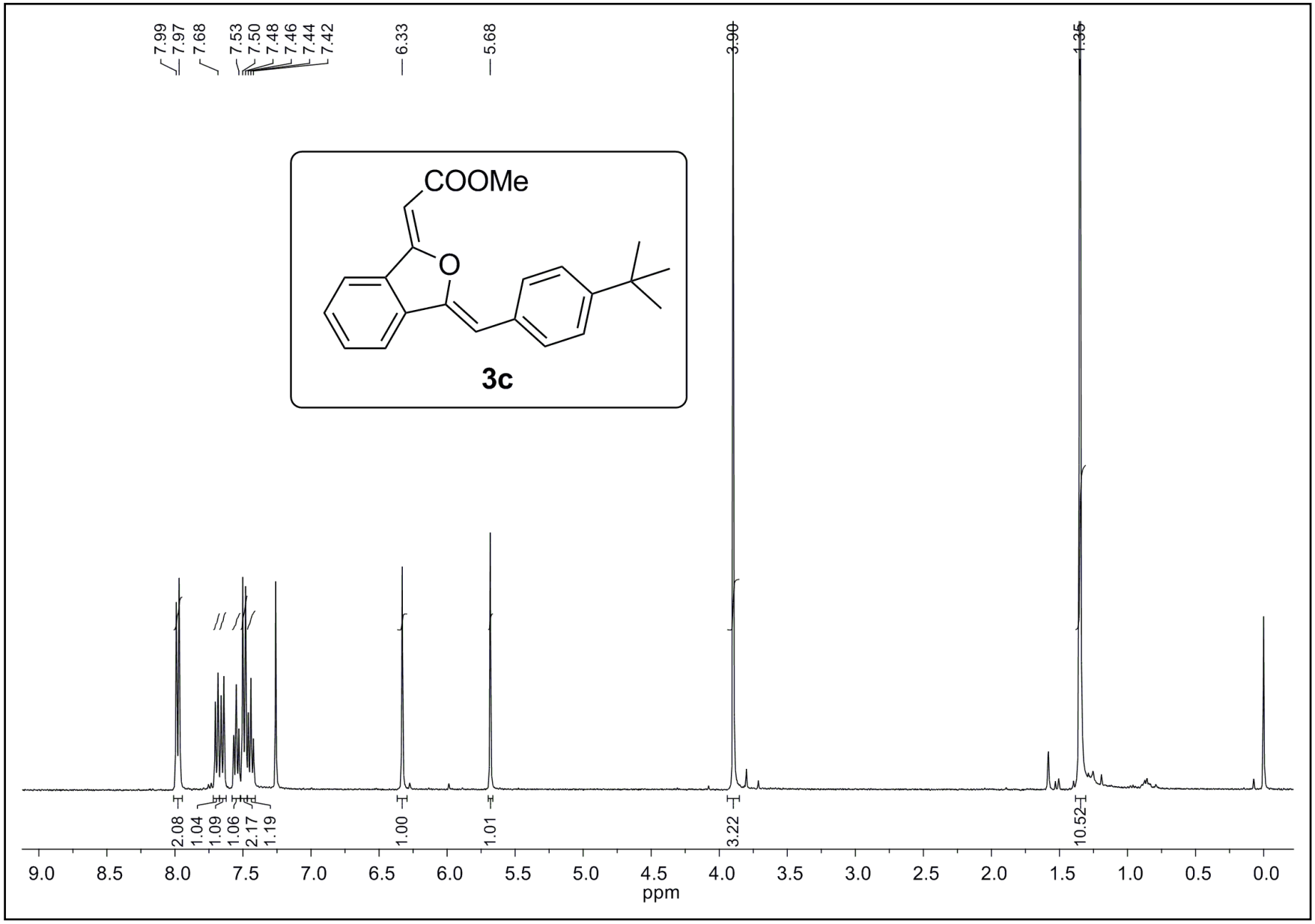
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1.35
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O
3c
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1.09
1.06
2.17
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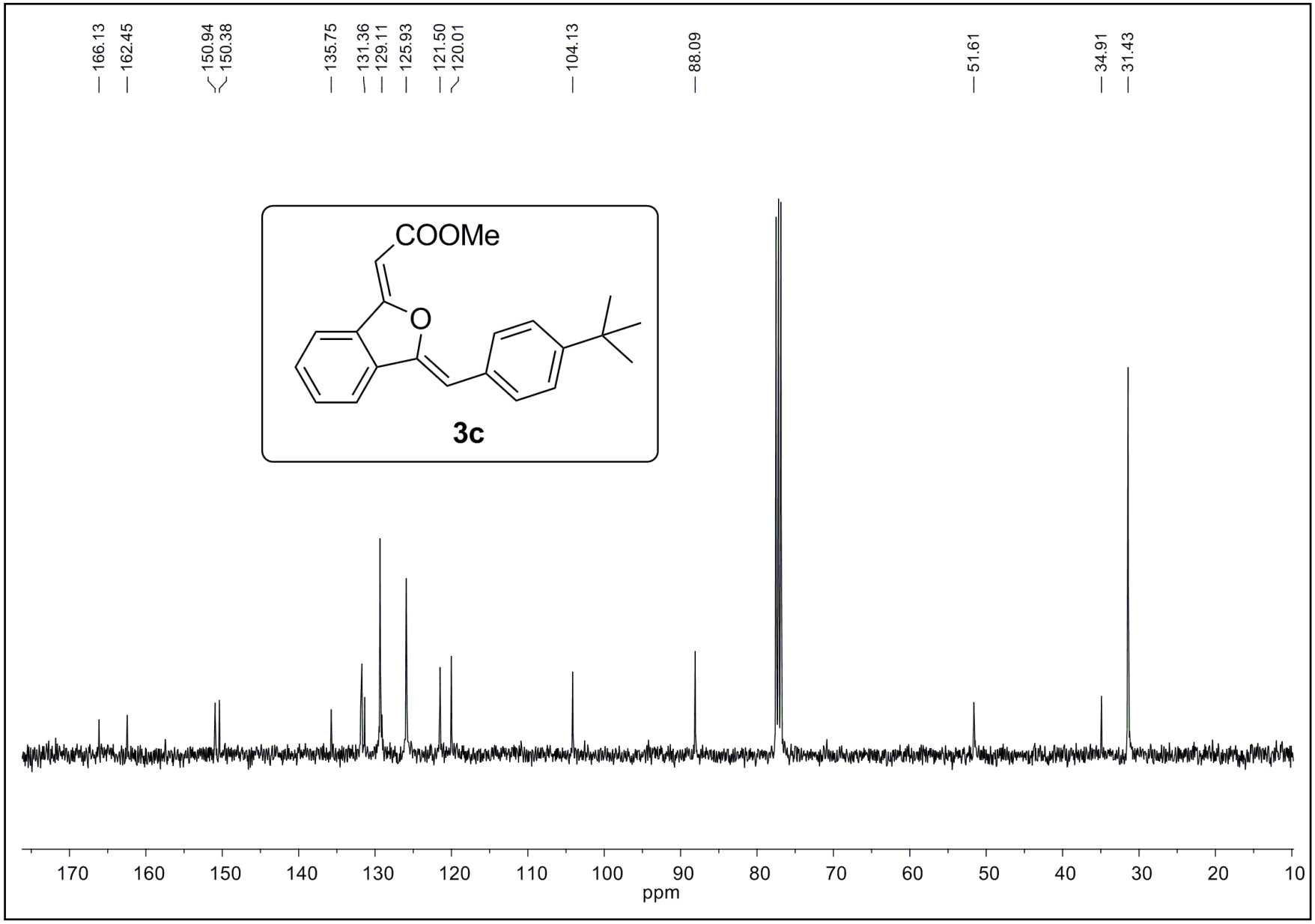
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31.43
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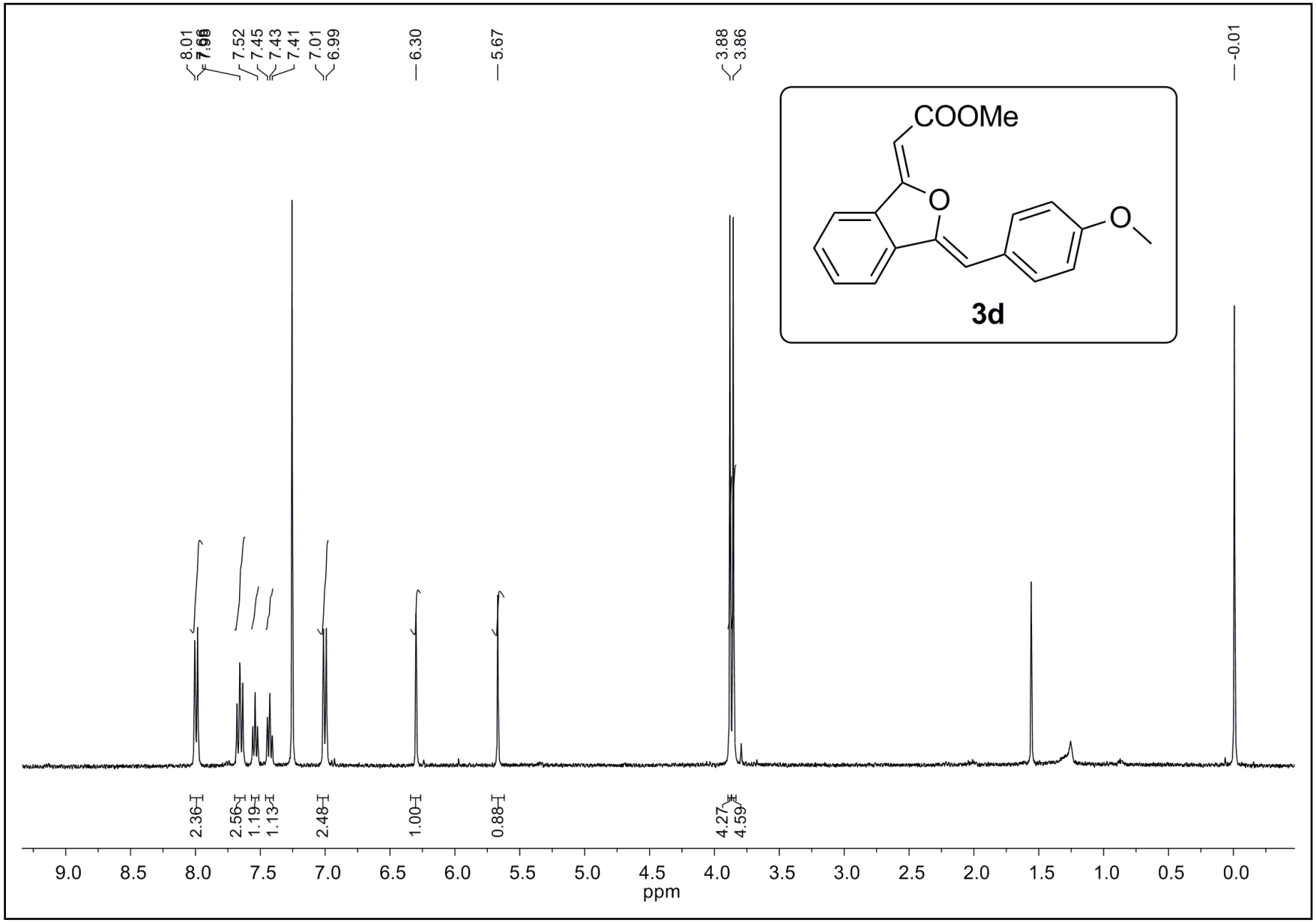
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COOMe
O
O
3d
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2.56
1.19
1.13
2.48
1.00
0.88
4.27
4.59
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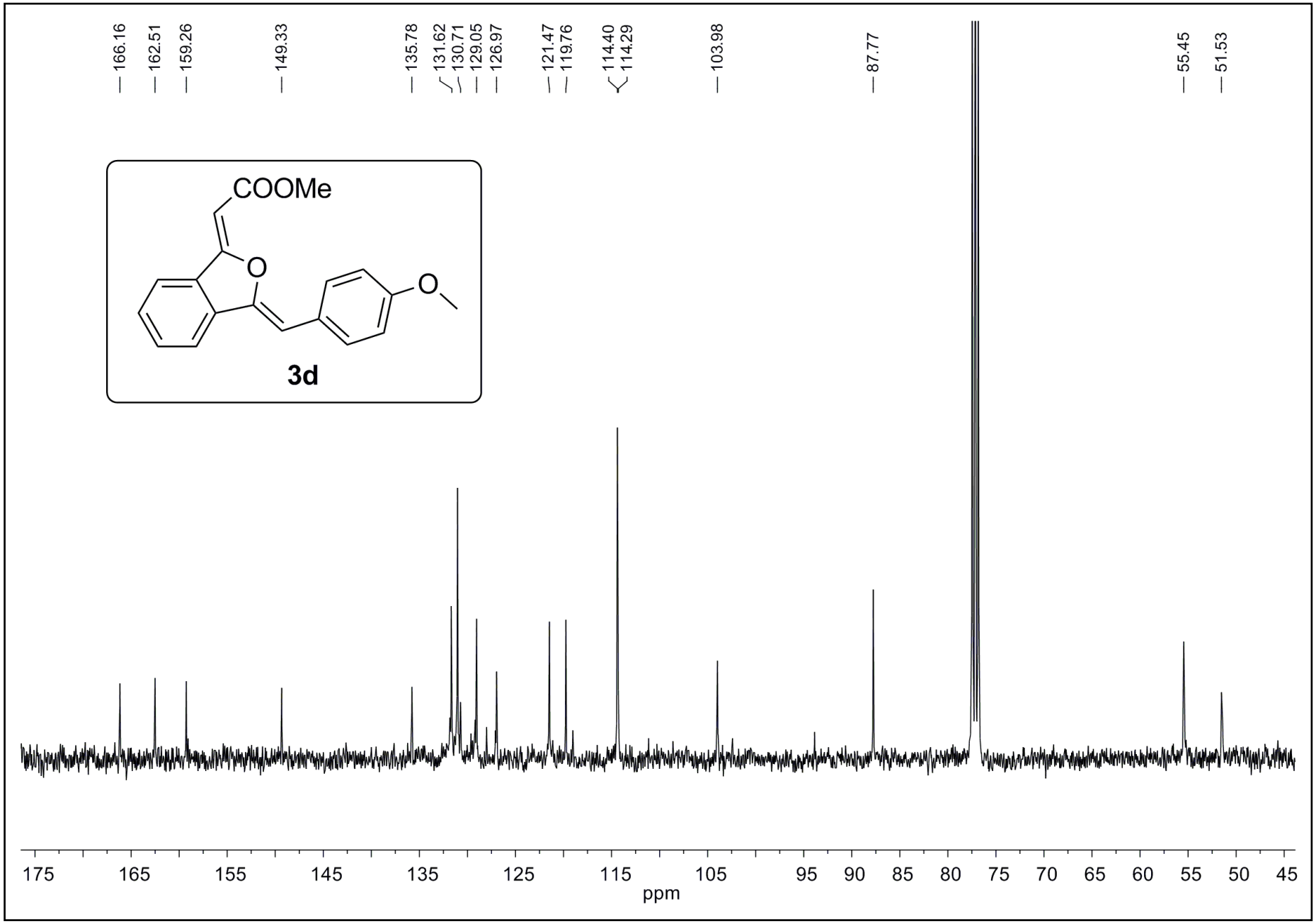
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O
3d
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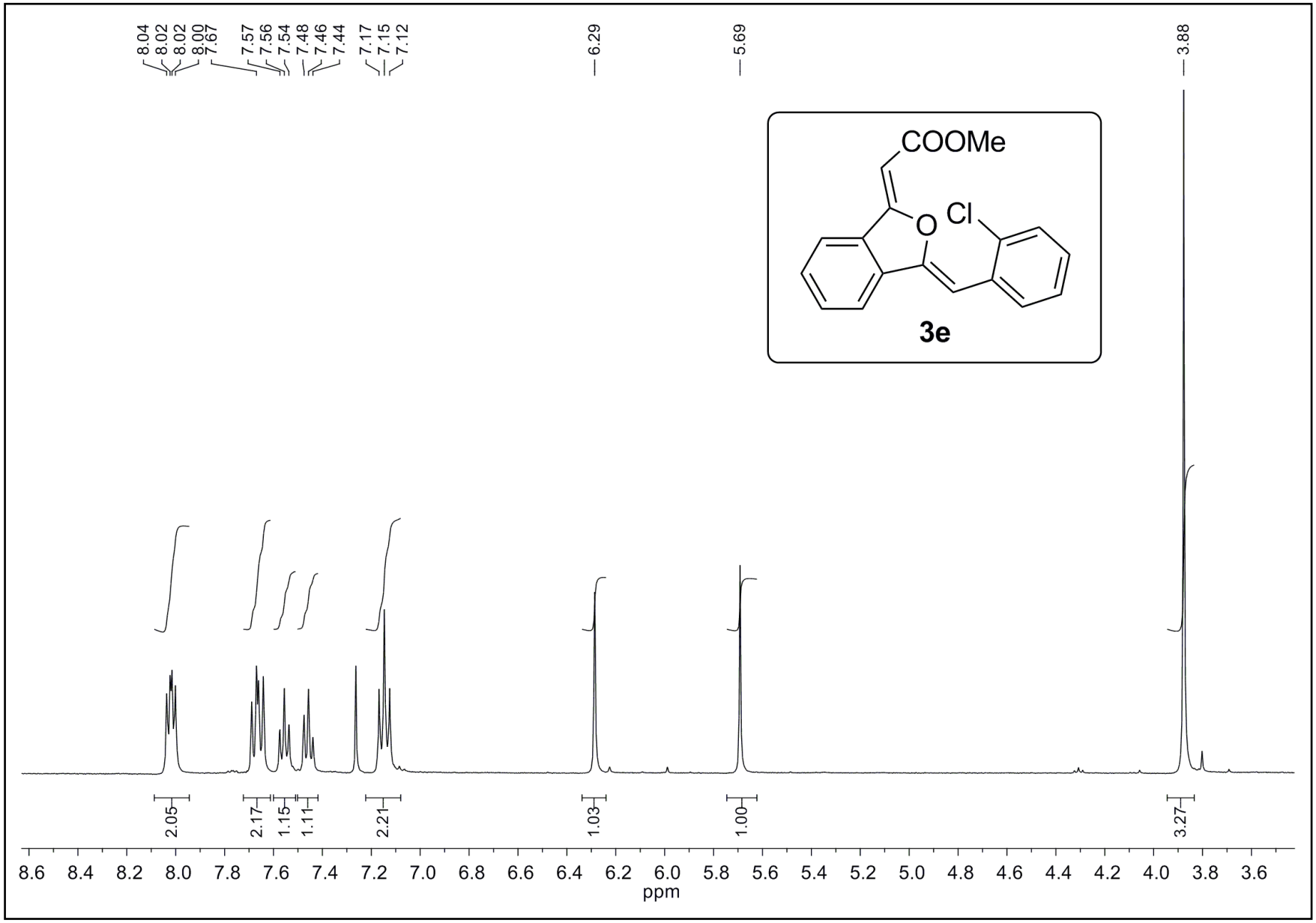
45
ppm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5.69
3.88
COOMe
O
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3e
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2.17
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1.11
2.21
1.03
1.00
3.27
8.6 8.4 8.2 8.0 7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6
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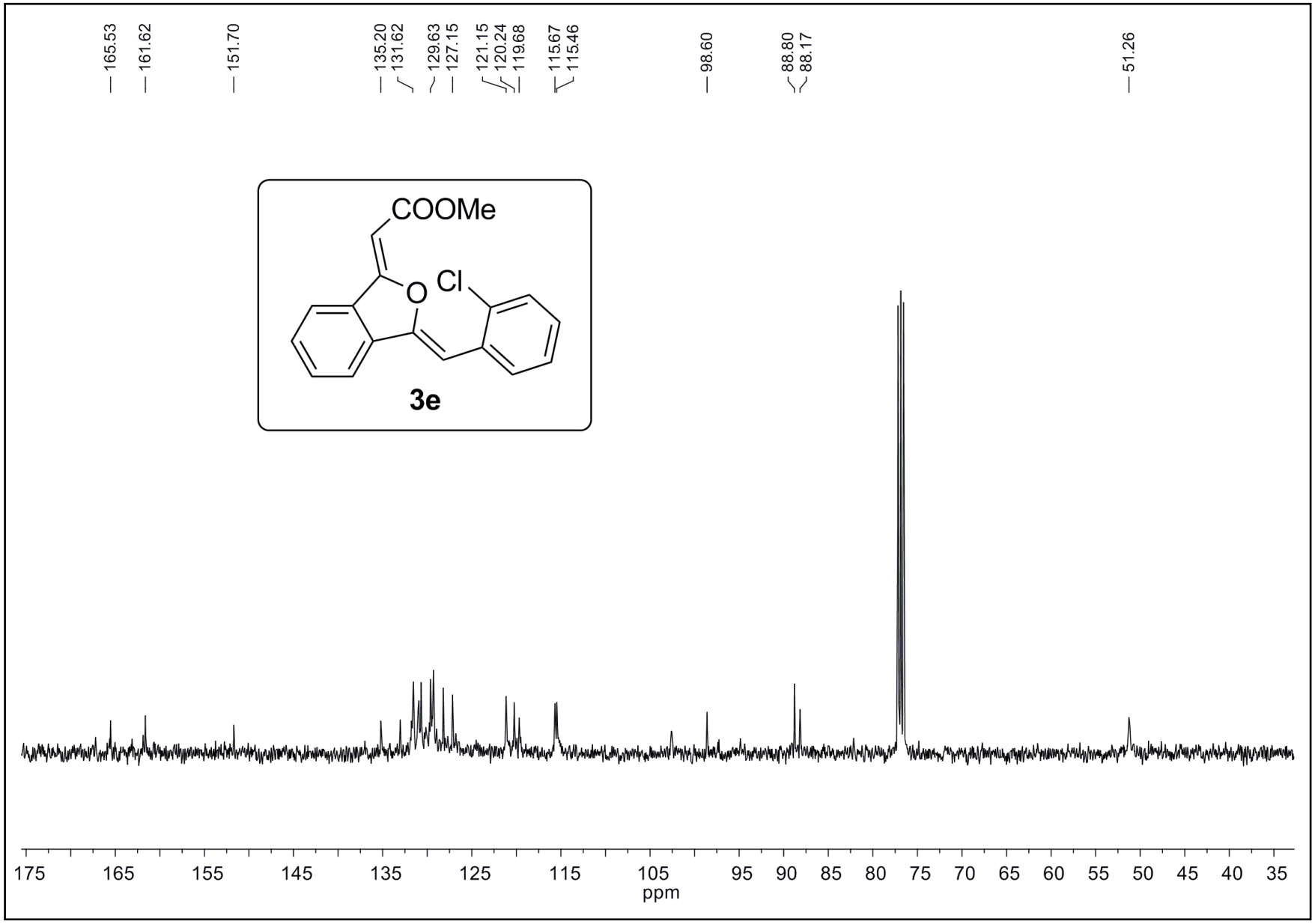
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88.17
51.26
COOMe
O
Cl
3e
175
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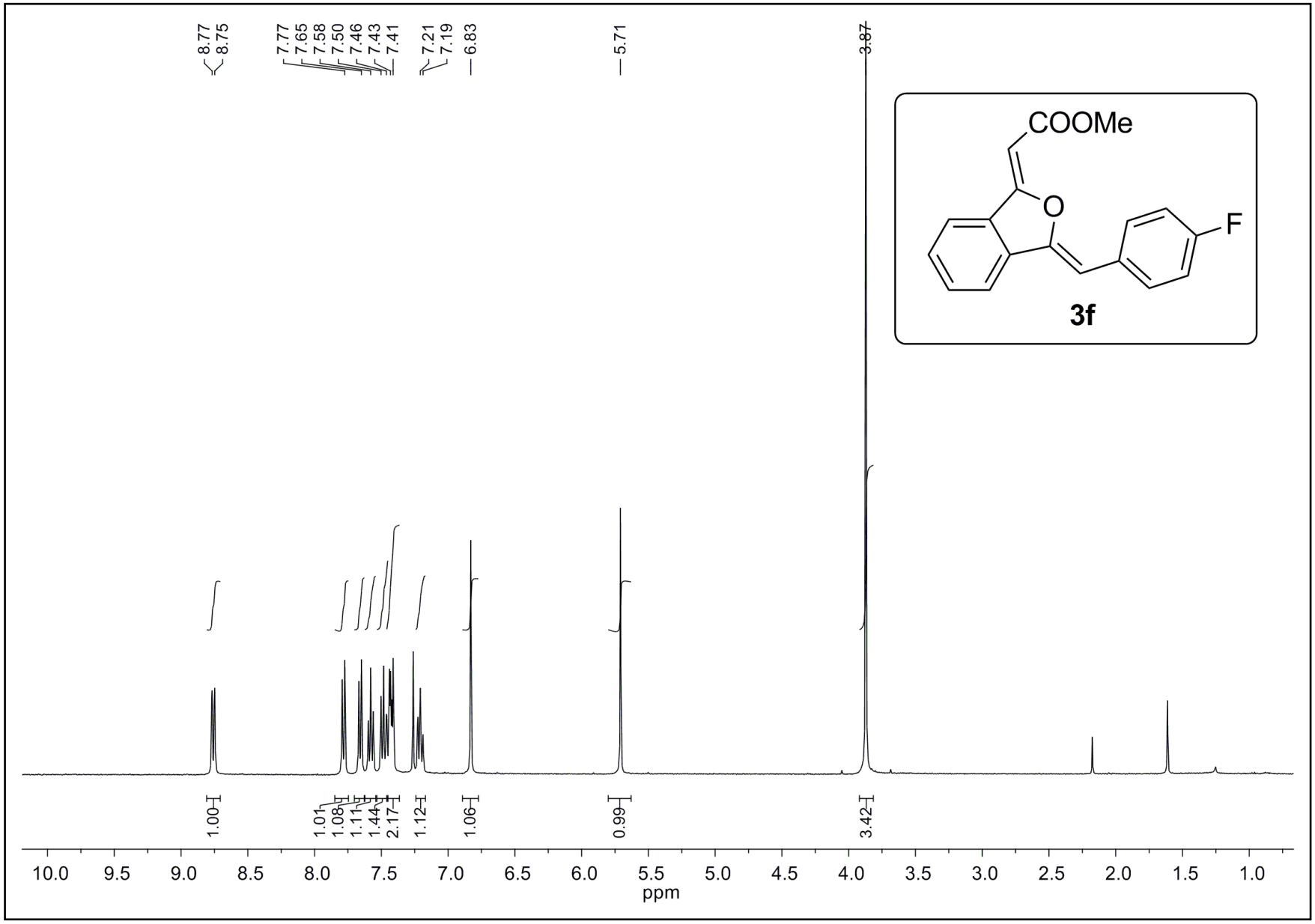
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1.44
2.17
1.12
1.06
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3.42
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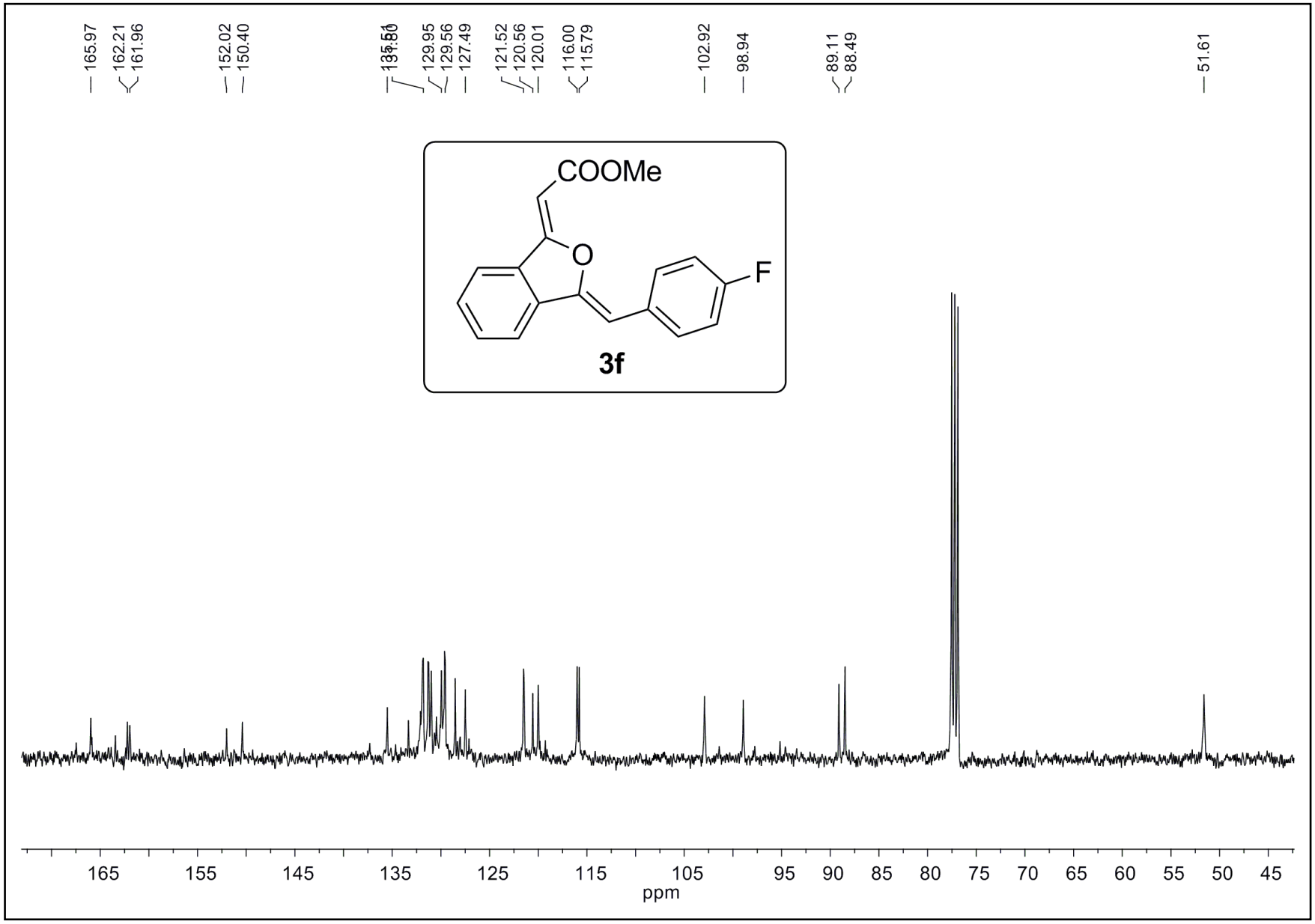
ppm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88.49
51.61
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O
F
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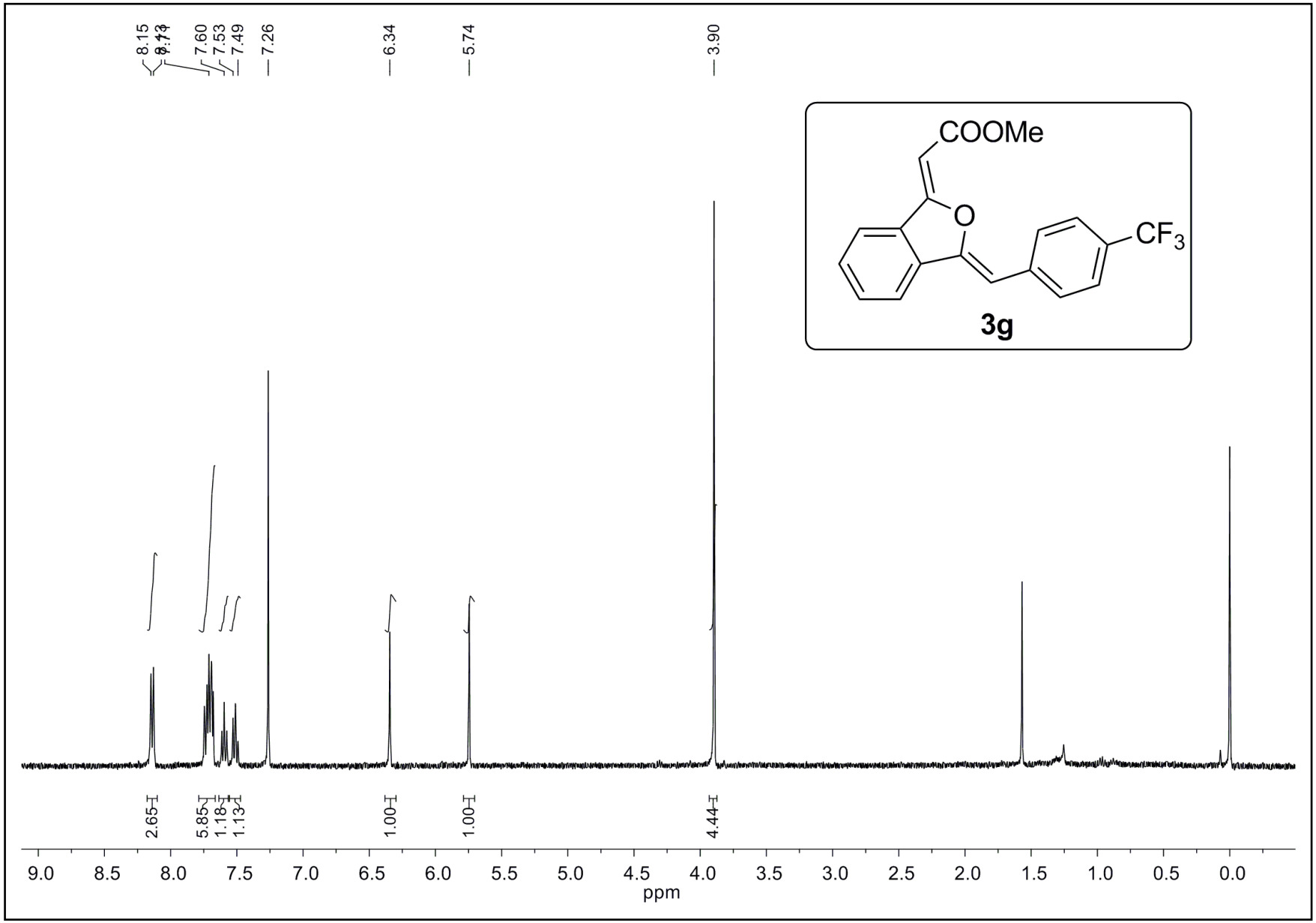
ppm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4.44
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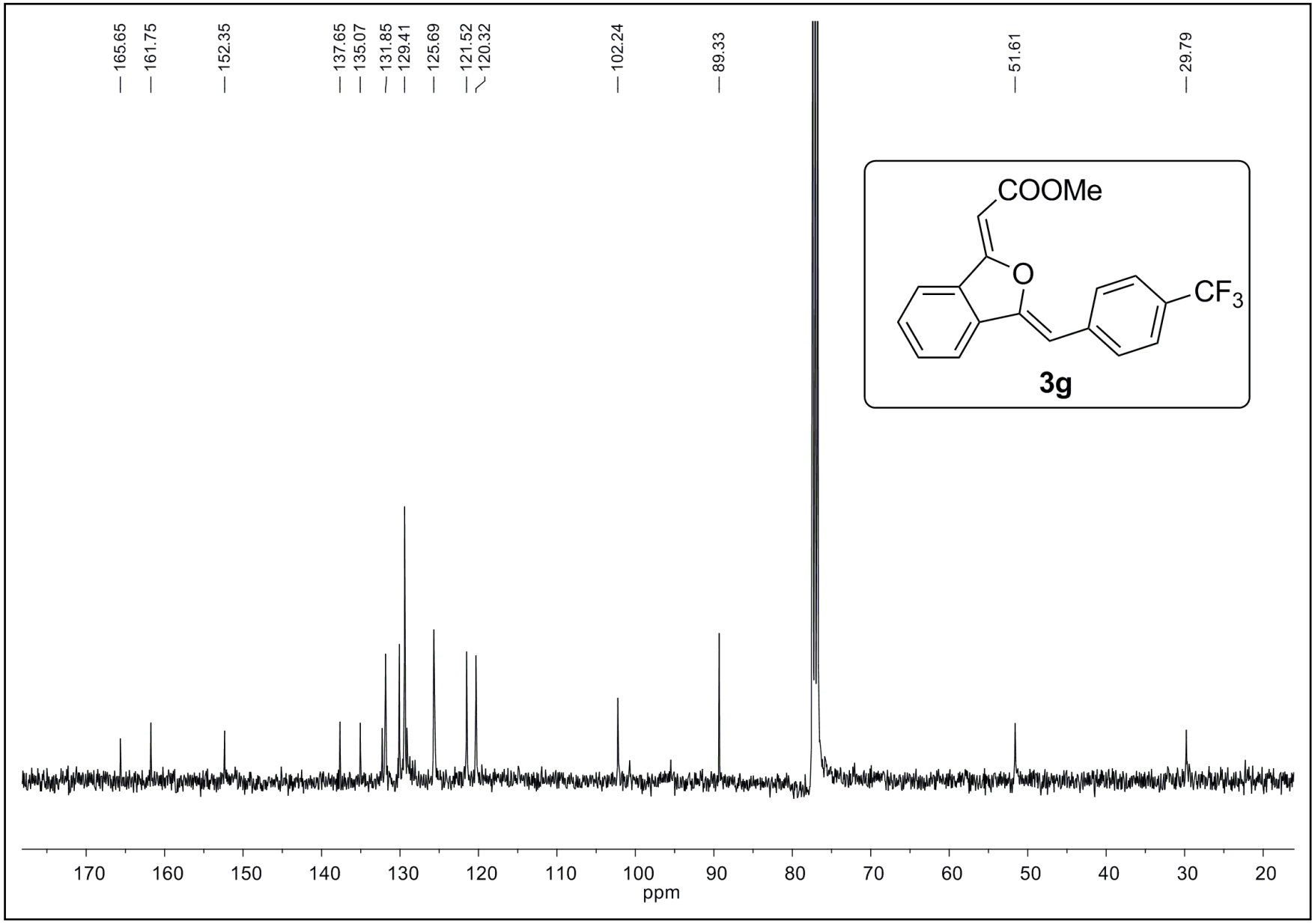
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120.32
102.24
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29.79
COOMe
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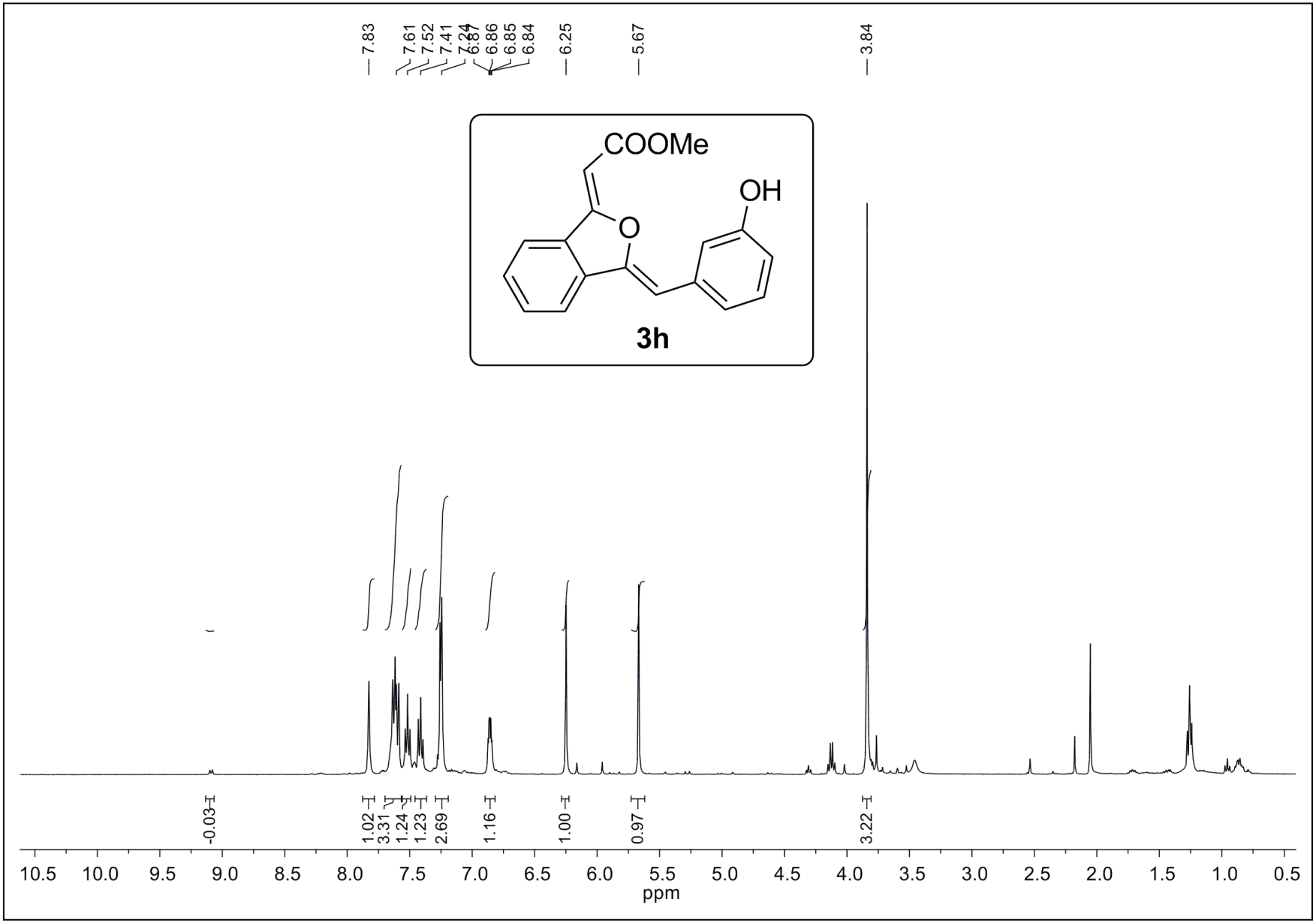
20
ppm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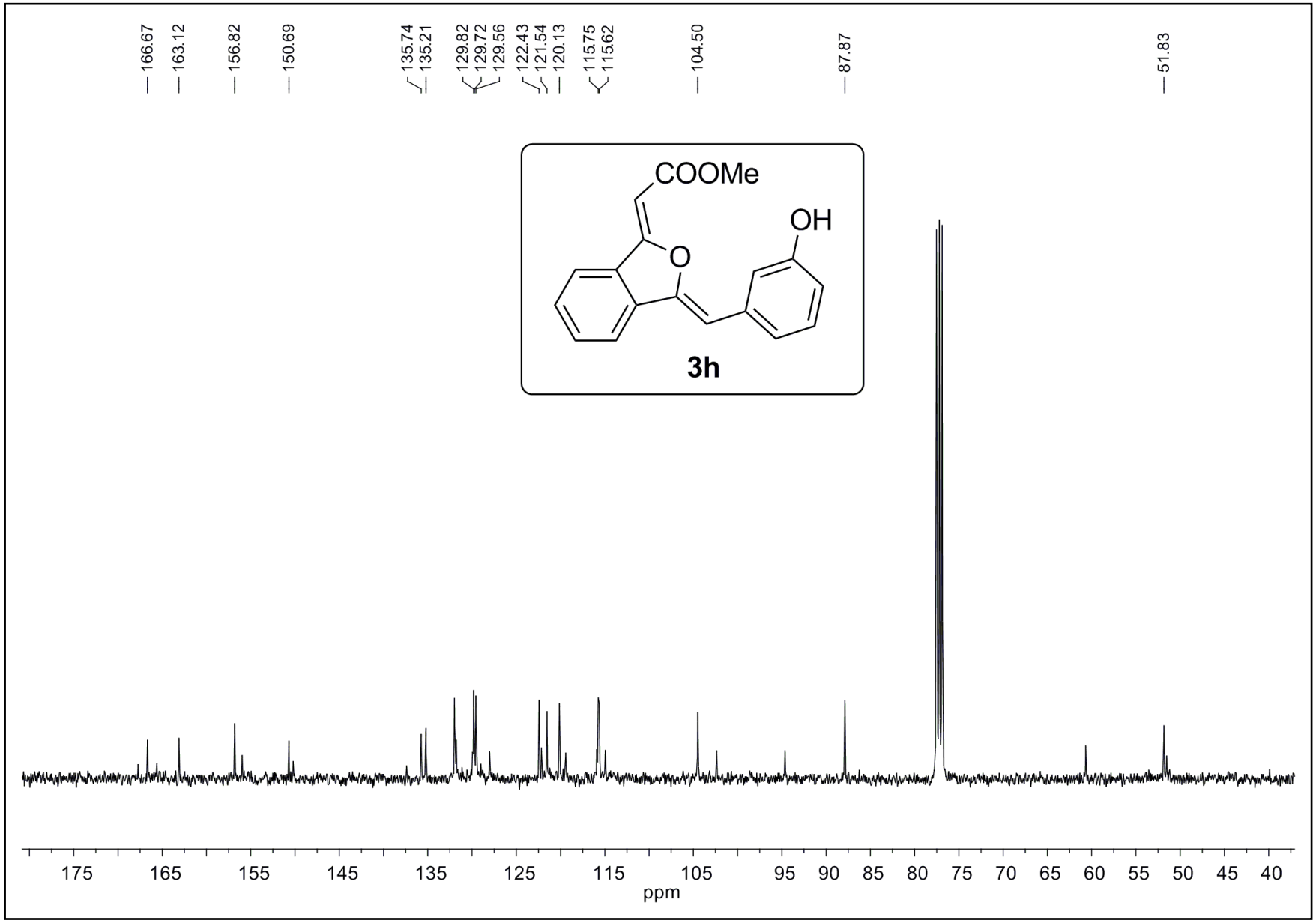
0.97
3.22
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
ppm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163.12
156.82
150.69
135.74
135.21
129.82
129.72
129.56
122.43
121.54
120.13
115.75
115.62
104.50
87.87
51.83
COOMe
OH
O
3h
175
165
155
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135
125
115
105
95
90
85
80
75
70
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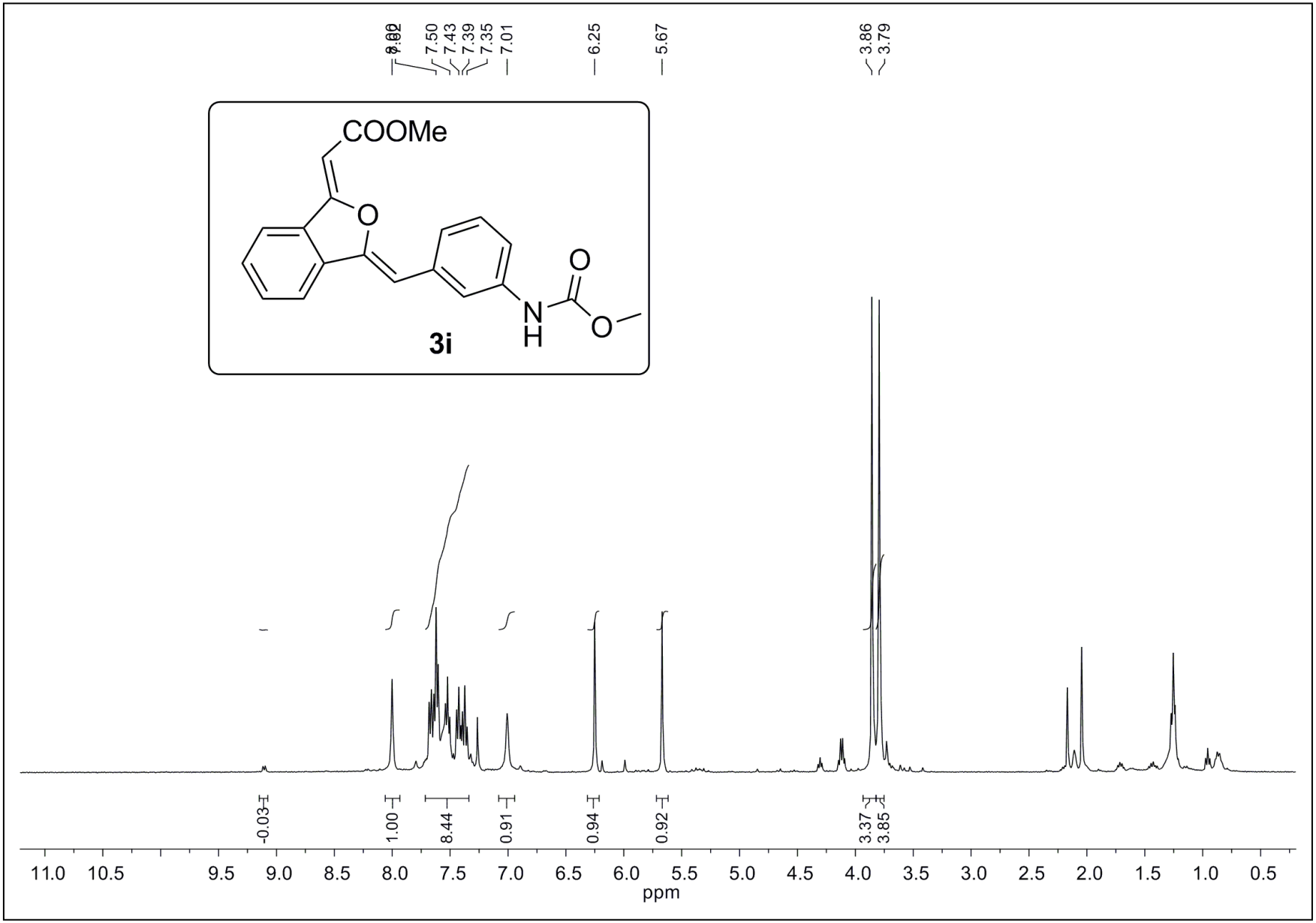
50
45
40
ppm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6.25
5.67
3.86
3.79
COOMe
O
N
H
O
O
3i
-0.03
1.00
8.44
0.91
0.94
0.92
3.37
3.85
11.0
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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4.5
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3.0
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2.0
1.5
1.0
0.5
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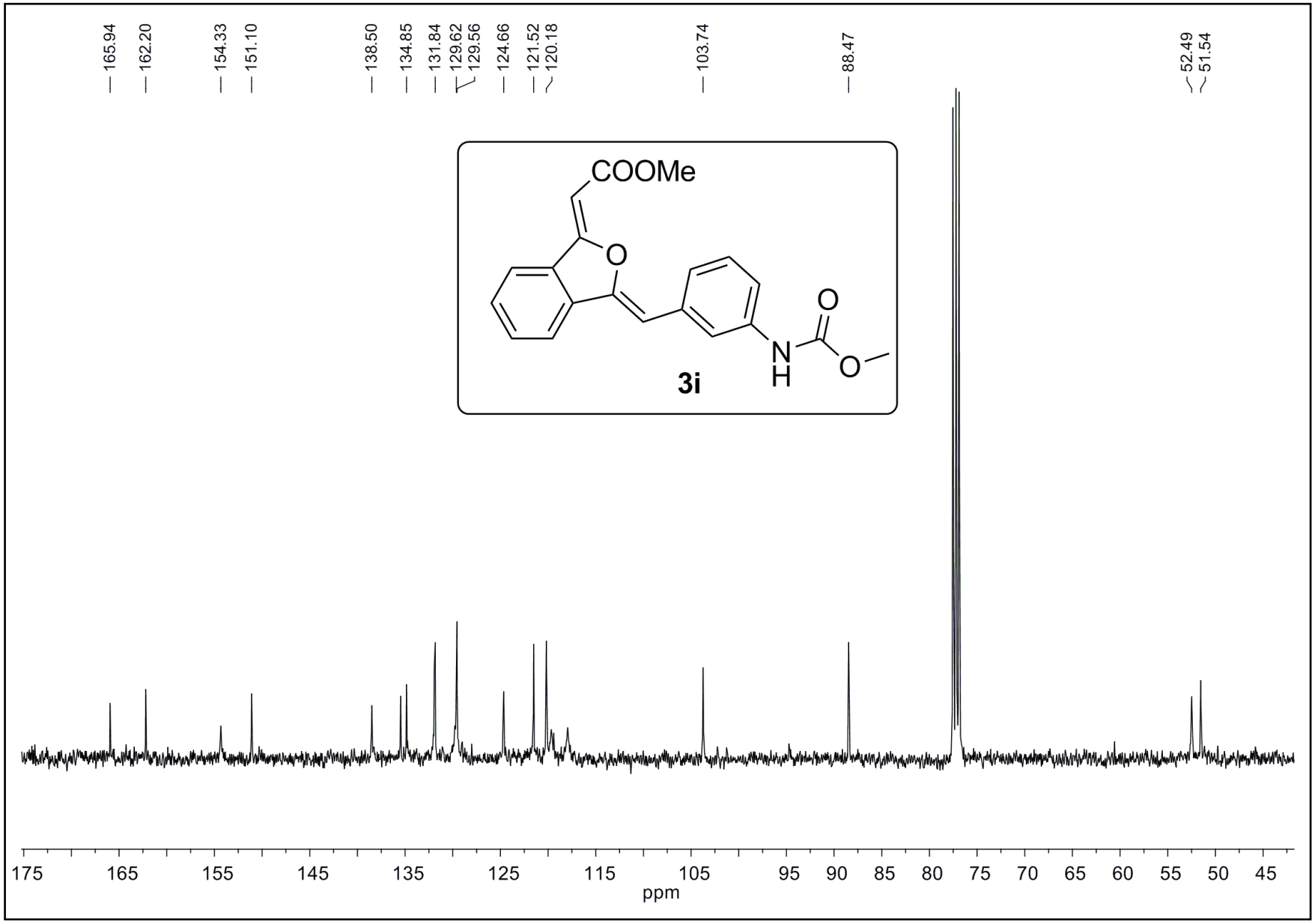
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154.33
151.10
138.50
134.85
131.84
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124.66
121.52
120.18
103.74
88.47
52.49
51.54
COOMe
O
N
H
O
O
3i
175
165
155
145
135
125
115
105
95
90
85
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75
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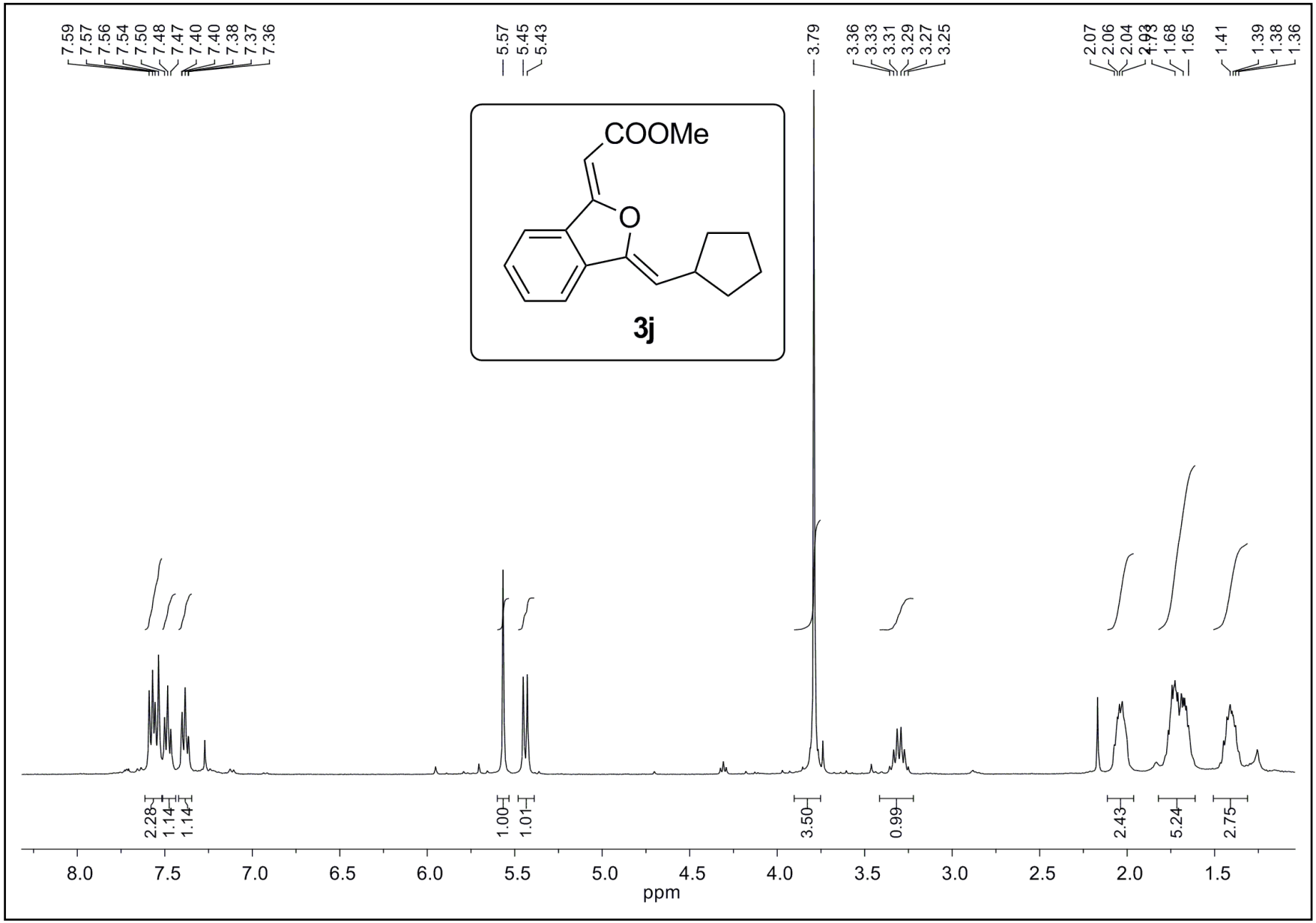
60
55
50
45
ppm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7.57
7.56
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7.38
7.37
7.36
5.57
5.45
5.43
3.79
3.36
3.33
3.31
3.29
3.27
3.25
2.07
2.06
2.04
1.68
1.65
1.41
1.39
1.38
1.36
COOMe
O
3j
2.28
1.14
1.14
1.00
1.01
3.50
0.99
2.43
5.24
2.75
8.0
7.5
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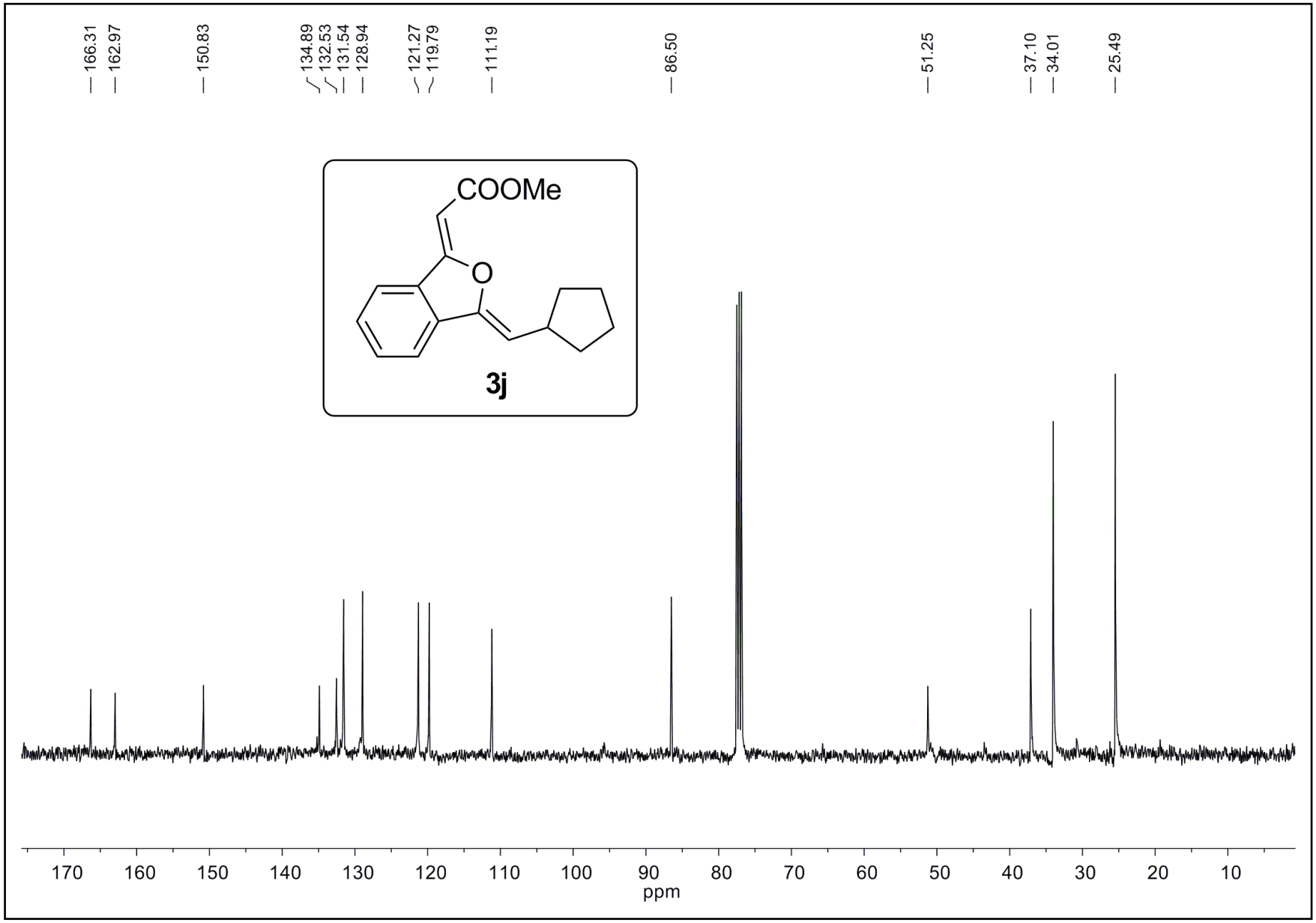
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm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162.97
150.83
134.89
132.53
131.54
128.94
121.27
119.79
111.19
86.50
51.25
37.10
34.01
25.49
COOMe
O
3j
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150
140
130
120
110
100
90
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70
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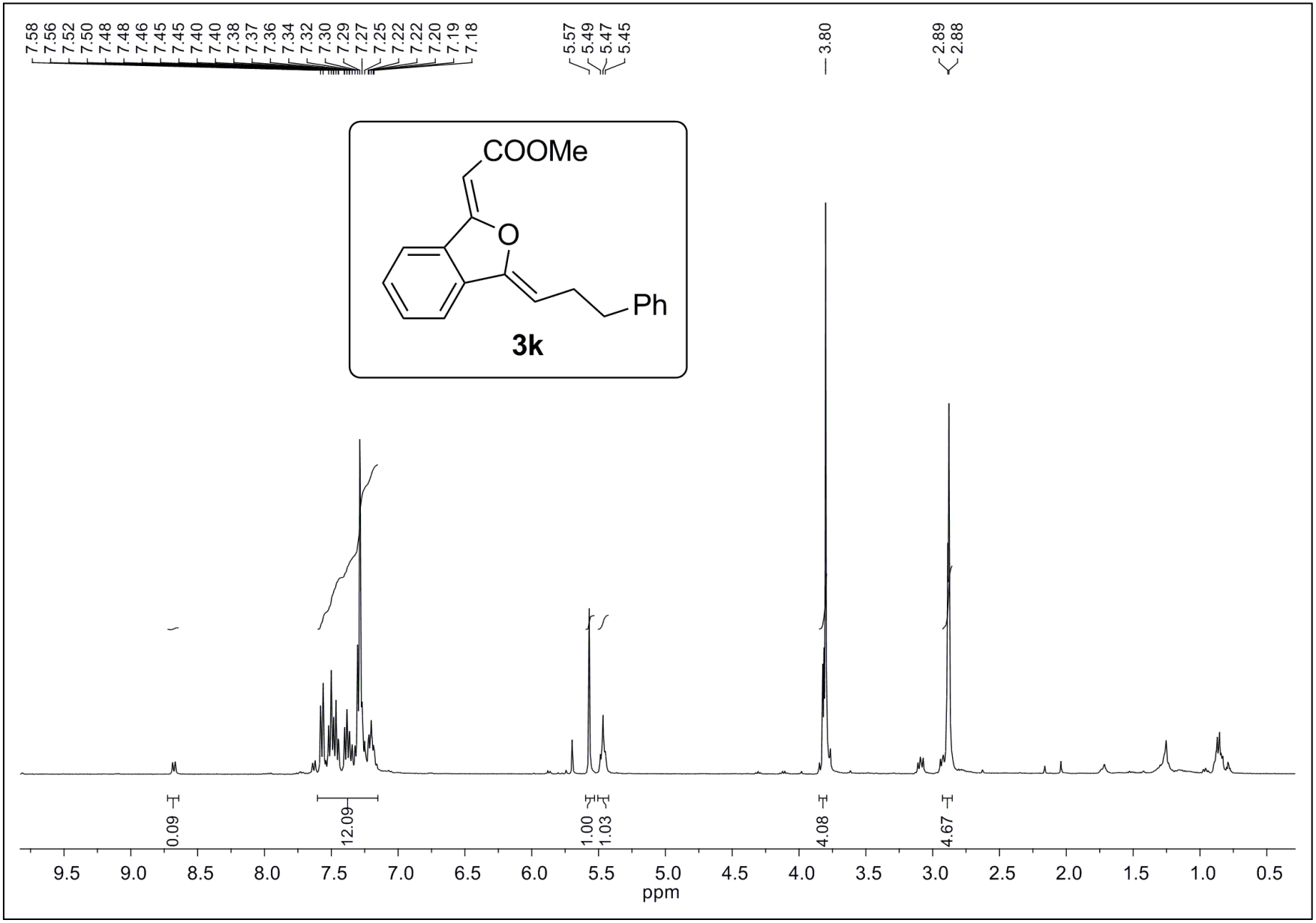
40
30
20
10
ppm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7.48
7.46
7.45
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7.40
7.40
7.38
7.37
7.36
7.34
7.32
7.30
7.29
7.27
7.25
7.22
7.22
7.20
7.19
7.18
5.57
5.49
5.47
5.45
3.80
2.89
2.88
COOMe
O
Ph
3k
0.09
12.09
1.00
1.03
4.08
4.67
9.5
9.0
8.5
8.0
7.5
7.0
6.5
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4.5
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2.0
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1.0
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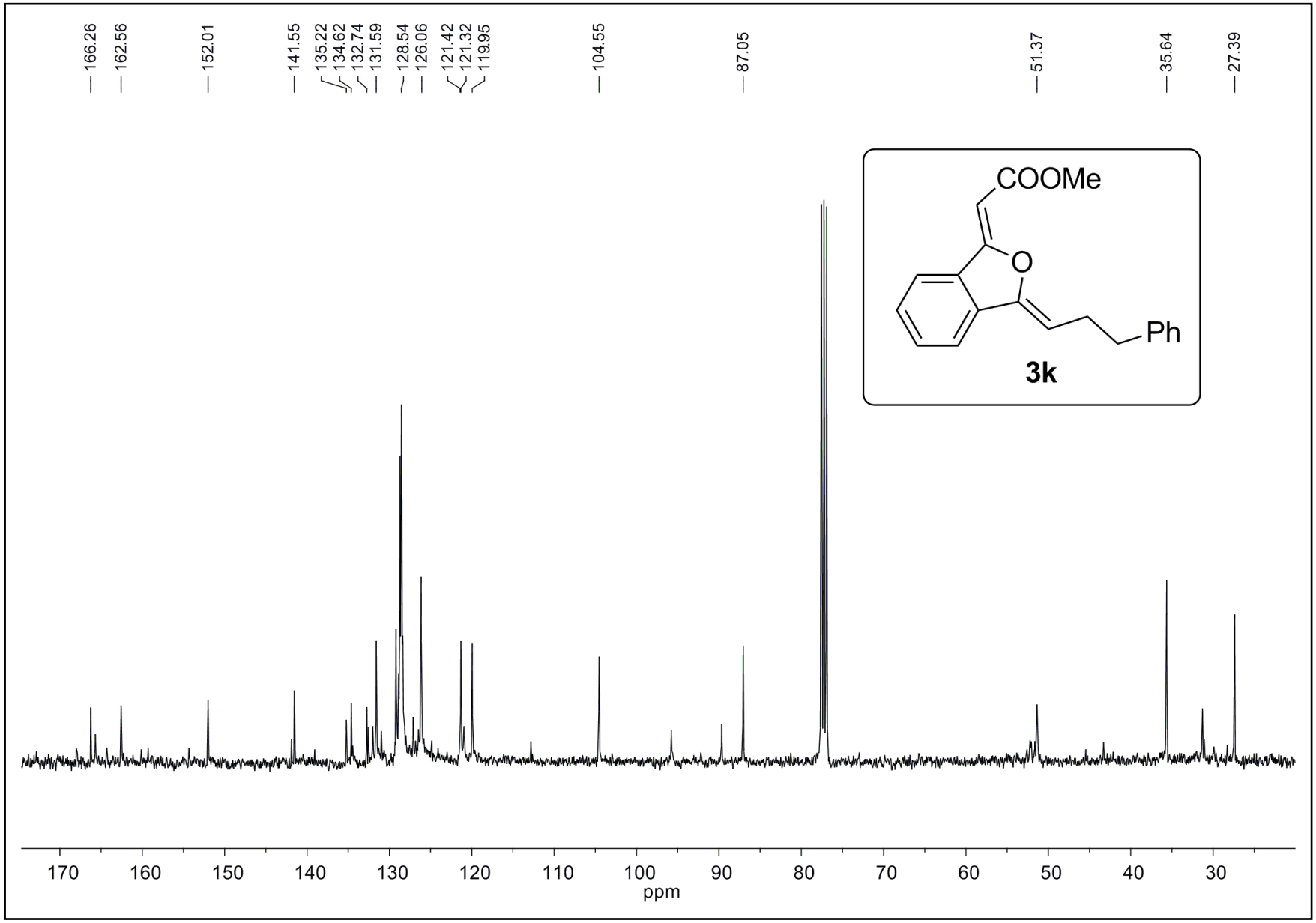
ppm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152.01
141.55
135.22
134.62
132.74
131.59
128.54
126.06
121.42
121.32
119.95
104.55
87.05
51.37
35.64
27.39
COOMe
O
Ph
3k
170
160
150
140
130
120
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90
80
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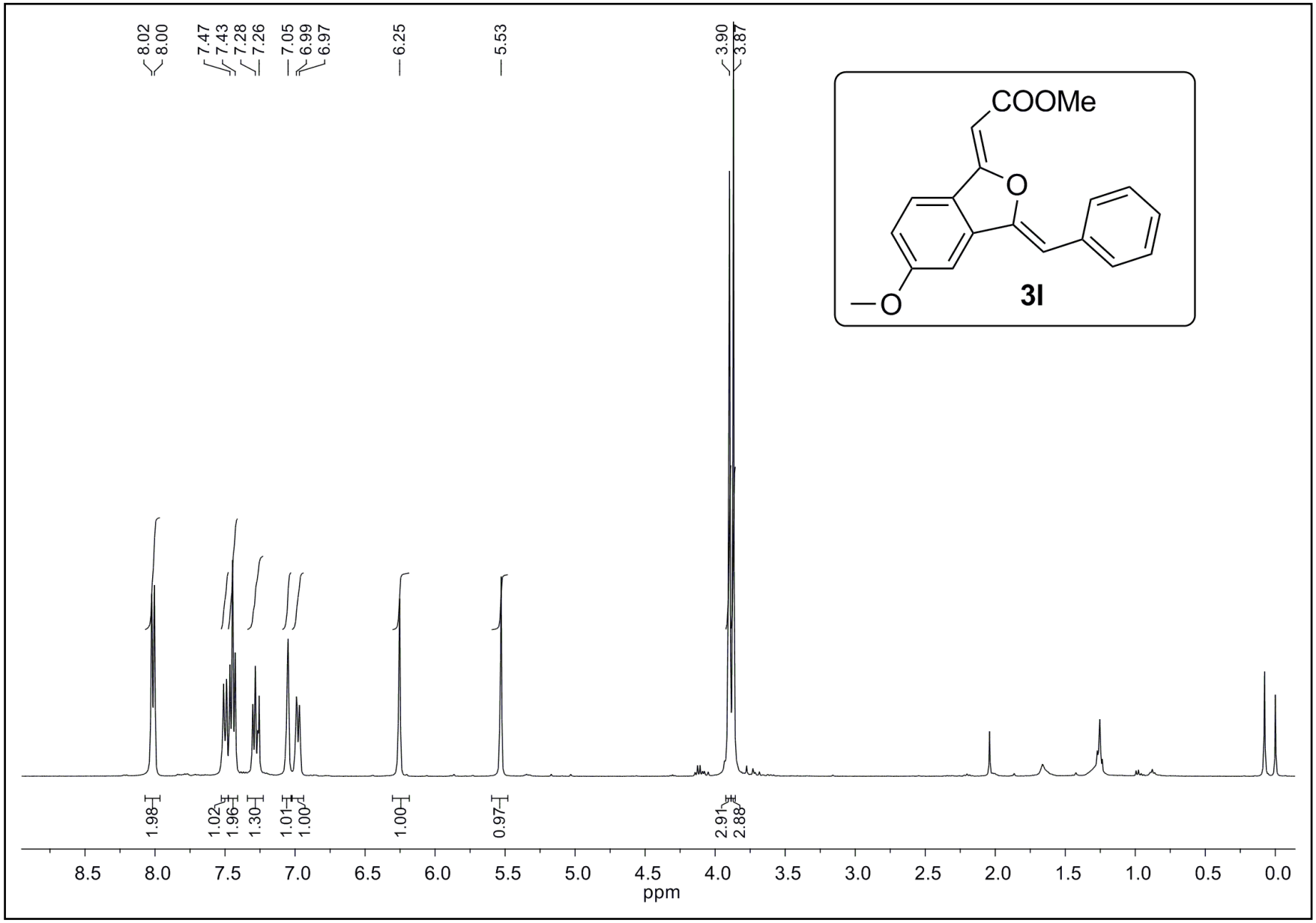
30
ppm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8.00
7.47
7.43
7.28
7.26
7.05
6.99
6.97
6.25
5.53
3.90
3.87
COOMe
O
O
3I
1.98
1.02
1.96
1.30
1.01
1.00
1.00
0.97
2.91
2.88
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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4.0
3.5
3.0
2.5
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1.5
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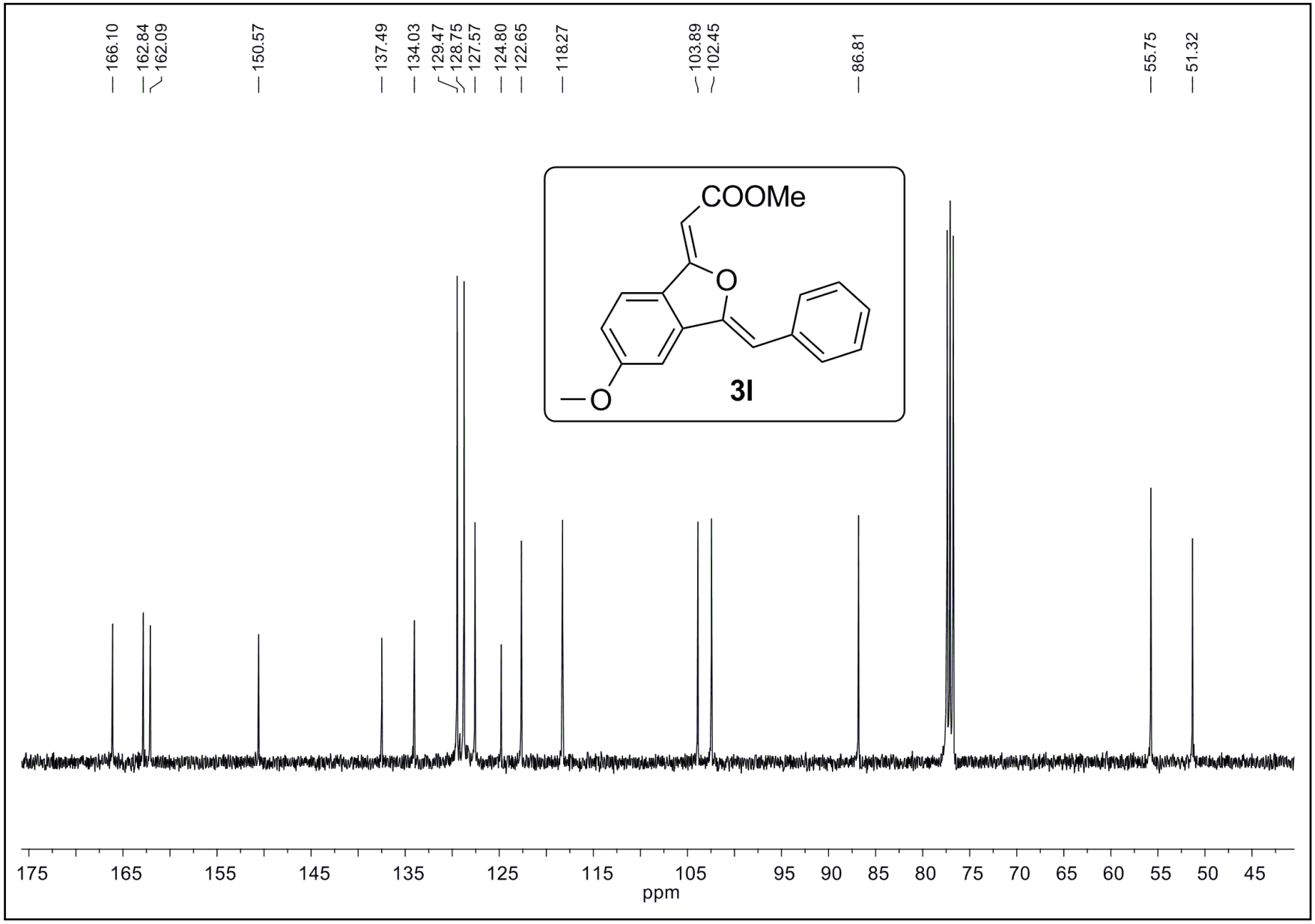
ppm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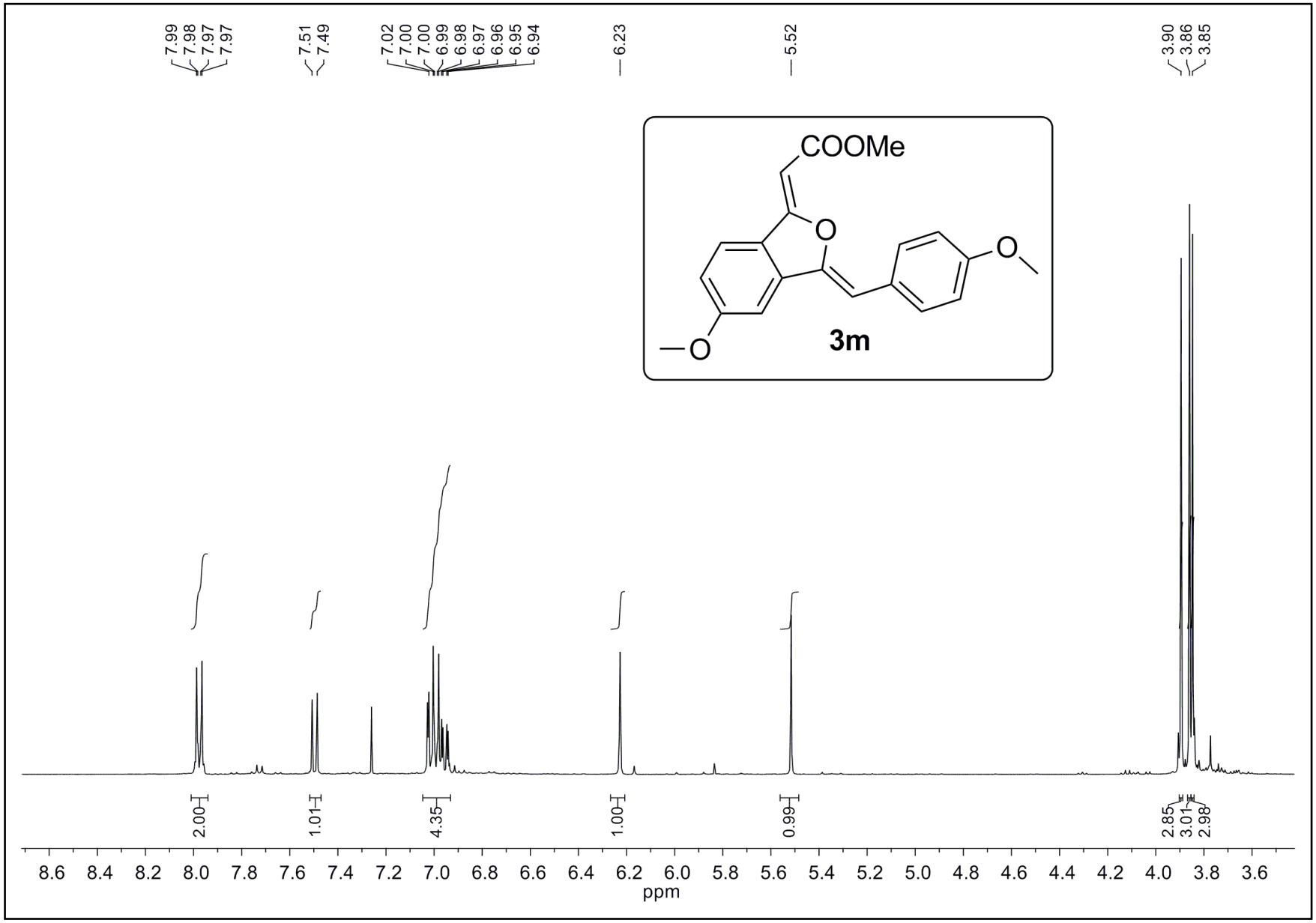
162.84
162.09
150.57
137.49
134.03
129.47
128.75
127.57
124.80
122.65
118.27
103.89
102.45
86.81
55.75
51.32
COOMe
O
O
3l
175
165
155
145
135
125
115
105
95
90
85
80
75
70
65
60
55
50
45
ppm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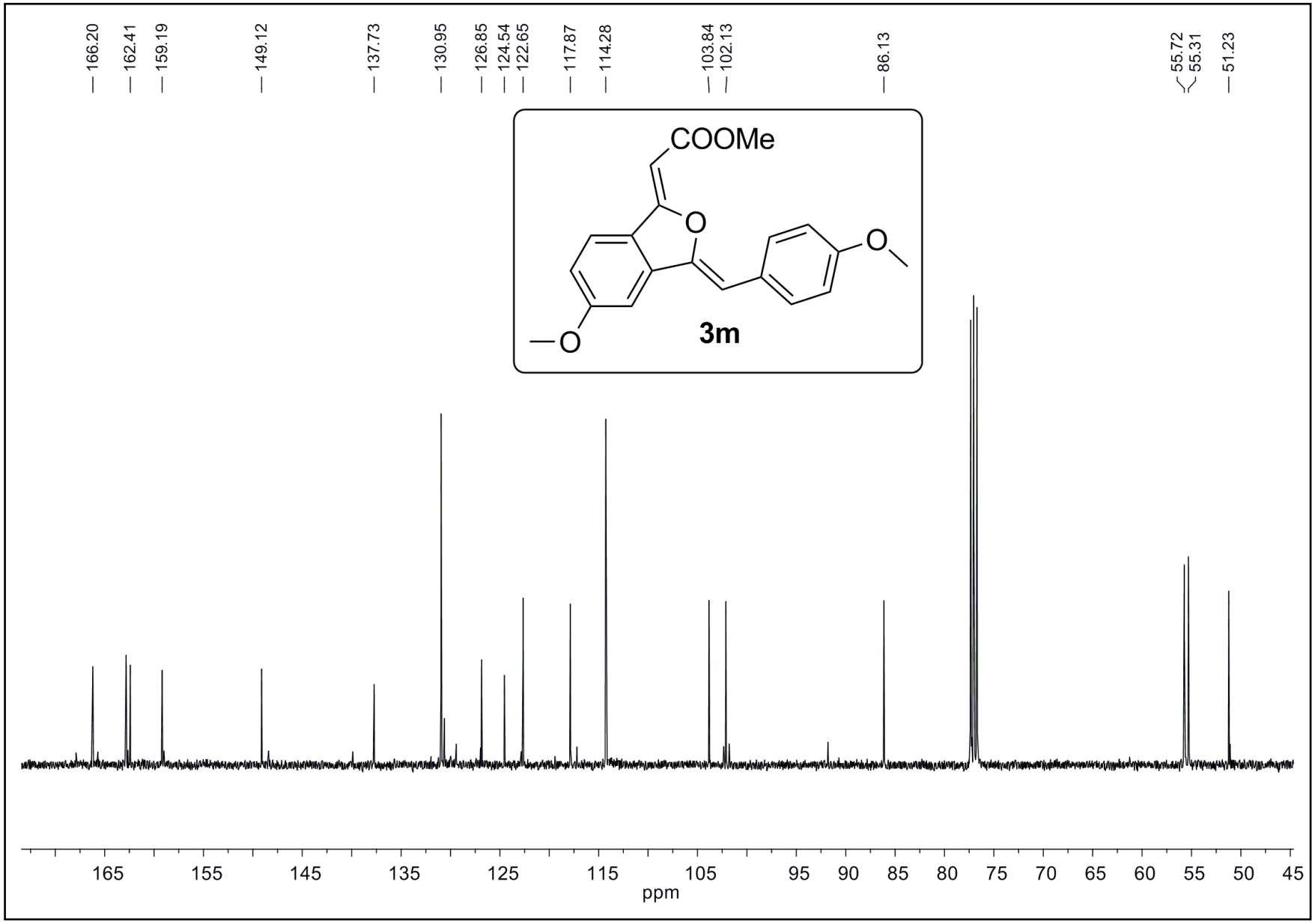
7.98
7.97
7.97
7.51
7.49
7.02
7.00
7.00
6.99
6.98
6.97
6.96
6.95
6.94
6.23
5.52
3.90
3.86
3.85
COOMe
O
O
O
3m
2.00
1.01
4.35
1.00
0.99
2.85
3.01
2.98
8.6 8.4 8.2 8.0 7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6
ppm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159.19
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124.54
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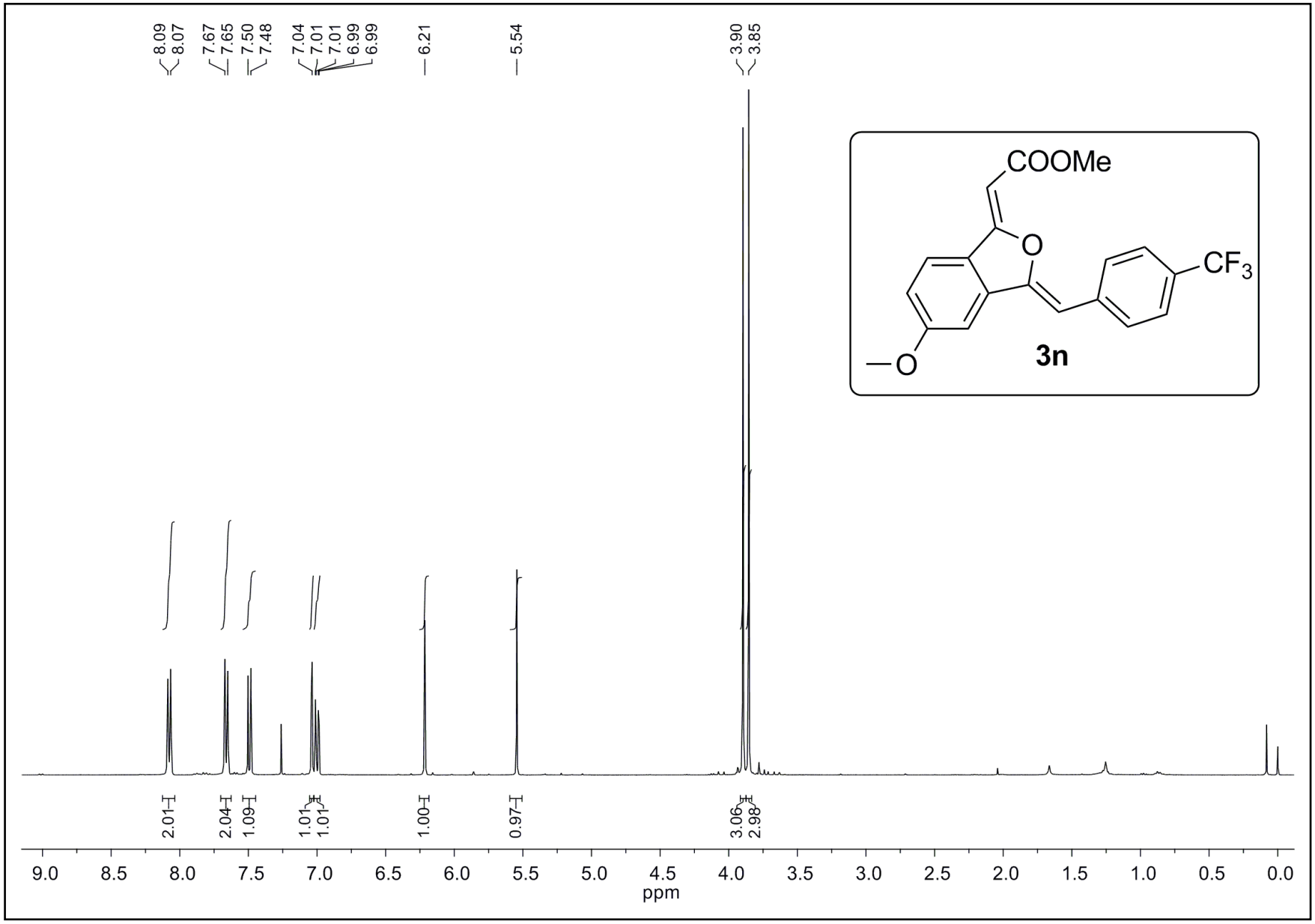
117.87
114.28
103.84
102.13
86.13
55.72
55.31
51.23
COOMe
O
O
O
3m
165
155
145
135
125
115
105
95
90
85
80
75
70
65
60
55
50
45
ppm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8.07
7.67
7.65
7.50
7.48
7.04
7.01
7.01
6.99
6.99
6.21
5.54
3.90
3.85
COOMe
O
CF3
O
3n
2.01
2.04
1.09
1.01
1.01
1.00
0.97
3.06
2.98
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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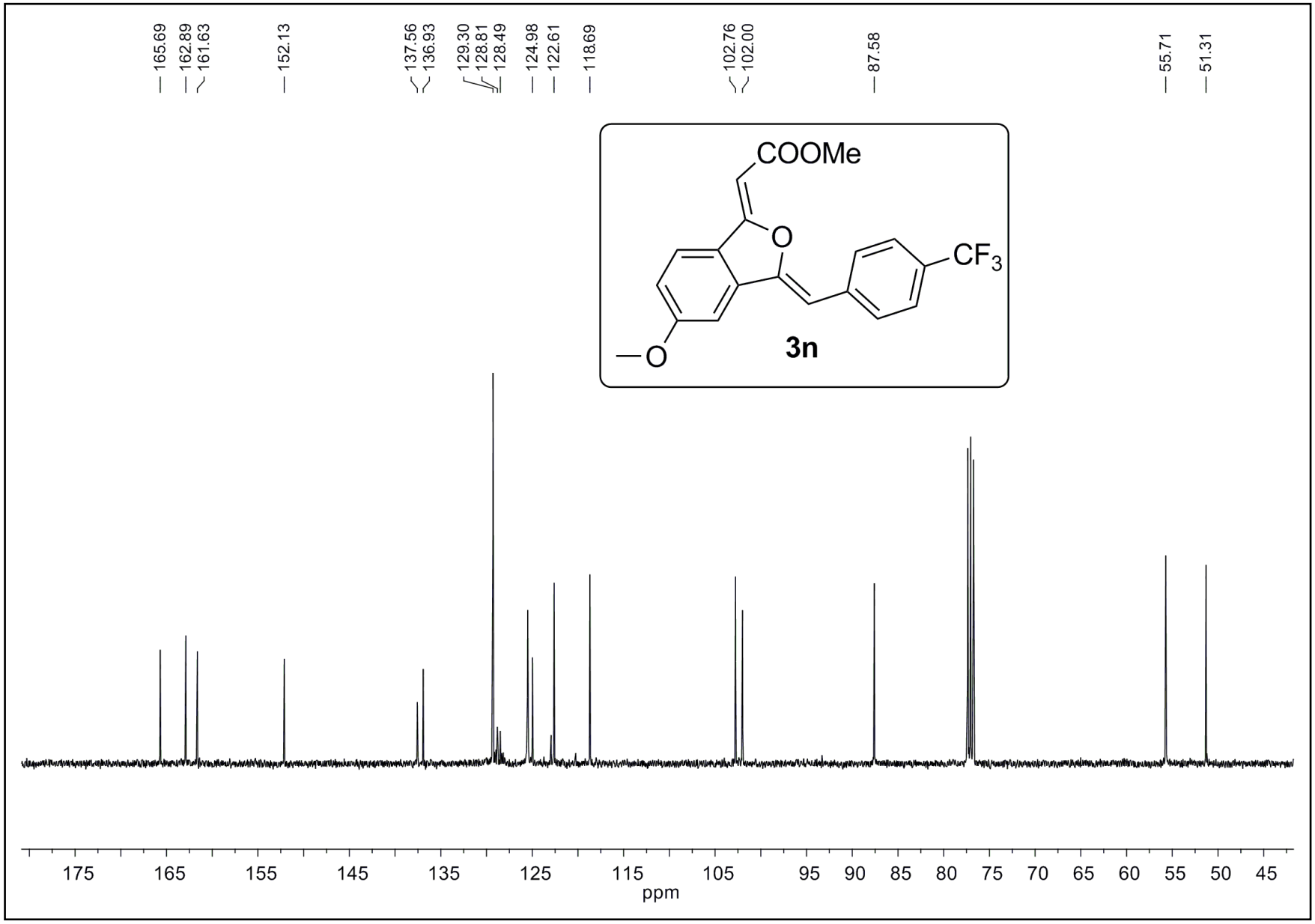
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm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124.98
122.61
118.69
102.76
102.00
87.58
55.71
51.31
COOMe
O
CF3
O
3n
175
165
155
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135
125
115
105
95
90
85
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75
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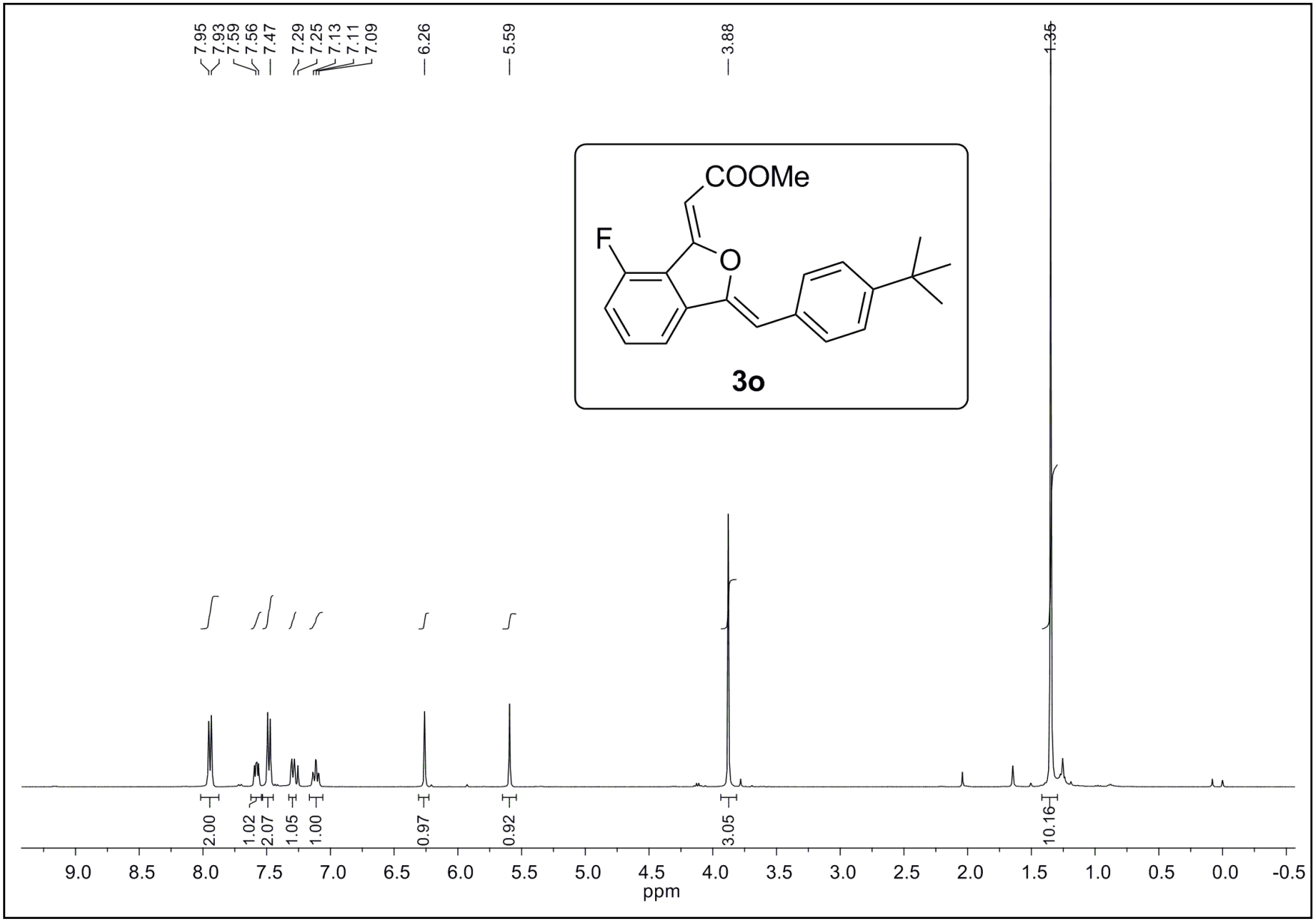
50
45
ppm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7.56
7.47
7.29
7.25
7.13
7.11
7.09
6.26
5.59
3.88
1.35
COOMe
F
O
3o
2.00
1.02
2.07
1.05
1.00
0.97
0.92
3.05
10.16
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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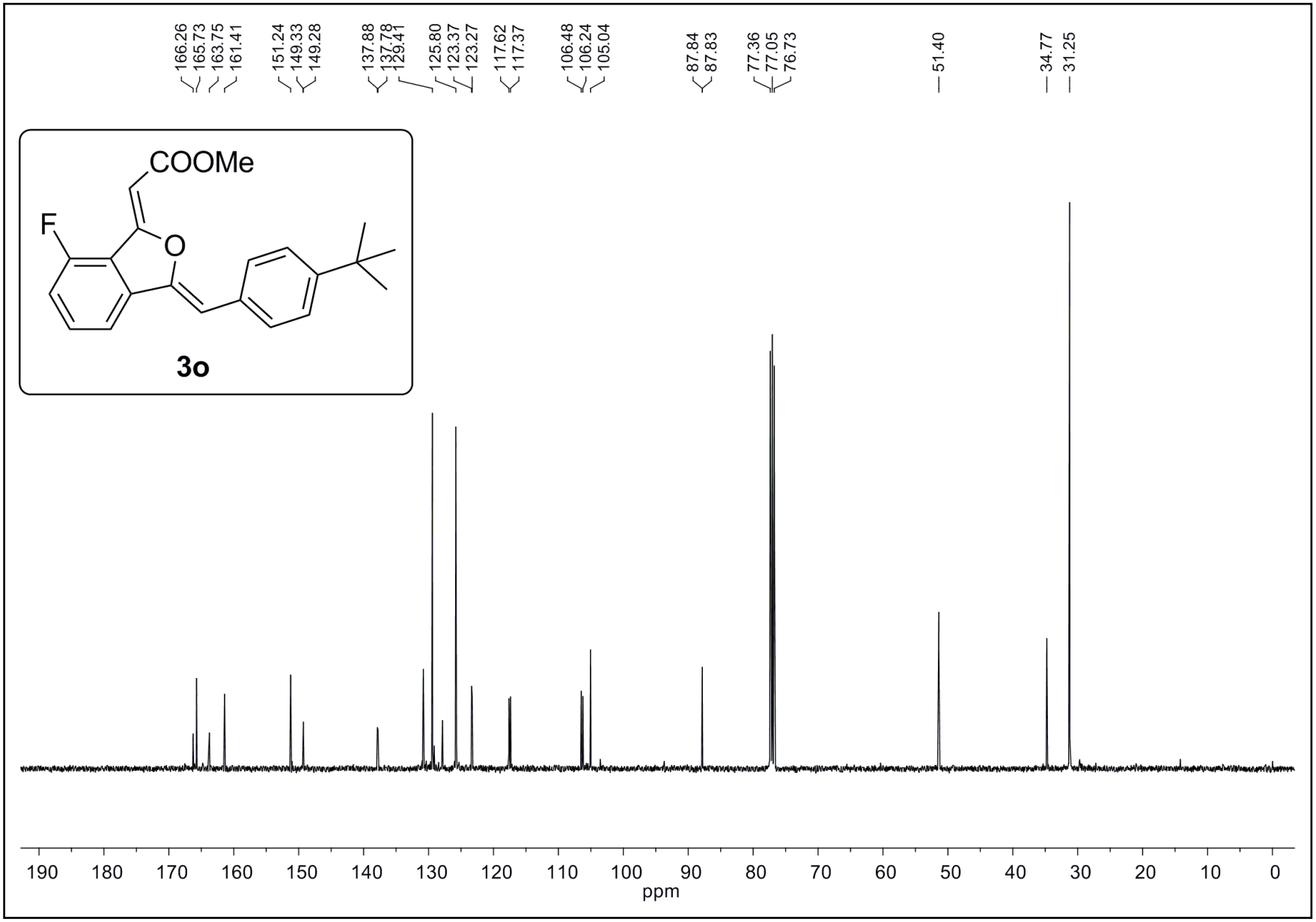
ppm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129.41
125.80
123.37
123.27
117.62
117.37
106.48
106.24
105.04
87.84
87.83
77.36
77.05
76.73
51.40
34.77
31.25
COOMe
F
O
3o
190
180
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140
130
120
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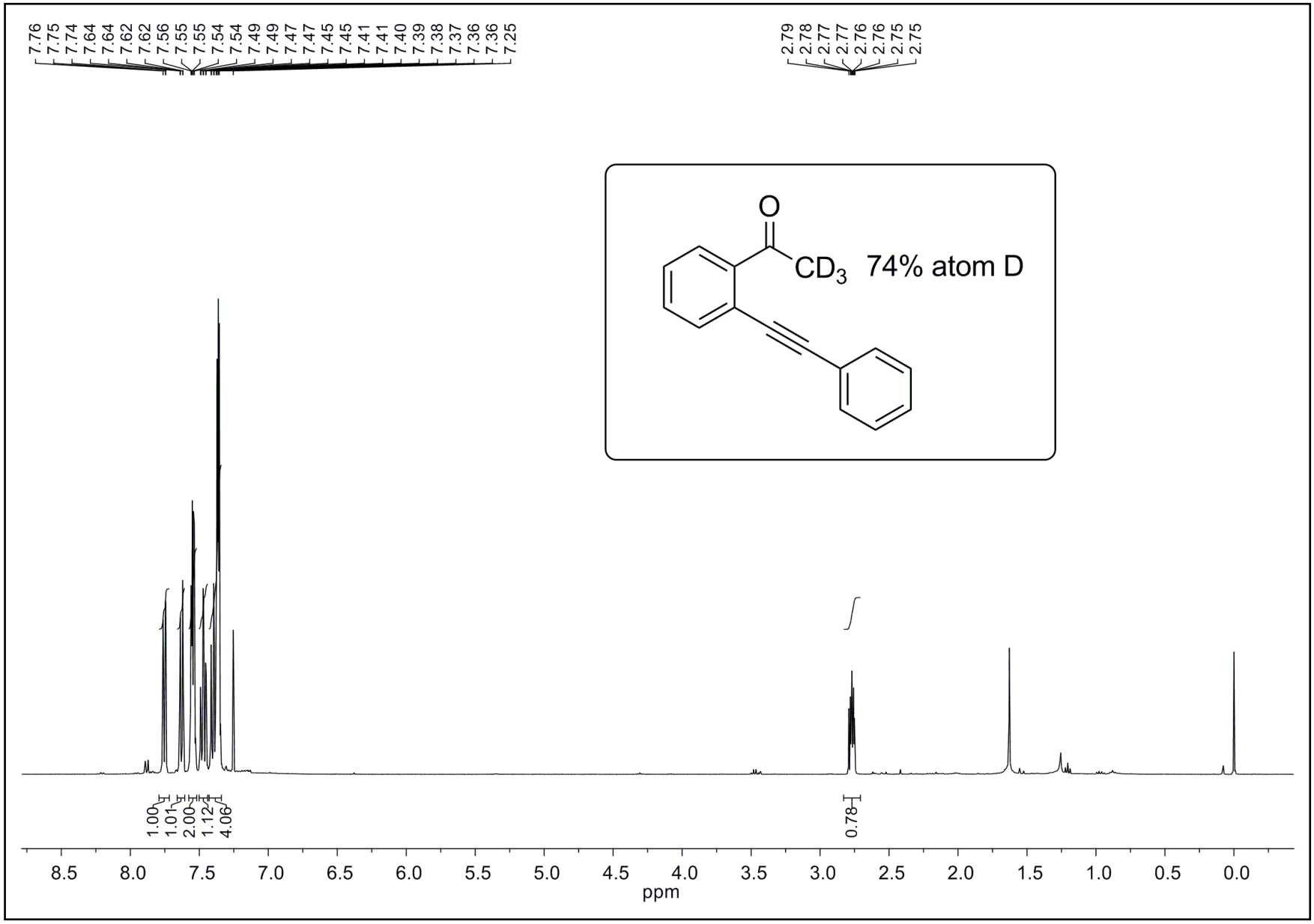
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7.54
7.49
7.49
7.47
7.47
7.45
7.45
7.41
7.41
7.40
7.39
7.38
7.37
7.36
7.36
7.25
2.79
2.78
2.77
2.77
2.76
2.76
2.75
2.75
O
CD3
74% atom D
1.00
1.01
2.00
1.12
4.06
0.78
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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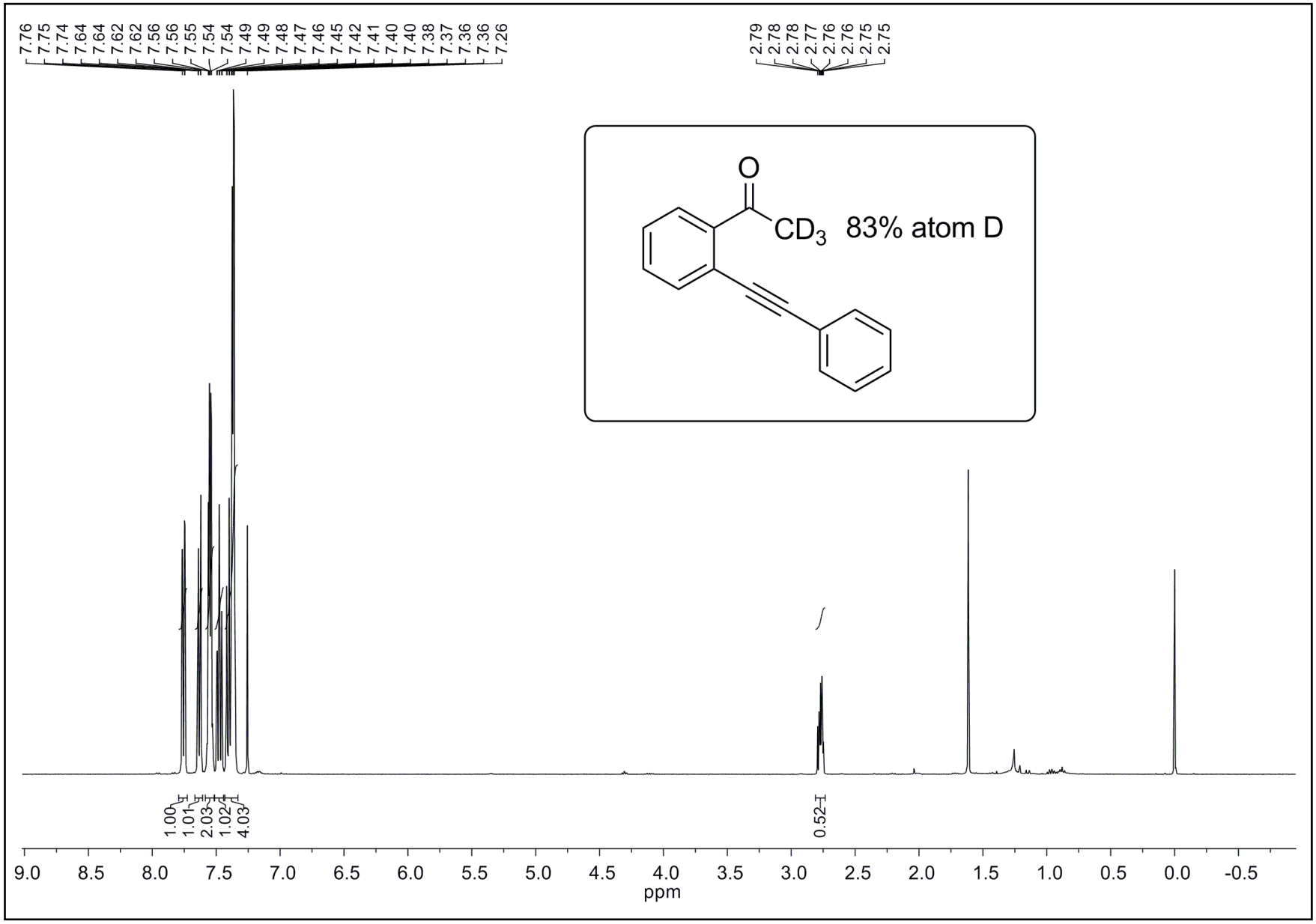
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm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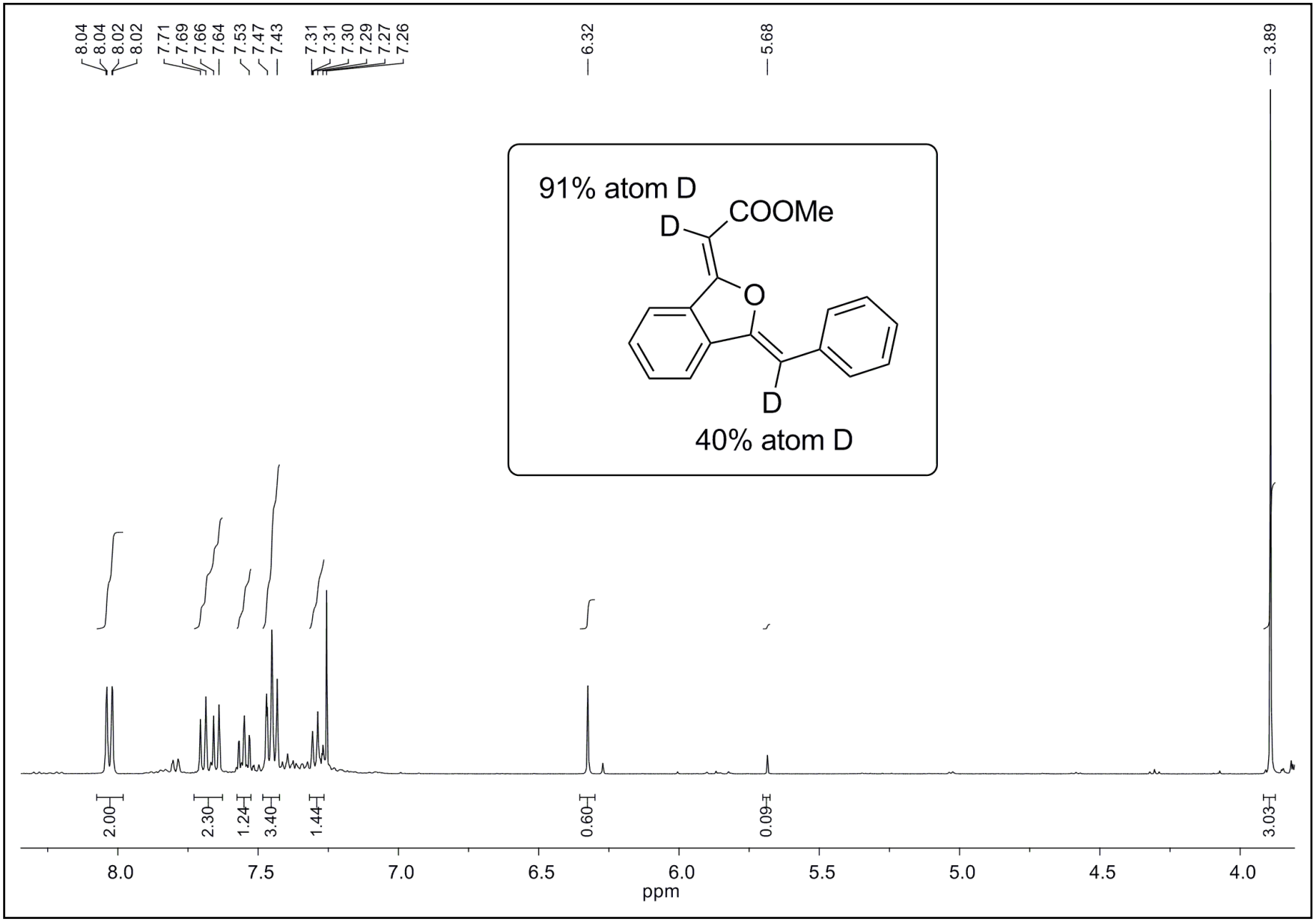
7.75
7.74
7.64
7.64
7.62
7.62
7.56
7.56
7.55
7.54
7.54
7.49
7.49
7.48
7.47
7.46
7.45
7.42
7.41
7.40
7.40
7.38
7.37
7.36
7.36
7.26
2.79
2.78
2.78
2.77
2.76
2.76
2.75
2.75
O
CD3 83% atom D
1.00
1.01
2.03
1.02
4.03
0.52
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
ppm


8.04
8.04
8.02
8.02
7.71
7.69
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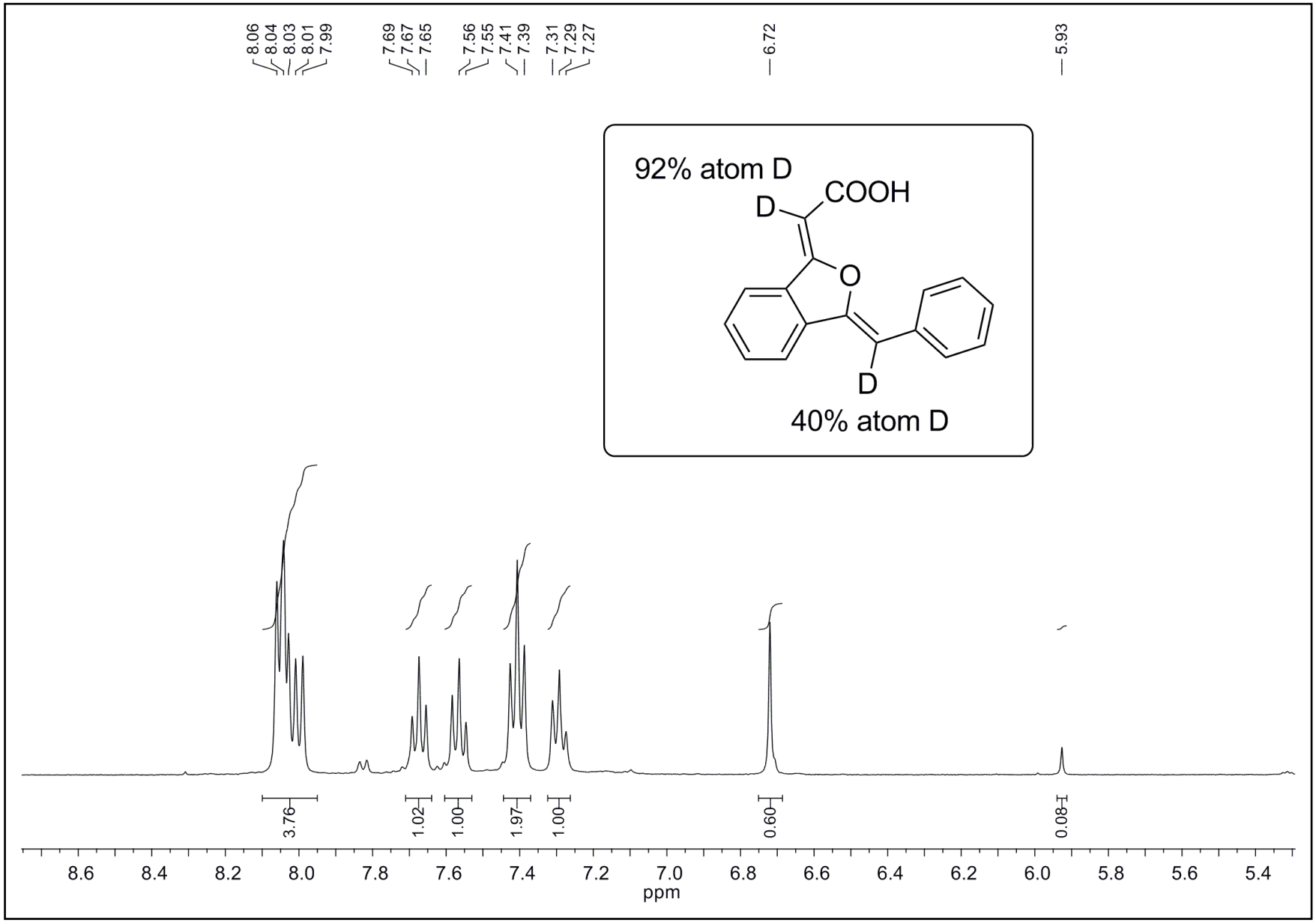
7.64
7.53
7.47
7.43
7.31
7.31
7.30
7.29
7.27
7.26
6.32
5.68
3.89
91% atom D
D
COOMe
O
D
40% atom D
2.00
2.30
1.24
3.40
1.44
0.60
0.09
3.03
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
ppm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8.04
8.03
8.01
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7.69
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7.65
7.56
7.55
7.41
7.39
7.31
7.29
7.27
6.72
5.93
92% atom D
D
COOH
O
D
40% atom D
3.76
1.02
1.00
1.97
1.00
0.60
0.08
8.6
8.4
8.2
8.0
7.8
7.6
7.4
7.2
7.0
6.8
6.6
6.4
6.2
6.0
5.8
5.6
5.4
ppm