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Electronic Supplementary Information (ESI)

Gated Access to α-Lithiated Phenyltetrahydrofuran: Functionalisation via Direct Lithiation of the Parent Oxygen Heterocycle

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1. General Methods

Tetrahydrofuran (THF), diethyl ether, toluene and hexane were freshly distilled under a nitrogen atmosphere: THF and diethyl ether over sodium/benzophenone ketyl, toluene and hexane over calcium hydride. For the ^{1}H and ^{13}C NMR spectra (^{1}H NMR 400 or 600 MHz; ^{13}C NMR 101 or 151 MHz), $CDCl_3$ was used as the solvent. GC-MS spectrometry analyses were performed on a gas chromatograph (dimethylsilicon capillary column, 30 m, 0.25 mm i.d.) equipped with a mass selective detector operating at 70 eV (EI). Elemental analyses were performed by using a Carlo Erba CHNS-O EA1108-Elemental Analyzer. Analytical thin layer chromatography (TLC) was carried out on precoated 0.25 mm thick plates of Kieselgel 60 F254; visualization was accomplished by UV light (254 nm) or by spraying with a solution of 5 % (w/v) ammonium molybdate and 0.2 % (w/v) cerium(III) sulfate in 100 ml 17.6 % (w/v) aq. sulphuric acid and heating to 473 K for some time until blue spots appear. All reactions involving air-sensitive reagents were performed under nitrogen in oven-dried glassware using syringe-septum cap technique. Lithiation-electrophilic trapping reactions were performed in a methanol/liquid N_2 (–98 °C), acetone/liquid N_2 (–90 °C) or acetone/dry ice (–78 °C) cold bath. The enantiomeric ratios were measured by GC analysis employing a Chirasil-DEX CB (250-0.25 mm, column head pressure 26 psi, He flow 1.7 mL min^{-1}). In particular, for compounds (*R*)-**3** and [D]-**3**: isothermal run at 110 °C (t_R = 12.4 min, t_R = 13.3 min); for compound **5d**: isothermal run at 110 °C (t_R = 16.3 min, t_R = 17.1 min).

Compounds **2**[1] and **3**[2] have been synthesized as reported.

Spectroscopic data of compounds **2**[3], **3**[2] and **6a**[4] have been reported.

[1] J. W. Hulshof, P. Casarosa, W. M. P. B. Menge, L. M. S. Kuusisto, H. van der Goot, M. J. Smit, I. J. P. de Esch, R. Leurs, *J. Med. Chem.* 2005, **48**, 6461.
[2] T. H. Chan, P. Pellon, *J. Am. Chem. Soc.* 1989, **111**, 8737.
[3] M. P. Gamble, A. R. C. Smith, M. Wills, *J. Org. Chem.* 1998, **63**, 6068.
[4] S. –i. Fukuzawa, K. Seki, M. Tatsuzawa, K. Mutoh *J. Am. Chem. Soc.* 1997, **119**, 1482.

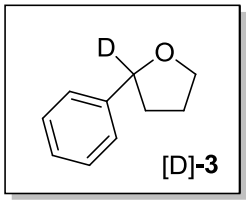
2. Experimental procedures and characterization data

Preparation of [D]-3 or 2-substituted-2-phenyltetrahydrofurans 5a–k – General procedure:

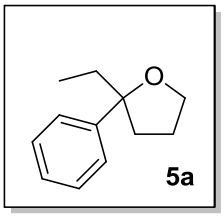
A solution of **3** (148 mg, 1.0 mmol) and TMEDA (0.23 mL, 1.5 mmol) in 5 mL of dry toluene was cooled to –78 °C and treated with *s*-BuLi (1.08 mL, 1.5 mmol, 1.4 M solution in cyclohexane) under N_2. The color of the mixture became green. After stirring for 2 min at the above temperature, MeOD (10 mmol) or the electrophile (2.0 mmol) (as pure liquid or as a solution in 1 mL of toluene if solid) was added all at once and the mixture was stirred for an additional 30 min at –78 °C. After this time, 5 mL of water was added and the reaction mixture was allowed to warm to room temperature and finally extracted with AcOEt (3 × 10 mL). The combined organic phases were dried over Na_2SO_4 and concentrated *in vacuo*. The crude product was purified by flash-chromatography (silica gel; hexane/AcOEt 9/1÷95/5).

Preparation of γ-butyrolactone 6a[4]

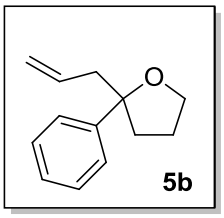
A suspension of $RuO_2{\cdot}H_2O$ (21 mg, 0.16 mmol) and $NaIO_4$ (1.04 g, 4.88 mmol) in H_2O (5 ml) was added to a solution of **5a** (1.0 mmol) in CCl_4 (5 mL) at room temperature. After stirring for 24 h, additional water was added (5 mL), and the resulting mixture was extracted with CH_2Cl_2 (3 x 5 mL). The combined organic phases were dried over Na_2SO_4, passed through a pad of celite, and concentrated *in vacuo*. The crude product was purified by flash-chromatography (silica gel; hexane/AcOEt 9/1) to afford the lactone **6** in 70% yield.



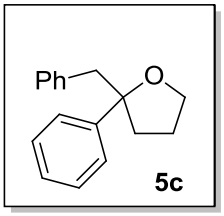
2-Deuterio-2-phenyltetrahydrofuran ([D]-3): colorless oil, >98 %. ^{1}H-NMR (600 MHz; $CDCl_3$): δ 1.80-1.85 (m, 1H), 1.98-2.08 (m, 2H), 2.32-2.36 (m, 1H), 3.94-3.98 (m, 1H), 4.10-4.12 (m, 1H), 7.25-7.28 (m, 1H), 7.35-7.36 (m, 4H); ^{13}C-NMR (151 MHz; $CDCl_3$): δ 26.0, 34.5, 68.7, 80.2 (t, $^1J_{C\text{-}D}$ = 23 Hz), 125.6, 127.1, 128.3, 143.4; GC-MS (70 eV) m/z (%): 149 (M^+, 15), 148 (13), 123 (41), 105 (100), 77 (38);



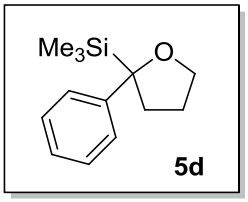
2-Ethyl-2-phenyltetrahydrofuran (5a): colorless oil, 74%. ^{1}H-NMR (400 MHz; $CDCl_3$): δ 0.76 (t, *J* = 7.4 Hz, 3H), 1.86-1.74 (m, 3H), 1.98-1.90 (m, 1H), 2.07-2.00 (m, 1H), 2.21-2.14 (m, 1H), 3.88 (td, *J* = 8.0, 5.7 Hz, 1H), 4.00-3.94 (m, 1H), 7.23-7.19 (m, 1H), 7.37-7.29 (m, 4H). ^{13}C-NMR (101 MHz; $CDCl_3$): δ 8.7, 25.6, 35.0, 37.7, 67.4, 77.4, 87.1, 125.3, 127.8, 146.5 GC-MS (70 eV) m/z (%): 176 (M^+, 3), 147 (100), 105 (55), 77 (16); FT-IR (film, cm^{-1}) 3024, 2967, 2929, 1492, 1446, 1057, 758, 701. Anal. Calcd. for $C_{12}H_{16}O$: C, 81.77; H, 9.15; Found: C, 81.93; H, 9.27.



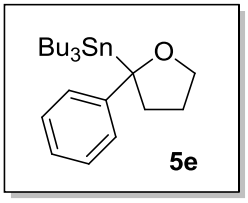
2-Allyl-2-phenyltetrahydrofuran (5b): colorless oil, >98%. ^{1}H-NMR (400 MHz; $CDCl_3$): δ 1.77-1.66 (m, 1H), 1.92-1.82 (m, 1H), 2.10-2.03 (m, 2H), 2.48-2.42 (m, 1H), 2.57-2.52 (m, 1H), 3.83 (td, *J* = 8.0, 5.8 Hz, 1H), 3.96-3.90 (m, 1H), 4.97-4.91 (m, 2H), 5.67-5.57 (m, 1H), 7.17-7.13 (m, 1H), 7.32-7.24 (m, 4H). ^{13}C-NMR (101 MHz; $CDCl_3$): δ 25.5, 37.2, 46.9, 67.7, 86.2, 117.4, 125.2, 126.3, 127.9, 134.3, 146.6; GC-MS (70 eV) m/z (%): 188 (M^+, 2), 147 (100), 105 (70), 77 (21); FT-IR (film, cm^{-1}) 2976, 2872, 1446, 1055, 914, 762, 703. Anal. Calcd. for $C_{13}H_{16}O$: C, 82.94; H, 8.57; Found: C, 82.80; H, 8.68.



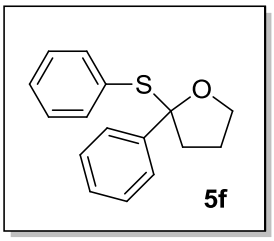
2-Benzyl-2-phenyltetrahydrofuran (5c): colorless oil, 90% yield. ^{1}H-NMR (600 MHz; $CDCl_3$): δ 1.75-1.80 (m, 2H), 2.12-2.22 (m, 2H), 3.03 (d, *J* = 13.5 Hz, 1H), 3.12 (d, *J* = 13.5 Hz, 1H), 3.85-3.89 (m, 1H), 3.91-3.94 (m, 1H), 7.04-7.05 (m, 2H), 7.18-7.24 (m, 4H), 7.28-7.32 (m, 4H). ^{13}C-NMR (101 MHz; $CDCl_3$): δ 25.5, 36.8, 48.6, 67.54, 87.0, 125.5, 126.0, 126.4, 127.6, 127.8, 130.6, 137.6, 146.7. GC-MS (70 eV) m/z (%): 238 (M+, 2), 147 (100), 105 (52), 77 (17); FT-IR (film, cm^{-1}) 2976, 1454, 1112, 1053, 909, 733, 701. Anal. Calcd. for $C_{17}H_{18}O$: C, 85.67; H, 7.61; Found: C, 85.57; H, 7.80.



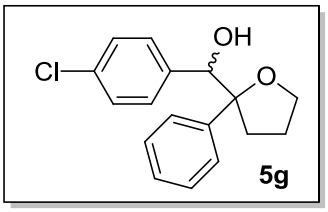
2-Phenyl-2-trimethylsilyltetrahydrofuran (5d): colorless oil, 70 %. ^{1}H-NMR (400 MHz; $CDCl_3$): δ –0.11 (s, 9H), 1.58-1.65 (m, 1H), 1.71-1.79 (m,1H), 2.01-2.09 (m, 1H), 2.15-2.22 (m, 1H); ^{13}C-NMR (101 MHz; $CDCl_3$): δ -4.0, 26.1, 34.6, 67.3, 80.9, 124.5, 125.0, 127.7, 146.3; GC-MS (70 eV) m/z (%): 220 (M^+, 11), 219 (18), 192 (58), 191 (100), 177 (73), 147 (97), 105 (82), 77 (30); FT-IR (film, cm^{-1}) 2926, 1445, 1246, 1030, 838, 758, 702. Anal. Calcd. for $C_{13}H_{20}OSi$: C, 70.85; H, 9.15; Found: C, 70.97; H, 9.40.



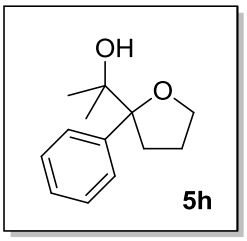
2-Phenyl-2-tributylstannyltetrahydrofuran (5e): colorless oil, 40 %. ^{1}H-NMR (400 MHz; $CDCl_3$): δ 0.77- 0.84 (m, 14H), 1.17-1.27 (m, 7H), 1.32-1.40 (m, 6H), 1.62-1.71 (m, 1H), 1.77-1.86 (m, 1H), 2.21-2.29 (m, 1H), 2.37-2.43 (m, 1H), 3.75-3.88 (m, 2H), 7.00-7.04 (m, 1H), 7.14-7.16 (m, 2H), 7.21-7.24 (m, 2H); ^{13}C-NMR (151 MHz; $CDCl_3$): δ 9.5, 13.6, 25.0, 27.4, 28.9, 37.3, 66.6, 85.5, 122.8, 124.1, 128.0, 149.5; GC-MS (70 eV) m/z (%): 220 (M^+, 11), 219 (18), 192 (58), 191 (100), 177 (73), 147 (97), 105 (82), 77 (30); FT-IR (film, cm^{-1}) 2926, 1445, 1246, 1030, 838, 758, 702. Anal. Calcd. for $C_{22}H_{38}OSn$: C, 60.43; H, 8.76; Found: C, 60.67; H, 8.95.



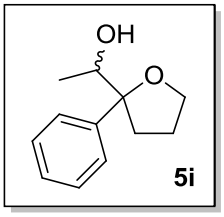
2-Phenyl-2-(phenylthio)tetrahydrofuran (5f): colorless oil**,** 85%, ^{1}H-NMR (400 MHz; $CDCl_3$): δ 1.92-2.00 (m, 1H), 2.11-2.21 (m, 1H), 2.55-2.61 (m, 1H), 3.10-3.19 (m, 1H), 4.11-4.17 (m, 1H), 4.26-4.31 (m, 1H), 7.09-7.31 (m, 8H), 7.37-7.39 (m, 2H). ^{13}C-NMR (101 MHz; $CDCl_3$): δ 24.7, 40.2, 67.7, 98.2, 125.7, 126.7, 127.3, 127.9, 132.6, 135.5, 144.0. GC-MS (70 eV) m/z (%): 256 (M^+, 2), 147 (100), 105 (35), 77 (20); FT-IR (film, cm^{-1}) 2966, 1583, 1438, 1060, 1027, 748. Anal. Calcd. for $C_{16}H_{16}OS$: C, 74.96; H, 6.29; Found: C, 75.14; H, 6.33.



(4-Chlorophenyl)(2-phenyltetrahydrofuran-2-yl)methanol (5g): Inseparable mixture of diastereomers, colorless oil, 45 % overall yield (dr 60/40). ^{1}H-NMR (600 MHz; $CDCl_3$): δ 1.69-1.95 (m, 2H major + 2H minor), 1.95-2.04 (m, 1H minor), 2.19-2.23 (m, 1H major), 2.33-2.38 (m, 1H minor), 2.48-2.53 (m, 1H major), 2.83 (br s, exchanges with D_2O , 1H major + 1H minor), 3.81-3.85 (m, 1H minor), 3.87-3.91 (m, 1H major), 3.98-4.02 (m, 1H minor), 4.03-4.07 (m, 1H major), 4.76 (s, 1H minor), 4.78 (s, 1H major), 6.95-6.98 (m, 2H major + 2H minor), 7.1-7.30 (m, 7H major + 7H minor). ^{13}C-NMR (151 MHz; $CDCl_3$): δ 25.4, 25.9, 30.4, 34.9, 67.8, 68.3, 78.8, 78.9, 89.4, 90.0, 126.4, 126.7, 126.9, 127.5, 127.6, 127.8, 128.9, 129.1, 133.0, 133.4, 137.5, 138.5, 142.3, 142.4. GC-MS (70 eV) m/z (%): 288 (M^+, 2), 270 (1), 147 (100), 15 (51), 77 (23). FT-IR (film, cm^{-1}) 3405, 2925, 1492, 1089, 1043, 1014, 829, 701. Anal. Calcd. for $C_{17}H_{17}ClO_2$: C, 70.71; H, 5.93; Found: C, 70.92; H, 6.11.

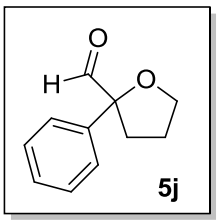


2-(2-Phenyltetrahydrofuran-2-yl)propan-2-ol (5h): white solid**,** 70%, mp 61-62 °C (from Et_2O) **,** ^{1}H-NMR (600 MHz; $CDCl_3$): δ 1.03 (s, 3H), 1.24 (s, 3H), 1.71-1.64 (m, 1H), 1.89-1.95 (m, 1H), 2.22-2.26 (m, 1H), 2.47-2.53 (m, 1H), 2.54 (br s, exchanges with D_2O, 1H), 3.80-3.84 (m, 1H), 3.97-4.00 (m, 1H), 7.24-7.27 (m, 1H), 7.31-7.34 (m, 2H), 7.46-7.47 (m, 2H). ^{13}C-NMR (151 MHz; $CDCl_3$): δ 24.7, 25.8, 26.1, 32.4, 67.6, 73.9, 92.1, 126.8, 126.9, 127.6, 143.2. GC-MS (70 eV) m/z (%): 206 (M^+, 2), 191 (12), 147 (100), 148 (34), 105 (53), 77 (17); FT-IR (film, cm^{-1}) 3467, 2969, 1442, 1364, 1178, 1045, 758, 702. Anal. Calcd. for $C_{13}H_{18}O_2$: C, 75.69; H, 8.80; Found: C, 75.91; H, 9.02.

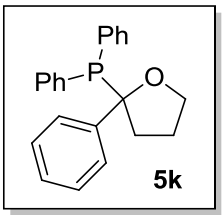


1-(2-Phenyltetrahydrofuran-2-yl)ethanol (5i): Inseparable mixture of diastereomers, colorless oil, 80 % overall yield (dr 60/40). ^{1}H-NMR (400 MHz; $CDCl_3$): δ 0.91 (d, *J* = 6.5 Hz, 3H minor), 1.02 (d, *J* = 6.4 Hz, 3H major), 1.70-1.79 (m, 1H major + 1H minor), 1.87-1.97 (m, 1H major + 1H minor), 2.07-2.13 (m, 1H minor), 2.18-2.30 (m, 1H major + 1H minor) , 2.38-2.45 (m, 1H major), 3.69-3.75 (m, 1H major), 3.79-4.01 (m, 2H major + 3H minor), 7.25-7.18 (m,

1H major + 1H minor), 7.32-7.28 (m, 2H major + 4H minor), 7.42-7.40 (m, 2H major). ^{13}C-NMR (101 MHz; CDCl3): δ 17.1, 18.5, 25.6, 26.0, 29.8, 35.2, 67.4, 68.3, 72.7, 72.8, 89.3, 90.0, 125.7, 126.4, 126.6, 127.1, 128.0, 143.1, 144.0. GC-MS (70 eV) m/z (%): 192 (M^+, 2), 147 (100), 105 (62), 77 (22). FT-IR (film, cm^{-1}) 2976, 2874, 1446, 1056, 760, 703. Anal. Calcd. for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39; Found: C, 75.12; H, 8.42.

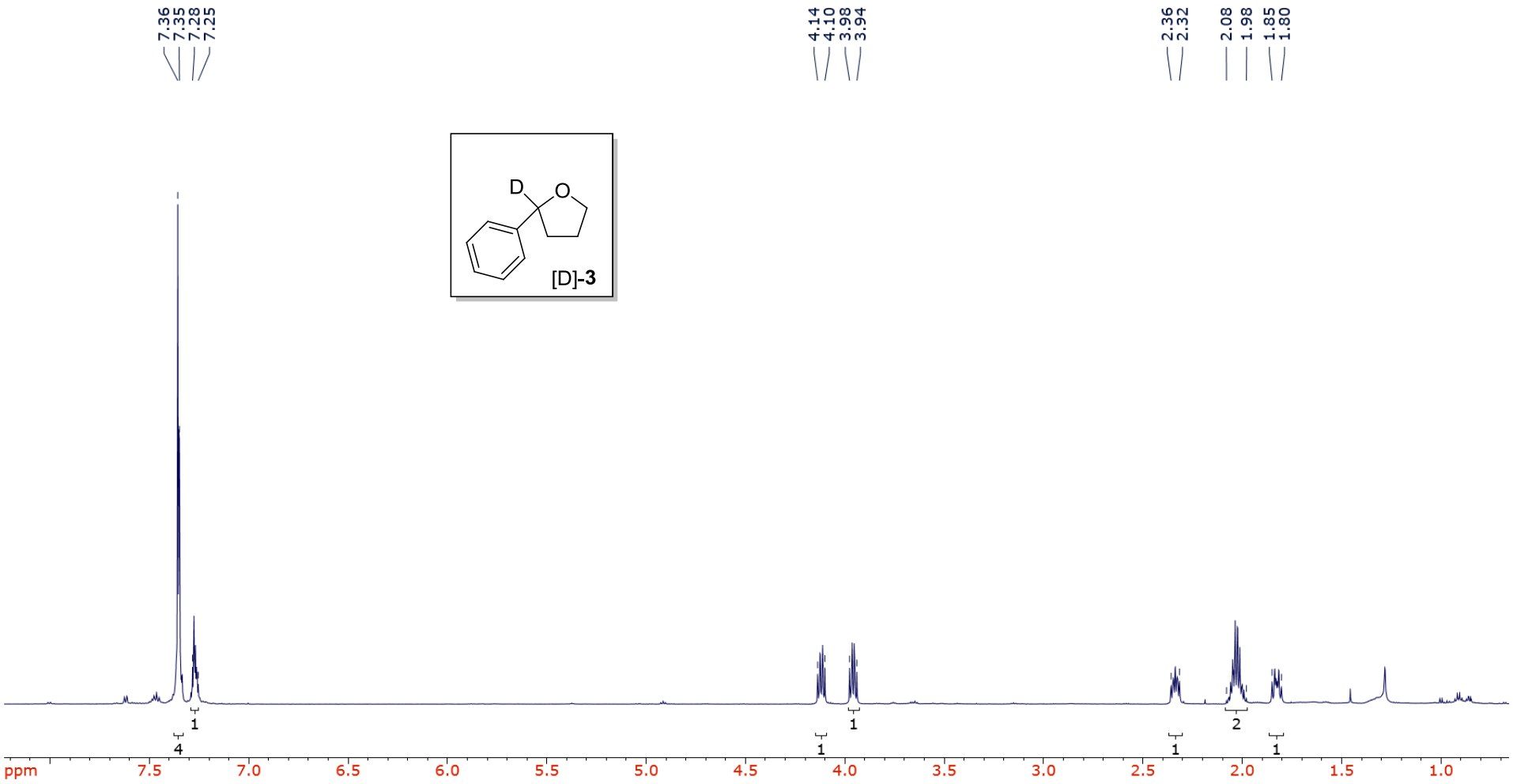


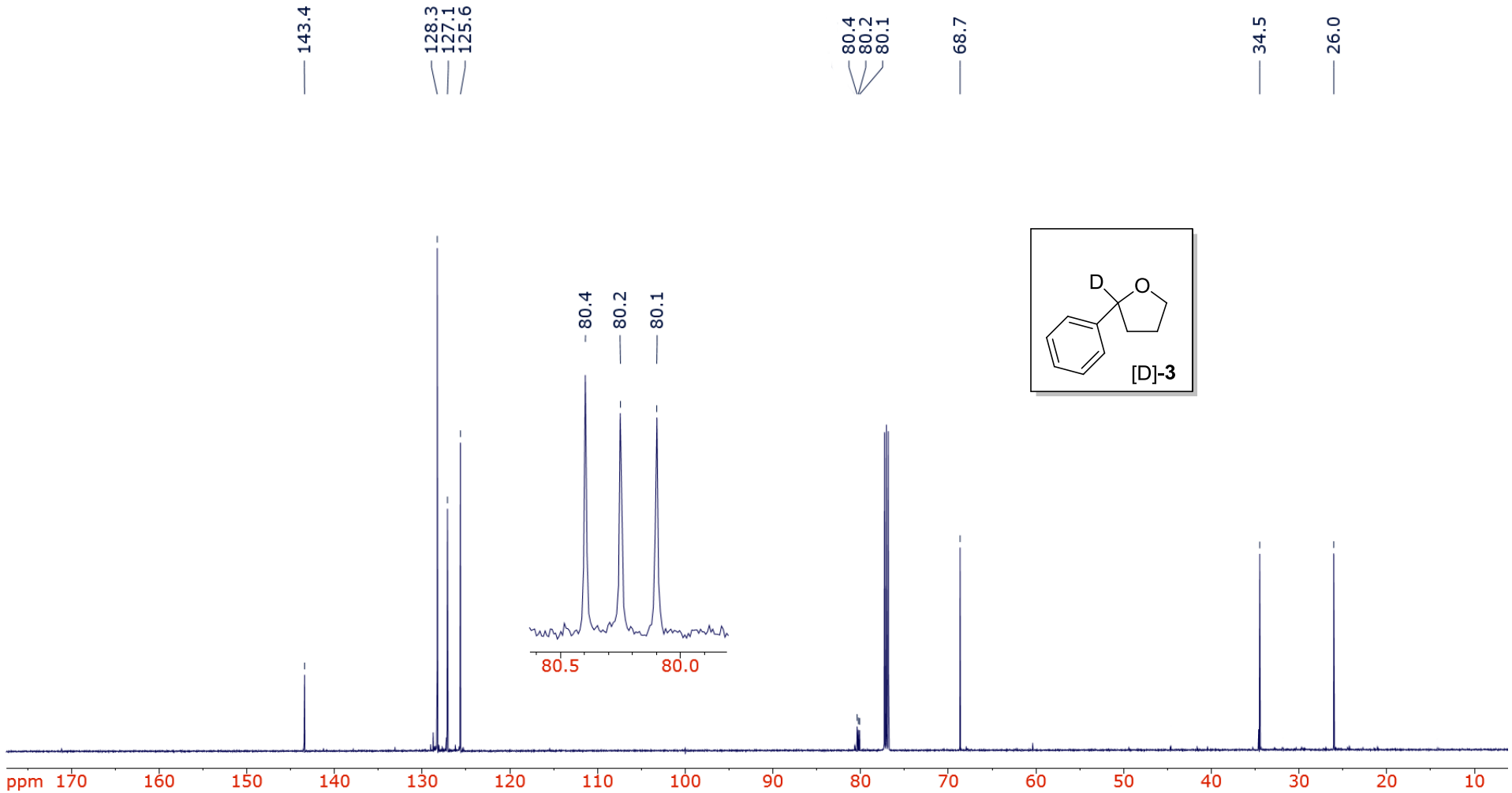
2-Phenyltetrahydrofuran-2-carbaldehyde (5j): colorless oil, 90 %. ^{1}H-NMR (600 MHz; $CDCl_3$): δ 2.05-1.91 (m, 3H), 2.78 (td, *J* = 9.9, 4.6 Hz, 1H), 4.12-4.05 (m, 2H), 7.33-7.30 (m, 1H), 7.40-7.37 (m, 2H), 7.45-7.43 (m, 2H), 9.53 (s, 1H). ^{13}C-NMR (151 MHz; $CDCl_3$): δ 25.9, 33.5, 69.0, 90.8, 125.7, 127.9, 128.6, 138.6, 199.5. GC-MS (70 eV) m/z (%): 176 (M^+, 3), 147 (100), 105 (94), 77 (33). FT-IR (film, cm^{-1}) 3059, 2954, 1731, 1448, 1060, 7600, 701. Anal. Calcd. for $C_{11}H_{12}O_2$: C, 74.98; H, 6.86; Found: C, 75.15; H, 7.08.



Diphenyl(2-phenyltetrahydrofuran-2-yl)phosphine (5k): colorless oil, 65 % yield. ^{1}H-NMR (400 MHz; $CDCl_3$): δ 1.41-1.49 (m, 1H), 1.58-1.66 (m, 1H), 2.33-2.41 (m, 1H), 2.52-2.63 (m, 1H), 3.62-3.68 (m, 1H), 3.95-4.01 (m ,1H), 7.14-7.23 (m, 5H), 7.41-7.51 (m, 6H), 7.70-7.75 (m, 2H), 8.05-8.10 (m, 2H). ^{13}C-NMR (101 MHz; $CDCl_3$): δ 25.0 (d, *J* = 5.1 Hz), 36.8 d, *J* = 3.9 Hz), 69.7 (d, *J* = 6.7 Hz), 86.8 (d, *J* = 90.8 Hz), 126.3 (d, *J* = 3.0 Hz), 127.0 (d, *J* = 2.2 Hz), 127.6, 127.7, 128.1 (d, *J* = 10.9 Hz), 130.2 (br s), 131.2 (d, *J* = 2.4 Hz), 131.6 (d, *J* = 2.5 Hz), 131.8 (d, *J* = 8.6 Hz), 133.0 (d, *J* = 7.9 Hz), 141.0 (d, *J* = 6.6 Hz). GC-MS (70 eV) m/z (%): 332 (M^+, 2), 105 (75), 77 (50). FT-IR (film, cm^{-1}) 3058, 2874, 1438, 1274, 1180, 1115, 756, 722. Anal. Calcd. for $C_{22}H_{21}OP$: C, 79.50; H, 6.37; Found: C, 79.72; H, 6.51.

3. ^{1}H and ^{13}C NMR spectra

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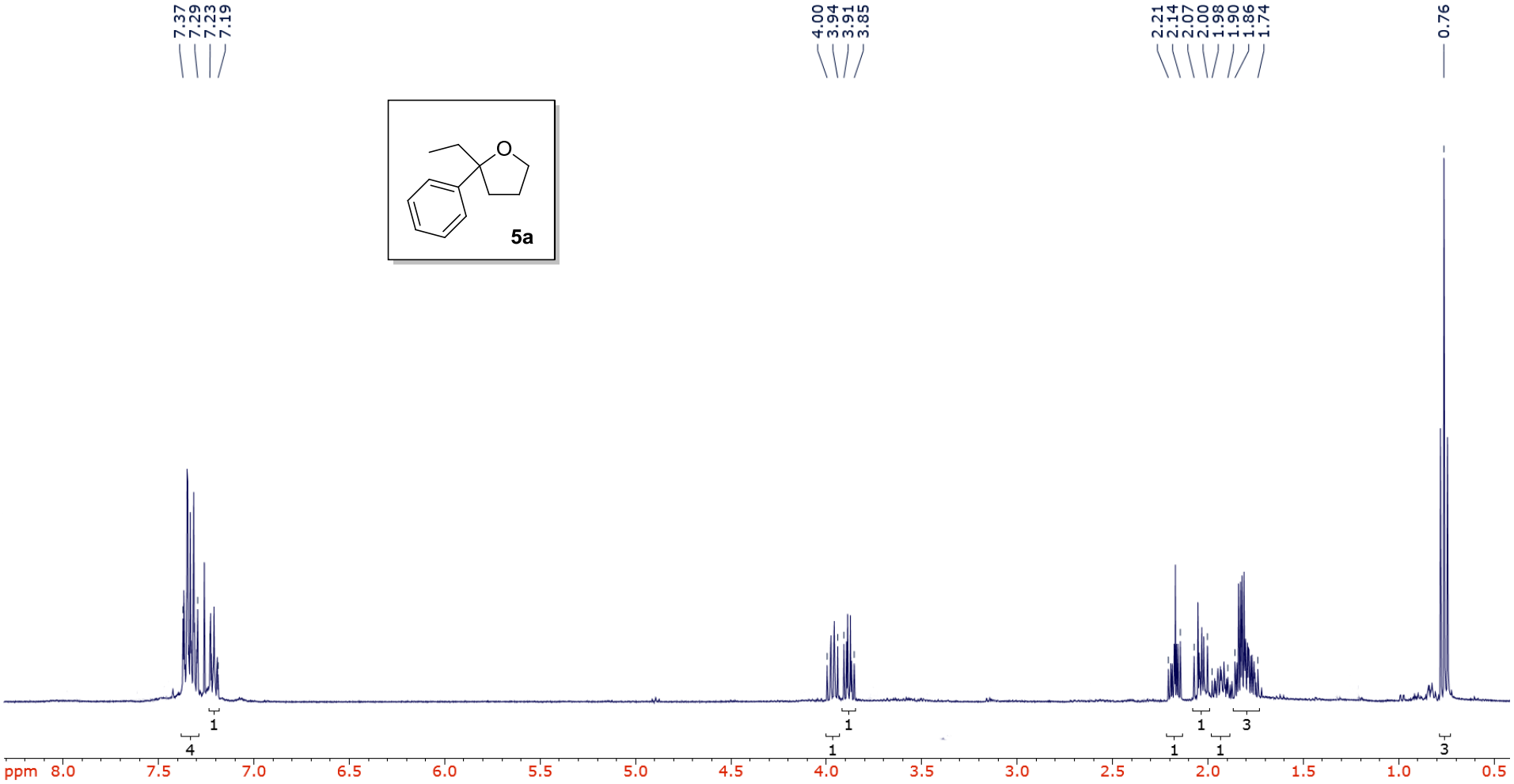
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1.90
1.86
1.74
0.76
O
5a
4
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1
1
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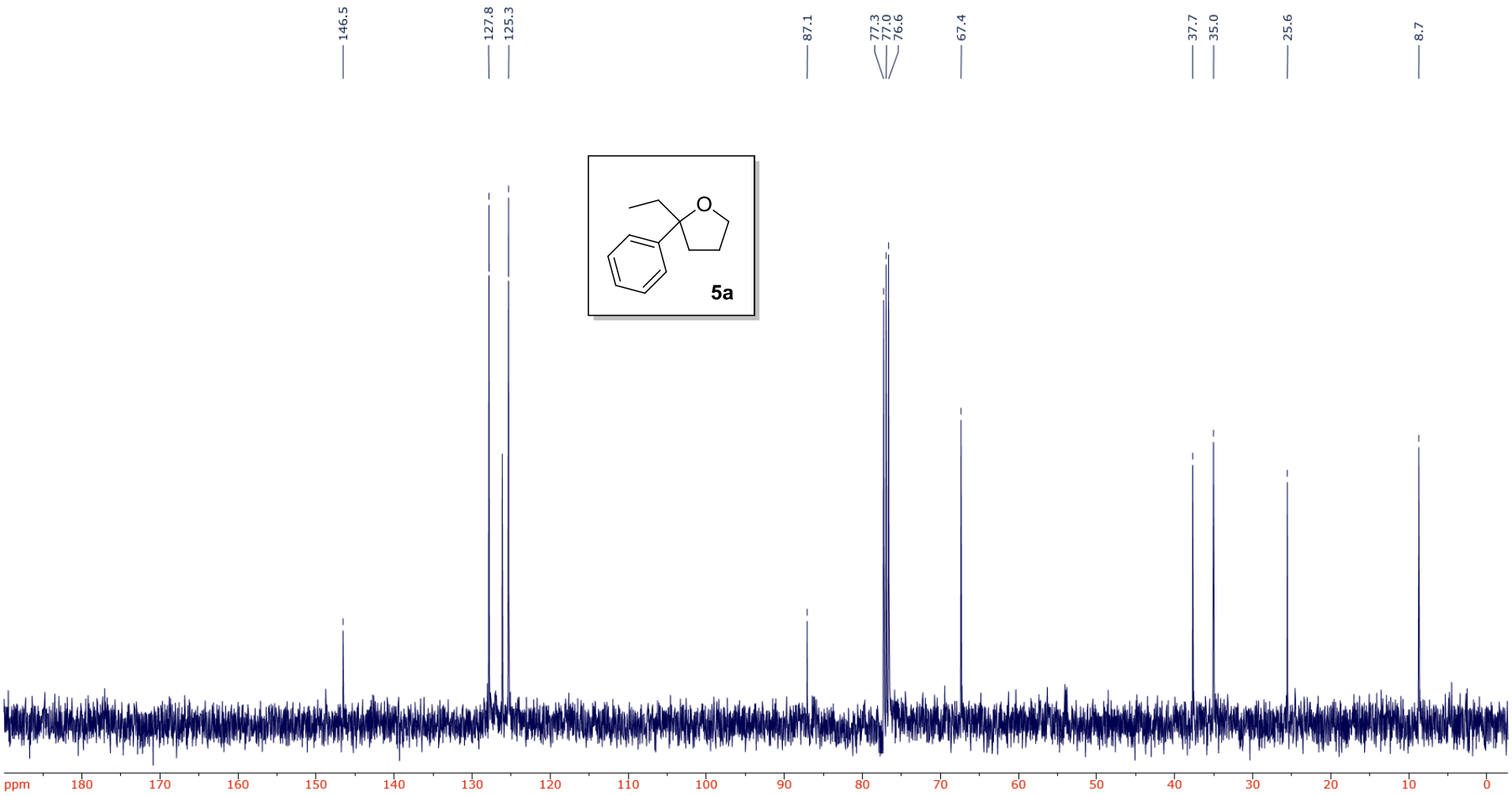
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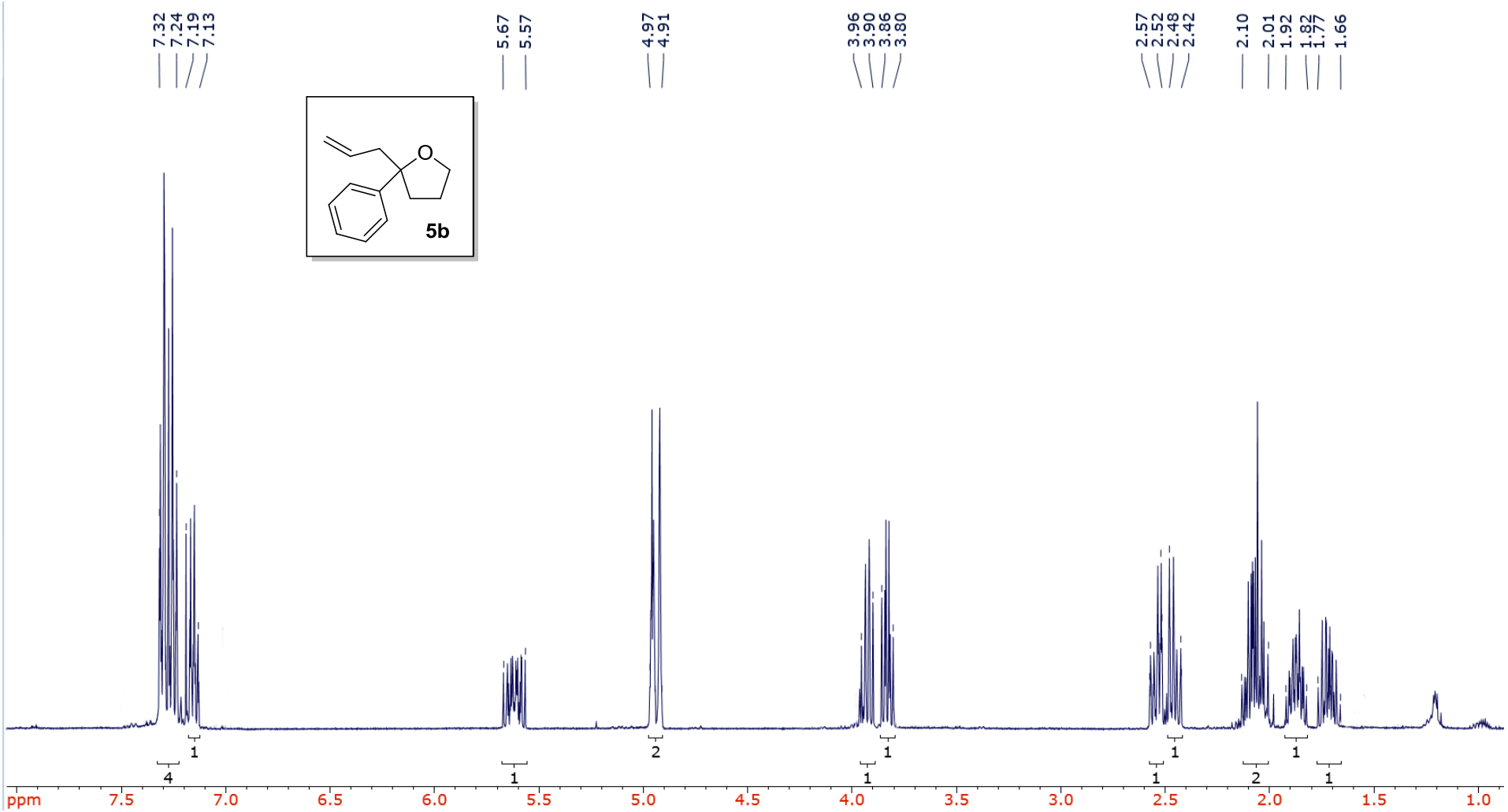
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2.48
2.42
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2.01
1.92
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1.77
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O
5b
4
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2
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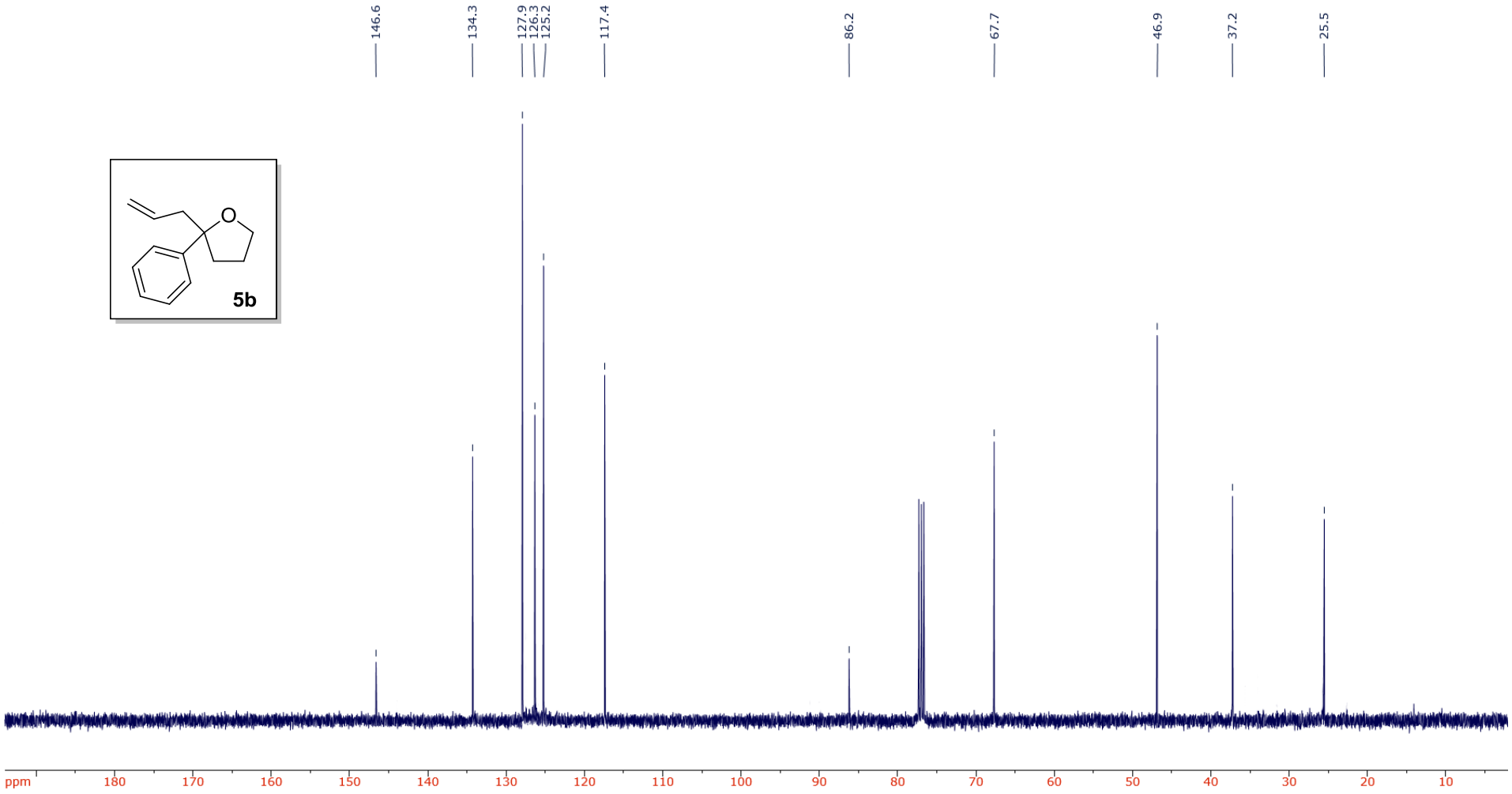
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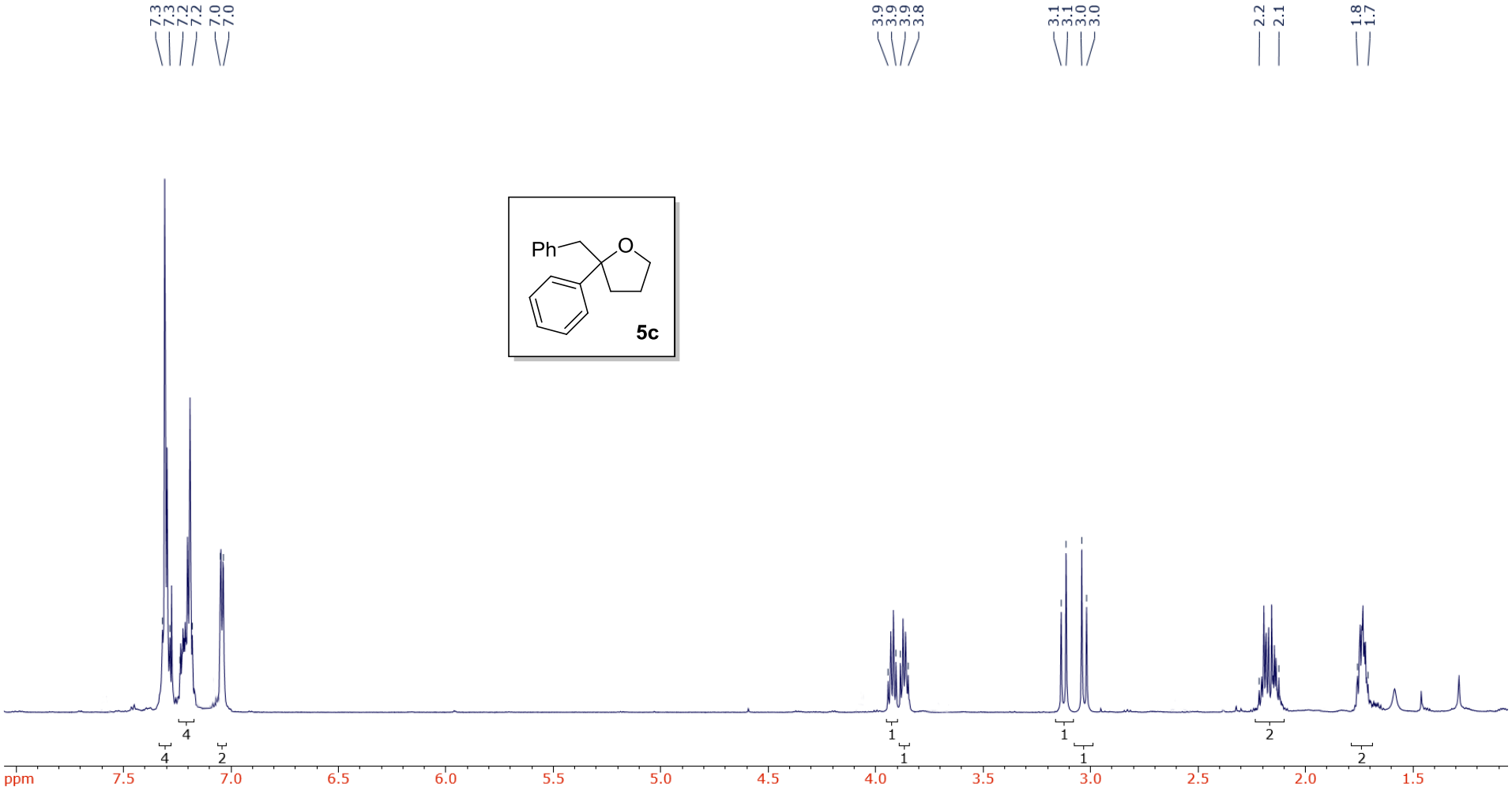
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3.0
3.0
2.2
2.1
1.8
1.7
Ph
O
5c
4
4
2
1
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1
1
2
2
ppm
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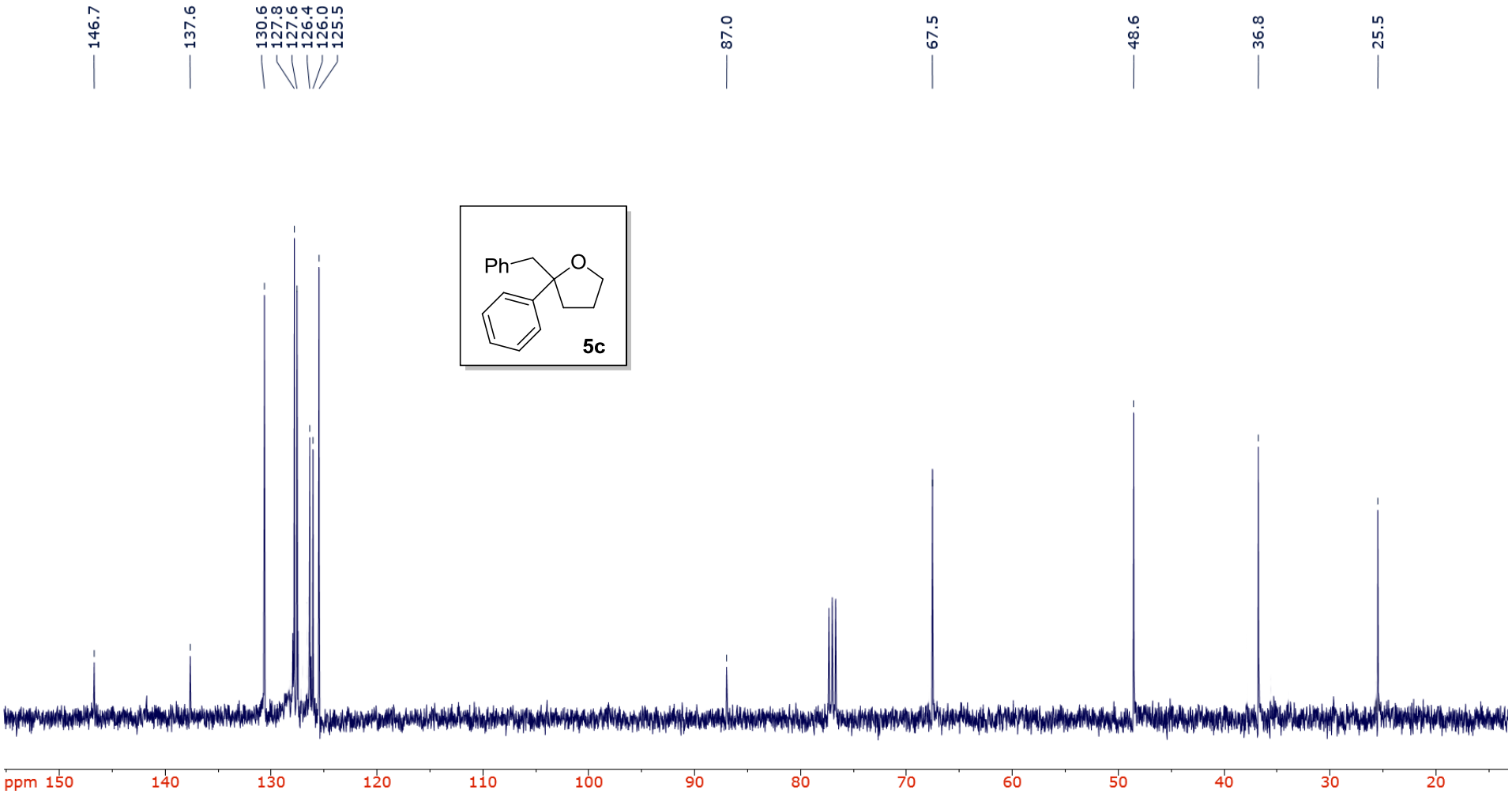
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67.5
48.6
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5c
ppm 150
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130
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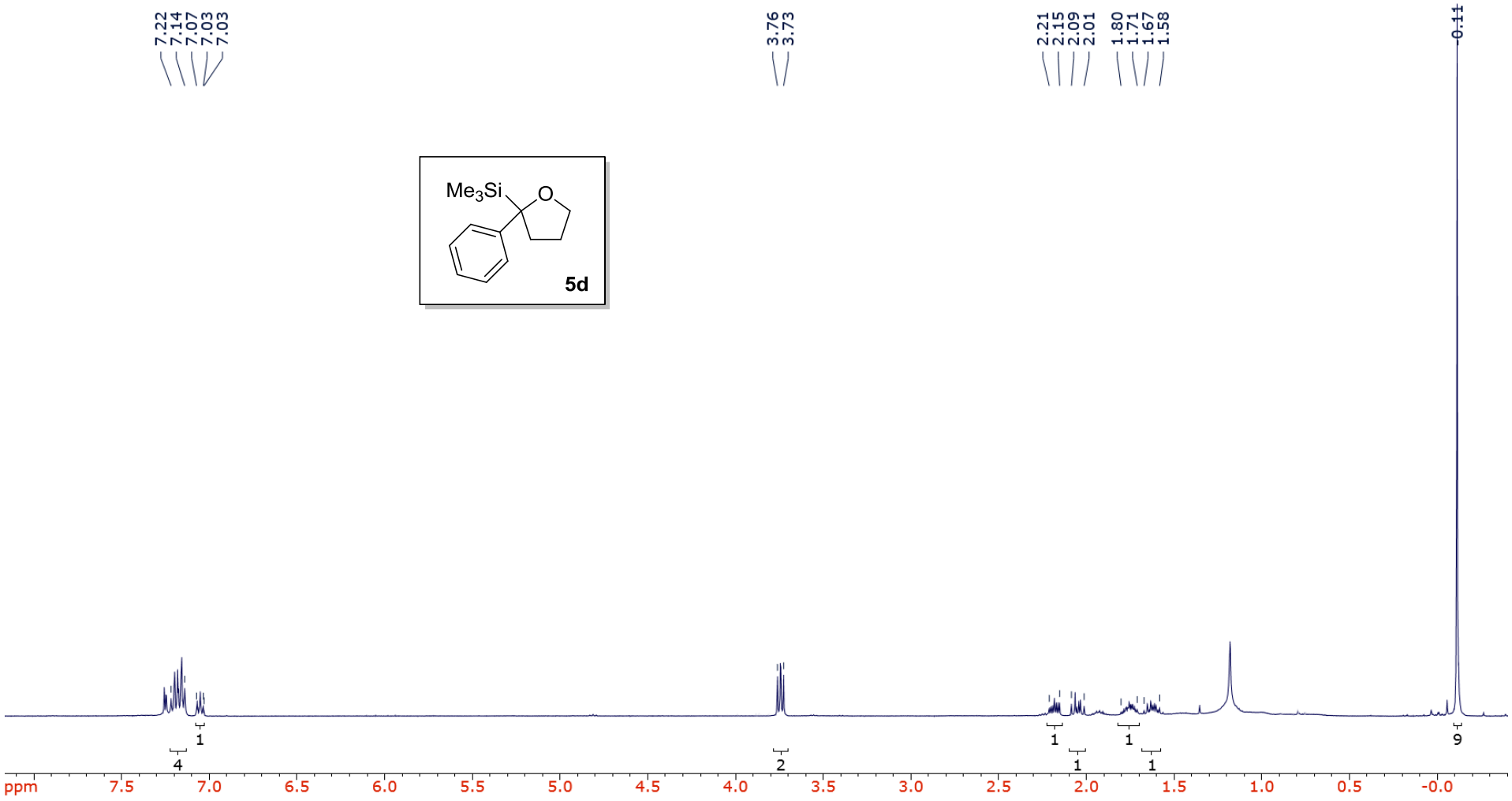
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1.71
1.67
1.58
0.11
Me3Si
O
5d
4
1
2
1
1
1
1
9
ppm
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7.0
6.5
6.0
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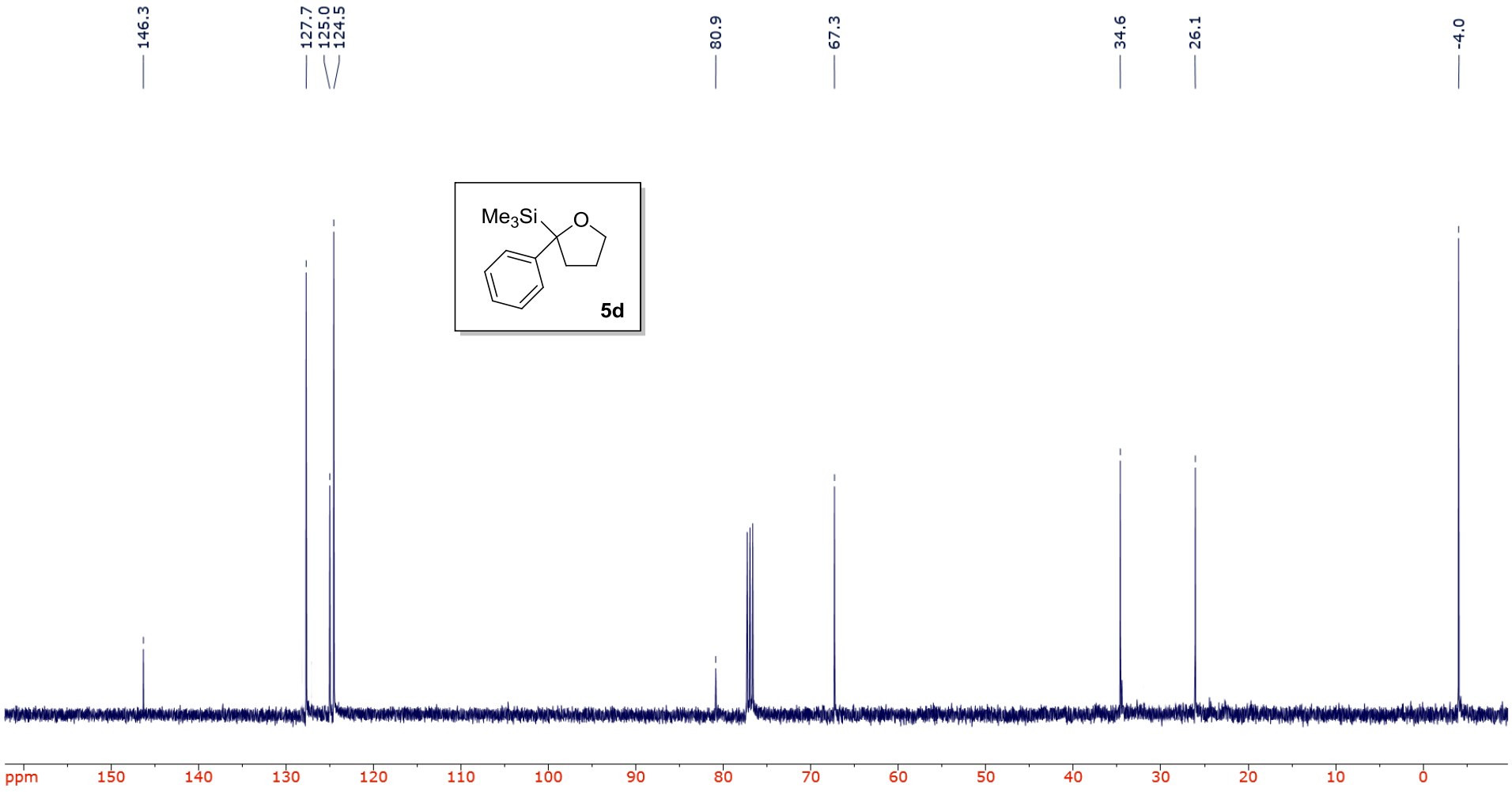
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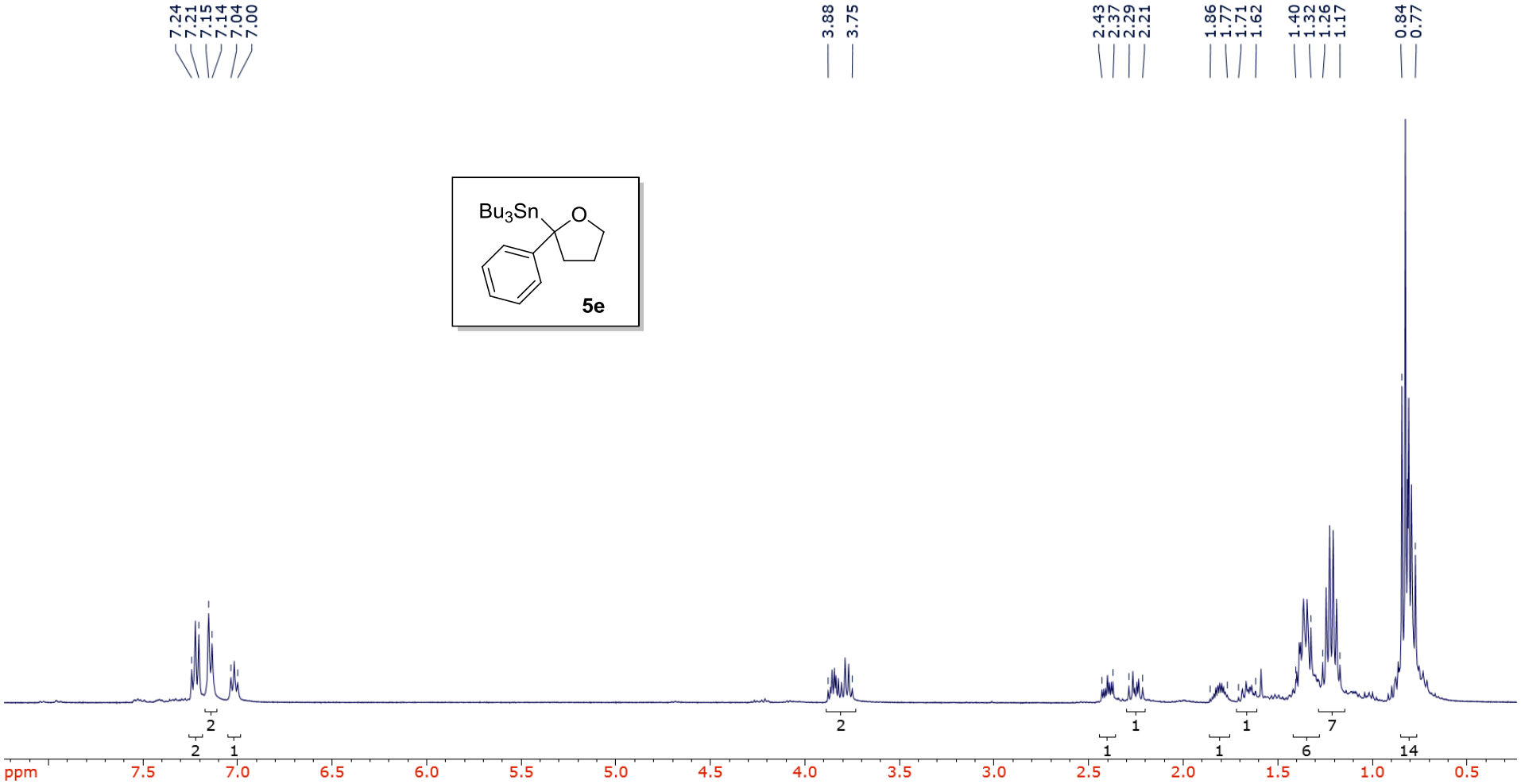
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2.21
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1.77
1.71
1.62
1.40
1.32
1.26
1.17
0.84
0.77
Bu3Sn
O
5e
2
2
1
2
1
1
1
1
7
6
14
ppm
7.5
7.0
6.5
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2.5
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1.0
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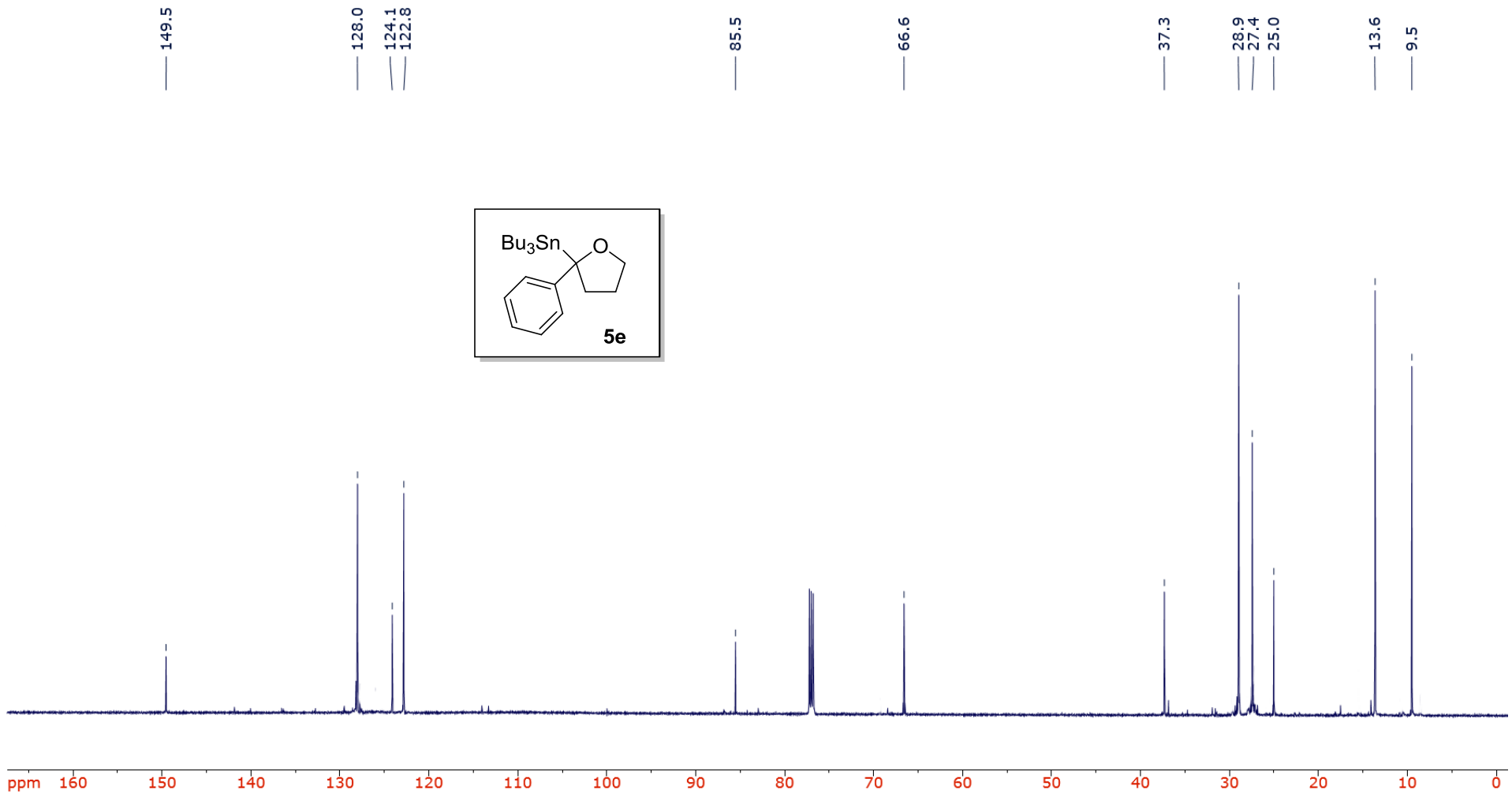
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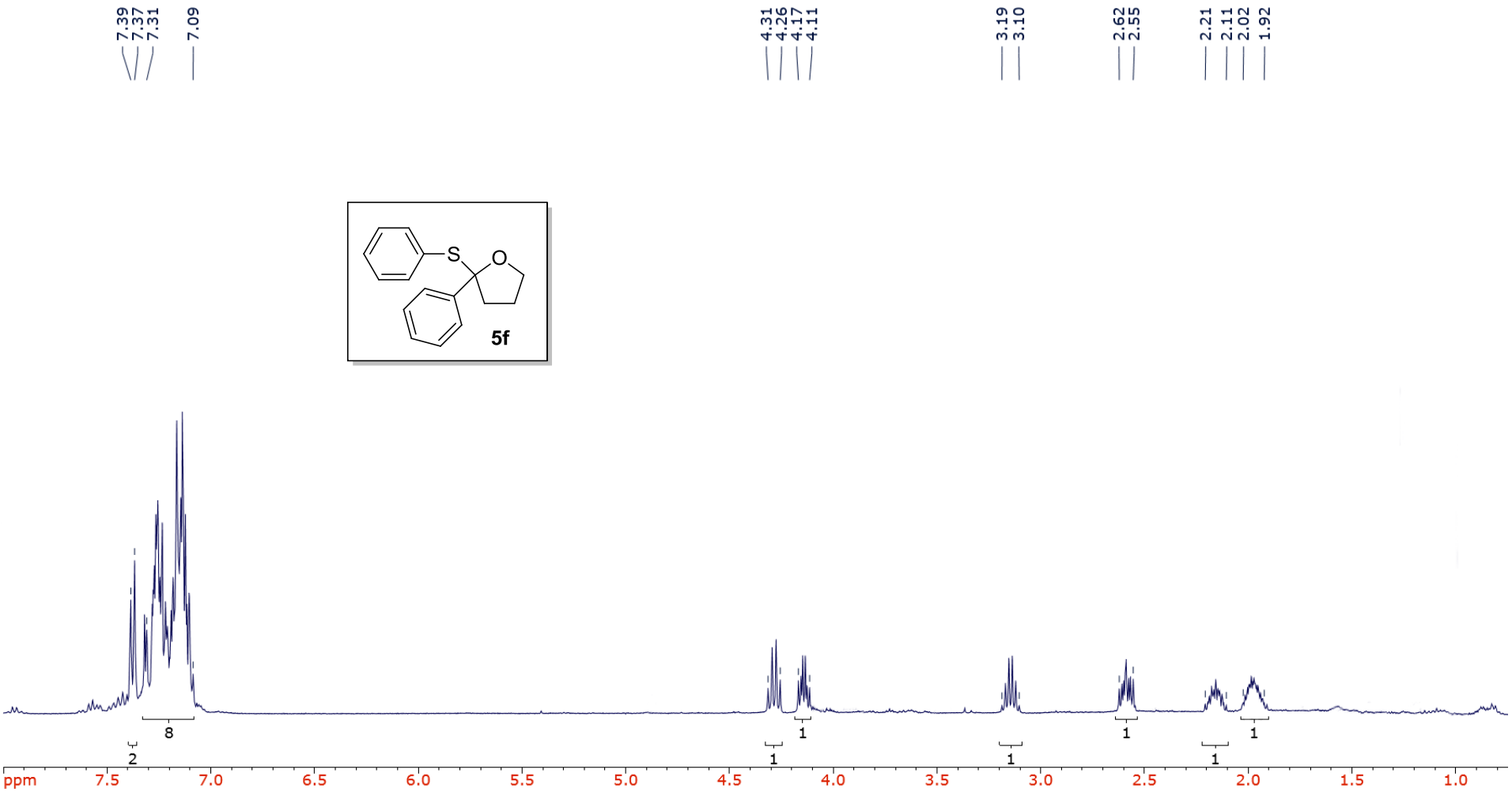
9.5
Bu3Sn
O
5e
ppm 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0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2.55
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2.11
2.02
1.92
S
O
5f
8
2
1
1
1
1
1
1
ppm
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7.0
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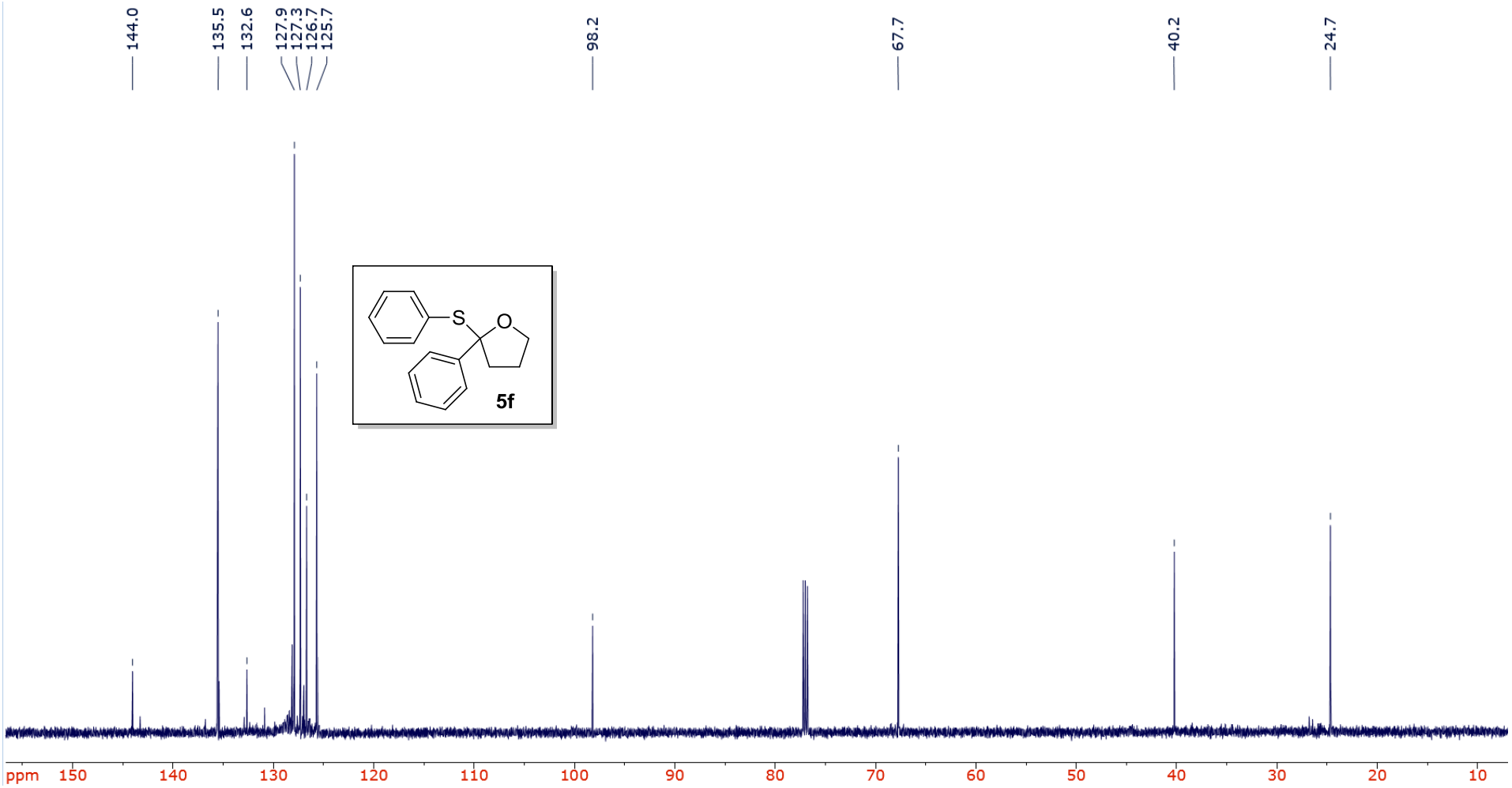
1.0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40.2
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ppm
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120
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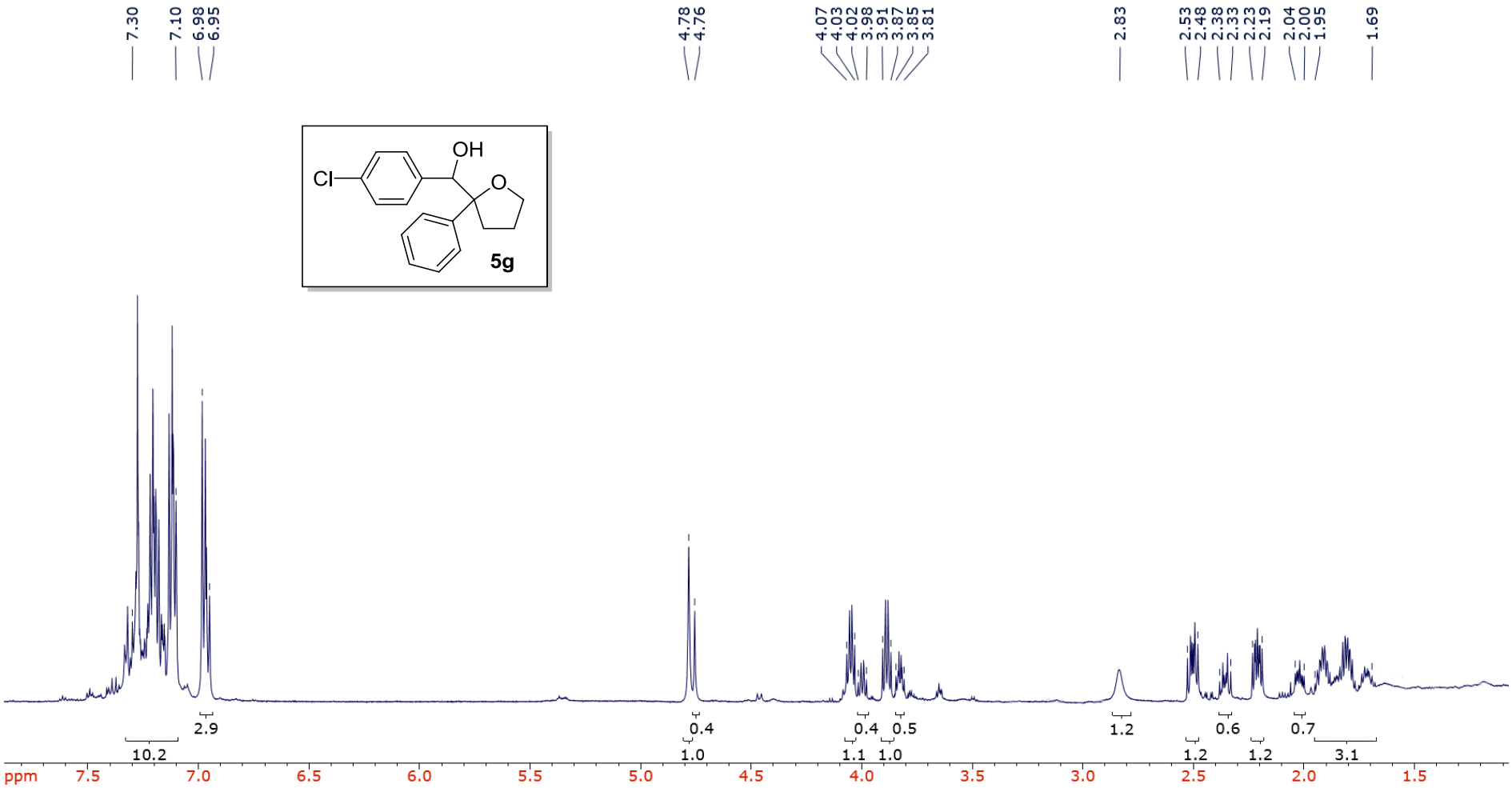
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2.53
2.48
2.38
2.33
2.23
2.19
2.04
2.00
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1.69
OH
Cl
O
5g
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0.4
0.5
1.1
1.0
1.2
0.6
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1.2
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3.1
ppm
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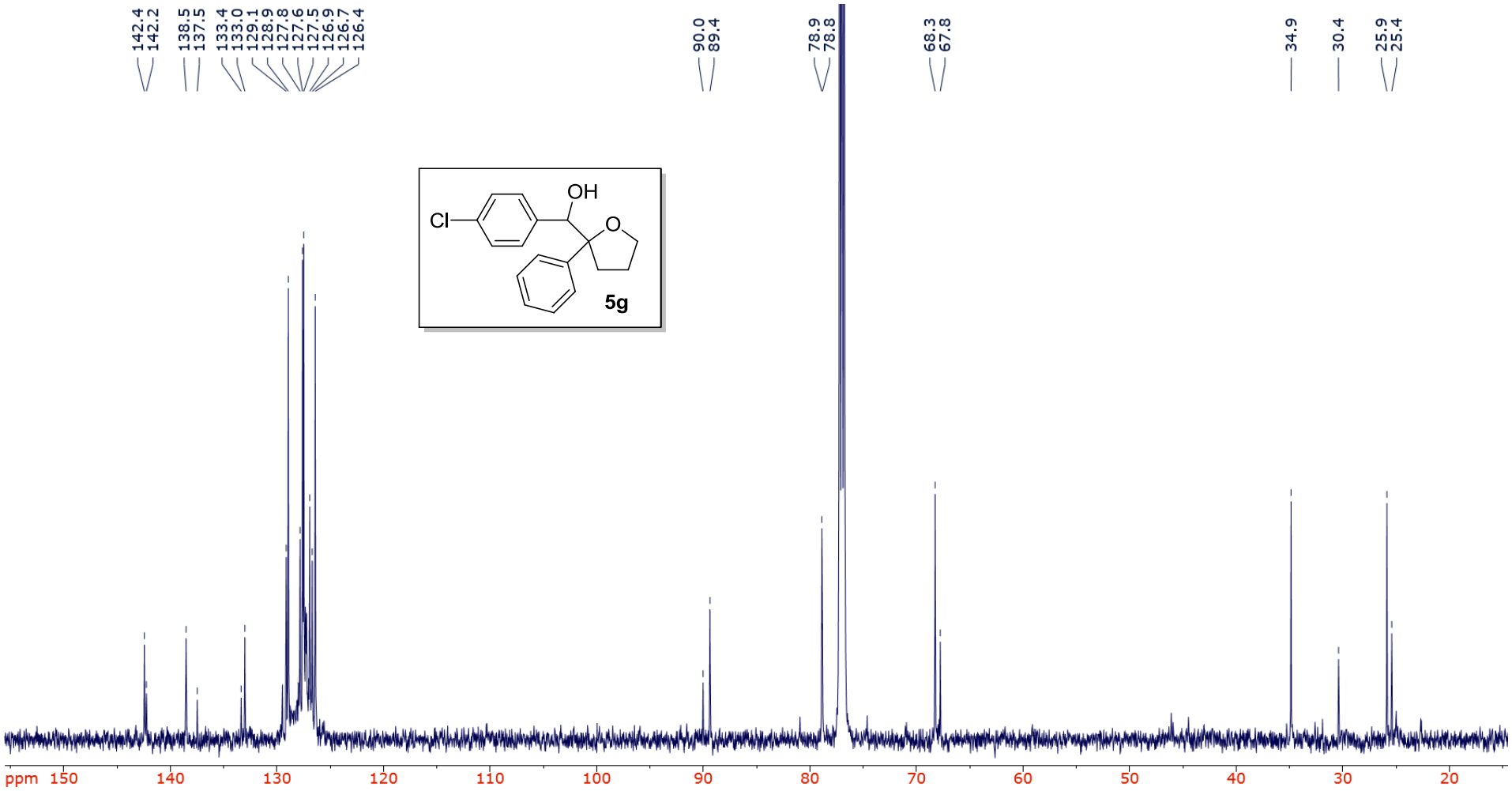
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89.4
78.9
78.8
68.3
67.8
34.9
30.4
25.9
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5g
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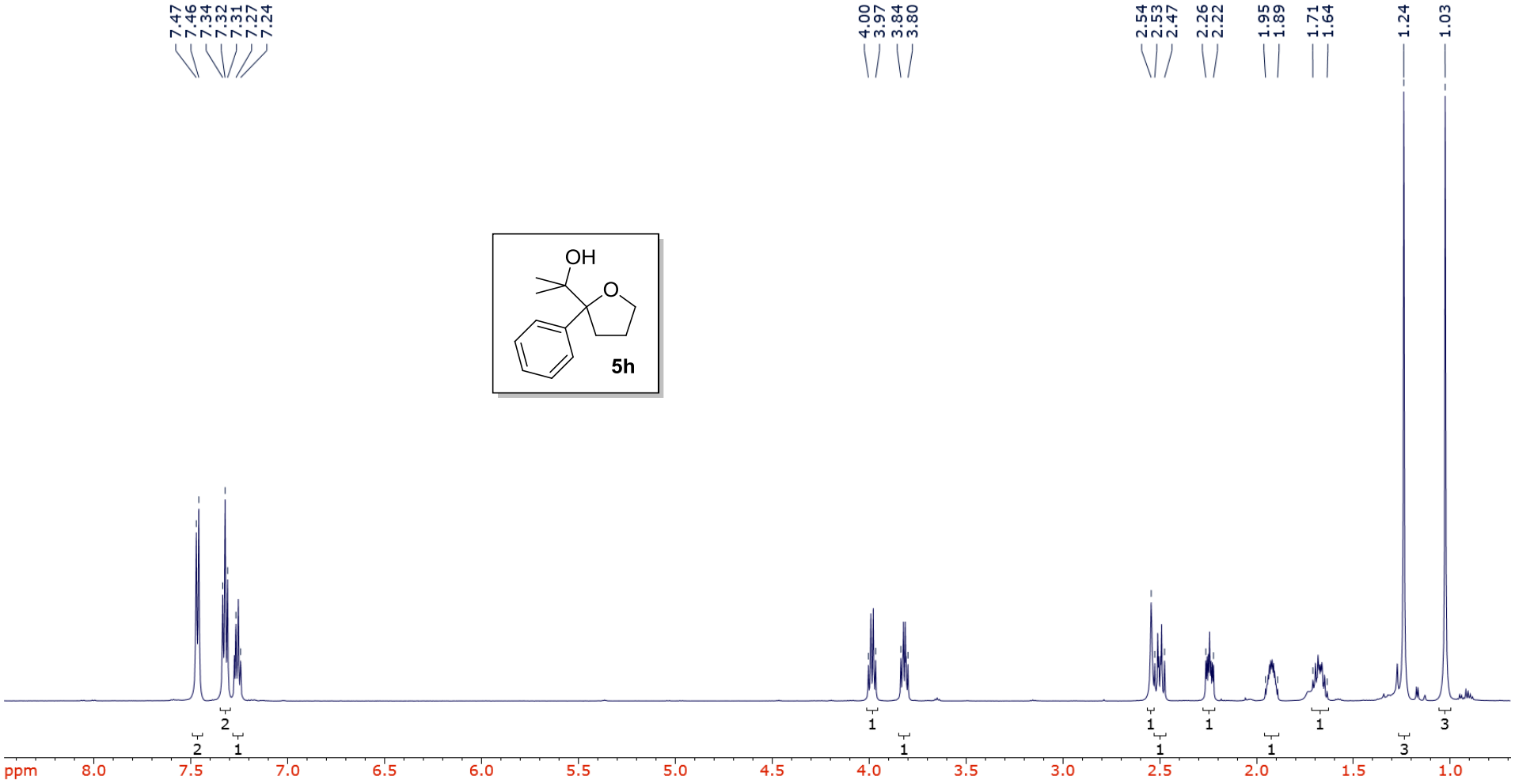
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2.22
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1.71
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O
5h
ppm
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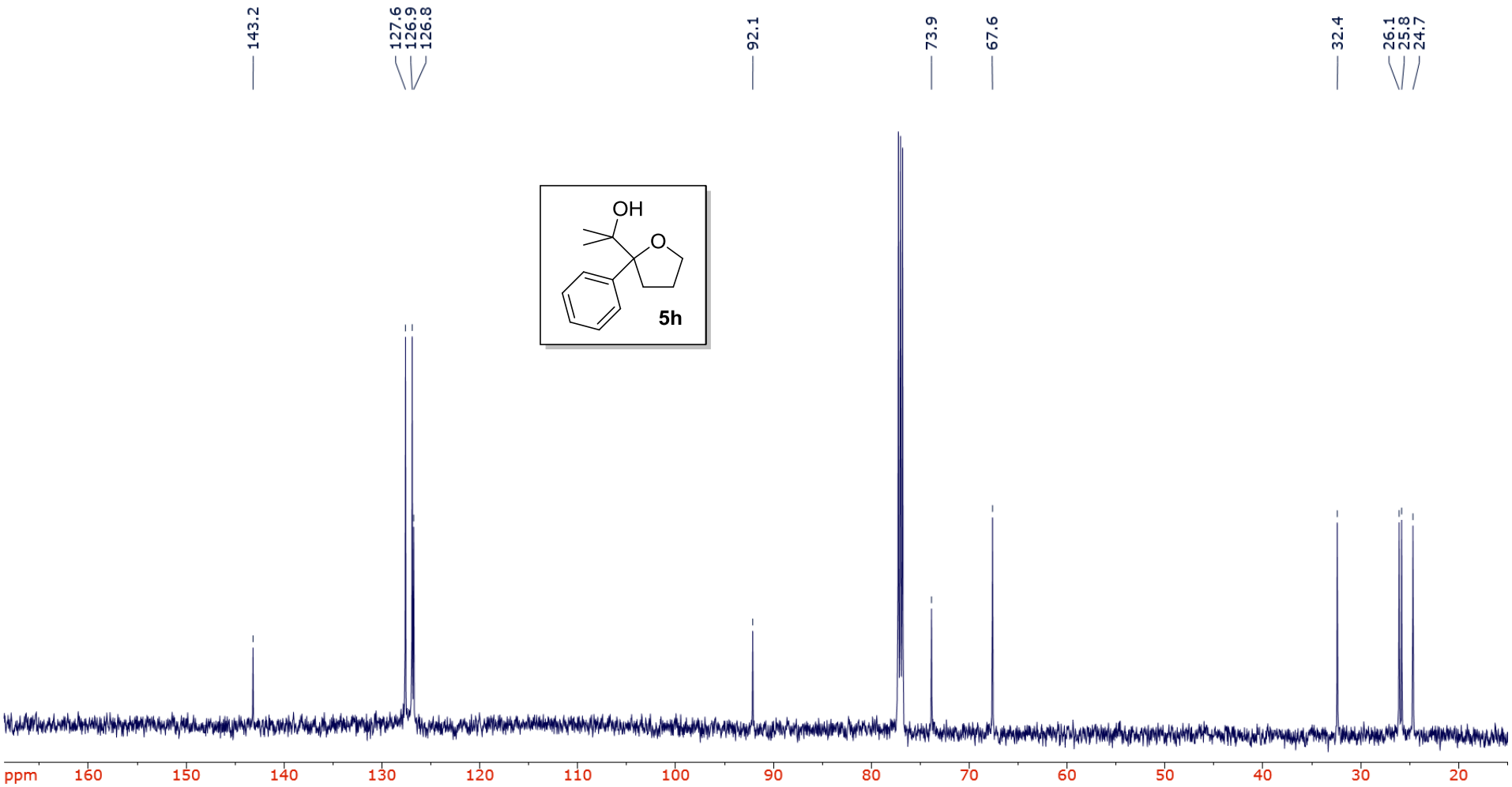
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25.8
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ppm
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150
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130
120
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80
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30
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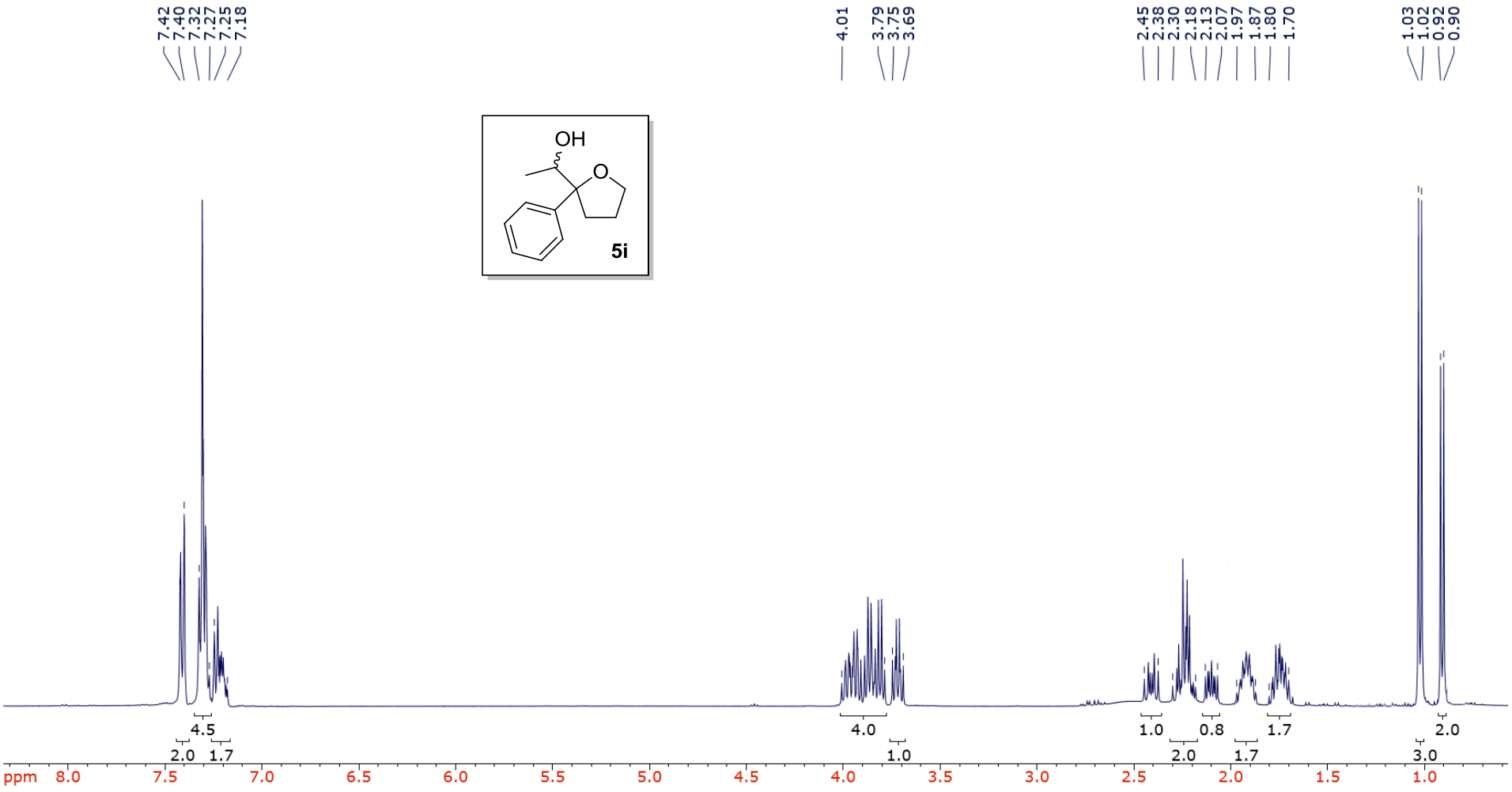
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2.13
2.07
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1.87
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1.70
1.03
1.02
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0.90
OH
O
5i
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1.0
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0.8
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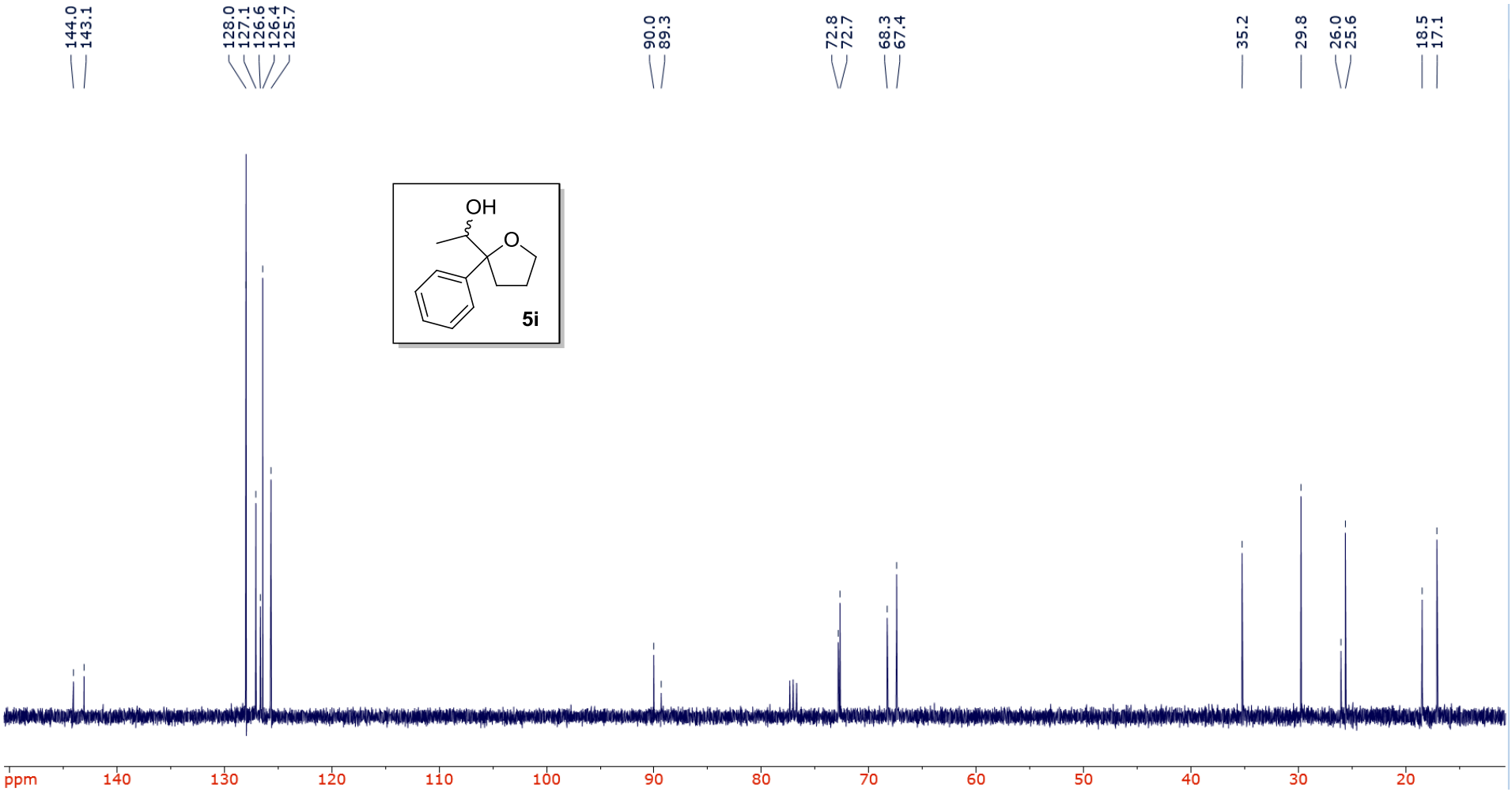
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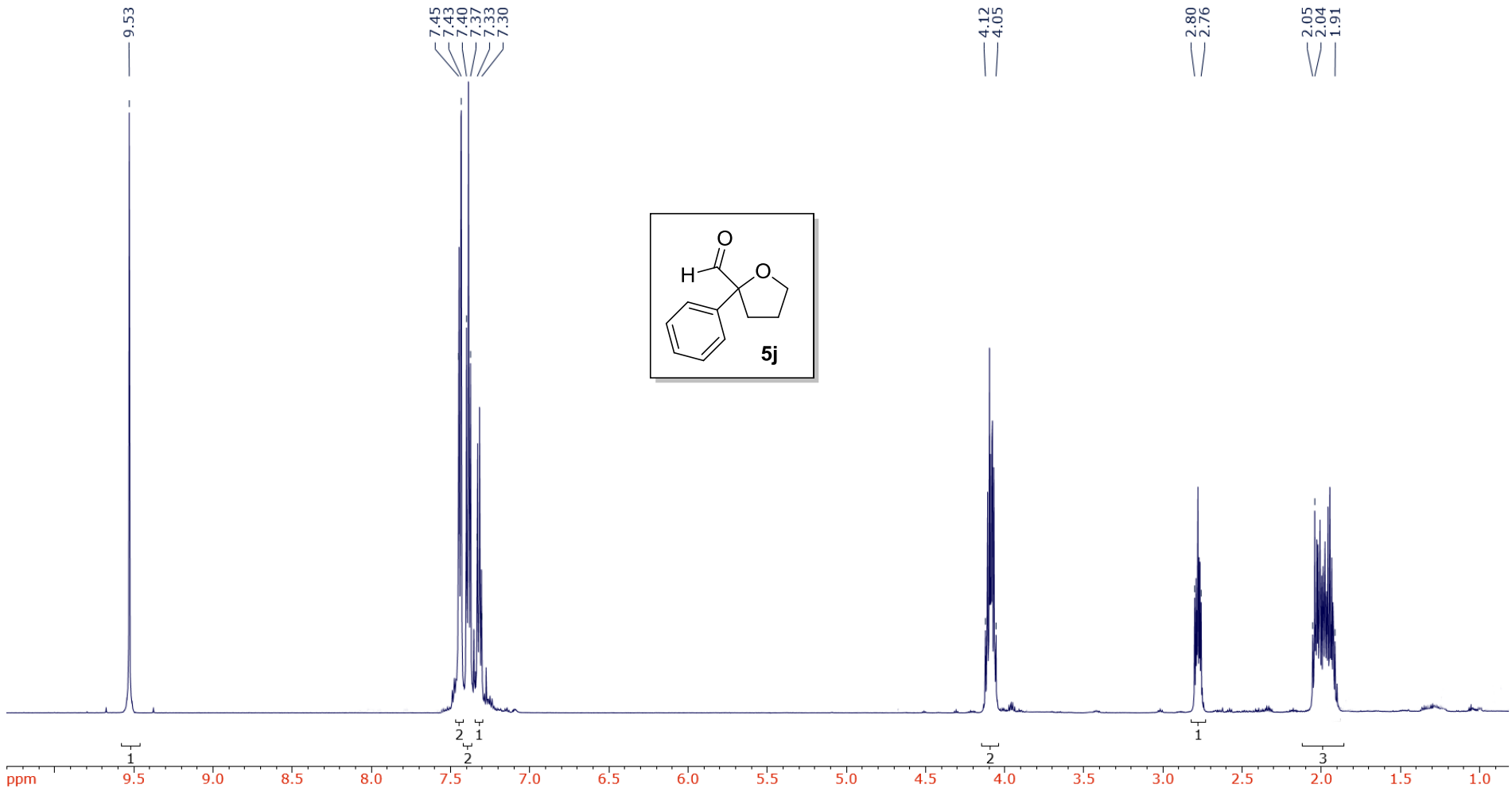
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2.05
2.04
1.91
O
H
O
5j
1
2
1
2
2
1
3
ppm
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9.0
8.5
8.0
7.5
7.0
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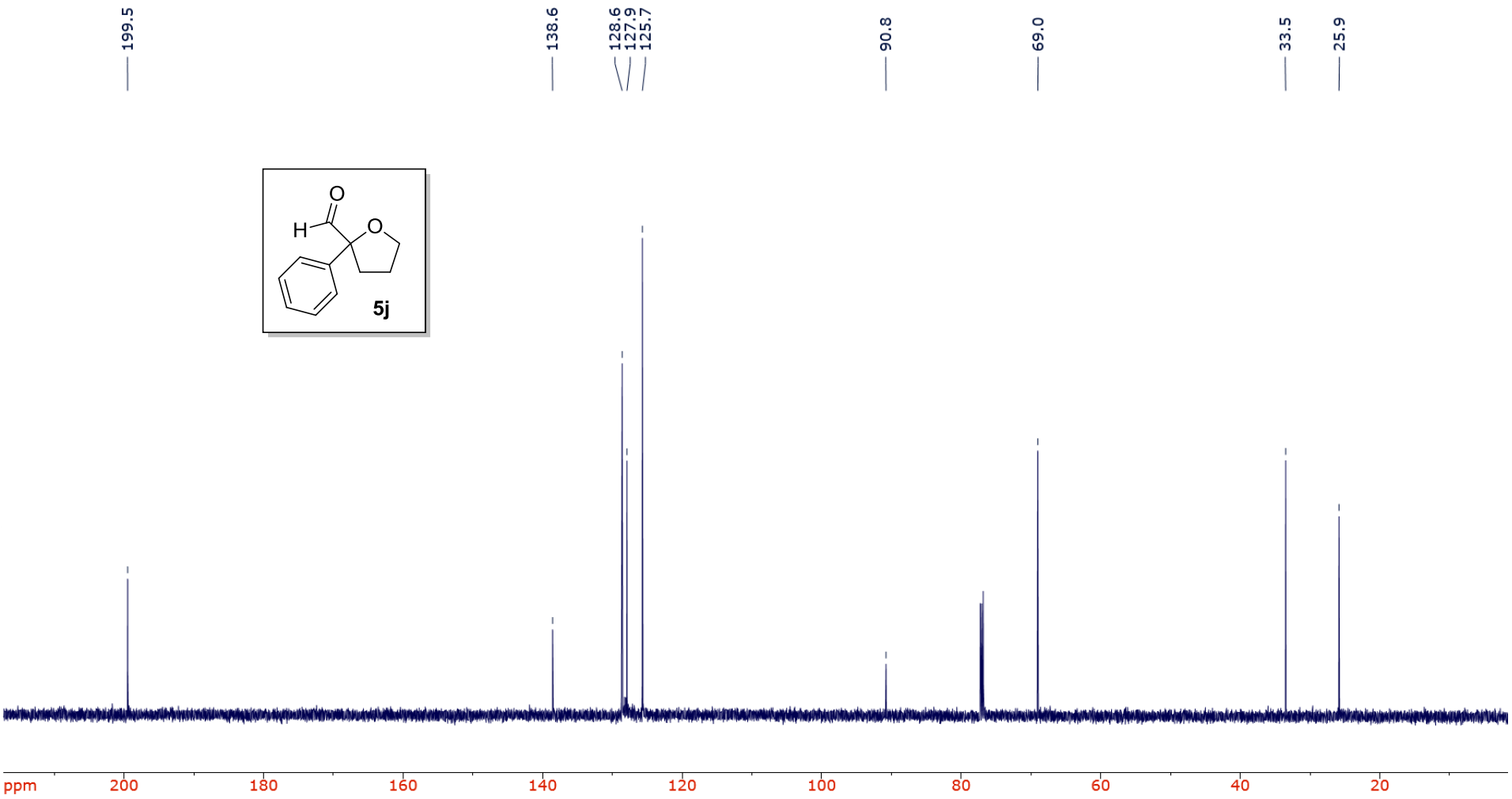
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O
H
O
5j
ppm
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140
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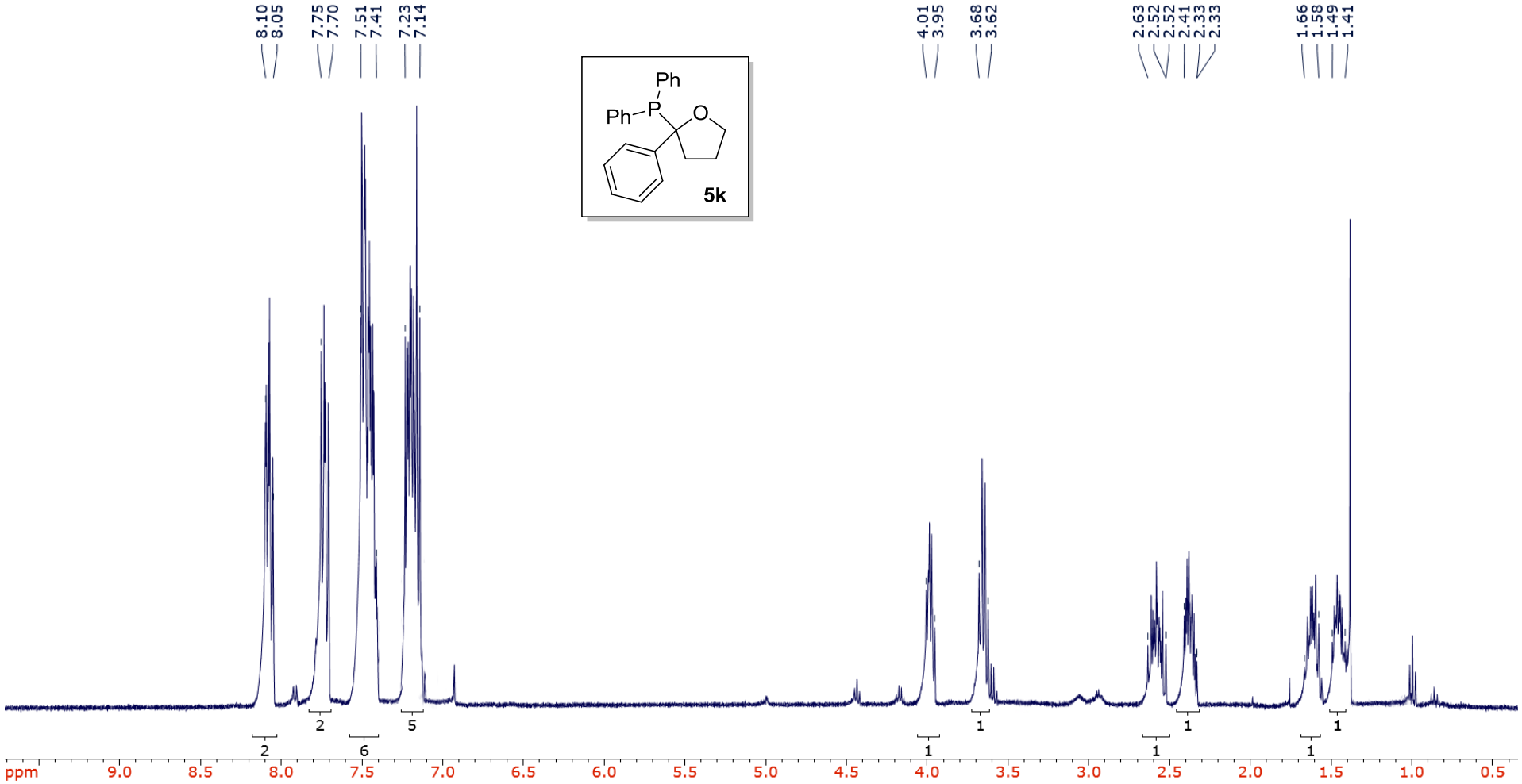
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2.63
2.52
2.52
2.41
2.33
2.33
1.66
1.58
1.49
1.41
Ph
Ph
P
O
5k
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1
1
1
1
1
1
ppm
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8.0
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7.0
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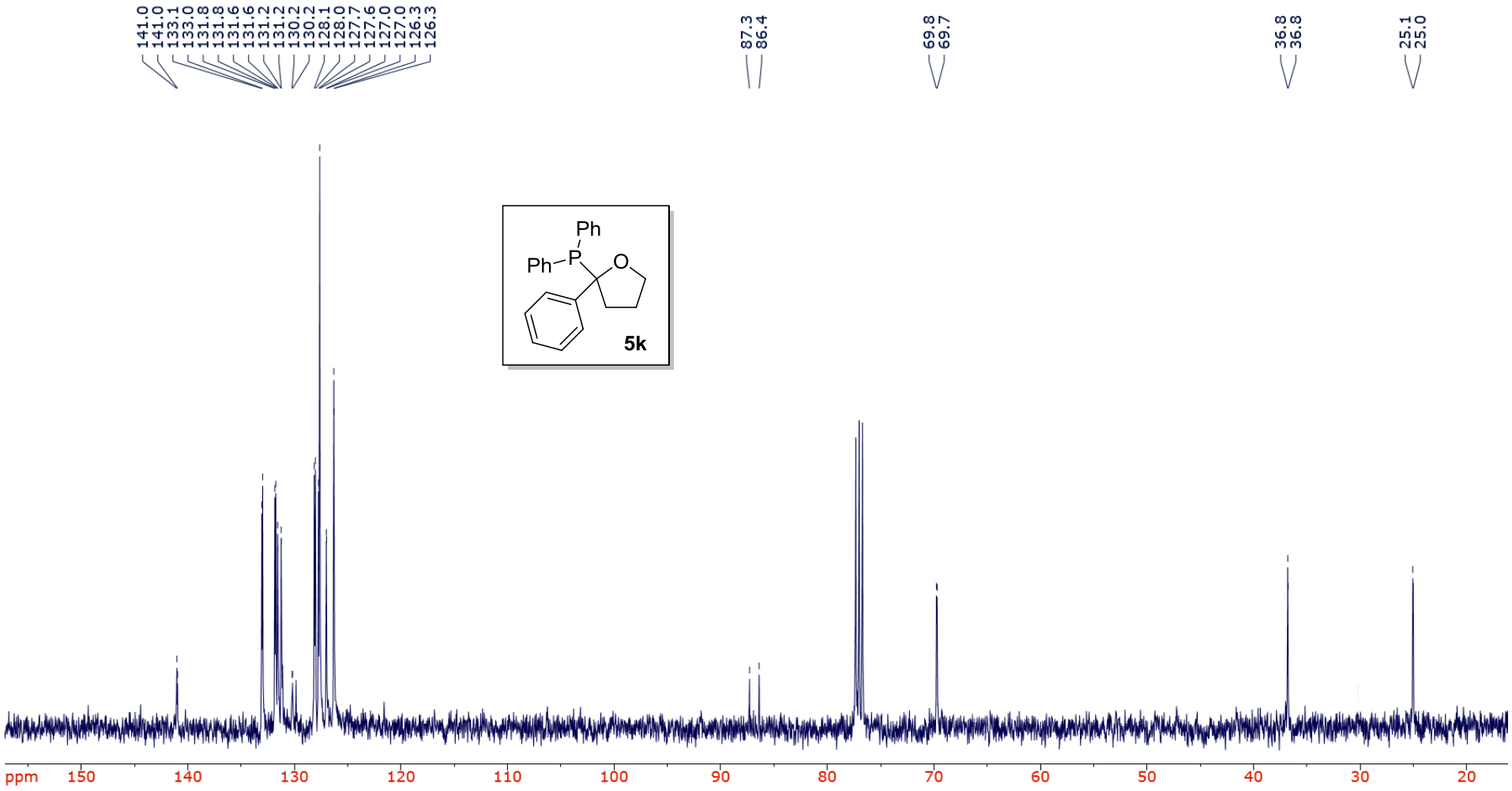
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128.0
127.7
127.6
127.0
127.0
126.3
126.3
87.3
86.4
69.8
69.7
36.8
36.8
25.1
25.0
Ph
Ph
P
O
5k
ppm
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80
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60
50
40
30
20