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Supporting Information

Palladium-catalyzed *ortho*-alkenylation of aryl hydrogen phosphates using a new *mono*-phosphoric acid directing group

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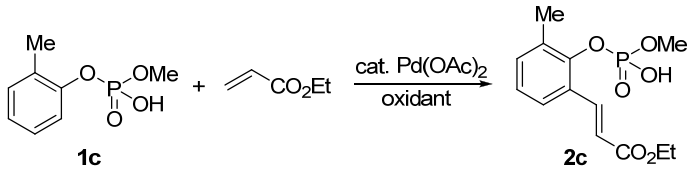
General methods:

All chemical reagents were obtained from Aldrich, Merck or Fluka and used without further purification. Analytical TLC was carried out on pre-coated plates (Merck silica gel 60, F254) and visualized with UV light or stained with potassium permanganate. ^{1}H and ^{13}C NMR spectra were measured at 298 K on a Bruker BBFO 400 Fourier Transform spectrometer. Chemical shifts were reported in δ (ppm), relative to the internal standard of TMS. The signals observed were described as: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplets). The number of protons (n) for a given resonance was indicated as nH. Coupling constants are reported as J value in Hz. ^{13}C NMR are reported as δ (ppm) in downfield from TMS and relative to the signal of chloroform-*d* (δ 77.00, triplet). Mass spectrometry was performed on a Finnigan MAT95XP GC/HRMS spectrometer under electron impact (ESI) ionization technique.

Additional data for optimization of reaction conditions

Table 1 Optimization of reaction conditions using **1c**[a]

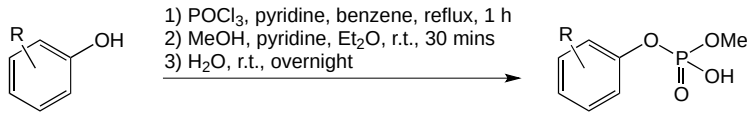


1c **2c**

Entry	Oxidant (equiv)	Base (1 equiv)	Ligand (20 mol %)	Temp (^{o}C)	Yield (%)[c]
1[b]	AgOAc (3)	-	-	110	0
2	AgOAc (3)	Li_2CO_3	-	110	100
3	AgOAc (3)	Li_2CO_3	Boc-Val-OH	110	100
4	AgOAc (3)	Li_2CO_3	Boc-Leu-OH	110	53
5	AgOAc (3)	Na_2CO_3	Boc-Val-OH	110	100
6	AgOAc (3)	-	-	110	100
7	AgOAc (2)	-	-	110	77
8	AgOAc (3)	-	-	60	18
9	O_2 (g)	-	-	110	0

[a] 0.15 mmol of **1c**, 2 equiv of ethyl acrylate, 10 mol % of $Pd(OAc)_2$, 20 mol % ligand, *x* equiv of oxidant, 1 equiv of base in 1 mL of dioxane for 15 h. [b] Reaction was carried out without $Pd(OAc)_2$ catalyst. [c] NMR yield.

GP1-General preparation of *mono*-phosphoric acid[1]

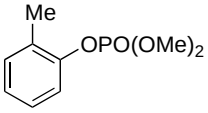


To a solution of phenol (5.0 mmol, 1.0 equiv) in benzene (5 mL) was added dropwise $POCl_3$ (0.47 mL, 5.0 mmol, 1.0 equiv), followed by pyridine (0.40 mL, 5.0 mmol, 1.0 equiv). The reaction mixture was cooled to room temperature after being stirred for 1 h at reflux, whereby the white precipitate of pyridine·HCl was filtered off and the filtrate concentrated *in vacuo*. The crude intermediate ($ArOPOCl_2$) was used without further purification.

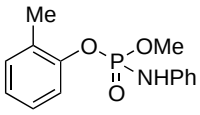
Anhydrous methanol (0.20 mL, 5.0 mmol, 1.0 equiv) was added slowly to an ice cooled solution of $ArOPOCl_2$ (5 mmol, 1.0 equiv) in diethyl ether (5 mL), followed by the subsequent addition of pyridine (0.40 mL, 5.0 mmol, 1.0 equiv). The white precipitate of pyridine·HCl was filtered off and the filtrate concentrated *in vacuo*. The crude intermediate (ArOPO(OMe)Cl) was used without further purification.

ArOPO(OMe)Cl (5.0 mmol), 1N NaOH (0.5 mL) was stirred in CH_2Cl_2:H_2O (1:2 v/v, 10 mL) under ambient

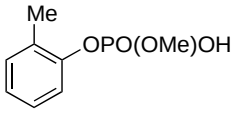
temperature overnight. The reaction was then extensively extracted with CH_2Cl_2 (10 mL x 5) and the combined organic extract was concentrated *in vacuo*. The crude residue was purified by flash chromatography (CH_2Cl_2/acetone = 1:2) *via* a short silica plug to afford the respective *mono*-phosphoric acid.



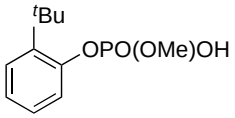
Dimethyl *o*-tolyl phosphate (1a). In GP1-step 2, anhydrous methanol (0.40 mL, 10.0 mmol, 2.0 equiv) and pyridine (0.80 mL, 10.0 mmol, 2.0 equiv) was used instead. The crude product was then purified by flash chromatography (hexane/EtOAc = 2:1) to afford **1a** without carrying out step 3. **1a** can also be obtained as a minor byproduct from the preparation of **1b** and **1c**; (1.01 g, 93% yield); yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (d, J = 8.5 Hz, 1H), 7.23 – 7.12 (m, 2H), 7.12 – 7.03 (m, 1H), 3.86 (d, J = 11.3 Hz, 6H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.0 (d, J = 7.0 Hz), 131.3, 129.1 (d, J_{CP} = 6.7 Hz), 127.0 (d, J_{CP} = 1.0 Hz), 125.0, 119.5 (d, J_{CP} = 2.2 Hz), 54.8 (d, J_{CP} = 6.2 Hz), 16.2; ^{31}P NMR (162 MHz, $CDCl_3$) δ -3.9; FTIR (NaCl, neat): ν 1585, 1493, 1462 cm^{-1}; HRMS (EI, $C_9H_{14}O_4P$ (M+)): calcd.: 217.0630; found: 217.0628.



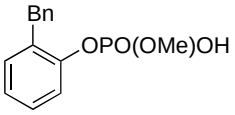
Methyl *o*-tolyl phenylphosphoramidate (1b). GP1-step 3 was modified. Aniline (0.40 mL, 6.0 mmol, 1.2 equiv), followed by the careful addition of triethylamine (0.80 mL, 7.5 mmol, 1.5 equiv) was added to a solution of ArOPO(OMe)Cl (5.0 mmol) in CH_2Cl_2 and stirred overnight at room temperature. The excess reagents and $Et_3N{\cdot}HCl$ was removed by washing the organic layer with water; brine; dried in Na_2SO_4; and concentrated *in vacuo*. The crude residue was then purified by flash chromatography (hexane/EtOAc = 1:2) to afford **1b** (0.89 g, 64% yield); yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 – 7.19 (m, 3H), 7.14 (d, J = 7.2 Hz, 1H), 7.11 – 6.70(m, 5H), 3.86 (d, J = 11.6 Hz, 3H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.0 (d, J_{CP} = 7.0 Hz), 139.2, 131.3, 129.5 (d, J_{CP} = 6.0 Hz), 129.3, 126.9, 124.9, 122.1, 119.8 (d, J_{CP} = 2.5 Hz), 117.9 (d, J_{CP} = 7.3 Hz, 5H), 53.5 (d, J_{CP} = 5.0 Hz), 16.4; ^{31}P NMR (162 MHz, $CDCl_3$) δ -0.5; FTIR (NaCl, neat): ν 3165, 1605, 1510, 1418 cm^{-1}; HRMS (EI, $C_{14}H_{17}NO_3P$ (M+)): calcd.: 278.0946; found: 278.0944.



Methyl *o*-tolyl hydrogen phosphate (1c). (0.82 g, 81% yield); yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.16 (m, 2H), 7.16 – 7.02 (m, 2H), 3.78 (d, J = 11.6 Hz, 3H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.1, 131.2, 129.4 (J_{CP}, J = 6.0 Hz), 126.9, 124.9, 119.7, 54.5 (d, J_{CP} = 6.0 Hz), 16.1; ^{31}P NMR (162 MHz, $CDCl_3$) δ -4.2; FTIR (NaCl, neat): ν 3339, 1585, 1493, 1454 cm^{-1}; HRMS (EI, $C_8H_{12}O_4P$ (M+)): calcd.: 203.0473; found: 203.0474.

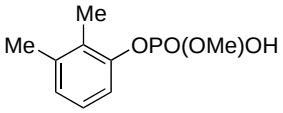


2-(*tert*-Butyl)phenyl methyl hydrogen phosphate (3a). (1.09 g, 89% yield); yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.29 (m, 2H), 7.31 – 7.01 (m, 2H), 3.82 (d, J = 11.2 Hz, 3H), 1.39 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.9 (d, J_{CP} = 6.0 Hz), 139.7 (d, J_{CP} = 8.0 Hz), 127.4, 127.2, 124.4, 119.2, 54.5 (d, J_{CP} = 6.0 Hz), 34.6, 30.0; FTIR (NaCl, neat): ν 3401, 1487, 1445, 1364 cm^{-1}; ^{31}P NMR (162 MHz, $CDCl_3$) δ -4.6; HRMS (EI, $C_{11}H_{18}O_4P$ (M+)): calcd.: 245.0943; found: 245.0939.

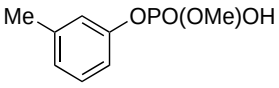


2-Benzylphenyl methyl hydrogen phosphate (3b). (1.07 g, 77% yield); yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.20 (m, 3H), 7.21 – 6.99 (m, 6H), 4.01 (s, 2H), 3.65 (d, J = 11.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.7, 139.9, 132.3 (d, J_{CP} = 7.0 Hz), 130.9,

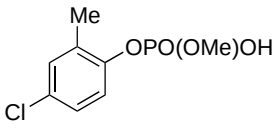
129.0, 128.4, 127.5, 126.1, 125.1, 119.6, 54.6 (d, J_{CP} = 6.0 Hz), 35.8; ^{31}P NMR (162 MHz, $CDCl_3$) δ -4.1; FTIR (NaCl, neat): ν 3408, 1489, 1452 cm^{-1}; HRMS (EI, $C_{14}H_{16}O_4P$ (M+)): calcd.: 279.0786; found: 279.0782.



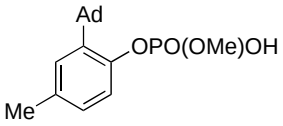
2,3-Dimethylphenyl methyl hydrogen phosphate (3c). (0.97 g 90% yield); yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 – 7.02 (m, 1H), 7.02 – 6.90 (m, 2H), 3.78 (d, J = 11.5 Hz, 3H), 2.26 (s, 3H), 2.18 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.8, 138.7, 128.1 (d, J_{CP} = 6.0 Hz), 126.5, 125.9, 117.4, 54.5 (d, J_{CP} = 5.0 Hz), 20.1, 12.3; ^{31}P NMR (162 MHz, $CDCl_3$) δ -3.4; FTIR (NaCl, neat): ν 3402, 1490, 1451 cm^{-1}; HRMS (EI, $C_9H_{14}O_4P$ (M+)): calcd.: 217.0630; found: 217.0628.



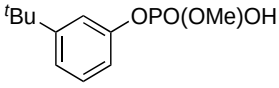
Methyl *m*-tolyl hydrogen phosphate (3d). (0.78 g 77% yield); yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (t, J = 7.7 Hz, 1H), 7.05 – 6.92 (m, 3H), 3.79 (d, J = 11.5 Hz, 3H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.4 (d, J_{CP} = 7.0 Hz), 139.9, 129.3, 125.9, 120.6 (d, J_{CP} = 5.0 Hz), 116.9 (d, J_{CP} = 5.0 Hz), 54.6 (d, J_{CP} = 6.0 Hz), 21.2; ^{31}P NMR (162 MHz, $CDCl_3$) δ -3.9; FTIR (NaCl, neat): ν 3401, 1488, 1455 cm^{-1}; HRMS (EI, $C_8H_{12}O_4P$ (M+)): calcd.: 203.0473; found: 203.0475.



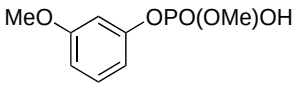
4-Chloro-2-methylphenyl methyl hydrogen phosphate (3e). (0.83 g, 70% yield); yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (s, 1H), 7.14 – 7.03 (m, 2H), 3.78 (d, J = 11.5 Hz, 3H), 2.23 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.6 (d, J_{CP} = 7.0 Hz), 131.6 (d, J_{CP} = 6.0 Hz), 131.1, 130.2, 126.9, 121.0, 54.8 (d, J_{CP} = 7.0 Hz), 16.2; ^{31}P NMR (162 MHz, $CDCl_3$) δ -4.3; FTIR (NaCl, neat): ν 3389, 1485, 1454 cm^{-1}; HRMS (EI, $C_8H_{11}ClO_4P$ (M+)): calcd.: 237.0084; found: 237.0091.



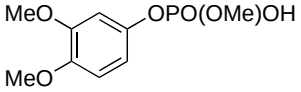
2-(Adamantan-1-yl)-4-methylphenyl methyl hydrogen phosphate (3f). 1 mmol scale was used instead; (0.22 g, 65% yield); white solid; m.p. 191 – 192 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (d, J = 8.2 Hz, 1H), 7.07 (s, 1H), 6.89 (d, J = 7.7 Hz, 1H), 3.83 (d, J = 11.5 Hz, 3H), 2.28 (s, 3H), 2.06 (s, 9H), 1.75 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.9 (d, J_{CP} = 7.0 Hz), 139.4 (d, J_{CP} = 8.0 Hz), 133.8, 128.1, 127.3, 119.1, 54.5 (d, J_{CP} = 6.0 Hz), 40.7, 36.9, 36.7, 29.0, 21.0; ^{31}P NMR (162 MHz, $CDCl_3$) δ -3.9; FTIR (NaCl, neat): ν 3424, 1495, 1454, 1244, 1070 cm^{-1}; HRMS (EI, $C_{18}H_{26}O_4P$ (M+)): calcd.: 337.1569; found: 337.1577.



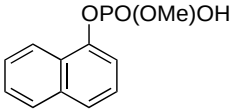
3-(*tert*-Butyl)phenyl methyl hydrogen phosphate (3g). (0.95 g, 78% yield); yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.14 (m, 3H), 7.03 (d, J = 7.6 Hz, 1H), 3.79 (d, J = 11.6 Hz, 3H), 1.29 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.5, 129.1, 127.2, 122.0, 117.3 (d, J_{CP} = 6.0 Hz), 116.8 (d, J_{CP} = 4.0 Hz), 54.6 (d, J_{CP} = 6.0 Hz), 34.7, 31.2; ^{31}P NMR (162 MHz, $CDCl_3$) δ -3.7; FTIR (NaCl, neat): ν 3366, 1487, 1429, 1364 cm^{-1}; HRMS (EI, $C_{11}H_{18}O_4P$ (M+)): calcd.: 245.0943; found: 245.0947.



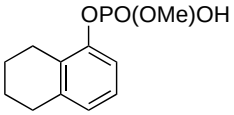
3-Methoxyphenyl methyl hydrogen phosphate (3h). (0.65 g, 60% yield); yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (t, J = 8.2 Hz, 1H), 6.85 – 6.65 (m, 3H), 3.80 (d, J = 11.2 Hz, 3H), 3.76 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.6, 151.4 (d, J_{CP} = 7.0 Hz), 130.0, 112.1 (d, J_{CP} = 5.0 Hz), 111.1, 106.1 (d, J_{CP} = 6.0 Hz), 55.4, 54.7 (d, J_{CP} = 6.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ -3.9; FTIR (NaCl, neat): ν 3366, 1607, 1493, 1454 cm^{-1}; HRMS (EI, $C_8H_{12}O_5P$ (M+)): calcd.: 219.0422; found: 219.0423.



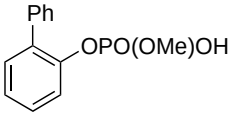
3,4-Dimethoxyphenyl methyl hydrogen phosphate (3i). (0.78 g, 63% yield); yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.81 – 6.71 (m, 3H), 3.83 (s, 6H), 3.79 (d, J = 11.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.3, 146.2, 144.3 (d, J_{CP} = 7.0 Hz), 111.2, 111.0 (d, J_{CP} = 5.0 Hz), 104.5 (d, J_{CP} = 4.0 Hz), 56.0, 55.8, 54.4 (d, J_{CP} = 5.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ -4.5; FTIR (NaCl, neat): ν 3478, 1605, 1504, 1454 cm^{-1}; HRMS (EI, $C_9H_{14}O_6P$ (M+)): calcd.: 249.0528; found: 249.0526.



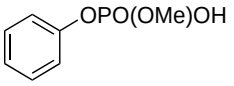
Methyl naphthalen-1-yl hydrogen phosphate (3j). (1.05 g, 88% yield); yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 – 8.07 (m, 1H), 7.86 – 7.74 (m, 1H), 7.62 (d, J = 8.1 Hz, 1H), 7.51 – 7.43 (m, 2H), 7.38 (d, J = 7.5 Hz, 1H), 7.35 – 7.27 (m, 1H), 3.78 (d, J = 11.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.4 (d, J_{CP} = 7.0 Hz), 134.7, 127.6, 126.6, 126.4, 125.4, 125.0, 121.7, 114.9 (d, J_{CP} = 3.0 Hz), 54.8 (d, J_{CP} = 6.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ -3.6; FTIR (NaCl, neat): ν 3393, 1599, 1393 cm^{-1}; HRMS (EI, $C_{11}H_{12}O_4P$ (M+)): calcd.: 239.0473; found: 239.0471.



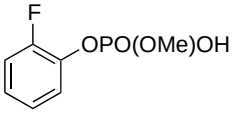
Methyl (5,6,7,8-tetrahydronaphthalen-1-yl) hydrogen phosphate (3k). (0.92 g, 76% yield); yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.06 (d, J = 8.0 Hz, 1H), 6.99 (t, J = 7.8 Hz, 1H), 6.87 (d, J = 7.5 Hz, 1H), 3.77 (d, J = 11.5 Hz, 3H), 2.85 – 2.64 (m, 4H), 1.85 – 1.59 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.8 (d, J_{CP} = 7.0 Hz), 139.3, 128.8 (d, J_{CP} = 6.0 Hz), 125.7, 116.5 (d, J_{CP} = 2.0 Hz), 54.5 (d, J_{CP} = 6.0 Hz), 29.4, 23.2, 22.6, 22.5; ^{31}P NMR (162 MHz, $CDCl_3$) δ -3.8; FTIR (NaCl, neat): ν 3402, 1643, 1454, 1333 cm^{-1}; HRMS (EI, $C_{11}H_{16}O_4P$ (M+)): calcd.: 243.0786; found: 243.0788.



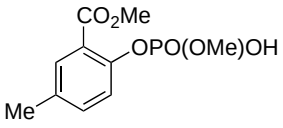
[1,1'-Biphenyl]-2-yl methyl hydrogen phosphate (3l). (0.85 g, 64% yield); yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, J = 7.4 Hz, 2H), 7.43 – 7.28 (m, 5H), 7.27 – 7.13 (m, 2H), 3.38 (d, J = 11.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.5 (d, J_{CP} = 6.0 Hz), 137.3, 133.6 (d, J_{CP} = 6.0 Hz), 131.1, 129.4, 128.6, 128.1, 127.4, 125.2, 120.4, 54.4 (d, J_{CP} = 6.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ -4.5; FTIR (NaCl, neat): ν 3402, 1498, 1445, 1250 cm^{-1}; HRMS (EI, $C_{13}H_{14}O_4P$ (M+)): calcd.: 265.0630; found: 265.0639.



Methyl phenyl hydrogen phosphate (3m). (0.86 g, 91% yield); yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.26 (m, 2H), 7.20 – 7.14 (m, 3H), 3.80 (d, J = 10.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.4, 129.7, 125.1, 120.1 (d, J_{CP} = 4.0 Hz), 54.7 (d, J_{CP} = 6.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ -3.9; FTIR (NaCl, neat): ν 3381, 1591, 1487 cm^{-1}; HRMS (EI, $C_7H_{10}O_4P$ (M+)): calcd.: 189.0317; found: 189.0315.



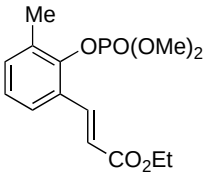
2-Fluorophenyl methyl hydrogen phosphate (3n). (0.69 g, 67% yield); yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.27 (m, 1H), 7.17 – 7.02 (m, 3H), 3.84 (d, J = 11.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.5 (dd, $J_{CF,\ CP}$ = 249.1, 5.8 Hz), 138.2 (d, J = 12.0 Hz), 126.0, 124.5 (d, J_{CP} = 4.0 Hz), 122.4 (d, J_{CP} = 2.0 Hz), 116.9 (d, J_{CP} = 19.0 Hz), 54.9 (d, J_{CP} = 6.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ -4.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ -130.92; FTIR (NaCl, neat): ν 3401, 1599, 1454 cm^{-1}; HRMS (EI, $C_7H_9FO_4$ (M+)): calcd.: 207.0223; found: 207.0224.



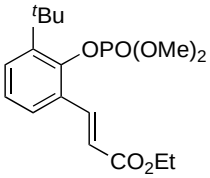
Methyl 2-((hydroxy(methoxy)phosphoryl)oxy)-5-methylbenzoate (3o). (0.78 g, 60% yield); yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (s, 1H), 7.37 – 7.20 (m, 2H), 3.89 (s, 3H), 3.86 (d, J = 11.6 Hz, 3H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 147.3 (d, J_{CP} = 7.0 Hz), 134.7, 134.2, 131.9, 122.6 (d, J_{CP} = 5.0 Hz), 121.6, 54.8 (d, J_{CP} = 6.0 Hz), 52.3, 20.5; ^{31}P NMR (162 MHz, $CDCl_3$) δ -4.7; FTIR (NaCl, neat): ν 3426, 1682, 1505, 1441 cm^{-1}; HRMS (EI, $C_{10}H_{14}O_6P$ (M+)): calcd.: 261.0528; found: 261.0530.

GP2-General experimental procedure for the palladium-catalyzed C-H alkenylation:

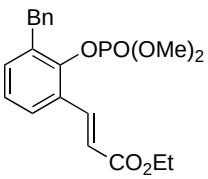
$Pd(OAc)_2$ (3.36 mg, 0.015 mmol, 10 mol % equiv) and AgOAc (75.1 mg, 0.45 mmol, 3.0 equiv) was carefully weighed to a vial equipped with a magnetic stirrer bar and a tightly-screwed cap. *Mono*-phosphoric acid (0.15 mmol, 1.0 equiv) in 1,4-dioxane (1 mL) was then added, followed by acrylates or styrene derivatives (0.30 mmol, 2.0 equiv). The reaction mixture was stirred at 110 ^{o}C for 15 h, and cooled to room temperature. The mixture was diluted with EtOAc (1 mL), quenched with 1N HCl (1 mL), and stirred at room temperature for 5 mins. The aqueous layer was further extracted with EtOAc (3 mL x 3), and the combined organic layer was concentrated *in vacuo*. No further purification was needed. TMS-diazomethane (0.4 mL, 0.75 mmol, 2.0 M in hexane, 5.0 equiv) was added to the crude product in MeOH (0.5 mL), and stirred at ambient temperature for 30 min. The residual crude product was concentrated *in vacuo* and purified by flash column chromatography (CH_2Cl_2:acetone = 20:1) to afford the desired alkenylated product.



(*E*)-Ethyl 3-(2-((dimethoxyphosphoryl)oxy)-3-methylphenyl)acrylate (2c-i). (37.7 mg, 80% yield); yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, J = 16.0 Hz, 1H), 7.46 (d, J = 7.4 Hz, 1H), 7.25 (d, J = 7.5 Hz, 1H), 7.12 (t, J = 7.8 Hz, 1H), 6.41 (d, J = 16.0 Hz, 1H), 4.26 (q, J = 7.1 Hz, 2H), 3.90 (d, J = 11.6 Hz, 6H), 2.41 (s, 3H), 1.34 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 147.8 (d, J_{CP} = 9.0 Hz), 139.0, 133.4 (d, J_{CP} = 1.0 Hz), 131.4 (d, J_{CP} = 4.0 Hz), 127.3 (d, J_{CP} = 4.0 Hz), 125.6, 124.8, 119.7, 60.4, 55.1 (d, J_{CP} = 6.0 Hz), 17.0, 14.2; ^{31}P NMR (162 MHz, $CDCl_3$) δ -4.0; FTIR (NaCl, neat): ν 1722, 1643, 1462 cm^{-1}; HRMS (EI, $C_{14}H_{20}O_6P$ (M+)): calcd.: 315.0998; found: 315.0993.

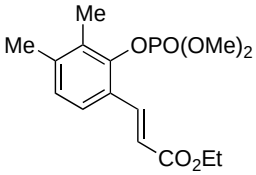


(*E*)-Ethyl 3-(3-(*tert*-butyl)-2-((dimethoxyphosphoryl)oxy)phenyl)acrylate (4a). (50.2 mg, 94% yield); yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, J = 15.9 Hz, 1H), 7.45 (d, J = 7.8 Hz, 2H), 7.16 – 7.14 (m, 1H), 6.37 (d, J = 15.8 Hz, 1H), 4.27 (q, J = 7.1 Hz, 2H), 3.87 (d, J = 11.2 Hz, 6H), 1.45 (s, 9H), 1.34 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 148.7 (d, J_{CP} = 9.0 Hz), 142.2 (d, J_{CP} = 5.0 Hz), 140.4, 130.0, 128.7, 125.8 (d, J_{CP} = 1.0 Hz), 125.3, 119.7, 60.4, 54.9 (d, J_{CP} = 6.0 Hz), 35.1, 30.6, 14.3; ^{31}P NMR (162 MHz, $CDCl_3$) δ -4.3; FTIR (NaCl, neat): ν 1713, 1636, 1423 cm^{-1}; HRMS (EI, $C_{17}H_{26}O_6P$ (M+)): calcd.: 357.1467; found: 357.1467.

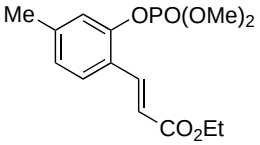


(*E*)-Ethyl 3-(3-benzyl-2-((dimethoxyphosphoryl)oxy)phenyl)acrylate (4b). (50.9 mg, 87% yield); yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, J = 16.0 Hz, 1H), 7.53 – 7.46 (m, 1H), 7.34 – 7.24 (m, 2H), 7.24 – 7.17 (m, 3H), 7.15 – 7.00 (m, 2H), 6.42 (d, J = 16.0 Hz, 1H), 4.26 (q, J = 7.1 Hz, 2H), 4.18 (s, 2H), 3.85 (d, J = 11.4 Hz, 6H), 1.33 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 147.4 (d, J_{CP} = 8.0 Hz), 139.5, 139.0, 134.4 (d, J_{CP} = 3.0 Hz), 133.1, 129.1, 128.4, 127.6 (d, J_{CP} = 3.0 Hz), 126.2, 125.8, 125.4, 119.8, 60.5, 55.2 (d, J_{CP} = 6.0 Hz), 36.0, 14.3; ^{31}P NMR (162

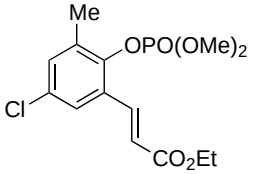
MHz, $CDCl_3$) δ -3.9; FTIR (NaCl, neat): ν 1712, 1634, 1454 cm^{-1}; HRMS (EI, $C_{20}H_{24}O_6P$ (M+)): calcd.: 391.1311; found: 391.1312.



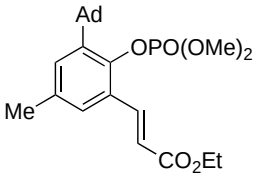
(*E*)-Ethyl 3-(2-((dimethoxyphosphoryl)oxy)-3,4-dimethylphenyl)acrylate (4c). (48.3 mg, 98% yield); yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, J = 16.0 Hz, 1H), 7.37 (d, J = 8.0 Hz, 1H), 7.02 (d, J = 8.0 Hz, 1H), 6.38 (d, J = 16.0 Hz, 1H), 4.26 (q, J = 7.1 Hz, 2H), 3.89 (d, J = 11.3 Hz, 6H), 2.29 (d, J = 7.4 Hz, 3H), 1.33 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.9, 147.7 (d, J_{CP} = 9.0 Hz), 141.5, 139.2, 129.9 (d, J_{CP} = 4.0 Hz), 127.2 (d, J_{CP} = 2.0 Hz), 124.9 (d, J_{CP} = 3.0 Hz), 123.8, 118.5, 60.3, 55.1 (d, J_{CP} = 6.0 Hz), 20.4, 14.2, 13.2; ^{31}P NMR (162 MHz, $CDCl_3$) δ -3.8; FTIR (NaCl, neat): ν 1713, 1634, 1454 cm^{-1}; HRMS (EI, $C_{15}H_{22}O_6P$ (M+)): calcd.: 329.1154; found: 329.1155.



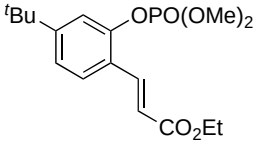
(*E*)-Ethyl 3-(2-((dimethoxyphosphoryl)oxy)-4-methylphenyl)acrylate (4d). (38.2 mg, 81% yield); yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, J = 16.1 Hz, 1H), 7.49 (d, J = 8.0 Hz, 1H), 7.22 (s, 1H), 7.01 (d, J = 8.0 Hz, 1H), 6.42 (d, J = 16.1 Hz, 1H), 4.26 (q, J = 7.1 Hz, 2H), 3.90 (d, J = 11.4 Hz, 6H), 2.37 (s, 3H), 1.33 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.9, 149.0 (d, J_{CP} = 7.0 Hz), 142.5, 137.9, 127.5, 126.3, 123.2 (d, J_{CP} = 7.0 Hz), 120.9 (d, J_{CP} = 2.0 Hz), 119.1, 60.4, 55.1 (d, J_{CP} = 6.0 Hz), 21.4, 14.3; ^{31}P NMR (162 MHz, $CDCl_3$) δ -4.5; FTIR (NaCl, neat): ν 1713, 1614, 1447 cm^{-1}; HRMS (EI, $C_{14}H_{20}O_6P$ (M+)): calcd.: 315.0998; found: 315.1000.



(*E*)-Ethyl 3-(5-chloro-2-((dimethoxyphosphoryl)oxy)-3-methylphenyl)acrylate (4e). (39.8 mg, 76% yield); yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, J = 16.0 Hz, 1H), 7.42 (d, J = 2.4 Hz, 1H), 7.22 (d, J = 1.9 Hz, 1H), 6.40 (d, J = 16.0 Hz,1H), 4.26 (q, J = 7.1 Hz, 2H), 3.89 (d, J = 11.6 Hz, 6H), 2.38 (s, 3H), 1.33 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 146.3 (d, J_{CP} = 8.0 Hz), 137.7, 133.3 (d, J_{CP} = 3.0 Hz), 132.8, 130.9 (d, J_{CP} = 2.0 Hz), 128.9, 124.5, 120.9, 60.6, 55.2 (d, J_{CP} = 6.0 Hz), 17.0, 14.2; ^{31}P NMR (162 MHz, $CDCl_3$) δ -3.9; FTIR (NaCl, neat): ν 1713, 1639, 1468 cm^{-1}; HRMS (EI, $C_{14}H_{19}ClO_6P$ (M+)): calcd.: 349.0608; found: 349.0605.

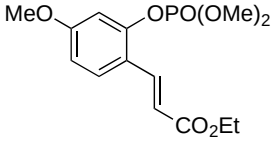


(*E*)-Ethyl 3-(3-(adamantan-1-yl)-2-((dimethoxyphosphoryl)oxy)-5-methylphenyl) acrylate (4f). (64.6 mg, 96% yield); yellow solid; m.p. 102 – 109 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, J = 15.8 Hz, 1H), 7.23 (s, 1H), 7.20 (s, 1H), 6.35 (d, J = 15.8 Hz, 1H), 4.26 (q, J = 7.1 Hz, 2H), 3.88 (d, J = 11.6 Hz, 6H), 2.31 (s, 3H), 2.11 (s, 9H), 1.84 – 1.72 (m, 6H), 1.33 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8, 147.0 (d, J_{CP} = 9.0 Hz), 141.8 (d, J_{CP} = 5.0 Hz), 140.7, 134.6, 130.9, 128.3, 125.9, 119.5, 60.3, 54.9 (d, J_{CP} = 6.0 Hz), 40.9, 37.3, 36.6, 29.0, 21.0, 14.3; ^{31}P NMR (162 MHz, $CDCl_3$) δ -4.0; FTIR (NaCl, neat): ν 1711, 1634, 1447 cm^{-1}; HRMS (EI, $C_{24}H_{34}O_6P$ (M+)): calcd.: 449.2093; found: 449.2090.

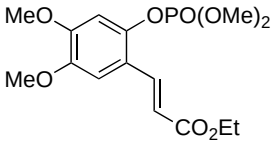


(*E*)-Ethyl 3-(4-(*tert*-butyl)-2-((dimethoxyphosphoryl)oxy)phenyl)acrylate (4g). (45.4 mg, 85% yield); yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, J = 16.1 Hz, 1H), 7.53 (d, J = 8.3 Hz, 1H), 7.40 (s, 1H), 7.22 (d, J = 8.0 Hz, 1H), 6.43 (d, J = 16.1 Hz, 1H), 4.26 (q, J = 7.1 Hz, 2H), 3.89 (d, J = 11.6 Hz, 6H), 1.34 – 1.30 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8, 155.7, 149.0 (d, J_{CP} = 6.0 Hz), 137.9, 127.3, 123.2 (d, J_{CP} = 7.0 Hz), 122.6, 119.2, 117.6 (d, J_{CP} = 2.0 Hz), 60.4, 55.0 (d, J

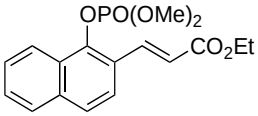
= 6.0 Hz), 35.0, 30.9, 14.2; ^{31}P NMR (162 MHz, $CDCl_3$) δ -4.4; FTIR (NaCl, neat): ν 1713, 1634, 1614, 1505 cm^{-1}; HRMS (EI, $C_{17}H_{26}O_6P$ (M+)): calcd.: 357.1467; found: 357.1468.



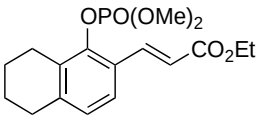
(*E*)-Ethyl 3-(2-((dimethoxyphosphoryl)oxy)-4-methoxyphenyl)acrylate (4h). (38.6 mg, 78% yield); yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, J = 16.1 Hz, 1H), 7.54 (d, J = 8.8 Hz, 1H), 6.97 (dd, J = 2.4, 1.0 Hz, 1H), 6.76 (dd, J = 8.8, 2.5 Hz, 1H), 6.35 (d, J = 16.0 Hz, 1H), 4.25 (q, J = 7.2 Hz, 2H), 3.90 (d, J = 11.2 Hz, 6H), 3.84 (s, 3H), 1.34 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.1, 162.1, 150.2 (d, J_{CP} = 7.0 Hz), 137.7, 128.6, 118.5 (d, J_{CP} = 7.0 Hz), 117.4, 111.8, 106.0 (d, J_{CP} = 2.0 Hz), 60.3, 55.6, 55.1 (d, J_{CP} = 7.0 Hz), 14.3; ^{31}P NMR (162 MHz, $CDCl_3$) δ -4.6; FTIR (NaCl, neat): ν 1713, 1614, 1505 cm^{-1}; HRMS (EI, $C_{14}H_{20}O_7P$ (M+)): calcd.: 331.0947; found: 331.0945.



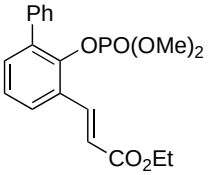
(*E*)-Ethyl 3-(2-((dimethoxyphosphoryl)oxy)-4,5-dimethoxyphenyl)acrylate (4i). (43.2 mg, 80% yield); brown solid; m.p. 62 – 64 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, J = 16.0 Hz, 1H), 7.03 (s, 1H), 6.97 (s, 1H), 6.34 (d, J = 16.0 Hz, 1H), 4.26 (q, J = 7.1 Hz, 2H), 3.92 (s, 3H), 3.90 (s, 3H), 3.89 (d, J = 6.0 Hz, 6H), 1.33 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.9, 151.6, 146.5, 143.7 (d, J_{CP} = 7.0 Hz), 137.6, 117.6 (d, J_{CP} = 6.0 Hz), 117.3, 108.3, 104.4, 60.4, 56.2, 56.1, 55.1 (d, J_{CP} = 7.0 Hz), 14.2; ^{31}P NMR (162 MHz, $CDCl_3$) δ -4.1; FTIR (NaCl, neat): ν 1707, 1634, 1609, 1514, 1445 cm^{-1}; HRMS (EI, $C_{15}H_{22}O_8P$ (M+)): calcd.: 361.1052; found: 361.1034.



(*E*)-Ethyl 3-(1-((dimethoxyphosphoryl)oxy)naphthalen-2-yl)acrylate (4j). (43.6 mg, 83% yield); yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 – 8.24 (m, 2H), 7.82 (d, J = 8.0 Hz, 1H), 7.73 – 7.63 (m, 2H), 7.63 – 7.51 (m, 2H), 6.54 (d, J = 16.1 Hz, 1H), 4.29 (q, J = 7.1 Hz, 2H), 3.92 (d, J = 11.4 Hz, 6H), 1.36 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 145.7 (d, J_{CP} = 9.0 Hz), 138.4, 135.5, 127.7 (d, J_{CP} = 2.0 Hz), 127.2, 127.2, 126.0, 123.2, 122.8 (d, J_{CP} = 4.0 Hz), 122.7 (d, J_{CP} = 2.0 Hz), 119.8, 60.5, 55.3 (d, J_{CP} = 6.0 Hz), 14.3; ^{31}P NMR (162 MHz, $CDCl_3$) δ -3.5; FTIR (NaCl, neat): ν 1712, 1634, 1470 cm^{-1}; HRMS (EI, $C_{17}H_{20}O_6P$ (M+)): calcd.: 351.0998; found: 351.0990.

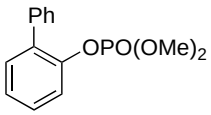


(*E*)-Ethyl 3-(1-((dimethoxyphosphoryl)oxy)-5,6,7,8-tetrahydronaphthalen-2-yl) acrylate (4k). (42.5 mg, 80% yield); yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, J = 16.0 Hz, 1H), 7.36 (d, J = 8.1 Hz, 1H), 6.94 (d, J = 8.1 Hz, 1H), 6.37 (d, J = 16.0 Hz, 1H), 4.25 (q, J = 7.1 Hz, 2H), 3.89 (d, J = 11.4 Hz, 6H), 2.81 (dd, J = 26.7, 5.8 Hz, 4H), 1.87 – 1.69 (m, 4H), 1.33 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.9, 147.7 (d, J_{CP} = 8.0 Hz), 142.2, 139.1, 130.7 (d, J_{CP} = 3.0 Hz), 126.7, 124.3 (d, J_{CP} = 4.0 Hz), 123.6, 118.4, 60.3, 55.1 (d, J_{CP} = 6.0 Hz), 29.7, 23.8, 22.3, 22.2, 14.3; ^{31}P NMR (162 MHz, $CDCl_3$) δ -4.1; FTIR (NaCl, neat): ν 1713, 1639, 1566, 1418 cm^{-1}; HRMS (EI, $C_{17}H_{24}O_6P$ (M+)): calcd.: 355.1311; found: 355.1298.

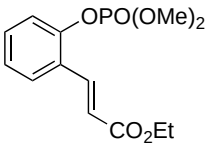


(*E*)-Ethyl 3-(2-((dimethoxyphosphoryl)oxy)-[1,1'-biphenyl]-3-yl)acrylate (4l). (37.3 mg, 66% yield); yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, J = 16.0 Hz, 1H), 7.62 (d, J = 7.8 Hz, 1H), 7.53 – 7.47 (m, 2H), 7.44 (t, J = 7.5 Hz, 2H), 7.40 – 7.32 (m, 2H), 7.31 – 7.23 (m, 1H), 6.47 (d, J = 16.0 Hz, 1H), 4.27 (q, J = 7.1 Hz, 2H), 3.44 (d, J = 11.5 Hz, 6H), 1.34 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 146.3 (d, J_{CP} = 8.0 Hz), 138.9, 137.4, 135.9 (d, J_{CP} = 4.0 Hz),

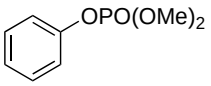
133.2, 129.6, 128.3 (d, J_{CP} = 3.0 Hz), 128.2, 127.6, 126.5, 125.8, 120.3, 60.5, 54.5 (d, J_{CP} = 6.0 Hz), 14.3; ^{31}P NMR (162 MHz, $CDCl_3$) δ -4.2; FTIR (NaCl, neat): ν 1712, 1634, 1427 cm^{-1}; HRMS (EI, $C_{19}H_{22}O_6P$ (M+)): calcd.: 377.1154; found: 377.1154.



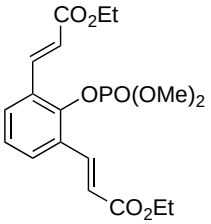
[1,1'-Biphenyl]-2-yl dimethyl phosphate (4l-i). (7.1 mg, 17% yield); yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.47 (m, 2H), 7.47 – 7.40 (m, 3H), 7.40 – 7.29 (m, 3H), 7.29 – 7.20 (m, 1H), 3.58 (d, J = 11.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.5, 137.3, 133.6, 131.2, 129.5, 128.8 (d, J_{CP} = 1.0 Hz), 128.1, 127.4, 125.4, 120.4 (d, J_{CP} = 2.0 Hz), 54.7 (d, J_{CP} = 6.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ -4.6; FTIR (NaCl, neat): ν 1732, 1645, 1479, 1435 cm^{-1}; HRMS (EI, $C_{14}H_{16}O_4P$ (M+)): calcd.: 279.0786; found: 279.0783.



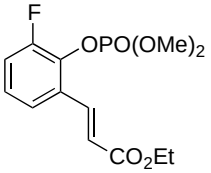
(*E*)-Ethyl 3-(2-((dimethoxyphosphoryl)oxy)phenyl)acrylate (4m). (24.8 mg, 55% yield); yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, J = 16.1 Hz, 1H), 7.61 (d, J = 7.8 Hz, 1H), 7.45 – 7.32 (m, 2H), 7.21 (t, J = 7.4 Hz, 1H), 6.47 (d, J = 16.0 Hz, 1H), 4.27 (q, J = 7.1 Hz, 2H), 3.90 (d, J = 11.4 Hz, 6H), 1.34 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 149.2 (d, J_{CP} = 7.0 Hz), 137.9, 131.4, 127.8, 126.2 (d, J_{CP} = 7.0 Hz), 125.4, 120.5 (d, J_{CP} = 2.0 Hz), 120.3, 60.6, 55.1 (d, J_{CP} = 7.0 Hz), 14.3; ^{31}P NMR (162 MHz, $CDCl_3$) δ -4.4; FTIR (NaCl, neat): ν 1713, 1634, 1487, 1454 cm^{-1}; HRMS (EI, $C_{13}H_{18}O_6P$ (M+)): calcd.: 301.0841; found: 301.0837.



Dimethyl phenyl phosphate (4m-i). (4.2 mg, 14% yield); yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.32 (m, 2H), 7.24 – 7.15 (m, 3H), 3.87 (d, J = 11.3 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.6 (d, J_{CP} = 7.0 Hz), 129.8, 125.1, 119.8 (d, J_{CP} = 5.0 Hz), 54.9 (d, J_{CP} = 6.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ -4.1; FTIR (NaCl, neat): ν 1639, 1593, 1489 cm^{-1}; HRMS (EI, $C_8H_{12}O_4P$ (M+)): calcd.: 203.0473; found: 203.0469.

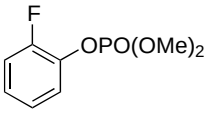


(2*E*,2'*E*)-Diethyl 3,3'-(2-((dimethoxyphosphoryl)oxy)-1,3-phenylene)diacrylate (4m-ii). (9.6 mg, 16% yield); yellow solid; m.p. 107 – 111 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, J = 15.4 Hz, 2H), 7.65 (d, J = 7.8 Hz, 2H), 7.28 – 7.20 (m, 1H), 6.44 (d, J = 11.5 Hz, 2H), 4.27 (q, J = 7.1 Hz, 4H), 3.93 (d, J = 11.4 Hz, 6H), 1.34 (t, J = 7.1 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 147.6 (d, J = 8.0 Hz), 138.1, 128.9, 128.6 (d, J = 4.0 Hz), 126.0, 120.9, 60.6, 55.4 (d, J = 6.0 Hz), 14.3; ^{31}P NMR (162 MHz, $CDCl_3$) δ -3.7; FTIR (NaCl, neat): ν 1711, 1636, 1435 cm^{-1}; HRMS (EI, $C_{18}H_{24}O_8P$ (M+)): calcd.: 399.1209; found: 399.1200.

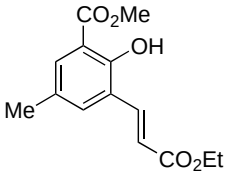


(*E*)-Ethyl 3-(2-((dimethoxyphosphoryl)oxy)-3-fluorophenyl)acrylate (4n). (23.4 mg, 49% yield); yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, J = 16.1 Hz, 1H), 7.47 – 7.34 (m, 1H), 7.25 – 7.09 (m, 2H), 6.47 (d, J = 16.1 Hz, 1H), 4.27 (q, J = 7.1 Hz, 2H), 3.96 (d, J = 11.5 Hz, 6H), 1.34 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 154.4 (d, J_{CF} = 252.6 Hz), 137.3 (dd, $J_{CF,\ CP}$ = 13.3, 7.7 Hz), 137.0 (d, J_{CP} = 3.0 Hz), 129.6 (d, J_{CP} = 3.0 Hz), 126.0 (d, J_{CP} = 7.0 Hz), 122.4, 121.5, 118.1 (d, J_{CF} = 19.0 Hz), 60.7, 55.3 (d, J_{CP} = 6.0 Hz), 14.2; ^{31}P NMR (162 MHz, $CDCl_3$) δ -3.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ -128.27; FTIR (NaCl, neat): ν 1713, 1643, 1479 cm^{-1}; HRMS (EI, $C_{13}H_{17}FO_6P$ (M+)):

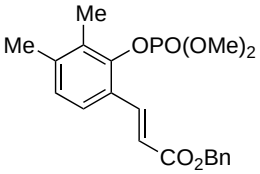
calcd.: 319.0747; found: 319.0747.



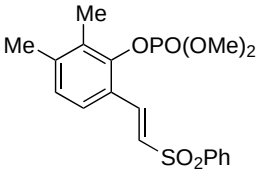
2-Fluorophenyl dimethyl phosphate (4n-i). (11.9 mg, 36% yield); yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (t, J = 7.9 Hz, 1H), 7.30 – 7.01 (m, 3H), 3.91 (d, J = 11.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.5 (dd, $J_{CF,\ CP}$ = 252.9, 4.2 Hz), 138.3, 126.1 (d, J_{CP} = 7.0 Hz), 124.6 (d, J_{CP} = 4.0 Hz), 122.4, 122.3, 117.0 (d, J_{CF} = 18.0 Hz), 55.2 (d, J_{CP} = 6.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ -4.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -131.33; FTIR (NaCl, neat): v 1715, 1639, 1611, 1504 cm^{-1}; HRMS (EI, $C_8H_{11}FO_4P$ (M+)): calcd.: 221.0379; found: 221.0387.



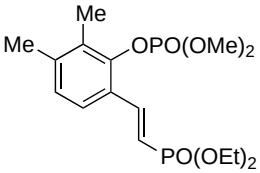
(*E*)-Methyl 3-(3-ethoxy-3-oxoprop-1-en-1-yl)-2-hydroxy-5-methylbenzoate (4o). (37.3 mg, 94% yield); white solid; m.p. 97 – 100 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.30 (s, 1H), 7.93 (d, J = 16.2 Hz, 1H), 7.68 (d, J = 1.6 Hz, 1H), 7.49 (d, J = 1.8 Hz, 1H), 6.62 (d, J = 16.2 Hz, 1H), 4.26 (q, J = 7.1 Hz, 2H), 3.96 (s, 3H), 2.29 (s, 3H), 1.34 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 167.3, 158.6, 138.8, 135.7, 131.7, 128.1, 123.1, 119.8, 112.6, 60.4, 52.4, 20.3, 14.3; FTIR (NaCl, neat): v 3426, 1672, 1441 cm^{-1}; HRMS (EI, $C_{14}H_{17}O_5$ (M+)): calcd.: 265.1076; found: 265.1074.



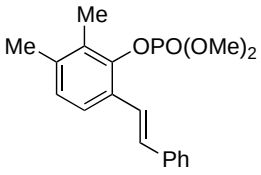
(*E*)-Benzyl 3-(2-((dimethoxyphosphoryl)oxy)-3,4-dimethylphenyl)acrylate (5a). (53.3 mg, 91% yield); yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, J = 16.0 Hz, 3H), 7.49 – 7.29 (m, 6H), 7.01 (d, J = 8.0 Hz, 1H), 6.42 (d, J = 16.0 Hz, 1H), 5.24 (s, 2H), 3.80 (d, J = 11.4 Hz, 6H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 147.7 (d, J_{CP} = 8.0 Hz), 141.7, 139.8, 136.0, 129.9 (d, J_{CP} = 3.0 Hz), 128.5, 128.2, 128.2, 127.2 (d, J_{CP} = 1.0 Hz), 124.8 (d, J_{CP} = 3.0 Hz), 123.9, 118.1, 66.2, 55.0 (d, J_{CP} = 6.0 Hz), 20.5, 13.3; ^{31}P NMR (162 MHz, $CDCl_3$) δ -3.9; FTIR (NaCl, neat): v 1713, 1634, 1607, 1454 cm^{-1}; HRMS (EI, $C_{20}H_{24}O_6P$ (M+)): calcd.: 391.1311; found: 391.1297.



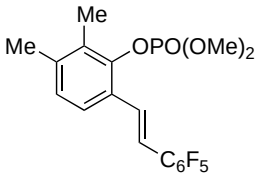
(*E*)-2,3-Dimethyl-6-(2-(phenylsulfonyl)vinyl)phenyl dimethyl phosphate (5b). (45.8 mg, 77% yield); yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, J = 15.4 Hz, 1H), 8.00 – 7.93 (m, 2H), 7.64 – 7.58 (m, 1H), 7.58 – 7.51 (m, 2H), 7.29 – 7.22 (m, 1H), 7.00 (d, J = 8.0 Hz, 1H), 6.81 (d, J = 15.4 Hz, 1H), 3.89 (d, J = 11.4 Hz, 6H), 2.30 (s, 3H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.9 (d, J_{CP} = 8.0 Hz), 142.8, 140.9, 137.8, 133.2, 130.4 (d, J_{CP} = 3.0 Hz), 129.2, 127.6, 127.3, 124.5, 123.0, 122.9, 55.2 (d, J_{CP} = 6.0 Hz), 20.5, 13.3; ^{31}P NMR (162 MHz, $CDCl_3$) δ -3.7; FTIR (NaCl, neat): v 1614, 1447, 1410, 1306 cm^{-1}; HRMS (EI, $C_{18}H_{22}O_6PS$ (M+)): calcd.: 397.0875; found: 397.0871.



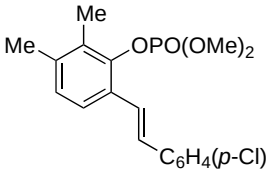
(*E*)-6-(2-(Diethoxyphosphoryl)vinyl)-2,3-dimethylphenyl dimethyl phosphate (5c). (45.9 mg, 78% yield); yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (dd, J = 22.7, 17.7 Hz, 1H), 7.34 (d, J = 7.9 Hz, 1H), 7.02 (d, J = 7.9 Hz, 1H), 6.20 (t, J = 18.1 Hz, 1H), 4.14 (dq, J = 14.0, 7.1 Hz, 4H), 3.89 (dd, J = 11.3, 1.3 Hz, 6H), 2.30 (s, 3H), 2.28 (s, 3H), 1.36 (t, J = 7.1 Hz, 3H), 1.35 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.3 (d, J_{CP} = 8.0 Hz), 143.1 (d, J_{CP} = 8.0 Hz), 143.1, 141.4, 129.8, 127.1, 125.4 (d, J_{CP} = 21.0 Hz), 123.7, 114.3 (d, J_{CP} = 191.9 Hz), 61.8 (d, J_{CP} = 5.0 Hz), 55.1 (d, J_{CP} = 6.0 Hz), 20.4, 16.3 (d, J_{CP} = 6.0 Hz), 13.2; ^{31}P NMR (162 MHz, $CDCl_3$) δ 19.4, -3.7; FTIR (NaCl, neat): v 1614, 1568, 1454, 1410 cm^{-1}; HRMS (EI, $C_{16}H_{27}O_7P_2$ (M+)): calcd.: 393.1232; found: 393.1222.



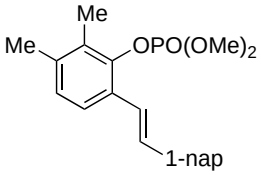
(*E*)-2,3-Dimethyl-6-styrylphenyl dimethyl phosphate (5d). (40.4 mg, 81% yield); yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.46 (m, 3H), 7.43 (d, J = 8.0 Hz, 1H), 7.35 (t, J = 7.6 Hz, 2H), 7.29 – 7.22 (m, 1H), 7.08 – 6.97 (m, 2H), 3.83 (d, J = 11.3 Hz, 6H), 2.30 (s, 3H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.9 (d, J_{CP} = 8.0 Hz), 138.3, 137.6, 129.4 (d, J_{CP} = 4.0 Hz), 129.2, 128.7, 127.6, 127.5, 127.1, 126.5, 123.3, 122.9 (d, J_{CP} = 1.0 Hz), 55.0 (d, J_{CP} = 6.0 Hz), 20.3, 13.3; ^{31}P NMR (162 MHz, $CDCl_3$) δ -3.4; FTIR (NaCl, neat): v 1636, 1452, 1277 cm^{-1}; HRMS (EI, $C_{18}H_{22}O_4P$ (M+)): calcd.: 333.1256; found: 333.1253.



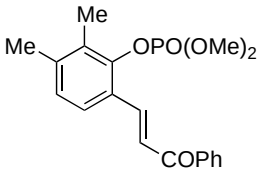
(*E*)-2,3-Dimethyl-6-(2-(perfluorophenyl)vinyl)phenyl dimethyl phosphate (5e). (46.2 g, 73% yield); yellow solid; m.p. 122 – 124 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, J = 16.8 Hz, 1H), 7.43 (d, J = 8.0 Hz, 1H), 7.04 (d, J = 8.0 Hz, 1H), 6.91 (d, J = 16.8 Hz, 1H), 3.86 (d, J = 11.3 Hz, 6H), 2.31 (s, 3H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.0 (d, J_{CP} = 9.0 Hz), 144.8 (d, J_{CF} = 247.0 Hz), 140.0 (d, J_{CP} = 1.0 Hz), 139.6 (d, J_{CF} = 254.0 Hz), 137.7 (d, J_{CF} = 251.6 Hz), 131.8 (t, J_{CF} = 7.9 Hz), 129.7 (d, J_{CP} = 4.0 Hz), 127.2 (d, J_{CP} = 2.0 Hz), 126.9 (d, J_{CP} = 3.0 Hz), 122.9, 113.0, 112.6 (td, $J_{CF,\ CP}$ = 13.7, 4.1 Hz), 54.9 (d, J_{CP} = 6.0 Hz), 20.3, 13.3; ^{31}P NMR (162 MHz, $CDCl_3$) δ -3.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ -142.94 (dd, J_{FF} = 21.5, 7.7 Hz), -156.72 (t, J_{FF} = 20.7 Hz), -163.04 (td, J_{FF} = 21.3, 7.5 Hz).; FTIR (NaCl, neat): v 1520, 1454, 1277 cm^{-1}; HRMS (EI, $C_{18}H_{17}F_5O_4P$ (M+)): calcd.: 423.0785; found: 423.0798.



(*E*)-6-(4-Chlorostyryl)-2,3-dimethylphenyl dimethyl phosphate (5f). (39.6 mg, 72% yield); yellow solid; m.p. 90 – 95 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.43 (m, 3H), 7.41 (d, J = 8.0 Hz, 1H), 7.35 – 7.28 (m, 2H), 7.01 (d, J = 8.0 Hz, 1H), 6.96 (d, J = 16.3 Hz, 1H), 3.83 (d, J = 11.3 Hz, 6H), 2.29 (s, 3H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.9, 138.6, 136.2, 133.1, 129.4 (d, J_{CP} = 4.0 Hz), 128.8, 127.8, 127.6, 127.3, 127.1, 124.1, 122.9, 55.0 (d, J_{CP} = 6.0 Hz), 20.3, 13.3; ^{31}P NMR (162 MHz, $CDCl_3$) δ -3.4; FTIR (NaCl, neat): v 1493, 1454, 1265 cm^{-1}; HRMS (EI, $C_{18}H_{21}ClO_4P$ (M+)): calcd.: 367.0866; found: 367.0865.



(*E*)-2,3-Dimethyl-6-(2-(naphthalen-2-yl)vinyl)phenyl dimethyl phosphate (5g). (36.7 mg, 64% yield); orange solid; m.p. 48 – 53 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.74 (m, 5H), 7.63 (d, J = 16.3 Hz, 1H), 7.53 – 7.40 (m, 3H), 7.19 (d, J = 16.3 Hz, 1H), 7.04 (d, J = 8.0 Hz, 1H), 3.84 (d, J = 11.3 Hz, 6H), 2.31 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.9 (d, J_{CP} = 9.0 Hz), 138.3, 135.1, 133.7, 133.0, 129.4 (d, J_{CP} = 4.0 Hz), 129.3, 128.3, 128.0, 127.7, 127.1, 126.7, 126.3, 125.8, 123.8, 123.4, 122.9, 55.0 (d, J_{CP} = 6.0 Hz), 20.3, 13.3; ^{31}P NMR (162 MHz, $CDCl_3$) δ -3.3; FTIR (NaCl, neat): v 1454, 1265, 1186 cm^{-1}; HRMS (EI, $C_{22}H_{24}O_4P$ (M+)): calcd.: 383.1412; found: 383.1409.

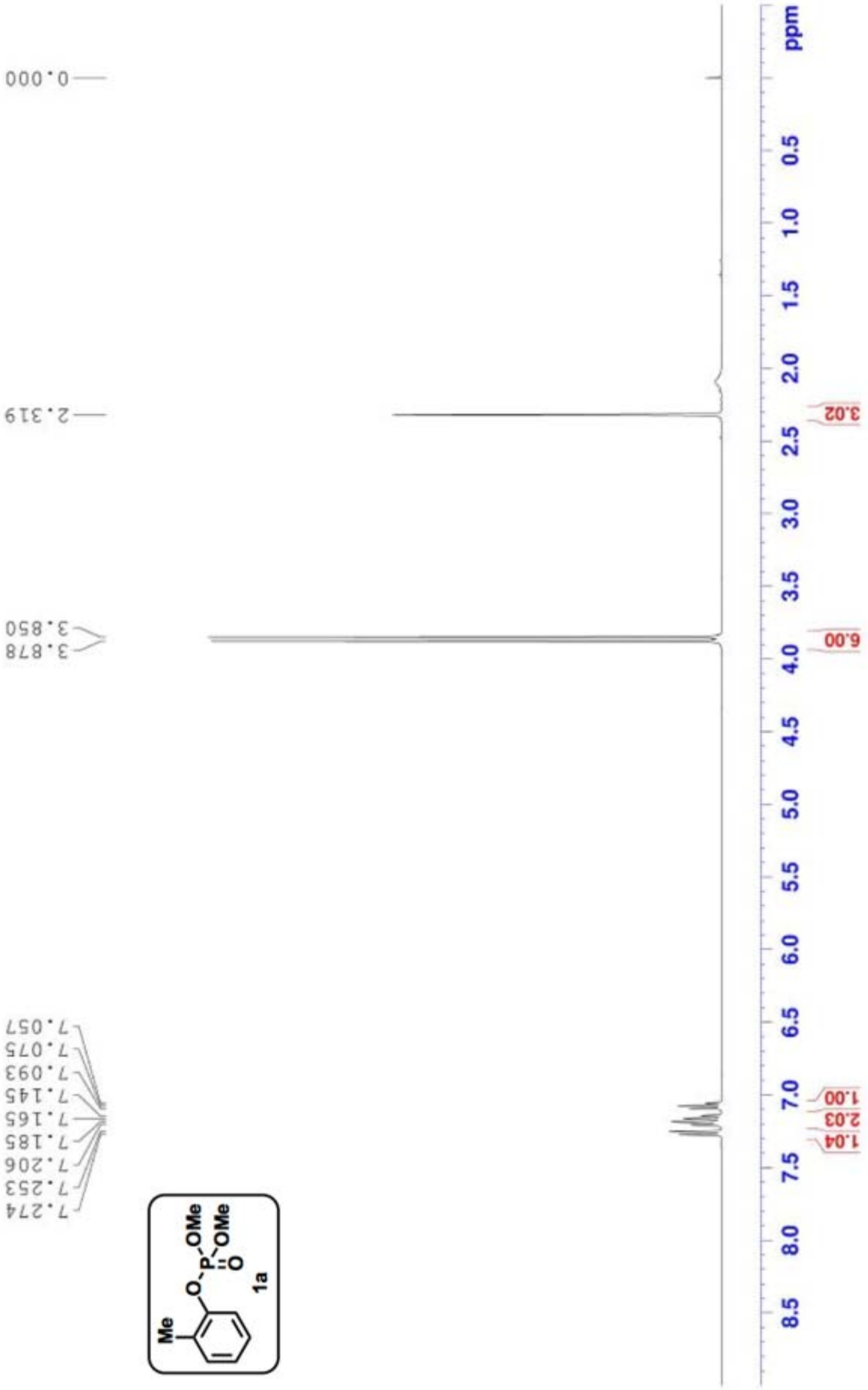


(*E*)-2,3-Dimethyl-6-(3-oxo-3-phenylprop-1-en-1-yl)phenyl dimethyl phosphate (5h). (36.2 mg, 67% yield); orange solid; m.p. 121 – 127 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, J = 15.8 Hz, 1H), 8.07 – 7.94 (m, 2H), 7.63 – 7.54 (m, 1H), 7.55 – 7.42 (m, 4H), 7.06 (d, J = 7.9 Hz, 1H), 3.86 (d, J = 11.4 Hz, 6H), 2.33 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.7, 148.3, 141.9, 139.8, 138.2, 132.6, 130.1, 128.6, 128.5, 127.2, 125.4, 124.1, 122.7, 55.1 (d, J_{CP} =

6.0 Hz), 20.6, 13.3; ^{31}P NMR (162 MHz, $CDCl_3$) δ -3.8; FTIR (NaCl, neat): ν 1663, 1603, 1449, 1265 cm^{-1}; HRMS (EI, $C_{19}H_{22}O_5P$ (M+)): calcd.: 361.1205; found: 361.1198.

Reference

1. M. F. Orrie and M. S. Arnold, *J. Am. Chem. Soc.,* 1950, **72**, 624.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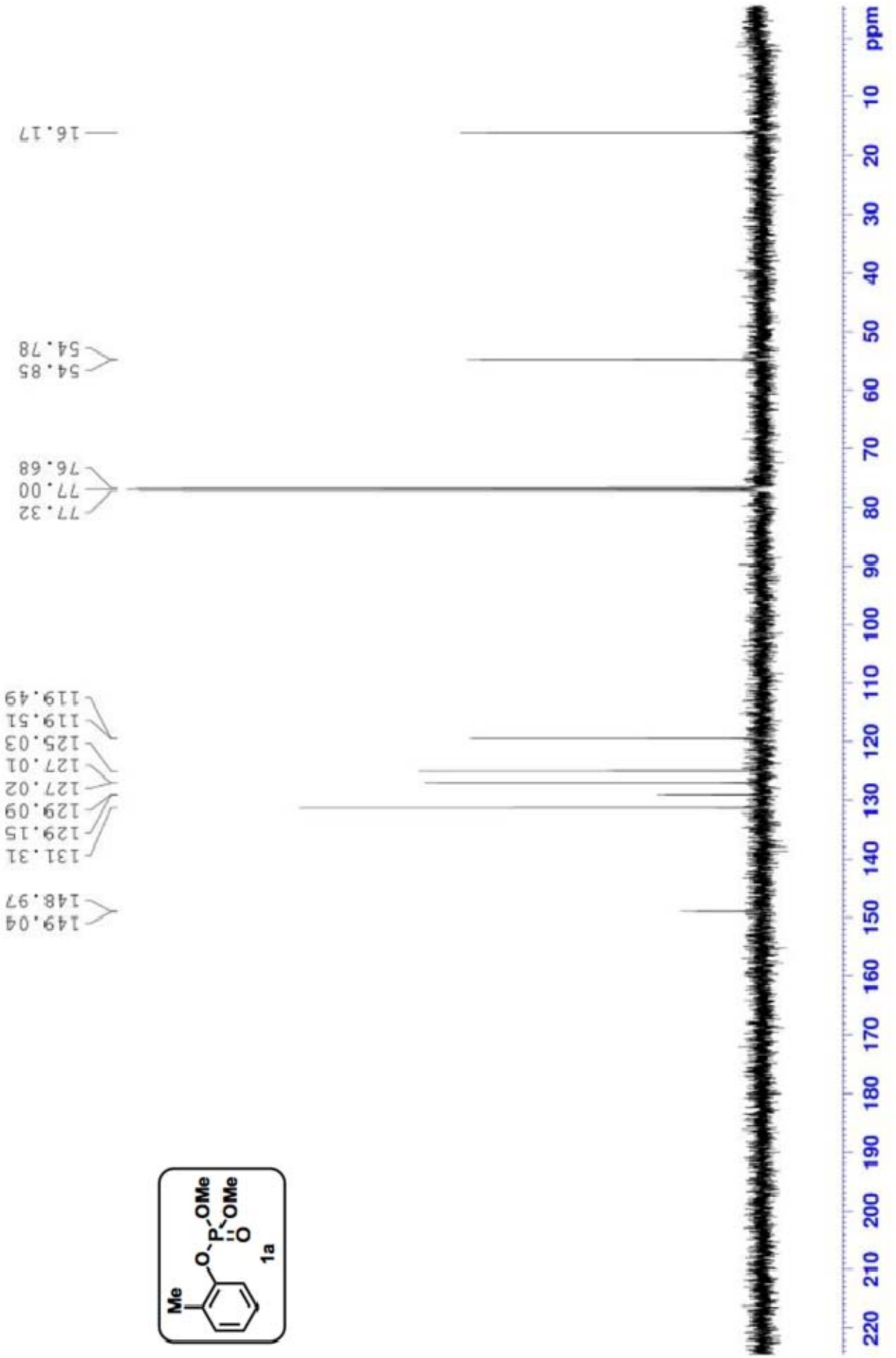

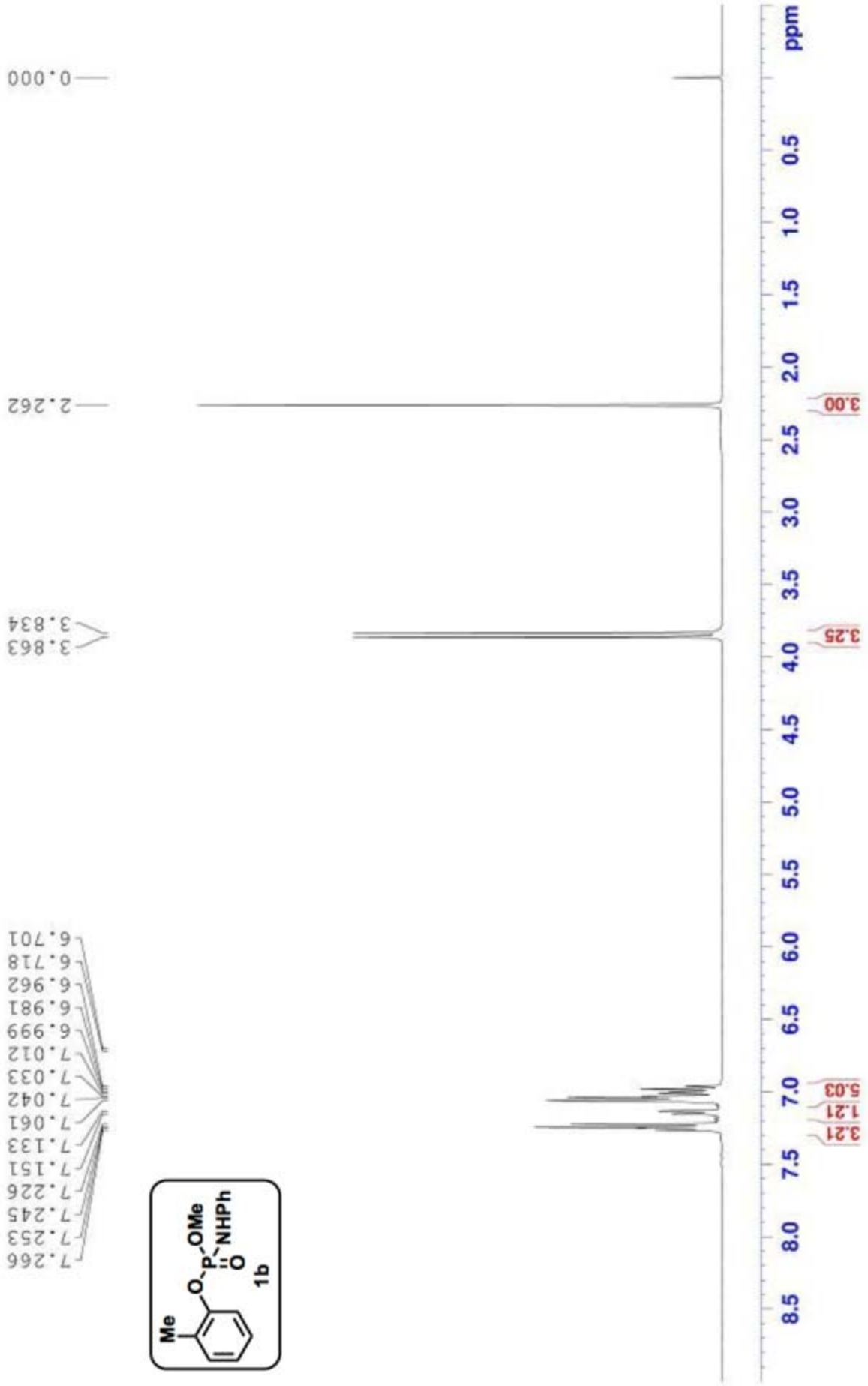
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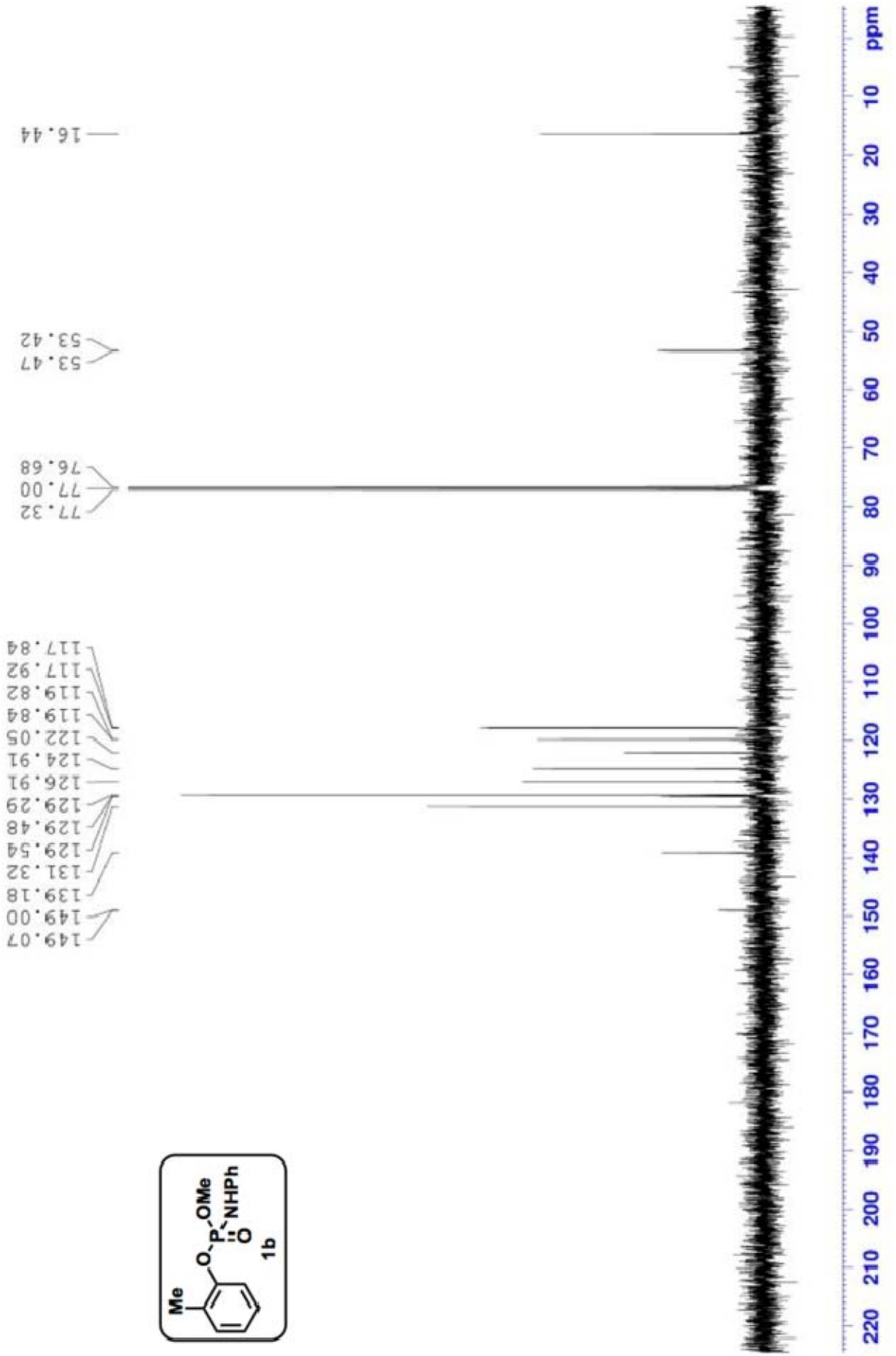

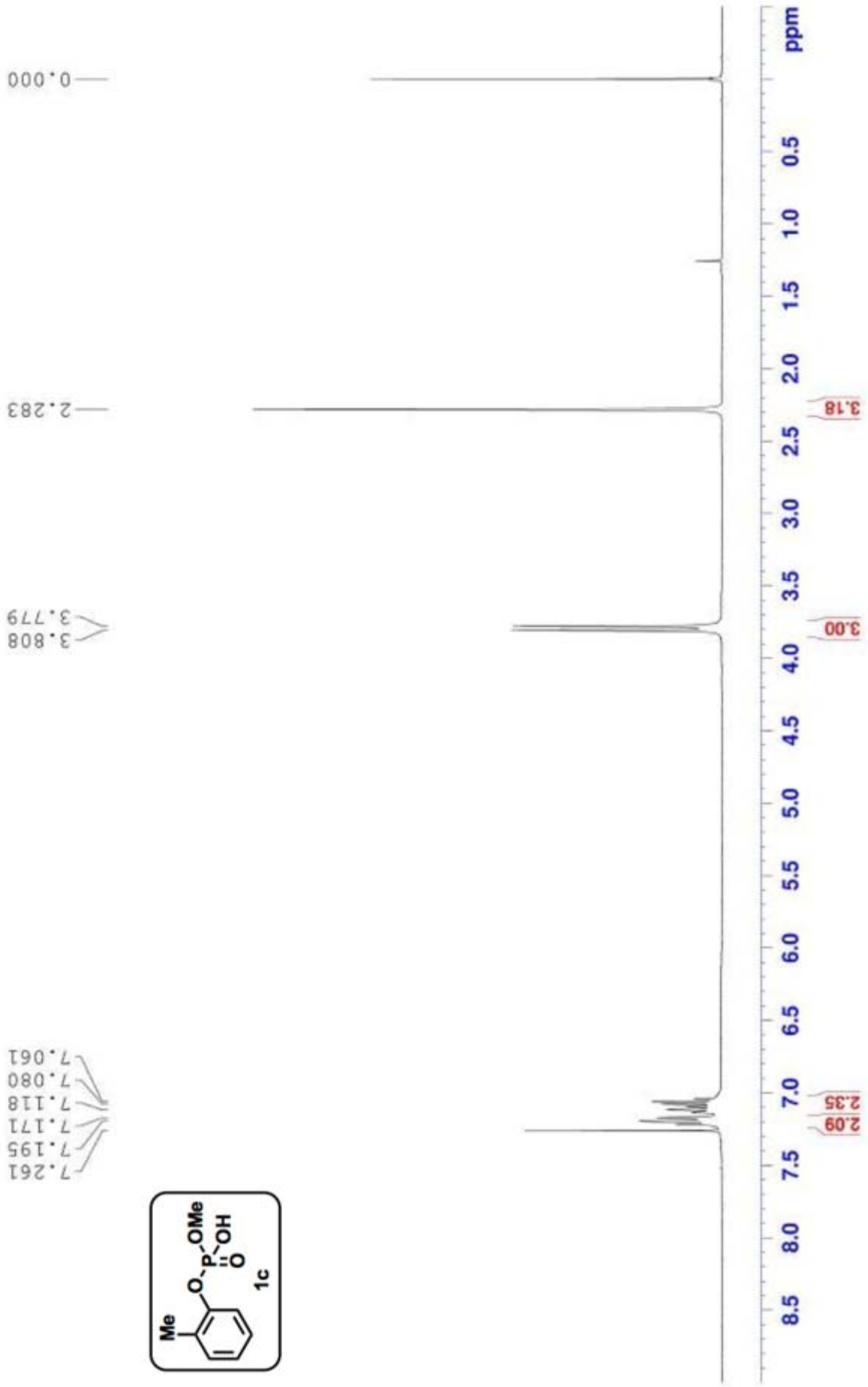
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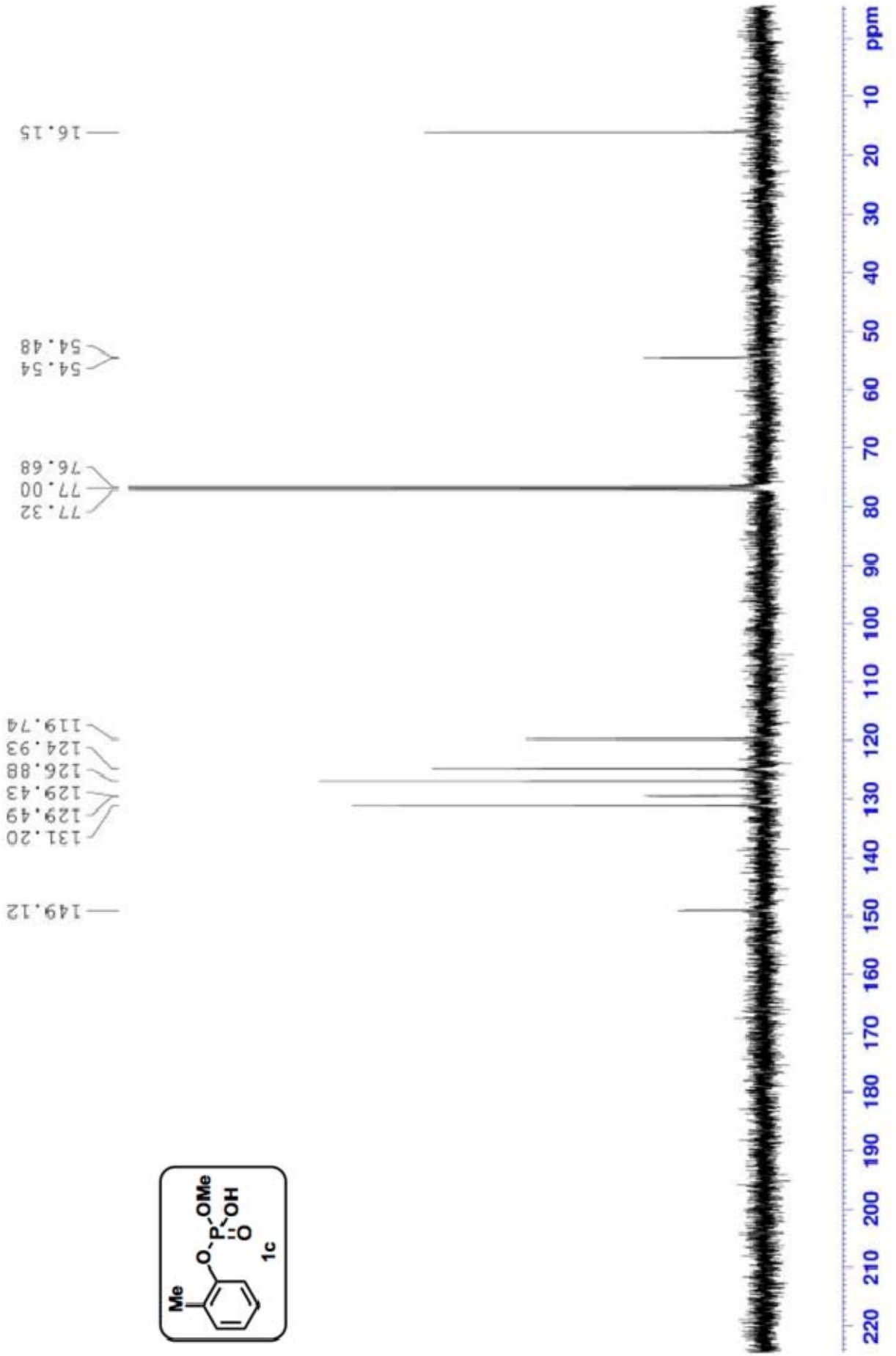
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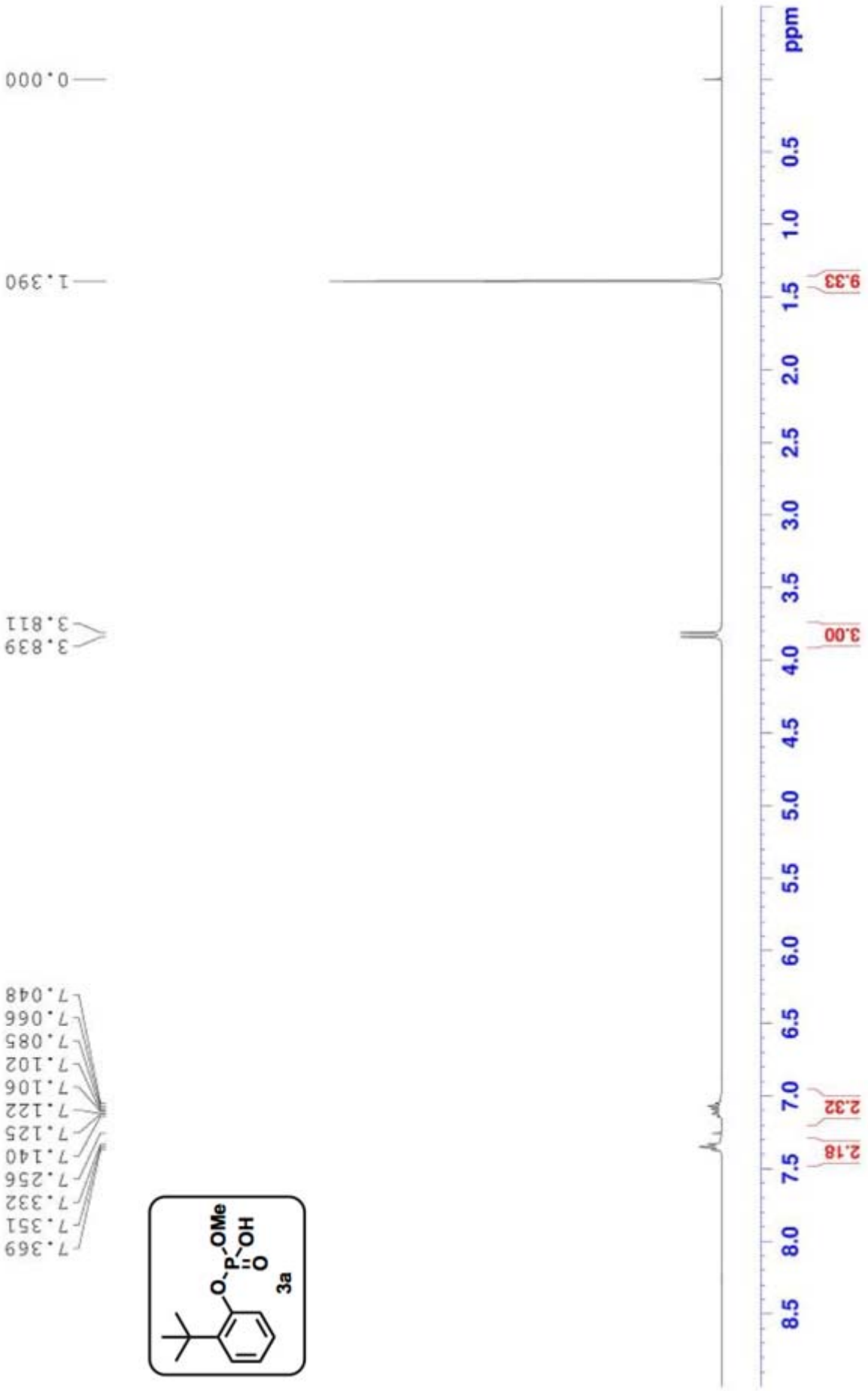
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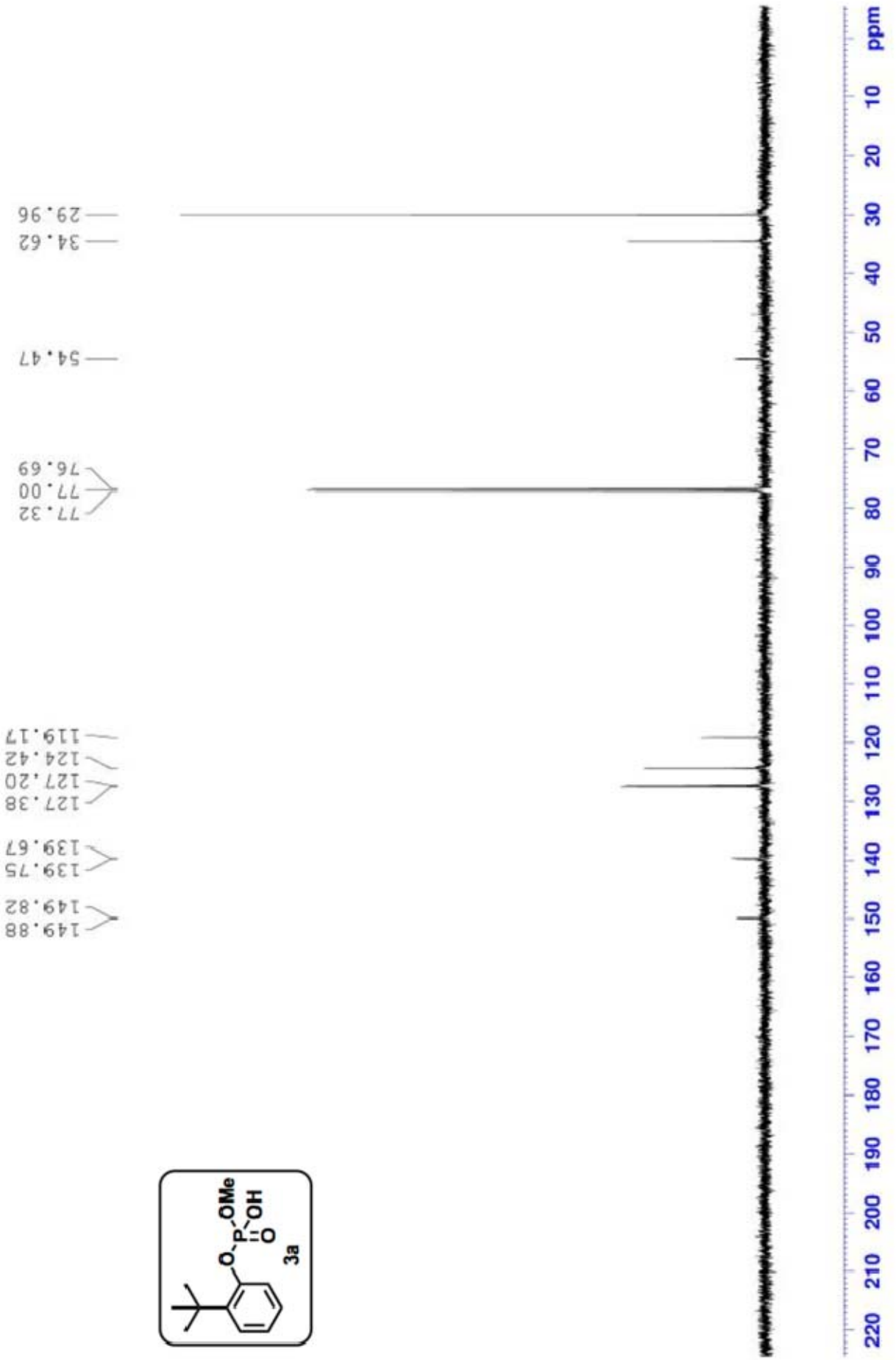

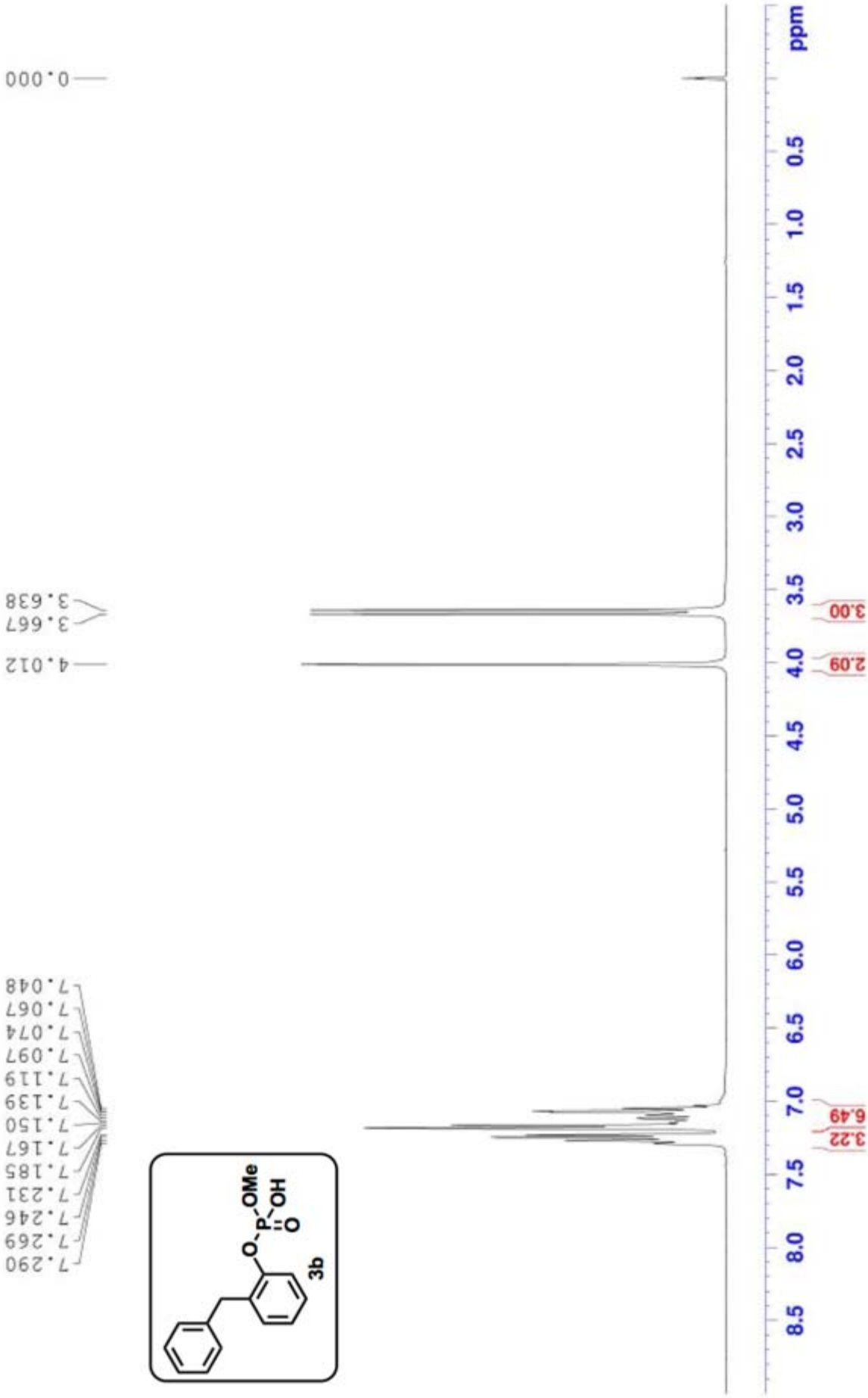
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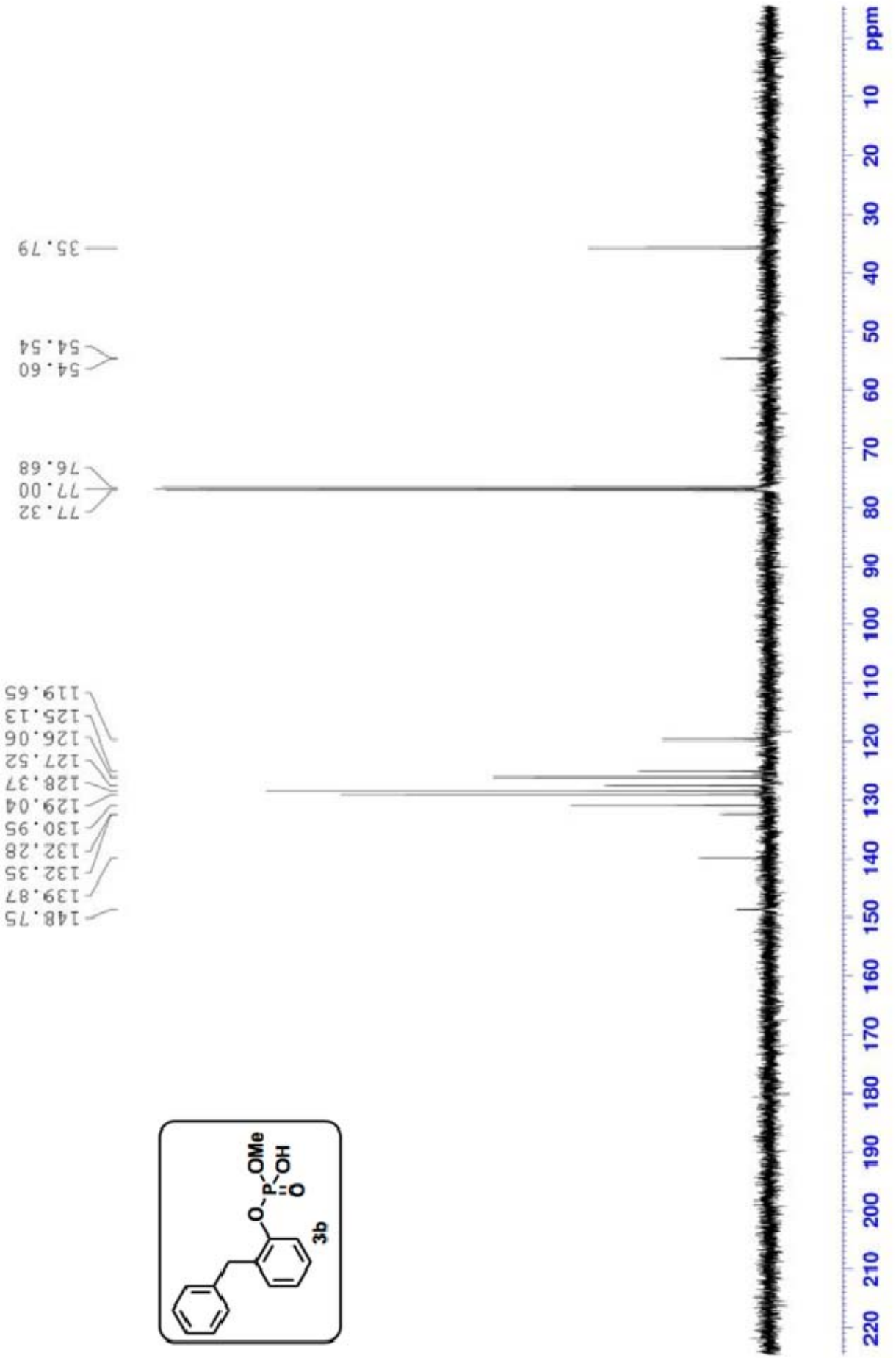
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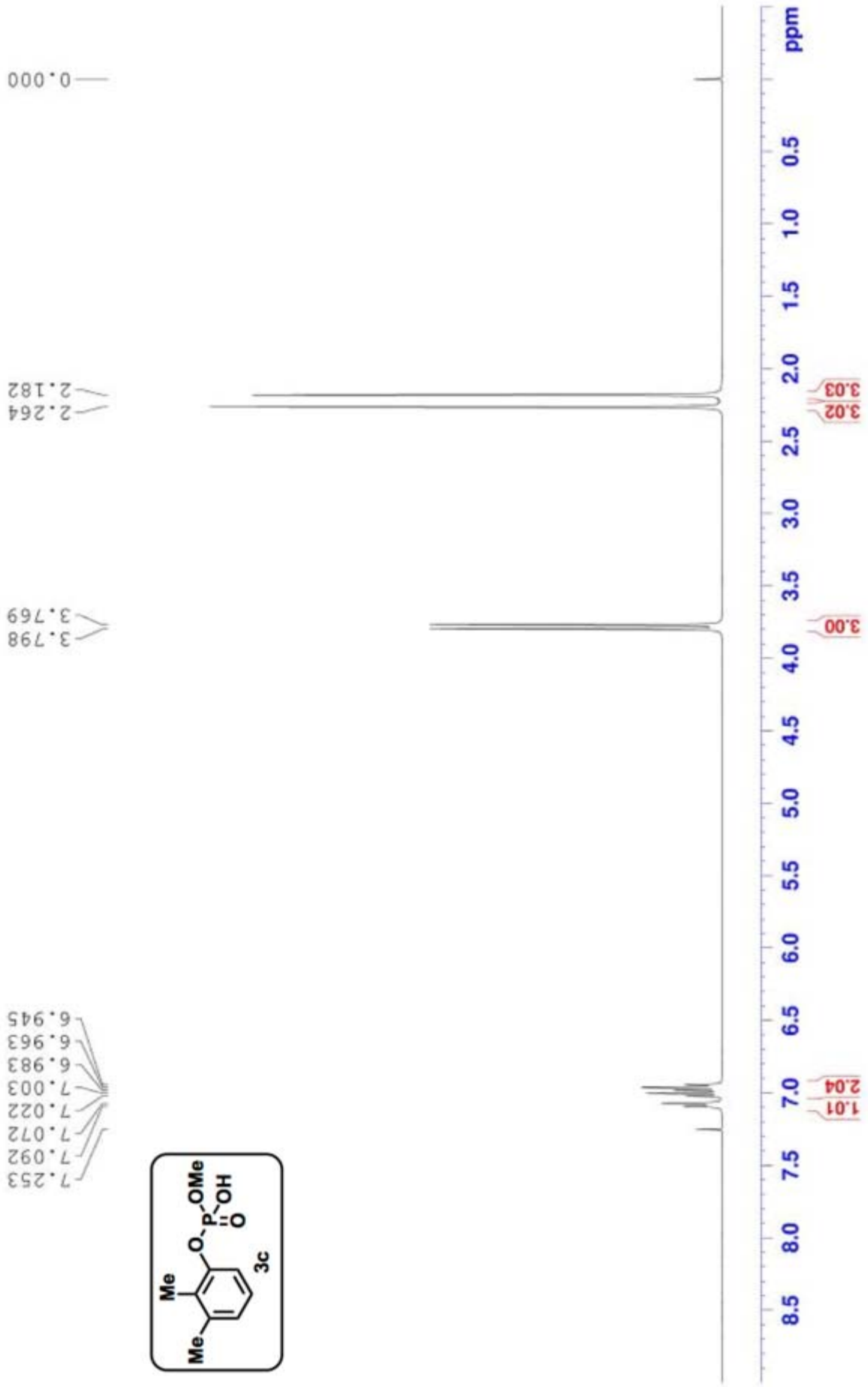

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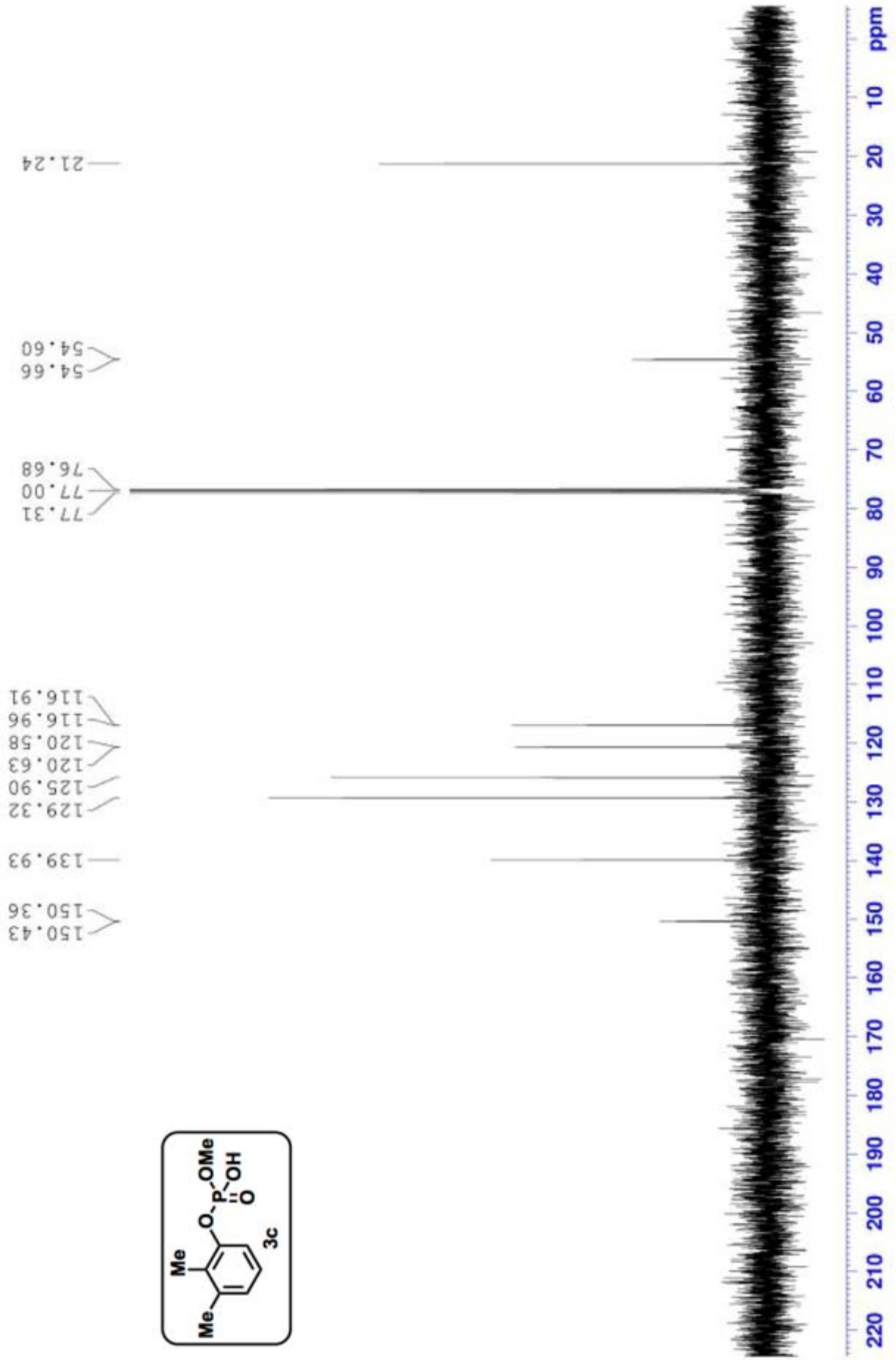

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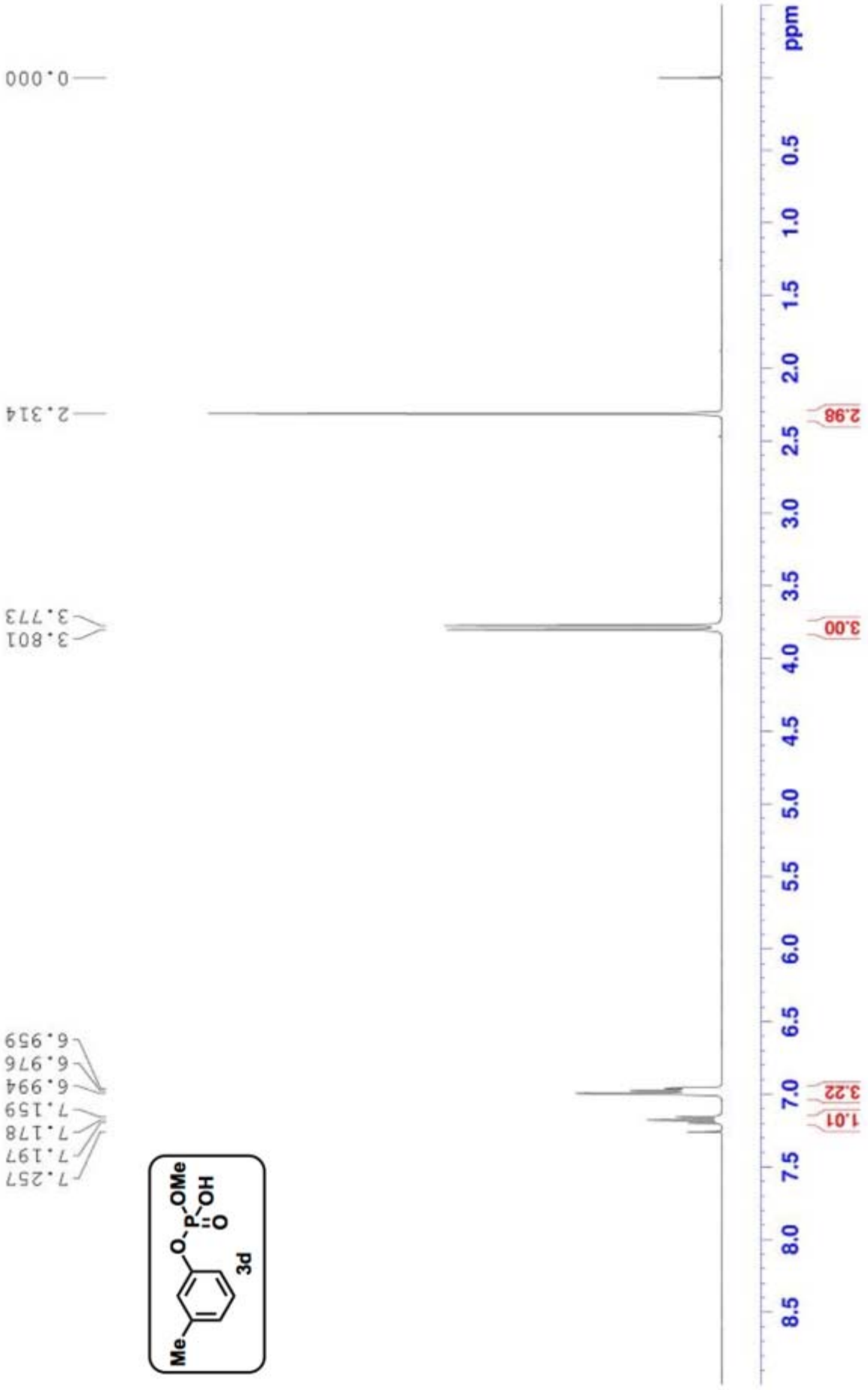

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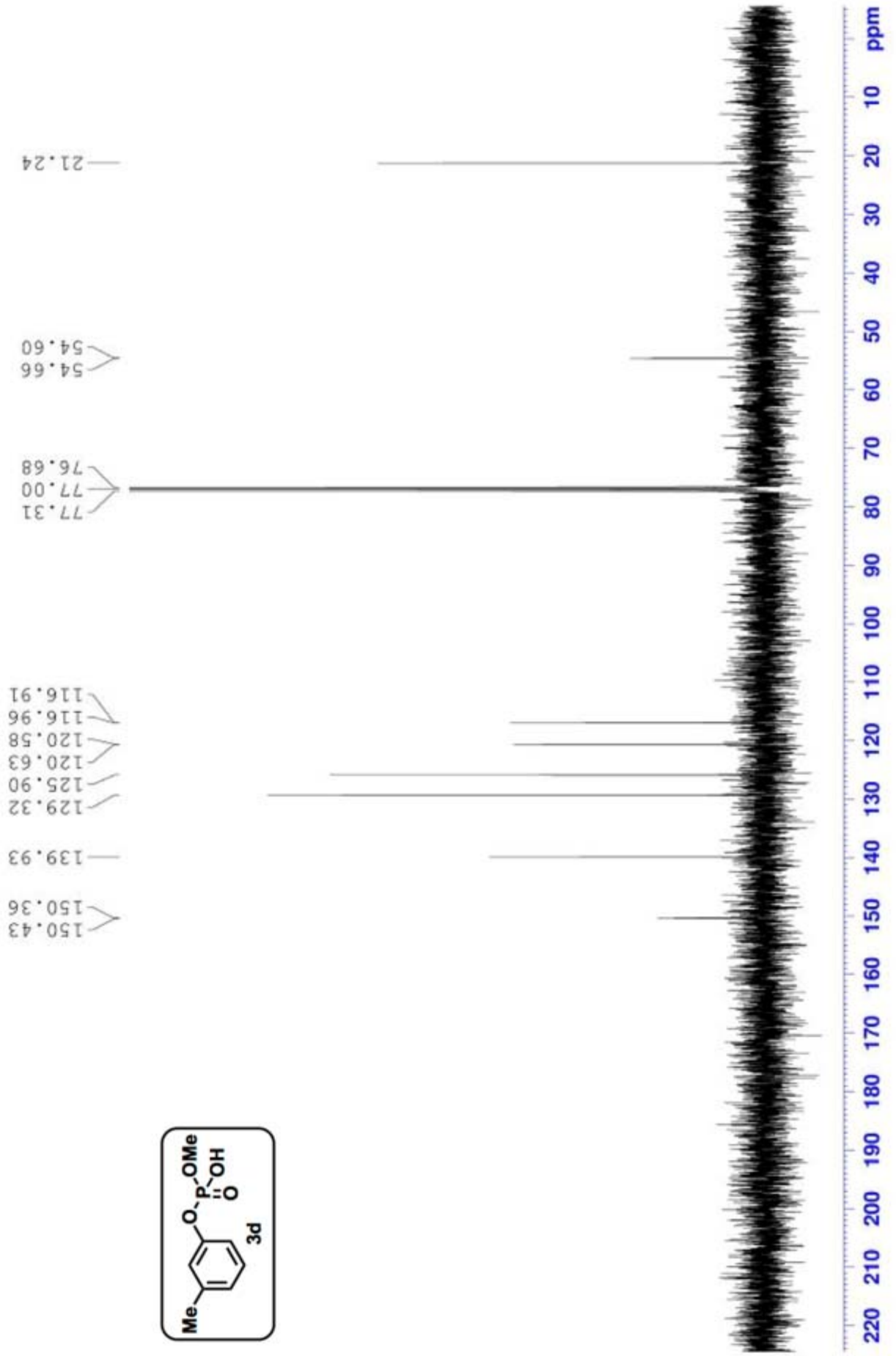

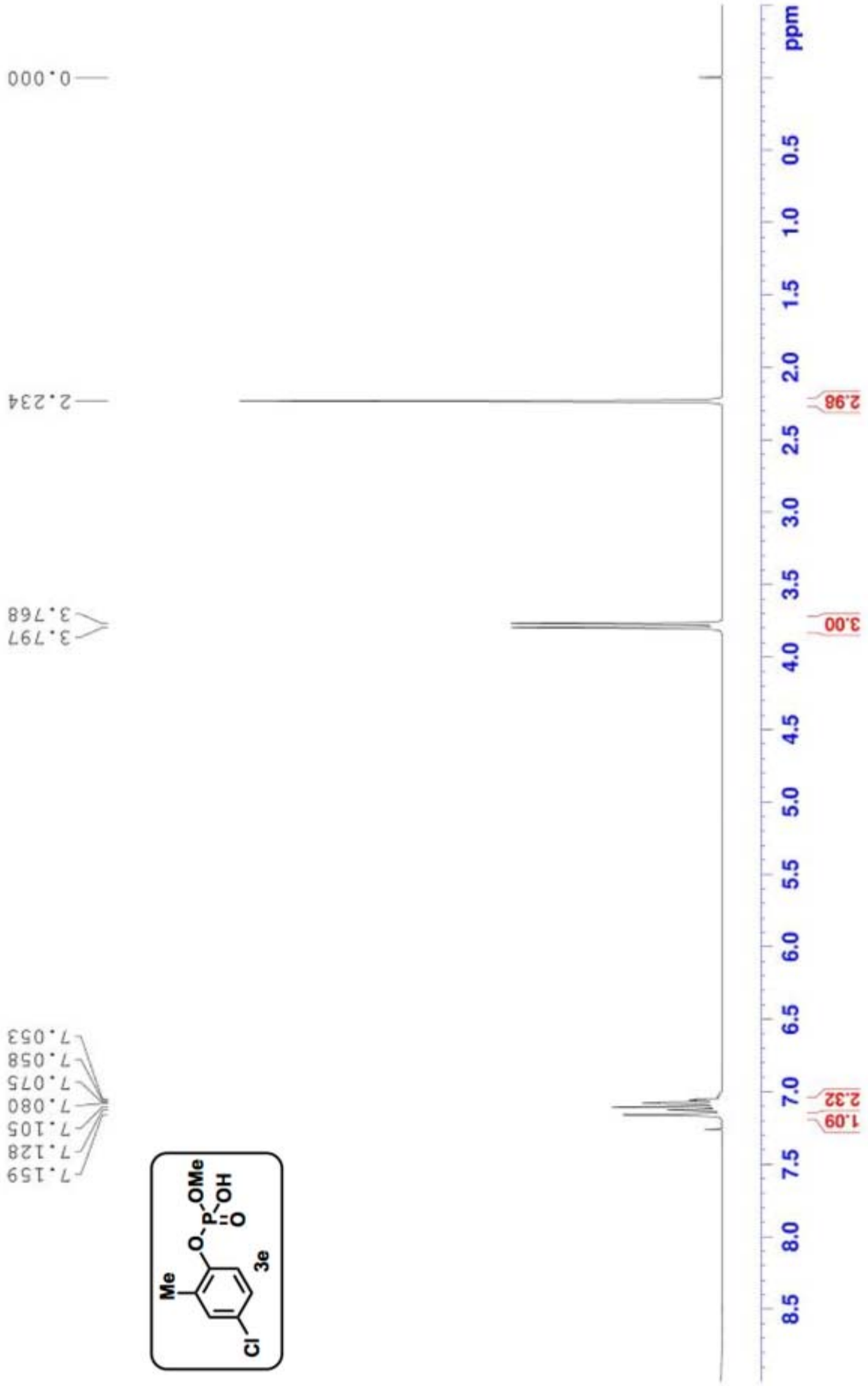
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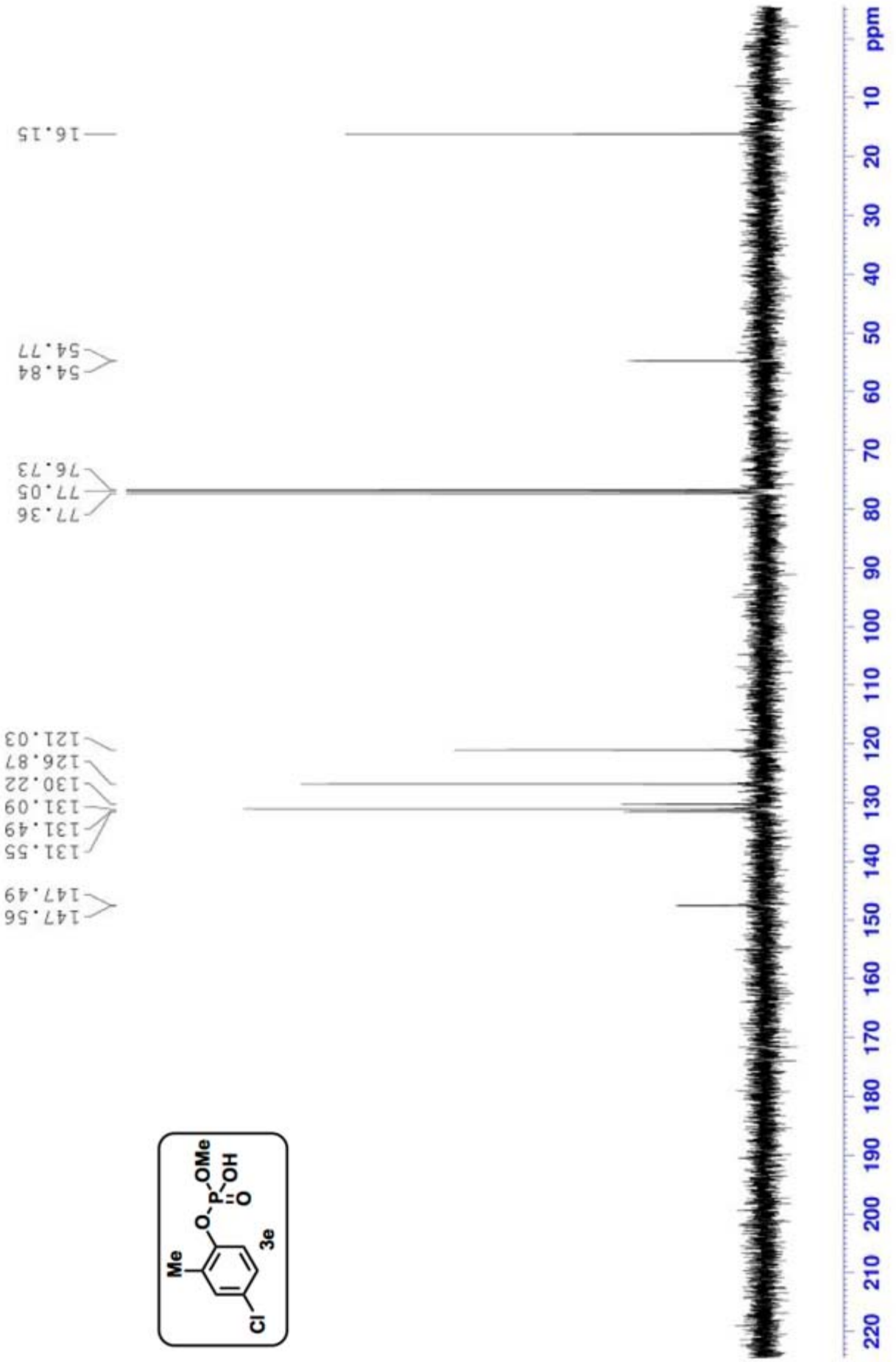

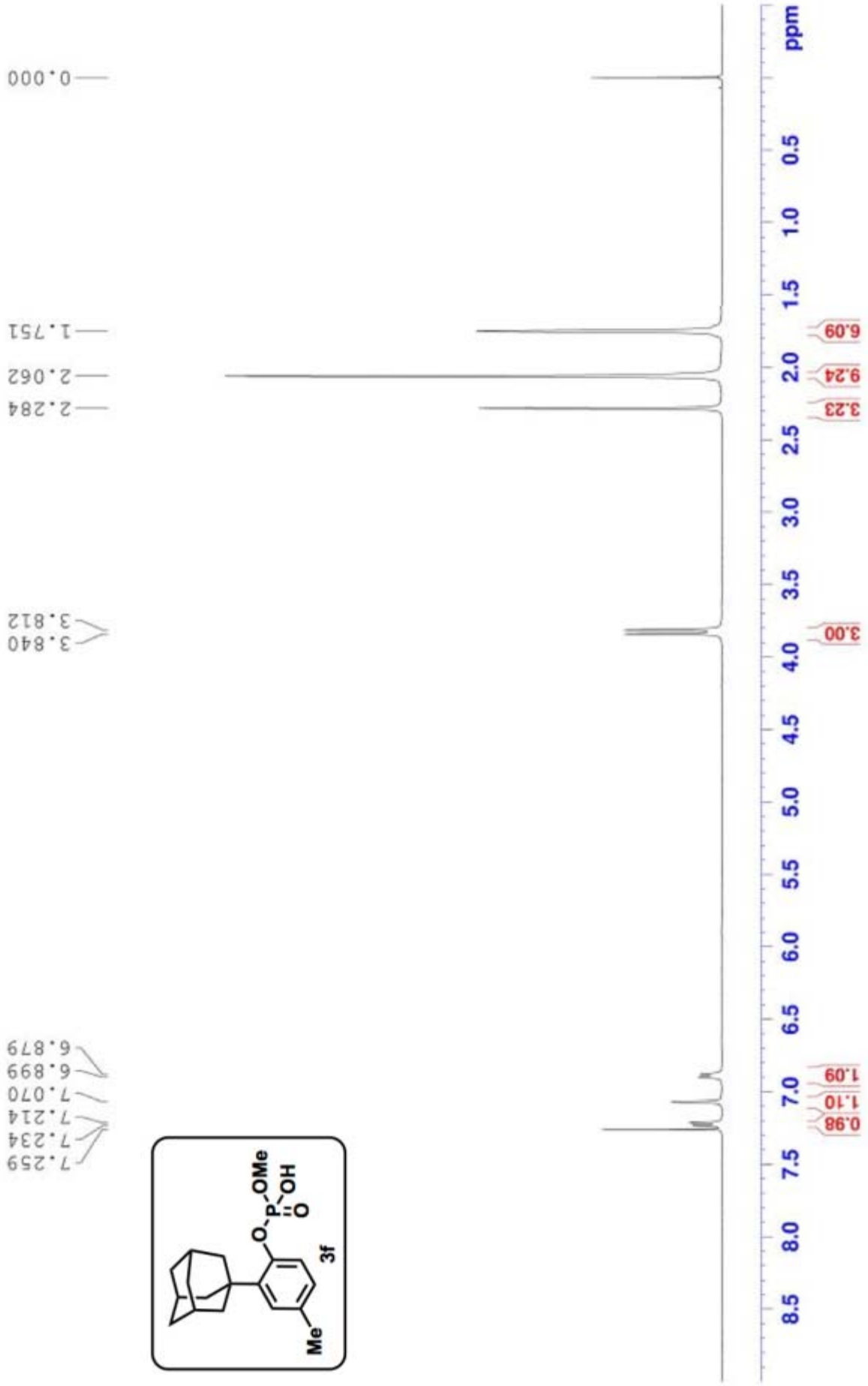
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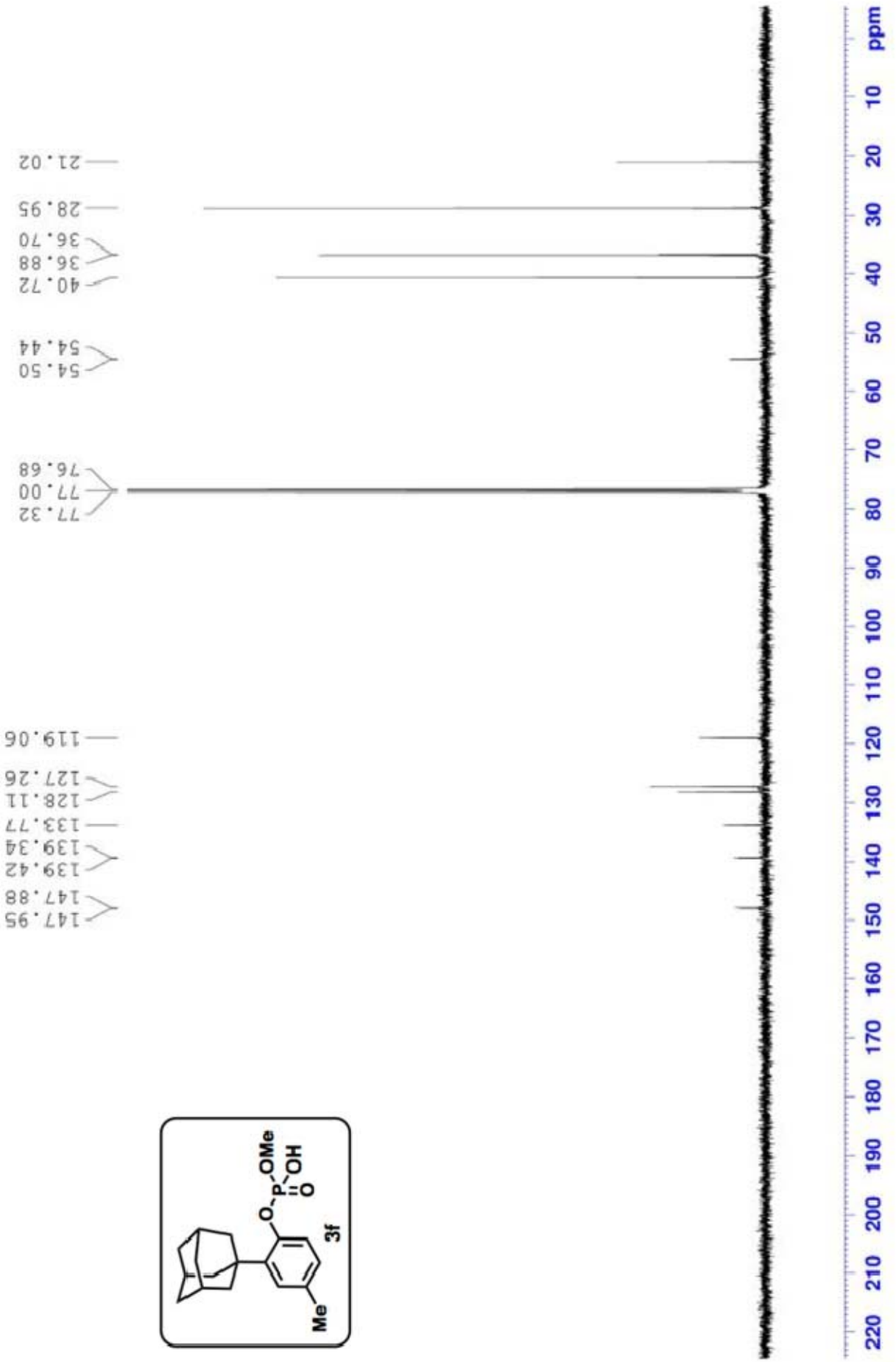
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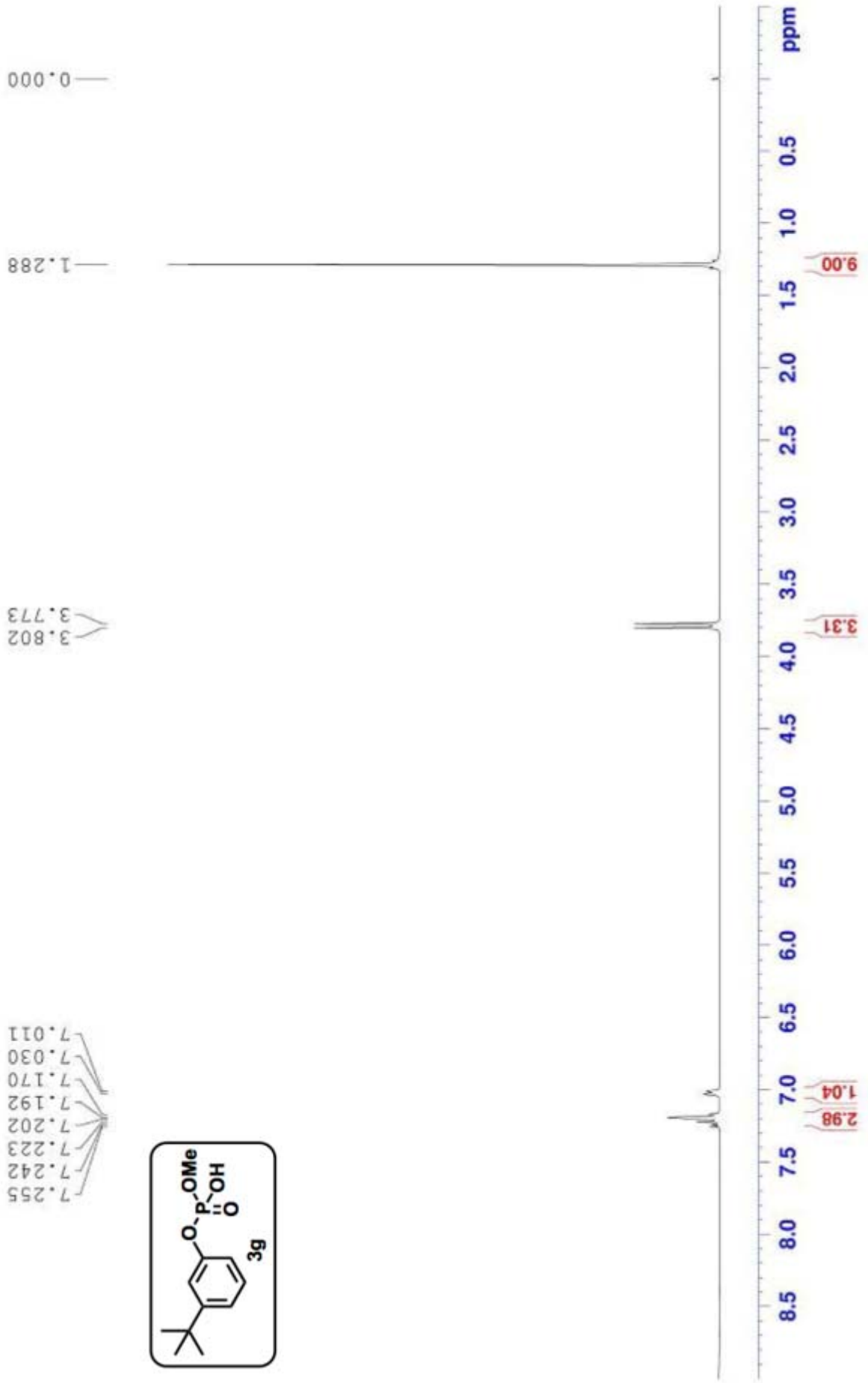
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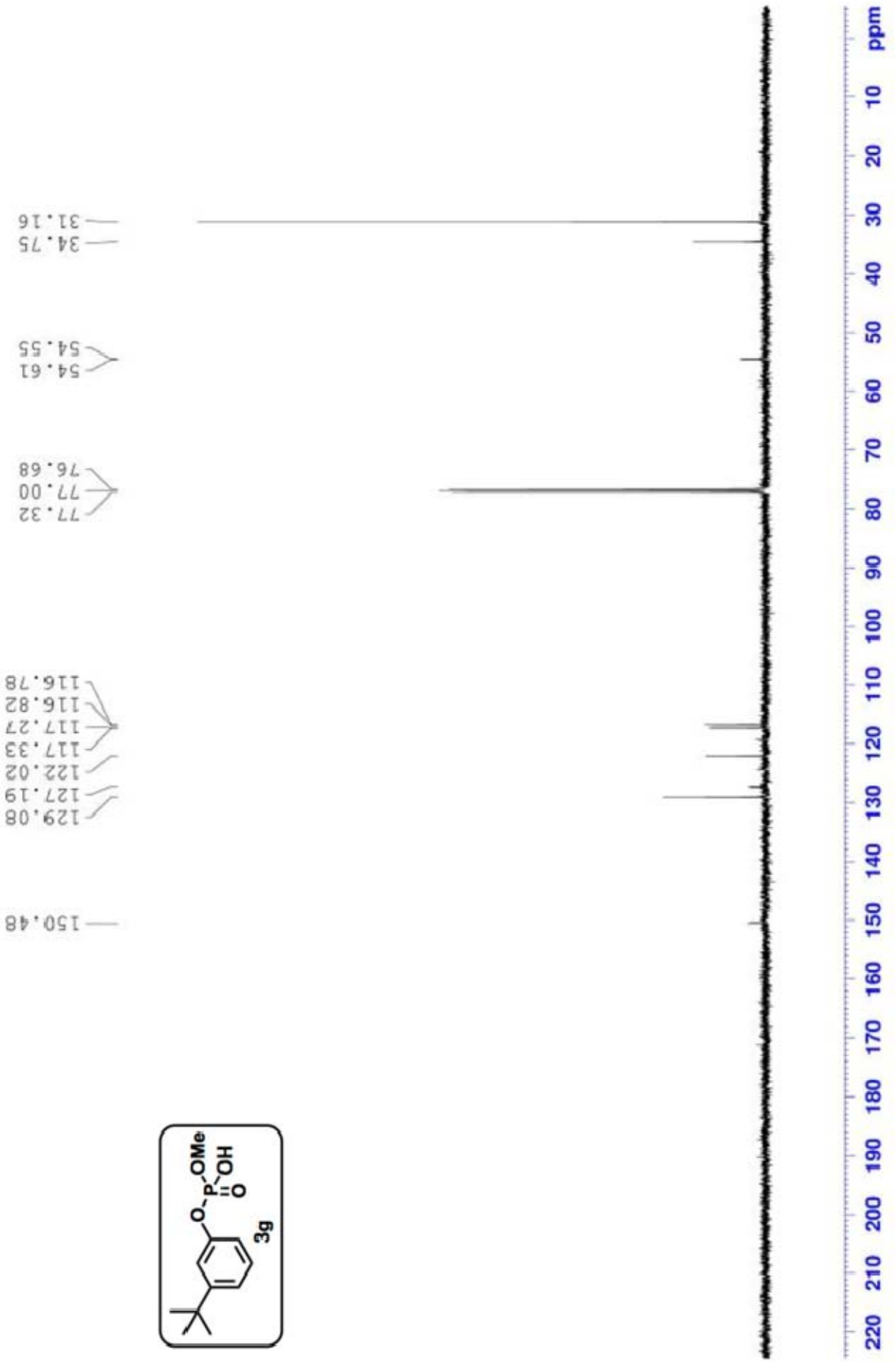
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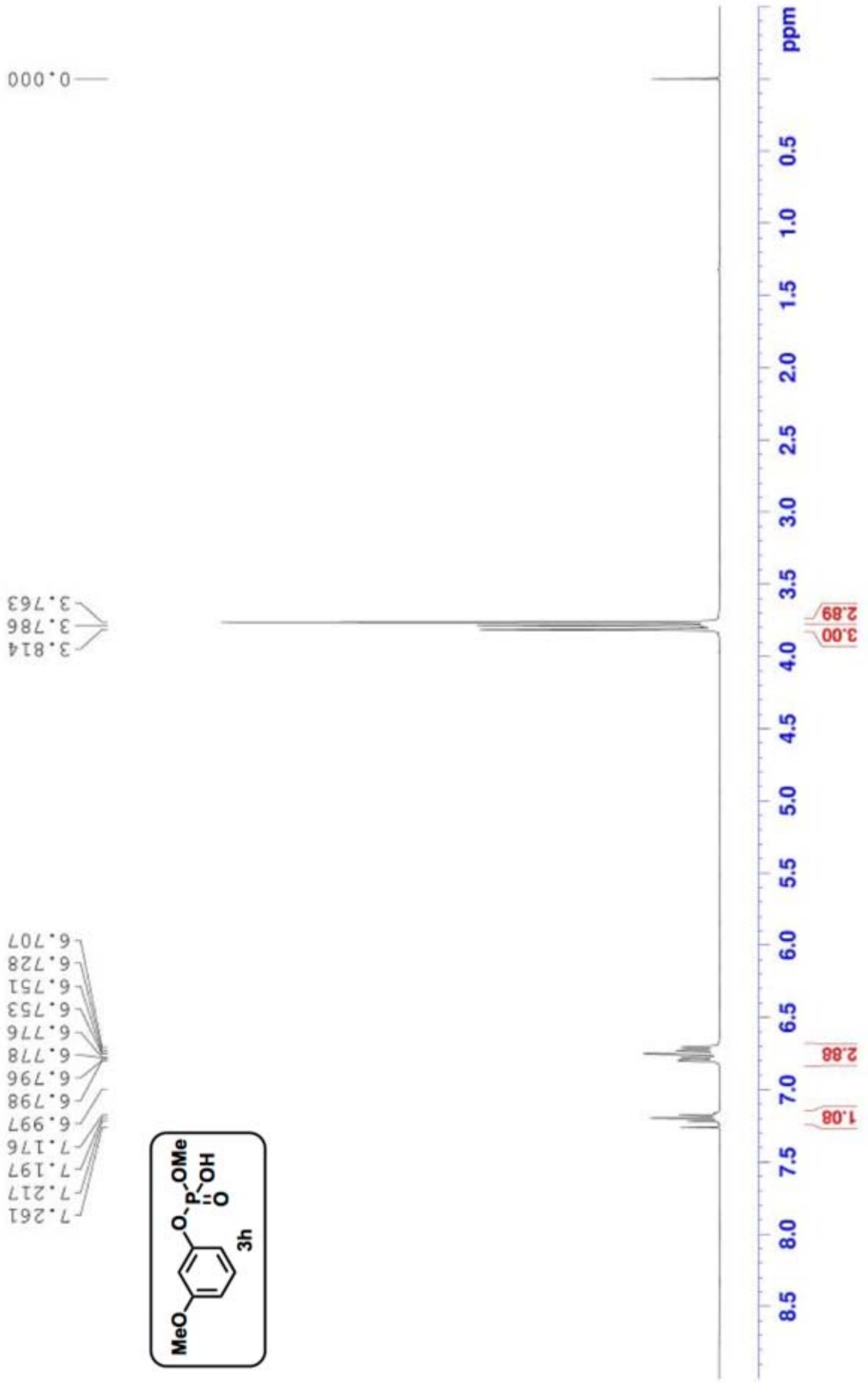
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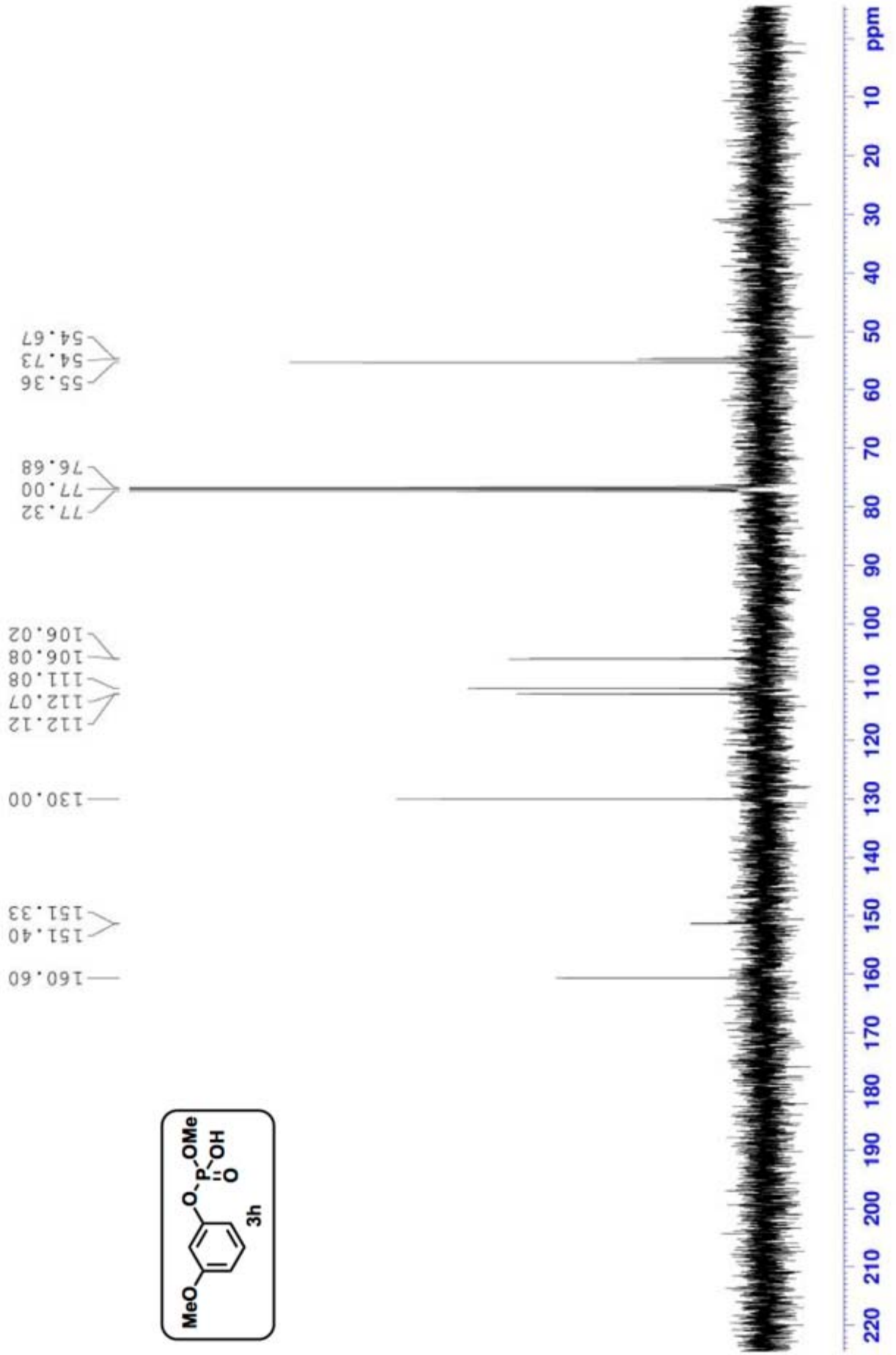


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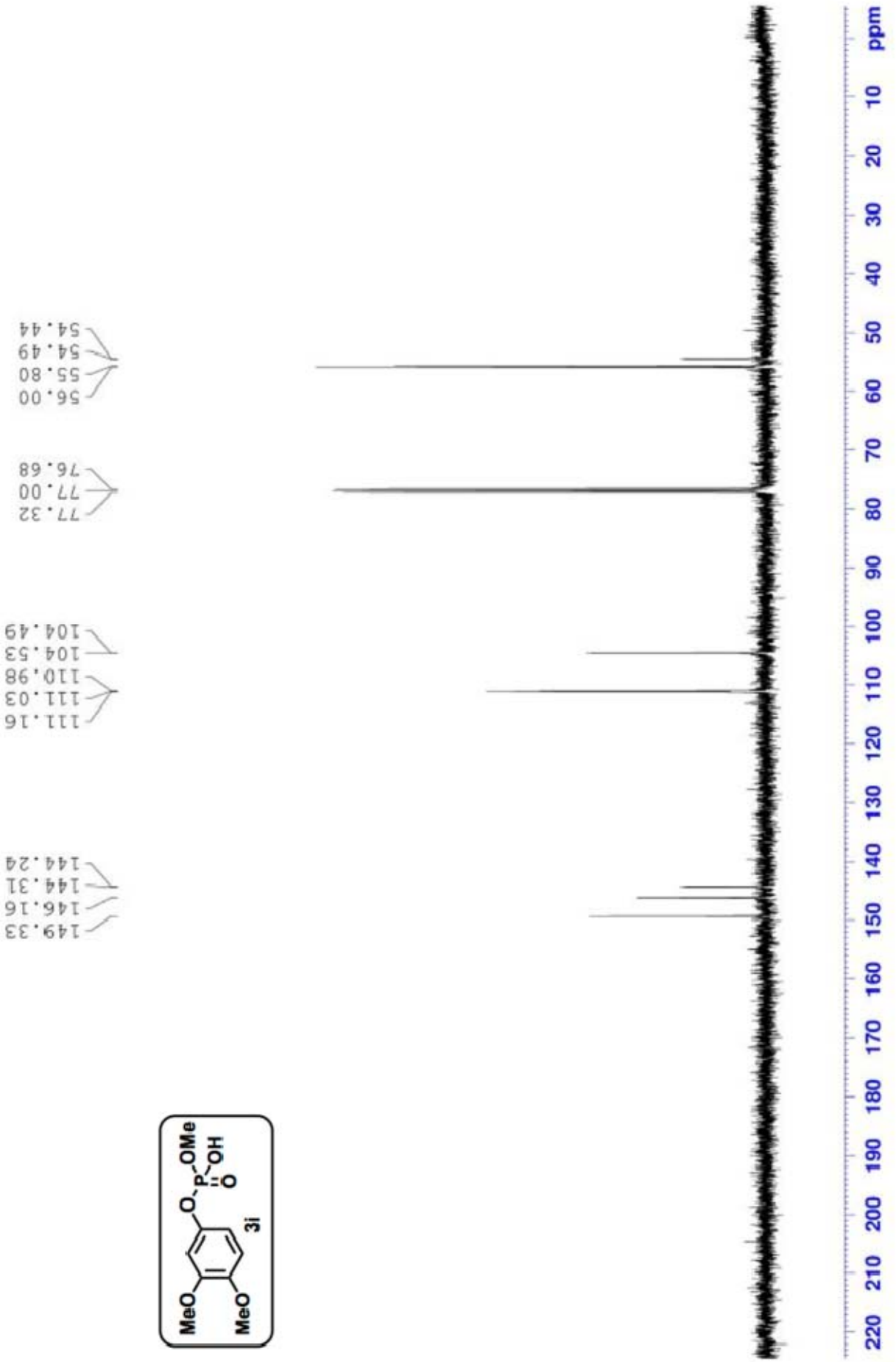
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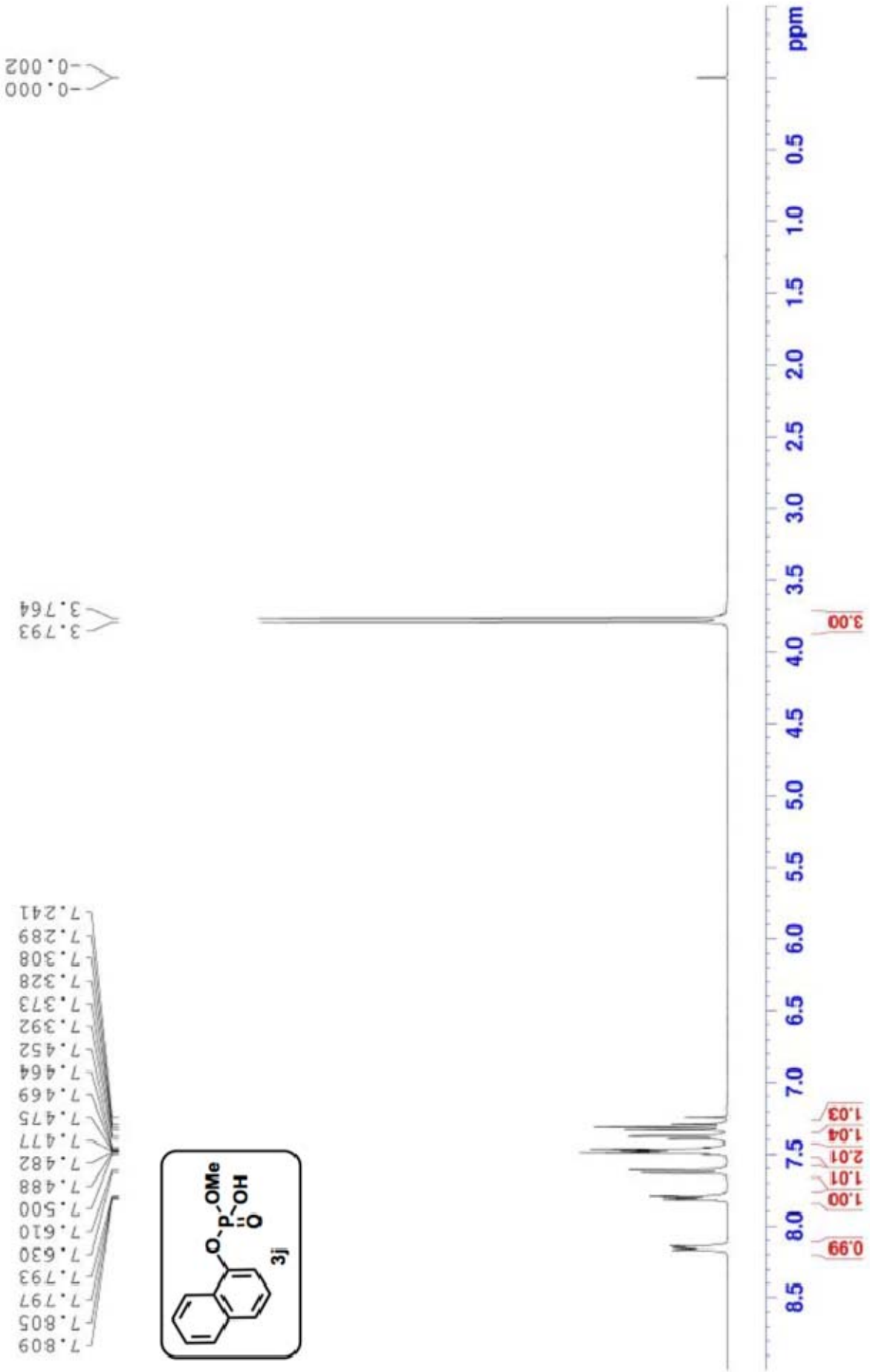
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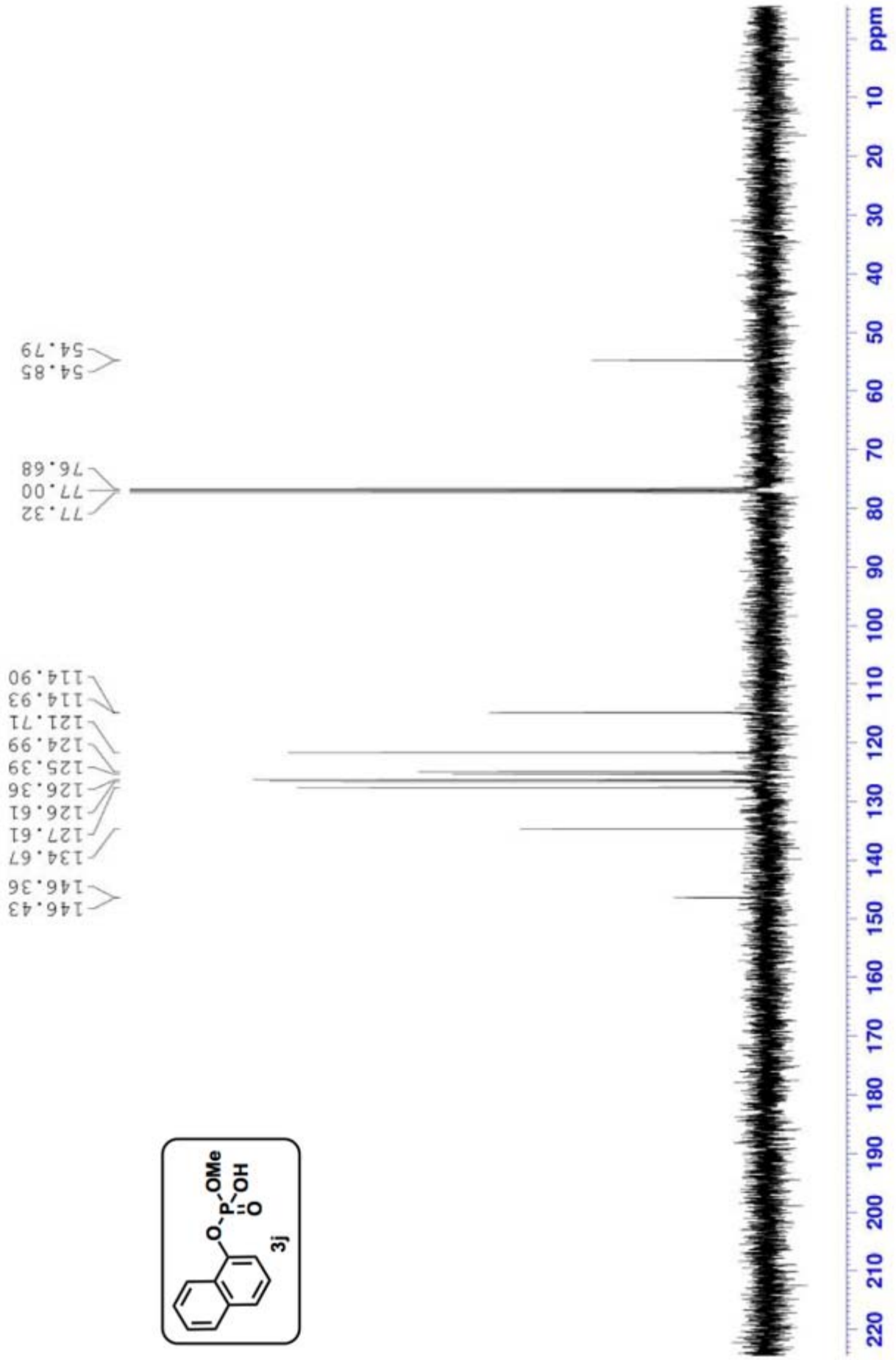

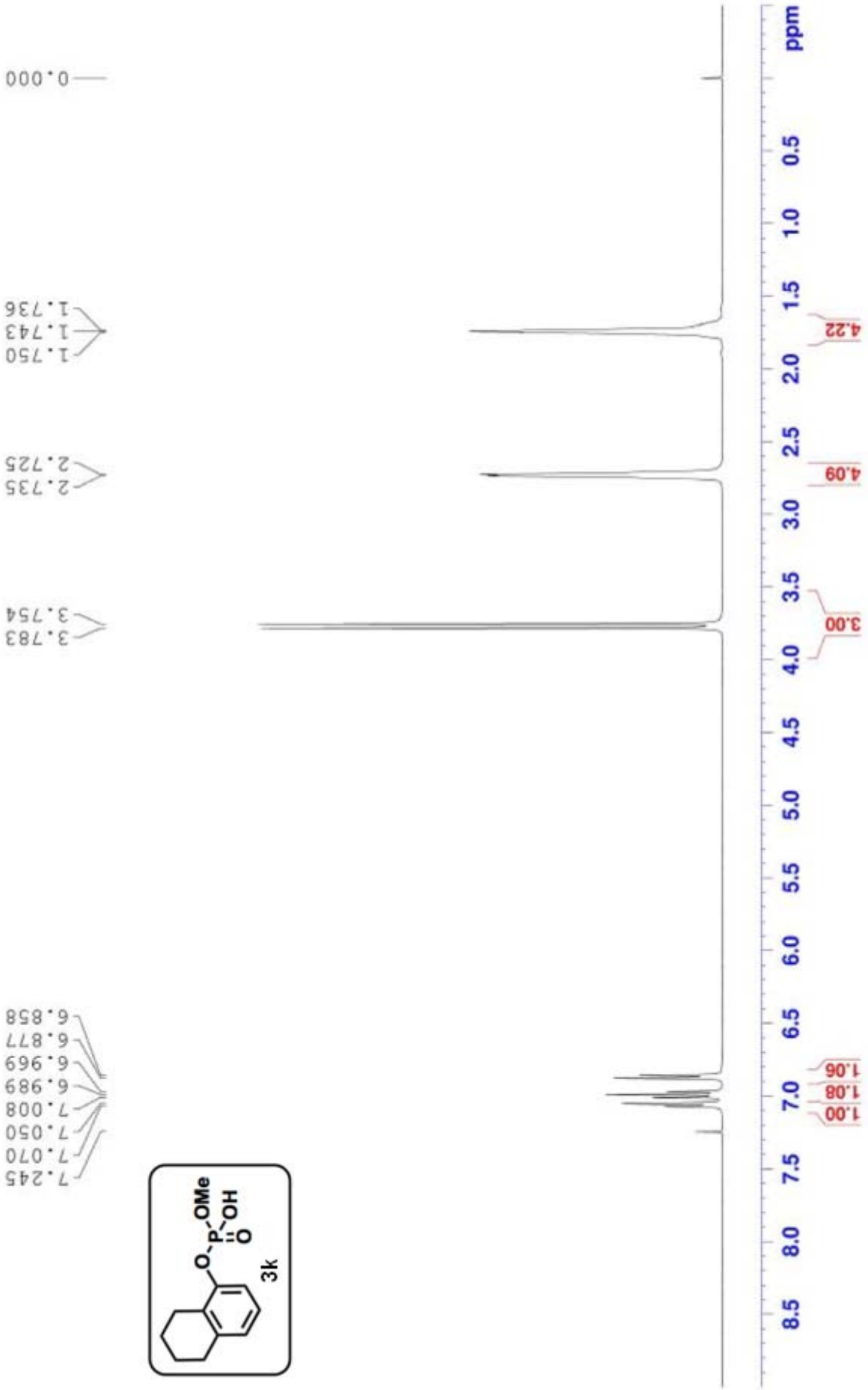
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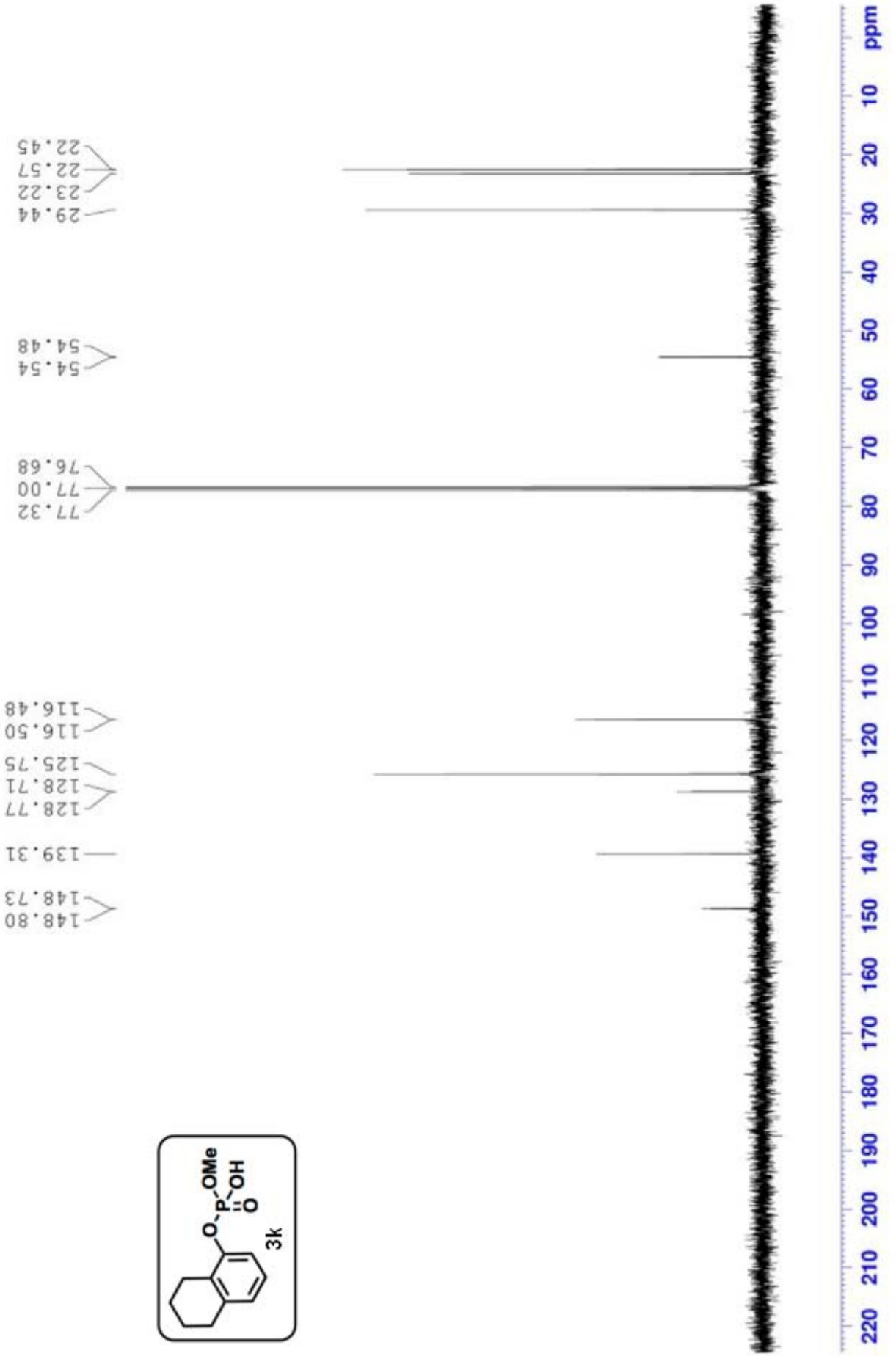
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50
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OH
O
P
O
3k

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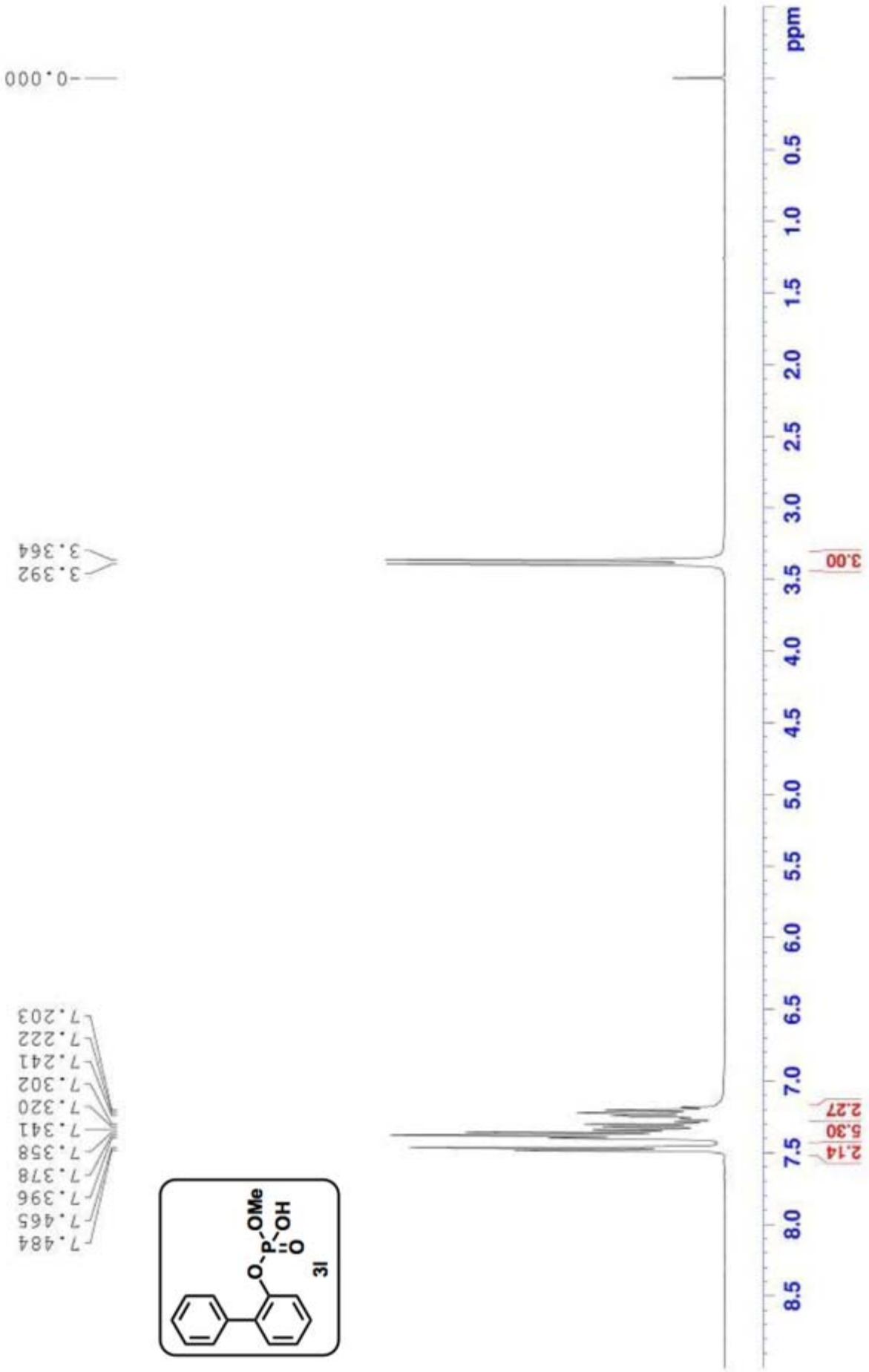

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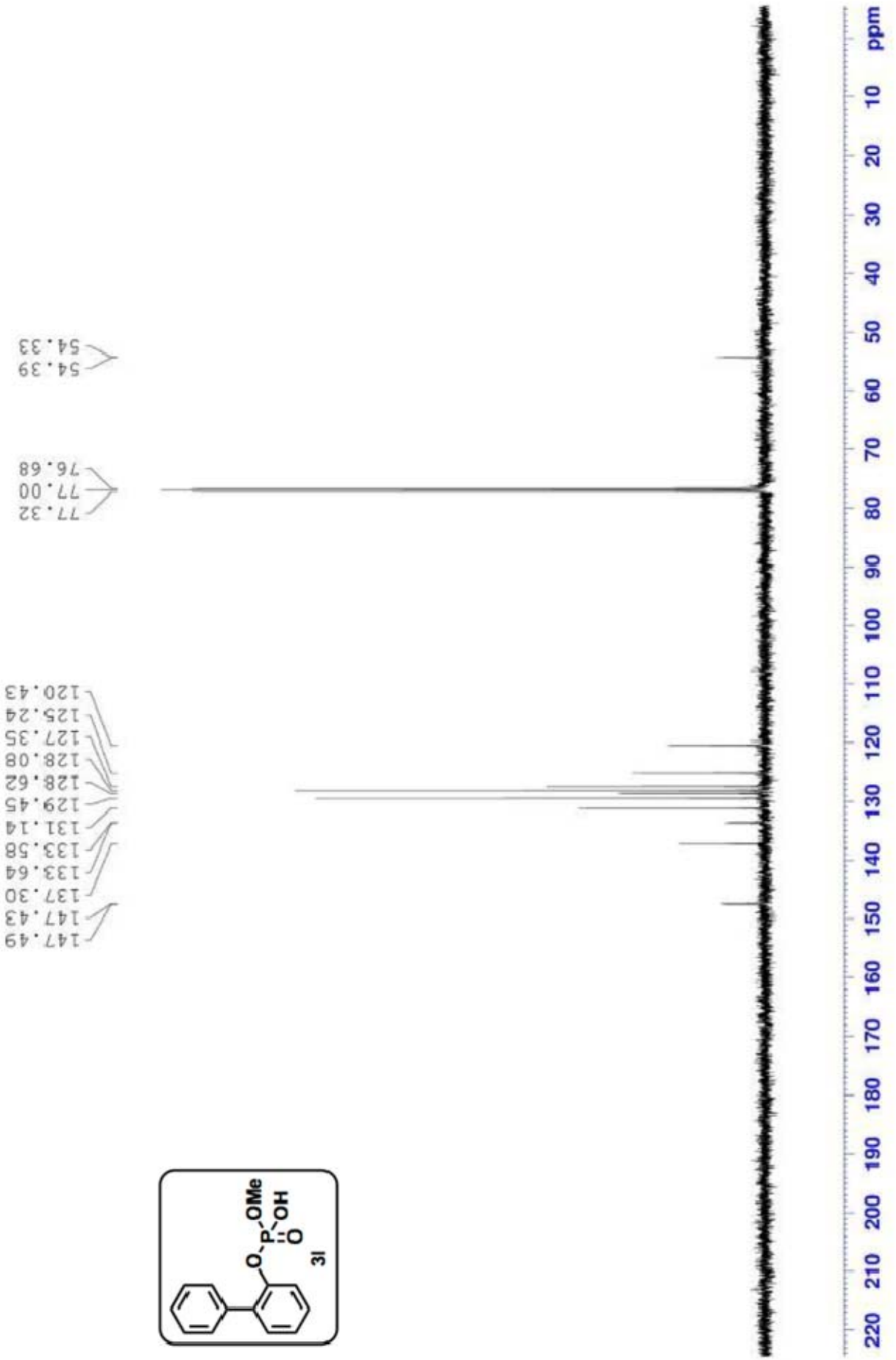

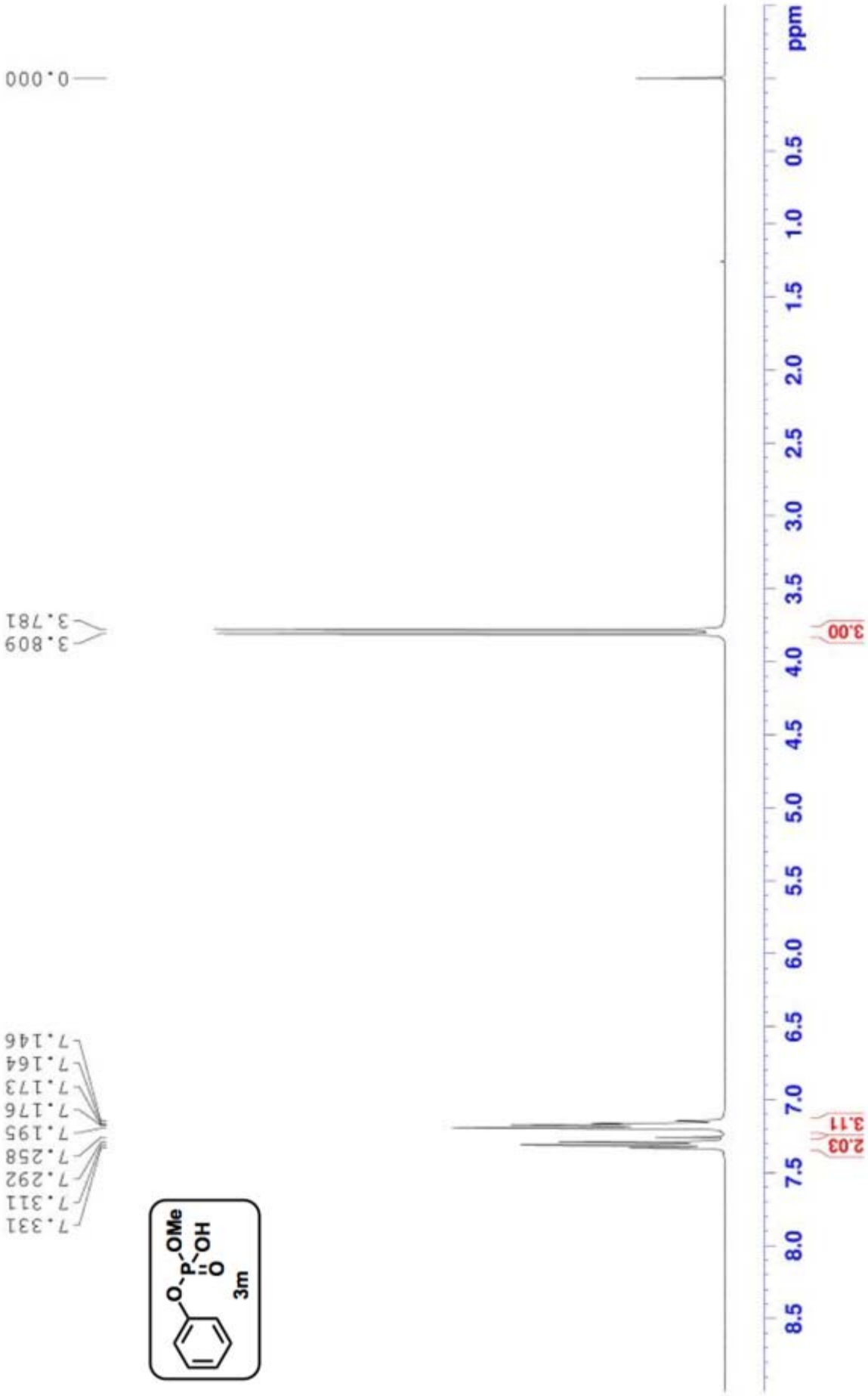
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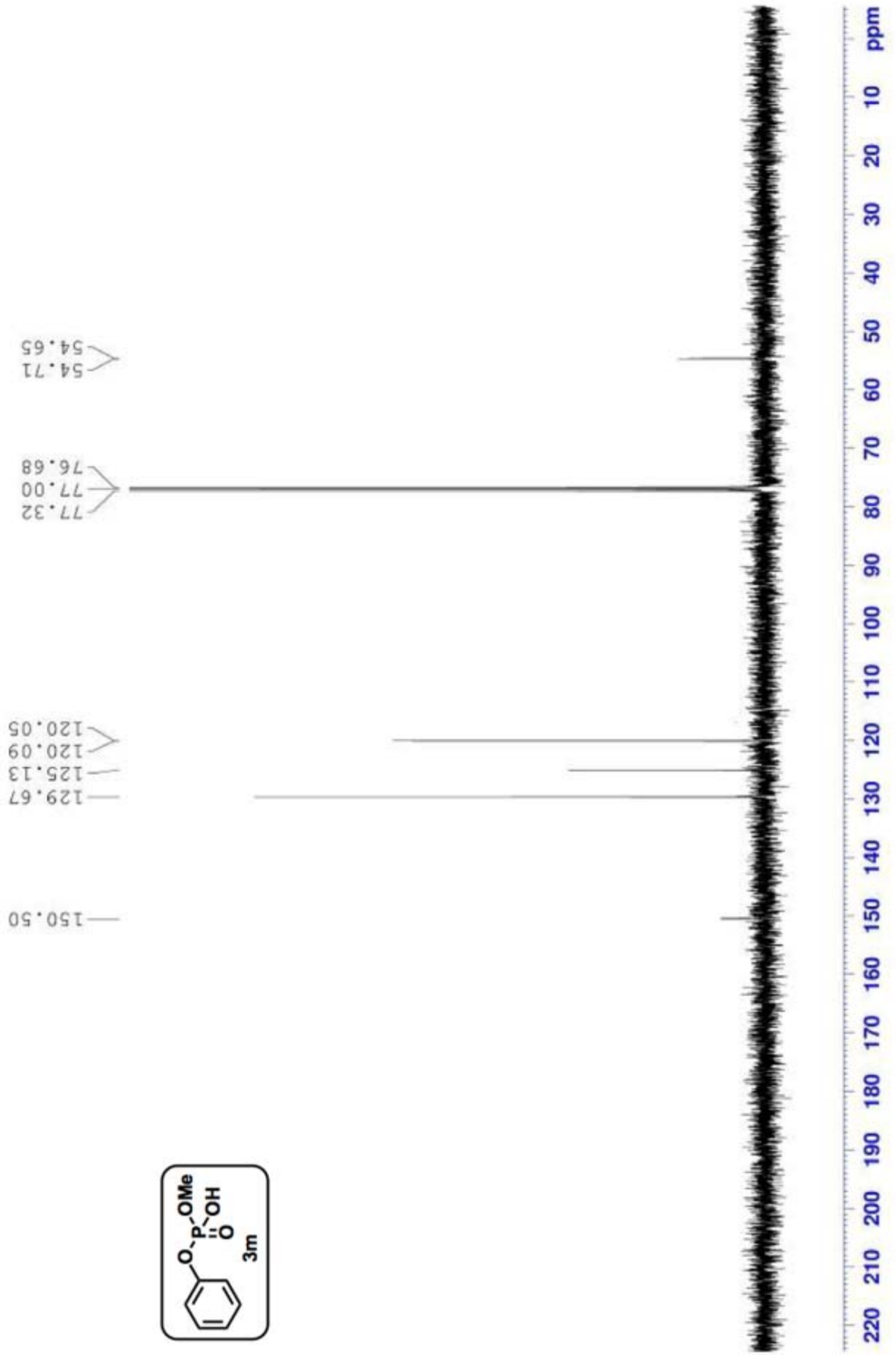
3.11
ppm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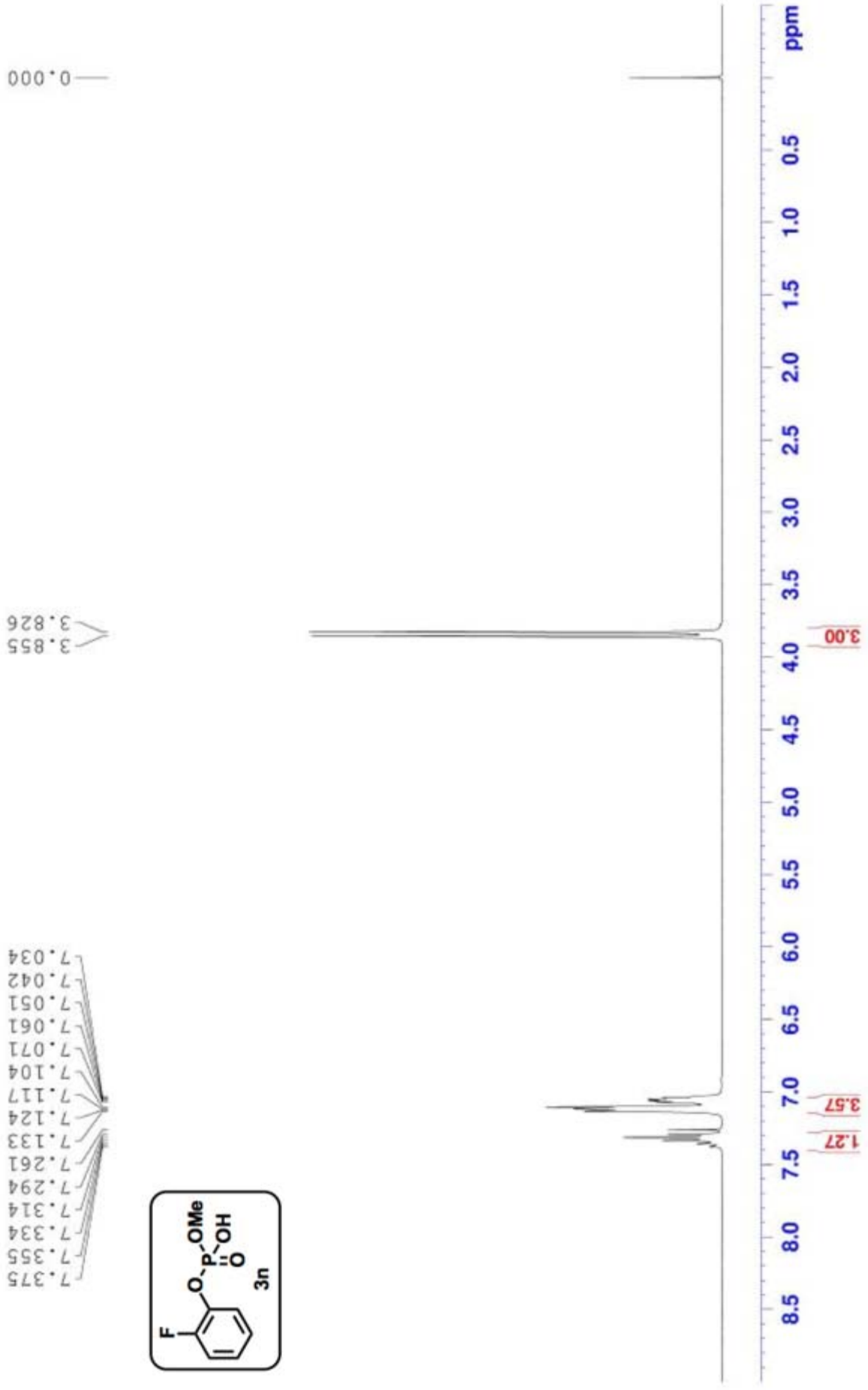
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O
P
OMe
OH
O
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ppm
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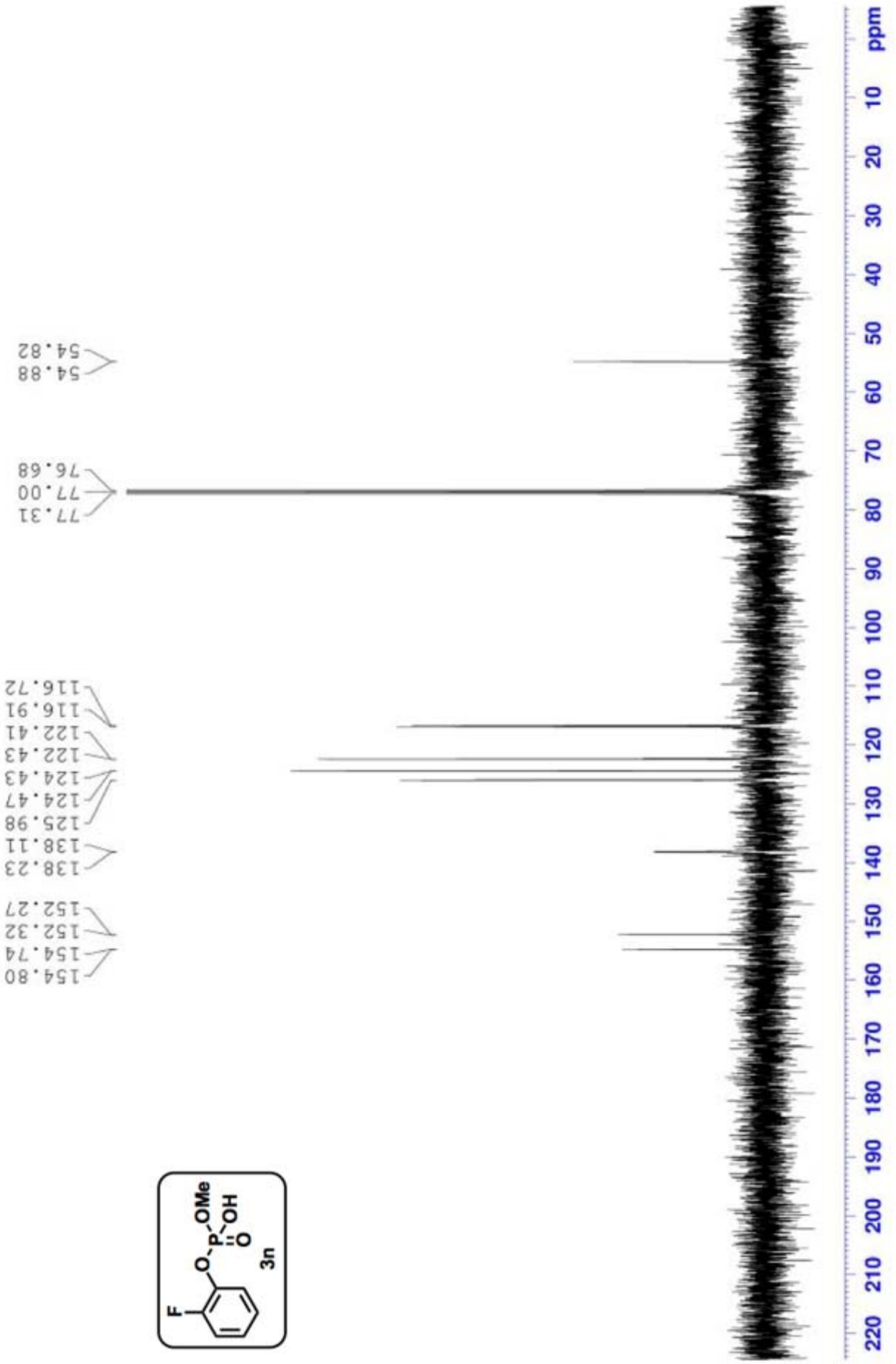

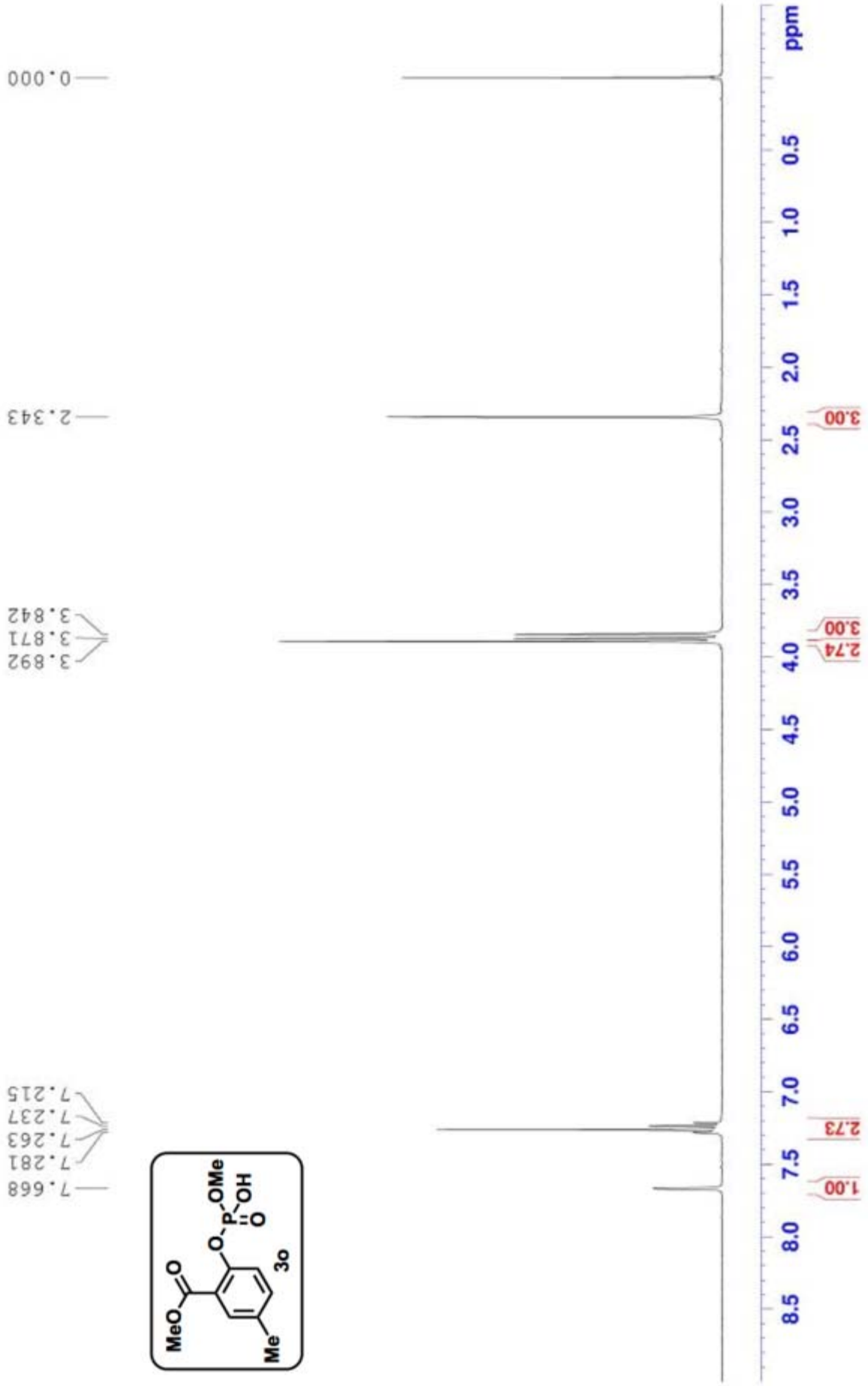
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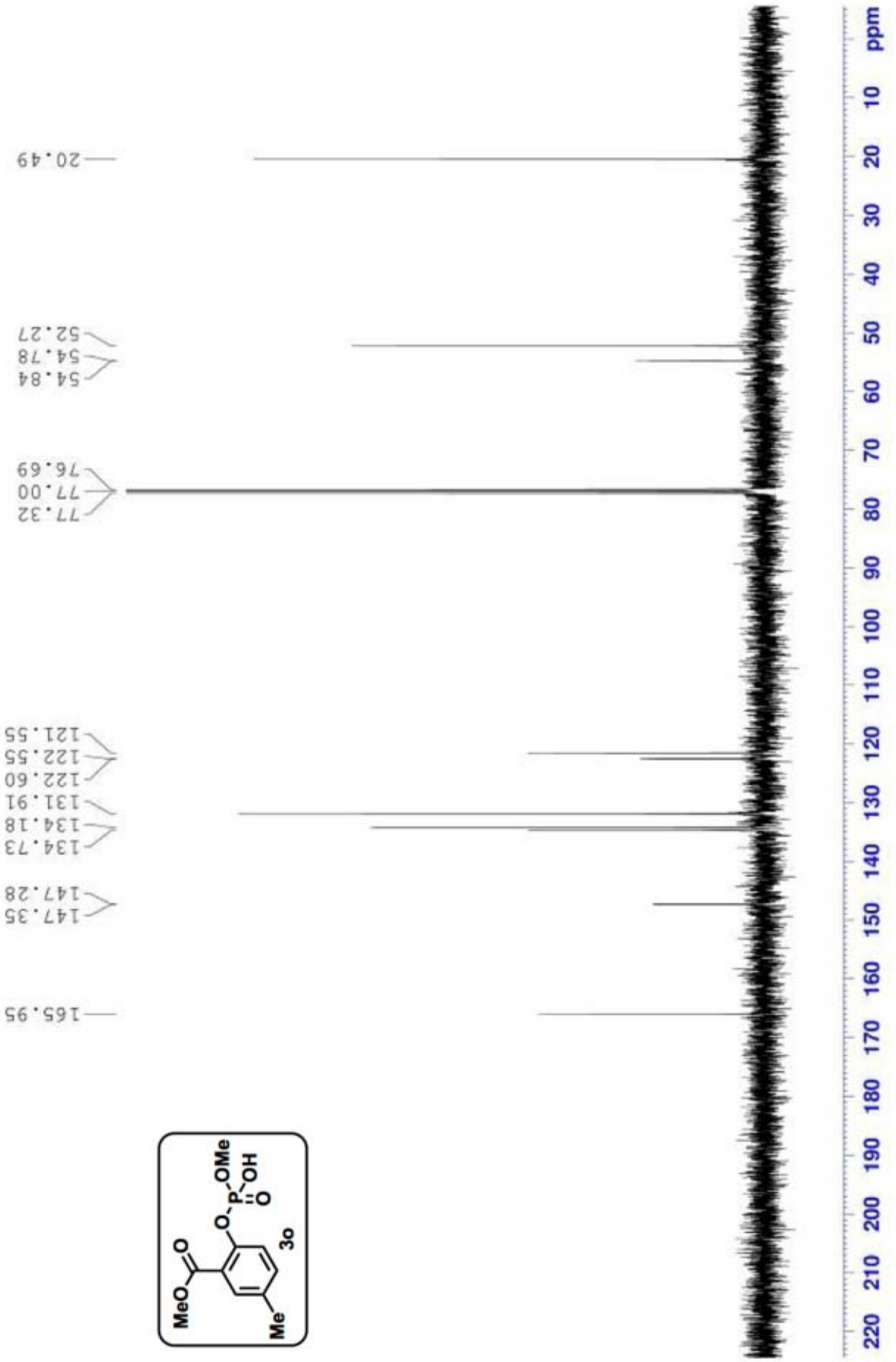

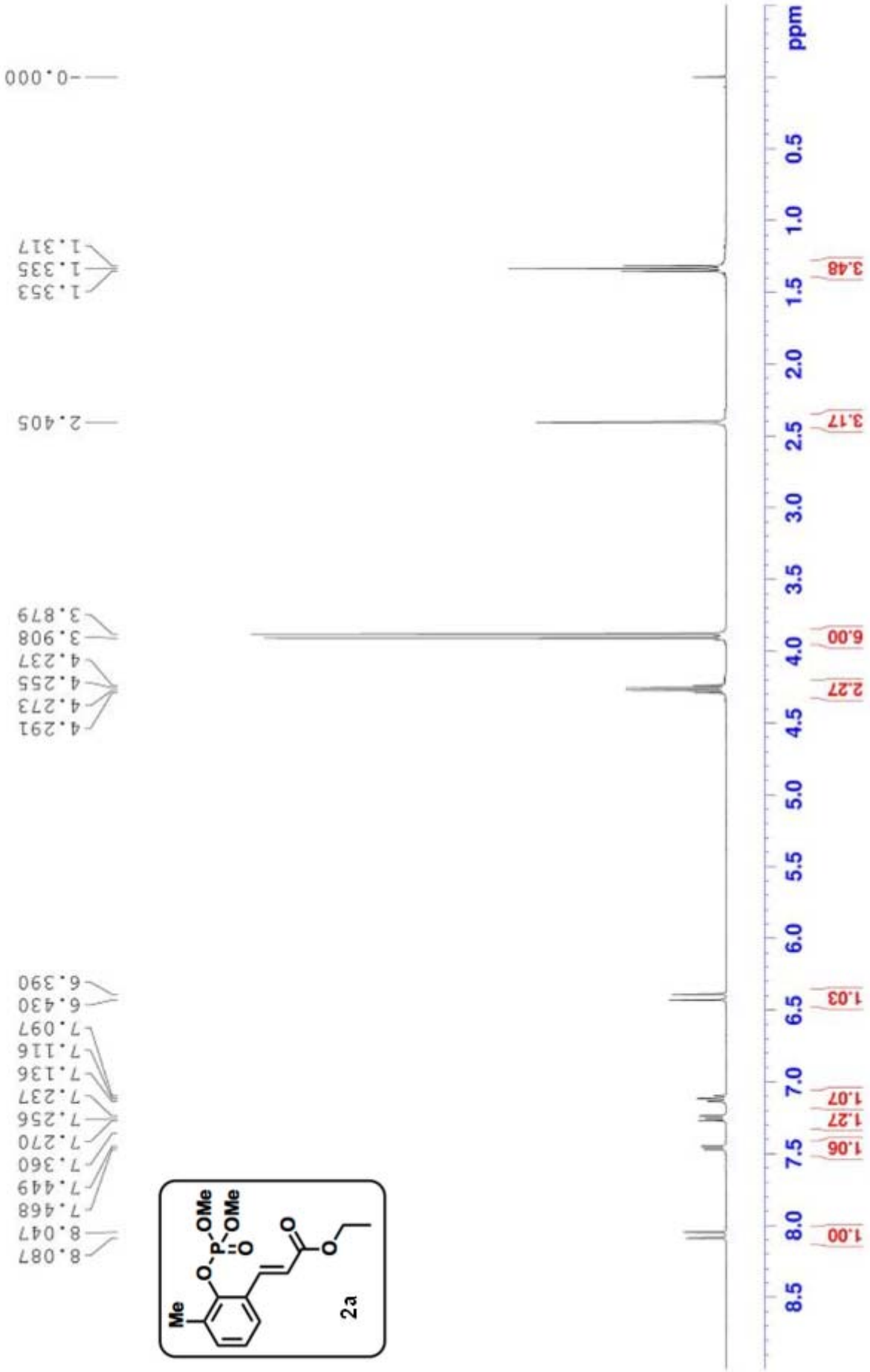
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6.00
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1.03
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O
O
Me
2a

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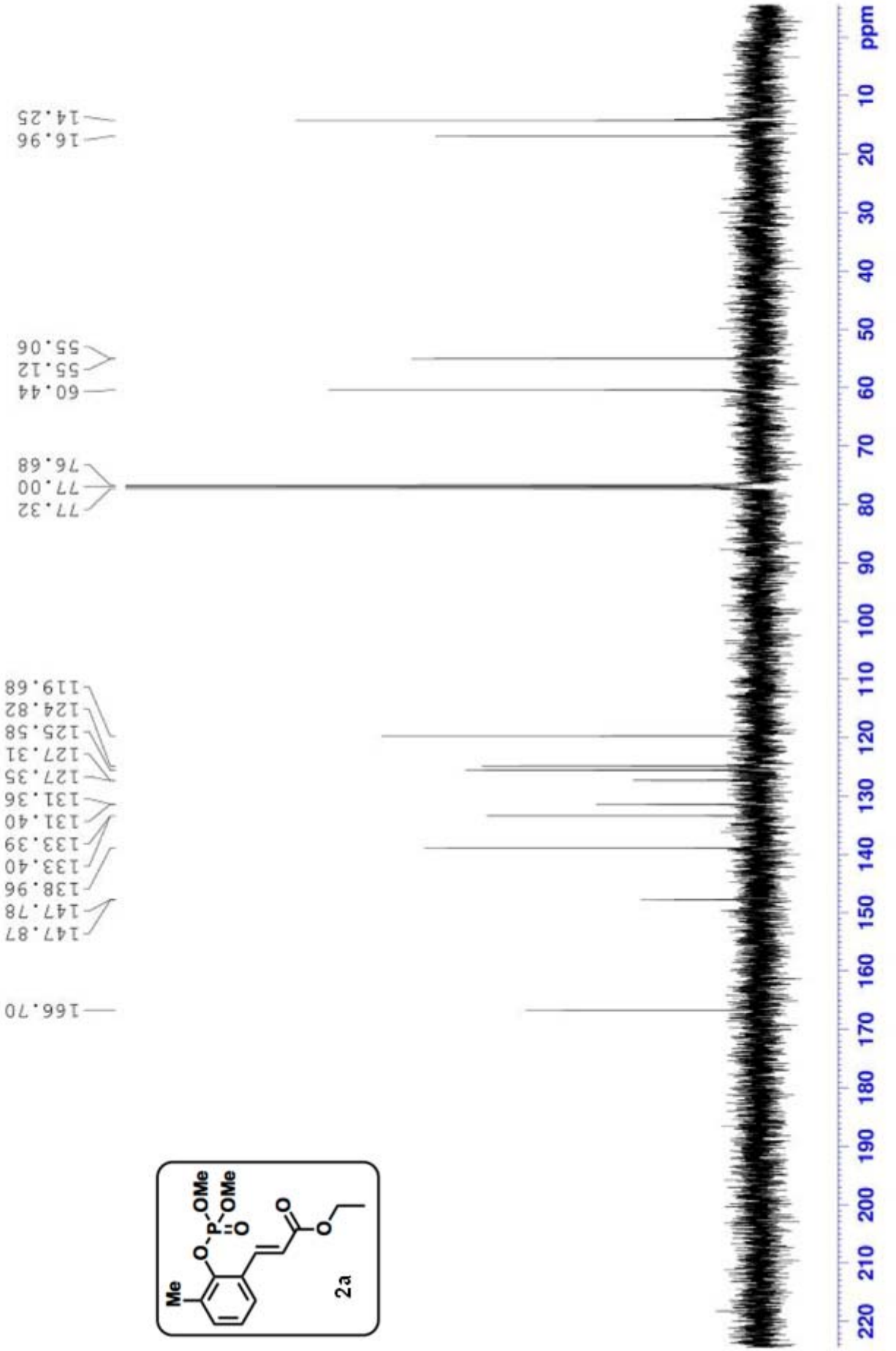

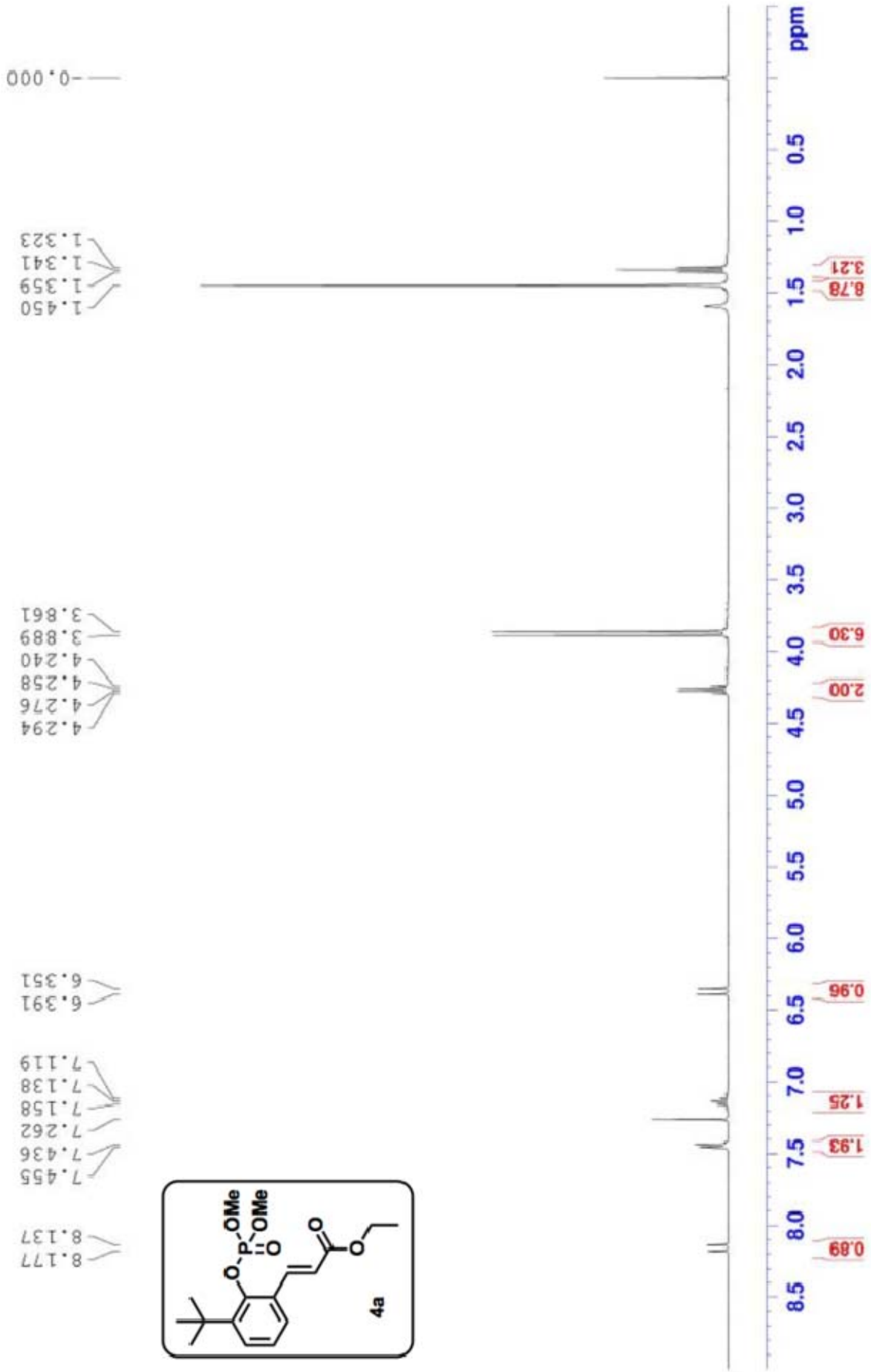
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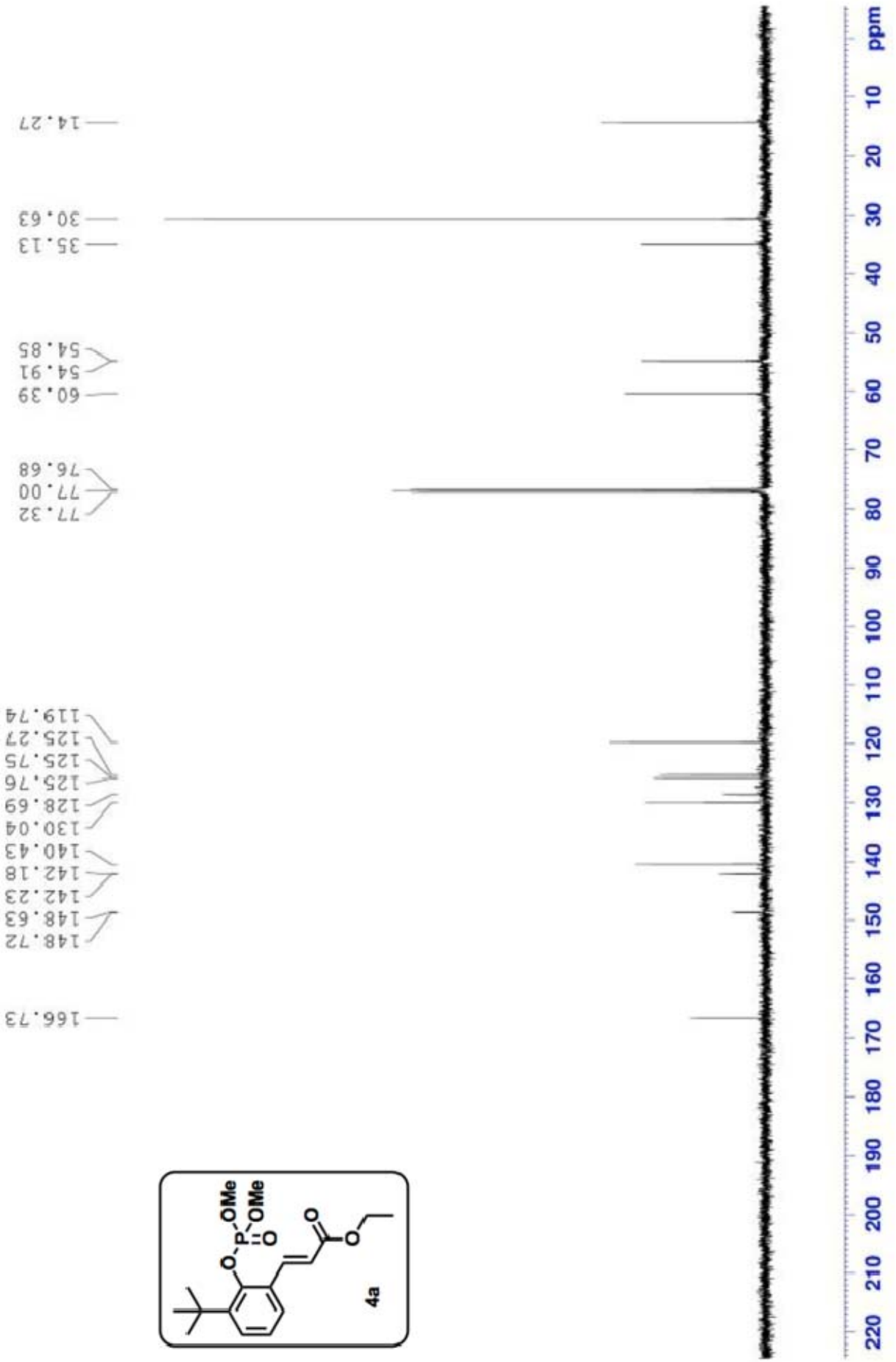

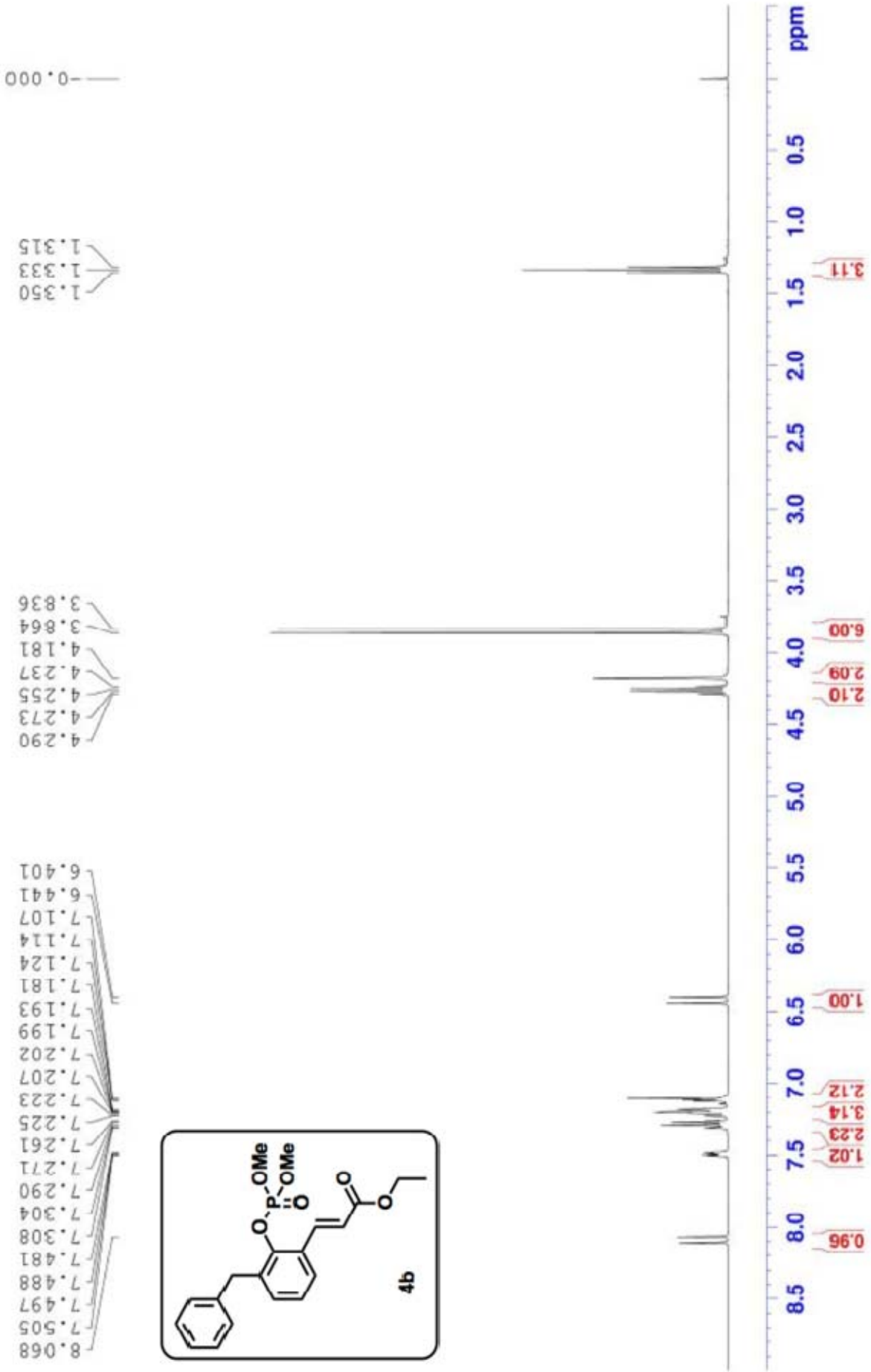
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OMe
OMe
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P
O
O
O
4b
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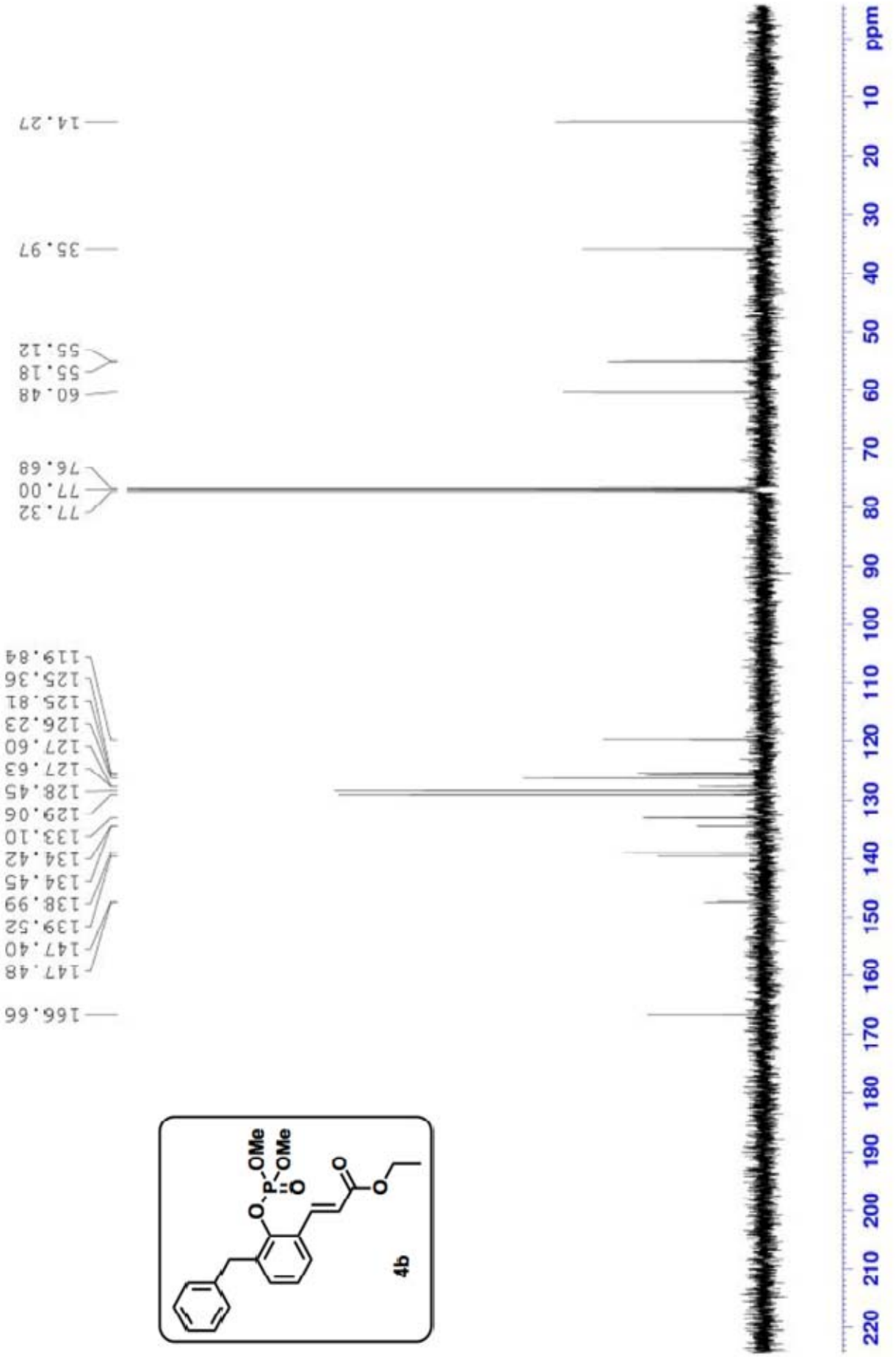

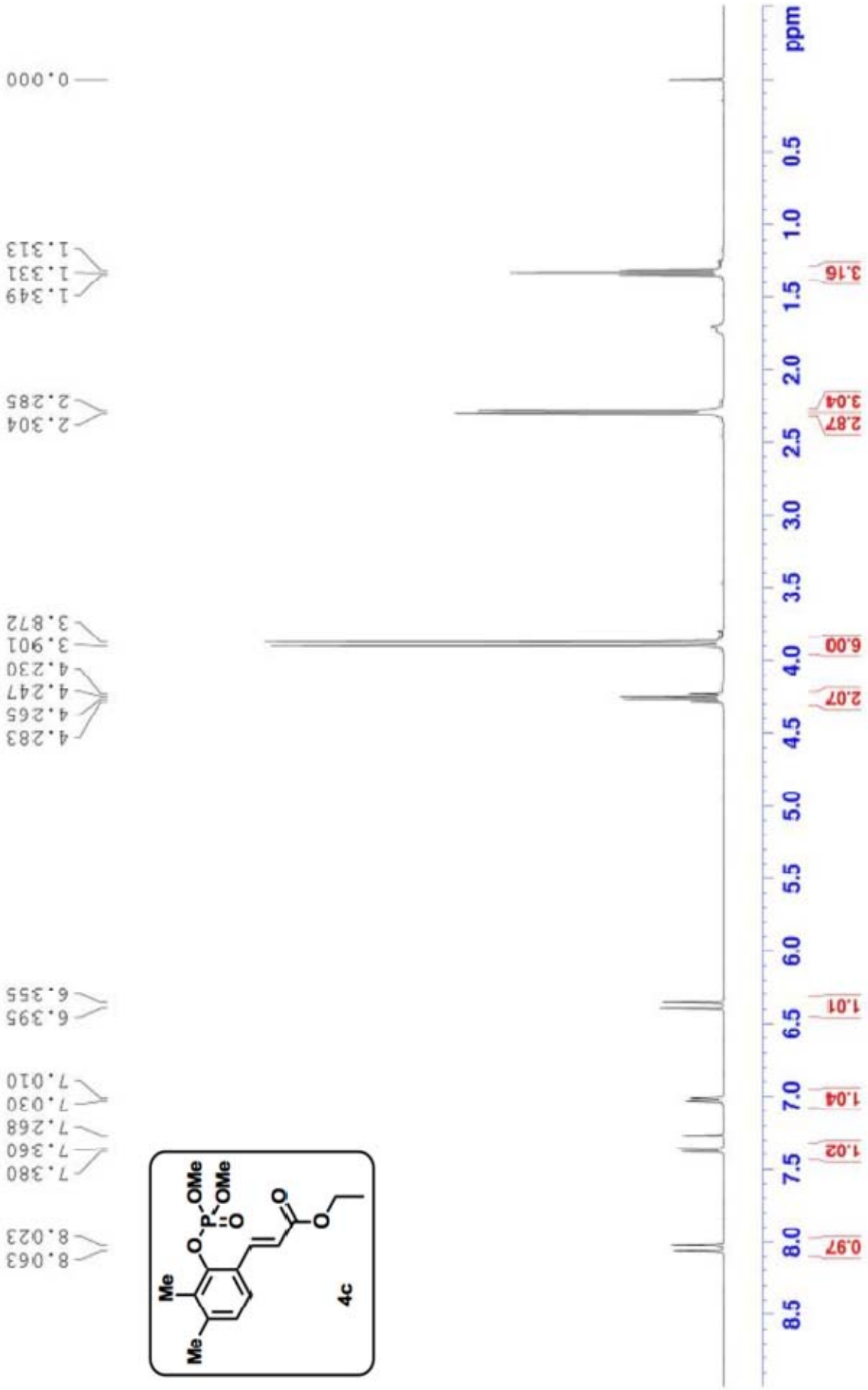
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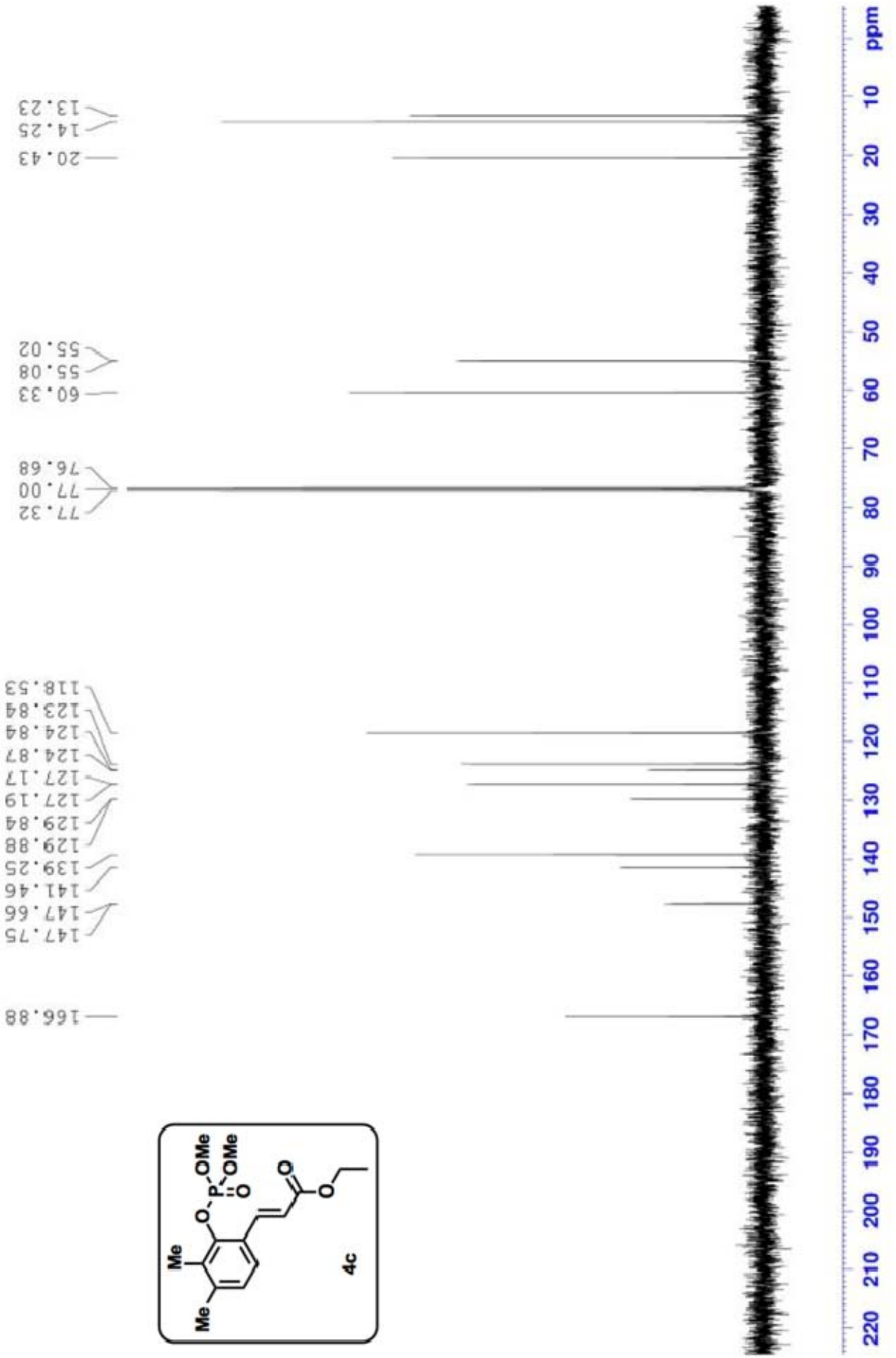
4c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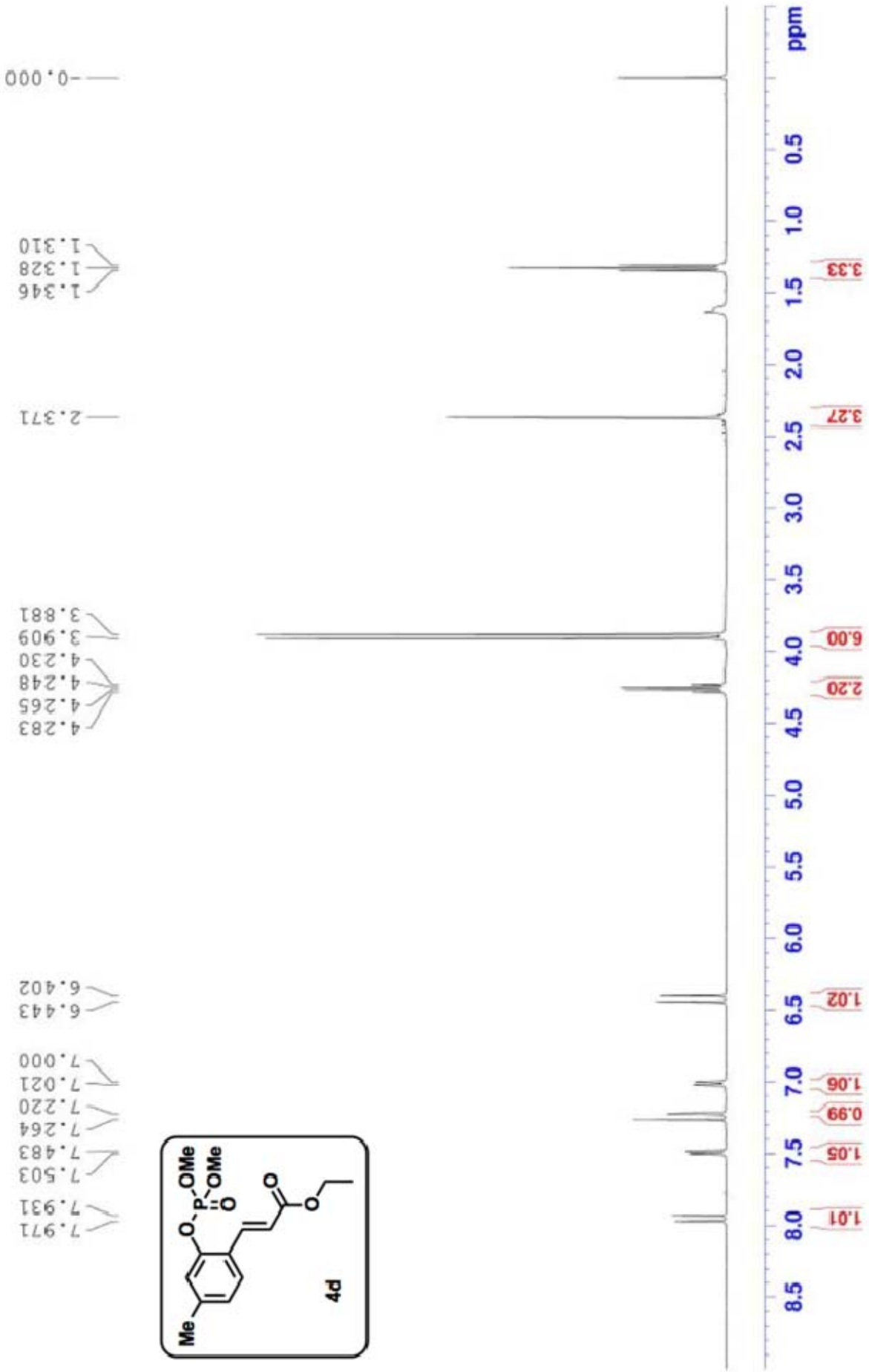
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O
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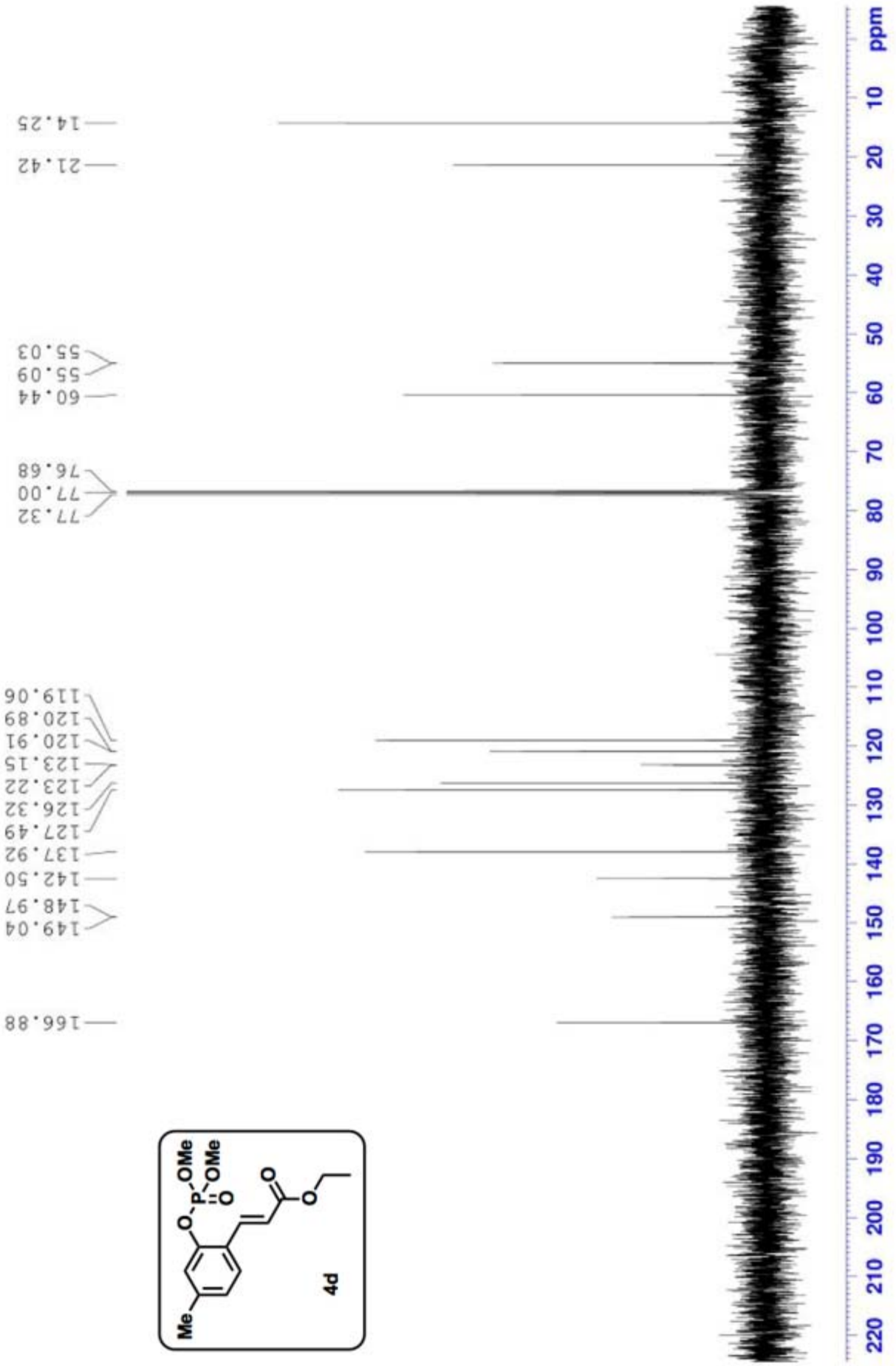

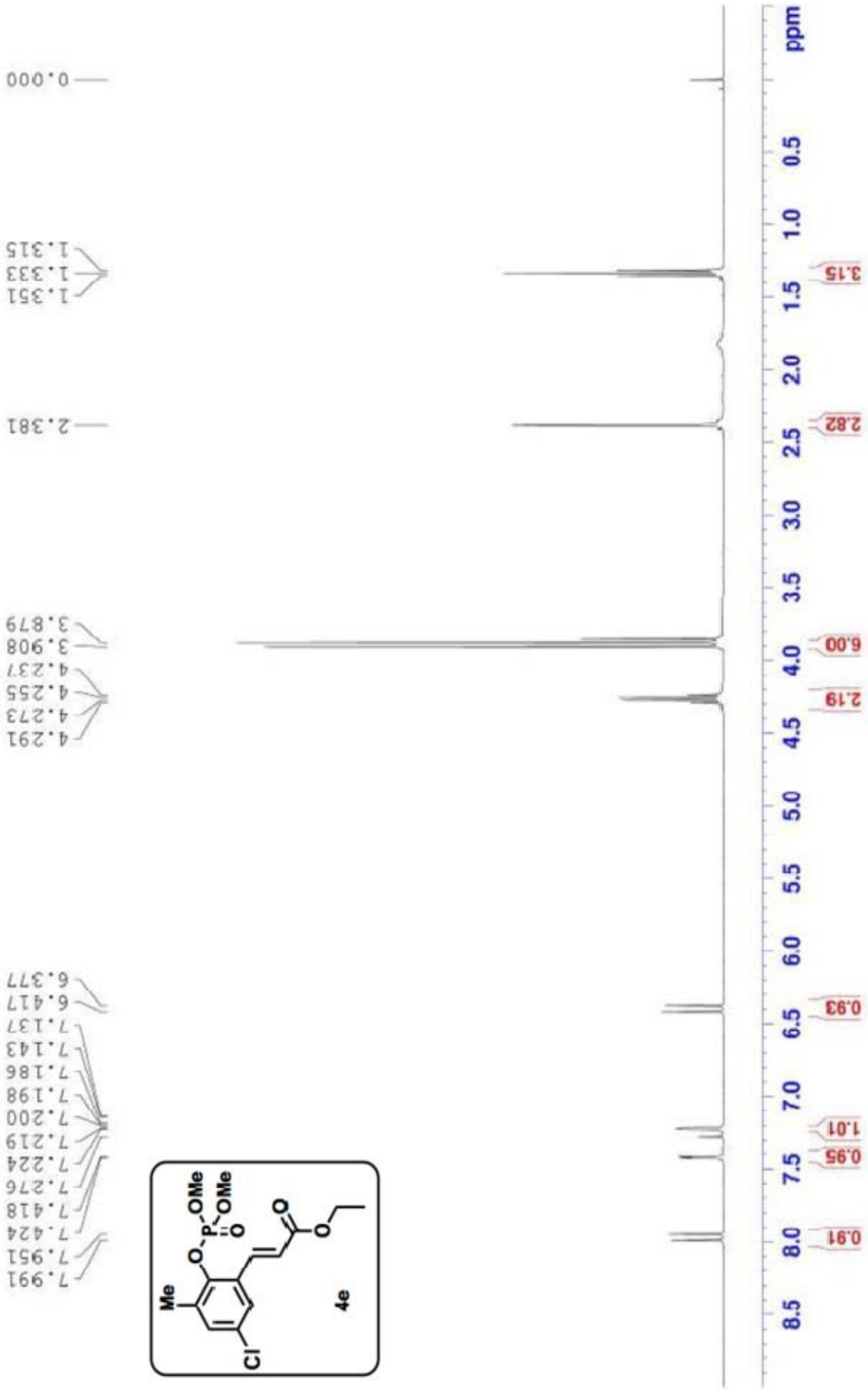
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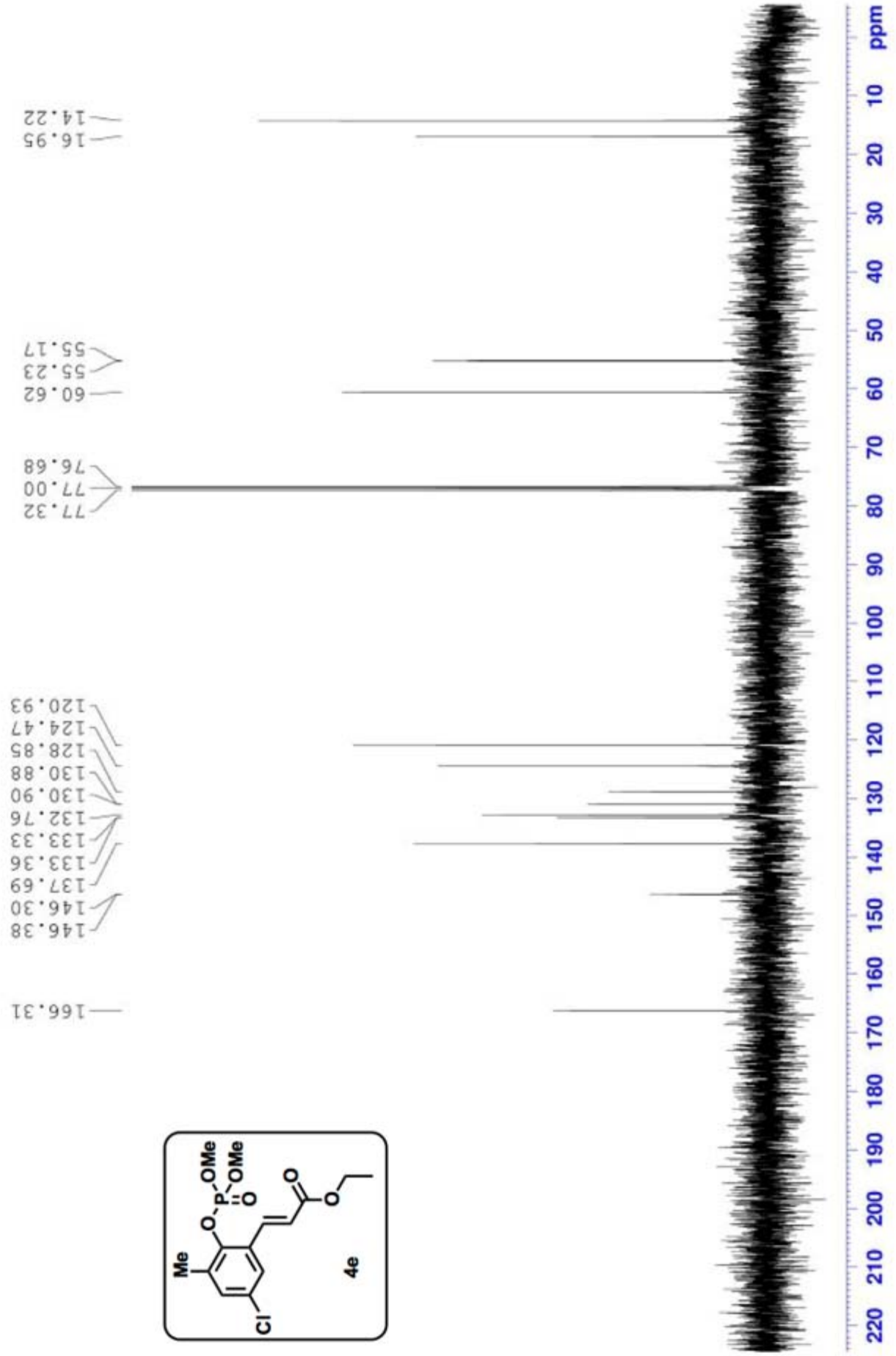

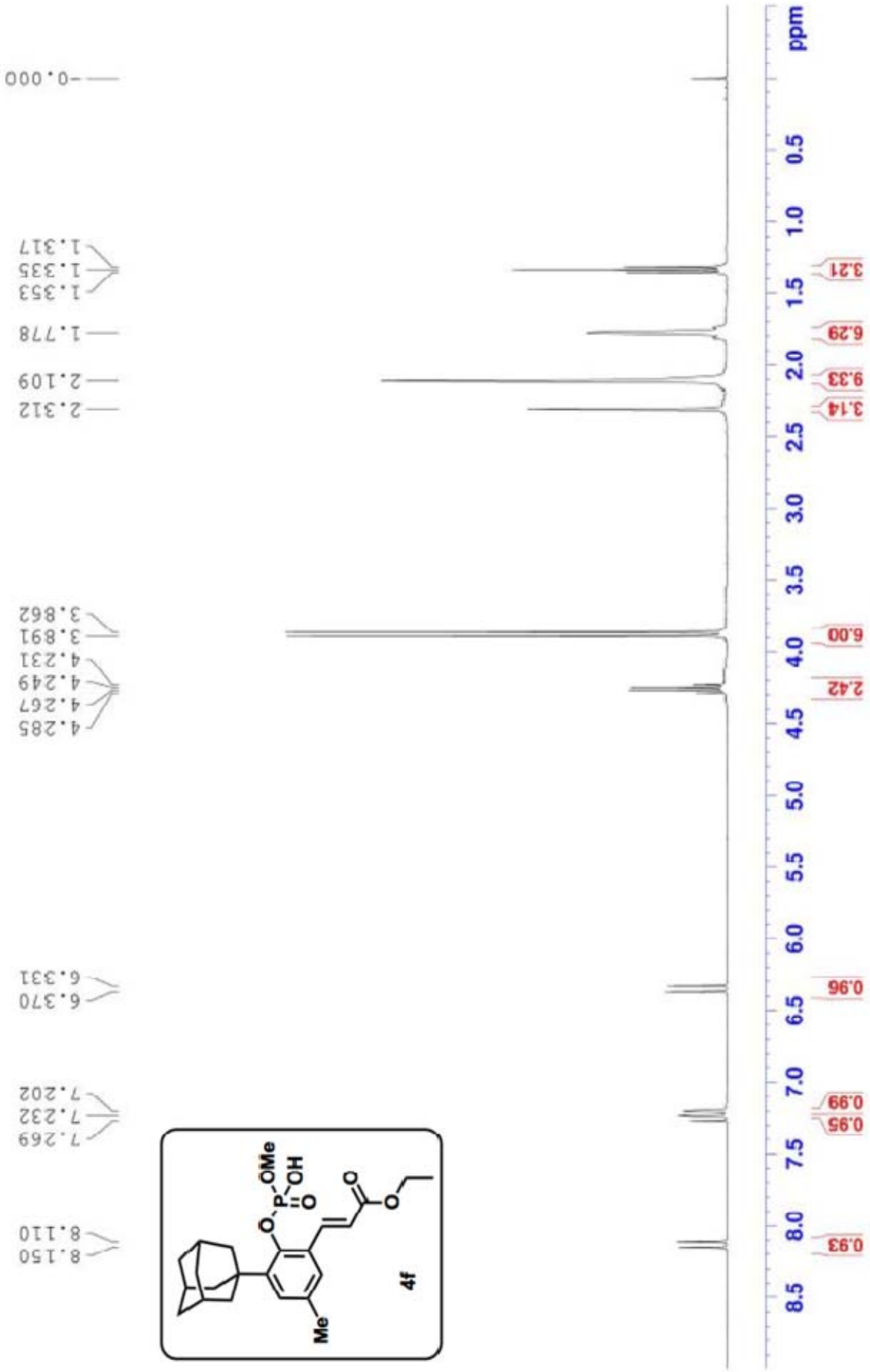
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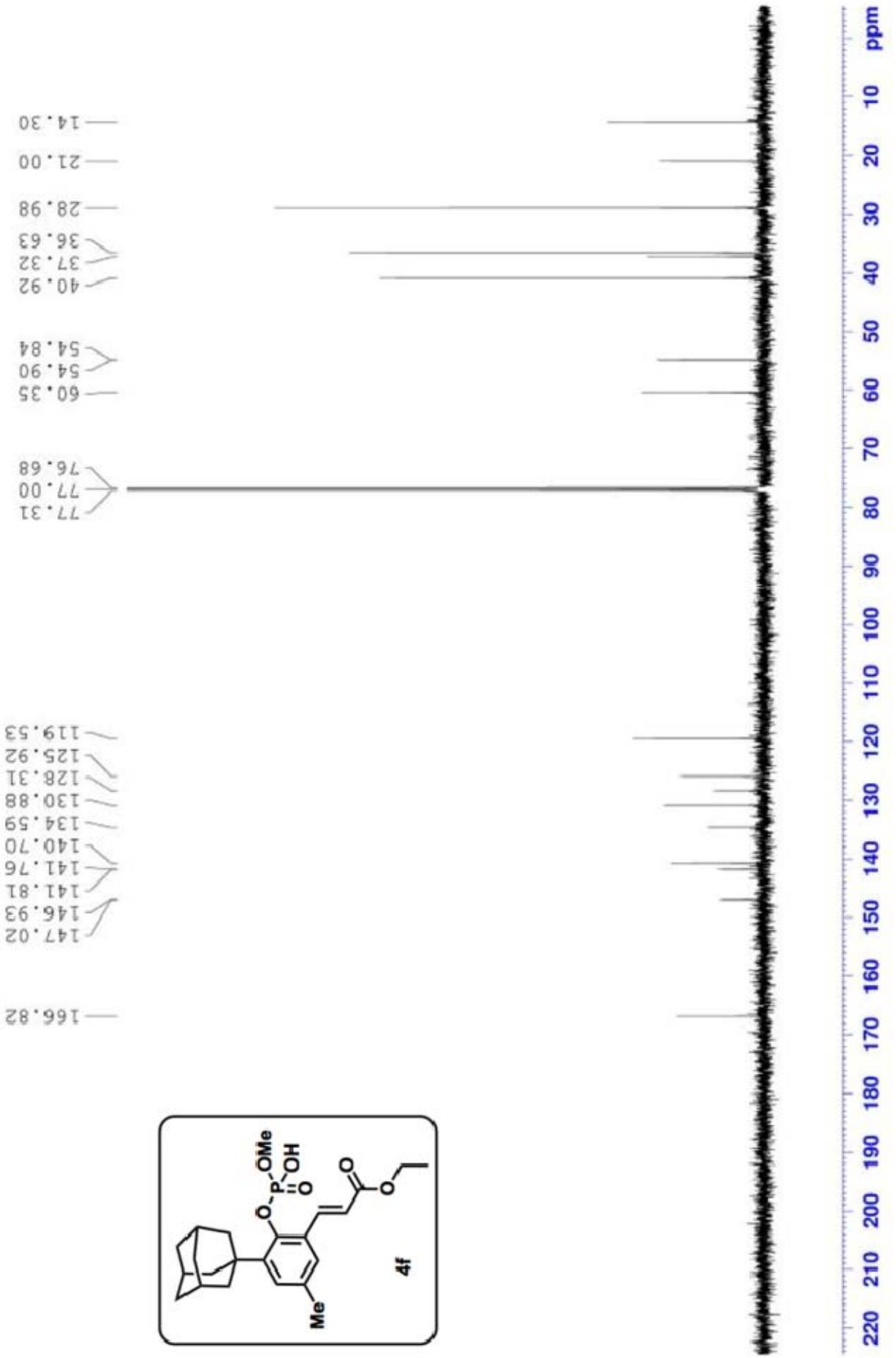
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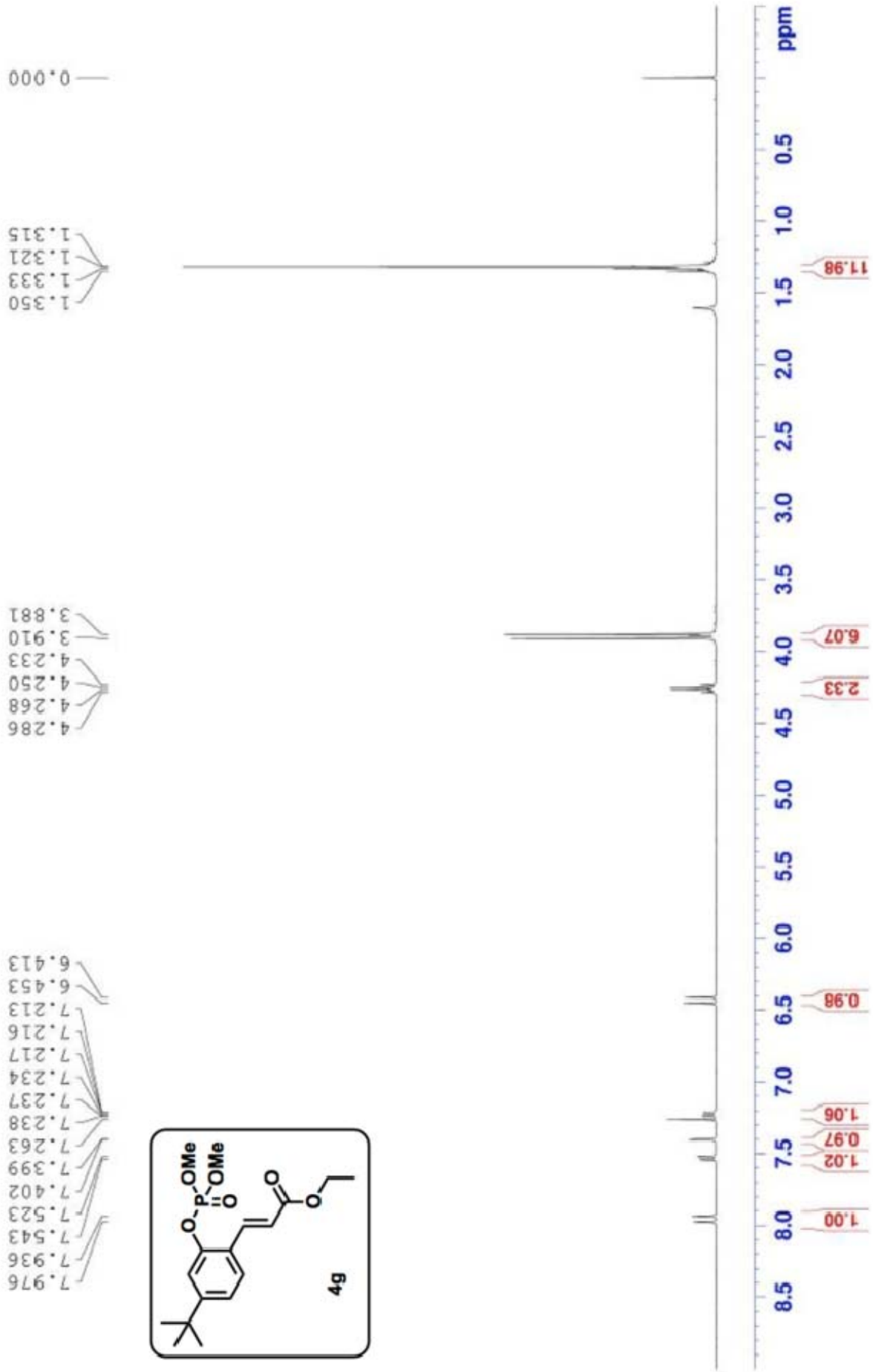
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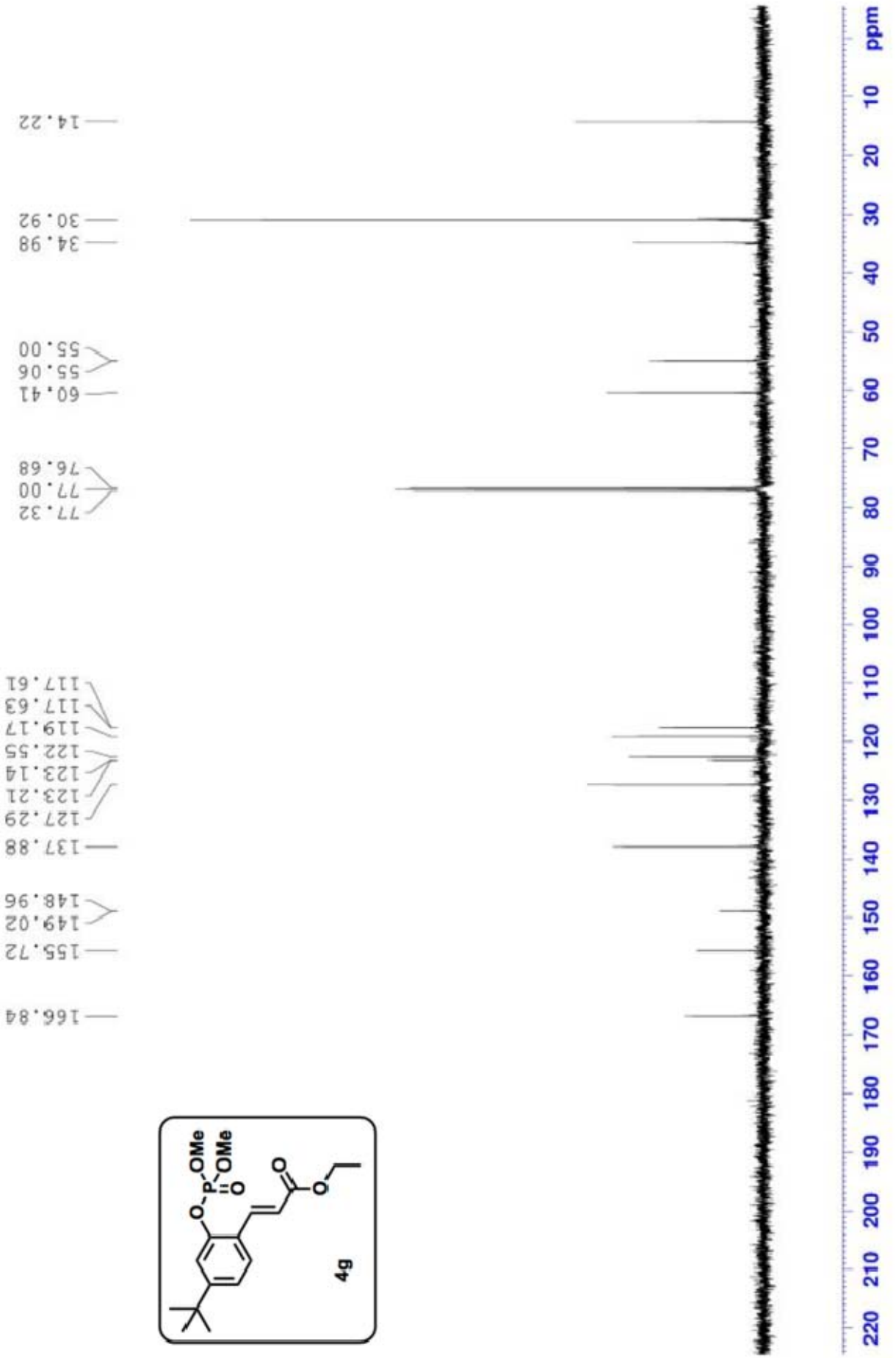

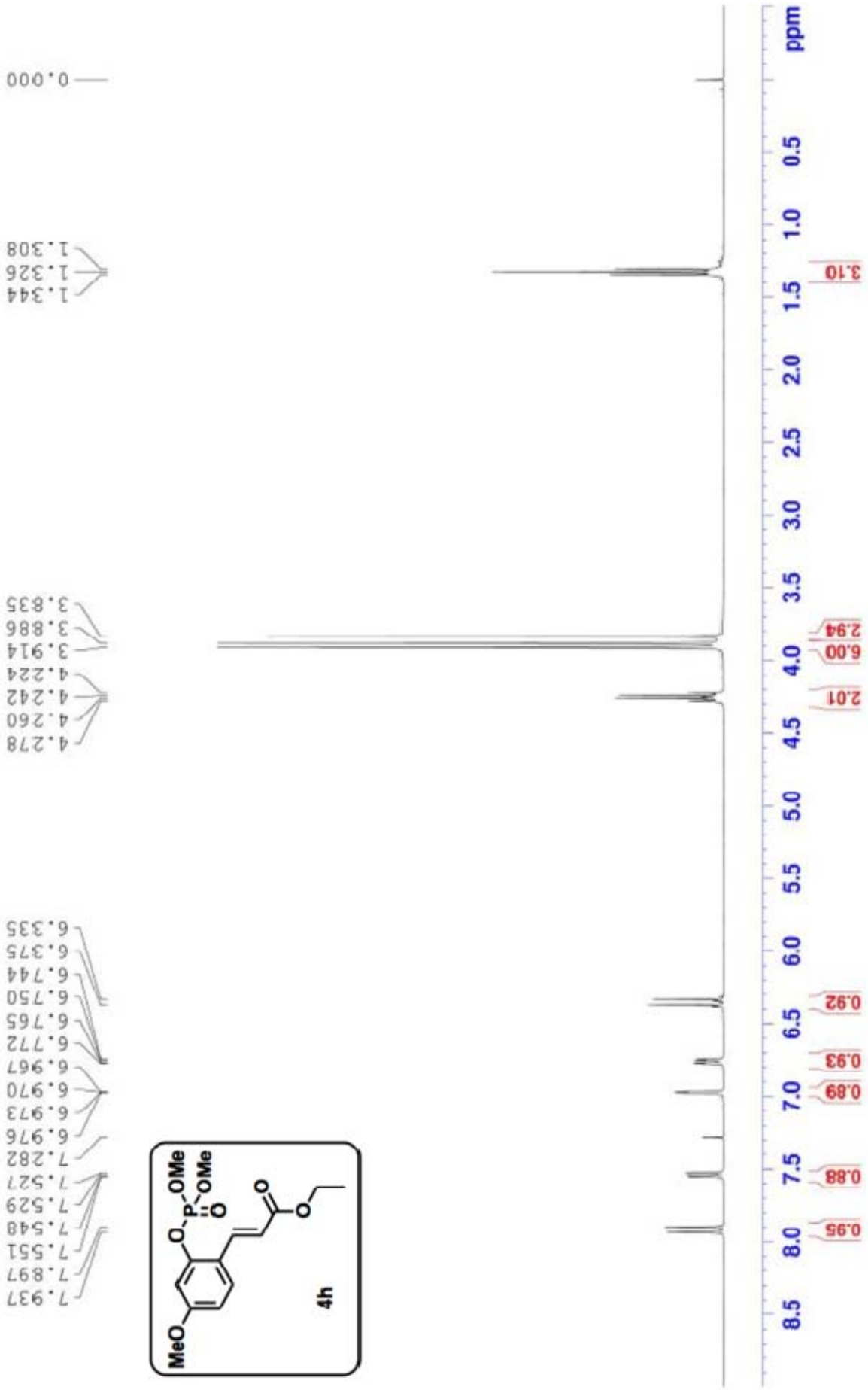
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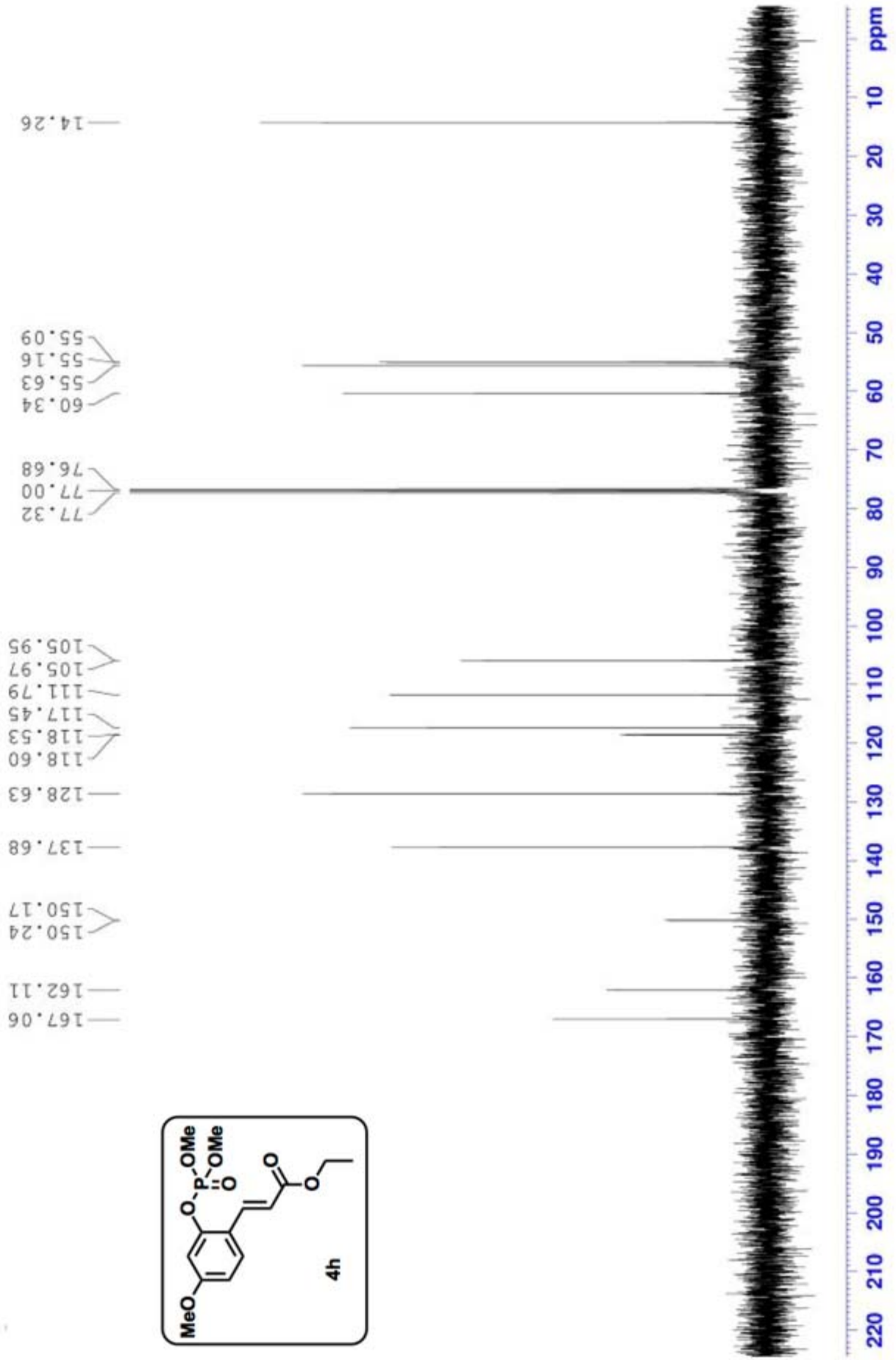

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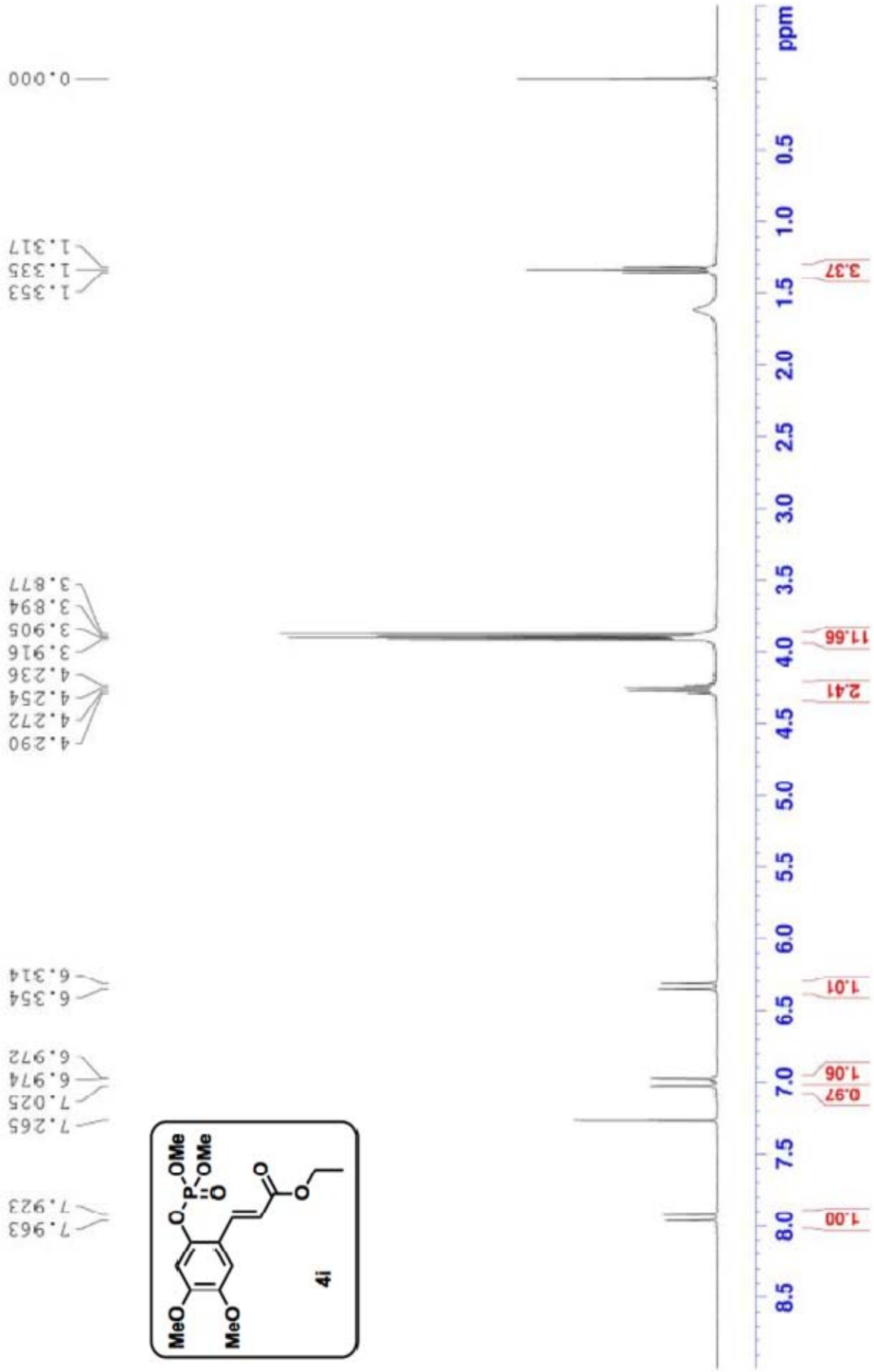

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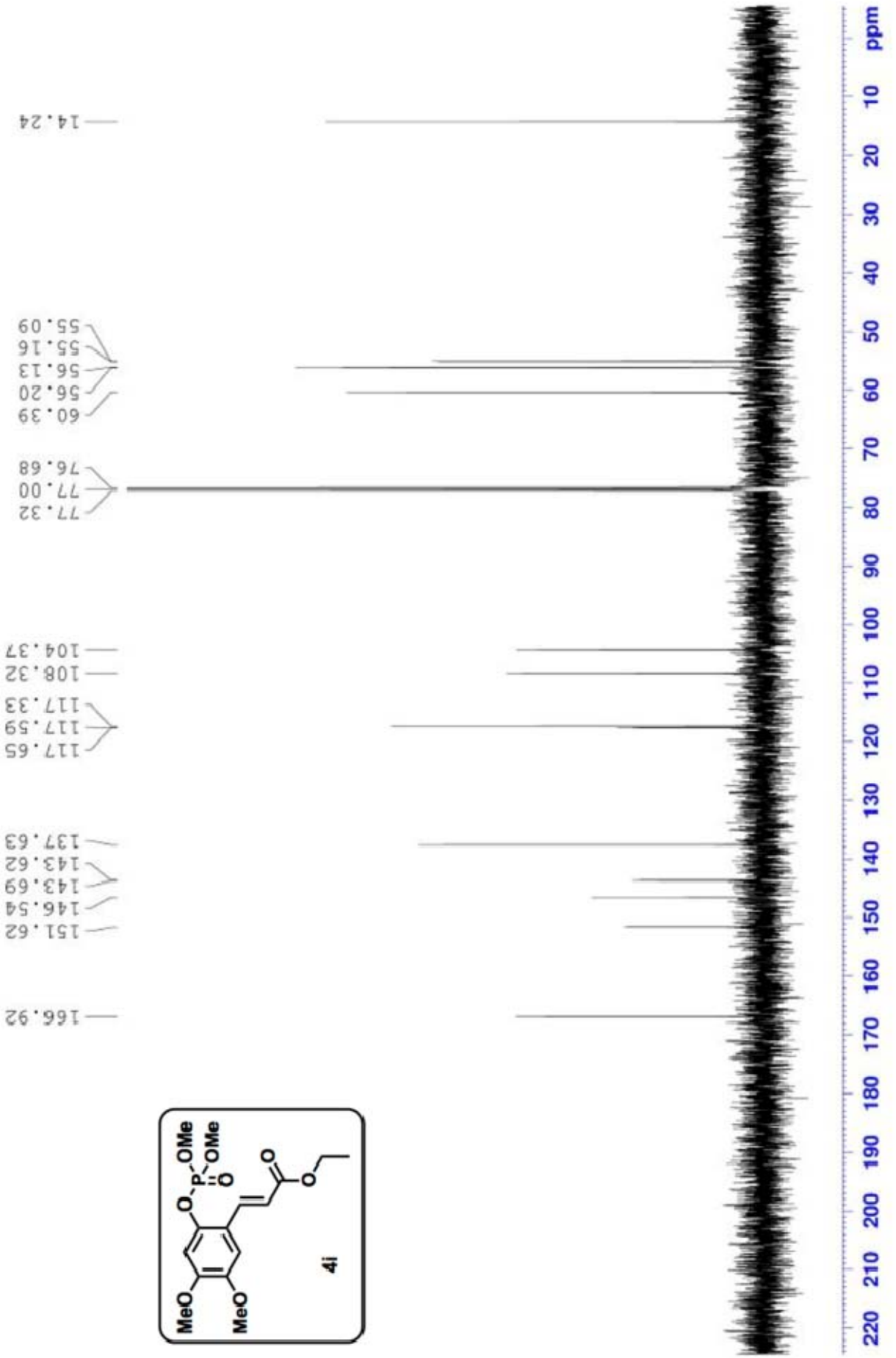

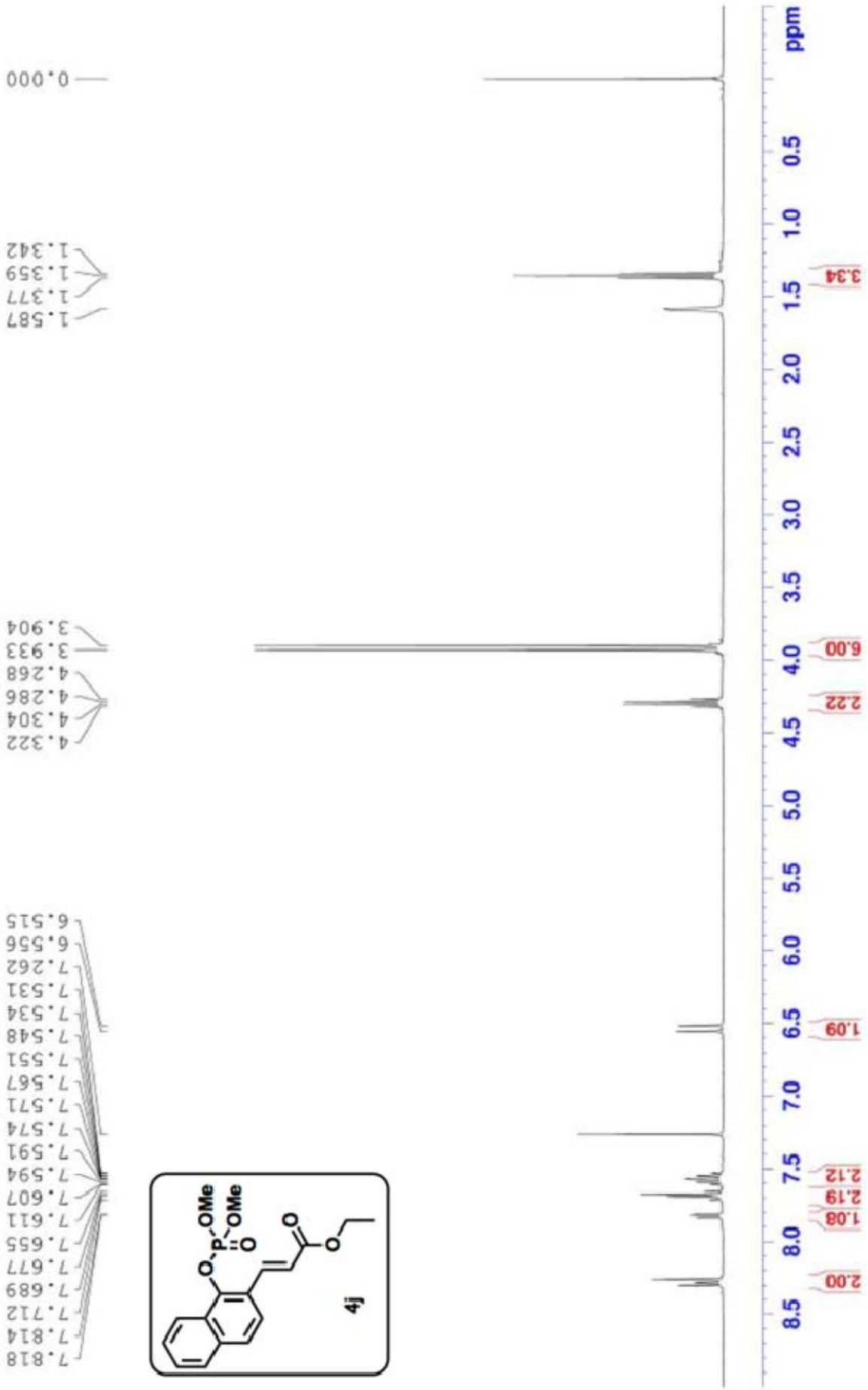
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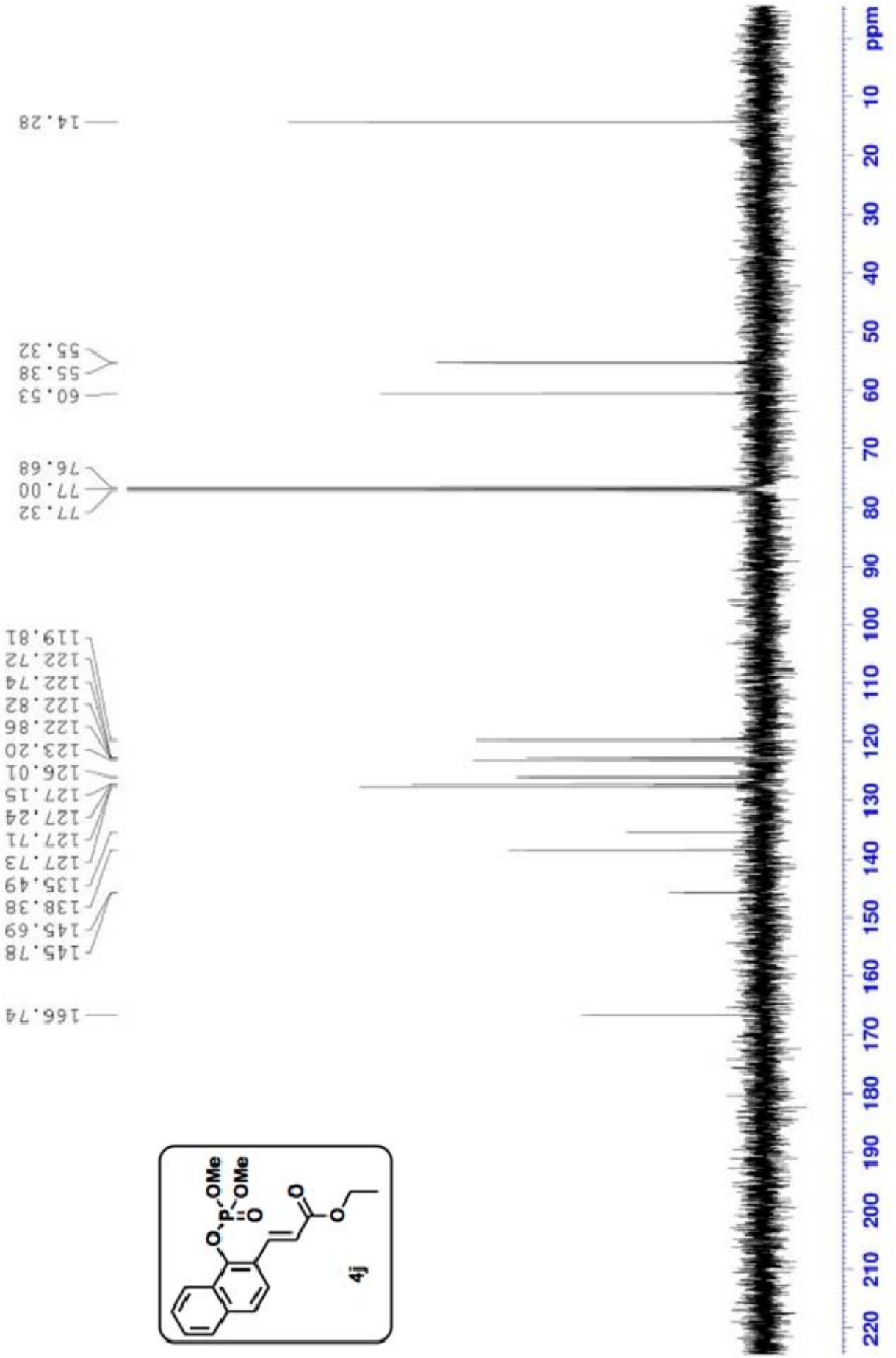

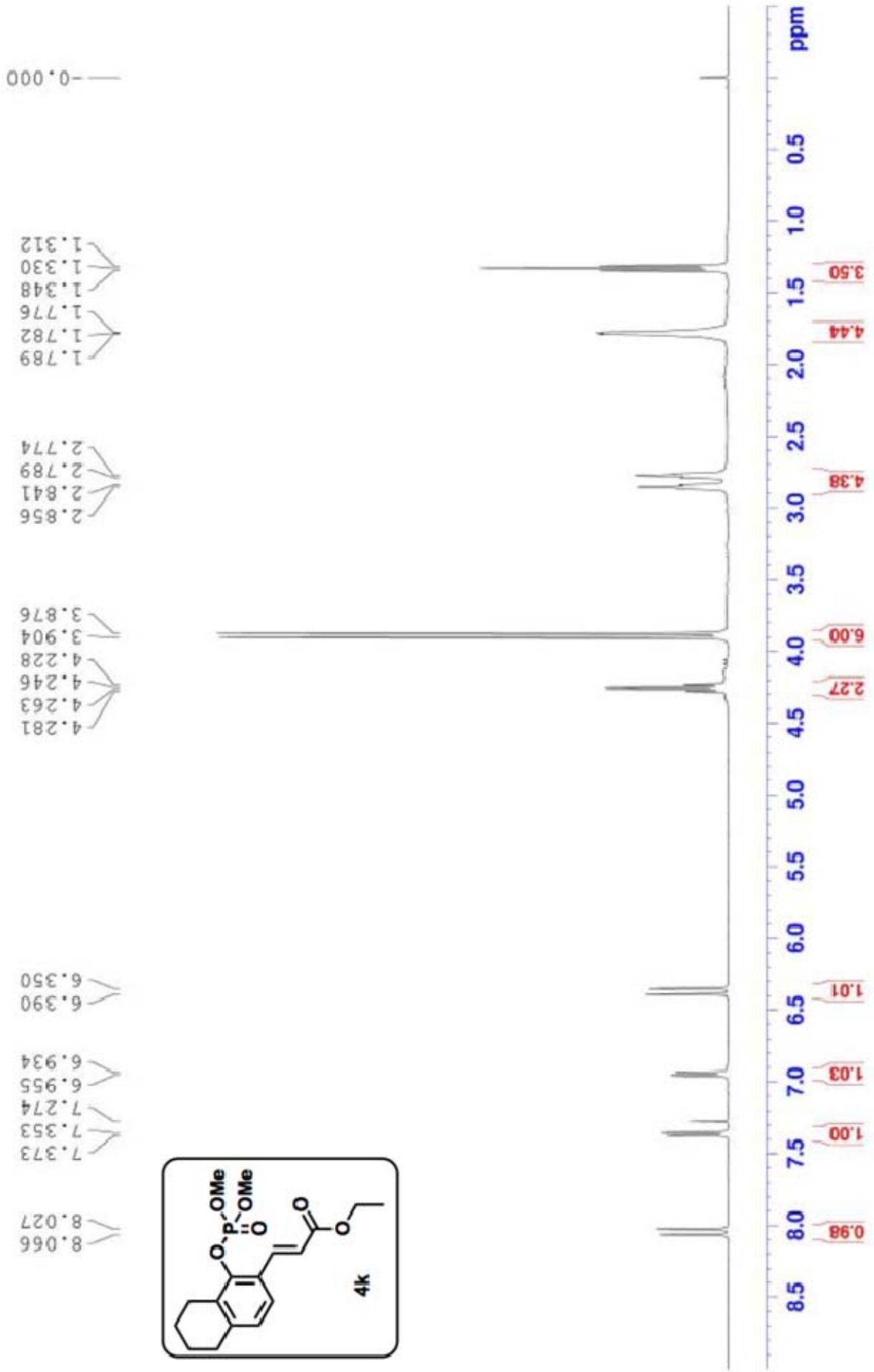
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O
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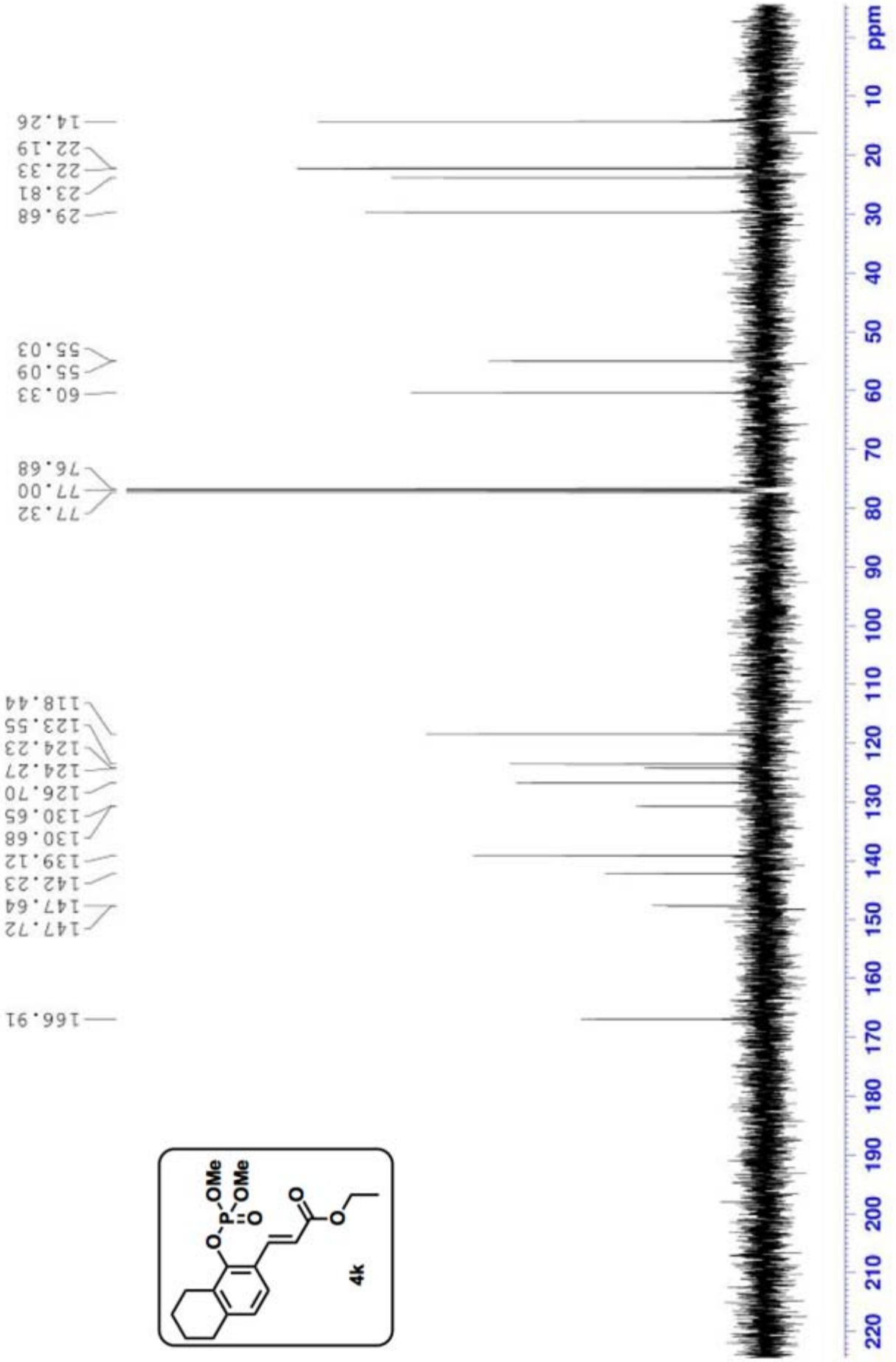

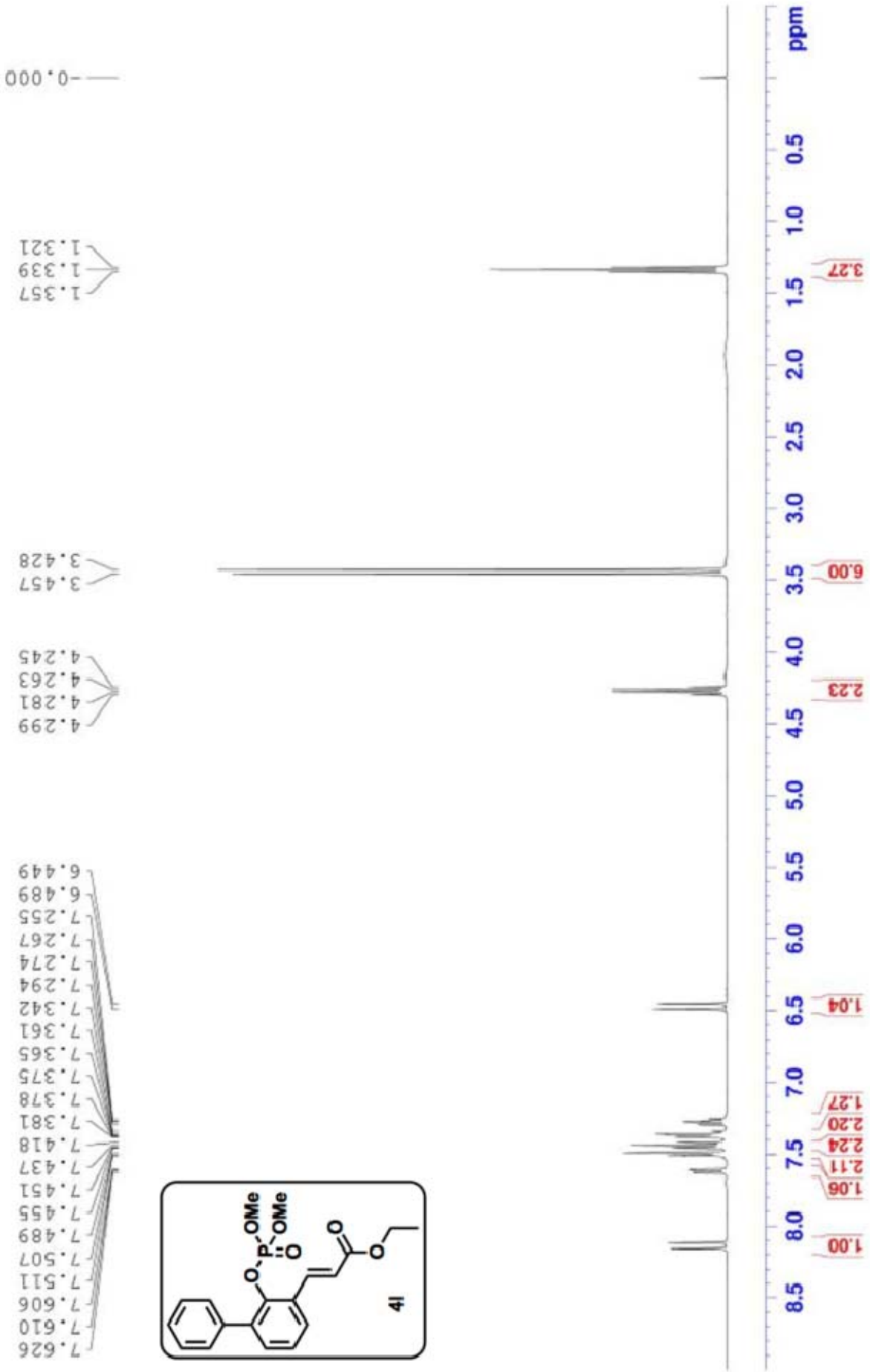
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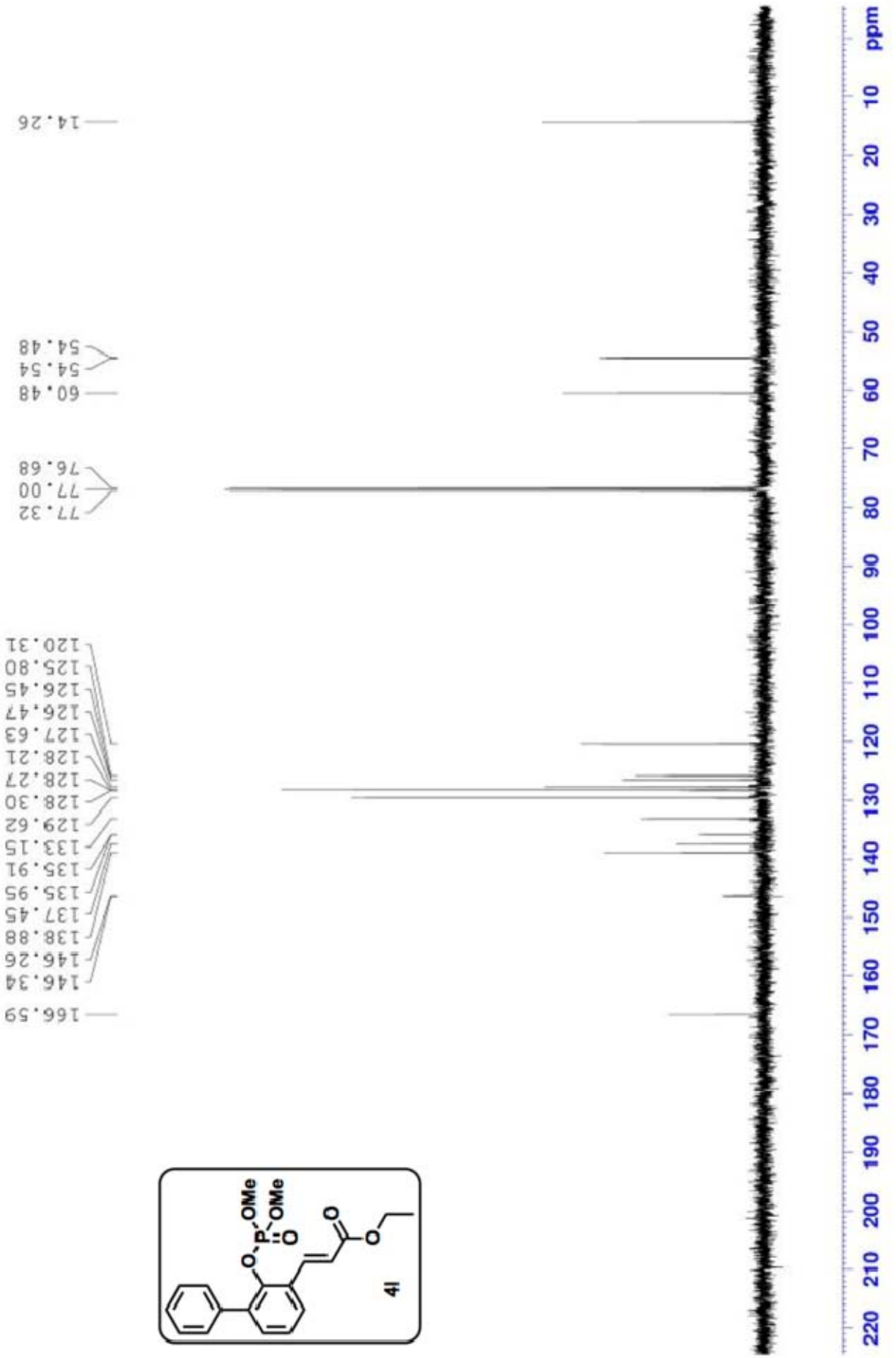
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OMe
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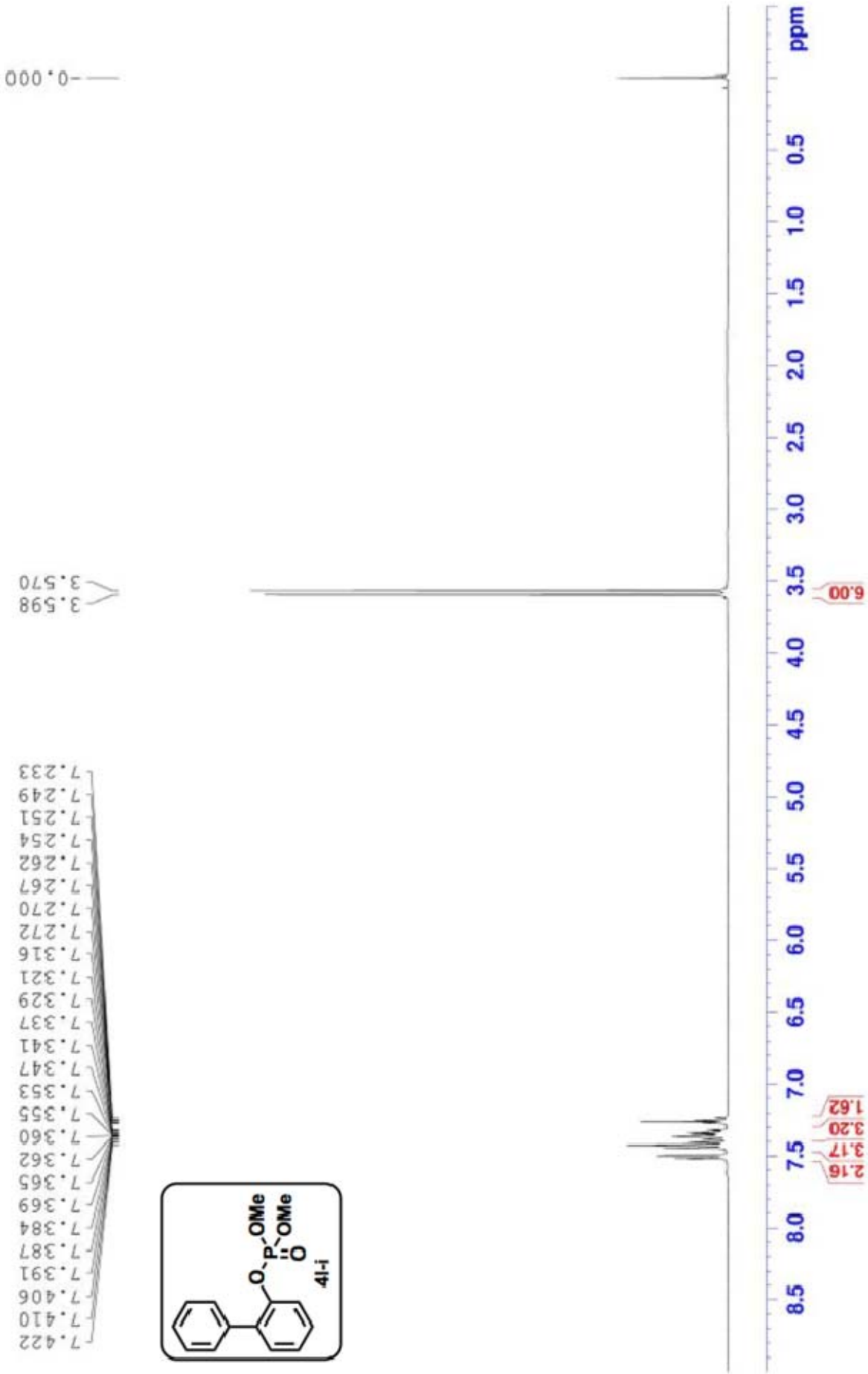
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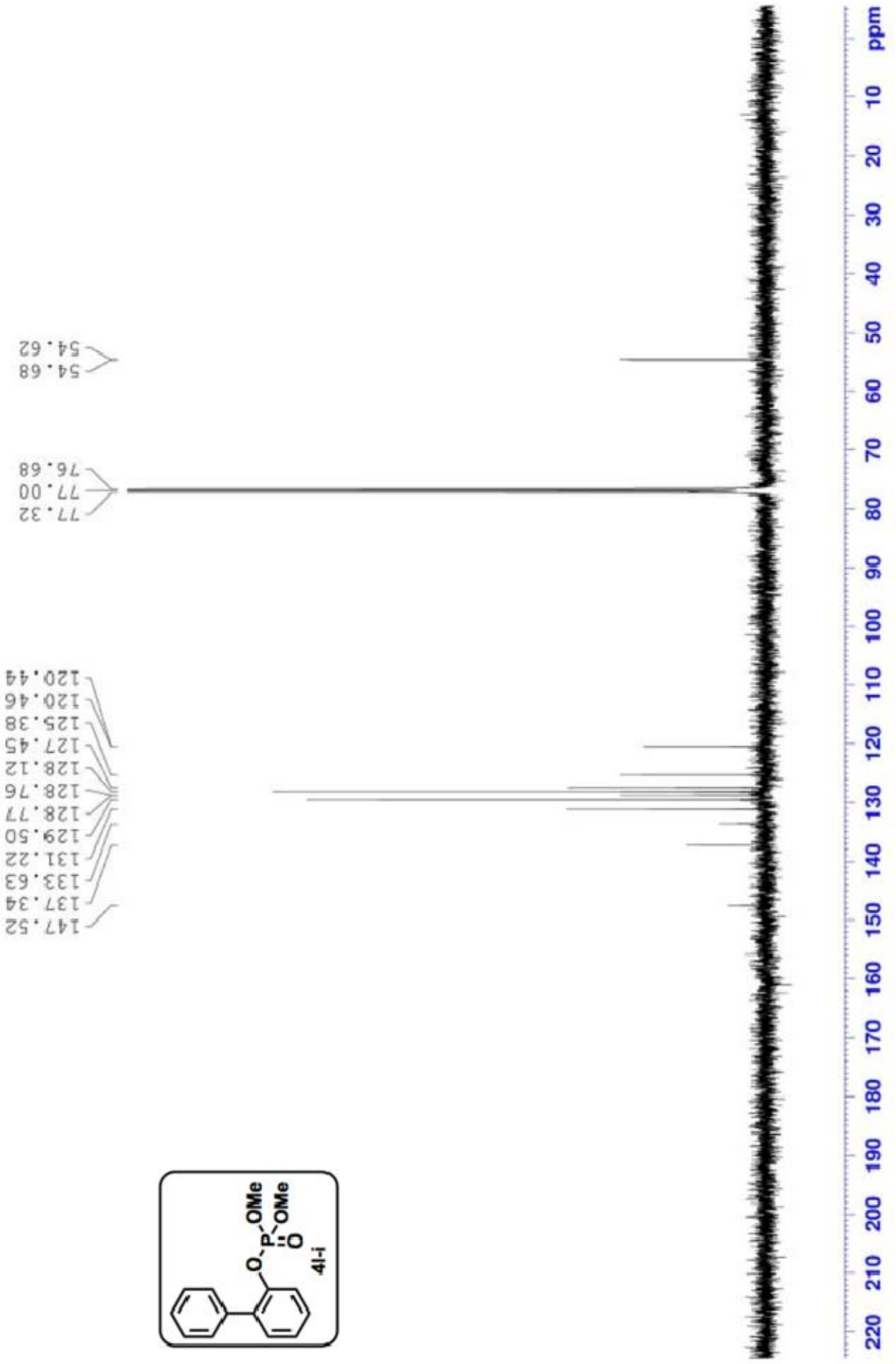

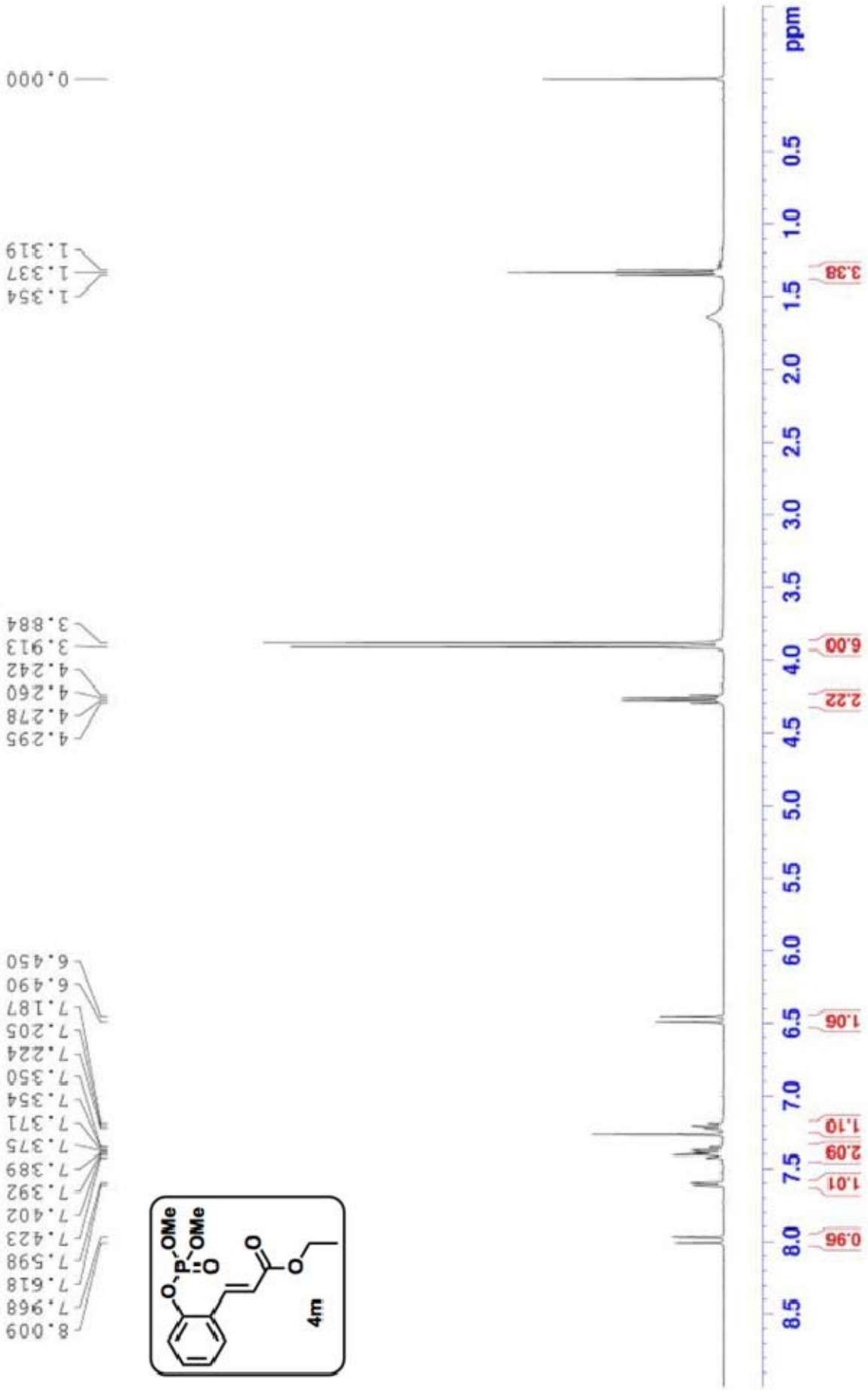
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7.354
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7.375
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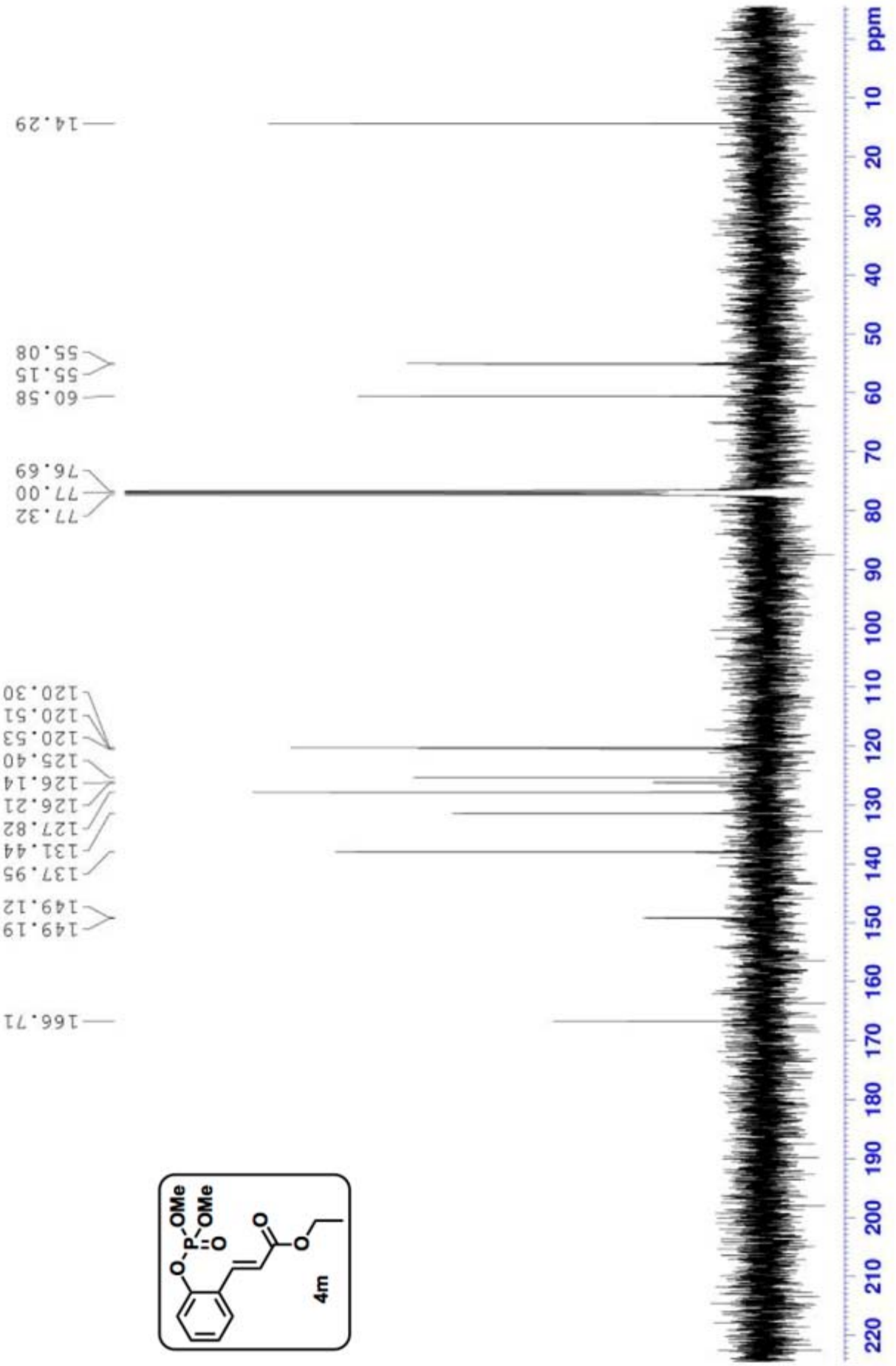

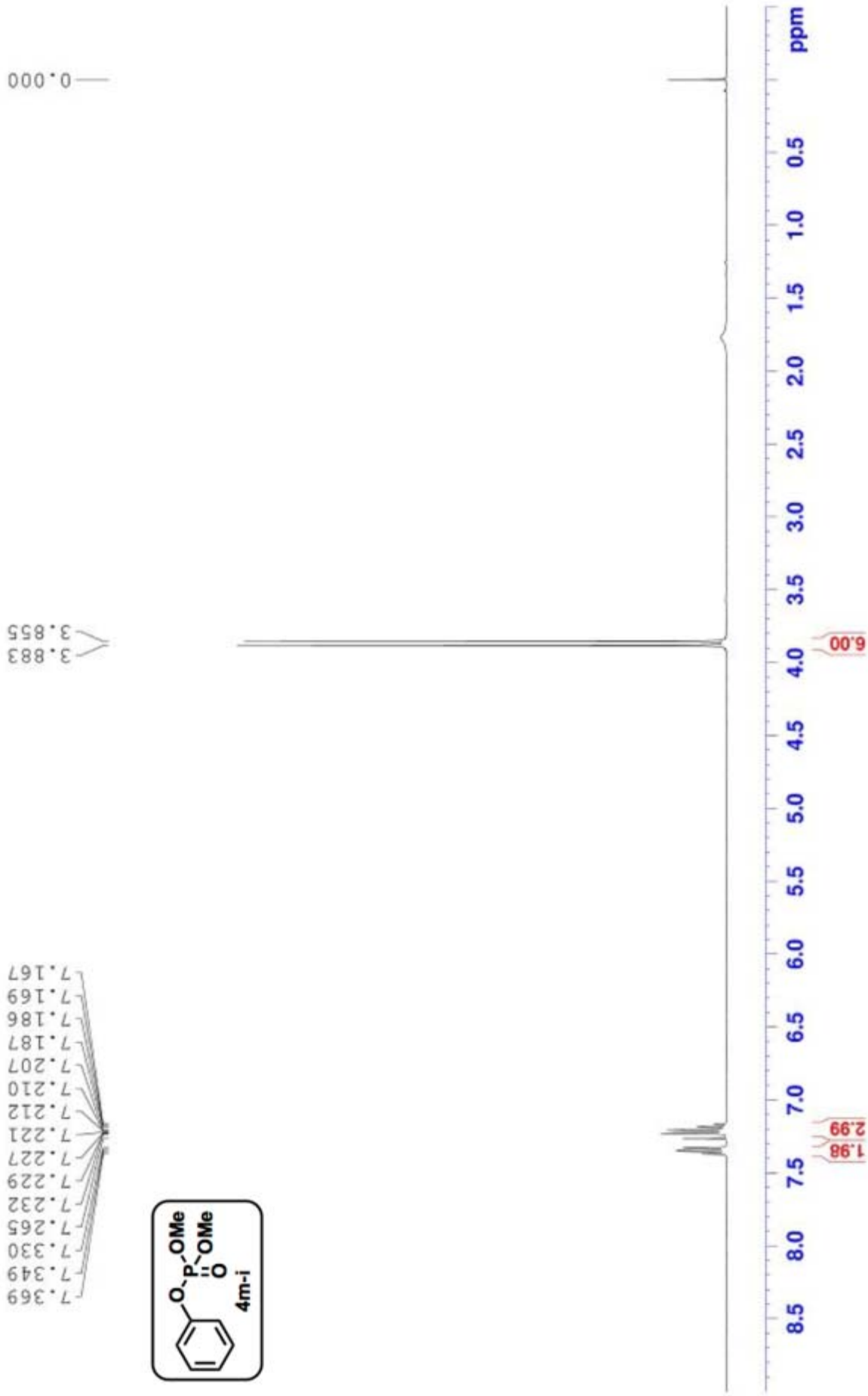
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P
OMe
OMe
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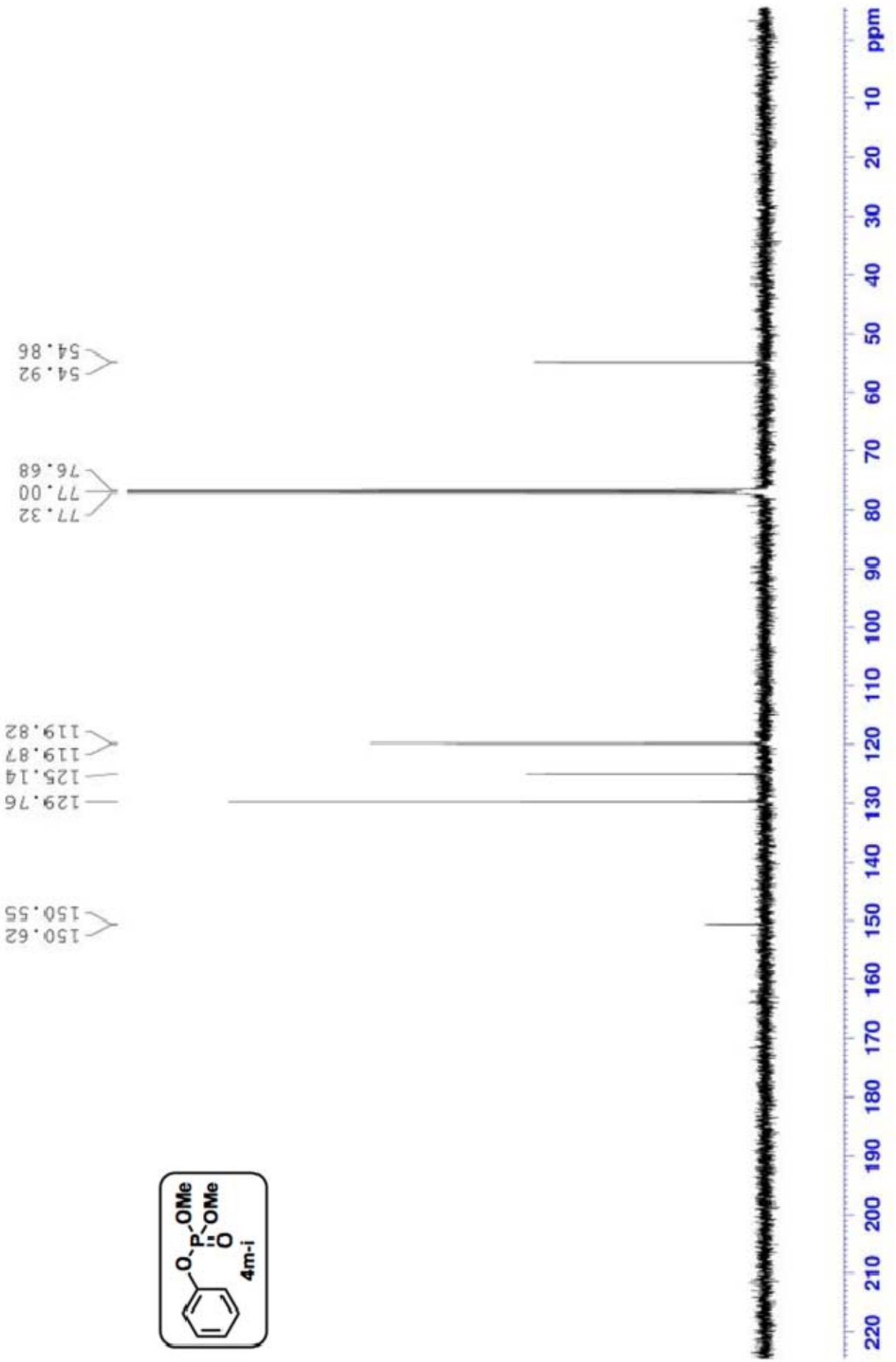
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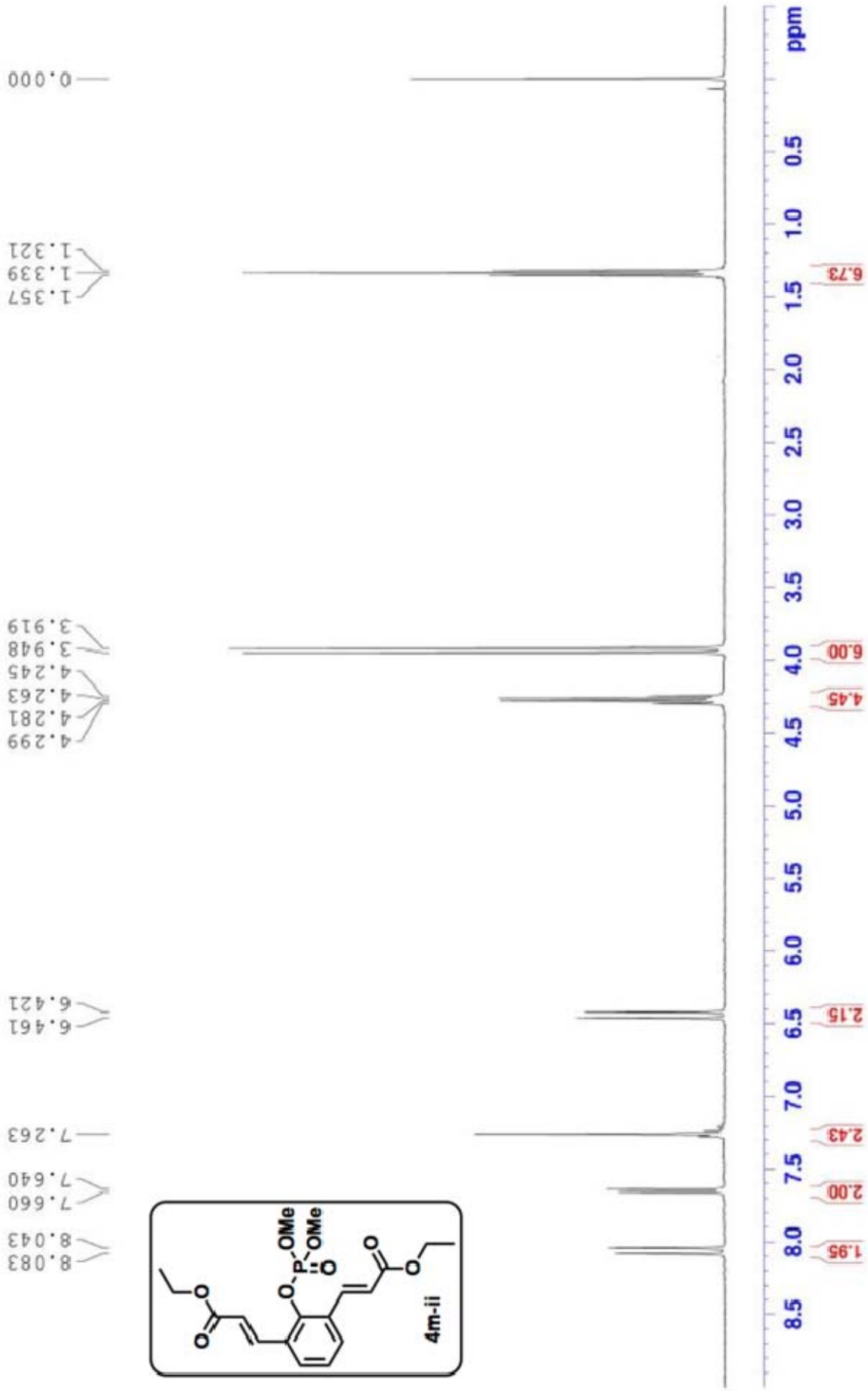

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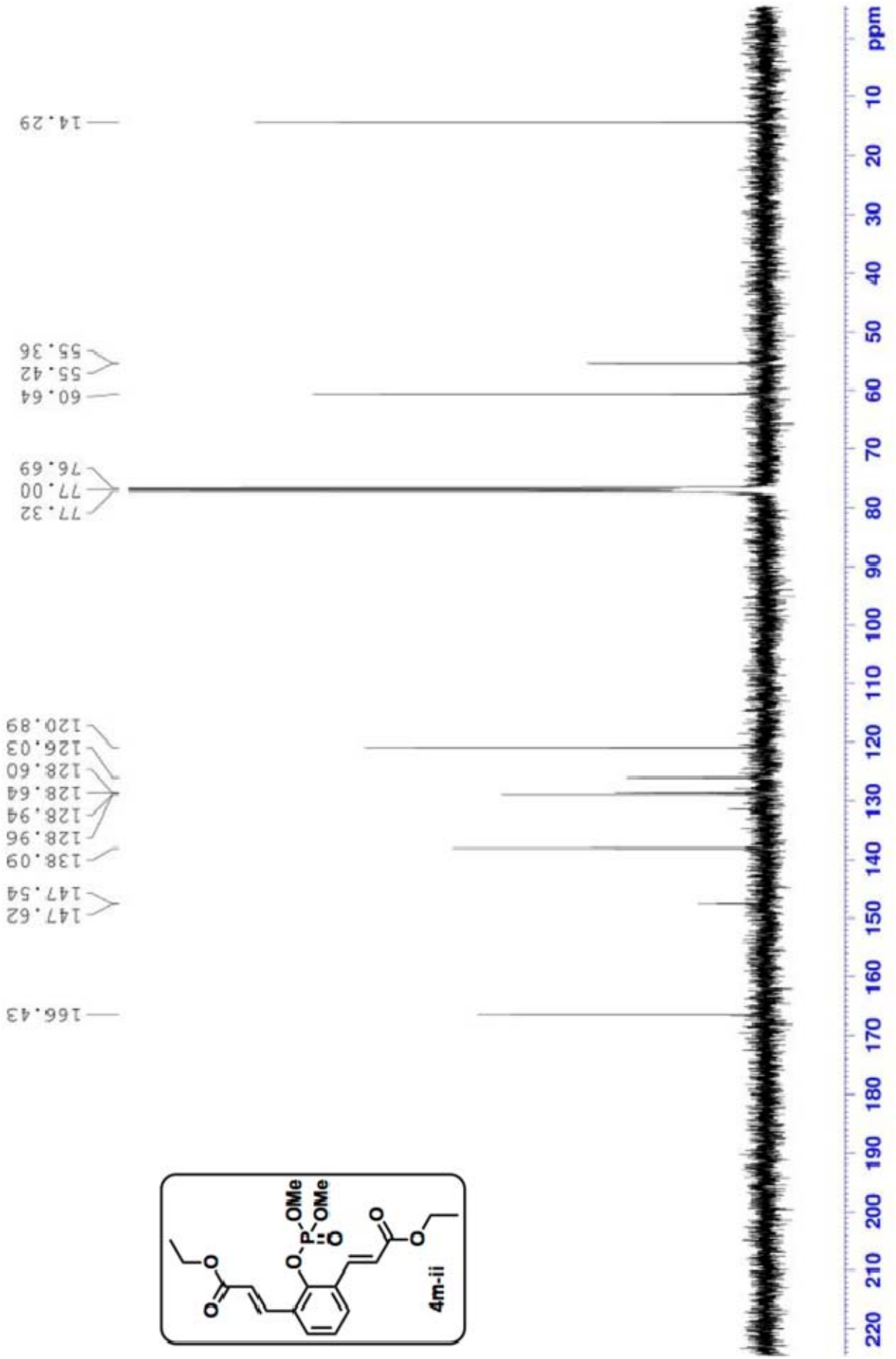

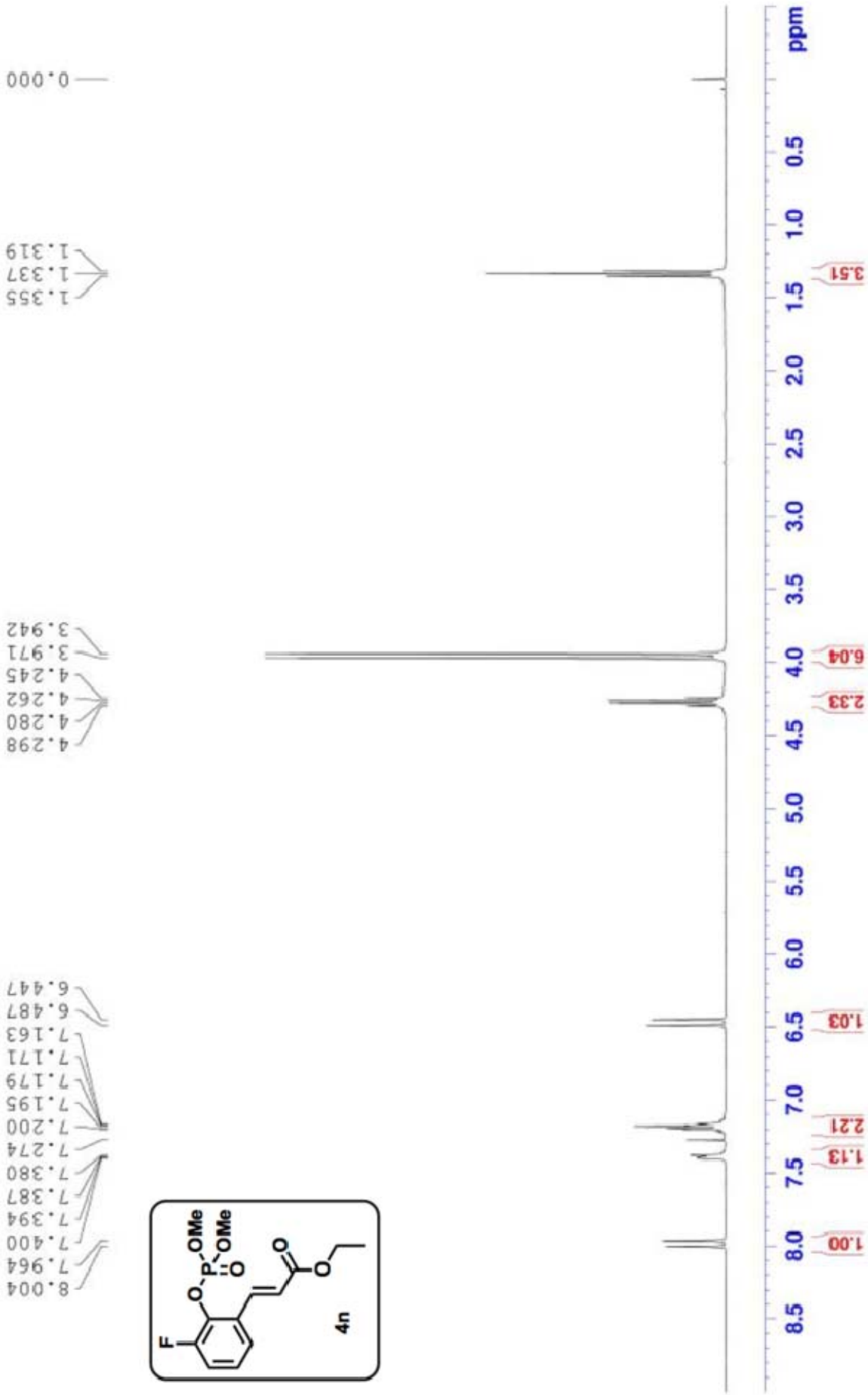
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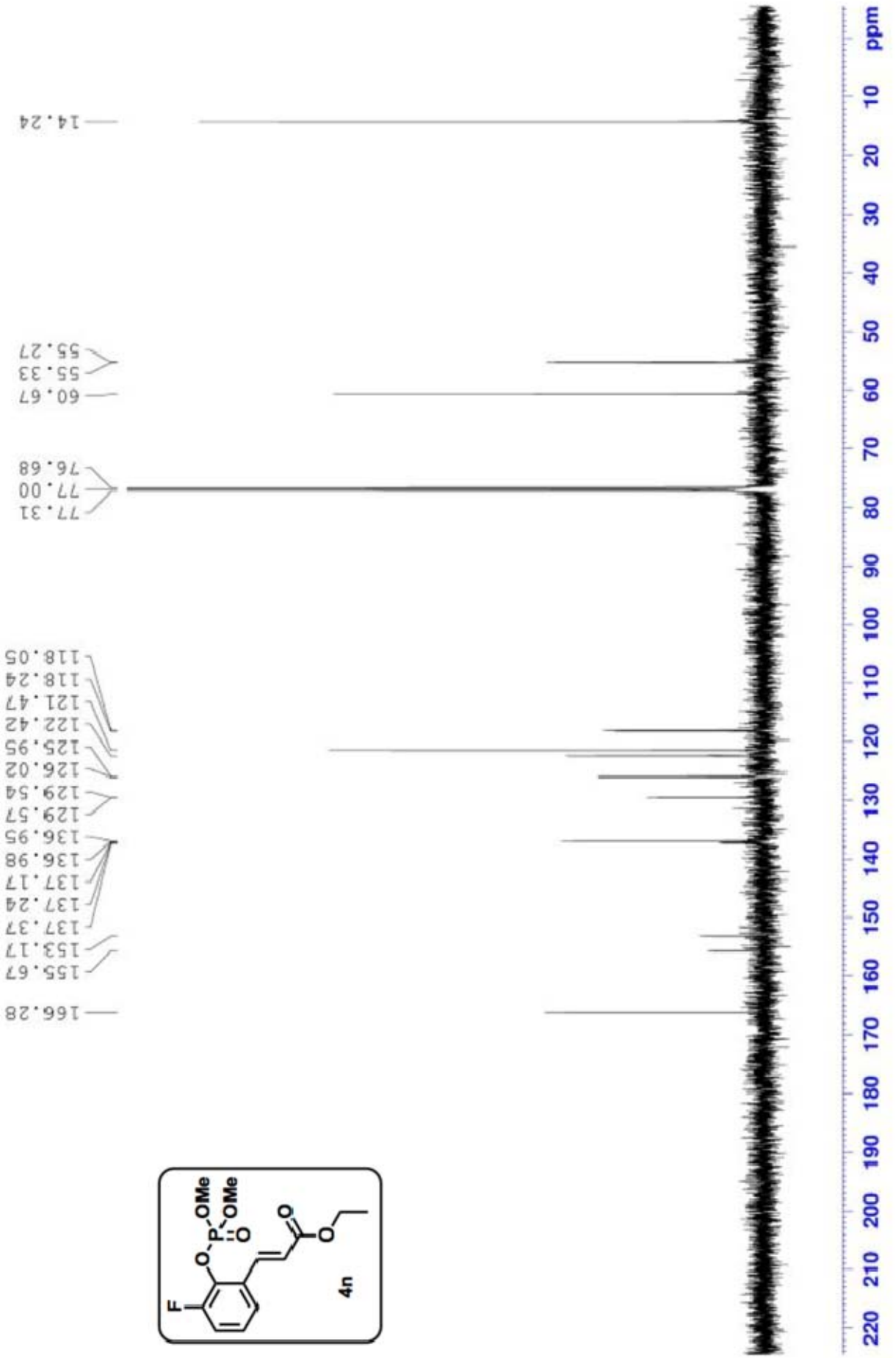

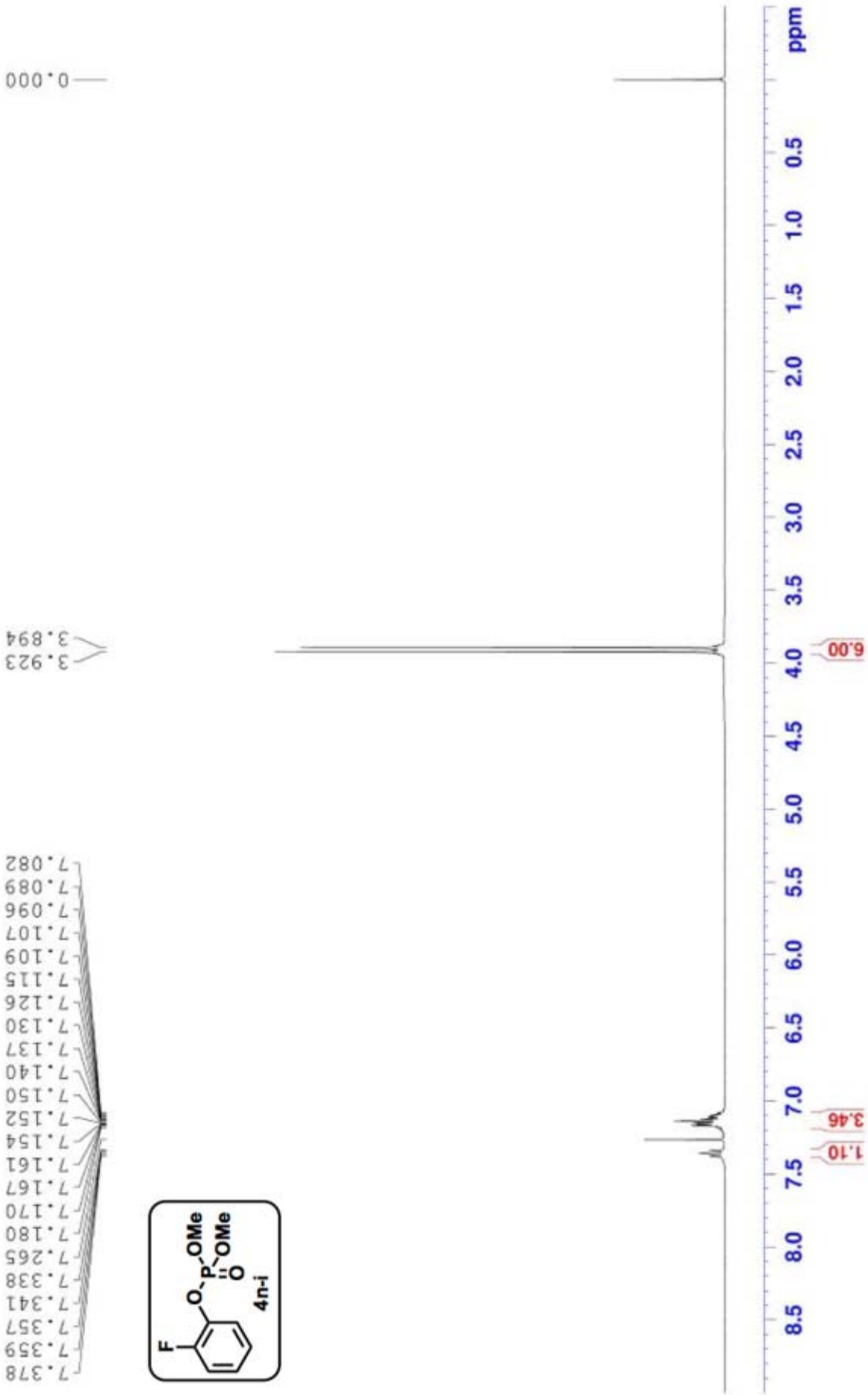
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P
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OMe
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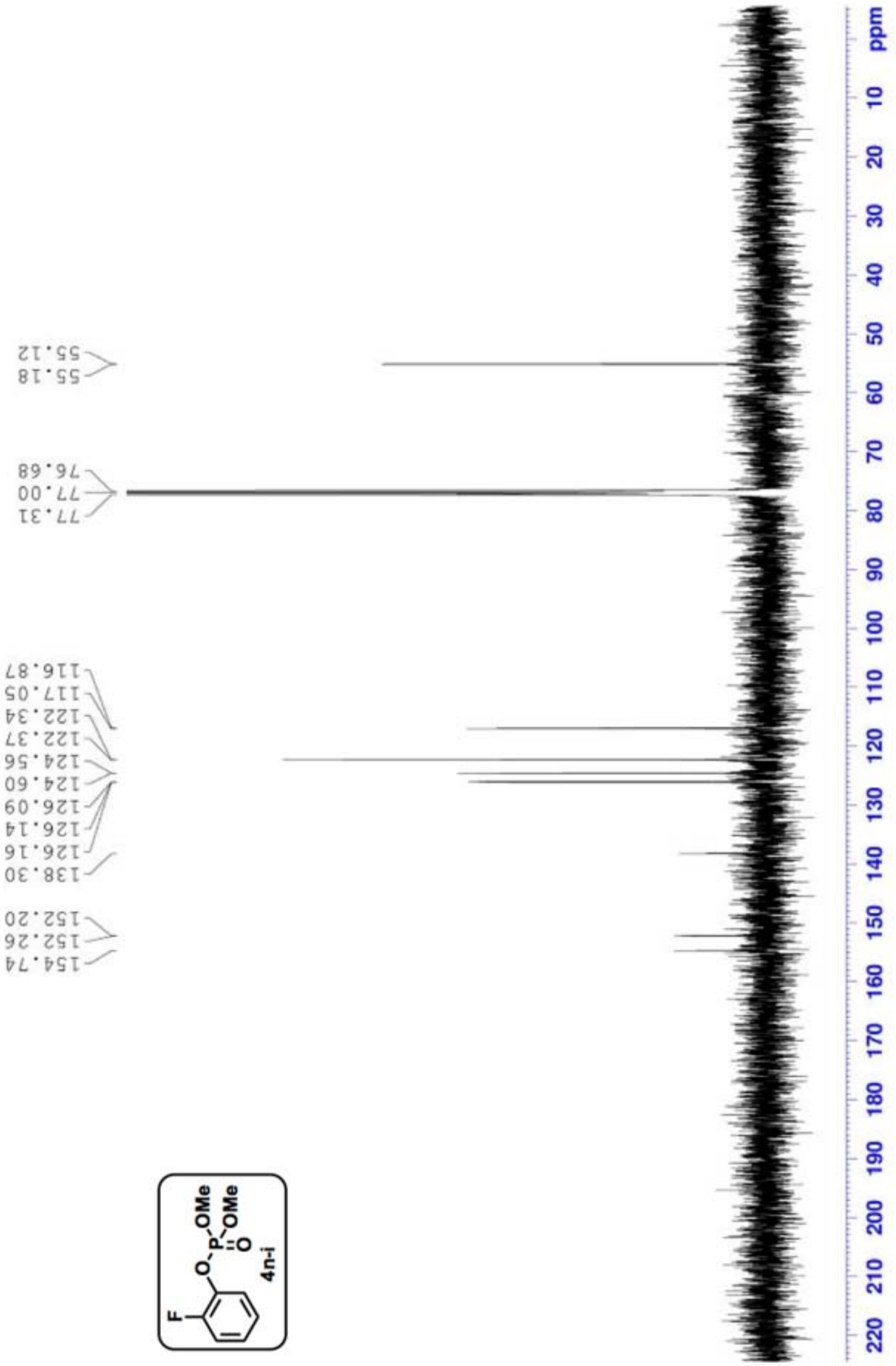

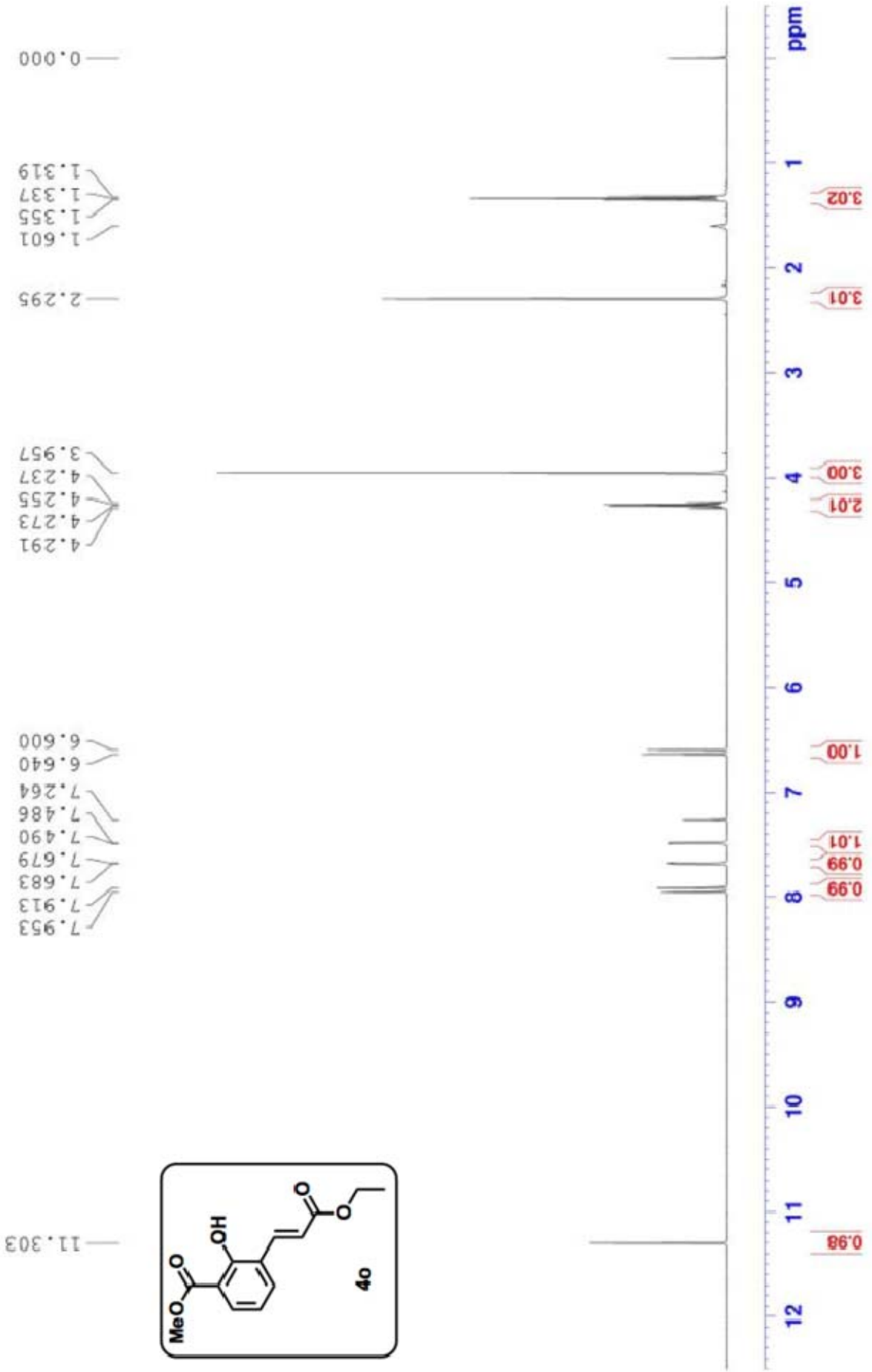
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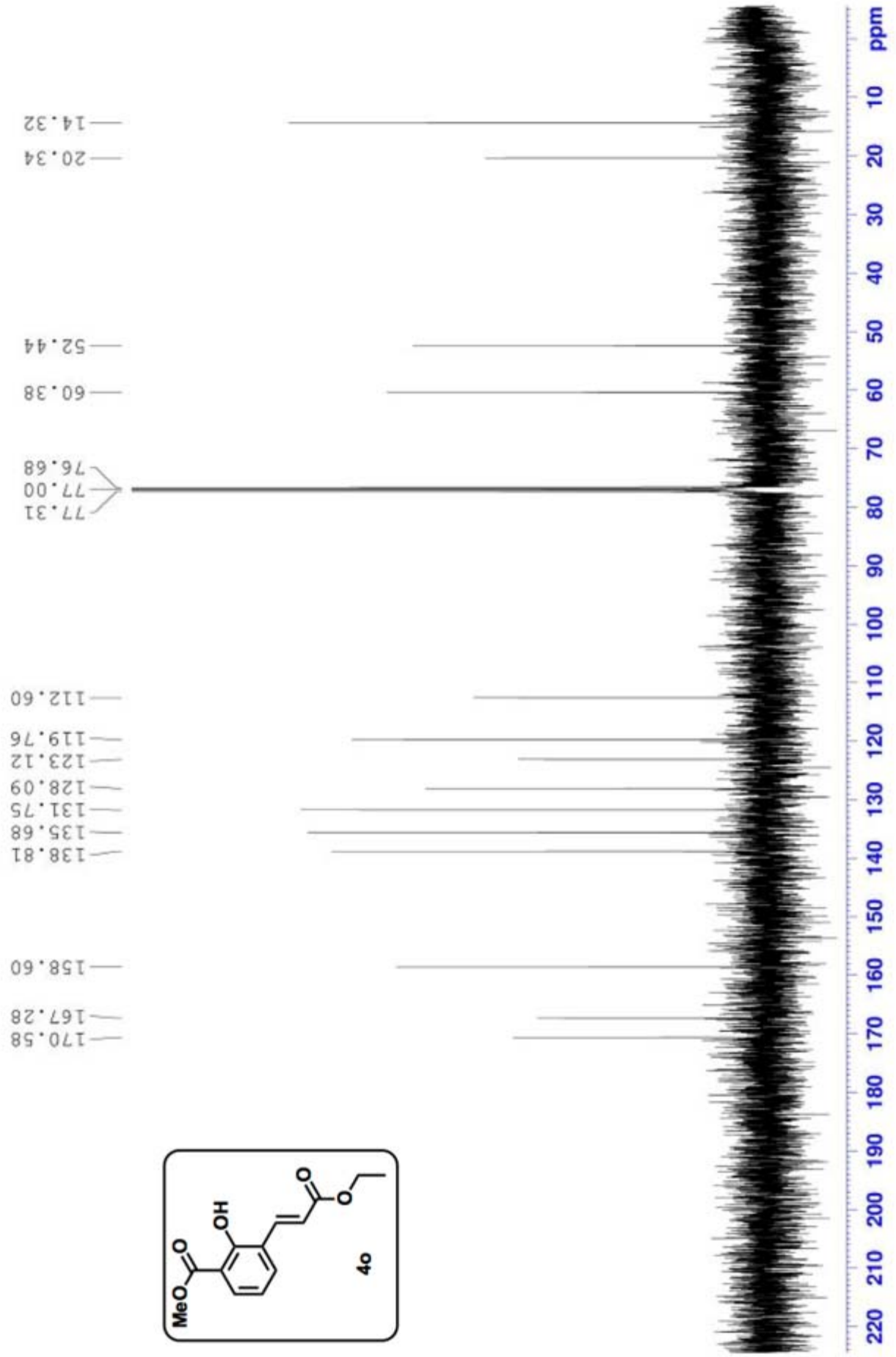

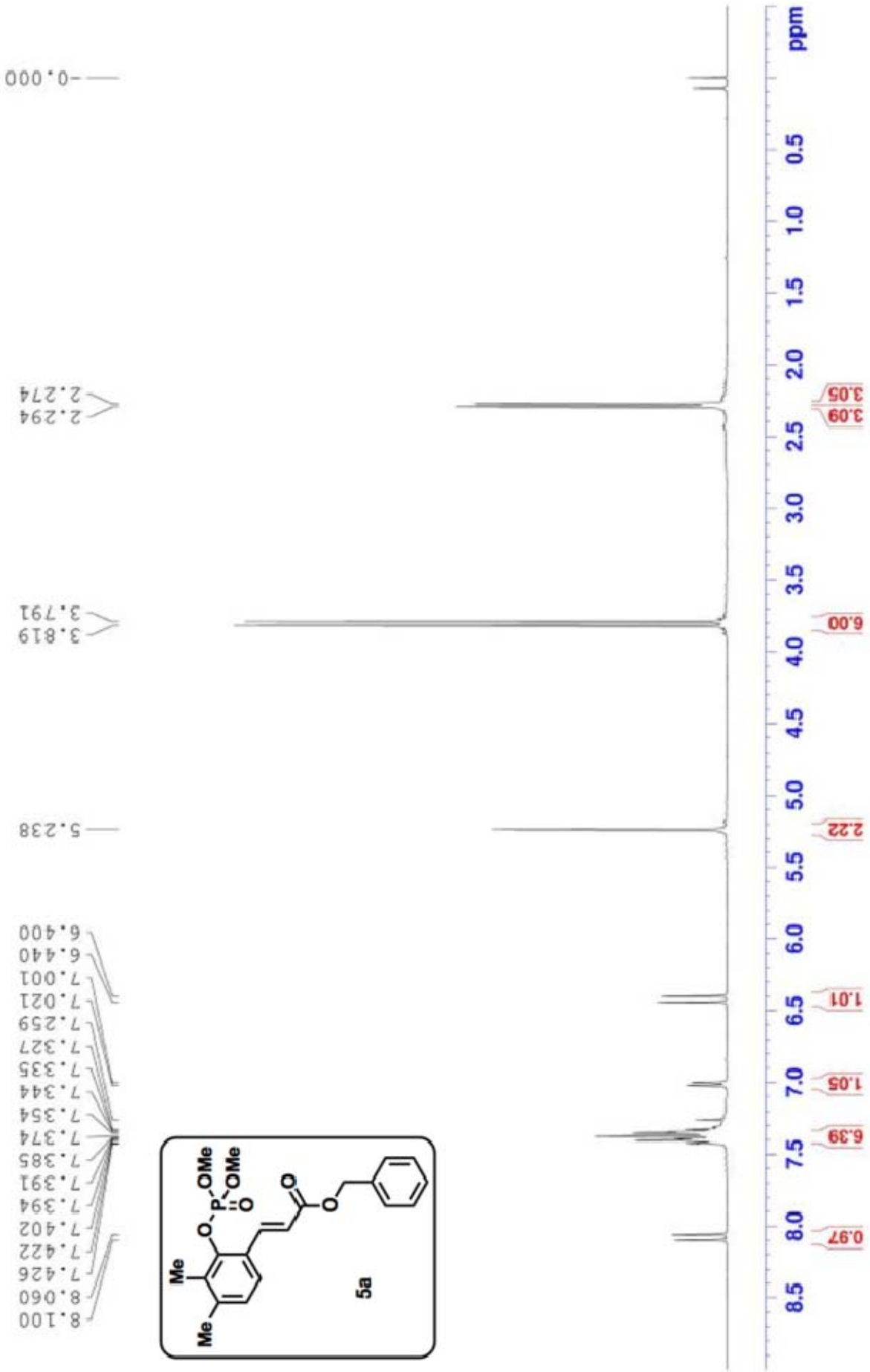
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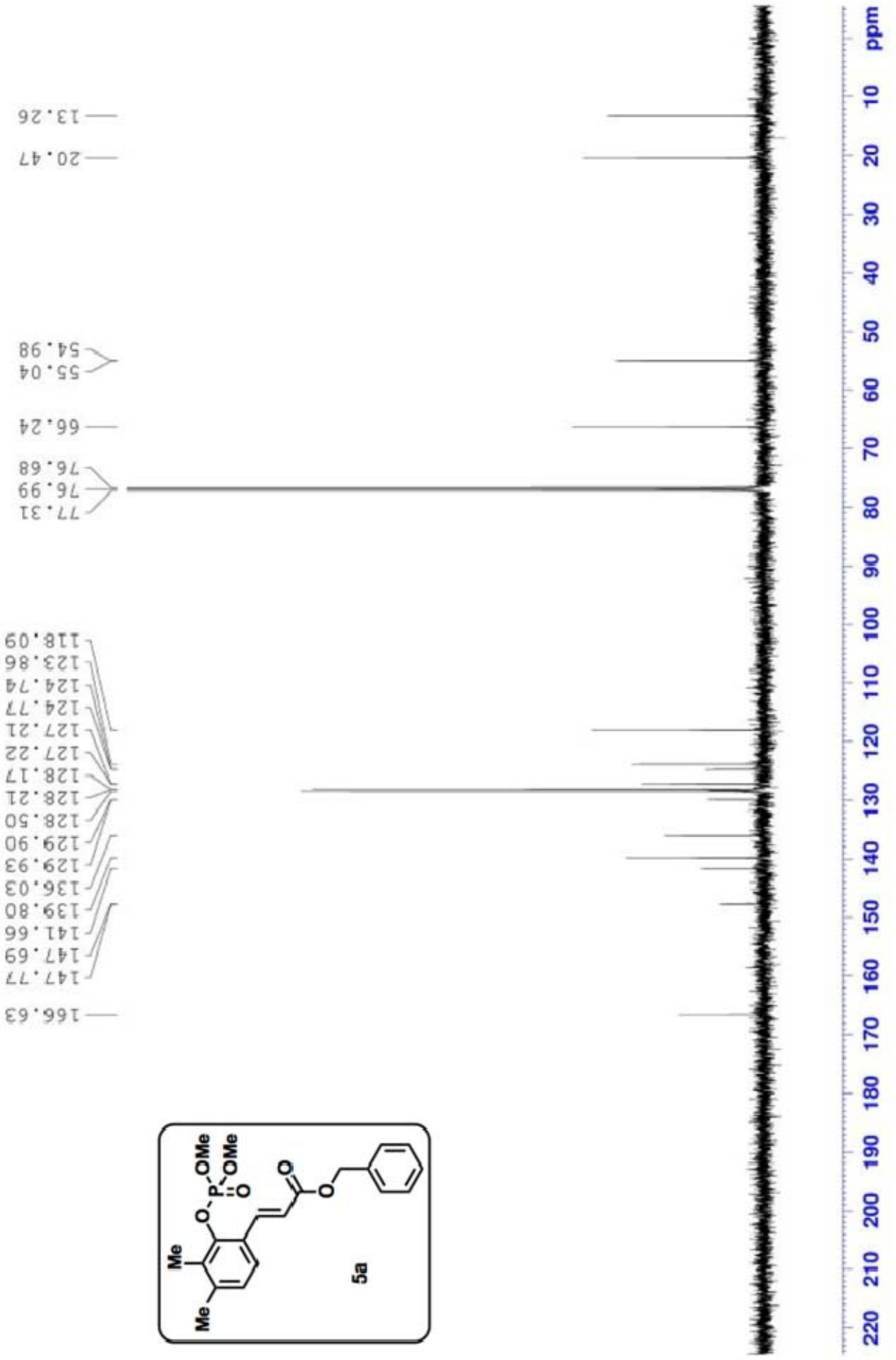

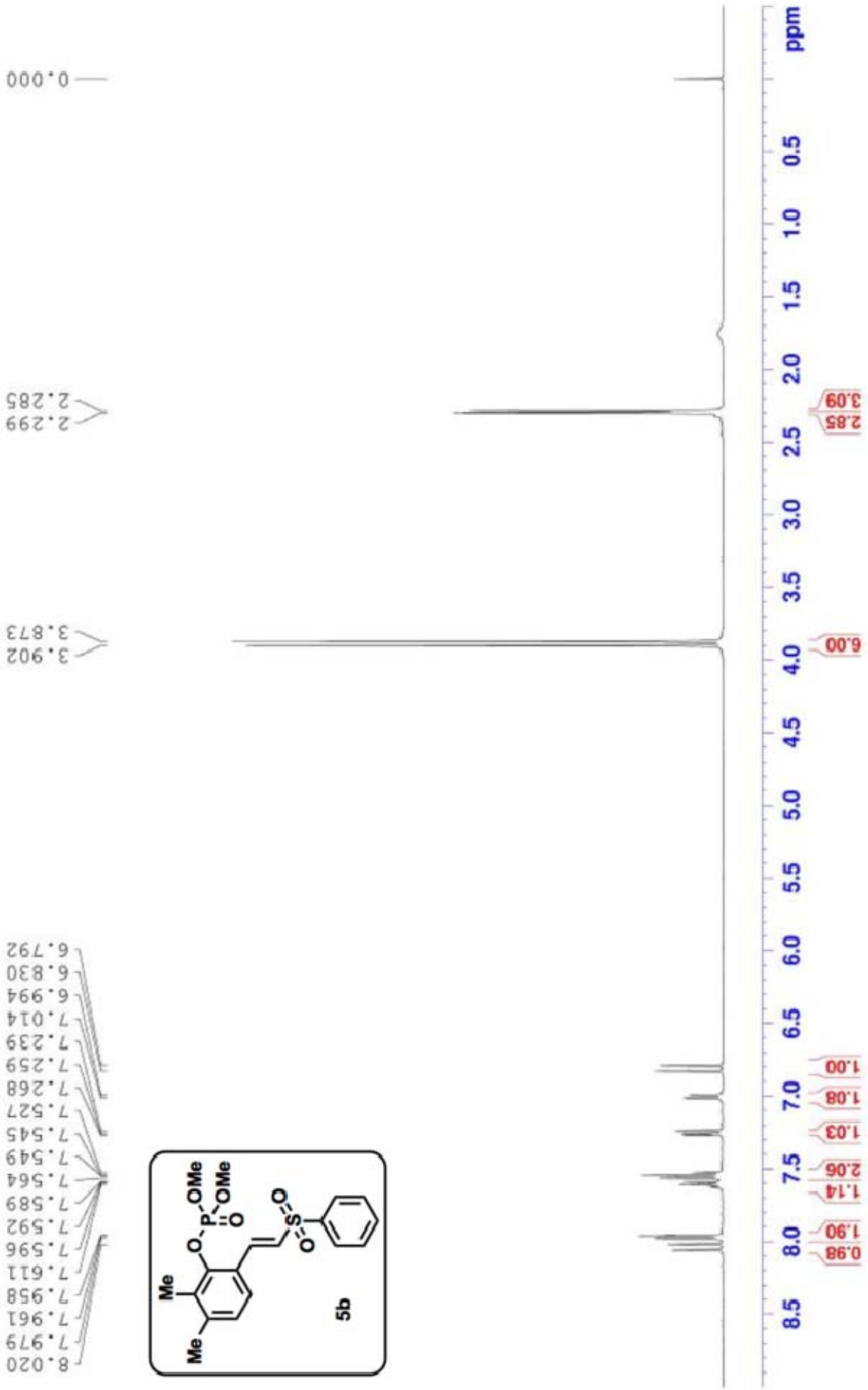
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Me
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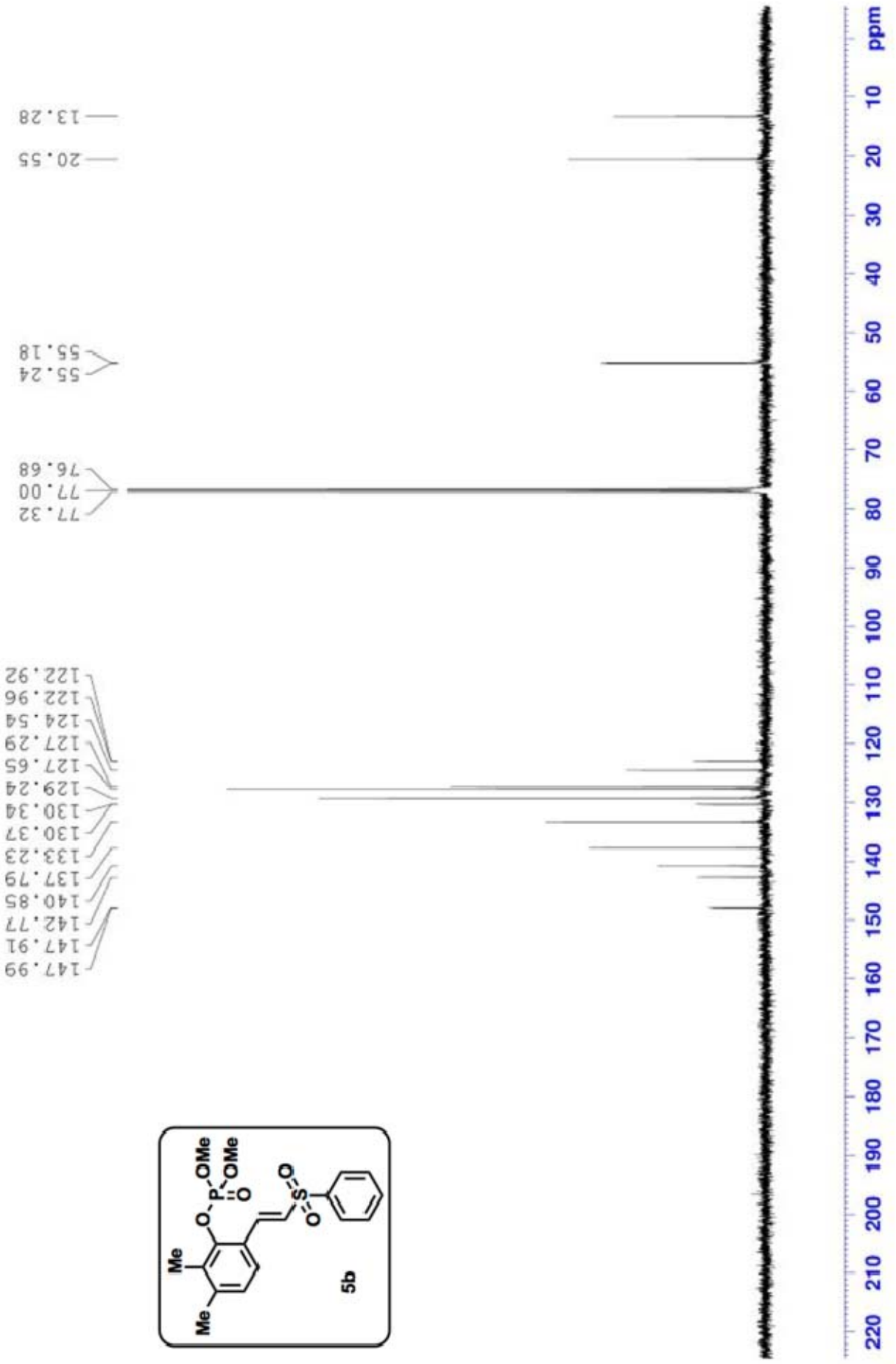

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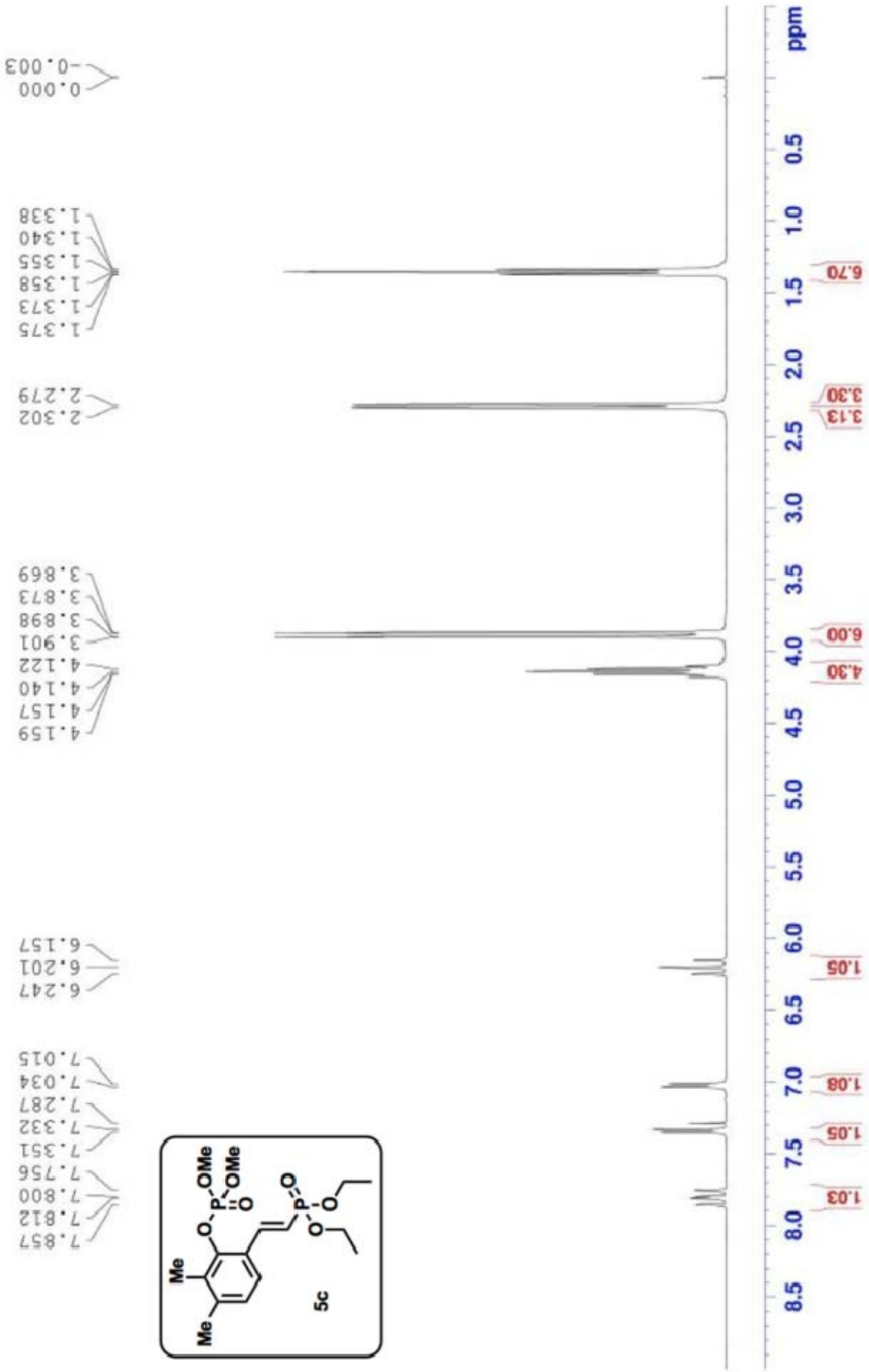

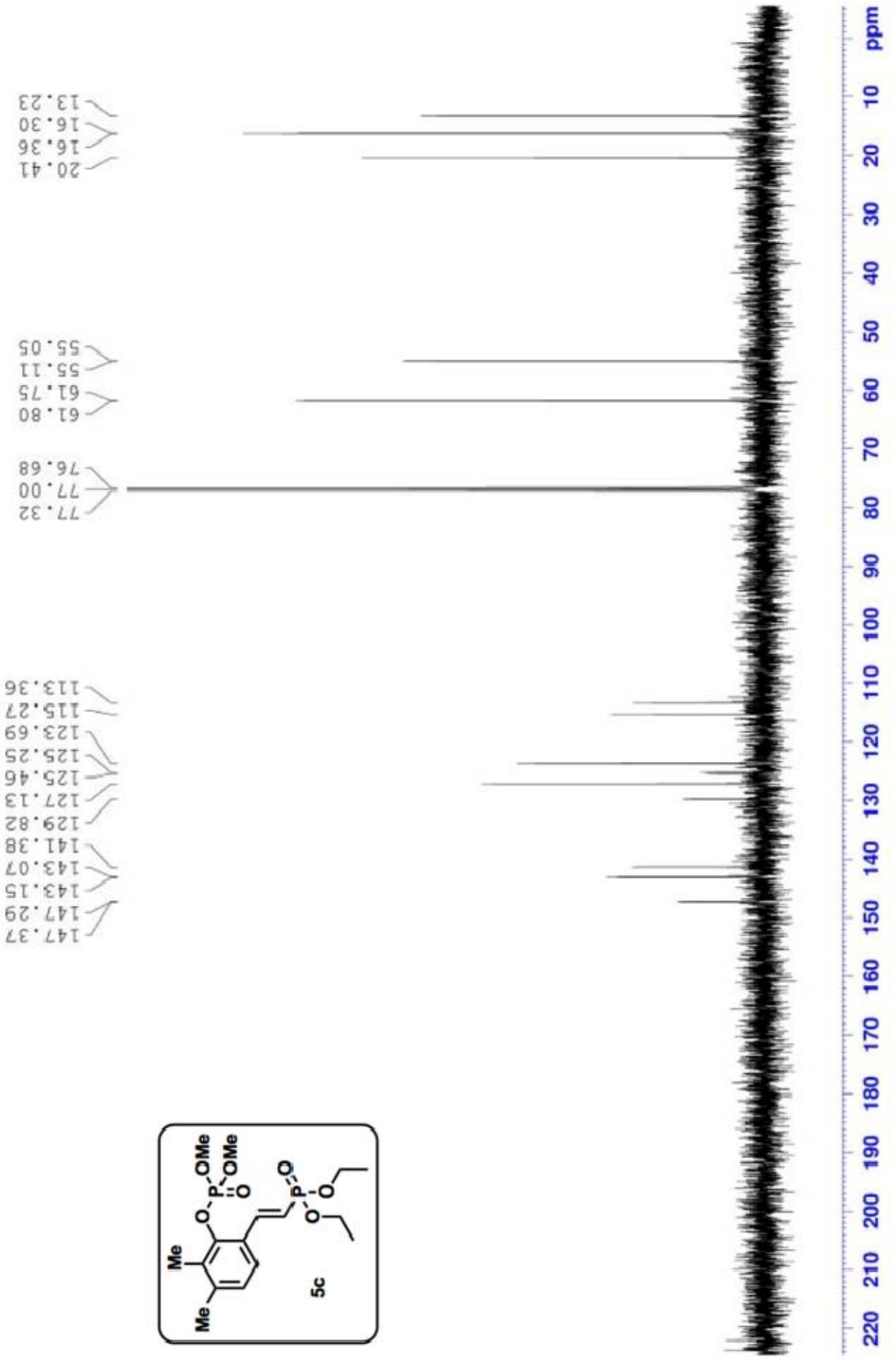
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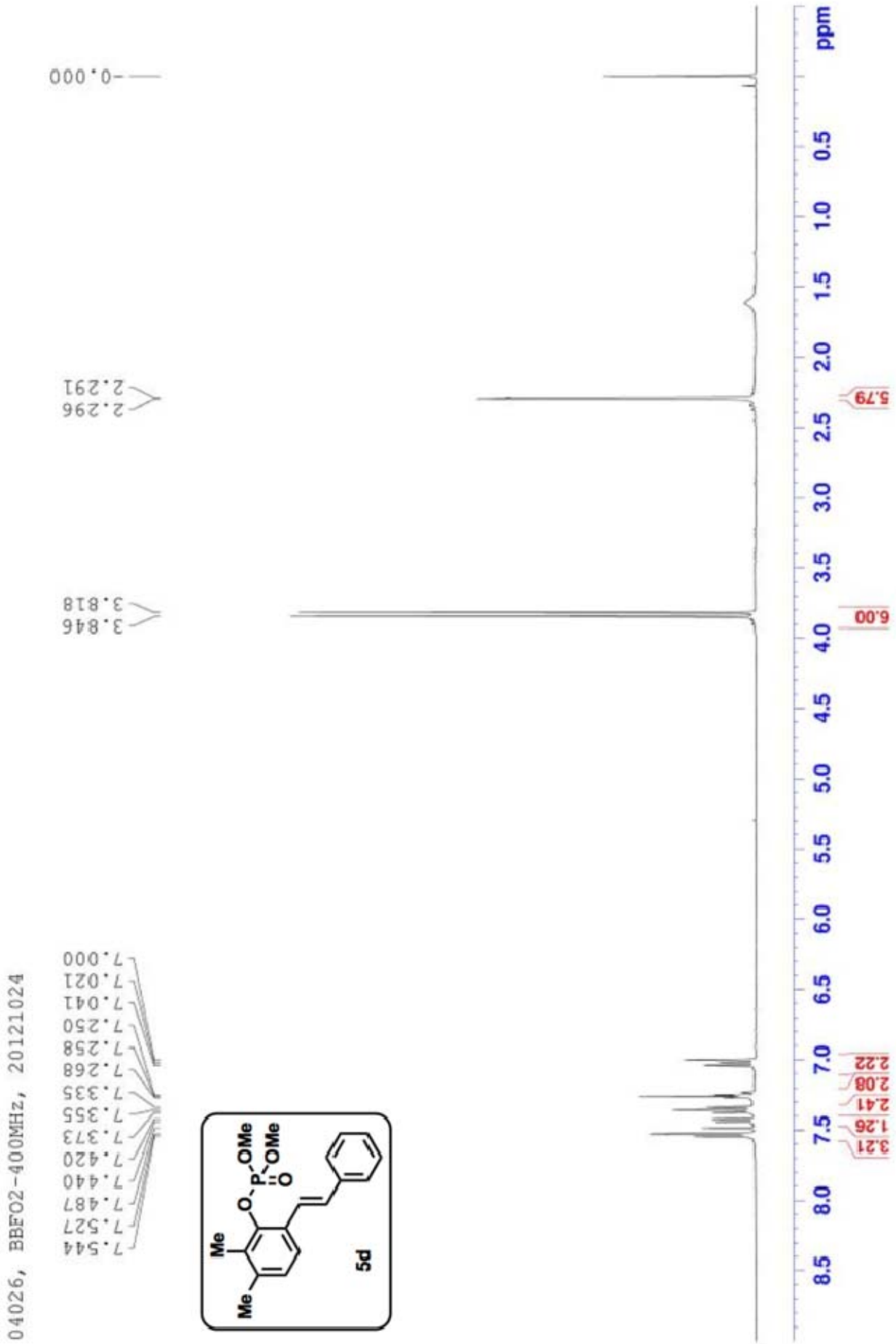
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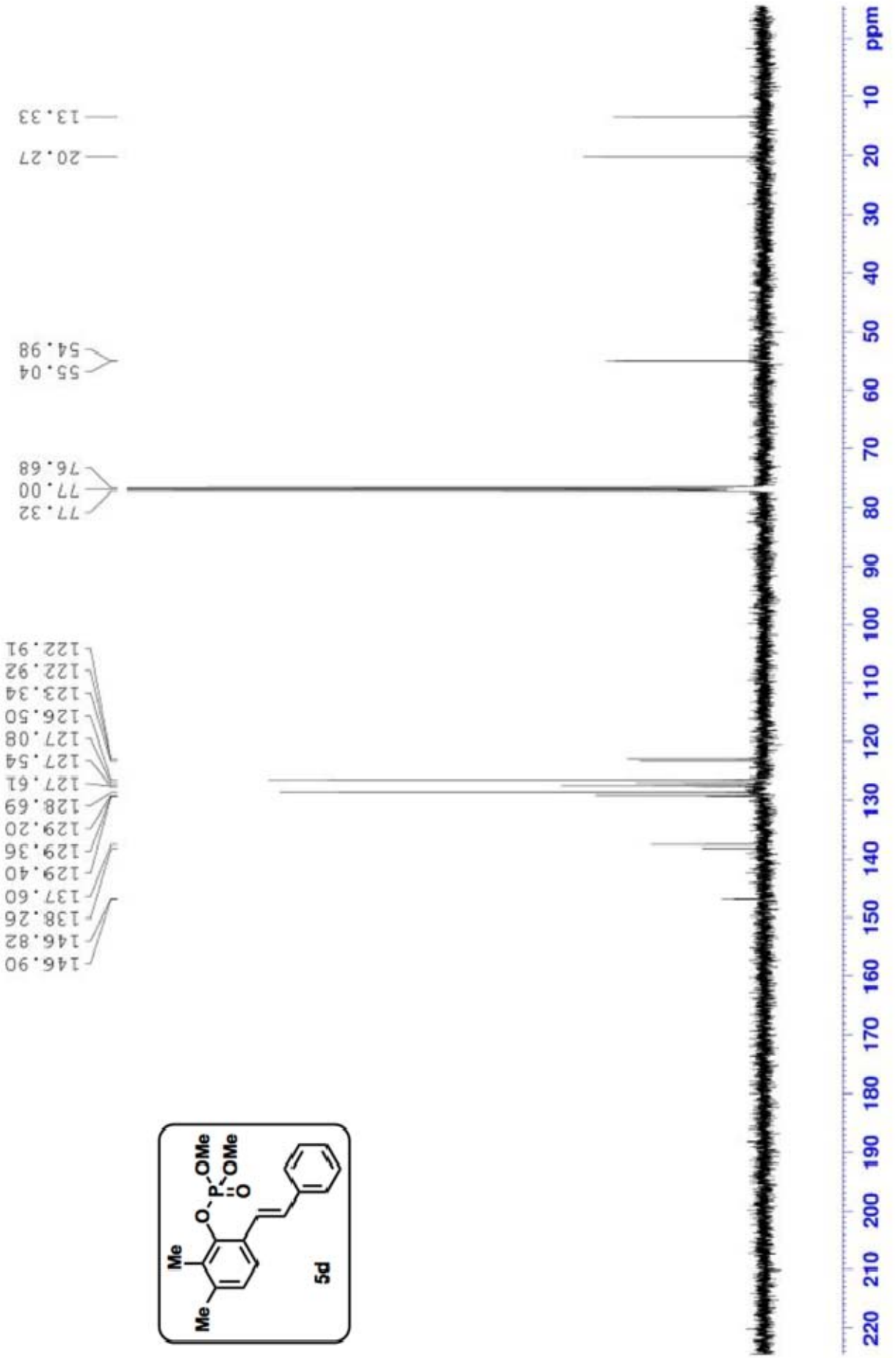

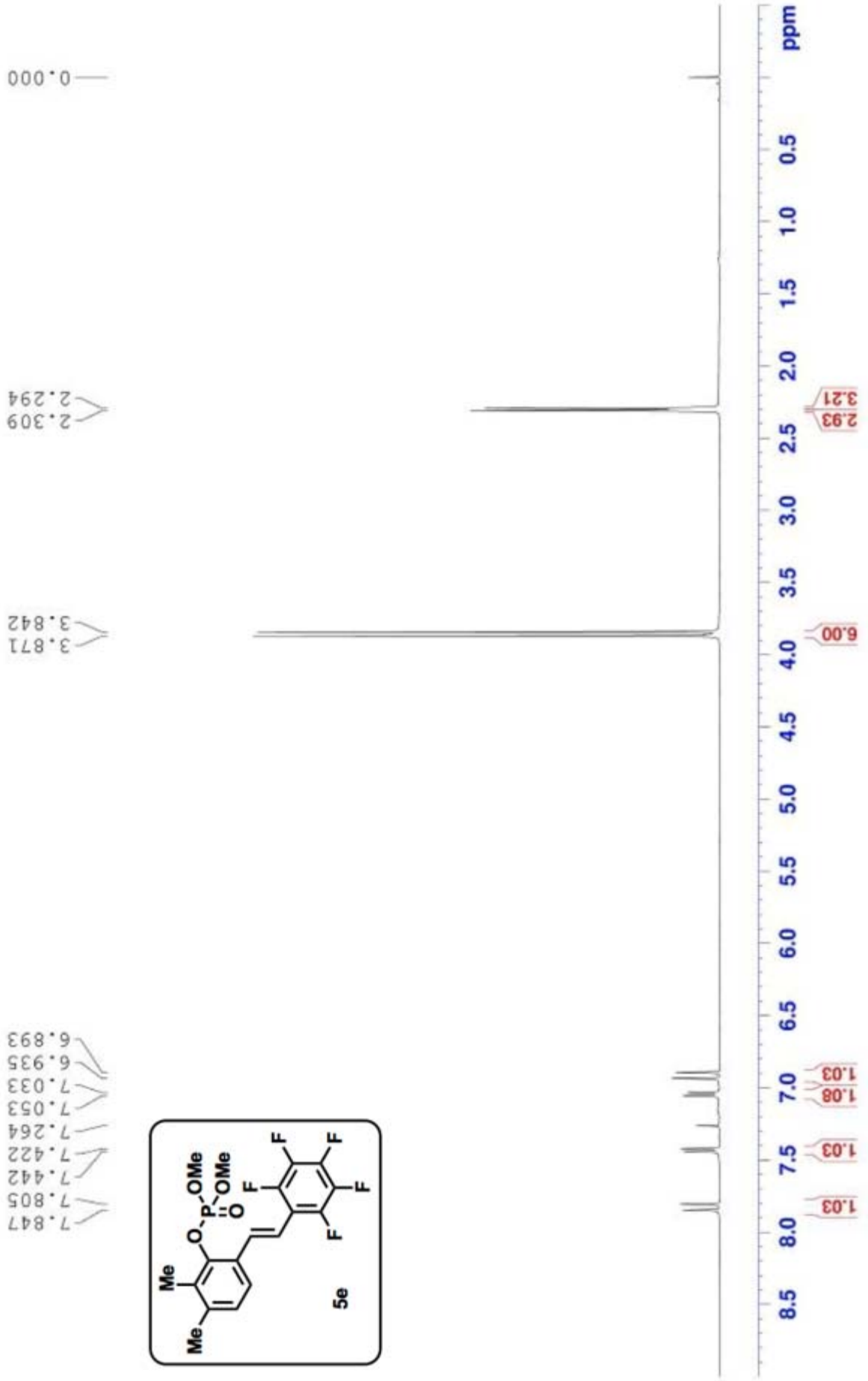
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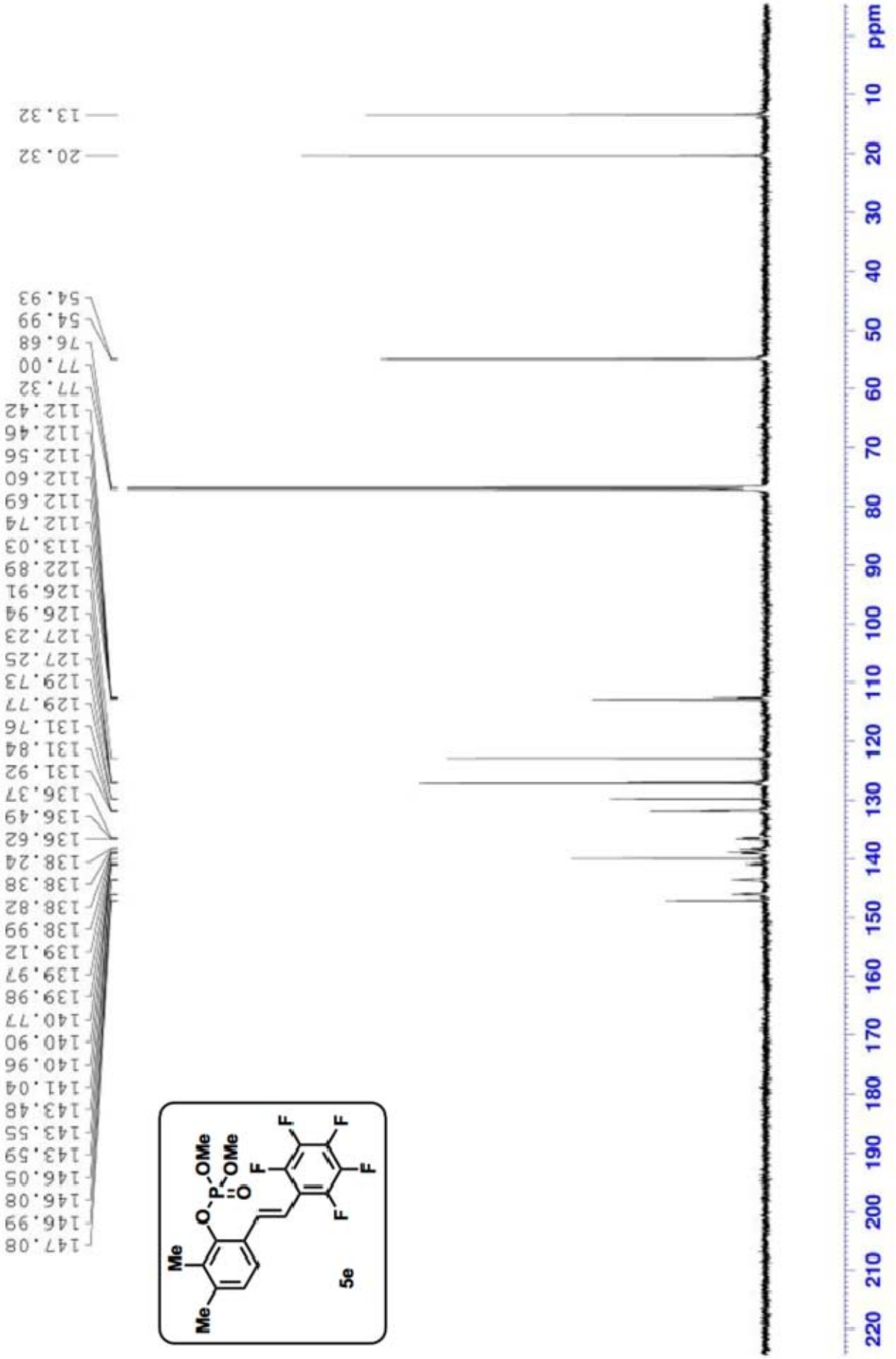

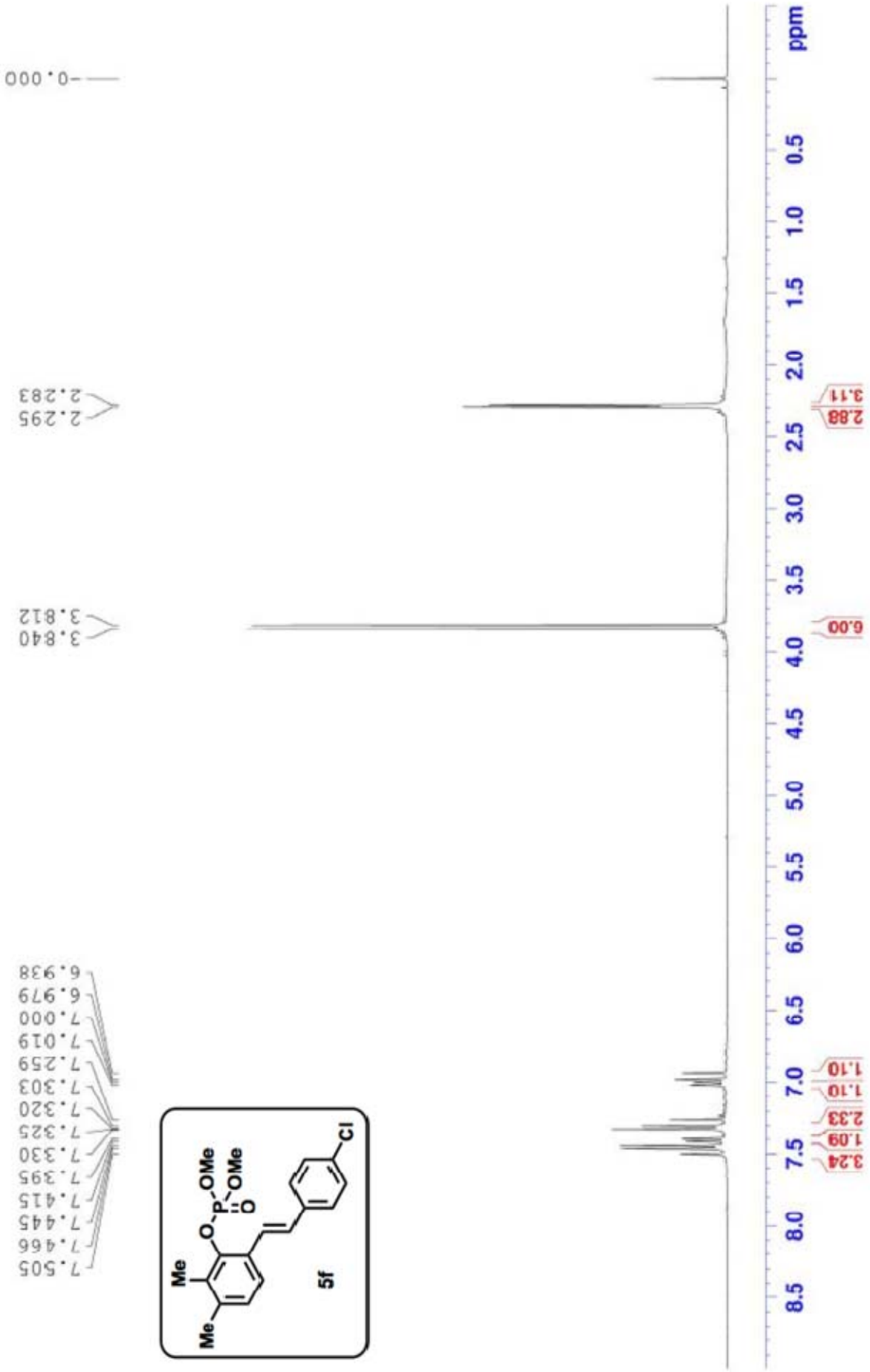
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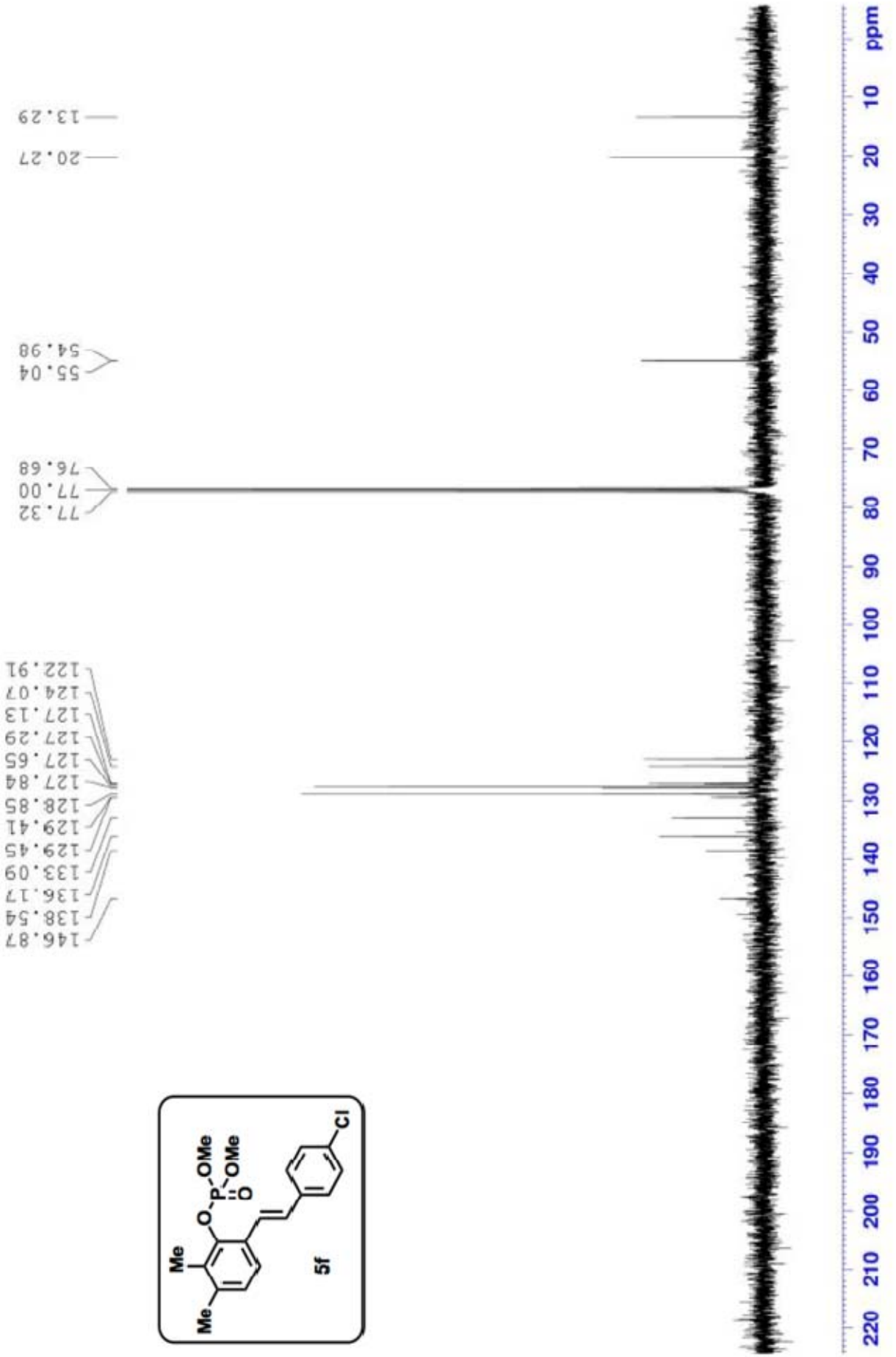

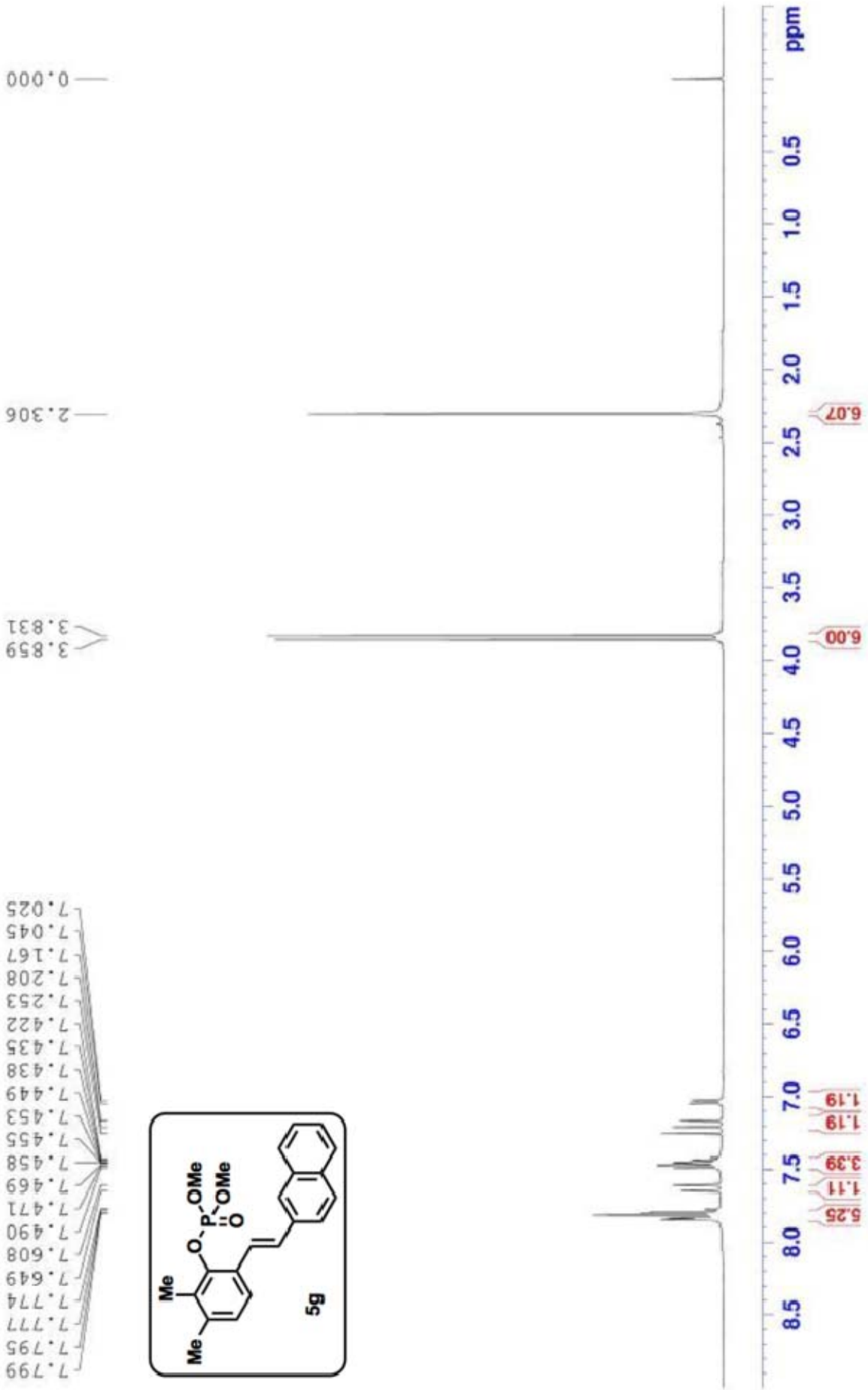
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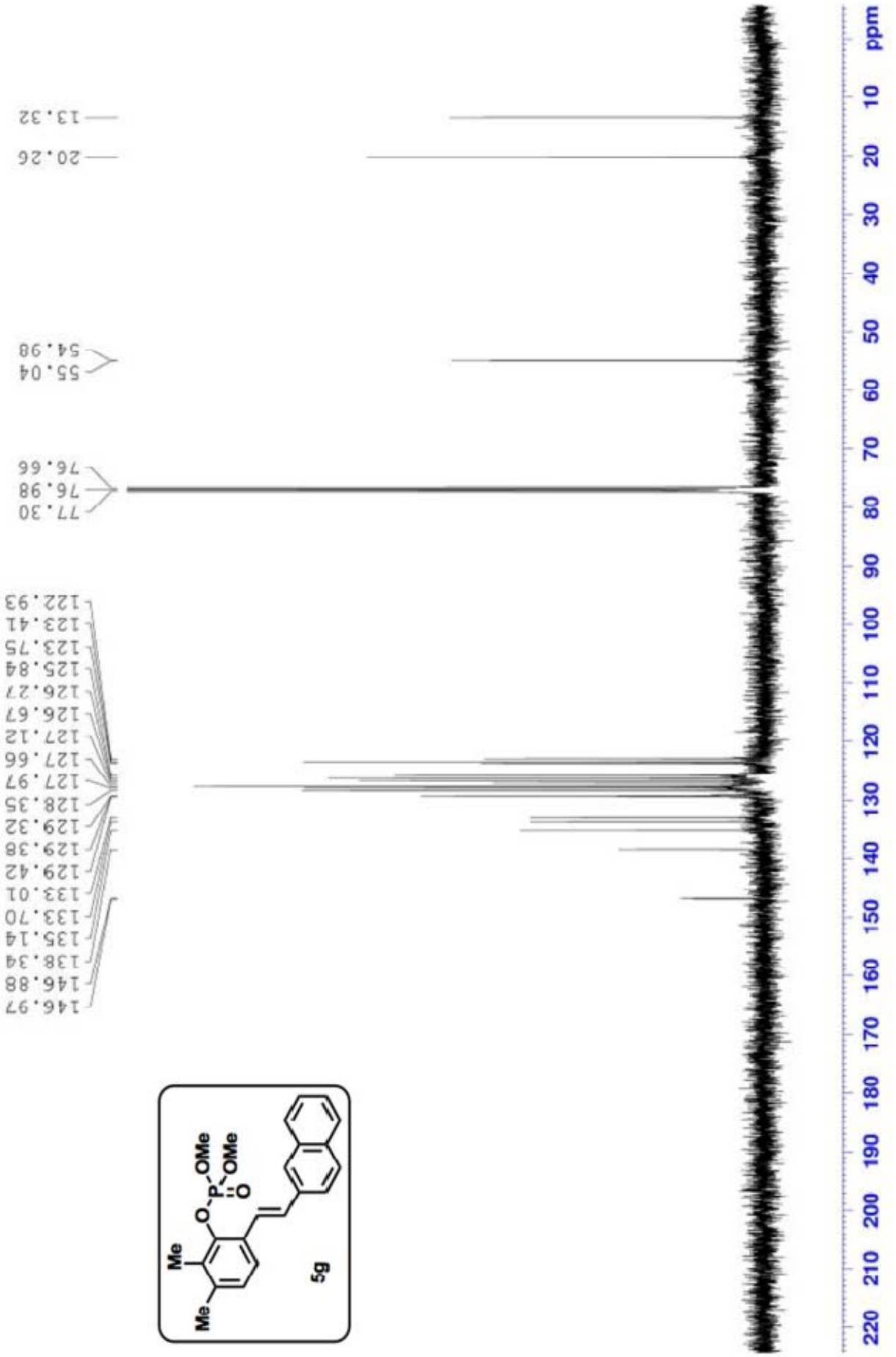

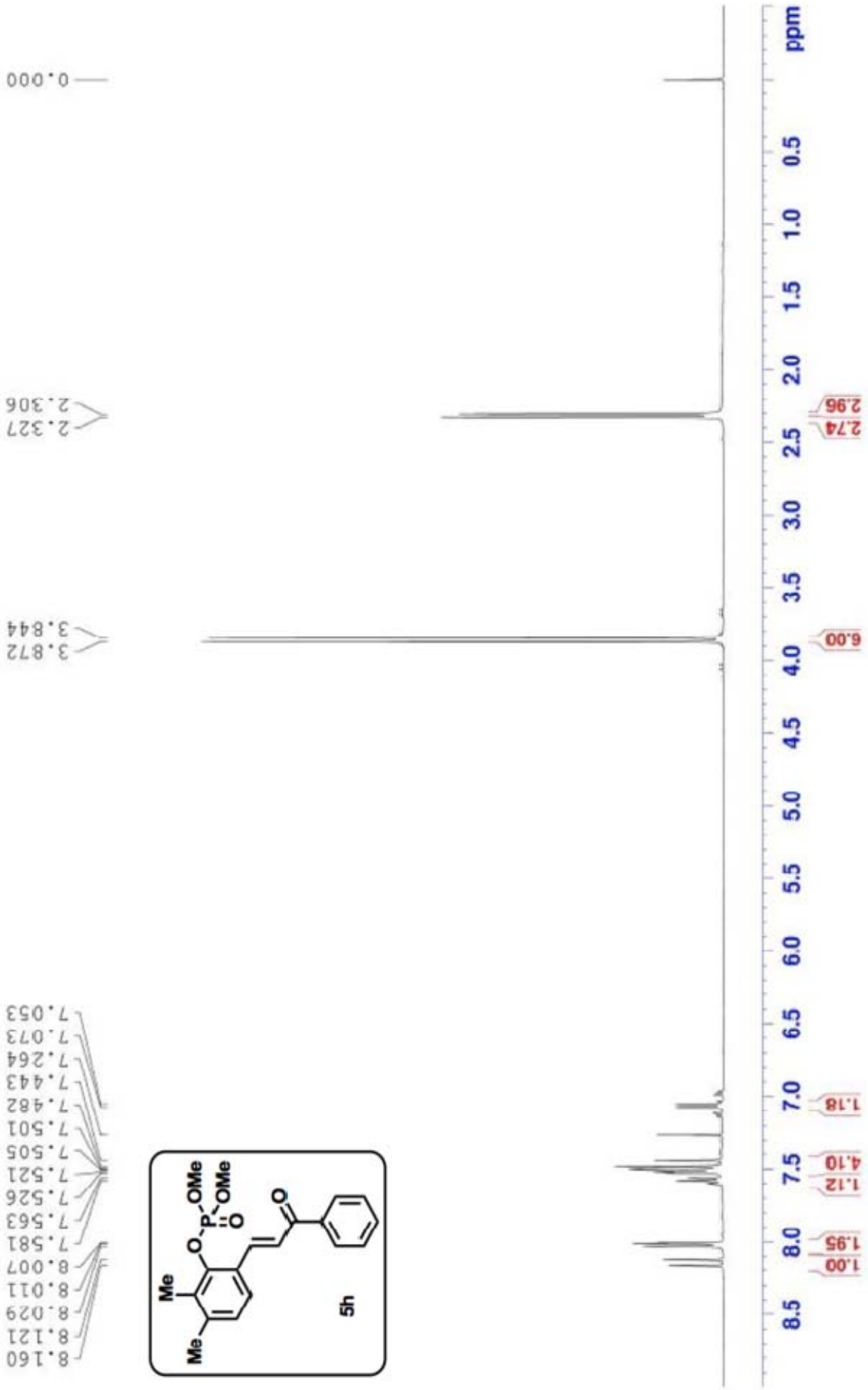
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