Electronic Supplementary Information

Hydrophosphinylation of Unactivated Alkenes with Secondary Phosphine Oxides Under Visible-Light Photocatalysis

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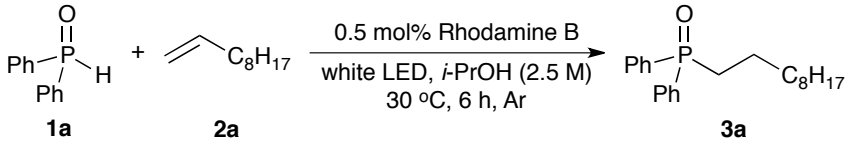
Contents

General Information: ^{1}H and ^{13}C NMR spectra were recorded on a JEOL ECX-500 in $CDCl_3$. Chemical shifts were reported in parts per million (ppm) from tetramethylsilane using the solvent resonance as the internal standard (chloroform: δ 7.26 ppm) for ^{1}H NMR and (deuterochloroform: δ 77.0 ppm) for ^{13}C NMR. ^{31}P NMR spectra were referenced to external H_3PO_4 (δ 0 ppm). IR spectra were measured on a JASCO FT/IR-610 spectrometer. High-resolution mass spectrometry was carried out using a JEOL JMS-T100TD (DART). Preparative thin-layer chromatography (PTLC) was carried out using Wakogel B-5F from Wako Pure Chemical Industries, Ltd.

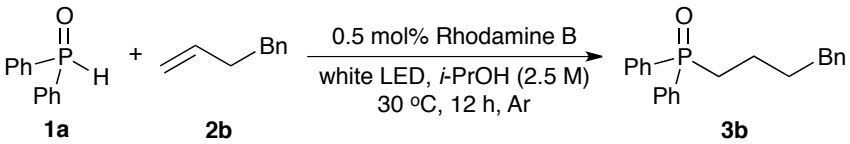
Reagents: Unless stated otherwise, commercial reagents were used as received. Secondary phosphine oxides **1b-1f** used in this study were prepared according to known literature procedure.[1]

Part I: Substrate Scope for the Hydrophosphinylation of SPOs to Unactivated Alkenes Using Rhodamine B as a Catalyst

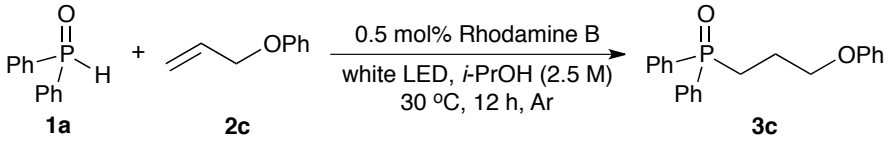


In a 2 mL screw-cap vial was added rhodamine B (0.0012 g, 0.0025 mmol, 0.5 mol%), SPO **1a** (0.1011 g, 0.5000 mmol), alkene **2a** (100 μL, 0.497 mmol), and *i*-PrOH (0.2 mL). The vial was quickly flushed with argon and then was stirred for 6 h in a water bath (30 °C) under a white LED lamp (Toshiba E-CORE LDA7N/2). Then, the reaction mixture was passed through a plug of silica gel, concentrated under reduced pressure, and the resulting residue was purified by preparative TLC (EtOAc) to afford the addition product **3a** (0.1526 g, 0.4456 mmol, 89%) as a white solid.

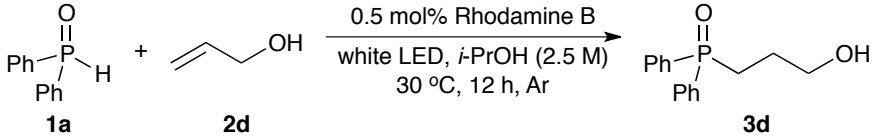
Decyldiphenylphosphine oxide (3a) (Table 3, entry 1). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.71-7.68 (m, 4H), 7.49-7.40 (m, 6H), 2.24-2.19 (m, 2H), 1.60-1.55 (m, 2H), 1.37-1.32 (m, 2H), 1.25-1.18 (m, 12H), 0.83 (t, 3H, J = 6.9 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 133.4 (d, $J_{C\text{-}P}$ = 98.0 Hz), 131.8, 130.9 (d, $J_{C\text{-}P}$ = 9.6 Hz), 128.8 (d, $J_{C\text{-}P}$ = 10.6 Hz), 32.0, 31.1 (d, $J_{C\text{-}P}$ = 15.0 Hz), 29.9 (d, $J_{C\text{-}P}$ = 72.0 Hz), 29.6 (d, $J_{C\text{-}P}$ = 19.2 Hz), 29.4, 29.2, 22.8, 21.6, 21.5, 14.3; ^{31}P NMR ($CDCl_3$, 200 MHz) δ 33.1. This is a known compound and the spectral data are identical to those reported in the literature.[2]



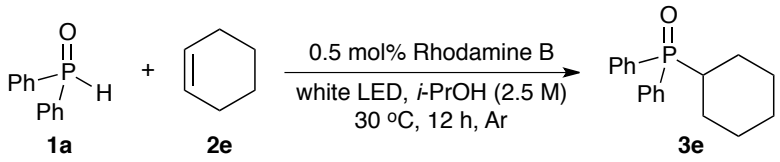
Diphenyl(4-phenylbutyl)phosphine oxide (3b) (Table 3, entry 2). Following the above general procedure with **2b** (75 μL, 0.499 mmol) for 12 h. The crude reaction mixture was purified by preparative TLC (EtOAc) to provide **3b** (0.0979 g, 0.293 mmol, 59%) as a white solid. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.76-7.71 (m, 4H), 7.54-7.45 (m, 6H), 7.28-7.24 (m, 2H), 7.19-7.11 (m, 3H), 2.60 (t, 2H, J = 7.4 Hz), 2.32-2.27 (m, 2H), 1.78-1.66 (m, 4H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 142.1, 133.3 (d, $J_{C\text{-}P}$ = 98.0 Hz), 131.8, 131.0 (d, $J_{C\text{-}P}$ = 8.8 Hz), 128.8 (d, $J_{C\text{-}P}$ = 11.4 Hz), 128.5, 126.0, 35.5, 32.9 (d, $J_{C\text{-}P}$ = 14.4 Hz), 29.8 (d, $J_{C\text{-}P}$ = 71.6 Hz), 21.4; ^{31}P NMR ($CDCl_3$, 200 MHz) δ 32.9. This is a known compound and the spectral data are identical to those reported in the literature.[3]



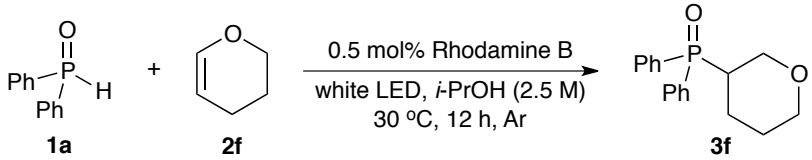
(3-Phenoxypropyl)diphenylphosphine oxide (3c) (Table 3, entry 3). Following the above general procedure with **2c** (69 μL, 0.503 mmol) for 12 h. The crude reaction mixture was purified by preparative TLC (EtOAc) to provide **3c** (0.1514 g, 0.450 mmol, 90%) as a white solid. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.76-7.71 (m, 4H), 7.51-7.41 (m, 6H), 7.25-7.21 (m, 2H), 6.92-6.89 (m, 1H), 6.83-6.81 (m, 2H), 3.98 (t, J = 5.9 Hz), 2.49-2.44 (m, 2H), 2.14-2.06 (m, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 158.8, 133.1 (d, $J_{C\text{-}P}$ = 98.4 Hz), 132.0, 131.0 (d, $J_{C\text{-}P}$ = 9.0 Hz), 129.6, 128.9 (d, $J_{C\text{-}P}$ = 12.0 Hz), 121.0, 114.6, 67.6 (d, $J_{C\text{-}P}$ = 14.4 Hz), 26.6 (d, $J_{C\text{-}P}$ = 73.2 Hz), 22.0; ^{31}P NMR ($CDCl_3$, 200 MHz) δ 33.0. This is a known compound and the spectral data are identical to those reported in the literature.[3]



(3-Hydroxypropyl)diphenylphosphine oxide (3d) (Table 3, entry 4). Following the above general procedure with **2d** (34 μL, 0.500 mmol) for 12 h. The crude reaction mixture was purified by preparative TLC (MeOH:DCM = 5:95) to provide **3d** (0.1145 g, 0.440 mmol, 88%) as a white solid. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.75-7.68 (m, 4H), 7.52-7.41 (m, 6H), 4.16 (bs, 1H), 3.66 (t, J = 5.6 Hz), 2.38 (m, 2H), 1.88-1.80 (m, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 132.5 (d, $J_{C\text{-}P}$ = 99.0 Hz), 132.0, 131.0 (d, $J_{C\text{-}P}$ = 10.0 Hz), 128.9 (d, $J_{C\text{-}P}$ = 11.4 Hz), 62.6 (d, $J_{C\text{-}P}$ = 10.2 Hz), 27.6 (d, $J_{C\text{-}P}$ = 72.0 Hz), 25.5; ^{31}P NMR ($CDCl_3$, 200 MHz) δ 35.3. This is a known compound and the spectral data are identical to those reported in the literature.[4]

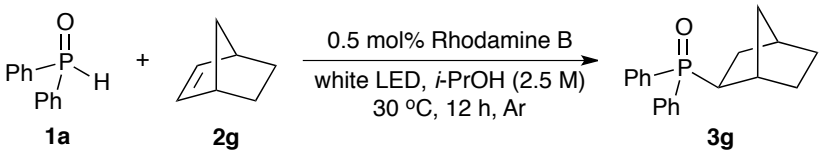


Cyclohexyldiphenylphosphine oxide (3e) (Table 3, entry 5). Following the above general procedure with **2e** (100 μL, 0.987 mmol) for 12 h. The crude reaction mixture was purified by preparative TLC (EtOAc) to provide **3e** (0.0916 g, 0.322 mmol, 64%) as a white solid. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.76-7.72 (m, 4H), 7.47-7.39 (m, 6H), 2.23-2.16 (m, 1H), 1.77-1.66 (m, 5H), 1.54-1.45 (m, 2H), 1.26-1.16 (m, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 132.2 (d, $J_{C\text{-}P}$ = 94.0 Hz), 131.6, 131.2 (d, $J_{C\text{-}P}$ = 9.0 Hz), 128.7 (d, $J_{C\text{-}P}$ = 10.8 Hz), 37.3 (d, $J_{C\text{-}P}$ = 74.0 Hz), 26.5 (d, $J_{C\text{-}P}$ = 13.0 Hz), 25.9, 24.9; ^{31}P NMR ($CDCl_3$, 200 MHz) δ 34.9. This is a known compound and the spectral data are identical to those reported in the literature.[3]



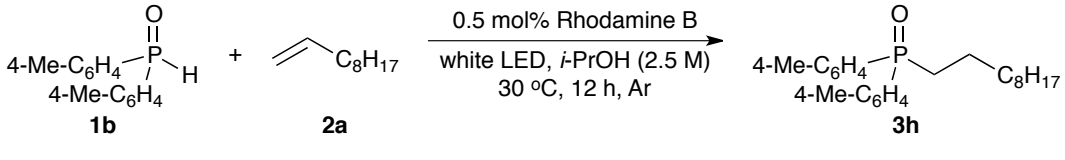
1a 2f 3f

Diphenyl(tetrahydro-2*H*-pyran-3-yl)phosphine oxide (3f) (Table 3, entry 6). Following the above general procedure with **2f** (91 μL, 1.00 mmol) for 12 h. The crude reaction mixture was purified by preparative TLC (MeOH:DCM = 1:9) to provide **3f** (0.0830 g, 0.290 mmol, 58%) as a white solid. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.79-7.70 (m, 4H), 7.51-7.43 (m, 6H), 3.91-3.89 (m, 2H), 3.66-3.61 (m, 1H), 3.36 (td, 1H, J = 10.9, 3.9 Hz), 2.62-2.55 (m, 1H), 1.91-1.62 (m, 4H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 132.1, 132.0, 131.9, 131.8, 131.1 (d, J_{C-P} = 6.4 Hz), 131.0 (d, J_{C-P} = 6.6 Hz), 129.0 (d, J_{C-P} = 8.2 Hz), 128.9 (d, J_{C-P} = 8.2 Hz), 68.2, 67.0, 36.7 (d, J_{C-P} = 70.4 Hz), 25.9 (d, J_{C-P} = 11.4 Hz), 22.3; ^{31}P NMR ($CDCl_3$, 200 MHz) δ 30.8. This is a known compound and the spectral data are identical to those reported in the literature.[3]



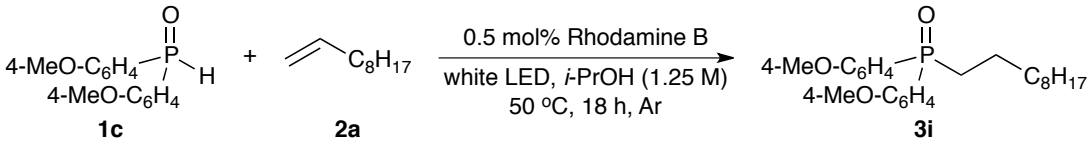
1a 2g 3g

Bicyclo[2.2.1]heptan-2-yldiphenylphosphine oxide (3g) (Table 3, entry 7). Following the above general procedure with **2g** (0.0942, 1.00 mmol) for 12 h. The crude reaction mixture was purified by preparative TLC (EtOAc) to provide **3g** (0.1262 g, 0.426 mmol, 85%) as a white solid. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.81-7.70 (m, 4H), 7.49-7.39 (m, 6H), 2.48 (bd, 1H, J = 7.9 Hz), 2.34 (bs, 1H), 2.27 (t, 1H, J = 7.9 Hz), 1.96-1.83 (m, 2H), 1.59-1.51 (m, 2H), 1.42-1.13 (m, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 133.9 (d, J_{C-P} = 95.4 Hz), 133.6 (d, J_{C-P} = 95.4 Hz), 131.54, 131.48, 131.14 (d, J_{C-P} = 8.4 Hz), 131.08 (d, J_{C-P} = 9.6 Hz), 128.7 (d, J_{C-P} = 12.0 Hz), 128.6 (d, J_{C-P} = 12.0 Hz), 40.1 (d, J_{C-P} = 72.8 Hz), 38.3, 37.5, 36.6, 32.3 (d, J_{C-P} = 15.0 Hz), 31.6 (d, J_{C-P} = 4.2 Hz), 28.8; ^{31}P NMR ($CDCl_3$, 200 MHz) δ 34.5. This is a known compound and the spectral data are identical to those reported in the literature.[5]



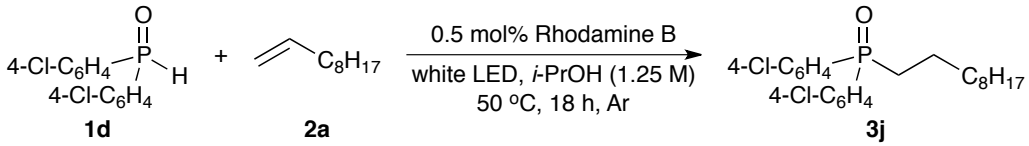
1b 2a 3h

Decyldi-*p*-tolylphosphine oxide (3h) (Table 3, entry 8). Following the above general procedure with **1b** (0.1151, 0.500 mmol) for 12 h. The crude reaction mixture was purified by preparative TLC (EtOAc) to provide **3h** (0.1167 g, 0.315 mmol, 63%) as a white solid (m.p. = 45-46 °C). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.57 (4H, dd, J = 11.3, 7.7 Hz), 7.23-7.21 (m, 4H), 2.34 (s, 6H), 2.20-2.14 (m, 2H), 1.56-1.53 (m, 2H), 1.34-1.11 (m, 14H), 0.82 (t, 3H, J = 7.0 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 142.0, 130.9 (d, J_{C-P} = 9.6 Hz), 130.3 (d, J_{C-P} = 100.2 Hz), 129.4 (d, J_{C-P} = 12.0 Hz), 32.0, 31.1 (d, J_{C-P} = 14.4 Hz), 30.1 (d, J_{C-P} = 72.0 Hz), 29.6, 29.5, 29.4, 29.2, 22.8, 21.7, 21.6 (d, J_{C-P} = 3.6 Hz), 14.2; ^{31}P NMR ($CDCl_3$, 200 MHz) δ 33.3; IR (KBr) cm^{-1} 3043 (s), 3021 (s), 2849 (w), 1926 (s), 1659 (w), 1604 (s), 1501 (m), 1467 (s), 1401 (s), 1380 (m), 1174 (s), 1116 (s), 1099 (s); DART-HRMS (m/z) calcd. for $C_{24}H_{36}O_1P_1$ [$(M+H)^+$]: 371.25038, found: 371.25003.



1c **2a** **3i**

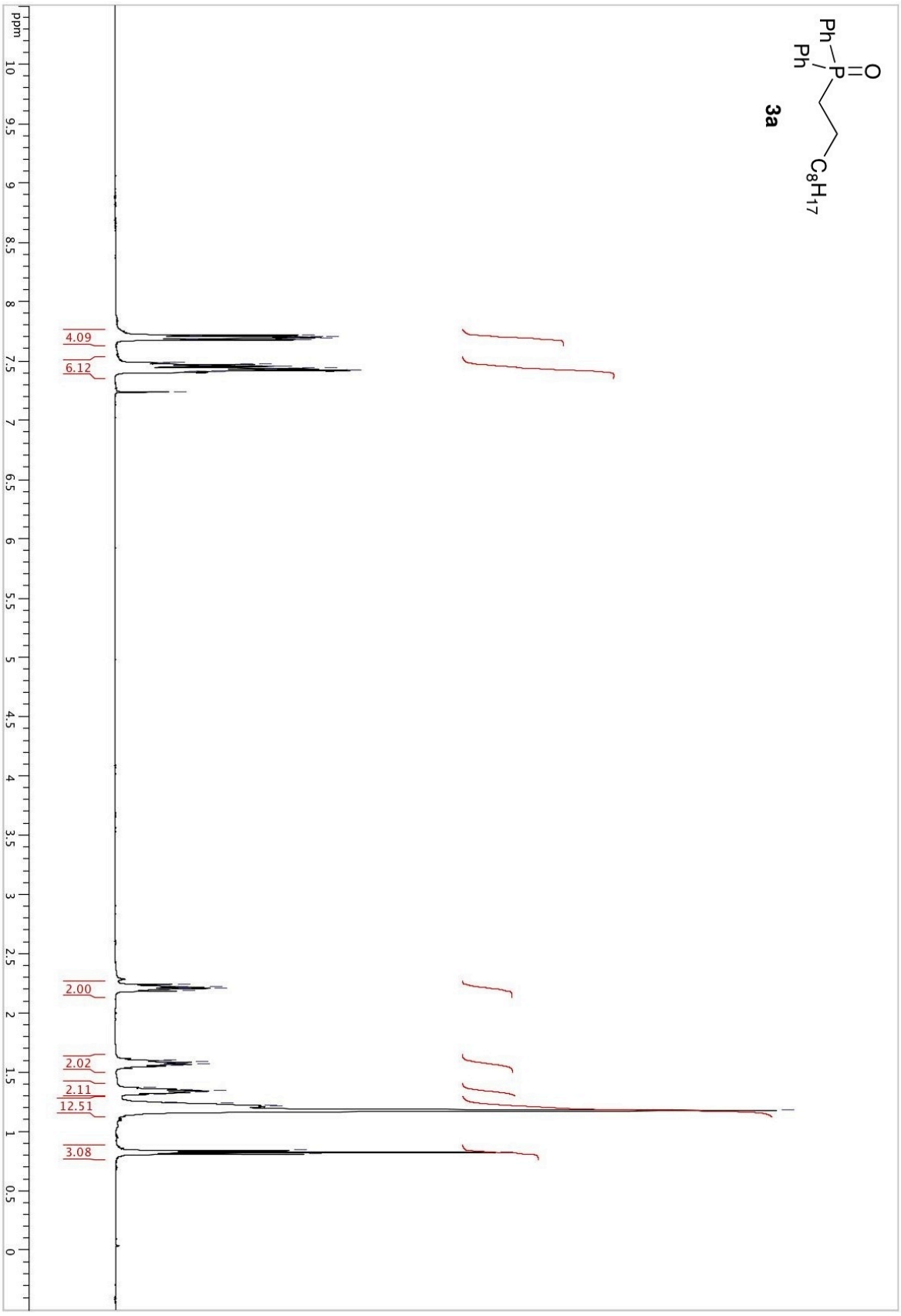
Decylbis(4-methoxyphenyl)phosphine oxide (3i) (Table 3, entry 9). Following the above general procedure with **1c** (0.1311, 0.500 mmol) and *i*-PrOH (0.4 mL) for 18 h at 50 °C. The crude reaction mixture was purified by preparative TLC (EtOAc) to provide **3i** (0.0547 g, 0.136 mmol, 27%) as a white solid (m.p. = 47-48 °C). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.60 (dd, 4H, J = 10.9, 8.3 Hz), 6.93-6.91 (m, 4H), 3.79 (s, 6H), 2.17-2.11 (m, 2H), 1.58-1.50 (m, 2H), 2.17-2.11 (m, 2H), 1.34-1.17 (m, 14H), 0.83 (t, 3H, J = 6.9 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 162.3, 132.7 (d, $J_{C\text{-}P}$ = 10.6 Hz), 124.9 (d, $J_{C\text{-}P}$ = 104.4 Hz), 114.3 (d, $J_{C\text{-}P}$ = 12.5 Hz), 55.5, 32.0, 31.2 (d, $J_{C\text{-}P}$ = 14.6 Hz), 30.4 (d, $J_{C\text{-}P}$ = 72.7 Hz), 29.7, 29.5, 29.4, 29.3, 22.8, 21.7, 14.3; ^{31}P NMR ($CDCl_3$, 200 MHz) δ 33.1; IR (KBr) cm^{-1} 2955 (m), 2921 (s), 2851 (s), 2050 (w), 1908 (w), 1599 (s), 1571 (m), 1501 (s), 1462 (m), 1295 (s), 1255 (s), 1174 (s); DART-HRMS (m/z) calcd. for $C_{24}H_{36}O_3P_1$ [$(M+H)^+$]: 403.24021, found: 403.24110.



1d **2a** **3j**

Bis(4-chlorophenyl)(decyl)phosphine oxide (3j) (Table 3, entry 10). Following the above general procedure with **1d** (0.1311, 0.500 mmol) and *i*-PrOH (0.4 mL) for 18 h at 50 °C. The crude reaction mixture was purified by preparative TLC (EtOAc) to provide **3j** (0.1295 g, 0.315 mmol, 63%) as a white solid (m.p. = 51-52 °C). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.63-7.59 (m, 4H), 7.43-7.39 (m, 4H), 2.21-2.15 (m, 2H), 1.57-1.51 (m, 2H), 1.36-1.31 (m, 2H), 1.25-1.00 (m, 12H), 0.82 (t, 3H, J = 7.0); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 138.6, 132.3 (d, $J_{C\text{-}P}$ = 10.0 Hz), 131.5 (d, $J_{C\text{-}P}$ = 99.0 Hz), 129.3 (d, $J_{C\text{-}P}$ = 12.0 Hz), 32.0, 31.1 (d, $J_{C\text{-}P}$ = 14.6 Hz), 30.1, 29.6, 29.5, 29.4, 29.2, 22.8, 21.4, 14.3; ^{31}P NMR ($CDCl_3$, 200 MHz) δ 32.0; IR (KBr) cm^{-1} 3052 (2), 2953 (s), 2850 (s), 1921 (w), 1718 (w), 1584 (m), 1483 (m), 1390 (m), 1184 (s), 1088 (s); DART-HRMS (m/z) calcd. for $C_{22}H_{30}Cl_2O_1P_1$ [$(M+H)^+$]: 411.14113, found: 411.14016.

Part III: NMR Spectra of **3a-j**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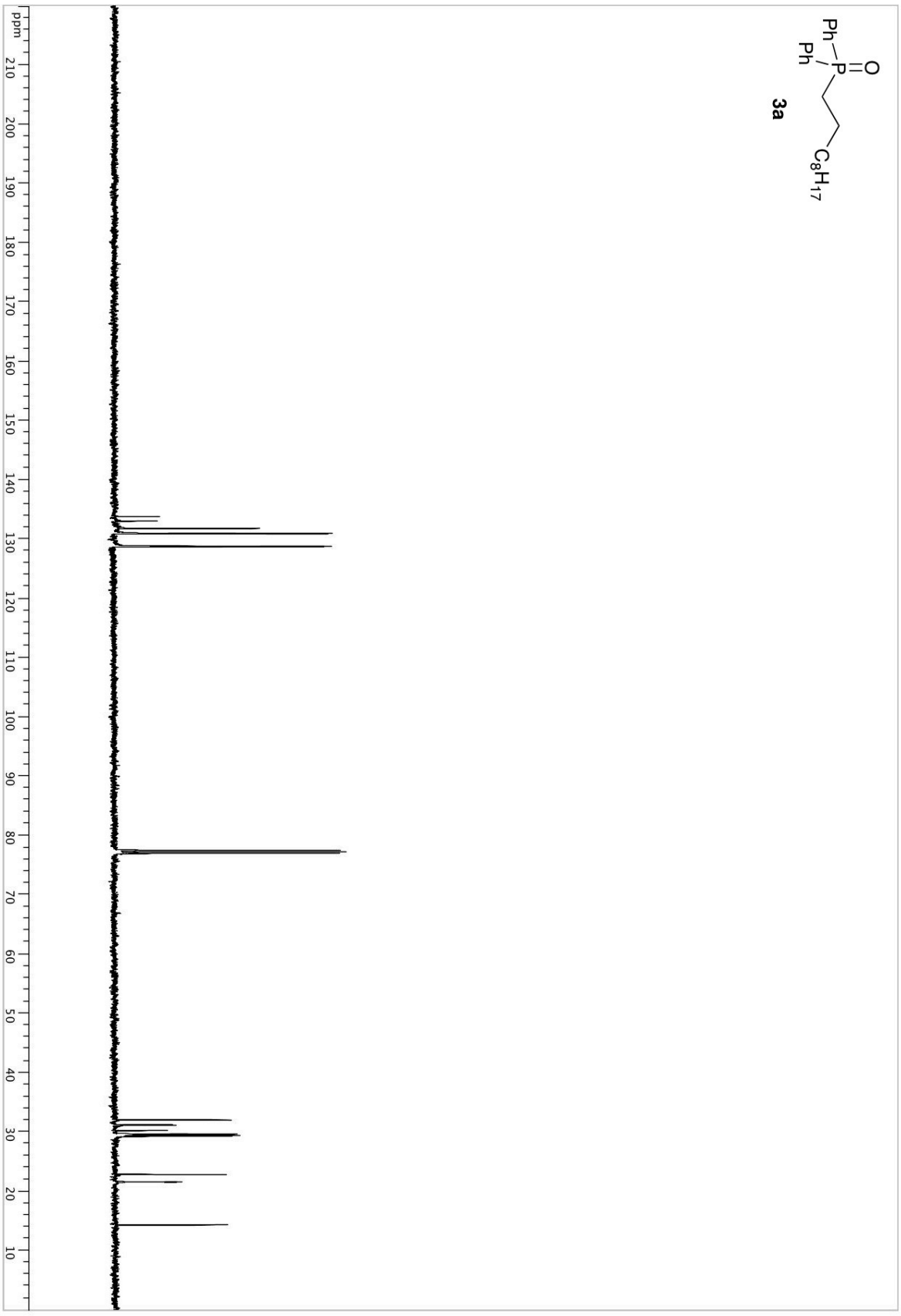
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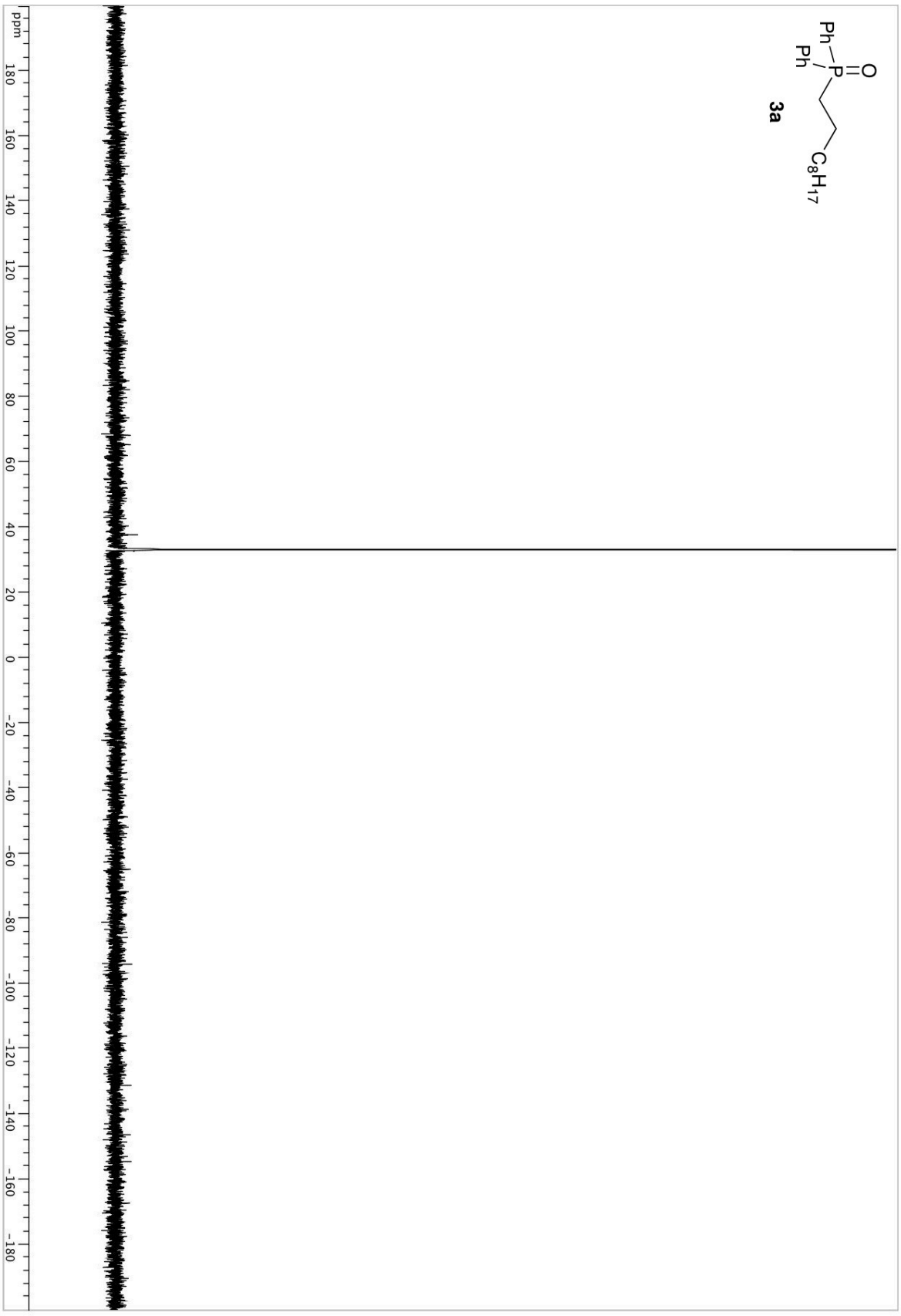

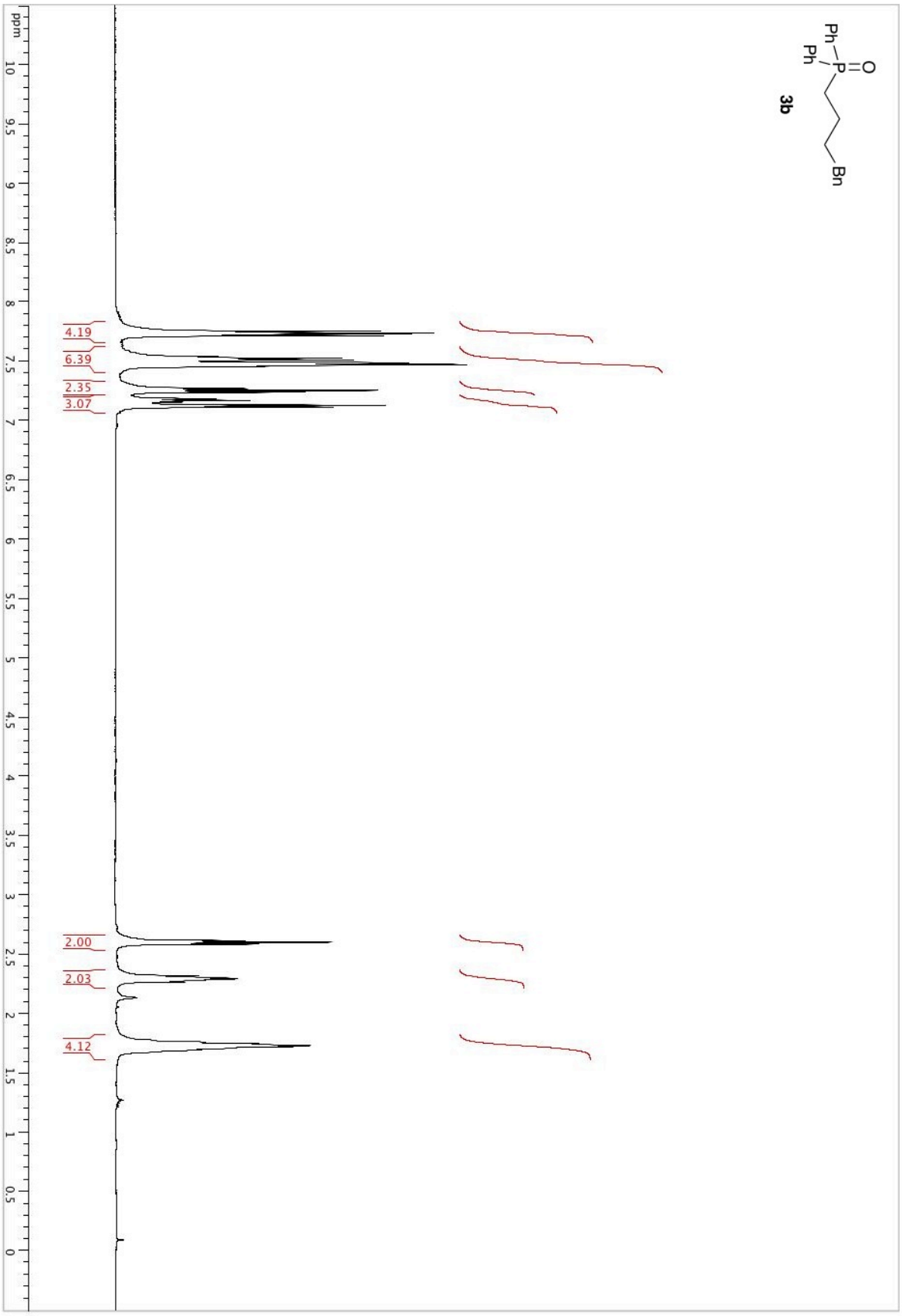
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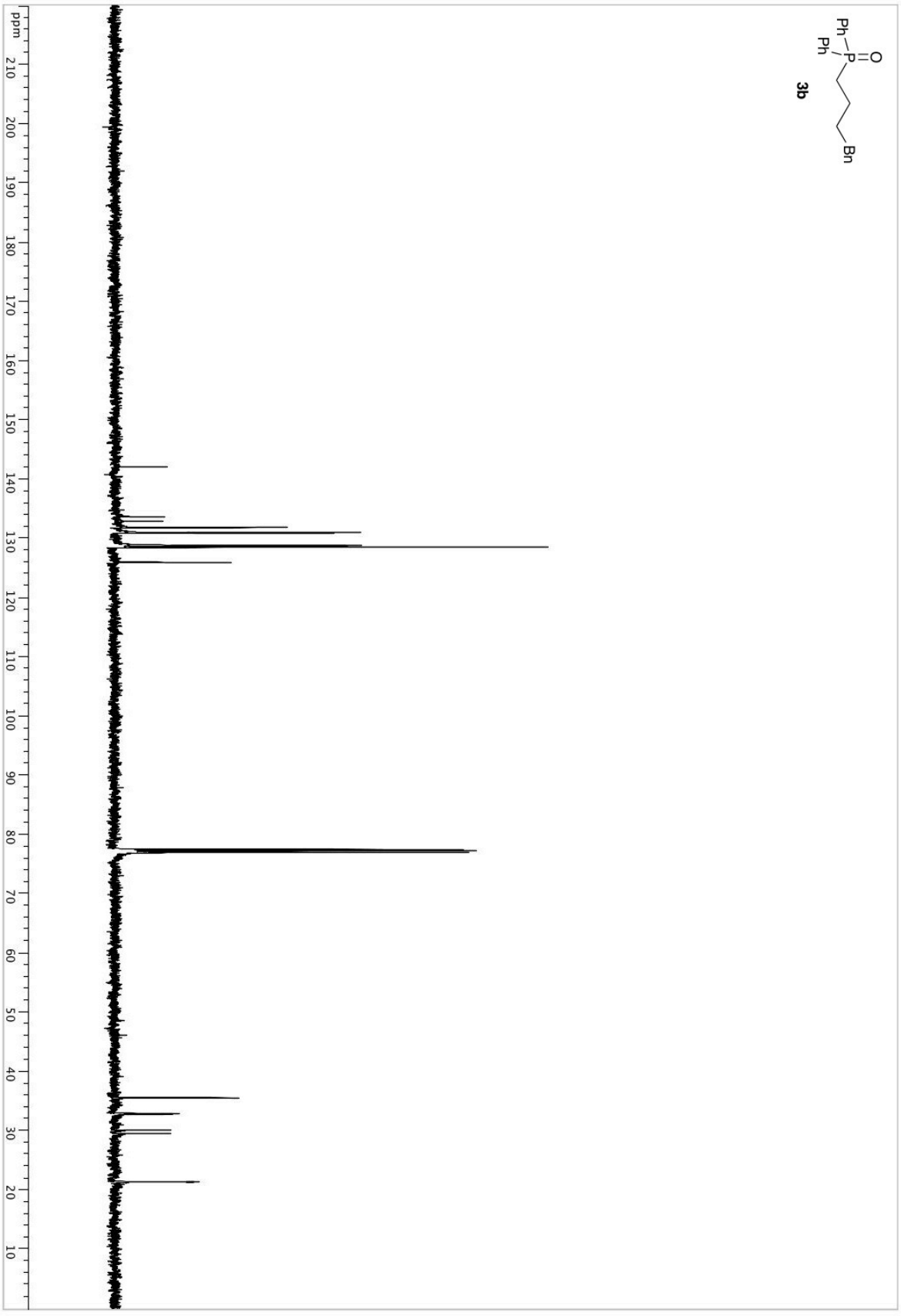
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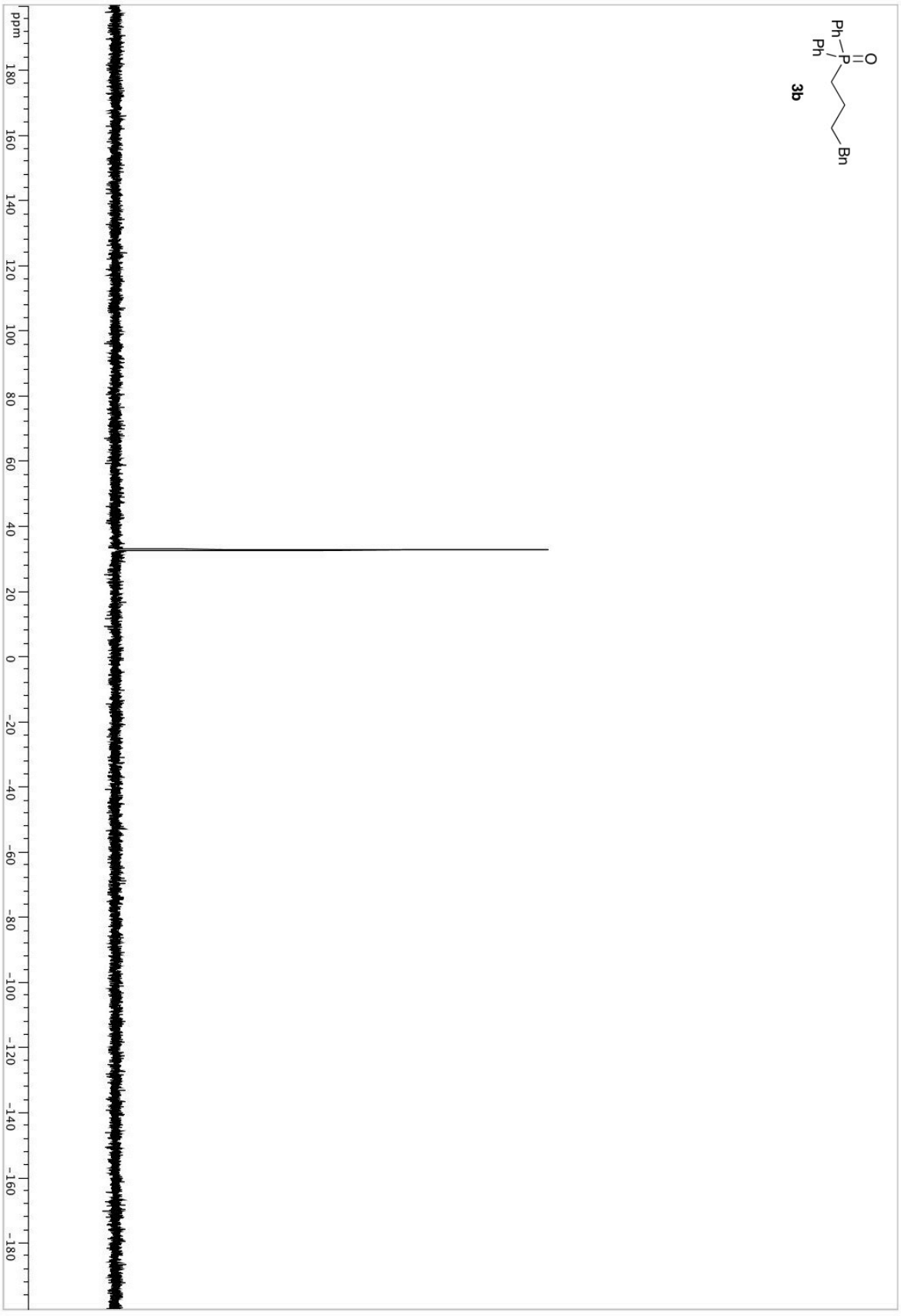

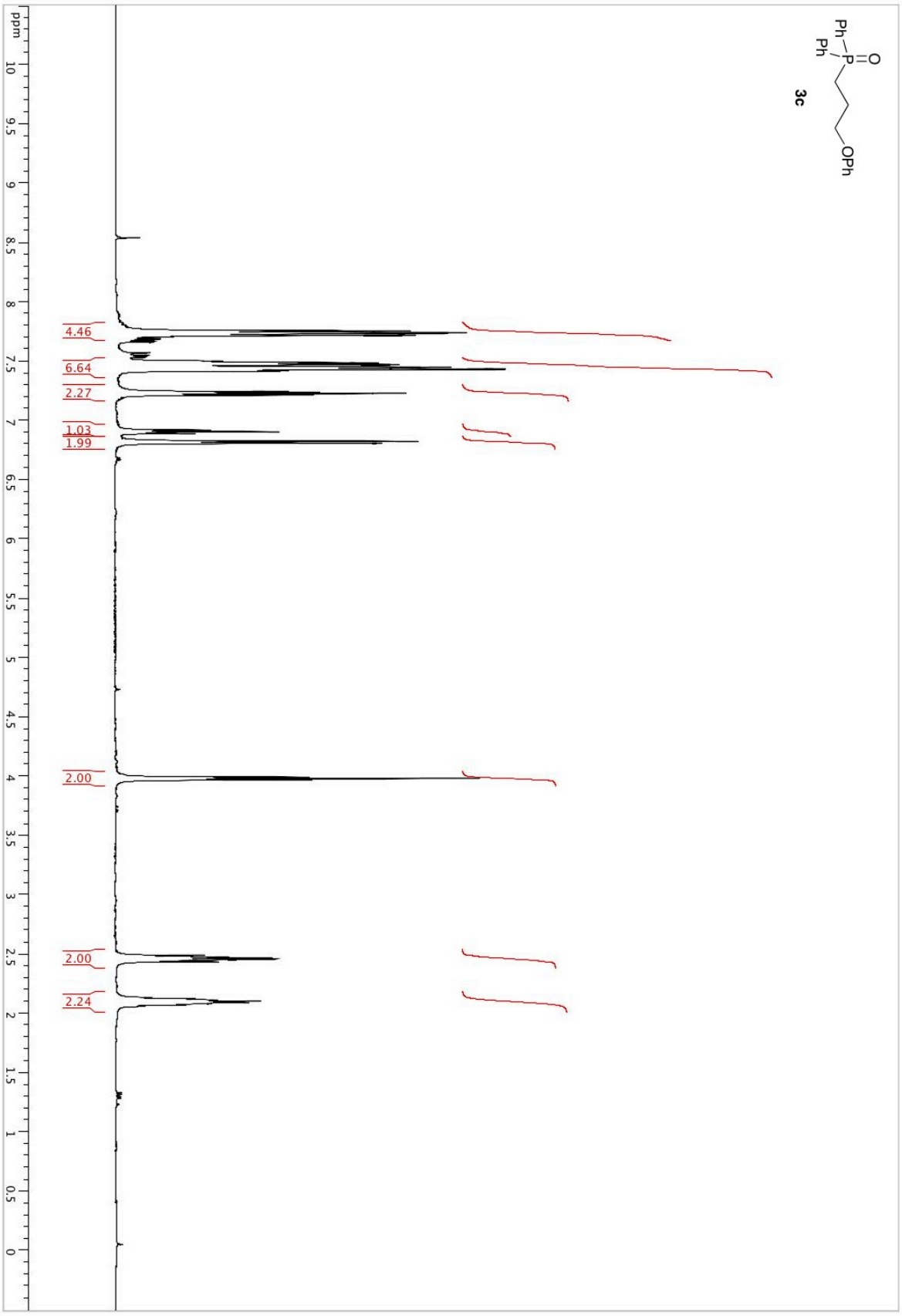
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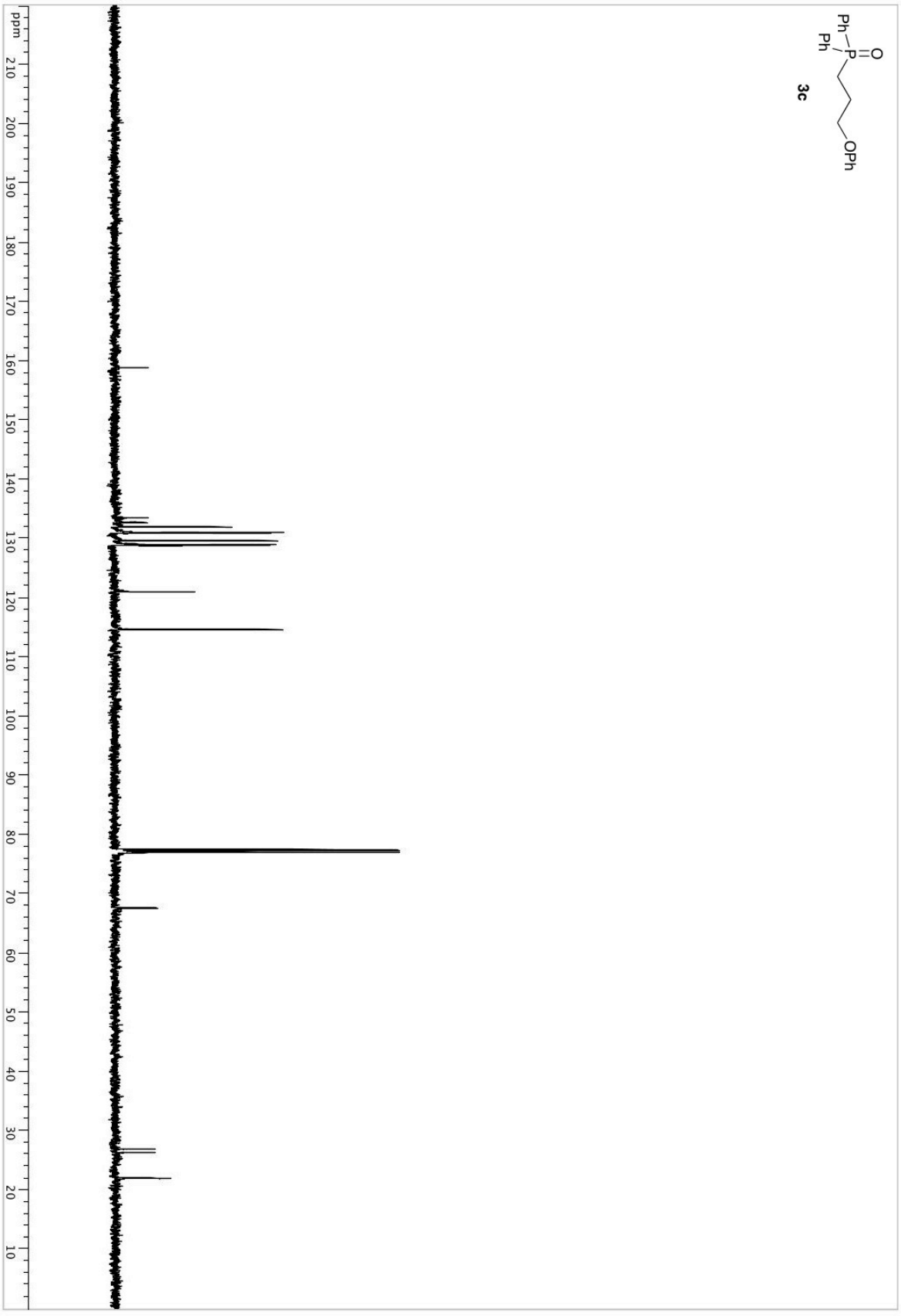
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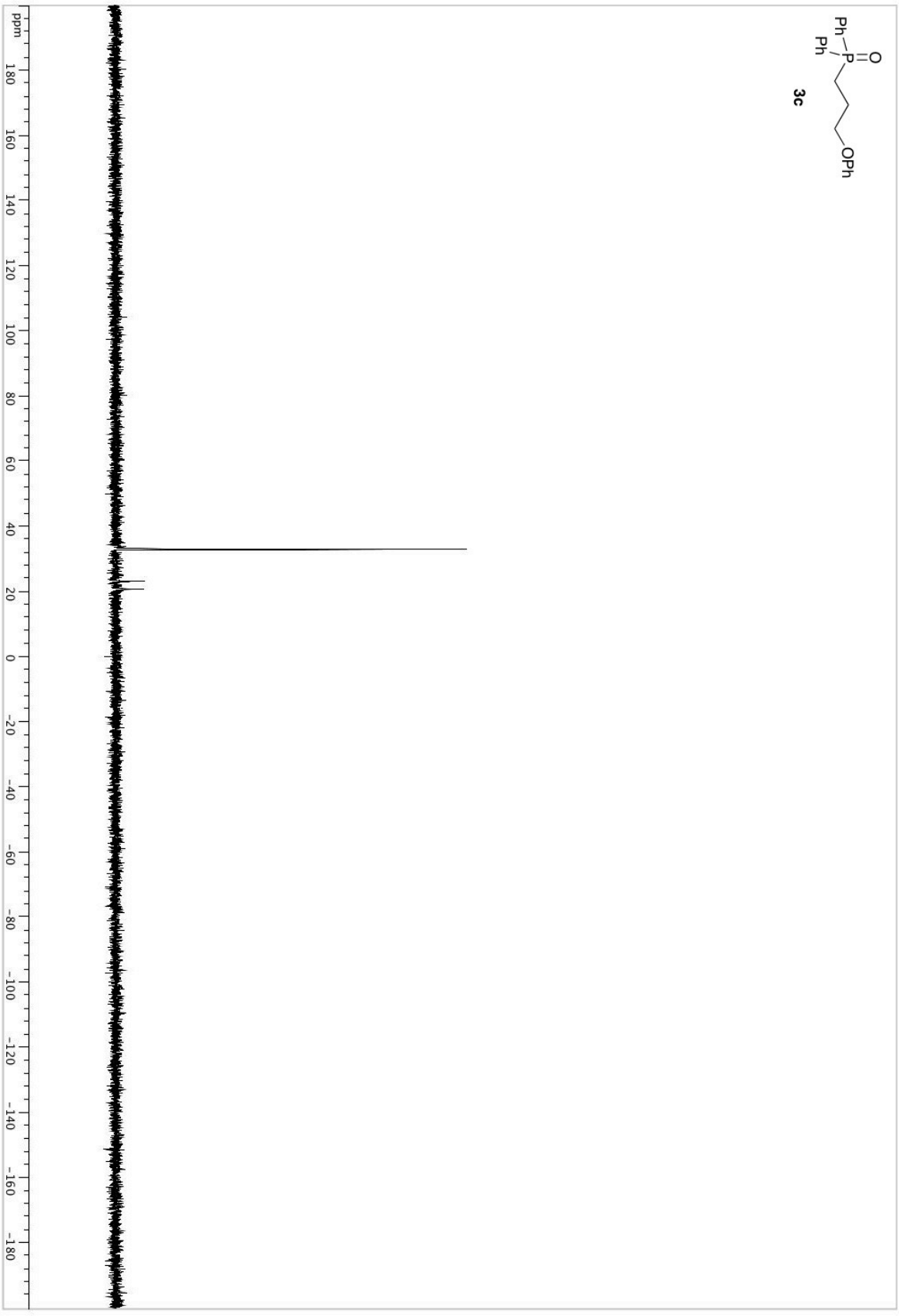

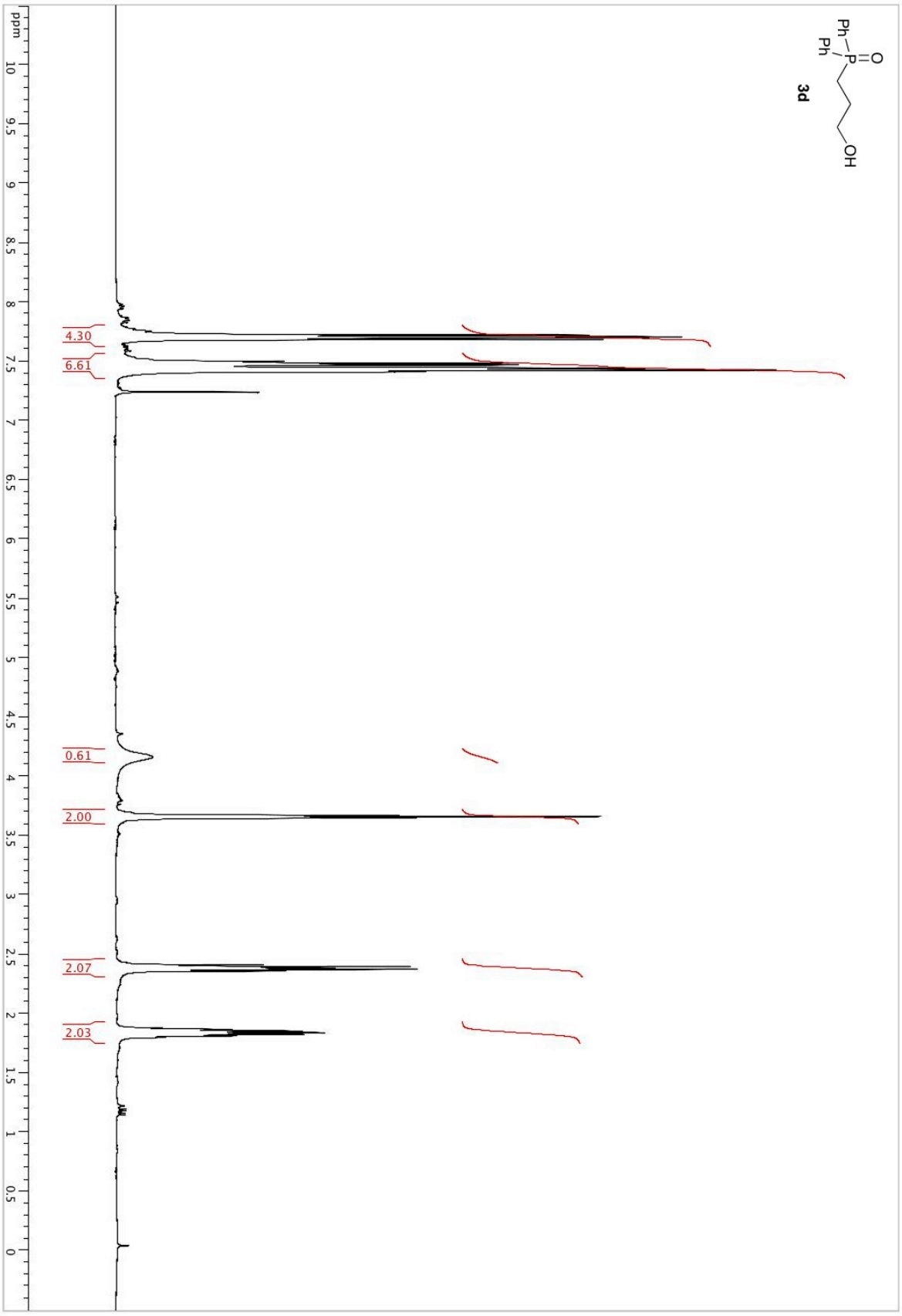
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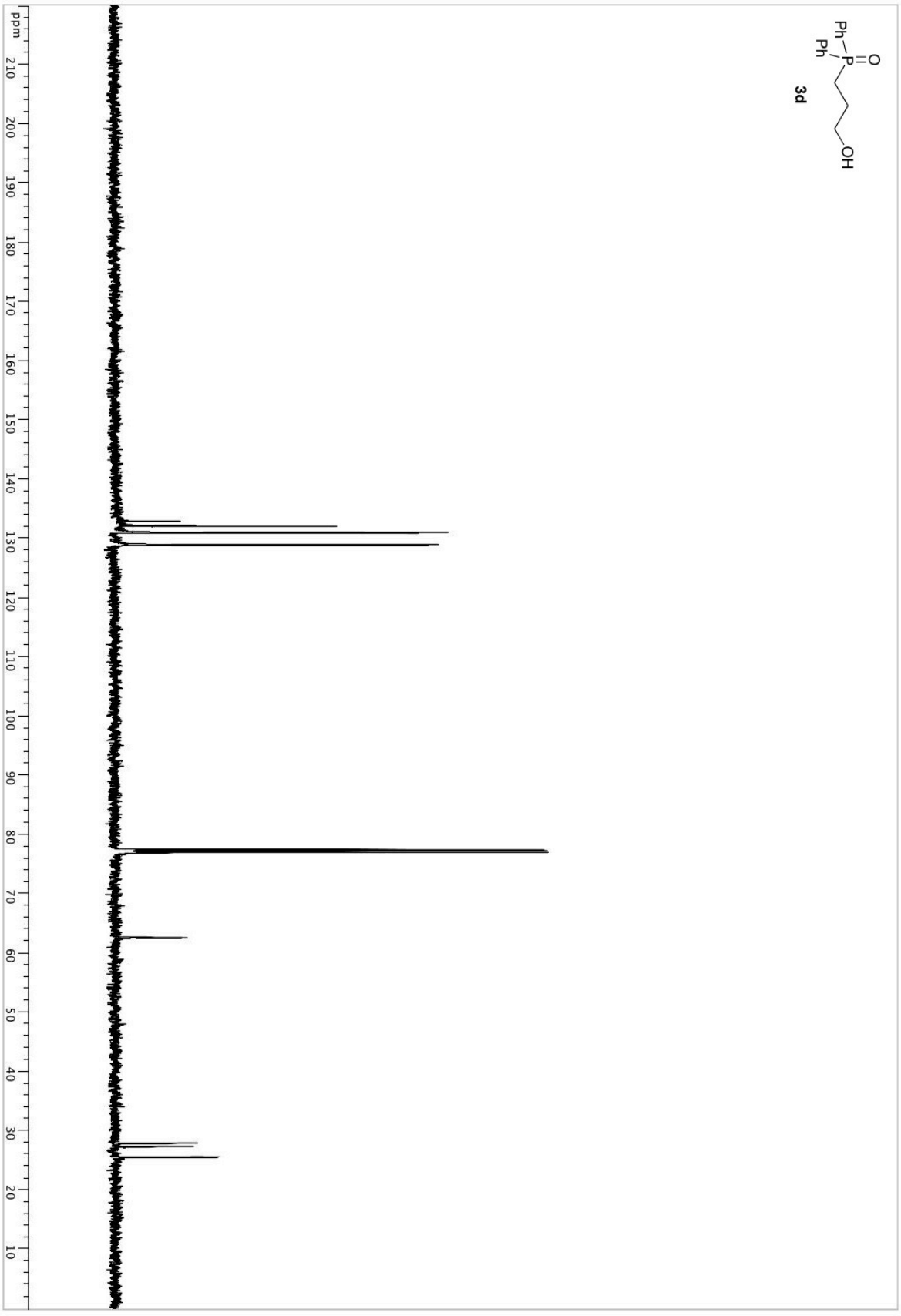
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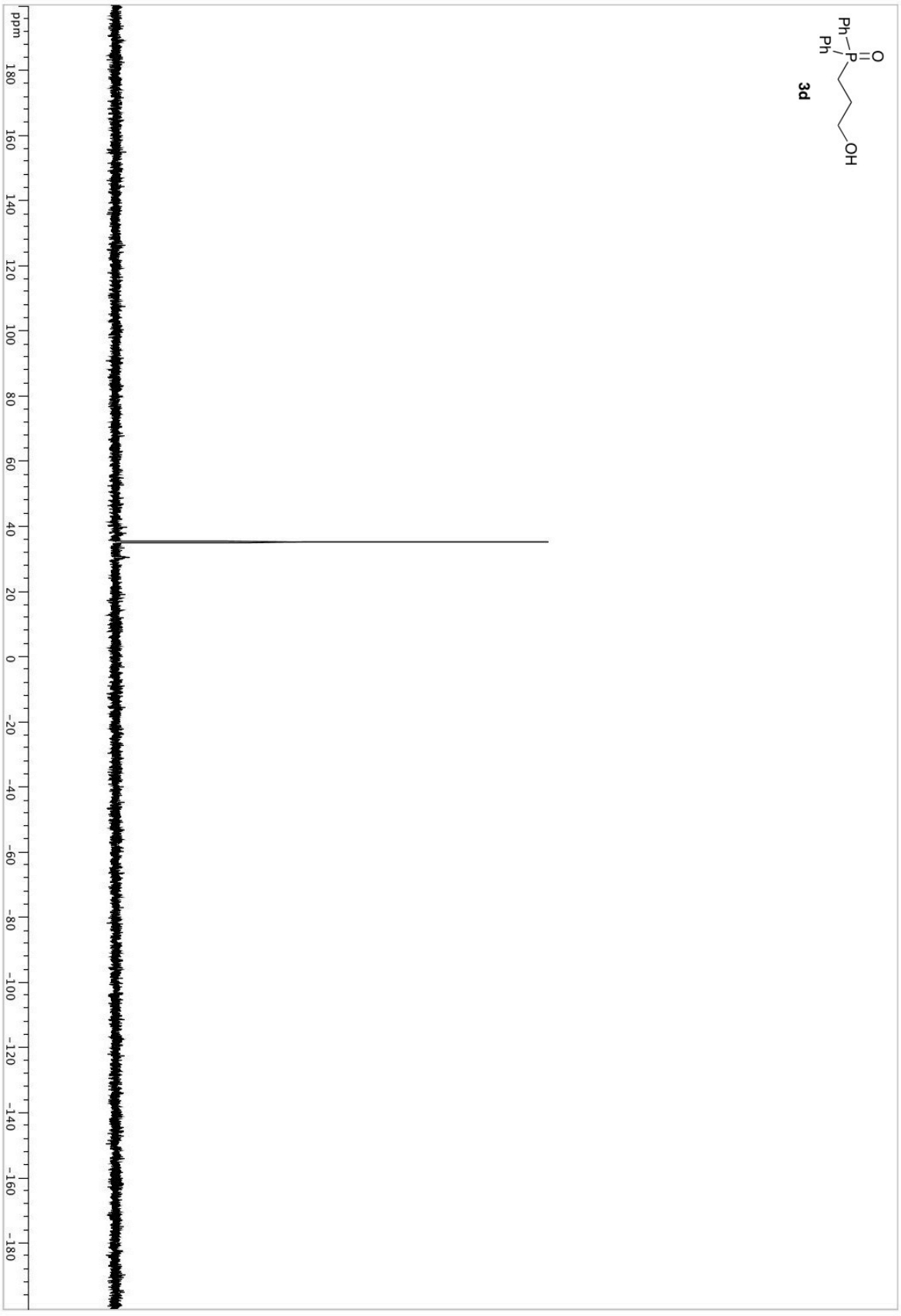
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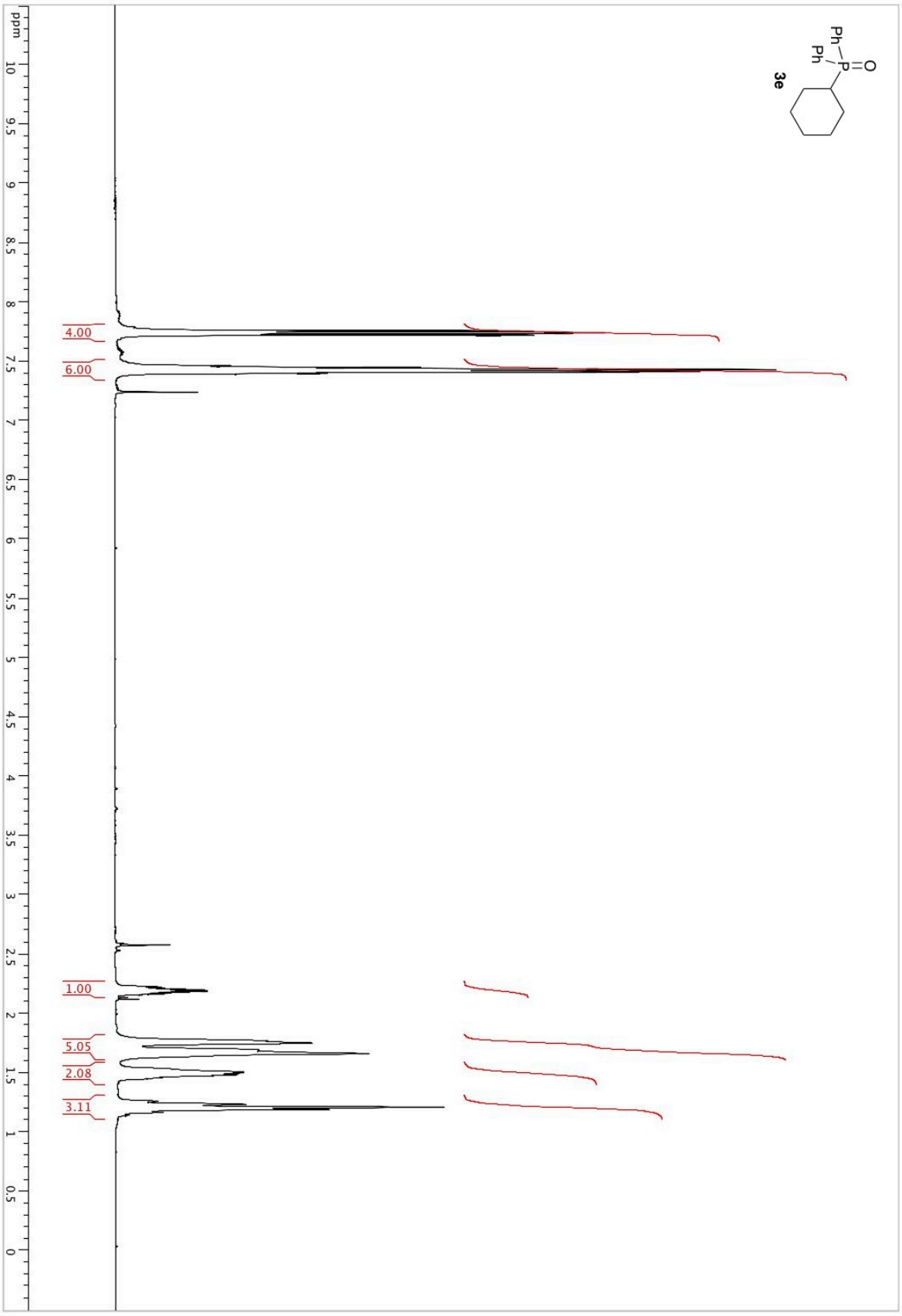

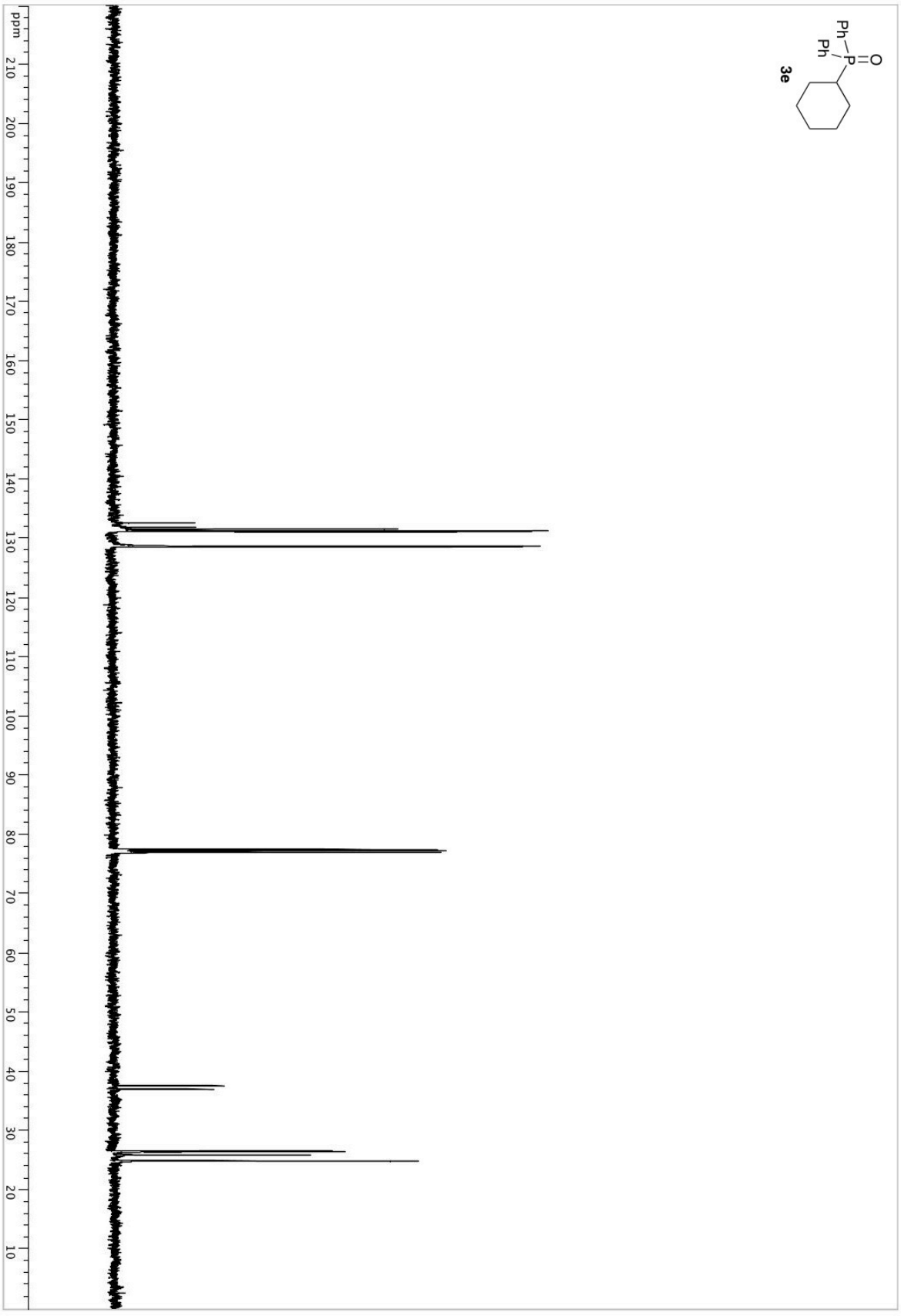
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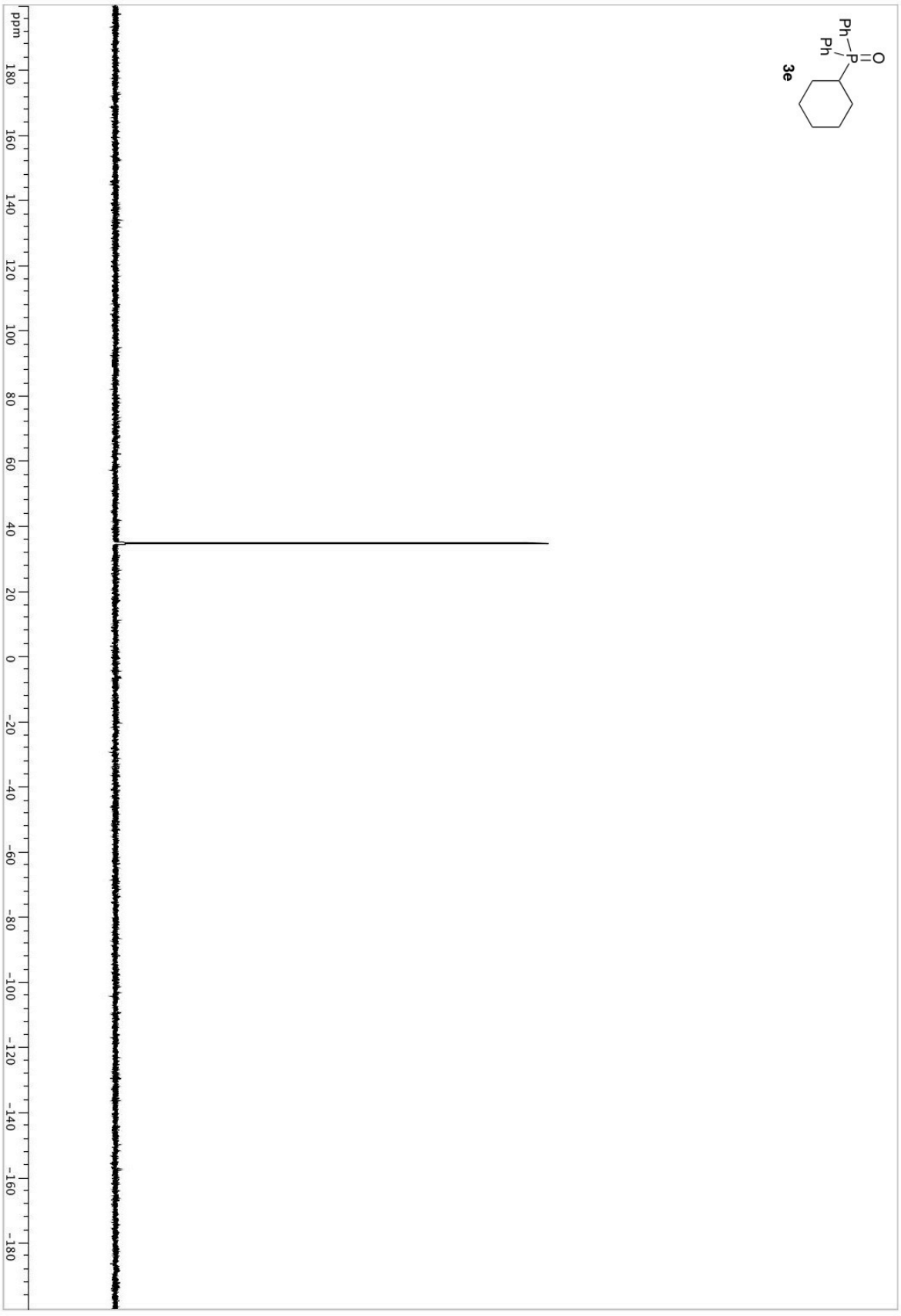
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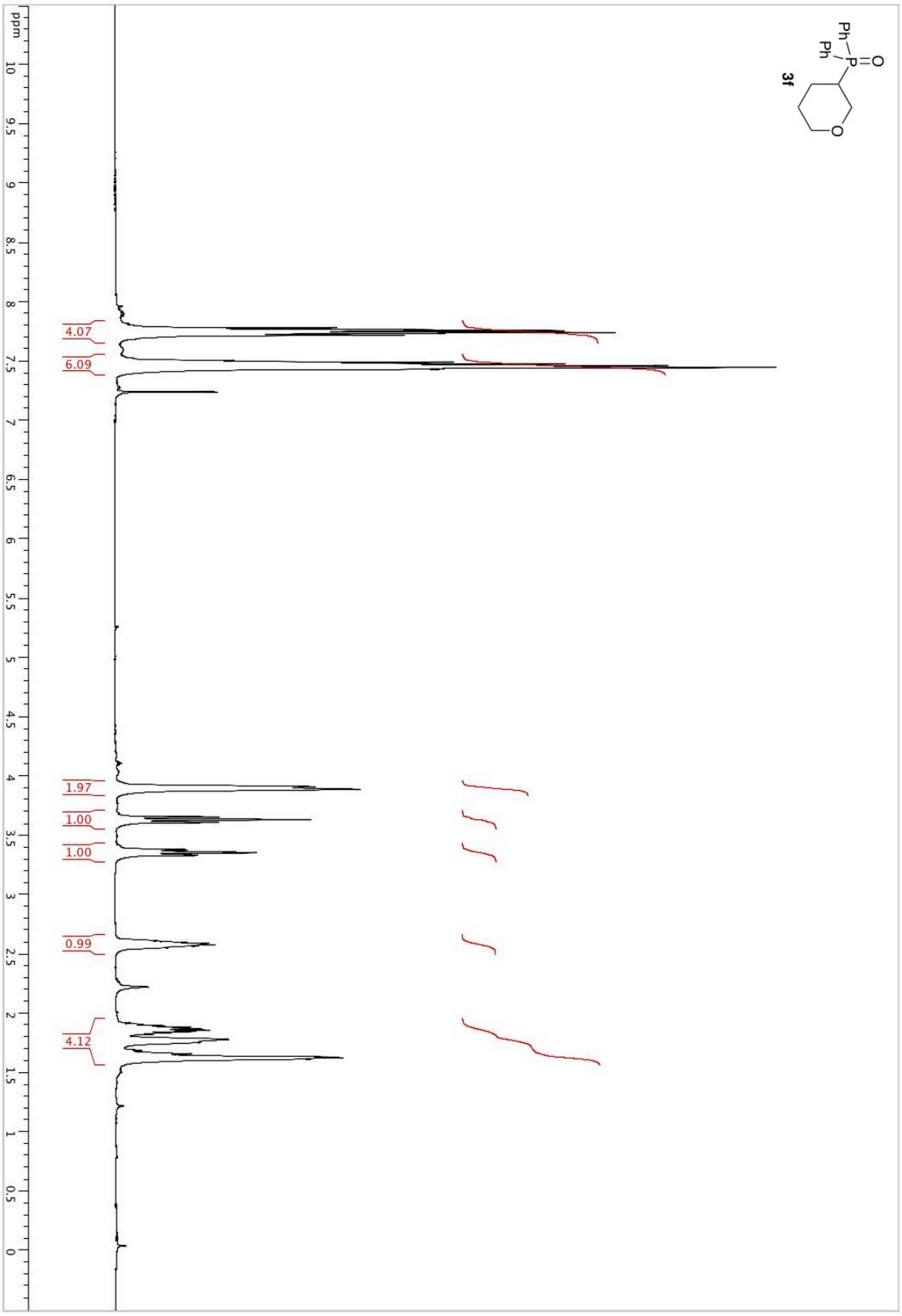

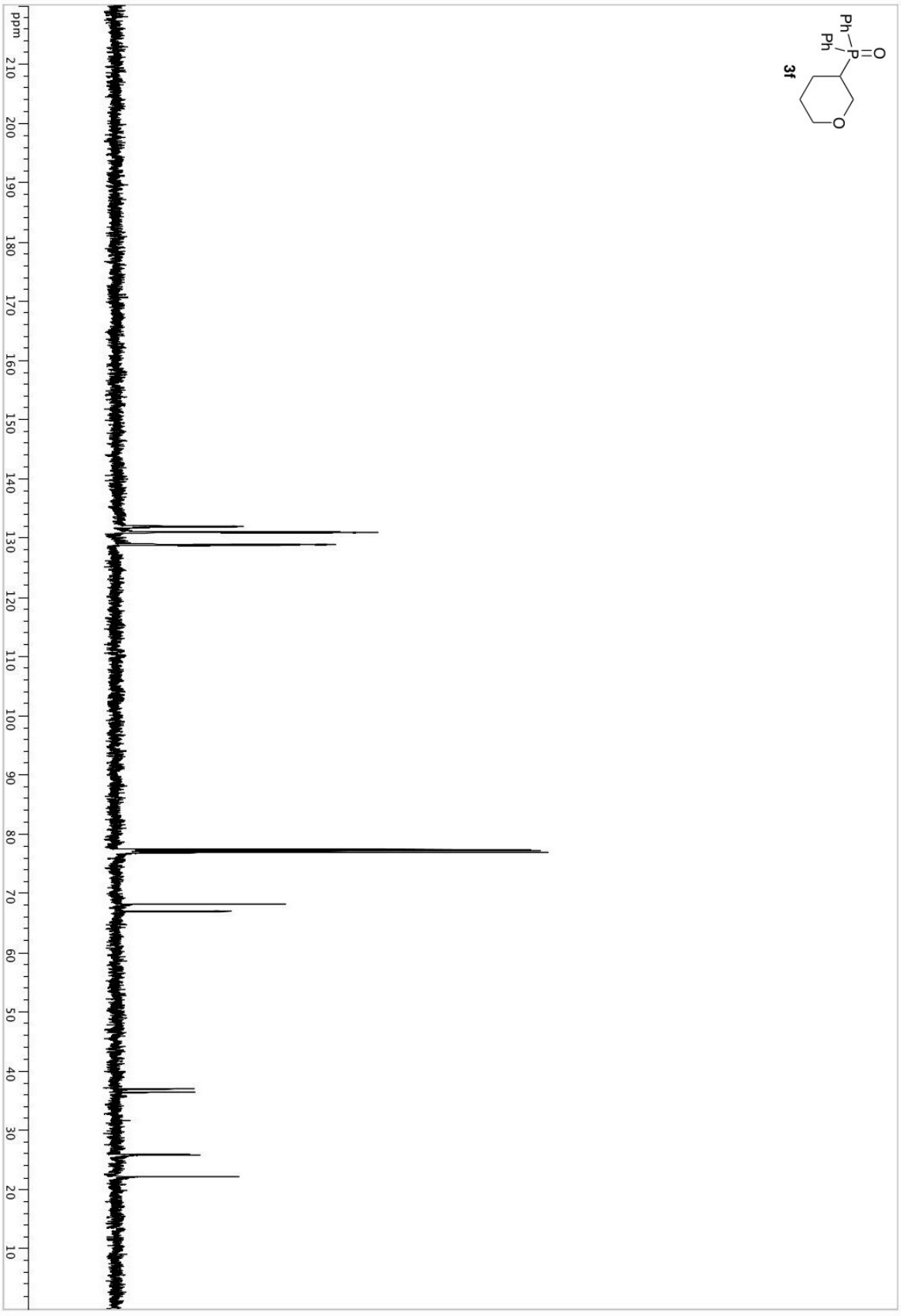
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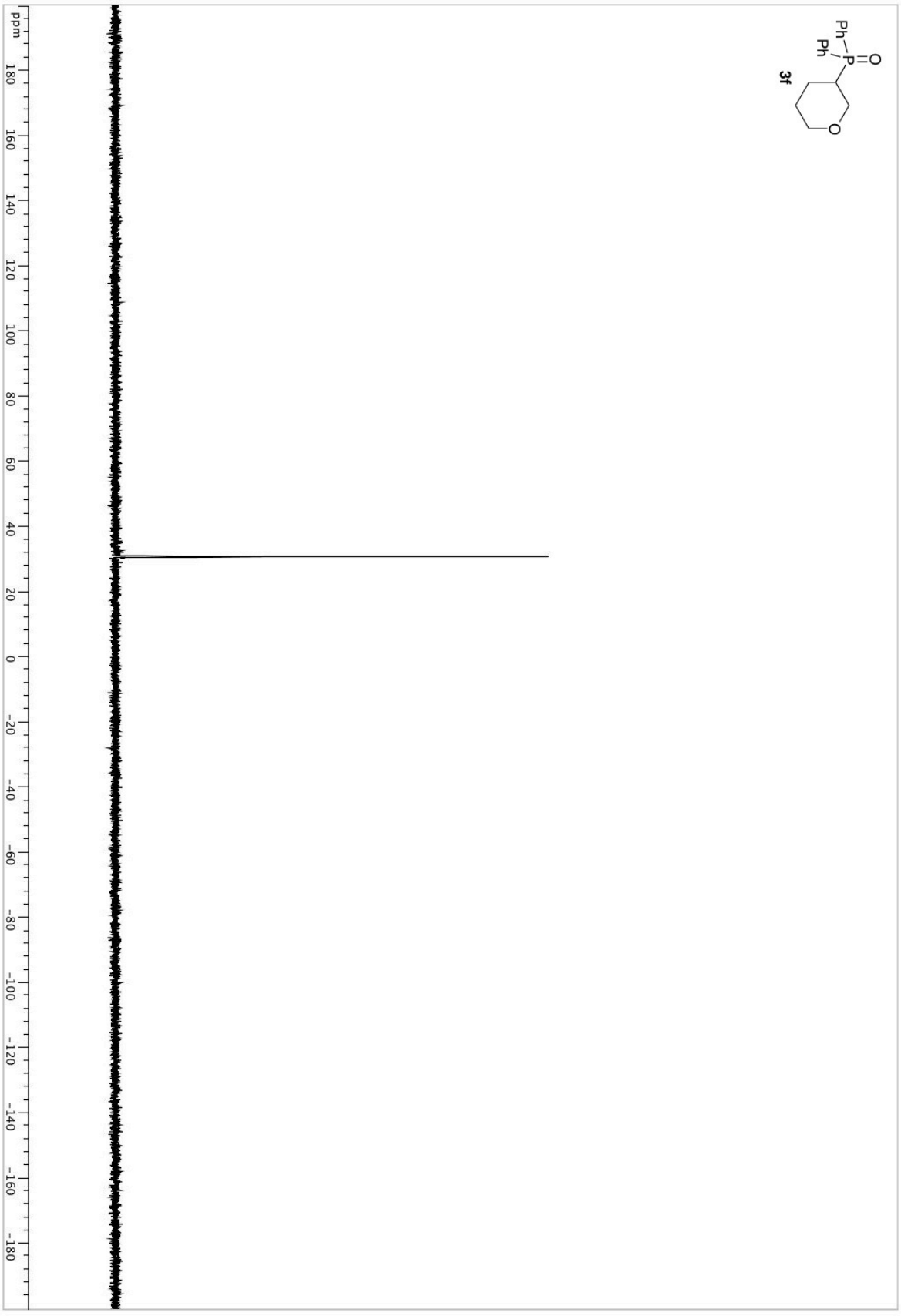
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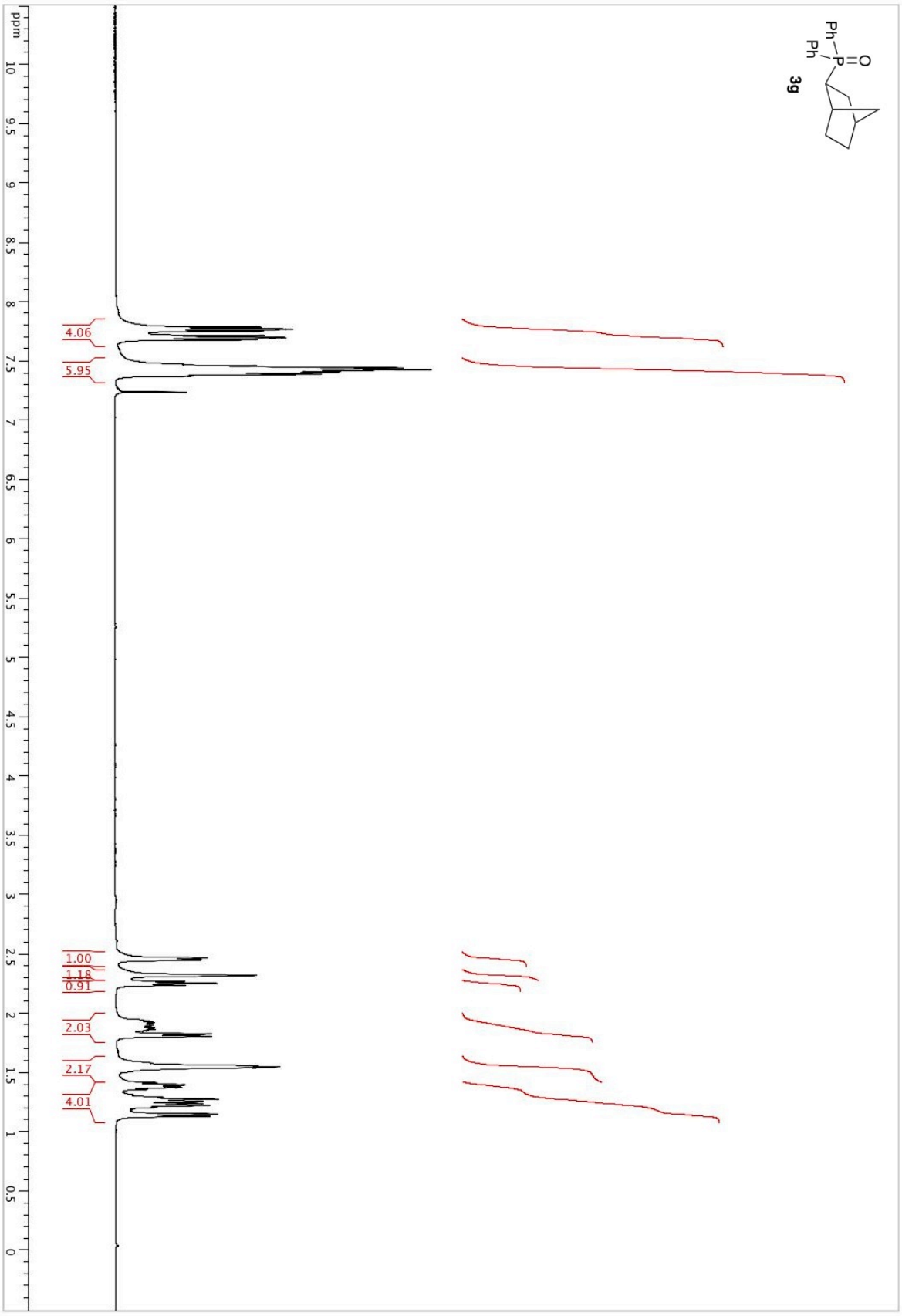
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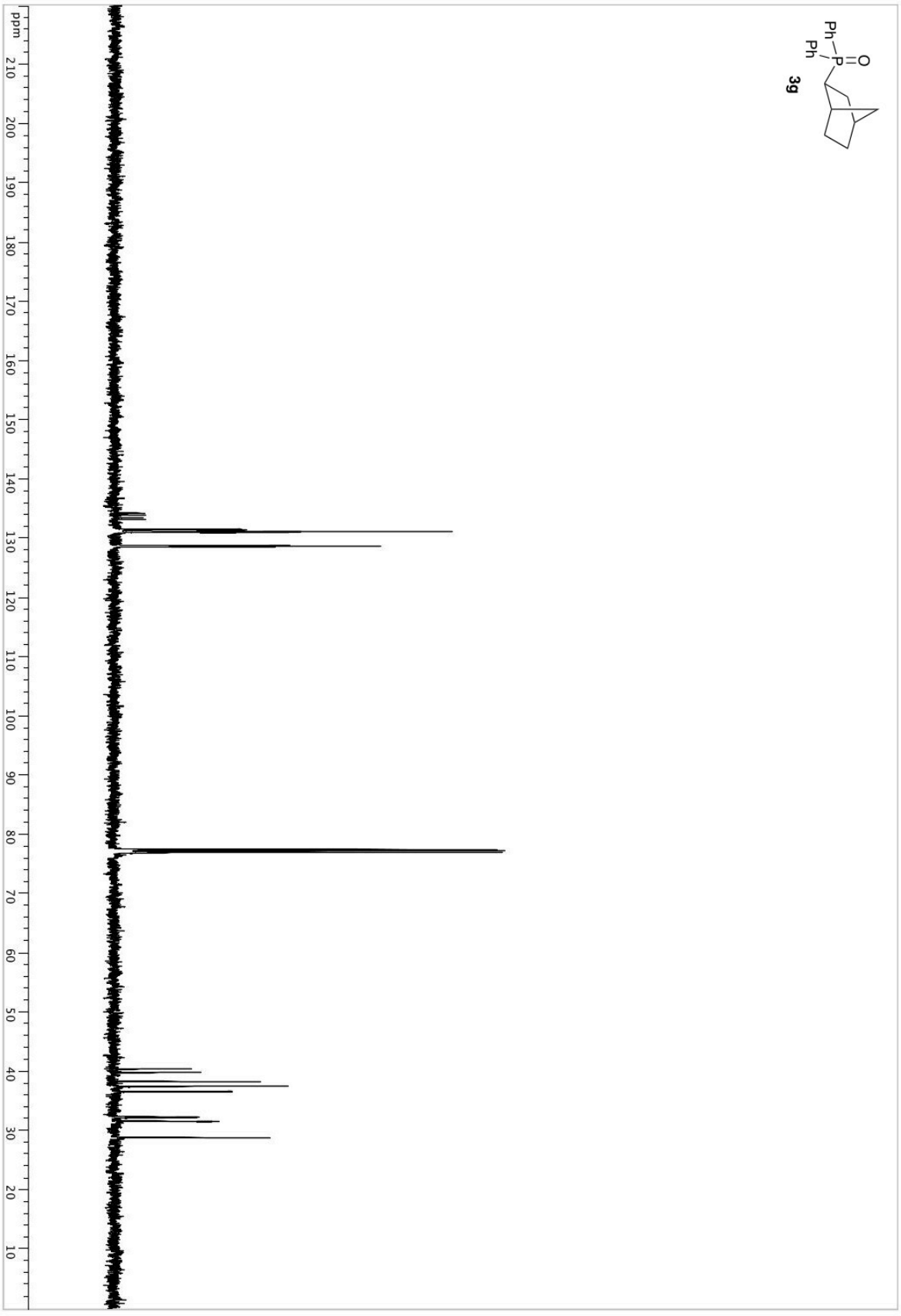
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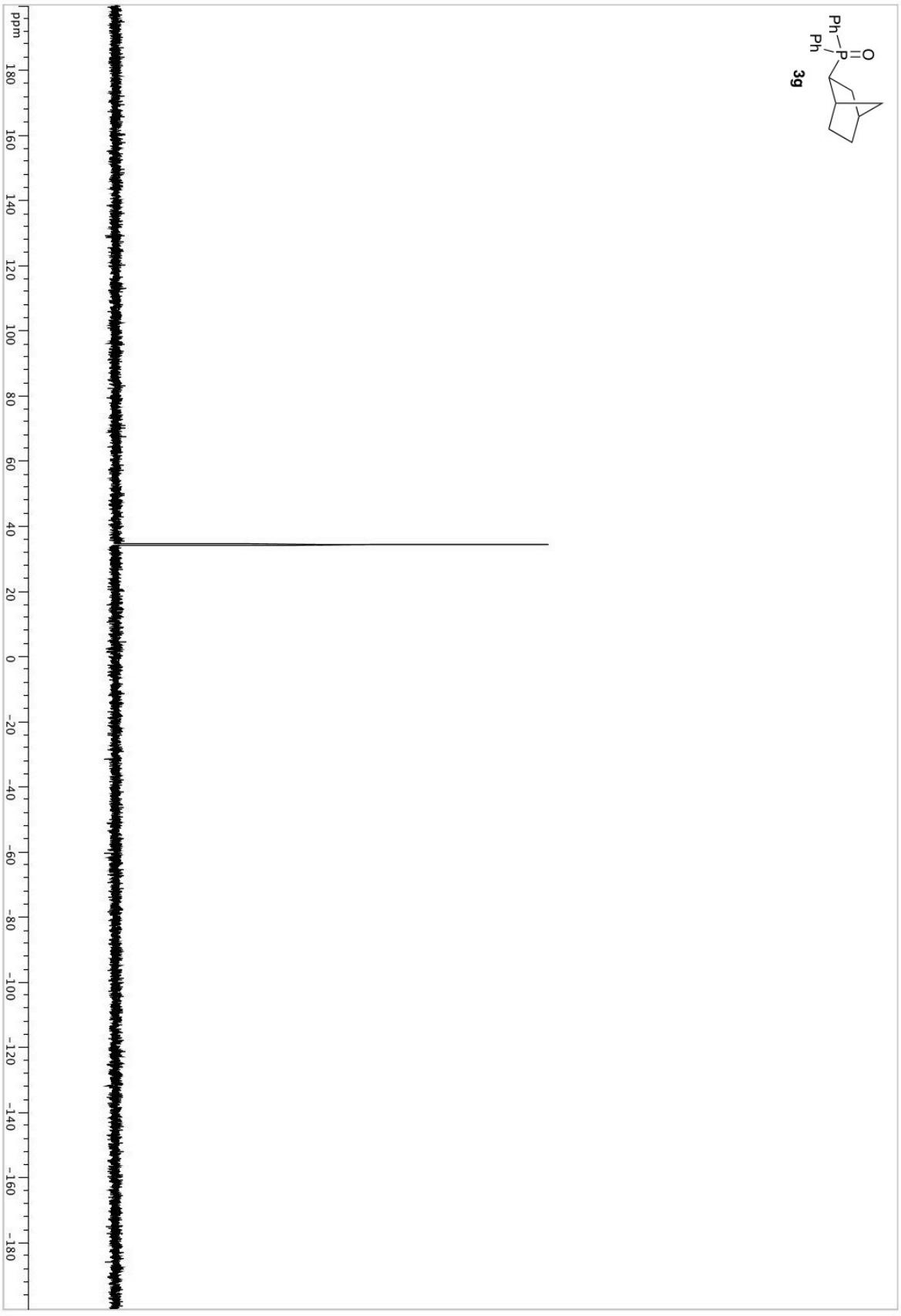
Ph
3g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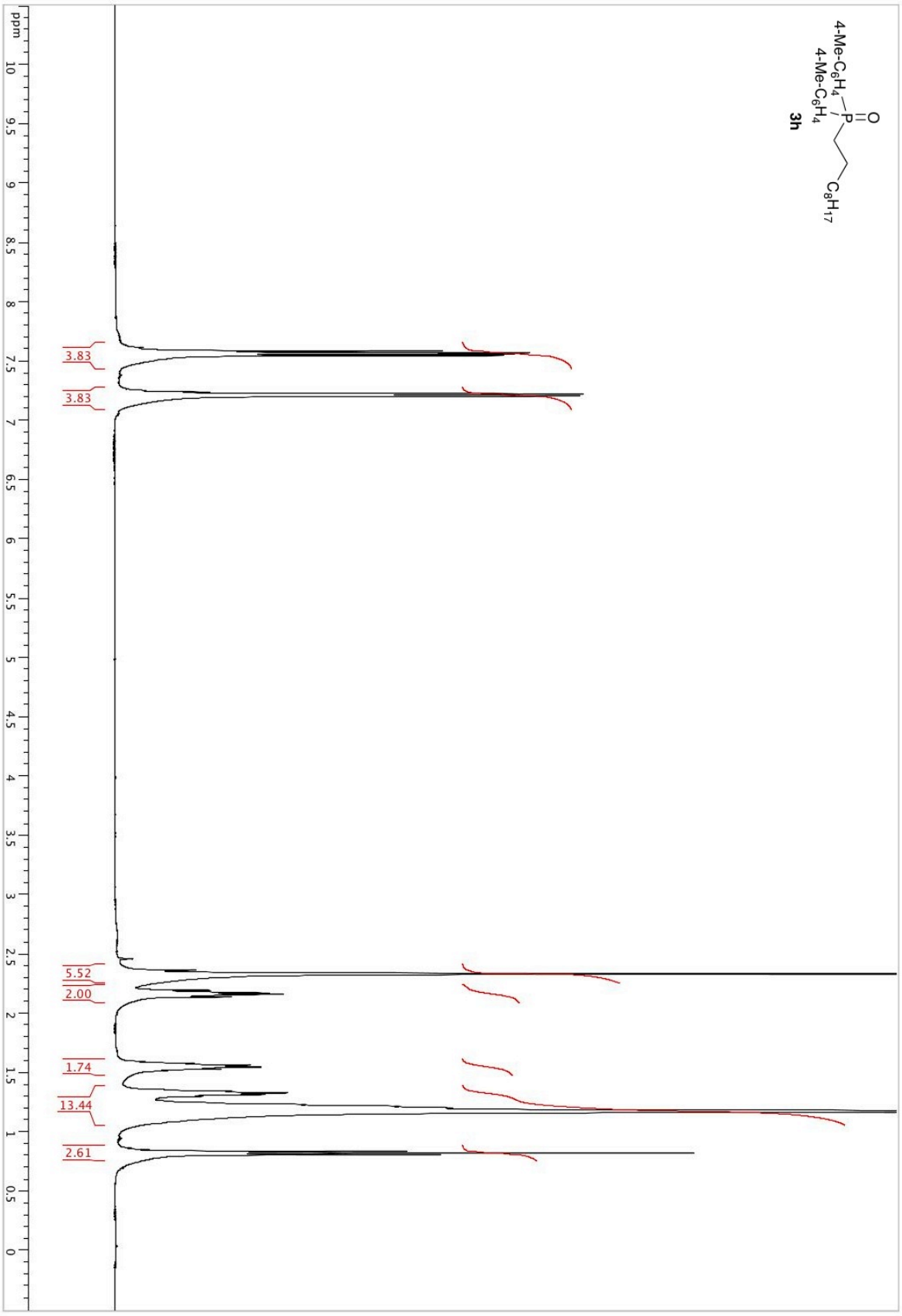
O
3g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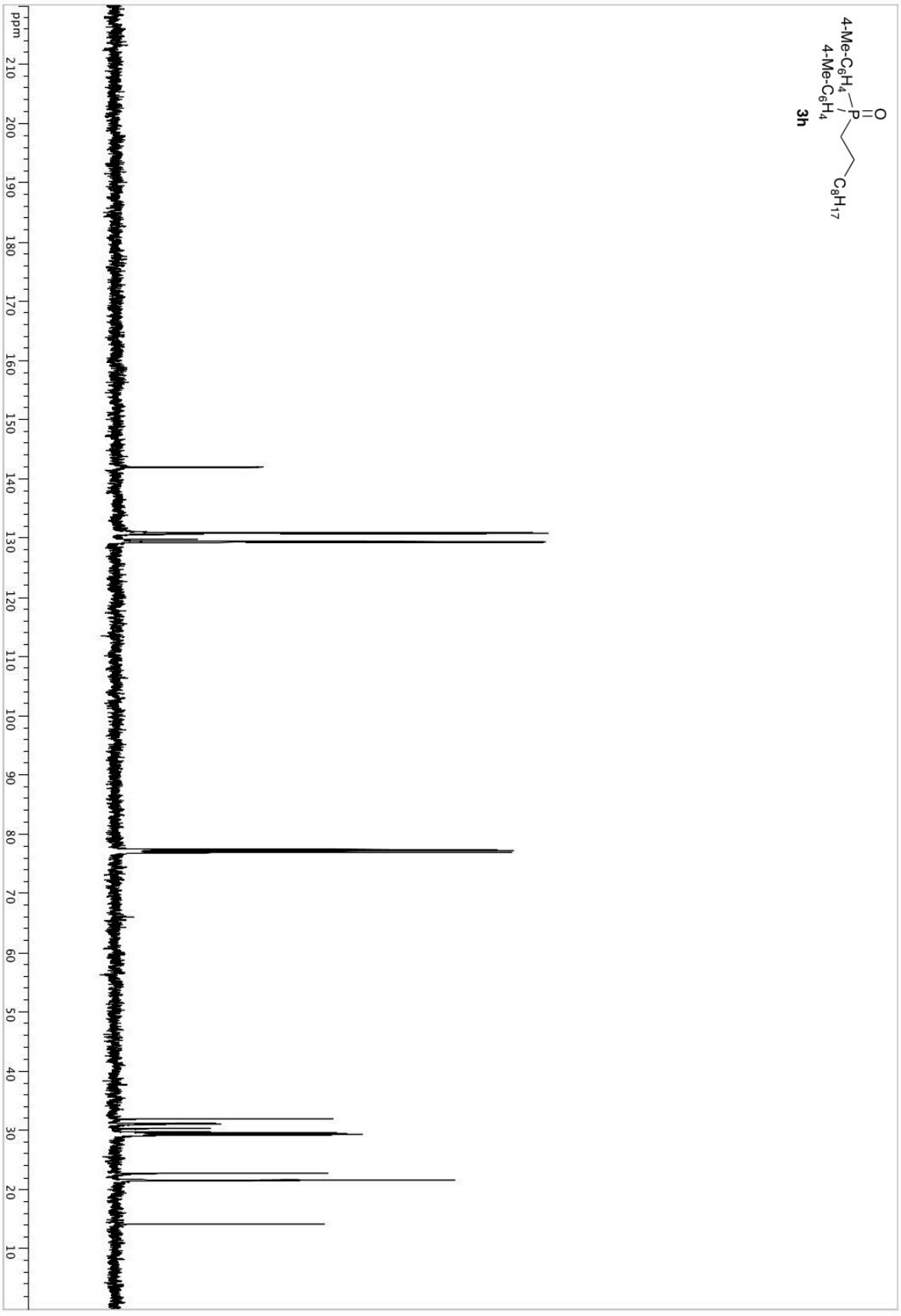
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4-Me-C6H4
C8H17
3h
ppm
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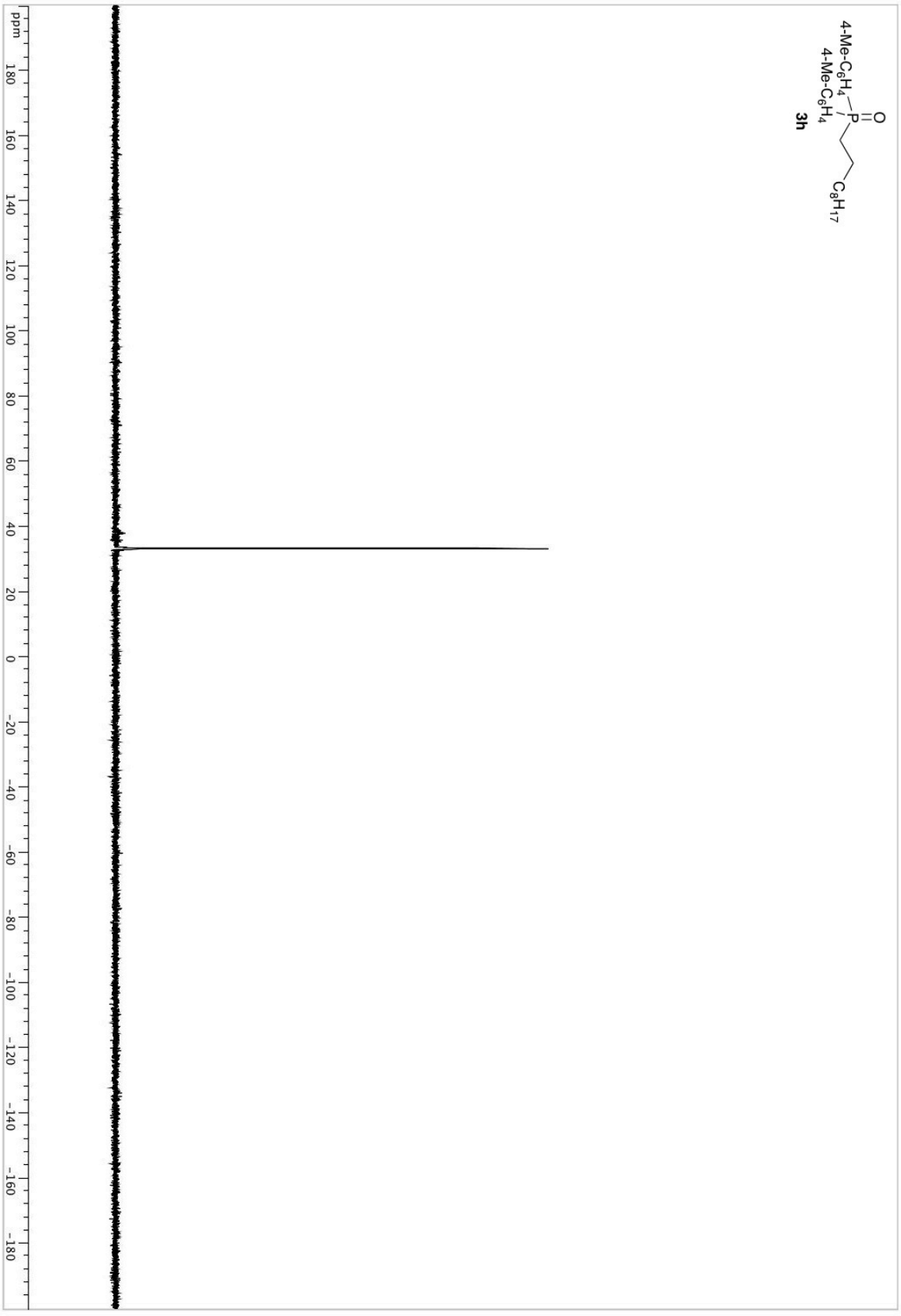
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P
C8H17
3h
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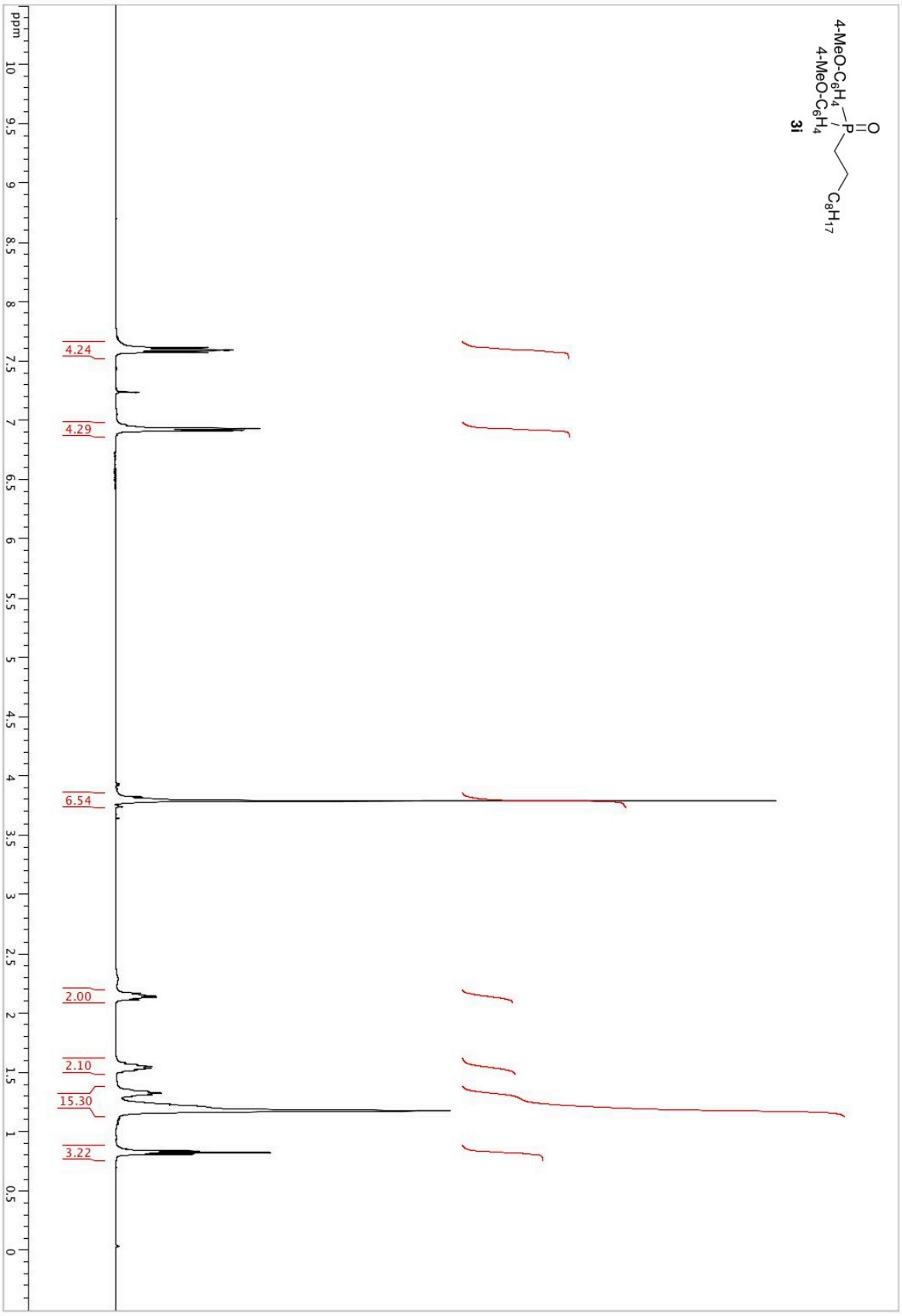
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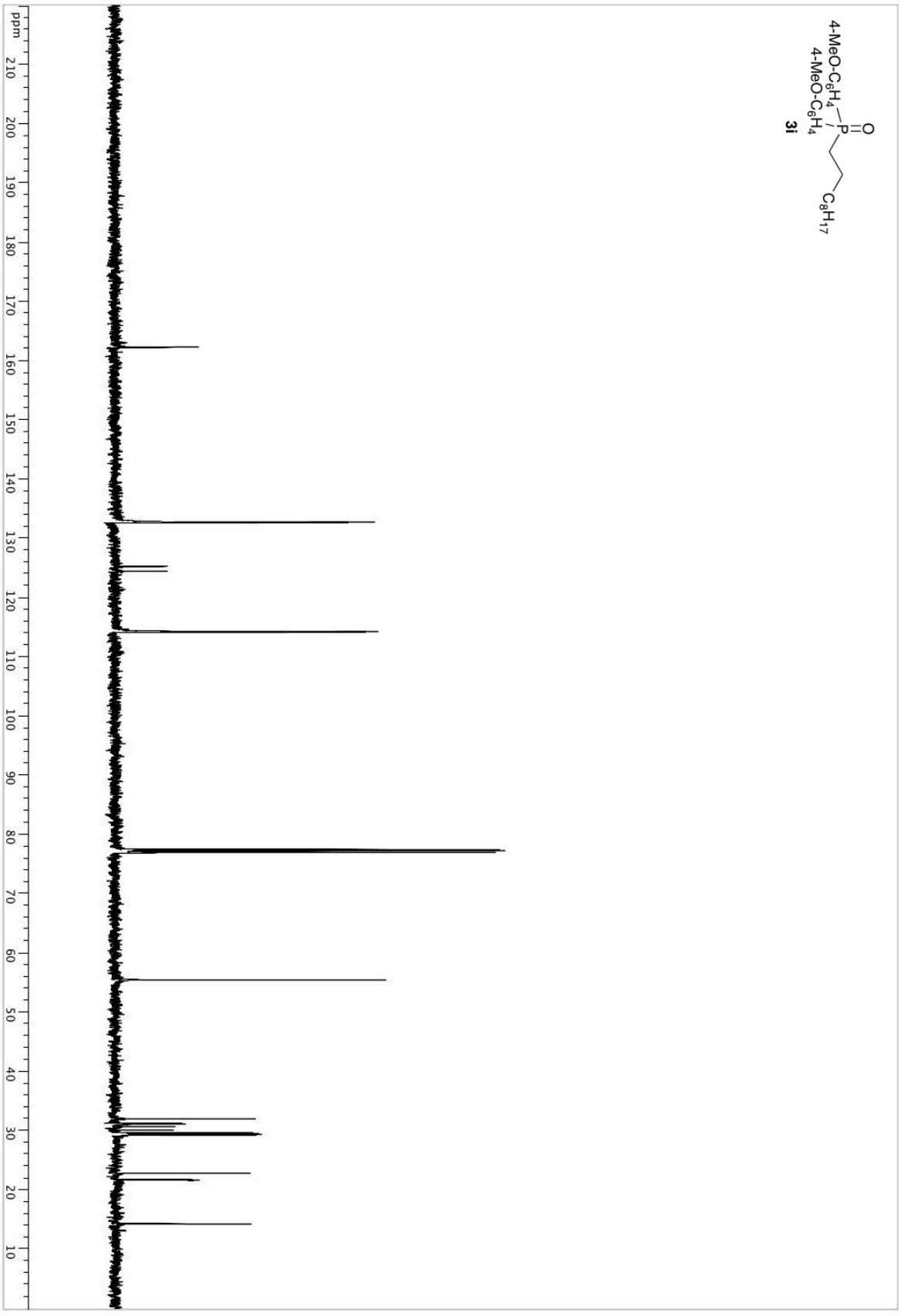
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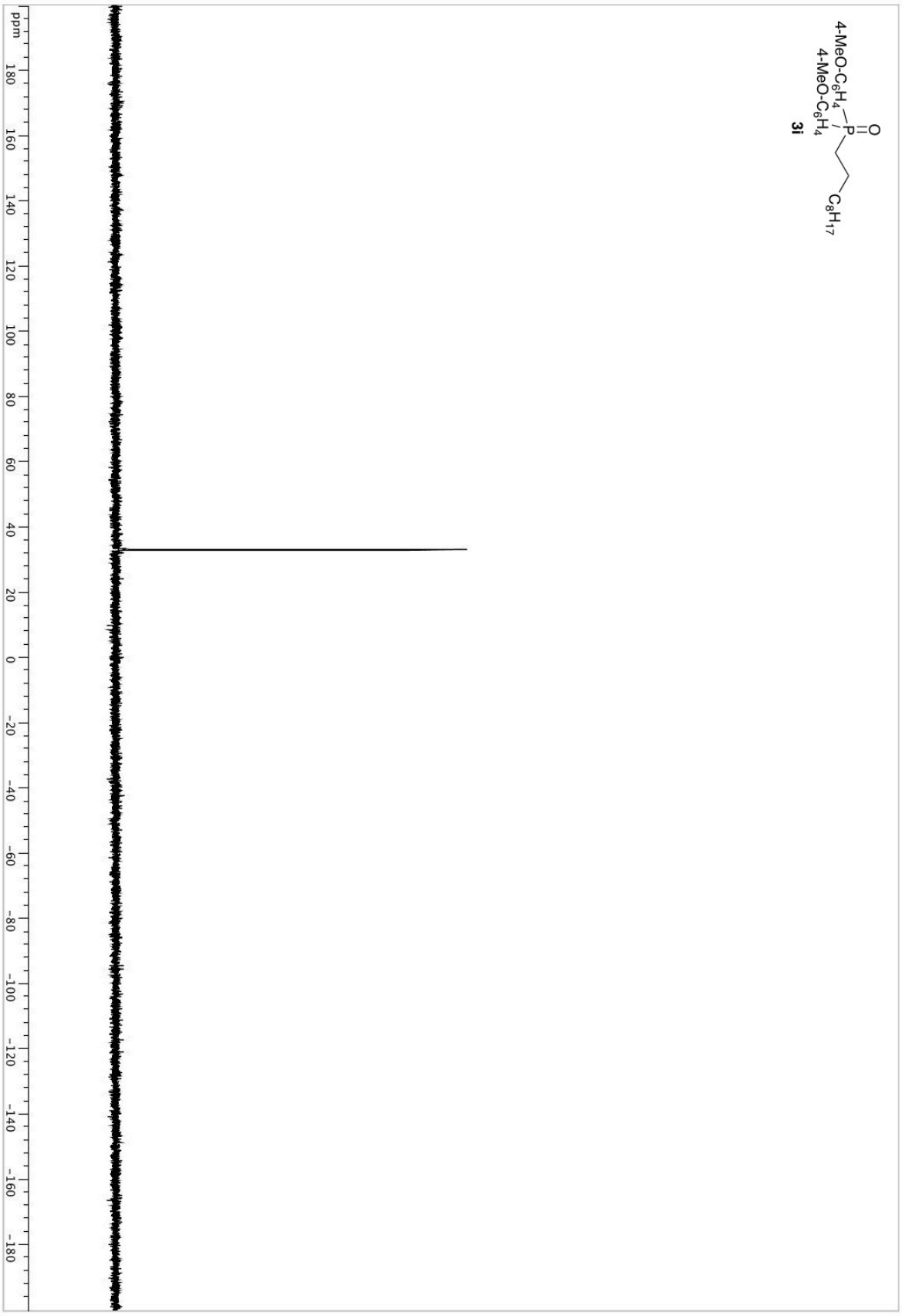

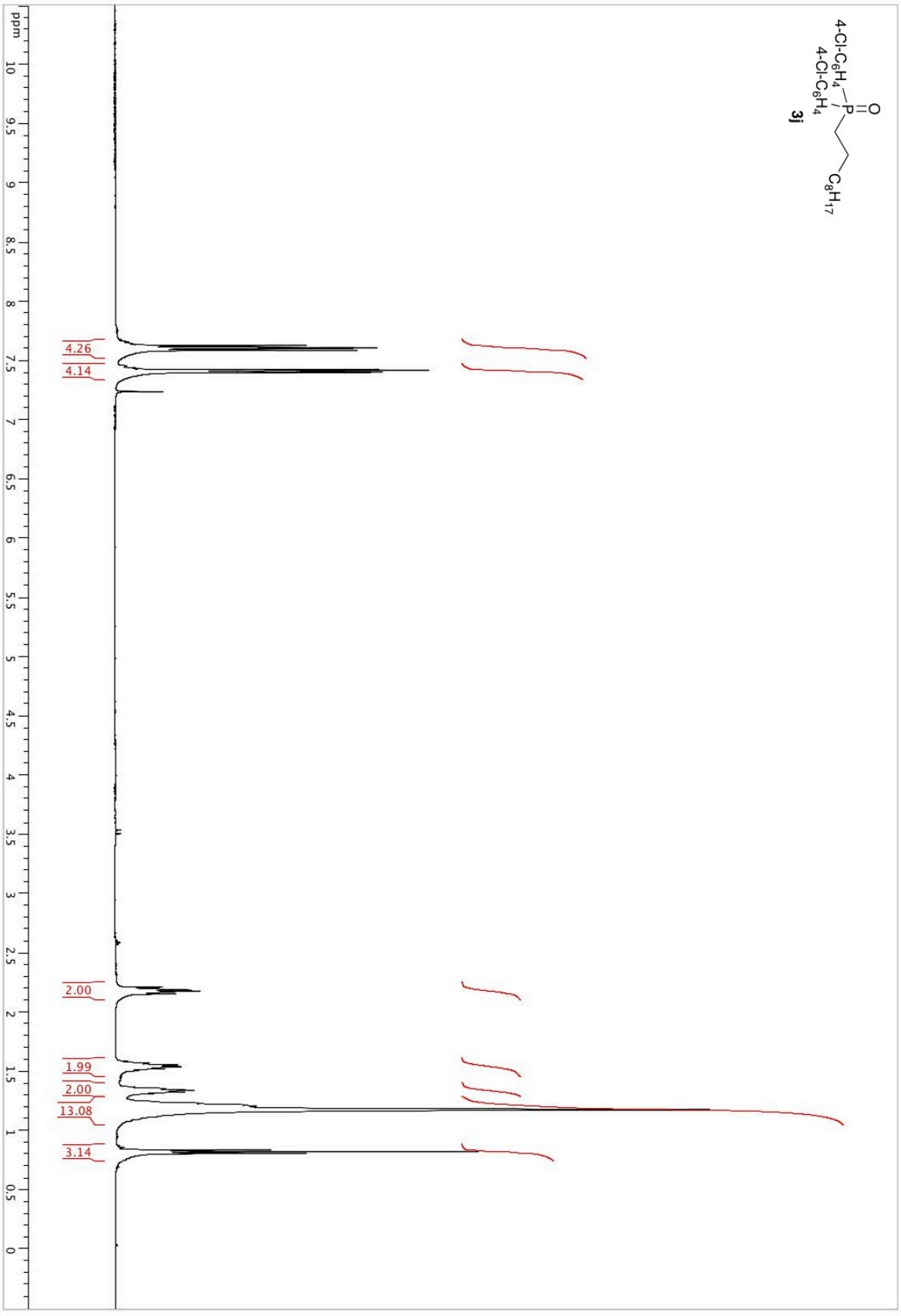

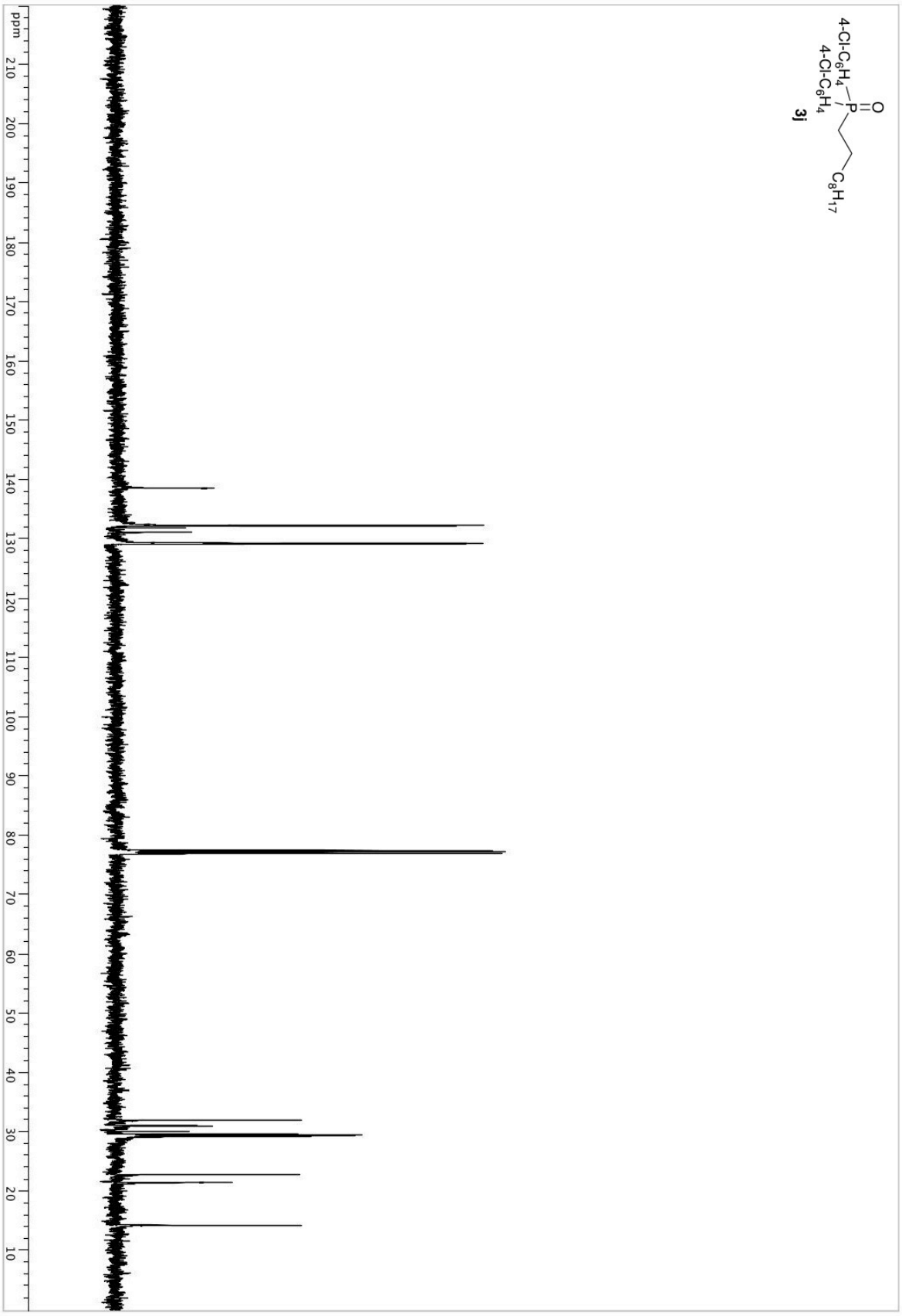
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C8H17
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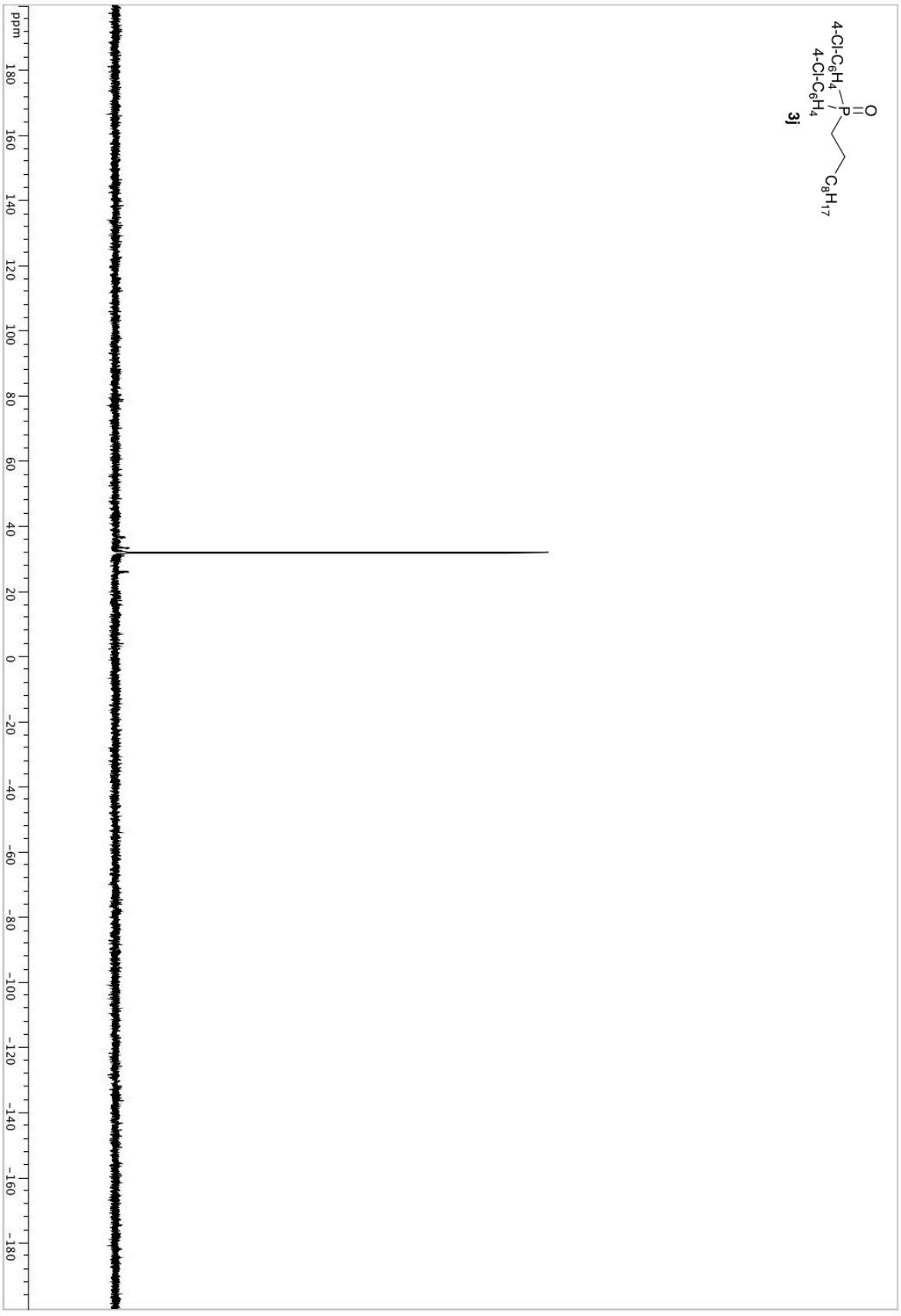

Part III: References

1. C. A. Busacca, J. C. Lorenz, N. Grinberg, N. Haddad, M. Hrapchak, B. Latli, H. Lee, P. Sabila, A. Saha, M. Sarvestani, S. Shen, R. Varsolona, X. Wei and C. H. Senanayake, *Org. Lett.*, 2005, **7**, 4277.
2. T. Hirai and L.-B. Han, *Org. Lett.*, 2007, **9**, 53.
3. S. Kawaguchi, A. Nomoto, M. Sonoda and A. Ogawa, *Tetrahedron Lett.*, 2009, **50**, 624.
4. S. Yamamoto, K. Okuma and H. Ohta, *Bull. Chem. Soc. Jpn.*, 1988, **61**, 4476.
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