Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Direct and Efficient Synthesis of Tetrasubstituted Allenyl organothiophosphates from Propargylic Alcohols under Catalyst- and Additive-Free Conditions

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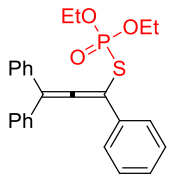
Table of Contents

General Remarks

Column chromatography was carried out on silica gel. ^{1}H NMR spectra were recorded on 400 MHz in $CDCl_3$ or DMSO and ^{13}C NMR spectra were recorded on 100 MHz in $CDCl_3$ or d-acetone. Chemical shifts (ppm) were recorded with tetramethylsilane (TMS) as the internal reference standard. Multiplicities are given as: s (singlet), d (doublet), t (triplet), dd (doublet of doublets), q (quartet) or m (multiplet). IR spectra were recorded on a FT-IR spectrometer and only major peaks are reported in cm^{-1}. HR-MS was obtained using a Q-TOF instrument equipped with ESI source. Copies of their ^{1}H NMR and ^{13}C NMR spectra are provided in the Supporting Information. Commercially available reagents were used without further purification. All solvents were dried under standard method.

General procedure for the preparation of product tetrasubstituted allenylorganothiophosphates 3: The mixture of propargylic alcohols (**1**) (0.1 mmol) and $(EtO)_2P(O)SH$ (0.2 mmol) was stirred in CH_3NO_2 (1.0 mL) at 60 °C under air. After 2.0 h, the completion of the reaction was monitored by TLC. Then, the solution was concentrated and the residue was purified by flash chromatography on silica gel to afford **3**.

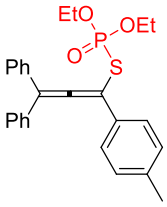
***O*,*O*-diethyl S-(1,3,3-triphenylpropa-1,2-dien-1-yl) phosphorothioate (3a):**



The resultant residue was purified by flash silica gel column chromatography (eluent: petroleum ether/EtOAc=50:1–10:1, v/v) to afford **3a**, white solid, mp: 118-120 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 1.00 (t, J = 7.2 Hz, 6 H), 3.83- 3.89 (m, 2 H), 4.02 – 4.08 (m, 2 H), 7.25 – 7.29 (m, 1 H), 7.33 – 7.40 (m, 8 H), 7.44 – 7.46 (m, 4 H), 7.71 (d, J = 7.6 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 15.6, 15.6, 63.8, 63.9, 98.0, 98.1, 113.3, 113.3, 127.0, 128.1, 128.3, 128.5, 128.6, 128.9,

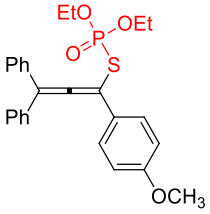
134.7, 211.6, 211.6. ^{31}P NMR (162 MHz, $CDCl_3$): δ 22.69. HRMS (ESI, m/z): calcd for $C_{25}H_{26}O_3PS$: M+H = 437.1335; found: 437.1331.

S-(3,3-diphenyl-1-(*p*-tolyl)propa-1,2-dien-1-yl) *O,O*-diethyl phosphorothioate (3b):



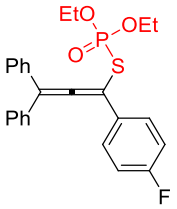
The resultant residue was purified by flash silica gel column chromatography (eluent: petroleum ether/EtOAc=50:1–10:1, v/v) to afford **3b**, colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 0.93 (t, *J* = 7.2 Hz, 6 H), 2.26 (s, 3 H), 3.76 – 3.84 (m, 2 H), 3.92 – 4.00 (m, 2 H), 7.07 – 7.09 (m, 2 H), 7.22 – 7.31 (m, 6 H), 7.36 – 7.37 (m, 4 H), 7.51 (d, *J* = 8.4 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): 15.6, 15.7, 21.1, 63.8, 63.9, 98.1, 98.2, 113.2, 113.3, 126.9, 128.2, 128.6, 128.9, 129.3, 131.8, 131.9, 135.0, 135.0, 138.2, 211.3, 211.3. ^{31}P NMR (162 MHz, $CDCl_3$): δ ppm 22.81. HRMS (ESI, m/z): calcd for $C_{26}H_{28}O_3PS$: M+H = 451.1491; found: 451.1485.

***O,O*-diethyl S-(1-(4-methoxyphenyl)-3,3-diphenylpropa-1,2-dien-1-yl) phosphorothioate (3c):**



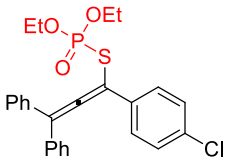
The resultant residue was purified by flash silica gel column chromatography (eluent: petroleum ether/EtOAc=30:1–10:1, v/v) to afford **3c**, yellow liquid.^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 1.02 (t, J = 7.2 Hz, 6 H), 3.81 (s, 3 H), 3.84 – 3.92 (m, 2 H), 4.00 – 4.10 (m, 2 H), 6.89 (d, *J* = 8.8 Hz, 2 H), 7.26 – 7.45 (m, 10 H), 7.63 (d, *J* = 8.8 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 15.6, 15.7, 55.4, 63.8, 63.9, 97.7, 113.1, 113.9, 126.9, 128.2, 128.3, 128.6, 128.9, 135.0, 135.0, 159.6, 211.0, 211.1. ^{31}P NMR (162 MHz, $CDCl_3$): δ ppm 22.74. HRMS (ESI, m/z): calcd for $C_{26}H_{28}O_4PS$: M+H = 467.1440; found: 467.1446.

***O,O*-diethyl S-(1-(4-fluorophenyl)-3,3-diphenylpropa-1,2-dien-1-yl) phosphorothioate (3d):**



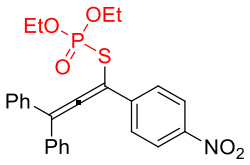
The resultant residue was purified by flash silica gel column chromatography (eluent: petroleum ether/EtOAc=50:1–10:1, v/v) to afford **3d**, yellow solid, mp: 86-88 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 1.03 (t, J = 7.2 Hz, 6 H), 3.83 – 3.93 (m, 2 H), 4.01 – 4.10 (m, 2 H), 7.05 (t, J = 8.4 Hz, 2 H), 7.32 – 7.45 (m, 10 H), 7.66 – 7.70 (m, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 15.7, 15.7, 63.9, 64.0, 97.2, 97.3, 113.4, 113.5, 115.4, 115.6, 128.4, 128.7, 128.8, 128.9, 128.9, 130.9, 134.7, 134.7, 161.4, 163.9, 211.4, 211.5. ^{31}P NMR (162 MHz, $CDCl_3$): δ ppm 22.42. HRMS (ESI, m/z): calcd for $C_{25}H_{24}FO_3PSNa$: M+Na = 477.1060; found: 477.1050.

S-(1-(4-chlorophenyl)-3,3-diphenylpropa-1,2-dien-1-yl) O,O-diethyl phosphorothioate (3e):



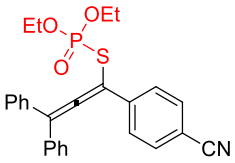
The resultant residue was purified by flash silica gel column chromatography (eluent: petroleum ether/EtOAc=50:1–10:1, v/v) to afford **3e**, yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 1.02 – 1.06 (m, 6 H), 3.83 – 3.93 (m, 2 H), 4.00 – 4.10 (m, 2 H), 7.31 – 7.44 (m, 12 H), 7.64 (d, J = 8.8 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 15.7, 15.8, 64.0, 64.0, 97.2, 97.3, 113.7, 113.7, 128.3, 128.5, 128.7, 128.9, 133.4, 134.0, 134.5, 134.5, 211.8, 211.8. ^{31}P NMR (162 MHz, $CDCl_3$): δ ppm 22.33. HRMS (ESI, m/z): calcd for $C_{25}H_{25}ClO_3PS$: M+H = 471.0945; found: 471.0947.

***O,O*-diethyl S-(1-(4-nitrophenyl)-3,3-diphenylpropa-1,2-dien-1-yl) phosphorothioate (3f):**



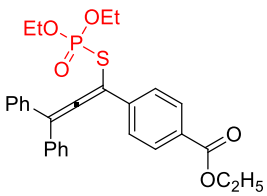
The resultant residue was purified by flash silica gel column chromatography (eluent: petroleum ether/EtOAc=30:1–10:1, v/v) to afford **3f**, yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 1.07 (t, J = 7.2 Hz, 6 H), 3.87 – 3.97 (m, 2 H), 4.02 – 4.12 (m, 2 H), 7.26 (s, 1 H), 7.37 – 7.45 (m, 9 H), 7.88 (d, J = 8.8 Hz, 2 H), 8.22 (d, J = 9.2 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 15.7, 15.8, 64.2, 64.3, 97.0, 114.4, 123.8, 127.8, 128.8, 128.9, 128.9, 133.8, 133.8, 141.8, 147.3, 213.7. ^{31}P NMR (162 MHz, $CDCl_3$): δ ppm 21.75. HRMS (ESI, m/z): calcd for $C_{25}H_{24}NO_5PSNa$: M+Na = 504.1005; found: 504.0997.

S-(1-(4-cyanophenyl)-3,3-diphenylpropa-1,2-dien-1-yl) *O,O*-diethyl phosphorothioate (3g):



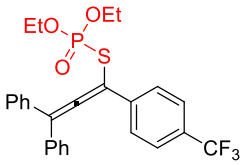
The resultant residue was purified by flash silica gel column chromatography (eluent: petroleum ether/EtOAc=30:1–10:1, v/v) to afford **3g**, yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 1.05 (t, J = 6.8 Hz, 6 H), 3.85 – 3.95 (m, 2 H), 4.01 – 4.11 (m, 2 H), 7.36 – 7.44 (m, 10 H), 7.64 (d, J = 8.4 Hz, 2 H), 7.82 (d, J = 8.4 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 15.7, 15.8, 64.1, 64.2, 97.1, 97.2, 111.5, 114.3, 118.7, 127.6, 128.8, 128.8, 128.9, 132.3, 133.9, 133.9, 139.8, 213.2. ^{31}P NMR (162 MHz, $CDCl_3$): δ ppm 21.81. HRMS (ESI, m/z): calcd for $C_{26}H_{24}NO_3PSNa$: M+Na = 484.1107; found: 484.1100.

Ethyl 4-(1-((diethoxyphosphoryl)thio)-3,3-diphenylpropa-1,2-dien-1-yl)benzoate (3h):



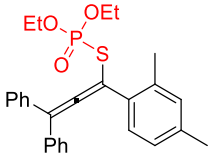
The resultant residue was purified by flash silica gel column chromatography (eluent: petroleum ether/EtOAc=30:1–10:1, v/v) to afford **3h**, yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 1.03 (t, *J* = 7.2 Hz, 6 H),1.39 (t, *J* = 7.2 Hz, 6 H), 3.83 – 3.93 (m, 2 H), 4.01 – 4.11 (m, 2 H), 4.37 (q, *J* = 6.8 Hz, 14.0 Hz, 2 H), 7.35 – 7.46 (m, 10 H), 7.78 (d, *J* = 8.4 Hz, 2 H), 8.03 (d, *J* = 8.4 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 14.3, 15.7, 15.7, 61.0, 64.0, 64.0, 97.6, 97.7, 113.8, 113.8, 126.9, 128.5, 128.7, 128.9, 129.8, 130.0, 134.3, 134.4, 139.4, 166.2, 212.7, 212.8. ^{31}P NMR (162 MHz, $CDCl_3$): δ pmm 22.28. HRMS (ESI, m/z): calcd for $C_{28}H_{29}O_5PSNa$: M+Na = 531.1366; found: 531.1370.

S-(3,3-diphenyl-1-(4-(trifluoromethyl)phenyl)propa-1,2-dien-1-yl) *O,O*-diethyl phosphorothioate (3i):



The resultant residue was purified by flash silica gel column chromatography (eluent: petroleum ether/EtOAc=50:1–10:1, v/v) to afford **3i**, yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 1.04 (t, *J* = 7.2 Hz, 6 H), 3.85 – 3.95 (m, 2 H), 4.01 – 4.11 (m, 2 H), 7.34 – 7.45 (m, 10 H), 7.61 (d, *J* = 8.4 Hz, 2 H), 7.83 (d, *J* = 8.0 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 15.7, 15.7, 64.0, 64.1, 97.2, 97.3, 114.0, 114.0, 122.7, 125.4, 125.5, 125.5, 129.8, 130.2, 134.2, 134.3, 138.7, 212.5. ^{31}P NMR (162 MHz, $CDCl_3$): δ ppm 22.08. HRMS (ESI, m/z): calcd for $C_{26}H_{24}F_3O_3PSNa$: M+Na = 527.1028; found: 527.1019.

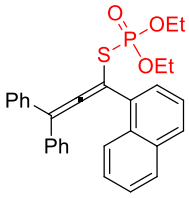
S-(1-(2,4-dimethylphenyl)-3,3-diphenylpropa-1,2-dien-1-yl) *O,O*-diethyl phosphorothioate (3j):



The resultant residue was purified by flash silica gel column chromatography (eluent: petroleum ether/EtOAc=50:1–10:1, v/v) to afford **3j**, yellow sold, mp: 72-74 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 1.05 (t, *J* = 7.2 Hz, 6 H), 2.24 (s, 3 H), 2.31 (s,

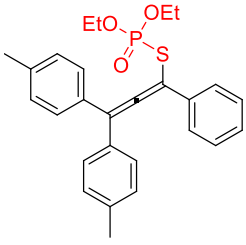
3 H), 3.72 – 3.82 (m, 2 H), 3.97 – 4.07 (m, 2 H), 6.98 (s, 1 H), 7.04 (d, *J* = 7.6 Hz, 1 H), 7.29 – 7.41 (m, 10 H), 7.49 (d, *J* = 7.6 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 15.6, 15.7, 20.5, 21.1, 63.6, 63.6, 96.1, 96.2, 110.9, 110.9, 126.6, 128.0, 128.5, 129.0, 129.5, 131.2, 132.4, 135.2, 135.2, 136.3, 138.1, 209.6, 209.6. ^{31}P NMR (162 MHz, $CDCl_3$): δ ppm 23.09. HRMS (ESI, m/z): calcd for $C_{27}H_{29}O_3PSNa$: M+Na = 487.1467; found: 487.1470.

***O,O*-diethyl S-(1-(naphthalen-1-yl)-3,3-diphenylpropa-1,2-dien-1-yl) phosphorothioate (3k):**



The resultant residue was purified by flash silica gel column chromatography (eluent: petroleum ether/EtOAc=50:1–10:1, v/v) to afford **3k**, yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 0.93 – 0.97 (m, 6 H), 3.63 – 3.73 (m, 2 H), 3.91 – 4.01 (m, 2 H), 7.31 – 7.52 (m, 13 H), 7.78 (d, *J* = 7.2 Hz, 1 H), 7.82 – 7.85 (m, 2 H), 8.09 (d, *J* = 8.4 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 15.5, 15.6, 63.6, 63.7, 95.2, 95.3, 111.4, 111.4, 125.3, 125.6, 126.1, 126.4, 127.5, 128.2, 128.4, 128.6, 129.0, 129.1, 130.7, 133.5, 133.5, 133.8, 135.1, 135.1, 210.2, 210.3. ^{31}P NMR (162 MHz, $CDCl_3$): δ ppm 22.59. HRMS (ESI, m/z): calcd for $C_{29}H_{28}O_3PS$: M+H = 487.1491; found: 487.1490.

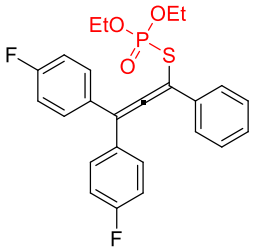
***O,O*-diethyl S-(1-phenyl-3,3-di-p-tolylpropa-1,2-dien-1-yl) phosphorothioate (3l):**



The resultant residue was purified by flash silica gel column chromatography (eluent: petroleum ether/EtOAc=50:1–10:1, v/v) to afford **3l**, yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 0.93 (t, *J* = 6.8 Hz, 6 H), 2.29 (s, 6 H), 3.76 – 3.84 (m, 2

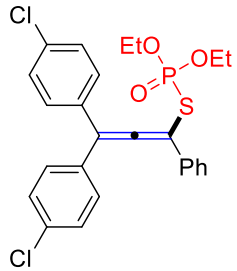
H), 3.93 – 4.03 (m, 2 H), 7.09 – 7.12 (m, 4 H), 7.18 – 7.20 (m, 1 H), 7.25 – 7.29 (m, 6 H), 7.62 (d, J = 7.6 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 15.6, 15.7, 21.2, 63.8, 63.9, 97.6, 97.6, 113.2, 127.0, 128.0, 128.5, 128.8, 129.3, 131.9, 131.9, 135.1, 138.2, 211.6, 211.7. ^{31}P NMR (162 MHz, $CDCl_3$): δ ppm 22.93. HRMS (ESI, m/z): calcd for $C_{27}H_{30}O_3PS$: M+H = 465.1648; found: 465.1647.

S-(3,3-bis(4-fluorophenyl)-1-phenylpropa-1,2-dien-1-yl) *O*,*O*-diethyl phosphorothioate (3m):



The resultant residue was purified by flash silica gel column chromatography (eluent: petroleum ether/EtOAc=50:1–10:1, v/v) to afford **3m**, yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 1.04 (t, J = 6.8 Hz, 6 H), 3.85 – 3.95 (m, 2 H), 4.05 – 4.10 (m, 2 H), 7.08 (t, J = 8.4 Hz, 4 H), 7.26 – 7.31 (m, 1 H), 7.35 – 7.43. (m, 6 H), 7.67 (d, J = 7.6 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 15.6, 15.7, 63.8, 63.9, 98.2, 98.3, 112.4, 112.5, 115.5, 115.7, 126.9, 128.2, 128.4, 128.6, 128.7, 128.8, 130.5, 130.6, 134.6, 161.4, 163.9, 211.3, 211.4. ^{31}P NMR (162 MHz, $CDCl_3$): δ ppm 22.57. HRMS (ESI, m/z): calcd for $C_{25}H_{24}F_2O_3PS$: M+H = 473.1146; found: 473.1146.

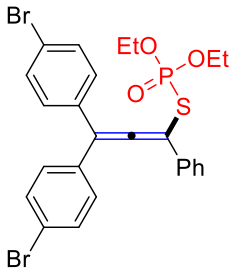
***S*-(3,3-bis(4-chlorophenyl)-1-phenylpropa-1,2-dien-1-yl) *O*,*O*-diethyl phosphorothioate (3n):**



The resultant residue was purified by flash silica gel column chromatography (eluent: petroleum ether/EtOAc=50:1–10:1, v/v) to afford **3n**, colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 1.05 (t, J = 7.2 Hz, 6 H), 3.85 - 3.95 (m, 2 H), 4.03 - 4.12 (m, 2

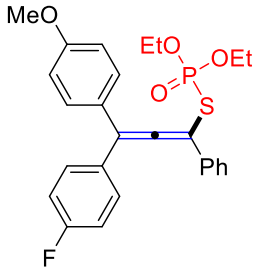
H), 7.26 - 7.39 (m, 11 H), 7.66 (d, *J* = 7.6 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 15.6, 15.7, 64.0, 64.1, 98.9, 99.0, 111.6, 111.7, 126.9, 128.5, 128.7, 129.0, 130.0, 132.9, 132.9, 134.1, 134.4, 211.1, 211.2. ^{31}P NMR (162 MHz, $CDCl_3$): δ ppm 22.52. HRMS (ESI, m/z): calcd for $C_{25}H_{24}Cl_2O_3PS$: M+H = 505.0555; found: 505.0550.

***S*-(3,3-bis(4-bromophenyl)-1-phenylpropa-1,2-dien-1-yl) *O*,*O*-diethyl phosphorothioate (3o):**



The resultant residue was purified by flash silica gel column chromatography (eluent: petroleum ether/EtOAc=50:1–10:1, v/v) to afford **3o**, colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 1.05 (t, *J* = 6.8 Hz, 6 H), 3.84 - 3.94 (m, 2 H), 4.02 - 4.12 (m, 2 H), 7.26 - 7.31 (m, 5 H), 7.35 - 7.39 (m, 2 H), 7.51 (d, *J* = 8.4 Hz, 4 H), 7.65 (d, *J* = 7.6 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 15.7, 15.7, 63.9, 64.0, 99.1, 99.1, 111.7, 111.7, 112.5, 126.9, 128.5, 128.6, 130.3, 131.9, 133.3, 133.3, 134.1, 211.0, 211.1. ^{31}P NMR (162 MHz, $CDCl_3$): δ ppm 22.34. HRMS (ESI, m/z): calcd for $C_{25}H_{23}Br_2O_3PSNa$: M+Na = 614.9364; found: 614.9356.

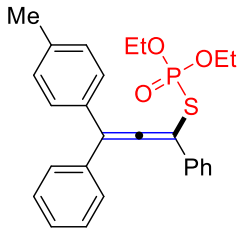
***O*,*O*-diethyl *S*-(3-(4-fluorophenyl)-3-(4-methoxyphenyl)-1-phenylpro pa-1,2-dien-1-yl) phosphorothioate (3p):**



The resultant residue was purified by flash silica gel column chromatography (eluent: petroleum ether/EtOAc=50:1–10:1, v/v) to afford **3p**, yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 1.03 (t, *J* = 7.2 Hz, 6 H), 3.78 - 3.92 (m, 5 H), 4.04 - 4.10 (m, 2 H), 6.92 (d, *J* = 8.4 Hz, 2 H), 7.07 (t, *J* = 8.4 Hz, 2 H), 7.26 - 7.45 (m, 7 H), 7.69 (d, *J*

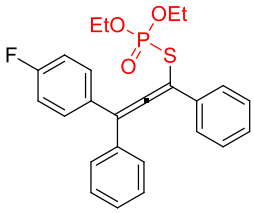
= 7.6 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 15.6, 15.7, 55.3, 63.8, 63.9, 97.9, 97.9, 112.2, 112.2, 114.1, 115.5, 115.7, 126.6, 126.9, 128.1, 128.5, 130.0, 130.5, 134.9, 159.8, 161.4, 163.9, 211.3, 211.3. ^{31}P NMR (162 MHz, $CDCl_3$): δ ppm 22.84. HRMS (ESI, m/z): calcd for $C_{26}H_{26}O_4FPSNa$: M+Na = 507.1166; found: 507.1160.

***S*-(1,3-diphenyl-3-(*p*-tolyl)propa-1,2-dien-1-yl) *O*,*O*-diethyl phosphorothioate (3q):**



The resultant residue was purified by flash silica gel column chromatography (eluent: petroleum ether/EtOAc=50:1–10:1, v/v) to afford **3q**, colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 1.00 (t, *J* = 7.2 Hz, 6 H), 2.37 (s, 3 H), 3.81 - 3.91 (m, 2 H), 4.01 - 4.10 (m, 2 H), 7.18 - 7.20 (m, 2 H), 7.25 - 7.39 (m, 8 H), 7.44 - 7.46 (m, 2 H), 7.71 (d, *J* = 7.6 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 15.5, 15.6, 21.2, 63.7, 63.8, 97.8, 97.8, 113.2, 113.2, 126.9, 128.0, 128.2, 128.5, 128.5, 128.7, 128.9, 129.3, 131.6, 131.7, 134.9, 138.2, 211.6, 211.6. ^{31}P NMR (162 MHz, $CDCl_3$): δ ppm 22.83. HRMS (ESI, m/z): calcd for $C_{26}H_{28}O_3PS$: M+H = 451.1491; found: 451.1485.

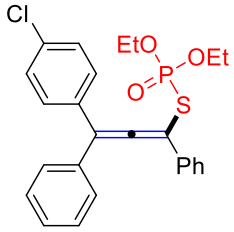
***O*,*O*-diethyl S-(3-(4-fluorophenyl)-1,3-diphenylpropa-1,2-dien-1-yl) phosphorothioate (3r):**



The resultant residue was purified by flash silica gel column chromatography (eluent: petroleum ether/EtOAc=50:1–10:1, v/v) to afford **3r**, colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 1.00 – 1.04 (m, 6 H), 3.82 – 3.93 (m, 2 H), 4.01 – 4.11 (m, 2 H), 7.08 (t, *J* = 8.8 Hz, 2 H), 7.26 – 7.44 (m, 10 H), 7.69 (d, *J* = 7.6 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 15.6, 15.7, 63.8, 63.9, 98.2, 98.3, 112.4, 112.5, 115.5, 115.7, 126.9, 128.2, 128.4, 128.6, 128.7, 128.8, 130.5, 130.6, 134.6, 161.4, 163.9, 211.3, 211.4. ^{31}P NMR (162 MHz, $CDCl_3$): δ ppm 22.63.

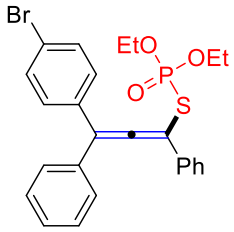
$C_{25}H_{24}FO_3PSNa$: M+Na = 477.1060; found: 477.1050.

***S*-(3-(4-chlorophenyl)-1,3-diphenylpropa-1,2-dien-1-yl) *O*,*O*-diethyl phosphorothioate (3s):**



The resultant residue was purified by flash silica gel column chromatography (eluent: petroleum ether/EtOAc=50:1–10:1, v/v) to afford **3s**, colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 1.00 - 1.04 (m, 6 H), 3.83 - 3.93 (m, 2 H), 4.02 - 4.11 (m, 2 H), 7.26 - 7.43 (m, 12 H), 7.68 (d, *J* = 7.6 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 15.6, 15.7, 63.9, 64.0, 98.4, 98.5, 112.4, 112.5, 127.0, 128.3, 128.5, 128.6, 128.7, 128.8, 128.8, 130.1, 133.2, 133.3, 134.1, 134.3, 134.4, 134.4, 211.3, 211.4. ^{31}P NMR (162 MHz, $CDCl_3$): δ ppm 22.62. HRMS (ESI, m/z): calcd for $C_{25}H_{25}ClO_3PS$: M+H = 471.0945; found: 471.0947.

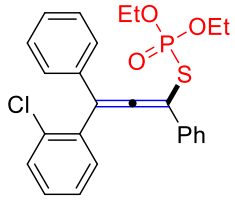
***S*-(3-(4-bromophenyl)-1,3-diphenylpropa-1,2-dien-1-yl) *O*,*O*-diethyl phosphorothioate (3t):**



The resultant residue was purified by flash silica gel column chromatography (eluent: petroleum ether/EtOAc=50:1–10:1, v/v) to afford **3t**, colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 1.00 - 1.04 (m, 6 H), 3.83 - 3.92 (m, 2 H), 4.01 - 4.11 (m, 2 H), 7.26 - 7.41 (m, 10 H), 7.43 - 7.52 (m, 2 H), 7.68 (d, *J* = 7.2 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 15.6, 15.7, 63.9, 63.9, 98.5, 98.6, 112.5, 112.5, 122.3, 127.0, 128.3, 128.5, 128.6, 128.7, 128.8, 130.4, 131.8, 133.8, 134.3, 134.3, 134.4, 211.3, 211.4. ^{31}P NMR (162 MHz, $CDCl_3$): δ ppm 22.58. HRMS (ESI, m/z): calcd for $C_{25}H_{25}BrO_3PS$: M+H = 515.0440; found: 515.0446.

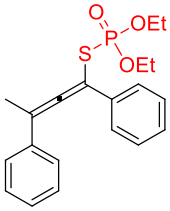
***S*-(3-(2-chlorophenyl)-1,3-diphenylpropa-1,2-dien-1-yl) *O*,*O*-diethyl**

phosphorothioate (3u):



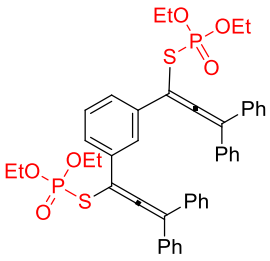
The resultant residue was purified by flash silica gel column chromatography (eluent: petroleum ether/EtOAc=50:1–10:1, v/v) to afford **3u**, yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 1.02 (t, *J* = 6.8 Hz, 6 H), 3.88 - 3.96 (m, 2 H), 4.05 - 4.13 (m, 2 H), 7.26 - 7.38 (m, 10 H), 7.45 - 7.48 (m, 2 H), 7.73 (d, *J* = 7.2 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 15.6, 15.6, 15.6, 15.7, 63.8, 63.8, 63.9, 64.0, 98.6, 98.7, 110.2, 110.2, 127.0, 127.2, 127.4, 128.1, 128.2, 128.5, 128.7, 129.6, 130.0, 131.8, 133.7, 133.7, 133.9, 134.0, 134.0, 134.5, 210.4, 210.5. ^{31}P NMR (162 MHz, $CDCl_3$): δ ppm 22.64. HRMS (ESI, m/z): calcd for $C_{25}H_{25}ClO_3PS$: M+H = 471.0945; found: 471.0949.

S-(1,3-diphenylbuta-1,2-dien-1-yl)*O,O*-diethyl phosphorothioate (3v):



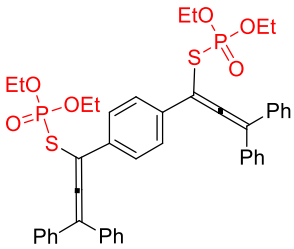
The resultant residue was purified by flash silica gel column chromatography (eluent: petroleum ether/EtOAc=50:1–10:1, v/v) to afford **3v**, colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 1.10 (t, *J* = 6.8 Hz, 3 H), 1.17 (t, *J* = 7.2 Hz, 3 H), 2.29 (s, 3 H), 3.93 – 4.03 (m, 2 H), 4.10 – 4.19 (m, 2 H), 7.26 – 7.29 (m, 2 H), 7.32 – 7.39 (m, 4 H), 7.49 (d, *J* = 7.6 Hz, 2 H), 7.63 (d, *J* = 7.6 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 15.7, 15.8, 15.9, 16.3, 16.3, 63.8, 63.8, 63.8, 63.9, 96.4, 96.5, 105.3, 105.3, 126.5, 127.0, 127.9, 127.9, 128.5, 128.6, 134.9, 134.9, 135.4, 210.4, 210.5. ^{31}P NMR (162 MHz, $CDCl_3$): δ ppm 23.38. HRMS (ESI, m/z): calcd for $C_{20}H_{24}O_3PS$: M+H = 375.1178; found: 375.1179.

S,S'-(1,3-phenylenebis(3,3-diphenylpropa-1,2-diene-1,1-diyl)) O,O,O',O'-tetraethyl diphosphorothioate (3aa):



The resultant residue was purified by flash silica gel column chromatography (eluent: petroleum ether/EtOAc=30:1–5:1, v/v) to afford **3aa**, colorless liquid. ^{1}H NMR (400 MHz, DMSO): δ ppm 0.91 (t, *J* = 6.8 Hz, 12 H), 3.79 – 3.89 (m, 4 H), 3.91 – 4.00 (m, 4 H), 7.25 – 7.28 (m, 8 H), 7.33 – 7.43 (m, 12 H), 7.56 (t, *J* = 8.0 Hz, 1 H), 7.67 – 7.69 (m, 2 H), 7.97 (s, 1 H). ^{13}C NMR (100 MHz, DMSO): δ ppm 20.6, 20.7, 68.9, 69.0, 102.3, 102.4, 118.5, 120.4, 131.7, 133.5, 133.8, 134.1, 134.6, 134.9, 139.0, 139.0, 139.7, 216.3. ^{31}P NMR (162 MHz, DMSO): δ ppm 20.72. HRMS (ESI, m/z): calcd for $C_{44}H_{45}O_6P_2S_2$: M+H = 795.2127; found: 795.2127.

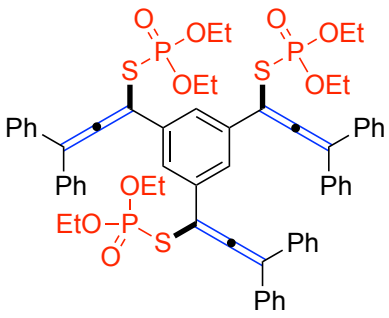
S,S'-(1,4-phenylenebis(3,3-diphenylpropa-1,2-diene-1,1-diyl)) O,O,O',O'-tetraethyl diphosphorothioate (3ab):



The resultant residue was purified by flash silica gel column chromatography (eluent: petroleum ether/EtOAc=30:1–5:1, v/v) to afford **3ab**, yellow solid, mp: 155-157 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 1.03 (t, *J* = 6.8 Hz, 12 H), 3.84 – 3.94 (m, 4 H), 4.01 – 4.11 (m, 4 H), 7.31 – 7.44 (m, 20 H), 7.71 (s, 4 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 15.7, 15.7, 63.9, 64.0, 97.7, 97.8, 113.7, 127.1, 128.4, 128.6, 128.9, 134.6, 212.0, 212.0. ^{31}P NMR (162 MHz, $CDCl_3$): δ ppm 20.33. HRMS (ESI, m/z): calcd for $C_{44}H_{45}O_6P_2S_2$: M+H = 795.2127; found: 795.2131.

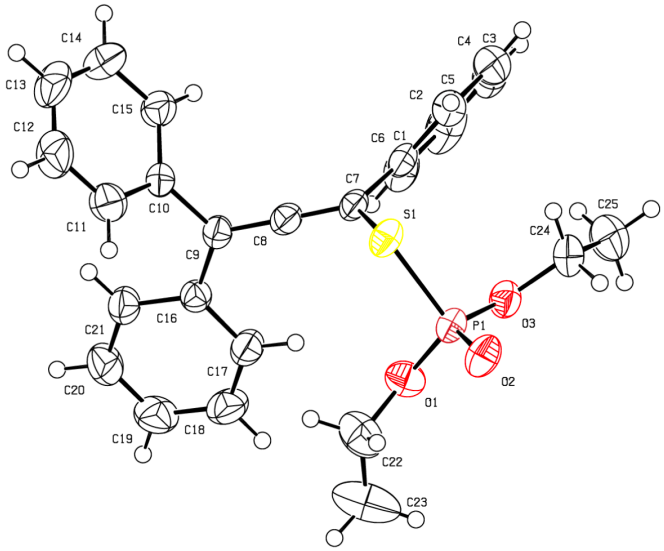
***S,S',S''*-(benzene-1,3,5-triyltris(3,3-diphenylpropa-1,2-diene-1,1-diyl))**

***O,O,O',O',O'',O''*-hexaethyl tris(phosphorothioate) (3ac):**



The resultant residue was purified by flash silica gel column chromatography (eluent: petroleum ether/EtOAc=30:1–5:1, v/v) to afford **3ac**, colorless liquid. ^{1}H NMR (400 MHz, DMSO): δ ppm 0.81 - 0.85 (m, 18 H), 3.67 - 3.74 (m, 6 H), 3.85 - 3.92 (m, 6 H), 7.17 - 7.25 (m, 30 H), 7.98 (d, *J* = 3.6 Hz, 3 H). ^{13}C NMR (100 MHz, DMSO): δ ppm 15.5, 15.6, 63.8, 63.8, 97.3, 97.4, 113.9, 113.9, 124.7, 128.3, 128.6, 128.8, 134.3, 135.5, 211.9, 212.0. ^{31}P NMR (162 MHz, DMSO): δ ppm 21.49. HRMS (ESI, m/z): calcd for $C_{63}H_{63}O_9P_3S_3$: M+H = 1153.2920; found: 1153.2922.

Crystal preparation and X-ray diffraction analysis of compound 3a



X-ray structure of 3a

Datablock: 1

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Cell:          a=9.7821(15)       b=10.8018(16)    c=12.4788(19)
               alpha=106.814(2)   beta=97.289(2)   gamma=108.910(2)
Temperature:   296 K

                 Calculated                Reported
Volume           1158.1(3)                 1158.1(3)
Space group      P -1                      P -1
Hall group       -P 1                      -P 1
Moiety formula   C25 H25 O3 P S            ?
Sum formula      C25 H25 O3 P S            C25 H25 O3 P S
Mr               436.48                    436.48
Dx,g cm-3        1.252                     1.252
Z                2                         2
Mu (mm-1)        0.232                     0.232
F000             460.0                     460.0
F000'            460.63
h,k,lmax         11,12,14                  11,12,14
Nref             4084                      4044
Tmin,Tmax        0.941,0.952
Tmin'            0.941

Correction method= Not given

Data completeness= 0.990          Theta(max)= 24.997

R(reflections)= 0.0350( 3587)     wR2(reflections)= 0.1014( 4044)

S = 1.038                 Npar= 274
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The following ALERTS were generated. Each ALERT has the format
      test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.
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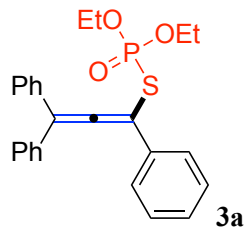
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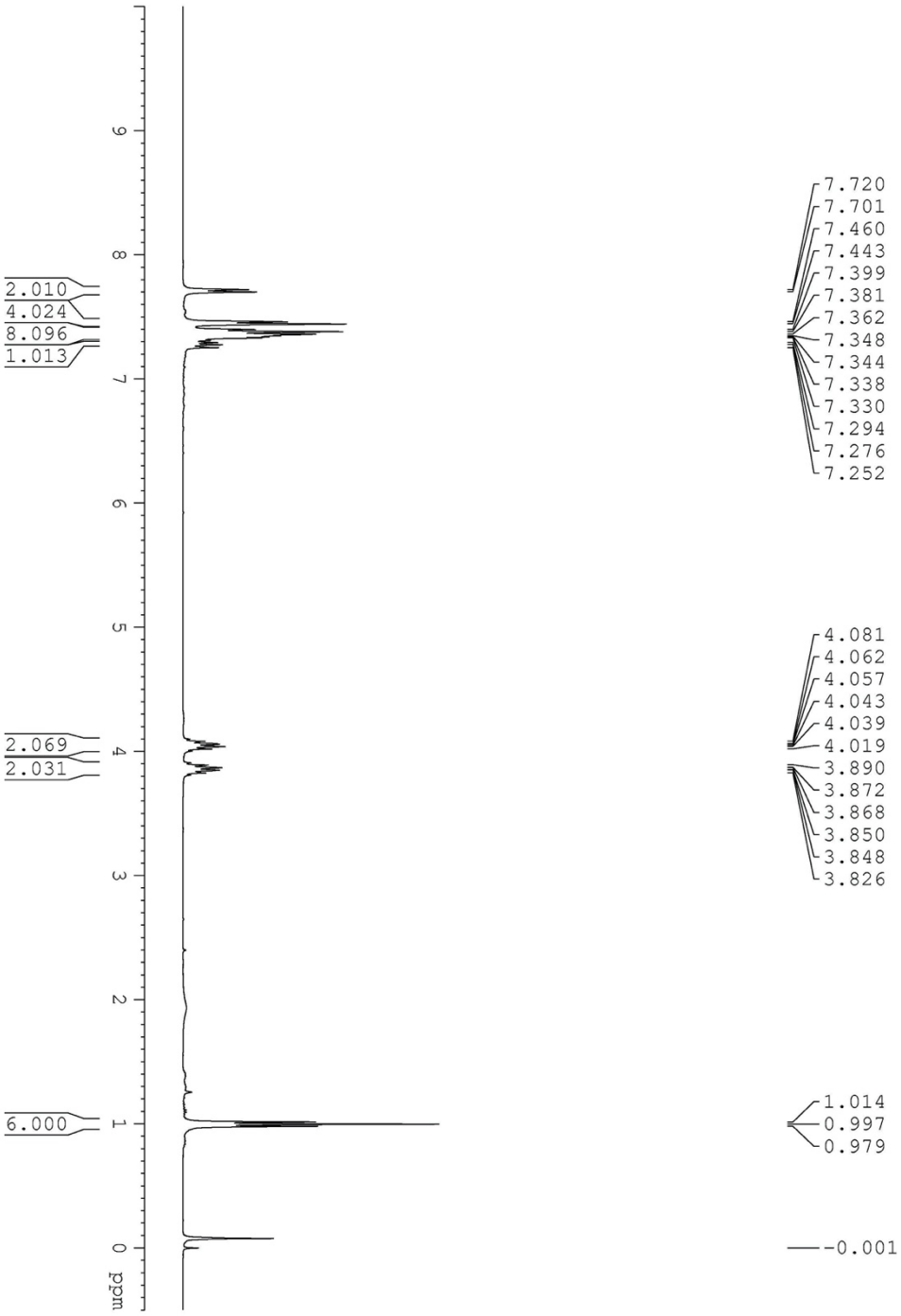
OEt
O
P
S
Ph
Ph

3a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4.062
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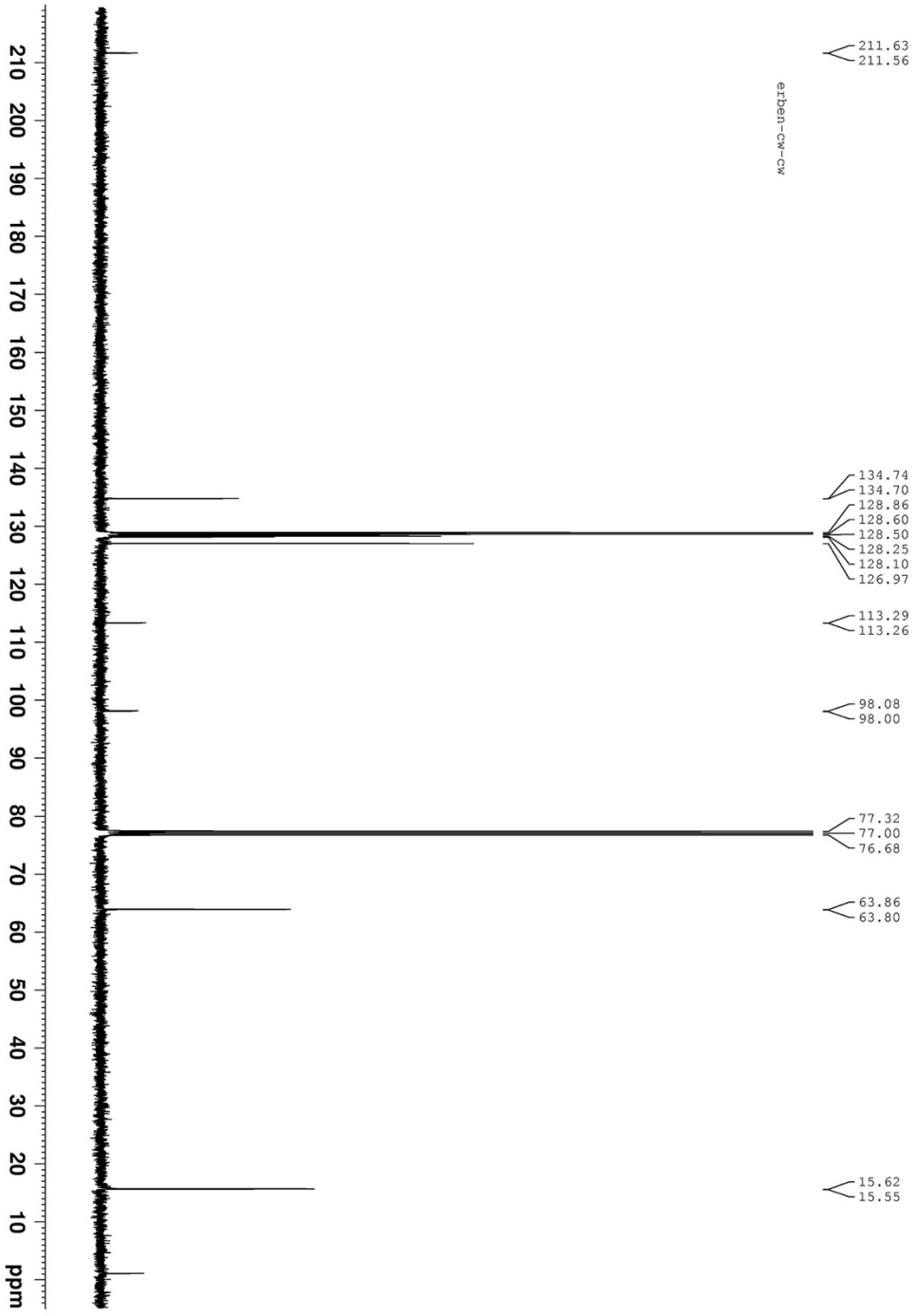
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113.26
98.08
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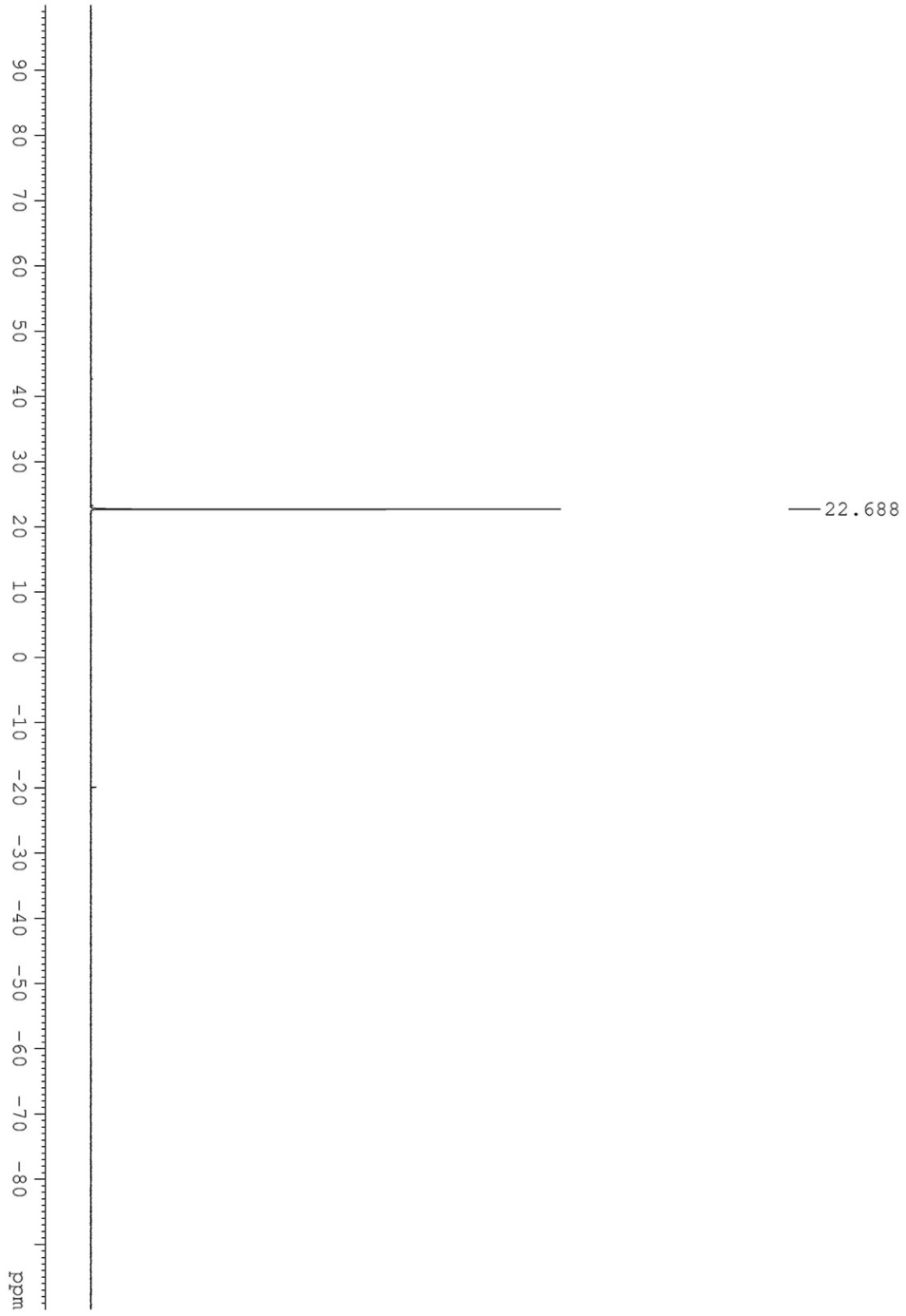
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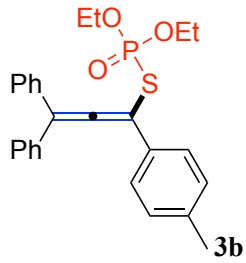
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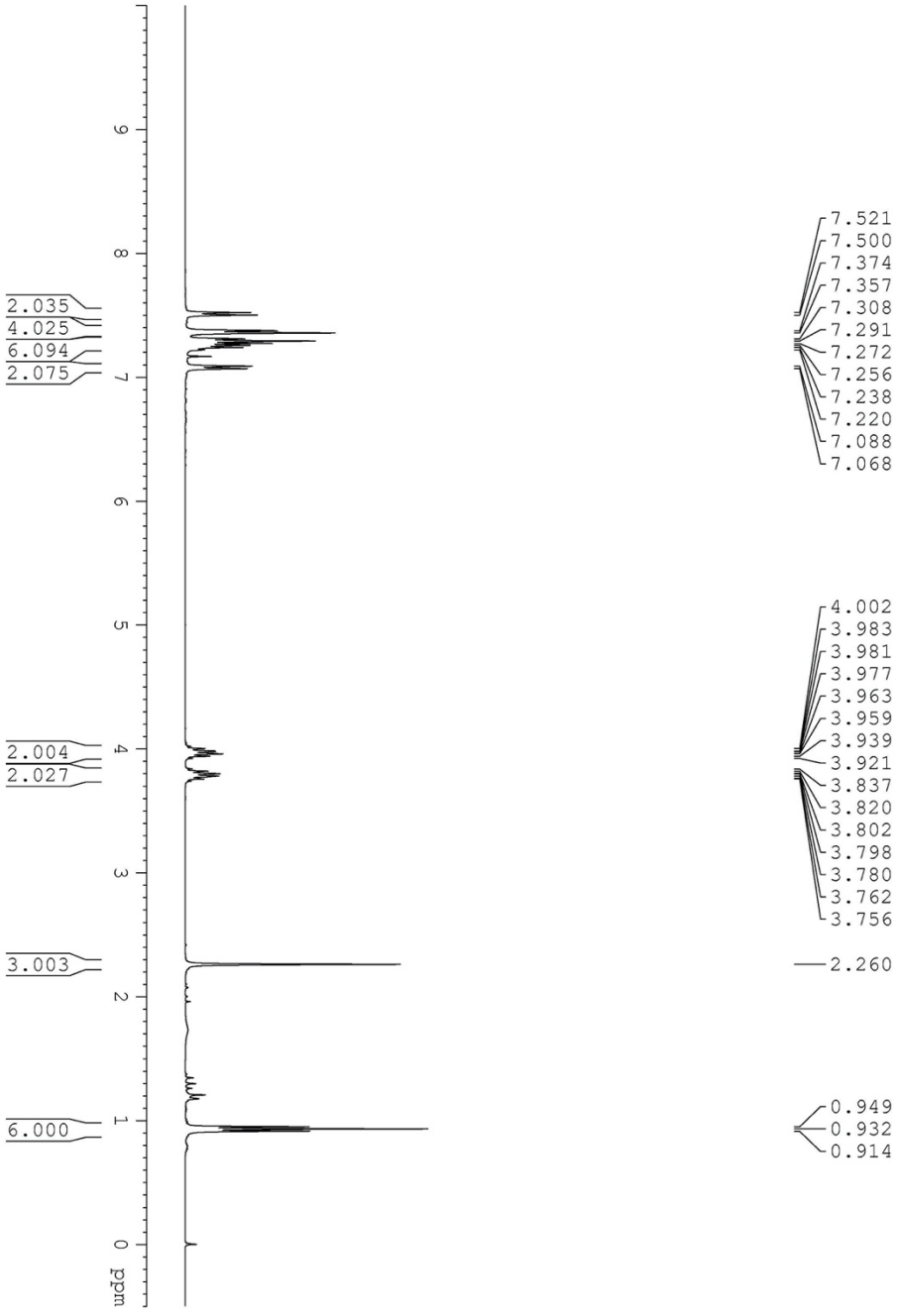
Ph
Ph

3b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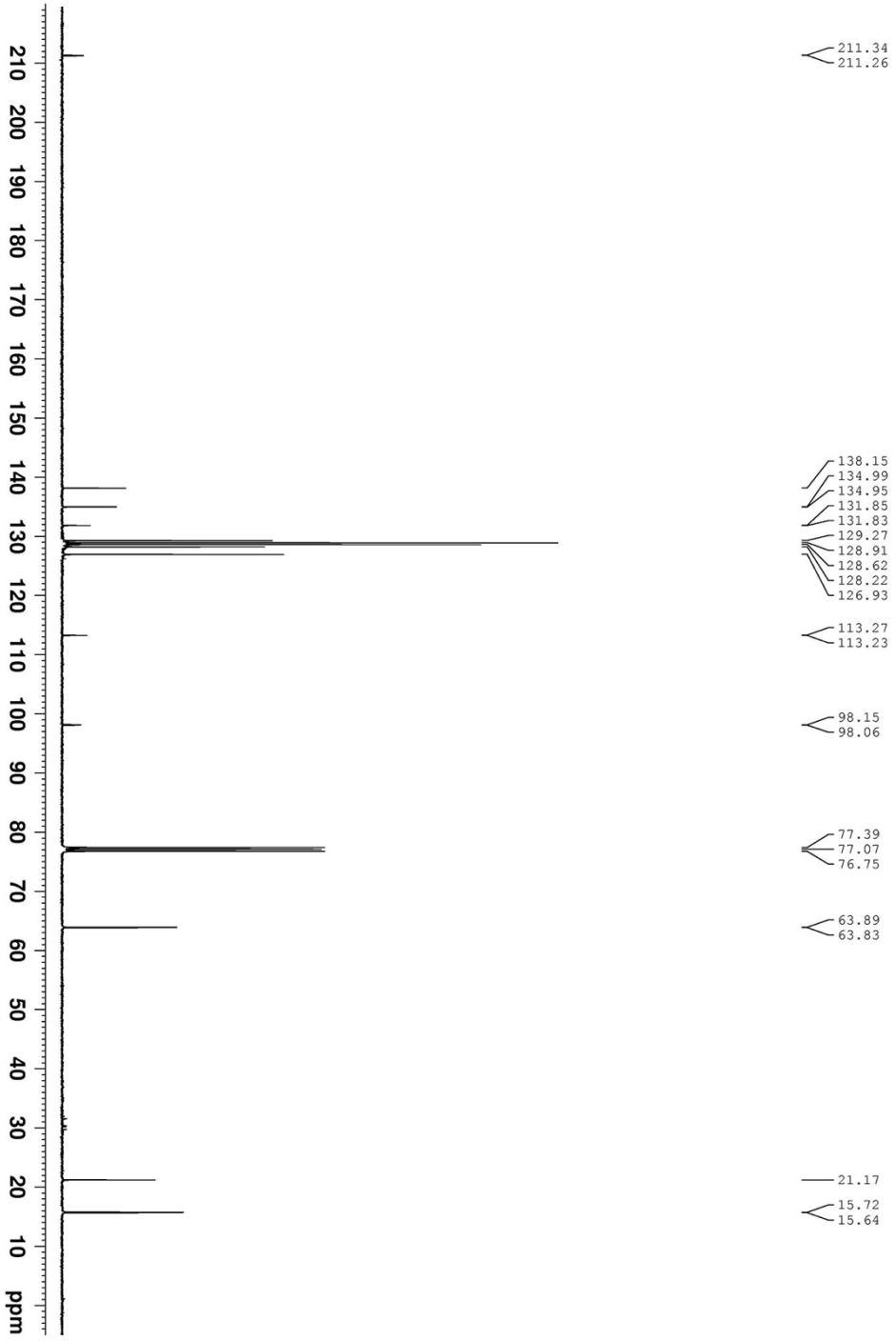
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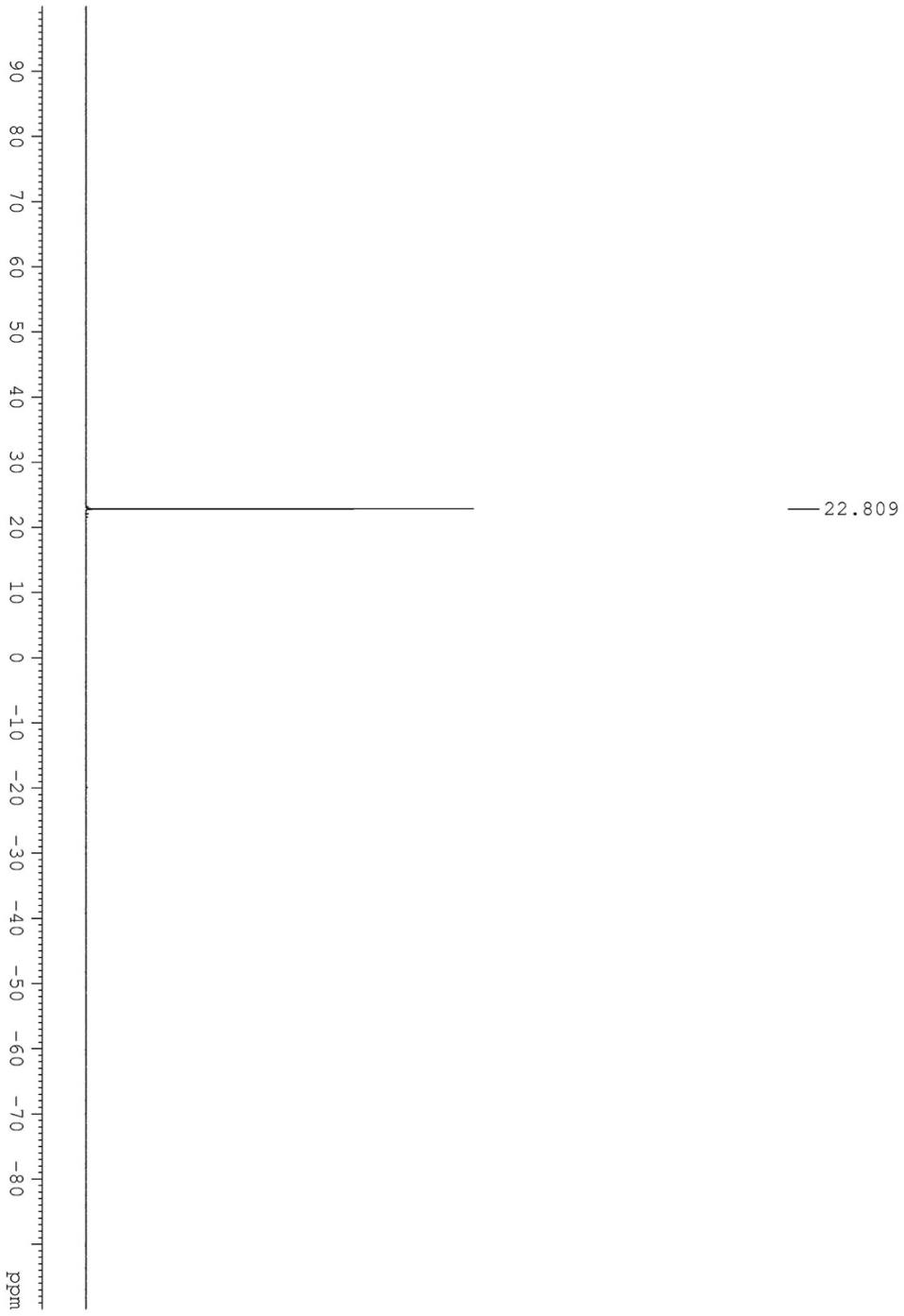
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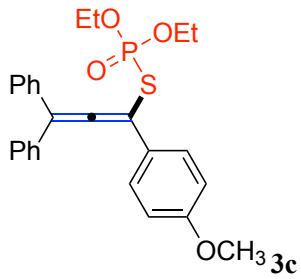
ppm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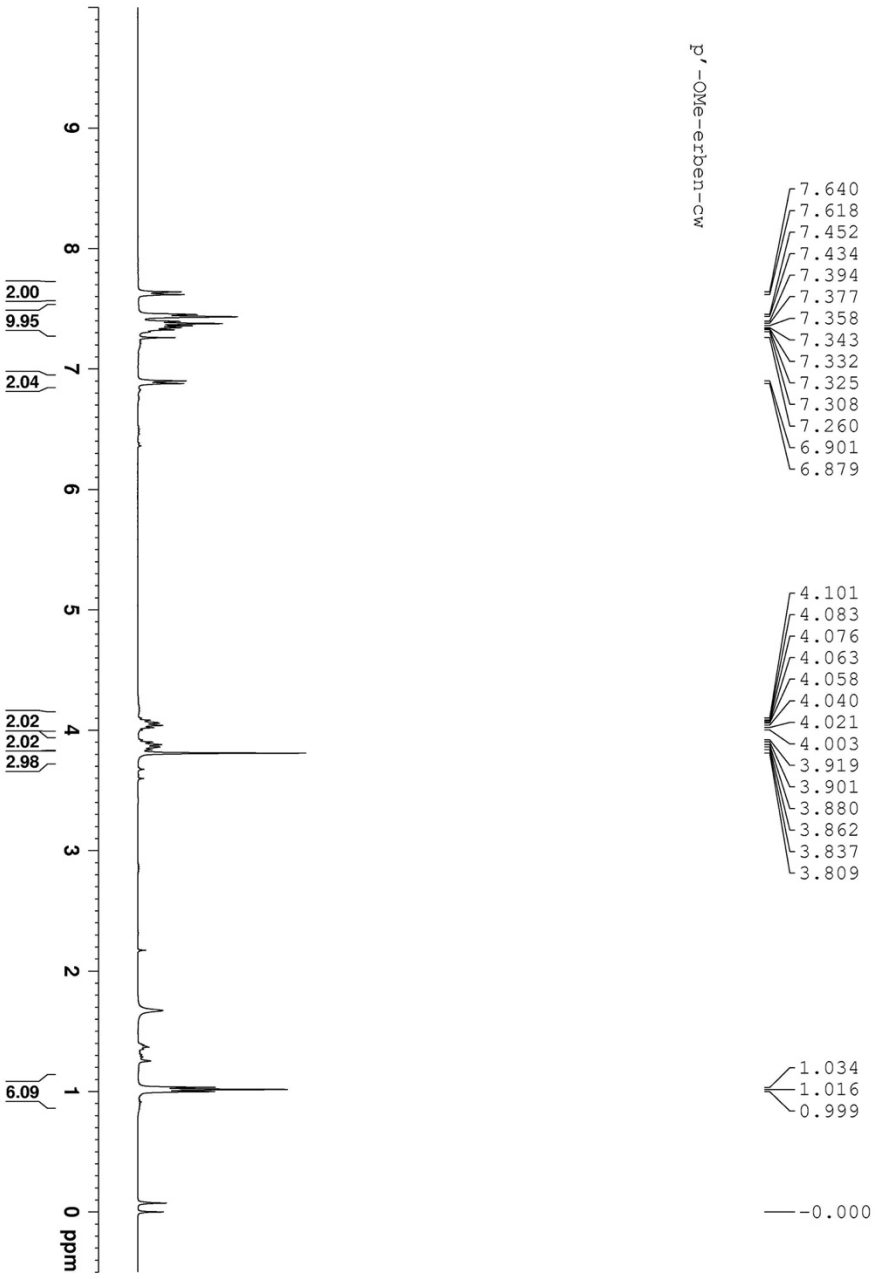
OCH3

3c


p'-OMe-erben-cw
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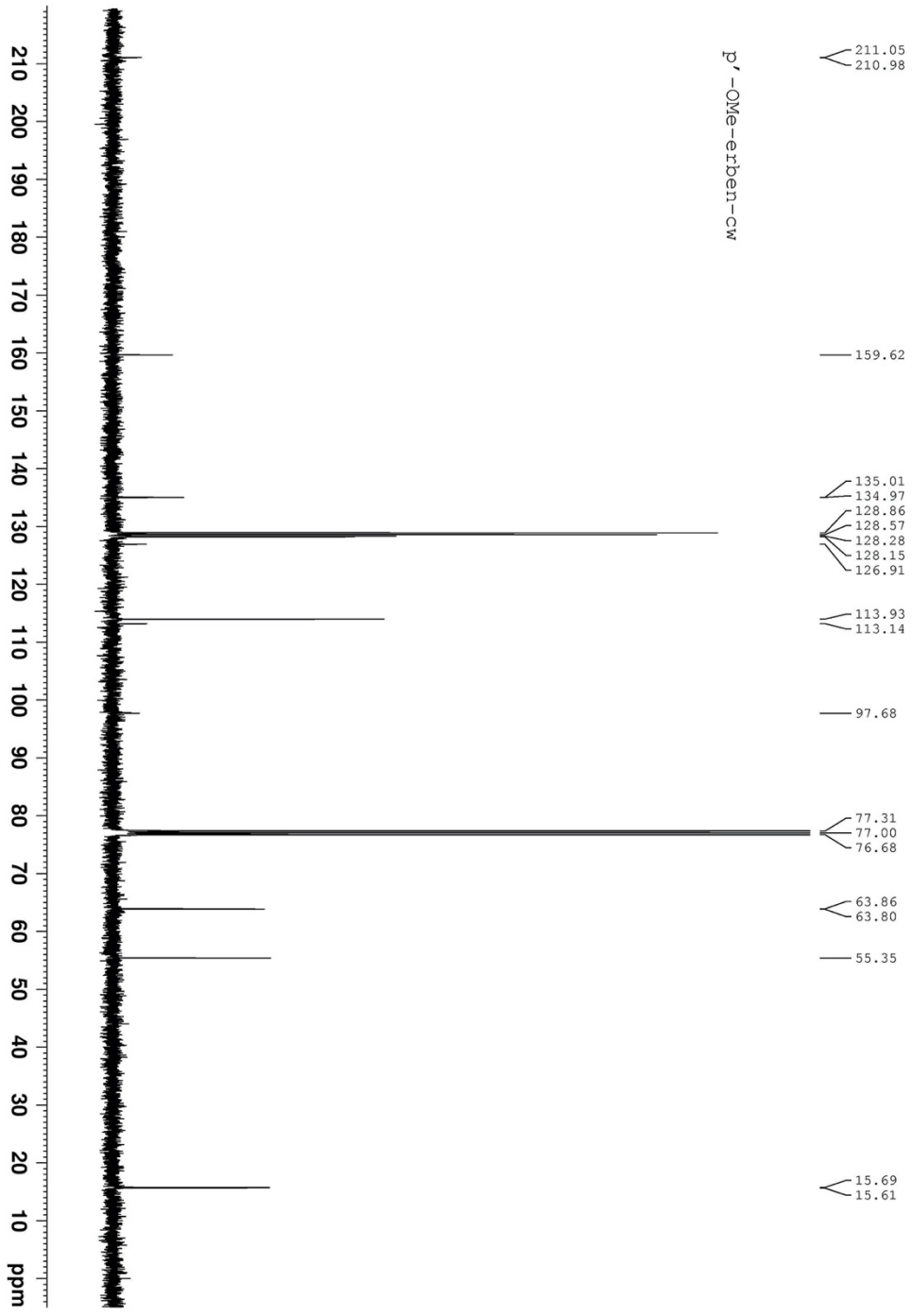
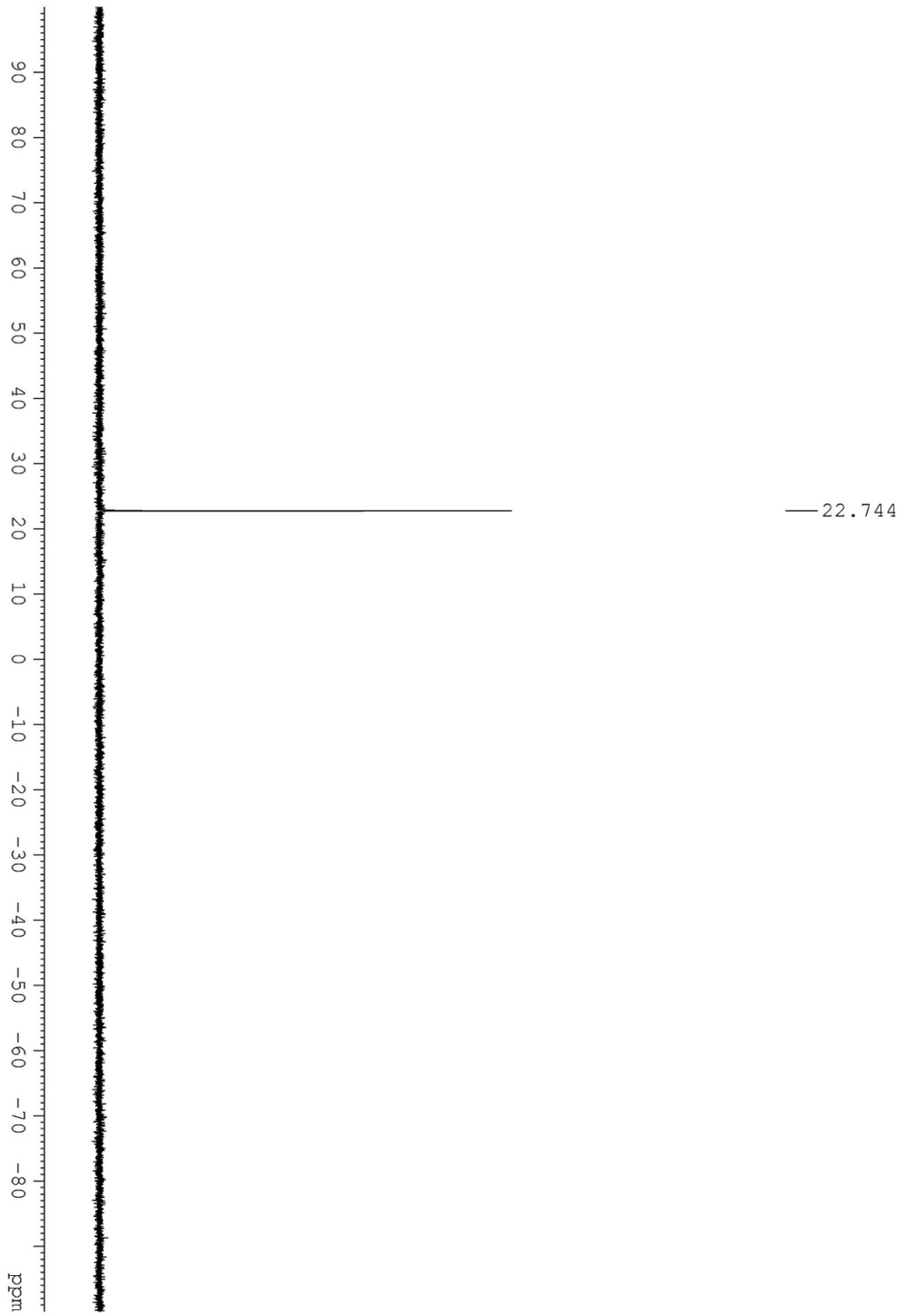
9.95
2.04
2.02
2.02
2.98
6.09
ppm
7.640
7.618
7.452
7.434
7.394
7.377
7.358
7.343
7.332
7.325
7.308
7.260
6.901
6.879
4.101
4.083
4.076
4.063
4.058
4.040
4.021
4.003
3.919
3.901
3.880
3.862
3.837
3.809
1.034
1.016
0.999
-0.000


p'-OMe-erben-cw
211.05
210.98
159.62
135.01
134.97
128.86
128.57
128.28
128.15
126.91
113.93
113.14
97.68
77.31
77.00
76.68
63.86
63.80
55.35
15.69
15.61
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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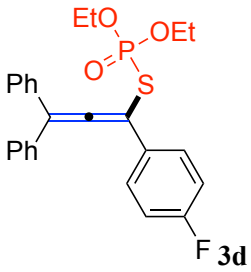
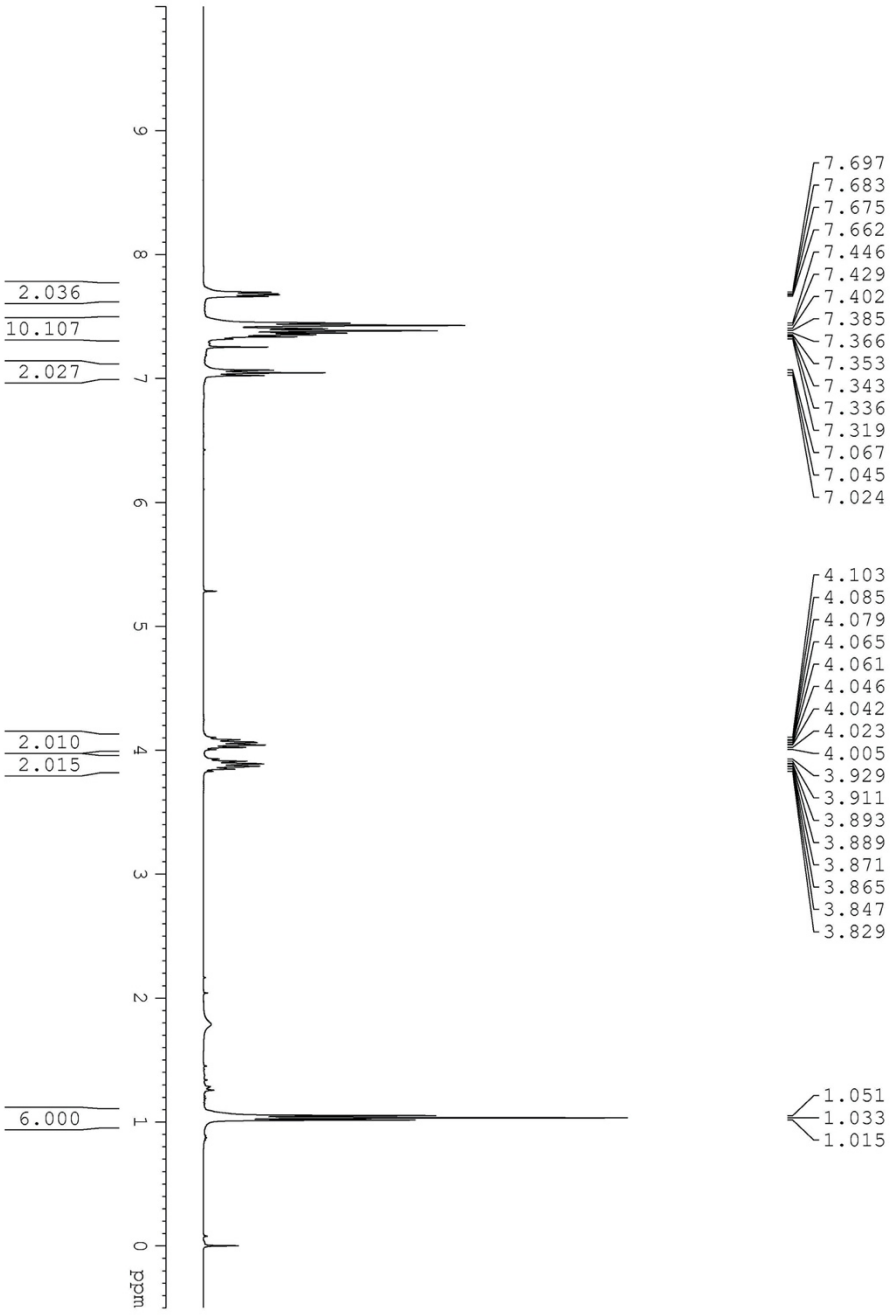
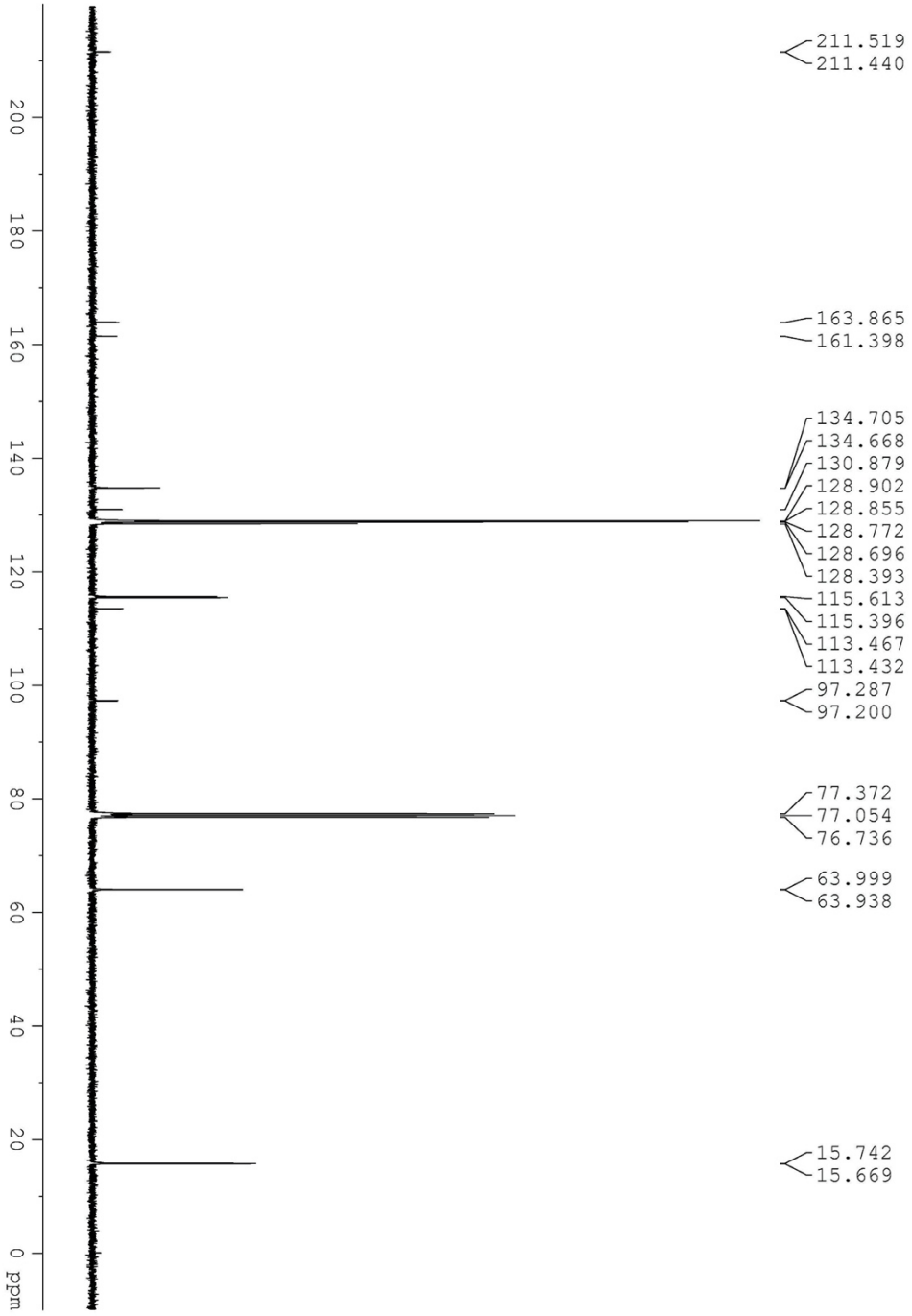
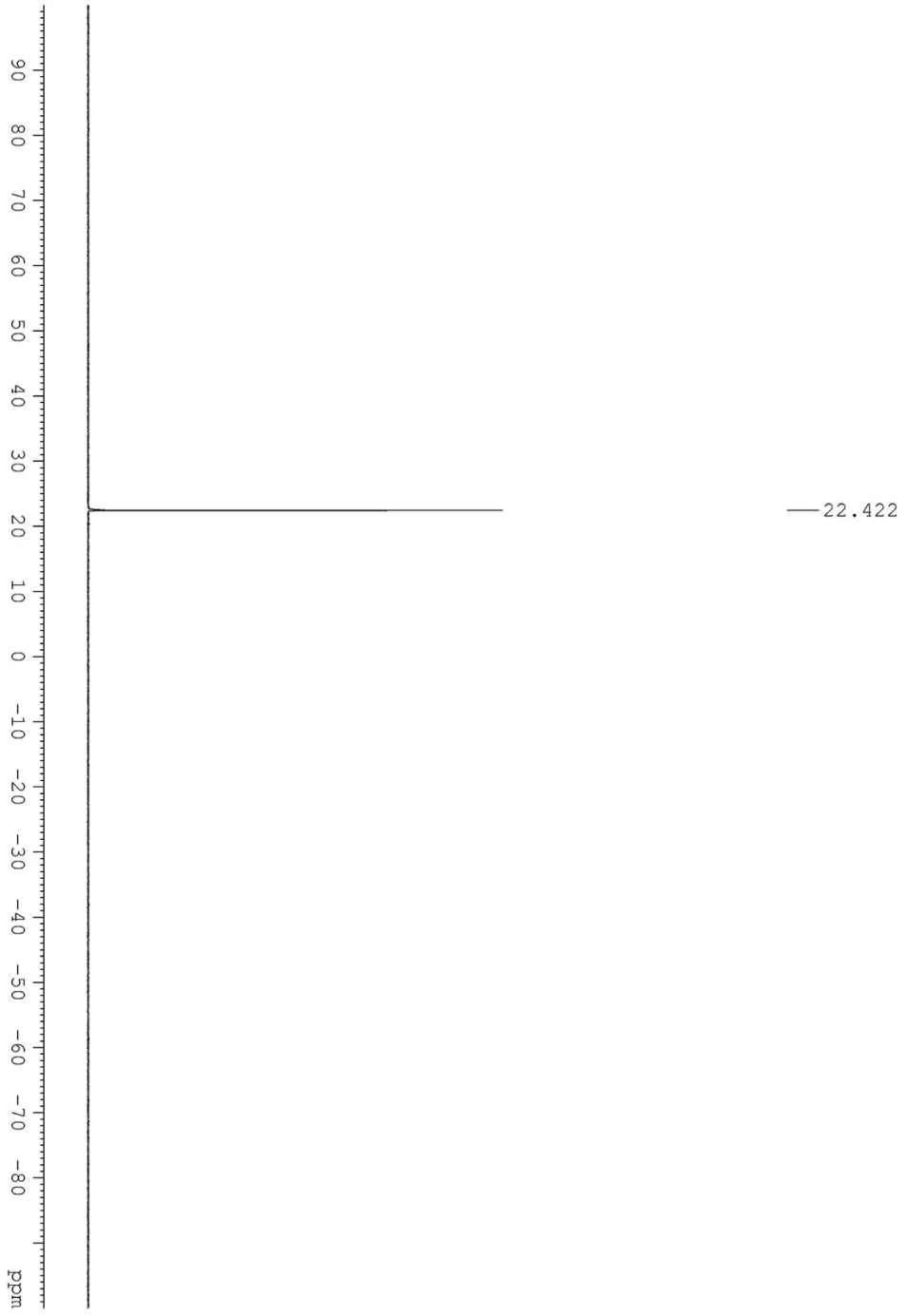
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
ppm


EtO
OEt
O
P
S
Ph
Ph
F

3d


2.036
10.107
2.027
2.010
2.015
6.000
7.697
7.683
7.675
7.662
7.446
7.429
7.402
7.385
7.366
7.353
7.343
7.336
7.319
7.067
7.045
7.024
4.103
4.085
4.079
4.065
4.061
4.046
4.042
4.023
4.005
3.929
3.911
3.893
3.889
3.871
3.865
3.847
3.829
1.051
1.033
1.015
ppm


211.519
211.440
163.865
161.398
134.705
134.668
130.879
128.902
128.855
128.772
128.696
128.393
115.613
115.396
113.467
113.432
97.287
97.200
77.372
77.054
76.736
63.999
63.938
15.742
15.669
200
180
160
140
120
100
80
60
40
20
0 ppm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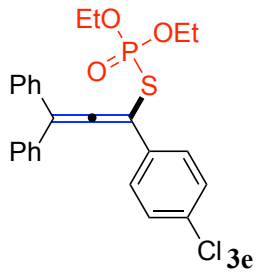
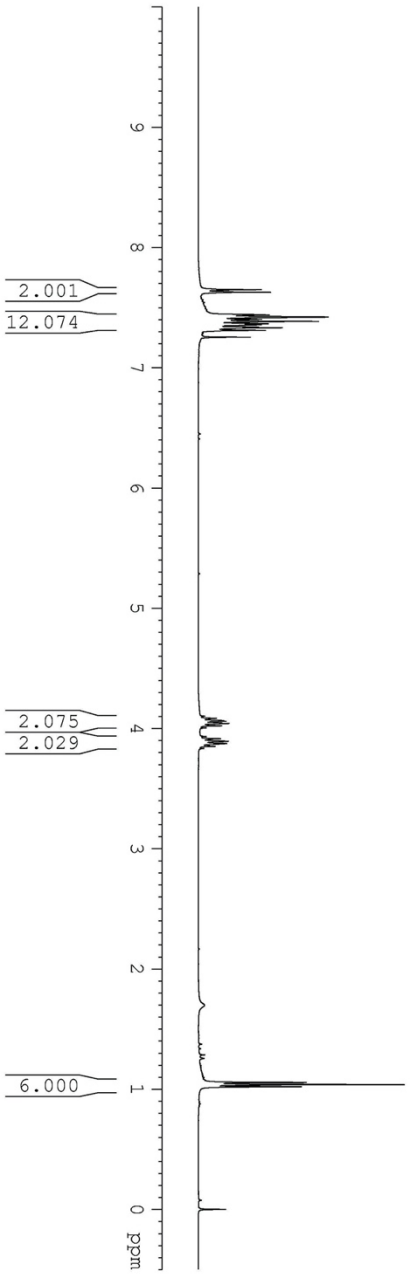
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
ppm


EtO
OEt
O
P
S
Ph
Ph
Cl

3e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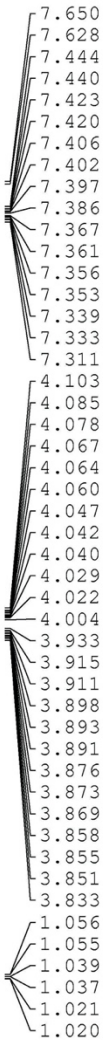
12.074
2.075
2.029
6.000
ppm


7.650
7.628
7.444
7.440
7.423
7.420
7.406
7.402
7.397
7.386
7.367
7.361
7.356
7.353
7.339
7.333
7.311
4.103
4.085
4.078
4.067
4.064
4.060
4.047
4.042
4.040
4.029
4.022
4.004
3.933
3.915
3.911
3.898
3.893
3.891
3.876
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3.855
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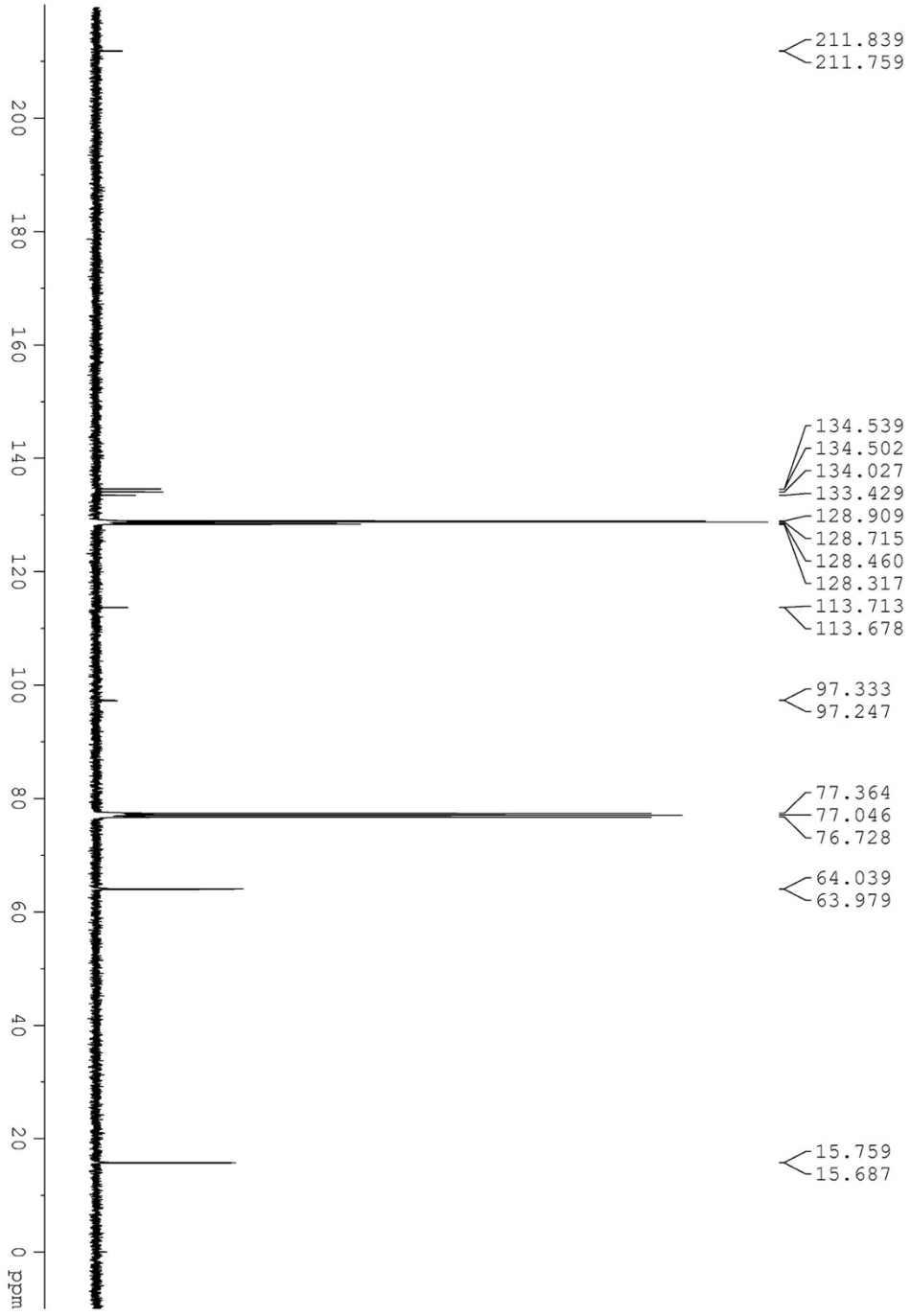
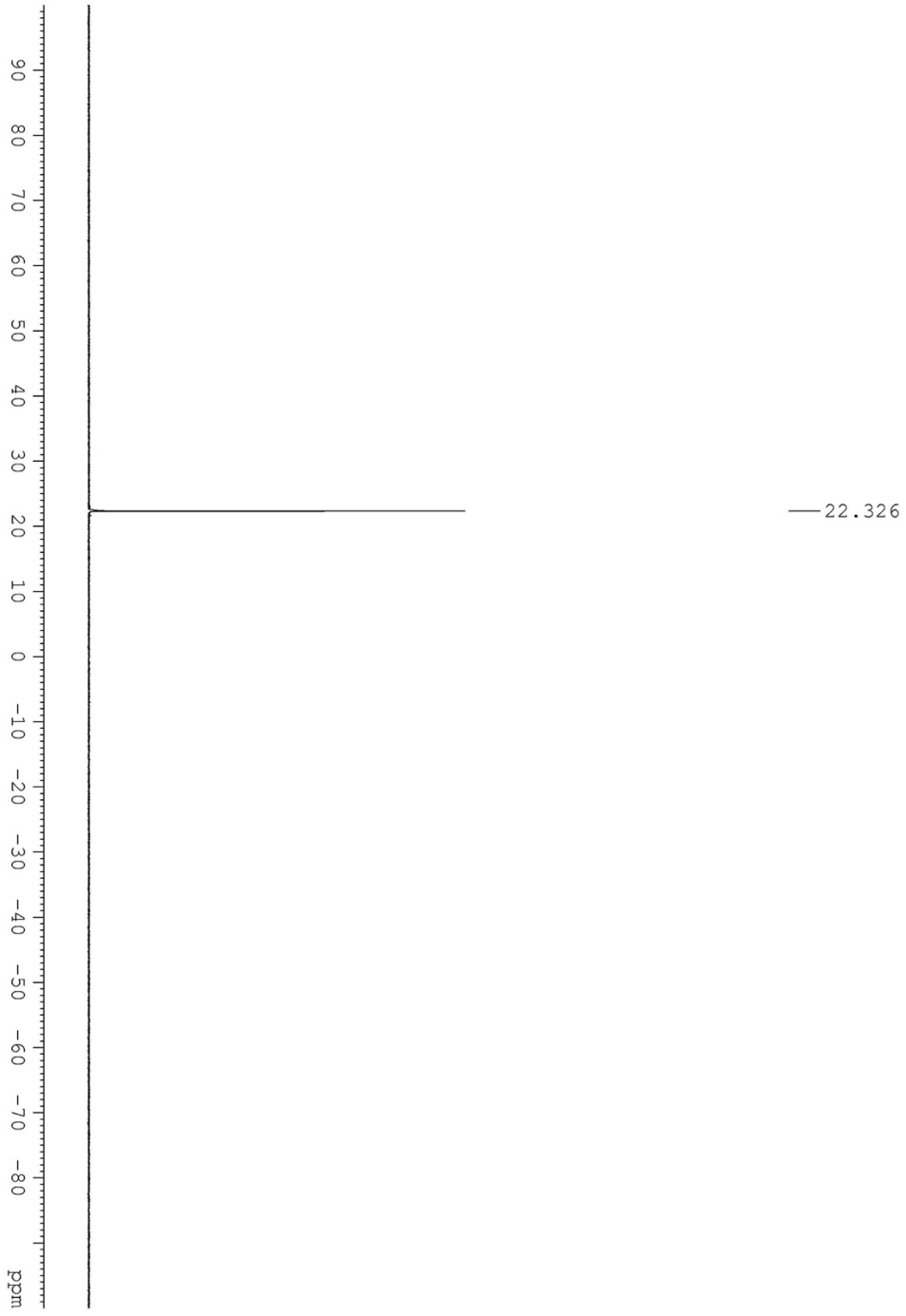
1.056
1.055
1.039
1.037
1.021
1.020


211.839
211.759
134.539
134.502
134.027
133.429
128.909
128.715
128.460
128.317
113.713
113.678
97.333
97.247
77.364
77.046
76.728
64.039
63.979
15.759
15.687
200
180
160
140
120
100
80
60
40
20
0 ppm


22.326
90
80
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60
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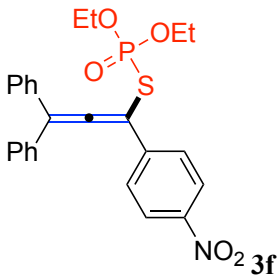
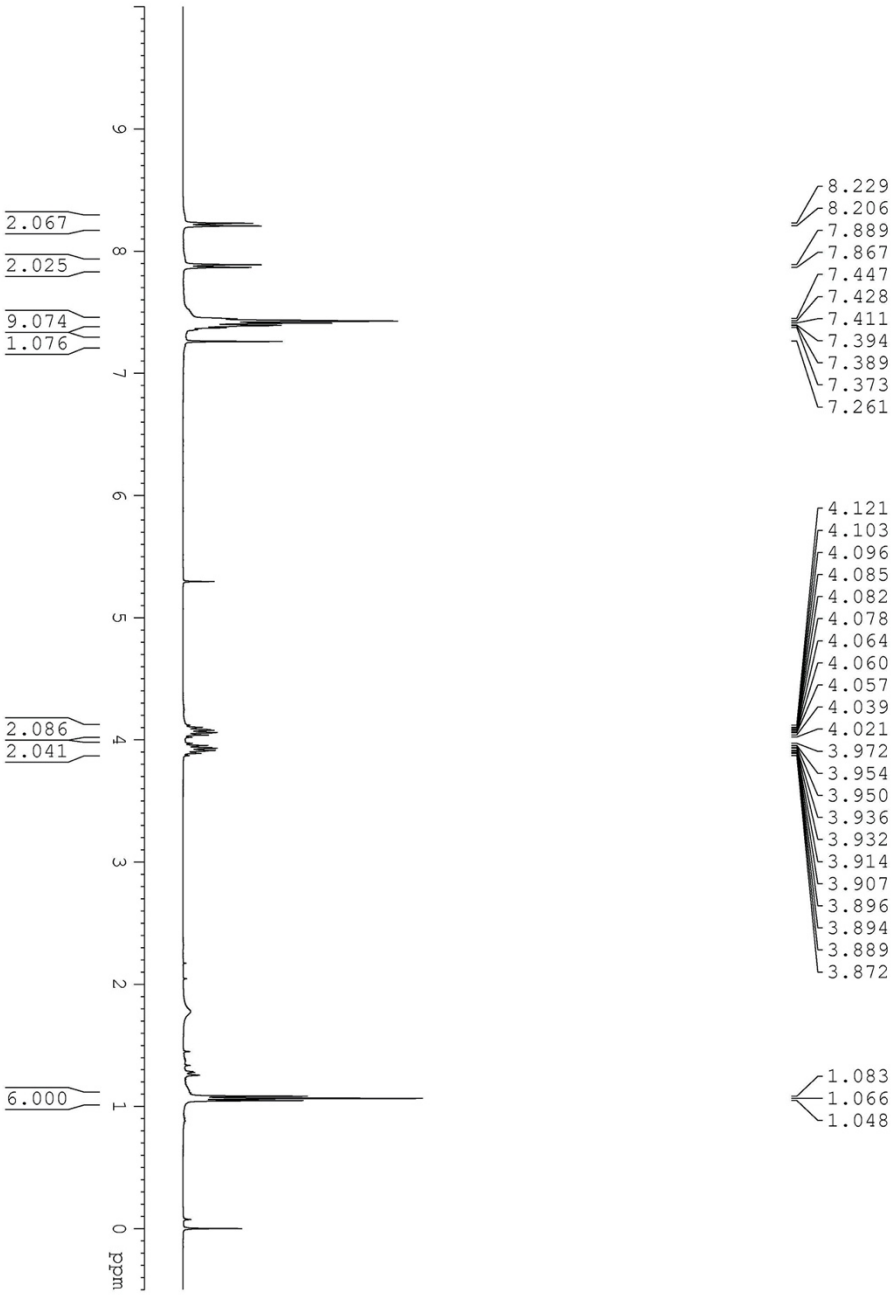
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
ppm


EtO
OEt
O
P
S
Ph
Ph
NO2

3f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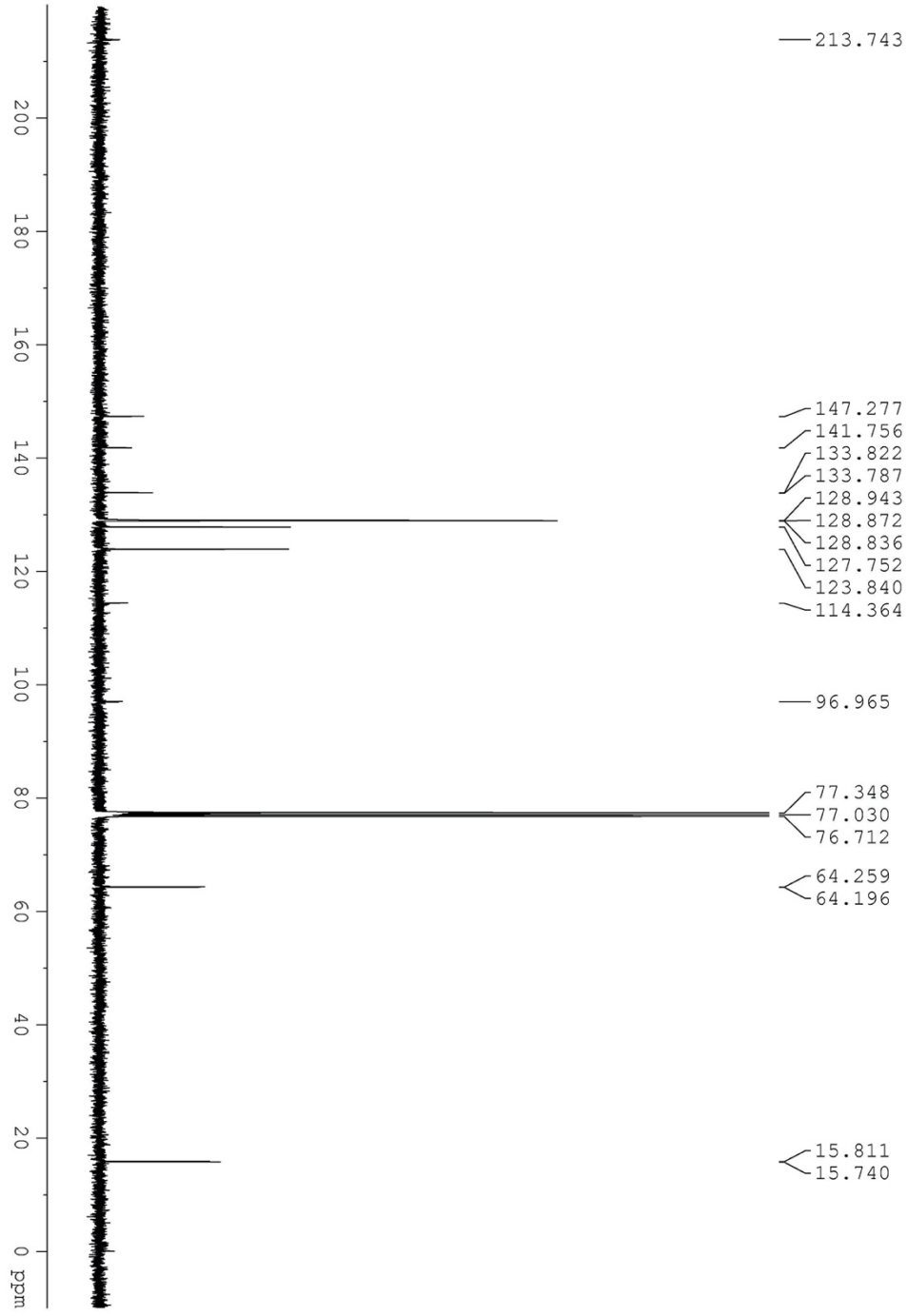
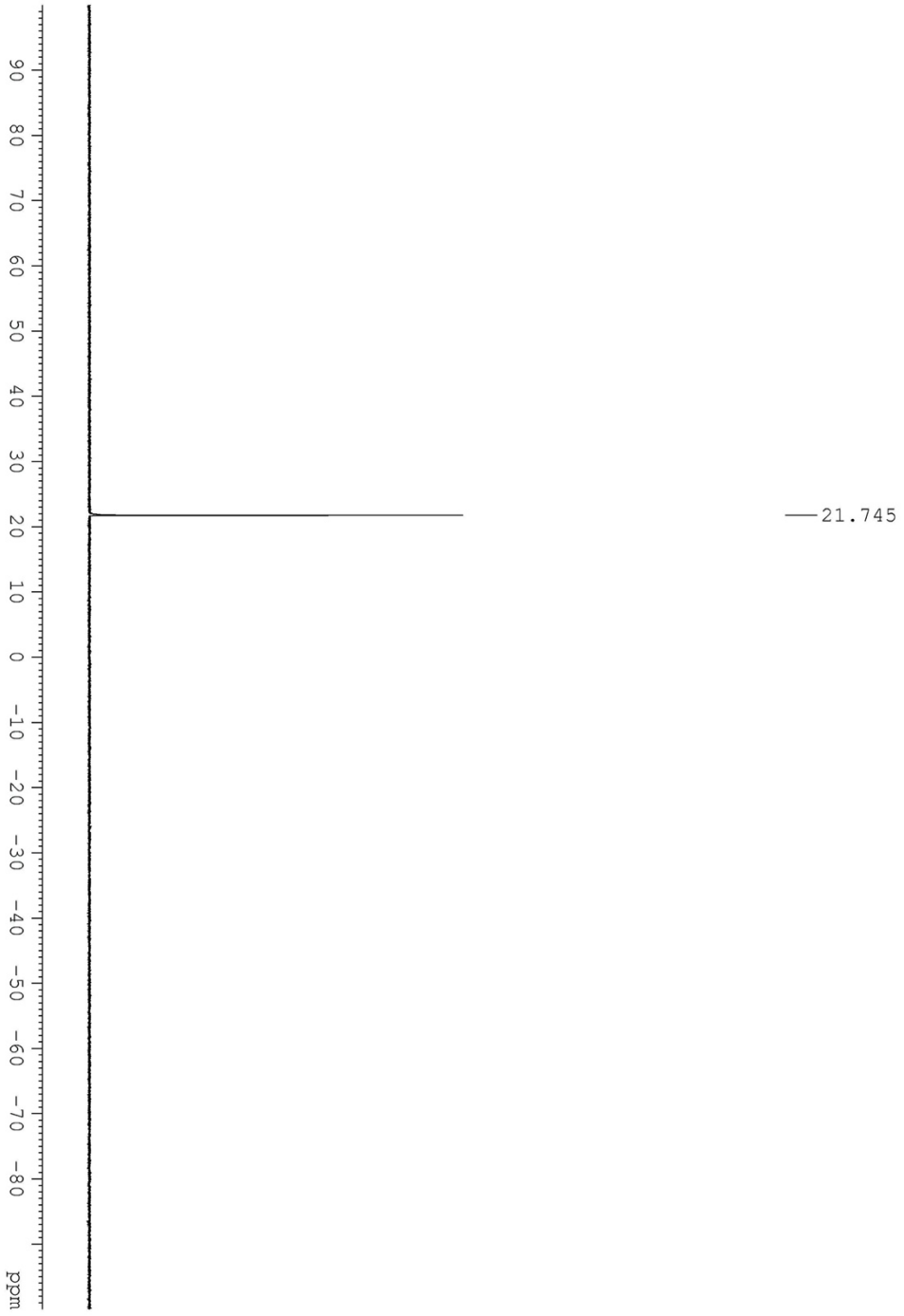
2.025
9.074
1.076
2.086
2.041
6.000
8.229
8.206
7.889
7.867
7.447
7.428
7.411
7.394
7.389
7.373
7.261
4.121
4.103
4.096
4.085
4.082
4.078
4.064
4.060
4.057
4.039
4.021
3.972
3.954
3.950
3.936
3.932
3.914
3.907
3.896
3.894
3.889
3.872
1.083
1.066
1.048
ppm


213.743
147.277
141.756
133.822
133.787
128.943
128.872
128.836
127.752
123.840
114.364
96.965
77.348
77.030
76.712
64.259
64.196
15.811
15.740
200
180
160
140
120
100
80
60
40
20
0 ppm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90
80
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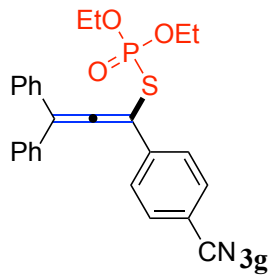
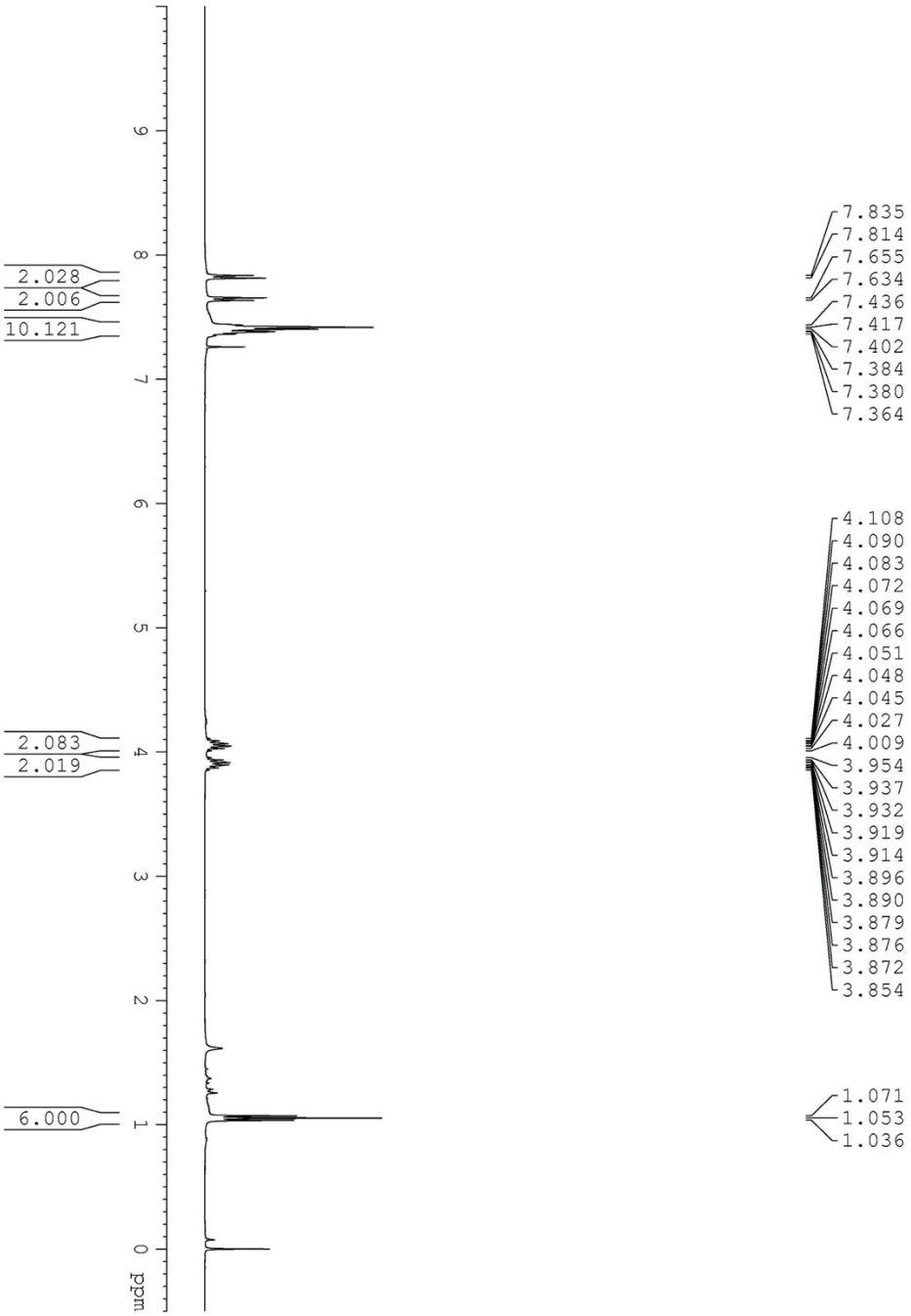
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
ppm


EtO
OEt
O
P
S
Ph
Ph
CN

3g


2.028
2.006
10.121
2.083
2.019
6.000
ppm
7.835
7.814
7.655
7.634
7.436
7.417
7.402
7.384
7.380
7.364
4.108
4.090
4.083
4.072
4.069
4.066
4.051
4.048
4.045
4.027
4.009
3.954
3.937
3.932
3.919
3.914
3.896
3.890
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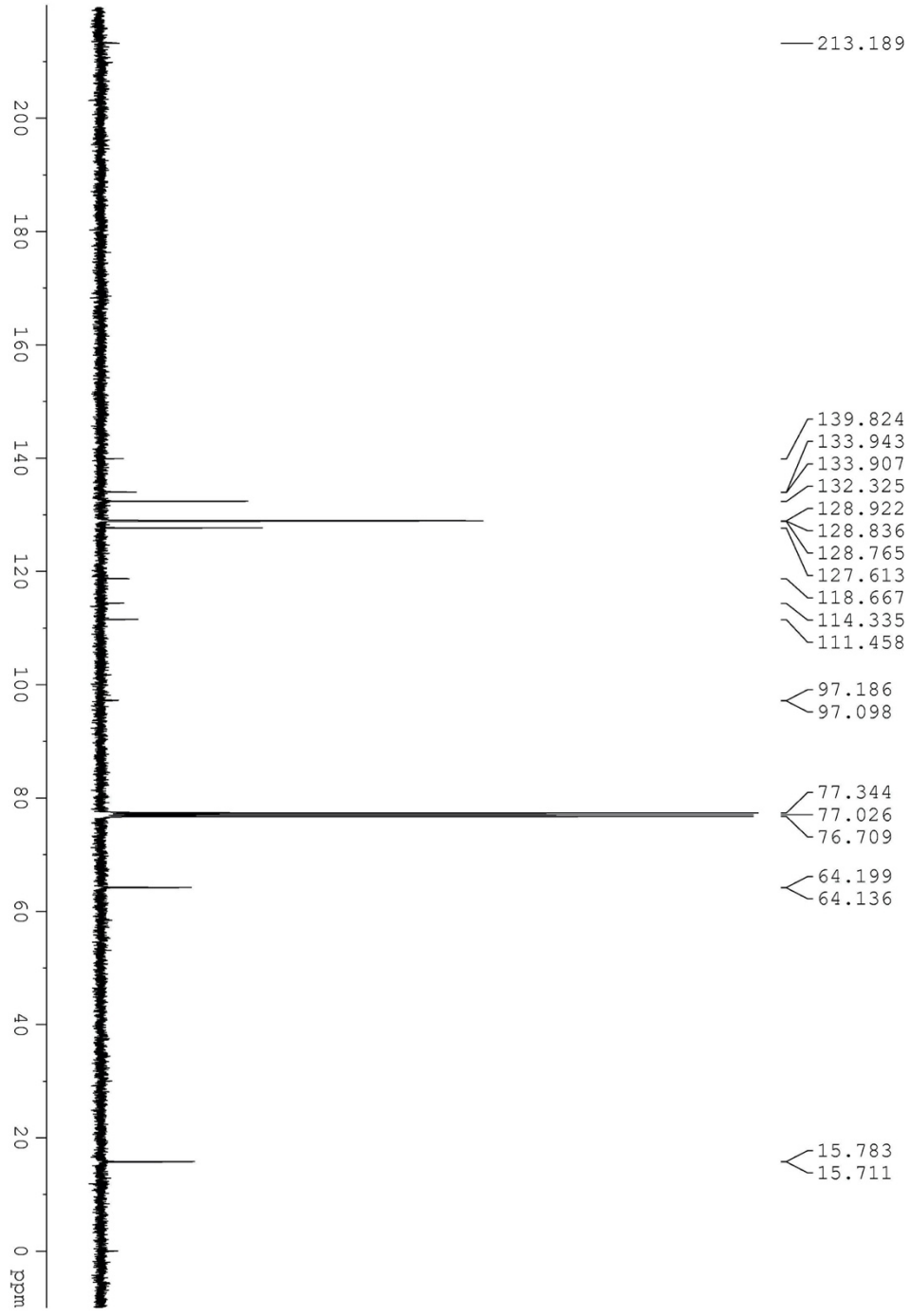
3.876
3.872
3.854
1.071
1.053
1.036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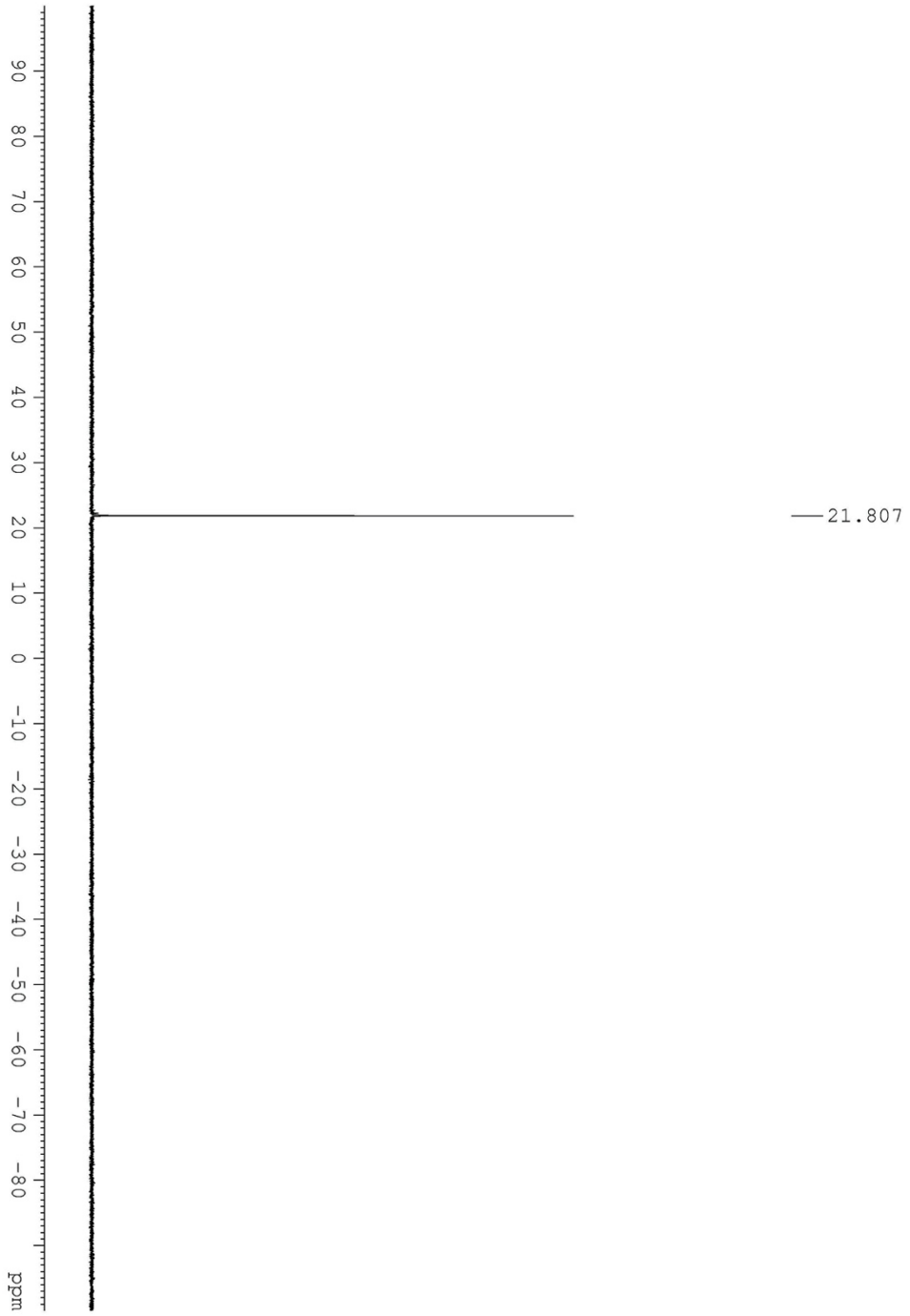
139.824
133.943
133.907
132.325
128.922
128.836
128.765
127.613
118.667
114.335
111.458
97.186
97.098
77.344
77.026
76.709
64.199
64.136
15.783
15.711
200
180
160
140
120
100
80
60
40
20
0 ppm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90
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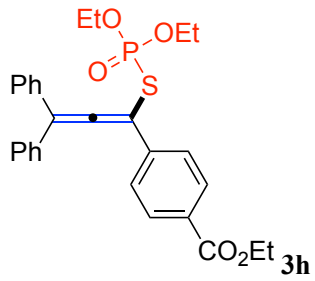
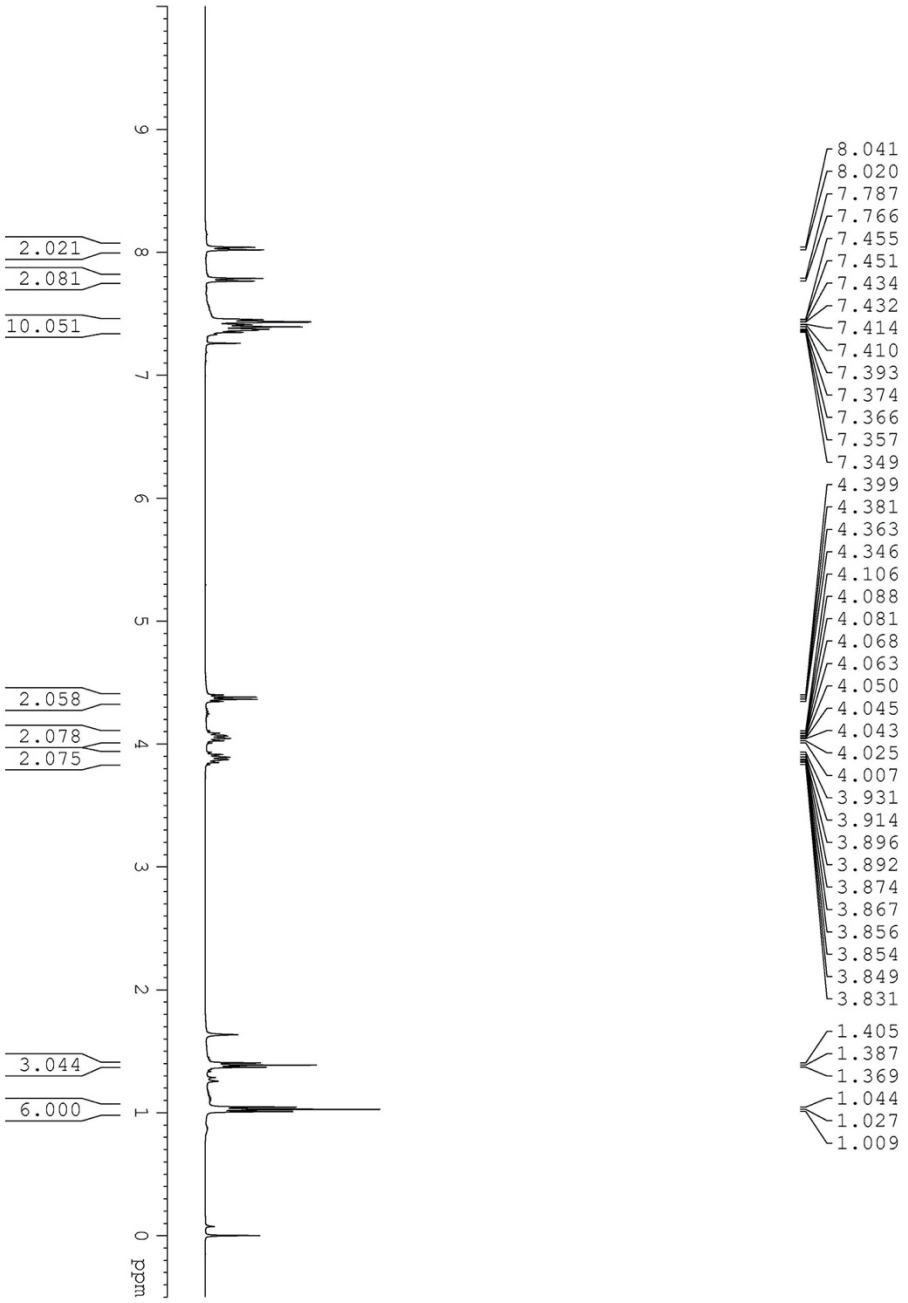
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
ppm


EtO
OEt
O
P
S
Ph
Ph
CO2Et

3h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2.081
10.051
2.058
2.078
2.075
3.044
6.000
ppm
8.041
8.020
7.787
7.766
7.455
7.451
7.434
7.432
7.414
7.410
7.393
7.374
7.366
7.357
7.349
4.399
4.381
4.363
4.346
4.106
4.088
4.081
4.068
4.063
4.050
4.045
4.043
4.025
4.007
3.931
3.914
3.896
3.892
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1.387
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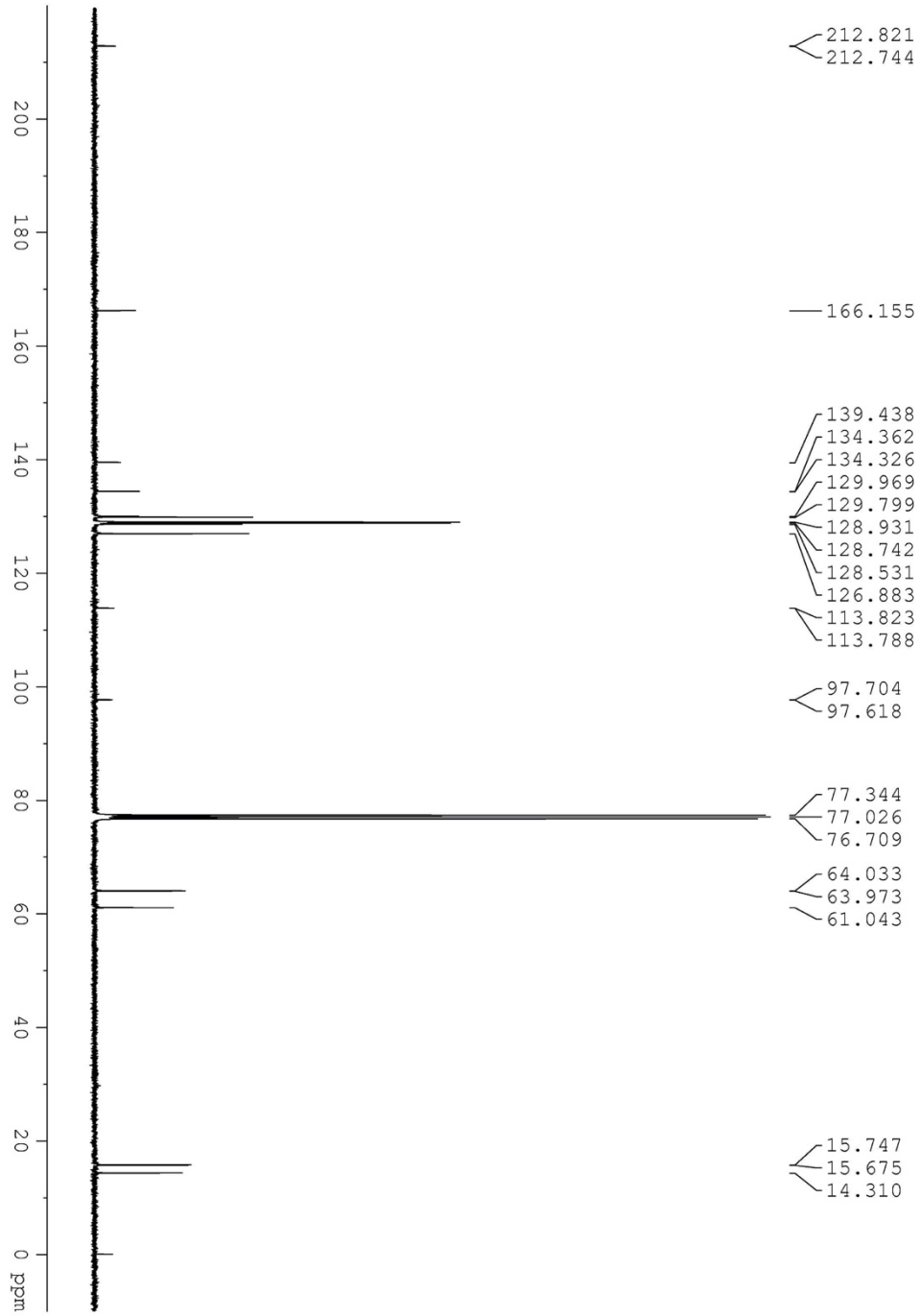
1.044
1.027
1.009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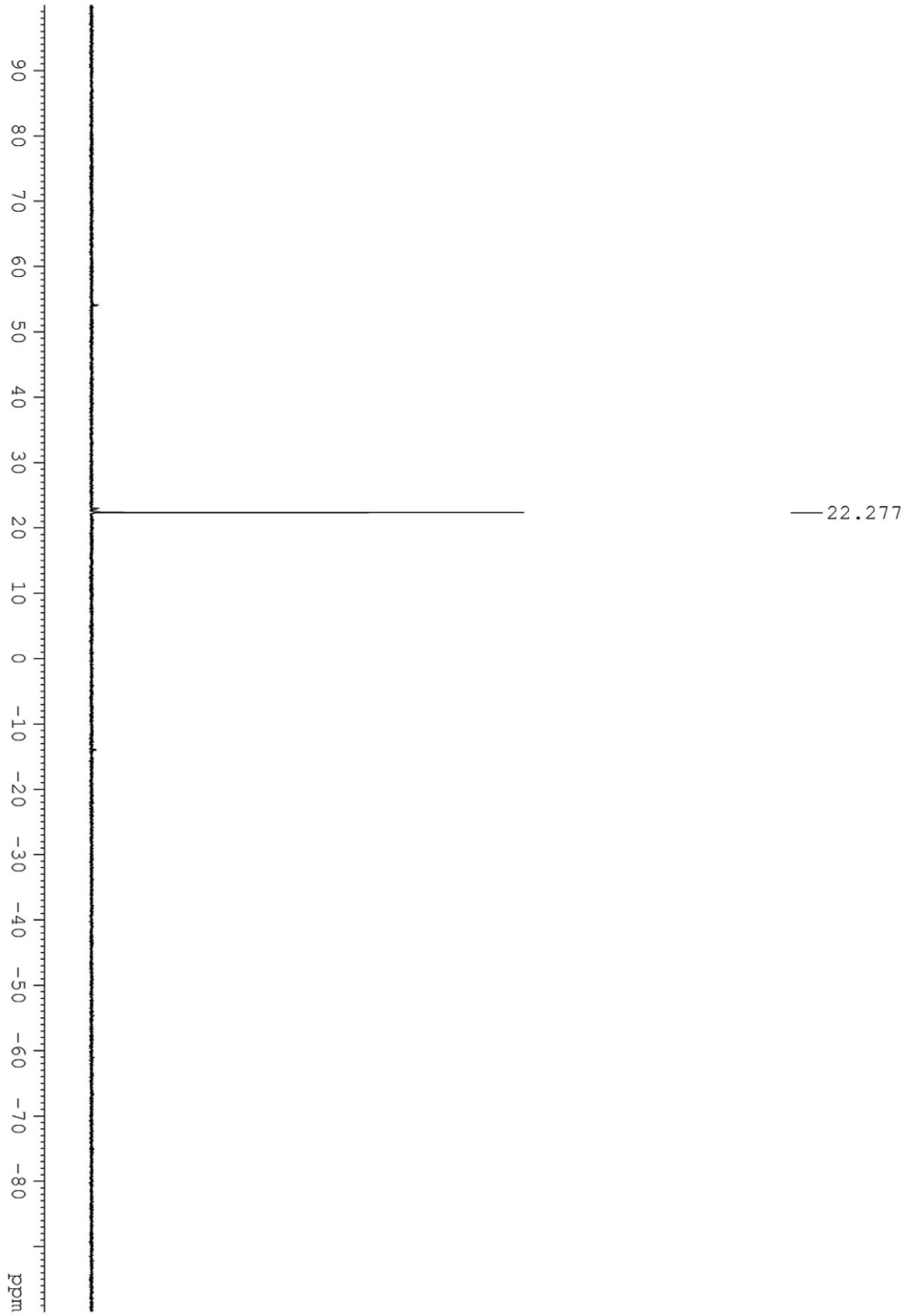
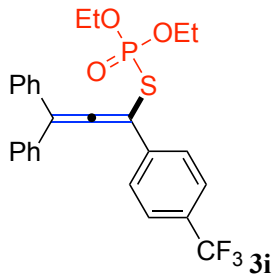
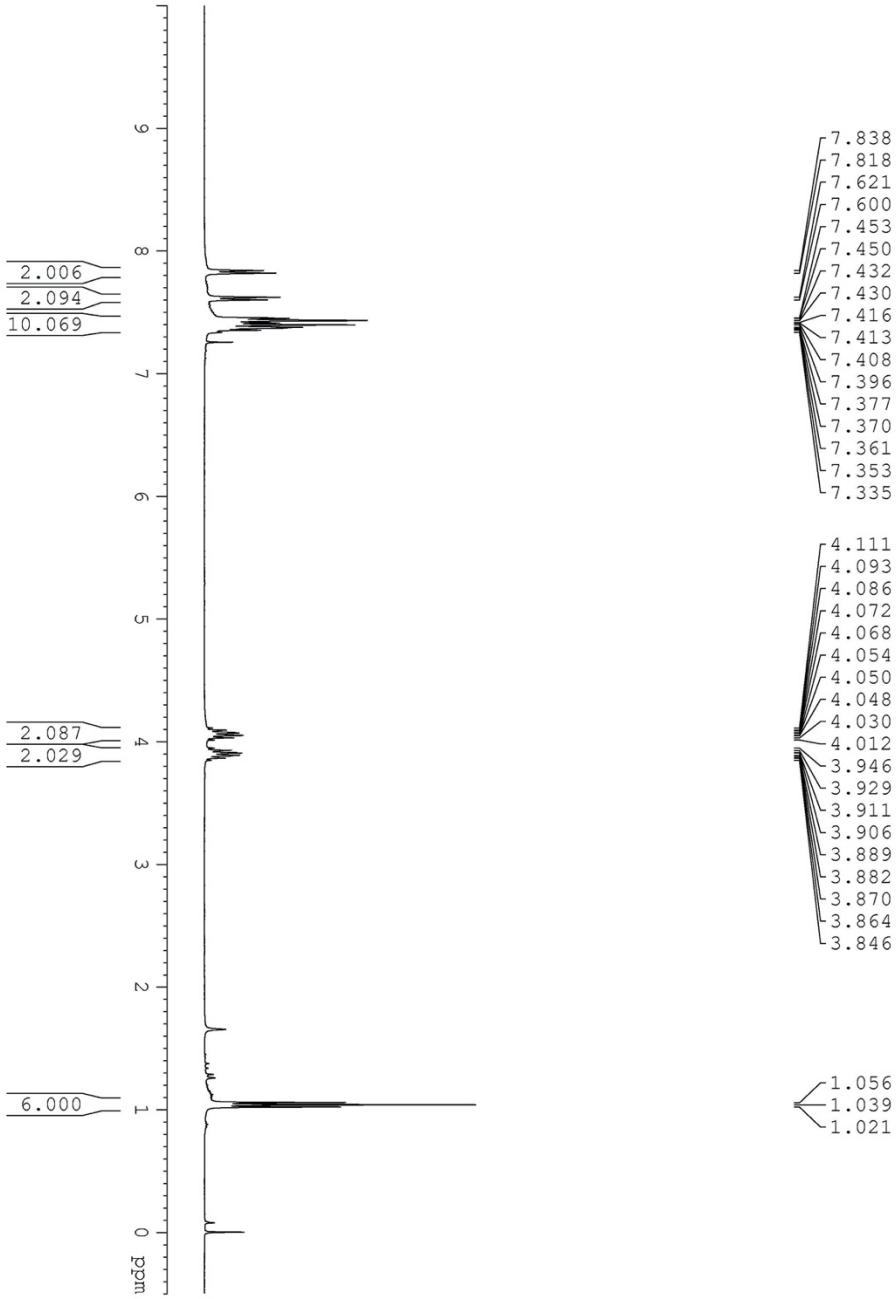
212.744
166.155
139.438
134.362
134.326
129.969
129.799
128.931
128.742
128.531
126.883
113.823
113.788
97.704
97.618
77.344
77.026
76.709
64.033
63.973
61.043
15.747
15.675
14.310
200
180
160
140
120
100
80
60
40
20
0 ppm


22.277
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
ppm


EtO
OEt
O
P
S
Ph
Ph
CF3

3i


2.006
2.094
10.069
2.087
2.029
6.000
7.838
7.818
7.621
7.600
7.453
7.450
7.432
7.430
7.416
7.413
7.408
7.396
7.377
7.370
7.361
7.353
7.335
4.111
4.093
4.086
4.072
4.068
4.054
4.050
4.048
4.030
4.012
3.946
3.929
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3.906
3.889
3.882
3.870
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3.846
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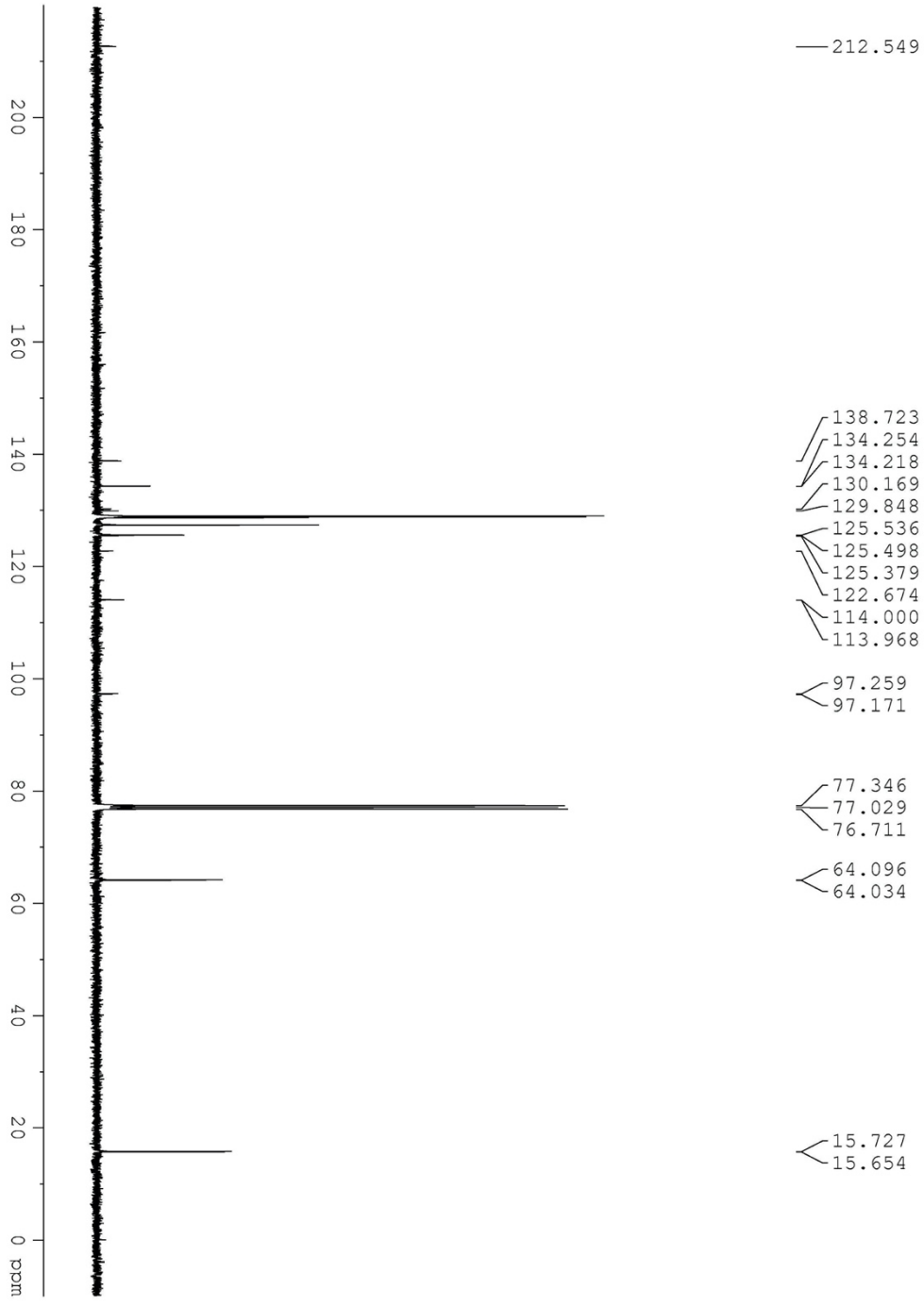
1.039
1.021
ppm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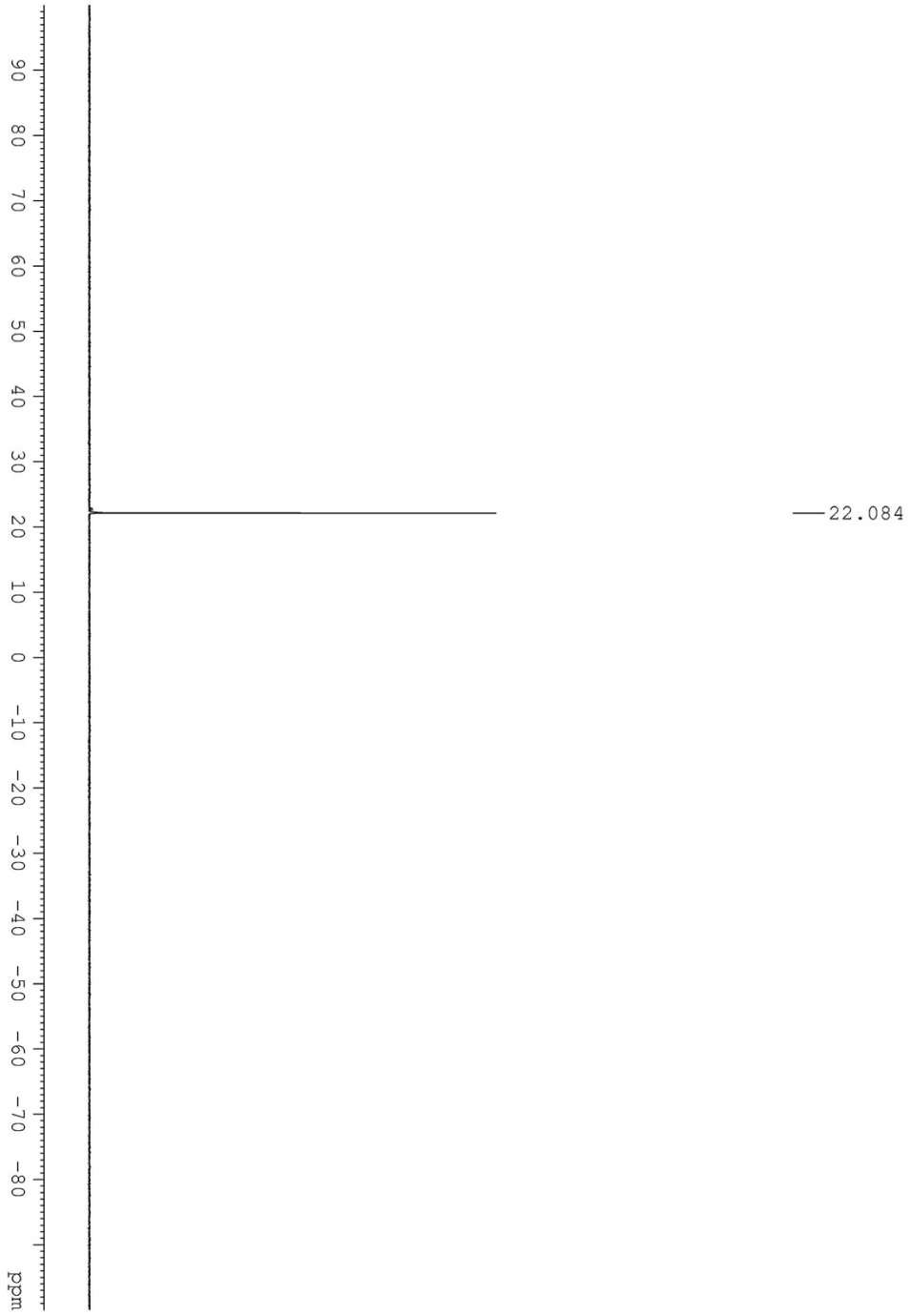
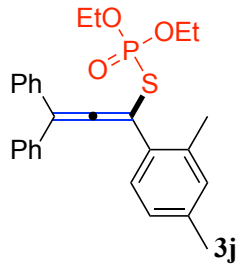
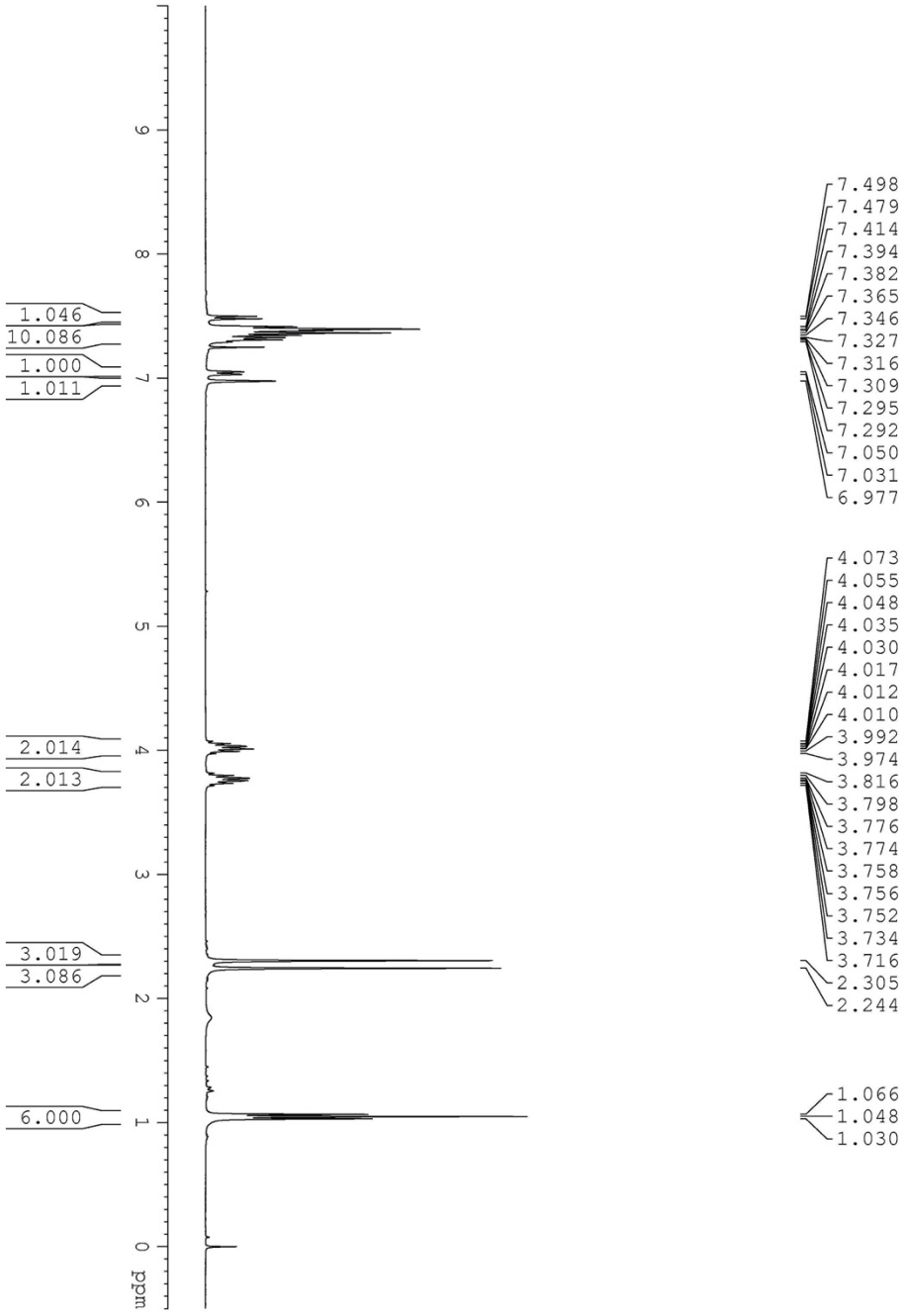
138.723
134.254
134.218
130.169
129.848
125.536
125.498
125.379
122.674
114.000
113.968
97.259
97.171
77.346
77.029
76.711
64.096
64.034
15.727
15.654
200
180
160
140
120
100
80
60
40
20
0 ppm


22.084
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
ppm


EtO
OEt
O
P
S
Ph
Ph

3j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10.086
1.000
1.011
2.014
2.013
3.019
3.086
6.000
ppm
7.498
7.479
7.414
7.394
7.382
7.365
7.346
7.327
7.316
7.309
7.295
7.292
7.050
7.031
6.977
4.073
4.055
4.048
4.035
4.030
4.017
4.012
4.010
3.992
3.974
3.816
3.798
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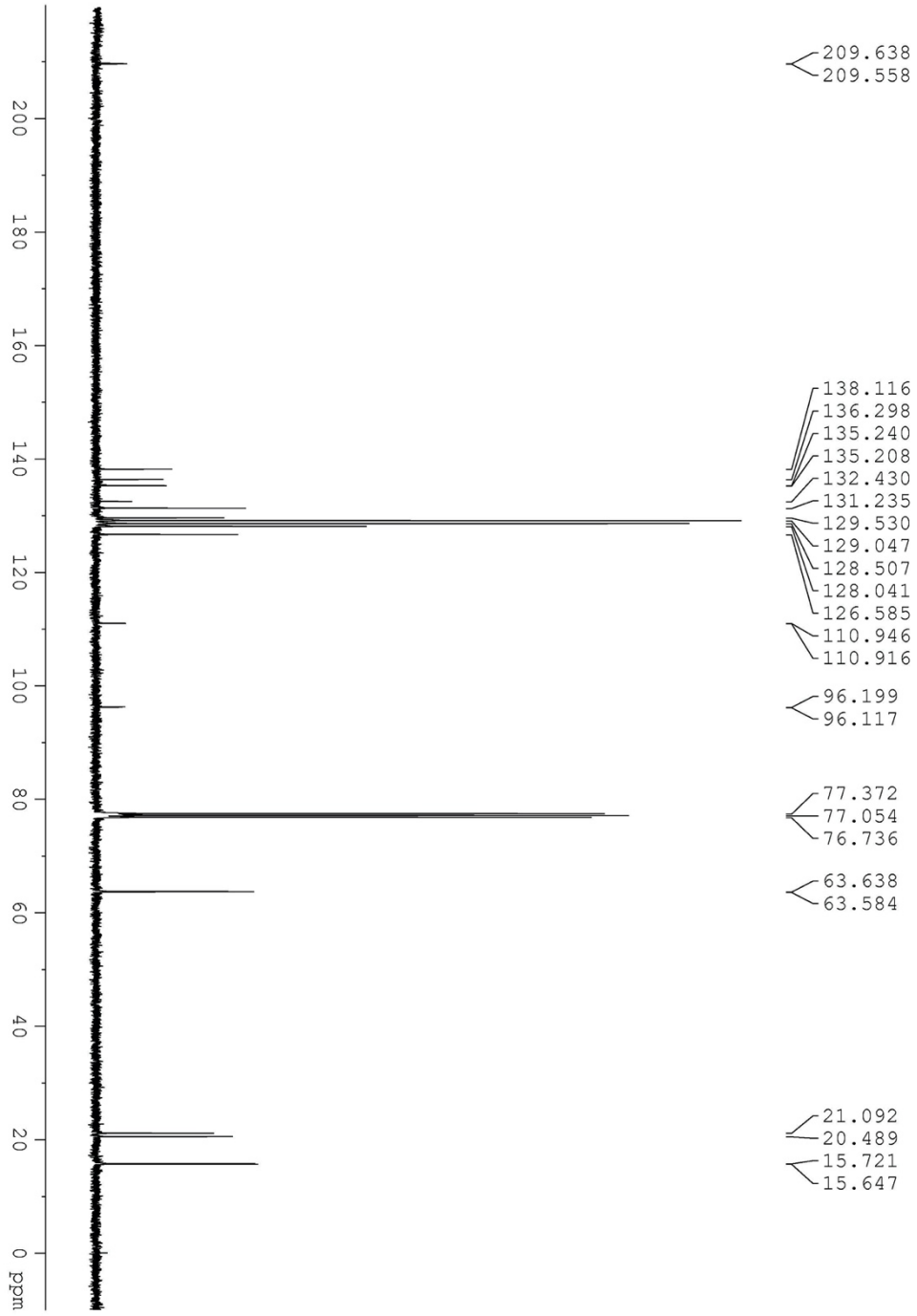
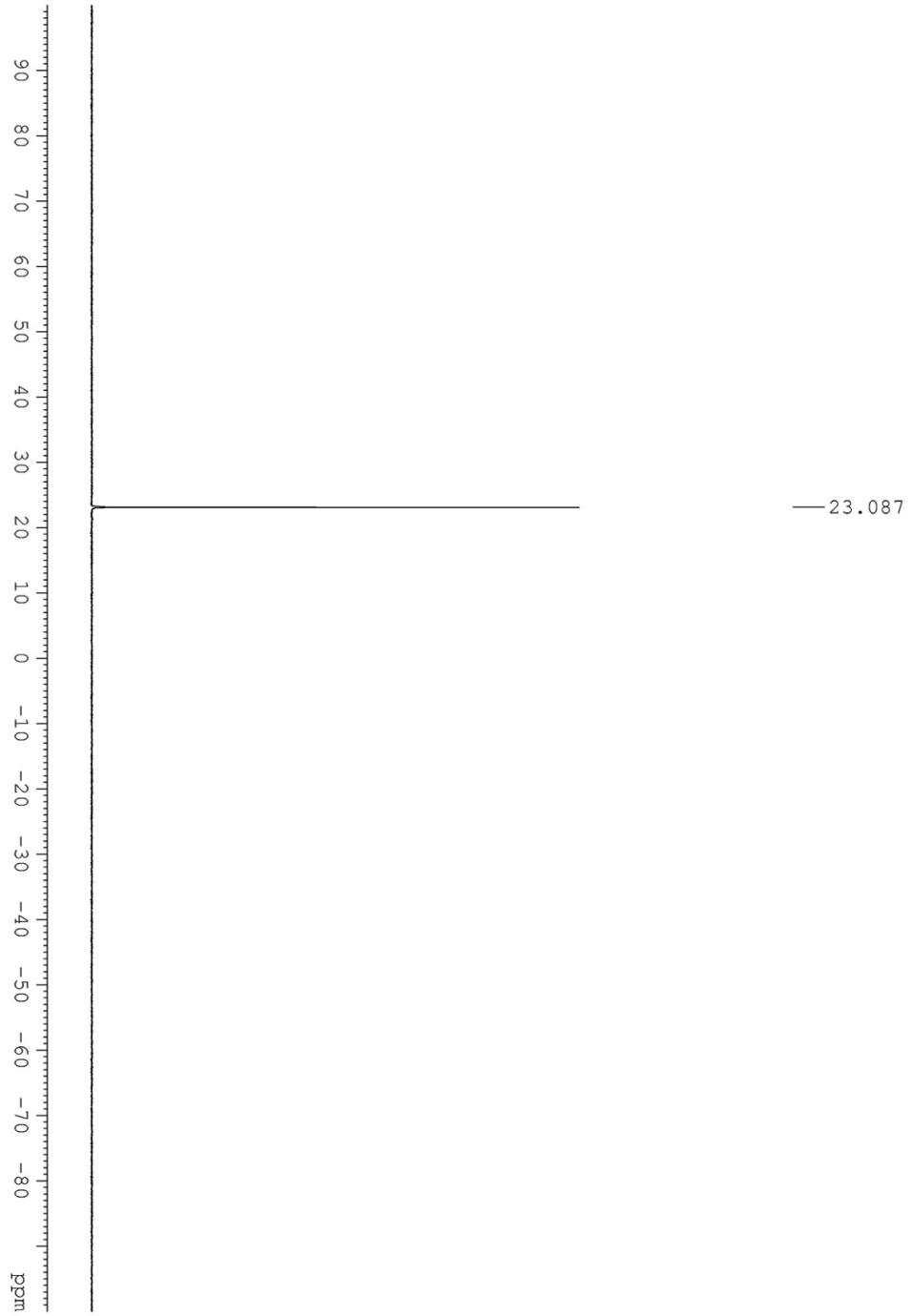
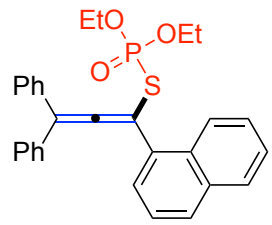
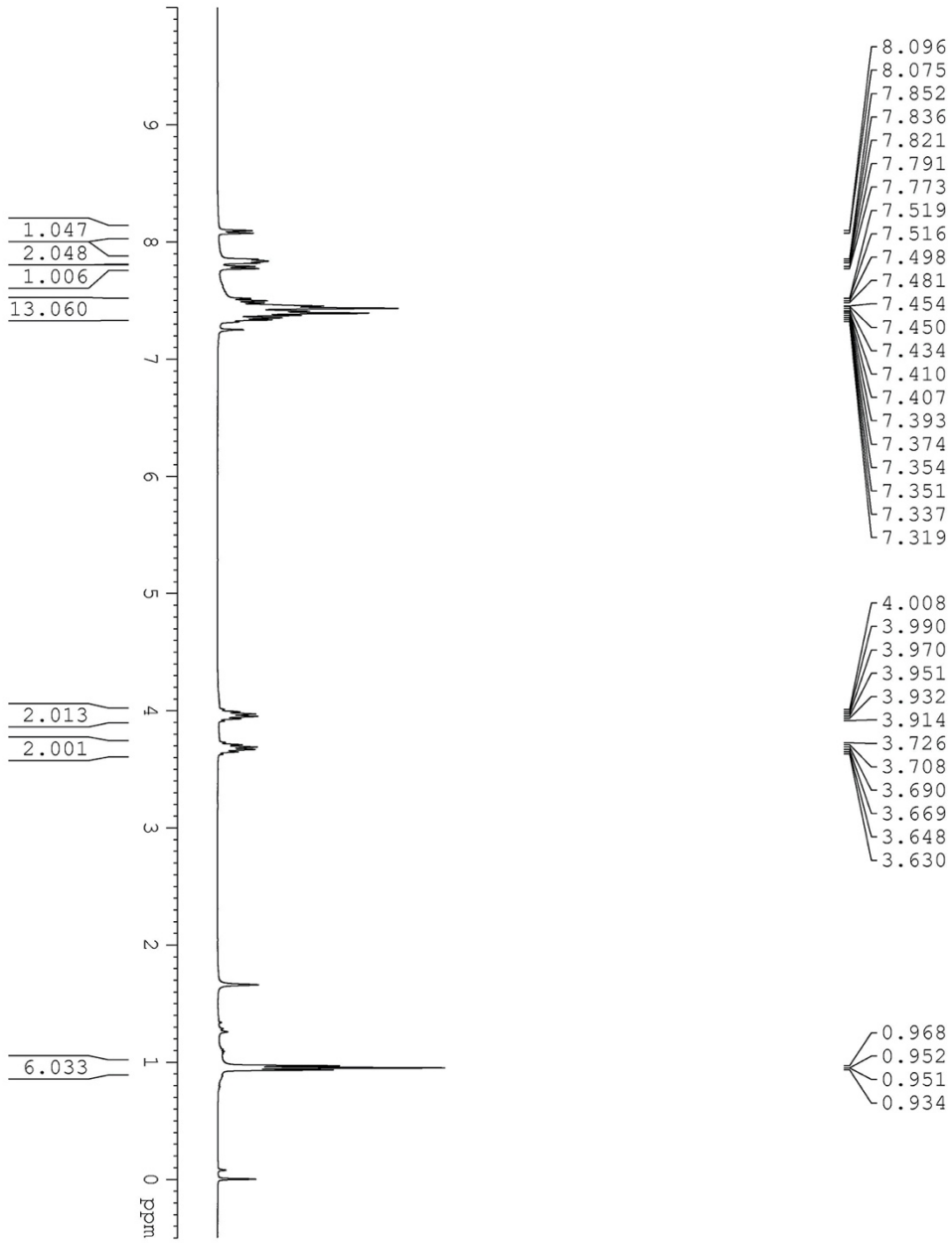
1.048
1.030

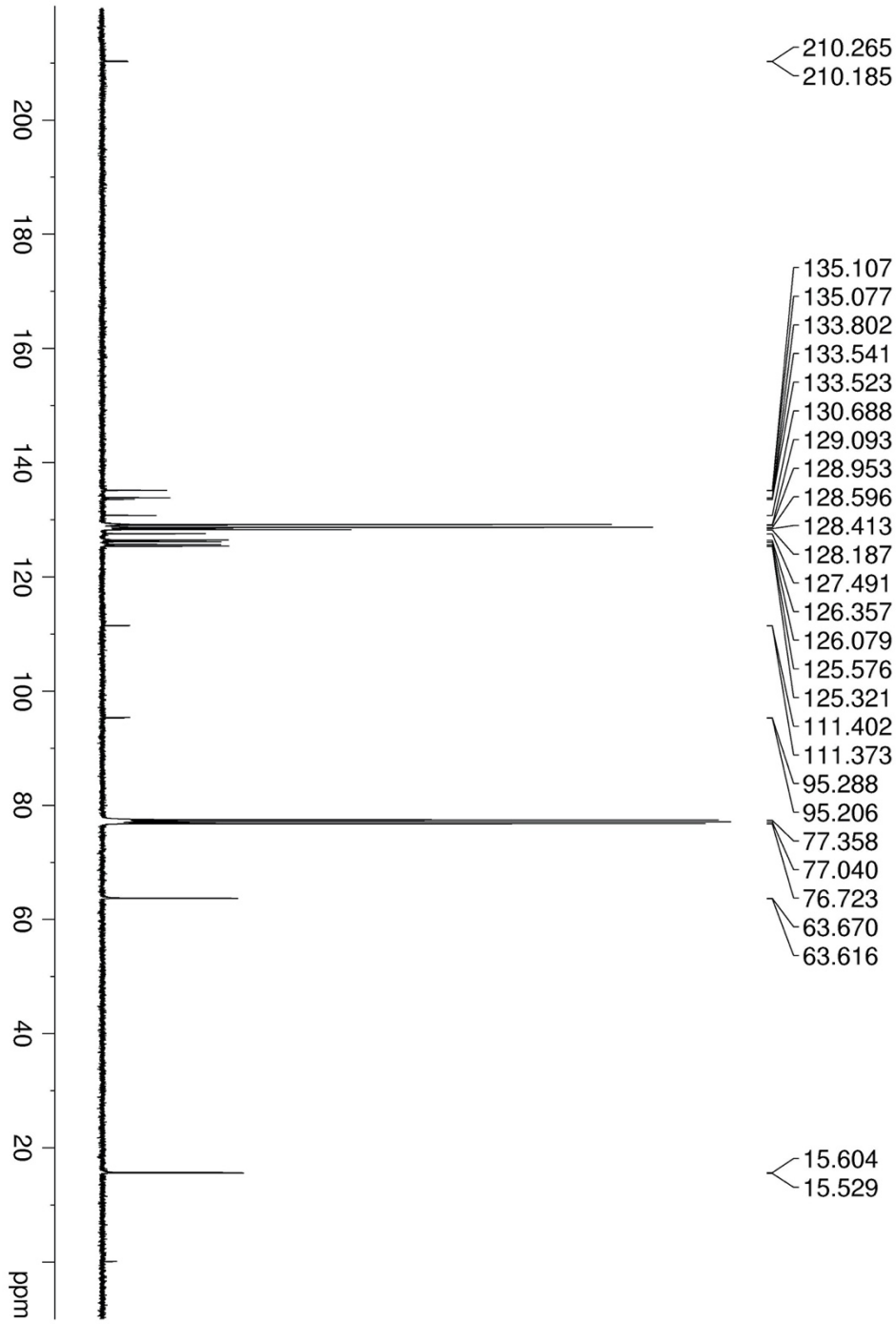

209.638
209.558
138.116
136.298
135.240
135.208
132.430
131.235
129.530
129.047
128.507
128.041
126.585
110.946
110.916
96.199
96.117
77.372
77.054
76.736
63.638
63.584
21.092
20.489
15.721
15.647
200
180
160
140
120
100
80
60
40
20
0 ppm

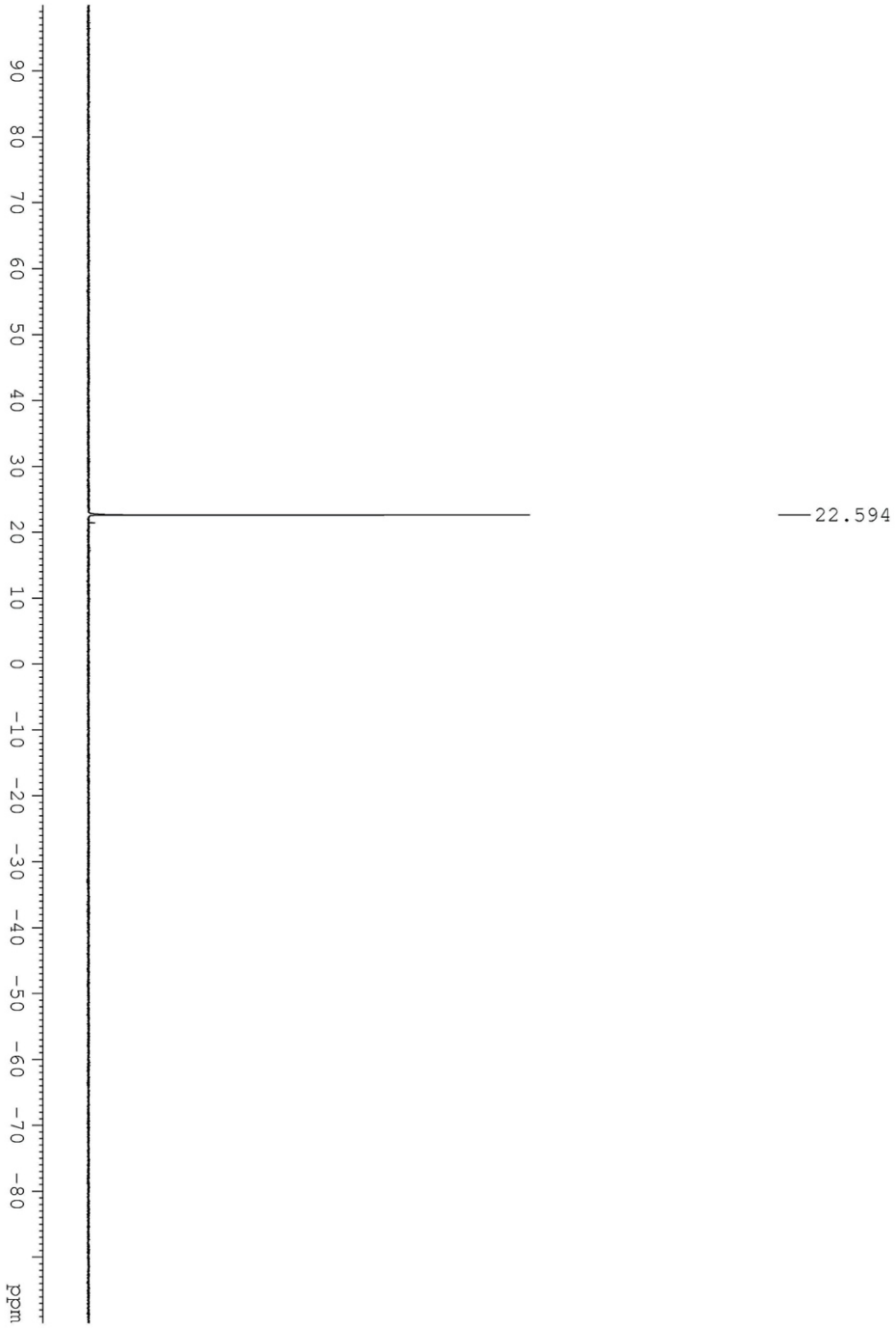

23.087
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
ppm

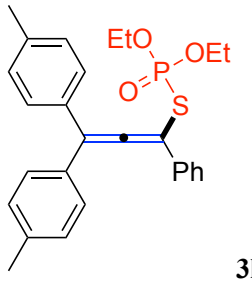

EtO
OEt
O
P
S
Ph
Ph

3k

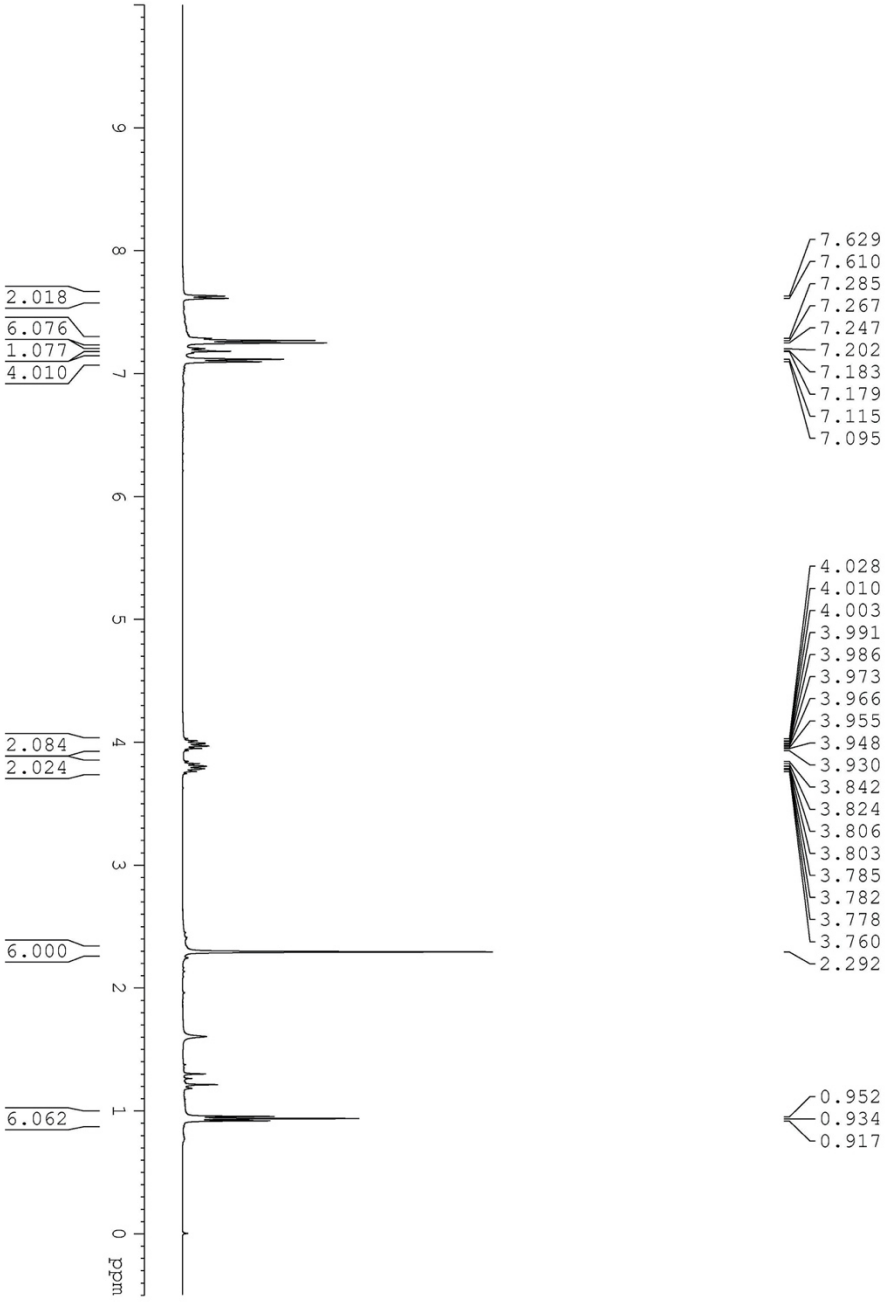

1.047
2.048
1.006
13.060
2.013
2.001
6.033
8.096
8.075
7.852
7.836
7.821
7.791
7.773
7.519
7.516
7.498
7.481
7.454
7.450
7.434
7.410
7.407
7.393
7.374
7.354
7.351
7.337
7.319
4.008
3.990
3.970
3.951
3.932
3.914
3.726
3.708
3.690
3.669
3.648
3.630
0.968
0.952
0.951
0.934
ppm

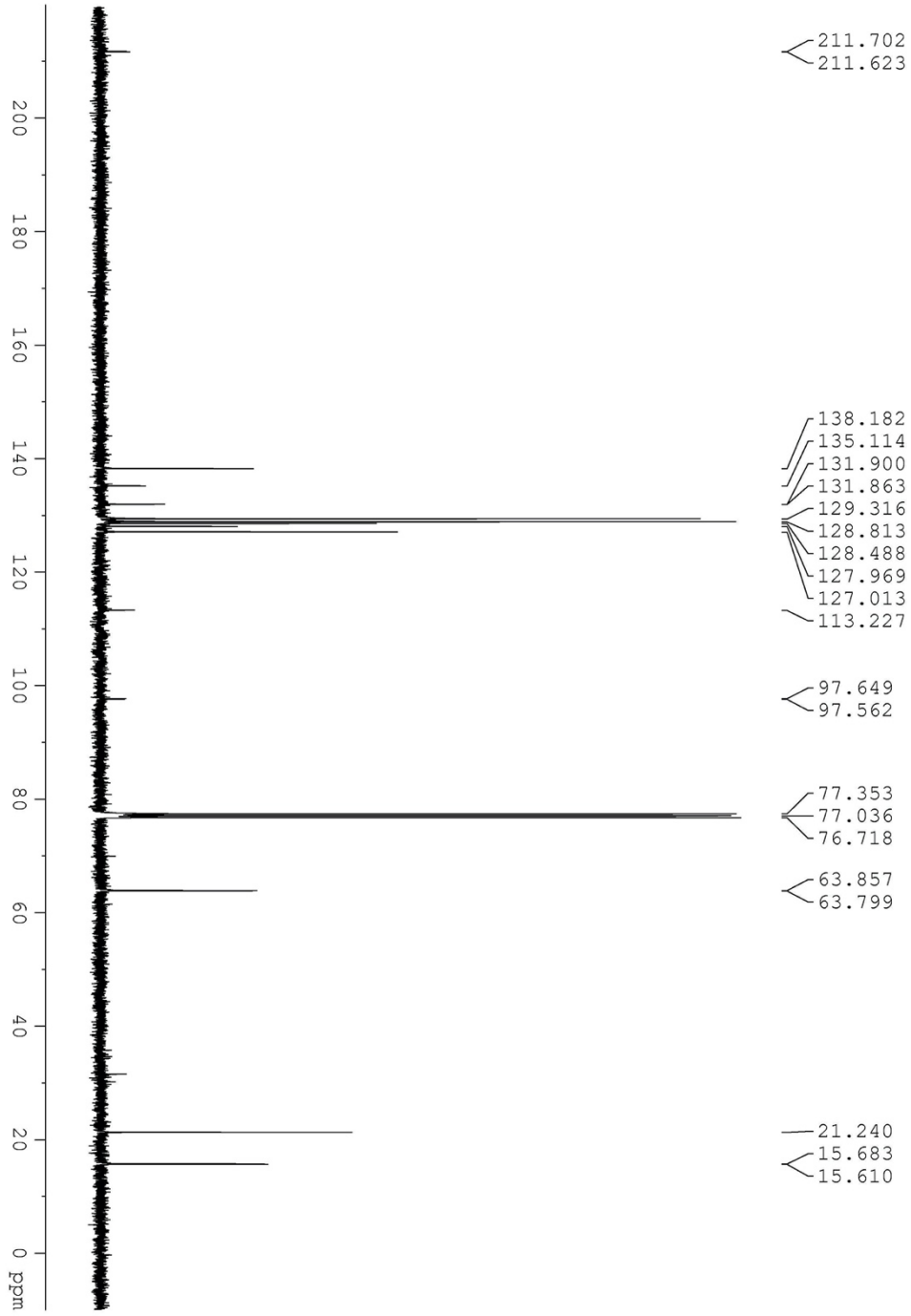

210.265
210.185
135.107
135.077
133.802
133.541
133.523
130.688
129.093
128.953
128.596
128.413
128.187
127.491
126.357
126.079
125.576
125.321
111.402
111.373
95.288
95.206
77.358
77.040
76.723
63.670
63.616
15.604
15.529
200
180
160
140
120
100
80
60
40
20
ppm

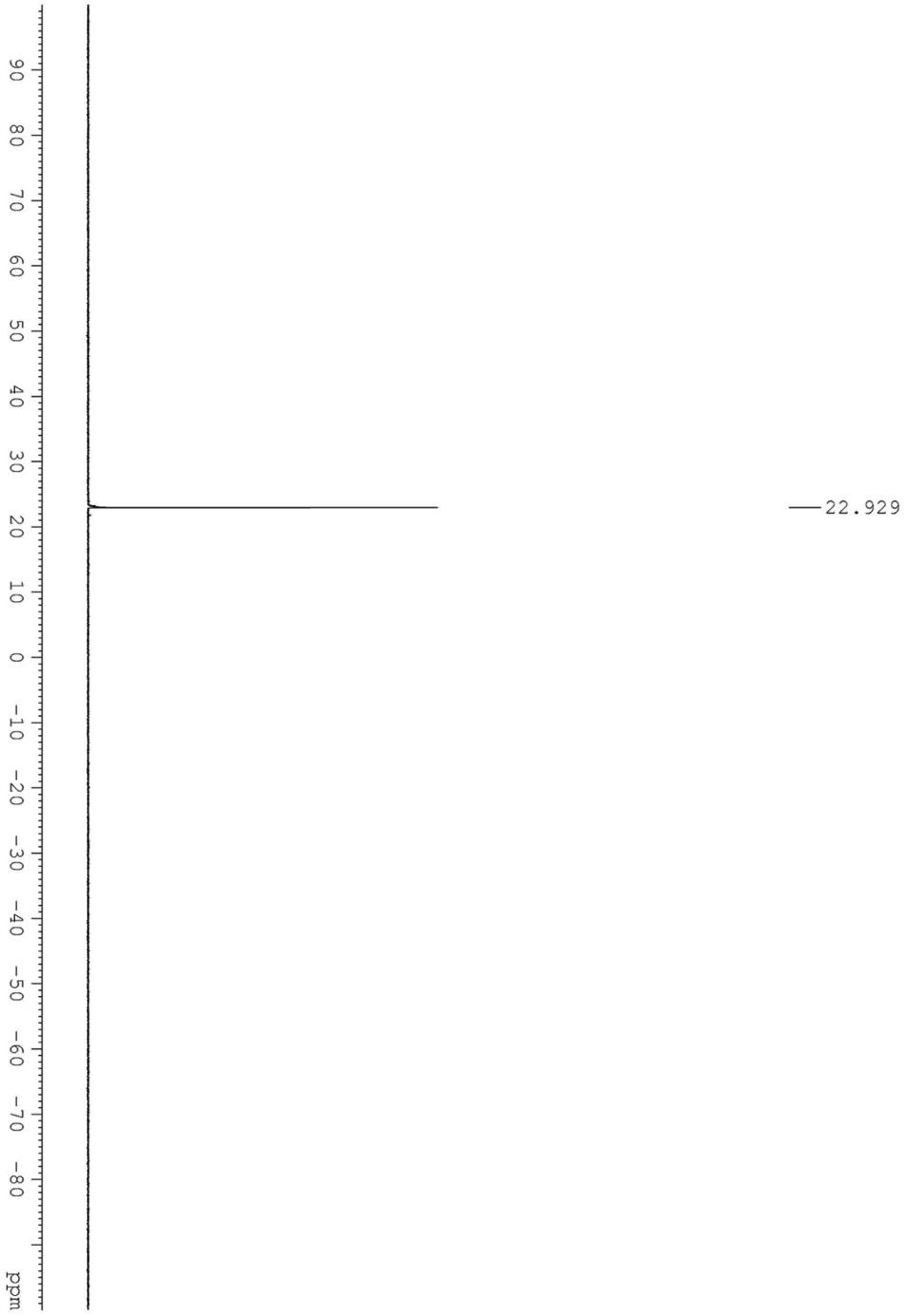

22.594
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
ppm

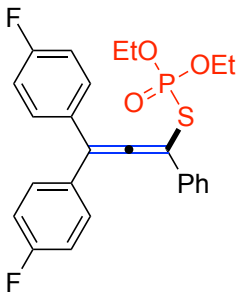

EtO
OEt
O
P
S
Ph

3l

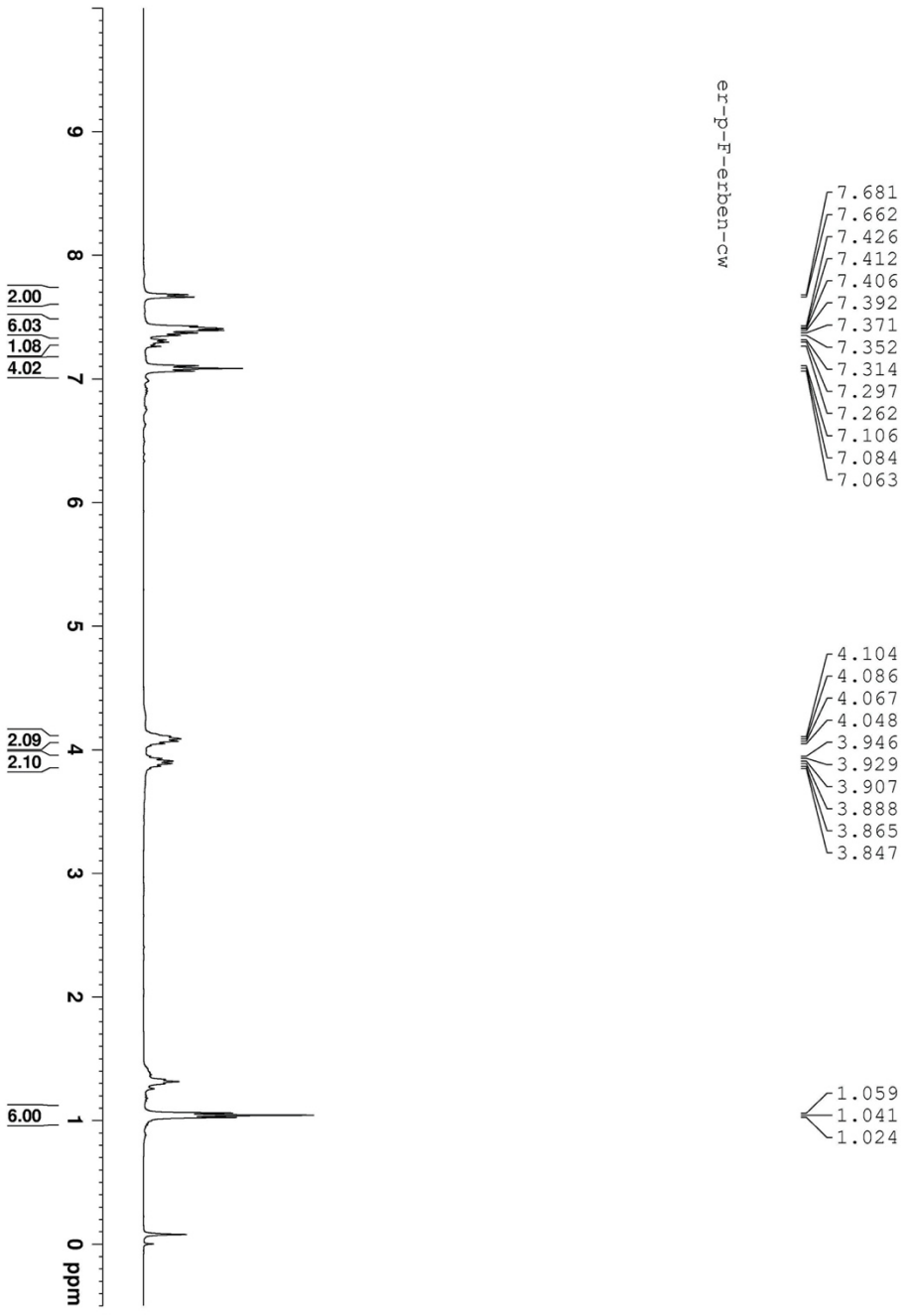

2.018
6.076
1.077
4.010
2.084
2.024
6.000
6.062
7.629
7.610
7.285
7.267
7.247
7.202
7.183
7.179
7.115
7.095
4.028
4.010
4.003
3.991
3.986
3.973
3.966
3.955
3.948
3.930
3.842
3.824
3.806
3.803
3.785
3.782
3.778
3.760
2.292
0.952
0.934
0.917
ppm

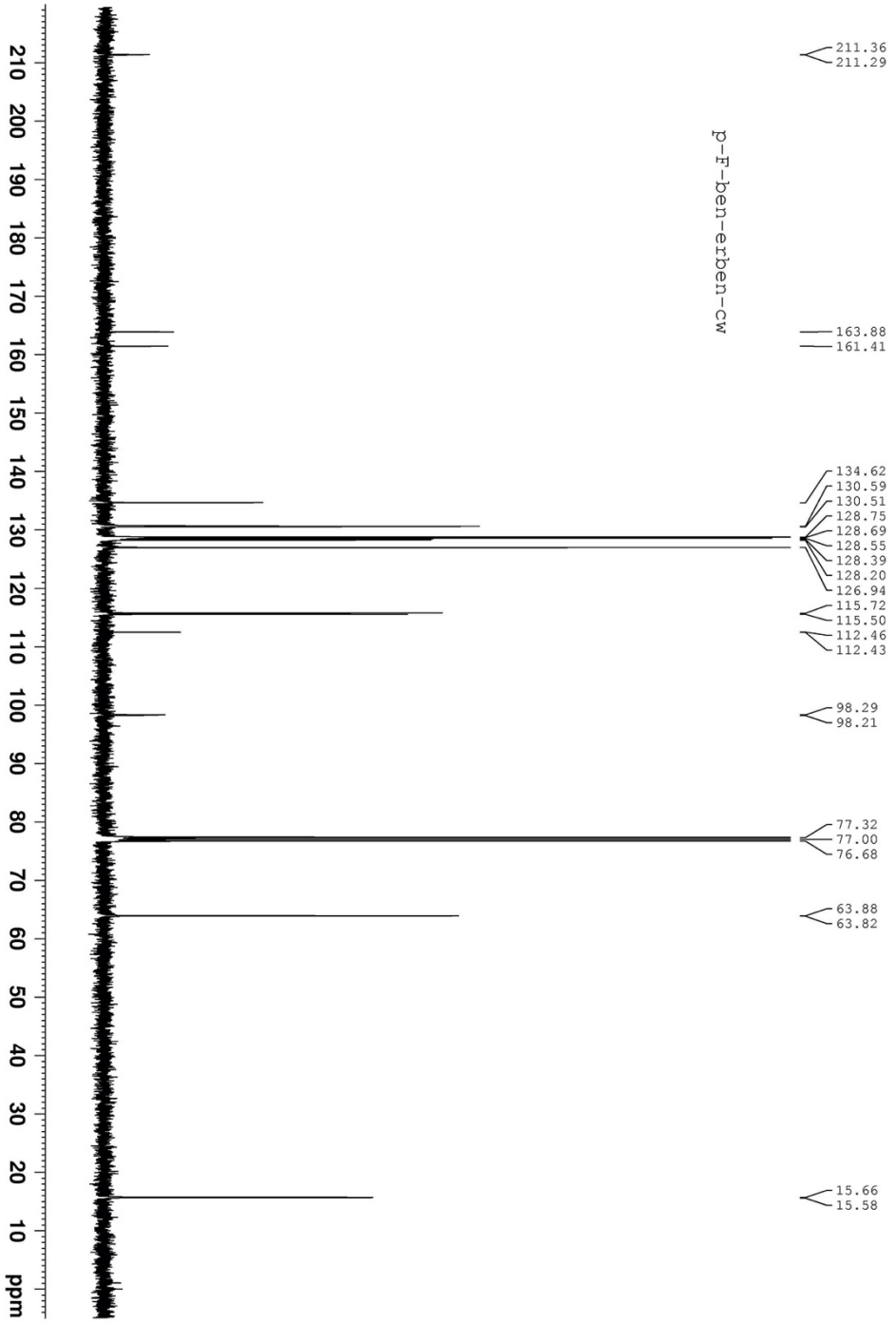

211.702
211.623
138.182
135.114
131.900
131.863
129.316
128.813
128.488
127.969
127.013
113.227
97.649
97.562
77.353
77.036
76.718
63.857
63.799
21.240
15.683
15.610
200
180
160
140
120
100
80
60
40
20
0 ppm

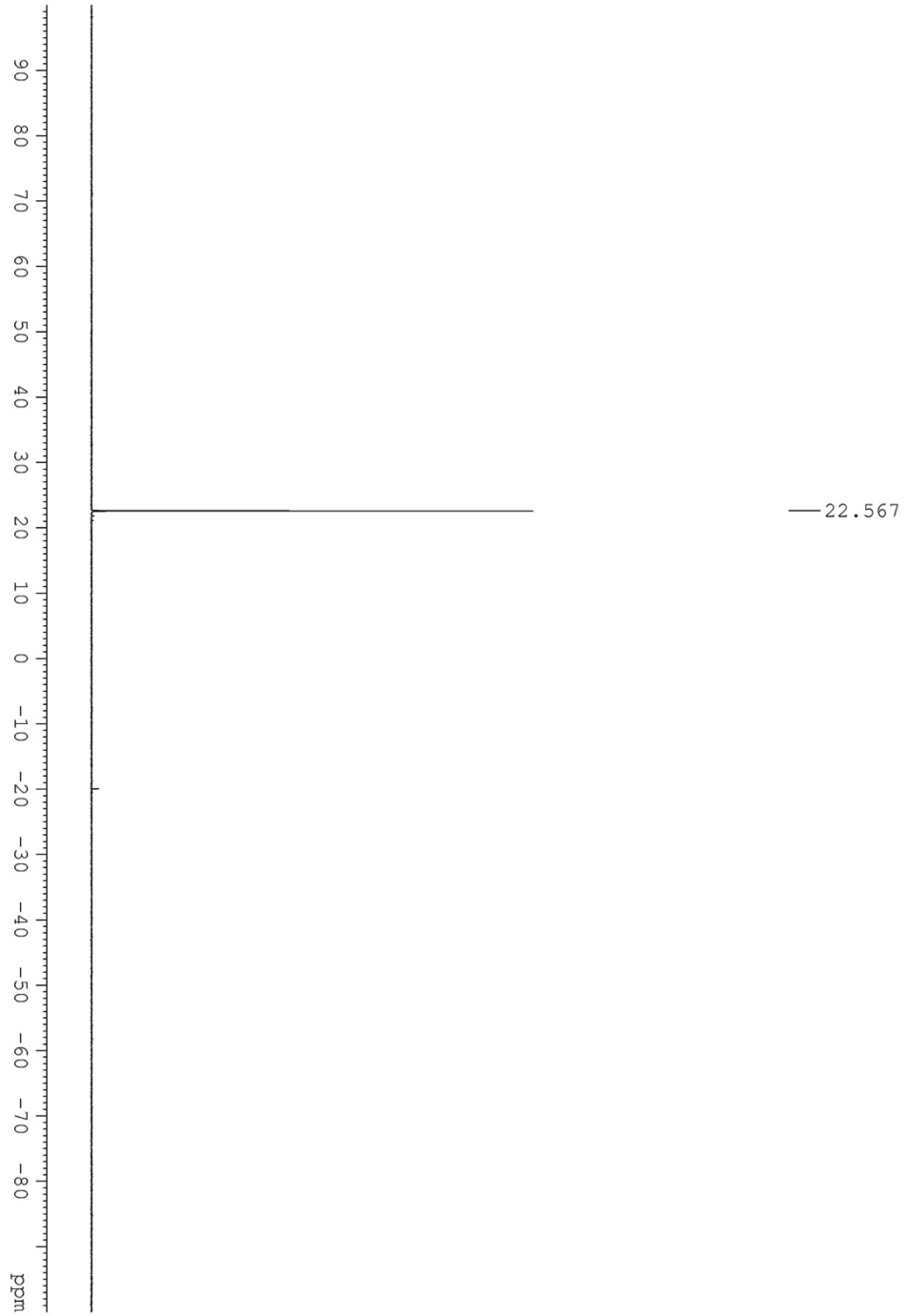

22.929
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
ppm

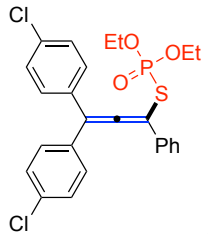

F
EtO
OEt
O
P
S
Ph
F

3m

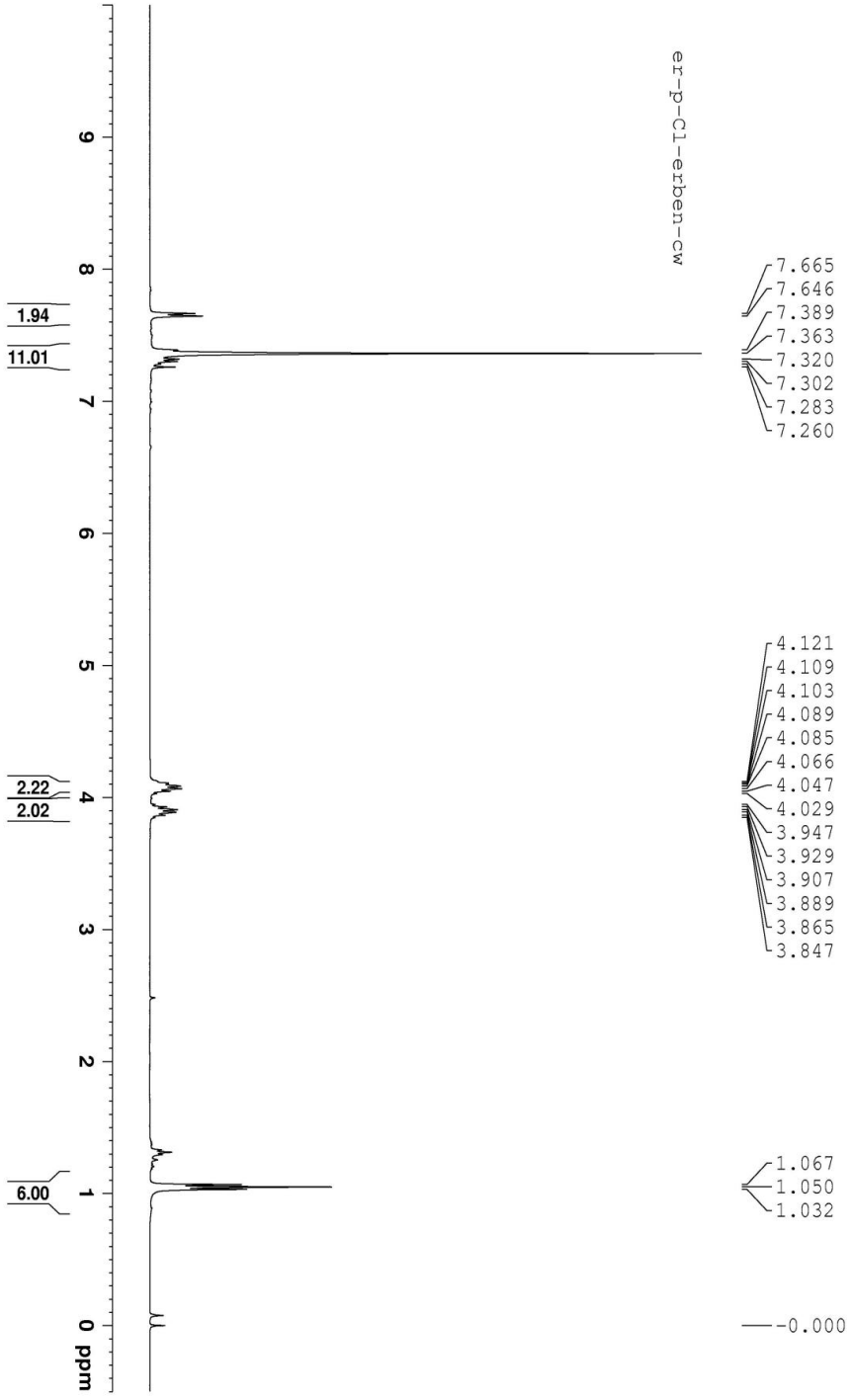

er-p-F-erben-cw
2.00
6.03
1.08
4.02
2.09
2.10
6.00
9
8
7
6
5
4
3
2
1
0
ppm
7.681
7.662
7.426
7.412
7.406
7.392
7.371
7.352
7.314
7.297
7.262
7.106
7.084
7.063
4.104
4.086
4.067
4.048
3.946
3.929
3.907
3.888
3.865
3.847
1.059
1.041
1.024

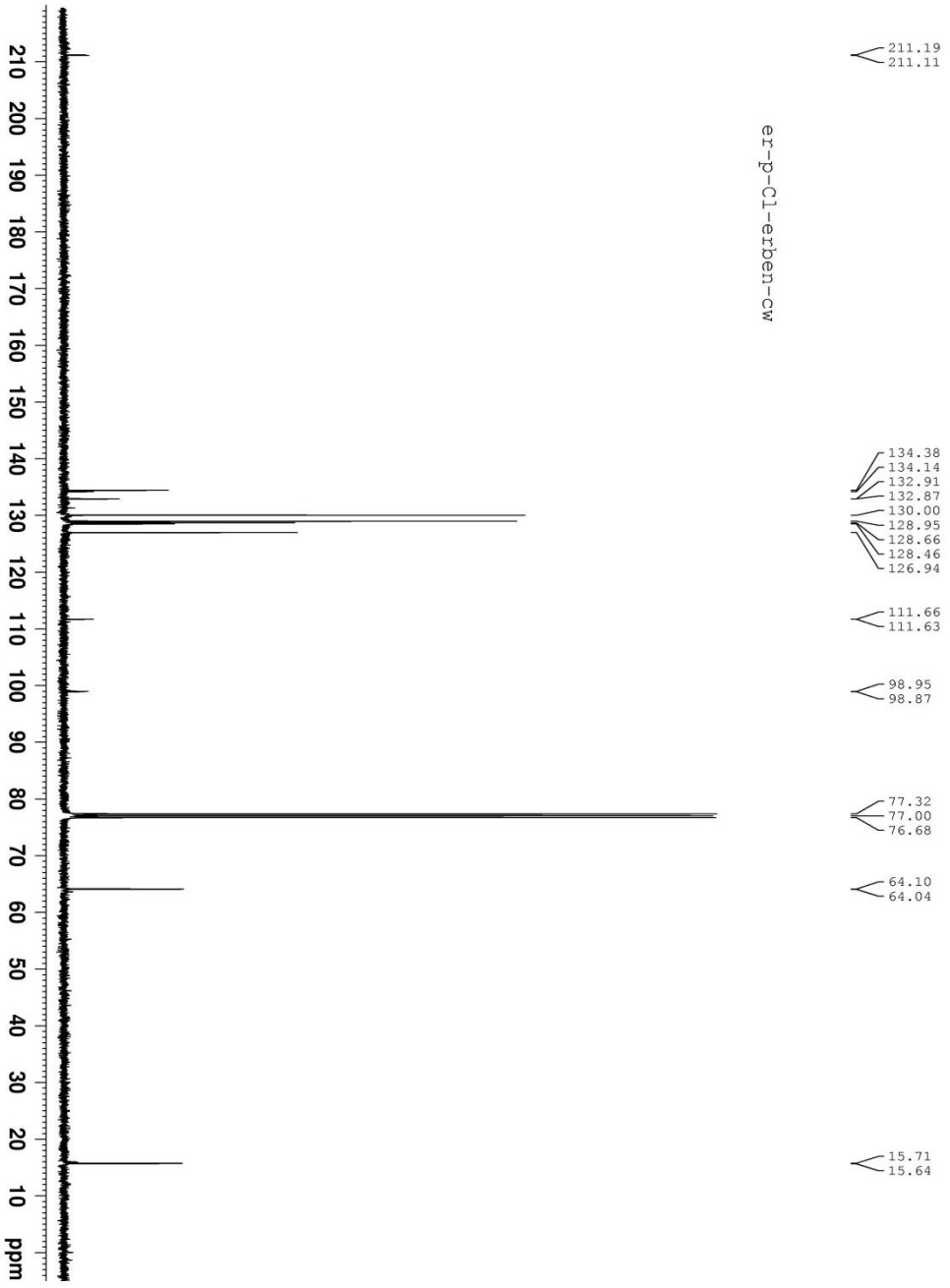

211.36
211.29
163.88
161.41
134.62
130.59
130.51
128.75
128.69
128.55
128.39
128.20
126.94
115.72
115.50
112.46
112.43
98.29
98.21
77.32
77.00
76.68
63.88
63.82
15.66
15.58
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

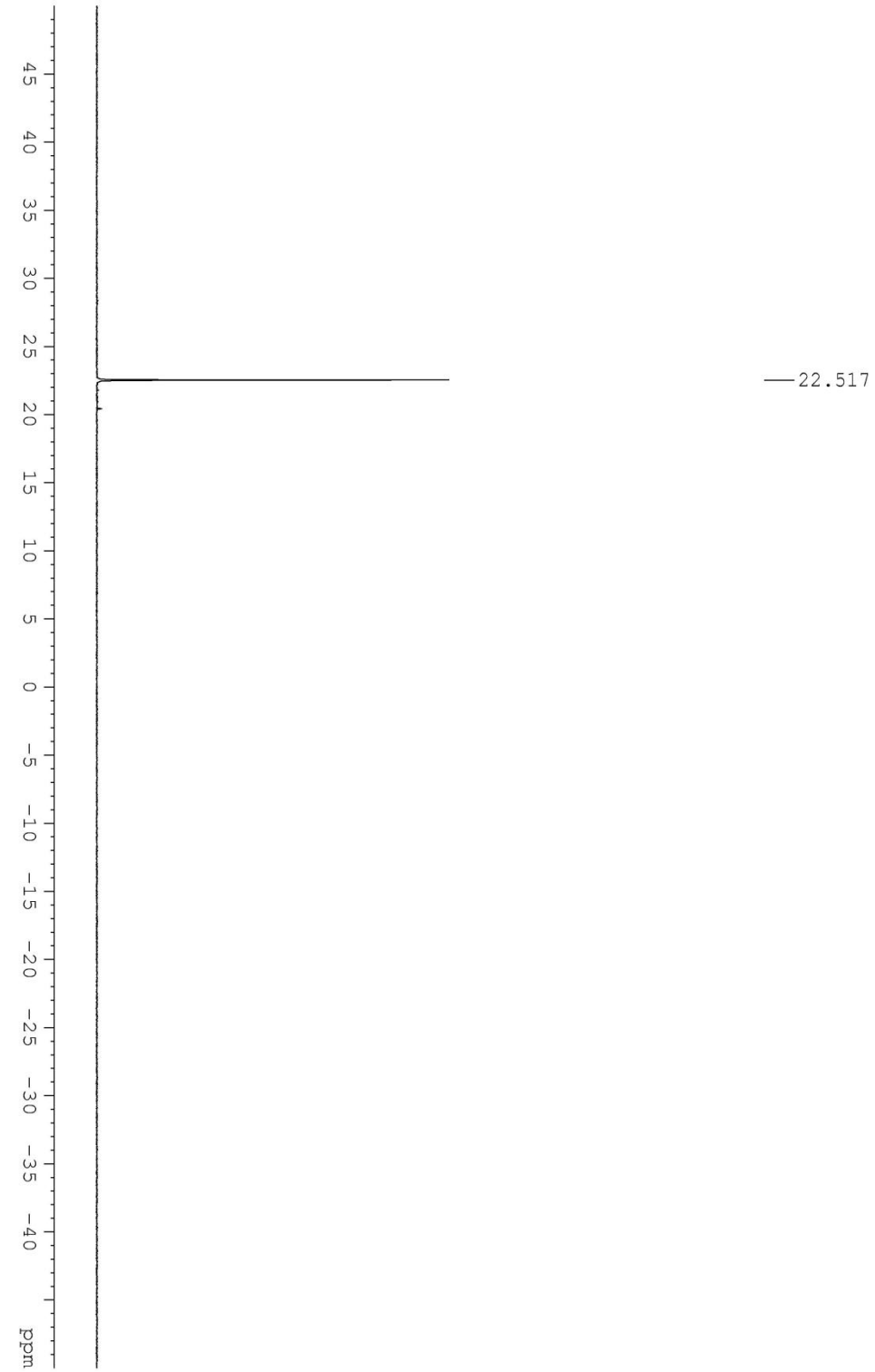

22.567
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
ppm

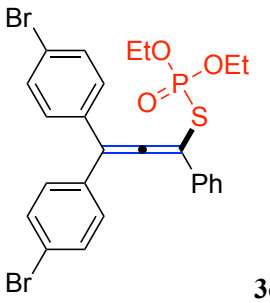

Cl
EtO
OEt
O
P
S
Ph
Cl

3n

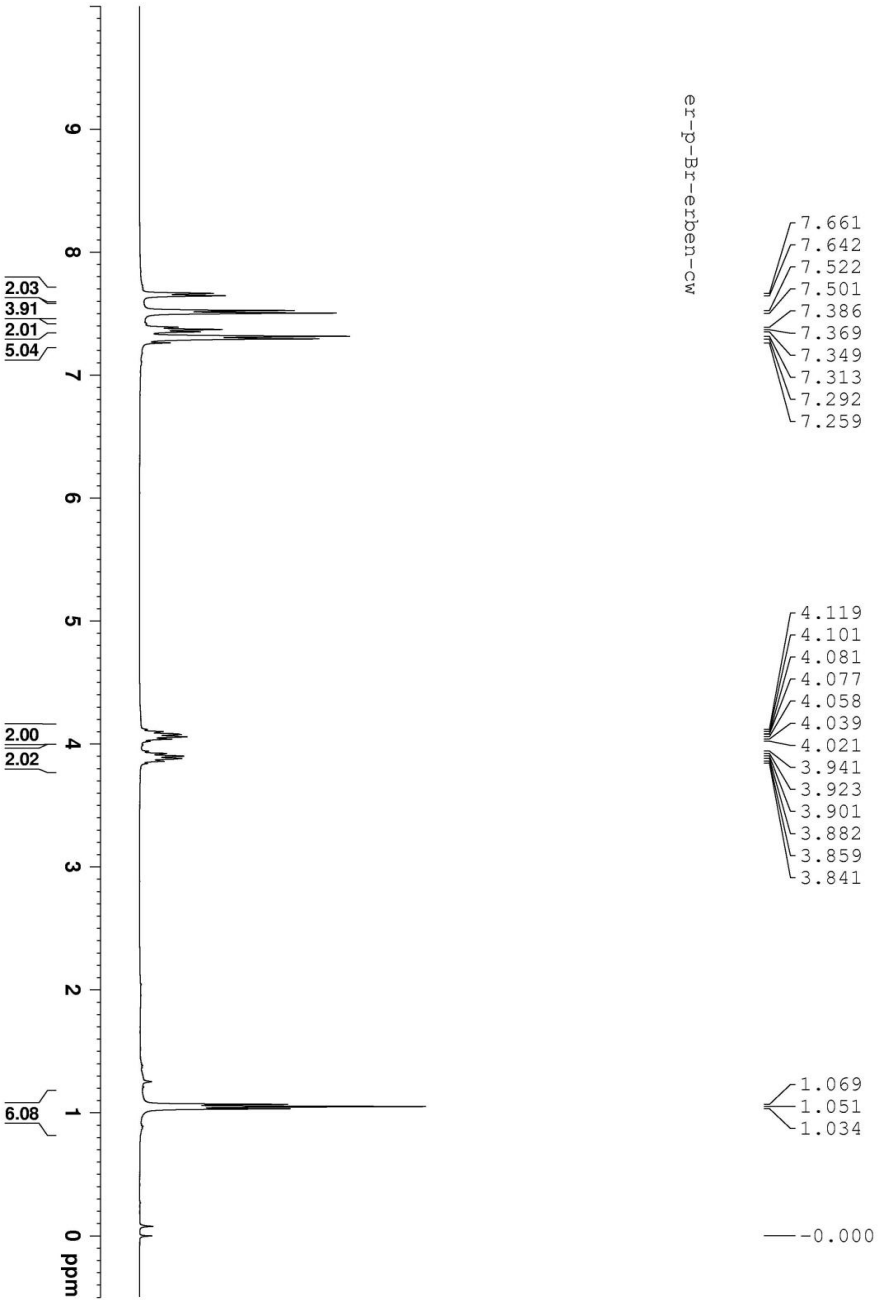

er-p-Cl-erben-cw
7.665
7.646
7.389
7.363
7.320
7.302
7.283
7.260
4.121
4.109
4.103
4.089
4.085
4.066
4.047
4.029
3.947
3.929
3.907
3.889
3.865
3.847
1.067
1.050
1.032
-0.000
1.94
11.01
2.22
2.02
6.00
ppm

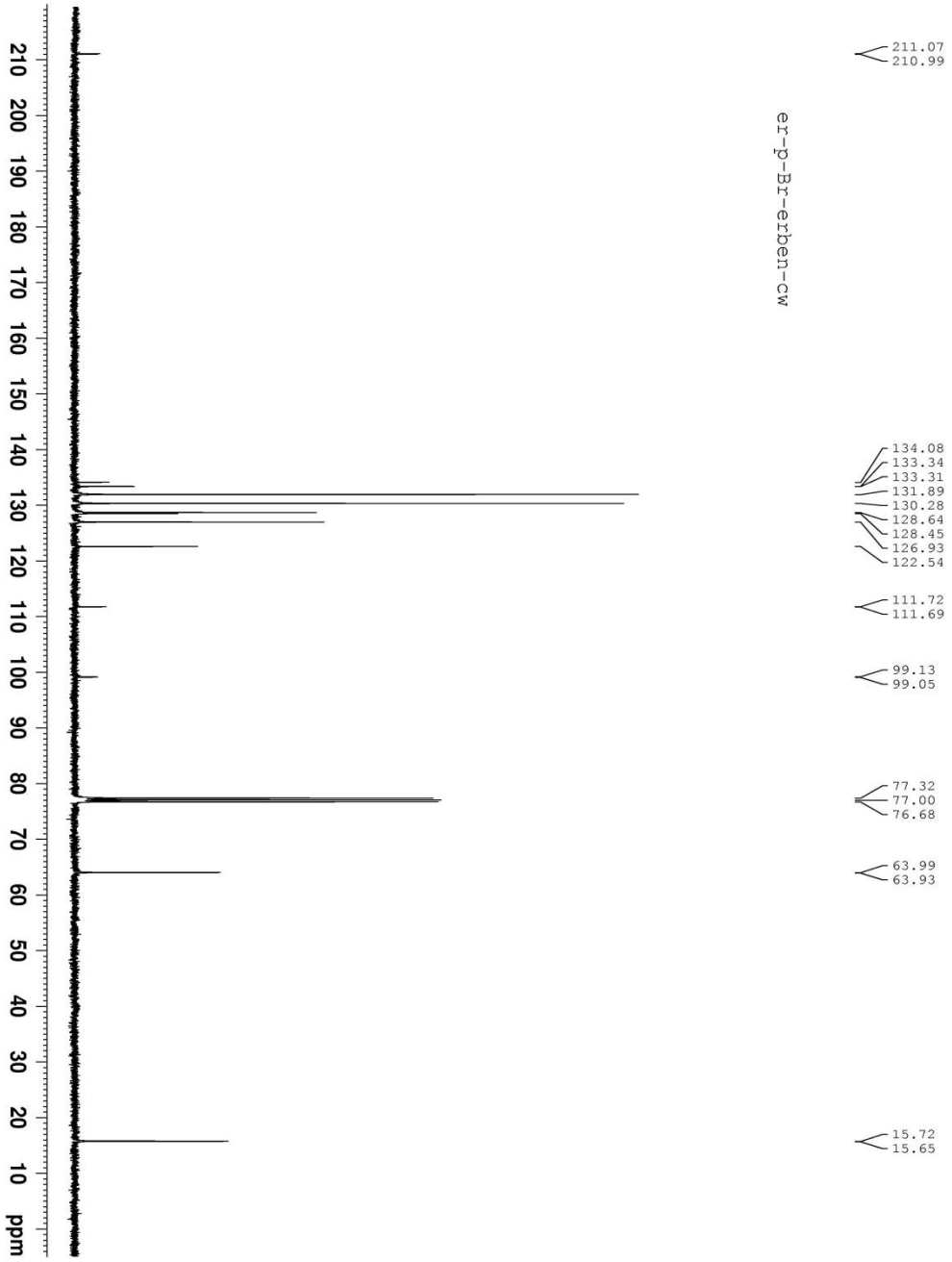

er-p-Cl-erben-cw
211.19
211.11
134.38
134.14
132.91
132.87
130.00
128.95
128.66
128.46
126.94
111.66
111.63
98.95
98.87
77.32
77.00
76.68
64.10
64.04
15.71
15.64
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


22.517
45
40
35
30
25
20
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
ppm

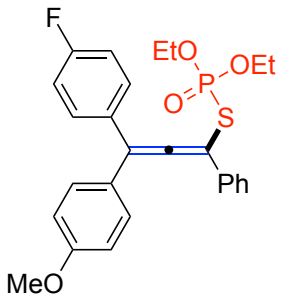

Br
EtO
OEt
O
P
S
Ph
Br

3o

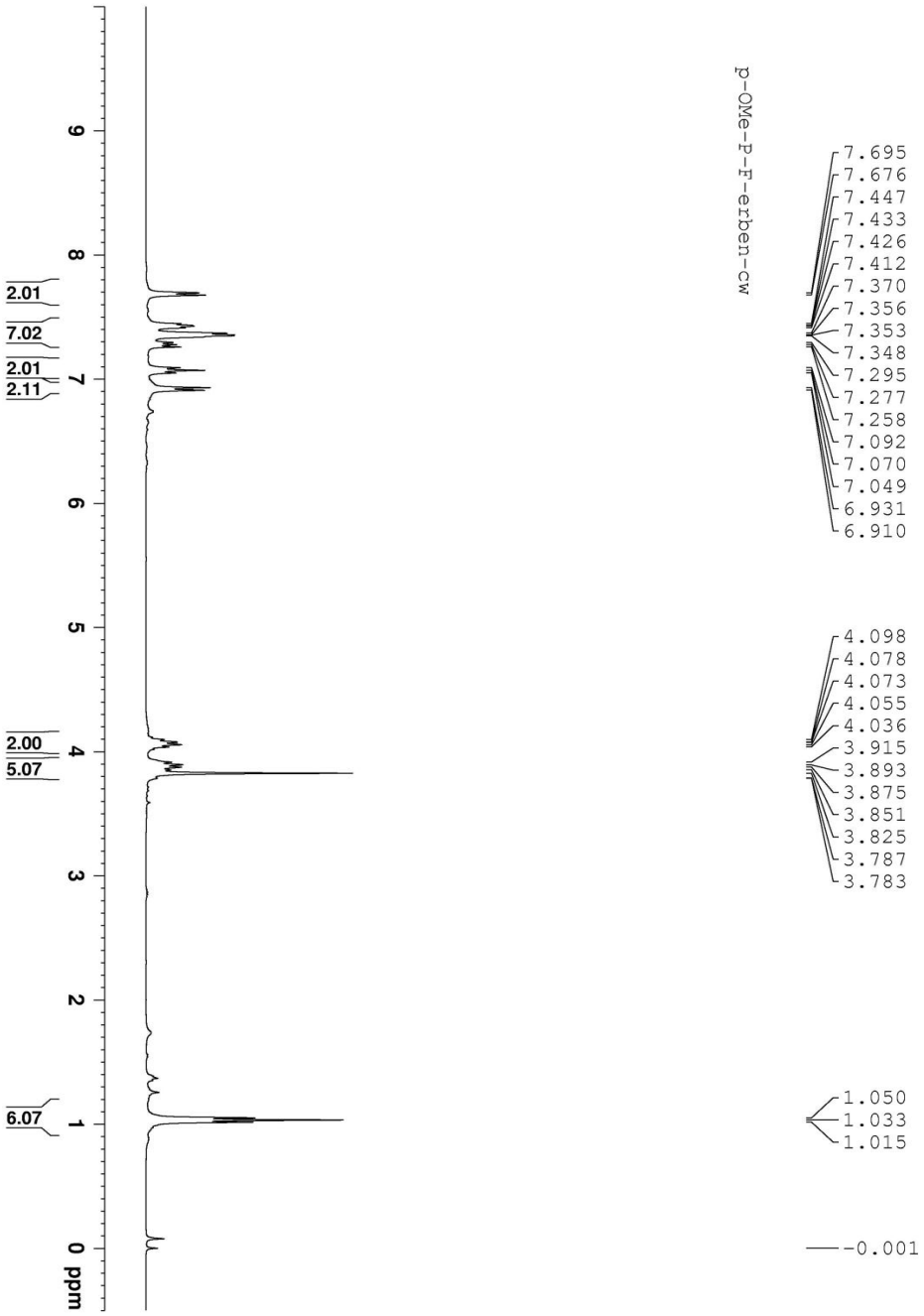

er-p-Br-erben-cw
7.661
7.642
7.522
7.501
7.386
7.369
7.349
7.313
7.292
7.259
4.119
4.101
4.081
4.077
4.058
4.039
4.021
3.941
3.923
3.901
3.882
3.859
3.841
1.069
1.051
1.034
-0.000
2.03
3.91
2.01
5.04
2.00
2.02
6.08
ppm

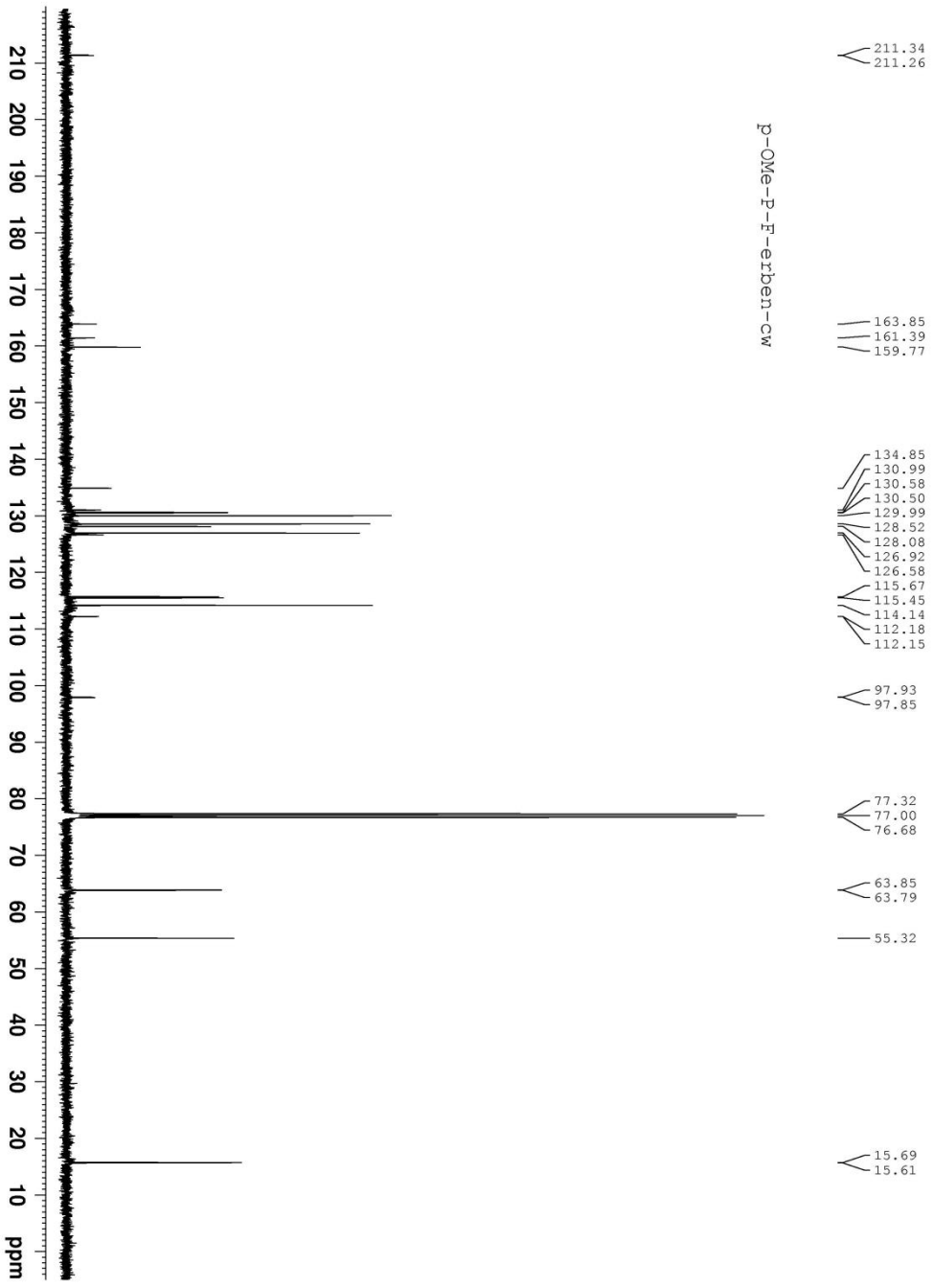

er-p-Br-erben-cw
211.07
210.99
134.08
133.34
133.31
131.89
130.28
128.64
128.45
126.93
122.54
111.72
111.69
99.13
99.05
77.32
77.00
76.68
63.99
63.93
15.72
15.65
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

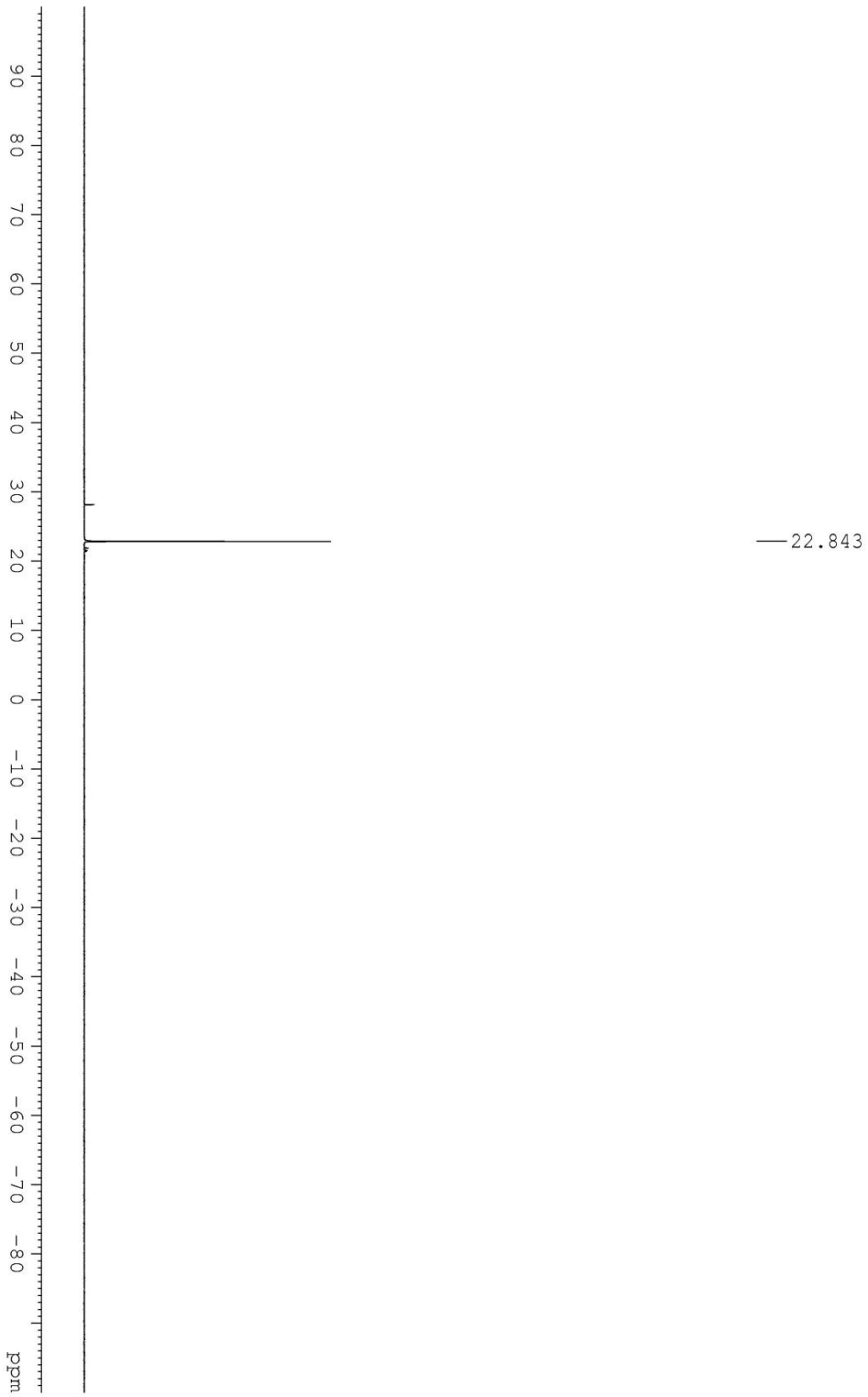
22.337
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
ppm

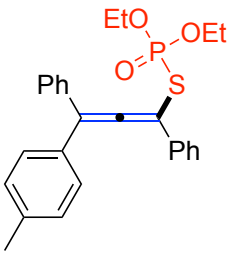

F
EtO
OEt
O
P
S
Ph
MeO

3p

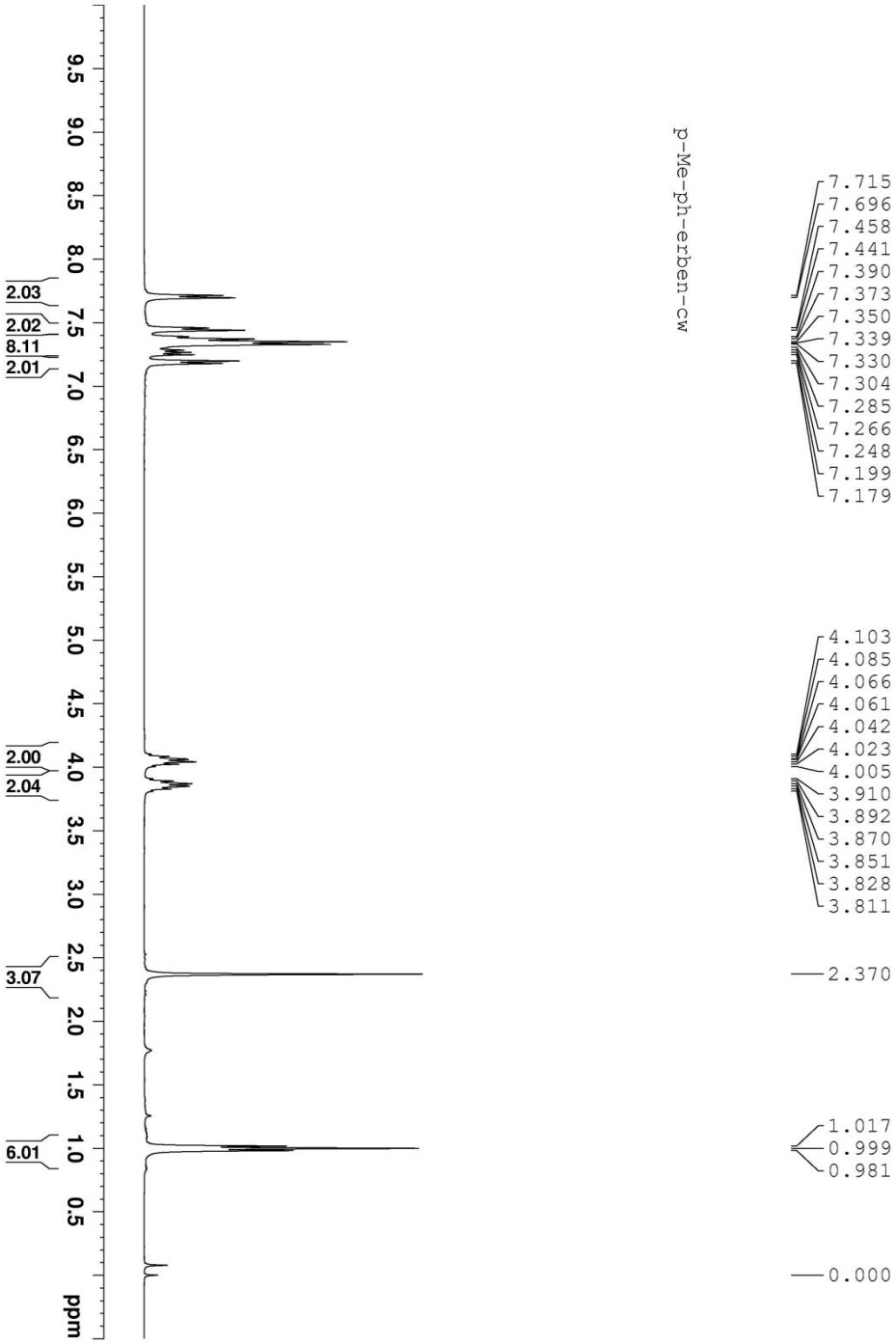

p-OMe-p-F-epen-cw
2.01
7.02
2.01
2.11
2.00
5.07
6.07
9
8
7
6
5
4
3
2
1
0
ppm
7.695
7.676
7.447
7.433
7.426
7.412
7.370
7.356
7.353
7.348
7.295
7.277
7.258
7.092
7.070
7.049
6.931
6.910
4.098
4.078
4.073
4.055
4.036
3.915
3.893
3.875
3.851
3.825
3.787
3.783
1.050
1.033
1.015
-0.001

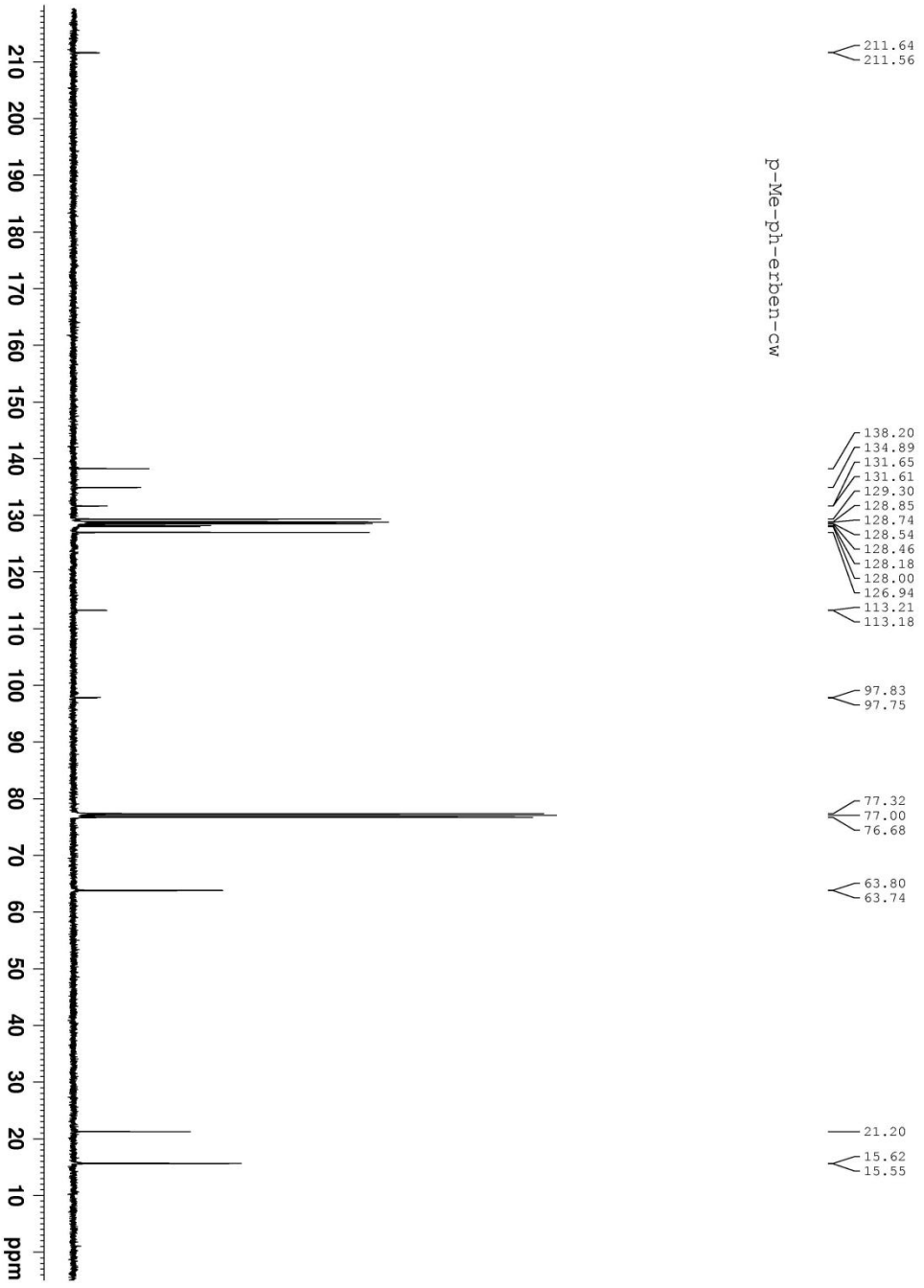

p-OMe-P-F-erben-cw
211.34
211.26
163.85
161.39
159.77
134.85
130.99
130.58
130.50
129.99
128.52
128.08
126.92
126.58
115.67
115.45
114.14
112.18
112.15
97.93
97.85
77.32
77.00
76.68
63.85
63.79
55.32
15.69
15.61
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

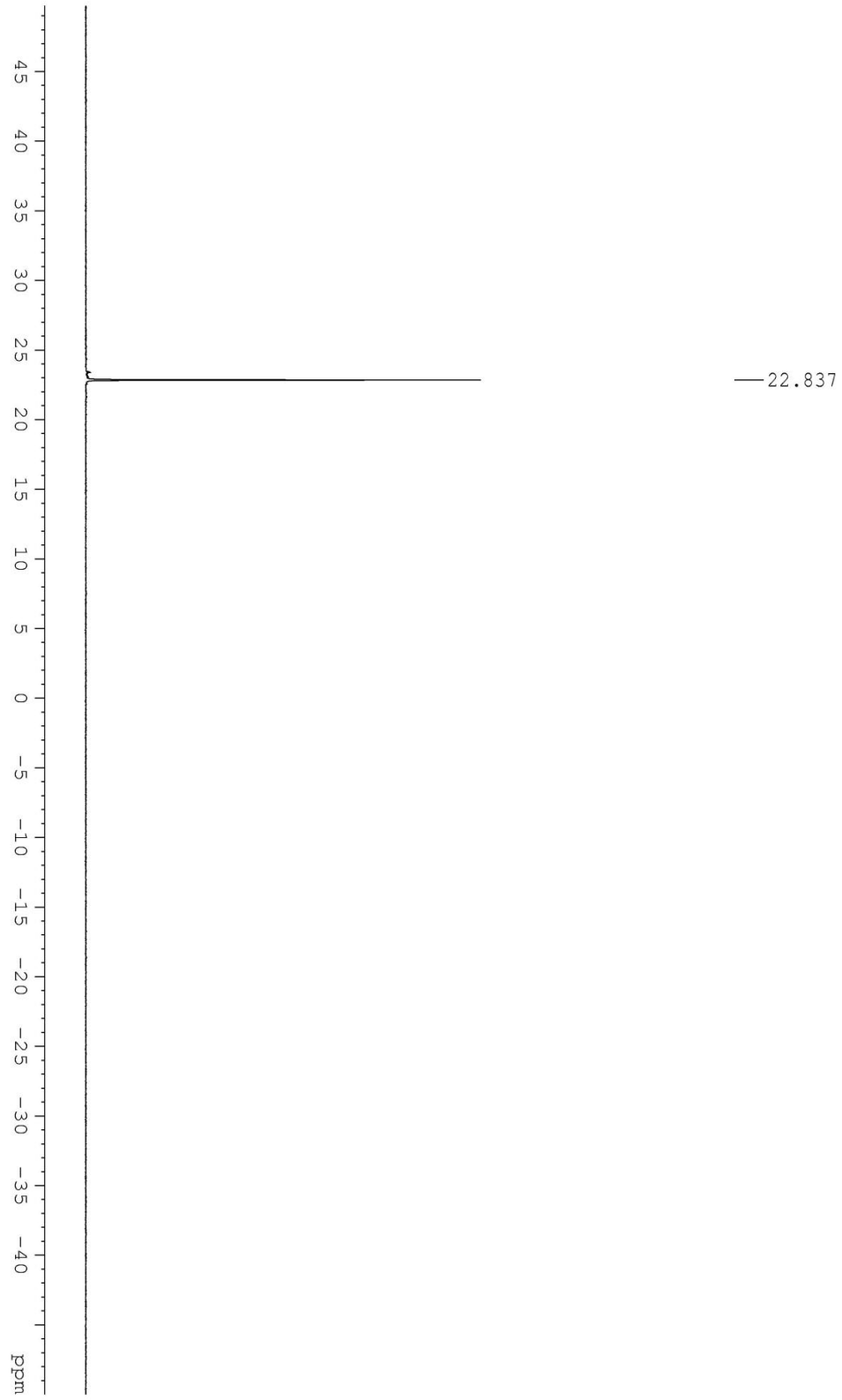

22.843
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
ppm

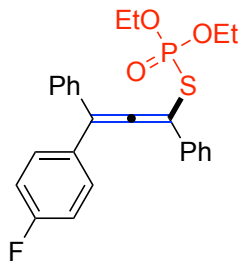

EtO
OEt
O
P
S
Ph
Ph

3q

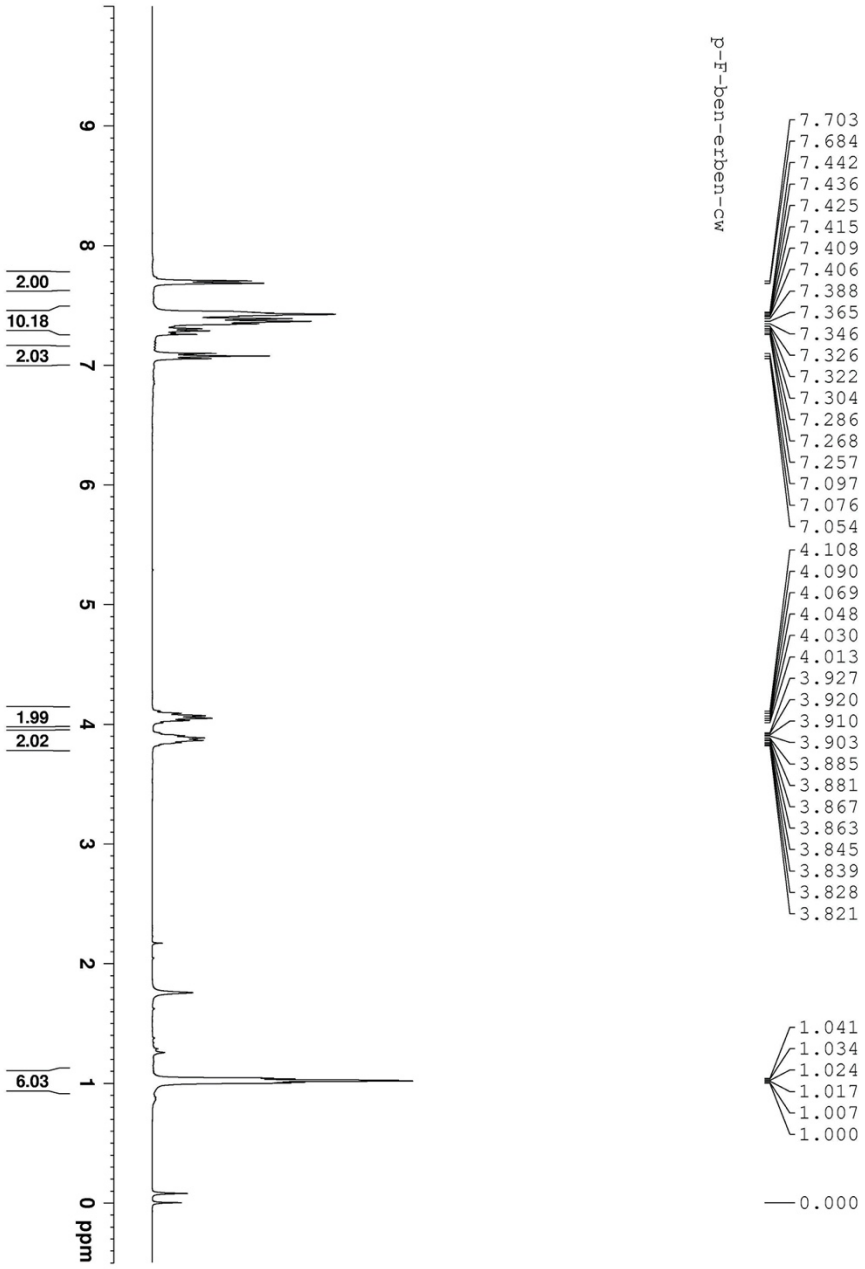

p-Me-ph-erben-cw
2.03
2.02
8.11
2.01
2.00
2.04
3.07
6.01
ppm
7.715
7.696
7.458
7.441
7.390
7.373
7.350
7.339
7.330
7.304
7.285
7.266
7.248
7.199
7.179
4.103
4.085
4.066
4.061
4.042
4.023
4.005
3.910
3.892
3.870
3.851
3.828
3.811
2.370
1.017
0.999
0.981
0.000

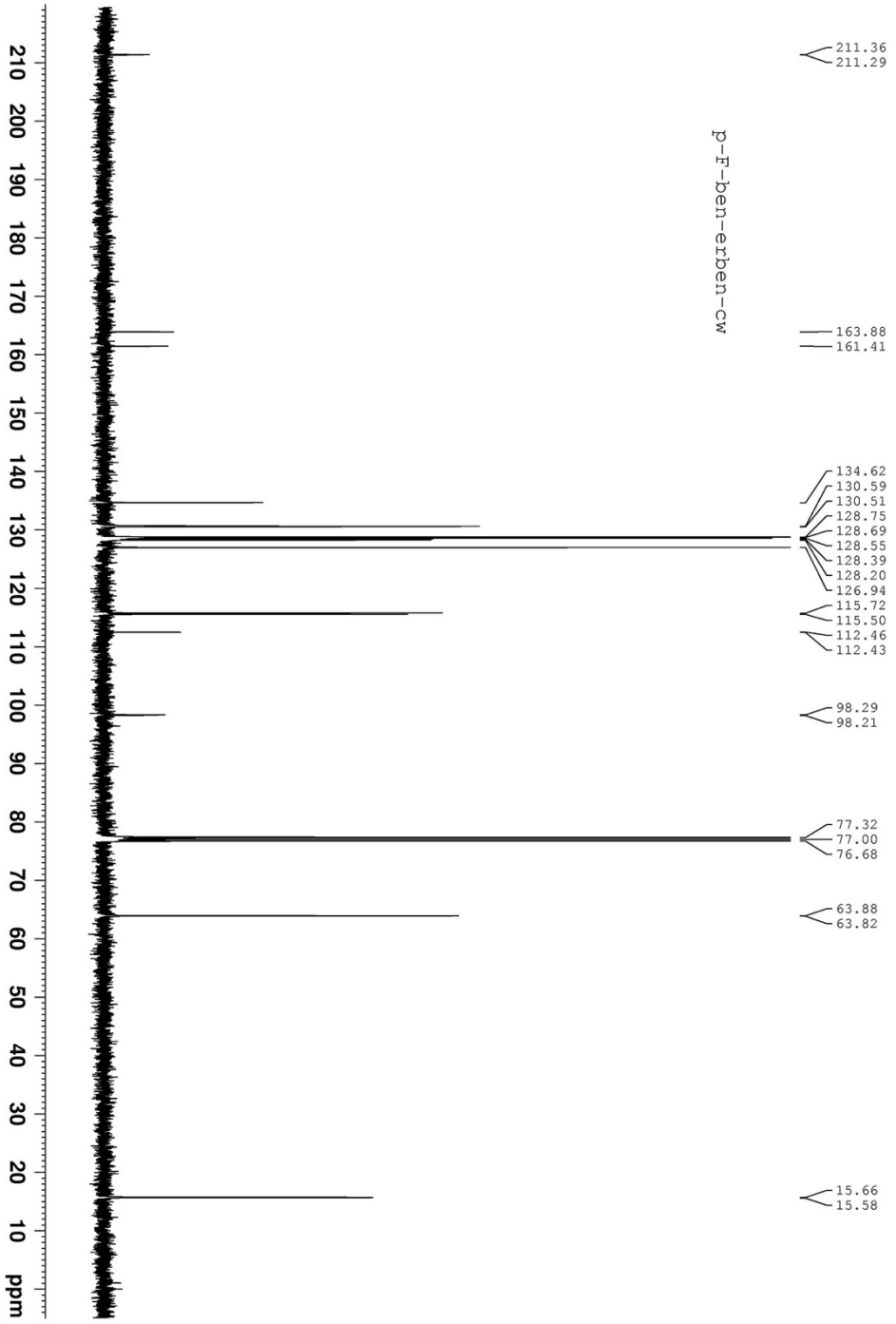

p-Me-ph-erben-cw
211.64
211.56
138.20
134.89
131.65
131.61
129.30
128.85
128.74
128.54
128.46
128.18
128.00
126.94
113.21
113.18
97.83
97.75
77.32
77.00
76.68
63.80
63.74
21.20
15.62
15.55
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

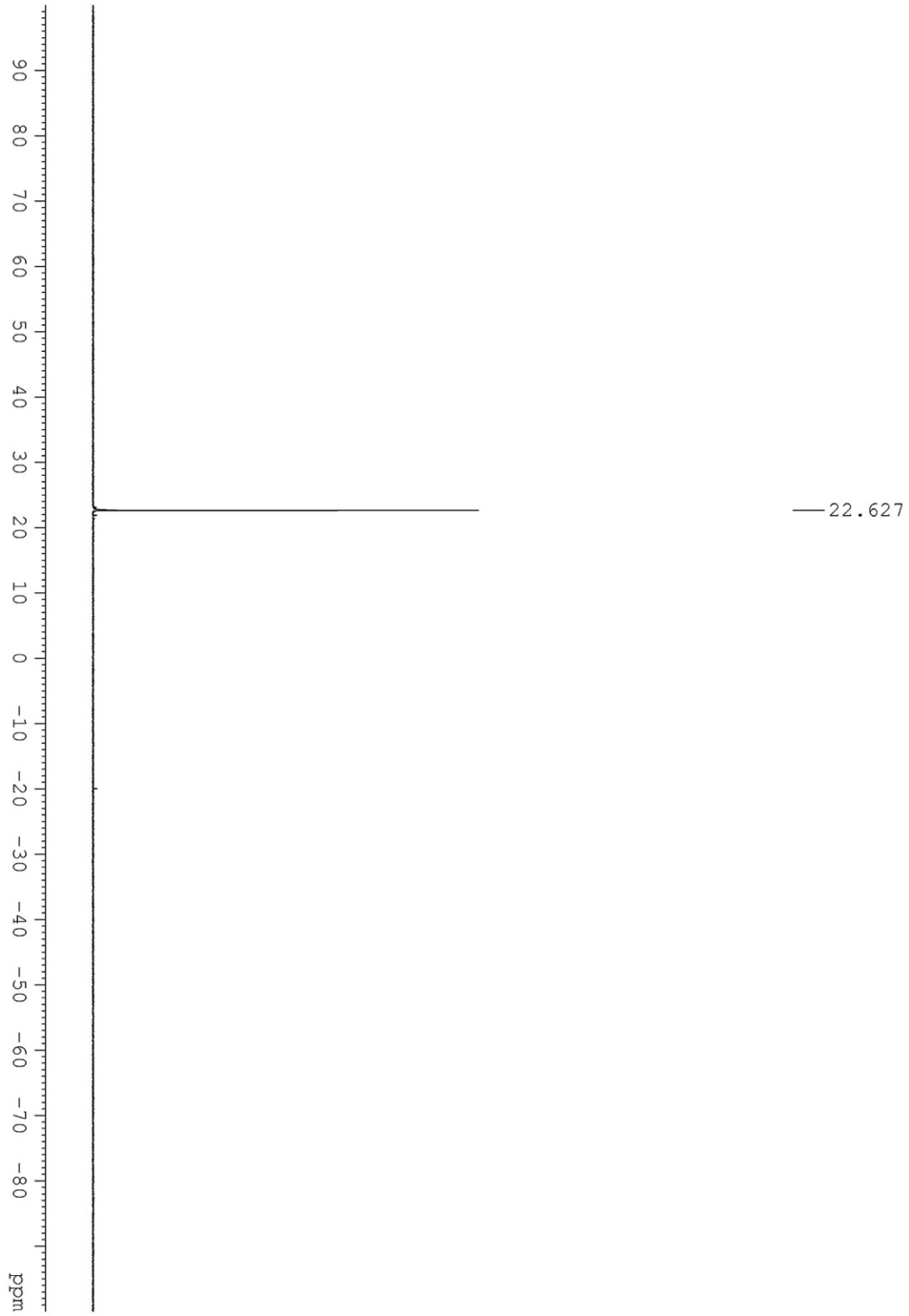

22.837
45
40
35
30
25
20
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
ppm

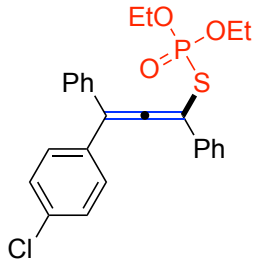

EtO
OEt
O
P
S
Ph
Ph
F

3r

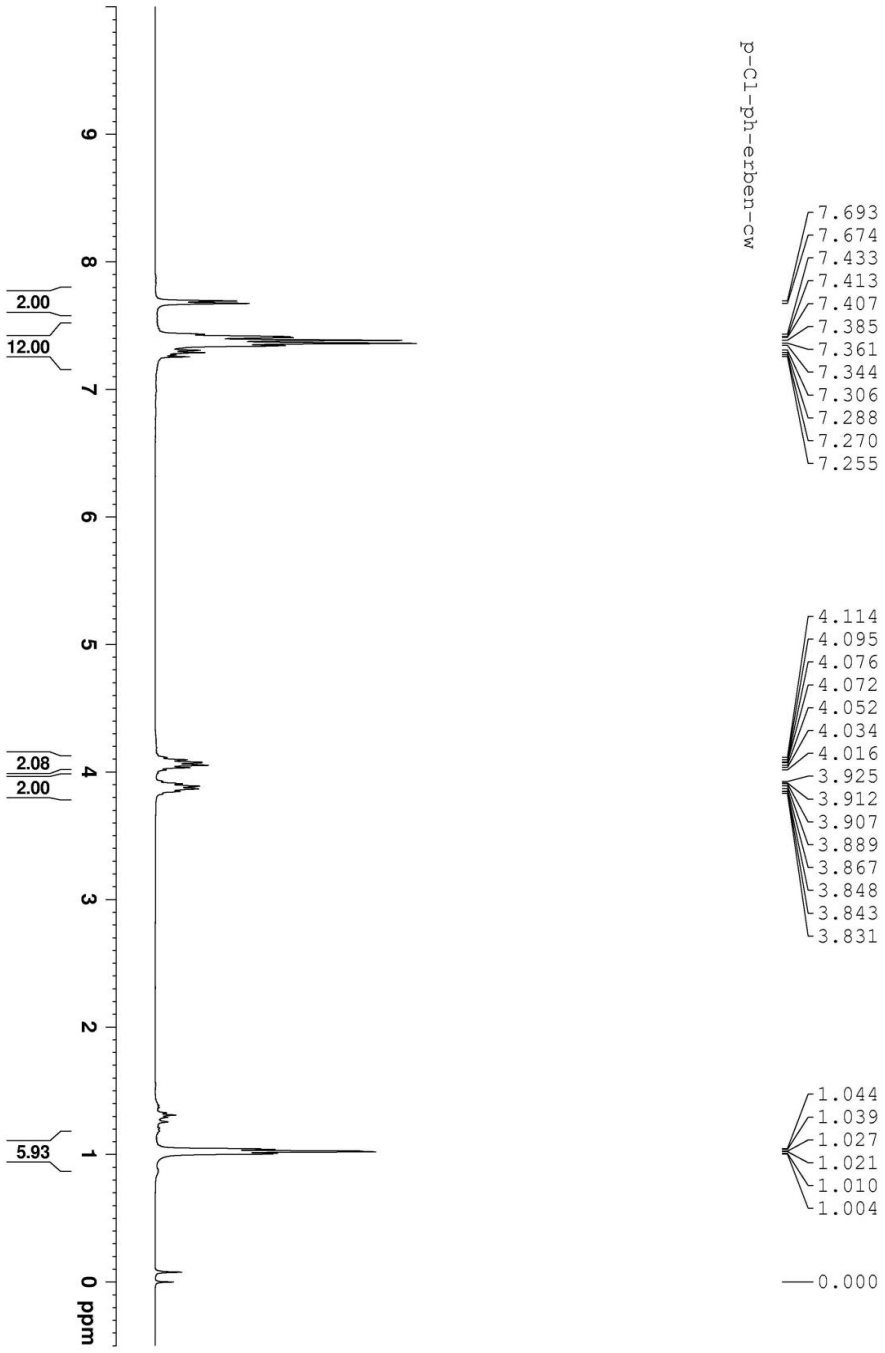

p-F-ben-erben-cw
2.00
10.18
2.03
1.99
2.02
6.03
9
8
7
6
5
4
3
2
1
0 ppm
7.703
7.684
7.442
7.436
7.425
7.415
7.409
7.406
7.388
7.365
7.346
7.326
7.322
7.304
7.286
7.268
7.257
7.097
7.076
7.054
4.108
4.090
4.069
4.048
4.030
4.013
3.927
3.920
3.910
3.903
3.885
3.881
3.867
3.863
3.845
3.839
3.828
3.821
1.041
1.034
1.024
1.017
1.007
1.000
0.000

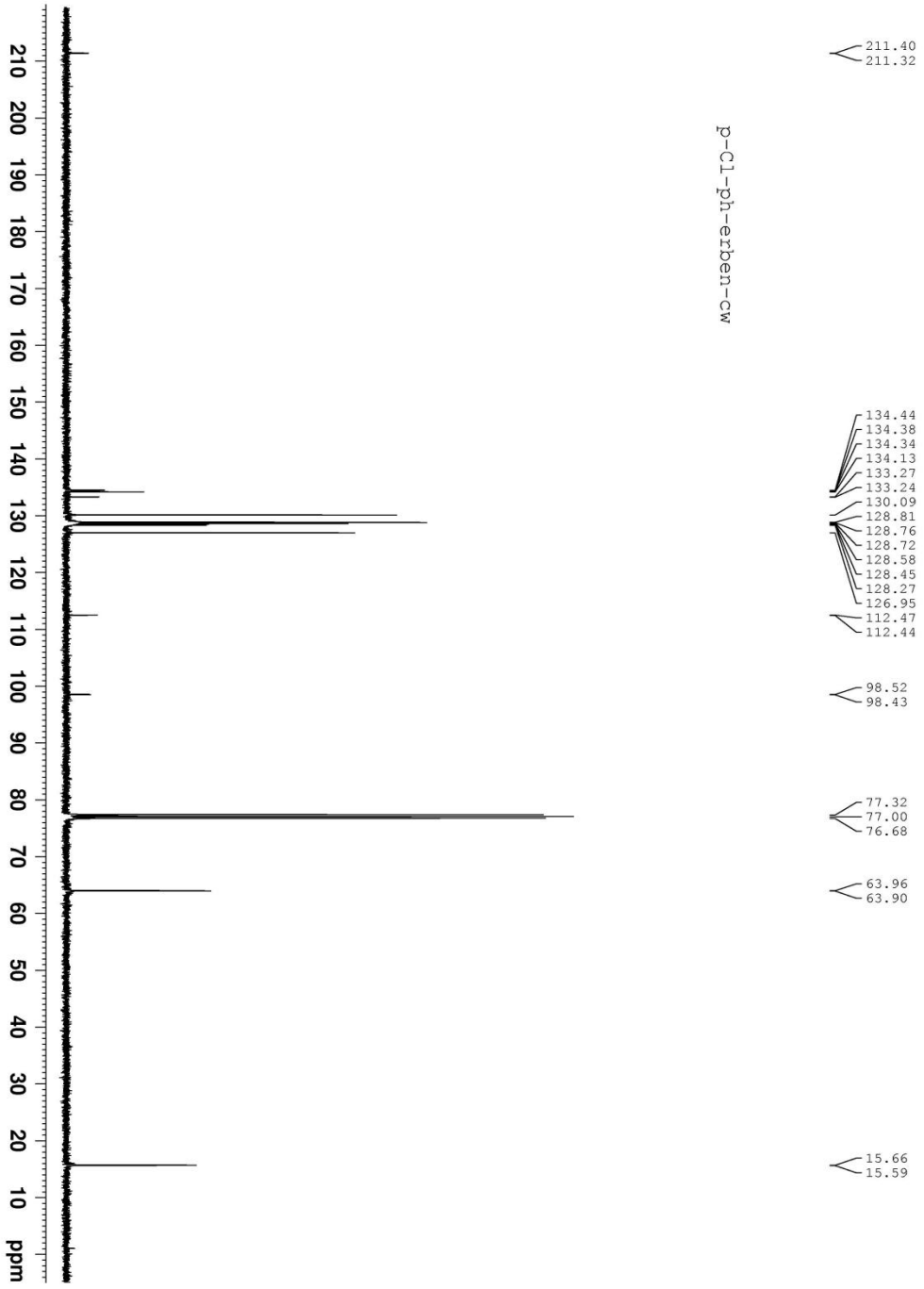

211.36
211.29
163.88
161.41
134.62
130.59
130.51
128.75
128.69
128.55
128.39
128.20
126.94
115.72
115.50
112.46
112.43
98.29
98.21
77.32
77.00
76.68
63.88
63.82
15.66
15.58
p-F-ben-erben-cm
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

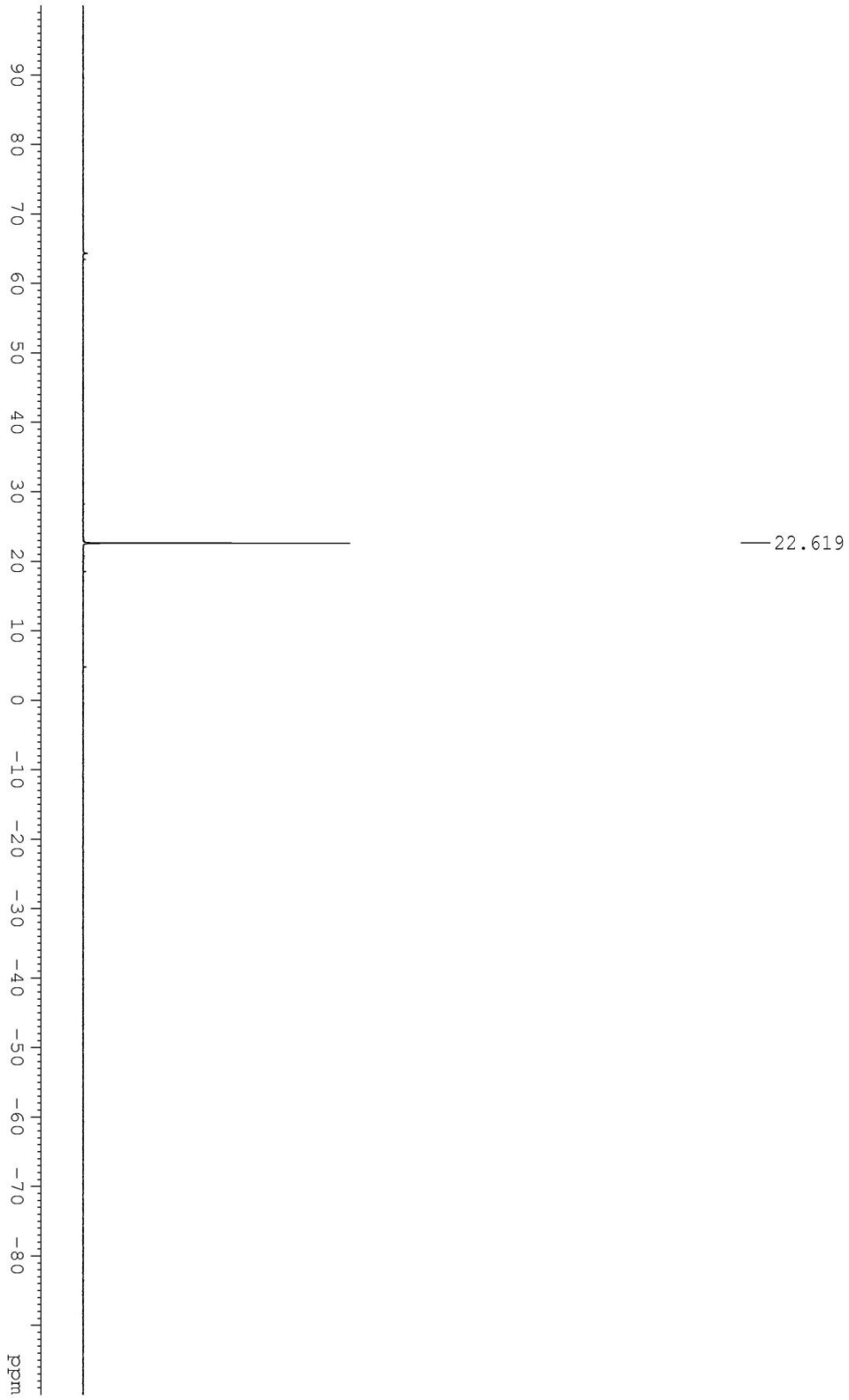

22.627
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
ppm

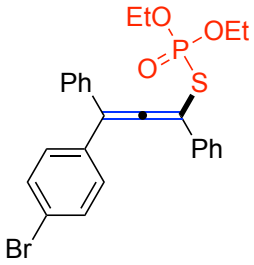

EtO
OEt
O
P
S
Ph
Ph
Cl

3s

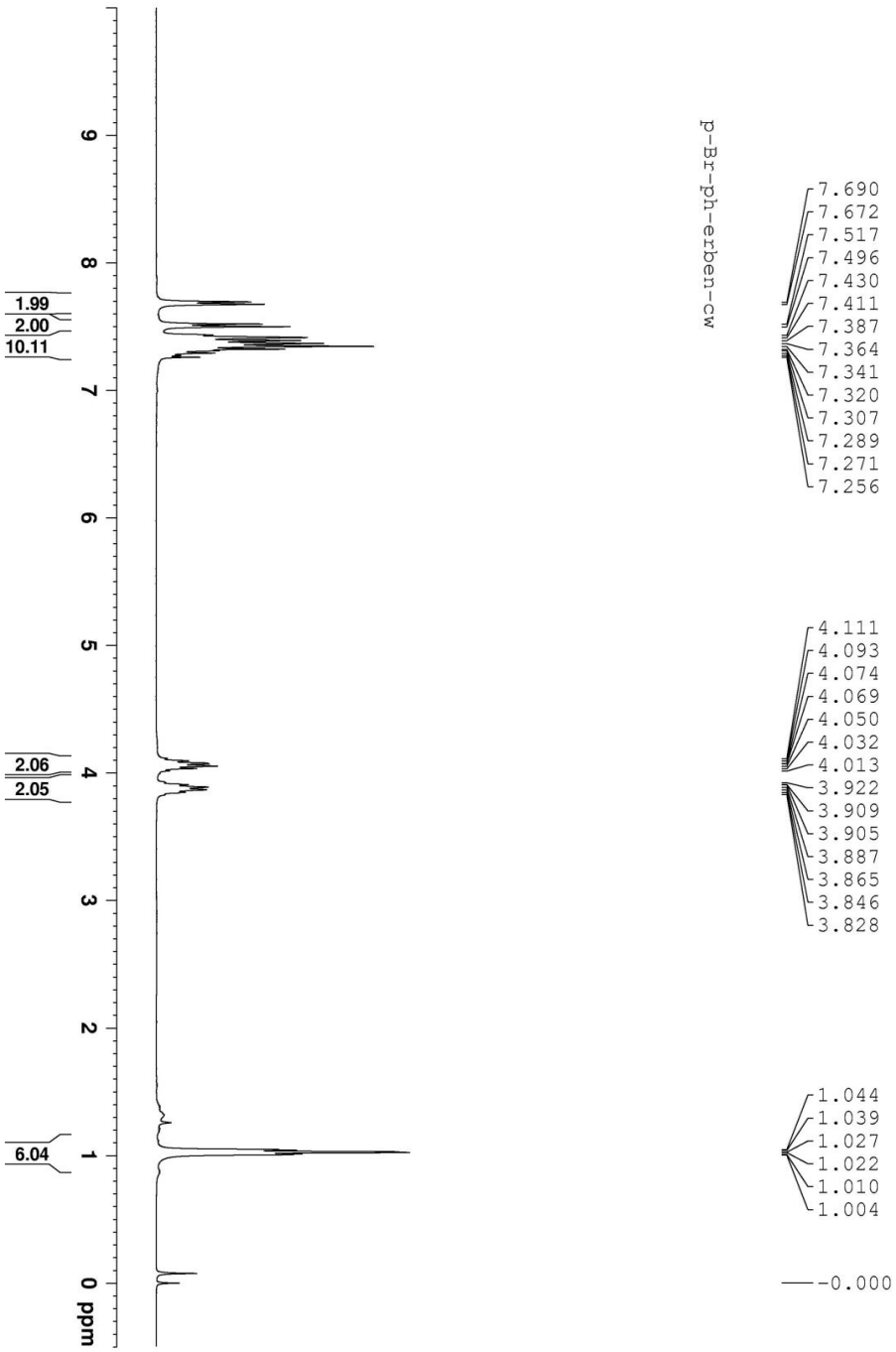

p-Cl-ph-erben-cw
7.693
7.674
7.433
7.413
7.407
7.385
7.361
7.344
7.306
7.288
7.270
7.255
4.114
4.095
4.076
4.072
4.052
4.034
4.016
3.925
3.912
3.907
3.889
3.867
3.848
3.843
3.831
1.044
1.039
1.027
1.021
1.010
1.004
0.000
2.00
12.00
2.08
2.00
5.93
ppm

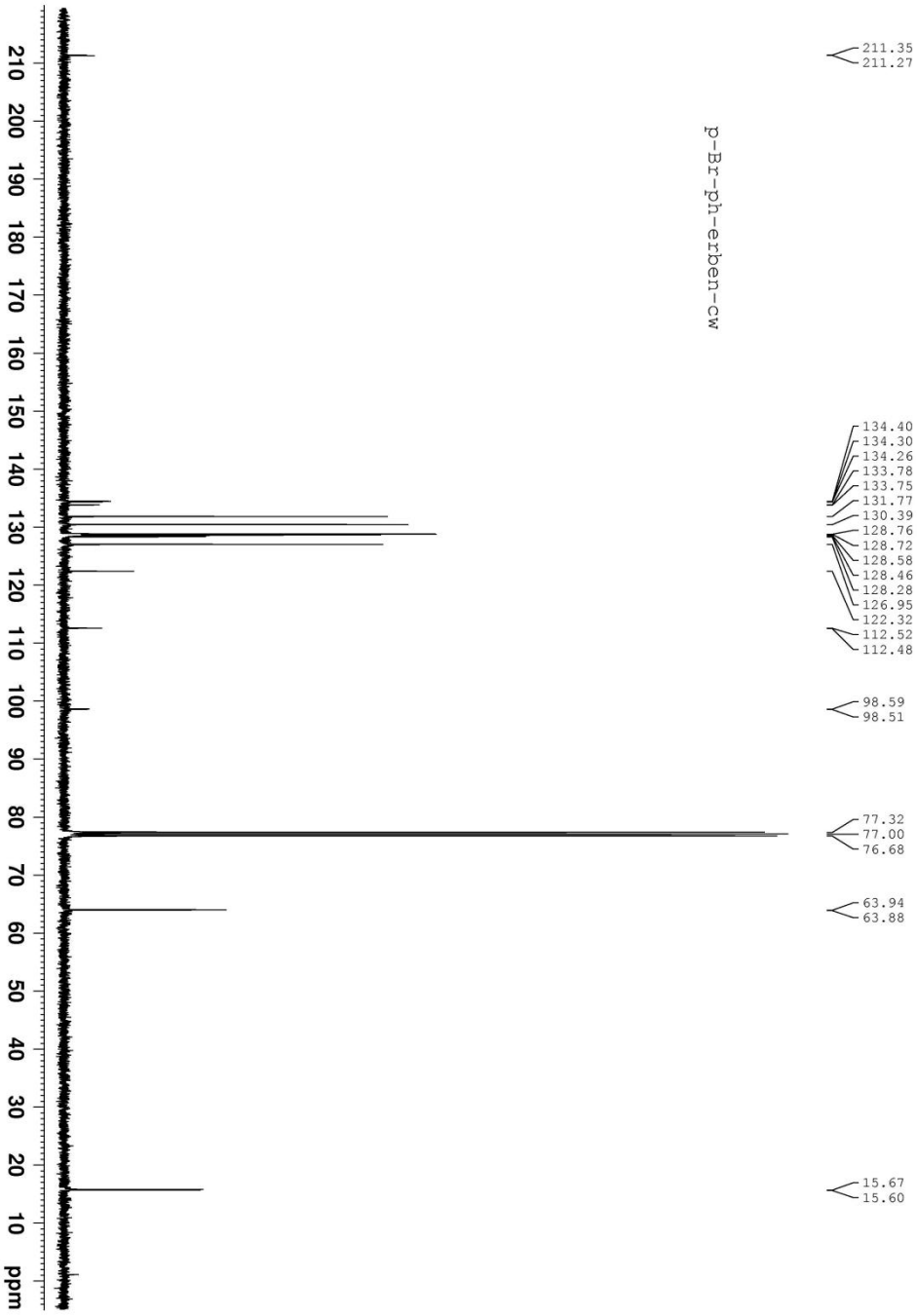

p-Cl-ph-erben-cw
211.40
211.32
134.44
134.38
134.34
134.13
133.27
133.24
130.09
128.81
128.76
128.72
128.58
128.45
128.27
126.95
112.47
112.44
98.52
98.43
77.32
77.00
76.68
63.96
63.90
15.66
15.59
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

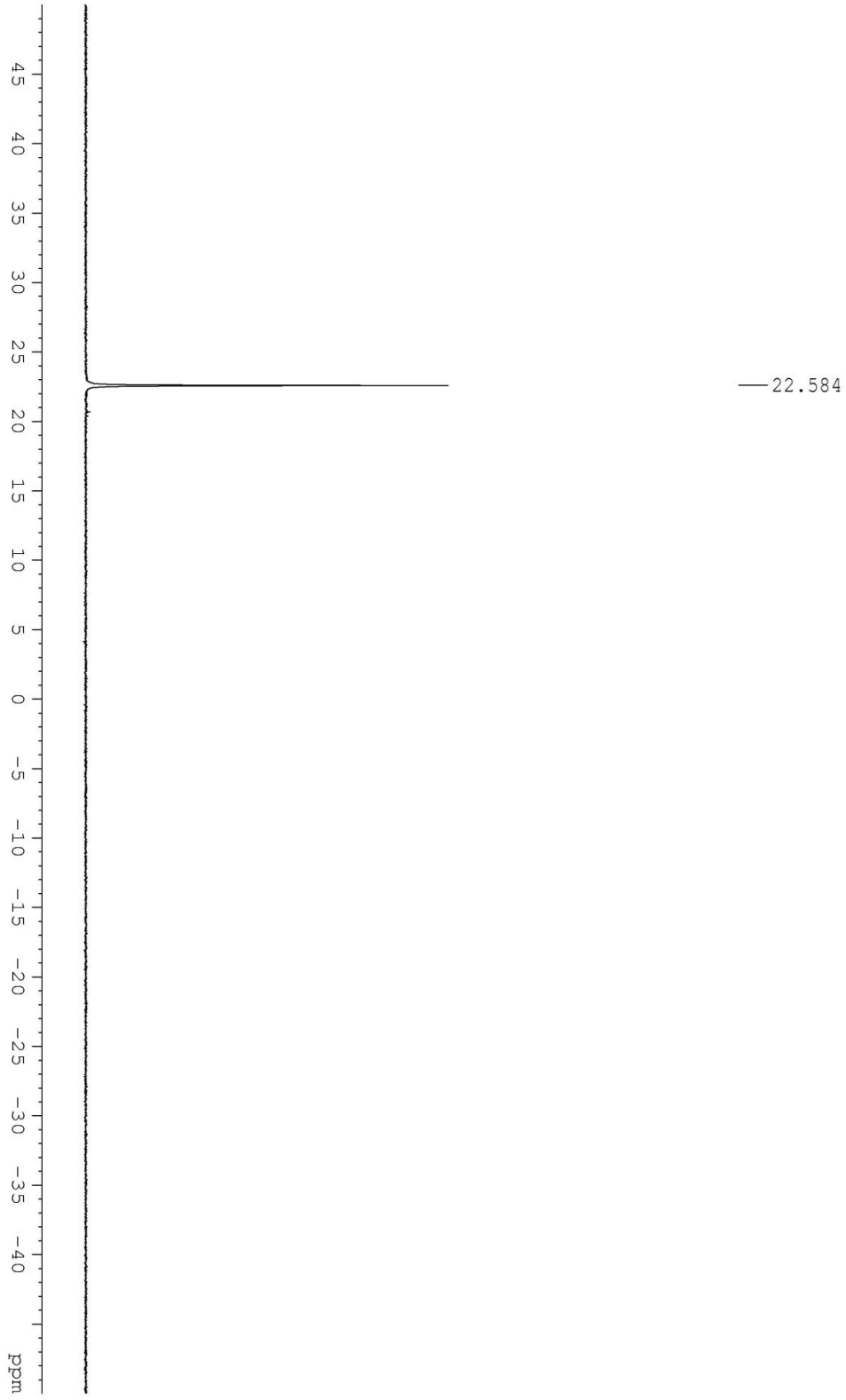

22.619
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
ppm

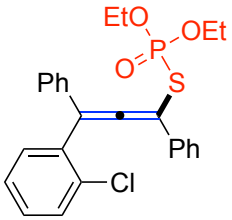

EtO
OEt
O
P
S
Ph
Ph
Br

3t

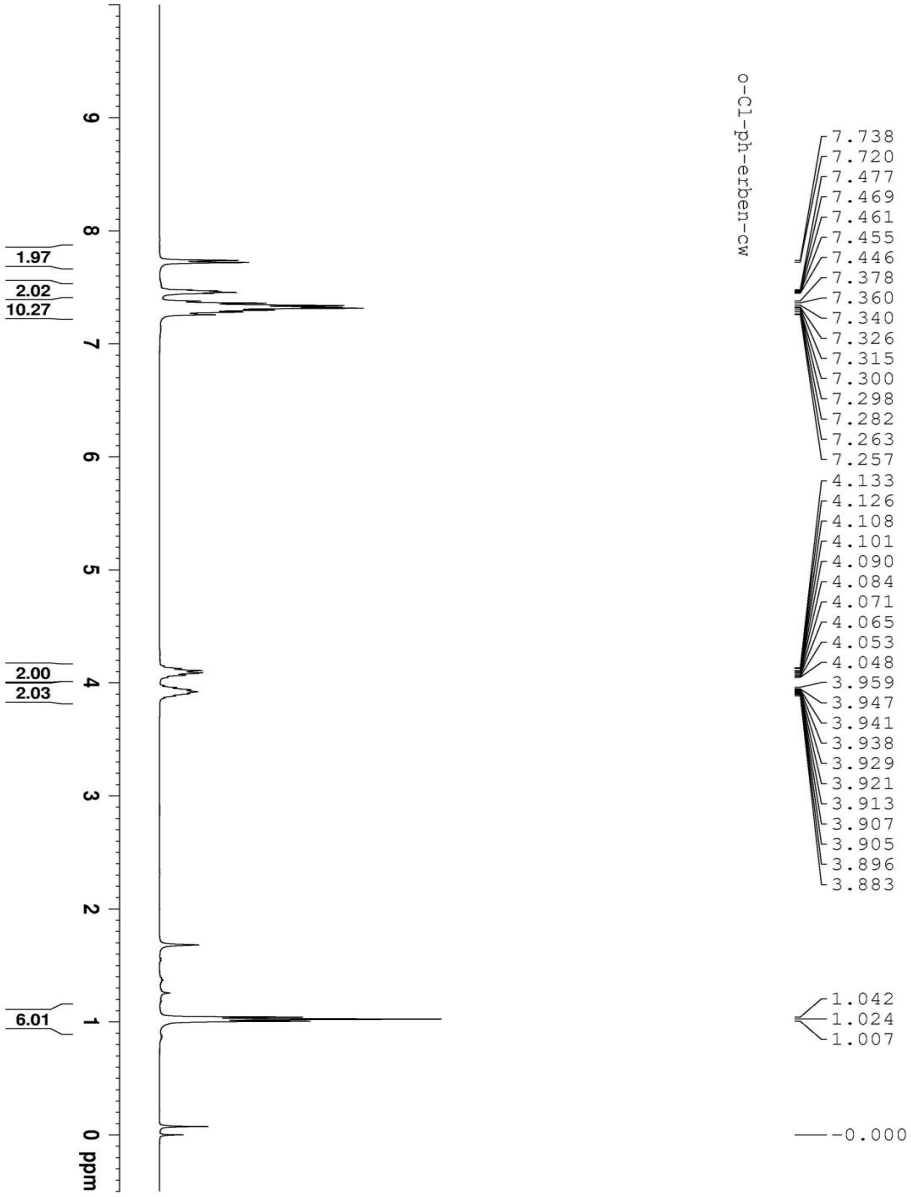

p-Br-ph-erben-cw
1.99
2.00
10.11
2.06
2.05
6.04
7.690
7.672
7.517
7.496
7.430
7.411
7.387
7.364
7.341
7.320
7.307
7.289
7.271
7.256
4.111
4.093
4.074
4.069
4.050
4.032
4.013
3.922
3.909
3.905
3.887
3.865
3.846
3.828
1.044
1.039
1.027
1.022
1.010
1.004
-0.000
ppm

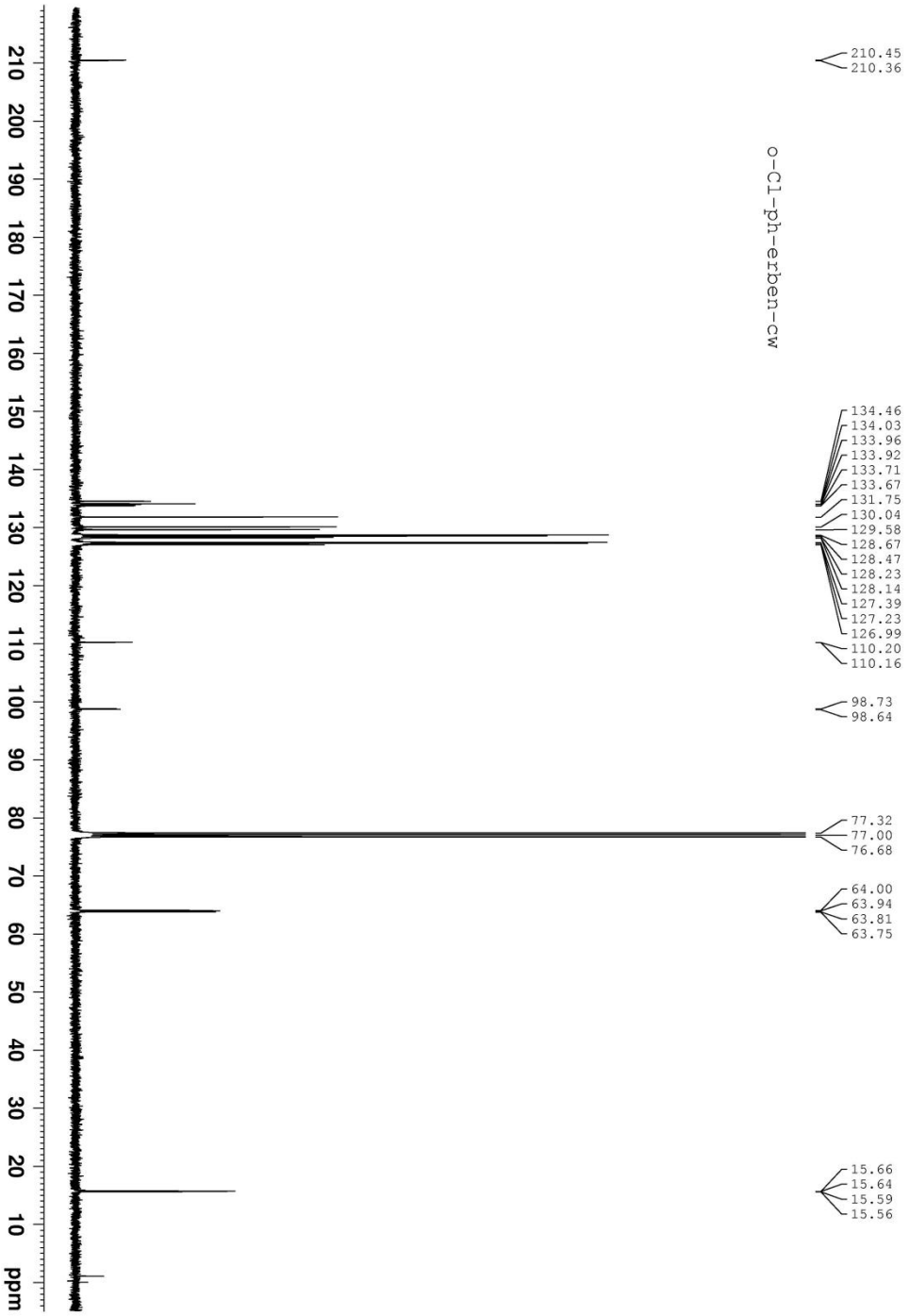

p-Br-ph-erben-cw
211.35
211.27
134.40
134.30
134.26
133.78
133.75
131.77
130.39
128.76
128.72
128.58
128.46
128.28
126.95
122.32
112.52
112.48
98.59
98.51
77.32
77.00
76.68
63.94
63.88
15.67
15.60
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

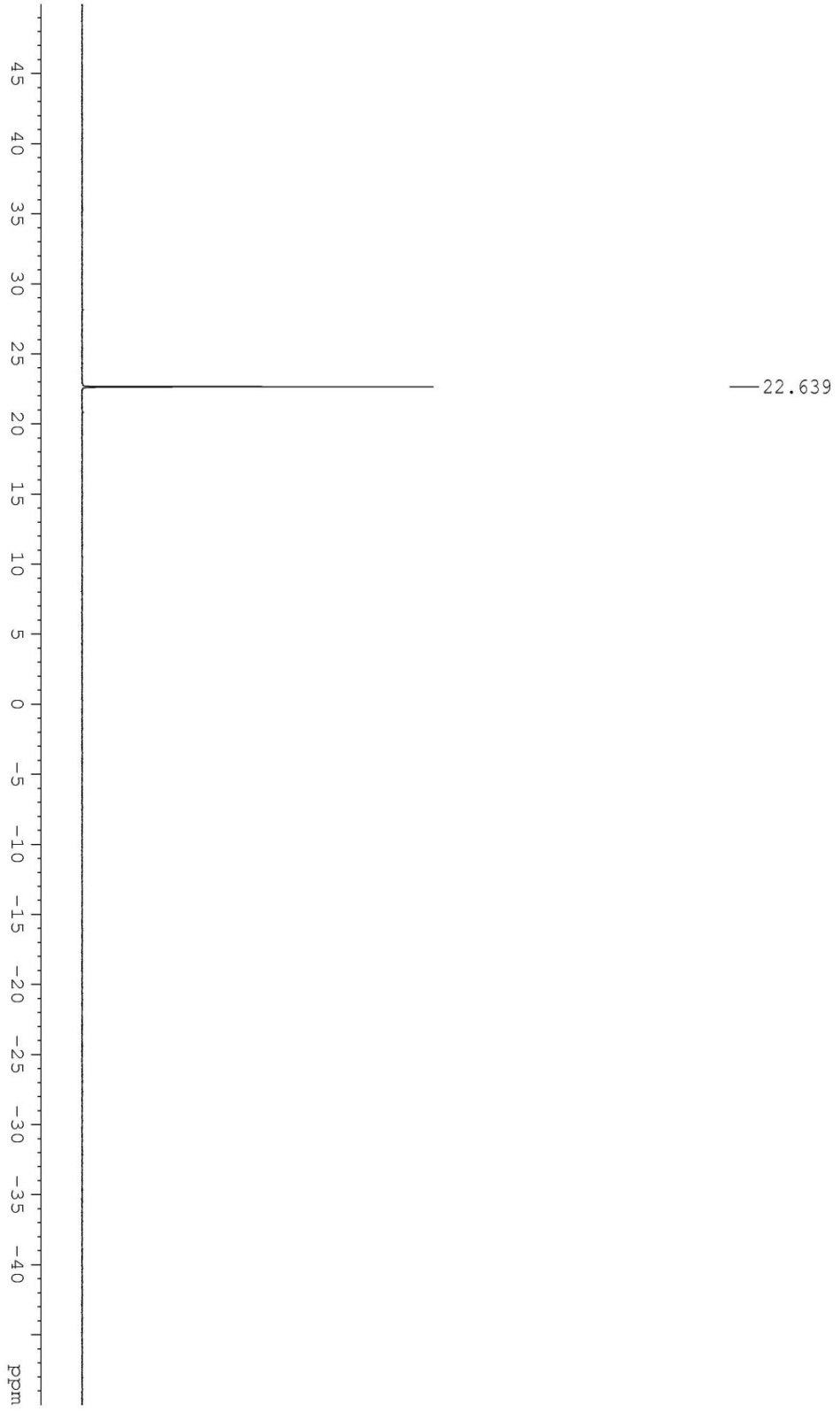

22.584
45
40
35
30
25
20
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
ppm

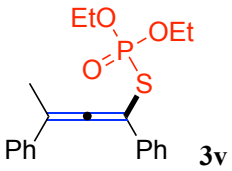

EtO
OEt
O
P
S
Ph
Ph
Cl

3u

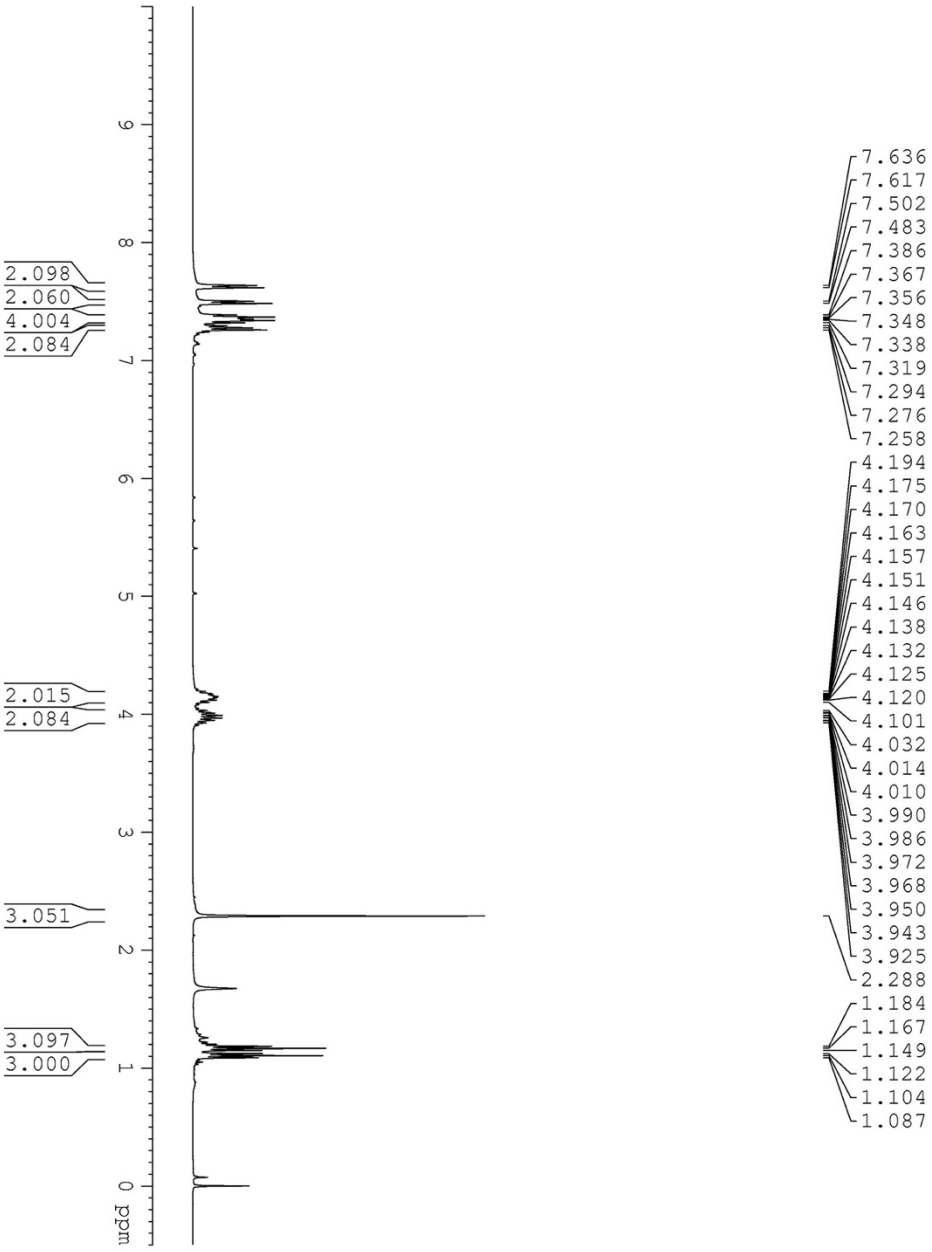

o-Cl-ph-erben-cw
1.97
2.02
10.27
2.00
2.03
6.01
9
8
7
6
5
4
3
2
1
0 ppm
7.738
7.720
7.477
7.469
7.461
7.455
7.446
7.378
7.360
7.340
7.326
7.315
7.300
7.298
7.282
7.263
7.257
4.133
4.126
4.108
4.101
4.090
4.084
4.071
4.065
4.053
4.048
3.959
3.947
3.941
3.938
3.929
3.921
3.913
3.907
3.905
3.896
3.883
1.042
1.024
1.007
0.000


o-Cl-ph-erben-cw
210.45
210.36
134.46
134.03
133.96
133.92
133.71
133.67
131.75
130.04
129.58
128.67
128.47
128.23
128.14
127.39
127.23
126.99
110.20
110.16
98.73
98.64
77.32
77.00
76.68
64.00
63.94
63.81
63.75
15.66
15.64
15.59
15.56
ppm


22.639
45
40
35
30
25
20
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
ppm


EtO
OEt
O
P
S
Ph
Ph

3v


2.098
2.060
4.004
2.084
2.015
2.084
3.051
3.097
3.000
ppm
7.636
7.617
7.502
7.483
7.386
7.367
7.356
7.348
7.338
7.319
7.294
7.276
7.258
4.194
4.175
4.170
4.163
4.157
4.151
4.146
4.138
4.132
4.125
4.120
4.101
4.032
4.014
4.010
3.990
3.986
3.972
3.968
3.950
3.943
3.925
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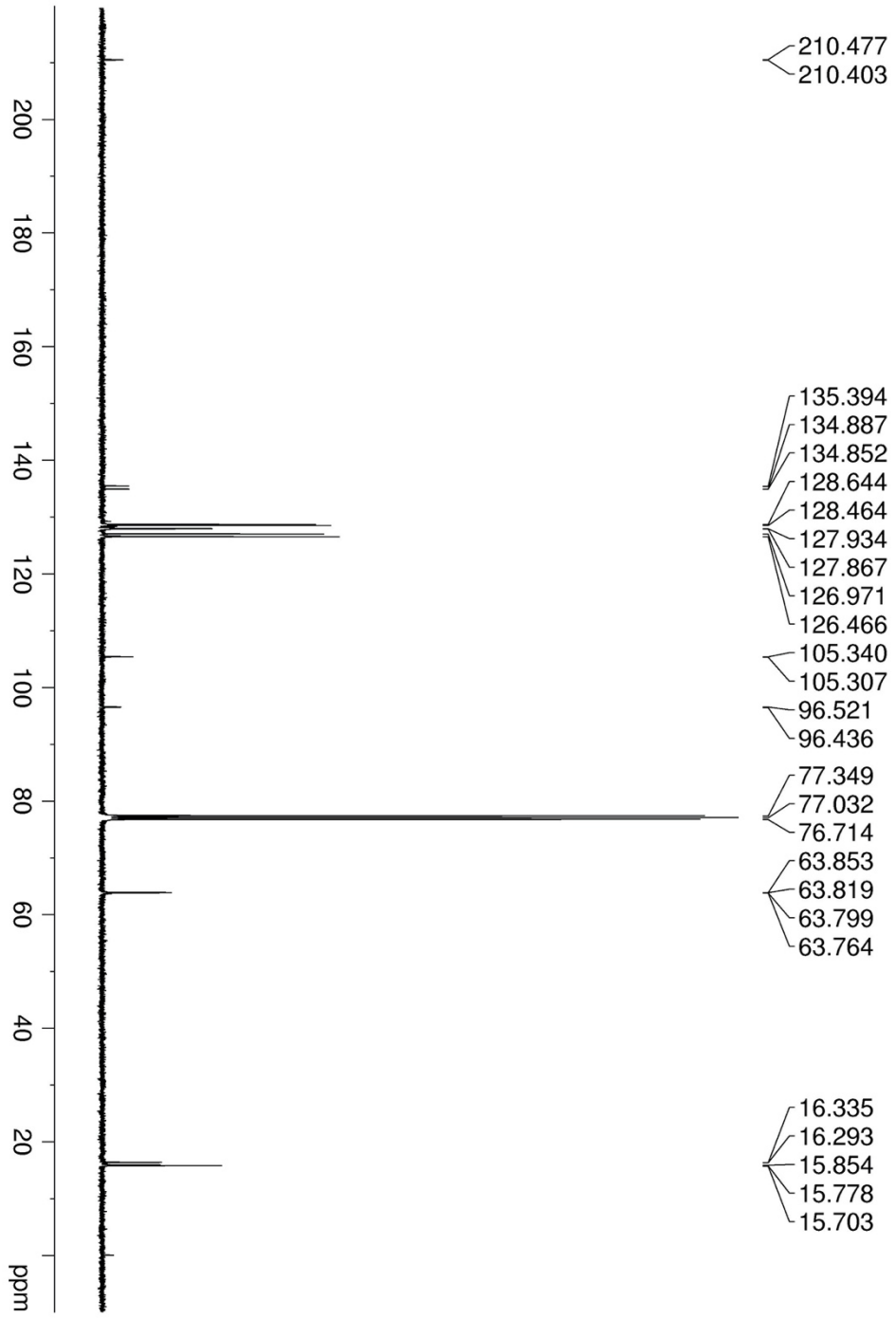
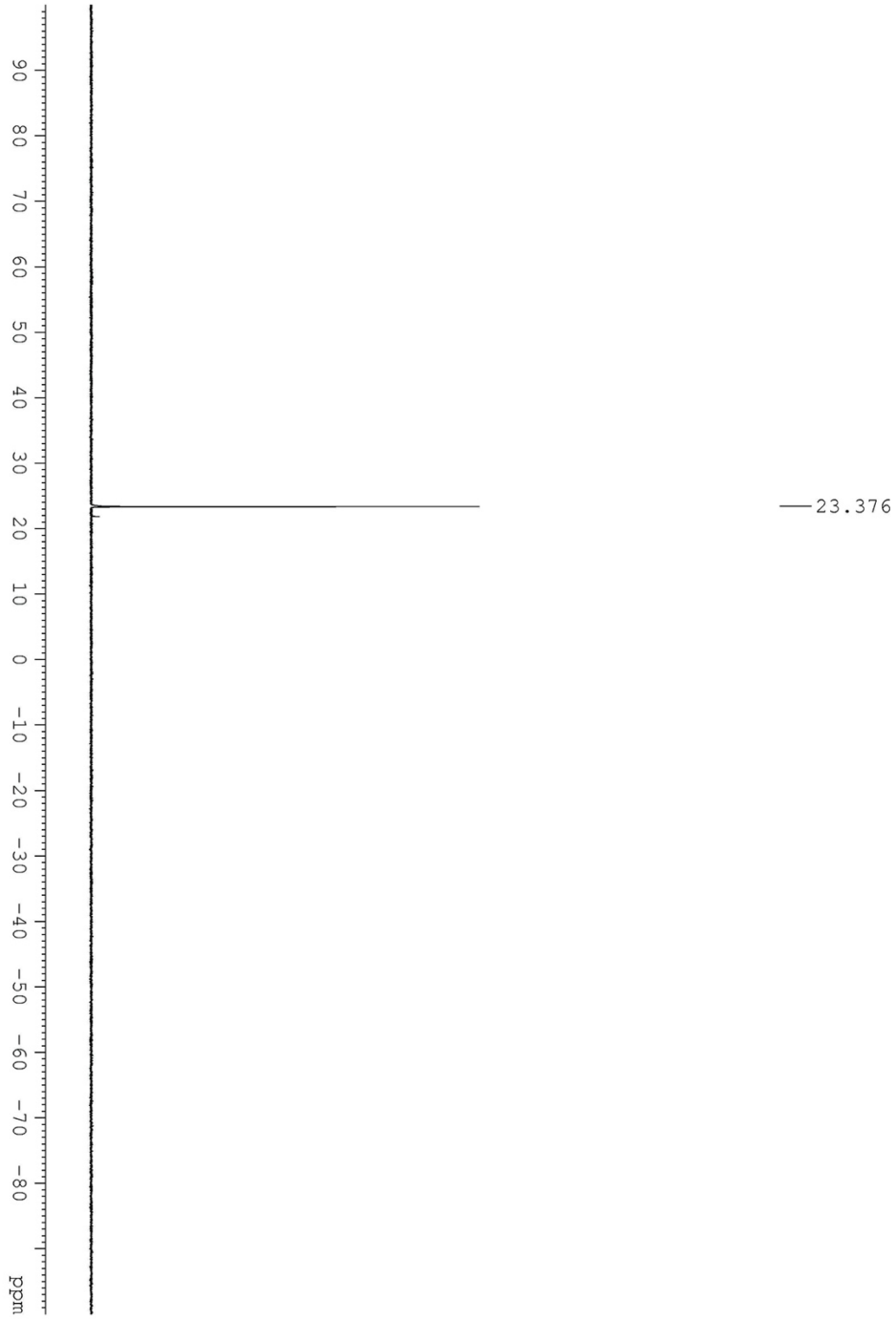
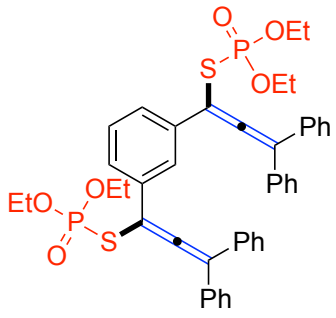
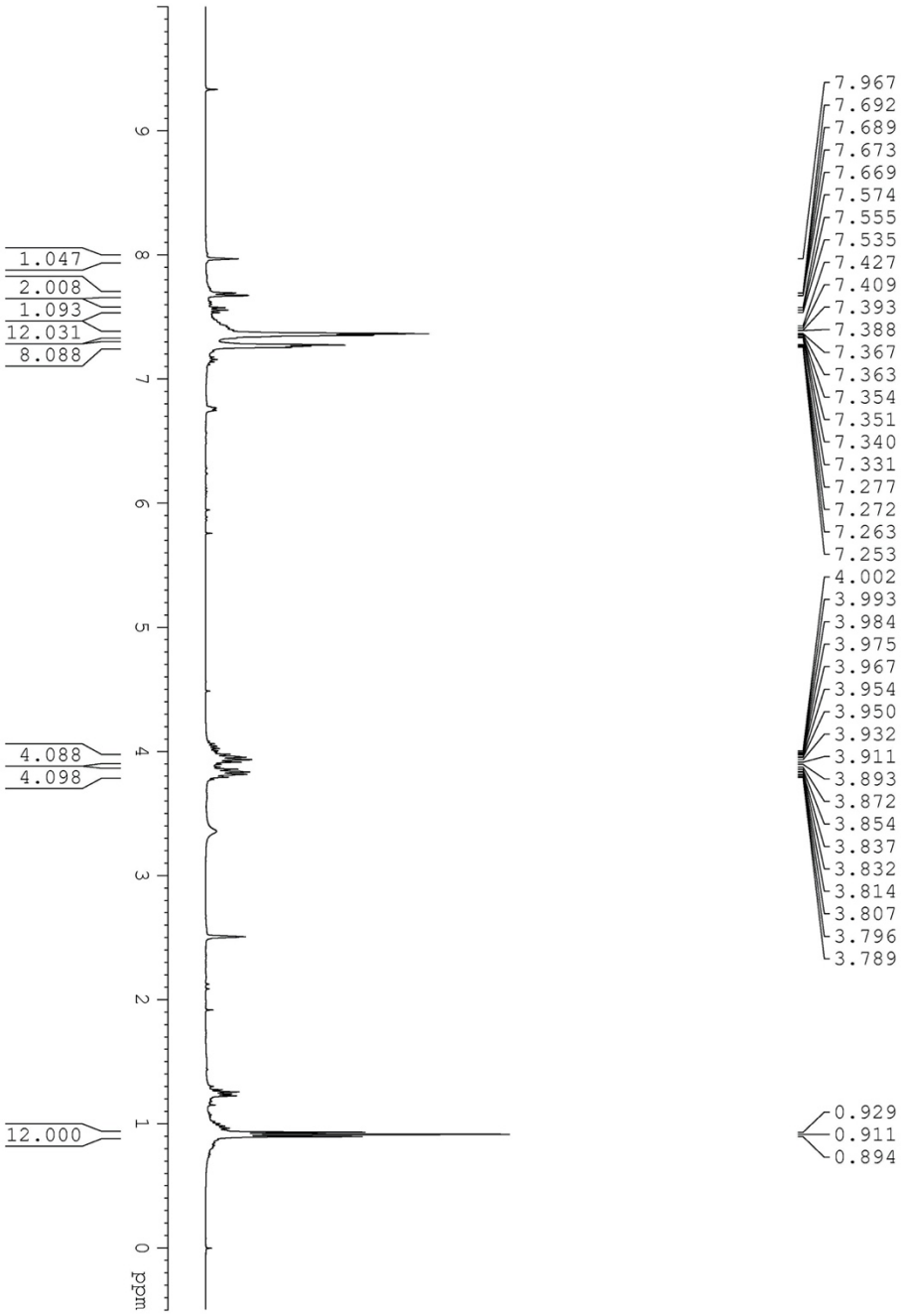
1.184
1.167
1.149
1.122
1.104
1.087

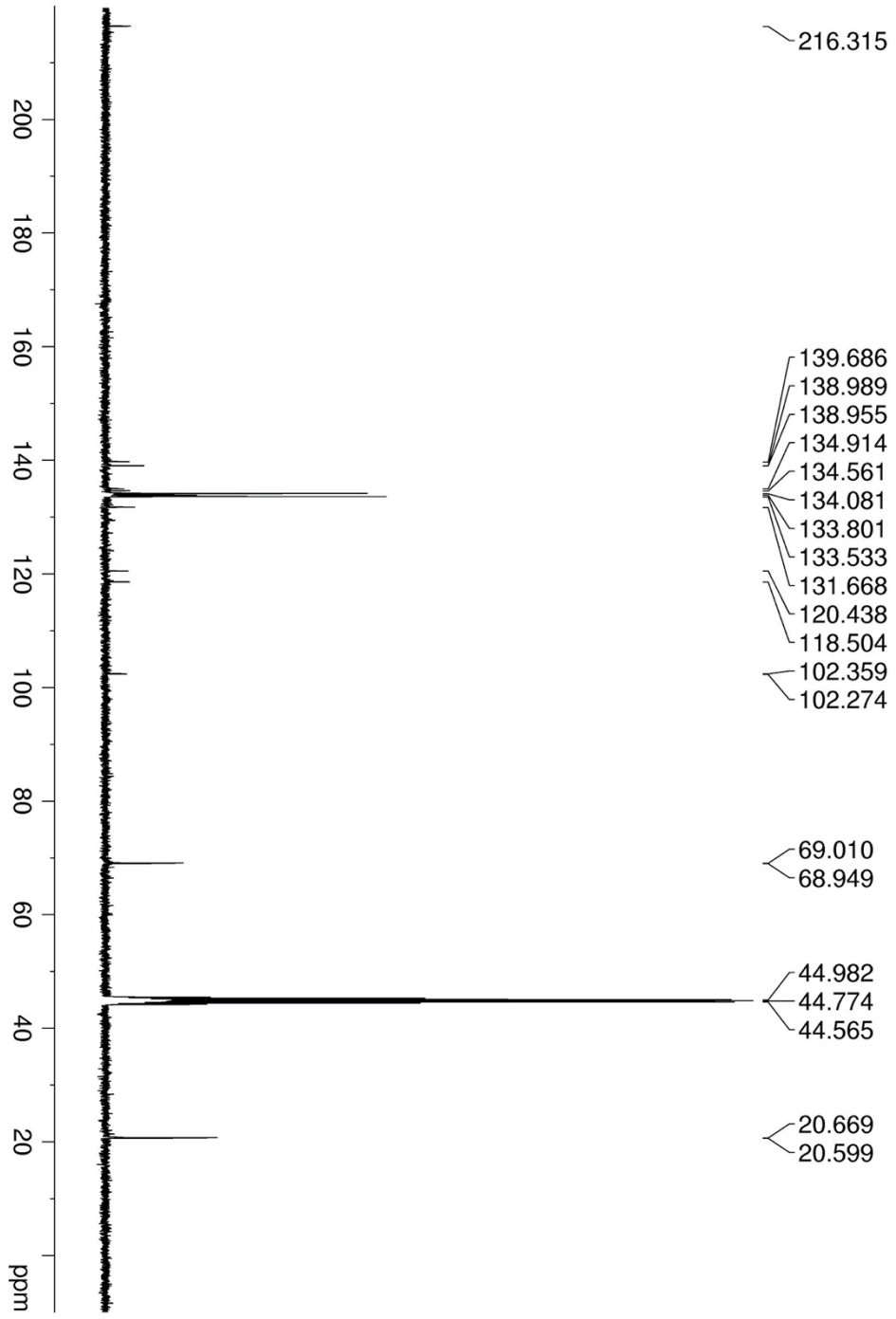

210.477
210.403
135.394
134.887
134.852
128.644
128.464
127.934
127.867
126.971
126.466
105.340
105.307
96.521
96.436
77.349
77.032
76.714
63.853
63.819
63.799
63.764
16.335
16.293
15.854
15.778
15.703
200
180
160
140
120
100
80
60
40
20
ppm

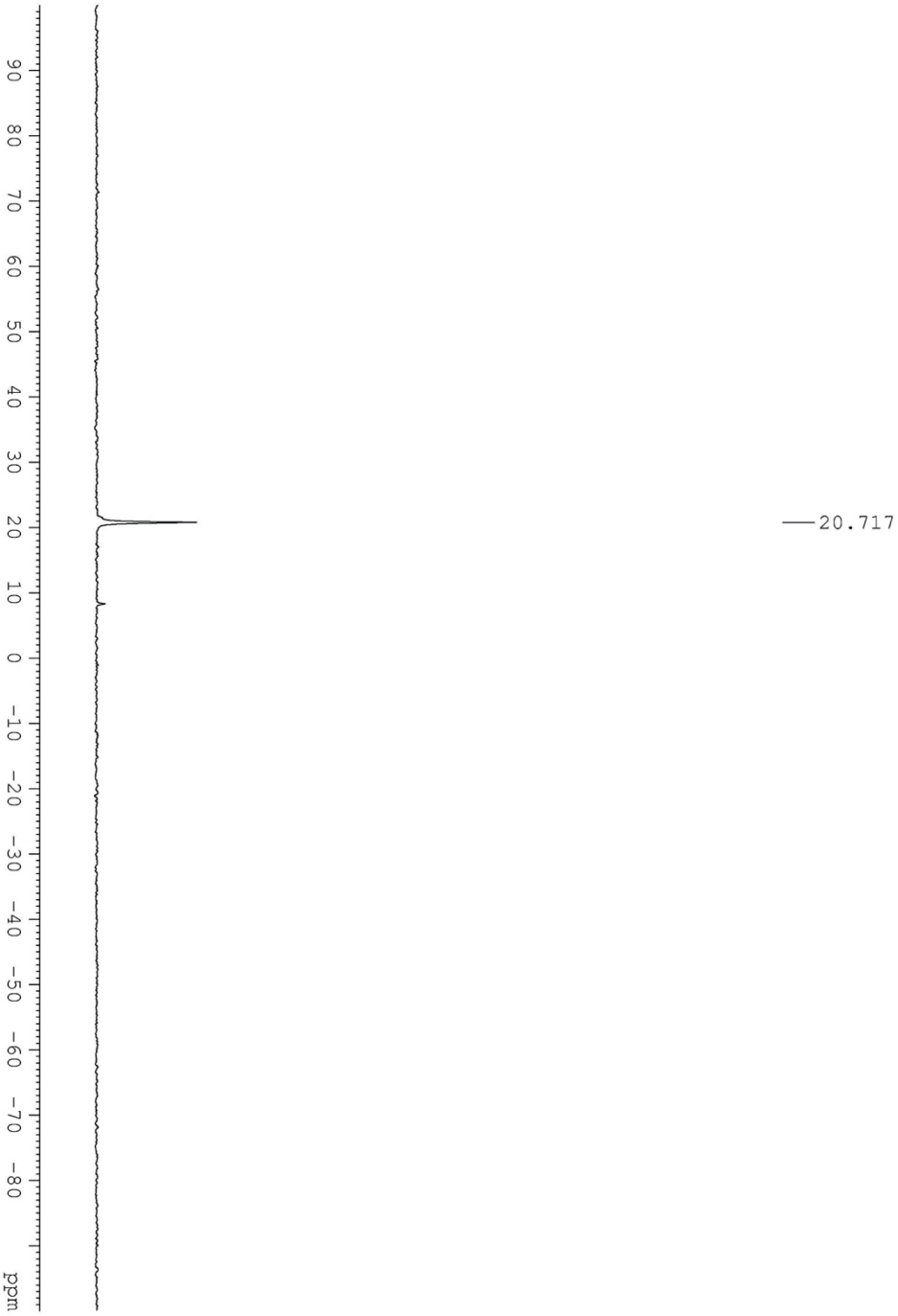

23.376
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
ppm

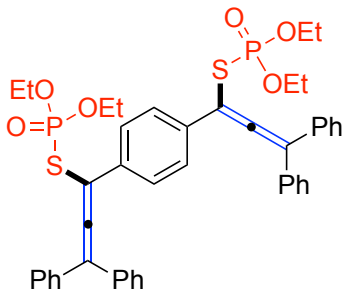

O
OEt
P
S
OEt
Ph
Ph
EtO
OEt
P
O
S
Ph
Ph

3aa

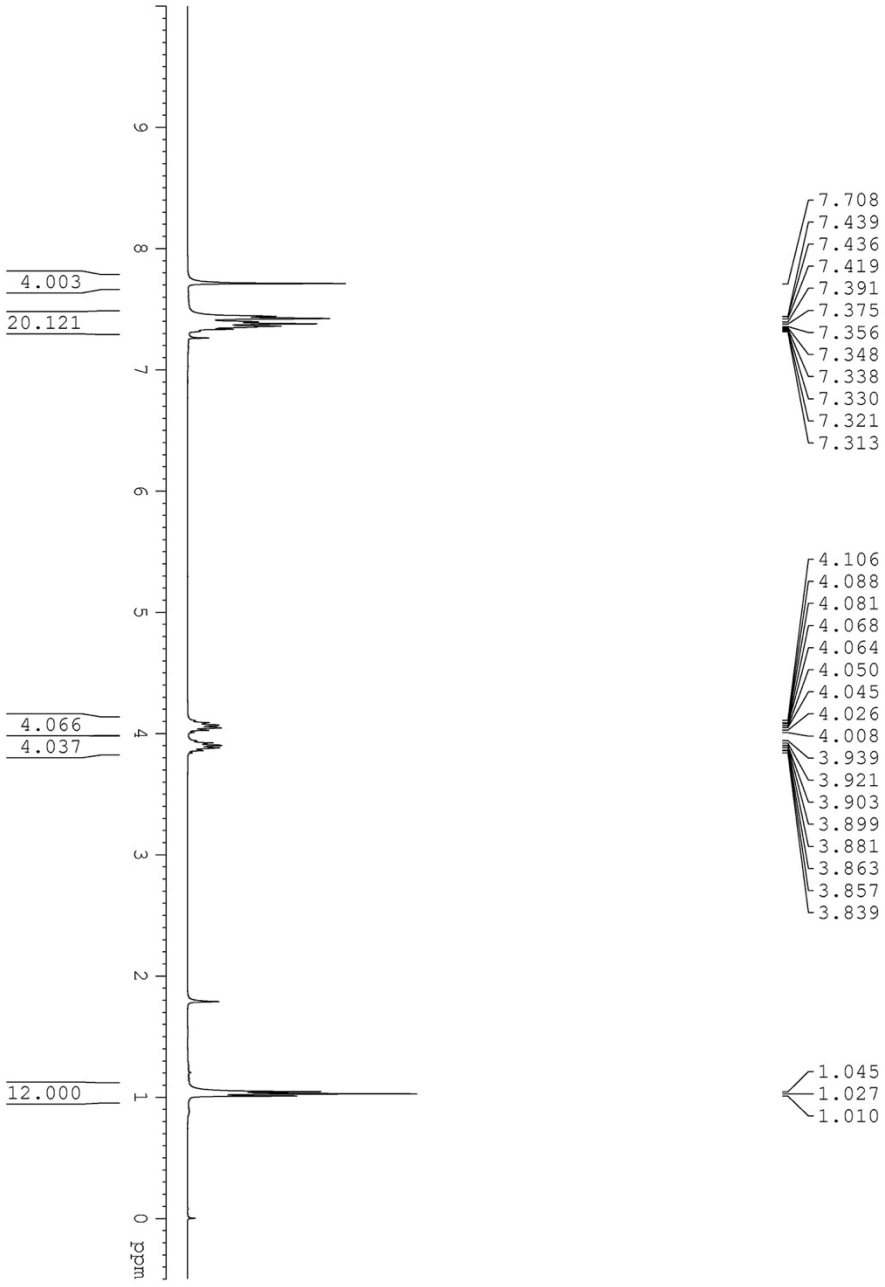

1.047
2.008
1.093
12.031
8.088
4.088
4.098
12.000
9
8
7
6
5
4
3
2
1
0
ppm
7.967
7.692
7.689
7.673
7.669
7.574
7.555
7.535
7.427
7.409
7.393
7.388
7.367
7.363
7.354
7.351
7.340
7.331
7.277
7.272
7.263
7.253
4.002
3.993
3.984
3.975
3.967
3.954
3.950
3.932
3.911
3.893
3.872
3.854
3.837
3.832
3.814
3.807
3.796
3.789
0.929
0.911
0.894

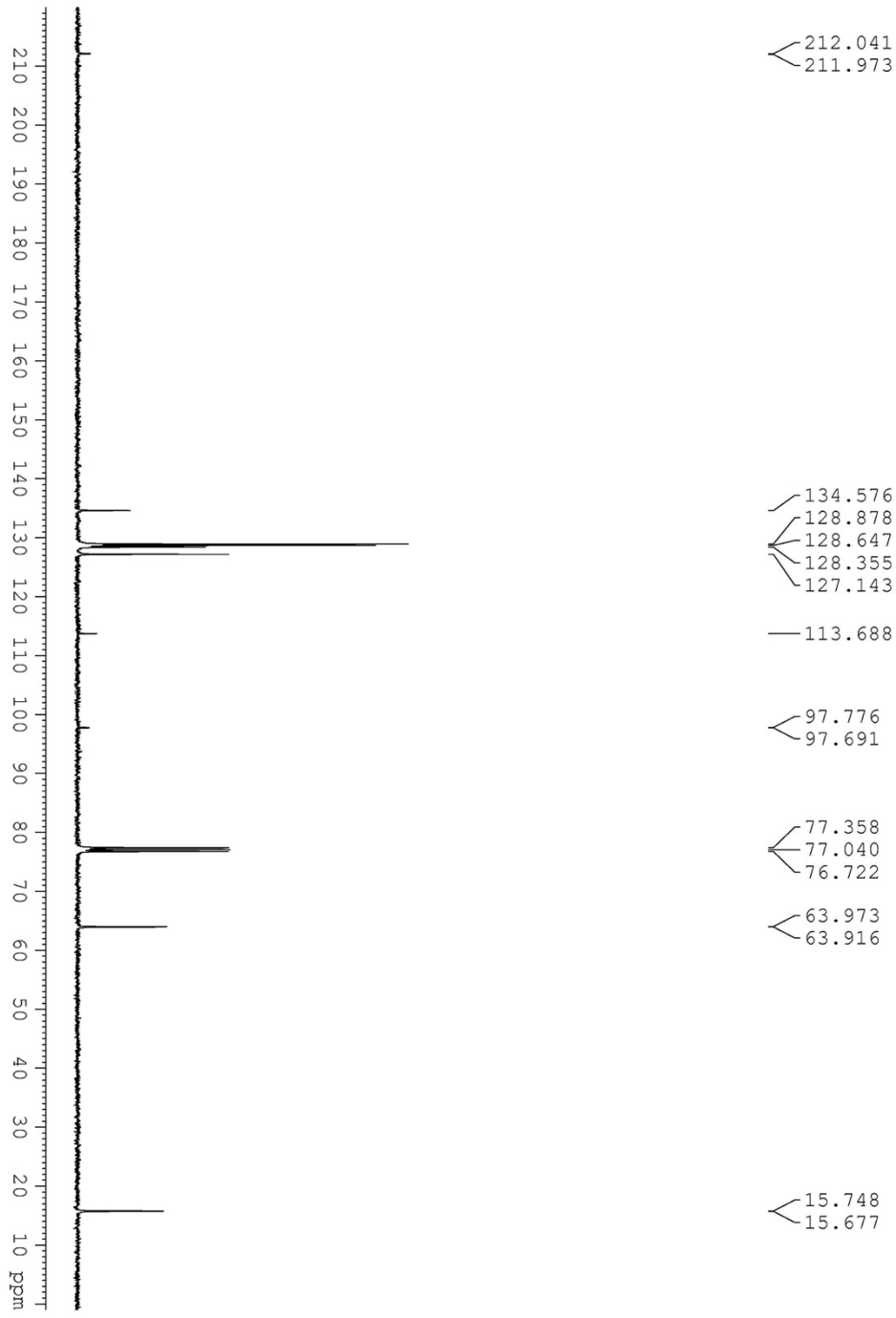

216.315
139.686
138.989
138.955
134.914
134.561
134.081
133.801
133.533
131.668
120.438
118.504
102.359
102.274
69.010
68.949
44.982
44.774
44.565
20.669
20.599
200
180
160
140
120
100
80
60
40
20
ppm

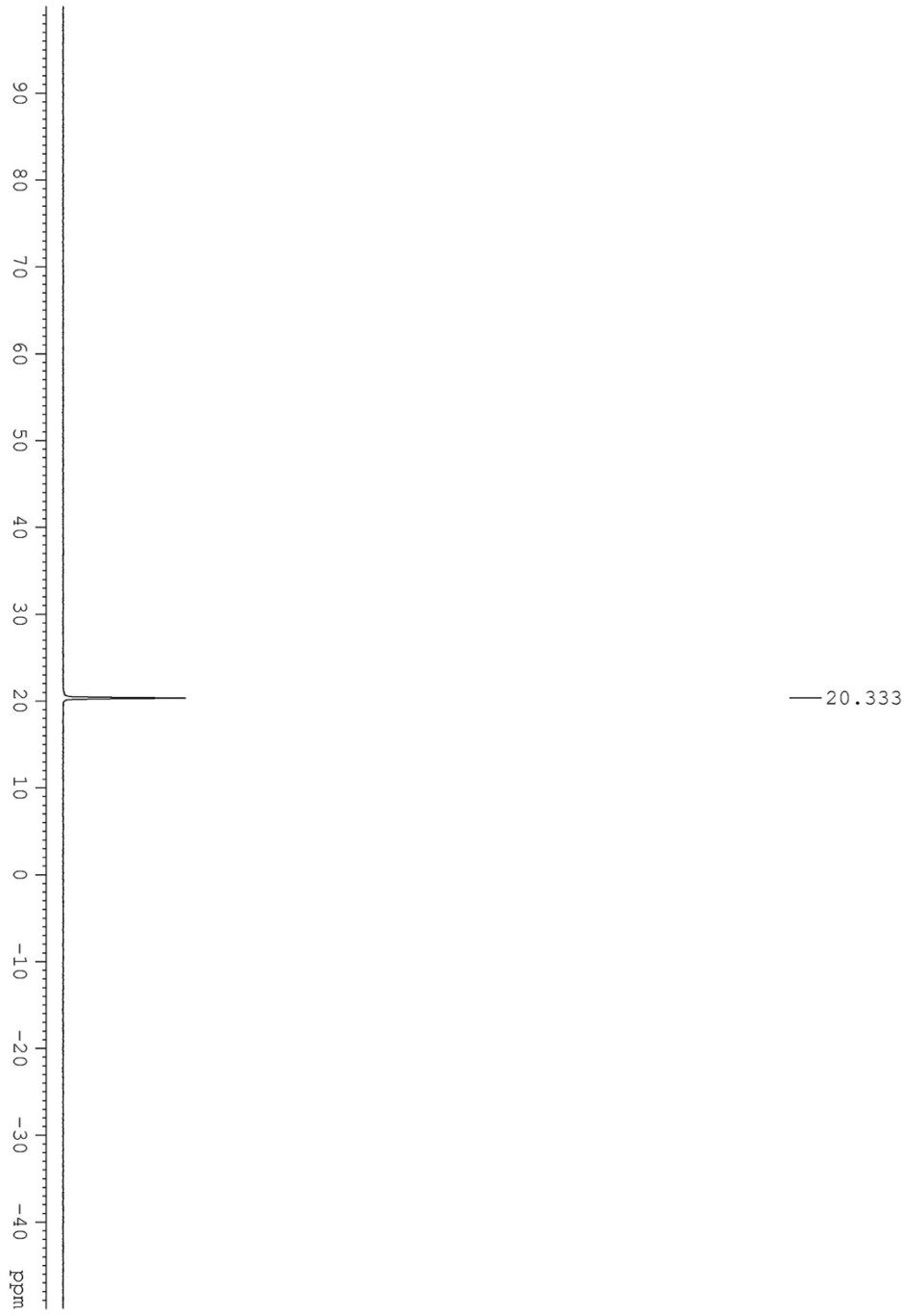

20.717
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
ppm

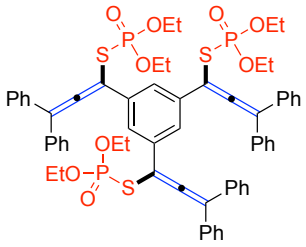

O
OEt
P
S
OEt
EtO
OEt
O=P
S
Ph
Ph
Ph
Ph

3ab

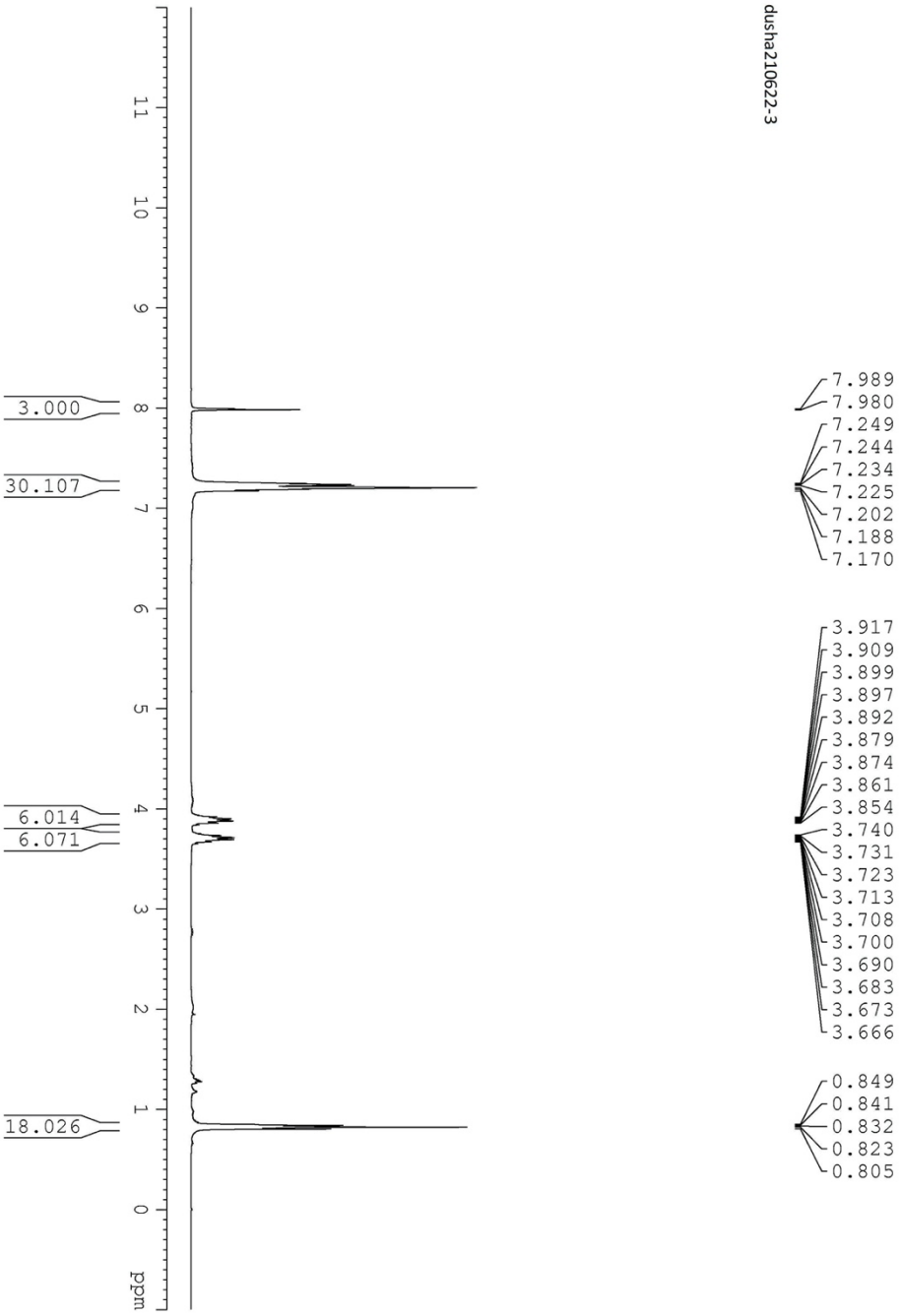

4.003
20.121
4.066
4.037
12.000
7.708
7.439
7.436
7.419
7.391
7.375
7.356
7.348
7.338
7.330
7.321
7.313
4.106
4.088
4.081
4.068
4.064
4.050
4.045
4.026
4.008
3.939
3.921
3.903
3.899
3.881
3.863
3.857
3.839
1.045
1.027
1.010
ppm

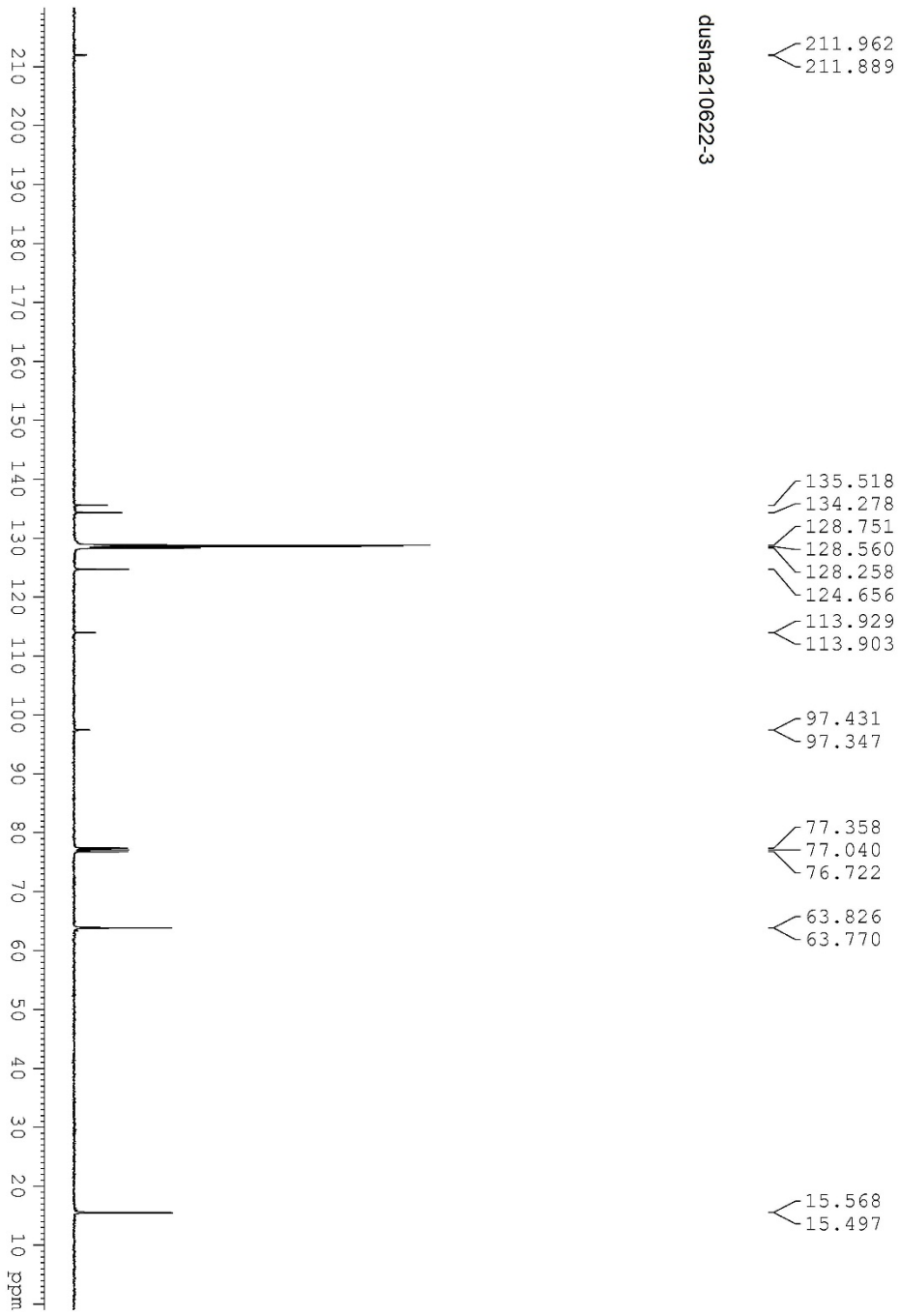

212.041
211.973
134.576
128.878
128.647
128.355
127.143
113.688
97.776
97.691
77.358
77.040
76.722
63.973
63.916
15.748
15.677
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

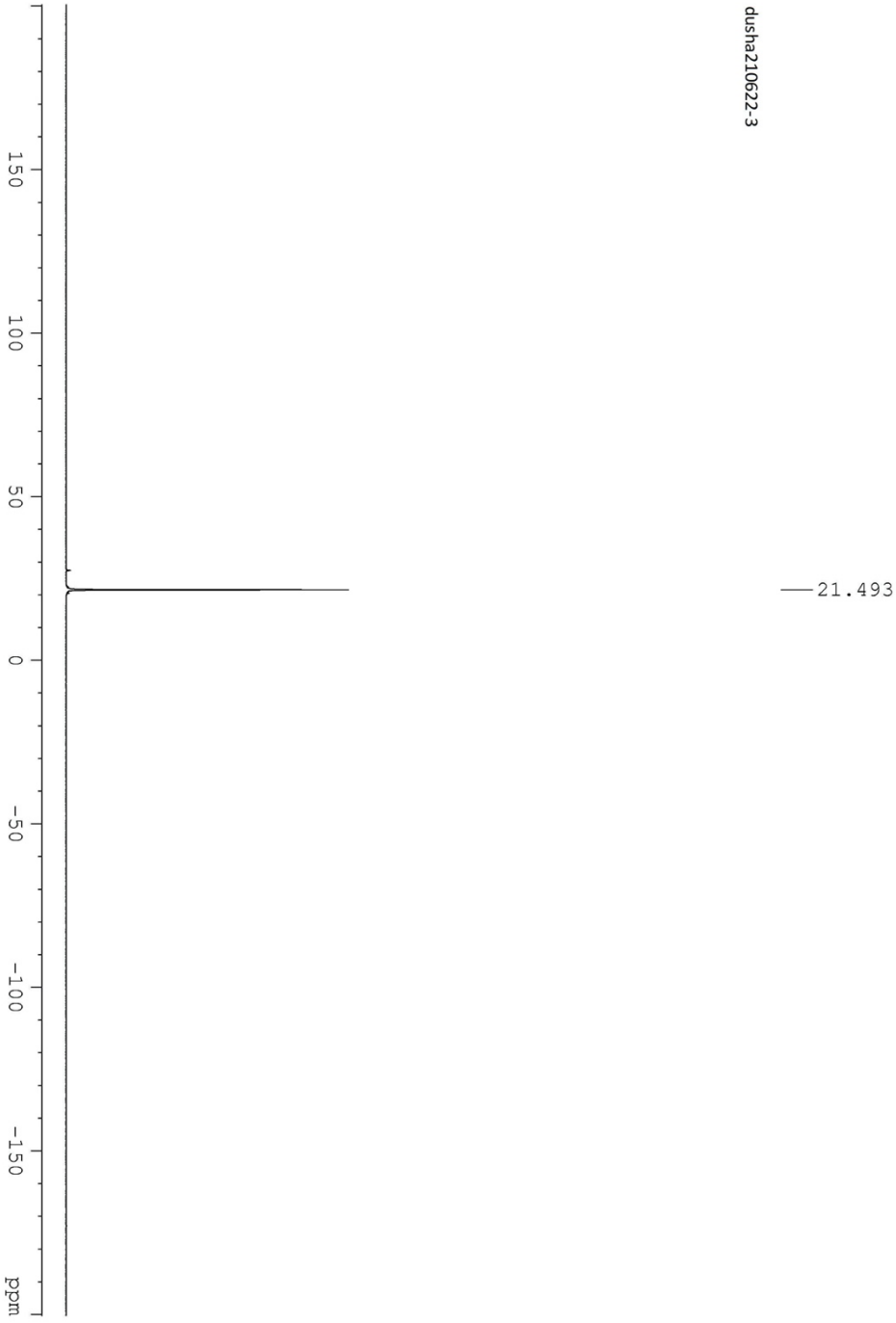

90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
ppm
20.333


O
OEt
P
S
OEt
Ph
Ph
OEt
EtO
P
O
S
Ph
Ph

3ac


dusha210622-3
7.989
7.980
7.249
7.244
7.234
7.225
7.202
7.188
7.170
3.917
3.909
3.899
3.897
3.892
3.879
3.874
3.861
3.854
3.740
3.731
3.723
3.713
3.708
3.700
3.690
3.683
3.673
3.666
0.849
0.841
0.832
0.823
0.805
3.000
30.107
6.014
6.071
18.026
ppm


dusha210622-3
211.962
211.889
135.518
134.278
128.751
128.560
128.258
124.656
113.929
113.903
97.431
97.347
77.358
77.040
76.722
63.826
63.770
15.568
15.497
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


dusha210622-3
21.493
150
100
50
0
-50
-100
-150
ppm