Electronic Supplementary Information
for
Phosphinative Cyclopropanation of Allyl Phosphates with Lithium Phosphides

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I. General

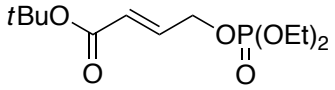
All reactions were carried out with standard Schlenk techniques under nitrogen unless otherwise noted. NMR spectra were recorded on JEOL JNM-ECS400 or Agilent Unity-Inova500 spectrometer. High resolution mass spectra were recorded on JEOL JMS700 spectrometer. X-ray crystallographic analysis was performed by RIGAKU XTaLAB P200. Preparative GPC was performed with JAI LaboACE LC-5060 equipped with JAIGEL-2HR columns using $CHCl_3$ as an eluent.

N,*N*-Diisopropylethylamine (Wako Chemicals) was distilled over KOH under vacuum. Pyridine (Nacalai Tesque) was dried over MS4A prior to use. Toluene (Wako Chemicals; dehydrated), CH_2Cl_2 (Kanto Chemical; dehydrated), Et_2O (Wako Chemicals; dehydrated), *tert*-butyl methyl ether (Wako Chemicals; dehydrated), cyclopentyl methyl ether (Wako Chemicals; dehydrated), THF (Kanto Chemical; dehydrated), *tert*-butyl bromoacetate (Wako Chemicals), glycoaldehyde (Aldrich), 4-dimethylaminopyridine (Wako Chemicals), diethyl chlorophosphate (Aldrich), triphenylphosphine (Wako Chemicals), dicyclohexylphosphine (Kanto Chemical), dicyclopentylphosphine (Strem Chemicals; 10 wt% solution in hexane), diisopropylphosphine (Acros Organics; 10 wt% solution in hexane), diisobutylphosphine (Strem Chemicals; 10 wt% solution in hexane), di-*tert*-butylphosphine (Acros Organics; 10 wt% solution in hexane), diphenylphosphine (TCI), *n*BuLi (Kanto Chemical; 1.57–1.59 M solution in hexane), hydrogen peroxide (Kishida Chemical; 30wt% solution in H_2O), *N*,*N'*-dimethylpropyleneurea (TCI), hexamethylphosphoric triamide (TCI), and lithium (Kishida Chemical; sticks in liquid paraffin) were used as received.

1a,[1] **1b**,[2] **1c**,[3] **1d**,[2] **1e**,[4] **1f**,[2] **1g**,[3] **1h**,[2] **1i**,[2] **1j**,[5] **1l**,[2] **1m**,[6] **5**,[7] **6**,[8] (*E*)-4-phenyl-3-buten-2-ol,[9] and 1,2-diphenyltetramethyldisilane[2] were synthesized following the literature procedures.

II. Synthesis of Substrates

Diethyl (*E*)-3-(*tert*-butoxycarbonyl)-2-propen-1-yl phosphate (1k)



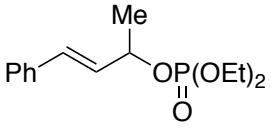
tert-Butyl bromoacetate (644 μL, 4.39 mmol) was added dropwise to a solution of triphenylphosphine (1.05 g, 4.00 mmol) in toluene (2.3 mL) at 0 °C, and the mixture was stirred for 8 h while gradually raising the temperature to room temperature. The precipitates that formed were collected by filtration with pentane and dried under vacuum. The solid thus obtained was dissolved in CH_2Cl_2 (26 mL) and 1.0 M NaOHaq (8.0 mL, 8.0 mmol) was added to it. The resulting mixture was stirred for 1 h at room temperature, and this was extracted with CH_2Cl_2. The organic layer was washed with H_2O and the aqueous layer was extracted with CH_2Cl_2 for 3 times. The combined organic layer was washed with saturated NaClaq, dried over Na_2SO_4, filtered, and concentrated under vacuum to afford *tert*-butyl (triphenylphosphoranylidene)acetate (CAS 35000-38-5) as a white solid (1.21g, 3.21 mmol; 80% yield). Without further purification, this was added with CH_2Cl_2 (8.0 mL) to a solution of glycolaldehyde (109 mg, 0.908 mmol) in CH_2Cl_2 (10.5 mL), and the mixture was stirred for 4 h at 40 °C. The solvent was removed under vacuum and the residue was chromatographed on silica gel with hexane/EtOAc = 3/1 to afford *tert*-butyl (*E*)-4-hydroxy-2-butenoate (CAS 528846-51-7) as a colorless oil (229 mg, 1.45 mmol; 80% yield).

^{1}H NMR ($CDCl_3$): δ 6.93 (dt, $^3J_{HH}$ = 15.6 and 4.3 Hz, 1H), 6.01 (d, $^3J_{HH}$ = 15.8 Hz and $^4J_{HH}$ = 1.9 Hz, 1H), 4.33 (dd, $^3J_{HH}$ = 4.1 Hz and $^4J_{HH}$ = 1.9 Hz, 2H), 1.54 (s, 1H), 1.49 (s, 9H).

N,*N*-Diisopropylethylamine (489 μL, 2.90 mmol) and 4-dimethylaminopyridine (36.0 mg, 0.295 mmol) were added to a solution of *tert*-butyl (*E*)-4-hydroxy-2-butenoate (229 mg, 1.45 mmol) in CH_2Cl_2 (8.0 mL). Diethyl chlorophosphate (327 μL, 2.28 mmol) was added dropwise to it and the mixture was stirred for 18 h at room temperature. The reaction was quenched with saturated $NaHCO_3$aq and this was extracted with CH_2Cl_2. The organic layer was washed with H_2O, and the aqueous layer was extracted with CH_2Cl_2 for 2 times. The combined organic layer was washed with saturated NH_4Claq, dried over $MgSO_4$, filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with hexane/EtOAc = 1/2 to afford compound **1k** (CAS 528846-27-7) as a yellow oil (383 mg, 1.30 mmol; 90% yield).

^{1}H NMR ($CDCl_3$): δ 6.82 (dtd, $^3J_{HH}$ = 15.6 and 4.4 Hz and $^4J_{HP}$ = 1.7 Hz, 1H), 6.03 (dt, $^3J_{HH}$ = 15.6 Hz and $^4J_{HH}$ = 1.9 Hz, 1H), 4.67 (ddd, $^3J_{HP}$ = 7.3 Hz, $^3J_{HH}$ = 4.4 Hz, and $^4J_{HH}$ = 1.9 Hz, 2H), 4.14 (dq, $^3J_{HP}$ = 8.0 Hz and $^3J_{HH}$ = 7.1 Hz, 4H), 1.49 (s, 9H), 1.35 (td, $^3J_{HH}$ = 7.1 Hz, $^4J_{HP}$ = 1.0 Hz, 6H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 165.1, 140.1 (d, $^3J_{CP}$ = 7.7 Hz), 124.2, 80.8, 65.5 (d, $^2J_{CP}$ = 4.8 Hz), 64.1 (d, $^2J_{CP}$ = 5.8 Hz), 28.2, 16.2 (d, $^3J_{CP}$ = 5.8 Hz).

Diethyl (*E*)-4-phenyl-3-buten-2-yl phosphate (1m)

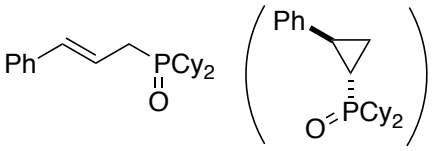


Pyridine (325 μL, 4.02 mmol) and 4-dimethylaminopyridine (49.3 mg, 0.404 mmol) were added to a solution of (*E*)-4-phenyl-3-buten-2-ol (298 mg, 2.01 mmol) in CH_2Cl_2 (2.0 mL). Diethyl chlorophosphate (434 μL, 3.02 mmol) was added dropwise to it at 0 °C and the mixture was stirred for 16 h while gradually raising the temperature to room temperature. The precipitates that formed were filtered off through Celite with Et_2O, and the solvent was removed under vacuum. The residue was purified by GPC with $CHCl_3$ to afford compound **1m** as a colorless oil (332 mg, 1.17 mmol; 58% yield).

^{1}H NMR ($CDCl_3$): δ 7.41-7.34 (m, 2H), 7.34-7.28 (m, 2H), 7.27-7.22 (m, 1H), 6.62 (d, $^3J_{HH}$ = 16.0 Hz, 1H), 6.22 (dd, $^3J_{HH}$ = 16.0 and 7.3 Hz, 1H), 5.15-5.04 (m, 1H), 4.17-4.03 (m, 4H), 1.50 (d, $^3J_{HH}$ = 6.4 Hz, 3H), 1.32 (td, $^3J_{HH}$ = 7.1 Hz and $^4J_{HP}$ = 0.9 Hz, 3H), 1.28 (td, $^3J_{HH}$ = 7.1 Hz and $^4J_{HP}$ = 0.9 Hz, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 136.3, 131.7, 129.4 (d, $^3J_{CP}$ = 5.8 Hz), 128.7, 128.2, 126.8, 75.9 (d, $^2J_{CP}$ = 4.8 Hz), 63.74 (d, $^2J_{CP}$ = 5.8 Hz), 63.69 (d, $^2J_{CP}$ = 4.8 Hz), 22.5 (d, $^3J_{CP}$ = 4.8 Hz), 16.2 (d, $^3J_{CP}$ = 6.7 Hz). HRMS (FAB) calcd for $C_{14}H_{21}O_4P$ (M^+) 284.1172, found 284.1176.

III. Cyclopropanation Reactions

Procedure for Table 1, Entry 4.



*n*BuLi (283 μL, 0.450 mmol; 1.59 M solution in hexane) was added to a solution of dicyclohexylphosphine (98.7 μL, 0.450 mmol) in cyclopentyl methyl ether (1.5 mL) at 0 °C. Compound **1a** (81.7 mg, 0.302 mmol) was added to it and the mixture was stirred for 3 h at 20 °C. H_2O_2 (221 μL, 2.16 mmol; 30 wt% solution in H_2O) was then added to it and the resulting mixture was stirred for 2 h at room temperature. This was extracted with Et_2O and the organic layer was washed with H_2O. The aqueous layer was extracted with Et_2O for 3 times, and the combined organic layer was washed with saturated NaClaq, dried over $MgSO_4$, filtered, and concentrated under vacuum. The residue was purified by GPC with $CHCl_3$ to afford a mixture of compounds **3aa**/**4aa** as a white solid (70.9 mg, 0.215 mmol; 71% yield, (**3aa**/**4aa** = 3/97).

4aa: ^{1}H NMR ($CDCl_3$): δ 7.35 (d, $^3J_{HH}$ = 7.3 Hz, 2H), 7.31 (t, $^3J_{HH}$ = 7.7 Hz, 2H), 7.23 (t, $^3J_{HH}$ = 7.2 Hz, 1H), 6.51 (dd, $^3J_{HH}$ = 15.8 Hz and $^4J_{HP}$ = 3.1 Hz, 1H), 6.25 (dtd, $^3J_{HH}$ = 15.8 and 7.6 Hz and $^3J_{HP}$ = 5.1 Hz, 1H), 2.74 (dd, $^2J_{HP}$ = 13.8 Hz and $^3J_{HH}$ = 7.5 Hz, 2H), 2.07-1.63 (m, 12H), 1.55-1.38

(m, 4H), 1.34-1.16 (m, 6H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 137.0 (d, $^{4}J_{CP}$ = 1.9 Hz), 134.1 (d, $^{2}J_{CP}$ = 11.5 Hz), 128.6, 127.5, 126.2, 120.6 (d, $^{3}J_{CP}$ = 7.7 Hz), 36.2 (d, $^{1}J_{CP}$ = 63.3 Hz), 30.0 (d, $^{1}J_{CP}$ = 57.5 Hz), 26.7 (d, J_{CP} = 12.5 Hz), 26.6 (d, J_{CP} = 11.5 Hz), 26.0, 25.9 (d, J_{CP} = 2.9 Hz), 25.5 (d, J_{CP} = 2.9 Hz). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ 49.5 (s). HRMS (FAB) calcd for $C_{21}H_{32}OP$ ($M+H^+$) 331.2185, found 331.2194.

General Procedure for Table 2, Equations 1–3, and Scheme 2.

Hexamethylphosphoric triamide (HMPA; 83.5 μL, 0.480 mmol) and THF (0.5 mL) were added to a solution of dicyclohexylphosphine (98.7 μL, 0.450 mmol) in THF (1.0 mL), and the mixture was cooled to 0 °C. *n*BuLi (287 μL, 0.450 mmol; 1.57 M solution in hexane) was added to it, and the mixture was cooled to –78 °C. Compound **1**, **5**, or **6** (0.300 mmol) was added to it and the resulting mixture was stirred for 3 h at –78 °C. H_2O_2 (110 μL, 1.08 mmol; 30 wt% solution in H_2O) was then added to it and the resulting mixture was stirred for 1 h at room temperature. This was extracted with Et_2O and the organic layer was washed with H_2O for 3 times. The aqueous layer was extracted with Et_2O, and the combined organic layer was washed with saturated NaClaq, dried over $MgSO_4$, filtered, and concentrated under vacuum. The residue was purified by GPC with $CHCl_3$ to afford compounds **3**/**4**.

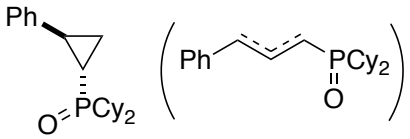


Table 2, Entry 1 (Compound 3aa). Colorless oil. 77% yield (**3aa**/(**4aa**+**4aa'**) = 92/8, **4aa**/**4aa'** = 88/12, containing ca. 4% inseparable dicyclohexyl(3-phenylpropyl)phosphine oxide).

^{1}H NMR ($CDCl_3$): δ 7.32-7.25 (m, 2H), 7.22-7.16 (m, 1H), 7.14-7.07 (m, 2H), 2.46-2.34 (m, 1H), 2.08-1.58 (m, 12H), 1.57-1.10 (m, 12H), 0.86-0.73 (m, 1H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 141.0 (d, $^{3}J_{CP}$ = 1.9 Hz), 128.7, 126.3, 126.0, 36.9 (d, $^{1}J_{CP}$ = 67.1 Hz), 36.4 (d, $^{1}J_{CP}$ = 68.1 Hz), 26.8 (d, J_{CP} = 13.4 Hz), 26.7, 26.64, 26.62 (d, J_{CP} = 11.5 Hz), 26.21 (d, J_{CP} = 1.9 Hz), 26.16, 26.04, 26.03 (d, J_{CP} = 2.9 Hz), 25.5 (d, J_{CP} = 2.9 Hz), 25.3 (d, J_{CP} = 2.9 Hz), 18.8 (d, $^{2}J_{CP}$ = 2.9 Hz), 13.8 (d, $^{1}J_{CP}$ = 84.4 Hz) 11.4 (d, $^{2}J_{CP}$ = 3.8 Hz). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ 48.0 (s). HRMS (FAB) calcd for $C_{21}H_{32}OP$ ($M+H^+$) 331.2185, found 331.2191.

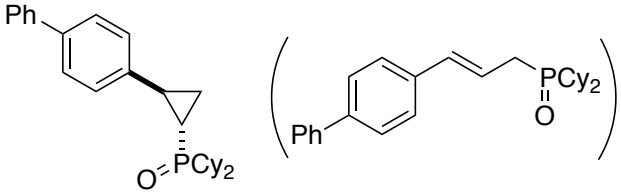


Table 2, Entry 2 (Compound 3ba). White solid. 80% yield (**3ba**/**4ba** = 97/3).

^{1}H NMR ($CDCl_3$): δ 7.61-7.55 (m, 2H), 7.52 (d, $^{3}J_{HH}$ = 8.2 Hz, 2H), 7.43 (t, $^{3}J_{HH}$ = 7.6 Hz, 2H),

7.36-7.30 (m, 1H), 7.18 (d, $^{3}J_{HH}$ = 8.2 Hz, 2H), 2.51-2.38 (m, 1H), 2.10-1.63 (m, 12H), 1.61-1.12 (m, 12H), 0.90-0.77 (m, 1H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 140.8, 140.1 (d, $^{3}J_{CP}$ = 1.9 Hz), 139.3, 128.8, 127.4, 127.3, 127.0, 126.4, 36.8 (d, $^{1}J_{CP}$ = 67.1 Hz), 36.4 (d, $^{1}J_{CP}$ = 68.1 Hz), 26.745 (d, J_{CP} = 12.5 Hz), 26.740, 26.62, 26.60 (d, J_{CP} = 12.5 Hz), 26.2 (d, J_{CP} = 2.9 Hz), 26.1, 26.0, 25.5 (d, J_{CP} = 3.8 Hz), 25.3 (d, J_{CP} = 3.8 Hz), 18.6 (d, $^{2}J_{CP}$ = 2.9 Hz), 13.9 (d, $^{1}J_{CP}$ = 83.4 Hz), 11.5 (d, $^{2}J_{CP}$ = 3.8 Hz). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ 48.1 (s). HRMS (FAB) calcd for $C_{27}H_{36}OP$ ($M+H^+$) 407.2498, found 407.2505.

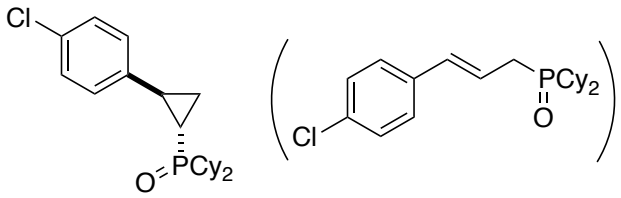


Table 2, Entry 3 (Compound 3ca). White solid. 76% yield (**3ca**/**4ca** = 99/1).

^{1}H NMR ($CDCl_3$): δ 7.25 (d, $^{3}J_{HH}$ = 8.7 Hz, 2H), 7.02 (d, $^{3}J_{HH}$ = 8.7 Hz, 2H), 2.43-2.28 (m, 1H), 2.07-1.59 (m, 12H), 1.57-1.05 (m, 12H), 0.81-0.67 (m, 1H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 139.6 (d, $^{3}J_{CP}$ = 2.9 Hz), 132.0, 128.8, 127.2, 36.8 (d, $^{1}J_{CP}$ = 67.1 Hz), 36.4 (d, $^{1}J_{CP}$ = 68.0 Hz), 26.71 (d, J_{CP} = 12.5 Hz), 26.70, 26.58, 26.56 (d, J_{CP} = 12.5 Hz), 26.2 (d, J_{CP} = 2.9 Hz), 26.10, 26.06 (d, J_{CP} = 2.9 Hz), 26.0, 25.5 (d, J_{CP} = 3.8 Hz), 25.3 (d, J_{CP} = 2.9 Hz), 18.3 (d, $^{2}J_{CP}$ = 2.9 Hz), 14.1 (d, $^{1}J_{CP}$ = 83.4 Hz), 11.6 (d, $^{2}J_{CP}$ = 4.8 Hz). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ 47.9 (s). HRMS (FAB) calcd for $C_{21}H_{31}ClOP$ ($M+H^+$) 365.1796, found 365.1795.

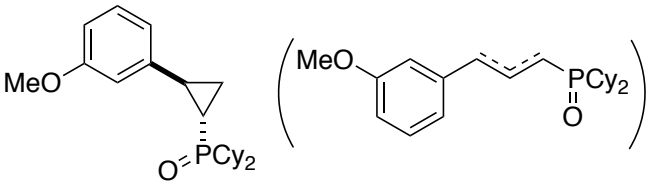


Table 2, Entry 4 (Compound 3da). Colorless oil. 86% yield (**3da**/(**4da**+**4da'**) = 90/10, **4da**/**4da'** = 89/11, containing ca. 3% inseparable dicyclohexyl(3-(3-methoxyphenyl)propyl)phosphine oxide).

^{1}H NMR ($CDCl_3$): δ 7.20 (t, $^{3}J_{HH}$ = 8.0 Hz, 1H), 6.74 (dd, $^{3}J_{HH}$ = 8.2 Hz and $^{4}J_{HH}$ = 2.3 Hz, 1H), 6.70 (d, $^{3}J_{HH}$ = 7.8 Hz, 1H), 6.65 (t, $^{4}J_{HH}$ = 2.1 Hz, 1H), 3.80 (s, 3H), 2.43-2.32 (m, 1H), 2.08-1.59 (m, 12H), 1.56-1.10 (m, 12H), 0.85-0.74 (m, 1H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 159.9, 142.6 (d, $^{3}J_{CP}$ = 1.9 Hz), 129.6, 118.2, 112.0, 111.4, 55.2, 36.7 (d, $^{1}J_{CP}$ = 67.1 Hz), 36.3 (d, $^{1}J_{CP}$ = 68.1 Hz), 26.646 (d, J_{CP} = 12.5 Hz), 26.645, 26.53, 26.52 (d, J_{CP} = 12.5 Hz), 26.08 (d, J_{CP} = 1.9 Hz), 26.05, 25.94, 25.92 (d, J_{CP} = 1.9 Hz), 25.4 (d, J_{CP} = 2.9 Hz), 25.2 (d, J_{CP} = 3.8 Hz), 18.8 (d, $^{2}J_{CP}$ = 2.9 Hz), 13.7 (d, $^{1}J_{CP}$ = 84.4 Hz), 11.4 (d, $^{2}J_{CP}$ = 4.8 Hz). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ 48.0 (s). HRMS (FAB) calcd for $C_{22}H_{34}O_2P$ ($M+H^+$) 361.2291, found 361.2292.

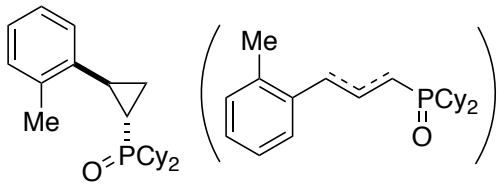


Table 2, Entry 5 (Compound 3ea). White solid. 67% yield (**3ea**/(**4ea**+**4ea'**) = 90/10, **4ea**/**4ea'** = 65/35, containing ca. 2% inseparable dicyclohexyl(3-(2-methylphenyl)propyl)phosphine oxide).

^{1}H NMR ($CDCl_3$): δ 7.20-7.09 (m, 3H), 6.91-6.85 (m, 1H), 2.51-2.40 (m, 1H), 2.43 (s, 3H), 2.08-1.15 (m, 23H), 1.08-0.96 (m, 1H), 0.94-0.84 (m, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 138.8 (d, $^{3}J_{CP}$ = 2.9 Hz), 138.1, 130.2, 126.3, 126.0, 124.4, 36.8 (d, $^{1}J_{CP}$ = 68.1 Hz), 36.7 (d, $^{1}J_{CP}$ = 67.1 Hz), 26.8 (d, J_{CP} = 3.8 Hz), 26.7 (d, J_{CP} = 12.5 Hz), 26.64 (d, J_{CP} = 1.9 Hz), 26.61 (d, J_{CP} = 11.5 Hz), 26.2 (d, J_{CP} = 2.9 Hz), 26.13, 26.08, 26.07 (d, J_{CP} = 1.9 Hz), 25.5 (d, J_{CP} = 3.8 Hz), 25.3 (d, J_{CP} = 2.9 Hz), 19.8, 16.7 (d, $^{2}J_{CP}$ = 2.9 Hz), 11.6 (d, $^{2}J_{CP}$ = 4.8 Hz), 10.4 (d, $^{1}J_{CP}$ = 84.4 Hz). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 48.3 (s). HRMS (FAB) calcd for $C_{22}H_{34}OP$ ($M+H^+$) 345.2342, found 345.2349.

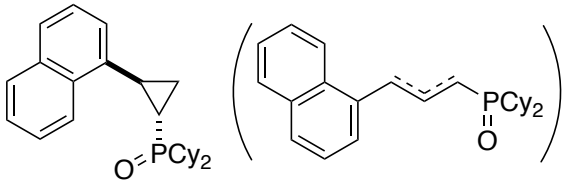


Table 2, Entry 6 (Compound 3fa). White solid. 97% yield (**3fa**/(**4fa**+**4fa'**) = 97/3, **4fa**/**4fa'** = 50/50).

^{1}H NMR ($CDCl_3$): δ 8.38 (d, $^{3}J_{HH}$ = 8.2 Hz, 1H), 7.88-7.83 (m, 1H), 7.75 (d, $^{3}J_{HH}$ = 8.3 Hz, 1H), 7.56 (ddd, $^{3}J_{HH}$ = 8.2 and 6.8 Hz and $^{4}J_{HH}$ = 1.4 Hz, 1H), 7.51 (td, $^{3}J_{HH}$ = 7.3 Hz and $^{4}J_{HH}$ = 1.4 Hz, 1H), 7.40 (t, $^{3}J_{HH}$ = 7.6 Hz, 1H), 7.16 (d, $^{3}J_{HH}$ = 6.8 Hz, 1H), 3.03-2.92 (m, 1H), 2.12-1.63 (m, 13H), 1.61-1.42 (m, 4H), 1.39-1.12 (m, 7H), 1.07-0.96 (m, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 136.9 (d, $^{3}J_{CP}$ = 2.9 Hz), 133.7, 133.3, 128.5, 127.3, 126.2, 126.1, 125.3, 124.4, 122.5, 36.9 (d, $^{1}J_{CP}$ = 68.1 Hz), 36.9 (d, $^{1}J_{CP}$ = 67.1 Hz), 26.8 (d, J_{CP} = 3.8 Hz), 26.7 (d, J_{CP} = 12.5 Hz), 26.64 (d, J_{CP} = 3.8 Hz), 26.61 (d, J_{CP} = 11.5 Hz), 26.21 (d, J_{CP} = 1.9 Hz), 26.16 (d, J_{CP} = 2.9 Hz), 26.12 (d, J_{CP} = 1.9 Hz), 26.10 (d, J_{CP} = 1.9 Hz), 25.5 (d, J_{CP} = 3.8 Hz), 25.4 (d, J_{CP} = 2.9 Hz), 16.6 (d, $^{2}J_{CP}$ = 2.9 Hz), 11.5 (d, $^{2}J_{CP}$ = 4.8 Hz), 9.7 (d, $^{1}J_{CP}$ = 85.3 Hz). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 48.4 (s). HRMS (FAB) calcd for $C_{25}H_{34}OP$ ($M+H^+$) 381.2342, found 381.2348.

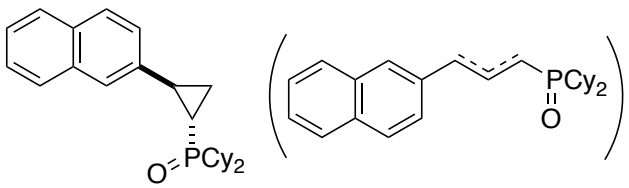


Table 2, Entry 7 (Compound 3ga). White solid. 86% yield (**3ga**/(**4ga**+**4ga'**) = 97/3, **4ga**/**4ga'** = 96/4).

^{1}H NMR ($CDCl_3$): δ 7.83-7.74 (m, 3H), 7.56 (s, 1H), 7.50-7.38 (m, 2H), 7.21 (dd, $^{3}J_{HH}$ = 8.7 Hz and $^{4}J_{HH}$ = 1.4 Hz, 1H), 2.63-2.52 (m, 1H), 2.11-1.07 (m, 24H), 0.98-0.85 (m, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 138.5 (d, $^{3}J_{CP}$ = 1.9 Hz), 133.6, 132.3, 128.3, 127.7, 127.4, 126.3, 125.4, 124.3, 124.2, 36.8

(d, J_{CP} = 68.1 Hz), 36.4 (d, J_{CP} = 68.1 Hz), 26.69 (d, J_{CP} = 13.4 Hz), 26.68 (d, J_{CP} = 2.9 Hz), 26.6 (d, J_{CP} = 2.9 Hz), 26.5 (d, J_{CP} = 12.5 Hz), 26.13 (d, J_{CP} = 2.9 Hz), 26.09 (d, J_{CP} = 1.9 Hz), 26.0 (d, J_{CP} = 2.9 Hz), 25.9, 25.5 (d, J_{CP} = 2.9 Hz), 25.3 (d, J_{CP} = 2.9 Hz), 19.0 (d, $^{2}J_{CP}$ = 2.9 Hz), 13.9 (d, $^{1}J_{CP}$ = 83.4 Hz), 11.6 (d, $^{2}J_{CP}$ = 4.8 Hz). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ 48.1 (s). HRMS (FAB) calcd for $C_{25}H_{34}OP$ ($M+H^+$) 381.2342, found 381.2343.

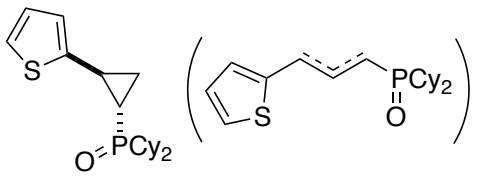


Table 2, Entry 8 (Compound 3ha). Colorless oil. 82% yield (**3ha**/(**4ha**+**4ha'**) = 90/10, **4ha**/**4ha'** = 80/20).

^{1}H NMR ($CDCl_3$): δ 7.09 (dd, $^{3}J_{HH}$ = 5.1 Hz and $^{4}J_{HH}$ = 1.2 Hz, 1H), 6.91 (dd, $^{3}J_{HH}$ = 5.1 and 3.4 Hz, 1H), 6.85-6.82 (m, 1H), 2.65-2.57 (m, 1H), 2.07-1.63 (m, 12H), 1.58-1.38 (m, 5H), 1.34-1.18 (m, 7H), 0.87-0.77 (m, 1H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 145.4 (d, $^{3}J_{CP}$ = 2.9 Hz), 127.0, 123.7, 122.8, 36.7 (d, $^{1}J_{CP}$ = 67.1 Hz), 36.5 (d, $^{1}J_{CP}$ = 68.0 Hz), 26.7 (d, J_{CP} =12.5 Hz), 26.6 (d, J_{CP} = 11.5 Hz), 26.13 (d, J_{CP} = 1.9 Hz), 26.06, 26.0 (d, J_{CP} = 1.9 Hz), 25.4 (d, J_{CP} = 2.9 Hz), 25.3 (d, J_{CP} = 3.8 Hz), 14.7 (d, $^{2}J_{CP}$ = 3.8 Hz), 14.5 (d, $^{1}J_{CP}$ = 82.4 Hz), 12.0 (d, $^{2}J_{CP}$ = 3.8 Hz). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ 47.6 (s). HRMS (FAB) calcd for $C_{19}H_{30}OPS$ ($M+H^+$) 337.1749, found 337.1756.

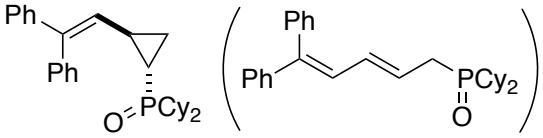


Table 2, Entry 9 (Compound 3ia). The reaction was conducted in the absence of HMPA. Colorless oil. 82% yield (**3ia**/**4ia** = 96/4, *trans*/*cis* = 96/4 for **3ia**).

^{1}H NMR ($CDCl_3$): δ 7.38 (t, $^{3}J_{HH}$ = 7.4 Hz, 1H), 7.34-7.18 (m, 8H), 5.46 (d, $^{3}J_{HH}$ = 10.2 Hz, 1H), 2.26-1.15 (m, 24H), 1.03-0.95 (m, 1H), 0.69-0.59 (m, 1H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 142.34, 142.26, 139.6, 131.0 (d, $^{3}J_{CP}$ = 2.9 Hz), 130.0, 128.5, 128.3, 127.4, 127.1, 127.0, 36.9 (d, $^{1}J_{CP}$ = 67.1 Hz), 36.4 (d, $^{1}J_{CP}$ = 68.1 Hz), 26.74 (d, J_{CP} = 10.5 Hz), 26.70 (d, J_{CP} = 12.5 Hz), 26.65 (d, J_{CP} = 3.8 Hz), 26.5 (d, J_{CP} = 3.8 Hz), 26.14, 26.12, 26.07 (d, J_{CP} = 1.9 Hz), 25.4 (d, J_{CP} = 3.8 Hz), 25.2 (d, J_{CP} = 2.9 Hz), 15.8 (d, $^{2}J_{CP}$ = 2.9 Hz), 12.2 (d, $^{1}J_{CP}$ = 83.4 Hz), 10.9 (d, $^{2}J_{CP}$ = 4.8 Hz). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ 47.5 (s). HRMS (FAB) calcd for $C_{29}H_{38}OP$ ($M+H^+$) 433.2655, found 433.2663.

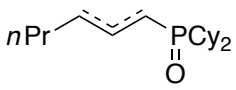


Table 2, Entry 10 (Compound 4ja). Yellow oil. 90% yield (**3ja**/(**4ja**+**4ja'**) = 0/100, **4ja**/**4ja'** = 94/6).

^{1}H NMR ($CDCl_3$): δ 5.64-5.53 (m, 1H), 5.52-5.40 (m, 1H), 2.55 (dd, $^{2}J_{HP}$ = 14.1 Hz and $^{3}J_{HH}$ = 7.3 Hz, 2H), 2.08-1.65 (m, 14H), 1.53-1.16 (m, 12H), 0.90 (t, $^{3}J_{HH}$ = 7.3 Hz, 3H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$):

δ 135.6 (d, $^2J_{CP}$ = 11.5 Hz), 120.1 (d, $^3J_{CP}$ = 8.6 Hz), 35.9 (d, $^1J_{CP}$ = 63.3 Hz), 34.8, 29.3 (d, $^1J_{CP}$ = 58.5 Hz), 26.7 (d, J_{CP} = 11.5 Hz), 26.6 (d, J_{CP} = 11.5 Hz), 26.1, 25.8, 25.5, 22.5, 13.7. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 49.5 (s). HRMS (FAB) calcd for $C_{18}H_{34}OP$ ($M+H^+$) 297.2342, found 297.2348.

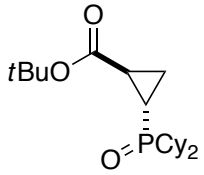


Table 2, Entry 11 (Compound 3ka). The reaction was conducted in the absence of HMPA. White solid. 70% yield (**3ka**/**4ka** = 100/0).

^1H NMR ($CDCl_3$): δ 2.30-1.15 (m, 25H), 1.45 (s, 9H), 1.13-0.90 (m, 1H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 172.3, 81.0, 36.9 (br), 36.1 (br), 28.1, 26.60, 26.58, 26.56, 26.12, 26.08, 26.0, 25.22, 25.17, 17.2, 12.6 (br), 9.6. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 47.9 (s). HRMS (FAB) calcd for $C_{20}H_{36}O_3P$ ($M+H^+$) 355.2397, found 355.2395.

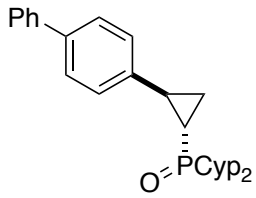


Table 2, Entry 12 (Compound 3bb). White solid. 70% yield (**3bb**/**4bb** = 100/0).

^1H NMR ($CDCl_3$): δ 7.60-7.54 (m, 2H), 7.51 (d, $^3J_{HH}$ = 8.2 Hz, 2H), 7.43 (t, $^3J_{HH}$ = 7.6 Hz, 2H), 7.33 (t, $^3J_{HH}$ = 7.3 Hz, 1H), 7.18 (d, $^3J_{HH}$ = 8.2 Hz, 2H), 2.58-2.47 (m, 1H), 2.25-2.04 (m, 2H), 2.03-1.47 (m, 17H), 1.30-1.19 (m, 1H), 0.97-0.84 (m 1H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 140.8, 140.3 (d, $^3J_{CP}$ = 2.9 Hz), 139.2, 128.8, 127.3, 127.2, 127.0, 126.3, 38.7 (d, $^1J_{CP}$ = 70.9 Hz), 38.5 (d, $^1J_{CP}$ = 71.9 Hz), 27.064, 27.055 (d, J_{CP} = 1.9 Hz), 26.6 (d, J_{CP} = 1.9 Hz), 26.5 (d, J_{CP} = 2.9 Hz), 26.43 (d, J_{CP} = 9.6 Hz), 26.42, 26.32, 26.30 (d, J_{CP} = 9.6 Hz), 18.8 (d, $^2J_{CP}$ = 2.9 Hz), 15.8 (d, $^1J_{CP}$ = 87.2 Hz), 11.5 (d, $^2J_{CP}$ = 4.8 Hz). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 48.2 (s). HRMS (FAB) calcd for $C_{25}H_{32}OP$ ($M+H^+$) 379.2185, found 379.2192.

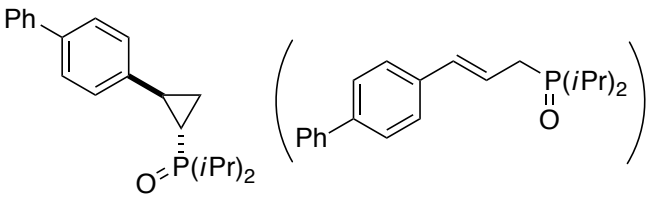


Table 2, Entry 13 (Compound 3bc). Colorless oil. 82% yield (**3bc**/**4bc** = 97/3).

^1H NMR ($CDCl_3$): δ 7.60-7.54 (m, 2H), 7.52 (d, $^3J_{HH}$ = 8.2 Hz, 2H), 7,43 (t, $^3J_{HH}$ = 7.6 Hz, 2H), 7.33 (t, $^3J_{HH}$ = 7.3 Hz, 1H), 7.18 (d, $^3J_{HH}$ = 8.2 Hz, 2H), 2.55-2.43 (m, 1H), 2.20-2.00 (m, 2H), 1.65-

1.51 (m, 1H), 1.36-1.14 (m, 13H), 0.95-0.80 (m, 1H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 140.7, 139.9 (d, $^{3}J_{CP}$ = 1.9 Hz), 139.2, 128.8, 127.3, 127.2, 126.9, 126.2, 26.5 (d, $^{1}J_{CP}$ = 67.1 Hz), 26.2 (d, $^{1}J_{CP}$ = 68.1 Hz), 18.4 (d, $^{2}J_{CP}$ = 2.9 Hz), 16.3 (d, $^{2}J_{CP}$ = 1.9 Hz), 16.2 (d, $^{2}J_{CP}$ = 1.9 Hz), 15.7 (d, $^{2}J_{CP}$ = 3.8 Hz), 15.6 (d, $^{2}J_{CP}$ = 2.9 Hz), 13.2 (d, $^{1}J_{CP}$ = 84.4 Hz), 11.3 (d, $^{2}J_{CP}$ = 4.8 Hz). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ 53.1 (s). HRMS (FAB) calcd for $C_{21}H_{28}OP$ ($M+H^+$) 327.1872, found 327.1869.

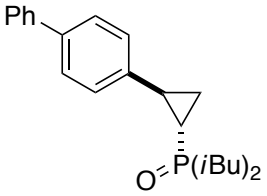


Table 2, Entry 14 (Compound 3bd). White solid. 86% yield (**3bd**/**4bd** = 100/0).

^{1}H NMR ($CDCl_3$): δ 7.60-7.55 (m, 2H), 7.52 (d, $^{3}J_{HH}$ = 8.5 Hz, 2H), 7.43 (t, $^{3}J_{HH}$ = 7.6 Hz, 2H), 7.33 (t, $^{3}J_{HH}$ = 7.4 Hz, 1H), 7.18 (d, $^{3}J_{HH}$ = 8.3 Hz, 2H), 2.59-2.50 (m, 1H), 2.27-2.08 (m, 2H), 1.83-1.55 (m, 5H), 1.33-1.24 (m, 1H), 1.12 (d, $^{3}J_{HH}$ = 6.6 Hz, 3H), 1.11 (d, $^{3}J_{HH}$ = 6.3 Hz, 3H), 1.08 (d, $^{3}J_{HH}$ = 6.6 Hz, 3H), 1.03 (d, $^{3}J_{HH}$ = 6.6 Hz, 3H), 1.00-0.89 (m, 1H). ^{13}C NMR ($CDCl_3$): δ 140.8, 140.0 (d, $^{3}J_{CP}$ = 2.9 Hz), 139.3, 128.8, 127.3, 127.2, 127.0, 126.3, 39.8 (d, $^{1}J_{CP}$ = 68.1 Hz), 39.7 (d, $^{1}J_{CP}$ = 67.1 Hz), 25.1 (d, $^{3}J_{CP}$ = 9.6 Hz), 25.0 (d, $^{3}J_{CP}$ = 8.6 Hz), 24.9 (d, $^{3}J_{CP}$ = 7.7 Hz), 24.8 (d, $^{3}J_{CP}$ = 7.7 Hz), 23.7 (d, $^{2}J_{CP}$ = 3.8 Hz), 23.6 (d, $^{2}J_{CP}$ = 3.8 Hz), 19.6 (d, $^{2}J_{CP}$ = 2.9 Hz), 19.2 (d, $^{1}J_{CP}$ = 87.2 Hz), 12.0 (d, $^{2}J_{CP}$ = 3.8 Hz). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ 42.9 (s). HRMS (FAB) calcd for $C_{23}H_{32}OP$ ($M+H^+$) 355.2185, found 355.2191.

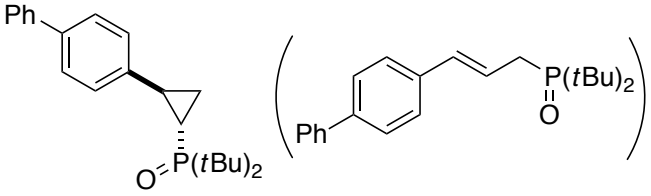


Table 2, Entry 15 (Compound 3be). Yellow solid. 88% yield (**3be**/(**4be**+**4be'**) = 89/11, **4ja**/**4ja'** = 62/38).

^{1}H NMR ($CDCl_3$): δ 7.57 (d, $^{3}J_{HH}$ = 6.9 Hz, 2H), 7.52 (d, $^{3}J_{HH}$ = 8.2 Hz, 2H), 7.43 (t, $^{3}J_{HH}$ = 7.8 Hz, 2H), 7.33 (t, $^{3}J_{HH}$ = 7.3 Hz, 1H), 7.18 (d, $^{3}J_{HH}$ = 8.2 Hz, 2H), 2.53-2.43 (m, 1H), 1.65-1.55 (m, 1H), 1.33-1.27 (m, 1H), 1.35 (d, $^{3}J_{HP}$ = 13.3 Hz, 9H), 1.28 (d, $^{3}J_{HP}$ = 13.3 Hz, 9H), 1.14-1.02 (m, 1H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 140.8, 140.1 (d, $^{3}J_{CP}$ = 1.9 Hz), 139.2, 128.8, 127.3, 127.2, 127.0, 126.2, 36.4 (d, $^{1}J_{CP}$ = 61.3 Hz), 36.1 (d, $^{1}J_{CP}$ = 62.3 Hz), 27.2, 19.9 (d, $^{2}J_{CP}$ = 2.9 Hz), 13.6 (d, $^{1}J_{CP}$ = 77.6 Hz), 13.1 (d, $^{2}J_{CP}$ = 4.8 Hz). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ 57.2 (s). HRMS (FAB) calcd for $C_{23}H_{32}OP$ ($M+H^+$) 355.2185, found 355.2202.

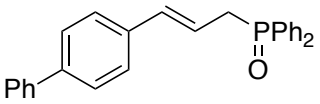


Table 2, Entry 16 (Compound 4bf). White solid. 80% yield (**3bf**/**4bf** = 0/100).

^{1}H NMR ($CDCl_3$): δ 7.87-7.73 (m, 4H), 7.63-7.45 (m, 10H), 7.42 (t, $^{3}J_{HH}$ = 7.6 Hz, 2H), 7.38-7.29 (m, 3H), 6.46 (dd, $^{3}J_{HH}$ = 15.6 Hz and $^{4}J_{HP}$ = 4.1 Hz, 1H), 6.23 (dtd, $^{3}J_{HH}$ = 15.6 and 7.6 Hz and $^{3}J_{HP}$ = 6.0 Hz, 1H), 3.32 (ddd, $^{2}J_{HP}$ = 14.7 Hz, $^{3}J_{HH}$ = 7.3 Hz, and $^{4}J_{HH}$ = 1.4 Hz, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 140.7, 140.5, 135.9 (d, J_{CP} = 2.9 Hz), 135.2 (d, J_{CP} = 12.5 Hz), 132.7 (d, $^{1}J_{CP}$ = 98.7 Hz), 132.0 (d, J_{CP} = 2.9 Hz), 131.2 (d, J_{CP} = 8.6 Hz), 128.9, 128.7 (d, J_{CP} = 11.5 Hz), 127.4, 127.3, 127.0, 126.8, 118.7 (d, $^{3}J_{CP}$ = 9.6 Hz), 35.8 (d, $^{1}J_{CP}$ = 68.1 Hz). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 30.0 (s). HRMS (FAB) calcd for $C_{27}H_{24}OP$ ($M+H^+$) 395.1559, found 395.1560.

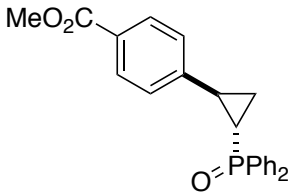
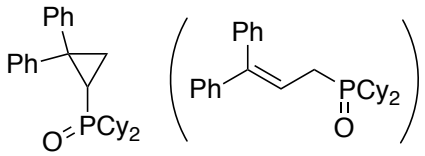


Table 2, Entry 17 (Compound 3nf). White solid. 76% yield (**3nf**/**4nf** = 100/0).

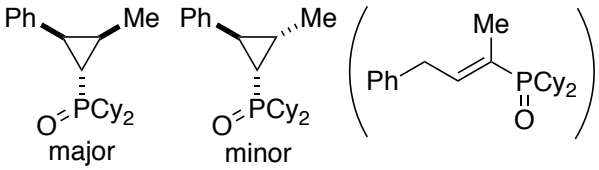
^{1}H NMR ($CDCl_3$): δ 7.94 (d, $^{3}J_{HH}$ = 7.8 Hz, 2H), 7.82-7.64 (m, 4H), 7.58-7.38 (m, 6H), 7.15 (d, $^{3}J_{HH}$ = 8.2 Hz, 2H), 3.89 (s, 3H), 2.77-2.63 (m, 1H), 1.84-1.72 (m, 1H), 1.71-1.58 (m, 1H), 1.52-1.40 (m, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 166.8, 145.9 (d, $^{3}J_{CP}$ = 2.9 Hz), 133.3 (d, $^{1}J_{CP}$ = 104 Hz), 131.98, 131.96, 131.9, 131.09 (d, J_{CP} = 9.6 Hz), 131.07 (d, J_{CP} = 9.6 Hz), 130.0, 128.70 (d, J_{CP} = 12.5 Hz), 128.68 (d, J_{CP} = 11.5 Hz), 128.5, 126.0, 52.1, 21.0 (d, $^{2}J_{CP}$ = 2.9 Hz), 19.9 (d, $^{1}J_{CP}$ = 99.7 Hz), 12.8 (d, $^{2}J_{CP}$ = 4.8 Hz). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 30.1 (s). HRMS (FAB) calcd for $C_{23}H_{22}O_3P$ ($M+H^+$) 377.1301, found 377.1307.



Equation 1 (Compound 3la). White solid. 92% yield (**3la**/**4la** = 85/15).

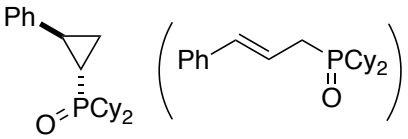
^{1}H NMR ($CDCl_3$): δ 7.36-7.28 (m, 6H), 7.25-7.19 (m, 3H), 7.15 (t, $^{3}J_{HH}$ = 7.1 Hz, 1H), 2.42 (ddd, $^{2}J_{HP}$ = 14.2 Hz and $^{3}J_{HH}$ = 7.4 and 4.6 Hz, 1H), 2.03-1.02 (m, 24H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 146.5 (d, $^{3}J_{CP}$ = 1.9 Hz), 139.7 (d, $^{3}J_{CP}$ = 2.9 Hz), 129.8, 128.9, 128.6, 127.8, 126.7, 126.6, 38.4 (d, $^{1}J_{CP}$ = 67.1 Hz), 37.9 (d, $^{1}J_{CP}$ = 67.1 Hz), 36.4 (d, $^{2}J_{CP}$ = 4.8 Hz), 27.0 (d, J_{CP} = 12.5 Hz), 26.9 (d, J_{CP} = 12.5 Hz), 26.8 (d, J_{CP} = 11.5 Hz), 26.7 (d, J_{CP} = 2.9 Hz), 26.6 (d, J_{CP} = 6.7 Hz), 26.4 (d, J_{CP} = 1.9 Hz), 26.23 (d, J_{CP} = 1.9 Hz), 26.21 (d, J_{CP} = 1.9 Hz), 26.1 (d, J_{CP} = 1.9 Hz), 26.0 (d, J_{CP} = 2.9 Hz), 19.1 (d, $^{1}J_{CP}$ = 81.5 Hz), 16.6 (d, $^{2}J_{CP}$ = 3.8 Hz). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 47.0 (s). HRMS (FAB) calcd for $C_{27}H_{36}OP$

(M+H$^+$) 407.2498, found 407.2506.

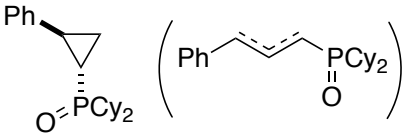


Equation 2 (Compound 3ma). White solid. 94% yield (**3ma**/**4ma'** = 97/3, dr = 87/13 for **3ma**). The relative configurations were assigned by coupling constants in ^{1}H NMR as well as HMQC data.

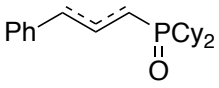
Major diastereomer: ^{1}H NMR ($CDCl_3$): δ 7.31 (t, $^3J_{HH}$ = 7.3 Hz, 2H), 7.25-7.20 (m, 1H), 7.20-7.15 (m, 2H), 2.66 (ddd, $^3J_{HP}$ = 11.4 Hz and $^3J_{HH}$ = 9.2 and 6.4 Hz, 1H), 2.09-1.04 (m, 23H), 0.90 (d, $^3J_{HH}$ = 6.4 Hz, 3H), 0.74 (dt, $^2J_{HP}$ = 14.2 Hz and $^3J_{HH}$ = 6.2 Hz, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 136.9 (d, $^3J_{CP}$ = 1.9 Hz), 129.0, 128.2, 126.3, 36.7 (d, $^1J_{CP}$ = 67.1 Hz), 36.5 (d, $^1J_{CP}$ = 68.0 Hz), 26.73 (d, J_{CP} = 12.5 Hz), 26.69 (d, J_{CP} = 12.4 Hz), 26.61 (d, J_{CP} = 11.5 Hz), 26.57 (d, J_{CP} = 10.5 Hz), 26.134 (d, J_{CP} = 4.8 Hz), 26.130, 26.10 (d, J_{CP} = 1.9 Hz), 26.08 (d, J_{CP} = 2.9 Hz), 25.34 (d, J_{CP} = 3.8 Hz), 25.27 (d, J_{CP} = 3.8 Hz), 24.7 (d, $^3J_{CP}$ = 3.8 Hz), 16.3 (d, $^2J_{CP}$ = 4.8 Hz), 14.6 (d, $^1J_{CP}$ = 85.3 Hz) 12.6 (d, $^2J_{CP}$ = 2.9 Hz). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 48.9 (s). HRMS (FAB) calcd for $C_{22}H_{34}OP$ (M+H$^+$) 345.2342, found 345.2355.



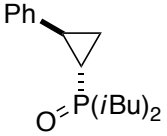
Equation 3, using substrate 5. White solid. 77% yield (**3aa**/**4aa** = 99/1).



Equation 3, using substrate 6. The reaction was conducted at 40 °C. White solid. 71% yield (**3aa**/(**4aa**+**4aa'**) = 90/10, **4aa**/**4aa'** = 71/29).



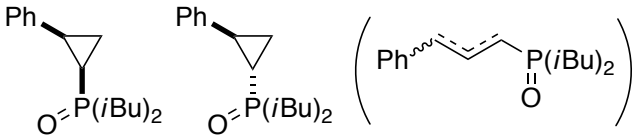
Equation 3, using substrate 7. 61% ^{1}H NMR yield (**3aa**/(**4aa**+**4aa'**) = 0/100, **4aa**/**4aa'** = 92/8).



Scheme 2a (Compound *trans*-3ad). White solid. 82% yield (**3ad**/**4ad** = 100/0).

^{1}H NMR ($CDCl_3$): δ 7.28 (t, $^3J_{HH}$ = 7.5 Hz, 2H), 7.20 (tt, $^3J_{HH}$ = 7.4 Hz and $^4J_{HH}$ = 1.7 Hz, 1H),

7.13-7.09 (m, 2H), 2.49 (ddt, $^3J_{HP}$ = 12.4 Hz, $^3J_{HH}$ = 8.8 Hz and 5.6 Hz, 1H), 2.25-2.06 (m, 2H), 1.80-1.61 (m, 4H), 1.60-1.52 (m, 1H), 1.28-1.21 (m, 1H), 1.11 (d, $^3J_{HH}$ = 6.6 Hz, 3H), 1.10 (d, $^3J_{HH}$ = 6.5 Hz, 3H), 1.06 (d, $^3J_{HH}$ = 6.6 Hz, 3H), 1.01 (d, $^3J_{HH}$ = 6.8 Hz, 3H), 0.94-0.86 (m, 1H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 140.8 (d, $^3J_{CP}$ = 1.9 Hz), 128.6, 126.3, 125.9, 39.8 (d, $^1J_{CP}$ = 68.1 Hz), 39.7 (d, $^1J_{CP}$ = 66.1 Hz), 25.0 (d, $^3J_{CP}$ = 9.6 Hz, 2C), 24.9 (d, $^3J_{CP}$ = 7.7 Hz), 24.7 (d, $^3J_{CP}$ = 7.7 Hz), 23.7 (d, $^2J_{CP}$ = 3.8 Hz), 23.6 (d, $^2J_{CP}$ = 4.8 Hz), 19.8 (d, $^2J_{CP}$ = 3.8 Hz), 19.0 (d, $^1J_{CP}$ = 88.2 Hz), 11.9 (d, $^2J_{CP}$ = 4.8 Hz). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 43.0 (s). HRMS (FAB) calcd for $C_{17}H_{28}OP$ ($M+H^+$) 279.1872, found 279.1878.

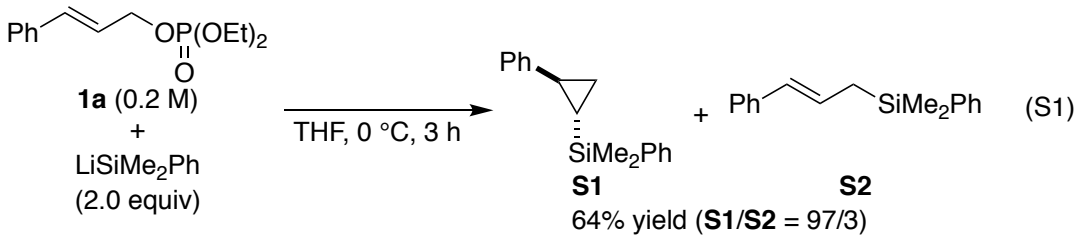


Scheme 2b (Compound *trans*/*cis*-3ad). Colorless oil. 82% yield (**3ad**/(**4ad**+**4ad'**) = 91/9, *trans*/*cis* = 33/67 for **3ad**, *E*/*Z* = 44/56 for **4ad**, **4ad**/**4ad'** = 94/6). Pure *cis*-**3ad** for analysis was obtained by GPC with $CHCl_3$.

cis-**3ad**: ^1H NMR ($CDCl_3$): δ 7.38 (d, $^3J_{HH}$ = 7.3 Hz, 2H), 7.30-7.25 (m, 2H), 7.19 (tt, $^3J_{HH}$ = 7.4 Hz and $^4J_{HH}$ = 1.2 Hz, 1H), 2.52-2.43 (m, 1H), 2.23-2.11 (m, 1H), 1.89-1.75 (m, 2H), 1.65-1.56 (m, 1H), 1.48 (ddd, $^2J_{HH}$ = 15.1 Hz, $^2J_{HP}$ = 10.0 Hz, and $^3J_{HH}$ = 7.0 Hz, 1H), 1.45-1.37 (m ,1H), 1.33 (td, ^2J = 14.6 Hz and $^3J_{HH}$ = 6.8 Hz, 1H), 1.14 (ddd, $^2J_{HH}$ = 15.1 Hz, $^2J_{HP}$ = 12.4 Hz, and $^3J_{HH}$ = 6.3 Hz, 1H), 1.10-0.99 (m, 1H), 1.06 (d, $^3J_{HH}$ = 6.6 Hz, 6H), 0.85 (d, $^3J_{HH}$ = 6.6 Hz, 3H), 0.83 (d, $^3J_{HH}$ = 6.6 Hz, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 136.8 (d, $^3J_{CP}$ = 4.8 Hz), 129.2, 128.0, 126.6, 40.4 (d, $^1J_{CP}$ = 67.1 Hz), 38.7 (d, $^1J_{CP}$ = 67.1 Hz), 25.0 (d, $^3J_{CP}$ = 8.6 Hz), 24.80 (d, $^3J_{CP}$ = 9.6 Hz), 24.76 (d, $^3J_{CP}$ = 7.7 Hz), 24.6 (d, $^3J_{CP}$ = 8.6 Hz), 23.6 (d, $^2J_{CP}$ = 4.8 Hz), 23.5 (d, $^2J_{CP}$ = 3.8 Hz), 23.3 (d, $^2J_{CP}$ = 4.8 Hz), 18.0 (d, $^1J_{CP}$ = 89.1 Hz), 8.6 (d, $^2J_{CP}$ = 3.8 Hz). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 43.6 (s). HRMS (FAB) calcd for $C_{17}H_{28}OP$ ($M+H^+$) 279.1872, found 279.1873.

Comparison between Silicon and Phosphorus Nucleophiles.

Previously, we reported a related cyclopropanation reaction of allyl phosphates using a silicon nucleophile derived from a silylboronate and $KN(SiMe_3)_2$, and we proposed that the effective nucleophile would be a silylpotassium species.[2] To make a direct comparison with the present reaction using lithium phosphides, we conducted a reaction of cinnamyl phosphate **1a** with $LiSiMe_2Ph$ in THF at 0 °C in the absence of HMPA (eqn (S1)). As a result, cyclopropanation product **S1** was selectively obtained along with a small amount of allylic substitution product **S2** in 64% combined yield in the ratio of 97/3. By comparing this result with the ones obtained in Table 1, entries 5, 6, and 8, a silyllithium is considered to be more nucleophilic than a lithium phosphide, and HMPA presumably coordinates to lithium to increase the nucleophilicity of the phosphide in the present reaction.

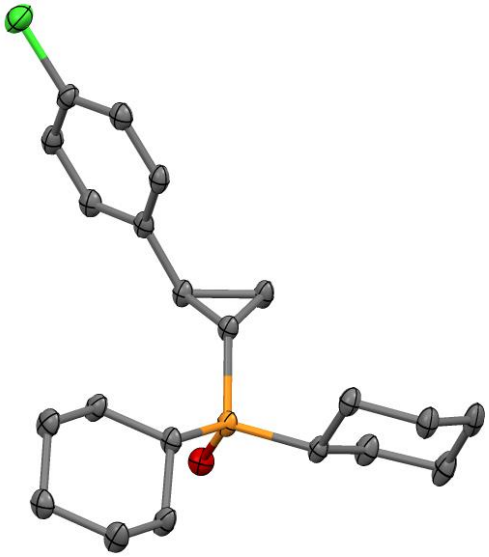


Lithium (38.7 mg, 0.990 mmol; cut in small pieces) was added to a solution of 1,2-diphenyltetramethyldisilane (163 mg, 0.603 mmol) in THF (2.0 mL) at –5 °C. The mixture was sonicated for 30 min at 0 °C and further stirred for 15 h at –5 °C to generate a solution of dimethylphenylsilyllithium. One half of this solution was taken and diluted with THF (0.5 mL). Compound **1a** (81.8 mg, 0.303 mmol) was then added to it at 0 °C, and the reaction mixture was stirred for 3 h at 0 °C. After dilution with Et_2O, the mixture was passed through a pad of silica gel with EtOAc, and the solvent was removed under vacuum. The residue was purified by silica gel preparative TLC with hexane to afford compounds **S1**/**S2** as a colorless oil (48.6 mg, 0.193 mmol; 64% yield, **S1**/**S2** = 97/3).

S1: ^{1}H NMR ($CDCl_3$): δ 7.61-7.53 (m, 2H), 7.40-7.33 (m, 3H), 7.28-7.22 (m, 2H), 7.17-7.07 (m, 3H), 1.84 (ddd, $^3J_{HH}$ = 7.3, 6.4, and 4.6 Hz, 1H), 1.06 (ddd, $^3J_{HH}$ = 10.1 and 4.6 Hz and $^2J_{HH}$ = 3.6 Hz, 1H), 0.94 (td, $^3J_{HH}$ = 7.6 Hz and $^2J_{HH}$ = 3.6 Hz, 1H), 0.29 (s, 3H), 0.28 (s, 3H), 0.31-0.23 (m, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 144.2, 138.7, 134.0, 129.2, 128.4, 127.9, 125.8, 125.6, 20.1, 13.1, 9.5, –3.5, –3.7.

IV. X-ray Crystal Structure

Compound 3ca



A colorless toluene/hexane solution of compound **3ca** was prepared. Crystals suitable for X-ray analysis were obtained by slow evaporation of the solvents at room temperature. The crystal structure has been deposited at the Cambridge Crystallographic Data Centre (deposition number: CCDC 2016109). The data can be obtained free of charge via the Internet at www.ccdc.cam.ac.uk/conts/retrieving.html.

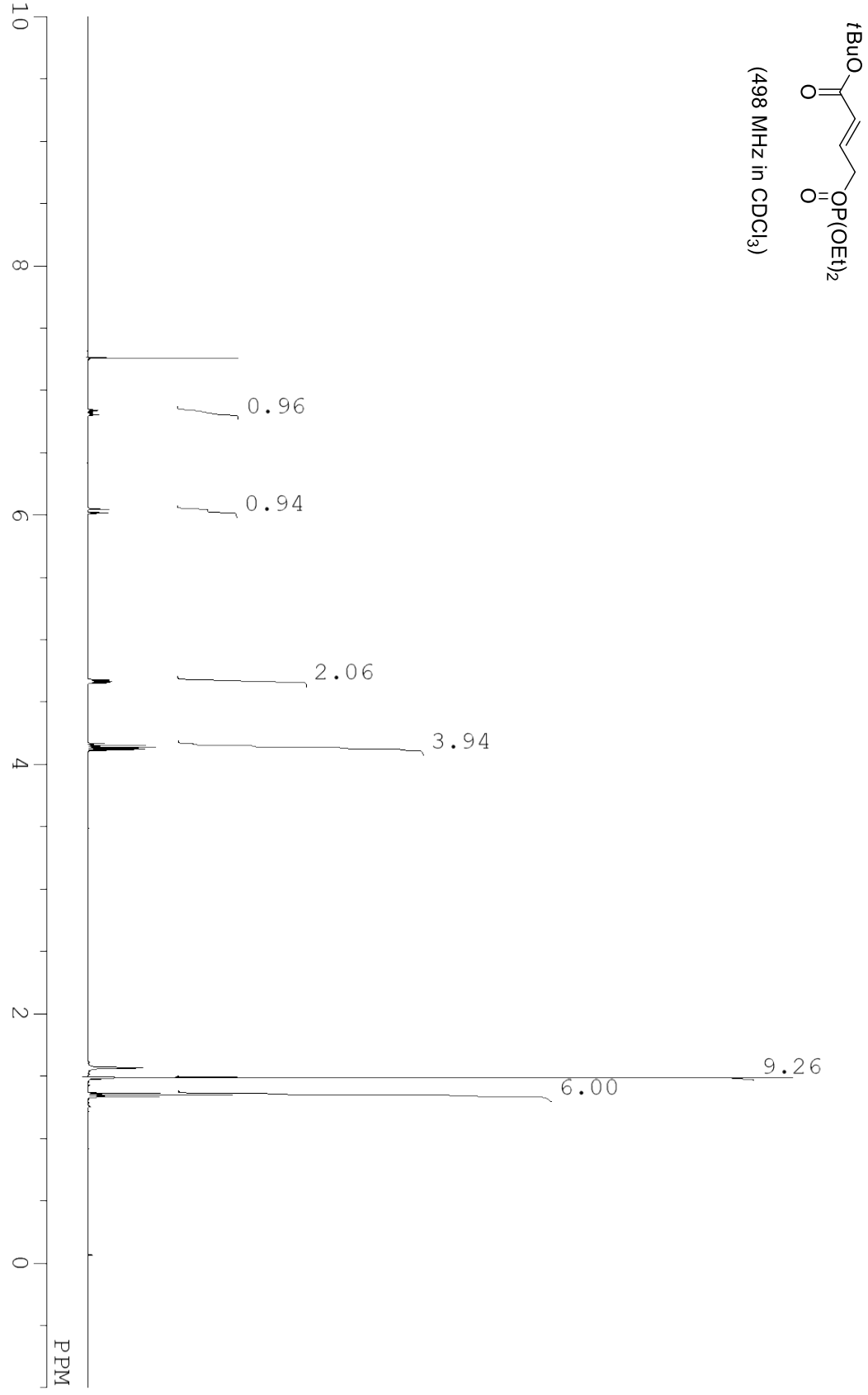
Crystal Data and Structure Refinement.

Empirical Formula	$C_{21}H_{30}ClOP$	
Formula Weight	364.87	
Temperature	113 ± 2 K	
Wavelength	0.71075 Å	
Crystal System	Trilinic	
Space Group	P–1	
Unit Cell Dimensions	a = 5.7668(15) Å	α = 95.169(6)°
	b = 11.743(3) Å	β = 90.067(6)°
	c = 28.998(7) Å	γ = 102.805(7)°

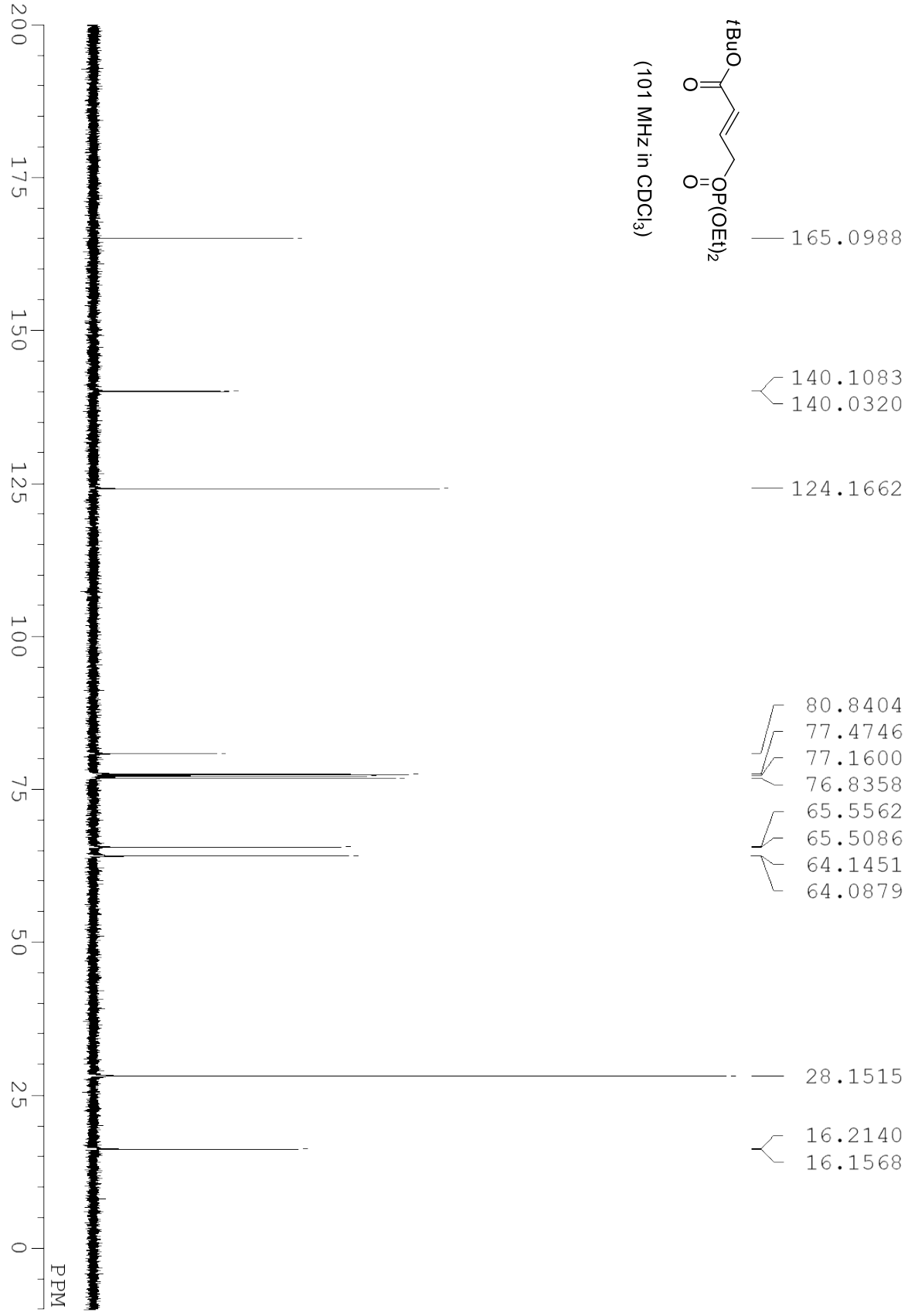
Volume	1906.7(8) $Å^3$
Z Value	4
Calculated Density	1.271 g/cm^3
Absorption coefficient	0.290 mm^{-1}
F(000)	784
Crystal size	0.300 x 0.250 x 0.200 mm
Theta Range for Data Collection	3.197–27.590°
Index Ranges	$-7 \leq h \leq 7, -15 \leq k \leq 15, -37 \leq l \leq 37$
Reflections Collected	31173
Independent Reflections	8342 [R(int) = 0.0822]
Completeness to Theta = 25.242°	96.0%
Absorption Correction	Semi-empirical from equivalents
Max. and Min. Transmission	1.000 and 0.667
Refinement Method	Full-matrix least-squares on F^2
Data / Restraints / Parameters	8342 / 0 / 433
Goodness-of-Fit on F^2	1.008
Final R Indices [I>2sigma(I)]	R1 = 0.0623, wR2 = 0.1669
R Indices (All Data)	R1 = 0.0731, wR2 = 0.1708
Largest Diff. Peak and Hole	1.411 and –0.511 $e^-/Å^3$

V. ^{1}H and ^{13}C NMR Spectra

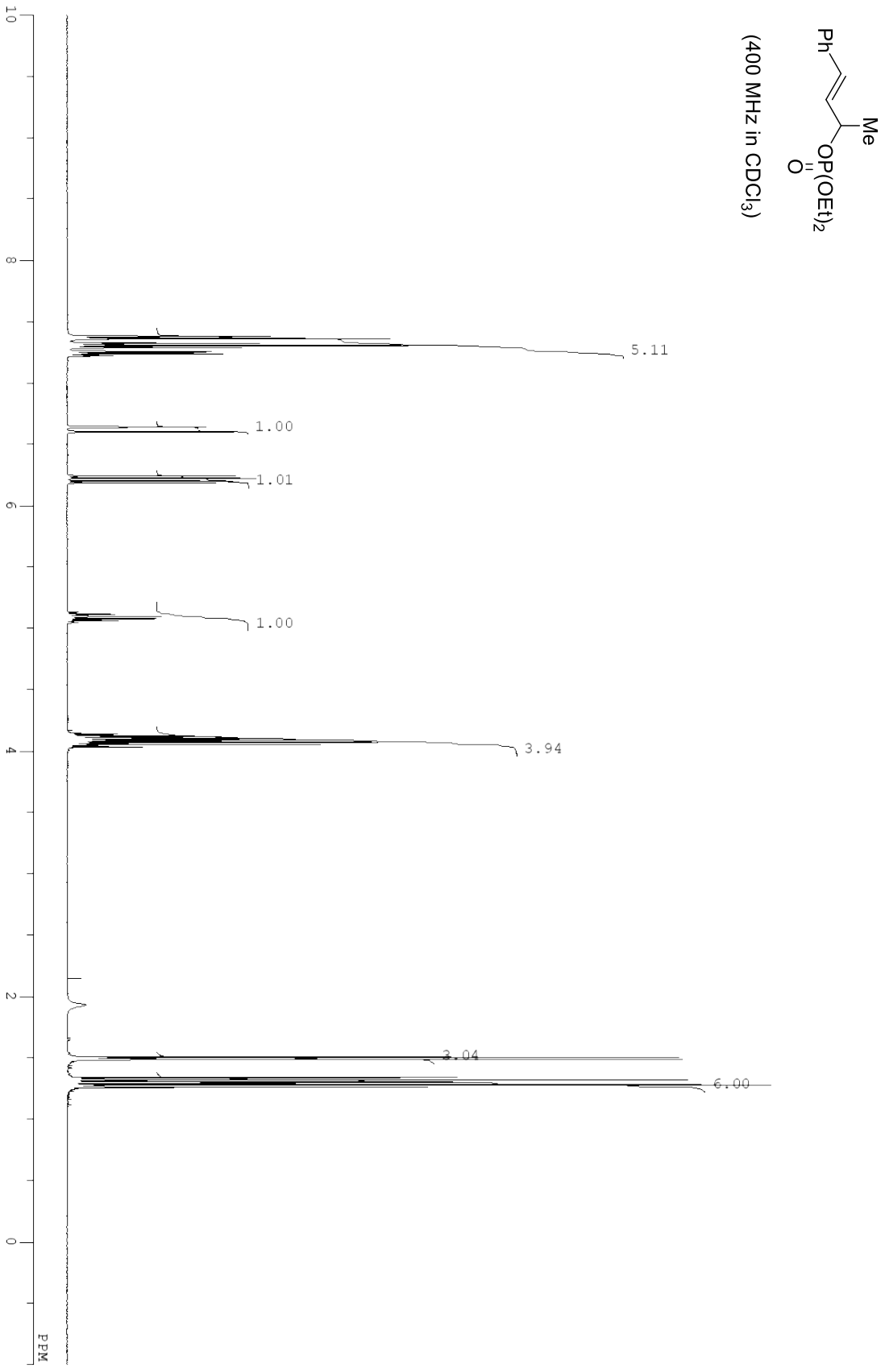
compound **1k**



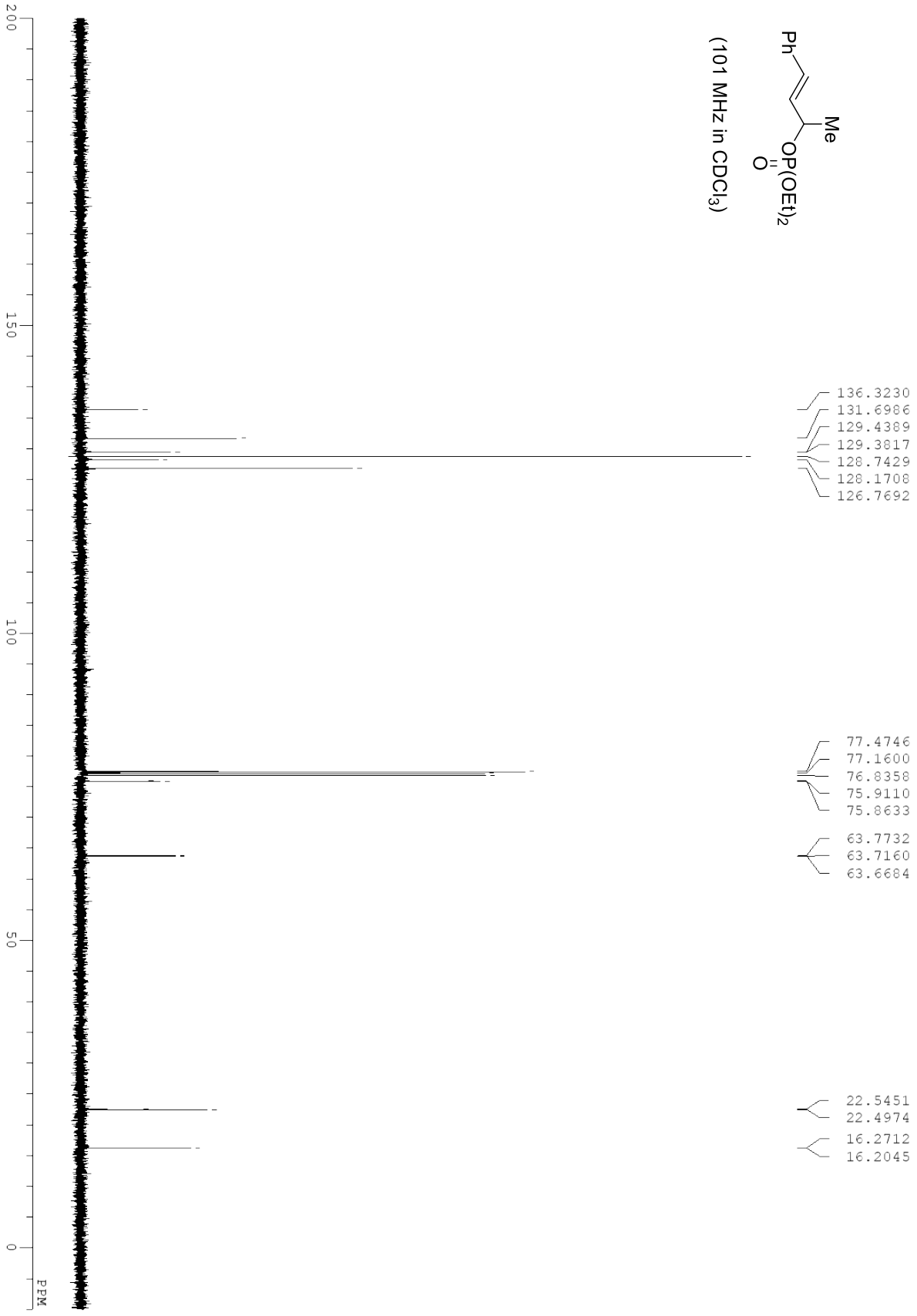
compound **1k**


(101 MHz in CDCl3)
tBuO
O
O
OP(OEt)2
165.0988
140.1083
140.0320
124.1662
80.8404
77.4746
77.1600
76.8358
65.5562
65.5086
64.1451
64.0879
28.1515
16.2140
16.1568
200
175
150
125
100
75
50
25
0
PPM

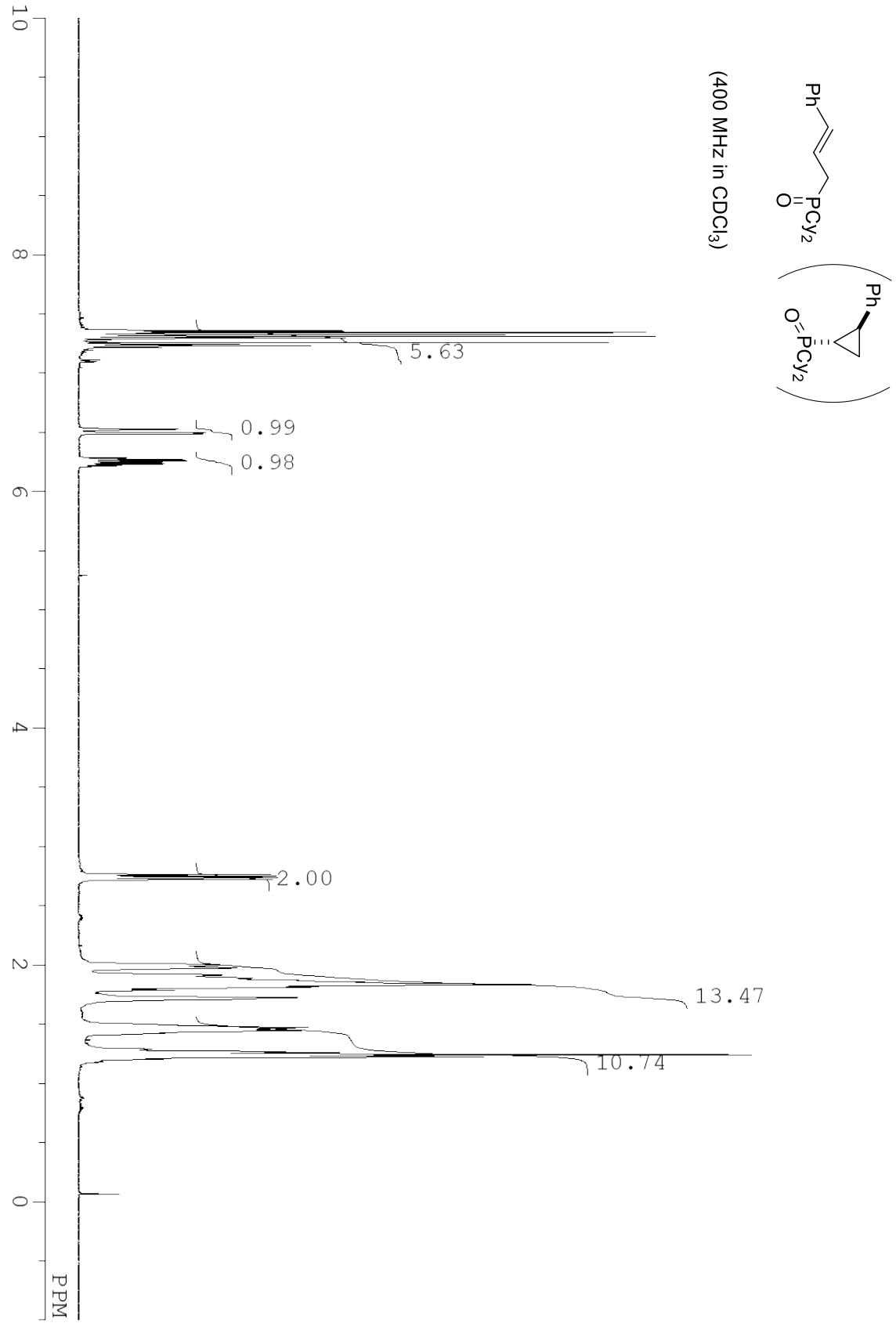
compound **1m**


Ph
Me
OP(OEt)2
O
(400 MHz in CDCl3)
10
8
6
4
2
0
PPM
5.11
1.00
1.01
1.00
3.94
3.04
6.00

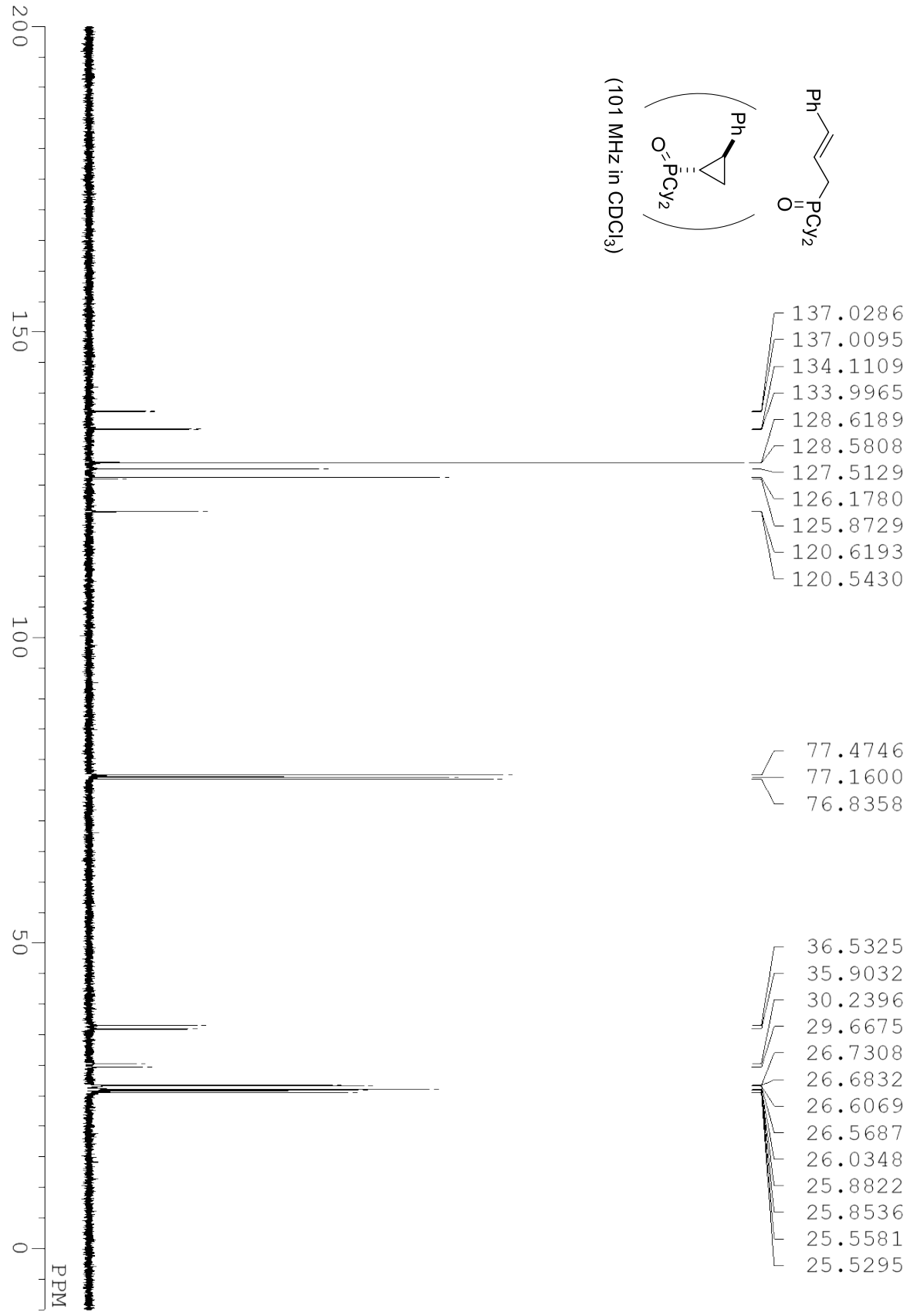
compound **1m**


(101 MHz in CDCl3)
Ph
Me
OP(OEt)2
O
136.3230
131.6986
129.4389
129.3817
128.7429
128.1708
126.7692
77.4746
77.1600
76.8358
75.9110
75.8633
63.7732
63.7160
63.6684
22.5451
22.4974
16.2712
16.2045
200
150
100
50
0
PPM

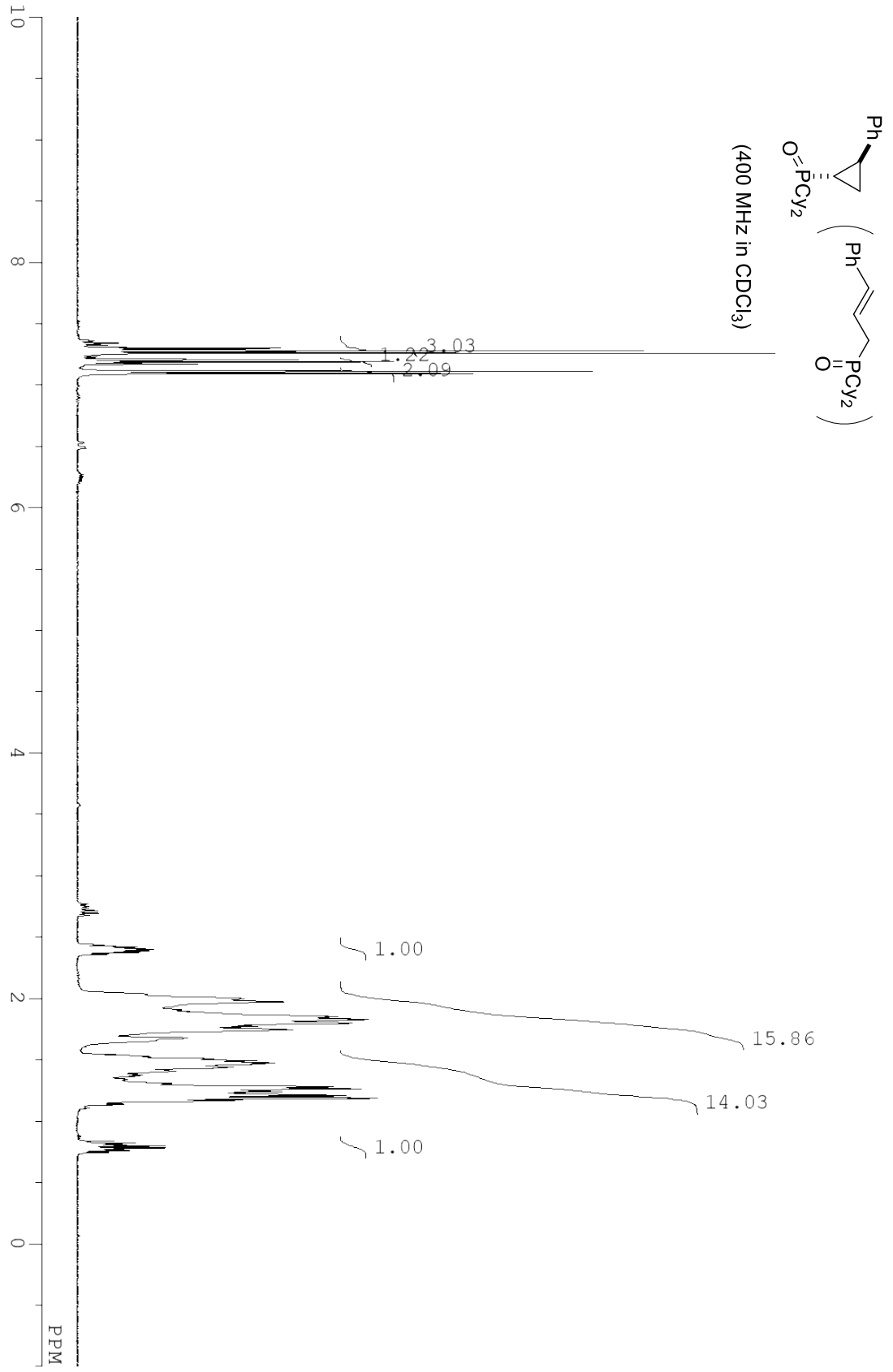
compound **4aa** (**3aa**)



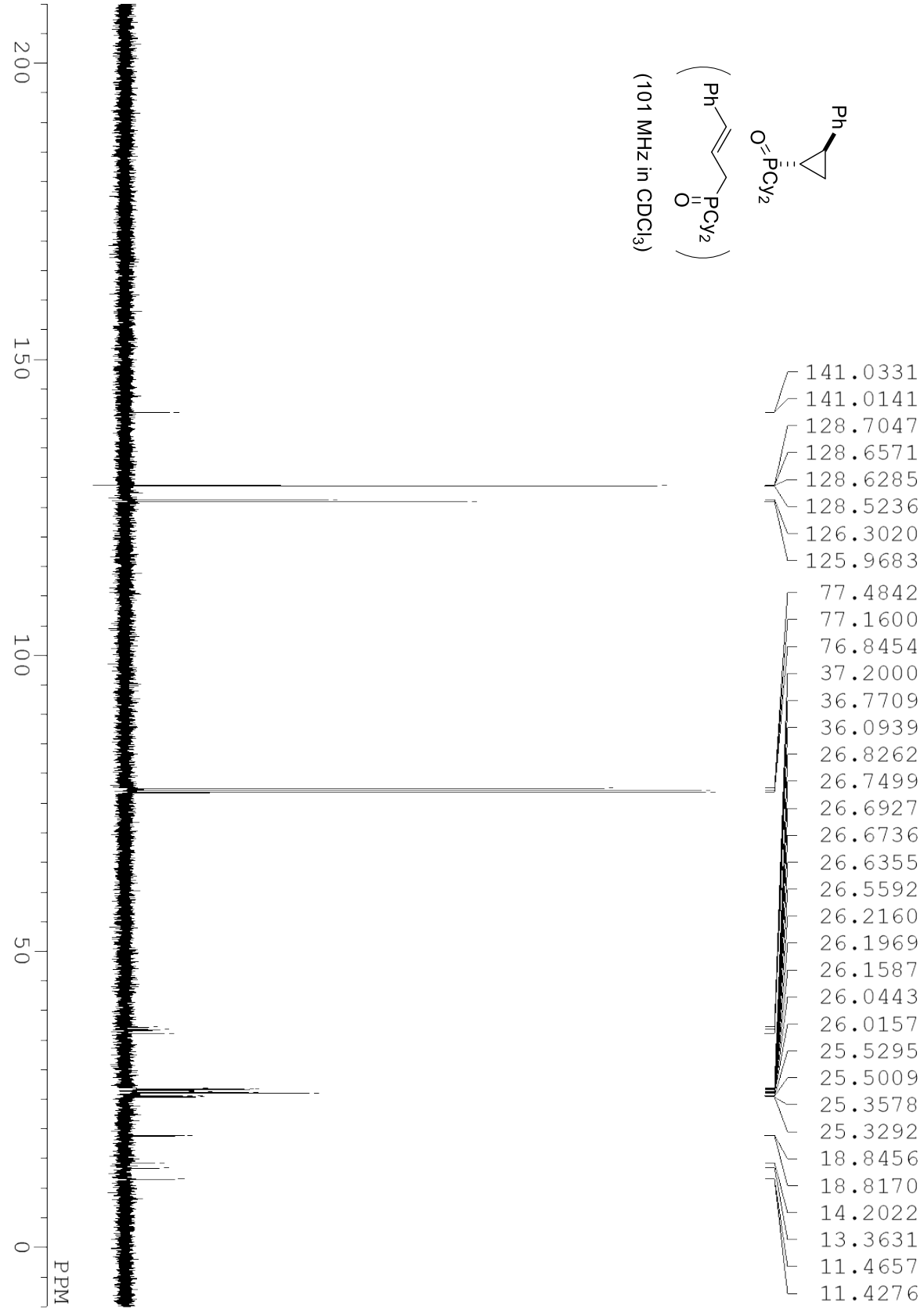
compound **4aa** (**3aa**)



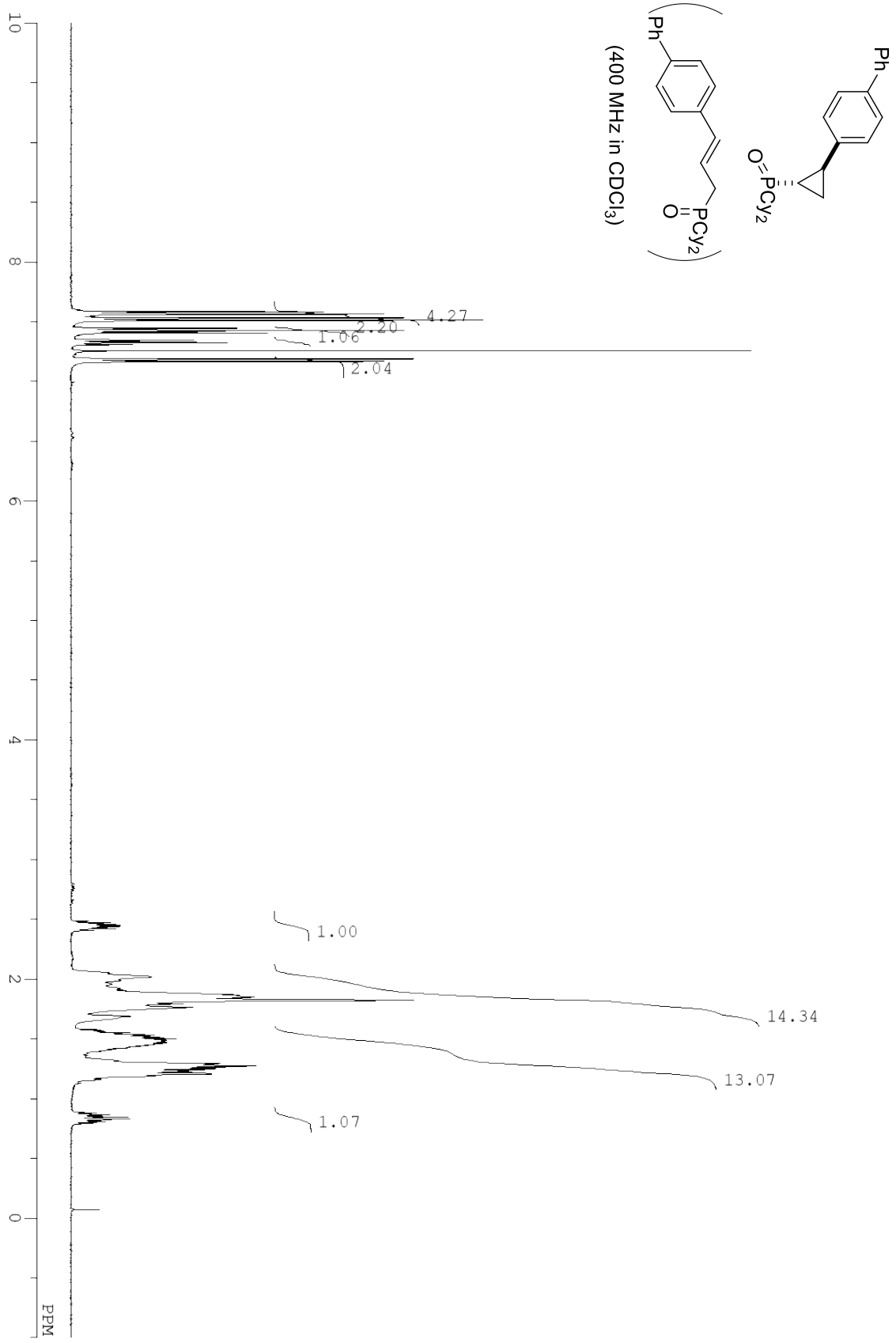
compound **3aa** (**4aa**)



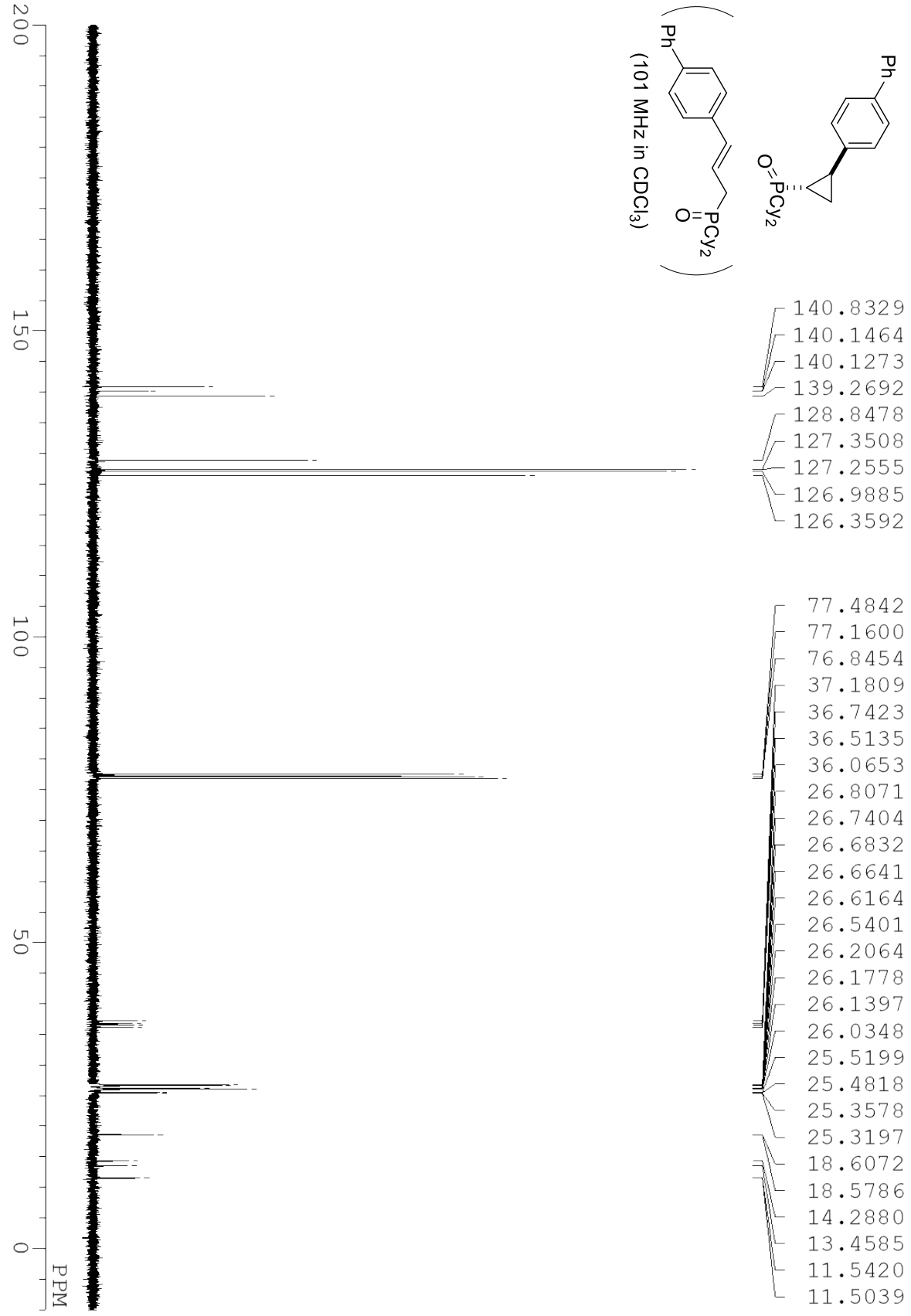
compound **3aa** (**4aa**)



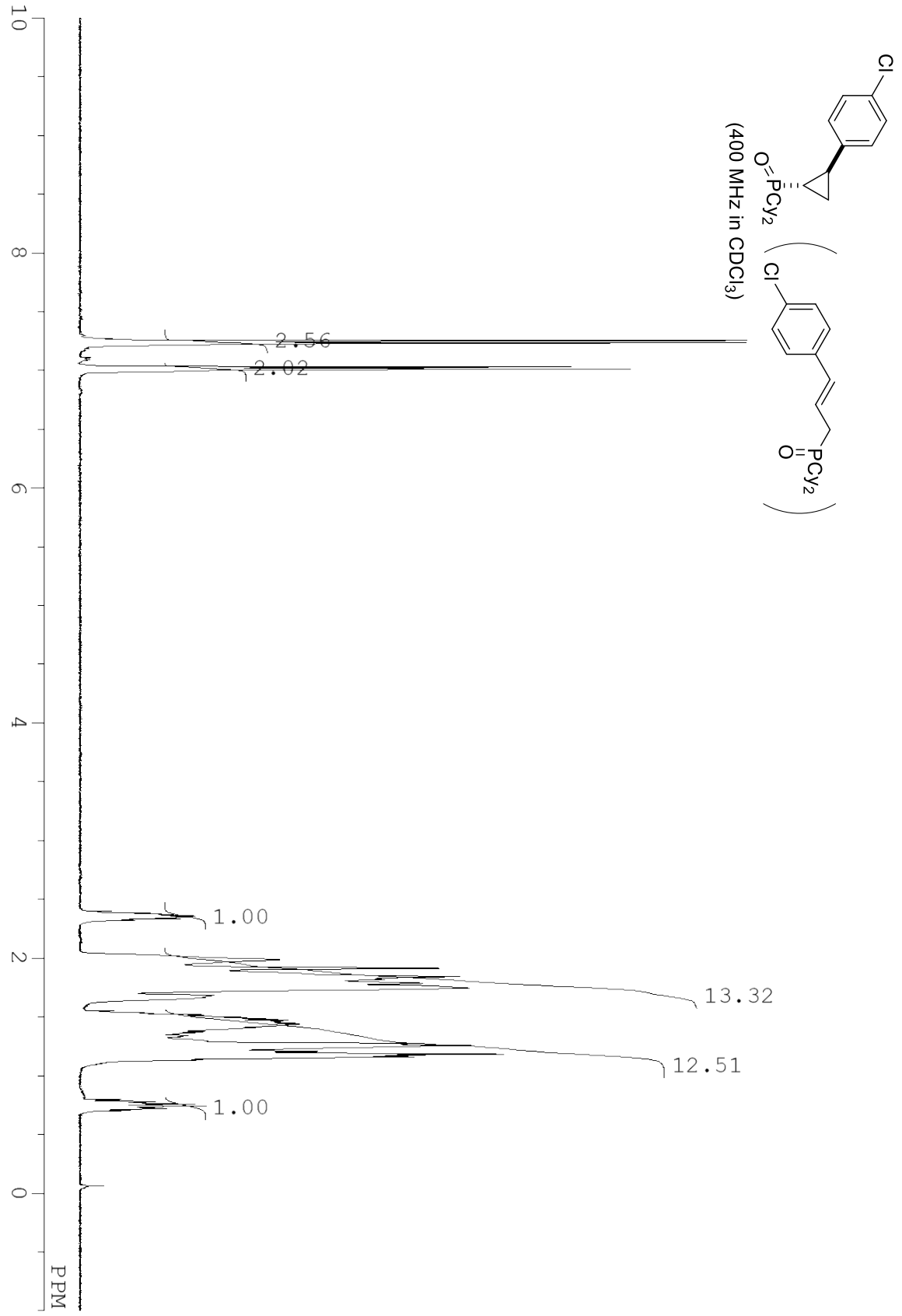
compound **3ba** (**4ba**)



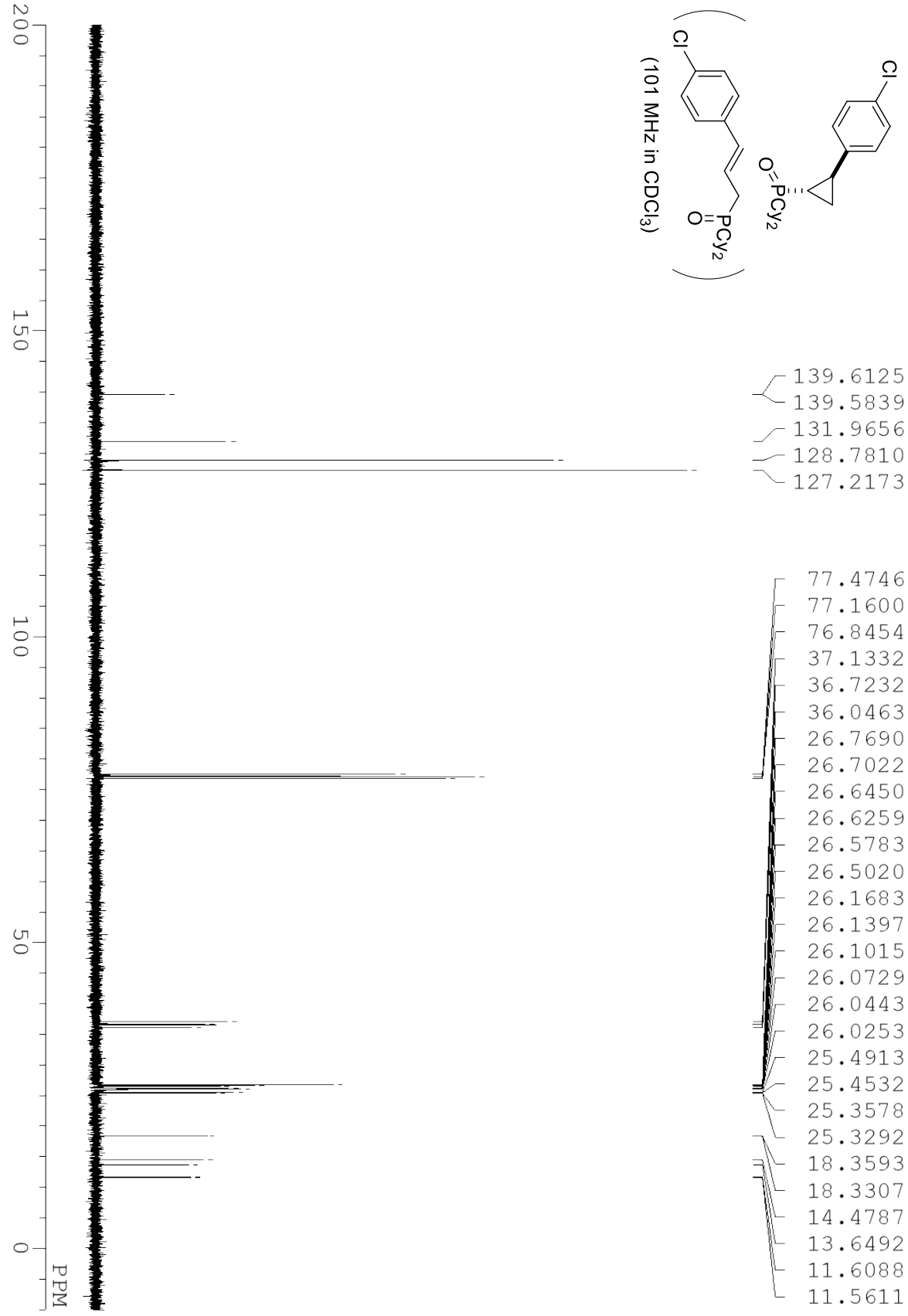
compound **3ba** (**4ba**)



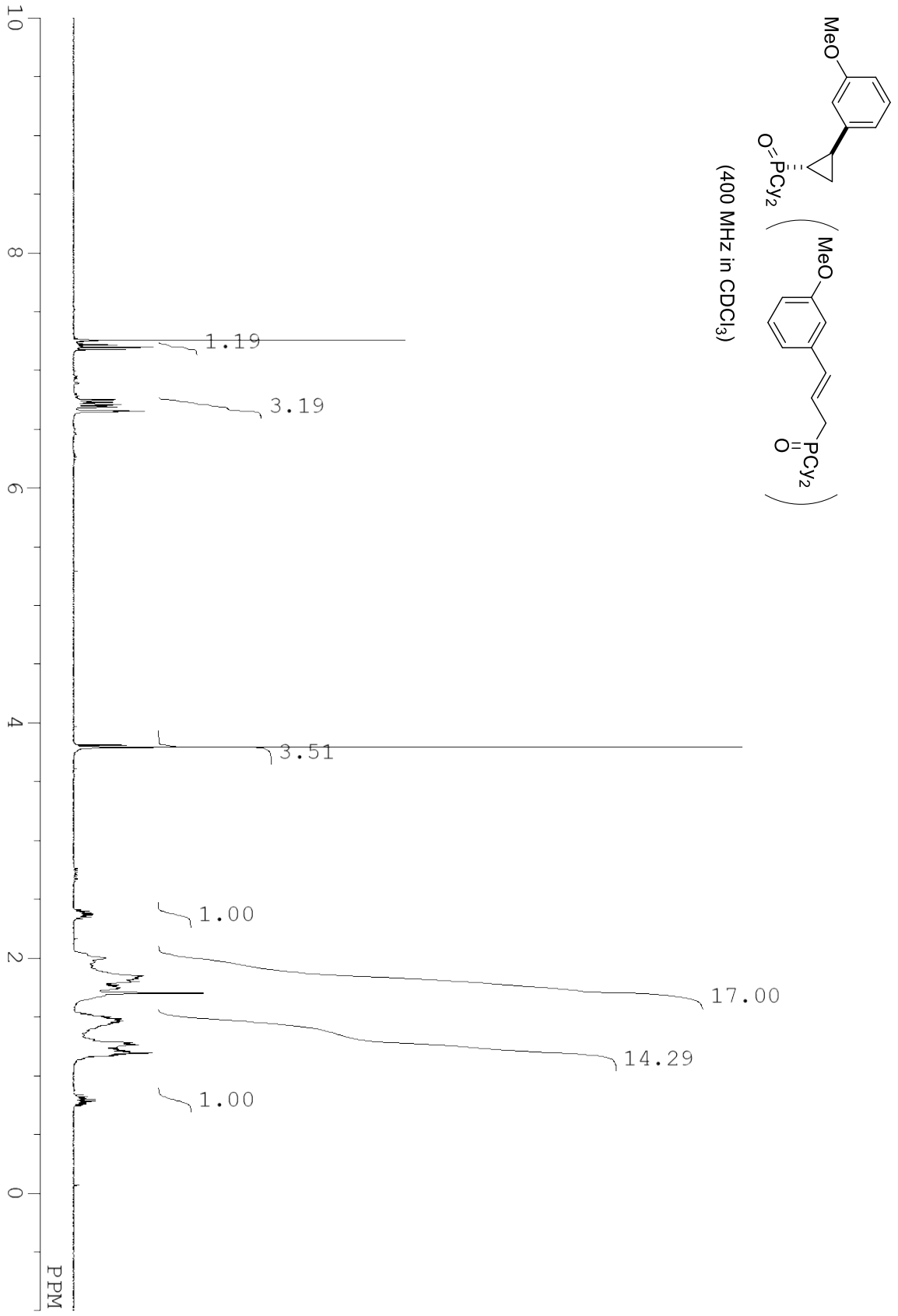
compound **3ca** (**4ca**)



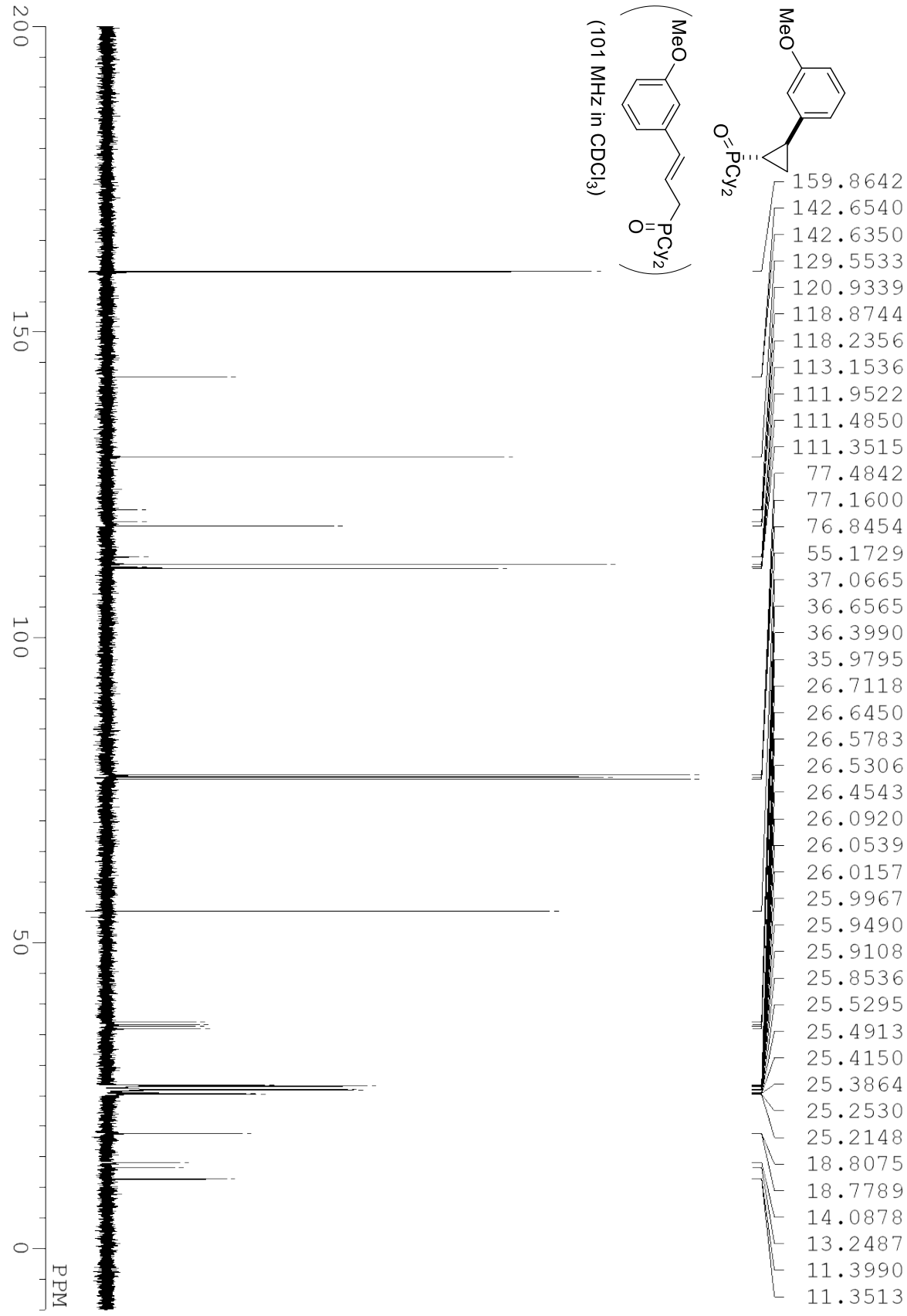
compound **3ca** (**4ca**)



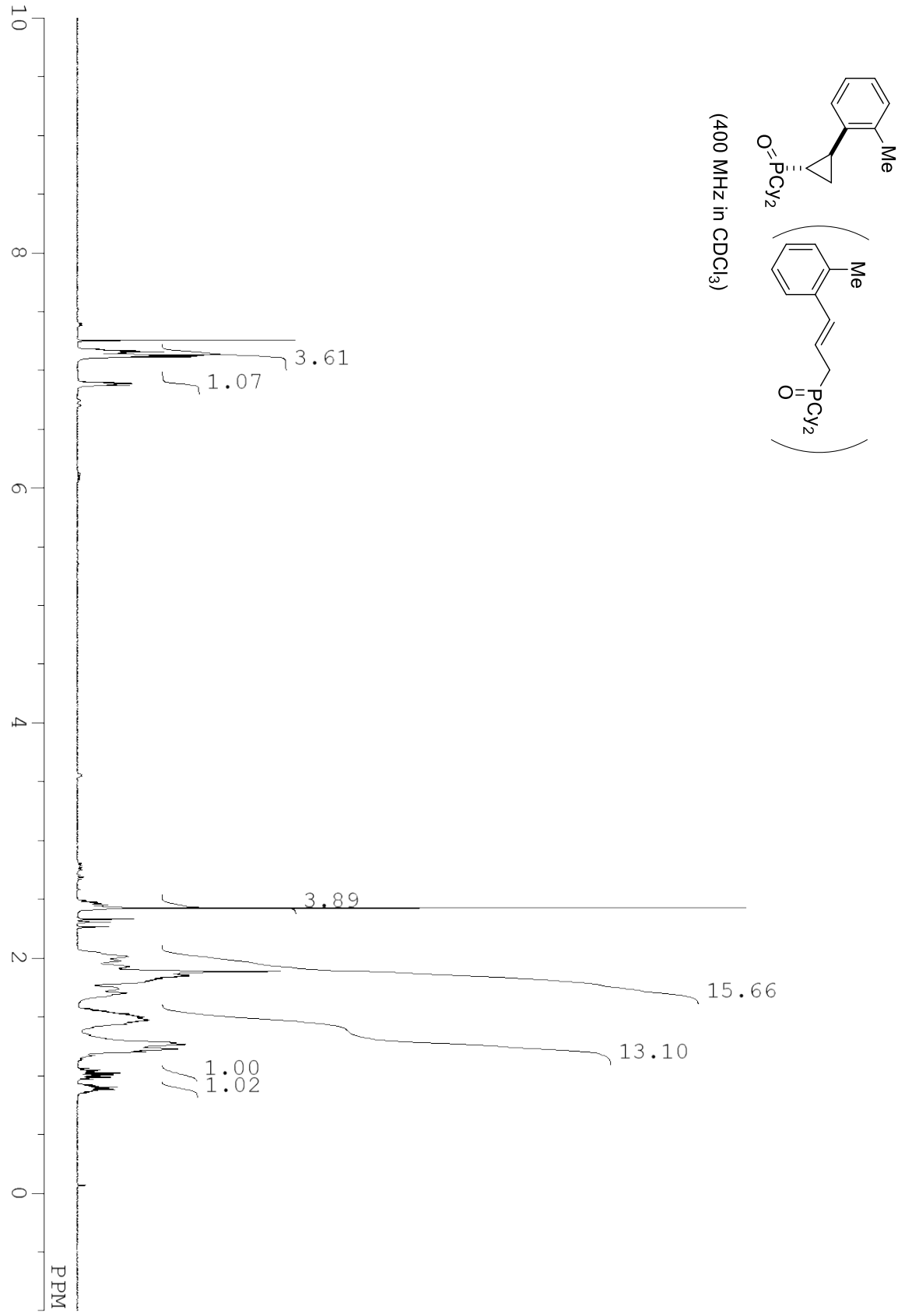
compound **3da** (**4da**)



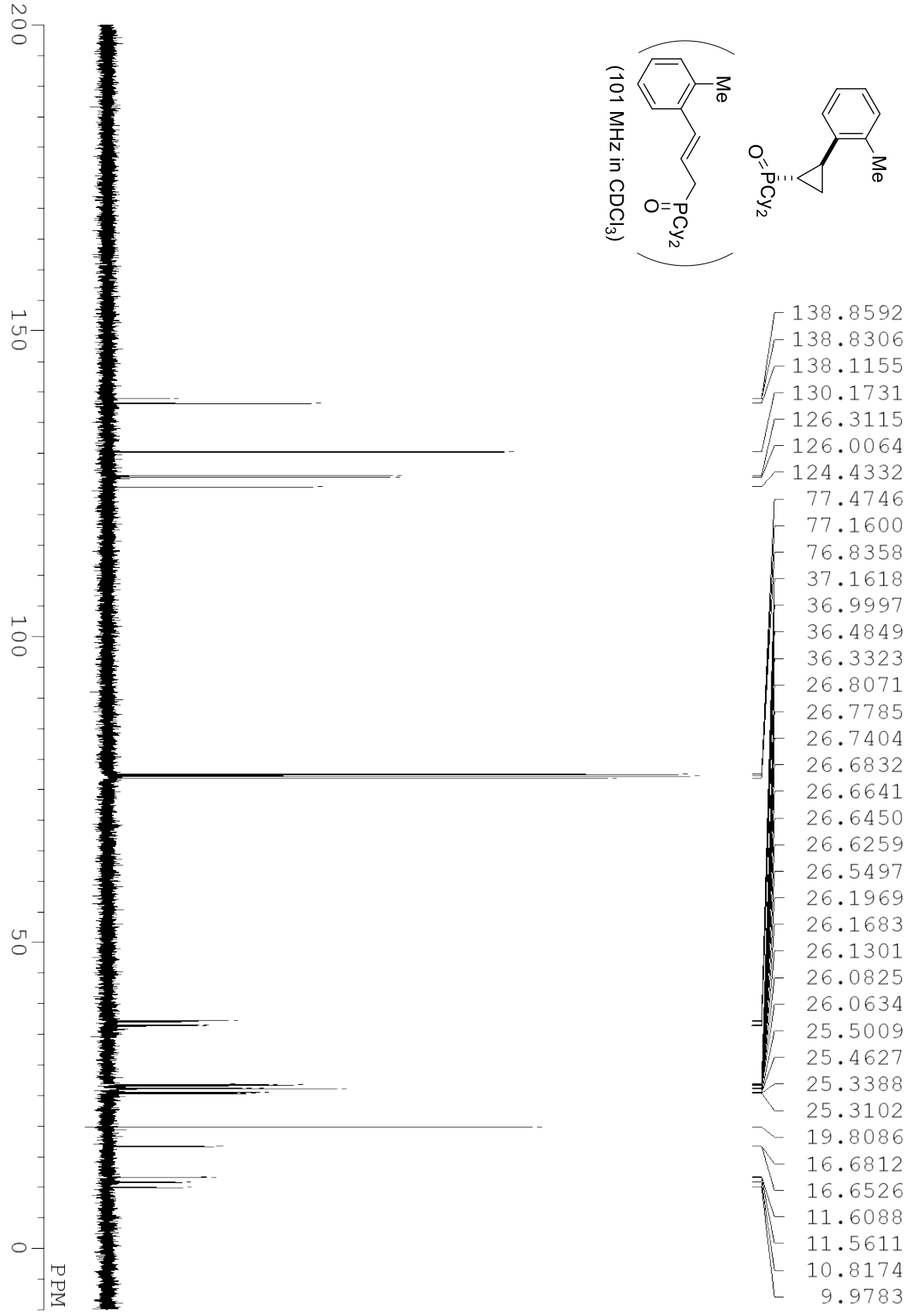
compound **3da** (**4da**)



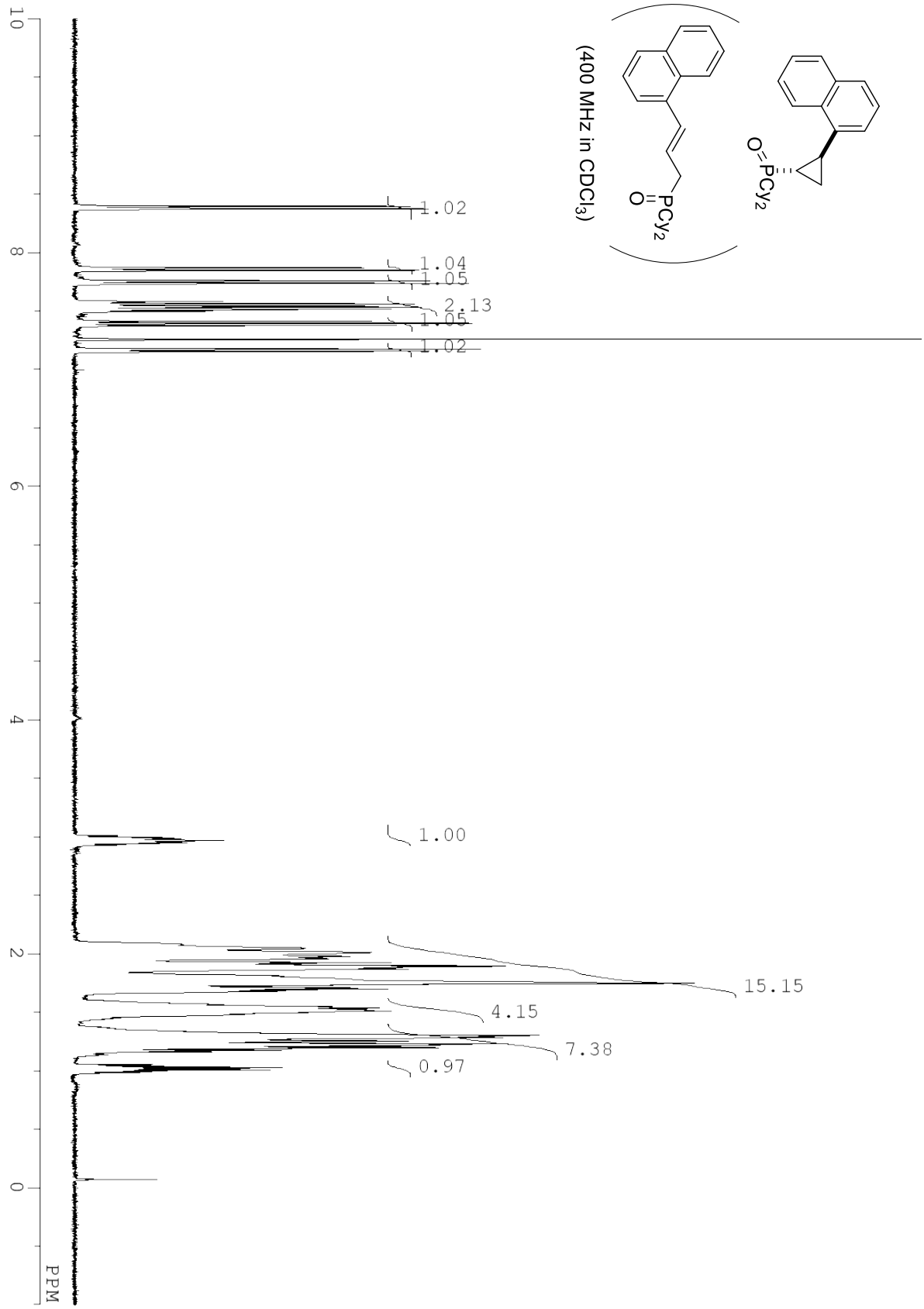
compound **3ea** (**4ea**)



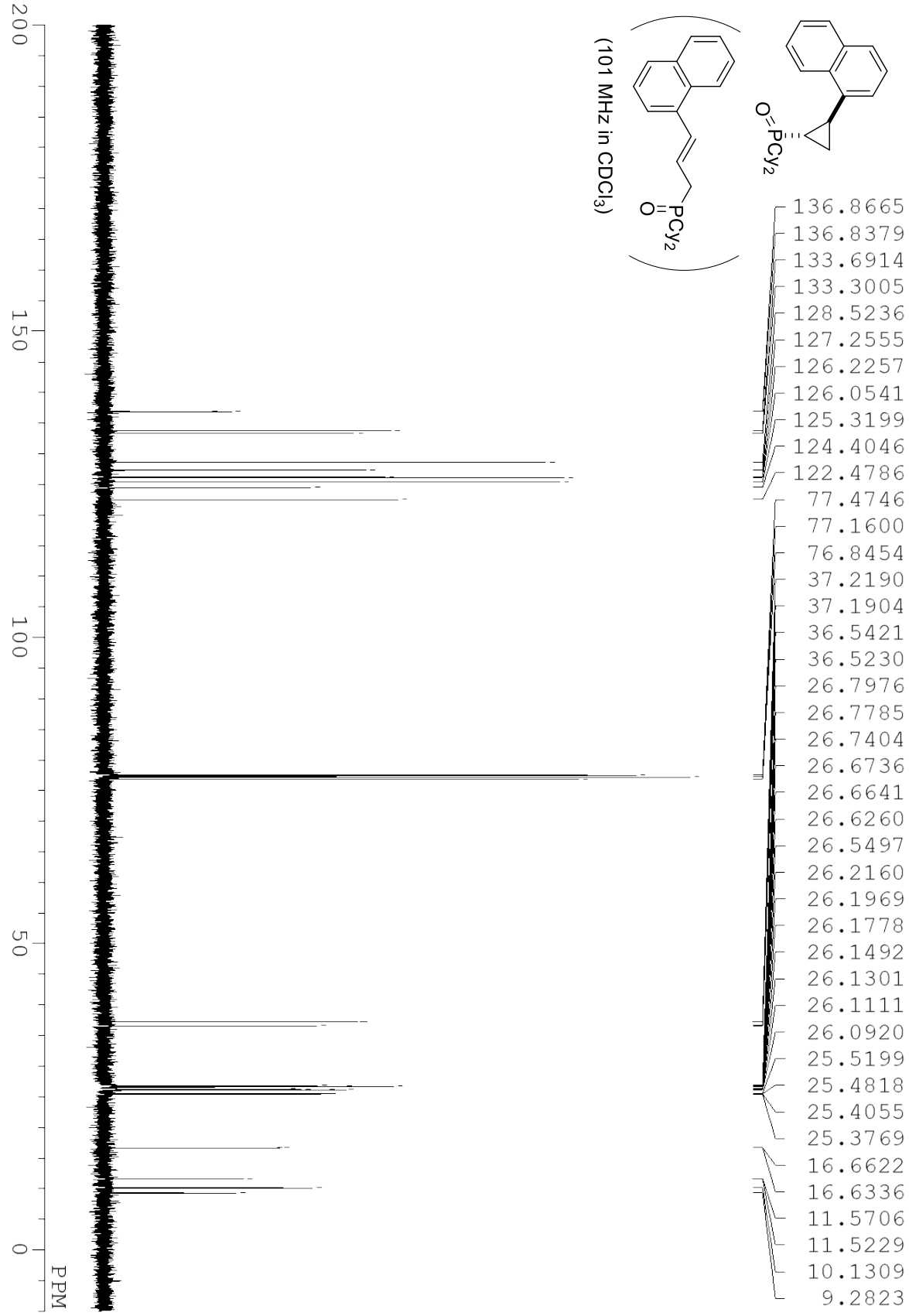
compound **3ea** (**4ea**)



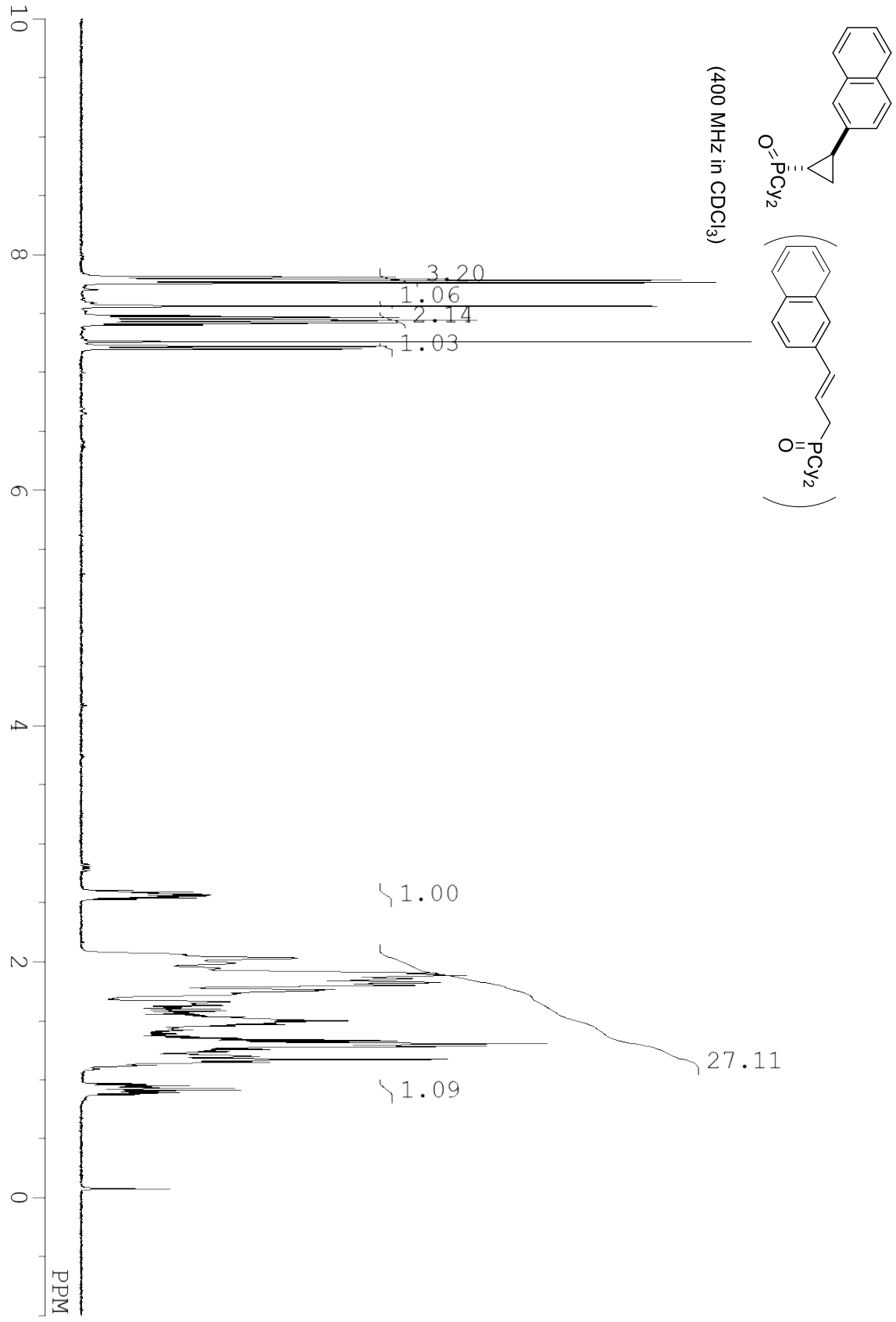
compound **3fa** (**4fa**)



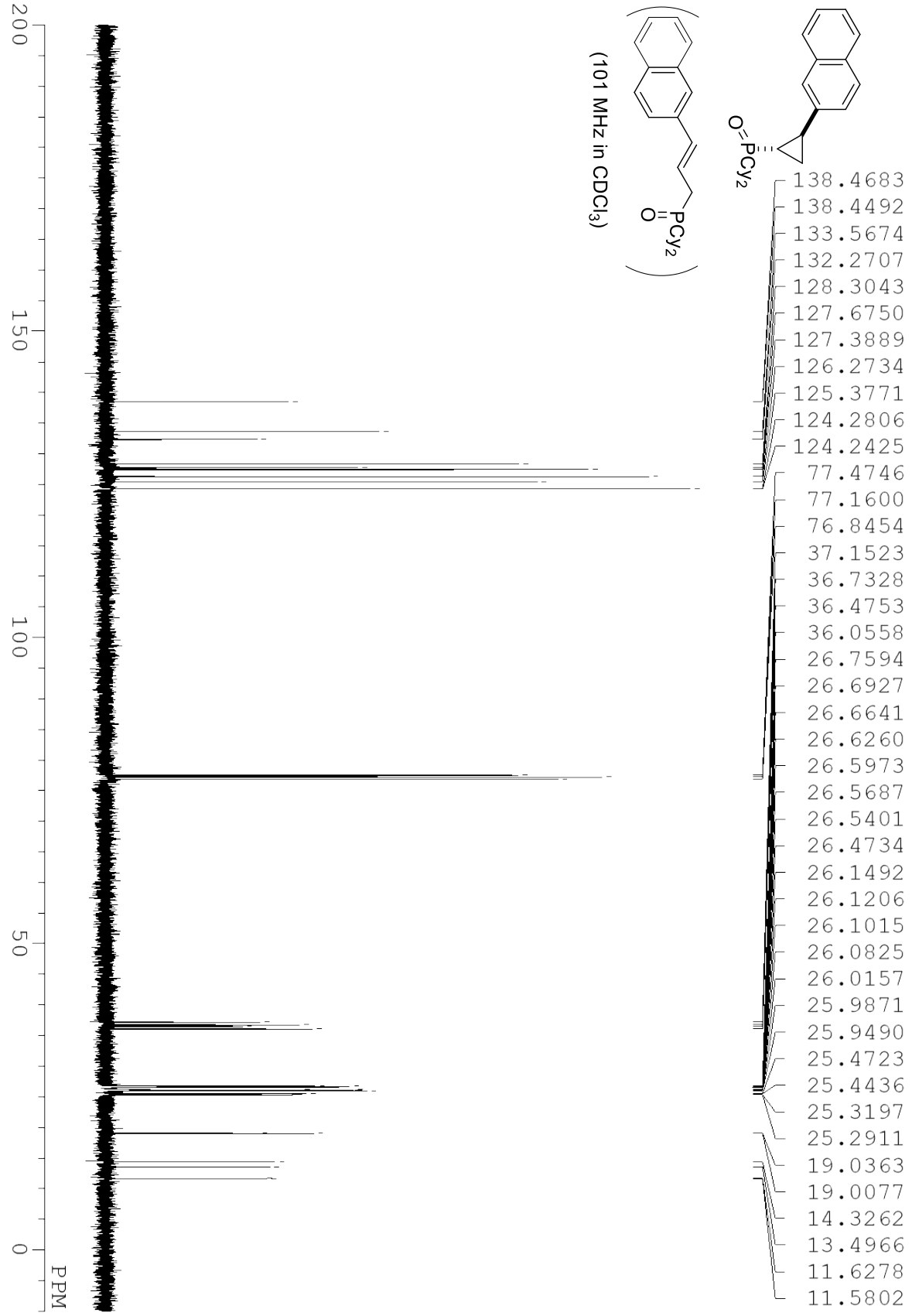
compound **3fa** (**4fa**)



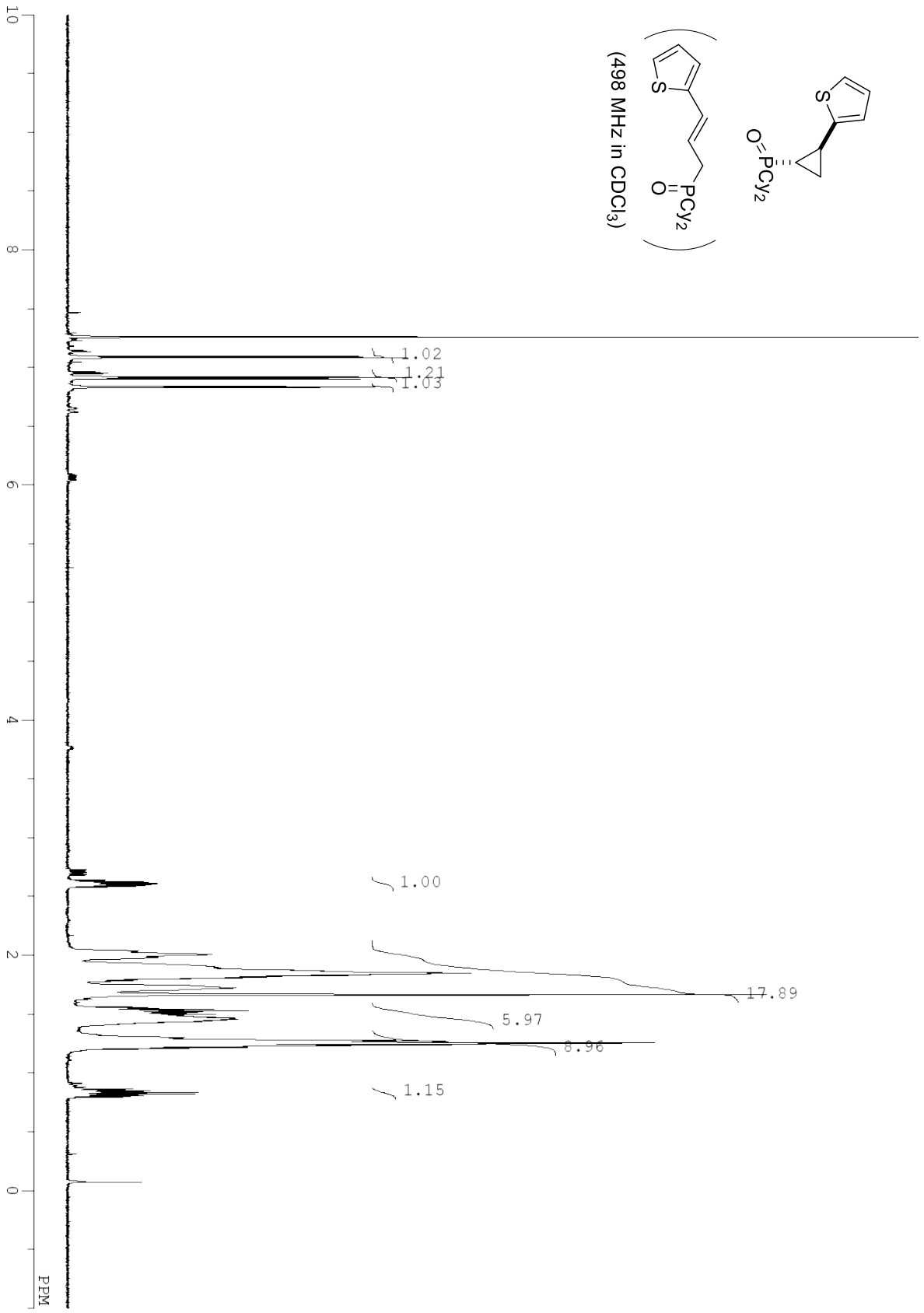
compound **3ga** (**4ga**)



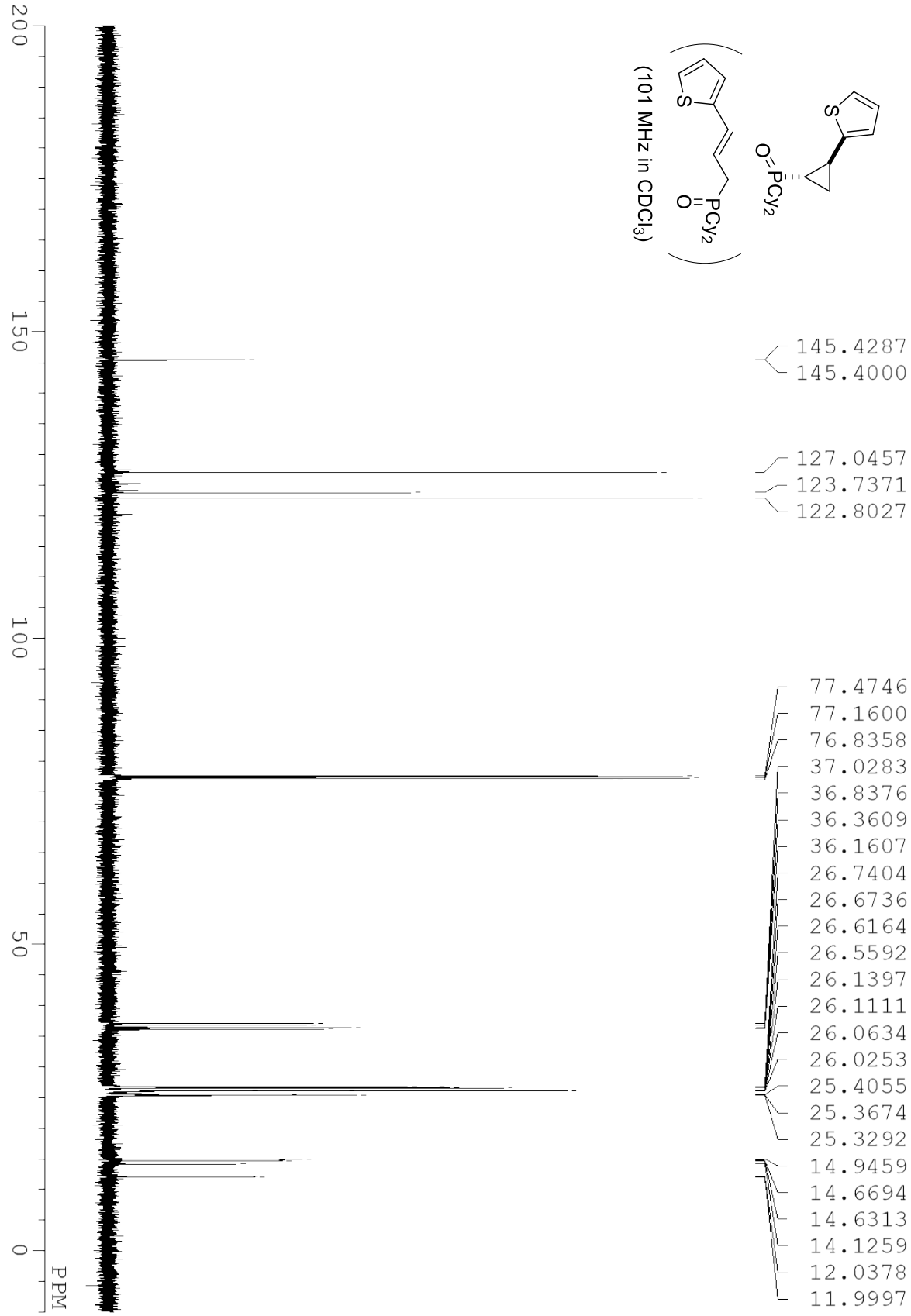
compound **3ga** (**4ga**)



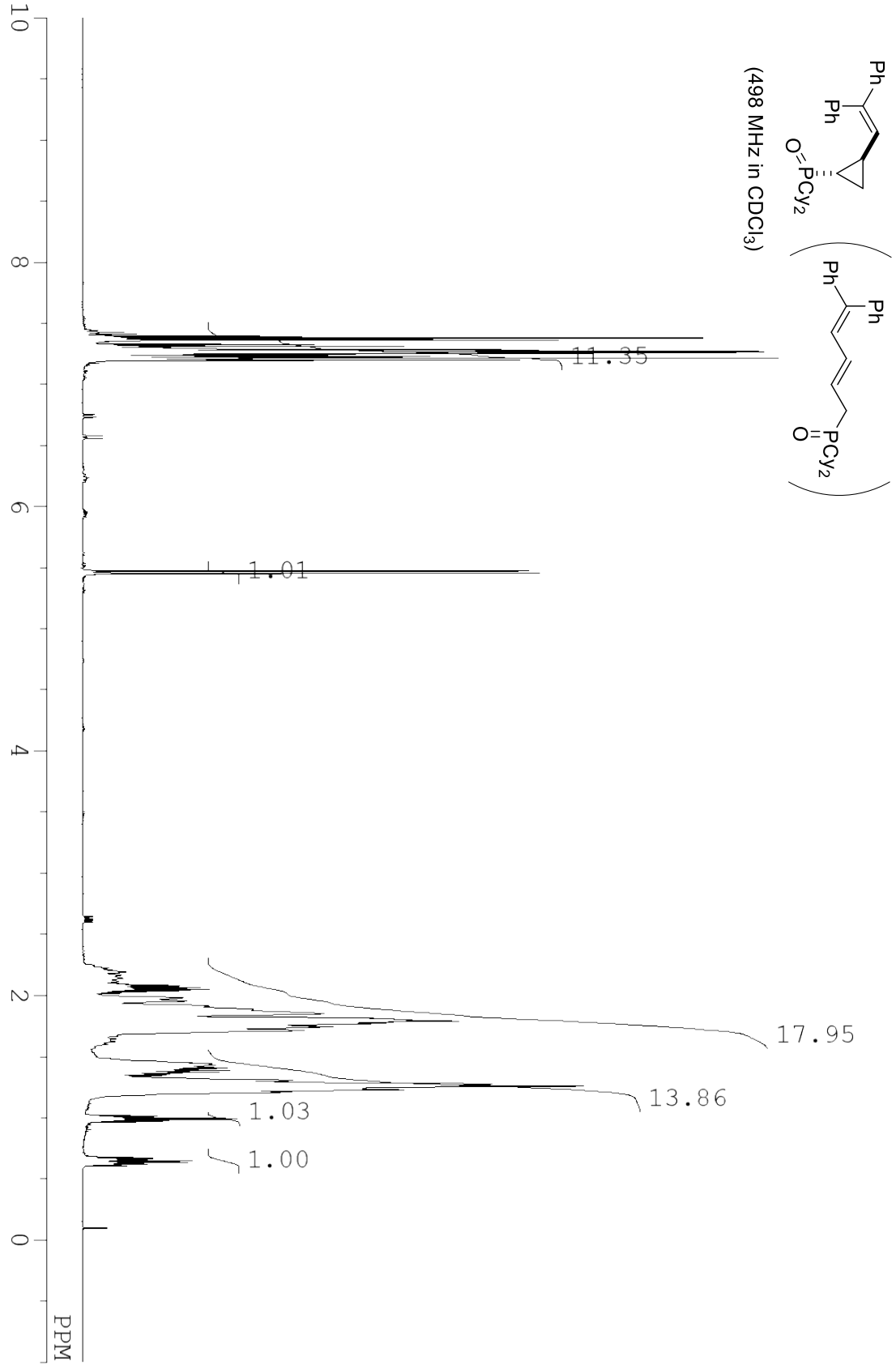
compound **3ha** (**4ha**)



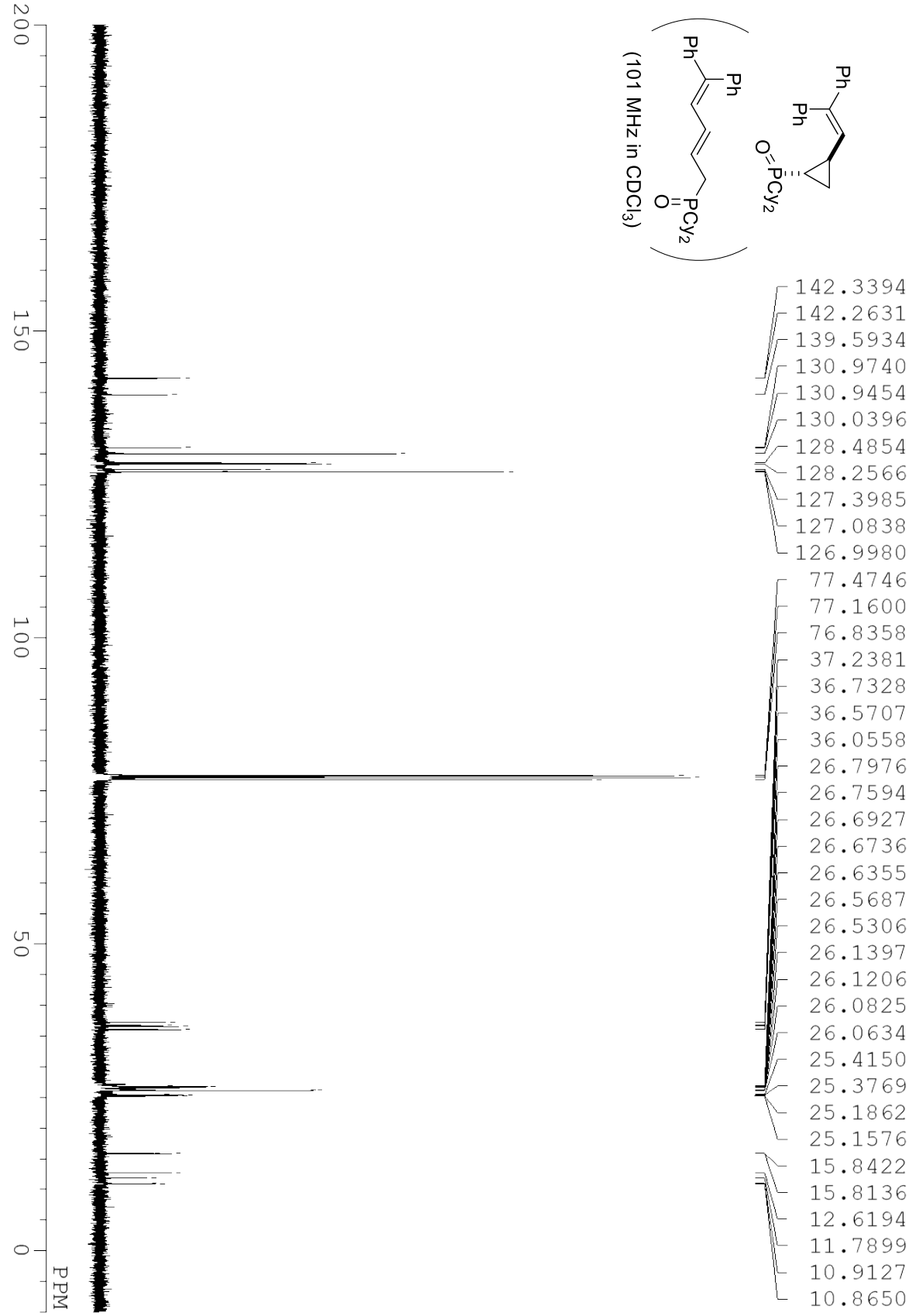
compound **3ha** (**4ha**)



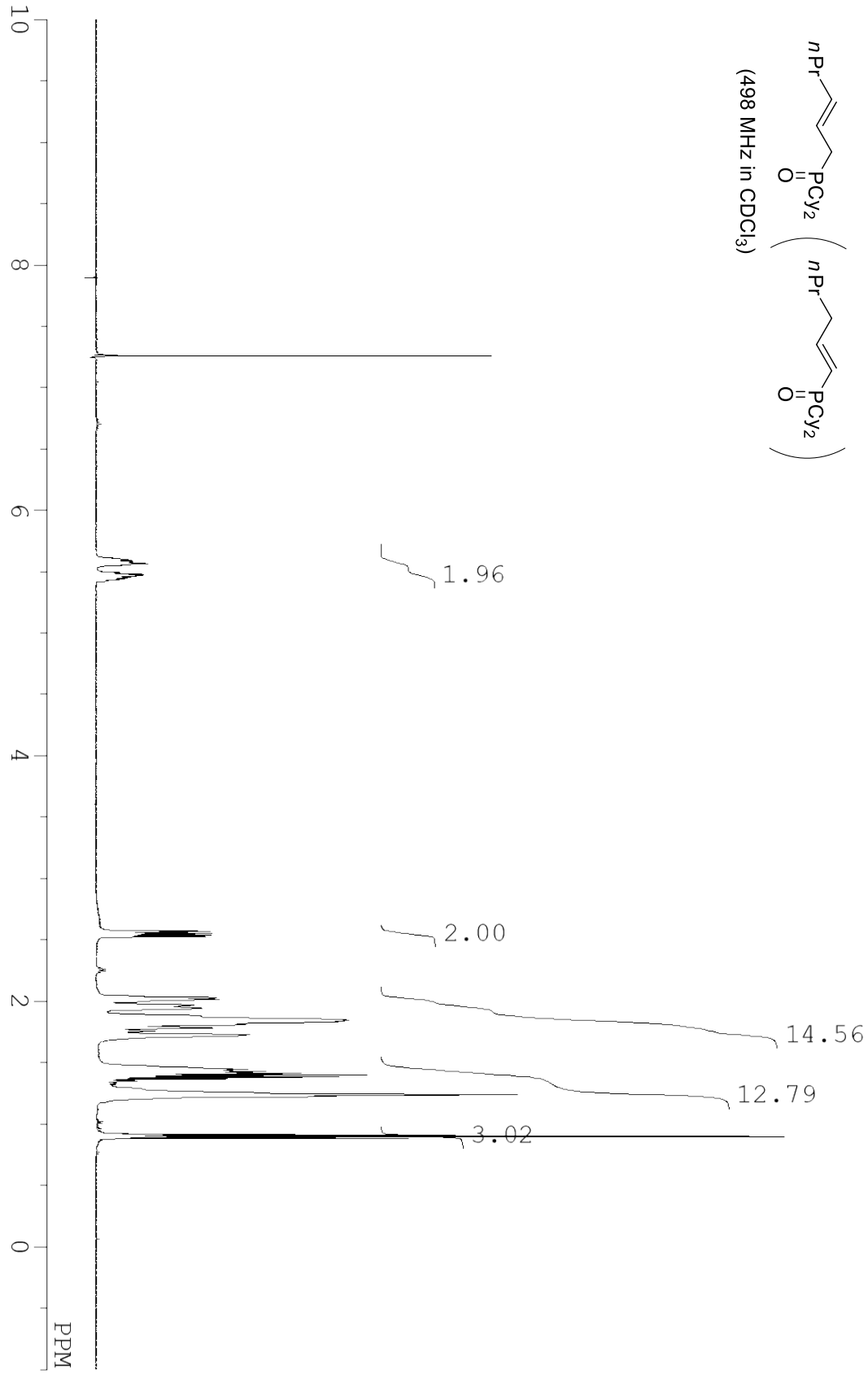
compound **3ia** (**4ia**)



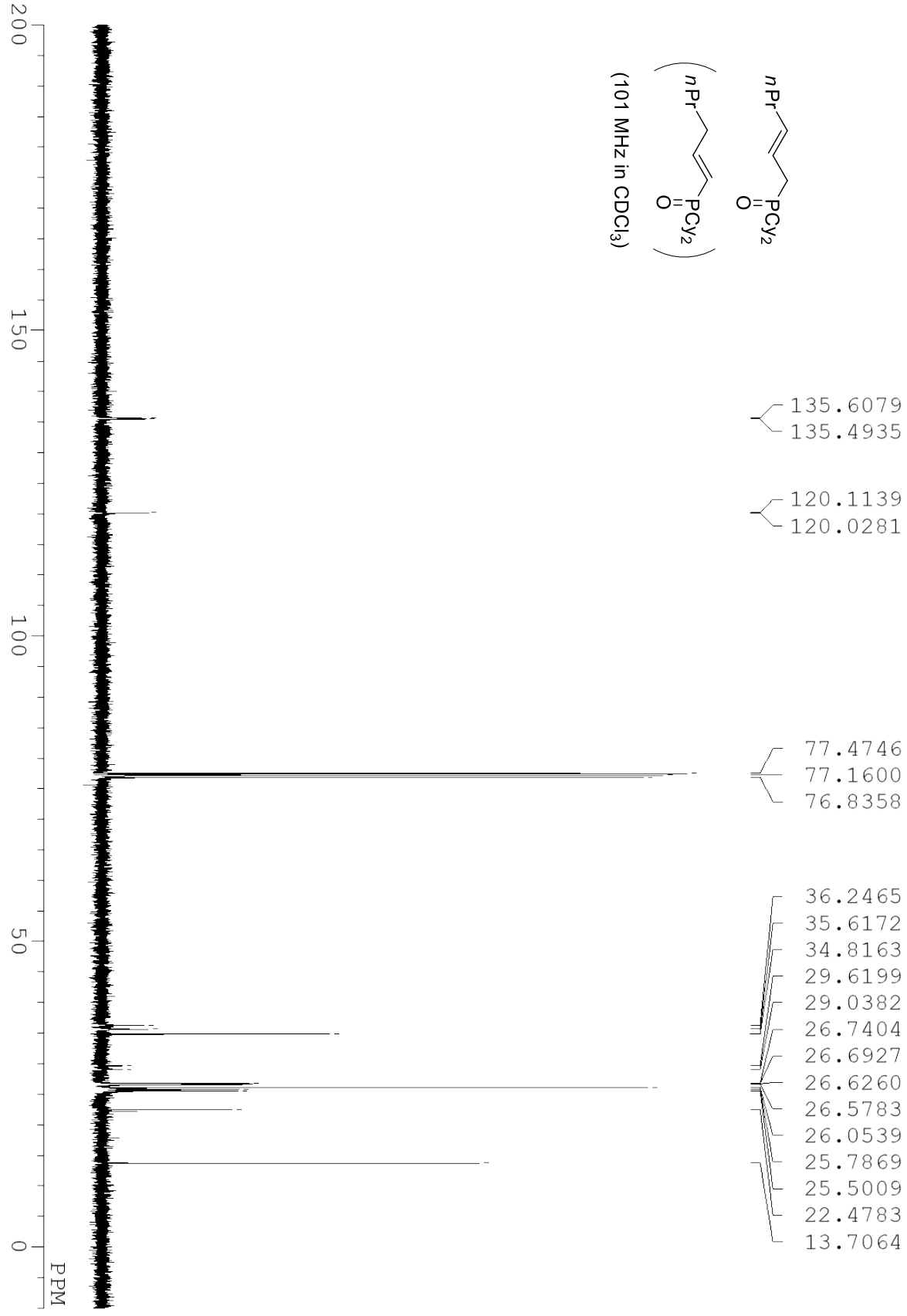
compound **3ia** (**4ia**)



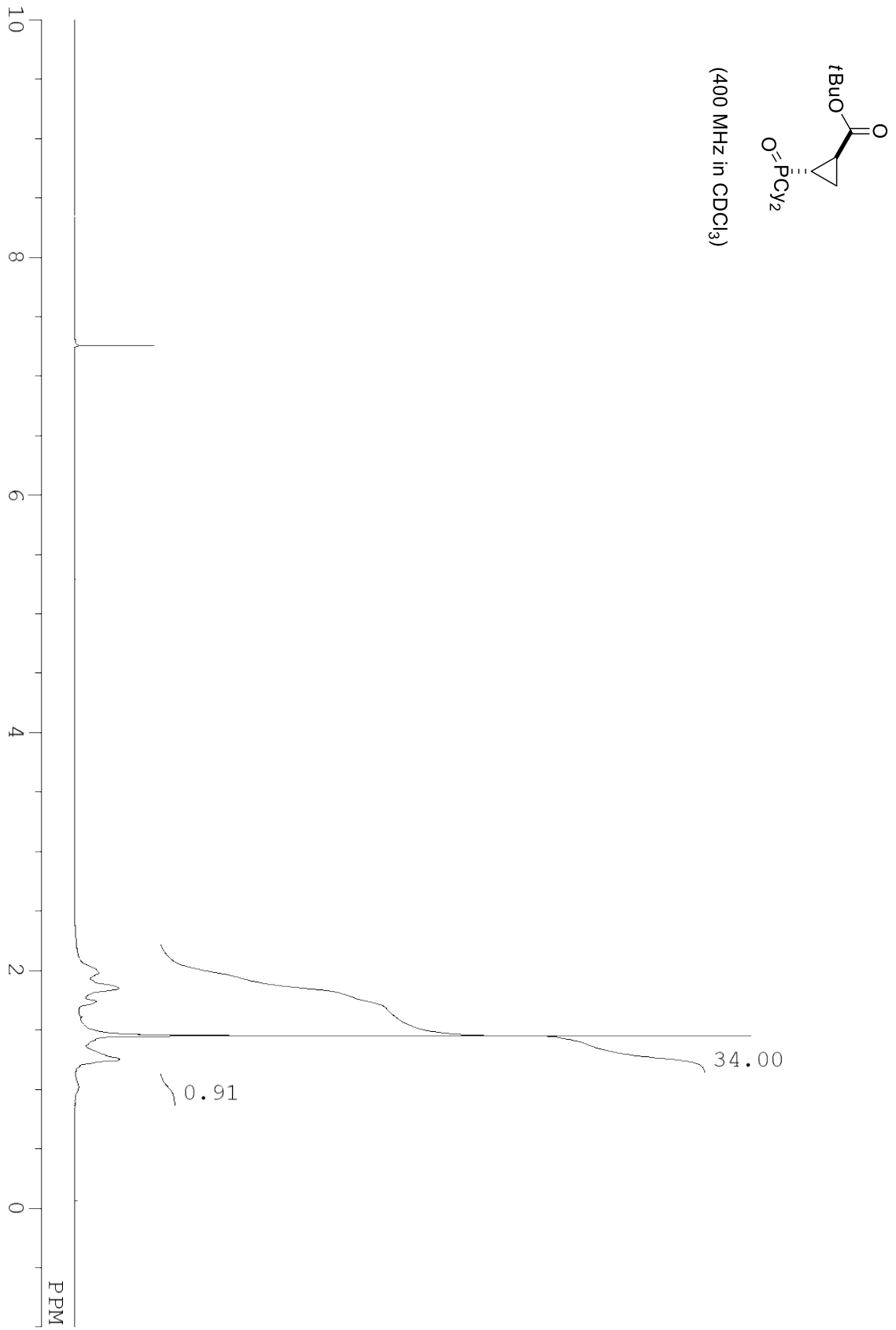
compound **4ja**



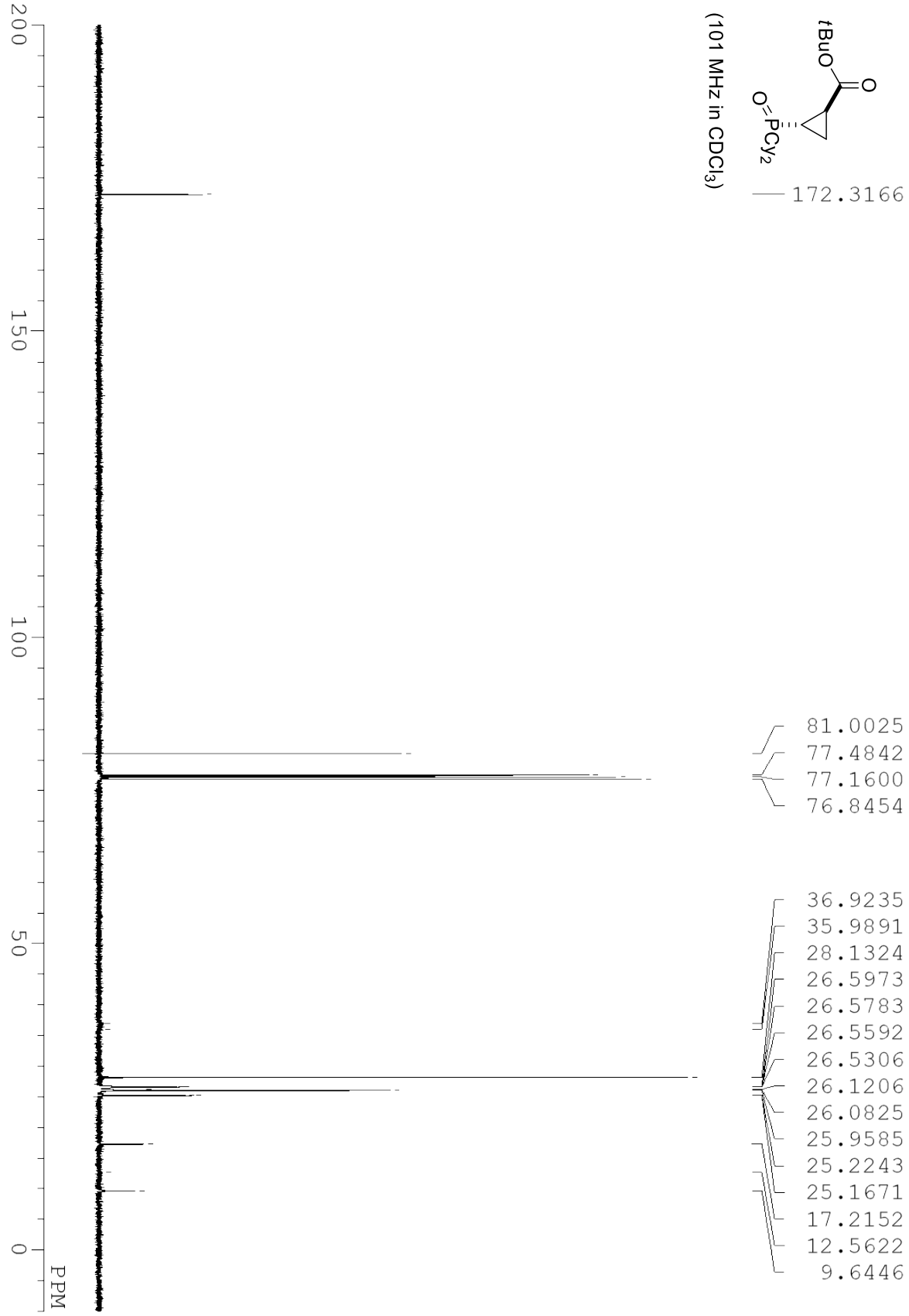
compound **4ja**



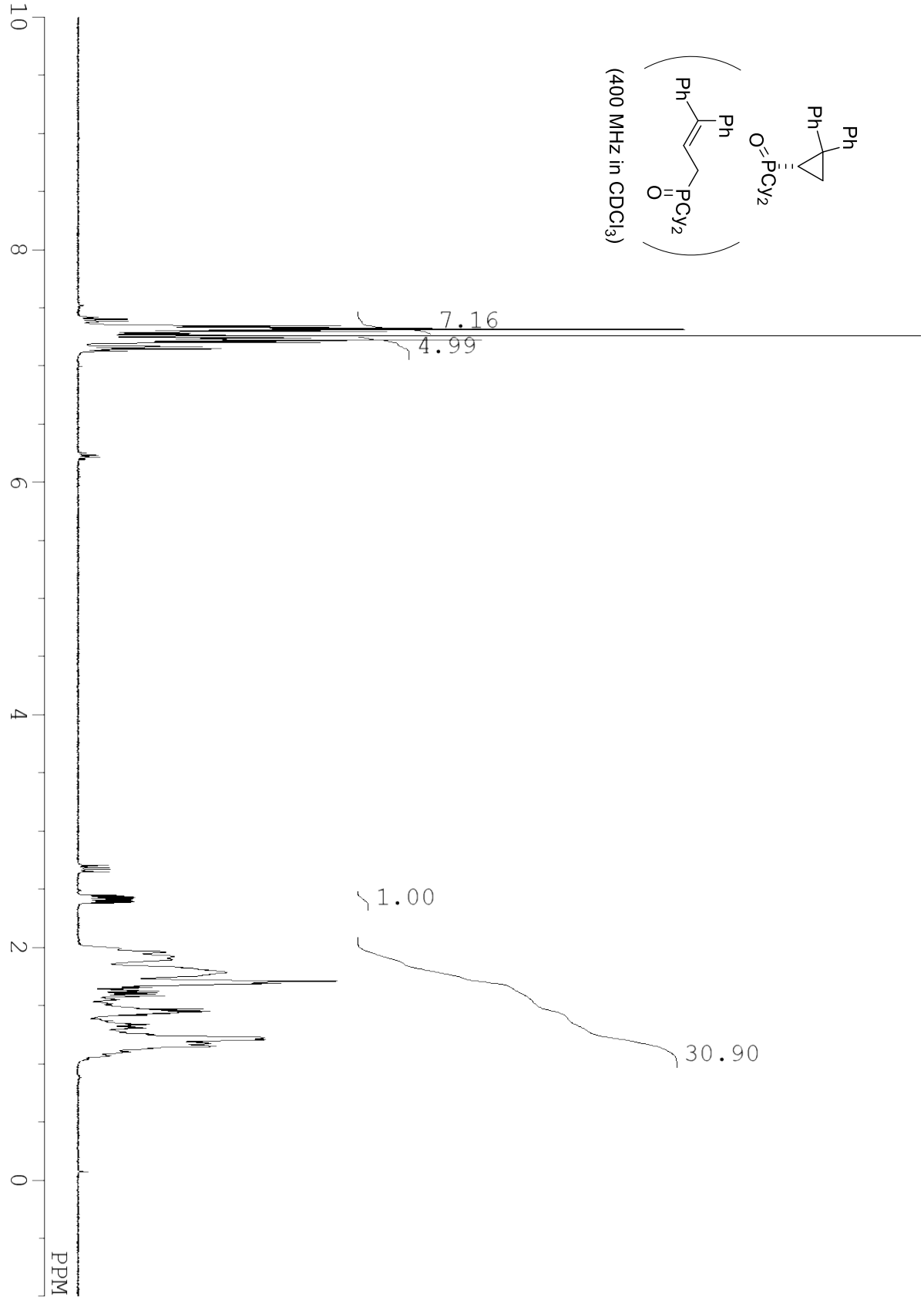
compound **3ka**



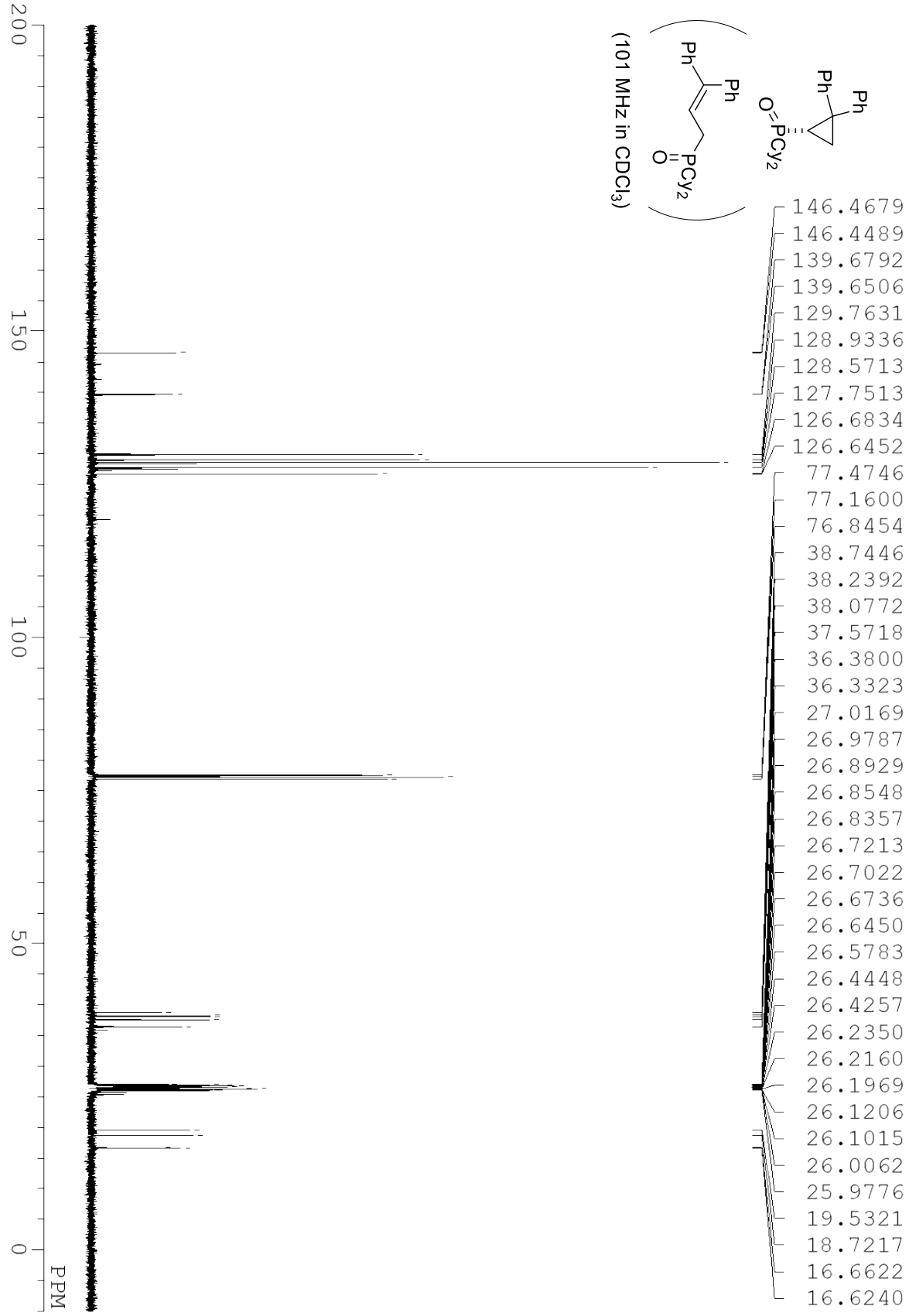
compound **3ka**



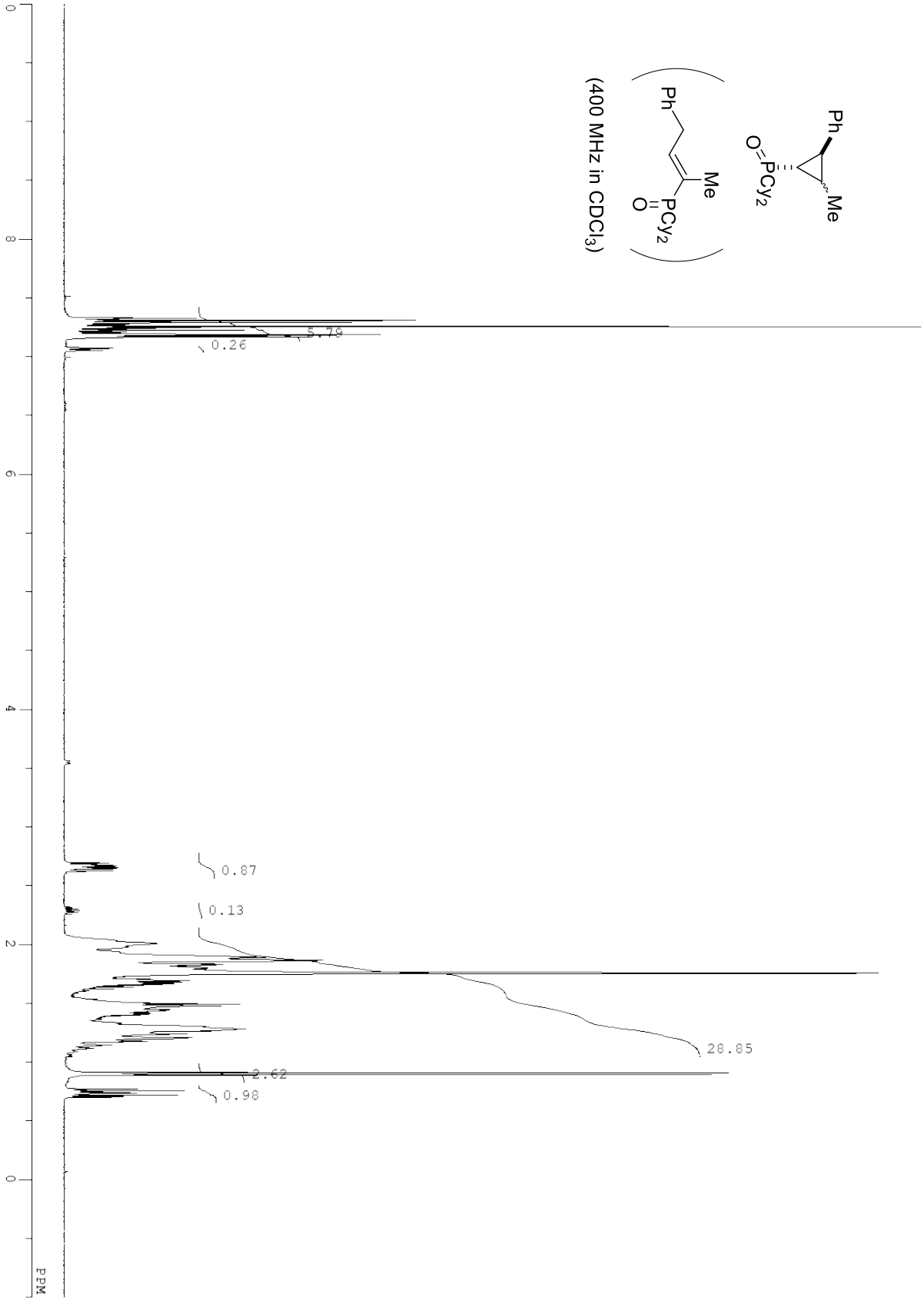
compound **3la** (**4la**)



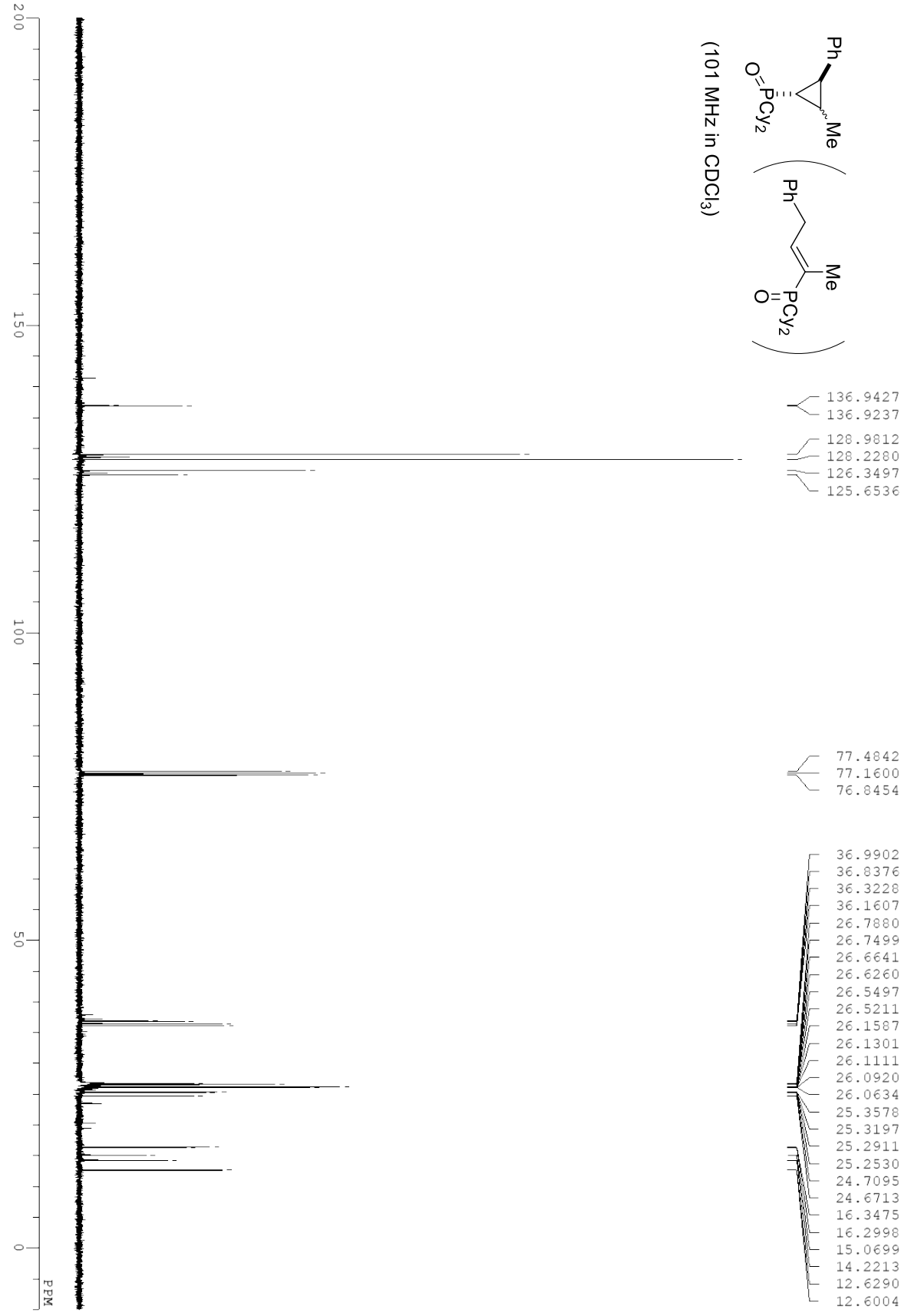
compound **3la** (**4la**)



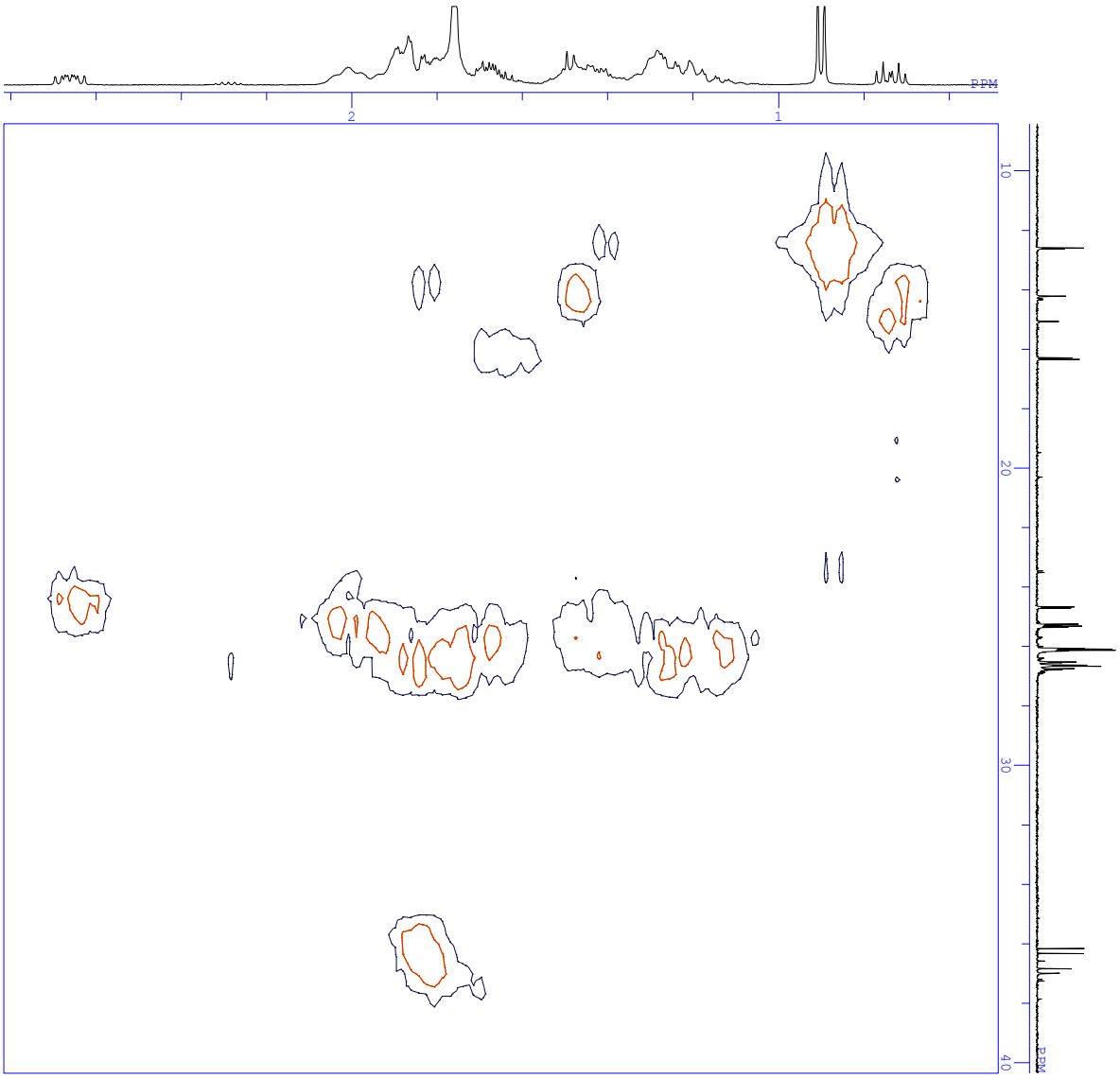
compound **3ma** (**4ma'**)



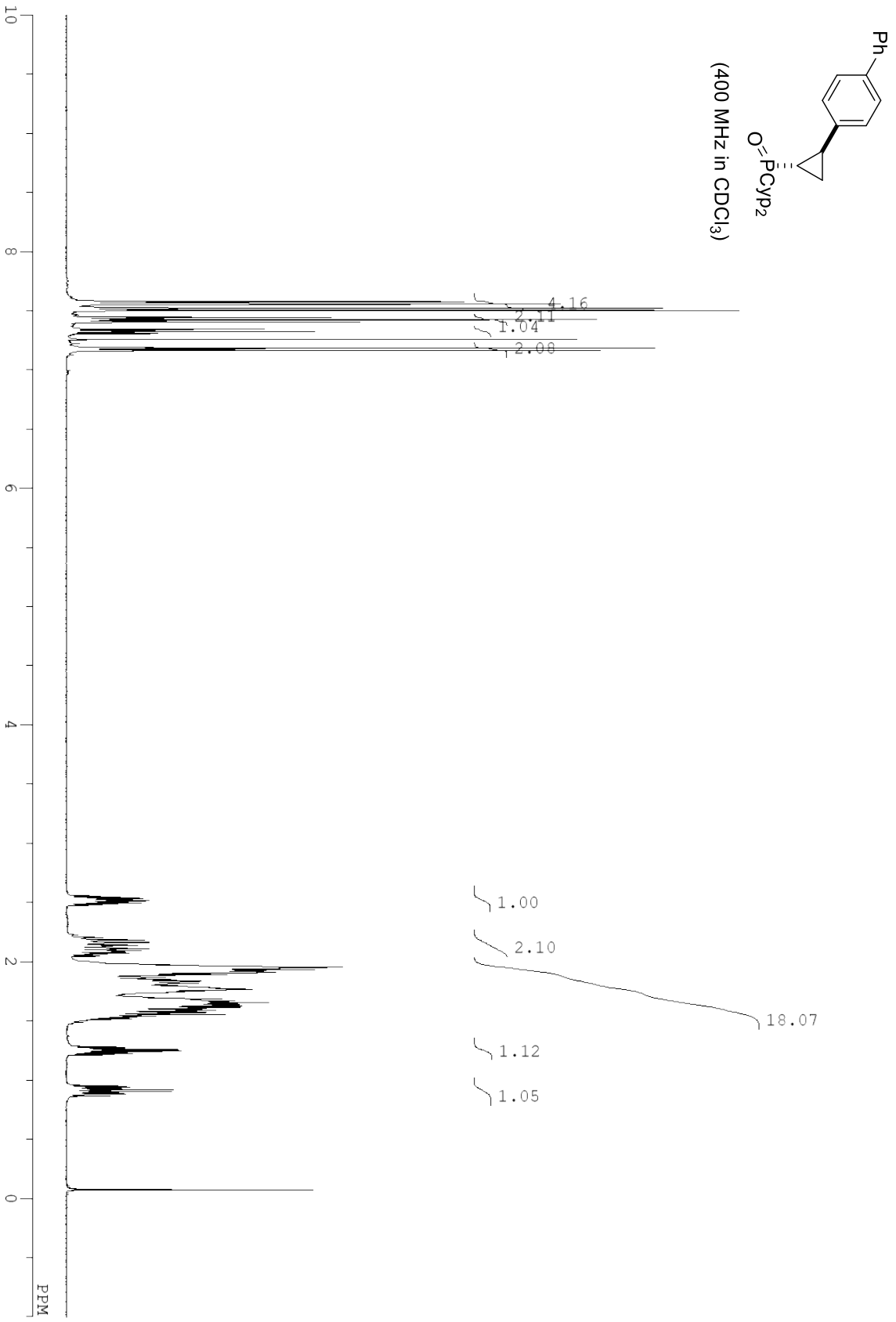
compound **3ma** (**4ma'**)



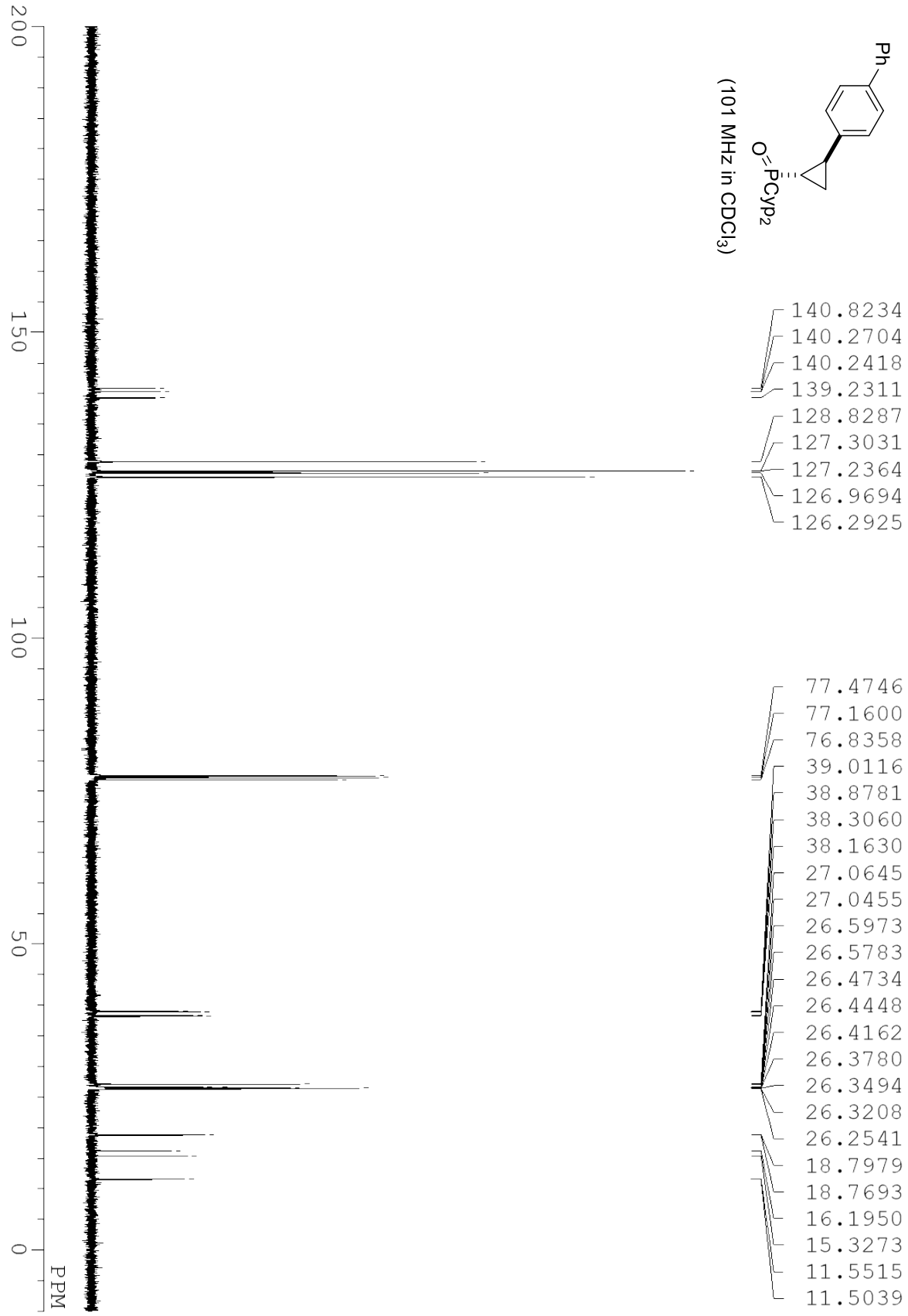
compound **3ma** (**4ma'**) HMQC spectrum (alkyl region)



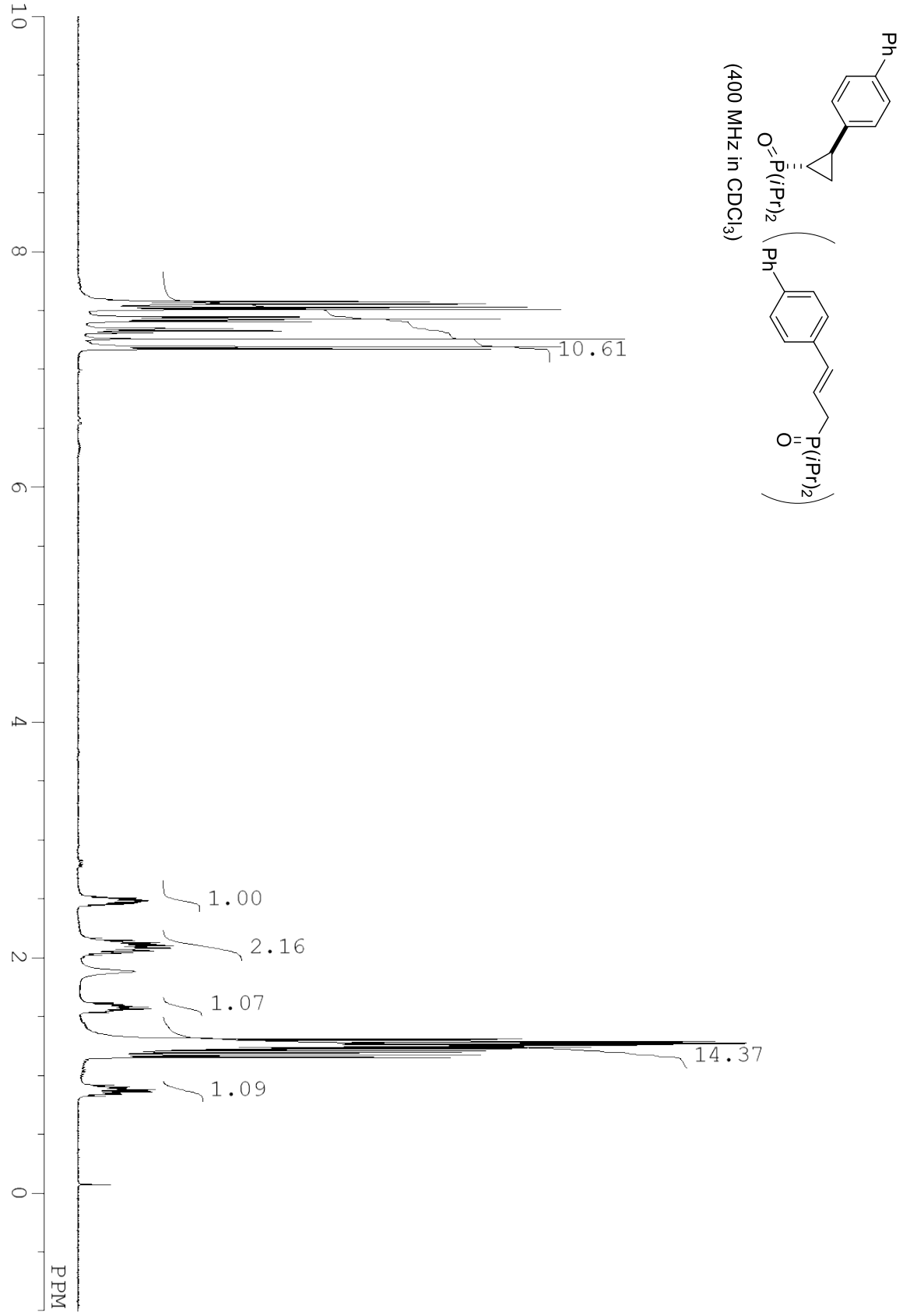
compound **3bb**



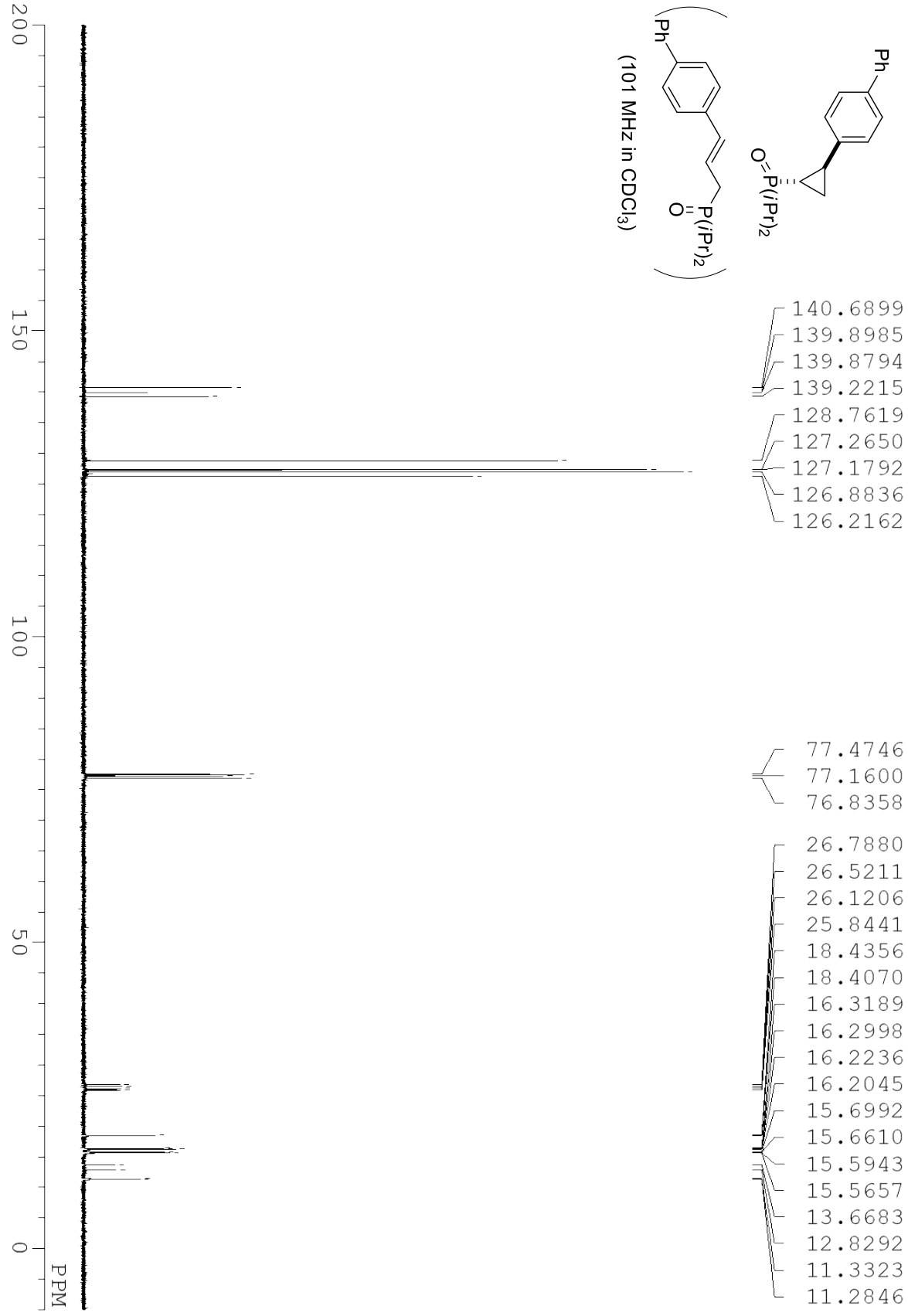
compound **3bb**



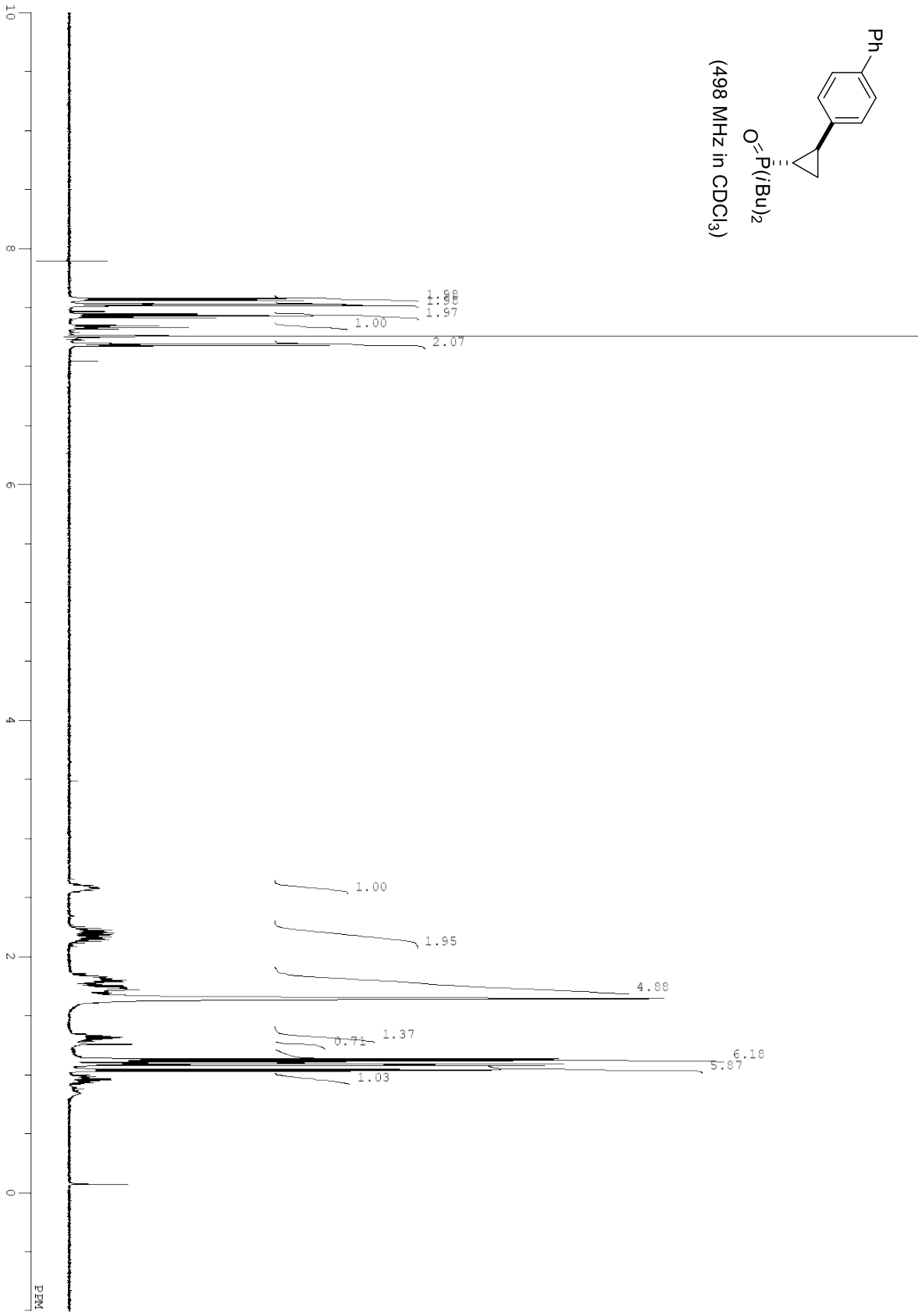
compound **3bc** (**4bc**)



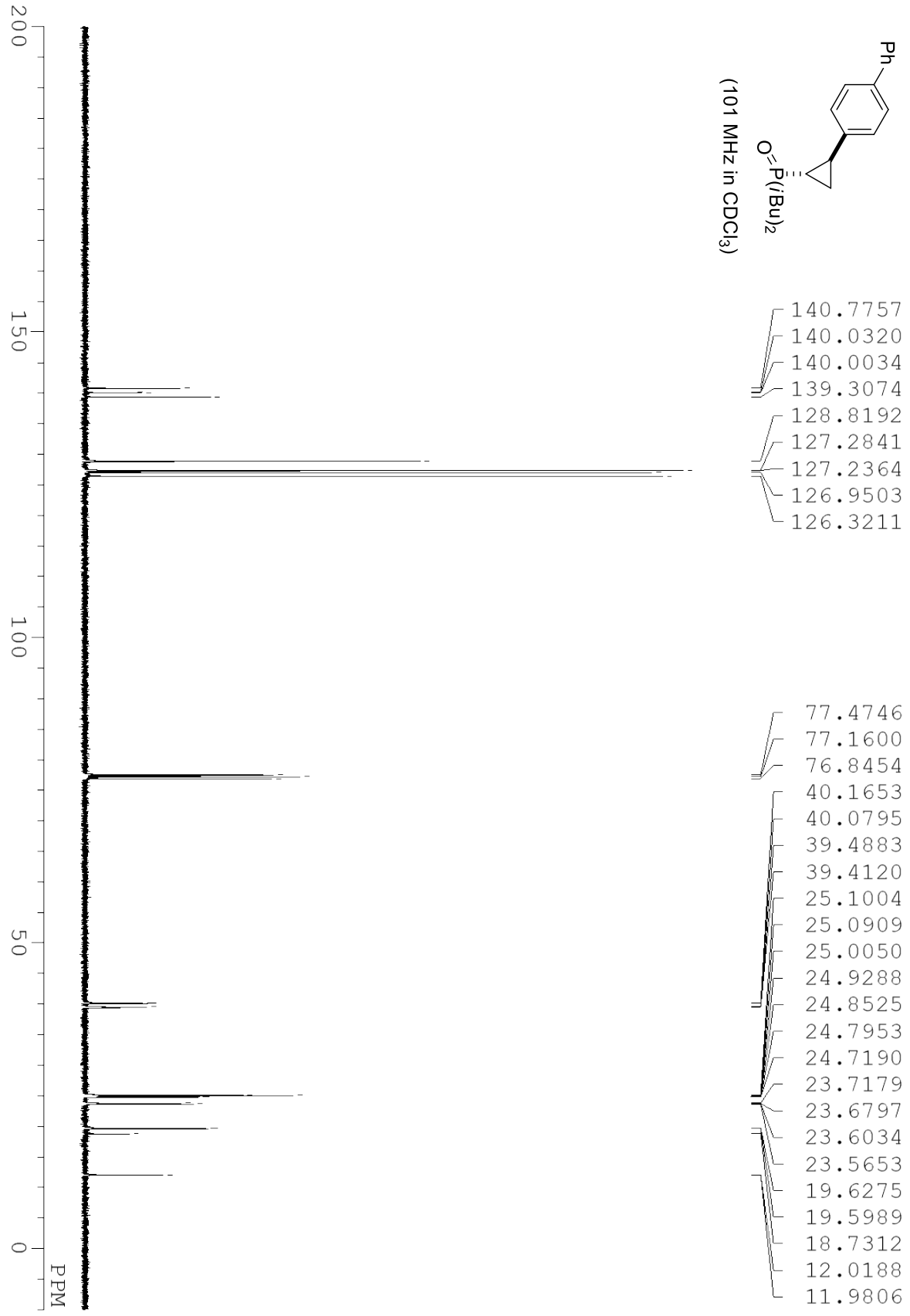
compound **3bc** (**4bc**)



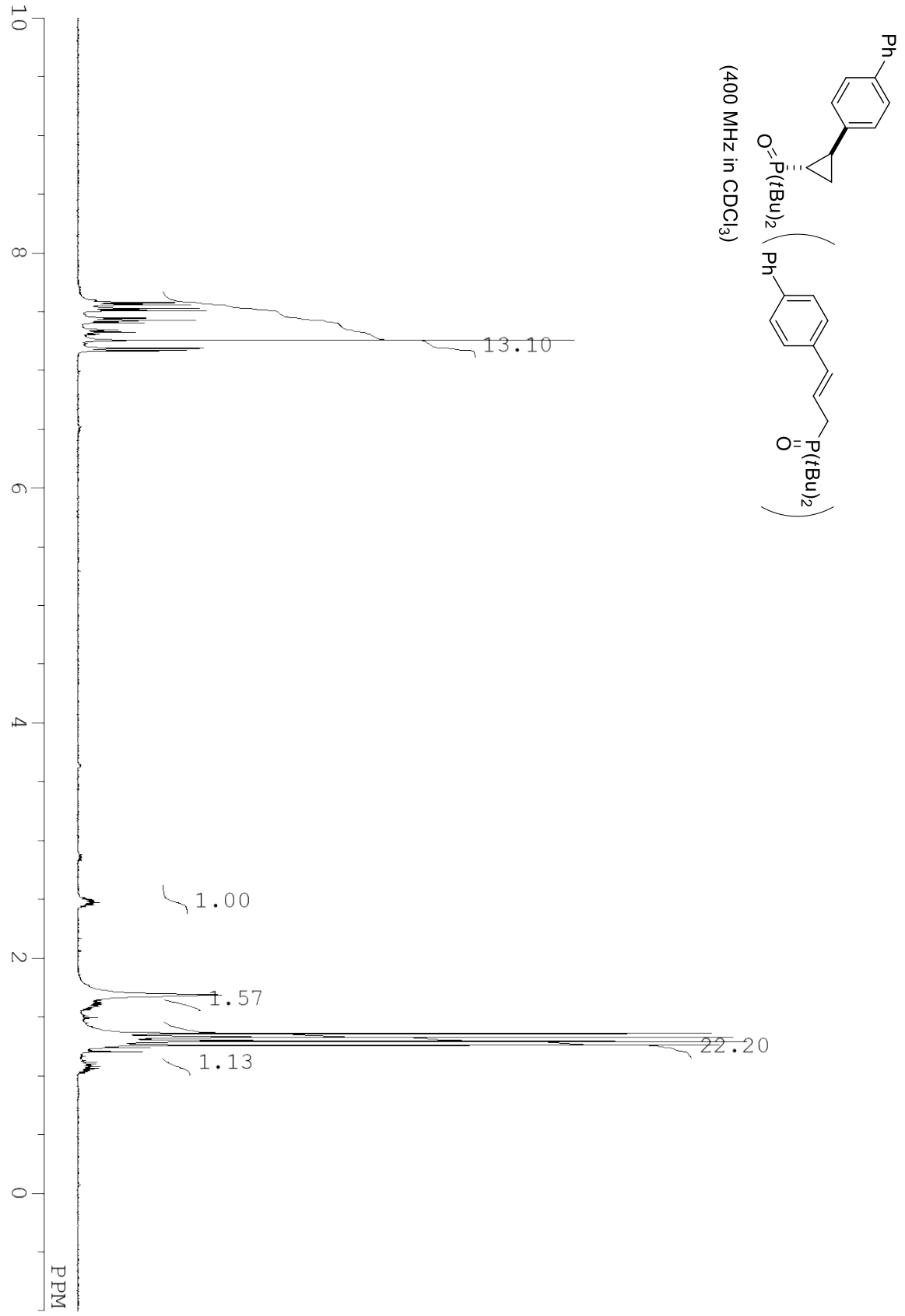
compound **3bd**



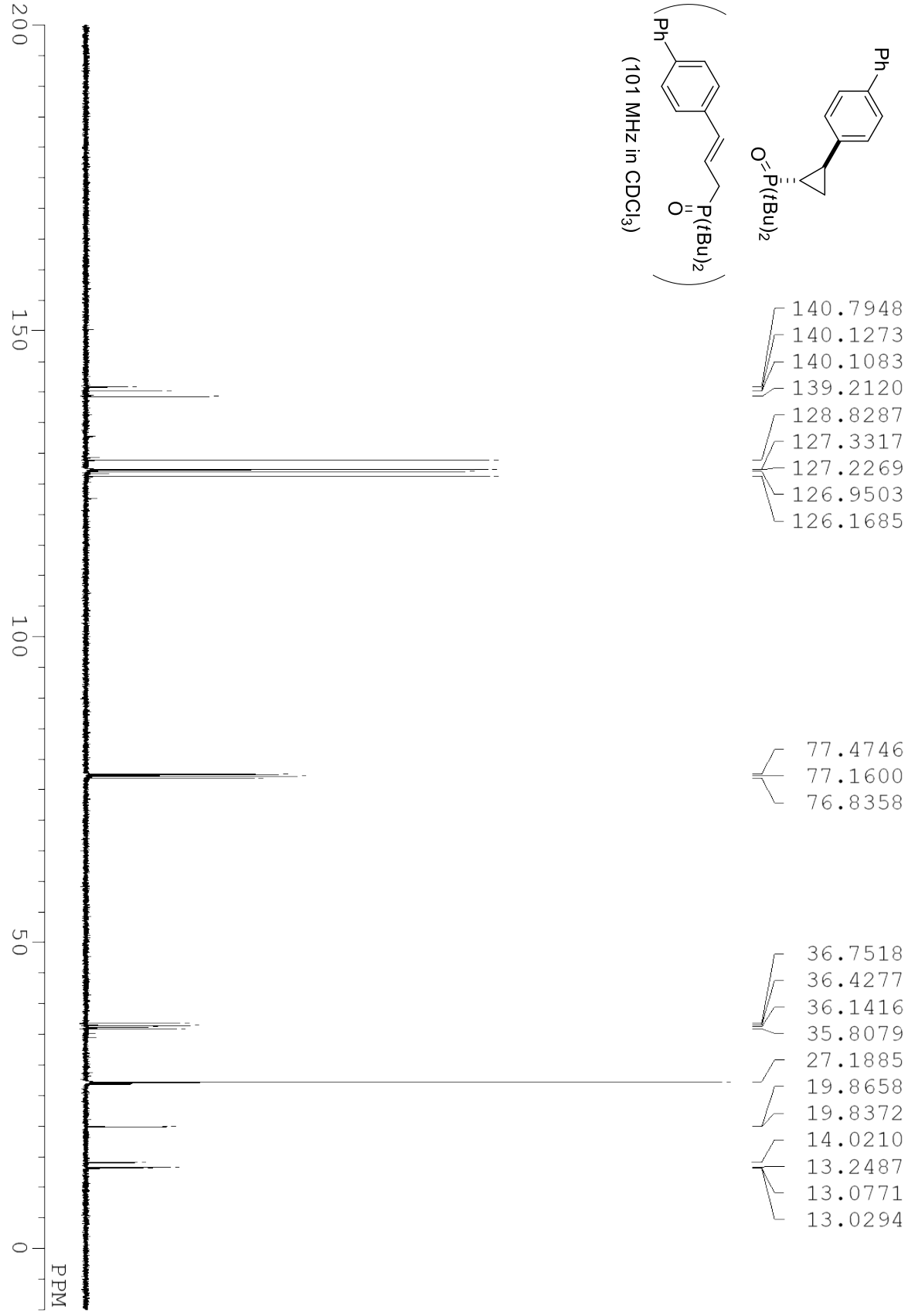
compound **3bd**



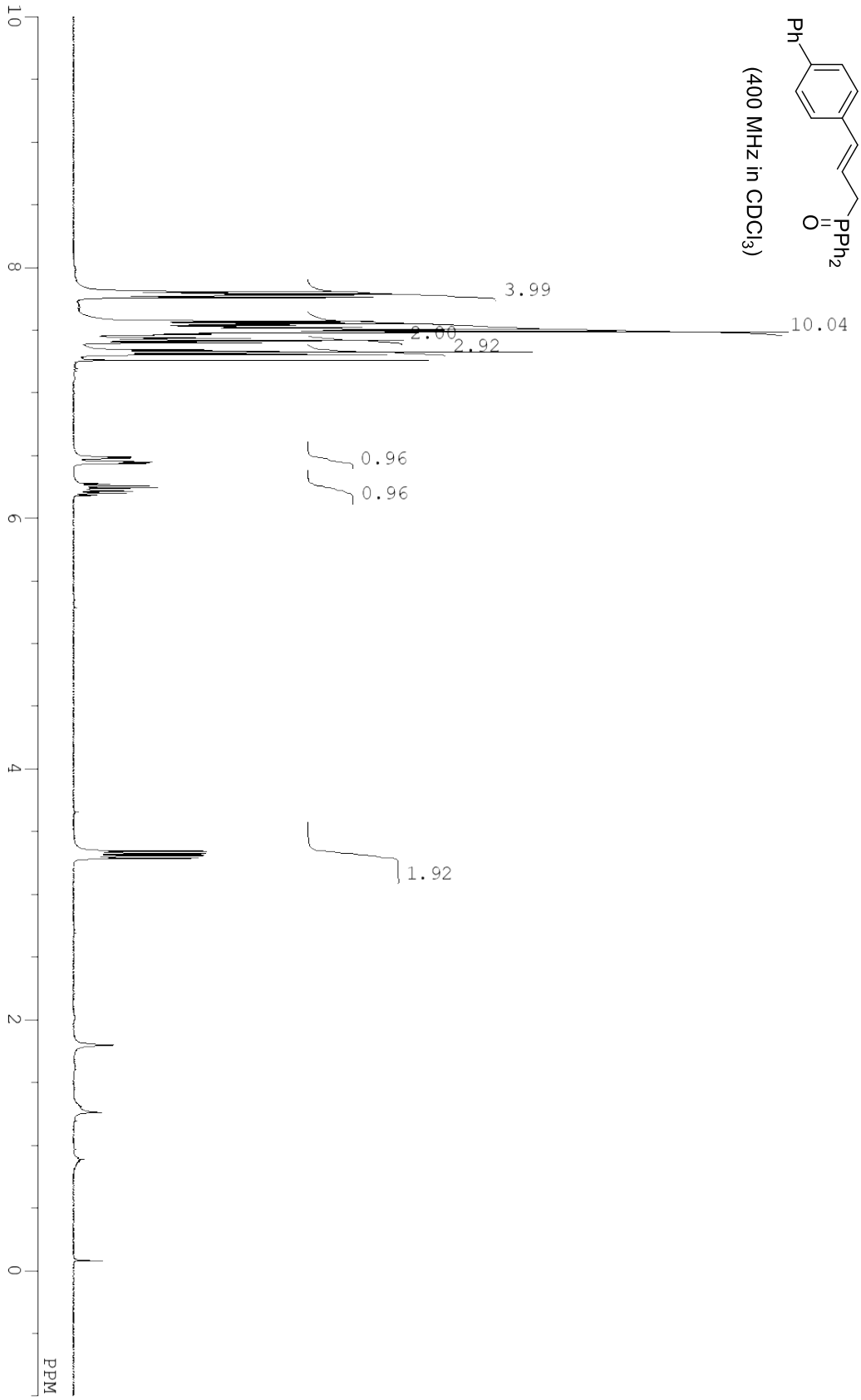
compound **3be** (**4be**)



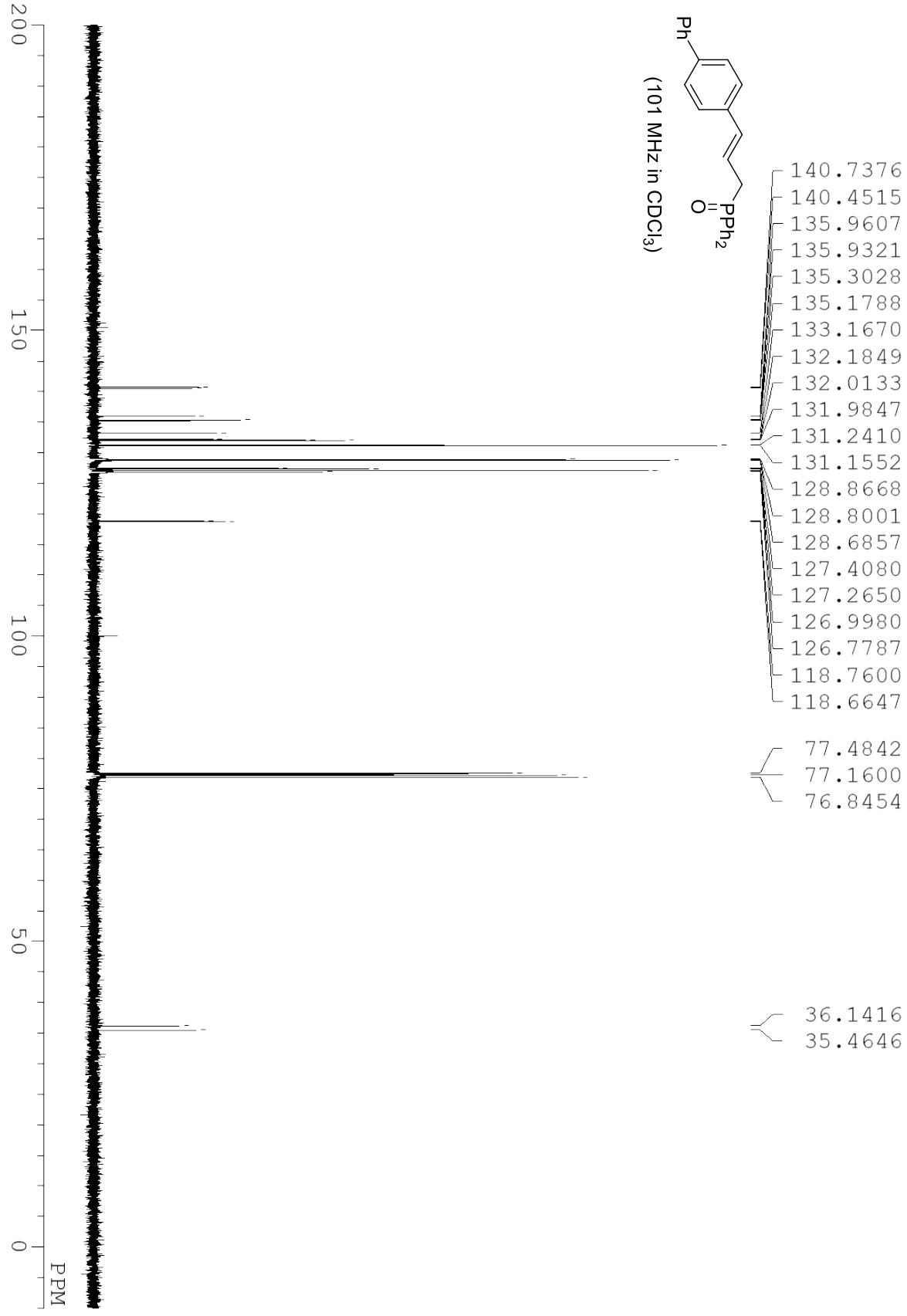
compound **3be** (**4be**)



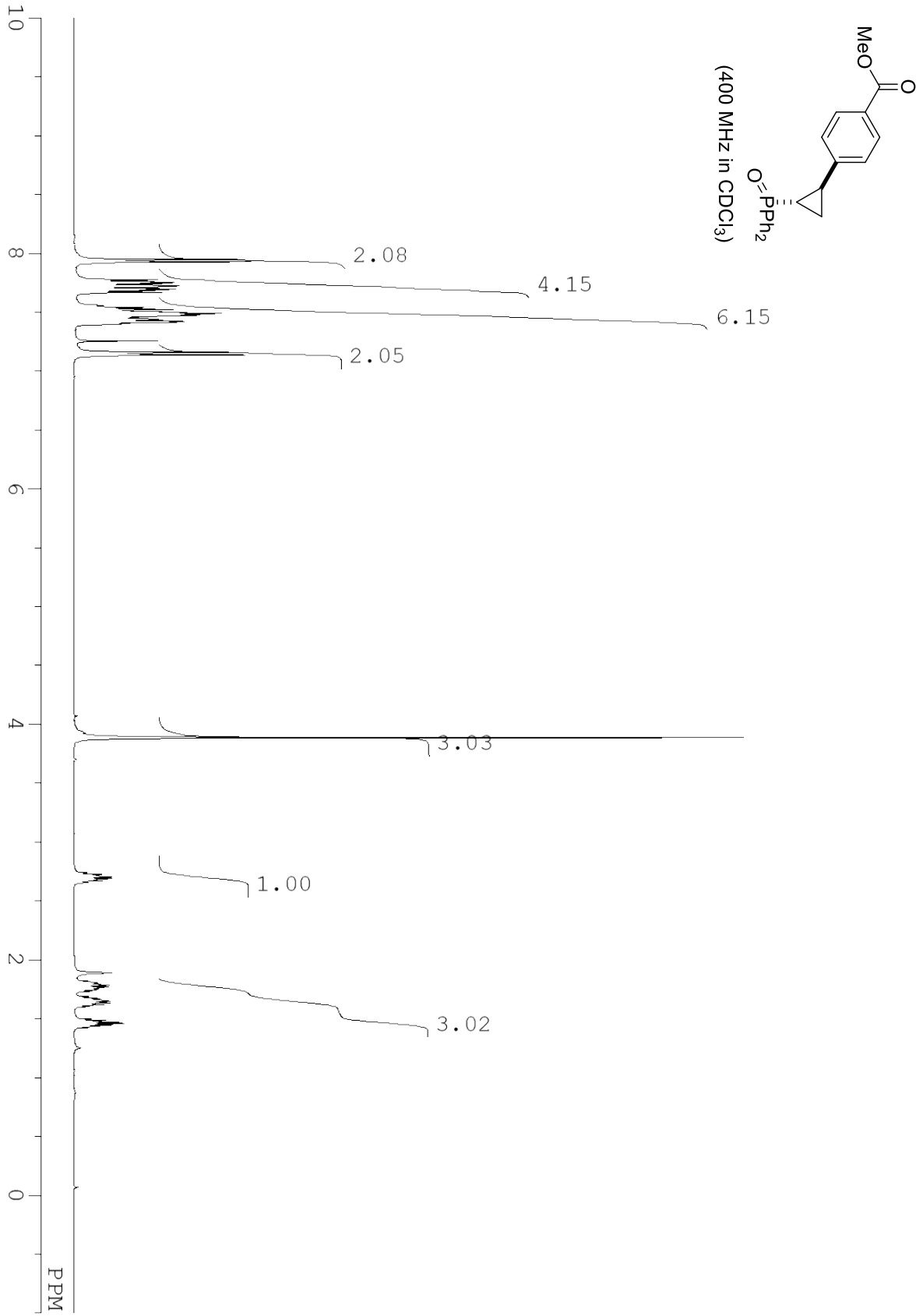
compound **4bf**



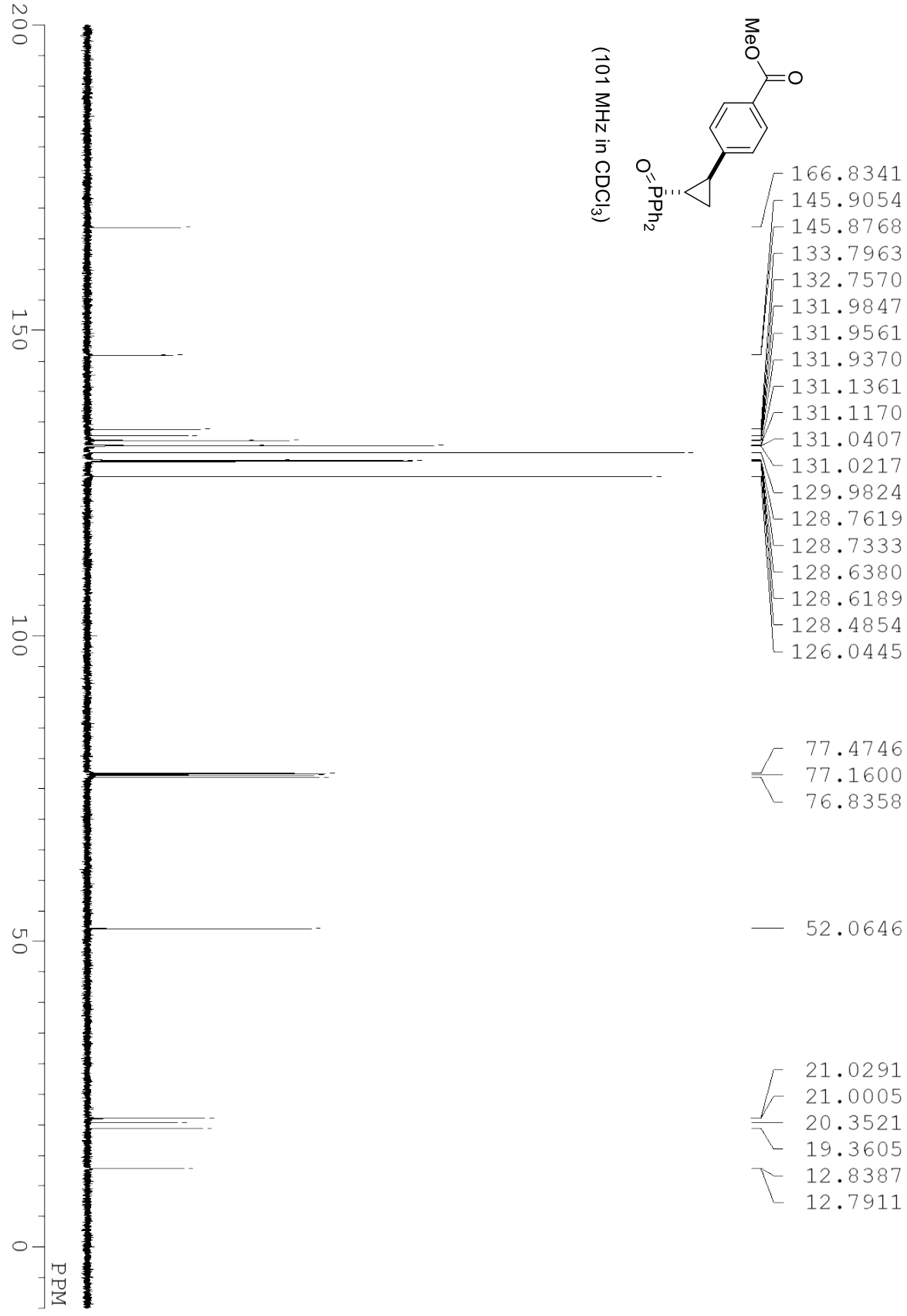
compound **4bf**



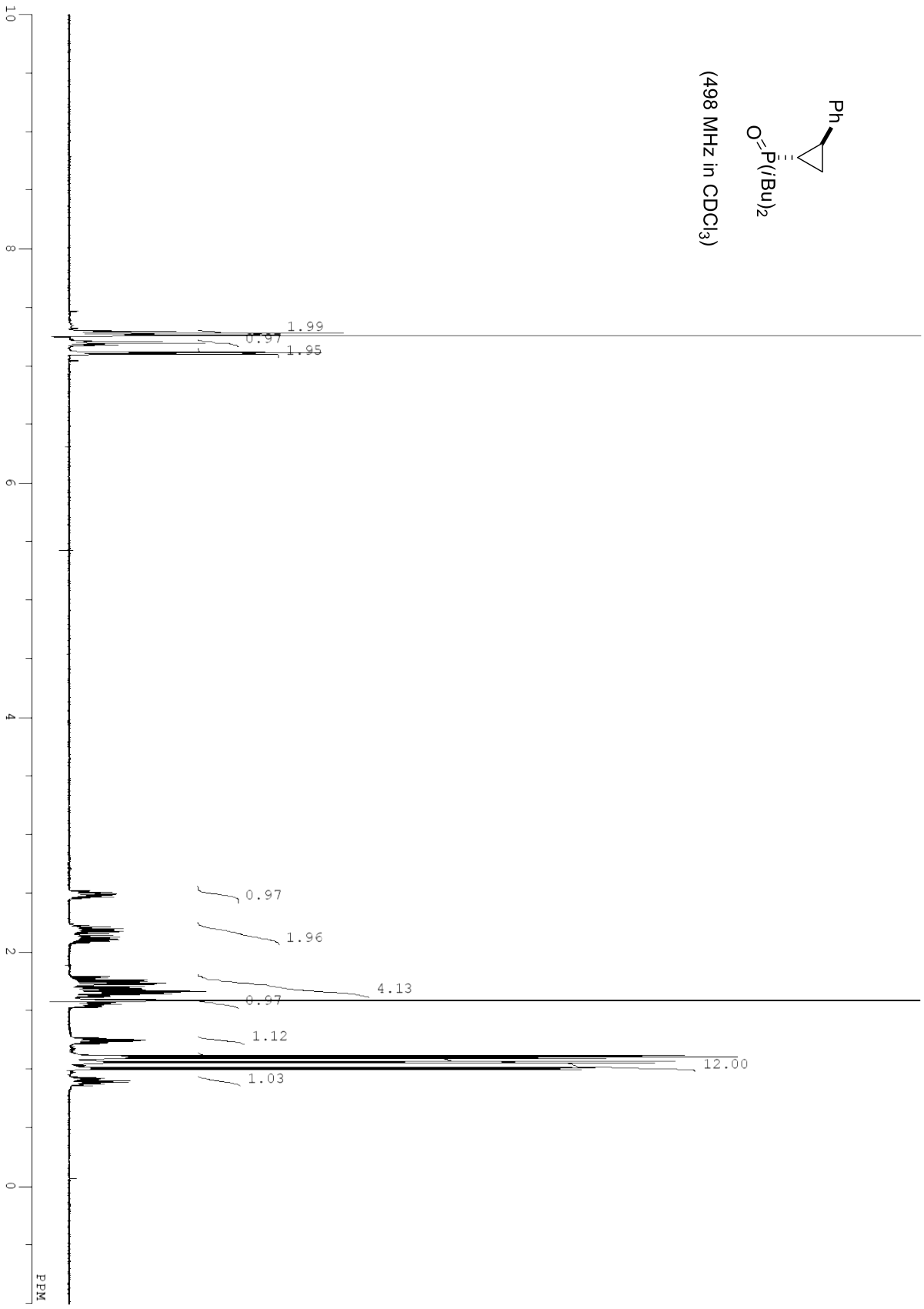
compound **3nf**



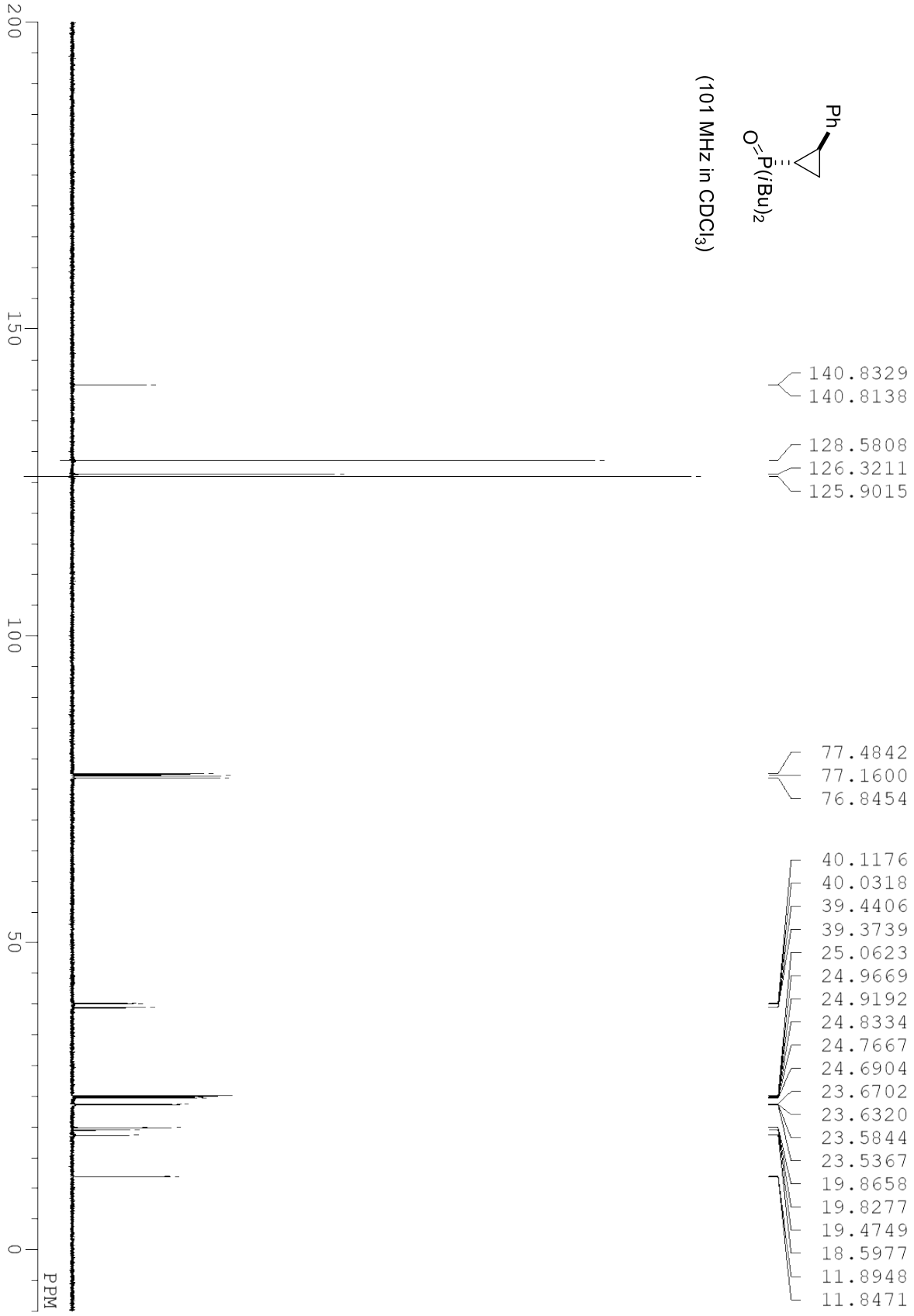
compound **3nf**



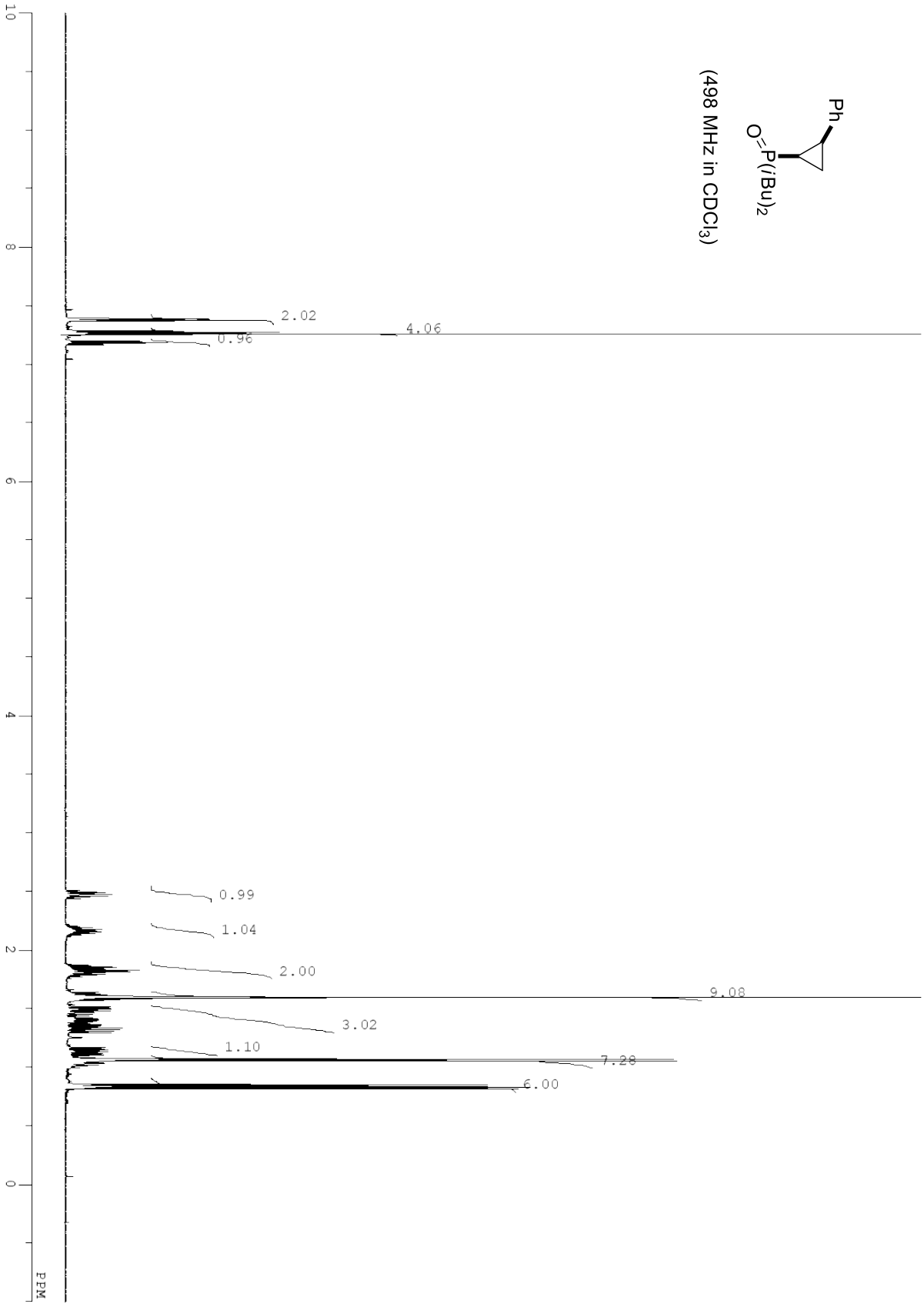
compound *trans*-**3ad**



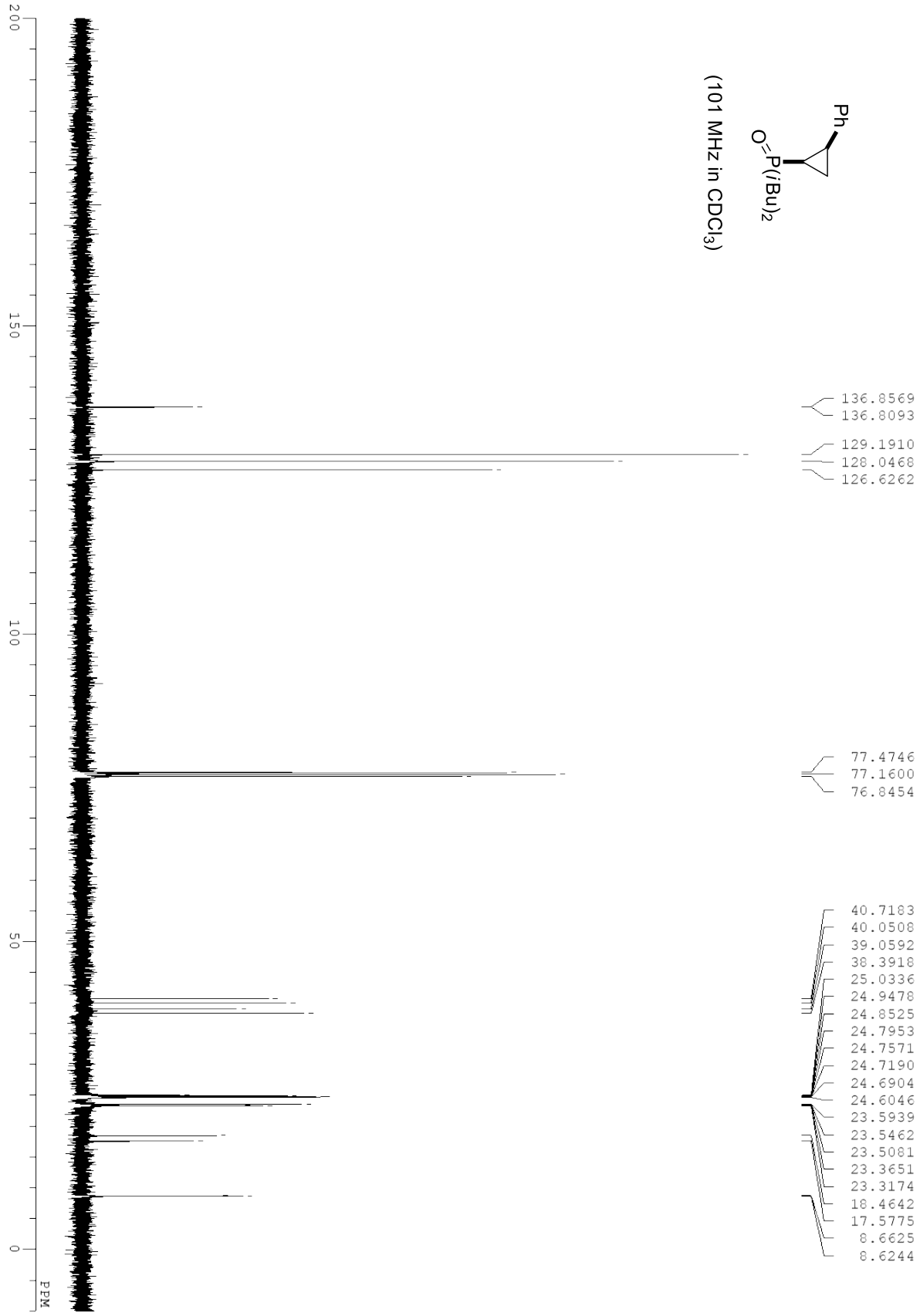
compound *trans*-**3ad**



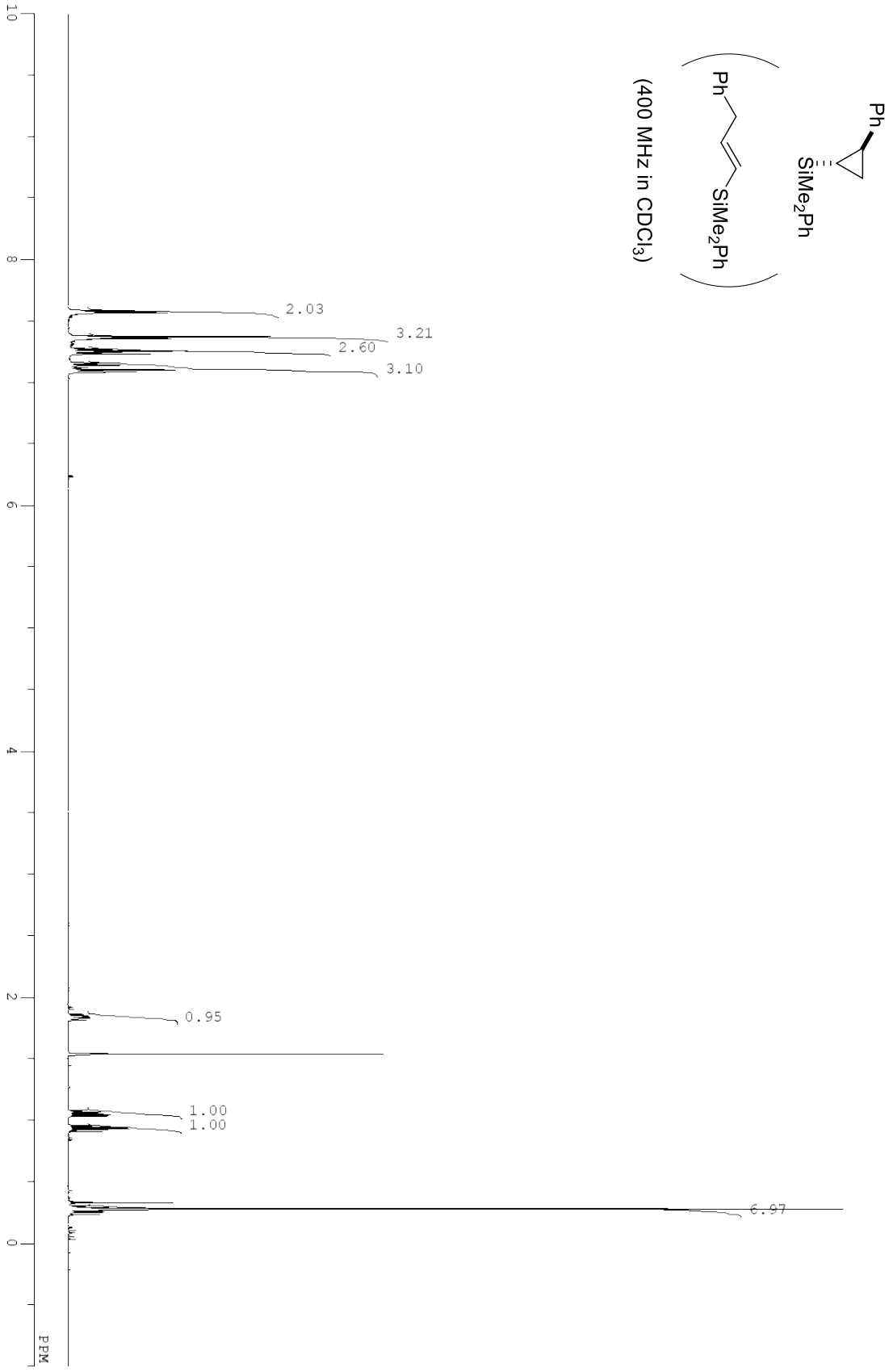
compound *cis*-**3ad**



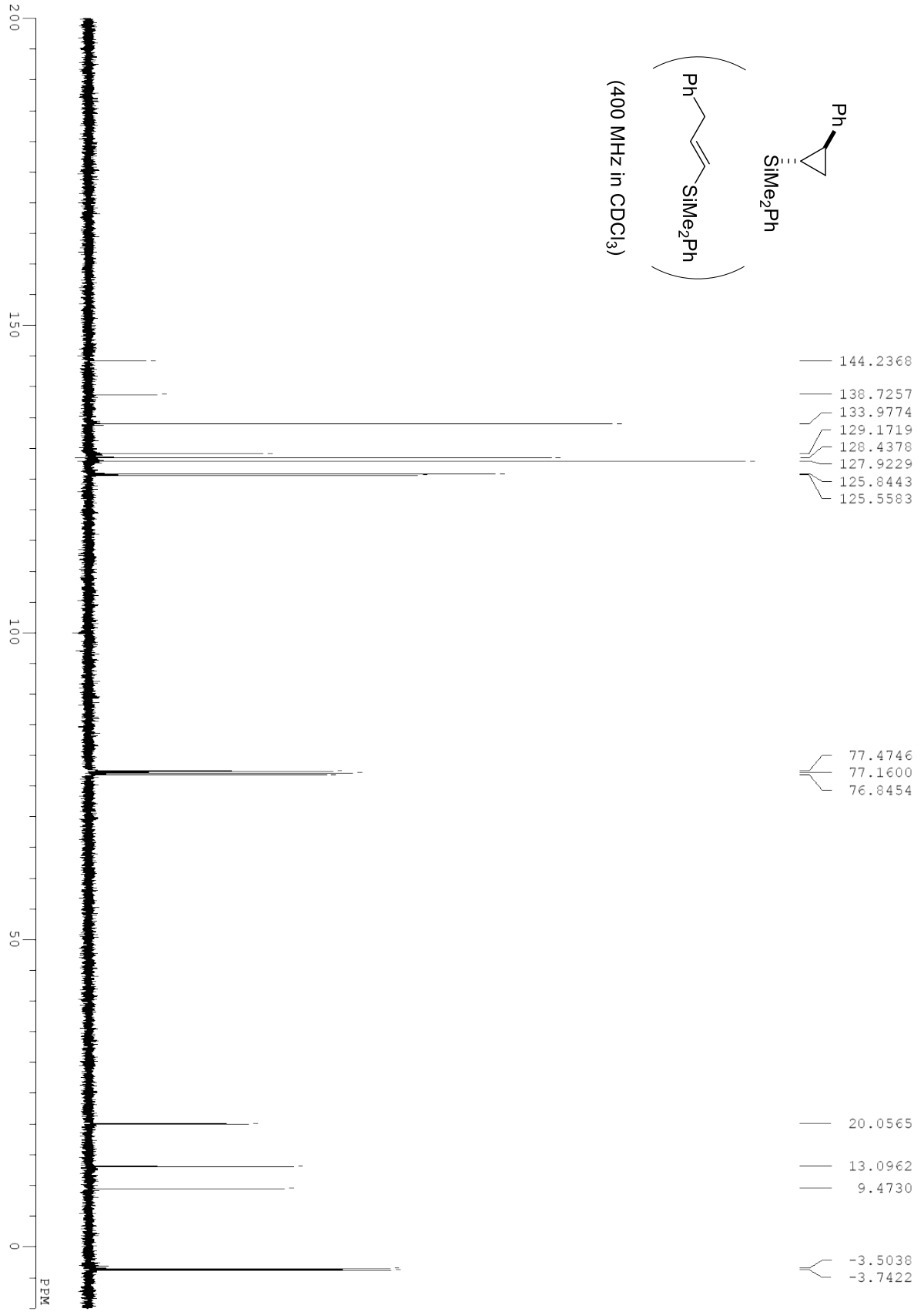
compound *cis*-**3ad**



compound **S1** (**S2**)



compound **S1** (**S2**)



VI. References

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