Supporting Information

Microwave-Promoted Tin-Free Iminyl Radical Cyclization with TEMPO Trapping: A Practical Synthesis of 2-Acylpyrroles

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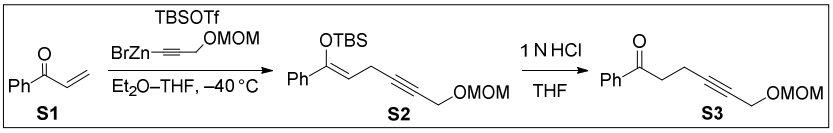
General Experimental Details

Dichloromethane, diethyl ether, and pyridine were dried by passage through a solvent drying system containing cylinders of activated alumina.[1] Other solvents and reagents were purchased from commercial vendors and used without purification. Flash chromatography was carried out using 60–230 mesh silica gel. ^{1}H NMR spectra were acquired on a 500 MHz spectrometer with chloroform (7.27 ppm) as internal reference. Signals are reported as follows: s (singlet), d (doublet), t (triplet), q (quartet), p (pentet), h (hextet), dd (doublet of doublets), dt (doublet of triplets), tt (triplet of triplets), qd (quartet of doublets), br s (broad singlet), m (multiplet). Coupling constants are reported in hertz (Hz). ^{13}C NMR spectra were acquired on a spectrometer operating at 125 MHz with chloroform (77.23 ppm) as internal reference. Infrared spectra were obtained on an FT-IR spectrometer. Mass spectral data were obtained using ESI techniques. Microwave-promoted reactions were carried out by irradiating sealed reaction mixtures inside a CEM Discover S-Class microwave reactor that was set at 300 W.

Synthesis of Ketone Precursors to *O*-Phenyl Oxime Ethers (note: all ketones not shown in this section are known compounds that were synthesized according to literature procedures)

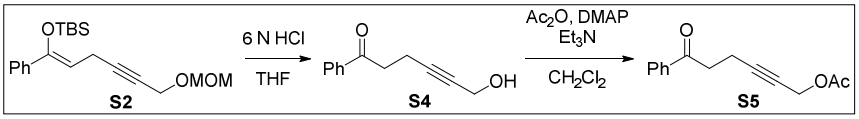


6-(Methoxymethoxy)-1-phenylhex-4-yn-1-one (S3). A solution of 3-(methoxymethoxy) prop-1-yne (114.1 mg, 1.14 mmol, 1.5 equiv) in anhydrous Et_2O (2.4 mL) at –40 °C under Ar was treated with *n*-butyllithium (1.57 M in hexane, 730 μL, 1.14 mmol, 1.5 equiv) and zinc

[1] Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518.

bromide (1.0 M in THF, 1.14 mL, 1.14 mmol, 1.5 equiv). The mixture was stirred at rt under Ar for 20 min, then cooled to –40 °C and treated with a solution of phenyl vinyl ketone (**S1**, 100.3 mg, 0.759 mmol, 1.0 equiv) in anhydrous THF (1.1 mL) followed by TBS-OTf (260 μL, 299 mg, 1.13 mmol, 1.5 equiv). The resulting mixture was stirred at rt for 3 h, then treated with sat aq $NaHCO_3$ (5 mL) and extracted with Et_2O (3 × 5 mL). The combined organic layers were washed with brine (5 mL), dried (Na_2SO_4), and concentrated *in vacuo* to give crude silyl enol ether **S2**.

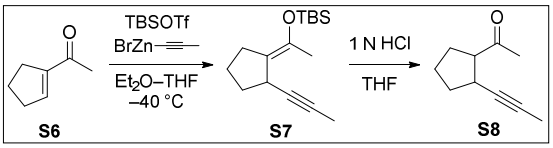
Crude **S2** was treated with 1 N HCl (3 mL) and THF (3 mL), and the resulting mixture was stirred at rt for 3 h. Sat aq $NaHCO_3$ (6 mL) was added to neutralize the reaction, and it was extracted with EtOAc (3 × 6 mL). The combined organic layers were dried (Na_2SO_4) and concentrated *in vacuo*. Flash chromatography (25 mL of SiO_2, 2–5% EtOAc in hexanes gradient elution) afforded **S3** (82.1 mg, 0.353 mmol, 47% from **S1**) as a colorless oil: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.98 (d, *J* = 7.8 Hz, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.8 Hz, 2H), 4.70 (s, 2H), 4.20 (t, *J* = 2.1 Hz, 2H), 3.38 (s, 3H), 3.25 (t, *J* = 7.4 Hz, 2H), 2.70–2.66 (m, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 197.8, 136.5, 133.3, 128.7 (2C), 128.0 (2C), 94.7, 85.6, 76.0, 55.5, 54.7, 37.7, 13.6; IR (film) ν_{max} 2931, 2237, 1686, 1597, 1449, 1360, 1207, 1180, 1046 cm^{-1}; HRMS (ESI) *m/z* 233.1162 (MH^+, $C_{14}H_{16}O_3H^+$ requires 233.1178).



6-Oxo-6-phenylhex-2-yn-1-yl acetate (S5). A solution of crude silyl enol ether **S2** (prepared as described above from **S1** (73.4 mg, 0.555 mmol, 1.0 equiv) and 3-(methoxymethoxy)prop-1-yne (84.1 mg, 0.840 mmol, 1.5 equiv)) in THF (3.0 mL) and H_2O (2.0 mL) was treated with 6 N HCl (5.0 mL) and heated at 55 °C for 8 h. The mixture was then

poured into brine (8.0 mL) and extracted with Et_2O (3 × 10 mL). The combined organic layers were dried (Na_2SO_4) and concentrated *in vacuo*. Flash chromatography (25 mL of SiO_2, 0.5–5% MeOH in CH_2Cl_2 gradient elution) afforded 6-hydroxy-1-phenylhex-4-yn-1-one (**S4**, 37.9 mg, 0.201 mmol, 36% from **S1**).

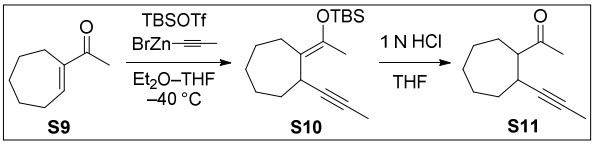
A solution of **S4** (32.1 mg, 0.171 mmol, 1.0 equiv) and Ac_2O (50 µL, 54 mg, 0.53 mmol, 3.1 equiv) in anhydrous CH_2Cl_2 (1.2 mL) at 0 °C under Ar was treated with Et_3N (71 µL, 52 mg, 0.51 mmol, 3.0 equiv) and DMAP (2.1 mg, 0.017 mmol, 0.1 equiv). The mixture was stirred at 0 °C for 5 min and at rt for 1.5 h. The reaction was quenched by the addition of sat aq $NaHCO_3$ (5 mL) and H_2O (5 mL), then extracted with Et_2O (3 × 6 mL). The combined organic layers were washed with 1 N HCl (4 mL) and brine (5 mL), dried (Na_2SO_4), and concentrated *in vacuo*. Flash chromatography (10 mL of SiO_2, 10–20% EtOAc in hexanes gradient elution) afforded **S5** (37.2 mg, 0.162 mmol, 95%) as a colorless oil: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.98 (d, J = 7.2 Hz, 2H), 7.59 (t, J = 7.4 Hz, 1H), 7.49 (t, J = 7.7 Hz, 2H), 4.66 (t, J = 2.0 Hz, 2H), 3.25 (t, J = 7.4 Hz, 2H) 2.71–2.66 (m, 2H), 2.10 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 197.7, 170.4, 136.4, 133.3, 128.7 (2C), 128.0 (2C), 86.3, 74.5, 52.7, 37.5, 20.8, 13.6; IR (film) ν_{max} 2923, 2360, 2342, 1742, 1686, 1225, 1024 cm^{-1}; HRMS (ESI) *m/z* 231.1009 (MH^+, $C_{14}H_{14}O_3H^+$ requires 231.1021).



1-(2-(Prop-1-yn-1-yl)cyclopentyl)ethan-1-one (S8). A solution of $ZnBr_2$ (1.0 M in THF, 2.5 mL, 2.5 mmol, 1.25 equiv) in anhydrous Et_2O (6 mL) at –40 °C under Ar was treated with 1-propynylmagnesium bromide (0.5 M in THF, 5.0 mL, 2.5 mmol, 1.25 equiv), and the mixture was stirred at rt for 20 min. The formed alkynylzinc reagent was then cooled to –40 °C and

treated with a solution of 1-acetyl-1-cyclopentene (**S6**, 230 μL, 220 mg, 1.99 mmol, 1.0 equiv) in anhydrous Et_2O (4.0 mL) followed by TBS-OTf (570 μl, 656 mg, 2.48 mmol, 1.24 equiv). The resulting mixture was stirred at 0 °C under Ar for 3 h, then treated with sat aq $NaHCO_3$ (12 mL) and extracted with Et_2O (3 × 12 mL). The combined organic layers were washed with brine (12 mL), dried (Na_2SO_4), and concentrated *in vacuo* to give crude silyl enol ether **S7**.

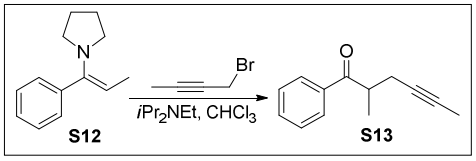
Crude **S7** was treated with 1 N HCl (6.0 mL) and THF (6.0 mL), and the resulting mixture was stirred at rt for 3 h. Sat aq $NaHCO_3$ (10 mL) was added to neutralize the reaction, and it was extracted with EtOAc (3 × 10 mL). The combined organic layers were dried (Na_2SO_4) and concentrated *in vacuo*. Flash chromatography (70 mL of SiO_2, 3–5 % EtOAc in hexanes gradient elution) afforded **S8** (189.4 mg, 1.26 mmol, 63% from **S6**) as a colorless oil: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.11–3.04 (m, 1H), 2.98–2.91 (m, 1H), 2.24 (s, 3H), 2.12–2.03 (m, 1H), 1.93–1.84 (m, 2H), 1.82–1.77 (m, 1H), 1.75 (d, J = 2.4 Hz, 3H), 1.72–1.64 (m, 1H), 1.62–1.55 (m, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 209.1, 79.1, 78.5, 56.5, 33.8, 33.7, 30.2, 25.3, 23.6, 3.5; IR (film) ν_{max} 2961, 2251, 1711, 1360, 1172 cm^{-1}; HRMS (ESI) *m/z* 151.1119 (MH^+, $C_{10}H_{14}OH^+$ requires 151.1123).



1-(2-(Prop-1-yn-1-yl)cycloheptyl)ethan-1-one (S11). A solution of $ZnBr_2$ (1.0 M in THF, 2.7 mL, 2.7 mmol, 1.26 equiv) in anhydrous Et_2O (6.8 mL) at –40 °C under Ar was treated with 1-propynylmagnesium bromide (0.5 M in THF, 5.4 mL, 2.7 mmol, 1.26 equiv), and the mixture was stirred at rt for 20 min. The formed alkynylzinc reagent was then cooled to –40 °C and

treated with a solution of 1-acetyl-1-cycloheptene[2] (**S9**, 296.4 mg, 2.14 mmol, 1.0 equiv) in anhydrous Et_2O (4.5 mL) followed by TBS-OTf (620 μL, 714 mg, 2.70 mmol, 1.26 equiv). The resulting mixture was stirred at 0 °C under Ar for 3 h, then treated with sat aq $NaHCO_3$ (12 mL) and extracted with Et_2O (3 × 12 mL). The combined organic layers were washed with brine (12 mL), dried (Na_2SO_4), and concentrated *in vacuo* to give crude silyl enol ether **S10**.

Crude **S10** was treated with 1 N HCl (6.5 mL) and THF (6.5 mL), and the resulting mixture was stirred at rt for 3 h. Sat aq $NaHCO_3$ (12 mL) was added to neutralize the reaction, and it was extracted with EtOAc (3 × 12 mL). The combined organic layers were dried (Na_2SO_4) and concentrated *in vacuo*. Flash chromatography (75 mL of SiO_2, 3–5 % EtOAc in hexanes gradient elution) afforded **S11** (153.5 mg, 0.861 mmol, 40% from **S9**) as a colorless oil: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.19–3.14 (m, 1H), 2.49 (dt, *J* = 10.5, 3.4 Hz, 1H), 2.20 (s, 3H), 1.95–1.81 (m, 3H), 1.79 (d, *J* = 2.6 Hz, 3H), 1.78–1.66 (m, 3H), 1.61–1.51 (m, 3H), 1.48–1.40 (m, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 210.5, 79.1, 79.0, 56.8, 33.9, 32.1, 28.2, 27.6, 26.3, 25.1, 24.6, 3.6; IR (film) ν_{max} 2923, 1711, 1446, 1353, 1178 cm^{-1}; HRMS (ESI) *m/z* 179.1434 (MH^+, $C_{12}H_{18}OH^+$ requires 179.1436).

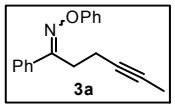


A solution of 1-bromo-2-butyne (68 μL, 103 mg, 0.78 mmol) and *i*Pr_2NEt (130 μL, 96 mg, 0.75 mmol) in $CHCl_3$ (1.0 mL) was treated with freshly prepared 1-(1-phenylprop-1-en-1-

[2] Hudlicky, T.; Srnak, T. *Tetrahedron Lett.* **1981**, *22*, 3351.

yl)pyrrolidine[3] (**S12**, ca. 70% purity, 201.1 mg, 0.75 mmol). The resulting mixture was refluxed for 12 h, then treated with 1N HCl (1.5 mL) and stirred at 65 °C for 4 h. The resulting biphasic mixture was extracted with diethyl ether (3 × 6 mL), and the combined organic layers were washed with water (5 mL) and brine (5 mL), then dried (Na_2SO_4) and concentrated *in vacuo*. Flash chromatography (18 mL of SiO_2, 0–5 % EtOAc in hexanes gradient elution) afforded **S13** (122.4 mg, 0.657 mmol, 87%) as a colorless oil: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.98 (d, J = 7.6 Hz, 2H), 7.58 (t, J = 7.4 Hz, 1H), 7.49 (t, J = 7.6 Hz, 2H), 3.64 (h, J = 7.0 Hz, 1H), 2.64–2.51 (m, 1H), 2.41–2.29 (m, 1H), 1.76 (t, J = 2.6 Hz, 3H), 1.30 (d, J = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 202.8, 136.1, 133.0, 128.6 (2C), 128.4 (2C), 77.1, 76.9, 40.7, 22.8, 17.4, 3.5; IR (film) ν_{max} 2973, 2359, 1683, 1448, 1199 cm^{-1}; HRMS (ESI) *m/z* 187.1151 (MH^+, $C_{13}H_{14}OH^+$ requires 187.1123).

Synthesis of *O*-Phenyl Oximes



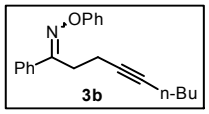
1-Phenylhex-4-yn-1-one *O*-phenyl oxime (3a). A solution of *O*-phenyl hydroxylamine hydrochloride[4] (288.3 mg, 1.98 mmol, 1.5 equiv) in anhydrous pyridine (5.4 mL) under Ar at rt was treated with 1-phenylhex-4-yn-1-one[5] (227.7 mg, 1.32 mmol, 1.0 equiv). The resulting mixture was stirred at rt for 16 h, then poured into H_2O (12 mL) and extracted with EtOAc (3 × 12 ml). The combined organic layers were washed with sat aq $CuSO_4$ (12 mL) to remove traces of pyridine, dried ($NaSO_4$), and concentrated *in vacuo*. Flash chromatography (30 mL of SiO_2, 1–5% EtOAc in hexanes gradient elution) afforded **3a** (254.7 mg, 0.967 mmol,

[3] Kawai, N.; Shioiri, T.; *Chem. Pharm. Bull.* **1983**, *31*, 2564.

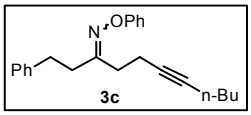
[4] Petrassi, H. M.; Sharpless, K. B.; Kelly, J. W. *Org. Lett.* **2001**, *3*, 139.

[5] Kusama, H.; Ishida, K.; Funami, H.; Iwasawa, N. *Angew. Chem., Int. Ed.* **2008**, *47*, 4903.

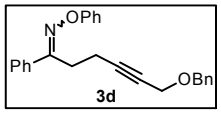
73%) as a colorless oil that was a 3.2:1 mixture of isomers: ^{1}H NMR ($CDCl_3$, 500 MHz) 7.85–7.79 (m, 2H), 7.52–7.42 (m, 3H), 7.39–7.33 (m, 2H), 7.32 and 7.19 (2d, J = 7.2 and 7.7 Hz, 2H), 7.06 and 7.02 (2t, J = 7.1 and 7.3 Hz, 1H), 3.17 and 2.89 (2t, J = 7.6 and 7.3 Hz, 2H), 2.57–2.51 and 2.50–2.42 (2m, 2H), 1.80 and 1.74 (2t, J = 2.4 and 2.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 160.2 and 159.9, 159.5 and 159.4, 134.9, 129.8, 129.3 and 129.2 (2C), 128.6 and 128.2 (2C), 127.8 and 126.8, 122.3 and 122.0 (2C), 114.9 and 114.7 (2C), 77.8 and 77.6, 76.9, 35.2 and 27.2, 16.4, 3.4; IR (film) ν_{max} 3060, 2917, 2361, 1593, 1490, 1214 cm^{-1}; HRMS (ESI) *m/z* 264.1373 (MH^+, $C_{18}H_{17}NOH^+$ requires 264.1388).



1-Phenylnon-4-yn-1-one *O*-phenyl oxime (3b). Subjection of 1-phenylnon-4-yn-1-one[5] (36.6 mg, 0.171 mmol) to the procedure described above for the synthesis of **3a** with purification by flash chromatography (10 mL of SiO_2, 1–5% EtOAc in hexanes gradient elution) afforded **3b** (43.7 mg, 0.143 mmol, 84%) as a colorless oil that was a 2.1:1 mixture of isomers: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.83–7.79 (m, 1H), 7.49–7.39 (m, 4H), 7.37–7.32 (m, 2H), 7.30 and 7.18 (2d, J = 7.6 and 7.7 Hz, 2H), 7.05 and 7.00 (2t, J = 7.1 and 7.3 Hz, 1H), 3.16 and 2.88 (2t, J = 7.7 and 7.5 Hz, 2H), 2.56 and 2.46 (2tt, J = 7.7, 2.2 Hz and 7.6, 2.2 Hz, 2H), 2.15 and 2.09 (2tt, J = 6.8, 2.3 Hz and 6.8, 2.3 Hz, 2H), 1.49–1.31 (m, 4H), 0.91–0.85 (m, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 160.3 and 159.8, 159.5 and 159.4, 135.0 and 133.1, 129.7 and 129.3 (2C), 129.2 and 129.1, 128.5 and 128.2 (2C), 127.8 and 126.9 (2C), 122.2 and 122.0, 114.9 and 114.7 (2C), 81.6, 78.4, 35.3 and 31.0, 31.1 and 27.3, 21.9, 18.4, 16.5 and 16.4, 13.6; IR (film) ν_{max} 2930, 2359, 1593, 1490, 1214, 1023 cm^{-1}; HRMS (ESI) *m/z* 306.1867 (MH^+, $C_{21}H_{23}NOH^+$ requires 306.1858).



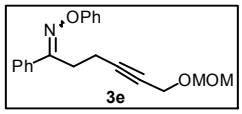
1-Phenylundec-6-yn-3-one *O*-phenyl oxime (3c). Subjection of 1-phenylundec-6-yn-3-one[6] (24.7 mg, 0.102 mmol) to the procedure described above for the synthesis of **3a** with purification by flash chromatography (8 mL of SiO_2, 1–5% EtOAc in hexanes gradient elution) afforded **3c** (27.7 mg, 0.0831 mmol, 82%) as a colorless oil that was a 1:1 mixture of isomers: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.34–7.28 (m, 4H), 7.27–7.22 (m, 3H), 7.20 and 7.14 (2d, *J* = 7.8 and 7.8 Hz, 2H), 7.04–6.98 (m, 1H), 2.99 and 2.93 (2t, *J* = 8.0, 8.0 Hz, 2H), 2.80 and 2.74 (2t, *J* = 7.9, 8.0 Hz, 2H), 2.70 and 2.54–2.43 (t and m, *J* = 7.3 Hz, 4H), 2.21–2.09 (m, 2H), 1.50–1.34 (m, 4H), 0.89 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 162.6 and 162.5, 159.5 and 159.4, 141.3 and 141.0, 129.2 (2C), 128.5 (2C), 128.4 and 128.3 (2C), 126.3 and 126.1, 121.9 and 121.8, 114.7 and 114.6 (2C), 81.4 and 81.2, 78.7 and 78.5, 36.6 and 34.4, 32.2 and 32.0, 31.3 and 31.1, 29.0, 22.0 and 21.9, 18.4, 16.0 and 15.7, 13.6; IR (film) ν_{max} 2930, 2360, 1591, 1489, 1213, 1072 cm^{-1}; HRMS (ESI) *m/z* 334.2143 (MH^+, $C_{23}H_{27}NOH^+$ requires 334.2171).



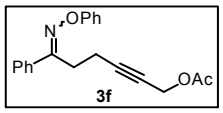
6-(Benzyloxy)-1-phenylhex-4-yn-1-one *O*-phenyl oxime (3d). Subjection of 6-(benzyloxy)-1-phenylhex-4-yn-1-one[6] (37.5 mg, 0.135 mmol) to the procedure described above for the synthesis of **3a** with purification by flash chromatography (18 mL of SiO_2, 3–5% EtOAc in hexanes gradient elution) afforded **3d** (35.6 mg, 0.964 mmol, 72%) as a colorless oil that was a 6.1:1 mixture of isomers: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.86–7.77 (m, 2H), 7.49 and 7.45–7.40 (d and m, *J* = 8.0 Hz, 4H), 7.38–7.28 and 7.17 (m and d, *J* = 7.9 Hz,

[6] Ishida, K.; Kusama, H.; Iwasawa, N. *J. Am. Chem. Soc.* **2010**, *132*, 8842.

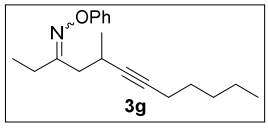
8H), 7.06 and 7.00 (2t, J = 7.1 and 7.2 Hz, 1H), 4.58 and 4.51 (2s, 2H), 4.16 and 4.10 (2t, J = 2.0 and 2.0 Hz, 2H), 3.21 and 2.94 (2t, J = 7.7 and 7.6 Hz, 2H), 2.66 and 2.58 (2tt, J = 7.7, 2.0 Hz and 7.5, 2.1 Hz, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 159.8, 159.4, 137.6, 134.8, 129.9, 129.3 and 129.2 (2C), 128.6 (2C), 128.4 and 128.3 (2C), 128.1 and 128.0 (2C), 127.9 and 127.8, 126.8 (2C), 122.4 and 122.1, 114.8 and 114.7 (2C), 85.4, 77.2, 71.5 and 71.4, 57.6, 34.7 and 26.7, 16.4; IR (film) ν_{max} 3062, 2360, 1653, 1489, 1351, 1214, 1072 cm^{-1}; HRMS (ESI) *m/z* 370.1780 (MH^+, $C_{25}H_{23}NO_2H^+$ requires 370.1807).



6-(Methoxymethoxy)-1-phenylhex-4-yn-1-one *O*-phenyl oxime (3e). Subjection of 6-(methoxymethoxy)-1-phenylhex-4-yn-1-one (**S3**, 33.2 mg, 0.143 mmol) to the procedure described above for the synthesis of **3a** with purification by flash chromatography (12 mL of SiO_2, 5–10% EtOAc in hexanes gradient elution) afforded **3e** (36.9 mg, 0.114 mmol, 80%) as a colorless oil that was a 4.7:1 mixture of isomers: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.83–7.77 (m, 2H), 7.46–7.41 (m, 3H), 7.38–7.33 (m, 2H), 7.30 and 7.18 (2d, J = 7.6 and 7.8 Hz, 2H), 7.06 and 7.01 (2t, J = 7.2 and 7.3 Hz, 1H), 4.70 and 4.65 (2s, 2H), 4.21 and 4.15 (2t, J = 2.0 and 2.0 Hz, 2H), 3.37 (s, 3H), 3.20 and 2.92 (2t, J = 7.8 and 7.5 Hz, 2H), 2.65–2.61 and 2.58–2.54 (2m, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 159.8, 159.4 and 159.3, 134.7 and 133.0, 129.9, 129.3 and 129.2 (2C), 128.6 and 128.3 (2C), 127.8 and 126.8 (2C), 122.4 and 122.1, 114.8 and 114.7 (2C), 94.7 and 94.6, 85.3 and 85.2, 76.7 and 76.6, 55.5, 54.6 and 54.5, 34.7 and 26.7, 16.4; IR (film) ν_{max} 2946, 2236, 1592, 1490, 1214, 1150, 1072 cm^{-1}; HRMS (ESI) *m/z* 324.1603 (MH^+, $C_{20}H_{21}NO_3H^+$ requires 324.1600).

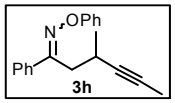


6-(Phenoxyimino)-6-phenylhex-2-yn-1-yl acetate (3f). Subjection of 6-oxo-6-phenylhex-2-yn-1-yl acetate (**S5**, 27.7 mg, 0.120 mmol) to the procedure described above for the synthesis of **3a** with purification by flash chromatography (25 mL of SiO_2, 1–5% EtOAc in hexanes gradient elution) afforded **3f** (35.1 mg, 0.109 mmol, 91%) as a colorless oil that was a 1.7:1 mixture of isomers: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.81–7.77 (m, 1H), 7.50–7.41 (m, 4H), 7.35 (t, *J* = 8.0 Hz, 1H), 7.32–7.28 (m, 2H), 7.17 (d, *J* = 7.7 Hz, 1H), 7.06 and 7.01 (2t, *J* = 7.2 and 7.3 Hz, 1H), 4.66 and 4.60 (2t, *J* = 2.2 and 2.1 Hz, 2H), 3.20 and 2.92 (2t, *J* = 7.8 and 7.4 Hz, 2H), 2.63 and 2.57 (2tt, *J* = 7.8, 2.2 Hz and 7.6, 2.1 Hz, 2H), 2.07 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 170.4 and 170.3, 159.6 and 159.4, 159.3 and 159.1, 134.7 and 132.9, 129.9 and 129.34, 129.30 and 129.2 (2C), 128.6 and 128.3 (2C), 127.8 and 126.8 (2C), 122.4 and 122.1, 114.8 and 114.7 (2C), 85.9 and 85.8, 75.2 and 75.1, 52.7 and 52.6, 34.5 and 26.5, 20.8, 16.4 and 16.3; IR (film) ν_{max} 2938, 2238, 1744, 1591, 1216, 1024 cm^{-1}; HRMS (ESI) *m/z* 322.1455 (MH^+, $C_{20}H_{19}NO_3H^+$ requires 322.1443).

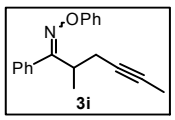


5-Methyldodec-6-yn-3-one *O*-phenyl oxime (3g). Subjection of 5-methyldodec-6-yn-3-one[5] (34.7 mg, 0.179 mmol) to the procedure described above for the synthesis of **3a** with purification by flash chromatography (12 mL of SiO_2, 1–5% EtOAc in hexanes gradient elution) afforded **3g** (49.8 mg, 0.174 mmol, 98%) as a colorless oil that was a 2.0:1 mixture of isomers: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.31 (t, *J* = 7.4 Hz, 2H), 7.20 (d, *J* = 7.5 Hz, 2H), 7.00 (t, *J* = 7.2 Hz, 1H), 3.00–2.92 and 2.91–2.82 (2m, 1H), 2.75–2.69 and 2.44–2.38 (2m, 1H), 2.60–2.47 (m, 3H), 2.20–2.10 (m, 2H), 1.53–1.44 (m, 2H), 1.38–1.30 (m, 4H), 1.27–1.16 (m, 6H), 0.96–0.85 (m, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 164.1 and 164.0, 159.6 and

159.5, 129.2 (2C), 121.7 and 121.6, 114.6 (2C), 83.6 and 83.4, 81.3 and 81.2, 41.1 and 36.2, 31.0, 28.7 and 28.6, 23.7 and 23.5, 22.4, 22.2, 21.9 and 21.4, 18.7, 14.0, 10.7 and 10.5; IR (film) ν_{max} 2932, 2360, 1592, 1489, 1211 cm^{-1}; HRMS (ESI) *m/z* 286.2149 (MH^+, $C_{19}H_{27}NOH^+$ requires 286.2171).

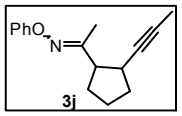


3-Methyl-1-phenylhex-4-yn-1-one *O*-phenyl oxime (3h). Subjection of 3-methyl-1-phenylhex-4-yn-1-one[5] (29.6 mg, 0.159 mmol) to the procedure described above for the synthesis of **3a** with purification by flash chromatography (12 mL of SiO_2, 1–5% EtOAc in hexanes gradient elution) afforded **3h** (39.1 mg, 0.141 mmol, 89%) as a colorless oil that was a 1.4:1 mixture of isomers: ^1H NMR ($CDCl_3$, 500 MHz) δ 7.87–7.75 (m, 1H), 7.49–7.40 (m, 4H), 7.37–7.28 (m, 3H), 7.18 (d, *J* = 8.2 Hz, 1H), 7.05 and 7.01 (2t, *J* = 7.2, 7.3 Hz, 1H), 3.19 and 2.88 (2dd, *J* = 10.4, 7.7 and 10.9, 7.7 Hz, 1H), 3.07 and 2.74 (2dd, *J* = 10.2, 7.5 and 10.6, 7.1 Hz, 1H), 2.99–2.91 and 2.70–2.57 (2m, 1H), 1.77 and 1.67 (2d, *J* = 2.2, 2.3 Hz, 3H), 1.22 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 159.9 and 159.8, 159.5 and 159.4, 135.4 and 133.2, 129.6 and 129.3, 129.2 and 129.1 (2C), 128.4, 128.2 and 127.9 (2C), 127.1, 122.2 and 122.0, 114.9 and 114.8 (2C), 82.6 and 82.3, 77.2 and 76.9, 42.7 and 34.5, 24.0 and 23.8, 21.3 and 20.9, 3.5 and 3.4; IR (film) ν_{max} 2968, 2360, 1593, 1490, 1216 cm^{-1}; HRMS (ESI) *m/z* 278.1575 (MH^+, $C_{19}H_{19}NOH^+$ requires 278.1545).

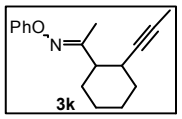


2-Methyl-1-phenylhex-4-yn-1-one *O*-phenyl oxime (3i). Subjection of 2-methyl-1-phenylhex-4-yn-1-one (**S13**, 23.7 mg, 0.127 mmol) to the procedure described above for the synthesis of **3a** with purification by flash chromatography (15 mL of SiO_2, 1–5% EtOAc

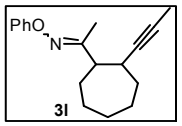
in hexanes gradient elution) afforded **3i** (29.3 mg, 0.106 mmol, 83%) as a colorless oil that was a 1.9:1 mixture of isomers: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.65–7.56 (m, 1H), 7.52–7.39 (m, 3H), 7.37 (d, *J* = 7.3 Hz, 1H), 7.35–7.25 (m, 3H), 7.15 (d, *J* = 7.8 Hz, 1H), 7.04 and 6.99 (2t, *J* = 7.2 and 7.2 Hz, 1H), 3.64 and 3.02 (2h, *J* = 7.2 and 7.0 Hz, 1H), 2.68–2.62 and 2.35–2.29 (2m, 1H), 2.57–2.51 (m, 1H), 1.82 and 1.75 (2t, *J* = 2.4 and 2.4 Hz, 3H), 1.42 and 1.32 (2d, *J* = 7.1 and 6.9 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 165.1 and 164.0, 159.5 and 159.3, 135.6 and 133.4, 129.2 and 129.14, 129.12 and 128.8 (2C), 128.3 and 128.1 (2C), 128.0 and 127.6 (2C), 122.2 and 121.9, 114.8 and 114.7 (2C), 77.3 and 77.2, 77.1, 40.1 and 35.9, 24.0 and 23.3, 17.9 and 17.0, 3.5; IR (film) ν_{max} 2918, 2359, 1594, 1490, 1215 cm^{-1}; HRMS (ESI) *m/z* 278.1543 (MH^+, $C_{19}H_{19}NOH^+$ requires 278.1545).



1-(2-(Prop-1-yn-1-yl)cyclopentyl)ethan-1-one *O*-phenyl oxime (3j). Subjection of 1-(2-(prop-1-yn-1-yl)cyclopentyl)ethan-1-one (**S8**, 38.6 mg, 0.257 mmol) to the procedure described above for the synthesis of **3a** with purification by flash chromatography (25 mL of SiO_2, 3–5% EtOAc in hexanes gradient elution) afforded **3j** (47.2 mg, 0.196 mmol, 76%) as a colorless oil that was a 4.6:1 mixture of isomers: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.31 (t, *J* = 8.0 Hz, 2H), 7.21 (d, *J* = 7.7 Hz, 2H), 6.99 (t, *J* = 7.3 Hz, 1H), 3.50 and 2.86 (2q, *J* = 8.6 and 8.0 Hz, 1H), 3.38–3.32 and 3.08–3.01 (2m, 1H), 2.12 and 2.10 (2s, 3H), 2.07–1.90 (m, 3H), 1.89–1.81 (m, 2H), 1.76 (d, *J* = 2.4 Hz, 3H), 1.68–1.61 (m, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 163.3 and 162.4, 159.7 and 159.5, 129.2 (2C), 121.8 and 121.5, 114.9 and 114.6 (2C), 80.5 and 79.7, 78.4, 49.9 and 43.4, 34.4, 33.4 and 33.2, 27.3 and 26.8, 23.6 and 23.5, 19.2 and 15.3, 3.6; IR (film) ν_{max} 2960, 2871, 1595, 1490, 1214, 1159 cm^{-1}; HRMS (ESI) *m/z* 242.1526 (MH^+, $C_{16}H_{19}NOH^+$ requires 242.1545).

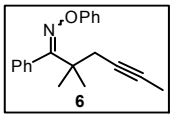


1-(2-(Prop-1-yn-1-yl)cyclohexyl)ethan-1-one *O*-phenyl oxime (3k). Subjection of 1-(2-(prop-1-yn-1-yl)cyclohexyl)ethan-1-one[5] (31.0 mg, 0.189 mmol) to the procedure described above for the synthesis of **3a** with purification by flash chromatography (25 mL of SiO_2, 3–5% EtOAc in hexanes gradient elution) afforded **3k** (47.6 mg, 0.186 mmol, 99%) as a colorless oil that was a 6.7:1 mixture of isomers: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.30 (t, J = 7.4 Hz, 2H), 7.20 (d, J = 7.7 Hz, 2H), 6.98 (t, J = 7.2 Hz, 1H), 3.29 and 2.40 (2dt, J = 12.7, 3.3 Hz and 12.1, 3.3 Hz, 1H), 3.19 and 3.01 (2 br s, 1H), 2.07 (s, 3H), 1.94–1.87 (m, 2H), 1.82 (d, J = 2.4 Hz, 3H), 1.78–1.69 (m, 2H), 1.61–1.52 (m, 2H), 1.33–1.22 (m, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 163.4, 159.7, 129.2 and 129.1 (2C), 121.8 and 121.5, 114.9 and 114.7 (2C), 79.2, 79.0, 47.1 and 40.2, 32.1 and 32.0, 31.4 and 29.8, 25.8, 24.5, 21.5 and 21.3, 18.3 and 13.5, 3.6; IR (film) ν_{max} 2932, 2362, 1594, 1490, 1212, 1158, 1023 cm^{-1}; HRMS (ESI) *m/z* 256.1680 (MH^+, $C_{17}H_{21}NOH^+$ requires 256.1701).



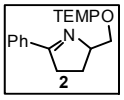
1-(2-(Prop-1-yn-1-yl)cycloheptyl)ethan-1-one *O*-phenyl oxime (3l). Subjection of 1-(2-(prop-1-yn-1-yl)cycloheptyl)ethan-1-one (**S11**, 31.6 mg, 0.177 mmol) to the procedure described above for the synthesis of **3a** with purification by flash chromatography (20 mL of SiO_2, 1–5% EtOAc in hexanes gradient elution) afforded **3l** (34.7 mg, 0.129 mmol, 73%) as a colorless oil that was a 5.7:1 mixture of isomers: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.30 (t, J = 7.9 Hz, 2H), 7.19 (d, J = 7.7 Hz, 2H), 6.99 (t, J = 7.3 Hz, 1H), 3.49–3.45 and 2.63–2.59 (2m, 1H), 3.09–3.05 and 3.02–2.96 (2m, 1H), 2.13 and 2.10 (2s, 3H), 2.02–1.89 (m, 2H), 1.84 (d, J = 2.4 Hz, 3H), 1.82–1.76 (m, 3H), 1.73–1.63 (m, 3H), 1.62–1.54 (m, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 165.9 and 164.9, 159.6 and 159.4, 129.2 (2C), 121.8 and 121.6, 114.8 (2C), 80.0 and

79.9, 79.3 and 79.0, 51.8 and 48.7, 34.4, 34.2, 28.0 and 27.4, 27.0 and 26.9, 26.3, 24.9 and 24.6, 17.8 and 13.2, 3.6; IR (film) ν_{max} 2924, 2360, 1594, 1489, 1213 cm^{-1}; HRMS (ESI) *m/z* 270.1875 (MH^+, $C_{18}H_{23}NOH^+$ requires 270.1858).



2,2-Dimethyl-1-phenylhex-4-yn-1-one *O*-phenyl oxime (6). Subjection of 2,2-dimethyl-1-phenylhex-4-yn-1-one[5] (35.4 mg, 0.177 mmol) to the procedure described above for the synthesis of **3a** with purification by flash chromatography (20 mL of SiO_2, 1–5% EtOAc in hexanes gradient elution) afforded **6** (34.5 mg, 0.118 mmol, 67%) as a colorless oil that was a single isomer of undetermined configuration about the C=N bond: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.46–7.39 (m, 3H), 7.28–7.18 (m, 4H), 7.09 (d, *J* = 7.7 Hz, 2H), 6.96 (t, *J* = 7.3 Hz, 1H), 2.39 (q, *J* = 2.4 Hz, 2H), 1.85 (t, *J* = 2.4 Hz, 3H), 1.33 (s, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 167.4, 159.6, 133.4, 129.0 (2C), 128.0, 127.9 (2C), 127.4 (2C), 121.7, 114.6 (2C), 78.3, 76.3, 41.5, 30.7, 25.8 (2C), 3.6; IR (film) ν_{max} 3059, 2970, 2919, 1594, 1490, 1213, cm^{-1}; HRMS (ESI) *m/z* 292.1679 (MH^+, $C_{20}H_{21}NOH^+$ requires 292.1701).

Iminyl radical cyclizations

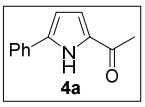


2,2,6,6-Tetramethyl-1-((5-phenyl-3,4-dihydro-2*H*-pyrrol-2-yl)methoxy)-piperidine (2). An oven-dried microwave reaction vessel was charged with 1-phenylpent-4-en-1-one *O*-phenyl oxime[7,8] (**1**, 21.6 mg, 0.0859 mmol, 1.0 equiv), TEMPO (20.1 mg, 0.129 mmol, 1.5 equiv), and trifluorotoluene (0.86 mL). The vessel was sealed under an Ar atmosphere and

[7] Portella-Cubillo, F.; Scott, J. S.; Walton, J. C. *Chem. Commum.* **2007**, 4041.

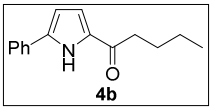
[8] Portella-Cubillo, F.; Scott, J. S.; Walton, J. C. *J. Org. Chem.* **2008**, *73*, 5558.

subjected to microwave irradiation (300 W) for 15 min at 98 ºC. The mixture was cooled to rt and concentrated *in vacuo*. Flash chromatography (10 mL of SiO_2, 0.5–5% MeOH in CH_2Cl_2 gradient elution) afforded **2** (24.4 mg, 0.0776 mmol, 90%) as a colorless oil: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.86 (d, *J* = 3.9 Hz, 2H), 7.46–7.38 (m, 3H), 4.45 (br s, 1H), 4.09 (dd, *J* = 8.7, 4.2 Hz, 1H), 3.98 (t, *J* = 5.1 Hz, 1H), 3.08–2.93 (m, 2H), 2.20–2.11 (m, 1H), 2.09–2.01 (m, 1H), 1.59–1.34 (m, 6H), 1.22 (s, 3H), 1.16 (s, 3H), 1.11 (s, 3H), 0.95 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 173.5, 134.7, 130.3, 128.4 (2C), 127.7 (2C), 79.1, 72.3, 59.9 (2C), 39.6, 35.4 (2C), 33.2, 33.0, 25.9, 20.3, 20.0, 17.1; IR (film) ν_{max} 2931, 1616, 1450, 1373, cm^{-1}; HRMS (ESI) *m/z* 315.2461 (MH^+, $C_{20}H_{30}N_2OH^+$ requires 315.2436).



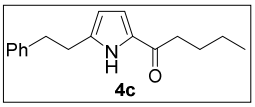
4a

1-(5-Phenyl-1*H*-pyrrol-2-yl)ethan-1-one (4a). An oven-dried microwave reaction vessel was charged with *O*-phenyl oxime **3a** (20.4 mg, 0.0775 mmol), TEMPO (18.2 mg, 0.116 mmol, 1.5 equiv), and trifluorotoluene (0.8 mL). The vessel was sealed under an Ar atmosphere and subjected to microwave irradiation (300 W) for 30 min at 98 ºC. The mixture was treated with additional TEMPO (18.2 mg, 0.116 mmol, 1.5 equiv) and irradiated by microwaves for 30 additional min at 98 °C. The mixture was then cooled to rt and concentrated *in vacuo*. Flash chromatography (15 mL of SiO_2, 5–20% EtOAc in hexanes gradient elution) afforded **4a** (11.9 mg, 0.0642 mmol, 83%) as a colorless powder: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 9.53 (br s, 1H), 7.60 (d, *J* = 8.0 Hz, 2H), 7.44 (t, *J* = 7.7 Hz, 2H), 7.34 (t, *J* = 7.4 Hz, 1H), 6.97 (dd, *J* = 3.1, 2.4 Hz, 1H), 6.58 (dd, *J* = 3.3, 2.8 Hz, 1H), 2.47 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 187.6, 138.2, 132.5, 130.9, 129.1 (2C), 128.2, 125.0 (2C), 118.2, 108.3, 25.3; IR (film) ν_{max} 3300, 2360, 1634, 1470, 1273 cm^{-1}; HRMS (ESI) *m/z* 186.0898 (MH^+, $C_{12}H_{11}NOH^+$ requires 186.0919).



4b

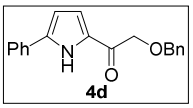
1-(5-phenyl-1*H*-pyrrol-2-yl)pentan-1-one (4b). An oven-dried microwave reaction vessel was charged with *O*-phenyl oxime **3b** (17.6 mg, 0.0576 mmol), TEMPO (27.0 mg, 0.173 mmol, 3.0 equiv), and trifluorotoluene (0.6 mL). The vessel was sealed under an Ar atmosphere and subjected to microwave irradiation (300 W) for 30 min at 98 ºC. The mixture was cooled to rt and concentrated *in vacuo*. Flash chromatography (8 mL of SiO_2, 5–20% EtOAc in hexanes gradient elution) afforded **4b** (9.9 mg, 0.044 mmol, 76%) as a white powder: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 9.43 (br s, 1H), 7.59 (d, *J* = 7.3 Hz, 2H), 7.44 (t, *J* = 7.7 Hz, 2H), 7.34 (t, *J* = 7.4 Hz, 1H), 6.97 (dd, *J* = 4.0, 2.4 Hz, 1H), 6.58 (dd, *J* = 4.2, 2.9 Hz, 1H), 2.79 (t, *J* = 7.6 Hz, 2H), 1.74 (p, *J* = 7.6 Hz, 2H), 1.43 (h, J = 7.4 Hz, 2H), 0.97 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 190.9, 137.9, 132.4, 131.0, 129.1 (2C), 128.1, 124.9 (2C), 117.4, 108.2, 37.6, 27.6, 22.6, 13.9; IR (film) ν_{max} 3322, 2360, 1638 cm^{-1}; HRMS (ESI) *m/z* 228.1382 (MH^+, $C_{15}H_{17}NOH^+$ requires 228.1388).



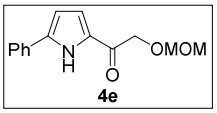
4c

1-(5-Phenethyl-1*H*-pyrrol-2-yl)pentan-1-one (4c). Subjection of *O*-phenyl oxime **3c** (11.7 mg, 0.0351 mmol) to the procedure described above for the synthesis of **4b** with purification by flash chromatography (8 mL of SiO_2, 5–20% EtOAc in hexanes gradient elution) afforded **4c** (8.2 mg, 0.032 mmol, 92%) as a yellow powder: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.98 (br s, 1H), 7.31 (t, *J* = 7.4 Hz, 2H), 7.23 (t, *J* = 7.3 Hz, 1H), 7.18 (d, *J* = 7.1 Hz, 2H), 6.82 (dd, *J* = 3.7, 2.6 Hz, 1H), 6.01 (t, *J* = 3.2 Hz, 1H), 2.96 (s, 4H), 2.71 (t, *J* = 7.6 Hz, 2H), 1.69 (p, *J* = 7.6 Hz, 2H), 1.39 (h, *J* = 7.5 Hz, 2H), 0.94 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 190.4, 140.7, 139.2, 131.0, 128.6 (2C), 128.3 (2C), 126.4, 116.7, 108.6,

37.4, 35.4, 29.7, 27.6, 22.6, 13.9; IR (film) ν_{max} 3261, 2951, 2359, 1623, 1496, 1203, 1054 cm^{-1}; HRMS (ESI) *m/z* 256.1711 (MH^+, $C_{17}H_{21}NOH^+$ requires 256.1701).

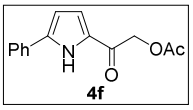


2-(Benzyloxy)-1-(5-phenyl-1*H*-pyrrol-2-yl)ethan-1-one (4d). Subjection of *O*-phenyl oxime **3d** (11.3 mg, 0.0306 mmol) to the procedure described above for the synthesis of **4a** with purification by flash chromatography (5 mL of SiO_2, 5–20% EtOAc in hexanes gradient elution) afforded **4d** (4.7 mg, 0.016 mmol, 53%) and **5** (1.4 mg, 0.0032 mmol, 11%). For **4d**: yellow powder, ^1H NMR ($CDCl_3$, 500 MHz) δ 9.68 (br s, 1H), 7.55 (d, *J* = 7.5 Hz, 2H), 7.46–7.37 (m, 6H), 7.34 (t, *J* = 7.4 Hz, 2H), 7.10 (dd, *J* = 3.1, 2.4 Hz, 1H), 6.58 (dd, *J* = 3.3, 2.7 Hz, 1H), 4.71 (s, 2H), 4.56 (s, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 186.2, 137.2, 130.7, 129.1 (3C), 128.6 (2C), 128.3, 128.1 (4C), 125.0 (2C), 118.5, 108.6, 77.2, 73.6; IR (film) ν_{max} 3315, 2923, 2359, 1653, 1265, 1078, 1018 cm^{-1}; HRMS (ESI) *m/z* 292.1345 (MH^+, $C_{19}H_{17}NO_2H^+$ requires 292.1338). For **5**: ^1H NMR ($CDCl_3$, 500 MHz) δ 8.00 (d, *J* = 6.7 Hz, 2H), 7.50–7.41 (m, 5H), 7.37 (t, *J* = 7.5 Hz, 2H), 7.34–7.31 (m, 1H), 5.11 (s, 2H), 4.97 (s, 2H), 3.06 (t, *J* = 7.0 Hz, 2H), 2.81 (t, *J* = 6.8 Hz, 2H), 1.50–1.41 (m, 4H), 1.35–1.30 (m, 2H), 1.15 (s, 6H), 1.13 (s, 6H); HRMS (ESI) *m/z* 433.2875 (MH^+, $C_{28}H_{36}N_2O_2H^+$ requires 433.2855).



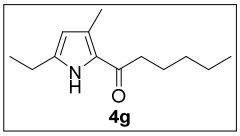
2-(Methoxymethoxy)-1-(5-phenyl-1*H*-pyrrol-2-yl)ethan-1-one (4e). Subjection of *O*-phenyl oxime **3e** (10.2 mg, 0.0315 mmol) to the procedure described above for the synthesis of **4b** with purification by flash chromatography (12 mL of SiO_2, 0–5% MeOH in CH_2Cl_2 gradient elution) afforded **4e** (4.8 mg, 0.020 mmol, 62%) as a white film: ^1H NMR ($CDCl_3$, 500 MHz) δ 9.60 (br s, 1H), 7.61 (d, *J* = 7.2 Hz, 2H), 7.45 (t, *J* = 7.7 Hz, 2H), 7.36 (t, *J*

= 7.4 Hz, 1H), 7.06 (dd, *J* = 4.2, 2.4 Hz, 1H), 6.60 (dd, *J* = 4.2, 2.7 Hz, 1H), 4.81 (s, 2H), 4.67 (s, 2H), 3.45 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 185.6, 138.6, 130.7, 130.0, 129.2 (2C), 128.4, 125.0 (2C), 118.0, 108.6, 96.7, 69.1, 55.8; IR (film) ν_{max} 3307, 2943, 2360, 1649, 1469, 1042 cm^{-1}; HRMS (ESI) *m/z* 246.1141 (MH^+, $C_{14}H_{15}NO_3H^+$ requires 246.1130).



4f

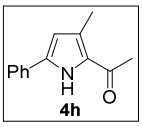
2-Oxo-2-(5-phenyl-1*H*-pyrrol-2-yl)ethyl acetate (4f). Subjection of *O*-phenyl oxime **3f** (11.9 mg, 0.0370 mmol) to the procedure described above for the synthesis of **4b** with purification by flash chromatography (12 mL of SiO_2, 10–30% EtOAc in hexanes gradient elution) afforded **4f** (8.3 mg, 0.034 mmol, 92%) as a yellow powder: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 9.47 (br s, 1H), 7.59 (d, *J* = 7.3 Hz, 2H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.37 (t, *J* = 7.4 Hz, 1H), 7.03 (dd, *J* = 3.9, 2.4 Hz, 1H), 6.61 (dd, *J* = 3.8, 2.7 Hz, 1H), 5.15 (s, 2H), 2.24 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 182.3, 170.5, 139.0, 130.6, 129.22, 129.20 (2C), 128.6, 125.1 (2C), 117.8, 108.7, 65.0, 20.7; IR (film) ν_{max} 3303, 1744, 1645, 1228 cm^{-1}; HRMS (ESI) *m/z* 244.0954 (MH^+, $C_{14}H_{13}NO_3H^+$ requires 244.0974).



4g

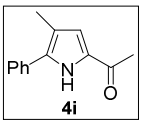
1-(5-Ethyl-3-methyl-1*H*-pyrrol-2-yl)hexan-1-one (4g). Subjection of *O*-phenyl oxime **3g** (16.4 mg, 0.0575 mmol) to the procedure described above for the synthesis of **4b** with purification by flash chromatography (10 mL of SiO_2, 5–20% EtOAc in hexanes gradient elution) afforded **4g** (9.7 mg, 0.047 mmol, 81%) as a yellow powder: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.97 (br s, 1H), 5.85 (d, *J* = 2.7 Hz, 1H), 2.70 (t, *J* = 7.6 Hz, 2H), 2.60 (q, *J* = 7.6 Hz, 2H), 2.37 (s, 3H), 1.77–1.69 (m, 2H), 1.40–1.34 (m, 4H), 1.25 (t, *J* = 7.7 Hz, 3H), 0.92 (t, *J* = 5.9 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 190.0, 139.9, 128.2, 127.4, 111.0, 39.5, 31.8,

24.4, 22.6, 20.8, 14.5, 14.0, 13.1; IR (film) ν_{max} 3269, 2953, 2360, 1619, 1491 cm^{-1}; HRMS (ESI) *m/z* 208.1715 (MH^+, $C_{13}H_{21}NOH^+$ requires 208.1701).



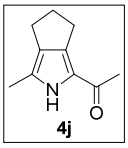
4h

1-(3-Methyl-5-phenyl-1*H*-pyrrol-2-yl)ethan-1-one (4h). Subjection of *O*-phenyl oxime **3h** (12.5 mg, 0.0451 mmol) to the procedure described above for the synthesis of **4b** with purification by flash chromatography (12 mL of SiO_2, 5–20% EtOAc in hexanes gradient elution) afforded **4h** (8.8 mg, 0.044 mmol, 98%) as a colorless powder: ^1H NMR ($CDCl_3$, 500 MHz) δ 9.35 (br s, 1H), 7.56 (d, *J* = 7.7 Hz, 2H), 7.42 (t, *J* = 7.7 Hz, 2H), 7.32 (t, *J* = 7.4 Hz, 1H), 6.42 (d, *J* = 2.8 Hz, 1H), 2.49 (s, 3H), 2.44 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 187.4, 136.2, 130.9, 130.1, 129.1 (2C), 128.6, 128.1, 124.8 (2C), 111.2, 27.9, 14.5; IR (film) ν_{max} 3311, 2360, 1636, 1448, 1271 cm^{-1}; HRMS (ESI) *m/z* 200.1053 (MH^+, $C_{13}H_{13}NOH^+$ requires 200.1075).

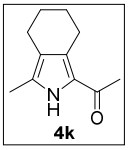


4i

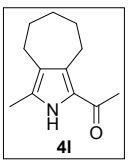
1-(4-Methyl-5-phenyl-1*H*-pyrrol-2-yl)ethan-1-one (4i). Subjection of *O*-phenyl oxime **3i** (12.7 mg, 0.0458 mmol) to the procedure described above for the synthesis of **4b** with purification by flash chromatography (12 mL of SiO_2, 10–20% EtOAc in hexanes gradient elution) afforded **4i** (8.0 mg, 0.040 mmol, 88%) as a white powder: ^1H NMR ($CDCl_3$, 500 MHz) δ 9.17 (br s, 1H), 7.51 (d, *J* = 7.2 Hz, 2H), 7.46 (t, *J* = 7.7 Hz, 2H), 7.36 (t, *J* = 7.3 Hz, 1H), 6.82 (d, *J* = 2.3 Hz, 1H), 2.44 (s, 3H), 2.29 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 187.4, 135.2, 131.9, 130.7, 128.9 (2C), 127.8, 127.0 (2C), 119.5, 118.7, 25.2, 12.5; IR (film) ν_{max} 3307, 1461, 1263, 1184 cm^{-1}; HRMS (ESI) *m/z* 200.1065 (MH^+, $C_{13}H_{13}NOH^+$ requires 200.1075).



1-(3-Methyl-2,4,5,6-tetrahydrocyclopenta[c]pyrrol-1-yl)ethan-1-one (4j). Subjection of *O*-phenyl oxime **3j** (20.2 mg, 0.0837 mmol) to the procedure described above for the synthesis of **4a** with purification by flash chromatography (10 mL of SiO_2, 5–20% EtOAc in hexanes gradient elution) afforded **4j** (7.0 mg, 0.0429 mmol, 51%) as a yellow powder: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.69 (br s, 1H), 2.88 (t, *J* = 7.3 Hz, 2H), 2.58 (t, *J* = 7.2 Hz, 2H), 2.40 (p, *J* = 7.2 Hz, 2H), 2.33 (s, 3H), 2.21 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 186.0, 139.6, 130.5, 127.6, 123.5, 30.8, 27.7, 26.2, 24.3, 12.2; IR (film) ν_{max} 3242, 2955, 1624, 1278, 1069 cm^{-1}; HRMS (ESI) *m/z* 164.1102 (MH^+, $C_{10}H_{13}NOH^+$ requires 164.1075).

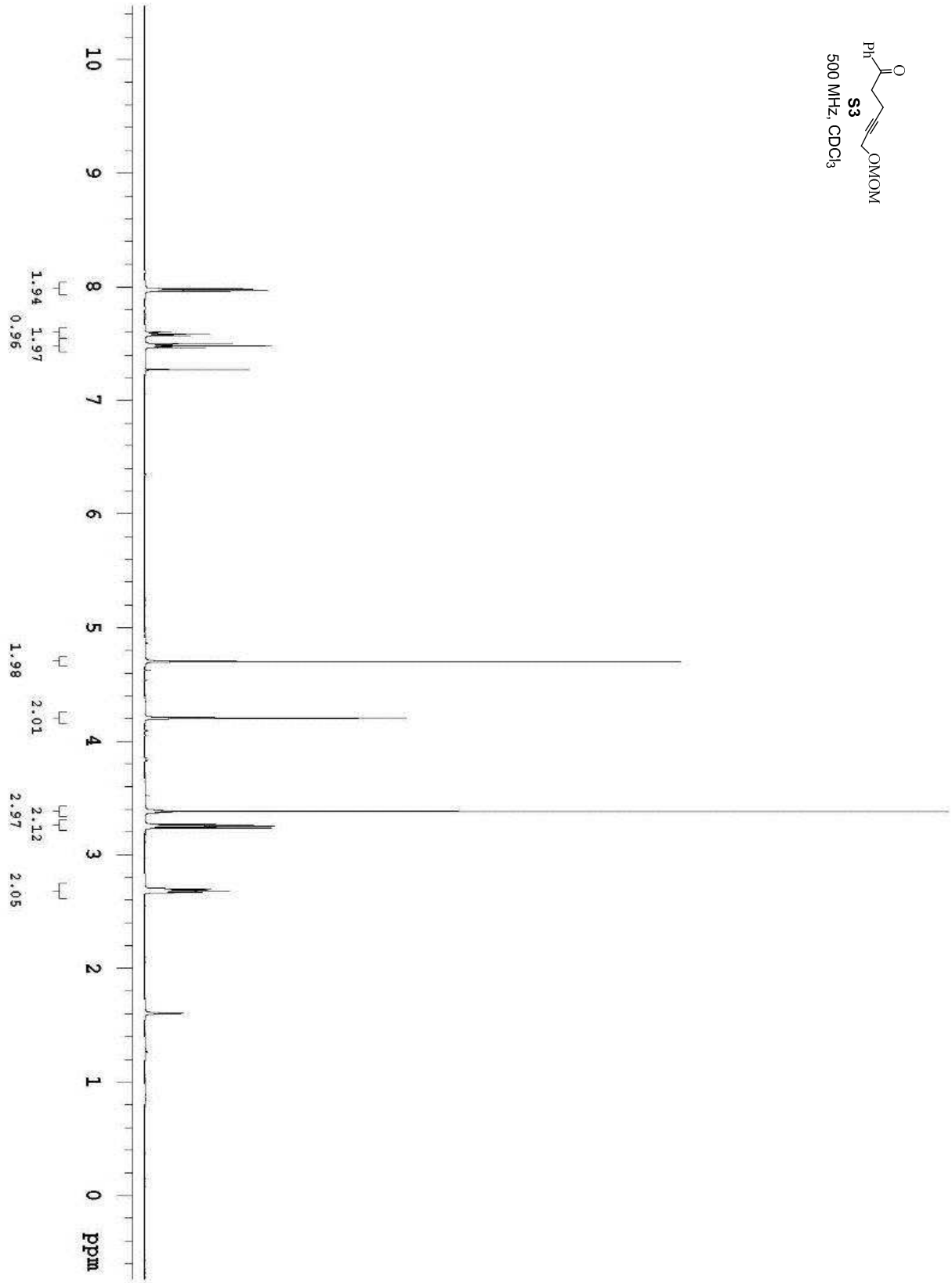


1-(3-Methyl-4,5,6,7-tetrahydro-2*H*-isoindol-1-yl)ethan-1-one (4k). Subjection of *O*-phenyl oxime **3k** (25.3 mg, 0.0991 mmol) to the procedure described above for the synthesis of **4b** with purification by flash chromatography (10 mL of SiO_2, 5–20% EtOAc in hexane gradient elution) afforded **4k** (16.5 mg, 0.0931 mmol, 94%) as a white powder: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.98 (br s, 1H), 2.81 (t, *J* = 6.2 Hz, 2H), 2.42 (t, *J* = 6.1 Hz, 2H), 2.36 (s, 3H), 2.17 (s, 3H), 1.84–1.71 (m, 4H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 186.0, 130.9, 128.7, 126.7, 119.8, 27.5, 24.3, 23.4, 23.0, 21.3, 11.2; IR (film) ν_{max} 3269, 2939, 1613, 1434, 1277 cm^{-1}; HRMS (ESI) *m/z* 178.1232 (MH^+, $C_{11}H_{15}NOH^+$ requires 178.1232).



1-(3-Methyl-2,4,5,6,7,8-hexahydrocyclohepta[c]pyrrol-1-yl)ethan-1-one (4l). Subjection of *O*-phenyl oxime **3l** (11.7 mg, 0.0434 mmol) to the procedure described above for

the synthesis of **4b** with purification by flash chromatography (12 mL of SiO_2, 10–20% EtOAc in hexanes gradient elution) afforded **4l** (7.9 mg, 0.041 mmol, 95%) as a yellow powder: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.67 (br s, 1H), 2.91 (t, J = 5.4 Hz, 2H), 2.49 (t, J = 5.6 Hz, 2H), 2.45 (s, 3H), 2.19 (s, 3H), 1.88–1.82 (m, 2H), 1.72–1.66 (m, 2H), 1.63–1.54 (m, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 186.8, 133.7, 130.3, 126.5, 125.2, 32.8, 28.7, 28.4, 28.1, 27.5, 25.8, 11.3; IR (film) ν_{max} 3311, 2918, 2360, 2342, 1616, 1496, 1420, 1273 cm^{-1}; HRMS (ESI) *m/z* 192.1386 (MH^+, $C_{12}H_{17}NOH^+$ requires 192.1388).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9
8
7
6
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4
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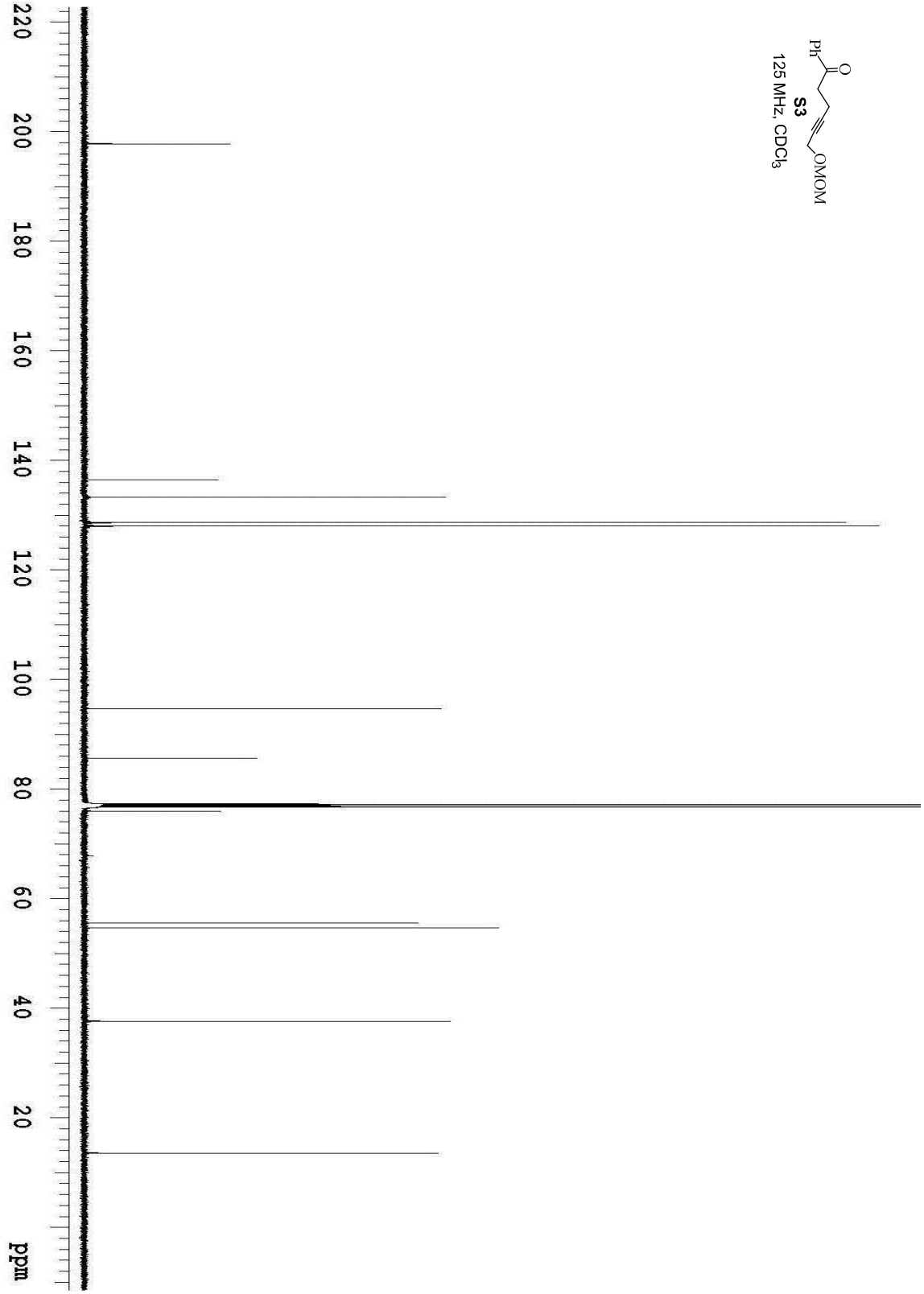
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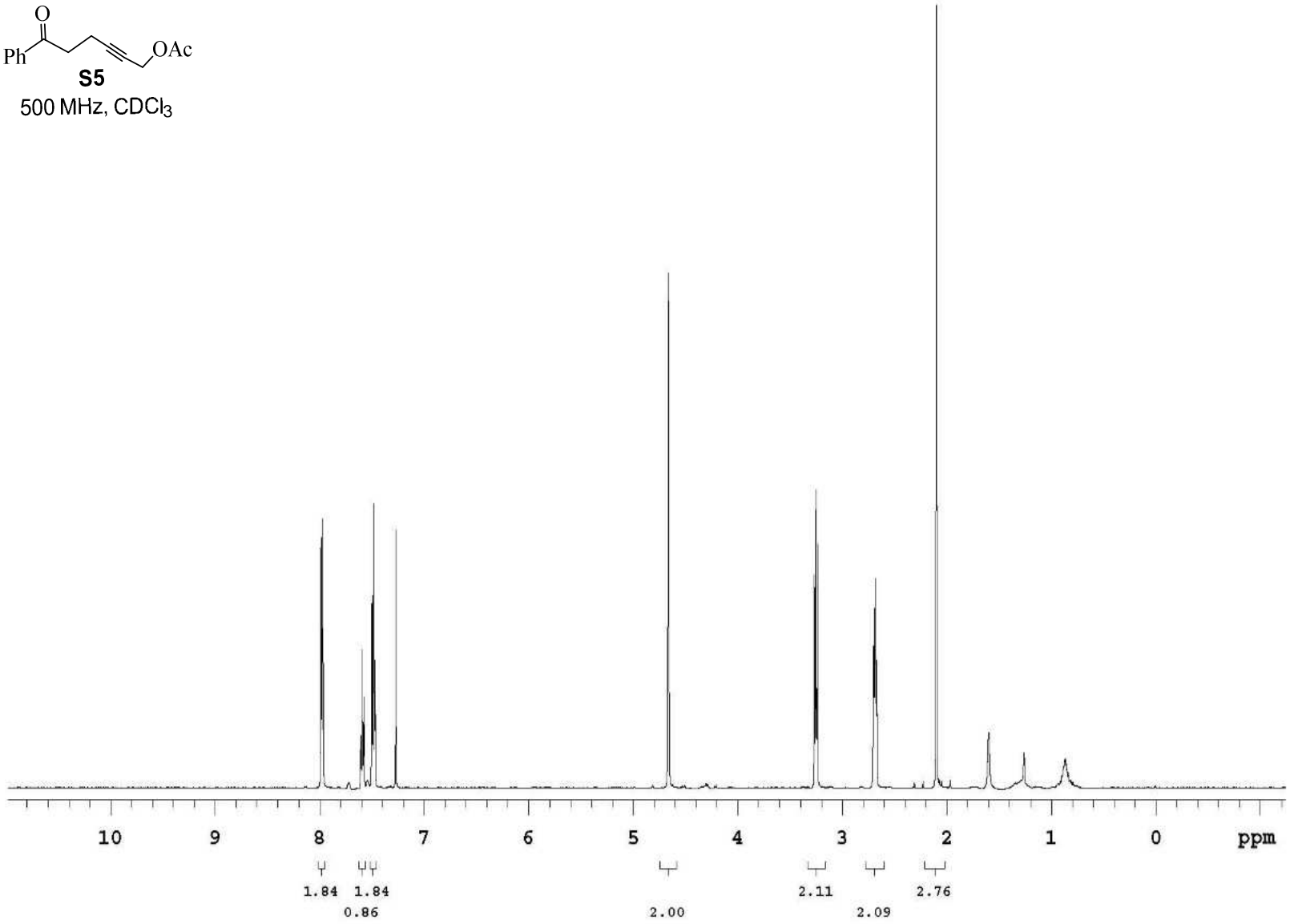
ppm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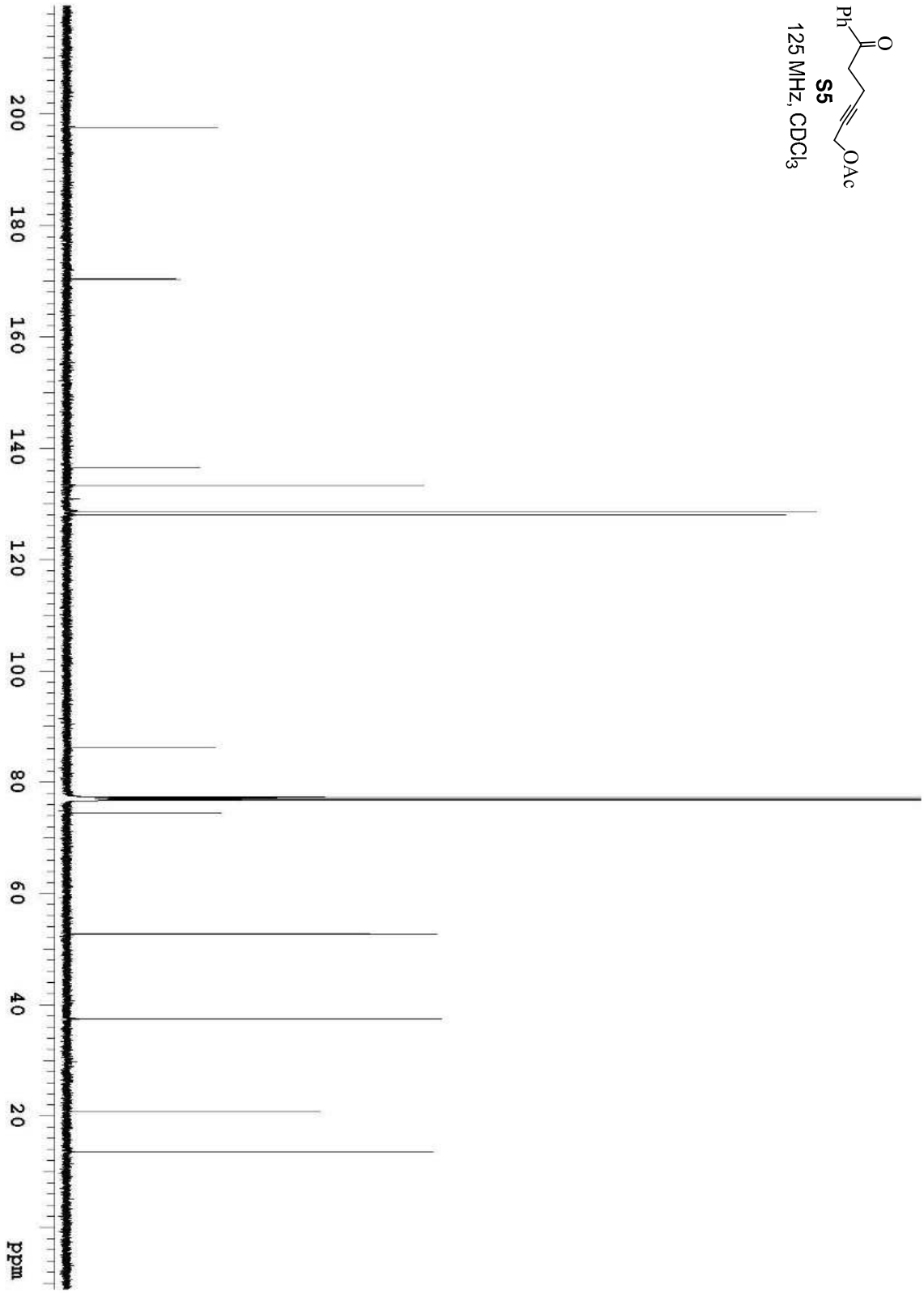
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140
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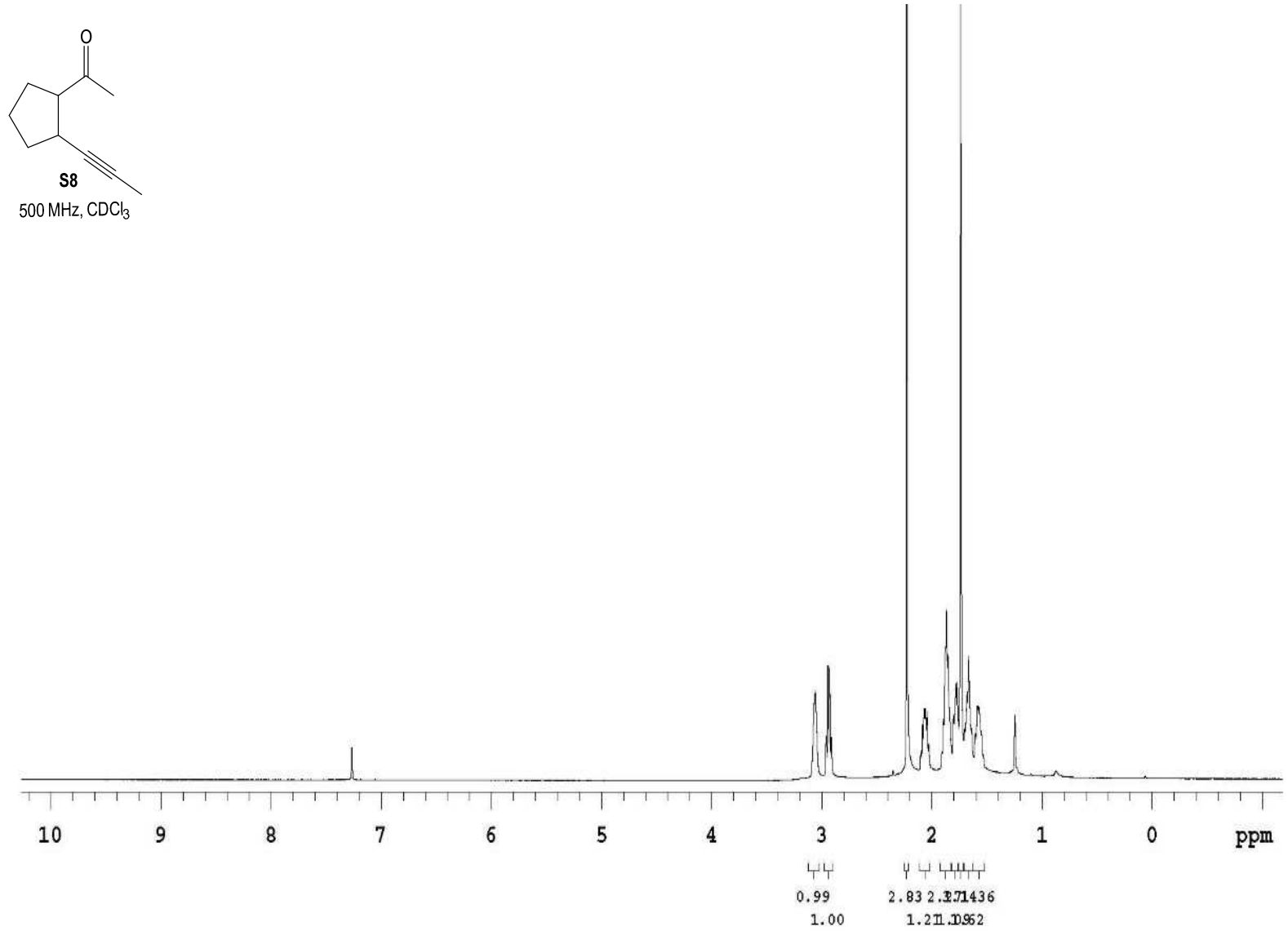
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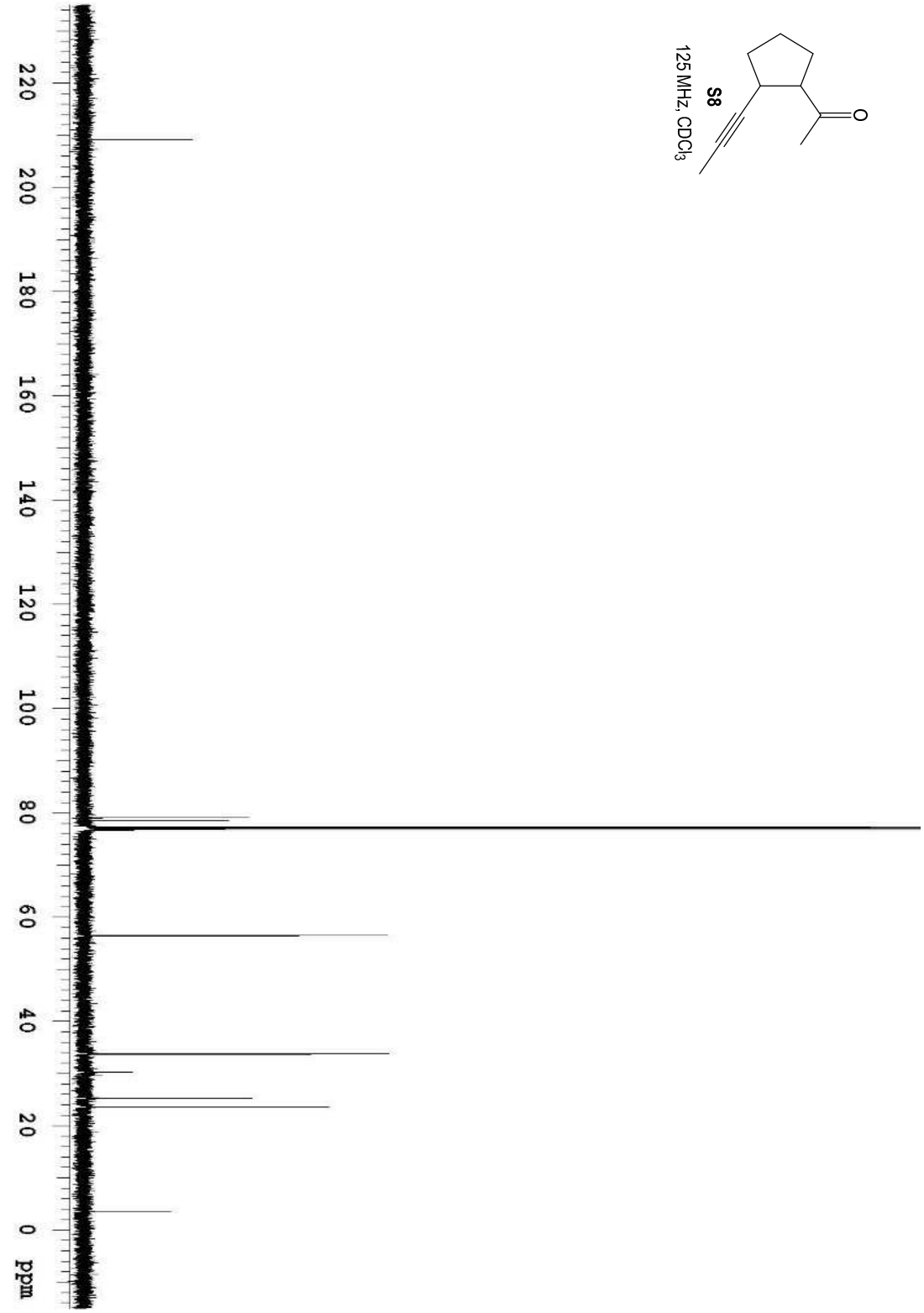
2.83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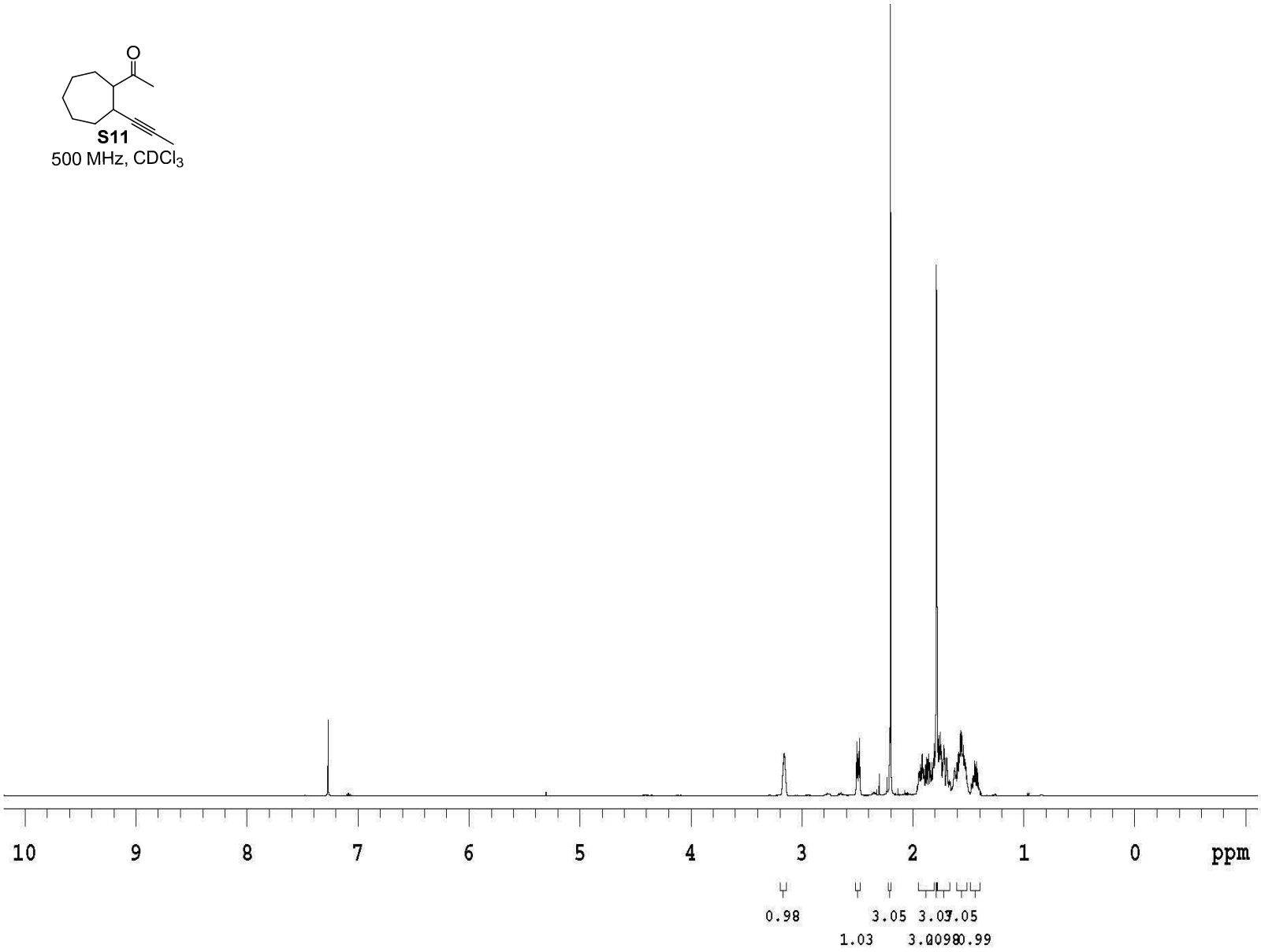
O
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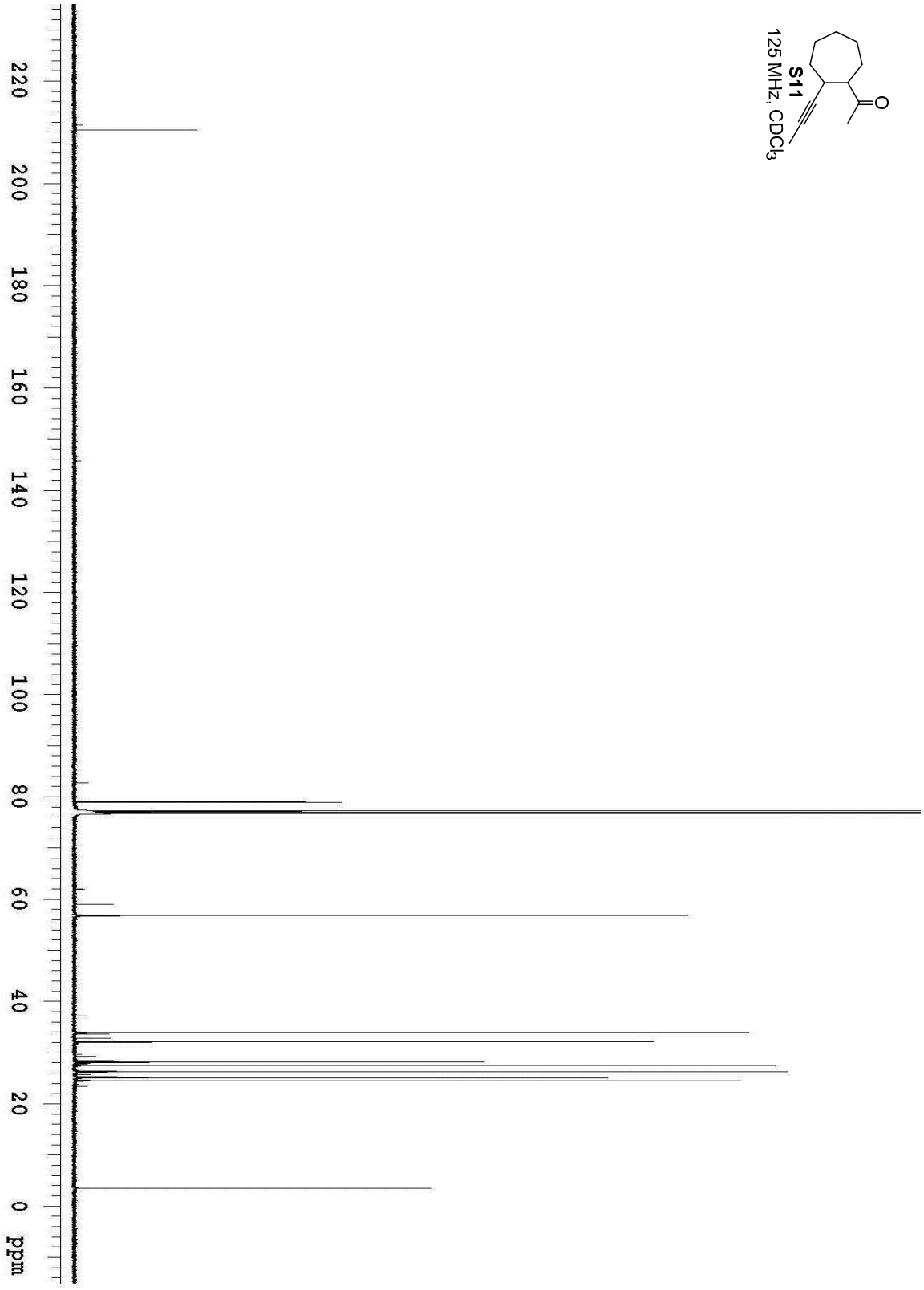
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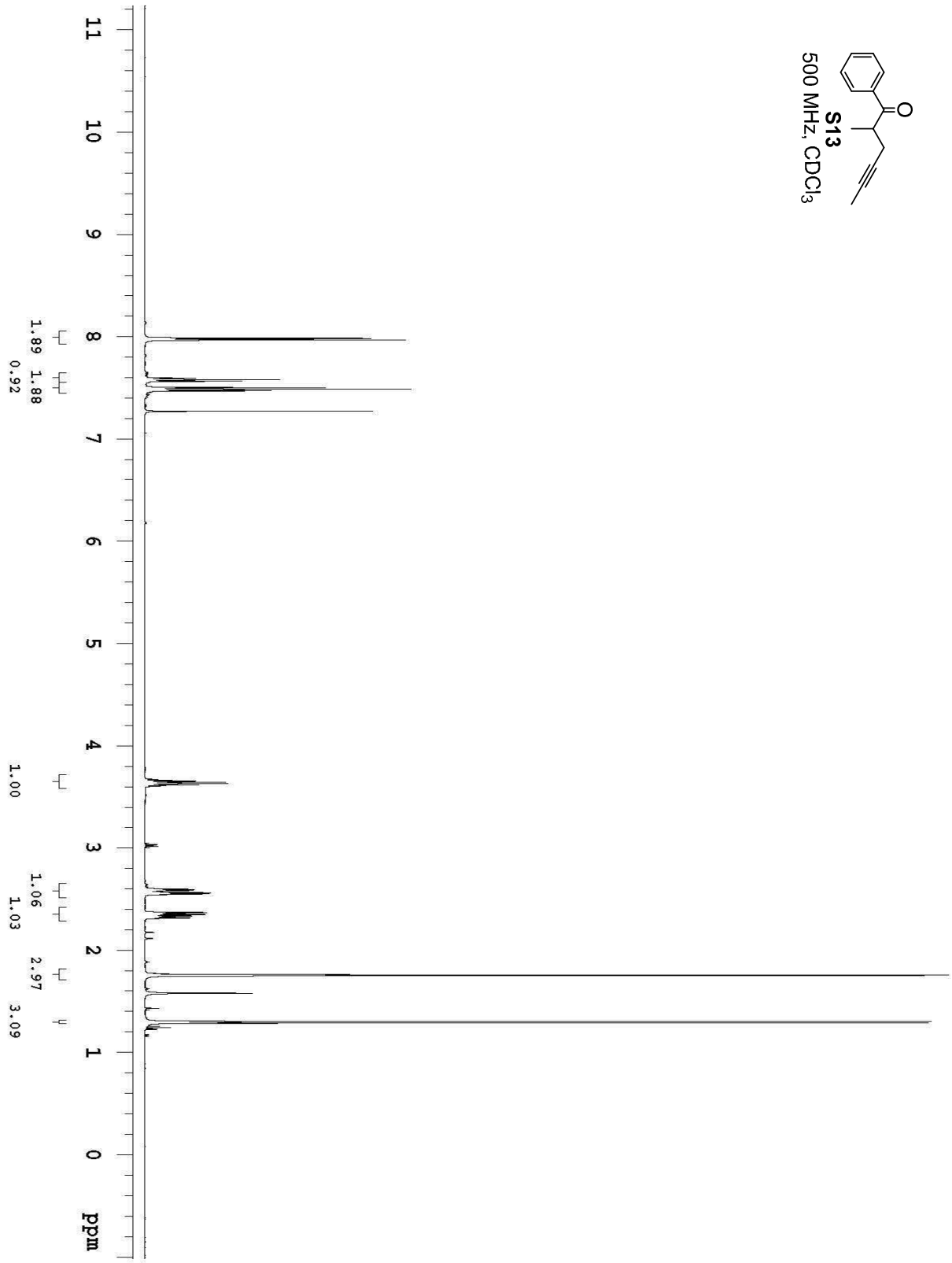
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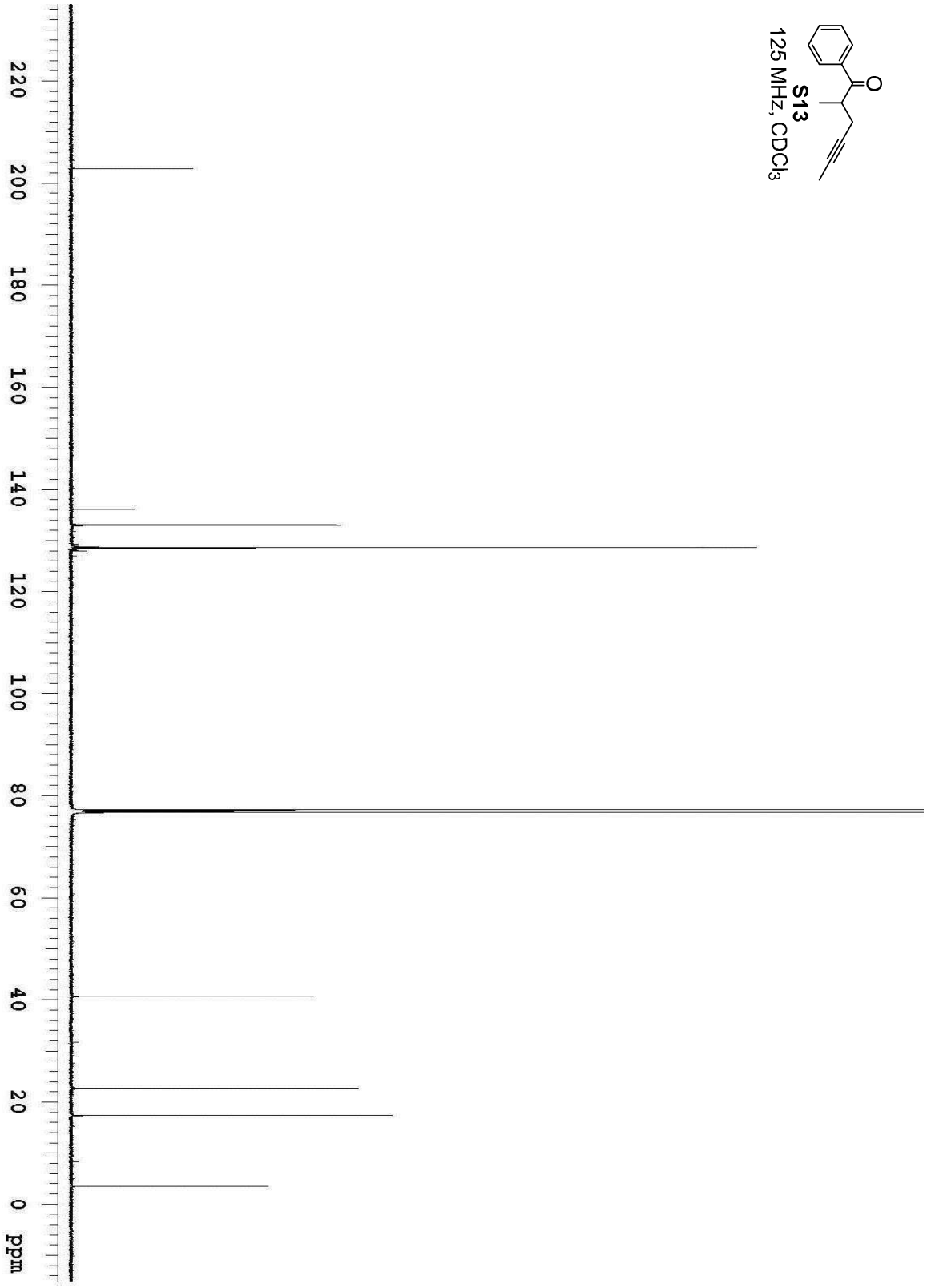
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125 MHz, CDCl3
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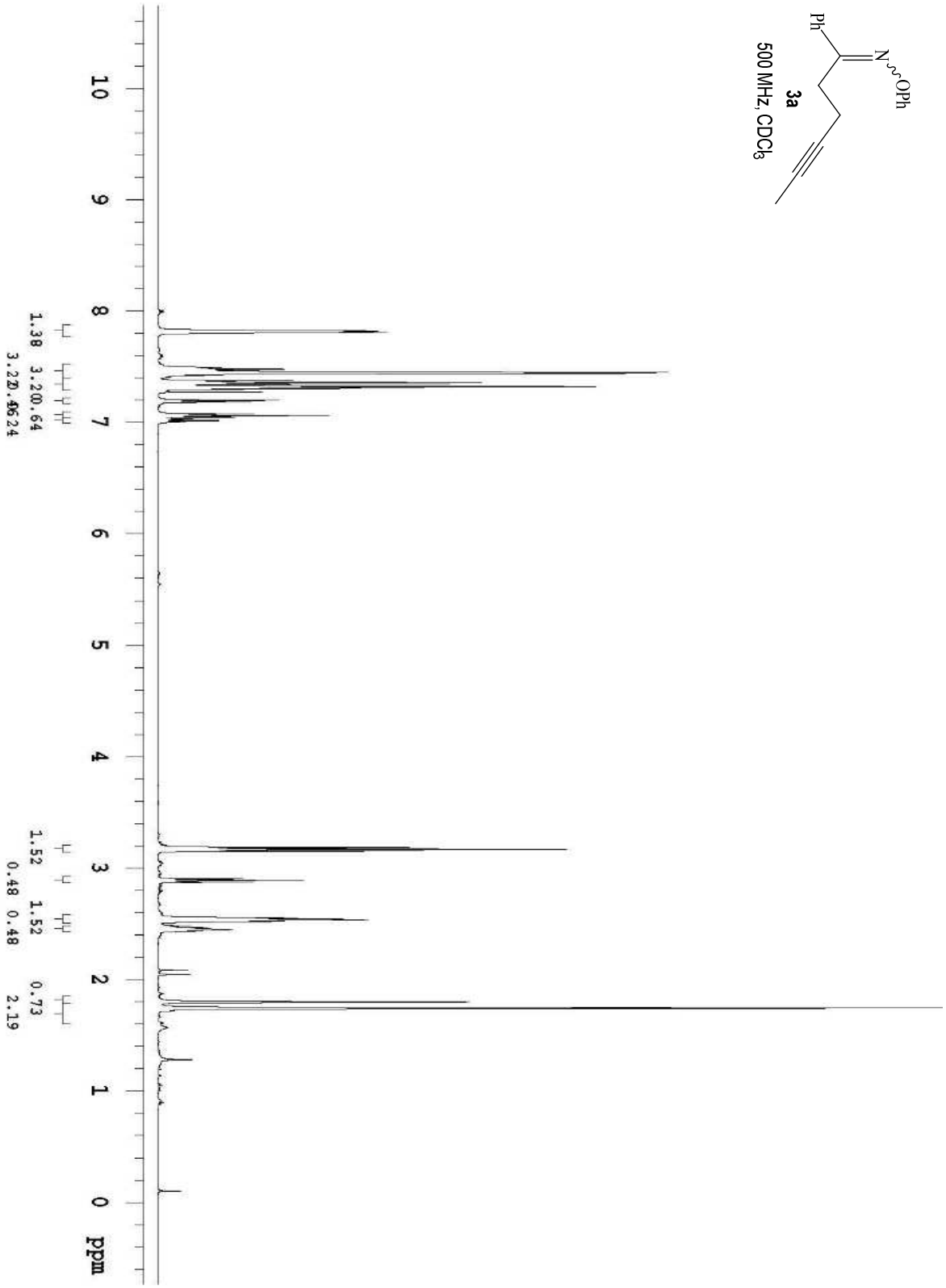
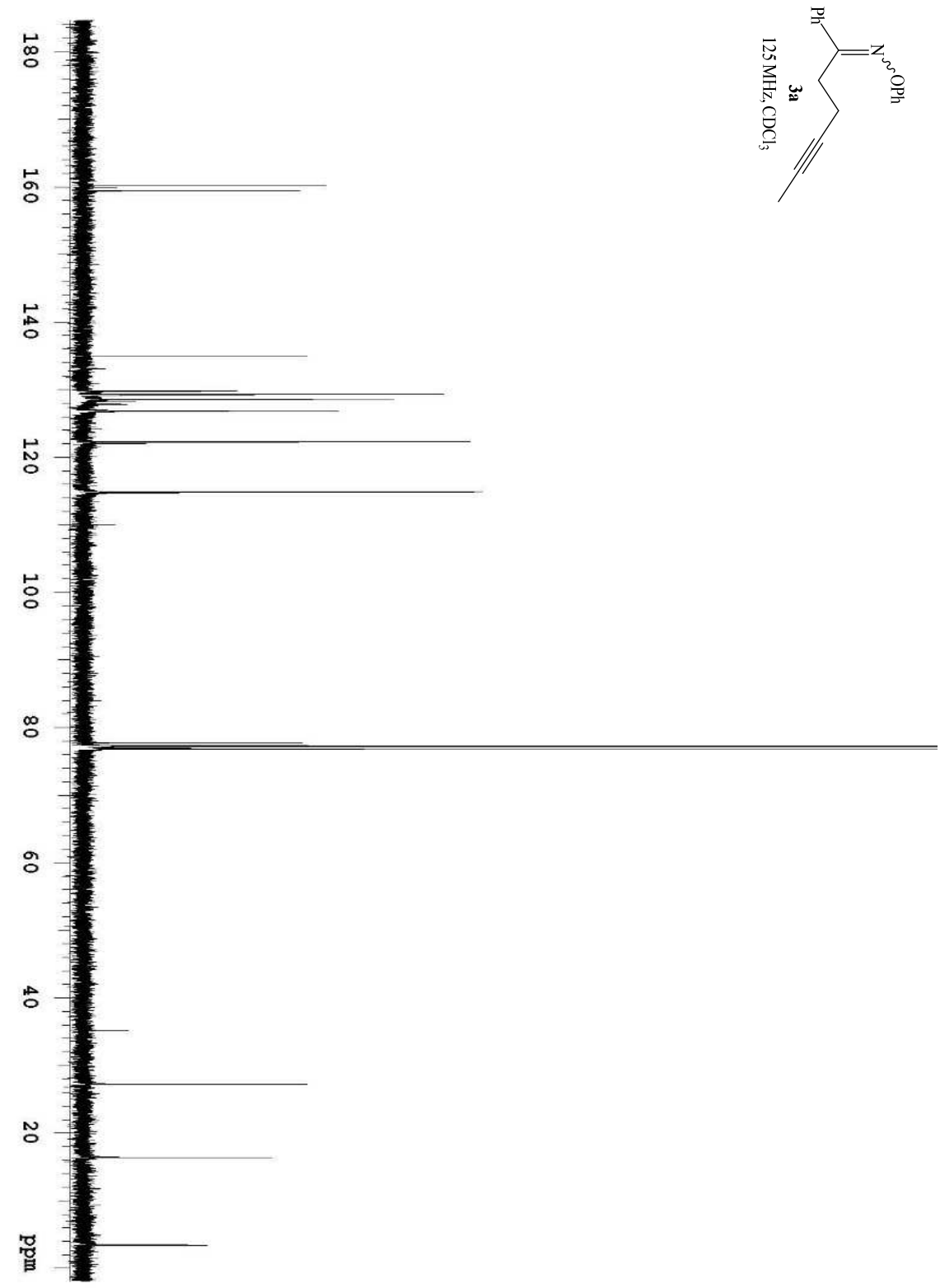
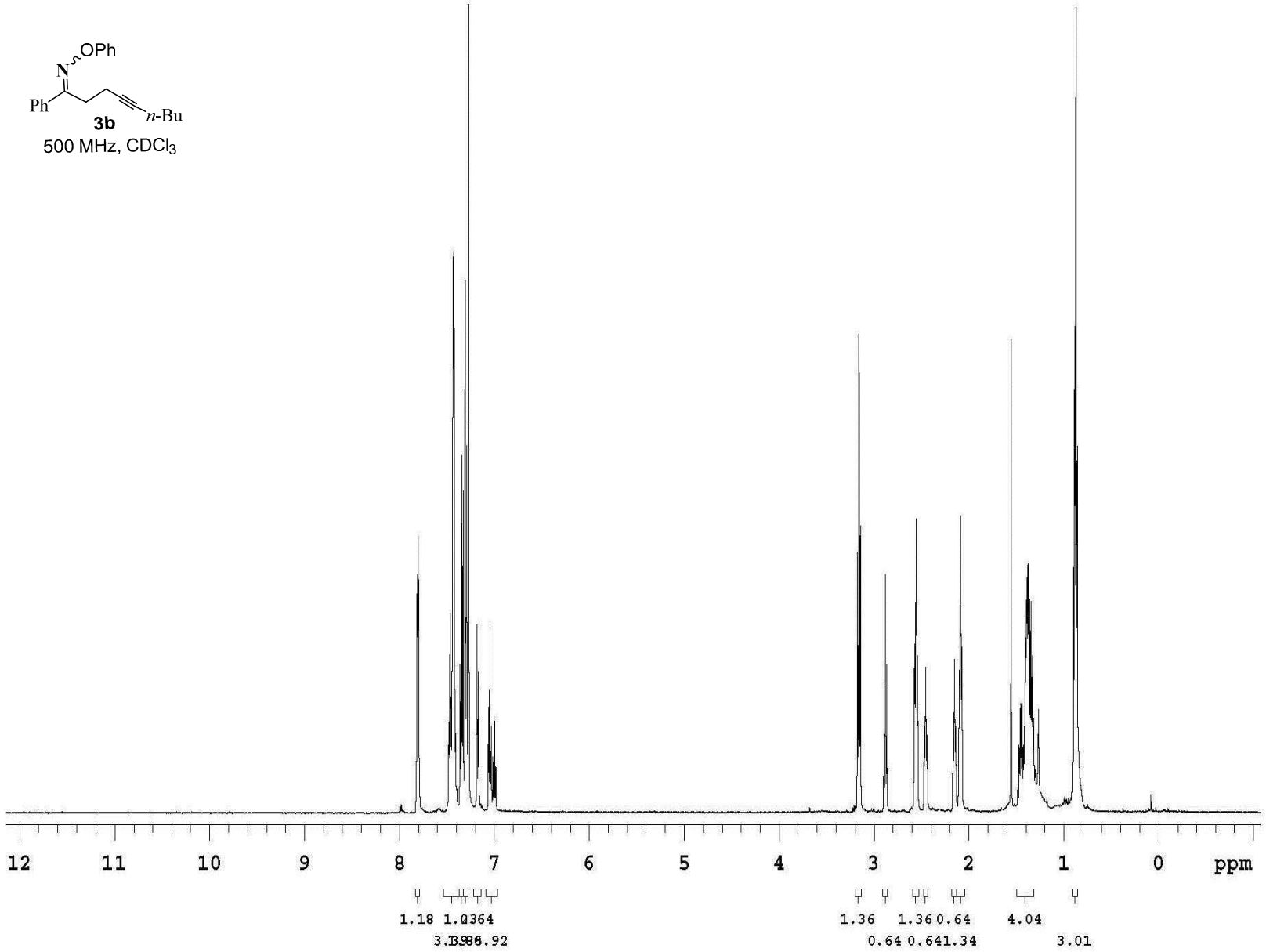
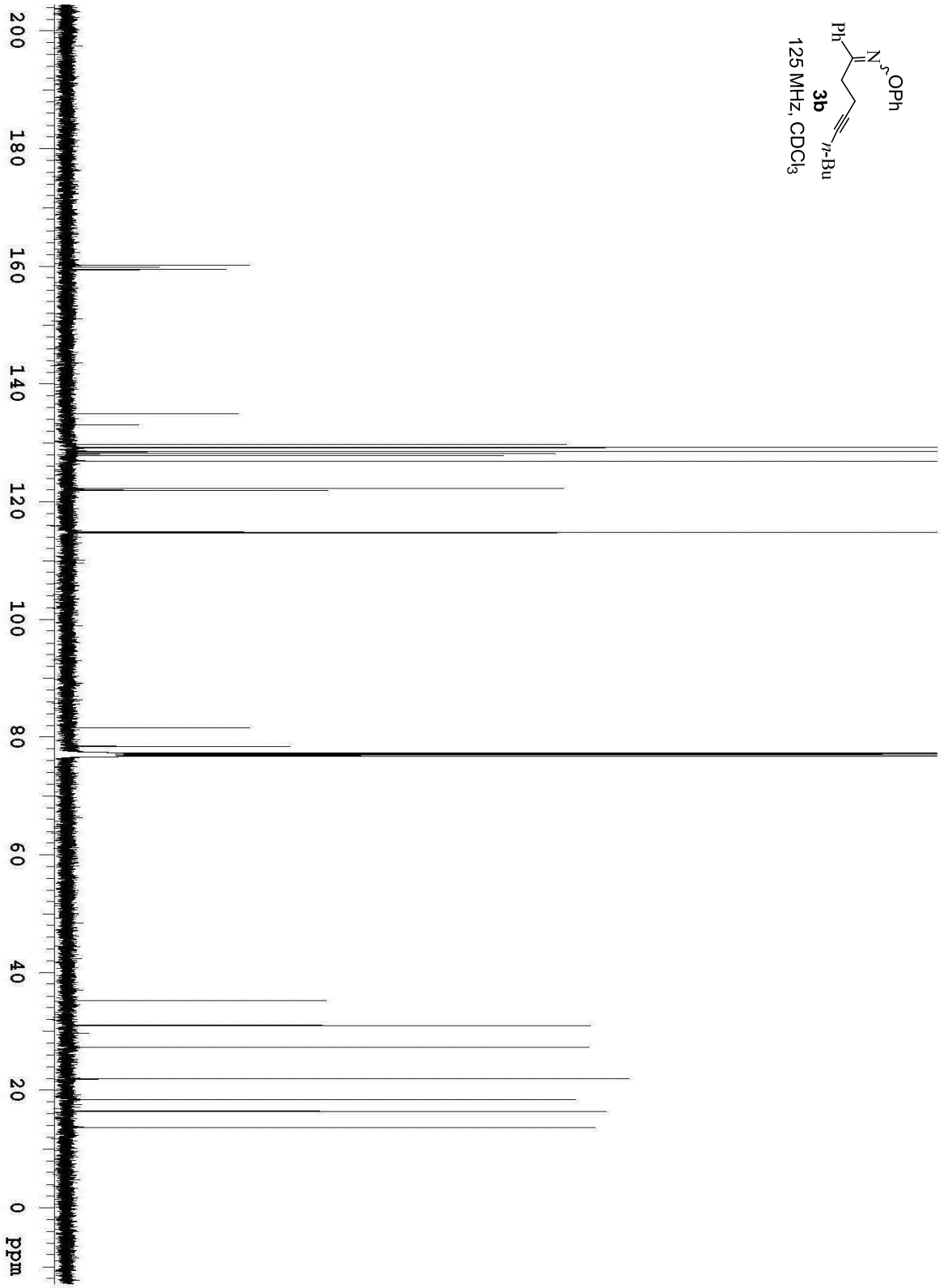
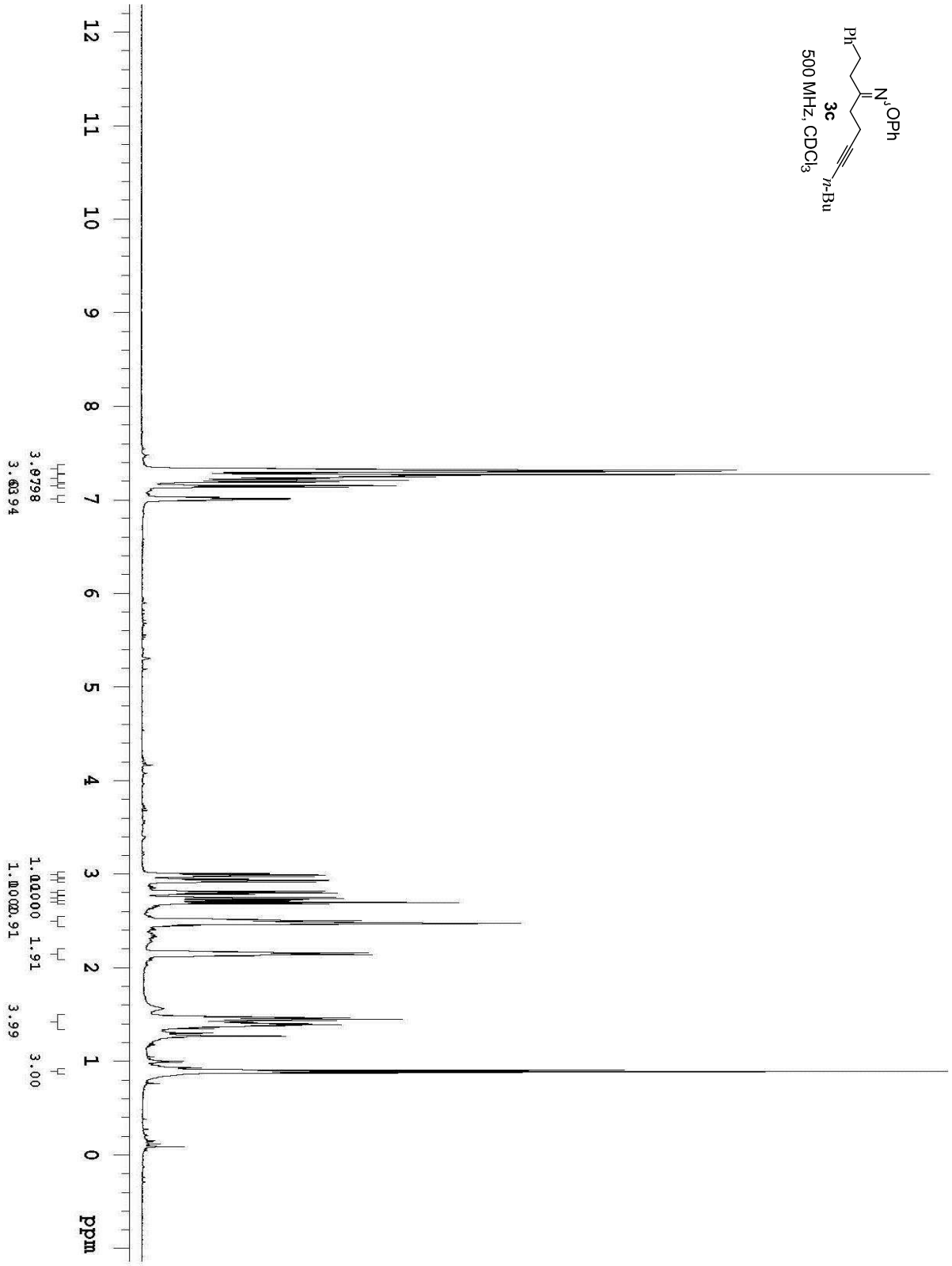
160
140
120
100
80
60
40
20
0
ppm

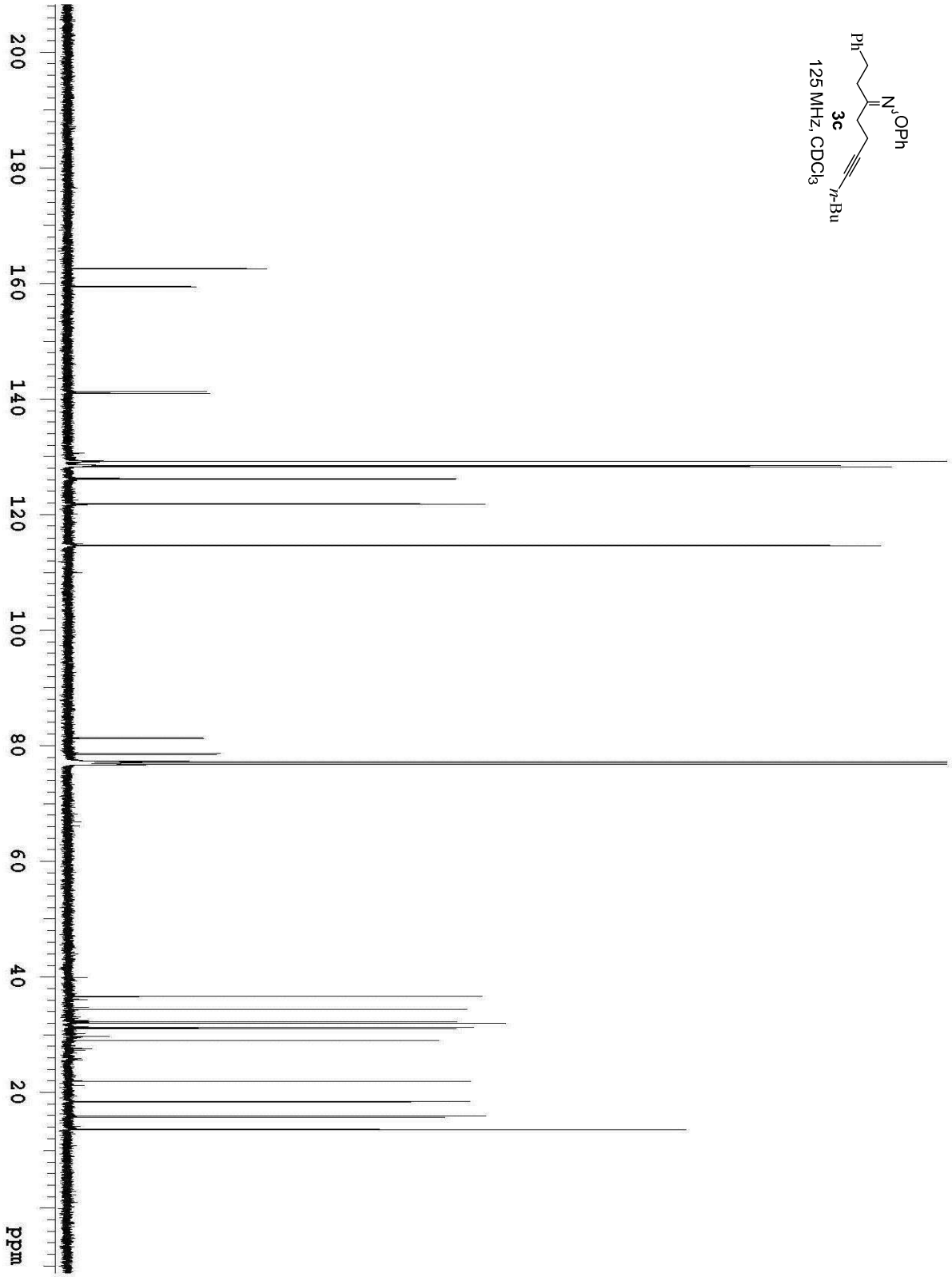

Ph
N
OPh
3a
500 MHz, CDCl3
10
9
8
7
6
5
4
3
2
1
0
ppm
1.38
3.20
0.64
1.52
1.52
0.48
0.48
0.73
2.19

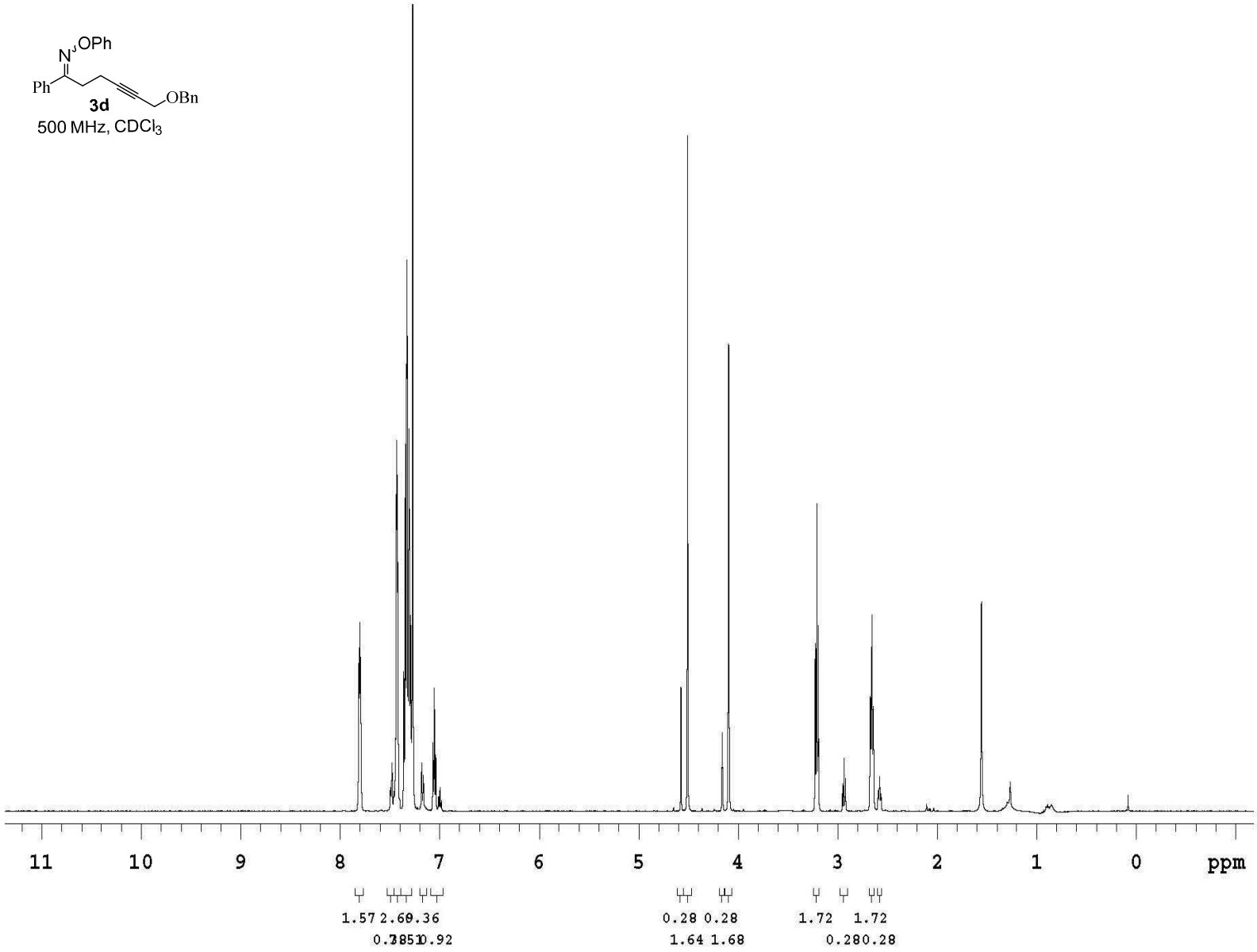

Ph
N
OPh
3a
125 MHz, CDCl3
180
160
140
120
100
80
60
40
20
ppm

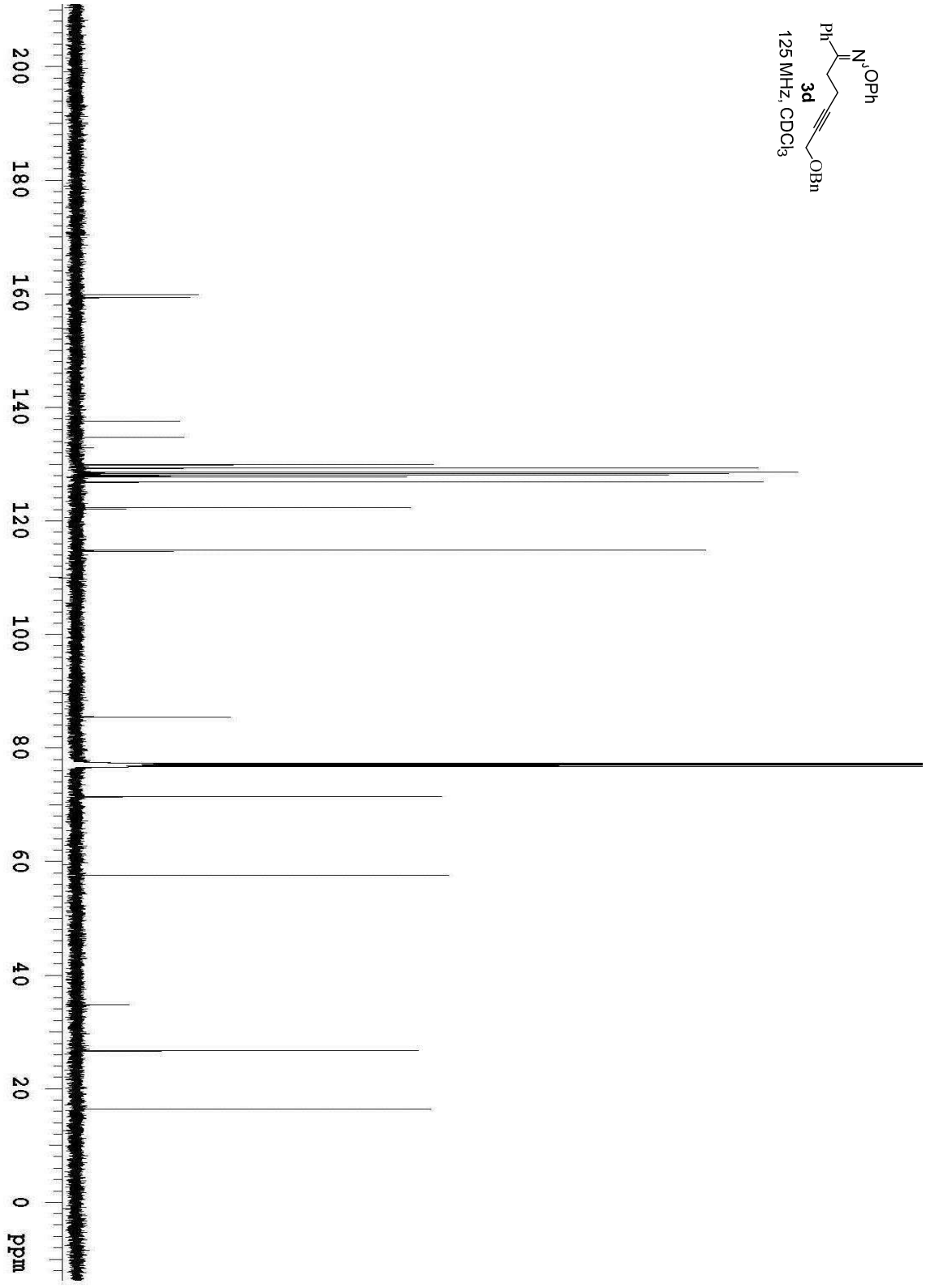

OPh
N
Ph
n-Bu
3b
500 MHz, CDCl3
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.18
1.36
1.36
0.64
4.04
0.64
0.64
1.34
3.01


Ph
N
OPh
n-Bu
3b
125 MHz, CDCl3
200
180
160
140
120
100
80
60
40
20
0
ppm


Ph
N
OPh
3c
500 MHz, CDCl3
n-Bu
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
3.99
3.00
1.91
1.00


Ph
N
OPh
3c
125 MHz, CDCl3
n-Bu
200
180
160
140
120
100
80
60
40
20
ppm


OPh
N
Ph
OBn
3d
500 MHz, CDCl3
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.57 2.69 0.36
0.38 1.51 0.92
0.28 0.28
1.64 1.68
1.72 1.72
0.28 0.28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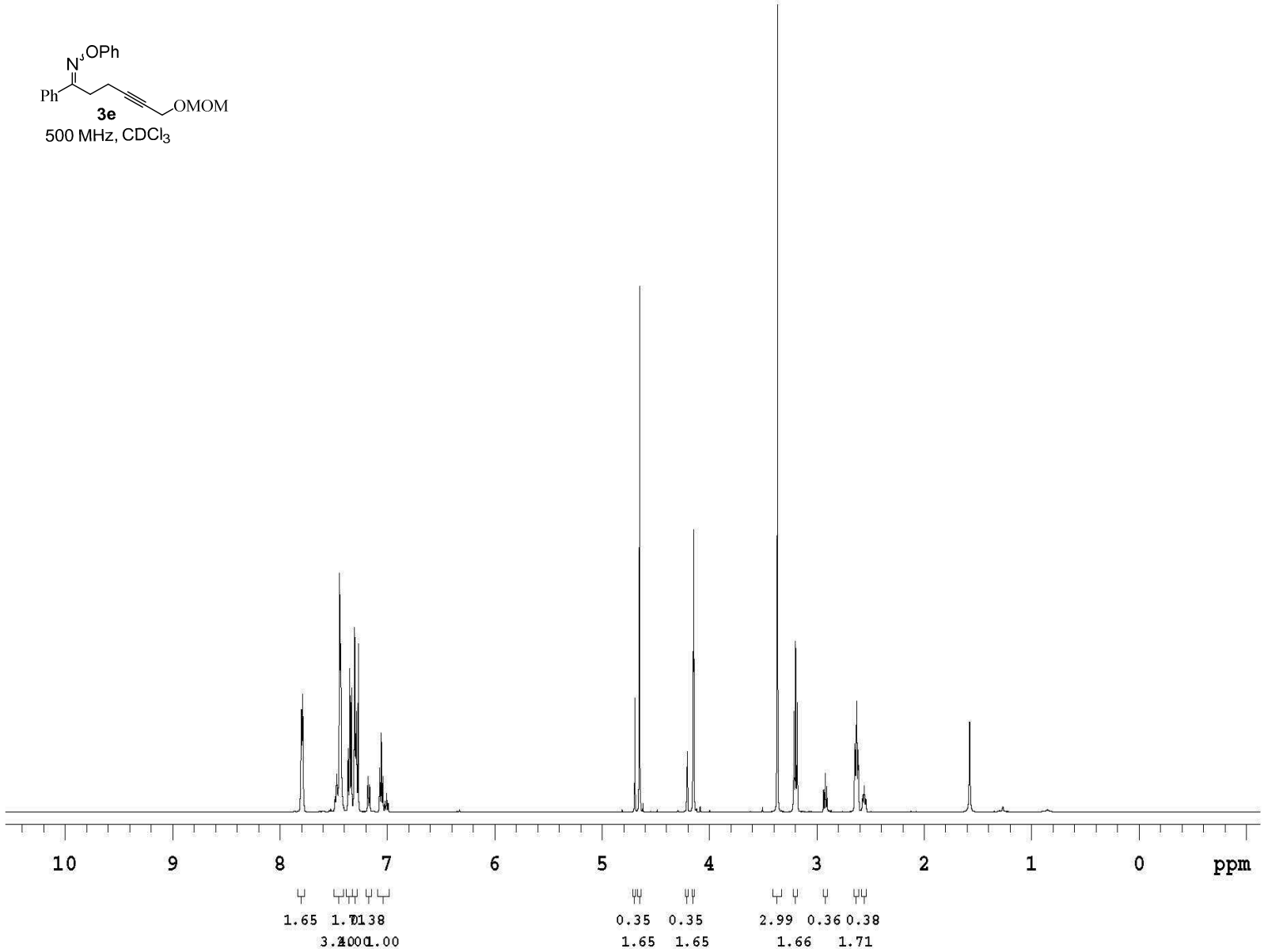
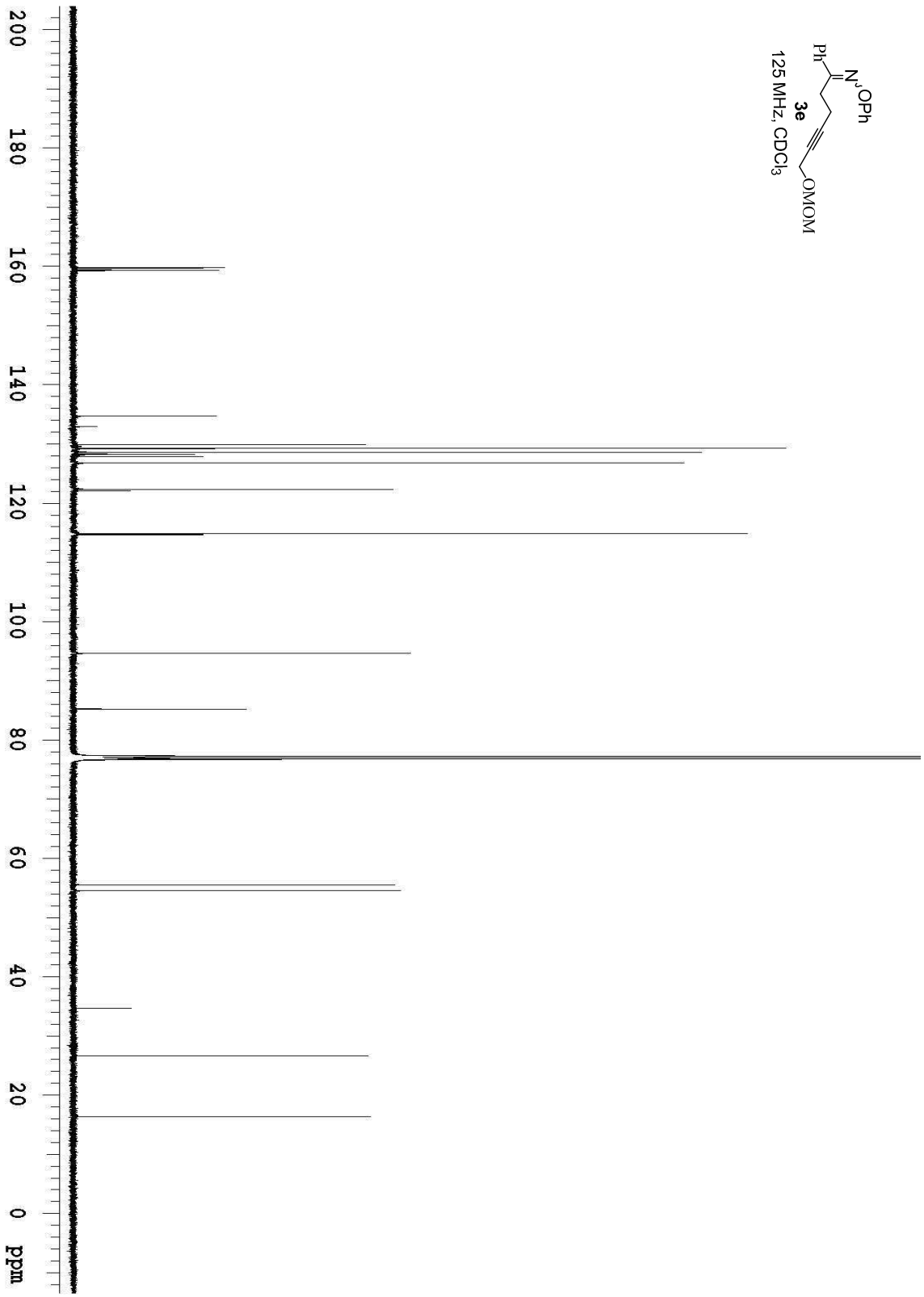
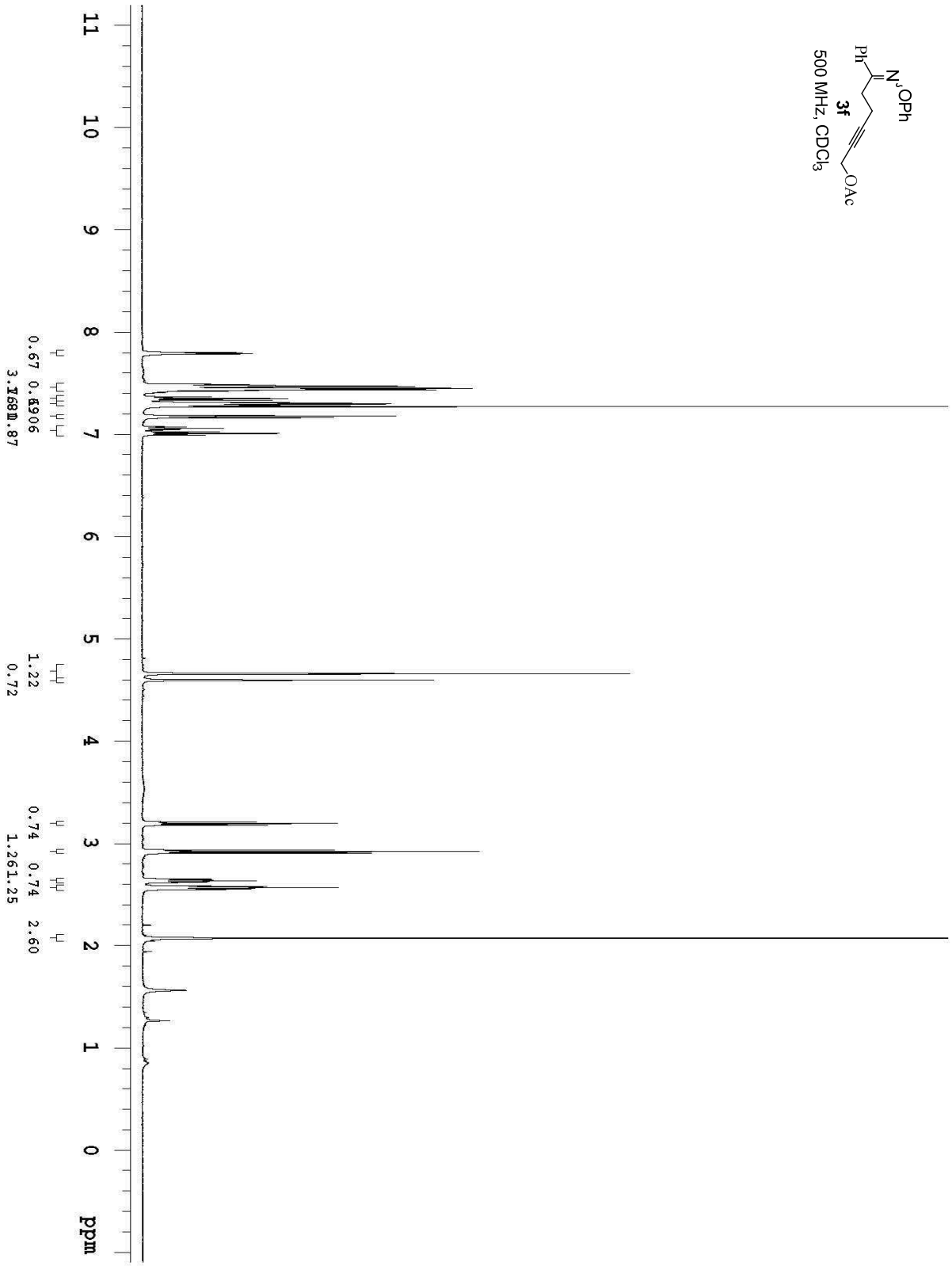
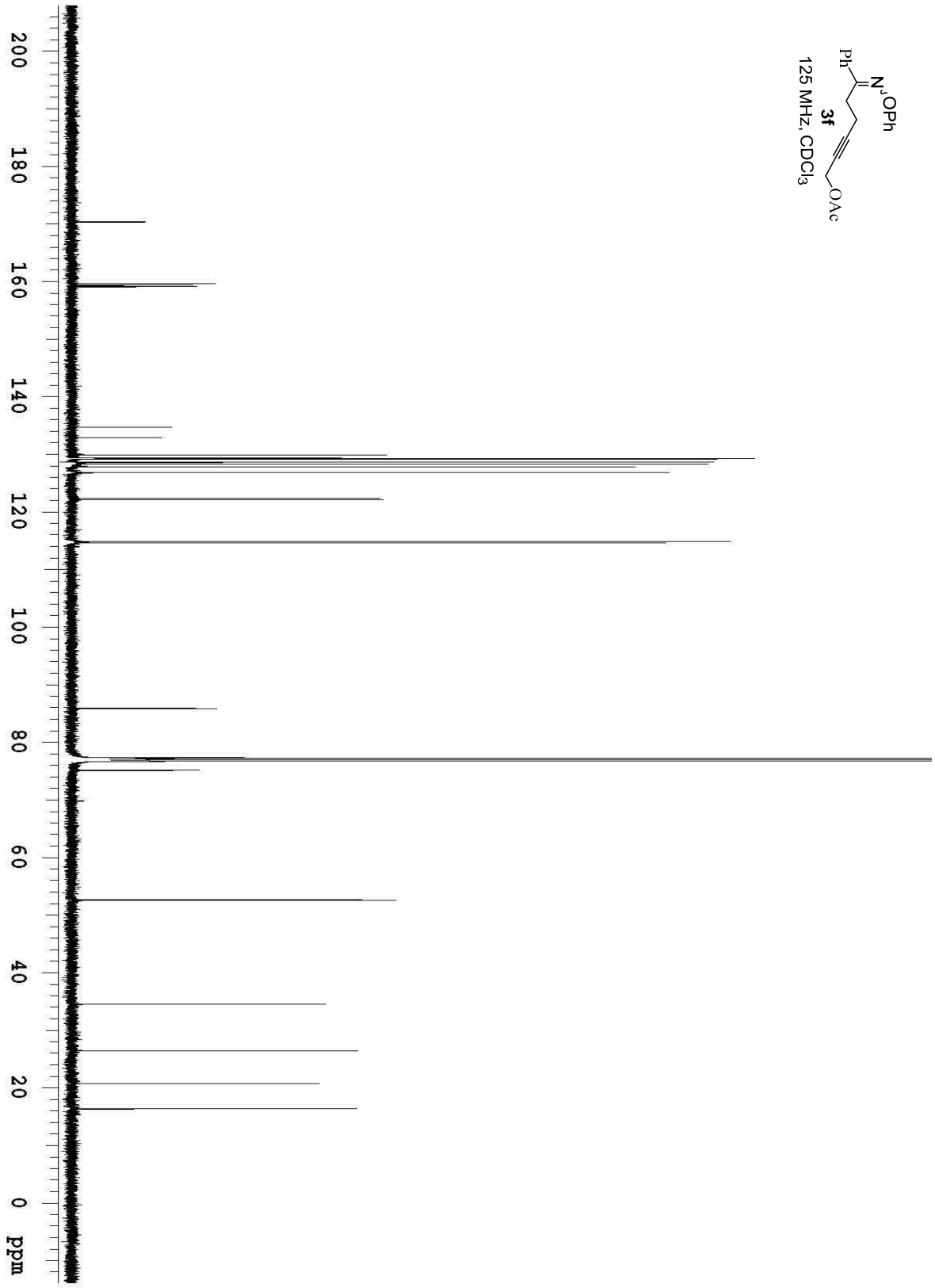
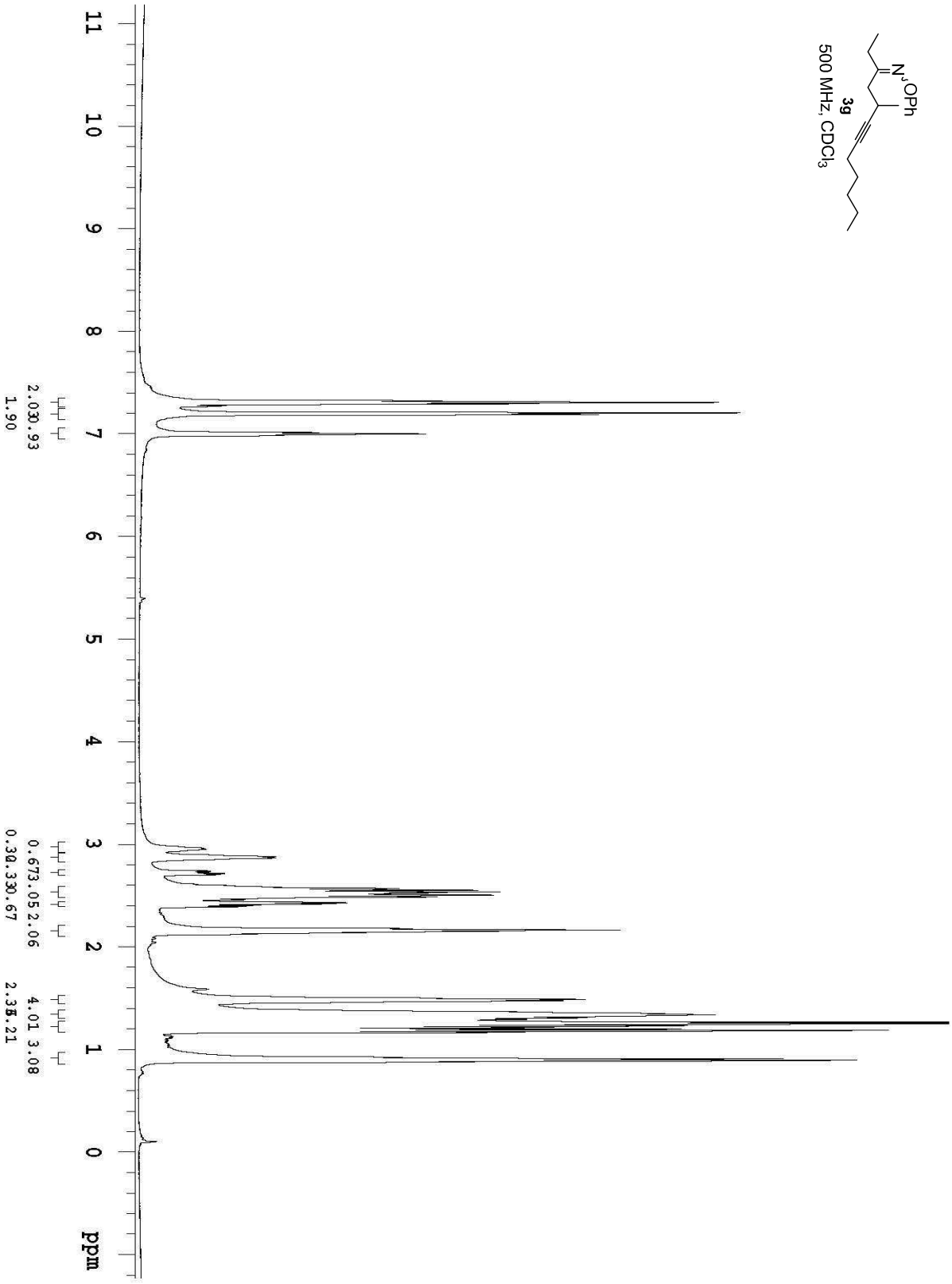
N
OPh
OBn
3d
125 MHz, CDCl3
200
180
160
140
120
100
80
60
40
20
0
ppm

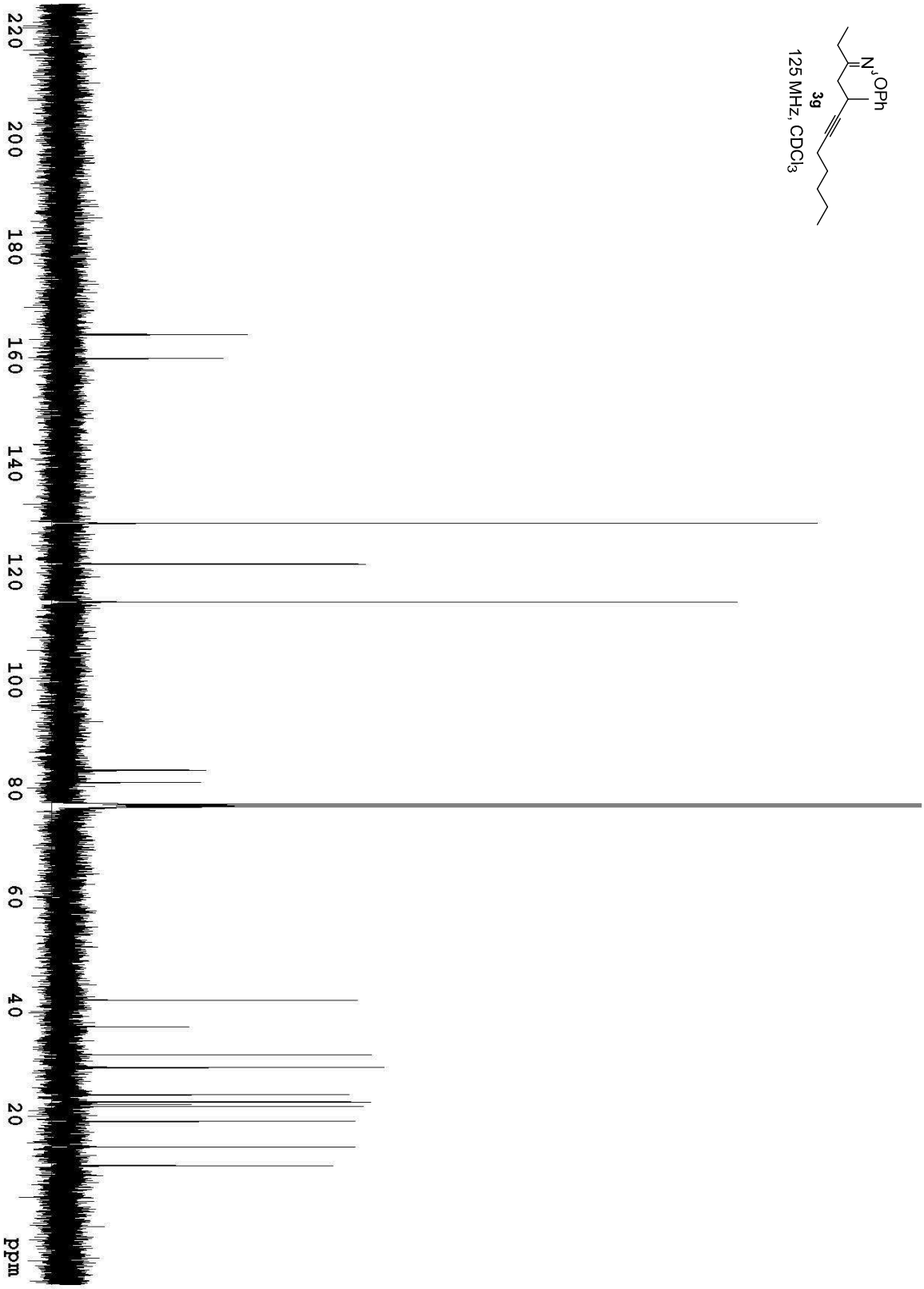

OPh
N
Ph
OMOM
3e
500 MHz, CDCl3
10
9
8
7
6
5
4
3
2
1
0
ppm
1.65
1.71
1.38
3.21
4.00
1.00
0.35
0.35
1.65
1.65
2.99
0.36
0.38
1.66
1.71

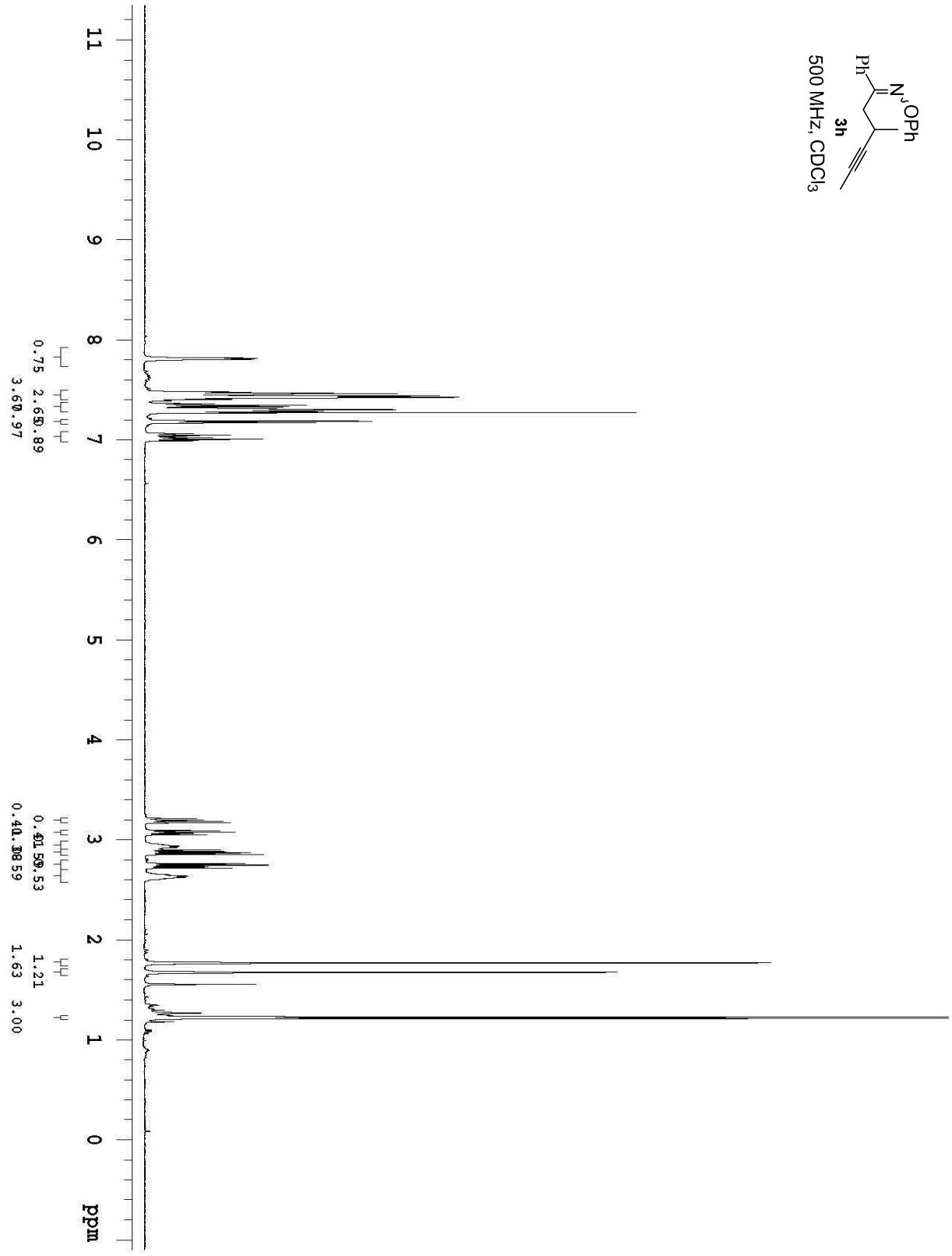

Ph
N
OPh
OMOM
3e
125 MHz, CDCl3
200
180
160
140
120
100
80
60
40
20
0
ppm

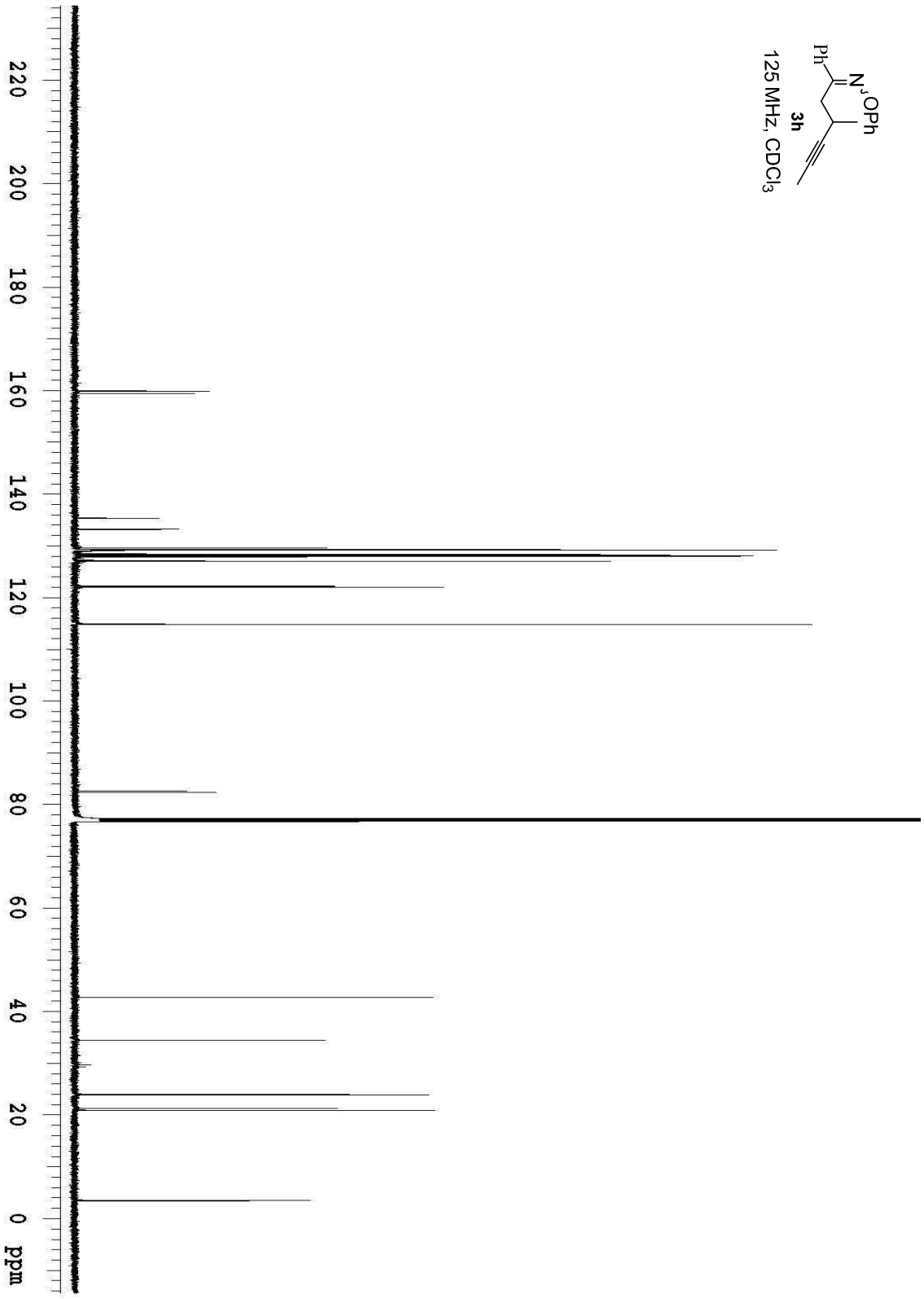

Ph
N
OPh
3f
OAc
500 MHz, CDCl3
11
10
9
8
7
6
5
4
3
2
1
0
ppm
0.67
0.72
1.22
0.74
0.74
2.60
1.26
1.25

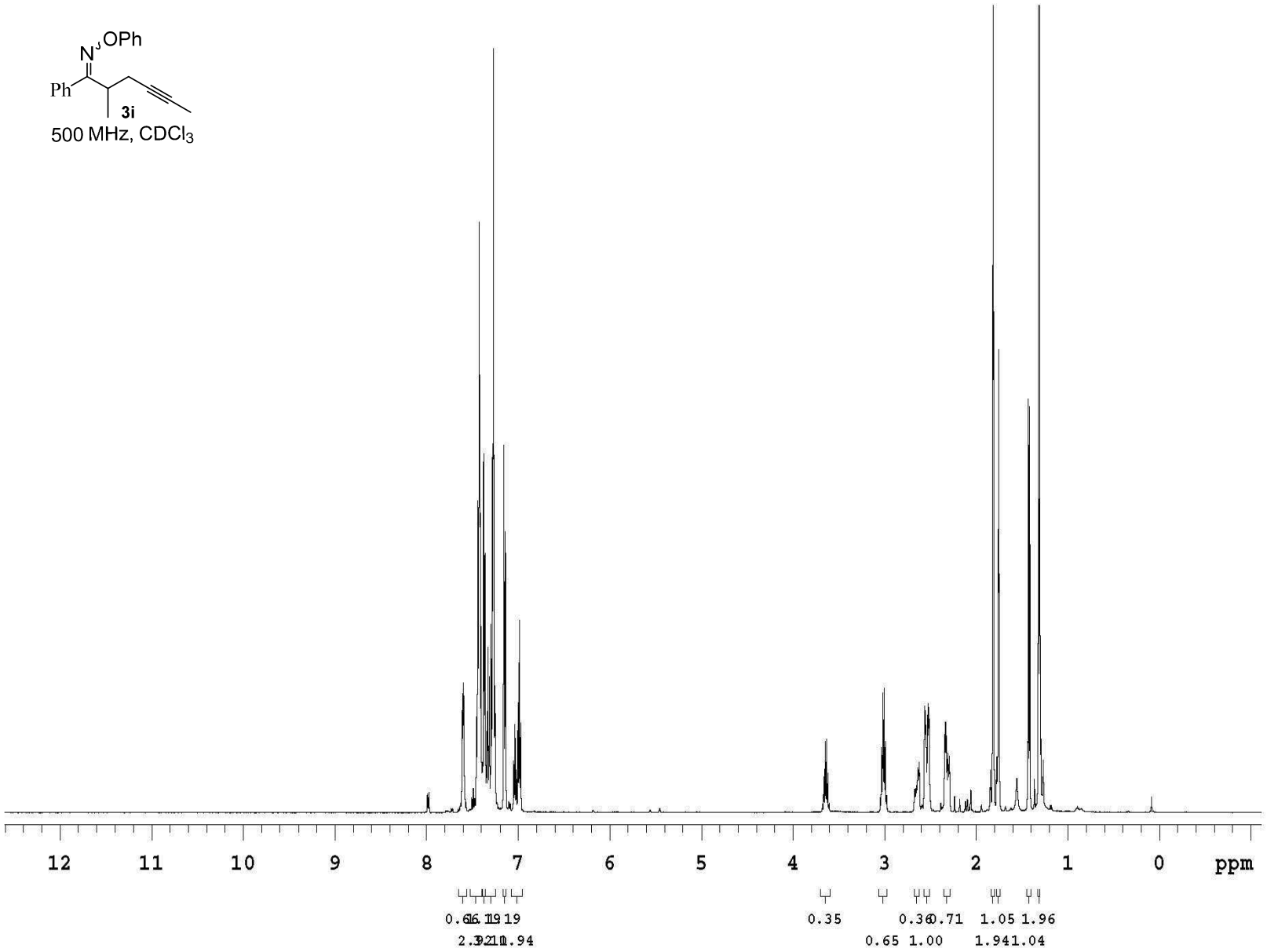

Ph
N
OPh
3f
125 MHz, CDCl3
OAc
200
180
160
140
120
100
80
60
40
20
0
ppm

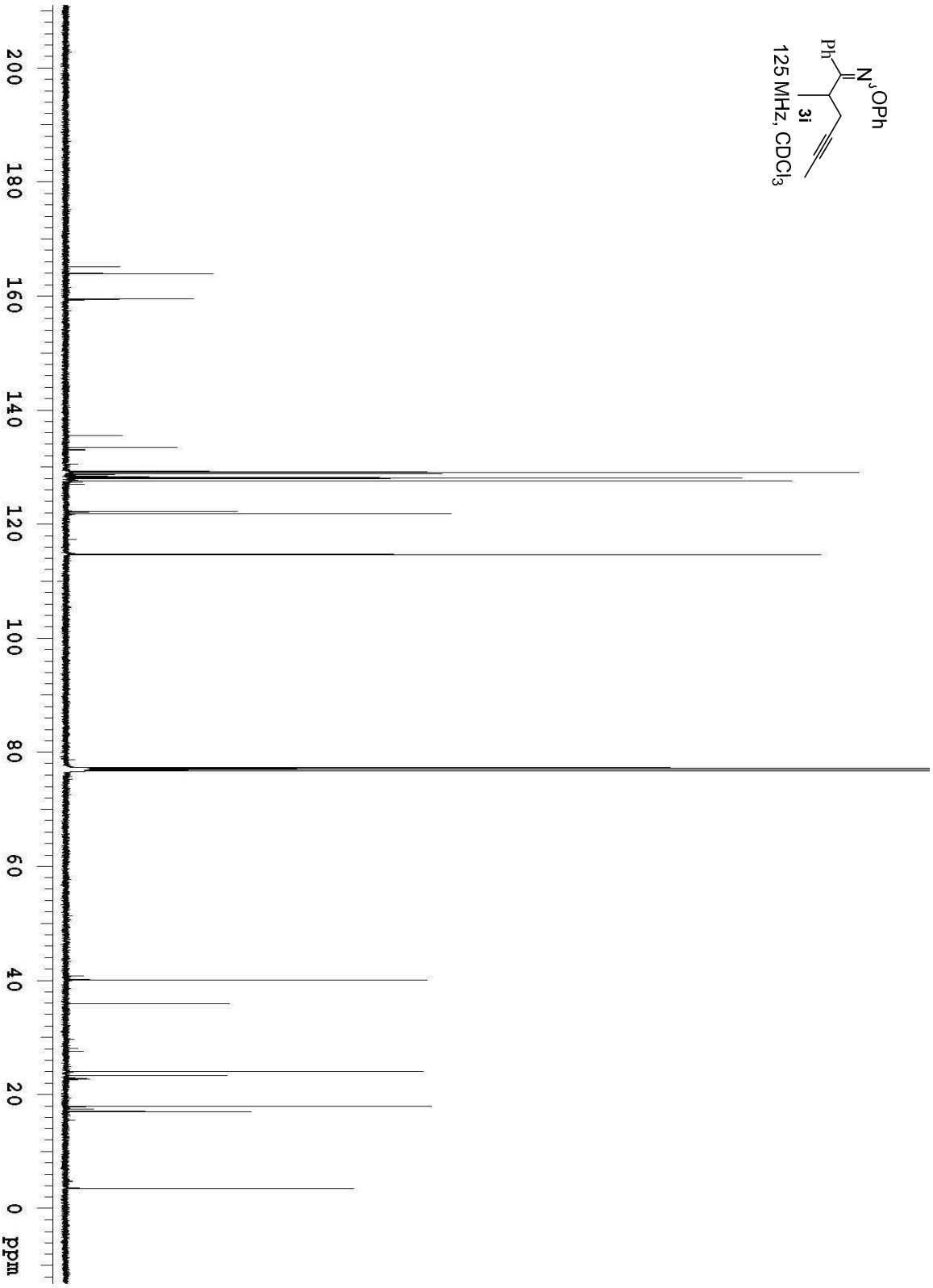

3g
500 MHz, CDCl3
OPh
11
10
9
8
7
6
5
4
3
2
1
0
ppm
2.03
0.93
1.90
0.67
3.05
2.06
0.30
0.33
0.67
4.01
3.08
2.38
5.21

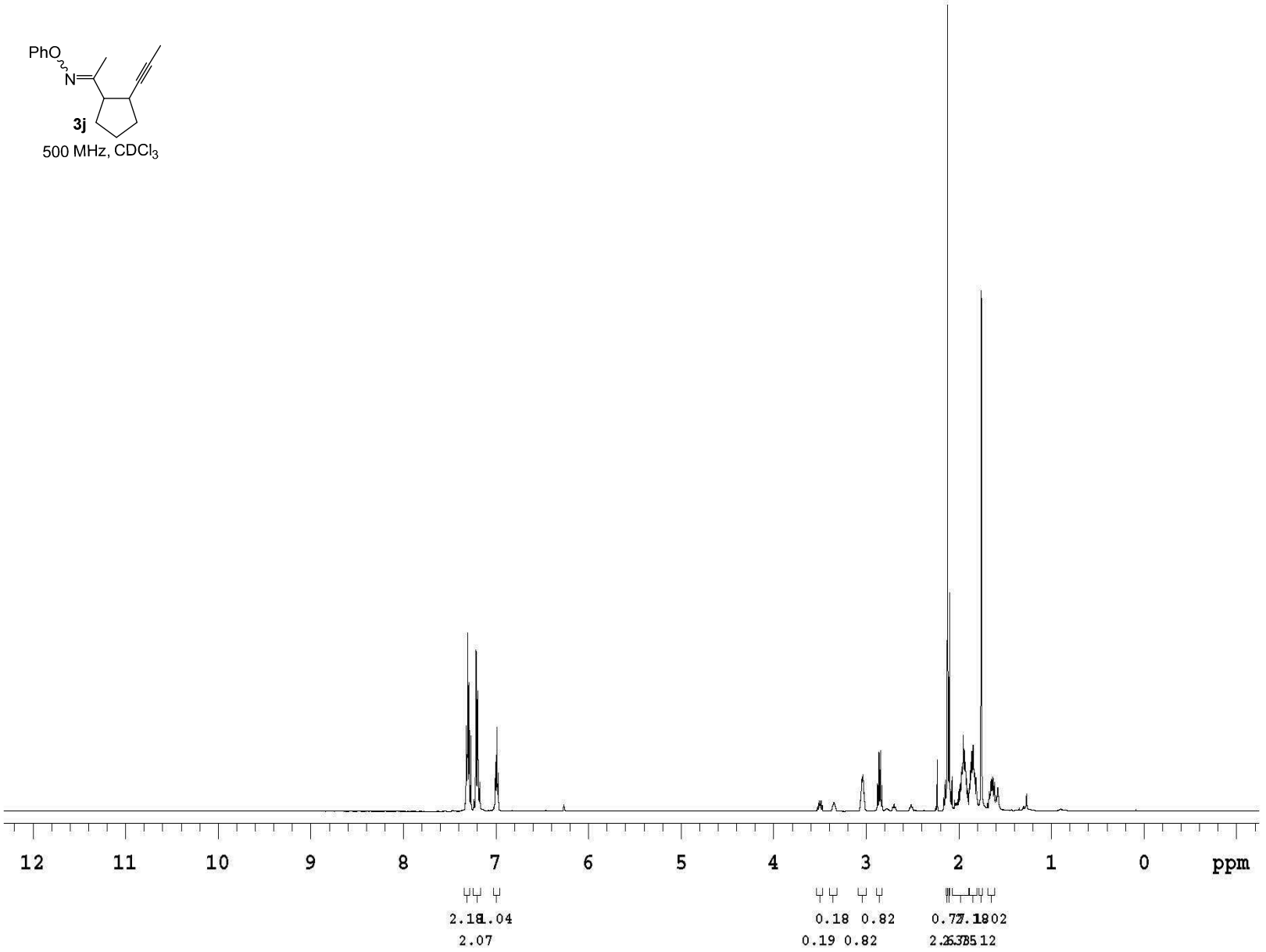

3g
125 MHz, CDCl3
OPh
220
200
180
160
140
120
100
80
60
40
20
ppm

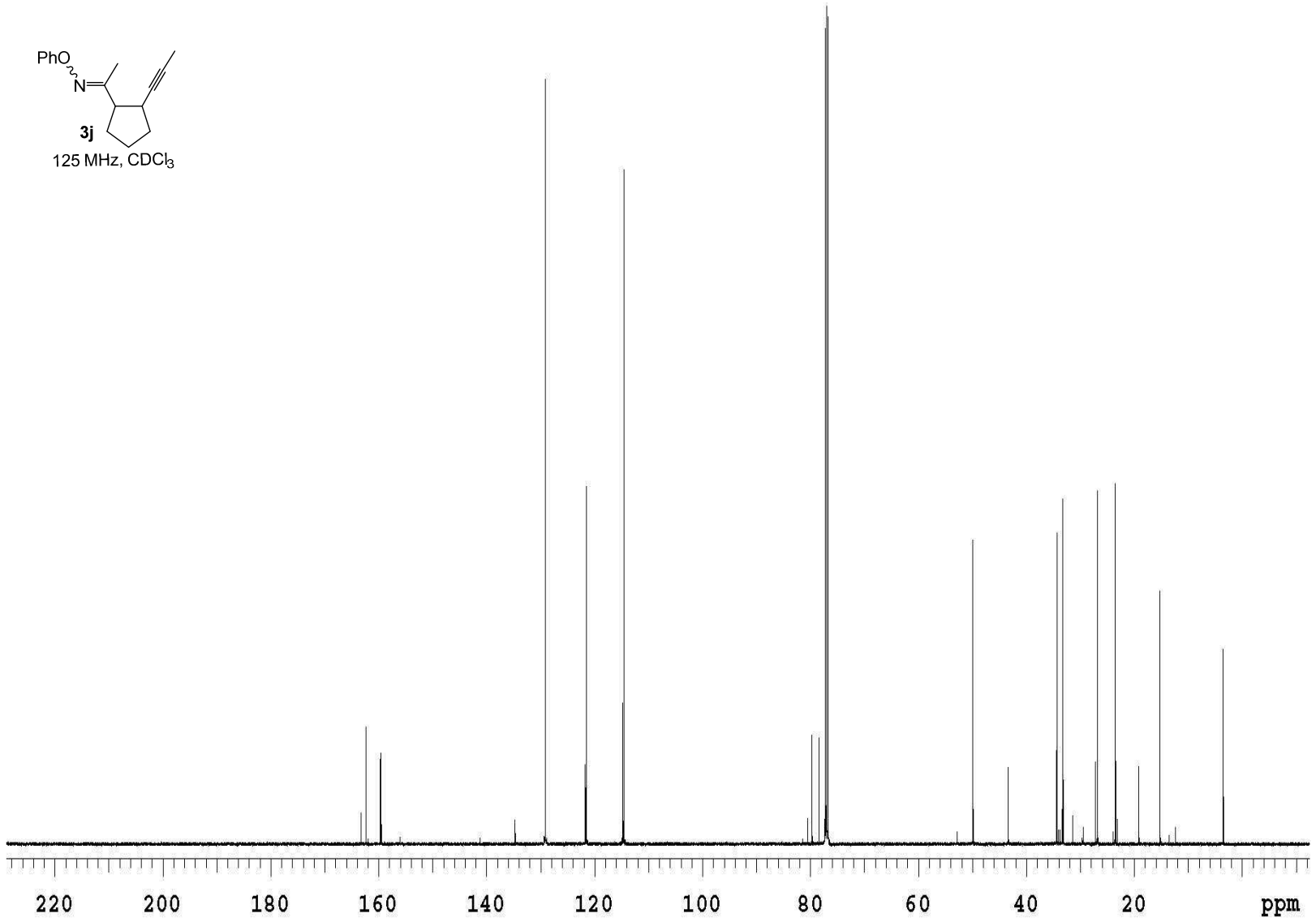

Ph
N
OPh
3h
500 MHz, CDCl3
11
10
9
8
7
6
5
4
3
2
1
0
ppm
0.75 2.65 5.89
3.60 7.97
0.41 1.59 0.53
0.40 1.38 0.59
1.21
1.63 3.00

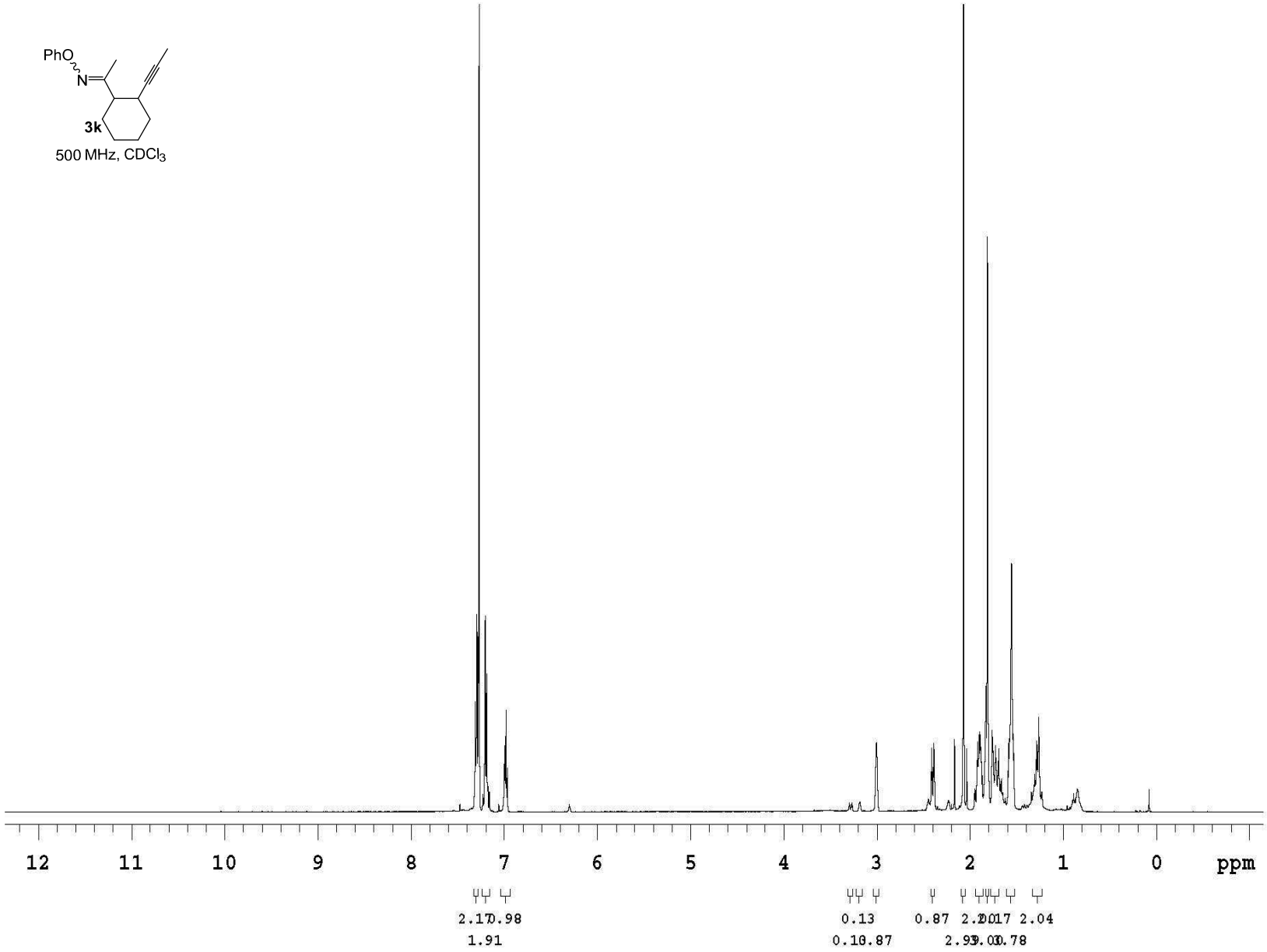

Ph
N
OPh
3h
125 MHz, CDCl3
220
200
180
160
140
120
100
80
60
40
20
0
ppm

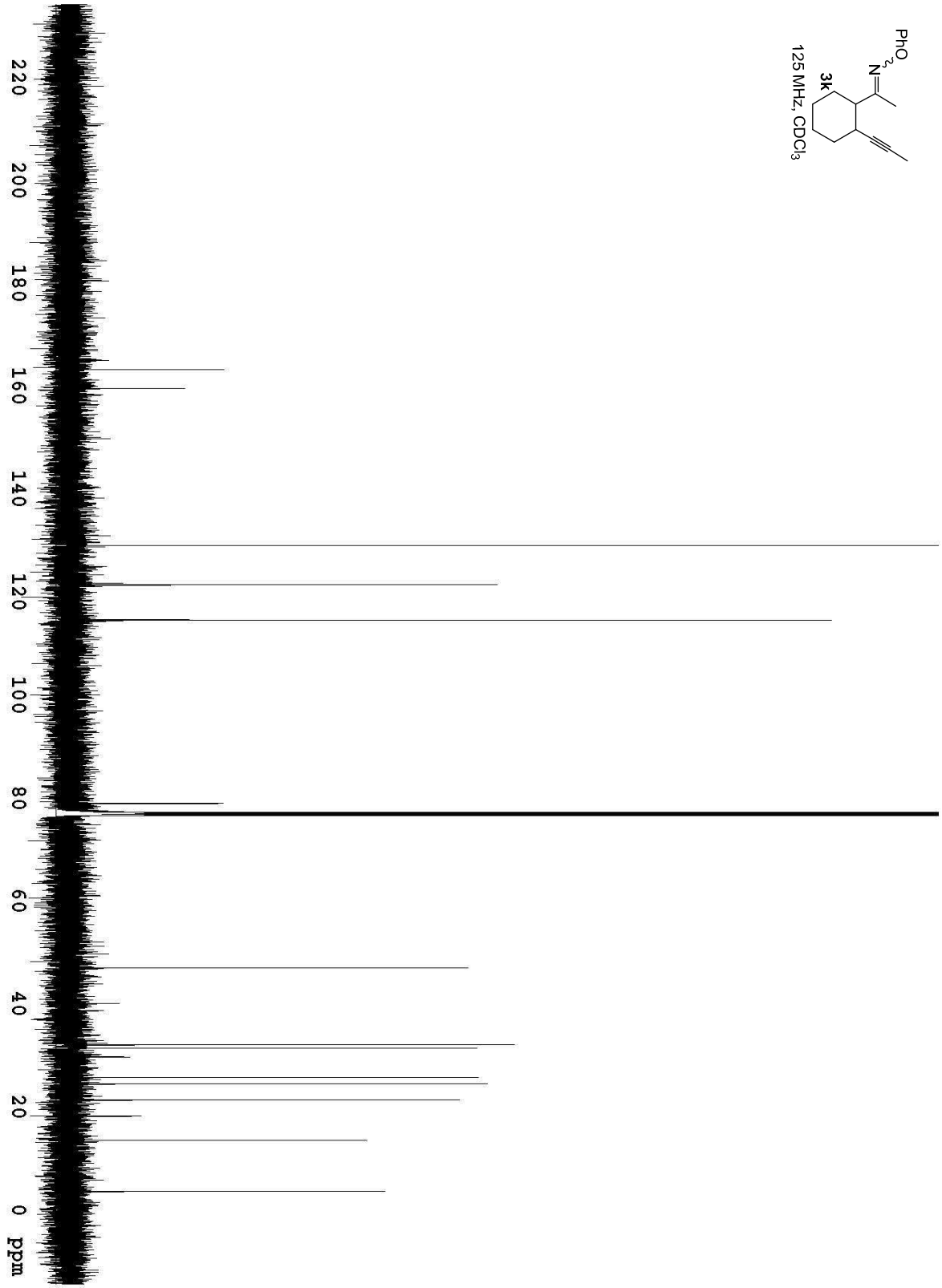

OPh
N
Ph
3i
500 MHz, CDCl3
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
0.35
0.65
1.00
1.94
1.04

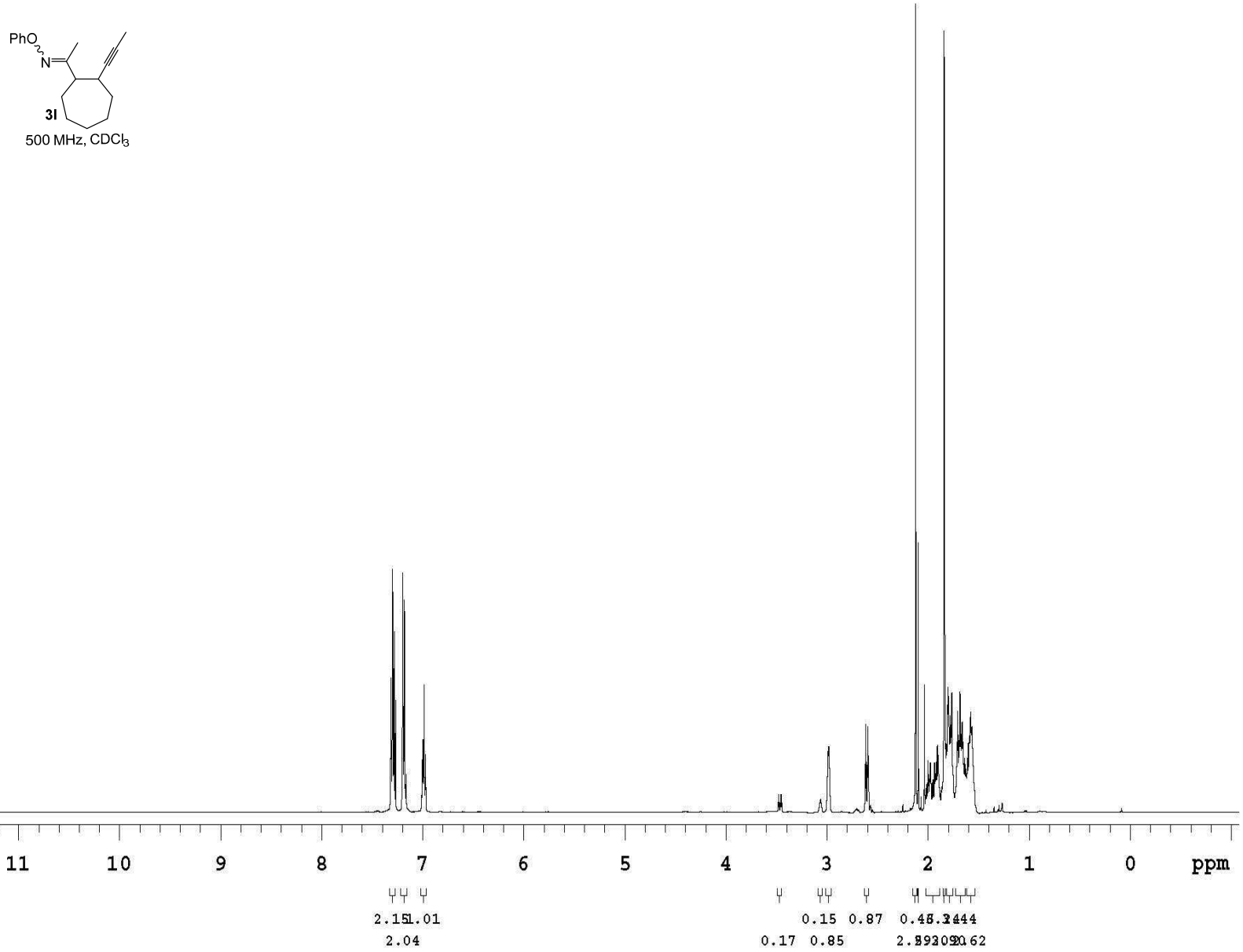

Ph
N
OPh
3i
125 MHz, CDCl3
200
180
160
140
120
100
80
60
40
20
0
ppm

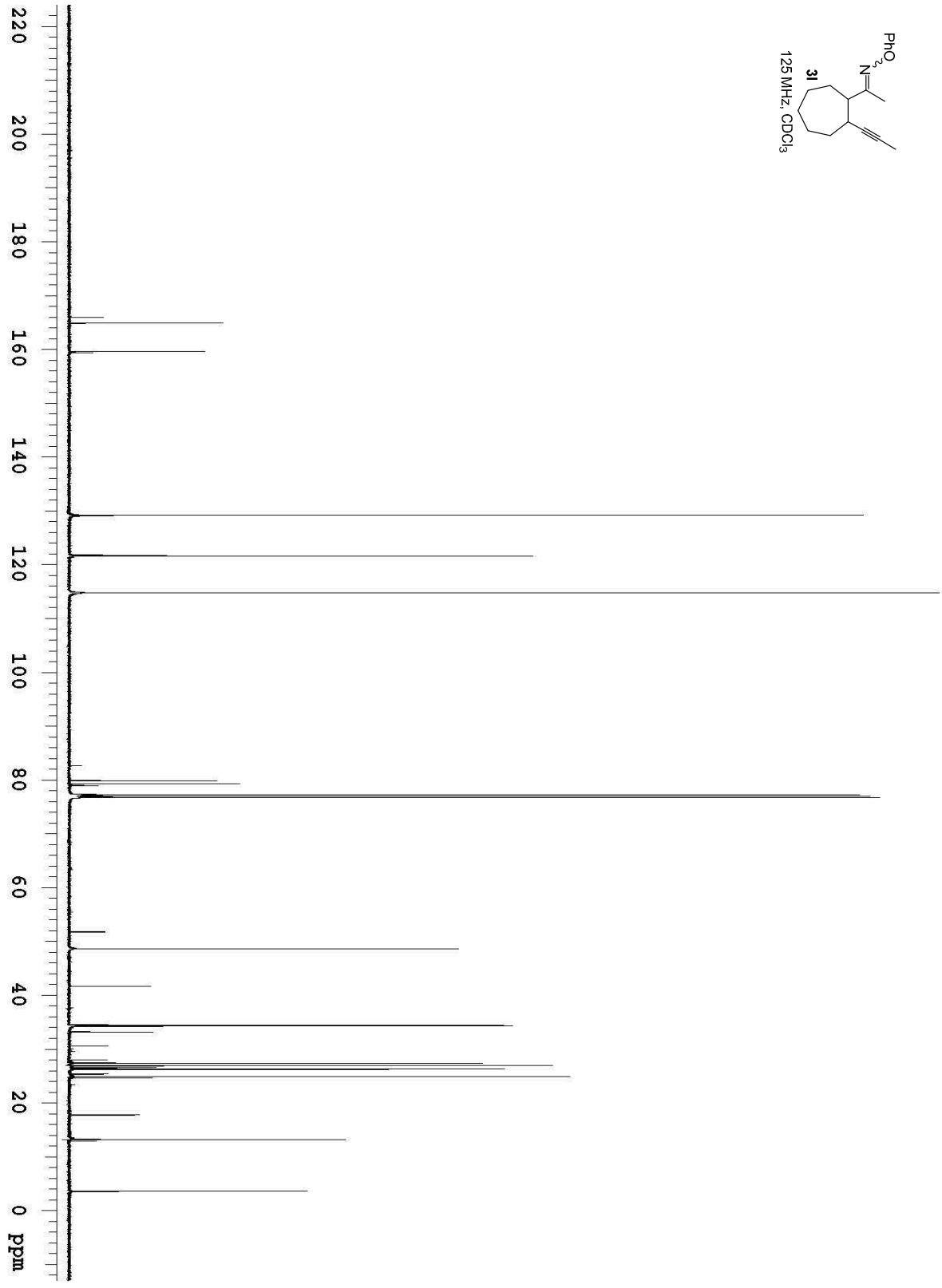

PhO
N
3j
500 MHz, CDCl3
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
2.18
1.04
2.07
0.18
0.82
0.19
0.82

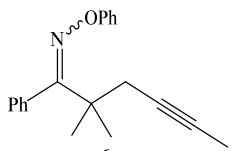

PhO
N
3j
125 MHz, CDCl3
220
200
180
160
140
120
100
80
60
40
20
ppm


PhO
N
3k
500 MHz, CDCl3
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
2.17
0.98
1.91
0.13
0.10
0.87
0.87
2.93
3.00
0.78
2.04


PhO
N
3k
125 MHz, CDCl3
220
200
180
160
140
120
100
80
60
40
20
0
ppm

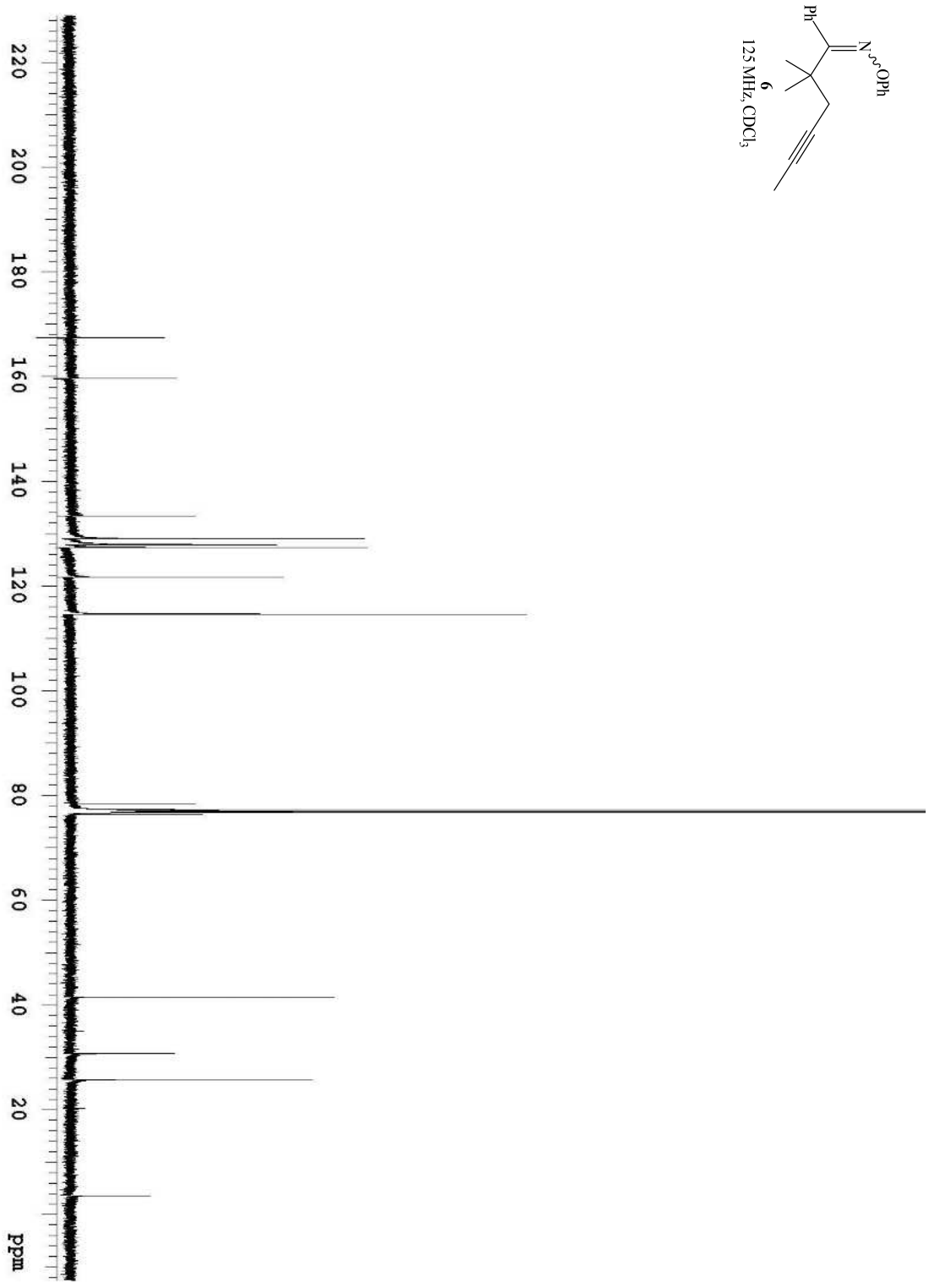

PhO
N
3l
500 MHz, CDCl3
11
10
9
8
7
6
5
4
3
2
1
0
ppm

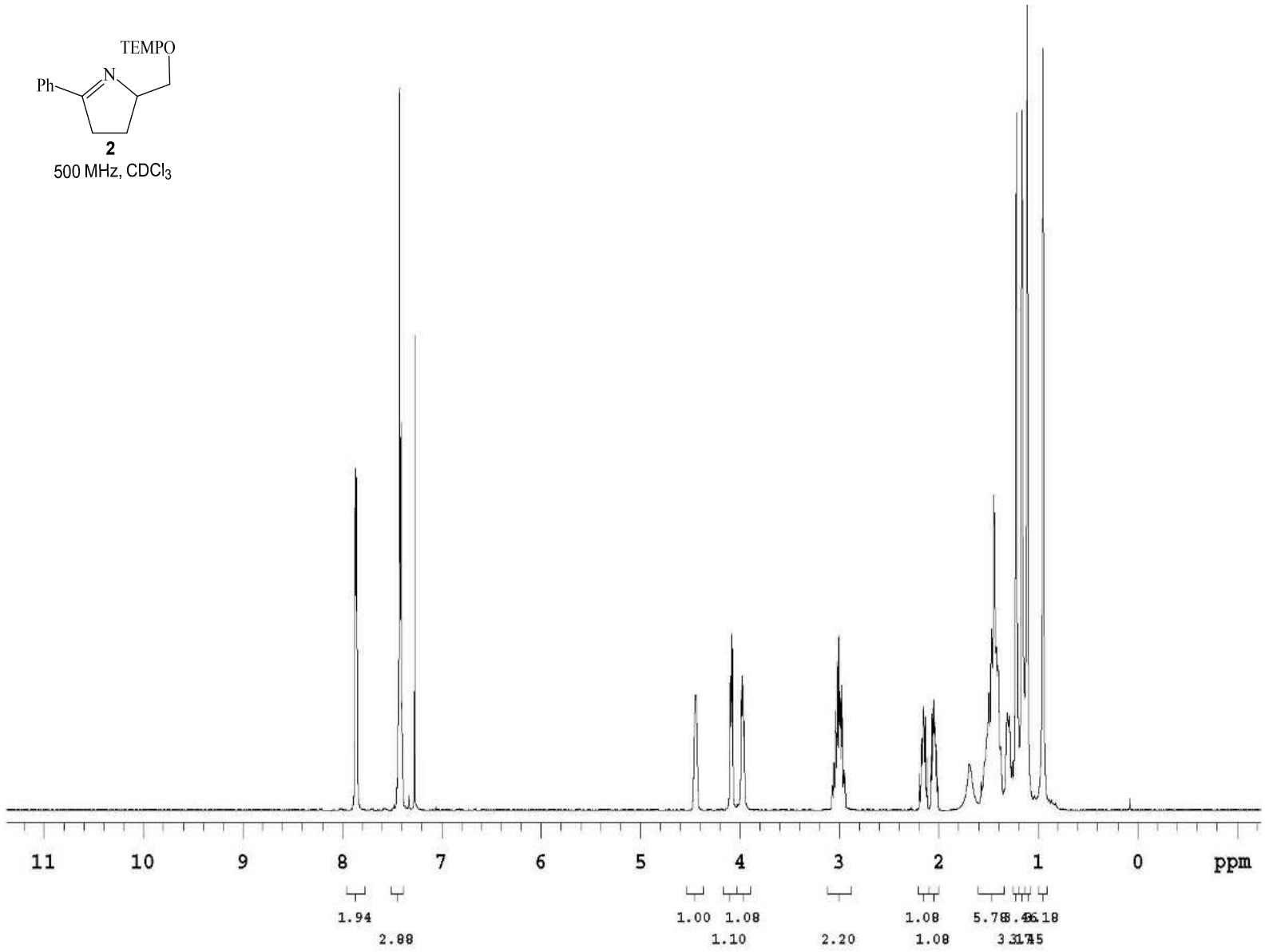

PhO2S
N
3l
125 MHz, CDCl3
220
200
180
160
140
120
100
80
60
40
20
0 ppm

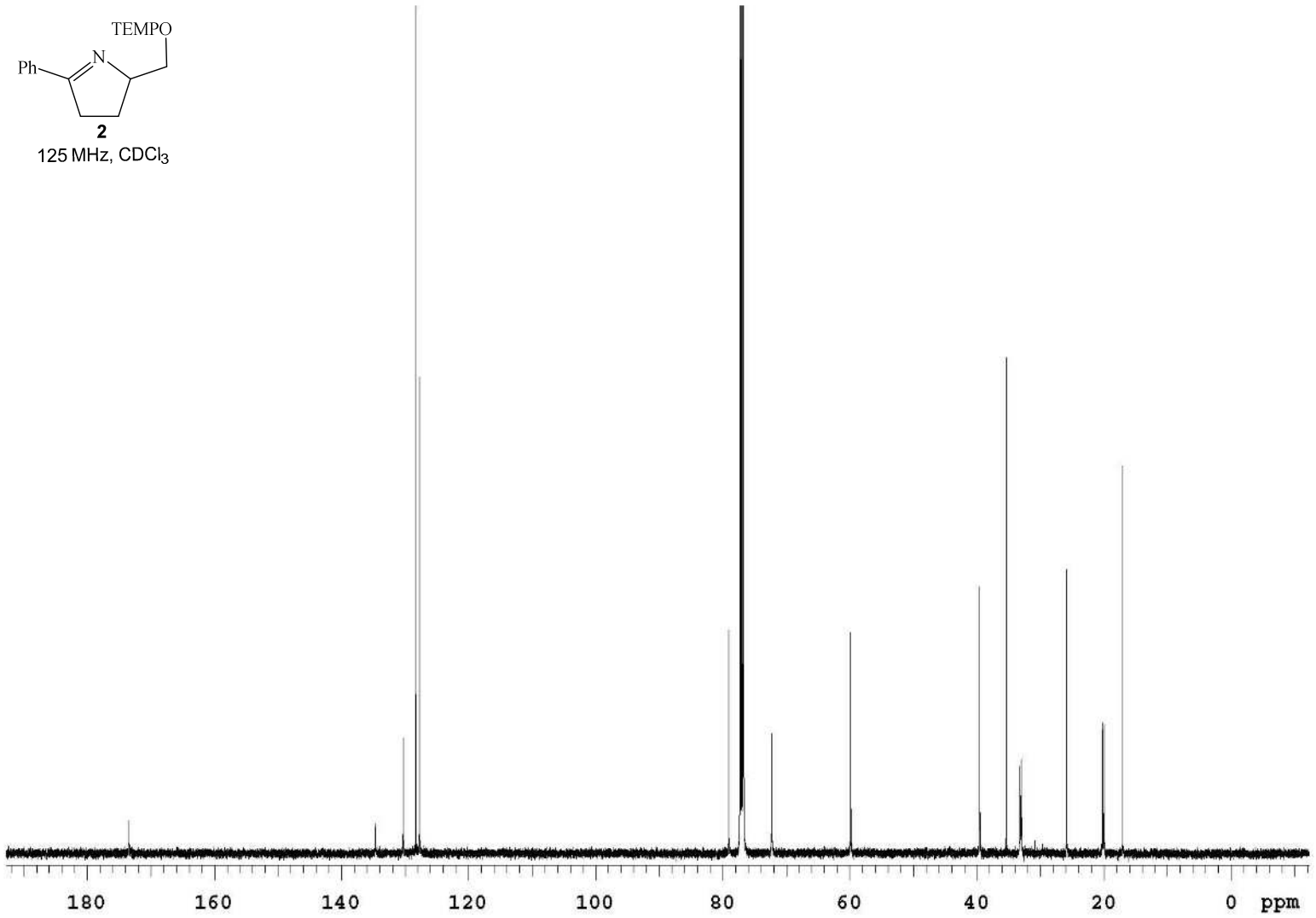


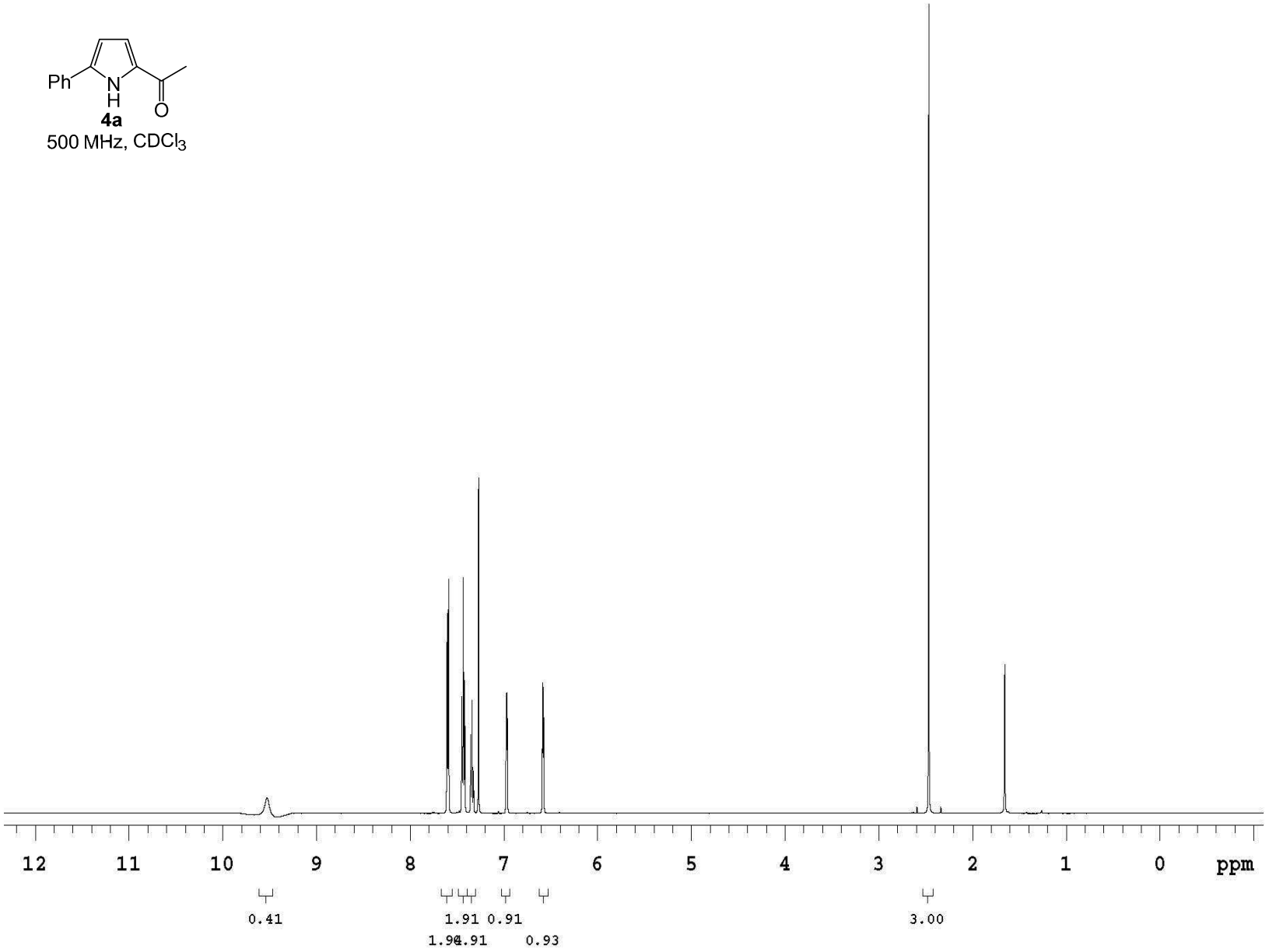
6

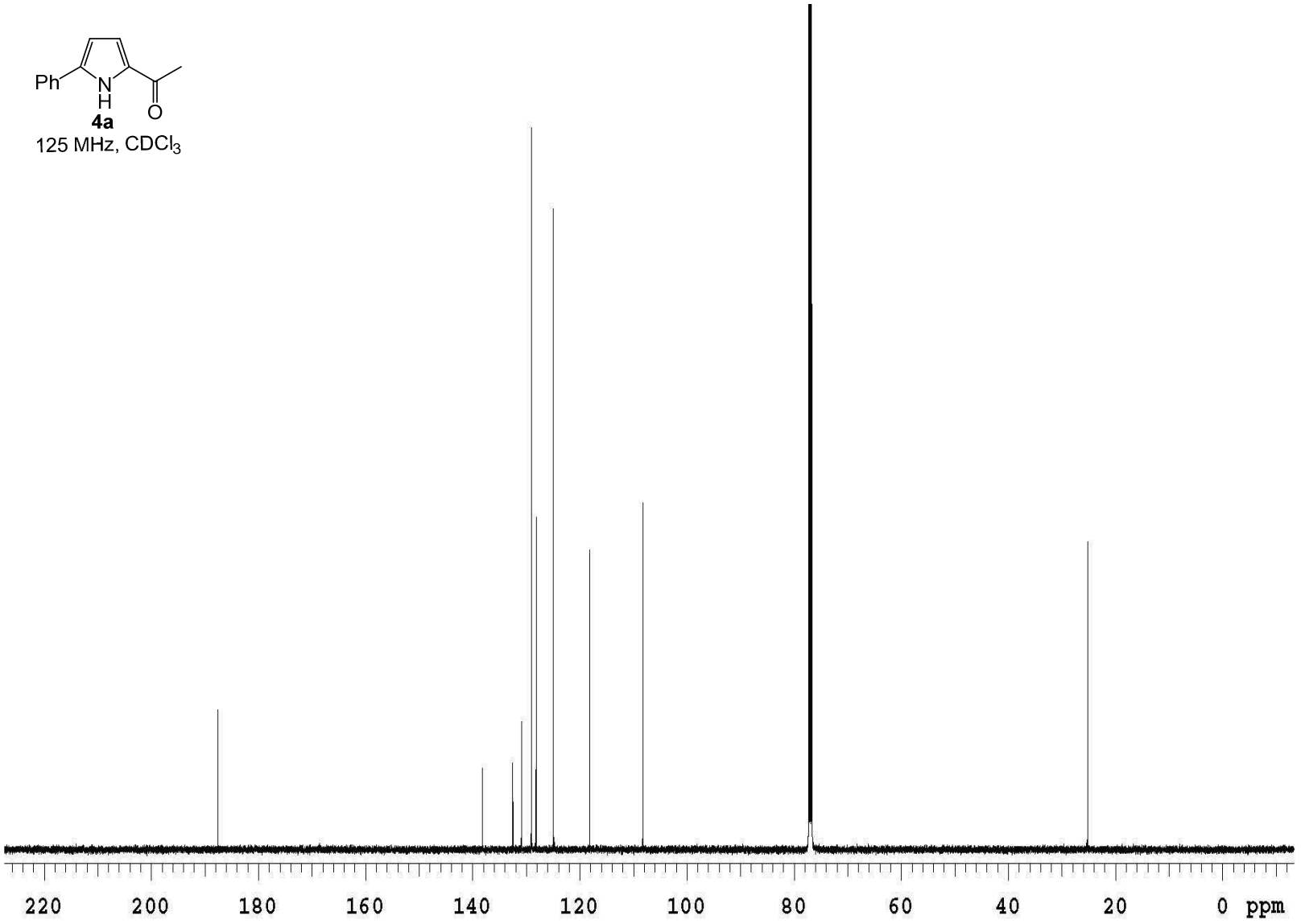
500 MHz, $CDCl_3$

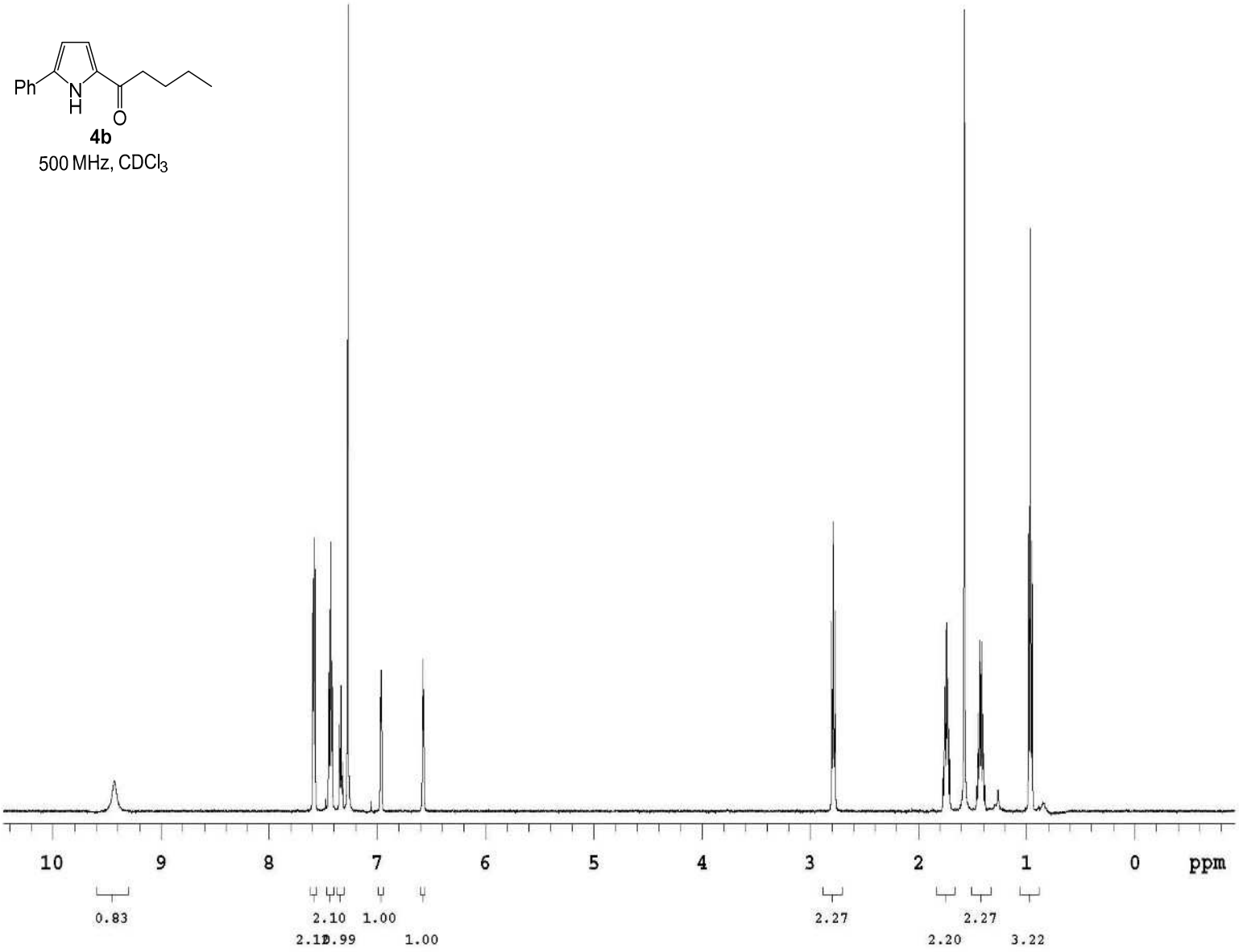

Ph
N
OPh
6
125 MHz, CDCl3
220
200
180
160
140
120
100
80
60
40
20
ppm

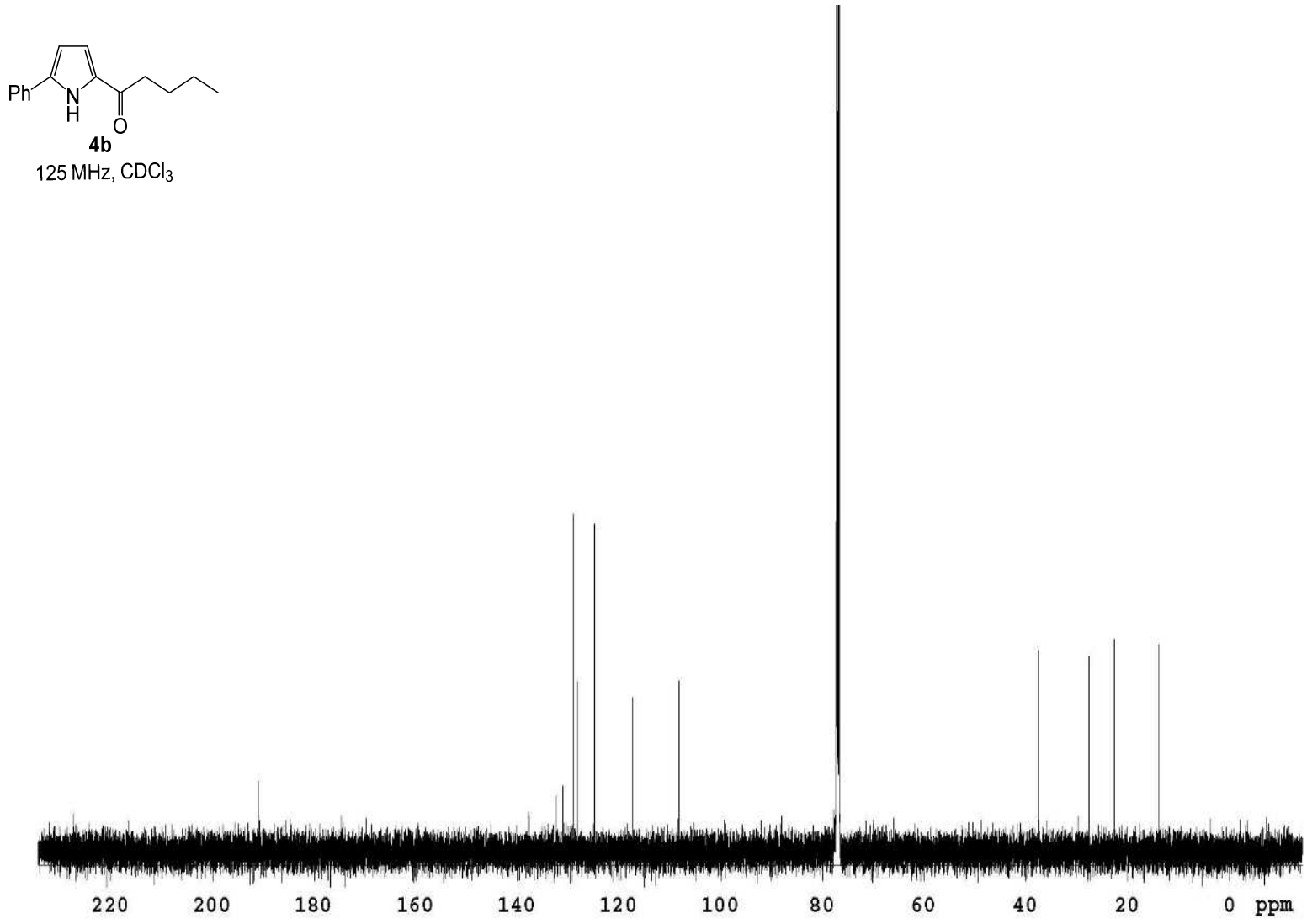

TEMPO
Ph
N
2
500 MHz, CDCl3
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.94
2.08
1.00
1.08
1.10
2.20
1.08
1.08
5.78
8.46
18
3.31
7.45

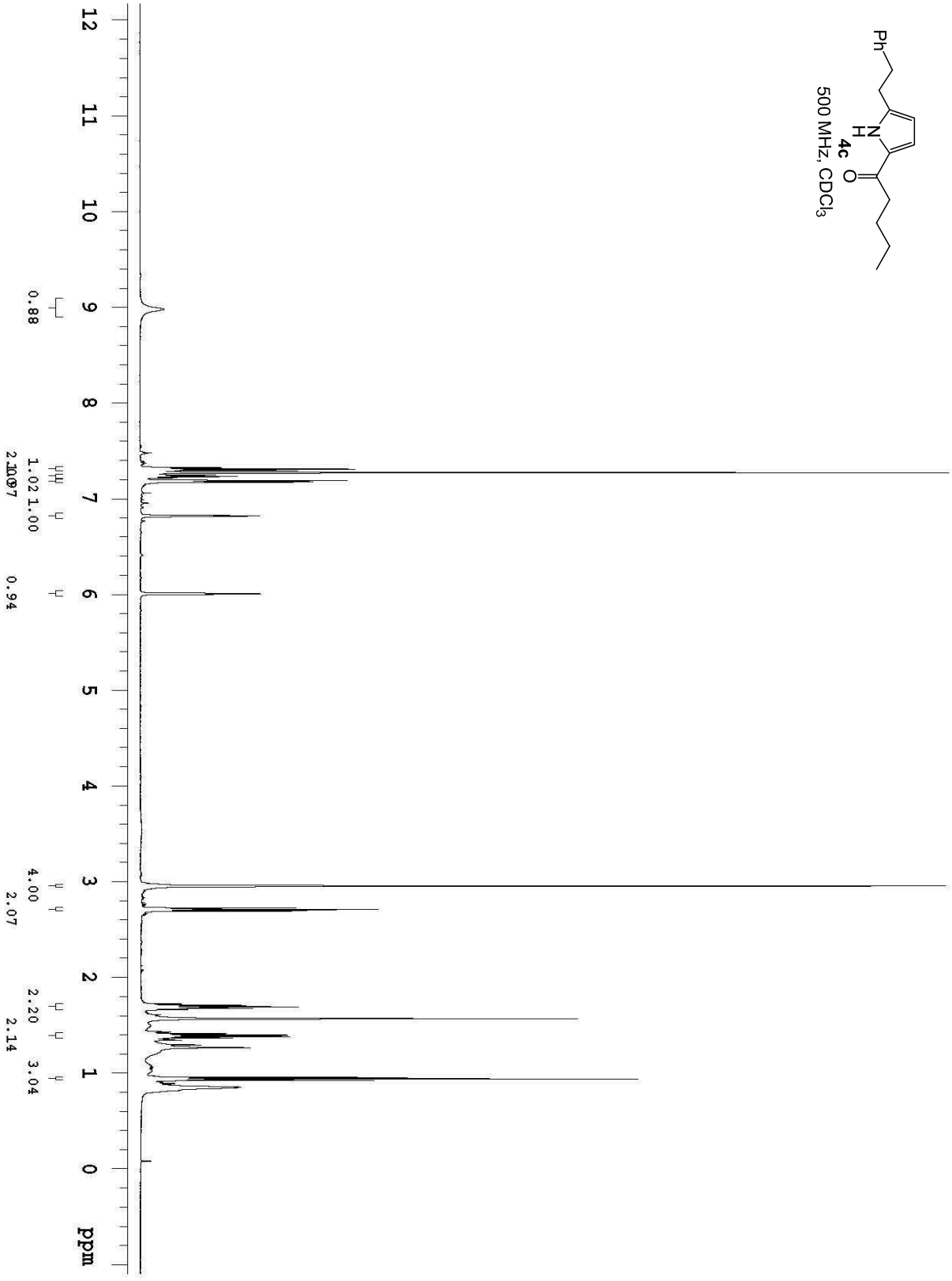

TEMPO
N
Ph
2
125 MHz, CDCl3
180
160
140
120
100
80
60
40
20
0
ppm

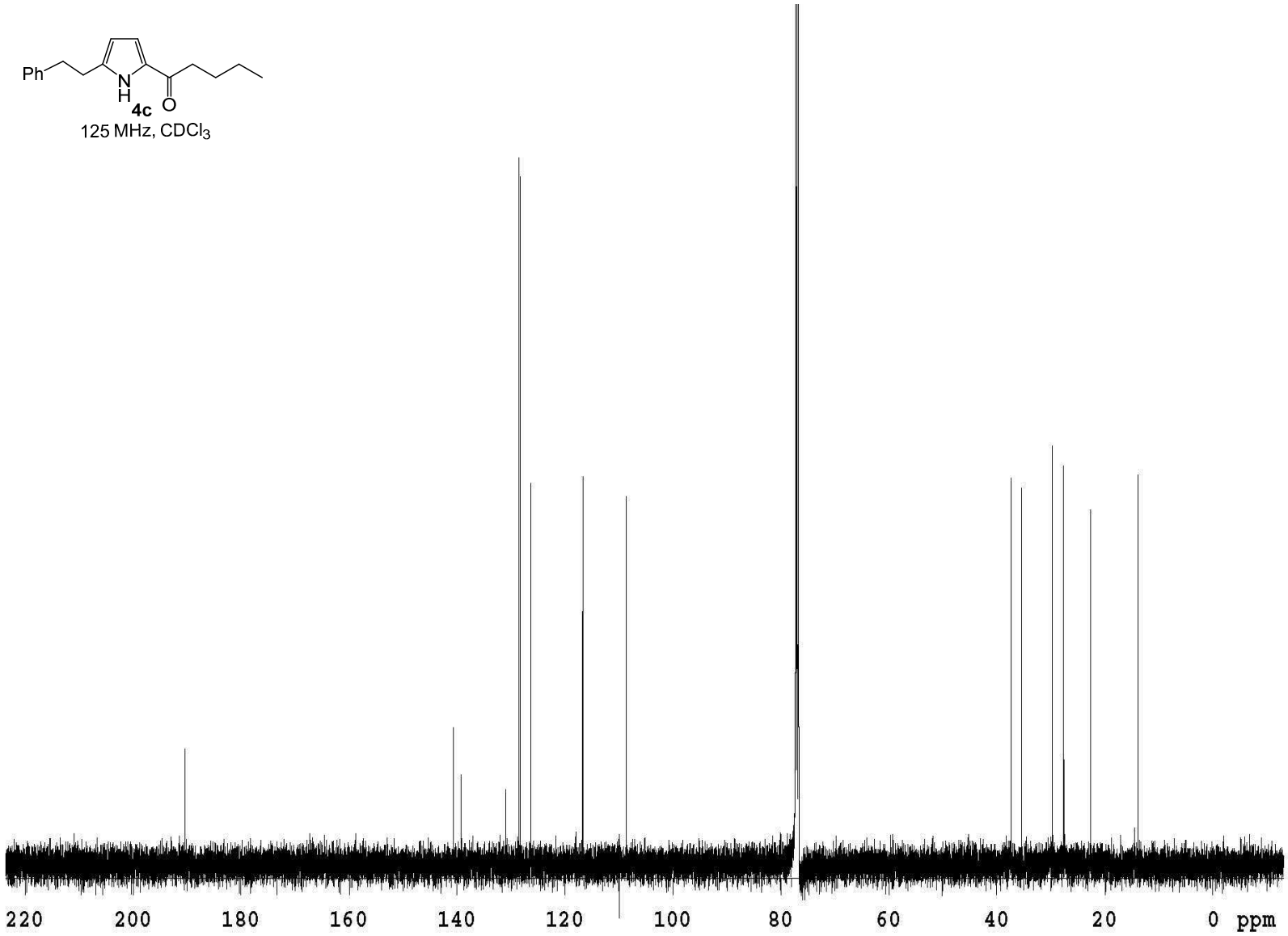

Ph
N
H
O
4a
500 MHz, CDCl3
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
0.41
1.91
1.94
1.91
0.91
0.93
3.00

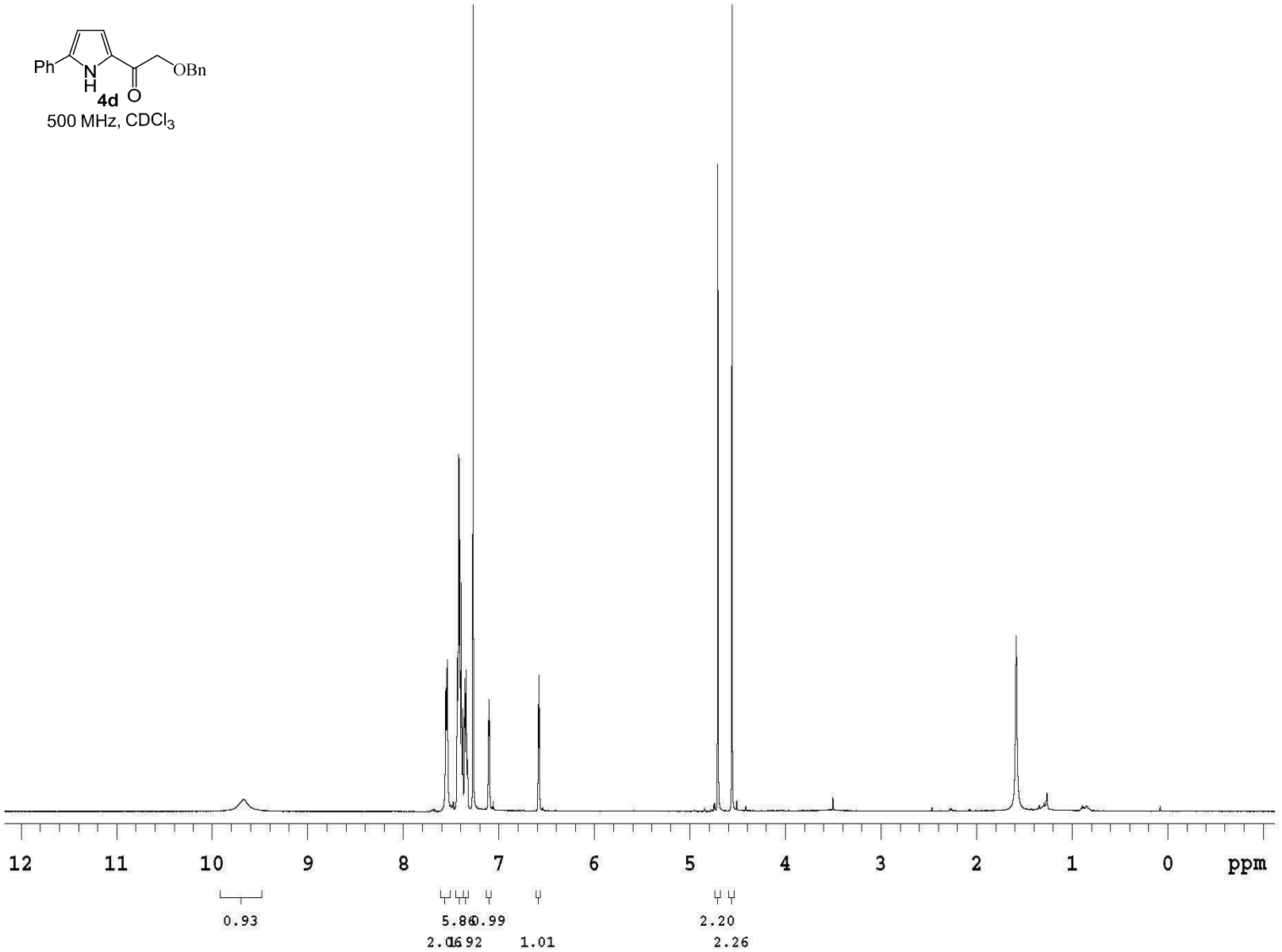

Ph
N
H
O
4a
125 MHz, CDCl3
220
200
180
160
140
120
100
80
60
40
20
0
ppm

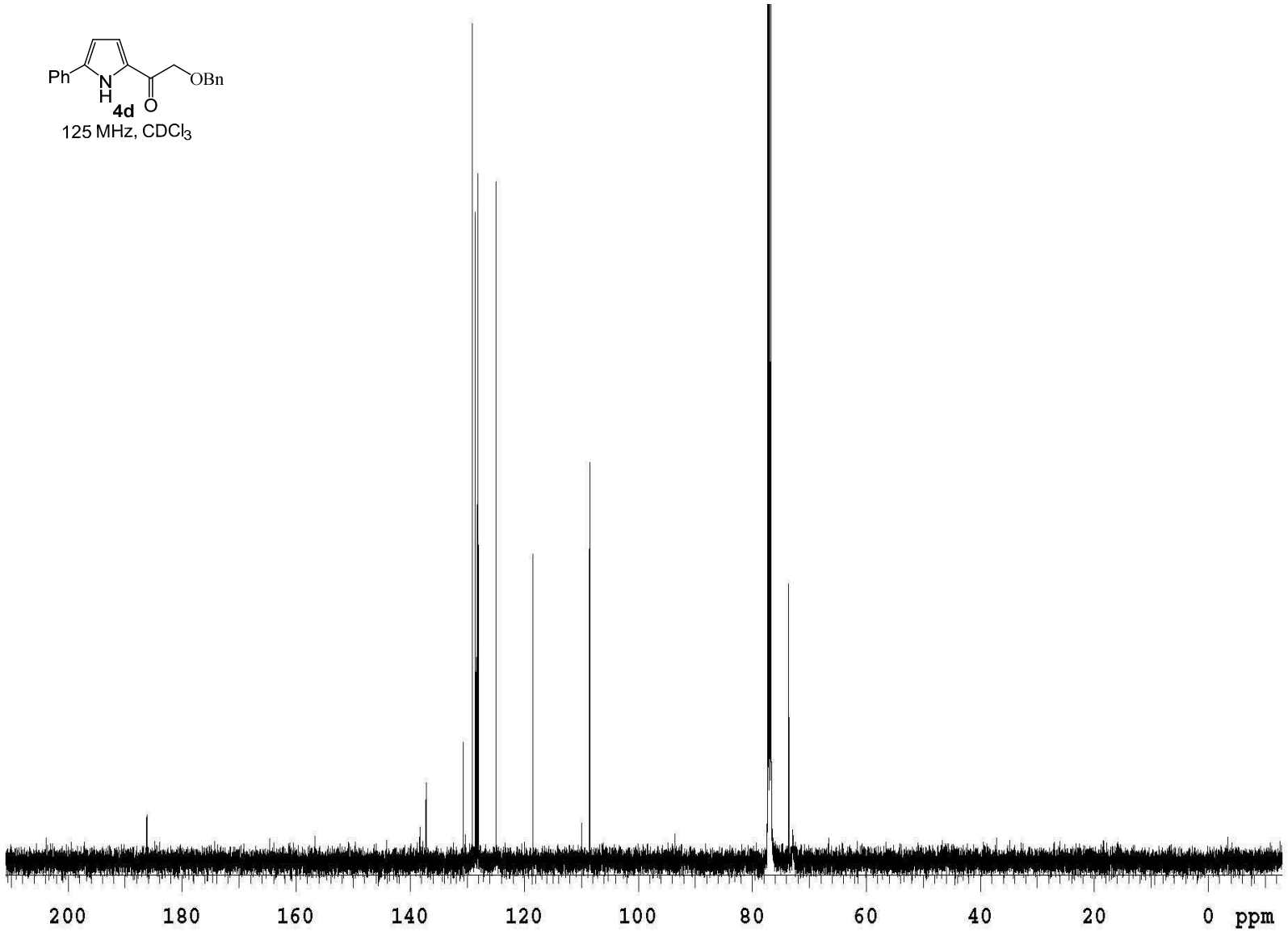

Ph
N
H
O
4b
500 MHz, CDCl3
10
9
8
7
6
5
4
3
2
1
0
ppm
0.83
2.10
1.00
2.27
2.27
3.22
1.00

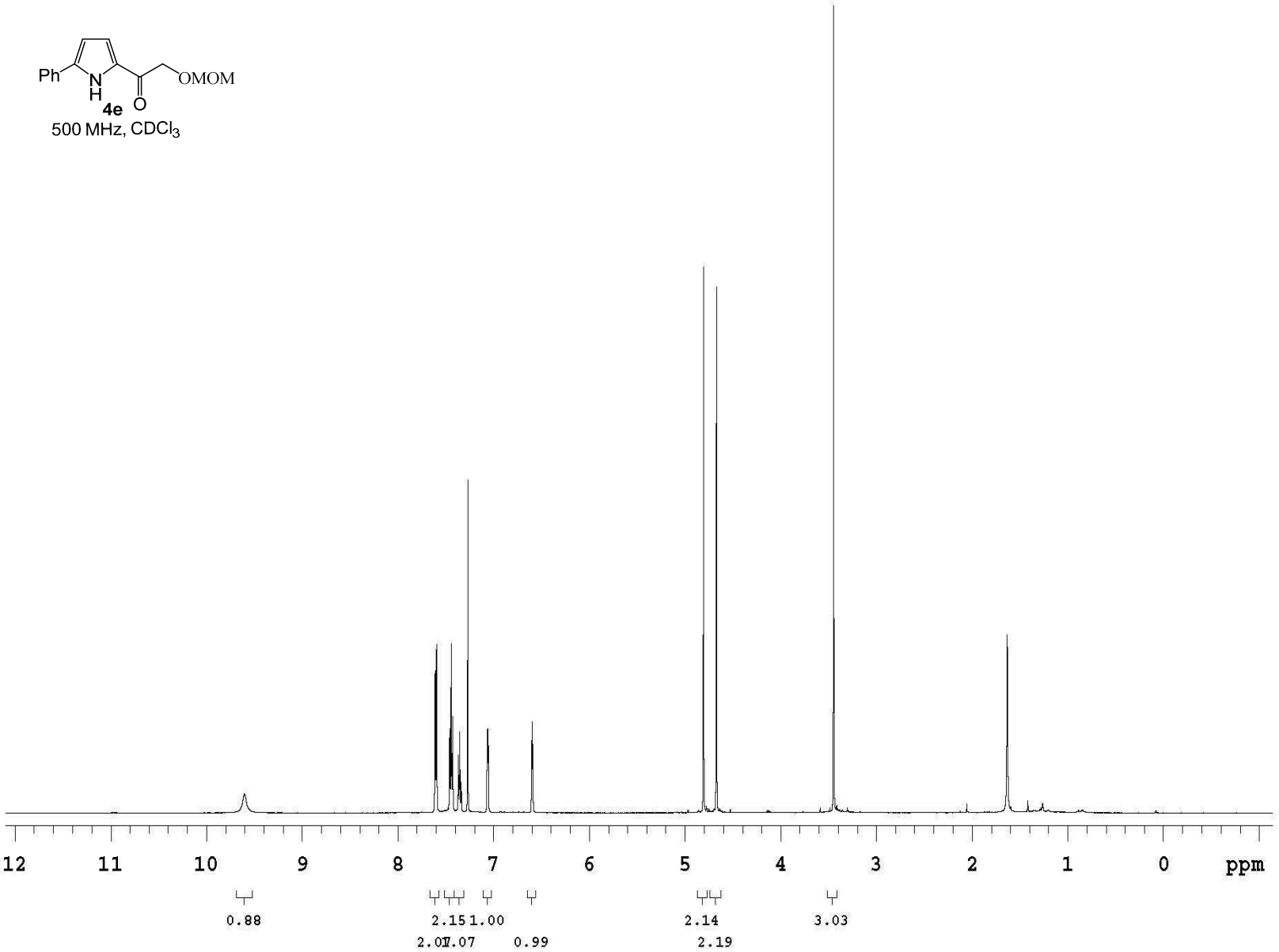

Ph
N
H
O
4b
125 MHz, CDCl3
220
200
180
160
140
120
100
80
60
40
20
0
ppm

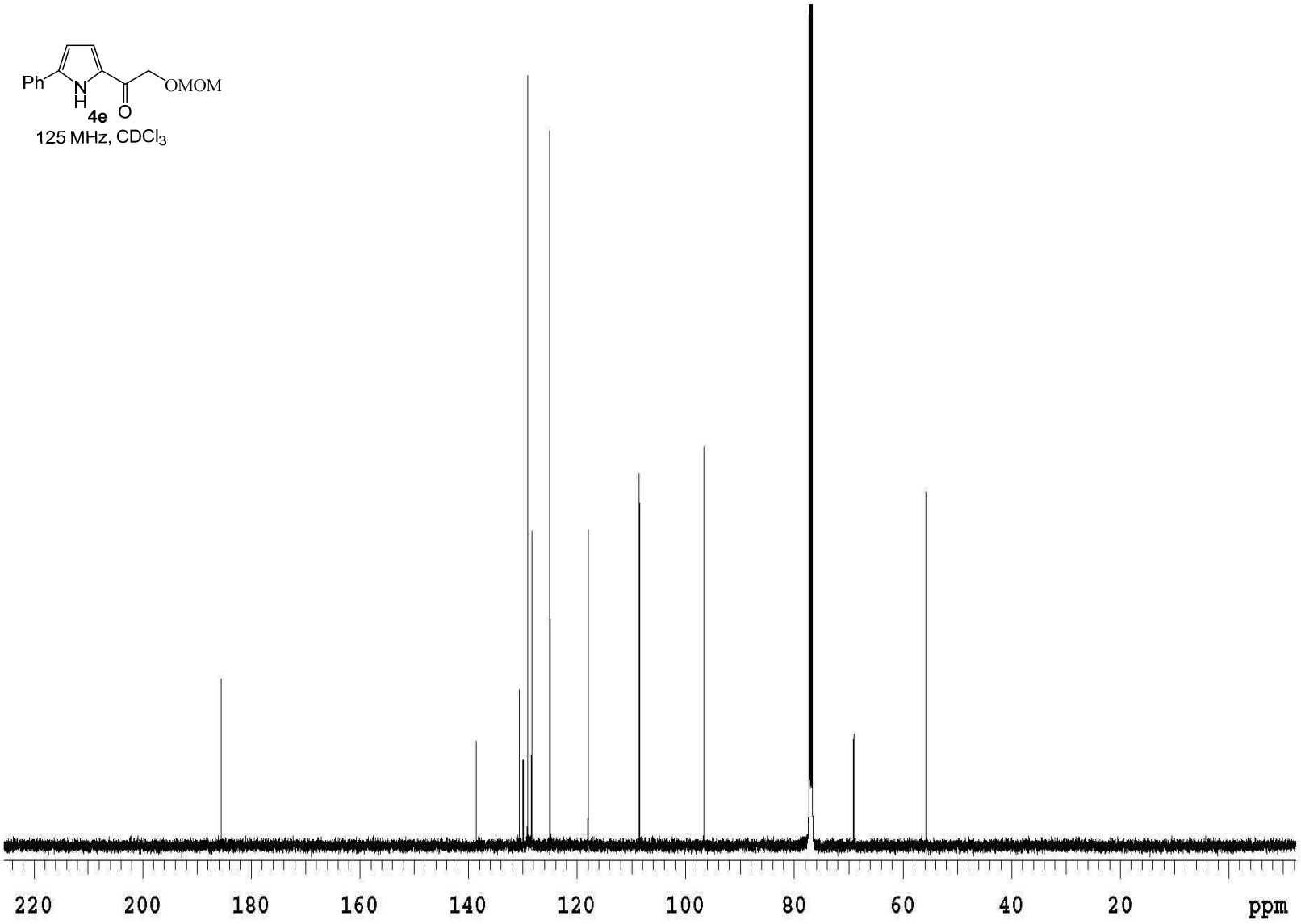

Ph
N
H
4c
O
500 MHz, CDCl3
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
0.88
1.02
1.00
2.07
0.94
4.00
2.07
2.20
3.04
2.14

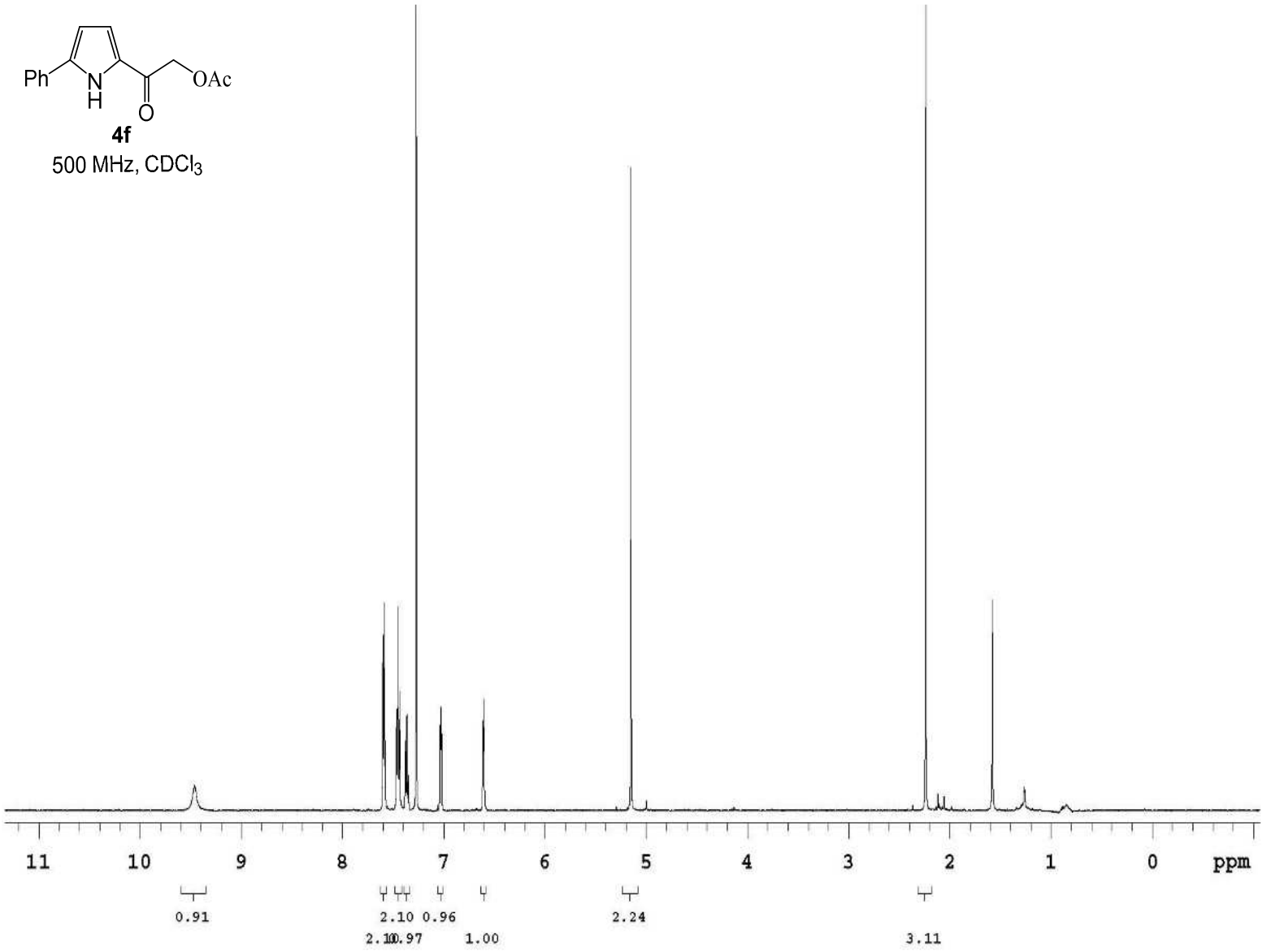

Ph
N
H
O
4c
125 MHz, CDCl3
220
200
180
160
140
120
100
80
60
40
20
0 ppm

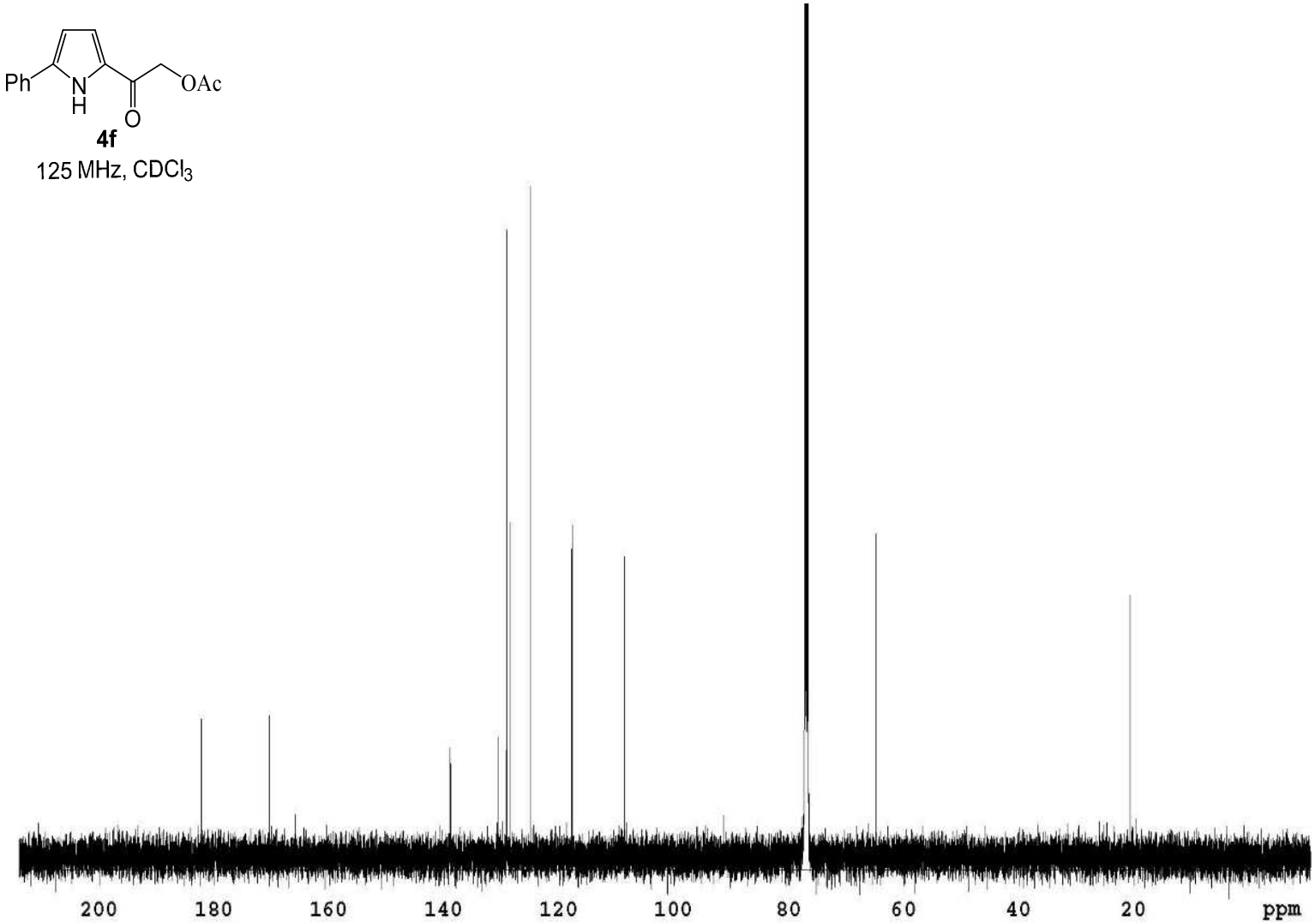

Ph
N
H
O
OBn
4d
500 MHz, CDCl3
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
0.93
5.86
0.99
2.20
2.01
1.92
1.01
2.26

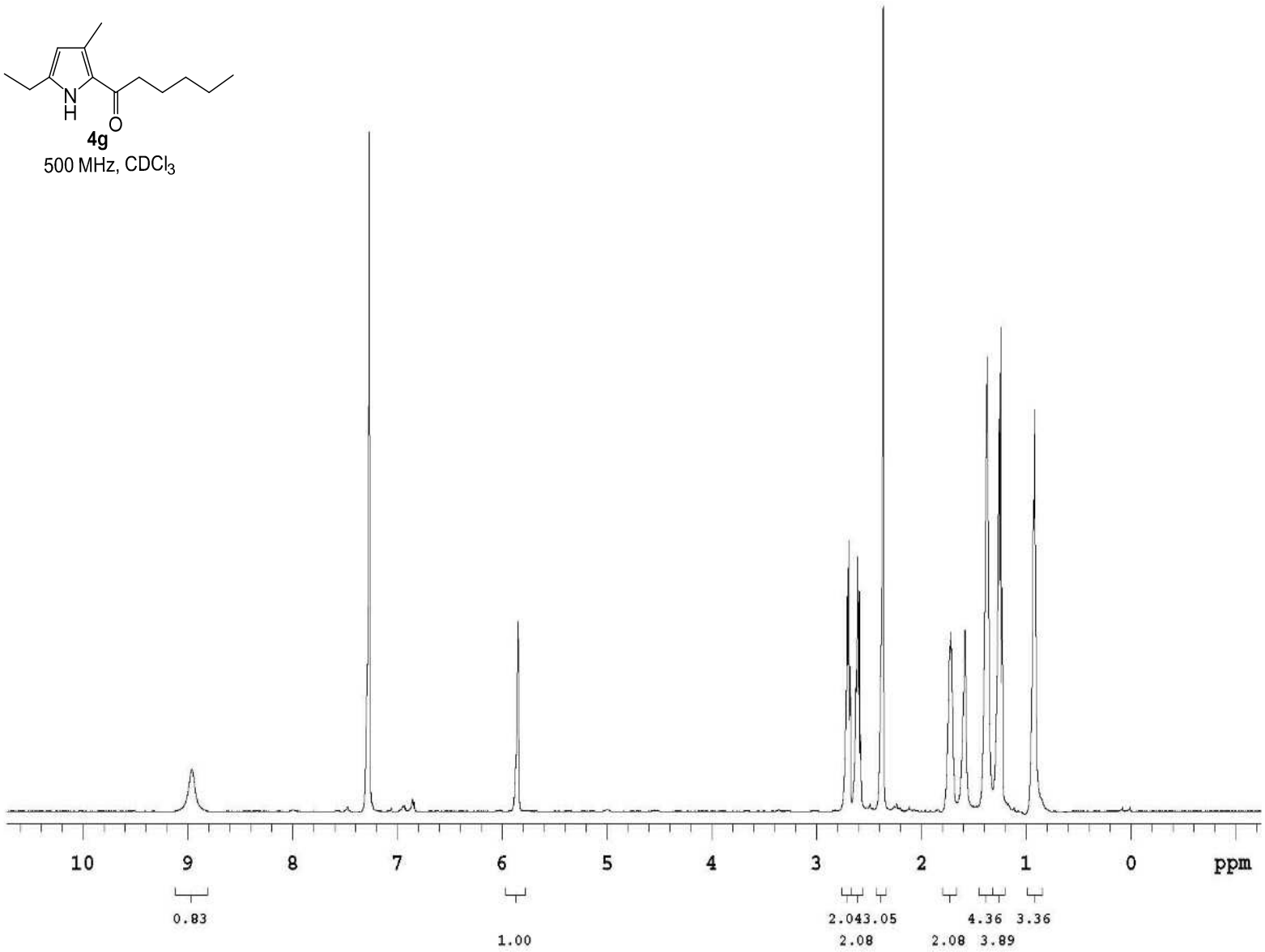

Ph
N
H
O
OBn
4d
125 MHz, CDCl3
200
180
160
140
120
100
80
60
40
20
0
ppm

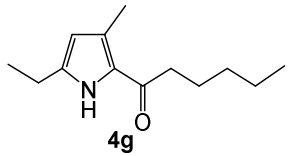

Ph
N
H
O
OMOM
4e
500 MHz, CDCl3
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
0.88
2.15
1.00
2.01
1.07
0.99
2.14
2.19
3.03


Ph
N
H
O
OMOM
4e
125 MHz, CDCl3
220
200
180
160
140
120
100
80
60
40
20
ppm


Ph
N
H
O
OAc
4f
500 MHz, CDCl3
11
10
9
8
7
6
5
4
3
2
1
0
ppm
0.91
2.10
0.96
2.10
0.97
1.00
2.24
3.11

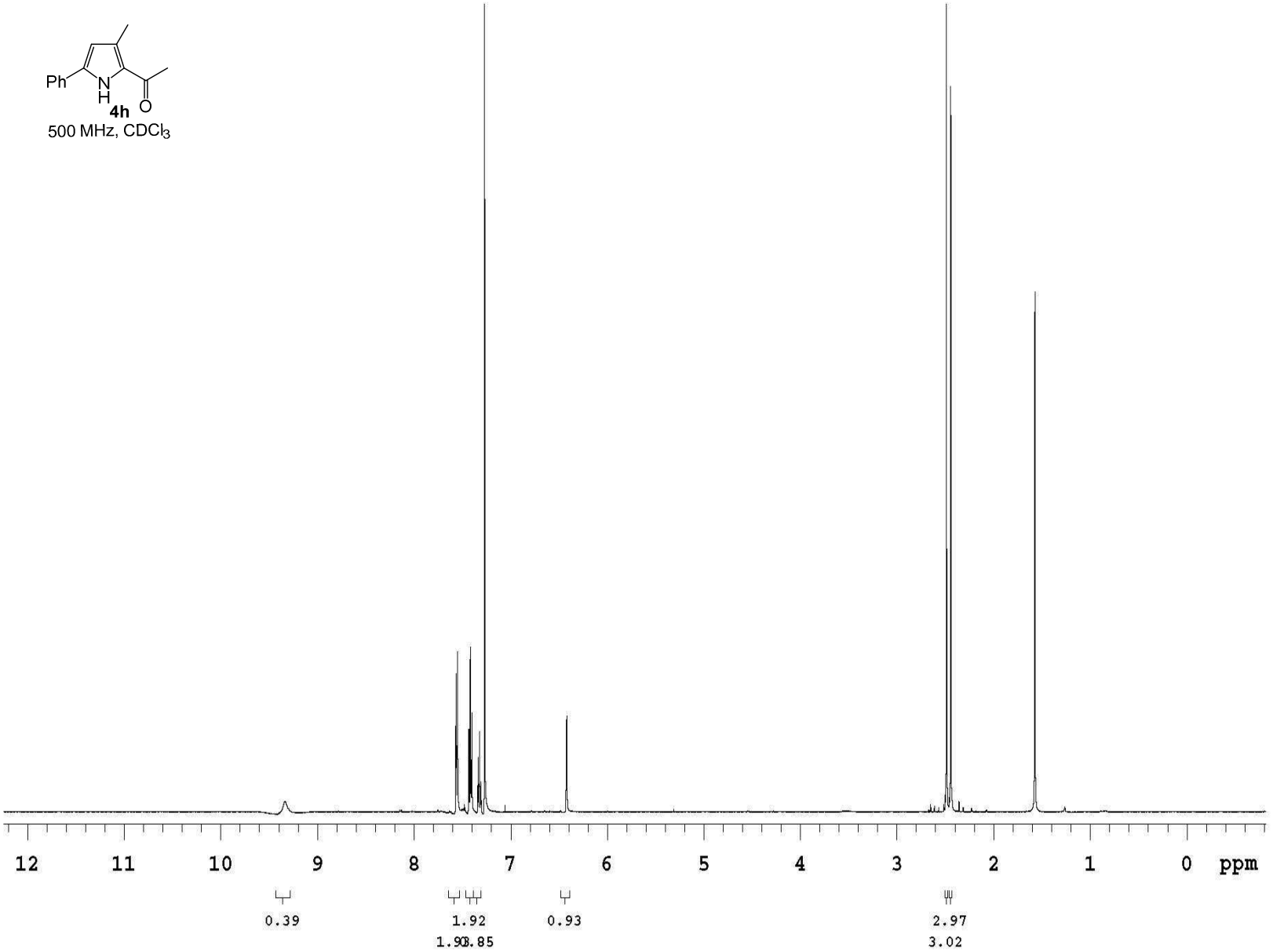

Ph
N
H
O
OAc
4f
125 MHz, CDCl3
200
180
160
140
120
100
80
60
40
20
ppm

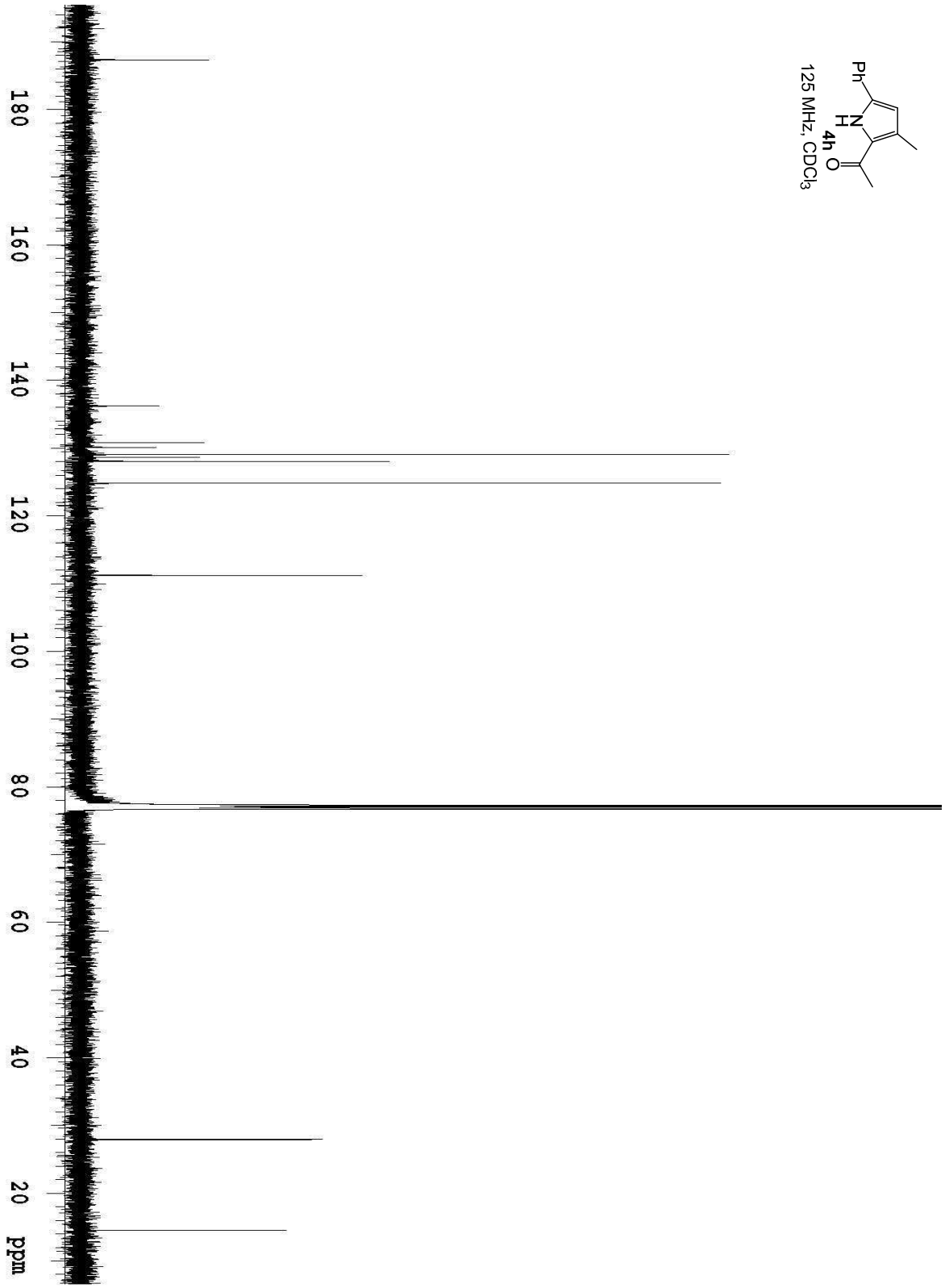

4g
500 MHz, CDCl3
10
9
8
7
6
5
4
3
2
1
0
ppm
0.83
1.00
2.04
3.05
2.08
2.08
4.36
3.89
3.36

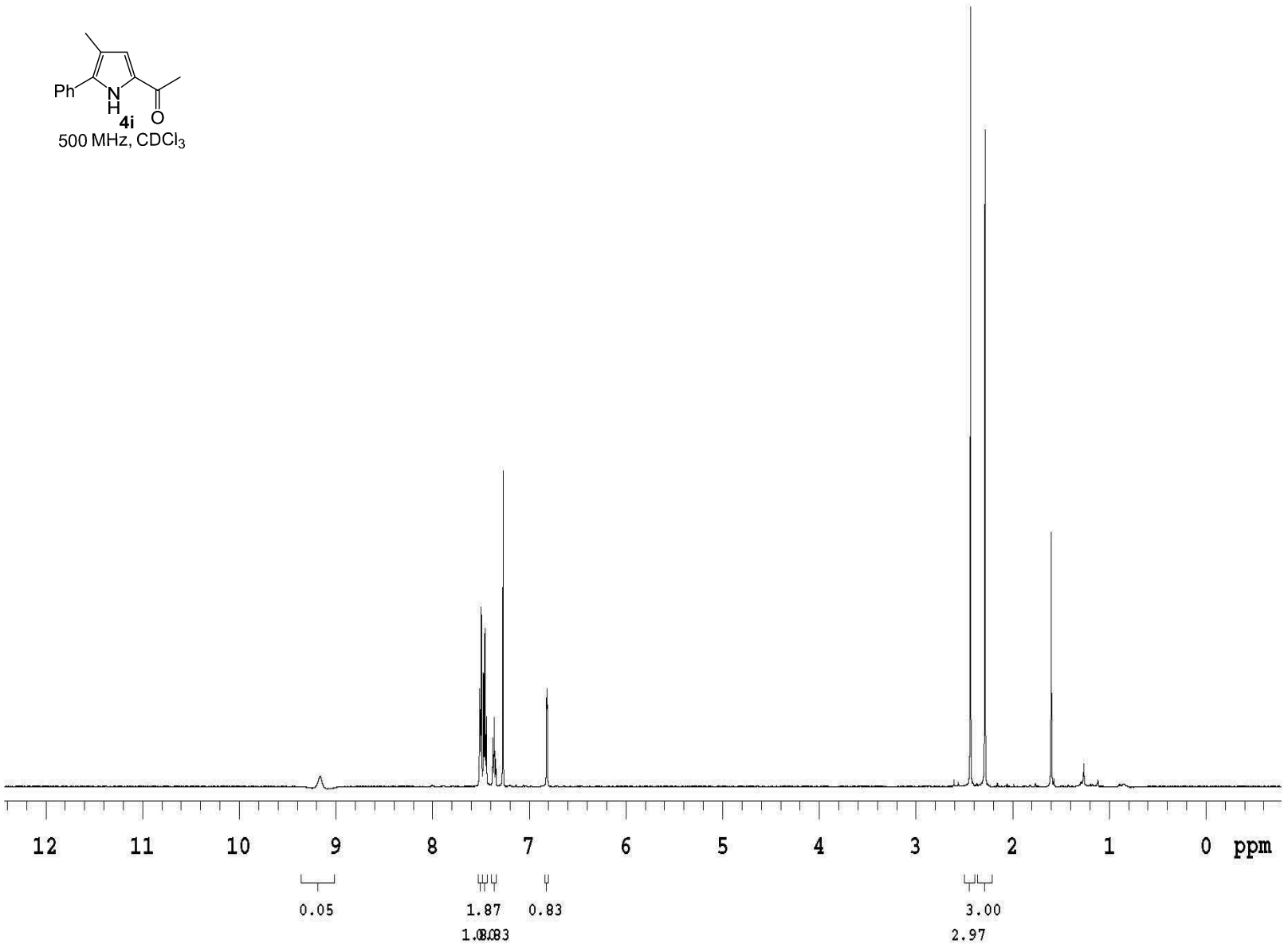


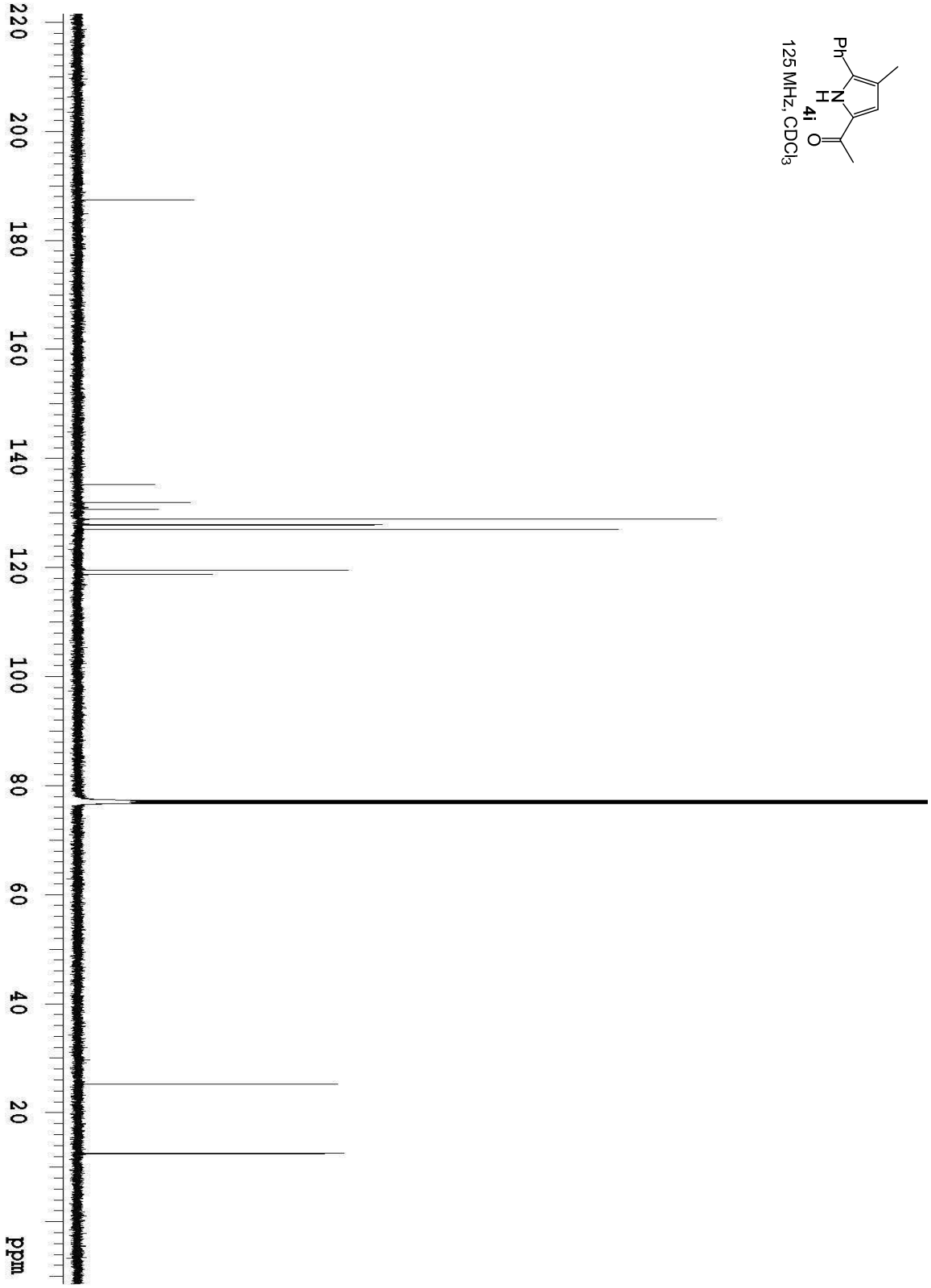
4g

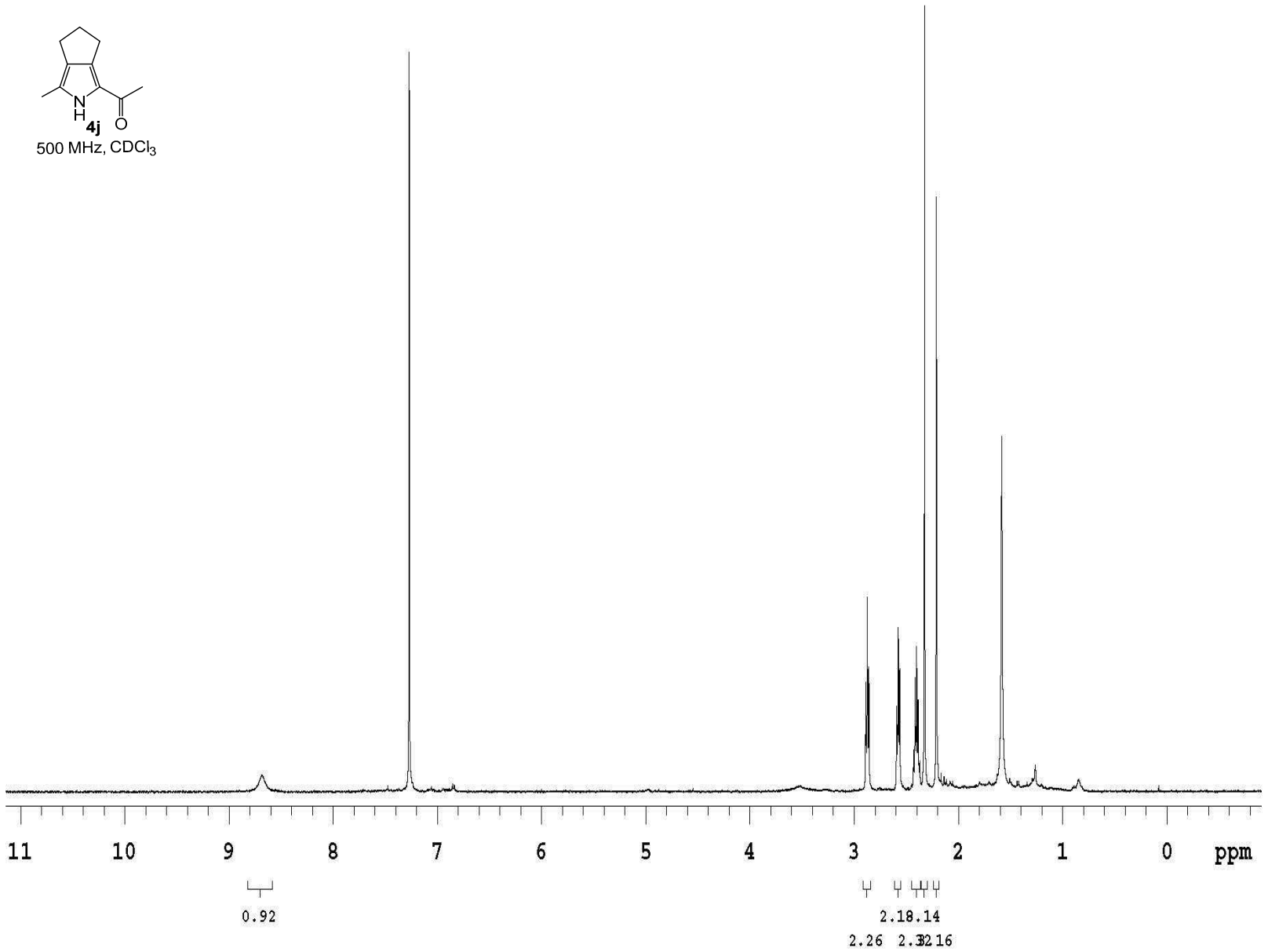
125 MHz, $CDCl_3$

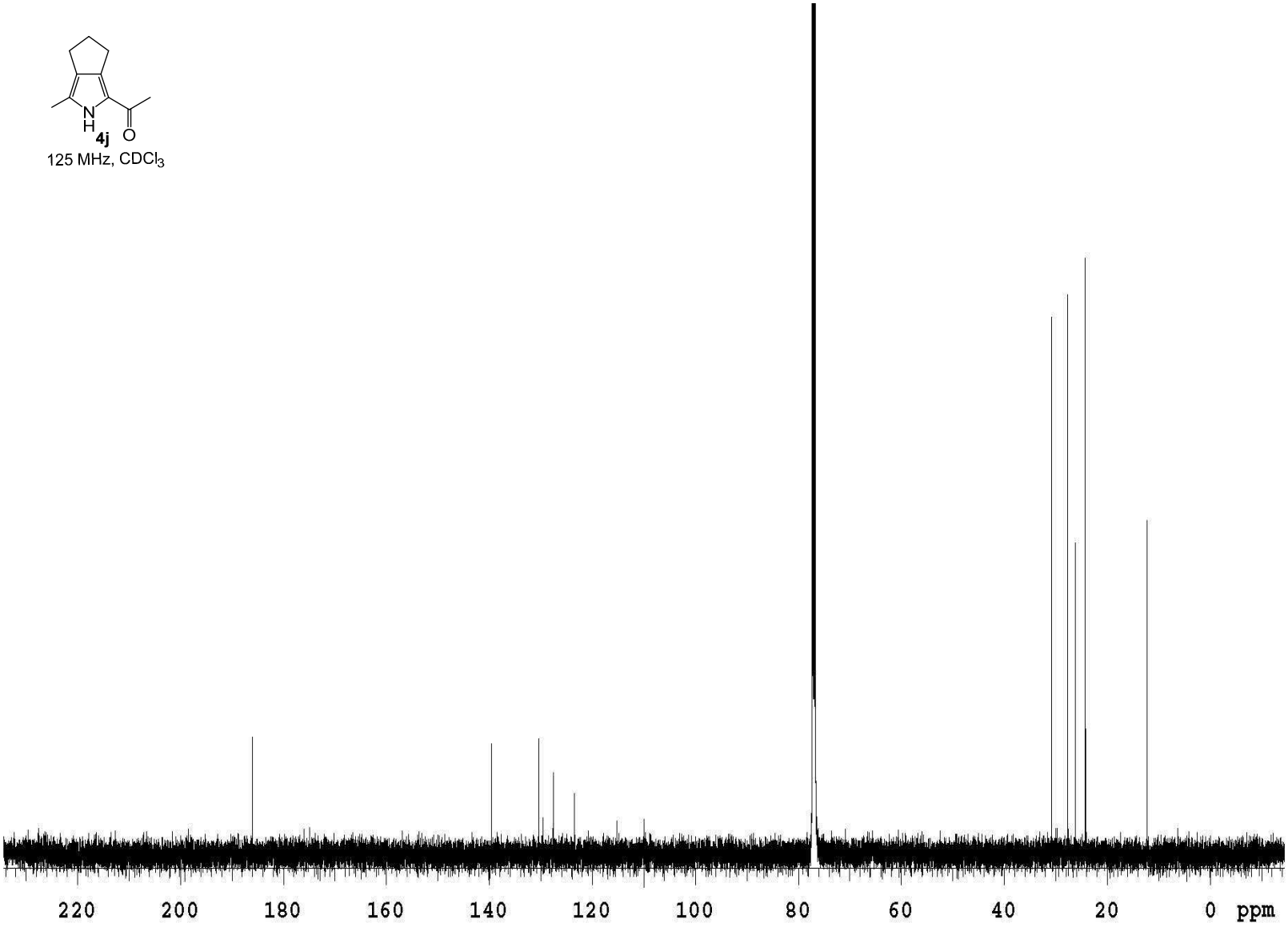

Ph
N
H
O
4h
500 MHz, CDCl3
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
0.39
1.92
1.90
3.85
0.93
2.97
3.02

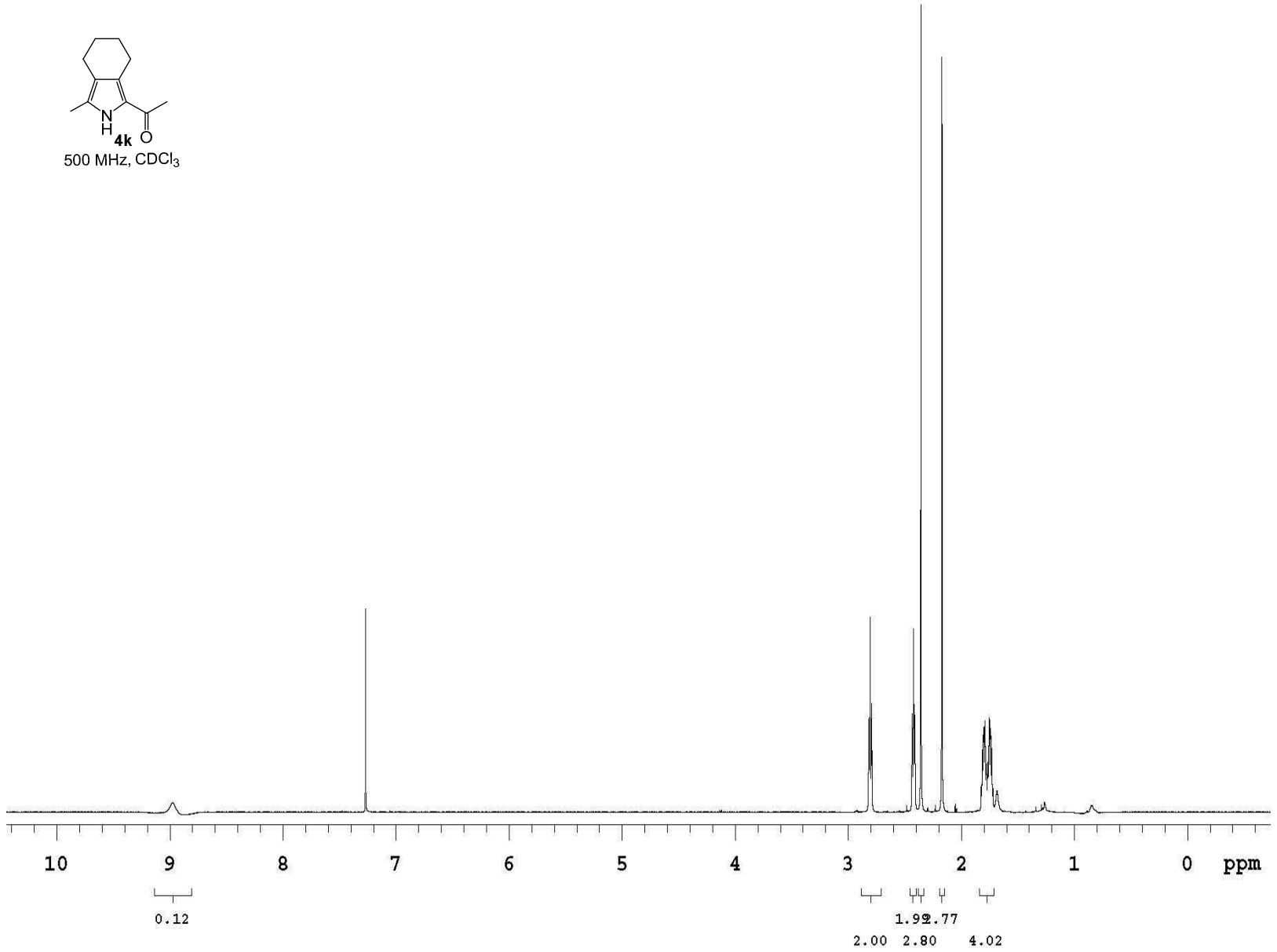

Ph
N
H
4h
O
125 MHz, CDCl3
180
160
140
120
100
80
60
40
20
ppm

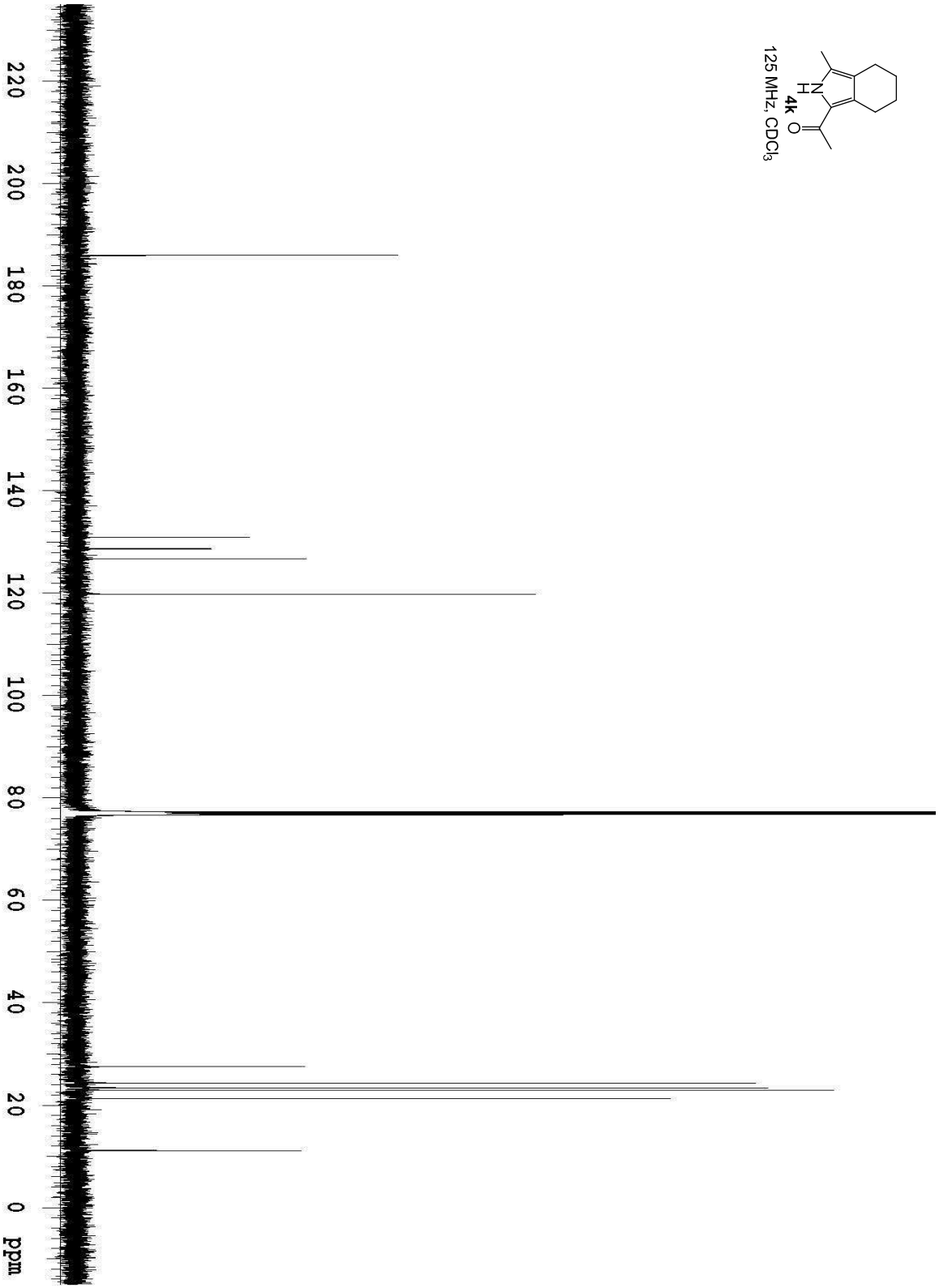

Ph
N
H
O
4i
500 MHz, CDCl3
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
0.05
1.87
0.83
3.00
2.97

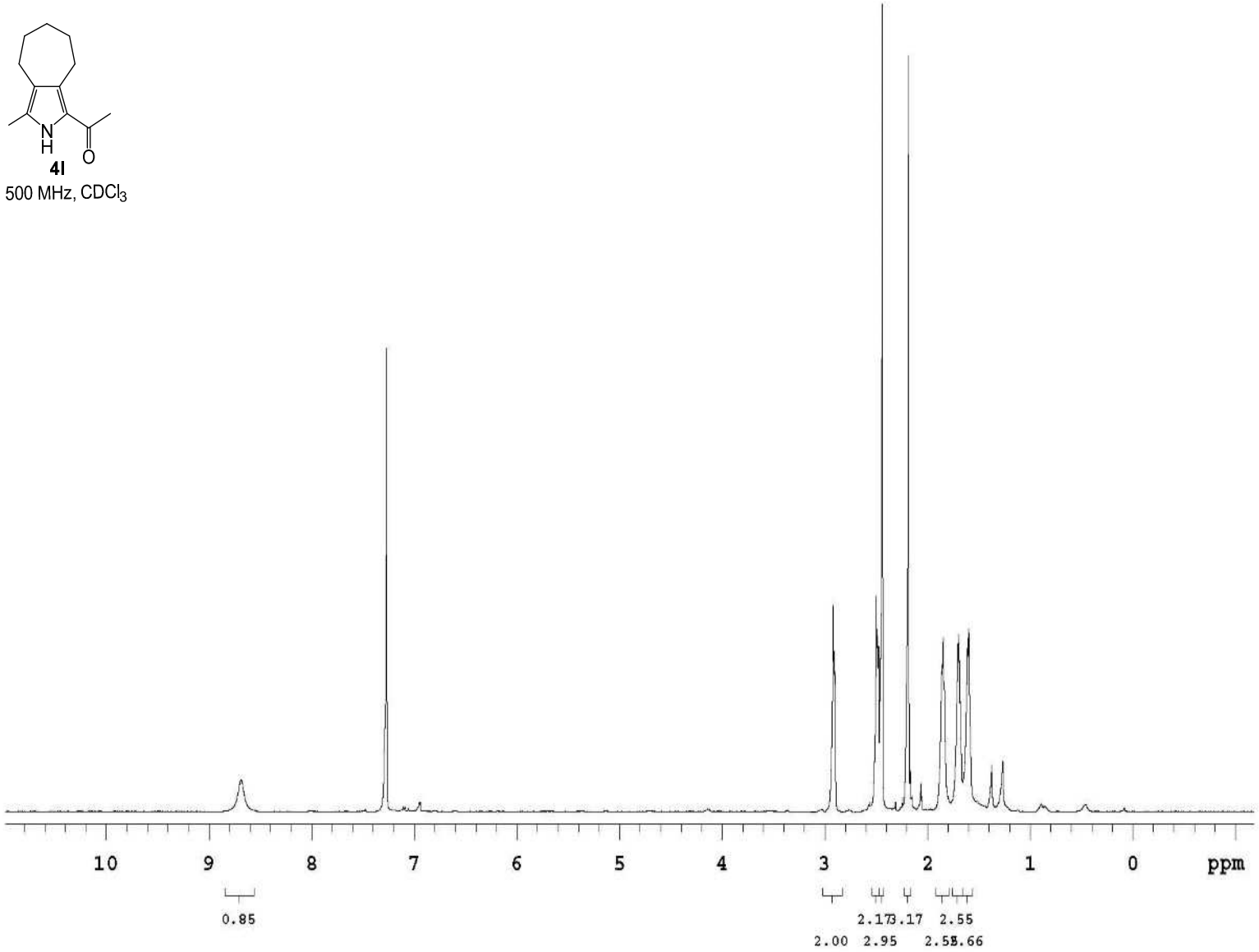

Ph
N
H
4i
O
125 MHz, CDCl3
220
200
180
160
140
120
100
80
60
40
20
ppm

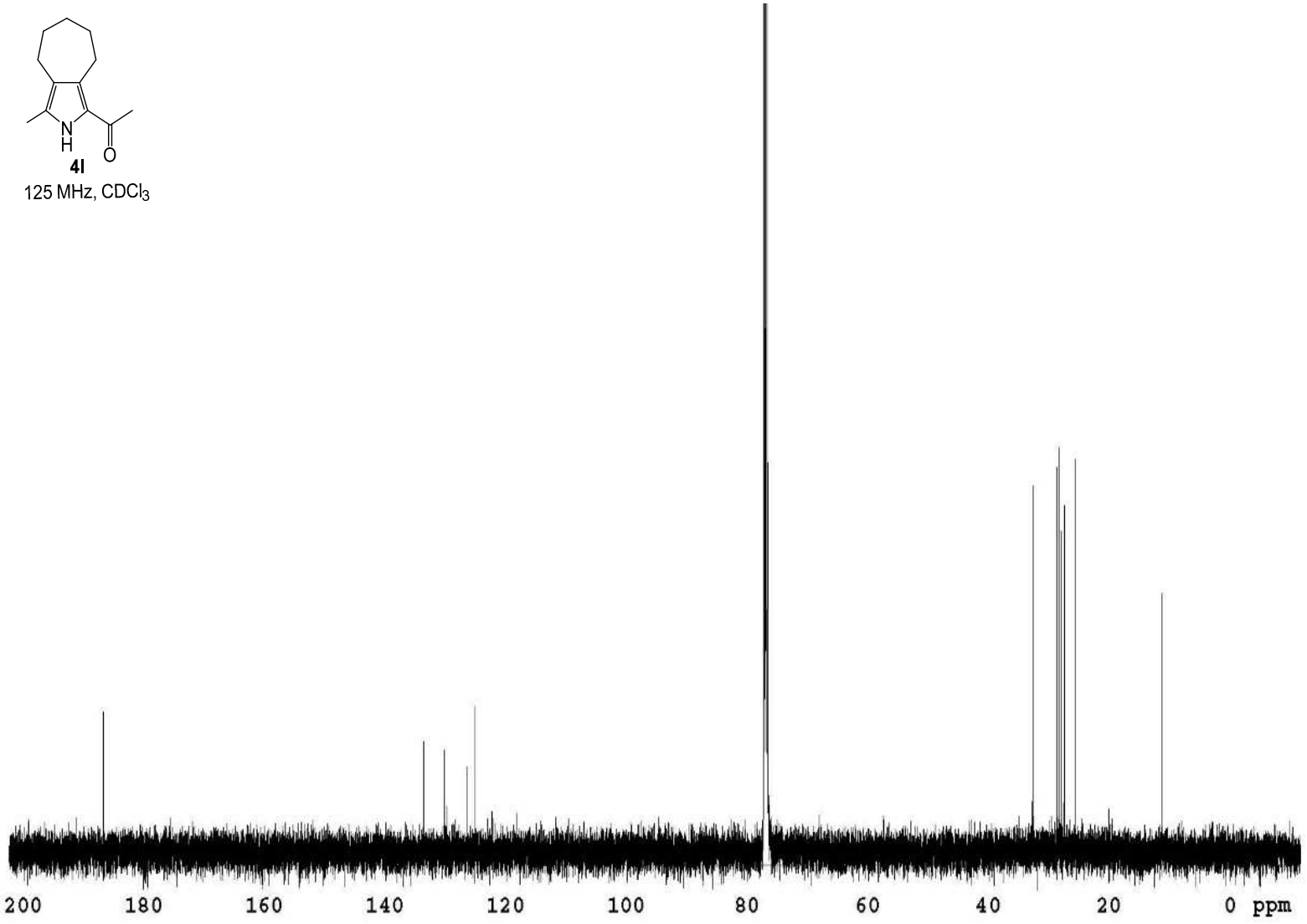

4j
500 MHz, CDCl3
11
10
9
8
7
6
5
4
3
2
1
0
ppm
0.92
2.18
2.14
2.26
2.16


4j
125 MHz, CDCl3
220
200
180
160
140
120
100
80
60
40
20
0
ppm


4k
500 MHz, CDCl3
10
9
8
7
6
5
4
3
2
1
0
ppm
0.12
2.00
1.99
2.80
2.77
4.02


4k
125 MHz, CDCl3
220
200
180
160
140
120
100
80
60
40
20
0
ppm


4l
500 MHz, CDCl3
10
9
8
7
6
5
4
3
2
1
0
ppm
0.85
2.00
2.95
2.17
3.17
2.55
2.55.66


4l
125 MHz, CDCl3
200
180
160
140
120
100
80
60
40
20
0 ppm