Supplemental material for:

Electronic Effects in the Pt-Catalyzed Cycloisomerization of Propargylic Esters: Synthesis of 2,3-Disubstituted Indolizines as a Mechanistic Probe

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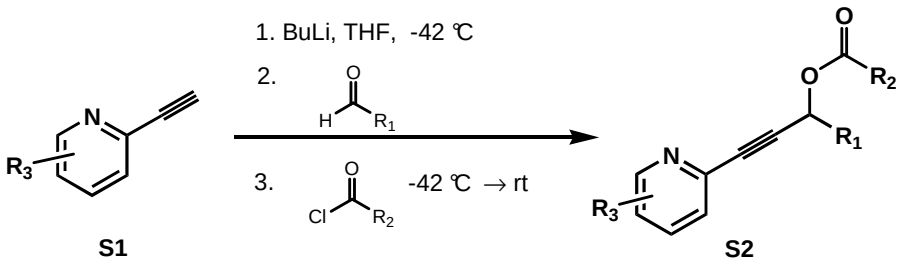
Experimental

Materials and Methods

Unless otherwise stated, reactions were performed in flame-dried glassware fitted with rubber septa under a nitrogen atmosphere. Liquid reagents and solvents were transferred via syringe under nitrogen. THF was distilled over sodium/benzophenone ketyl; dichloromethane, benzene and toluene were distilled over calcium hydride. All other solvents were used as received unless otherwise noted. Reaction temperatures above 23 °C were controlled by an IKA® temperature modulator. Reactions were monitored by thin layer chromatography using SiliCycle silica gel 60 F254 precoated plates (0.25 mm) which were visualized using UV irradiation, anisaldehyde stain or $KMnO_4$ stain. SiliCycle Silica-P silica gel (particle size 40-63 μm) was used for flash chromatography. ^1H and ^{13}C NMR were recorded on Bruker AVB-400 or DRX-500 MHz spectrometers with ^{13}C operating frequencies of 100 and 125 MHz, respectively, in benzene-d_6 at 23 °C. Chemical shifts (δ) are reported in ppm relative to the residual solvent signal (δ = 7.15 for ^1H NMR and δ = 128.02 ^{13}C NMR). Data for ^1H NMR are reported as follows: chemical shift (multiplicity, coupling constant, number of hydrogens). Multiplicity is abbreviated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet). IR spectra were recorded on a Nicolet MAGNA-IR 850 spectrometer and are reported in frequency of absorption (cm^{-1}). Mass spectral data were obtained from the Mass Spectral Facility at the University of California, Berkeley.

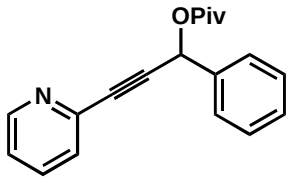
Scheme S1



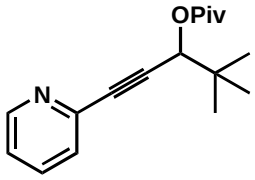
Representative Procedure for the Synthesis of Substrates

A flame-dried, round-bottom flask was charged with anhydrous THF (50 mL) and 2-ethynylpyridine (490 μL, 4.85 mmol). The solution was cooled to -42 °C and BuLi (2.5 M in hexanes, 2.3 mL, 5.82 mmol) was added dropwise. The solution was allowed to stir at -42 °C for 90 min, and then benzaldehyde (700 μL, 6.79 mmol) was added dropwise to the reaction mixture. The mixture was stirred at -42 °C for 2 h, then pivaloyl chloride (900 μL, 7.28 mmol) was added dropwise. The mixture was stirred for an additional 45 min at this temperature, then allowed to warm to rt. After 3 h, saturated aqueous NH_4Cl solution (30 mL) was added slowly and stirring was continued for 10 min. The mixture was diluted with EtOAc (50 mL), and the aqueous layer was extracted with EtOAc (3 x 30 mL). The organic layers were combined, washed with brine (60 mL) and dried over $MgSO_4$. The solvent was removed under reduced pressure and the crude mixture was purified by flash chromatography (4:1 hexanes/EtOAc) to obtain a yellow crystalline solid (1.18 g, 83% yield).

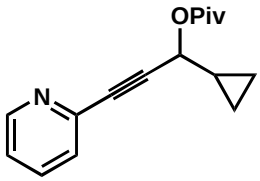
Spectral Data for Substrates



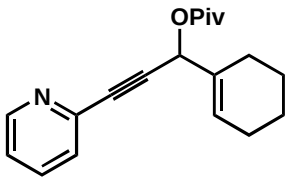
1-Phenyl-3-(pyridin-2-yl)prop-2-ynyl pivalate (18b): Yellow oil, 83% yield; $\mathbf{R_f}$ (3:1 hexanes/EtOAc) 0.24; **^{1}H NMR** (300 MHz, C_6D_6) δ 8.32 (d, *J* = 4.8 Hz, 1H), 7.58 (dd, *J* = 7.9, 1.2 Hz, 2H), 7.12-6.96 (m, 4H), 6.93 (s, 1H), 6.75 (dt, *J* = 7.8, 1.7 Hz, 1H), 6.47-6.39 (m, 1H), 1.10 (s, 9H); **^{13}C NMR** (125 MHz, C_6D_6) δ 176.6, 150.3, 143.2, 137.7, 135.5, 129.0, 128.9, 128.3, 127.3, 123.0, 87.0, 85.9, 66.0, 38.8, 27.0; **IR** (film) υ_{max} 2974, 1734, 1583, 1464, 1428, 1275, 1138, 697 cm^{-1}; **MS** (EI^+): *m/z* 293 (M^+); **HRMS** (EI^+) calcd for $[C_{19}H_{19}NO_2]^+$: *m/z* 293.1416, found 293.1411.



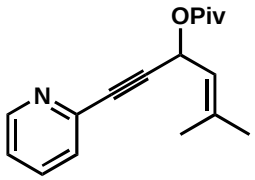
4,4-Dimethyl-1-(pyridin-2-yl)pent-1-yn-3-yl pivalate (Table 2, entry 1): Yellow oil, 69% yield; $\mathbf{R_f}$ (3:1 hexanes/EtOAc) 0.36; **^{1}H NMR** (400 MHz, C_6D_6) δ 8.32 (d, *J* = 4.14 Hz, 1H), 7.02 (d, *J* = 7.8 Hz, 1H), 6.77 (dt, *J* = 7.7, 1.8 Hz, 1H), 6.44 (ddd, *J* = 7.6, 4.8, 1.1Hz, 1H), 5.58 (s, 1H), 1.16 (s, 9H), 1.03 (s, 9H); **^{13}C NMR** (100 MHz, C_6D_6) δ 176.6 150.2 143.4 135.5 128.3 127.3 122.8 85.9 72.0, 35.7, 27.2, 25.7; **IR** (film) υ_{max} 2971, 1735, 1583, 1464, 1428, 1278, 1147, 973, 780 cm^{-1}; **MS** (EI$^+$): *m/z* 273 (M$^+$); **HRMS** (EI$^+$) calcd for $[C_{17}H_{23}NO_2]^+$: *m/z* 273.1729, found 273.1725.



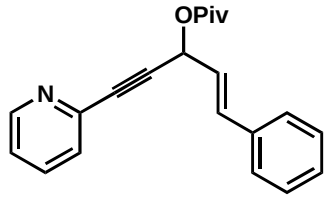
1-Cyclopropyl-3-(pyridin-2-yl)prop-2-ynyl pivalate (Table 2, entry 2): Yellow oil, 56% yield; $\mathbf{R_f}$ (3:1 hexanes/EtOAc) 0.33; **^{1}H NMR** (500 MHz, C_6D_6) δ 8.32 (d, *J* = 4.4 Hz, 1H), 7.02 (d, *J* = 7.8 Hz, 1H), 6.76 (dt, *J* = 7.7, 1.8 Hz, 1H), 6.43 (ddd, *J* = 7.6, 4.8, 1.1 Hz, 1H), 5.59 (d, *J* = 7.2 Hz, 1H), 1.28-1.21 (m, 1H), 1.18 (s, 9H), 0.51-0.47 (m, 2H), 0.35-0.25 (m, 2H); **^{13}C NMR** (125 MHz, C_6D_6) δ 176.9, 150.3, 143.3, 135.5, 127.3, 122.8, 85.4, 67.6, 38.9, 27.2, 15.1, 3.7, 2.6; **IR** (film) υ_{max} 2974, 1731, 1582, 1464, 1429, 1278, 1148, 1031, 968, 780 cm^{-1}; **MS** (FAB$^+$): *m/z* 258 (M+H$^+$); **HRMS** (FAB$^+$) calcd for $[C_{16}H_{20}NO_2]^+$ (M+H$^+$): *m/z* 258.1494, found 258.1487.



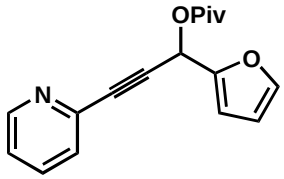
1-Cyclohexenyl-30(pyridine-2-yl)prop-2-ynyl pivalate (Table 2, entry 3): Yellow oil, 72% yield; $\mathbf{R_f}$ (3:1 hexanes/EtOAc) 0.28; **^{1}H NMR** (400 MHz, C_6D_6) δ 8.36-8.32 (m, 1H), 7.04 (td, *J* = 7.8, 1.0 Hz, 1H), 6.75 (dt, *J* = 7.8, 1.8 Hz, 1H), 6.42 (ddd, *J* = 7.6, 4.9, 1.2 Hz, 1H), 6.34 (s, 1H), 6.04 (d, *J* = 1.0 Hz, 1H), 2.42-2.01 (m, 2H), 1.86-1.73 (m, 2H), 1.54-1.41 (m, 2H), 1.39-1.27 (m, 2H), 1.16 (s, 9H); **^{13}C NMR** (100 MHz, C_6D_6) δ 176.6, 150.2, 143.4, 135.5, 133.7, 127.3, 122.8, 86.2, 85.8, 68.2, 39.0, 27.3, 27.2, 25.2, 24.9, 22.7, 22.3; **IR** (film) υ_{max} 2932, 1733, 1582, 1463, 1428, 1274, 1143, 1030, 779 cm^{-1}; **MS** (EI^+): *m/z* 297 (M^+); **HRMS** (EI^+) calcd for $[C_{19}H_{23}NO_2]^+$: *m/z* 297.1729, found 297.1733.



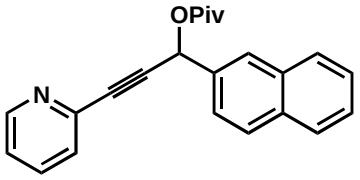
5-Methyl-1-(pyridine-2-yl)hex-4-en-1-yn-3-yl pivalate (Table 2, entry 4): Yellow oil, 82% yield; $\mathbf{R_f}$ (3:1 hexanes/EtOAc) 0.40; **^{1}H NMR** (400 MHz, C_6D_6) δ 8.33 (dd, *J* = 4.8, 0.7 Hz, 1H), 7.06 (d, *J* = 7.8 Hz, 1H), 6.76 (dt, *J* = 7.7, 1.8 Hz, 1H), 6.63 (d, *J* = 9.0 Hz, 1H), 6.43 (ddd, *J* = 7.6, 4.8, 1.1 Hz, 1H), 5.58-5.53 (m, 1H), 1.54 (d, *J* = 1.2 Hz, 3H), 1.41 (d, *J* = 1.2 Hz, 3H), 1.16 (s, 9H); **^{13}C NMR** (100 MHz, C_6D_6) δ 176.7, 150.3, 143.5, 139.3, 135.5, 127.3, 122.8, 121.2, 86.8, 85.2, 61.6, 38.9, 27.2, 25.5, 18.2; **IR** (film) υ_{max} 2973, 1730, 1582, 1463, 1428, 1275, 1145, 924, 778 cm^{-1}; **MS** (EI^+): *m/z* 271 (M^+); **HRMS** (EI^+) calcd for $[C_{17}H_{21}NO_2]^+$: *m/z* 271.1572, found 271.1573.



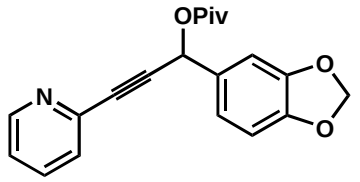
(*E*)-5-Phenyl-1-(pyridin-2-yl)pent-4-en-1-yn-3-yl pivalate (Table 2, entry 5): Yellow oil, 56% yield; $\mathbf{R_f}$ (3:1 hexanes/EtOAc) 0.36; **^{1}H NMR** (500 MHz, C_6D_6) δ 8.34 (d, *J* = 4.2 Hz, 1H), 7.11-7.05 (m, 3H), 7.04-6.97 (m, 3H), 6.87 (d, *J* = 15.7 Hz, 1H), 6.77 (dt, *J* = 7.7, 1.8 Hz, 1H), 6.48 (dd, *J* = 6.7, 0.9 Hz, 1H), 6.44 (ddd, *J* = 7.6, 4.8, 1.0 Hz, 1H), 6.29 (dd, *J* = 15.8, 6.7 Hz, 1H), 1.17 (s, 9H); **^{13}C NMR** (125 MHz, C_6D_6) δ 176.7, 150.4, 143.3, 136.2, 135.5, 135.1, 128.7, 128.5, 128.3, 127.3, 124.1, 123.0, 86.9, 85.2, 64.9, 38.9, 27.1; **IR** (film) υ_{max} 2973, 1732, 1582, 1464, 1428, 1273, 1140, 965, 779, 693 cm^{-1}; **MS** (EI$^+$): *m/z* 319 (M^+); **HRMS** (EI$^+$) calcd for $[C_{21}H_{21}NO_2]^+$: *m/z* 319.1572, found 319.1573.



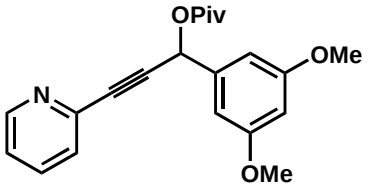
1-(Furan-2-yl)-3-(pyridin-2-yl)prop-2-ynyl pivalate (Table 2, entry 6): Orange oil, 70% yield; $\mathbf{R_f}$ (3:1 hexanes/EtOAc) 0.23; **^{1}H NMR** (400 MHz, C_6D_6) δ 8.32 (d, *J* = 4.2 Hz, 1H), 7.04-6.95 (m, 3H), 6.76 (dt, *J* = 7.8, 1.7 Hz, 1H), 6.49 (d, *J* = 3.3 Hz, 1H), 6.44 (dd, *J* = 7.6, 4.9 Hz, 1H), 5.93 (dd, *J* = 3.2, 1.9 Hz, 1H), 1.10 (s, 9H); **^{13}C NMR** (100 MHz, C_6D_6) δ 176.6, 150.3, 149.9, 143.7, 142.9, 135.5, 127.5, 123.1, 110.8, 110.5, 86.1, 83.5, 59.2, 38.9, 27.0; **IR** (film) υ_{max} 2974, 1737, 1583, 1464, 1429, 1273, 1135, 1008, 919, 779, 741 cm^{-1}; **MS** (EI$^+$): *m/z* 283 (M^+); **HRMS** (EI$^+$) calcd for $[C_{17}H_{17}NO_3]^+$: *m/z* 283.1208, found 283.1205.



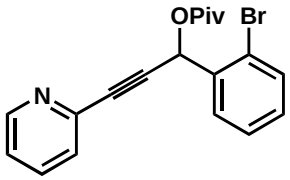
1-(Naphthalen-3-yl)-3-(pyridine-2-yl)prop-2-ynyl pivalate (Table 2, entry 7): Yellow oil, 68% yield; $\mathbf{R_f}$ (3:1 hexanes/EtOAc) 0.27; **^{1}H NMR** (400 MHz, C_6D_6) δ 8.34 (dd, *J* = 4.8, 0.8 Hz, 1H), 8.00 (d, *J* = 0.5 Hz, 1H), 7.72 (dd, *J* = 8.5, 1.7 Hz, 1H), 7.58 (d, *J* = 8.6 Hz, 1H), 7.53 (dd, *J* = 5.9, 3.3 Hz, 2H), 7.21-7.17 (m, 2H), 7.09 (s, 1H), 7.04 (td, *J* = 7.8, 1.0, 1.0 Hz, 1H), 6.75 (dt, *J* = 7.7, 1.8 Hz, 1H), 6.43 (ddd, *J* = 7.6, 4.8, 1.2 Hz, 1H), 1.13 (s, 9H); **^{13}C NMR** (125 MHz, C_6D_6) δ 176.6, 150.3, 143.2, 135.5, 135.0, 133.9, 133.6, 129.0, 128.7, 128.3, 127.6, 127.4, 126.7, 126.5, 125.4, 123.0, 87.3, 86.0, 66.3, 38.9, 27.0; **IR** (film) υ_{max} 2973, 1732, 1582, 1463, 1428, 1274, 1138 cm^{-1}; **MS** (EI$^+$): *m/z* 343 (M$^+$); **HRMS** (EI$^+$) calcd for $[C_{23}H_{21}NO_2]^+$: *m/z* 343.1572, found 343.1577.



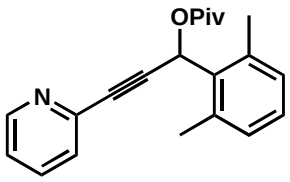
1-(Benzo[d][1,3]dioxol-5-yl)-3-(pyridine-2-yl)prop-2-ynyl pivalate (Table 2, entry 8): Yellow oil, 92% yield; $\mathbf{R_f}$ (3:1 hexanes/EtOAc) 0.23; **^{1}H NMR** (400 MHz, C_6D_6) δ 8.33 (d, *J* = 3.3 Hz, 1H), 7.18 (d, *J* = 1.7 Hz, 1H), 7.03-6.97 (m, 2H), 6.83 (s, 1H), 6.75 (dt, *J* = 7.7, 1.6 Hz, 1H), 6.52 (d, *J* = 8.0 Hz, 1H), 6.43 (dd, *J* = 7.4, 4.9 Hz, 1H), 5.20 (d, *J* = 3.6 Hz, 2H), 1.10 (s, 9H); **^{13}C NMR** (125 MHz, C_6D_6) δ 176.6, 150.3, 148.6, 148.4, 143.2, 135.5, 131.5, 127.3, 123.0, 122.1, 108.5, 108.4, 101.2, 86.9, 86.0, 65.9, 38.8, 27.0,; **IR** (film) υ_{max} 2974, 1732, 1582, 1489, 1464, 1249, 1140, 1038, 936, 779 cm^{-1}; **MS** (EI$^+$): *m/z* 337 (M$^+$); **HRMS** (EI$^+$) calcd for $[C_{20}H_{19}NO_4]^+$: *m/z* 337.1314, found 337.1311.



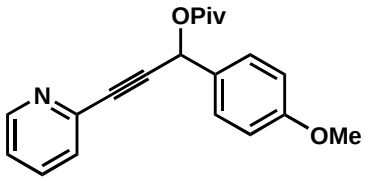
1-(3,5-dimethoxyphenyl)-3-(pyridin-2-yl)prop-2-ynyl pivalate (Table 2, entry 9): Yellow oil, 90% yield; $\mathbf{R_f}$ (3:1 hexanes/EtOAc) 0.15; **^{1}H NMR** (400 MHz, C_6D_6) δ 8.31 (d, *J* = 4.8 Hz, 1H), 7.00 (d, *J* = 7.8 Hz, 1H), 6.97-6.94 (m, 3H), 6.75 (dt, *J* = 7.7, 1.6 Hz, 1H), 6.49 (t, *J* = 2.2 Hz, 1H), 6.43 (dd, *J* = 7.1, 5.3 Hz, 1H), 3.27 (s, 6H), 1.13 (s, 9H); **^{13}C NMR** (125 MHz, C_6D_6) δ 176.6, 161.7, 150.3, 143.2, 140.0, 135.5, 128.6, 127.4, 122.9, 105.8, 101.5, 86.0, 66.0, 54.9, 38.9, 27.1,; **IR** (film) υ_{max} 2971, 1735, 1598, 1464, 1429, 1274, 1206, 1139, 1068, 779 cm^{-1}; **MS** (EI$^+$): *m/z* 353 (M$^+$); **HRMS** (EI$^+$) calcd for $[C_{21}H_{23}NO_4]^+$: *m/z* 353, 1627, found 353.1628.



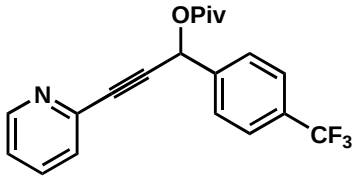
1-(2-Bromophenyl)-3-(pyridin-2-yl)prop-2-ynyl pivalate (Table 2, entry 10): Yellow oil, 83% yield; $\mathbf{R_f}$ (3:1 hexanes/EtOAc) 0.23; **^{1}H NMR** (400 MHz, C_6D_6) δ 8.32 (d, *J* = 4.1 Hz, 1H), 7.95 (d, *J* = 7.7 Hz, 1H), 7.29 (s, 1H), 7.24 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.00 (d, *J* = 7.8 Hz, 1H), 6.87 (dt, *J* = 7.7, 1.1 Hz, 1H), 6.74 (dt, *J* = 7.8, 1.6 Hz, 1H), 6.62 (dt, *J* = 7.9, 1.6 Hz, 1H), 6.46-6.40 (m, 1H), 1.14 (s, 9H); **^{13}C NMR** (100 MHz, C_6D_6) δ 176.2, 150.2, 136.6, 135.5, 133.3, 130.5, 130.2, 123.8, 123.0, 87.4, 85.0, 65.8, 60.0, 38.9, 27.1, 20.5, 14.2; **IR** (film) υ_{max} 2973, 1737, 1582, 1464, 1429, 1275, 1135, 1028, 779 cm^{-1}; **MS** (EI$^+$): *m/z* 371 (M$^+$); **HRMS** (EI$^+$) calcd for $[C_{19}H_{18}BrNO_2]^+$: *m/z* 371.0520, found 371.0511.



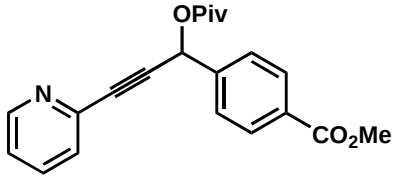
1-(2,6-dimethylphenyl)-3-(pyridin-2-yl)prop-2-ynyl pivalate (Table 2, entry 11): Yellow oil, 80% yield; $\mathbf{R_f}$ (3:1 hexanes/EtOAc) 0.23; **^{1}H NMR** (400 MHz, C_6D_6) δ 8.30 (d, *J* = 4.8 Hz, 1H), 7.44 (s, 1H), 6.99-6.91 (m, 2H), 6.89-6.84 (m, 2H), 6.74 (dt, *J* = 7.7, 1.8 Hz, 1H), 6.42 (ddd, *J* = 7.6, 4.8, 1.1 Hz, 1H), 2.65 (s, 6H), 1.07 (s, 9H); **^{13}C NMR** (100 MHz, C_6D_6) δ 176.6, 150.3, 143.3, 137.8, 135.5, 134.1, 129.5, 129.0, 127.2, 122.8, 86.4, 85.7, 62.4, 38.9, 27.1, 20.5; **IR** (film) υ_{max} 2974, 1732, 1582, 1463, 1428, 1275, 1141, 1032, 938, 777 cm^{-1}; **MS** (EI$^+$): *m/z* 321 (M^+); **HRMS** (EI$^+$) calcd for $[C_{21}H_{23}NO_2]^+$: *m/z* 321.1729, found 321.1724.



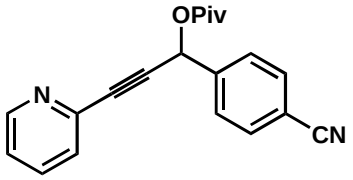
1-(4-Methoxyphenyl)-3-(pyridine-2-yl)prop-2-ynyl pivalate (Table 2, entry 12b): Yellow oil, 81% yield; $\mathbf{R_f}$ (3:1 hexanes/EtOAc) 0.33; **^{1}H NMR** (400 MHz, C_6D_6) δ 8.33 (d, *J* = 4.3 Hz, 1H), 7.54 (d, *J* = 8.7 Hz, 2H), 7.04 (d, *J* = 7.8 Hz, 1H), 6.94 (s, 1H), 6.78 (dt, *J* = 7.7, 1.8 Hz, 1H), 6.68 (d, *J* = 8.7 Hz, 2H), 6.45 (ddd, *J* = 7.6, 4.8, 1.1 Hz, 1H), 3.21 (s, 3H), 1.12 (s, 9H); **^{13}C NMR** (125 MHz, C_6D_6) δ 176.7, 160.5, 150.3, 143.3, 135.5, 129.8, 129.6, 127.3, 122.9, 114.3, 86.9, 86.3, 65.8, 54.7, 38.8, 27.0; **IR** (film) υ_{max} 2972, 1732, 1582, 1464, 1251, 1140, 1032, 833, 779 cm^{-1}; **MS** (EI$^+$): *m/z* 323 (M^+); **HRMS** (EI$^+$) calcd for $[C_{20}H_{21}NO_3]^+$: *m/z* 323.1521, found 323.1517.



1-(4-(trifluoromethyl)phenyl)-3-(pyridine-2-yl)prop-2-ynyl pivalate (Table 2, entry 12c): Yellow oil, 78% yield; $\mathbf{R_f}$ (3:1 hexanes:EtOAc) 0.27; **mp** 109-111 °C; **^{1}H NMR** (400 MHz, C_6D_6) δ 8.33 (d, *J* = 4.6 Hz, 1H), 7.36 (d, *J* = 8.2 Hz, 2H), 7.24 (d, *J* = 8.2 Hz, 2H), 7.02 (d, *J* = 7.8 Hz, 1H), 6.80-6.73 (m, 2H), 6.50-6.38 (m, 1H), 1.10 (s, 9H); **^{13}C NMR** (100 MHz, C_6D_6) δ 176.3, 150.3, 142.7, 141.1, 135.5, 128.0, 127.8, 127.2, 125.7, 125.7, 123.1, 87.3, 84.9, 65.0, 38.7, 26.8; **IR** (film) υ_{max} 2976, 1737, 1583, 1464, 1429, 1326, 1132, 1068, 1019, 779 cm^{-1}; **MS** (EI$^+$): *m/z* 361 (M$^+$); **HRMS** (EI$^+$) calcd for $[C_{20}H_{18}F_3NO_2]^+$: *m/z* 361.1299, found 361.1302.

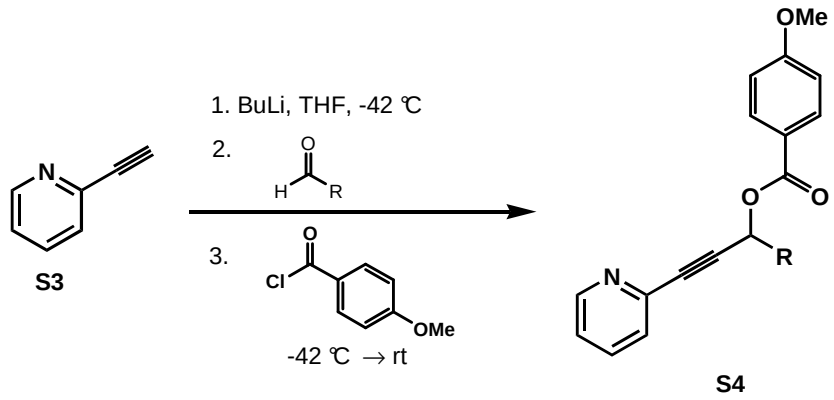


Methyl 4-(1-(pivaloyloxy)-3-(pyridin-2-yl)prop-2-ynyl)benzoate (Table 2, entry 12d): White solid, 73% yield; $\mathbf{R_f}$ (3:1 hexanes/EtOAc) 0.17; **mp** 97-100 °C; **^{1}H NMR** (500 MHz, C_6D_6) δ 8.31 (d, *J* = 4.1 Hz, 1H), 8.03 (d, *J* = 8.4 Hz, 2H), 7.49 (d, *J* = 8.2 Hz, 2H), 7.00 (d, *J* = 7.8 Hz, 1H), 6.82 (s, 1H), 6.76 (dt, *J* = 7.7, 1.8 Hz, 1H), 6.44 (ddd, *J* = 7.6, 4.8, 1.1 Hz, 1H), 3.44 (s, 3H), 1.09 (s, 9H); **^{13}C NMR** (125 MHz, C_6D_6) δ 176.4, 166.1, 150.4, 143.0, 142.1, 135.5, 131.1, 130.3, 127.3, 123.1, 87.4, 85.2, 65.4, 51.6, 38.8, 27.0; **IR** (film) υ_{max} 2974, 1727, 1582, 1464, 1429, 1278, 1137, 1021, 779, 704 cm^{-1}; **MS** (EI$^+$): *m/z* 351 (M$^+$); **HRMS** (EI$^+$) calcd for $[C_{21}H_{21}NO_4]^+$: *m/z* 351.1471, found 351.1470.



1-(4-Cyanophenyl)-3-(pyridin-2-yl)prop-2-ynyl pivalate (Table 2, entry 12e): Yellow solid, 77% yield; $\mathbf{R_f}$ (3:1 hexanes/EtOAc) 0.20; **^{1}H NMR** (500 MHz, C_6D_6) δ 8.30 (d, *J* = 4.8 Hz, 1H), 7.16 (d, *J* = 8.3 Hz, 2H), 7.01 (d, *J* = 7.8 Hz, 1H), 6.92 (d, *J* = 8.3 Hz, 2H), 6.78 (dt, *J* = 7.7, 1.7 Hz, 1H), 6.63 (s, 1H), 6.45 (ddd, *J* = 7.6, 4.8, 0.8 Hz, 1H), 1.08 (s, 9H); **^{13}C NMR** (125 MHz, C_6D_6) δ 176.3, 150.5, 142.7, 141.7, 135.6, 132.4, 128.3, 127.3, 123.3, 118.3, 113.2, 87.6, 84.5, 65.1, 38.8, 26.9; **IR** (film) υ_{max} 2974, 2230, 1737, 1582, 1464, 1429, 1276, 1135, 1032, 780 cm^{-1}; **MS** (EI$^+$): *m/z* 318 (M$^+$); **HRMS** (EI$^+$) calcd for $[C_{20}H_{18}N_2O_2]^+$: *m/z* 318.1368, found 318.1368.

Scheme S2

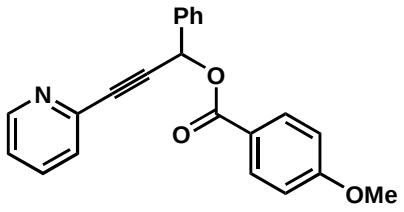


Representative Procedure for 4-Methoxybenzoate Substrates

A flame-dried, round-bottom flask was charged with anhydrous THF (27 mL) and 2-ethynylpyridine (280 μL, 2.75 mmol). The solution was cooled to -42 °C and BuLi (1.21 mL, 3.03 mmol, 2.5 M in hexanes) was added dropwise. The solution was allowed to stir at this temperature for 90 min, and then benzaldehyde (335 μL, 3.30 mmol) was added dropwise to the reaction mixture. The mixture was stirred at -42 °C for 2 h, then 4-methoxybenzoyl chloride (521 μL, 3.85 mmol) was added dropwise. The mixture was stirred for an additional 90 min, then allowed to warm to rt. After 3 h, saturated aqueous

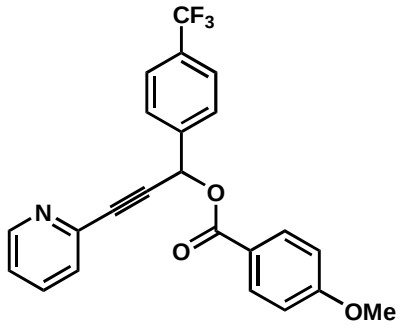
NH_4Cl solution (25 mL) was added slowly and stirring continued for 10 min. The mixture was diluted with EtOAc (20 mL), and the aqueous layer was extracted with EtOAc (3 x 20 mL). The combined organic phase was washed with brine (30 mL) and dried over $MgSO_4$. The solvent was removed under reduced pressure and the crude mixture was purified via flash chromatography (4:1 hexanes/EtOAc) to obtain a yellow oil (724.6 mg, 77% yield).

Spectral Data for 4-Methoxybenzoate Substrates



21b

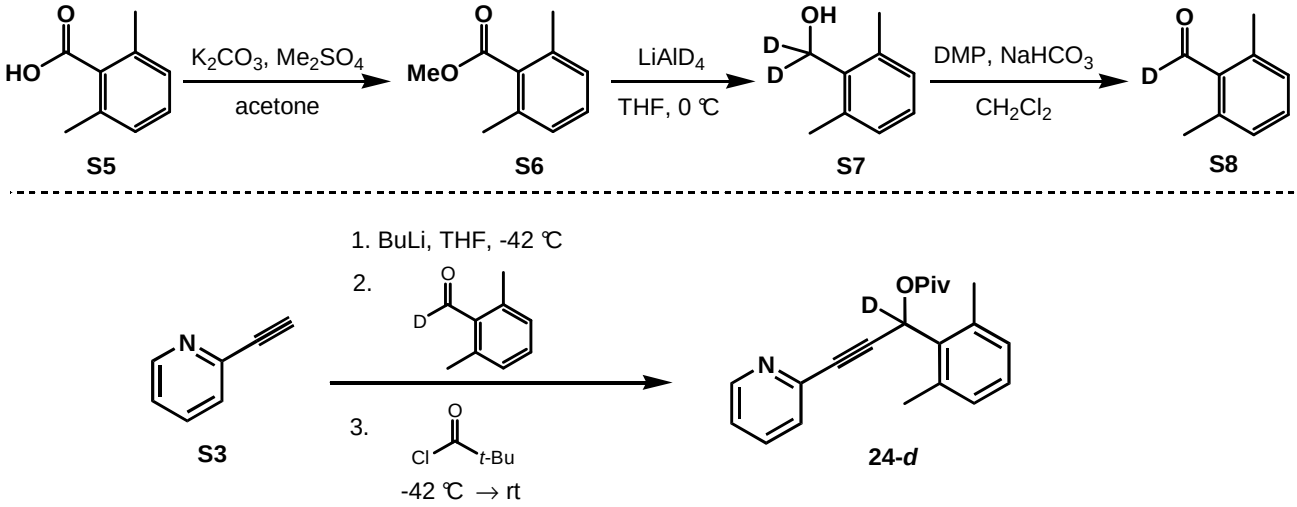
1-Phenyl-3-(pyridin-2-yl)prop-2-ynyl 4-methoxybenzoate (21b): Yellow oil, 77% yield; $\mathbf{R_f}$ (3:1 hexanes/EtOAc) 0.10; **^{1}H NMR** (400 MHz, C_6D_6) δ 8.34 (d, *J* = 4.1 Hz, 1H), 8.10 (d, *J* = 9.0 Hz, 2H), 7.69 (d, *J* = 7.1 Hz, 2H), 7.20 (s, 1H), 7.12-7.01 (m, 3H), 6.98 (td, *J* = 7.8, 1.0 Hz, 1H), 6.75 (dt, *J* = 7.8, 1.8 Hz, 1H), 6.56-6.51 (m, 2H), 6.43 (ddd, *J* = 7.6, 4.9, 1.1 Hz, 1H), 3.08 (s, 3H); **^{13}C NMR** (100 MHz, C_6D_6) δ 165.1, 163.9, 150.2, 143.2, 137.6, 135.5, 132.4, 129.0, 128.9, 127.9, 127.4, 123.0, 122.6, 113.9, 87.3, 86.1, 66.5, 54.8; **IR** (film) υ_{max} 2974, 1716, 1606, 1582, 1511, 1463, 1253, 1167, 1091, 768 cm^{-1}; **MS** (EI$^+$): *m/z* 343 (M$^+$); **HRMS** (EI$^+$) calcd for $[C_{22}H_{17}NO_3]^+$: *m/z* 343.1208, found 343.1205.



21d

1-(4-(trifluoromethyl)phenyl)-3-(pyridin-2-yl)prop-2-ynyl 4-methoxybenzoate (21d): Yellow oil, 91% yield; $\mathbf{R_f}$ (3:1 hexanes/EtOAc) 0.15; **^{1}H NMR** (500 MHz, C_6D_6) δ 8.33 (d, *J* = 4.7 Hz, 1H), 8.11 (d, *J* = 8.5 Hz, 2H), 7.46 (d, *J* = 8.0 Hz, 2H), 7.24 (d, *J* = 8.1 Hz, 2H), 7.05-7.00 (m, 2H), 6.77 (t, *J* = 7.7 Hz, 1H), 6.58 (d, *J* = 8.5 Hz, 2H), 6.45 (dd, *J* = 7.5, 4.9 Hz, 1H), 3.09 (s, 3H); **^{13}C NMR** (125 MHz, C_6D_6) δ 164.9, 164.1, 150.4, 142.9, 141.2, 135.6, 132.380, 128.4, 128.3, 127.9, 127.4, 125.9, 123.2, 122.2, 114.1, 87.7, 85.1, 65.6, 54.8; **IR** (film) υ_{max} 2937, 2841, 1719, 1606, 1511, 1464, 1326, 1254, 1168, 1091, 1020, 846, 771 cm^{-1}; **MS** (EI^+): *m/z* 411 (M^+); **HRMS** (EI^+) calcd for $[C_{23}H_{16}F_3NO_3]^+$: *m/z* 411.1082, found 411.1079.

Scheme S3



Synthesis of the Deuterated Substrate (24-*d*)

2,6-dimethylbenzoic acid **(S5)** (1.00 g, 6.7 mmol), potassium carbonate (1.40 g, 10.1 mmol), dimethyl sulfate (700 μL, 7.4 mmol) and acetone (33 mL) were combined in a round-bottom flask and stirred under a nitrogen atmosphere at rt for 4 h. The solvent was removed under reduced pressure and the resulting residue was taken up in ethyl acetate (20 mL). The solution was diluted with water (20 mL), and the aqueous layer was extracted with ethyl acetate (3 x 15 mL). The organic layers were combined, washed with brine (30 mL), and dried over $MgSO_4$. The solvent was removed under reduced pressure to yield a peach oil, which was purified via flash chromatography (9:1 hexanes/EtOAc) to give a light peach oil (1.02 g, 93% yield).

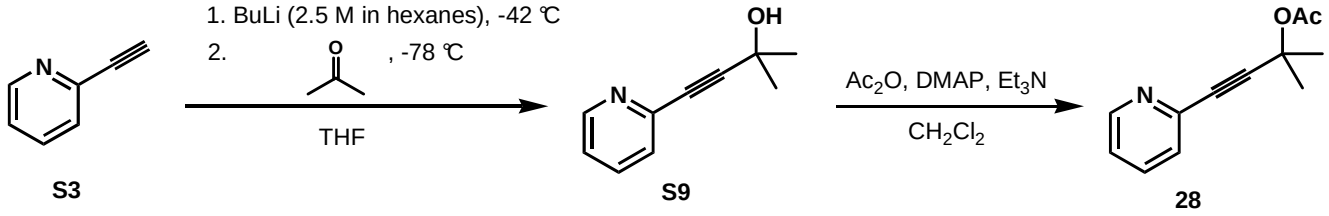
Lithium aluminum deuteride (51.2 mg, 1.22 mmol) was added in three portions to a round-bottom flask containing methyl ester **S6** (200 mg, 1.22 mmol) in THF (6 mL) at 0 °C. The mixture was stirred at 0 °C for 2 h under a nitrogen atmosphere. Water (51 μL) was added dropwise over 1 min followed by 10% sodium hydroxide aqueous solution (51 μL). Then, an additional 153 μL of water was added dropwise. The salts were removed via vacuum filtration and the solvent was removed under reduced pressure to yield a white crystalline solid (144.9 mg, 86% yield).

The deutrated alcohol **S7** (441.9 mg, 3.2 mmol), sodium bicarbonate (806.5 mg, 9.6 mmol) and dichloromethane (16 mL) were combined in a flame-dried, round-bottom flask. Dess Martin periodinane (1.612 g, 3.8 mmol) was added to the mixture in five portions over 5 min. The mixture was stirred at rt under a nitrogen atmosphere for 1 h. Saturated aqueous sodium sulfite solution (20 mL) was then added, and the aqueous layer was extracted with dichloromethane (3 x 20 mL). The organic layers were combined and washed with saturated aqueous sodium bicarbonate solution (1 x 30 mL), brine (1 x 30 mL) and dried over $MgSO_4$. The solvent was removed under reduced pressure, and the resulting crude aldehyde was purified via flash chromatography (4:1 hexanes/EtOAc). The deuterated aldehyde **S8** was obtained as a colorless oil (315.3 mg, 73% yield).

2-ethynylpyridine was added into **S8** using the previously described protocol (Scheme S1) to give the deuterated substrate (**24-*d***) as a colorless oil (306.2 mg, 63% yield). **^{1}H**

NMR (500 MHz, C_6D_6) δ 8.32 (d, *J* = 4.8 Hz, 1H), 6.97-6.92 (m, 2H), 6.87 (d, *J* = 7.5 Hz, 2H), 6.74 (dt, *J* = 7.7, 1.4 Hz, 1H), 6.45-6.41 (m, 1H), 2.65 (s, 6H), 1.07 (s, 9H); **^{13}C NMR** (125 MHz, C_6D_6) δ 176.6, 150.2, 143.2, 137.8, 135.5, 134.0, 129.8, 129.0, 128.3, 127.3, 122.9, 86.4, 85.7, 38.9, 27.1, 20.5; **IR** (film) υ_{max} 2973, 1732, 1582, 1463, 1276, 1149, 1084, 778 cm^{-1}; **MS** (EI$^+$): *m/z* 322 (M$^+$); **HRMS** (EI$^+$) calcd for $[C_{21}H_{22}DNO_2]^+$: *m/z* 322.1792, found 322.1789.

Scheme S4



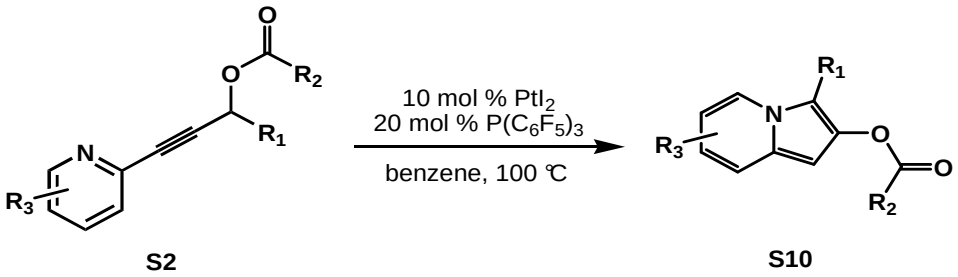
Synthesis of Tertiary Substrate (28)

2-Methyl-4-(pyridin-2-yl)but-3-yn-2-yl acetate: A flame-dried, round-bottom flask was charged with anhydrous THF (20 mL) and 2-ethynylpyridine (**S3**) (202 μL, 2.0 mmol). The solution was cooled to -42 °C and BuLi (880 μL, 2.2 mmol, 2.5 M in hexanes) was added dropwise. The solution was allowed to stir at this temperature for 90 min, and then was further cooled to -78 °C. Acetone (177 μL, 2.4 mmol) was added dropwise at -78 °C, and the mixture was stirred for 4 h and then allowed to warm to rt. After 3 h, saturated aqueous NH_4Cl solution (20 mL) was added slowly and stirring continued for 10 min. The mixture was diluted with EtOAc (15 mL) and the aqueous layer was extracted with EtOAc (3 x 15 mL). The organic layers were combined, washed with brine (30 mL) and dried over $MgSO_4$. Concentration under reduced pressure gave the crude product, which was purified via flash chromatography (1:1 hexanes/EtOAc) to obtain **S9** as a yellow oil (258.8 mg, 80% yield).

The propargylic alcohol **S9** (258 mg, 1.6 mmol), acetic anhydride (190 μL, 2.0 mmol), DMAP (9.8 mg, 0.1 mmol), triethylamine (670 μL, 3.0 mmol) and dichloromethane (16 mL) were combined in a flame-dried, round-bottom flask and stirred under an nitrogen atmosphere at rt for 4 d. Saturated aqueous ammonium chloride solution (15 mL) was

added, and the aqueous layer was extracted with dichloromethane (3 x 15 mL). The organic layers were combined, washed with brine (30 mL) and dried over $MgSO_4$. The solvent was removed under reduced pressure, and the crude oil was purified via flash chromatography (2:1 hexanes/EtOAc) to give **28** as a light yellow oil (212.9 mg, 66% yield). **^{1}H NMR** (400 MHz, C_6D_6) δ 8.33 (d, *J* = 4.8 Hz, 1H), 7.17 (d, *J* = 8.2 Hz, 1H), 6.81-6.74 (m, 1H), 6.45-6.41 (m, 1H), 1.63-1.62 (m, 9H); **^{13}C NMR** (125 MHz, C_6D_6) δ 168.6, 150.2, 143.8, 135.4, 127.3, 122.6, 90.3, 84.6, 72.0, 28.8, 21.4; **IR** (film) υ_{max} 2989, 1739, 1582, 1464, 1428, 1281, 1245, 1135, 1016, 781 cm^{-1}; **MS** (EI$^+$): *m/z* 203 (M$^+$); **HRMS** (EI$^+$) calcd for $[C_{12}H_{13}NO_2]^+$: *m/z* 203.0946, found 203.0952.

Scheme S5

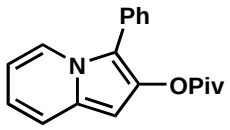


S2 **S10**

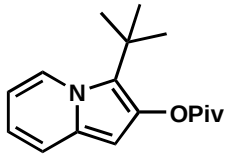
Representative Procedure for the Formation of 2,3-Disubstituted Indolizines

1-Phenyl-3-(pyridin-2-yl)prop-2-ynyl pivalate (**S2**) (80 mg, 0.272 mmol), platinum(II) iodide (12 mg, 0.027 mmol) and tris(pentafluoro)phenyl phosphine (28 mg, 0.054 mmol) were combined in an oven-dried 4 mL vial equipped with a stir bar. The vial was evacuated and backfilled with nitrogen (3x). Benzene (2 mL) was added via syringe, and the vial was capped with a Teflon® cap and heated at 100 °C for 24 h. The vial was removed from the oil bath and allowed to cool to rt. Concentration under reduced pressure gave the crude product, which was purified using flash chromatography (9:1 hexanes/EtOAc) to yield **S10**.

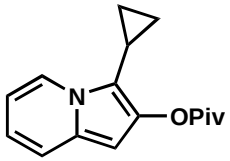
Spectral Data for Indolizine Products



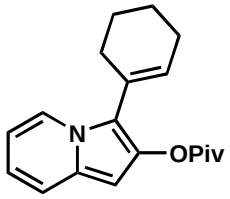
3-Phenylindolizin-2-yl pivalate (19b): Yellow oil, 75% yield; $\mathbf{R_f}$ (3:1 hexanes/EtOAc) 0.61; **^{1}H NMR** (500 MHz, C_6D_6) δ 7.72 (d, *J* = 7.1 Hz, 1H), 7.32 (dd, *J* = 8.0, 1.0 Hz, 2H), 7.16-7.11 (m, 2H), 7.06-6.99 (m, 2H), 6.68 (s, 1H), 6.35 (ddd, *J* = 8.9, 6.6, 0.9 Hz, 1H), 5.98 (dt, *J* = 7.1, 1.3 Hz, 1H), 1.13 (s, 9H); **^{13}C NMR** (100 MHz, C_6D_6) δ 175.9, 140.0, 130.7, 129.9, 129.6, 129.0, 127.6, 122.2, 119.4, 117.7, 114.9, 110.7, 93.5, 39.1, 27.2; **IR** (film) υ_{max} 2974, 1751, 1479, 1432, 1351, 1312, 1275, 1110, 759, 700 cm^{-1}; **MS** (EI$^+$): *m/z* 293 (M$^+$); **HRMS** (EI$^+$) calcd for $[C_{19}H_{19}NO_2]^+$: *m/z* 293.1416, found 293.1411.



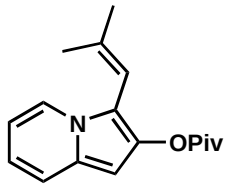
3-*tert*-butylindolizin-2-yl pivalate (Table 2, entry 1): Yellow oil, 11% yield; $\mathbf{R_f}$ (3:1 hexanes/EtOAc) 0.50; **^{1}H NMR** (500 MHz, C_6D_6) δ 7.61 (d, *J* = 7.4 Hz, 1H), 7.34 (d, *J* = 9.0 Hz, 1H), 6.85 (s, 1H), 6.38-6.30 (m, 1H), 6.10-6.06 (m, 1H), 1.29 (s, 9H), 1.15 (s, 9H); **^{13}C NMR** (125 MHz, C_6D_6) δ 176.1, 128.3, 123.9, 123.1, 116.9, 114.1, 109.7, 104.6, 39.2, 31.8, 28.6, 28.2, 27.4; **IR** (film) υ_{max} 2969, 1750, 1479, 1417, 1366, 1343, 1278, 1120 cm^{-1}; **MS** (EI$^+$): *m/z* 273 (M$^+$); **HRMS** (EI$^+$) calcd for $[C_{17}H_{23}NO_2]$: *m/z* 273.1729, found 273.1727.



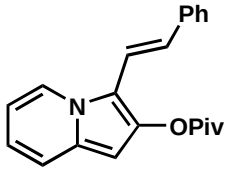
3-Cyclopropylindolizin-2-yl pivalate (Table 2, entry 2): Yellow oil, 49% yield; $\mathbf{R_f}$ (3:1 hexanes/EtOAc) 0.57; **^{1}H NMR** (500 MHz, C_6D_6) δ 7.66 (dd, *J* = 7.0, 0.8 Hz, 1H), 7.07 (d, *J* = 8.9 Hz, 1H), 6.52 (s, 1H), 6.47-6.42 (m, 1H), 6.23 (dt, *J* = 6.9, 1.2 Hz, 1H), 1.40-1.33 (m, 1H), 1.31 (s, 9H), 0.60-0.54 (m, 2H), 0.46-0.41 (m, 2H); **^{13}C NMR** (125 MHz, C_6D_6) δ 175.7, 140.5, 129.4, 122.6, 119.0, 116.7, 110.0, 92.0, 39.2, 27.4, 5.1, 3.8; **IR** (film) υ_{max} 2974, 1751, 1455, 1439, 1341, 1277, 1143, 1111 cm^{-1}; **MS** (EI$^+$): *m/z* 257 (M$^+$); **HRMS** (EI$^+$) calcd for [$C_{16}H_{19}NO_2$]: *m/z* 257.1416, found 257.1412.



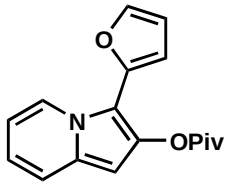
3-Cyclohexenylindolizin-2-yl pivalate (Table 2, entry 3): Yellow oil, 74% yield; $\mathbf{R_f}$ (3:1 hexanes/EtOAc) 0.66; **^{1}H NMR** (400 MHz, C_6D_6) δ 7.66 (dd, *J* = 7.1, 0.9 Hz, 1H), 7.04 (dt, *J* = 9.0, 1.0 Hz, 1H), 6.58 (s, 1H), 6.38 (ddd, *J* = 8.9, 6.5, 1.0 Hz, 1H), 6.13 (td, *J* = 7.1, 1.3 Hz, 1H), 5.84-5.80 (m, 1H), 2.25-2.19 (m, 2H), 2.01-1.94 (m, 2H), 1.61-1.46 (m, 4H), 1.28 (s, 9H); **^{13}C NMR** (100 MHz, C_6D_6) δ 175.9, 139.2, 131.0, 129.9, 127.5, 123.1, 119.3, 117.0, 116.7, 110.2, 92.9, 39.2, 27.7, 27.4, 25.8, 23.2, 22.5; **IR** (film) υ_{max} 2932, 1752, 1480, 1437, 1276, 1137, 1110 cm^{-1}; **MS** (EI$^+$): *m/z* 297 (M$^+$); **HRMS** (EI$^+$) calcd for [$C_{19}H_{23}NO_2$]$^+$: *m/z* 297.1729, found 297.1730.



3-(2-Methylprop-1-enyl)indolizin-2-yl pivalate (Table 2, entry 4): Yellow oil, 54% yield; $\mathbf{R_f}$ (3:1 hexanes/EtOAc) 0.64; **^{1}H NMR** (500 MHz, *C_6D_6)* δ 7.31 (d, *J* = 7.0 Hz, 1H), 7.06 (d, *J* = 8.9 Hz, 1H), 6.67 (s, 1H), 6.43-6.38 (m, 1H), 6.13 (dt, *J* = 7.0, 6.9, 1.2 Hz, 1H), 5.86 (s, 1H), 1.73 (s, 3H), 1.62 (s, 3H), 1.26 (s, 9H); **^{13}C NMR** (125 MHz, C_6D_6) δ 175.7, 141.0, 139.8, 130.1, 122.7, 119.0, 117.0, 112.3, 112.1, 110.2, 92.8, 39.2, 27.4, 25.4, 20.7; **IR** (film) υ_{max} 2973, 1752, 1480, 1455, 1351, 1275, 1143, 1109, 755 cm^{-1}; **MS** (EI$^+$): *m/z* 271 (M^+); **HRMS** (EI$^+$) calcd for [$C_{17}H_{21}NO_2$]: *m/z* 271.1572, found 271.1567.

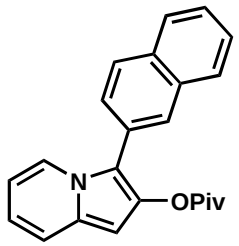


3-Styrylindolizin-2-yl pivalate (Table 2, entry 5): Yellow oil, 56% yield; $\mathbf{R_f}$ (3:1 hexanes/EtOAc) 0.55; **^{1}H NMR** (500 MHz, C_6D_6) δ 7.45-7.38 (m, 3H), 7.25-7.19 (m, 3H), 7.09 (t, *J* = 7.3 Hz, 1H), 6.99-6.95 (m, 2H), 6.81 (s, 1H), 6.37 (td, *J* = 11.8, 5.9 Hz, 1H), 6.12-6.07 (m, 1H), 1.27 (s, 9H); **^{13}C NMR** (125 MHz, C_6D_6) δ 175.3, 141.5, 138.8, 131.2, 129.0, 127.3, 126.8, 126.2, 122.4, 119.2, 118.0, 114.2, 113.1, 111.1, 94.5, 39.4, 27.4; **IR** (film) υ_{max} 2973, 1752, 1455, 1437, 1269, 1141, 1105 cm^{-1}; **MS** (EI$^+$): *m/z* 319 (M^+); **HRMS** (EI$^+$) calcd for [$C_{21}H_{21}NO_2$]: *m/z* 319.1572, found 319.1573.

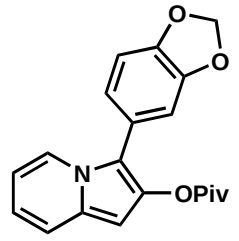


3-(Furan-2-yl)indolizin-2-yl pivalate (Table 2, entry 6): Brown oil, 34% yield; $\mathbf{R_f}$ (3:1 hexanes/EtOAc) 0.56; **^{1}H NMR** (500 MHz, C_6D_6) δ 8.24 (dd, *J* = 7.1, 0.7 Hz, 1H), 7.11 (d, *J* = 1.2 Hz, 1H), 6.97 (d, *J* = 8.9 Hz, 1H), 6.74 (s, 1H), 6.51 (d, *J* = 3.3 Hz, 1H), 6.36 (ddd, *J* = 8.8, 6.6, 0.8 Hz, 1H), 6.23 (dd, *J* = 3.3, 1.9 Hz, 1H), 6.10 (dt, *J* = 7.1, 1.3 Hz,

1H), 1.24 (s, 9H); **^{13}C NMR** (125 MHz, C_6D_6) δ 175.4, 145.5, 141.2, 140.7, 131.3, 124.1, 119.1, 118.3, 111.4, 111.2, 107.7, 93.8, 39.3, 27.3; **IR** (film) υ_{max} 2973, 1754, 1479, 1431, 1311, 1275, 1139, 1108 cm^{-1}; **MS** (EI^+): *m/z* 283 (M^+); **HRMS** (EI^+) calcd for [$C_{17}H_{17}NO_3$]: *m/z* 283.1208, found 283.1208.

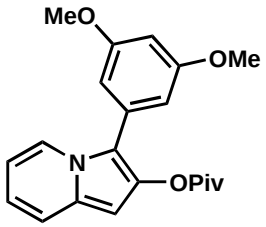


3-(Naphthalen-2-yl)indolizin-2-yl pivalate (Table 2, entry 7): Yellow oil; 73% yield; **R_f** (3:1 hexanes/EtOAc) 0.55; **^{1}H NMR** (500 MHz, C_6D_6) δ 7.85 (d, *J* = 7.1 Hz, 1H), 7.77 (s, 1H), 7.64-7.54 (m, 3H), 7.47 (dd, *J* = 8.5, 1.5 Hz, 1H), 7.28-7.21 (m, 2H), 7.09 (d, *J* = 9.0 Hz, 1H), 6.78 (s, 1H), 6.41 (dd, *J* = 8.5, 6.8 Hz, 1H), 6.06-6.01 (m, 1H), 1.15 (s, 9H); **^{13}C NMR** (125 MHz, C_6D_6) δ 175.9, 140.3, 134.1, 133.0, 130.9, 128.7, 128.5, 128.3, 127.3, 127.2, 126.6, 126.4, 122.2, 119.4, 117.9, 114.9, 110.8, 93.7, 39.2, 27.2; **IR** (film) υ_{max} 2973, 1754, 1466, 1310, 1110, 751 cm^{-1}; **MS** (EI^+): *m/z* 343 (M^+); **HRMS** (EI^+) calcd for [$C_{23}H_{21}NO_2$]: *m/z* 343.1572, found 343.1572.

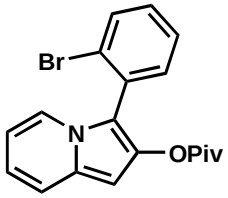


3-(Benzo[d][1,3]dioxol-6-yl)indolizin-2-yl pivalate (Table 2, entry 8): Yellow oil, 67% yield; **R_f** (3:1 hexanes/EtOAc) 0.50; **^{1}H NMR** (500 MHz, C_6D_6) δ 7.72 (d, *J* = 7.1 Hz, 1H), 7.05 (d, *J* = 8.9 Hz, 1H), 6.86 (d, *J* = 1.3 Hz, 1H), 6.78 (dd, *J* = 8.0, 1.5 Hz, 1H), 6.70-6.63 (m, 2H), 6.38 (dd, *J* = 8.2, 7.2 Hz, 1H), 6.05-6.01 (m, 1H), 5.32-5.28 (m, 2H), 1.19 (s, 9H); **^{13}C NMR** (125 MHz, C_6D_6) δ 176.0, 148.5, 147.5, 139.8, 130.4, 123.6, 123.4, 122.2, 119.3, 117.5, 114.6, 110.6, 110.0 , 108.9, 101.2, 93.3, 39.2, 27.3; **IR** (film)

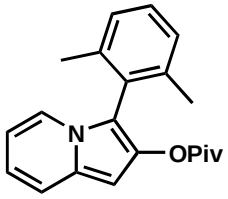
υ_{max} 2974, 1751, 1481, 1237, 1142, 1110, 1038 cm^{-1}; **MS** (EI^+): *m/z* 337 (M^+); **HRMS** (EI^+) calcd for [$C_{20}H_{19}NO_4$]: *m/z* 337.1314, found 337.1310.



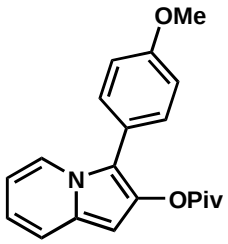
3-(3,5-Dimethoxyphenyl)indolizin-2-yl pivalate (Table 2, entry 9): Yellow oil, 76% yield; $\mathbf{R_f}$ (3:1 hexanes/EtOAc) 0.62; ; **^{1}H NMR** (500 MHz, C_6D_6) δ 7.91 (d, *J* = 7.1 Hz, 1H), 7.06 (d, *J* = 8.9 Hz, 1H), 6.72 (d, *J* = 2.2 Hz, 2H), 6.70 (s, 1H), 6.56 (t, *J* = 2.1 Hz, 1H), 6.38 (dd, *J* = 8.4, 7.1 Hz, 1H), 6.04 (t, *J* = 6.8 Hz, 1H), 3.32 (s, 6H), 1.21 (s, 9H); **^{13}C NMR** (125 MHz, C_6D_6) δ 176.0, 161.8, 140.0, 131.7, 130.7, 122.6, 119.3, 117.7, 110.7, 107.5, 100.7, 93.5, 54.9, 39.2, 27.3; **IR** (film) υ_{max} 2971, 1751, 1593, 1455, 1419, 1282, 1205, 1156, 1111 cm^{-1}; **MS** (EI^+): *m/z* 353 (M^+); **HRMS** (EI^+) calcd for [$C_{21}H_{23}NO_4$]: *m/z* 353.1627, found 353.1620.



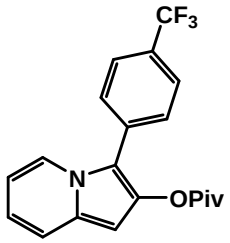
3-(2-Bromophenyl)indolizin-2-yl pivalate (Table 2, entry 10): Yellow oil, 72% yield; $\mathbf{R_f}$ (3:1 hexanes/EtOAc) 0.50; **^{1}H NMR** (500 MHz, C_6D_6) δ 7.44 (d, *J* = 8.8 Hz, 1H), 7.23 (d, *J* = 7.0 Hz, 1H), 7.18 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.08 (d, *J* = 9.0 Hz, 1H), 6.91 (dt, *J* = 7.6, 1.1 Hz, 1H), 6.78-6.73 (m, 2H), 6.44-6.39 (m, 1H), 6.11-6.06 (m, 1H), 1.12 (s, 9H); **^{13}C NMR** (125 MHz, C_6D_6) δ 175.8, 140.3, 134.1, 133.4, 131.1, 130.8, 130.2, 127.5, 126.5, 123.0, 119.2, 117.9, 113.8, 110.565, 93.0, 39.2, 27.2; **IR** (film) υ_{max} 2973, 1752, 1463, 1431, 1313, 1111, 1028, 756 cm^{-1}; **MS** (EI^+): *m/z* 371 (M^+); **HRMS** (EI^+) calcd for [$C_{19}H_{18}BrNO_2$]: *m/z* 371.0521, found 371.0522.



3-(2,6-dimethylphenyl)indolizin-2-yl pivalate (Table 2, entry 11): Yellow oil, 91% yield; $\mathbf{R_f}$ (3:1 hexanes/EtOAc) 0.63; **^{1}H NMR** (400 MHz, C_6D_6) δ 7.31-7.21 (m, 3H), 7.17-7.11 (m, 2H), 6.83 (s, 1H), 6.54 (ddd, *J* = 8.9, 6.6, 0.9 Hz, 1H), 6.18 (dt, *J* = 6.8, 1.2 Hz, 1H), 2.16 (s, 6H), 1.18 (s, 9H); **^{13}C NMR** (100 MHz, C_6D_6) δ 175.9, 140.5, 139.7, 130.4, 129.3, 128.4, 122.2, 119.3, 117.0, 113.724, 110.7, 92.8, 39.0, 27.0, 19.8; **IR** (film) υ_{max} 2973, 1754, 1461, 1347, 1276, 1138, 1110, 757 cm^{-1}; **MS** (EI$^+$): *m/z* 321 (M^+); **HRMS** (EI$^+$) calcd for [$C_{21}H_{23}NO_2$]: *m/z* 321.1729, found 321.1729.

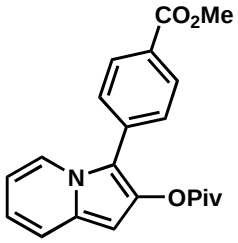


3-(4-Methoxyphen yl)indolizin-2-yl pivalate (Table 2, entry 12b): Yellow oil, 74% yield; $\mathbf{R_f}$ (3:1 hexanes: EtOAc) 0.59; **^{1}H NMR** (400 MHz, C_6D_6) δ 7.76 (d, *J* = 6.3 Hz, 1H), 7.27 (d, *J* = 8.8 Hz, 2H), 7.08 (d, *J* = 9.0 Hz, 1H), 6.78 (d, *J* = 8.8 Hz, 2H), 6.73 (s, 1H), 6.42-6.36 (m, 1H), 6.08-6.02 (m, 1H), 3.28 (s, 3H), 1.19 (s, 9H); **^{13}C NMR** (100 MHz, C_6D_6) δ 176.0, 159.6, 139.8, 131.2, 130.3, 122.2, 122.1, 119.4, 117.4, 114.9, 114.6, 110.5, 93.3, 54.8, 39.2, 27.3; **IR** (film) υ_{max} 2968, 1751, 1602, 1494, 1349, 1248, 1177, 1111, 1031 cm^{-1}; **MS** (EI$^+$): *m/z* 323 (M^+); **HRMS** (EI$^+$) calcd for [$C_{20}H_{21}NO_3$]: *m/z* 323.1521, found 323.1520.

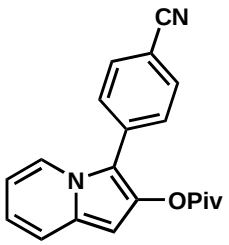


3-(4-(Trifluoromethyl)phenyl)indolizin-2-yl pivalate (Table 2, entry 12c): Yellow solid, 58% yield; $\mathbf{R_f}$ (3:1 hexanes/EtOAc) 0.61; **mp** 88-91 °C; **^{1}H NMR** (500 MHz, C_6D_6) δ 7.59 (d, *J* = 7.2 Hz, 1H), 7.37 (d, *J* = 8.1 Hz, 2H), 7.30 (d, *J* = 8.5 Hz, 1H), 7.20 (d, *J* = 8.0 Hz, 2H), 6.67 (s, 1H), 6.40 (ddd, *J* = 8.9, 6.6, 0.8 Hz, 1H), 6.04 (dt, *J* = 7.1, 1.3 Hz, 1H), 1.13 (s, 9H); **^{13}C NMR** (125 MHz, C_6D_6) δ 175.9, 175.7, 140.5, 133.5, 133.5, 131.4, 129.2, 128.3, 127.9, 126.0, 126.0, 125.9, 125.9, 124.4, 121.9, 121.5, 119.5, 118.5, 117.0, 116.7, 113.3, 111.4, 111.2, 108.1, 93.9, 39.3, 39.1, 27.4, 27.1; **IR** (film) υ_{max} 2976, 1753, 1480, 1325, 1111, 1068, 761 cm^{-1}; **MS** (EI$^+$): *m/z* 361 (M$^+$); **HRMS** (EI$^+$) calcd for [$C_{20}H_{18}F_3NO_2$]: *m/z* 361.1290, found 361.1285.

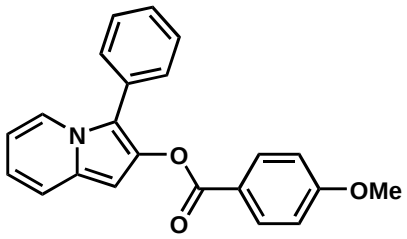
(**Note: this is a 2:1 mixture of 2,3- and 1,3-disubstituted indolizine)



Methyl 4-(2-pivaloyloxy)indolizin-3-yl)benzoate (Table 2, entry 12d): Green oil, 78% yield; $\mathbf{R_f}$ (3:1 hexanes/EtOAc) 0.44; **^{1}H NMR** (400 MHz, C_6D_6) δ 8.16 (d, *J* = 8.5 Hz, 2H), 7.71 (dd, *J* = 7.1, 0.7 Hz, 1H), 7.32 (d, *J* = 8.5 Hz, 2H), 7.02 (d, *J* = 9.1 Hz, 1H), 6.70 (s, 1H), 6.39 (ddd, *J* = 8.9, 6.7, 0.8 Hz, 1H), 6.02 (dt, *J* = 7.1, 1.3 Hz, 1H), 3.52 (s, 3H), 1.15 (s, 9H); **^{13}C NMR** (100 MHz, C_6D_6) δ 175.7, 166.4, 140.6, 134.4, 131.5, 130.3, 129.1, 128.6, 122.2, 119.4, 118.5, 113.8, 111.1, 94.0, 51.6, 39.2, 27.2; **IR** (film) υ_{max} 2974, 1753, 1721, 1607, 1438, 1276, 1140, 1108, 771 cm^{-1}; **MS** (EI$^+$): *m/z* 351 (M$^+$); **HRMS** (EI$^+$) calcd for [$C_{21}H_{21}NO_4$]: *m/z* 351.1471, found 351.1466.

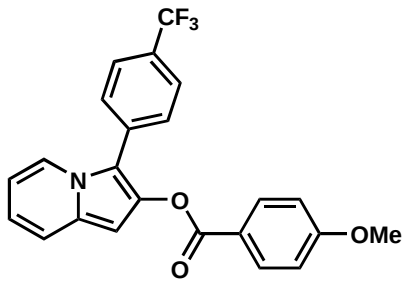


3-(4-Cyanophenyl)indolizin-2-yl pivalate (Table 2, entry 12e): Green oil, 31% yield; $\mathbf{R_f}$ (3:1 hexanes/EtOAc) 0.47; **^{1}H NMR** (500 MHz, C_6D_6) δ 7.52 (d, *J* = 7.2 Hz, 1H), 7.04-6.96 (m, 4H), 6.78 (d, *J* = 8.5 Hz, 1H), 6.64 (s, 1H), 6.38 (ddd, *J* = 8.9, 6.7, 0.8 Hz, 1H), 6.01 (dt, *J* = 7.1, 1.2 Hz, 1H), 1.13 (s, 9H); **^{13}C NMR** (125 MHz, C_6D_6) δ 175.5, 140.7, 133.8, 132.4, 131.7, 128.7, 128.3, 127.4, 121.9, 119.5, 118.9, 111.4, 110.8, 94.1, 39.1, 27.1; **IR** (film) υ_{max} 2975, 2225, 1752, 1605, 1511, 1479, 1439, 1314, 1275, 1139, 1109 cm^{-1}; **MS** (EI^+): *m/z* 318 (M^+); **HRMS** (EI^+) calcd for [$C_{20}H_{18}N_2O_2$]: *m/z* 318.1368, found 318.1369.



3-Phenylindolizin-2-yl 4-methoxybenzoate (22b): This indolizine was prepared according to the general procedure except the cycloimoserization was run for 2 d. Yellow oil, 67% yield; $\mathbf{R_f}$ (3:1 hexanes/EtOAc) 0.60; **^{1}H NMR** (500 MHz, C_6D_6) δ 8.17 (d, *J* = 8.7 Hz, 2H), 7.82 (d, *J* = 7.1 Hz, 1H), 7.45 (d, *J* = 7.6 Hz, 2H), 7.17-7.12 (m, 2H), 7.09 (d, *J* = 8.9 Hz, 1H), 7.03 (t, *J* = 7.5 Hz, 1H), 6.93 (s, 1H), 6.55 (d, *J* = 8.7 Hz, 2H), 6.40 (dd, *J* = 8.4, 7.0 Hz, 1H), 6.04 (t, *J* = 6.8 Hz, 1H), 3.10 (s, 3H); **^{13}C NMR** (125 MHz, C_6D_6) δ 164.4, 163.9, 140.0, 132.6, 130.8, 130.1, 129.4, 129.1, 127.6, 122.5, 122.2, 119.5, 117.8, 115.0, 114.1, 110.7, 93.9, 54.8; **IR** (film) υ_{max} 2360, 1732, 1606, 1510,

1254, 1167, 1070, 761 cm^{-1}; **MS** (EI^+): *m/z* 343 (M^+); **HRMS** (EI^+) calcd for [$C_{22}H_{17}NO_3$]: *m/z* 343.1208, found 343.1206.



3-(4-trifluoromethyl)phenyl)indolizin-2-yl 4-methoxybenzoate (22d): This indolizine was prepared according to the general procedure except the cycloimoserization was run for 2 d. Yellow oil, 56% yield; $\mathbf{R_f}$ (3:1 hexanes/EtOAc) 0.55; **^{1}H NMR** (400 MHz, C_6D_6) δ 8.15 (d, *J* = 8.7 Hz, 2H), 7.64 (d, *J* = 7.1 Hz, 1H), 7.31 (q, *J* = 8.6 Hz, 4H), 7.05 (d, *J* = 9.6 Hz, 1H), 6.87 (s, 1H), 6.57 (d, *J* = 8.8 Hz, 2H), 6.42 (dd, *J* = 8.9, 6.6 Hz, 1H), 6.06 (t, *J* = 6.9 Hz, 1H), 3.10 (s, 3H); **^{13}C NMR** (100 MHz, C_6D_6) δ 163.9, 163.9, 140.2, 133.4, 132.2, 131.2, 128.7, 128.4, 125.7, 125.701, 121.8, 121.7, 119.3, 118.2, 113.9, 113.1, 110.9, 94.0, 54.5; **IR** (film) υ_{max} 2360, 1734, 1607, 1511, 1325, 1252, 1167, 1122, 1068, 763 cm^{-1}; **MS** (EI^+): *m/z* 411 (M^+); **HRMS** (EI^+) calcd for [$C_{23}H_{16}F_3NO_3$]: *m/z* 411.1082, found 411.1084.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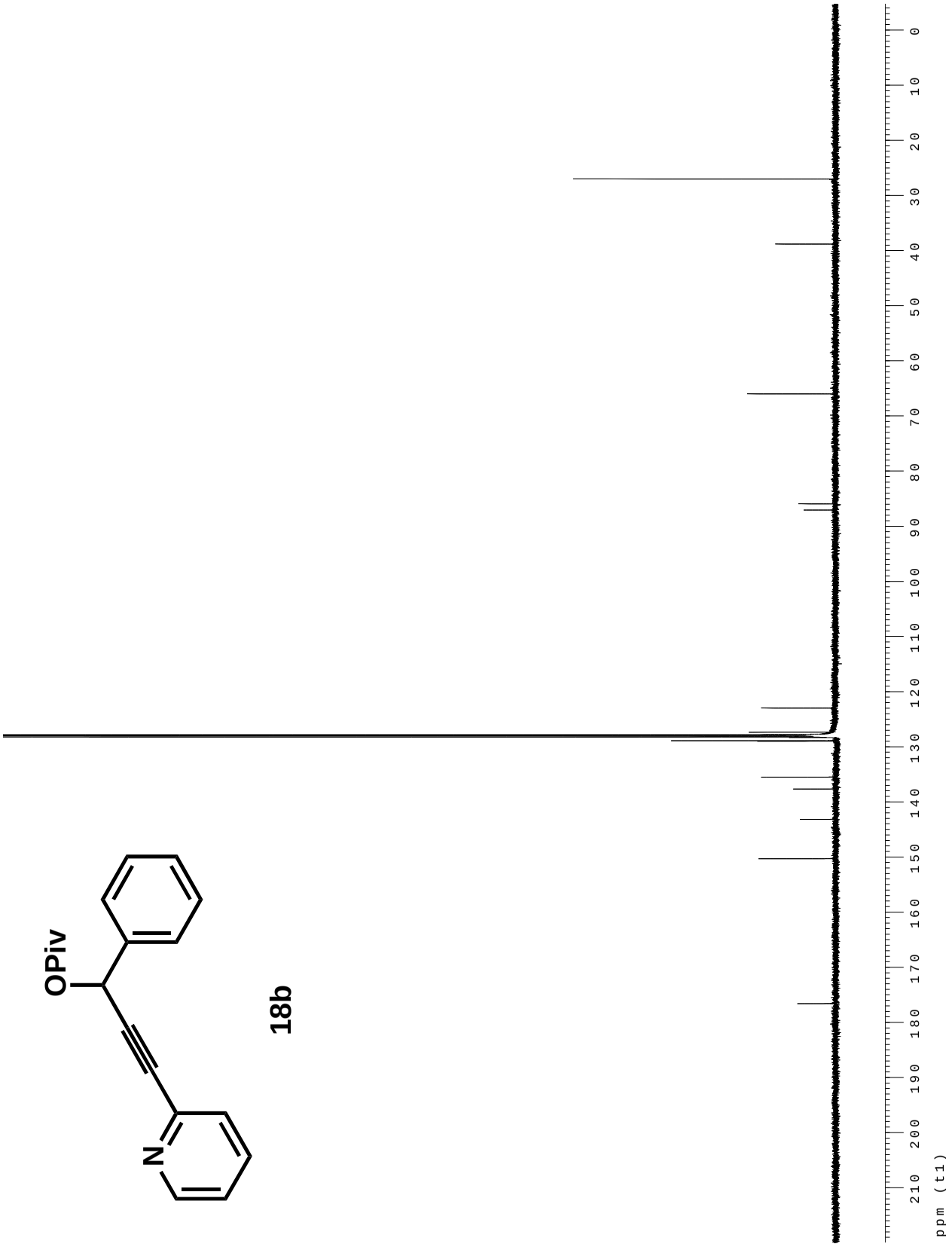
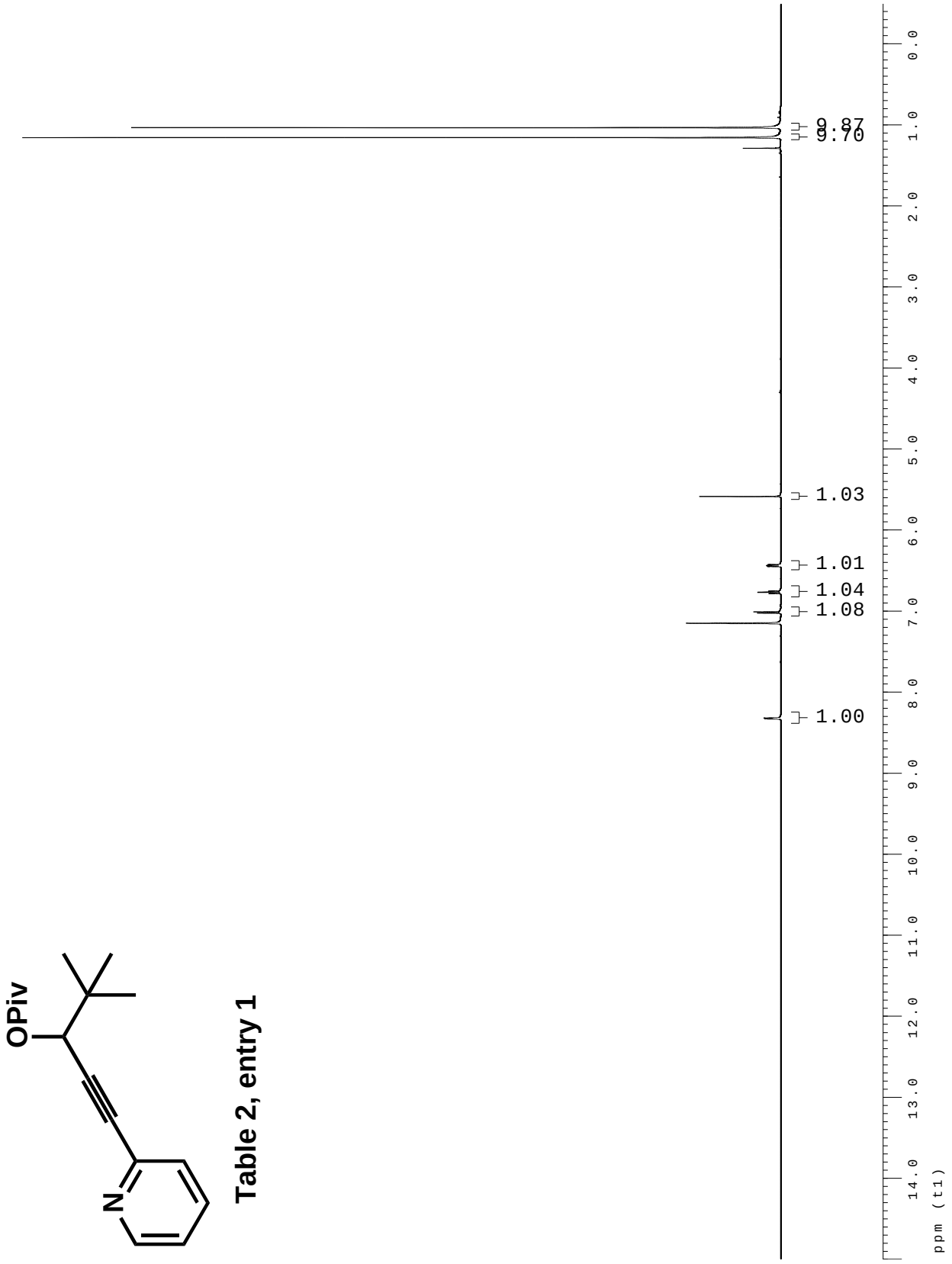
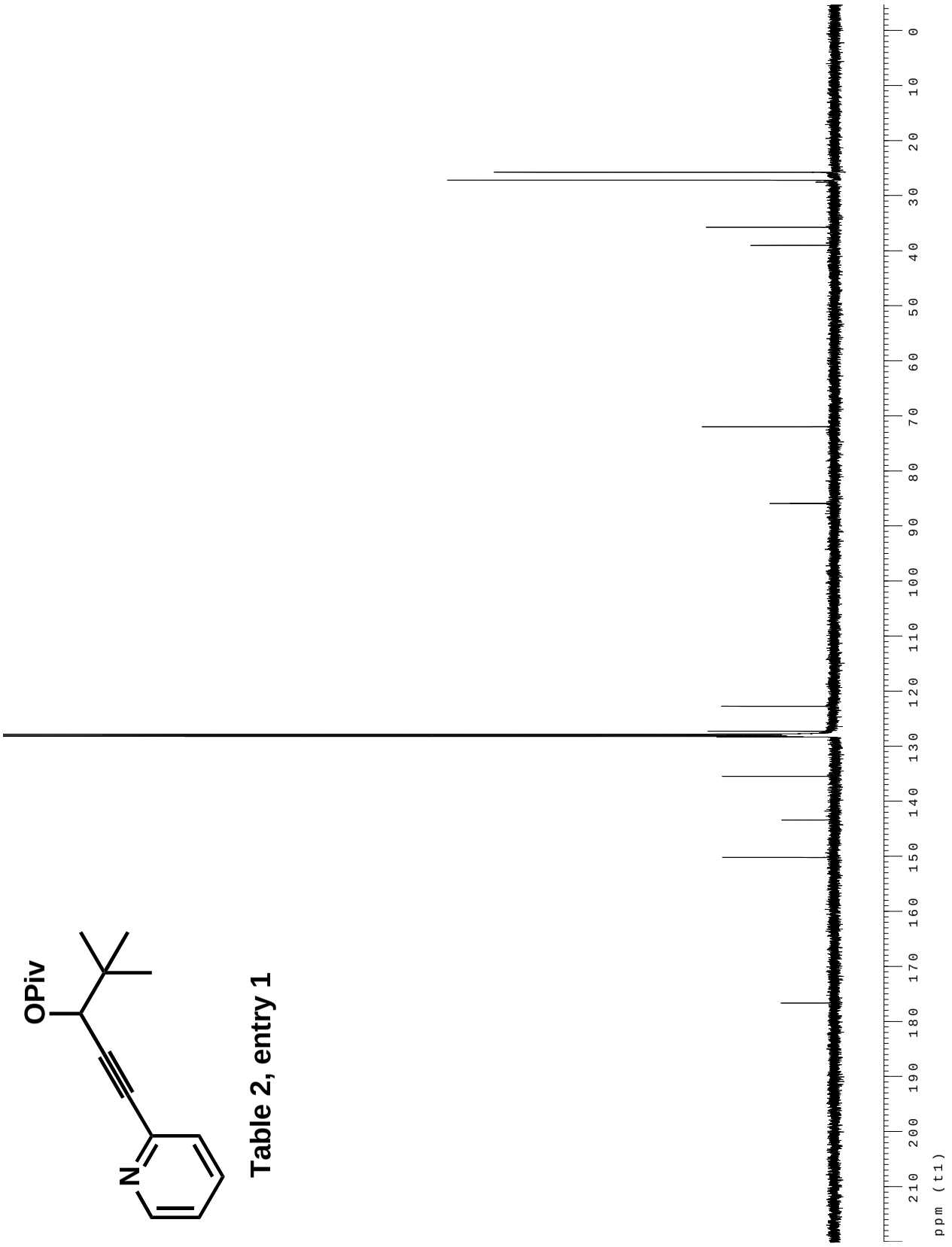
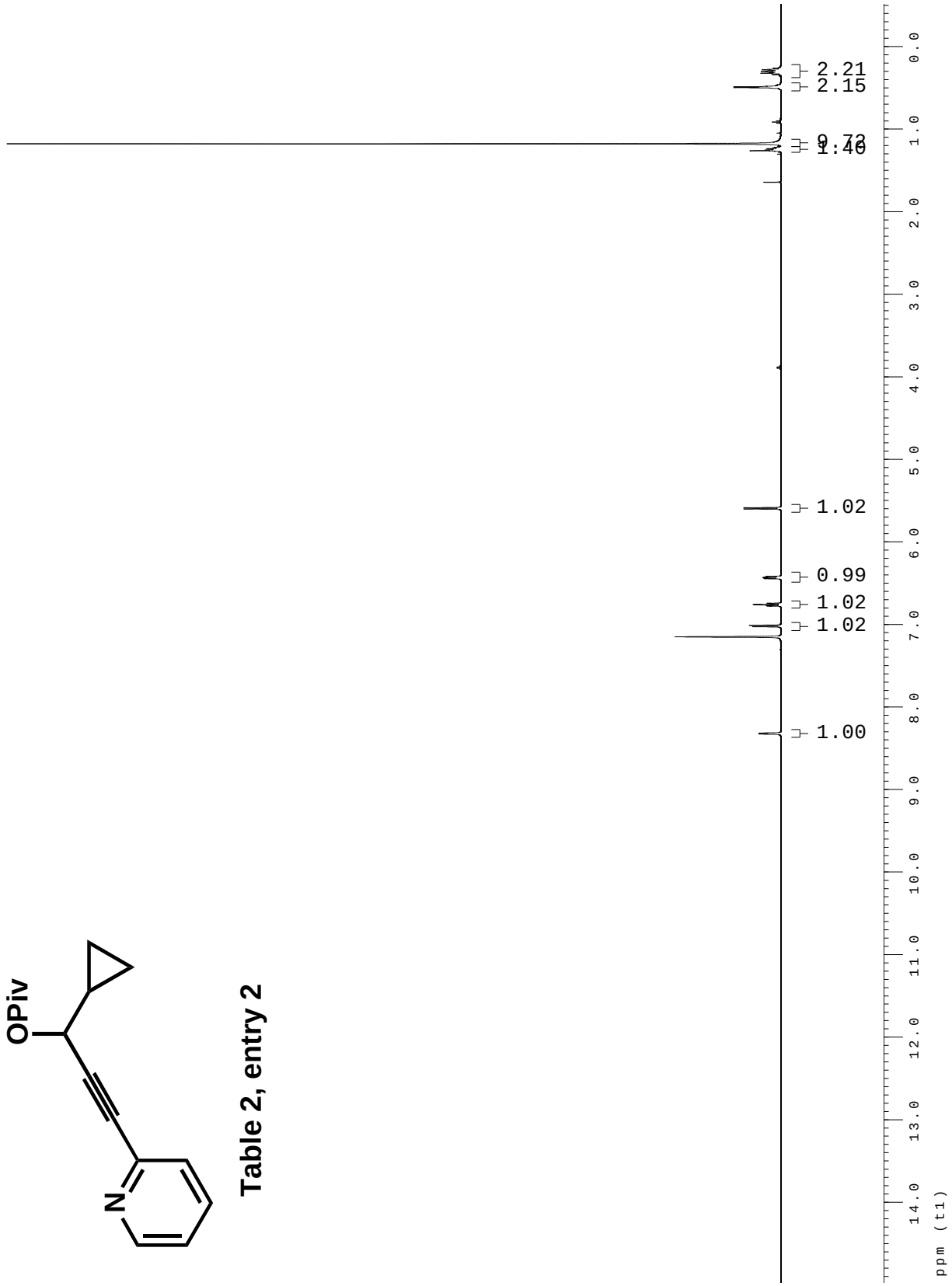
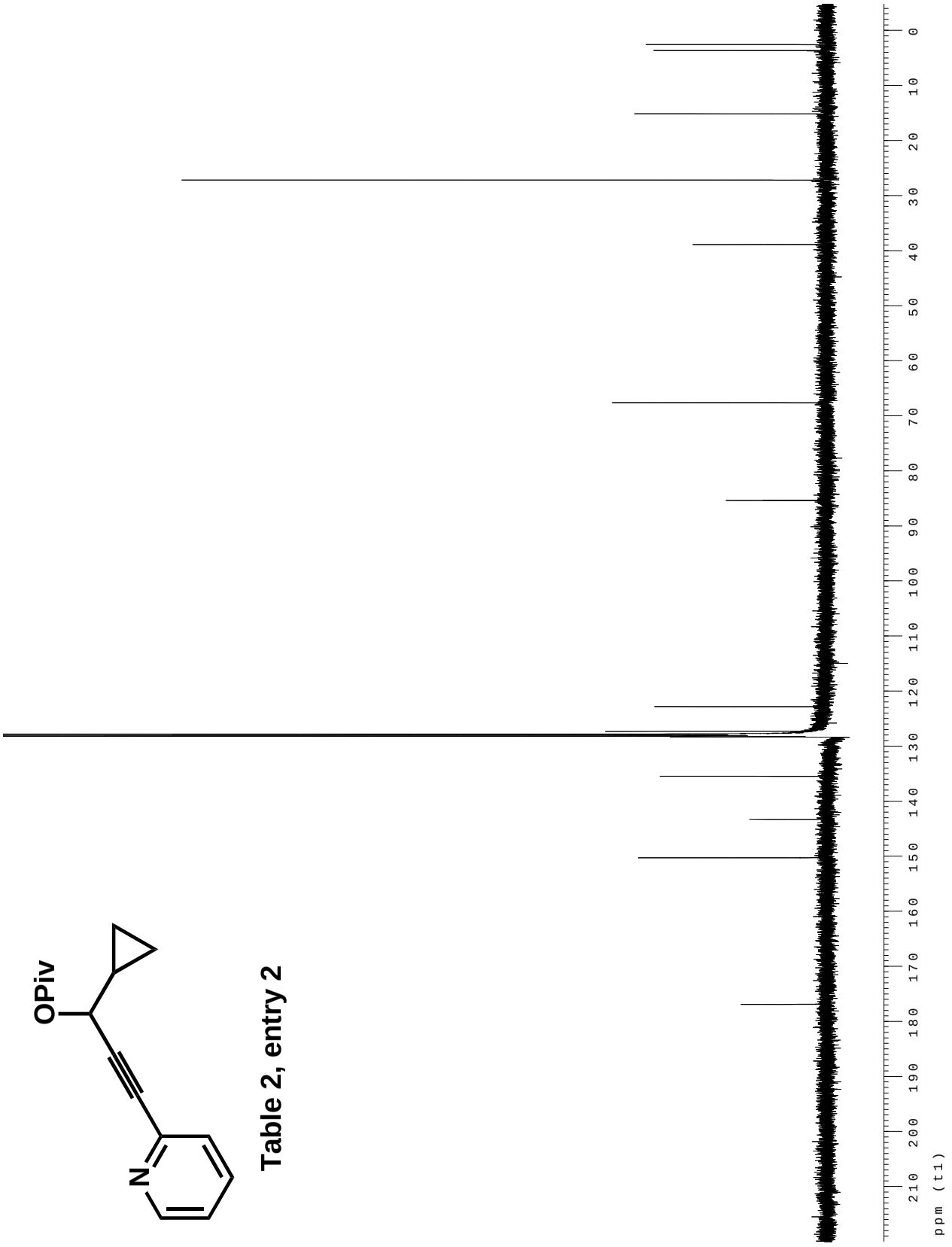
14.0
ppm (f1)

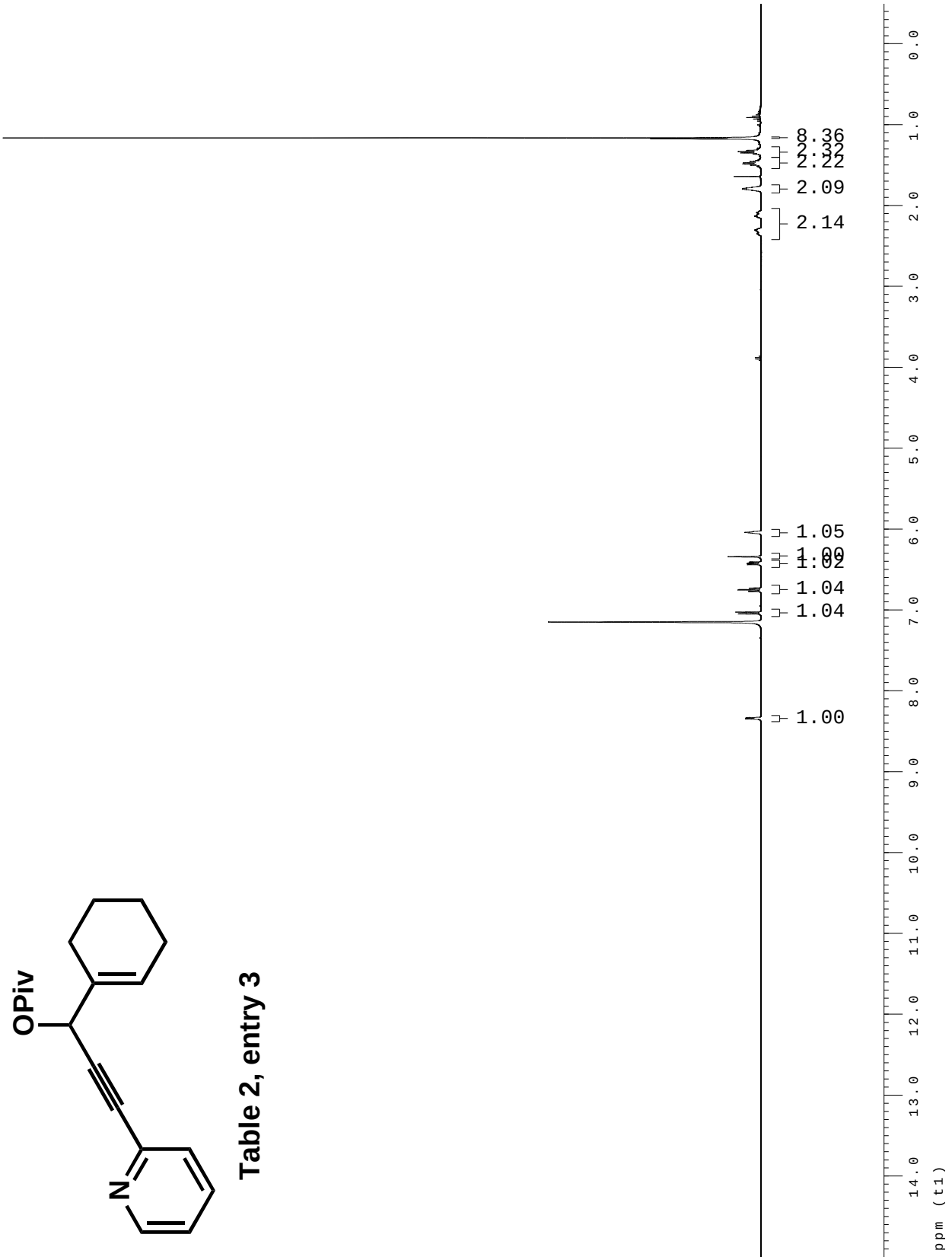

OPiv
N
18b
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm (t1)

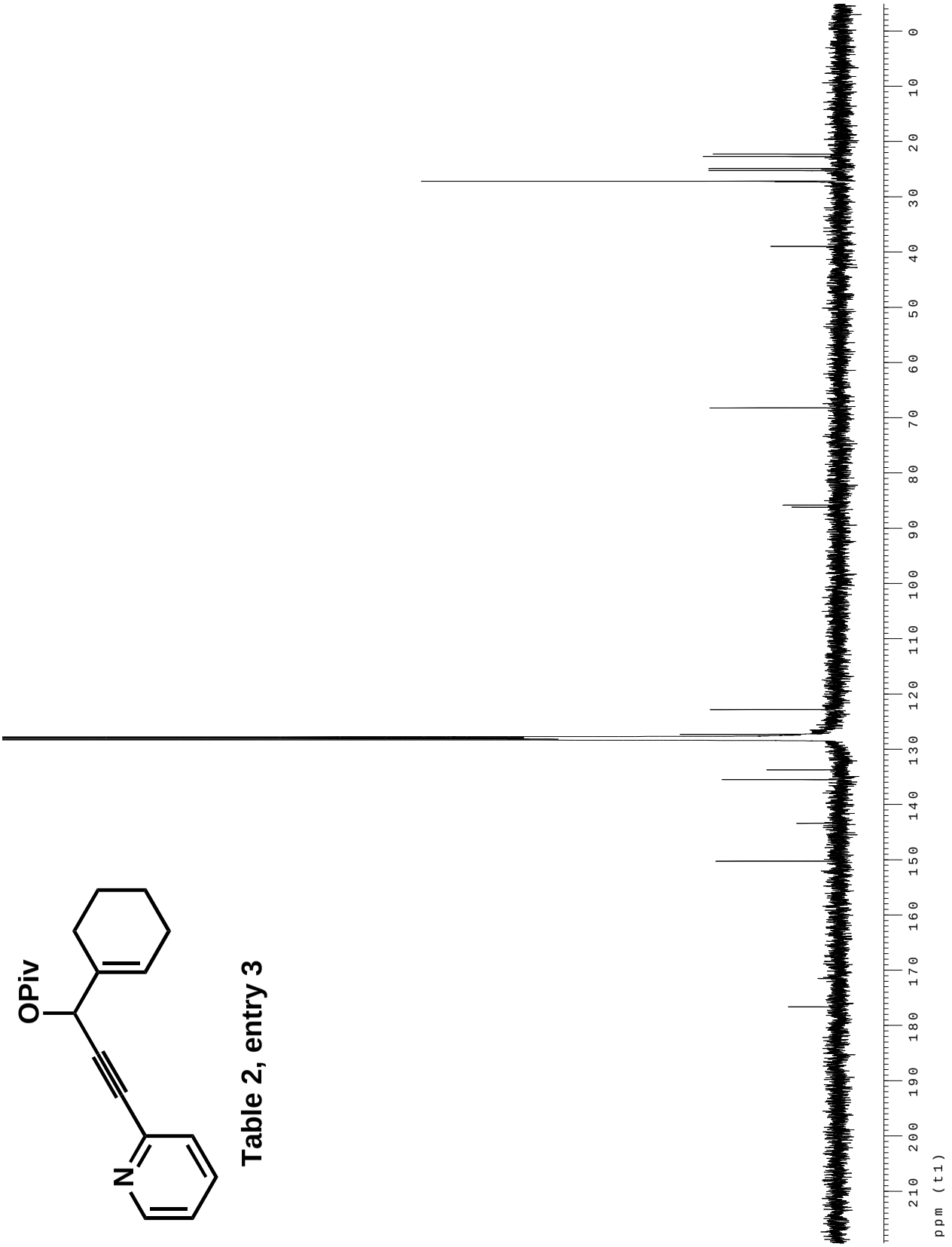

OPiv
N
Table 2, entry 1
9.87
9.70
1.03
1.01
1.04
1.08
1.00
ppm (t1)

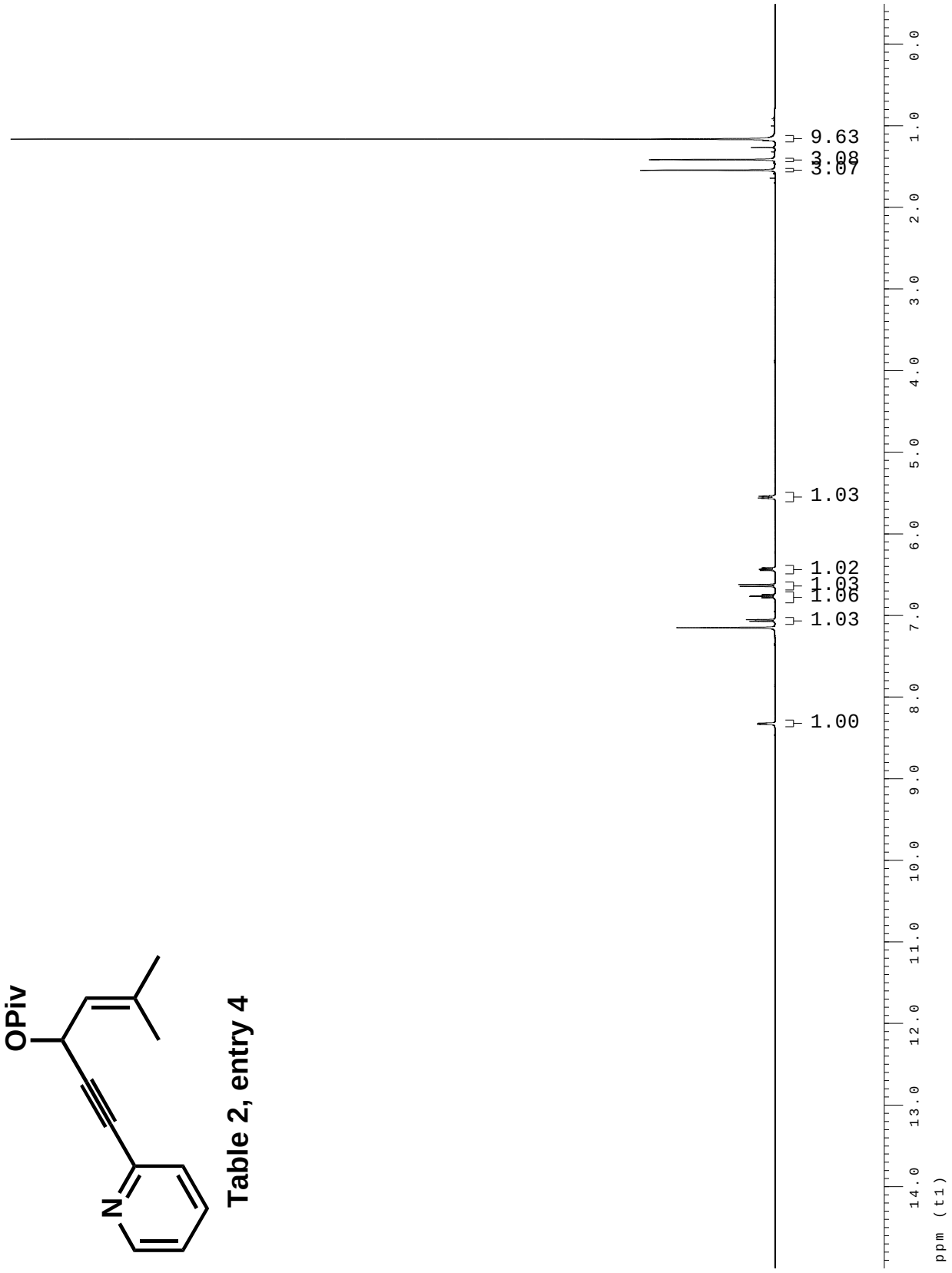

OPiv
N
Table 2, entry 1
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm (t1)

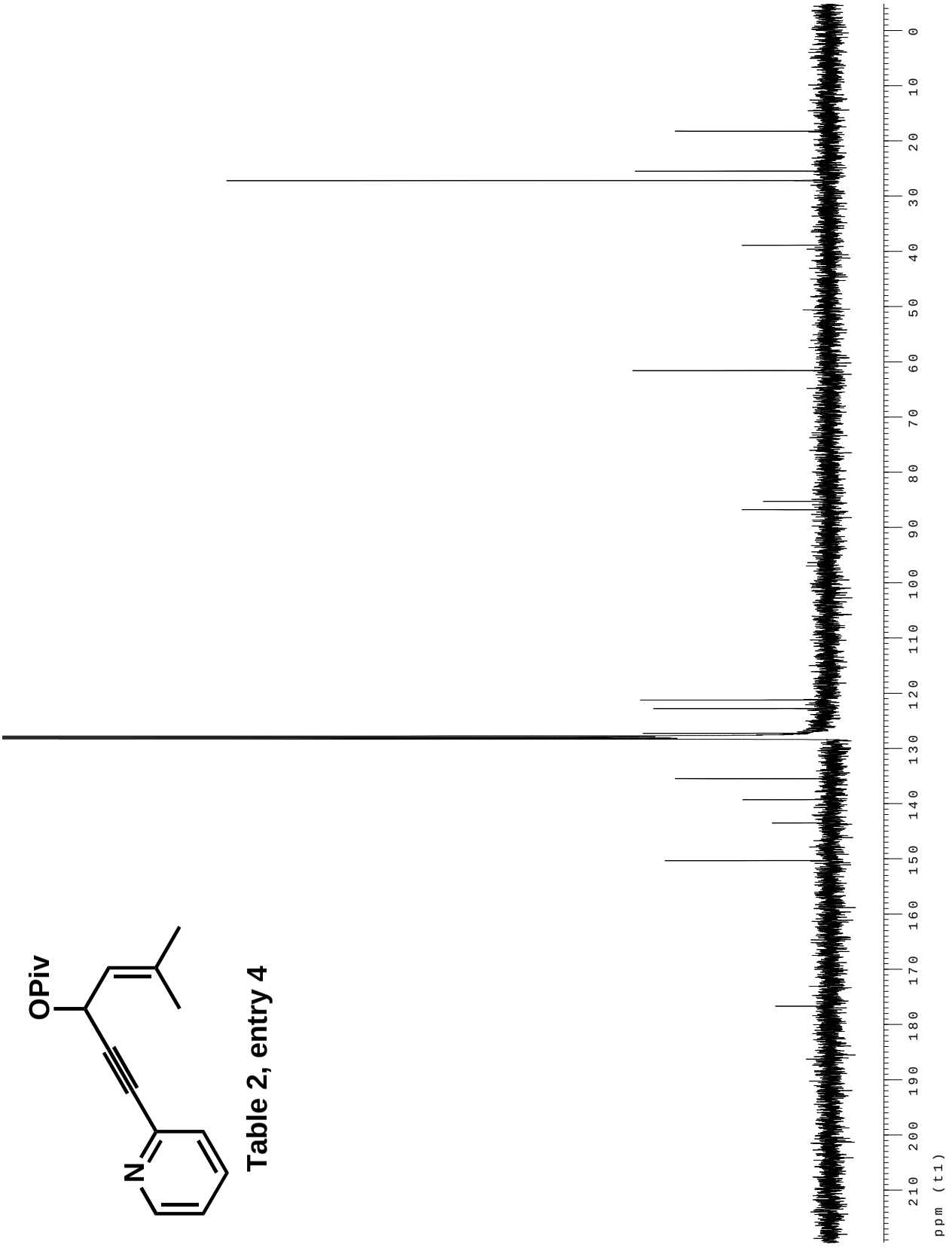

OPiv
N
Table 2, entry 2
2.21
2.15
9.72
1.46
1.02
0.99
1.02
1.02
1.00
ppm (t1)

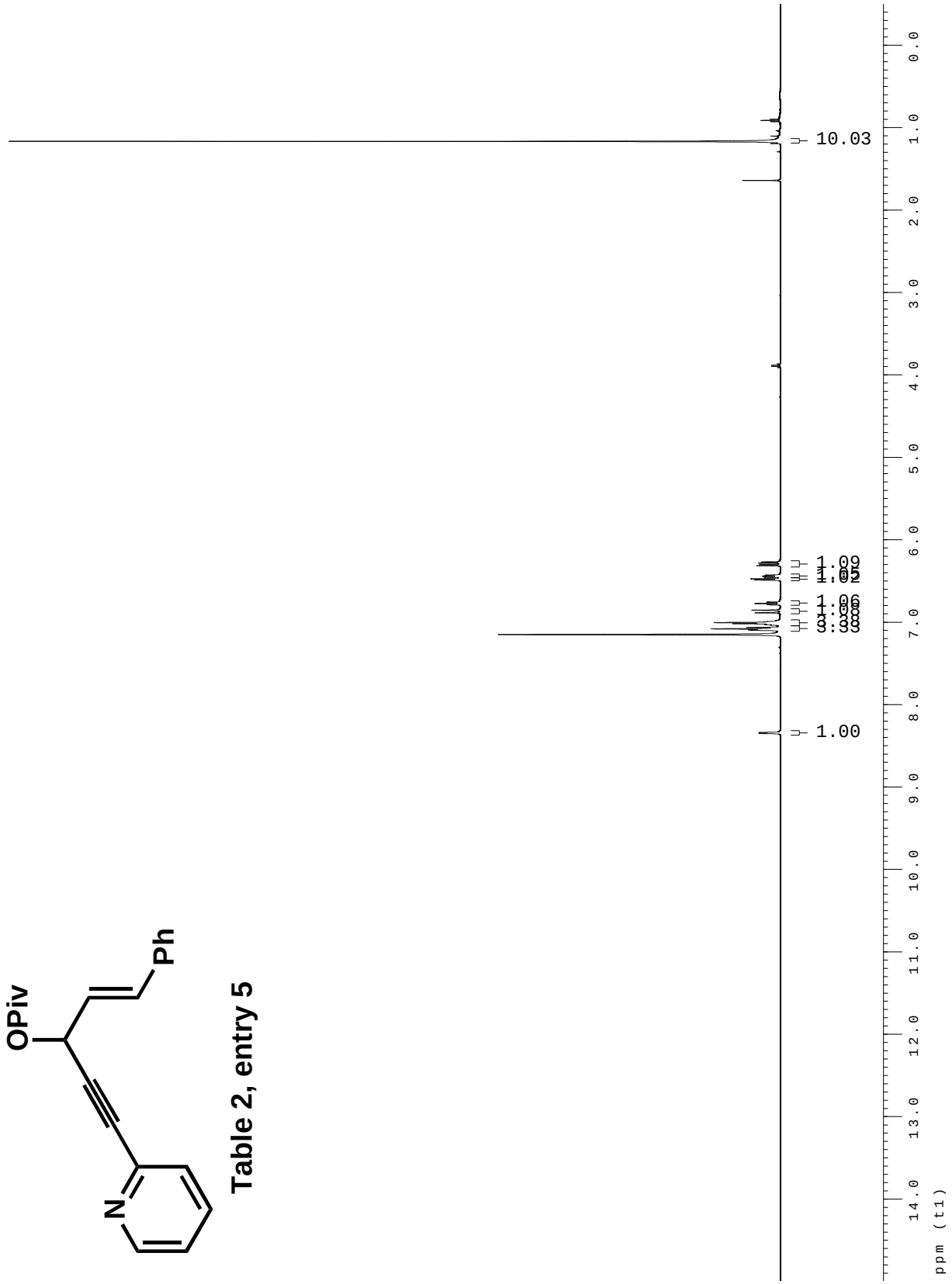

OPiv
N
Table 2, entry 2
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm (t1)

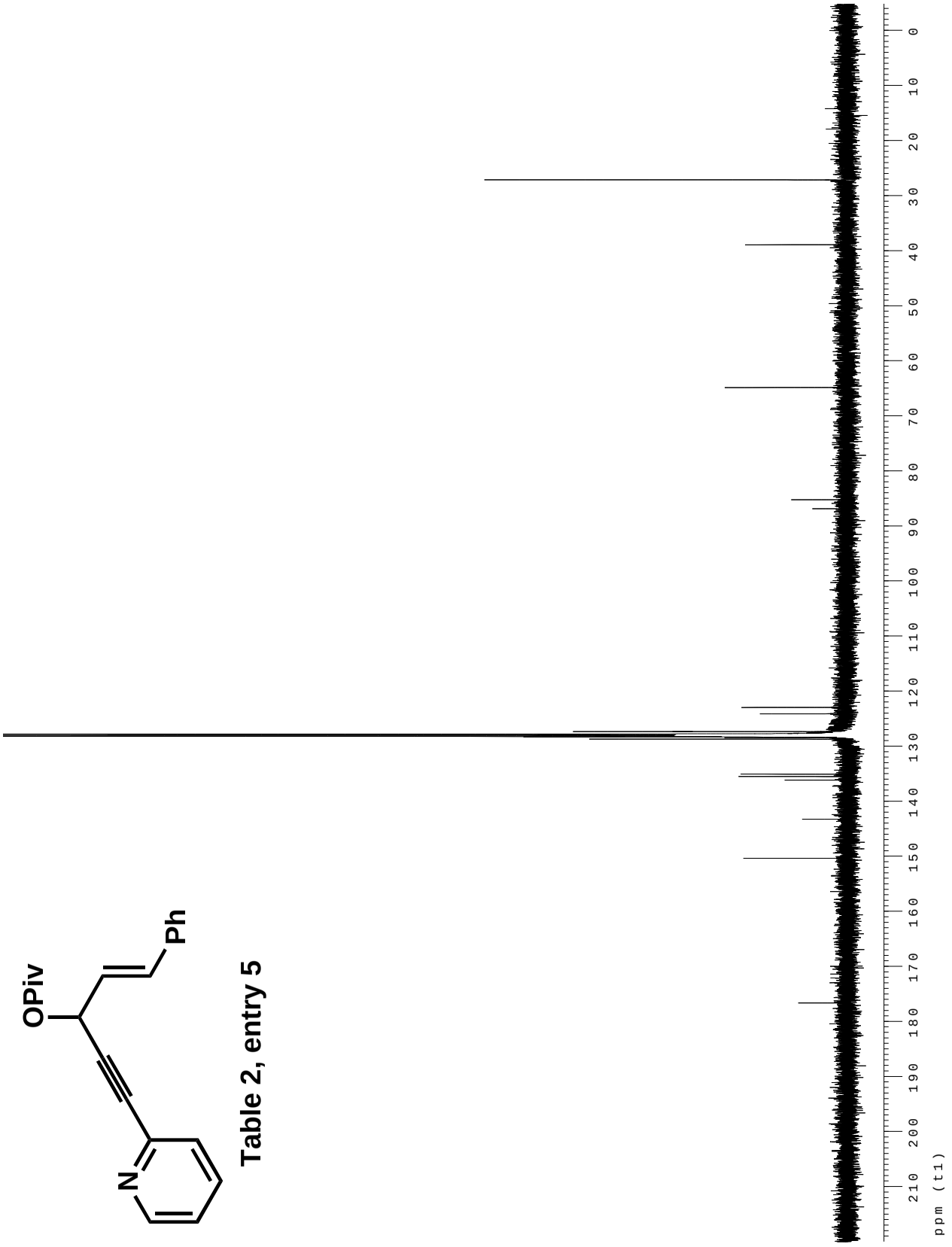

8.36
2.32
2.22
2.09
2.14
1.05
1.00
1.02
1.04
1.04
1.00
OPiv
N
Table 2, entry 3
ppm (t1)


OPiv
N
Table 2, entry 3
ppm (t1)


OPiv
N
Table 2, entry 4
9.63
3.08
3.07
1.03
1.02
1.03
1.06
1.03
1.00
ppm (t1)


OPiv
N
Table 2, entry 4
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm (t1)


OPiv
Ph
N
Table 2, entry 5
10.03
1.09
1.05
1.06
3.33
1.00
14.0
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


OPiv
Ph
N
Table 2, entry 5
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm (t1)

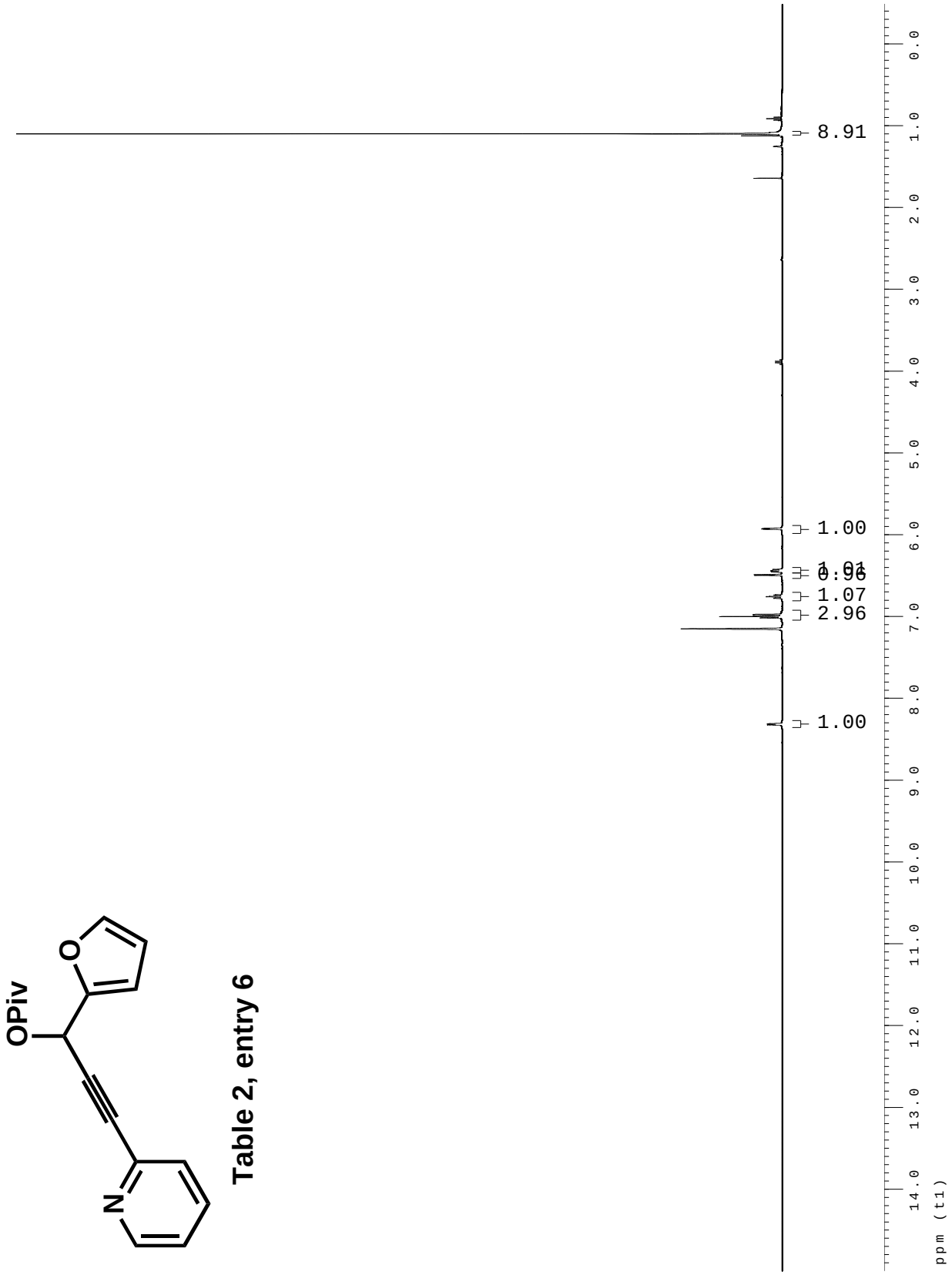
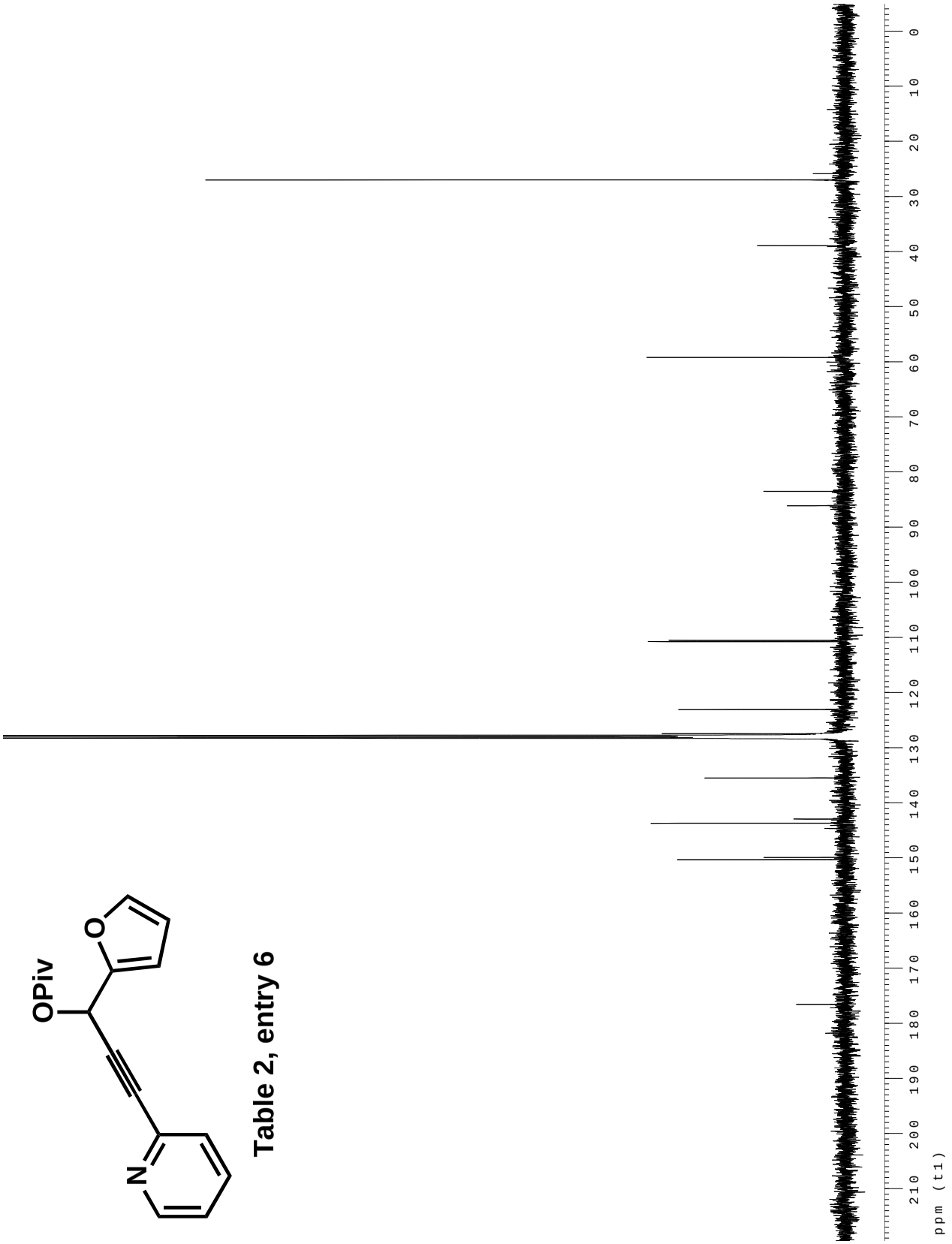
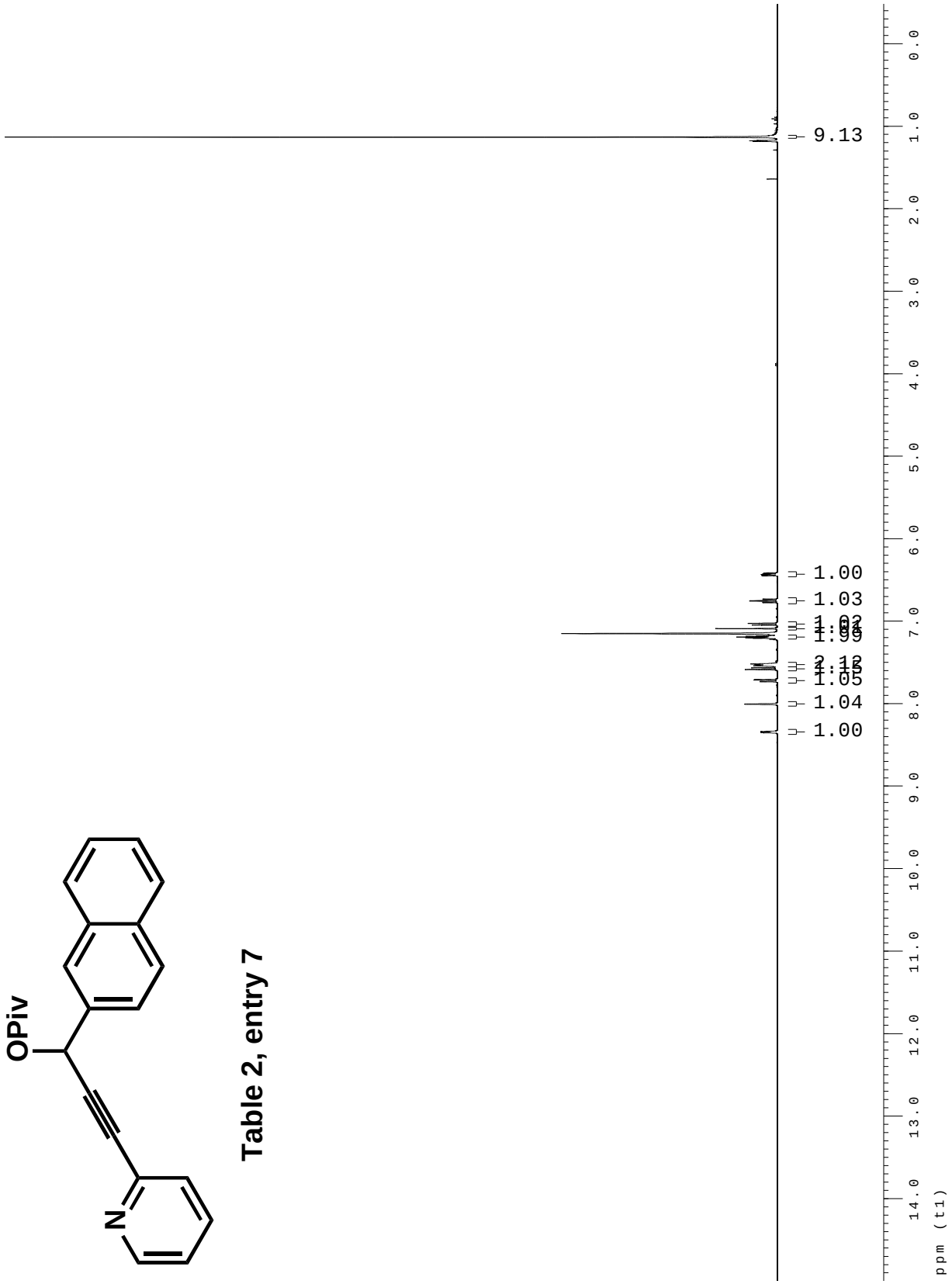
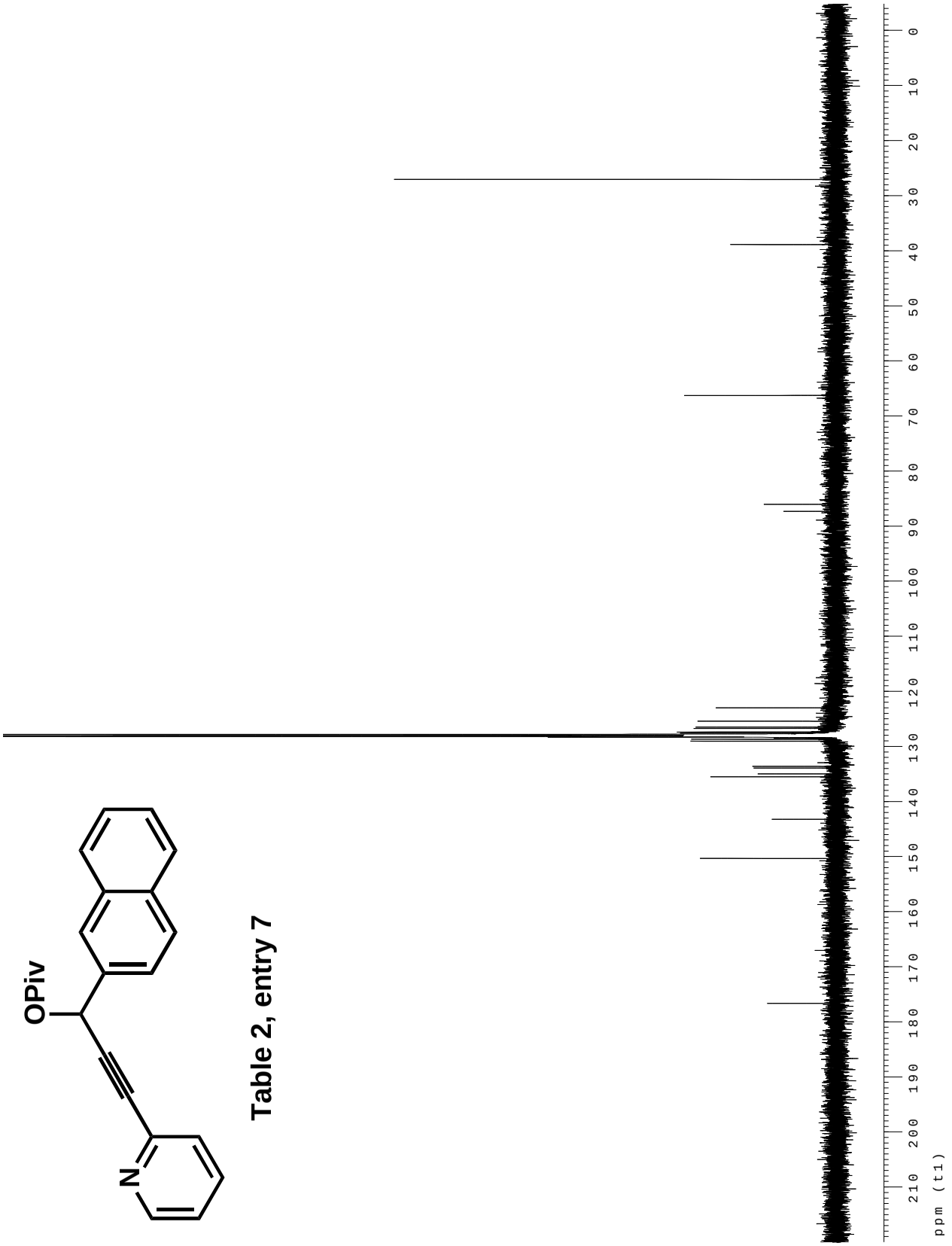
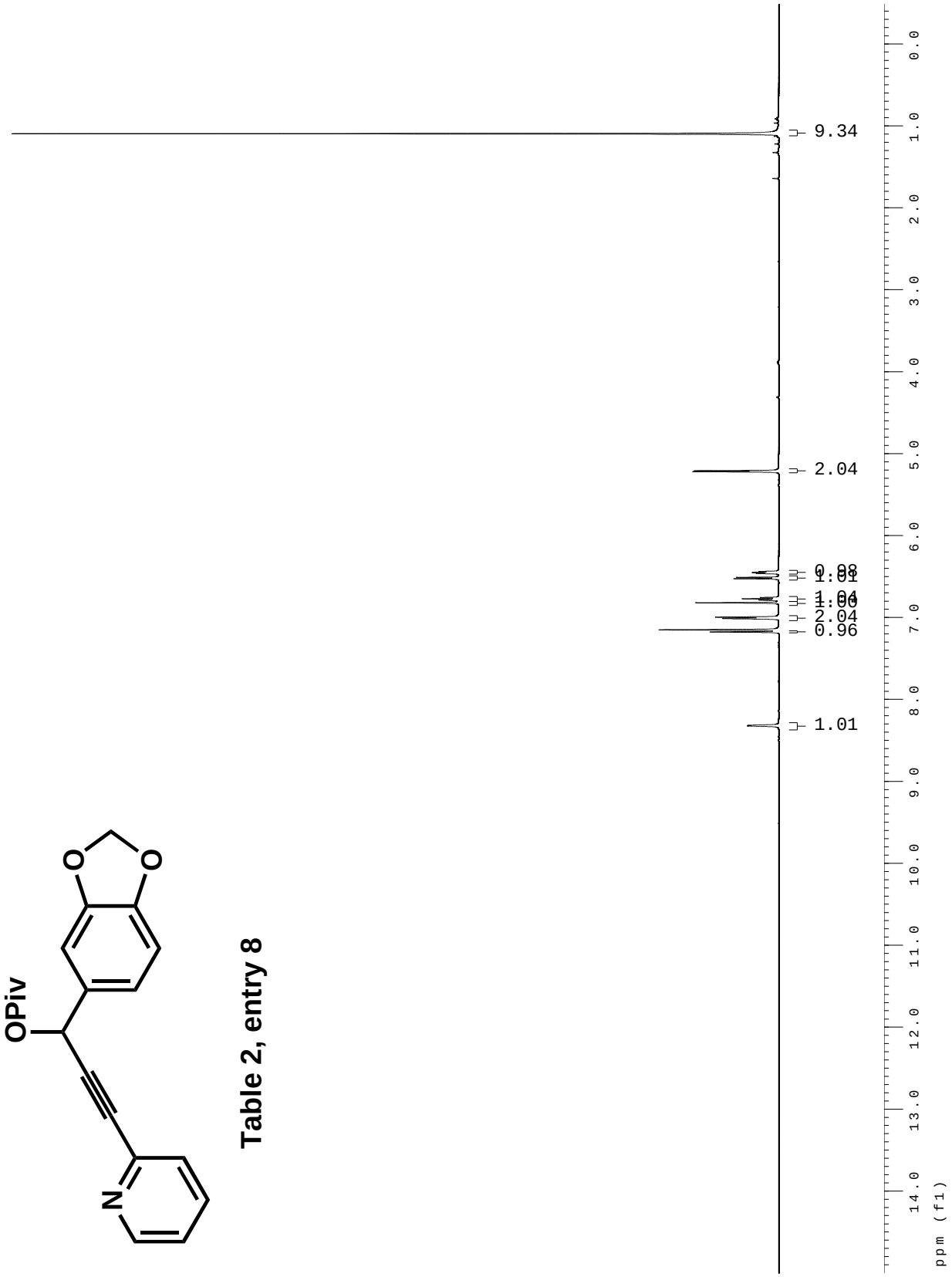


Table 2, entry 6


OPiv
O
N
Table 2, entry 6
ppm (t1)


OPiv
N
Table 2, entry 7
9.13
1.00
1.03
1.02
1.99
2.12
1.05
1.04
1.00
14.0
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


OPiv
N
Table 2, entry 7
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm (t1)


OPiv
N
O
O
Table 2, entry 8
9.34
2.04
0.88
1.01
1.04
1.00
2.04
0.96
1.01
14.0
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

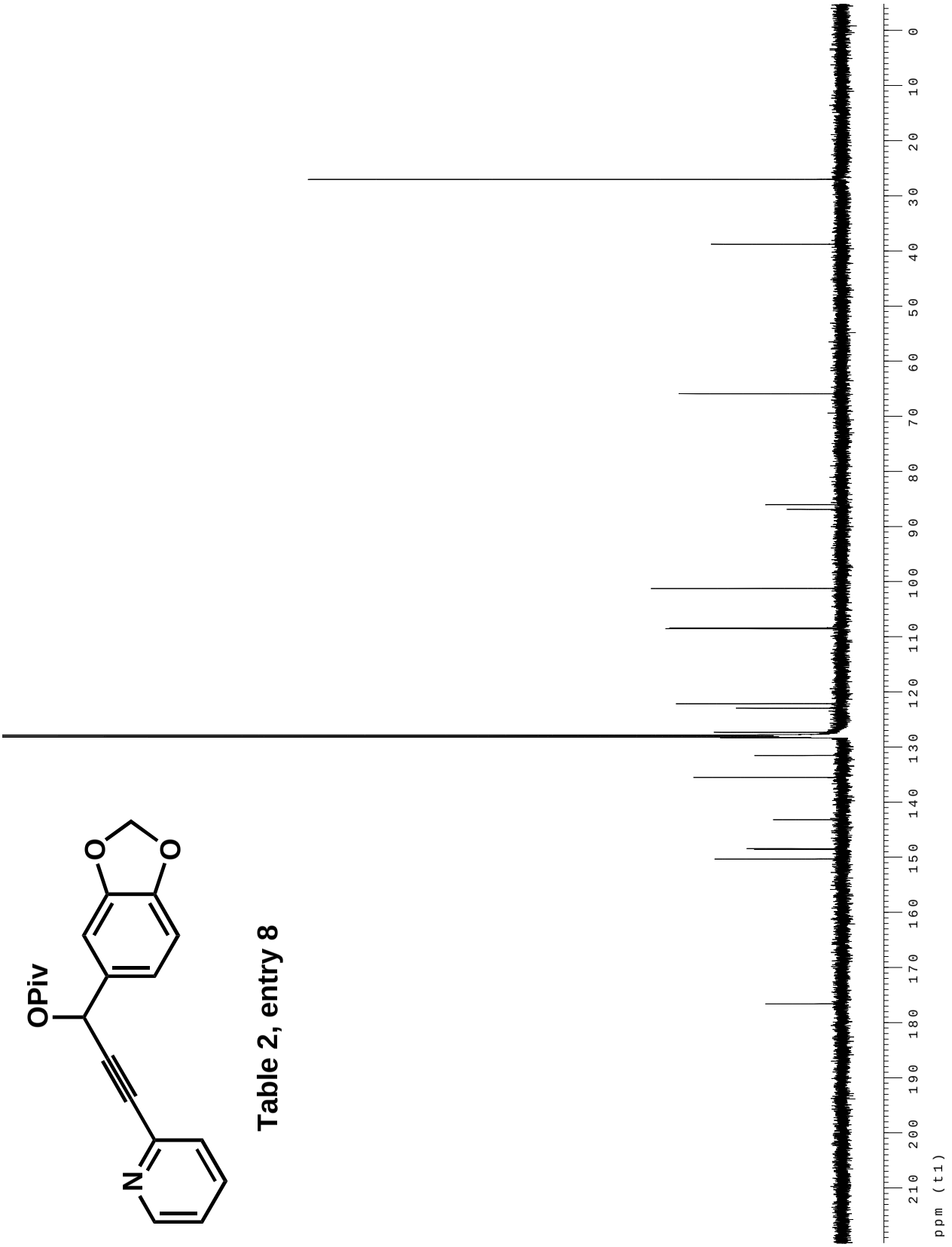
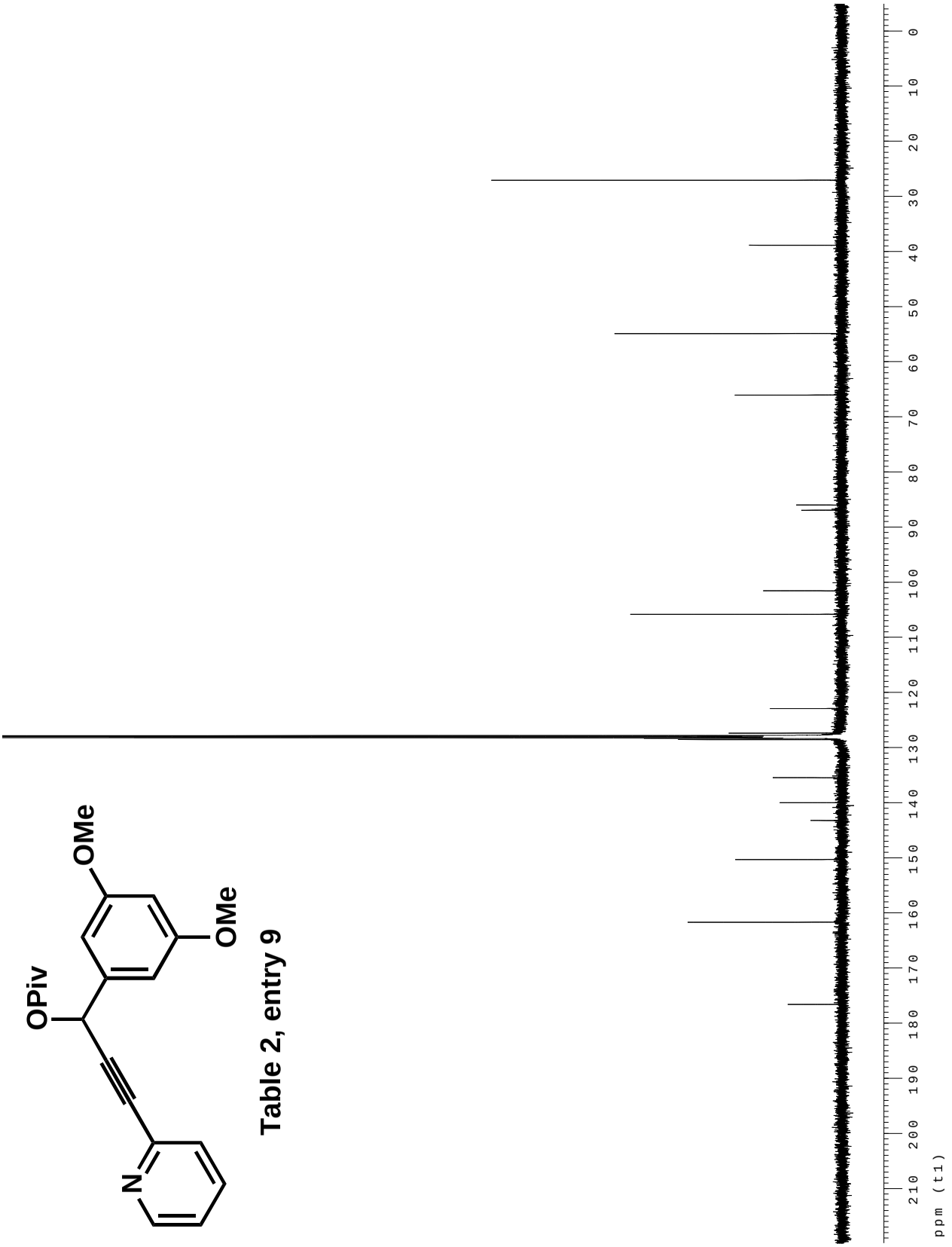
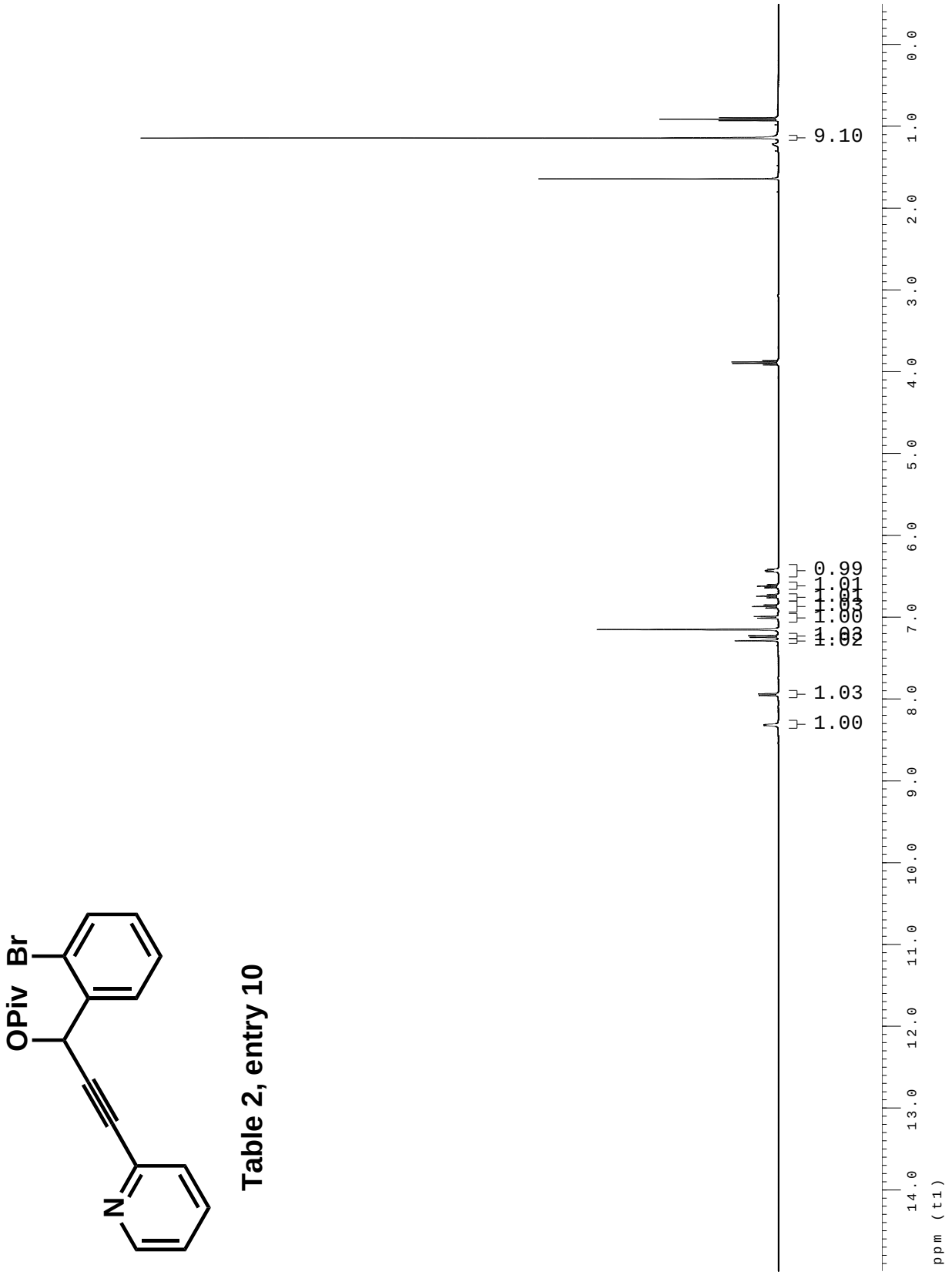
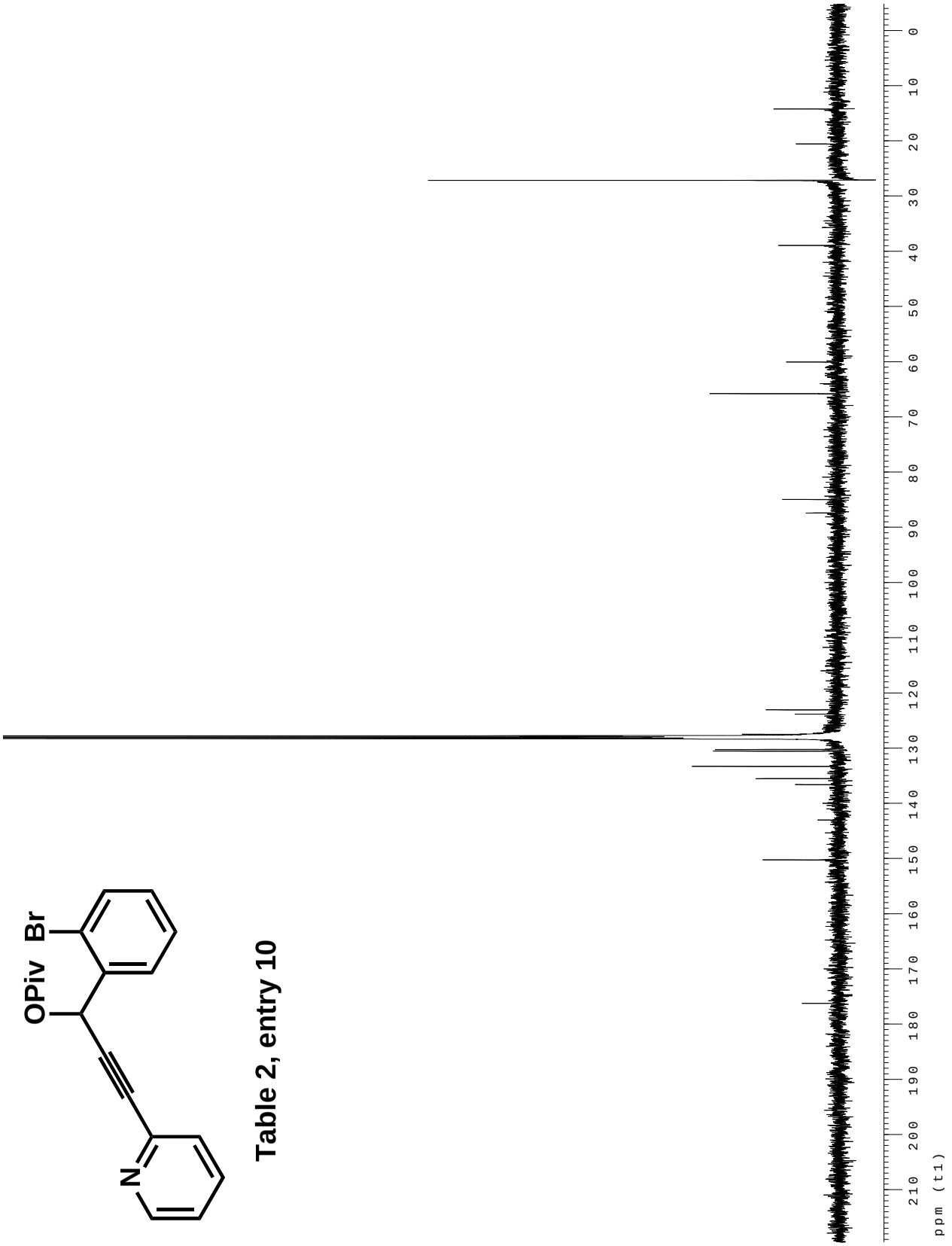
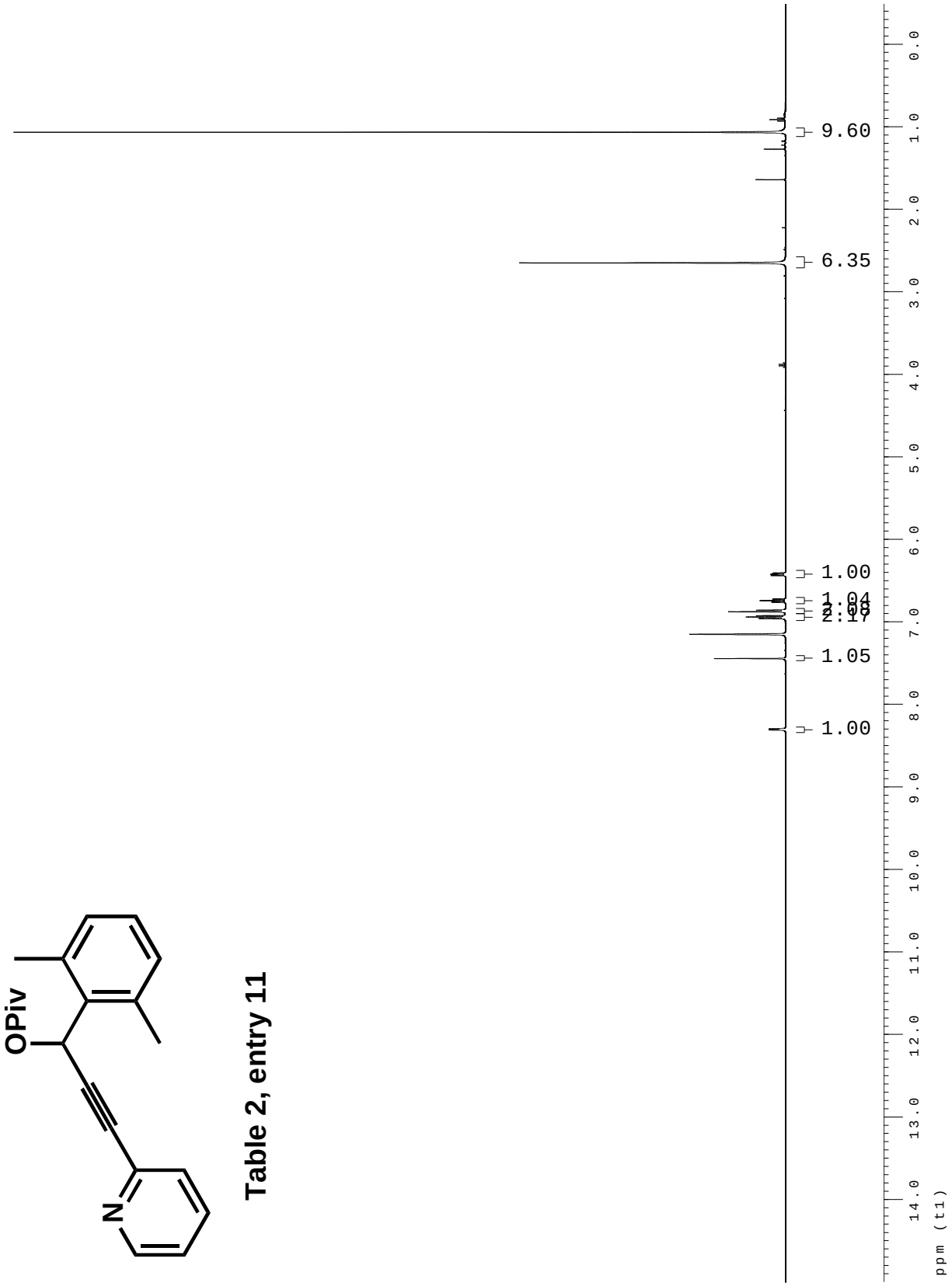

OPiv
O
O
N
Table 2, entry 8
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm (t1)

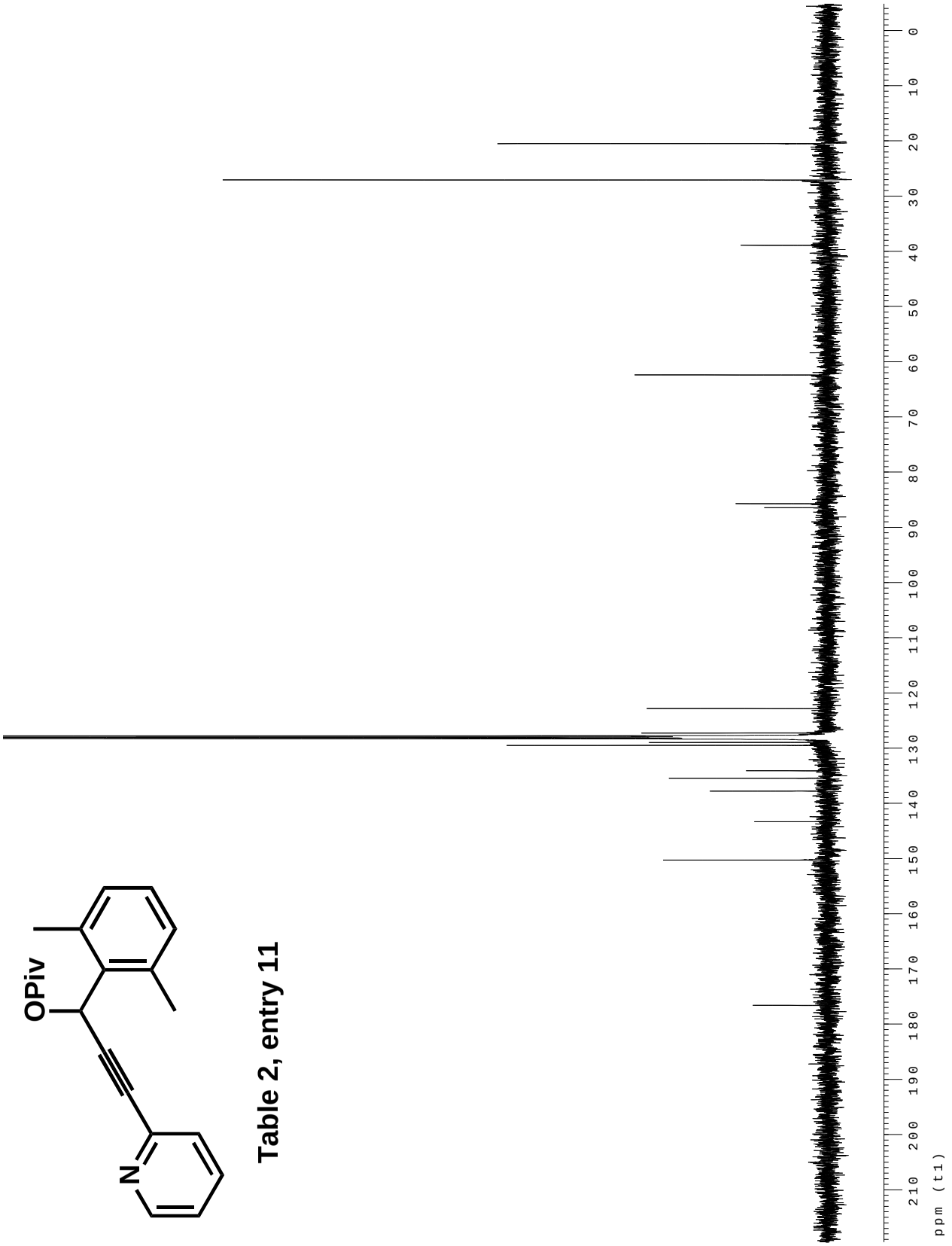
Table 2, entry 9

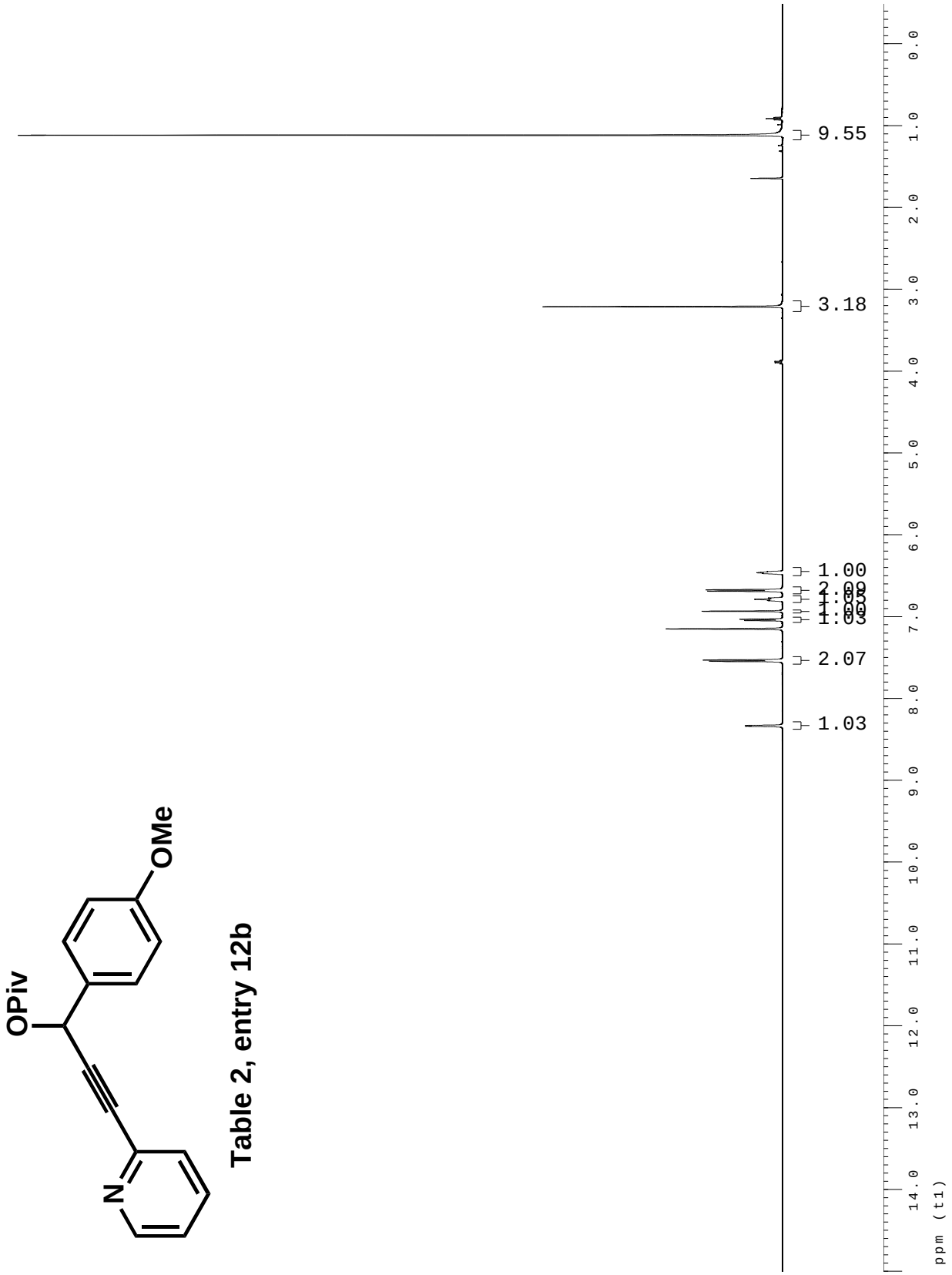

OPiv
OMe
OMe
N
Table 2, entry 9
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm (t1)

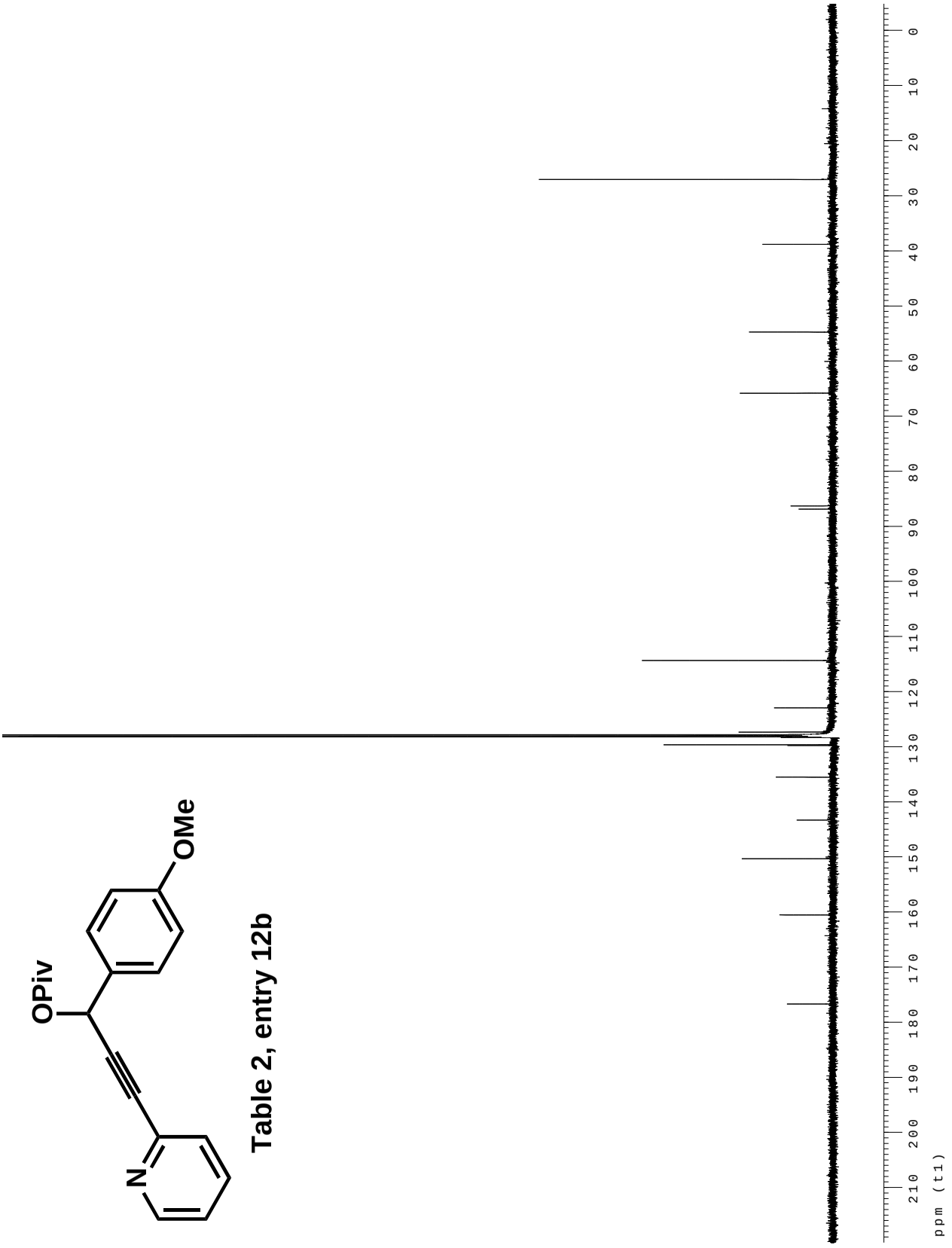

OPiv
Br
N
Table 2, entry 10
9.10
0.99
1.01
1.01
1.03
1.00
1.03
1.02
1.03
1.00
14.0
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

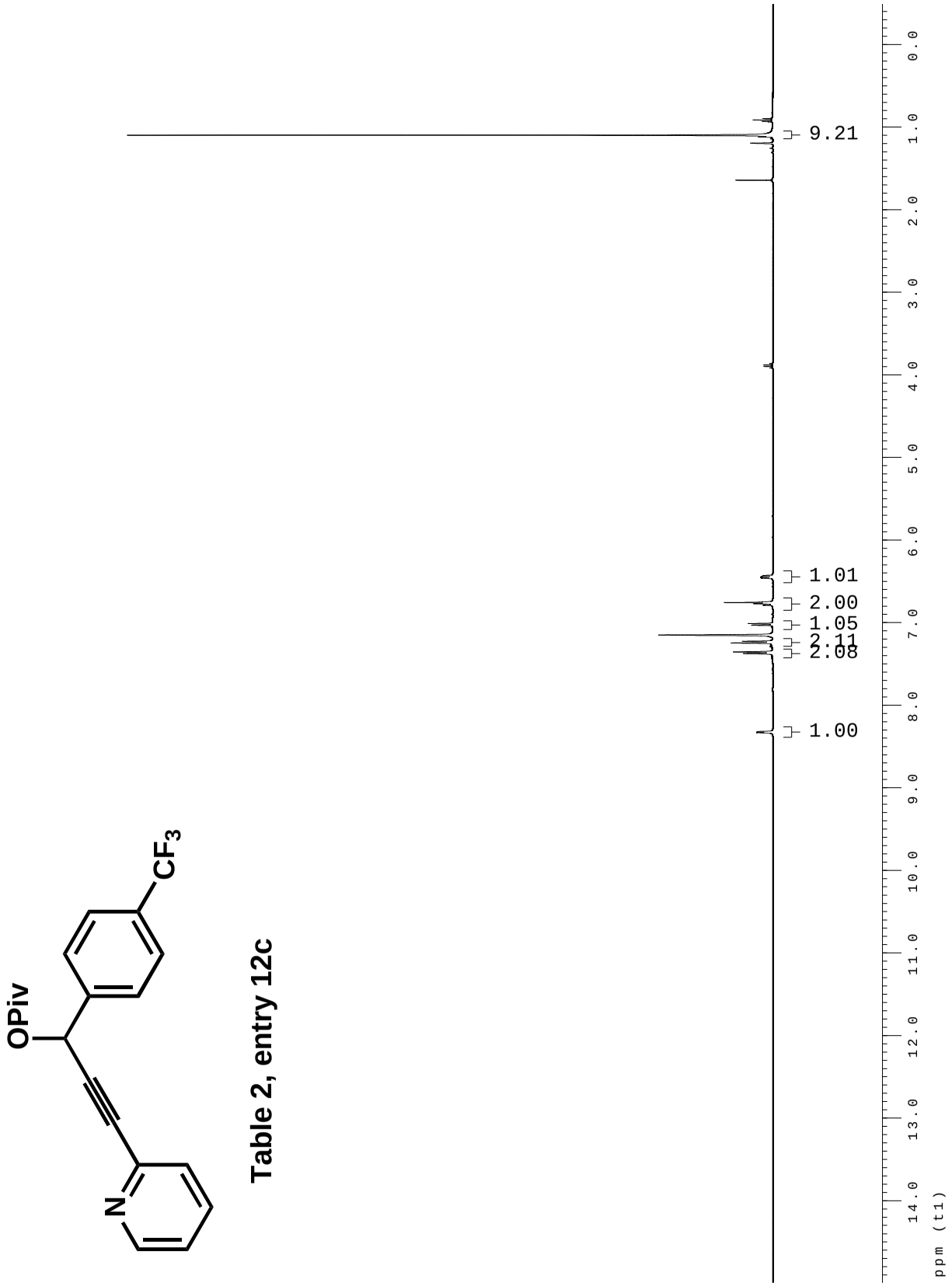

OPiv
Br
N
Table 2, entry 10
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm (t1)

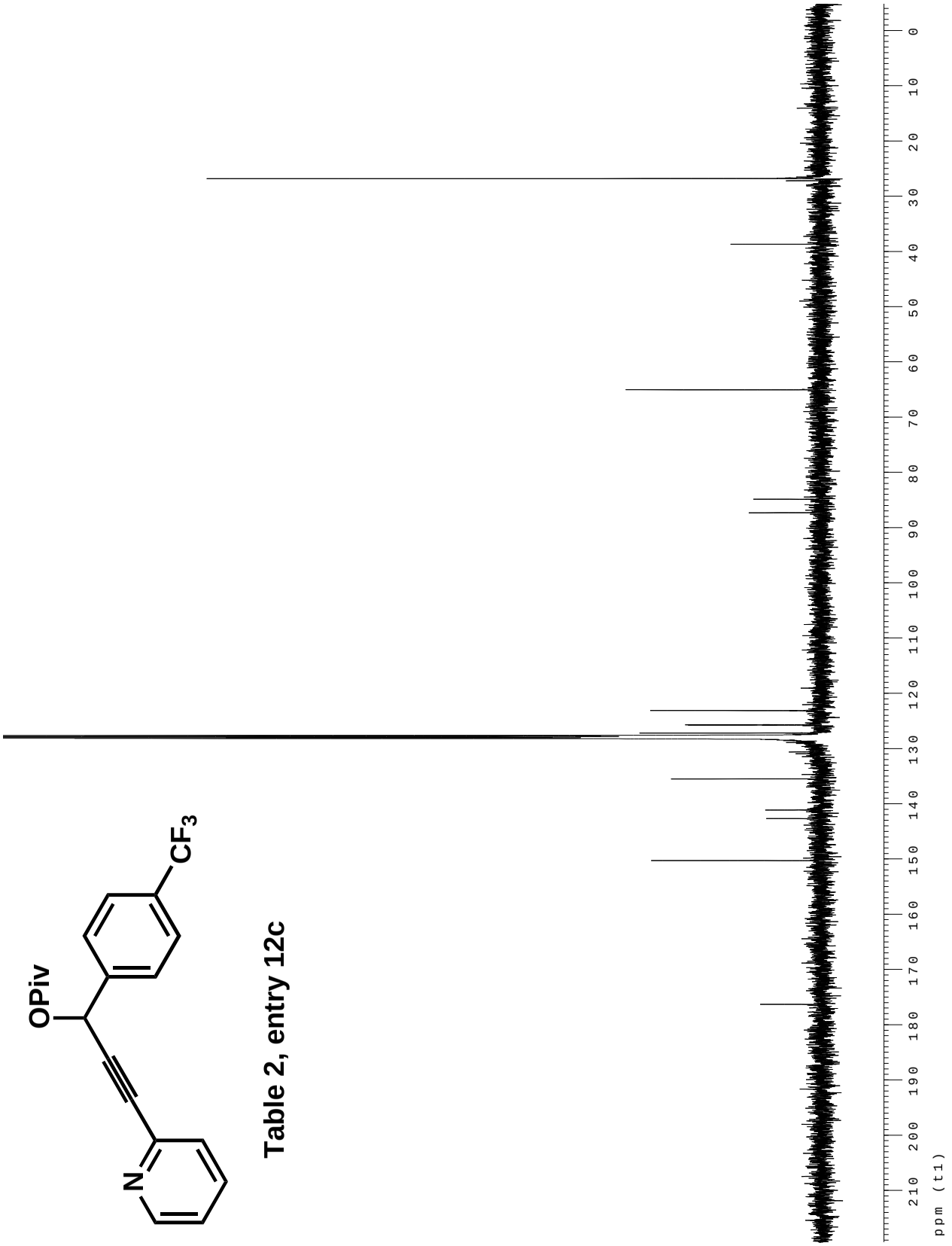

OPiv
N
Table 2, entry 11
9.60
6.35
1.00
1.04
2.08
2.17
1.05
1.00
14.0
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

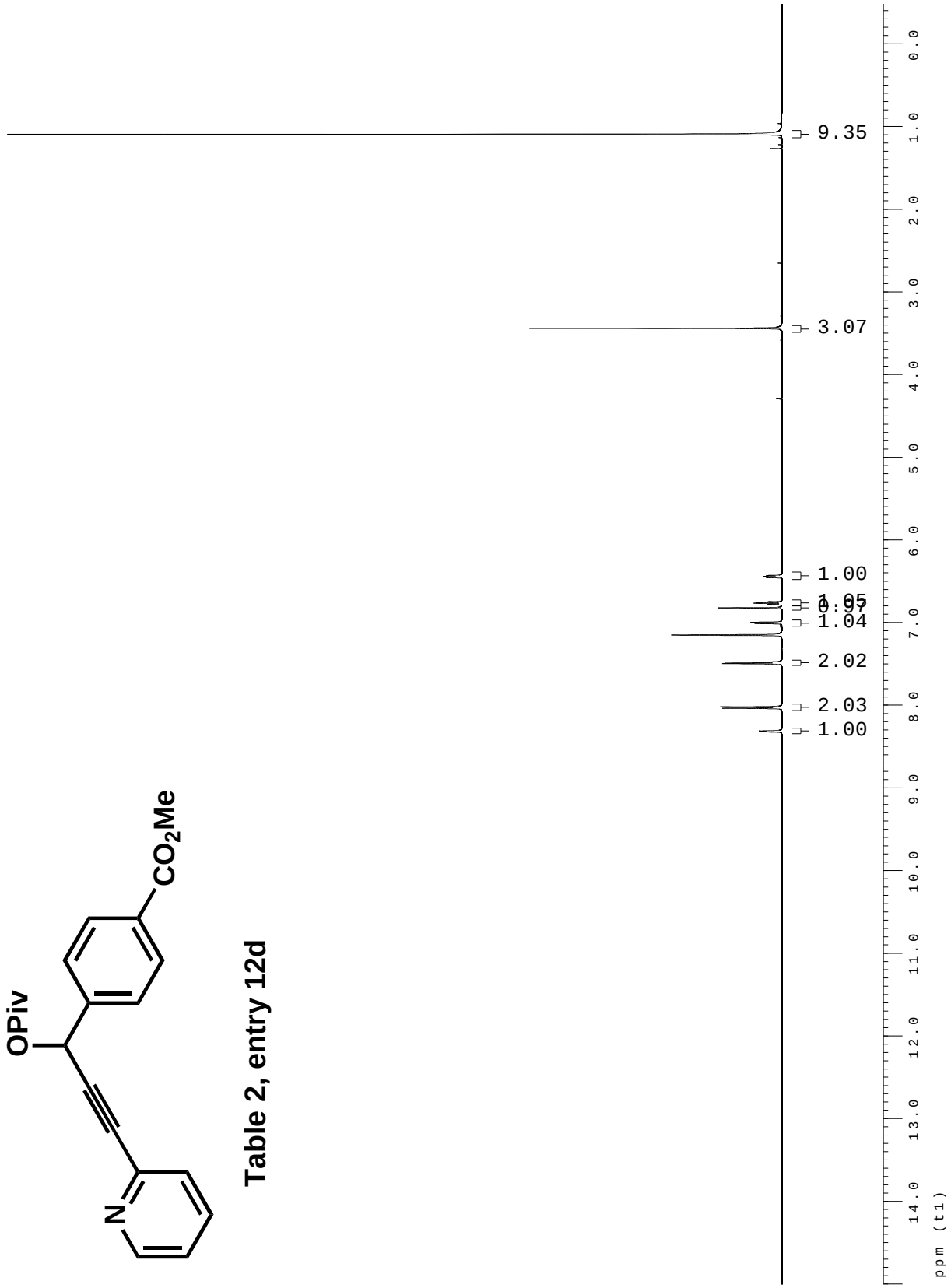

OPiv
N
Table 2, entry 11
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm (t1)

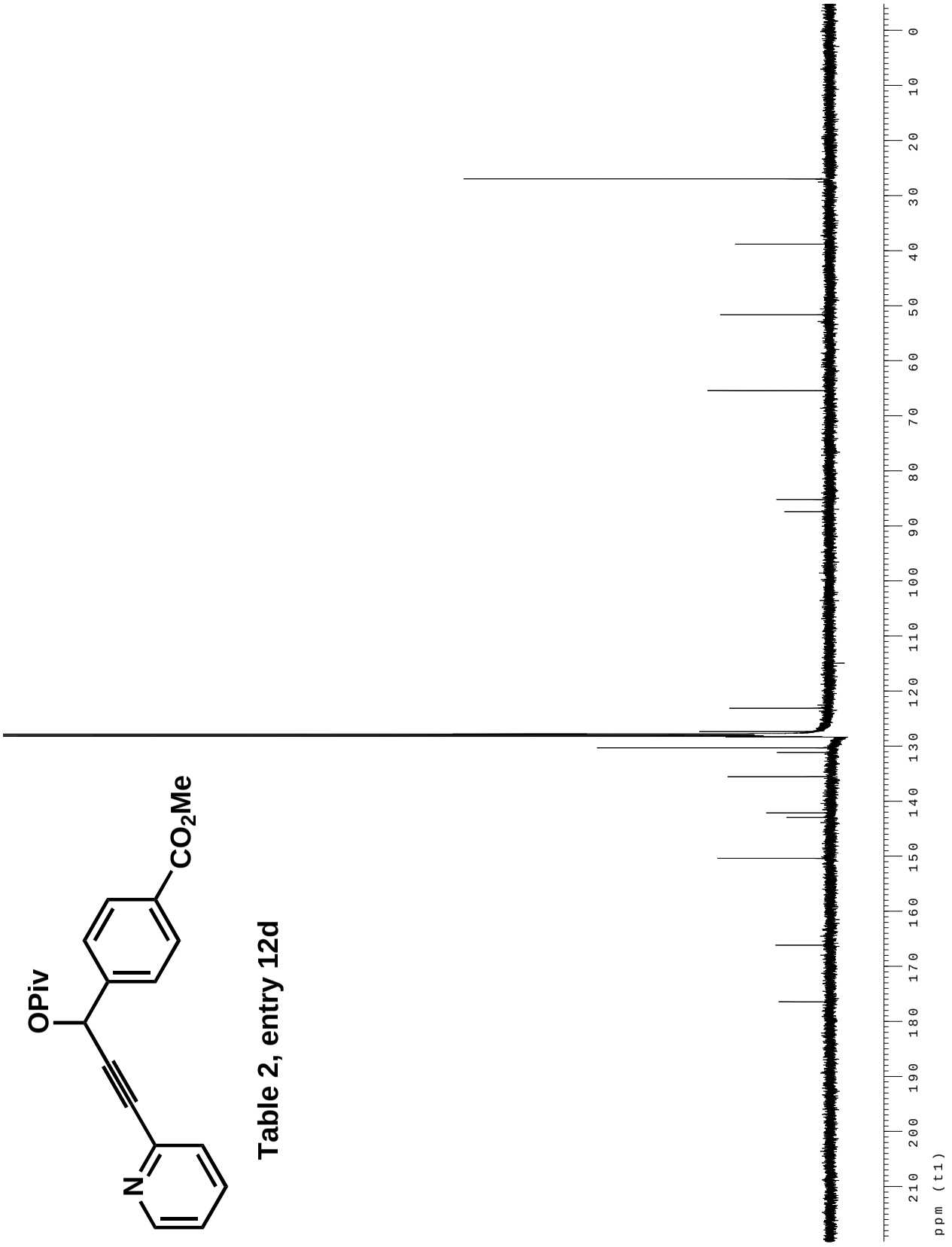

OPiv
OMe
N
Table 2, entry 12b
9.55
3.18
1.00
2.00
1.03
2.07
1.03
ppm (t1)


OPiv
OMe
N
Table 2, entry 12b
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm (t1)

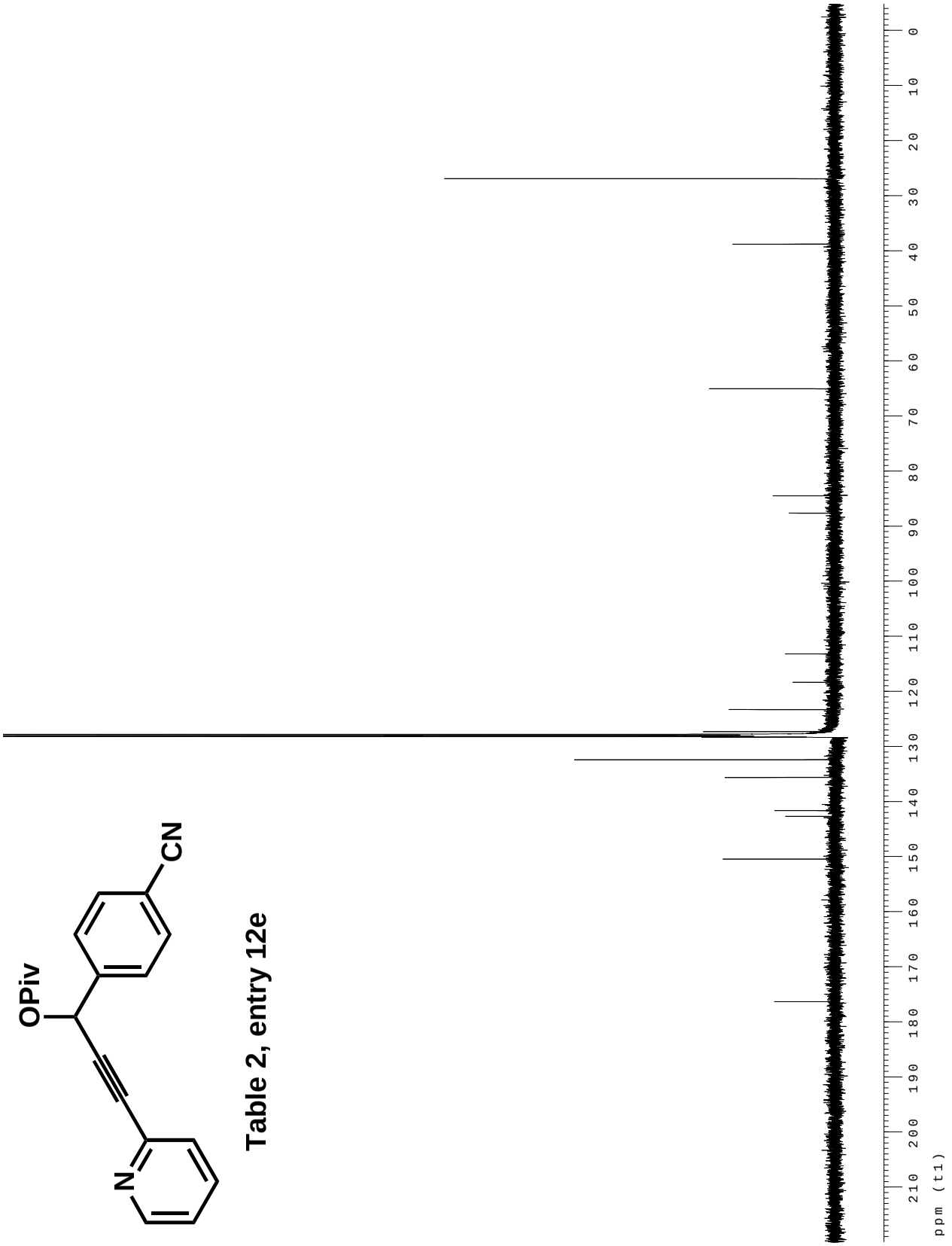

OPiv
CF3
N
Table 2, entry 12c
9.21
1.01
2.00
1.05
2.11
2.08
1.00
14.0
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

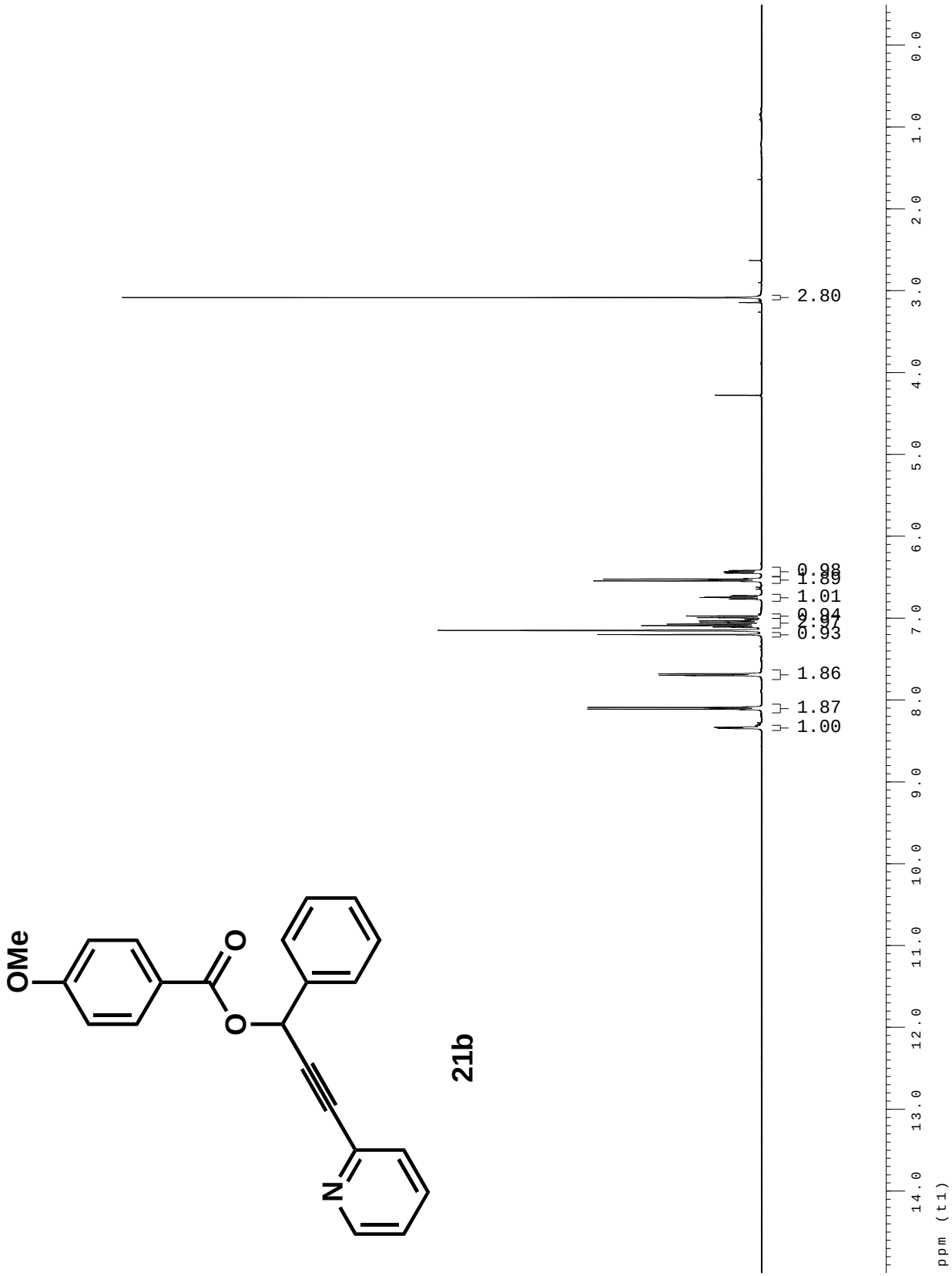

OPiv
CF3
N
Table 2, entry 12c
ppm (t1)

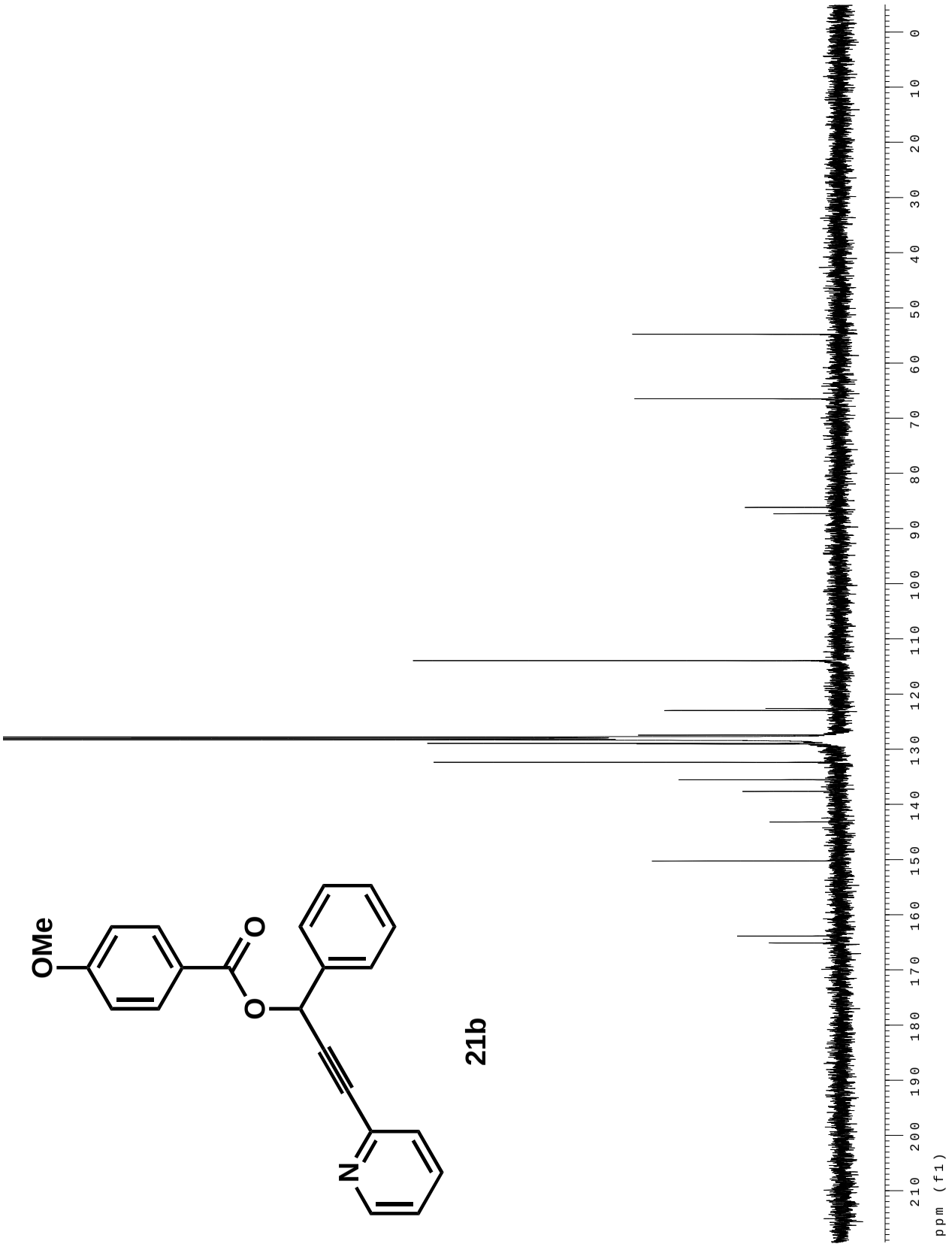

OPiv
CO2Me
N
Table 2, entry 12d
9.35
3.07
1.00
1.05
0.97
1.04
2.02
2.03
1.00
ppm (t1)

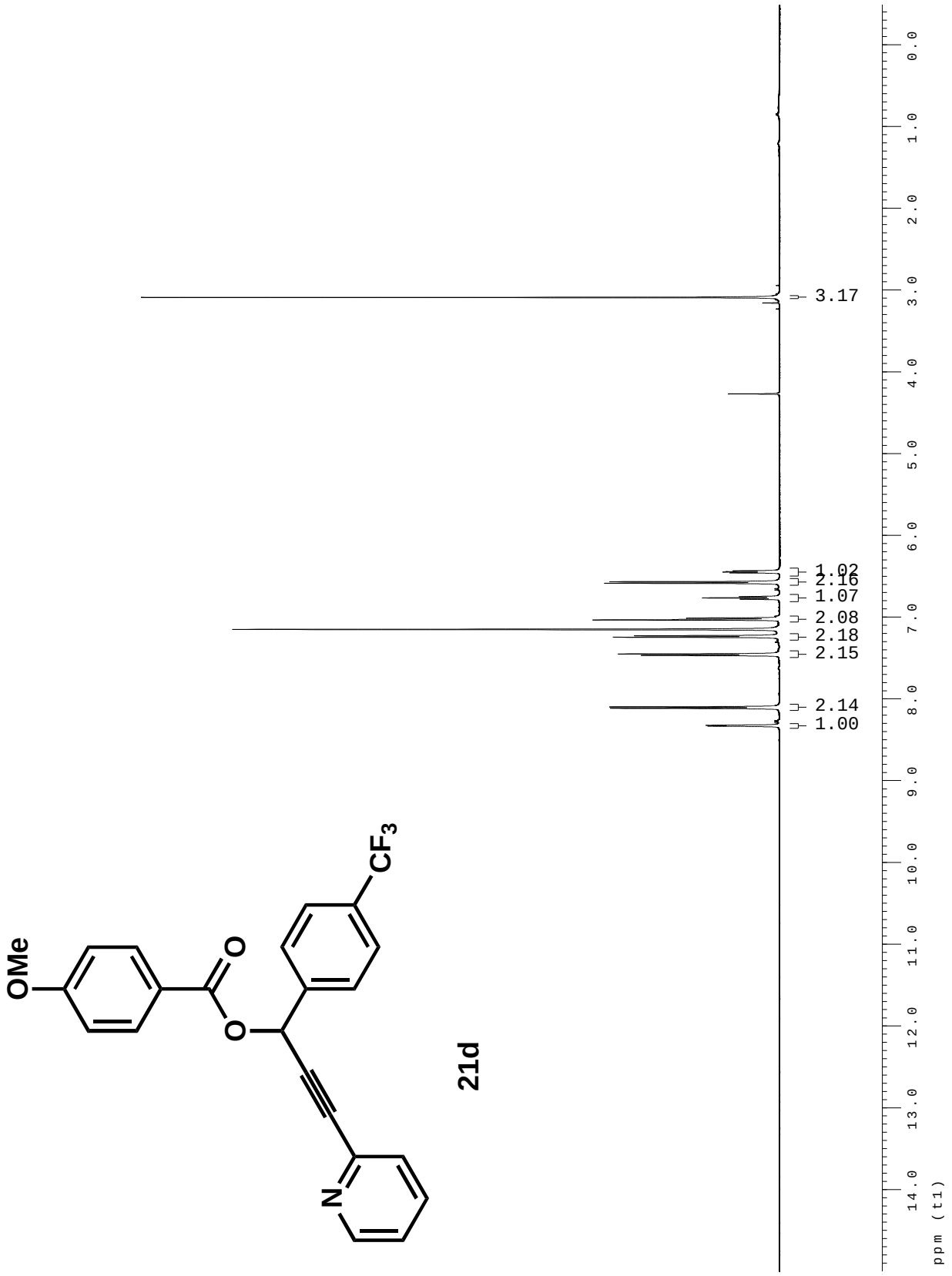

OPiv
CO2Me
N
Table 2, entry 12d
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm (t1)

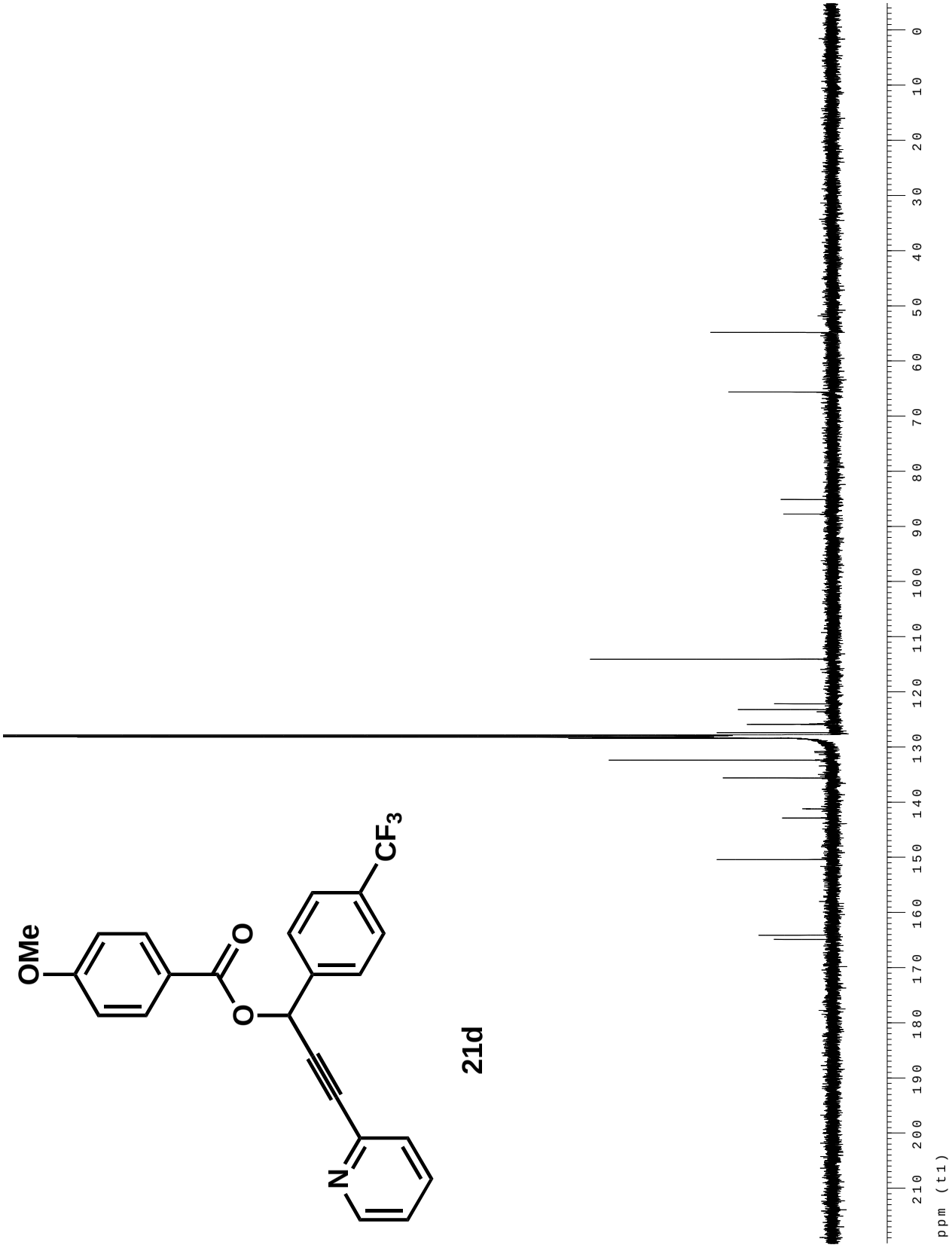

OPiv
CN
N
Table 2, entry 12e
9.23
1.01
0.95
1.06
2.04
1.06
5.21
1.00
14.0
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

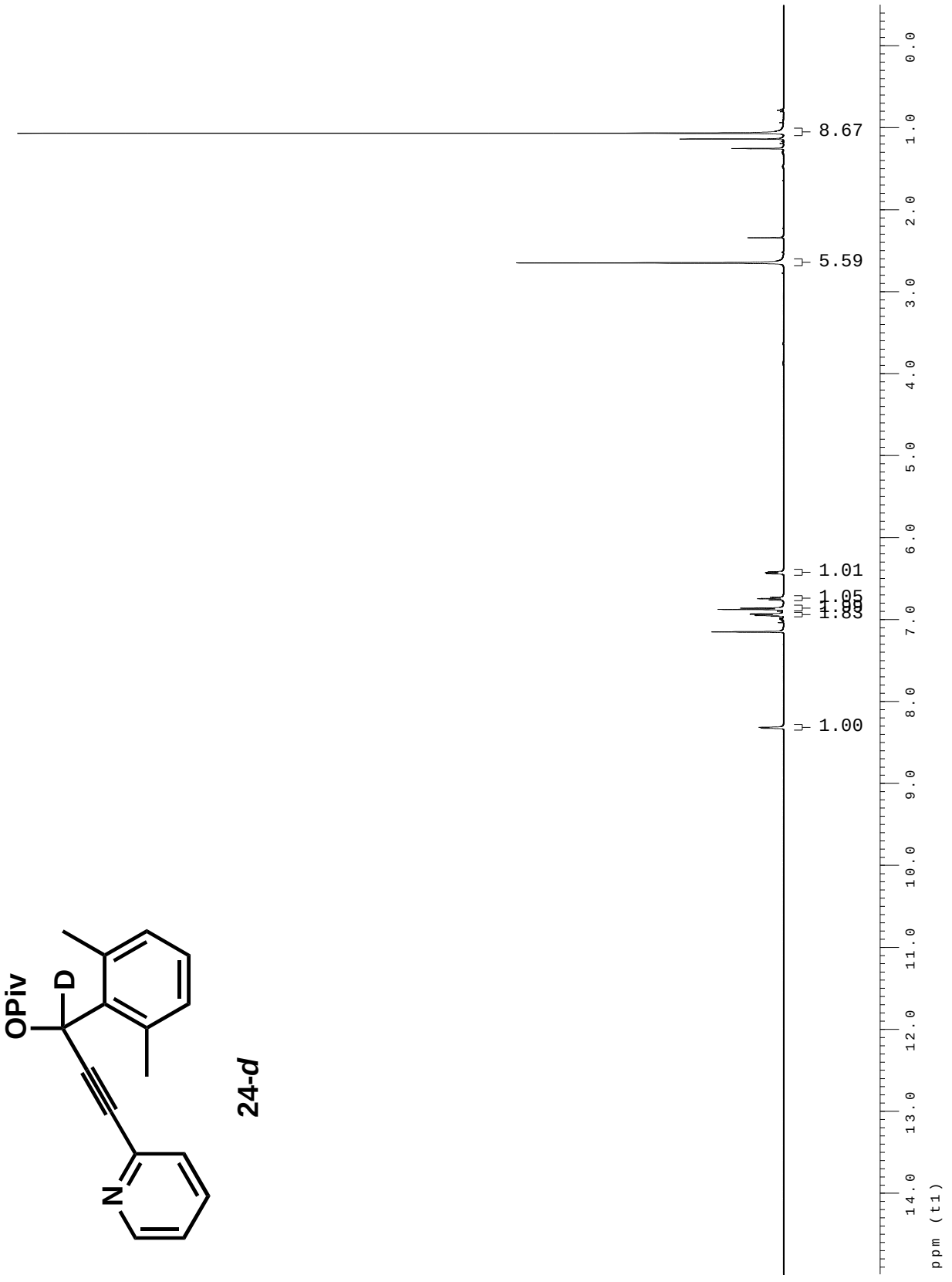

OPiv
CN
N
Table 2, entry 12e
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm (t1)


2.80
0.98
1.89
1.01
0.94
2.97
0.93
1.86
1.87
1.00
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
13.0
14.0
ppm (t1)
OMe
O
O
N
21b

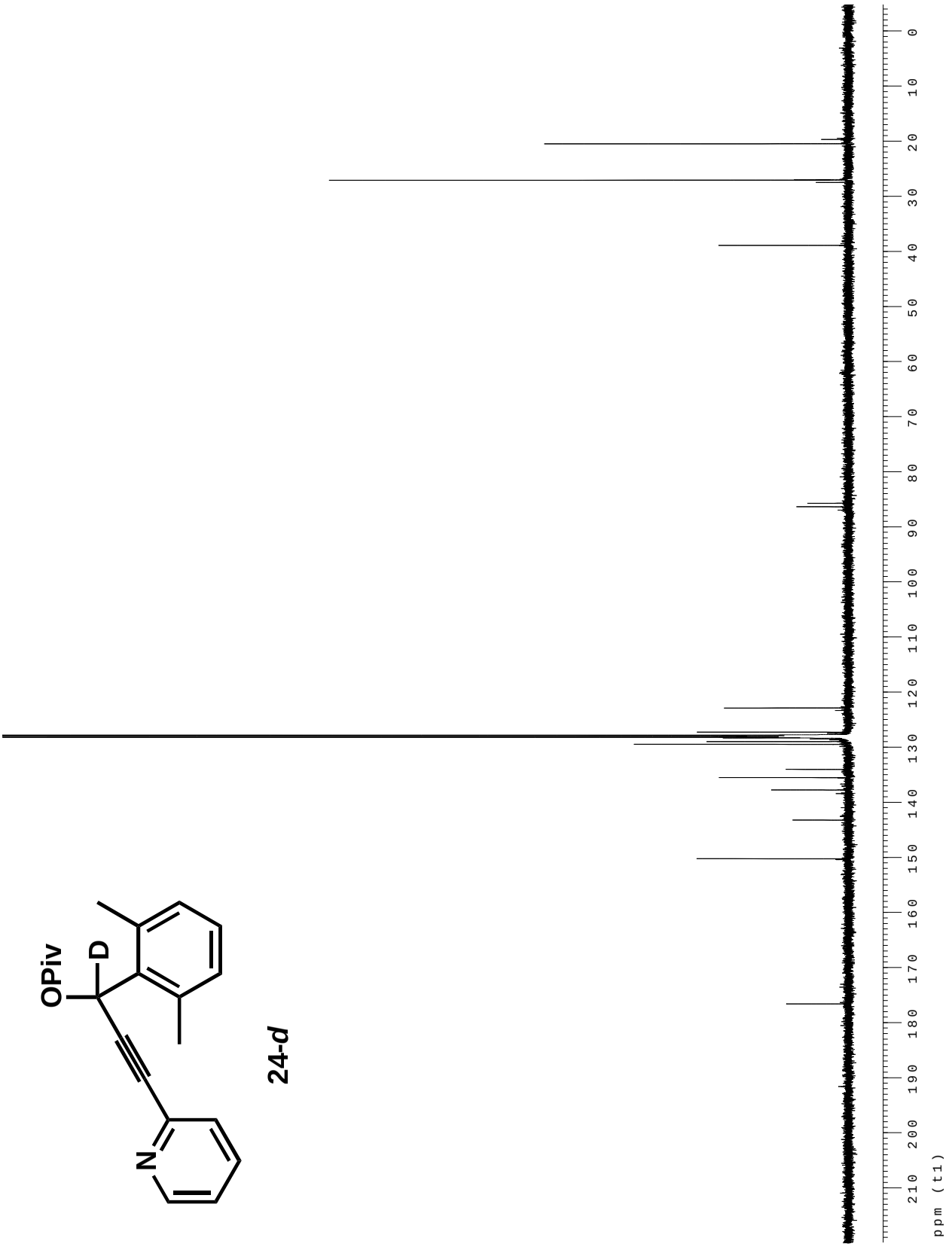

OMe
O
O
N
21b
ppm (f1)

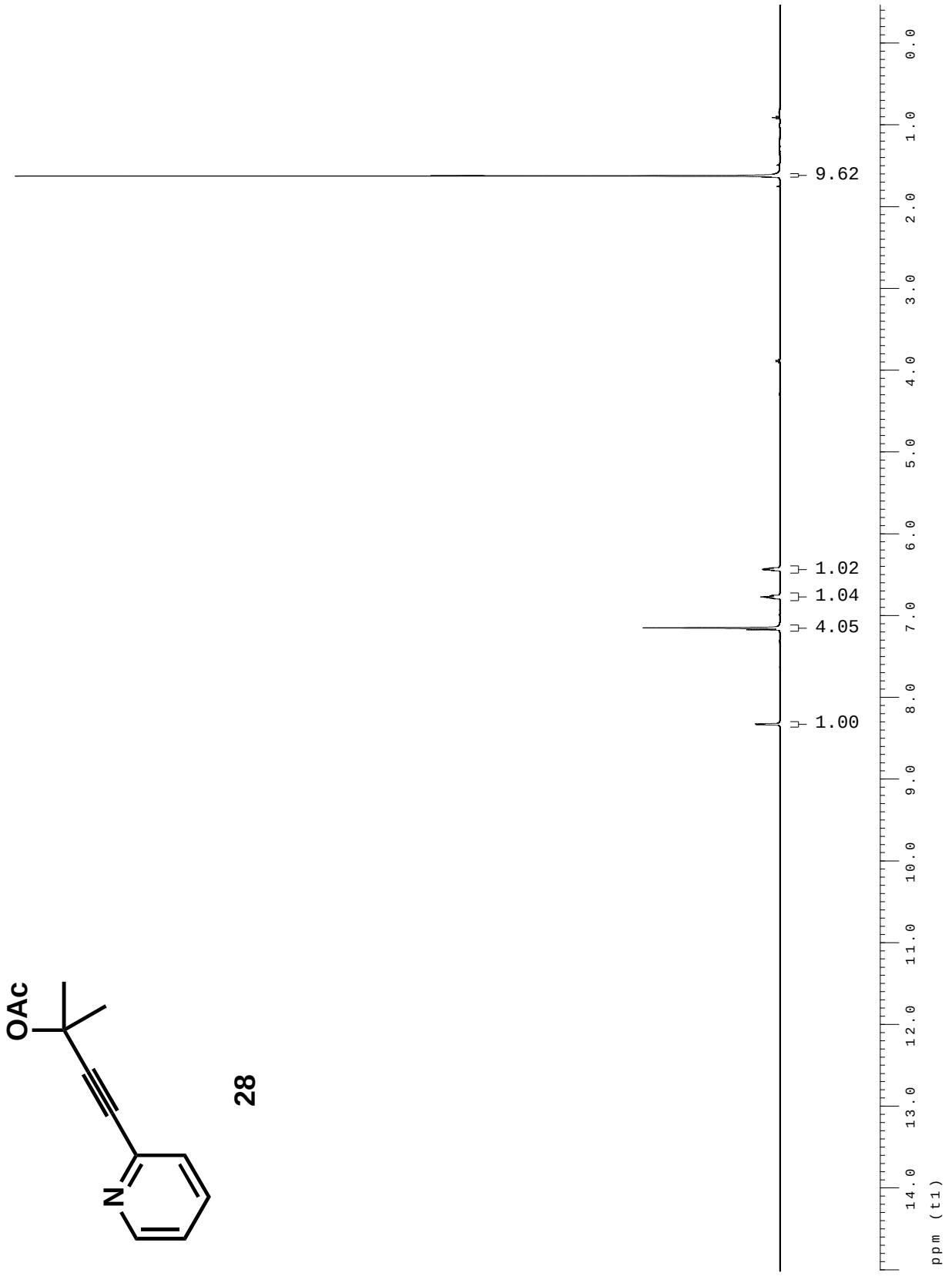

OMe
O
O
CF3
N
21d
3.17
1.02
2.16
1.07
2.08
2.18
2.15
2.14
1.00
14.0
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


OMe
O
O
CF3
N
21d
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm (t1)

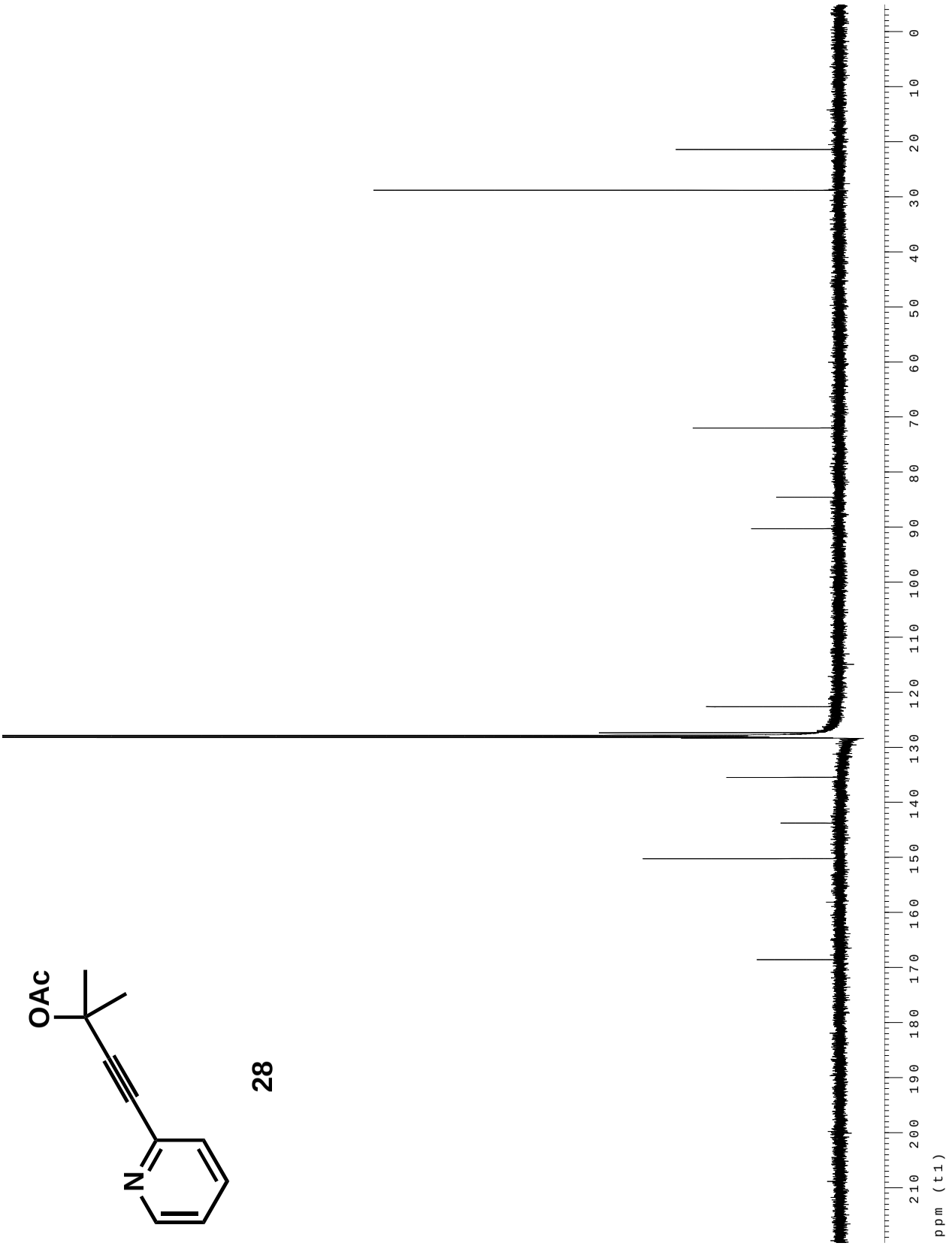


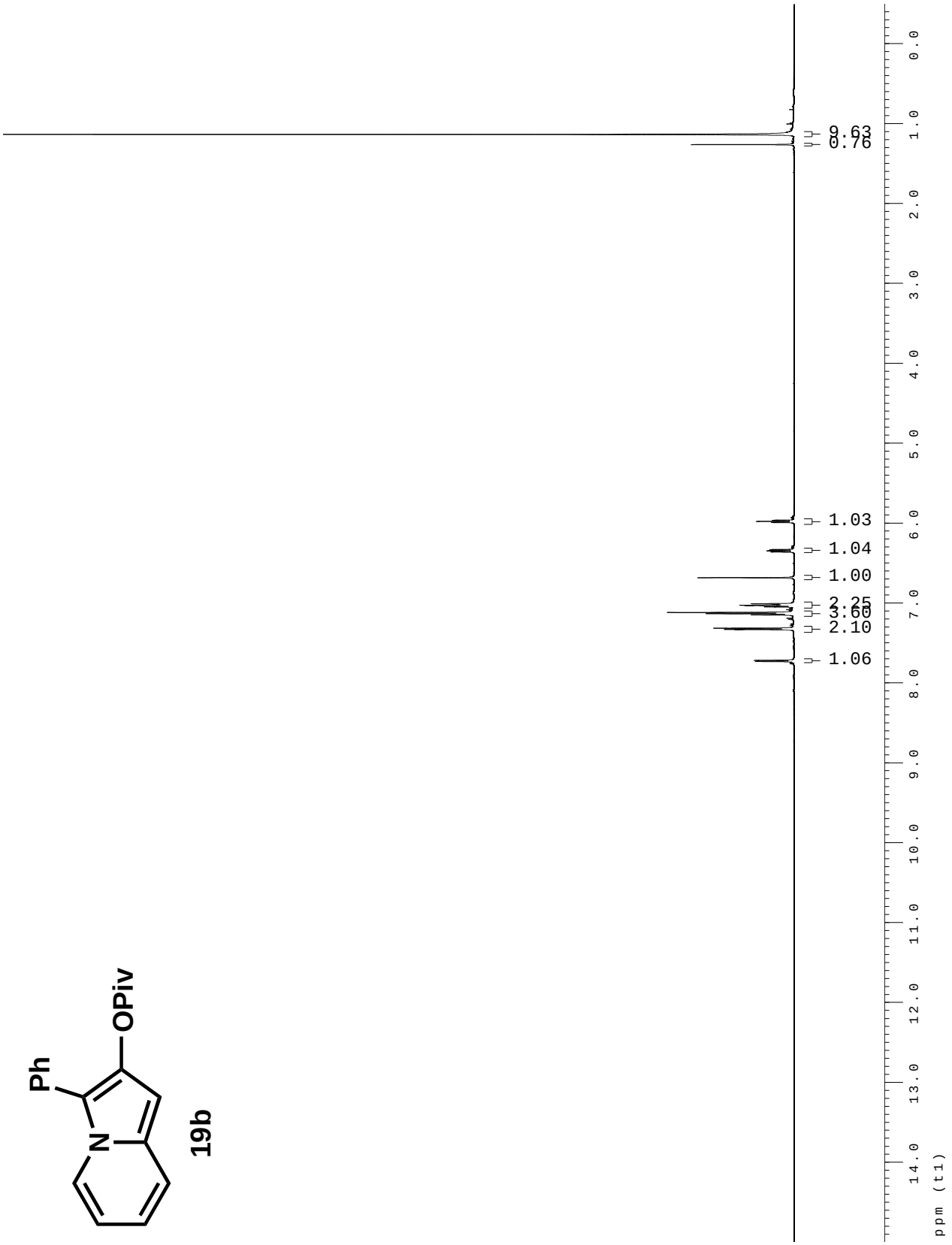
24-*d*


OPiv
D
N
24-*d*
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm (t1)


9.62
1.02
1.04
4.05
1.00
14.0
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)
OAc
N

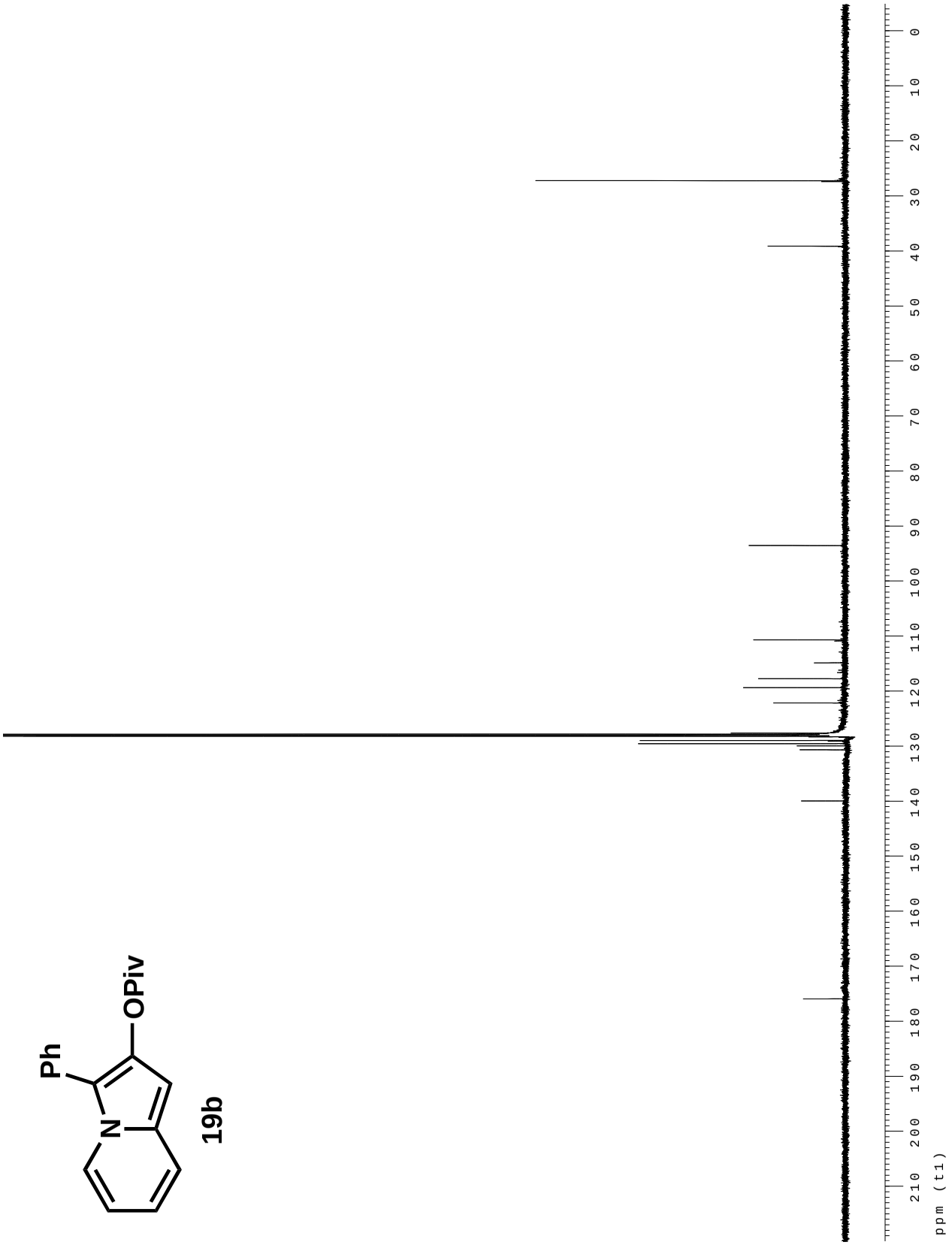
28

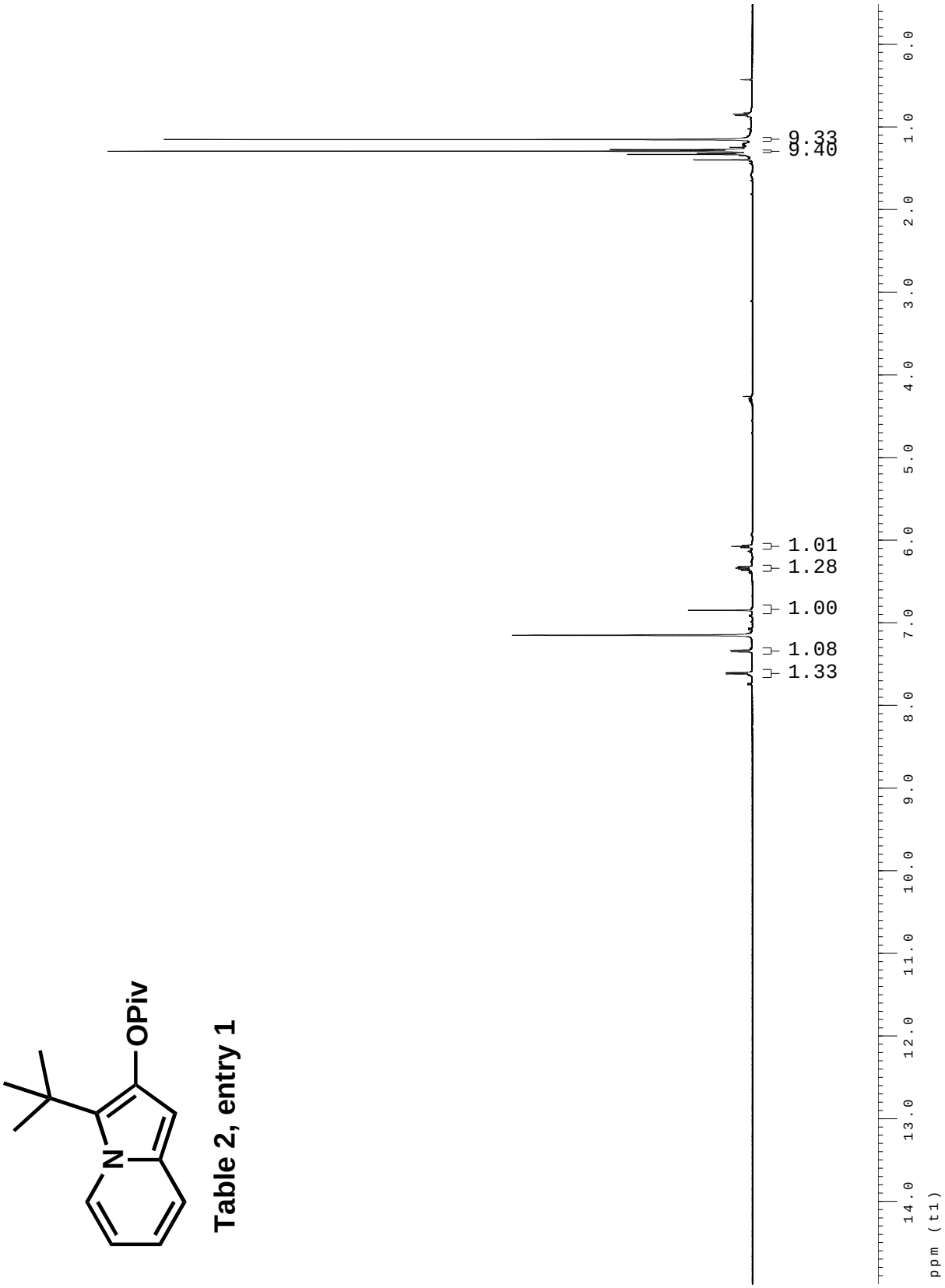

OAc
N
28
ppm (t1)

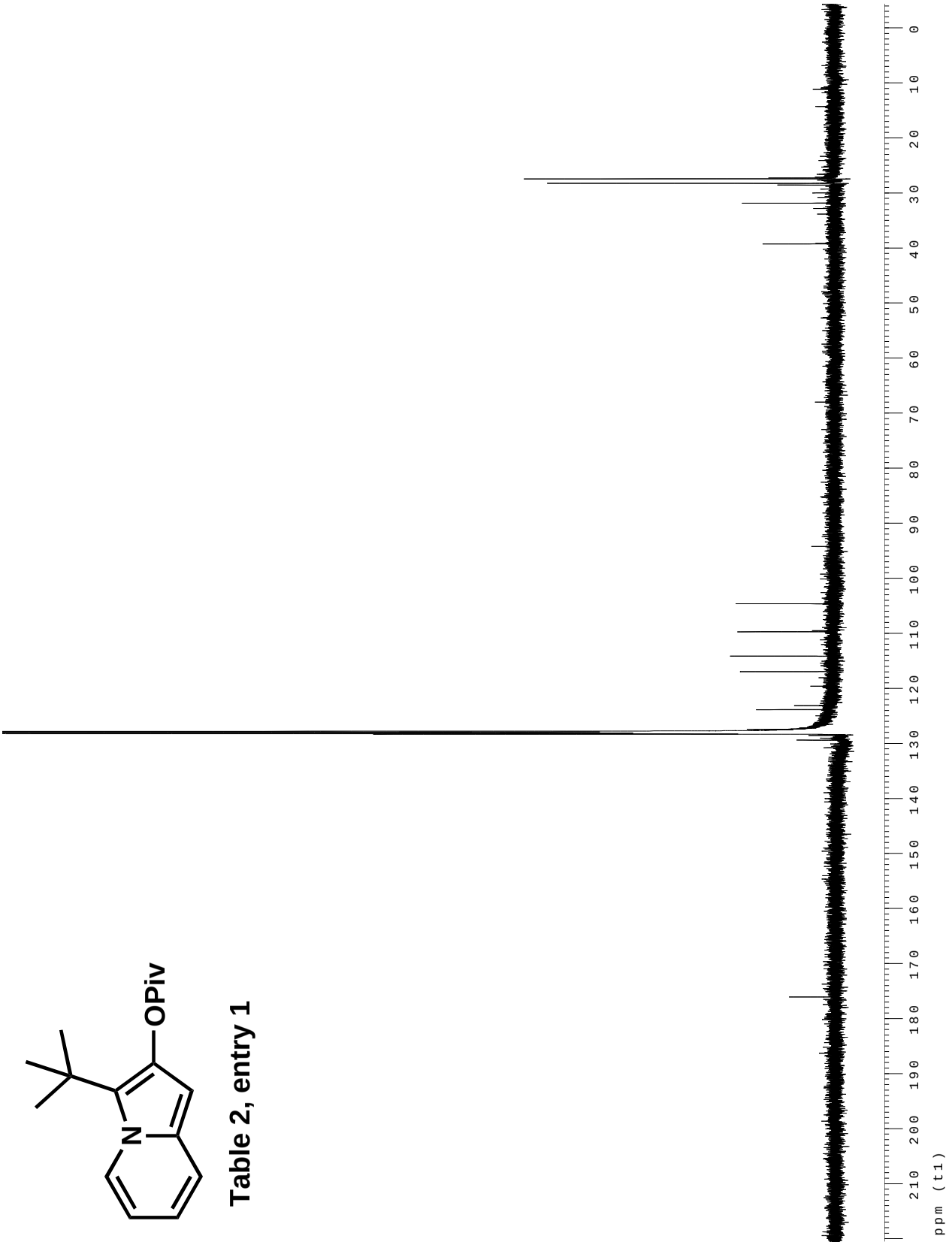

9.63
0.76
1.03
1.04
1.00
2.25
3.60
2.10
1.06
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
13.0
14.0
ppm (t1)

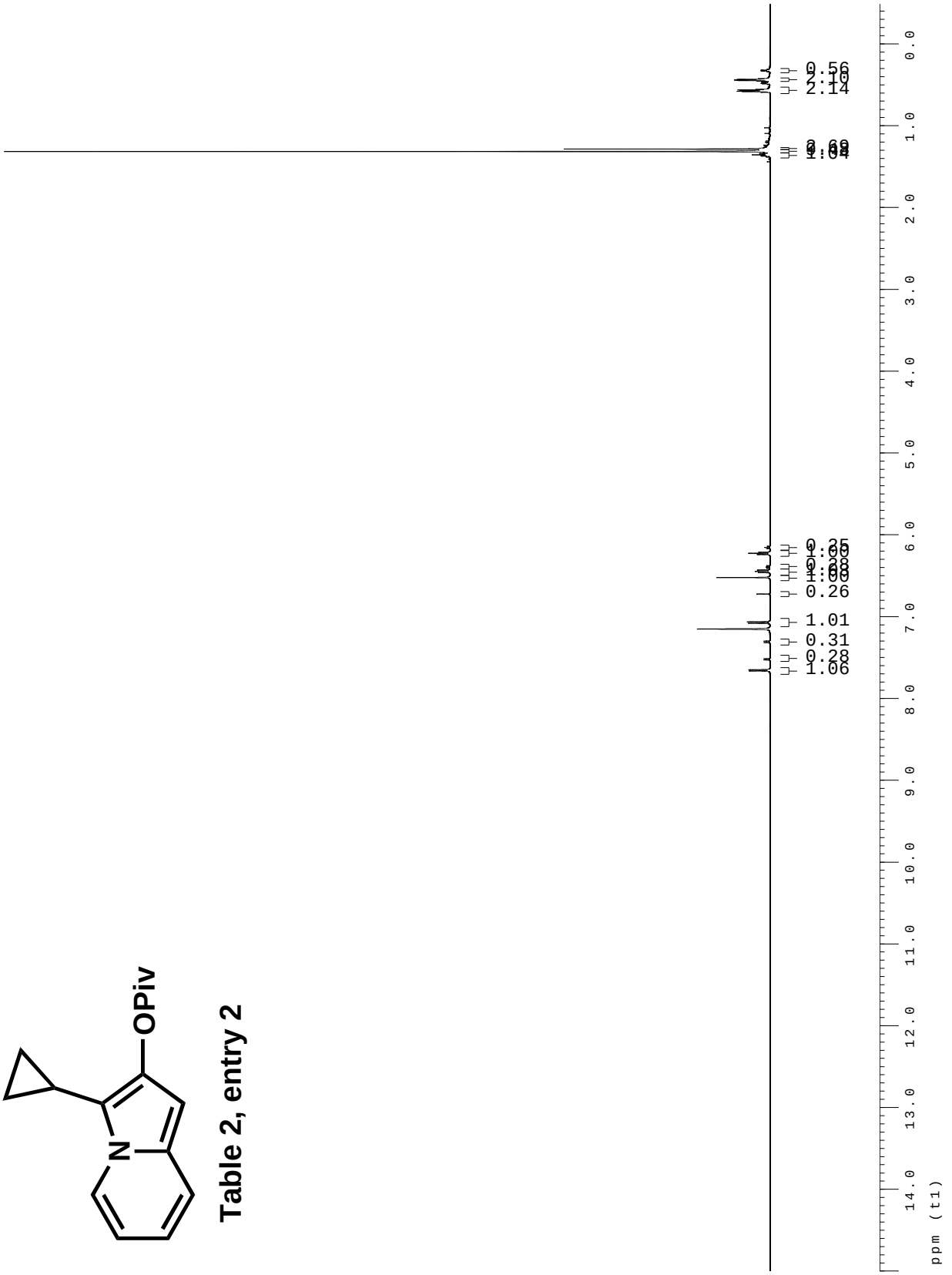
Ph
OPiv
N

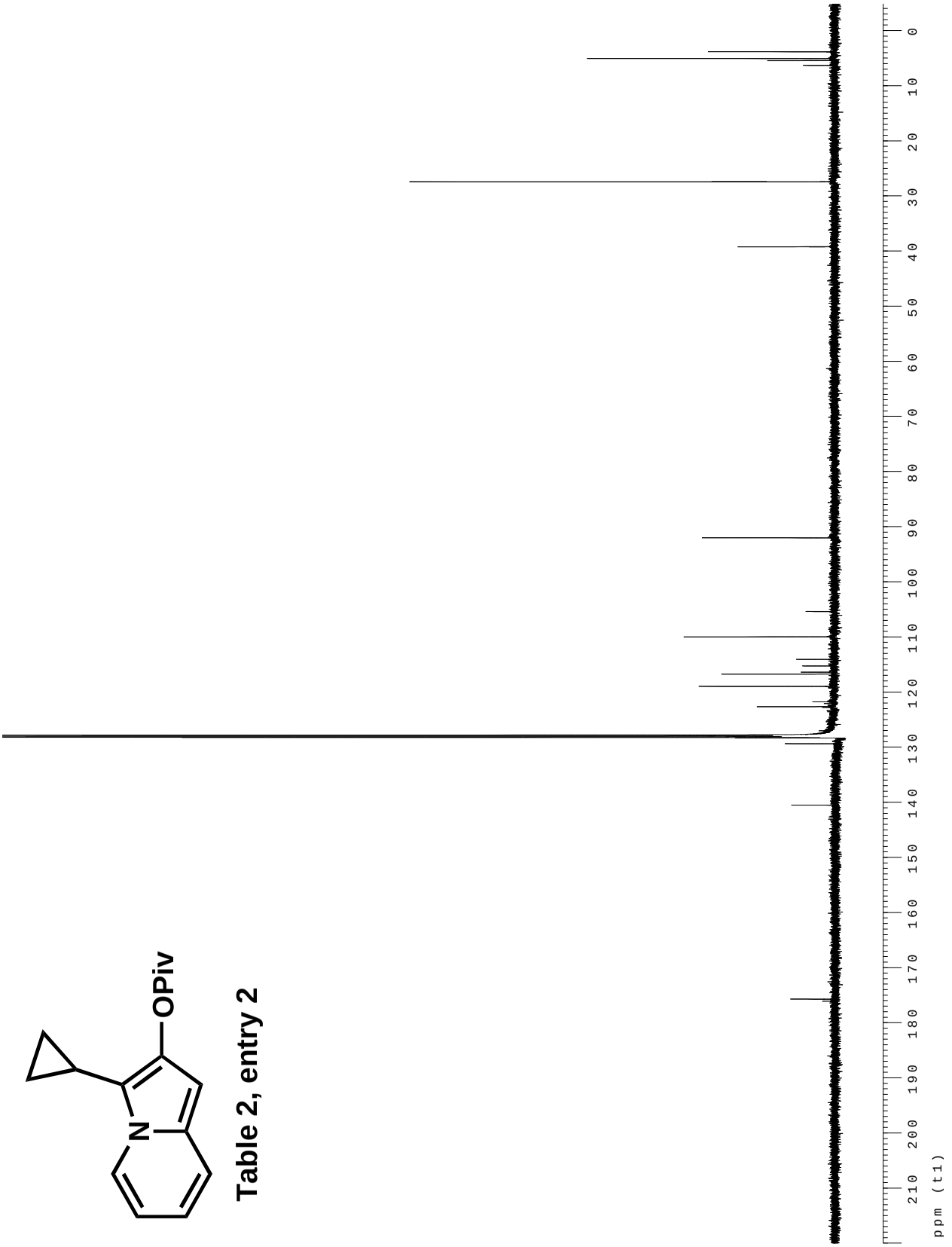
19b


Ph
OPiv
N
19b
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
ppm (t1)


OPiv
N
Table 2, entry 1
9.33
9.40
1.01
1.28
1.00
1.08
1.33
14.0
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


OPiv
N
Table 2, entry 1
ppm (t1)


OPiv
N
Table 2, entry 2
0.56
2.10
2.14
1.04
0.25
1.00
0.28
1.00
0.26
1.01
0.31
0.28
1.06
14.0
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


OPiv
N
Table 2, entry 2
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
ppm (t1)

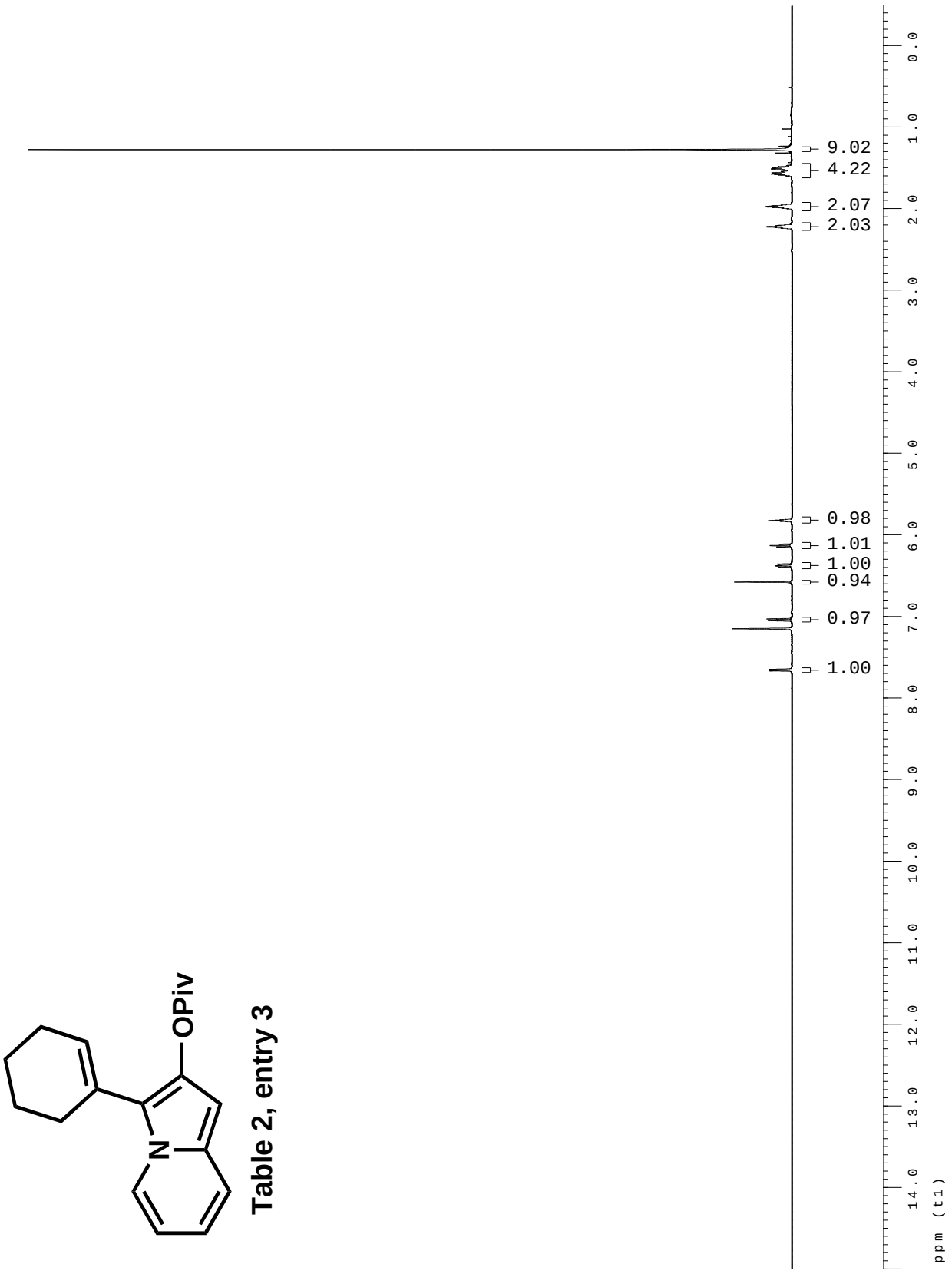
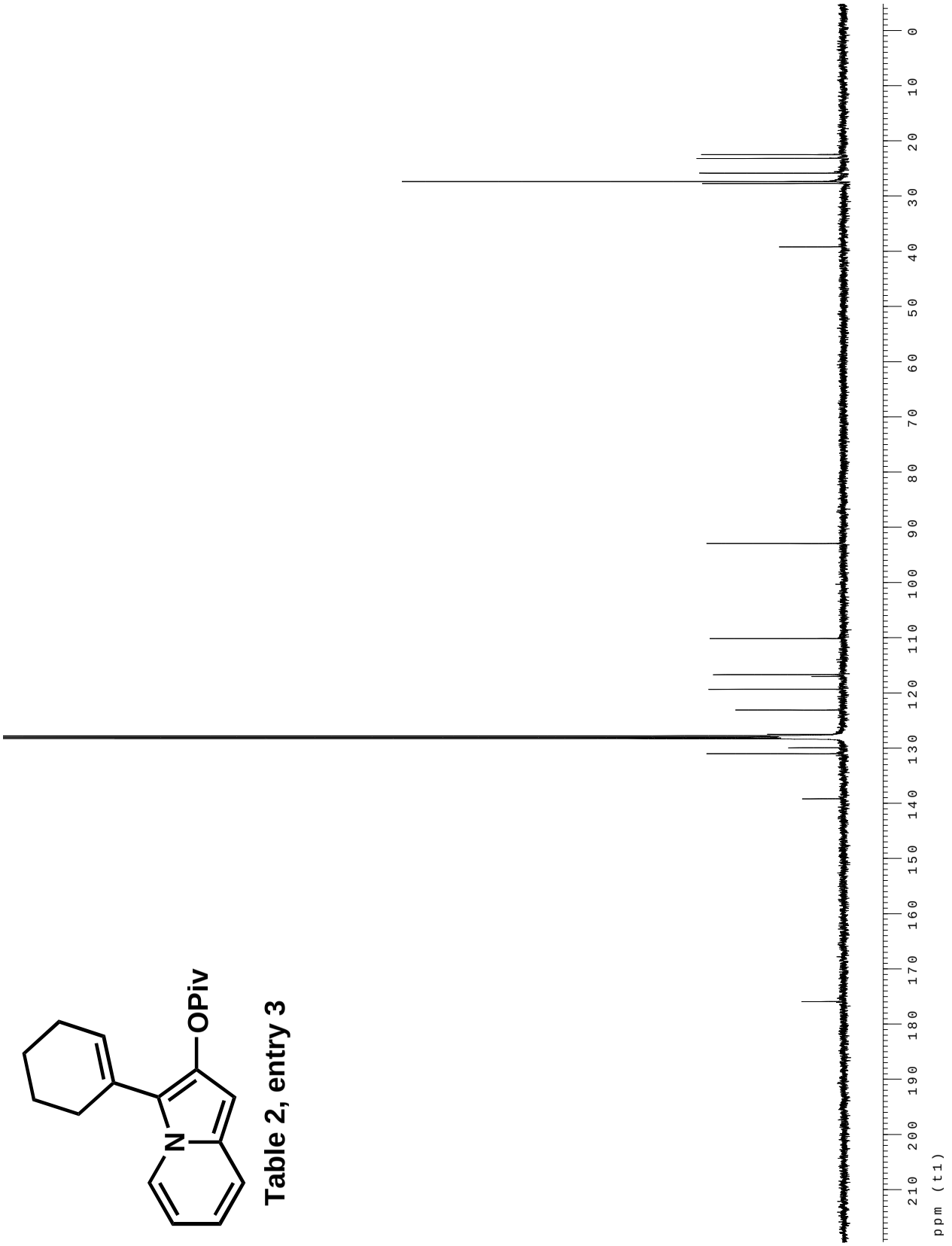


Table 2, entry 3


OPiv
N
Table 2, entry 3
ppm (t1)

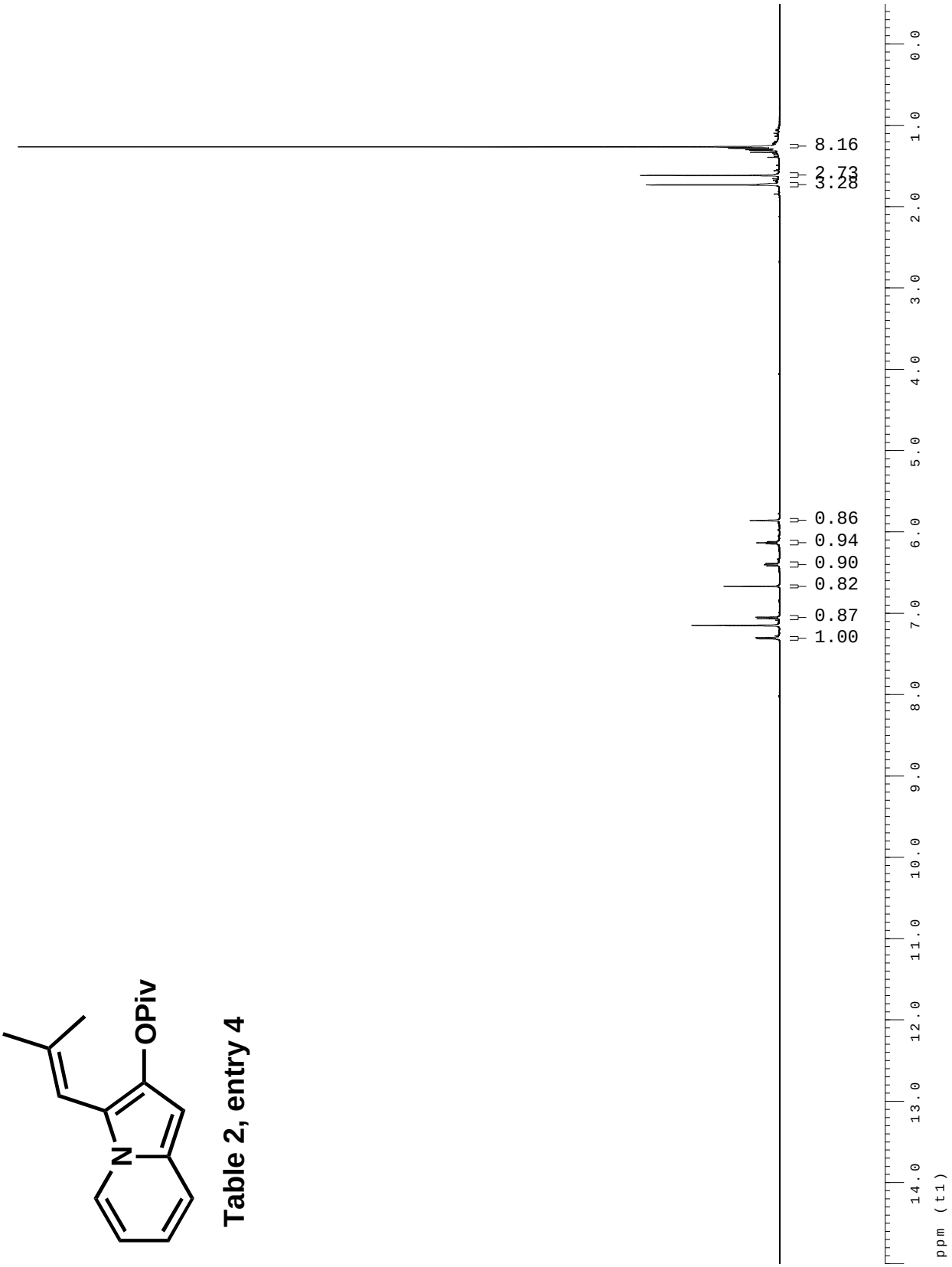
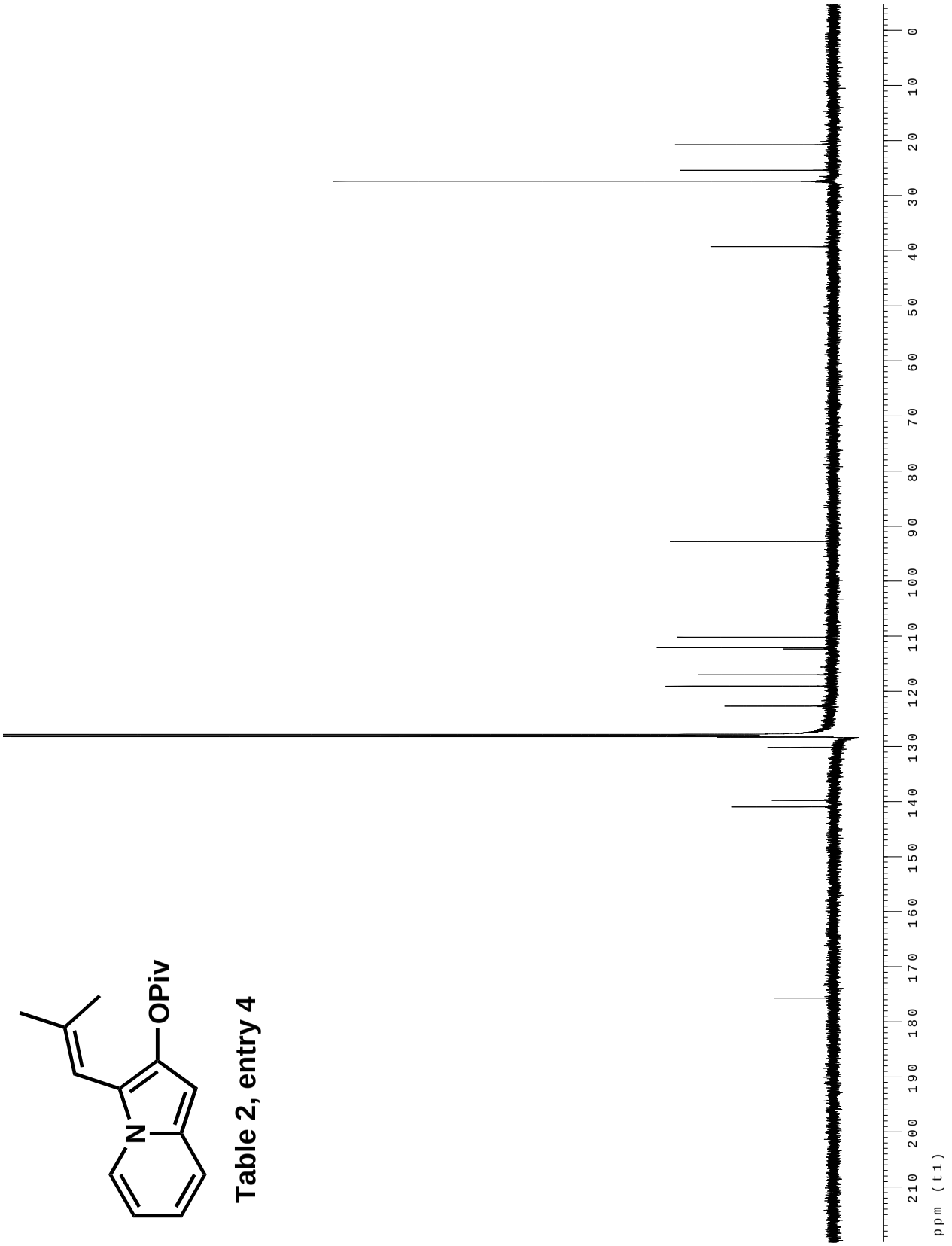
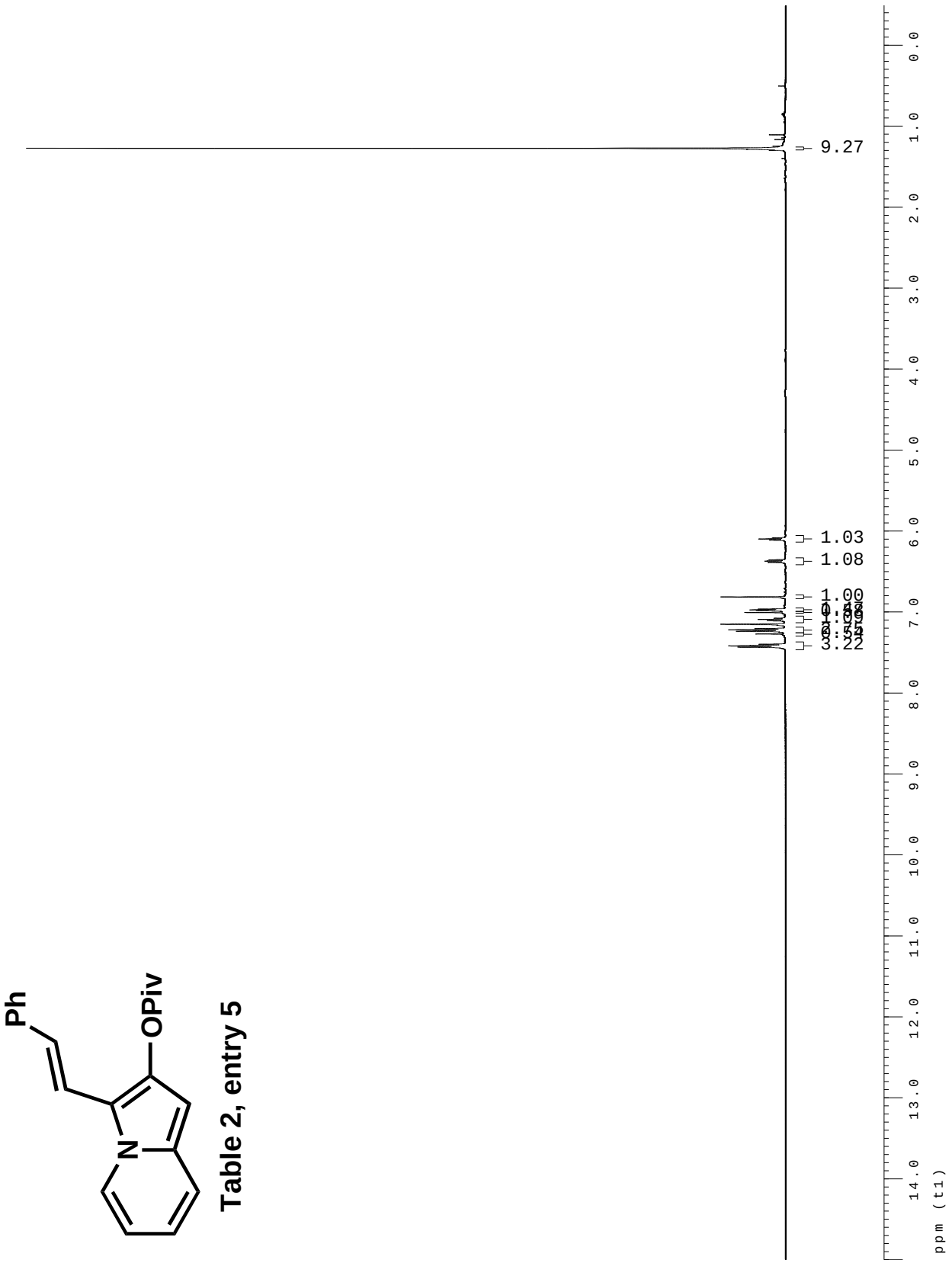
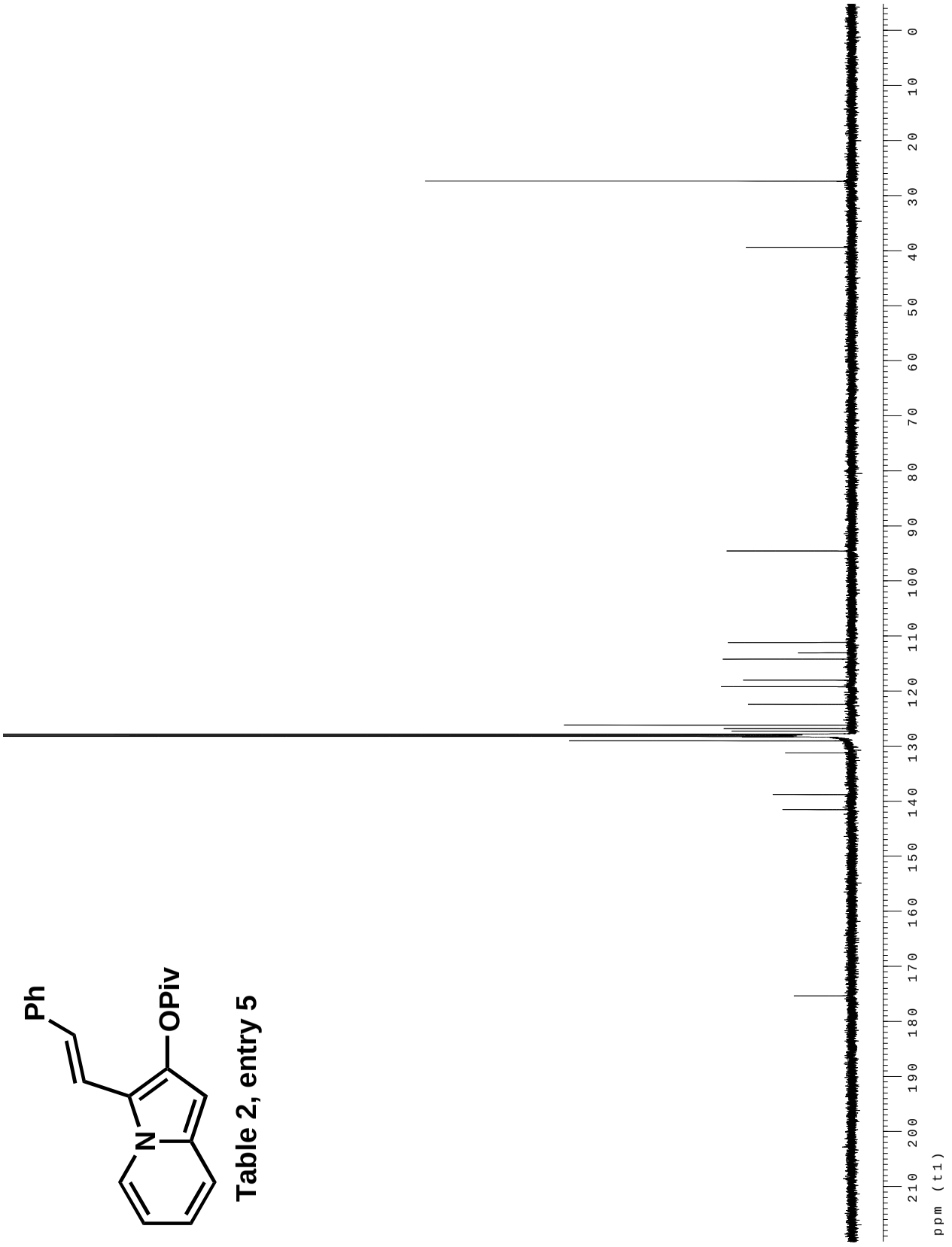


Table 2, entry 4


OPiv
N
Table 2, entry 4
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
ppm (t1)


Ph
OPiv
N
Table 2, entry 5
9.27
1.03
1.08
1.00
3.22
ppm (t1)


Ph
OPiv
N
Table 2, entry 5
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm (t1)

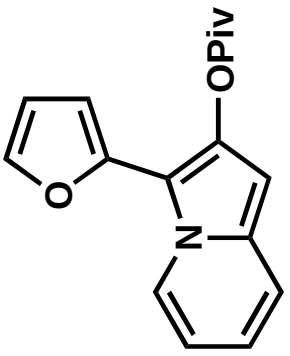
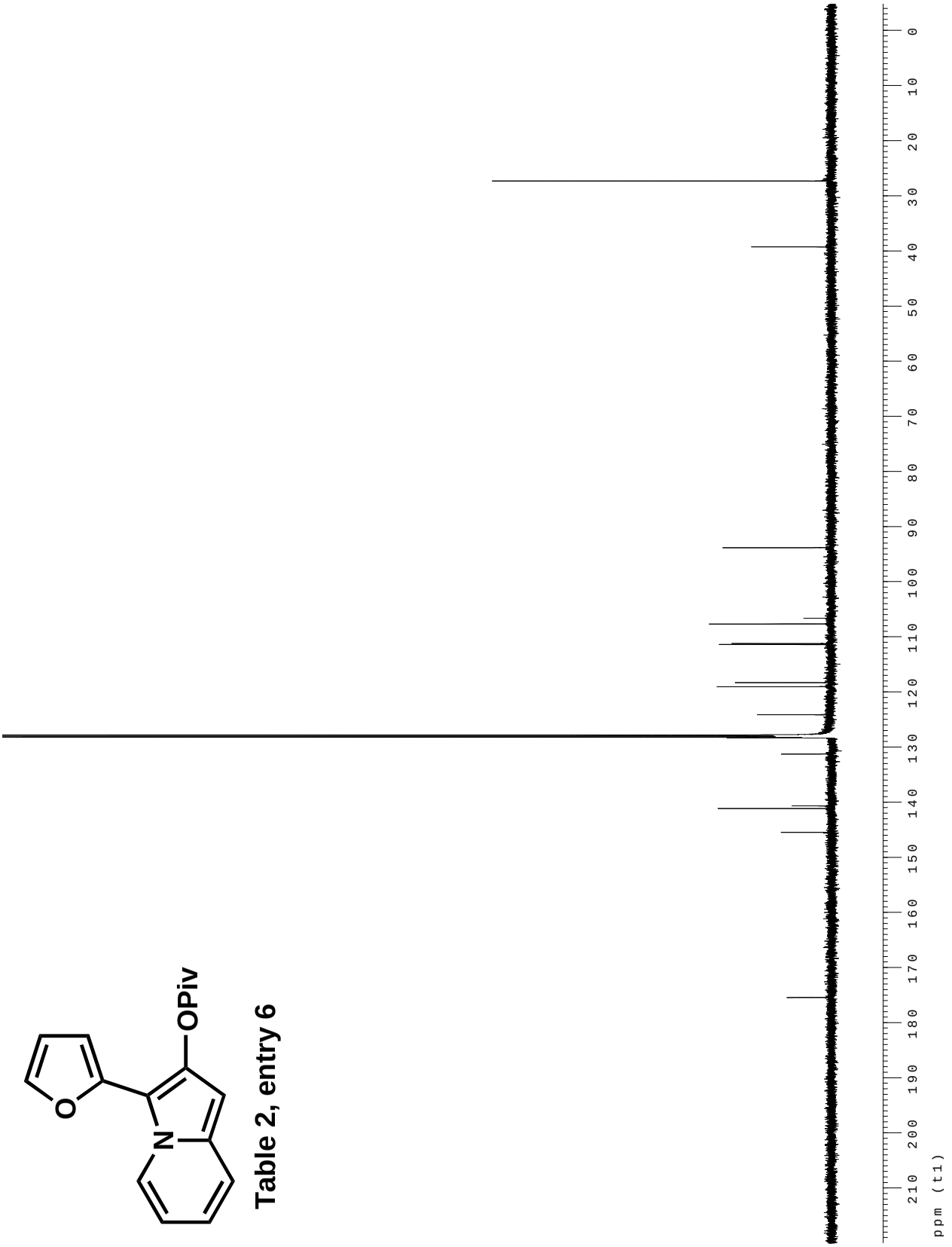


Table 2, entry 6


OPiv
O
N
Table 2, entry 6
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm (t1)

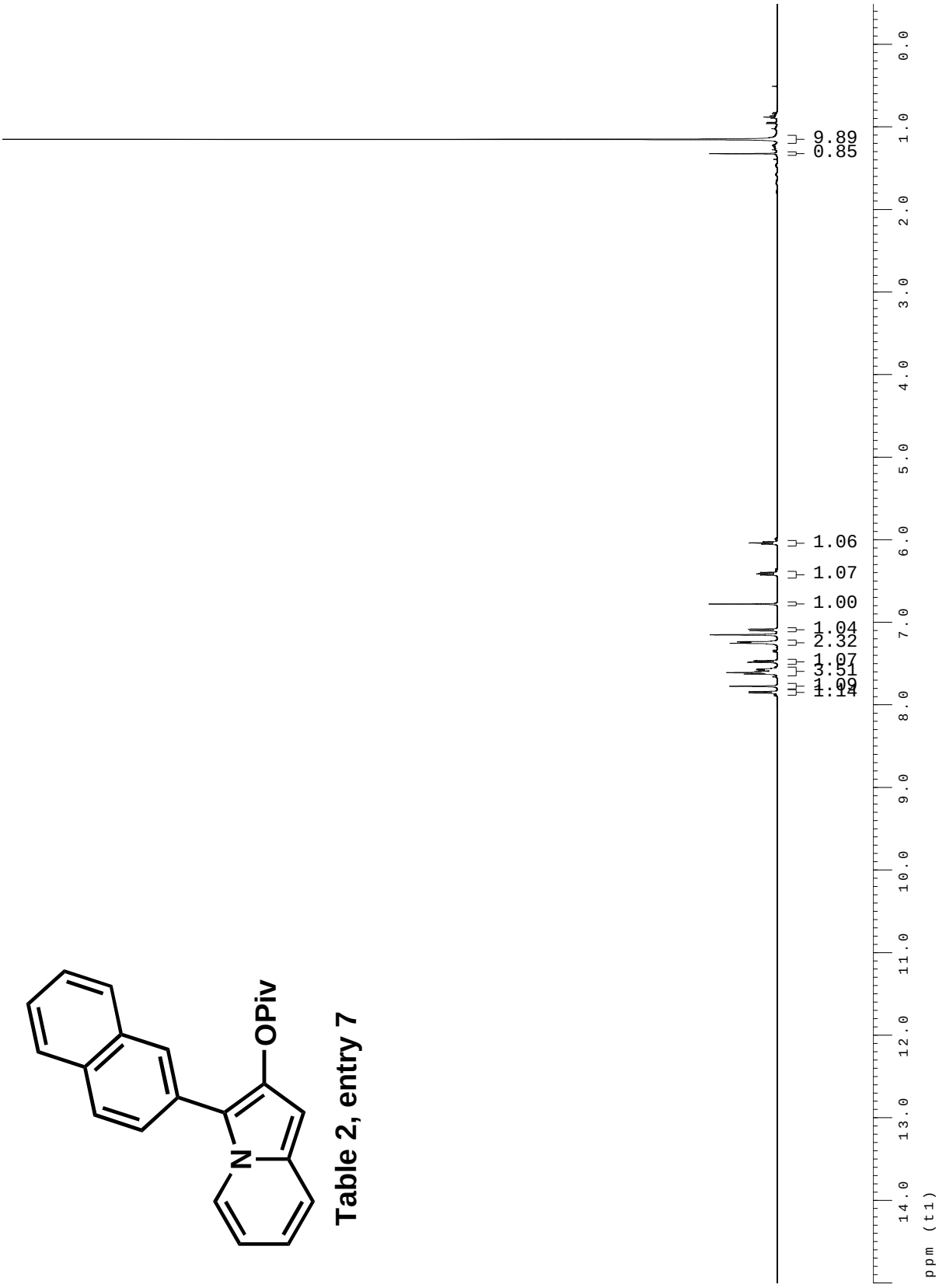
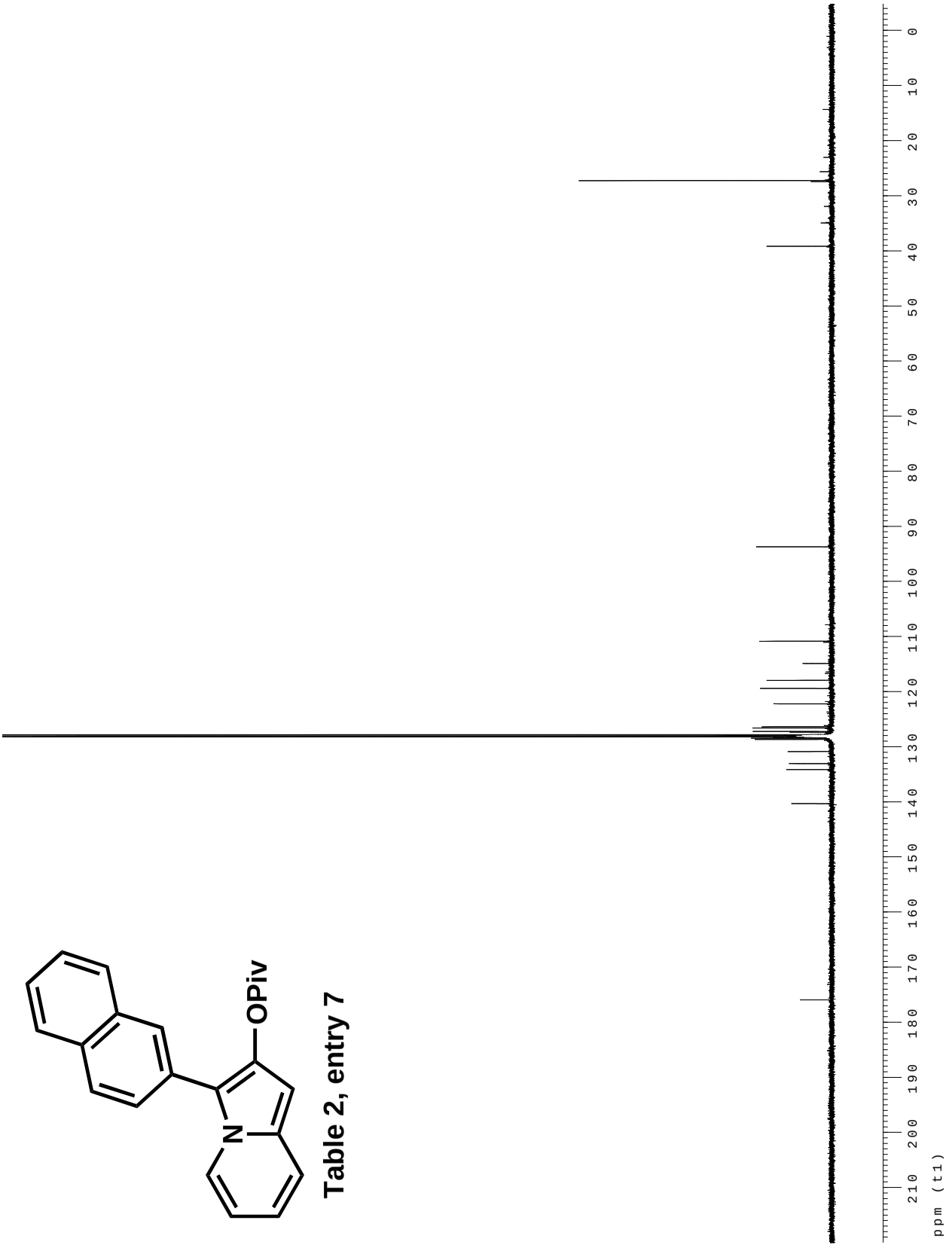


Table 2, entry 7


OPiv
N
Table 2, entry 7
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm (t1)

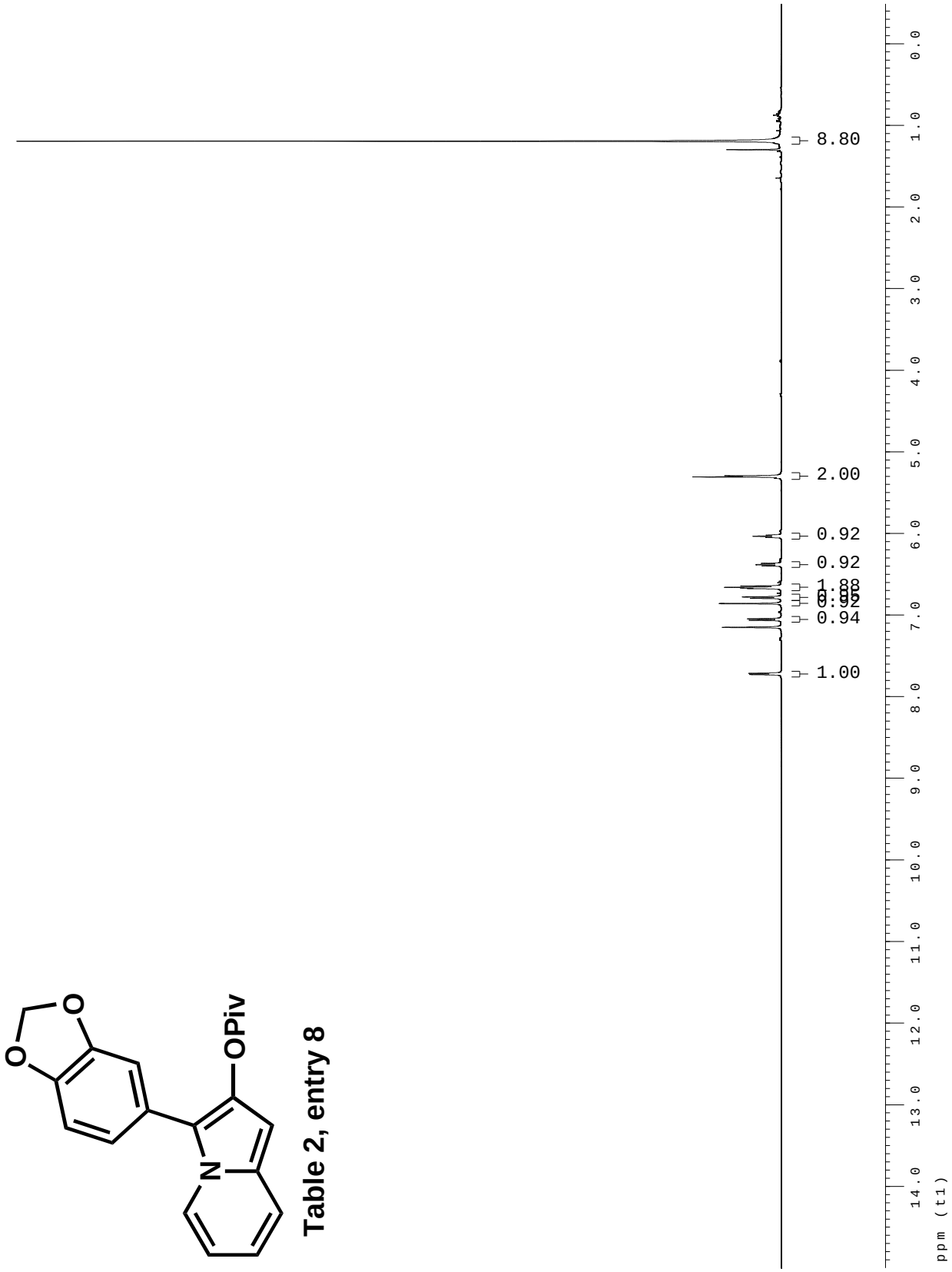
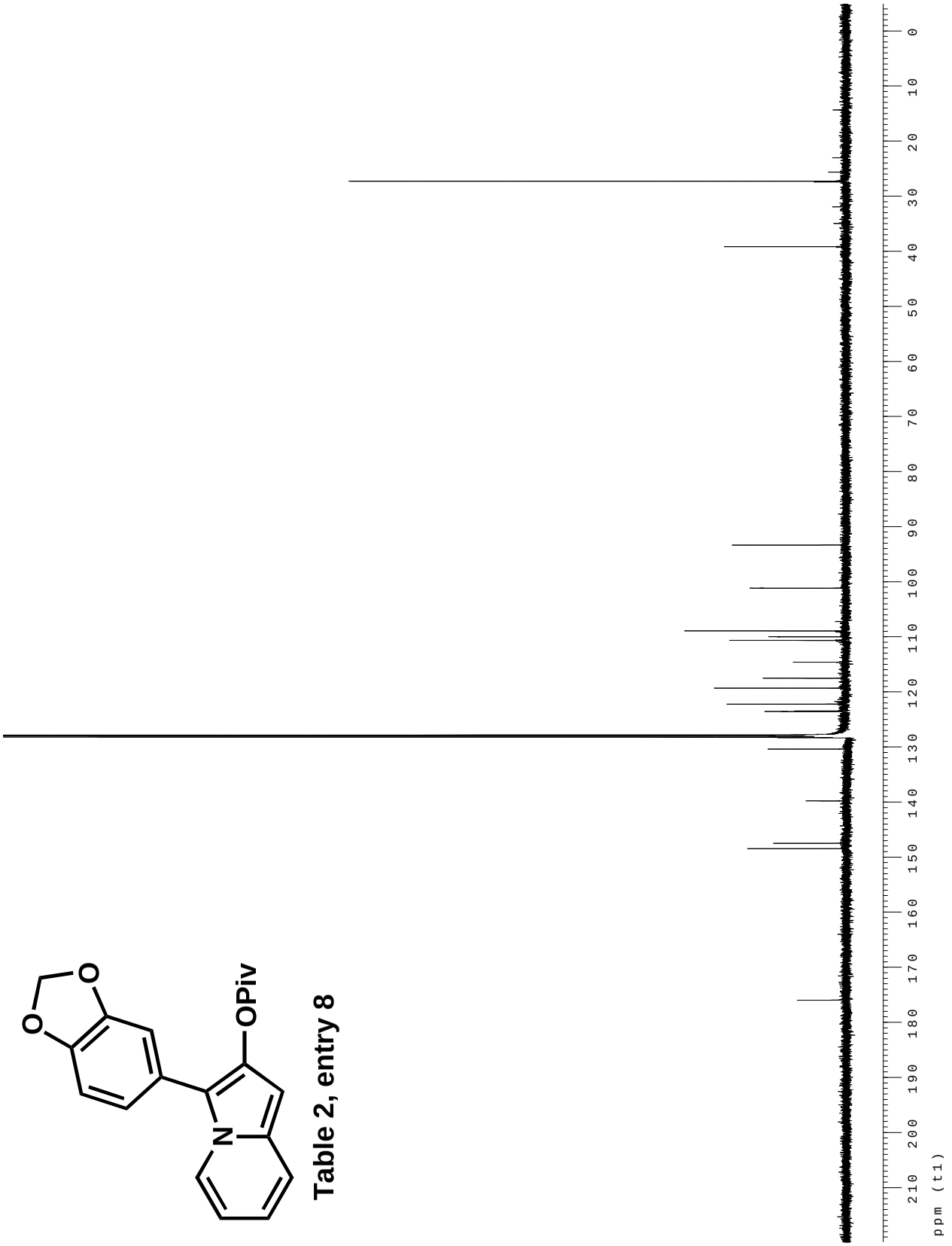


Table 2, entry 8


O
O
OPiv
N
Table 2, entry 8
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm (t1)

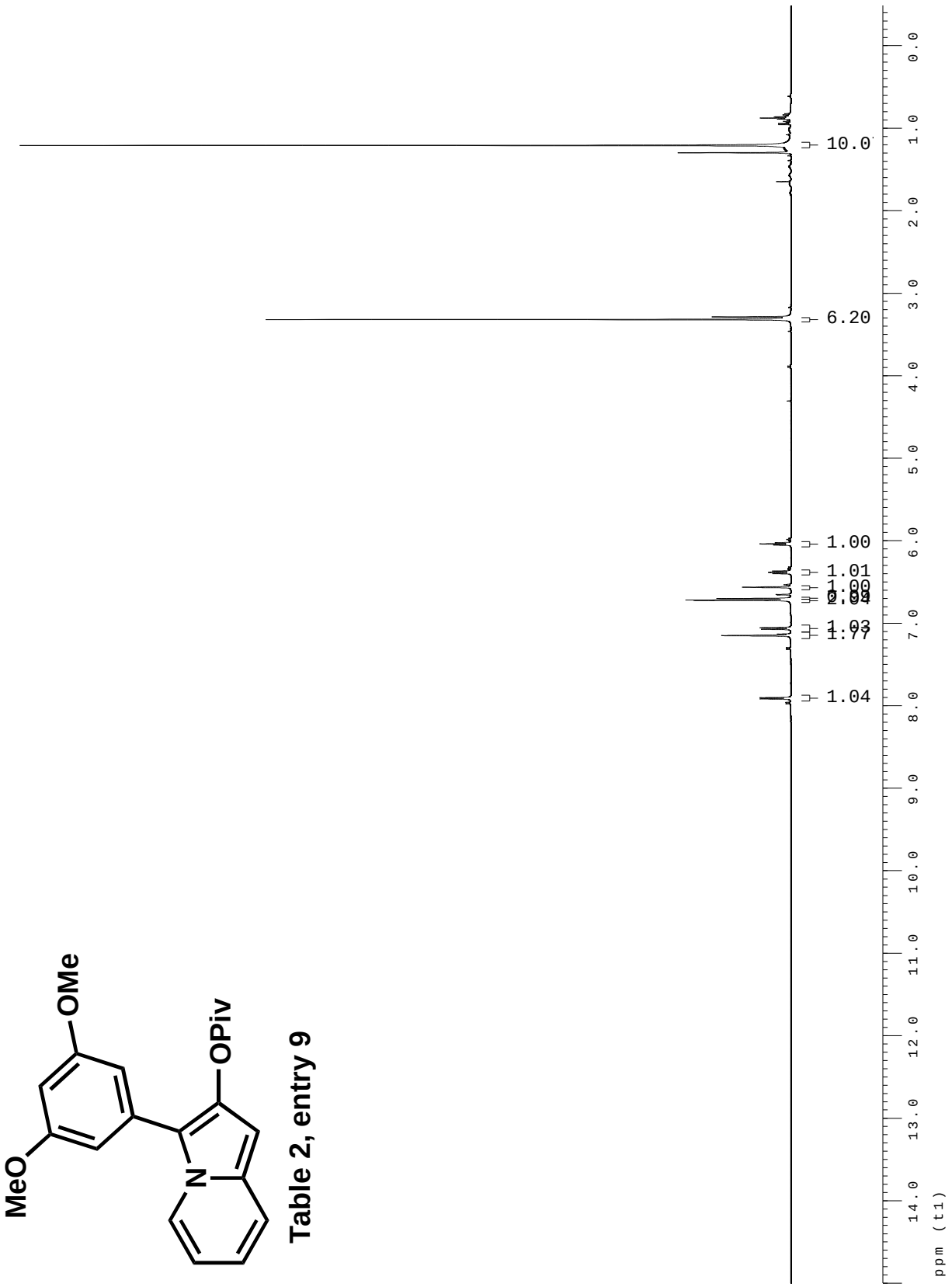
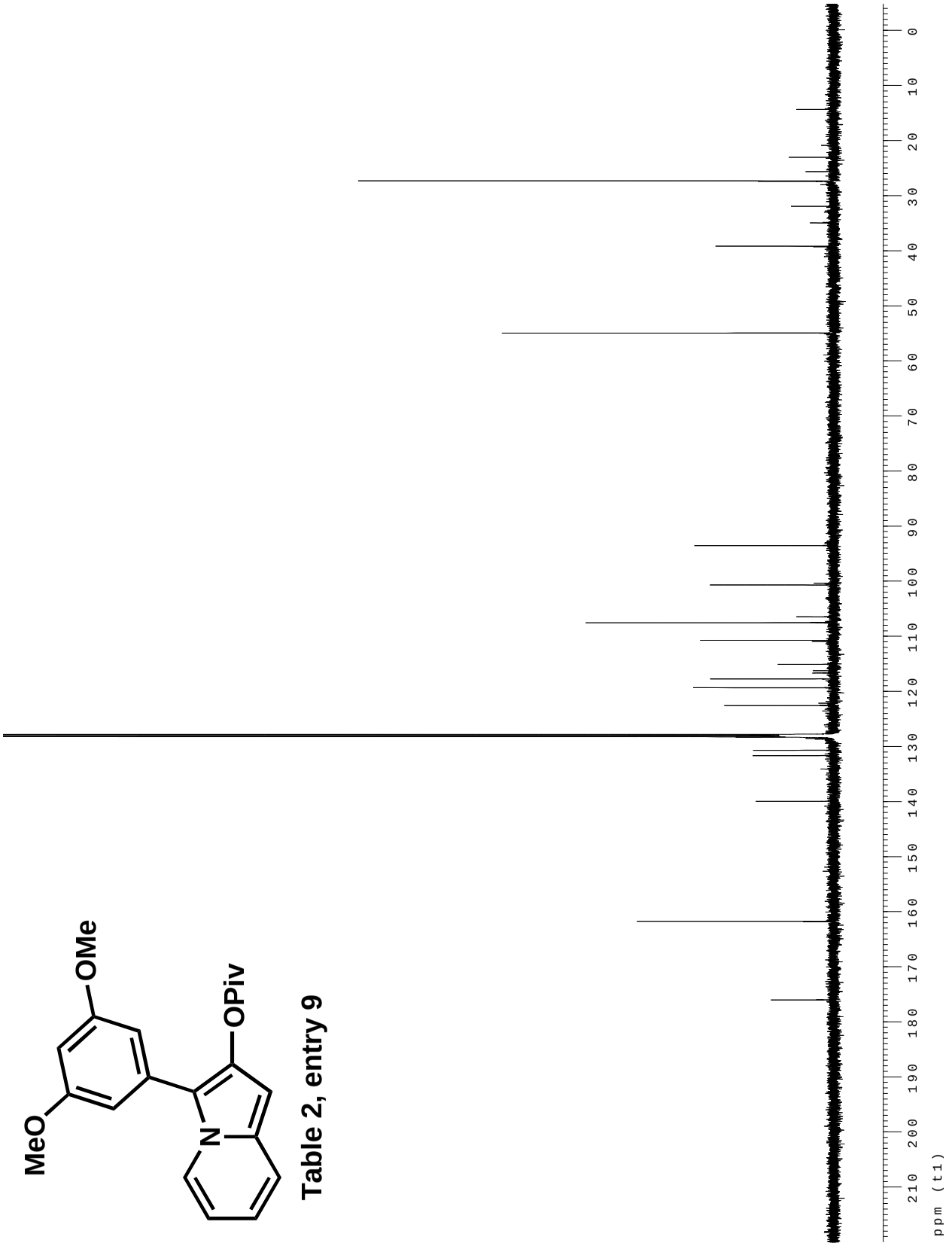
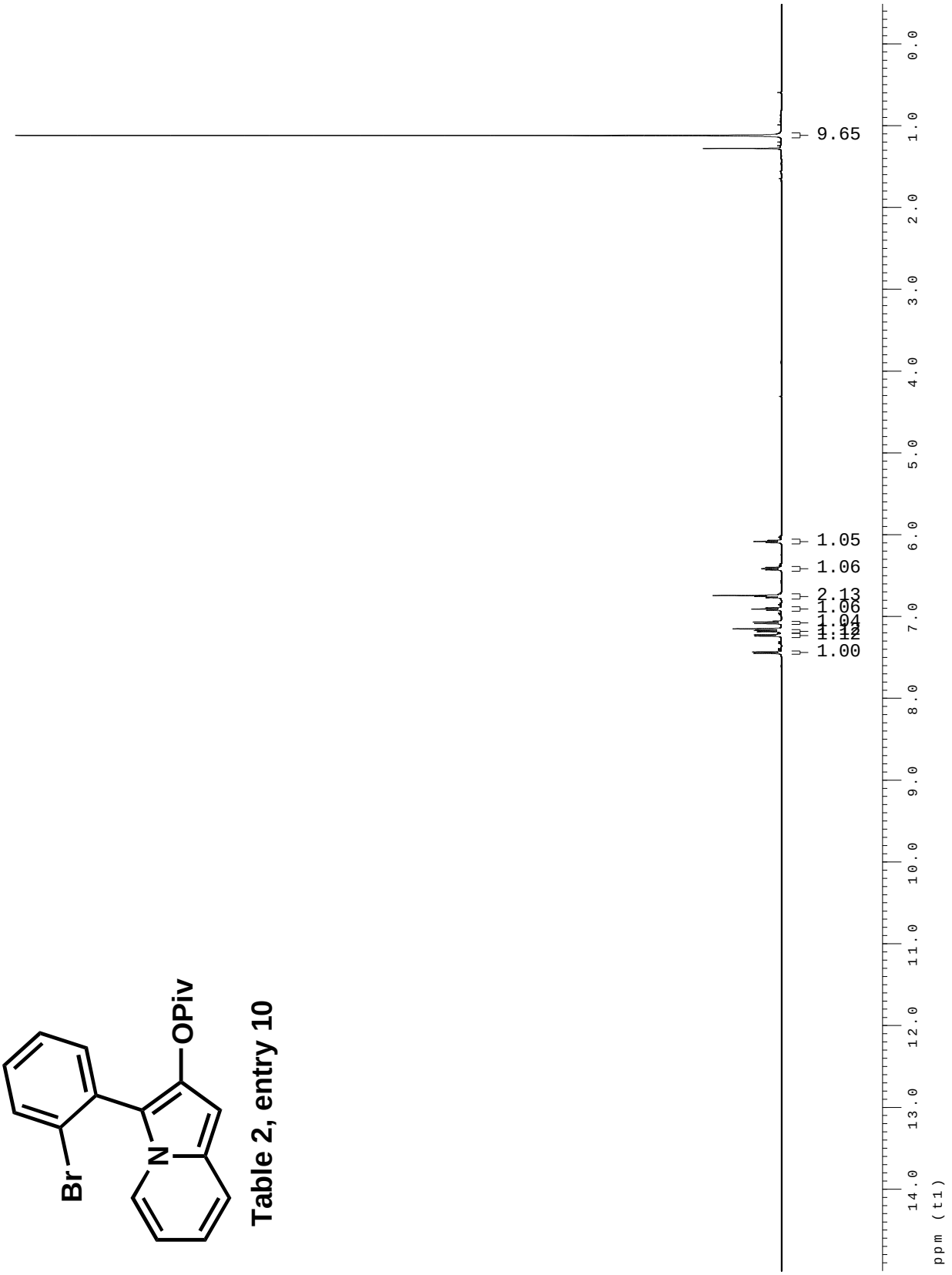
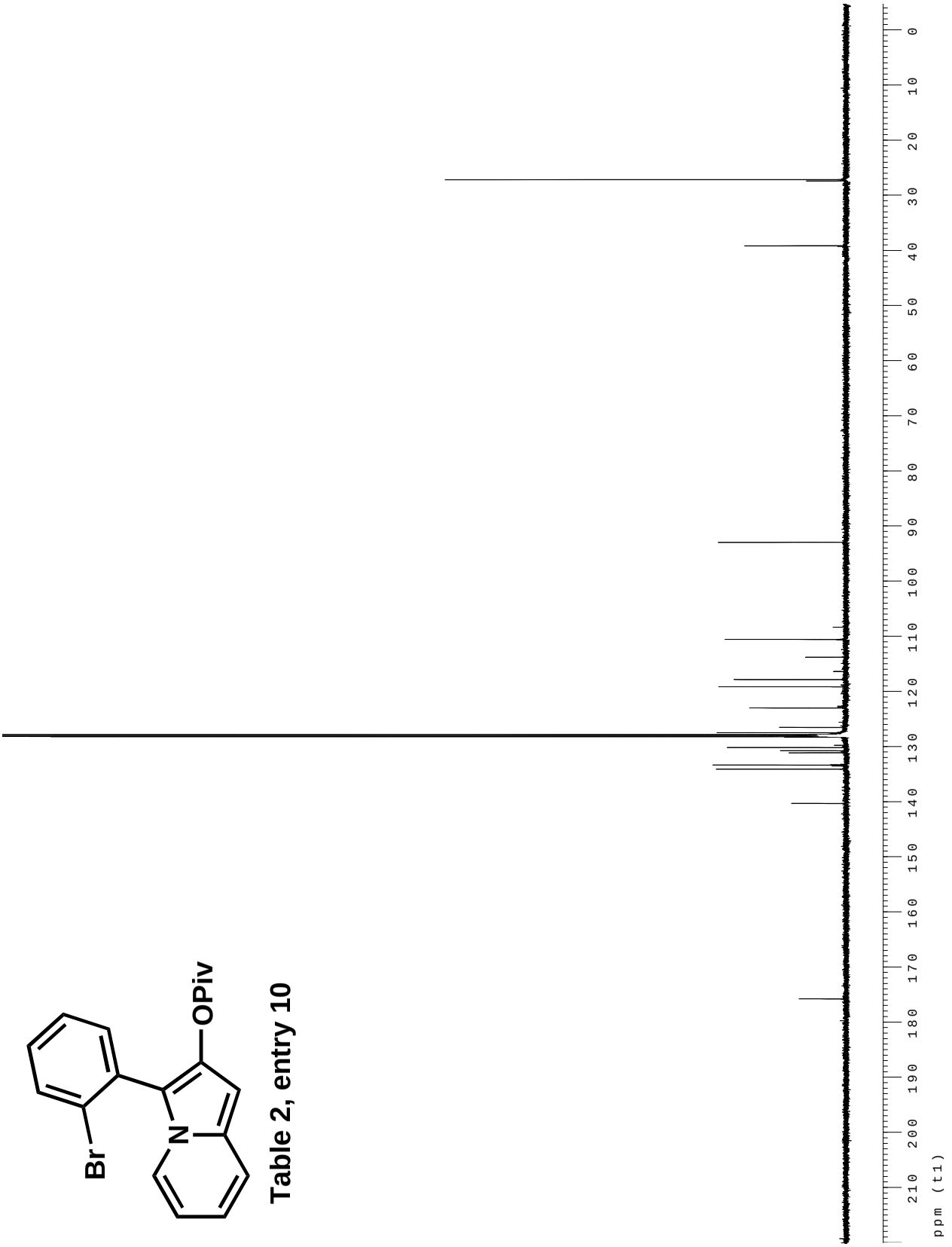


Table 2, entry 9


MeO
OMe
N
OPiv
Table 2, entry 9
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm (t1)


9.65
1.05
1.06
2.13
1.06
1.04
1.12
1.00
14.0
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)
Br
N
OPiv
Table 2, entry 10


OPiv
Br
N
Table 2, entry 10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
ppm (t1)

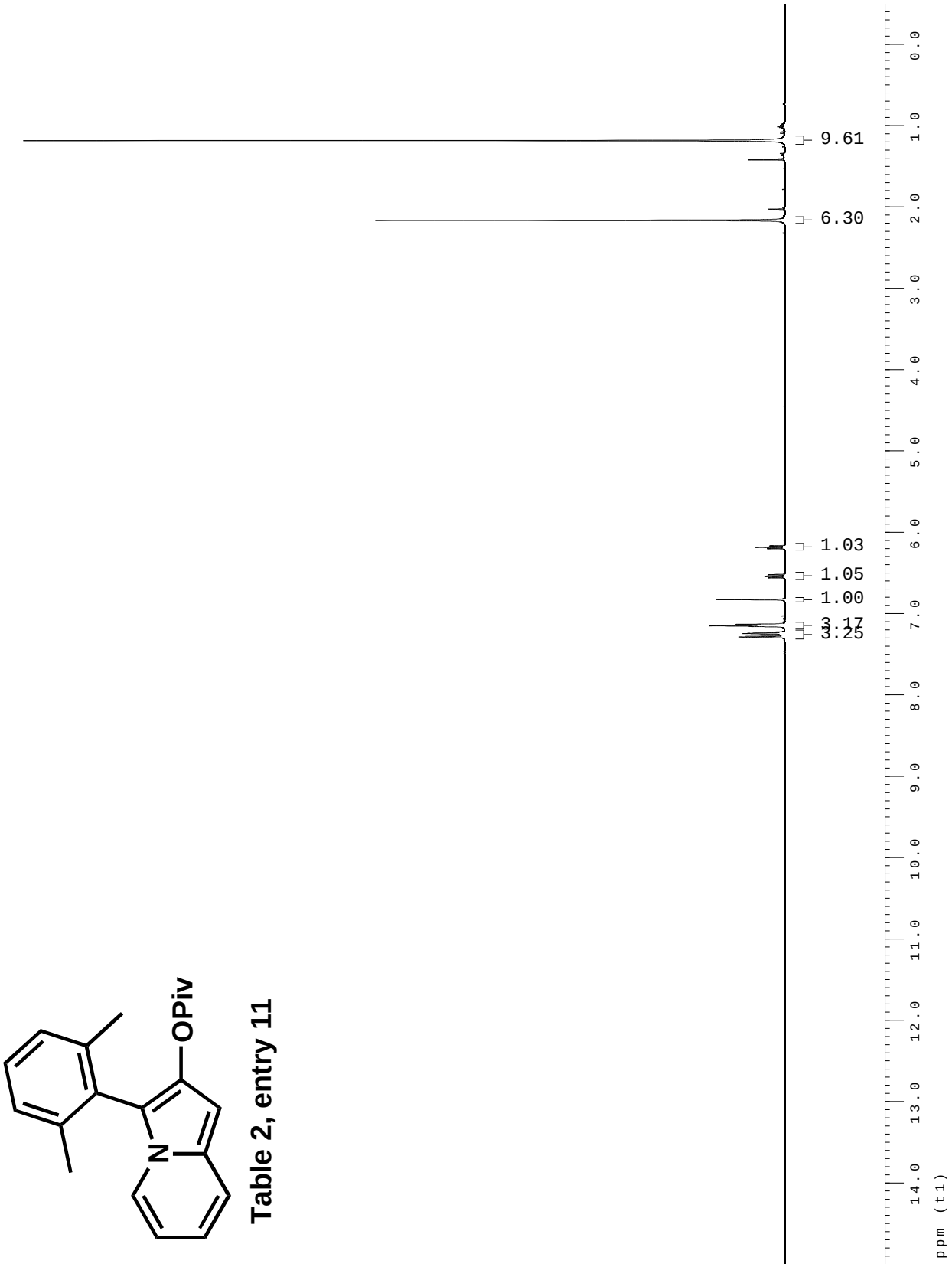
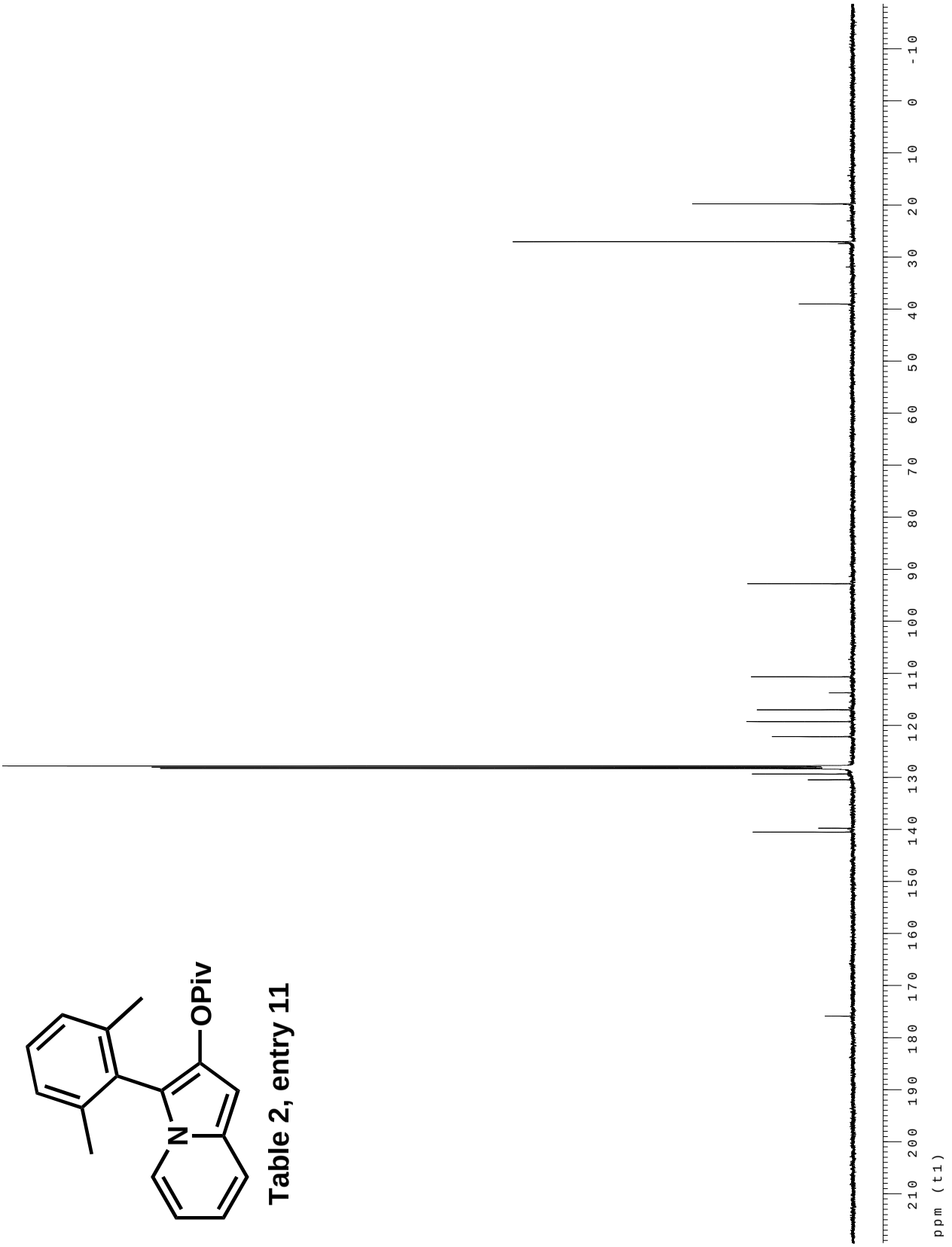
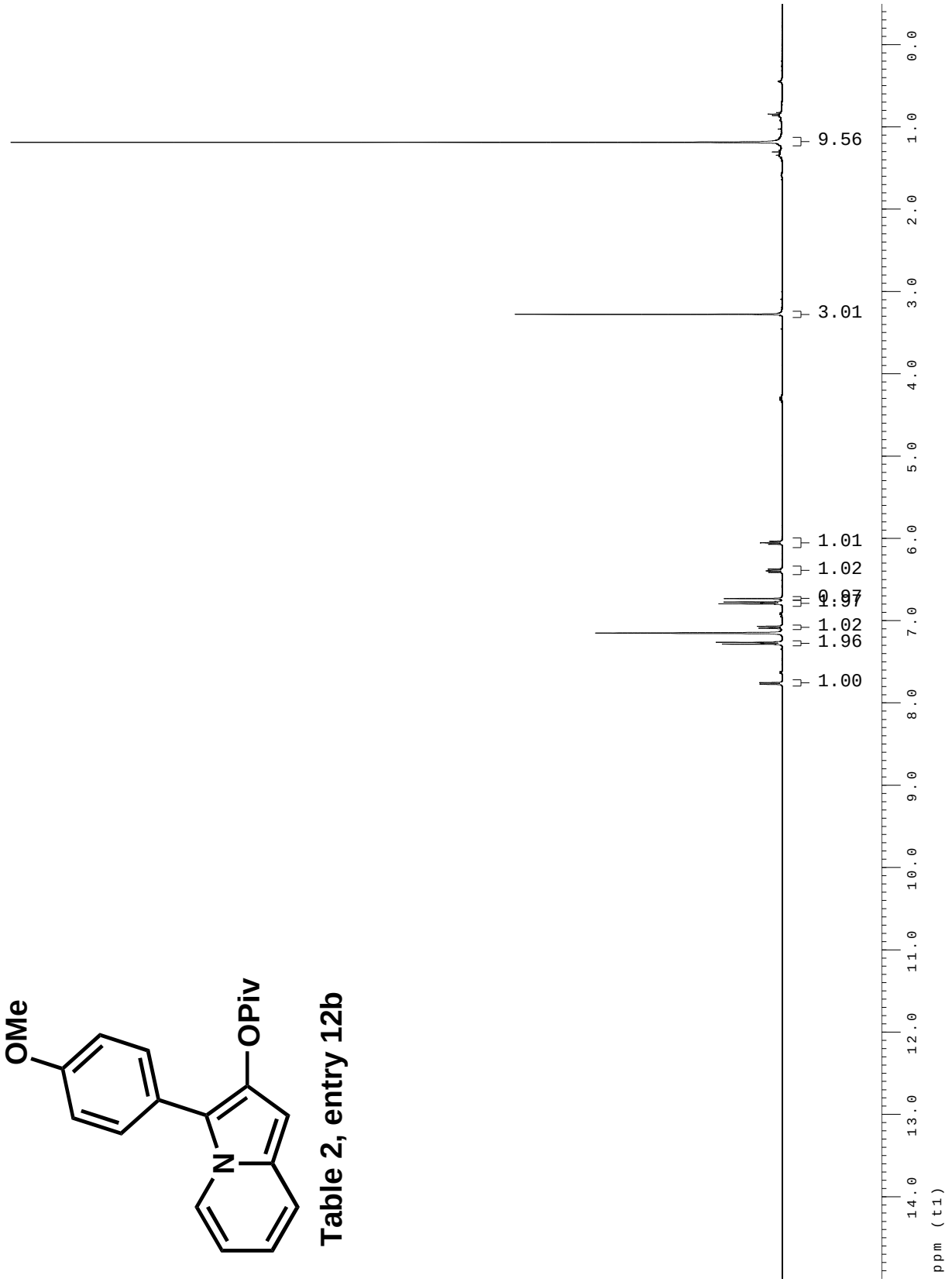
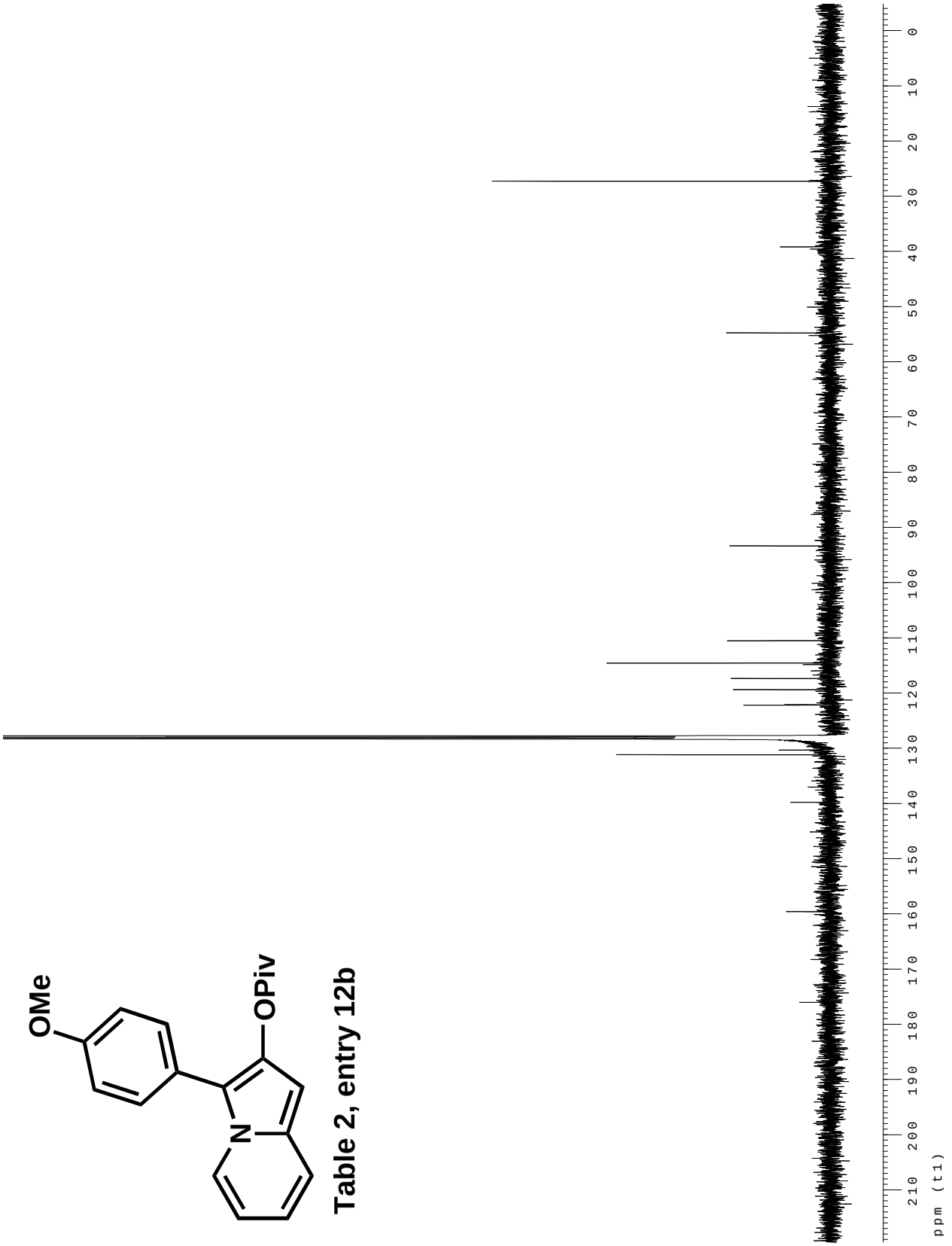
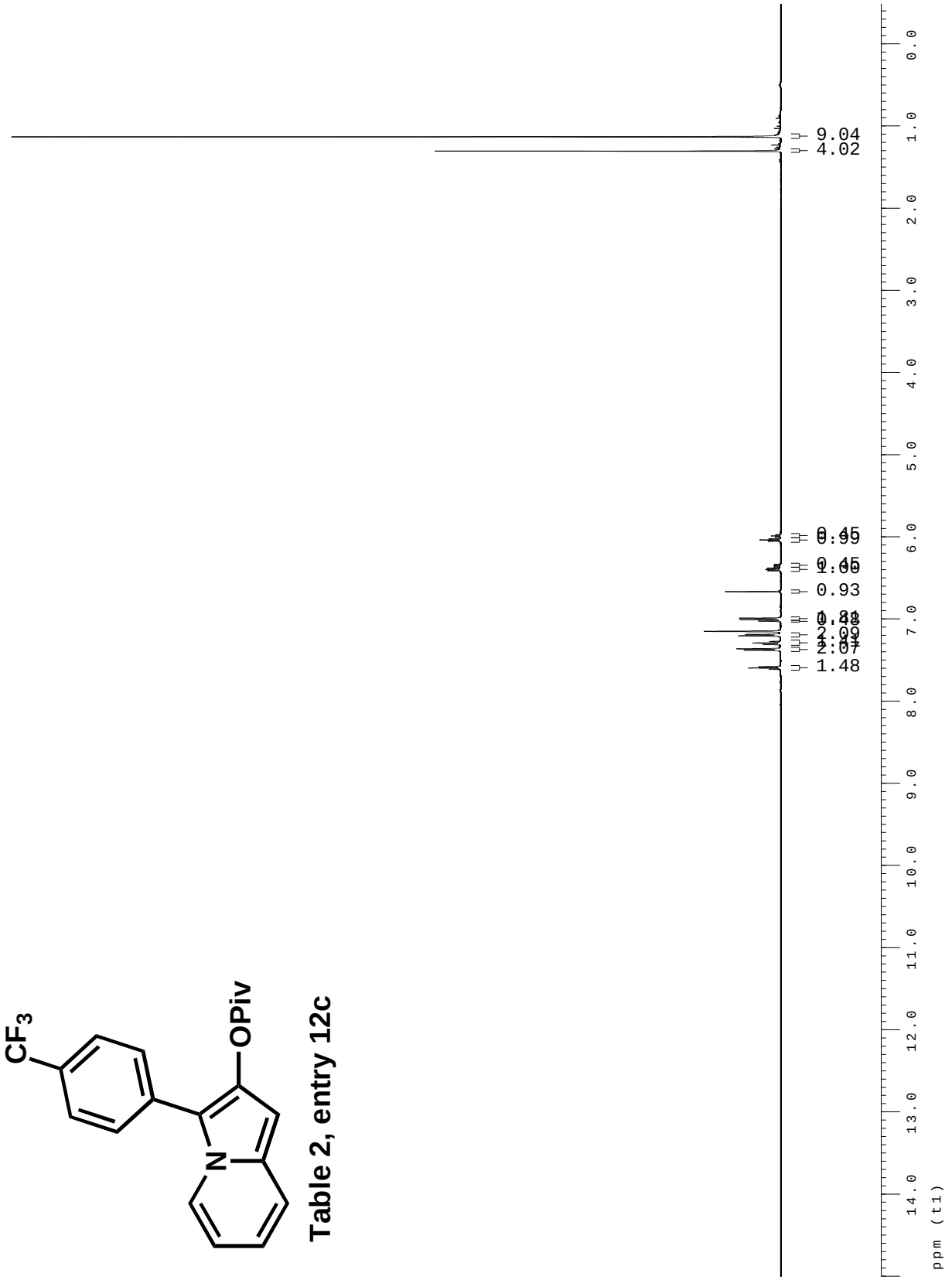


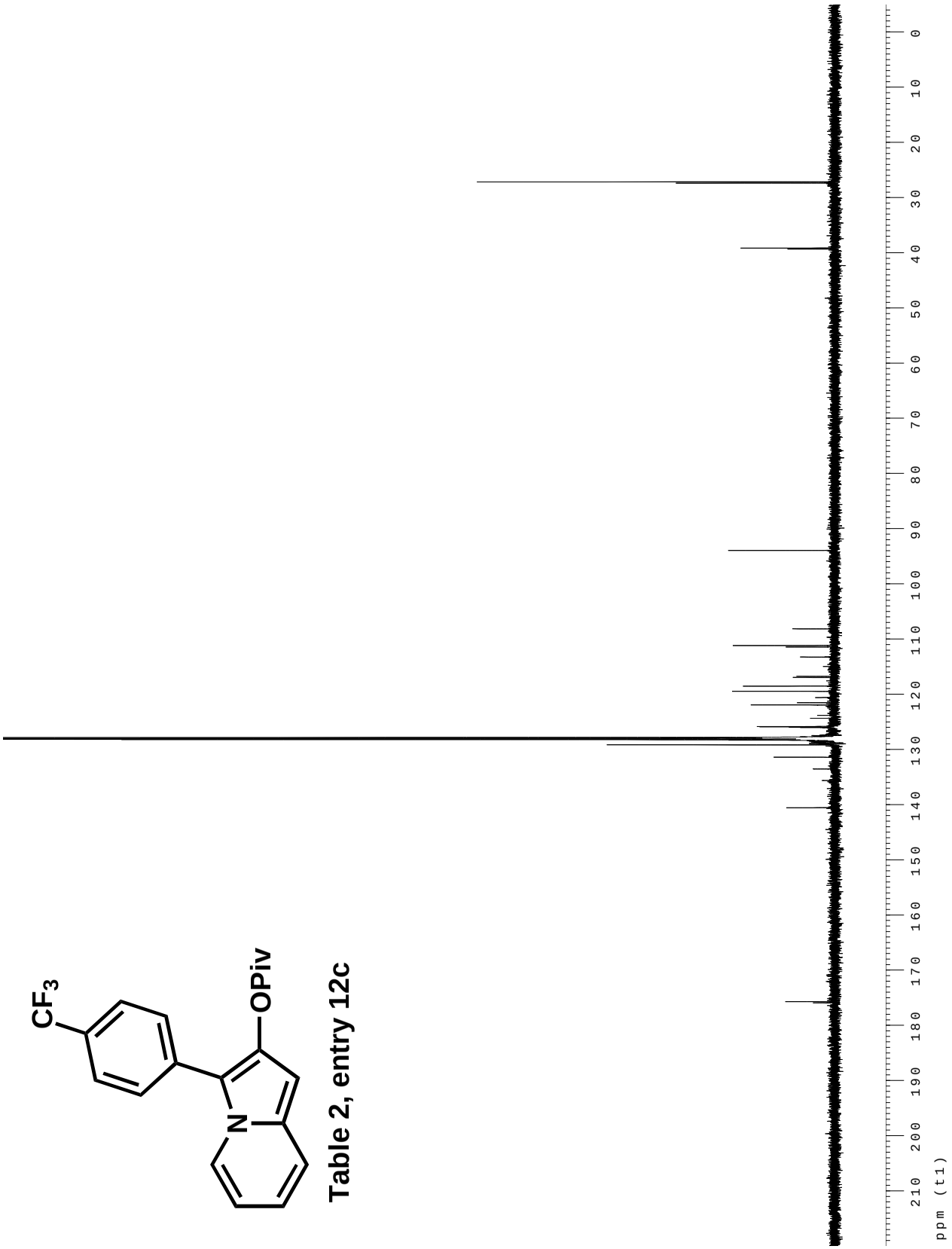
Table 2, entry 11

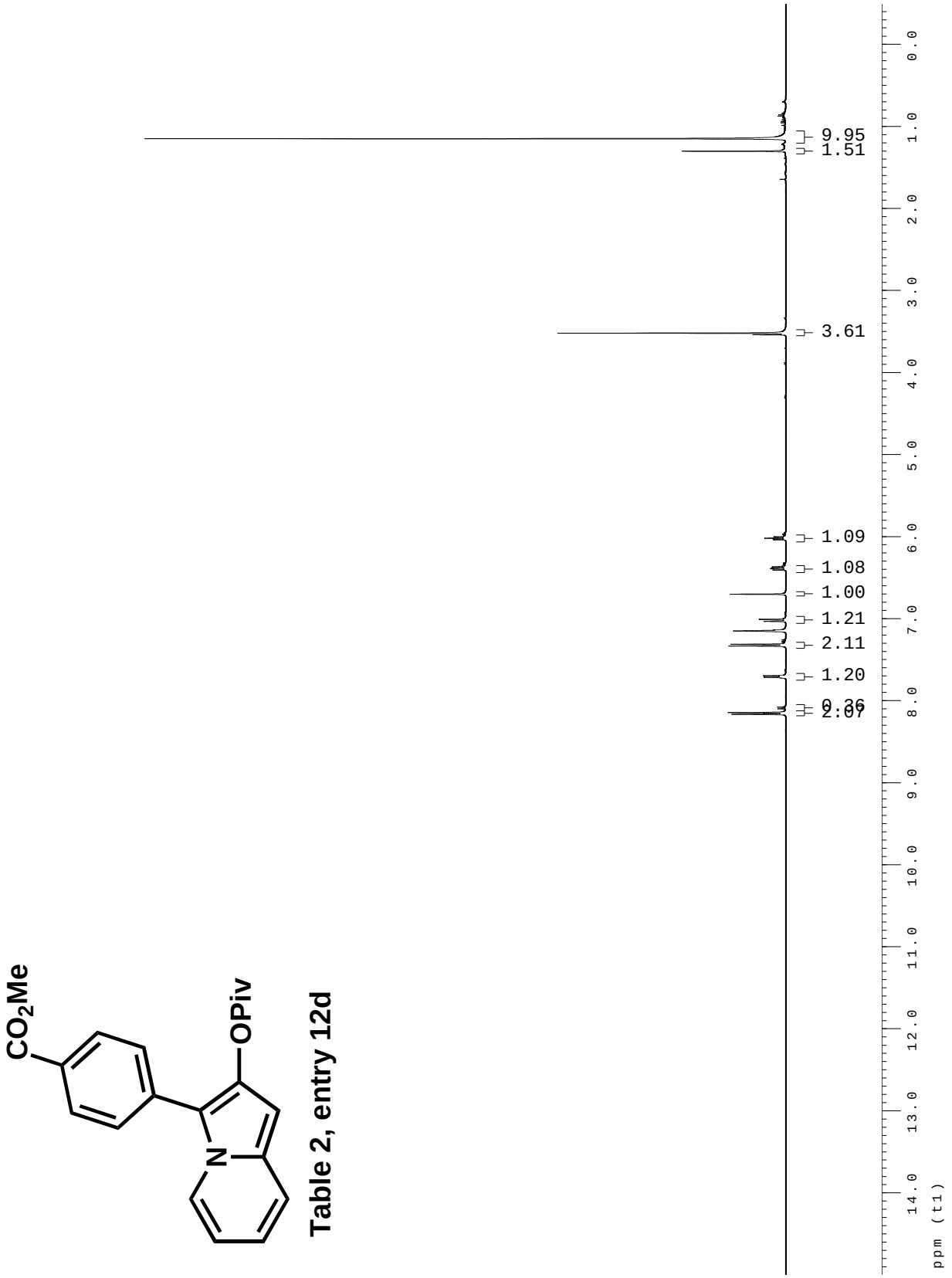

OPiv
N
Table 2, entry 11
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm (t1)

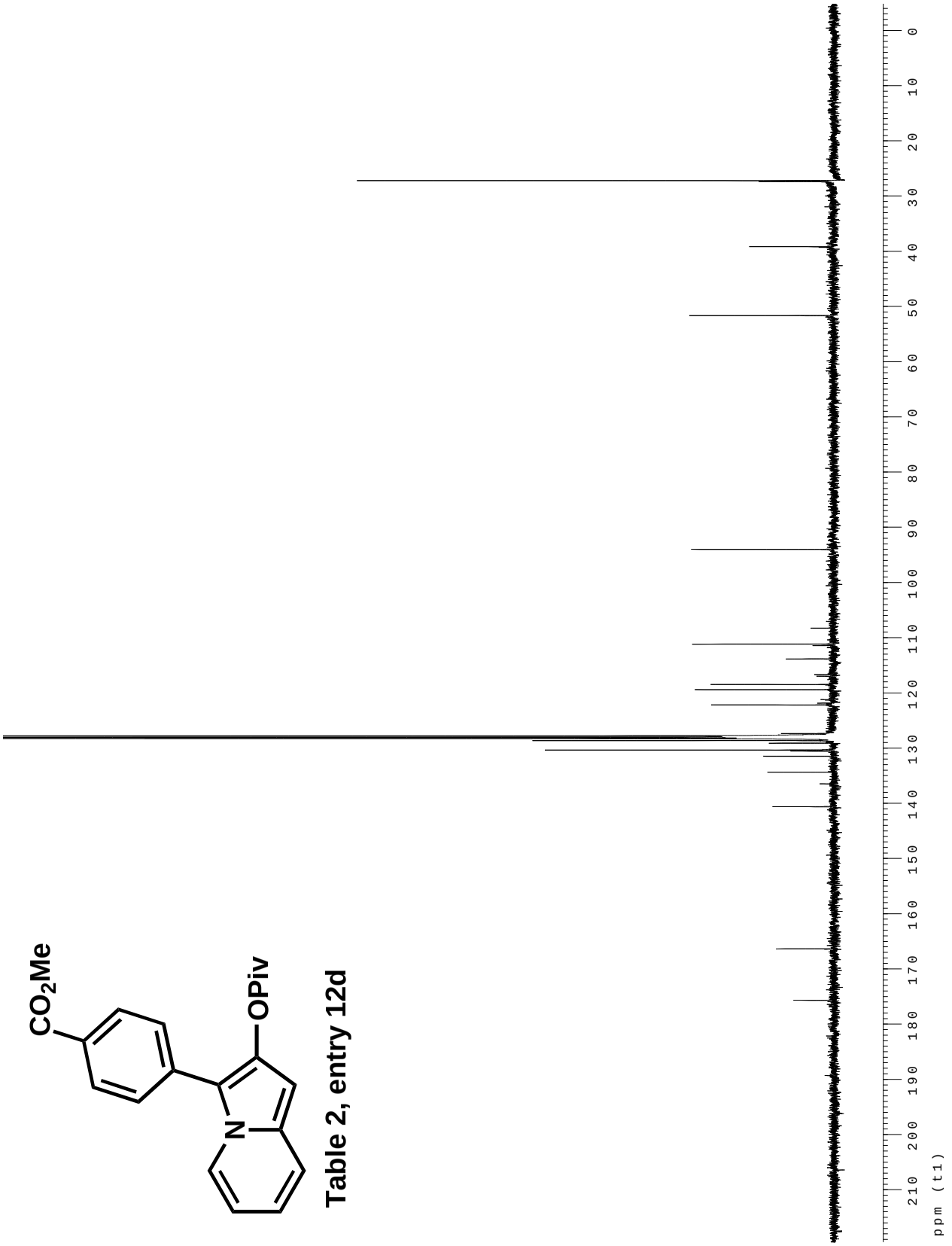

OMe
OPiv
N
Table 2, entry 12b
9.56
3.01
1.01
1.02
0.97
1.97
1.02
1.96
1.00
14.0
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


OMe
OPiv
N
Table 2, entry 12b
ppm (t1)


CF3
OPiv
N
Table 2, entry 12c
9.04
4.02
0.45
0.99
0.45
1.00
0.93
1.84
2.09
2.07
1.48
14.0
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


CF3
OPiv
N
Table 2, entry 12c
ppm (t1)


CO2Me
OPiv
N
Table 2, entry 12d
9.95
1.51
3.61
1.09
1.08
1.00
1.21
2.11
1.20
0.36
2.07
14.0
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


CO2Me
OPiv
N
Table 2, entry 12d
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm (t1)

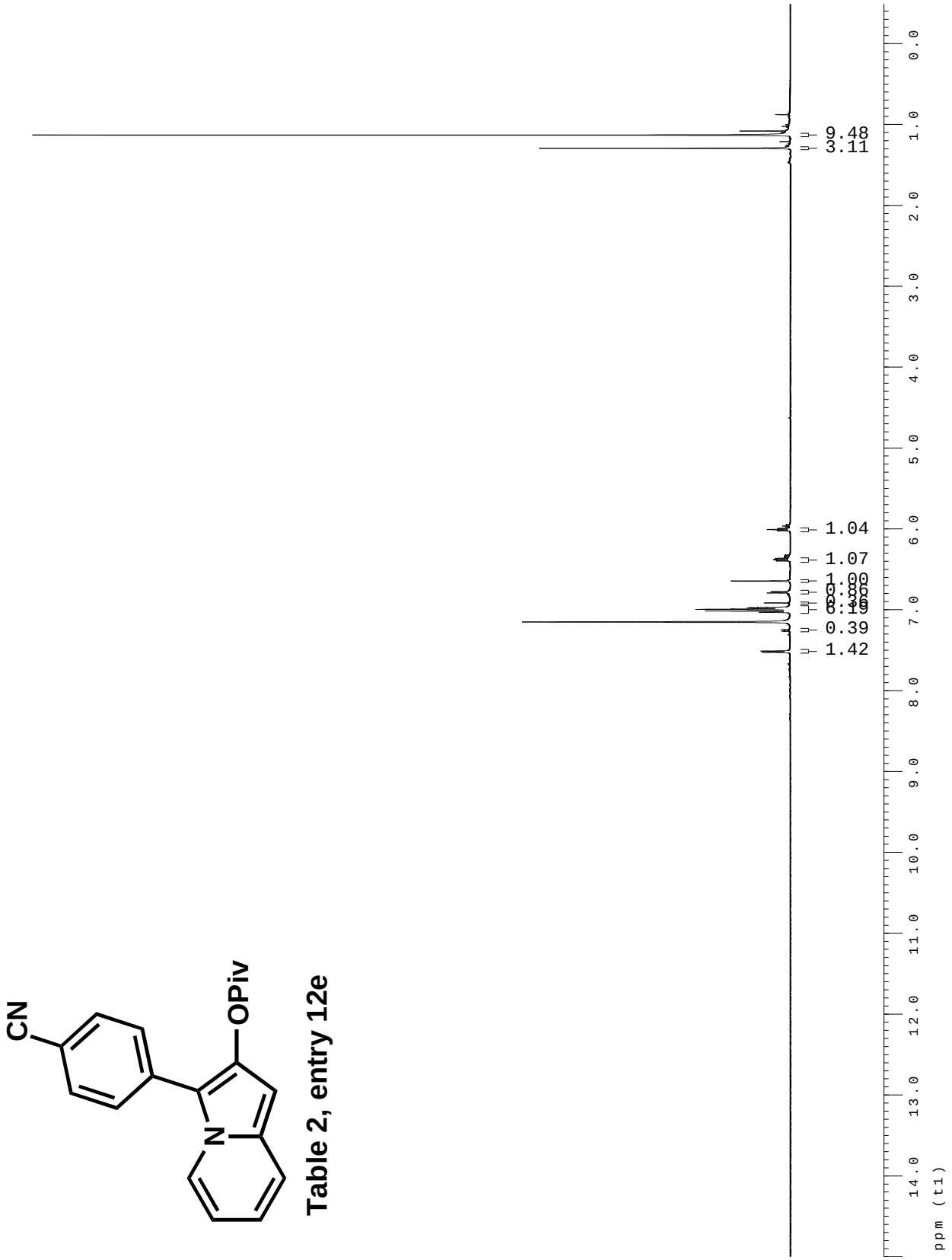
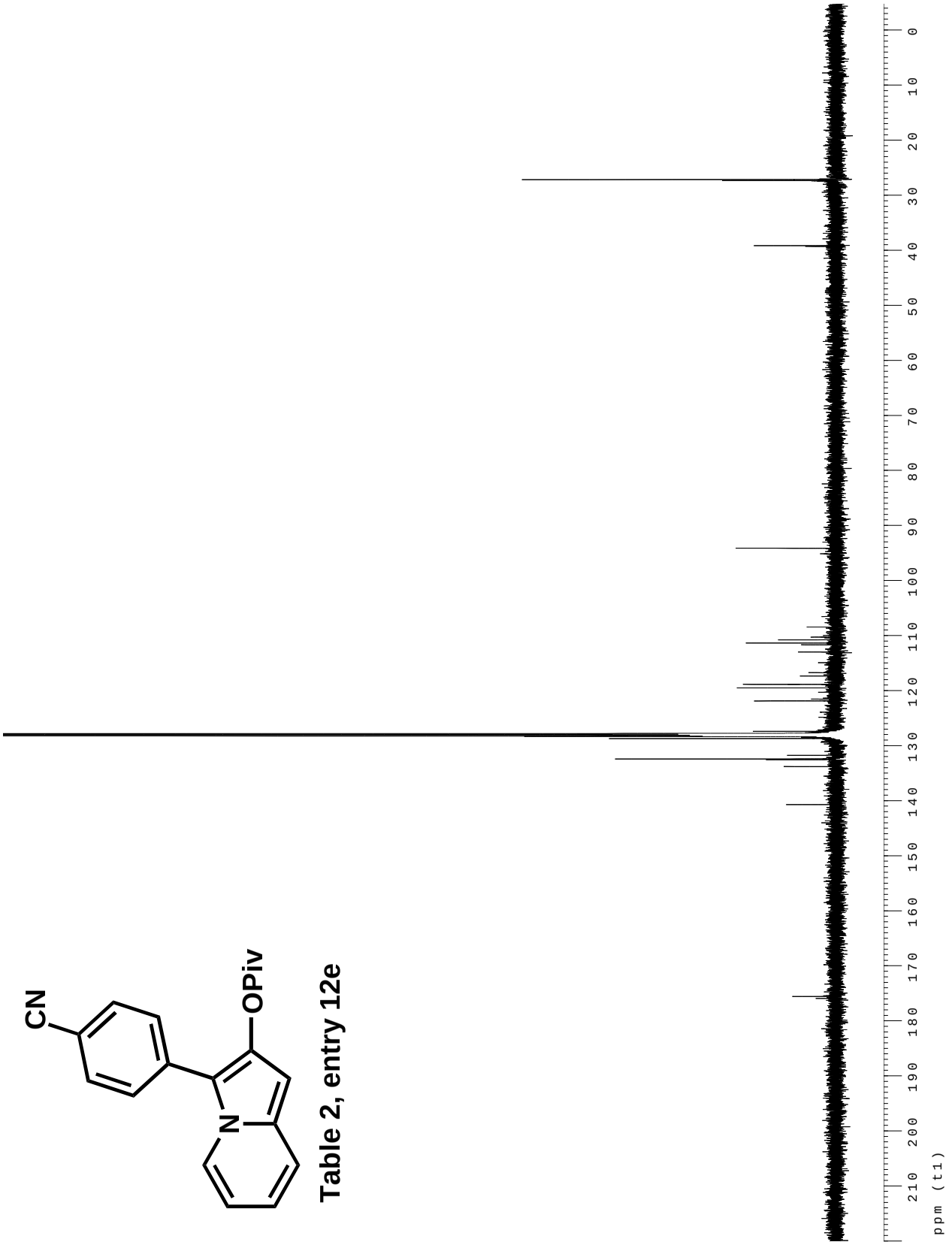
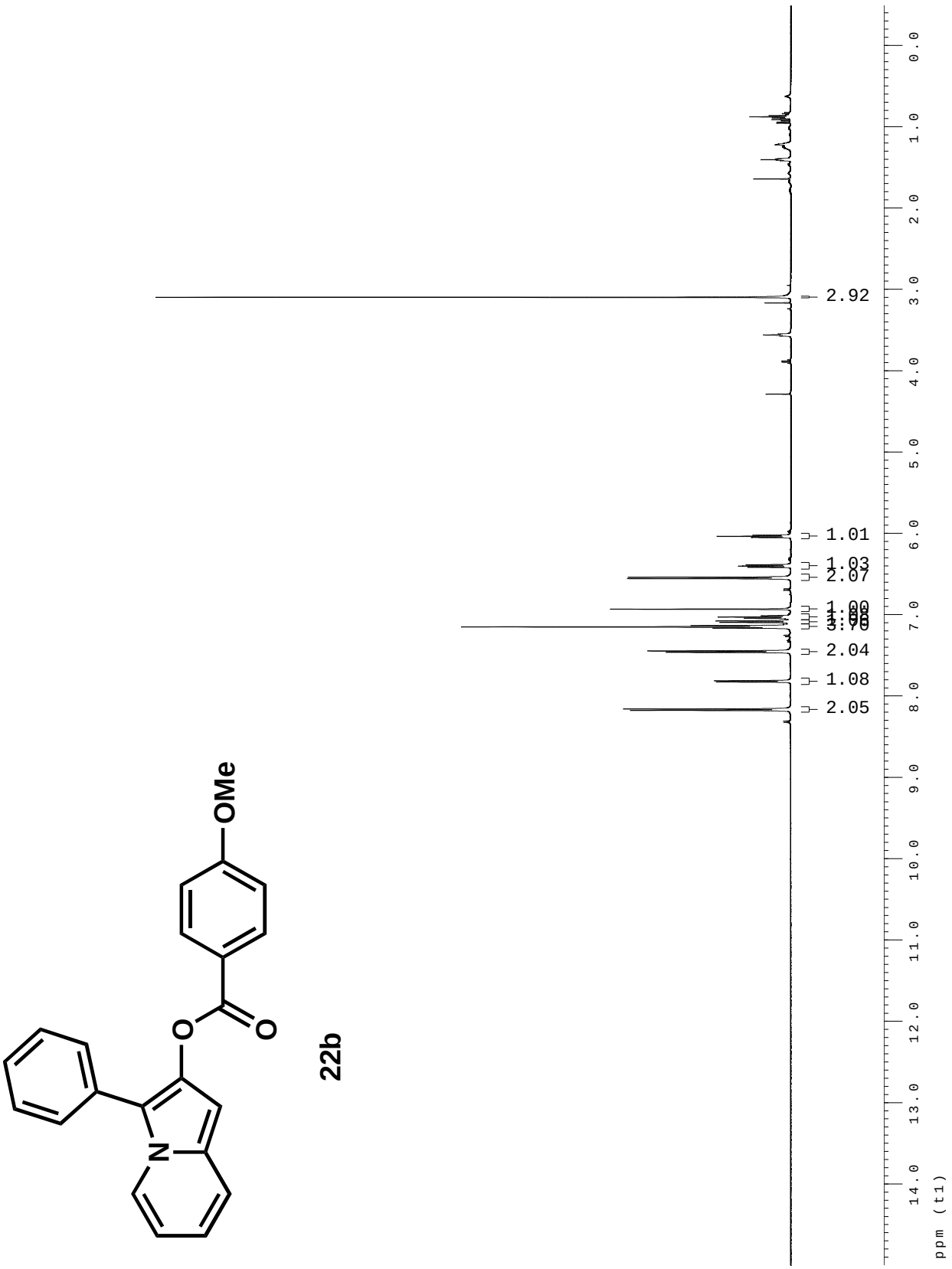
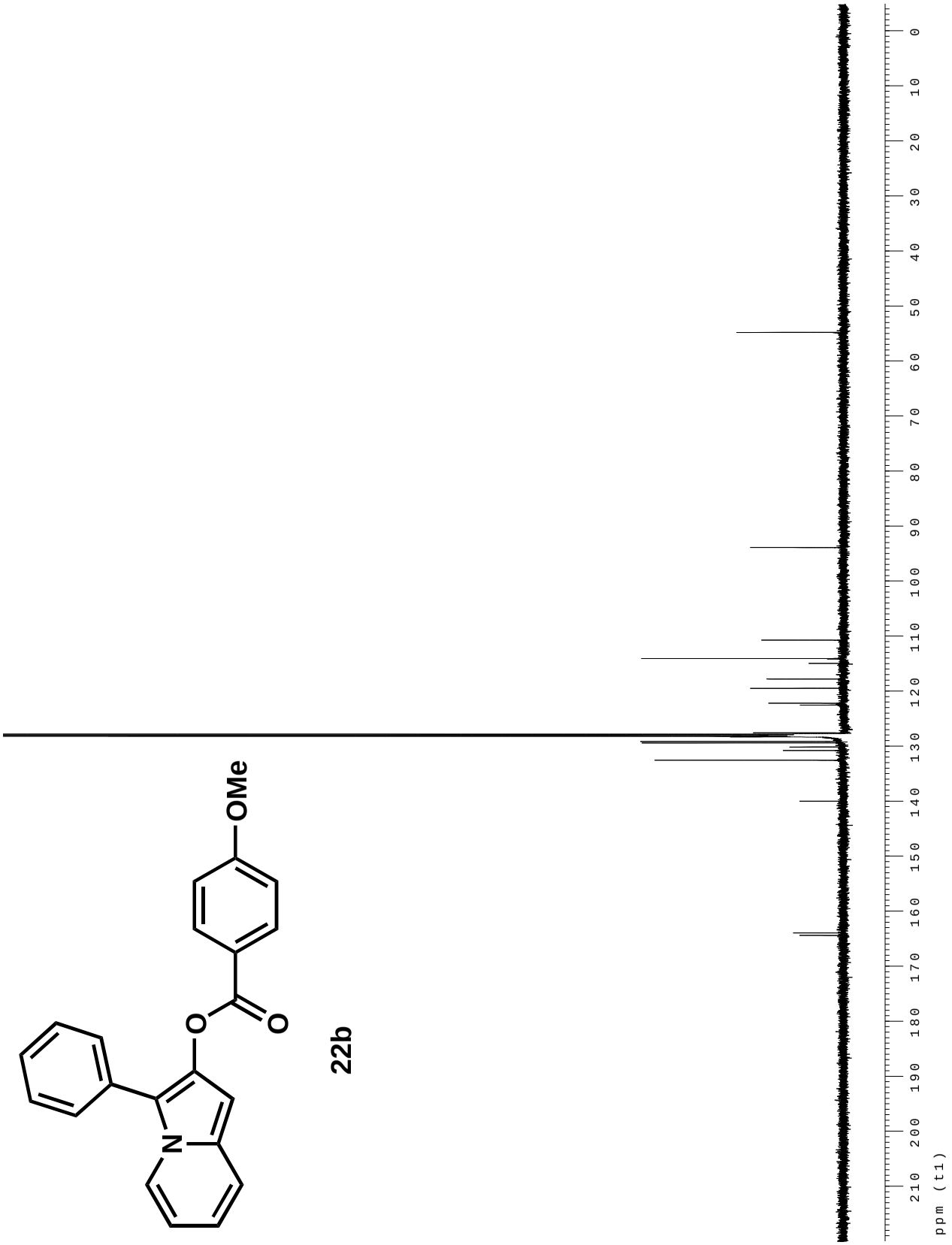
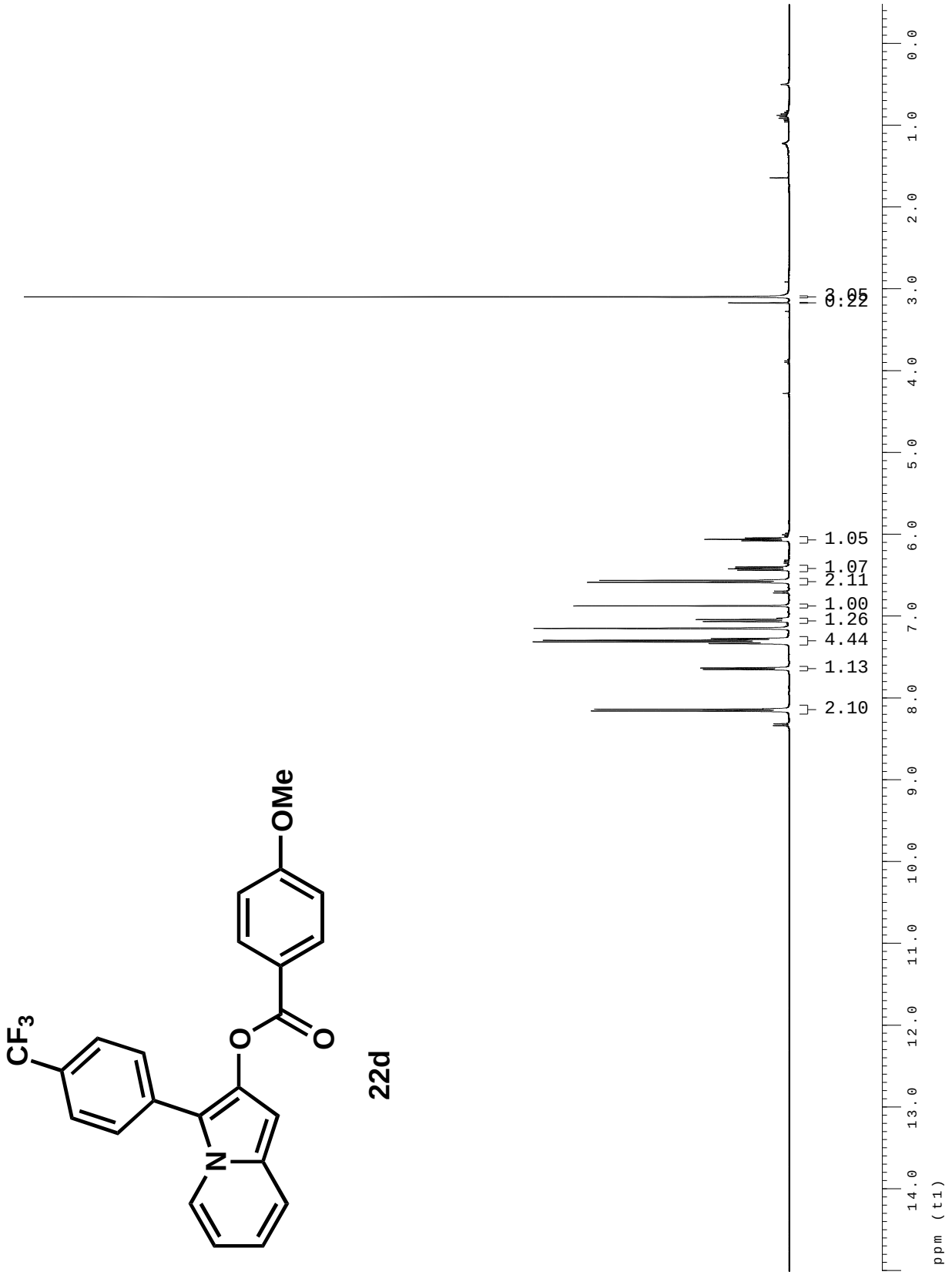


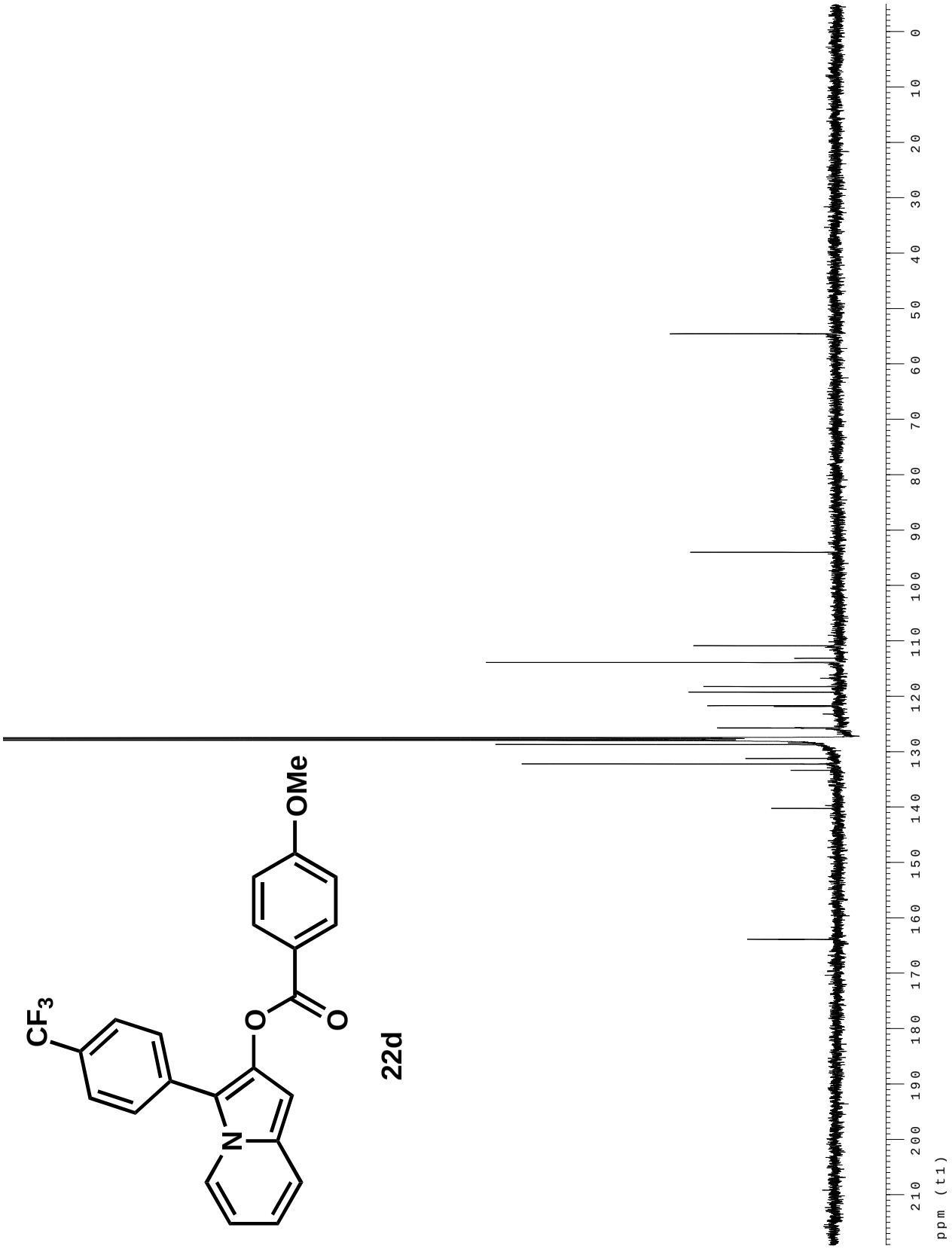
Table 2, entry 12e

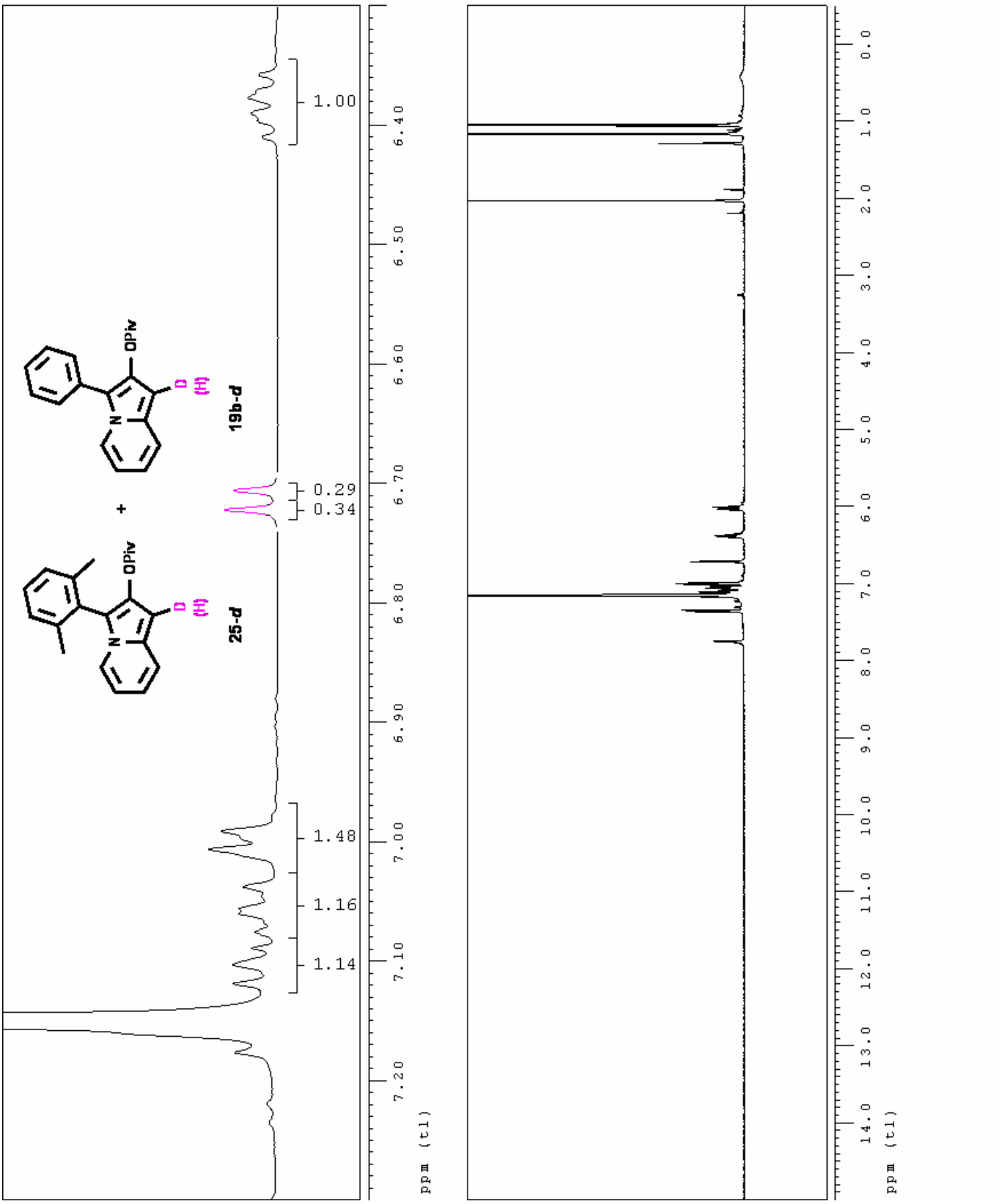

CN
OPiv
N
Table 2, entry 12e
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm (t1)


OMe
O
O
N
22b
2.92
1.01
1.03
2.07
1.00
3.78
2.04
1.08
2.05
ppm (t1)


OMe
O
O
N
22b
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
ppm (t1)


3.05
0.22
1.05
1.07
2.11
1.00
1.26
4.44
1.13
2.10
ppm (t1)
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
13.0
14.0
OMe
O
O
CF3
N
22d


OMe
O
O
CF3
N
22d
ppm (t1)


OPiv
D
(H)
19b-d
+
OPiv
D
(H)
25-d
1.00
0.29
0.34
1.48
1.16
1.14
6.40
6.50
6.60
6.70
6.80
6.90
7.00
7.10
7.20
ppm (t1)
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
13.0
14.0
ppm (t1)