



Supporting Information

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## Nickel-Catalyzed Addition of Pyridine-*N*-oxides Across Alkynes

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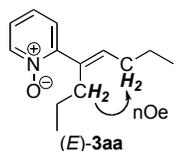
**General.** All manipulations of oxygen- and moisture-sensitive materials were conducted with a standard Schlenk technique or in a dry box under an argon atmosphere. Flash column chromatography was performed using Kanto Chemical silica gel (spherical, 40–50  $\mu\text{m}$ ). Analytical thin layer chromatography (TLC) was performed on Merck Kieselgel 60 F<sub>254</sub> (0.25 mm) plates. Visualization was accomplished with UV light (254 nm) and/or an aqueous alkaline KMnO<sub>4</sub> solution followed by heating.

**Apparatus.** Proton and carbon nuclear magnetic resonance spectra (<sup>1</sup>H and <sup>13</sup>C NMR) were recorded on a Varian Mercury 400 (<sup>1</sup>H NMR, 400 MHz; <sup>13</sup>C NMR 101 MHz) spectrometer with solvent resonance as the internal standard (<sup>1</sup>H NMR, CHCl<sub>3</sub> at 7.26 ppm; <sup>13</sup>C NMR, CDCl<sub>3</sub> at 77.0 ppm). <sup>1</sup>H NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sext = sextet, br = broad, m = multiplet), coupling constants (Hz), and integration. Mass spectra were obtained with a JEOL JMS-700 (EI) or JEOL JMS-HMS-HX110A (FAB+) spectrometer. GC analysis was performed on a Shimadzu GC 2010 equipped with a DB-5 column (30 m x 0.53 mm, pressure = 31.7 kPa, detector = FID, 290 °C) with helium gas as a carrier.

**Chemicals.** Unless otherwise noted, commercially available reagents were used without purification. All alkynes were distilled before use. Anhydrous toluene purchased from Kanto Chemical was degassed vigorously with argon for 20 min and further purified by passage through activated alumina under positive argon pressure as described by Grubbs et al.<sup>1</sup>

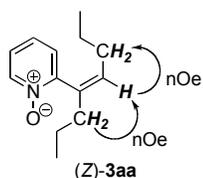
**Representative procedure for the synthesis of pyridine-*N*-oxides.**<sup>2</sup> Pyridine was dissolved in dry CH<sub>2</sub>Cl<sub>2</sub> and then *m*-chloroperobenzoic acid (1.2 equiv) was added in one portion. The reaction mixture was stirred at room temperature overnight, concentrated in vacuo, and purified by flash chromatography on silica gel (CH<sub>2</sub>Cl<sub>2</sub>–acetone as an eluent).

**Nickel-catalyzed hydroheteroarylation of alkynes using pyridine-*N*-oxides. A general Procedure.** A pyridine-*N*-oxide (1.0 mmol) and an alkyne (1.5 mmol) were added sequentially to a solution of Ni(cod)<sub>2</sub> (28 mg, 0.10 mmol) and PCyp<sub>3</sub> (24 mg, 0.10 mmol) in toluene (2.5 mL) in a dry box. The vial was taken outside the dry box and heated at 35 °C for the time specified in Table 1. The resulting mixture was filtered through a pad of silica gel, concentrated in vacuo, and purified by flash chromatography on silica gel to give the corresponding hydroheteroarylation products in yields listed in Table 1.



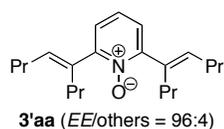
**(*E*)-2-(4-Octen-4-yl)pyridine-*N*-oxide [(*E*)-3aa].** A colorless oil,  $R_f$  0.40 (CH<sub>2</sub>Cl<sub>2</sub>–acetone = 3:2), <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.18 (dt,  $J$  = 6.2, 1.0 Hz, 1H), 7.24–7.06 (m, 3H), 5.62 (t,  $J$  = 7.2 Hz, 1H), 2.65 (t,  $J$  = 7.3 Hz, 2H), 2.20 (q,  $J$  = 7.4 Hz, 2H), 1.49 (sext,  $J$  = 7.4 Hz, 2H), 1.26 (sext,  $J$  = 7.5 Hz, 2H), 0.97 (t,  $J$  = 7.3 Hz, 3H), 0.86 (t,  $J$  = 7.3 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  152.8, 139.7, 136.3, 135.0, 127.2, 125.4, 123.9, 30.1, 29.5, 22.7, 22.0, 14.12, 14.07; Anal. Calcd for C<sub>13</sub>H<sub>19</sub>NO: C, 76.06; H, 9.33.

Found [as a mixture with (*Z*)-**3aa**]: C, 75.82; H, 9.49.

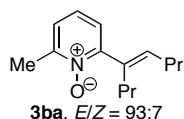


21.6, 14.0, 13.8.

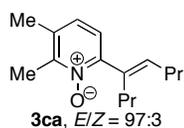
**(Z)-2-(4-Octen-4-yl)pyridine-N-oxide [(Z)-3aa].** A colorless oil,  $R_f$  0.40 ( $\text{CH}_2\text{Cl}_2$ -acetone = 3:2),  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.27 (d,  $J = 5.9$  Hz, 1H), 7.25–7.08 (m, 3H), 5.73 (t,  $J = 7.5$  Hz, 1H), 2.70–2.30 (br, 2H), 1.87 (q,  $J = 7.3$  Hz, 2H), 1.43–1.20 (m, 4H), 0.89 (t,  $J = 7.3$  Hz, 3H), 0.86 (t,  $J = 7.3$  Hz, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  149.8, 140.1, 134.1, 132.5, 127.6, 124.9, 124.1, 36.5, 31.4, 22.8,



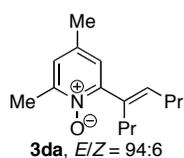
**2,6-Di(4-octen-4-yl)pyridine-N-oxide (3'aa, *EE*/others = 94:6).** A colorless oil,  $R_f$  0.70 ( $\text{CH}_2\text{Cl}_2$ -acetone = 3:2),  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.12–7.05 (m, 3H), 5.70–5.64 (m, 0.08H), 5.61 (t,  $J = 7.2$  Hz, 1.92H), 2.65 (t,  $J = 7.8$  Hz, 4H), 2.21 (q,  $J = 7.4$  Hz, 4H), 1.48 (sext,  $J = 7.2$  Hz, 4H), 1.25 (sext,  $J = 7.5$  Hz, 4H), 0.97 (m, 6H), 0.85 (m, 6H);  $^{13}\text{C}$  NMR [for (*E,E*)-**3'aa**, 101 MHz,  $\text{CDCl}_3$ ]  $\delta$  152.8, 136.8, 134.1, 125.2, 124.4, 30.1, 29.5, 22.6, 21.8, 14.1, 14.0; HMRS (FAB+) Calcd for  $\text{C}_{21}\text{H}_{33}\text{NO}$ :  $M^+$ , 315.2562. Found:  $m/z$  315.2569.



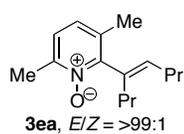
**6-Methyl-2-(4-octen-4-yl)pyridine-N-oxide (3ba, *E/Z* = 93:7).** A colorless oil,  $R_f$  0.45 ( $\text{CH}_2\text{Cl}_2$ -acetone = 3:2),  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.20–6.93 (m, 3H), 5.65 (t,  $J = 7.5$ , 0.07H), 5.57 (t,  $J = 7.2$  Hz, 0.93H), 2.61 (t,  $J = 7.8$  Hz, 2H), 2.51 (s, 0.21H), 2.49 (s, 2.79H), 2.19 (q,  $J = 7.4$  Hz, 2H), 1.45 (sext,  $J = 7.4$  Hz, 2H), 1.24 (sext,  $J = 7.5$  Hz, 2H), 0.95 (t,  $J = 7.5$  Hz, 3H), 0.84 (t,  $J = 7.4$  Hz, 3H);  $^{13}\text{C}$  NMR [for (*E*)-**3ba**, 101 MHz,  $\text{CDCl}_3$ ]  $\delta$  152.7, 148.8, 136.7, 133.9, 124.6, 124.5, 124.3, 29.9, 29.6, 22.5, 21.8, 18.1, 14.0, 13.9; HMRS (FAB+) Calcd for  $\text{C}_{14}\text{H}_{21}\text{NO}$ :  $M^+$ , 219.1623. Found:  $m/z$  219.1613.



**5,6-Dimethyl-2-(4-octen-4-yl)pyridine-N-oxide (3ca, *E/Z* = 97:3).** A colorless oil,  $R_f$  0.40 ( $\text{CH}_2\text{Cl}_2$ -acetone = 3:2),  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.97 (d,  $J = 8.0$  Hz, 1H), 6.93 (d,  $J = 8.4$  Hz, 1H), 5.65 (t,  $J = 7.3$  Hz, 0.03H), 5.54 (t,  $J = 7.3$  Hz, 0.97H), 2.63 (t,  $J = 7.8$  Hz, 2H), 2.52 (s, 0.09H), 2.50 (s, 2.91H), 2.34 (s, 0.09H), 2.32 (s, 2.91H), 2.20 (q,  $J = 7.3$  Hz, 2H), 1.47 (sext,  $J = 7.4$  Hz, 2H), 1.25 (sext,  $J = 7.5$  Hz, 2H), 0.97 (t,  $J = 7.4$  Hz, 3H), 0.86 (t,  $J = 7.4$  Hz, 3H);  $^{13}\text{C}$  NMR [for (*E*)-**3ca**, 101 MHz,  $\text{CDCl}_3$ ]  $\delta$  150.2, 147.8, 136.9, 133.4, 132.3, 126.2, 123.0, 29.9, 29.7, 22.6, 21.8, 19.5, 14.0, 13.9; Anal. Calcd for  $\text{C}_{15}\text{H}_{23}\text{NO}$ : C, 77.21; H, 9.93. Found: C, 76.96; H, 10.20.

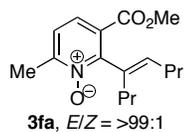


**4,6-Dimethyl-2-(4-octen-4-yl)pyridine-N-oxide (3da, *E/Z* = 94:6).** A colorless oil,  $R_f$  0.30 ( $\text{CH}_2\text{Cl}_2$ -acetone = 3:2),  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.97 (d,  $J = 2.2$  Hz, 1H), 6.85 (d,  $J = 2.8$  Hz, 1H), 5.65 (t,  $J = 7.3$ , 0.06H), 5.57 (t,  $J = 7.2$  Hz, 0.94H), 2.64 (t,  $J = 7.8$  Hz, 2H), 2.51 (s, 0.18H), 2.49 (s, 2.82H), 2.31 (s, 0.18), 2.29 (s, 2.82H), 2.20 (q,  $J = 7.3$  Hz, 2H), 1.48 (sext,  $J = 7.4$  Hz, 2H), 1.27 (sext,  $J = 7.5$  Hz, 2H), 0.98 (t,  $J = 7.4$  Hz, 3H), 0.87 (t,  $J = 7.3$  Hz, 3H);  $^{13}\text{C}$  NMR [for (*E*)-**3da**, 101 MHz,  $\text{CDCl}_3$ ]  $\delta$  152.1, 148.1, 137.0, 135.6, 133.9, 125.4, 125.2, 30.1, 29.8, 22.8, 22.0, 20.3, 18.2, 14.20, 14.16; HMRS (FAB+) Calcd for  $\text{C}_{15}\text{H}_{23}\text{NO}$ :  $M^+$ , 233.1780. Found:  $m/z$  233.1776.



**(E)-3,6-Dimethyl-2-(4-octen-4-yl)pyridine-N-oxide (3ea).** A colorless oil,  $R_f$  0.50 ( $\text{CH}_2\text{Cl}_2$ -acetone = 3:2),  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.01 (d,  $J = 8.1$  Hz, 1H), 7.00 (d,  $J = 8.1$  Hz, 1H), 5.38 (t,  $J = 7.3$  Hz, 1H), 2.54–2.41 (m, 2H), 2.45 (s, 3H), 2.24 (s, 3H), 2.32–2.22 (m, 2H), 1.56–1.36 (m, 2H), 1.34–1.18 (m, 2H), 0.96 (t,  $J = 7.4$  Hz, 3H), 0.88 (t,  $J = 7.2$  Hz, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  151.9, 146.0, 133.8, 133.0, 132.3, 126.6,

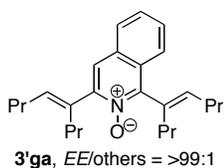
123.2, 31.1, 30.0, 22.7, 22.1, 19.9, 18.0, 14.6, 14.2; HMRS (FAB+) Calcd for C<sub>15</sub>H<sub>23</sub>NO: M<sup>+</sup>, 233.1780. Found: *m/z* 233.1786.



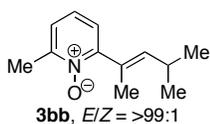
**(E)-3-(Methoxycarbonyl)-6-methyl-2-(4-octen-4-yl)pyridine-*N*-oxide (3fa).** A colorless oil, *R<sub>f</sub>* 0.60 (CH<sub>2</sub>Cl<sub>2</sub>–acetone = 3:2), <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.36 (d, *J* = 8.0 Hz, 1H), 7.20 (d, *J* = 8.0 Hz, 1H), 5.40 (t, *J* = 7.2 Hz, 1H), 3.80 (s, 3H), 2.52 (s, 3H), 2.74–2.30 (m, 2H), 2.24–2.08 (m, 2H), 1.48–1.30 (m, 4H), 0.94 (t, *J* = 6.6 Hz, 3H), 0.91 (t, *J* = 7.1 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 166.3, 152.3, 151.2, 134.4, 134.0, 129.6, 124.3, 123.7, 52.5, 31.2, 30.3, 22.5, 21.7, 18.6, 14.7, 14.1; Anal. Calcd for C<sub>16</sub>H<sub>23</sub>NO<sub>3</sub>: C, 68.99; H, 8.29. Found: C, 69.29; H, 8.36.



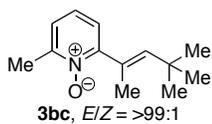
**(E)-1-(4-Octen-4-yl)-isoquinoline-*N*-oxide (3ga).** A colorless oil, *R<sub>f</sub>* 0.40 (CH<sub>2</sub>Cl<sub>2</sub>–acetone = 1:1), <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.13 (d, *J* = 7.1, 1H), 7.94 (d, *J* = 7.8 Hz, 1H), 7.30 (d, *J* = 7.4 Hz, 1H), 7.59–7.48 (m, 3H), 5.58 (t, *J* = 7.2 Hz, 1H), 2.80–2.57 (m, 2H), 2.48–2.28 (m, 2H), 1.64–1.48 (m, 2H), 1.38–1.16 (m, 2H), 1.03 (t, *J* = 7.3 Hz, 3H), 0.87 (t, *J* = 7.3 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 148.9, 136.9, 135.9, 132.1, 129.5, 129.0, 128.5, 127.8, 126.6, 125.8, 122.3, 30.6, 30.3, 22.8, 21.9, 14.6, 14.2; HMRS (FAB+) Calcd for C<sub>17</sub>H<sub>21</sub>NO: M<sup>+</sup>, 255.1623. Found: *m/z* 255.1618.



**(E)-1,3-Di(4-octen-4-yl)isoquinoline-*N*-oxide (3'ga).** A colorless oil, *R<sub>f</sub>* 0.75 (CH<sub>2</sub>Cl<sub>2</sub>–acetone = 1:1), <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.93–7.87 (m, 1H), 7.74–7.67 (m, 1H), 7.53–7.44 (m, 3H), 5.69 (t, *J* = 7.2 Hz, 1H), 5.57 (t, *J* = 7.2 Hz, 1H), 2.84–2.54 (m, 4H), 2.50–2.16 (m, 4H), 1.68–1.42 (m, 4H), 1.38–1.16 (m, 4H), 1.10–0.94 (m, 6H), 0.92–0.80 (m, 6H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 150.2, 148.9, 136.9, 135.4, 134.2, 132.6, 129.2, 128.7, 127.5, 127.4, 126.3, 125.6, 122.3, 30.6, 30.4, 30.3, 22.84, 22.76, 21.83, 21.81, 14.6, 14.3, 14.2; HMRS (FAB+) Calcd for C<sub>25</sub>H<sub>35</sub>NO: M<sup>+</sup>, 365.2719. Found: *m/z* 365.2709.

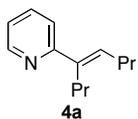


**(E)-6-Methyl-2-(4-methyl-2-penten-2-yl)pyridine-*N*-oxide (3bb).** A colorless oil, *R<sub>f</sub>* 0.60 (CH<sub>2</sub>Cl<sub>2</sub>–acetone = 3:2), <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.17–7.04 (m, 3H), 5.50 (dq, *J* = 9.2, 1.3 Hz, 1H), 2.80–2.64 (m, 1H), 2.51 (s, 3H), 2.07 (d, *J* = 1.5 Hz, 3H), 1.05 (d, *J* = 6.8 Hz, 6H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 153.7, 149.0, 141.5, 129.6, 124.7, 124.4, 123.8, 27.4, 22.6, 18.2, 14.4; HMRS (FAB+) Calcd for C<sub>12</sub>H<sub>17</sub>NO: M<sup>+</sup>, 191.1310. Found: *m/z* 191.1303.

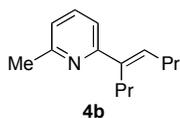


**(E)-2-(4,4-Dimethyl-2-penten-2-yl)-6-methylpyridine-*N*-oxide (3bc).** A colorless oil, *R<sub>f</sub>* 0.40 (CH<sub>2</sub>Cl<sub>2</sub>–acetone = 3:2), <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.15–7.00 (m, 3H), 5.57 (q, *J* = 1.4 Hz, 1H), 2.49 (s, 3H), 2.12 (d, *J* = 1.5 Hz, 3H), 1.20 (s, 9H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 154.8, 148.9, 143.7, 130.8, 124.7, 124.2, 123.7, 33.2, 30.5, 18.2, 15.7; Anal. Calcd for C<sub>13</sub>H<sub>19</sub>NO: C, 76.05; H, 9.21. Found: C, 76.06; H, 9.33.

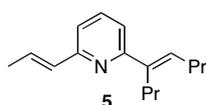
**Deoxygenation of 3aa and 3ba. A general Procedure.** To a solution of **3** (1.10 mmol) in toluene (5.0 mL), PCl<sub>3</sub> (0.11 g, 1.30 mmol) was added dropwise, and the resulting mixture was stirred for 15 min at room temperature. Saturated NaHCO<sub>3</sub> was then added carefully, and the whole was stirred for further 5 min. After extraction with CH<sub>2</sub>Cl<sub>2</sub>/H<sub>2</sub>O, the organic layers were washed with brine, concentrated in vacuo, and purified by flash silica gel chromatography to afford the corresponding deoxygenated 2-(4-octen-4-yl)pyridines **4**.



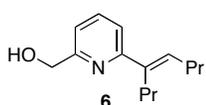
**(E)-2-(4-Octen-4-yl)pyridine (4a).** A colorless oil,  $R_f$  0.60 (hexane–ethyl acetate = 9/1),  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.54 (ddd,  $J = 4.8, 1.8, 0.9$  Hz, 1H), 7.58 (ddd,  $J = 8.0, 6.8, 1.9$  Hz, 1H), 7.35 (ddd,  $J = 8.0, 2.0, 1.0$  Hz, 1H), 7.08 (ddd,  $J = 7.4, 4.9, 1.1$  Hz, 1H), 6.21 (t,  $J = 7.4$  Hz, 1H), 2.61 (t,  $J = 7.7$  Hz, 2H), 2.24 (q,  $J = 7.4$  Hz, 2H), 1.51 (sext,  $J = 7.4$  Hz, 2H), 1.42 (sext,  $J = 7.5$  Hz, 2H), 0.98 (t,  $J = 7.3$  Hz, 3H), 0.92 (t,  $J = 7.3$  Hz, 3H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  159.8, 148.6, 139.5, 136.0, 132.1, 121.0, 120.2, 30.9, 30.2, 22.9, 22.2, 14.22, 14.18; HMRS (FAB+) Calcd for  $\text{C}_{13}\text{H}_{19}\text{N}$ :  $M^+$ , 189.1517. Found:  $m/z$  189.1525.



**(E)-2-(4-Octen-4-yl)-6-methylpyridine (4b).** A colorless oil,  $R_f$  0.40 (hexane–ethyl acetate = 9:1),  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.48 (t,  $J = 7.6$  Hz, 1H), 7.13 (d,  $J = 7.9$  Hz, 1H), 6.95 (d,  $J = 7.7$  Hz, 1H), 6.22 (t,  $J = 7.3$  Hz, 1H), 2.60 (t,  $J = 7.6$  Hz, 2H), 2.54 (s, 3H), 2.23 (q,  $J = 7.4$  Hz, 2H), 1.50 (sext,  $J = 7.4$  Hz, 2H), 1.41 (sext,  $J = 7.5$  Hz, 2H), 0.98 (t,  $J = 7.4$  Hz, 3H), 0.92 (t,  $J = 7.3$  Hz, 3H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  159.3, 157.1, 139.7, 136.1, 131.6, 120.5, 117.2, 30.9, 30.5, 24.9, 23.0, 22.2, 14.3, 14.2; HMRS (FAB+) Calcd for  $\text{C}_{14}\text{H}_{21}\text{N}$ :  $M^+$ , 203.1674. Found:  $m/z$  203.1676.



**Synthesis of (E)-2(4-octen-4-yl)-6-(propen-1-yl)pyridine (5).**<sup>3</sup> To a solution of **3aa** (1.0 mmol) in THF (5 mL) were added allyl(trimethyl)silane (0.40 g, 2.5 mmol) and a 1.0 M solution of  $\text{Bu}_4\text{NF}$  in THF (0.10 mL, 0.10 mmol) at 0 °C, and the resulting mixture was stirred at 0–5 °C for 2 hours. The whole was diluted with  $\text{CH}_2\text{Cl}_2$ , and the organic layers were washed with brine, dried over anhydrous  $\text{Na}_2\text{SO}_4$ , and concentrated in vacuo. The residue was purified by flash chromatography on silica gel (hexane–ethyl acetate as an eluent) to give the title compound (0.12 g, 51%) as a colorless oil,  $R_f$  0.65 (hexane–ethyl acetate = 9/1).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.51 (t,  $J = 7.7$  Hz, 1H), 7.18 (d,  $J = 7.9$  Hz, 1H), 7.01 (d,  $J = 7.7$  Hz, 1H), 6.79 (dq,  $J = 15.4, 6.8$  Hz, 1H), 6.50 (dq,  $J = 14.1, 1.6$  Hz, 1H), 6.27 (t,  $J = 7.4$  Hz, 1H), 2.63 (t,  $J = 7.7$  Hz, 2H), 2.25 (q,  $J = 7.5$  Hz, 2H), 1.94 (dd,  $J = 6.7, 1.8$  Hz, 3H), 1.58–1.38 (m, 4H), 0.99 (t,  $J = 7.4$  Hz, 3H), 0.94 (t,  $J = 7.3$  Hz, 3H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  159.1, 154.6, 139.7, 136.3, 131.6, 131.5, 129.9, 118.2, 118.0, 30.9, 30.3, 23.0, 22.3, 18.4, 14.4, 14.2; HMRS (FAB+) Calcd for  $\text{C}_{16}\text{H}_{23}\text{N}$ :  $M^+$ , 229.1830. Found:  $m/z$  229.1836.



**Synthesis of (E)-2-hydroxymethyl-6-(4-octen-4-yl)pyridine (6).**<sup>4</sup> Trifluoroacetic anhydride (0.24 mL, 1.63 mmol) was added dropwise to **3ba** (70 mg, 0.33 mmol). The resulting orange mixture was stirred for 30 min at room temperature, and then refluxed for further 30 min. After cooling the mixture to room temperature, a saturated  $\text{NaHCO}_3$  aqueous solution was added slowly until the solution indicated pH 8, then stirred for 5 min. The mixture was extracted with  $\text{CH}_2\text{Cl}_2$ , and the combined organic layers were washed with brine, dried over anhydrous  $\text{Na}_2\text{SO}_4$ , and concentrated in vacuo. The residue was purified by flash chromatography on silica gel to afford **6** (58 mg, 81%) as a colorless oil,  $R_f$  0.35 (hexane–ethyl acetate = 1:1).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.60 (t,  $J = 7.7$  Hz, 1H), 7.30 (d,  $J = 7.9$  Hz, 1H), 7.00 (d,  $J = 7.7$  Hz, 1H), 6.29 (t,  $J = 7.4$  Hz, 1H), 4.73 (s, 2H), 4.60–4.40 (br, 1H), 2.62 (t,  $J = 7.2$  Hz, 2H), 2.25 (q,  $J = 7.0$  Hz, 2H), 1.58–1.38 (m, 4H), 0.99 (t,  $J = 7.3$  Hz, 3H), 0.94 (t,  $J = 7.4$  Hz, 3H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  158.2, 156.8, 138.9, 136.8, 132.5, 118.5, 117.6, 63.5, 30.9, 30.2, 23.0, 22.3, 14.3, 14.2; HMRS (FAB+) Calcd for  $\text{C}_{14}\text{H}_{21}\text{NO}$ :  $M^+$ , 219.1623. Found:  $m/z$  219.1615.

## References

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2. L.-C. Campeau, S. Rousseaux, K. Fagnou, *J. Am. Chem. Soc.* **2005**, *127*, 18020.

3. H. Vorbruggen, K. Krolikiewicz, *Tetrahedron Lett.* **1983**, 9, 889.
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7109-74-3

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

File: 7109-74-3-Fvr+2PrCCPr-clean-H

Mercury-400BB "m400"

Relax. delay 1.500 sec

Pulse 45.0 degrees

Acq. time 3.502 sec

Width 5995.2 Hz

16 repetitions

OBSERVE H1, 399.9480258 MHz

DATA PROCESSING

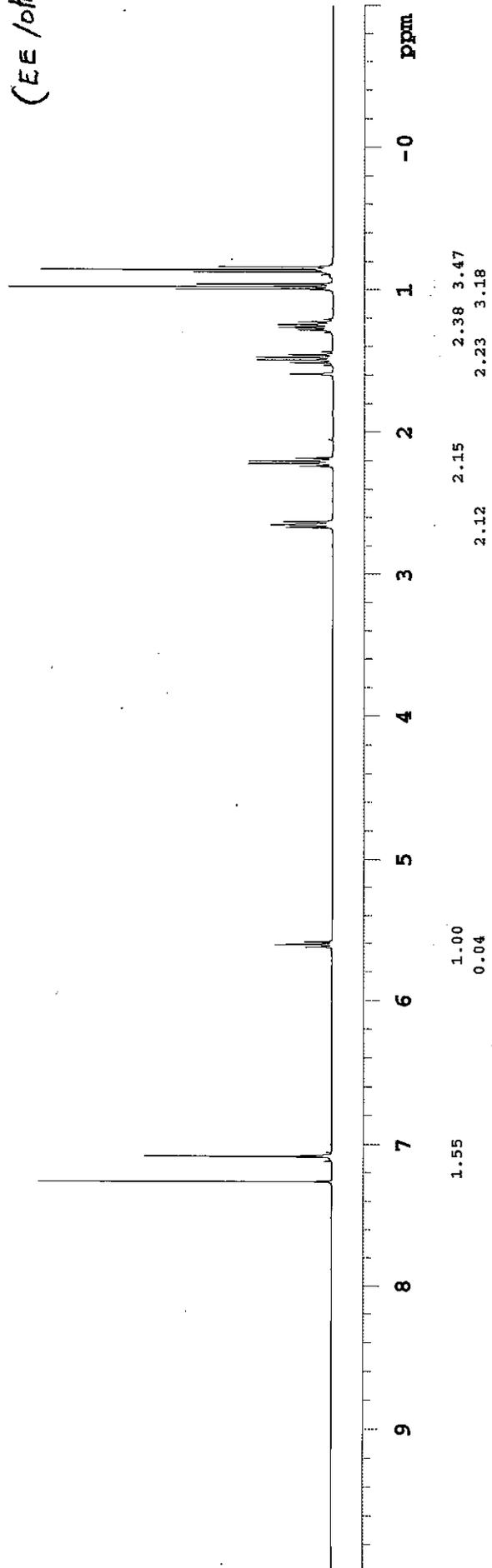
Line broadening 0.2 Hz

FT size 65536

Total time 2 min, 4 sec



3'aa  
(EE / OTHERS = 96:4)



7109-74-3-pyrNO-2PrCCPr-C

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

File: 7109-74-3-PyrNO-2PrCCPr-C

Mercury-400BB "M400"

Relax. delay 0.801 sec

Pulse 45.0 degrees

Acq. time 1.199 sec

Width 25125.6 Hz

68 repetitions

OBSERVE C13, 100.5670285 MHz

DECOUPLE H1, 399.9500406 MHz

Power 36 dB

continuously on

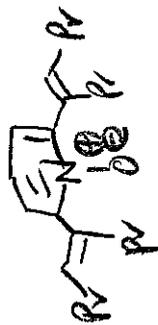
WALTZ-16 modulated

DATA PROCESSING

Line broadening 1.0 Hz

Ft size 65536

Total time 1 hr, 39 min, 10 sec



3'aa

(EE / others = 96:4)

14.035  
14.065  
21.766  
22.605  
29.521  
30.062

76.680  
77.000  
77.313

124.433  
125.249  
134.109  
136.831

152.813

180 160 140 120 100 80 60 40 20 0 ppm

6805-74-3-2mepic-PrCCPr-H

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

File: 6805-74-3-2mepic-PrCCPr-1H

Mercury-400BB "m400"

Relax. delay 1.500 sec

Pulse 45.0 degrees

Acq. time 3.502 sec

Width 5995.2 Hz

16 repetitions

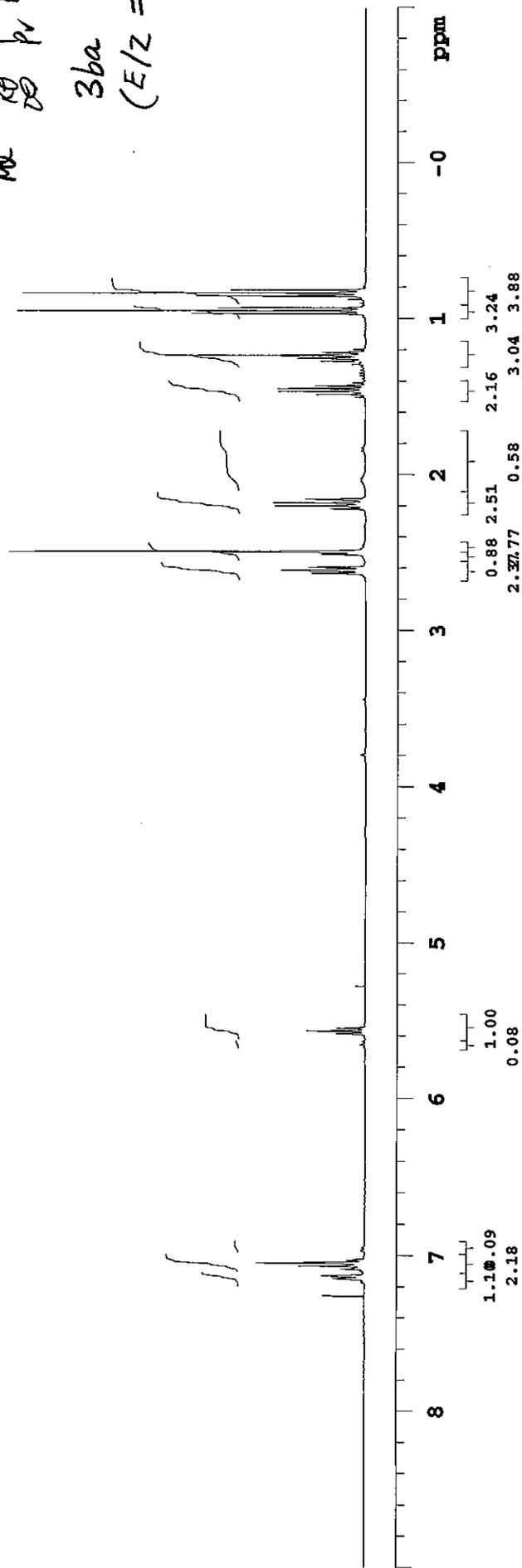
OBSERVE H1, 399.9480275 MHz

DATA PROCESSING

Line broadening 0.2 Hz

FT size 65536

Total time 2 min, 4 sec



13C OBSERVE

Pulse Sequence: s2pul

Solvent: CDC13

Ambient temperature

Mercury-400BE "m400"

Relax. delay 0.801 sec

Pulse 45.0 degrees

Acq. time 1.199 sec

Width 25125.6 Hz

113 repetitions

OBSERVE C13, 100.5670331 MHZ

DECOUPLE H1, 399.9500406 MHZ

Power 36 dB

continuously on

WALTZ-16 modulated

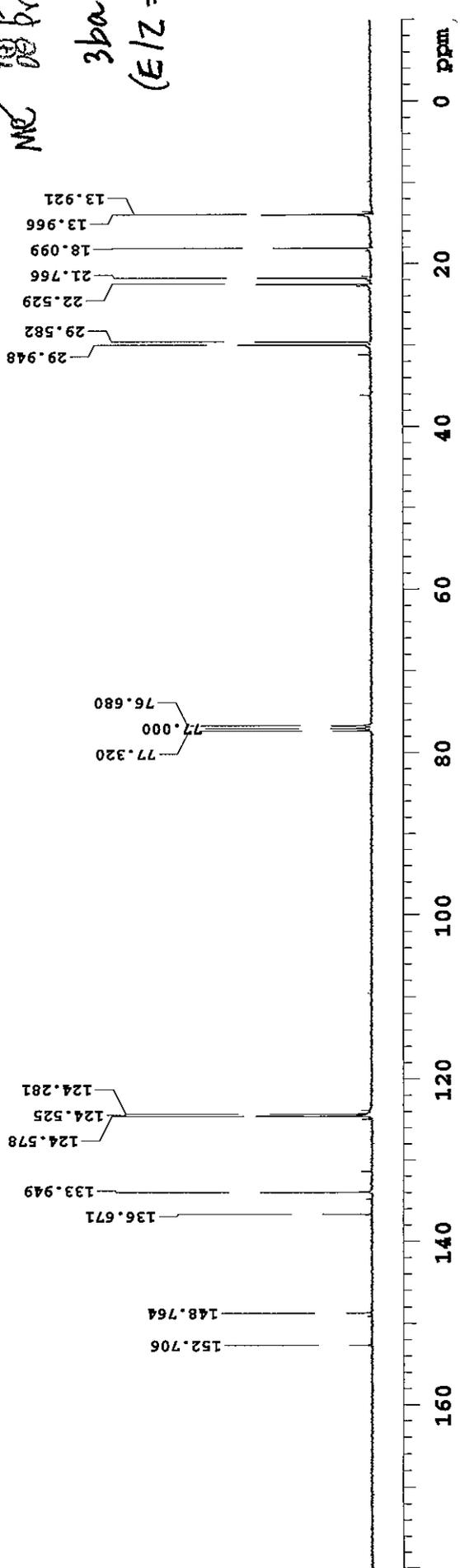
DATA PROCESSING

Line broadening 1.0 Hz

FF size 65536

Total time 1 hr, 39 min, 10 sec

NR  
3ba  
(E/Z = 93:7)



7416-74-4-pg42-H

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

Mercury-400BB "m400"

Relax. delay 1.500 sec

Pulse 45.0 degrees

Acq. time 3.502 sec

Width 5995.2 Hz

16 repetitions

OBSERVE H1, 399.9480254 MHz

DATA PROCESSING

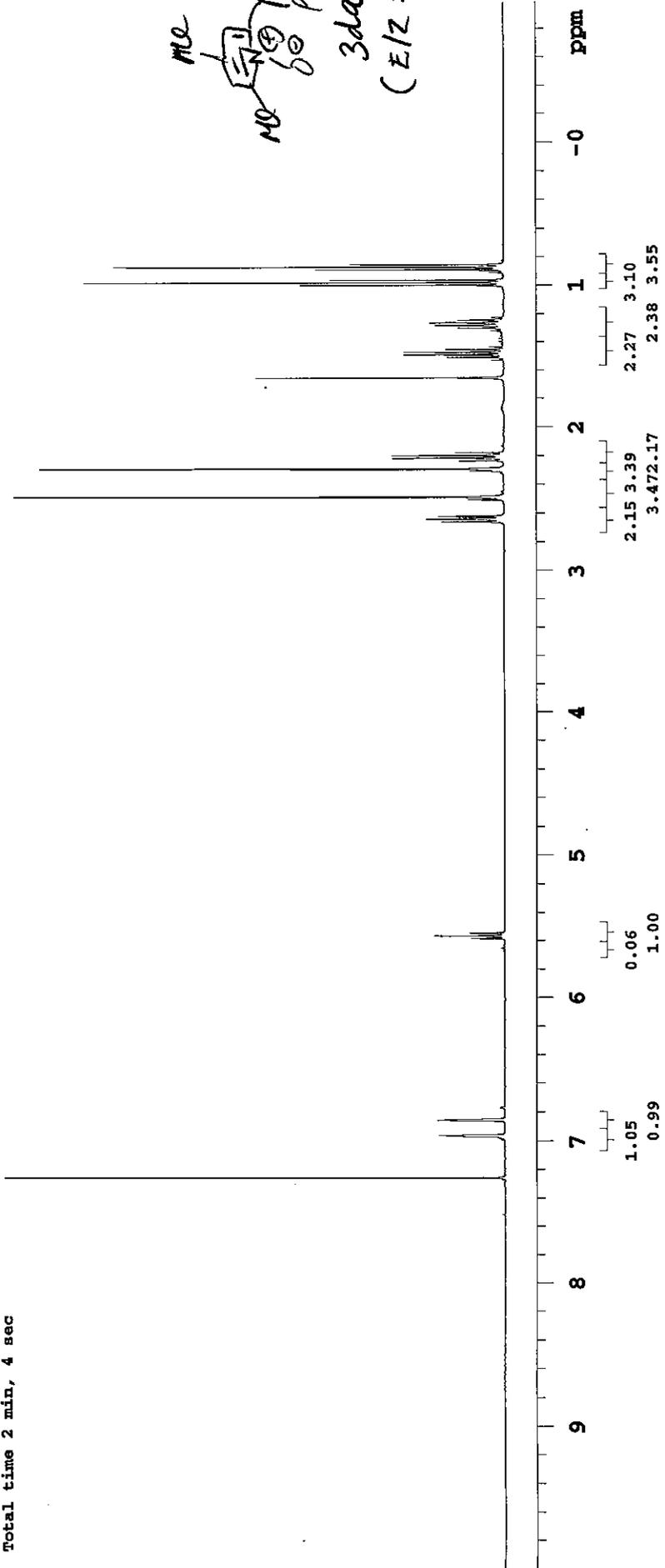
Line broadening 0.2 Hz

FT size 65536

Total time 2 min, 4 sec



3da  
(E/Z = 94:6)



7416-74-P942-C

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

Mercury-400BB "m400"

Relax. delay 0.801 sec

Pulse 45.0 degrees

Acq. time 1.199 sec

Width 25125.6 Hz

1024 repetitions

OBSERVE C13, 100.5670200 MHz

DECOUPLE H1, 399.9500406 MHz

Power 36 dB

continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening 1.0 Hz

Ft size 65536

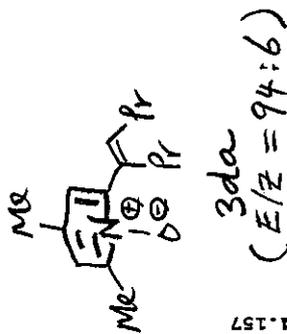
Total time 56 min, 12 sec

77.320  
77.000  
76.687

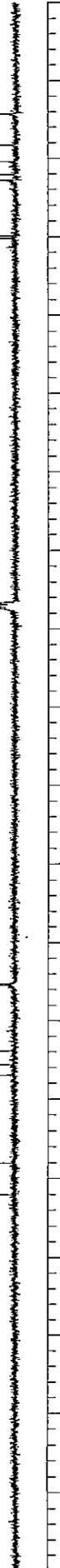
136.969  
135.619  
133.865  
125.432  
125.204

152.073  
148.055

30.146  
29.849  
22.758  
22.003  
20.341  
18.206  
14.203  
14.157



180 160 140 120 100 80 60 40 20 ppm



6z19-74-3-pg132-H

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

Mercury-400BB "m400"

Relax. delay 1.500 sec

Pulse 45.0 degrees

Acq. time 3.502 sec

Width 5995.2 Hz

16 repetitions

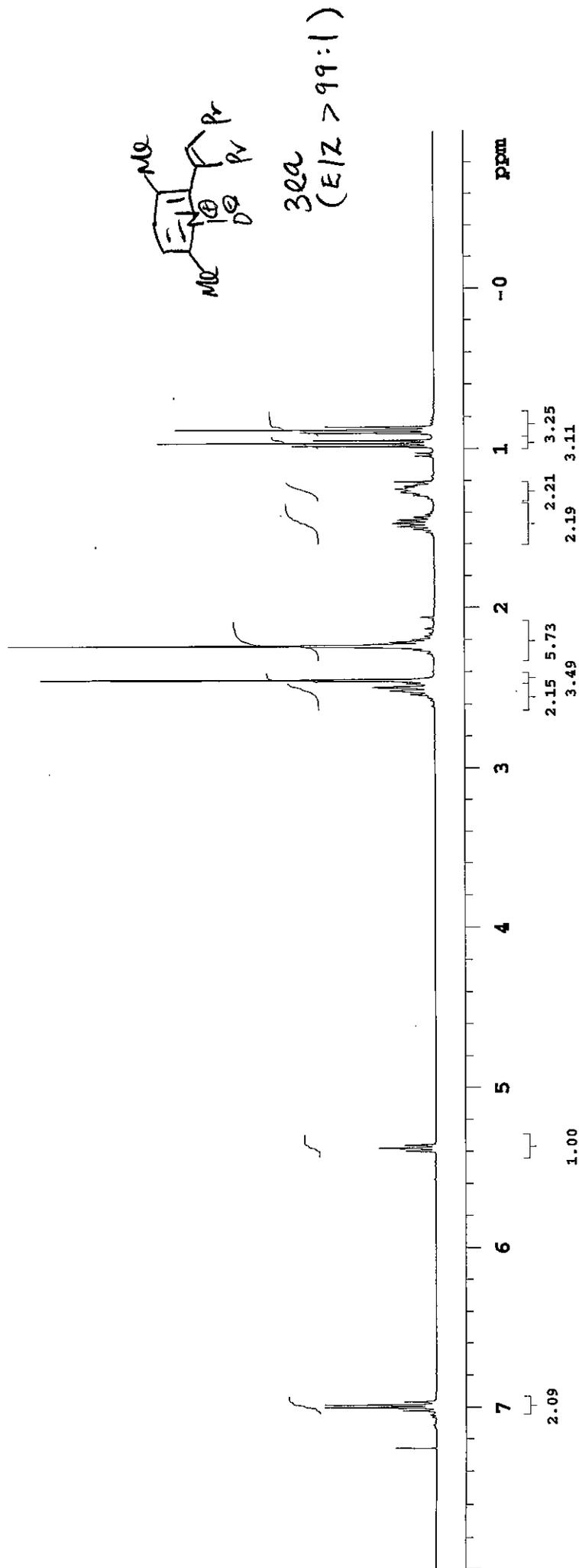
OBSERVE H1, 399.9480262 MHz

DATA PROCESSING

Line broadening 0.2 Hz

FT size 65536

Total time 2 min, 4 sec



13C OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

Mercury-400BB "m400"

Relax. delay 0.801 sec

Pulse 45.0 degrees

Acq. time 1.199 sec

Width 25125.6 Hz

111 repetitions

OBSERVE C13, 100.5670246 MHz

DECOUPLE H1, 399.9500406 MHz

Power 36 dB

continuously on

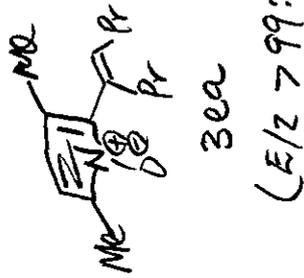
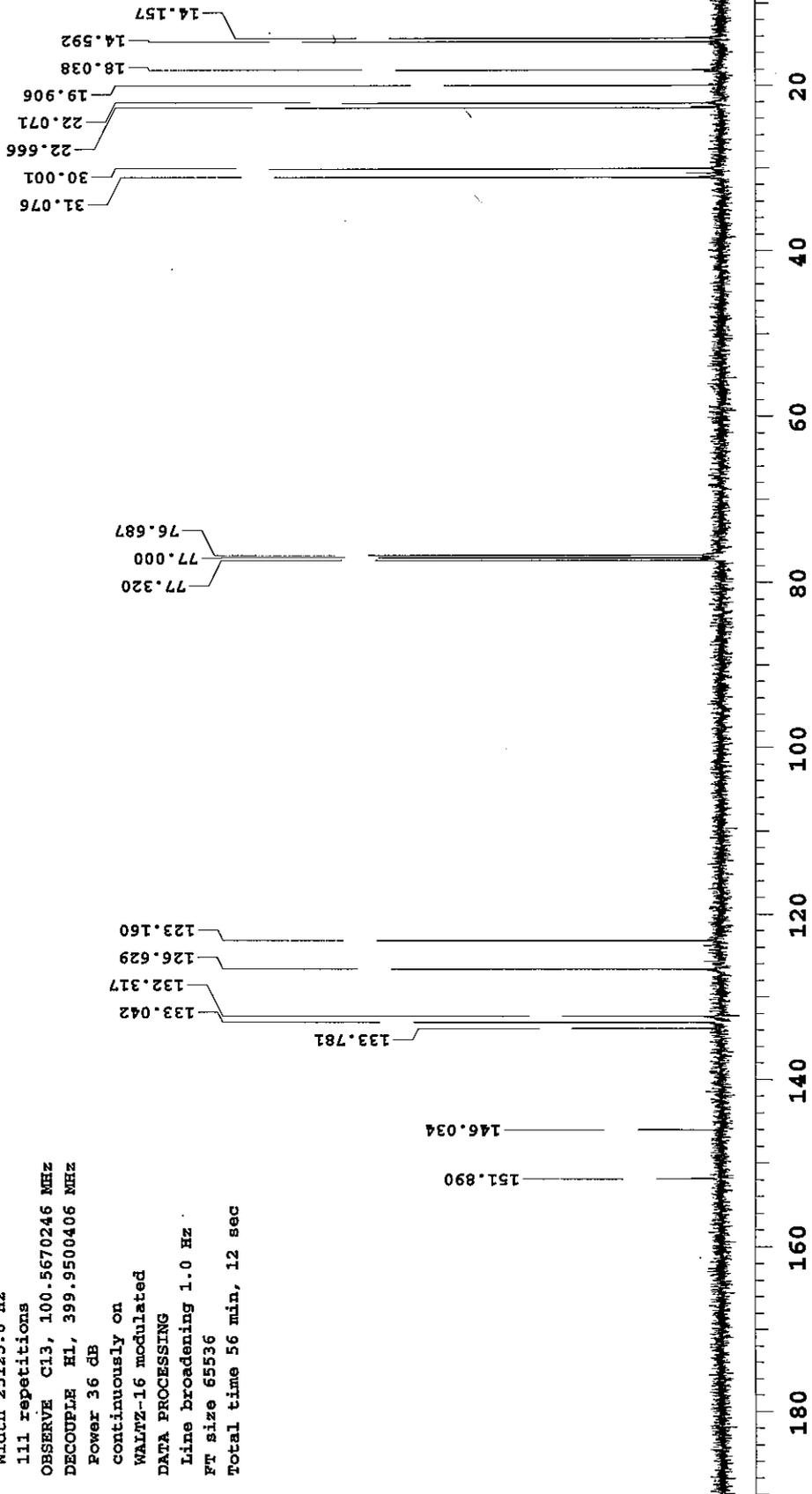
WALTZ-16 modulated

DATA PROCESSING

Line broadening 1.0 Hz

FT size 65536

Total time 56 min, 12 sec



6818-74-3-pg31-2-H

Pulse Sequence: s2pu1

Solvent: CDCl3

Ambient temperature

Mercury-400BB "m400"

Relax. delay 1.500 sec

Pulse 45.0 degrees

Acq. time 3.502 sec

Width 5995.2 Hz

16 repetitions

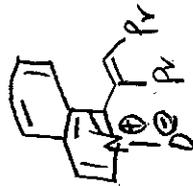
OBSERVE H1, 399.9480256 MHz

DATA PROCESSING

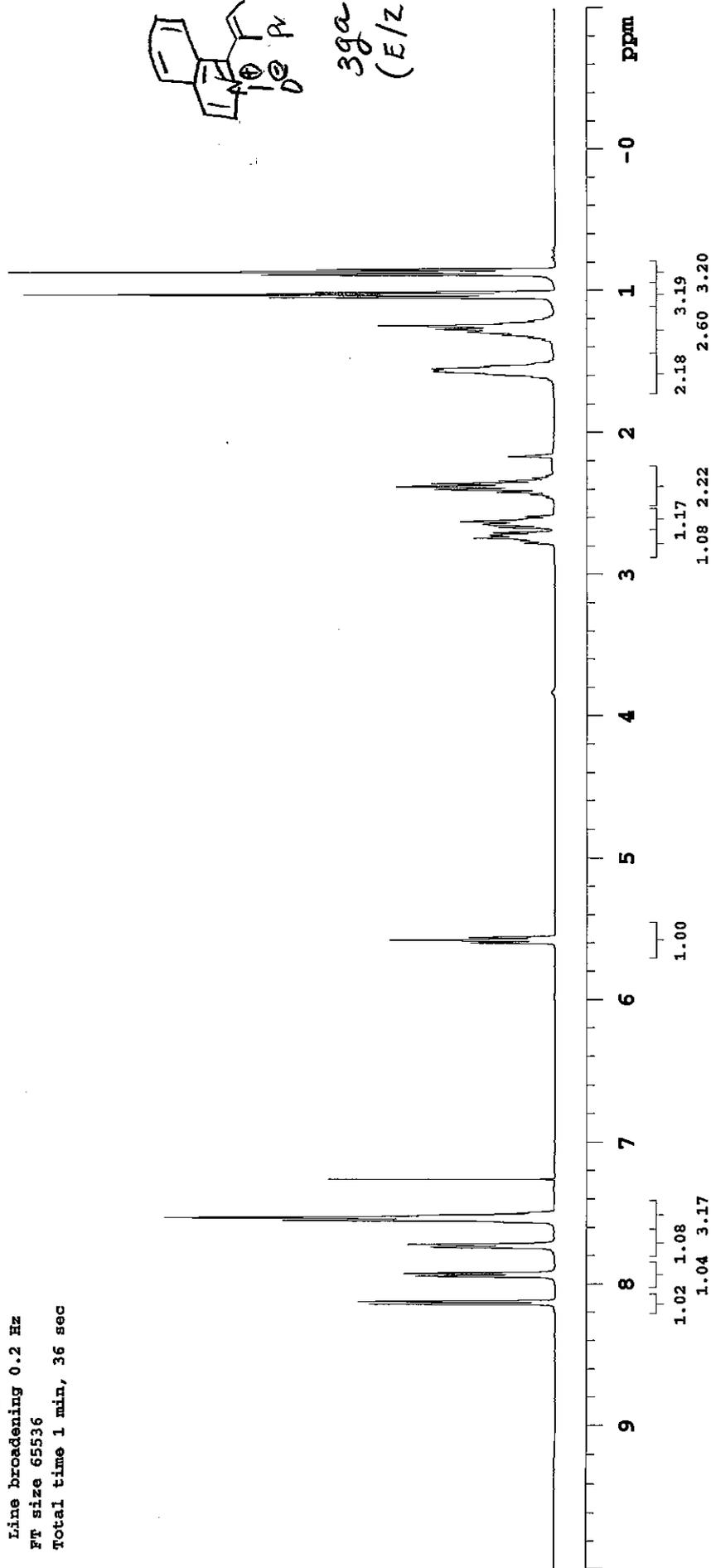
Line broadening 0.2 Hz

Ft size 65536

Total time 1 min, 36 sec



3ga  
(E/Z > 99:1)



13C OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

Mercury-400BE "m400"

Relax. delay 0.801 sec

Pulse 45.0 degrees

Acq. time 1.199 sec

Width 25125.6 Hz

156 repetitions

OBSERVE C13, 100.5670239 MHz

DECOUPLE H1, 399.9500406 MHz

Power 36 dB

continuously on

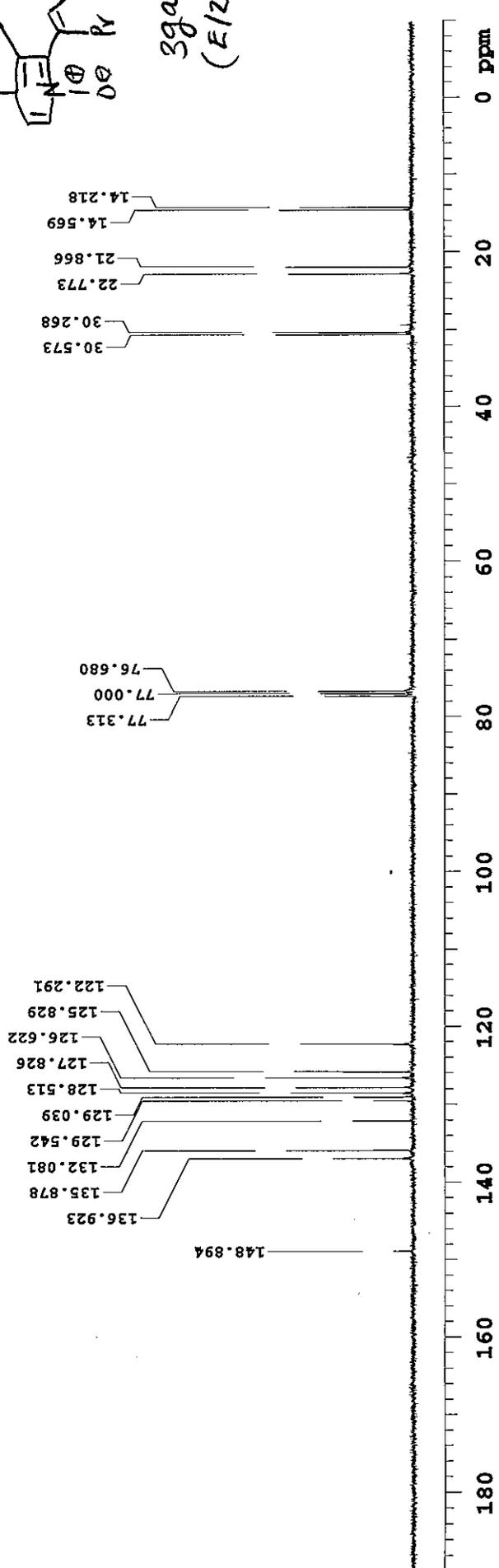
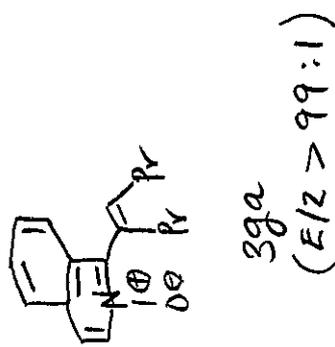
WALTZ-16 modulated

DATA PROCESSING

Line broadening 1.0 Hz

FT size 65536

Total time 56 min, 12 sec



STANDARD 1H OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

Mercury-400BB "m400"

Relax. delay 1.500 sec

Pulse 45.0 degrees

Acq. time 3.502 sec

Width 5995.2 Hz

16 repetitions

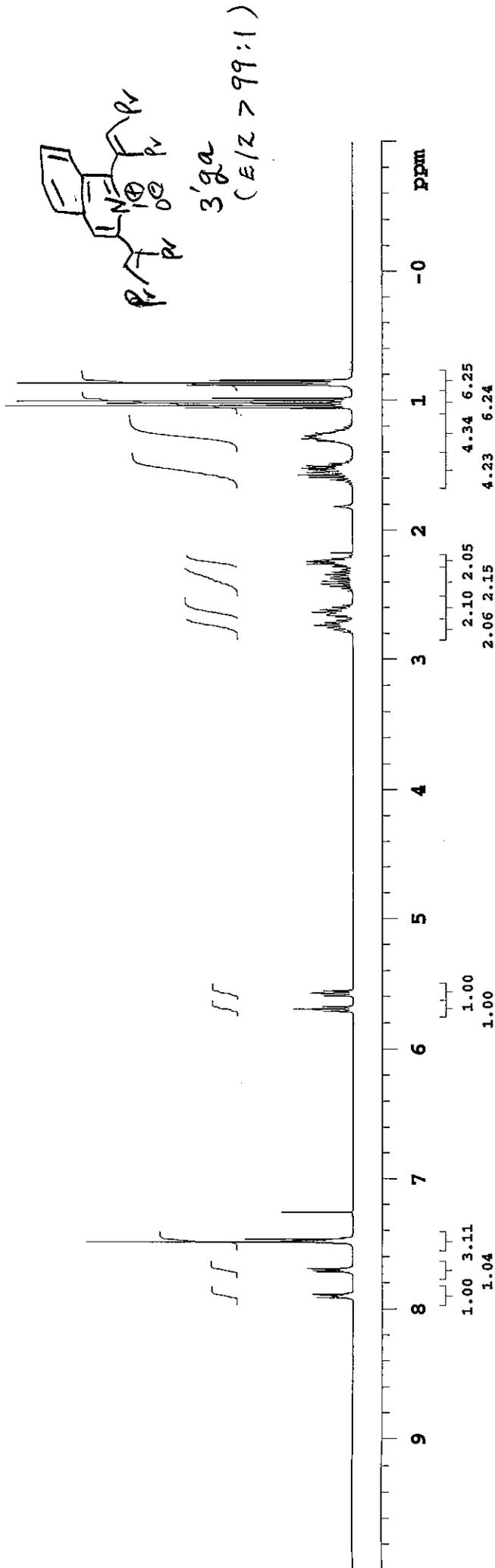
OBSERVE H1, 399.9480256 MHz

DATA PROCESSING

Line broadening 0.2 Hz

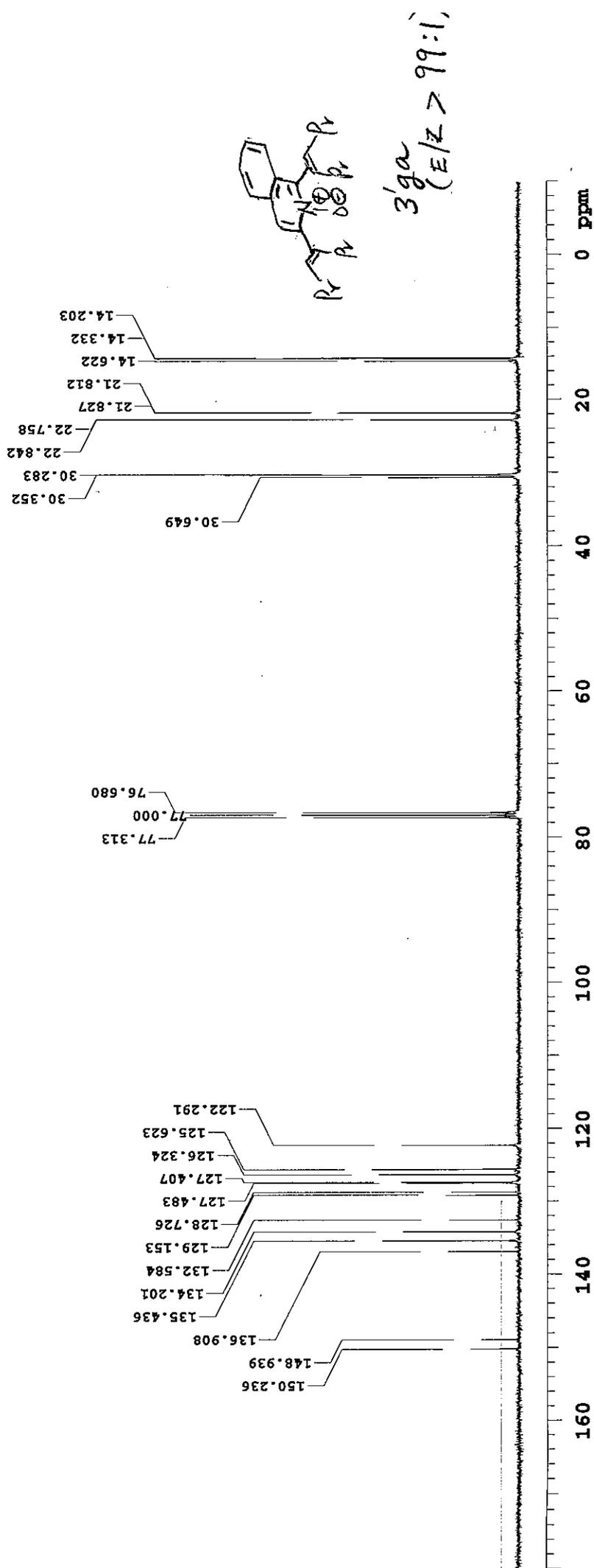
FT size 65536

Total time 1 min, 23 sec



13C OBSERVE

Pulse Sequence: s2pul



STANDARD 1H OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

File: 6815-74-3-pg25-H

Mercury-400BB "m400"

Relax. delay 1.500 sec

Pulse 45.0 degrees

Acq. time 3.502 sec

Width 5995.2 Hz

9 repetitions

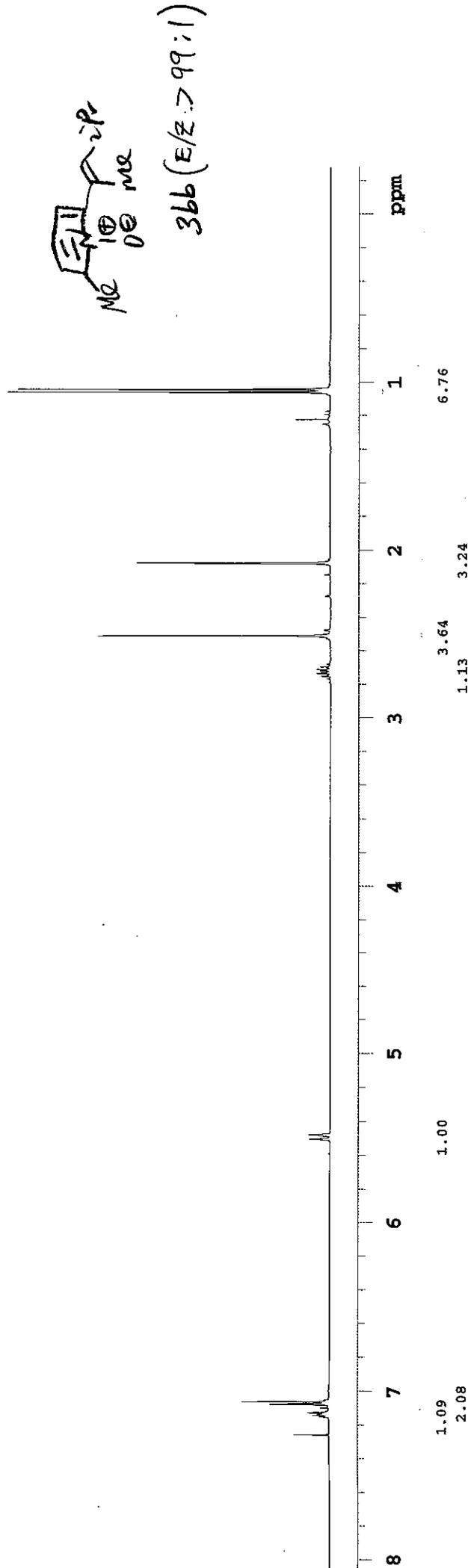
OBSERVE H1, 399.9480256 MHz

DATA PROCESSING

Line broadening 0.2 Hz

FT size 65536

Total time 2 min, 4 sec



13C OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

Mercury-400BB "m400"

Relax. delay 0.801 sec

Pulse 45.0 degrees

Acq. time 1.199 sec

Width 25125.6 Hz

465 repetitions

OBSERVE C13, 100.5670216 MHz

DECOUPLE H1, 399.9500406 MHz

Power 36 dB

continuously on

WALTZ-16 modulated

DATA PROCESSING

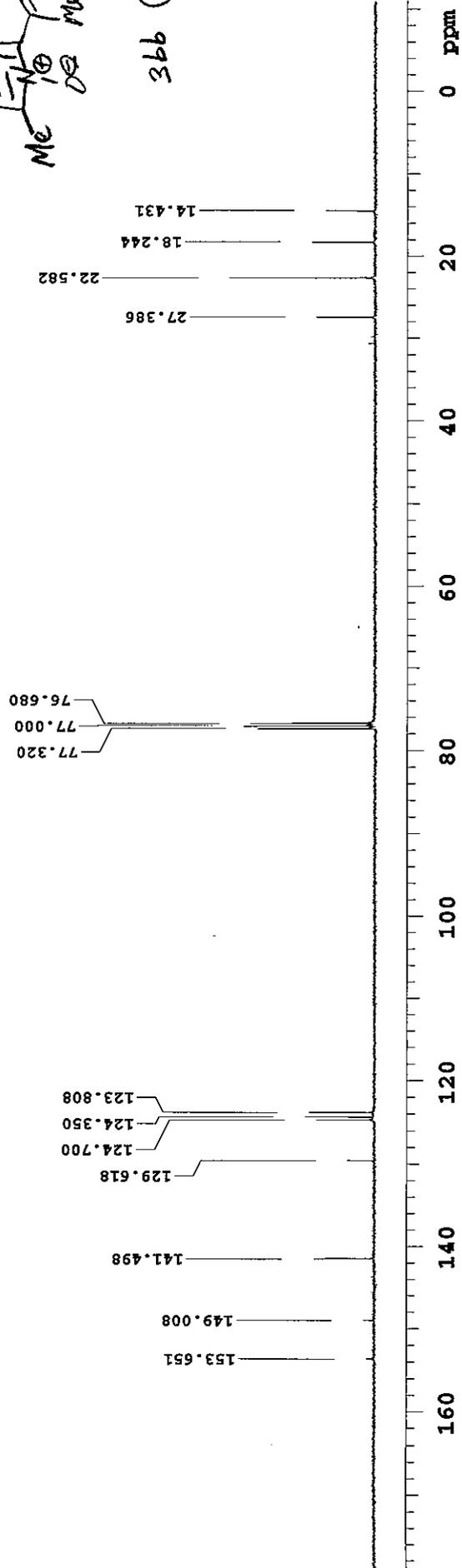
Line broadening 1.0 Hz

FT size 65536

Total time 56 min, 12 sec



366 (E/Z > 99:1)



deoxidation

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

File: 6x20-74-3-Fyr-ErCCPr-Hclean

Mercury-400BB "m400"

Relax. delay 1.500 sec

Pulse 45.0 degrees

Acq. time 3.502 sec

Width 5995.2 Hz

16 repetitions

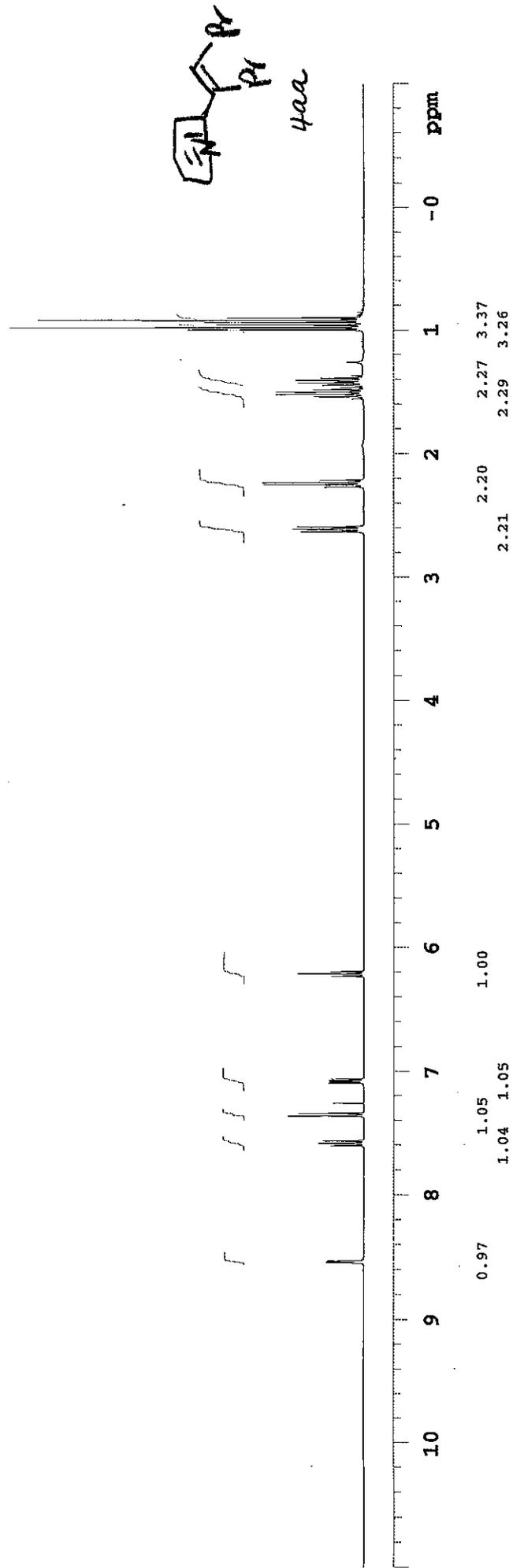
OBSERVE H1, 399.9480256 MHz

DATA PROCESSING

Line broadening 0.2 Hz

FT size 65536

Total time 2 min, 4 sec

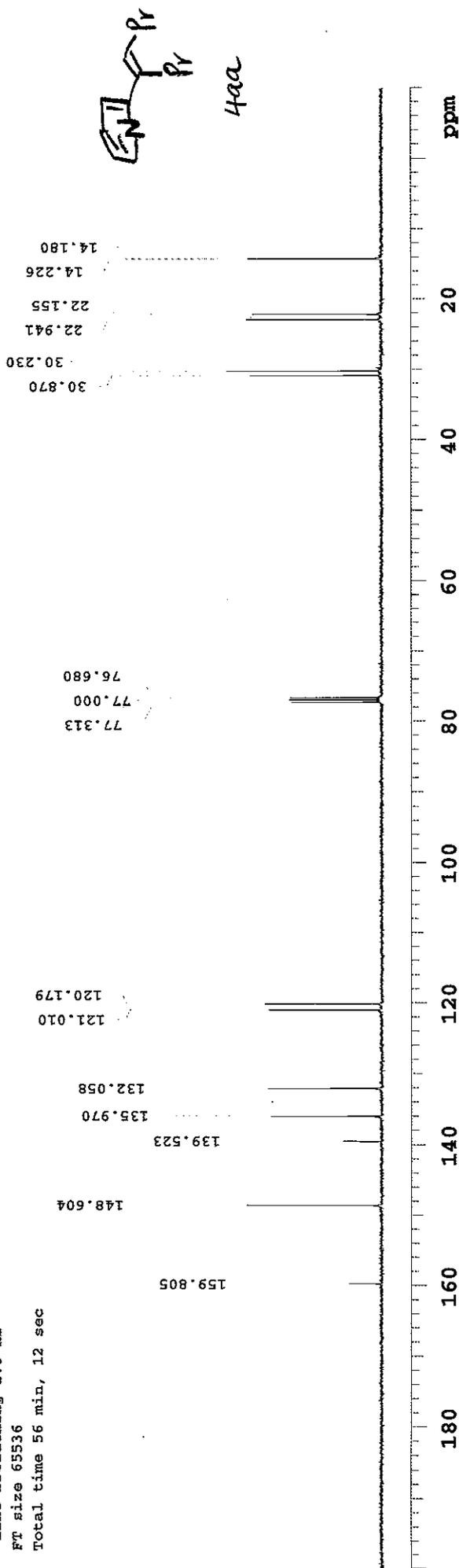


13C OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl3  
Ambient temperature  
File: 6z20-74-3-Pyr-PrCCPr-Cclean  
Mercury-400BE "m400"

Relax. delay 0.801 sec  
Pulse 45.0 degrees  
Acq. time 1.199 sec  
Width 25125.6 Hz  
165 repetitions  
OBSERVE C13, 100.5670223 MHz  
DECOUPLE H1, 399.9500406 MHz  
Power 36 dB  
continuously on  
WALTZ-16 modulated  
DATA PROCESSING  
Line broadening 1.0 Hz  
Ft size 65536  
Total time 56 min, 12 sec



<sup>1</sup>H OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

File: 7119-74-3-deoxygenation-2picpyrNO-PrCCPr-H

Mercury-400BB "m400"

Relax. delay 1.500 sec

Pulse 45.0 degrees

Acq. time 3.502 sec

Width 5995.2 Hz

16 repetitions

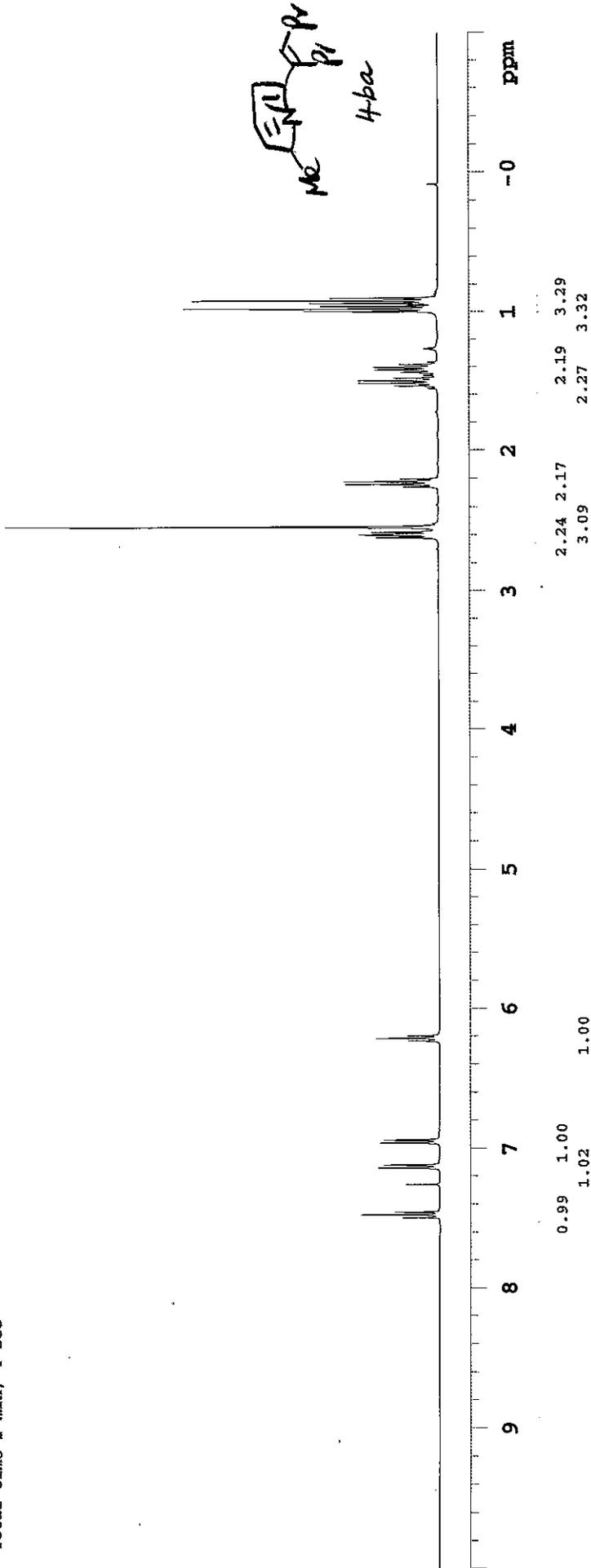
OBSERVE F1, 399.9480256 MHz

DATA PROCESSING

Line broadening 1.0 Hz

FT size 65536

Total time 2 min, 4 sec



deoxygenation

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

File: 7119-74-3-deoxyg-2picNO-PrCCPr-C

Mercury-400BB "m400"

Relax. delay 0.801 sec

Pulse 45.0 degrees

Acq. time 1.199 sec

Width 25125.6 Hz

192 repetitions

OBSERVE C13, 100.5670208 MHz

DECOUPLE H1, 399.9500406 MHz

Power 36 dB

continuously on

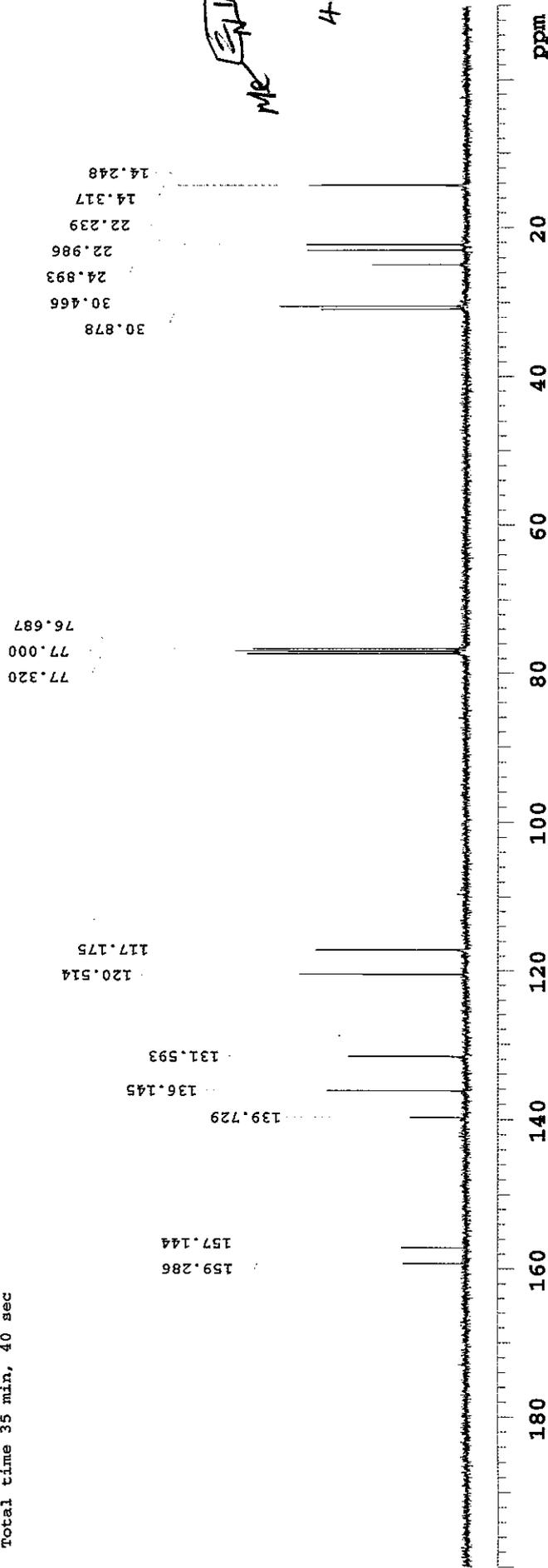
WALTZ-16 modulated

DATA PROCESSING

Line broadening 1.0 Hz

FT size 65536

Total time 35 min, 40 sec



7126-74-3-2picNO-PrCCPr+Me3siallyl-H

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

File: 7126-74-3-2picNO-PrCCPr-Me3siallyl-H

Mercury-400BB "M400"

Relax. delay 1.500 sec

Pulse 45.0 degrees

Acq. time 3.502 sec

Width 5995.2 Hz

16 repetitions

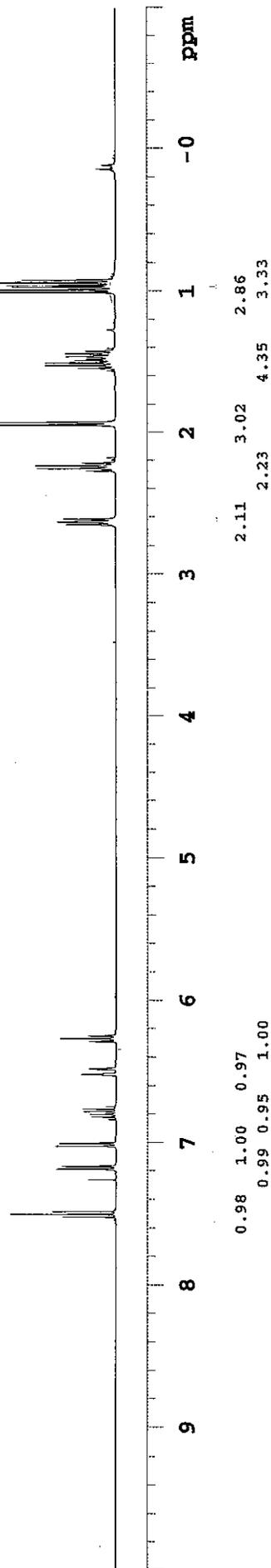
OBSERVE H1, 399.9480258 MHz

DATA PROCESSING

Line broadening 0.2 Hz

Ft size 65536

Total time 2 min, 4 sec



13C OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

File: 7126-74-3-PyrNO-PrCCPr+Me3Siallyl-C

Mercury-400BB "m400"

Relax. delay 0.801 sec

Pulse 45.0 degrees

Acq. time 1.199 sec

Width 25125.6 Hz

219 repetitions

OBSERVE C13, 100.5670223 MHz

DECOUPLE H1, 399.9500406 MHz

Power 36 dB

continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening 1.0 Hz

FT size 65536

Total time 56 min, 12 sec

30.901  
30.329  
22.994  
22.331  
18.434  
14.393  
14.233

77.320  
77.000  
76.687

117.960  
118.196

131.624  
131.540  
129.931

136.290  
139.744

159.096  
154.612



7117-74-3-pg159-H

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

Mercury-400BB "m400"

Relax. delay 1.500 sec

Pulse 45.0 degrees

Acq. time 3.502 sec

Width 5995.2 Hz

16 repetitions

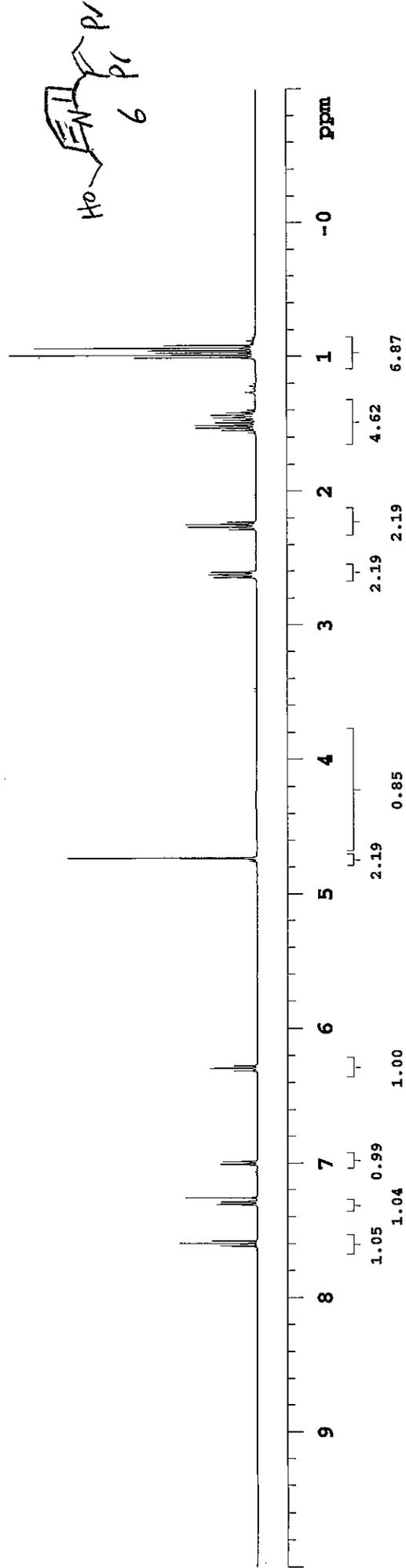
OBSERVE H1, 399.9480254 MHz

DATA PROCESSING

Line broadening 0.2 Hz

FT size 65536

Total time 2 min, 4 sec



7117-74-3-pgi59-C

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

Mercury-400BE "m400"

Relax. delay 0.801 sec

Pulse 45.0 degrees

Acq. time 1.199 sec

Width 25125.6 Hz

156 repetitions

OBSERVE C13, 100.5670208 MHz

DECOUPLE H1, 399.9500406 MHz

Power 36 dB

continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening 1.0 Hz

FT size 65536

Total time 56 min, 12 sec

