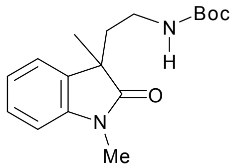
Synthetic studies on vincorine: access to 3a,8a-dialkyl-1,2,3,3a,8,8a-hexahydropyrrolo[2,3-b]indole skeleton

Yoshizumi Yasui, Tomoyo Kinugawa and Yoshiji Takemoto*

SUPPORTING INFORMATION

General. Unless otherwise noted, all reactions were performed under argon. $Pd(PPh_3)_4$ was prepared by using the reported protocol.[1] Analytical thin-layer chromatography was performed with Merck Silica gel 60 and Merck 25 DC-Alufolein. Flash silica gel column chromatography was performed with Kanto Silica gel 60 (spherical, 63-210 μm). Proton nuclear magnetic resonance (^1H NMR) spectra were recorded on a JEOL JNM-ECA500 KP at 500 MHz. Chemical shifts are reported relative to Me_4Si (δ 0.00) and toluene-d_8 (δ, 7.09). Multiplicity is indicated by one or more of the following: s (singlet); d (doublet); t (triplet); q (quartet); m (multiplet); br (broad). Carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on a JEOL JNM-ECA500 KP at 126 MHz. Chemical shifts are reported relative to $CDCl_3$ (δ, 77.2) and toluene-d_8 (δ, 20.4). Unless otherwise noted, all NMR spectra were recorded at room temperature. Infrared spectra were recorded on a FT/IR-410 (JASCO). Low resolution mass spectra (LRMS) were recorded on a SHIMADZU PARVUM 2 mass spectrometer or on a JEOL JMS-HX211A.

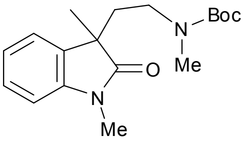


Carbamate 15: $NaBH_4$ (1.84 g, 48.8 mmol) was added to a mixture of (1,3-dimethyl-2-oxoindolin-3-yl)acetonitrile[2] (1.95 g, 9.75 mmol), Boc_2O (8.50 g, 39 mmol), and $CoCl_2 \cdot 6H_2O$ (5.80 g, 24.4 mmol) in MeOH (30 mL) at 0 °C. After stirring for 2 hr at room temperature, H_2O, brine, 0.1 M aqueous ethylenediamine tetraacetic acid, and 1.0 M aqueous K_2CO_3 was added. The aqueous layer was extracted with AcOEt, and the combined organic layers were washed with brine and dried over Na_2SO_4. Removal of the solvent under reduced pressure afforded the crude product, which was purified by

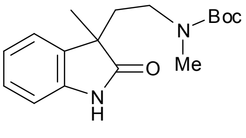
---

[1] Coulson, D. R. *Inorg. Synth.* **1972**, *13*, 121.
[2] Yasui, Y.; Kamisaki, H.; Takemoto, Y. *Org. Lett.* **2008**, *15*, 3303.

silica gel column chromatography (hexane/AcOEt = 10/0→5/5) to give oxindole **15** (2.45 g, 83%) as a colorless oil. Rf 0.38 (silica, hexane/AcOEt = 6/4); ^{1}H NMR (δ, $CDCl_3$) 7.27 (dd, $J_1 = J_2 = 7.5$ Hz, 1H), 7.21 (d, $J = 7.5$ Hz, 1H), 7.08 (dd, $J_1 = J_2 = 7.5$ Hz, 1H), 6.84 (d, $J_1 = 7.5$ Hz, 1H) 4.52 (br s, 1H), 3.21 (s, 3H), 2.95–2.72 (m, 2H), 2.16–1.93 (m, 2H), 1.38 (s, 9H), 1.37 (s, 3H); ^{13}C NMR (δ, $CDCl_3$) 180.5, 155.7, 143.1, 133.3, 128.1, 122.9, 122.8, 108.3, 79.1, 47.1, 37.7, 37.0, 28.5, 26.4, 24.2; IR (NaCl) 3352, 2974, 1703 cm^{-1}; LRMS (FAB$^+$) *m/z* = 305 (M+H$^+$); Anal. Calced for $C_{17}H_{24}N_2O_3$: C, 67.08; H, 7.95; N, 9.20. Found: C, 66.84; H, 8.10; N, 8.90.



Oxindole 13: To a solution of oxindole **15** (2.25 g, 7.40 mmol) in THF (25 mL) was added NaH (ca 60% purity, 444 mg, 11 mmol) at 0 °C. After stirring for 30 min, MeI (0.60 mL, 1.4 g, 9.6 mmol) was added. The reaction mixture was stirred for 7 hr at room temperature, and saturated aqueous $NaHCO_3$ was added. The mixture was extracted with AcOEt, and the combined organic layers were washed with brine and dried over Na_2SO_4. Removal of the solvent under reduced pressure afforded the crude product, which was purified by silica gel column chromatography (hexane/AcOEt = 10/0→5/5) to give oxindole **13** (2.15 g, 91%) as a colorless oil. Rf 0.45 (silica, hexane/AcOEt = 6/4); ^{1}H NMR (δ, $CDCl_3$) 7.27–7.21 (m, 2H), 7.08 (dd, $J_1 = J_2 = 7.5$ Hz, 1H), 6.85 (br s, 1H), 3.22 (s, 3H), 3.12 (br s)*, 2.86–2.69 (m, 5H), 2.14–1.93 (m, 2H), 1.39 (s, 9H), 1.38 (s, 3H); ^{13}C NMR (δ, $CDCl_3$) 180.2, 179.9, 155.5, 143.1, 133.3, 128.0, 122.7, 122.6, 108.2, 79.4, 46.8, 45.1, 44.8, 35.9, 35.1, 34.2, 28.5, 26.3, 24.2; IR (NaCl) 2973, 1697 cm^{-1}; LRMS (FAB$^+$) *m/z* = 319 (M+H$^+$); Anal. Calced for $C_{18}H_{26}N_2O_3$: C, 67.90; H, 8.23; N, 8.80. Found: C, 67.63; H, 8.01; N, 8.67. (* Peak of minor rotamer)

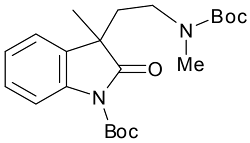


Oxindole S1[3]: A solution of carbamate **13** (404 mg, 1.27 mmol) and benzoylperoxide (include ca. 25% water, 1.2 g, 3.8 mmol) in CH_2Cl_2 (12 mL) was heated in a sealed tube for 20 hr at 80 °C. After concentrating the reaction mixture, a solution of 2.0 M NH_3 in

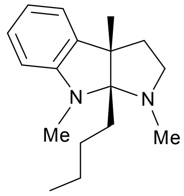
---

[3] (a) Nakatsuka, S.; Asano, O.; Goto, T. *Heterocycles* **1986**, *24*, 2791. (b) van Henegouwen, W. G. B.; Fieseler, R. M.; Rutjes, F. P. J. T.; Hiemstra, H. *J. Org. Chem.* **2000**, *65*, 8317.

MeOH (20 mL) was added, and the mixture was stirred for 18 hr at room temperature. After concentrating the reaction mixture, saturated aqueous $NaHCO_3$ was added. The mixture was extracted with AcOEt, and the combined organic layers were washed with brine and dried over Na_2SO_4. Removal of the solvent under reduced pressure afforded the crude product, which was purified by silica gel column chromatography (hexane/AcOEt = 10/0→5/5) to give oxindole **S1** (235 mg, 61%) as a colorless oil. Rf 0.48 (silica, hexane/AcOEt = 5/5); ^{1}H NMR (δ, $CDCl_3$) 8.95 (br s, 1H), 8.83 (br s)*, 7.20 (br s, 2H), 7.05 (dd, $J_1 = J_2 = 7.5$ Hz, 1H), 6.94 (br s, 1H), 3.15 (br s)*, 2.89 (br s, 2H), 2.75 (br s, 3H), 2.71 (br s)*, 2.15–1.97 (m, 2H), 1.41 (s, 3H), 1.39 (s, 9H); ^{13}C NMR (δ, $CDCl_3$) 183.0, 182.7, 155.6, 140.5, 140.4, 133.8, 128.1, 123.2, 122.9, 122.7, 110.2, 79.6, 79.4, 47.4, 45.2, 44.9, 35.9, 35.1, 34.3, 28.6, 24.3; IR (NaCl) 3247, 2974, 1710 cm^{-1}; LRMS (FAB$^+$) *m/z* = 305 (M+H$^+$); Anal. Calced for $C_{17}H_{24}N_2O_3$: C, 67.08; H, 7.95; N, 9.20. Found: C, 66.84; H, 7.96; N, 8.87. (* Peak of minor rotamer)



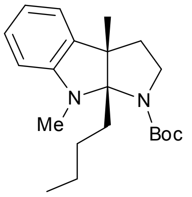
Imide 9: A mixture of oxindole **S1** (180 mg, 0.592 mmol), Na_2CO_3 (365 mg, 3.44 mmol), and Boc_2O (313 mg, 1.43 mmol) in THF (5.0 mL) was refluxed for 5 hr. The solid was filtered off, and the filtrate was concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexane/AcOEt = 10/0→7/3) to give imide **9** (221 mg, 92%) as a colorless oil. Rf 0.42 (silica, hexane/AcOEt = 8/2); ^{1}H NMR (δ, $CDCl_3$) 7.85 (br s, 1H), 7.29–7.16 (m, 3H), 3.13 (br s)*, 2.86 (br s, 2H), 2.72 (br s, 3H), 2.26–2.11 (m, 1H), 2.11–1.89 (m, 1H), 1.65 (s, 9H), 1.43 (s, 3H), 1.39 (s, 9H); ^{13}C NMR (δ, $CDCl_3$) 178.9, 178.5, 155.5, 149.4, 139.1, 132.1, 128.3, 124.7, 122.8, 122.5, 115.2, 84.4, 79.5, 47.2, 45.1, 36.7, 35.8, 34.4, 34.1, 28.5, 28.2, 25.4, 22.8; IR (NaCl) 2977, 2251, 1766, 1730, 1697 cm^{-1}; LRMS (FAB$^+$) *m/z* = 405 (M+H$^+$); Anal. Calced for $C_{22}H_{32}N_2O_5$: C, 65.32; H, 7.97; N, 6.93. Found: C, 65.41; H, 8.00; N, 6.84.



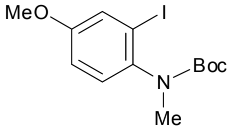
Hexahydropyrroindole 12 from imide 9: To a solution of imide **9** (135mg, 0.334 mmol) and LiCl (75.6 mg, 1.73 mmol) in toluene (4.0 mL) was added *n*-BuLi in hexane (1.6 M, 0.43 mL, 0.69 mmol) at –78 °C. After stirring for 15 min, saturated aqueous $NaHCO_3$ was added. The mixture was warmed to room temperature, and the aqueous layer was extracted with AcOEt. The combined organic layers were washed with brine and dried over Na_2SO_4. Removal of the solvent under reduced pressure afforded the crude product, which was subjected to silica gel chromatography (hexane/AcOEt = 10/0→8/2) to give a colorless oil. To a solution of this oil in CH_2Cl_2 (2.5 mL) was added TFA (0.11 mL, 170 mg, 1.5 mmol) at 0 °C. After stirring at room temperature for 30 min, saturated aqueous $NaHCO_3$ was added, and the mixture was extracted with AcOEt. The combined organic layers were washed with brine and dried over Na_2SO_4. Removal of the solvent under reduced pressure afforded the crude product. To a solution of the crude mixture and MeI (0.050 mL, 114 mg, 0.80 mmol) in toluene (2.5 mL) was added a solution of KHMDS in toluene (0.50 M, 0.78 mL, 0.39 mmol) at 0 °C. After stirring for 12 hr at room temperature, H_2O was added, and the mixture was extracted with AcOEt. The combined organic layers were washed with brine and dried over Na_2SO_4. Removal of the solvent under reduced pressure afforded the crude product, which was purified by silica gel column chromatography (hexane/AcOEt = 10/0→0/10) to give pyrroindole **12** (21.6 mg, 26%) as a colorless oil.

Hexahydropyrroindole 12 from carbamate 13 (two-pot method): To a solution of carbamate **13** (198 mg, 0.621 mmol) and LiCl (181 mg, 3.91 mmol) in THF (3.5 mL) was added *n*-BuLi in hexane (1.6 M, 1.0 mL, 1.6 mmol) at –78 °C. After stirring for 15 min, H_2O was added, and the mixture was extracted with AcOEt. The combined organic layers were washed with brine and dried over Na_2SO_4. Removal of the solvent under reduced pressure afforded the crude product. To a solution of the crude mixture in CH_2Cl_2 (3.0 mL) was added TFA (0.180 mL, 276 mg, 2.48 mmol) at 0 °C. After stirring for 2 hr at room temperature, saturated aqueous $NaHCO_3$ was added, and the mixture was extracted with AcOEt. The combined organic layers were washed with brine and dried over Na_2SO_4. Removal of the solvent under reduced pressure afforded the crude product, which was purified by silica gel column chromatography (hexane/AcOEt = 10/0→0/10) to give pyrroindole **12** (140 mg, 87%) as a colorless oil.

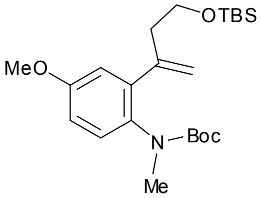
Hexahydropyrroindole 12 from carbamate 13 (one-pot method): To a solution of carbamate **13** (151 mg, 0.480 mmol) and LiCl (135 mg, 2.88 mmol) in THF (3.0 mL) was added a solution of *n*-BuLi in hexane (1.6 M, 0.73 mL, 1.2 mmol) at –78 °C. After stirring for 15 min, the reaction mixture was warmed to 0 °C, and farther *n*-BuLi in hexane (1.6 M, 0.870 mL, 1.44 mmol) was added. After stirring for 5 min, H_2O was added, and mixture was extracted with AcOEt. The combined organic layers were washed with brine and dried over Na_2SO_4. Removal of the solvent under reduced pressure afforded the crude product, which was purified by silica gel column chromatography (hexane/AcOEt = 10/0→0/10) to give pyrroindole **12** (112 mg, 92%) as a colorless oil. ^{1}H NMR (δ, $CDCl_3$) 7.04 (dd, $J_1 = J_2$ = 7.5 Hz, 1H), 6.93 (d, J = 7.5 Hz, 1H), 6.58 (dd, $J_1 = J_2$ = 7.5 Hz, 1H), 6.21 (d, J_1 = 7.5 Hz, 1H), 2.87 (s, 3H), 2.79–2.76 (m, 1H), 2.45 (s, 3H), 2.43–2.39 (m, 1H), 2.03 (ddd, J_1 = 15.5 Hz, J_2 = 12.0 Hz, J_3 = 5.0 Hz, 1H), 1.91–1.84 (m, 2H), 1.71 (ddd, J_1 = 15.5 Hz, J_2 = 12.0 Hz, J_3 = 4.5 Hz, 1H), 1.46 (s, 3H), 1.33–1.26 (m, 2H), 1.26–1.16 (m, 1H), 1.07–0.99 (m, 1H), 0.86 (t, J = 7.5 Hz, 3H); ^{13}C NMR (δ, $CDCl_3$) 152.0, 136.3, 127.8, 121.5, 116.1, 103.1, 94.2, 55.1, 52.7, 42.3, 36.0, 32.5, 31.4, 25.9, 24.2, 23.6, 14.2; Rf 0.28 (silica, hexane/AcOEt = 5/5); IR (NaCl) 2955, 1604, 1495 cm^{-1}; LRMS (FAB$^+$) *m/z* = 258 (M$^+$); Anal. Calced for $C_{17}H_{26}N_2$: C, 79.02; H, 10.14; N, 10.84. Found: C, 78.86; H, 9.99; N, 10.81.



Hexahydropyrroindole 16: To a solution of oxindole **15** (256 mg, 0.842 mmol) and LiCl (348 mg, 8.21 mmol) in THF (3.0 mL) was added *n*-BuLi in hexane (1.6 M, 2.0 mL, 3.4 mmol) at –78 °C. After stirring for 2 hr, saturated aqueous $NaHCO_3$ was added. The mixture was warmed to room temperature, and extracted with AcOEt. The combined organic layers were washed with brine and dried over Na_2SO_4. Removal of the solvent under reduced pressure afforded the crude product, which was purified by silica gel column chromatography (hexane/AcOEt = 10/0→9/1) to give pyrroindole **16** (285 mg, 96%) as a colorless oil. Rf 0.85 (silica, hexane/AcOEt = 8/2); ^{1}H NMR (δ, toluene, 100 °C) 7.03 (dd, $J_1 = J_2$ = 7.5 Hz, 1H), 6.81 (d, J = 7.5 Hz, 1H), 6.65 (d, $J_1 = J_2$ = 7.5 Hz, 1H), 6.26 (d, J = 7.5 Hz, 1H), 3.54 (dd, $J_1 = J_2$ = 9.0 Hz, 1H), 3.02 (s, 3H), 3.00–2.92 (m, 2H), 1.93–1.89 (m, 1H), 1.86–1.80(m, 1H), 1.76–1.70(m, 1H), 1.41 (s, 9H), 1.38–1.29 (m, 4H), 1.15 (s, 3H), 0.95 (t, J = 7.5 Hz, 3H); ^{13}C NMR (δ, toluene, 100 °C) 154.5, 150.6, 135.1, 125.1, 121.3, 117.9, 106.2, 92.7, 78.8, 56.6, 47.4, 36.8, 30.9, 30.8, 28.7, 27.5, 23.6, 22.7, 14.2; IR (NaCl) 2961, 2360, 1699 cm^{-1}; LRMS (FAB$^+$) *m/z* = 344 (M$^+$); Anal. Calced for $C_{21}H_{32}N_2O_2$: C, 73.22; H, 9.36; N, 8.13. Found: C, 73.19; H, 9.28; N, 8.21.



Carbamate 18: To a solution of *tert*-butyl 2-iodo-4-methoxyphenylcarbamate[4](1.69 g, 4.86 mmol) in DMF (16 mL) was added a suspension of NaH (55% pure, 303 mg, 6.94 mmol) in DMF (5.0 mL) at 0 °C. After stirring for 30 min, MeI (0.46 mL, 1.0 g, 7.4 mmol) was added. The reaction mixture was stirred for 3 hr at room temperature, and H_2O was added. The mixture was extracted with AcOEt, and the combined organic layers were washed with brine and dried over Na_2SO_4. Removal of the solvent under reduced pressure afforded the crude product, which was purified by silica gel column chromatography (hexane/AcOEt = 10/0→8/2) to give carbamate **18** (1.61 mg, 91%) as a yellow oil. Rf 0.57 (silica, hexane/AcOEt = 8/2); ^{1}H NMR (δ, $CDCl_3$) 7.37 (s)*, 7.35 (s, 1H), 7.16 (d, *J*= 8.5 Hz)*, 7.08 (d, *J*= 8.5 Hz, 1H), 6.88–6.86 (m, 1H), 3.80 (s, 3H), 3.77 (s)*, 3.12 (s)*,3.11 (s, 3H), 1.53 (s)*, 1.36 (s, 9H); ^{13}C NMR (δ, $CDCl_3$) 158.8*, 158.5, 154.7, 139.2, 129.2*, 128.6, 124.5*, 124.1, 115.4*, 115.0, 99.8*, 99.7, 80.5*, 80.1, 55.9*, 55.8, 37.7*, 36.7, 28.6*, 28.4; IR (NaCl) 2975, 1703 cm^{-1}; LRMS (FAB$^+$) *m/z* = 363 (M$^+$); Anal. Calced for $C_{13}H_{18}INO_3$: C, 42.99; H, 5.00; N, 3.86. Found: C, 43.12; H, 4.89; N, 3.84. (* Peak of minor rotamer)

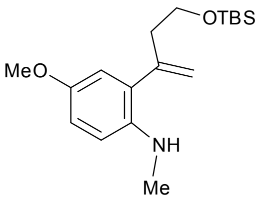


Alkenylaniline 20: To a solution of [(3-bromo-3-butenyl)oxy]-*tert*-butyl dimethylsilane (**19**) (272 mg, 1.33 mmol)[5] in THF (5.0 mL) was added *n*-BuLi in hexane (2.8 M, 0.60 mL, 1.7 mmol) at −78 °C. After stirring the mixture for 45 min at −78 °C, a solution of $ZnCl_2$ (210 mg, 1.54 mmol) in THF (5.0 mL) was added. The reaction mixture was stirred for 15 min at 0 °C, and a solution of iodoaniline **18** (301 mg, 0.829 mmol) in THF (5.0 mL) and $Pd(PPh_3)_4$ (105 mg, 0.0908 mmol) was added. After refluxing for 16 hr, the mixture

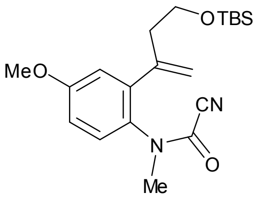
---

[4] Kondo, Y.; Kojima, S.; Sakamoto, T. *J. Org. Chem.* **1997**, *62*, 6507.
[5] Magus, P.; Quagliato, D. *J. Org. Chem.* **1985**, *50*, 1621.

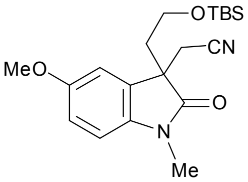
was cooled to room temperature and H_2O was added, and the mixture was extracted with AcOEt. The combined organic layers were washed with brine and dried over Na_2SO_4. Removal of the solvent under reduced pressure afforded the crude product, which was purified by silica gel column chromatography (hexane/AcOEt = 10/0→9/1) to give alkenylaniline **20** (323 mg, 93%) as a colorless oil. Rf 0.85 (silica hexane/AcOEt = 8/2); ^{1}H NMR (δ, $CDCl_3$) 7.09 (d, J = 8.5 Hz)*, 6.97 (d, J = 8.5 Hz, 1H), 6.82–6.70 (m, 2H), 5.17 (s, 1H), 5.05 (s, 1H), 3.80 (s, 3H), 3.67–3.59 (m, 2H), 3.05 (s, 3H), 2.57–2.55 (m, 2H), 1.48 (s)*, 1.34 (s, 9H), 0.88 (s, 9H), 0.00 (s, 6H); ^{13}C NMR (δ, $CDCl_3$) 158.1, 155.5, 146.0, 141.4, 134.1, 129.5, 116.5, 115.1, 113.3, 79.9, 61.8, 55.5, 39.6, 37.5, 28.6, 28.5, 26.1, 18.4, –5.2; IR (NaCl) 2929, 1700 cm^{-1}; LRMS (FAB^+) m/z = 422 ($M+H^+$); Anal. Calcd for $C_{23}H_{39}NO_4Si$: C, 65.52; H, 9.32; N, 3.32. Found: C, 65.41; H, 9.28; N, 3.44. (* Peak of minor rotamer)



Aniline 21: To a solution of TMSOTf (0.750 mL, 4.16 mmol) in CH_2Cl_2 (4.0 mL) was added a solution of alkenylaniline **20** (1.46 g, 3.47 mmol) and 2,6-lutidine (0.610 mL, 5.24 mmol) in CH_2Cl_2 (11 mL) at 0 °C. After stirring for 30 min, the reaction mixture was poured into saturated aqueous $NaHCO_3$. The mixture was extracted with AcOEt, and the combined organic layers were washed with brine and dried over Na_2SO_4. Removal of the solvent under reduced pressure afforded the crude product, which was purified by silica gel column chromatography (hexane/AcOEt = 10/0→9/1) to give aniline **21** (1.10 g, 95%) as a colorless oil. Rf 0.72 (silica, hexane/AcOEt = 8/2); ^{1}H NMR (δ, $CDCl_3$) 6.77 (dd, J_1 = 8.5 Hz, J_2 = 2.9 Hz, 1H), 6.61 (d, J = 2.9 Hz, 1H), 6.55 (d, J = 8.5 Hz, 1H), 5.29 (s, 1H), 5.10 (s, 1H), 3.98 (s, 1H), 3.74 (s, 3H), 3.65 (t, J = 6.3 Hz, 2H), 2.77 (s, 3H), 2.54 (t, J = 6.3 Hz, 2H), 0.89 (s, 9H), 0.03 (s, 6H); ^{13}C NMR (δ, $CDCl_3$) 151.3, 144.6, 141.0, 129.7, 117.2, 115.2, 113.3, 111.0, 61.3, 56.0, 40.8, 31.8, 26.1, 18.5, –5.1; IR (NaCl) 3393, 2929 cm^{-1}; LRMS (FAB^+) m/z = 321 (M^+); Anal. Calced for $C_{18}H_{31}NO_2Si$: C, 67.24; H, 9.72; N, 4.36. Found: C, 67.51; H, 9.68; N, 4.36.



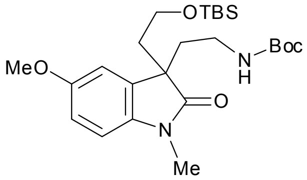
Cyanoformamide 22: To a solution of carbonyl cyanide[6] (ca. 1 M in Et_2O, 15 mL) was added a solution of aniline **21** (358 mg, 1.12 mmol) in Et_2O (3.0 mL) at 0 °C. After stirring for 15 min, the reaction mixture was concentrated under reduced pressure and the obtained residue was purified by silica gel column chromatography (hexane/AcOEt = 10/0→7/3) to give cyanoformamide **22** (408 mg, 97%) as a colorless oil. Rf 0.52 (silica, hexane/AcOEt = 8/2); ^{1}H NMR (δ, $CDCl_3$) 7.14 (d, J = 8.5 Hz, 1H), 7.03 (d, J = 8.5 Hz)*, 6.89 (dd, J_1 = 8.5 Hz, J_2 = 2.9 Hz, 1H), 6.85 (d, J = 2.9 Hz, 1H), 6.81 (d, J = 2.9 Hz)*, 5.34 (s, 1H), 5.25 (s)*, 5.13 (s, 1H), 5.04 (s)*, 3.84 (s, 3H), 3.81(s)*, 3.75–3.66 (m, 2H), 3.49 (s)*, 3.23 (s, 3H), 2.51 (t, J = 6.3 Hz, 2H), 0.87 (s, 9H), 0.02 (s, 6H); ^{13}C NMR (δ, $CDCl_3$) 160.5, 145.7, 143.6, 143.1, 130.0, 129.9, 118.8, 116.3, 114.0, 111.2, 61.3, 55.7, 40.0, 37.0, 26.0, 18.4, –5.2; IR (NaCl) 2929, 1686 cm^{-1}; LRMS (FAB$^+$) = 375 (M+H$^+$); Anal. Calced for $C_{20}H_{30}N_2O_3Si$: C, 64.13; H, 8.07; N, 7.48. Found: C, 64.00; H, 7.91; N, 7.50. (* Peak of minor rotamer)



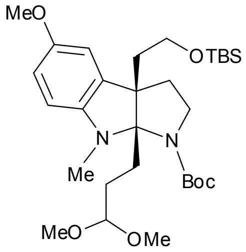
Oxindole 23: A solution of cyanoformamide **22** (444 mg, 1.19 mmol) and $Pd(PPh_3)_4$ (141 mg, 0.122 mmol) in xylene (5.0 mL) was stirred for 30 min at 130 °C, and the mixture was subjected directly to silica gel column chromatography (hexane/AcOEt = 10/0→5/5) to give oxindole **23** (440 mg, 98%) as a colorless oil. Rf 0.35 (silica, hexane/AcOEt = 8/2); ^{1}H NMR (δ, $CDCl_3$) 7.04 (d, J = 2.9 Hz, 1H), 6.87 (dd, J_1 = 8.5 Hz, J_2 = 2.9 Hz, 1H), 6.79 (d, J = 8.5 Hz, 1H), 3.82 (s, 3H), 3.50–3.42 (m, 2H), 3.19 (s, 3H), 2.74 (d, J = 16.5 Hz, 1H), 2.43 (d, J = 16.5 Hz, 1H), 2.26 (ddd, J_1 = 14.0 Hz, J_2 = 8.0 Hz, J_3 = 6.5 Hz, 1H), 2.16 (ddd, J_1 = 14.0 Hz, J_2 = J_3 = 5.0 Hz, 1H), 0.78 (s, 9H), –0.11 (s, 6H); ^{13}C NMR (δ, $CDCl_3$) 176.7, 156.4, 137.1, 130.2, 116.7, 113.7, 111.2, 109.1, 59.2, 56.0, 48.0, 38.0, 26.8, 26.7, 25.9, 18.3, –5.5; IR (NaCl) 2360, 1720 cm^{-1}; LRMS (EI$^+$) m/z = 375 (M+H$^+$); Anal. Calced for $C_{20}H_{30}N_2O_3Si$: C, 64.13; H, 8.07; N, 7.48. Found: C, 63.19; H, 7.68; N, 7.23.

---

[6] Linn, W. J.; Webster, O. W.; Benson, R. E. *J. Am Chem. Soc.* **1965**, *87*, 3651.



Carbamate 24: $NaBH_4$ (448 mg, 11.9 mmol) was added to a solution of oxindole **23** (885 mg, 3.74 mmol), Boc_2O (2.06 g, 9.48 mmol), and $CoCl_2 \cdot 6H_2O$ (1.41 g, 5.95 mmol) in MeOH (23 mL) at 0 °C. After stirring for 2 hr at room temperature, H_2O, brine, 0.1 M aqueous ethylenediamine tetraacetic acid and 1.0 M aqueous K_2CO_3 were added successively. The mixture was extracted with AcOEt, and the combined organic layers were washed with brine and dried over Na_2SO_4. Removal of the solvent under reduced pressure afforded the crude product, which was purified by silica gel column chromatography (hexane/AcOEt = 10/0→5/5) to give oxindole **24** (1.03g, 91%) as a colorless oil. Rf 0.45 (silica $CHCl_3$/AcOEt = 9/1); ^1H NMR (δ, $CDCl_3$) 6.79 (s, 1H), 6.78 (d, J = 8.0 Hz, 1H), 6.71 (d, J = 8.0 Hz, 1H), 4.40 (br s, 1H), 3.80 (s, 3H), 3.38–3.29 (m, 2H), 3.16 (s, 3H), 2.89–2.70 (m, 2H), 2.21 (ddd, J_1 = 14.0, J_2 = J_3 = 7.0, 1H), 2.08 (ddd, J_1 = 14.0, J_2 = J_3 = 7.0 Hz, 1H), 2.01–1.92 (m, 2H), 1.37 (s, 9H), 0.77 (s, 9H), –0.13 (s, 6H); ^{13}C NMR (δ, $CDCl_3$) 178.9, 156.1, 155.6, 137.2, 132.3, 112.1, 110.7, 108.3, 78.8, 59.1, 55.7, 50.0, 40.1, 38.0, 36.4, 28.4, 26.2, 25,8, 18.1, –5.58, –5.62; IR (NaCl) 3352, 2929, 1703 cm^{-1}; LRMS (FAB^+) m/z = 478 (M^+); Anal. Calced for $C_{25}H_{42}N_2O_5Si$: C, 62.73; H, 8.84; N, 5.85. Found: C, 62.74; H, 9.05; N, 5.72.

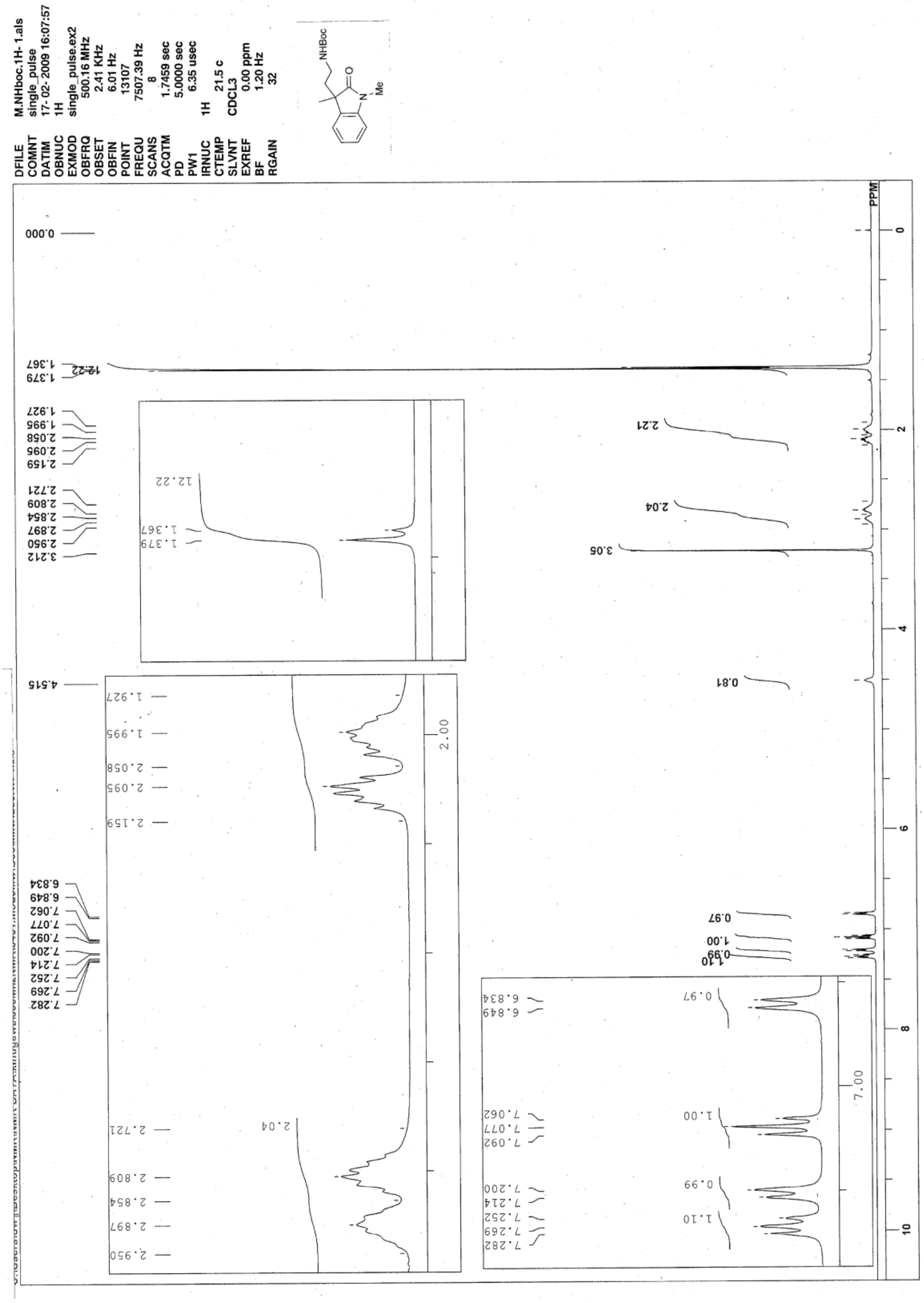


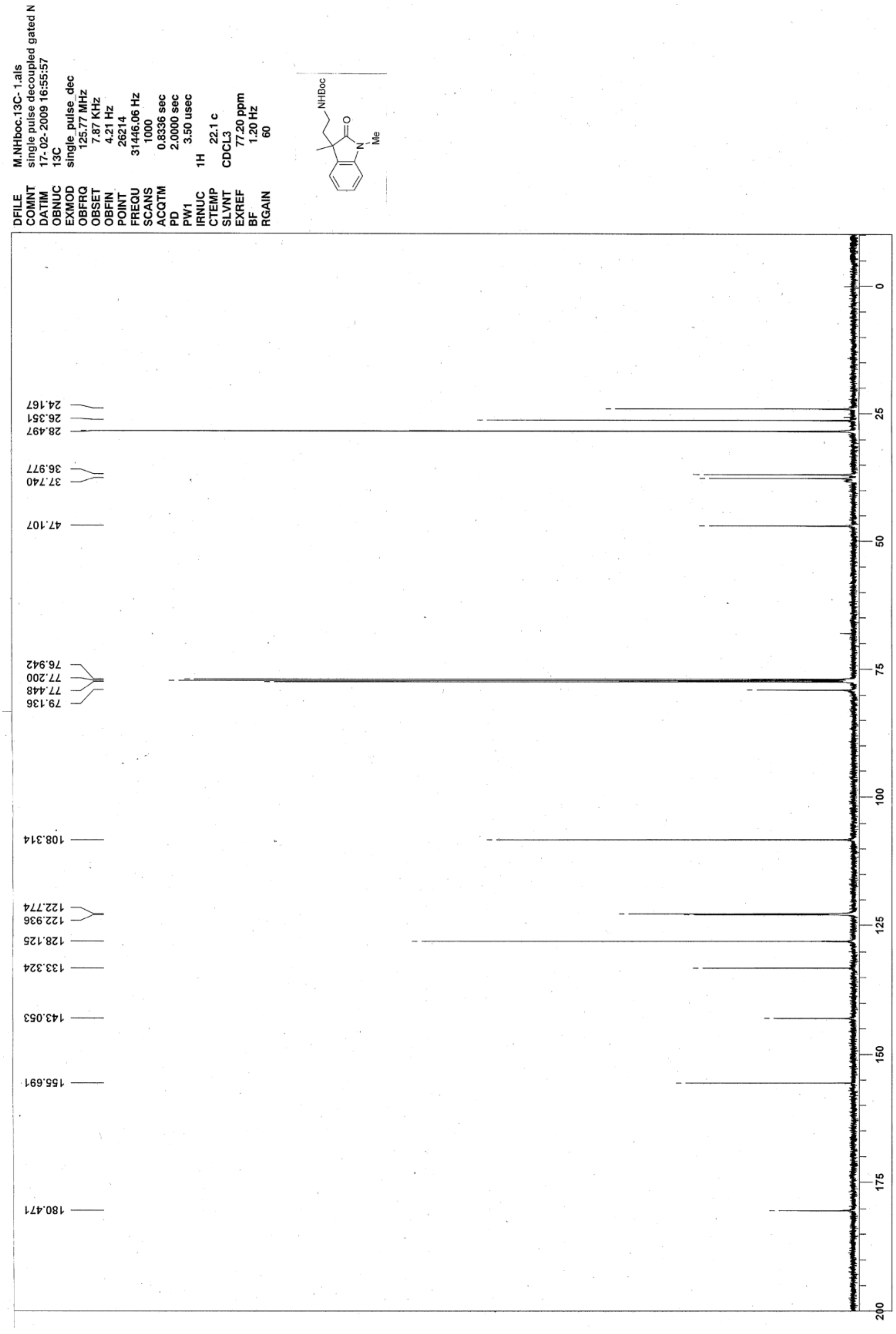
Pyrroloindole 25: To a solution of 3,3-dimethoxypropyl bromide[7] (1.25 g, 6.83 mmol) in Et_2O was added t-BuLi in pentane (1.8 M, 7.7 mL, 13.9 mmol) at –78 °C. After Stirring for 10 min at –78 °C, the reaction mixture was slowly warmed to 0 °C. The solvent was evaporated at 0 °C and THF (5.0 mL) was added. The concentration of the alkyl lithium in this reaction mixture was determined to be 0.80 M by titration. At –78 °C, to a solution of oxindole **24** (256 mg, 0.842 mmol) and LiCl (348 mg, 8.21 mmol) in THF (3.0 mL) was added the solution of 3,3-dimethoxypropyl lithium in THF (0.80 M, 2.6 mL, 2.1 mmol) that prepared above. After stirring for 16 hr at –60 °C, saturated aqueous

---

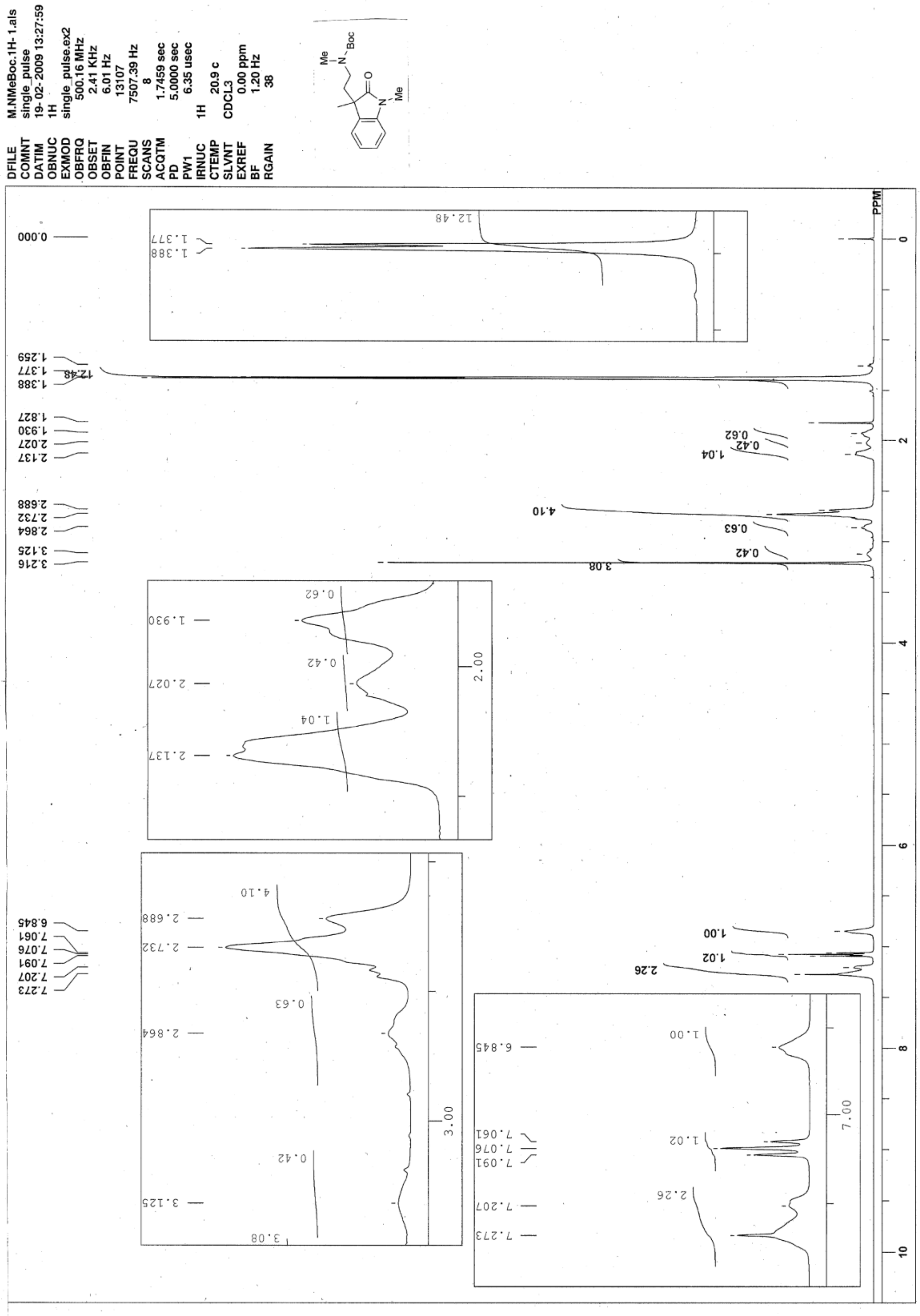
[7] Lee, T. V.; Porter, J. R. *Org. Synth.* **1995**, *72,* 189.

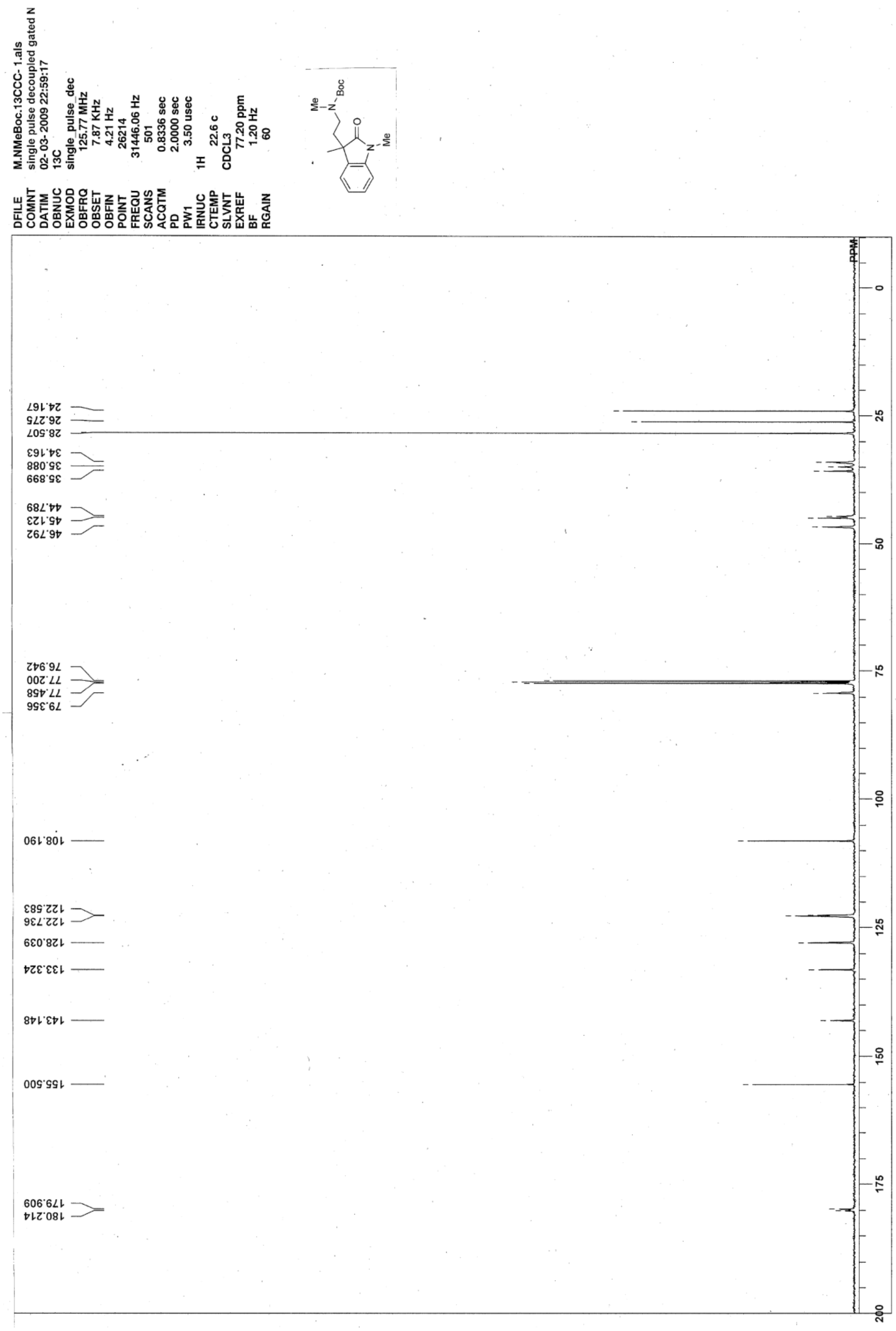
$NaHCO_3$ was added. The mixture was warmed to room temperature, and extracted with AcOEt. The combined organic layers were washed with brine and dried over Na_2SO_4. Removal of the solvent under reduced pressure afforded the crude product, which was purified by silica gel column chromatography (hexane/AcOEt = 10/0→9/1) to give pyrroloindole **25** (285 mg, 96%) as a colorless oil. Rf 0.82 (silica, hexane/AcOEt = 8/2); f 0.82 (silica, hexane/AcOEt = 8/2); ^{1}H NMR (δ, toluene, 100 ^{o}C) 6.72 (d, $J = 2.5$ Hz, 1H), 6.61 (dd, $J_1 = 8.0$ Hz, $J_2 = 2.5$ Hz, 1H), 6.19 (d, $J = 8.0$ Hz, 1H), 4.41 (t, $J = 5.5$ Hz, 1H), 3.73–3.68 (m, 1H), 3.61–3.53 (m, 1H), 3.53 (s, 3H), 3.26 (s, 6H), 3.17 (br s, 1H), 3.02–2.96 (m, 1H), 2.99 (br s, 3H), 2.13–2.08 (m, 2H), 2.01–1.94 (m, 2H), 1.90–1.79 (m, 3H), 1.76–1.69 (m, 1H), 1.40 (s, 9H), 0.93 (s, 9H), 0.02 (s, 6H); ^{13}C HMR (δ, toluene, 100 ^{o}C); 154.5, 153.9, 145.6, 133.6, 113.7, 111.4, 106.8, 105.9, 93.9, 78.9, 60.2, 56.1, 53.3, 52.4, 48.1, 38.5, 35.1, 31.6, 29.1, 28.6, 26.3, 25.8, 18.6, –5.06, –5.10; IR (NaCl) 2954, 1698 cm^{-1}; LRMS (FAB$^+$) $m/z = 564$ (M$^+$); Anal. Calced for $C_{30}H_{52}N_2O_6Si$: C, 63.79; H, 9.28; N, 4.96. Found: C, 63.88; H, 9.38; N, 4.90.


DFILE M.NHboc.1H- 1.als
COMNT single_pulse
DATIM 17- 02- 2009 16:07:57
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 500.16 MHz
OBSET 2.41 KHz
OBFIN 6.01 Hz
POINT 13107
FREQU 7507.39 Hz
SCANS 8
ACQTM 1.7459 sec
PD 5.0000 sec
PW1 6.35 usec
IRNUC 1H
CTEMP 21.5 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 1.20 Hz
RGAIN 32
NHBoc
O
N
Me
0.000
1.367
1.379
1.927
1.995
2.058
2.095
2.159
2.721
2.809
2.854
2.897
2.950
3.212
4.515
6.834
6.849
7.062
7.077
7.092
7.200
7.214
7.252
7.269
7.282
12.22
2.21
2.04
3.05
0.81
0.97
1.00
0.99
1.10
2.00
7.00
PPM
0
2
4
6
8
10

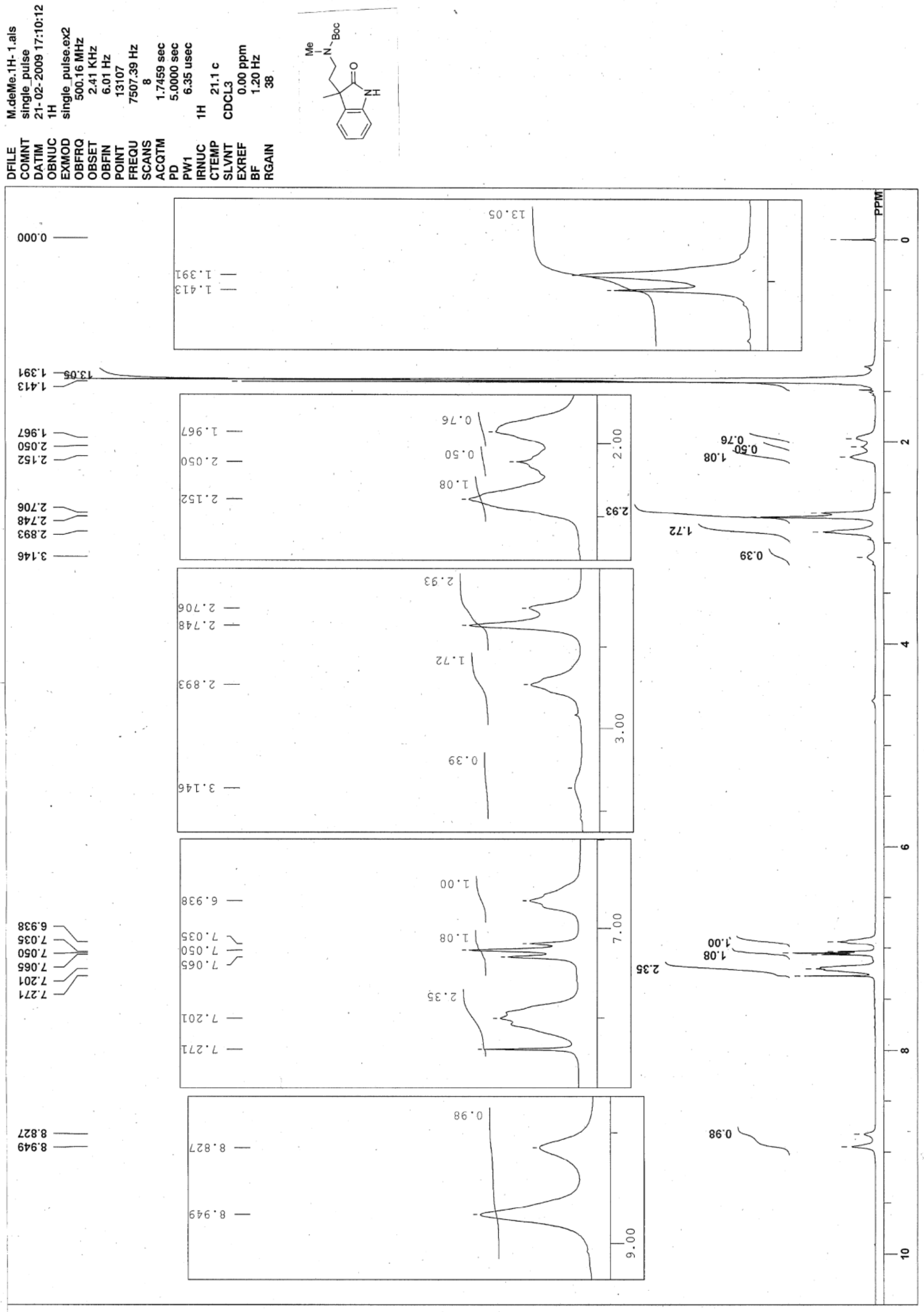


DFILE M.NHboc.13C- 1.als
COMNT single pulse decoupled gated N
DATIM 17- 02- 2009 16:55:57
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 125.77 MHz
OBSET 7.87 KHz
OBFIN 4.21 Hz
POINT 26214
FREQU 31446.06 Hz
SCANS 1000
ACQTM 0.8336 sec
PD 2.0000 sec
PW1 3.50 usec
IRNUC 1H
CTEMP 22.1 c
SLVNT CDCL3
EXREF 77.20 ppm
BF 1.20 Hz
RGAIN 60


DFILE M.NMeBoc.1H- 1.als
COMNT single_pulse
DATIM 19- 02- 2009 13:27:59
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 500.16 MHz
OBSET 2.41 KHz
OBFIN 6.01 Hz
POINT 13107
FREQU 7507.39 Hz
SCANS 8
ACQTM 1.7459 sec
PD 5.0000 sec
PW1 6.35 usec
IRNUC 1H
CTEMP 20.9 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 1.20 Hz
RGAIN 38
Me
N
Boc
O
N
Me
0.000
1.259
1.377
1.388
1.827
1.930
2.027
2.137
2.688
2.732
2.864
3.125
3.216
6.845
7.061
7.076
7.091
7.207
7.273
12.48
0.62
0.42
1.04
4.10
0.63
0.42
3.08
1.00
1.02
2.26
2.00
3.00
7.00
PPM
0
2
4
6
8
10

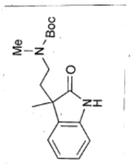


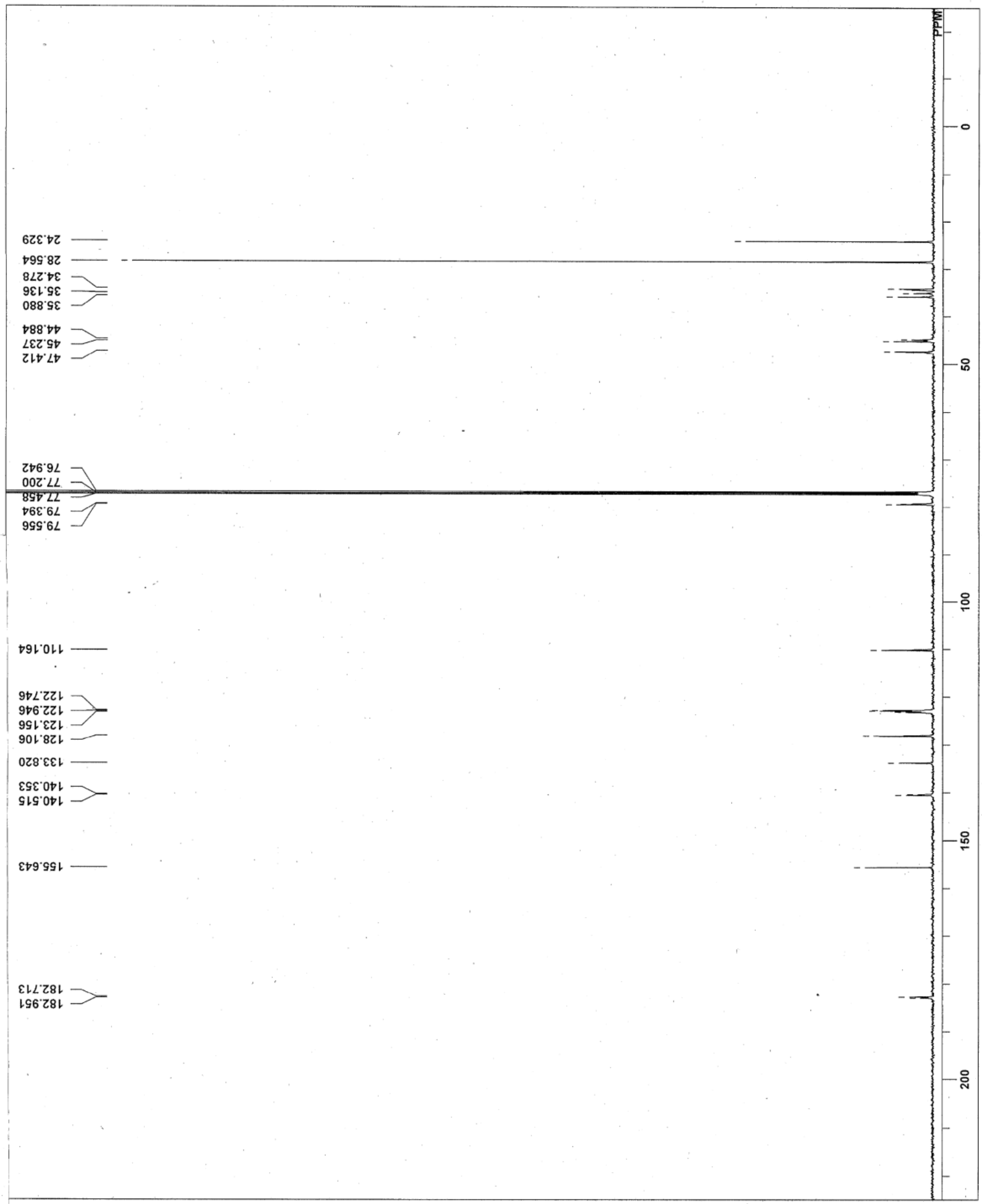
DFILE M.NMeBoc.13CCC- 1.als
COMNT single pulse decoupled gated N
DATIM 02- 03- 2009 22:59:17
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 125.77 MHz
OBSET 7.87 KHz
OBFIN 4.21 Hz
POINT 26214
FREQU 31446.06 Hz
SCANS 501
ACQTM 0.8336 sec
PD 2.0000 sec
PW1 3.50 usec
IRNUC 1H
CTEMP 22.6 c
SLVNT CDCL3
EXREF 77.20 ppm
BF 1.20 Hz
RGAIN 60

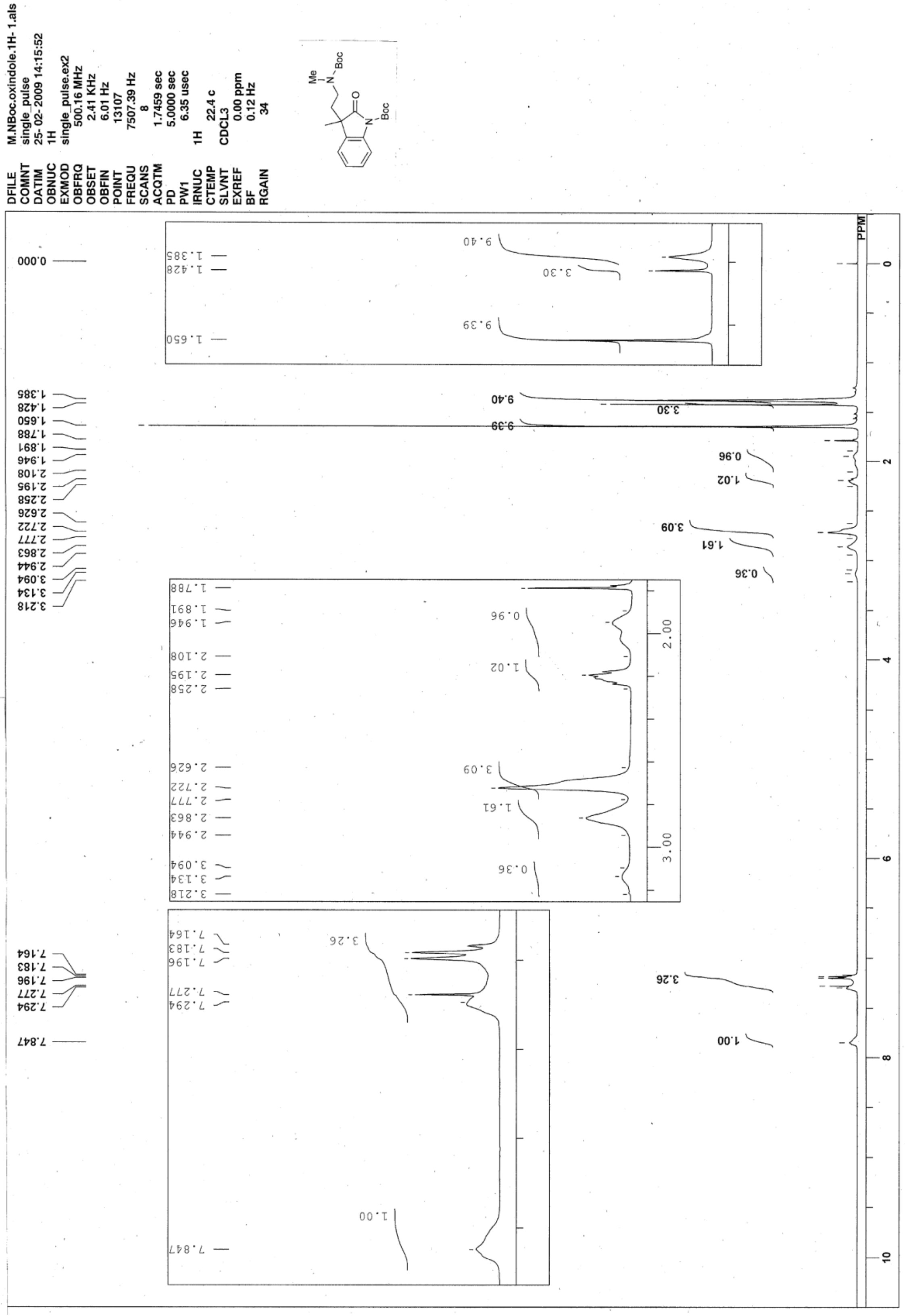


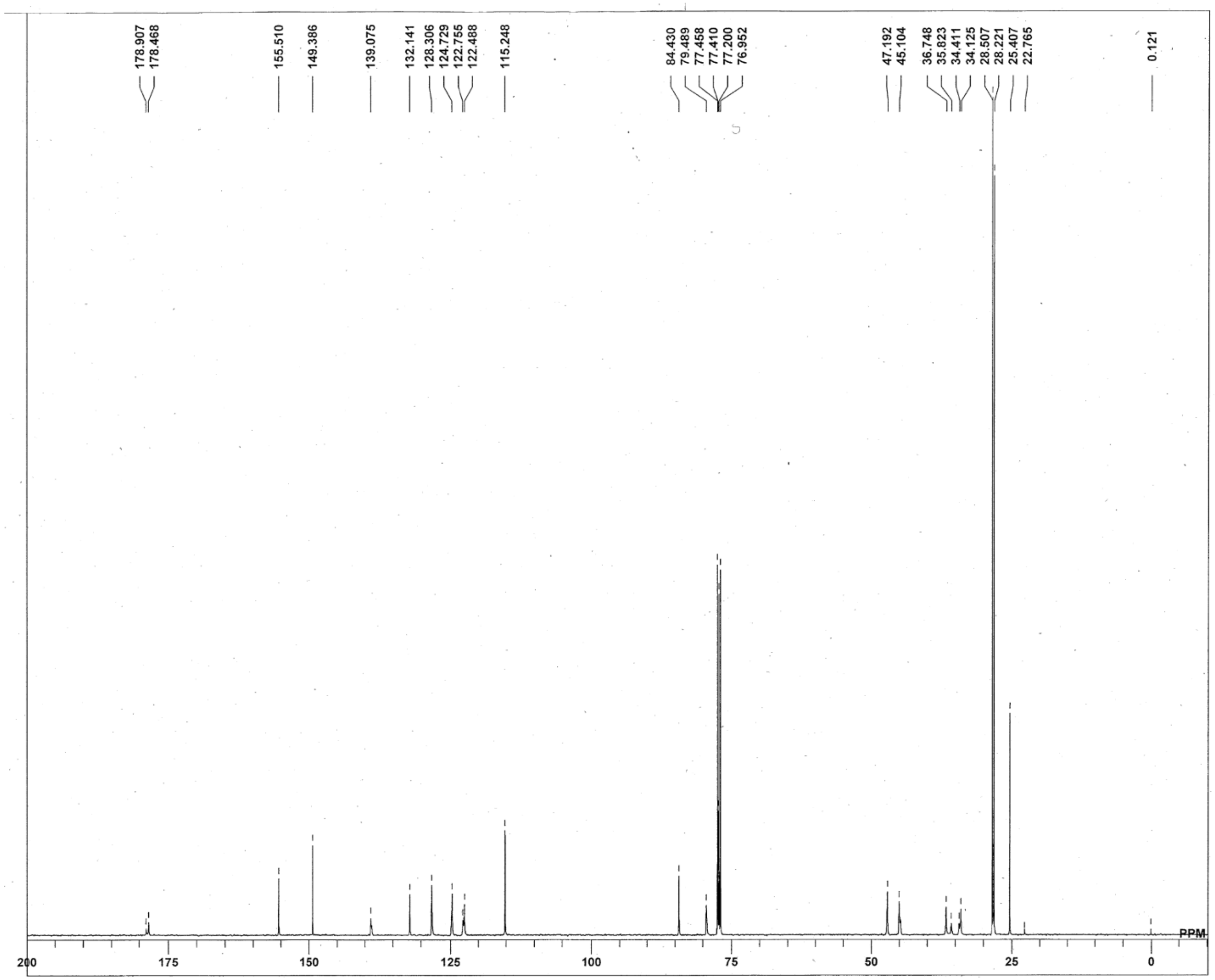
DFILE M.deMe.1H-1.als
COMNT single_pulse
DATIM 21-02-2009 17:10:12
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 500.16 MHz
OBSET 2.41 KHz
OBFIN 6.01 Hz
POINT 13107
FREQU 7507.39 Hz
SCANS 8
ACQTM 1.7459 sec
PD 5.0000 sec
PW1 6.35 usec
IRNUC 1H
CTEMP 21.1 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 1.20 Hz
RGAIN 38

DFILE	M.deMe.13C- 1.als
COMNT	single pulse decoupled gated N
DATIM	21- 02- 2009 17:58:12
OBNUC	13C
EXMOD	single_pulse_dec
OBFRQ	125.77 MHz
OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	26214
FREQU	31446.06 Hz
SCANS	1000
ACQTM	0.8336 sec
PD	2.0000 sec
PW1	3.50 usec
IRNUC	1H
CTEMP	21.6 c
SLVNT	CDCL3
EXREF	77.20 ppm
BF	1.20 Hz
RGAIN	60

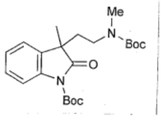


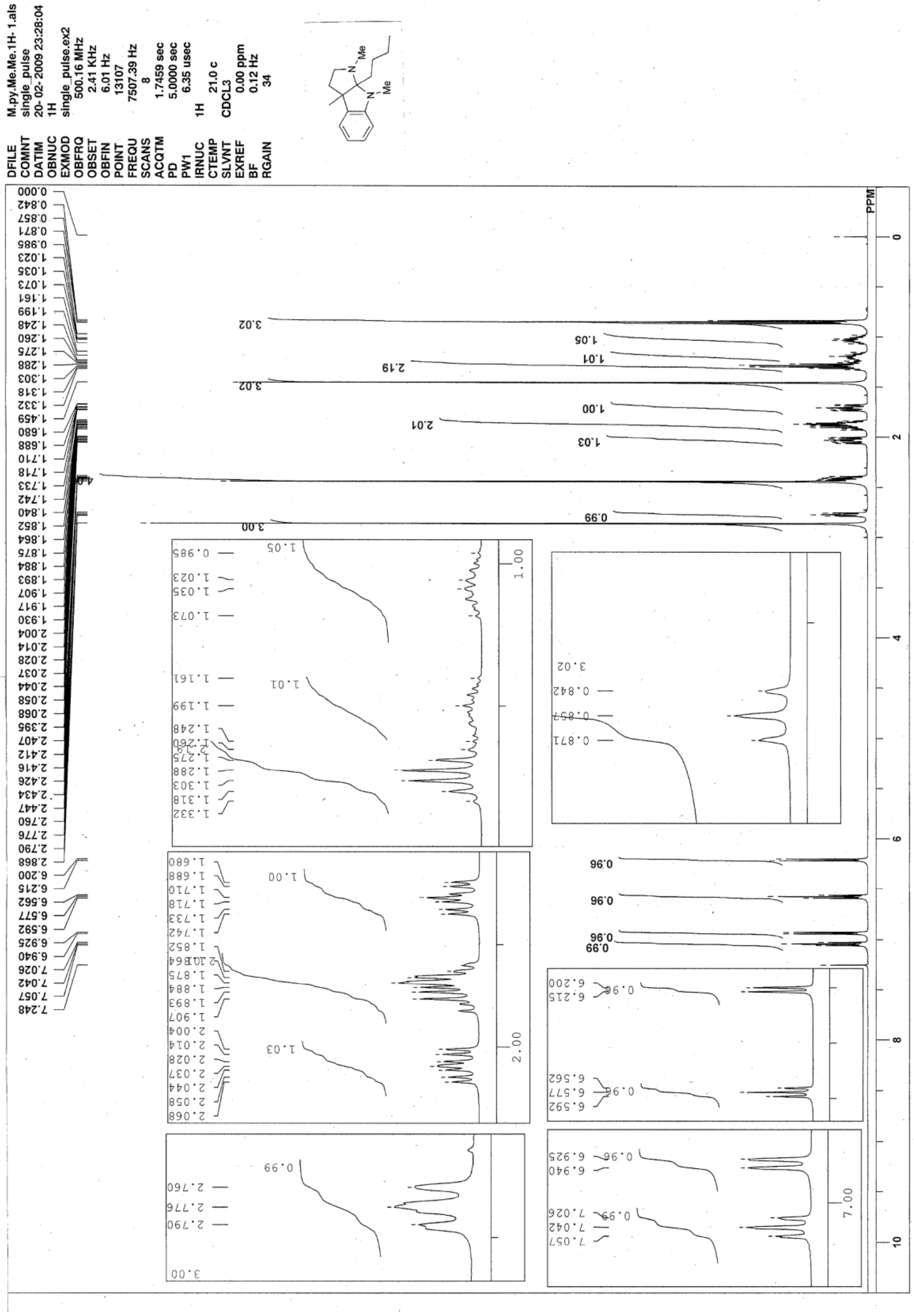


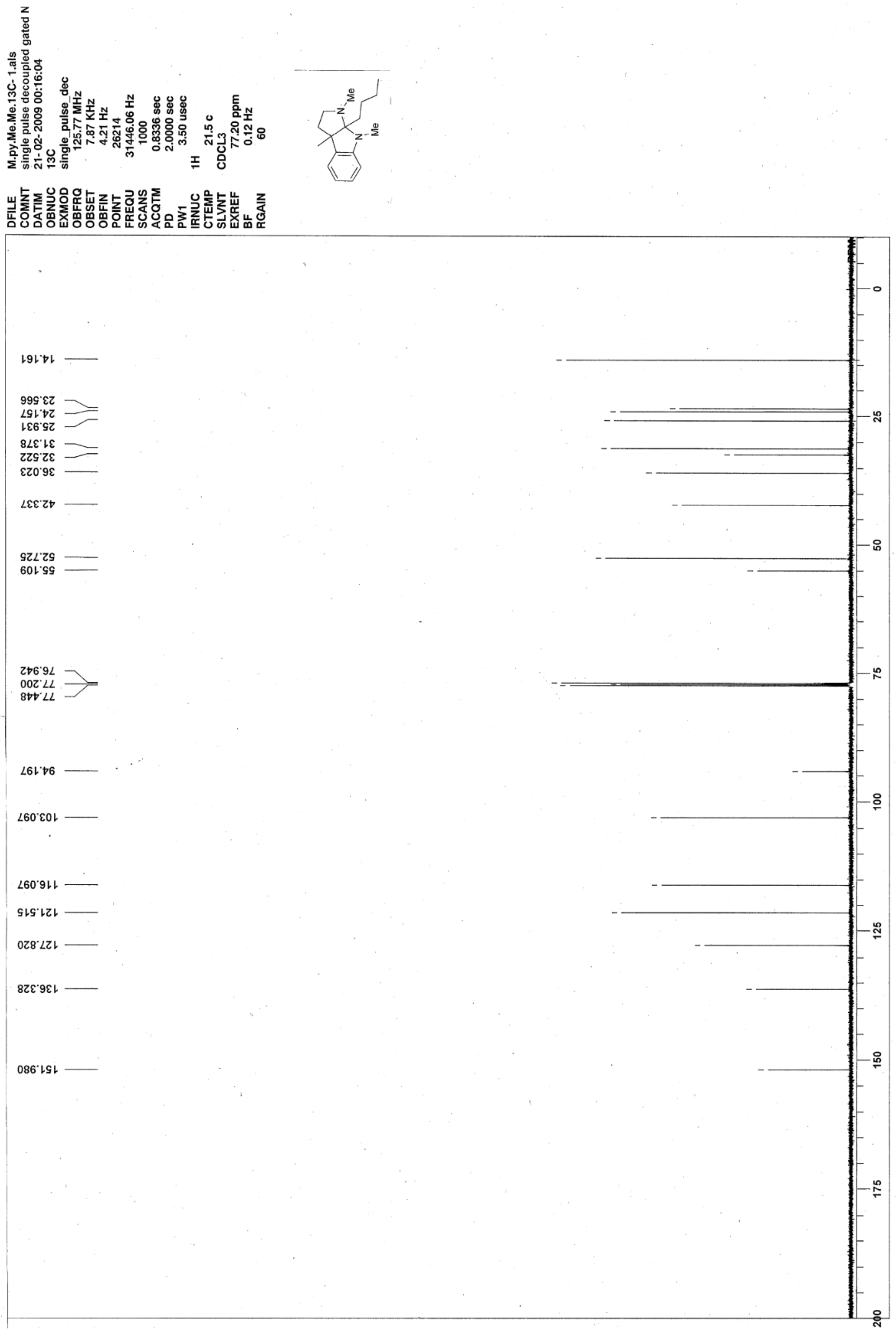

DFILE M.NBoc.oxindole.1H- 1.als
COMNT single_pulse
DATIM 25- 02- 2009 14:15:52
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 500.16 MHz
OBSET 2.41 KHz
OBFIN 6.01 Hz
POINT 13107
FREQU 7507.39 Hz
SCANS 8
ACQTM 1.7459 sec
PD 5.0000 sec
PW1 6.35 usec
IRNUC 1H
CTEMP 22.4 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 34
Me
N
Boc
O
N
Boc
0.000
1.385
1.428
1.650
1.788
1.891
1.946
2.108
2.195
2.258
2.626
2.722
2.777
2.863
2.944
3.094
3.134
3.218
7.164
7.183
7.196
7.277
7.294
7.847
9.40
3.30
9.39
0.96
1.02
3.09
1.61
0.36
3.26
1.00
2.00
3.00
PPM
0
2
4
6
8
10



DFILE	M.NBoc.oxindole.13C- 2.als
COMNT	single pulse decoupled gated N
DATIM	07- 03- 2009 15:53:55
OBNUC	13C
EXMOD	single_pulse_dec
OBFRQ	125.77 MHz
OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	26214
FREQU	31446.06 Hz
SCANS	990
ACQTM	0.8336 sec
PD	2.0000 sec
PW1	3.50 usec
IRNUC	1H
CTEMP	23.9 c
SLVNT	CDCL3
EXREF	77.20 ppm
BF	1.20 Hz
RGAIN	60

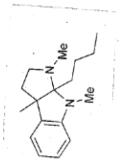


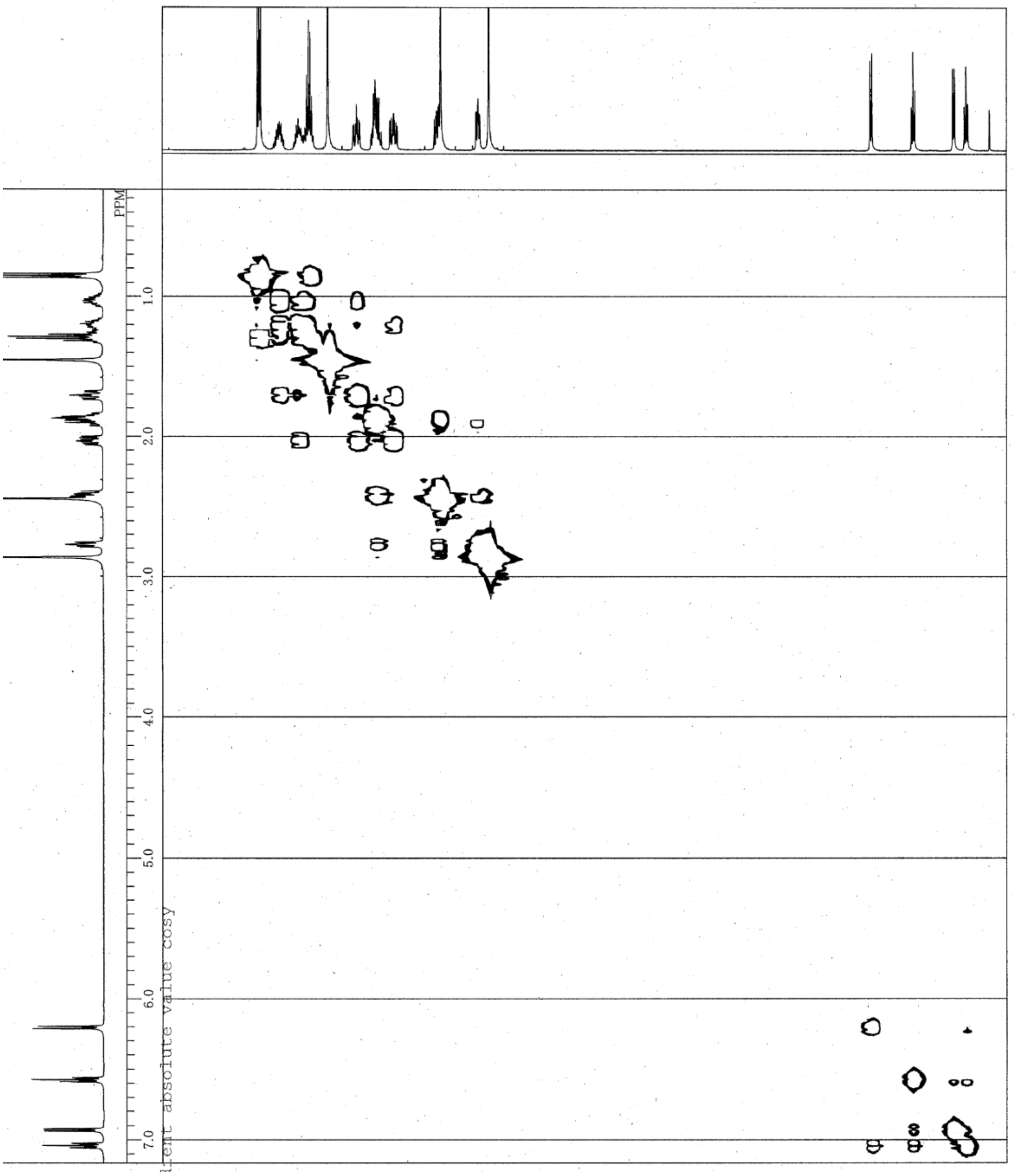

DFILE M.py.Me.Me.1H- 1.als
COMNT single_pulse
DATIM 20- 02- 2009 23:28:04
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 500.16 MHz
OBSET 2.41 KHz
OBFIN 6.01 Hz
POINT 13107
FREQU 7507.39 Hz
SCANS 8
ACQTM 1.7459 sec
PD 5.0000 sec
PW1 6.35 usec
IRNUC 1H
CTEMP 21.0 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 34
N
Me
N
Me
PPM

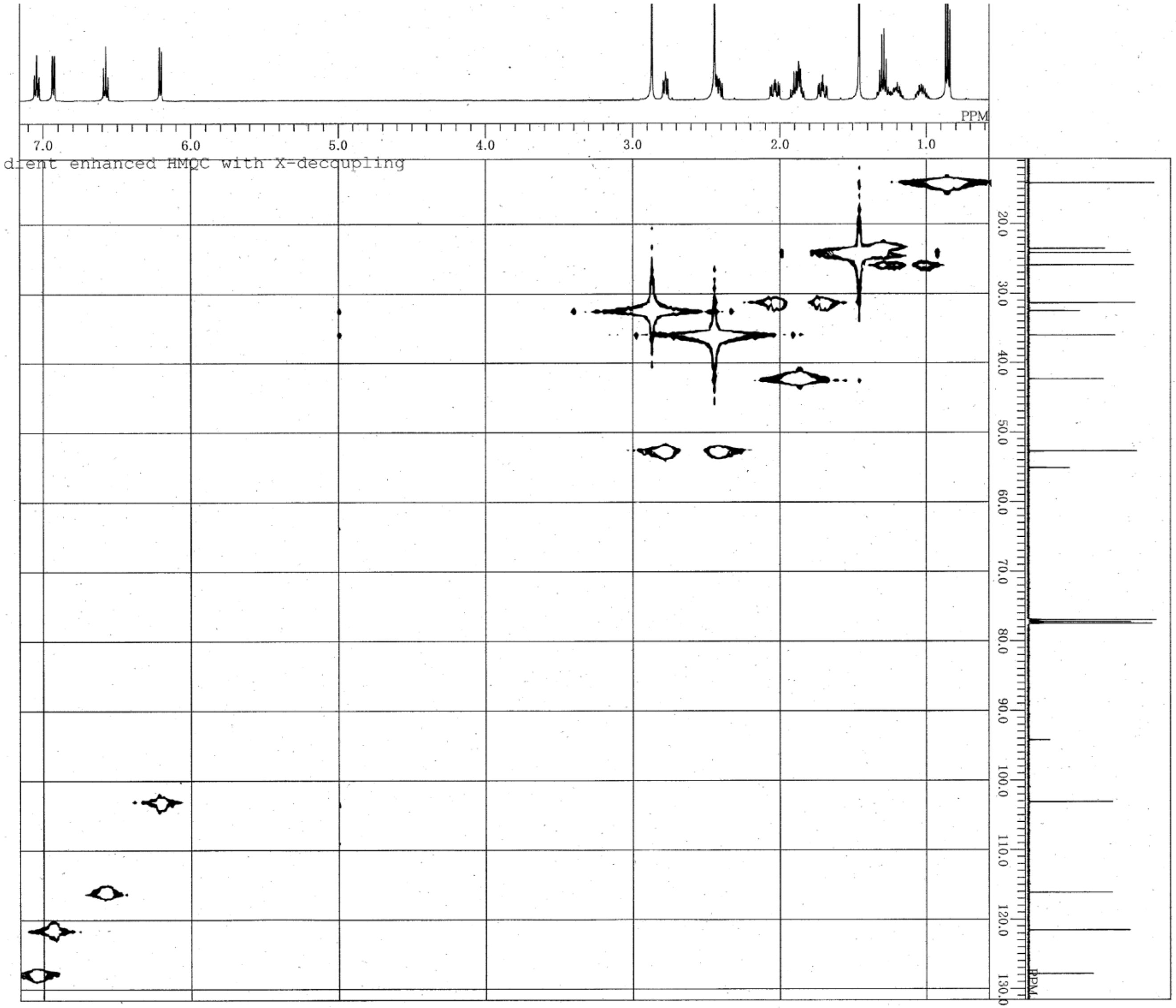


```
DFILE   M.py.Me.Me.13C-1.als
COMNT   single pulse decoupled gated N
DATIM   21-02-2009 00:16:04
OBNUC   13C
EXMOD   single_pulse_dec
OBFRQ   125.77 MHz
OBSET     7.87 KHz
OBFIN     4.21 Hz
POINT   26214
FREQU   31446.06 Hz
SCANS     1000
ACQTM   0.8336 sec
PD      2.0000 sec
PW1       3.50 usec
IRNUC   1H
CTEMP     21.5 c
SLVNT   CDCL3
EXREF   77.20 ppm
BF        0.12 Hz
RGAIN     60
```

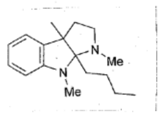
```
DFILE   M.py.Me.Me.cosy-1.als
COMNT   gradient absolute value cosy
DATIM   21-02-2009 00:23:28
EXMOD   cosy_pfg.ex2
OBNUC   1H
OBFRQ       500.16 MHz
OBSET         2.41 KHz
OBFIN         6.01 Hz
POINT         1024
FREQU      7507.51 Hz
CLPNT          256
TODAT          256
CLFRQ      7503.00 Hz
SCANS            1
ACQTM       0.1364 sec
PD          1.5000 sec
PW1          12.70 usec
PW2           0.00 usec
PW3           0.00 usec
PI1         0.0000 msec
PI2         0.0000 msec
PI3         0.0000 msec
IRNUC   1H
CTEMP         21.2 c
SLVNT   CDCL3
EXREF         0.00 ppm
CLEXR         0.00
RGAIN           50
```

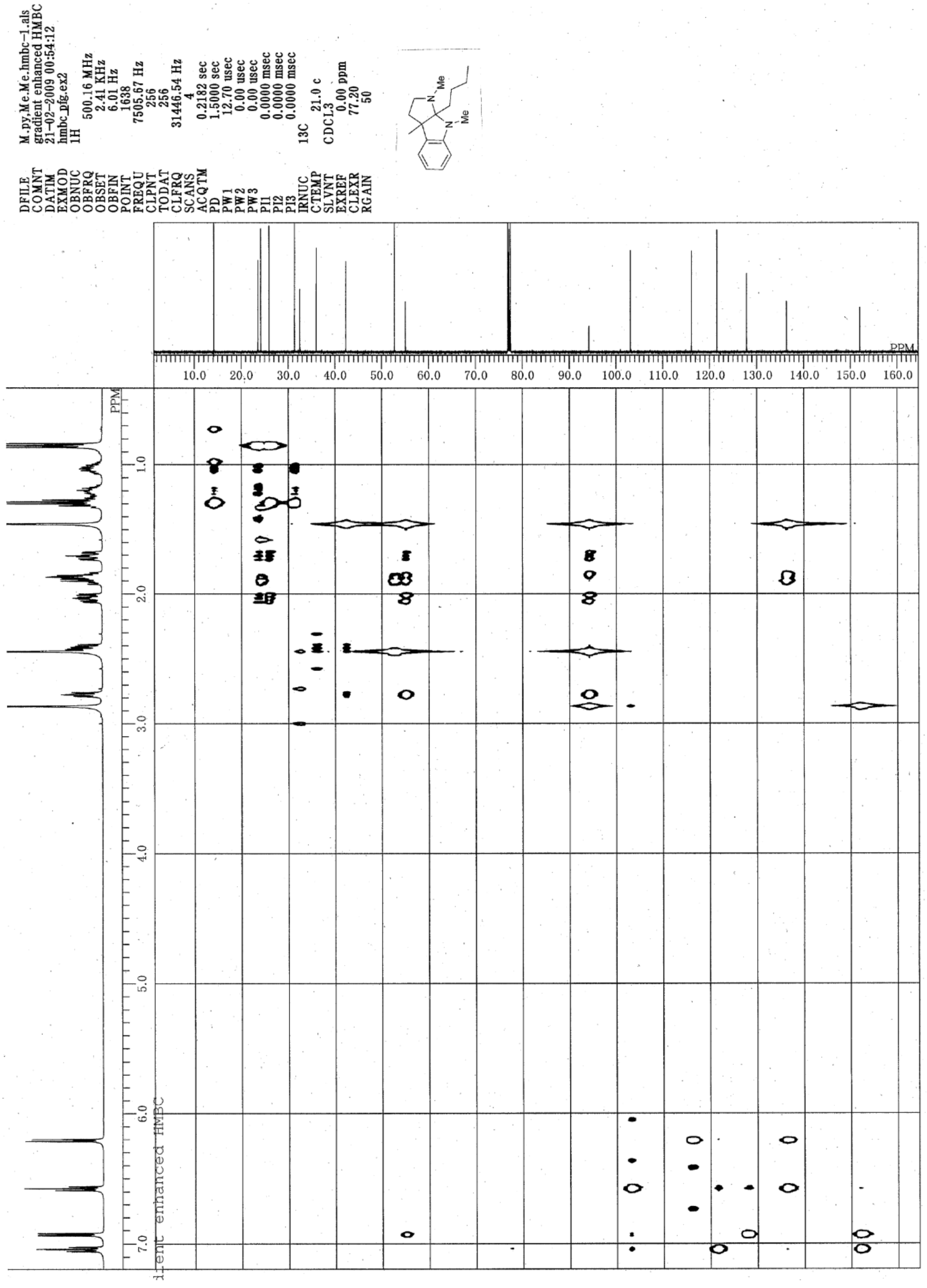




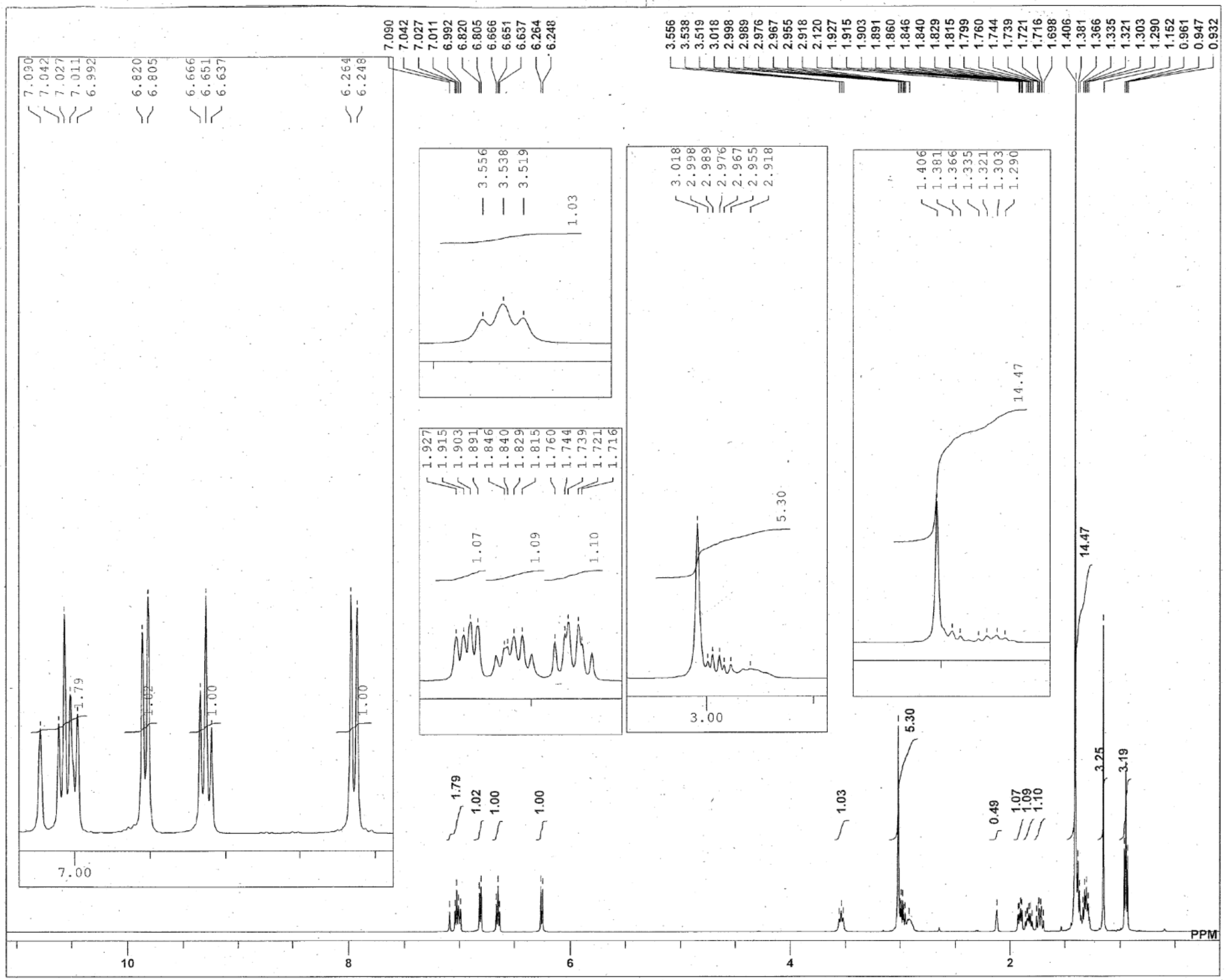


```
DFILE   M.py.Me.Me.hmqc-1.als
COMNT   gradient enhanced HMQC w
DATIM   21-02-2009 01:01:22
EXMOD   hmqc_pfg.ex2
OBNUC   1H
OBFRQ     500.16 MHz
OBSET       2.41 KHz
OBFIN       6.01 Hz
POINT        819
FREQU    7505.67 Hz
CLPNT        256
TODAT        256
CLFRQ   21385.80 Hz
SCANS          1
ACQTM     0.1091 sec
PD        1.5000 sec
PW1        12.70 usec
PW2         0.00 usec
PW3         0.00 usec
PI1       0.0000 msec
PI2       0.0000 msec
PI3       0.0000 msec
IRNUC   13C
CTEMP       21.1 c
SLVNT   CDCL3
EXREF       0.00 ppm
CLEXR      77.20
RGAIN         50
```

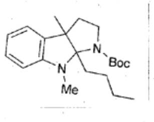


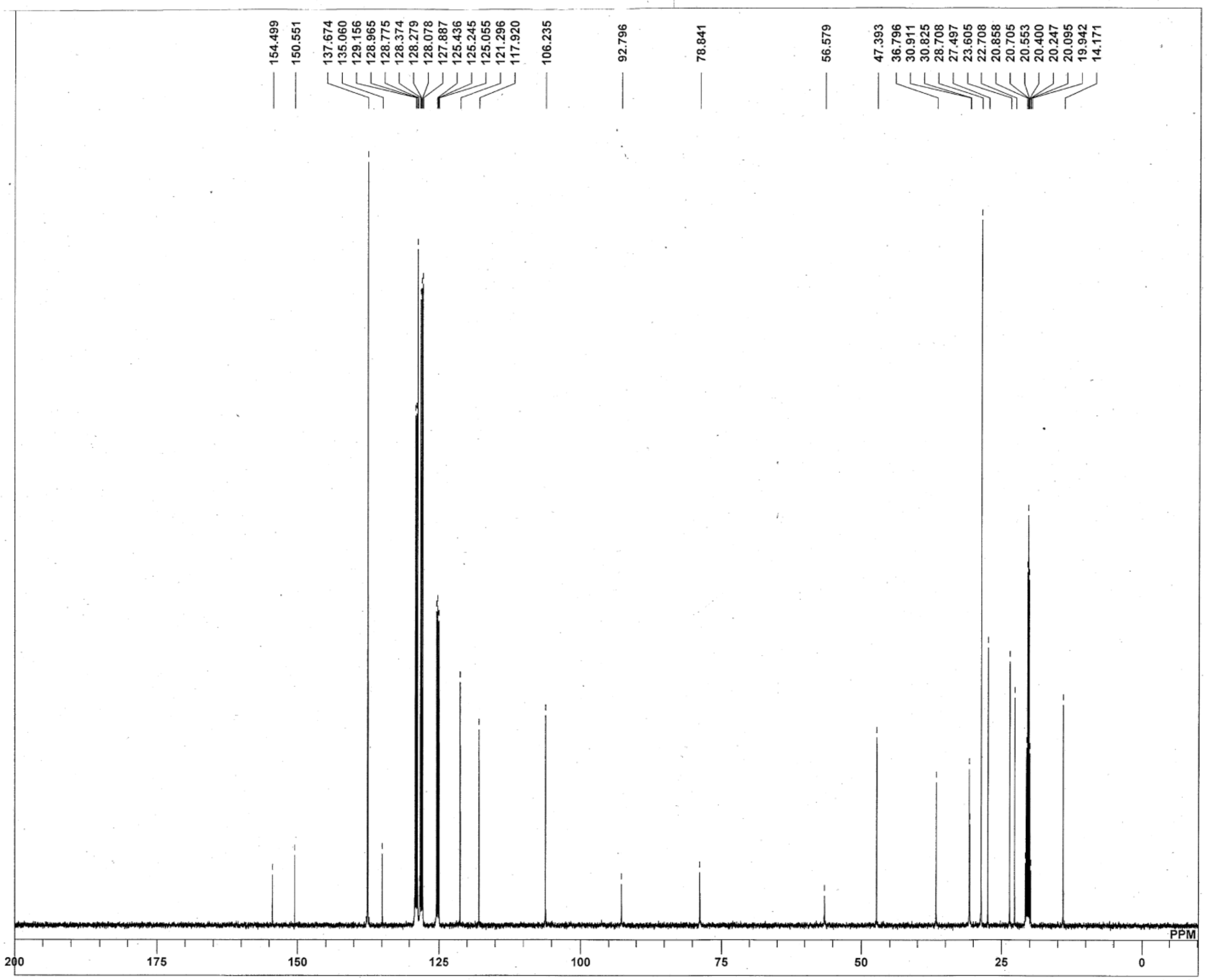


```
DFILE   M.py,Me.Me.hmbc-1.als
COMNT   gradient enhanced HMBC
DATIM   21-02-2009 00:54:12
EXMOD   hmbc_pfg.ex2
OBNUC   1H
OBFRQ      500.16 MHz
OBSET        2.41 KHz
OBFIN        6.01 Hz
POINT        1638
FREQU     7505.67 Hz
CLPNT         256
TODAT         256
CLFRQ    31446.54 Hz
SCANS           4
ACQTM      0.2182 sec
PD         1.5000 sec
PW1         12.70 usec
PW2          0.00 usec
PW3          0.00 usec
PI1        0.0000 msec
PI2        0.0000 msec
PI3        0.0000 msec
IRNUC   13C
CTEMP        21.0 c
SLVNT   CDCL3
EXREF        0.00 ppm
CLEXR       77.20
RGAIN          50
```

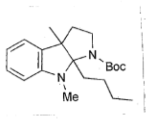


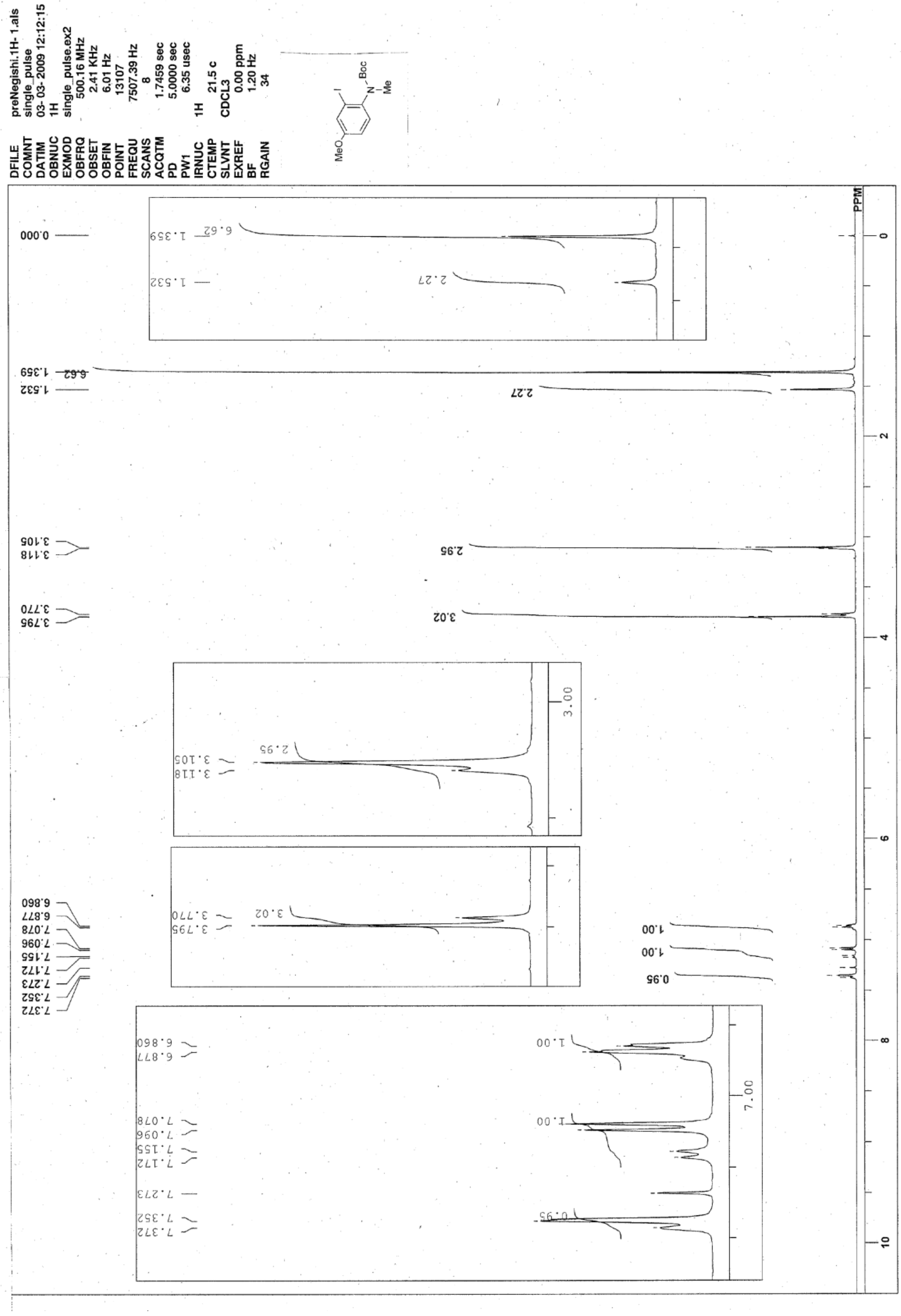
DFILE	M.py.Me.Boc.t.temp- 1.als
COMNT	single_pulse
DATIM	28- 02- 2009 15:23:13
OBNUC	1H
EXMOD	single_pulse.ex2
OBFRQ	500.16 MHz
OBSET	2.41 KHz
OBFIN	6.01 Hz
POINT	13107
FREQU	7507.39 Hz
SCANS	8
ACQTM	1.7459 sec
PD	5.0000 sec
PW1	6.35 usec
IRNUC	1H
CTEMP	100.0 c
SLVNT	C6D5CD3
EXREF	7.09 ppm
BF	1.20 Hz
RGAIN	32

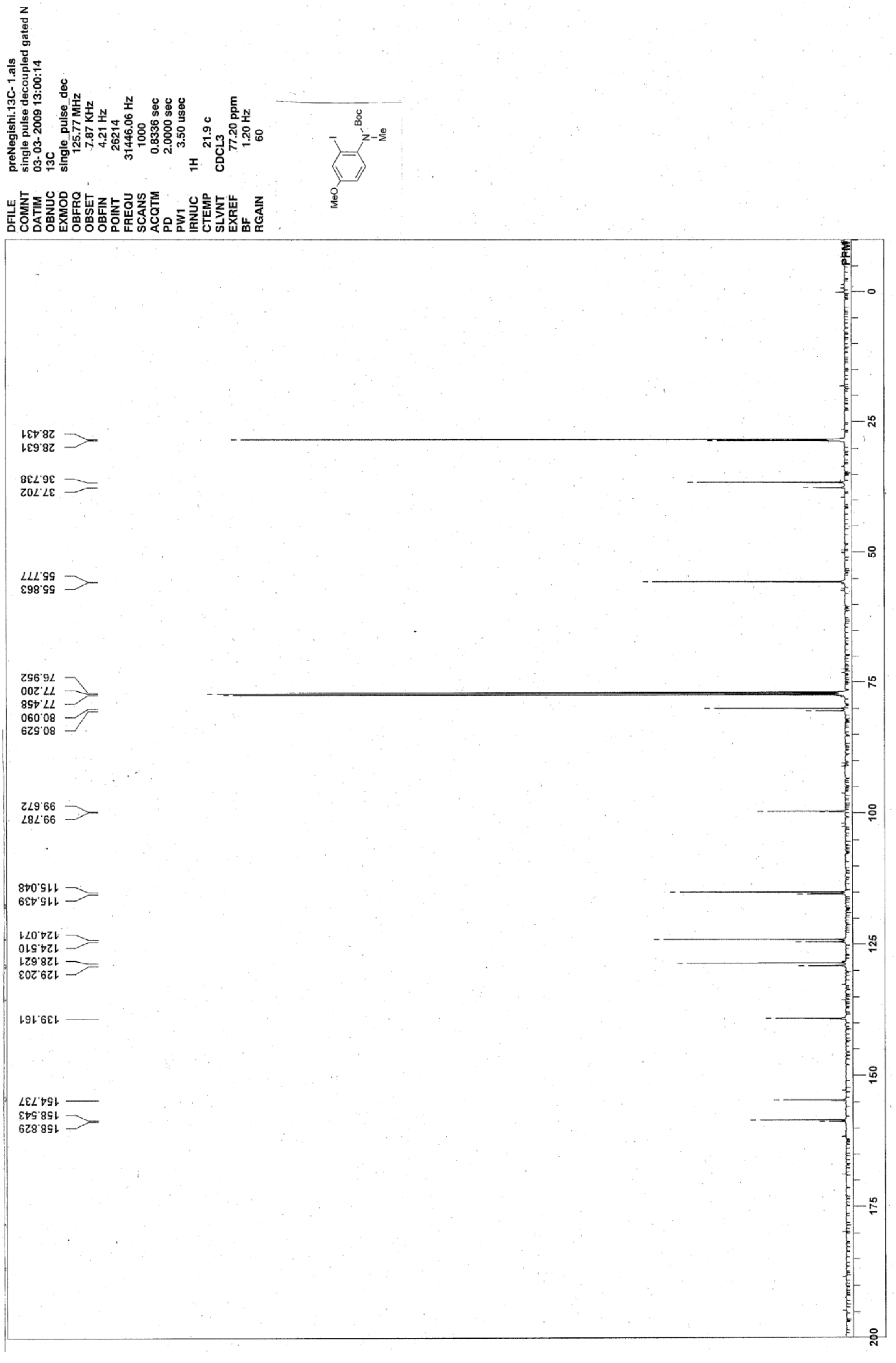




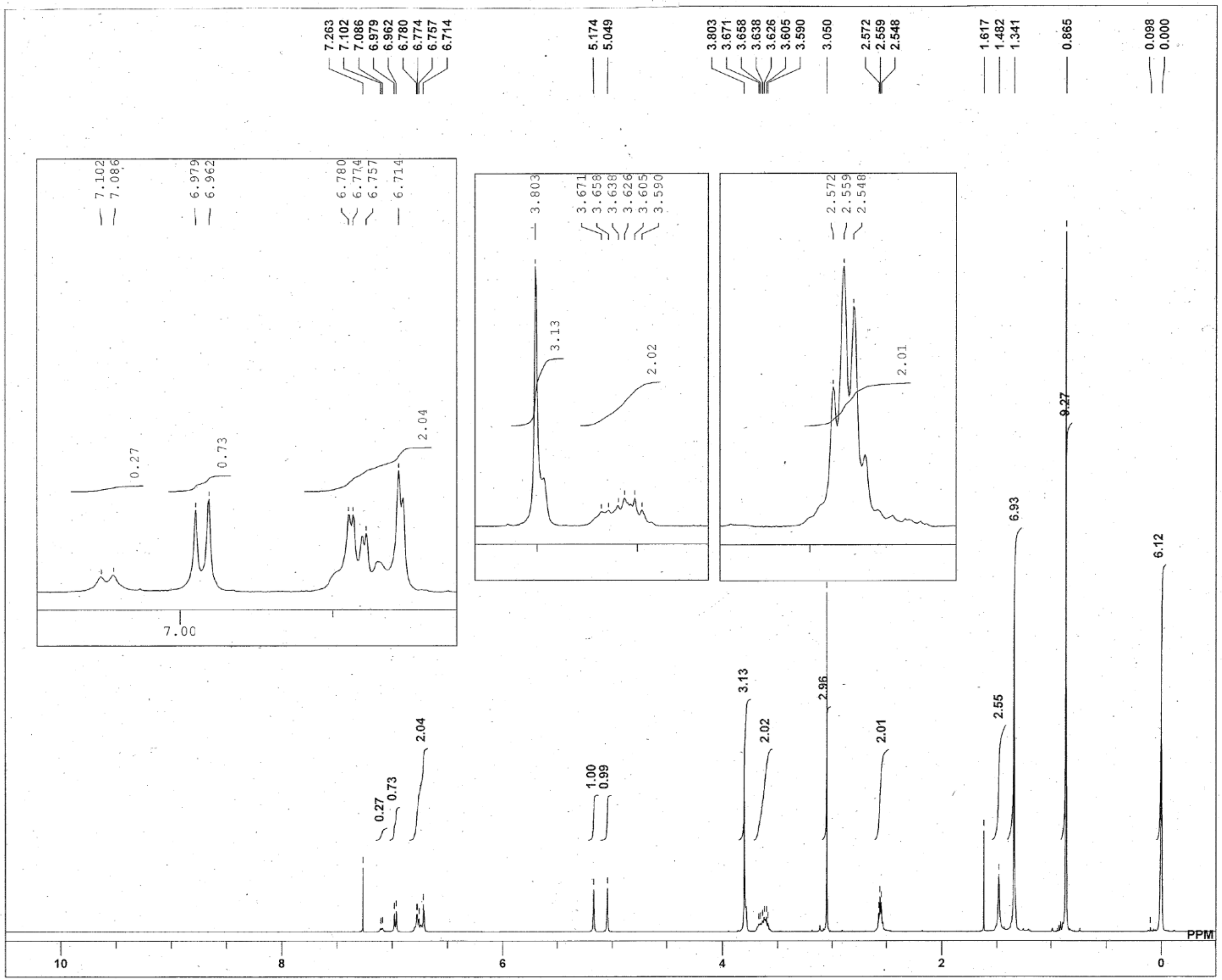
DFILE	M.py.Me.Boc.13C.t.temp- 1.als
COMNT	single pulse decoupled gated N
DATIM	28- 02- 2009 19:11:47
OBNUC	13C
EXMOD	single_pulse_dec
OBFRQ	125.77 MHz
OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	26214
FREQU	31446.06 Hz
SCANS	1000
ACQTM	0.8336 sec
PD	2.0000 sec
PW1	3.50 usec
IRNUC	1H
CTEMP	100.0 c
SLVNT	C6D5CD3
EXREF	20.40 ppm
BF	1.20 Hz
RGAIN	60



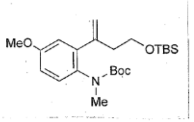

DFILE preNegishi.1H- 1.als
COMNT single_pulse
DATIM 03- 03- 2009 12:12:15
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 500.16 MHz
OBSET 2.41 KHz
OBFIN 6.01 Hz
POINT 13107
FREQU 7507.39 Hz
SCANS 8
ACQTM 1.7459 sec
PD 5.0000 sec
PW1 6.35 usec
IRNUC 1H
CTEMP 21.5 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 1.20 Hz
RGAIN 34
MeO
I
N
Boc
Me
0.000
1.359
1.532
3.105
3.118
3.770
3.795
6.860
6.877
7.078
7.096
7.155
7.172
7.273
7.352
7.372
6.62
2.27
2.95
3.02
1.00
1.00
0.95
3.00
7.00
PPM
0
2
4
6
8
10

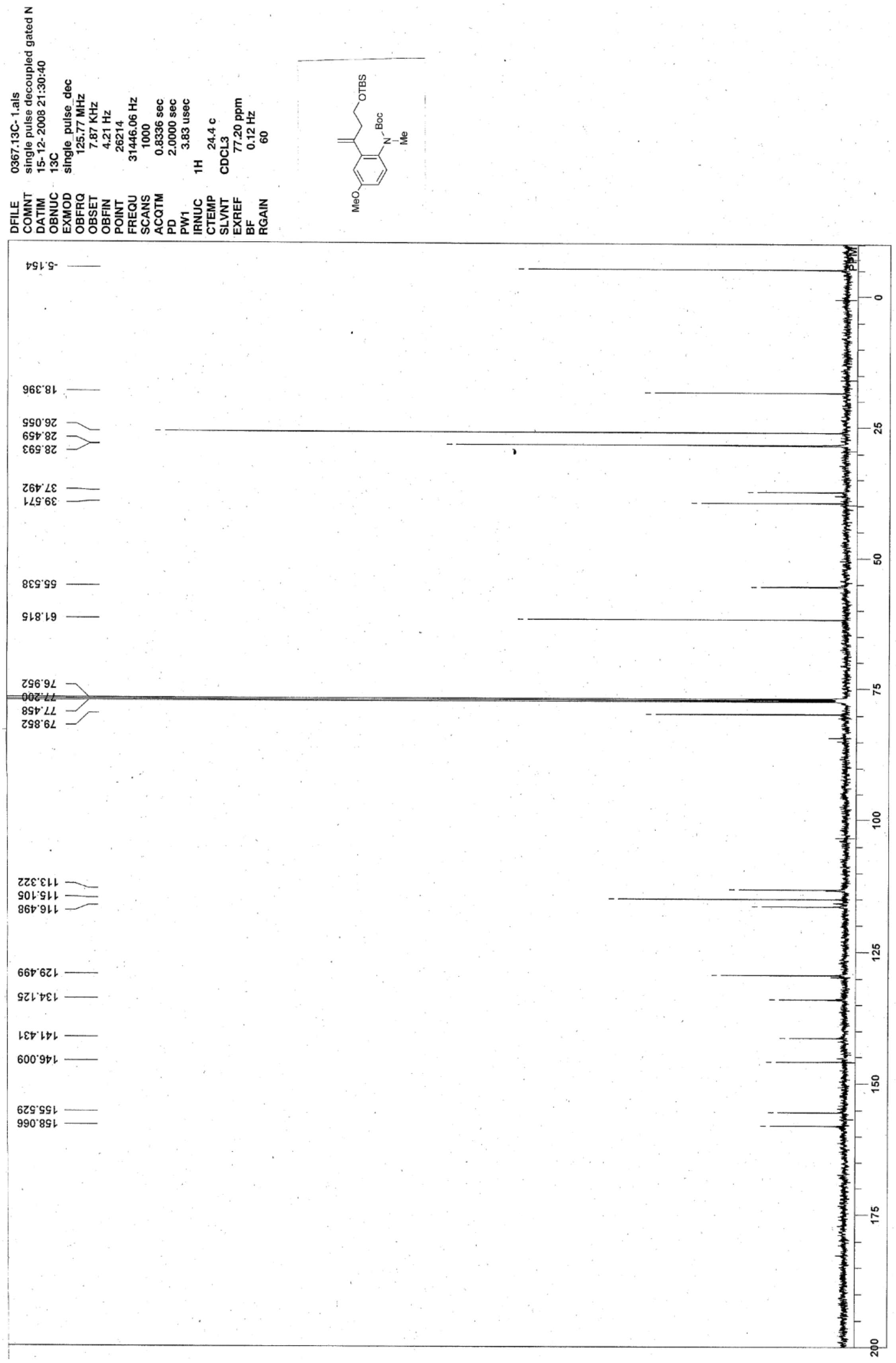


DFILE preNegishi.13C- 1.als
COMNT single pulse decoupled gated N
DATIM 03- 03- 2009 13:00:14
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 125.77 MHz
OBSET 7.87 KHz
OBFIN 4.21 Hz
POINT 26214
FREQU 31446.06 Hz
SCANS 1000
ACQTM 0.8336 sec
PD 2.0000 sec
PW1 3.50 usec
IRNUC 1H
CTEMP 21.9 c
SLVNT CDCL3
EXREF 77.20 ppm
BF 1.20 Hz
RGAIN 60

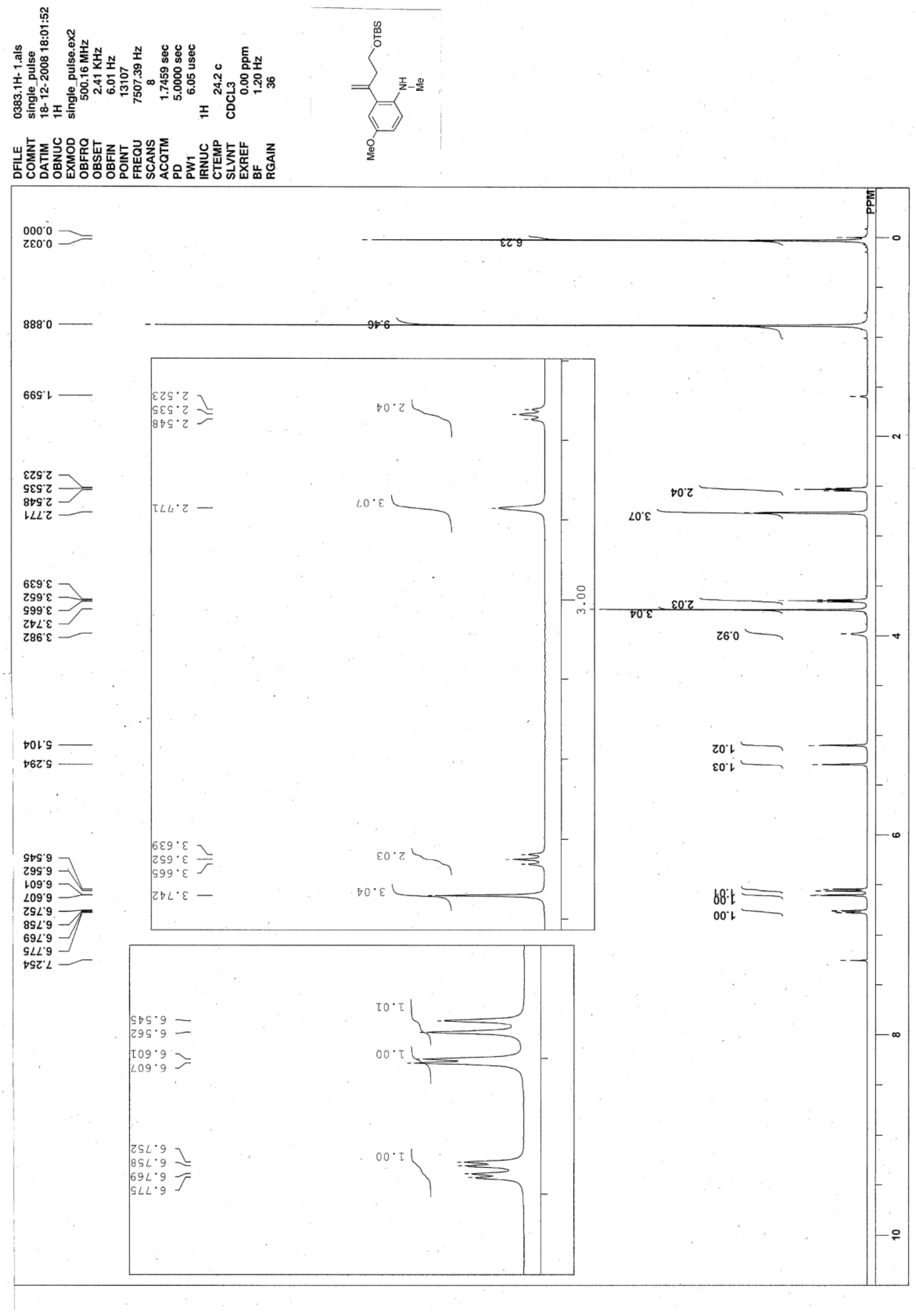


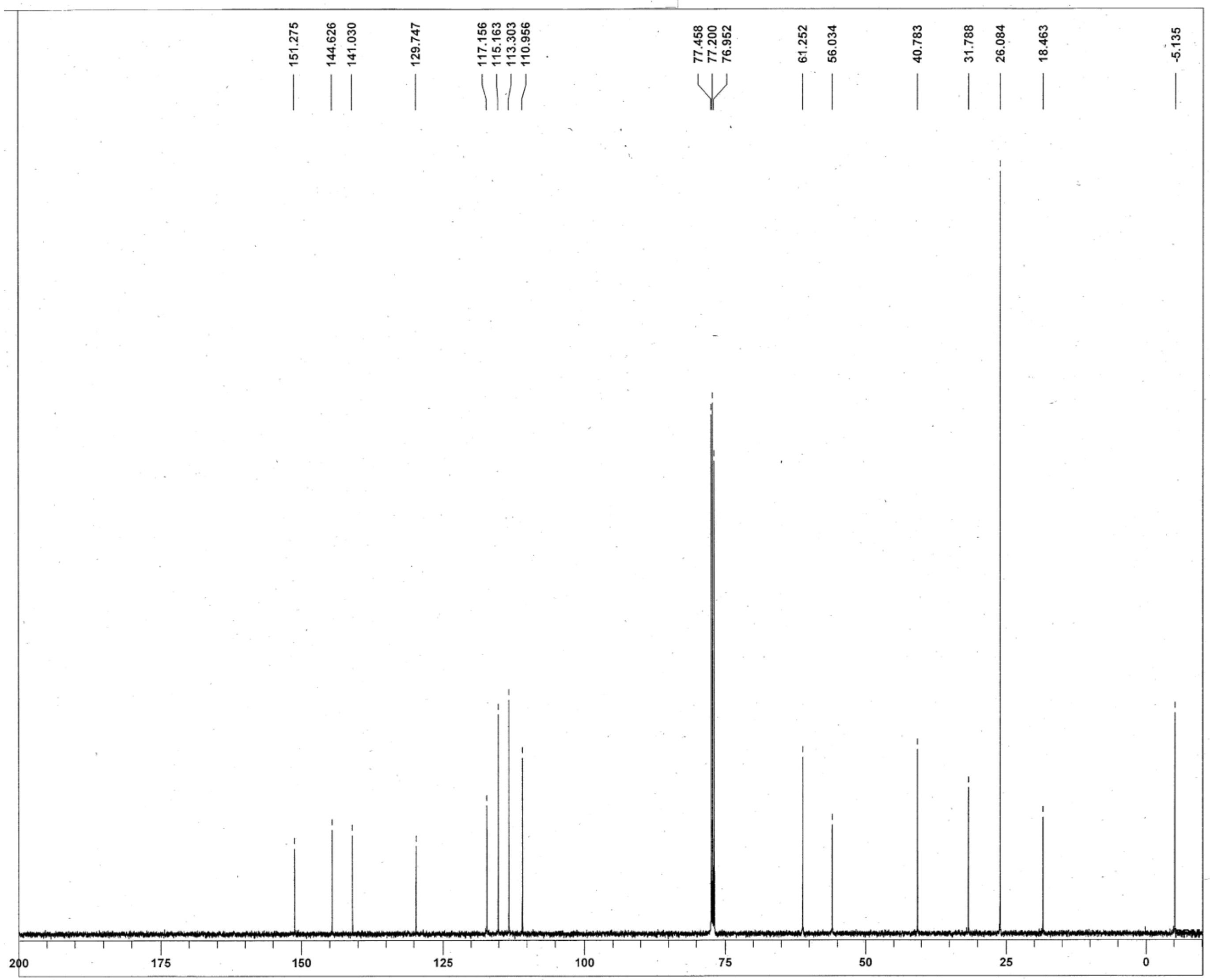
DFILE	0367.1H- 1.als
COMNT	single_pulse
DATIM	15- 12- 2008 20:42:42
OBNUC	1H
EXMOD	single_pulse.ex2
OBFRQ	500.16 MHz
OBSET	2.41 KHz
OBFIN	6.01 Hz
POINT	13107
FREQU	7507.39 Hz
SCANS	8
ACQTM	1.7459 sec
PD	5.0000 sec
PW1	6.05 usec
IRNUC	1H
CTEMP	24.0 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	38



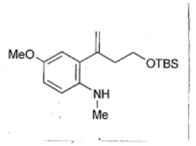


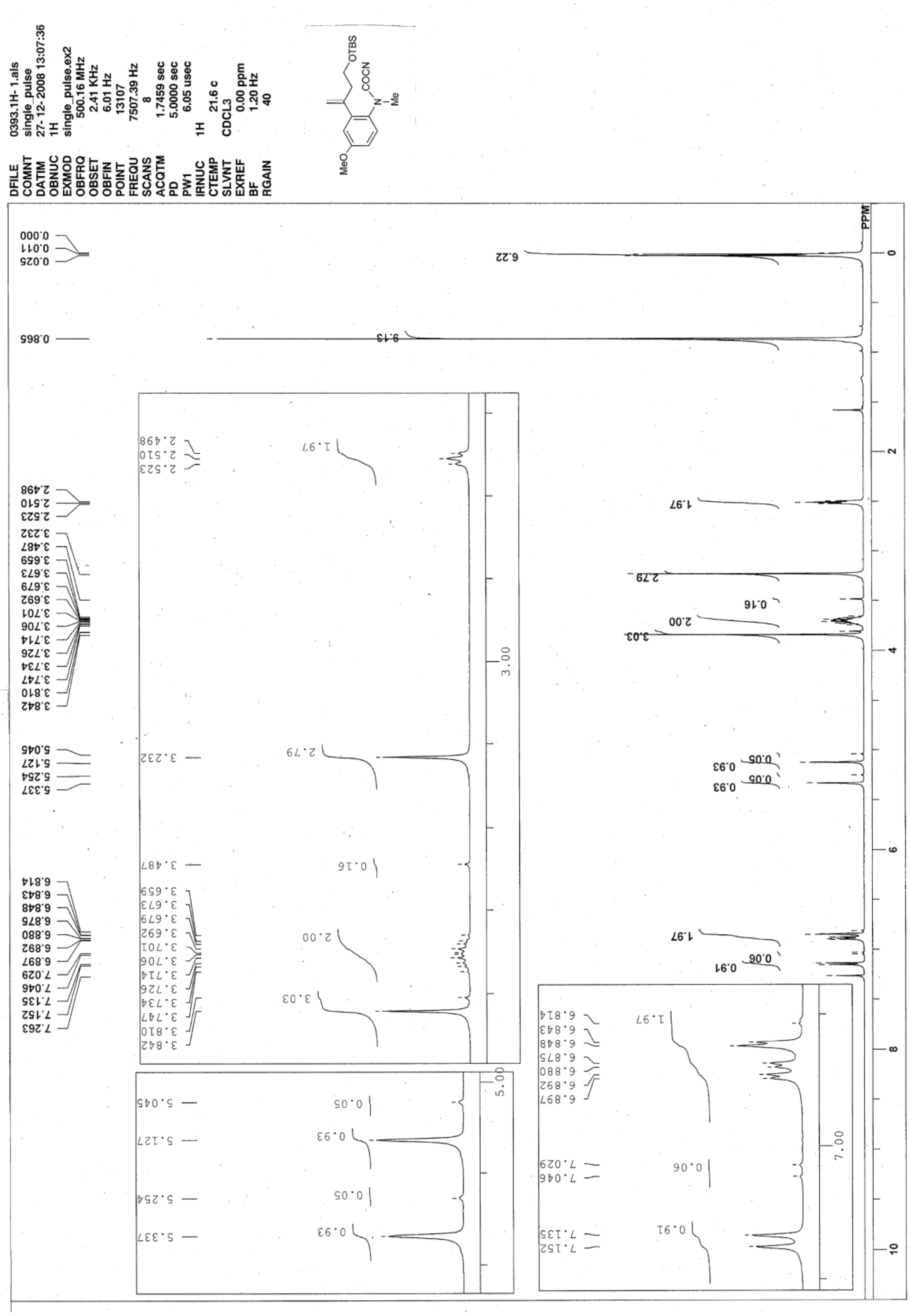
```
DFILE   0367.13C-1.als
COMNT   single pulse decoupled gated N
DATIM   15-12-2008 21:30:40
OBNUC   13C
EXMOD   single_pulse_dec
OBFRQ   125.77 MHz
OBSET   7.87 KHz
OBFIN   4.21 Hz
POINT   26214
FREQU   31446.06 Hz
SCANS   1000
ACQTM   0.8336 sec
PD      2.0000 sec
PW1     3.83 usec
IRNUC   1H
CTEMP   24.4 c
SLVNT   CDCL3
EXREF   77.20 ppm
BF      0.12 Hz
RGAIN   60
```

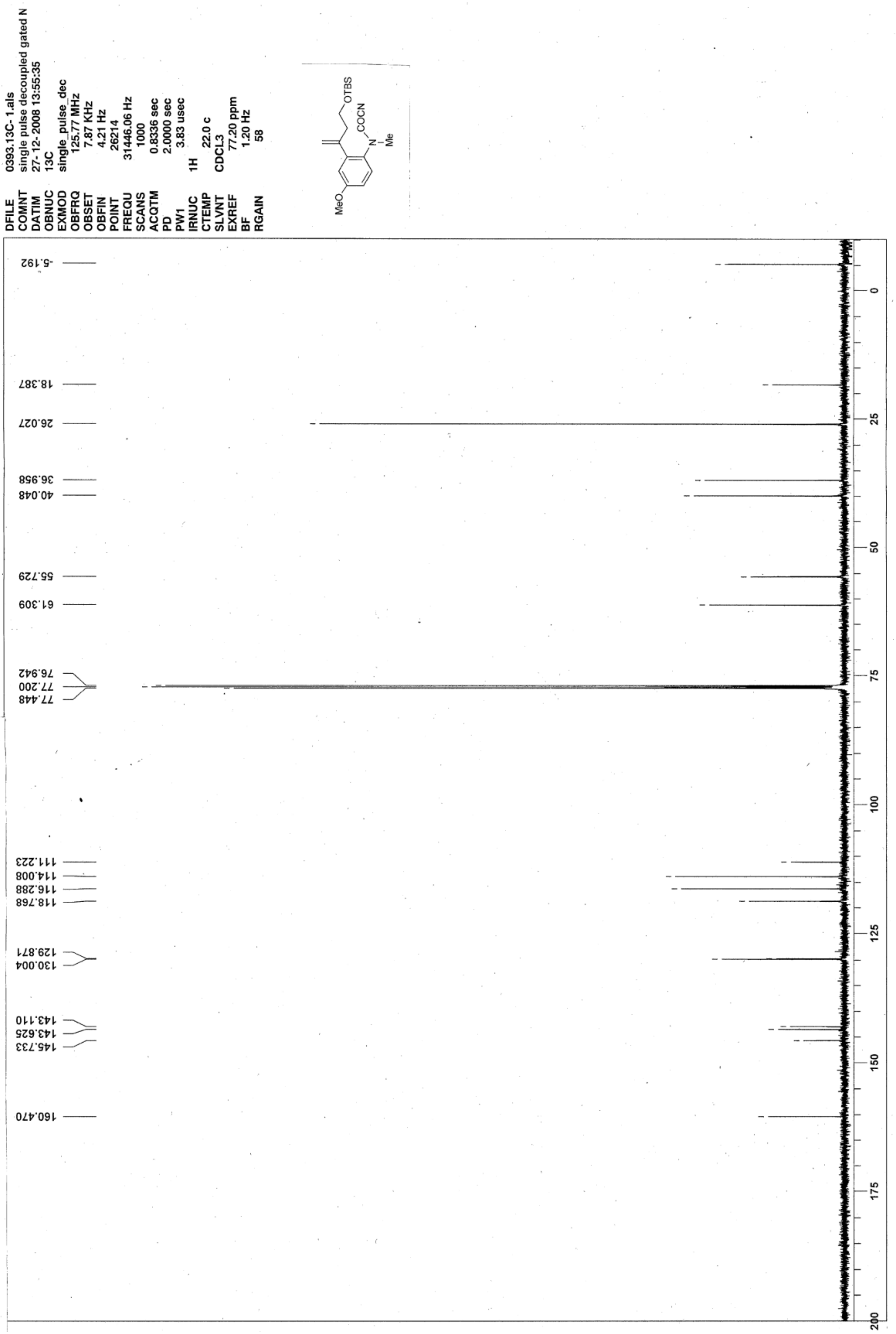

DFILE 0383.1H- 1.als
COMNT single_pulse
DATIM 18- 12- 2008 18:01:52
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 500.16 MHz
OBSET 2.41 KHz
OBFIN 6.01 Hz
POINT 13107
FREQU 7507.39 Hz
SCANS 8
ACQTM 1.7459 sec
PD 5.0000 sec
PW1 6.05 usec
IRNUC 1H
CTEMP 24.2 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 1.20 Hz
RGAIN 36
MeO
NH
Me
OTBS
0.000
0.032
0.888
1.599
2.523
2.535
2.548
2.771
3.639
3.652
3.665
3.742
3.982
5.104
5.294
6.545
6.562
6.601
6.607
6.752
6.758
6.769
6.775
7.254
6.23
9.46
2.04
3.07
2.03
3.04
0.92
1.02
1.03
1.01
1.00
1.00
3.00
PPM
0
2
4
6
8
10

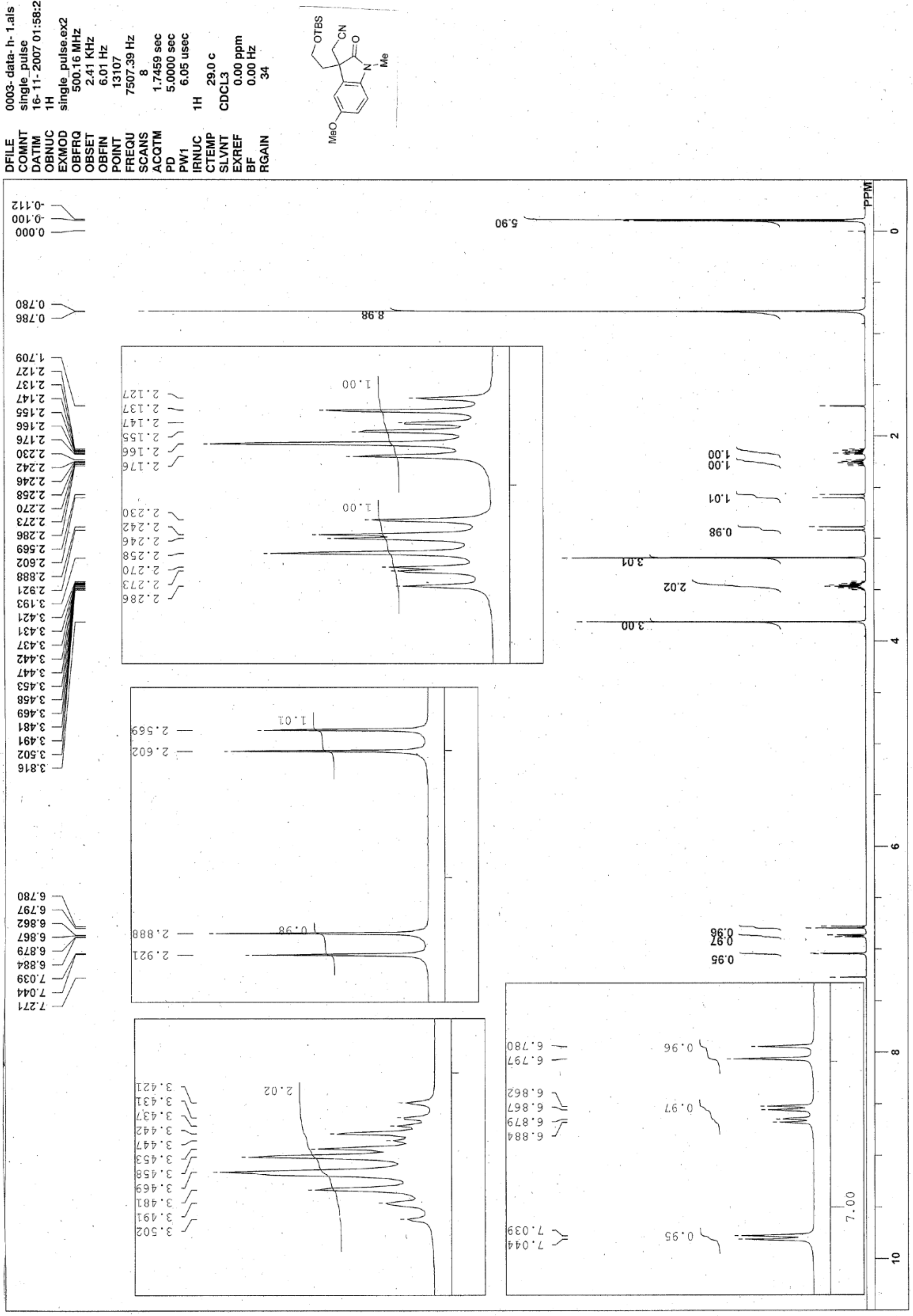


DFILE	0383.13C- 1.als
COMNT	single pulse decoupled gated N
DATIM	18- 12- 2008 18:49:51
OBNUC	13C
EXMOD	single_pulse_dec
OBFRQ	125.77 MHz
OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	26214
FREQU	31446.06 Hz
SCANS	1000
ACQTM	0.8336 sec
PD	2.0000 sec
PW1	3.83 usec
IRNUC	1H
CTEMP	24.6 c
SLVNT	CDCL3
EXREF	77.20 ppm
BF	1.20 Hz
RGAIN	60



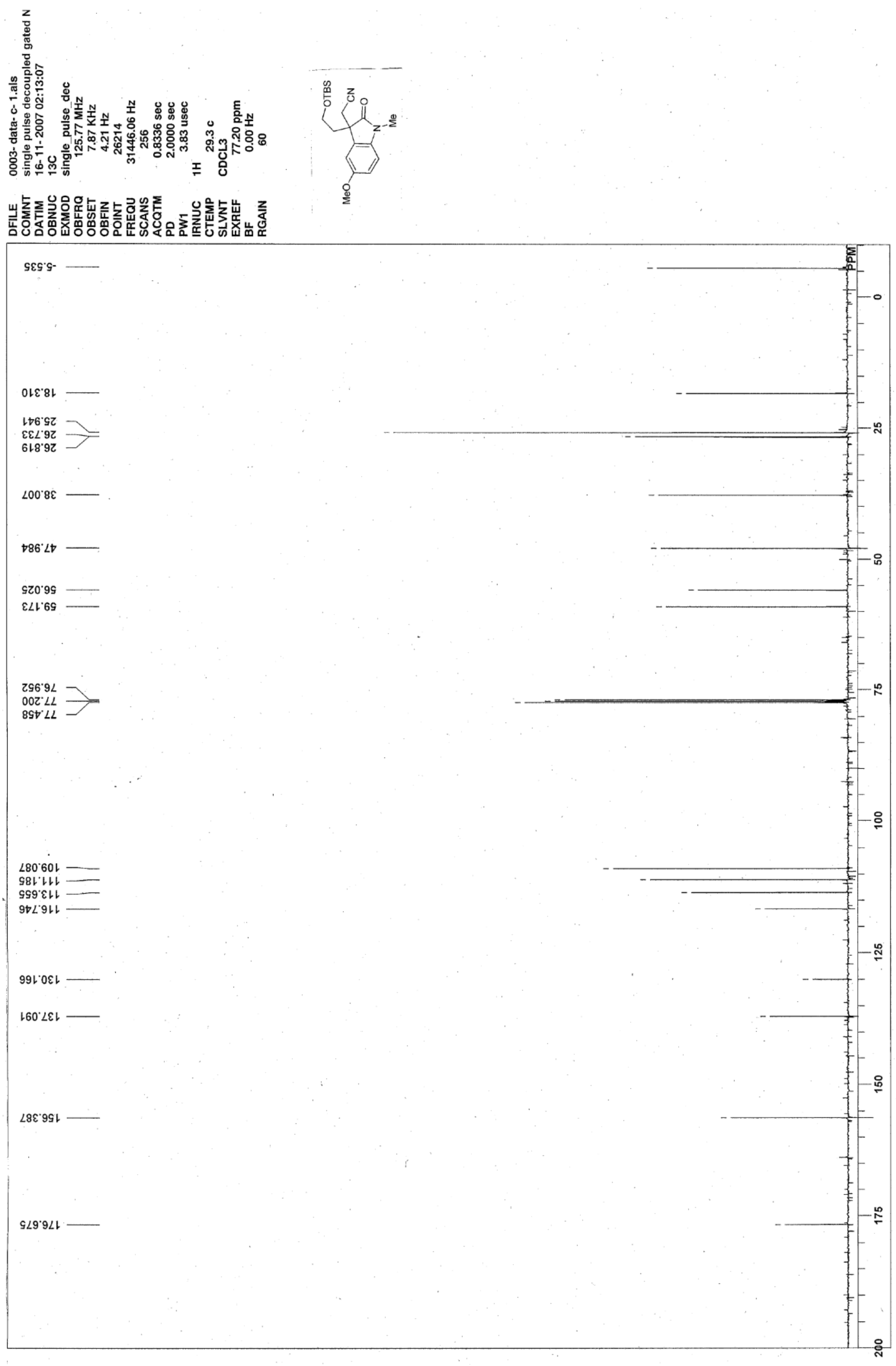

DFILE 0393.1H-1.als
COMNT single_pulse
DATIM 27-12-2008 13:07:36
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 500.16 MHz
OBSET 2.41 KHz
OBFIN 6.01 Hz
POINT 13107
FREQU 7507.39 Hz
SCANS 8
ACQTM 1.7459 sec
PD 5.0000 sec
PW1 6.05 usec
IRNUC 1H
CTEMP 21.6 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 1.20 Hz
RGAIN 40
MeO
OTBS
COCN
N
Me
0.000
0.011
0.025
0.865
2.498
2.510
2.523
3.232
3.487
3.659
3.673
3.679
3.692
3.701
3.706
3.714
3.726
3.734
3.747
3.810
3.842
5.045
5.127
5.254
5.337
6.814
6.843
6.848
6.875
6.880
6.892
6.897
7.029
7.046
7.135
7.152
7.263
6.22
9.13
1.97
2.79
0.16
2.00
3.03
0.05
0.93
0.05
0.93
1.97
0.06
0.91
3.00
5.00
7.00
PPM
0
2
4
6
8
10


DFILE 0393.13C- 1.als
COMNT single pulse decoupled gated N
DATIM 27- 12- 2008 13:55:35
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 125.77 MHz
OBSET 7.87 KHz
OBFIN 4.21 Hz
POINT 26214
FREQU 31446.06 Hz
SCANS 1000
ACQTM 0.8336 sec
PD 2.0000 sec
PW1 3.83 usec
IRNUC 1H
CTEMP 22.0 c
SLVNT CDCL3
EXREF 77.20 ppm
BF 1.20 Hz
RGAIN 58
MeO
OTBS
COCN
N
Me
-5.192
18.387
26.027
36.958
40.048
55.729
61.309
76.942
77.200
77.448
111.223
114.008
116.288
118.768
129.871
130.004
143.110
143.625
145.733
160.470
0
25
50
75
100
125
150
175
200

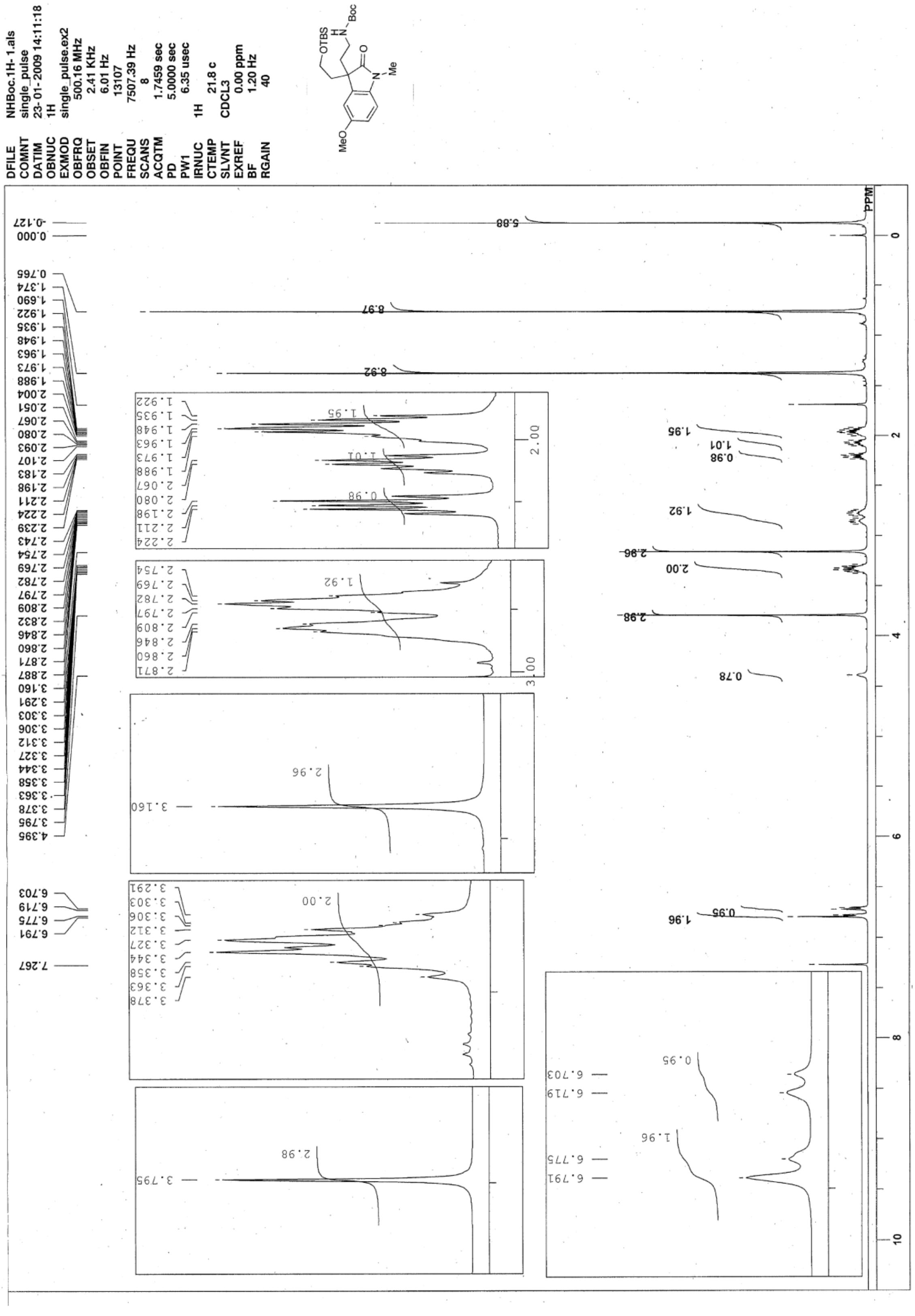


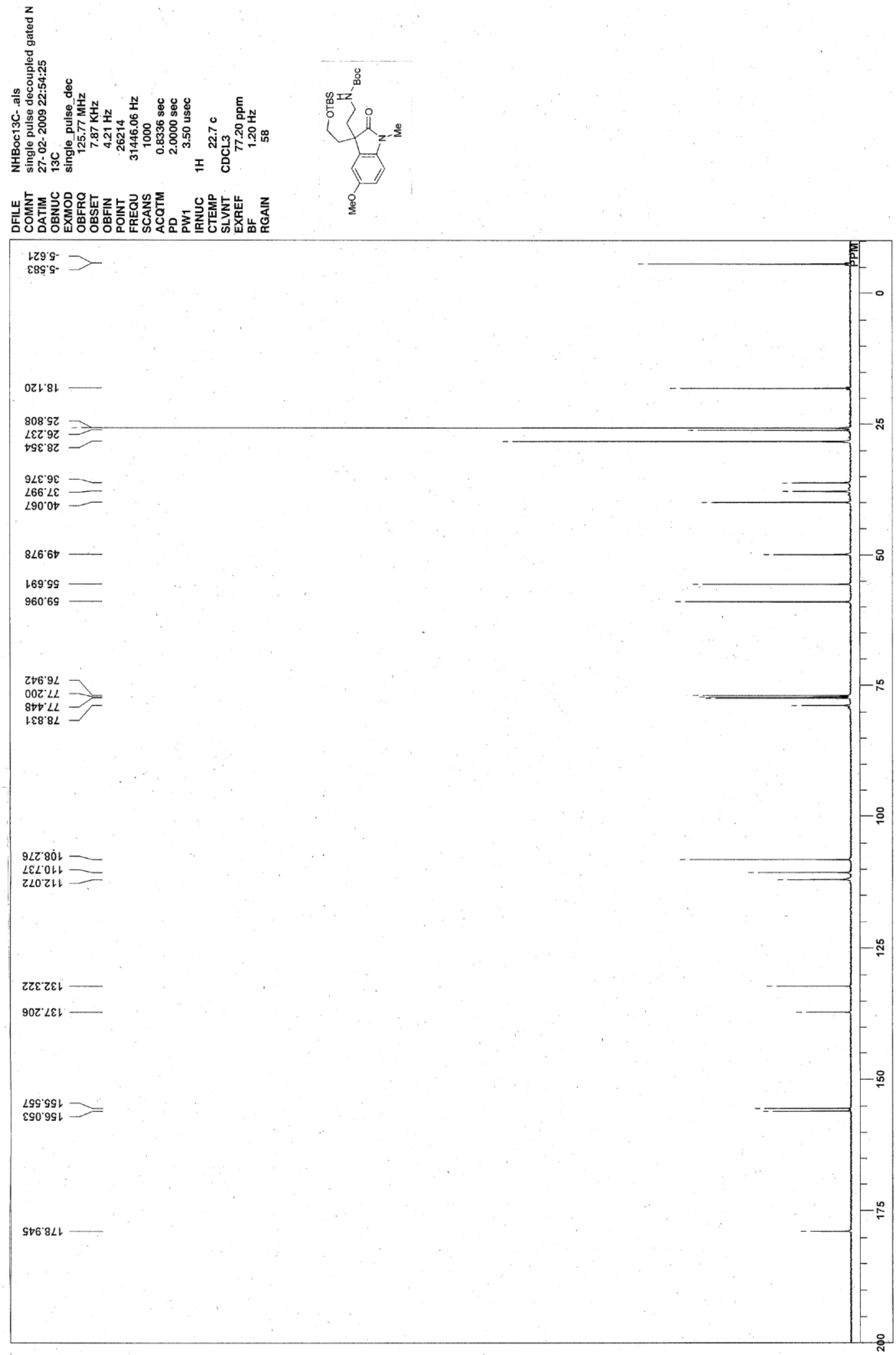
DFILE 0003-data-h-1.als
COMNT single_pulse
DATIM 16-11-2007 01:58:21
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 500.16 MHz
OBSET 2.41 KHz
OBFIN 6.01 Hz
POINT 13107
FREQU 7507.39 Hz
SCANS 8
ACQTM 1.7459 sec
PD 5.0000 sec
PW1 6.05 usec
IRNUC 1H
CTEMP 29.0 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.00 Hz
RGAIN 34

Supplementary Material (ESI) for Chemical Communications



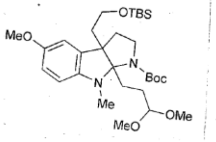
DFILE 0003-data-c-1.als
COMNT single pulse decoupled gated N
DATIM 16-11-2007 02:13:07
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 125.77 MHz
OBSET 7.87 KHz
OBFIN 4.21 Hz
POINT 26214
FREQU 31446.06 Hz
SCANS 256
ACOTM 0.8336 sec
PD 2.0000 sec
PW1 3.83 usec
IRNUC 1H
CTEMP 29.3 c
SLVNT CDCL3
EXREF 77.20 ppm
BF 0.00 Hz
RGAIN 60

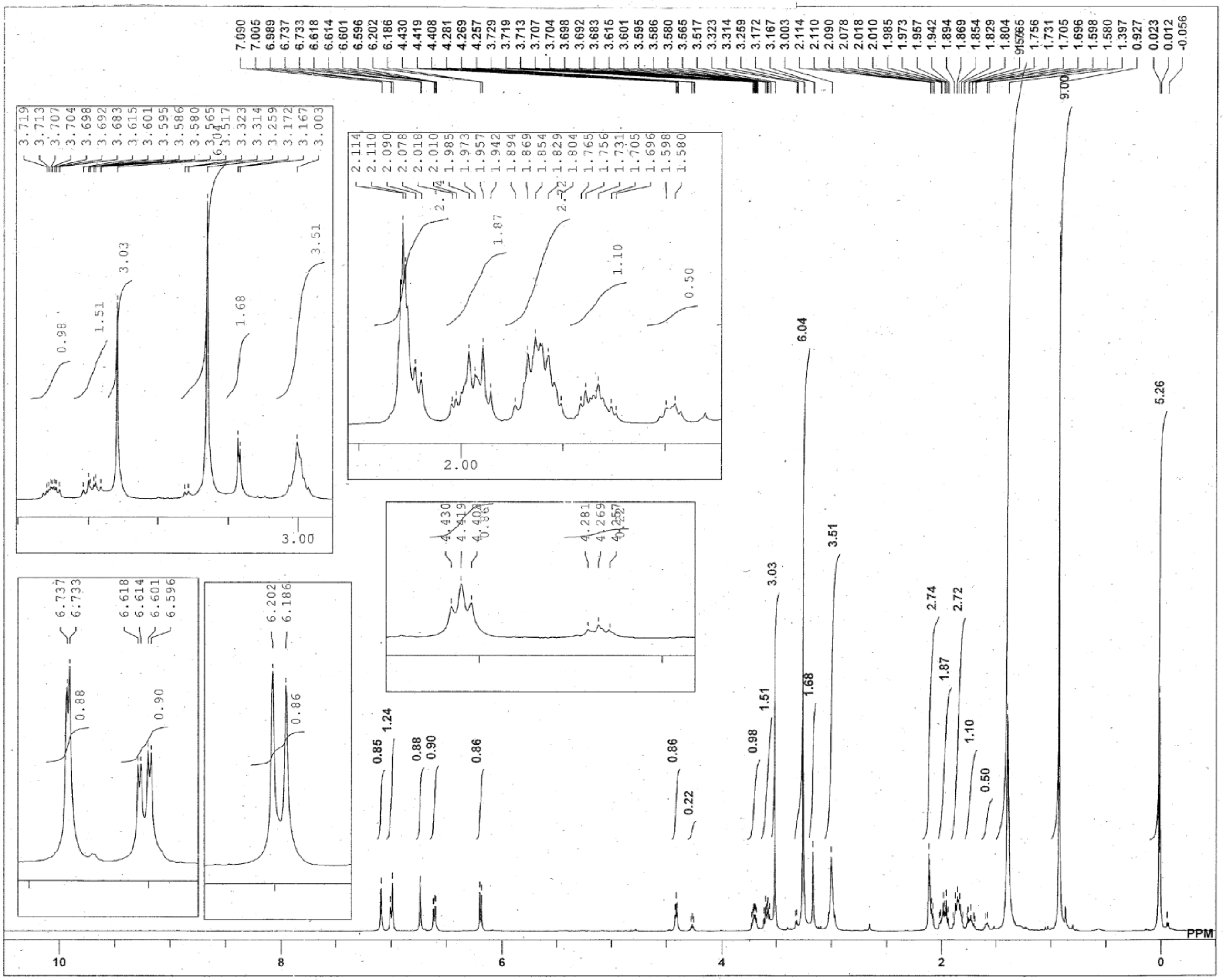

DFILE NHBoc.1H-1.als
COMNT single_pulse
DATIM 23-01-2009 14:11:18
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 500.16 MHz
OBSET 2.41 KHz
OBFIN 6.01 Hz
POINT 13107
FREQU 7507.39 Hz
SCANS 8
ACQTM 1.7459 sec
PD 5.0000 sec
PW1 6.35 usec
IRNUC 1H
CTEMP 21.8 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 1.20 Hz
RGAIN 40
OTBS
H
N
Boc
O
N
Me
MeO
PPM
-0.127
0.000
0.765
1.374
1.690
1.922
1.935
1.948
1.963
1.973
1.988
2.004
2.051
2.067
2.080
2.093
2.107
2.183
2.198
2.211
2.224
2.239
2.743
2.754
2.769
2.782
2.797
2.809
2.832
2.846
2.860
2.871
2.887
3.160
3.291
3.303
3.306
3.312
3.327
3.344
3.358
3.363
3.378
3.795
4.395
6.703
6.719
6.775
6.791
7.267
5.88
8.97
8.92
1.95
1.01
0.98
1.92
2.96
2.00
2.98
0.78
0.95
1.96
0
2
4
6
8
10

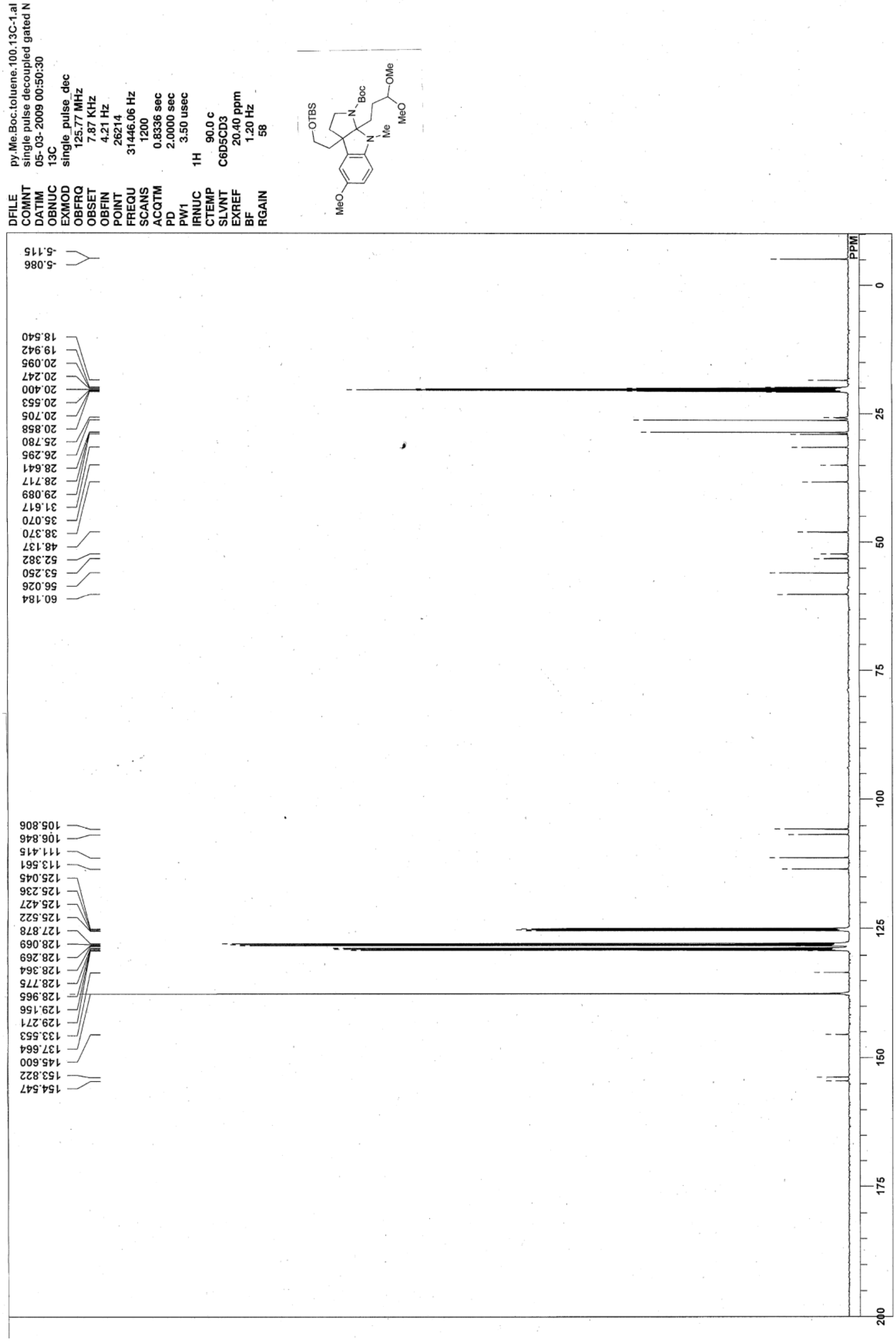


DFILE NHBoc13C-.als
COMNT single pulse decoupled gated N
DATIM 27-02-2009 22:54:25
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 125.77 MHz
OBSET 7.87 KHz
OBFIN 4.21 Hz
POINT 26214
FREQU 31446.06 Hz
SCANS 1000
ACQTM 0.8336 sec
PD 2.0000 sec
PW1 3.50 usec
IRNUC 1H
CTEMP 22.7 c
SLVNT CDCL3
EXREF 77.20 ppm
BF 1.20 Hz
RGAIN 58

DFILE	py.Me.Boc.toluene.100.1H- 1.al
COMNT	single_pulse
DATIM	04- 03- 2009 23:52:58
OBNUC	1H
EXMOD	single_pulse.ex2
OBFRQ	500.16 MHz
OBSET	2.41 KHz
OBFIN	6.01 Hz
POINT	13107
FREQU	7507.39 Hz
SCANS	8
ACQTM	1.7459 sec
PD	5.0000 sec
PW1	6.35 usec
IRNUC	1H
CTEMP	90.0 c
SLVNT	C6D5CD3
EXREF	7.09 ppm
BF	1.20 Hz
RGAIN	42






DFILE py.Me.Boc.toluene.100.13C-1.al
COMNT single pulse decoupled gated N
DATIM 05-03-2009 00:50:30
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 125.77 MHz
OBSET 7.87 KHz
OBFIN 4.21 Hz
POINT 26214
FREQU 31446.06 Hz
SCANS 1200
ACQTM 0.8336 sec
PD 2.0000 sec
PW1 3.50 usec
IRNUC 1H
CTEMP 90.0 c
SLVNT C6D5CD3
EXREF 20.40 ppm
BF 1.20 Hz
RGAIN 58
OTBS
N
Boc
OMe
MeO
N
Me
MeO
-5.115
-5.086
18.540
19.942
20.095
20.247
20.400
20.553
20.705
20.858
25.780
26.295
28.641
28.717
29.089
31.617
35.070
38.370
48.137
52.382
53.250
56.026
60.184
105.806
106.846
111.415
113.561
125.045
125.236
125.427
125.522
127.878
128.069
128.269
128.364
128.775
128.965
129.156
129.271
133.553
137.664
145.600
153.822
154.547
PPM
0
25
50
75
100
125
150
175
200