Supporting Information

Highly Efficient Recognition of Native TpT by Artificial Ditopic Hydrogen-Bonding Receptors Possessing a Conformationally Well-Defined Linkage

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Synthetic procedures and spectroscopic data (mp, IR, ^{1}H NMR, ^{13}C NMR, MS, and elemental analysis)

Ferrocene-Linked Ditopic Reoceptor 2. To a THF (16 mL) solution of **12**[16] (176 mg, 0.72 mmol), **15**[17] (314 mg, 1.50 mmol), and *N,N,N',N'*-tetramethylazodicarboxamide (259 mg, 1.51 mmol) was added *n*-Bu_3P (305 mg, 1.51 mmol) at room temperature. The solution was stirred for 6 h at the same temperature. After removal of the solvent, the residue was poured into water and extracted with CH_2Cl_2. The CH_2Cl_2 extract was evaporated and chromatographed (silica gel; eluent, CH_2Cl_2/MeOH/Et_3N 40:2:1) to give **2**: yield 44% (200 mg); mp > 180 °C (dec); IR (KBr) 1670, 1579 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.61 (br s, 4 H), 7.55 (br s, 4 H), 4.90 (s, 4 H), 4.37 (s, 4 H), 4.24 (s, 4 H), 2.20 (s, 12 H); ^{13}C NMR (DMSO-d_6) δ 169.40, 166.78, 151.37, 95.72, 81.78, 70.39, 69.27, 65.78, 24.05; FABMS (in 3-nitrobenzyl alcohol) *m/e* (rel intensity) 628 (M^+, 100%). Anal. Calcd for $C_{30}H_{34}FeN_6O_6$: C, 57.15; H, 5.44; N, 13.33.

Found: C, 56.42; H, 5.09; N, 13.12.

Lipophilic TpT Analogue 3. To a THF (13 mL) solution of dichlorodi-*n*-hexylsilane (404 mg, 1.50 mmol) and pyridine (3.1 mL) was added a THF (10 mL) solution of 5'-*O*-(*tert*-butyldimethylsilyl)thymidine[23] (500 mg, 1.40 mmol) dropwise at -78 °C over a 30 min period. After the reaction mixture was stirred at -78 °C for 2 h, to the mixture was added a THF (10 mL) solution of 3'-*O*-(*tert*-butyldimethylsilyl)thymidine[23] (463 mg, 1.30 mmol) dropwise at the same temperature over a 10 min period. The reaction mixture was then allowed to warm slowly to room temperature with stirring and evaporated. The residue was poured into brine and extracted with $CHCl_3$. The $CHCl_3$ extract was evaporated and chromatographed (silica gel; eluent, CH_2Cl_2/MeOH 30:1) to afford crude **3**. The crude **3** was purified by HPLC (ODS; eluent, MeOH) to give pure **3**: yield 15% (193 mg); mp 48–50 °C; IR (KBr) 3419, 1699, 1277, 1255 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.87 (br s, 2 H), 7.47 (br s, 1 H), 7.41 (br s, 1 H), 6.38–6.24 (m, 2 H), 4.55–4.46 (m, 1 H), 4.42–4.33 (m, 1 H), 4.00 (br s, 1 H), 3.96–3.69 (m, 5 H), 2.34–2.22 (m, 2 H), 2.09–1.97 (m, 2 H), 1.92 (s, 6 H), 1.40–1.21 (m, 16 H), 0.97–0.82 (m, 24 H), 0.70–0.62 (m, 4 H), 0.114 (s, 3H), 0.109 (s, 3H), 0.82 (s, 3H), 0.77 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 163.66, 150.22, 135.52, 135.21, 110.92, 110.77, 87.77, 87.12, 84.93, 84.86, 72.88, 71.85, 63.33, 62.20, 41.20, 40.89, 33.04, 33.01, 31.39, 25.87, 25.68, 22.71, 22.66, 22.52, 18.33, 17.93, 14.05, 12.64, 12.51, 12.46, -4.68, -4.84, -5.37, -5.54; FABMS (in 3-nitrobenzyl alcohol) *m/e* (rel intensity) 909 (MH^+, 100%). Anal. Calcd for $C_{46}H_{82}N_2O_{10}Si_3$: C, 60.89; H, 9.11; N, 3.09 Found: C, 59.34; H, 8.87; N, 5.80.

Naphthalene-Linked U-U Dinucleotide Derivative 5. To a DMF–Et_2NH (2 + 2 mL) mixed solution of **26**[19] (152 mg, 0.40 mmol), $(Ph_3P)_2PdCl_2$ (28 mg, 40 μmol), and CuI (3.8 mg, 20 μmol) was added a DMF (2 mL) solution of **25** (248 mg, 1.0 mmol) dropwise at 0 °C. The reaction mixture was stirred at room temperature for 5 h and evaporated. The residue was poured into water and extracted with CH_2Cl_2. The CH_2Cl_2 extract was evaporated and chromatographed (silica gel; eluent, ether/hexane 4:1)

to give **5**: yield 24% (150 mg); mp 174–175 °C; IR (KBr) 3419, 1699 cm^{-1}; ^1H NMR ($CDCl_3$) δ 9.84 (s, 2 H), 7.83 (d, J = 7.8 Hz, 2 H), 7.80 (d, J = 7.1 Hz, 2 H), 7.57 (s, 2 H), 7.44 (dd, J = 7.8, 7.1 Hz, 2 H), 3.78 (t, J = 7.3 Hz, 4 H), 1.77–1.64 (m, 4 H), 1.40–1.15 (m, 20 H), 0.86 (t, J = 6.5 Hz, 6 H); ^{13}C NMR ($CDCl_3$) δ 161.33, 150.61, 147.40, 134.93, 133.90, 132.25, 130.08, 125.51, 120.09, 100.89, 92.90, 87.33, 49.17, 31.74, 29.14, 29.04, 26.49, 22.60, 14.07; FABMS (in 3-nitrobenzyl alcohol) *m/e* (rel intensity) 621 (MH^+, 100%). Anal. Calcd for $C_{38}H_{44}N_4O_4$: C, 73.52; H, 7.14; N, 9.03. Found: C, 73.58; H, 7.02; N, 8.81.

Biphenylene-Linked U-U Dinucleotide Derivative 6. An Et_3N (11 mL) solution of **25** (738 mg, 2.97 mmol), **28** (300 mg, 0.74 mmol), $(Ph_3P)_2PdCl_2$ (13 mg, 18 μmol), and CuI (3.4 mg, 18 μmol) was stirred at 40 °C for 1 h. After removal of the solvent, the residue was recrystallized from $CHCl_3$ to give **6**: yield 81% (385 mg); mp 237–239 °C; IR (KBr) 3446, 2219, 1705, 1689 cm^{-1}; ^1H NMR (DMSO-d_6) δ 11.55 (s, 2 H), 7.99 (s, 2 H), 6.90–6.76 (m, 6 H), 3.55 (t, J = 7.1 Hz, 4 H), 1.57–1.46 (m, 4 H), 1.30–1.16 (m, 20 H), 0.84 (t, J = 6.6 Hz, 6 H); ^{13}C NMR (DMSO-d_6) δ 161.58, 150.87, 149.83, 149.60, 148.95, 131.50, 129.78, 117.80, 112.96, 97.10, 87.84, 85.92, 48.14, 31.20, 28.56, 28.50, 28.23, 25.77, 22.07, 13.93; FABMS (in 3-nitrobenzyl alcohol) *m/e* (rel intensity) 645 (MH^+, 100%). Anal. Calcd for $C_{40}H_{44}N_4O_4$: C, 74.51; H, 6.88; N, 8.69. Found: C, 74.27; H, 6.92; N, 8.80.

Anthracene-Linked U-U Dinucleotide Derivative 7. A CH_3CN–Et_3N (7 + 7 mL) mixed solution of **23** (1.86 g, 5.31 mmol), **29**[21] (400 mg, 1.77 mmol), $(Ph_3P)_2PdCl_2$ (31 mg, 44 μmol), and CuI (8 mg, 44 μmol) was stirred at 60 °C for 2 h. After removal of the solvent, the residue was poured into water and extracted with $CHCl_3$. The $CHCl_3$ extract was evaporated and chromatographed (silica gel; eluent, CH_2Cl_2/MeOH 40:1) to give **7**: yield 26% (311 mg); mp 254–255 °C; IR (KBr) 3415, 2207, 1687 cm^{-1}; ^1H NMR (DMSO-d_6) δ 11.68 (s, 2 H), 9.31 (s, 1 H), 8.74 (s, 1 H), 8.27 (s, 2 H), 8.17 (d, J = 8.3 Hz, 2 H), 7.80 (d, J = 7.0 Hz, 2 H), 7.58 (dd, J = 8.3, 7.0 Hz, 2 H), 3.70 (t, J = 7.1 Hz, 4 H),

1.67–1.50 (m, 4 H), 1.35–1.15 (m, 20 H), 0.82 (d, J = 6.7 Hz, 6 H); ^{13}C NMR (DMSO-d_6) δ 161.99, 149.92, 149.08, 131.12, 130.99, 130.32, 129.09, 128.17, 125.65, 122.76, 120.53, 97.49, 90.03, 88.21, 79.17, 48.23, 31.21, 28.58, 28.41, 25.77, 22.07, 13.91; FABMS (in 3-nitrobenzyl alcohol) *m/e* (rel intensity) 671 (MH^+, 100%). Anal. Calcd for $C_{42}H_{46}N_4O_4$: C, 75.20; H, 6.91; N, 8.35. Found: C, 74.21; H, 6.90; N, 8.34.

Naphthalene-Linked Ditopic Receptor 8. A DMF–Et_3N (3 + 1 mL) mixed solution of **14** (335 mg, 1.11 mmol), **26**[19] (141 mg, 0.37 mmol), $(Ph_3P)_2PdCl_2$ (16 mg, 22 μmol), and CuI (2 mg, 11 μmol) was stirred at 55 °C for 9 h. After removal of the solvent, the residue was poured into water and extracted with CH_2Cl_2. The CH_2Cl_2 extract was evaporated and chromatographed (silica gel; eluent, CH_2Cl_2/MeOH 100:1) to give **8**: yield 74% (200 mg); mp 170–171 °C; IR (KBr) 3295, 2203, 1678, 1553 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.90–7.84 (m, 4 H), 7.76 (br s, 4 H), 7.63 (br s, 4 H), 7.49 (dd, J = 7.8, 7.5 Hz, 2 H), 2.38–2.28 (m, 8 H), 1.72–1.59 (m, 8 H), 1.45–1.30 (m, 8 H), 0.98–0.88 (m, 12 H); ^{13}C NMR ($CDCl_3$) δ 171.62, 149.46, 136.27, 135.59, 133.99, 131.37, 130.56, 125.84, 119.74, 112.10, 94.66, 94.43, 37.37, 27.58, 22.64, 14.12; FABMS (in 3-nitrobenzyl alcohol) *m/e* (rel intensity) 727 (MH^+, 100%). Anal. Calcd for $C_{44}H_{50}N_6O_4$: C, 72.70; H, 6.93; N, 11.56. Found: C, 72.12; H, 6.95; N, 11.54.

Biphenylene-Linked Ditopic Receptor 9. A THF–Et_3N (3 + 3 mL) mixed solution of **14** (333 mg, 1.10 mmol), **28** (113 mg, 0.28 mmol), $(Ph_3P)_4Pd$ (26 mg, 22 μmol), and $Cu(OAc)_2 \cdot H_2O$ (4 mg, 22 μmol) was stirred at 60 °C for 4 h. After removal of the solvent, the residue was poured into water and extracted with $CHCl_3$. The $CHCl_3$ extract was evaporated and chromatographed (silica gel; eluent, hexane/AcOEt 1:1) to give **9**: yield 95% (199 mg); mp 205–206 °C; IR (KBr) 3281, 2215, 1678, 1552 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.67 (br s, 4 H), 7.61 (br s, 4 H), 6.86–6.75 (m, 4H), 6.63 (dd, J = 6.3, 1.2 Hz, 2 H), 2.34–2.23 (m, 8 H), 1.72–1.56 (m, 8 H), 1.44–1.29 (m, 8 H), 1.01–0.84 (m, 12 H); ^{13}C NMR ($CDCl_3$) δ 171.32, 152.34, 150.54, 149.26, 135.64, 131.53, 129.17, 117.54, 113.14, 112.02, 90.95, 90.53, 37.42, 27.51, 22.68, 14.13; FABMS (in 3-

nitrobenzyl alcohol) *m/e* (rel intensity) 750 (MH^+, 100%). Anal. Calcd for $C_{46}H_{50}N_6O_4$: C, 73.57; H, 6.71; N, 11.19. Found: C, 72.52; H, 6.72; N, 11.00.

Anthracene-Linked Ditopic Receptor 10. A THF–Et_3N (4 + 1 mL) mixed solution of **19** (1.86 g, 5.31 mmol), **29**[21] (111 mg, 0.49 mmol), and $(Ph_3P)_2PdCl_2$ (17 mg, 24 μmol) was stirred at 70 °C for 2 h. After removal of the solvent, the residue was poured into water and extracted with CH_2Cl_2. The CH_2Cl_2 extract was evaporated and chromatographed (silica gel; eluent, CH_2Cl_2/MeOH 50:1) to give **10**: yield 64% (240 mg); mp 229–231 °C; IR (KBr) 3299, 2207, 1676, 1552 cm^{-1}; ^1H NMR ($CDCl_3$) δ 9.47 (s, 1 H), 8.48 (s, 1 H), 8.06 (d, J = 8.7 Hz, 2 H), 7.92 (br s, 4 H), 7.82 (d, J = 7.5 Hz, 2 H), 7.67 (br s, 4 H), 7.50 (dd, J = 8.7, 7.1 Hz, 2 H), 2.36–2.24 (m, 8 H), 1.70–1.45 (m, 8 H), 1.44–1.29 (m, 8 H), 0.98–0.86 (m, 12 H); ^{13}C NMR ($CDCl_3$) δ 171.37, 149.59, 136.09, 131.71, 131.55, 131.47, 129.95, 127.79, 125.35, 123.99, 120.71, 111.92, 93.17, 92.49, 37.45, 27.53, 22.69, 14.13; FABMS (in 3-nitrobenzyl alcohol) *m/e* (rel intensity) 777 (MH^+, 100%). Anal. Calcd for $C_{48}H_{52}N_6O_4$: C, 74.20; H, 8.24; N, 10.82. Found: C, 73.90; H, 8.06; N, 10.53.

2,6-Di-*n*-pentamido-4-ethynylpyridine (14). This compound was synthesized from 4-(allyloxy)-2,6-diaminopyridine[18] (**16**) in 5 steps in a manner similar to that described for **13**.[13] To a CH_2Cl_2 (140 mL) solution of **16** (2.3 g, 13.9 mmol) and Et_3N (5.3 mL) was added *n*-valeryl chloride (3.7 g, 30.6 mmol) dropwise at 0 °C. The reaction mixture was stirred at room temperature for 5 h, washed with water, and evaporated. The residue was subjected to column chromatography (silica gel; eluent, $CHCl_3$/AcOEt 50:1) to give 4-(allyloxy)-2,6-di-*n*-pentamidopyridine (**17**): yield 93% (4.3 g); mp 47–49 °C; IR (KBr) 3421, 1687, 1585 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.57 (br s, 4 H), 6.07–5.96 (m, 1 H), 5.43 (dd, J = 17.2, 1.3 Hz, 1 H), 5.30 (dd, J = 10.6, 1.3 Hz, 1 H), 4.61 (dd, J = 5.4, 1.5 Hz, 2 H), 2.35 (t, J = 7.3 Hz, 4 H), 1.74–1.65 (m, 4 H), 1.45–1.34 (m, 4 H), 0.94 (t, J = 7.3 Hz, 6 H); ^{13}C NMR ($CDCl_3$) δ 171.67, 168.47, 150.51, 132.05, 118.32, 96.37, 69.03, 37.61, 27.37, 22.31, 13.79; FABMS (in 3-nitrobenzyl alcohol) *m/e* (rel

intensity) 334 (MH^+, 100%). Anal. Calcd for $C_{18}H_{27}N_3O_3$: C, 64.84; H, 8.16; N, 12.60. Found: C, 64.58; H, 8.20; N, 12.38. A CH_3CN–EtOH–H_2O (15 + 15 + 15 mL) mixed solution of **17** (2.3 g, 90 mmol), $(Ph_3P)_3RhCl$ (511 mg, 0.55 mmol), and DABCO (77 mg, 0.69 mmol) was stirred at 70 °C for 18 h. After removal of the solvent, the residue was subjected to column chromatography (silica gel; eluent, CH_2Cl_2/MeOH 20:1) to give 2,6-di-*n*-pentamido-4-pyridone (**18**): yield 79% (1.6 g); mp 168–169 °C; IR (KBr) 1662 cm^{-1}; ^1H NMR (DMSO-d_6) δ 10.47 (s, 1 H), 9.74 (s, 2 H), 7.25 (s, 2 H), 2.34 (t, J = 7.3 Hz, 4 H), 1.57–1.48 (m, 4 H), 1.34–1.22 (m, 4 H), 0.87 (t, J = 7.3 Hz, 6 H); ^{13}C NMR (DMSO-d_6) δ 172.07, 166.55, 151.24, 96.84, 35.86, 27.18, 21.73, 13.72; FABMS (in 3-nitrobenzyl alcohol) *m/e* (rel intensity) 294 (MH^+, 100%). Anal. Calcd for $C_{15}H_{23}N_3O_3$: C, 61.41; H, 7.90; N, 14.32. Found: C, 60.84; H, 7.90; N, 14.27. To a pyridine (10 mL) solution of **18** (2.3 g, 7.84 mmol) was added trifluoromethanesulfonic anhydride (2.9 g, 10.2 mmol) dropwise at 0 °C over a 5 min period. The reaction mixture was stirred at room temperature for 5 h. After removal of the solvent, the residue was poured into water and extracted with ether. The ether extract was evaporated and chromatographed (silica gel; eluent, CH_2Cl_2/MeOH 30:1) to give 4-(2,6-di-*n*-pentamidopyridyl) trifluoromethanesulfonate (**19**): yield 87% (2.8 g); mp 72–73 °C; IR (KBr) 3396, 1672, 1217 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.95 (s, 2 H), 7.72 (s, 2 H), 2.39 (t, J = 7.6 Hz, 4 H), 1.76–1.63 (m, 4 H), 1.47–1.33 (m, 4 H), 0.95 (t, J = 7.3 Hz, 6 H); ^{13}C NMR ($CDCl_3$) δ 171.82, 158.65, 151.12, 118.61 (q, $J_{C\text{-}F}$ = 321 Hz), 102.14, 37.42, 27.11, 22.26, 13.76; FABMS (in 3-nitrobenzyl alcohol) *m/e* (rel intensity) 426 (MH^+, 100%). Anal. Calcd for $C_{16}H_{22}F_3N_3O_5S$: C, 45.17; H, 5.21; N, 9.88. Found: C, 45.03; H, 5.10; N, 9.84. To an Et_3N (18 mL) solution of **19** (1.7 g, 4.13 mmol) and $(Ph_3P)_2PdCl_2$ (58 mg, 83 μmol) was added (trimethylsilyl)acetylene (811 mg, 8.26 mmol) at 40 °C. The reaction mixture was stirred at 70 °C for 2 h. After removal of the solvent, the residue was poured into water and extracted with CH_2Cl_2. The CH_2Cl_2 extract was evaporated and chromatographed (silica gel; eluent, CH_2Cl_2) to give 2,6-di-*n*-pentamido-4-[(trimethylsilyl)ethynyl]pyridine (**20**): yield 94% (1.5 g); mp 126–128 °C; IR (KBr) 3423, 2164, 1699, 1556, 849, 764 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.98 (s, 2 H), 7.50 (s, 2 H), 2.37 (t, J

= 7.6 Hz, 4 H), 1.75–1.66 (m, 4 H), 1.46–1.35 (m, 4 H), 0.95 (t, J = 7.3 Hz, 6 H), 0.24 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 171.68, 149.45, 135.53, 111.70, 102.25, 99.56, 37.26, 27.24, 22.17, 13.68, -0.48; FABMS (in 3-nitrobenzyl alcohol) *m/e* (rel intensity) 374 (MH^+, 100%). Anal. Calcd for $C_{20}H_{31}N_3O_2Si$: C, 64.30; H, 8.36; N, 11.25. Found: C, 64.31; H, 8.25; N, 11.13. To a THF (30 mL) solution of **20** (1.3 g, 3.53 mmol) was added tetra-*n*-butylammonium fluoride (1.4 mg, 5.30 mmol) and a few drops of water at room temperature. The reaction mixture was stirred at the same temperature for 1.5 h. After removal of the solvent, the residue was poured into water and extract with CH_2Cl_2. The CH_2Cl_2 extract was evaporated and chromatographed (silica gel; eluent, CH_2Cl_2) to give **14**: yield 96% (1.0 g); mp 135–136 °C; IR (KBr) 3423, 3255, 2104, 1699, 1560 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.01 (s, 2 H), 7.54 (br s, 2 H), 3.24 (s, 1 H), 2.37 (t, J = 7.3 Hz, 4 H), 1.75–1.65 (m, 4 H), 1.46–1.35 (m, 4 H), 0.95 (t, J = 7.3 Hz, 6 H); ^{13}C NMR ($CDCl_3$) δ 171.51, 149.51, 134.81, 112.02, 81.49, 81.37, 37.55, 27.36, 22.30, 13.79; FABMS (in 3-nitrobenzyl alcohol) *m/e* (rel intensity) 302 (MH^+, 100%). Anal. Calcd for $C_{17}H_{23}N_3O_2$: C, 67.75; H, 7.69; N, 13.94. Found: C, 68.15; H, 7.80; N, 13.91.

1-*n*-Octyluracil (22). To a DMSO (100 mL) suspension of uracil (**21**: 10 g, 89 mmol) and finely ground K_2CO_3 (62 g, 450 mmol) was added a DMSO (50 mL) solution of 1-bromooctane (21 g, 110 mmol) dropwise at 0 °C. The reaction mixture was stirred at room temperature for 12 h and filtered. The filtrate was evaporated, and the residue was poured into water and extracted with $CHCl_3$ (ca. 200 mL). The $CHCl_3$ extract was concentrated to one-tenth of its original volume and dropped into a large quantity of cold (ca. 0 °C) hexane with stirring. The resulting precipitate was filtered and washed with hexane to give **22**: yield 39% (7.8 g); mp 69–70 °C; IR (KBr) 1693, 1649 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 9.54 (br s, 1 H), 7.16 (d, J = 7.8 Hz, 1 H), 5.71 (d, J = 7.8 Hz, 1 H), 3.72 (t, J = 7.3 Hz, 2 H), 1.77–1.60 (m, 2 H), 1.40–1.20 (m, 10 H), 0.88 (t, J = 6.8 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 163.94, 150.90, 144.41, 102.03, 48.86, 31.66, 29.07, 29.04, 29.00, 26.36, 22.54, 14.01; FABMS (in 3-nitrobenzyl alcohol) *m/e* (rel intensity) 225 (MH^+, 100%). Anal. Calcd for $C_{12}H_{20}N_2O_2$: C, 64.26; H, 8.99; N, 12.49. Found: C,

64.08; H, 9.04; N, 12.56.

5-Iodo-1-*n*-octyluracil (23). To a MeOH (30 mL) solution of **22** (5.0 g, 22 mmol) was added ICl (7.0 g, 44 mmol) dropwise at room temperature. The reaction mixture was stirred at the same temperature for 10 h and cooled to -78 °C. The resulting precipitate was filtered and washed with cold (ca. 0 °C) hexane to give **23**: yield 75% (5.8 g); mp 152–154 °C; IR (KBr) 1703, 1674 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.83 (s, 1 H), 7.61 (s, 1 H), 3.74 (t, J = 7.3 Hz, 2 H), 1.75–1.62 (m, 2 H), 1.41–1.20 (m, 10 H), 6.88 (t, J = 6.5 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 160.33, 150.30, 148.87, 67.45, 49.23, 31.68, 29.17, 29.04, 26.31, 22.58, 14.05; FABMS (in 3-nitrobenzyl alcohol) *m/e* (rel intensity) 351 (MH^+, 100%). Anal. Calcd for $C_{12}H_{19}IN_2O_2$: C, 41.16; H, 5.47; N, 8.00. Found: C, 41.84; H, 5.48; N, 8.18.

1-*n*-Octyl-5-[(trimethylsilyl)ethynyl]uracil (24). To an Et_3N (140 mL) solution of **23** (5.0 g, 14.3 mmol), $(Ph_3P)_2PdCl_2$ (200 mg, 0.29 mmol), and CuI (27 mg, 0.14 mmol) was added (trimethylsilyl)acetylene (5.6 g, 57 mmol) dropwise at 40 °C. The reaction mixture was stirred at 60 °C for 2 h and evaporated. The residue was poured into water and extracted with CH_2Cl_2. The CH_2Cl_2 extract was evaporated and chromatographed (silica gel; eluent, $CHCl_3$/AcOEt 15:1) to give **24**: yield 85% (3.9 g); mp 94–95 °C; IR (KBr) 3419, 2158, 1713, 1678 cm^{-1}; ^1H NMR ($CDCl_3$) δ 9.06 (br s, 1 H), 7.47 (s, 1 H), 3.73 (t, J = 7.3 Hz, 2 H), 1.74–1.64 (m, 2 H), 1.36–1.21 (m, 10 H), 0.88 (t, J = 6.7 Hz, 3 H), 0.23 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 161.62, 149.67, 147.68, 99.89, 99.65, 94.99, 49.29, 31.66, 29.07, 29.04, 26.30, 22.56, 14.04, -0.19; FABMS (in 3-nitrobenzyl alcohol) *m/e* (rel intensity) 321 (MH^+, 100%). Anal. Calcd for $C_{17}H_{28}N_2O_2Si$: C, 63.71; H, 8.81; N, 8.74. Found: C, 63.66; H, 8.85; N, 8.84.

5-Ethynyl-1-*n*-octyluracil (25). To a THF (100 mL) solution of **24** (3.9 g, 12.2 mmol) was added tetra-*n*-butylammonium fluoride (4.8 g, 18.3 mmol) and a few drops of water at room temperature. The reaction mixture was stirred at the same

temperature for 1.5 h. After removal of the solvent, the residue was chromatographed (silica gel; eluent, $CHCl_3$/AcOEt 10:1) to give **25**: yield 69% (2.1 g); mp 116–118 °C; IR (KBr) 3242, 2115, 1705, 1672 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.40 (s, 1 H), 7.50 (s, 1 H), 3.78–3.67 (m, 2 H), 3.21 (s, 1 H), 1.78–1.64 (m, 2 H), 1.41–1.20 (m, 10 H), 1.00–0.75 (m, 3 H); ^{13}C NMR ($CDCl_3$) δ 162.06, 149.81, 148.08, 98.64, 82.08, 74.41, 49.35, 31.62, 28.99, 26.26, 22.51, 13.98; FABMS (in 3-nitrobenzyl alcohol) *m/e* (rel intensity) 249 (MH^+, 100%). Anal. Calcd for $C_{14}H_{20}N_2O_2$: C, 67.71; H, 8.12; N, 11.28. Found: C, 67.73; H, 8.01; N, 11.31.

1,8-Diiodobiphenylene (28). This compound was synthesized from 1,8-dibromobiphenylene[20] (**27**) by a modification of our published procedure,[24] in which DMF was used as a solvent instead of carcinogenic HMPA. Indeed, most iodoarenes may satisfactorily be prepared from the corresponding bromoarenes by this modified method. Details will be reported elsewhere. A DMF (30 mL) suspension of **27** (800 mg, 2.58 mmol), CuI (7.7 g, 39 mmol), and KI (16g, 97 mmol) was stirred at 140 °C for 22 h. The reaction mixture was filtered, and the filtrate was evaporated. The residue was poured into water and extracted with CH_2Cl_2. The CH_2Cl_2 extract was evaporated to give **28**: yield 92% (963 mg); mp 181–183 °C; ^1H NMR ($CDCl_3$) δ 7.03 (d, J = 8.5 Hz, 2 H), 6.59 (d, J = 6.8 Hz, 2 H), 6.48 (dd, J = 8.5, 6.8 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 154.89, 151.79, 139.03, 129.98, 116.31, 80.51; FABMS (in 3-nitrobenzyl alcohol) *m/e* (rel intensity) 404 (M^+, 58%). Anal. Calcd for $C_{12}H_6I_2$: C, 35.68; H, 1.50. Found: C, 35.59; H, 1.55.

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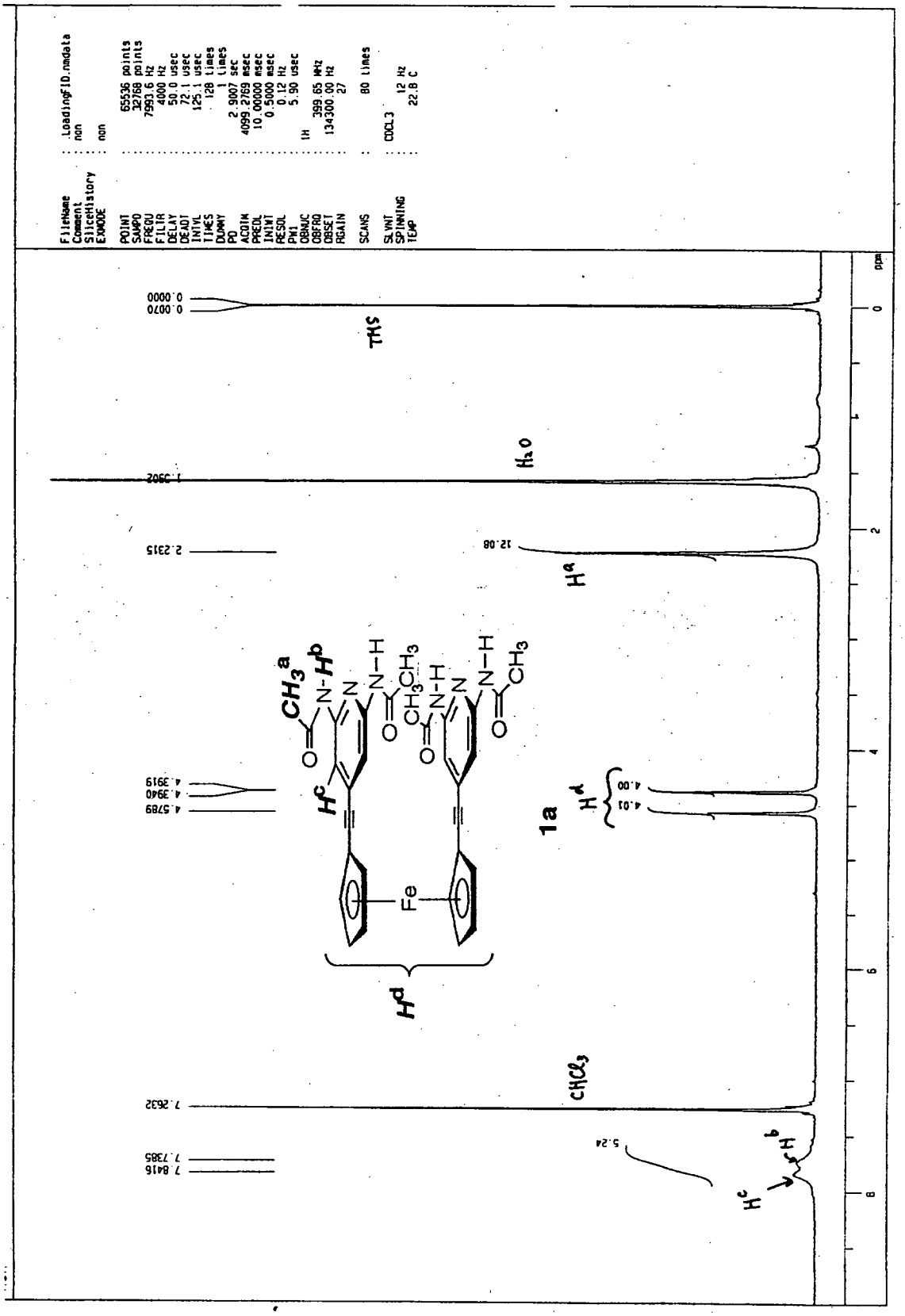
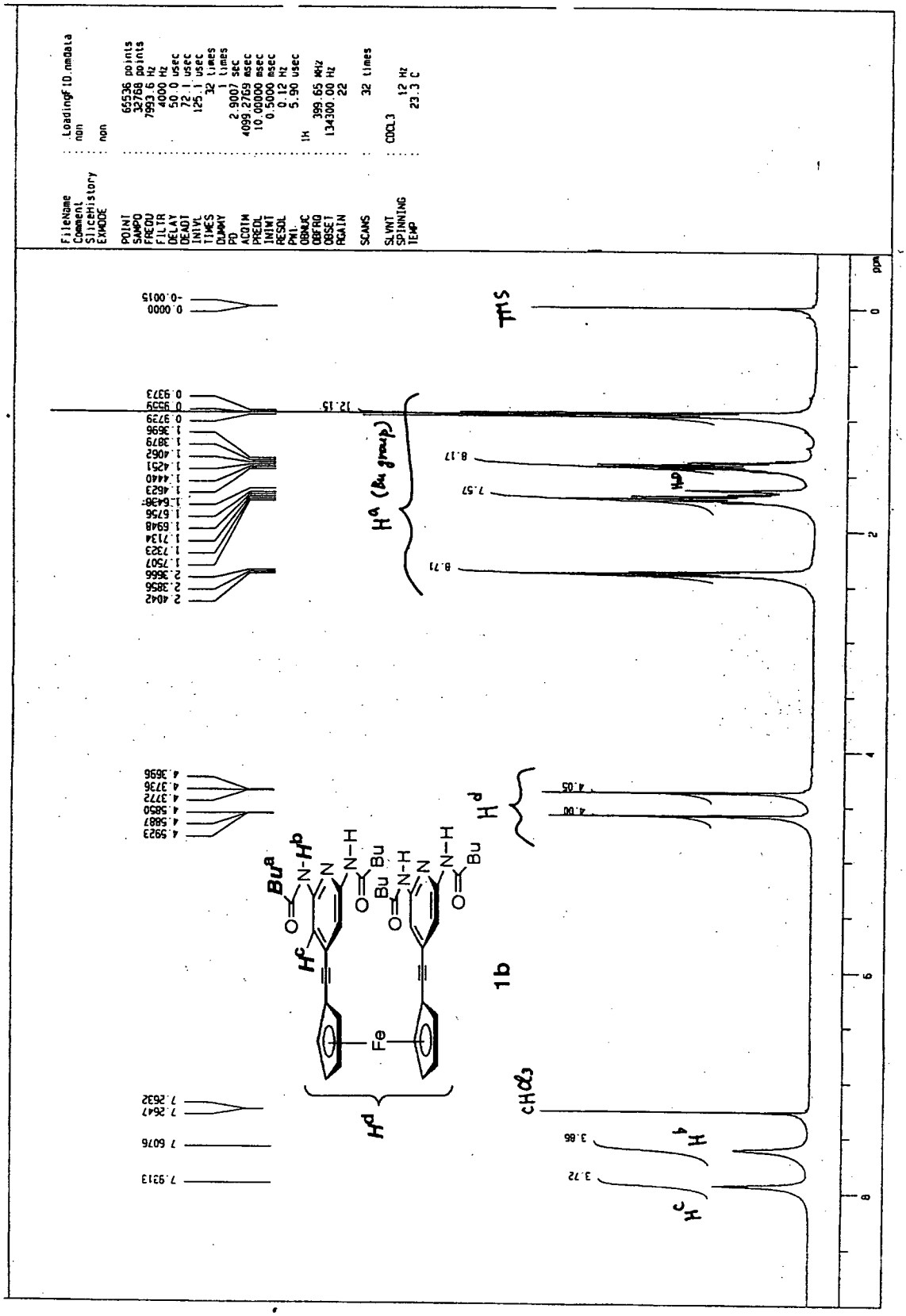
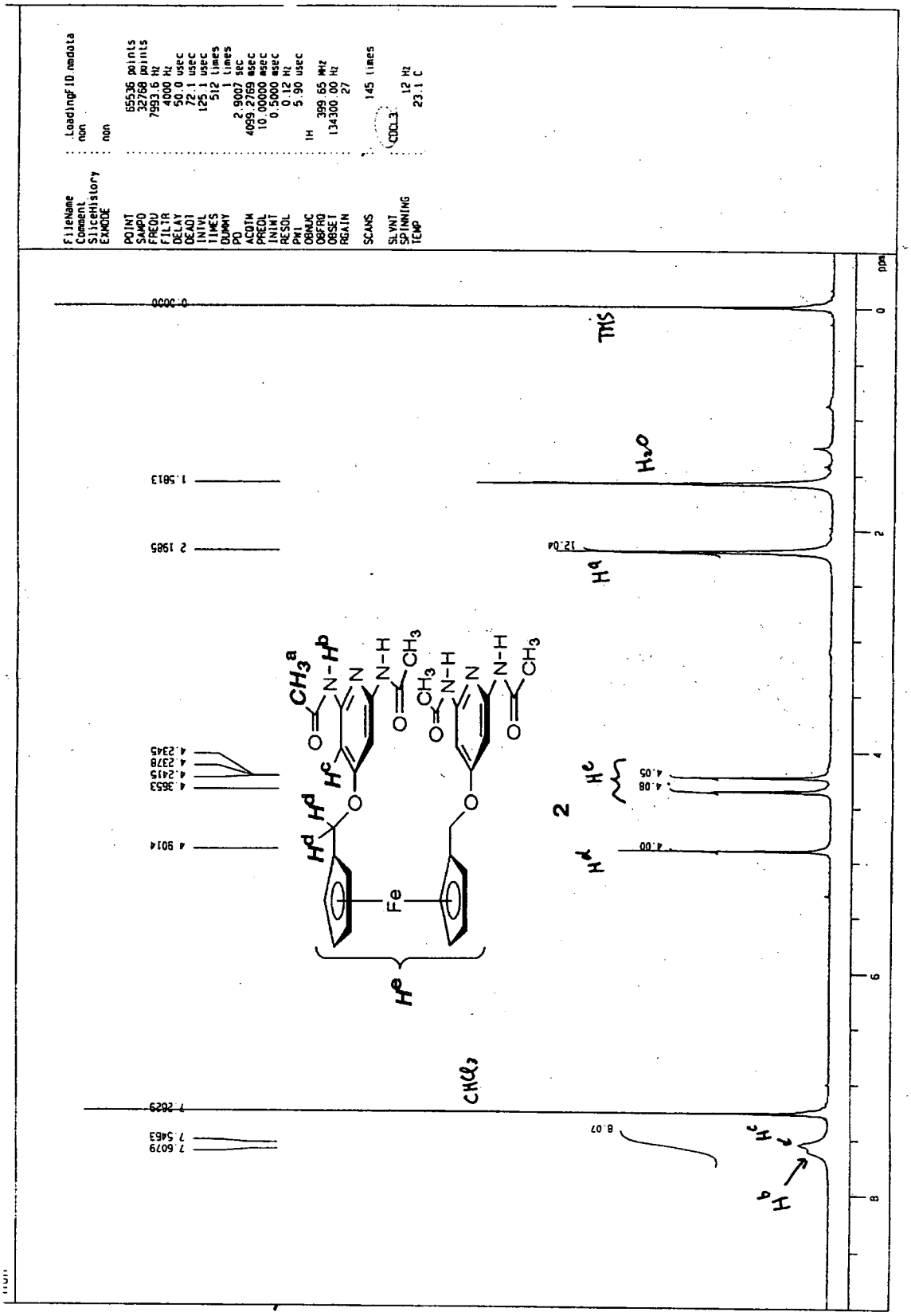
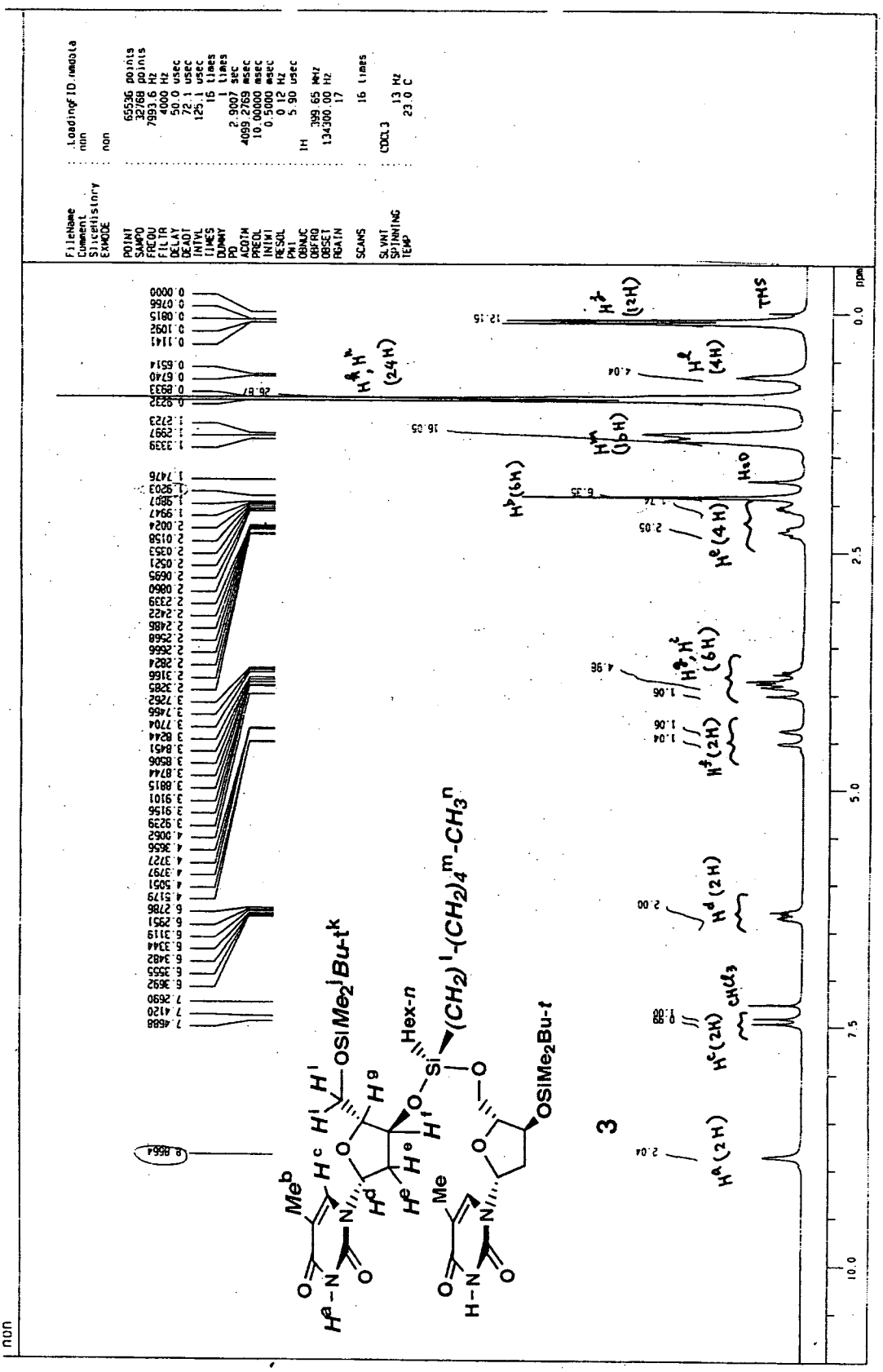
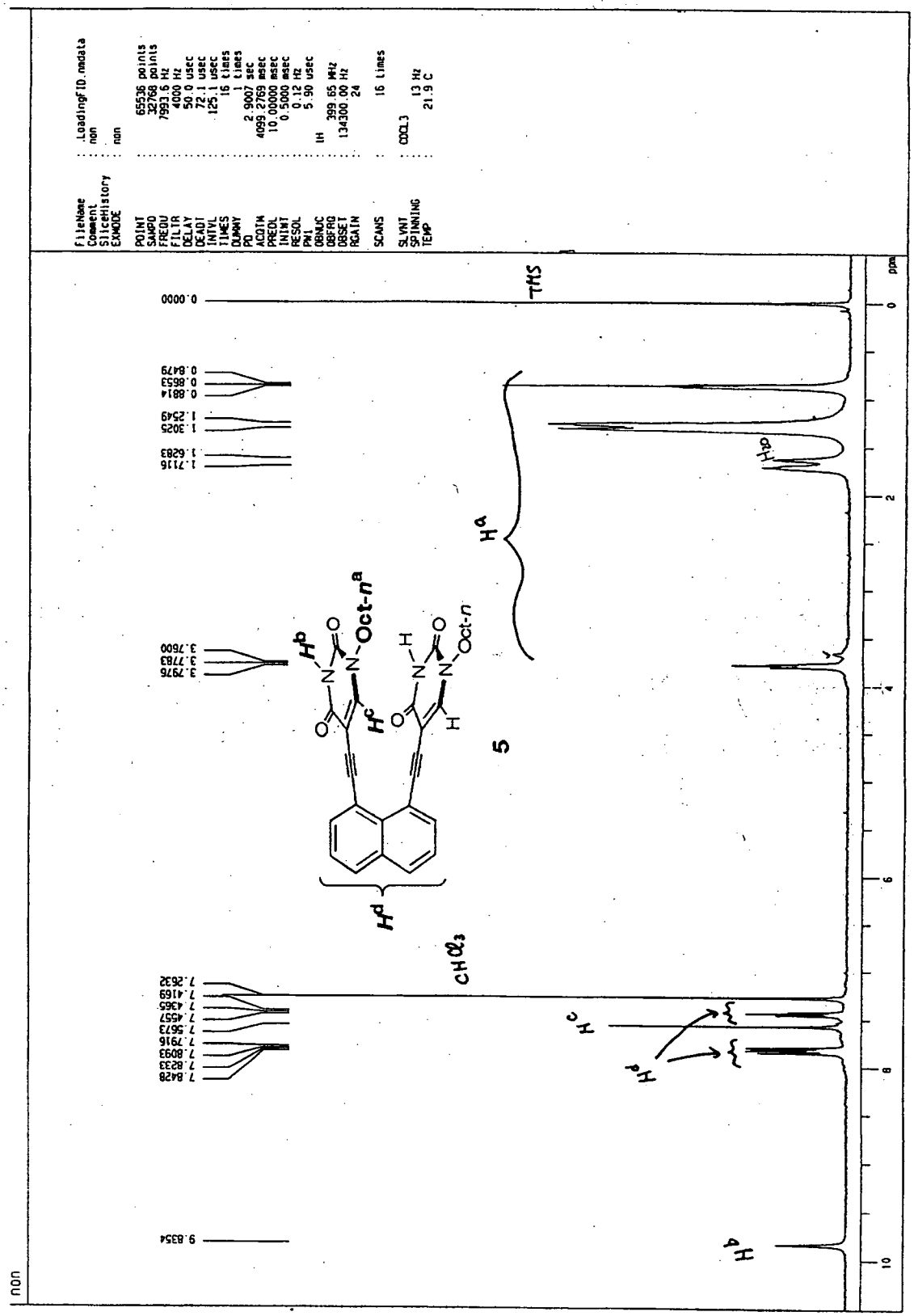
^{1}H NMR spectra of all new compounds

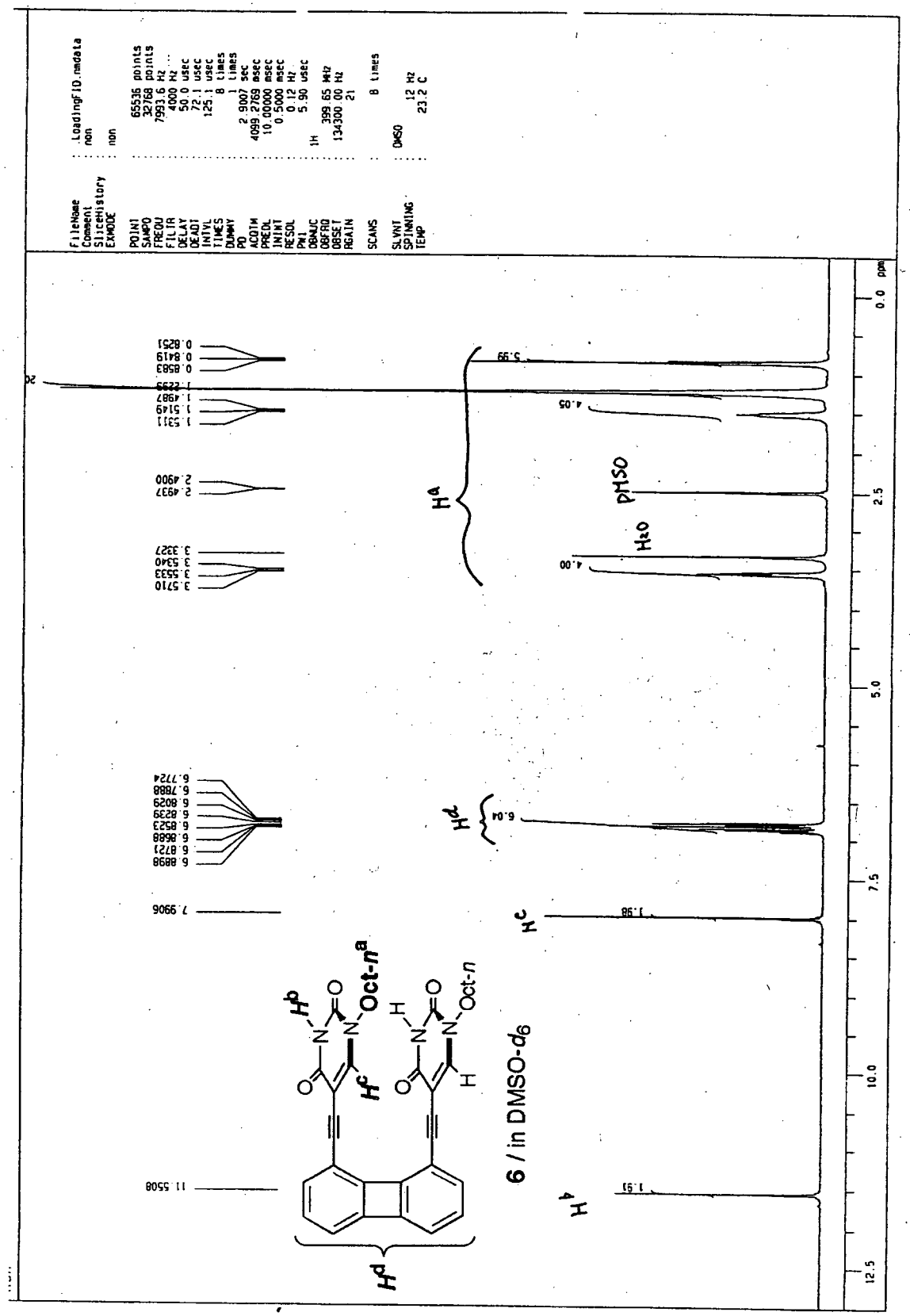


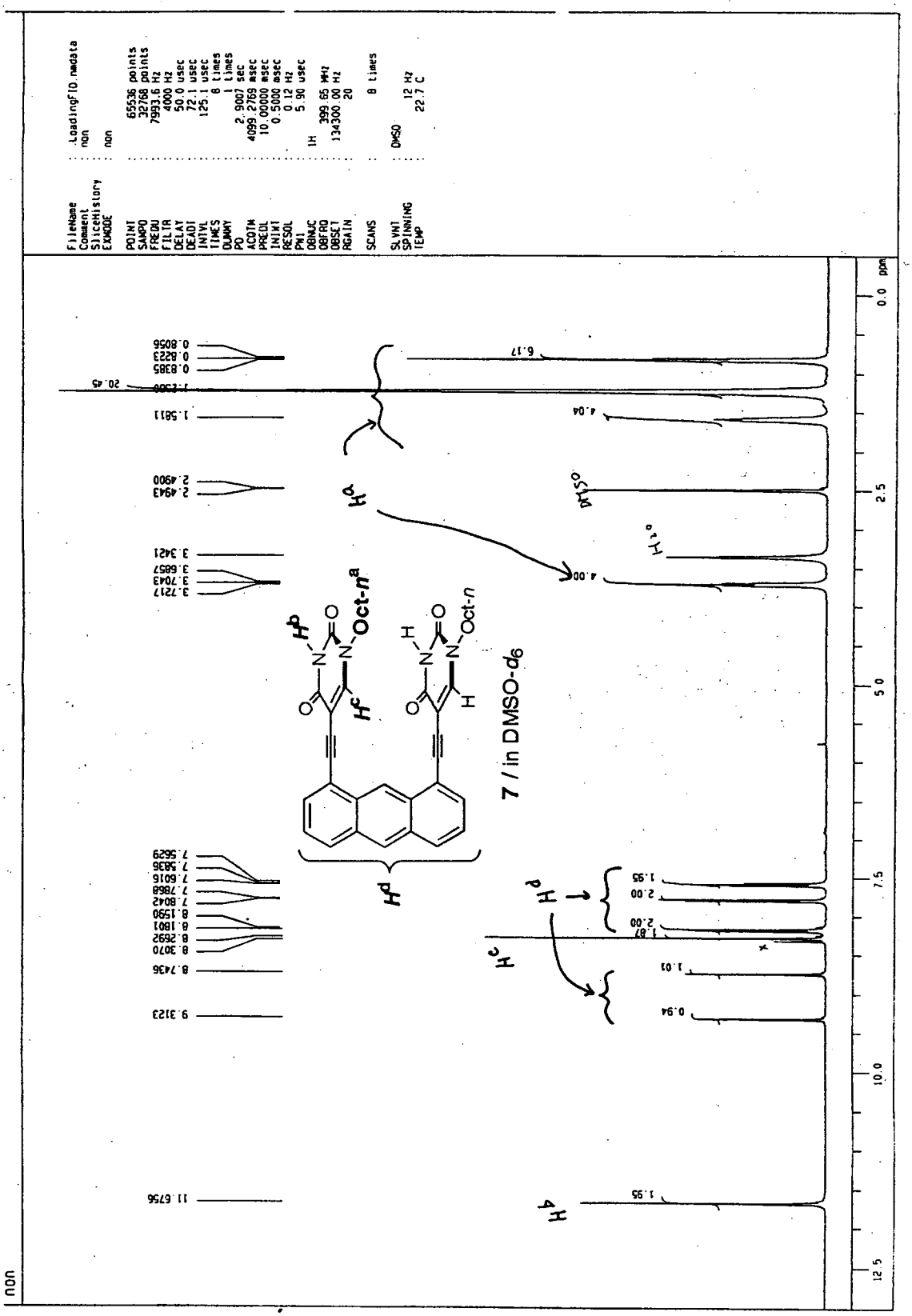


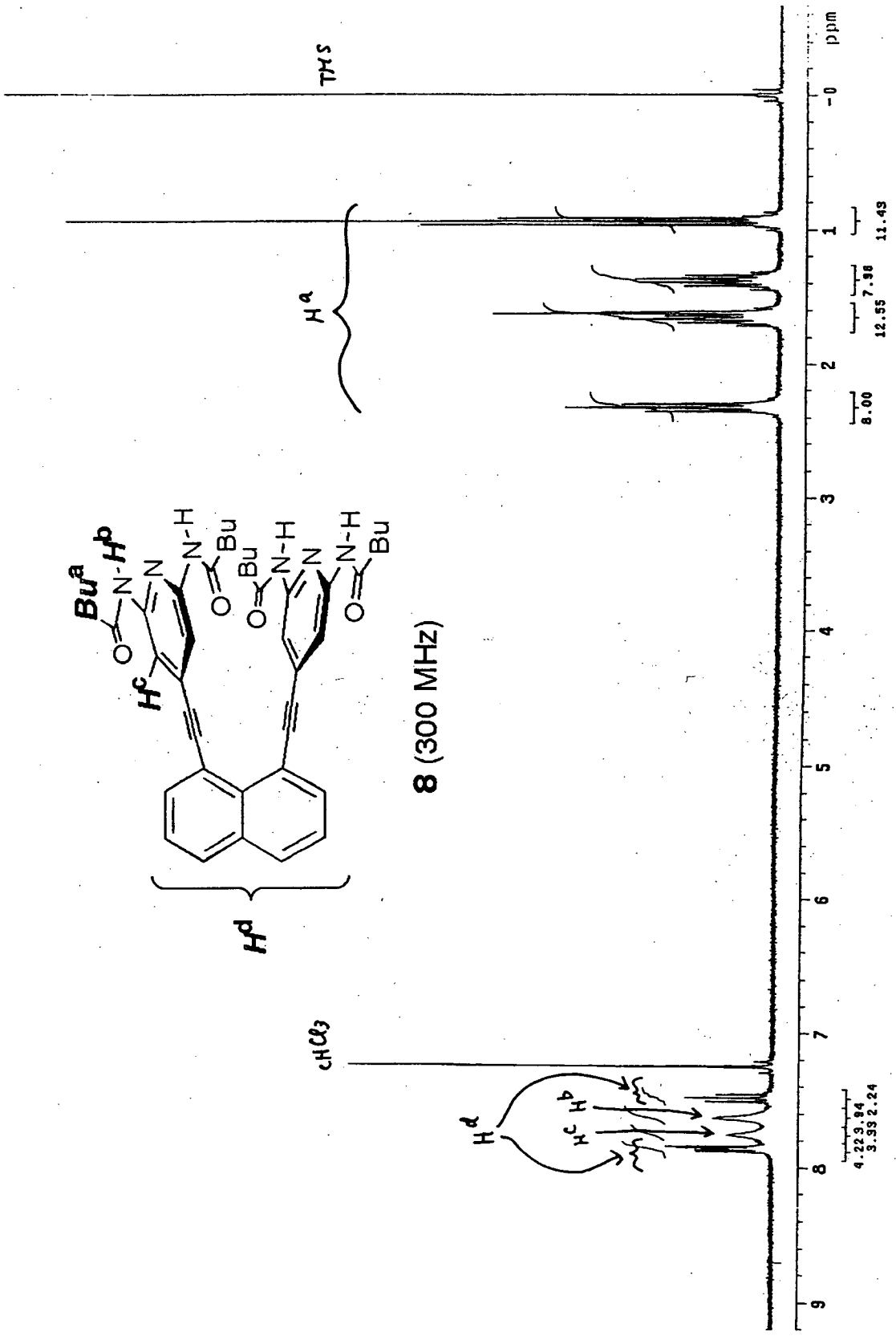


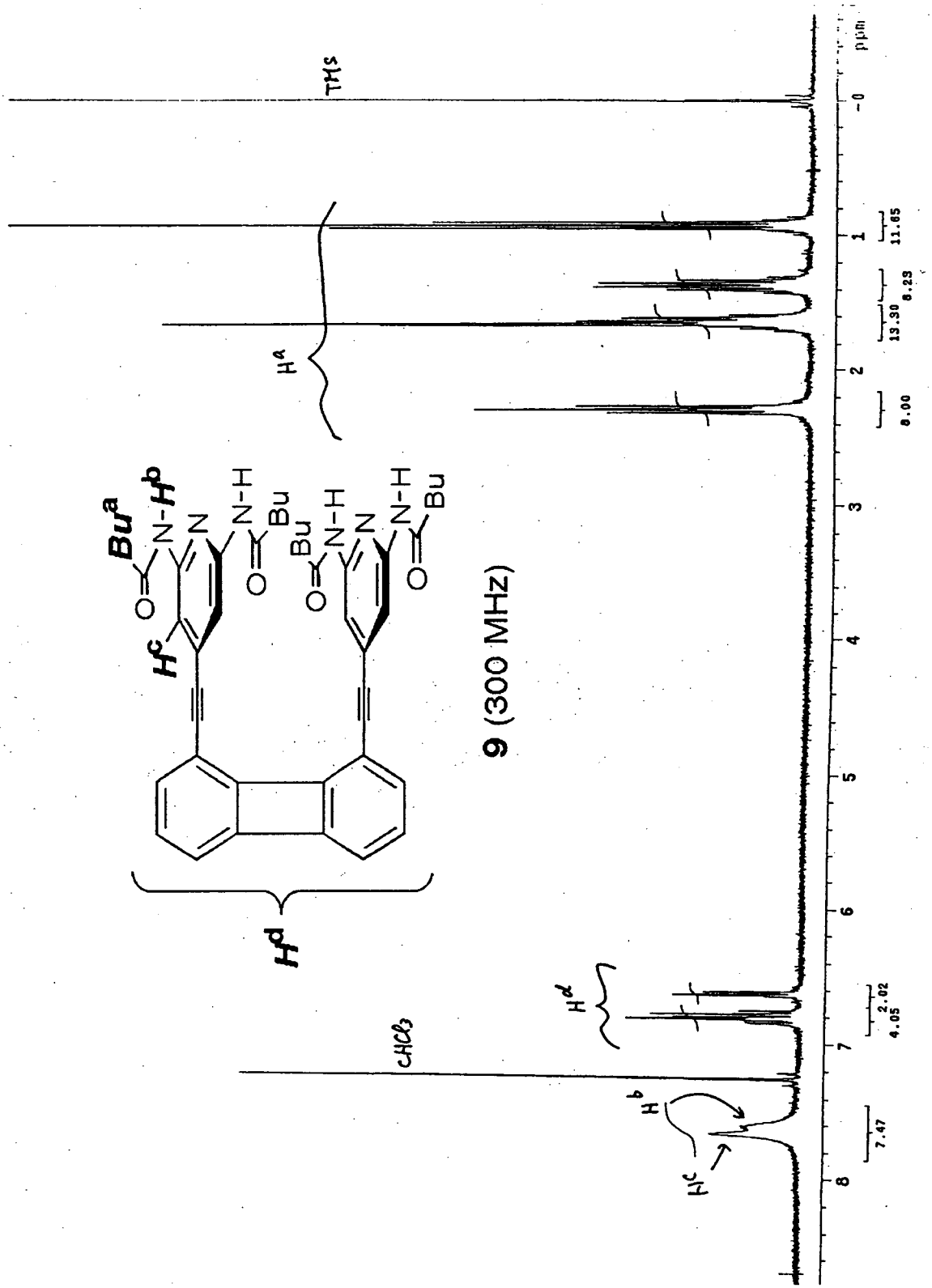


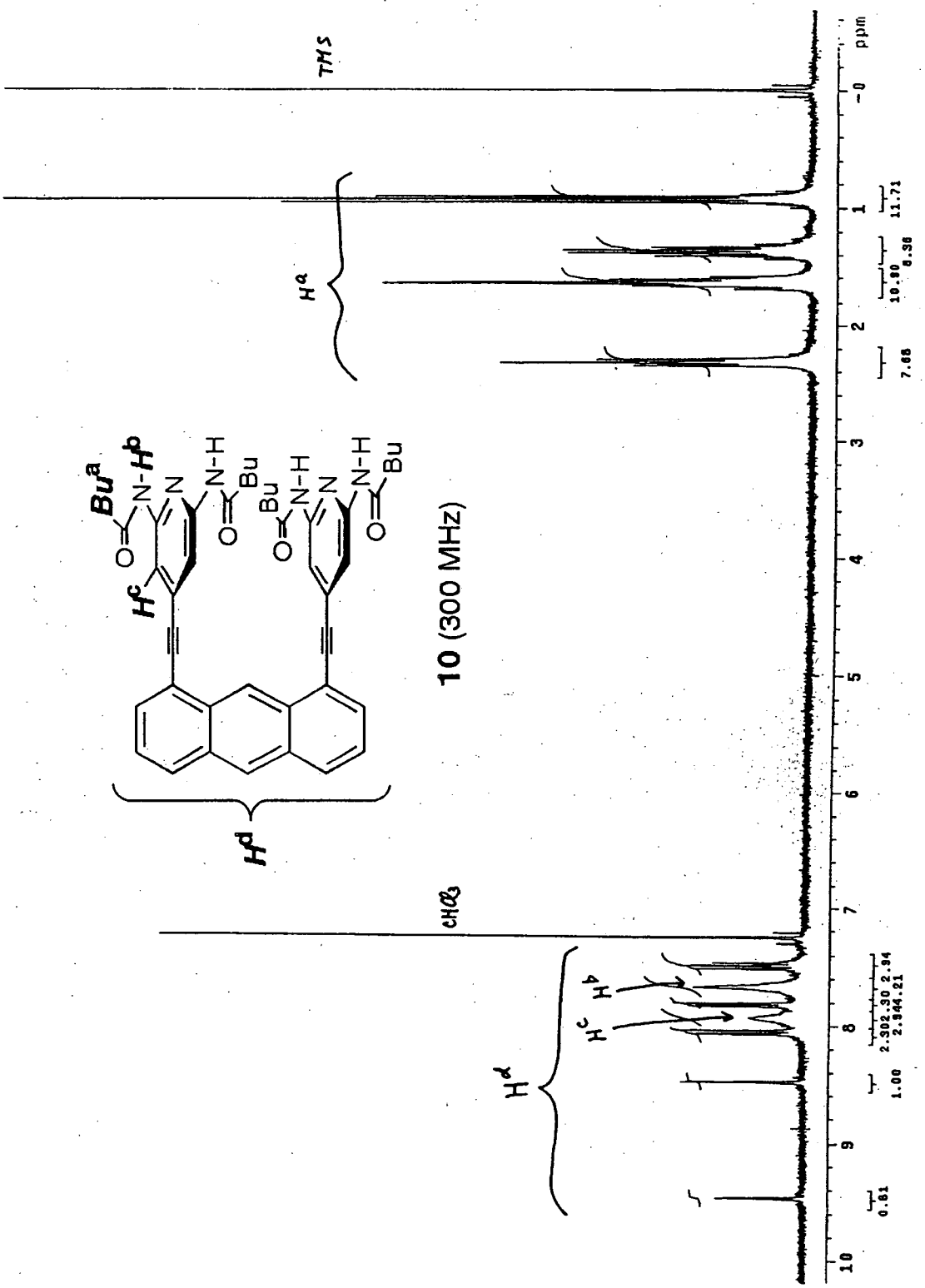


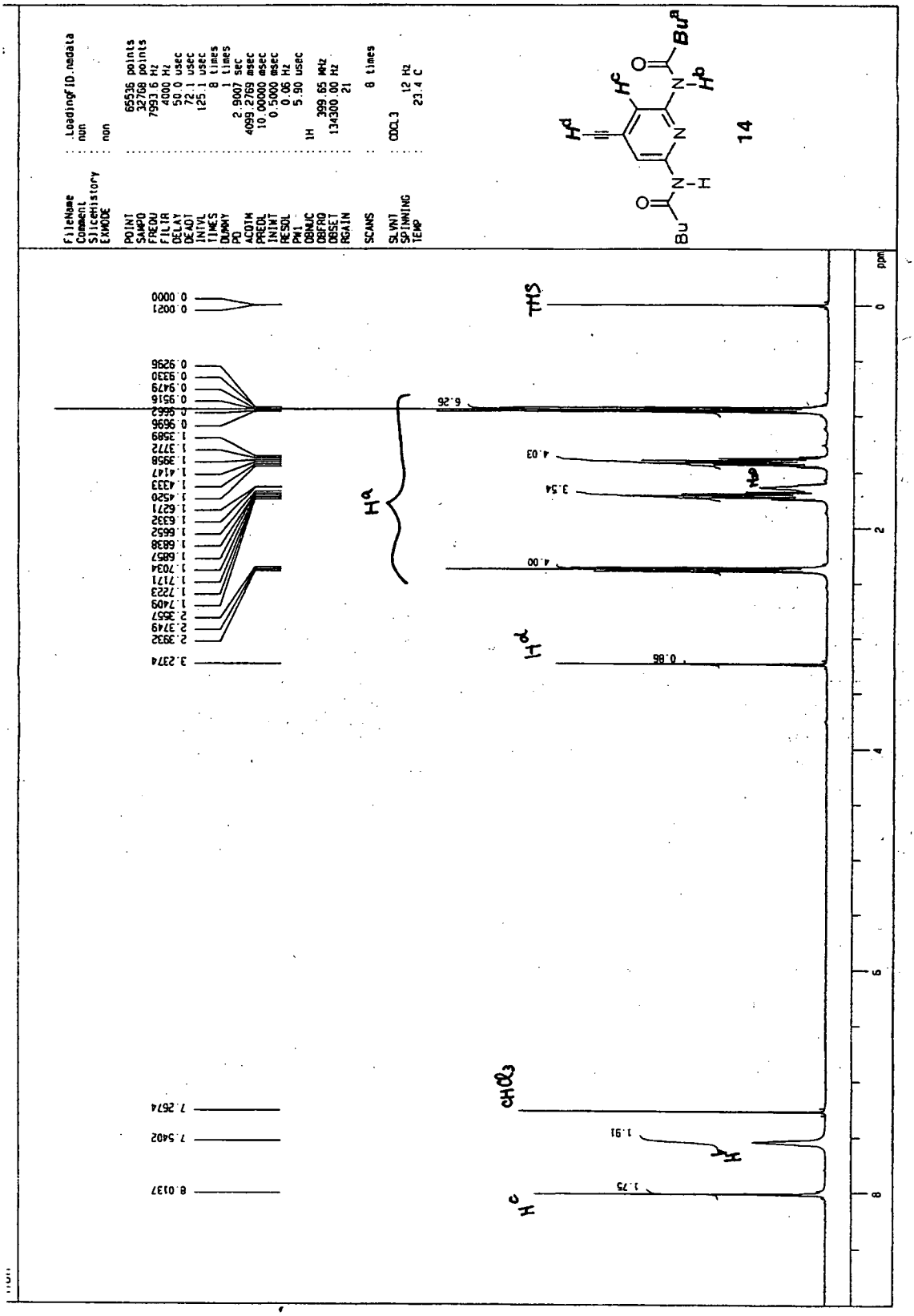


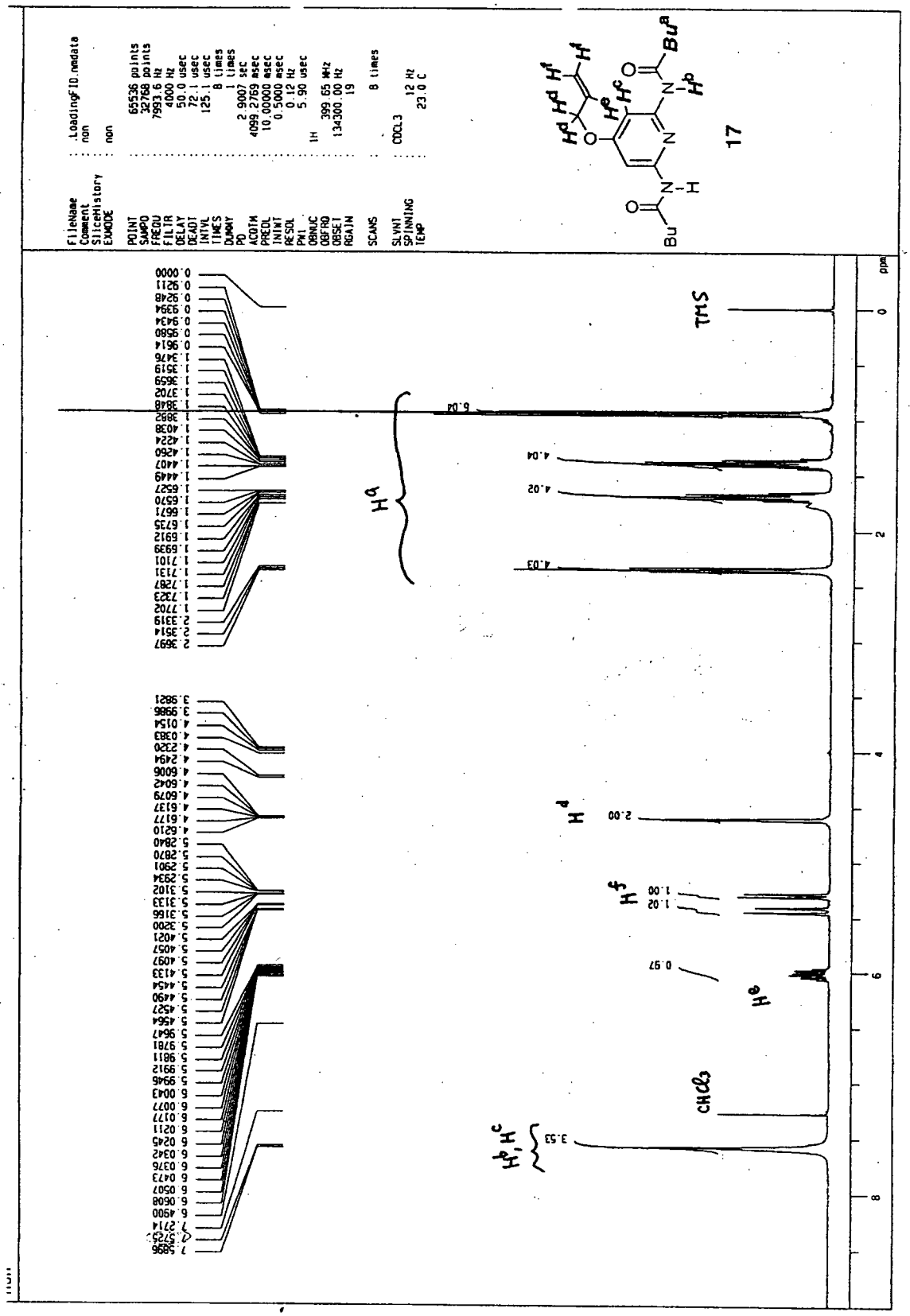


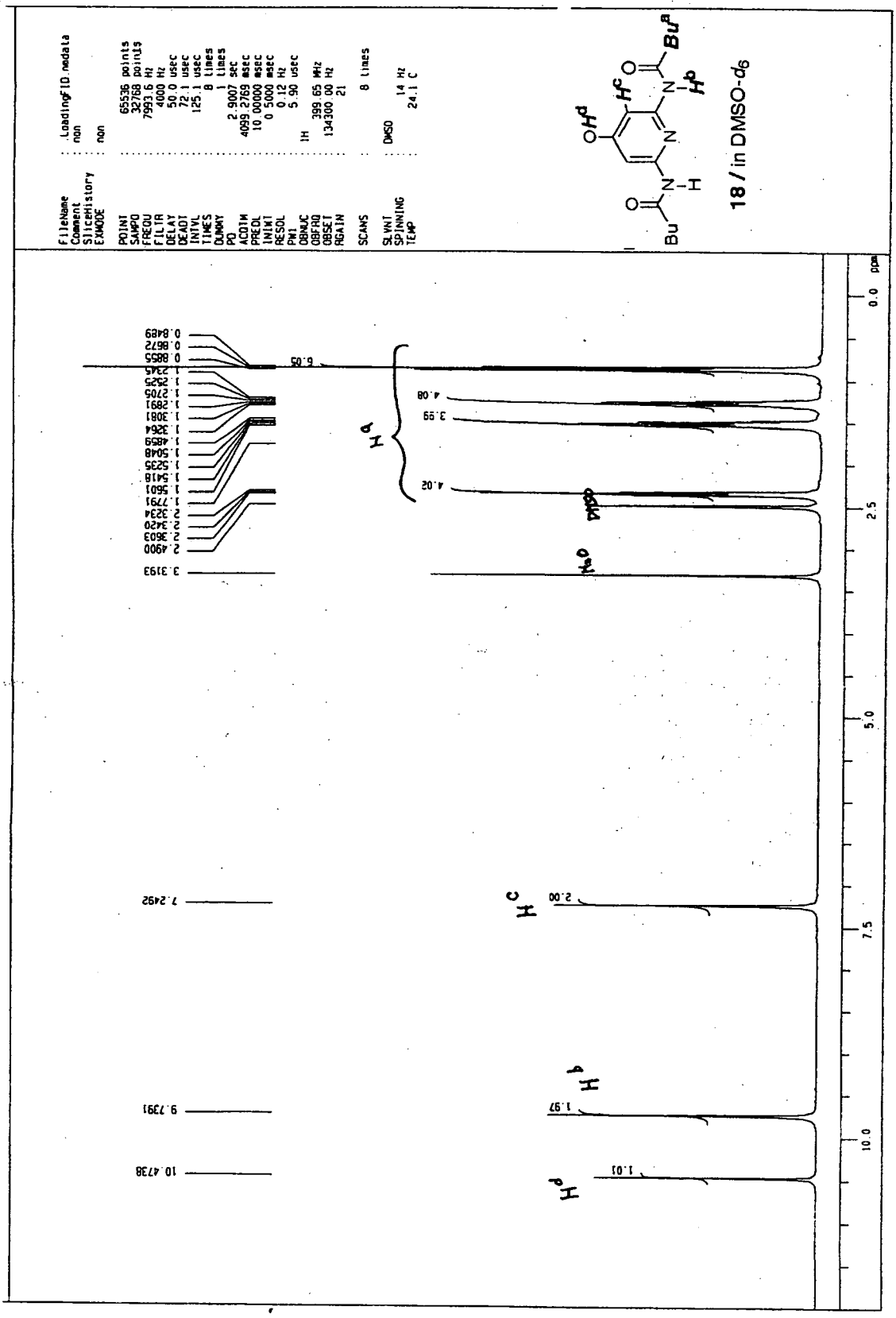








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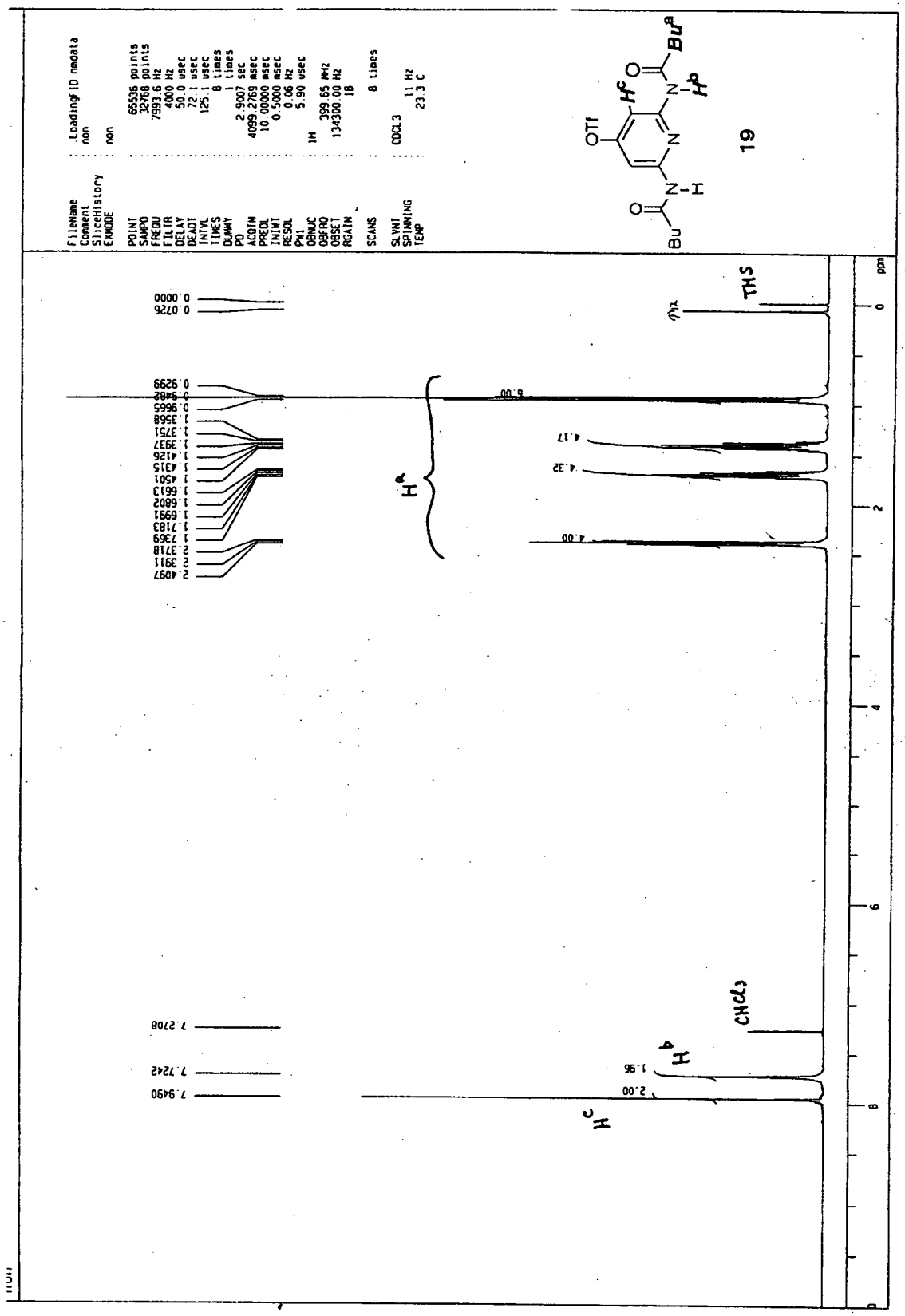

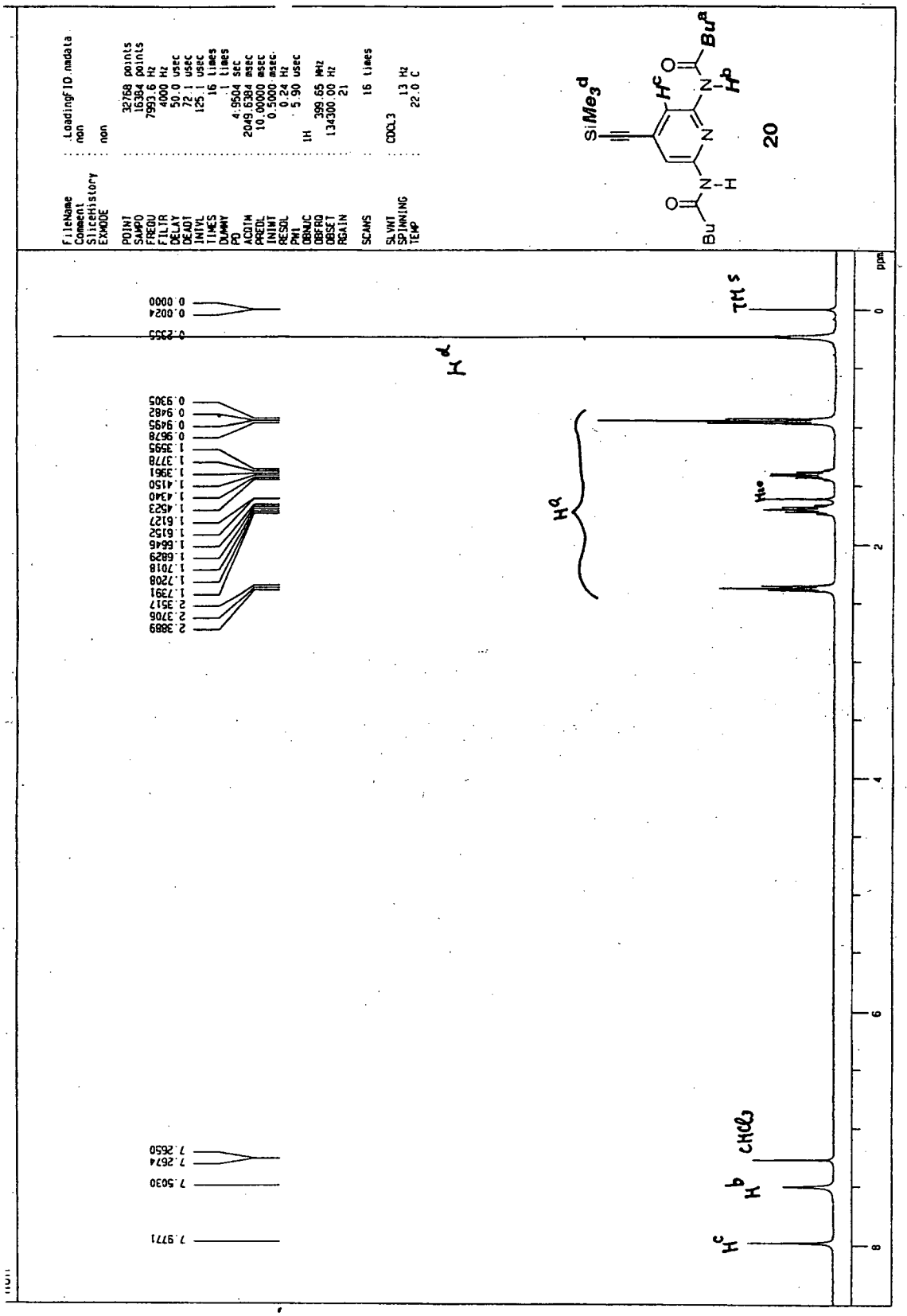

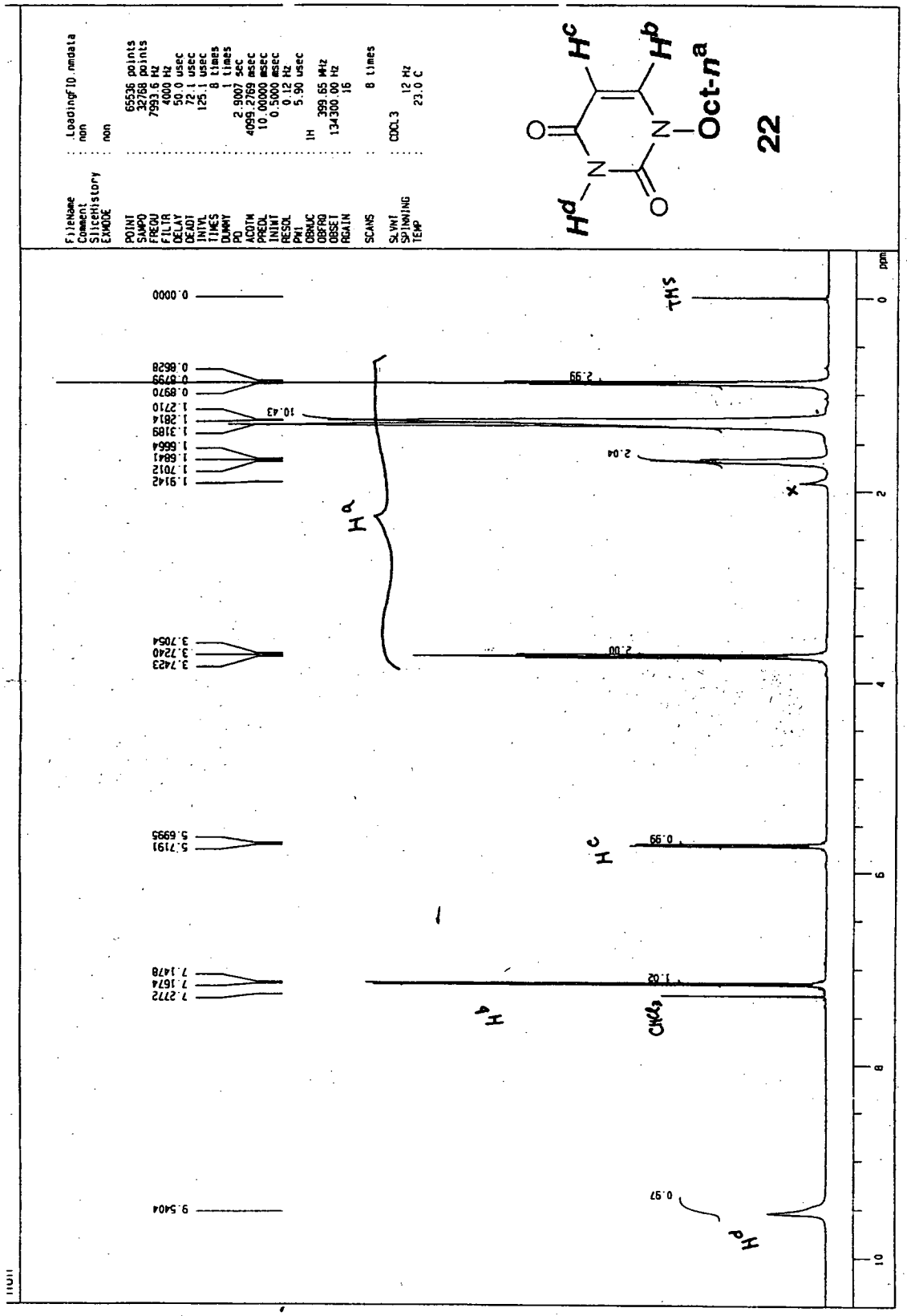

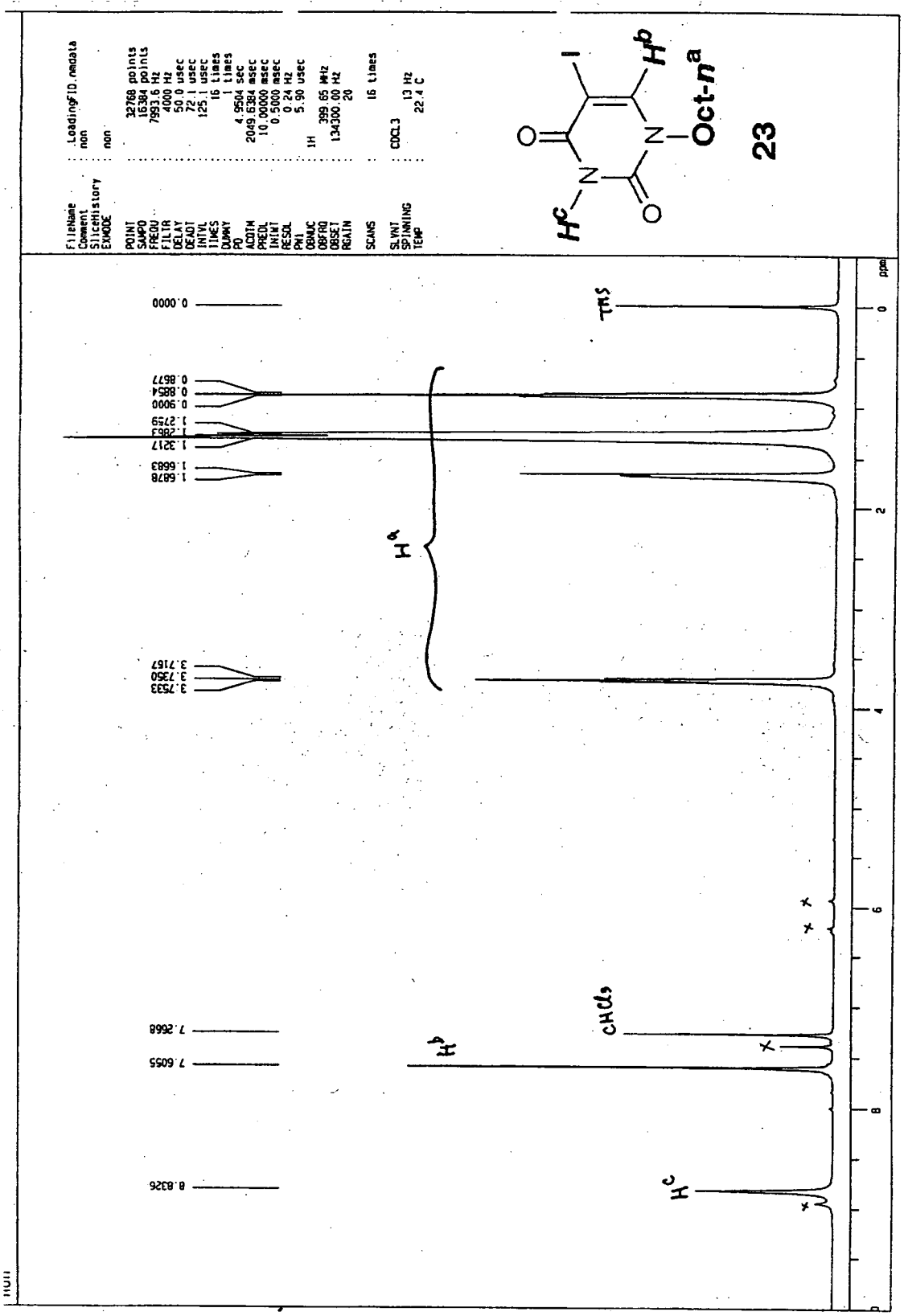

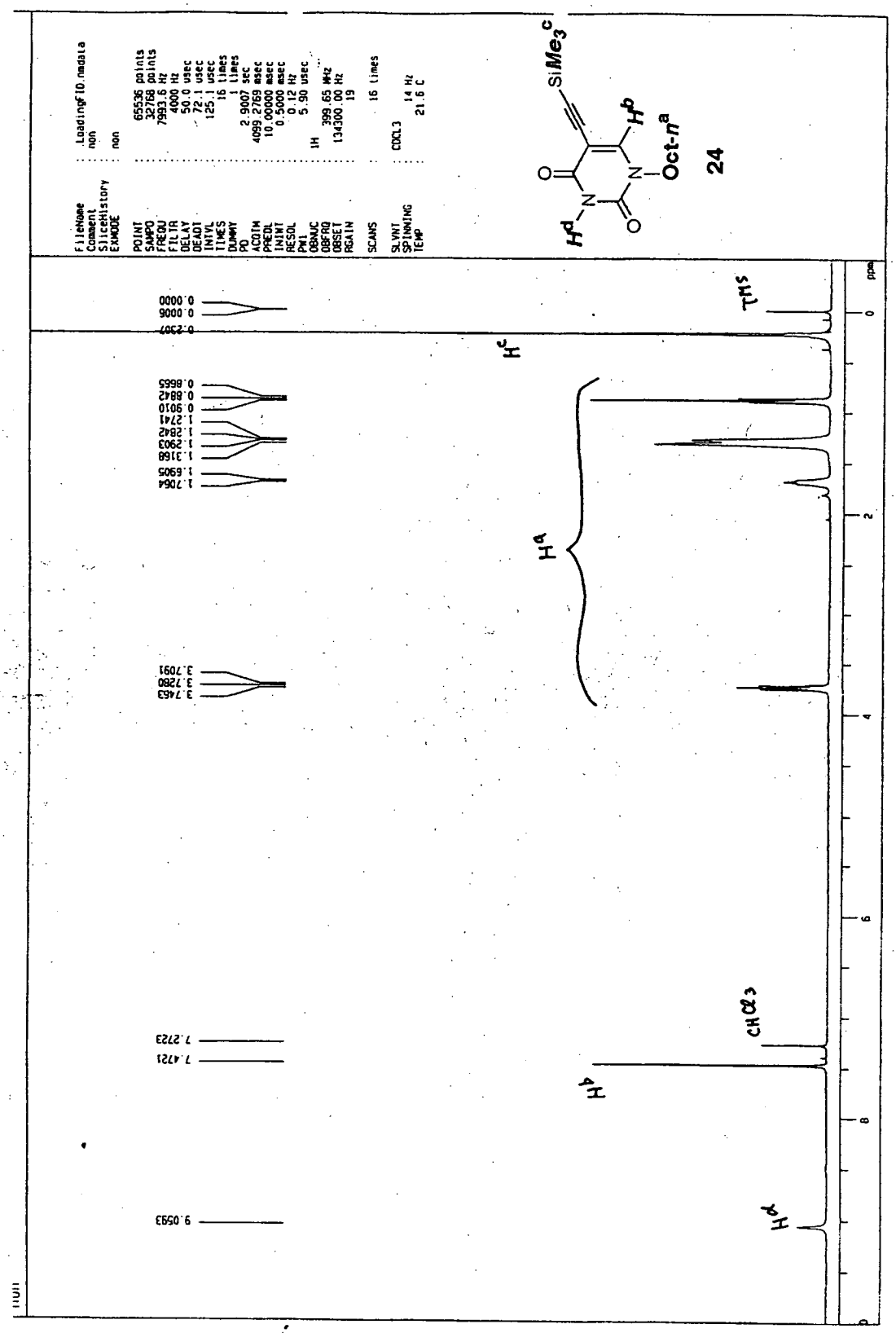

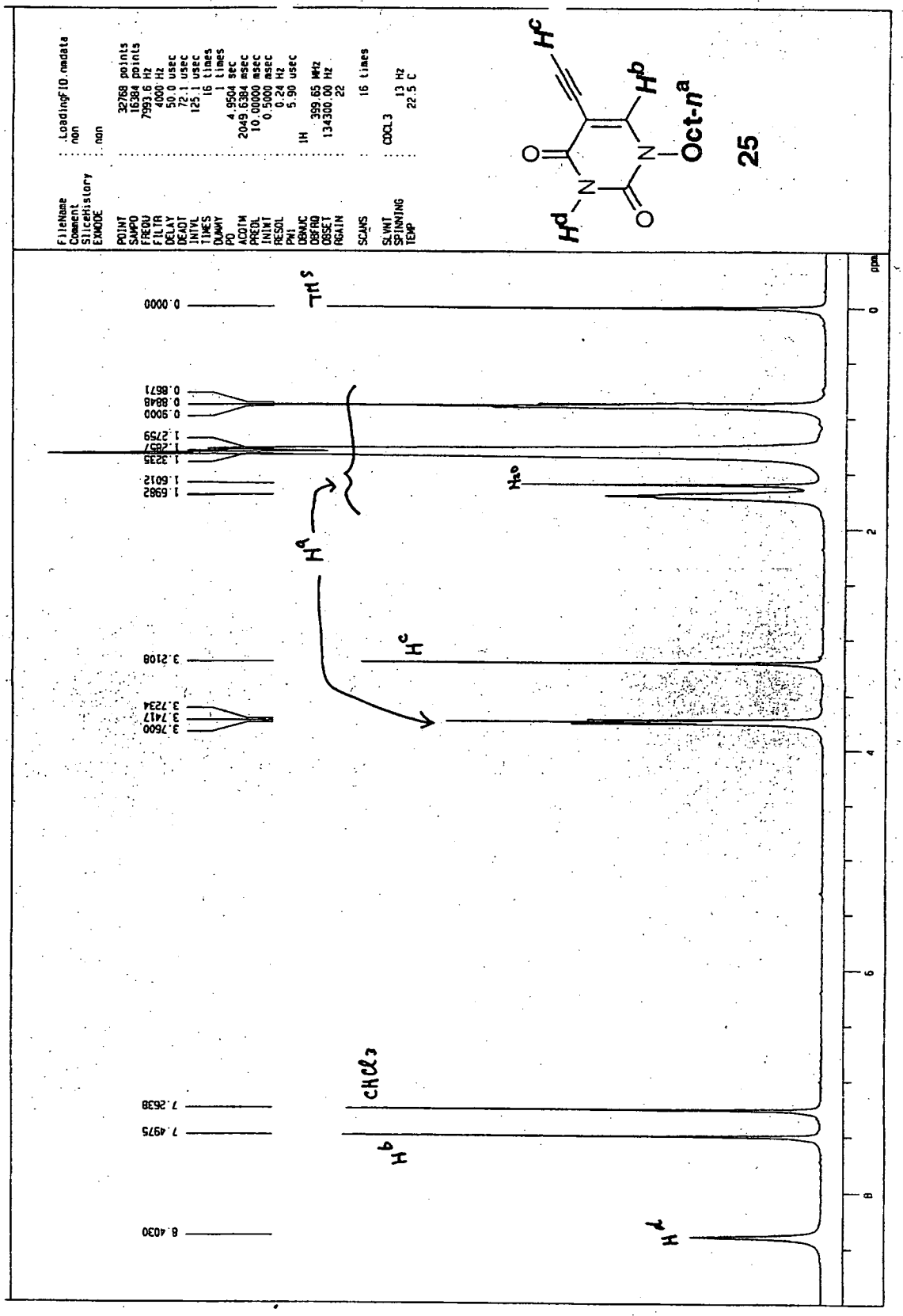
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