Supplementary Material (ESI) for Chemical Communications

Chemical Communications

Capturing a [*c*2]Daisy Chain Using the Threading-Followed-by-Swelling Approach

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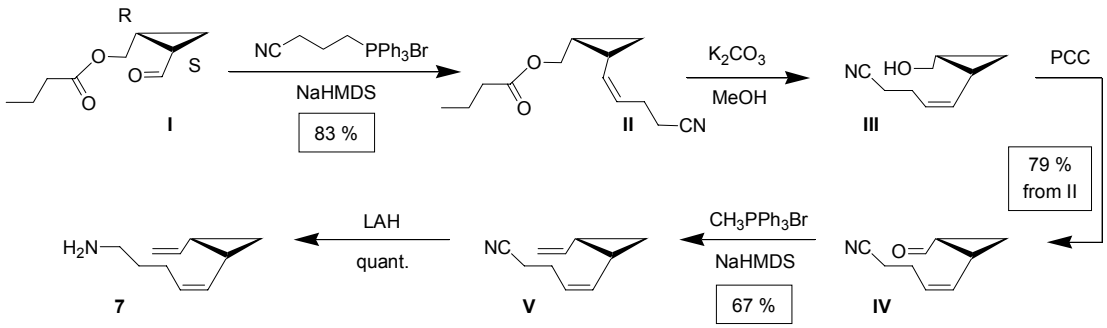
Macrocycle 2. Sodium hydride (0.72 g, 30.0 mmol) was added to a DMF solution (600 mL) of the diol **4** (0.83 g, 6.0 mmol) and then the mixture was stirred at room temperature for 20 min. A solution of the dichloride **3**[1] (2.32 g, 6 mmol) in DMF (60 mL) was slowly added over 2 h and then the mixture was stirred at room temperature for 10 days. The organic solvent was evaporated under reduced pressure and the yellow residue was then partitioned between ethyl acetate (300 mL) and water (100 mL). The organic layer was washed with water (2 × 100 mL), dried ($MgSO_4$), and concentrated. The crude product was purified (SiO_2; hexane/ethyl acetate, 6/4) to afford the macrocycle **2** as a yellow solid (0.19 g, 7%). M.p. 131–133 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.41 (s, 4 H), 4.51 (s, 4 H), 5.18 (s, 4 H), 6.73 (d, *J* = 8.1 Hz, 4 H), 7.12 (d, *J* = 8.1 Hz, 4 H), 7.28 (d, *J* = 7.7 Hz, 2 H), 7.30 (s, 4 H), 7.64 (t, *J* = 7.7 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 69.2, 71.3, 71.6, 115.4, 120.3, 126.8, 129.6, 136.9, 136.9, 157.4, 157.5 (one carbon signal is missing, possibly because of signal overlapping); HRMS (ESI): *m/z* $[M + Na]^+$ $C_{29}H_{27}NO_4Na$ calcd. 476.1838, found 476.1812.



Scheme S1. Synthesis of the amine **7**

(1*S*,2*R*)-*cis*-2-Butyryloxymethyl-1-[(*Z*)-4-cyanobut-1-enyl]cyclopropane (II). A solution of (3-cyanopropyl)triphenylphosphonium bromide (53.1 g, 130 mmol) in THF (650 mL) was cooled to 0 °C; NaHMDS (2 M in THF, 69 mL, 138 mmol) was added and then the mixture was stirred for 10 min. A solution of the aldehyde **I**[2] (14.7 g, 86.3 mmol) in THF (130 mL) was added and then the mixture was stirred at 0 °C for 3.5 h before being poured into petroleum ether (1 L). The precipitate was filtered off, and the filtrate was concentrated and purified (SiO_2; hexane/ethyl acetate, 7:3 then 6:4) to afford the alkene **II** as a yellow oil (15.9 g, 83%). $[\alpha]_D^{23}$ = –75.0°; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.45 (q, *J* = 4.8 Hz, 1 H), 0.94 (t, *J* = 7.2 Hz, 3 H), 1.09 (td, *J* = 8.0, 4.8 Hz, 1 H), 1.39–1.44 (m, 1 H), 1.59–1.71 (m; overlapped with a sextet at 1.62, *J* = 7.2 Hz, 3 H), 2.28 (t, *J* = 7.2 Hz, 2 H), 2.39–2.43 (m, 2 H), 2.49–2.55 (m, 2 H), 3.92 (dd, *J* = 11.8, 8.8 Hz, 1 H), 4.18 (dd, *J* = 11.8, 7.0 Hz, 1 H), 5.23 (t, *J* = 9.8 Hz, 1H), 5.45 (td, *J* = 9.8, 7.6 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.5, 13.7,

14.2, 17.1, 17.4, 18.5, 23.6, 36.1, 64.6, 119.1, 126.6, 131.1, 173.3; HRMS (ESI) *m/z* $[M + Na]^+$ $C_{13}H_{19}NaNO_2$ calcd. 244.1314, found 244.1318.

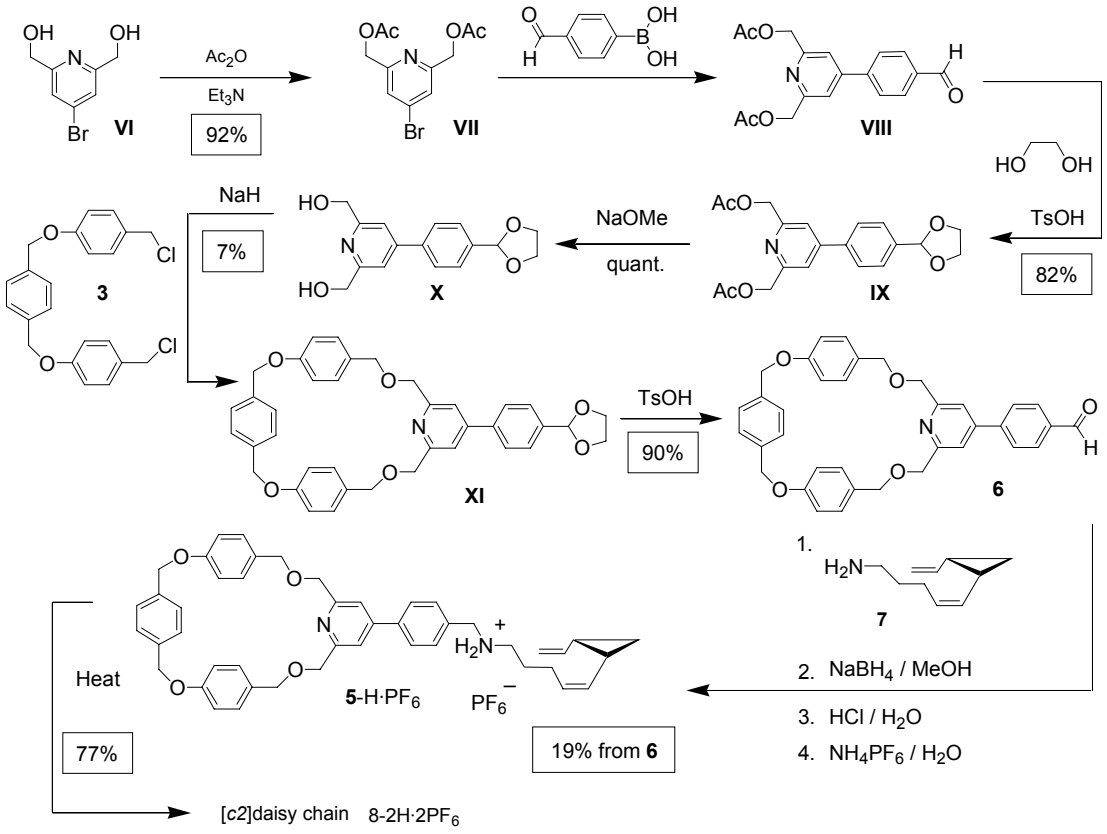
(1*S*,2*R*)-*cis*-1-[(*Z*)-4-Cyanobut-1-enyl]-2-hydroxymethylcyclopropane (III). Alkene **II** (15.9 g, 71.8 mmol) and K_2CO_3 (29.8 g, 216 mmol) were stirred in MeOH (72 mL) at room temperature for 1.5 h. The mixture was then partitioned between CH_2Cl_2 (300 mL) and H_2O (200 mL) and the organic layer was dried ($MgSO_4$) and concentrated to give the crude alcohol **III** as a colorless oil (10.9 g, quant.). $[\alpha]_D^{23}$ –73.9°; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.43 (q, *J* = 5.2 Hz, 1 H), 1.06 (td, *J* = 8.8, 5.2 Hz, 1 H), 1.37–1.47 (m, 1 H), 1.53 (br s, 1 H), 1.62–1.75 (m, 1 H), 2.41–2.46 (m, 2 H), 2.48–2.61 (m, 2 H), 3.46 (t, *J* = 8.8 Hz, 1 H), 3.76–3.82 (m, 1 H), 5.30 (t, *J* = 10.4 Hz, 1 H), 5.47 (dt, *J* = 10.4, 7.2 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.7, 13.5, 16.8, 20.2, 22.9, 61.7, 119.1, 125.5, 131.1; HRMS (ESI): *m/z* $[M + Na]^+$ $C_9H_{13}NaNO$ calcd. 174.0895, found 174.0920.

(1*R*,2*S*)-*cis*-1-Formyl-2-[(*Z*)-4-cyanobut-1-enyl]cyclopropane (IV). A solution of the alcohol **III** (15 g, 87.2 mmol) in CH_2Cl_2 (45 mL) was added to a mixture of PCC (37.6 g, 174 mmol), NaOAc (4.3 g, 52.3 mmol), 4 Å molecular sieves (15.0 g), and Celite (15 g) in CH_2Cl_2 (45 mL) and then the mélange was stirred at room temperature for 2 h. After additional Celite (90 g) and ethyl ether (300 mL) had been added, the mixture was filtered through a pad of silica gel; the filtrate was concentrated and purified (SiO_2; hexane/ethyl acetate, 7:3) to afford the desired aldehyde **IV** as a colorless oil (11.8 g, 79% from **II**). $[\alpha]_D^{23}$ –231.9°; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.48 (t, *J* = 7.2 Hz, 2 H), 2.17–2.30 (m, 2 H), 2.37–2.47 (m, 2 H), 2.47–2.60 (m, 2 H), 5.43–5.55 (m, 2 H), 9.36 (d, *J* = 5.2 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.5, 17.2, 21.5, 23.5, 30.0, 119.0, 128.0, 128.9, 200.0; HRMS (ESI): *m/z* $[M + Na]^+$ $C_9H_{11}NaNO$ calcd. 172.0738, found 172.0762.

(1*S*,2*R*)-*cis*-1-[(*Z*)-4-Cyanobut-1-enyl]-2-ethenylcyclopropane (V). NaHMDS (2 M in THF, 24.3 mL, 48.6 mmol) was added to a THF solution (320 mL) of methyltriphenylphosphonium bromide (17.4 g, 48.6 mmol) at –78 °C and then the mixture was stirred for 10 min. A solution of the aldehyde **IV** (6.04 g, 40.5 mmol) in THF (80.0 mL) was added and then the mixture was stirred at –78 °C for 0.5 h and then warmed to 0 °C for 3.5 h. The mixture was poured into petroleum ether (500 mL) and filtered. The filtrate was concentrated and the residue purified (SiO_2; hexane/ethyl acetate, 9:1) to afford the desired product **V** as a yellow oil (4.0 g, 67%). $[\alpha]_D^{23}$ –133.2°; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.61 (q, *J* = 5.6 Hz, 1 H), 1.19 (td, *J* = 8.0, 5.6 Hz, 1 H), 1.71–1.85 (m, 2 H), 2.35–2.47 (m, 2 H), 2.45–2.57 (m, 2 H), 5.00 (d,

J = 10.4 Hz, 1 H), 5.12 (d, *J* = 17.2 Hz, 1 H), 5.19–5.30 (m, 1 H), 5.40–5.50 (m, 1 H), 5.50–5.60 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.8, 17.1, 17.5, 22.6, 23.7, 114.8, 119.3, 125.7, 132.1, 137.2; HRMS (ESI): *m/z* $[M + Na]^+$ $C_{10}H_{13}NaN$ calcd. 170.0945, found 170.0924.

(1*S*,2*R*)-*cis*-1-[(*Z*)-5-Aminopent-1-enyl]-2-ethenylcyclopropane (7). Lithium aluminum hydride (2.51 g, 66.0 mmol) was added in small portions to a THF solution (200 mL) of the nitrile **V** (2.0 g, 13.2 mmol) at 0 °C. The mixture was stirred at 0 °C for 5 h and then wet THF (100 mL), water (2 mL), and $MgSO_4$ (20 g) were added sequentially. The suspension was filtered and the filtrate concentrated to afford the crude amine **7** as a yellow oil (2.05 g, quant.), which was used in the next reaction without further purification. $[\alpha]_D^{22}$ –129.7°; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.48–0.62 (m, 1 H), 1.05–1.23 (m, 1 H), 1.53 (quintet, *J* = 7.5 Hz, 2 H), 1.64–1.75 (m, 1 H), 1.75–1.90 (m, 1 H), 2.18 (q, *J* = 7.5 Hz, 2 H), 2.70 (t, *J* = 7.5 Hz, 2 H), 4.98 (d, *J* = 11.6 Hz, 1 H), 5.03–5.18 (two overlapped doublets: *J* = 10.8 Hz at 5.05 and *J* = 16.4 Hz at 5.11, 2 H), 5.38–5.45 (m, 1 H), 5.45–5.60 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.8, 17.2, 22.5, 25.0, 33.7, 41.8, 114.3, 128.8, 130.1, 137.8; HRMS (ESI): *m/z* $[M + H]^+$ $C_{10}H_{18}N$ calcd. 152.1439, found 152.1380.



Scheme S2. Synthesis of the [*c*2]daisy chain **8**-2H·2PF_6

2,6-Bis(acetoxymethyl)-4-bromopyridine (VII). Acetic anhydride (14.8 mL, 16.1 g, 158 mmol) was added to a solution of 2,6-bis(hydroxymethyl)-4-bromopyridine (**VI**, 8.60 g, 39.4 mmol) and triethylamine (24.9 mL, 17.9 g, 177 mmol) in CH_2Cl_2 (200 mL) and then the mixture was heated under reflux for 2 h. After cooling to room temperature, the mixture was partitioned between CH_2Cl_2 (200 mL) and saturated aqueous $NaHCO_3$ (100 mL). The organic layer was washed with water (2 × 100 mL), dried ($MgSO_4$), and concentrated to afford **VII** as a yellow solid (11.0 g, 92%). M.p. 78–80 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.13 (s, 6 H), 5.13 (s, 4 H), 7.41 (s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.9, 65.9, 123.8, 134.2, 157.1, 170.4; HRMS (ESI): *m/z* $[M + H]^+$ $C_{11}H_{13}BrNO_4$ calcd. 302.0028, found 302.0008.

2,6-Bis(acetoxymethyl)-4-[4-(formyl)phenyl]pyridine (VIII). A mixture of 4-formylphenylboronic acid (0.76 g, 5.1 mmol), bromide **VI** (1.39 g, 4.6 mmol), and $Pd(PPh)_4$ (0.11 g, 92 μmol) in degassed toluene (37 mL) and saturated aqueous $NaHCO_3$ (31 mL) was stirred at 50 °C for 72 h. After cooling to room temperature, the reaction mixture was extracted with ethyl acetate (3 × 30 mL); the organic layers were combined, dried ($MgSO_4$), and concentrated. The crude product was purified (SiO_2; hexane/ethyl acetate, 1:1) to afford the aldehyde **VIII** as a white solid (1.22 g, 81%). M.p. 76–78 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.14 (s, 6 H), 5.25 (s, 4 H), 7.49 (s, 2 H), 7.76 (d, *J* = 8.2 Hz, 2 H), 7.97 (d, *J* = 8.2 Hz, 2 H), 10.05 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.9, 66.6, 119.1, 127.9, 130.3, 136.5, 143.7, 148.8, 156.5, 170.5, 191.5; HRMS (ESI): *m/z* $[M + H]^+$ $C_{18}H_{18}NO_5$ calcd. 328.1185, found 328.1191.

2,6-Bis(acetoxymethyl)-4-[4-(1,3-dioxolanyl)phenyl)]pyridine (IX). A mixture of the aldehyde **VIII** (5.2 g, 15.9 mmol), ethylene glycol (1.97 g, 31.8 mmol), and $TsOH·H_2O$ (0.3 g, 1.59 mmol) was heated under reflux in toluene (100 mL) for 16 h in a Dean–Stark apparatus. After cooling to room temperature, the mixture was partitioned between ethyl acetate (200 mL) and water (100 mL). The organic layer was washed with water (2 × 100 mL), dried ($MgSO_4$), and concentrated. The crude product was then purified (SiO_2; hexane/ethyl acetate, 1:1) to afford the acetal **IX** as a yellow oil (4.82 g, 82%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.14 (s, 6 H), 3.95–4.20 (m, 4 H), 5.23 (s, 4 H), 5.84 (s, 1 H), 7.45 (s, 2 H), 7.57 (d, *J* = 8.5 Hz, 2 H), 7.61 (d, *J* = 8.5 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.8, 65.3, 66.7, 103.1, 119.0, 127.1, 127.1, 138.7, 139.1, 149.8, 156.1, 170.5; HRMS (ESI): *m/z* $[M + H]^+$ $C_{20}H_{22}NO_6$ calcd. 372.1447, found 372.1436.

2,6-Bis(methanol)-4-[4-(1,3-dioxolanyl)phenyl)]pyridine (X). Sodium methoxide (0.28 g, 5.2 mmol) was added to a MeOH solution (65 mL) of the acetal **IX** (4.82 g, 13.0 mmol) and then the mixture was heated under reflux for 4 h. After cooling to room temperature, IR-120 (H^+) resin was added to the mixture until the pH reached 6.0–7.0. The suspension was filtered and the filtrate concentrated to afford the diol **X** as a white solid (3.16 g, quant.). M.p. 123–125 °C; ^{1}H NMR (400 MHz, $CDCl_3$/CD_3CN, 1:1) δ 3.62 (br s, 2 H), 3.73–3.95 (m, 4 H), 4.48 (s, 4 H), 5.56 (s, 1 H), 7.26 (s, 2 H), 7.33 (d, *J* = 8.2 Hz, 2 H), 7.46 (d, *J* = 8.2 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$/CD_3CN, 1:1) δ 63.6, 64.5, 102.3, 115.8, 126.2, 126.5, 138.2, 138.4, 148.2, 159.4; HRMS (ESI): *m/z* $[M + H]^+$ $C_{16}H_{18}NO_4$ calcd. 288.1236, found 288.1228.

Macrocycle XI. Sodium hydride (1.3 g, 54.0 mmol) was added to a solution of diol **X** (4.18 g, 10.8 mmol) in DMF (1.08 L) and then the mixture was stirred at room temperature for 20 min. A solution of the dichloride **3**[1] (2.63 g, 10.8 mmol) in DMF (150 mL) was added slowly to the alkoxide solution over 2 h and then the mixture was stirred at room temperature for 10 d. After evaporating the organic solvent under reduced pressure, the yellow residue was suspended in ethyl acetate (300 mL) and washed with water (3 × 100 mL); the solution was dried ($MgSO_4$) and concentrated. The crude product was purified (SiO_2; CH_2Cl_2/MeOH, 98:2) to afford the macrocycle **XI** as a white solid (0.44 g, 7%). M.p. 180–182 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.00–4.23 (m, 4 H), 4.45 (s, 4 H), 4.53 (s, 4 H), 5.18 (s, 4 H), 5.86 (s, 1 H), 6.73 (d, *J* = 8.6 Hz, 4 H), 7.12 (d, *J* = 8.6 Hz, 4 H), 7.28 (s, 4 H), 7.49 (s, 2 H), 7.57 (d, *J* = 8.3 Hz, 2 H), 7.67 (d, *J* = 8.3 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 65.4, 69.3, 71.4, 71.8, 103.3, 115.4, 118.4, 126.9, 127.1, 127.2, 129.7, 129.8, 137.0, 138.7, 139.3, 149.1, 157.6, 158.3; HRMS (ESI): *m/z* $[M+H]^+$ $C_{38}H_{36}NO_6$ calcd. 602.2543, found 602.2528.

Aldehyde 6. $TsOH{\cdot}H_2O$ (0.13 g, 0.66 mmol) was added to a solution of the macrocycle **XI** (0.4 g, 0.66 mmol) in acetone/water (10:1, 4.4 mL) and then the mixture was stirred at room temperature for 16 h before being partitioned between CH_2Cl_2 (30 mL) and water (10 mL). The organic layer was washed with water (2 × 10 mL), dried ($MgSO_4$), and concentrated. The crude product was purified (SiO_2; CH_2Cl_2/MeOH, 98:2) to afford the aldehyde **6** as a white solid (0.33 g, 90%). M.p. 67–69 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.46 (s, 4 H), 4.54 (s, 4 H), 5.18 (s, 4 H), 6.73 (d, *J* = 8.1 Hz, 4 H), 7.12 (d, *J* = 8.1 Hz, 4 H), 7.28 (s, 4 H), 7.52 (s, 2 H), 7.81 (d, *J* = 8.0 Hz, 2 H), 7.97 (d, *J* = 8.0 Hz, 2 H), 10.1 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 69.2, 71.2, 71.9, 115.4, 118.4, 126.9, 127.8, 129.5, 129.8, 130.3, 136.4, 137.0, 144.4, 148.1, 157.6, 158.6, 191.7; HRMS (ESI): *m/z* $[M + H]^+$ $C_{36}H_{32}NO_5$ calcd. 558.2280,

found 558.2275.

Hermaphroditic Monomer 5-H·PF_6. Macrocycle **6** (0.33 g, 0.59 mmol), the amine **7** (0.11 g, 0.71 mmol), and potassium carbonate (49 mg, 0.35 mmol) were stirred in CH_2Cl_2 (10 mL) at 0 °C and then slowly warmed to room temperature over 16 h. The mixture was then filtered and the filtrate concentrated to give a solid residue. The residue was dissolved in MeOH/CH_2Cl_2 (10:3, 13 mL) at 0 °C and then $NaBH_4$ (45 mg, 1.18 mmol) was added; the mixture was then stirred for 4 h at 0 °C. The mixture was then partitioned between CH_2Cl_2 (30 mL) and water (10 mL); the organic layer was washed with water (2 × 10 mL), dried ($MgSO_4$), and concentrated. The crude product was purified (SiO_2; CH_2Cl_2/MeOH, 96:4) to afford the amine **5** as a yellow residue (90.0 mg, 23%). $[\alpha]_D^{25}$ –36.0 °; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.55 (q, *J* = 5.2 Hz, 1 H), 1.13 (td, *J* = 8.2, 5.2 Hz, 1 H), 1.63 (quintet, *J* = 7.2 Hz, 2 H), 1.65–1.80 (m, 1 H), 1.80–1.92 (m, 1 H), 2.20 (q, *J* = 7.2 Hz, 2 H), 2.67 (t, *J* = 7.2 Hz, 2 H), 3.84 (s, 2 H), 4.45 (s, 4 H), 4.53 (s, 4 H), 4.98 (d, *J* = 10.5 Hz, 1 H), 5.02–5.15 (m, 2 H), 5.18 (s, 4 H), 5.44 (dt, *J* = 10.5, 7.3 Hz, 1 H), 5.48–5.60 (m, 1 H), 6.72 (d, *J* = 8.6 Hz, 4 H), 7.12 (d, *J* = 8.6 Hz, 4 H), 7.28 (s, 4 H), 7.42 (d, *J* = 8.0 Hz, 2 H), 7.49 (s, 2 H), 7.62 (d, *J* = 8.0 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.7, 17.1, 22.4, 25.3, 29.8, 48.9, 53.5, 69.2, 71.4, 71.7, 114.4, 115.4, 118.2, 126.9, 127.1, 128.7, 129.1, 129.7, 130.2, 137.0, 138.0, 141.4, 149.2, 157.5, 158.1 (two carbon signals are missing, possibly because of signal overlapping); HRMS (ESI): *m/z* $[M + Na]^+$ $C_{46}H_{48}N_2O_4Na$ calcd. 715.3512, found 715.3501. 1 N HCl (57 μL) was added to a solution of the amine **5** (40 mg, 57 μmol) in CH_2Cl_2 (1 mL) and CH_3CN (10 mL) and then saturated aqueous KPF_6 solution (20 mL) was added. The organic solvent was evaporated under reduced pressure and the precipitate was filtered off to give the monomer **5**-H·PF_6 as a white solid (40 mg, 84%). M.p. >230 °C; $[\alpha]_D^{25}$ –13.0°; ^{1}H NMR (400 MHz, $CDCl_3$/CD_3CN, 10:1) δ –0.25 to –0.50 (m, 2 H), 0.67 (q, *J* = 5.3 Hz, 1 H), 1.11–1.25 (m, 2 H), 1.30 (td, *J* = 8.2, 5.3 Hz, 1 H), 1.40–1.55 (m, 2 H), 1.80–1.95 (m, 2 H), 2.27–2.42 (m, 2 H), 4.38 (br t, *J* = 7.0 Hz, 2 H), 4.53–4.69 (m, 4 H), 4.77 (br d, *J* = 8.0 Hz, 2 H), 5.02 (d, *J* = 10.2 Hz, 1 H), 5.10–5.30 (m, 7 H), 5.48–5.63 (m, 1 H), 6.82–6.91 (m, 2 H), 6.93–7.07 (m, 4 H), 7.10–7.20 (m, 6 H), 7.27 (s, 4 H), 7.42 (br s, 2 H), 7.55 (br d, *J* = 5.6 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$/CD_3CN, 5:1) δ 15.0, 17.2, 22.7, 23.7, 26.3, 46.4, 50.6, 67.4, 73.6, 73.8, 114.1, 115.2, 119.2, 126.6, 126.9, 127.2, 128.0, 129.0, 129.2, 129.7, 130.5, 135.8, 136.7, 136.9, 147.7, 154.6, 156.8; HRMS (ESI): *m/z* [**5**-H]$^+$ $C_{46}H_{49}N_2O_4$ calcd. 693.3693, found 693.3674.

[*c*2]Daisy Chain 8-2H·2PF_6. A solution of monomer **5**-H·PF_6 (40 mg, 48 μmol) in chloroform/acetonitrile (10:1, 4.4 mL) was heated at 40 °C for 120 h. The solution

was concentrated and the residue purified (SiO_2; CH_2Cl_2/MeOH, 96:4) to afford **8**-2H·2PF_6 as a white solid (31 mg, 77%). M.p. >235 °C; ^{1}H NMR (400 MHz, $CDCl_3$/CD_3CN, 5:1) δ –0.42 to –0.25 (m, 4 H), 0.38–0.62 (m, 4 H), 0.92–1.08 (m, 4 H), 2.00–2.15 (m, 2 H), 2.17–2.32 (m, 4 H), 2.35–2.45 (m, 4 H), 2.67–3.02 (m, 4 H), 4.34 (dd, *J* = 9.0, 6.4 Hz, 4 H), 4.55 (s, 8 H), 4.69 (d, *J* = 9.0 Hz, 8 H), 5.16 (s, 8 H), 5.52 (dd, *J* = 11.3, 4.3 Hz, 2 H), 5.61–5.77 (m, 6 H), 6.82 (d, *J* = 8.0 Hz, 4 H), 6.94 (d, *J* = 6.9 Hz, 4 H), 7.02 (s, 4 H), 7.04–7.15 (m, 8 H), 7.22 (s, 8 H), 7.30 (d, *J* = 6.9 H, 4 H), 7.46 (d, *J* = 8.0 Hz, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$/CD_3CN, 5:1) δ 23.8, 28.6, 31.8, 32.4, 36.7, 46.6, 50.6, 67.4, 73.7, 73.8, 115.4, 119.6, 127.1, 127.4, 127.9, 128.4, 128.5, 128.6, 129.5, 130.2, 130.9, 134.3, 136.3, 137.3, 148.2, 155.2, 157.4; HRMS (ESI): *m/z* [**8**-2H·PF_6]$^+$ $C_{92}H_{98}F_6N_4O_8P$ calcd. 1531.7028, found 1531.7066.

[1] A. Kannan and P. Rajakumar *Synth. Commun.*, 1995, **25**, 3053–3065.
[2] D. Grandjean, P. Pale and J. Chuche, *Tetrahedron*, 1991, **47**, 1215–1230.

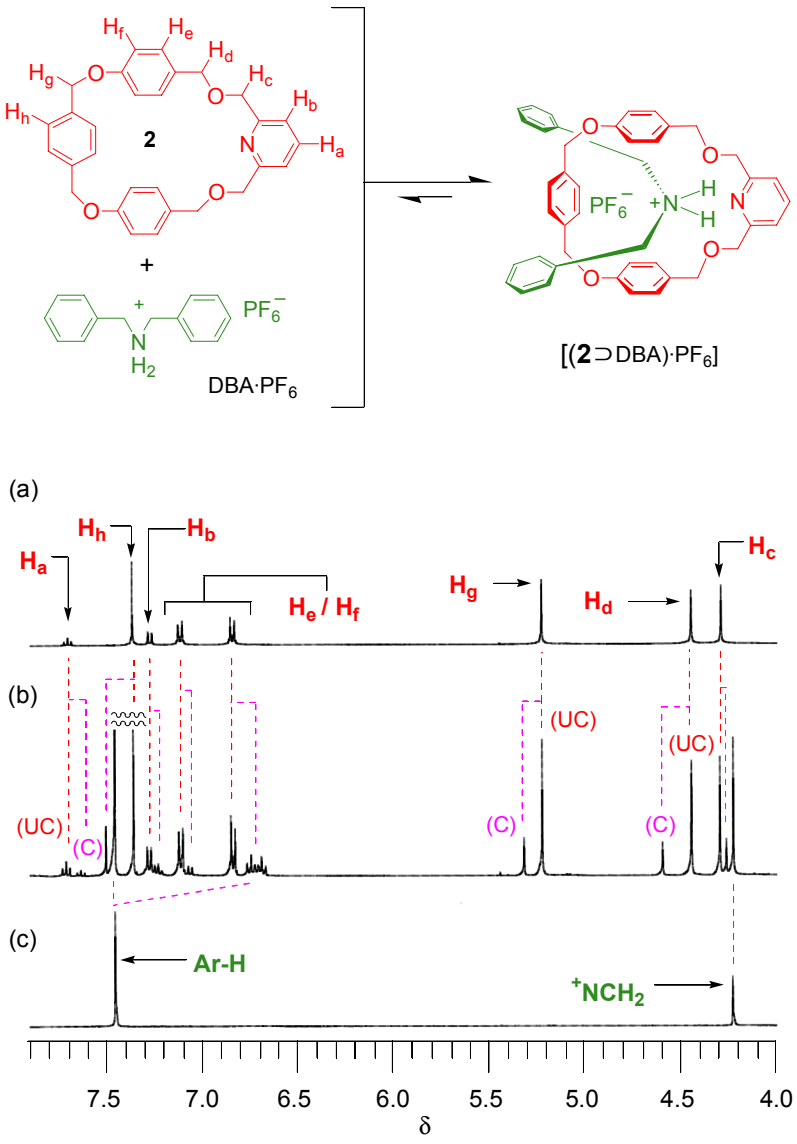
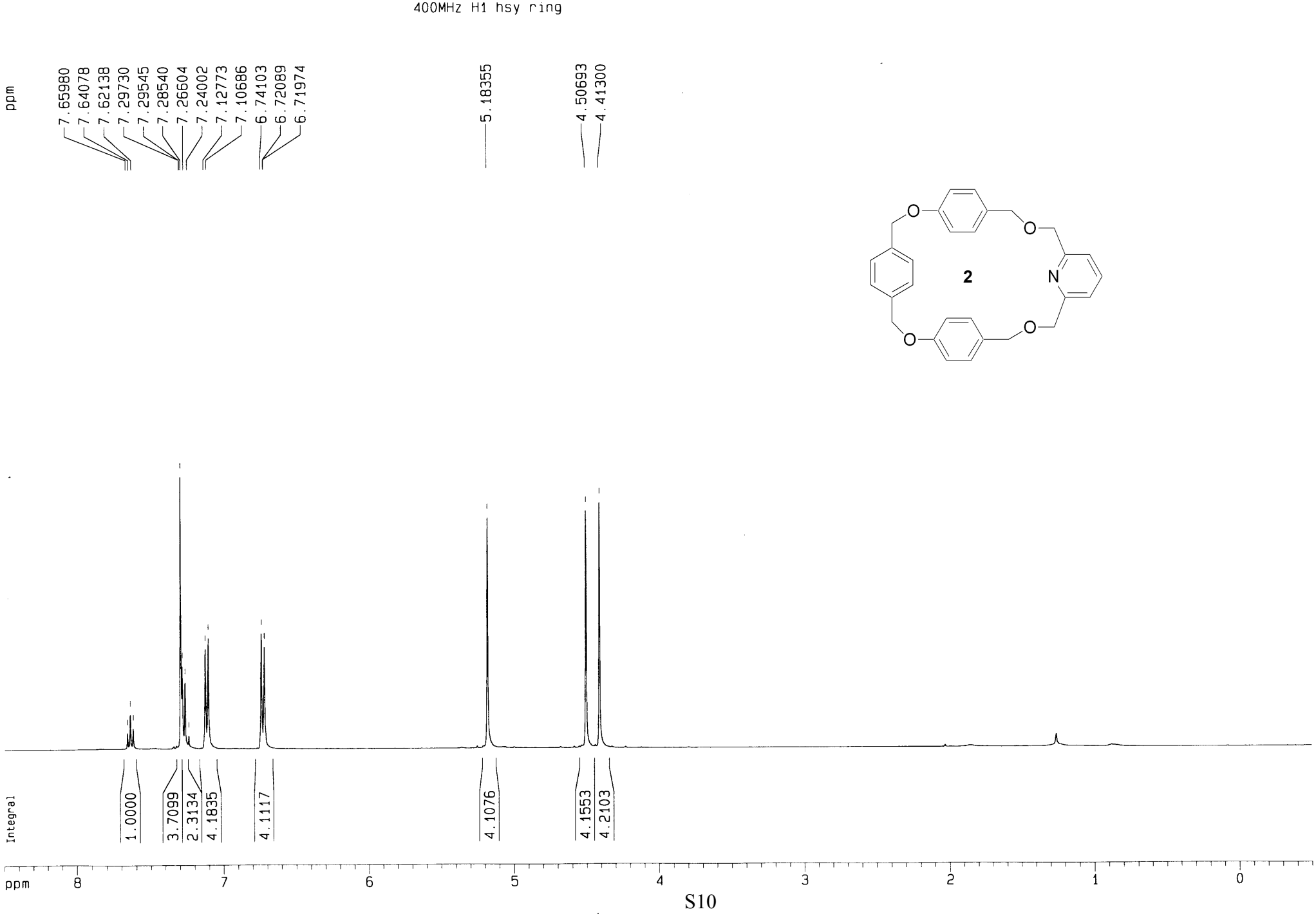
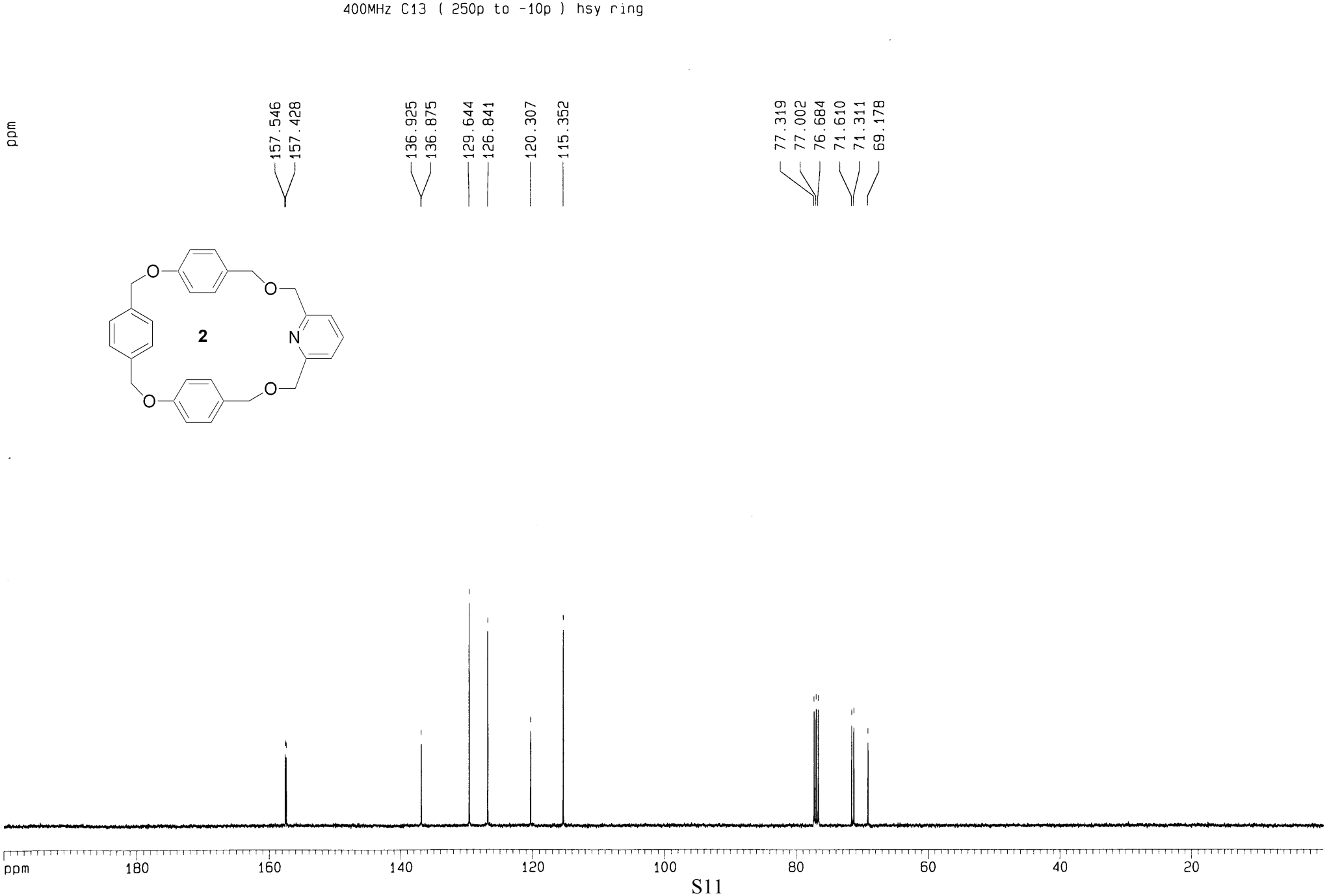


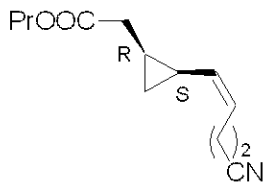
Figure 1. Partial ^{1}H NMR spectra (400 MHz, CD_3CN, 298 K) of (a) macrocycle **2**, (b) an equimolar mixture of **2** and DBA·PF_6 (10 mM), and (c) DBA·PF_6. The descriptors "UC" and "C" refer to the uncomplexed and complexed states, respectively.


400MHz H1 hsy ring
ppm
7.65980
7.64078
7.62138
7.29730
7.29545
7.28540
7.26604
7.24002
7.12773
7.10686
6.74103
6.72089
6.71974
5.18355
4.50693
4.41300
2
N
O
Integral
1.0000
3.7099
2.3134
4.1835
4.1117
4.1076
4.1553
4.2103
ppm
8
7
6
5
4
3
2
1
0


400MHz C13 (250p to -10p) hsy ring
ppm
157.546
157.428
136.925
136.875
129.644
126.841
120.307
115.352
77.319
77.002
76.684
71.610
71.311
69.178
2
N
O
ppm
180
160
140
120
100
80
60
40
20

STANDARD 1H OBSERVE

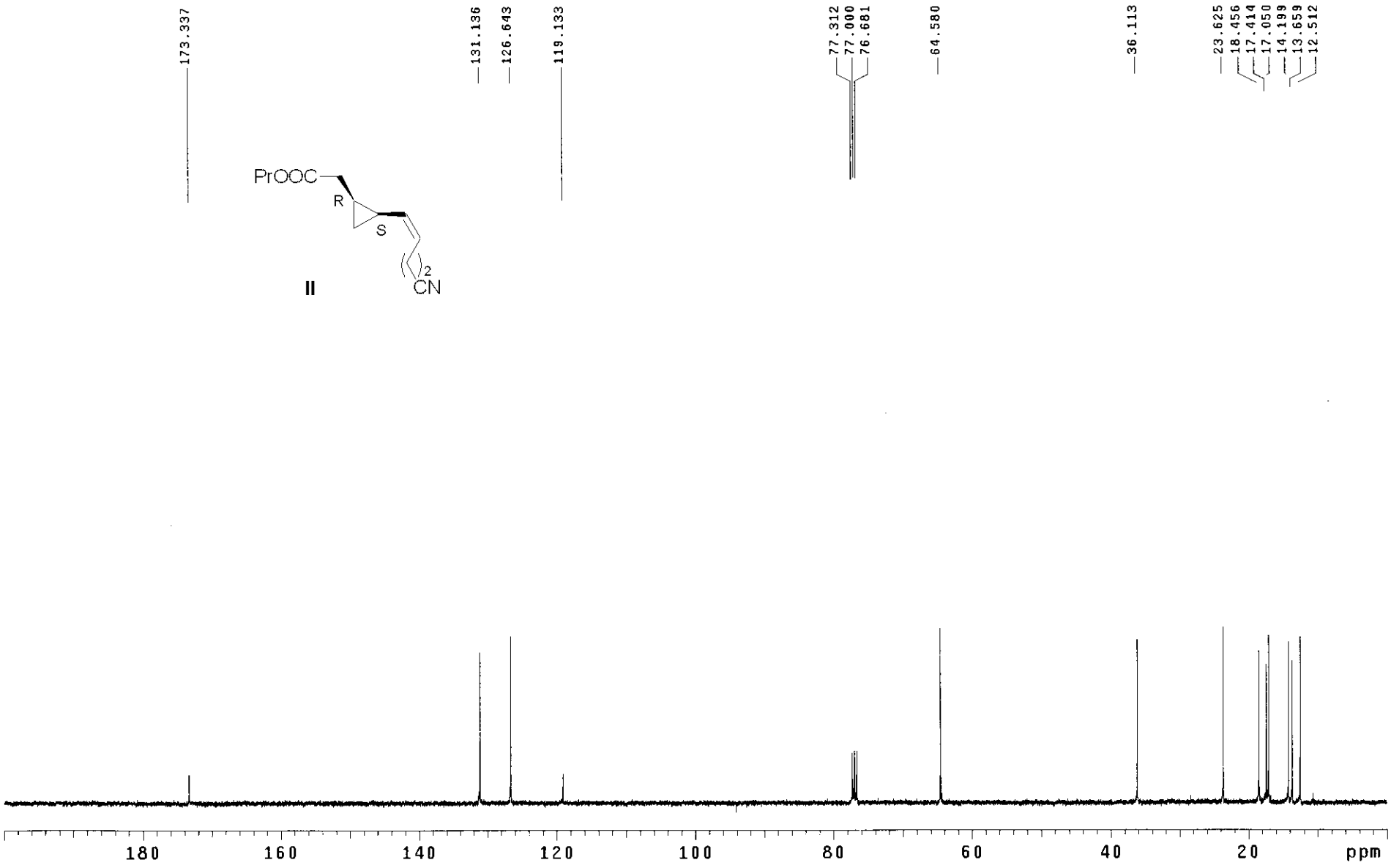
Pulse Sequence: s2pul



II

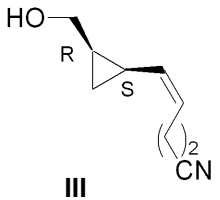
13C OBSERVE

Pulse Sequence: s2pul



STANDARD 1H OBSERVE

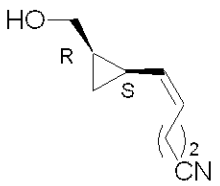
Pulse Sequence: s2pul



III

13C OBSERVE

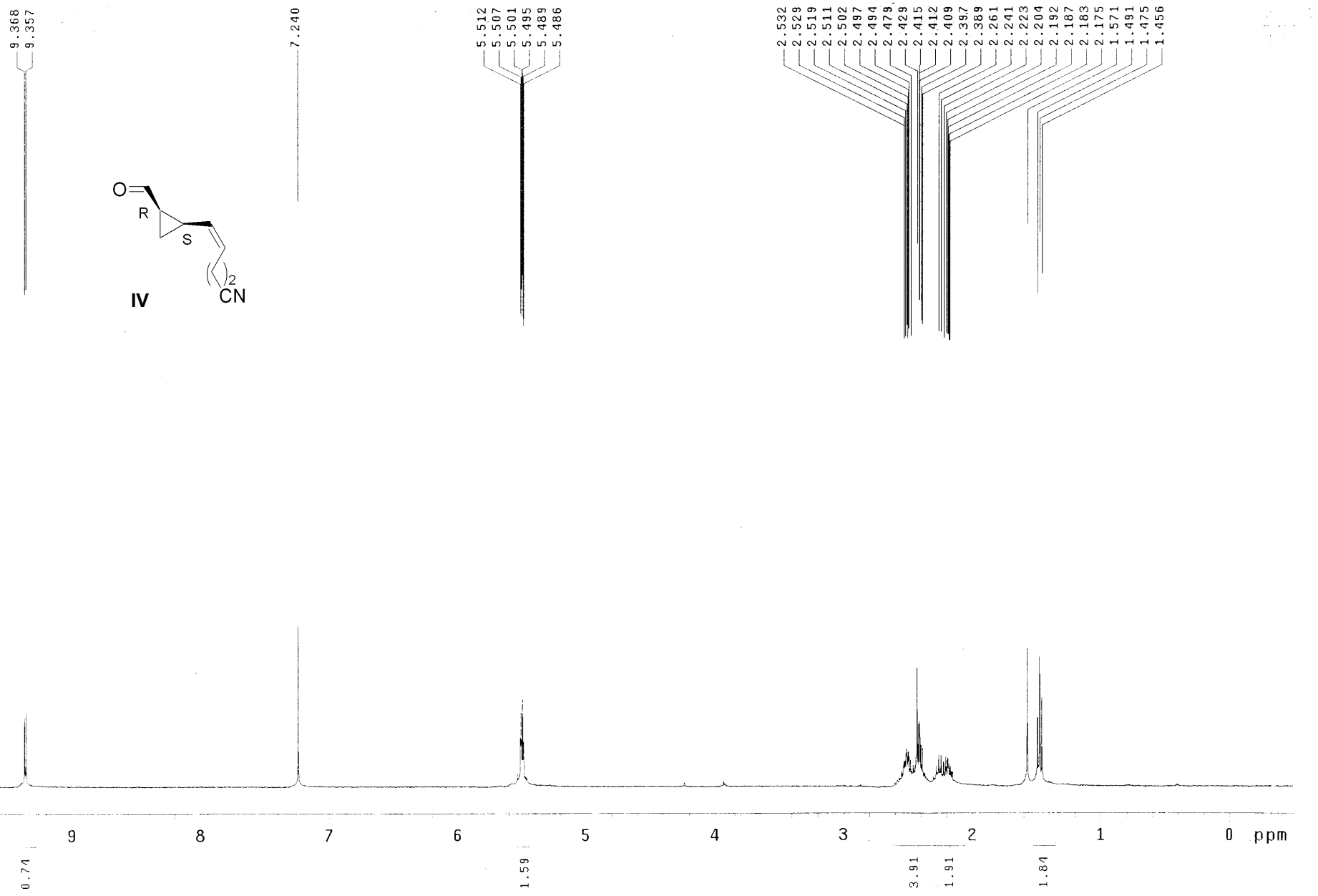
Pulse Sequence: s2pul



III

STANDARD 1H OBSERVE

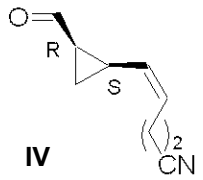
Pulse Sequence: s2pul



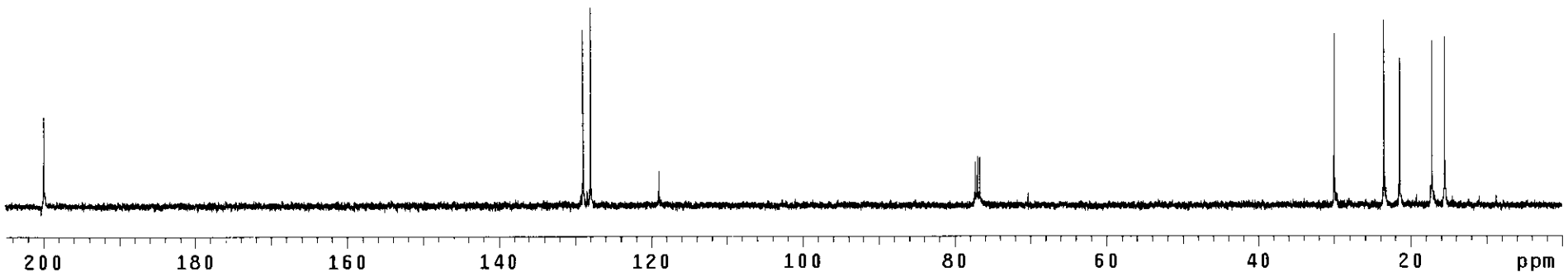
13C OBSERVE

Pulse Sequence: s2pul

199.964
128.939
127.958
118.981
77.319
77.000
76.681
29.994
23.526
21.458
17.194
15.507

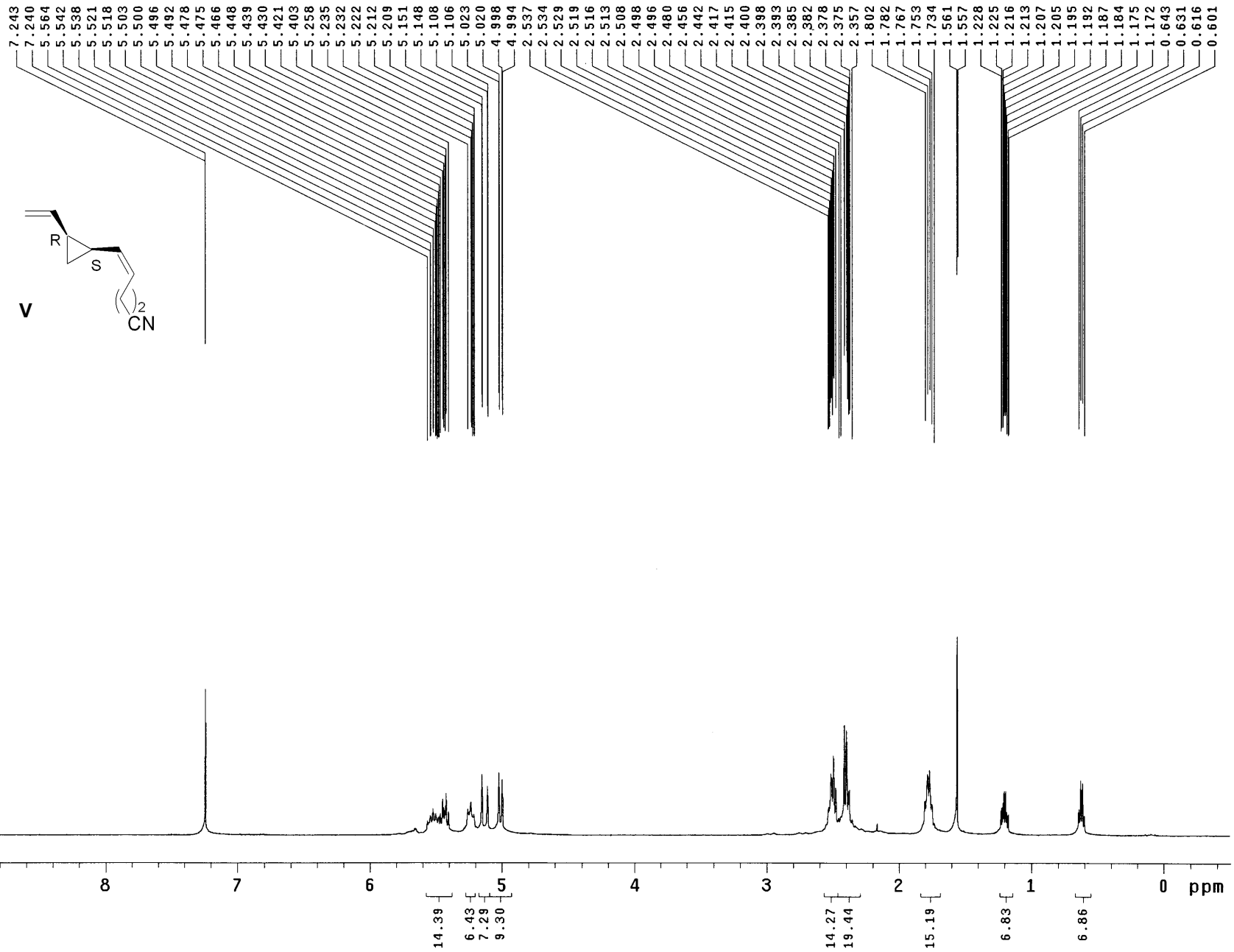


IV



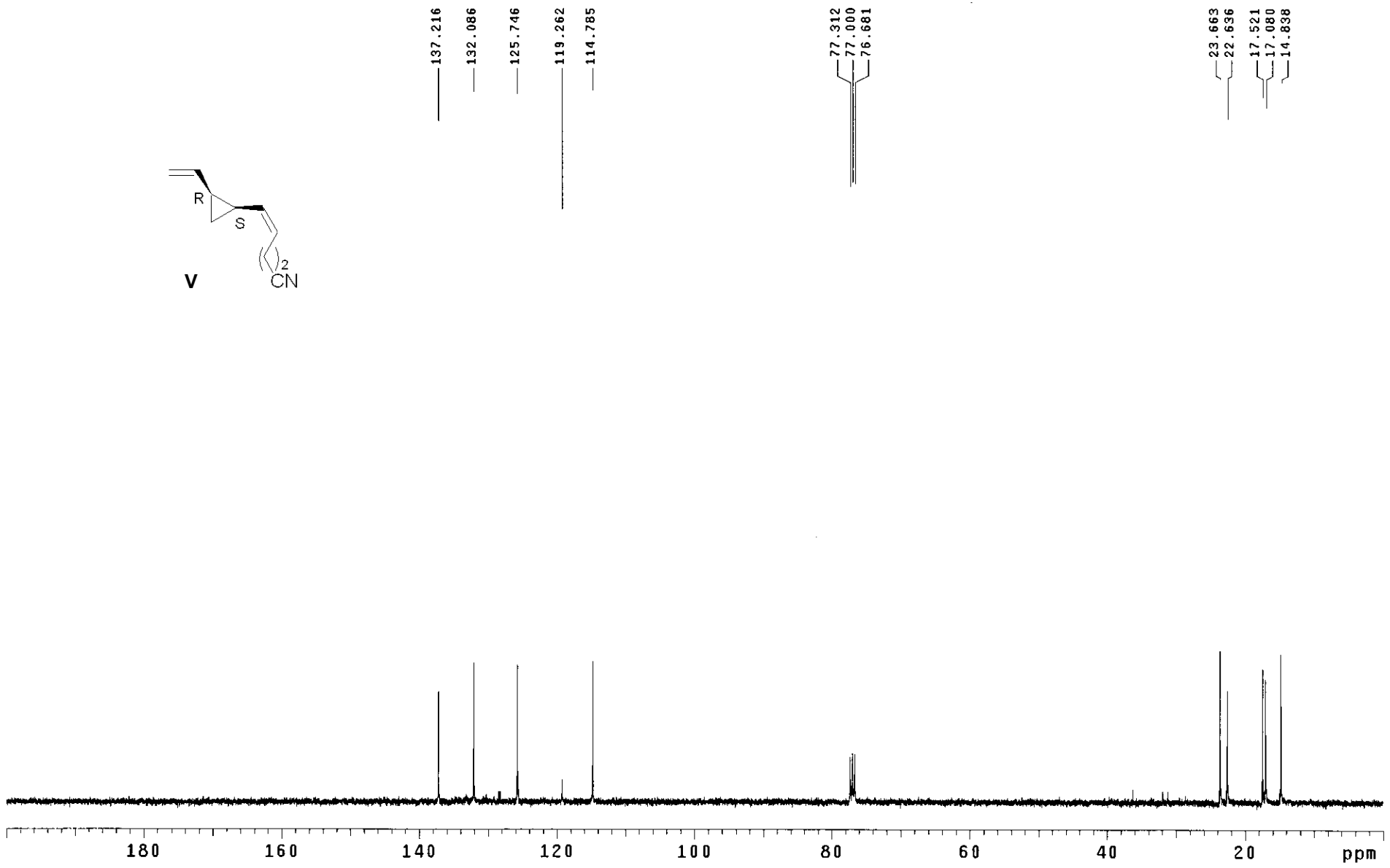
STANDARD 1H OBSERVE

Pulse Sequence: s2pul



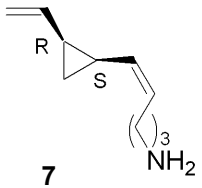
13C OBSERVE

Pulse Sequence: s2pul

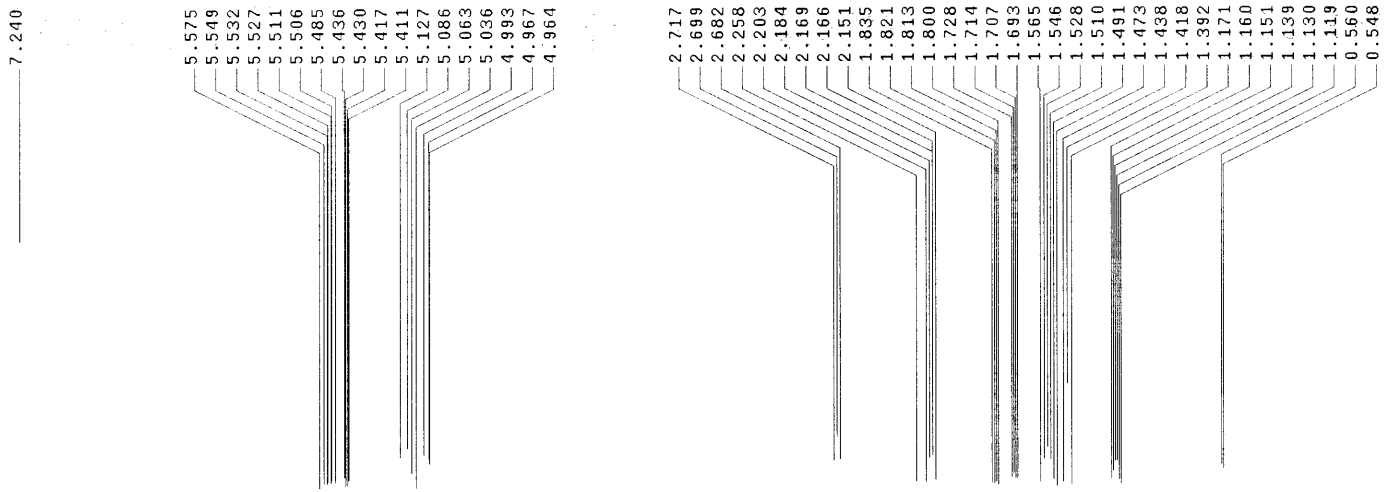


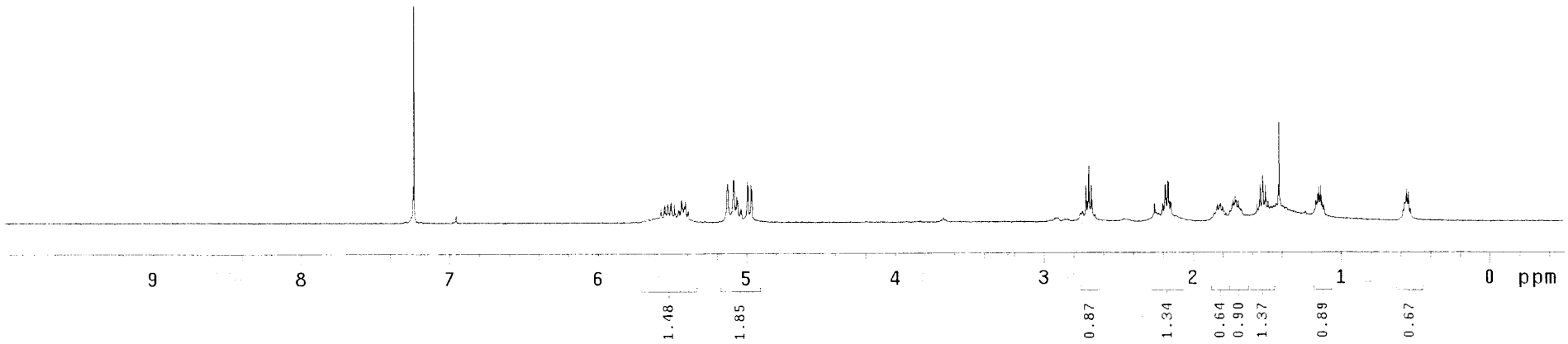
STANDARD 1H OBSERVE

Pulse Sequence: s2pul



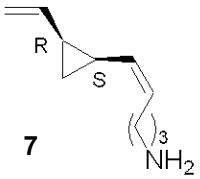
7





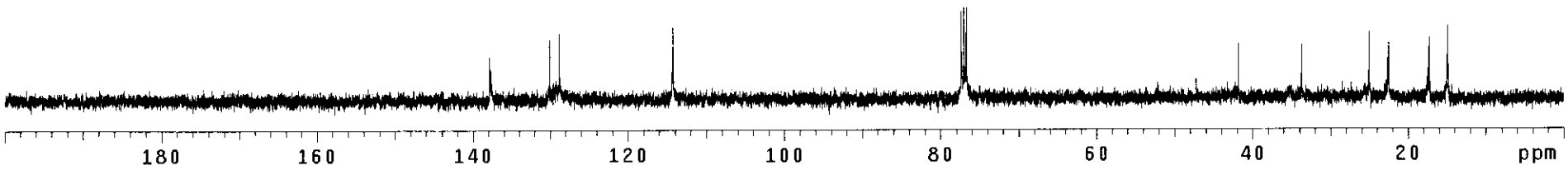
13C OBSERVE

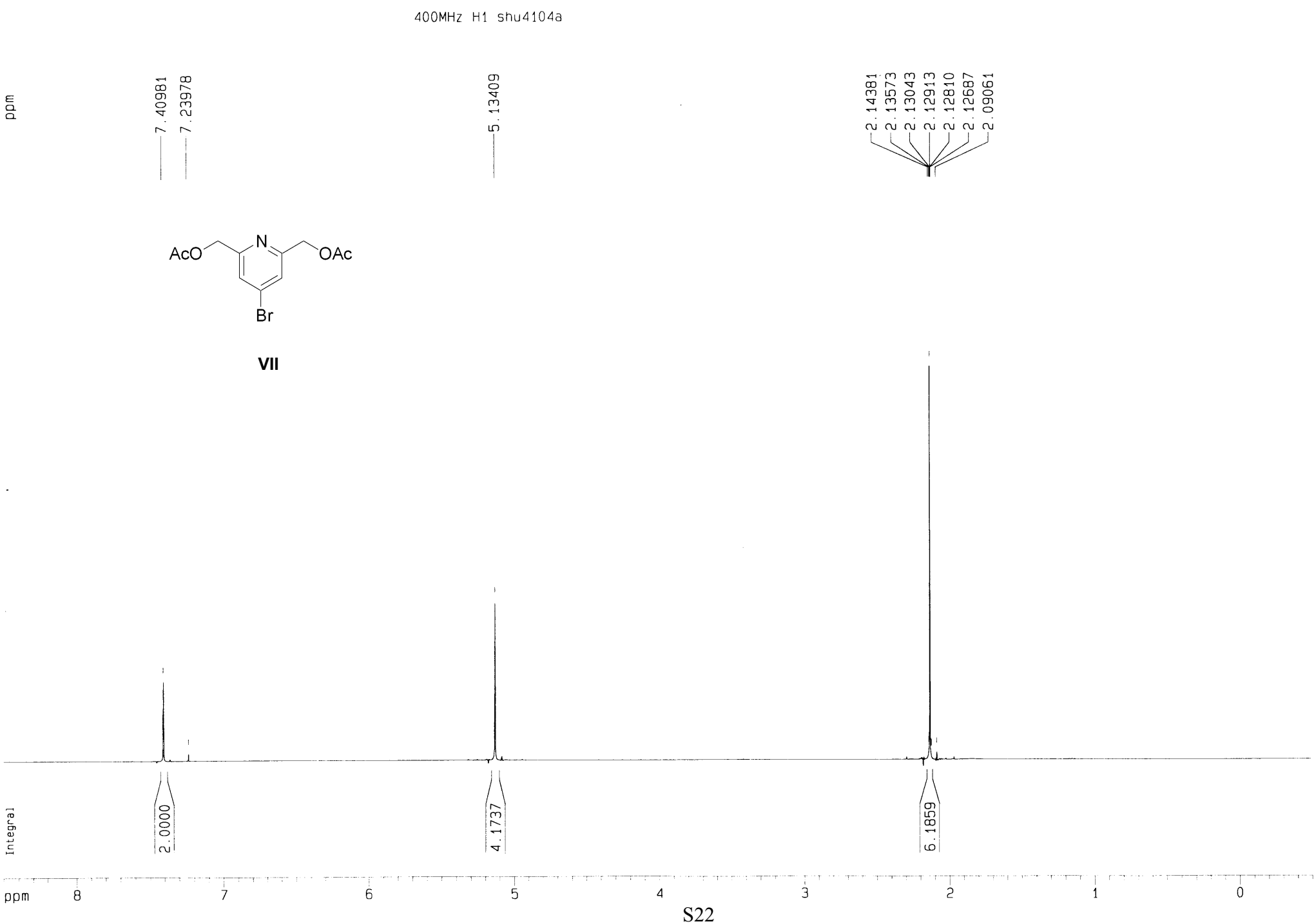
Pulse Sequence: s2pul



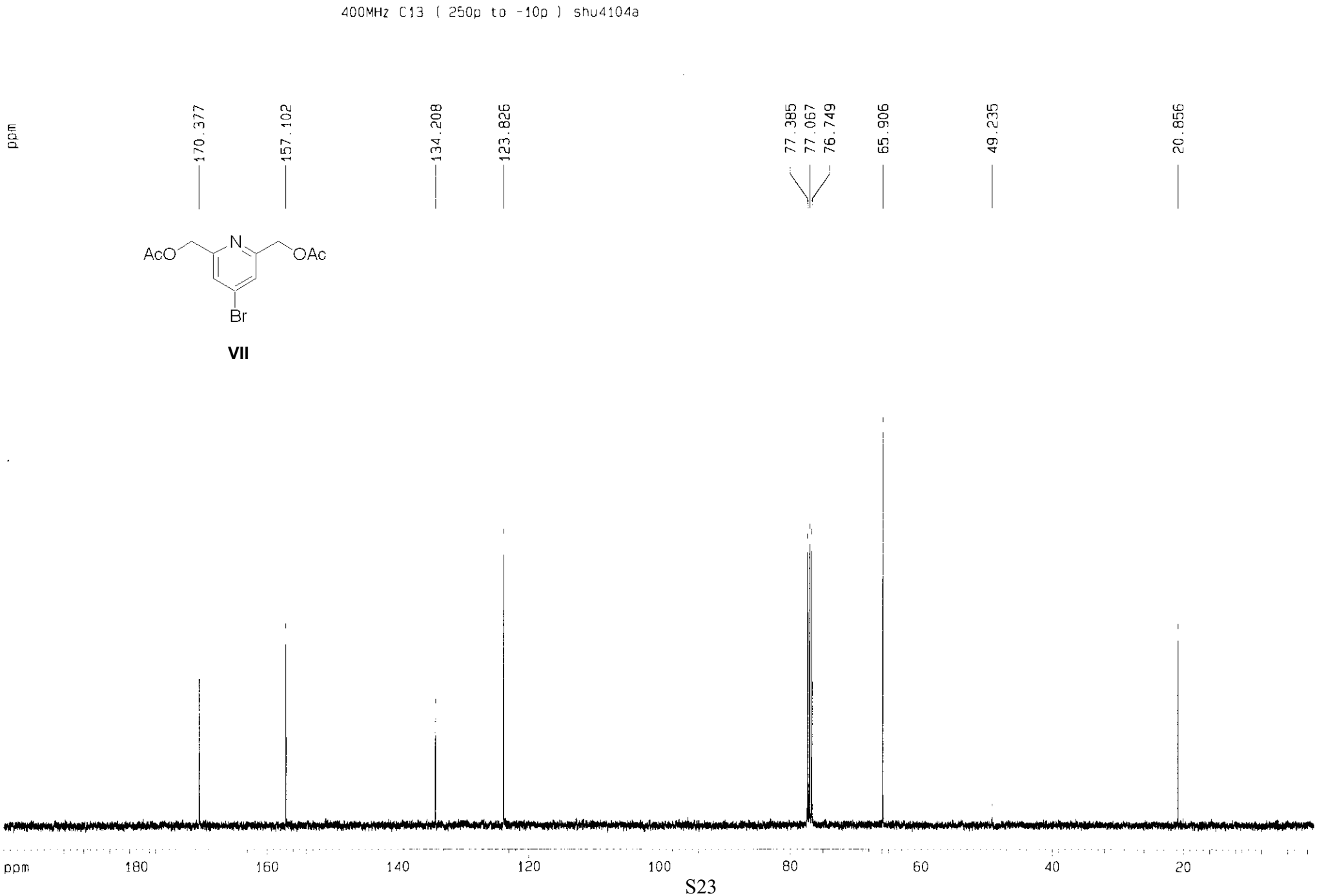
7

137.817
130.071
128.802
114.261
77.319
77.000
76.681
41.814
33.681
24.993
22.462
17.300
17.240
14.845

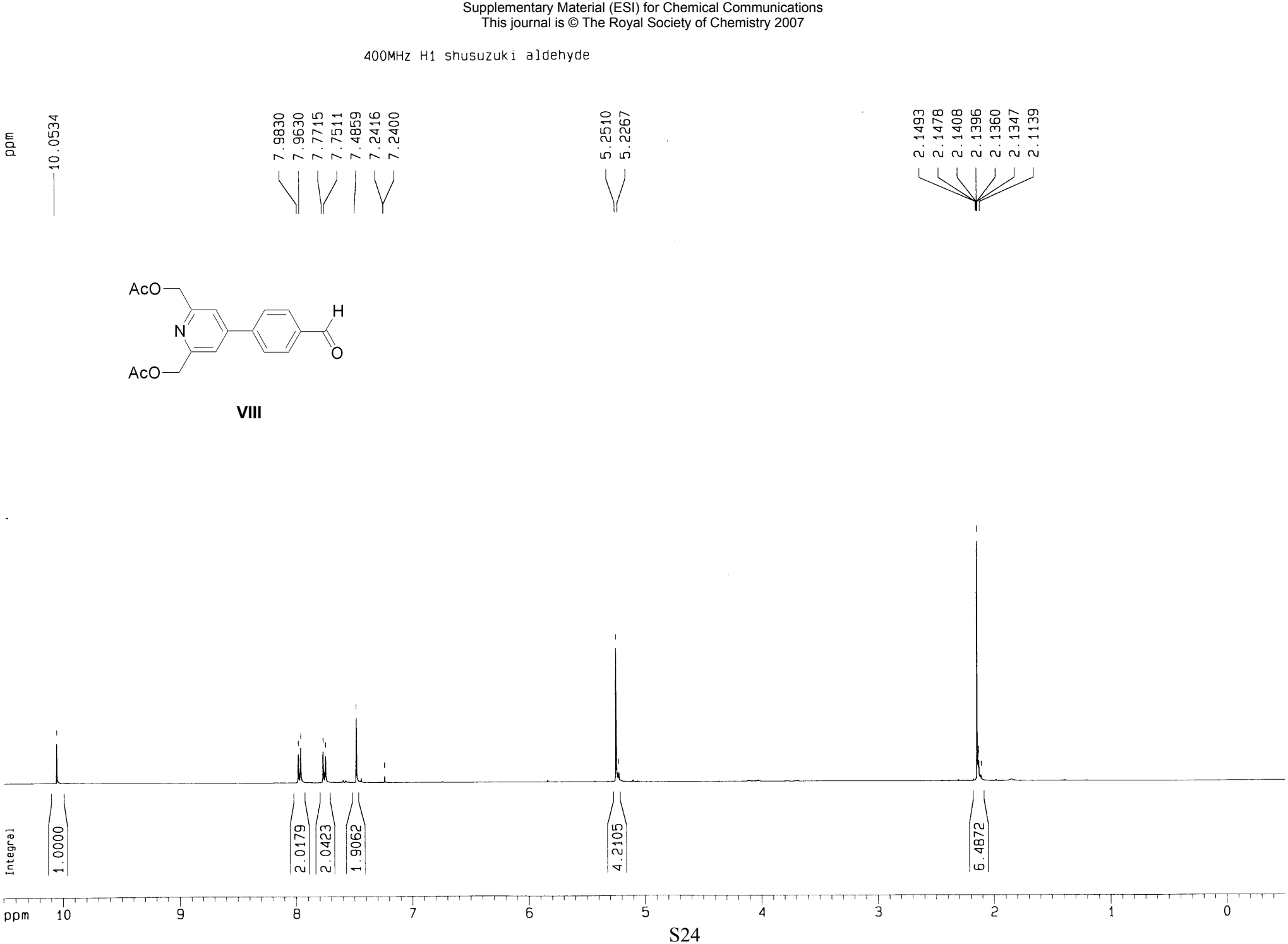



400MHz H1 shu4104a
ppm
7.40981
7.23978
5.13409
2.14381
2.13573
2.13043
2.12913
2.12810
2.12687
2.09061
AcO
N
OAc
Br
Integral
2.0000
4.1737
6.1859
ppm
8
7
6
5
4
3
2
1
0

VII

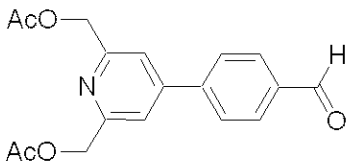

400MHz C13 (250p to -10p) shu4104a
ppm
170.377
157.102
134.208
123.826
77.385
77.067
76.749
65.906
49.235
20.856
AcO
N
OAc
Br
ppm
180
160
140
120
100
80
60
40
20

VII

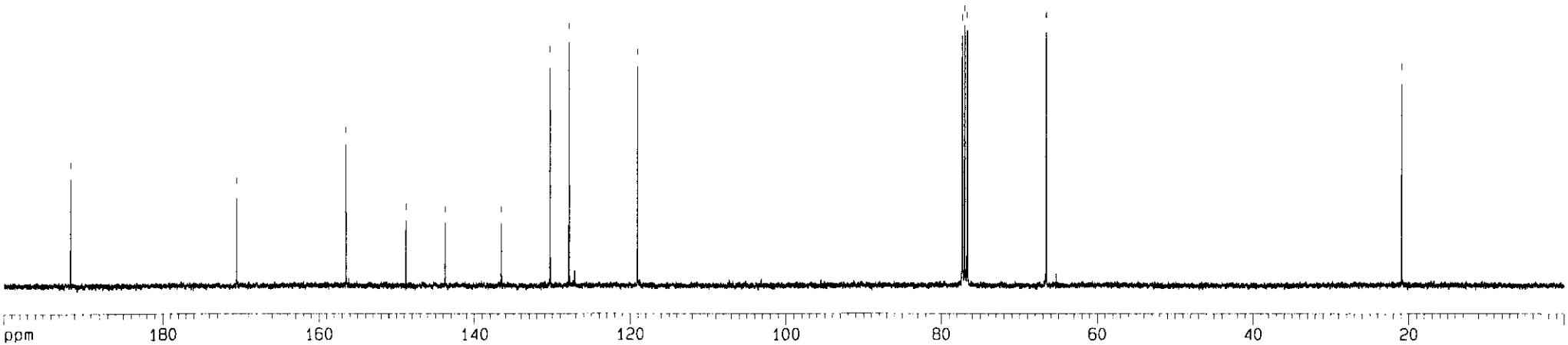

400MHz H1 shusuzuki aldehyde
ppm
10.0534
7.9830
7.9630
7.7715
7.7511
7.4859
7.2416
7.2400
5.2510
5.2267
2.1493
2.1478
2.1408
2.1396
2.1360
2.1347
2.1139
AcO
AcO
N
H
O
Integral
1.0000
2.0179
2.0423
1.9062
4.2105
6.4872
ppm
10
9
8
7
6
5
4
3
2
1
0

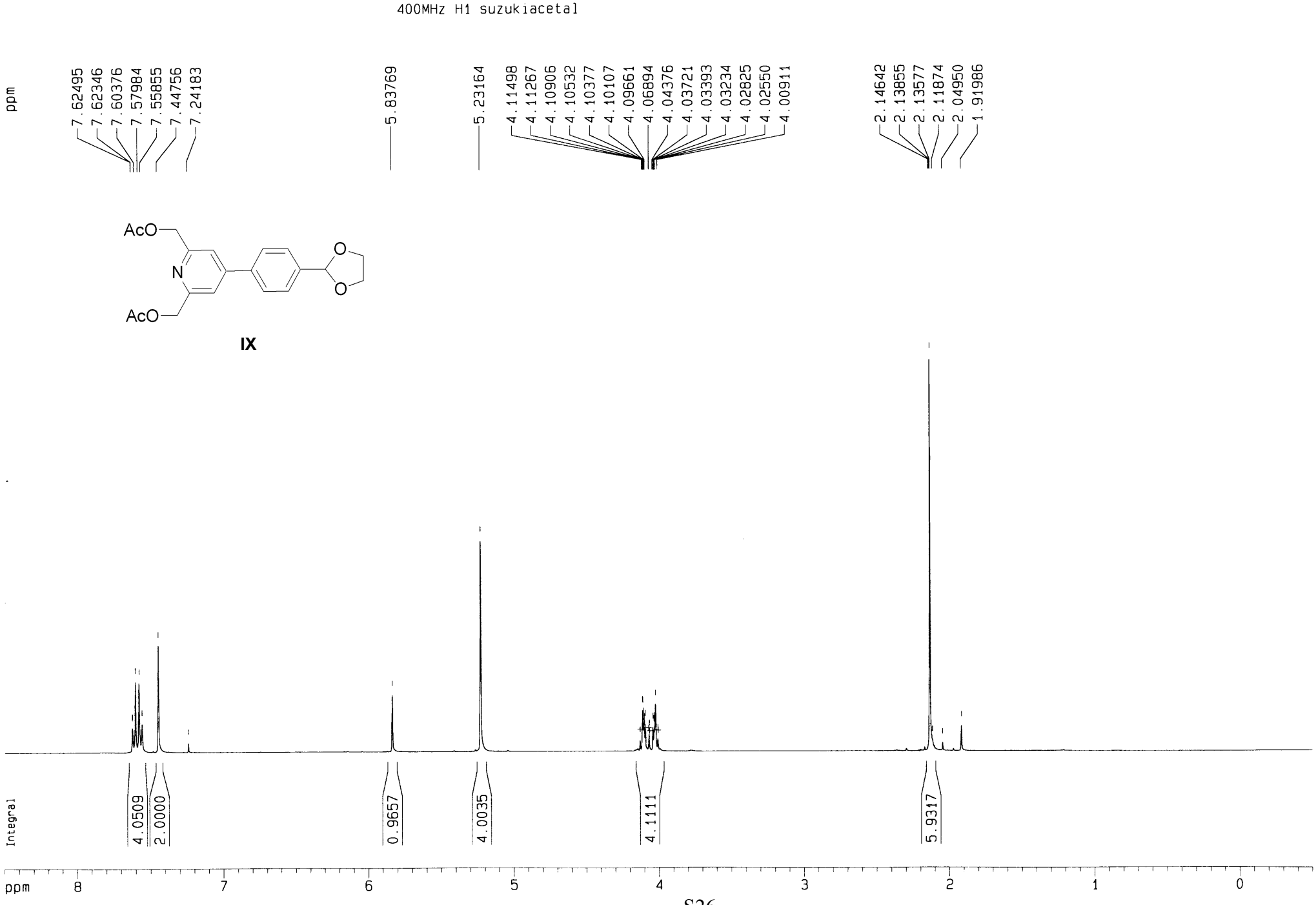
VIII

400MHz C13 (250p to -10p) suzuki aldehyde



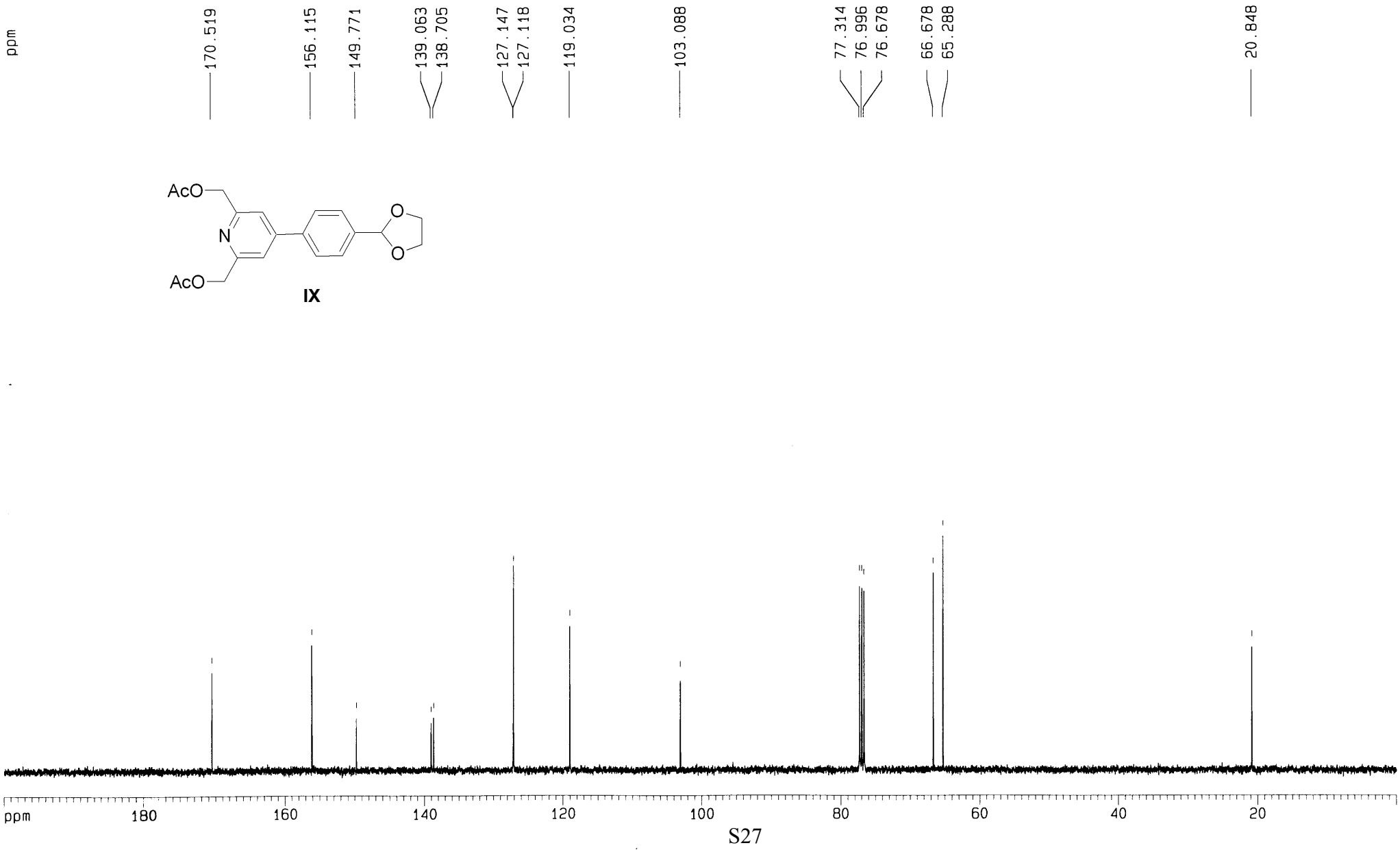
VIII



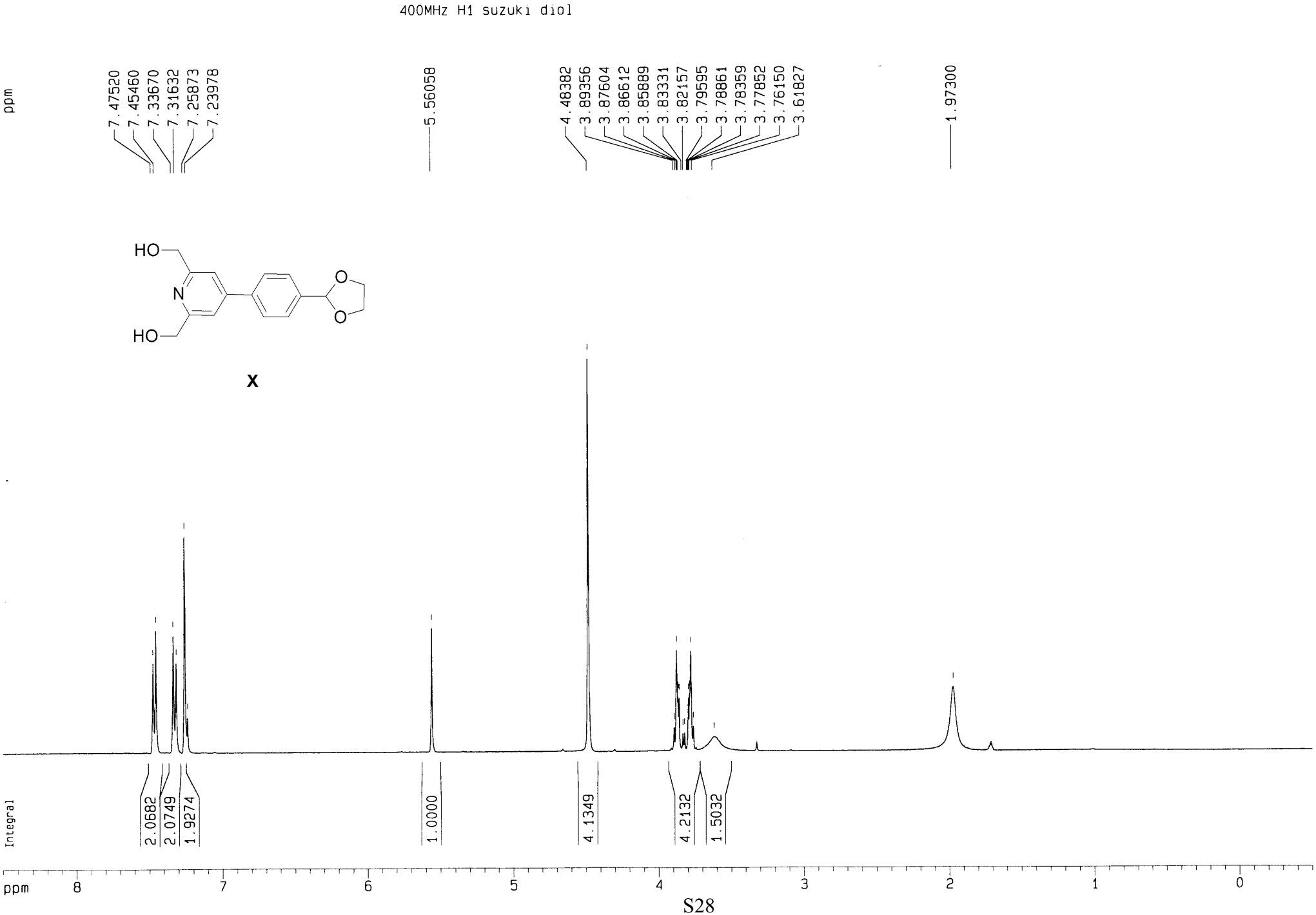

400MHz H1 suzukiacetal
ppm
7.62495
7.62346
7.60376
7.57984
7.55855
7.44756
7.24183
5.83769
5.23164
4.11498
4.11267
4.10906
4.10532
4.10377
4.10107
4.09661
4.06894
4.04376
4.03721
4.03393
4.03234
4.02825
4.02550
4.00911
2.14642
2.13855
2.13577
2.11874
2.04950
1.91986
AcO
N
O
O
AcO
Integral
4.0509
2.0000
0.9657
4.0035
4.1111
5.9317
ppm
8
7
6
5
4
3
2
1
0

IX

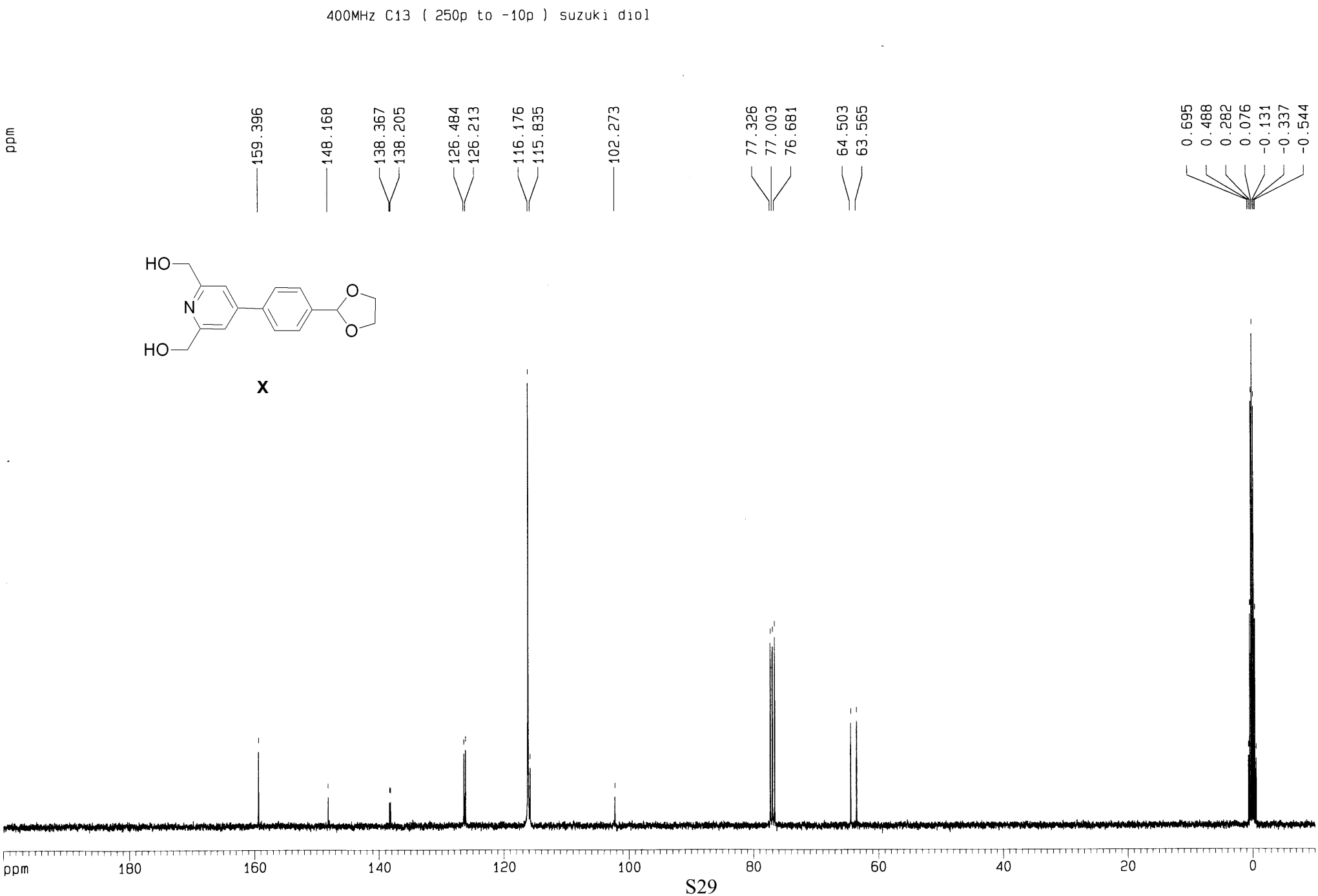
400MHz C13 (250p to -10p) suzuki acetal

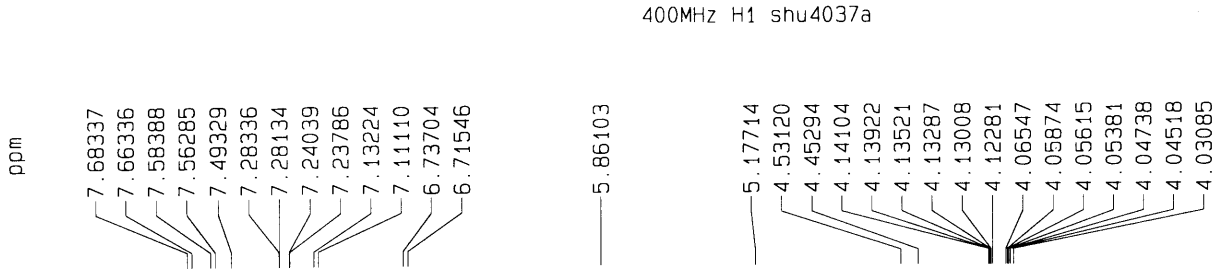


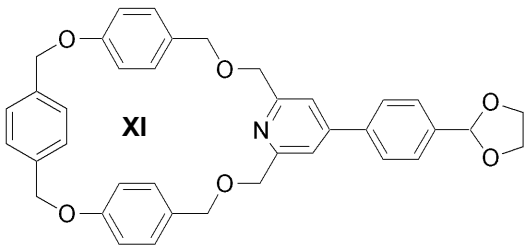
IX


400MHz H1 suzuki diol
ppm
7.47520
7.45460
7.33670
7.31632
7.25873
7.23978
5.56058
4.48382
3.89356
3.87604
3.86612
3.85889
3.83331
3.82157
3.79595
3.78861
3.78359
3.77852
3.76150
3.61827
1.97300
HO
N
HO
O
O
Integral
2.0682
2.0749
1.9274
1.0000
4.1349
4.2132
1.5032
ppm
8
7
6
5
4
3
2
1
0

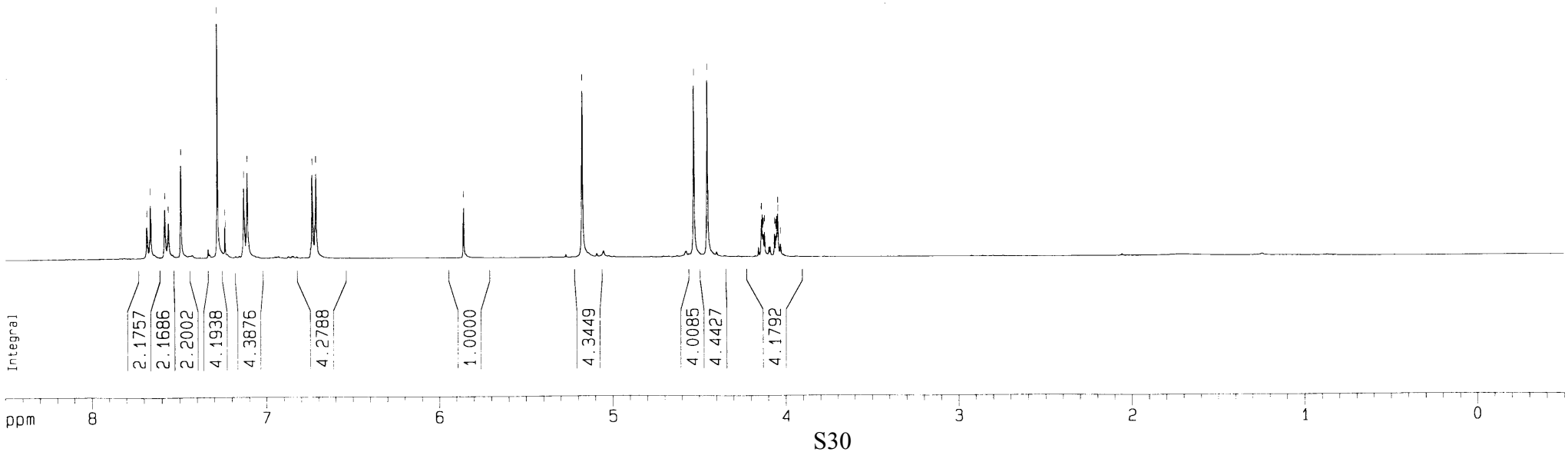
X

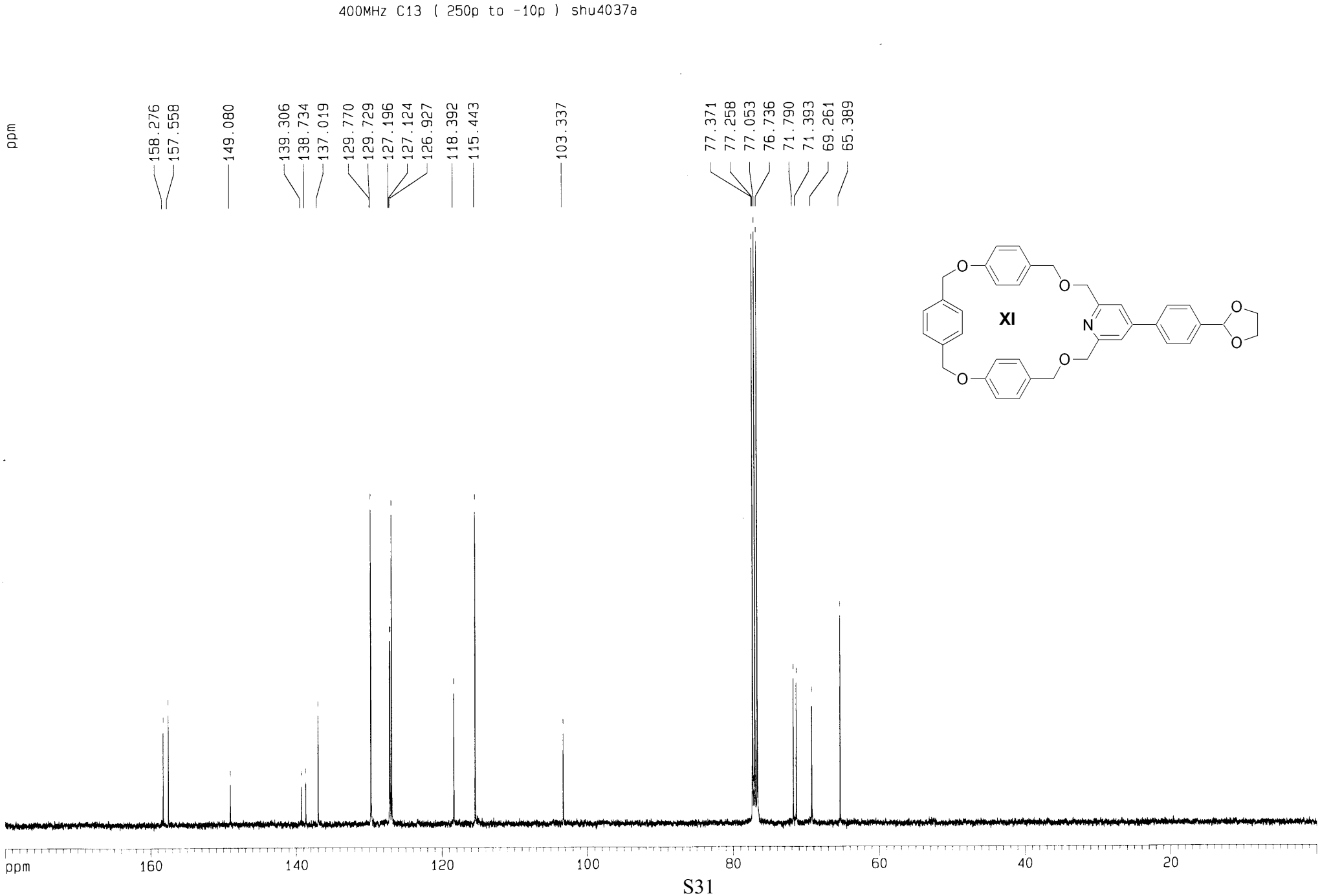

400MHz C13 (250p to -10p) suzuki diol
ppm
159.396
148.168
138.367
138.205
126.484
126.213
116.176
115.835
102.273
77.326
77.003
76.681
64.503
63.565
0.695
0.488
0.282
0.076
-0.131
-0.337
-0.544
HO
N
HO
O
O
X
ppm
180
160
140
120
100
80
60
40
20
0

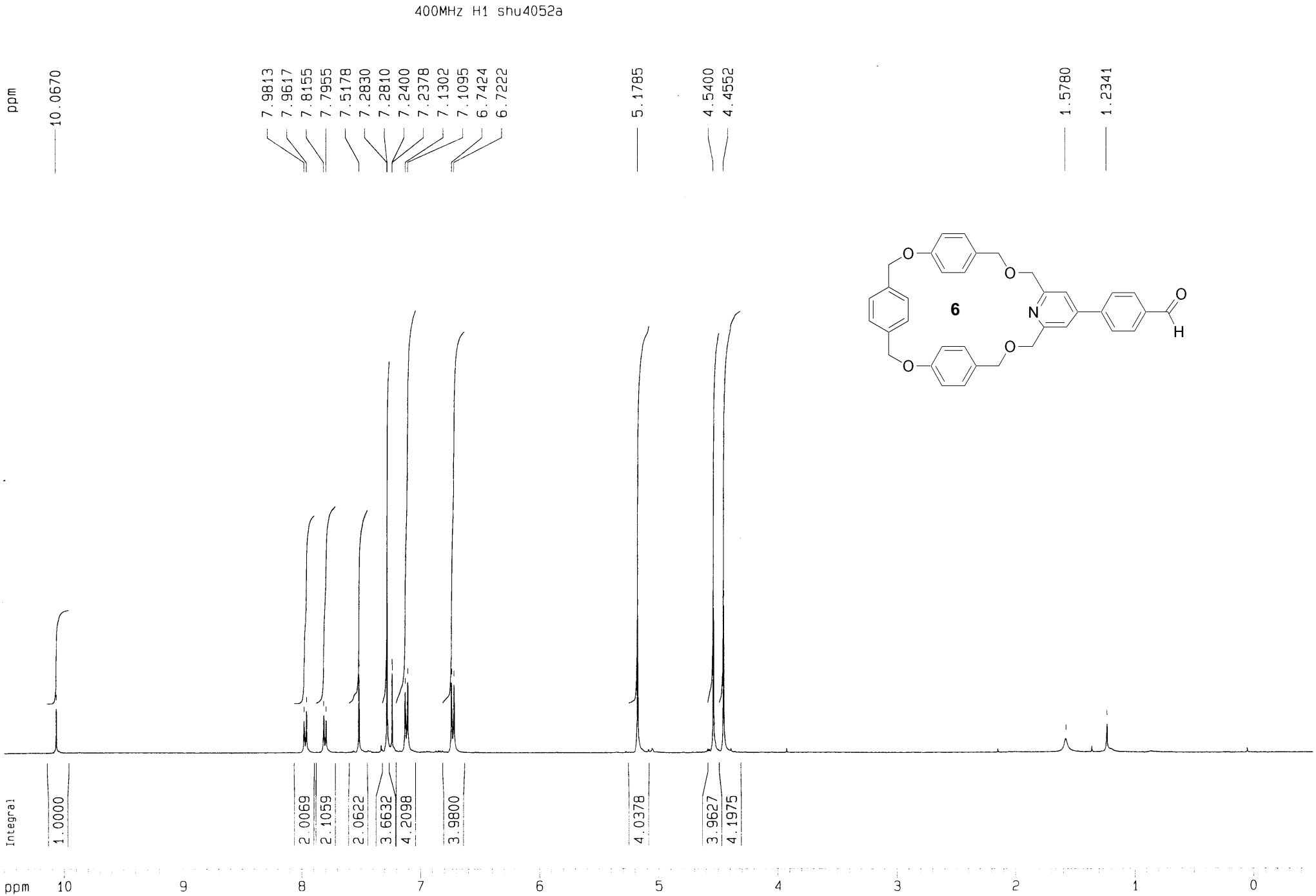

400MHz H1 shu4037a
ppm
7.68337
7.66336
7.58388
7.56285
7.49329
7.28336
7.28134
7.24039
7.23786
7.13224
7.11110
6.73704
6.71546
5.86103
5.17714
4.53120
4.45294
4.14104
4.13922
4.13521
4.13287
4.13008
4.12281
4.06547
4.05874
4.05615
4.05381
4.04738
4.04518
4.03085

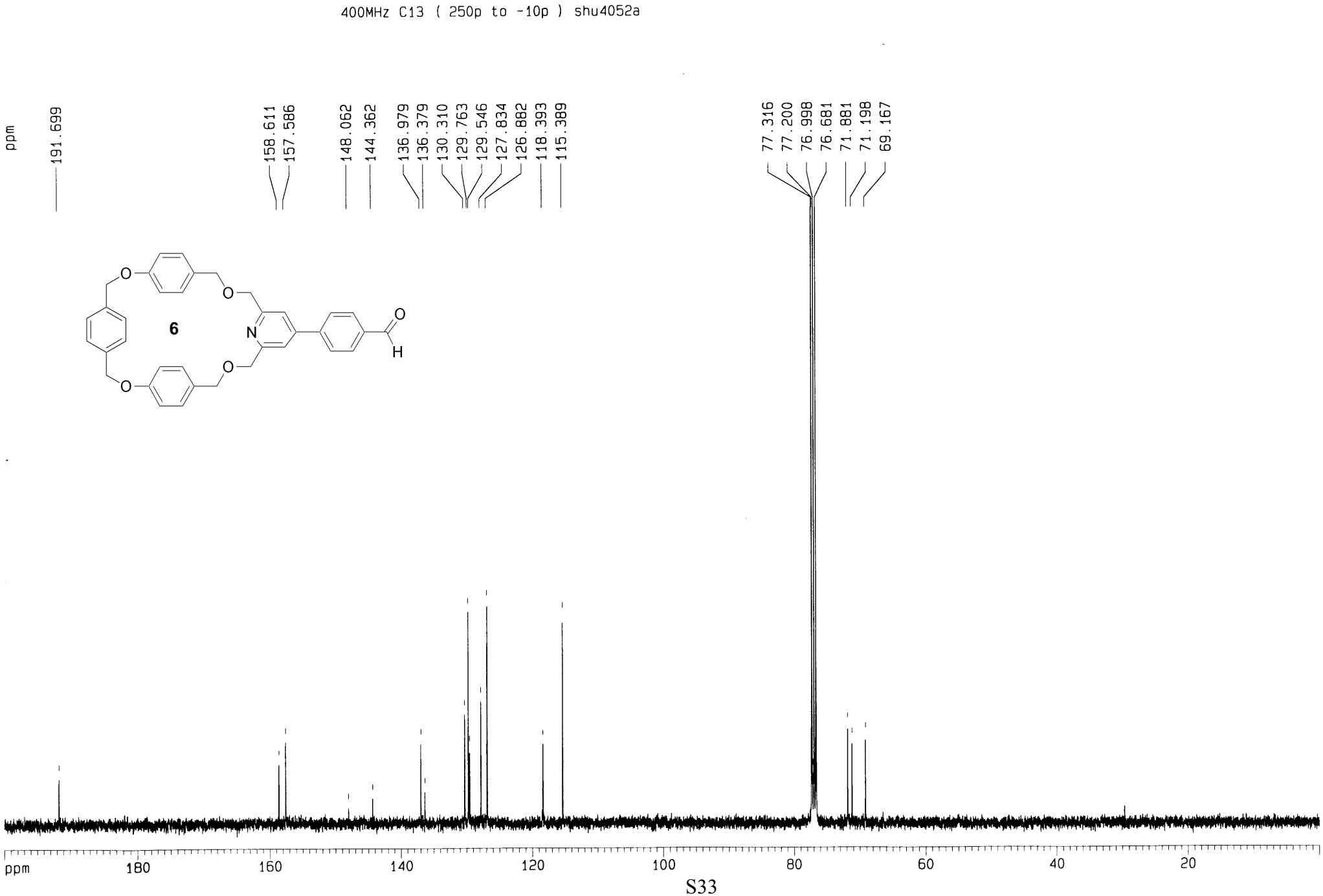

O
O
O
O
O
O
N
O
O

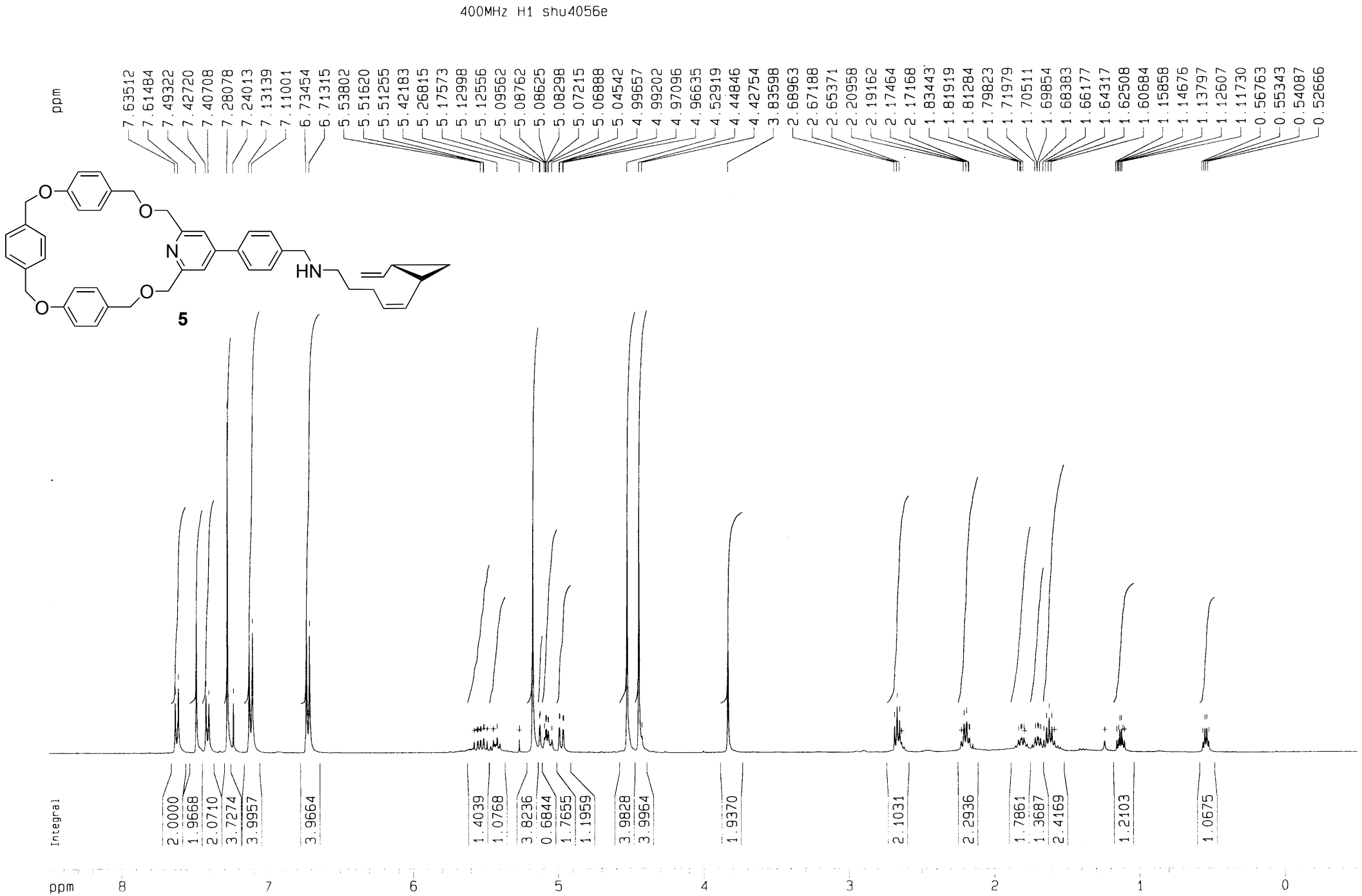
XI


Integral
2.1757
2.1686
2.2002
4.1938
4.3876
4.2788
1.0000
4.3449
4.0085
4.4427
4.1792
ppm
8
7
6
5
4
3
2
1
0

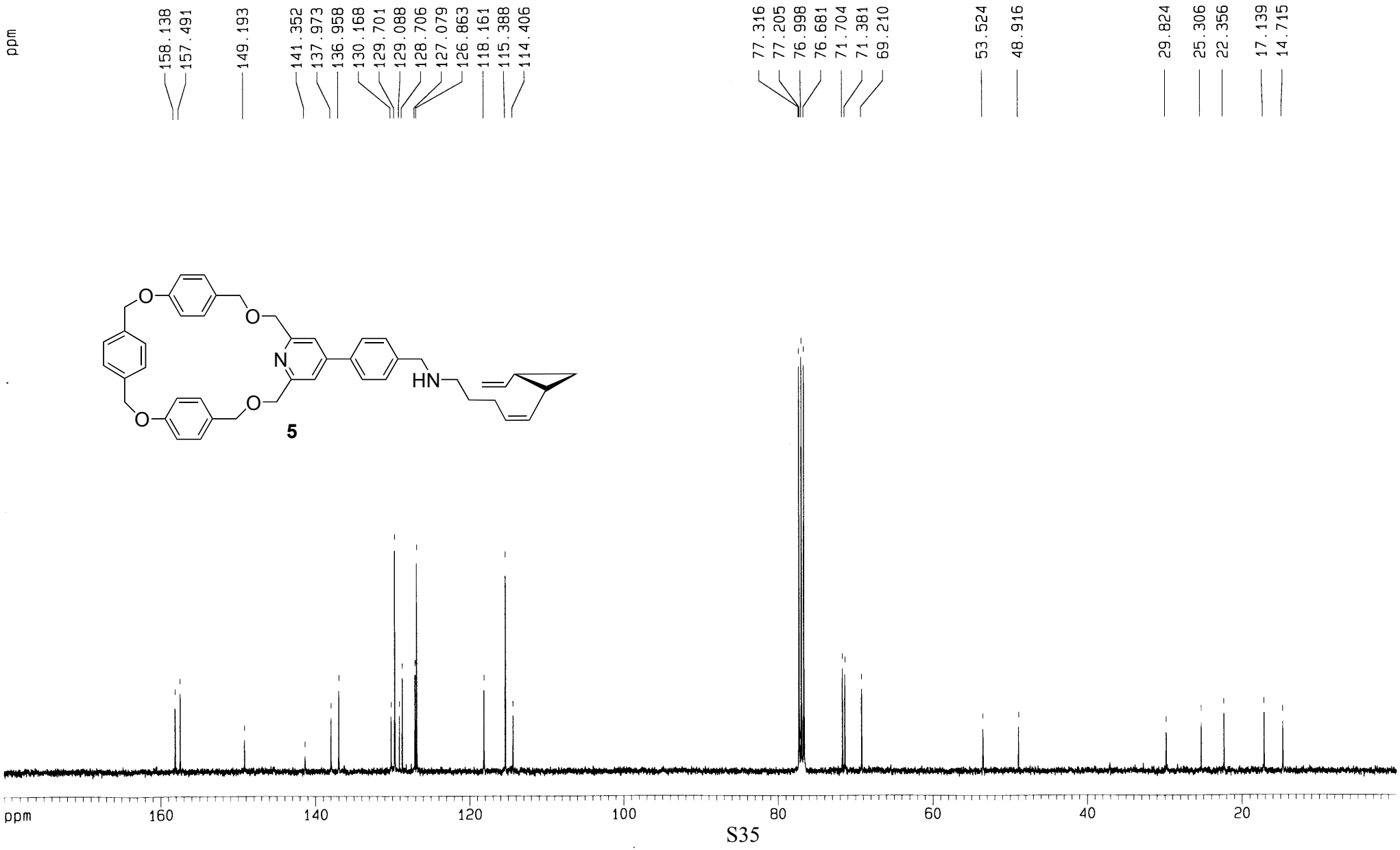

400MHz C13 (250p to -10p) shu4037a
ppm
158.276
157.558
149.080
139.306
138.734
137.019
129.770
129.729
127.196
127.124
126.927
118.392
115.443
103.337
77.371
77.258
77.053
76.736
71.790
71.393
69.261
65.389
XI
ppm
160
140
120
100
80
60
40
20

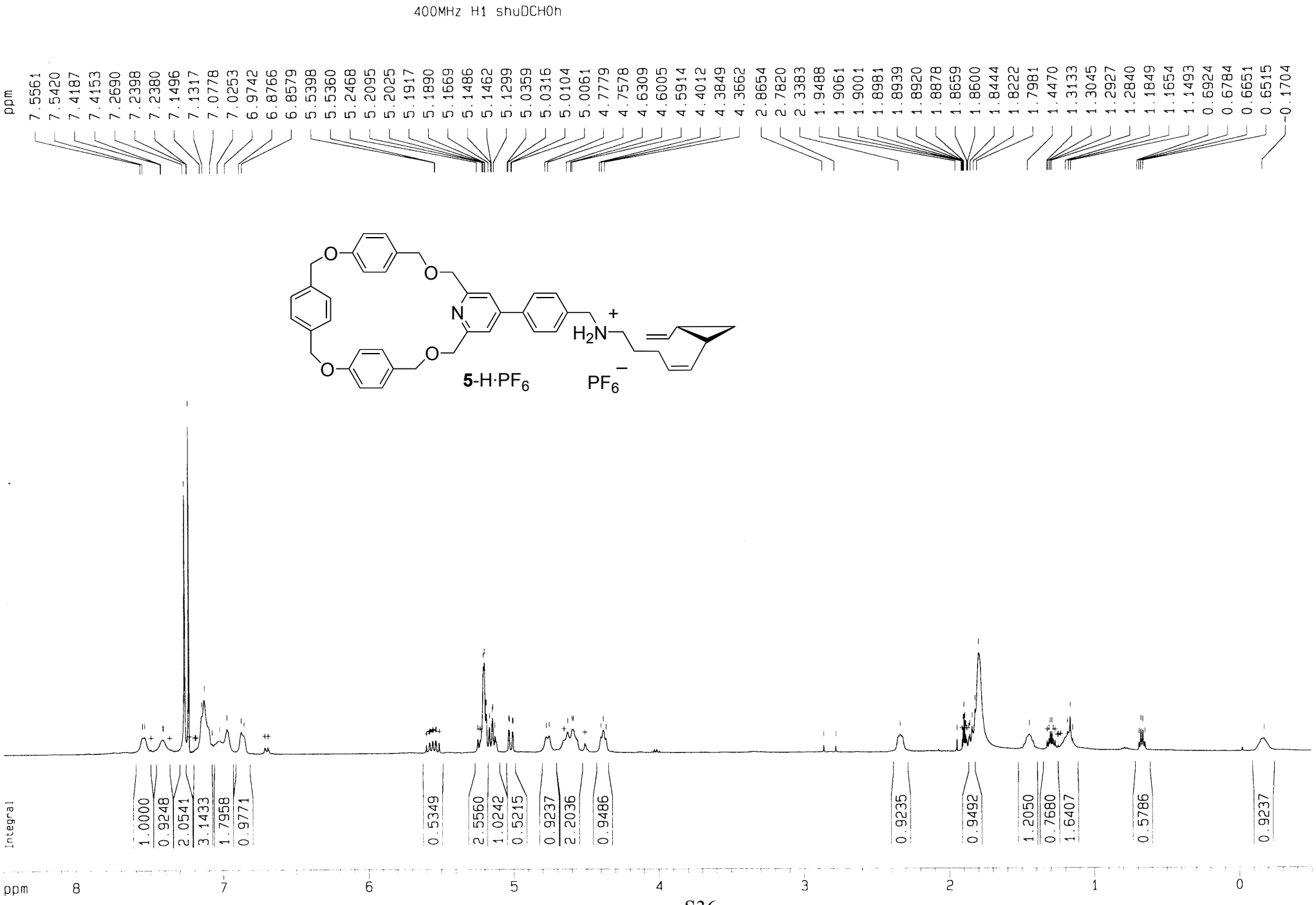

400MHz H1 shu4052a
ppm
10.0670
7.9813
7.9617
7.8155
7.7955
7.5178
7.2830
7.2810
7.2400
7.2378
7.1302
7.1095
6.7424
6.7222
5.1785
4.5400
4.4552
1.5780
1.2341
6
Integral
1.0000
2.0069
2.1059
2.0622
3.6632
4.2098
3.9800
4.0378
3.9627
4.1975
ppm
10
9
8
7
6
5
4
3
2
1
0

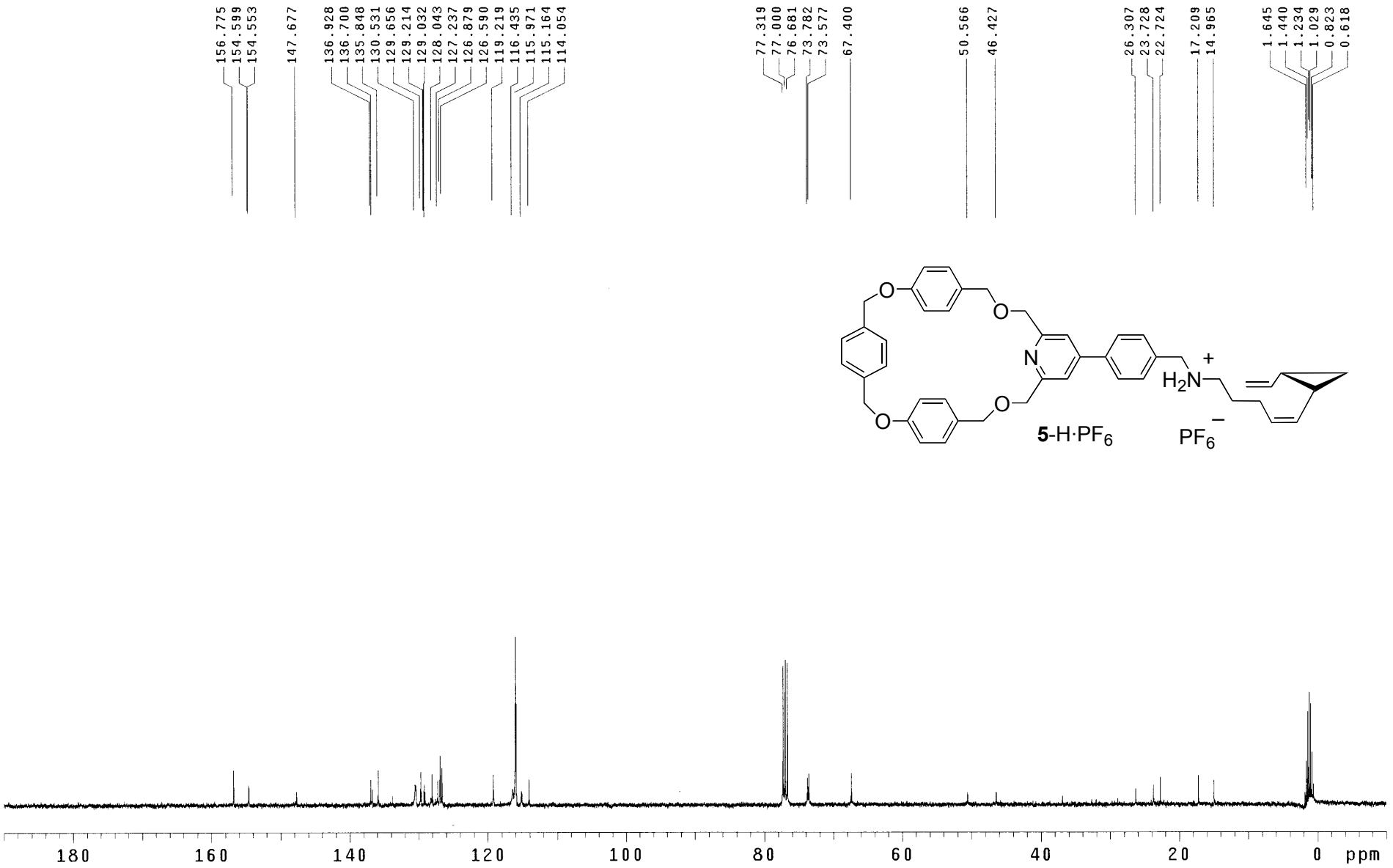

400MHz C13 (250p to -10p) shu4052a
ppm
191.699
158.611
157.586
148.062
144.362
136.979
136.379
130.310
129.763
129.546
127.834
126.882
118.393
115.389
77.316
77.200
76.998
76.681
71.881
71.198
69.167
6
O
N
H
ppm
180
160
140
120
100
80
60
40
20


400MHz H1 shu4056e
ppm
7.63512
7.61484
7.49322
7.42720
7.40708
7.28078
7.24013
7.13139
7.11001
6.73454
6.71315
5.53802
5.51620
5.51255
5.42183
5.26815
5.17573
5.12998
5.12556
5.09562
5.08762
5.08625
5.08298
5.07215
5.06888
5.04542
4.99657
4.99202
4.97096
4.96635
4.52919
4.44846
4.42754
3.83598
2.68963
2.67188
2.65371
2.20958
2.19162
2.17464
2.17168
1.83443
1.81919
1.81284
1.79823
1.71979
1.70511
1.69854
1.68383
1.66177
1.64317
1.62508
1.60684
1.15858
1.14676
1.13797
1.12607
1.11730
0.56763
0.55343
0.54087
0.52666
O
O
N
HN
O
O
5
Integral
2.0000
1.9668
2.0710
3.7274
3.9957
3.9664
1.4039
1.0768
3.8236
0.6844
1.7655
1.1959
3.9828
3.9964
1.9370
2.1031
2.2936
1.7861
1.3687
2.4169
1.2103
1.0675
ppm
8
7
6
5
4
3
2
1
0

400MHz C13 (250p to -10p) shu4056e



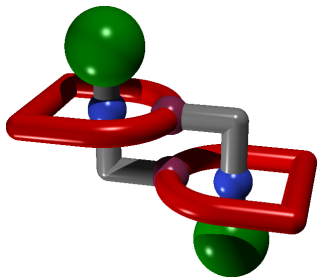

400MHz H1 shuDCH0h
ppm
7.5561
7.5420
7.4187
7.4153
7.2690
7.2398
7.2380
7.1496
7.1317
7.0778
7.0253
6.9742
6.8766
6.8579
5.5398
5.5360
5.2468
5.2095
5.2025
5.1917
5.1890
5.1669
5.1486
5.1462
5.1299
5.0359
5.0316
5.0104
5.0061
4.7779
4.7578
4.6309
4.6005
4.5914
4.4012
4.3849
4.3662
2.8654
2.7820
2.3383
1.9488
1.9061
1.9001
1.8981
1.8939
1.8920
1.8878
1.8659
1.8600
1.8444
1.8222
1.7981
1.4470
1.3133
1.3045
1.2927
1.2840
1.1849
1.1654
1.1493
0.6924
0.6784
0.6651
0.6515
-0.1704
O
O
O
O
N
+
H2N
5-H·PF6
PF6 −
Integral
1.0000
0.9248
2.0541
3.1433
1.7958
0.9771
0.5349
2.5560
1.0242
0.5215
0.9237
2.2036
0.9486
0.9235
0.9492
1.2050
0.7680
1.6407
0.5786
0.9237
ppm
8
7
6
5
4
3
2
1
0


156.775
154.599
154.553
147.677
136.928
136.700
135.848
130.531
129.656
129.214
129.032
128.043
127.237
126.879
126.590
119.219
116.435
115.971
115.164
114.054
77.319
77.000
76.681
73.782
73.577
67.400
50.566
46.427
26.307
23.728
22.724
17.209
14.965
1.645
1.440
1.234
1.029
0.823
0.618
O
O
O
O
N
+
H2N
PF6
180
160
140
120
100
80
60
40
20
0
ppm

5-H·PF_6

400MHz H1 shuDC dimer

8-2H·2PF_6



400MHz C13 (250p to -10p) shuDC dimer

ppm

157.409 155.235 155.187 148.224 137.262 136.327 136.306 134.279 130.915 130.162 129.452 128.636 128.466 128.362 127.937 127.376 127.058 119.550 116.283 115.423

77.324 77.198 77.003 76.682 73.848 73.814 73.661 67.395

50.605 46.598

36.683 32.409 31.786 28.595 23.784

1.376 1.169 0.963 0.757 0.551 0.344 0.138

8-2H·2PF$_6$