Supplementary Material (ESI) for Chemical Communications


# Cobalt(II) phthalocyanine catalyzed efficient reduction of flavones with sodium borohydride

**Pratibha Kumari, Poonam and Shive M.S. Chauhan***

Department of Chemistry, University of Delhi, Delhi-110 007, India

*Corresponding author. Tel.: +91-11-27666845; fax: +91-11-27666845;

e-mail: smschauhan@chemistry.du.ac.in.

## 1. Experimental

### 1.1 Materials and Methods

All the melting points are uncorrected and were determined on a *Thomas Hoover* Unimelt capillary melting point apparatus. The IR spectra were recorded on a Perkin Elmer 1710 FTIR spectrometer and the $\nu_{max}$ are expressed in $cm^{-1}$. The electronic spectra were recorded on a Perkin Elmer Lambda-35 UV/Vis spectrophotometer and the $\lambda_{max}$ are expressed in nanometers. The $^{1}H$ NMR, $^{13}C$ NMR, $^{1}H$-$^{1}H$ COSY and $^{1}H$-$^{13}C$ COSY spectra were recorded on Bruker Avance-300 and Bruker Avance-400 spectrometer using TMS as internal standard (chemical shifts in ppm). The TOF LC/ MS spectra were recorded on Hybrid Quadruple- TOF LC/MS mass spectrometer 1011273/A using ion spray. ESI-MS spectra were recorded on Micromass LCT KC 455 using electrospray positive ion mass spectra. Elemental analyses were obtained on GmbH Vario EL-III elemental analyzing system.

Flavone (**1a**), 4'-methoxyflavone (**1b**), 4'-methylflavone (**1c**), 4'-chloroflavone (**1d**) and 3-hydroxyflavone (**1e**), were prepared according to the literature methods.[1S] Chalcone (**S3**) was prepared by condensation of corresponding acetophenones with corresponding aldehydes by the general procedure of Kohler and Chadwell.[2S] The α-naphthoflavone (**2**) was obtained from SISCO Chemicals Ltd. and morin hydrate (**1f**) was obtained from Fluka. Metallophthalocyanines (**3a-3g**) were prepared according to the method reported by us.[3S]

Data for **3f**: IR (KBr): 2925, 2854, 1610, 1462, 1387, 1278, 1240, 1097, 826, 750 $cm^{-1}$. $^1H$ NMR (300 MHz, $CDCl_3$): δ = 0.87 (br, 12 H, $CH_3$), 1.24-1.90 (m, 48 H, $CH_2$), 4.06 (m, 8 H, $OCH_2$), 7.12-8.00 (m, 12 H, Ar H). $^{13}C$ NMR (100 MHz, $CDCl_3$): δ = 14.12-14.70 (4 × C), 22.68-32.50 (24 × C), 68.48 (4 × C), 104.21 (4 × C), 113.68 (4 × C), 123.16 (4 × C), 132.63 (4 × C), 135.79 (4 × C), 159.79 (4 × C), 161.05 (4 × C), 161.574 × C). UV-vis ($CHCl_3$): $\lambda_{max}$ (log ε) = 289 (4.74), 323 (4.75), 612 (4.25), 675 (4.74).

## 1.2 Reduction of flavones (1a-1f, 2) with $NaBH_4$ catalyzed by metallophthalocyanines (MPc) (3a-3g)

To the solution of flavone (**1a-1f, 2**) (1.0 mmol) in dry methanol (20 ml), MPc (**3a-3g**) (0.1 mmol) was added. The solution was stirred at room temperature under nitrogen atmosphere and $NaBH_4$ (8 mmol) was added in portions. The progress of the reaction was checked by TLC. The reaction mixture was filtered to remove the catalyst **3a-3g** and the filtrate was concentrated under reduced pressure. The resulting solid was chromatographed over silica gel (230-400 mesh) and the column was eluted with ethyl acetate/ petroleum ether (varying from 1: 99 to 10: 90, v/v) to give flavan-4-ols (**4a-4f, 5**). The products were crystallized with chloroform/ petroleum (1:1, v/v). The recovered catalyst was washed with methanol and reused to catalyze further reduction reactions.

**Flavan-4-ol (4a)**

mp 146°C (lit mp[4S] 148°C). IR (KBr): 3303, 2959, 2918, 1580, 1484, 1454, 1343, 1228, 1065, 1038, 905, 758, 703 $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$): δ = 1.92 (d, J = 8.4 Hz, 1H, OH), 2.12 (ddd, J = 13.2, 11.6, 10.8 Hz, 1H, $H_a$-3), 2.49 (ddd, J = 13.2, 6.4, 2.0 Hz, 1H, $H_e$-3), 5.08 (m, 1H, H-4), 5.16 (m, 1H, H-2), 6.89 (dd, J = 8.2, 0.8 Hz, 1H, H-8), 6.98 (dt, J = 7.4, 1.2 Hz, 1H, H-6), 7.20 (m, 1H, H-7), 7.32-7.45 (m, 5H, H-2'- 6'), 7.51 (d, J = 7.6 Hz, 1H, H-5). $^{13}C$ NMR (75 MHz, $CDCl_3$): δ = 40.03 (C-3), 65.80 (C-4), 76.82 (C-2), 116.72 (C-8), 120.96 (C-6), 125.70 (C-4a), 126.06 (C-5), 126.95 (C-2', 6'), 128.21 (C-4'), 128.65 (C-3', 5'), 129.17 (C-7), 140.47 (C-1'), 154.45 (C-8a). MS (LC-MS): *m*/*z* calcd for $C_{15}H_{14}O_2H$: 226; found: 227 [M + $H^+$]. UV-vis ($CHCl_3$): $\lambda_{max}$ (log ε) = 242

(3.19), 278 (3.31), 285 nm (3.29). *Anal.* Calc for $C_{15}H_{14}O_2$: C, 79.62; H, 6.24. Found: C, 79.52; H, 6.32.

**4'-methoxyflavan-4-ol (4b)**

mp 150-151°C (lit mp[4S] 150-151°C). IR (nujol): 3361, 3309, 1610, 1580, 1518, 1458, 1297, 1255, 1228, 1176, 1062, 1035, 1000, 832, 815, 762 $cm^{-1}$. $^1H$ NMR (300 MHz, $CDCl_3$): δ = 1.74 (d, J = 8.7 Hz, 1H, OH), 2.19 (ddd, J = 13.05, 11.55, 10.8-10.5 Hz, 1H, $H_a$-3), 2.53 (ddd, J = 13.05, 6.45, 2.0 Hz, 1H, $H_e$-3), 3.84 (s, 3H, $OCH_3$), 5.12 (m, 1H, H-4), 5.15 (m, 1H, H-2), 6.90 (dd, J = 8.1, 0.9 Hz, 1H, H-8), 6.94 (m, 1H, H-6), 6.96-7.03 (m, 2H, H-3', 5'), 7.22 (m, 1H, H-7), 7.37-7.41 (m, 2H, H-2', 6'), 7.54 (d, J = 7.5 Hz, 1H, H-5). $^{13}C$ NMR (100 MHz, $CDCl_3$): δ = 39.85 (C-3), 55.34 (C-4', $OCH_3$), 65.91 (C-4), 76.72 (C-2), 114.04 (C-8), 116.73 (C-6), 120.91 (C-3', 5'), 125.72 (C-4a), 126.97 (C-2', 6'), 127.57 (C-5), 129.16 (C-7), 132.53 (C-1'), 154.58 (C-8a), 159.55 (C-4'). MS (LC-MS): *m*/*z* calcd for $C_{16}H_{16}O_3$: 256; found: 257 [M + $H^+$]. UV-vis ($CHCl_3$): $\lambda_{max}$ (log ε) = 242 (3.46), 276 nm (3.48). *Anal.* Calc for $C_{16}H_{16}O_3$: C, 74.98; H, 6.29. Found: C, 75.13; H, 6.31.

**4'-methylflavan-4-ol (4c)**

mp 108-109°C (lit mp[4S] 109-110°C). IR (film): 3366, 2921, 1625, 1581, 1518, 1485, 1458, 1270, 1231, 1068, 1040, 906, 812, 757 $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$): δ = 2.01 (d, J = 8.0 Hz, 1H, OH), 2.11 (ddd, J = 13.0, 11.6, 10.8 Hz, 1H, $H_a$-3), 2.36 (s, 3H, $CH_3$), 2.45 (ddd, J = 13.0, 6.2, 2 Hz, 1H, $H_e$-3), 5.04 (m, 1H, H-4), 5.11 (dd, J – 11.6, 2.0 Hz, 1H, H-2), 6.66 (dd, J = 8.2, 1.0 Hz, 1H, H-8), 6.96 (dt, J = 7.4, 1.2 Hz, 1H, H-6), 7.17 (m, 3H, H-7, H3', 5'), 7.31 (m, 2H, H-2'-6'), 7.51 (d, J = 7.8 Hz, 1H, H-5). $^{13}C$ NMR (100 MHz, $CDCl_3$): δ = 21.22 ($CH_3$), 39.90 (C-3), 65.85 (C-4), 76.77 (C-2), 116.76 (C-8), 120.92 (C-6), 125.76 (C-5), 126.13 (C-2', 6'), 127.01 (C-4a), 127.01 (C-7), 129.35 (C-3', 5'), 137.50 (C-4'), 138.06 (C-1'), 154.57 (C-8a). MS (LC-MS): *m*/*z* calcd for $C_{16}H_{16}O_2$: 240; found: 240 [$M^+$]. UV-vis ($CHCl_3$): $\lambda_{max}$ (log ε) = 241 (4.02), 261 (3.85), 279 (4.06), 286 (4.12), 299 nm (3.89). *Anal.* Calc for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. Found: C, 80.14; H, 6.88.

**4'-chloroflavan-4-ol (4d)**

mp 160-161°C (lit mp[4S] 160-161°C). IR (KBr): 3382, 2924, 1581, 1485, 1459, 1303, 1270, 1227, 1065, 1039, 1012, 904, 864, 820, 755 $cm^{-1}$. $^1H$ NMR (300 MHz, $CDCl_3$): δ =

1.75 (d, J = 8.6 Hz, 1H, OH), 2.10 (m, 1H, $H_a$-3), 2.50 (ddd, J = 13.1, 6.1, 1.6 Hz, 1H, $H_e$-3), 5.10 (m, 1H, H-4), 5.16 (dd, J= 11.7, 1.6 Hz, 1H, H-2), 6.88 (d, J = 8.2 Hz, 1H, H-8), 7.00 (m, 1H, H-7), 7.22 (m, 1H, H-6), 7.38 (m, 4H, H-2'-6'), 7.52 (d, J = 7.6 Hz, 1H, H-5). $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 40.05 (C-3), 65.68 (C-4), 76.85 (C-2), 116.71 (C-8), 121.18 (C-6), 125.61 (C-4a), 126.96 (C-5), 127.46 (C-2', 6'), 128.84 (C-3', 5'), 129.27 (C-7), 133.94 (C-4'), 139.04 (C-1'), 154.23 (C-8a). MS (LC-MS): *m*/*z* calcd for $C_{15}H_{13}ClO_2$: 260.71; found: 261 [$M^+$]. UV-vis ($CHCl_3$): $\lambda_{max}$ (log ε) = 239 (3.25), 277 (3.33), 285 nm (3.29). *Anal.* Calc for $C_{15}H_{13}ClO_2$: C, 69.10; H, 5.03. Found: C, 69.43; H, 5.12.

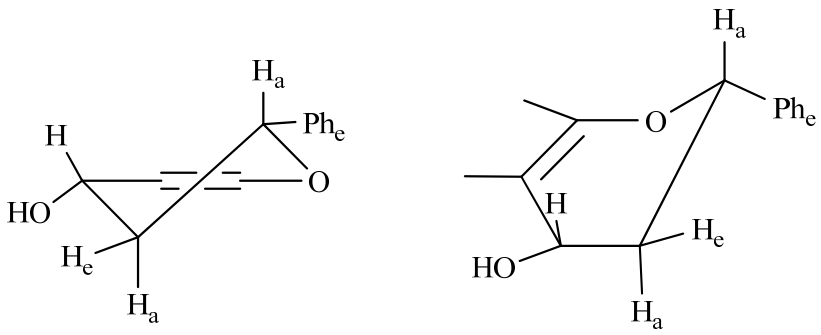
**α-Naphthoflavan-4-ol (5)**

mp 168-169$^o$C. IR (KBr): 3338, 3062, 2947, 1574, 1508, 1439, 1393, 1308, 1221, 1189, 1097, 1051, 937, 878, 807, 752, 697 $cm^{-1}$. $^1$H NMR (300 MHz, $CDCl_3$): δ = 1.75 (d, J = 8.8 Hz, 1H, OH), 2.26 (ddd, J = 13.2, 11.2, 9.8 Hz, 1H, $H_a$-3), 2.67 (ddd, J = 13.2, 6.3, 2.1 Hz, 1H, $H_e$-3), 5.24 (m, 1H, H-4), 5.39 (dd, J= 11.2, 1.6 Hz, 1H, H-2), 7.34-7.61 (m, 9H, ArH), 7.77-7.80 (m, 1H, H-7), 8.22-8.25 (m, 1H, H-10). $^{13}$C NMR (75 MHz, $CDCl_3$): δ = 40.03 (C-3), 65.82 (C-4), 76.90 (C-2), 119.04 (C-4a), 120.42 (C-6), 122.23 (C-10), 124.33 (C-9), 124.77 (C-8), 125.52 (C-10a), 125.94 (C-4'), 126.54 (C-7), 127.44 (C-5), 128.07 (C-2', 6'), 128.65 (C-3', 5'), 134.08 (C-6a), 140.66 (C-1'), 149.55 (C-4b). MS (LC-MS): *m*/*z* calcd for $C_{19}H_{16}O_2$: 276; found: 277 [$M + H^+$], 301 [$M + Na^+ + 2H^+$]. UV-vis ($CHCl_3$): $\lambda_{max}$ (log ε) = 243 (4.36), 298 (3.72), 311(3.61), 326 nm (3.48). *Anal.* Calc for $C_{19}H_{16}O_2$: C, 82.58; H, 5.84. Found: C, 82.75; H, 5.94.

### 1.2.1 Configuration of 4a-4d and 5

The stereochemical aspects of **4a-4d** and **5** were ascertained on the basis of their physical and spectroscopic data that are consistent with the literature values. For instance, the melting point of **4a** (146$^o$C) closely corresponded to the literature value of *cis*-flavan-4-ol (mp 140$^o$C) (mp of *trans*-flavan-4-ol = 118$^o$C).[5S] The chemical shift for C-2 in the $^{13}$C NMR of **4a** being notably different for *cis* and *trans* isomers,[5S] was in good agreement with *cis*-flavan-4-ol. Moreover, the coupling constants $J_{3a,3e}$ = 13.2 Hz, $J_{3a,2a}$ = 11.6 Hz, $J_{3e,2a}$ = 2 Hz, $J_{3a,4a}$ = 10.8 Hz and $J_{3e,4a}$ = 6.4 Hz were in conformity with the biologically important *cis*-form of **4a** ring with 2-phenyl group in equatorial position

(either the half-chair or the sofa conformation) (Fig.A).[6S] The formation of *cis*-form of **4a** is believed to be stereospecific as the $^1$H NMR of the reaction mixture of **2** (Fig. S37 and S38) after removing the catalyst (**3a**) showed only the presence of *cis*- isomer in the reaction mixture based on the coupling constants ($J_{3a,3e}$ = 13.2 Hz, $J_{3a,2a}$ = 11.4 Hz, $J_{3e,2a}$ = 2.0 Hz, $J_{3a,4a}$ = 10.2 Hz and $J_{3e,4a}$ = 6.4 Hz) which are according to that for isolated and purified product **5** and are remarkably different from the *trans*-isomer (for *trans*- isomer, $J_{3a,3e}$ = 14.4 Hz, $J_{3a,2a}$ = 12.4 Hz, $J_{3e,2a}$ = 1.9 Hz, $J_{3a,4a}$ = 3.2 Hz and $J_{3e,4a}$ = 2.7 Hz).[7S]




Half chair conformation Sofa conformation

**Fig. A** Conformations of flavan-4-ol (**4a**)

### 1.2.2 Reduction of flavone (1a) with equimolar amount of $NaBH_4$ catalyzed by cobalt(II) phthalocyanines (3a) in methanol

To a mixture flavone (**1a**) (1 mmol) and **3a** (0.1 mmol), $NaBH_4$ (1 mmol) was added in methanol under nitrogen atmosphere. The reaction mixture was stirred at room temperature for 1 hr. After removing the catalyst **3a** by filtration, the filtrate was concentrated under reduced pressure. The reduced product flavanone (**6a**) (20 % yield) and **4a** (5 % yield) were separated by preparative TLC (solvent system: ethyl acetate/ hexane 5: 95, v/v). Data for **6a**: mp 76-77 $^o$C (lit mp[8S] 76-77$^o$C). IR (KBr): 3038, 2897, 1689, 1606, 1461, 1303, 1227, 1148, 1114, 1066, 985, 907, 766, 700 cm$^{-1}$. $^1$H NMR (300 MHz, $CDCl_3$): δ = 2.88 (dd, J = 16.9, 3 Hz, 1H, $H_e$-3), 3.08 (dd, J = 16.9, 13.2 Hz, 1H, $H_a$-3), 5.48 (dd, J = 13.2, 2.4 Hz, 1H, CH), 7.03-7.07 (m, 2H, Ar H), 7.38-7.53 (m, 6H, Ar H), 7.94 (d, J = 8.1 Hz, 1H, ArH).

**1.3 Reduction of flavone (2) with $NaBD_4$ catalyzed by cobalt(II) phthalocyanines (3a) in methanol**

The reduction of **2** was carried out using $NaBD_4$ following the procedure as described above to give **7** in 96 % yield. Data for **7**: mp 168-170$^oC$. IR (KBr): 3233, 2943, 1573, 1508, 1449, 1390, 1324, 1273, 1244, 1188, 1114, 1071, 999, 956, 805, 761, 750, 696 $cm^{-1}$. $^1H$ NMR (300 MHz, $CDCl_3$): δ = 1.81 (s, 1H, OH), 2.27 (m, 1H, $H_a$-3), 2.66 (m, 1H, $H_e$-3), 7.37-7.62 (m, 9H, ArH), 7.79-7.81 (m, 1H, H-7), 8.25-8.27 (m, 1H, H-10). $^{13}C$ NMR (100 MHz, $CDCl_3$): δ = 39.82 (C-3), 65.85 (C-4), 76.70 (C-2), 118.96 (C-4a), 120.44 (C-6), 122.26 (C-10), 124.37 (C-9), 124.79 (C-8), 125.54 (C-10a), 125.96 (C-4'), 126.57 (C-7), 127.46 (C-5), 128.11 (C-2', 6'), 128.68 (C-3', 5'), 134.11 (C-6a), 140.62 (C-1'), 149.61 (C-4b). MS (ESI-MS): *m*/*z* calcd for $C_{19}H_{14}D_2O_2$: 278; found: 279 [M + $H^+$], 303 [M + $Na^+$ + $2H^+$].

**1.4 Reduction of flavone (2) with $NaBH_4$ catalyzed by cobalt(II) phthalocyanines (3a) in $CD_3OD$**

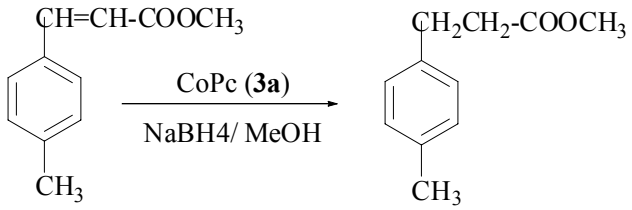
Flavone **2** (1.0 mmol) was dissolved in $CD_3OD$ (20 ml) and **3a** (0.1 mmol) was added. The reaction mixture was stirred at room temperature under nitrogen atmosphere and $NaBH_4$ (8 mmol) was added in portions. The product (**8**) was isolated in 98 % yield following the same procedure as described above. Data for **8**: IR (KBr): 3537, 2924, 1573, 1392, 1317, 1190, 1097, 931, 808, 749, 697 $cm^{-1}$. $^1H$ NMR (300 MHz, $CDCl_3$): δ = 2.23 (m, 1H, $H_a$-3), 5.23 (m, 1H, H-4), 5.37 (m, 1H, H-2), 7.39-7.62 (m, 9H, ArH), 7.77-7.79 (m, 1H, H-7), 8.22-8.25 (m, 1H, H-10). $^{13}C$ NMR (75 MHz, $CDCl_3$): δ = 40.08 (C-3), 65.87 (C-4), 76.93 (C-2), 119.05 (C-4a), 120.46 (C-6), 122.27 (C-10), 124.37 (C-9), 124.80 (C-8), 125.55 (C-10a), 125.97 (C-4'), 126.58 (C-7), 127.47 (C-5), 128.11 (C-2', 6'), 128.69 (C-3', 5'), 134.12 (C-6a), 140.69 (C-1'), 149.59 (C-4b). MS (ESI-MS): *m*/*z* calcd for $C_{19}H_{14}D_2O_2$: 278; found: 279 [M + $H^+$], 278 [$M^+$].

**1.5 Reduction of methyl 3-(4-methylphenyl)prop-2-enoate (S1) with sodium borohydride catalyzed by cobalt(II) phthalocyanine (3a) in methanol**

**(a) Preparation of methyl 3-(4-methylphenyl)prop-2-enoate (S1)**

Dimethylsulphate (1.5 mmol) was added dropwise to a mixture of 4-methyl cinnamic acid (1 mmol) and $K_2CO_3$ (5 mmol) in dry acetone (20 ml) in 15-20 min. Reaction mixture was stirred for 4 hr and the reaction was monitored by TLC. After the reaction was completed, reaction mixture was stirred for 15 min and filtrate was evaporated to dryness. White solid was obtained in 98% yield. mp 55-56$^oC$, IR (KBr): 2924, 2854, 1711, 1633, 1512, 1459, 1377, 1316, 1276, 1167, 1001, 816, 723 $cm^{-1}$. $^1H$ NMR (300 MHz, $CDCl_3$): δ = 2.37 (s, 3H, $CH_3$), 3.80 (s, 3H, $COOCH_3$), 6.40 (d, J = 16.0 Hz, 1H, CH=CH), 7.19 (d, J = 8.0 Hz, 2H, ArH), 7.42 (d, J = 8.1 Hz, 2H, ArH), 7.65 (d, J = 16.0 Hz, 1H, =CHCOOCH$_3$).

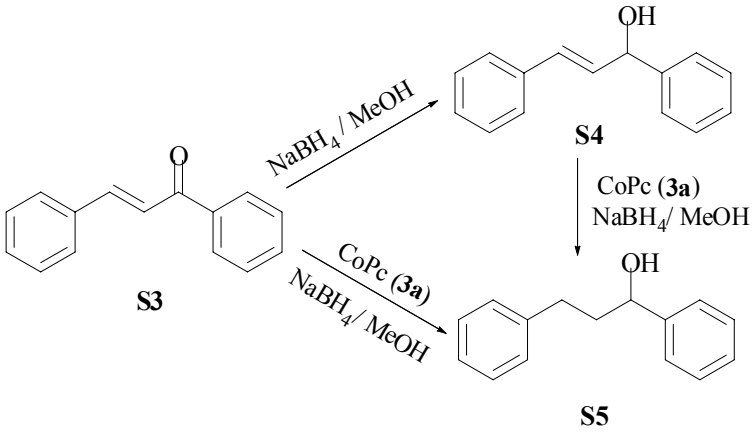
**(b) Reduction of methyl 3-(4-methylphenyl)prop-2-enoate (S1)**




**S1** **S2**

Sodium borohydride (6 mmol) was added to a mixture of methyl 3-(4-methylphenyl)prop-2-enoate (**S1**) (1 mmol) and **3a** (0.1 mmol) in methanol under nitrogen atmosphere. The reaction was stirred for 3 hr at room temperature. The progress of the reaction was monitored by TLC. After the completion of reaction, the catalyst was separated by filtration. The solvent (filtrate) was removed under reduced pressure and the residue was chromatographed on silica gel (230-400 mesh) (eluent: varying from hexane to hexane/ ethyl acetate, 92: 8, v/v) to give 3-(4-methylphenyl)prop-2-enoate (**S2**) in 63 % yield. Data for **S2**: colorless liquid, IR (Film): 2952, 1739, 1516, 1438, 1394, 1200, 1167, 986, 815 $cm^{-1}$. $^1H$ NMR (300 MHz, $CDCl_3$): δ = 2.32 (s, 3H, $CH_3$), 2.62 (t, J = 8 Hz, 2H, $CH_2$), 2.92 (t, J = 8 Hz, 2H, $CH_2$-$COOCH_3$), 3.67 (s, 3H, $COOCH_3$), 7.10 (m, 4H, Ar H).

**1.6 Reduction of chalcone (S3) with $NaBH_4$ in absence or presence of cobalt(II) phthalocyanine (3a)**




**1.6.a Reduction in absence of 3a:** Sodium borohydride (15 mmol) was added to the chalcone (**S3**) (1 g, 5 mmol) in methanol (20 ml). After 30 min the reaction mixture was diluted with water (20 ml), acidified with aqueous HCl (pH 4) and extracted with ethyl acetate (3 x 50 ml). The combined extracts were dried over anhydrous $Na_2SO_4$ and evaporated. Purification by chromatography over silica gel (230-400 mesh) yielded 1,3-diphenyl-2-propenol (**S4**) in 85% yield. Data for **S4**: mp 56-57 $^oC$. IR (Film): 3362, 3083, 3060, 3028, 1600, 1494, 1451, 1305, 1191, 1093, 1067, 1011, 966, 745, 697 $cm^{-1}$. $^1H$ NMR (300 MHz, $CDCl_3$): δ = 2.02 (s, 1H, OH), 5.34 (d, J = 6.3 Hz, 1H, CHOH), 6.35 (dd, J = 15.9, 6.6 Hz, 1H, CH=CH), 6.67 (d, J = 15.9 Hz, 1H, =CHPh), 7.20-7.45 (m, 10H, Ar H). $^{13}C$ NMR ($CDCl_3$, 75 MHz): δ = 143.0, 136.7, 131.7, 130.8, 128.9, 128.8, 128.0, 128.0, 126.8, 126.6, 75.4.

**1.6.b Reduction in presence of 3a:** The reaction of chalcone (**S3**) or 1,3-diphenyleth-2-en-1-ol (**S4**) (2 mmol) with sodium borohydride (8 mmol) catalyzed by **3a** (0.2 mmol) in methanol (5 ml) gave 1,3-diphenyl -1-propanol (**S5**) in 98% yield. The work up and purification procedure is same as described above for **S4**. Data for **S5**: bp 193 $^oC$. IR (Film): 3369, 3084, 3062, 3027, 2928, 2861, 1603, 1494, 1453, 1393, 1339, 1203, 108, 914, 747, 699 $cm^{-1}$. $^1H$ NMR (300 MHz, $CDCl_3$): δ = 2.18 (m, 2H, $PhCH_2$), 2.85 (m, 2H, $CH_2CH_2$), 3.06 (s, 1H, OH), 4.75 (m, 1H, CHOH), 7.27-7.47 (m, 10H, Ar H). $^{13}C$ NMR (75 MHz, $CDCl_3$): δ = 31.8, 40.2, 73.4, 125.6, 125.8, 127.3, 128.2, 128.2, 128.3, 141.6, 144.4.

**1.7 Uv-Vis spectral studies of cobalt(II) phthalocyanine (3a) on addition of sodium borohydride in methanol and propanol**

The UV-visible spectra of **3a** in methanol showed Q band at 662 nm which shifted to 705 nm on addition of $NaBH_4$ accompanied by a new band at 464 nm (Fig. S39). This change is ascribed to the formation of Co(I)Pc intermediate (**9**) in the reaction. Gradually, the intensity of band at 705 nm decreased and new bands at 656 nm and 594 nm appeared with increased absorption intensity. This blue shift from 662 nm to 656 nm could be attributed to the generation of hydridocobalt(III) phthalocyanine (**10**) intermediate. Similar spectral study of **3a** was carried out in propanol on addition of $NaBH_4$ to further investigate the role of solvent in the catalytic reaction (Fig. S40). However, the solubility of **3a** in propanol was poor, the Uv-Vis spectrum exhibited Q band at 662 nm. The addition of $NaBH_4$ showed a similar red shift in Q band from 662 nm to 708 nm due to formation of intermediate **9**. The reduction of Co(II) to Co(I) in propanol proceeded slowly and the intermediate **9** remained stable for a longer period of time as compared to that in methanol. This justifies the slow proton transfer from propanol to **9** to form intermediate **10**.

**References**


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Fig. S1: $^{1}$H NMR of **4a**

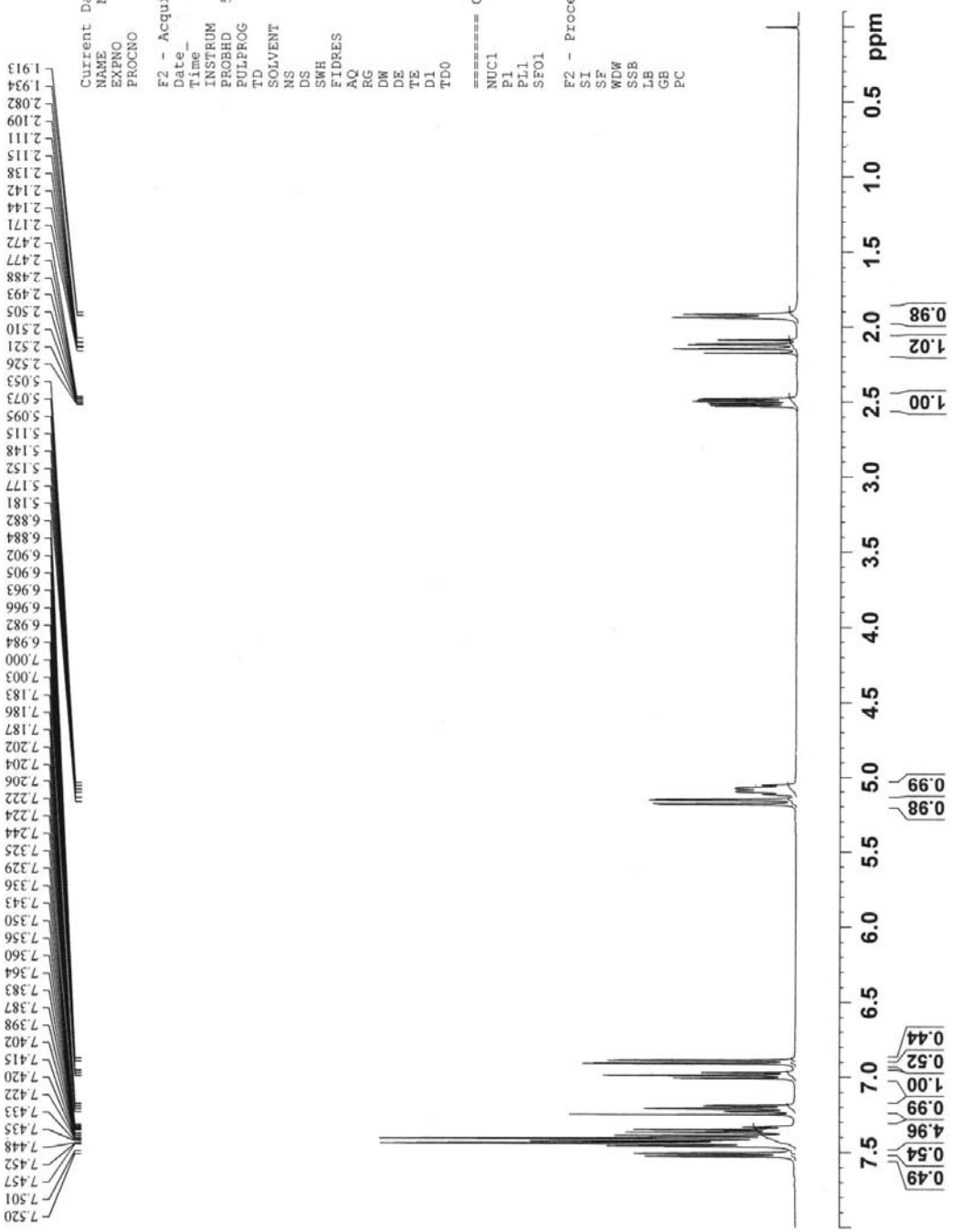


Fig. S2: $^{1}$H NMR of **4a**

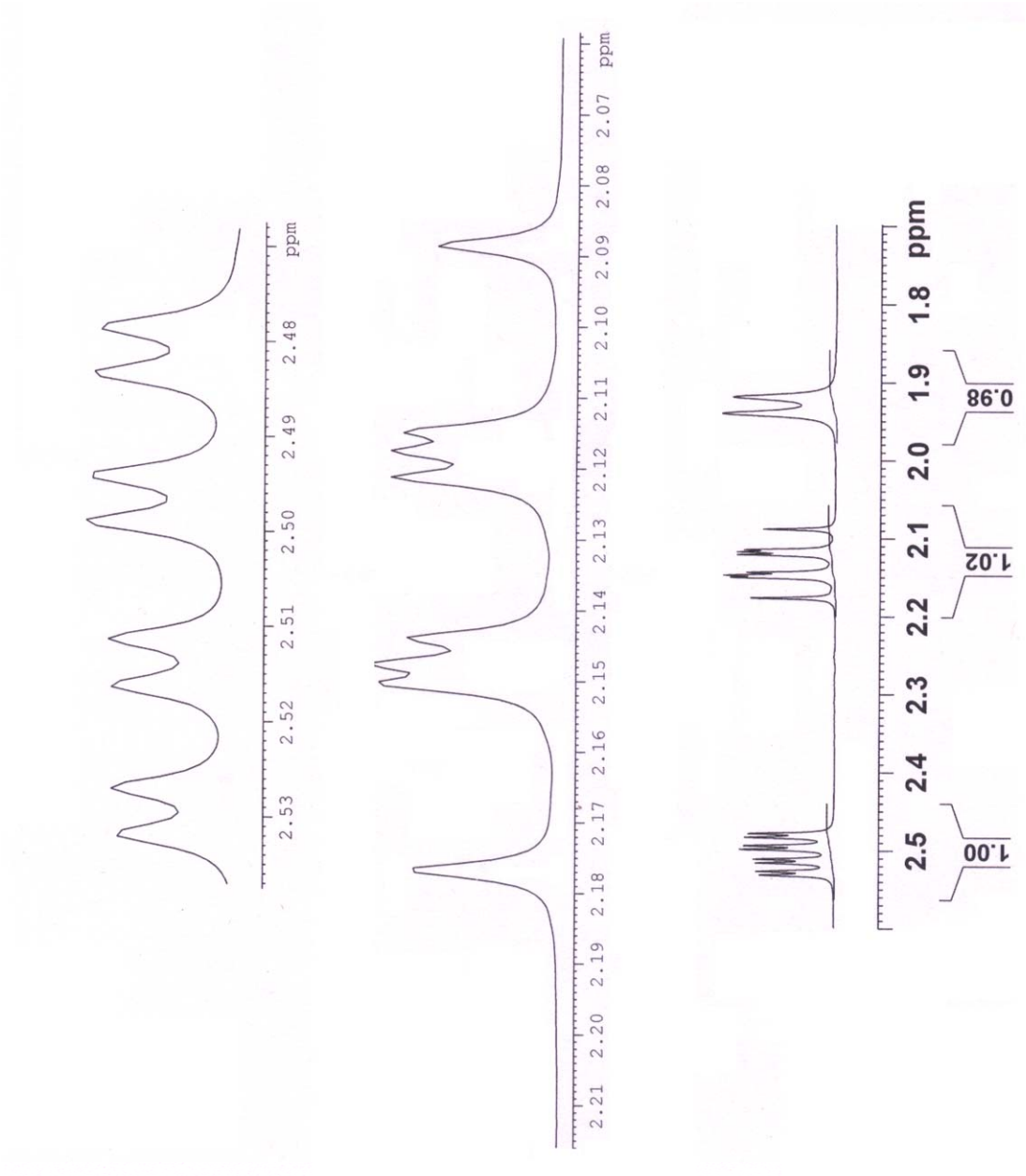


Fig. S3: $^{1}$H NMR of **4a**

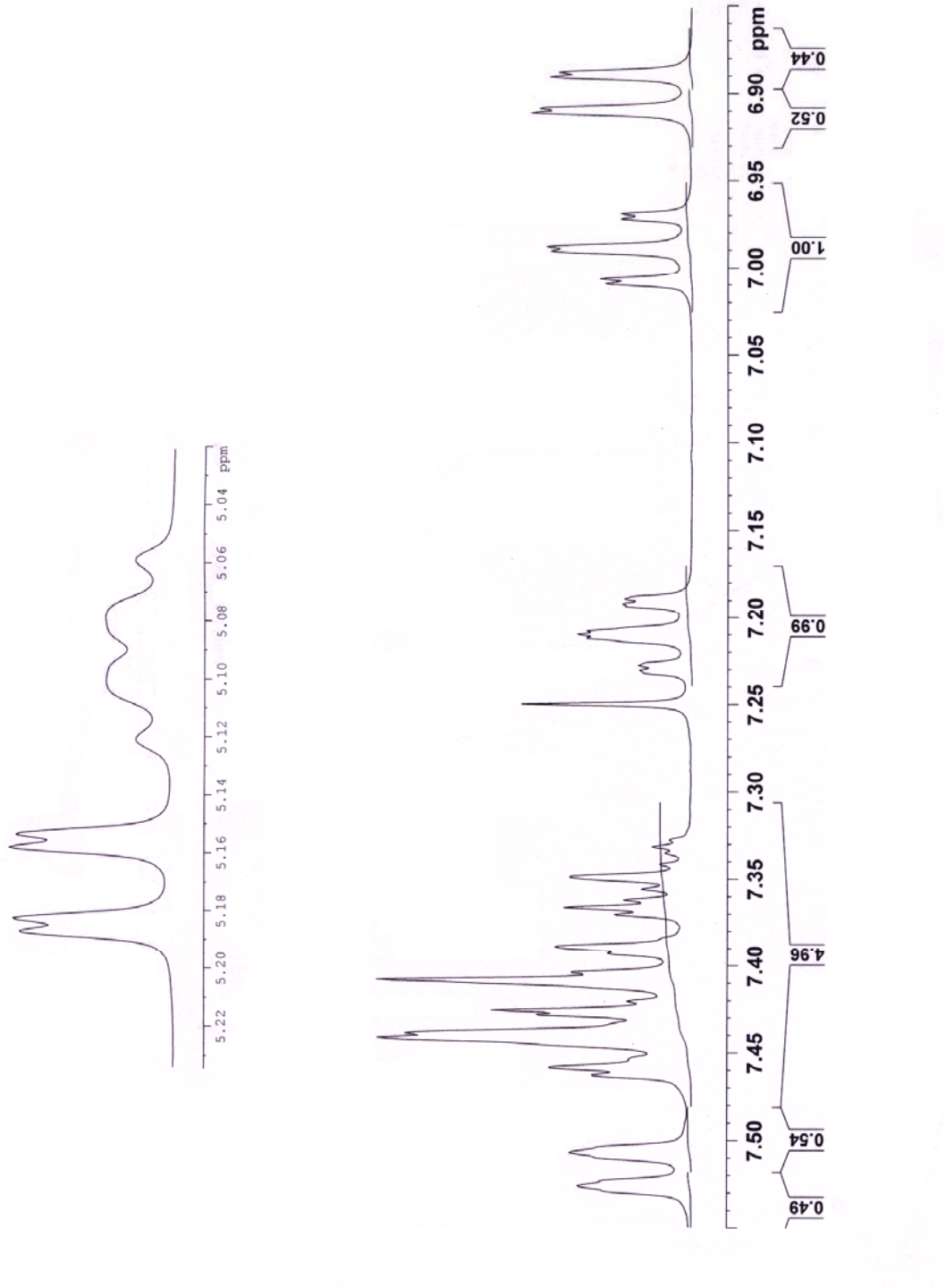


Fig. S4: $^{13}C$ NMR of **4a**

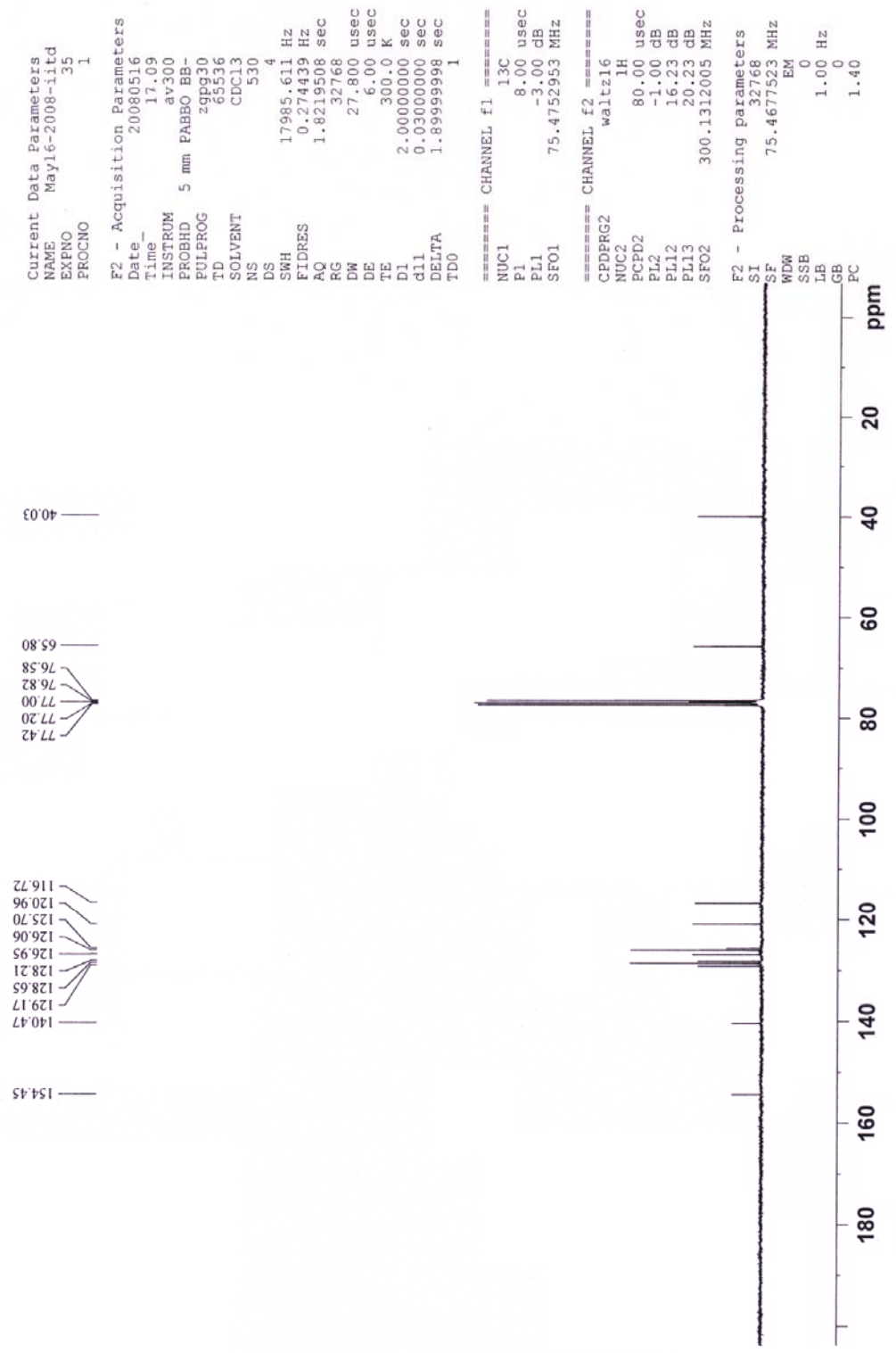


Fig. S5: $^{1}$H-$^{1}$H COSY of **4a**

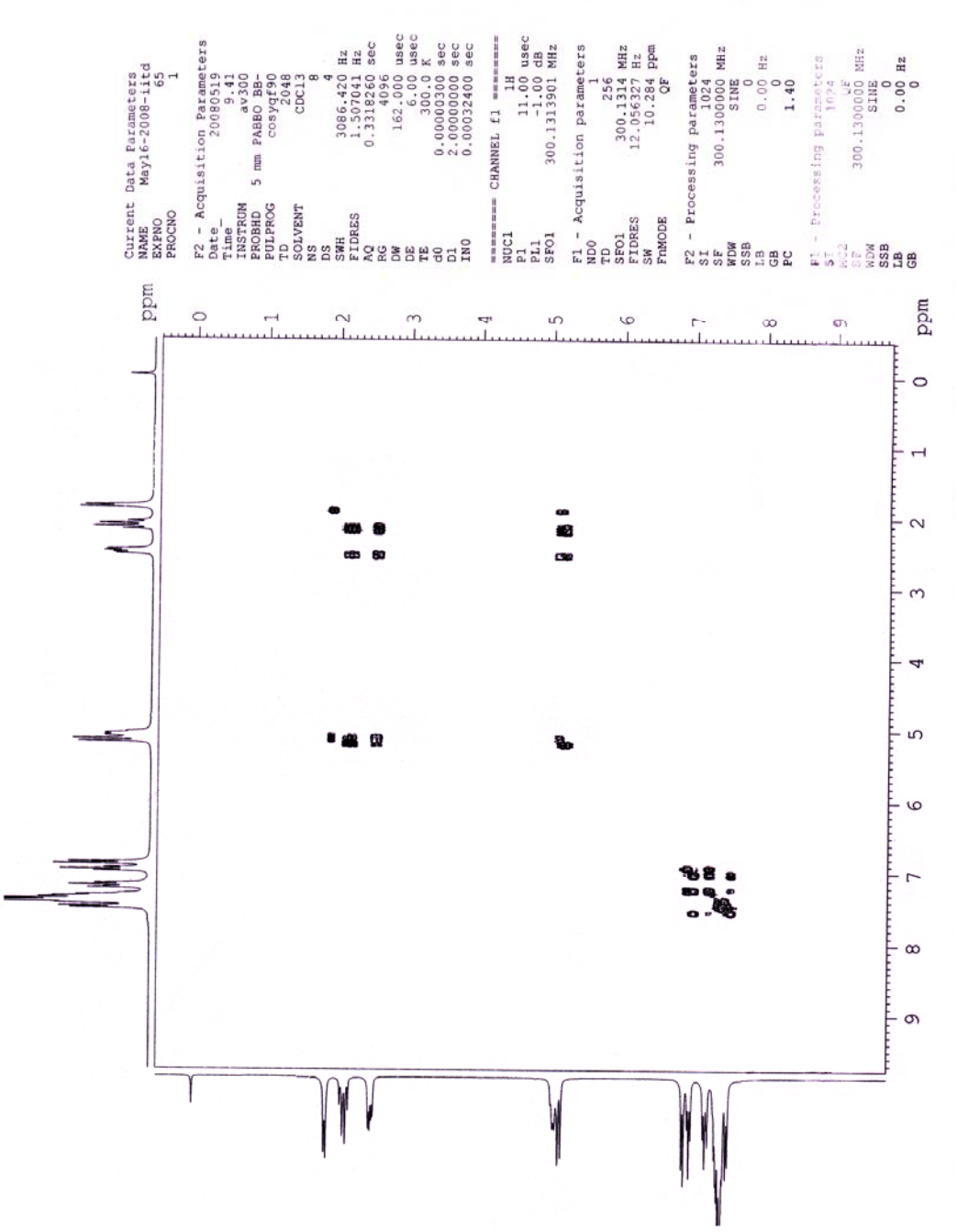


Fig. S6: $^{1}$H-$^{1}$H COSY of **4a**

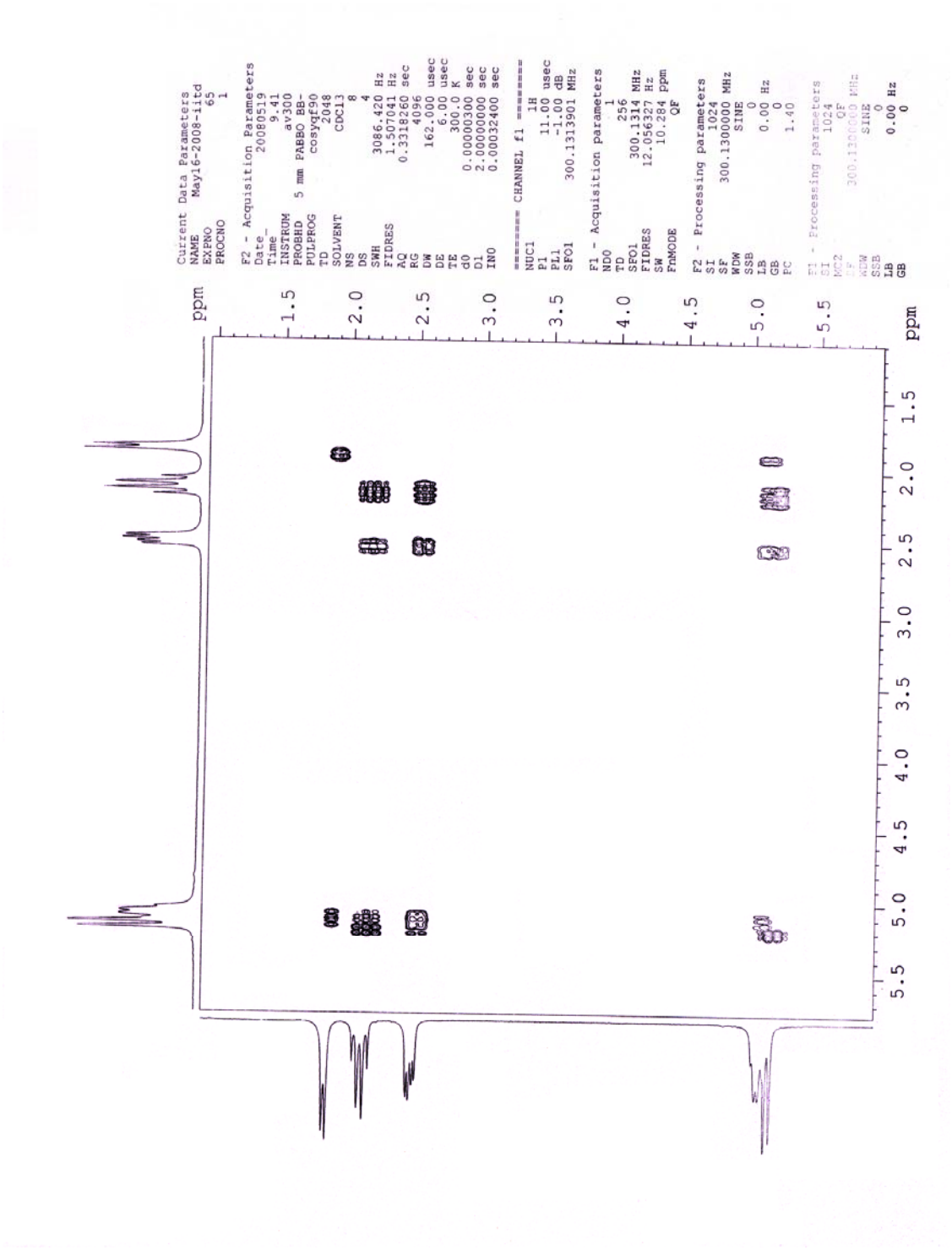


Fig. S7: $^{1}H$-$^{13}C$ COSY of **4a**

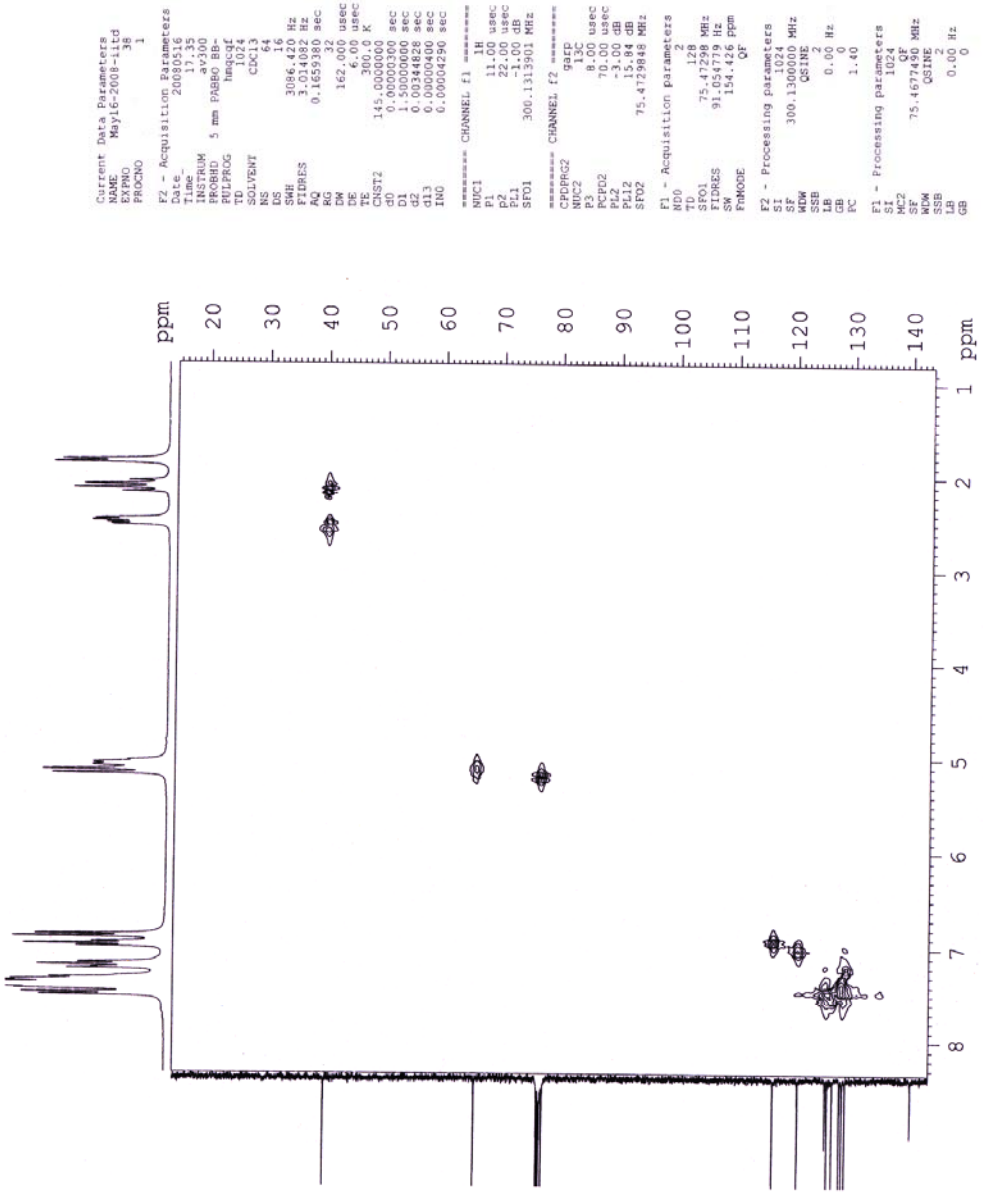


Fig. S8: $^{1}$H NMR of **4b**

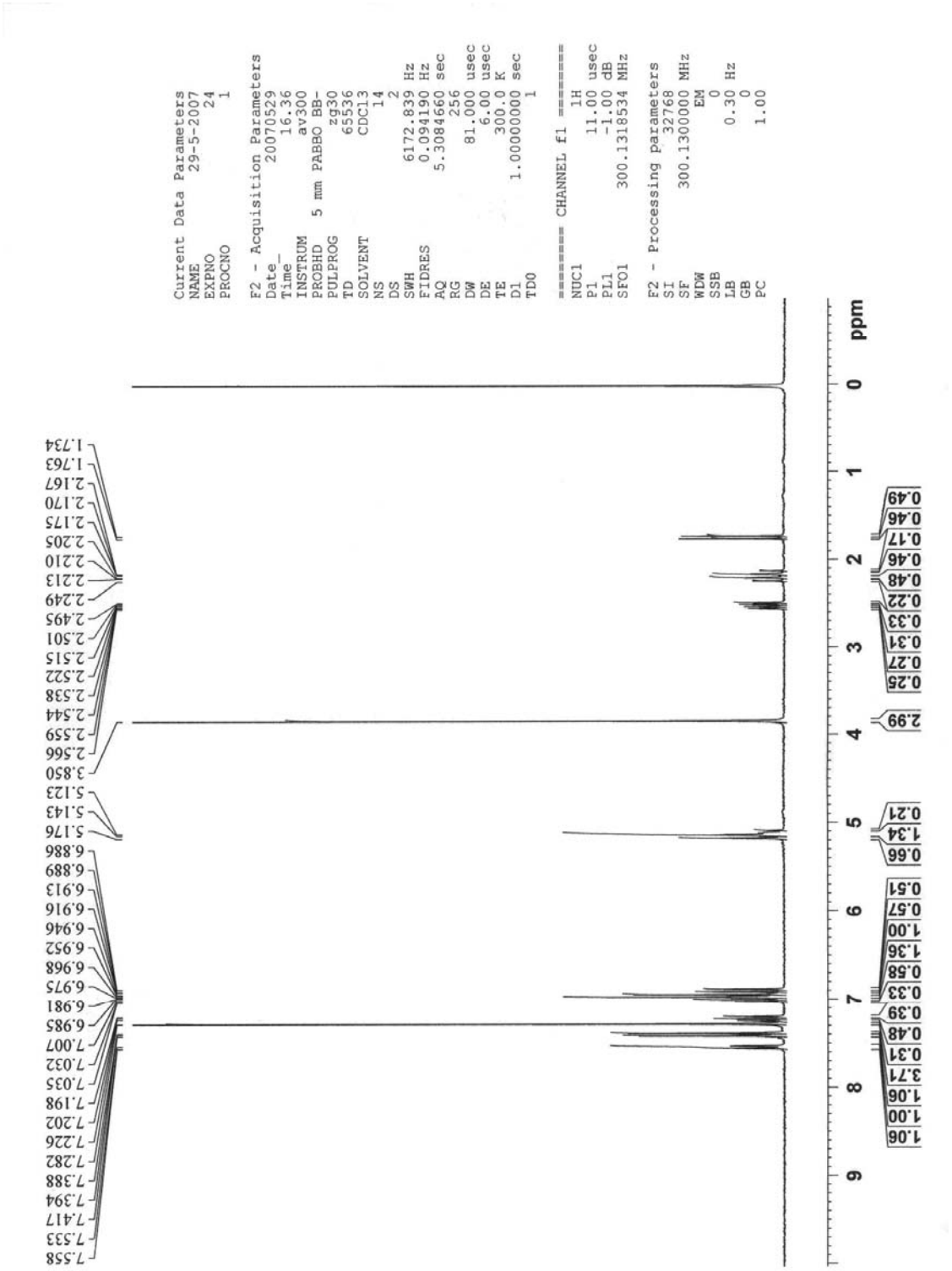


Fig. S9: $^{1}$H NMR of **4b**

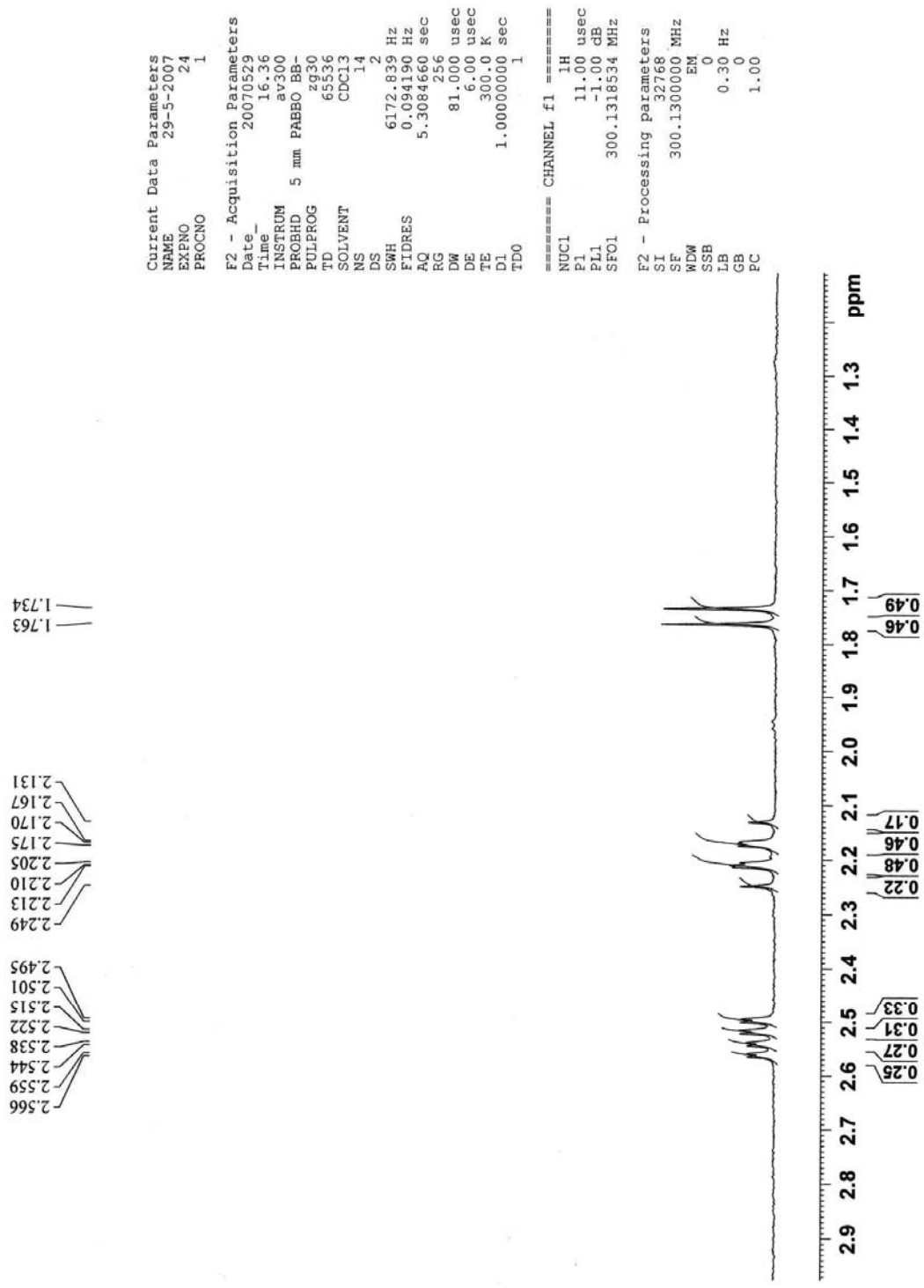


Fig. S10: $^{13}$C NMR of **4b**

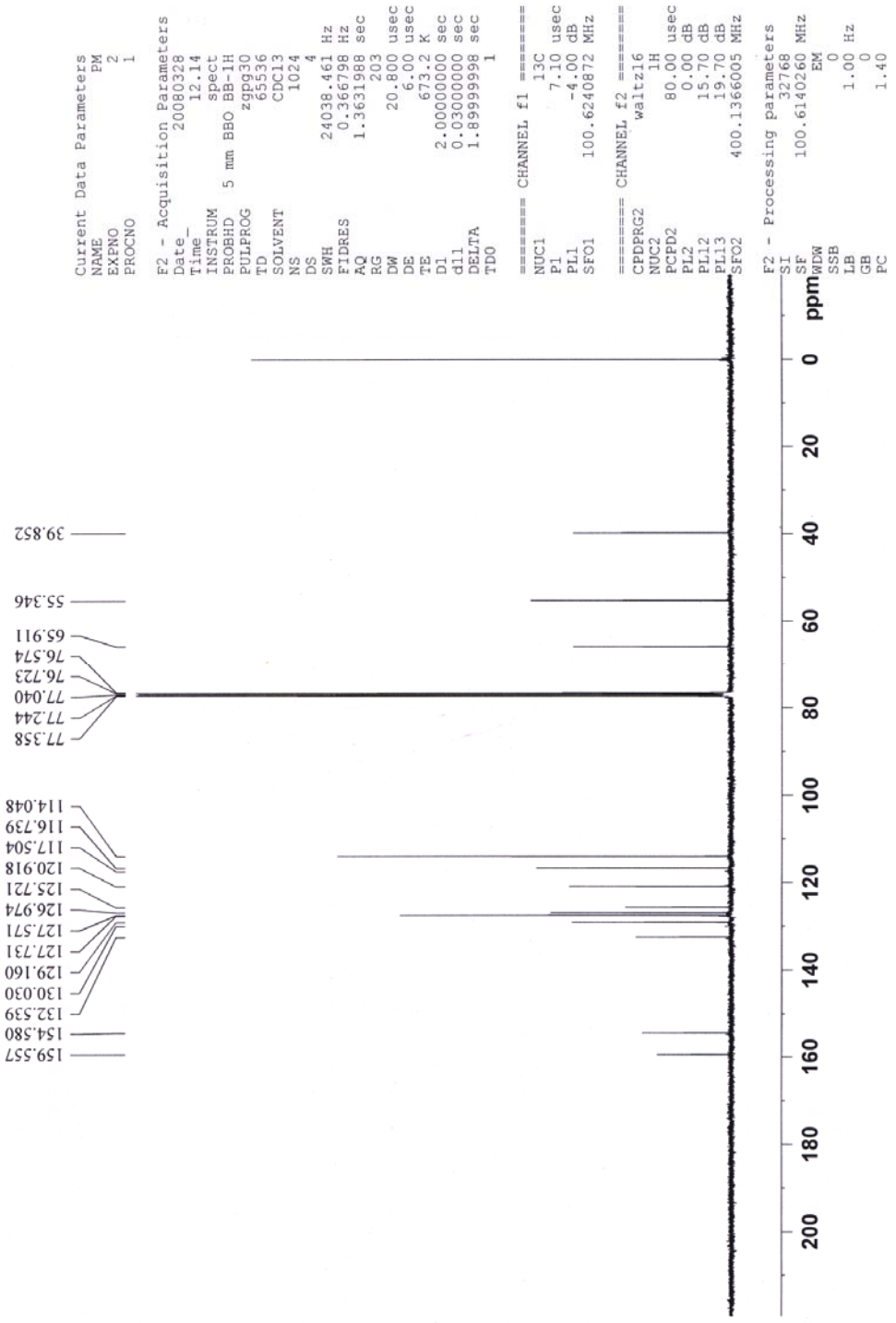


Fig. S11: $^{1}$H NMR of **4c**

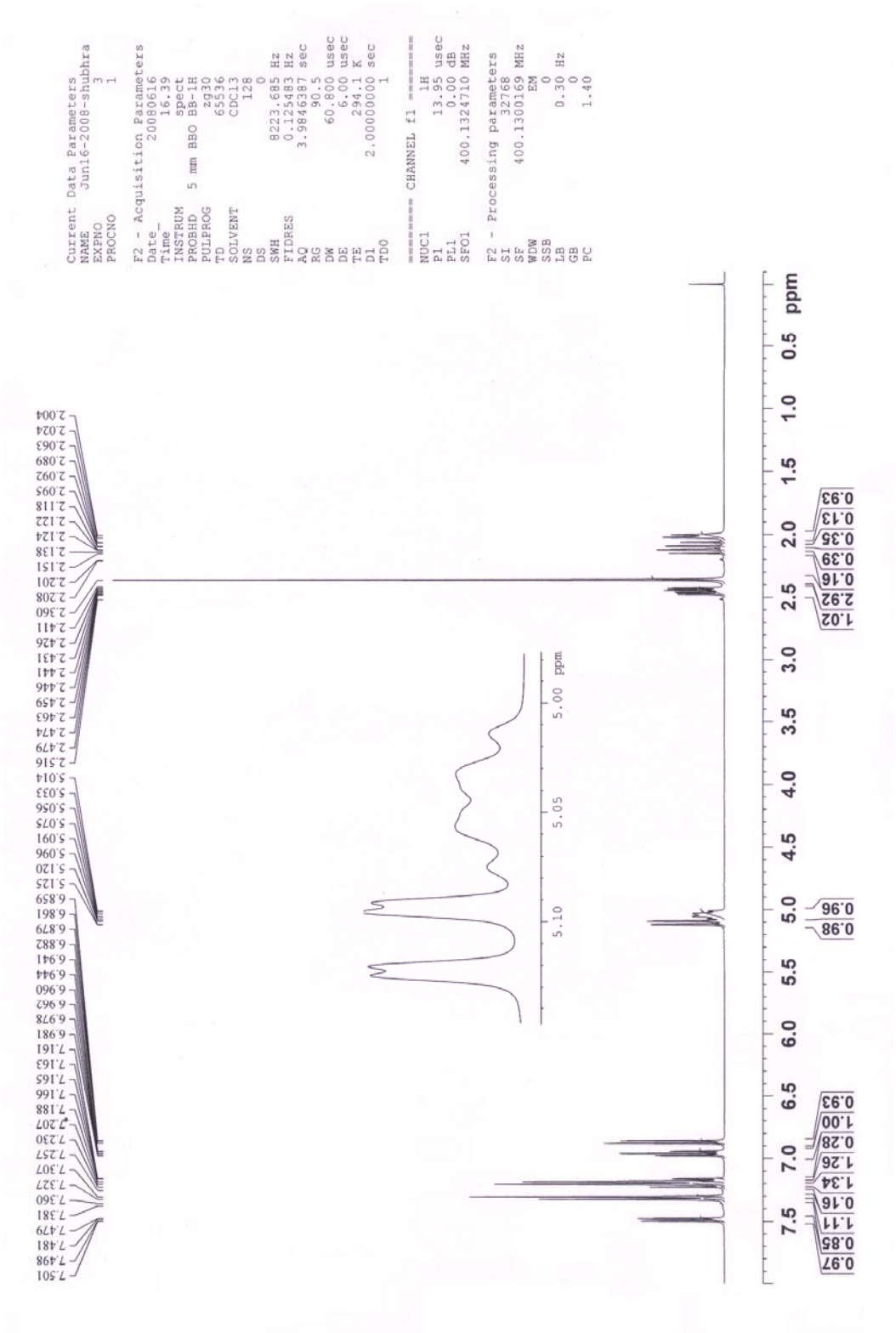


Fig. S12: $^{1}$H NMR of **4c**

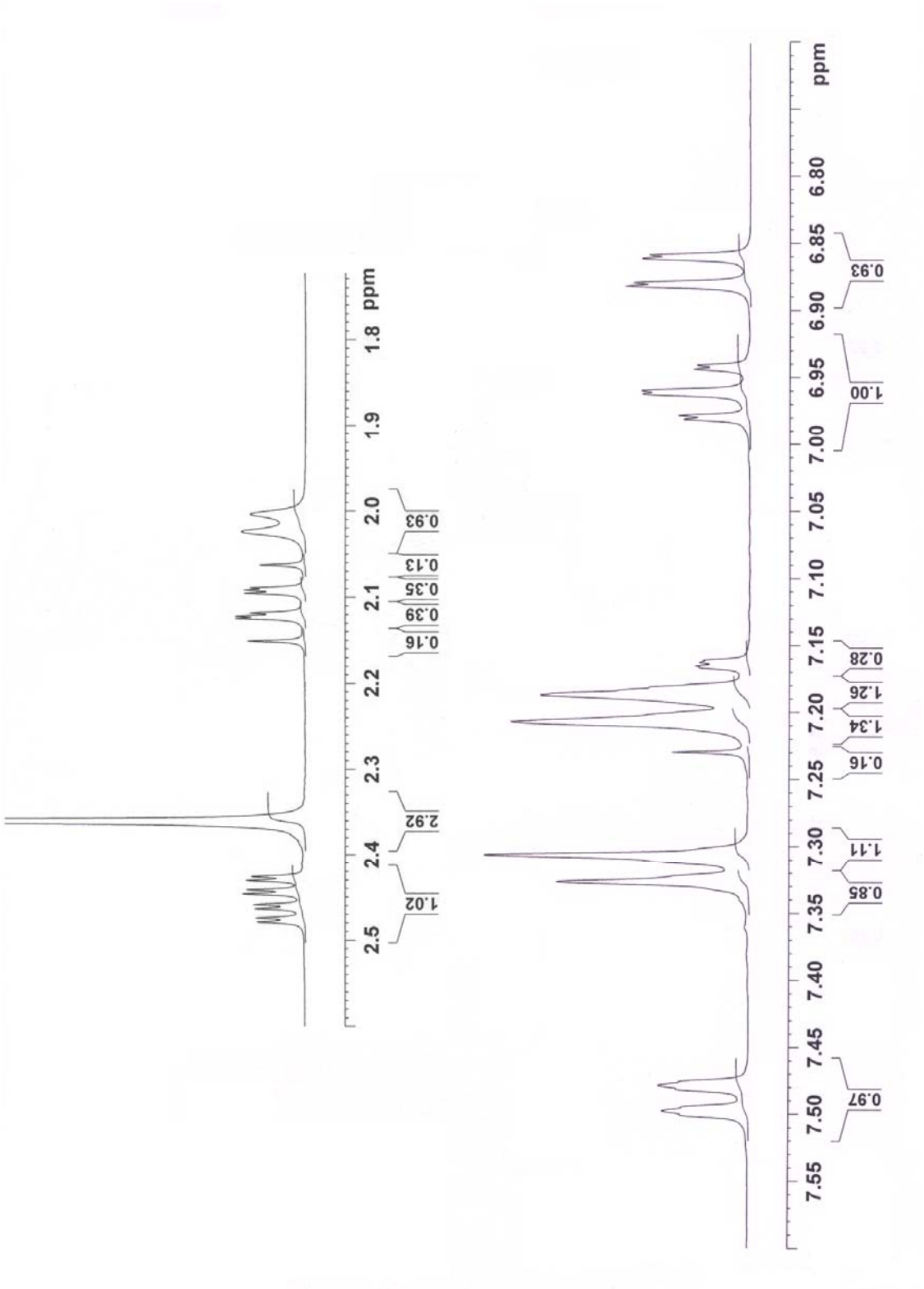


Fig. S13: $^{13}C$ NMR of **4c**

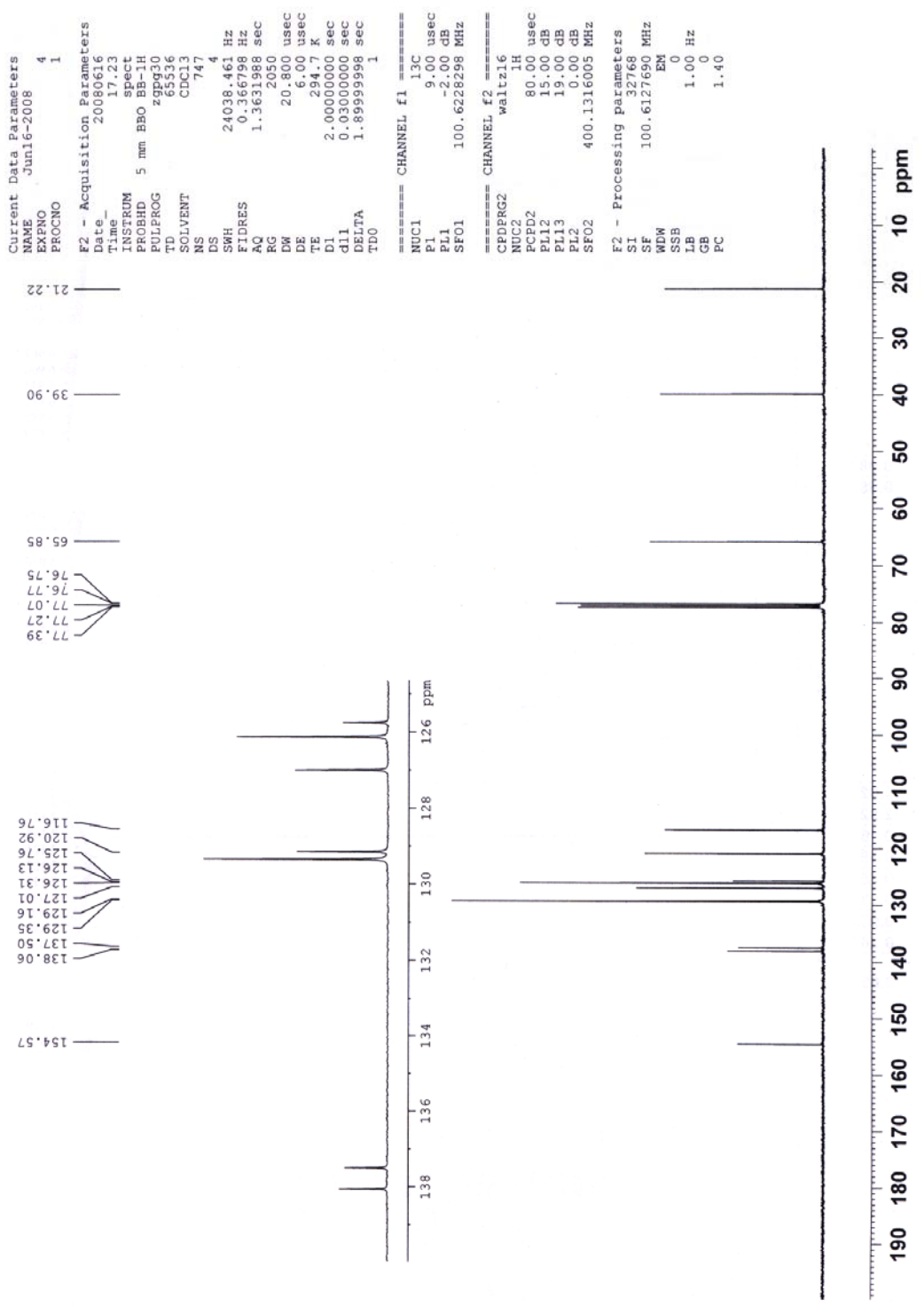


Fig. S14: $^{1}$H NMR of **4d**

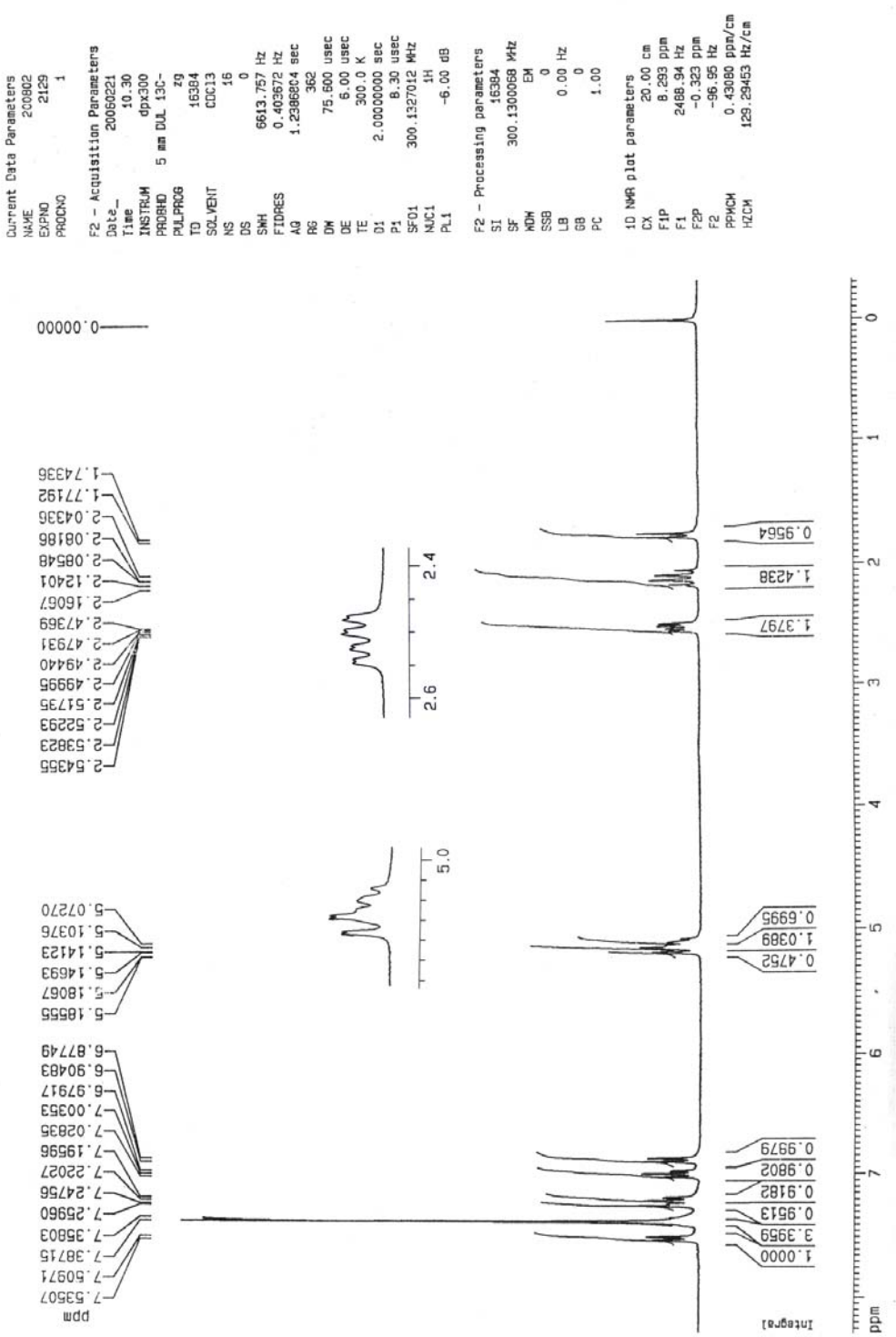


Fig. S15: $^{13}$C NMR of **4d**

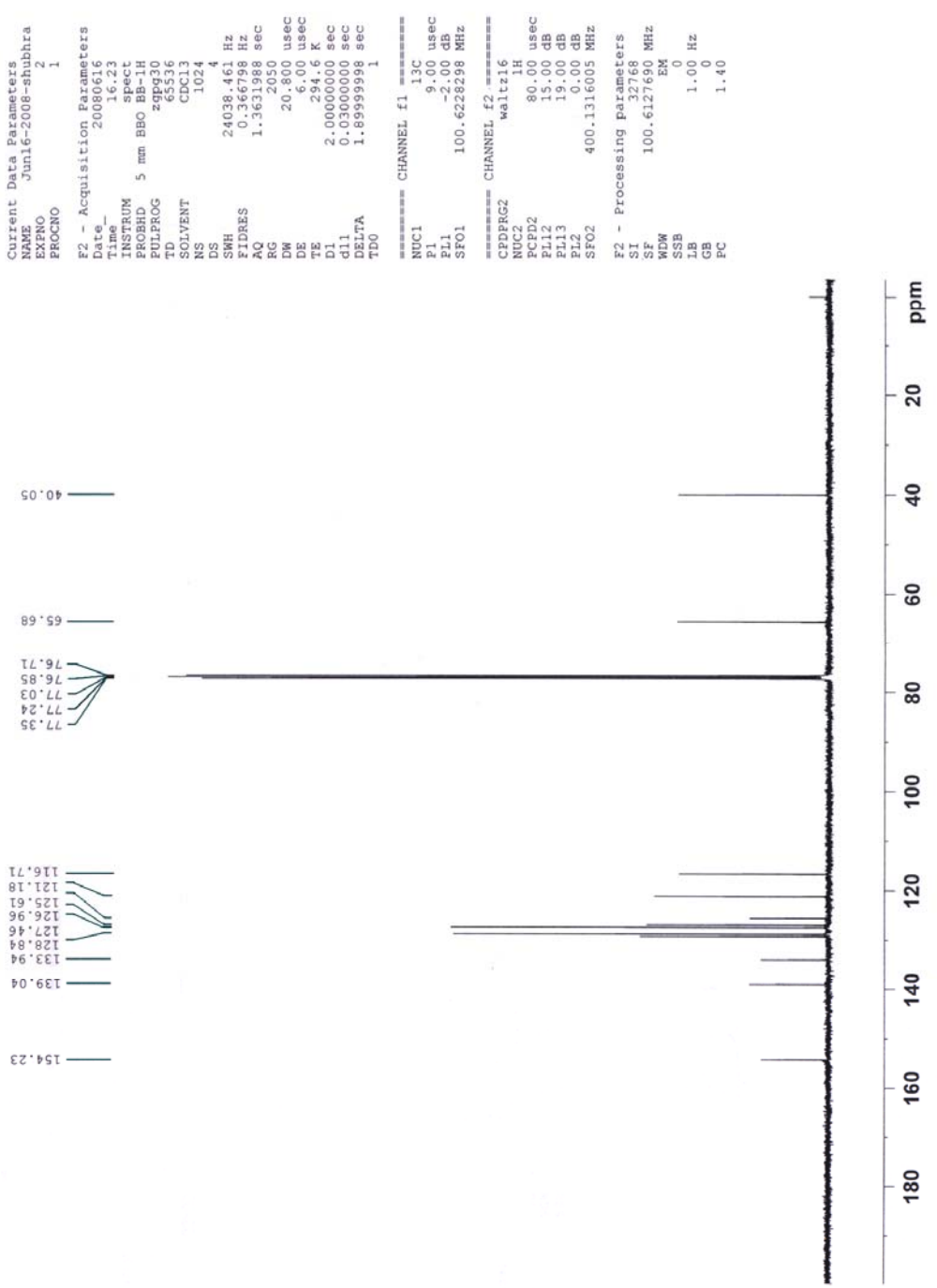


Fig. S16: $^{1}$H NMR of **5**

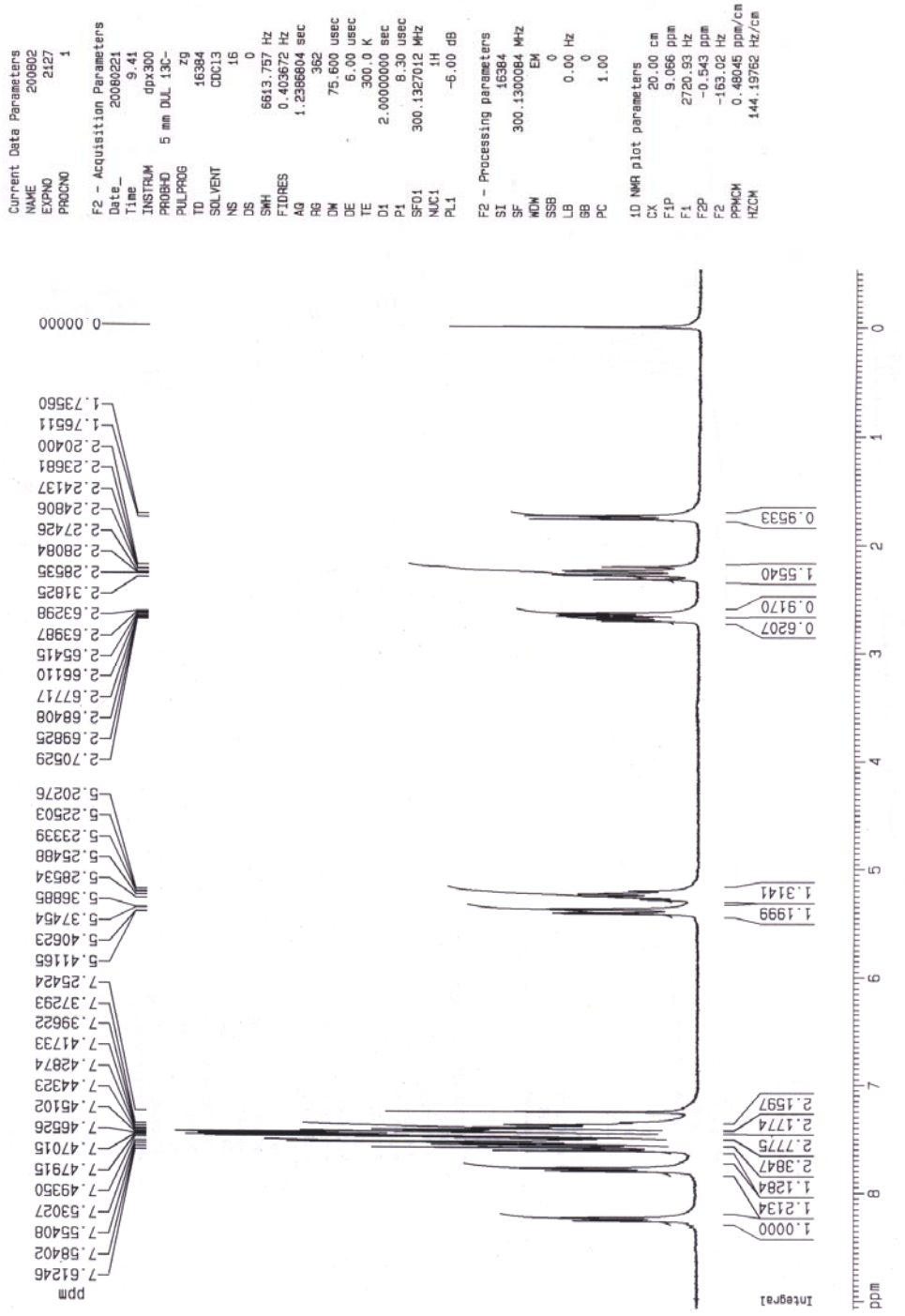


Fig. S17: $^{1}$H NMR of **5**

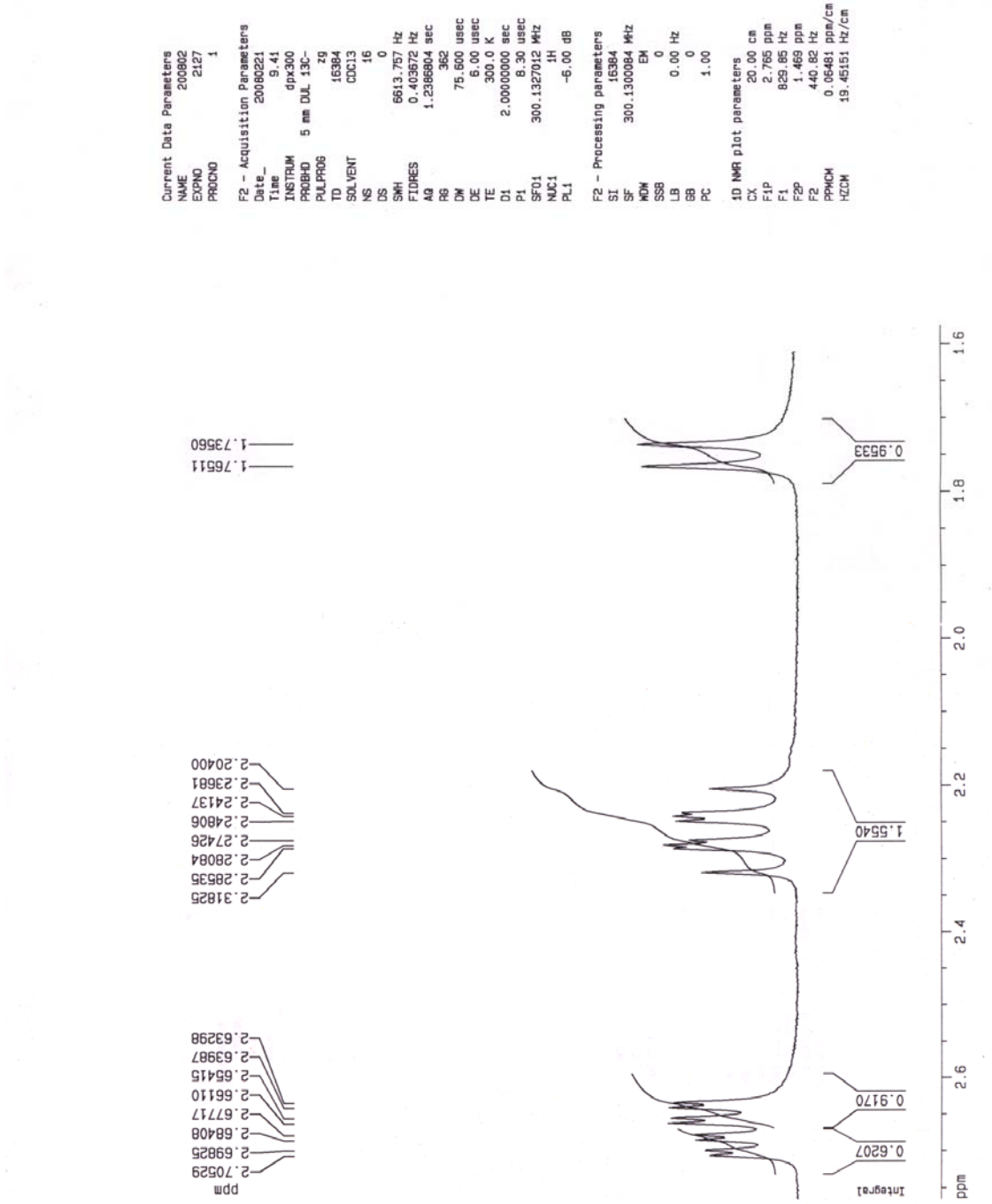


Fig. S18: $^{1}$H NMR of **5**

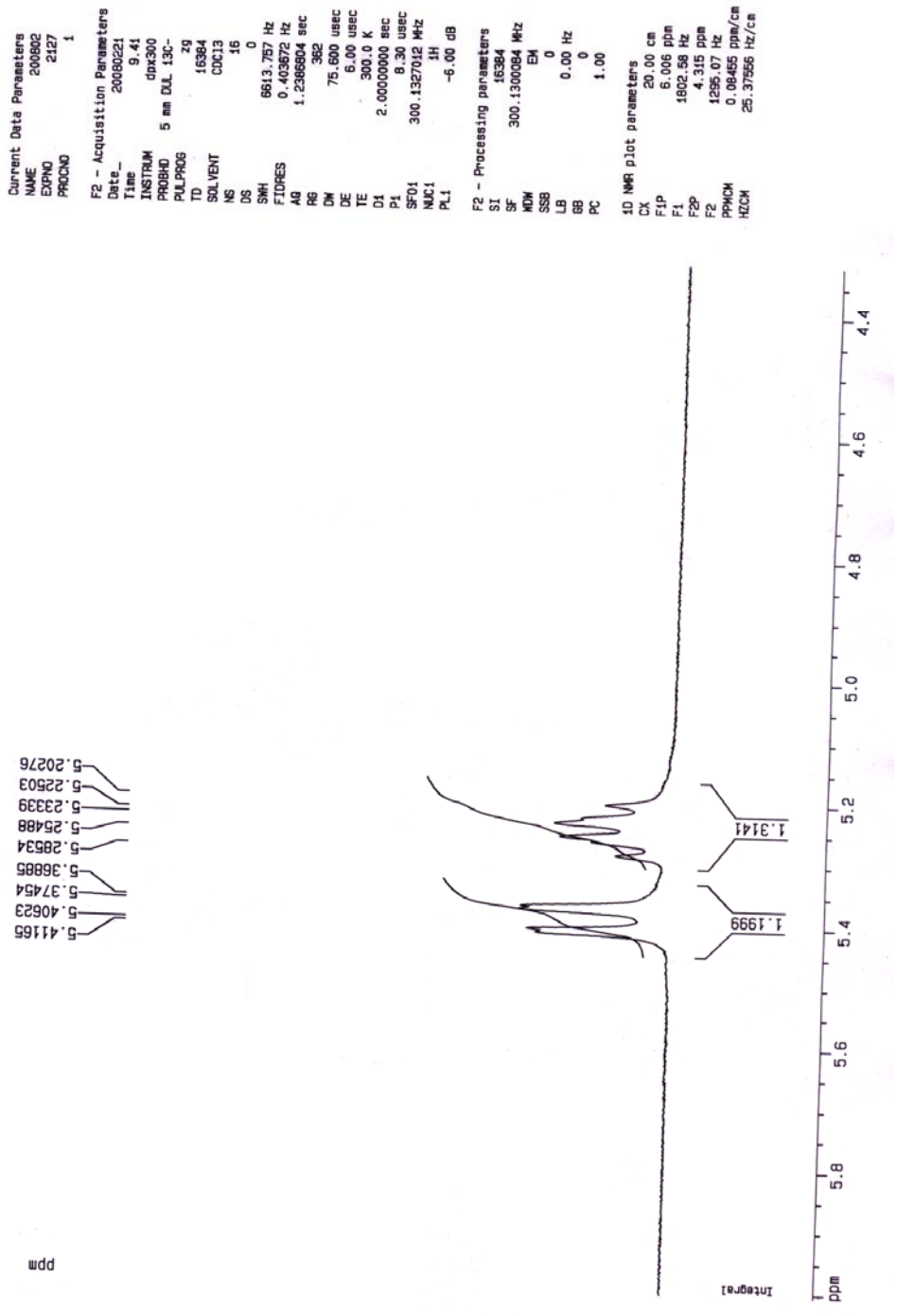


Fig. S19: $^{13}$C NMR of **5**

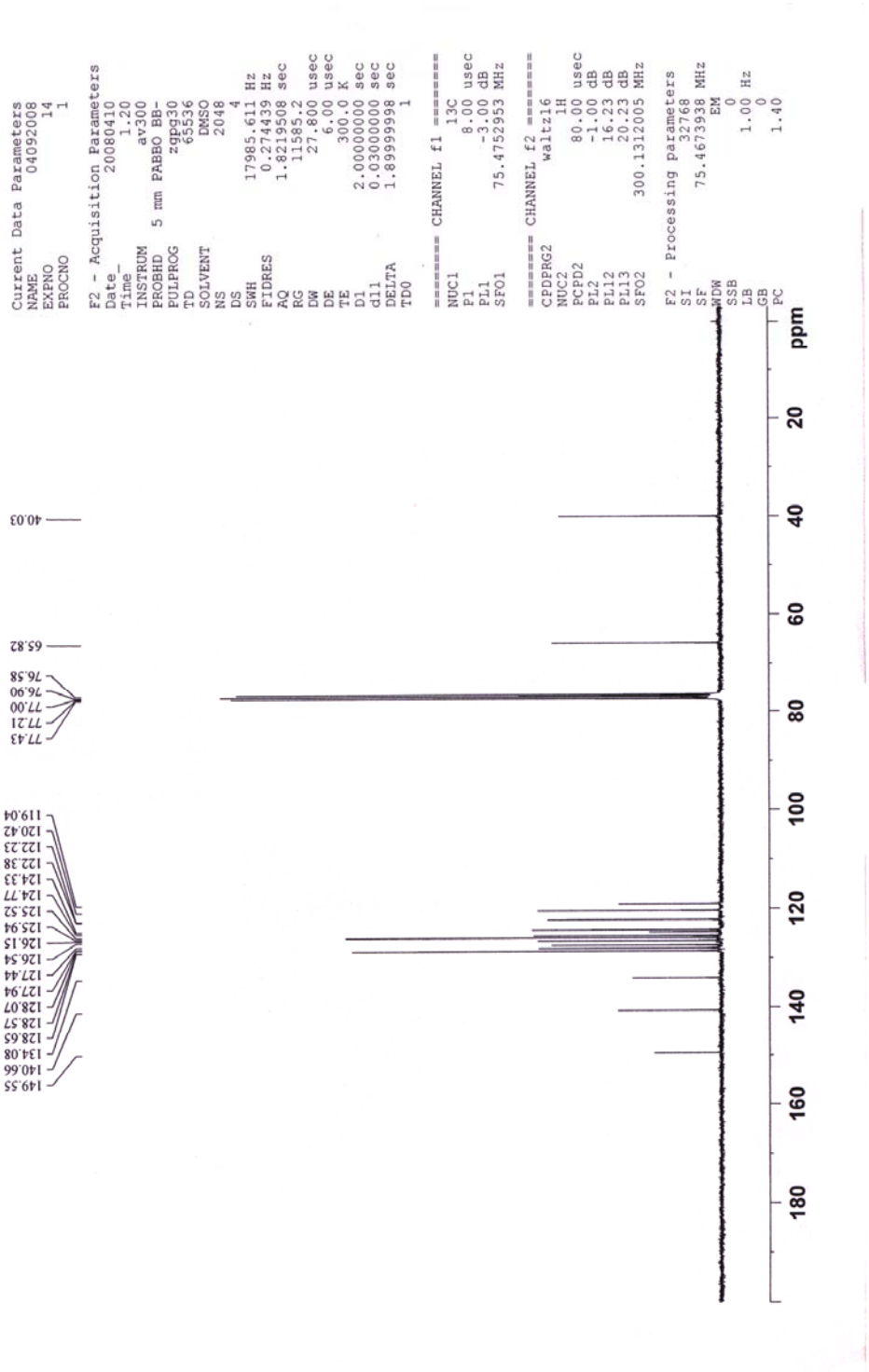


Fig. S20: $^{1}$H - H COSY of **5**

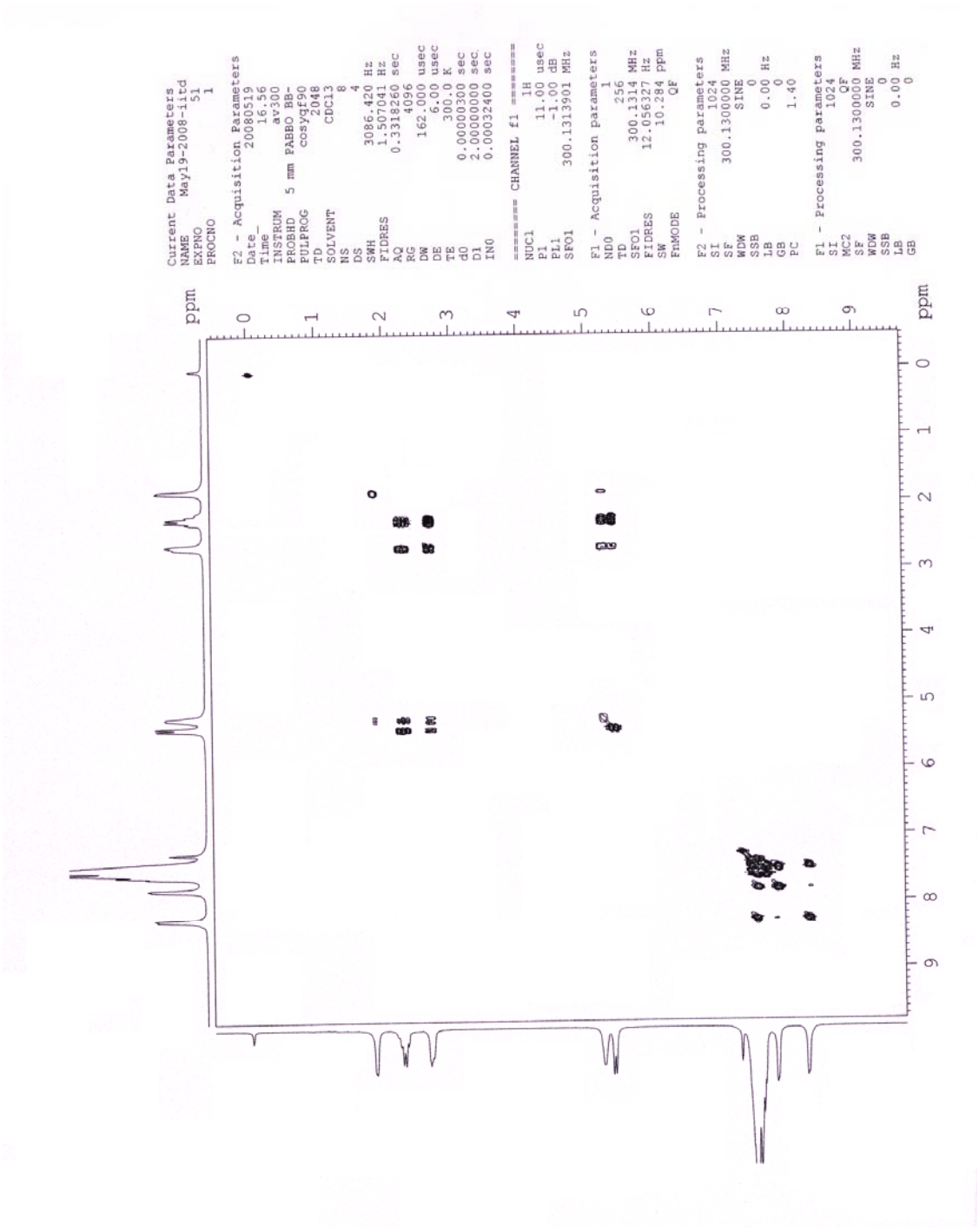


Fig. S21: $^{1}H - ^{13}C$ COSY of **5**

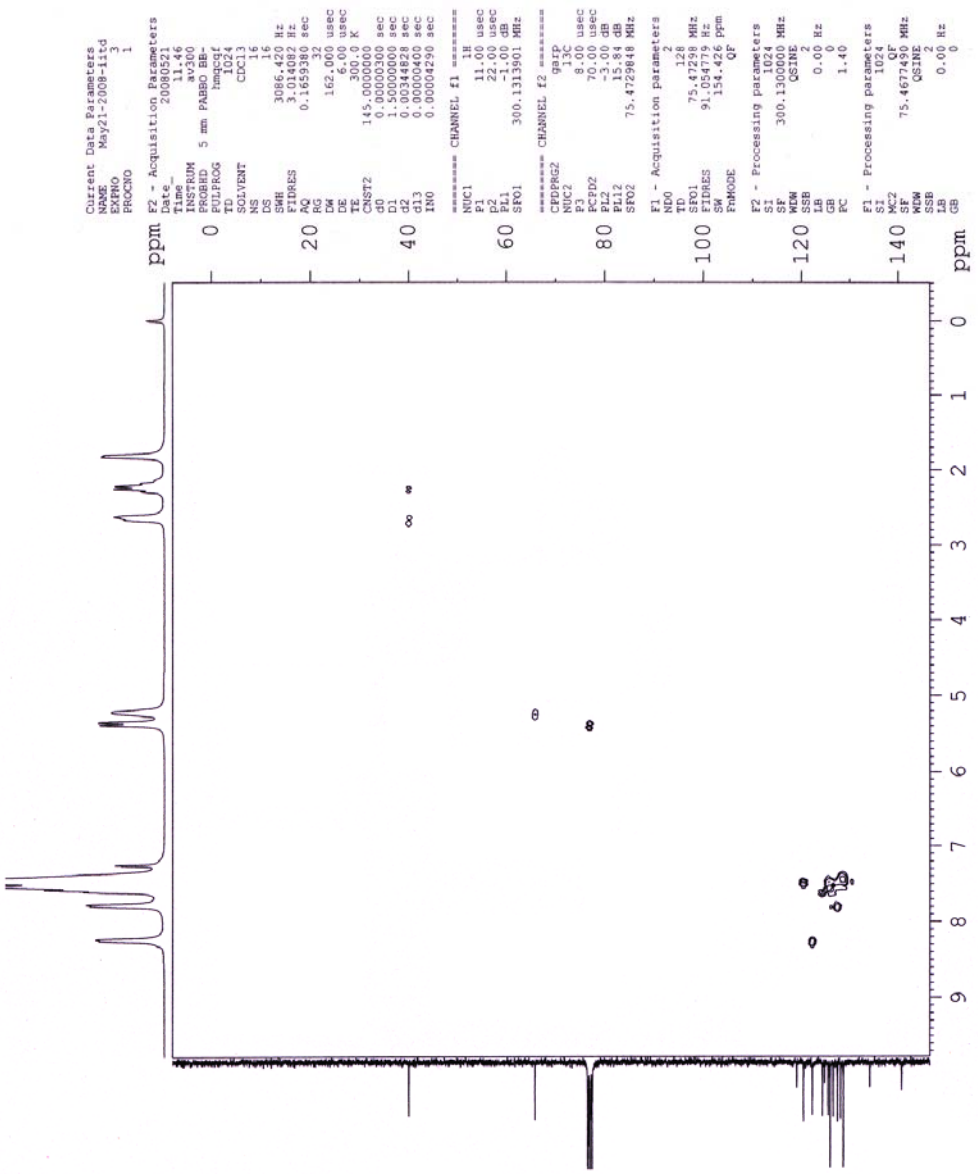


Fig. S22: $^{1}$H NMR of **6a**

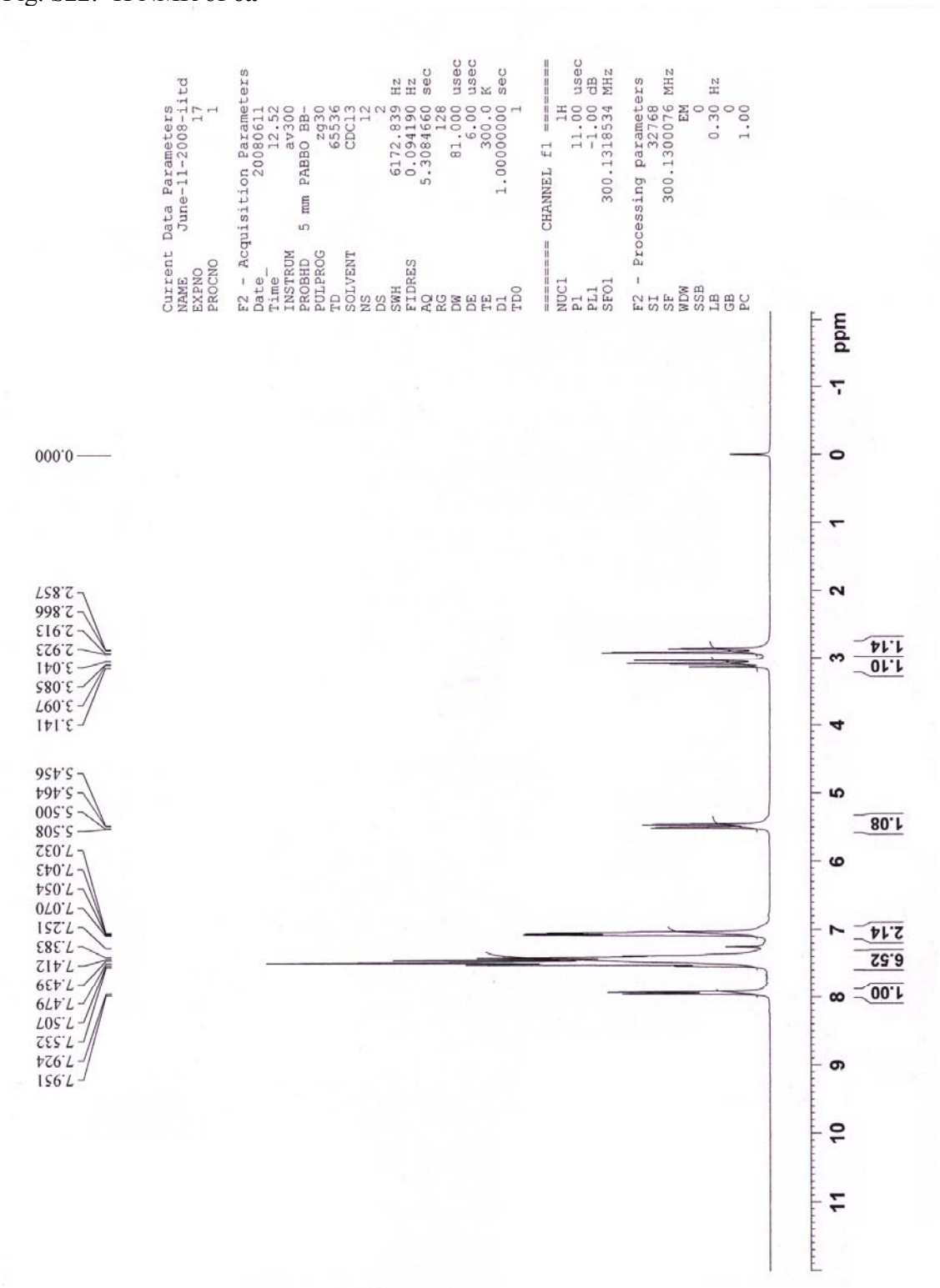


Fig. S23: $^{1}$H NMR of **6a**

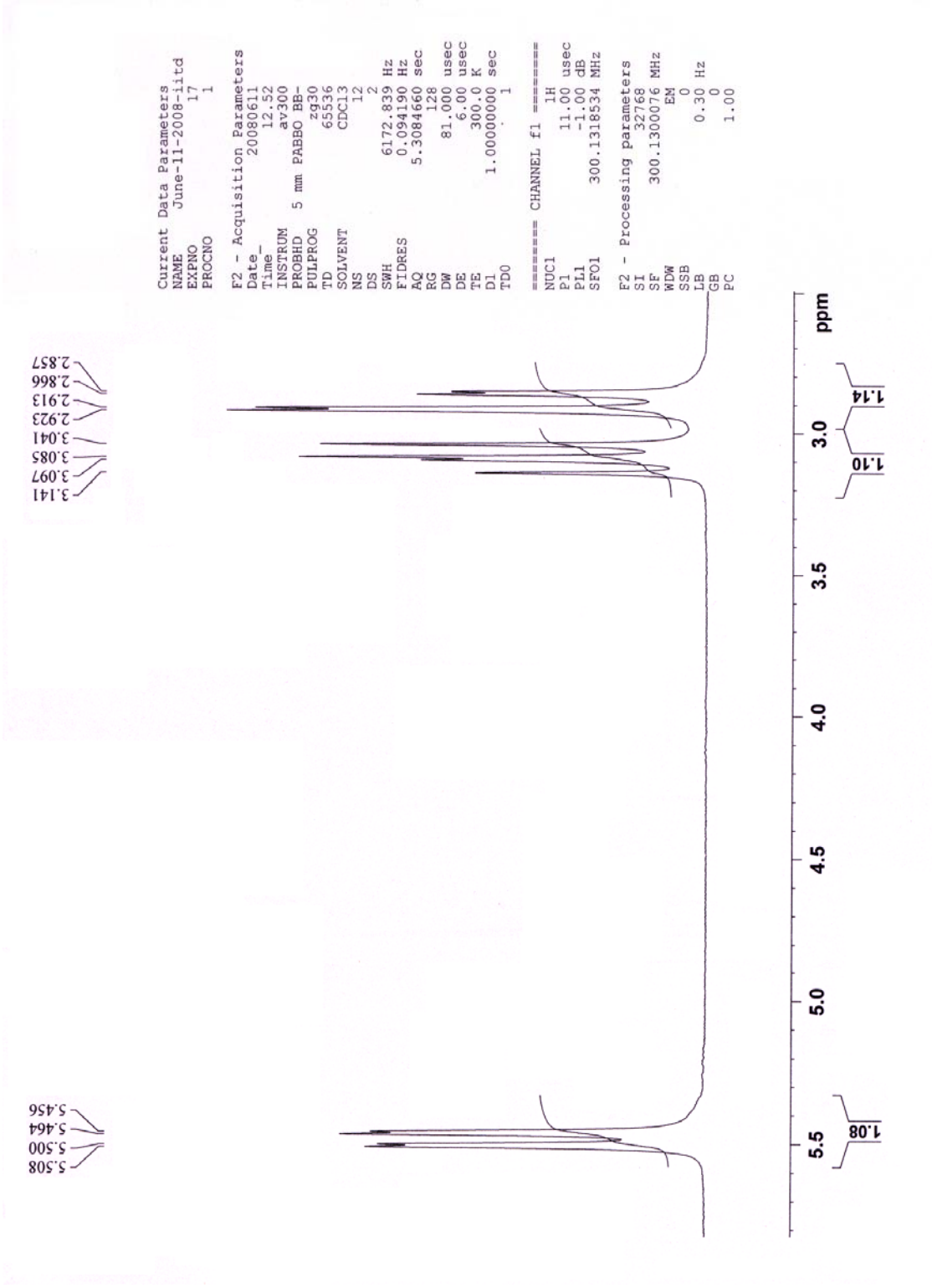


Fig. S24: $^{1}$H NMR of methyl 3-(4-methylphenyl)prop-2-enoate (**S1)**

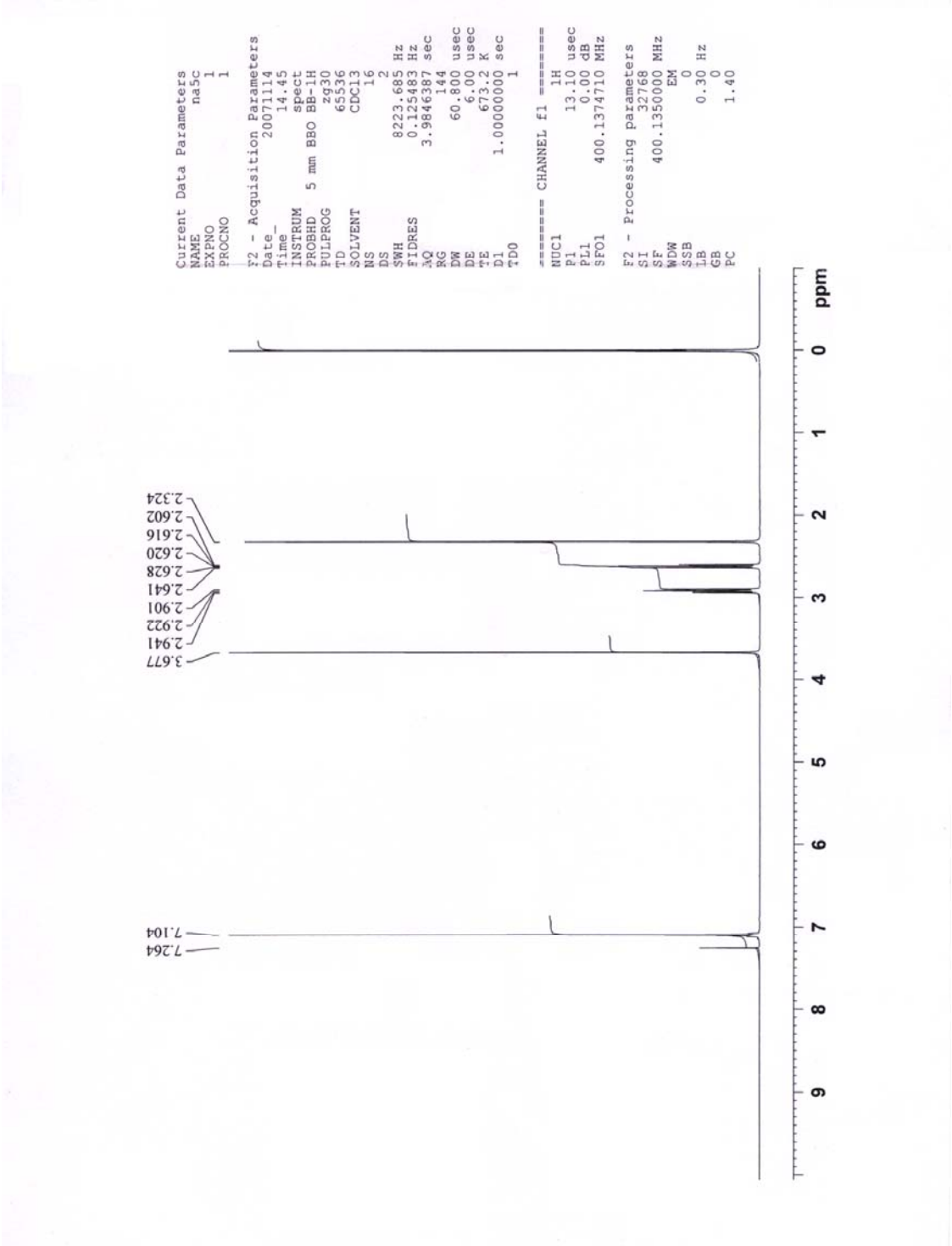


Fig. S25: $^{1}$H NMR of methyl 3-(4-methylphenyl)prop-2-enoate (**S1**)

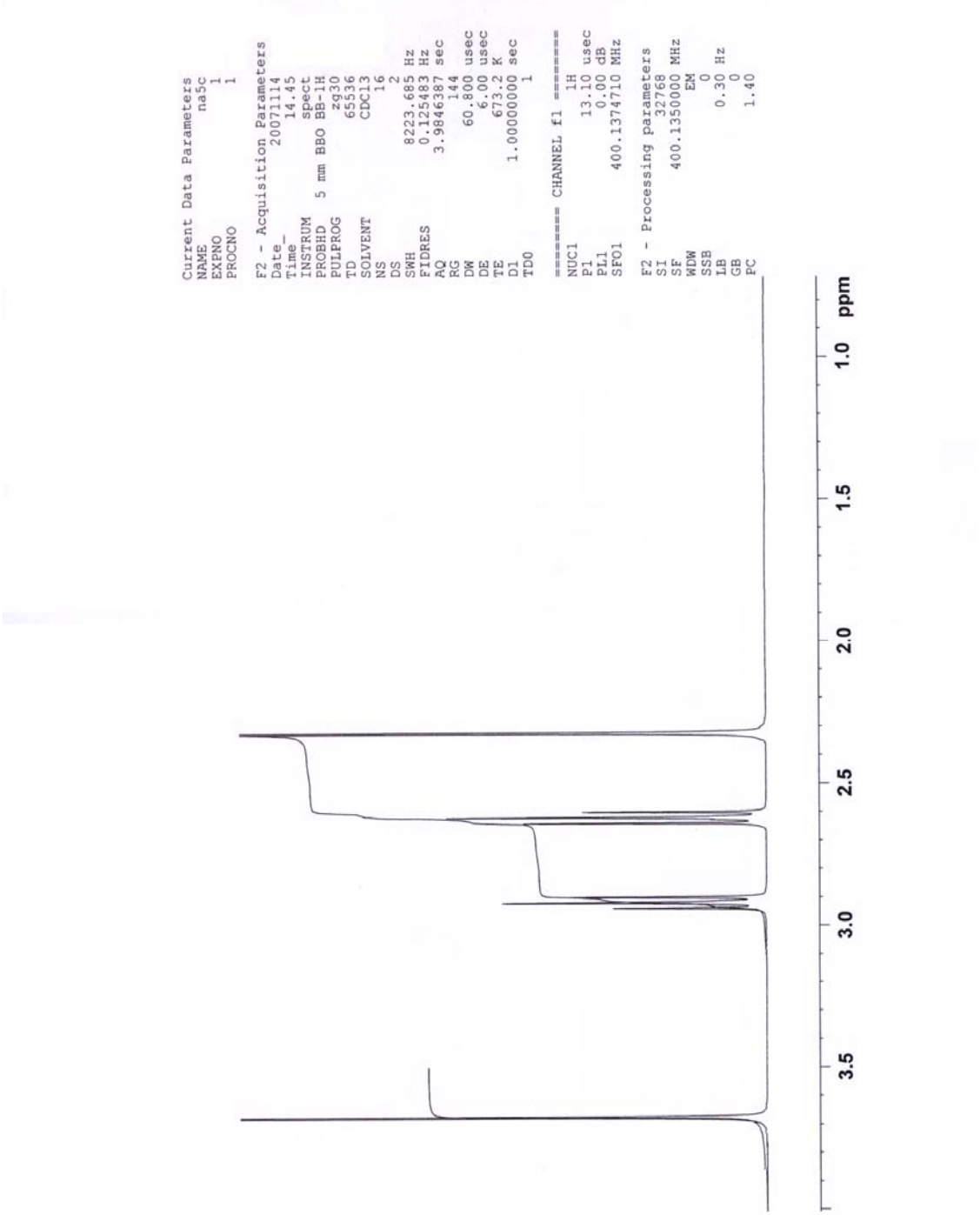


Fig. S26: $^{1}$H NMR of **S3**

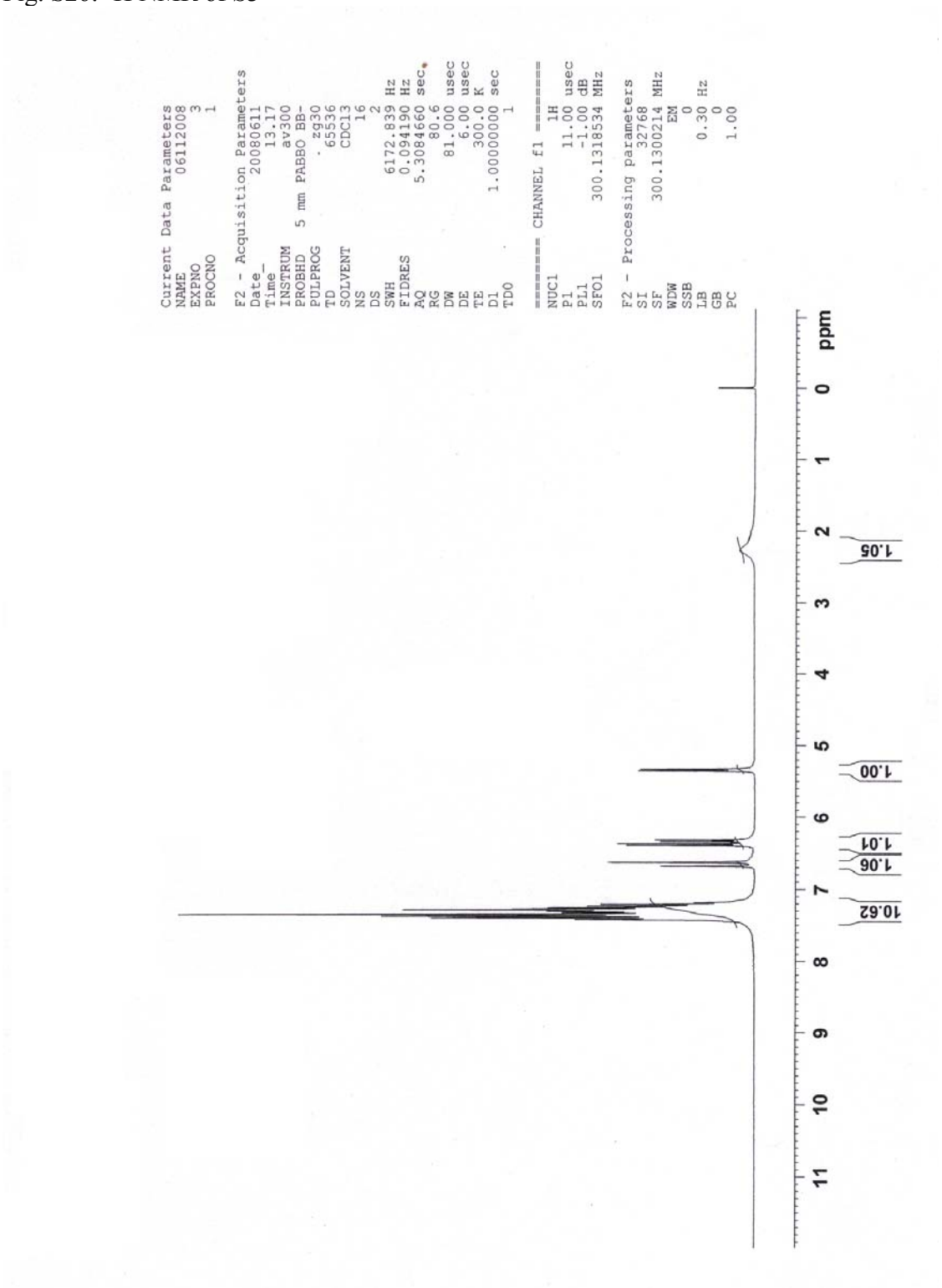


Fig. S27: $^{1}$H NMR of **S4**

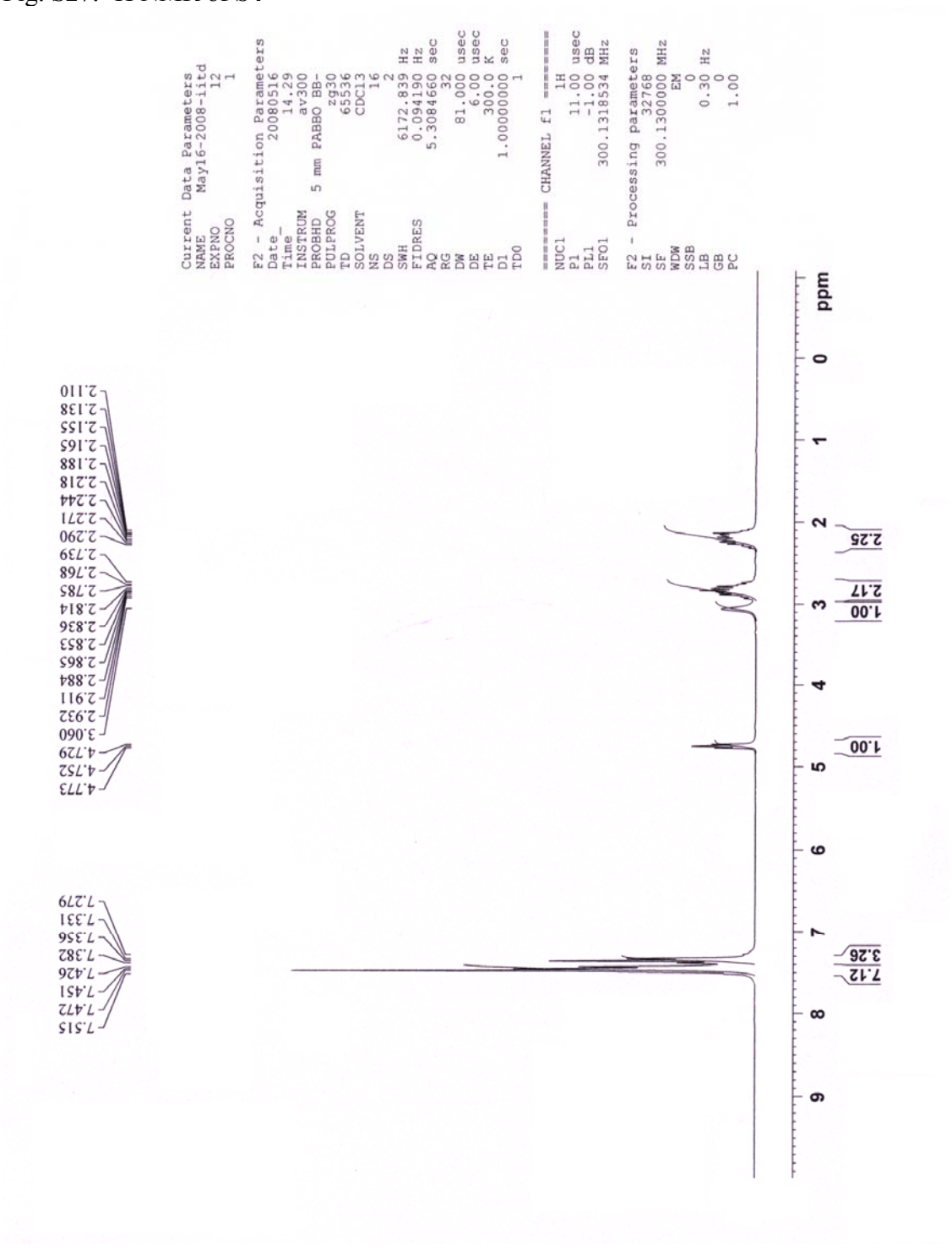


Fig. S28: $^{13}C$ NMR of **S4**

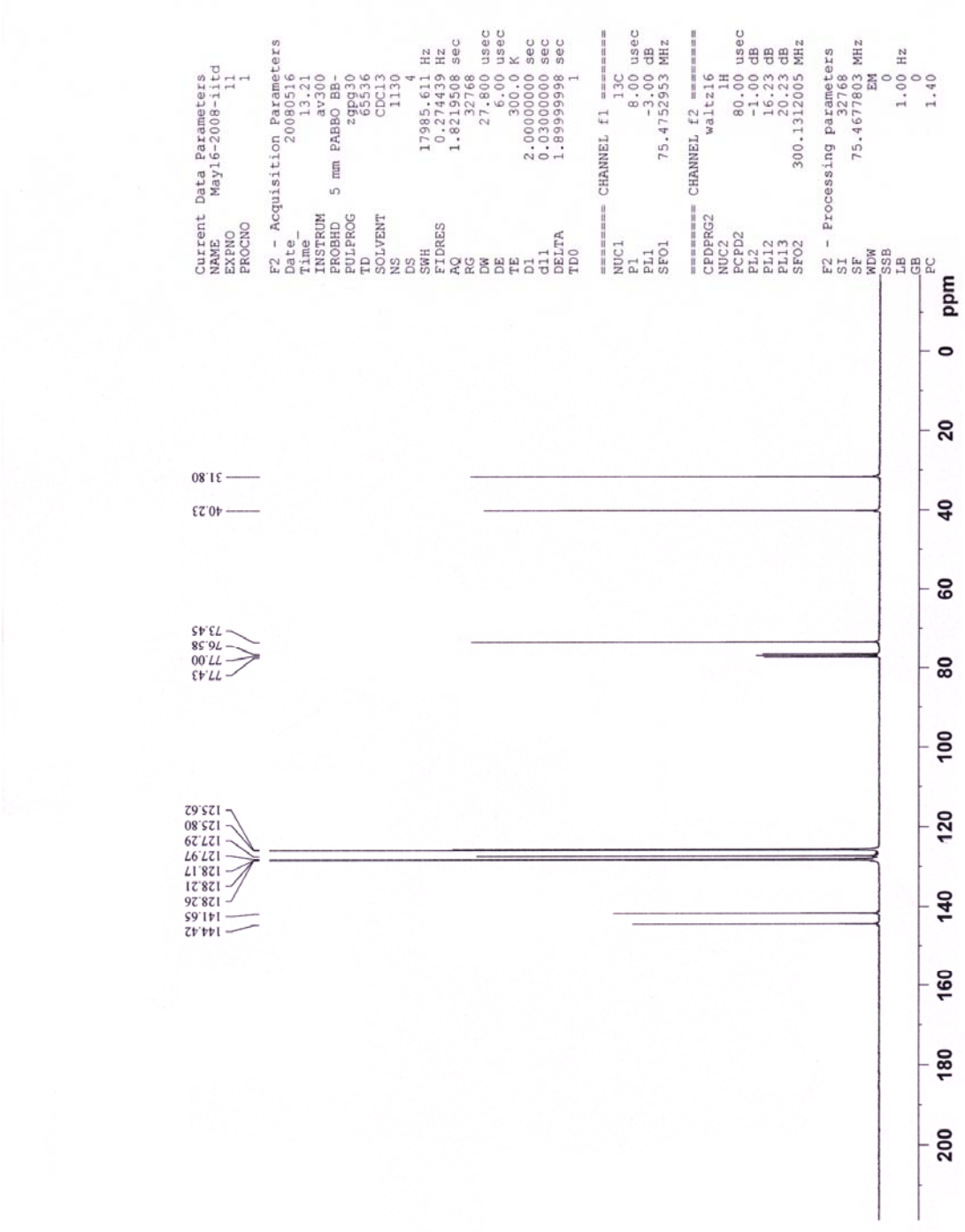


Fig. S29: IR spectra of **8**

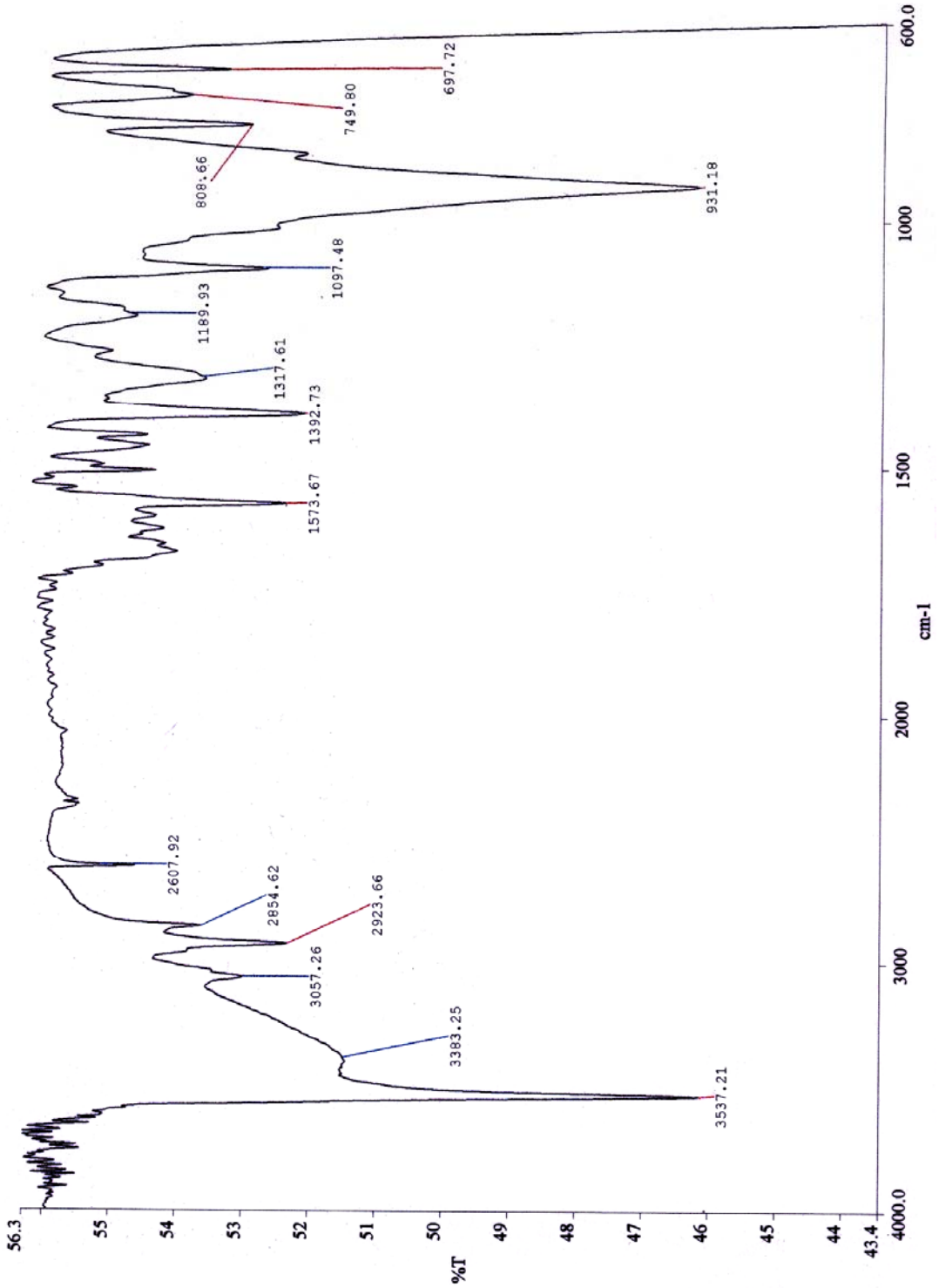


Fig. S30: $^{1}$H NMR spectra of **8**

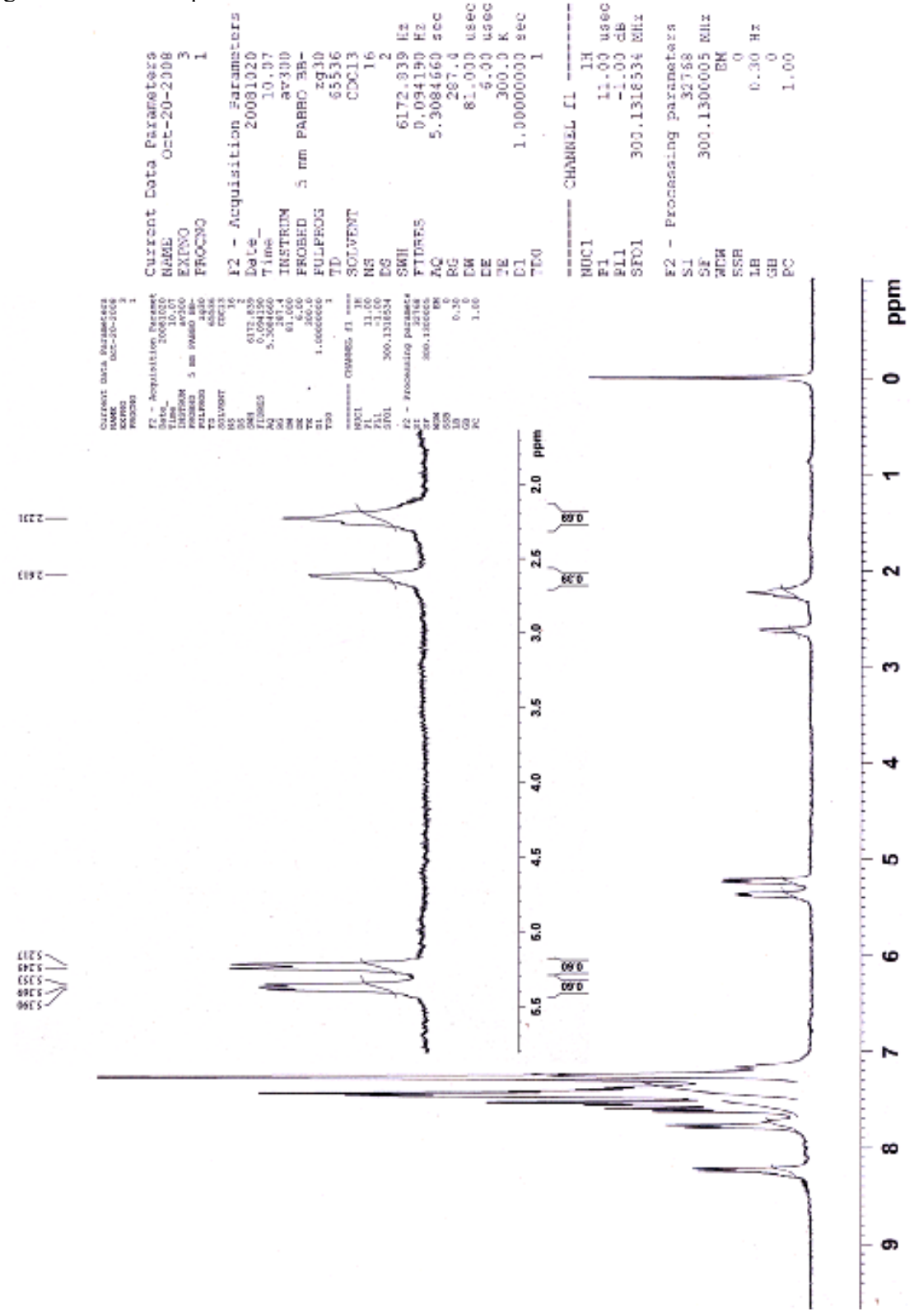


Fig. S31: $^{13}C$ NMR spectra of **8**

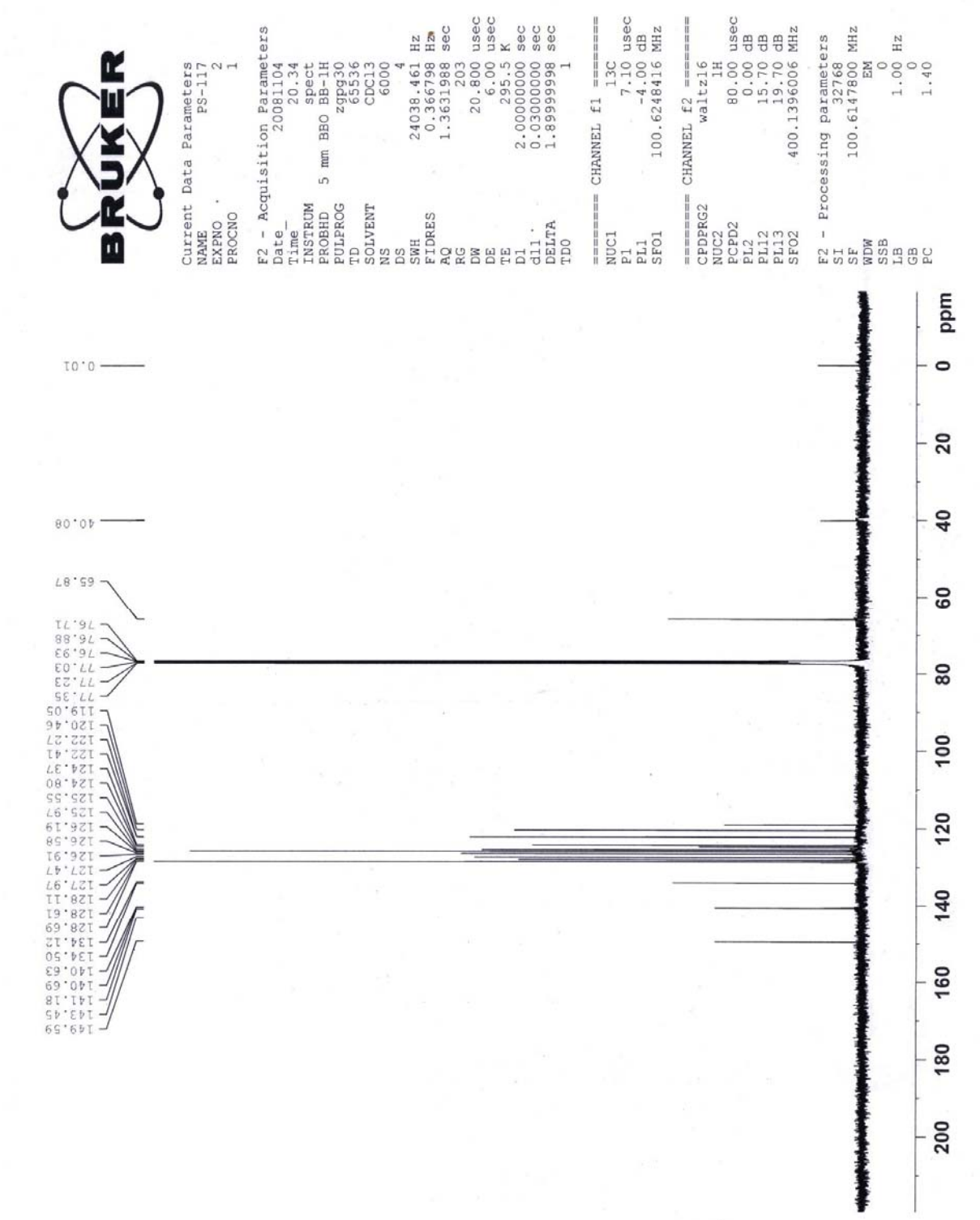


Fig. S32: IR spectra of **7**

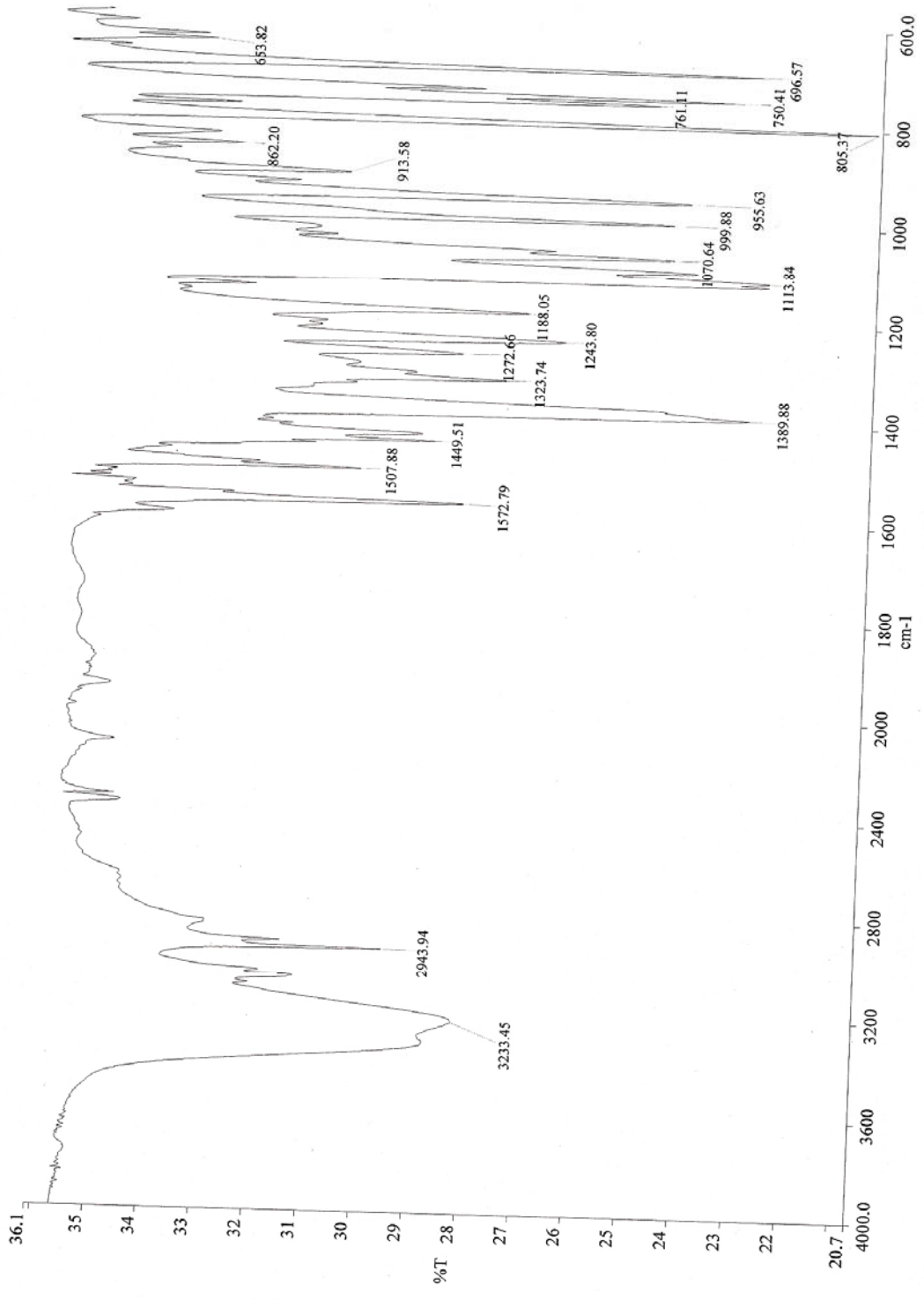


Fig. S33: $^{1}$H NMR spectra of **7**

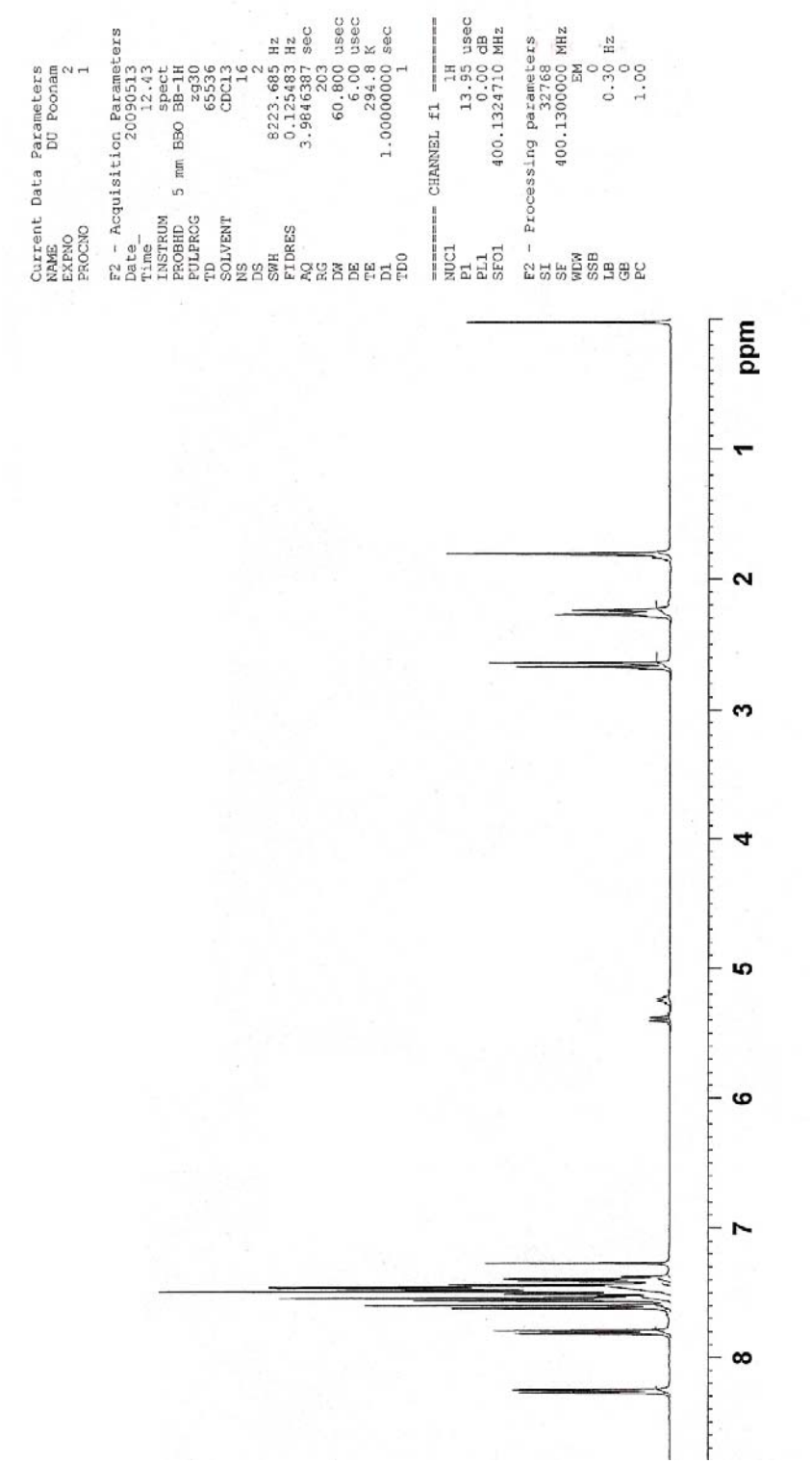


Fig. S34: $^{1}$H NMR spectra of **7**

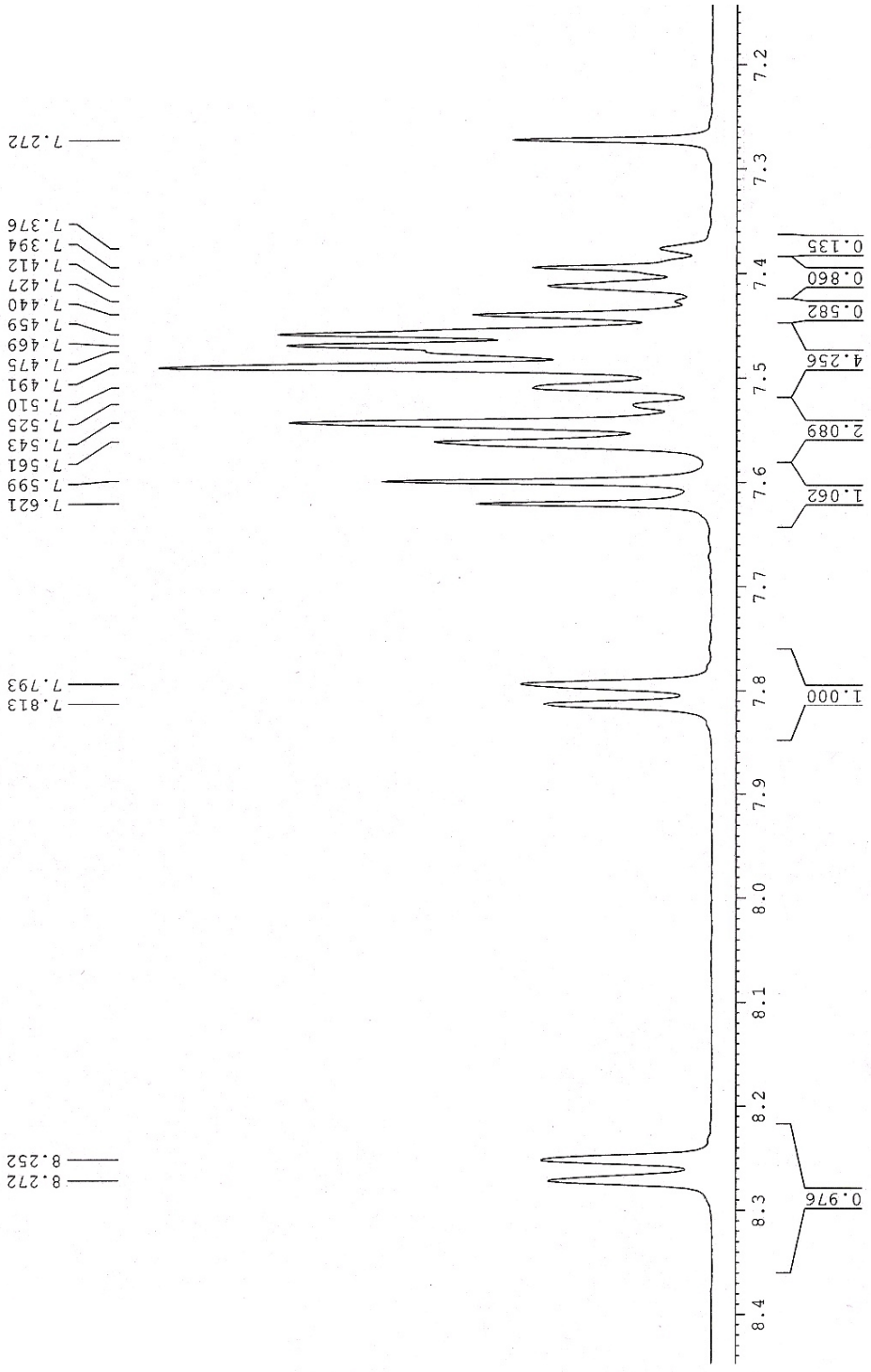


Fig. S35: $^{1}$H NMR spectra of **7**

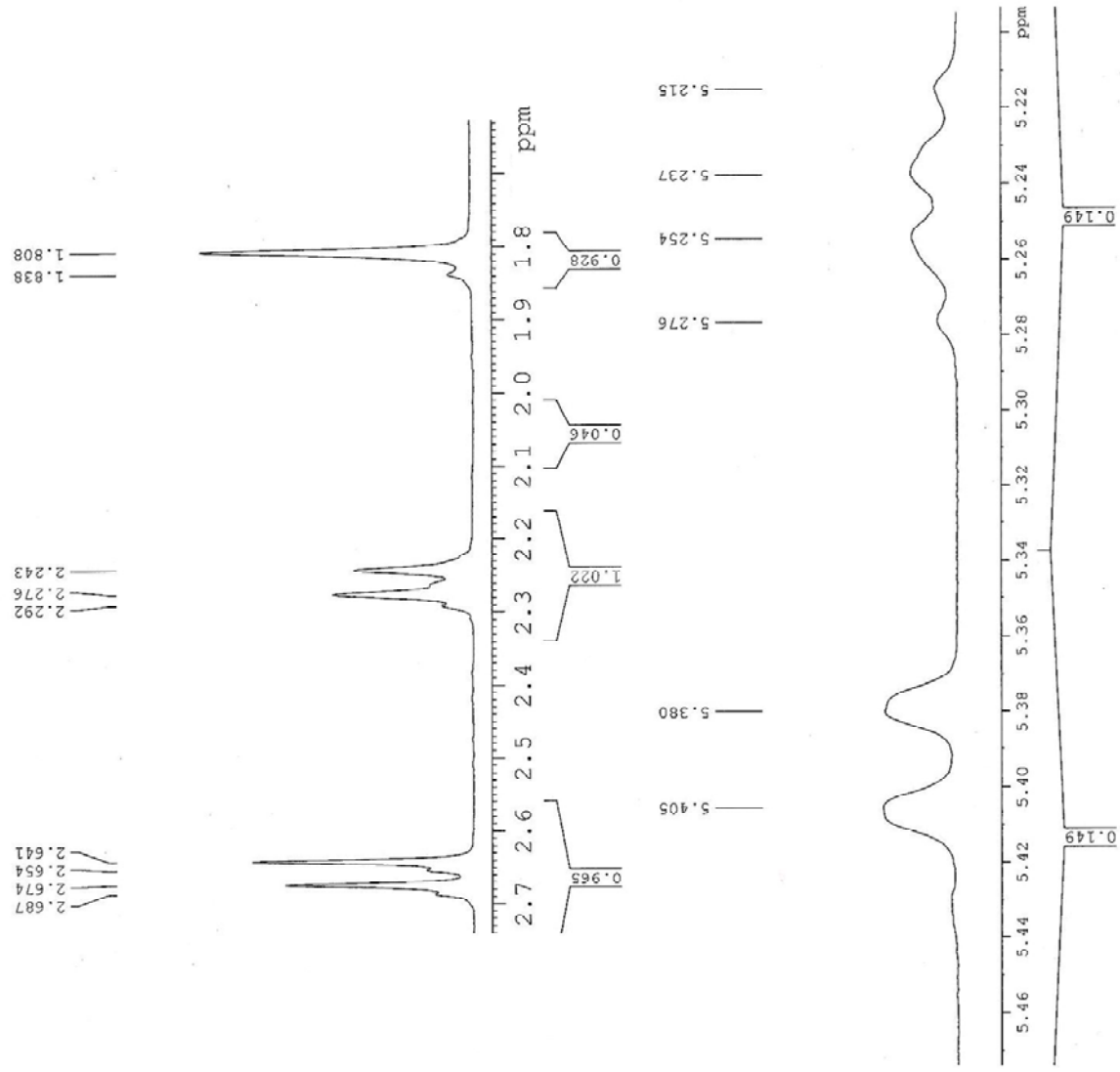


Fig. S36: $^{13}$C NMR spectra of **7**

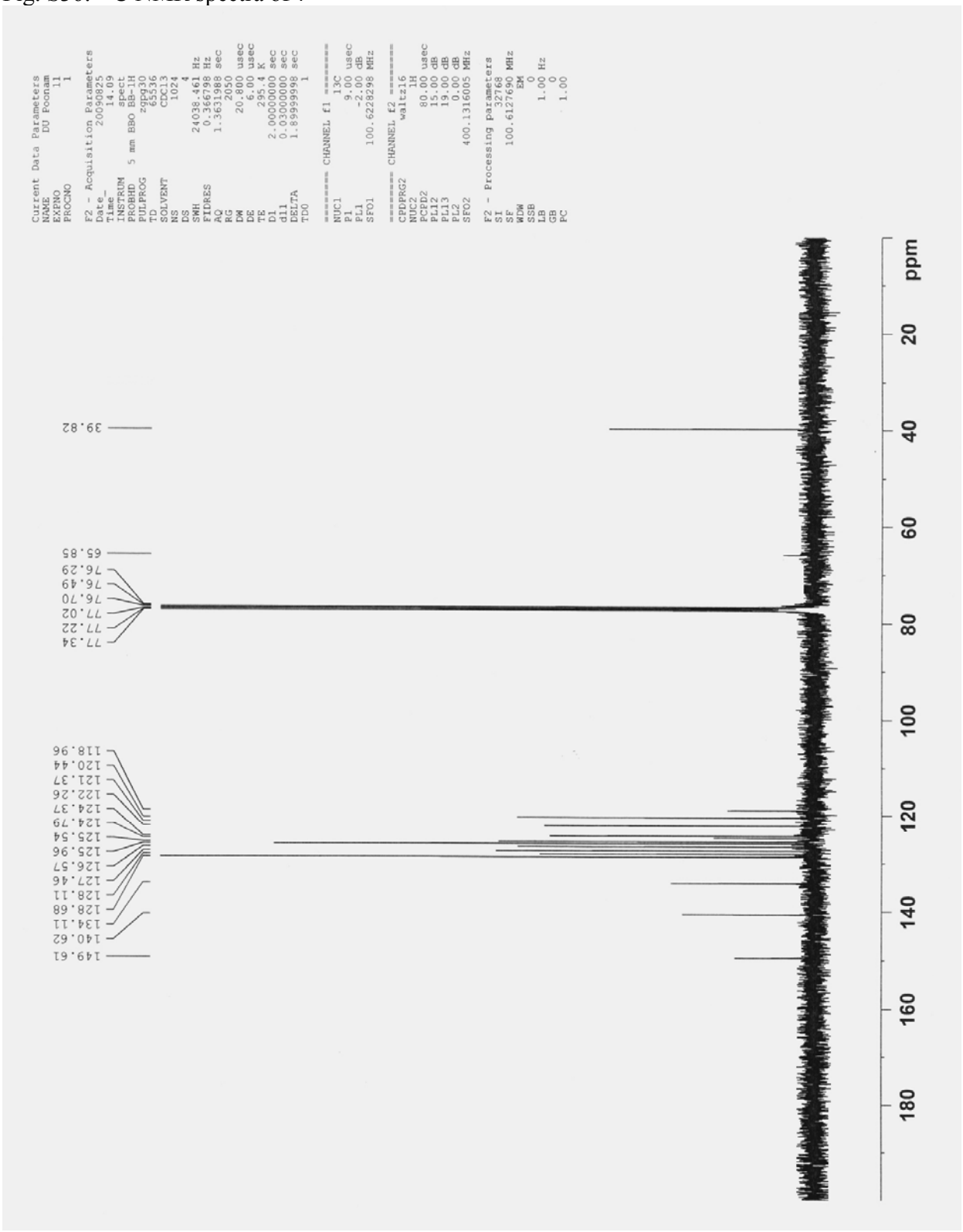
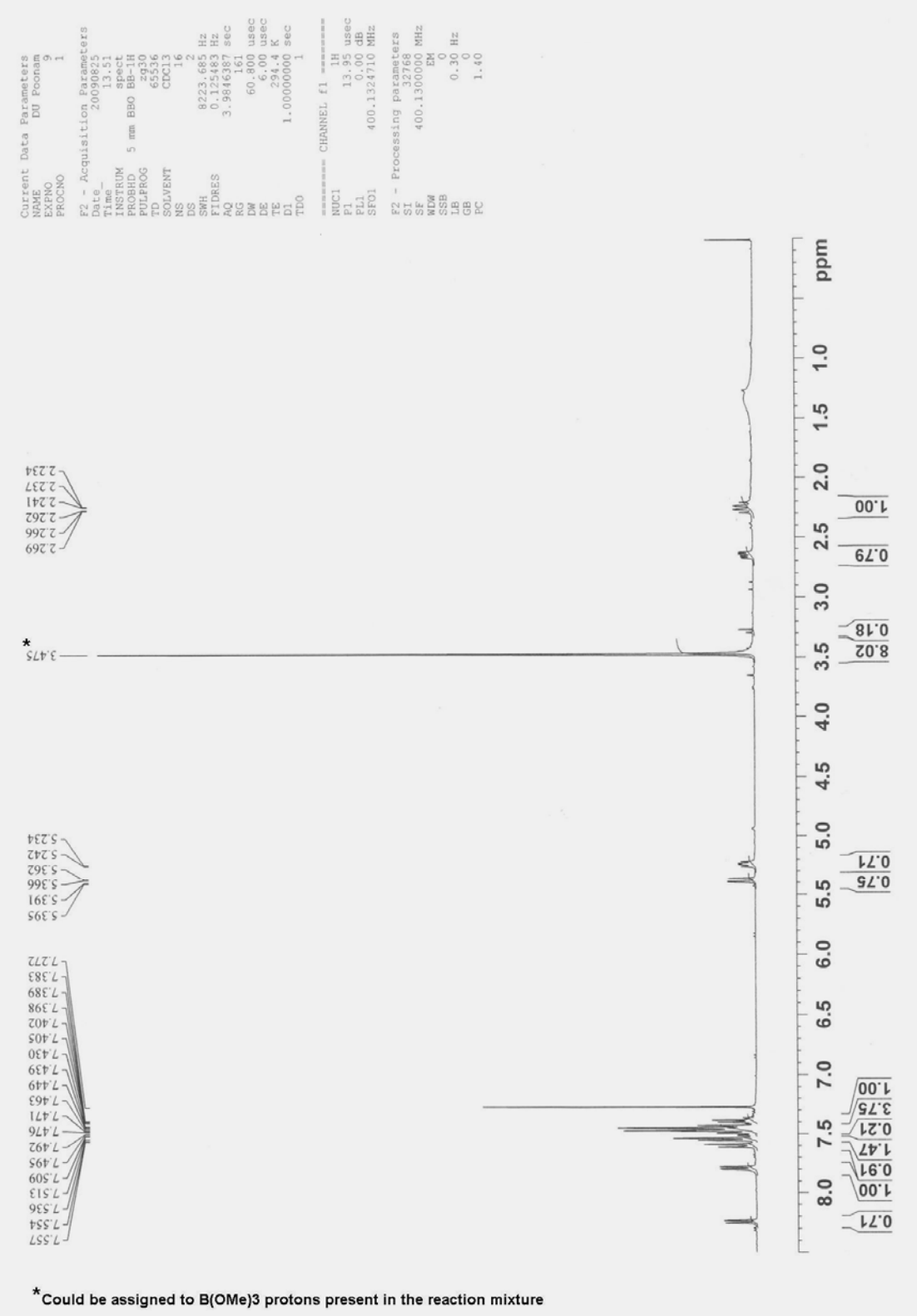


Fig. S37: $^{1}$H NMR spectrum of the reaction mixture of **2** with $NaBH_4$ in methanol




*Could be assigned to B(OMe)3 protons present in the reaction mixture

Fig. S38: $^{1}H$ NMR spectrum of the reaction mixture of **2** with $NaBH_4$ in methanol

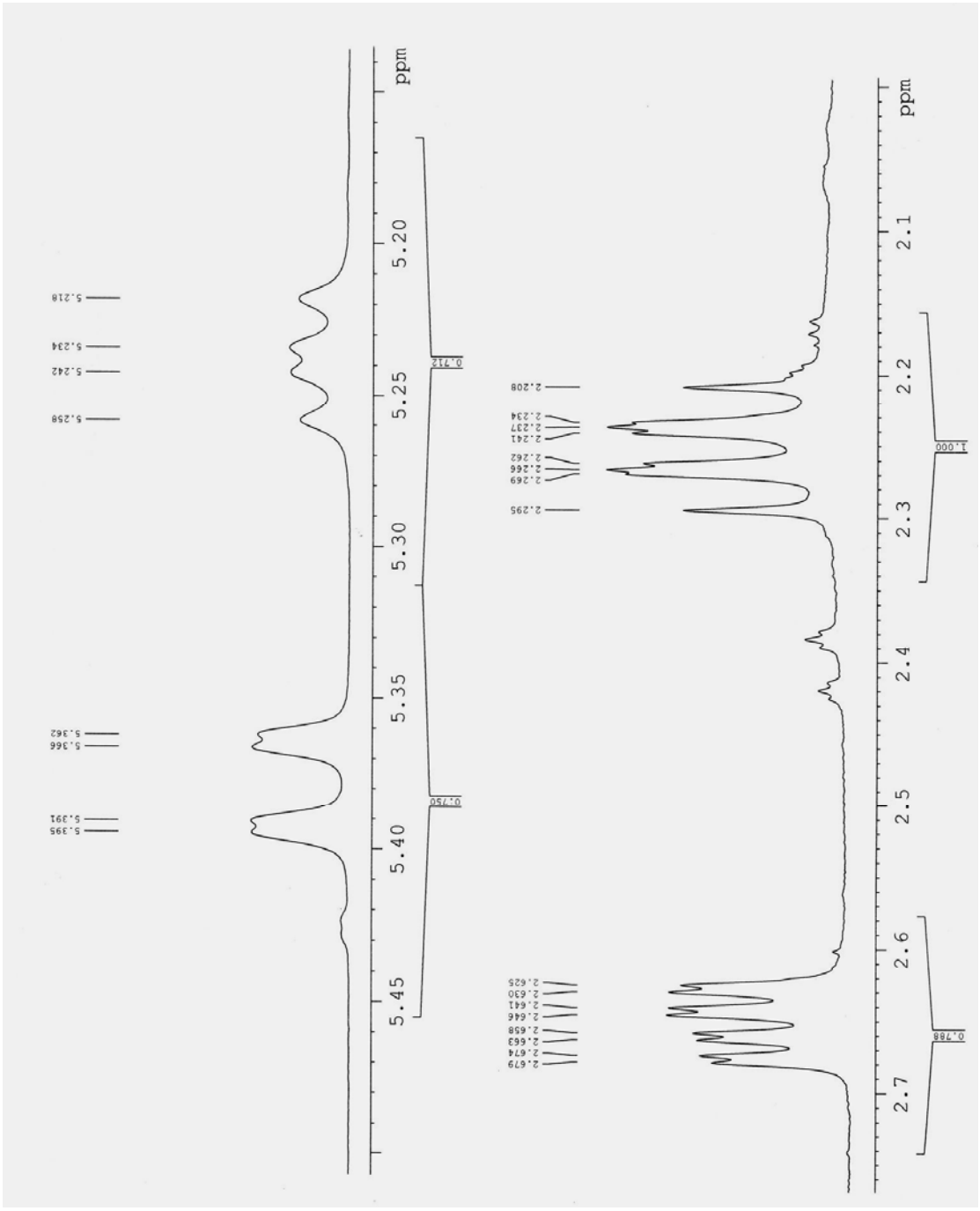


Fig. S39: UV-vis spectra of **3a** (a) on addition of $NaBH_4$ (b- i) at an interval of 1 min in methanol

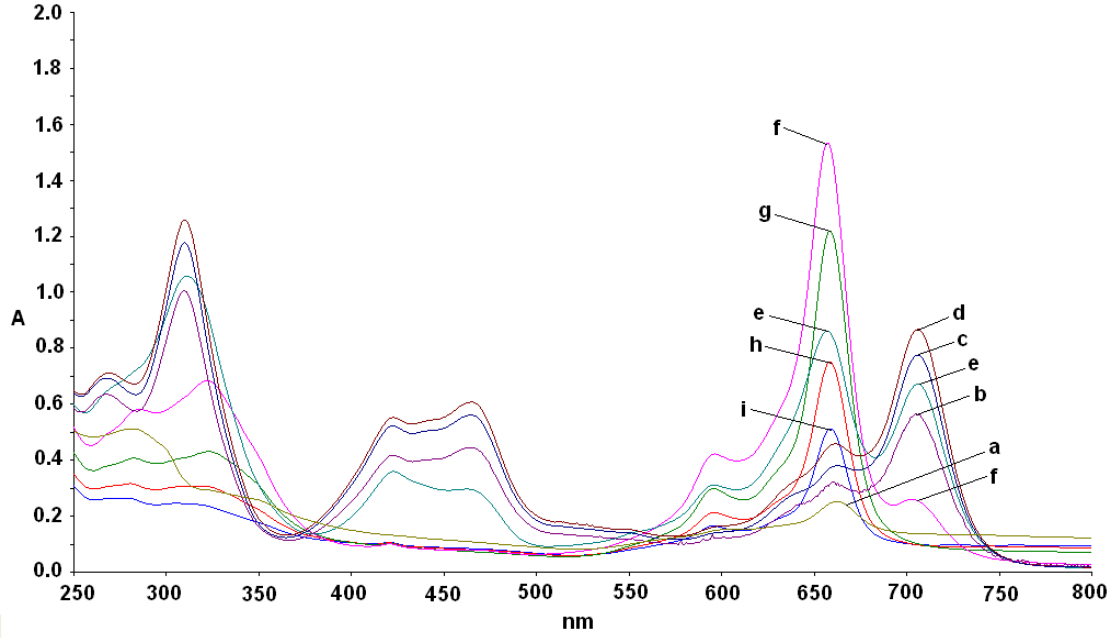



Fig. S40: UV-vis spectra of **3a** (a) on addition of $NaBH_4$ in propanol (b- n) at the time intervals of 1 min (a- b), 2 min (b- c and c- d), 6 min (d- e and e- f), 8 min (f- g and g- h), 10 min (h- i), 8 min (i- j), 10 min (j- k), 30 min (k- l), 10 min (l –m), 10 min (m- n).