

Supporting Information:

Suzuki Coupling Reaction of 1,6,7,12-Tetrabromoperylene Bisimide

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General Experimental Methods

¹H NMR and ¹³C NMR were measured with Bruker 300 MHz or 400 MHz spectrometers. Mass spectra were recorded on AEI-MS50-MS spectrometer for EI MS and Bruker BIFLEXIII spectrometer for MALDI-TOF-MS. Elemental analysis was performed on Carlo-Erba-1106 instrument. Infrared spectra were determined with Pekin-Elmer Tensor 27 spectrometer. Electronic absorption spectra were measured on a Jasco V570 UV-vis spectrophotometer. The photoluminescence spectra were recorded on Jasco FP-6600 spectrofluometer. 2-Ethylhexylamine, tetrakis(triphenylphosphine)palladium, cesium fluoride, and phenylboronic acid were purchased from Acros. Dehydrated 1,2-dimethoxyethane (DME), toluene, THF and N,N-dimethylformamide (DMF) were freshly distilled before reactions with common treatment methods. Fluorescence quantum yields were determined by the optically dilute method with Rhodamine B in ethanol solution as reference (quantum yield: 0.70, using an excitation wavelength of 510 nm).

Experimental Section

Synthesis of 1,6,7,12-Tetrabromoperylene-3,4,9,10-tetracarboxylic acid bisanhydride **2**

A mixture of 19.6 g (50 mmol) perylene-3,4,9,10-tetracarboxylic acid bisanhydride, 220 mL 98 wt% sulfuric acid and 40 mL fuming sulfuric acid was stirred at room temperature for 12 h. The mixture was then heated to 80 °C and 0.31 g I₂ (1.2 mmol) was added. Subsequently, 5.4 mL (16.8 g, 105 mmol, 2.1 equiv.) Br₂ was added dropwise over 8 h and the reaction mixture was heated for 24 h at 80 °C. Then 0.31 g I₂ (1.2 mmol) was added and the reaction temperature was raised to 100 °C. 5.4 mL (16.8 g, 105 mmol, 2.1 equiv.) Br₂ was added dropwise over 12 h and the reaction mixture was heated for an additional 80 h at 100 °C. After being cooled to room temperature, the excess bromine was removed by a gentle stream of N₂ gas, and 80 g of ice was added slowly. The resultant precipitate was filtered through G4 funnel, washed with 200 mL 86 % sulfuric acid and a large amount of water until the filtrate became neutral. The solid residue was dried in a vacuum at 120 °C for 8 h to give 34.1 g (96 %) of a red-brown powder. The crude product was used directly in the later reaction without further purification. Due to its insolubility in organic solvents, only MS was recorded. MS (EI): m/z 708 (M⁺).

Synthesis of N,N'-Di(2-ethylhexyl)-1,6,7,12-tetrabromoperylene-3,4,9,10-tetracarboxylic acid bisimide **3**

2-Ethylhexylamine (4.4 g, 34 mmol) was added to a mixture of 1,6,7,12-tetrabromoperylene-3,4,9,10-tetracarboxylic acid bisanhydride 4.0 g (5.6 mmol) and 100 mL propionic acid under N₂ atmosphere, the reaction mixture was stirred and heated at 140 °C for 4 h. After being cooled to room temperature, the solvent was removed by rotary evaporation, the crude product was purified by silica gel column chromatography with toluene as eluent to yield perylene bisimide product as a red-brown solid (5.0 g, 95%).

3: UV-vis (CHCl₃): [λ_{\max} nm (log ϵ)] 529 (4.52), 499 (4.38), 439 (4.11). FT-IR (KBr, cm⁻¹) ν 3055, 2958, 2927, 2859, 1705 (s, C=O), 1663 (s, C=O), 1582, 1436, 1411, 1384, 1363, 1278, 1232, 1180, 1154, 925, 804, 646. MS (MALDI-TOF): m/z 930.3 (M⁺). ¹H NMR (400 MHz, CDCl₃, 25 °C): δ = 8.83 (s, 4H, perylene-H), 4.10-4.20 (m, 4H, N-CH₂-), 1.94 (m, 2H, -CH-), 1.33-1.41 (m, 16H, -CH₂-), 0.95 (m, 12H, -CH₃) ppm. ¹³C NMR (100 MHz, CDCl₃, 25 °C): δ = 162.5 (C=O), 136.2, 131.6, 131.4, 124.0, 122.7, 44.6, 38.0, 30.7, 28.6, 24.0, 23.1, 14.2, 10.6 ppm.

Elemental analysis (%), calcd. for (C₄₀H₃₈Br₄N₂O₄): C, 51.64; H, 4.12; N, 3.01; Found: C, 51.50; H, 4.24; N, 2.92. Fluorescence (CH₂Cl₂): λ_{max} 566 nm, fluorescence quantum yield Φ_f 0.62.

Typical procedure of the coupling reaction with condition D.

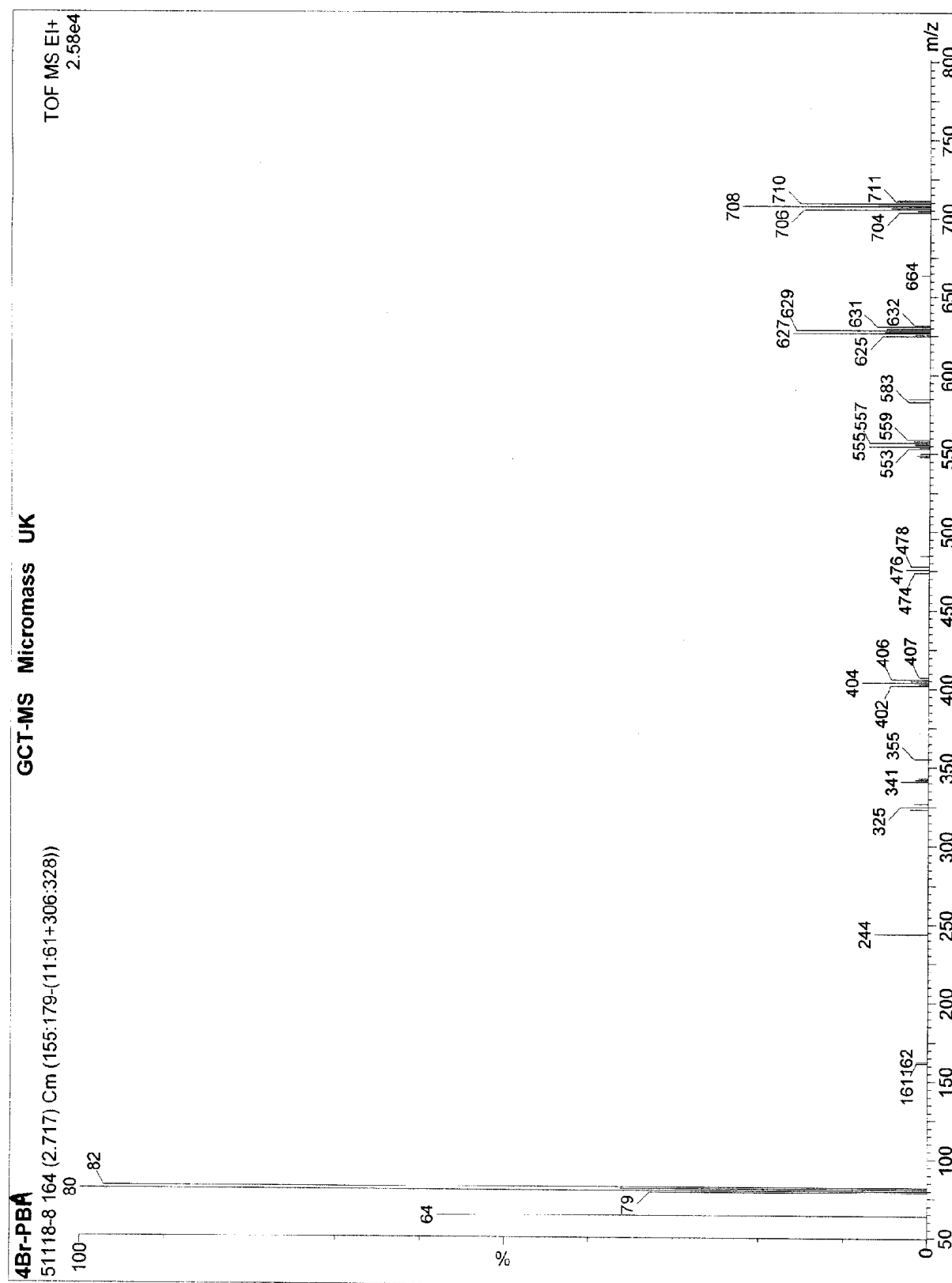
A three-neck flask was charged with N,N'-di(2-ethylhexyl)-1,6,7,12-tetrabromoperylene-3,4,9,10-tetracarboxylic acid bisimide (420 mg, 0.45 mmol, 1 equiv.), phenylboronic acid (330 mg, 2.7 mmol, 6 equiv.), cesium fluoride (550 mg, 3.6 mmol, 8 equiv.), and silver(I) oxide (460 mg, 2.0 mmol, 4.4 equiv.), and the flask was evacuated and backfilled with nitrogen two times. Tetrakis(triphenylphosphine)palladium (52 mg, 0.045 mmol, 10% equiv.) was added with a gentle flow of nitrogen. The flask was evacuated and backfilled with nitrogen three times. Subsequently, DME (15 mL) was added by syringe. The flask was cooled to -78 °C and further evacuated and backfilled with nitrogen three times. Subsequently, the reaction mixture was stirred at 80°C for 24 h with vigorous stirring. After being cooled to room temperature, the crude product was purified by silica gel column chromatography with toluene as eluent. The first band was collected, removal of the solvent yielded 1,6,7,12-tetraphenylperylene bisimide as a blue-purple solid (195 mg, 47%). The second band was collected and characterized to be 1,6,7-triphenyl perylene bisimide as a red solid (126 mg, 33%).

N,N'-Di(2-ethylhexyl)-1,6,7,12-tetraphenylperylene-3,4,9,10-tetracarboxylic acid bisimide 4:

UV-vis (CHCl₃): [λ_{max} nm (log ϵ)] 603 (4.36), 568 (4.24), 449 (4.16). FT-IR (KBr, cm⁻¹) ν 3058, 2958, 2929, 2861, 1699 (s, C=O), 1660 (s, C=O), 1592, 1491, 1443, 1410, 1317, 1268, 1226, 1184, 1150, 1034, 912, 732, 697. MS (MALDI-TOF): m/z 919.3 (M⁺). ¹H NMR (300 MHz, CDCl₃, 25 °C): δ = 8.30 (s, 4H, perylene-H), 7.20 (m, 4H, Ph-H), 7.08 (s, br, 8H, Ph-H), 6.70 (m, 8H, Ph-H), 4.15 (d, 4H, J = 6.69 Hz, N-CH₂-), 1.98 (s, br, 2H, -CH-), 1.25–1.46 (m, br, 16H, -CH₂-), 0.96 (m, 12H, -CH₃) ppm. ¹³C NMR (75 MHz, CDCl₃, 25 °C): δ = 164.6 (C=O), 143.1, 140.9, 134.2, 132.3, 131.7, 130.8, 129.2, 128.0, 126.5, 122.7, 44.8, 38.6, 31.4, 31.2, 29.5, 29.1, 24.7, 24.6, 23.6, 14.7, 11.3, 11.0 ppm. Elemental analysis (%), calcd. for (C₆₄H₅₈N₂O₄): C, 83.63; H, 6.36; N, 3.05; Found: C, 83.17; H, 6.38; N, 3.22. Fluorescence (CH₂Cl₂): λ_{max} 665 nm, fluorescence quantum yield Φ_f 0.29.

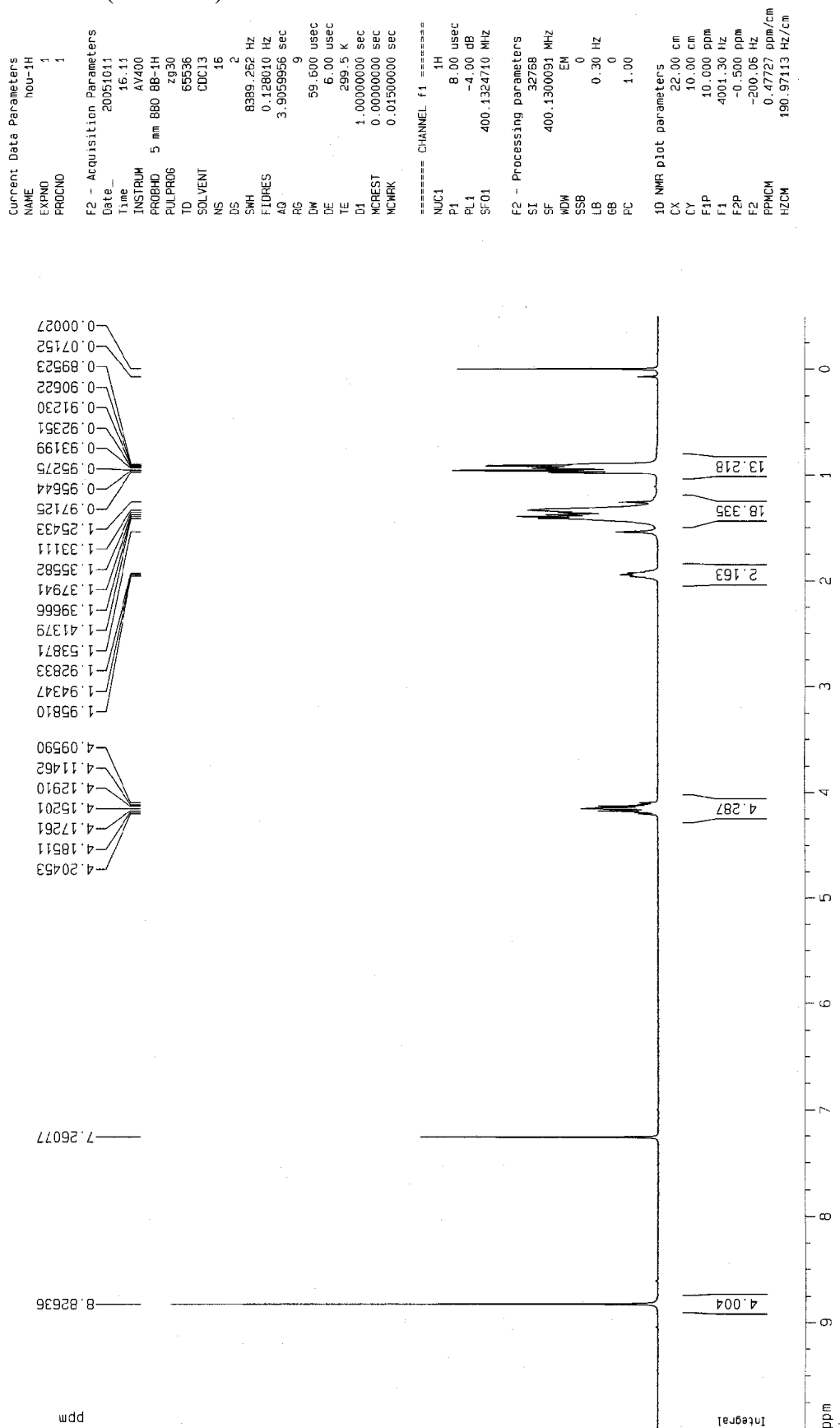
N,N'-Di(2-ethylhexyl)-1,6,7-triphenylperylene-3,4,9,10-tetracarboxylic acid bisimide 5:

UV-vis (CHCl_3): [λ_{max} nm (log ϵ)] 579 (4.40), 549 (4.31), 428 (4.04). FT-IR (KBr, cm^{-1}) ν 3058, 2958, 2929, 2861, 1699 (s, C=O), 1660 (s, C=O), 1592, 1490, 1449, 1413, 1347, 1303, 1223, 1184, 1150, 912, 733, 696. MS (MALDI-TOF): m/z 842.5 (M^+). ^1H NMR (300 MHz, CDCl_3 , 25 $^\circ\text{C}$): δ = 8.65 (s, 1H, perylene-H), 8.28 (d, 2H, J = 5.91 Hz, perylene-H), 8.16 (d, 1H, J = 7.86 Hz, perylene-H), 7.73 (d, 1H, J = 7.89 Hz, perylene-H), 7.48 (s, br, 2H, Ph-H), 6.90–7.30 (m, br, 9H, Ph-H), 6.80 (s, br, 2H, Ph-H), 6.61 (d, 2H, J = 6.72 Hz, Ph-H), 4.11–4.17 (m, 4H, N- CH_2 -), 1.95 (s, br, 2H, -CH-), 1.30–1.50 (s, br, 16H, - CH_2 -), 0.91 (t, 12H, - CH_3) ppm. ^{13}C NMR (75 MHz, CDCl_3 , 25 $^\circ\text{C}$): δ = 164.6 (C=O), 164.5 (C=O), 143.8, 143.2, 142.6, 141.9, 141.2, 140.7, 135.2, 135.0, 134.7, 133.1, 132.8, 132.4, 130.9, 130.7, 130.6, 130.4, 130.3, 130.1, 129.7, 129.6, 129.1, 128.7, 128.6, 128.0, 127.6, 123.0, 122.9, 122.6, 122.0, 44.7, 38.5, 31.2, 29.4, 29.1, 24.7, 24.5, 23.6, 14.6, 11.3, 11.2, 11.1 ppm. Elemental analysis (%), calcd. for ($\text{C}_{58}\text{H}_{54}\text{N}_2\text{O}_4$): C, 82.64; H, 6.46; N, 3.32; Found: C, 82.30; H, 6.41; N, 3.43. Fluorescence (CH_2Cl_2): λ_{max} 642 nm, fluorescence quantum yield Φ_f 0.39.

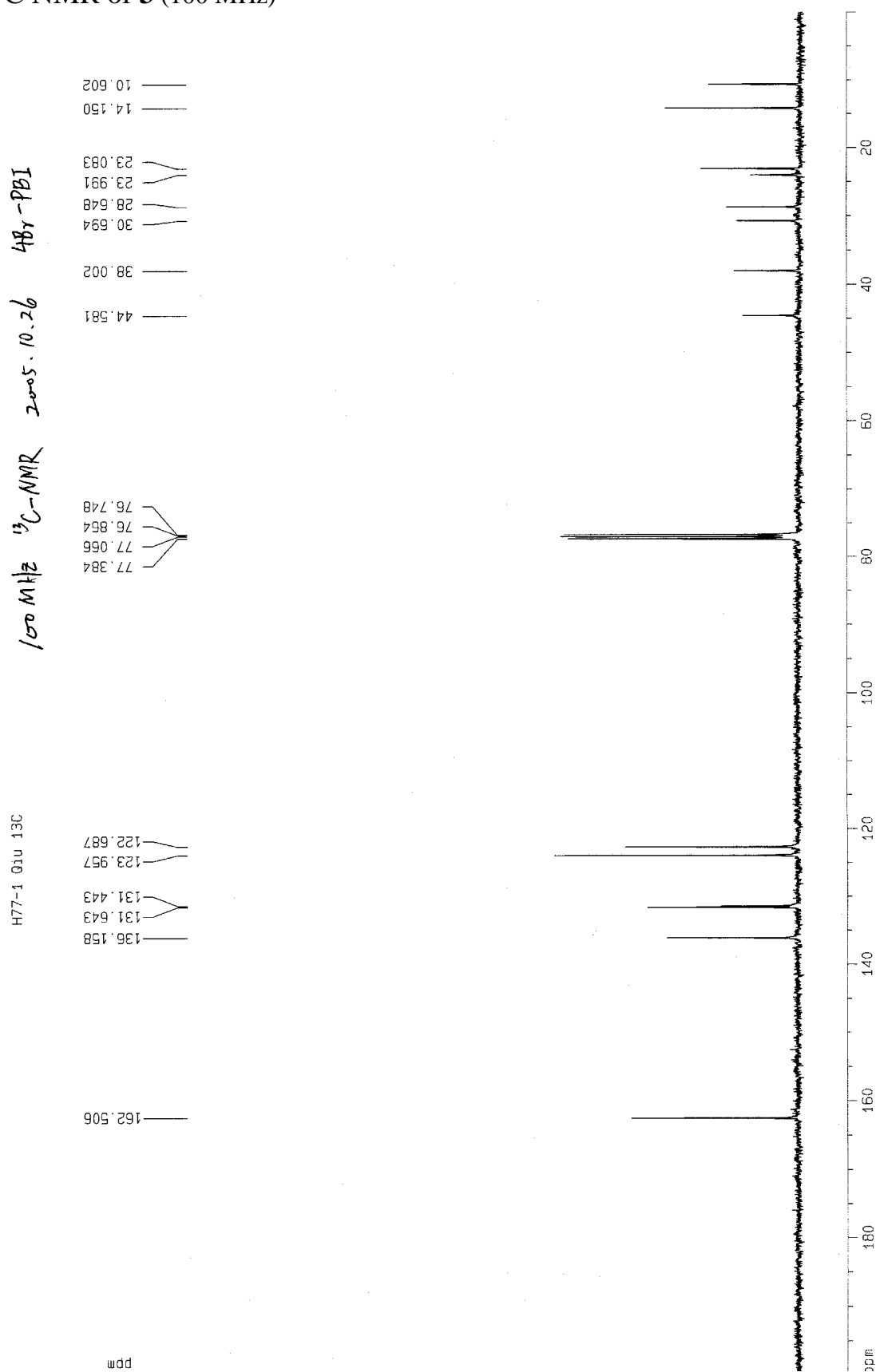


¹H NMR of **3** (400 MHz)

05-10-11-qiu-H77-1

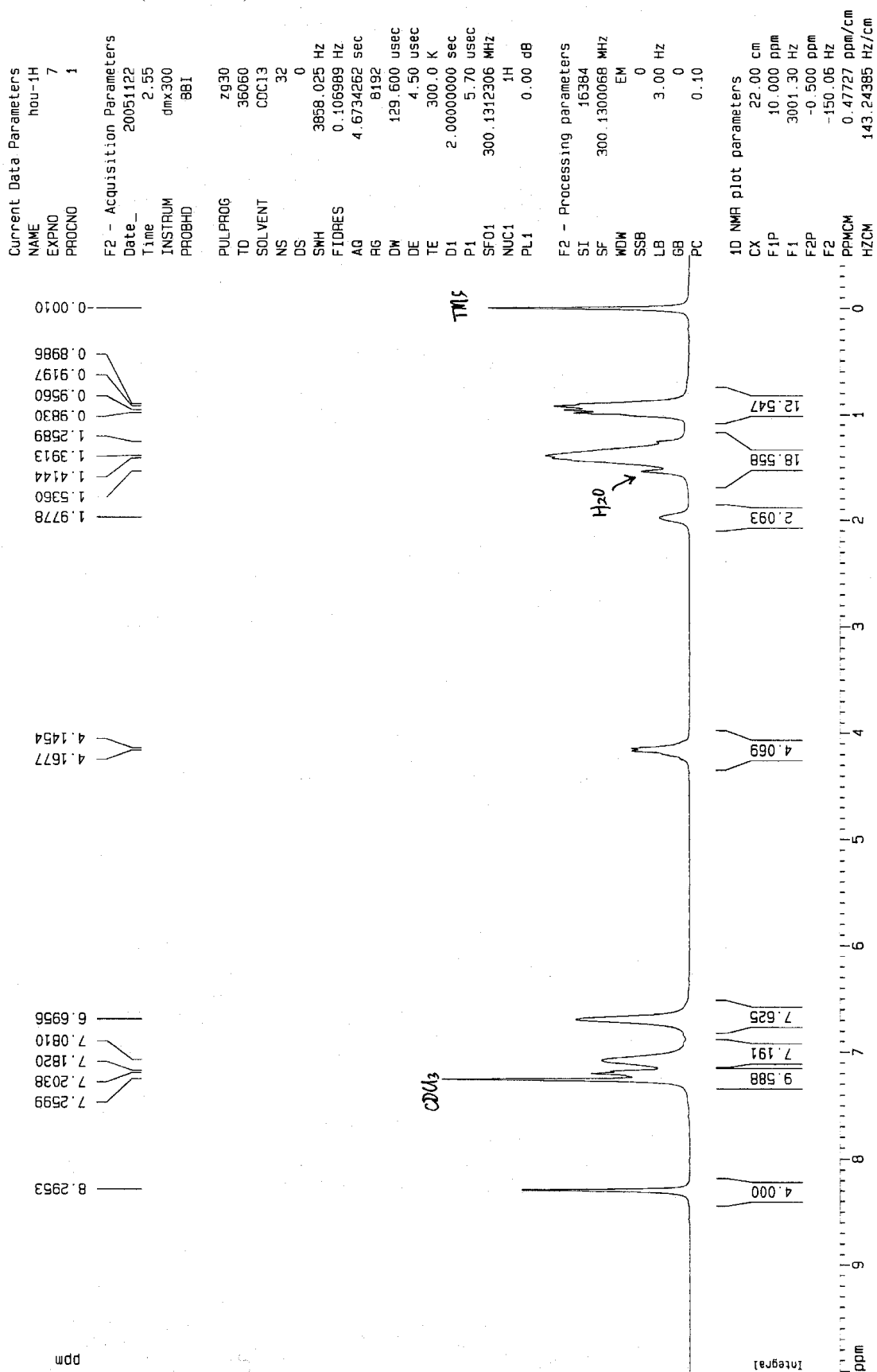


^{13}C NMR of **3** (100 MHz)



¹H NMR H85-2 Qiu

¹H NMR of 4 (300 MHz)



¹³C NMR of **4** (75 MHz)

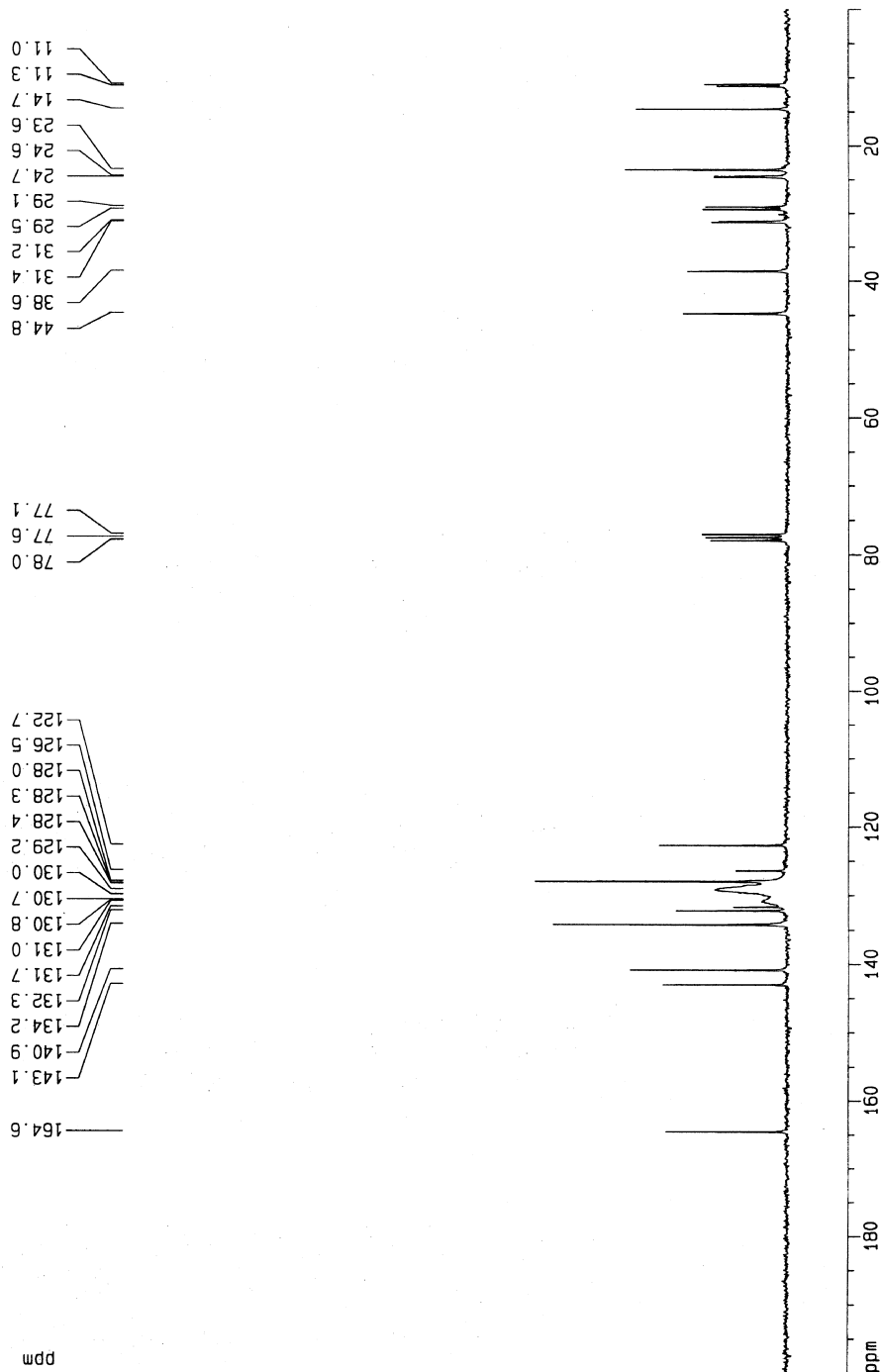
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 F2 0.00 Hz
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¹³C NMR of **4** (75 MHz, 110 ppm – 180 ppm)

2005.11.23 13C NMR H85-2 Qiu

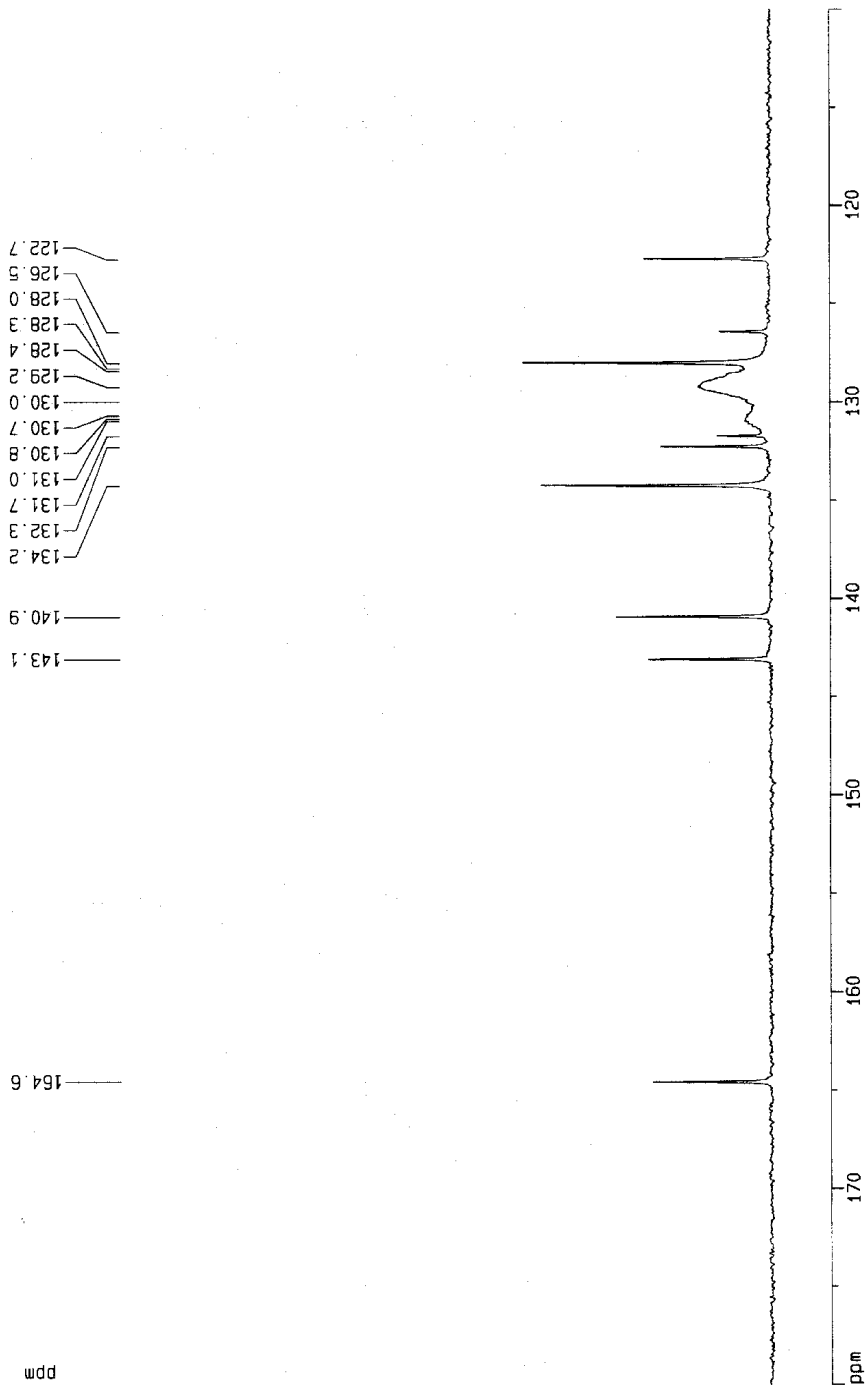
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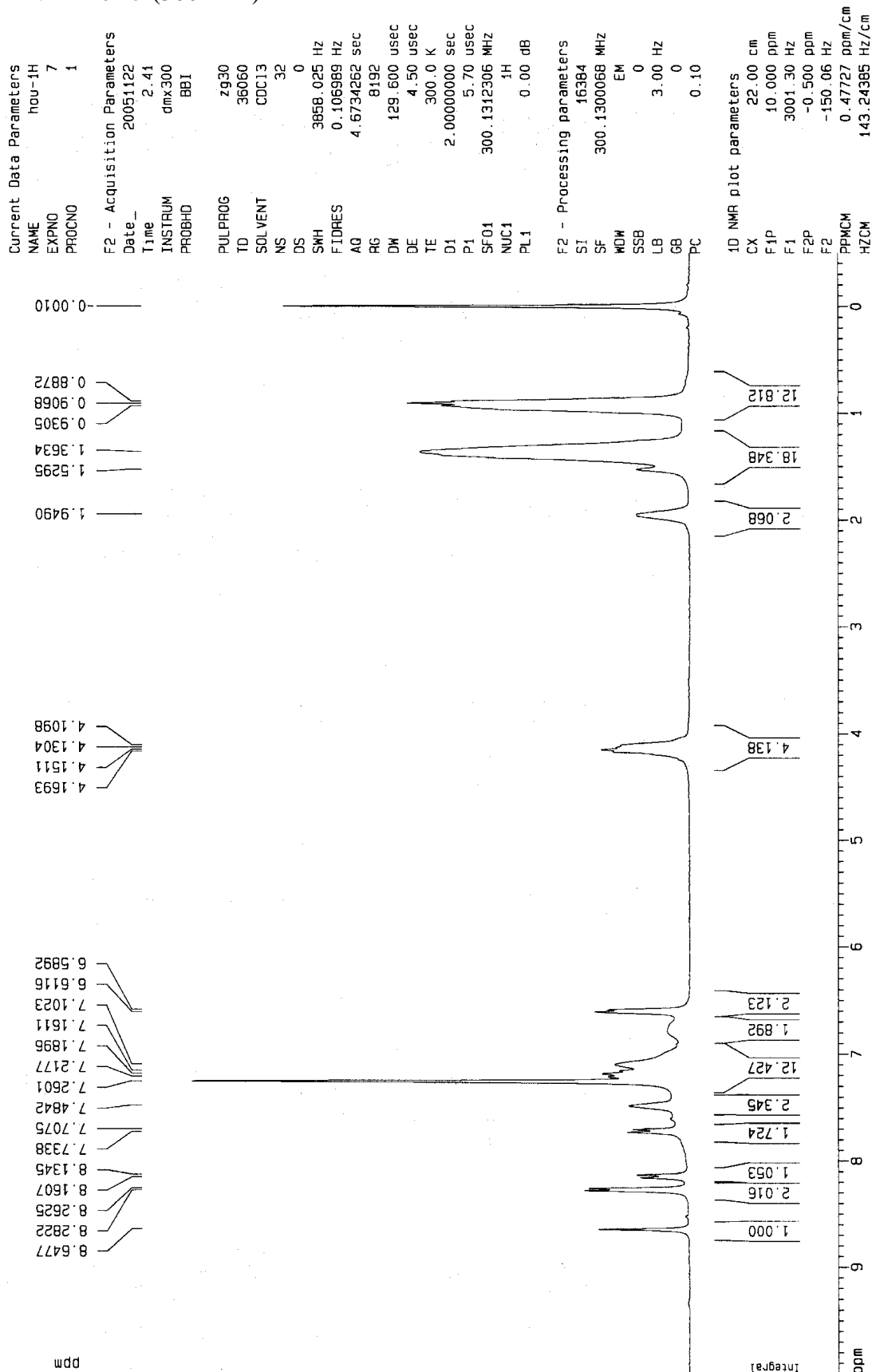
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¹H NMR H85-3 Qiu

¹H NMR of **5** (300MHz)



2005.11.23 13C NMR H85-3 Qiu

¹³C NMR of **5** (75 MHz)

Current Data Parameters
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F2 - Processing parameters

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1D NMR plot parameters
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F1 15093.54 Hz
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F2 0.00 Hz
PPMCM 9.30233 ppm/cm
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