SUPPORTING INFORMATION

Overcoming Regioselectivity Issues Inherent in BisTröger's Base Preparation

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CONTENTS

Experimental part

The combination of g-HMBC, g-HSQC, g-COSY and 1D NOESY spectra were used for assignment of chemical shifts in ^{1}H and ^{13}C NMR spectra. The geometry parameters from computer model (geometry optimization by semiempirical PM3 method done by HyperChem 7.5 was used) were helpful in case of bisTB derivatives.[3]

*3,6-dinitrobenzene-1,2-dioic acid (**2**).*[10] 1,5-Dinitronaphthalene (20.0 g, 92 mmol) was treated with mixture of fuming nitric acid (6 mL) and concentrate sulfuric acid (100 mL). The reaction mixture was stirred and kept under 30 °C by water cooling bath for 3 h. The mixture was poured onto ice. Precipitated 1,4,5-trinitronaphthalene was filtered off and washed with water, and dried *in vacuo* (22.1 g, 91 %). Obtained trinitronaphthalene was treated with fuming nitric acid (100 mL) and water (10 ml) at 120-130 °C for 24 h. The mixture was cooled to room temperature and diluted with water (100 mL). The precipitated 1,4,5,7-tetranitronaphthalene was filtered off and washed with water (12.6 g, 48.7 %). The filtrate was evaporated to dryness *in vacuo* and acid **2** was obtained and purified by crystallization from diethylether/petrolether 11.7 g (54 %). *1,4,5-trinitronaphthalene*: ^{1}H NMR ($CDCl_3$): 8.67 (1H, d, 8.8), 8.43 (1H, d, 7.7), 8.36 (1H, d, 8.3), 8.28 (1H, d, 8.3), 7.97 (1H, t, 8.3). *3,6-dinitrobenzene-1,2-dioic acid (**2**)*: ^{1}H NMR (DMSO-d_6): 8.39 (2H, s), 3.79 (2H, bs). ^{13}C APT NMR (DMSO-d_6): 164.05 (C), 148.91 (C), 129.59 (C), 127.11 (CH).

*4,6-dinitrobenzene-1,3-dioic acid (**9**).*[15] 2,4-Dimethyl-1-nitrobenzene (40 g, 0.26 mol) was treated with fuming nitric acid (100 mL) at room temperature for 1 h. The mixture was poured onto ice. The precipitate was filtered off and well washed with water. The crude product was treated with boiling ethanol and insoluble 2,4-dimethyl-1,3,5-trinitrobenzene was filtered off. Filtrate was allowed to cool down and 1,3-dimethyl-4,6-dinitrobenzene precipitated (26.3 g, 51 %). The mater liquors contained mainly 1,5-dimethyl-2,4-dinitrobenzene. 1,3-Dimethyl-4,6-dinitrobenzene (10 g, 51 mmol) was dissolved in sulfuric acid (75 mL) was carefully added into solution of CrO_3 (25 g) in sulfuric acid (75 mL) at -10 °C. The mixture was stirred at under -10 °C for 3 h and at room temperature for 2 h. The mixture was poured into water with ice. Precipitated 5-methyl-2,4-dinitrobenzoic acid was filtered off and washed with water. The filtrate was

extracted with diethylether. The organic layer was evaporated to dryness and obtained crude product **9** (6.66 g, 51 %) was purified by crystallization of diethylether/petrolether. *2,4-dimethyl-1,3,5-trinitrobenzene*: ^{1}H NMR (acetone-d_6): 8.81 (1H, s), 2.56 (1H, s). *1,3-dimethyl-4,6-dinitrobenzene*: ^{1}H NMR (acetone-d_6): 8.64 (1H, s), 7.67 (1H,s), 2.67 (6H, s). ^{13}C APT NMR (Acetone-d_6, it is good to increase the relaxation time from common 1 s to 20 s): 148.42 (C), 140.34 (C), 138.90 (CH), 122.76 (CH), 20.92 (C). *1,5-dimethyl-2,4-dinitrobenzene*: ^{1}H NMR (acetone-d_6): 8.09 (1H, d, 8.5), 7.60 (1H, d, 8.5), 2.42 (3H, s), 2.40 (3H, s). *5-methyl-2,4-dinitrobenzoic acid*: ^{1}H NMR (DMSO-d_6): 8.65 (1H, s), 8.01 (1H, s), 4.07 (1H, bs), 2.63 (3H, s). *4,6-dinitrobenzene-1,3-dioic acid (**9**)*: ^{1}H NMR (DMSO-d_6): 8.74 (1H, s), 8.29 (1H, s), 5.92 (2H, bs). ^{13}C APT NMR (DMSO-d_6): 163.84 (C), 148.82 (C), 131.82 (CH), 130.66 (C), 120.28 (CH).

*Preparation of diamide **3***. Dinitrophthalic acid **2** (5.00 g, 19.5 mmol) was treated with $SOCl_2$ (60 mL) at 80 °C for 2 h. Resulted solution was evaporated *in vacuo* to dryness. The residual solid (probably 3,6-dinitrobenzene-1,2-dioyl anhydride) was dissolved in ethyl acetate (20 mL), and solution of *p*-anisidine (2.40 g, 19.5 mmol) in ethyl acetate (20 mL) was added. The mixture was stirred at room temperature for 2 h. Evaporation to dryness *in vacuo* gave 7.05 g (100 %) of monoamide **4** was obtained. Monoamide **4** (2.00 g, 5.5 mmol) was dissolved in THF (60 mL), and solution of $(COCl)_2$ (0.70 g, 5.5 mmol) in THF (80 mL) in THF (80 mL) was added, followed by addition of 1 mL of DMF. After 10 min at rt the solution of *p*-anisidine (1.36 g, 11.0 mmol) was added, followed by addition of Et_3N (1.12 g, 11.0 mmol) in THF (50 mL). The reaction mixture was stirred 2 h at room temperature. The resulted solution was evaporated *in vacuo* to oily residue, and diluted HCl (1:10, 30 mL) was added. The precipitated solid was filtered off and washed with diluted HCl (1:30), water, and chloroform, and dried *in vacuo* to obtain 1.74 g (67 %) of diamide **3**. *N^1,N^2-bis(4-methoxyphenyl)-3,6-dinitrobenzene-1,2-diamide (**3**)*: ^{1}H NMR (DMSO-d_6): 10.60 (2H, s), 8.48 (2H, s), 7.40 (4H, d, 9.1), 6.89 (4H, d, 9.1), 3.72 (6H, s). ^{13}C APT NMR (DMSO-d_6): 159.98 (C), 155.94 (C), 148.60 (C), 132.69 (C), 131.30 (C), 121.37 (CH), 114.46 (CH), 113.98 (CH), 55.22 (CH_3). *2-(4-methoxyphenylcarbamoyl)-3,6-dinitrobenzoic acid (**4**)*: ^{1}H NMR (DMSO-d_6): 10.68 (1H, s), 8.45 (1H, d, 8.8), 8.36 (1H, d, 8.8), 7.45 (2H, d, 9.1), 6.94 (2H, d, 9.1), 3.74 (3H, s). ^{13}C APT NMR (DMSO-d_6): 163.95 (C), 160.06 (C), 155.98 (C), 149.47 (C), 148.29 (C), 132.42 (C), 131.46 (C), 129.94 (C), 127.29 (CH), 126.21 (CH), 121.24 (CH), 114.07 (CH), 55.26 (CH_3). The possible by-product *2-(4-methoxyphenyl)-*

*4,7-dinitroisoindoline-1,3-dione (**5a**)*: ^{1}H NMR ($CDCl_3$): 8.19 (2H, s), 7.30 (2H, d, 9.1), 7.01 (2H, d, 9.1), 3.85 (3H, s).

*Preparations of diamides **10a-e***. 4,6-dinitrobenzene-1,3-dioic acid (**2**, 0.69 g, 2.7 mmol) was treated with thionyl chloride (15 mL) at 75 °C for 3 h. Resulted solution was evaporated *in vacuo* to dryness. The oily residue (4,6-dinitrobenzene-1,3-dioyl dichloride) was dissolved in ethyl acetate (20 mL) and added into solution of *p*-anisidine (1.00 g, 8.1 mmol) and triethylamine (1.07 g, 10.6 mmol) in ethyl acetate (20 mL). The reaction mixture was stirred at rt for 3 h. The resulted solution was evaporated *in vacuo* and diluted with HCl (1:10, 50 mL). The precipitated product was filtered off and washed with diluted HCl (1:10), water and dichlormethane, and dried *in vacuo* to gave 1.05 g (83 %) of **10a** was obtained. *N^1,N^3-bis(4-methoxyphenyl)-4,6-dinitrobenzene-1,3-diamide (**10a**)*: ^{1}H NMR (DMSO-d_6): 10.74 (2H, s), 8.83 (1H, s), 8.26 (1H, s), 7.56 (4H, d, 8.8), 6.96 (4H, d, 8.8), 3.75 (6H, s). ^{13}C APT NMR (DMSO-d_6): 161.44 (C), 156.22 (C), 146.64 (C), 136.38 (C), 131.41 (C), 130.57 (CH), 121.68 (CH), 121.09 (CH), 114.21 (CH), 55.37 (CH_3). *N^1,N^3-di(naphtalen-2-yl)-4,6-dinitrobenzene-1,3-diamide (**10b**)*: Analogously to procedure for **10a**, diacid **2** (0.72 g, 2.81 mmol), 2-aminonaphtalene (1.00 g, 8.12 mmol) and triethylamine (0.85 g, 8.40 mmol) gave 1.12 g (79 %) of **10b**. ^{1}H NMR (DMSO-d_6): 11.16 (2H, s), 8.92 (1H, s), 8.47 (1H, s), 8.38 (2H, d, 1.7) 7.95 (2H, d, 9.1), 7.91 (2H, d, 8.0), 7.90 (2H d, 7.4), 7.66 (2H, dd, 8.8, 1.7), 7.50 (4H, m). ^{13}C APT NMR (DMSO-d_6): 161.93 (C), 146.59 (C), 136.16 (C), 135.87 (C), 133.24 (C), 130.74 (CH), 130.28 (C), 128.68 (CH), 127.55 (CH), 127.53 (CH), 126.68 (CH), 125.21 (CH), 121.19 (CH), 120.08 (CH), 116.36 (CH). *N^1,N^3-di(anthracen-2-yl)-4,6-dinitrobenzene-1,3-diamide (**10c**)*: Analogously to procedure for **10a**, diacid **2** (0.53 g, 2.07 mmol), 2-aminoanthracene (1.00 g, 5.18 mmol) and triethylamine (0.63 g, 6.23 mmol) gave 1.14 g (91 %) of **10c**. Due to low solubility of the amine ethyl acetate with DMF (2:1) was used as reaction solvent. ^{1}H NMR (DMSO-d_6): 11.25 (2H, s), 8.95 (1H, s), 8.60 (2H, s), 8.56 (4H, s), 8.53 (1H, s), 8.14 (2H, d, 9.1), 8.07 (4H, m), 7.66 (2H, d, 9.4), 7.51 (4H, m). ^{13}C APT NMR (DMSO-d_6): 162.04 (C), 146.66 (C), 136.06 (C), 135.35 (C), 131.77 (C), 131.29 (C), 130.97 (CH), 130.74 (C), 129.17 (CH), 128.81 (C), 128.10 (CH), 127.78 (CH), 126.02 (CH), 125.80 (CH), 125.50 (CH), 125.28 (CH), 121.22(CH), 120.82 (CH), 115.37 (CH). *N^1,N^3-di(fluoren-2-yl)-4,6-dinitrobenzene-1,3-diamide (**10d**)*: Analogously to procedure for **10a**, diacid **2** (0.60 g, 2.34 mmol), 2-aminofluoren (0.93 g, 5.13 mmol) and triethylamine (0.68 g, 6.72 mmol) gave

1.28 g (94 %) of **10d**. ^{1}H NMR (DMSO-d_6): 11.01 (2H, s), 8.90 (s, 1H), 8.38 (s, 1H), 8.01 (2H, s), 7.91 (2H, d, 8.3), 7.86 (2H, d, 7.4), 7.61 (2H, d, 8.5), 7.58 (2H, d, 7.4), 7.34 (4H, m), 3.96 (4H, s). ^{13}C APT NMR (DMSO-d_6): 161.62 (C), 146.54 (C), 143.94 (C), 142.99 (C), 140.76 (C), 137.50 (C), 137.25 (C), 136.26 (C), 130.66 (CH), 126.79 (CH), 126.43 (CH), 125.08 (CH), 121.15 (CH), 120.32 (CH), 119.71 (CH), 118.70 (CH), 116.70 (CH), 36.56 (CH_2). *N^1,N^3-di(pyrrene-1-yl)-4,6-dinitrobenzene-1,3-diamide (**10e**)*: Analogously to procedure for **10a**, diacid **2** (0.47 g, 1.84 mmol), 1-aminopyrrene (1.00 g, 4.60 mmol) and triethylamine (0.56 g, 5.53 mmol) gave 1.05 g (87 %) of **10e**. ^{1}H NMR (DMSO-d_6): 11.41 (2H, s), 9.05 (s, 1H), 8.87 (s, 1H), 8.49-8.26 (12H, m), 8.23 (4H, s), 8.12 (2H, t, 7.7). ^{13}C APT NMR (DMSO-d_6): 163.31 (C), 146.52 (C), 136.97 (C), 131.30 (CH), 130.79 (C), 130.47 (C), 130.48 (C), 129.07 (C), 127.58 (CH), 127.24 (CH), 127.16 (CH), 126.59 (CH), 125.55 (CH), 125.28 (CH), 125.12 (CH), 124.62 (C), 124.38 (C), 123.77 (C), 123.64 (CH), 122.34 (CH), 121.17 (CH).

*Preparation of aminoamides **7** and **11a-e***: Compound **3** (62 mg, 0.13 mmol) and catalyst (5% Pd/C, 32 mg) were added into mixture of methanol (2 mL) and DMF (5 mL). The reaction mixture was stirred under hydrogen atmosfere over night. The catalyst was filtered off, and the filtrate was evaporated to dryness *in vacuo* to give 54 mg of **7** (92 %). The reaction temperature as well as the temperature during work-up procedures, has to be keep at least less than 40 °C, else aminoimide **5b** is formed. *3,6-diamino-N^1,N^2-bis(4-methoxyphenyl)-benzene-1,2-diamide (**7**)*: ^{1}H NMR (DMSO-d_6): 9.68 (2H, s), 7.42 (4H, d, 8.8), 6.79 (4H, d, 8.8), 6.67 (2H, s), 4.60 (4H, bs), 3.68 (6H, s). *4,7-diamino-2-(4-methoxyphenyl)isoindoline-1,3-dione (**5b**)*: ^{1}H NMR (DMSO-d_6): 7.27 (2H, d, 9.1), 7.03 (2H, d, 9.1), 6.91 (2H, s), 5.91 (4H, bs), 3.80 (3H, s). ^{13}C APT NMR (DMSO-d_6): 167.88 (C), 158.31 (C), 138.95 (C), 128.46 (CH), 125.68 (CH), 125.00 (C), 113.96 (CH), 106.40 (C), 55.33 (CH_3). *4,6-diamino-N^1,N^3-bis(4-methoxyphenyl)benzene-1,3-diamide (**11a**)*: Analogously to procedure for **7**, the stirring of nitroamide **10a** (0.53 g, 1.14 mmol) in 20 mL of methanol-DMF (1:1) with catalyst (5% Pd/C, 100 mg) under hydrogen atmosphere gave 0.44 g of **11a** (95 %). ^{1}H NMR (DMSO-d_6): 9.66 (2H, s), 8.04 (1H, s), 7.59 (4H, d, 8.5), 6.91 (4H, d, 8.5), 6.70 (4H, bs), 5.92 (1H, s), 3.74 (6H, s). ^{13}C APT NMR (DMSO-d_6): 167.17 (C), 155.12 (C), 152.99 (C), 132.50 (C), 131.22 (CH), 122.02 (CH), 113.64 (CH), 104.71 (C), 98.60 (CH), 55.14 (CH_3). *4,6-diamino-N^1,N^3-di(naphtalen-2-yl)benzene-1,3-diamide (**11b**)*: Analogously to procedure for **11a**, 0.50 g (0.99 mmol) of **10b** and 0.20 g of catalyst (2 days) gave

0.39 g of **11b** (89%). ^{1}H NMR (DMSO-d_6): 10.02 (2H, s), 8.34 (2H, s), 8.21 (1H, s), 7.86 (6H, m), 7.44 (4H, m), 6.80 (4H, bs), 5.97 (1H, s). ^{13}C APT NMR (DMSO-d_6): 167.66 (C), 153.34 (C), 137.30 (C), 133.45 (C), 132.01 (CH), 129.65 (C), 127.97 (CH), 127.44 (CH), 127.24 (CH) 126.28 (CH), 124.43 (CH), 121.23 (CH), 116.02 (CH), 104.62 (C), 98.53 (CH). *4,6-diamino-N^1,N^3-di(anthracen-2-yl)benzene-1,3-diamide (**11c**)*: Analogously to procedure for **11a**, 0.30 g (0.50 mmol) of **10c** and 0.10 g of catalyst (3 days) gave 0.20 g of **11c** (74 %). ^{1}H NMR (DMSO-d_6): 9.77 (2H, s), 8.52 (4H, m), 8.43 (s, 1H), 8.31-7.84 (14H, m), 7.50 (4H, bs), 6.50 (1H, s). *4,6-diamino-N^1,N^3-di(fluoren-2-yl)benzene-1,3-diamide (**11d**)*: Analogously to procedure for **11a**, 0.30 g (0.51 mmol) of **10d** and 0.15 g of catalyst (3 days) gave 0.20 g of **11d** (72 %). ^{1}H NMR (DMSO-d_6): 9.89 (2H, s), 8.13 (1H, s), 8.01 (2H, s), 7.84 (2H, d, 7.9), 7.82 (2H, d, 4.4), 7.62 (2H, d, 7.9), 7.56 (2H, d, 7.3), 7.31 (4H, m), 6.75 (4H, bs), 5.89 (1H, s), 3.92 (4H, s). *4,6-diamino-N^1,N^3-di(pyrren-1-yl)benzene-1,3-diamide (**11e**)*: Analogously to procedure for **11a**, 0.30 g (0.46 mmol) of **10e** and 0.15 g of catalyst (2 days) gave 0.24 g of **11e** (88 %). ^{1}H NMR (DMSO-d_6): 10.31 (2H, s), 8.81 (1H, s), 8.40-8.04 (18H, m), 6.94 (4H, bs), 6.06 (1H, s).

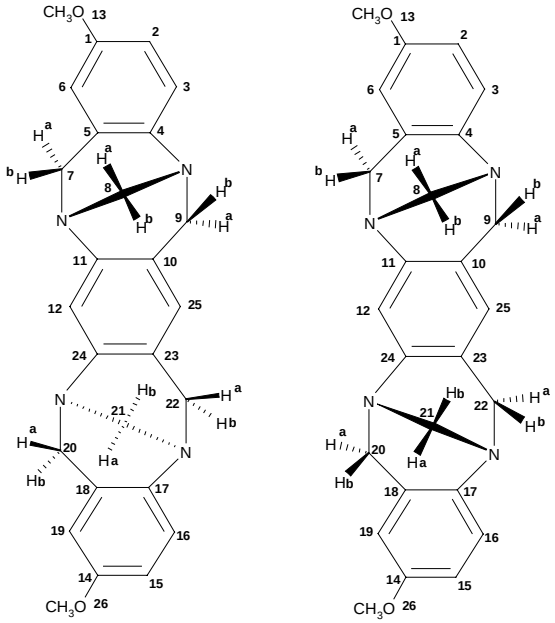
*2,3-bis((4-methoxyphenylamino)methyl)benzene-1,4-diamine (**8**)*. Procedure A: Solution of $LiAlH_4$ in THF (2.0 M, 6.4 mL, 12.9 mmol) was added into solution of **3** (0.30 g, 0.67 mmol) in anhydrous dioxane (30 mL). The reaction mixture was heated at 90 °C for 5 h. After cooling to rt 10 mL of water was added, followed by adding of 5 mL of 15% solution of NaOH. The insoluble part was filtered off and washed with chloroform. Filtrate with organic parts was extracted by water, dried over $MgSO_4$ and evaporated to dryness to give 0.12 g (50%) of **8**. Procedure B: Analogously to procedure A, 50 mg of **7** (0.12 mmol) and 1.3 mL of $LiAlH_4$ in THF (2.0 M, 2.48 mmol) in anhydrous dioxane (5 mL) gave 29 mg of tetraamine **8** (62%). The tetramine **8** was used immediately for next trogeration into **1**. *4,6-bis((4-methoxyphenylamino)methyl)benzene-1,3-diamine (**13a**)*: Analogously to procedure for **8**, 10 mL (20 mmol) of 2.0 M LAH and 0.21 g (2.84 mmol) of **11a** gave 0.12 g of **13a** (61 %). ^{1}H NMR ($CDCl_3$): 6.88 (1H, s), 6.80 (4H, d, 8.5), 6.64 (4H d, 8.5), 5.99 (1H, s), 4.03 (4H, s), 3.74 (6H, s). ^{13}C APT NMR ($CDCl_3$): 152.34 (C), 146.44 (C), 142.55 (C), 131.91 (CH), 114.67 (CH), 114.64 (CH), 113.30 (C), 102.98 (CH), 55.57 (CH_3), 47.30 (CH_2). *4,6-bis((naphthalen-2-ylamino)methyl)benzene-1,3-diamine (**13b**)*: Analogously to procedure for **8**, 16 mL (31.2 mmol) of 2.0 M LAH and 0.35 g (0.78 mmol) of **11b** gave 0.26 g of **13b** (78 %) with 2-aminonaphthalene as impurity (about 15 %mol by NMR).

^{1}H NMR ($CDCl_3$): 7.66 (6H, m), 7.39 (2H, m), 7.23 (2H, m), 7.03 (1H, s), 6.94 (4H, m), 6.11 (1H, s), 4.23 (4H, s). ^{13}C APT NMR ($CDCl_3$): 146.48 (C), 145.95 (C), 135.01 (C), 132.35 (CH), 128.87 (C), 127.73 (CH), 127.60 (CH), 126.37 (CH), 126.04 (CH), 122.26 (CH), 118.19 (CH), 113.06 (C), 105.23 (CH), 103.04 (CH), 46.15 (CH_2).

*10,23-Dimethoxy-1,6,14,19-tetraazaheptacyclo[17.7.1.1^{6,14}.0^{2,17}.0^{5,16}.0^{8,13}.0^{20,25}]hexacosa-2,4,8,10,12,16,20,22,24-nonaene (**1**)*. Compound **8** (0.11 g, 0.26 mmol) and paraformaldehyd (0.10 g) were dissolved in 15 mL of trifluoroacetic acid, and stirred at 60 °C for 2 h. The mixture was cool to rt and diluted with water and ice, and alkalinized by conc. aqueous ammonia. Product was extracted into chloroform. The organic part was washed with brine, dried over Na_2SO_4 and evaporated *in vacuo* to dryness. The residue was separated by preparation TLC (CH_2Cl_2/methanol 95:5) to obtain 4 mg (4% yield) of less polar *anti*-**1** 4 mg (4% yield) of more polar *syn*-**1**.[3]

*9,23-Dimethoxy-4,15-didehydro-1,5,13,19-tetraazaheptacyclo[17.7.1.1^{5,13}.0^{2,17}.0^{4,15}.0^{7,12}.0^{20,25}]-hexacosa-2,4,7,9,11,16,20,22,24-nonaene (**14a**)*. Procedure A: Analogously to procedure for **1**, 0.12 g (0.32 mmol) of tetraamine **13a**, 0.12 g of paraformaldehyd (120 mg) and 20 mL of trifluoroacetic acid gave two isomers of **14a**; 15 mg (11 %) of **14a-1** and 12 mg (9 %) of **14a-2**. Procedure B:[9] Tetraamin **13a** (100 mg, 0.26 mmol) was dissolved in 15 mL of TFA, and hexamethylentetramine (82 mg, 0.58 mmol) was added at 0 °C under argon. The mixture was stirred at rt for 70 h, and then poured into cold water. The solution was carefully alkalinized at 0 °C by 25% aq. NH_3 (pH 11) and extracted with CH_2Cl_2. The organic parts were extracted by water, dried over Na_2SO_4, and evaporated to dryness *in vacuo*. The residue was separated by preparation TLC (CH_2Cl_2/methanol 95:5) and was obtained 20 mg of **14a** (purity about 80%). *BisTB **14a-1***: ^{1}H NMR ($CDCl_3$): 7.09 (2H, d, 8.8, H^{3}, H^{16}), 7.00 (1H, s, H^{12}), 6.75 (2H, dd, 8.8, 2.8, H^{2}, H^{15}), 6.48 (1H, s, H^{25}), 6.44 (2H, d, 2.8, H^{6}, H^{19}), 4.70 (2H, d, 16.5, H^{7b}, H^{20b}), 4.57 (2H, d, 16.5, H^{9b}, H^{22b}), 4.34 (2H, d, 12.4, H^{8a}, H^{21a}), 4.26 (2H, d, 12.4, H^{8b}, H^{21b}), 4.21 (2H, d, 16.5, H^{7a}, H^{20a}), 4.04 (2H, d, 16.5, H^{9a}, H^{22a}), 3.64 (6H, s, H^{13}, H^{26}). ^{13}C APT NMR ($CDCl_3$): 156.63 (C^{1}, C^{14}), 146.49 (C^{11}, C^{24}), 138.99 (C^{4}, C^{17}), 128.17 (C^{5}, C^{18}), 125.79 (C^{3}, C^{16}), 125.37 (C^{25}), 123.49 (C^{10}, C^{23}), 120.64 (C^{12}), 114.32 (C^{2}, C^{15}), 110.87 (C^{6}, C^{19}), 66.95 (C^{8}, C^{21}), 58.97 (C^{7}, C^{20}), 58.05 (C^{9}, C^{22}), 55.37 (C^{13}, C^{26}). HRMS (EI^{+}): for $C_{26}H_{26}N_4O_2$ [M^{+}] calcd: 426.2056; Found: 426.2054. *BisTB **14a-2***: ^{1}H NMR ($CDCl_3$): 7.02 (2H, d, 8.8, H^{3}, H^{16}), 6.89 (1H, s, H^{12}),

6.70 (2H, dd, 8.8, 2.8, H^2, H^{15}), 6.43 (1H, s, H^{25}), 6.41 (2H, d, 2.8, H^6, H^{19}), 4.66 (2H, d, 16.5, H^{7b}, H^{20b}), 4.58 (2H, d, 16.5, H^{9b}, H^{22b}), 4.27 (2H, d, 12.4, H^{8a}, H^{21a}), 4.25 (2H, d, 12.4, H^{8b}, H^{21b}), 4.05 (2H, d, 16.5, H^{7a}, ^{H20a}), 3.97 (2H, d, 16.5, H^{9a}, H^{22a}), 3.69 (6H, s, H^{13}, H^{26}). ^{13}C APT NMR ($CDCl_3$): 156.08 (C^1, C^{14}), 147.31 (C^{11}, C^{24}), 140.56 (C^4, C^{17}), 128.57 (C^5, C^{18}), 125.93 (C^3, C^{16}), 125.09 (C^{25}), 123.86 (C^{10}, C^{23}), 120.76 (C^{12}), 113.86 (C^2, C^{15}), 110.92 (C^6, C^{19}), 66.87 (C^8, C^{21}), 58.91 (C^7, C^{20}), 58.17 (C^9, C^{22}), 55.32 (C^{13}, C^{26}). HRMS (EI^+): for $C_{26}H_{26}N_4O_2$ [M^+] calcd: 426.2056, Found: 426.2048.

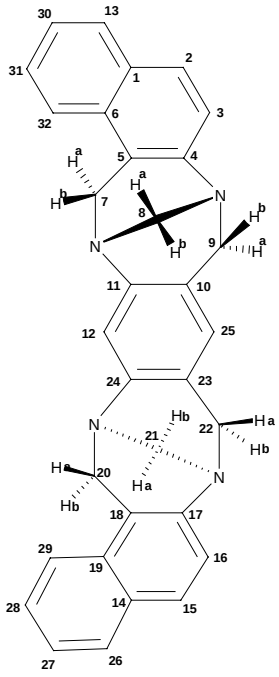


anti-**14a** *syn*-**14a**

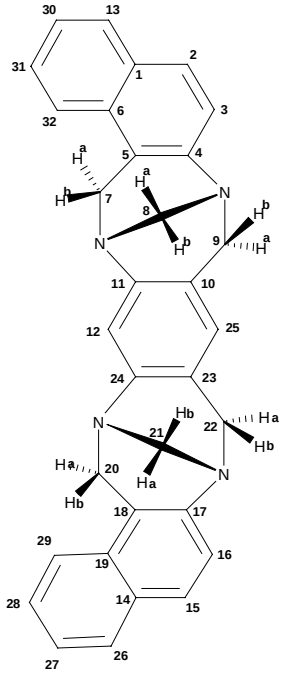
*4,19-Didehydro-1,5,17,23-tetraazanonacyclo[21.11.1.1^{5,17}.0^{2,21}.0^{4,19}.0^{7,16}.0^{8,13}.0^{24,33}.0^{27,32}]tetra-tricosa-2,5,9,11,13,15,20,24,26,28,30,32-tridecaene (**14b**)*. Procedure A: Analogously to procedure A for **14a**, 250 mg (0.60 mmol) of tetraamine **13b**, 230 mg of paraformaldehyde and 30 mL of trifluoroacetic acid gave two isomers of **14b**; 10 mg (2 %) of **14b-1** and 14 mg (5 %) of **14b-2**. In addition, common Tröger's base of 2-aminonaphthalene[17] was isolated (60 mg), as the result of contamination of tetraamine **13b** by 2-aminonaphthalene. Procedure B:[9] Tetraamin **13b** (140 mg, 0.33 mmol) was dissolved in 10 mL of TFA, and hexamethylentetramine (103 mg, 0.74 mmol) was added at 0 °C under argon. The mixture was stirred at rt for 60 h, and then poured into cold water. The solution was carefully alkalinized at 0 °C by 25% aq. NH_3 (pH 11) and

extracted with CH_2Cl_2. The organic parts were extracted by water, dried over Na_2SO_4, and evaporated to dryness *in vacuo*. The residue was separated by preparation TLC (CH_2Cl_2/methanol 95:5) to give common Tröger's base of 2-aminonaphthalene[17] (20 mg) and only traces of **14b**.

*BisTB **14b-1***: ^{1}H NMR ($CDCl_3$): 7.73 (2H, d, 8.0, H^{13}, H^{26}) 7.66 (2H, d, 8.5, H^2, H^{15}), 7.65 (2H, d, 8.0, H^{29}, H^{32}), 7.46 (2H, t, 8.5, H^{28}, H^{31}), 7.38 (2H, t, 8.3, H^{27}, H^{30}), 7.23 (2H, d, 8.8, H^3, H^{16}) 7.08 (1H, s, H^{12}), 6.47 (1H, s, H^{25}), 4.97 (2H, d, 16.8, H^{7b}, H^{20b}), 4.66 (2H, d, 16.8 H^{7a}, H^{20a}), 4.55 (2H, d, 16.5, H^{9b}, H^{22b}), 4.36 (2H, d, 12.1 H^{8a}, H^{21a}), 4.26 (2H, d, 12.1, H^{8b}, H^{21b}), 4.22 (2H, d, 16.5, H^{9a}, H^{22a}). ^{13}C APT NMR ($CDCl_3$): 147.16 (C^{11}, C^{24}), 144.64 (C^4, C^{17}), 131.20 (C^6, C^{19}), 130.79 (C^1, C^{14}), 128.53 (C^{13}, C^{26}), 127.98 (C^2, C^{15}), 126.57 (C^{28}, C^{31}), 125.18 (C^{25}), 124.85 (C^{27}, C^{30}), 124.30 (C^3, C^{16}), 123.92 (C^{10}, C^{23}), 121.28 (C^{29}, C^{32}), 121.21 (C^5, C^{18}), 121.04 (C^{12}), 66.59 (C^8, C^{21}), 57.14 (C^9, C^{22}), 56.98 (C^7, C^{20}). HRMS (EI^+): for $C_{32}H_{26}N_4$ [M^+] calcd: 466.2157, Found: 466.2166. *BisTB **14b-2***: ^{1}H NMR ($CDCl_3$): 7.54 (2H, d, 8.1, H^{13}, H^{26}) 7.51 (2H, d, 7.7, H^{29}, H^{32}), 7.48 (2H, d, 8.2, H^2, H^{15}), 7.29 (2H, t, 7.6, H^{28}, H^{31}), 7.18 (2H, t, 8.8, H^{27}, H^{30}), 7.10 (2H, d, 8.8, H^3, H^{16}) 6.96 (1H, s, H^{12}), 6.41 (1H, s, H^{25}), 4.89 (2H, d, 16.8, H^{7b}, H^{20b}), 4.56 (2H, d, 16.8, H^{9b}, H^{22b}), 4.35 (2H, d, 16.8, H^{7a}, H^{20a}), 4.28 (2H, d, 12.1, H^{8ab}, H^{21ab}), 4.26 (2H, d, 12.1, H^{8ab}, H^{21ab}), 4.11 (2H, d, 16.8 H^{9a}, H^{22a}). ^{13}C APT NMR ($CDCl_3$): 147.64 (C^{11}, C^{24}), 144.98 (C^4, C^{17}), 131.12 (C^6, C^{19}), 130.62 (C^1, C^{14}), 128.43 (C^{13}, C^{26}), 127.71 (C^2, C^{15}), 126.36 (C^{28}, C^{31}), 124.97 (C^{25}), 124.56 (C^{27}, C^{30}), 124.30 (C^3, C^{16}), 124.00 (C^{10}, C^{23}), 121.34 (C^{12}), 121.27 (C^{29}, C^{32}), 121.22 (C^5, C^{18}), 66.65 (C^8, C^{21}), 56.91 (C^9, C^{22}), 56.85 (C^7, C^{20}). HRMS (EI^+): for $C_{32}H_{26}N_4$ [M^+] calcd: 466.2157, Found: 466.2162.

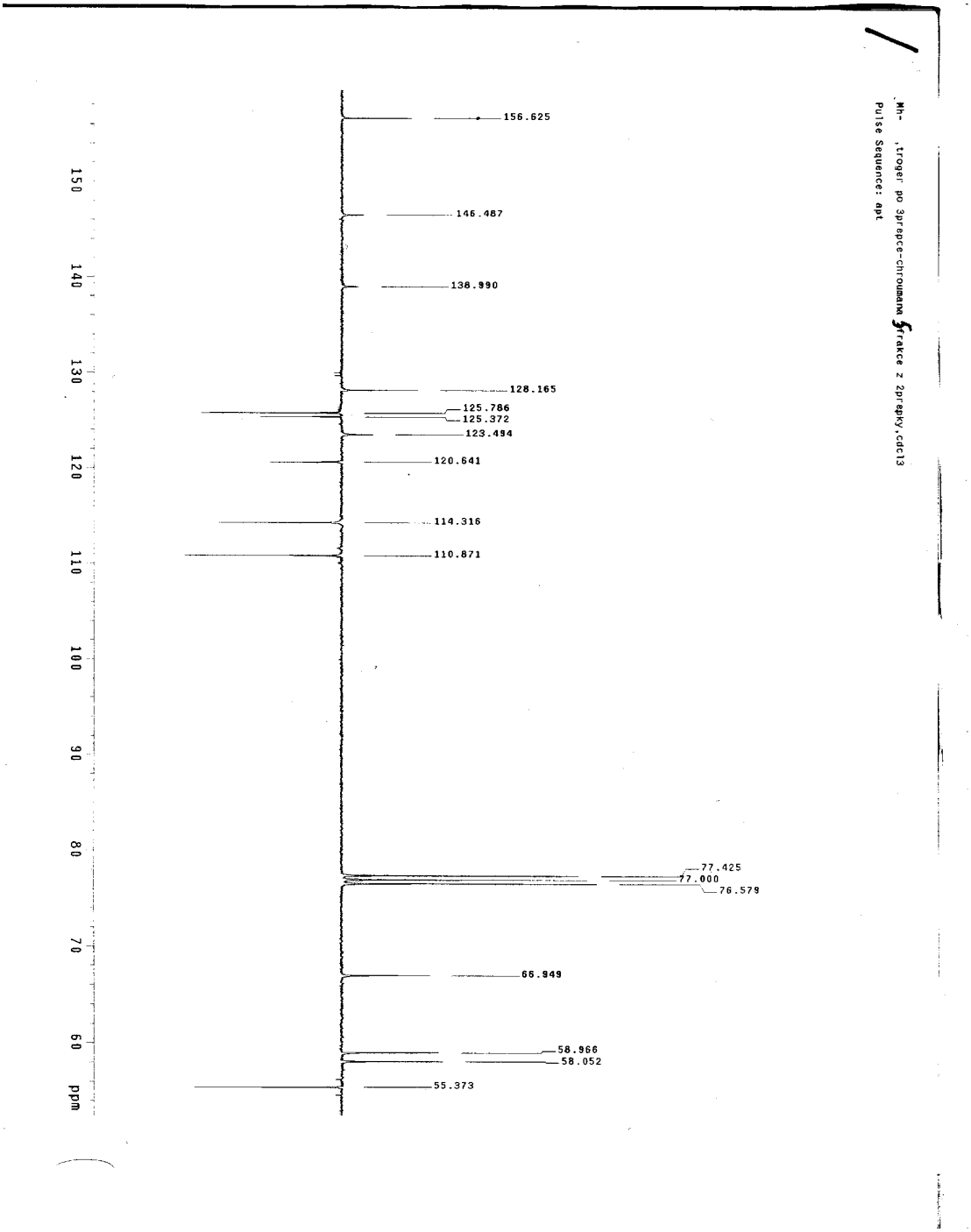


anti-**14b**

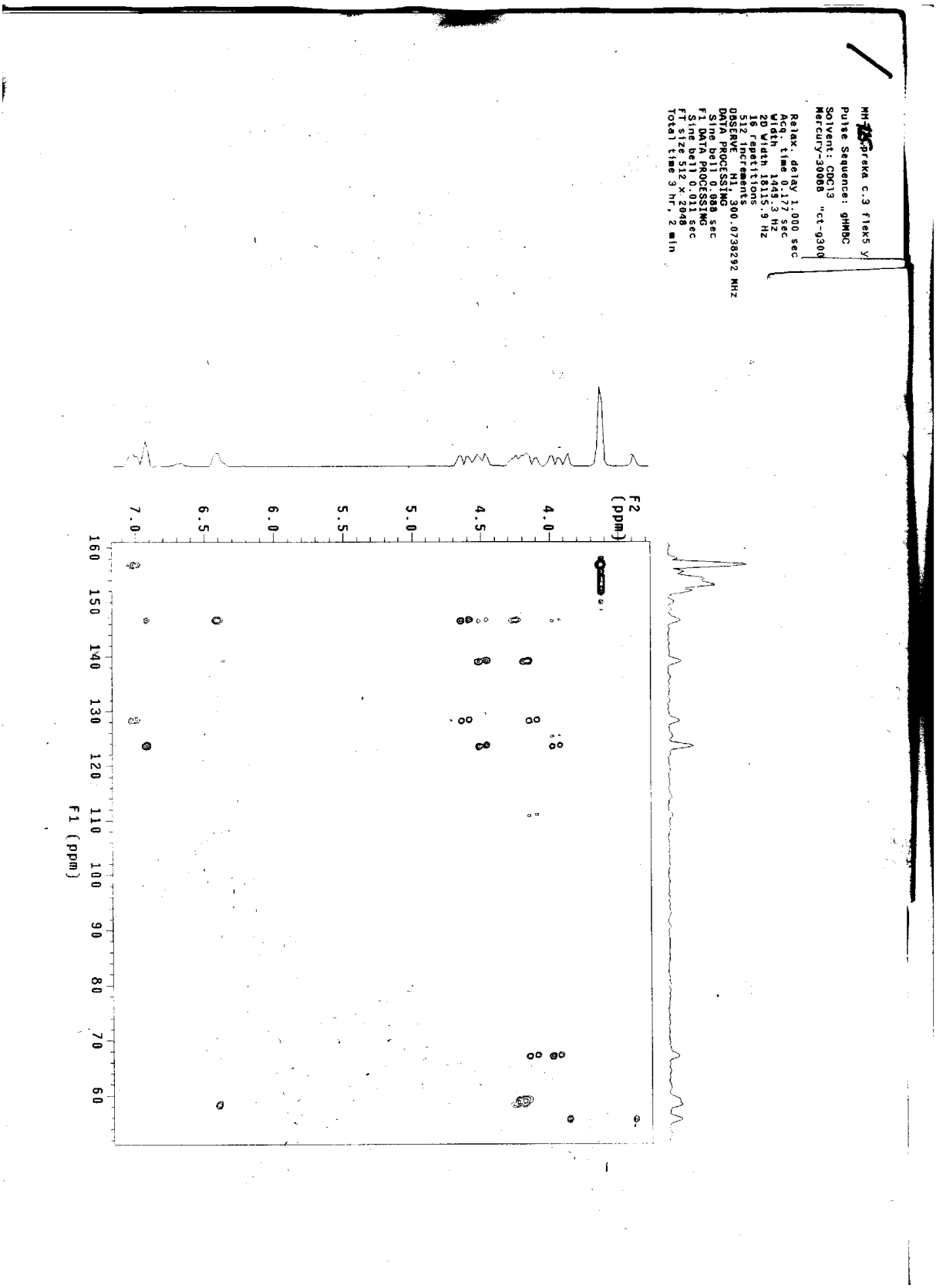


syn-**14b**

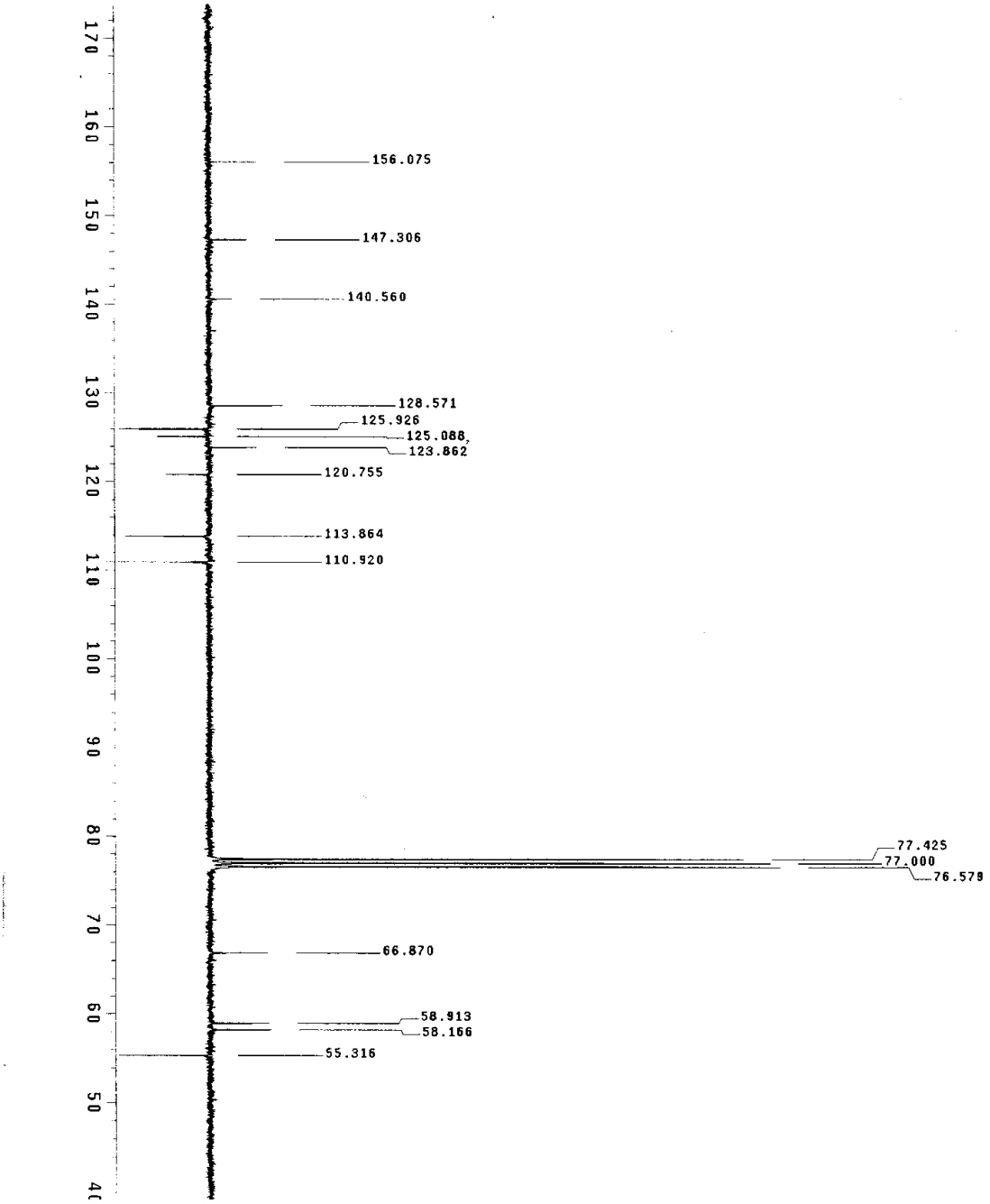
^{13}C NMR spectrum of **14a-1**



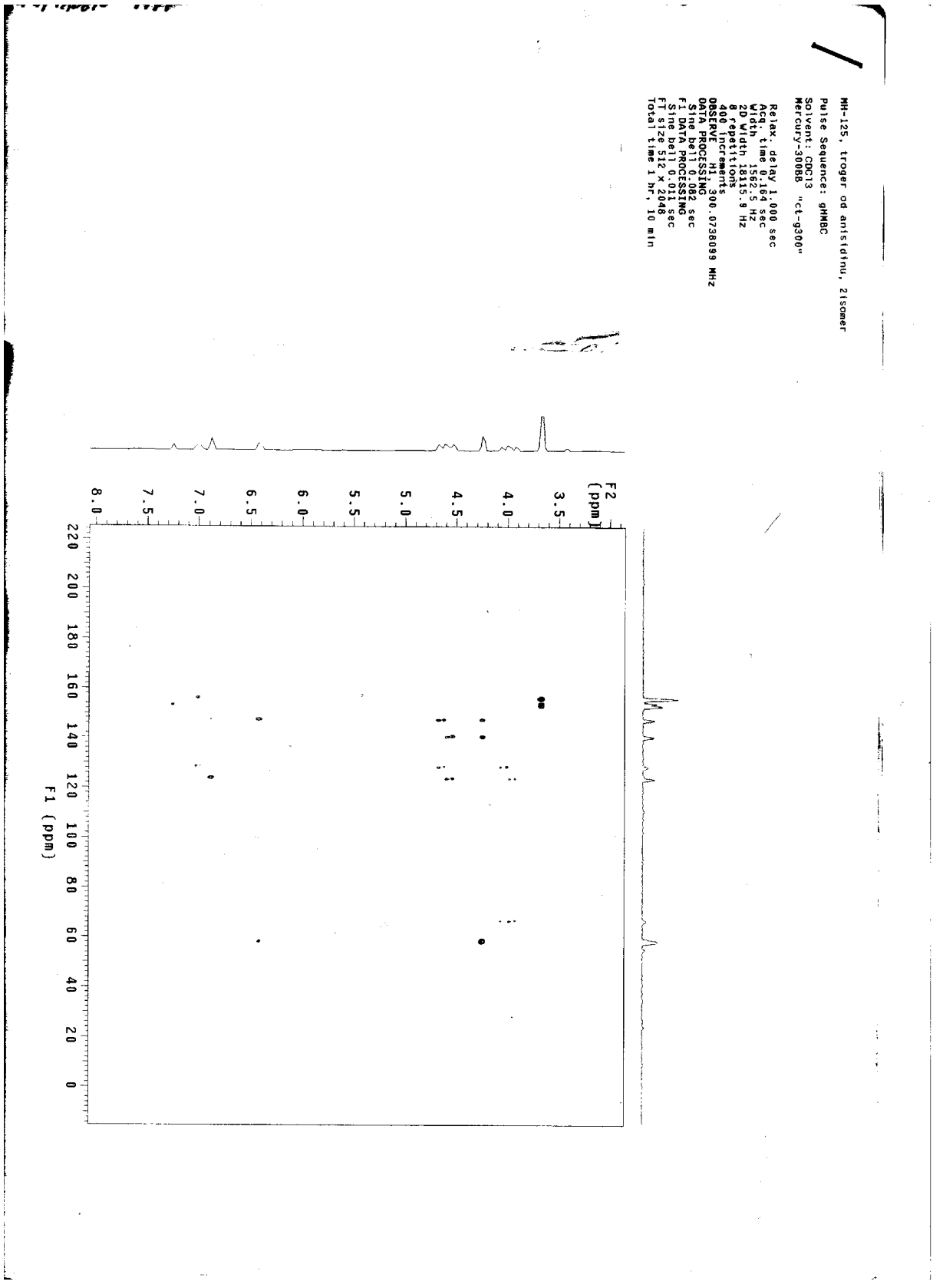
g-HMBC spectrum of **14a-1**



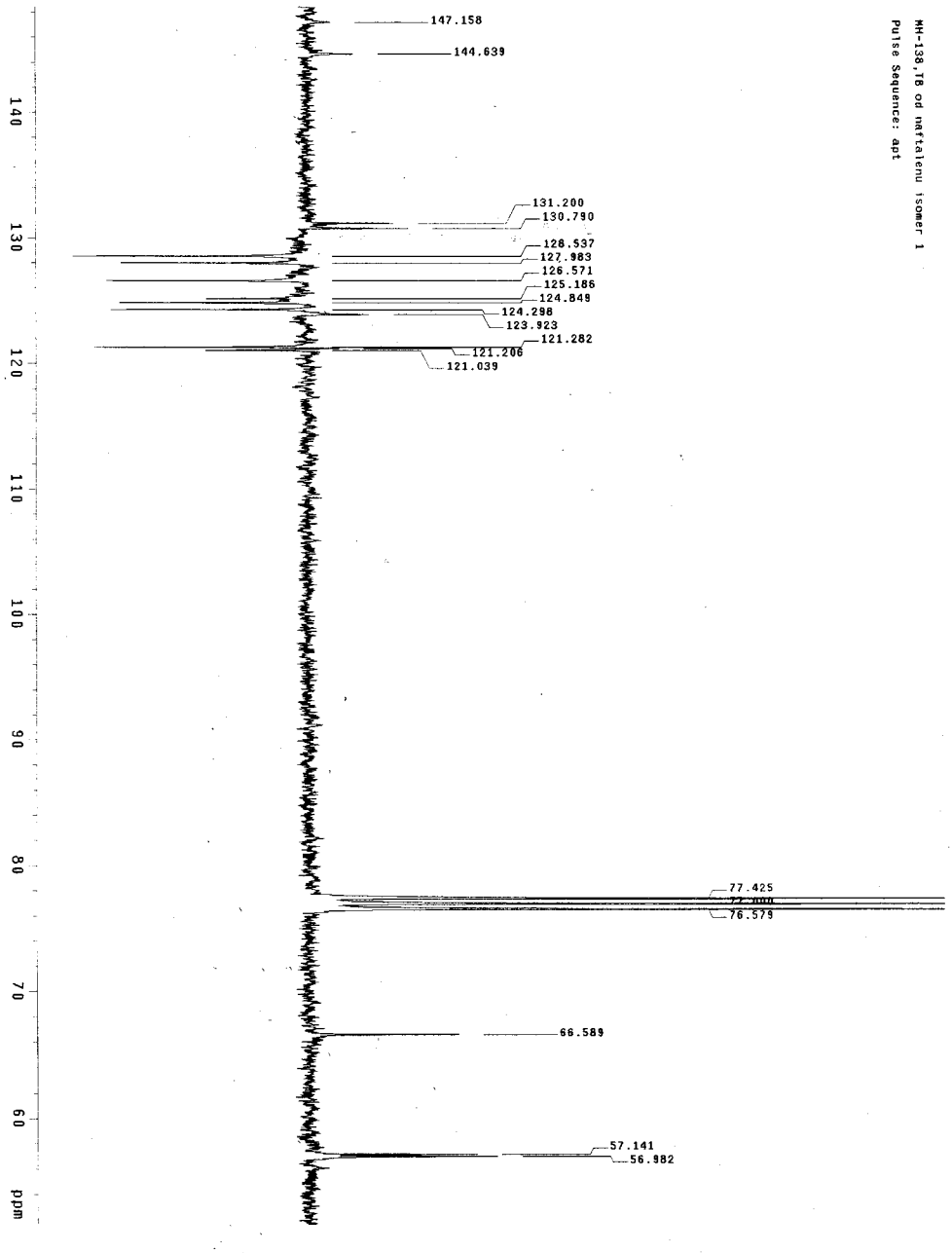
^{13}C NMR spectrum of **14a-2**



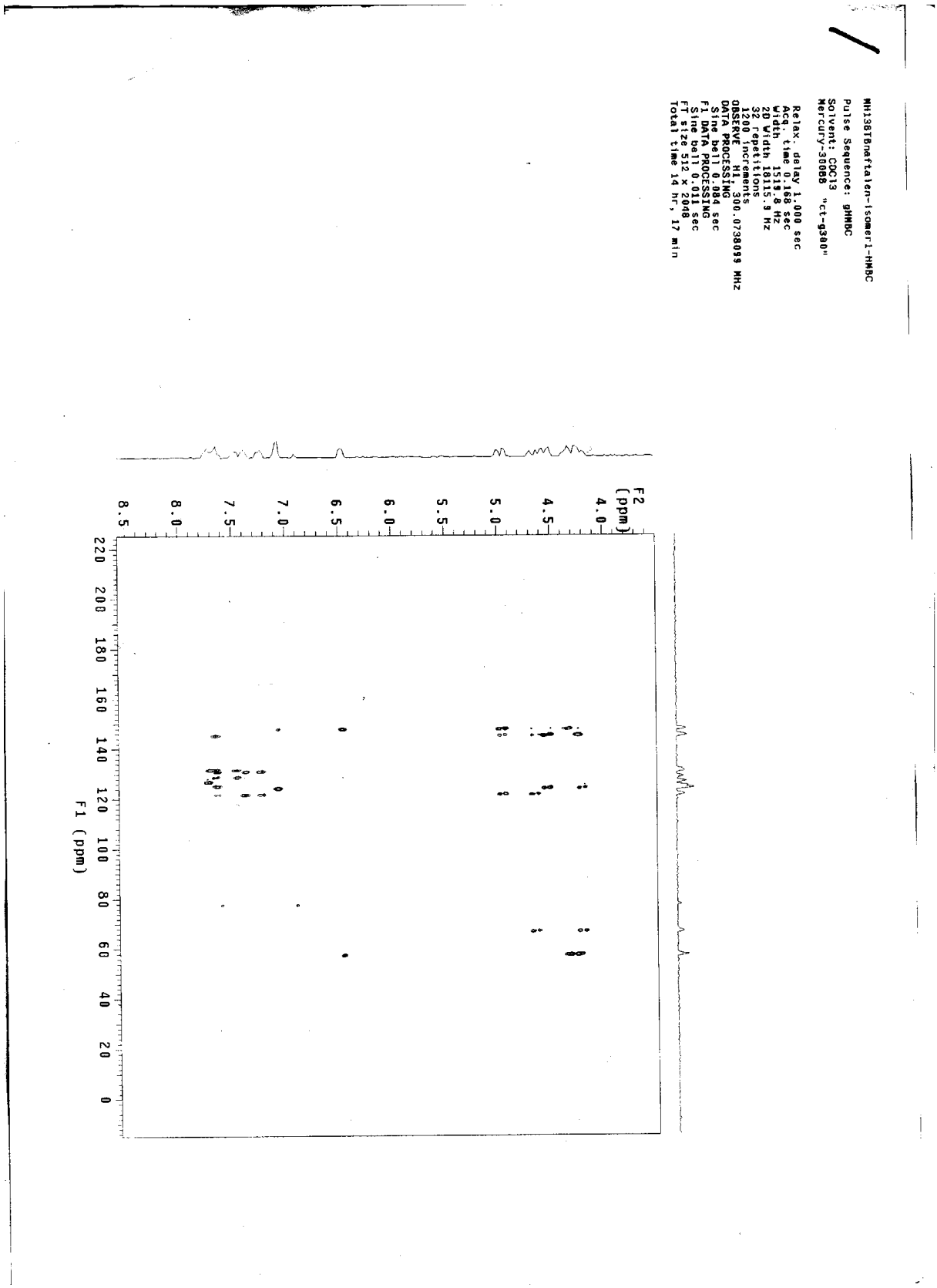
g-HMBC spectrum of **14a-2**



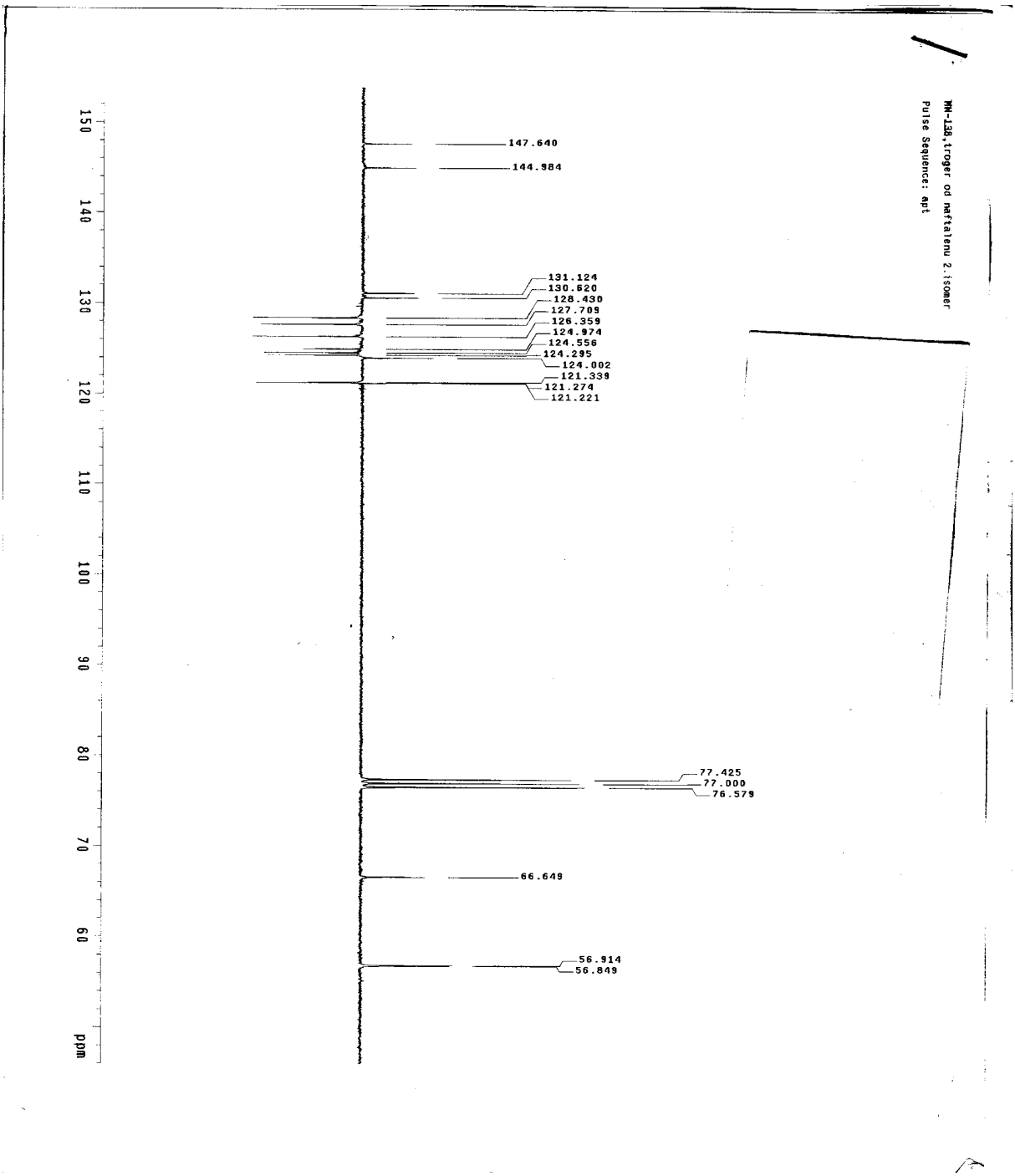
^{13}C NMR spectrum of **14b-1**



g-HMBC spectrum of **14b-1**



^{13}C NMR spectrum of **14b-2**



g-HMBC spectrum of **14b-2**