Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Asymmetric Suzuki-Miyaura Cross-Coupling of 1-Bromo-2-naphthoates using the Helically Chiral Polymer Ligand PQXphos

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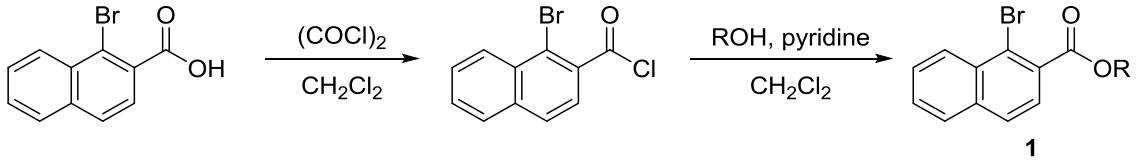
1. General

All reactions were carried out under an atmosphere of nitrogen with magnetic stirring. ^{1}H and ^{13}C NMR spectra were recorded on a Varian 400-MR spectrometer at ambient temperature. ^{1}H NMR data are reported as follows: chemical shift in ppm downfield from tetramethylsilane (δ scale), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, m = multiplet, and br = broad), coupling constant (Hz), and integration. ^{13}C NMR chemical shifts are reported in ppm downfield from tetramethylsilane (δ scale). ^{31}P NMR chemical shifts are reported in ppm downfield from H_3PO_4 (85%). All ^{13}C NMR and ^{31}P NMR spectra were obtained with complete proton decoupling.

Toluene and THF were dried and deoxygenized using an alumina/catalyst column system (GlassContour Co.)., $[PdCl(\eta^3\text{-}C_3H_5)]_2$ (TCI), distilled water (Nacalai tesque), 1-bromo-2-naphthoic acid (TCI), methanol (Nacalai tesque), ethanol (Nacalai tesque), 2-propanol (Nacalai tesque), 3-pentanol (TCI), 2,4-dimethyl-3-pentanol (TCI), dicyclohexylmethanol (Aldrich), cyclohexanol (Wako), cyclooctanol (TCI), t-butyl alcohol (Wako), phenol (TCI), 2,6-dimethylphenol (TCI), oxalyl chloride (Wako), 1-naphthaleneboronic acid (Wako), 2-methylphenylboronic acid (Wako), 4-methyl-1-naphthaleneboronic acid (Alfa Aesar), 4-methoxy-1-naphthaleneboronic acid (Aldrich), 4-fluoro-1-naphthaleneboronic acid (Aldrich), 1-pyreneboronic acid (Wako), 2,3-dimethylphenylboronic acid (Wako), 2,5-dimethylphenylboronic acid (Wako), 5-fluoro-2-methylphenylboronic acid (Wako), 4-fluoro-2-methylphenylboronic acid (Alfa Aesar), lithium alminium hydride (Wako), and potassium hydroxide (Nacalai tesque) were used as received from the commercial sources. 1,1,2-trichloroethane (Wako), dimethylformamide (Nacalai tesque), and pyridine (Wako) were purchased from the commercial sources and distilled before use. Potassium phosphate (Nacalai tesque) was purchased and dried prior to use. PQXphos **L1**-**L6** were synthesized by the method reported previously.[S1]

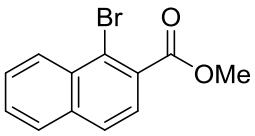
2. Experimental Procedures and Spectral Data for New Compounds

2.1 Preparation of Aryl Bromide

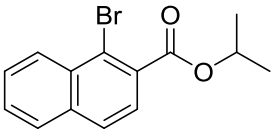


Scheme S1. Synthesis of aryl bromide **1**

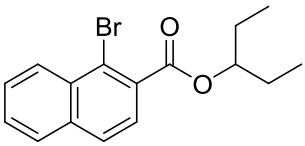
General procedure: To a solution of 1-bromo-2-naphthoic acid (1.11 g, 4.40 mmol) in CH_2Cl_2 (20 mL) was added oxalyl chloride (416 μL, 4.84 mmol) at 0 °C. The mixture was stirred at room temperature for 1 h. After evaporation of the solvent, to the mixture was added pyridine (1.0 mL, 13.3 mmol), alcohol (13.3 mmol), and CH_2Cl_2 (20 mL). The mixture was stirred at room temperature for 18 h. The resulting mixture was quenched by water and extracted with CH_2Cl_2. After drying with anhydrous $MgSO_4$, the concentrated mixture was purified by column chromatography (hexane:CH_2Cl_2 = 2:1) to give a desired product.



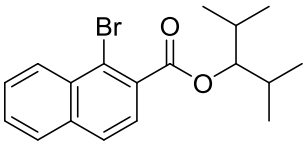
Methyl 1-bromo-2-naphthoate (1A): 95% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (d, J = 8.4 Hz, 1H), 7.85 (d, J = 8.0 Hz, 1H), 7.84 (d, J = 8.4 Hz, 1H), 7.58-7.70 (m, 3H), 4.01 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.9, 135.2, 132.3, 131.2, 128.6, 128.2, 128.1, 128.1, 127.8, 125.7, 122.6, 52.7; IR (ATR) ν 2925, 1717, 1456, 1429, 1265, 1234, 1219, 1126, 1003, 866, 827, 760 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{12}H_9BrO_2$+H^+ (M+H^+): 264.9859, found: 264.9851.



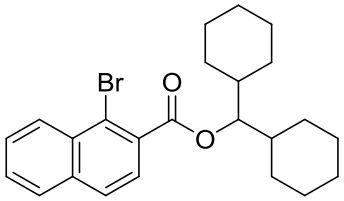
Isopropyl 1-bromo-2-naphthoate (1B): 82% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (d, J = 8.8 Hz, 1H), 7.84 (d, J = 8.0 Hz, 1H), 7.83 (d, J = 8.8 Hz, 1H), 7.56-7.67 (m, 3H), 5.36 (sep, J = 6.0 Hz, 1H), 1.44 (d, J = 6.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.1, 135.0, 132.2, 132.2, 128.4, 128.2, 128.0, 127.9, 127.8, 125.6, 122.0, 69.7, 21.8 (2C); IR (ATR) ν 2986, 1722, 1460, 1373, 1271, 1242, 1172, 1099, 978, 926, 823, 788, 762 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{14}H_{13}BrO_2$+H^+ (M+H^+): 293.0172, found: 293.0162.



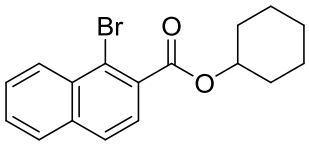
Pentan-3-yl 1-bromo-2-naphthoate (1C): 87% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (d, J = 8.0 Hz, 1H), 7.85 (dd, J = 8.0 Hz, 1.2 Hz, 1H), 7.84 (d, J = 8.4 Hz, 1H), 7.56-7.67 (m, 3H), 5.12 (quin, J = 6.0 Hz, 1H), 1.77 (dq, J = 7.6 Hz, 6.0 Hz, 4H), 1.03 (t, J = 7.6 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.5, 134.9, 132.4, 132.3, 128.4, 128.2, 128.0, 127.9, 127.8, 125.5, 121.9, 78.8, 26.5 (2C), 9.8 (2C); IR (ATR) ν 2966, 1728, 1558, 1456, 1265, 1234, 1150, 1136, 1109, 1045, 974, 930, 822, 758 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{16}H_{17}BrO_2$+H^+ (M+H^+): 321.0485, found: 321.0475.



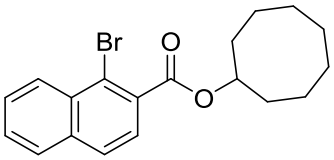
2,4-Dimethylpentan-3-yl 1-bromo-2-naphthoate (1D): 80% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (d, J = 8.4 Hz, 1H), 7.84 (dd, J = 7.2 Hz, 0.8 Hz, 1H), 7.84 (d, J = 8.4 Hz, 1H), 7.56-7.70 (m, 3H), 4.97 (t, J = 6.0 Hz, 1H), 2.07 (dsep, J = 6.4 Hz, 6.0 Hz, 2H), 1.03 (t, J = 6.4 Hz, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.5, 135.0, 132.4, 132.3, 128.5, 128.1, 128.0, 127.9, 127.8, 125.7, 122.1, 84.7, 26.6 (2C), 19.7 (2C), 17.5 (2C); IR (ATR) ν 2963, 1717, 1558, 1325, 1276, 1240, 1171, 1117, 972, 935, 893, 810, 754 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{18}H_{21}BrO_2$+H^+ (M+H^+): 349.0798, found: 349.0787.



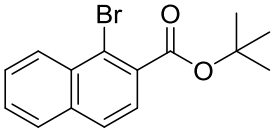
Dicyclohexylmethyl 1-bromo-2-naphthoate (1E): 80% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (d, J = 8.4 Hz, 1H), 7.84 (d, J = 8.0 Hz, 2H), 7.56-7.72 (m, 3H), 5.00-5.04 (m, 1H), 1.56-1.78 (m, 12H), 1.15-1.34 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.3, 135.0, 132.4, 132.1, 128.6, 128.1, 128.0, 127.9, 127.8, 125.8, 122.3, 83.3, 38.6 (2C), 30.0 (2C), 27.7 (2C), 26.4 (2C), 26.3 (2C), 26.1 (2C); IR (ATR) ν 2929, 2851, 1728, 1683, 1653, 1558, 1265, 1238, 1167, 1124, 975, 754 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{24}H_{29}BrO_2$+H^+ (M+H^+): 429.1424, found: 429.1411.



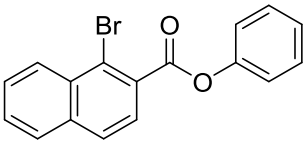
Cyclohexyl 1-bromo-2-naphthoate (1F): 92% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (d, *J* = 8.4 Hz, 1H), 7.84 (dd, *J* = 8.0 Hz, 1.2 Hz, 1H), 7.83 (d, *J* = 8.4 Hz, 1H), 7.56-7.67 (m, 3H), 5.13 (sep, *J* = 4.0 Hz, 1H), 2.02-2.07 (m, 2H), 1.80-1.85 (m, 2H), 1.51-1.70 (m, 3H), 1.41-1.51 (m, 2H), 1.29-1.39 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.1, 135.0, 132.3 (2C), 128.4, 128.2, 128.0, 127.9, 127.8, 125.7, 122.0, 74.5, 31.6 (2C), 25.4, 23.7 (2C); IR (ATR) ν 2933, 1717, 1558, 1506, 1456, 1285, 1248, 1170, 1128, 1011, 980, 824, 756 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{17}H_{17}BrO_2$+H^+ (M+H^+): 333.0485, found: 333.0473.



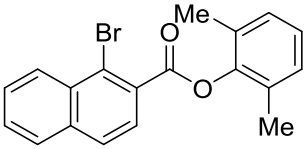
Cyclooctyl 1-bromo-2-naphthoate (1G): 93% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (d, *J* = 8.4 Hz, 1H), 7.84 (d, *J* = 8.4 Hz, 1H), 7.83 (d, *J* = 8.4 Hz, 1H), 7.56-7.66 (m, 3H), 5.30 (sep, *J* = 4.0 Hz, 1H), 1.90-2.07 (m, 4H), 1.74-1.83 (m, 2H), 1.55-1.66 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 135.0, 132.4, 132.2, 128.4, 128.1, 128.0, 127.9, 127.8, 125.6, 122.0, 77.2, 31.4 (2C), 27.1 (2C), 25.4, 23.0 (2C); IR (ATR) ν 2920, 1717, 1558, 1273, 1244, 1169, 1138, 1031, 976, 924, 826, 758, 746 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{19}H_{21}BrO_2$+H^+ (M+H^+): 361.0798, found: 361.0784.



***tert*-Butyl 1-bromo-2-naphthoate (1H)**: 63% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (d, *J* = 8.0 Hz, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.82 (d, *J* = 8.4 Hz, 1H), 7.55-7.65 (m, 3H), 1.67 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.9, 134.8, 133.4, 132.2, 128.3, 128.1, 127.9, 127.8, 127.7, 125.5, 121.3, 82.9, 28.2 (3C); IR (ATR) ν 1724, 1684, 1558, 1506, 1456, 1367, 1294, 1248, 1126, 822, 754, 654 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{15}H_{15}BrO_2$+H^+ (M+H^+): 307.0328, found: 307.0317.

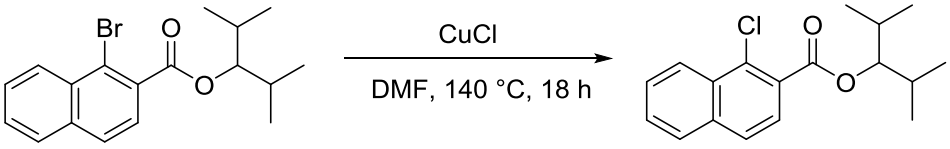


Phenyl 1-bromo-2-naphthoate (1I): 79% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (dd, J = 8.4 Hz, 0.8 Hz, 1H), 7.87-7.93 (m, 3H), 7.69 (ddd, J = 8.4 Hz, 7.2 Hz, 1.2 Hz, 1H), 7.64 (ddd, J = 8.0 Hz, 6.8 Hz, 1.2 Hz, 1H), 7.45-7.50 (m, 2H), 7.29-7.35 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 150.8, 135.4, 132.4, 130.5, 129.6 (2C), 128.7, 128.4, 128.3, 128.3, 128.0, 126.2, 125.9, 123.4, 121.6 (2C); IR (ATR) ν 1734, 1718, 1684, 1558, 1489, 1456, 1229, 1190, 1109, 968, 822, 758, 745, 691 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{17}H_{11}BrO_2$+H^+ (M+H^+): 307.0015, found: 307.0003.



2,6-Dimethylphenyl 1-bromo-2-naphthoate (1J): 78% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (d, J = 8.4 Hz, 1H), 7.99 (d, J = 8.4 Hz, 1H), 7.93 (d, J = 8.8 Hz, 1H), 7.90 (d, J = 8.8 Hz, 1H), 7.70 (ddd, J = 8.4 Hz, 6.8 Hz, 1.2 Hz, 1H), 7.65 (ddd, J = 8.0 Hz, 6.8 Hz, 1.2 Hz, 1H), 7.12-7.19 (m, 3H), 2.36 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.9, 148.2, 135.4, 132.4, 130.3, 130.2 (2C), 128.8 (2C), 128.4, 128.3, 128.2, 128.0, 126.1, 125.8 (2C), 123.5, 16.7 (2C); IR (ATR) ν 2358, 1684, 1653, 1647, 1558, 1506, 754 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{19}H_{15}BrO_2$+H^+ (M+H^+): 355.0328, found: 355.0316.

2.2 Preparation of Aryl Chloride 1D′



2,4-Dimethylpentan-3-yl 1-chlolro-2-naphthoate: To a solution of **1D** (349 mg, 1.0 mmol) in DMF (1.0 mL) was added CuCl (109 mg, 1.1 mmol). The mixture was stirred at 140 ^{o}C for 18 h. After filtration of the reaction mixture with Et_2O, the filtrate was extracted by Et_2O and washed by water, dried over $MgSO_4$. After evaporation of the solvent, the residue was purified by column chromatography (hexane:CH_2Cl_2 = 2:1) to give a desired product (254 mg, 84%).; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (d, J = 8.0 Hz, 1H), 7.87 (d, J = 8.0 Hz, 1H), 7.80 (d, J = 8.4 Hz, 1H), 7.77 (d, J = 8.4 Hz, 1H), 7.66 (dd, J = 6.8 Hz, 6.4 Hz, 1H), 7.61 (dd, J = 6.8 Hz, 6.4

Hz, 1H), 4.97 (t, J = 6.0 Hz, 1H), 2.06 (dsep, J = 6.4 Hz, 6.0 Hz, 2H), 1.01 (t, J = 6.4 Hz, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 135.1, 131.5, 131.2, 128.9, 128.1 (2C), 127.7, 126.9, 125.8, 125.7, 84.5, 29.6 (2C), 19.7 (2C), 17.4 (2C); IR (ATR) ν 2963, 1717, 1464, 1331, 1272, 1242, 1120, 989, 893, 812, 754 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{18}H_{21}ClO_2$+Na^+ (M+Na^+): 327.1122, found: 327.1118.

2.3 General Procedure for Asymmetric Suzuki-Miyaura Cross-coupling (Tables 1−3 and Eq 1)

To a solution of (*P*)-(*R*)-PQXphos (27 mg, 4.0 μmol phosphorous atom) in THF (300 μL) was added [PdCl(η^3-C_3H_5)]$_2$ (0.01 M in THF, 100 μL, 1 μmol), K_3PO_4 (43 mg, 0.2 mmol), **1** (0.10 mmol), **2** (0.15 mmol), H_2O (40 μL) in this order. The reaction was stirred at 40 ^{o}C for 24−48 h. After the reaction, subsequent addition of MeCN (10 mL) resulted in precipitation of the polymer complex. The suspension was passed through a pad of Celite® using MeCN as an eluent. The crude product was subjected to PTLC (hexane/Et_2O = 4/1) to give a desired product. Further purification was performed by GPC if necessary. The enantiomeric excesses of the products were determined by HPLC or SFC with a chiral stationary phase.

2.4 Gram-Scale Reaction (Table 3, ently 6)

To a solution of (*P*)-(*R*)-PQXphos (595 mg, 96 μmol phosphorous atom) in THF (16 mL) was added [PdCl(η^3-C_3H_5)]$_2$ (14.6 mg, 40 μmol), K_3PO_4 (1.70 g, 8.0 mmol), **1** (1.40 g, 4.0 mmol), **2** (900 mg, 6.0 mmol), H_2O (1.6 mL) in this order. The reaction was stirred at 40 ^{o}C for 72 h. After the reaction, subsequent addition of MeCN (30 mL) resulted in precipitation of the PQXphos. The suspension was passed through a pad of Celite® using MeCN as an eluent. The crude product was isolated by column chromatography (hexane/Et_2O = 4/1) to give a desired product **3Dg** (1.31 g, 87% yield). The enantiomeric excess of this compound was determined by SFC analysis.

2.5 Reuse of Catalyst (Scheme 1)

[**Initial Run**] To a solution of (*P*)-(*R*)-PQXphos (27 mg, 4.0 μmol phosphorous atom) in THF (300 μL) was added [PdCl(η^3-C_3H_5)]$_2$ (0.01 M in THF, 100 μL, 1 μmol), K_3PO_4 (43 mg, 0.2 mmol), **1D** (0.12 mmol, 42 mg), **2g** (0.10 mmol, 15 mg), H_2O (40 μL) in this order. The reaction was stirred at 40 ^{o}C for 40 hours. After the reaction, acetonitrile was added to the mixture to precipitate polymer complex. The insoluble materials were washed by acetonitrile to extract the product. After evaporation of the extract, the residue was purified by by PTLC (hexane/Et_2O = 4/1) to give a desired product (20 mg, 53%). The enantiomeric excesses of the

products were determined by SFC with a chiral stationary phase. The polymer catalyst remainning in the reaction vessel was dried under vacuum and used for the next run.

[2nd and 3rd Runs] To a mixture of polymer catalyst and THF (400 μL) was added K_3PO_4 (43 mg, 0.2 mmol), **1D** (0.12 mmol, 42 mg), **2g** (0.10 mmol, 15 mg), H_2O (40 μL) in this order. The reaction was stirred at 40 ^{O}C. After the reaction, acetonitrile was added to the mixture to precipitate polymer complex. The insoluble materials were washed by acetonitrile to extract the product. After evaporation of the extract, the residue was purified by by PTLC (hexane/Et_2O = 4/1) to give a desired product (2nd run, 25 mg, 66%; 3rd run, 26 mg 69%). The enantiomeric excesses of the products were determined by SFC with a chiral stationary phase.

2.6 Asymmetric Suzuki-Miyaura Coupling Using Helically Inversed PQXphos (Scheme 2)

(*R*)-**L6** (27 mg, 4.0 μmol phosphorus atom) in 1,1,2-trichloroethane (0.6 mL) and THF (0.2 mL) was stirred at 60 °C for 24 h. To the mixture was added [PdCl(η^3-C_3H_5)]$_2$ [0.01 M in THF/1,1,2-TCE (5/2), 100 μL, 1 μmol], and the solution was stirred at 60 °C for 10 min. To the mixture was added K_3PO_4 (43 mg, 0.2 mmol), **1D** (35 mg, 0.1 mmol), **2f** (37 mg, 0.15 mmol), and H_2O (40 μL). The mixture was stirred at 40 °C for 48 h. After the reaction, subsequent addition of MeCN (10 mL) resulted in precipitation of the PQXphos. The suspension was passed through a pad of Celite® using MeCN as an eluent. The crude product was subjected to PTLC (hexane/Et_2O = 4/1). Further purification was performed by GPC to give a desired product (44 mg, 93% yield). The enantiomeric excesses of the products were determined by SFC with a chiral stationary phase.

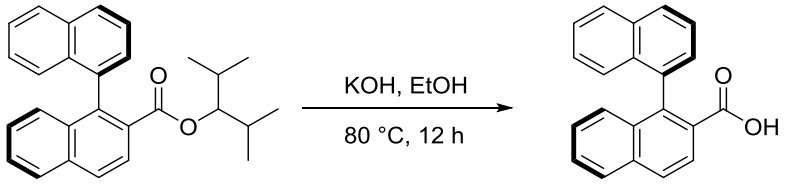
2.7 Reduction and Hydrolysis of (*S*)-3Dg (Scheme 3)

[Reduction] To a solution of (*S*)-**3Dg** (35 mg, 0.094 mmol) in Et_2O (7.0 mL) was added lithium aluminum hydride (7 mg, 0.20 mmol) at 0 °C. The mixture was stirred at 80 °C for 1 h. After the reaction, the mixture was quenched by water and extracted with Et_2O. After drying with anhydrous $MgSO_4$, the concentrated mixture was purified by column chromatography (hexane/Et_2O = 3/1) to give a desired product (*S*)-**4** (21 mg, 84% yield). The enantiomeric excess of this compound was determined by SFC analysis.

[Hydrolysis] To a solution of (*S*)-**3Dg** (131 mg, 0.35 mmol) in EtOH (30.0 mL) was added KOH (11 g, 200 mmol). The mixture was stirred at 80 °C for 12 hours. After the reaction, the mixture was extracted with Et_2O and the extracts were washed with water. After drying with anhydrous $MgSO_4$, the concentrated mixture was purified by column chromatography (hexane:Et_2O = 1:1) to give a desired product (*S*)-**5** (94 mg, 98% yield). The enantiomeric

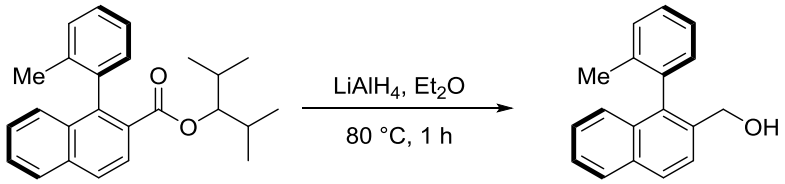
excess of this compound was determined by SFC analysis.

2.8 Determination of Absolute Configuration



3Da **S1**

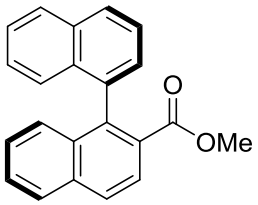
To a solution of **3Da** (26 mg, 0.066 mmol, 84% ee) in EtOH (7.0 mL) was added KOH (3.0 g, 53 mmol). The mixture was stirred at 80 °C for 12 hours. After the reaction, the mixture was extracted with Et_2O and the extracts were washed with water. After drying with anhydrous $MgSO_4$, the concentrated mixture was purified by column chromatography (hexane:Et_2O = 1:1) to give a desired product **6** (16 mg, 83% yield). The enantiomeric excess of this compound was determined by SFC analysis. The absolute configuration was determined by comparing its optical rotation with reported data.[S2a] **(S1):** ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, J = 8.4 Hz, 1H), 7.98 (d, J = 8.8 Hz, 1H), 7.92-7.95 (m, 3H), 7.52-7.57 (m, 2H), 7.45 (ddd, J = 8.4 Hz, 6.8 Hz, 1.2 Hz, 1H), 7.33 (dd, J = 6.8 Hz, 0.8 Hz, 1H), 7.21-7.30 (m, 3H), 7.15 (d, J = 8.0 Hz, 1H); $[\alpha]^{23}_D$ −20.1 [c 0.810, CH_2Cl_2, 84% ee (*S*)].



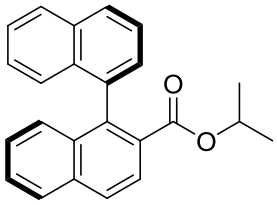
3Da **S2**

To a solution of **3Db** (42 mg, 0.12 mmol, 82% ee) in Et_2O (7.0 mL) was added lithium aluminum hydride (9 mg, 0.24 mmol) at 0 °C. The mixture was stirred at 80 °C for 1 h. After the reaction, the mixture was quenched by water and extracted with Et_2O. After drying with anhydrous $MgSO_4$, the concentrated mixture was purified by column chromatography (hexane/Et_2O = 3/1) to give a desired product **7** (23 mg, 80% yield). The enantiomeric excess of this compound was determined by SFC analysis. The absolute configuration was determined by comparing its optical rotation with reported data.[S2b] **(S2):** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, J = 8.8 Hz, 1H), 7.78 (d, J = 9.6 Hz, 1H), 7.61 (d, J = 8.4 Hz, 1H), 7.36 (ddd, J = 7.6 Hz, 6.8 Hz, 0.8 Hz, 1H), 7.15-7.28 (m, 5H), 7.05 (d, J = 7.2 Hz, 1H), 4.39 (d, J = 5.6 Hz, 2H), 1.82 (s, 3H); $[\alpha]^{22}_D$ −33.7 [c 1.070, CH_2Cl_2, 81% ee (*S*)].

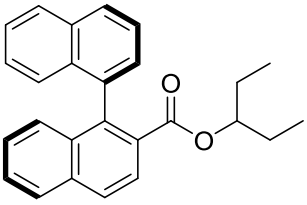
2.9 Spectral Data for New Compounds



Methyl 1-(1-naphthyl)-2-naphthoate (3Aa): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, J = 8.4 Hz, 1H), 8.01 (d, J = 8.4 Hz, 1H), 7.94-7.98 (m, 3H), 7.59 (dd, J = 8.4 Hz, 6.8 Hz, 1H), 7.55 (ddd, J = 8.0 Hz, 5.2 Hz, 2.4 Hz, 1H), 7.46 (ddd, J = 8.4 Hz, 6.8 Hz, 1.6 Hz, 1H), 7.37 (dd, J = 6.8 Hz, 1.2 Hz, 1H), 7.29-7.32 (m, 2H), 7.25−7.28 (m, 1H), 7.22 (d, J = 8.4 Hz, 1H), 3.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.0, 140.2, 136.9, 134.8, 133.2, 133.1, 132.9, 128.7, 128.2, 128.1, 128.0, 127.8, 127.8, 127.6, 126.9, 126.7, 126.0, 126.0, 125.7, 125.7, 125.2, 51.8; IR (ATR) ν 3057, 2947, 2841, 1724, 1712, 1504, 1431, 1280, 1240, 1122, 831, 798, 763, 731 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{22}H_{16}O_2$+H^+ (M+H^+): 313.1223, found: 313.1215; $[\alpha]^{27}_D$ −20.1 [c 1.240, CH_2Cl_2, 70% ee (*S*)].

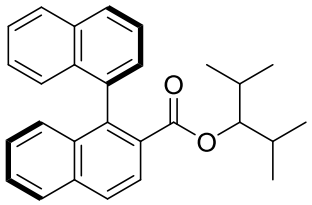


Isopropyl 1-(1-naphthyl)-2-naphthoate (3Ba): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, J = 8.8 Hz, 1H), 8.00 (d, J = 8.8 Hz, 1H), 7.92-7.99 (m, 3H), 7.56 (dd, J = 8.0 Hz, 6.8 Hz, 1H), 7.53 (ddd, J = 8.4 Hz, 6.4 Hz, 2.0 Hz, 1H), 7.45 (ddd, J = 8.4 Hz, 5.2 Hz, 3.2 Hz, 1H), 7.25-7.35 (m, 5H), 4.74 (sep, J = 6.4 Hz, 1H), 0.57 (d, J = 6.4 Hz, 3H), 0.54 (d, J = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.7, 139.3, 137.3, 134.7, 133.3, 133.3, 133.1, 129.8, 128.0, 128.0, 127.9, 127.9, 127.6, 127.4, 127.1, 126.6, 126.4, 125.9, 125.8, 125.7, 125.1, 67.9, 20.8, 20.8; IR (ATR) ν 3057, 2977, 2931, 1699, 1371, 1278, 1103, 822, 766 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{24}H_{20}O_2$+H^+ (M+H^+): 341.1536, found: 341.1530; $[\alpha]^{28}_D$ −7.3 [c 1.050, CH_2Cl_2, 79% ee (*S*)].

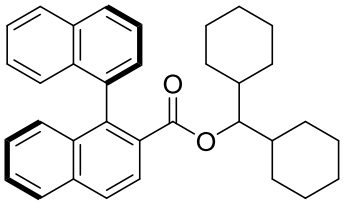


3-pentyl 1-(1-naphthyl)-2-naphthoate (3Ca): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, J = 8.4

Hz, 1H), 8.02 (d, *J* = 8.8 Hz, 1H), 7.94 (m, 3H), 7.56 (dd, *J* = 8.4 Hz, 7.2 Hz, 1H), 7.54 (ddd, *J* = 8.4 Hz, 5.2 Hz, 4.8 Hz, 1H), 7.45 (ddd, *J* = 8.0 Hz, 4.4 Hz, 3.2 Hz, 1H), 7.36 (dd, *J* = 6.8 Hz, 1.2 Hz, 1H), 7.28-7.30 (m, 2H), 7.24-7.27 (m, 2H), 4.58 (sep, *J* = 2.4 Hz, 1H), 0.74-1.09 (m, 4H), 0.54 (t, *J* = 7.2 Hz, 3H), 0.43 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.9, 139.5, 137.4, 134.8, 133.3, 133.3, 133.2, 129.5, 128.1, 128.0 (2C), 127.8, 127.6, 127.5, 127.0, 126.6, 126.4, 126.1, 125.9, 125.7, 125.1, 77.4, 25.9, 25.7, 9.5, 9.2; IR (ATR) ν 3057, 2966, 2933, 1699, 1327, 1269, 1136, 833, 766 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{26}H_{24}O_2$+H^+ (M+H^+): 369.1849, found: 369.1841; $[\alpha]^{29}_D$ −6.4 [c 1.105, CH_2Cl_2, 82% ee (*S*)].

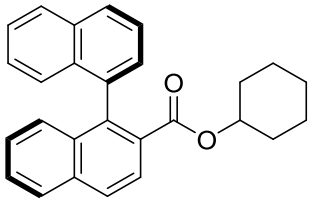


2,4-Dimethylpentan-3-yl 1-(1-naphthyl)-2-naphthoate (3Da): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.8 Hz, 1H), 8.01 (d, *J* = 8.4 Hz, 1H), 7.95 (d, *J* = 2.4 Hz, 1H), 7.93 (d, *J* = 2.0 Hz, 1H), 7.92 (d, *J* = 8.4 Hz, 1H), 7.56 (dd, *J* = 8.0 Hz, 6.8 Hz, 1H), 7.52 (ddd, *J* = 8.0 Hz, 6.4 Hz, 1.6 Hz, 1H), 7.43 (ddd, *J* = 8.0 Hz, 5.2 Hz, 2.8 Hz, 1H), 7.38 (dd, *J* = 6.8 Hz, 1.2 Hz, 1H), 7.20-7.29 (m, 4H), 4.55 (t, *J* = 6.0 Hz, 1H), 1.46 (sep, *J* = 6.4 Hz, 1H), 1.39 (sep, *J* = 6.4 Hz, 1H), 0.66 (d, *J* = 6.8 Hz, 3H), 0.63 (d, *J* = 6.8 Hz, 3H) 0.50 (d, *J* = 6.4 Hz, 3H), 0.30 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.1, 139.4, 137.1, 134.7, 133.4, 133.3, 133.1, 129.6, 128.1, 128.0, 127.8, 127.8, 127.4, 127.3, 126.6, 126.4, 126.2, 126.0, 125.7, 125.2, 83.7, 29.1, 19.2, 19.2, 17.4 (2C), 16.5 (2C); IR (ATR) ν 2963, 2359, 1726, 1699, 1558, 1506, 1456, 1232, 1117, 800, 770 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{28}H_{28}O_2$+H^+ (M+H^+): 397.2162, found: 397.2155; $[\alpha]^{29}_D$ −6.7 [c 1.030, CH_2Cl_2, 87% ee (*S*)].

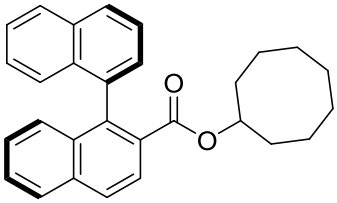


Dicyclohexylmethyl 1-(1-naphthyl)-2-naphthoate (3Ea): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.8 Hz, 1H), 8.01 (d, *J* = 8.8 Hz, 1H), 7.95 (d, *J* = 1.6 Hz, 1H), 7.94 (s, 1H), 7.92 (d, *J* = 8.4 Hz, 1H), 7.56 (dd, *J* = 8.0 Hz, 6.8 Hz, 1H), 7.52 (ddd, *J* = 8.0 Hz, 6.8 Hz, 1.2 Hz, 1H), 7.44 (ddd, *J* = 8.0 Hz, 6.0 Hz, 2.4 Hz, 1H), 7.38 (dd, *J* = 6.8 Hz, 1.2 Hz, 1H), 7.19-7.28 (m, 4H), 4.59 (t, *J* = 6.0 Hz, 1H), 0.03-1.57 (m, 22H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.2, 139.3, 137.2,

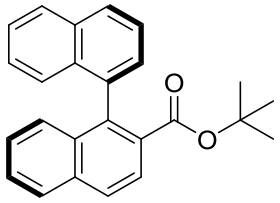
134.7, 133.4, 133.3, 133.2, 129.4, 128.1 (2C), 128.0, 127.8, 127.6, 127.4, 127.2, 126.5 (2C), 126.5, 126.0, 125.6, 125.1, 82.3, 37.9 (2C), 29.5, 29.2, 27.7, 26.2, 26.2, 26.1, 26.1, 26.0, 25.9, 25.8; IR (ATR) ν 2924, 2849, 1726, 1699,1446, 1271, 1121, 907, 766, 729 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{34}H_{36}O_2+H^+$ ($M+H^+$): 477.2788, found: 477.2777; $[\alpha]^{29}_D$ −1.2 [c 1.735, CH_2Cl_2, 82% ee (*S*)].



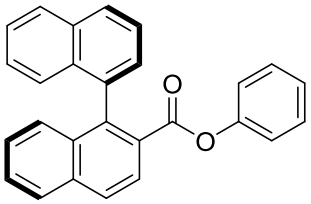
Cyclohexyl 1-(1-naphthyl)-2-naphthoate (3Fa): ^1H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.4 Hz, 1H), 8.00 (d, *J* = 8.4 Hz, 1H), 7.96 (d, *J* = 4.0 Hz, 1H), 7.94 (d, *J* = 4.0 Hz, 1H), 7.93 (d, *J* = 8.0 Hz, 1H), 7.56 (dd, *J* = 8.0 Hz, 6.8 Hz, 1H), 7.53 (ddd, *J* = 8.0 Hz, 4.8 Hz, 2.8 Hz, 1H), 7.45 (ddd, *J* = 8.0 Hz, 3.6 Hz, 3.6 Hz, 1H), 7.35 (dd, *J* = 6.8 Hz, 1.2 Hz, 1H), 7.25-7.29 (m, 4H), 4.53 (tt, *J* = 9.6 Hz, 4.0 Hz, 1H), 1.25-1.34 (m, 5H), 0.99-1.12 (m, 2H), 0.87-0.97 (m, 1H) 0.52-0.65 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.7, 139.2, 137.3, 134.7, 133.3, 133.2, 133.1, 129.9, 128.0 (2C), 127.9, 127.7, 127.4, 127.1, 126.6, 126.4, 125.9 (2C), 125.7, 125.2, 73.1, 30.7 (2C), 25.1 (2C), 23.4, 23.4; IR (ATR) ν 2930, 1699, 1327, 1279, 1111, 912, 764 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{27}H_{24}O_2+H^+$ ($M+H^+$): 381.1849, found: 381.1840; $[\alpha]^{30}_D$ −5.2 [c 1.030, CH_2Cl_2, 80% ee (*S*)].



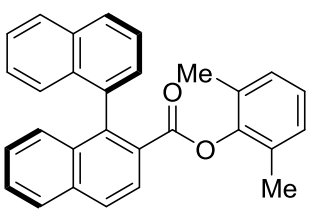
Cyclooctyl 1-(1-naphthyl)-2-naphthoate (3Ga): ^1H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.8 Hz, 1H), 8.00 (d, *J* = 8.8 Hz, 1H), 7.95 (dd, *J* = 6.0 Hz, 0.8 Hz, 1H), 7.92-7.94 (m, 2H), 7.56 (dd, *J* = 8.0 Hz, 6.8 Hz, 1H), 7.52 (ddd, *J* = 8.0 Hz, 4.0 Hz, 4.0 Hz, 1H), 7.46 (ddd, *J* = 8.0 Hz, 4.8 Hz, 2.8 Hz, 1H), 7.34 (dd, *J* = 7.2 Hz, 1.2 Hz, 1H), 7.25-7.29 (m, 4H), 4.72 (sep, *J* = 4.0 Hz, 1H), 1.10-1.31 (m, 12H), 0.80-1.02 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.7, 139.0, 137.3, 134.7, 133.4, 133.3, 133.1, 130.0, 128.0, 128.0, 127.9, 127.9, 127.7, 127.3, 127.1, 126.5, 126.4, 126.0, 125.9, 125.7, 125.2, 75.7, 30.0, 30.0, 27.1, 27.1, 25.0, 22.4, 22.3; IR (ATR) ν 2922, 1705, 1335, 1269, 1134, 945, 762 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{29}H_{28}O_2+H^+$ ($M+H^+$): 409.2162, found: 409.2152; $[\alpha]^{30}_D$ −10.5 [c 1.240, CH_2Cl_2, 80% ee (*S*)].



***tert*-Butyl 1-(1-naphthyl)-2-naphthoate (3Ha):** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92-7.99 (m, 5H), 7.56 (dd, *J* = 8.4 Hz, 6.8 Hz, 1H), 7.51 (ddd, *J* = 8.4 Hz, 6.0 Hz, 2.4 Hz, 1H), 7.46 (ddd, *J* = 8.0 Hz, 5.6 Hz, 2.4 Hz, 1H), 7.35 (dd, *J* = 6.8 Hz, 1.2 Hz, 1H), 7.24-7.31 (m, 4H), 0.81 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.0, 138.2, 137.4, 134.5, 133.4, 133.3, 133.0, 131.4, 128.0, 127.9, 127.9, 127.8, 127.6, 127.3, 127.2, 126.6, 126.5, 126.0, 125.8, 125.7, 125.2, 80.9, 27.1 (3C); IR (ATR) ν 2976, 1699, 1367, 1334, 1286, 1124, 853, 766 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{25}H_{22}O_2$+Na^+ (M+Na^+): 377.1512, found: 377.1502; $[\alpha]^{27}_{D}$ −21.5 [c 0.810, CH_2Cl_2, 68% ee (*S*)].

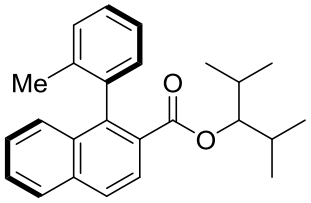


Phenyl 1-(1-naphthyl)-2-naphthoate (3Ia): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 8.4 Hz, 1H), 8.08 (d, *J* = 8.4 Hz, 1H), 8.00 (d, *J* = 8.0 Hz, 1H), 7.96 (d, *J* = 8.4 Hz, 1H), 7.94 (d, *J* = 8.8 Hz, 1H), 7.56-7.61 (m, 2H), 7.44-7.48 (m, 2H), 7.39 (d, *J* = 8.0 Hz, 1H), 7.27-7.36 (m, 3H), 7.13-7.19 (m, 2H), 7.06 (dddd, *J* = 8.8 Hz, 6.8Hz, 1.2 Hz, 1.2 Hz, 1H), 6.46-6.49 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 150.4, 140.3, 136.6, 135.0, 133.3, 130.0, 132.9, 129.0 (2C), 128.4, 128.2, 128.1, 128.0, 128.0, 127.9, 127.8, 127.3, 126.8, 126.2, 126.0, 125.8, 125.8, 125.4, 125.1, 121.0 (2C); IR (ATR) ν 2962, 1728, 1591, 1265, 1188, 1099, 1068, 798, 762 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{27}H_{18}O_2$+H^+ (M+H^+): 375.1380, found: 375.1370; $[\alpha]^{30}_{D}$ +29.7 [c 0.640, CH_2Cl_2, 78% ee (*S*)].

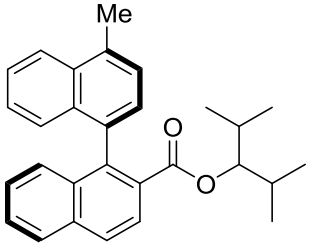


2,6-Dimethylphenyl 1-(1-naphthyl)-2-naphthoate (3Ja): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32

(d, *J* = 8.8 Hz, 1H), 8.09 (d, *J* = 8.8 Hz, 1H), 8.01 (d, *J* = 8.0 Hz, 1H), 7.92 (d, *J* = 8.4 Hz, 1H), 7.90 (d, *J* = 8.4 Hz, 1H), 7.55-7.61 (m, 2H), 7.48 (dd, *J* = 6.8 Hz, 1.2 Hz, 1H), 7.43 (ddd, *J* = 8.4 Hz, 6.0 Hz, 2.0 Hz, 1H), 7.24-7.34 (m, 4H), 6.88-6.92 (m, 3H), 1.83 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.2, 148.2, 140.9, 136.5, 135.0, 133.4, 133.1, 130.0, 128.3 (2C), 128.2, 128.2, 128.2, 128.1, 127.9, 127.9, 127.9, 127.3, 126.8, 126.1 (2C), 126.1, 125.9, 125.7, 125.5 (2C), 125.1, 16.1 (2C); IR (ATR) ν 2926, 1746, 1230, 1159, 1109, 800, 772, 764 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{29}H_{22}O_2$+H^+ (M+H^+): 403.1693, found: 403.1682; $[\alpha]^{30}_D$ +29.7 [c 0.945, CH_2Cl_2, 85% ee (*S*)].

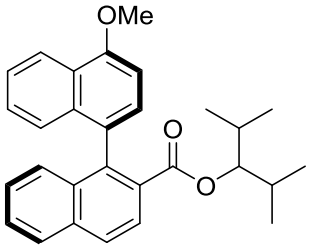


2,4-Dimethylpentan-3-yl 1-(2-methylphenyl)-2-naphthoate (3Db): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.8 Hz, 1H), 7.91 (d, *J* = 8.4 Hz, 1H), 7.91 (d, *J* = 8.0 Hz, 1H), 7.54 (ddd, *J* = 8.0 Hz, 6.4 Hz, 0.8 Hz, 1H), 7.40 (ddd, *J* = 8.4 Hz, 6.4 Hz, 1.2 Hz, 1H), 7.29-7.36 (m, 3H), 7.25 (ddd, *J* = 7.2 Hz, 1.6 Hz, 0.8 Hz, 1H), 7.12 (dd, *J* = 6.8 Hz, 1.2 Hz, 1H), 4.71 (t, *J* = 6.4 Hz, 1H), 1.97 (s, 3H), 1.79 (sep, *J* = 6.8 Hz, 1H), 1.71 (sep, *J* = 6.8 Hz, 1H), 0.81 (d, *J* = 6.8 Hz, 3H), 0.80 (d, *J* = 6.8 Hz, 3H), 0.74 (d, *J* = 6.8 Hz, 3H), 0.74 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.1, 140.7, 138.7, 136.7, 134.6, 132.4, 129.6, 129.5, 128.4, 127.9, 127.6, 127.5, 127.4, 127.3, 126.6, 125.9, 125.4, 83.6, 29.4, 29.4, 20.0, 19.4, 19.4, 17.5, 17.2; IR (ATR) ν 2922, 1695, 1558, 1261, 1118, 937, 770, 760, 731 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{25}H_{28}O_2$+H^+ (M+H^+): 361.2162, found: 361.2151; $[\alpha]^{25}_D$ −40.5 [c 1.020, CH_2Cl_2, 88% ee (*S*)]

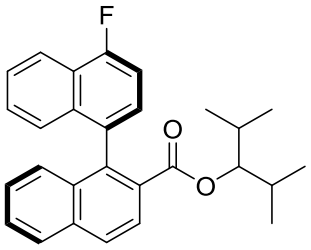


2,4-Dimethylpentan-3-yl 1-(4-methyl-1-naphthyl)-2-naphthoate (3Dc): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.4 Hz, 1H), 8.05 (d, *J* = 8.4 Hz, 1H), 7.97 (d, *J* = 8.8 Hz, 1H), 7.91 (d, *J* = 8.4 Hz, 1H), 7.50 (dd, *J* = 8.0 Hz, 4.0 Hz, 1H), 7.45 (ddd, *J* = 8.4 Hz, 4.8 Hz, 2.8 Hz, 1H), 7.38 (dd, *J* = 7.2 Hz, 0.8 Hz, 1H), 7.21-7.26 (m, 5H), 4.53 (t, *J* = 6.4 Hz, 1H), 2.78 (d, *J* = 0.4 Hz, 3H), 1.49 (sep, *J* = 6.8 Hz, 1H), 1.42 (sep, *J* = 6.8 Hz, 1H), 0.65 (d, *J* = 6.8 Hz, 3H), 0.61 (d,

J = 6.8 Hz, 3H), 0.47 (d, *J* = 6.8 Hz, 3H), 0.36 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.1, 139.7, 135.3, 134.6, 134.0, 133.5, 133.2, 132.5, 129.7, 128.1, 127.8, 127.7, 127.3, 127.0, 126.9, 126.5, 126.1, 125.9, 125.6, 125.5, 124.2, 83.5, 29.1, 29.1, 19.5, 19.2, 19.2, 17.2, 16.6; IR (ATR) ν 2962, 1699, 1456, 1271, 1236, 1124, 947, 827, 750 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{29}H_{30}O_2$+H^+ (M+H^+): 411.2319, found: 411.2308; $[\alpha]^{29}_D$ −5.6 [c 0.815, CH_2Cl_2, 92% ee (*S*)].

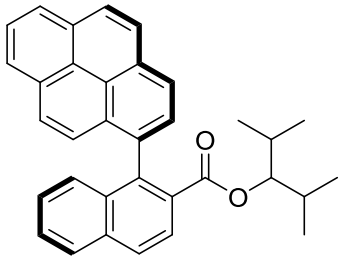


2,4-Dimethylpentan-3-yl 1-(4-methoxy-1-naphthyl)-2-naphthoate (3Dd): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (d, *J* = 8.4 Hz, 1H), 8.07 (d, *J* = 8.8 Hz, 1H), 7.98 (d, *J* = 8.4 Hz, 1H), 7.93 (d, *J* = 8.0 Hz, 1H), 7.51 (ddd, *J* = 8.0 Hz, 6.0 Hz, 1.6 Hz, 1H), 7.42 (ddd, *J* = 8.0 Hz, 6.8 Hz, 1.2 Hz, 1H), 7.23-7.32 (m, 4H), 7.17 (d, *J* = 8.4 Hz, 1H), 6.91 (d, *J* = 8.0 Hz, 1H), 4.55 (t, *J* = 6.0 Hz, 1H), 4.08 (s, 3H), 1.53 (sep, *J* = 6.8 Hz, 1H), 1.44 (sep, *J* = 6.8 Hz, 1H), 0.69 (d, *J* = 6.8 Hz, 3H), 0.62 (d, *J* = 6.8 Hz, 3H), 0.48 (d, *J* = 6.8 Hz, 3H), 0.41 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4, 155.2, 139.3, 134.6, 134.0, 133.7, 130.2, 129.1, 128.1, 127.8, 127.8, 127.3, 127.2, 126.5, 126.5, 126.3, 126.0, 125.4, 125.0, 122.0, 103.3, 83.5, 55.6, 29.2, 29.2, 19.3, 19.2, 17.2, 16.6; IR (ATR) ν 2924, 1718, 1683, 1558, 1506, 1456, 1236, 1088, 762 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{29}H_{30}O_3$+H^+ (M+H^+): 427.2268, found: 427.2260; $[\alpha]^{30}_D$ +1.7 [c 1.870, CH_2Cl_2, 88% ee (*S*)].

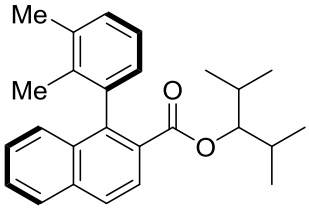


2,4-Dimethylpentan-3-yl 1-(4-fluoro-1-naphthyl)-2-naphthoate (3De): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 8.4 Hz, 1H), 8.11 (d, *J* = 8.8 Hz, 1H), 8.01 (d, *J* = 8.4 Hz, 1H), 7.95 (d, *J* = 8.0 Hz, 1H), 7.53 (ddd, *J* = 8.4 Hz, 6.8 Hz, 1.2 Hz, 1H), 7.50 (ddd, *J* = 8.4 Hz, 6.8 Hz, 1.2 Hz, 1H), 7.20-7.32 (m, 6H), 4.56 (t, *J* = 6.4 Hz, 1H), 1.53 (sep, *J* = 6.8 Hz, 1H), 1.48 (sep, *J* = 6.8 Hz, 1H), 0.68 (d, *J* = 6.8 Hz, 3H), 0.65 (d, *J* = 7.2 Hz, 3H), 0.54 (d, *J* = 6.8 Hz, 3H), 0.37 (d, *J* =

6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.0, 158.5 (J_{CF} = 250.1 Hz), 138.5, 134.7, 134.4 (J_{CF} = 4.7 Hz), 133.4, 133.0 (J_{CF} = 4.6 Hz), 129.9, 128.2, 127.9, 127.8, 127.5, 127.0, 126.8 (J_{CF} = 8.5 Hz), 126.7, 126.4 (J_{CF} = 2.3 Hz), 126.1, 126.0 (J_{CF} = 1.5 Hz), 123.6 (J_{CF} = 16.3 Hz), 120.6 (J_{CF} = 5.4 Hz), 108.8 (J_{CF} = 20.1 Hz), 83.7, 29.2 (2C), 19.3, 19.2, 17.3, 16.5; IR (ATR) ν 2966, 1718, 1684, 1558, 1506, 1456, 1246, 1126, 953, 841, 759 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{28}H_{27}O_2F+H^+$ ($M+H^+$): 415.2068, found: 415.2057; $[\alpha]^{30}_D$ −7.1 [c 1.955, CH_2Cl_2, 90% ee (*S*)].

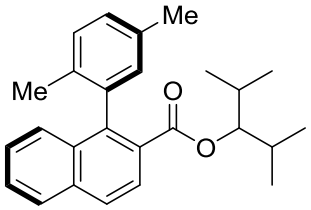


2,4-Dimethylpentan-3-yl 1-(1-pyrenyl)-2-naphthoate (3Df): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, *J* = 7.6 Hz, 1H), 8.06-8.23 (m, 6H), 8.01 (d, *J* = 7.6 Hz, 1H), 7.99 (d, *J* = 7.6 Hz, 1H), 7.94 (d, *J* = 8.0 Hz, 1H), 7.85 (d, *J* = 9.2 Hz, 1H), 7.53 (ddd, *J* = 8.4 Hz, 6.8 Hz, 1.2 Hz, 1H), 7.48 (d, *J* = 9.2 Hz, 1H), 7.23 (ddd, *J* = 8.4 Hz, 6.4 Hz, 1.2 Hz, 1H), 7.12 (dd, *J* = 8.4 Hz, 0.8 Hz, 1H), 4.48 (t, *J* = 6.8 Hz, 1H), 1.41 (sep, *J* = 6.8 Hz, 1H), 1.38 (sep, *J* = 6.4 Hz, 1H), 0.59 (d, *J* = 6.8 Hz, 3H), 0.56 (d, *J* = 6.8 Hz, 3H), 0.45 (d, *J* = 6.8 Hz, 3H), 0.27 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.9, 139.8, 134.6, 134.4, 133.5, 131.3, 130.9, 130.8, 129.9, 129.7, 128.1, 128.0, 127.8, 127.8, 127.4, 127.4 (2C), 127.2, 126.6, 126.0, 125.8, 125.5, 125.0, 124.9, 124.7, 124.6, 124.2, 83.5, 29.0, 29.0, 19.1, 19.1, 17.0, 16.5; IR (ATR) ν 2964, 1716, 1699, 1456, 1276, 1186, 847, 750, 721, 667 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{34}H_{30}O_2+H^+$ ($M+H^+$): 471.2319, found: 471.2307; $[\alpha]^{30}_D$ −67.1 [c 2.165, CH_2Cl_2, 95% ee (*S*)].

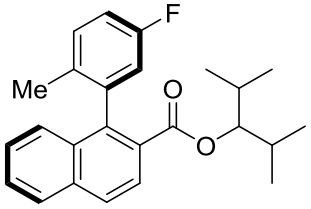


2,4-Dimethylpentan-3-yl 1-(2,3-dimethylphenyl)-2-naphthoate (3Dg): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.8 Hz, 1H), 7.91 (d, *J* = 8.0 Hz, 1H), 7.90 (d, *J* = 8.8 Hz, 1H), 7.53 (ddd, *J* = 8.4 Hz, 6.8 Hz, 1.6 Hz, 1H), 7.32-7.40 (m, 2H), 7.22 (d, *J* = 7.6 Hz, 1H), 7.14 (dd, *J* = 7.6 Hz, 7.6 Hz, 1H), 6.98 (d, *J* = 7.6 Hz, 1H), 4.71 (t, *J* = 6.0 Hz, 1H), 2.36 (s, 3H), 1.87 (s, 3H), 1.76 (sep, *J* = 6.8 Hz, 1H), 1.69 (sep, *J* = 6.8 Hz, 1H), 0.81 (d, *J* = 7.2 Hz, 3H), 0.79 (d, *J* = 6.8 Hz, 3H), 0.72 (d, *J* = 6.8 Hz, 3H), 0.72 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ

168.3, 141.3, 138.7, 136.3, 135.1, 134.6, 132.6, 129.1, 128.5, 127.8, 127.6, 127.5, 127.3, 127.3, 126.5, 126.0, 125.0, 83.5, 29.4, 29.3, 20.4, 19.4, 19.4, 17.4, 17.1, 16.7; IR (ATR) ν 2958, 1695, 1558, 1456, 1327, 1273, 1265, 1119, 891, 772 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{26}H_{30}O_2+H^+$ ($M+H^+$): 375.2319, found: 375.2309; $[\alpha]^{26}_D$ −44.6 [c 1.460, CH_2Cl_2, 96% ee (*S*)].

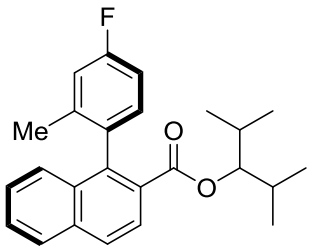


2,4-Dimethylpentan-3-yl 1-(2,5-dimethylphenyl)-2-naphthoate (3Dh): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.8 Hz, 1H), 7.90 (d, *J* = 8.4 Hz, 2H), 7.53 (ddd, *J* = 8.4 Hz, 6.0 Hz, 2.4 Hz, 1H), 7.34-7.41 (m, 2H), 7.19 (d, *J* = 7.6 Hz, 1H), 7.13 (dd, *J* = 8.0 Hz, 1.6 Hz, 1H), 6.94 (d, *J* = 1.2 Hz, 1H), 4.71 (t, *J* = 6.0 Hz, 1H), 2.31 (s, 3H), 1.93 (s, 3H), 1.78 (sep, *J* = 6.8 Hz, 1H), 1.69 (sep, *J* = 6.8 Hz, 1H), 0.81 (d, *J* = 6.8 Hz, 6H), 0.74 (d, *J* = 6.8 Hz, 3H), 0.73 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.3, 140.8, 138.5, 134.6, 134.6, 133.6, 132.4, 130.3, 129.4, 128.5, 128.3, 127.9, 127.5, 127.4, 127.3, 126.6, 126.0, 83.6, 29.4 (2C), 20.9, 19.5, 19.4, 19.4, 17.4, 17.1; IR (ATR) ν 2962, 1699, 1558, 1464, 1329, 1261, 1234, 1121, 1096, 943, 899, 810, 768 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{26}H_{30}O_2+H^+$ ($M+H^+$): 375.2319, found: 375.2309; $[\alpha]^{27}_D$ −44.2 [c 0.965, CH_2Cl_2, 91% ee (*S*)].

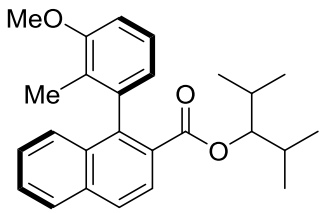


2,4-Dimethylpentan-3-yl 1-(5-fluoro-2-methylphenyl)-2-naphthoate (3Di): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.4 Hz, 1H), 7.93 (d, *J* = 8.4 Hz, 1H), 7.92 (d, *J* = 6.4 Hz, 1H), 7.56 (ddd, *J* = 8.4 Hz, 6.8 Hz, 1.2 Hz, 1H), 7.41 (ddd, *J* = 8.4 Hz, 6.8 Hz, 1.2 Hz, 1H), 7.33 (d, *J* = 8.0 Hz, 1H), 7.26 (dd, *J* = 8.4 Hz, 6.4 Hz, 1H), 7.04 (ddd, *J* = 8.4 Hz, 8.4 Hz, 2.8 Hz, 1H), 6.87 (dd, *J* = 9.2 Hz, 2.8 Hz, 1H), 4.73 (t, *J* = 6.4 Hz, 1H), 1.91 (s, 3H), 1.80 (sep, *J* = 6.8 Hz, 1H), 1.75 (sep, *J* = 6.8 Hz, 1H), 0.84 (d, *J* = 6.8 Hz, 3H), 0.83 (d, *J* = 6.8 Hz, 3H), 0.81 (d, *J* = 7.2 Hz, 3H), 0.75 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.7, 160.9 (J_{CF} = 243.1 Hz), 140.5 (J_{CF} = 7.8 Hz), 139.5, 134.7, 132.4 (J_{CF} = 3.1 Hz), 132.0, 130.8 (J_{CF} = 8.5 Hz), 128.2, 128.0, 127.9, 127.6, 127.1, 126.9, 126.0, 116.5 (J_{CF} = 20.9 Hz), 114.2 (J_{CF} = 20.9 Hz), 83.8, 29.4, 29.4, 19.4 (2C), 19.1, 17.4, 17.2; IR (ATR) ν 2924, 1717, 1558, 1488, 1254, 1130, 951,

889, 804, 760 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{25}H_{27}FO_2+H^+$ ($M+H^+$): 379.2068, found: 379.2059; $[\alpha]^{28}_D$ −37.5 [c 1.705, CH_2Cl_2, 93% ee (*S*)].

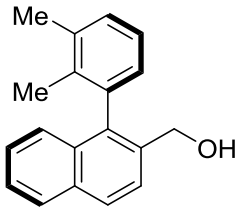


(2,4-Dimethylpentan-3-yl 1-(4-fluoro-2-methylphenyl)-2-naphthoate (3Dj): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.8 Hz, 1H), 7.92 (d, *J* = 8.4 Hz, 1H), 7.91 (d, *J* = 8.4 Hz, 1H), 7.55 (ddd, *J* = 8.0 Hz, 6.8 Hz, 1.2 Hz, 1H), 7.42 (ddd, *J* = 8.4 Hz, 6.8 Hz, 1.2 Hz, 1H), 7.31 (dd, *J* = 8.0 Hz, 0.4 Hz, 1H), 7.08 (dd, *J* = 8.4 Hz, 6.0 Hz, 1H), 7.04 (dd, *J* = 9.6 Hz, 2.4 Hz, 1H), 6.96 (ddd, *J* = 8.8 Hz, 8.8 Hz, 2.4 Hz, 1H), 4.72 (t, *J* = 6.4 Hz, 1H), 1.96 (s, 3H), 1.83 (sep, *J* = 6.8 Hz, 1H), 1.77 (sep, *J* = 6.8 Hz, 1H), 0.83 (d, *J* = 6.8 Hz, 6H), 0.77 (d, *J* = 6.8 Hz, 3H), 0.77 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.9, 162.3 (J_{CF} = 243.9 Hz), 139.6, 139.2 (J_{CF} = 7.7 Hz), 134.7, 134.5 (J_{CF} = 3.1 Hz), 132.5, 130.9 (J_{CF} = 7.7 Hz), 128.8, 128.0, 127.8, 127.4, 127.1, 126.8, 125.9, 116.3 (J_{CF} = 20.9 Hz), 112.2 (J_{CF} = 20.9 Hz), 83.7, 29.4 (2C), 20.1, 19.4, 19.4, 17.4, 17.2; IR (ATR) ν 2923, 1684, 1558, 1506, 1456, 1329, 1238, 1110, 895, 770 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{25}H_{27}FO_2+H^+$ ($M+H^+$): 379.2068, found: 379.2060; $[\alpha]^{28}_D$ −34.1 [c 1.730, CH_2Cl_2, 87% ee (*S*)].

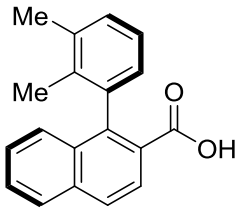


2,4-Dimethylpentan-3-yl 1-(3-methoxy-2-methylphenyl)-2-naphthoate (3Dk): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.8 Hz, 1H), 7.90 (d, *J* = 10.8 Hz, 1H), 7.90 (d, *J* = 6.0 Hz, 1H), 7.53 (ddd, *J* = 8.0 Hz, 5.2 Hz, 3.2 Hz, 1H), 7.36-7.38 (m, 2H), 7.21 (dd, *J* = 8.4 Hz, 8.0 Hz, 1H), 6.92 (d, *J* = 8.0 Hz, 1H), 6.76 (dd, *J* = 7.6 Hz, 0.8 Hz, 1H), 4.71 (t, *J* = 6.0 Hz, 1H), 3.90 (s, 3H), 1.83 (s, 3H), 1.79 (sep, *J* = 6.8 Hz, 1H), 1.71 (sep, *J* = 6.8 Hz, 1H), 0.82 (d, *J* = 6.8 Hz, 3H), 0.79 (d, *J* = 6.8 Hz, 3H), 0.74 (d, *J* = 6.8 Hz, 3H) , 0.73 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.1, 157.5, 140.6, 139.9, 134.6, 132.5, 128.3, 127.8, 127.6, 127.4, 127.3, 126.6, 125.9, 125.8, 125.5, 122.2, 109.2, 83.5, 55.4, 29.4, 29.3, 19.4, 19.4, 17.4, 17.1, 13.0; IR (ATR) ν 2960, 1730, 1684, 1653, 1558, 1456, 1242, 1126, 1088, 945, 835, 775 cm^{-1}; HRMS

(ESI) *m/z* calcd for $C_{26}H_{30}O_3+H^+$ ($M+H^+$): 391.2268, found: 391.2257; $[\alpha]^{29}_D$ −33.7 [c 1.725, CH_2Cl_2, 91% ee (*S*)].



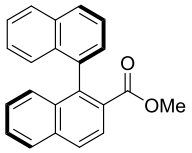
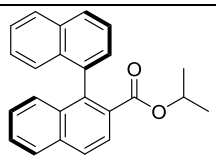
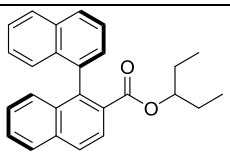
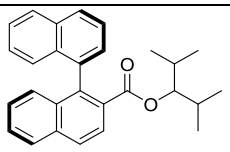
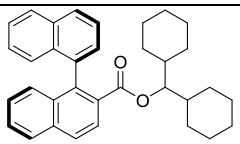
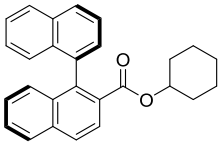
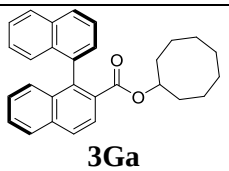
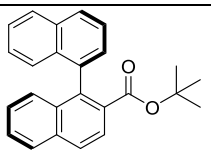
[1-(2,3-dimethylphenyl)naphthalen-2-yl]methanol (4): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.4 Hz, 1H), 7.89 (d, *J* = 8.8 Hz, 1H), 7.71 (d, *J* = 8.4 Hz, 1H), 7.46 (ddd, *J* = 8.0 Hz, 6.8 Hz, 1.6 Hz, 1H), 7.35 (ddd, *J* = 8.4 Hz, 6.8 Hz, 1.2 Hz, 1H), 7.26-7.30 (m, 2H), 7.21 (dd, *J* = 7.6 Hz, 7.2 Hz, 1H), 7.00 (d, *J* = 7.2 Hz, 1H), 4.50 (s, 2H), 2.39 (s, 3H), 1.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.8, 137.6, 137.2, 135.5, 135.4, 132.9, 132.5, 129.3, 127.9, 127.8, 127.7, 126.3, 126.1, 125.7, 125.7, 125.6, 63.5, 20.5, 16.4; IR (ATR) ν 3192, 2923, 2362, 1446, 1068, 1014, 827, 815, 744, 723 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{19}H_{18}O+Na^+$ ($M+Na^+$): 285.1250, found: 285.1243; $[\alpha]^{24}_D$ −49.6 [c 1.040, CH_2Cl_2, 96% ee (*S*)].

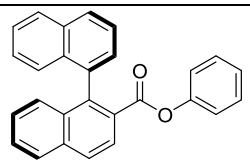
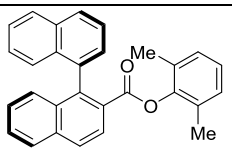
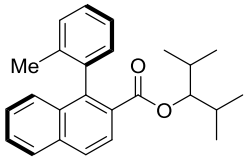
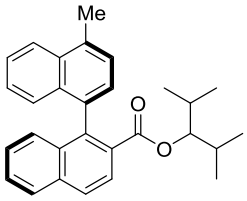
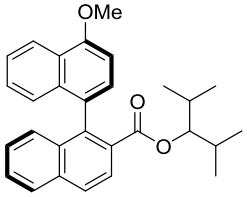
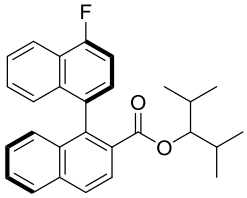
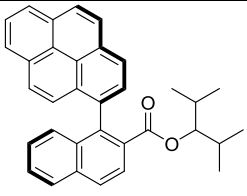
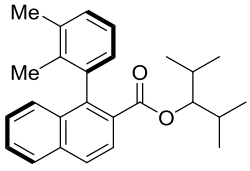


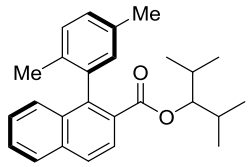
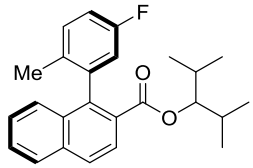
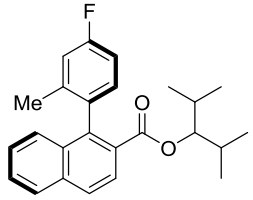
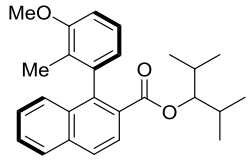
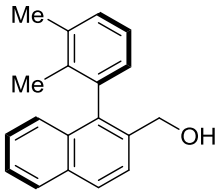
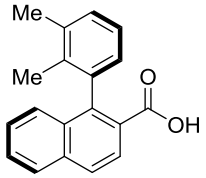
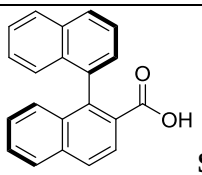
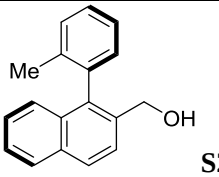
1-(2,3-dimethylphenyl)-2-naphthoic acid (5): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.8 Hz, 1H), 7.91 (d, *J* = 8.8 Hz, 2H), 7.56 (ddd, *J* = 10.0 Hz, 8.0 Hz, 1.6 Hz, 1H), 7.34-7.41 (m, 2H), 7.25 (d, *J* = 8.8 Hz, 1H), 7.17 (dd, *J* = 8.0 Hz, 7.2 Hz, 1H), 6.94 (d, *J* = 7.2 Hz, 1H), 2.38 (s, 3H), 1.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.5, 143.1, 138.1, 136.5, 135.3, 135.2, 132.6, 129.3, 127.9, 127.9, 127.5, 127.1, 126.7, 126.2, 126.1, 125.1, 20.4, 16.5; IR (ATR) ν 2924, 2359, 1695, 1666, 1558, 1288, 939, 773 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{19}H_{16}O_2-H^-$ ($M-H^-$): 275.1078, found: 275.1082; $[\alpha]^{25}_D$ −48.0 [c 0.695, CH_2Cl_2, 97% ee (*S*)].

3. Determination of the Enantiomeric Excesses of the Products by HPLC or SFC with a Chiral Stationary Phase

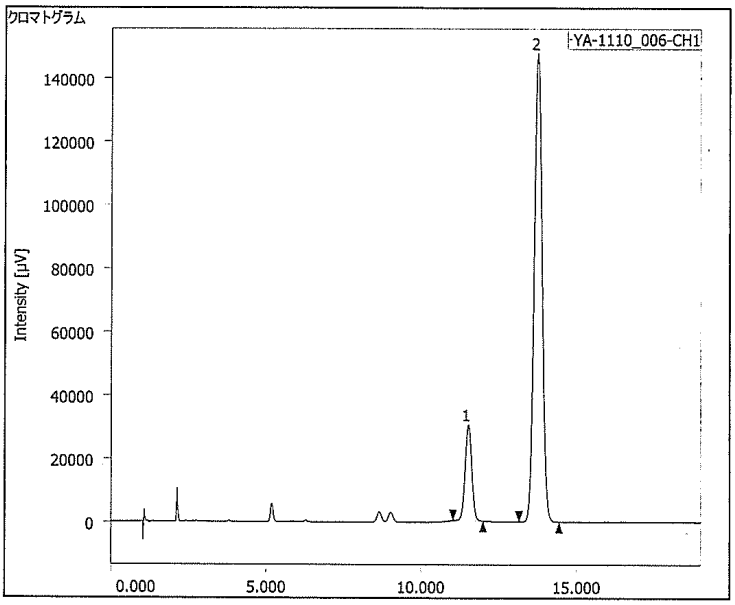
Table S1. SFC separation conditions and retention times of products

entry	Compound	column	Eluent	Flow rate (mL/min)	t_R of (*R*)-isomer (min)	t_R of (*S*)-isomer (min)
1	 **3Aa**	AD-H	*i*-PrOH/CO_2 1/20	3.15	11.5	13.7
2	 **3Ba**	AD-H	*i*-PrOH/CO_2 1/10	3.3	5.3	6.7
3	 **3Ca**	AD-H	*i*-PrOH/CO_2 1/10	3.3	6.3	7.1
4	 **3Da**	AD-H	*i*-PrOH/CO_2 1/10	3.3	6.2	7.0
5	 **3Ea**	AD-H	*i*-PrOH/CO_2 1/5	3.6	8.8	7.3
6	 **3Fa**	AD-H	*i*-PrOH/CO_2 1/5	3.6	5.0	6.8
7	 **3Ga**	AD-H	*i*-PrOH/CO_2 1/5	3.6	6.2	7.9
8	 **3Ha**	AD-H	*i*-PrOH/CO_2 1/10	3.3	5.6	9.1

9	 **3Ia**	AD-H	*i*-PrOH/CO_2 1/5	3.6	7.0	10.0
10	 **3Ja**	AD-H	*i*-PrOH/CO_2 1/5	3.6	8.2	13.2
11	 **3Db**	AD-H	*i*-PrOH/CO_2 1/5	3.6	2.1	1.9
12[a]	 **3Dc**	AD-H	*i*-PrOH/hexane 1/19	0.6	8.2	12.0
13	 **3Dd**	AD-H	*i*-PrOH/CO_2 1/10	3.3	8.6	7.4
14	 **3De**	AZ-H	*i*-PrOH/CO_2 1/20	3.15	6.7	6.1
15	 **3Df**	AD-H	*i*-PrOH/CO_2 1/5	3.6	7.1	10.8
16	 **3Dg**	OZ-H	*i*-PrOH/CO_2 1/20	3.15	3.9	3.4

17[a]	 **3Dh**	AD-H	*i*-PrOH/hexane 1/49	0.6	10.4	7.8
18	 **3Di**	AD-H	*i*-PrOH/CO_2 1/20	3.15	3.4	3.1
19	 **3Dj**	AD-H	*i*-PrOH/CO_2 1/20	3.15	3.1	2.6
20	 **3Dk**	OZ-H	*i*-PrOH/CO_2 1/20	3.15	5.7	4.6
21	 **4**	AZ-H	*i*-PrOH/CO_2 1/10	3.3	8.3	9.2
22	 **5**	AD-H	*i*-PrOH/CO_2 1/10	3.3	9.2	10.3
23	 **S1**	AD-H	*i*-PrOH/CO_2 1/5	3.6	9.3	10.3
24	 **S2**	AD-H	*i*-PrOH/CO_2 1/5	3.6	6.9	5.6

[a] Determined by chiral HPLC.

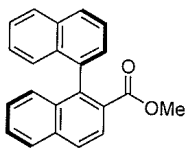


クロマトグラム情報

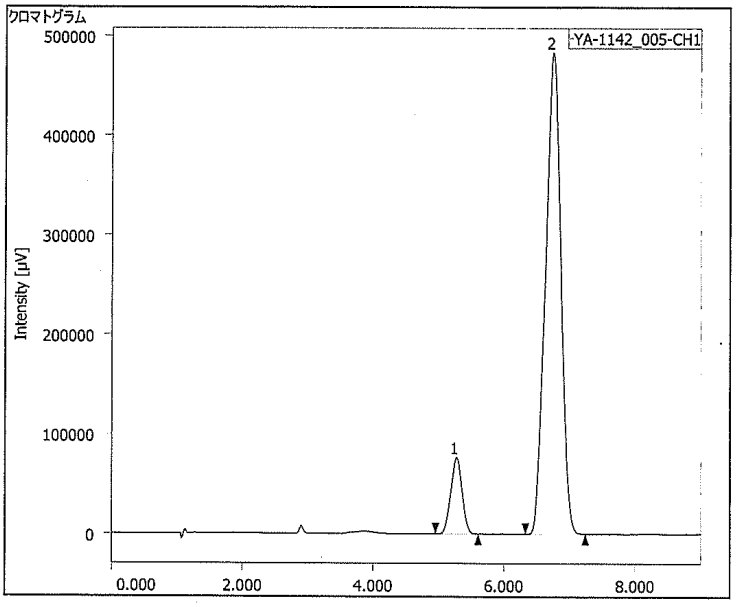
ユーザー名	JASCO
更新日時	2012/10/12 19:51:37
コメント	
HPLC システム名	JASCO SFC
測定日	2012/10/12 19:32:36
注入量	1.00 [μL]
サンプル#	47
プロジェクト名	Akai
取込時間	19.0 [min]
測定シーケンス	
コントロールメソッド	P2_IPA5%_20min_220nm

ピーク情報

#	ピーク名	tR [min]	面積 [μV·sec]	高さ [μV]	面積%	高さ%	定量値	NTP	分離度
1	Unknown	11.517	452360	30353	14.713	17.042	N/A	13887	5.196
2	Unknown	13.743	2622203	147749	85.287	82.958	N/A	13777	N/A



SFC trace for **3Aa**

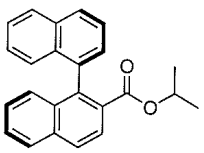


クロマトグラム情報

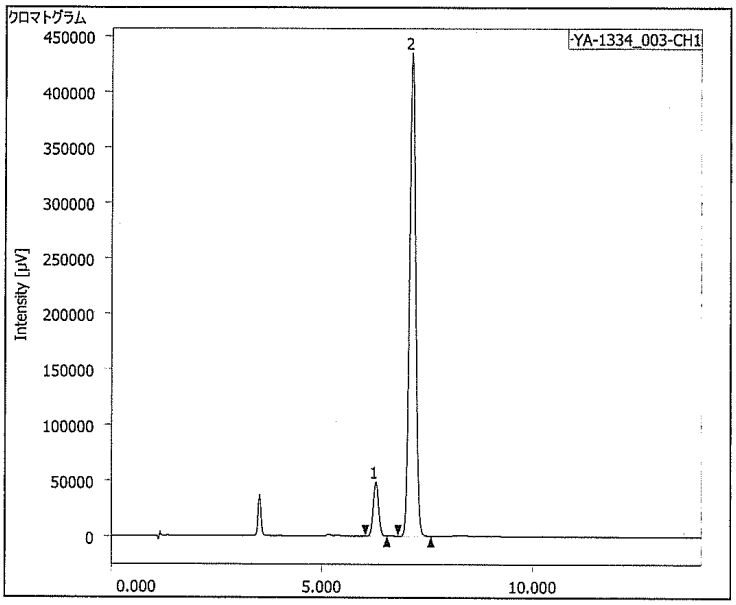
ユーザー名	JASCO
更新日時	2012/11/01 18:41:48
コメント	
HPLC システム名	JASCO SFC
測定日	2012/11/01 18:32:46
注入量	1.00 [μL]
サンプル#	12
プロジェクト名	Akai
取込時間	9.0 [min]
測定シーケンス	
コントロールメソッド	P2_IPA10%_10min_230nm

ピーク情報

#	ピーク名	tR [min]	面積 [μV·sec]	高さ [μV]	面積%	高さ%	定量値	NTP	分離度
1	Unknown	5.273	915145	76705	10.423	13.696	N/A	4391	3.909
2	Unknown	6.740	7865264	483333	89.577	86.304	N/A	3859	N/A



SFC trace for **3Ba**

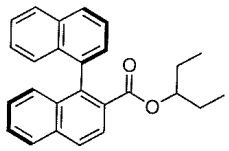


クロマトグラム情報

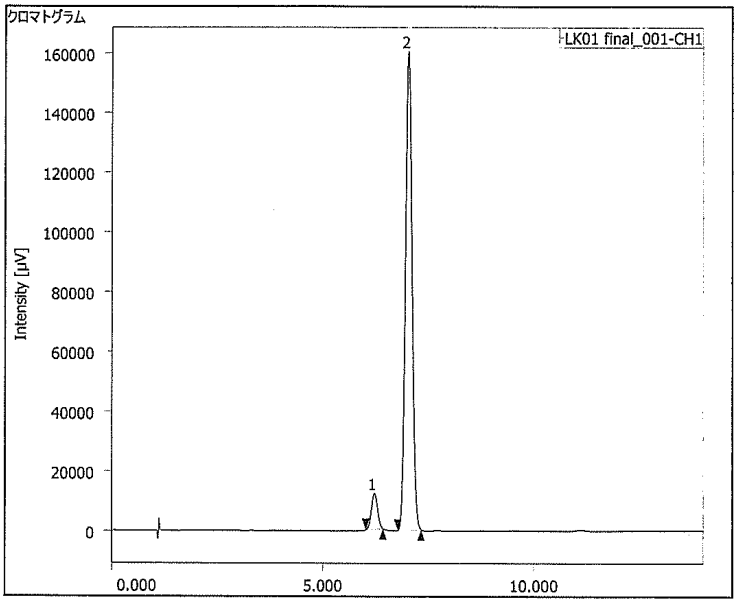
ユーザー名	JASCO
更新日時	2013/03/08 16:46:39
コメント	
HPLC システム名	JASCO SFC
測定日	2013/03/08 16:32:37
注入量	1.00 [μL]
サンプル#	2
プロジェクト名	Akai
取込時間	14.0 [min]
測定シーケンス	
コントロールメソッド	P2_IPA10%_15min_220nm

ピーク情報

#	ピーク名	tR [min]	面積 [μV·sec]	高さ [μV]	面積%	高さ%	定量値	NTP	分離度
1	Unknown	6.283	426305	48403	8.803	10.016	N/A	11668	3.433
2	Unknown	7.140	4416613	434882	91.197	89.984	N/A	11377	N/A



SFC trace for **3Ca**

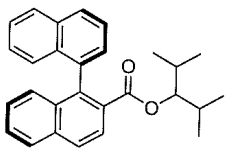


クロマトグラム情報

ユーザー名	JASCO
更新日時	2014/06/24 15:20:14
コメント	
HPLC システム名	JASCO SFC
測定日	2014/06/24 14:52:50
注入量	1.00 [μL]
サンプル#	1
プロジェクト名	Akai
取込時間	14.0 [min]
測定シーケンス	
コントロールメソッド	P2_IPA10%_15min_220nm

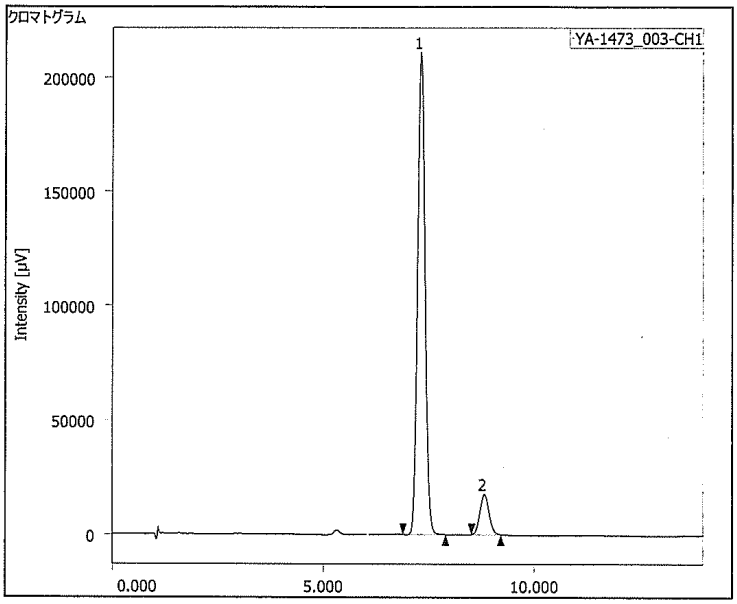
ピーク情報

#	ピーク名	tR [min]	面積 [μV·sec]	高さ [μV]	面積%	高さ%	定量値	NTP	分離度
1	Unknown	6.227	121323	12000	6.483	6.975	N/A	9558	2.903
2	Unknown	7.033	1750166	160039	93.517	93.025	N/A	9542	N/A



SFC trace for **3Da**

0726 YA-1473_003 2014/11/08 16:33:22

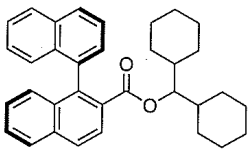


クロマトグラム情報

ユーザー名	JASCO
更新日時	2013/07/26 18:36:16
コメント	
HPLC システム名	JASCO SFC
測定日	2013/07/26 18:22:14
注入量	1.00 [μL]
サンプル#	22
プロジェクト名	Akai
取込時間	14.0 [min]
測定シーケンス	
コントロールメソッド	P2_IPA20%_15min_220nm

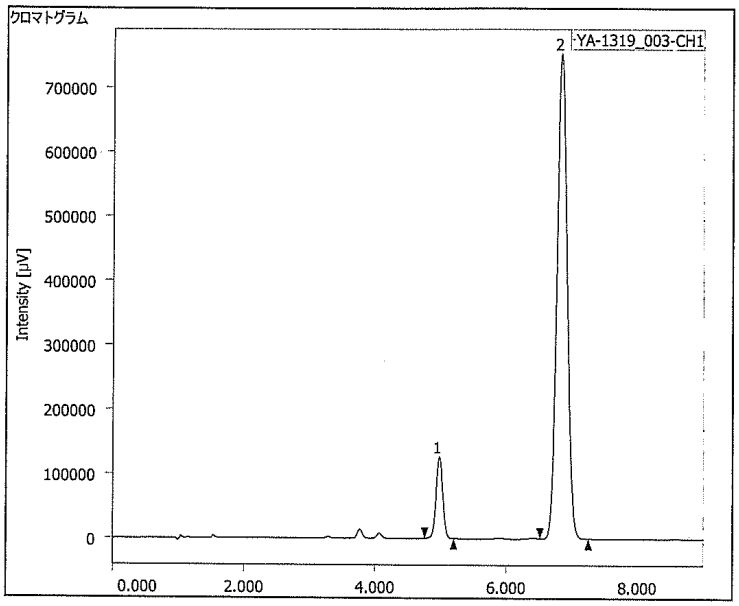
ピーク情報

#	ピーク名	tR [min]	面積 [μV*sec]	高さ [μV]	面積%	高さ%	定量値	NTP	分離度
1	Unknown	7.313	2600063	211016	90.815	92.307	N/A	8202	4.209
2	Unknown	8.820	262973	17586	9.185	7.693	N/A	7986	N/A



1 / 1

SFC trace for **3Ea**

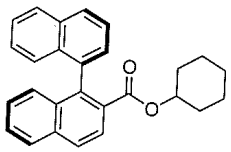


クロマトグラム情報

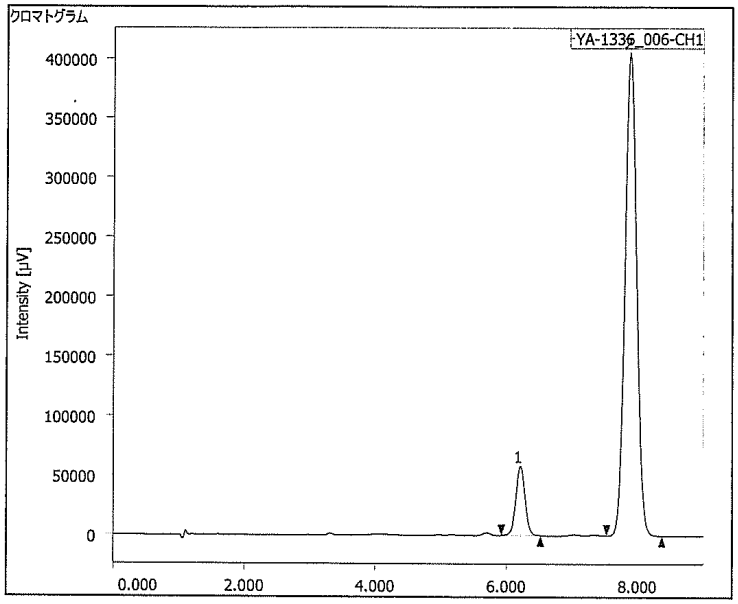
ユーザー名	JASCO
更新日時	2013/02/28 20:35:01
コメント	
HPLC システム名	JASCO SFC
測定日	2013/02/28 20:25:59
注入量	1.00 [μL]
サンプル#	2
プロジェクト名	Akai
取込時間	9.0 [min]
測定シーケンス	
コントロールメソッド	P2_IPA20%_10min_220nm

ピーク情報

#	ピーク名	tR [min]	面積 [μV·sec]	高さ [μV]	面積%	高さ%	定量値	NTP	分離度
1	Unknown	4.973	903083	126722	10.031	14.413	N/A	11325	7.890
2	Unknown	6.830	8099978	752520	89.969	85.587	N/A	9192	N/A



SFC trace for **3Fa**

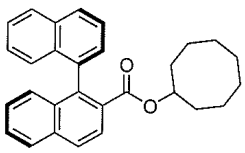


クロマトグラム情報

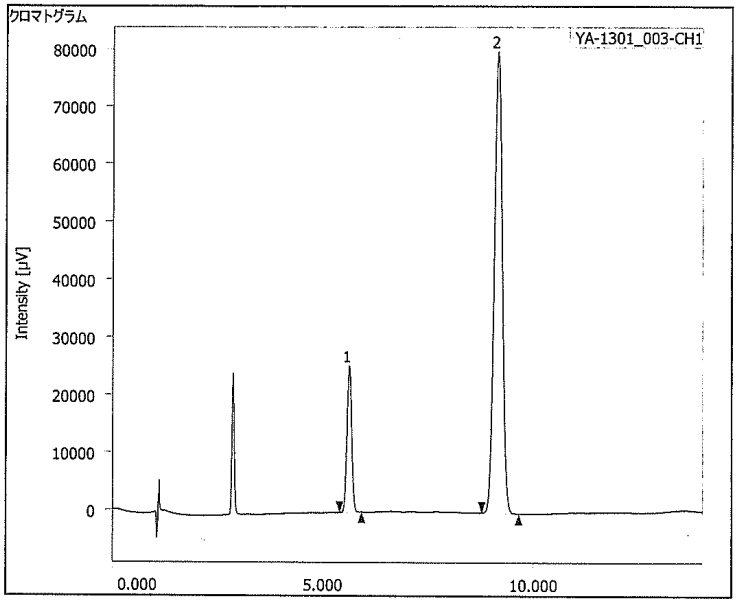
ユーザー名	JASCO
更新日時	2013/03/08 18:57:57
コメント	
HPLC システム名	JASCO SFC
測定日	2013/03/08 18:48:54
注入量	1.00 [μL]
サンプル#	4
プロジェクト名	Akai
取込時間	9.0 [min]
測定シーケンス	
コントロールメソッド	P2_IPA20%_10min_220nm

ピーク情報

#	ピーク名	tR [min]	面積 [μV·sec]	高さ [μV]	面積%	高さ%	定量値	NTP	分離度
1	Unknown	6.210	564870	57952	10.063	12.506	N/A	9509	5.738
2	Unknown	7.880	5048657	405427	89.937	87.494	N/A	9185	N/A



SFC trace for **3Ga**

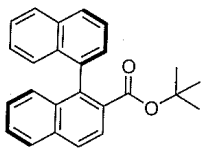


クロマトグラム情報

ユーザー名	JASCO
更新日時	2013/02/21 18:50:21
コメント	
HPLC システム名	JASCO SFC
測定日	2013/02/21 18:36:19
注入量	1.00 [μL]
サンプル#	2
プロジェクト名	Akai
取込時間	14.0 [min]
測定シーケンス	
コントロールメソッド	P2_IPA10%_15min_220nm

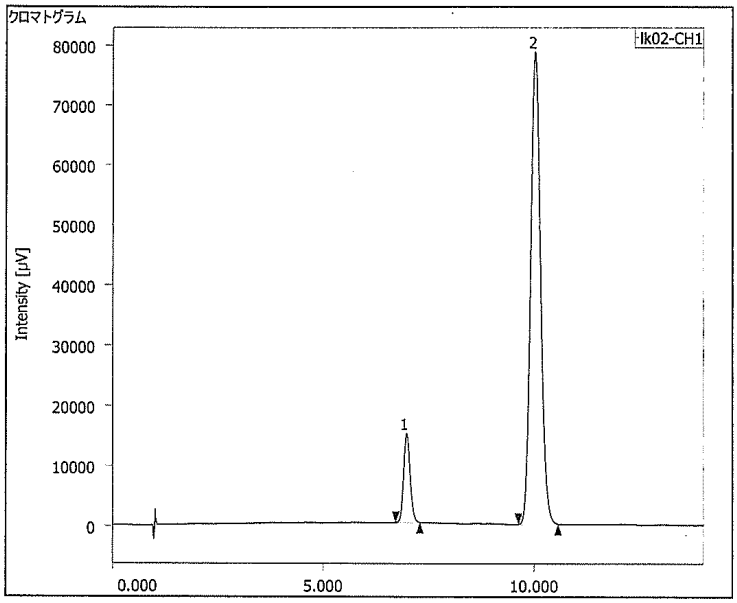
ピーク情報

#	ピーク名	tR [min]	面積 [μV·sec]	高さ [μV]	面積%	高さ%	定量値	NTP	分離度
1	Unknown	5.620	199526	25444	15.979	24.109	N/A	11739	12.759
2	Unknown	9.147	1049122	80095	84.021	75.891	N/A	11128	N/A



SFC trace for **3Ha**

Akai-1 Ik02 2014/11/08 16:34:18

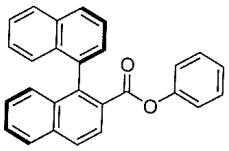


クロマトグラム情報

ユーザー名	JASCO
更新日時	2014/06/26 15:41:21
コメント	
HPLC システム名	JASCO SFC
測定日	2014/06/26 15:03:09
注入量	1.00 [μL]
サンプル#	2
プロジェクト名	Akai
取込時間	14.0 [min]
測定シーケンス	Akai-1
コントロールメソッド	P2_IPA20%_15min_220nm

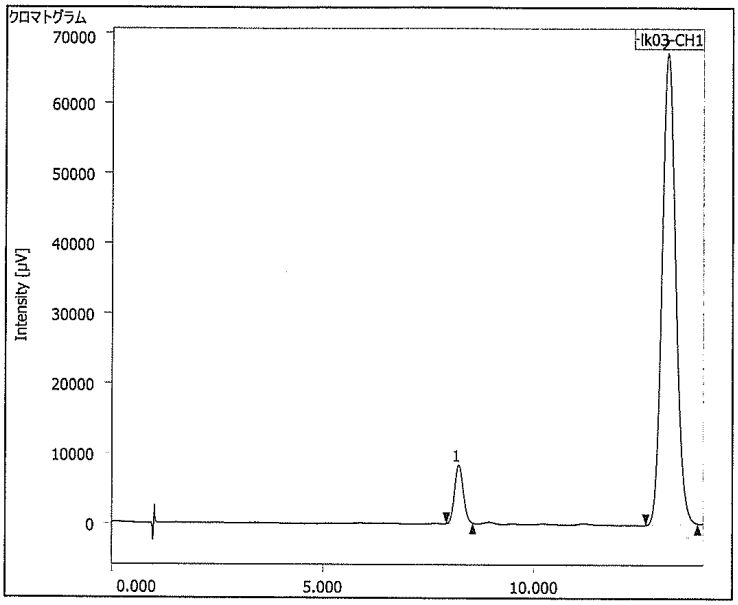
ピーク情報

#	ピーク名	tR [min]	面積 [μV·sec]	高さ [μV]	面積%	高さ%	定量値	NTP	分離度
1	Unknown	6.980	157362	14817	10.988	15.875	N/A	10148	8.687
2	Unknown	10.017	1274750	78518	89.012	84.125	N/A	8936	N/A



1 / 1

SFC trace for **3Ia**

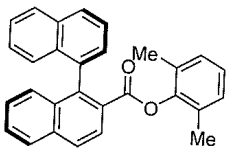


クロマトグラム情報

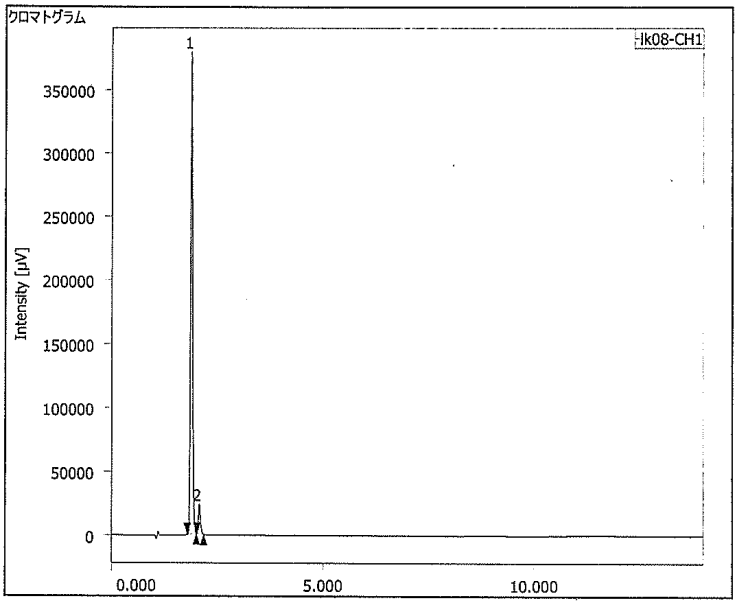
ユーザー名	JASCO
更新日時	2014/06/26 15:41:20
コメント	
HPLC システム名	JASCO SFC
測定日	2014/06/26 15:18:13
注入量	1.00 [μL]
サンプル#	3
プロジェクト名	Akai
取込時間	14.0 [min]
測定シーケンス	Akai-1
コントロールメソッド	P2_IPA20%_15min_220nm

ピーク情報

#	ピーク名	tR [min]	面積 [μV·sec]	高さ [μV]	面積%	高さ%	定量値	NTP	分離度
1	Unknown	8.220	118561	8306	7.305	10.995	N/A	7513	10.267
2	Unknown	13.163	1504346	67238	92.695	89.005	N/A	8067	N/A



SFC trace for **3Ja**

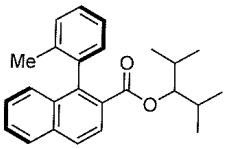


クロマトグラム情報

ユーザー名	JASCO
更新日時	2014/07/03 18:36:12
コメント	
HPLC システム名	JASCO SFC
測定日	2014/07/03 17:37:54
注入量	1.00 [μL]
サンプル#	4
プロジェクト名	Akai
取込時間	14.0 [min]
測定シーケンス	Akai-1
コントロールメソッド	P2_IPA20%_15min_220nm

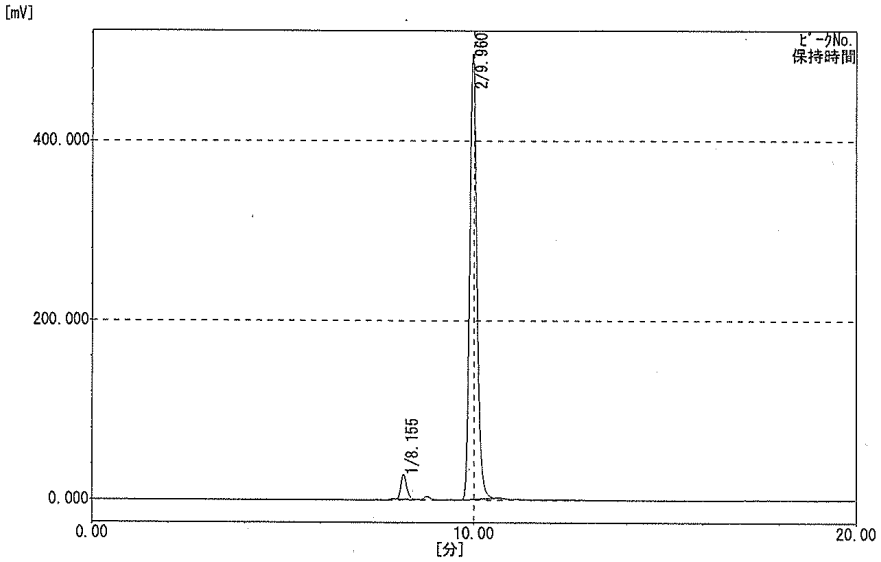
ピーク情報

#	ピーク名	tR [min]	面積 [μV·sec]	高さ [μV]	面積%	高さ%	定量値	NTP	分離度
1	Unknown	1.877	1241115	378550	94.159	94.306	N/A	7994	2.333
2	Unknown	2.077	76990	22856	5.841	5.694	N/A	8917	N/A



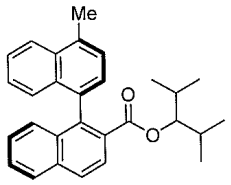
SFC trace for **3Db**

タイトル　　：
データ　　：C:¥HPLCData¥data_nishikawa.mdb　TN0540　Ik29
日時　　：収集 2014/07/26 10:46:52　計算 2014/07/26 13:05:57
カップ番号　：12
収集属性　　：独立　0.00 - 20.00 min
計算方法　　：百分率法



No.	Ch	時間[分]	高さ[mV]	半値幅[秒]	面積[mVx秒]	面積%	理論段数	分離能	非対称係数
1	1	8.155	27.17	9.51	284.70	4.17	14679	0.00	1.44
2	1	9.960	496.85	11.97	6545.35	95.83	13812	5.94	1.48

CH.1 Peak Not Found.



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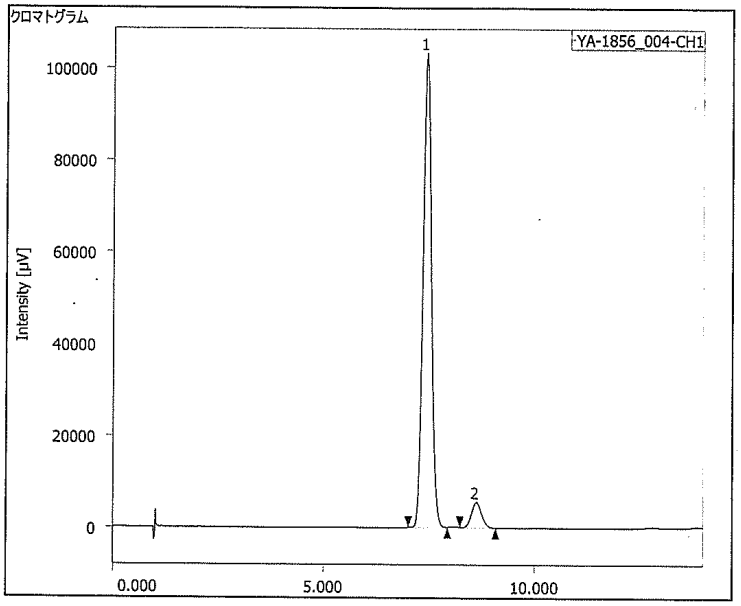
SFC trace for **3Dc**

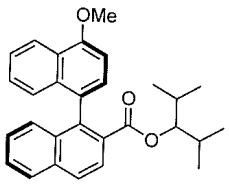


クロマトグラム情報

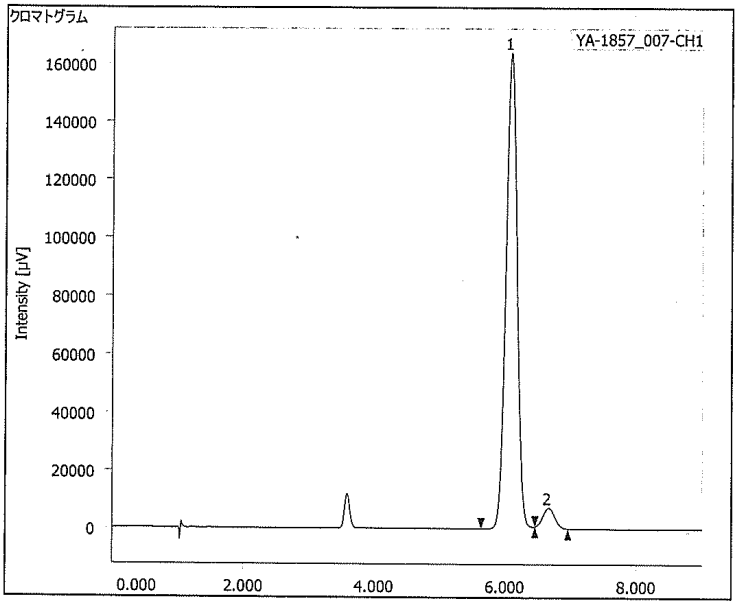
ユーザー名	JASCO
更新日時	2014/09/02 12:37:23
コメント	
HPLC システム名	JASCO SFC
測定日	2014/09/02 12:23:22
注入量	1.00 [μL]
サンプル#	3
プロジェクト名	Akai
取込時間	14.0 [min]
測定シーケンス	
コントロールメソッド	P2_IPA10%_15min_220nm

ピーク情報

#	ピーク名	tR [min]	面積 [μV·sec]	高さ [μV]	面積%	高さ%	定量値	NTP	分離度
1	Unknown	7.427	1408857	103072	93.941	94.960	N/A	6928	3.034
2	Unknown	8.630	90868	5471	6.059	5.040	N/A	6202	N/A



SFC trace for **3Dd**

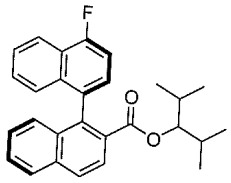


クロマトグラム情報

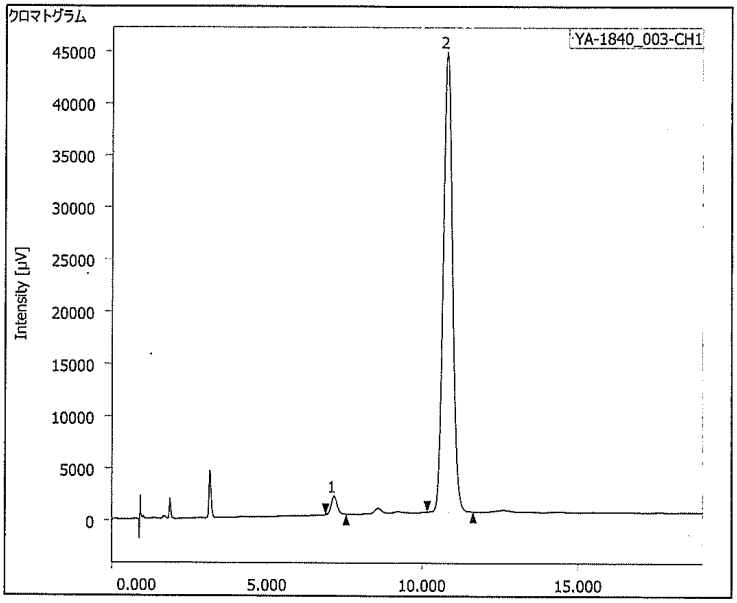
ユーザー名	JASCO
更新日時	2014/09/03 12:48:20
コメント	
HPLC システム名	JASCO SFC
測定日	2014/09/03 12:34:58
注入量	1.00 [μL]
サンプル#	5
プロジェクト名	Akai
取込時間	9.0 [min]
測定シーケンス	
コントロールメソッド	P4_IPA5%_10min_220nm

ピーク情報

#	ピーク名	tR [min]	面積 [μV·sec]	高さ [μV]	面積%	高さ%	定量値	NTP	分離度
1	Unknown	6.080	1927675	163845	95.357	95.787	N/A	6102	1.780
2	Unknown	6.663	93850	7206	4.643	4.213	N/A	5943	N/A



SFC trace for **3De**

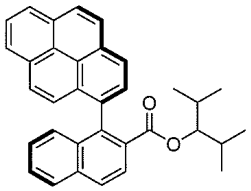


クロマトグラム情報

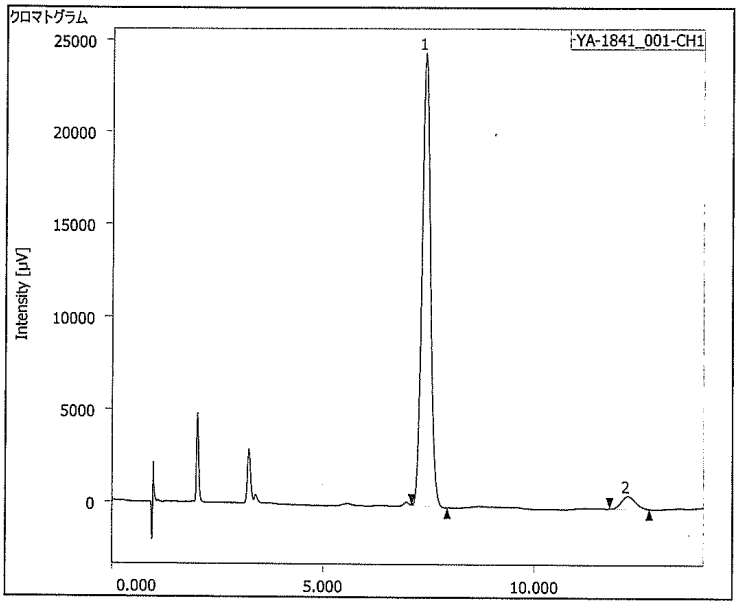
ユーザー名	JASCO
更新日時	2014/08/23 16:31:32
コメント	
HPLC システム名	JASCO SFC
測定日	2014/08/23 16:12:31
注入量	1.00 [μL]
サンプル#	5
プロジェクト名	Akai
取込時間	19.0 [min]
測定シーケンス	
コントロールメソッド	P2_IPA20%_20min_220nm

ピーク情報

#	ピーク名	tR [min]	面積 [μV·sec]	高さ [μV]	面積%	高さ%	定量値	NTP	分離度
1	Unknown	7.143	23328	1750	2.505	3.819	N/A	6678	8.234
2	Unknown	10.797	907947	44072	97.495	96.181	N/A	6394	N/A



SFC trace for (*S*)-**3Df**

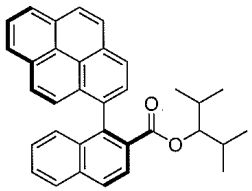


クロマトグラム情報

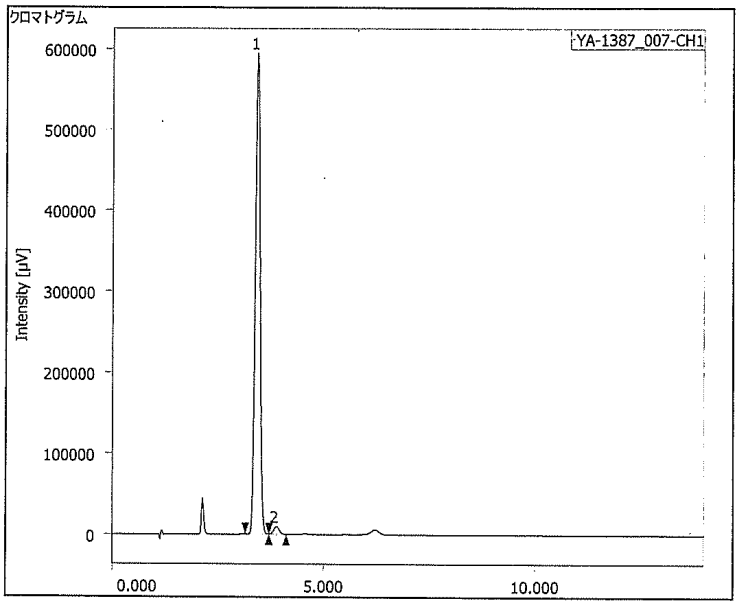
ユーザー名	JASCO
更新日時	2014/08/28 11:01:47
コメント	
HPLC システム名	JASCO SFC
測定日	2014/08/28 10:05:23
注入量	1.00 [μL]
サンプル#	23
プロジェクト名	Akai
取込時間	14.0 [min]
測定シーケンス	
コントロールメソッド	P2_IPA20%_15min_220nm

ピーク情報

#	ピーク名	tR [min]	面積 [μV·sec]	高さ [μV]	面積%	高さ%	定量値	NTP	分離度
1	Unknown	7.413	337963	24454	95.618	97.284	N/A	6722	9.909
2	Unknown	12.207	15489	683	4.382	2.716	N/A	6441	N/A



SFC trace for (*R*)-**3Df**

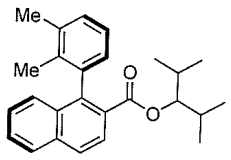


クロマトグラム情報

ユーザー名	JASCO
更新日時	2013/05/11 12:07:52
コメント	
HPLC システム名	JASCO SFC
測定日	2013/05/11 11:53:51
注入量	1.00 [μL]
サンプル#	22
プロジェクト名	Akai
取込時間	14.0 [min]
測定シーケンス	
コントロールメソッド	P6_IPA5%_15min_220nm

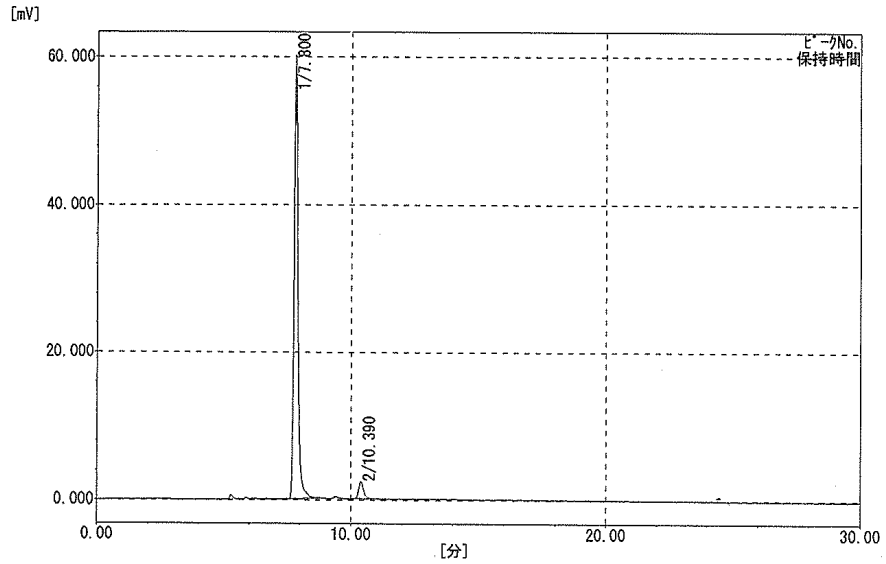
ピーク情報

#	ピーク名	tR [min]	面積 [μV·sec]	高さ [μV]	面積%	高さ%	定量値	NTP	分離度
1	Unknown	3.427	4676967	594042	98.250	98.453	N/A	4325	2.059
2	Unknown	3.887	83296	9337	1.750	1.547	N/A	4210	N/A



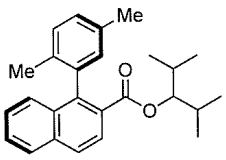
SFC trace for **3Dg**

タイトル　　：
データ　　：C:¥HPLCData¥data_Ke.mdb　yz01660022　lk43
日時　　：収集 2014/08/02 11:11:25　計算 2014/08/02 11:44:49
カップ番号　：11
収集属性　　：独立　0.00 - 30.00 min
計算方法　　：百分率法



No.	Ch	時間[分]	高さ[mV]	半値幅[秒]	面積[mVx秒]	面積%	理論段数	分離能	非対称係数
1	1	7.800	60.16	9.18	638.77	95.48	14393	0.00	1.66
2	1	10.390	2.34	11.78	30.26	4.52	15524	8.73	1.46

CH.1 Peak Not Found.



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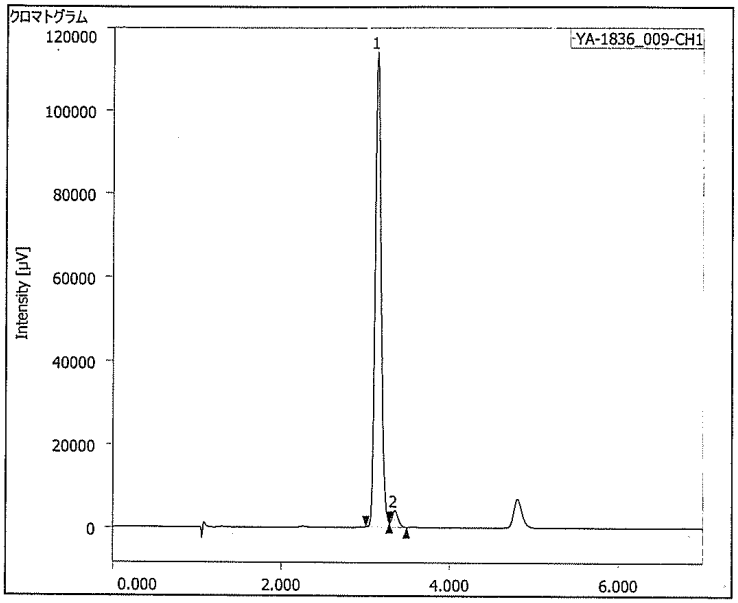
SFC trace for **3Dh**

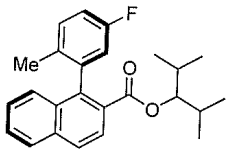


クロマトグラム情報

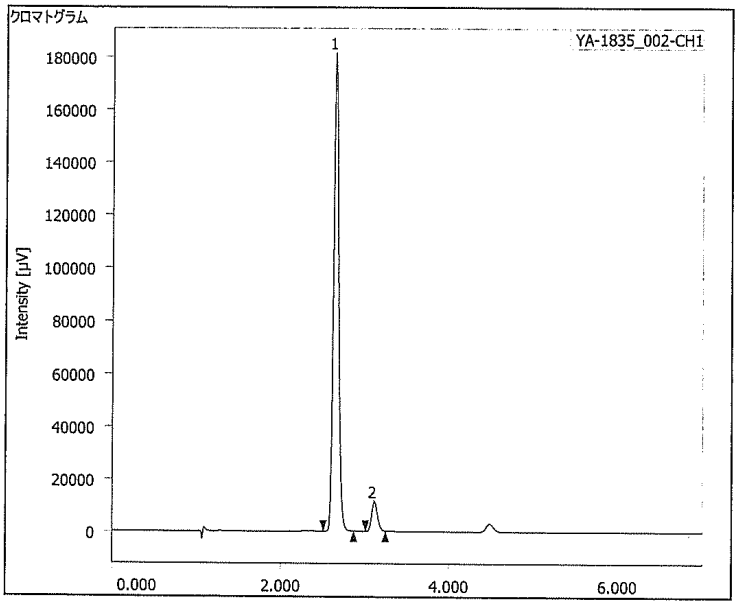
ユーザー名	JASCO
更新日時	2014/08/24 20:20:52
コメント	
HPLC システム名	JASCO SFC
測定日	2014/08/24 20:03:26
注入量	1.00 [μL]
サンプル#	14
プロジェクト名	Akai
取込時間	7.0 [min]
測定シーケンス	
コントロールメソッド	P2_IPA5%_8min_220nm

ピーク情報

#	ピーク名	tR [min]	面積 [μV·sec]	高さ [μV]	面積%	高さ%	定量値	NTP	分離度
1	Unknown	3.140	559165	113951	96.427	96.640	N/A	9853	1.601
2	Unknown	3.350	20722	3962	3.573	3.360	N/A	9626	N/A



SFC trace for **3Di**

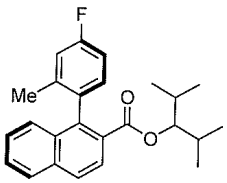


クロマトグラム情報

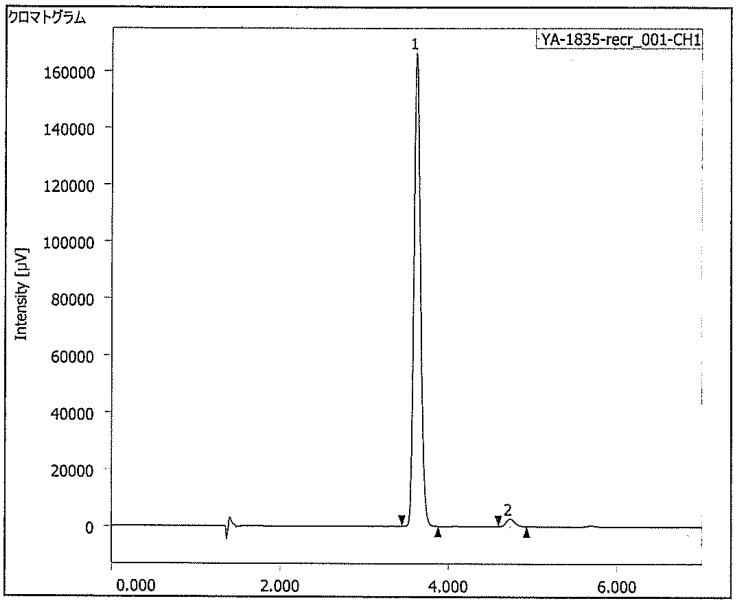
ユーザー名	JASCO
更新日時	2014/08/24 20:20:49
コメント	
HPLC システム名	JASCO SFC
測定日	2014/08/24 18:24:32
注入量	1.00 [μL]
サンプル#	13
プロジェクト名	Akai
取込時間	7.0 [min]
測定シーケンス	
コントロールメソッド	P2_IPA5%_8min_220nm

ピーク情報

#	ピーク名	tR [min]	面積 [μV·sec]	高さ [μV]	面積%	高さ%	定量値	NTP	分離度
1	Unknown	2.640	768743	181372	93.367	94.156	N/A	9310	3.973
2	Unknown	3.110	54613	11257	6.633	5.844	N/A	9474	N/A



SFC trace for **3Dj**



クロマトグラム情報

ユーザー名	JASCO
更新日時	2014/10/07 18:22:03
コメント	
HPLC システム名	JASCO SFC
測定日	2014/10/07 14:44:59
注入量	1.00 [μL]
サンプル#	23
プロジェクト名	Akai
取込時間	7.0 [min]
測定シーケンス	
コントロールメソッド	P2_IPA5%_8min_220nm

ピーク情報

#	ピーク名	tR [min]	面積 [μV*sec]	高さ [μV]	面積%	高さ%	定量値	NTP	分離度
1	Unknown	3.617	910535	166423	97.956	98.428	N/A	10349	6.727
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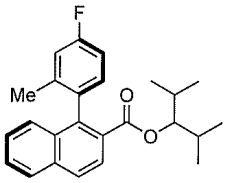
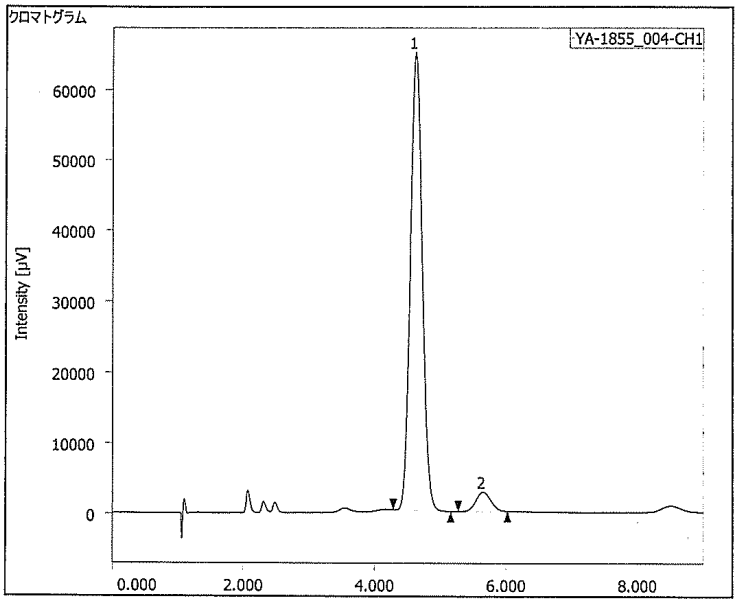


SFC trace for **3Dj** (after single recrystallization)

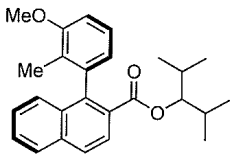


クロマトグラム情報

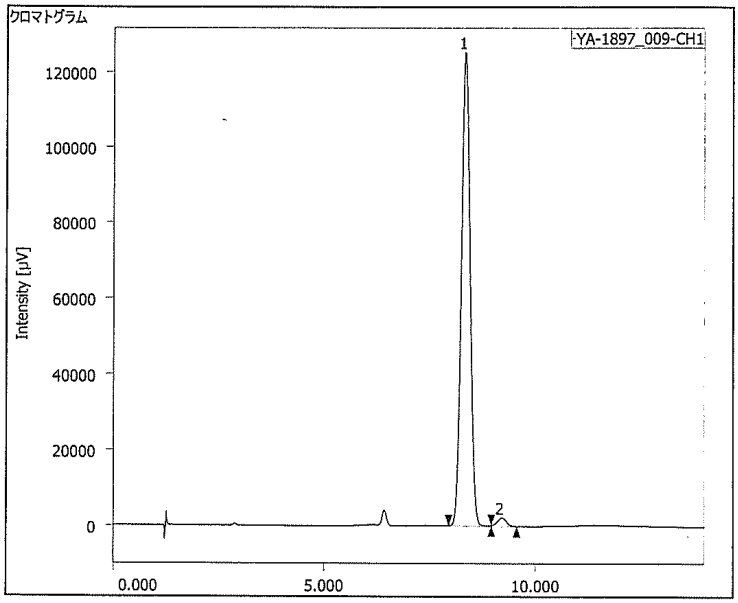
ユーザー名	JASCO
更新日時	2014/09/03 12:48:19
コメント	
HPLC システム名	JASCO SFC
測定日	2014/09/03 11:47:48
注入量	1.00 [μL]
サンプル#	12
プロジェクト名	Akai
取込時間	9.0 [min]
測定シーケンス	
コントロールメソッド	P6_IPA5%_10min_220nm

ピーク情報

#	ピーク名	tR [min]	面積 [μV*sec]	高さ [μV]	面積%	高さ%	定量値	NTP	分離度
1	Unknown	4.623	818450	64828	94.976	95.944	N/A	3085	2.742
2	Unknown	5.653	43293	2741	5.024	4.056	N/A	2893	N/A



SFC trace for **3Dk**



クロマトグラム情報

ユーザー名	JASCO
更新日時	2014/10/07 18:22:05
コメント	
HPLC システム名	JASCO SFC
測定日	2014/10/07 18:01:54
注入量	1.00 [μL]
サンプル#	25
プロジェクト名	Akai
取込時間	14.0 [min]
測定シーケンス	
コントロールメソッド	P4_IPA10%_15min_220nm

ピーク情報

#	ピーク名	tR [min]	面積 [μV·sec]	高さ [μV]	面積%	高さ%	定量値	NTP	分離度
1	Unknown	8.337	1806464	125188	98.198	98.279	N/A	7651	2.223
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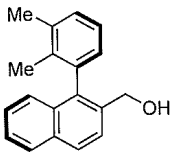
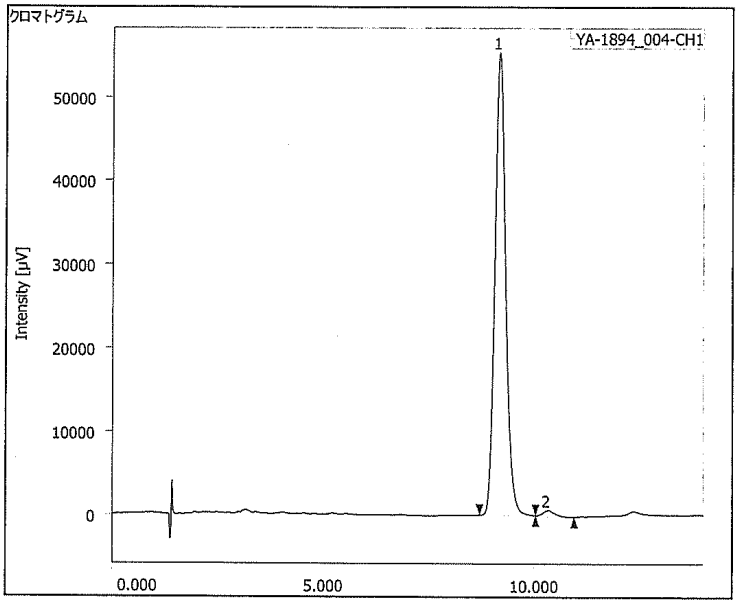


SFC trace for **4Dg**

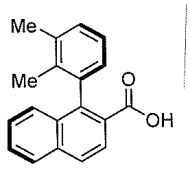


クロマトグラム情報

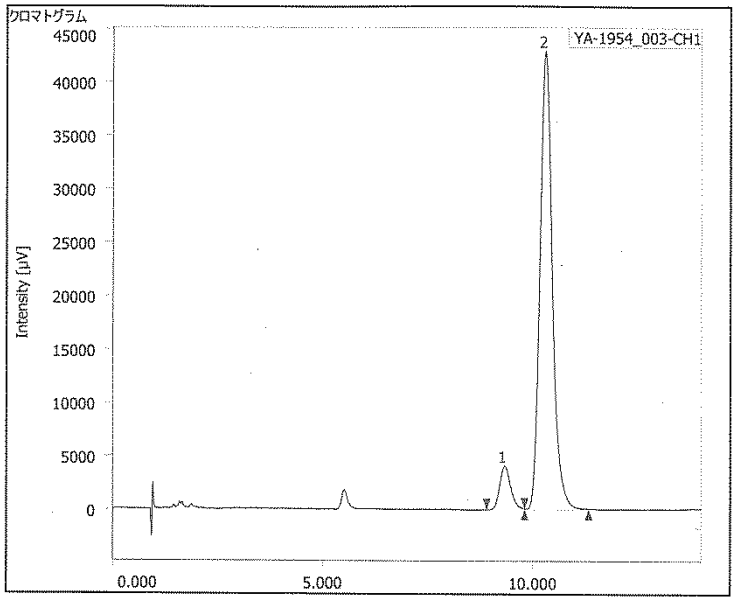
ユーザー名	JASCO
更新日時	2014/10/06 12:03:20
コメント	
HPLC システム名	JASCO SFC
測定日	2014/10/06 11:45:15
注入量	1.00 [μL]
サンプル#	24
プロジェクト名	Akai
取込時間	14.0 [min]
測定シーケンス	
コントロールメソッド	P2_IPA10%_15min_220nm

ピーク情報

#	ピーク名	tR [min]	面積 [μV·sec]	高さ [μV]	面積%	高さ%	定量値	NTP	分離度
1	Unknown	9.173	983210	55411	98.561	98.697	N/A	6539	2.428
2	Unknown	10.323	14352	731	1.439	1.303	N/A	6933	N/A



SFC trace for **5Dg**

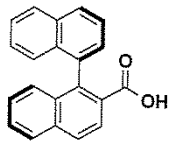


クロマトグラム情報

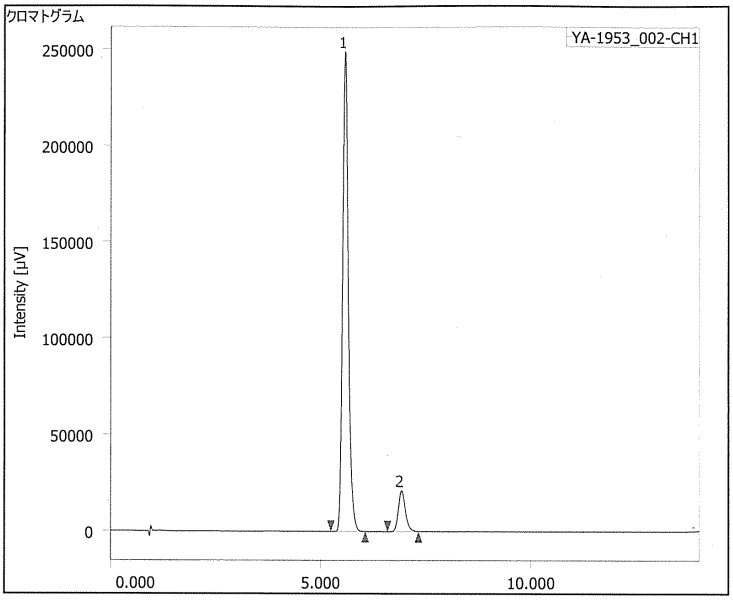
ユーザー名	JASCO
更新日時	2015/01/20 19:41:52
コメント	
HPLC システム名	JASCO SFC
測定日	2015/01/20 19:25:48
注入量	1.00 [μL]
サンプル#	28
プロジェクト名	Akai
取込時間	14.0 [min]
測定シーケンス	
コントロールメソッド	P2_IPA20%_15min_220nm

ピーク情報

#	ピーク名	tR [min]	面積 [μV*sec]	高さ [μV]	面積%	高さ%	定量値	NTP	分離度
1	Unknown	9.327	73766	4089	7.831	8.719	N/A	6478	1.969
2	Unknown	10.287	868200	42806	92.169	91.281	N/A	6408	N/A



SFC trace for **S1**

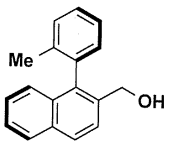


クロマトグラム情報

ユーザー名	JASCO
更新日時	2015/01/20 19:41:51
コメント	
HPLC システム名	JASCO SFC
測定日	2015/01/20 19:08:49
注入量	1.00 [μL]
サンプル#	27
プロジェクト名	Akai
取込時間	14.0 [min]
測定シーケンス	
コントロールメソッド	P2_IPA20%_15min_220nm

ピーク情報

#	ピーク名	tR [min]	面積 [μV·sec]	高さ [μV]	面積%	高さ%	定量値	NTP	分離度
1	Unknown	5.577	2359878	249387	90.548	92.136	N/A	8632	5.041
2	Unknown	6.923	246353	21287	9.452	7.864	N/A	8774	N/A



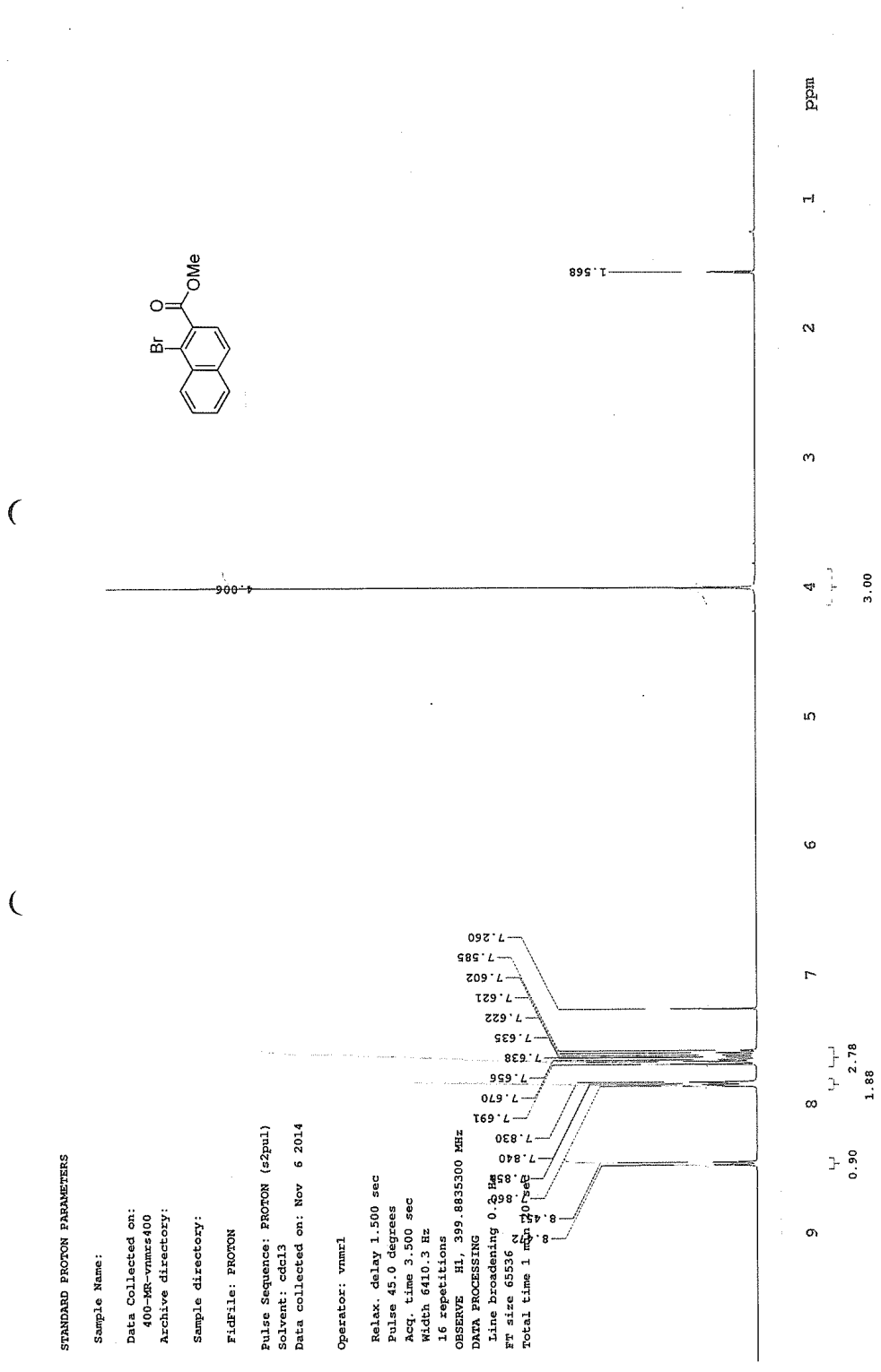
SFC trace for **S2**

4. References

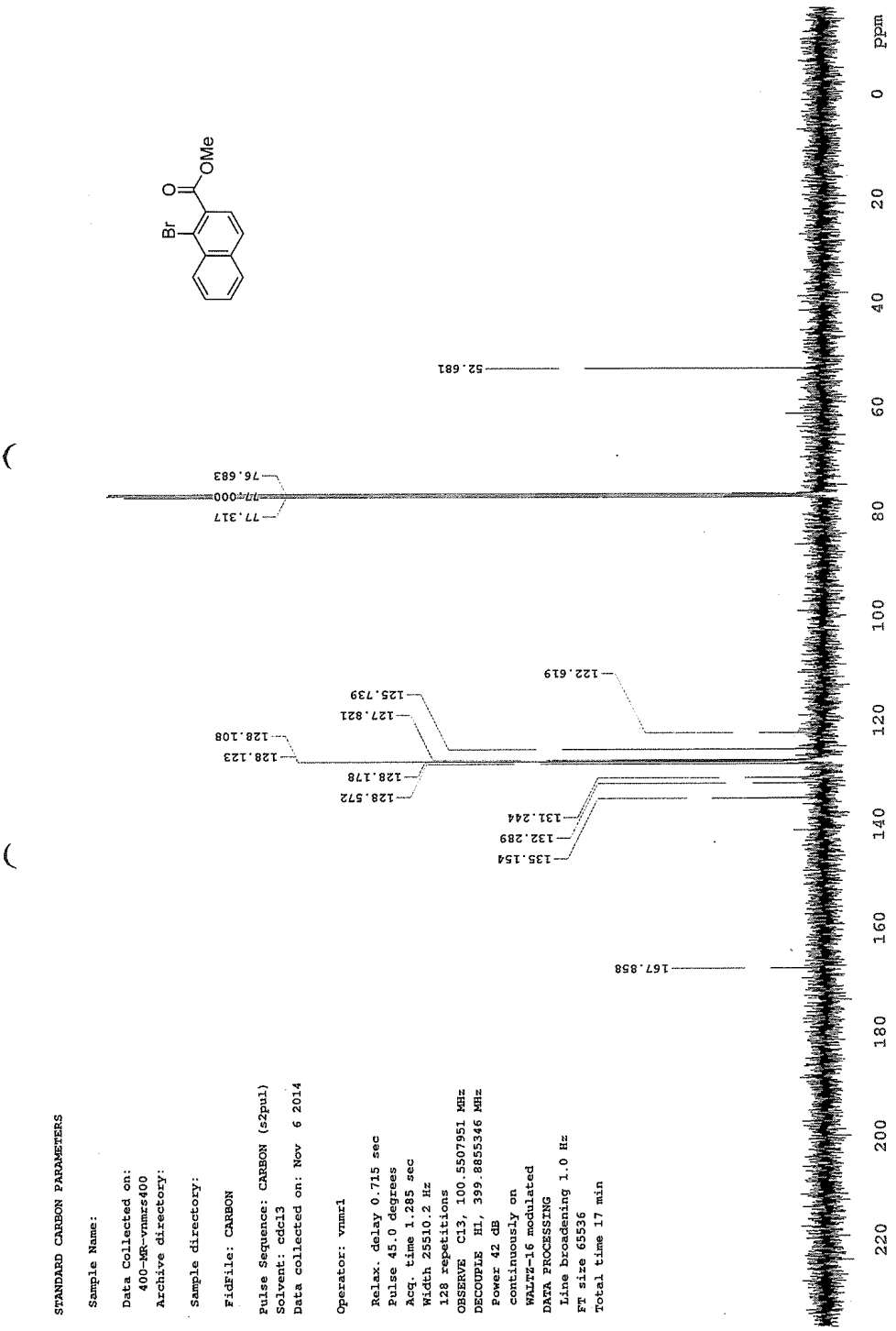
[S1] a) Yamamoto, T.; Akai, Y.; Nagata, Y.; Suginome, M. *Angew. Chem., Int. Ed.* **2011,** *50*, 8844.
b) Yamamoto, T.; Akai, Y.; Suginome, M. *Angew. Chem., Int. Ed.* **2014,** *53*, 12785.

[S2] a) Tang, W.; Patel, N. D.; Xu, G.; Xu, X.; Savoie, J.; Ma, S.; Hao, M.-H.; Keshipeddy, S.; Capacci, A. G.; Wei, X.; Zhang, Y.; Gao, J. J.; Li, W.; Rodriguez, S.; Lu, B. Z.; Yee, N. K.; Senanayake, C. H., *Org. Lett.* **2012**, *14*, 2258.
b) Sun, L.; Dai, W.-M. *Tetrahedron* **2011,** *67*, 9072.

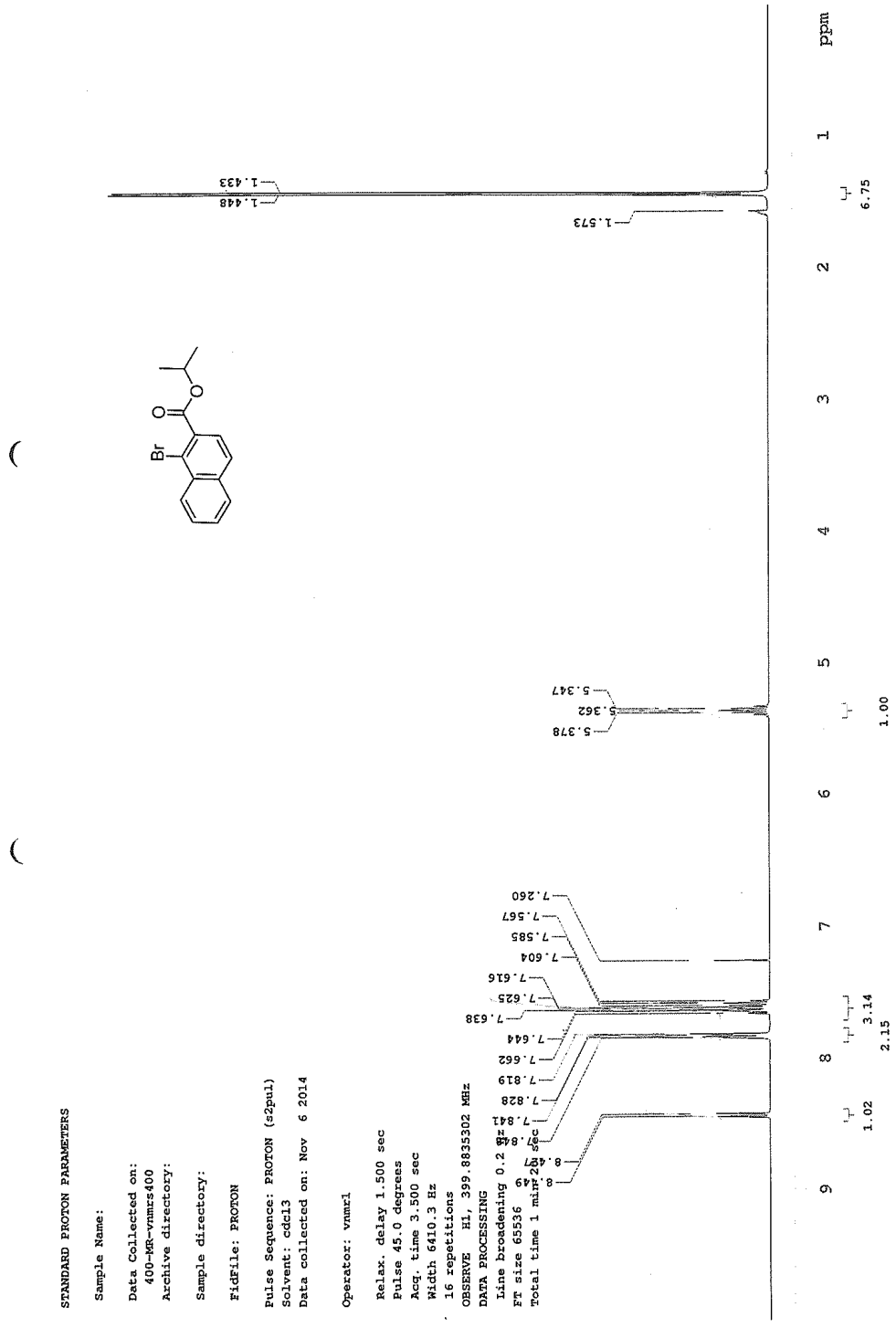
5. NMR Spectra and GPC Chart of New Compounds



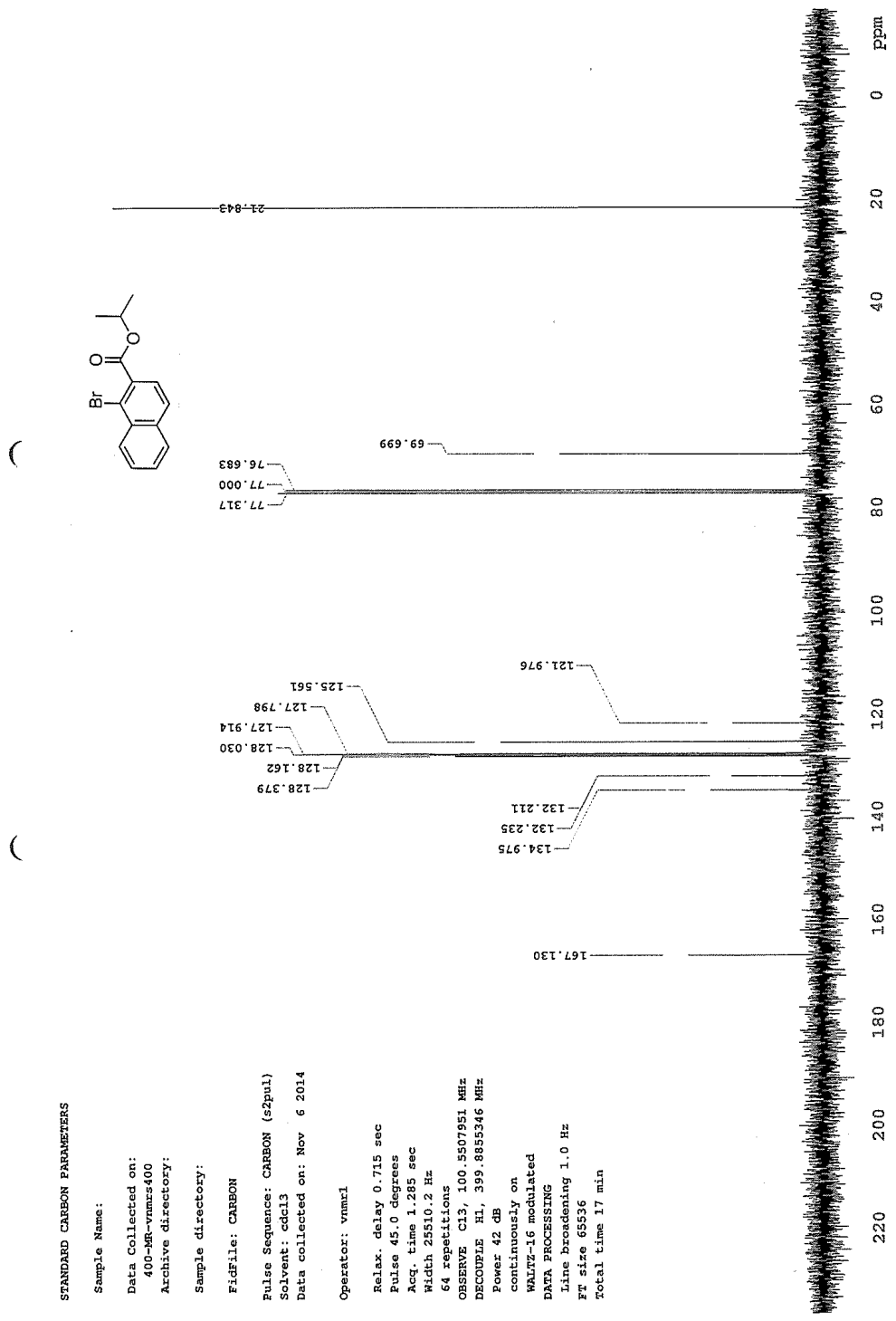
^{1}H NMR of compound **1A**



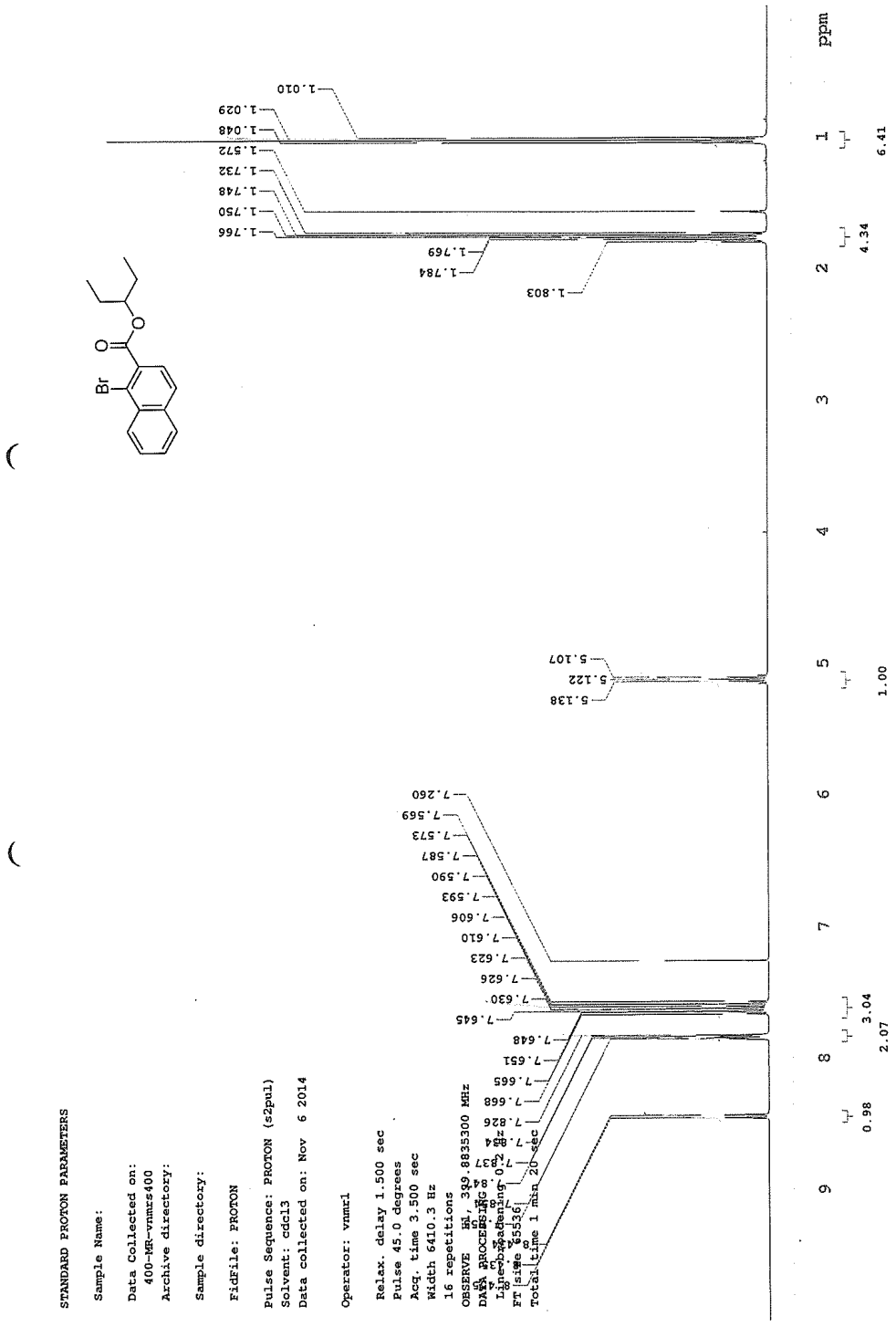
^{13}C NMR of compound **1A**



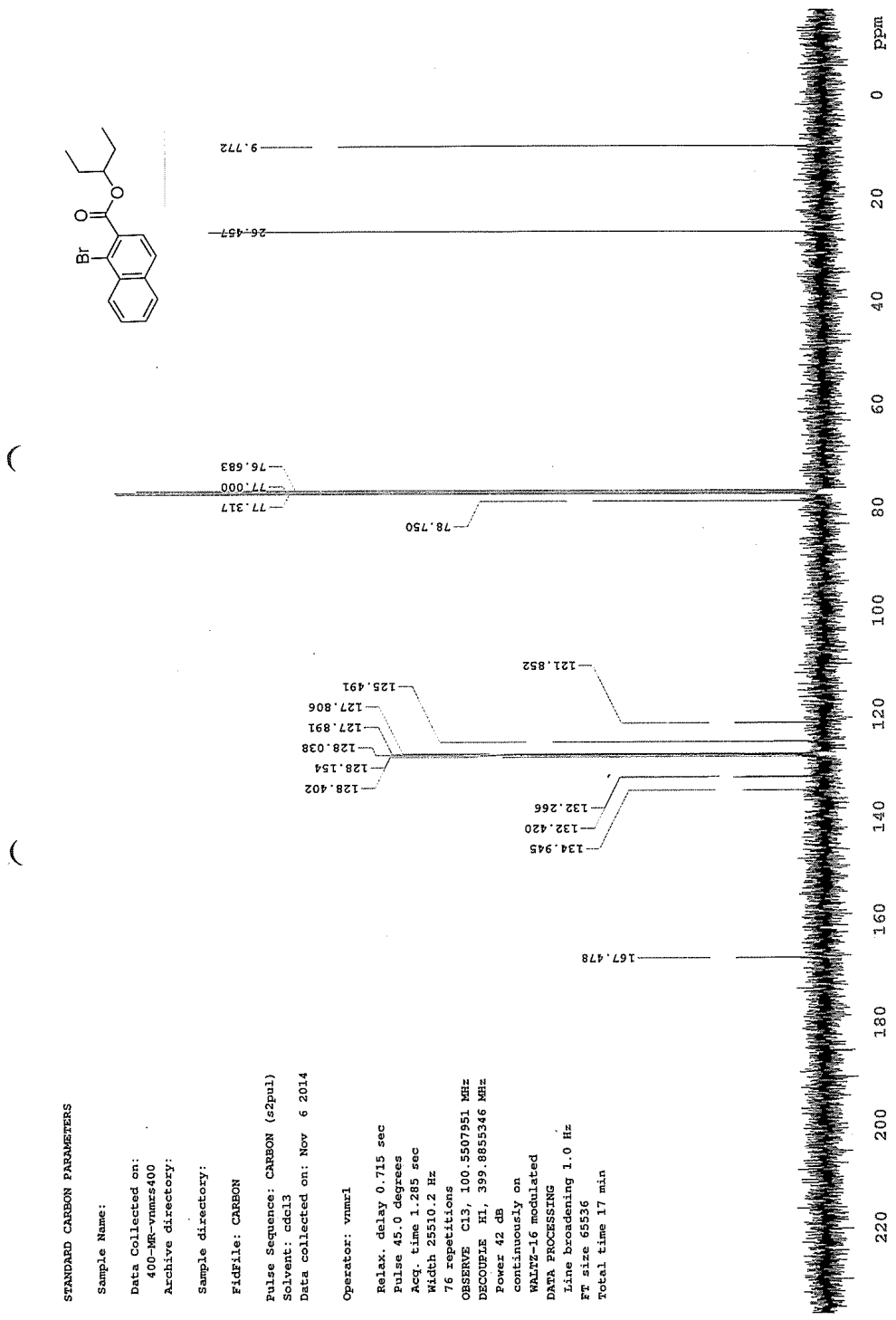
^{1}H NMR of compound **1B**



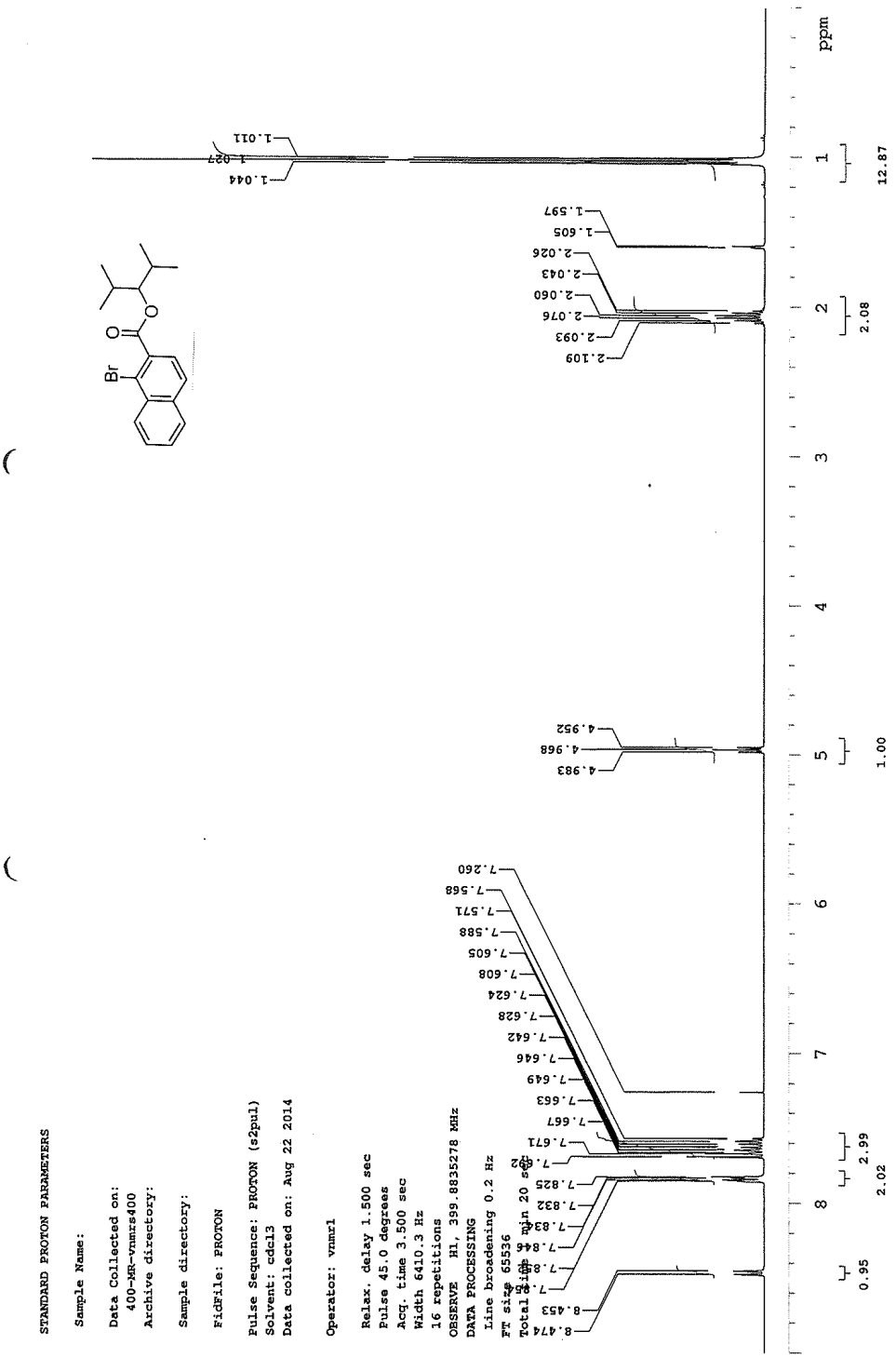
^{13}C NMR of compound **1B**



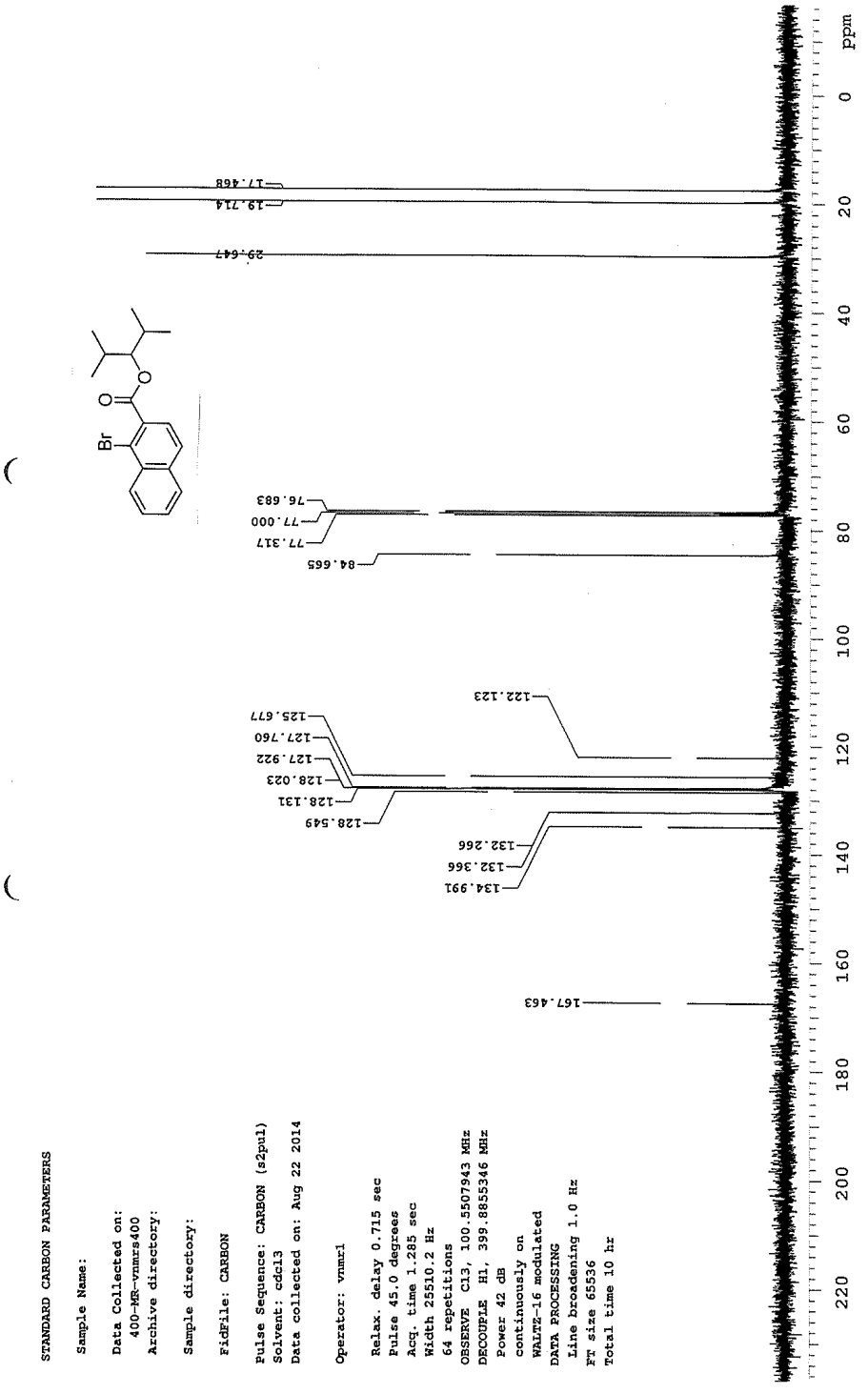
^{1}H NMR of compound **1C**



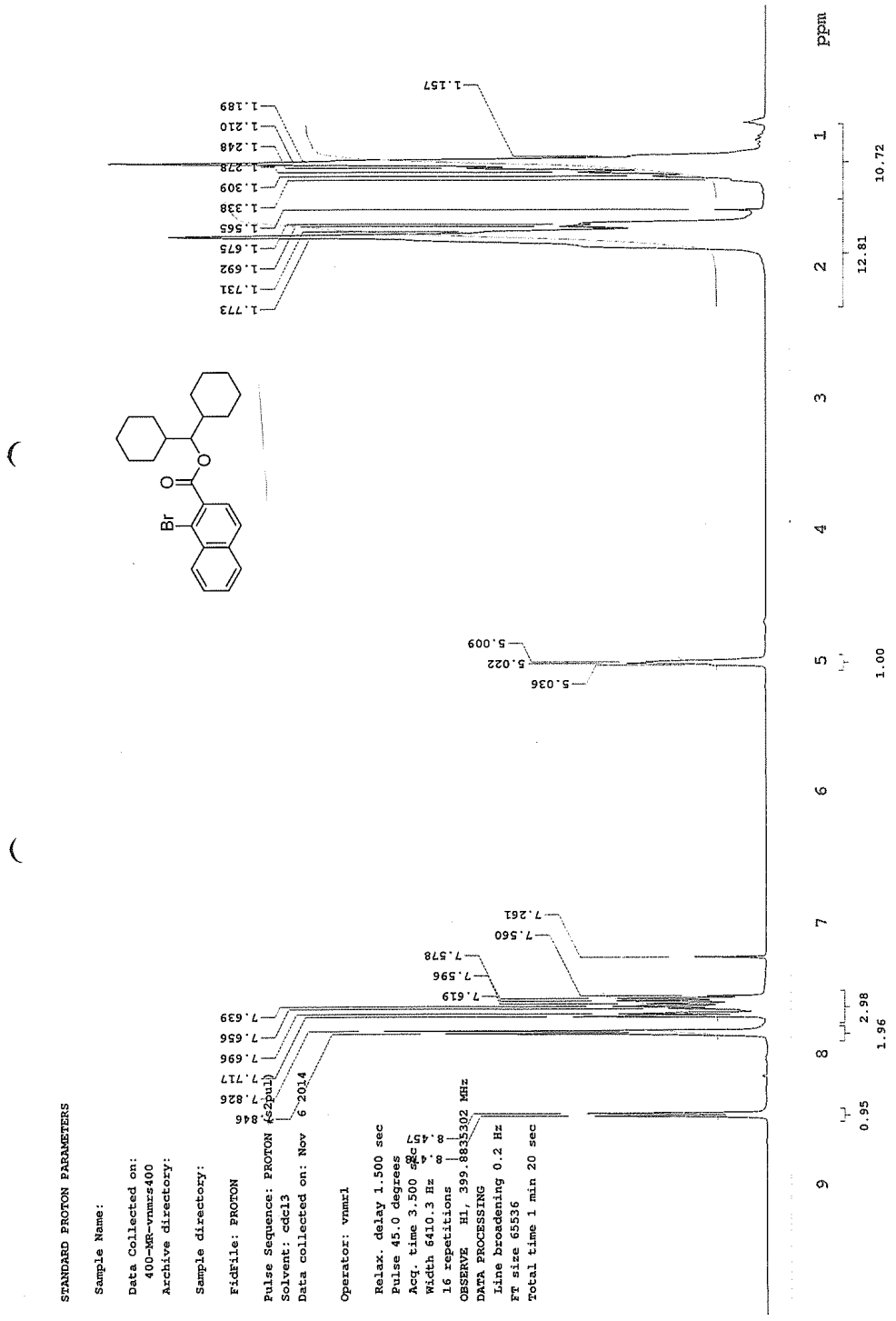
^{13}C NMR of compound **1C**



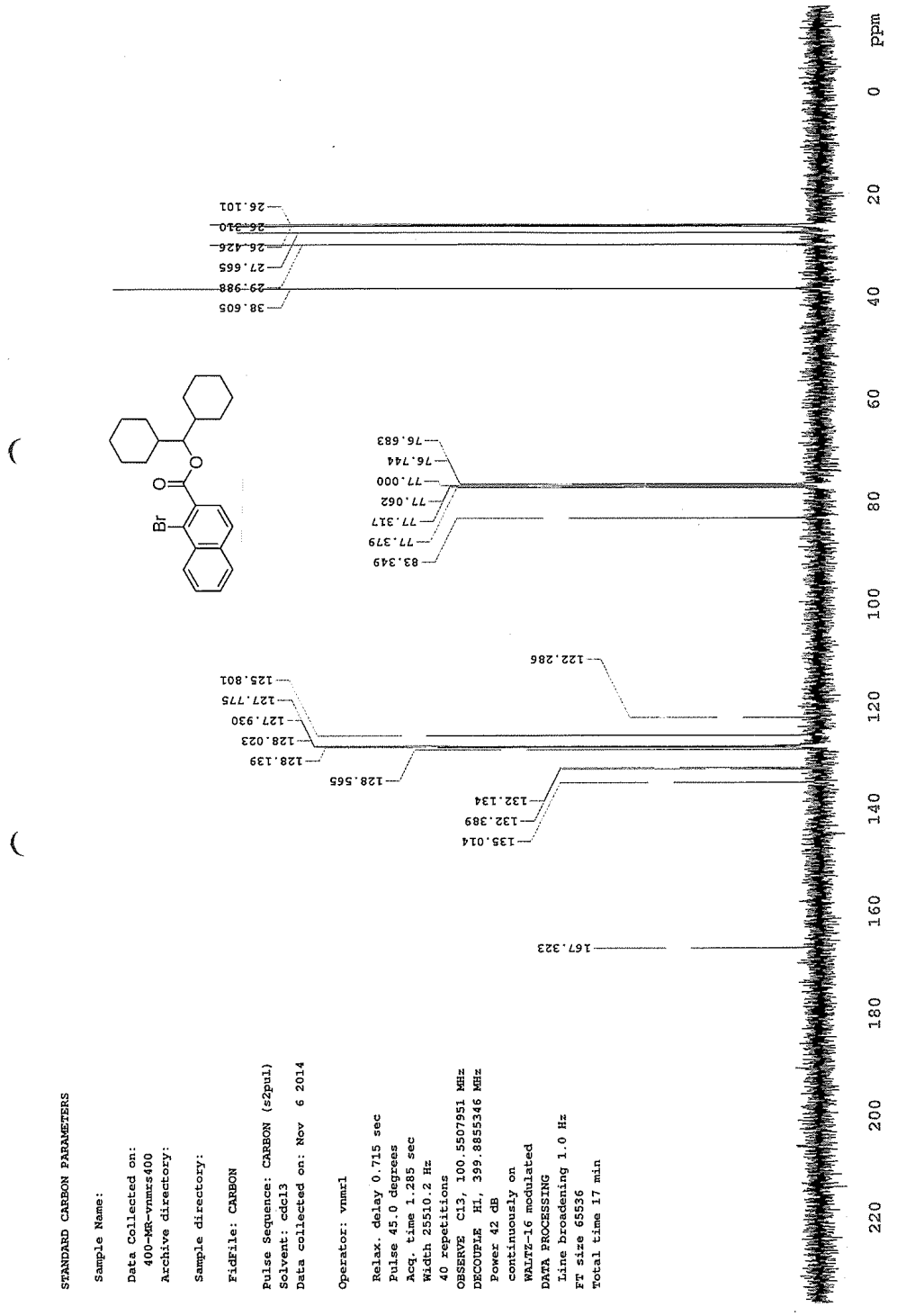
^{1}H NMR of compound **1D**



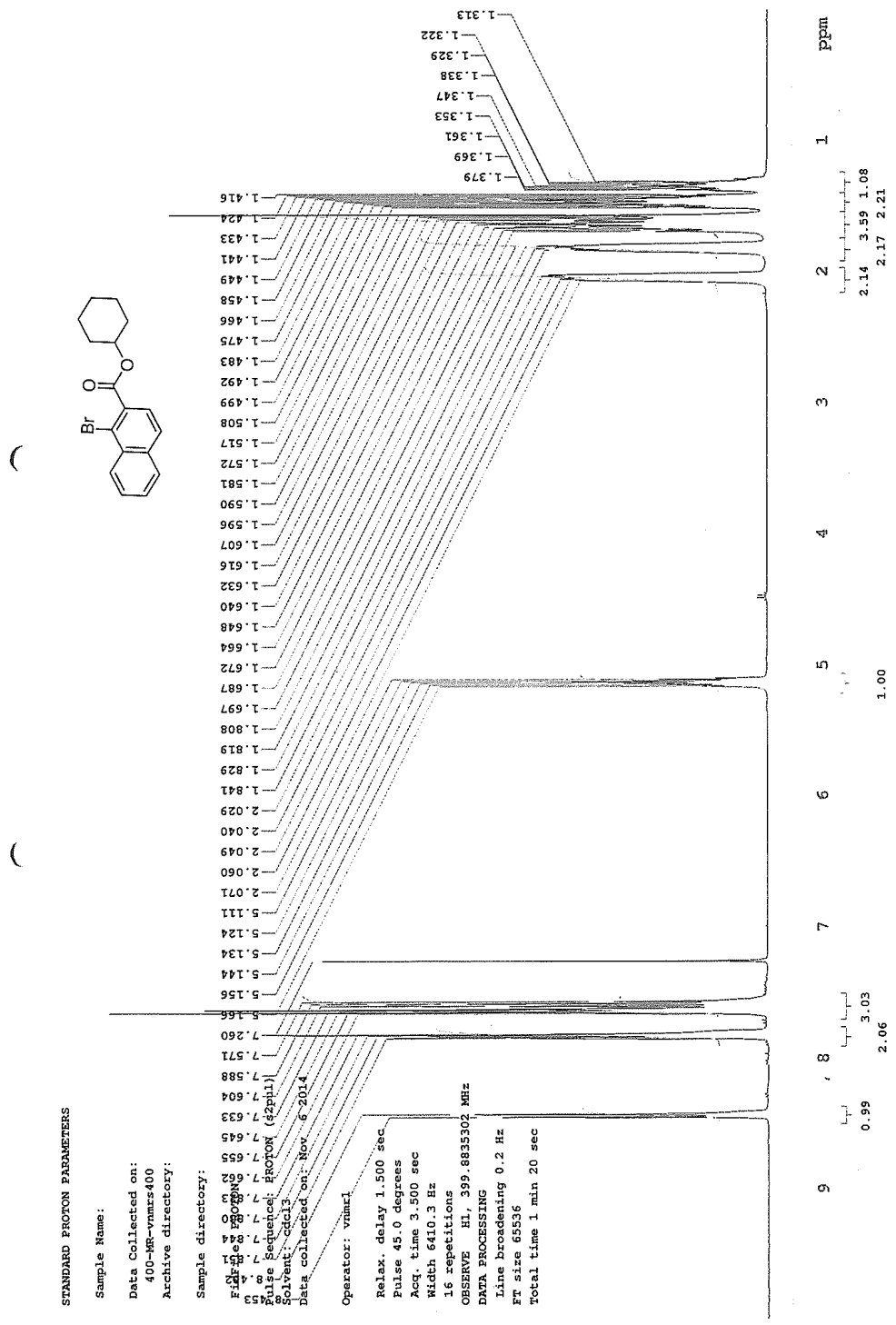
^{13}C NMR of compound **1D**



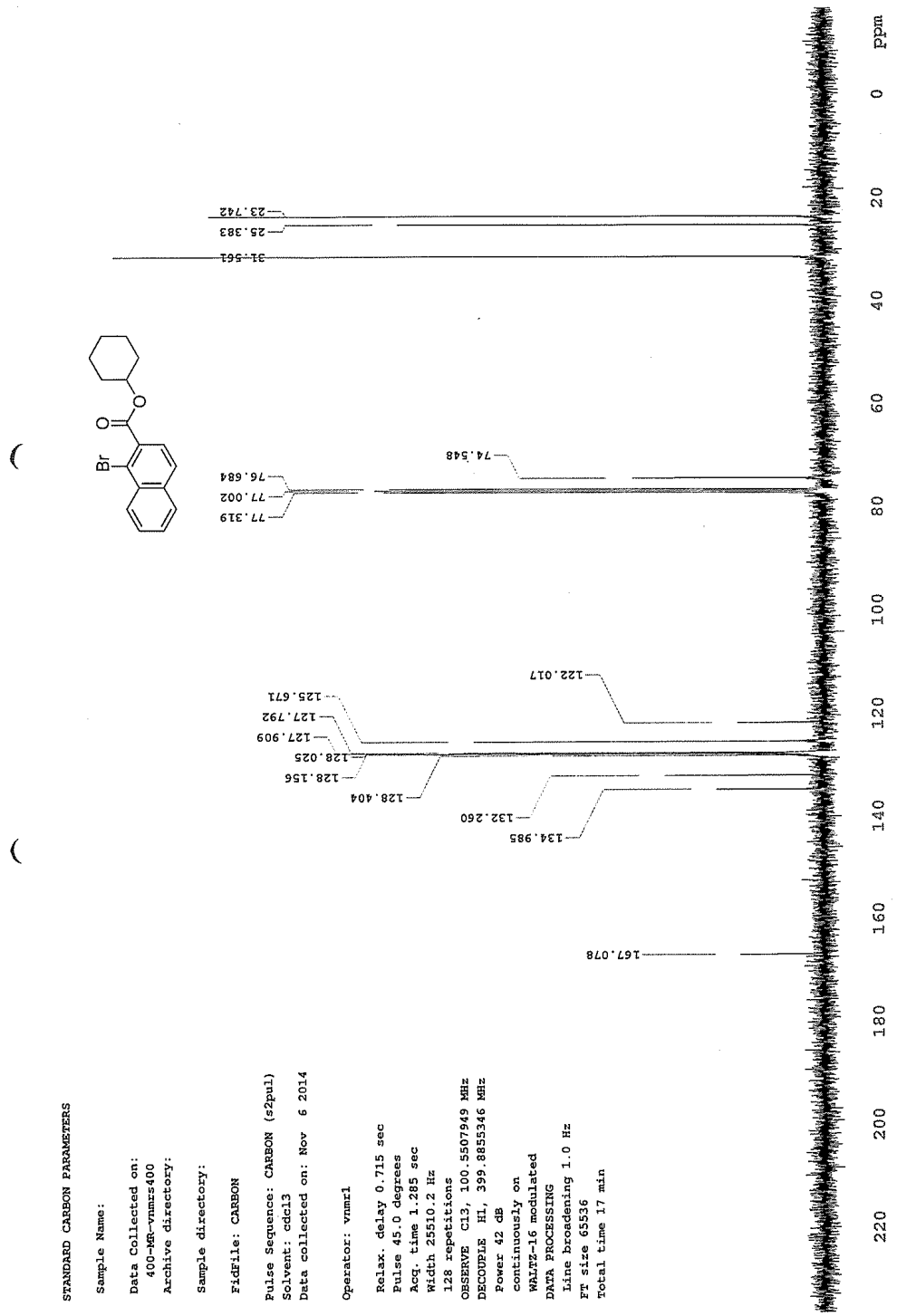
^{1}H NMR of compound **1E**



^{13}C NMR of compound **1E**

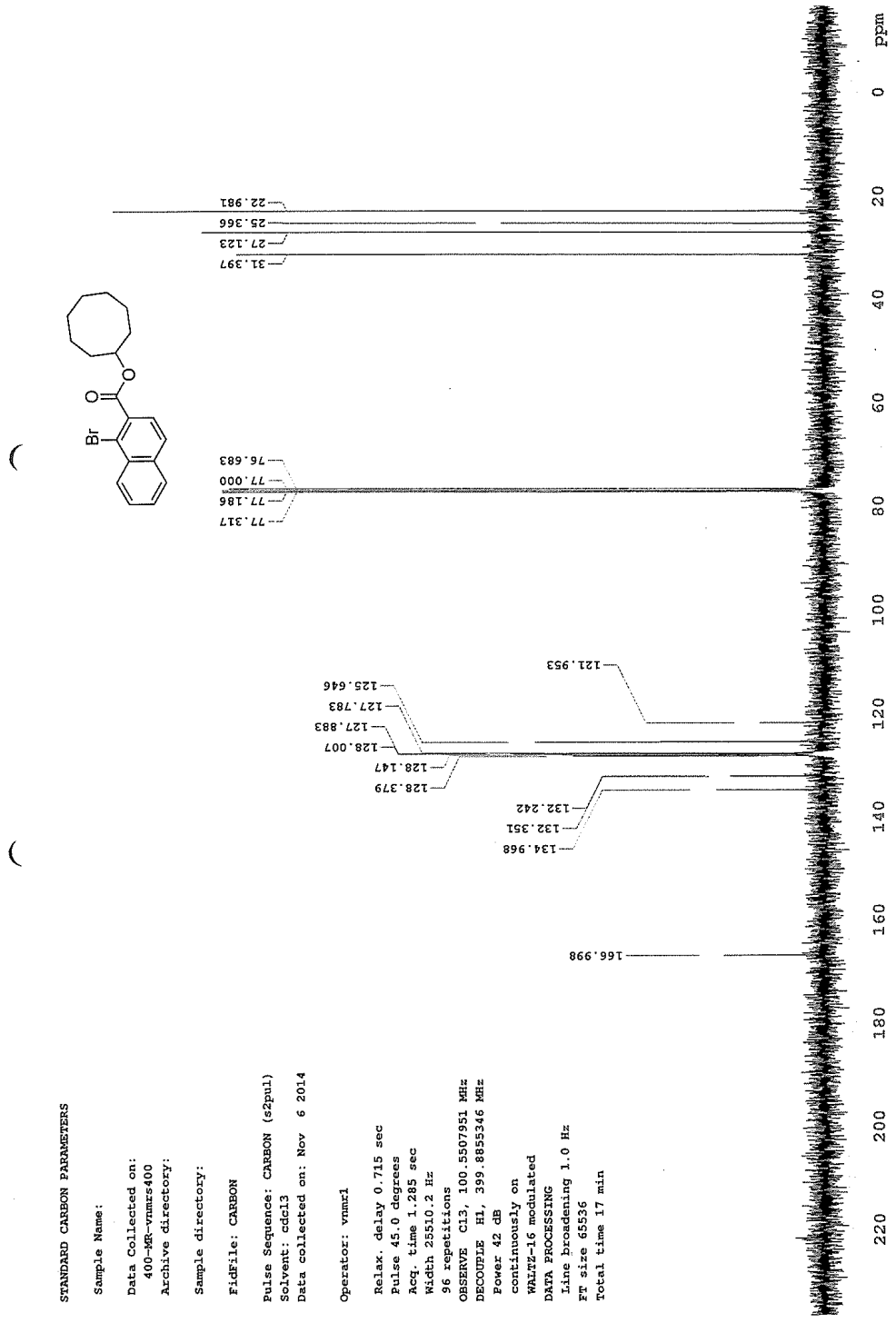


^{1}H NMR of compound **1F**

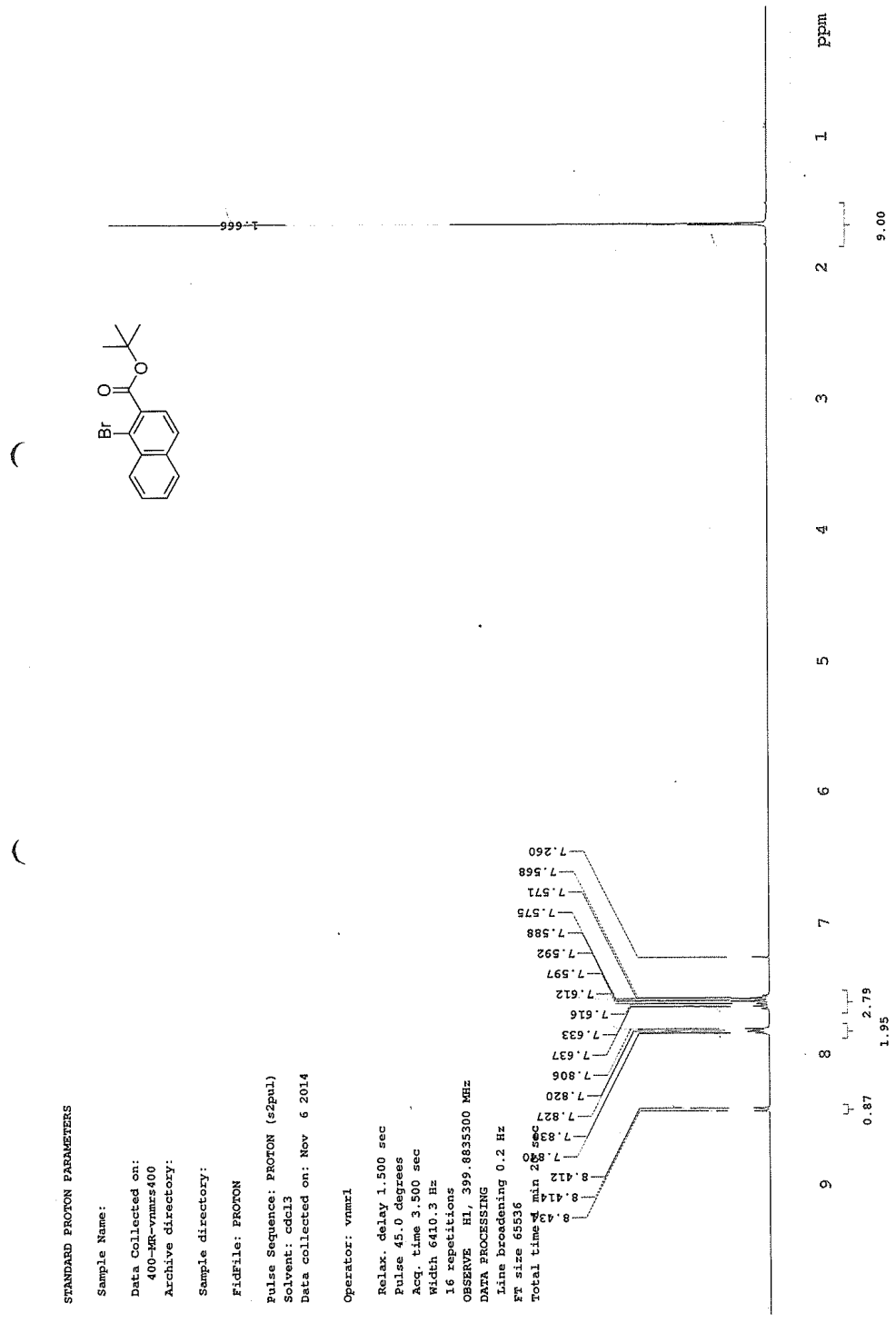


^{13}C NMR of compound **1F**

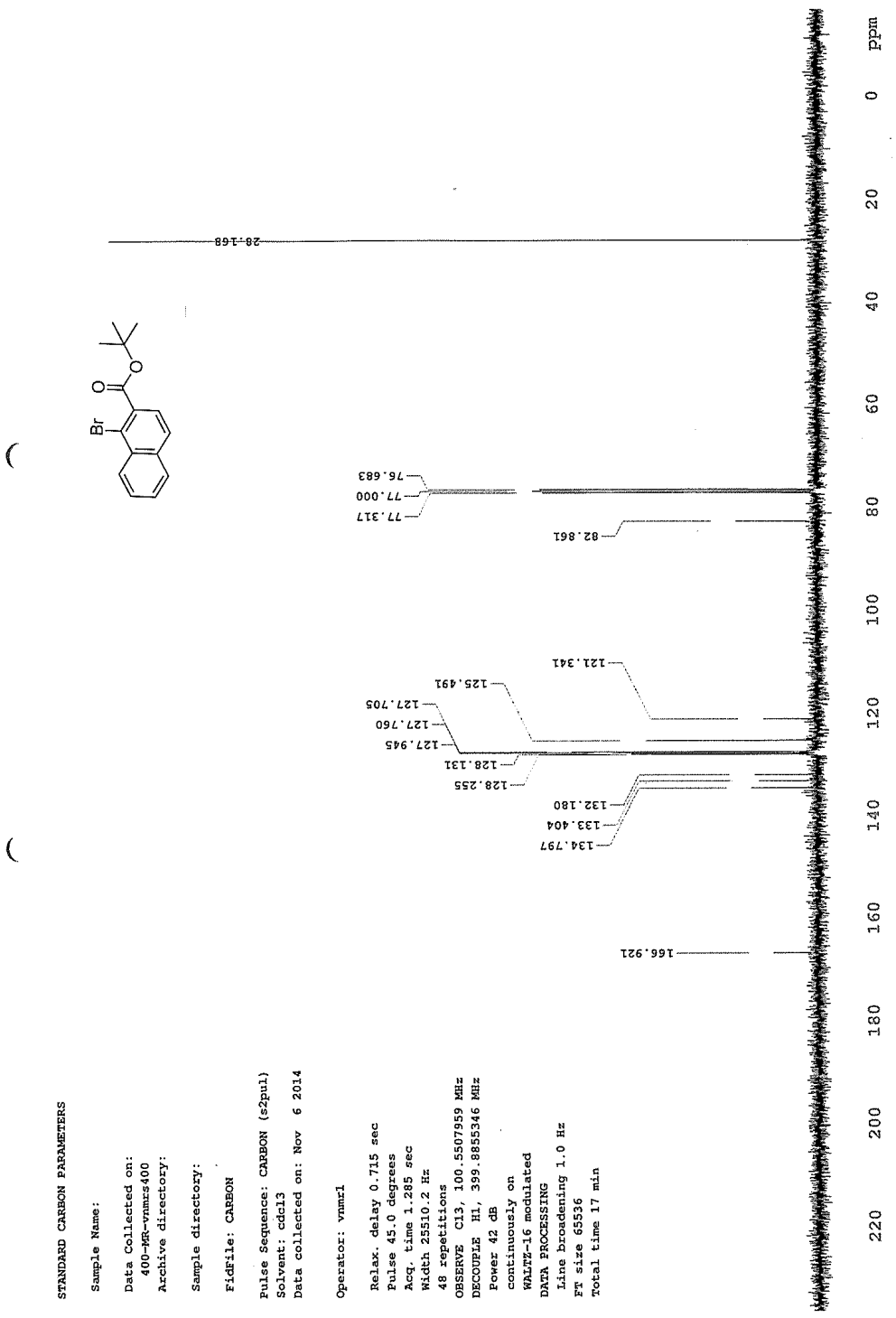
^{1}H NMR of compound **1G**



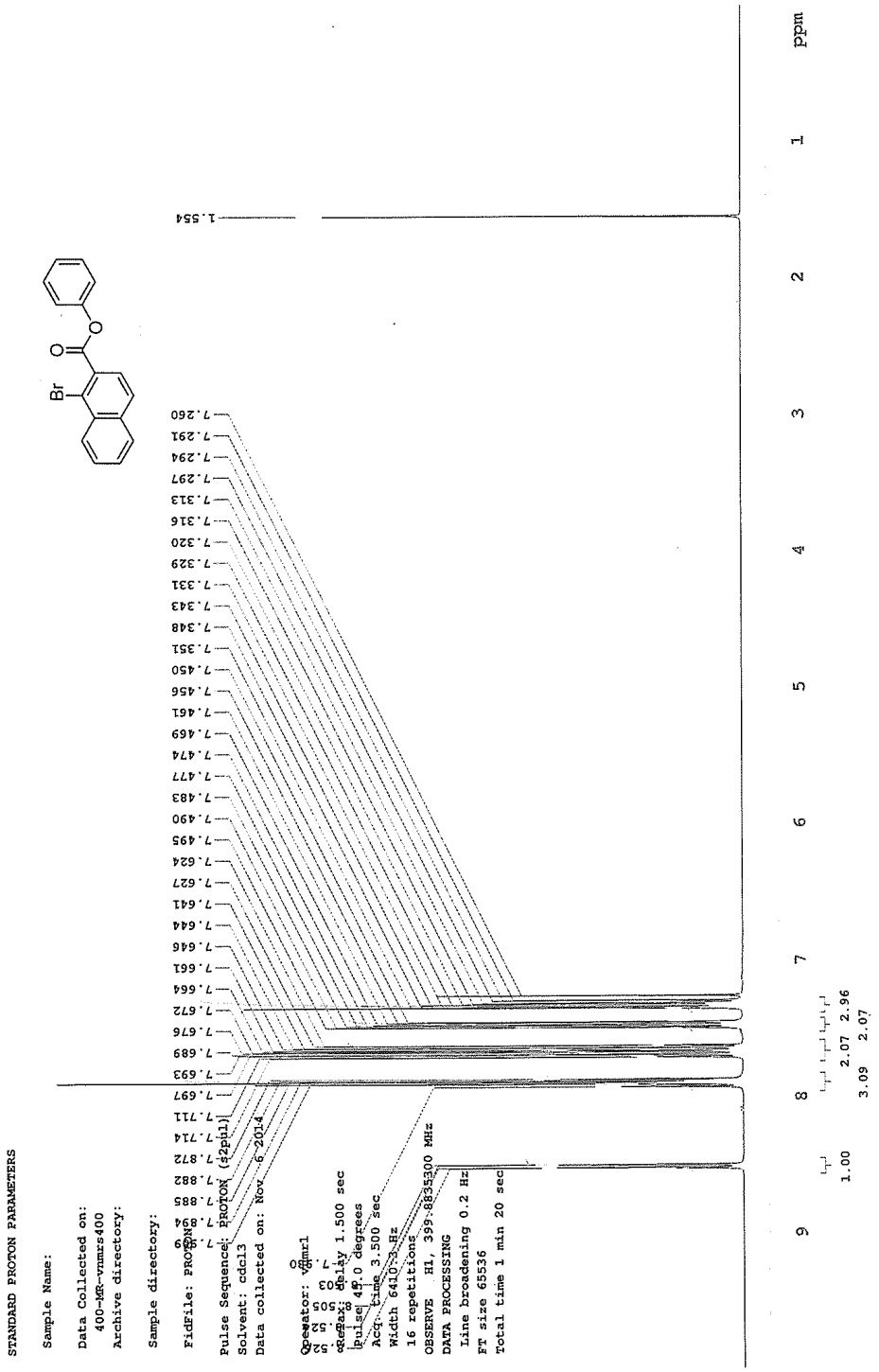
^{13}C NMR of compound **1G**



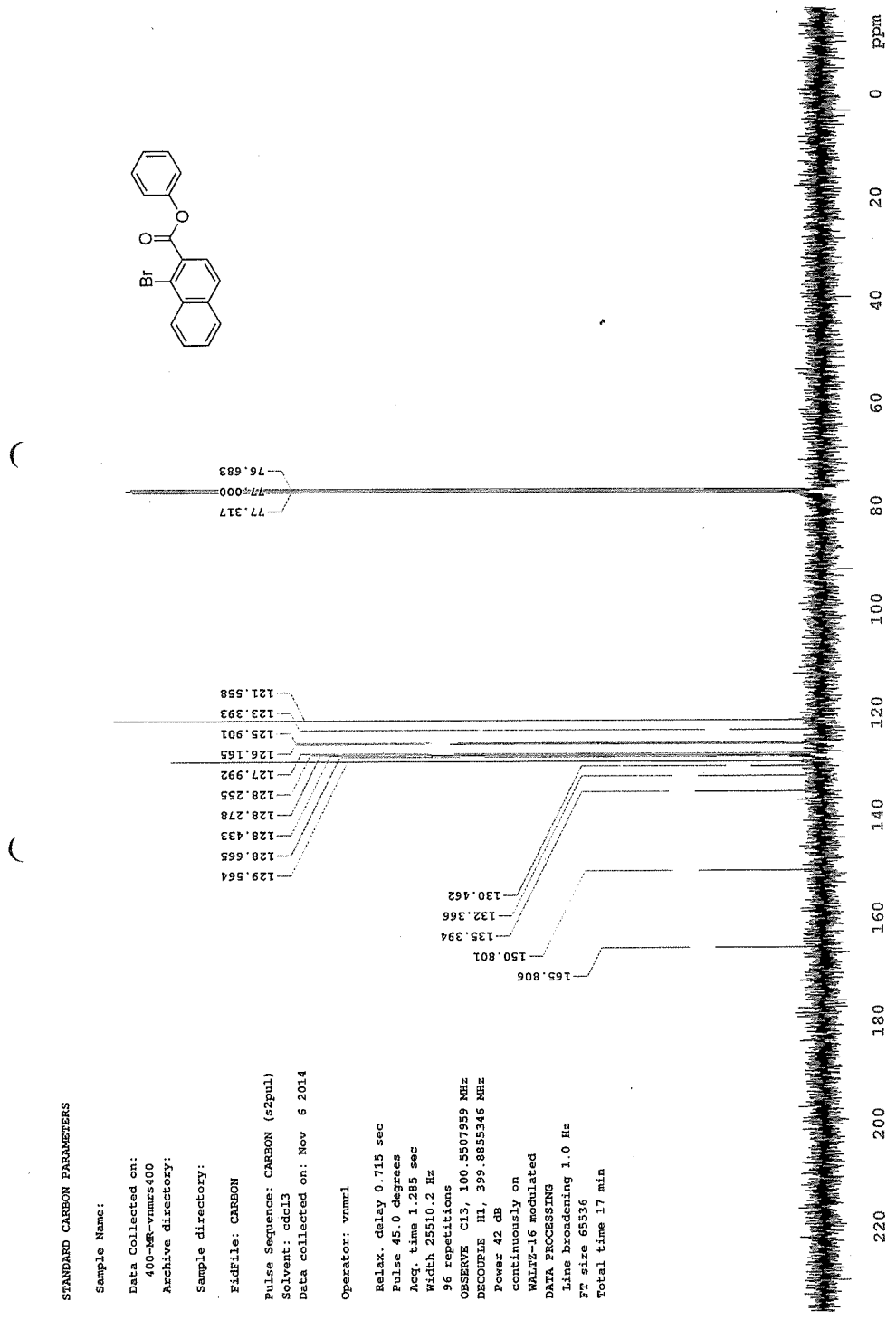
^{1}H NMR of compound **1H**



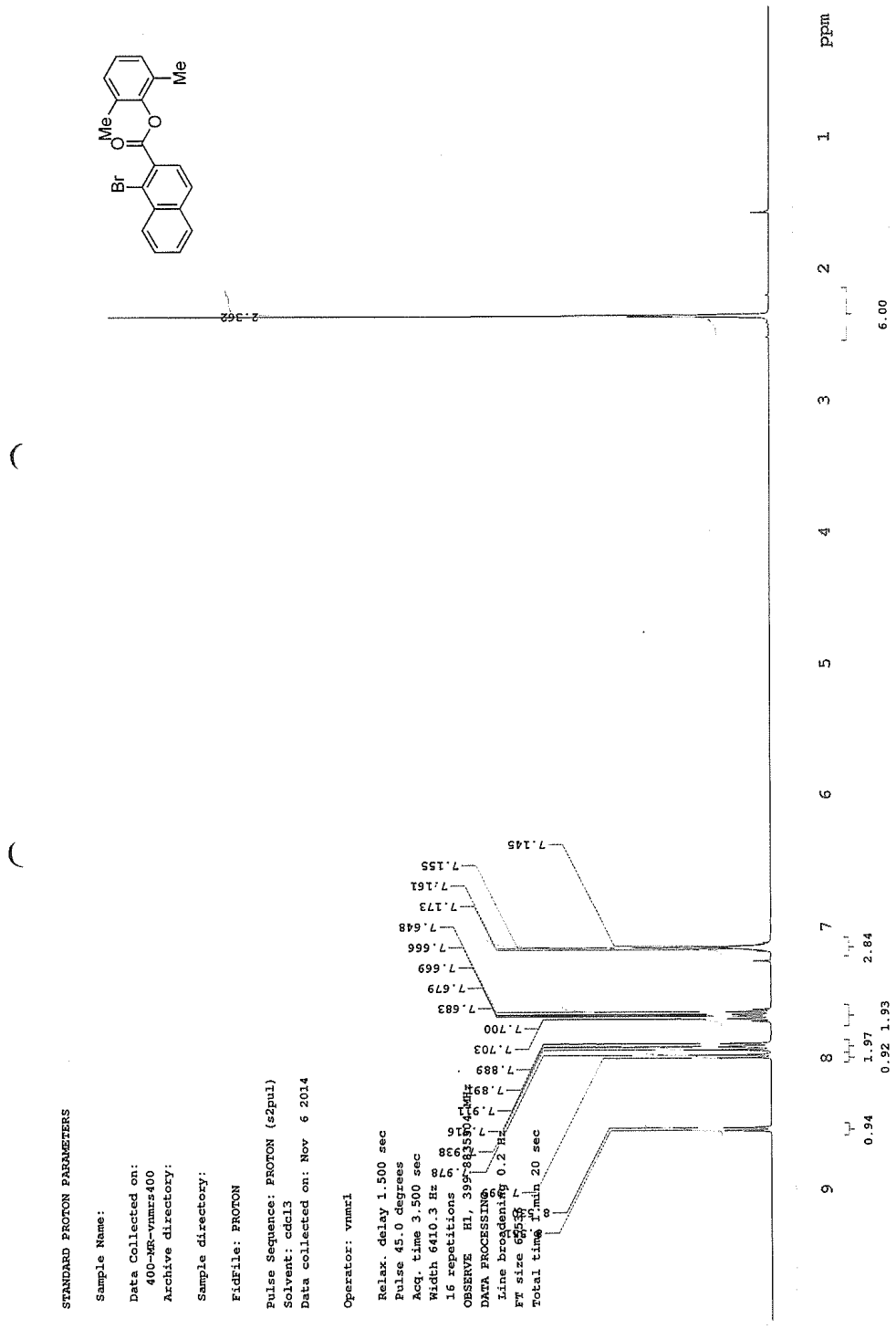
^{13}C NMR of compound **1H**



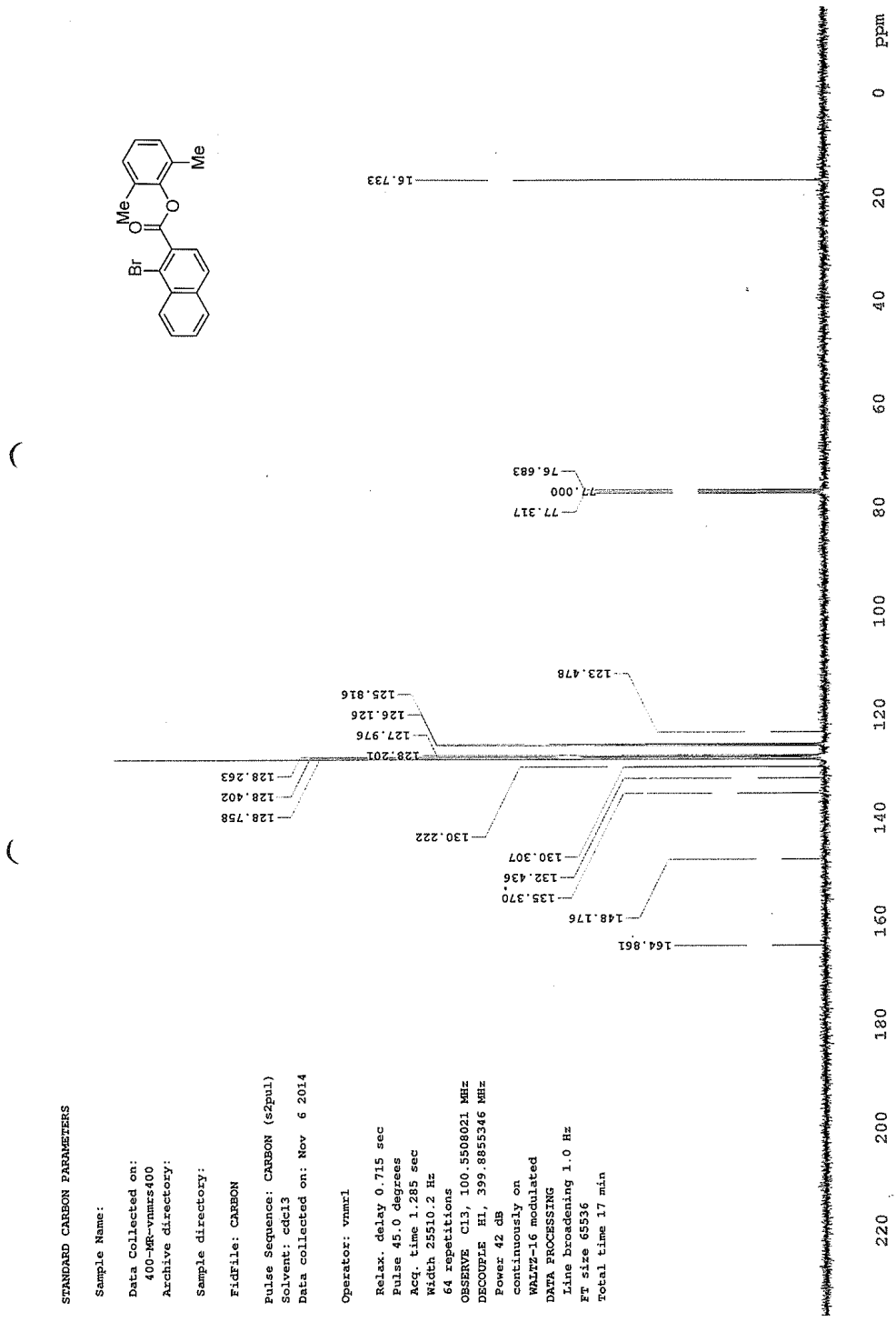
^{1}H NMR of compound **1I**



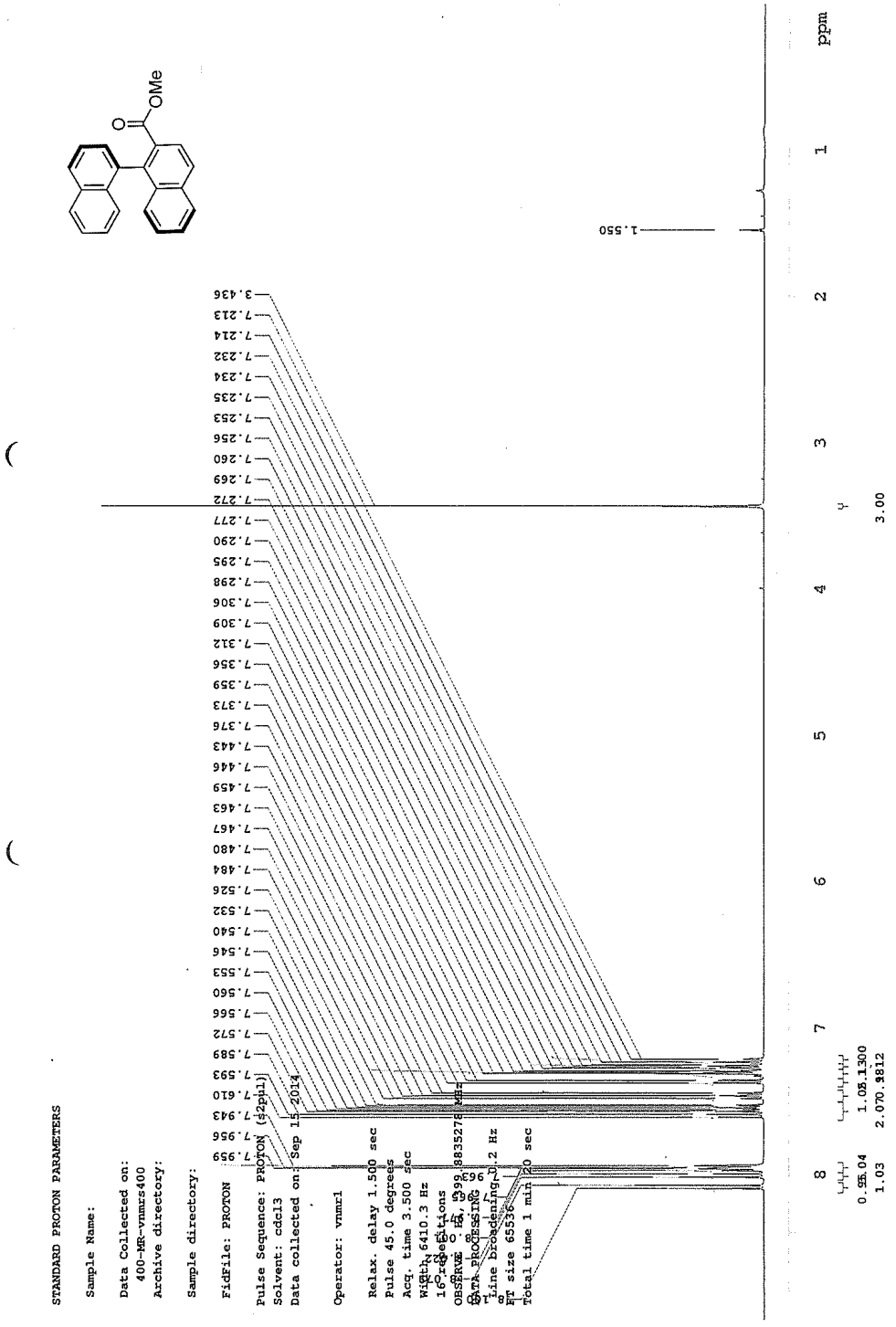
^{13}C NMR of compound **1I**



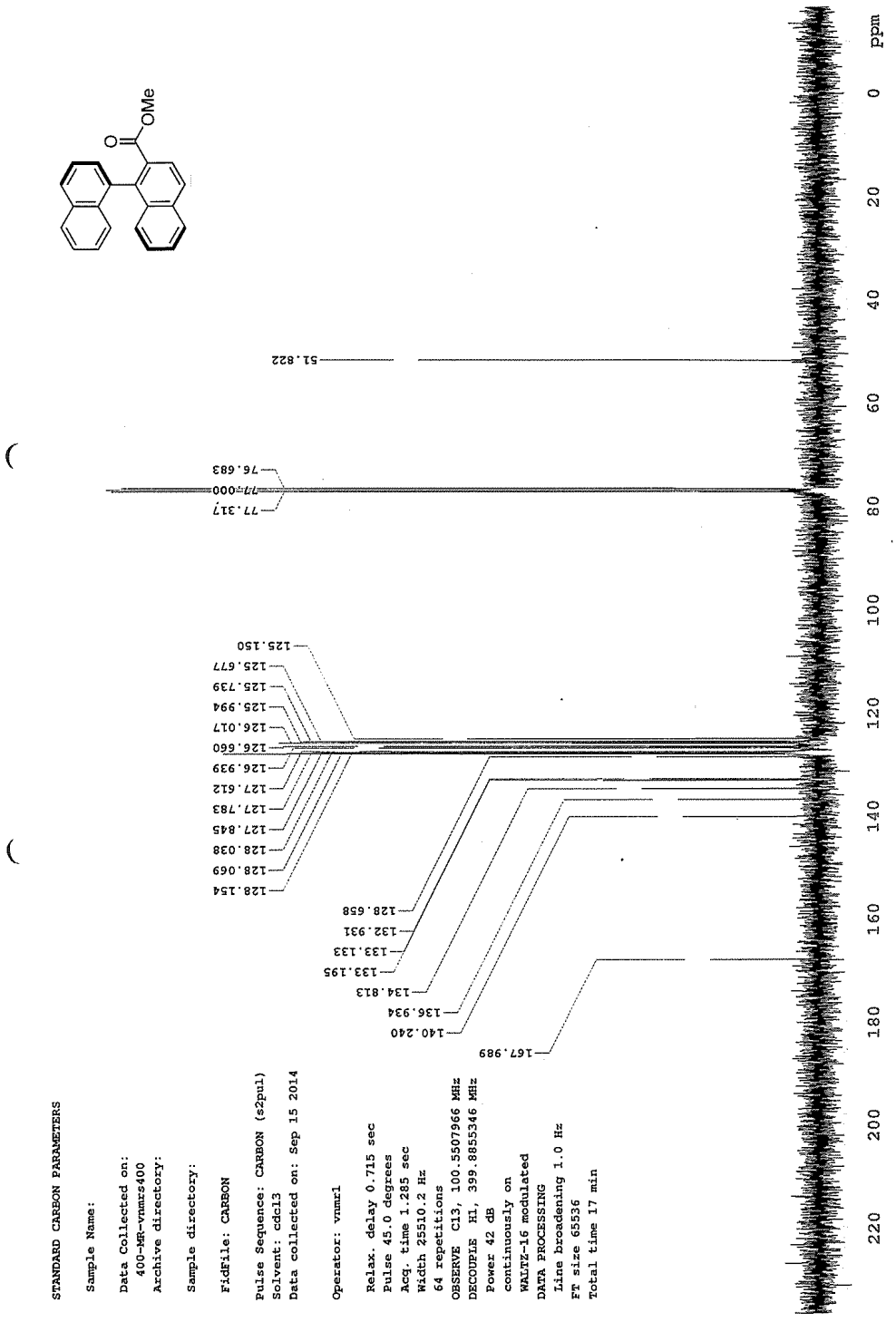
^{1}H NMR of compound **1J**



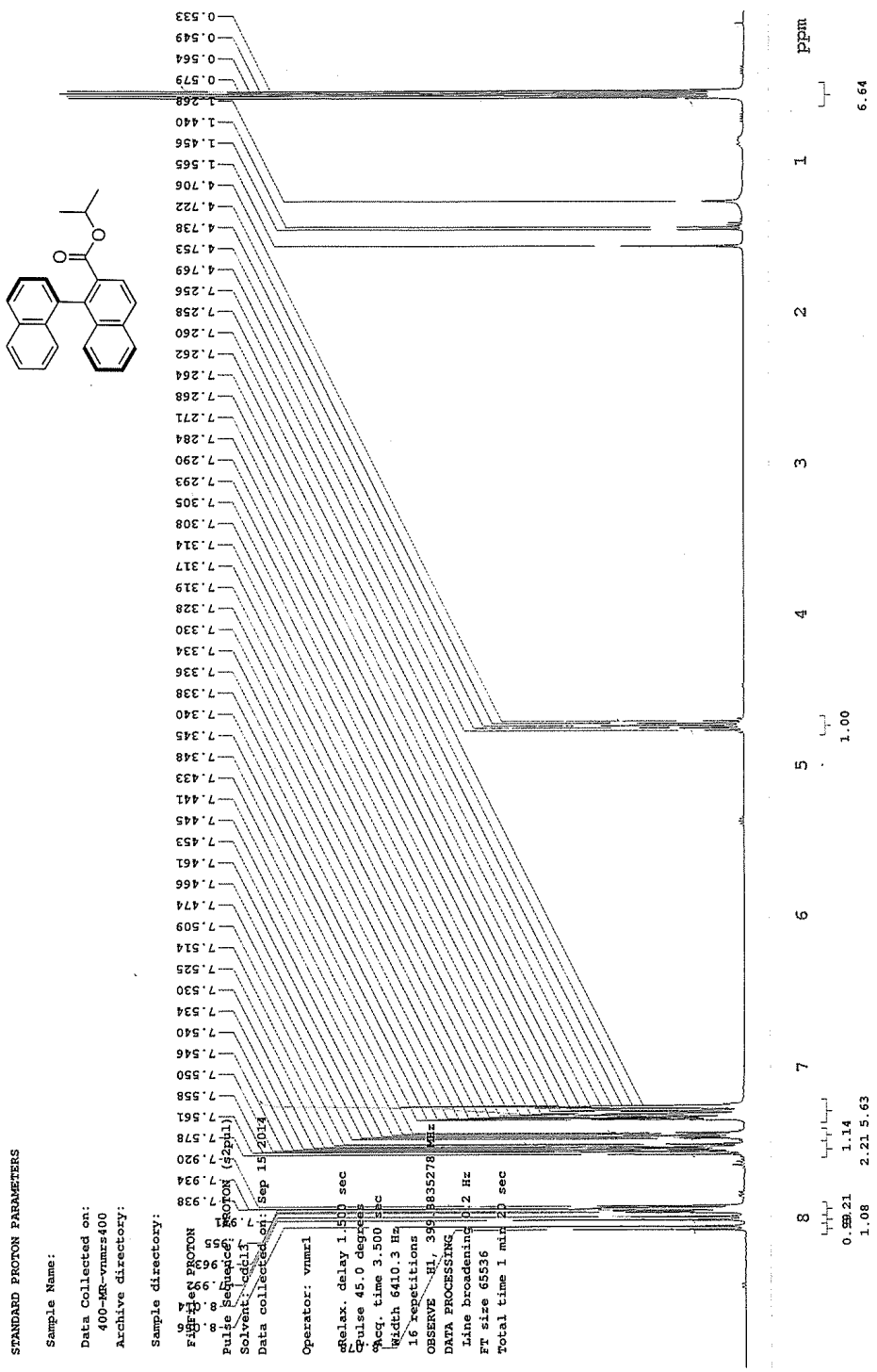
^{13}C NMR of compound **1J**



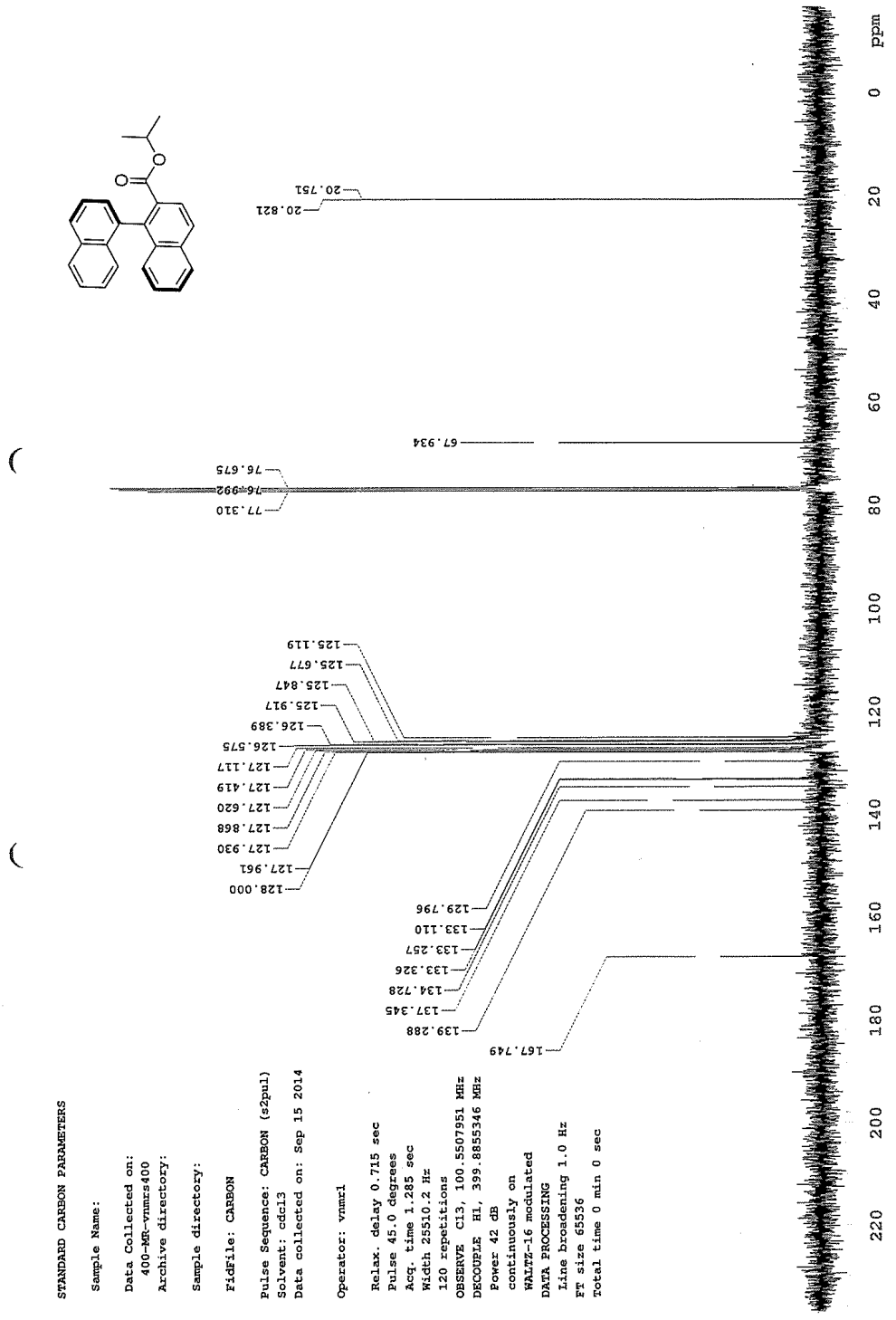
^{1}H NMR of compound **3Aa**



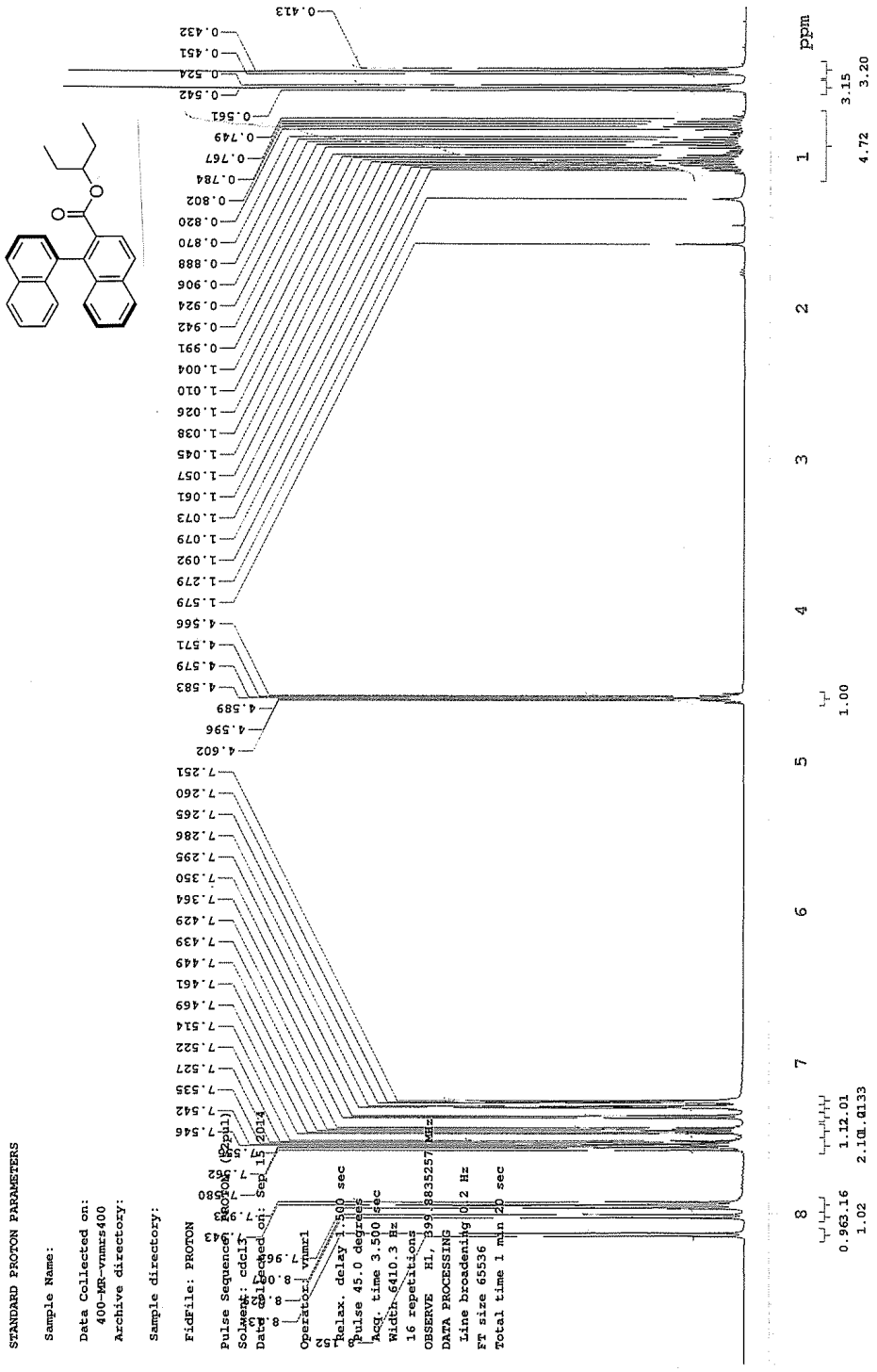
^{13}C NMR of compound **3Aa**



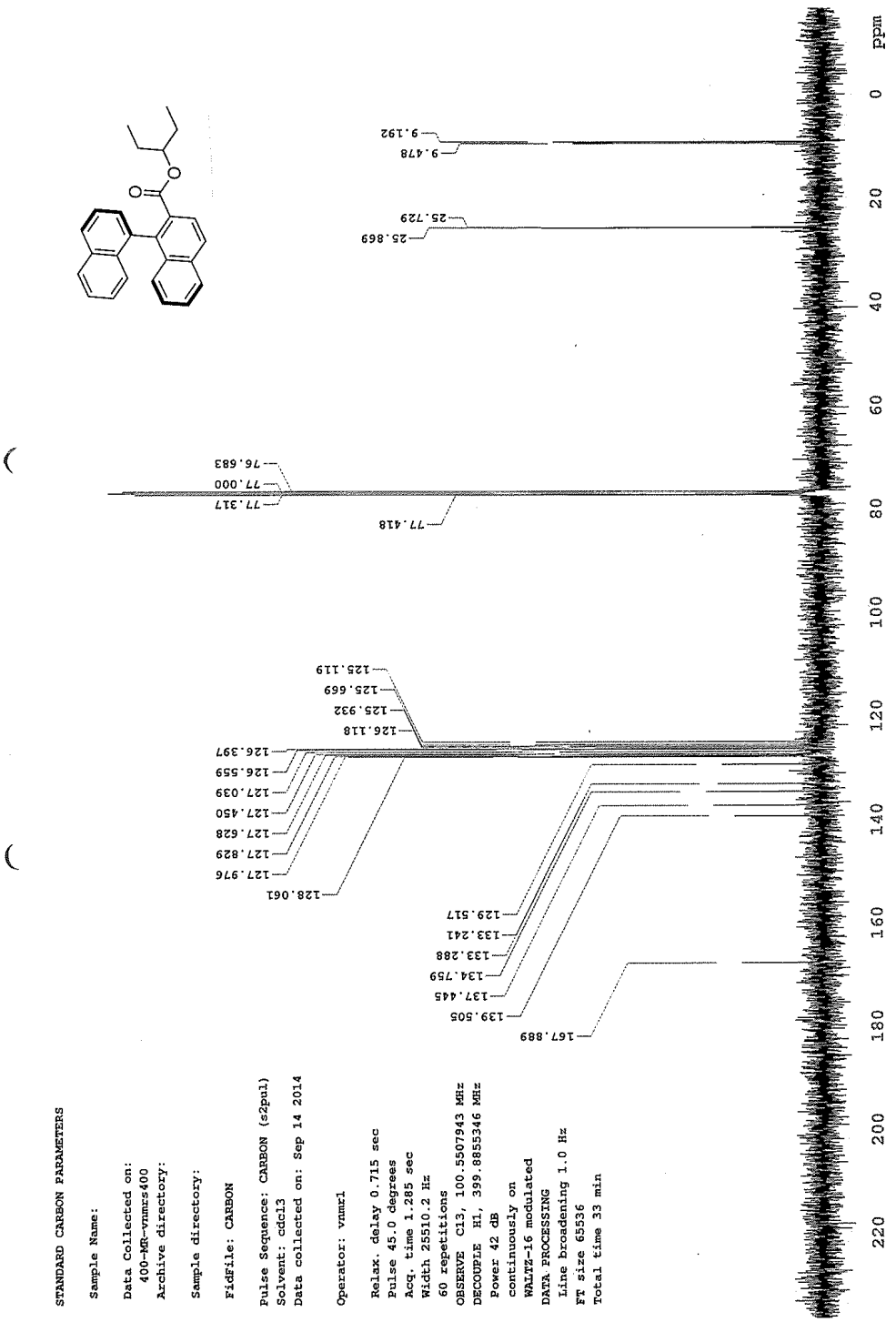
^{1}H NMR of compound **3Ba**



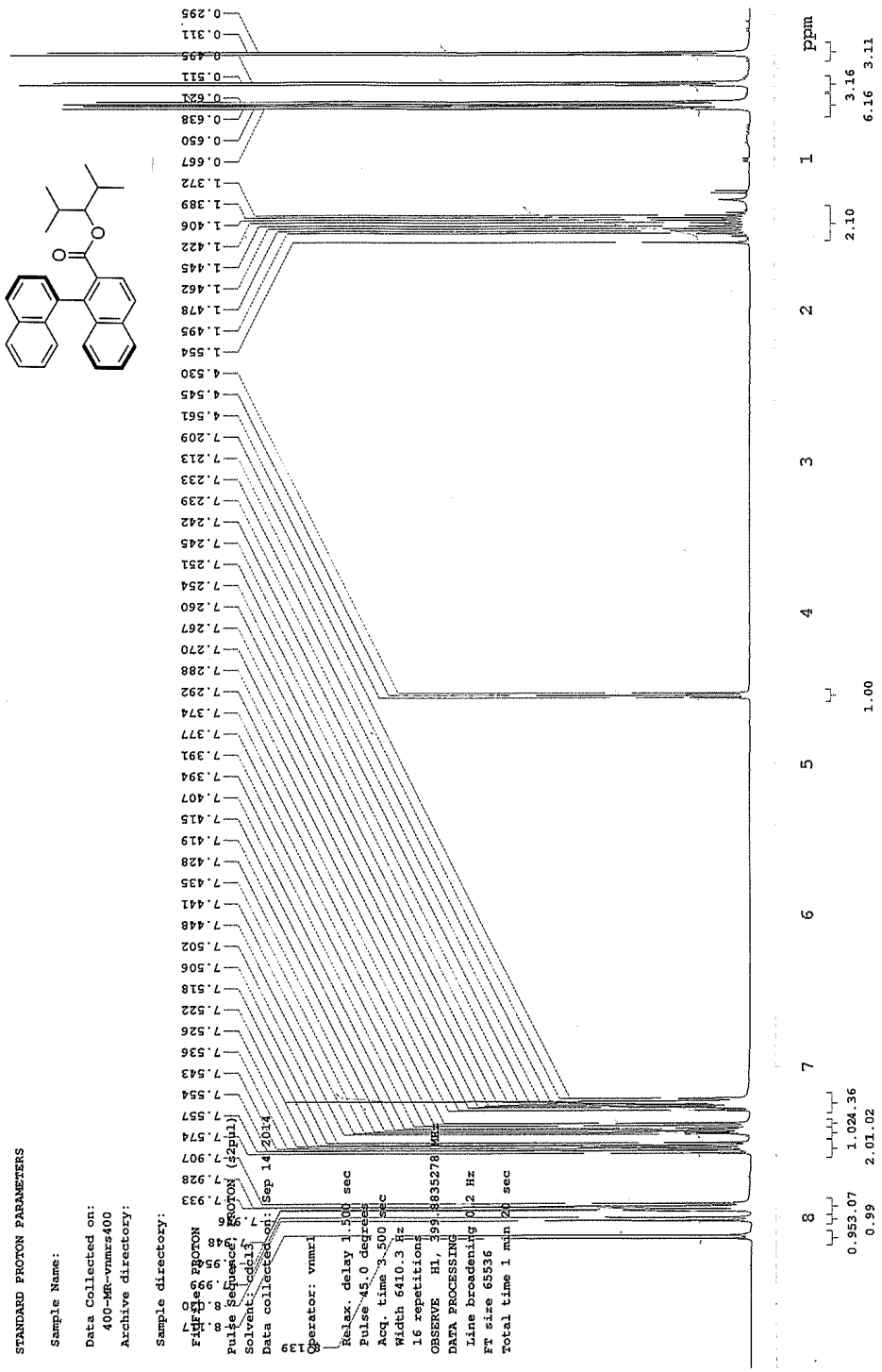
^{13}C NMR of compound **3Ba**



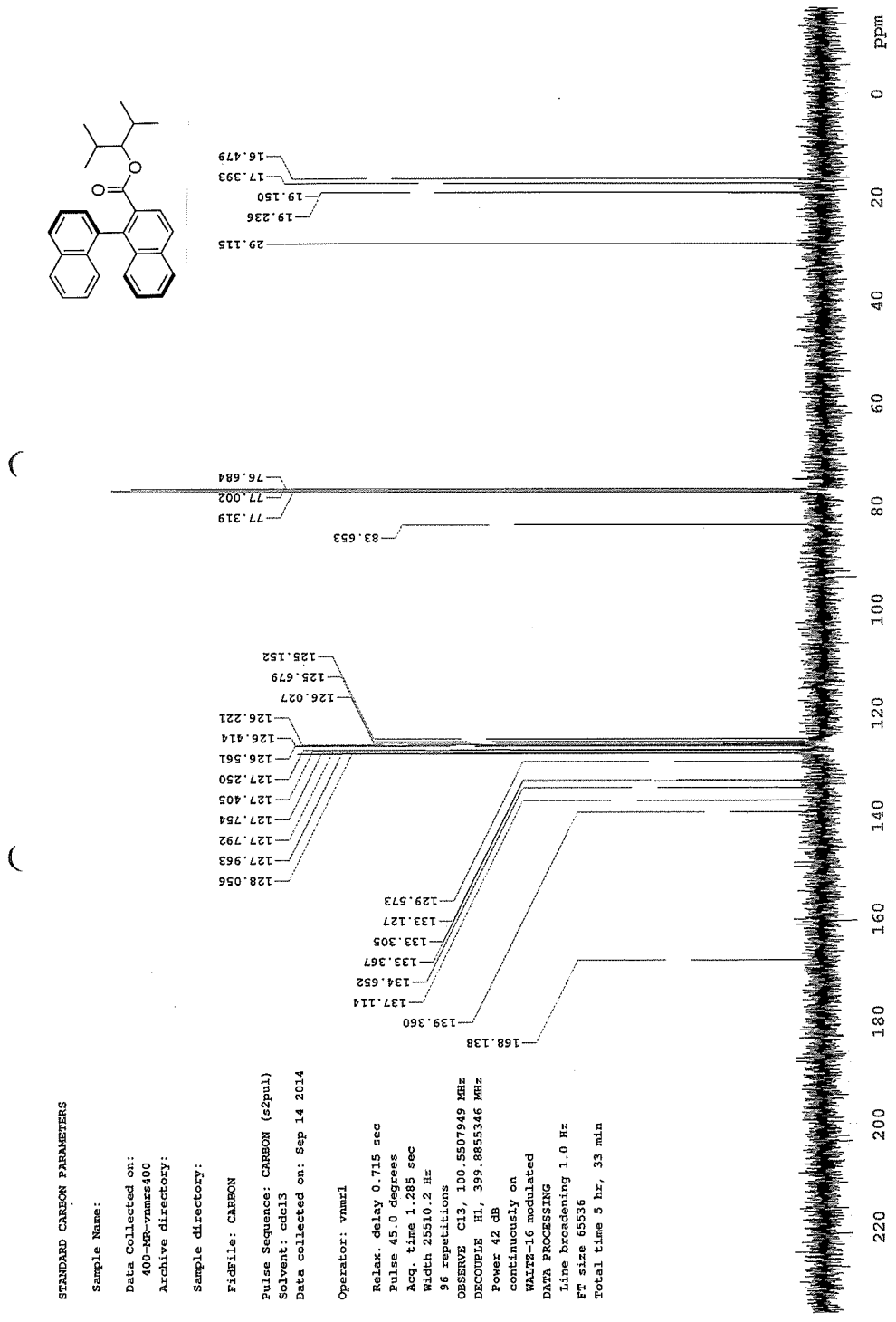
^{1}H NMR of compound **3Ca**



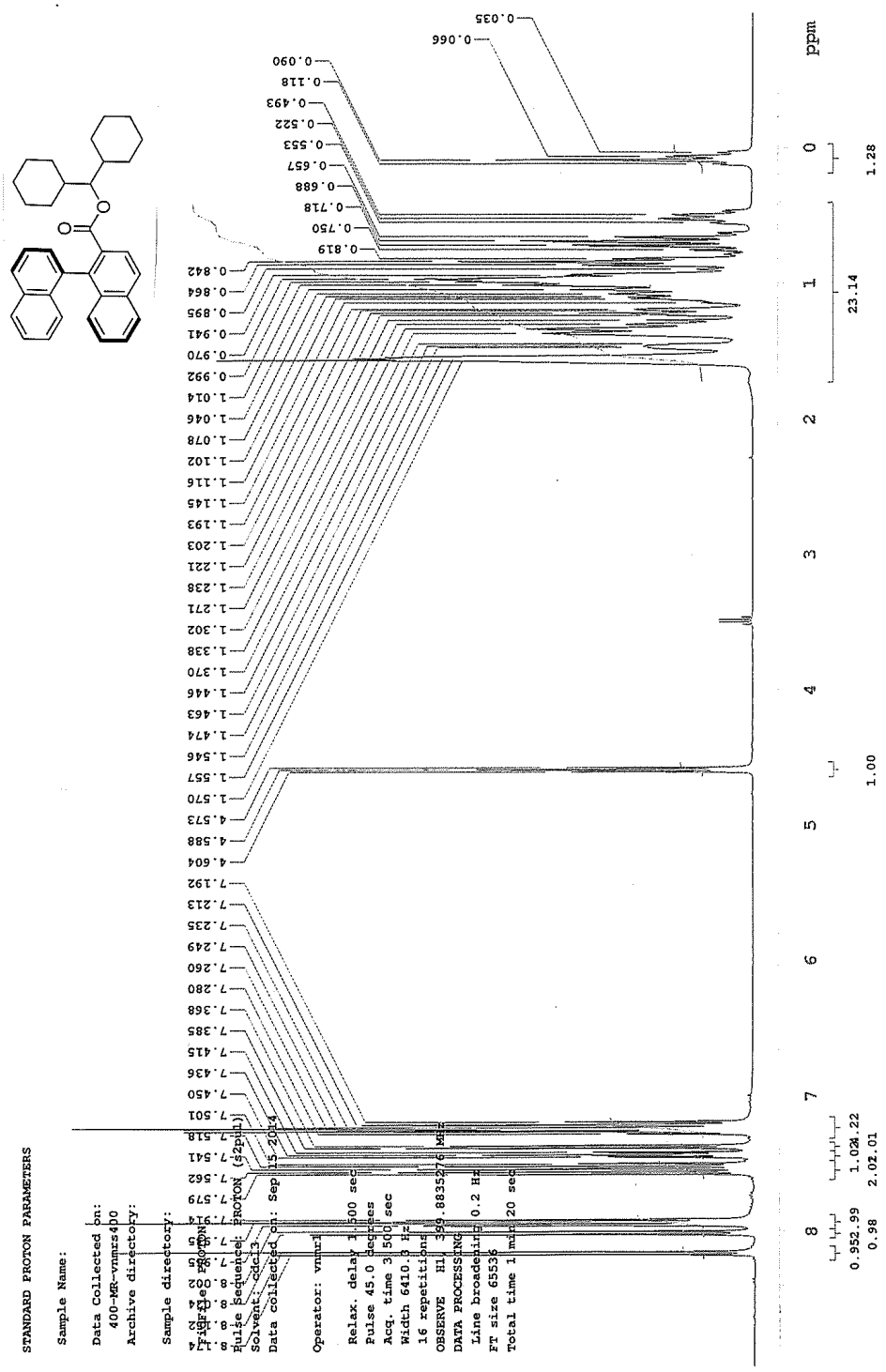
^{13}C NMR of compound **3Ca**



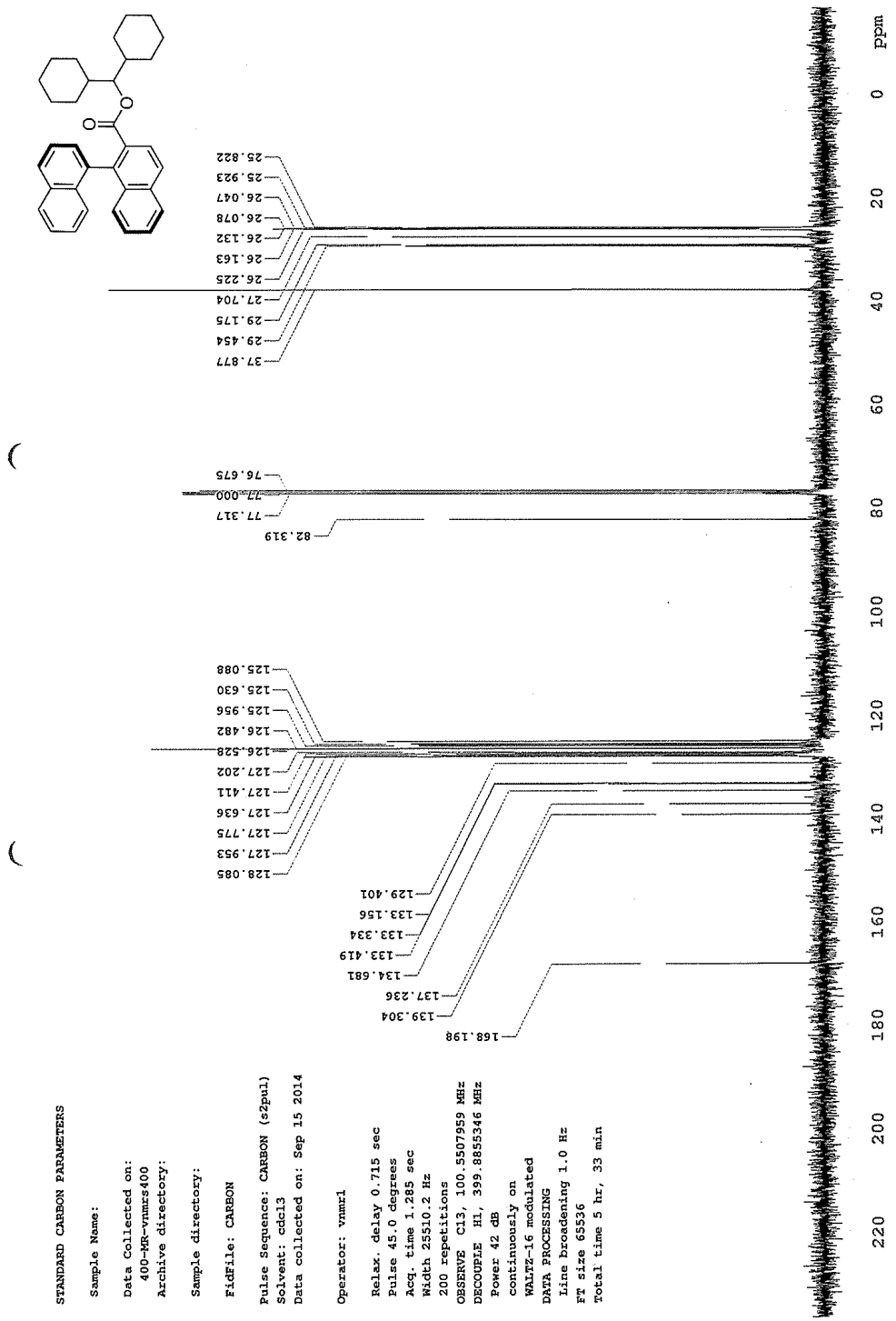
^{1}H NMR of compound **3Da**



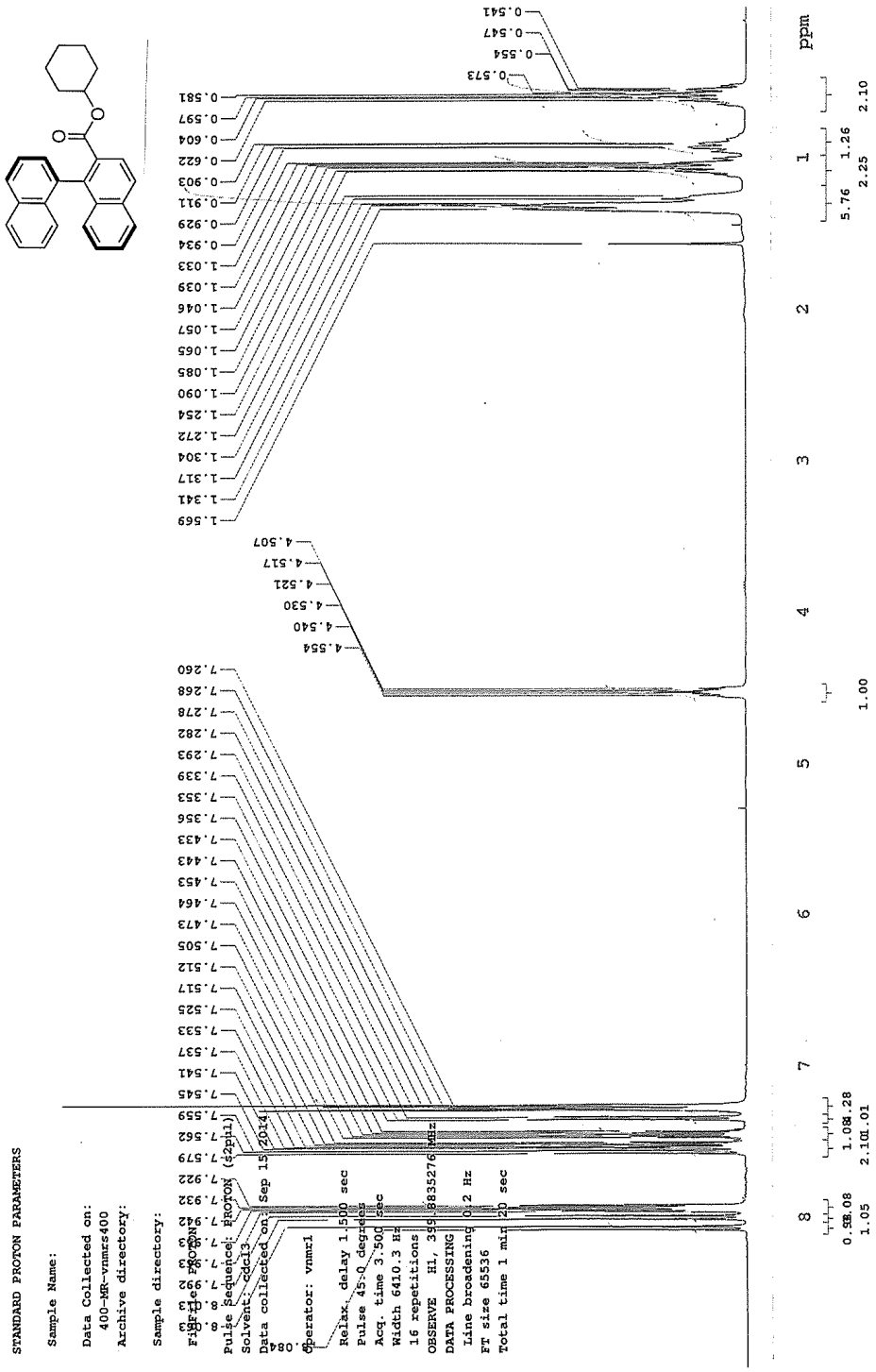
^{13}C NMR of compound **3Da**



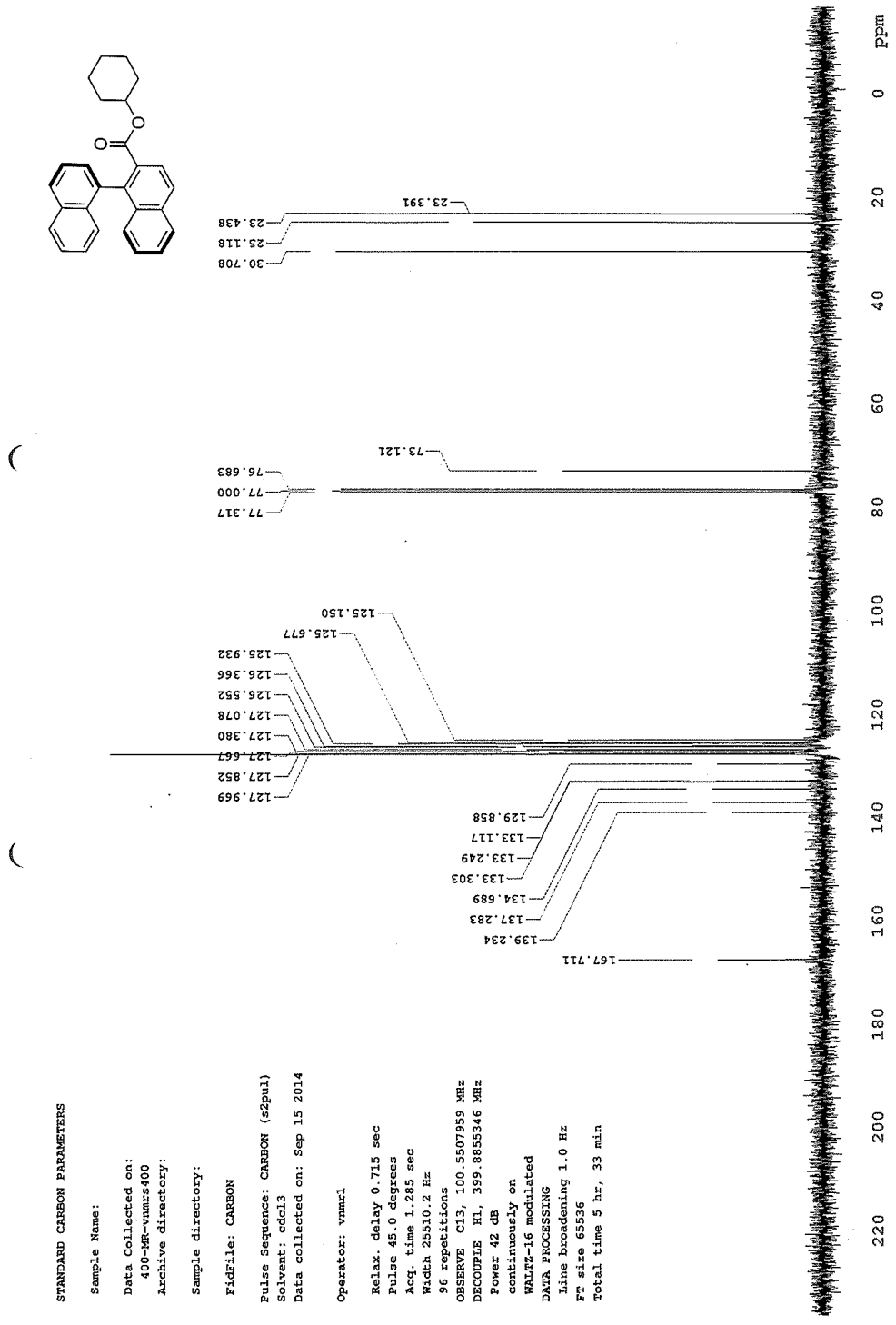
^{1}H NMR of compound **3Ea**



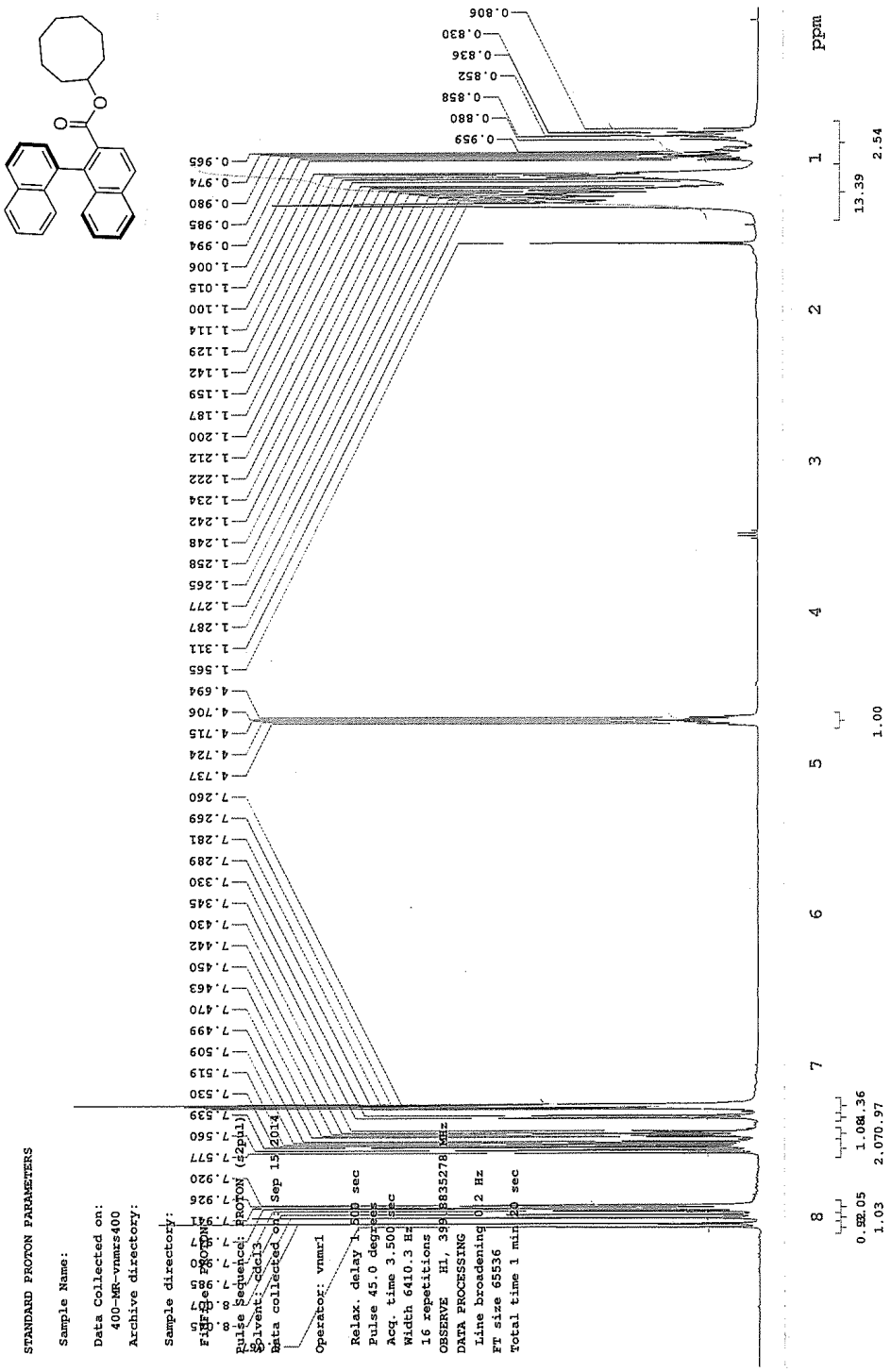
^{13}C NMR of compound **3Ea**



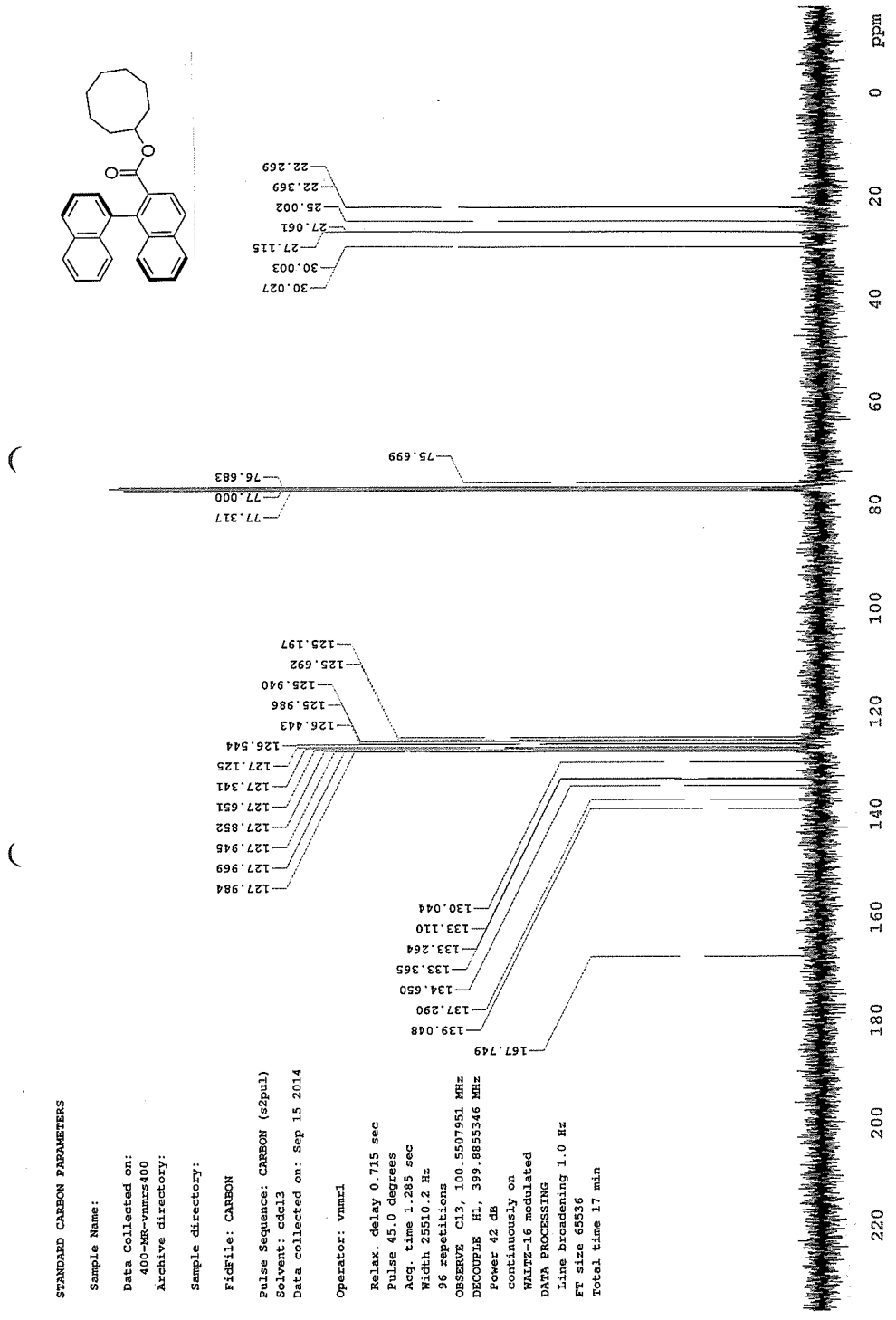
^{1}H NMR of compound **3Fa**



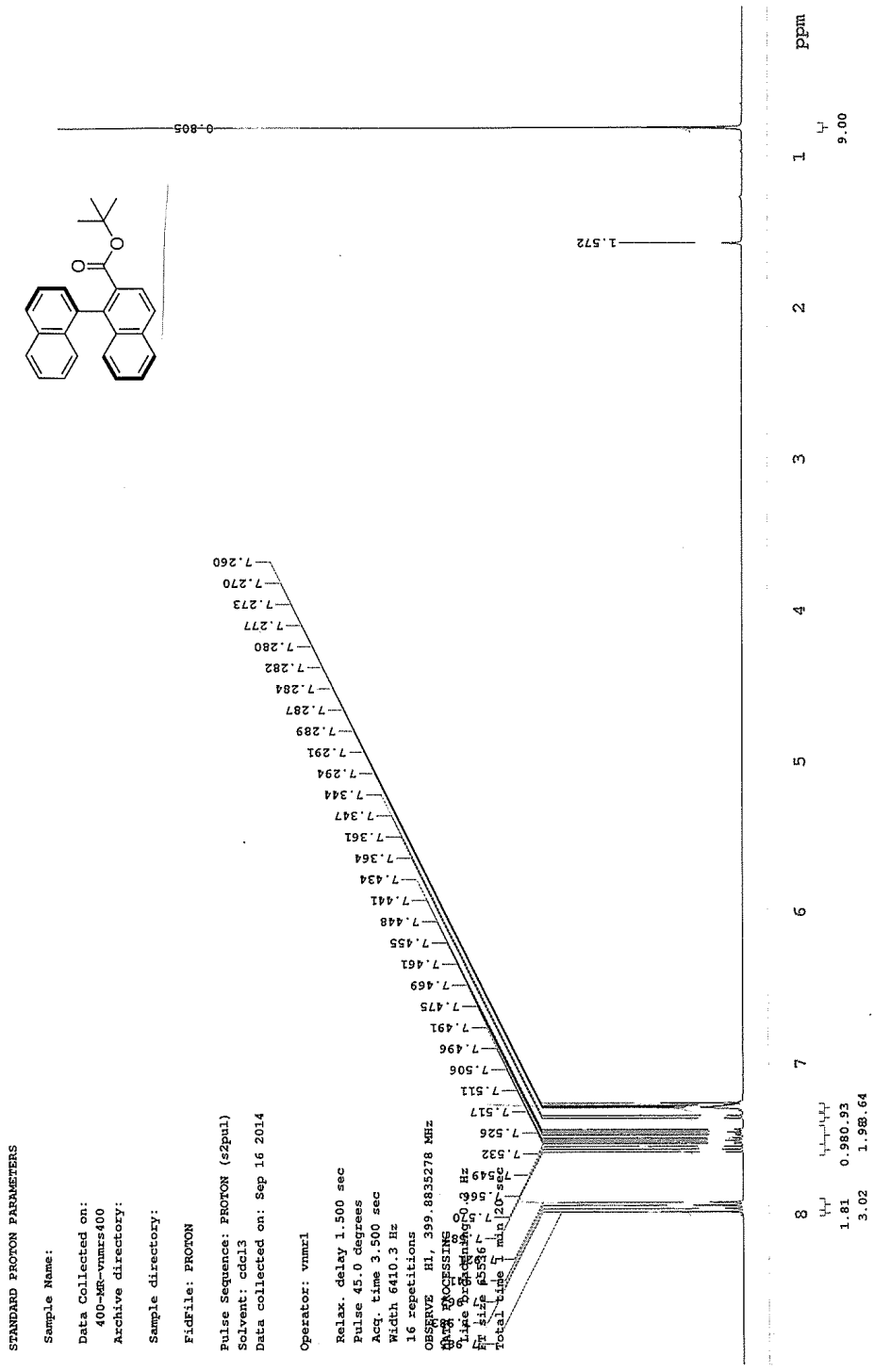
^{13}C NMR of compound **3Fa**



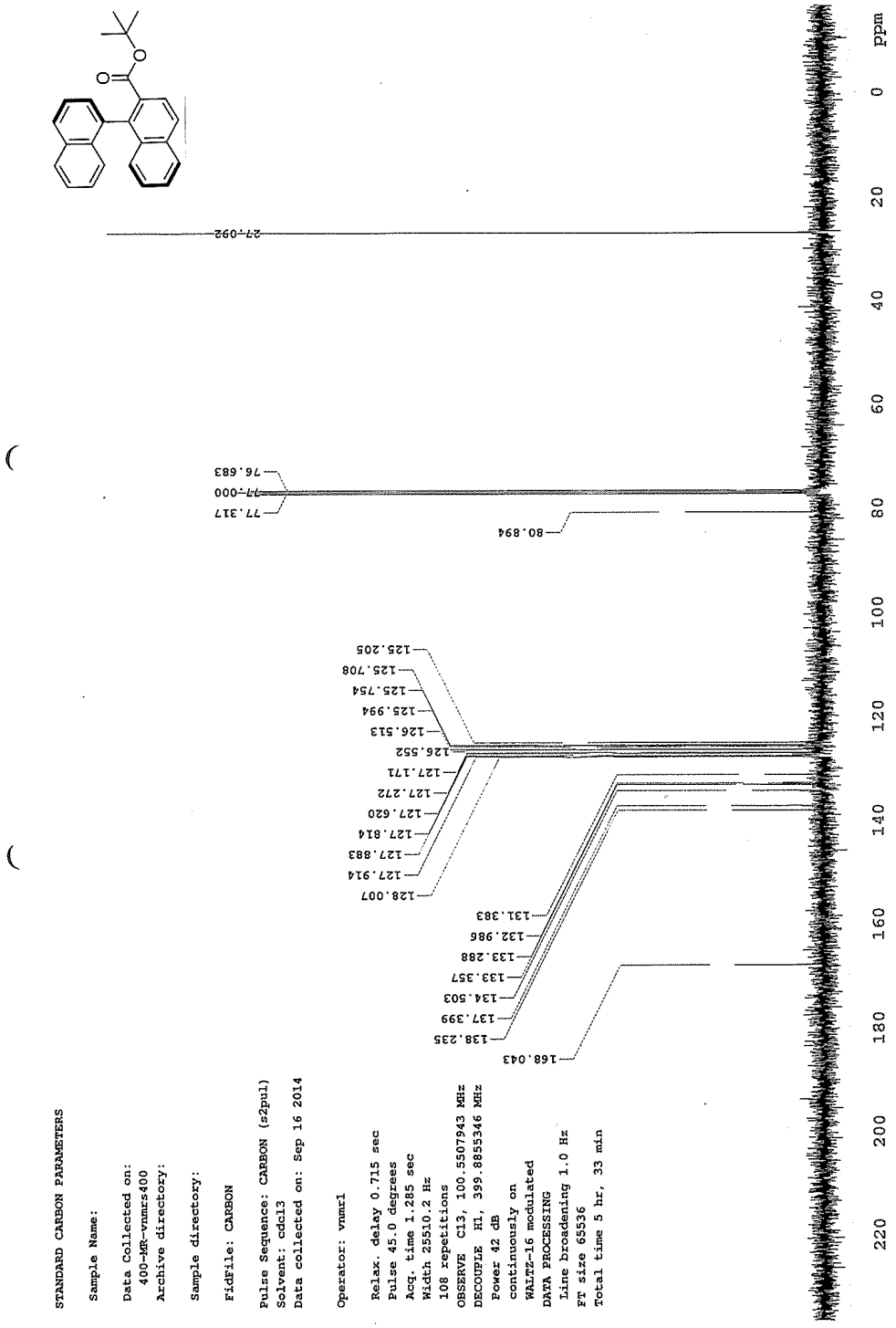
^{1}H NMR of compound **3Ga**



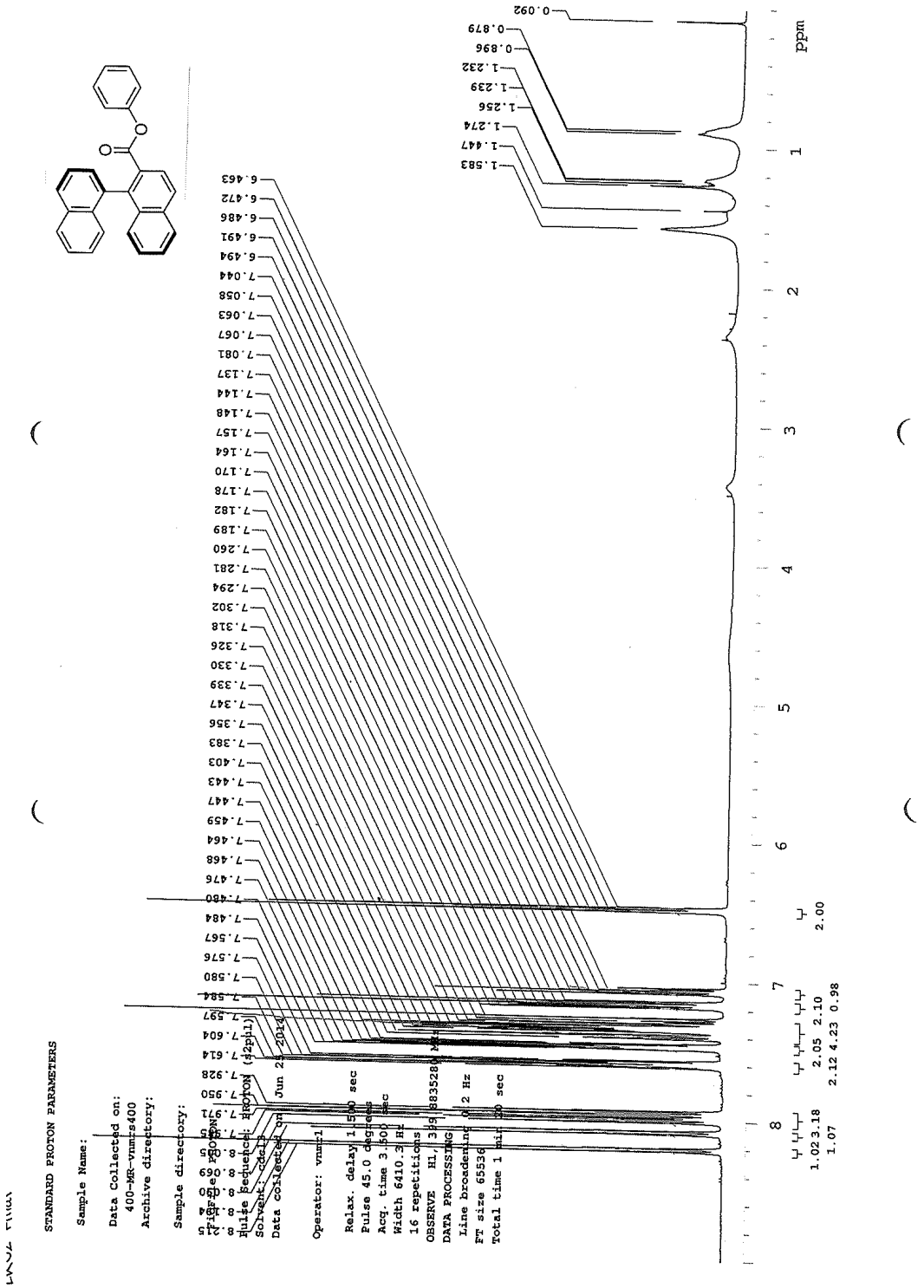
^{13}C NMR of compound **3Ga**



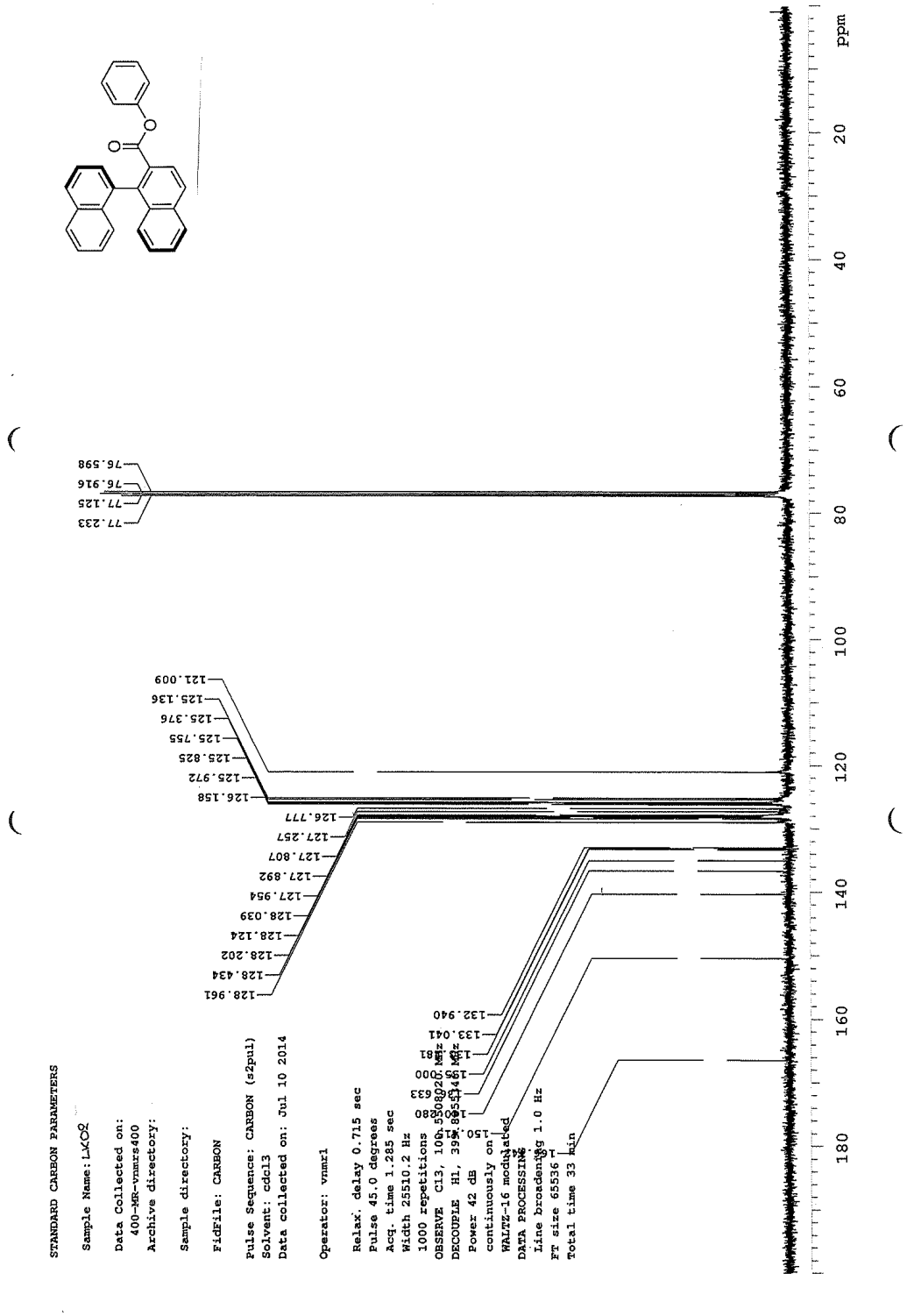
^{1}H NMR of compound **3Ha**



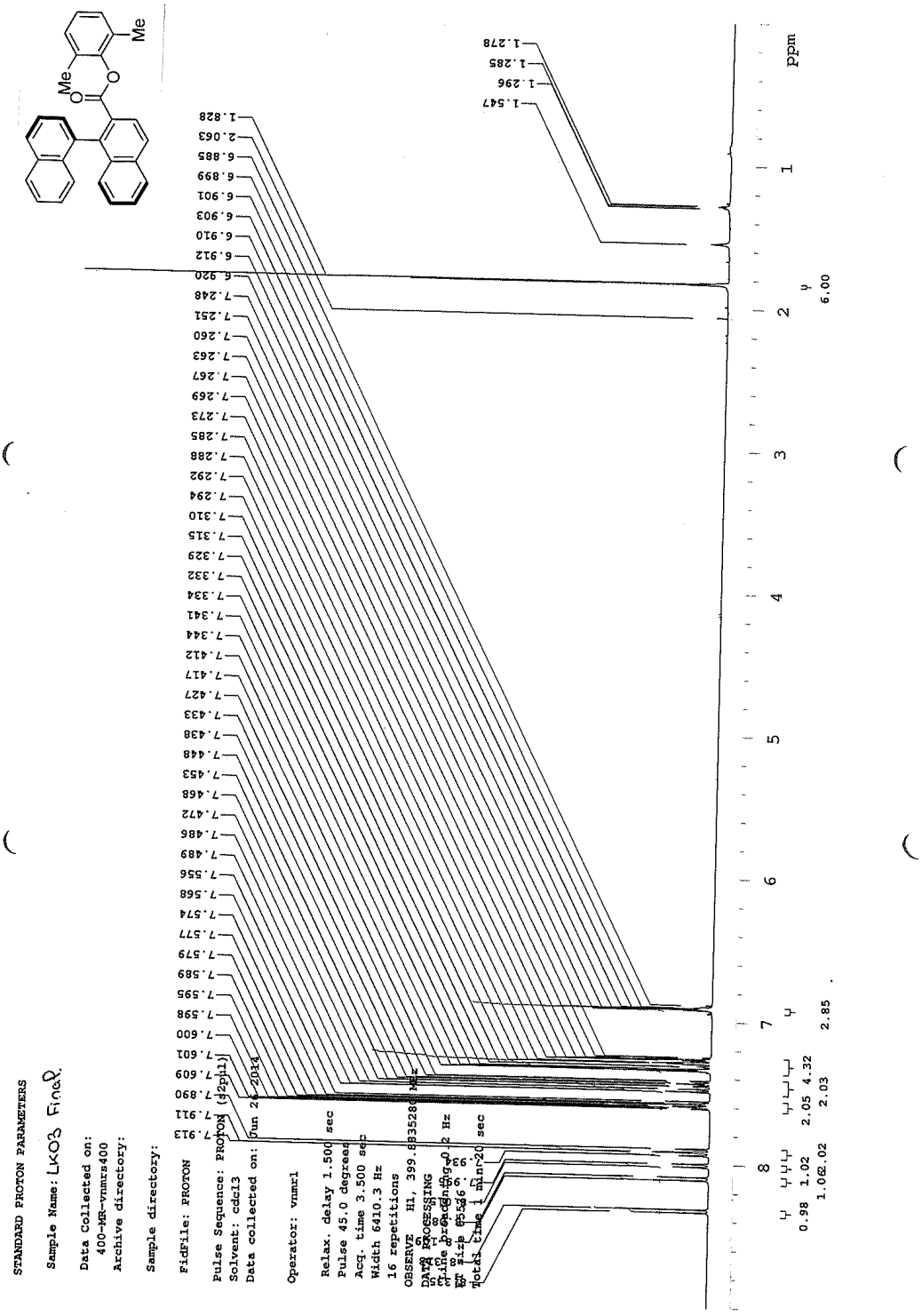
^{13}C NMR of compound **3Ha**



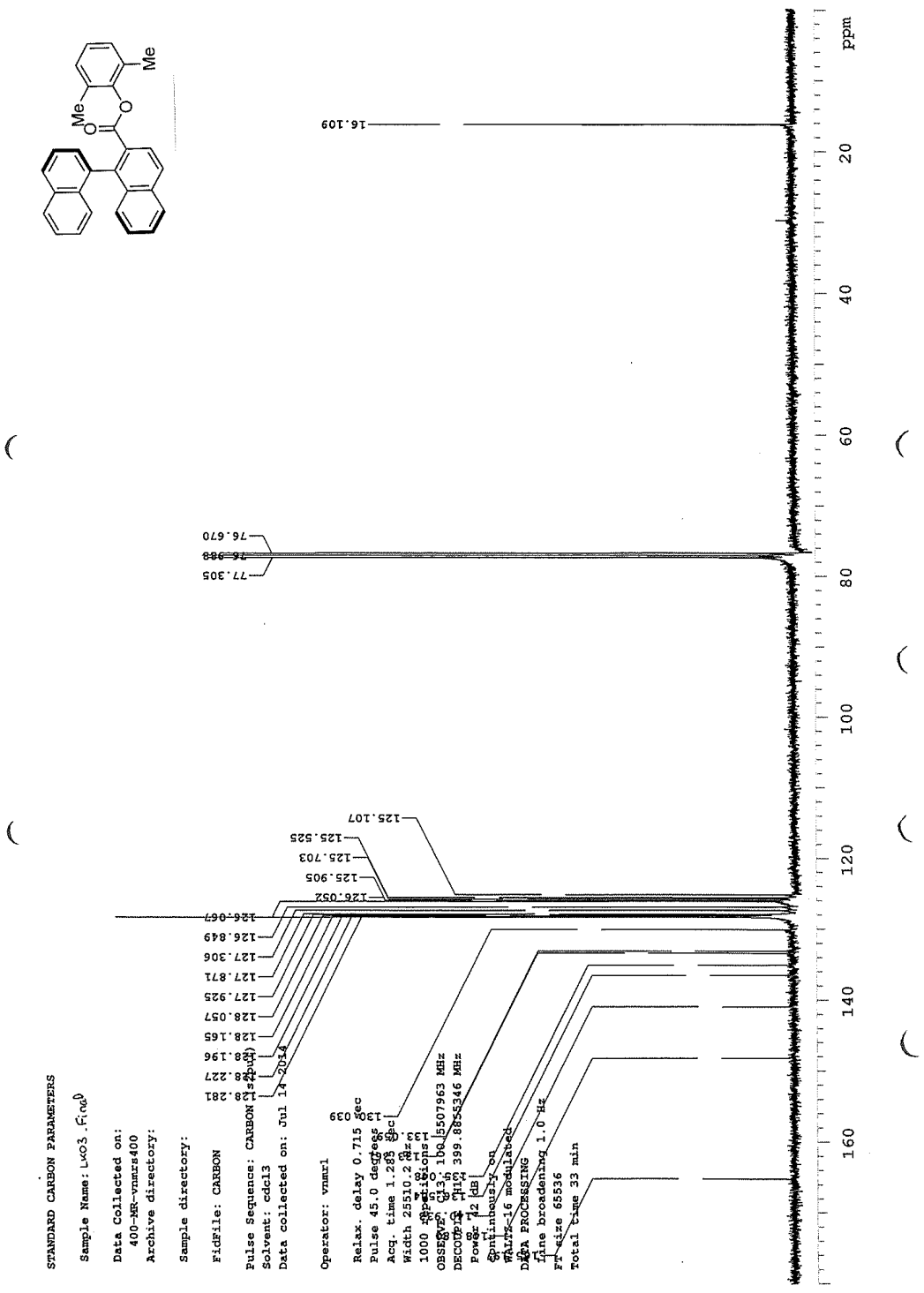
^{1}H NMR of compound **3Ia**



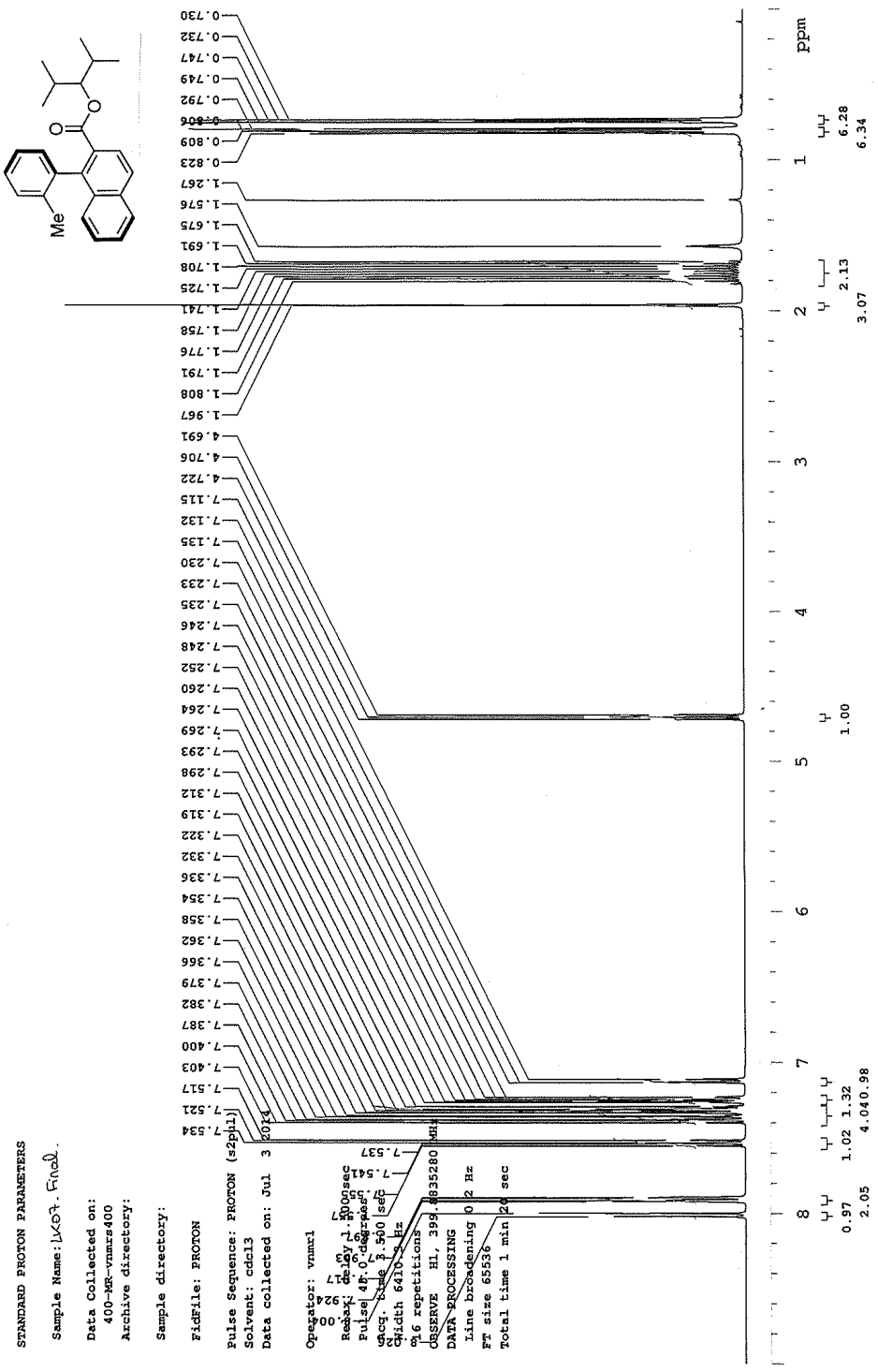
^{13}C NMR of compound **3Ia**



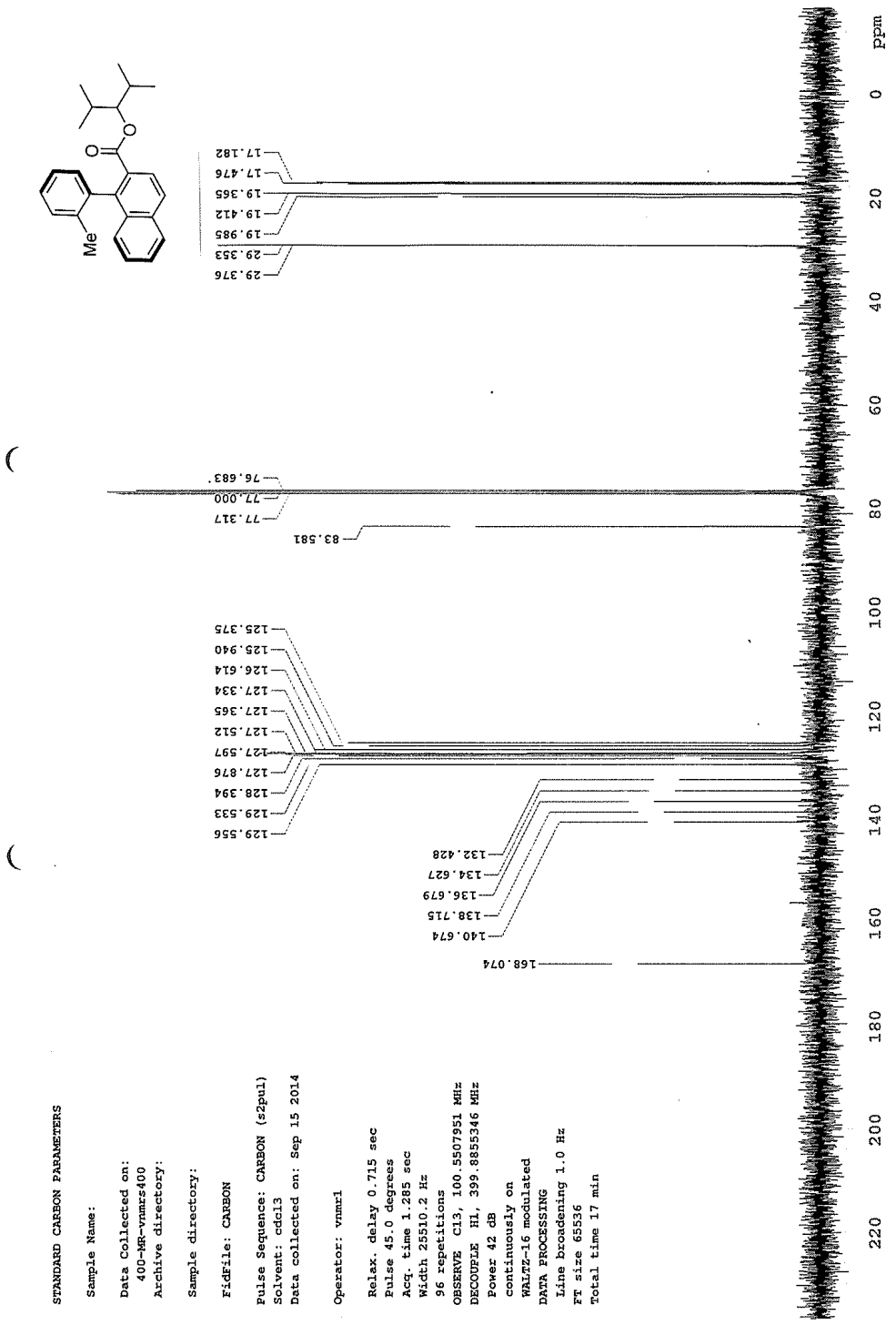
^{1}H NMR of compound **3Ja**



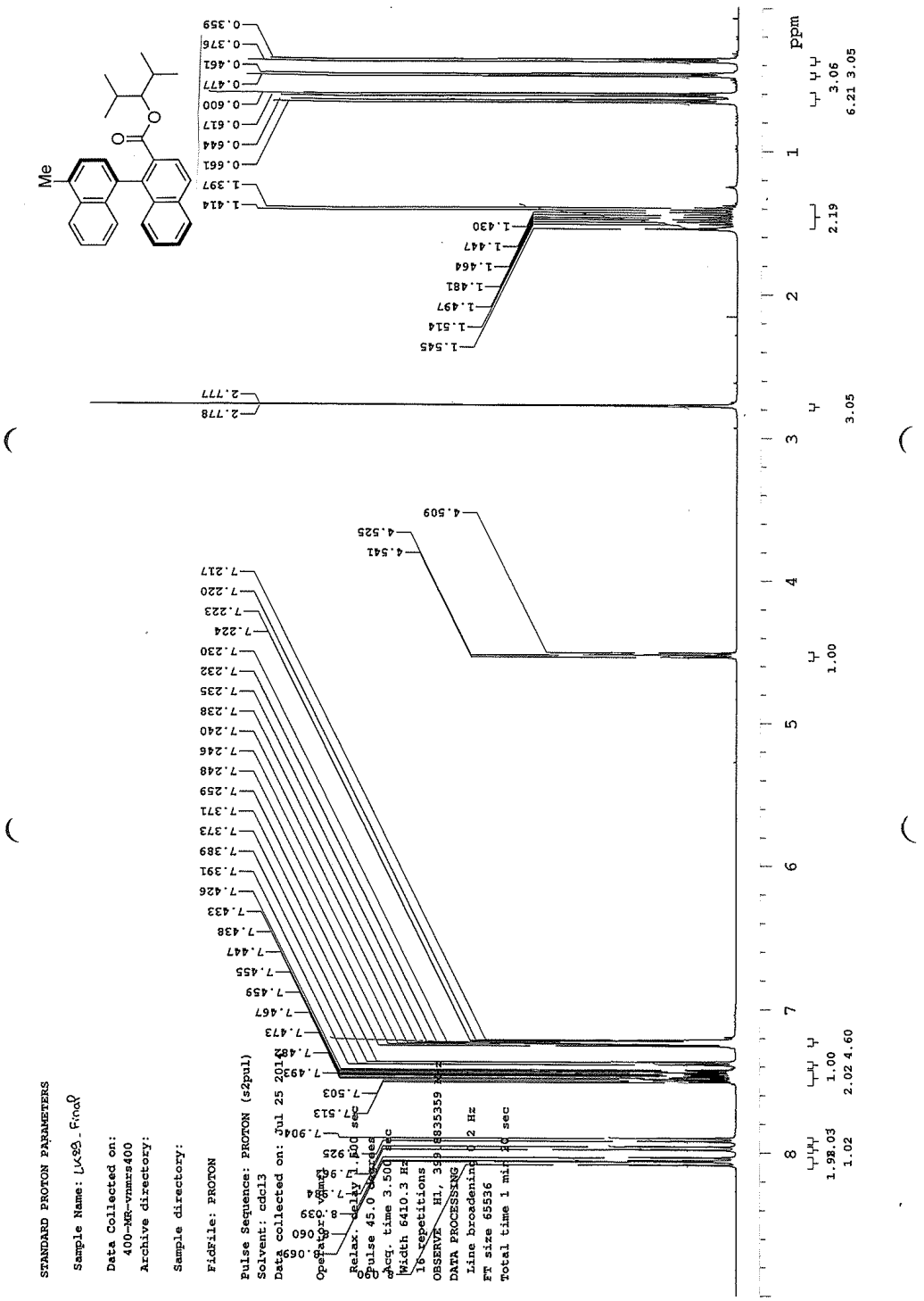
^{13}C NMR of compound **3Ja**



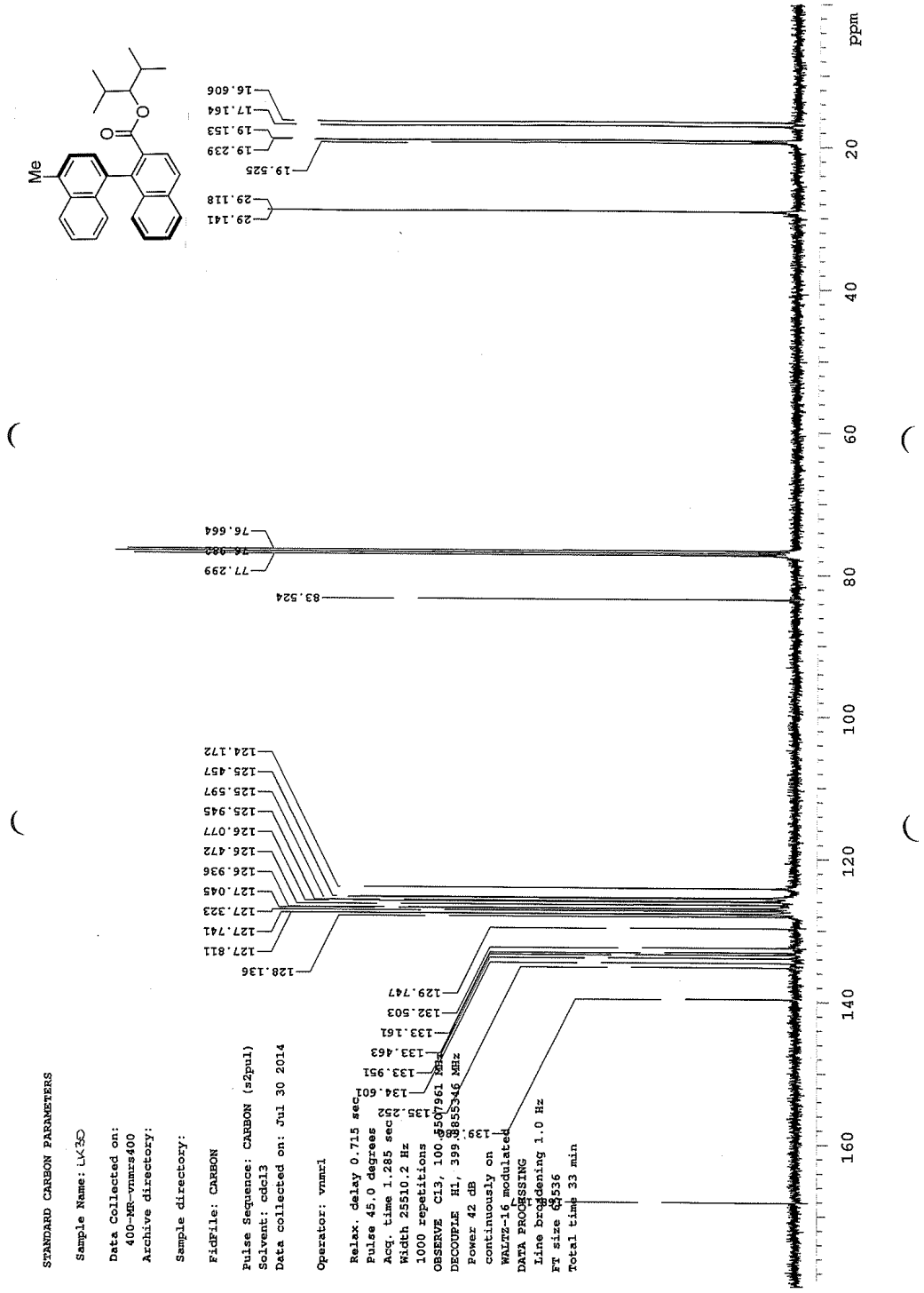
^{1}H NMR of compound **3Db**



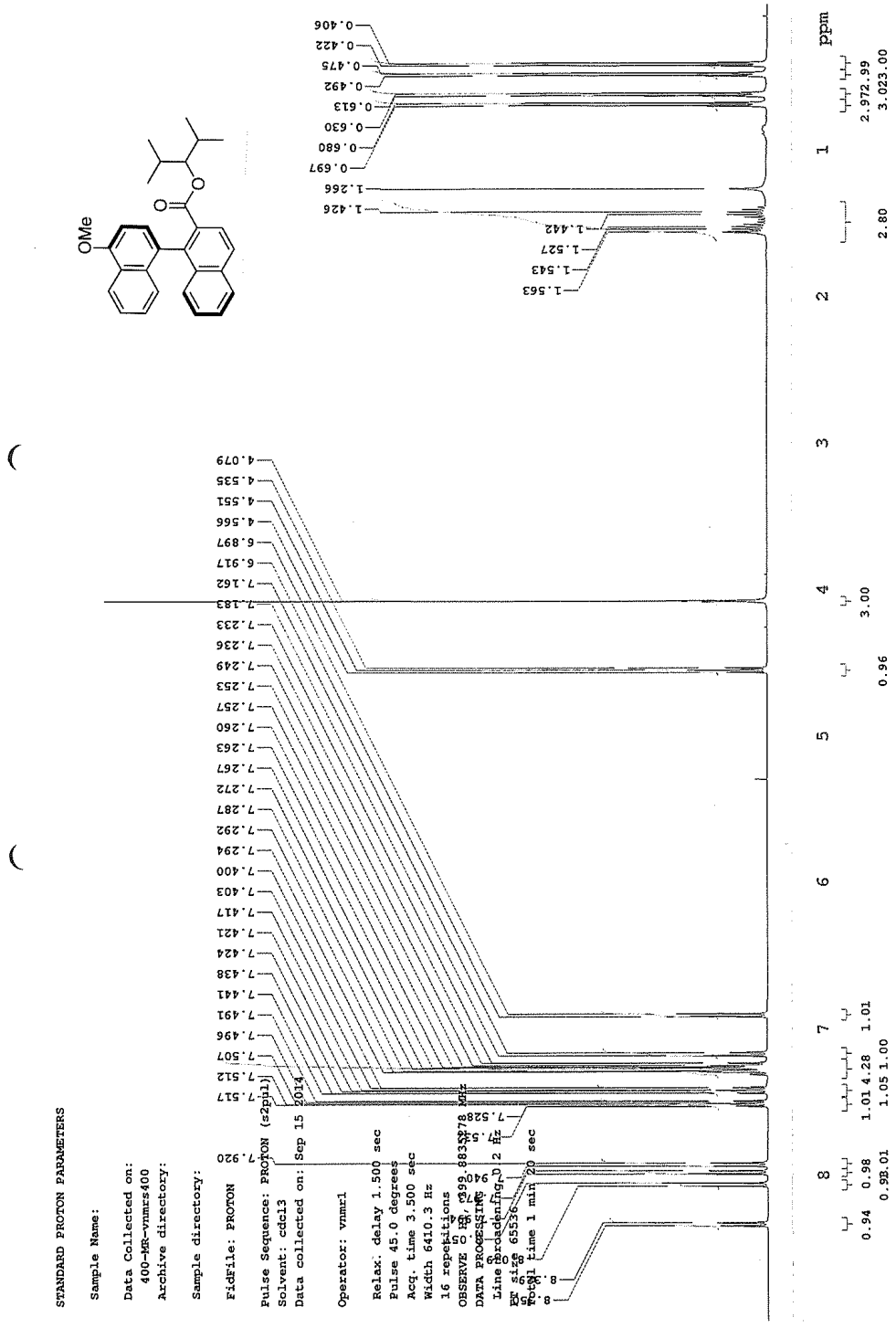
^{13}C NMR of compound **3Db**



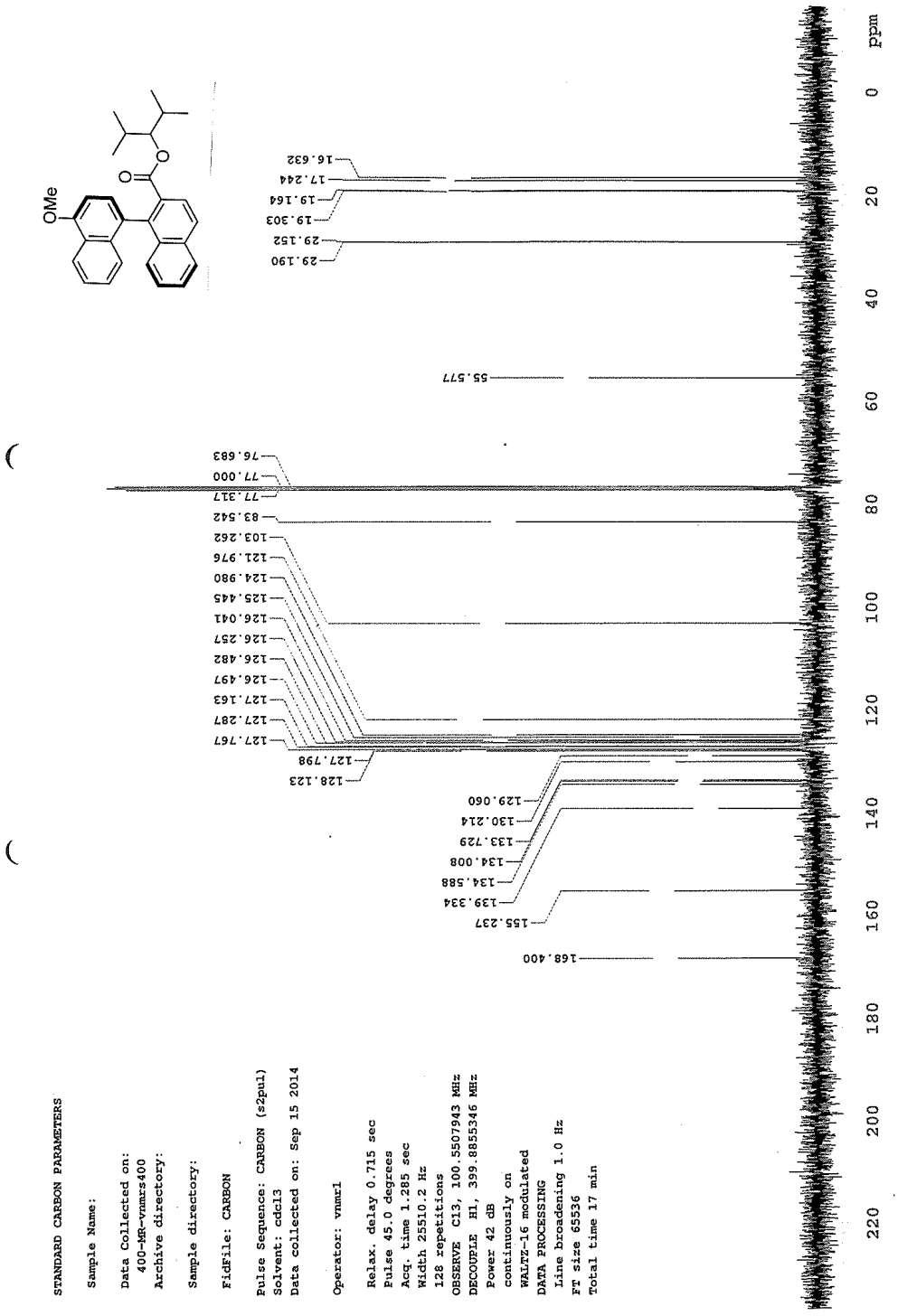
^{1}H NMR of compound **3Dc**



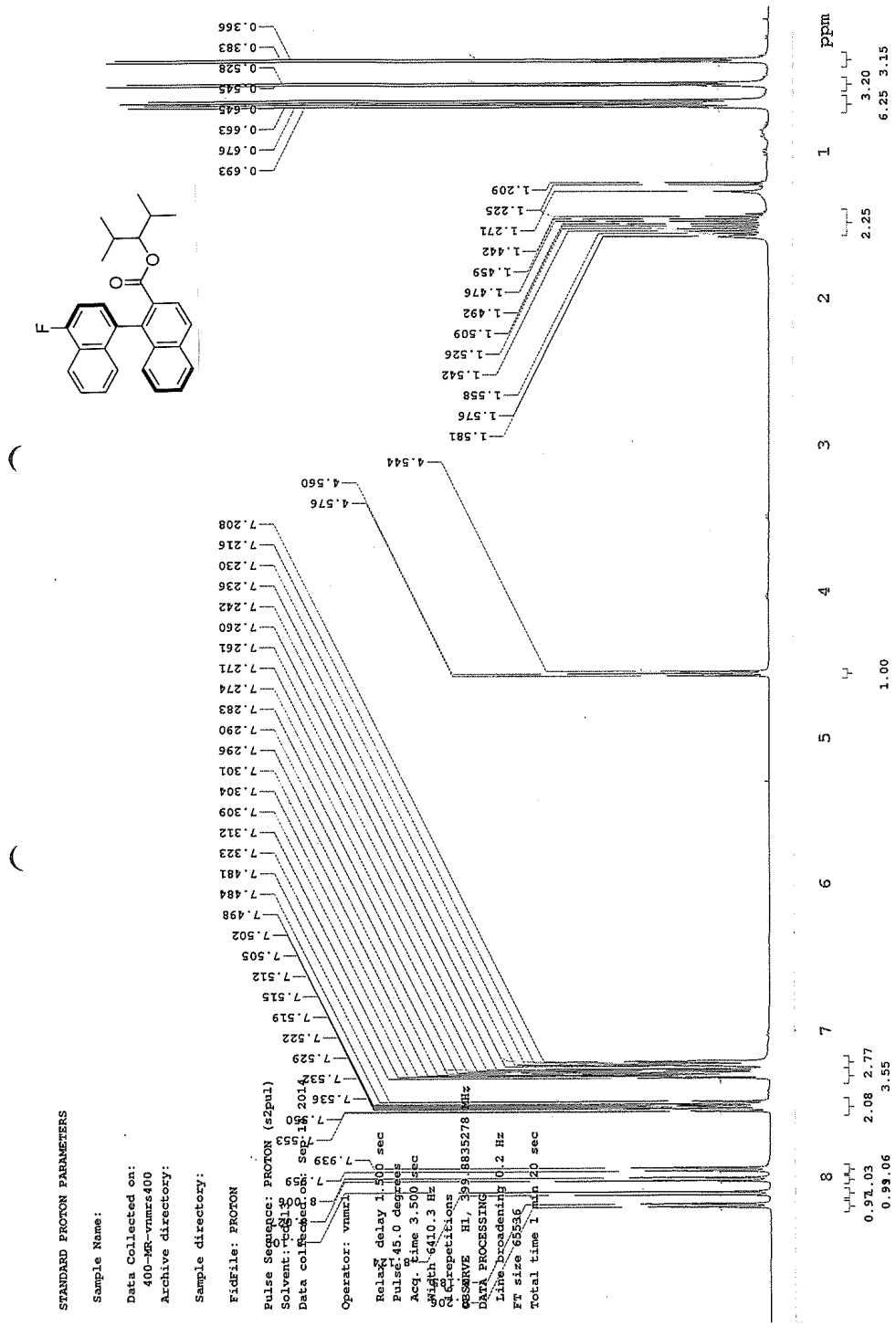
^{13}C NMR of compound **3Dc**



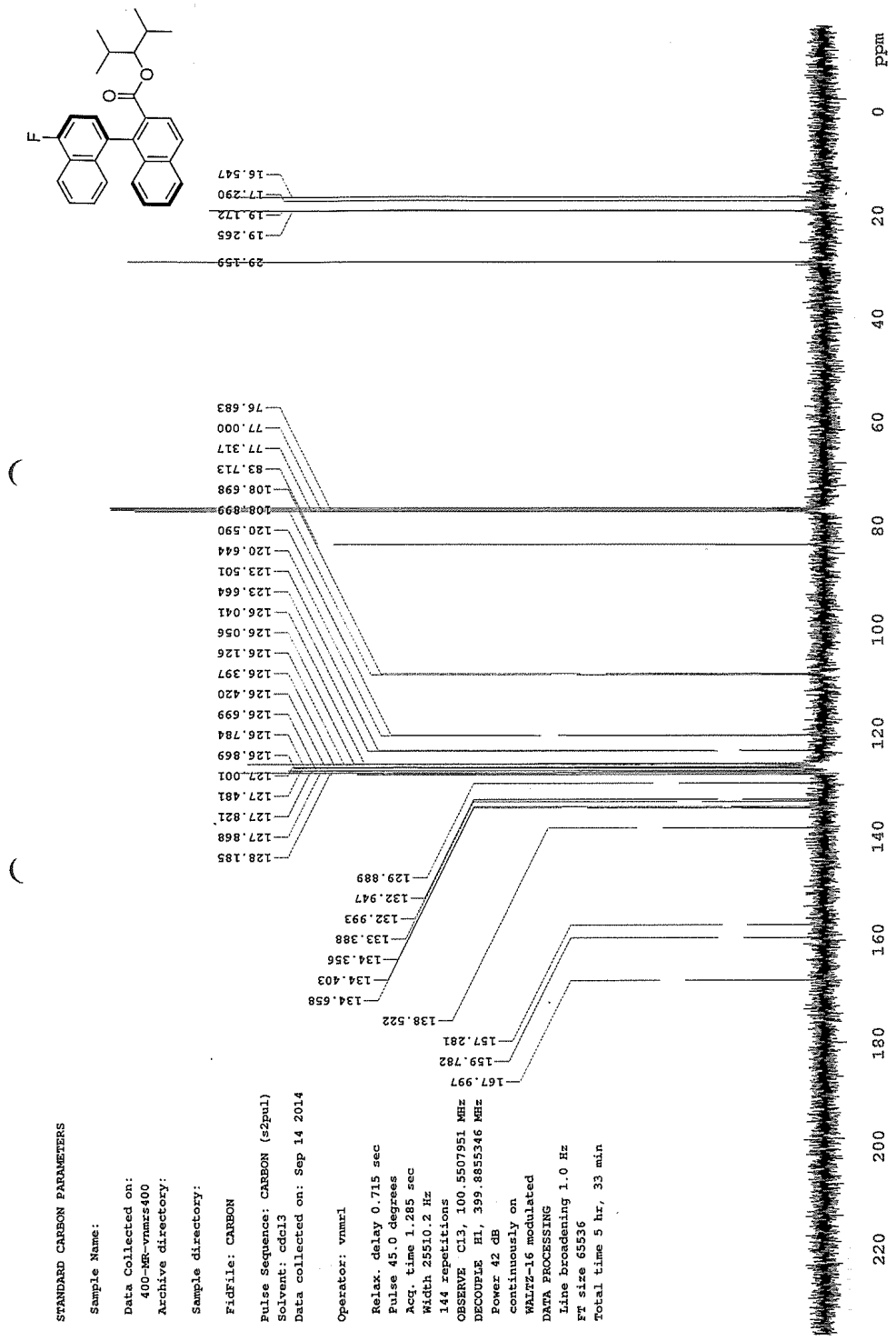
^{1}H NMR of compound **3Dd**



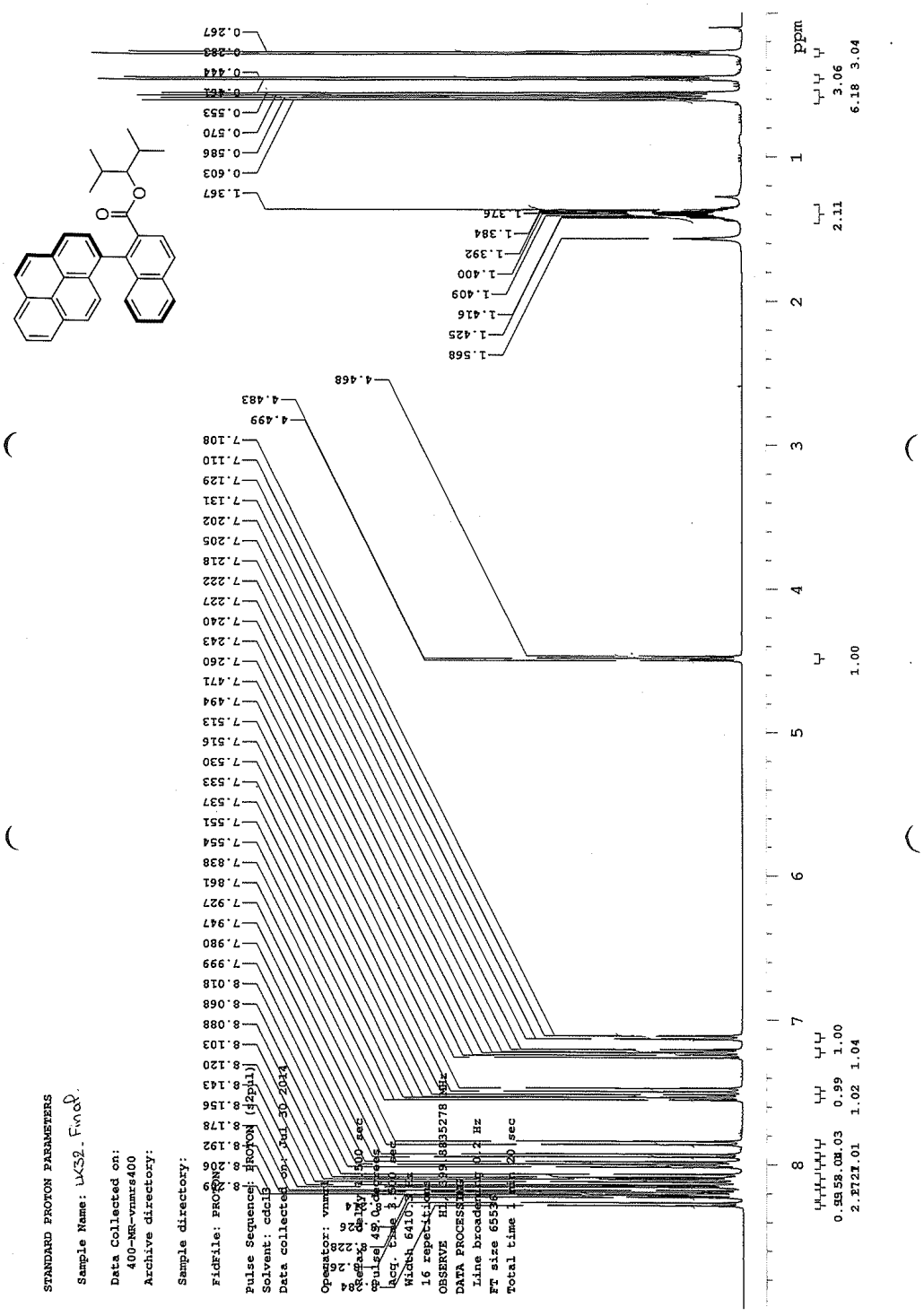
^{13}C NMR of compound **3Dd**



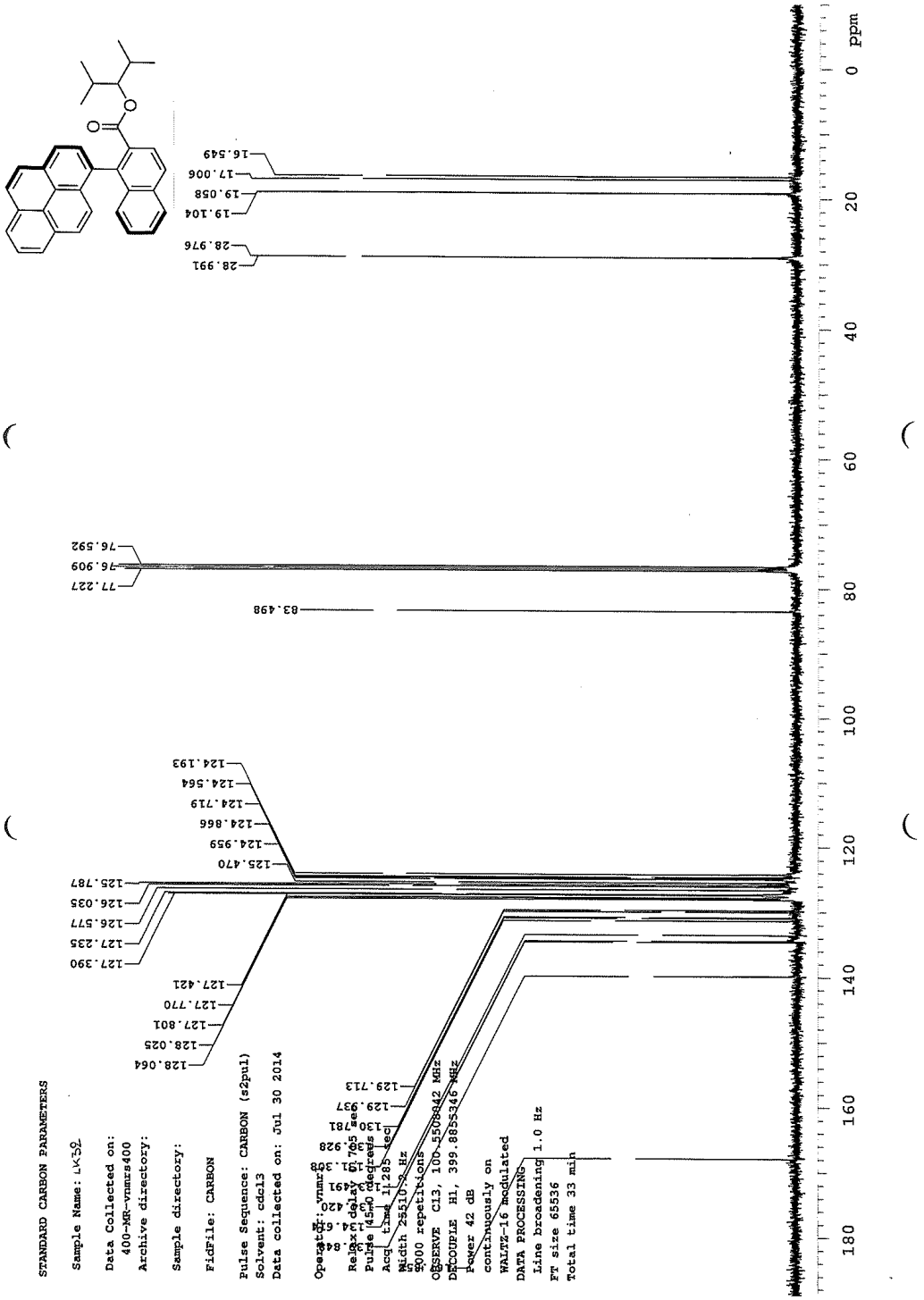
^{1}H NMR of compound **3De**



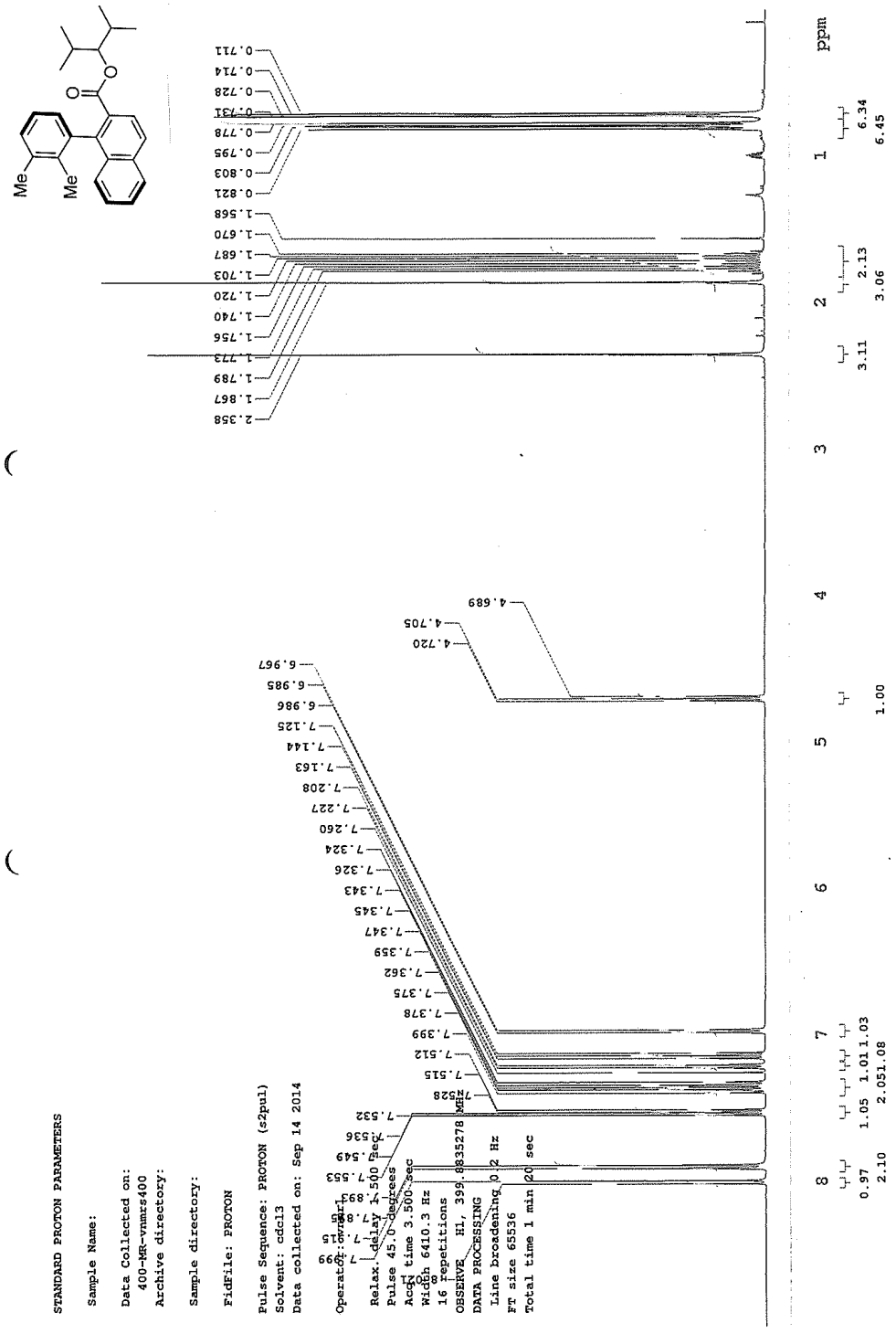
^{13}C NMR of compound **3De**



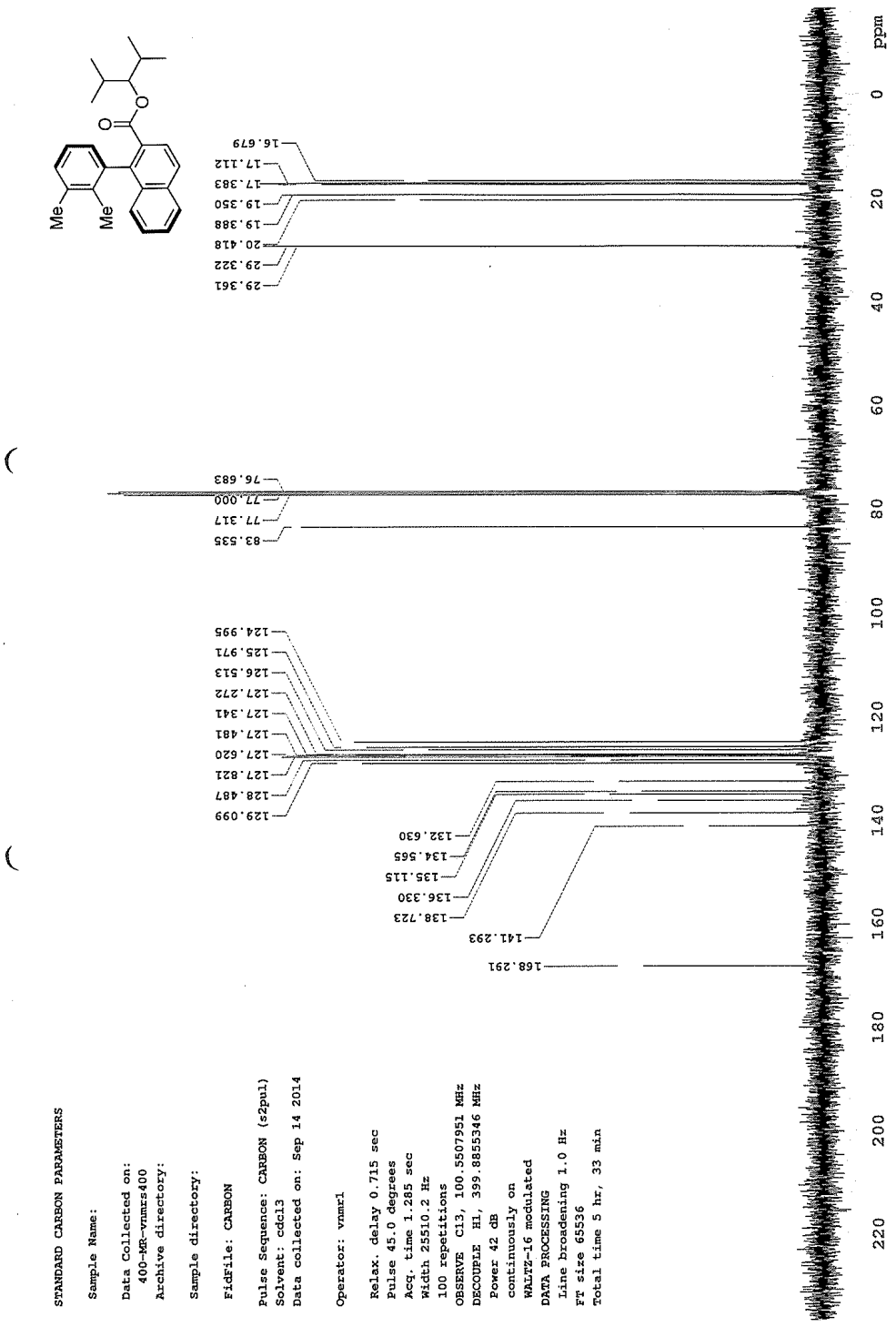
^{1}H NMR of compound **3Df**



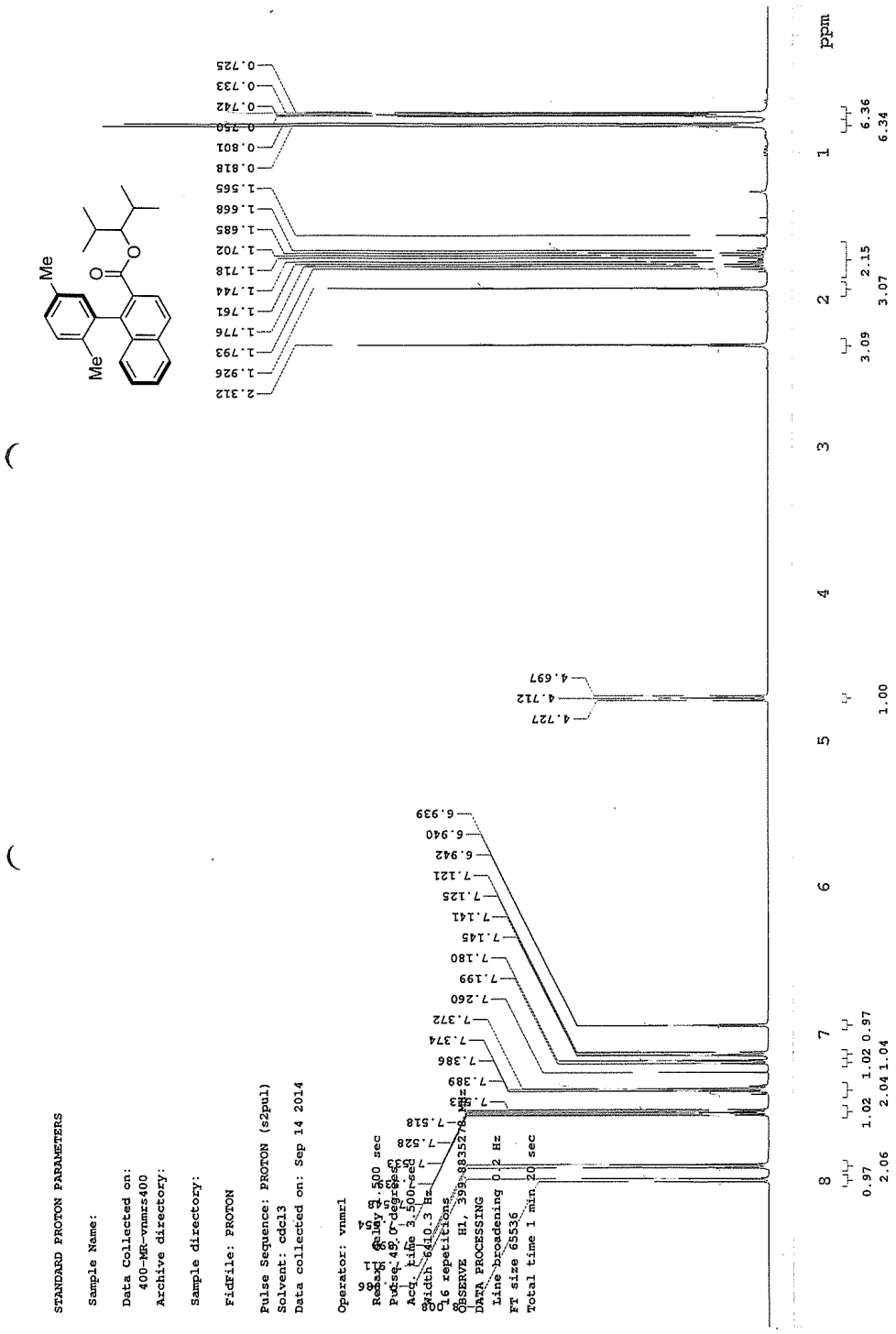
^{13}C NMR of compound **3Df**



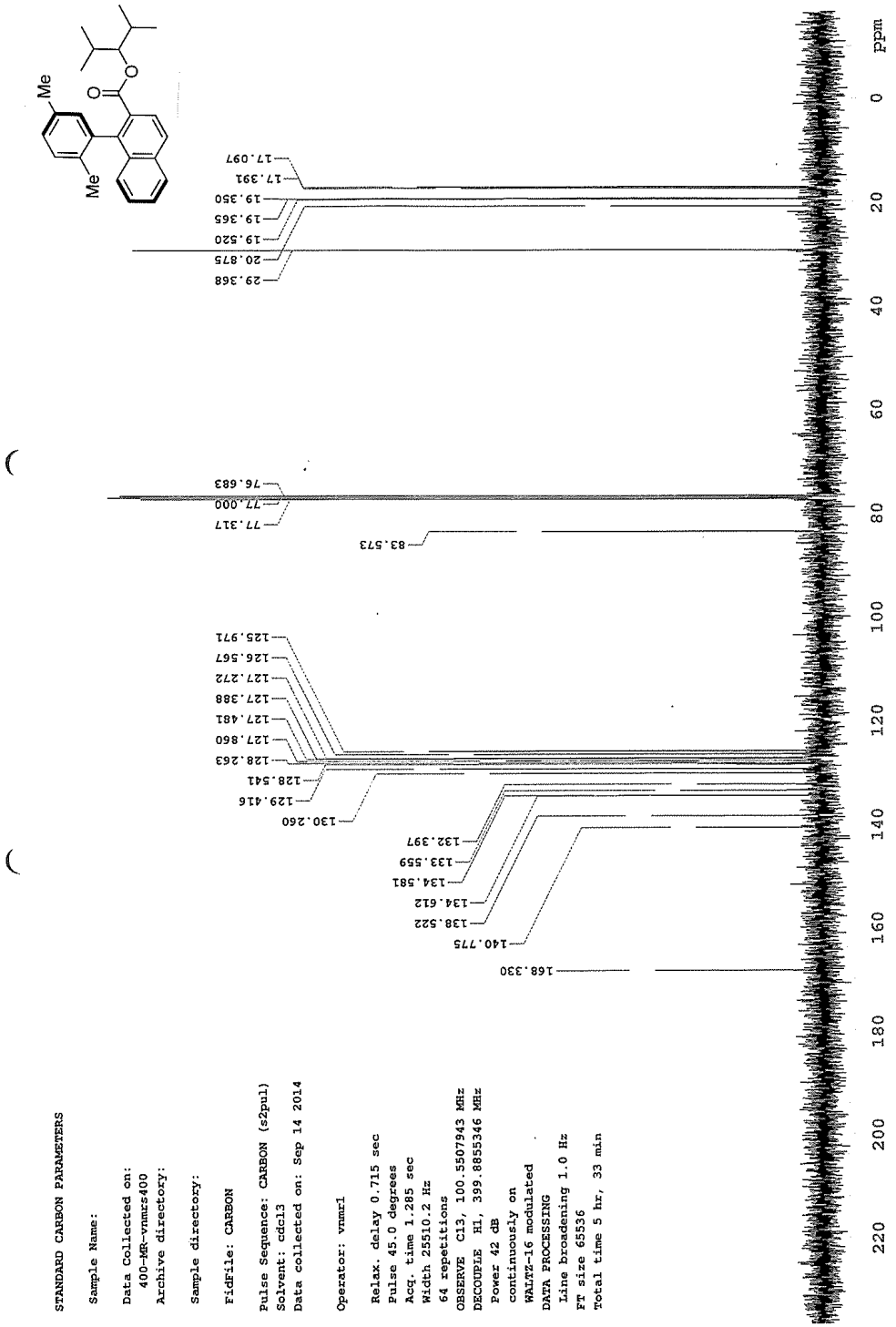
^{1}H NMR of compound **3Dg**



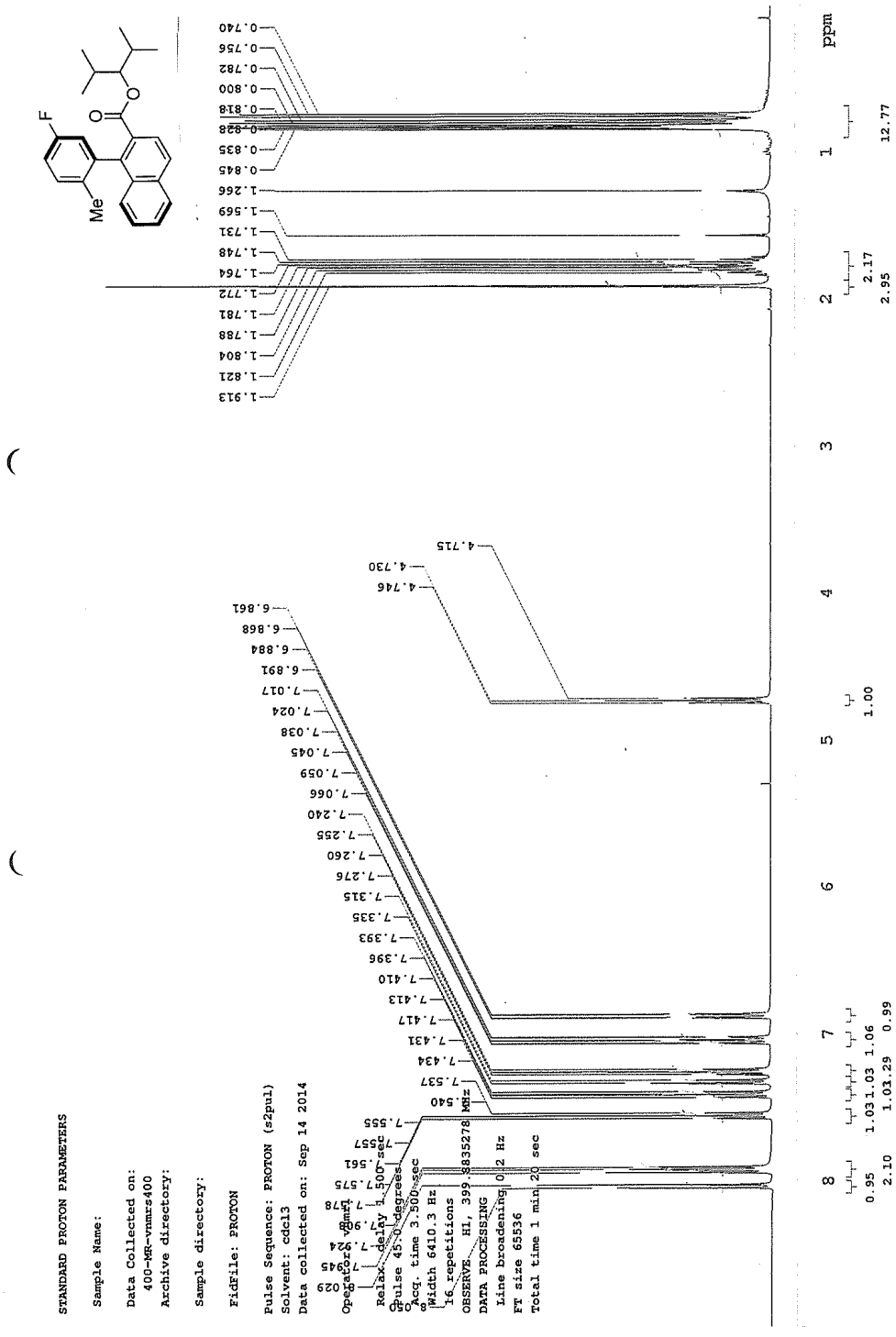
^{13}C NMR of compound **3Dg**



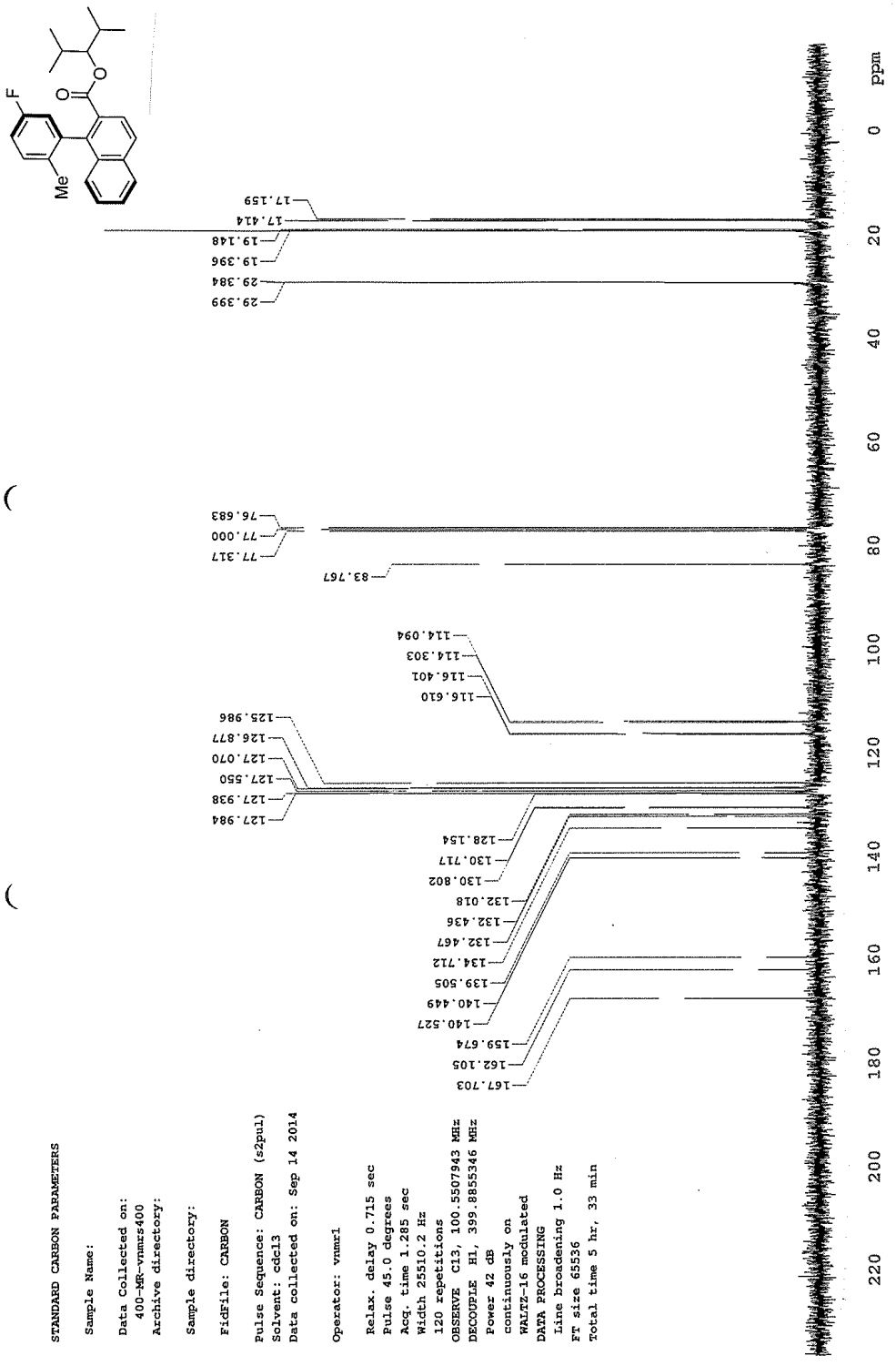
^{1}H NMR of compound **3Dh**



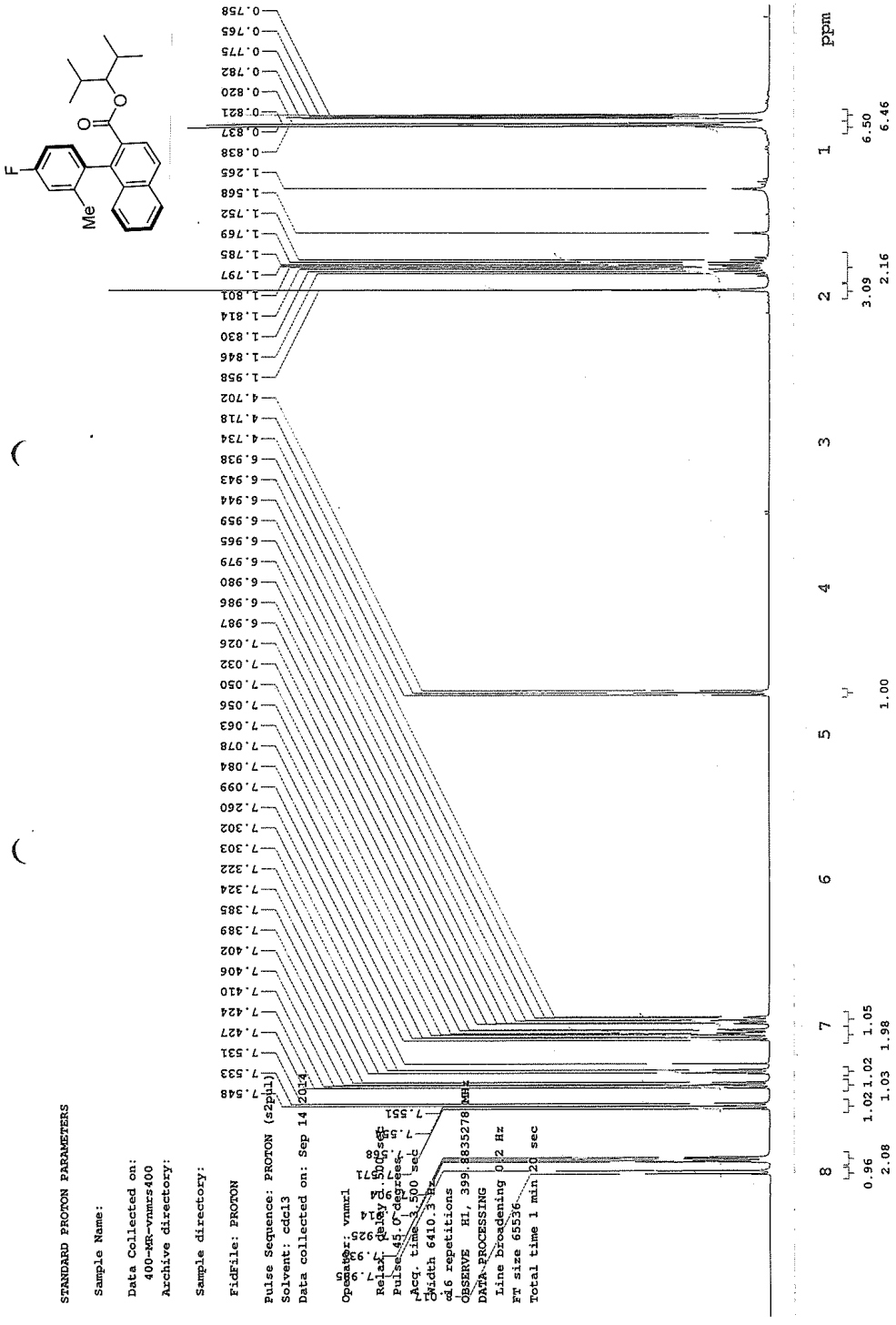
^{13}C NMR of compound **3Dh**



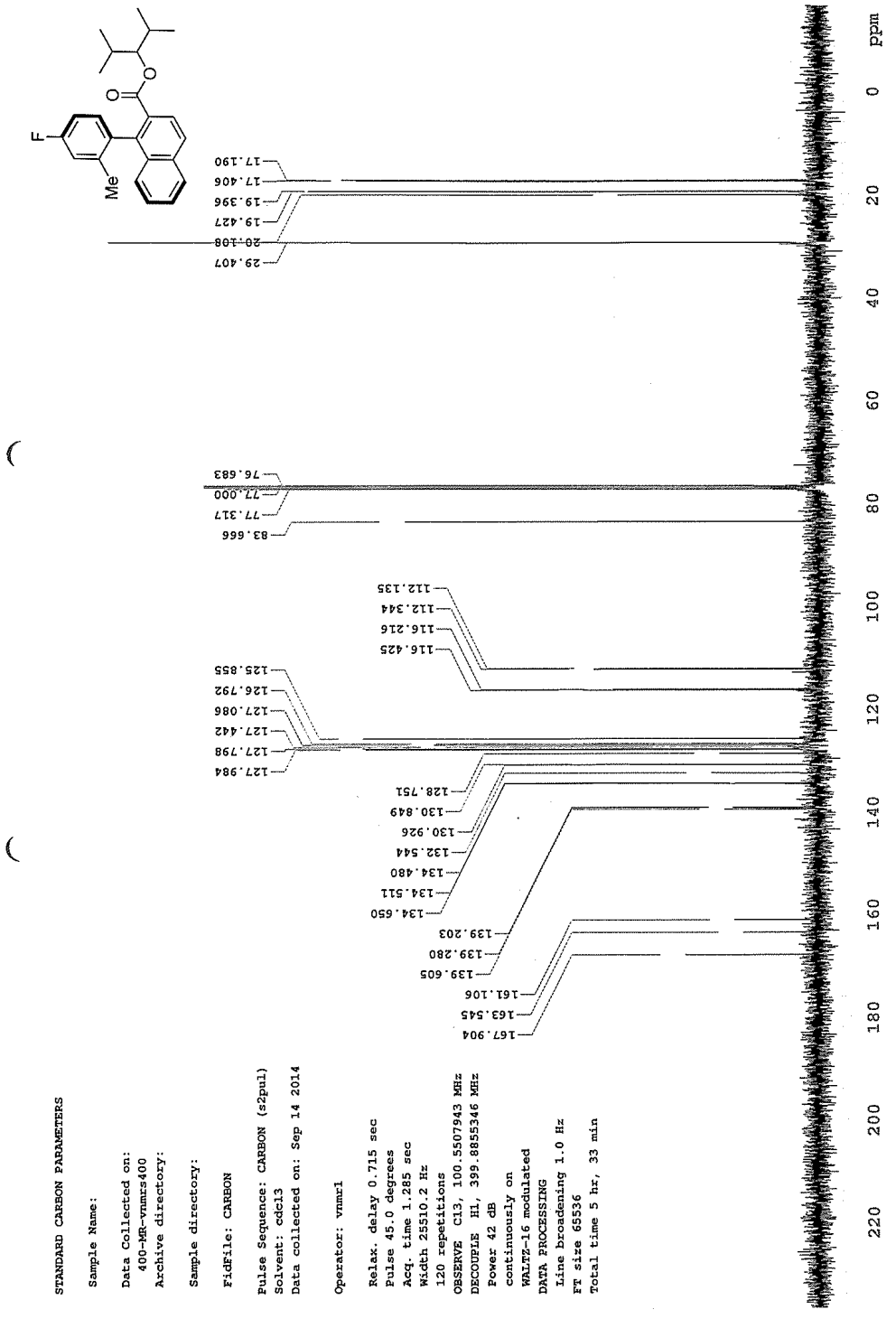
^{1}H NMR of compound **3Di**



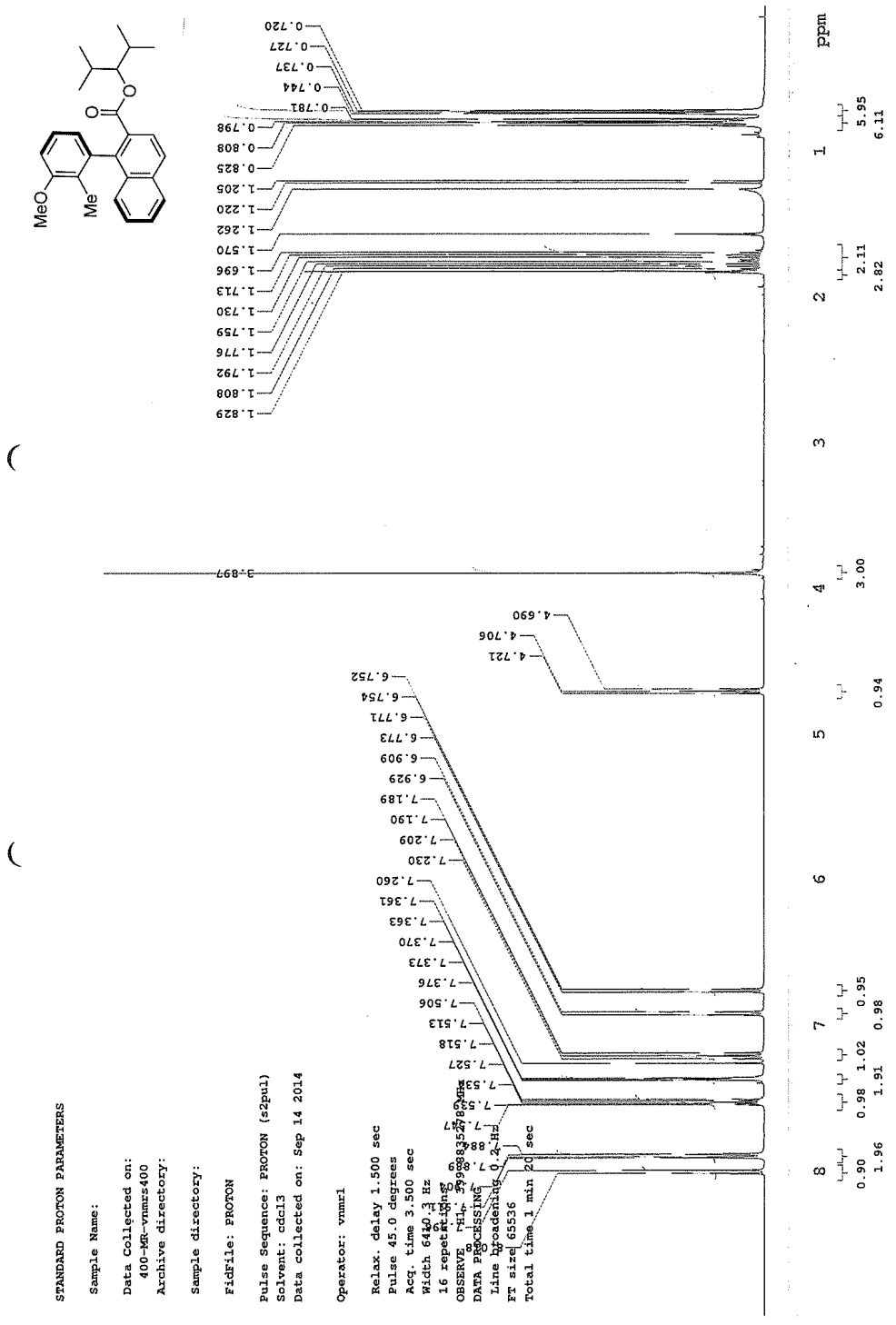
^{13}C NMR of compound **3Di**



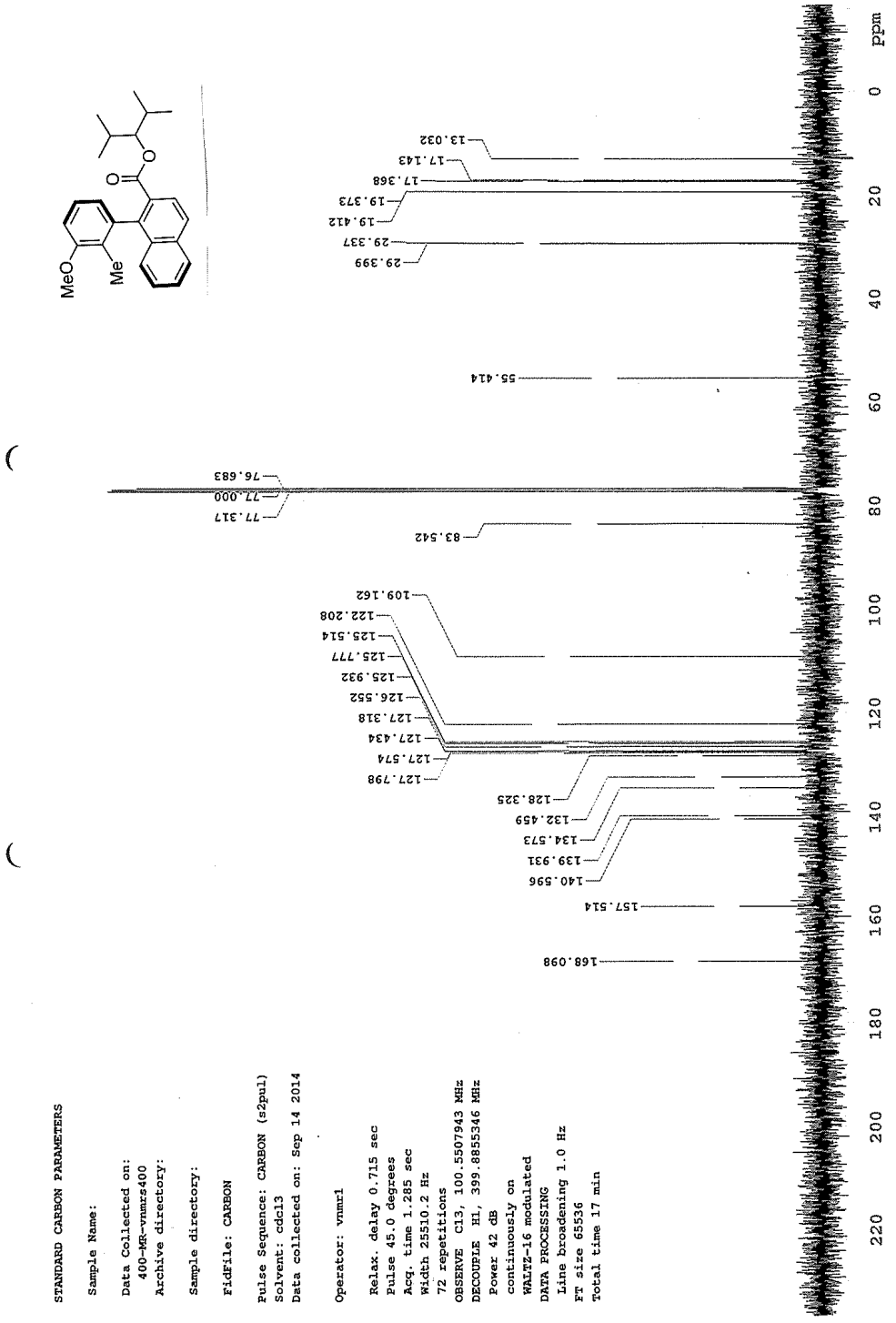
^{1}H NMR of compound **3Dj**



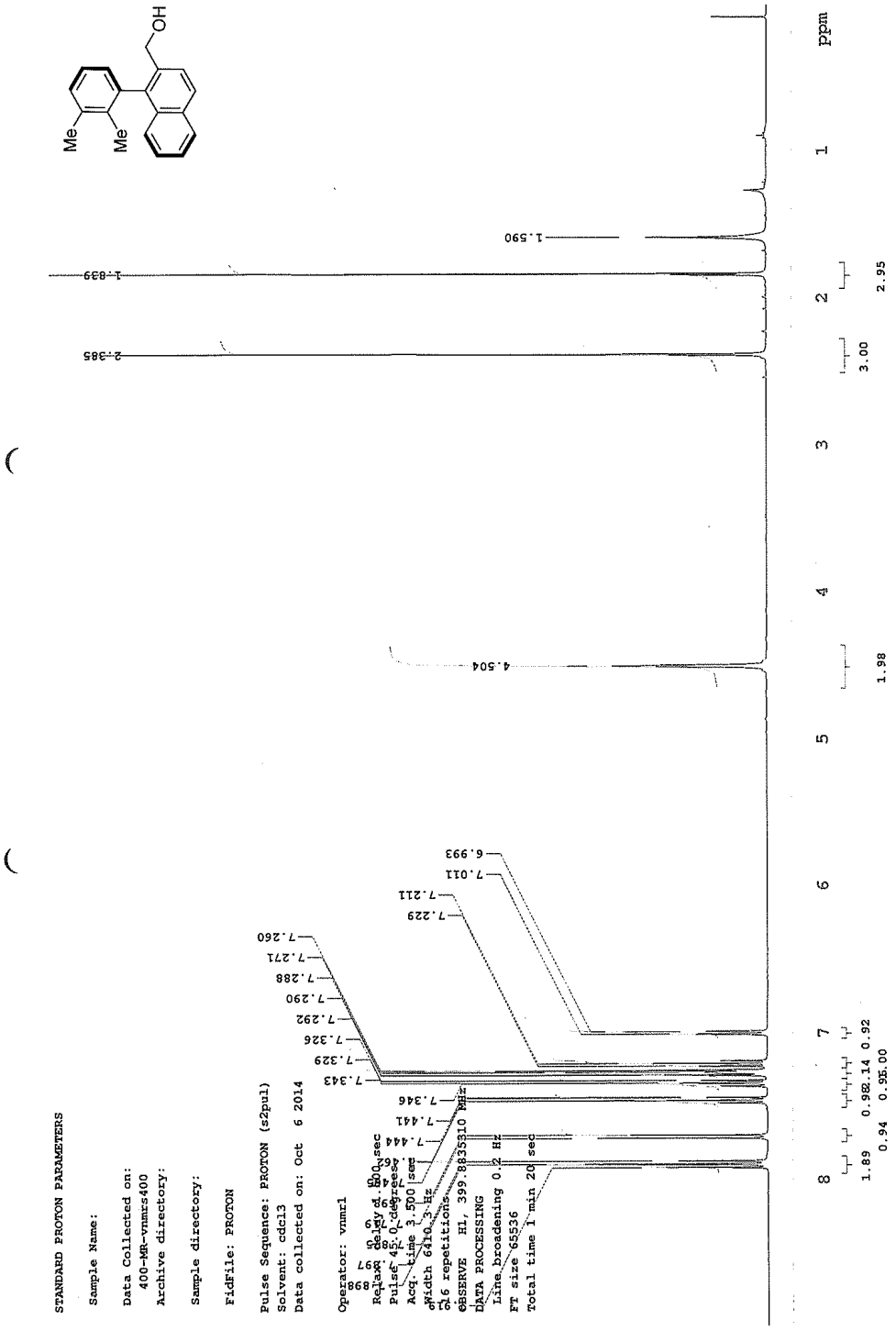
^{13}C NMR of compound **3Dj**



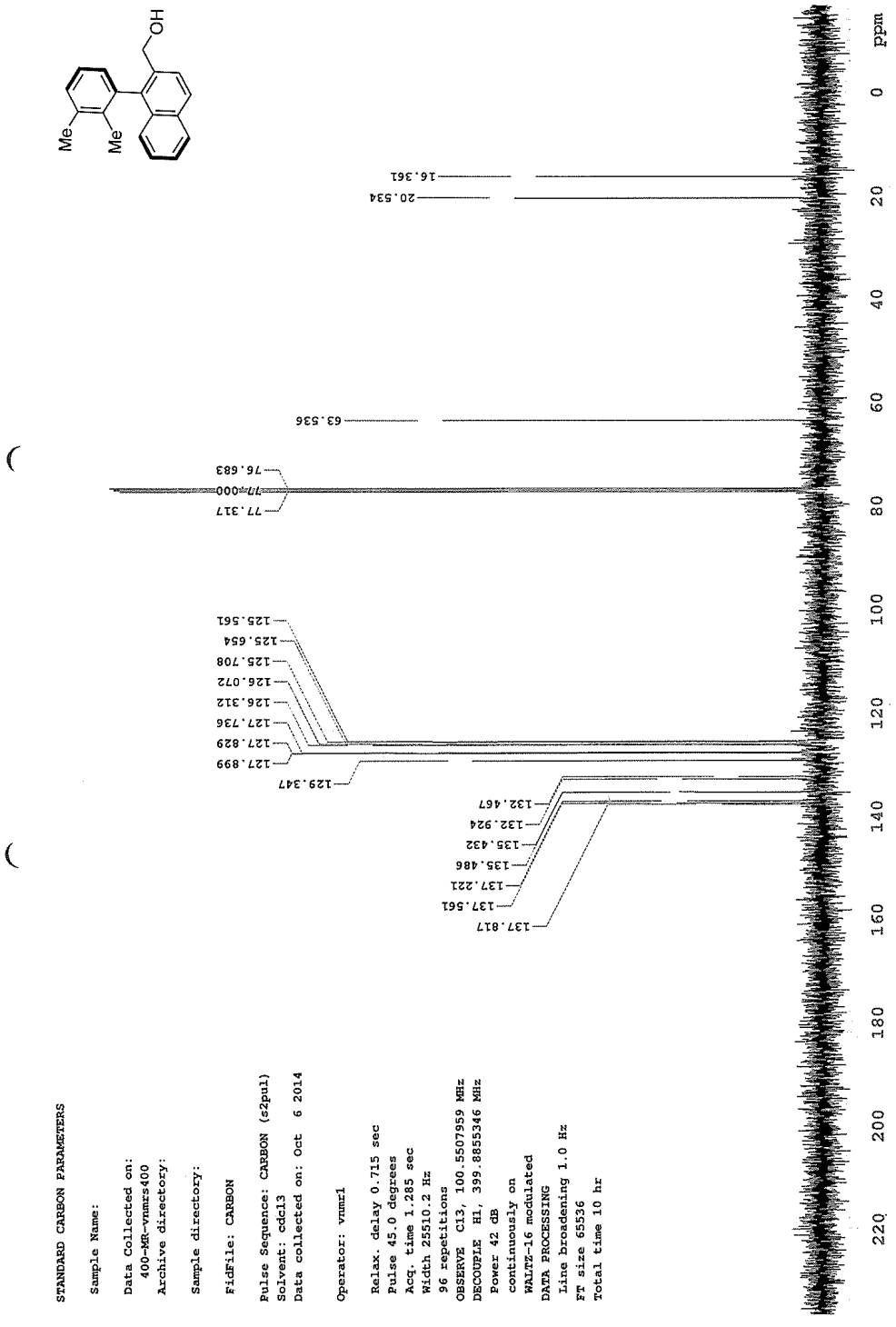
^{1}H NMR of compound **3Dk**



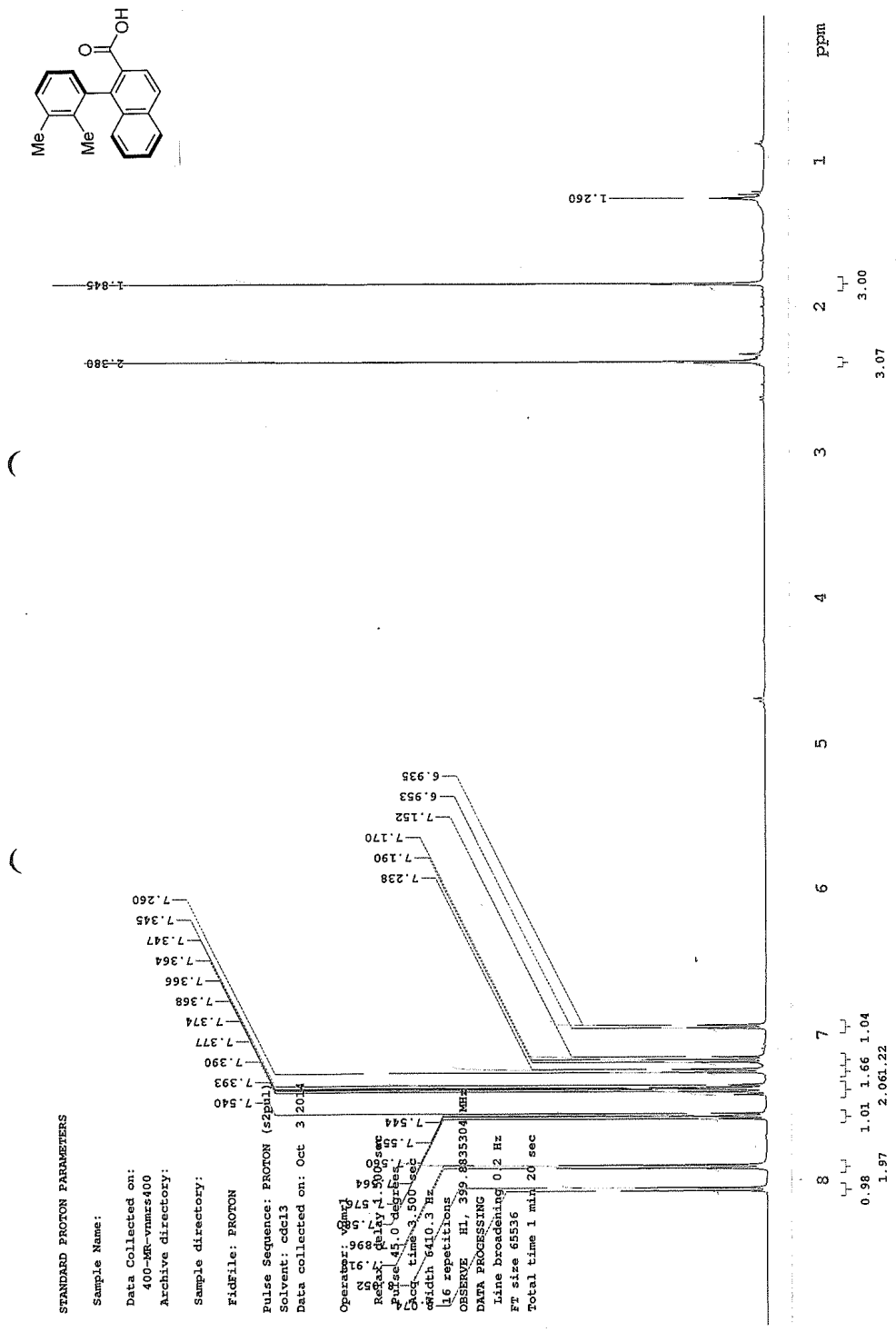
^{13}C NMR of compound **3Dk**



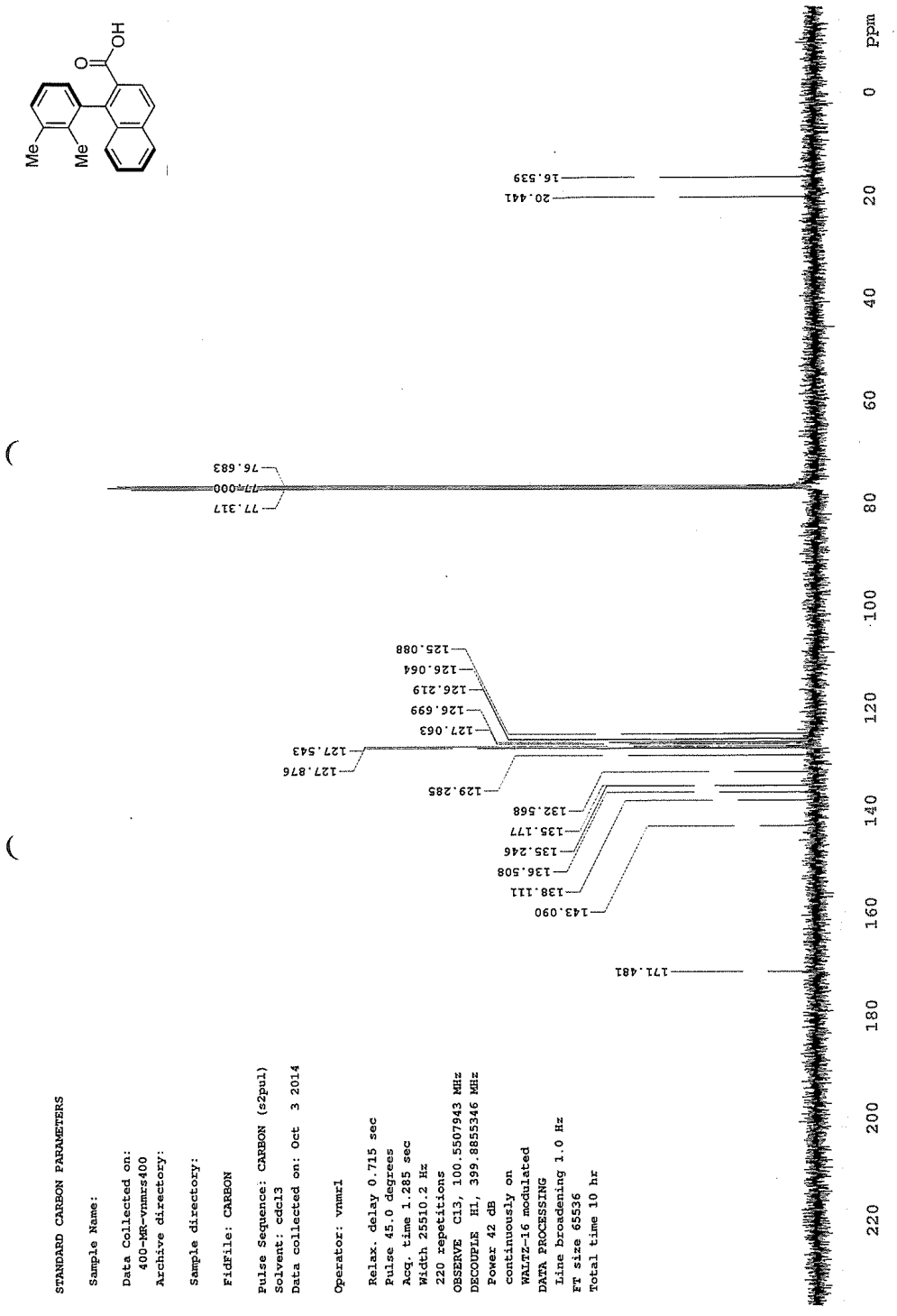
^{1}H NMR of compound **4Dg**



^{13}C NMR of compound **4Dg**



^{1}H NMR of compound **5Dg**



^{13}C NMR of compound **5Dg**