Supporting Information

Copper-Catalyzed Annulative Amination of ortho-Alkynylphenols with Hydroxylamines: Synthesis of 3-Aminobenzofurans by Umpolung Amination Strategy

Koji Hirano,* Tetsuya Satoh, and Masahiro Miura*

Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565-0871, Japan

Contents

Instrumentation and Chemicals

^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded at 400 or 600 MHz, 100 or 150 MHz, and 373 MHz, respectively, for $CDCl_3$ solutions. MS data were obtained by EI. GC analysis was carried out using a silicon OV-17 column (i. d. 2.6 mm x 1.5 m) or a CBP-1 capillary column (i. d. 0.5 mm x 25 m). TLC analyses were performed on commercial glass plates bearing a 0.25-mm layer of Merck Silica gel $60F_{254}$. Silica gel 60 N (spherical neutral, obtained from Kanto Chemical) was used for column chromatography.

Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. NMP was freshly distillated from CaH_2 and stored over MS4A strictly under nitrogen. $Cu(OTf)_2$ was purchased from TCI. LiO-*t*-Bu and Grubbs 2nd generation catalyst were obtained from Aldrich. *ortho*-Alkynylphenols **1** were prepared according to the literature.[1] *O*-Benzoyl-*N*,*N*-diethylhydroxylamine (**2a**) was obtained by the reaction of *N*,*N*-diethylhydroxylamine with benzoyl chloride, while other hydroxylamines **2b–l** were synthesized through the nucleophilic substitution of the corresponding amines with benzoyl peroxide.[2] Unless otherwise noted, all reactions were carried out under nitrogen atmosphere.

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[1] Yoneda, E.; Sugioka, T.; Hirao, K.; Zhang, S. W.; Takahashi, S. *J. Chem. Soc., Perkin Trans. 1* **1998**, *3*, 477.

[2] (a) Berman, A. M.; Johnson, J. S. *J. Am. Chem. Soc.* **2004**, *126*, 5680. (b) Berman, A. M.; Johnson, J. S. *J. Org. Chem.* **2006**, *71*, 219.

Experimental Procedure

Synthesis of 3aa (Table 1, entry 14): $Cu(OTf)_2$ (18 mg, 0.050 mmol) and LiO-*t*-Bu (80 mg, 1.0 mmol) were placed in a 20 mL two-necked reaction flask, which is filled with nitrogen using the standard Schlenk technique. NMP (1.0 mL) was added, and the suspension was stirred for 10 min at room temperature. A solution of 2-(phenylethynyl)phenol (**1a**, 97.1 mg, 0.50 mmol) and *O*-benzoyl-*N*,*N*-diethylhydroxylamine (**2a**, 116 mg, 0.60 mmol) in NMP (2.0 mL) was then added dropwise. After being stirred for 4 h at the same temperature, the resulting mixture was poured into saturated aq. NaCl and extracted with dichloromethane. The combined organic layer was dried over sodium sulfate and concentrated in vacuo. Subsequent silica gel column purification with hexane/Et_3N (200/1, v/v) afforded *N*,*N*-diethyl-2-phenylbenzofuran-3-amine (**3aa**, 81 mg, 0.31 mmol) in 61% yield. The optimization studies for chromatographic purification were summarized below (The yields based on GC method for all trials were >90%.).

conditions	acidic silica gel with Hex	neutral silica gel with Hex	neutral silica gel with Hex/Et_3N (200/1)
isolated yield of **3aa**	23%	52%	61%

Synthesis of 4 (Scheme 2): With $Cu(OTf)_2$ (36 mg, 0.10 mmol), under the otherwise identical conditions mentioned above, the oxyamination of 2-(3-methylbut-3-en-1-yn-1-yl)phenol (**1l**, 79 mg, 0.50 mmol) with *N*-allyl-*O*-benzoyl-*N*-methylhydroxylamine (**2g**, 191.2 mg, 1.0 mmol) proceeded to furnish *N*-allyl-*N*-methyl-2-(1-propen-2-yl)benzofuran-3-amine (**3lg**, 58 mg, 0.26 mmol) in 51% yield.

Grubbs 2nd generation catalyst (3.7 mg, 4.4 μmol) was placed in a 5 mL Schlenk tube, which is then filled with nitrogen. Trimethyl(vinyloxy)silane (0.013 mL, 0.087 mmol) and a solution of **3lg** (20 mg, 0.087 mmol) in toluene (1.0 mL) were subsequently added dropwise. The solution was heated at 110 ˚C for 2 h. The resulting mixture was allowed to cool to room temperature and filtered through a pad of neutral alumina. Concentration under reduced pressure followed by column chromatography on silica gel with hexane/EtOAc/Et_3N (400/20/2.5, v/v/v) produced 1,3,5-trimethyl-2,3-dihydro-1*H*-benzofuro[3,2-*b*]azepine (**4**, 15 mg, 0.067 mmol) in 77% yield.

Characterization Data for Products

^{1}H and ^{13}C NMR spectra for all compounds are attached in the last part.

***N,N*-Diethyl-2-phenylbenzofuran-3-amine (3aa)**; oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.05 (t, *J* = 7.4 Hz, 6H), 3.26 (q, *J* = 7.4 Hz, 4H), 7.16 (t, *J* = 7.3 Hz, 1H), 7.26–7.31 (m, 2H), 7.40-7.49 (m, 3H), 7.66 (d, *J* = 7.8 Hz, 1H), 8.40 (d, *J* = 7.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.66, 48.77, 111.73, 120.97, 122.01, 124.02, 125.91, 127.09, 127.73, 127.94, 128.19, 131.12, 149.16, 153.26; HRMS *m/z* (M^+) calcd for $C_{18}H_{19}NO$: 265.1467, found: 265.1466.

***N,N*-Diethyl-2-(4-methoxylphenyl)benzofuran-3-amine (3ba)**; oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.04 (t, *J* = 7.4 Hz, 6H), 3.24 (q, *J* = 7.4 Hz, 4H), 3.85 (s, 3H), 6.95 (dt, *J* = 8.7, 1.8 Hz, 2H), 7.14 (t, *J* = 7.3 Hz, 1H), 7.21 (t, *J* = 8.2 Hz, 1H), 7.45 (d, *J* = 7.8 Hz, 1H), 7.64 (d, *J* = 7.8 Hz, 1H), 8.34 (dt, *J* = 8.7, 2.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.68, 48.80, 55.23, 111.53, 113.61, 120.65, 121.90, 123.50, 124.00, 125.26, 127.44, 128.03, 149.52, 153.07, 159.21; HRMS *m/z* (M^+) calcd for $C_{19}H_{21}NO_2$: 295.1572, found: 295.1571.

***N,N*-Diethyl-2-{(4-trifluoromethyl)phenyl}benzofuran-3-amine (3ca)**; oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.05 (t, *J* = 7.3 Hz, 6H), 3.27 (q, *J* = 7.3 Hz, 4H), 7.19 (t, *J* = 7.8 Hz, 1H), 7.28–7.32 (m, 1H), 7.50 (d, *J* = 8.2 Hz, 1H), 7.66 (d, *J* = 8.2 Hz, 2H), 7.70 (d, *J* = 7.8 Hz, 1H), 8.52 (d, *J* = 8.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.60, 48.84, 111.96, 121.32, 122.35, 124.24 (q, *J* = 270.8 Hz), 124.86, 125.14 (q, *J* = 3.8 Hz), 125.78, 127.59, 129.09 (q, *J* = 32.4 Hz), 129.21, 134.36, 147.59, 153.53; ^{19}F NMR (373 MHz, $CDCl_3$) δ –62.47; HRMS *m/z* (M^+) calcd for $C_{19}H_{18}F_3NO$: 333.1340, found: 333.1338.

2-(4-Chlorophenyl)-*N,N*-diethylbenzofuran-3-amine (3da); oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.04 (t, *J* = 7.3 Hz, 6H), 3.25 (q, *J* = 7.3 Hz, 4H), 7.17 (t, *J* = 7.3 Hz, 1H), 7.26 (t, *J* = 7.8 Hz, 1H), 7.38 (dt, *J* = 8.8, 2.2 Hz, 2H), 7.47 (d, *J* = 8.1 Hz, 1H), 7.67 (d, *J* = 7.3 Hz, 1H), 8.35 (dt, *J* = 8.8, 2.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.61, 48.82, 111.77, 121.03, 122.18, 124.31, 127.12, 127.50, 127.69, 128.40, 129.57, 133.31, 148.24, 153.27; HRMS *m/z* (M^+) calcd for $C_{18}H_{18}ClNO$: 299.1077, found: 299.1070.

***N,N*-Diethyl-2-(3-thienyl)benzofuran-3-amine (3ea)**; oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.04 (t, *J* =

7.3 Hz, 6H), 3.24 (q, *J* = 7.3 Hz, 4H), 7.15 (t, *J* = 7.3 Hz, 1H), 7.21–7.25 (m, 1H), 7.34 (dd, *J* = 5.0, 3.2 Hz, 1H), 7.45 (d, *J* = 7.8 Hz, 1H), 7.64 (d, *J* = 7.8 Hz, 1H), 7.99 (d, *J* = 5.0 Hz, 1H), 8.05 (d, *J* = 3.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.75, 48.83, 111.66, 120.74, 122.06, 122.07, 123.78, 125.07, 125.35, 126.12, 127.53, 132.00, 147.92, 153.33; HRMS *m/z* (M^+) calcd for $C_{16}H_{17}NOS$: 271.1031, found: 271.1032.

2-(1-Cyclohexen-1-yl)-*N*,*N*-diethylbenzofuran-3-amine (3fa); oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.01 (t, *J* = 7.3 Hz, 6H), 1.59–1.69 (m, 2H), 1.71–1.77 (m, 2H), 2.2.4–2.27 (m, 2H), 2.64–2.66 (m, 2H), 3.15 (q, *J* = 7.3 Hz, 4H), 6.67–6.70 (m, 1H), 7.09 (t, *J* = 8.0 Hz, 1H), 7.17 (t, *J* = 8.4 Hz, 1H), 7.36 (d, *J* = 8.4 Hz, 1H), 7.58 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.79, 22.11, 22.65, 25.64, 25.71, 48.73, 111.29, 120.61, 121.56, 123.31, 125.15, 127.56, 128.01, 128.74, 151.57, 152.77; HRMS *m/z* (M^+) calcd for $C_{18}H_{23}NO$: 269.1780, found: 269.1783.

2-Butyl-*N*,*N*-diethylbenzofuran-3-amine (3ga); oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.95 (t, *J* = 7.3 Hz, 3H), 0.97 (t, *J* = 7.3 Hz, 6H), 1.38–1.44 (m, 2H), 1.60–1.73 (m, 2H), 2.76 (t, *J* = 7.3 Hz, 2H), 3.12 (q, *J* = 7.3 Hz, 4H), 7.11 (td, *J* = 7.3, 1.4 Hz, 1H), 7.17 (td, *J* = 7.3, 1.4 Hz, 1H), 7.38 (d, *J* = 7.8 Hz, 1H), 7.56 (d, *J* = 6.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.92, 14.06, 22.63, 25.42, 30.18, 49.28, 111.31, 119.92, 121.59, 122.69, 124.15, 126.80, 153.45, 155.78; HRMS *m/z* (M^+) calcd for $C_{16}H_{23}NO$: 245.1780, found: 245.1782.

2-Cyclohexyl-*N*,*N*-diethylbenzofuran-3-amine (3ha); oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.96 (t, *J* = 7.3 Hz, 6H), 1.26–1.44 (m, 4H), 1.65–1.85 (m, 6H), 3.01 (tt, *J* = 11.4, 3.6 Hz, 1H), 3.12 (q, *J* = 7.3 Hz, 4H), 7.10 (td, *J* = 7.3, 0.9 Hz, 1H), 7.17 (td, *J* = 7.3, 1.3 Hz, 1H), 7.38 (d, *J* = 8.0 Hz, 1H), 7.56 (d, *J* = 7.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.14, 25.98, 26.35, 31.22, 34.89, 49.39, 111.41, 120.04, 121.50, 122.18, 122.64, 126.55, 153.41, 159.70; HRMS *m/z* (M^+) calcd for $C_{18}H_{25}NO$: 271.1936, found: 271.1935.

2-(*tert*-Butyl)-*N*,*N*-diethylbenzofuran-3-amine (3ia); oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.04 (t, *J* = 7.3 Hz, 6H), 1.44 (s, 9H), 3.12 (bs, 4H), 7.09 (t, *J* = 7.3 Hz, 1H), 7.16 (t, *J* = 7.3 Hz, 1H), 7.36 (d, *J* = 7.8 Hz, 1H), 7.57 (d, *J* = 7.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.09, 29.59, 34.03, 48.90, 111.26, 120.79, 121.27, 122.74, 124.45, 127.62, 152.63, 160.06; HRMS *m/z* (M^+) calcd for $C_{16}H_{23}NO$: 245.1780, found: 245.1782.

2-Butyl-5,7-dichloro-*N,N*-diethylbenzofuran-3-amine (3ja); oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.96 (t, *J* = 7.3 Hz, 9H), 1.38–1.47 (m, 2H), 1.67–1.74 (m, 2H), 2.77 (t, *J* = 7.7 Hz, 2H), 3.07 (q, *J* = 7.3 Hz, 4H), 7.19 (d, *J* = 2.2 Hz, 1H), 7.42 (d, *J* = 2.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.84, 13.94, 22.63, 25.58, 29.99, 49.06, 117.30, 118.05, 122.92, 124.75, 127.49, 129.48, 147.68, 158.56; HRMS *m/z* (M^+) calcd for $C_{16}H_{21}Cl_2NO$: 313.1000, found: 313.1002.

5,7-Di-*tert*-butyl-2-butyl-*N,N*-diethylbenzofuran-3-amine (3ka); oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.94 (t, *J* = 7.3 Hz, 3H), 0.99 (t, *J* = 7.3 Hz, 6H), 1.37 (s, 9H), 1.40–1.44 (m, 2H), 1.50 (s, 9H), 1.66–1.70 (m, 2H), 2.76 (t, *J* = 7.3 Hz, 2H), 3.13 (q, *J* = 7.3 Hz, 4H), 7.15 (d, *J* = 1.8 Hz, 1H), 7.39 (d, *J* = 1.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.94, 14.27, 22.46, 25.42, 29.95, 30.26, 31.96, 34.32, 34.71, 49.16, 113.88, 117.46, 124.10, 126.79, 133.45, 144.03, 149.81, 154.53; HRMS *m/z* (M^+) calcd for $C_{24}H_{39}NO$: 357.3032, found: 357.3027.

***N,N*-Diallyl-2-butylbenzofuran-3-amine (3gb)**; oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.95 (t, *J* = 7.3 Hz, 3H), 1.29–1.43 (m, 2H), 1.64–1.72 (m, 2H), 2.76 (t, *J* = 7.3 Hz, 2H), 3.69 (d, *J* = 6.6 Hz, 4H), 5.00–5.03 (m, 2H), 5.07–5.13 (m, 2H), 5.83 (ddt, *J* = 16.5, 10.2, 6.2 Hz, 2H), 7.12–7.18 (m, 2H), 7.34–7.36 (m, 1H), 7.55–7.57 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.88, 22.52, 25.65, 30.15, 57.33, 111.23, 116.80, 119.67, 121.75, 122.75, 126.10, 127.19, 135.96, 153.18, 154.34; HRMS *m/z* (M^+) calcd for $C_{18}H_{23}NO$: 269.1780, found: 269.1781.

***N*-Benzyl-2-butyl-*N*-methylbenzofuran-3-amine (3gc)**; oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.91 (t, *J* = 7.3 Hz, 3H), 1.26–1.38 (m, 2H), 1.51–1.59 (m, 2H), 2.68 (t, *J* = 7.7 Hz, 2H), 2.83 (s, 3H), 4.21 (s, 2H), 7.14–7.37 (m, 8H), 7.62–7.64 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.82, 22.48, 25.75, 30.18, 42.32, 61.28, 111.31, 119.67, 121.74, 122.85, 126.75, 127.03, 128.03, 128.17, 128.75, 139.15, 152.81, 153.23; HRMS *m/z* (M^+) calcd for $C_{20}H_{23}NO$: 293.1780, found: 293.1775.

1-(2-Butylbenzofuran-3-yl)piperidine (3gd); oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.94 (t, *J* = 7.3 Hz, 3H), 1.35–1.43 (m, 2H), 1.58–1.60 (m, 2H), 1.64–1.70 (m, 6H), 2.79 (t, *J* = 7.3 Hz, 2H), 3.08–3.11 (m, 4H), 7.11–7.18 (m, 2H), 7.34 (d, *J* = 7.3 Hz, 1H), 7.60 (d, *J* = 7.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.81, 22.30, 24.36, 25.95, 26.86, 30.51, 53.72, 111.13, 119.82, 121.58, 122.71, 126.99, 129.30, 151.17, 153.13; HRMS *m/z* (M^+) calcd for $C_{17}H_{23}NO$: 257.1780, found: 257.1777.

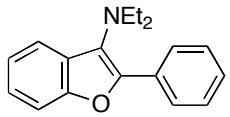
4-(2-Butylbenzofuran-3-yl)morpholine (3ge); oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.95 (t, *J* = 7.3 Hz, 3H), 1.38 (tq, *J* = 7.3, 7.4 Hz, 2H), 1.65 (tt, *J* = 7.3, 7.4 Hz, 2H), 2.80 (t, *J* = 7.3 Hz, 2H), 3.15 (t, *J* = 4.6 Hz, 4H), 3.85 (t, *J* = 4.6 Hz, 4H), 7.14–7.21 (m, 2H), 7.37 (d, *J* = 7.8 Hz, 1H), 7.62 (d, *J* = 8.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.78, 22.29, 25.70, 30.36, 52.60, 67.75, 111.35, 119.59, 121.88, 123.02, 126.38, 127.92, 152.43, 153.19; HRMS *m/z* (M^+) calcd for $C_{16}H_{21}NO_2$: 259.1572, found: 259.1573.

2-(2-Butylbenzofuran-3-yl)-1,2,3,4-tetrahydroisoquinoline (3gf); oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.92 (t, *J* = 7.3 Hz, 3H), 1.34–1.40 (m, 2H), 1.67–1.71 (m, 2H), 2.80 (t, *J* = 7.3 Hz, 2H), 3.01 (bs, 2H), 3.47 (bs, 2H), 4.34 (s, 2H), 7.04–7.06 (m, 1H), 7.13–7.23 (m, 5H), 7.39 (d, *J* = 7.8 Hz, 1H), 7.55 (d, *J* = 7.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.82, 22.32, 25.75, 30.10, 30.40, 50.38, 54.52, 111.33, 119.61, 121.85, 122.97, 125.72, 126.11, 126.31, 126.62, 128.05, 129.05, 134.58, 135.38, 152.45, 153.27; HRMS *m/z* (M^+) calcd for $C_{21}H_{23}NO$: 305.1780, found: 305.1778.

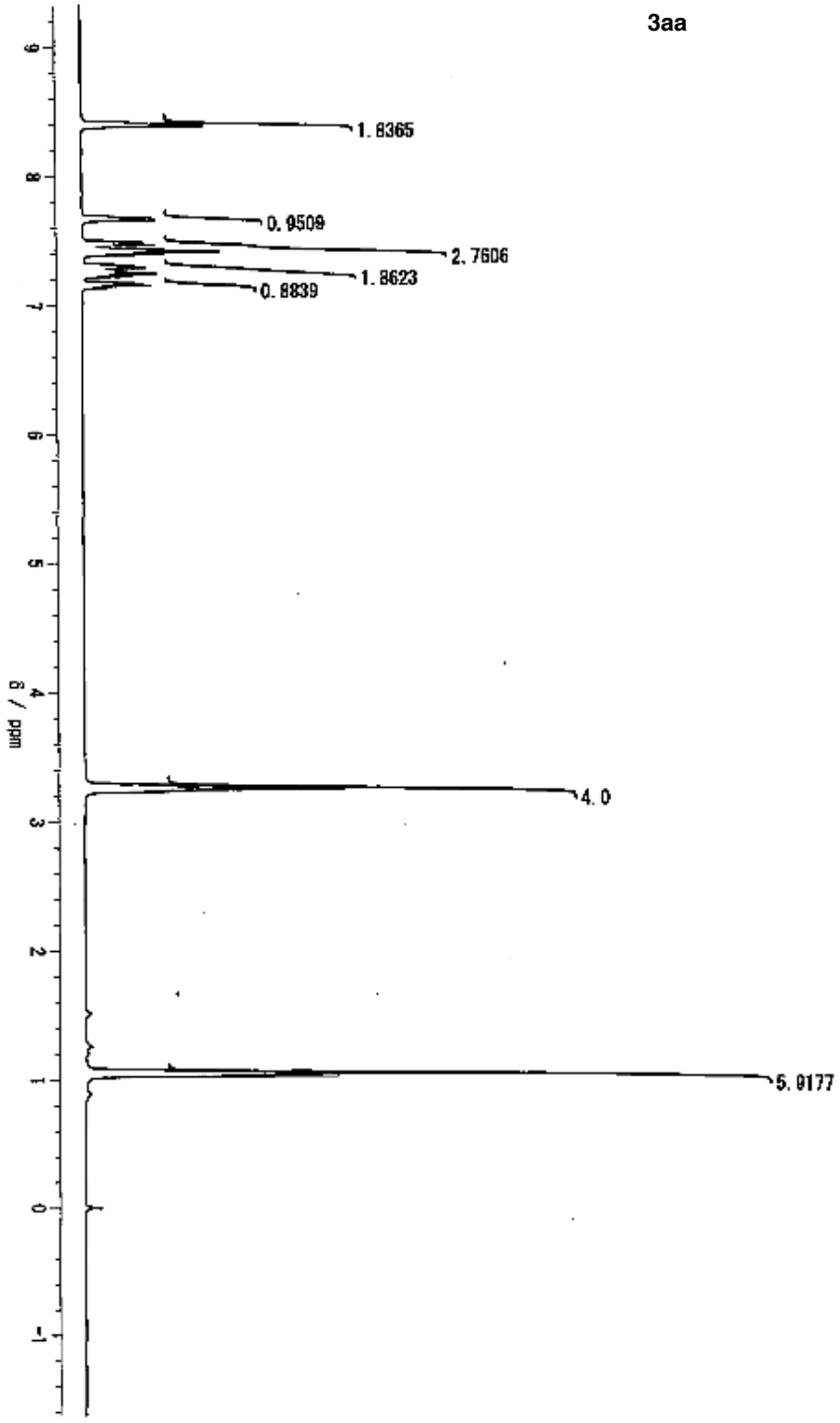
***N*-Allyl-*N*-methyl-2-(1-propen-2-yl)benzofuran-3-amine (3lg)**; oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.25 (s, 3H), 2.84 (s, 3H), 3.74 (d, *J* = 6.2 Hz, 2H), 5.09 (dd, *J* = 10.2, 1.4 Hz, 1H), 5.17–5.20 (m, 1H), 5.20 (s, 1H), 5.81 (s, 1H), 5.88 (ddt, *J* = 17.0, 10.2, 6.2 Hz, 1H), 7.15 (t, *J* = 7.3 Hz, 1H), 7.23 (t, *J* = 7.3 Hz, 1H), 7.39 (d, *J* = 8.2 Hz, 1H), 7.66 (d, *J* = 8.2 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 20.47, 41.45, 59.64, 111.57, 114.94, 117.06, 120.76, 121.87, 124.08, 127.29, 130.04, 134.25, 135.74, 148.64, 152.72; HRMS *m/z* (M^+) calcd for $C_{15}H_{17}NO$: 227.1310, found: 227.1307.

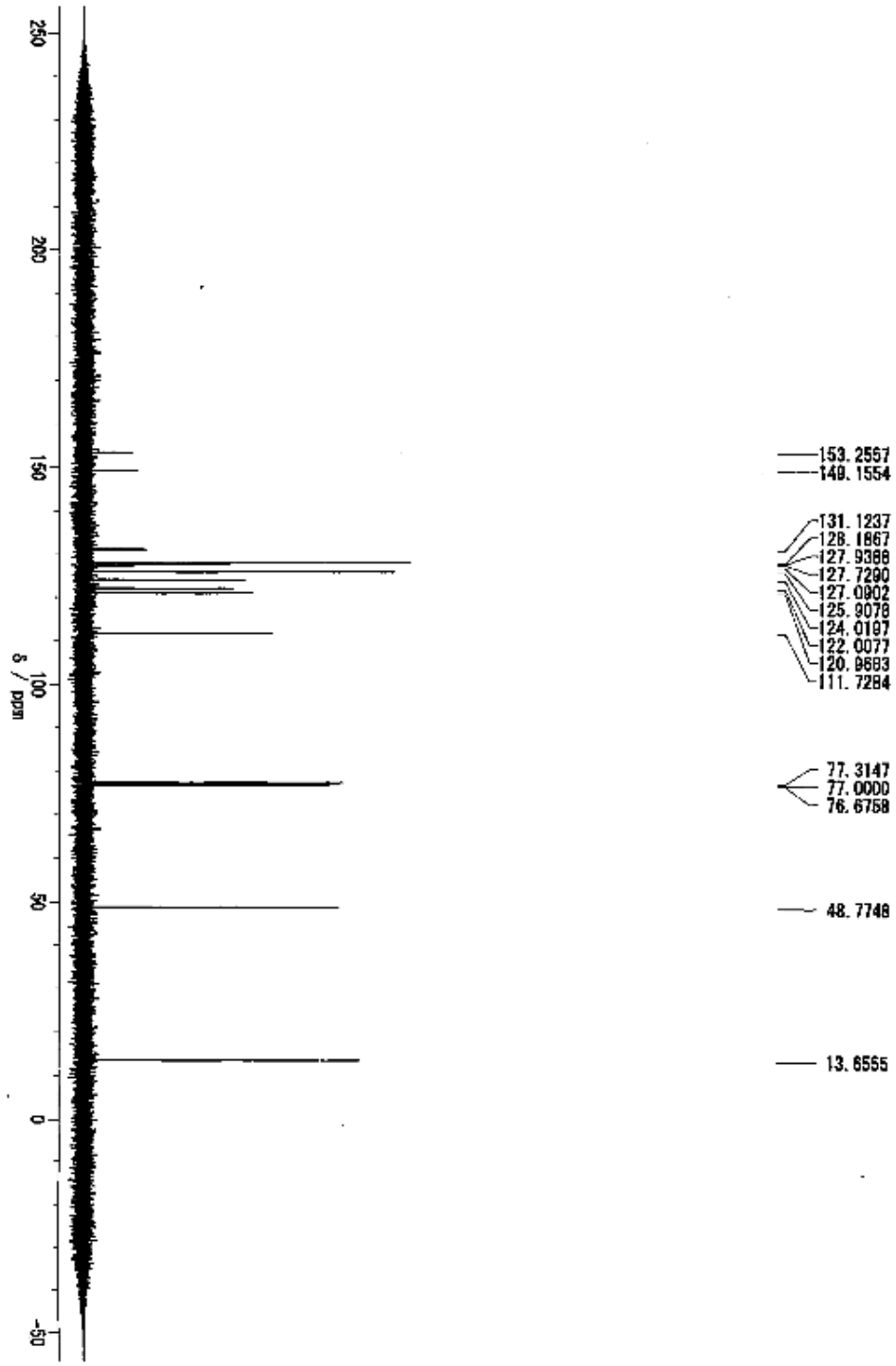
1,3,5-Trimethyl-2,3-dihydro-1*H*-benzofuro[3,2-*b*]azepine (4); oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.22 (d, *J* = 7.4 Hz, 3H), 2.22 (t, *J* = 1.8 Hz, 3H), 2.38–2.50 (m, 1H), 2.58 (dd, *J* = 13.3, 7.8 Hz, 1H), 2.99 (s, 3H), 3.12 (dt, *J* = 13.3, 1.4 Hz, 1H), 5.55–5.56 (m, 1H), 7.17 (td, *J* = 6.8, 0.9 Hz, 1H), 7.23 (td, *J* = 7.8, 1.4 Hz, 1H), 7.38 (d, *J* = 7.8 Hz, 1H), 7.63 (d, *J* = 8.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.38, 20.55, 32.03, 43.58, 59.63, 111.38, 119.58, 121.66, 124.12, 125.93, 130.36, 132.51, 141.96, 152.83 (One sp^2 ^{13}C signal was overlapped by other one.); HRMS *m/z* (M^+) calcd for $C_{15}H_{17}NO$: 227.1310, found: 227.1308.

[^{1}H and ^{13}C NMR spectra of **3aa**]



3aa

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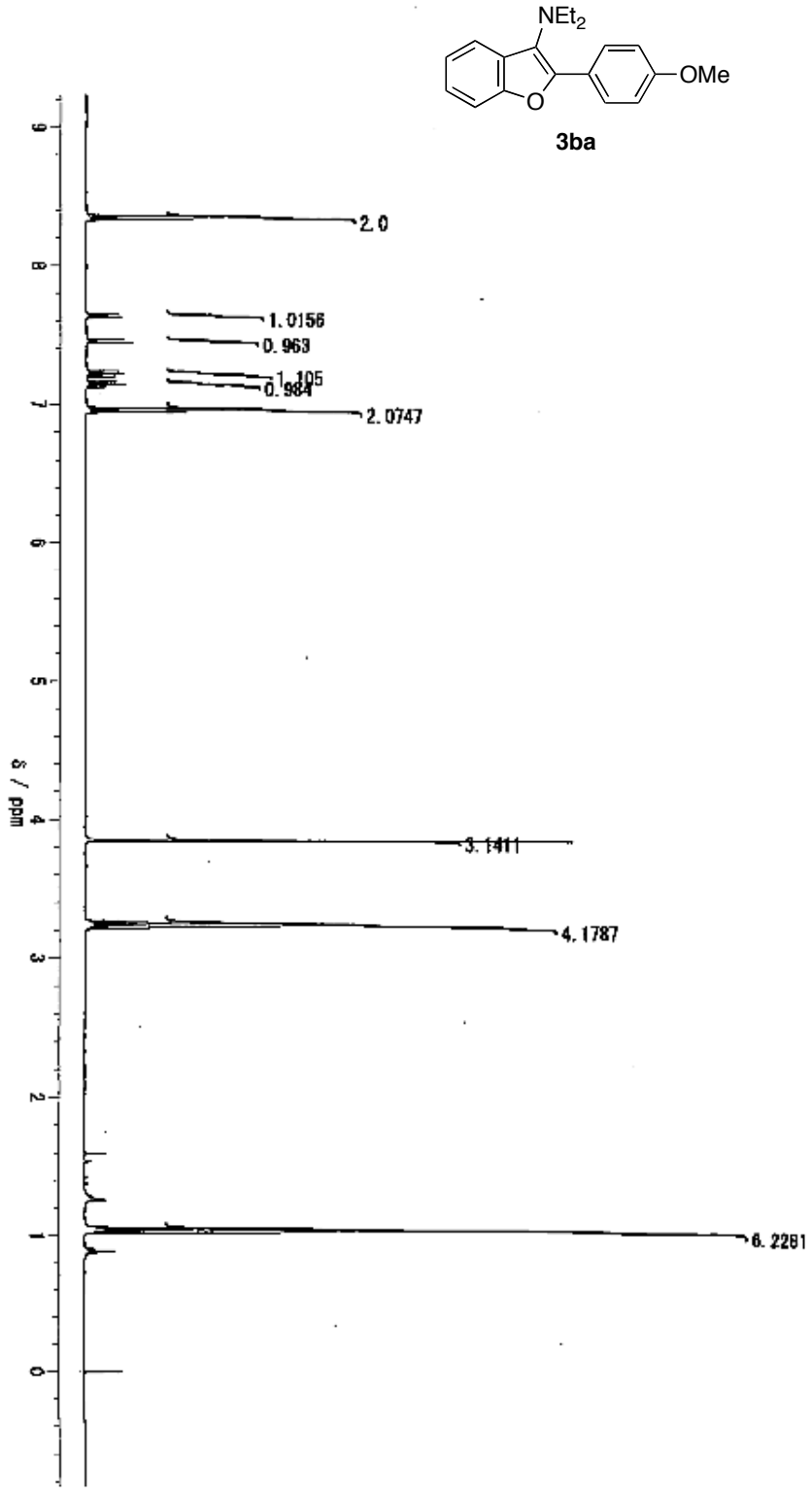
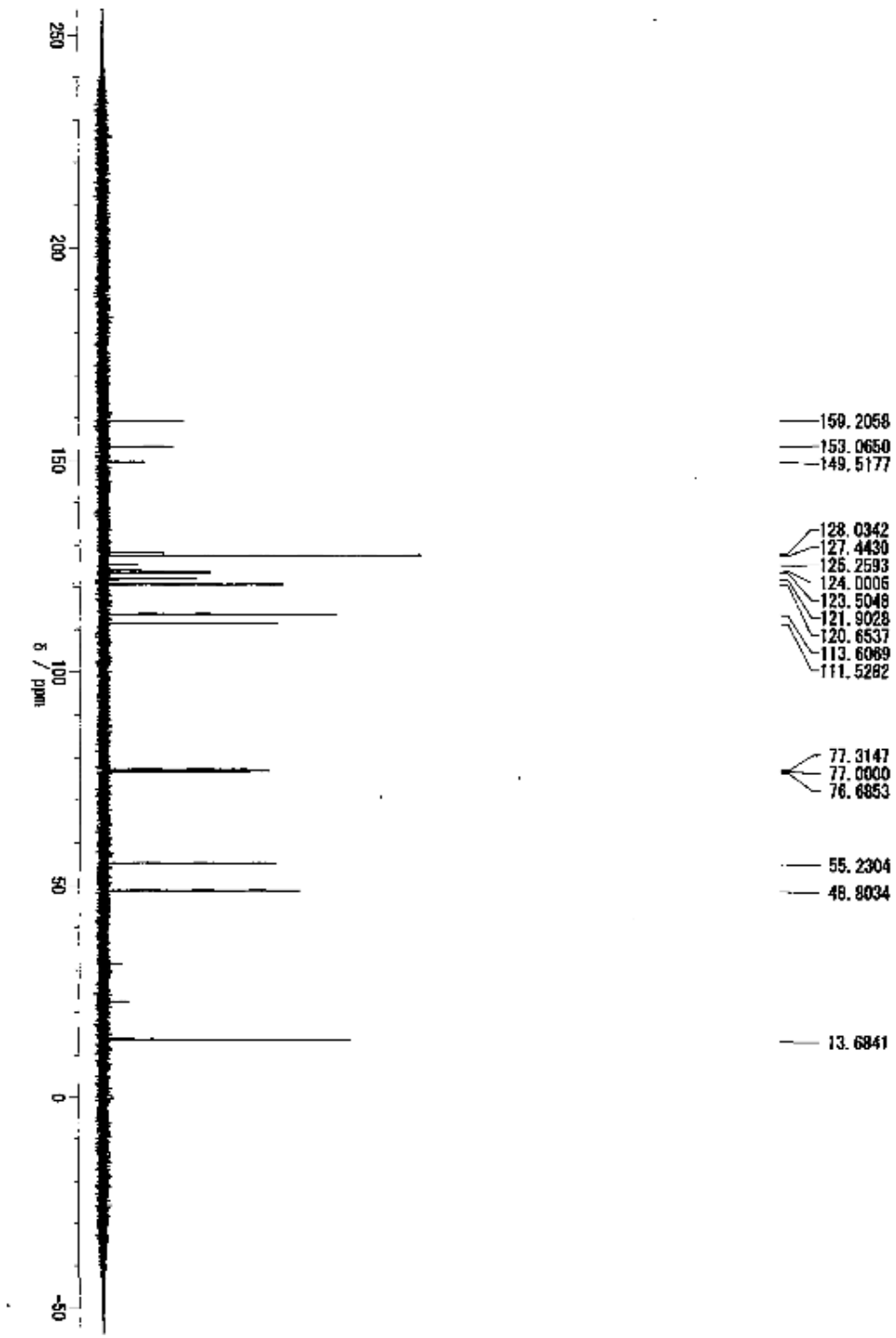
[^{1}H and ^{13}C NMR spectra of **3ba**]

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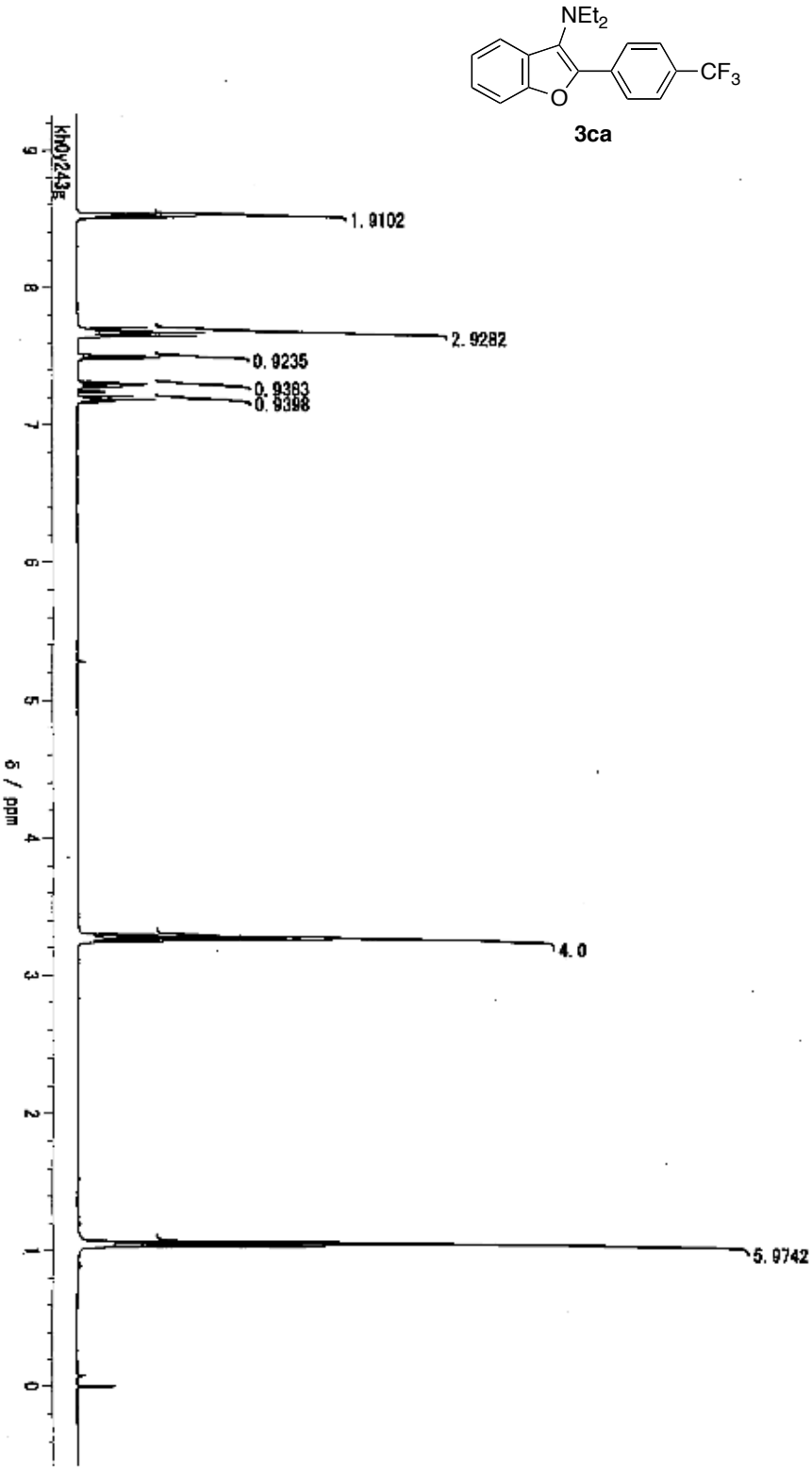
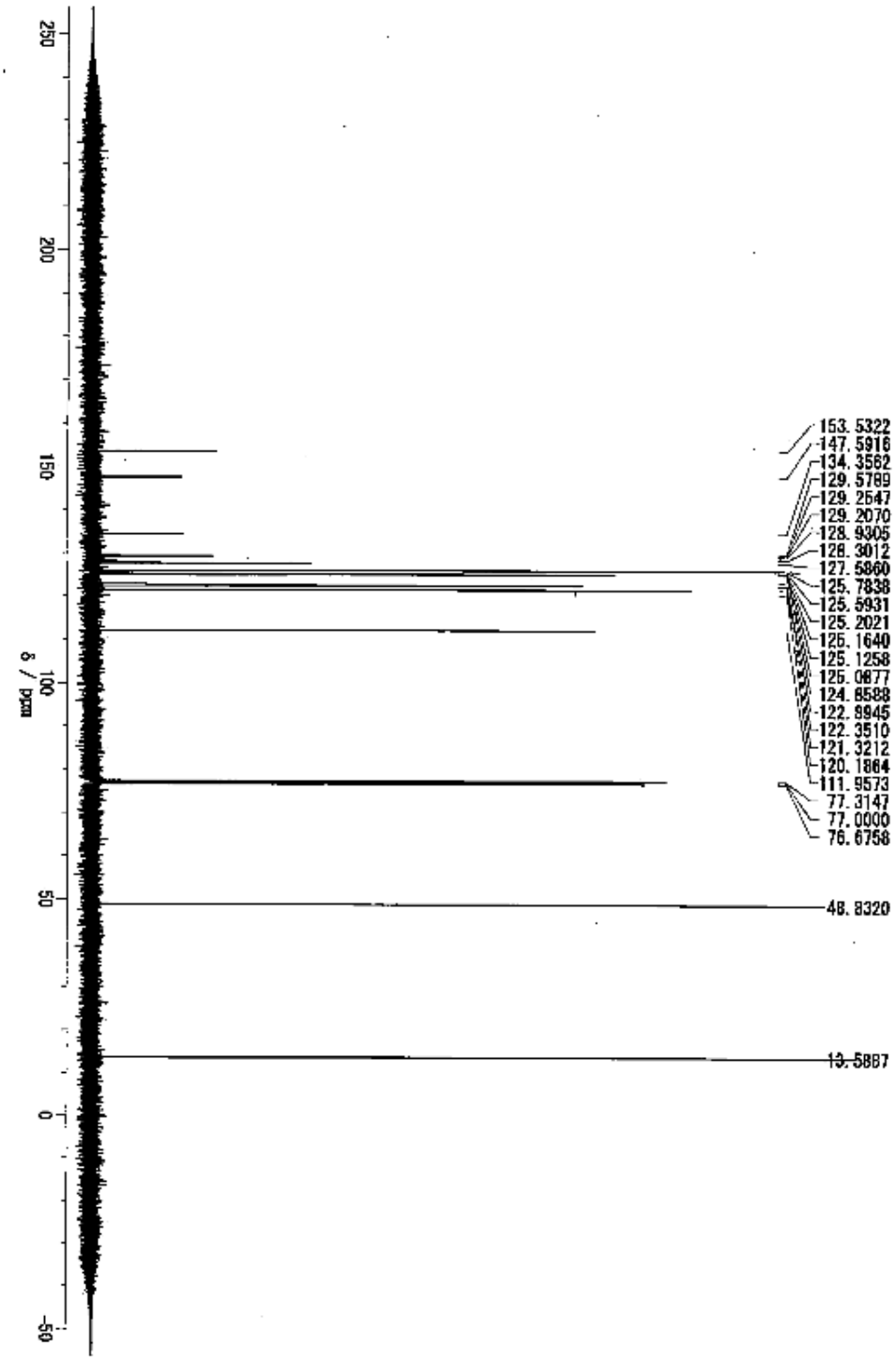
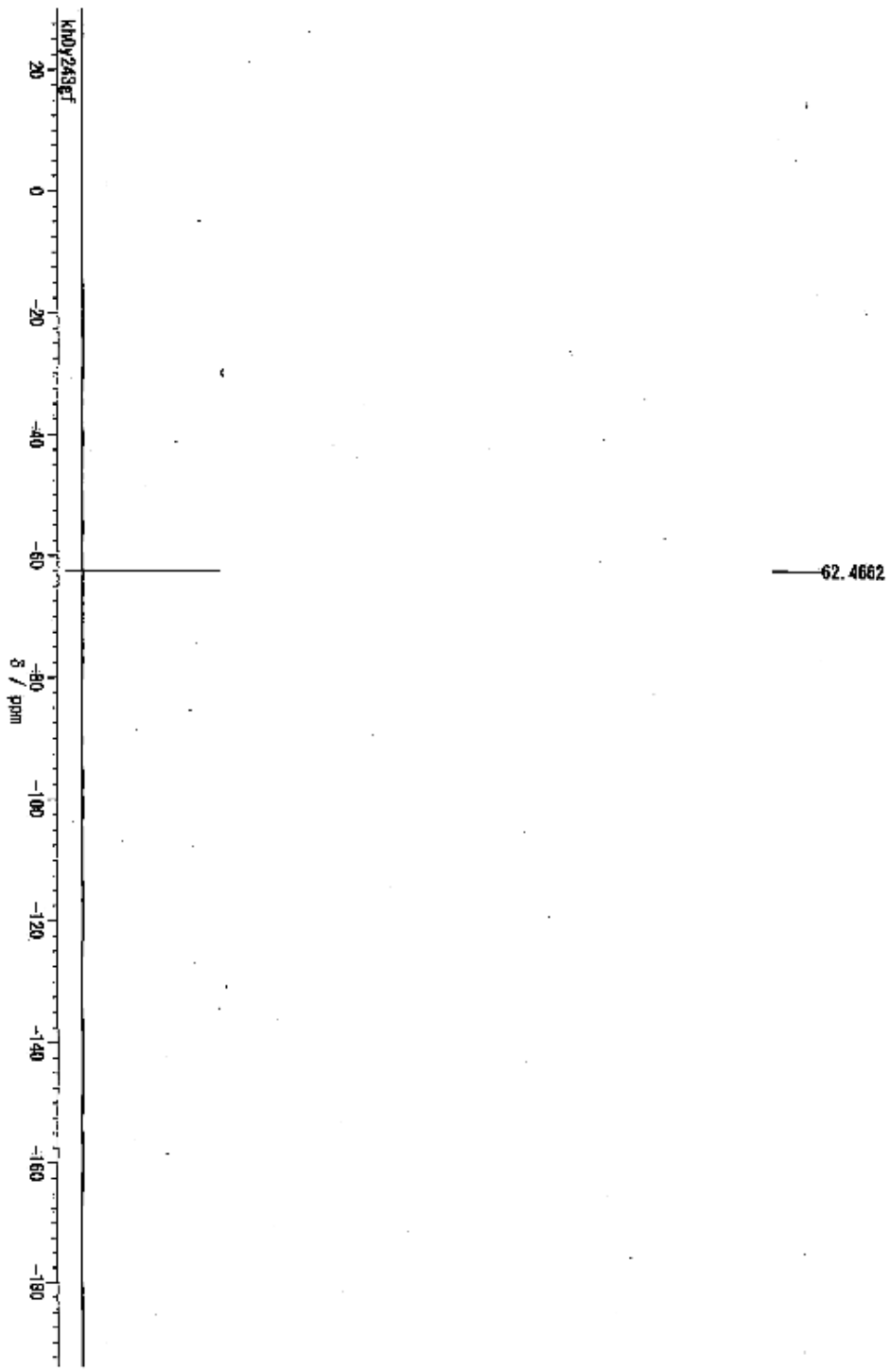
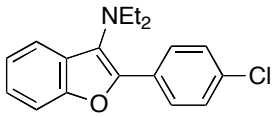
[^{1}H, ^{13}C, and ^{19}F NMR spectra of **3ca**]



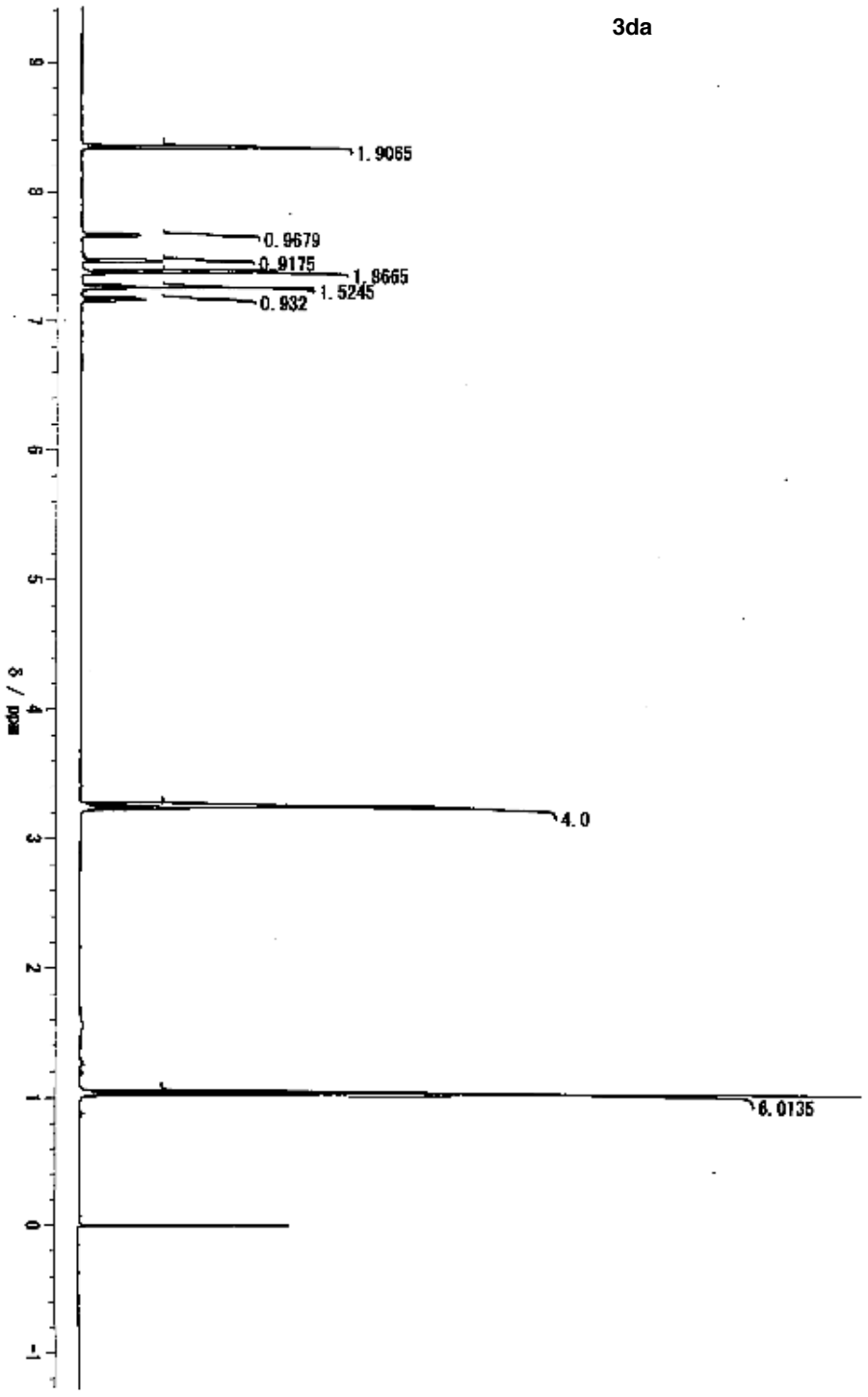

δ / ppm
250
200
150
100
50
0
-50
153.5322
147.5916
134.3562
129.5789
129.2647
129.2070
128.9305
128.3012
127.5860
125.7838
125.5931
125.2021
125.1640
125.1258
125.0877
124.8588
122.9945
122.3510
121.3212
120.1864
111.9573
77.3147
77.0000
76.6758
48.8320
13.5887

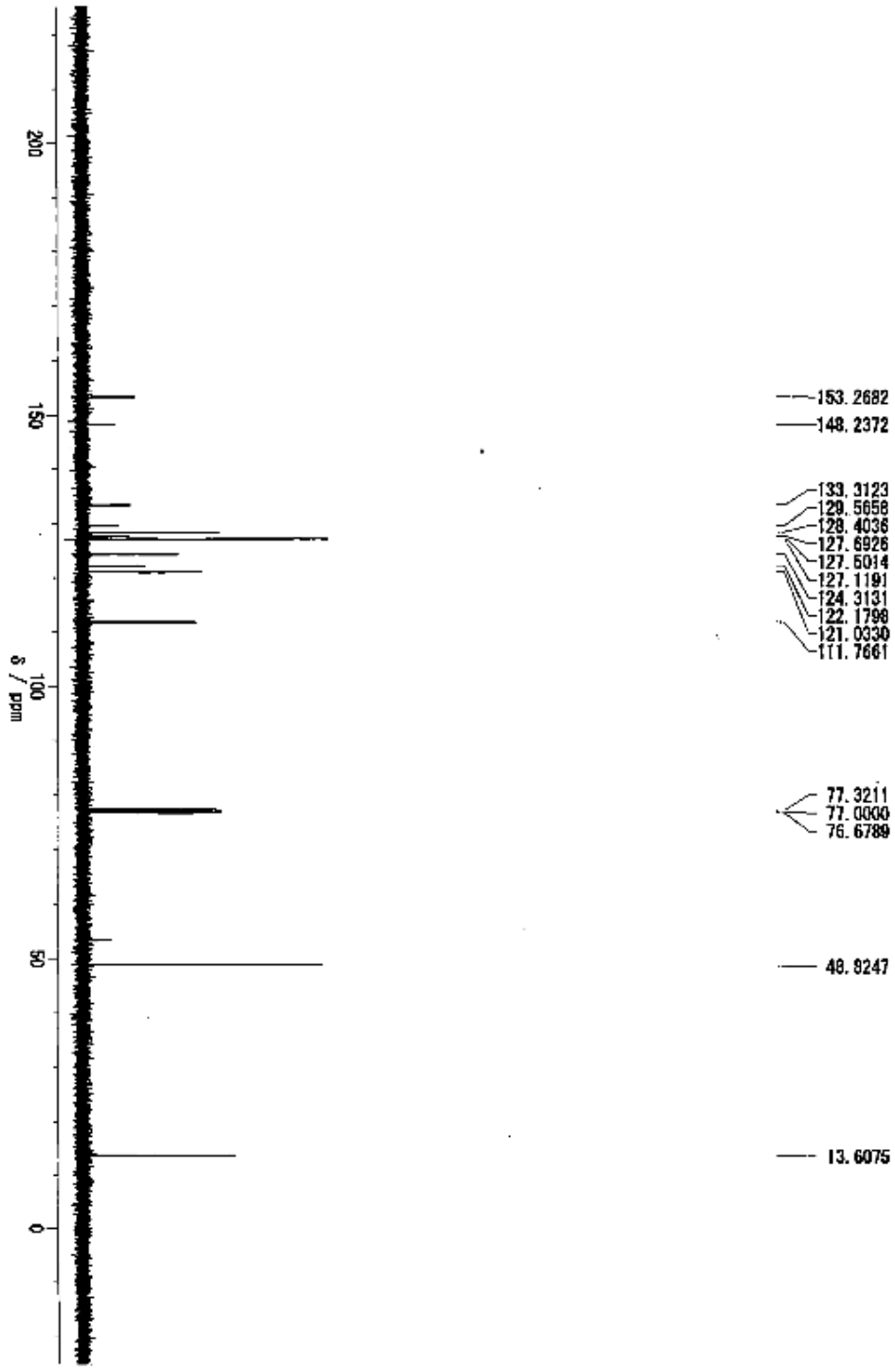

KhDy243gf
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
δ / ppm
62.4662

[^{1}H and ^{13}C NMR spectra of **3da**]

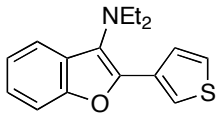


3da

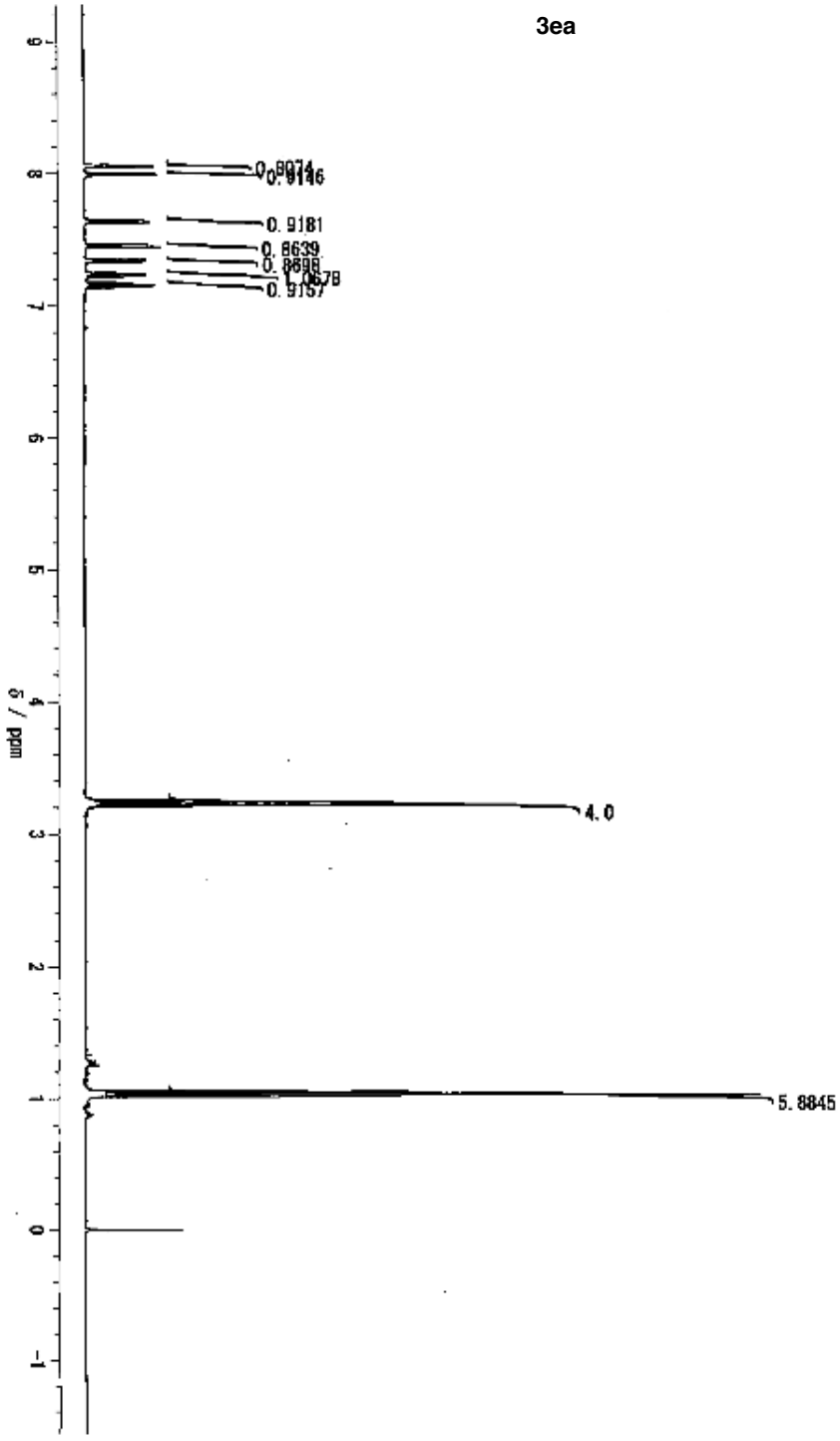


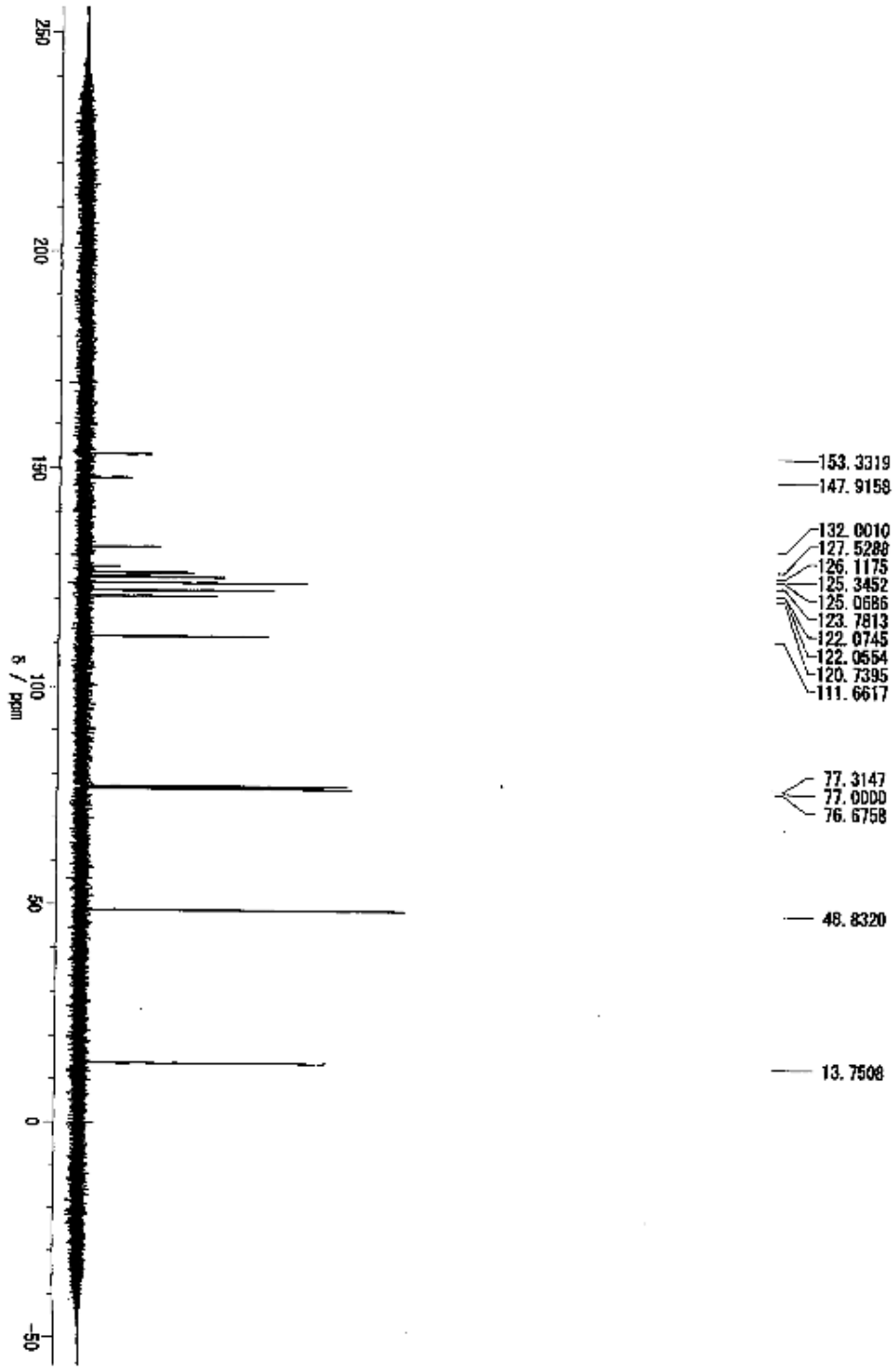

200
150
100
50
0
δ / ppm
153.2682
148.2372
133.3123
129.5658
128.4036
127.6926
127.5014
127.1191
124.3131
122.1798
121.0330
111.7661
77.3211
77.0000
76.6789
48.9247
13.6075

[^{1}H and ^{13}C NMR spectra of **3ea**]

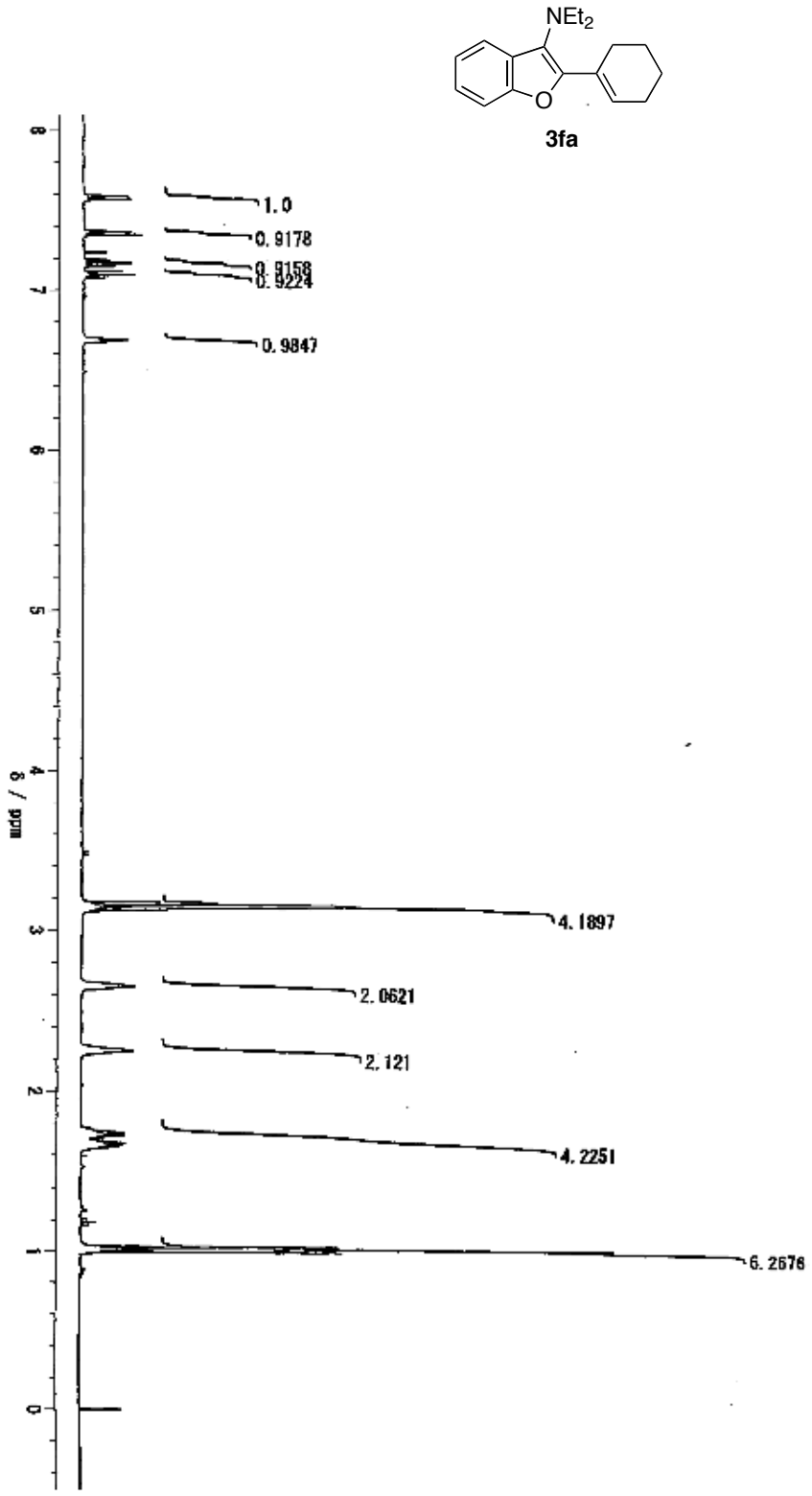


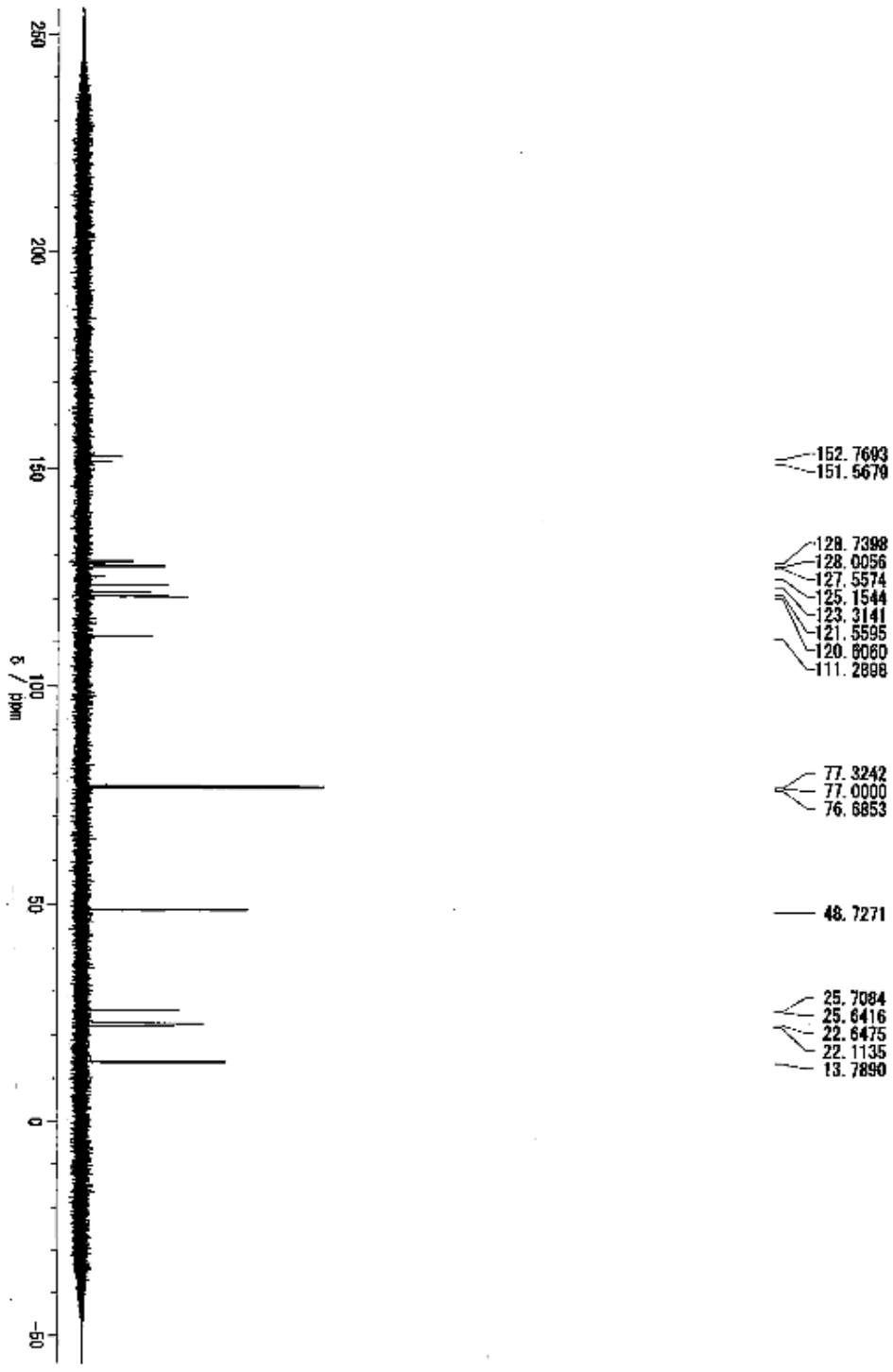
3ea



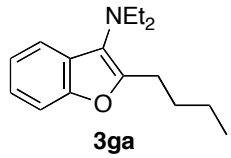

250
200
150
100
50
0
-50
δ / ppm
153.3319
147.9158
132.0010
127.5288
126.1175
125.3452
125.0686
123.7813
122.0745
122.0554
120.7395
111.6617
77.3147
77.0000
76.6758
48.8320
13.7508

[^{1}H and ^{13}C NMR spectra of **3fa**]

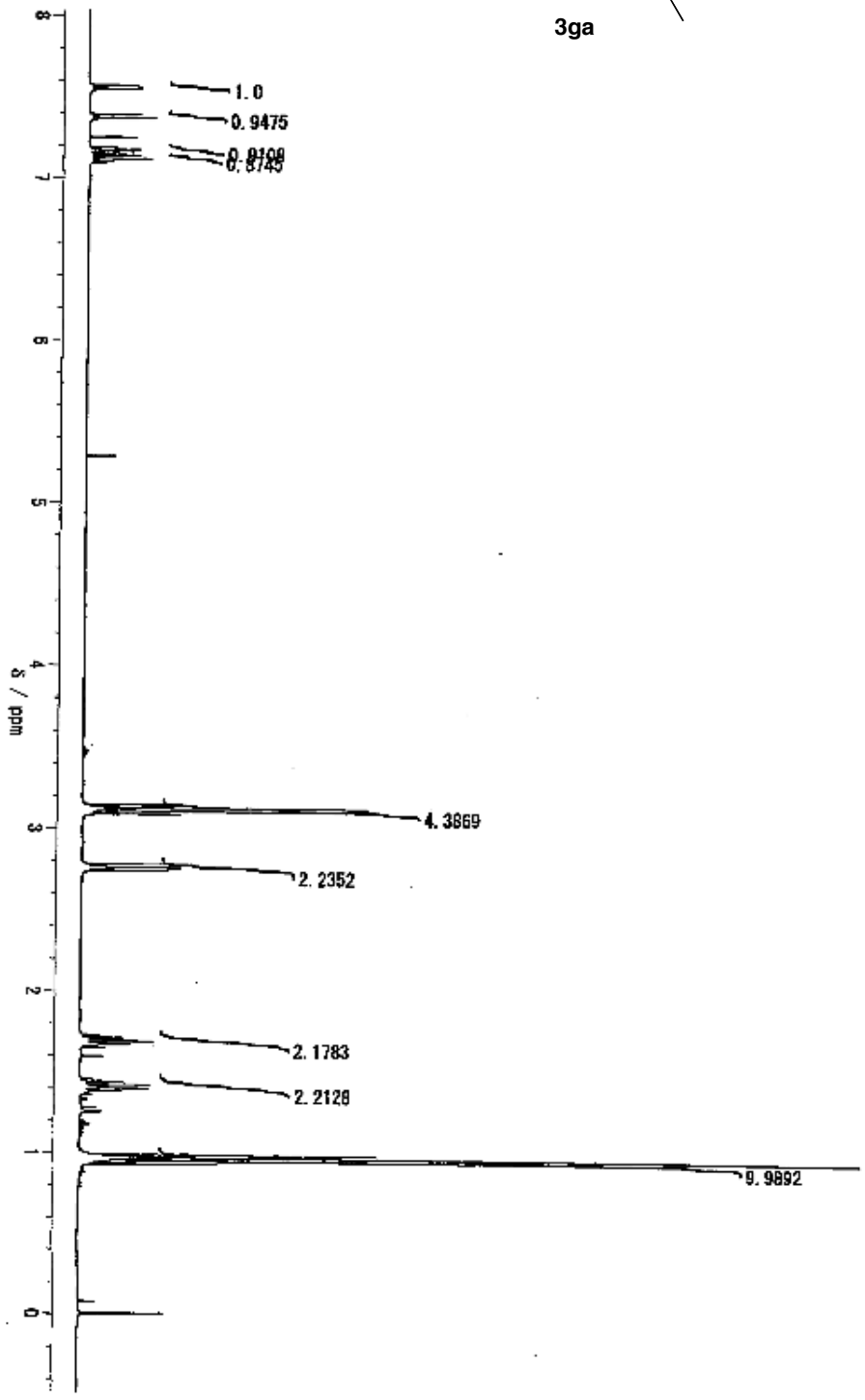


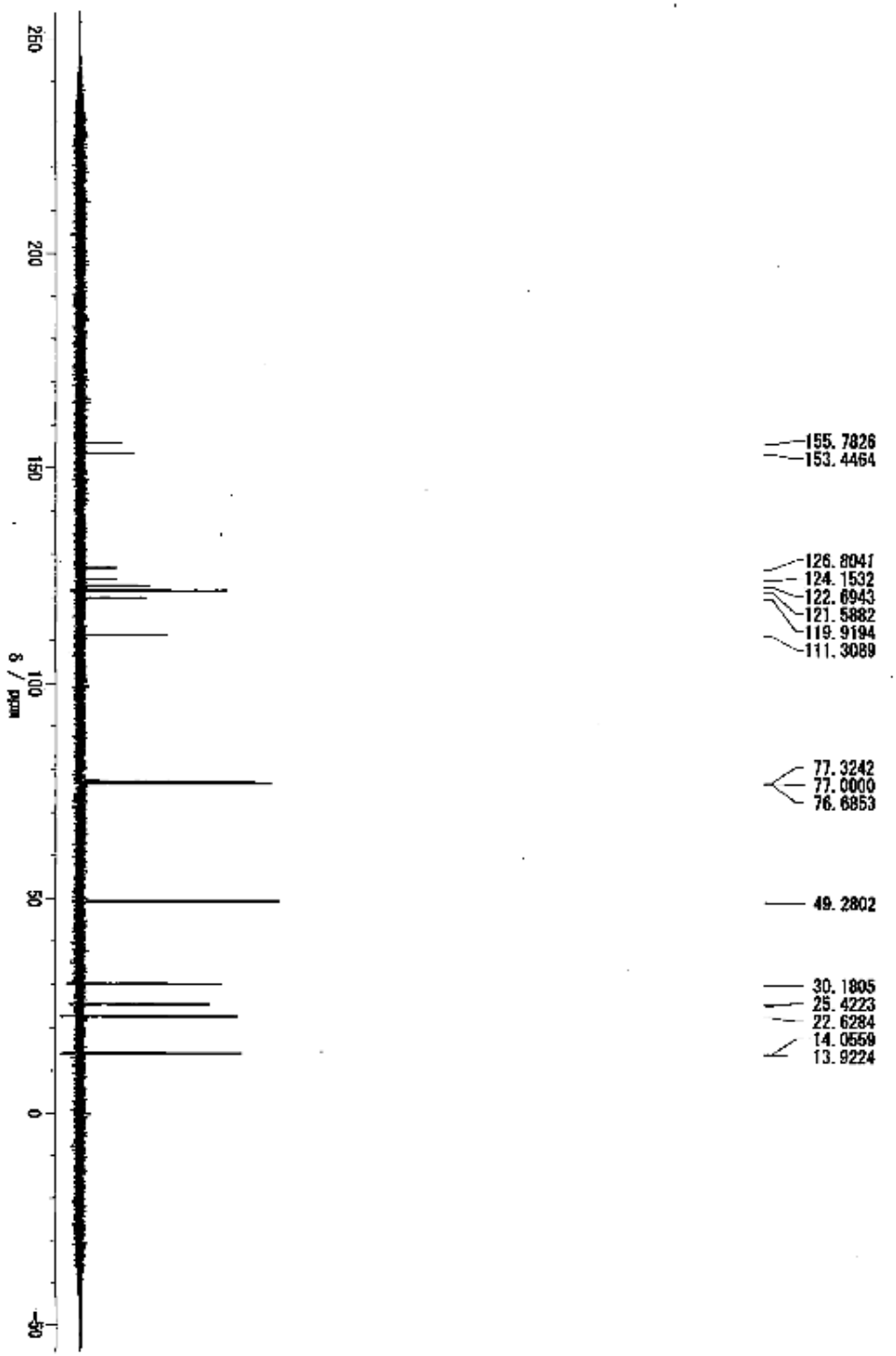

250
200
150
100
50
0
-50
δ / ppm
152.7693
151.5679
128.7398
128.0056
127.5574
125.1544
123.3141
121.5595
120.8060
111.2898
77.3242
77.0000
76.6853
48.7271
25.7084
25.6416
22.6475
22.1135
13.7890

[^{1}H and ^{13}C NMR spectra of **3ga**]

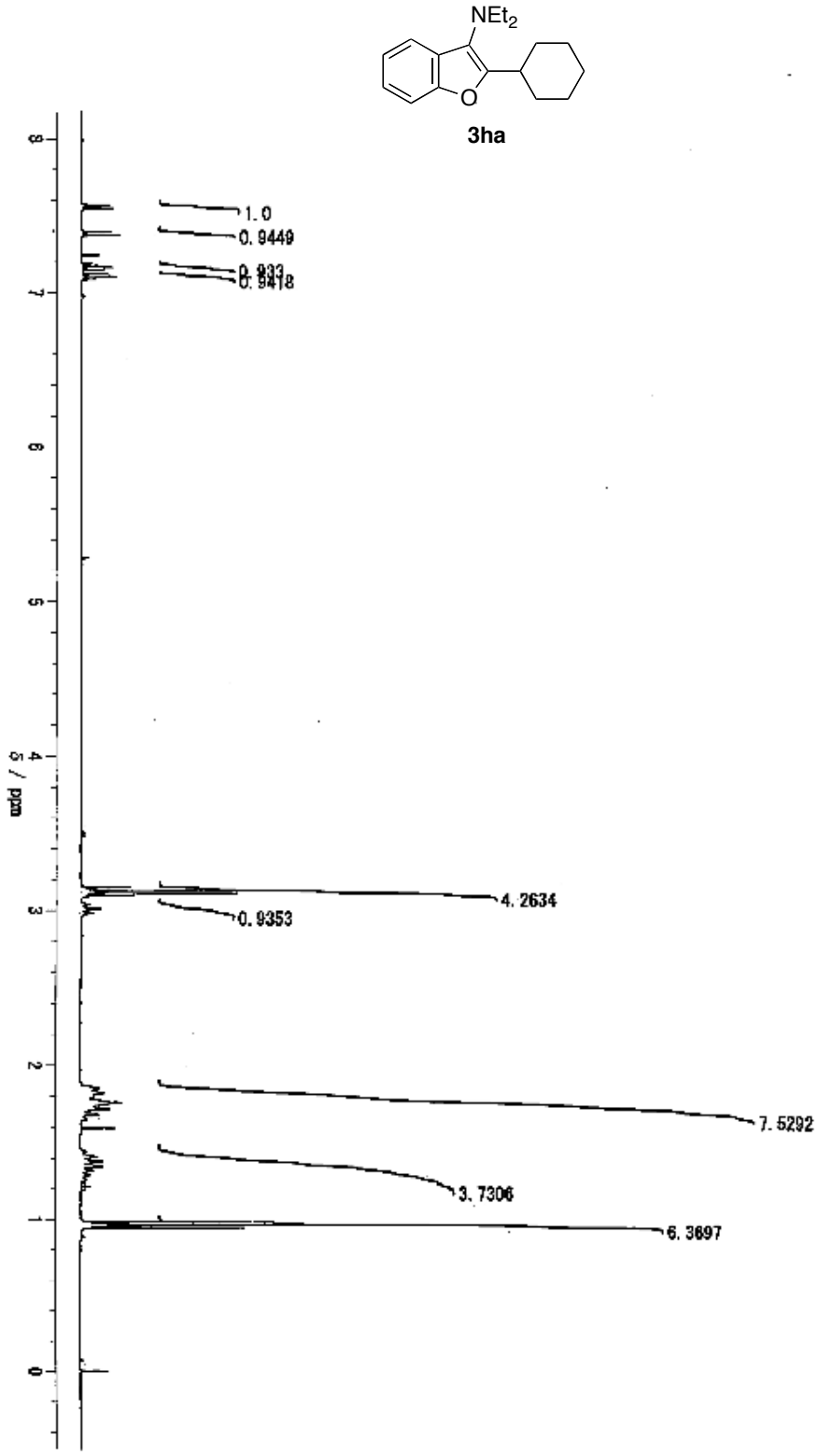


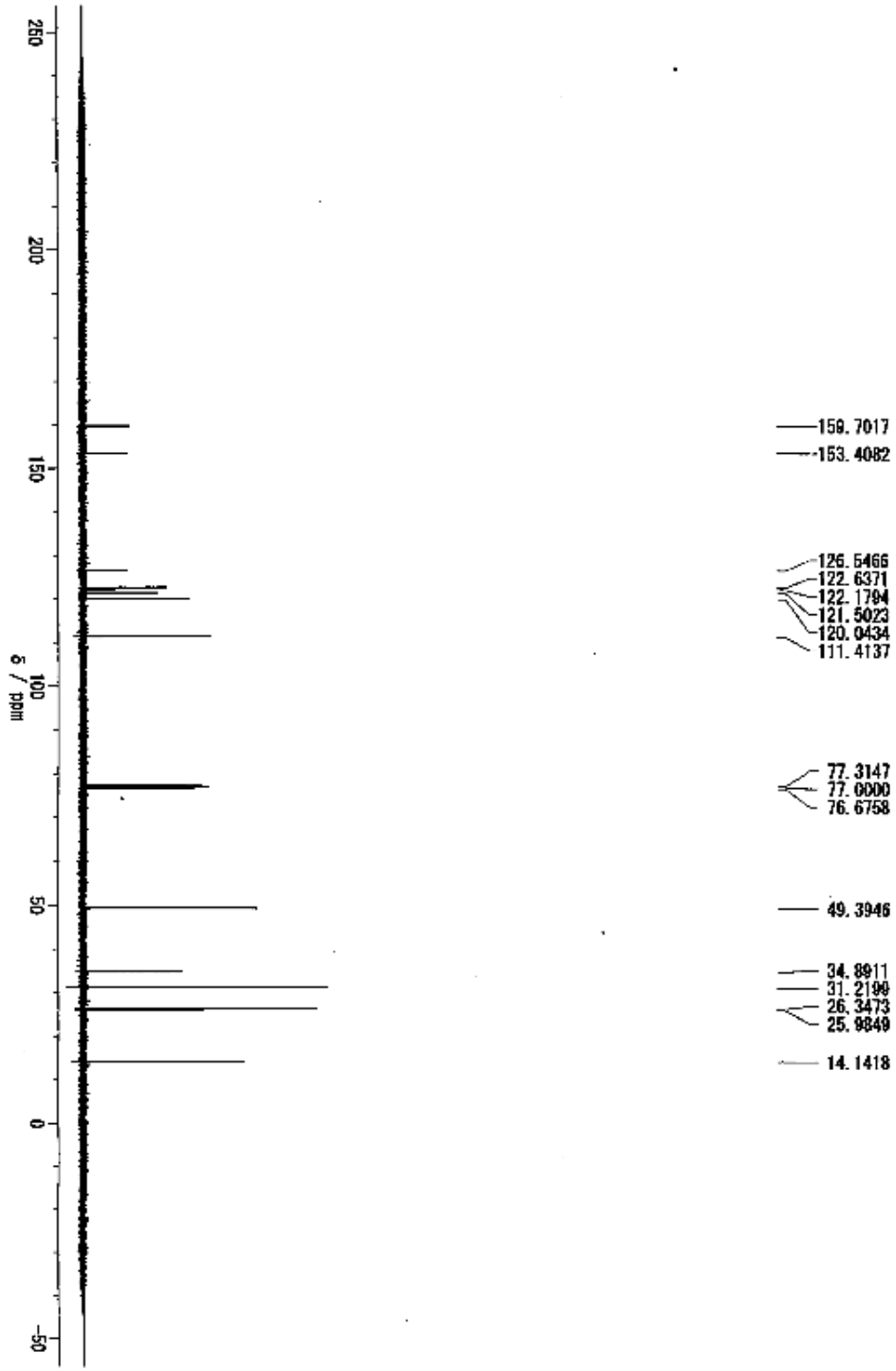
3ga



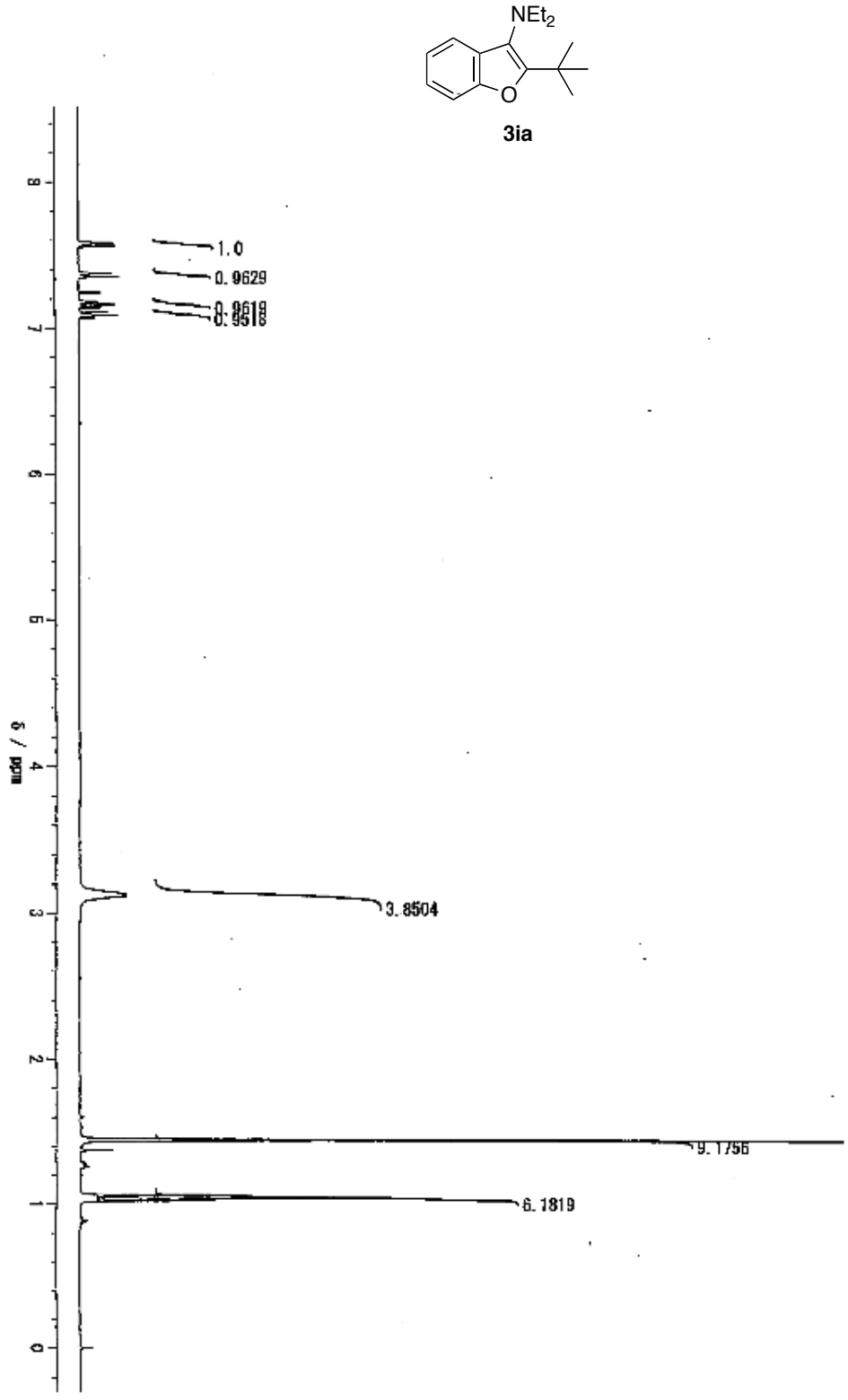

250
200
150
100
50
0
-50
δ / ppm
155.7826
153.4464
126.8041
124.1532
122.6943
121.5882
119.9194
111.3089
77.3242
77.0000
76.6853
49.2802
30.1805
25.4223
22.6284
14.0559
13.9224

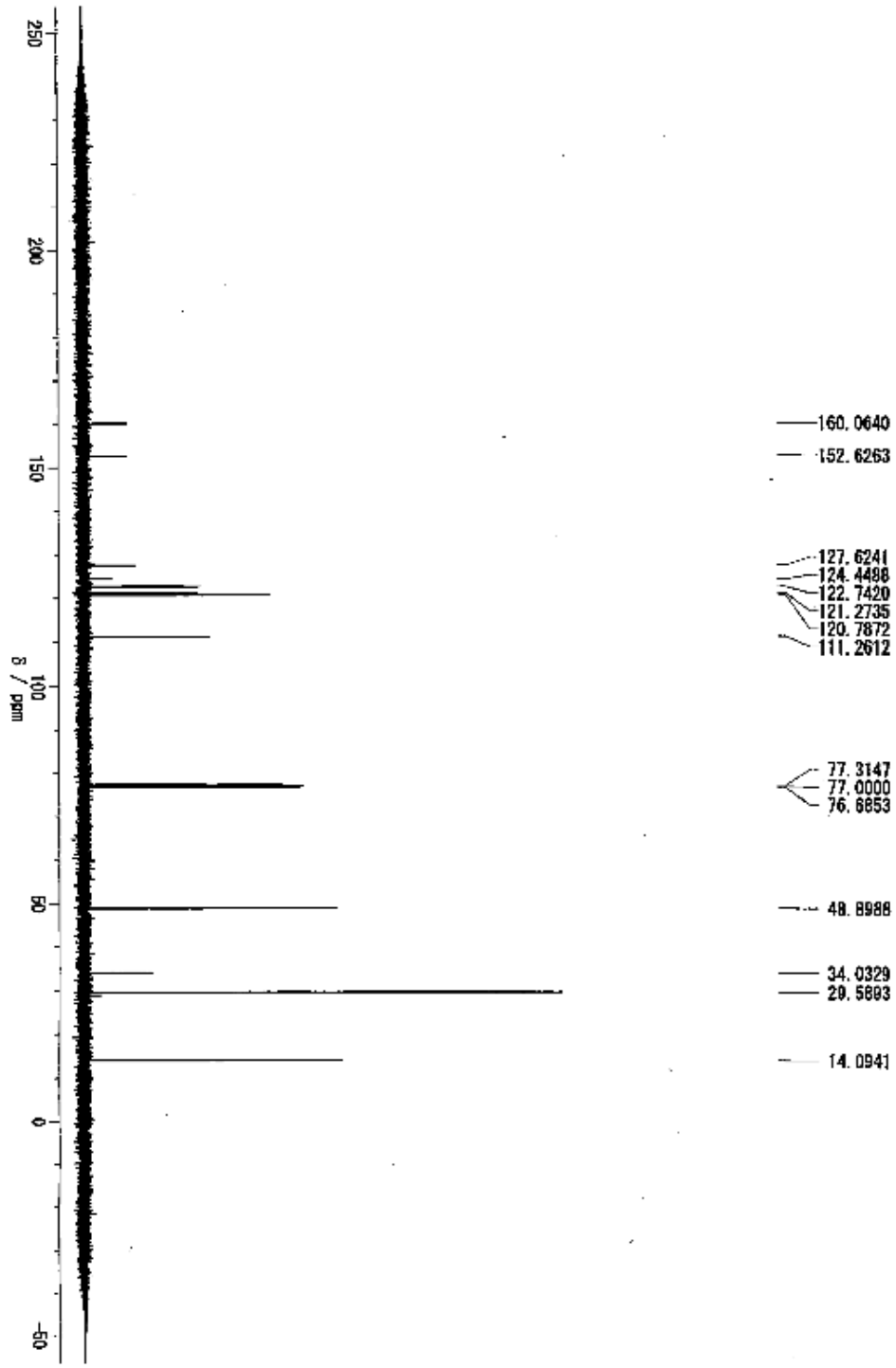
[^{1}H and ^{13}C NMR spectra of **3ha**]



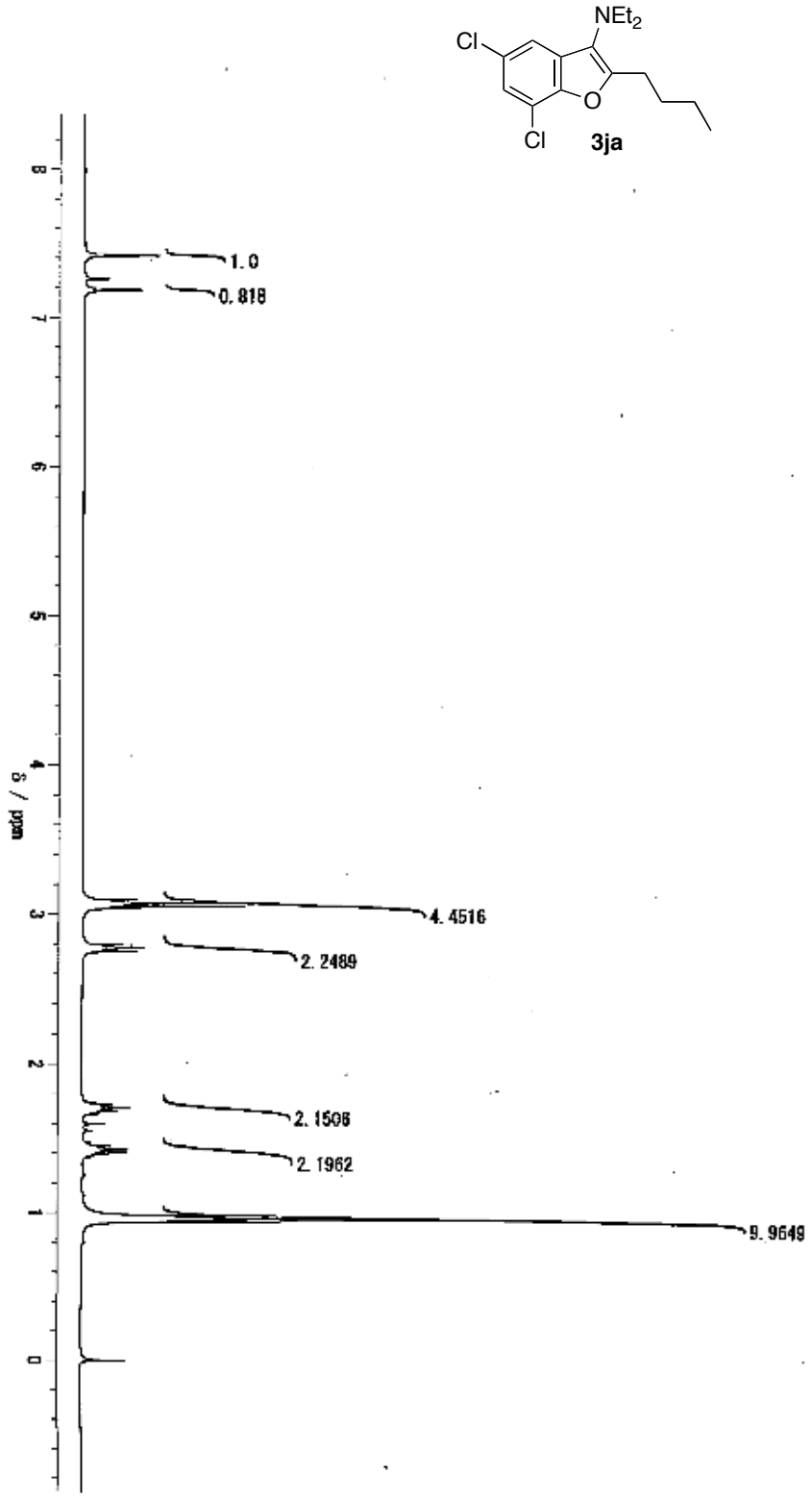

159.7017
153.4082
126.5466
122.6371
122.1794
121.5023
120.0434
111.4137
77.3147
77.0000
76.6758
49.3946
34.8911
31.2199
26.3473
25.9849
14.1418
δ / ppm
250
200
150
100
50
0
-50

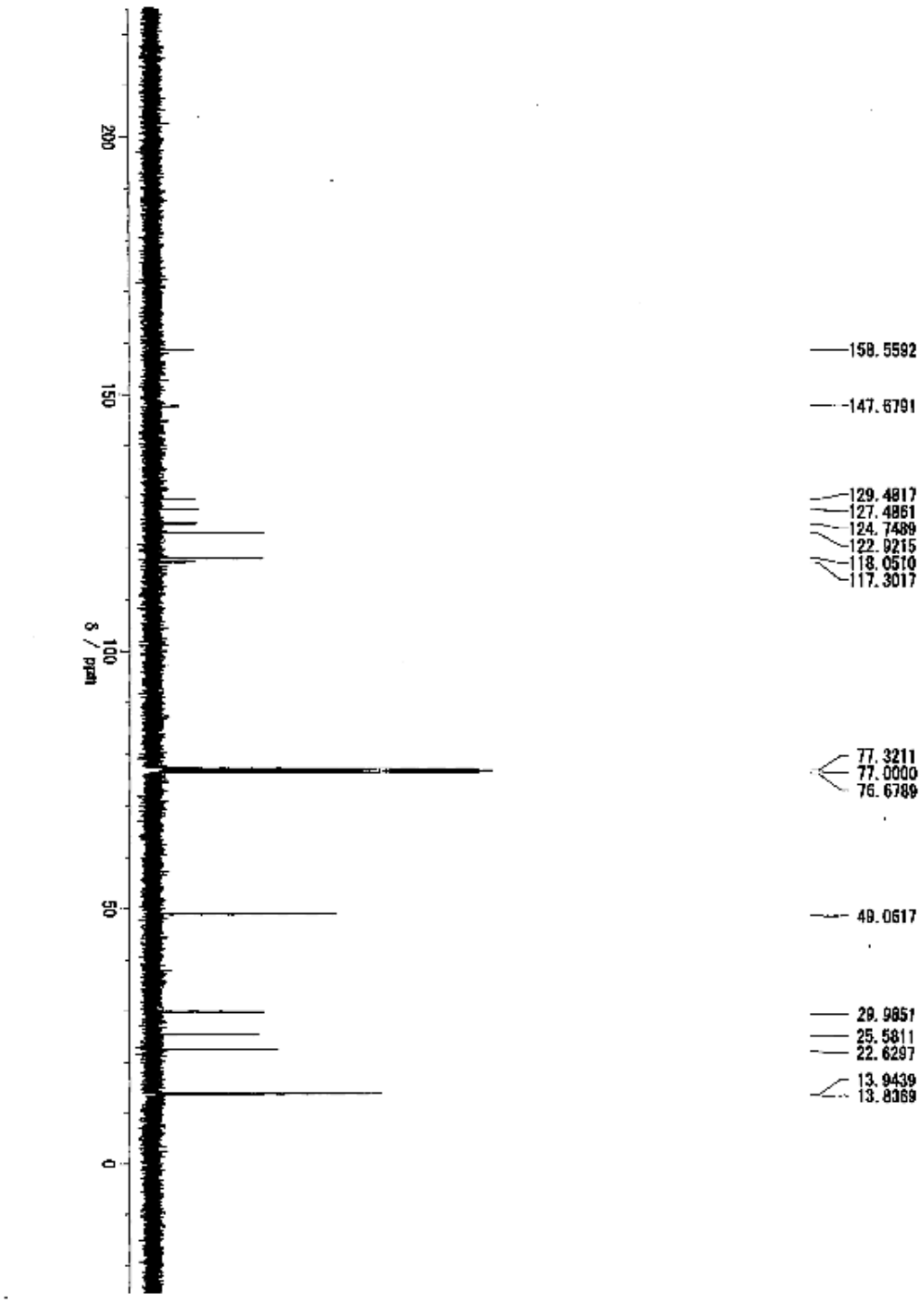
[^{1}H and ^{13}C NMR spectra of **3ia**]



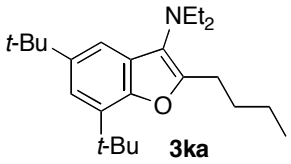

250
200
150
100
50
0
-50
δ / ppm
160.0640
152.6263
127.6241
124.4488
122.7420
121.2735
120.7872
111.2612
77.3147
77.0000
76.6853
48.8988
34.0329
29.5893
14.0941

[^{1}H and ^{13}C NMR spectra of **3ja**]

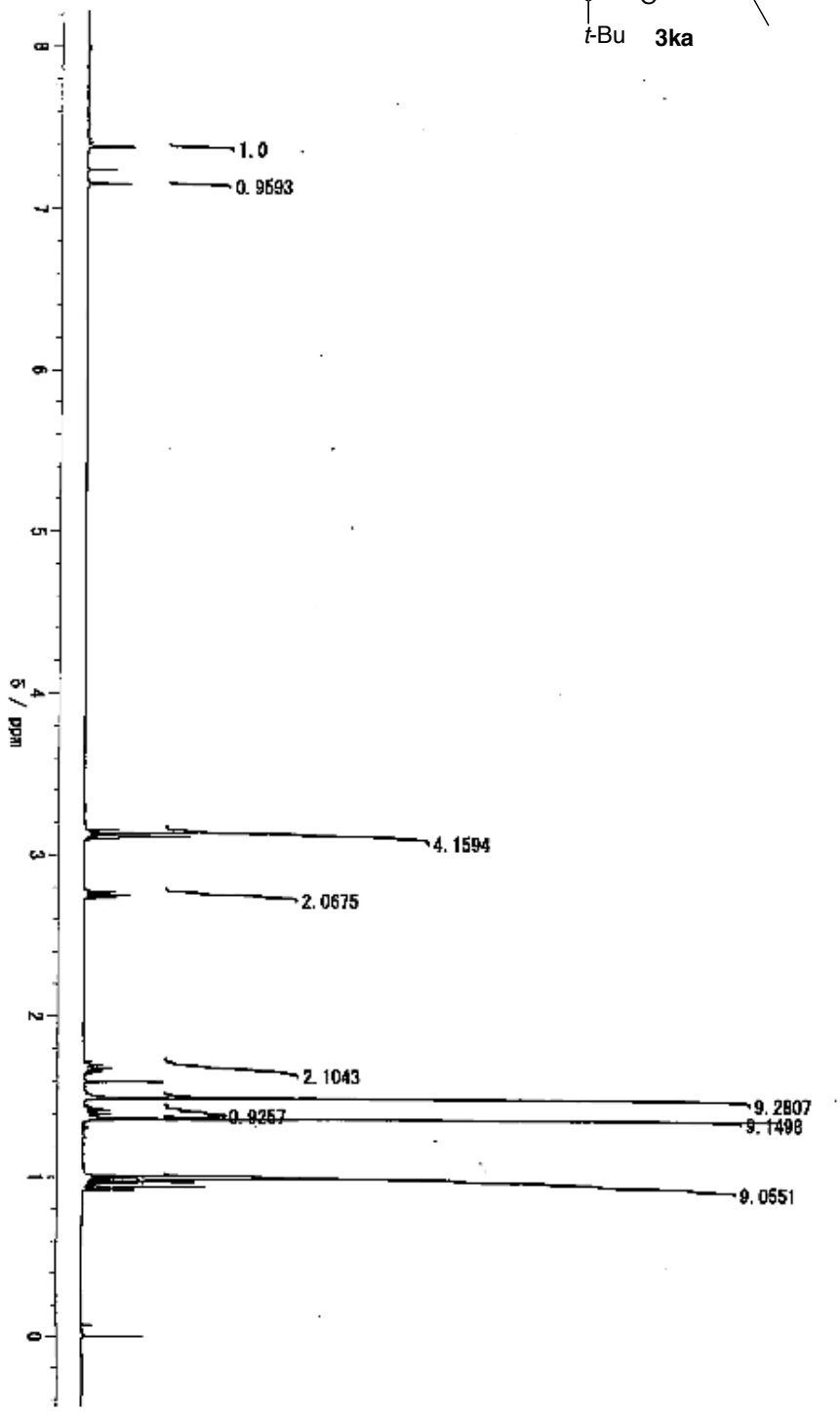


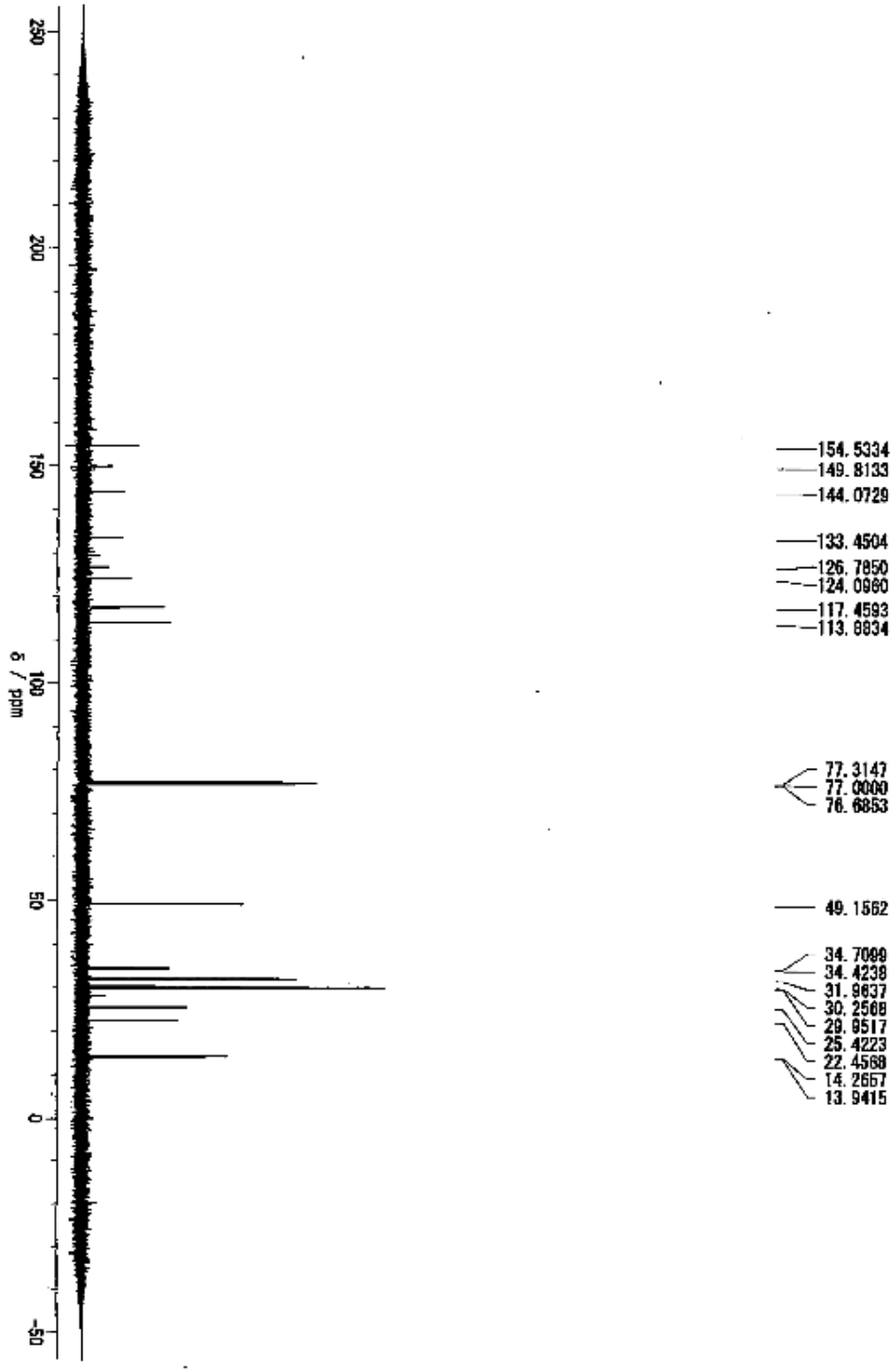

158.5592
147.6791
129.4817
127.4861
124.7489
122.9215
118.0510
117.3017
77.3211
77.0000
76.6789
49.0617
29.9851
25.5811
22.6297
13.9439
13.8369
200
150
100
50
0
S / ppm

[^{1}H and ^{13}C NMR spectra of **3ka**]

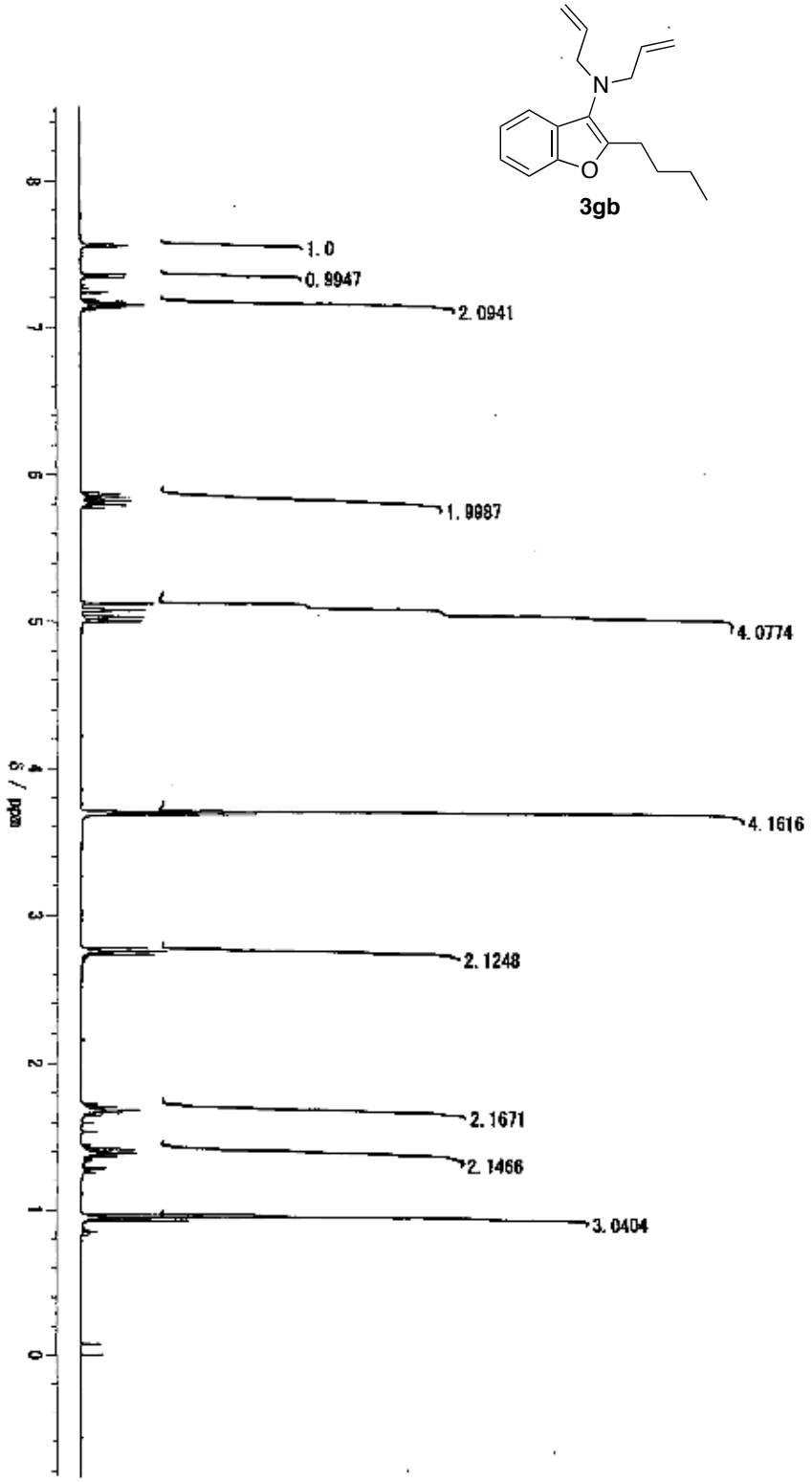


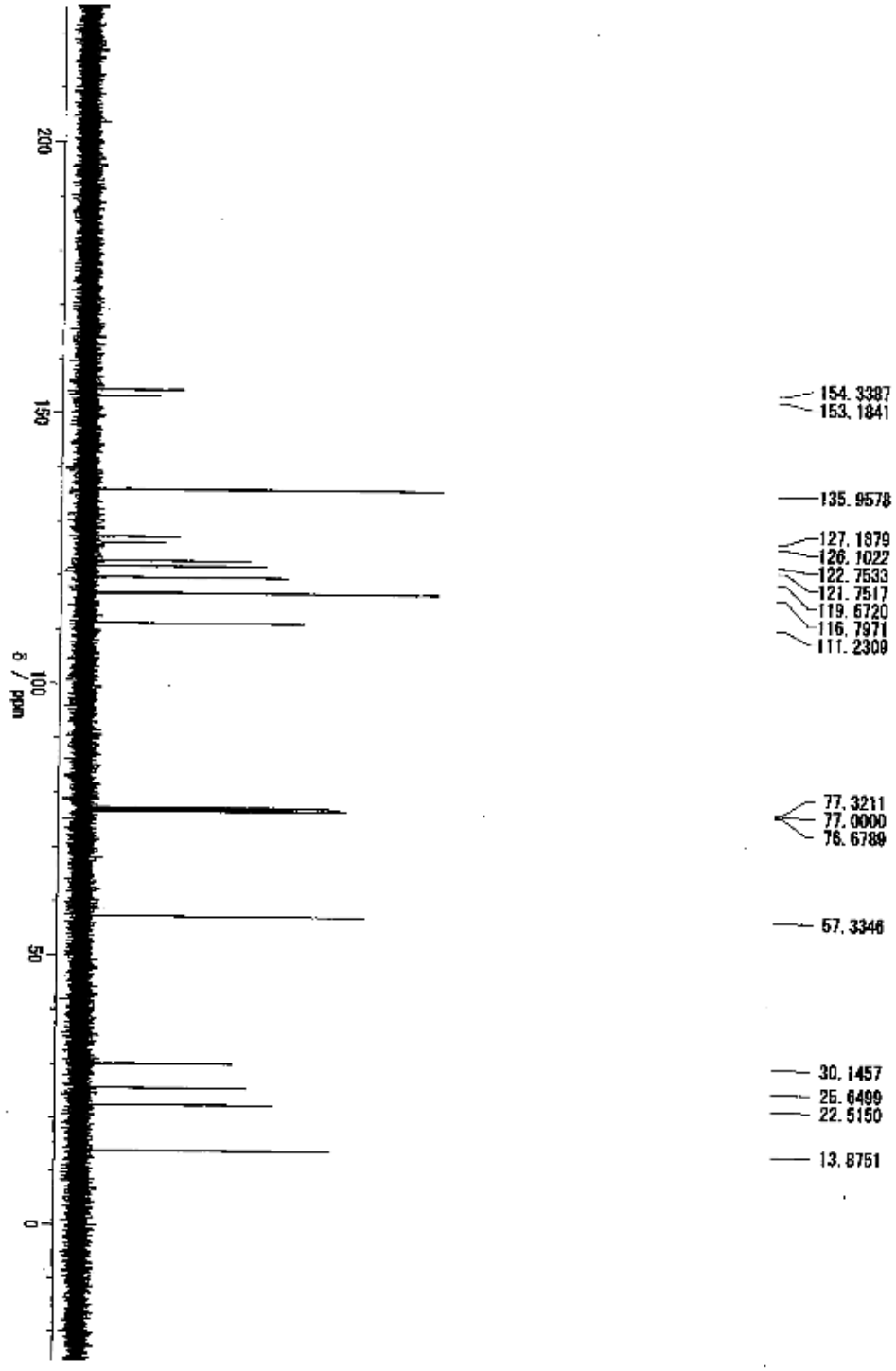
3ka



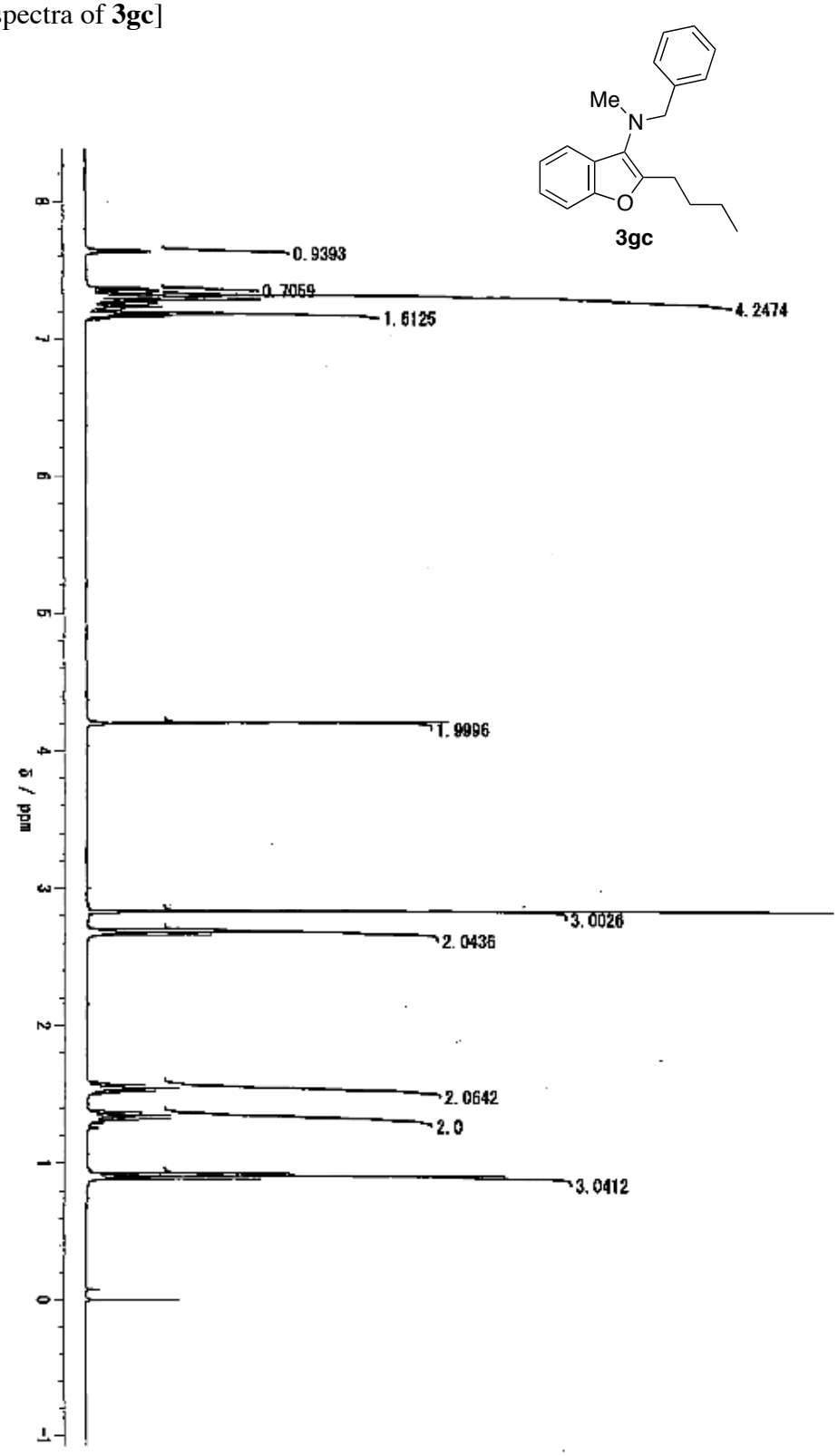

δ / ppm
250
200
150
100
50
0
-50
154.5334
149.8133
144.0729
133.4504
126.7850
124.0980
117.4593
113.8834
77.3147
77.0000
76.6853
49.1562
34.7099
34.4238
31.9637
30.2568
29.9517
25.4223
22.4588
14.2667
13.9415

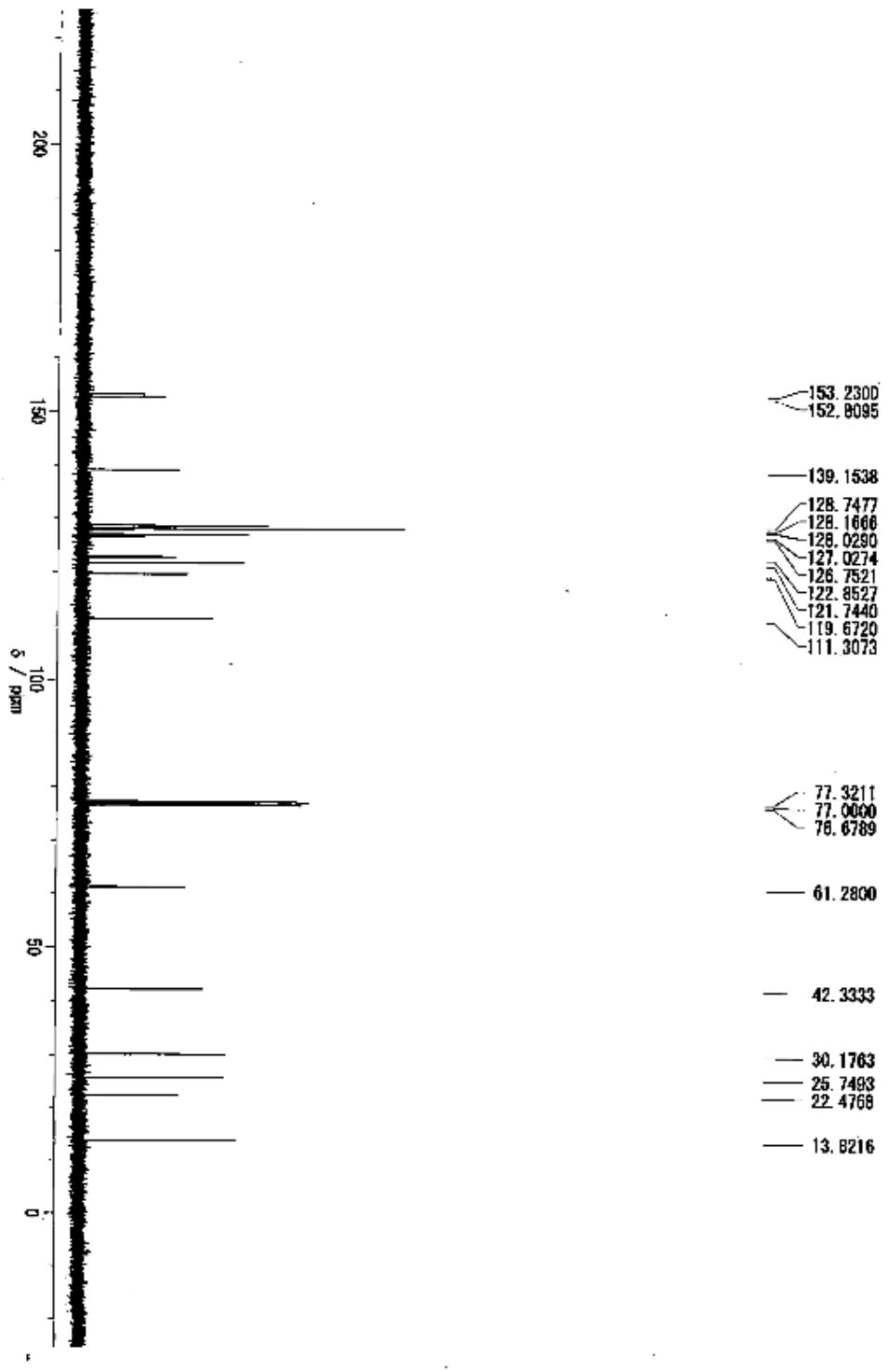
[^{1}H and ^{13}C NMR spectra of **3gb**]



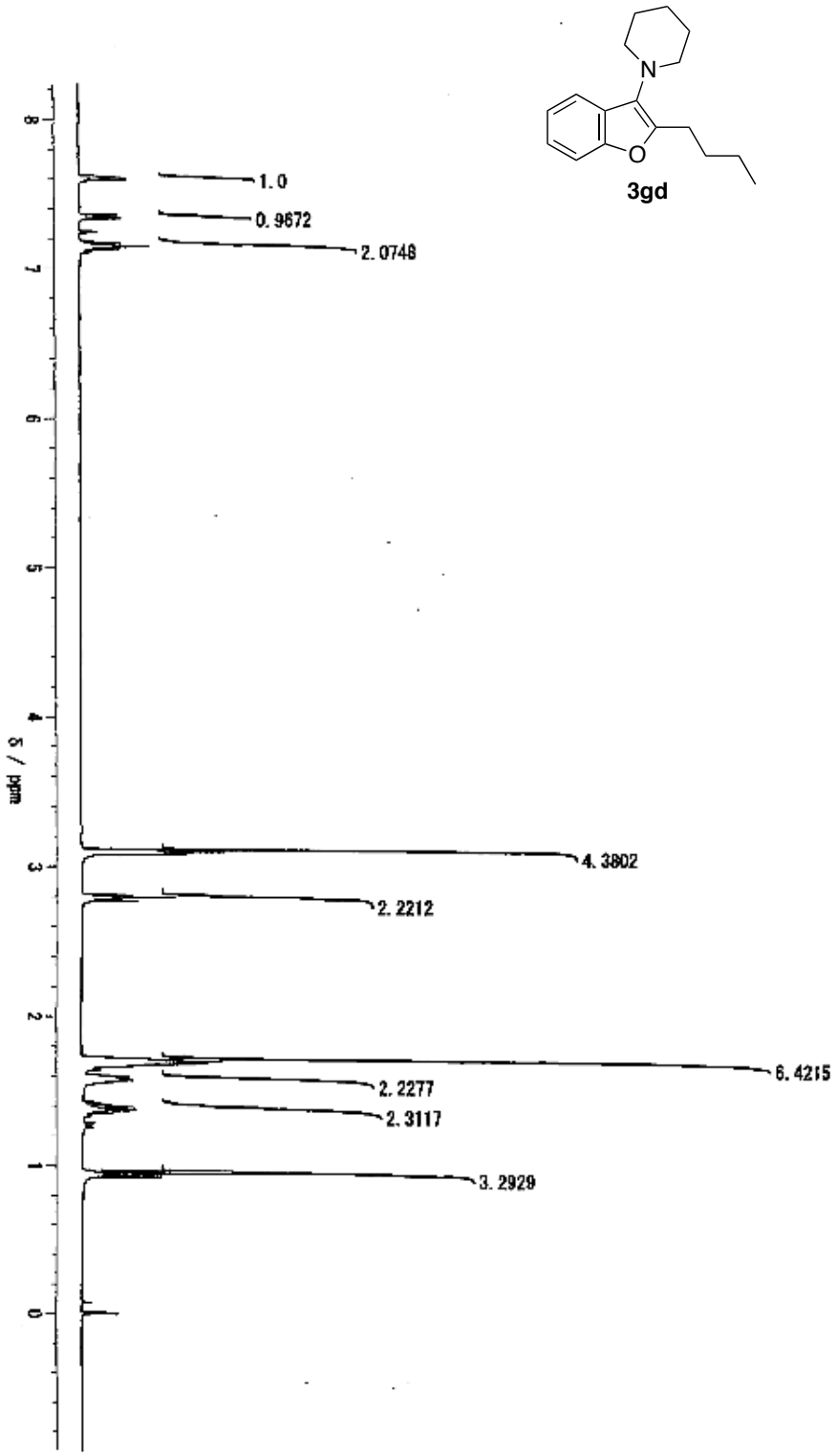

200
150
100
50
0
δ / ppm
154.3387
153.1841
135.9578
127.1879
126.1022
122.7533
121.7517
119.6720
116.7971
111.2309
77.3211
77.0000
76.6789
57.3346
30.1457
25.6499
22.5150
13.8751

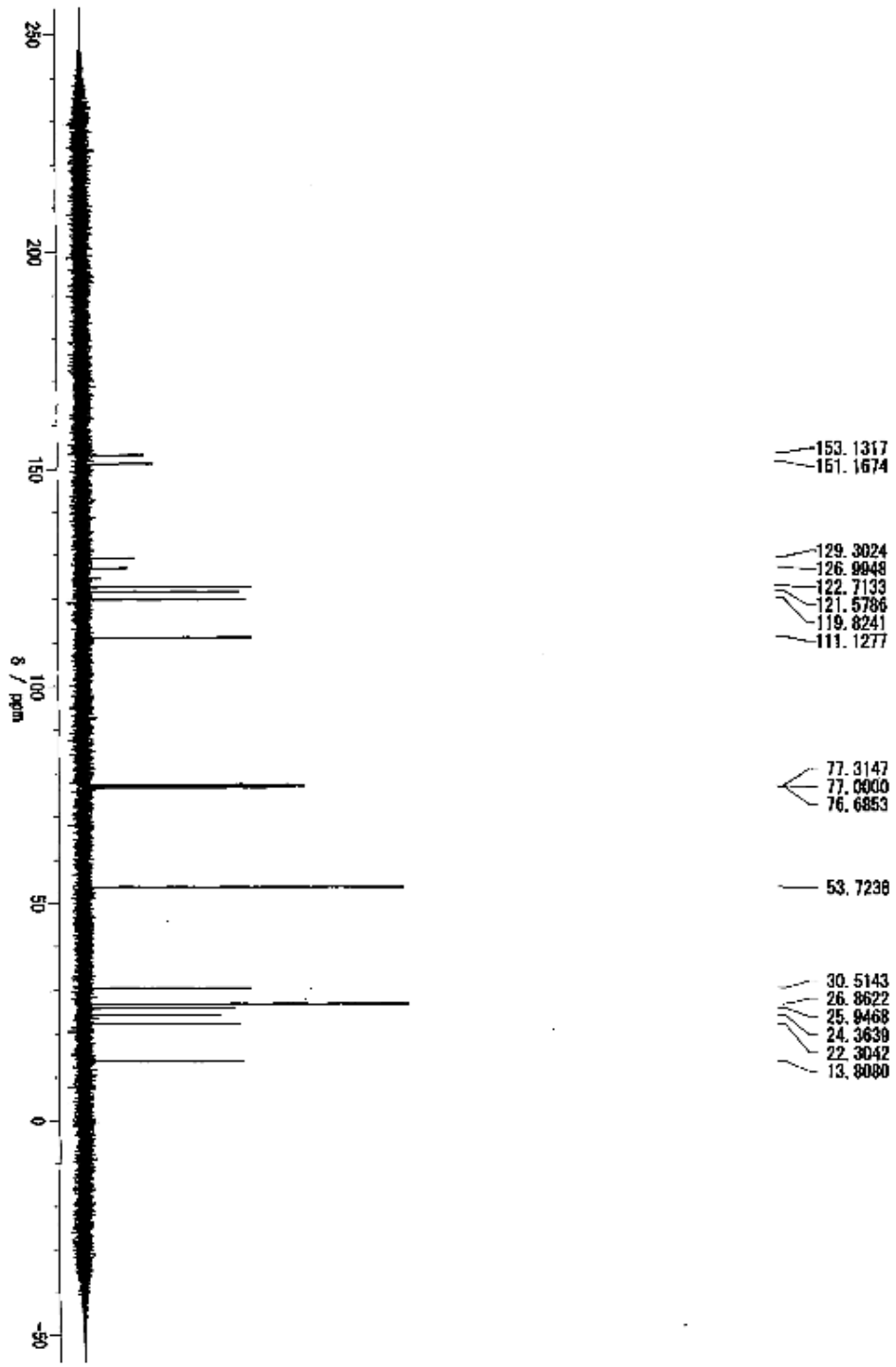
[^{1}H and ^{13}C NMR spectra of **3gc**]



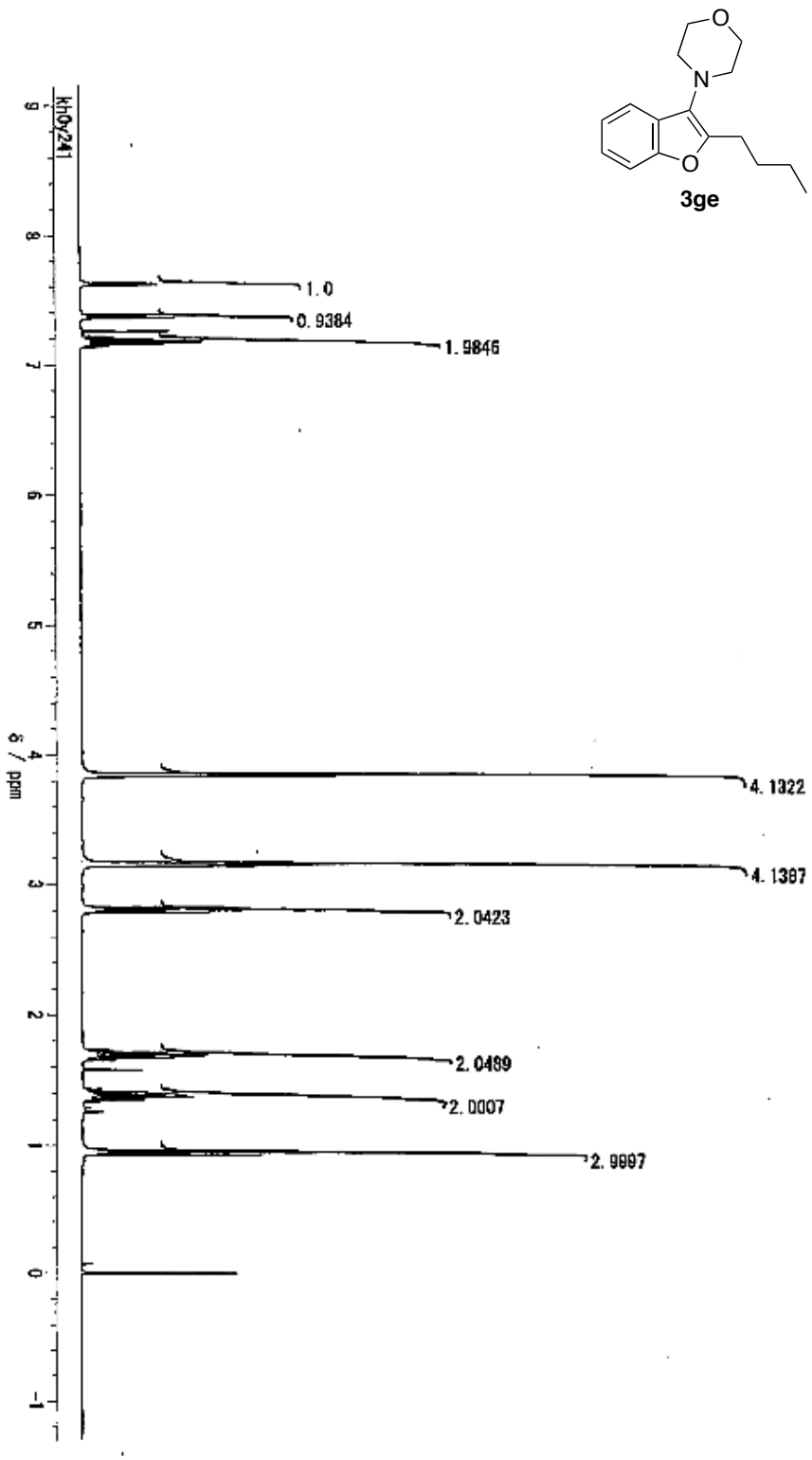

200
150
100
50
0
δ / ppm
153.2300
152.8095
139.1538
128.7477
128.1666
128.0280
127.0274
126.7521
122.8527
121.7440
119.6720
111.3073
77.3211
77.0000
76.6789
61.2800
42.3333
30.1763
25.7493
22.4768
13.8216

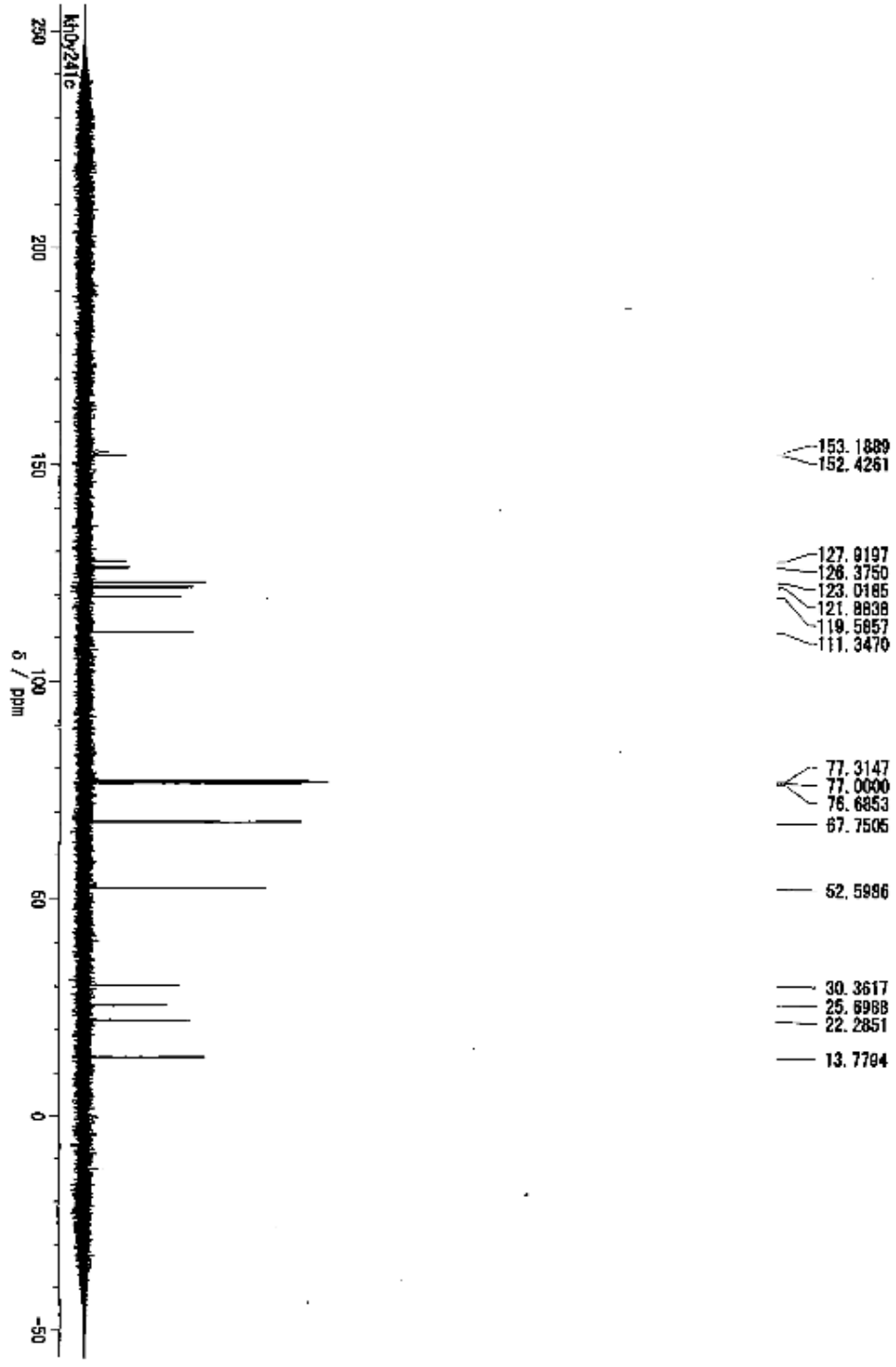
[^{1}H and ^{13}C NMR spectra of **3gd**]



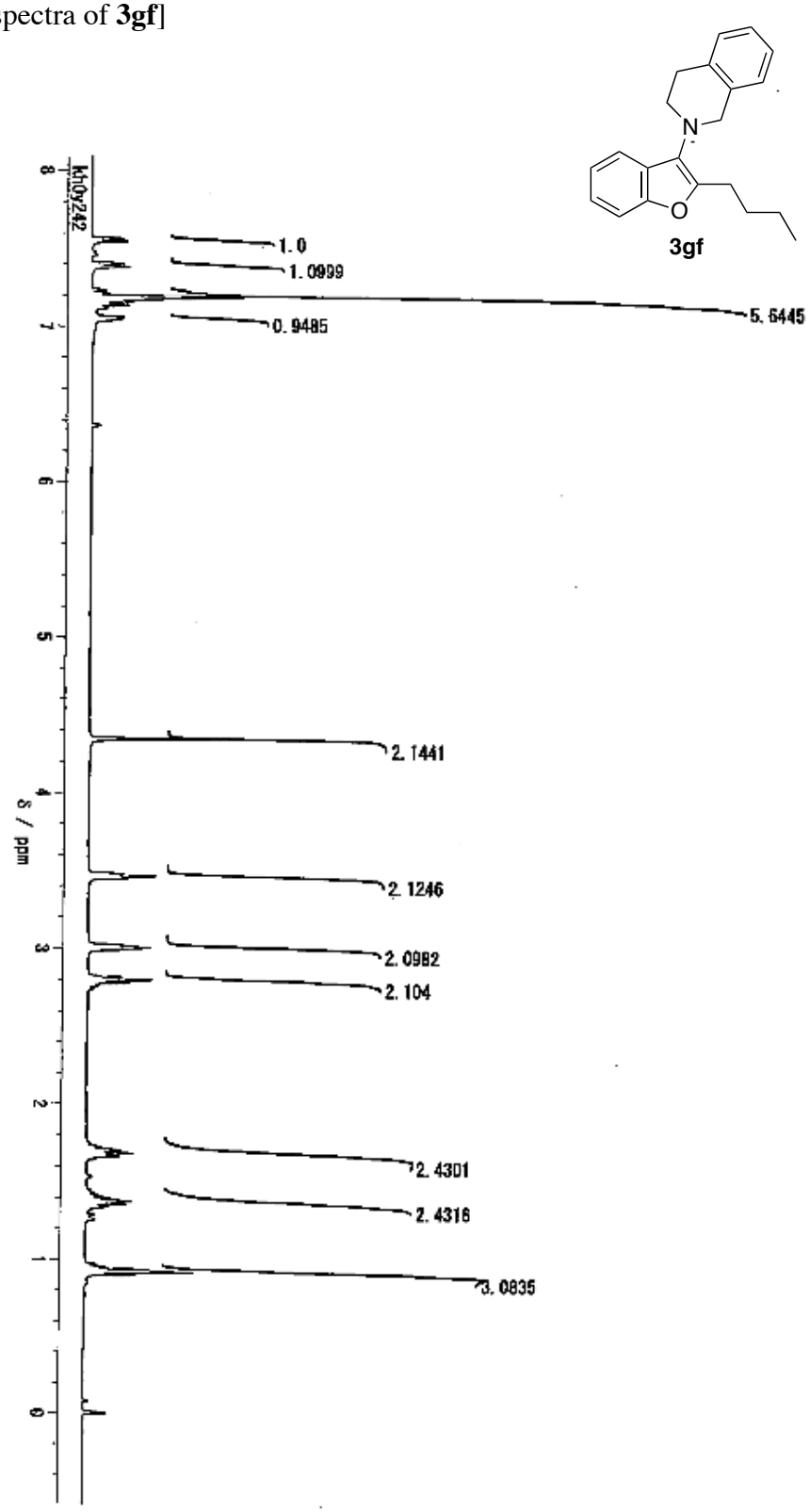

250
200
150
100
50
0
-50
δ / ppm
153.1317
151.1674
129.3024
126.9948
122.7133
121.5786
119.8241
111.1277
77.3147
77.0000
76.6853
53.7238
30.5143
26.8622
25.9468
24.3639
22.3042
13.8080

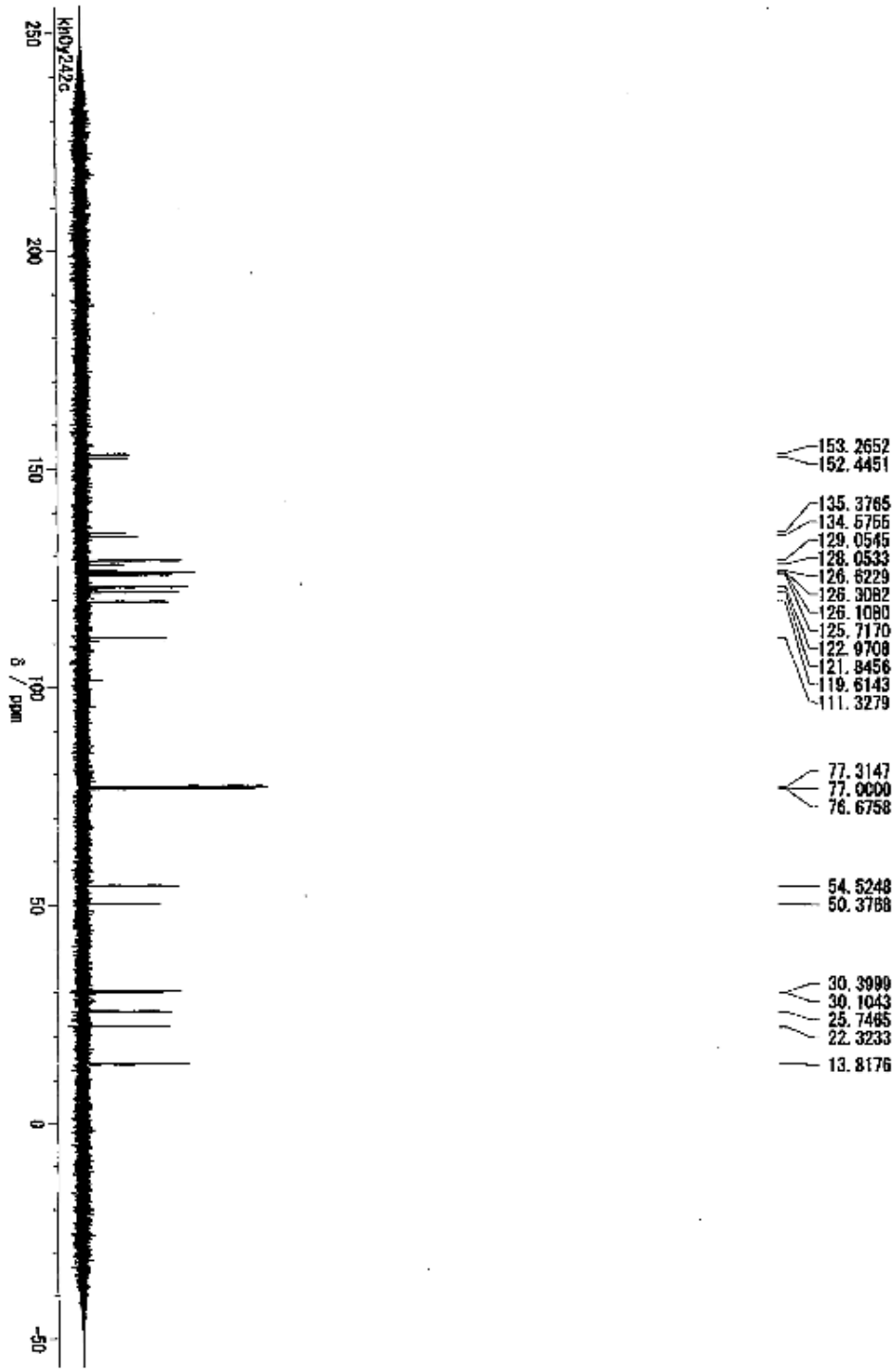
[^{1}H and ^{13}C NMR spectra of **3ge**]



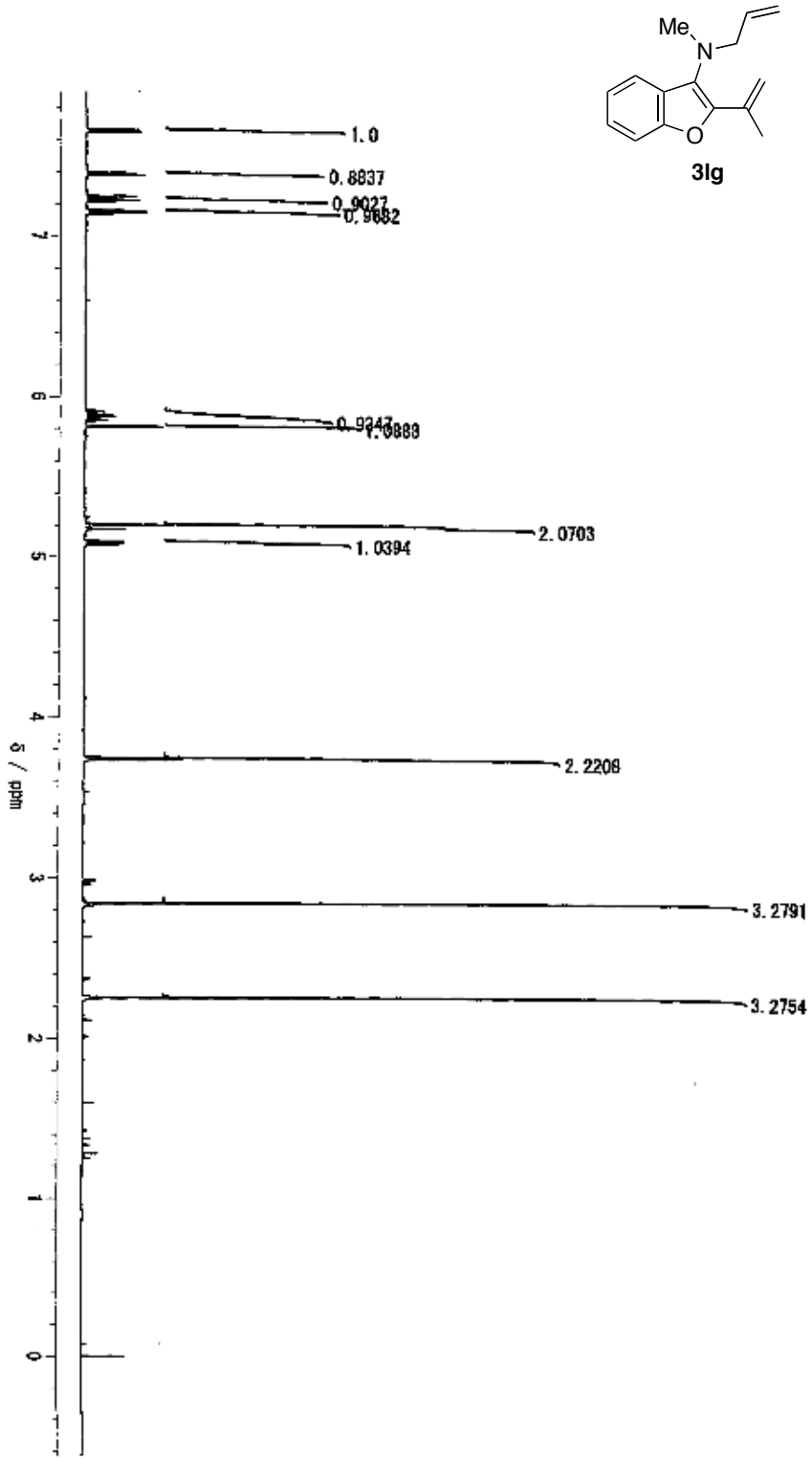

kt10y241c
250
200
150
100
50
0
-50
δ / ppm
153.1889
152.4261
127.9197
126.3750
123.0185
121.8838
119.5857
111.3470
77.3147
77.0000
76.6853
67.7505
52.5986
30.3617
25.6988
22.2851
13.7704

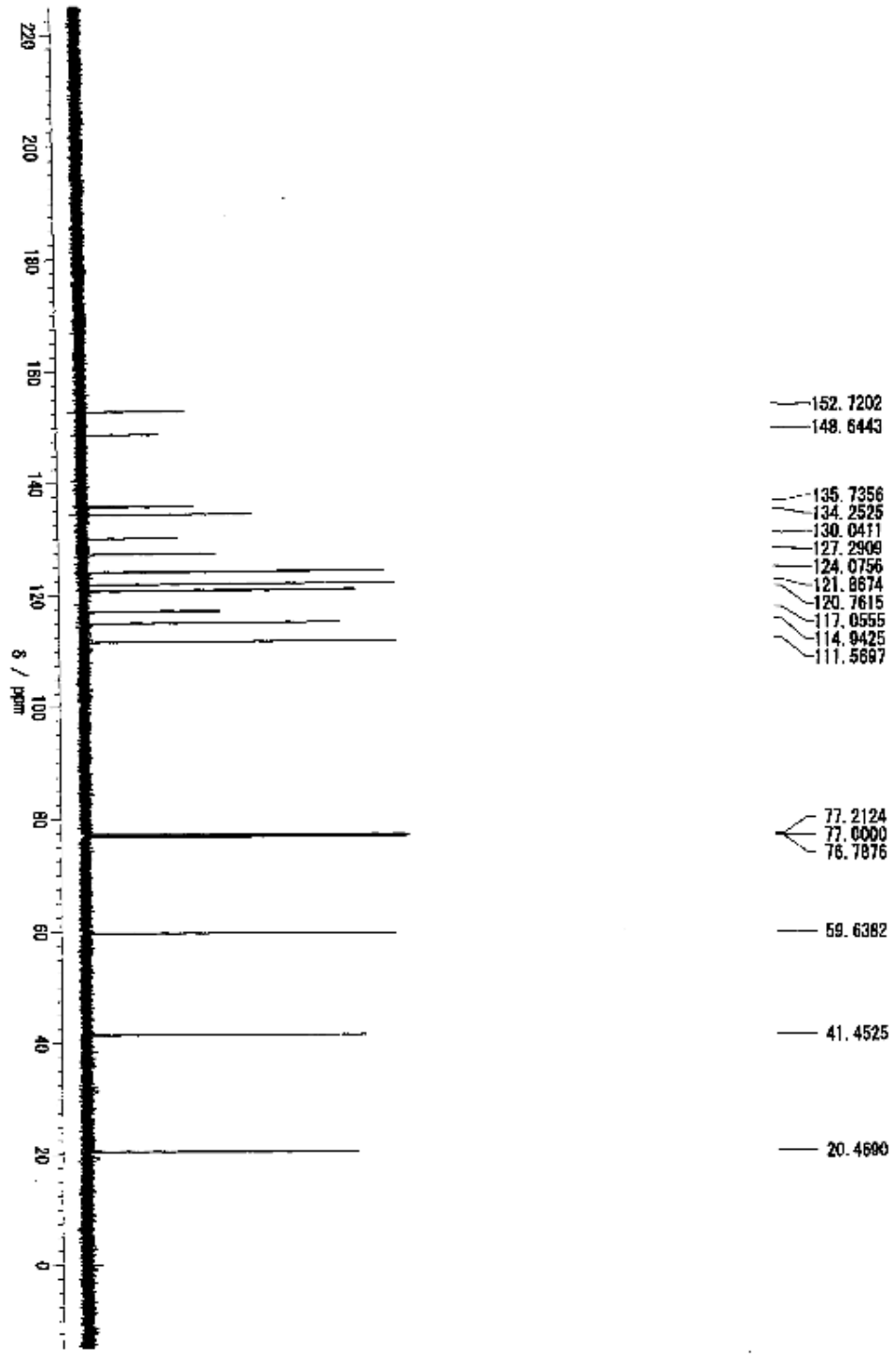
[^{1}H and ^{13}C NMR spectra of **3gf**]



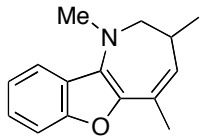

KthOy242c
250
200
150
100
50
0
-50
δ / ppm
153.2652
152.4451
135.3765
134.5755
129.0545
128.0533
126.6229
126.3082
126.1080
125.7170
122.9708
121.8456
119.6143
111.3279
77.3147
77.0000
76.6758
54.5248
50.3768
30.3999
30.1043
25.7465
22.3233
13.8176

[^{1}H and ^{13}C NMR spectra of **3lg**]

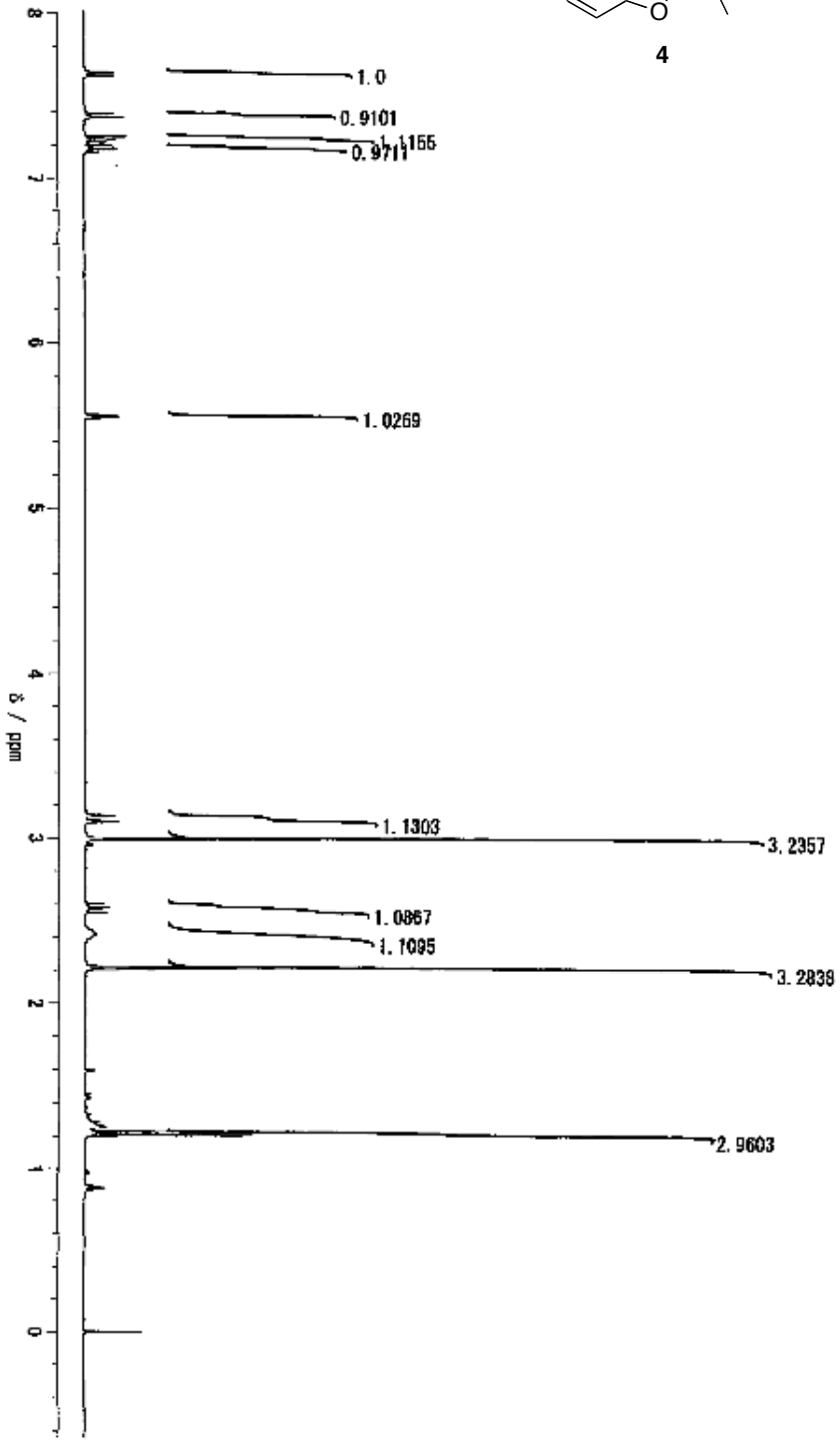


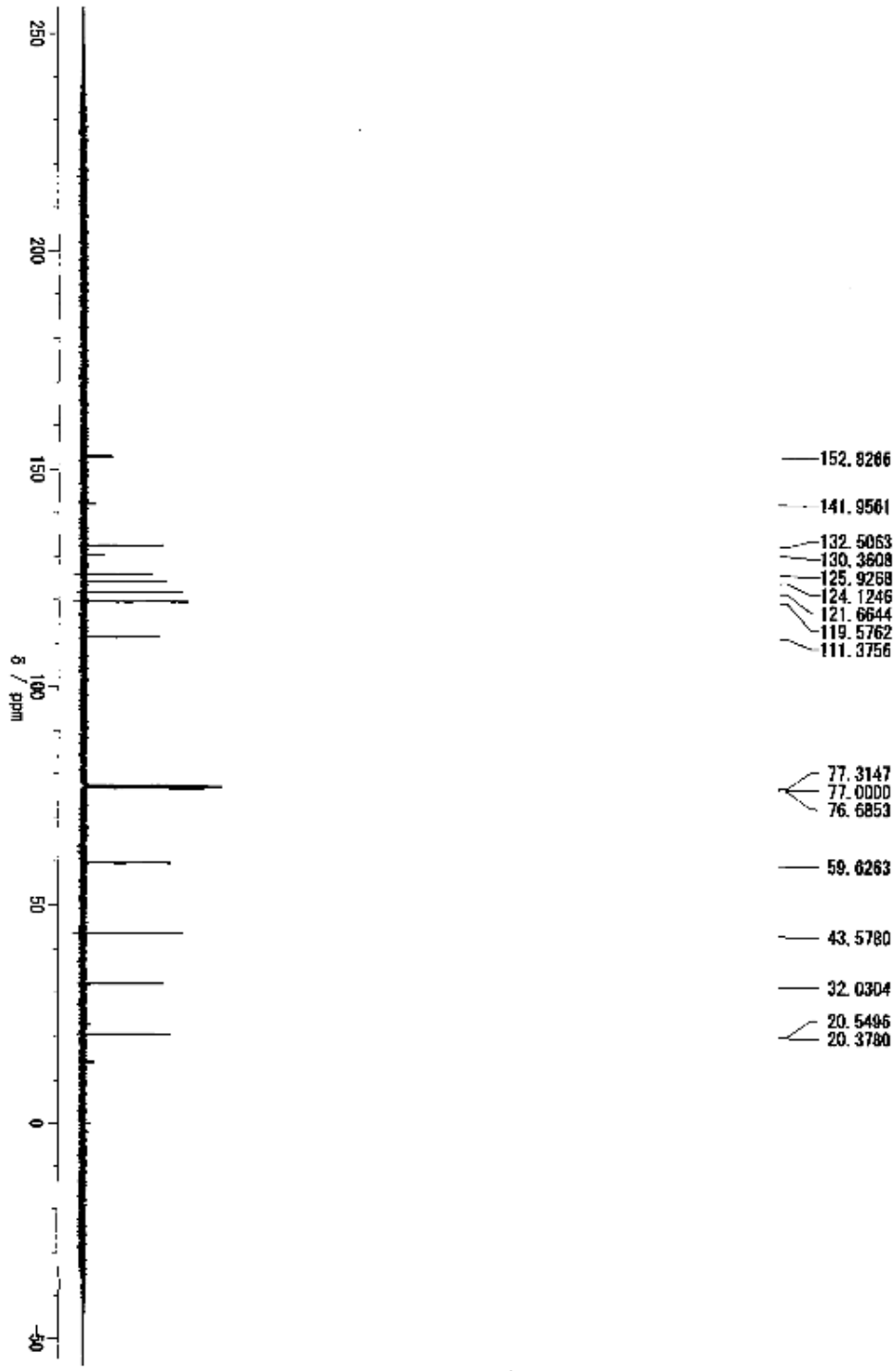

δ / ppm
220
200
180
160
140
120
100
80
60
40
20
0
152.7202
148.6443
135.7356
134.2525
130.0411
127.2909
124.0756
121.8674
120.7615
117.0555
114.9425
111.5697
77.2124
77.0000
76.7876
59.6382
41.4525
20.4590

[^{1}H and ^{13}C NMR spectra of **4**]



4




250
200
150
100
50
0
-50
δ / ppm
152.8266
141.9561
132.5063
130.3608
125.9268
124.1246
121.6644
119.5762
111.3756
77.3147
77.0000
76.6853
59.6263
43.5780
32.0304
20.5496
20.3780