Supporting Information

# Synthesis of Dihydrobenzo[*b*]furans by Diastereoselective Acyloxyarylation

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## 1. General

All reactions involving air- or moisture-sensitive reagents or intermediates were carried out in heat-gun-dried glassware under an argon atmosphere and were performed using standard Schlenk techniques. All solvents for extraction and flash chromatography were distilled before use. Acetic acid was purchased from *Acros* and used as received.

$^{1}$H NMR and $^{13}$C NMR spectra were recorded on a *Bruker DPX 300*, a *Bruker Varian 300*, a *Bruker Varian 400* or a *Varian Inova 500* spectrometer. Chemical shifts $\delta$ in ppm are referenced to the TMS peak as an internal standard. TLC was carried out on *Merck* silica gel 60 $F_{254}$ plates; detection by UV or dipping into a solution of $Ce(SO_4)_2 \cdot H_2O$ (10 g), phosphormolybdic acid hydrate (25 g), conc. $H_2SO_4$ (60 mL) and $H_2O$ (0.94 L) or $NaHCO_3$ (5.0 g), $KMnO_4$ (1.5 g) and $H_2O$ (0.20 L) followed by heating. Flash chromatography (FC) was carried out on *Merck* or *Fluka* silica gel 60 (40 - 63 μm) with an argon pressure of about 1.1 - 1.5 bar. ESI-MS and HRMS were performed using a *Bruker MicroTof*. Melting points were determined on a *Stuart SMP10* and are uncorrected. IR spectra were recorded on a *Digilab* Varian 3100 FT-IR Excalibur Series.

The reactants or reagents are purchased or prepared by following literatures.

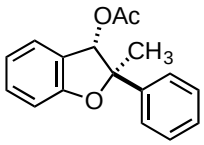
2-methylbenzofuran (*Aldrich*), 2-*n*-butylbenzofuran (*Aldrich*), benzene boronic acid (*Aldrich*), 4-fluorophenylboronic acid (*Alfa Aesar*), 4-chlorophenylboronic acid (*Alfa Aesar*), 4-bromophenylboronic acid (*Alfa Aesar*), 4-methylphenylboronic acid (*Alfa Aesar*), 3-methylphenylboronic acid (*Alfa Aesar*), 4-methoxyphenylboronic acid (*ABCR*), palladium acetate (*TCI*), palladium trifluoroacetate (*Aldrich*), acetic acid (*Acros*), propionic acid (*Acros*), potassium fluoride (*Aldrich*), 2,2,6,6-tetramethylpiperidin-*N*-oxyl radical (TEMPO, *CIBA*, *Specialty Chemicals*); 4-methoxyl-2-methy-benzofuran,[1] 5-methoxyl-2-methy-benzofuran,[1,2] 7-methoxyl-2-methy-benzofuran,[1] 2,7-dimethylbenzofuran,[1] 2,4,6-trimethylbenzofuran,[3] 2-methylnaphtho[2,1-*b*]furan.[1]

1. A. I. Roshchin, S. M. Kel'chevski, N. A. Bumagin, *J. Organomet. Chem.*, 1998, 163-167.
2. M. E. Meza-Aviñez, M. Ordoñez, Ma. Fernández-Zertuche, L. Rodríguez-Fragoso, J. Reyes-Esparza and J. Reyes-Esparza, 2005, *Bioorg. Med. Chem.*, 2005, 6521-6528.
3. S. W. Youn and J. I. Eom, *Org. Lett.*, 2005, **7**, 3355-3358.

## 2. General Procedure for the Acyloxyarylation of Benzofurans

An arylboronic acid (0.3 mmol, 1.5 equiv), TEMPO (94 mg, 0.6 mmol, 3.0 equiv), palladium acetate (2.2 mg, 0.01 mmol, 5 mol%), benzofuran derivative (0.2 mmol, 1.0 equiv) and acetic acid (0.4 mL) were stirred in a sealed tube at room temperature for 5 h. A saturated solution of $K_2CO_3$ (2 mL) was added and the mixture was extracted with $CH_2Cl_2$ (3 x 4 mL). The combined organic layers were dried over $MgSO_4$ and the volatiles were removed under reduced pressure. The residue was purified by FC.

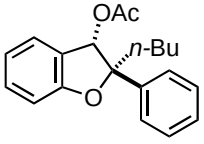
### 2-Methyl-2-phenyl-2,3-dihydrobenzofuran-3-yl acetate (4aaa)




According to the General Procedure with 2-methylbenzofuran (26 mg, 0.2 mmol) and phenylboronic acid (37 mg, 0.3 mmol). FC (pentane/$Et_2O$ 200:1 → 10:1) gave **4aaa** as a colorless oil (46 mg, 0.17 mmol, 86%, dr 93:7).

**$^1$H NMR** ($CDCl_3$, 300 MHz) δ 7.57 (dd, *J* = 8.4 Hz, *J* = 1.2 Hz, 2H), 7.38 - 7.27 (m, 5H), 7.05 (d, *J* = 8.4 Hz, 1H), 6.94 (t, *J* = 7.5 Hz, 1H), 6.37 (d, *J* = 1.2 Hz, 1H), 2.22 (d, *J* = 1.2 Hz, 3H), 1.77 (d, *J* = 1.8 Hz, 3H); **$^{13}$C NMR** ($CDCl_3$, 75 MHz) δ 170.8 (C), 160.2 (C), 144.1 (C), 131.3 (CH), 128.4 (CH), 127.4 (CH), 127.0 (CH), 125.1 (CH), 124.2 (C), 121.2 (CH), 110.2 (CH), 91.1 (C), 80.5 (CH), 23.1 ($CH_3$), 21.0 ($CH_3$); **HRMS** (**ESI**) *m/z* = 291.0992 calcd for $C_{17}H_{16}O_3$ $[M+Na]^+$, found: 291.0982. **IR** (neat): 2360, 2342, 1736, 1600, 1478, 1371, 1230, 1017, 977, 923, 752, 700.

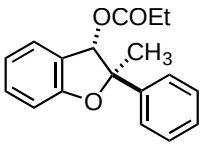
### 2-Butyl-2-phenyl-2,3-dihydrobenzofuran-3-yl acetate (4baa)




According to the General Procedure with 2-butylbenzofuran (35 mg, 0.2 mmol) and phenylboronic acid (37 mg, 0.3 mmol). FC (pentane/$Et_2O$ 200:1 → 10:1) gave **4baa** as a colorless solid (55 mg, 0.18 mmol, 89%, dr 89:11). The crystal suitable for X-ray analysis was obtained from hexane.

**$^1$H NMR** ($CDCl_3$, 300 MHz) δ 7.54 (dd, *J* = 7.2 Hz, *J* = 1.5Hz, 2H), 7.37 - 7.26 (m, 5H), 7.06 (d, *J* = 8.1 Hz, 1H), 6.95 - 6.90 (m, 1H), 6.40 (s, 1H), 2.25 - 2.14 (m, 1H), 2.21 (s, 3H), 2.03 - 1.93 (m, 1H), 1.53 - 1.29 (m, 3H), 1.04 - 0.93 (m, 1H), 0.87 (t, *J* = 7.5 Hz, 3H); **$^{13}$C NMR** ($CDCl_3$, 75 MHz) δ ; 170.7 (C), 160.1 (C), 142.3 (C), 131.1 (CH), 128.2 (CH), 127.2 (CH), 126.8 (CH), 125.6 (CH), 124.2 (C), 121.0 (CH), 110.1 (CH), 93.4 (C), 80.9 (CH), 34.8 ($CH_2$), 25.6 ($CH_2$), 22.9 ($CH_2$), 20.9 ($CH_3$), 13.8 ($CH_3$); mp: 73 - 74 °C; **HRMS** (**ESI**) *m/z* = 333.1461 calcd for $C_{20}H_{22}O_3$ $[M+Na]^+$, found: 333.1454; **IR** (neat): 2930, 2871, 2360, 2342, 1737, 1479, 1229, 1025, 963, 750, 702.

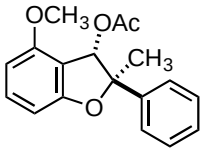
**2-Methyl-2-phenyl-2,3-dihydrobenzofuran-3-yl propionate (4aab)**




According to the General Procedure with 2-methylbenzofuran (26 mg, 0.2 mmol), phenylboronic acid (37 mg, 0.3 mmol) and propionic acid (0.4 mL) instead of acetic acid. FC (pentane/$Et_2O$ 200:1 → 10:1) gave **4aab** as a colorless oil (35 mg, 0.12 mmol, 62%, dr 85:15). The diastereomers were additionally separated with FC to give nearly pure major isomer (20 mg, 0.071 mmol, 35%, dr 97:3).

**$^1$H NMR** ($CDCl_3$, 300 MHz) δ 7.57 (dd, *J* = 7.2 Hz, *J* = 1.5 Hz, 2H), 7.37 - 7.27 (m, 5H), 7.04 (d, *J* = 8.1 Hz, 1H), 6.95 - 6.90 (m, 1H), 6.37 (s, 1H), 2.48 (q, *J* = 7.5 Hz, 2H), 1.75 (s, 3H), 1.25 (t, *J* = 7.5 Hz, 3H); **$^{13}$C NMR** ($CDCl_3$, 75 MHz) δ 174.4 (C), 160.2 (C), 144.2 (C), 131.3 (CH), 128.4 (CH), 127.5 (CH), 127.0 (CH), 125.1 (CH), 124.3 (C), 121.3 (CH), 110.2 (CH), 91.2 (C), 80.4 (CH), 27.7 ($CH_2$), 23.1 ($CH_3$), 9.1 ($CH_3$); **HRMS** (**ESI**) *m/z* = 305.1148 calcd for $C_{18}H_{18}O_3$ $[M+Na]^+$, found: 305.1140; **IR** (neat): 2983, 2941, 2361, 2342, 1734, 1600, 1478, 1254, 1169, 1063, 922, 750, 700.

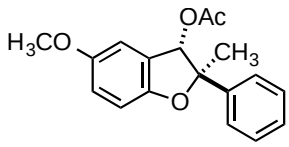
**4-Methoxy-2-methyl-2-phenyl-2,3-dihydrobenzofuran-3-yl acetate (4caa)**




According to the General Procedure with 4-methoxy-2-methylbenzofuran (32 mg, 0.2 mmol) and phenylboronic acid (37 mg, 0.3 mmol). FC (pentane/$Et_2O$ 200:1 → 10:1) gave **4caa** as a colorless oil (52 mg, 0.17 mmol, 87%, dr 85:15).

**$^1$H NMR** ($CDCl_3$, 300 MHz) δ 7.70 (d, *J* = 7.2 Hz, 2H), 7.43 - 7.31 (m, 4H), 6.75 (d, *J* = 7.8 Hz, 1H), 6.60 (s, 1H), 6.50 (d *J* = 8.4 Hz, 1H), 3.84 (s, 3H), 2.29 (s, 3H), 1.79 (s, 3H); **$^{13}$C NMR** ($CDCl_3$, 75 MHz) δ 169.2 (C), 160.0 (C), 156.0 (C), 142.5 (C), 130.9 (CH), 126.7 (CH), 127.5 (CH), 123.4 (CH), 109.3 (C), 101.7 (CH), 101.4 (CH), 90.2 (C), 76.8 (CH), 53.78 ($CH_3$), 21.5 ($CH_3$), 19.3 ($CH_3$); **HRMS** (**ESI**) *m/z* = 321.1097 calcd for $C_{18}H_{18}O_4$ $[M+Na]^+$, found: 321.1099; **IR** (neat): 2360, 2342, 1736, 1611, 1495, 1465, 1372, 1334, 1221, 1082, 1060, 1017, 974, 920, 763, 722, 701.

**5-Methoxy-2-methyl-2-phenyl-2,3-dihydrobenzofuran-3-yl acetate (4daa)**

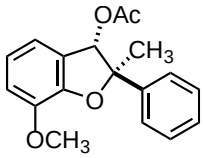



According to the General Procedure with 5-methoxy-2-methylbenzofuran (32 mg, 0.2 mmol) and phenylboronic acid (37 mg, 0.3 mmol). FC (pentane/$Et_2O$ 200:1 → 10:1) gave **4daa** as a colorless oil (57 mg, 0.19 mmol, 96%, dr 89:11).

**$^1$H NMR** ($CDCl_3$, 300 MHz) δ 7.41 (d, *J* = 7.5 Hz, 2H), 7.20 (t, *J* = 7.5 Hz, 2H), 7.13 (t, *J* = 6.0 Hz, 1H), 6.80 (s, 1H), 6.78 - 6.70 (m 2H), 6.17 (s, 1H), 3.60 (s, 3H), 2.07 (s, 3H), 1.60 (s, 3H);

**$^{13}$C NMR** ($CDCl_3$, 75 MHz) δ 170.7 (C), 154.4 (C), 154.3 (C), 144.1 (C), 128.3 (CH), 127.3 (CH), 125.0 (CH), 124.6 (C), 117.7 (CH), 111.50 (CH), 110.40 (CH), 91.7 (C), 80.8 (CH), 55.9 ($CH_3$), 23.0 ($CH_3$), 20.9 ($CH_3$); **HRMS** (**ESI**) *m/z* = 321.1097 calcd for $C_{18}H_{18}O_4$ $[M+Na]^+$, found: 321.1097; **IR** (neat): 2361, 2342, 1737, 1371, 1227, 1018, 933, 801, 761, 701.

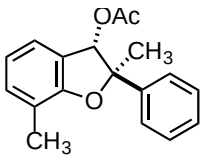
**7-Methoxy-2-methyl-2-phenyl-2,3-dihydrobenzofuran-3-yl acetate (4eaa)**




According to the General Procedure with 7-methoxy-2-methylbenzofuran (32 mg, 0.2 mmol) and phenylboronic acid (37 mg, 0.3 mmol). FC (pentane/$Et_2O$ 200:1 → 10:1) gave **4eaa** as a colorless oil (53 mg, 0.18 mmol, 89%, dr 91:9).

**$^1$H NMR** ($CDCl_3$, 300 MHz) δ 7.61 (d, *J* = 7.5 Hz, 2H), 7.38 (t, *J* = 7.5 Hz, 2H), 7.29 (t, *J* = 7.5 Hz, 1H), 6.98 - 6.10 (m, 3H), 6.41 (s, 1H), 4.03 (s, 3H), 2.23 (s, 3H), 1.83 (s, 3H); **$^{13}$C NMR** ($CDCl_3$, 75 MHz) δ 170.3 (C), 148.6 (C), 144.2 (C), 143.4 (C), 128.0 (CH), 127.0 (CH), 124.7 (C), 124.5 (CH), 121.4 (CH), 118.1 (CH), 113.0 (CH), 91.5 (C), 80.4 (CH), 55.6 ($CH_3$), 22.7 ($CH_3$), 20.6 ($CH_3$); **HRMS** (**ESI**) *m/z* = 321.1097 calcd for $C_{18}H_{18}O_4$ $[M+Na]^+$, found: 321.1096; **IR** (neat): 2361, 2342, 1733, 1602, 1478, 1371, 1230, 1013, 921, 828, 752.

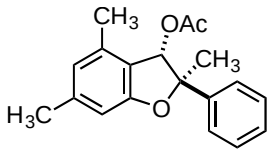
**2,7-Dimethyl-2-phenyl-2,3-dihydrobenzofuran-3-yl acetate (4faa)**




According to the General Procedure with 2,7-dimethylbenzofuran (29 mg, 0.2 mmol) and phenylboronic acid (37 mg, 0.3 mmol). FC (pentane/$Et_2O$ 200:1 → 10:1) gave **4faa** as a colorless oil (51 mg, 0.18 mmol, 90%, dr 94:6).

**$^1$H NMR** ($CDCl_3$, 300 MHz) δ 7.61 (d, *J* = 7.2 Hz, 2H), 7.39 (t, *J* = 7.2 Hz, 2H), 7.33 - 7.28 (m, 1H), 7.19 (t, *J* = 7.5 Hz, 2H), 6.89 (t, *J* = 7.5 Hz, 1H), 6.41 (s, 1H), 2.48 (s, 3H), 2.25 (s, 3H), 1.82 (s, 3H); **$^{13}$C NMR** ($CDCl_3$, 75 MHz) δ 170.1 (C), 158.0 (C), 143.6 (C), 131.5 (CH), 127.7 (CH), 126.7 (CH), 124.2 (CH), 123.5 (CH), 122.6 (C), 120.5 (CH), 119.6 (C), 90.1 (C), 80.2 (CH), 22.5 ($CH_3$), 20.4 ($CH_3$), 14.5 ($CH_3$); **HRMS** (**ESI**) *m/z* = 305.1148 calcd for $C_{18}H_{18}O_3$ $[M+Na]^+$, found: 305.1149, **IR** (neat): 2361, 2342, 1734, 1370, 1220, 1016, 924, 753, 699.

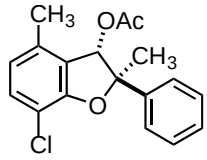
**2,4,6-Trimethyl-2-phenyl-2,3-dihydrobenzofuran-3-yl acetate (4gaa)**




According to the General Procedure with 2,4,6-trimethylbenzofuran (32 mg, 0.2 mmol) and phenylboronic acid (37 mg, 0.3 mmol). FC (pentane/$Et_2O$ 200:1 → 10:1) gave **4gaa** as a colorless oil (51 mg, 0.17 mmol, 86%, dr 90:10).

**$^1$H NMR** ($CDCl_3$, 300 MHz) δ 7.61 (dd, *J* = 7.2 Hz, *J* = 1.2 Hz, 2H), 7.34 (t, *J* = 7.2 Hz, 2H), 7.25 (m, 1H), 6.70 (s, 1H), 6.57 (s, 1H), 6.42 (s, 1H), 2.34 (s, 3H), 2.21 (s, 3H), 2.14 (s, 3H), 1.70 (s, 3H); **$^{13}$C NMR** ($CDCl_3$, 75 MHz) δ 170.8 (C), 160.3 (C), 144.2 (C), 141.6 (C), 136.3 (C), 128.2 (CH), 127.1 (CH), 125.0 (CH), 123.2 (CH), 119.4 (C), 107.9 (CH), 91.1 (C), 79.5 (CH), 23.0 ($CH_3$), 21.5 ($CH_3$), 20.6 ($CH_3$), 17.6 ($CH_3$); **HRMS** (**ESI**) *m/z* = 319.1305 calcd for $C_{19}H_{20}O_3$ $[M+Na]^+$, found: 319.1304; **IR** (neat): 2381, 2343, 1736, 1692, 1445, 1371, 1232, 1214, 1015, 971, 834, 762, 701.

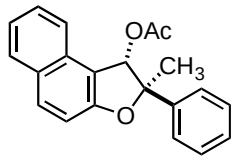
**7-Chloro-2,4,-dimethyl-2-phenyl-2,3-dihydrobenzofuran-3-yl acetate (4haa)**




According to the General Procedure with 7-chloro-2, 4-dimethylbenzofuran (29 mg, 0.16 mmol) and phenylboronic acid (37 mg, 0.3 mmol). FC (pentane/$Et_2O$ 200:1 → 10:1) gave **4haa** as a colorless oil (36 mg, 0.11 mmol, 66%, dr 76:24).

**$^1$H NMR** ($CDCl_3$, 300 MHz) δ 7.59 (dd, *J* = 6.9 Hz, *J* = 1.5 Hz, 2H), 7.38 - 7.34 (m, 3H), 7.22 (d, *J* = 8.1 Hz, 1H), 6.67 (d, *J* = 8.1 Hz, 1H), 6.47 (s, 1H), 2.22 (s, 3H), 2.14 (s, 3H), 1.74 (s, 3H); **$^{13}$C NMR** ($CDCl_3$, 75 MHz) δ 170.6 (C), 155.8 (C), 143.4 (C), 135.4 (C), 130.9 (CH), 128.5 (CH), 127. 5(CH), 124.9 (CH), 124.1 (C), 123.2 (CH), 112.7 (C), 92.2 (C), 79.9 (CH), 23.0 ($CH_3$), 20.5 ($CH_3$), 17.4 ($CH_3$); **HRMS** (**ESI**) *m/z* = 339.0758 calcd for $C_{18}H_{17}ClO_3$ $[M+Na]^+$, found: 339.0759; **IR** (neat): 2360, 2342, 1740, 1227, 1019, 911, 679.

**2-Methyl-2-phenyl-1,2-dihydronaphtho[2,1-*b*]furan-1-yl acetate (4iaa)**

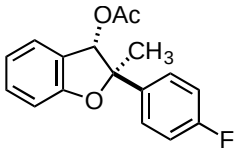



According to the General Procedure with 2-methylnaphtho[2,1-*b*]furan (29 mg, 0.2 mmol) and phenylboronic acid (37 mg, 0.3 mmol). FC (pentane/$Et_2O$ 200:1 → 10:1) gave **4iaa** as a colorless oil (56 mg, 0.18 mmol, 88%, dr 78:22).

**$^1$H NMR** ($CDCl_3$, 300 MHz) δ 7.73 (d, *J* = 8.7 Hz, 1H), 7.67 (d, *J* = 7.8 Hz, 1H), 7.51 (d, *J* = 7.5 Hz, 2H), 7.43 (d, *J* = 8.4 Hz, 1H), 7.70 (d, *J* = 8.4 Hz, 1H) 7.42 (t, *J* = 7.5 Hz, 1H), 7.34 - 7.08 (m, 4H), 6.76 (s, 1H), 2.08 (s, 3H), 1.58 (s, 3H); **$^{13}$C NMR** ($CDCl_3$, 75 MHz) δ 168.6 (C), 156.3 (C), 141.6 (C), 130.2 (CH), 128.3 (C), 127.1 (C), 126.4 (C), 126.0 (CH), 125.1 (CH),

125.0 (CH), 122.5 (CH), 121.0 (CH), 119.5 (CH), 112.6 (CH), 109.7 (CH), 89.8 (C), 77.4 (CH), 20.6 ($CH_3$), 18.5 ($CH_3$); **HRMS** (**ESI**) *m/z* = 341.1148 calcd for $C_{21}H_{18}O_3$ $[M+Na]^+$, found: 341.1148; **IR** (neat): 2361, 2342, 1734, 1636, 1370, 1218, 1016, 970, 809, 700.

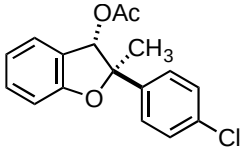
**(4-Fluorophenyl)-2-methyl-2,3-dihydrobenzofuran-3-yl acetate (4aba)**




According to the General Procedure with 2-methylbenzofuran (26 mg, 0.2 mmol) and *p*-fluorophenylboronic acid (42 mg, 0.3 mmol). FC (pentane/$Et_2O$ 200:1 → 10:1) gave **4aba** as a colorless oil (48 mg, 0.17 mmol, 84%, dr 91:9).

**$^1$H NMR** ($CDCl_3$, 300 MHz) δ 7.54 - 7.50 (m, 2H), 7.33 - 7.28 (m, 2H), 7.03 - 6.97 (m, 3H), 6.97 - 6.91 (m, 1H), 6.29 (s, 1H), 2.19 (s, 3H), 1.72 (s, 1H); **$^{13}$C NMR** ($CDCl_3$, 75 MHz) δ 170.8 (C) 163.6 (C, *J* = 245 Hz, C–F) 160.4 (C, *J* = 245 Hz, C–F), 160.0 (C), 139.8(C), 131.3 (CH), 126.9 (CH), 123.9 (C), 121.3 (CH), 115.3 (CH) 115.1 (CH), 110.1 (CH), 90.8 (C), 80.4 (CH), 23.1 ($CH_3$), 20.9 ($CH_3$); **HRMS** (**ESI**) *m/z* = 309.0897 calcd for $C_{17}H_{15}FO_3$ $[M+Na]^+$, found: 309.0902. **IR** (neat): 2361, 2342, 1734, 1603, 1509, 1480, 1372, 1227, 1070, 1015, 836, 751.

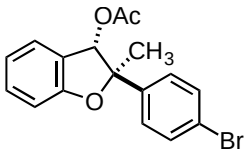
**(4-Chlorophenyl)-2-methyl-2,3-dihydrobenzofuran-3-yl acetate (4aca)**




According to the General Procedure with 2-methylbenzofuran (26 mg, 0.2 mmol) and *p*-chlorophenylboronic acid (47 mg, 0.3 mmol). FC (pentane/$Et_2O$ 200:1 → 10:1) gave **4aca** as a colorless oil (29 mg, 0.095 mmol, 48%, dr 89:11).

**$^1$H NMR** ($CDCl_3$, 300 MHz) δ 7.50 (dd, *J* = 6.6 Hz, *J* = 2.1 Hz, 2H), 7.41 - 7.26 (m, 4H), 7.01 (d, *J* = 7.8 Hz, 1H), 6.95 - 6.90 (m, 1H), 6.30 (s, 1H), 2.19 (s, 3H), 1.71 (s, 3H); **$^{13}$C NMR** ($CDCl_3$, 75 MHz) δ 170.8 (C), 159.9 (C), 142.6 (C), 133.3 (C), 131.3 (CH), 128.5 (CH), 126.9 (CH), 126.5 (CH), 123.8 (C), 121.4 (CH), 110.1 (CH), 90.7 (C), 80.2 (CH), 22.9 ($CH_3$), 20.9 ($CH_3$); **HRMS** (**ESI**) *m/z* = 325.0602 calcd for $C_{17}H_{15}ClO_3$ $[M+Na]^+$, found: 325.0601. **IR** (neat): 2361, 2342, 1734, 1481, 1231, 1013, 753.

**(4-Bromophenyl)-2-methyl-2,3-dihydrobenzofuran-3-yl acetate (4ada)**

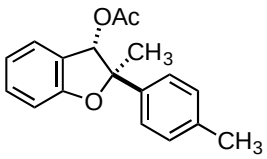



According to the General Procedure with 2-methylbenzofuran (26 mg, 0.2 mmol) and *p*-bromophenylboronic acid (60 mg, 0.3 mmol). FC (pentane/$Et_2O$ 200:1 → 10:1) gave **4ada** as a colorless oil (38 mg, 0.11

mmol, 55%, dr 89:11).

**$^1$H NMR** ($CDCl_3$, 300 MHz) δ 7.54 - 7.44 (m, 4H), 7.38 - 7.30 (m, 2H), 7.05 (d, *J* = 8.1 Hz, 1H), 6.97 (t, *J* = 7.2 Hz, 1H), 6.30 (s, 1H), 2.22 (s, 3H), 1.73 (s, 3H); **$^{13}$C NMR** ($CDCl_3$, 75 MHz) δ 170.2 (C), 159.3 (C), 142.6 (C), 130.9 (CH), 130.8 (CH), 130.2 (C), 127.4 (CH), 126.3 (CH), 123.1 (C), 120.8 (CH), 109.5 (CH), 90.1 (C), 79.6 (CH), 22.3 ($CH_3$), 20.3 ($CH_3$); **HRMS** (**ESI**) *m/z* = 369.0097 calcd for $C_{17}H_{15}BrO_3$ $[M+Na]^+$, found: 325.0101. **IR** (neat): 2361, 2342, 1738, 1481, 1230, 1009, 753.

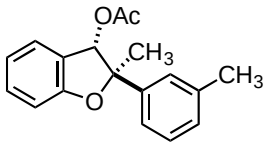
**2-Methyl-(*p*-tolyl)-2,3-dihydrobenzofuran-3-yl acetate (4aea)**




According to the General Procedure with 2-methylbenzofuran (26 mg, 0.2 mmol) and *p*-tolylboronic acid (41 mg, 0.3 mmol). FC (pentane/$Et_2O$ 200:1 → 10:1) gave **4aea** as a colorless oil (33 mg, 0.12 mmol, 58%, dr 88:12).

**$^1$H NMR** ($CDCl_3$, 300 MHz) δ 7.43 (d, *J* = 8.1 Hz, 2H), 7.26 - 7.16 (m, 2H), 7.04 (d, *J* = 8.0 Hz, 2H), 7.02 (d, *J* = 8.0 Hz, 1H), 6.93 - 6.88 (m, 1H), 6.32 (s, 1H), 2.31 (s, 3H), 2.18 (s, 3H), 1.73 (s, 3H); **$^{13}$C NMR** ($CDCl_3$, 75 MHz) δ 170.7 (C), 160.2 (C), 141.1 (C), 137.1 (C), 131.2 (CH), 129.0 (CH), 126.9 (CH), 124.9 (CH), 124.3 (C), 121.3 (CH), 110.1 (CH), 91.1 (C), 80.5 (CH), 23.1 ($CH_3$), 21.0 ($CH_3$), 20.9 ($CH_3$); **HRMS** (**ESI**) *m/z* = 305.1148 calcd for $C_{18}H_{18}O_3$ $[M+Na]^+$, found: 305.1151. **IR** (neat): 1734, 1601, 1479, 1230, 1016, 919, 817, 751.

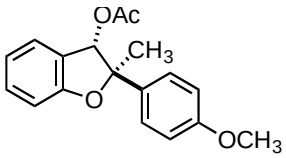
**2-Methyl-(*m*-tolyl)-2,3-dihydrobenzofuran-3-yl acetate (4afa)**




According to the General Procedure with 2-methylbenzofuran (26 mg, 0.2 mmol) and *m*-tolylboronic acid (41 mg, 0.3 mmol). FC (pentane/$Et_2O$ 200:1 → 10:1) gave **4afa** as a colorless oil (29 mg, 0.10 mmol, 51%, dr 86:14).

**$^1$H NMR** ($CDCl_3$, 300 MHz) δ 7.25 - 7.18 (m, 5H), 7.15 - 7.10 (m, 1H), 7.05 (d, *J* = 7.8 Hz, 2H), 7.02 (d, *J* = 8.4 Hz, 1H), 6.93 - 6.88 (m, 1H), 6.33 (s, 1H), 2.33 (s, 3H), 2.17 (s, 3H), 1.72 (s, 3H); **$^{13}$C NMR** ($CDCl_3$, 75 MHz) δ 170.8 (C), 160.3 (C), 144.1 (C), 138.1 (C), 131.3(CH), 128.4(CH), 128.3 (CH), 127.0 (CH), 125.7 (CH), 124.4 (C), 122.2 (CH), 121.1 (CH), 110.2 (CH), 91.2 (C), 80.5 (CH), 23.2 ($CH_3$), 21.6 ($CH_3$), 21.0 ($CH_3$); **HRMS** (**ESI**) *m/z* = 305.1148 calcd for $C_{18}H_{18}O_3$ $[M+Na]^+$, found: 305.1149; **IR** (neat): 2361, 2342, 1736, 1479, 1219, 1017, 751, 706.

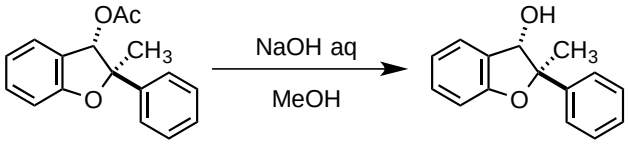
**2-(4-Methoxyphenyl)-methyl-2,3-dihydrobenzofuran-3-yl acetate (4aga)**




According to the General Procedure with 2-methylbenzofuran (26 mg, 0.2 mmol) and 4-methoxyphenylboronic acid (46 mg, 0.3 mmol). FC (pentane/$Et_2O$ 200:1 → 10:1) gave **4aga** as a colorless oil (17 mg, 0.057 mmol, 28%, dr 83:17).

**$^1$H NMR** ($CDCl_3$, 300 MHz) δ 7.46 (dd, *J* = 5.1 Hz, *J* = 3.0 Hz, 2H), 7.39 - 7.27 (m, 2H), 7.02 - 6.89 (m, 2H), 6.85 (dd, *J* = 5.1 Hz, *J* = 3.0 Hz, 2H), 6.30 (s, 1H), 3.77 (s, 3H), 2.18 (s, 3H), 1.72 (s, 3H); **$^{13}$C NMR** ($CDCl_3$, 75 MHz) δ 170.7 (C), 160.1 (C), 158.8 (C), 136.0 (C), 131.1 (CH), 126.9 (CH), 126.1 (CH), 124.2 (C), 121.1 (CH), 113.7 (CH), 110.0 (CH), 90.9 (C), 80.4 (CH), 55.1 ($CH_3$), 23.0 ($CH_3$), 20.9 ($CH_3$); **HRMS** (**ESI**) *m/z* = 321.1097 calcd for $C_{18}H_{18}O_4$ $[M+Na]^+$, found: 321.1097; **IR** (neat): 2361, 2342, 1734, 1812, 1512, 1372, 1231, 1019, 753.

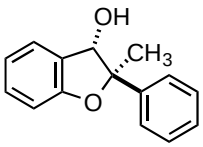
**Hydrolysis of 4aaa**




**4aaa**
dr (90:10)

90%
dr (90:10)

**2-Methyl-2-phenyl-2,3-dihydrobenzofuran-3-ol**




**4aaa** (127 mg, 0.47 mmol, dr 90:10), MeOH (15mL) and 1M NaOH solution (3.7 mL) were added to a reaction tube and stirred overnight at room temperature. The mixture was extracted with $CH_2Cl_2$ (3 x 5 mL). The combined organic layers were dried over $MgSO_4$ and the volatiles were removed under reduced pressure to afford 2-methyl-2-phenyl-2,3-dihydrobenzofuran-3-ol as a colorless solid (96 mg, 0.42 mmol, 90%, dr 90:10). The solid was recrystallized from hexane solution to give diastereoisomerically pure alcohol as colorless crystals (45 mg, 0.20 mmol, 42%).

**$^1$H NMR** ($CDCl_3$, 300 MHz) δ 7.43 (m, 2H), 7.35 - 7.21 (m, 5H), 6.99 (d, 8.1 Hz, 1H), 6.94 - 6.89 (m, 1H), 5.14 (d, *J* = 8.7 Hz, 1H), 2.04 (d, *J* = 8.7 Hz, 1H), 1.70 (s, 3H); **$^{13}$C NMR** ($CDCl_3$, 75 MHz) δ 159.3(C), 145.1 (C), 130.8 (CH), 128.4 (CH), 128.0 (C), 127.2 (CH), 126.1 (CH), 124.7 (CH), 121.2 (CH), 110.4 (CH), 92.3 (C), 80.4 (CH), 22.5 ($CH_3$); **HRMS** (**ESI**) *m/z* = 249.0886 calcd for $C_{15}H_{14}O_2$ $[M+Na]^+$, found: 249.0889; mp: 102 - 103 °C; **IR** (neat): 3328, 2361, 2342, 1599, 1477, 1252, 1022, 919, 752, 700.

### 3. X-ray Crystallography

X-ray data set was collected with a Nonius KappaCCD diffractometer. Programs used: data collection COLLECT (Nonius B.V., 1998), data reduction Denzo-SMN (Z. Otwinowski, W. Minor, *Methods in Enzymology*, **1997**, *276*, 307-326), absorption correction Denzo (Z.Otwinowski, D. Borek, W. Majewski & W. Minor, *Acta Cryst.* **2003**, *A59*, 228-234), structure solution SHELXS-97 (G.M. Sheldrick, *Acta Cryst.* **1990**, *A46*, 467-473), structure refinement SHELXL-97 (G.M. Sheldrick, *Acta Cryst.* **2008**, *A64*, 112-122), graphics XP (BrukerAXS, 2000). *R* values are given for the observed reflections, $wR^2$ values for all reflections.

X-ray crystal structure analysis for **4baa**: formula $C_{20}H_{22}O_3$, $M$ = 310.38, colourless crystal, 0.30 x 0.23 x 0.10 mm, $a$ = 12.9968(1), $b$ = 13.4352(1), $c$ = 10.0076(1) Å, $\beta$ = 101.394(1)°, $V$ = 1713.03(3) Å$^3$, $\rho_{calc}$ = 1.203 gcm$^{-3}$, $\mu$ = 0.636 mm$^{-1}$, empirical absorption correction ($0.832 \leq T \leq 0.939$), $Z$ = 4, monoclinic, space group $P2_1/c$ (No. 14), $\lambda$ = 1.54178 Å, $T$ = 223(2) K, $\omega$ and $\varphi$ scans, 13135 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sin$\theta$)/$\lambda$] = 0.60 Å$^{-1}$, 2981 independent ($R_{int}$ = 0.040) and 2678 observed reflections [$I>2\sigma(I)$], 210 refined parameters, $R$ = 0.045, $wR^2$ = 0.122, max. (min.) residual electron density 0.20 (-0.19) e.Å$^{-3}$, hydrogen atoms calculated and refined as riding atoms.

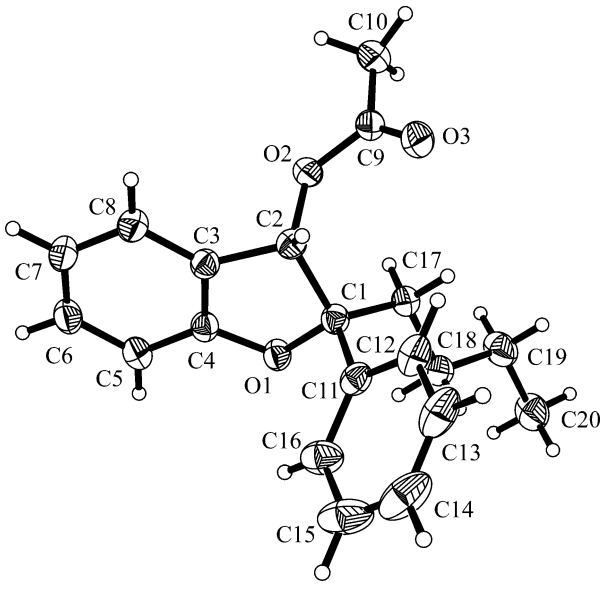



Figure S1. X-ray structure of **4baa** (thermals ellipsoids are shown with 30% probability).

X-ray crystal structure analysis for 2-methyl-2-phenyl-2,3-dihydrobenzofuran-3-ol: formula $C_{15}H_{14}O_2$, $M$ = 293.26, colourless crystal, 0.62 x 0.12 x 0.10 mm, $a$ = 25.2302(7), $b$ = 25.2302(7), $c$ = 10.3026(6) Å, α = 90, $\beta$ = 90, γ = 120°, $V$ = 5679.6(4) Å$^3$, $\rho_{calc}$ = 1.191 gcm$^{-3}$, μ = 0.623 mm$^{-1}$, empirical absorption correction (0.698 ≤ T ≤ 0.940), $Z$ = 18, trigonal, space group $R$-3 (No. 148), λ = 1.54178 Å, $T$ = 223(2) K, ω and φ scans, 16174 reflections collected (±$h$, ±$k$, ±$l$), [(sinθ)/λ] = 0.60 Å$^{-1}$, 2209 independent ($R_{int}$ = 0.054) and 1829 observed reflections [$I$>2σ($I$)], 159 refined parameters, $R$ = 0.041, $wR^2$ = 0.103, max. (min.) residual electron density 0.11 (-0.15) e.Å$^{-3}$, the hydrogen at O2 atom was refined freely; others were calculated and refined as riding atoms.

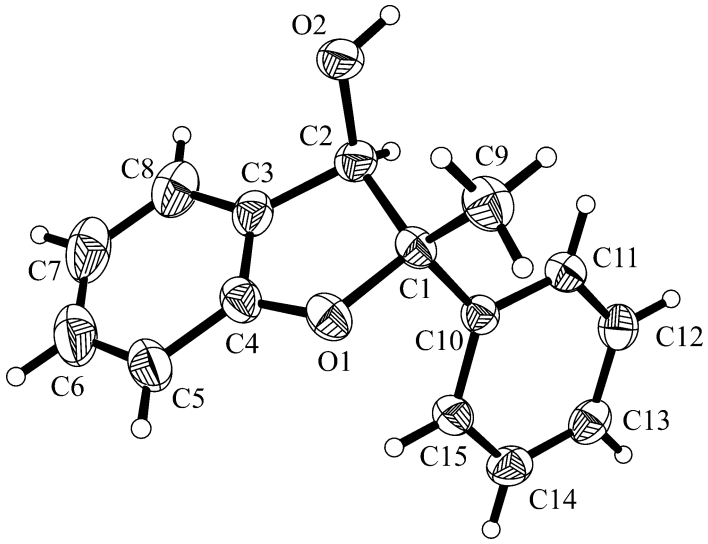
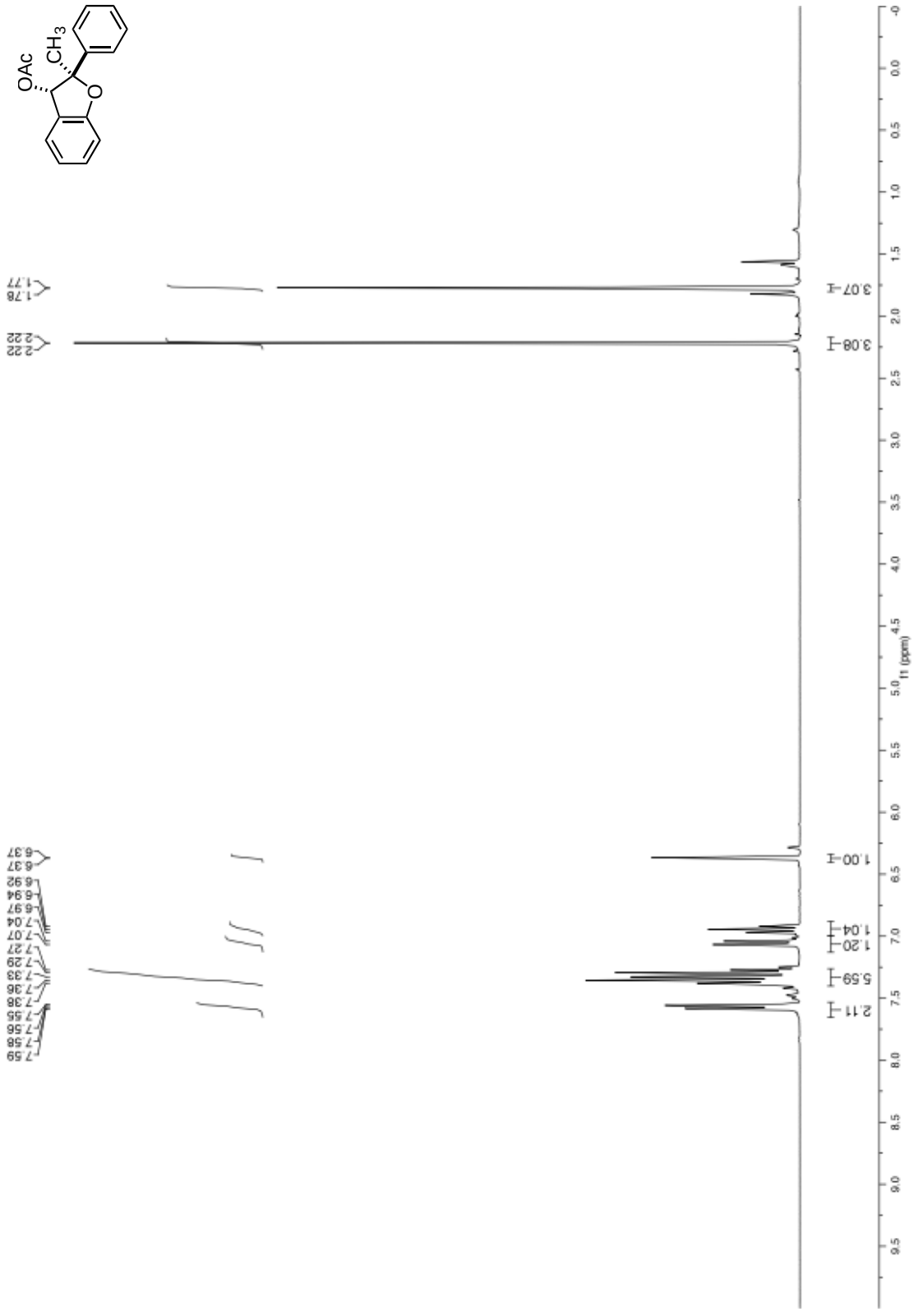



Figure S2. X-ray structure of 2-methyl-2-phenyl-2,3-dihydrobenzofuran-3-ol (thermals ellipsoids are shown with 30% probability)

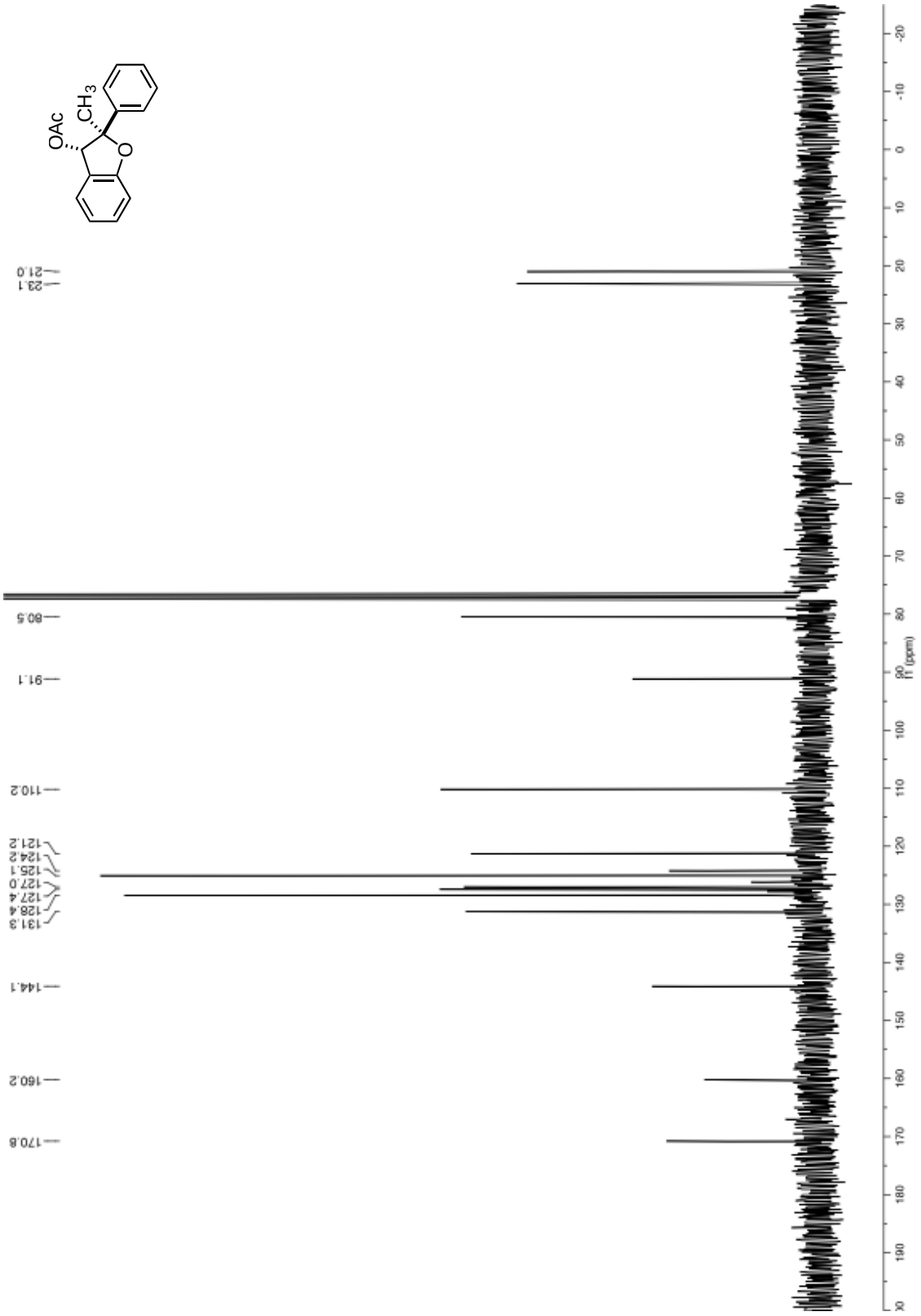
CCDC 963178 (**4baa**) and 963177 (2-methyl-2-phenyl-2,3-dihydrobenzofuran-3-ol) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44(1223)336-033, E-mail: deposit@ccdc.cam.ac.uk].

## 4. $^{1}$H and $^{13}$C NMR Spectra

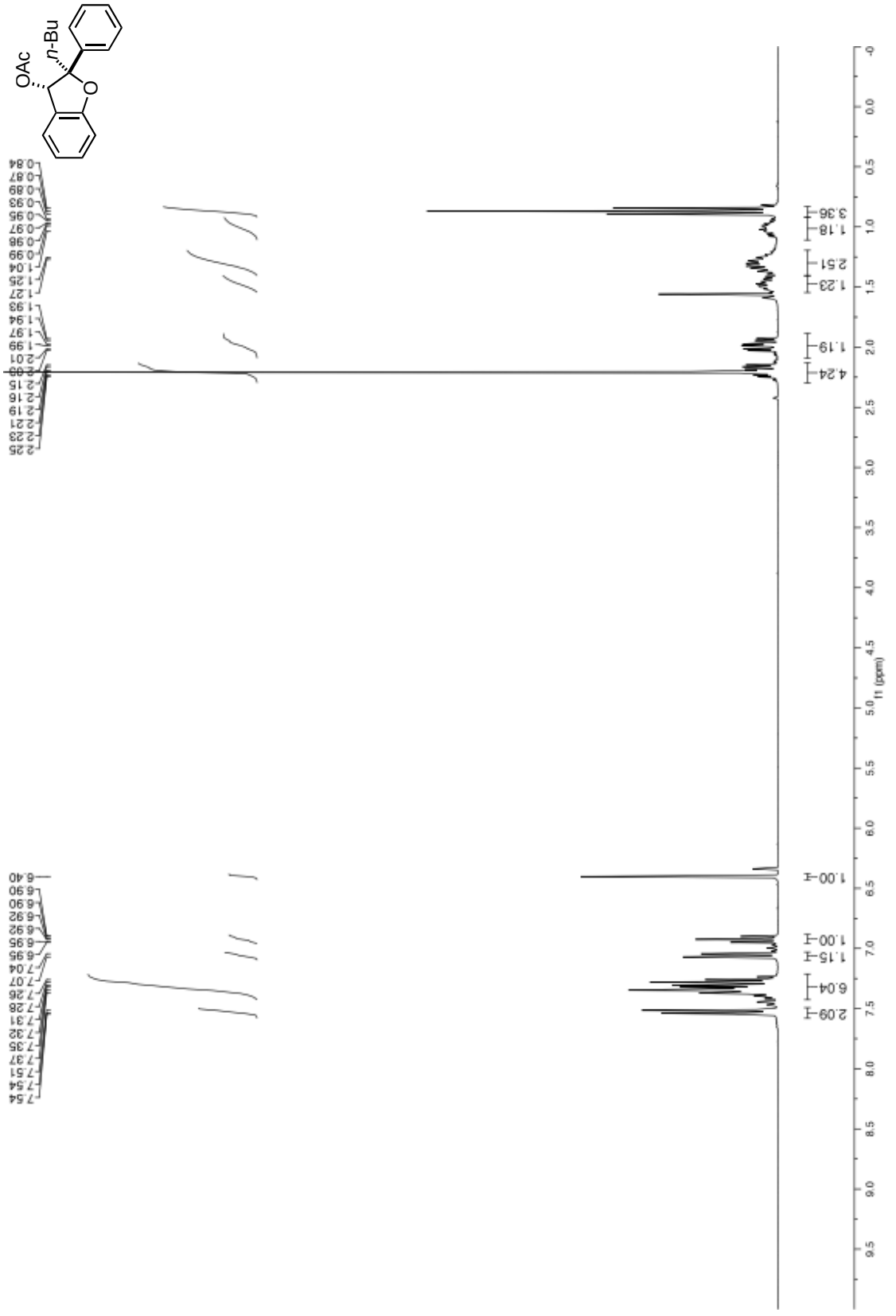
$^{1}$H NMR spectrum of **4aaa** (300 MHz, $CDCl_3$)



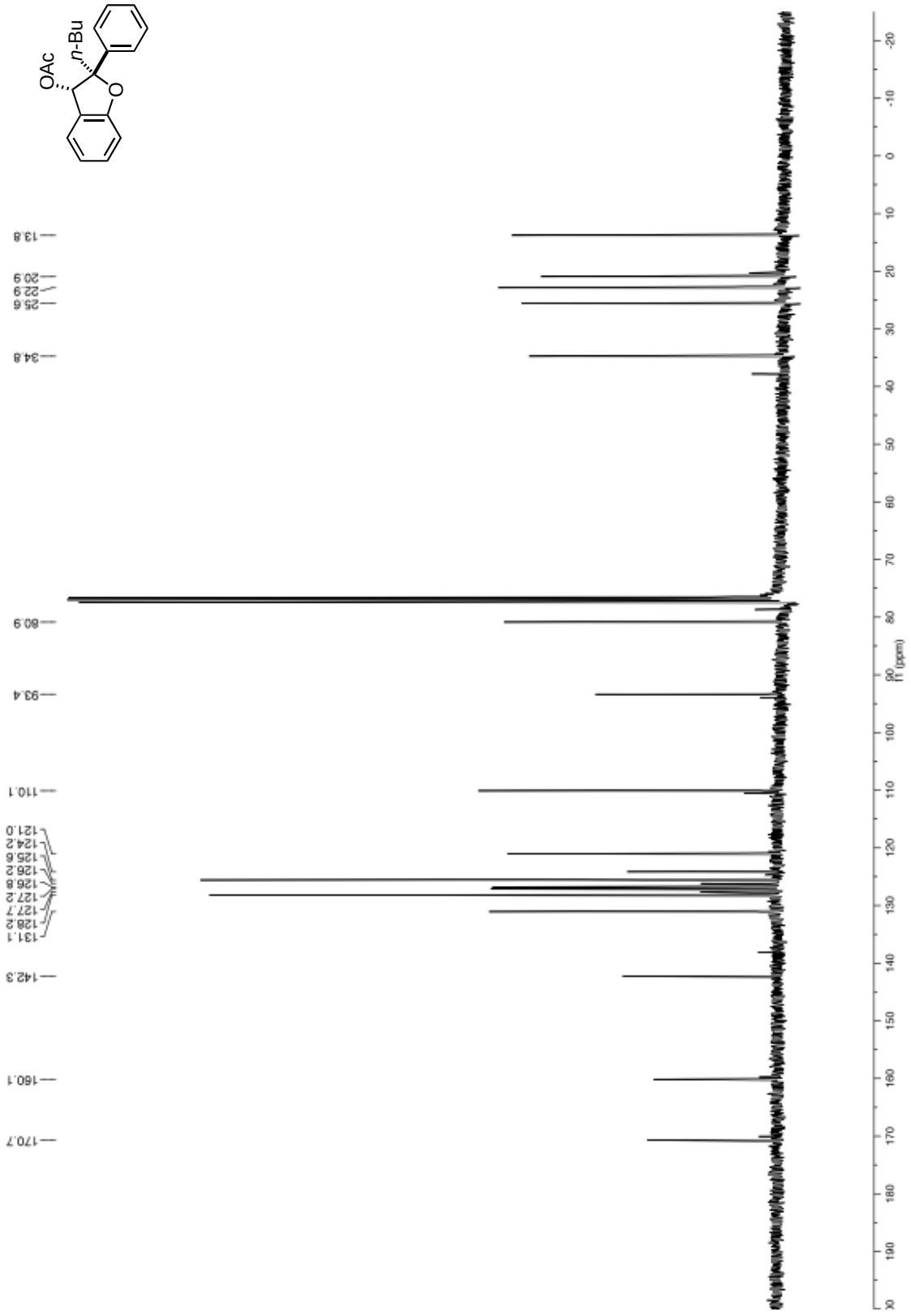
$^{13}$C NMR spectrum of **4aaa** (75 MHz, $CDCl_3$)



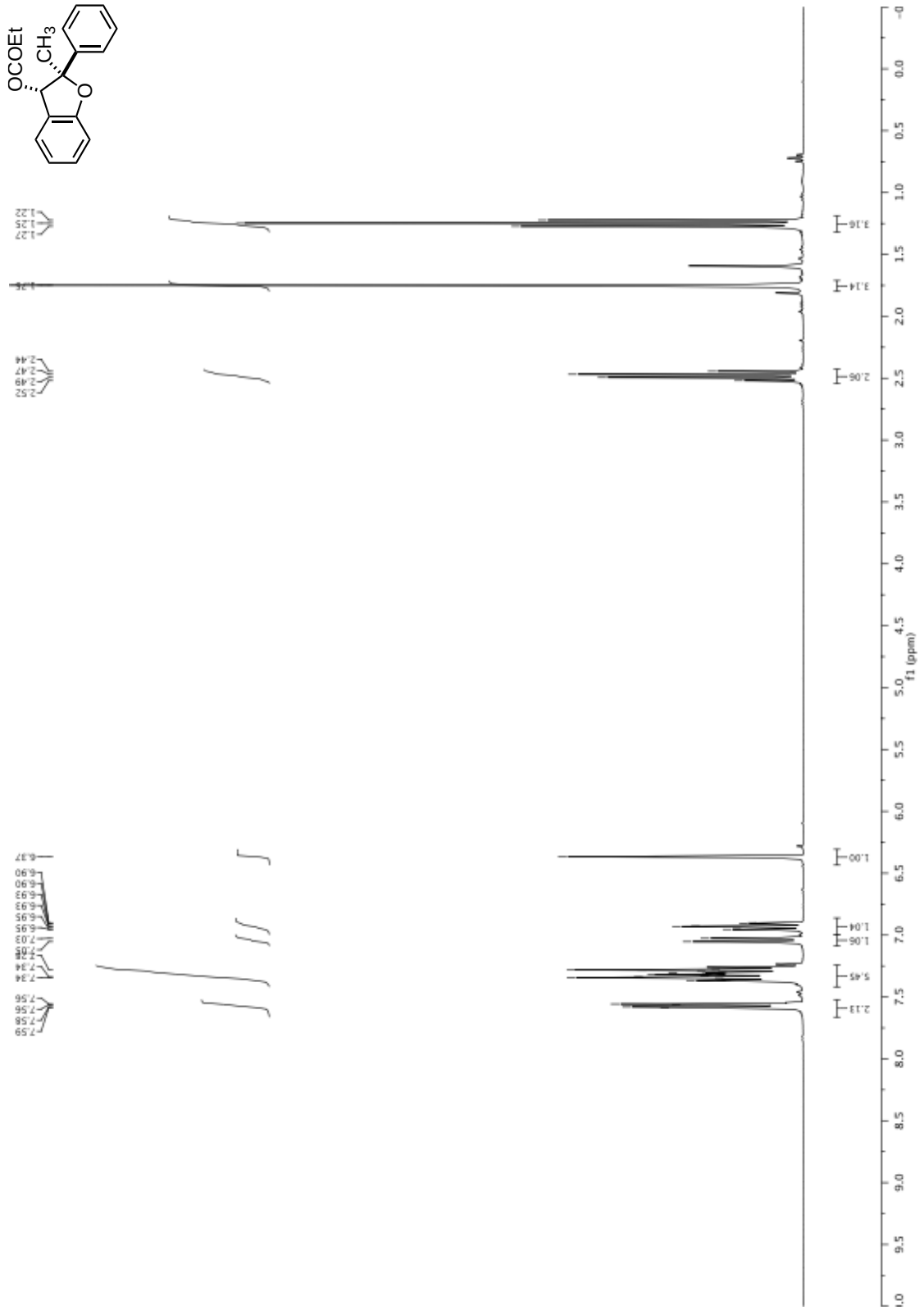
$^1$H NMR spectrum of **4baa** (300 MHz, $CDCl_3$)



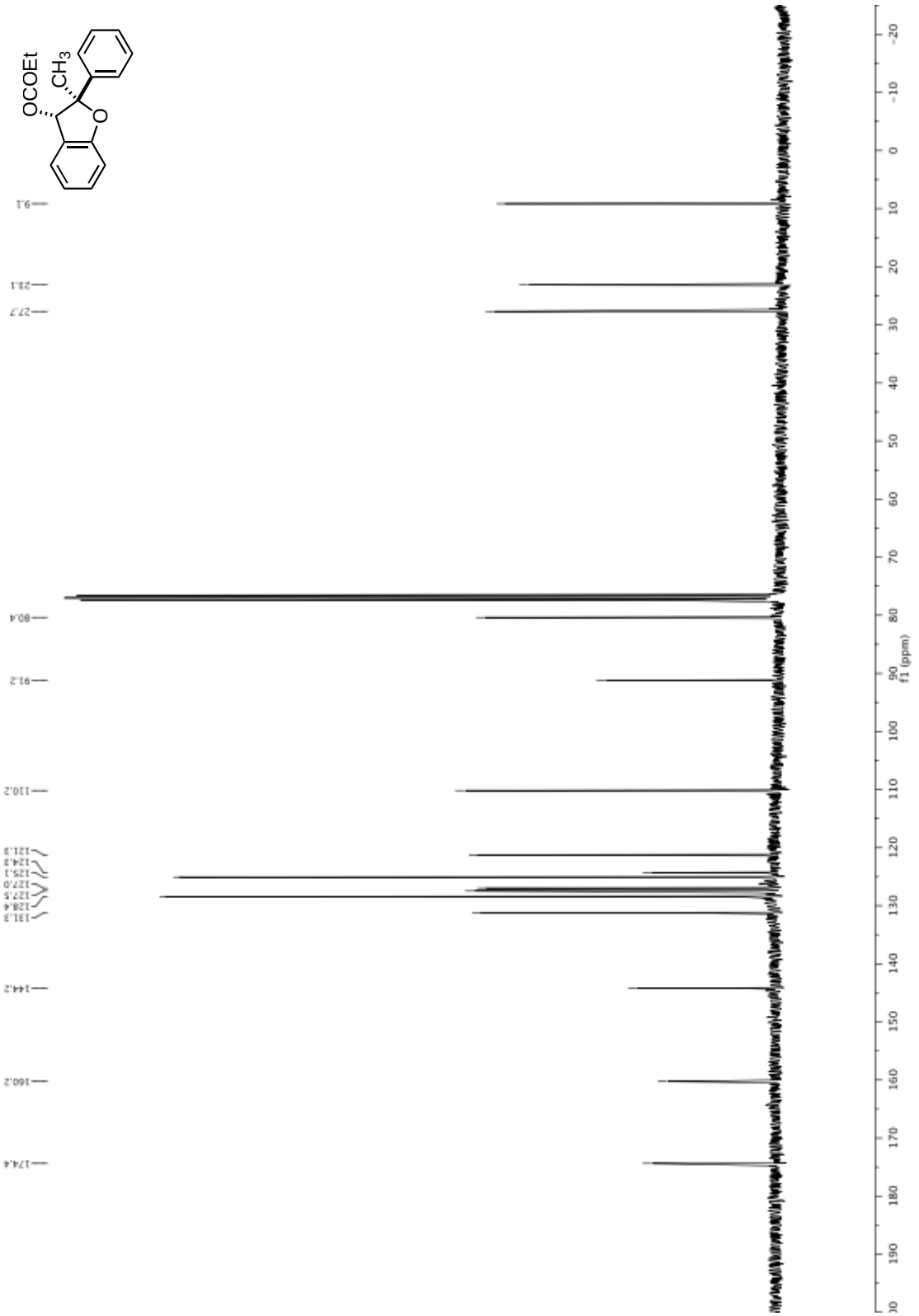
$^{13}$C NMR spectrum of **4baa** (75 MHz, $CDCl_3$)



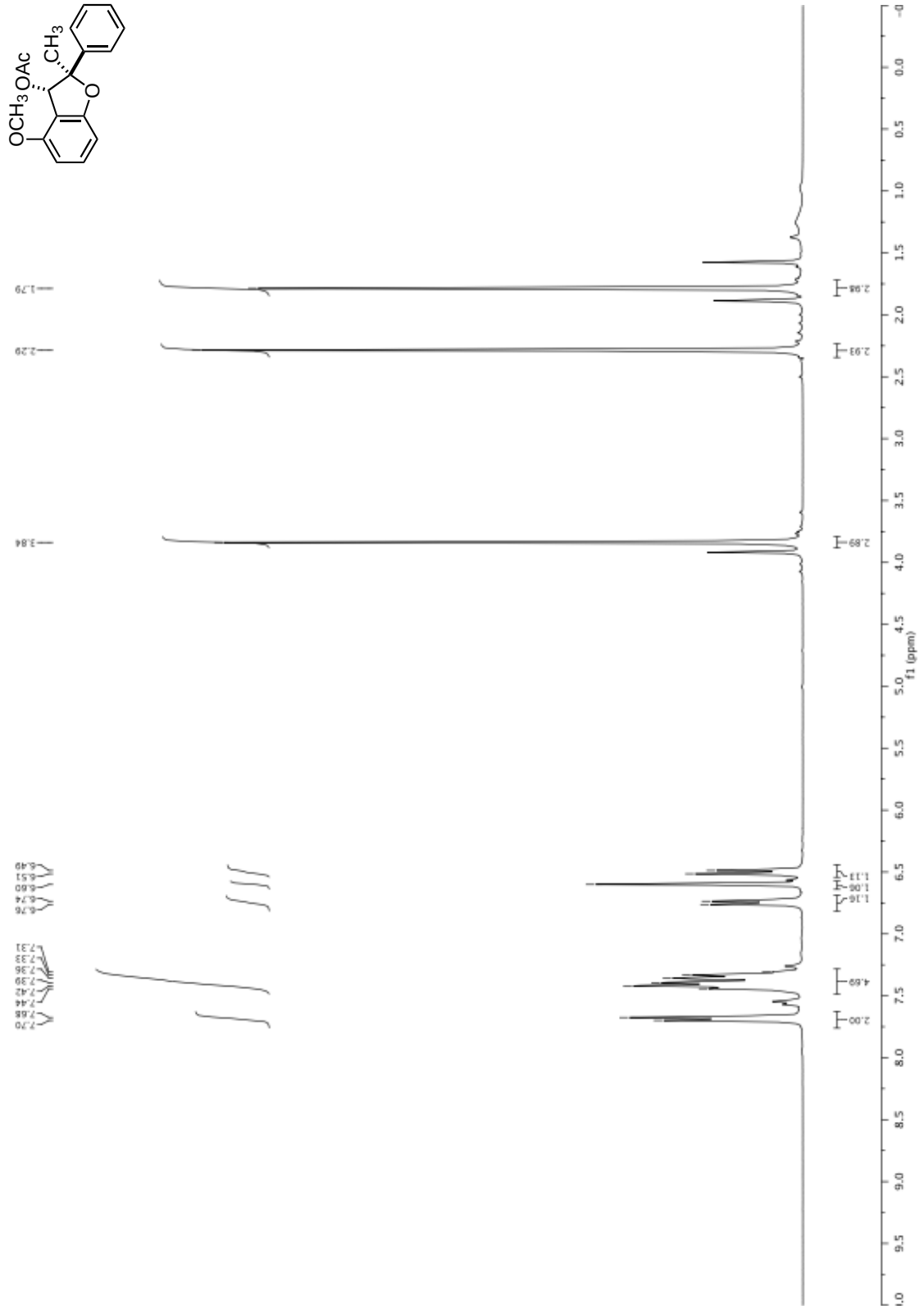
$^1$H NMR spectrum of **4aab** (300 MHz, $CDCl_3$)



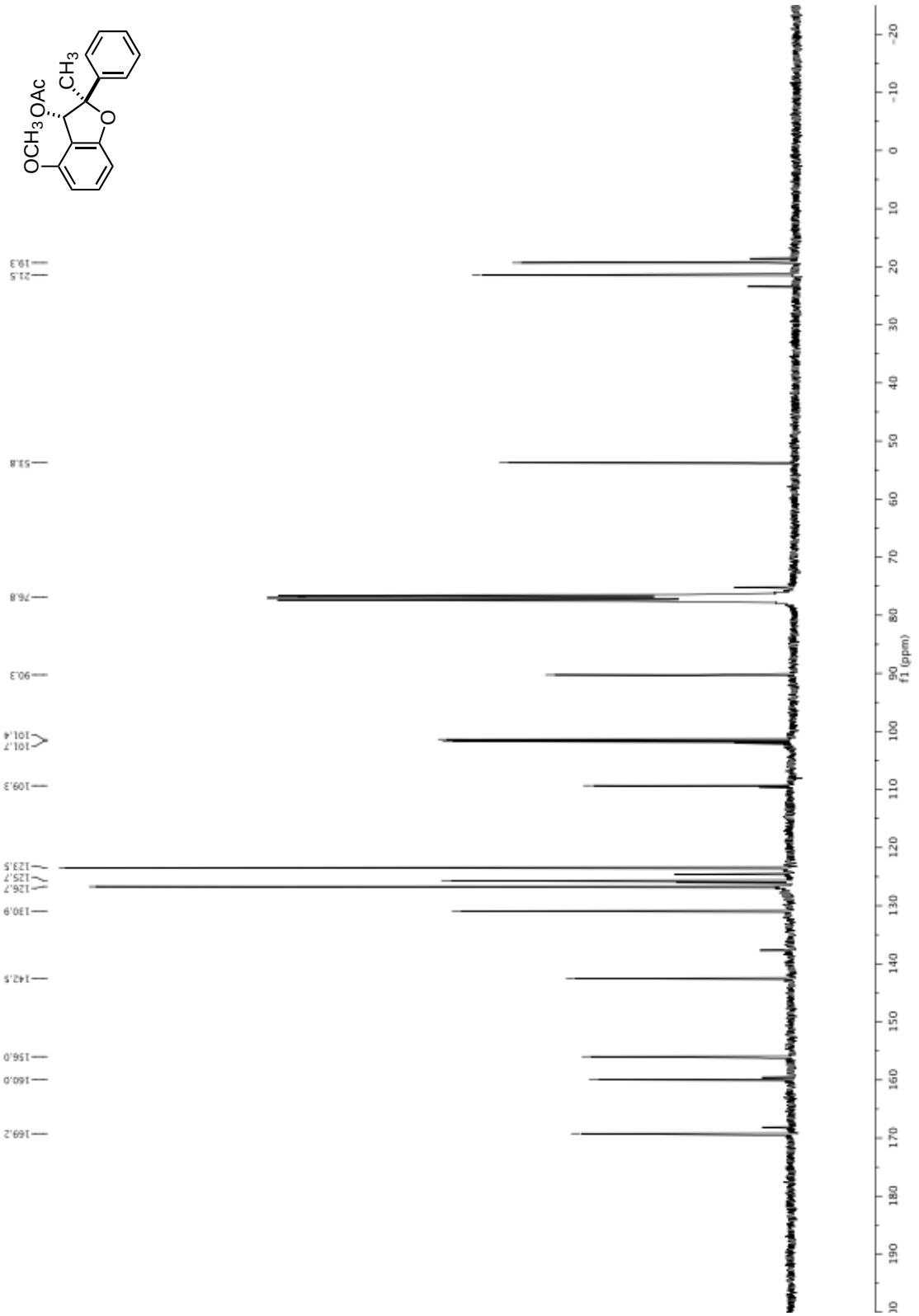
$^{13}$C NMR spectrum of **4aab** (75 MHz, $CDCl_3$)



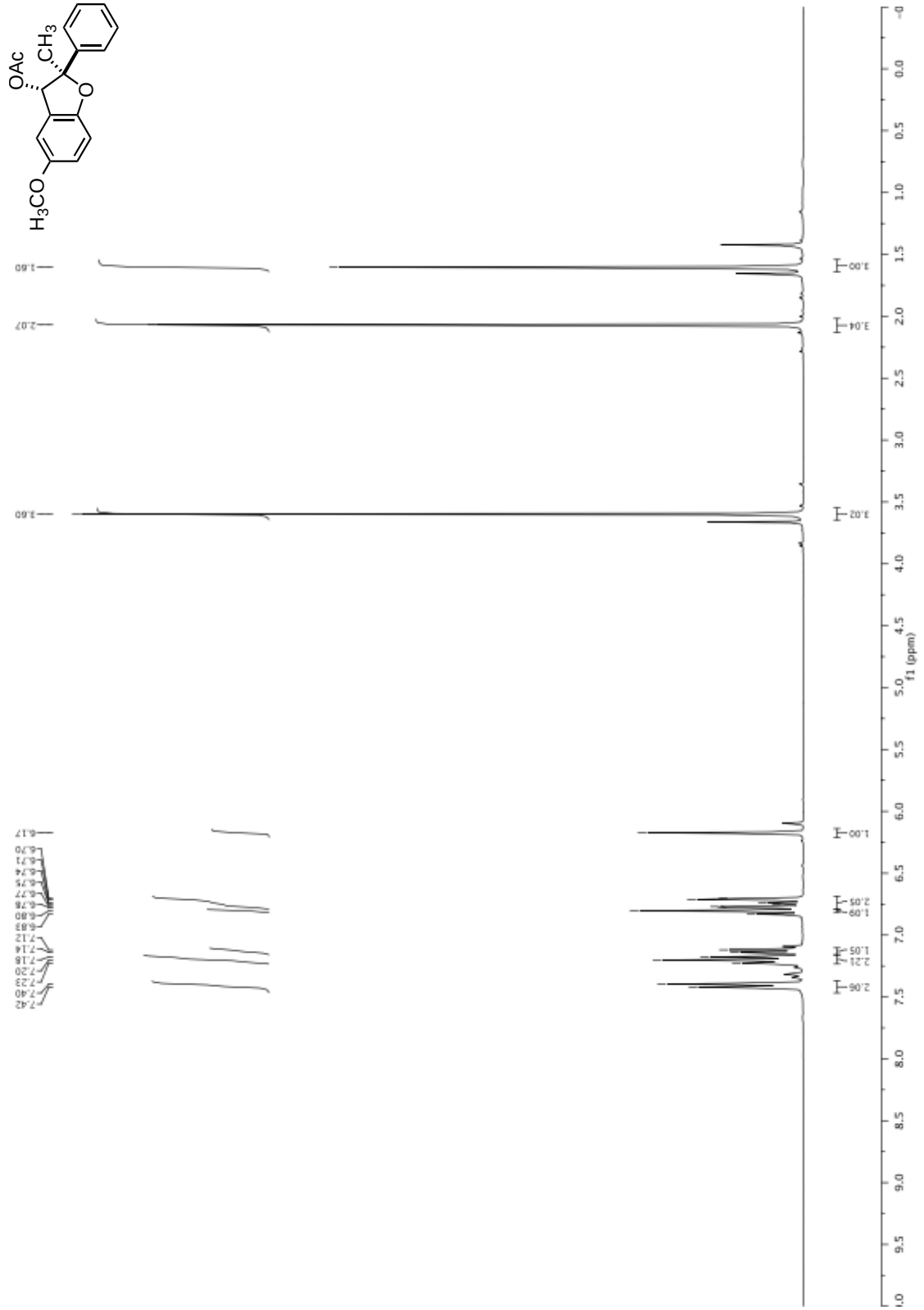
$^1$H NMR spectrum of **4caa** (300 MHz, $CDCl_3$)



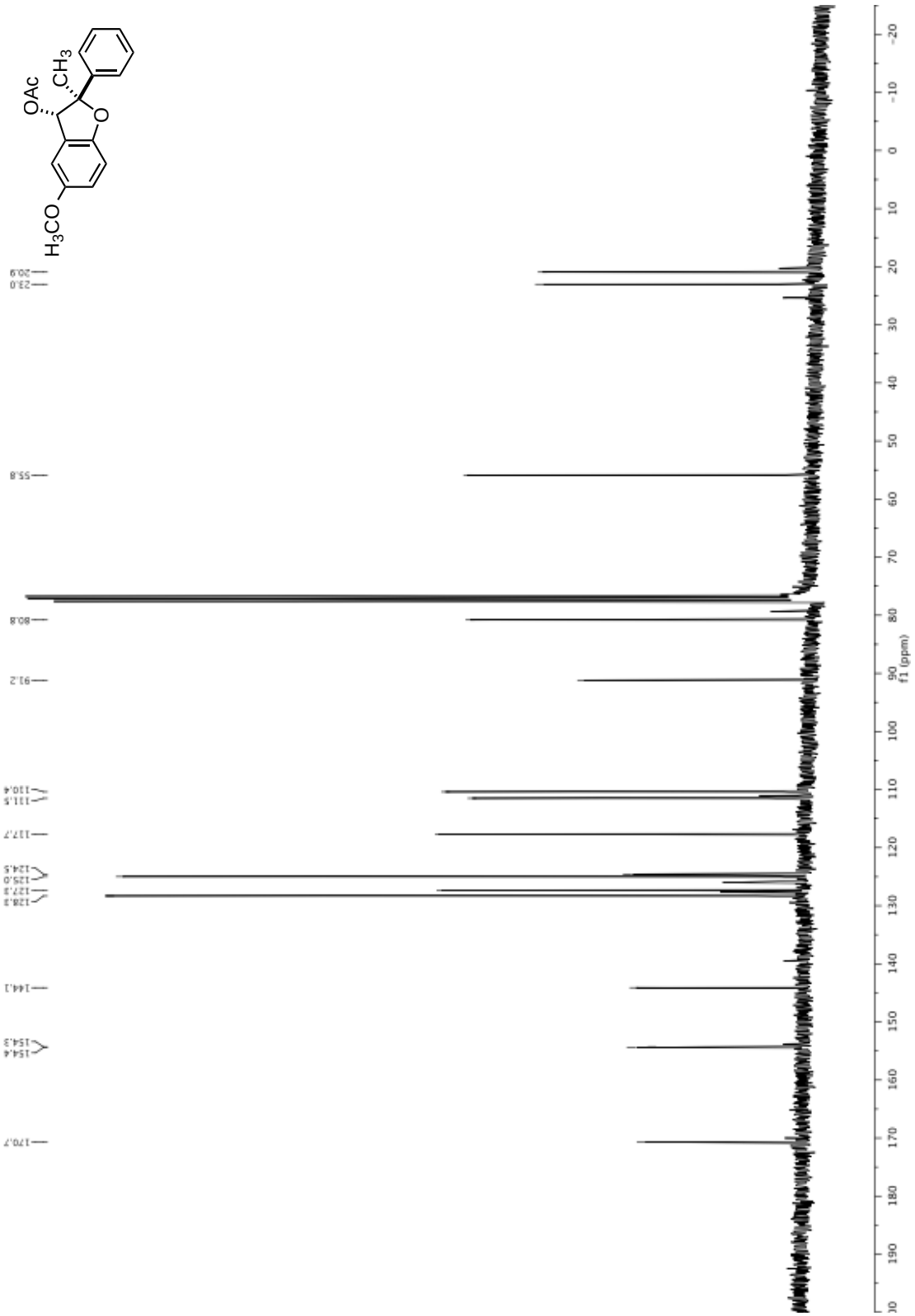
$^{13}$C NMR spectrum of **4caa** (75 MHz, $CDCl_3$)



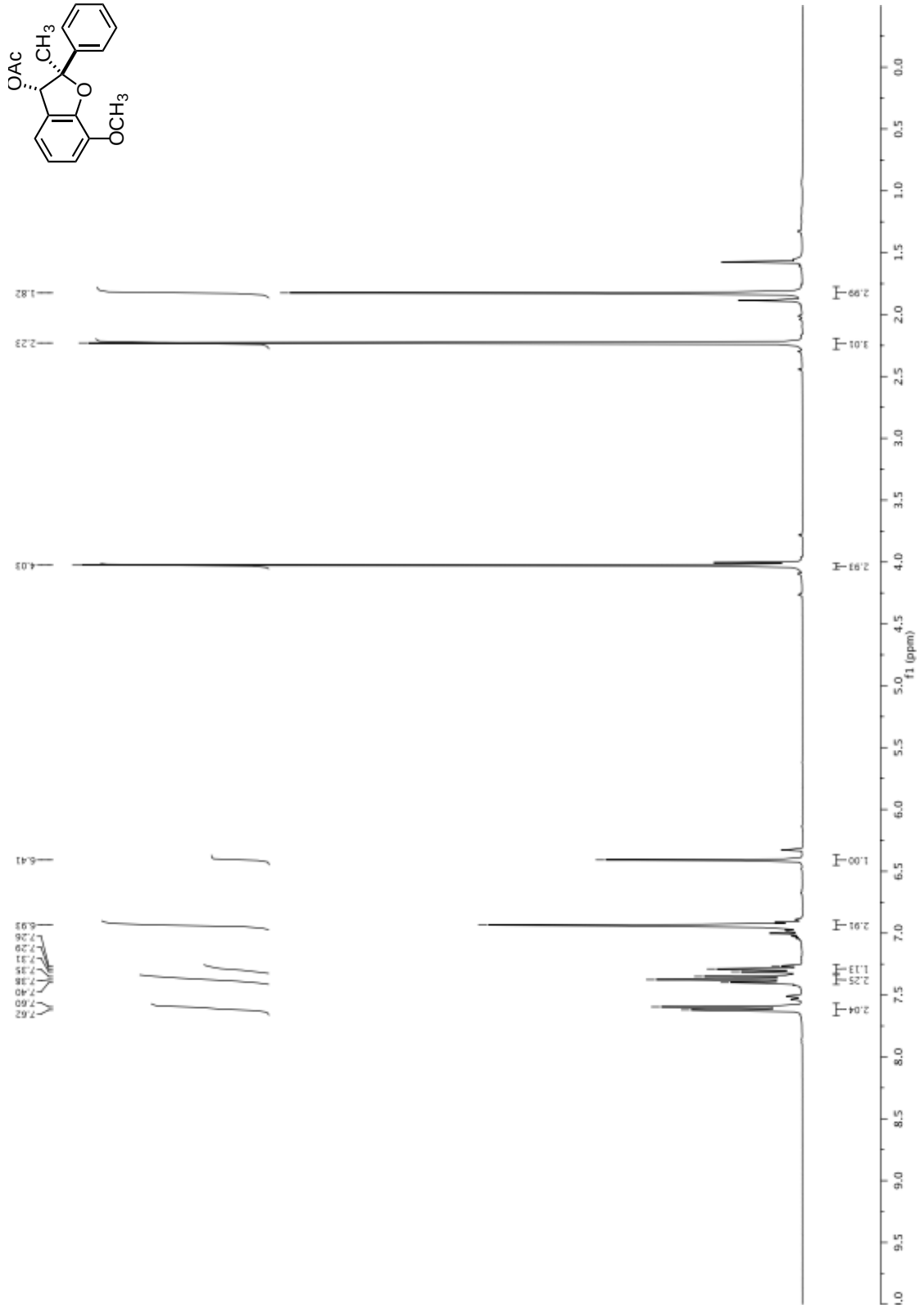
$^1$H NMR spectrum of **4daa** (300 MHz, $CDCl_3$)



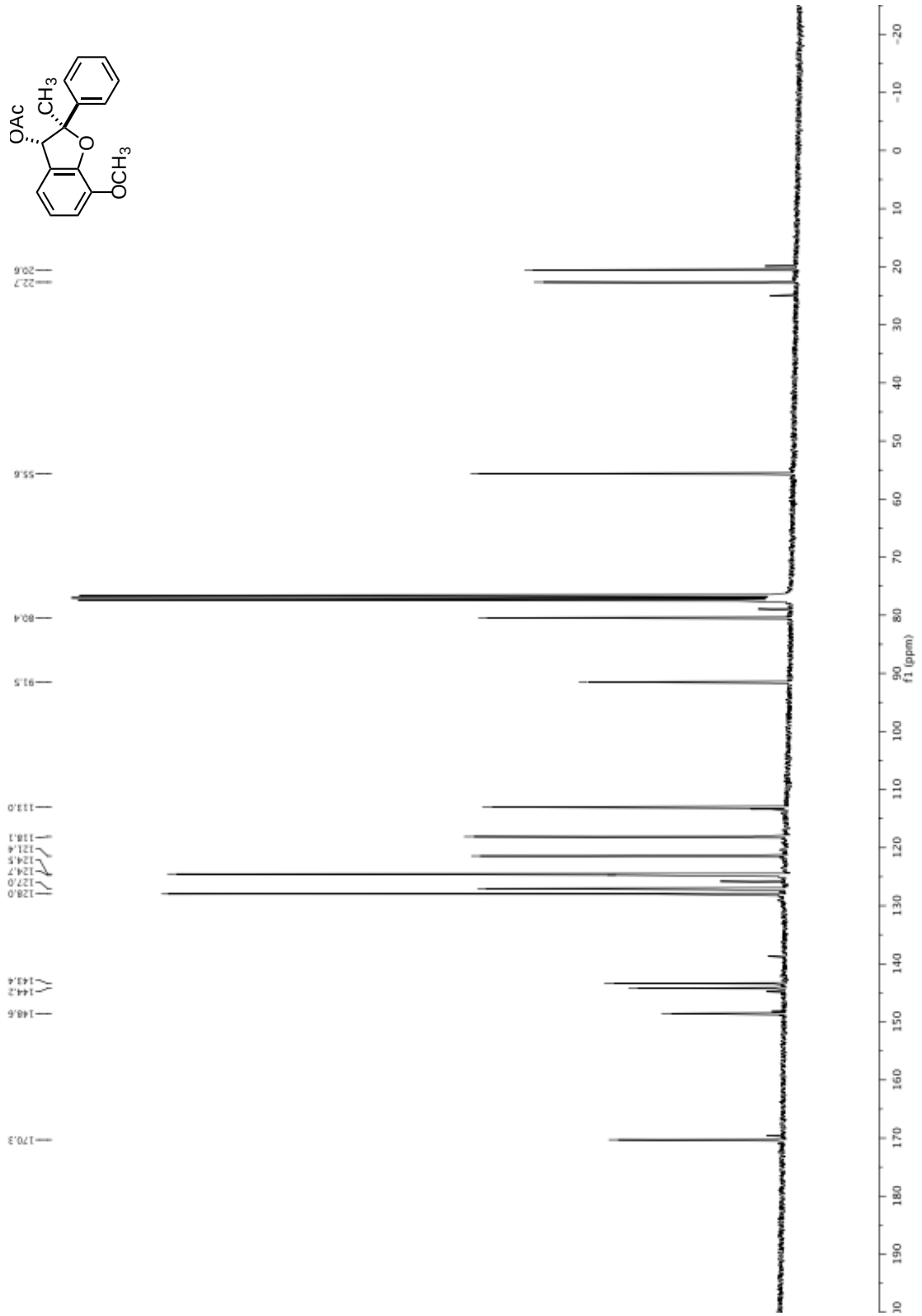
$^{13}$C NMR spectrum of **4daa** (75 MHz, $CDCl_3$)



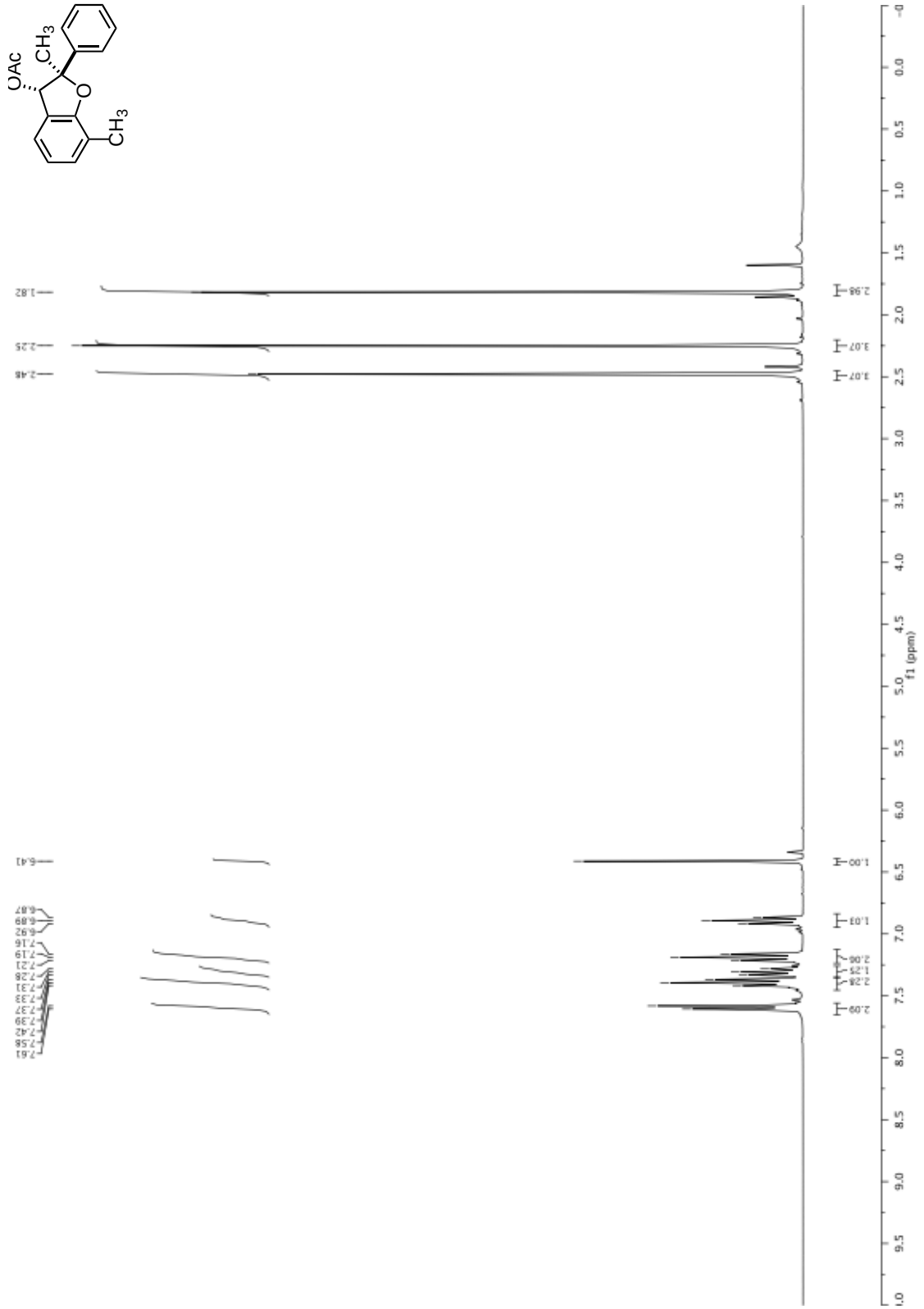
$^1$H NMR spectrum of **4eaa** (300 MHz, $CDCl_3$)



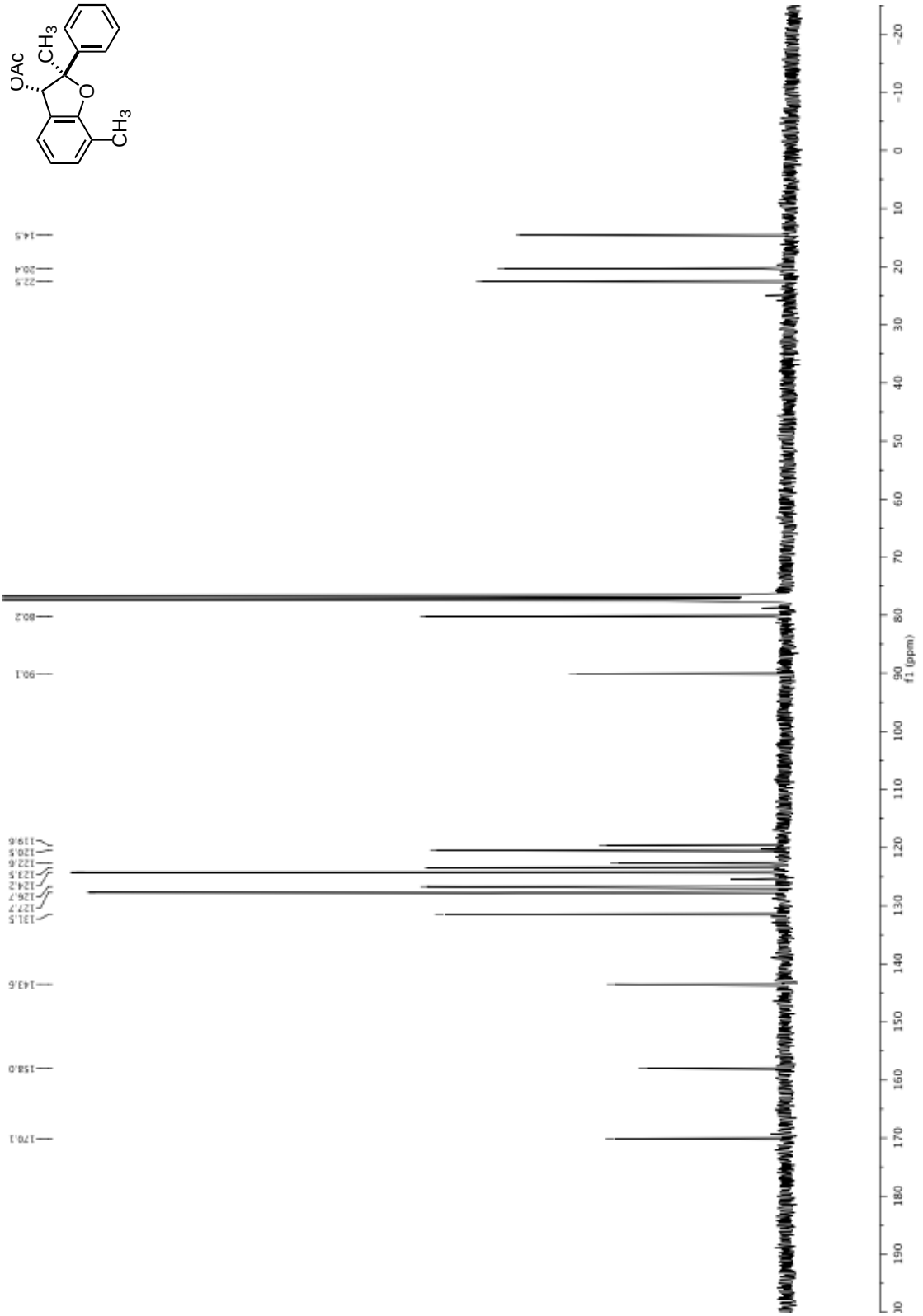
$^{13}$C NMR spectrum of **4eaa** (75 MHz, $CDCl_3$)



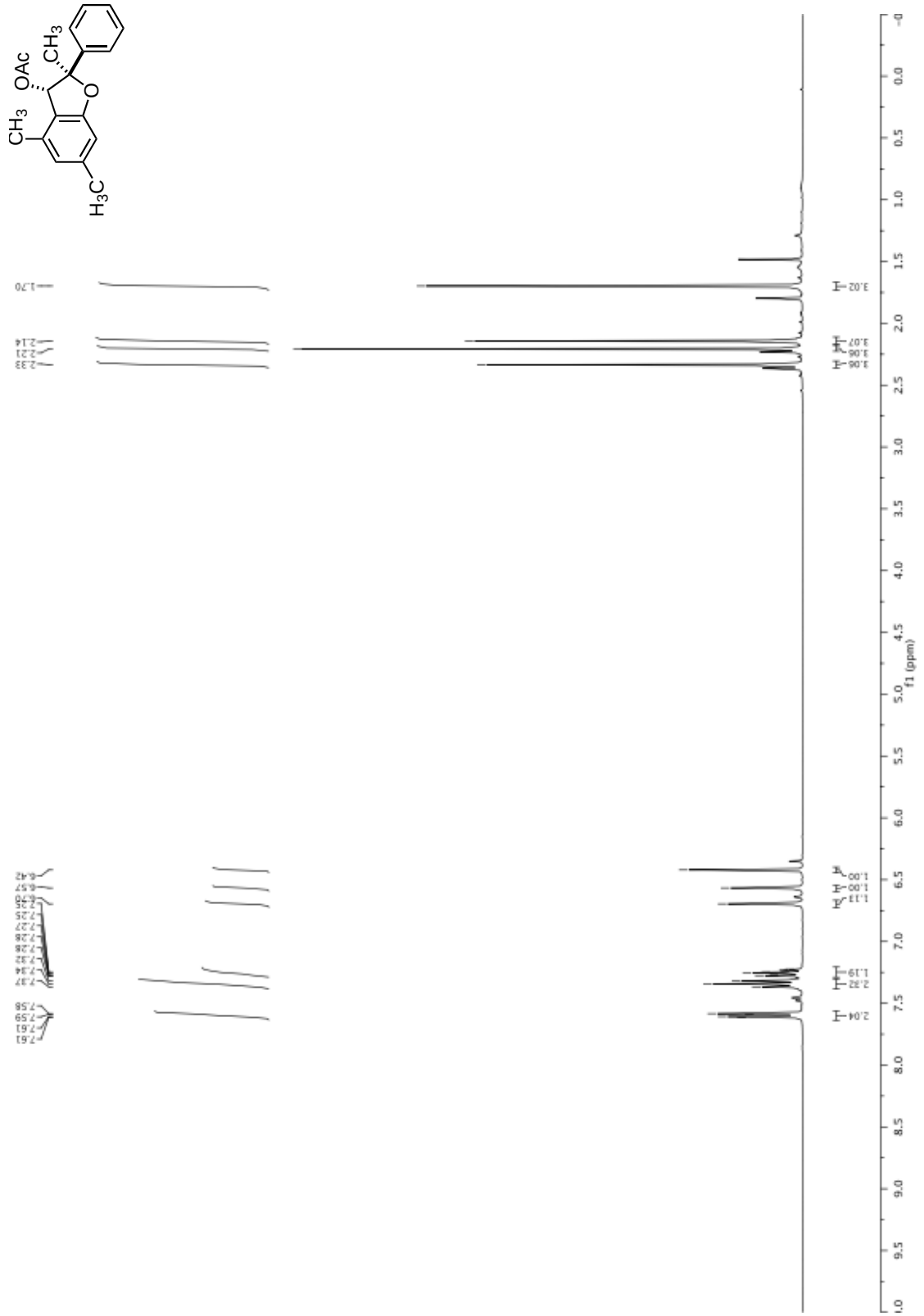
$^1$H NMR spectrum of **4faa** (300 MHz, $CDCl_3$)



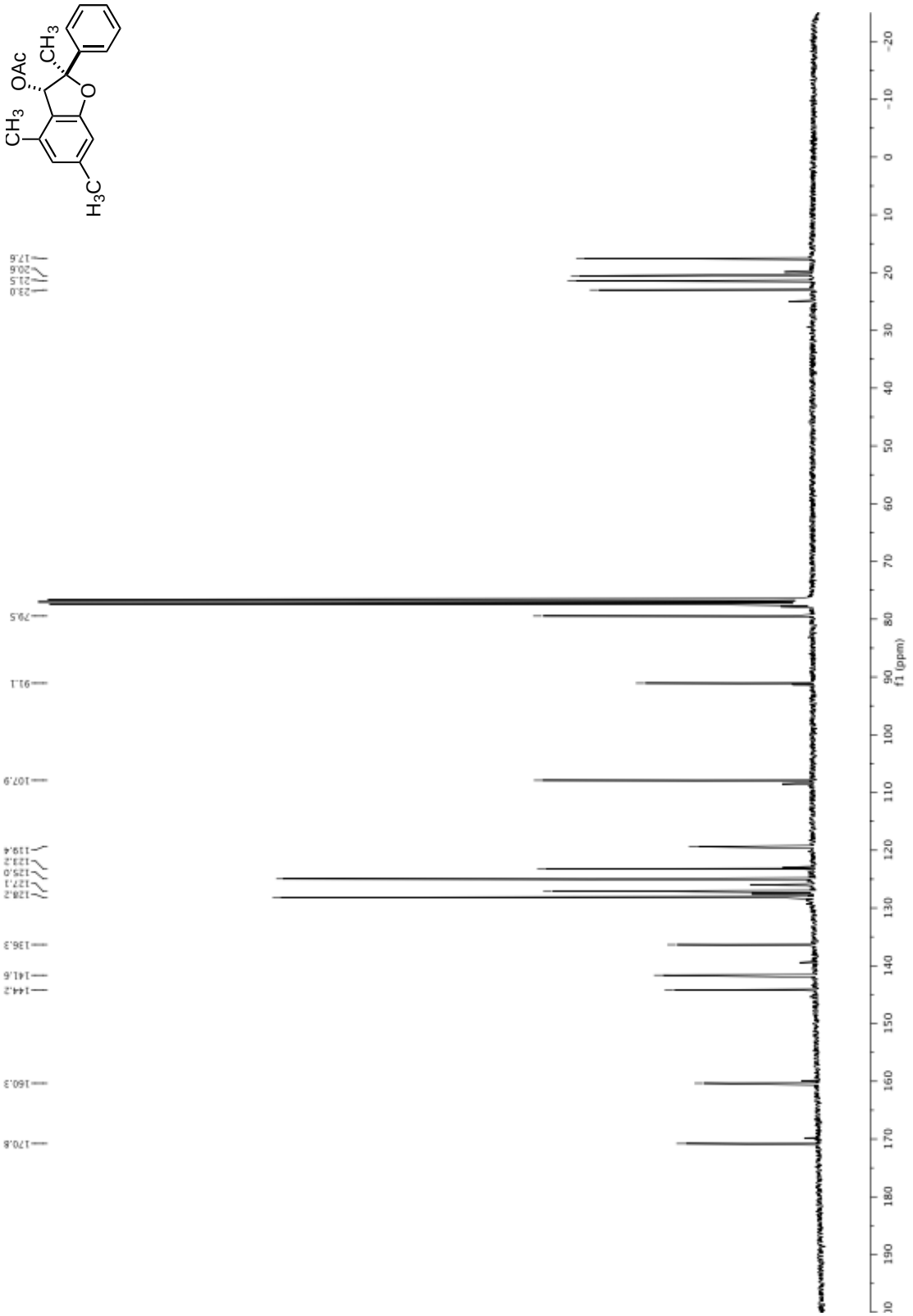
$^{13}$C NMR spectrum of **4faa** (75 MHz, $CDCl_3$)



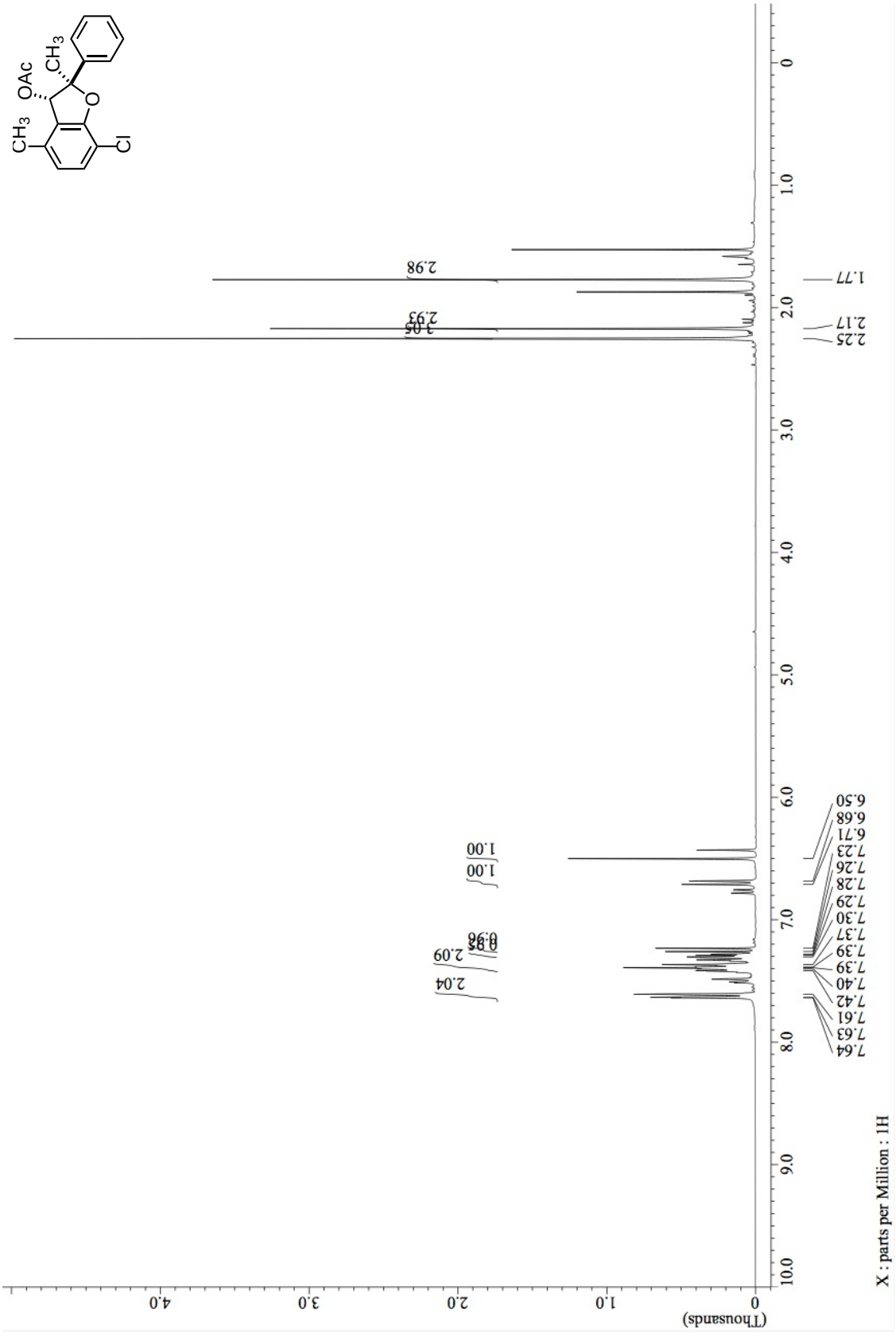
$^1$H NMR spectrum of **4gaa** (300 MHz, $CDCl_3$)



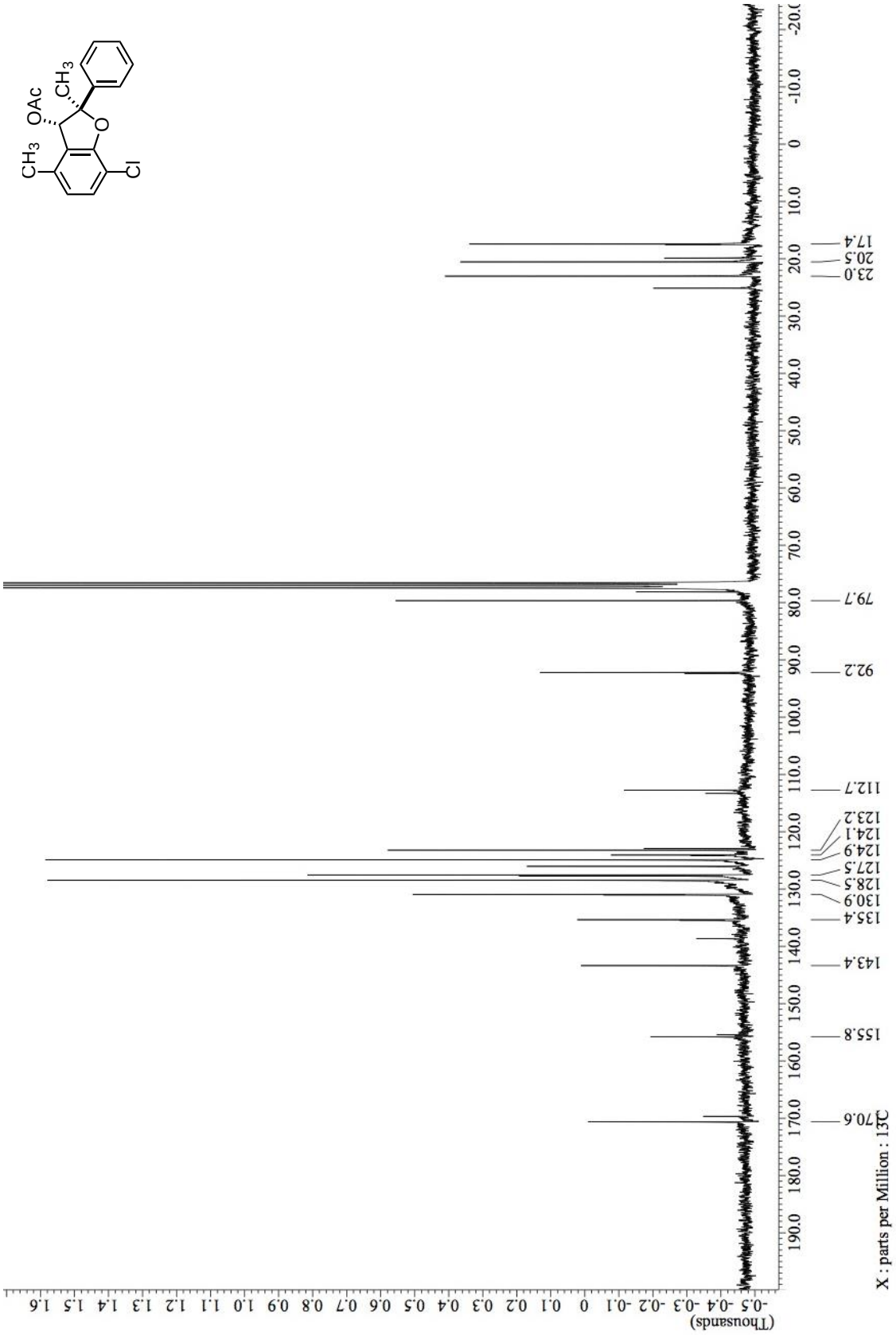
$^{13}$C NMR spectrum of **4gaa** (75 MHz, $CDCl_3$)



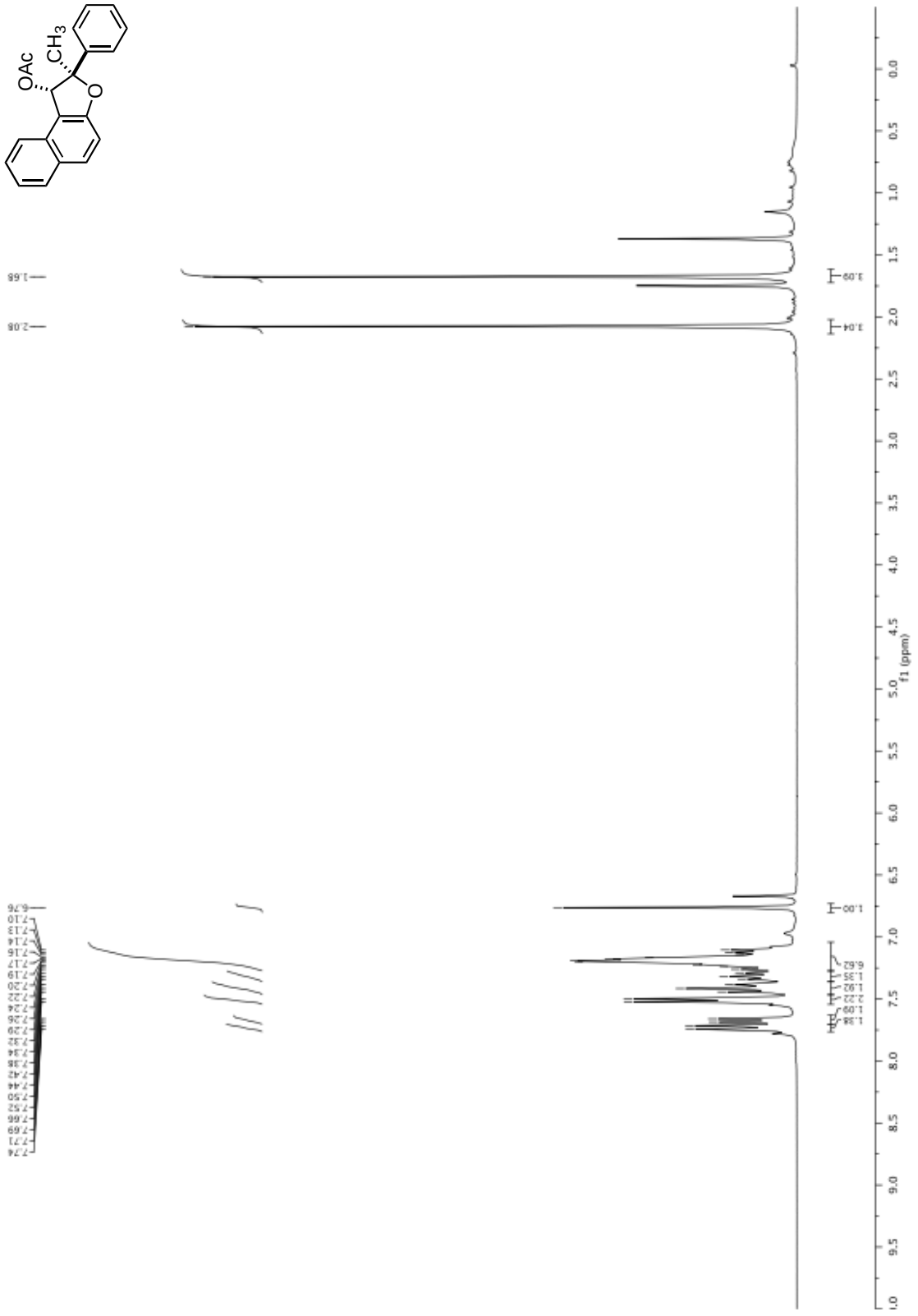
$^1$H NMR spectrum of **4haa** (300 MHz, $CDCl_3$)



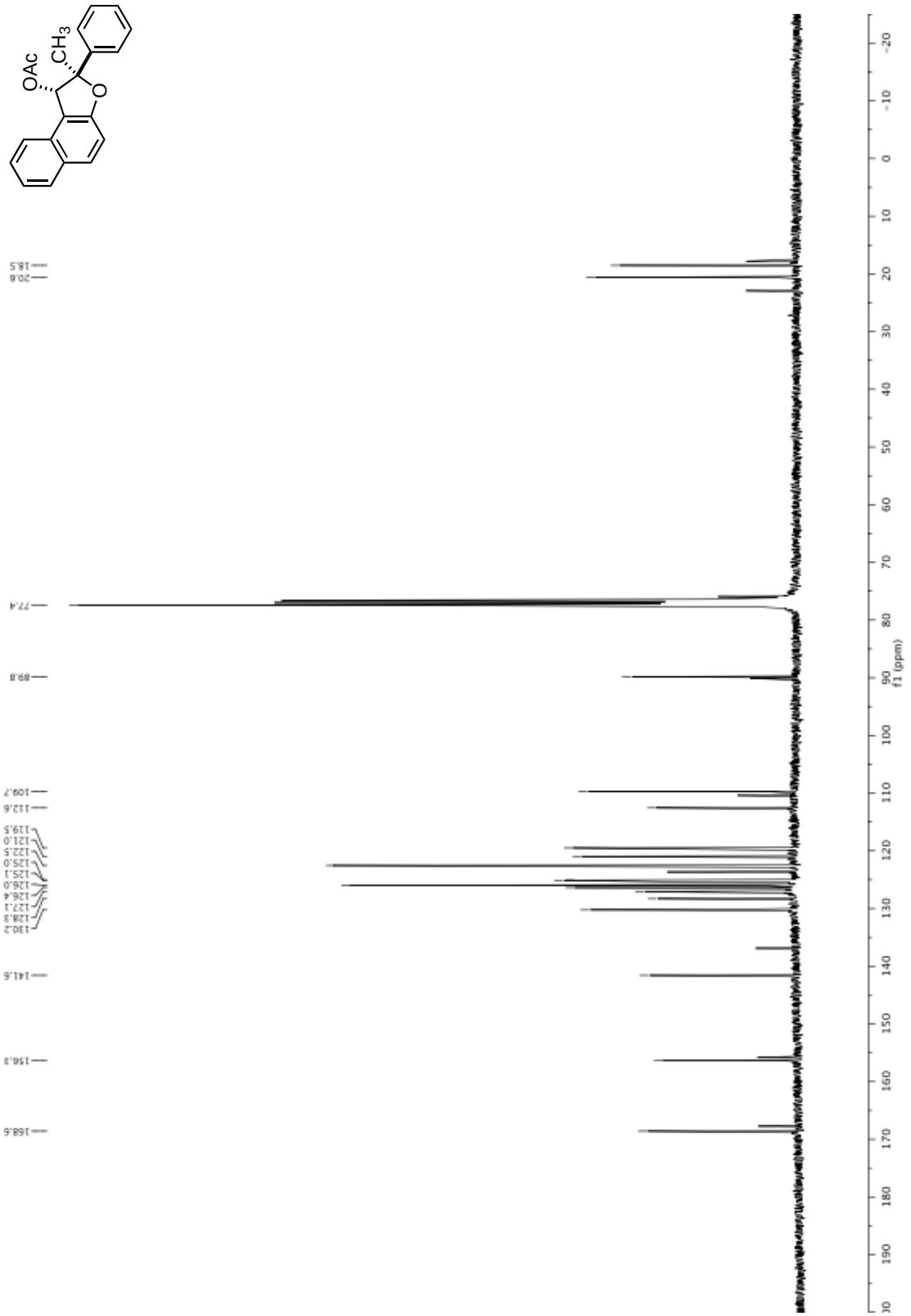
$^{13}$C NMR spectrum of **4haa** (75 MHz, $CDCl_3$)



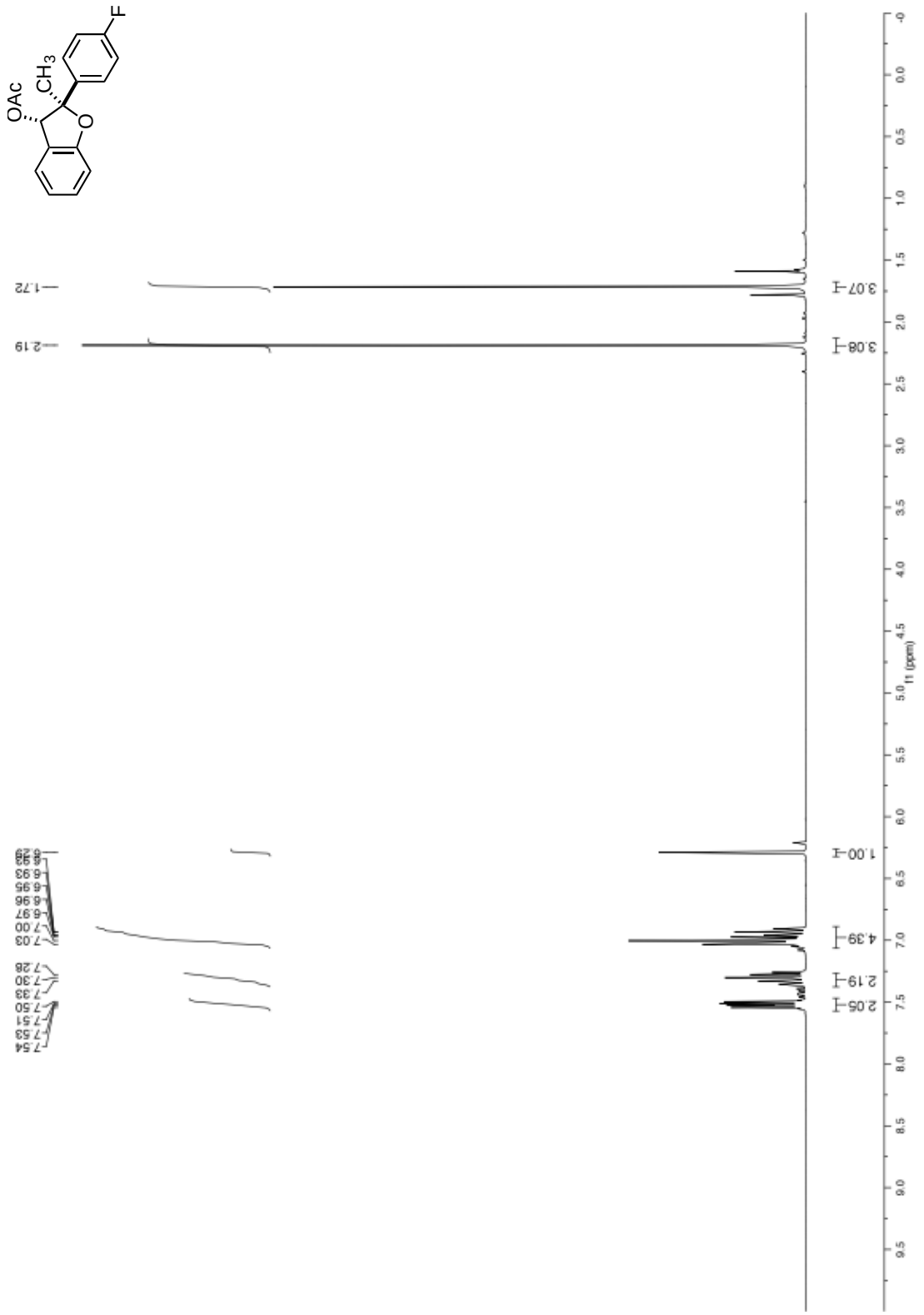
$^1$H NMR spectrum of **4iaa** (300 MHz, $CDCl_3$)



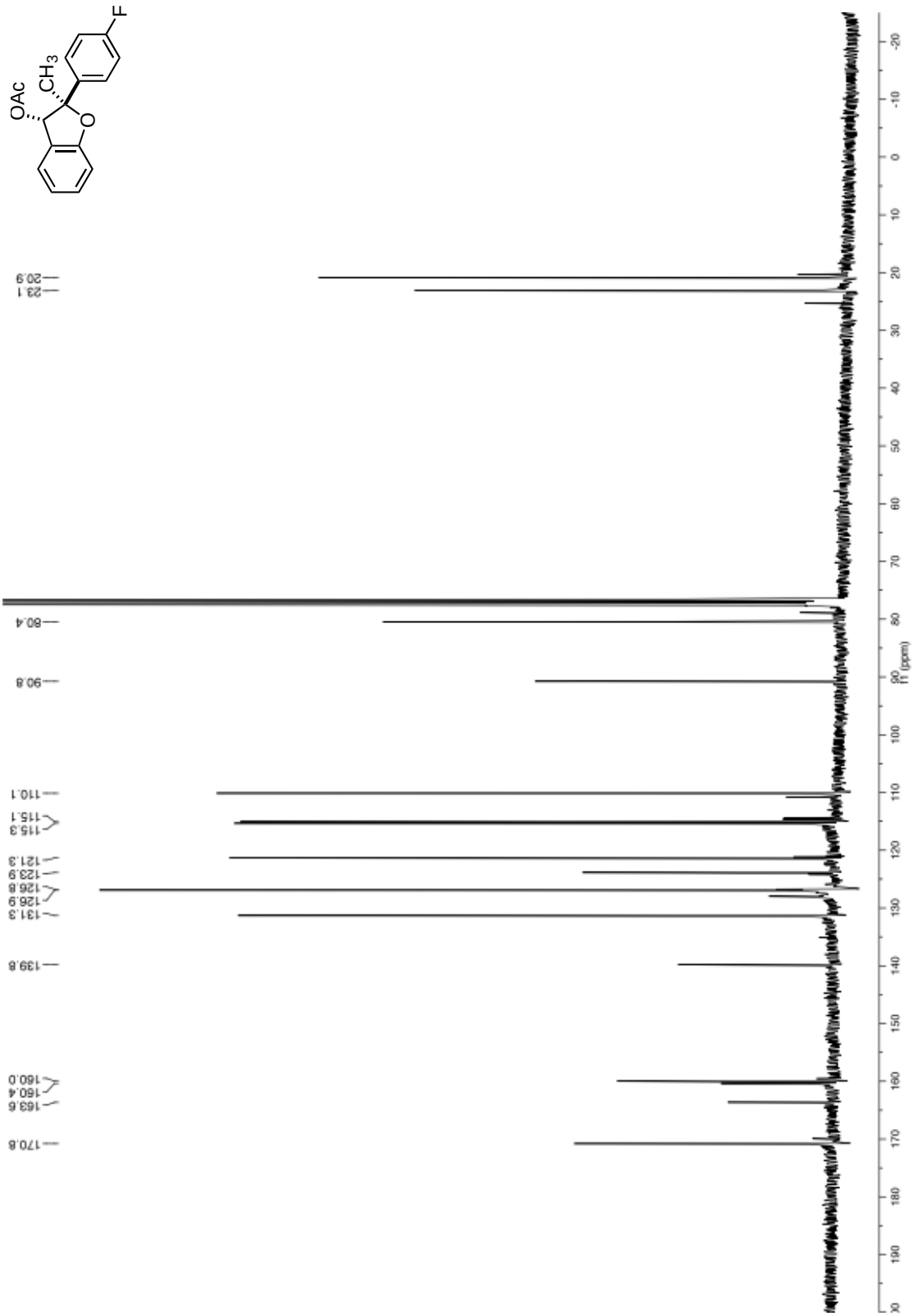
$^{13}$C NMR spectrum of **4iaa** (75 MHz, $CDCl_3$)



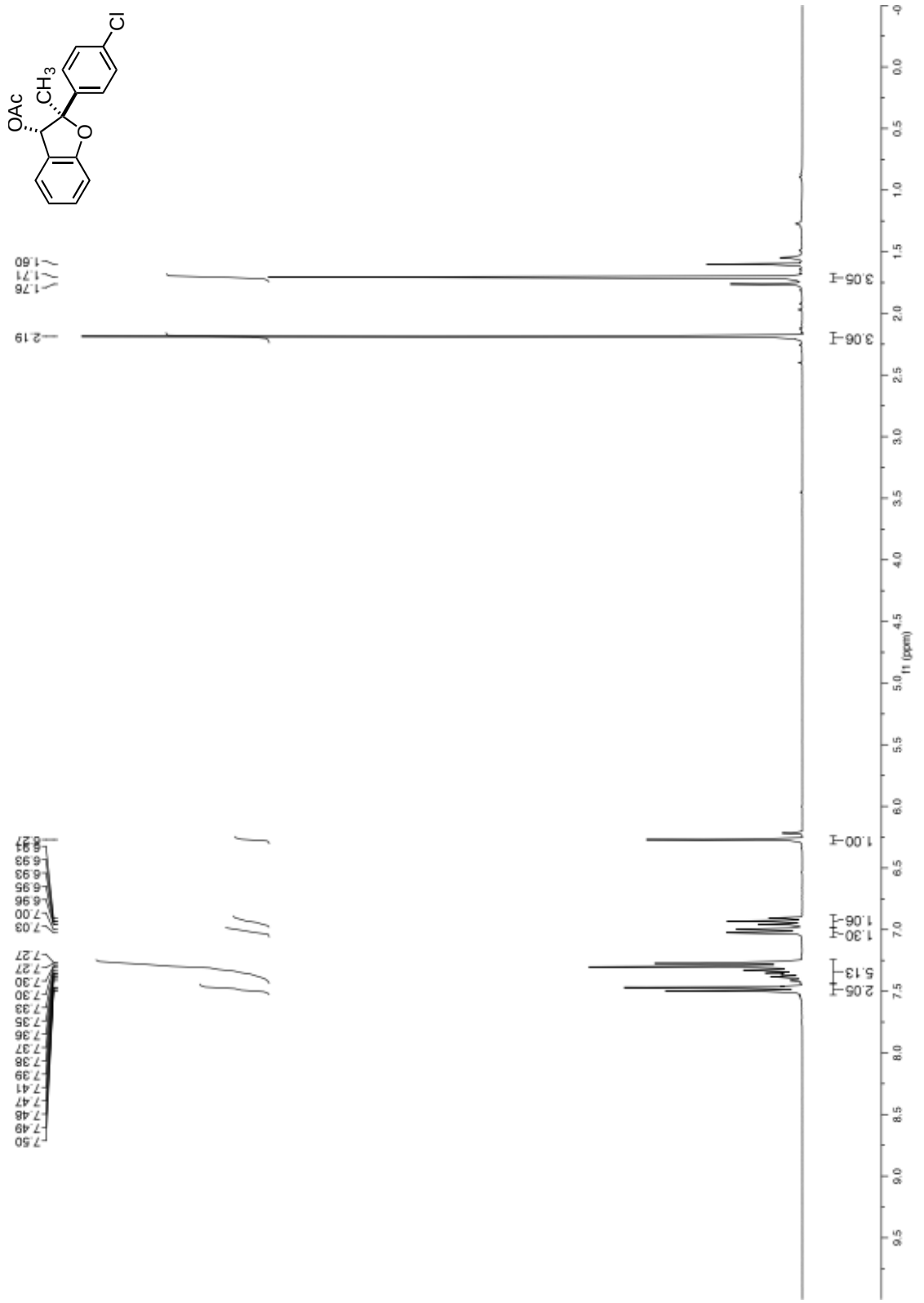
$^1$H NMR spectrum of **4aba** (300 MHz, $CDCl_3$)



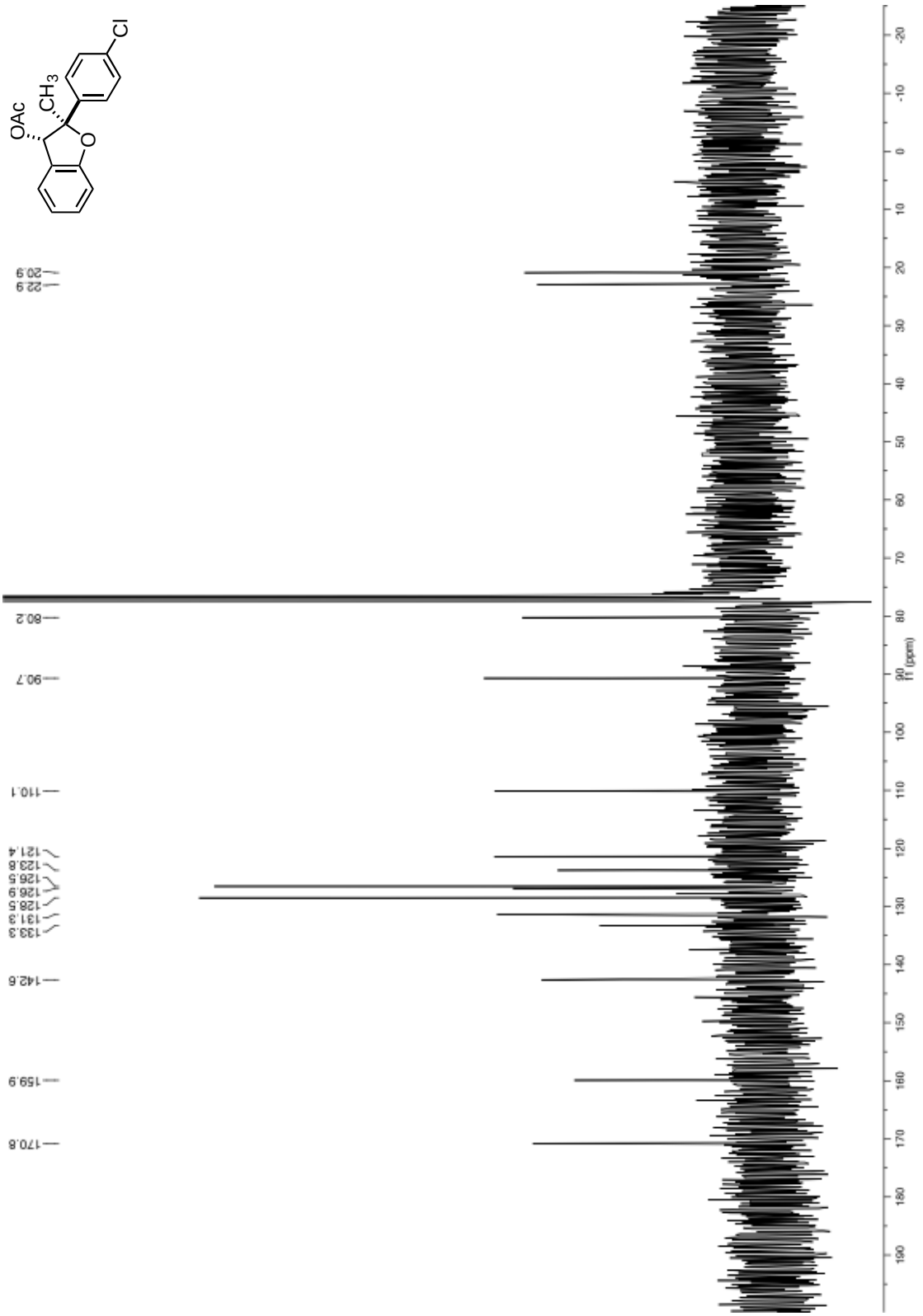
$^{13}$C NMR spectrum of **4aba** (75 MHz, $CDCl_3$)



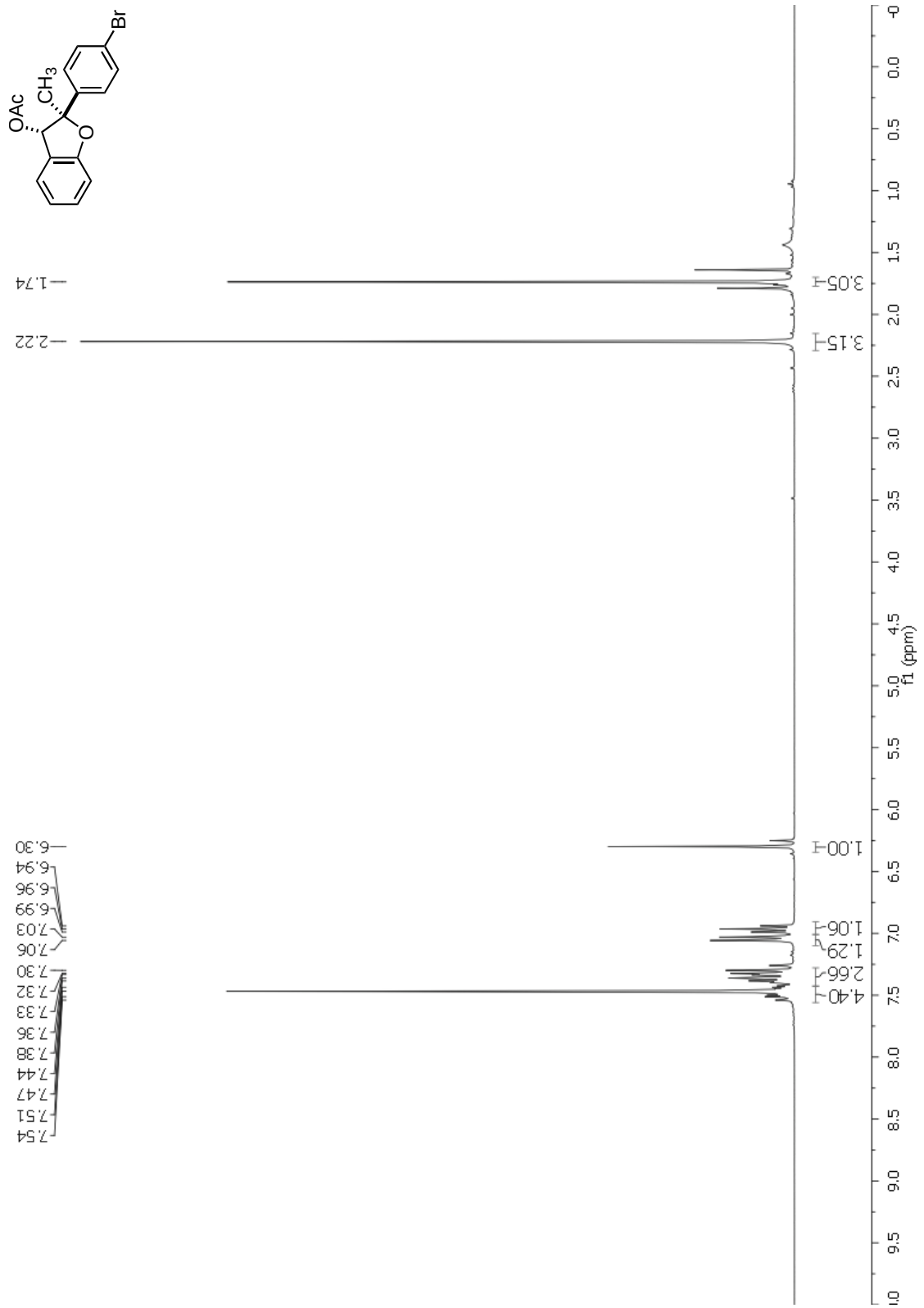
$^1$H NMR spectrum of **4aca** (300 MHz, $CDCl_3$)



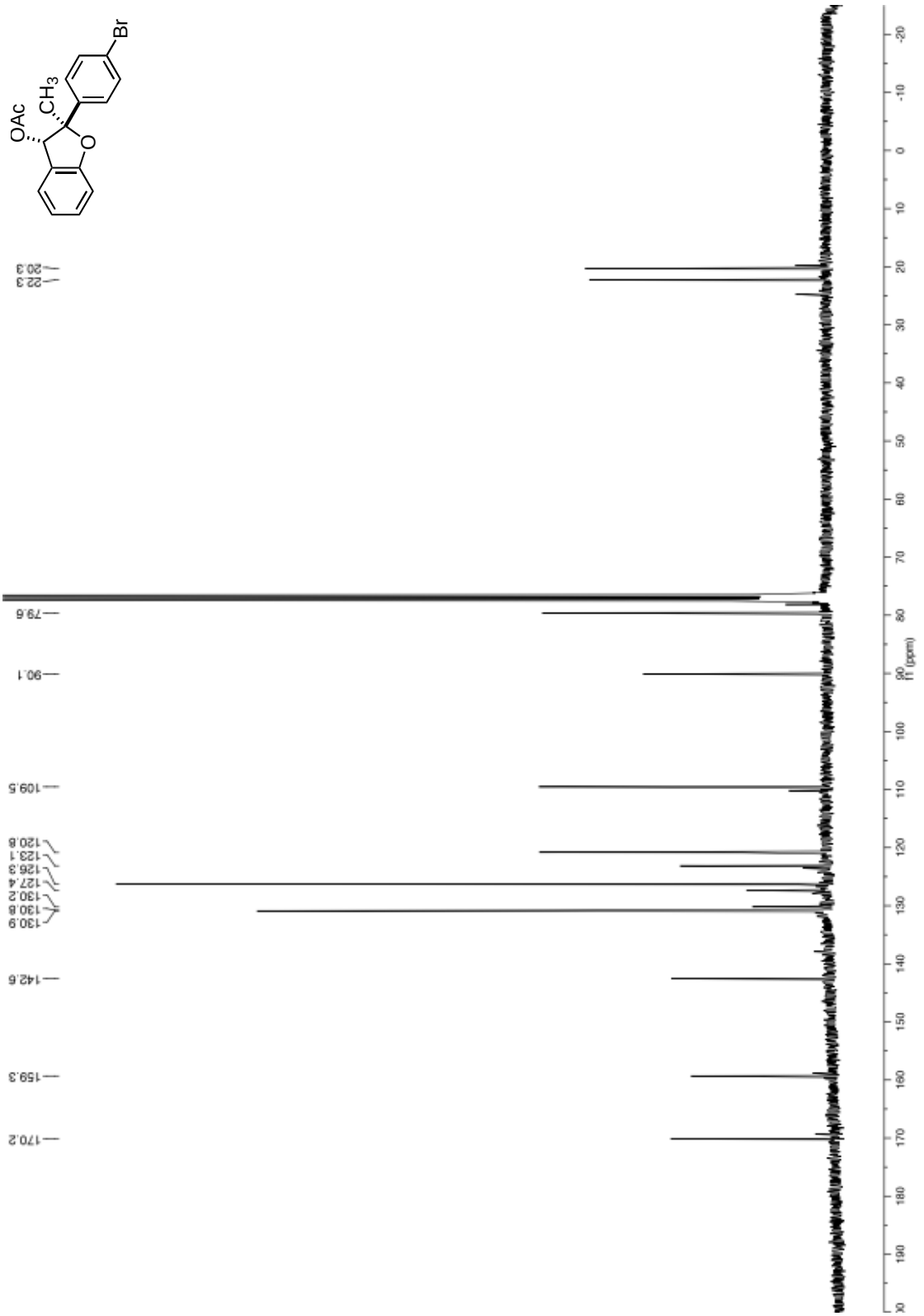
$^{13}$C NMR spectrum of **4aca** (75 MHz, $CDCl_3$)



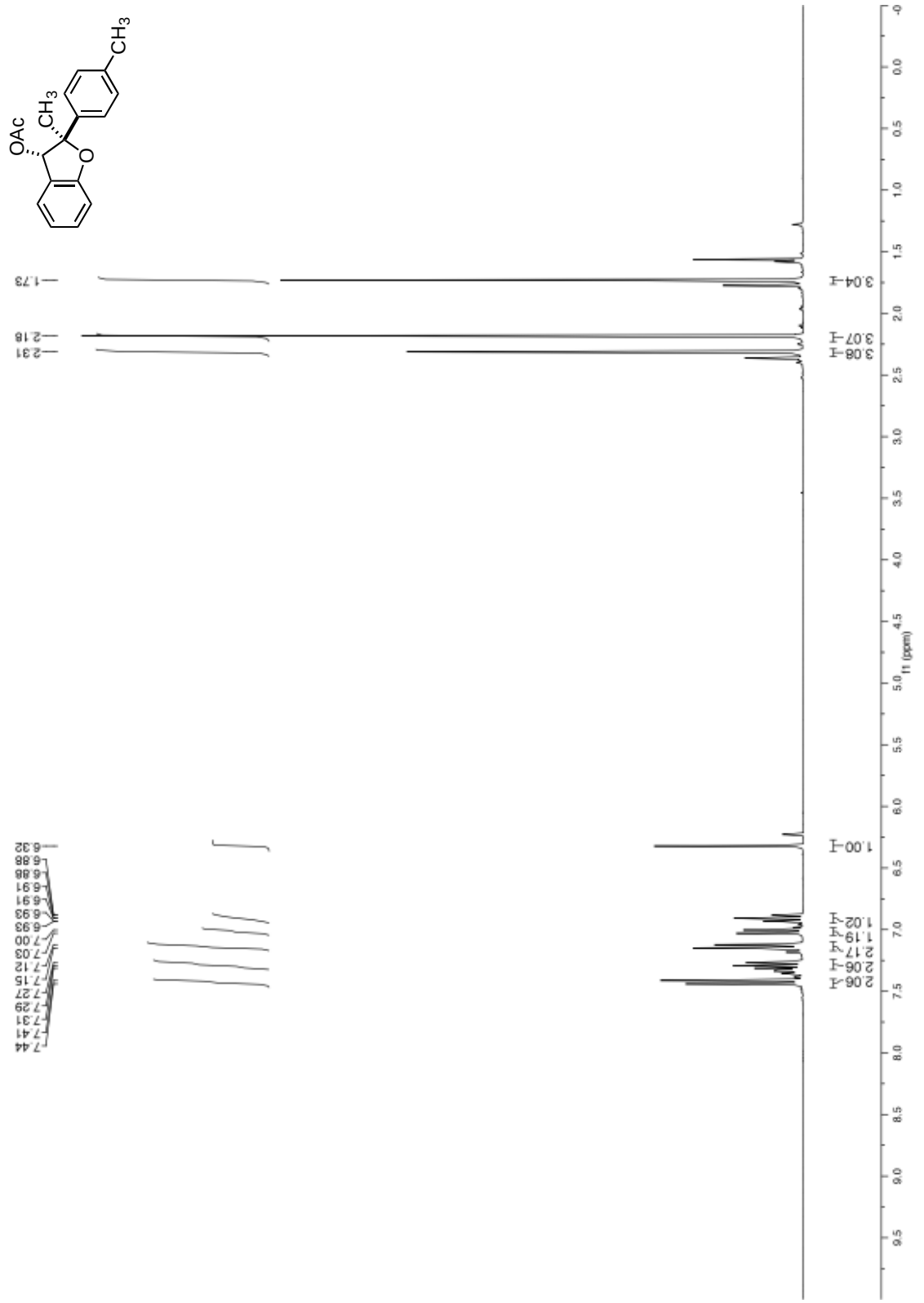
$^1$H NMR spectrum of **4ada** (300 MHz, $CDCl_3$)



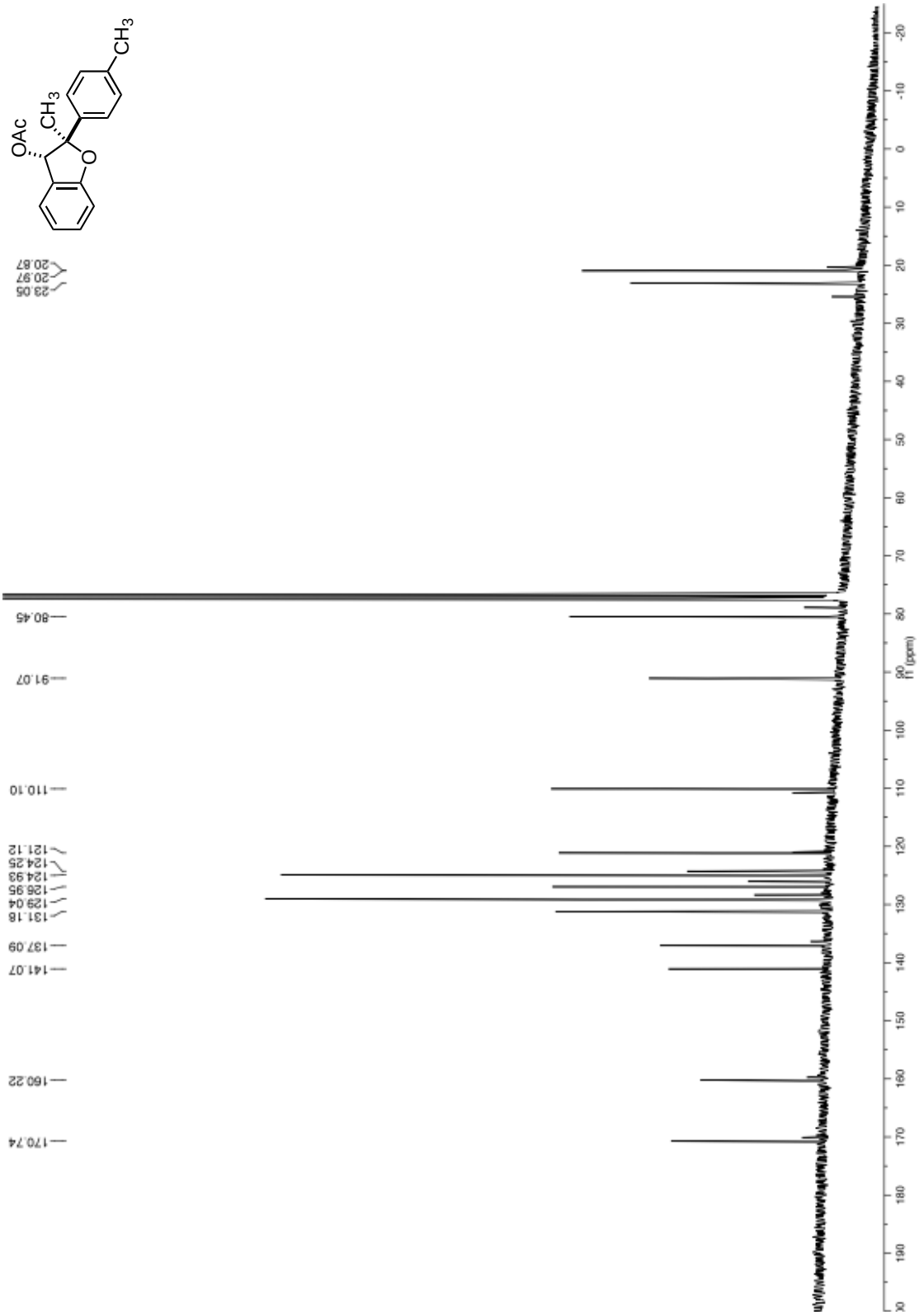
$^{13}$C NMR spectrum of **4ada** (75 MHz, $CDCl_3$)



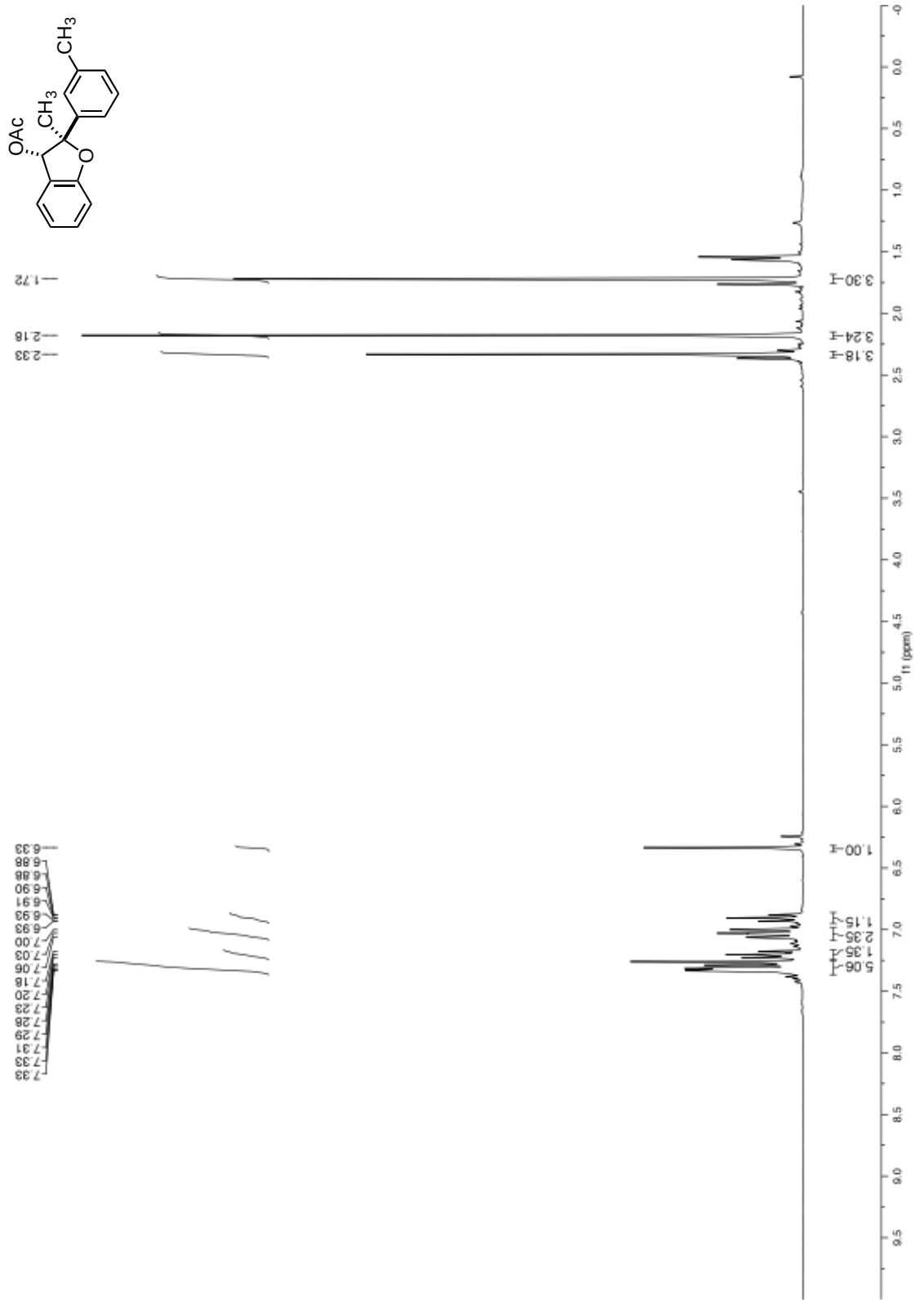
$^1$H NMR spectrum of **4aea** (300 MHz, $CDCl_3$)



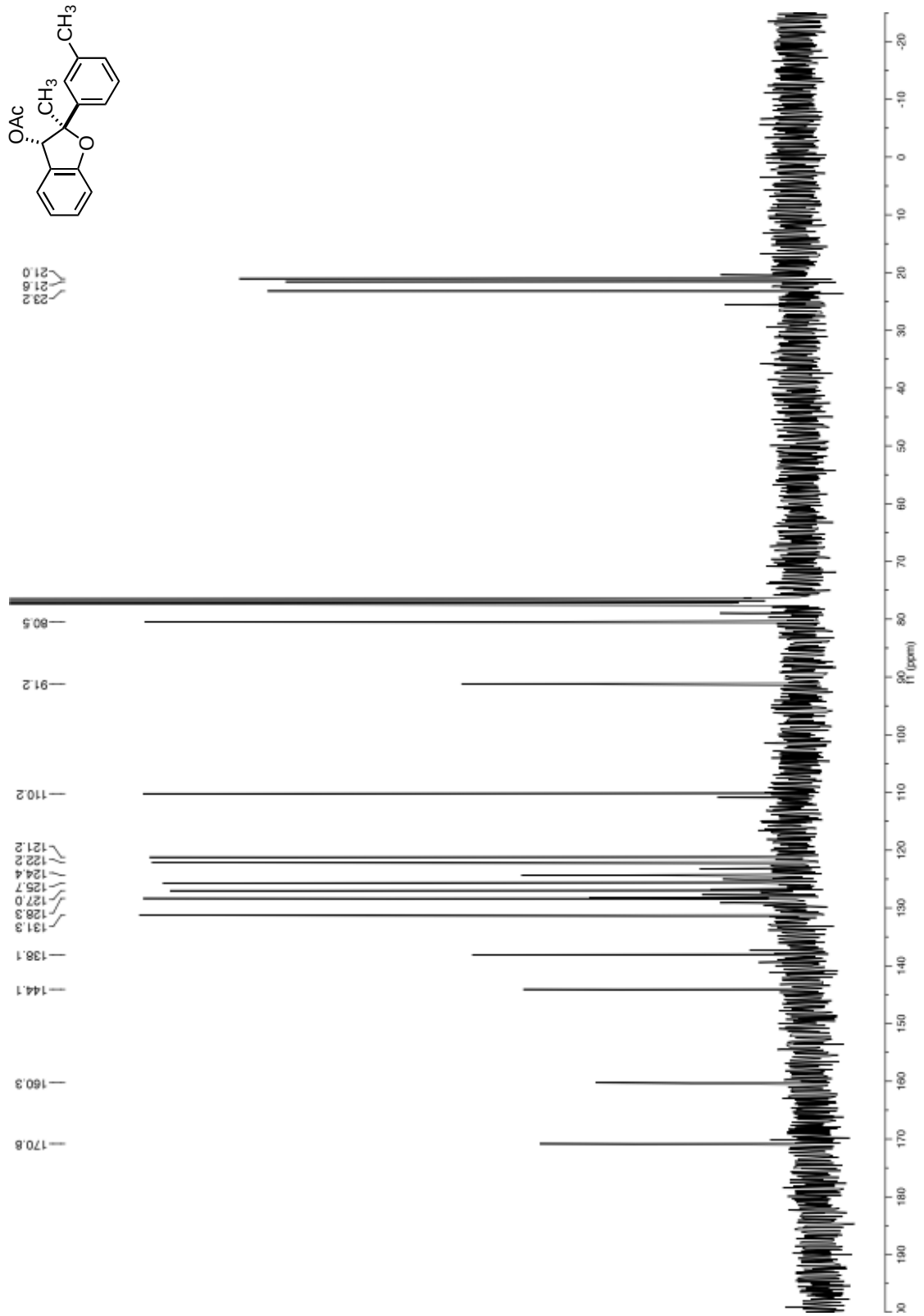
$^{13}$C NMR spectrum of **4aea** (75 MHz, $CDCl_3$)



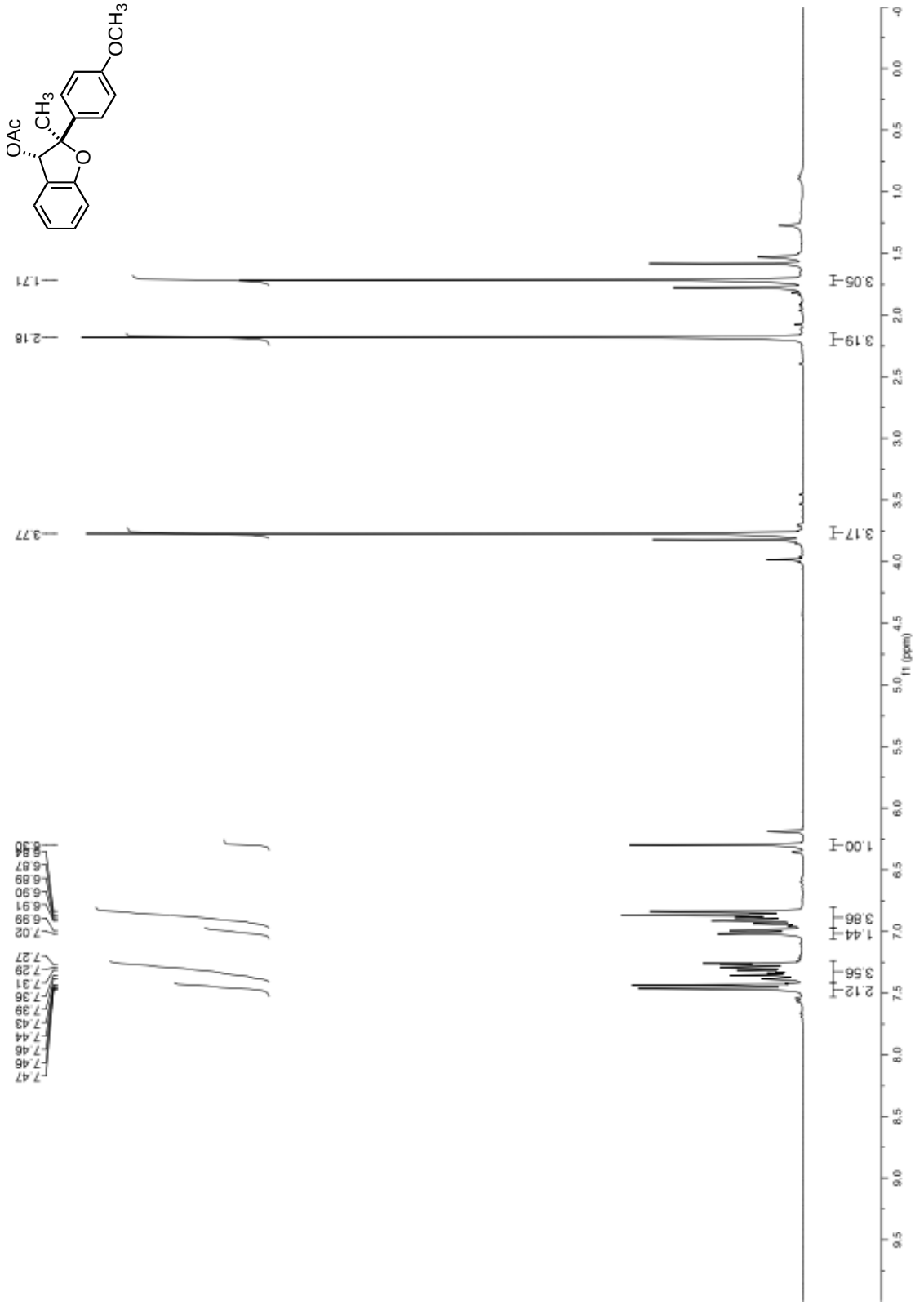
$^1$H NMR spectrum of **4afa** (300 MHz, $CDCl_3$)



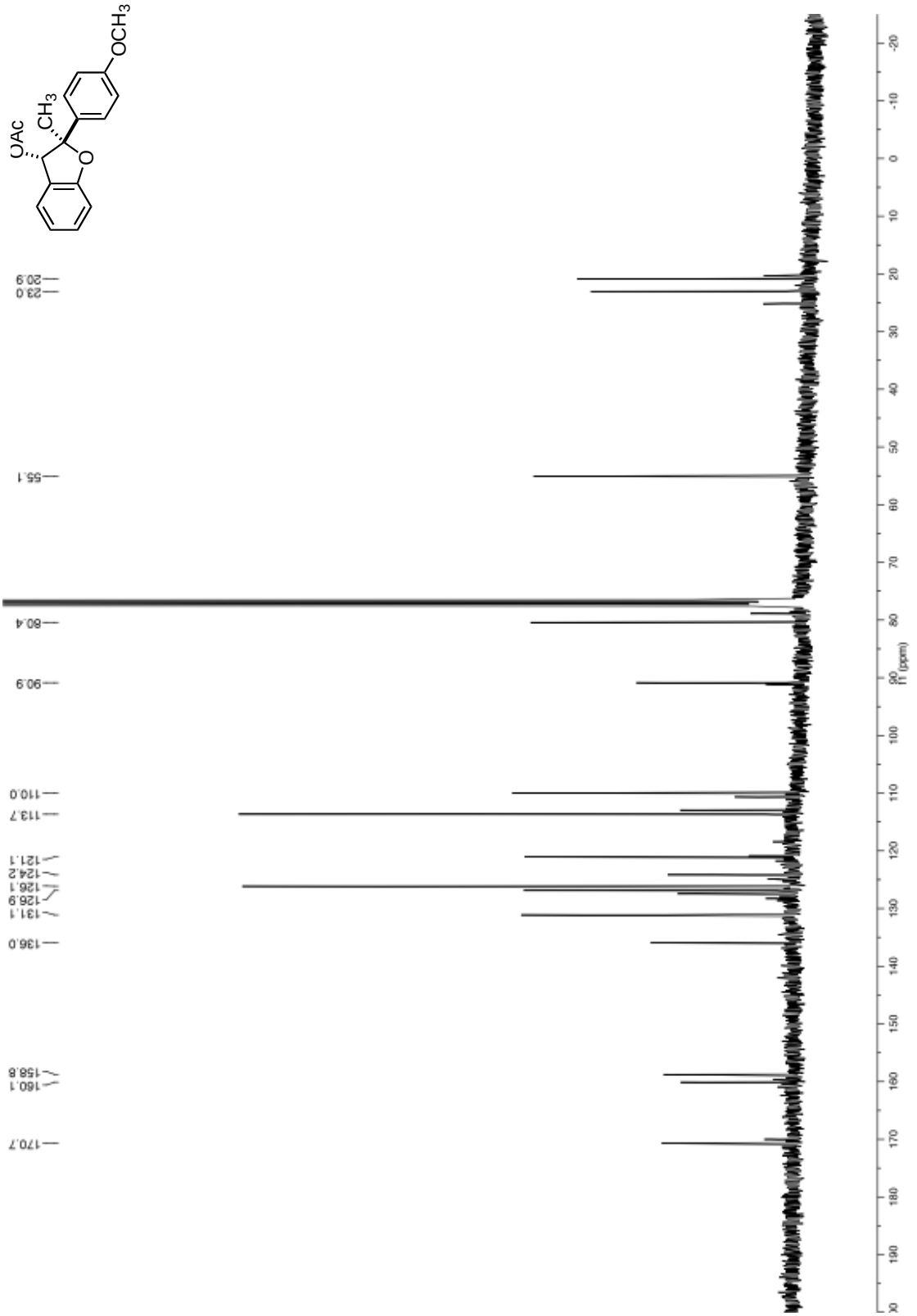
$^{13}$C NMR spectrum of **4afa** (75 MHz, $CDCl_3$)



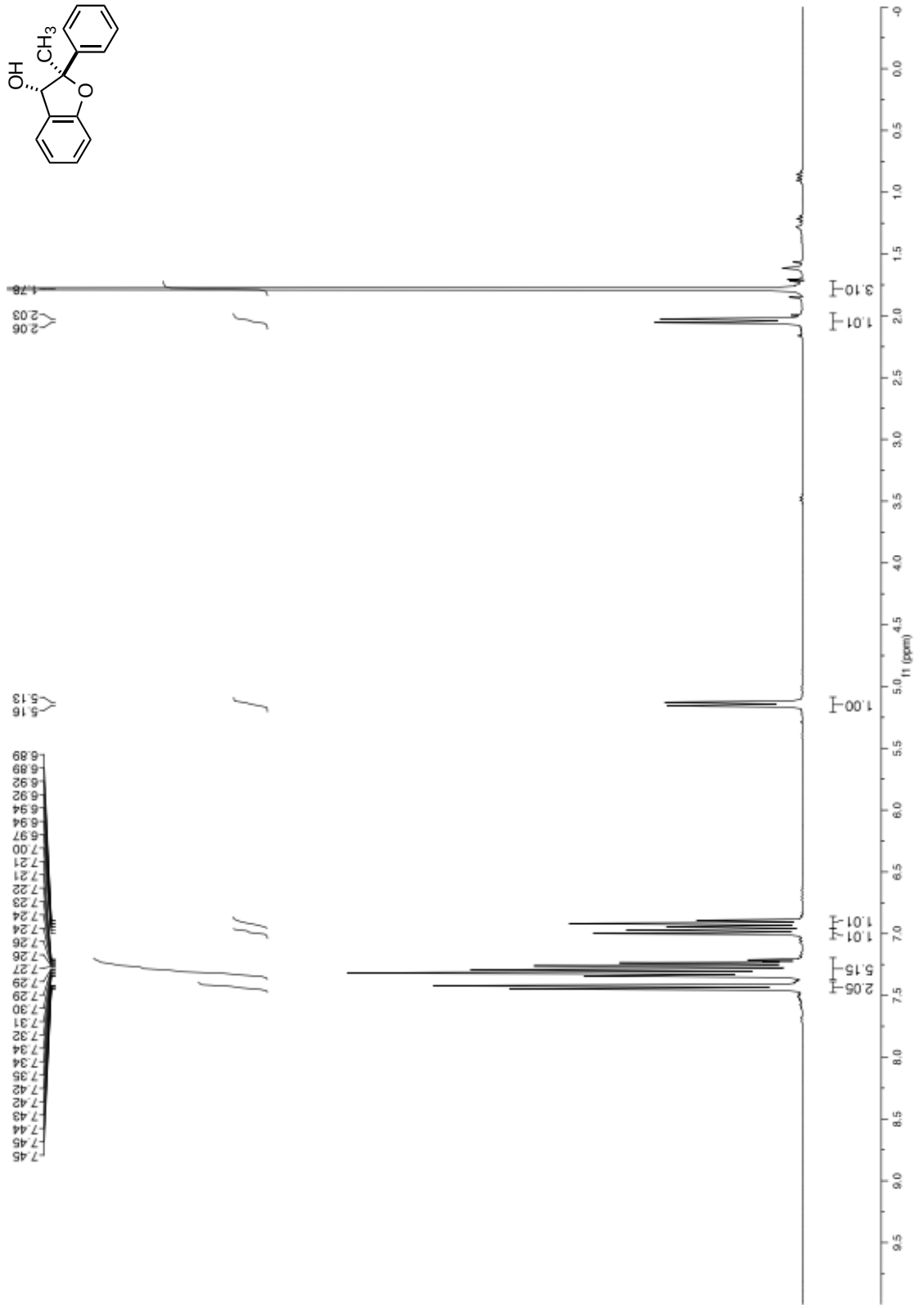
$^1$H NMR spectrum of **4aga** (300 MHz, $CDCl_3$)



$^{13}$C NMR spectrum of **4aga** (75 MHz, $CDCl_3$)



$^1$H NMR spectrum of 2-methyl-2-phenyl-2,3-dihydrobenzofuran-3-ol (300 MHz, $CDCl_3$)



$^{13}$C NMR spectrum of 2-methyl-2-phenyl-2,3-dihydrobenzofuran-3-ol (75 MHz, $CDCl_3$)