*Electronic Supplementary Information*

# Deoxygenative $CO_2$ conversions with triphenylborane and phenylsilane in the presence of secondary amines or nitrogen-containing aromatics

Takumi Murata,[a] Mahoko Hiyoshi,[a] Shinsuke Maekawa,[a] Yuta Saiki,[a] Manussada Ratanasak,[b] Jun-ya Hasegawa[b] and Tadashi Ema*[a]

[a] *Division of Applied Chemistry, Graduate School of Natural Science and Technology, Okayama University, Tsushima, Okayama 700-8530, Japan*

[b] *Institute for Catalysis, Hokkaido University, Kita 21, Nishi 10, Kita-ku, Sapporo, Hokkaido 001-0021, Japan*

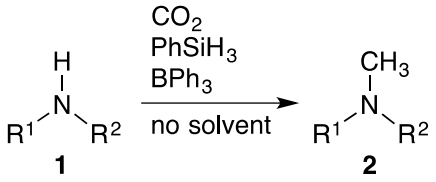
## Table of contents

**[A] General methods.**

NMR spectra were measured on a JEOL JNM-ECS400 spectrometer, and chemical shifts are reported as the delta scale in ppm using an internal reference ($\delta$ = 7.26 ppm ($CDCl_3$) for $^1H$ NMR and $\delta$ = 77.16 ppm ($CDCl_3$) for $^{13}C$ NMR). IR spectra were recorded on a Shimadzu IRAffinity-1 spectrophotometer. Melting points were measured on a Yanaco melting point apparatus (uncorrected). Column chromatography on silica gel and alumina was carried out using Fuji Silysia BW-127 ZH (100–270 mesh) and Merck Aluminium oxide 90 active basic 1.01076.1000 (0.063–0.200 mm), respectively. $^{13}CO_2$ (99%) purchased from Taiyo Nippon Sanso Corporation was used for the isotope labeling experiments.

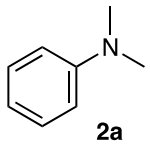
**[B] *N*-Methylation of amines with $CO_2$.**

**General procedure.** In a glovebox (purge type) under $N_2$ atmosphere, $BPh_3$ (24.2 mg, 0.10 mmol, 5 mol% based on $PhSiH_3$) was put in a 30 mL Schlenk flask, and the flask was taken out from the glovebox. After the flask was evacuated and filled with $CO_2$ (1 atm, balloon, ca. 1.6 L), amine **1** (0.50 mmol) and $PhSiH_3$ (250 μL, 2.0 mmol, stored over molecular sieves 3A) were added in this order via syringes. The mixture was stirred at constant temperature for reaction time. Purification by column chromatography on silica gel (eluent shown below) gave *N*-methylated product **2**.



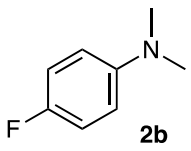

**Product characterizations.** Products **2a**,[S1] **2b**,[S2] **2c**,[S1] **2d**,[S3] **2e**,[S3] **2f**,[S1] **2g**,[S1] **2h**,[S1] **2i**,[S1] and **2l**[S1] were characterized according to the literature, while **2j** and **2k** were confirmed to be identical to commercial samples by means of NMR spectra.

***N*,*N*-Dimethylaniline (2a).**



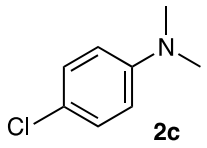

30 °C, 8 h; Eluent = hexane/EtOAc (20:1); 34.4 mg (0.284 mmol, 57% yield); Colorless oil; $^1H$ NMR ($CDCl_3$, 400 MHz) $\delta$ 2.95 (s, 6H), 6.73–6.76 (m, 3H), 7.23–7.27 (m, 2H); $^{13}C$ NMR ($CDCl_3$, 100 MHz) $\delta$ 40.8, 112.8, 116.8, 129.2, 150.8; IR (neat) 3094, 3061, 3026, 2924, 2803, 2174, 2083, 1919, 1732, 1601, 1576, 1507, 1445, 1344, 1229, 1192, 1165, 1128, 1061, 1034, 991, 945, 862, 806, 750, 691, 515 $cm^{-1}$.

**4-Fluoro-*N*,*N*-dimethylaniline (2b).**




30 °C, 8 h; Eluent = hexane/EtOAc (20:1); 62.5 mg (0.449 mmol, 90% yield); Colorless oil; $^1H$ NMR ($CDCl_3$, 400 MHz) $\delta$ 2.90 (s, 6H), 6.67–6.70 (m, 2H), 6.92–6.97 (m, 2H); $^{13}C$ NMR ($CDCl_3$, 100 MHz) $\delta$ 41.5, 114.1 (d, $J$ = 7.6 Hz), 115.5 (d, $J$ = 22.0 Hz), 147.7, 155.8 (d, $J$ = 234 Hz); IR (KBr) 3051, 2988, 2887, 2805, 2178, 1848, 1611, 1514, 1447, 1414, 1348, 1227, 1157, 1107, 1063, 945, 843, 816, 741, 687, 637, 517 $cm^{-1}$.

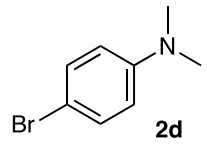
**4-Chloro-*N*,*N*-dimethylaniline (2c).**



**2c**

40 °C, 8 h; Eluent = hexane/EtOAc (20:1); 61.9 mg (0.399 mmol, 80% yield); White solid; mp 25–26 °C; $^{1}$H NMR ($CDCl_3$, 400 MHz) $\delta$ 2.93 (s, 6H), 6.64 (d, $J$ = 8.8 Hz, 2H), 7.17 (d, $J$ = 8.8 Hz, 2H); $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ 40.8, 113.8, 121.5, 128.9, 149.3. IR (KBr) 3094, 3049, 2990, 2920, 2886, 2855, 2805, 1865, 1734, 1595, 1564, 1504, 1445, 1352, 1223, 1190, 1125, 1098, 1061, 945, 849, 808, 762, 698, 611, 511 cm$^{-1}$.

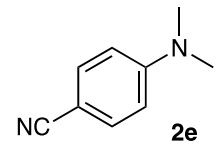
**4-Bromo-*N*,*N*-dimethylaniline (2d).**



**2d**

40 °C, 8 h; Eluent = hexane/EtOAc (10:1); 88.5 mg (0.442 mmol, 88% yield); White solid; mp 47–48 °C; $^{1}$H NMR ($CDCl_3$, 400 MHz) $\delta$ 2.92 (s, 6H), 6.60 (d, $J$ = 8.4 Hz, 2H), 7.30 (d, $J$ = 9.2 Hz, 2H); $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ 40.7, 108.8, 114.3, 131.8, 149.5; IR (KBr) 3092, 2920, 2886, 2806, 2172, 1865, 1734, 1593, 1501, 1447, 1356, 1312, 1223, 1190, 1125, 1063, 989, 945, 849, 806, 752, 696, 581, 509 cm$^{-1}$.

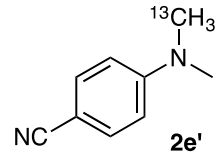
**4-Cyano-*N*,*N*-dimethylaniline (2e).**



**2e**

30 °C, 8 h; Eluent = hexane/EtOAc (3:1); 59.3 mg (0.406 mmol, 81% yield); White solid; mp 70–71 °C; $^{1}$H NMR ($CDCl_3$, 400 MHz) $\delta$ 3.04 (s, 6H), 6.64 (d, $J$ = 9.2 Hz, 2H), 7.47 (d, $J$ = 9.2 Hz, 2H); $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ 40.0, 97.5, 111.5, 120.9, 133.5, 152.6; IR (KBr) 3073, 3051, 3005, 2951, 2911, 2868, 2824, 2739, 2212, 1900, 1609, 1526, 1447, 1371, 1227, 1180, 1125, 1067, 941, 849, 818, 741, 698, 646, 546 cm$^{-1}$; HRMS (EI) calcd for $C_9H_{10}N_2$ 146.0844, found 146.0841 ($M^+$).

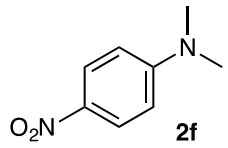
**4-Cyano-*N*,*N*-dimethylaniline labelled with $^{13}$C (2e').**



**2e'**

30 °C, 18 h; Eluent = hexane/EtOAc (3:1); 58.2 mg (0.395 mmol, 79% yield); White solid; mp 67–68 °C; $^{1}$H NMR ($CDCl_3$, 400 MHz) $\delta$ 3.04 (d, $^{1}J_{CH}$ = 136 Hz, 3H), 3.04 (d, $^{3}J_{CH}$ = 3.7 Hz, 3H), 6.64 (d, $J$ = 9.1 Hz, 2H), 7.47 (d, $J$ = 9.1 Hz, 2H); $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ 40.1, 97.5, 111.5, 120.9, 133.5, 152.6; IR (KBr) 3090, 3053, 2957, 2918, 2824, 2212, 1900, 1609, 1526, 1445, 1431, 1416, 1368, 1325, 1261, 1223, 1180, 1169, 1061, 947, 935, 849, 818, 785, 739, 698, 654, 646 cm$^{-1}$; HRMS (EI) calcd for $^{12}C_8{}^{13}CH_{10}N_2$ 147.0878, found 147.0880 ($M^+$).

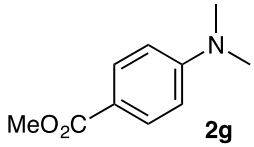
**4-Nitro-*N*,*N*-dimethylaniline (2f).**



**2f**

30 °C, 8 h; Eluent = hexane/EtOAc (3:1); 71.7 mg (0.431 mmol, 86% yield); Yellow solid; mp 161–162 °C; $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 3.12 (s, 6H), 6.61 (d, $J$ = 9.2 Hz, 2H), 8.13 (d, $J$ = 9.2 Hz, 2H); $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ 40.4, 110.4, 126.3, 137.1, 154.4; IR (KBr) 3088, 2922, 2830, 2696, 1917, 1603, 1531, 1487, 1456, 1383, 1323, 1234, 1202, 1117, 1069, 941, 822, 752, 696, 606, 540 cm$^{-1}$.

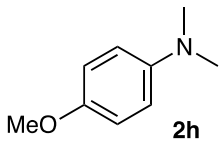
**4-Methoxycarbonyl-*N*,*N*-dimethylaniline (2g).**



**2g**

40 °C, 24 h; Eluent = hexane/EtOAc (3:1); 84.8 mg (0.473 mmol, 95% yield); White solid; mp 90–91 °C; $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 3.04 (s, 6H), 3.86 (s, 3H), 6.65 (d, $J$ = 9.1 Hz, 2H), 7.91 (d, $J$ = 9.1 Hz, 2H); $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ 40.1, 51.6, 110.8, 117.1, 131.3, 153.4, 167.6; IR (KBr) 3071, 3051, 3019, 2988, 2947, 2903, 1701, 1612, 1530, 1439, 1375, 1317, 1283, 1233, 1186, 1132, 1111, 1065, 966, 829, 772, 700, 503 cm$^{-1}$.

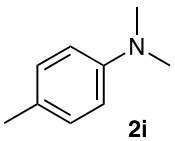
**4-Methoxy-*N*,*N*-dimethylaniline (2h).**



**2h**

30 °C, 8 h; Eluent = hexane/EtOAc (10:1); 49.4 mg (0.327 mmol, 65% yield); Yellow oil; $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 2.87 (s, 6H), 3.77 (s, 3H), 6.78 (d, $J$ = 9.1 Hz, 2H), 6.84–6.86 (m, 2H); $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ 42.0, 55.9, 114.8, 115.1, 145.8, 152.2; IR (neat) 3073, 3046, 2995, 2949, 2884, 2832, 2801, 2176, 2064, 1877, 1852, 1825, 1616, 1595, 1514, 1445, 1341, 1300, 1246, 1182, 1132, 1065, 1038, 947, 818, 754, 702, 685, 648, 604, 527 cm$^{-1}$.

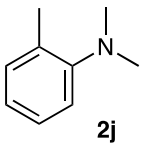
**4-*N*,*N*-Trimethylaniline (2i).**



**2i**

30 °C, 8 h; Eluent = hexane/EtOAc (20:1); 37.9 mg (0.280 mmol, 56% yield); Yellow oil; $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 2.26 (s, 3H), 2.90 (s, 6H), 6.69 (d, $J$ = 8.7 Hz, 2H), 7.06 (d, $J$ = 8.4 Hz, 2H); $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ 20.4, 41.2, 113.4, 126.2, 129.7, 149.0; IR (neat) 3096, 3071, 3007, 2918, 2797, 2176, 1861, 1618, 1570, 1522, 1477, 1445, 1429, 1341, 1260, 1227, 1192, 1163, 1130, 1098, 1061, 997, 947, 841, 804, 756, 739, 700, 687, 667, 642, 517 cm$^{-1}$.

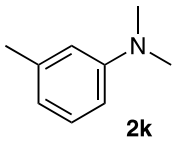
**2-*N*,*N*-Trimethylaniline (2j).**



**2j**

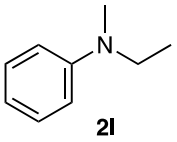
30 °C, 24 h; Eluent = hexane/EtOAc (30:1); 15.1 mg (0.112 mmol, 22% yield); Colorless oil; $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 2.33 (s, 3H), 2.70 (s, 6H), 6.95 (t, $J$ = 7.3 Hz, 1H), 7.03 (d, $J$ = 7.4 Hz, 1H), 7.14–7.17 (m, 2H); $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ 18.5, 44.4, 118.5, 122.7, 126.6, 131.3, 132.3, 152.9.

**3-*N*,*N*-Trimethylaniline (2k).**




30 °C, 6 h; Eluent = hexane/EtOAc (30:1); 38.0 mg (0.281 mmol, 56% yield); Colorless oil; $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 2.32 (s, 3H), 2.93 (s, 6H), 6.55–6.57 (m, 3H), 7.14 (t, $J$ = 8.1 Hz, 1H); $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ 22.0, 40.8, 110.1, 113.6, 117.8, 129.1, 138.8, 150.9.

***N*-Ethyl-*N*-methylaniline (2l).**




30 °C, 8 h; Eluent = hexane/EtOAc (10:1); 16.3 mg (0.121 mmol, 24% yield); Colorless oil; $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 1.12 (t, $J$ = 7.0 Hz, 3H), 2.90 (s, 3H), 3.40 (q, $J$ = 7.0 Hz, 2H), 6.66–6.73 (m, 3H), 7.21–7.25 (m, 2H); $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ 11.3, 37.6, 46.9, 112.5, 116.2, 129.3, 149.3; IR (neat) 3092, 3061, 3024, 2970, 2928, 2868, 2816, 2351, 2158, 1682, 1651, 1601, 1572, 1506, 1472, 1449, 1429, 1371, 1348, 1308, 1271, 1217, 1192, 1157, 1125, 1080, 1034, 995, 953, 891, 841, 793, 748, 691, 637 cm$^{-1}$.

**Control experiments in Scheme 3.**

The control experiments were done according to the general procedure described above, with each reagent deleted or replaced by another one as shown in Scheme 3 in the main text.

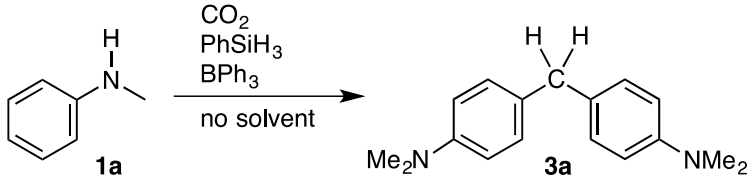
**[C] *C*-Methylenation of aromatic compounds with $CO_2$.**

**(a) Synthesis of diarylmethanes 3.**

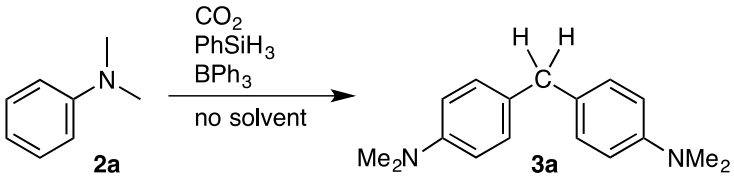
**Product characterizations.** Products **3a**,[S4] **3b**,[S5] **3d**,[S5] **3e**,[S4] **3f**,[S4] and **3g**[S6] were characterized according to the literature.

**Conversion of 1a into 4,4'-methylenebis(*N*,*N*-dimethylaniline) (3a).**

In a glovebox (purge type) under $N_2$ atmosphere, $BPh_3$ (48.4 mg, 0.20 mmol, 5 mol% based on $PhSiH_3$) was put in a 30 mL Schlenk flask, and the flask was taken out from the glovebox. After the flask was evacuated and filled with $CO_2$ (1 atm, balloon, ca. 1.6 L), **1a** (55 μL, 0.50 mmol) and $PhSiH_3$ (500 μL, 4.0 mmol, stored over molecular sieves 3A) were added in this order via syringes, and the mixture was stirred at 40 °C for 24 h. After addition of mesitylene (internal standard) and $CDCl_3$ with stirring, a small portion of the mixture was added to $CDCl_3$ in an NMR tube, and the yield of **3a** was determined by $^1$H NMR (29% yield).

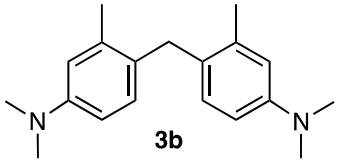


**Conversion of 2a into 3a (Typical procedure).**



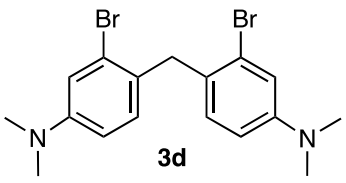

In a glovebox (purge type) under $N_2$ atmosphere, $BPh_3$ (48.4 mg, 0.20 mmol, 10 mol% based on $PhSiH_3$) was put in a 30 mL Schlenk flask, and the flask was taken out from the glovebox. After the flask was evacuated and filled with $CO_2$ (1 atm, balloon, ca. 1.6 L), **2a** (63 μL, 0.50 mmol) and $PhSiH_3$ (250 μL, 2.0 mmol, stored over molecular sieves 3A) were added in this order via syringes, and the mixture was stirred at 40 °C for 24 h. Purification by column chromatography on basic alumina (short column, $CHCl_3$) and silica gel (hexane/EtOAc (10:1)) afforded **3a** as a white solid (33.9 mg, 0.135 mmol, 54% yield). mp 89–90 °C; $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 2.90 (s, 12H), 3.81 (s, 2H), 6.68 (d, $J$ = 8.7 Hz, 4H), 7.05 (d, $J$ = 8.7 Hz, 4H); $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ 40.0, 41.1, 113.2, 129.6, 130.5, 149.2; IR (KBr) 3092, 3075, 3005, 2887, 2805, 1902, 1883, 1852, 1722, 1614, 1564, 1522, 1481, 1445, 1356, 1342, 1310, 1233, 1190, 1169, 1123, 1070, 949, 943, 901, 829, 795, 739, 714, 702, 687, 637, 569, 505 cm$^{-1}$; HRMS (FAB) calcd for $C_{17}H_{22}N_2$ 254.1783, found 254.1783 ($M^+$).

**4,4'-Methylenebis(*N*,*N*,3-trimethylaniline) (3b).**



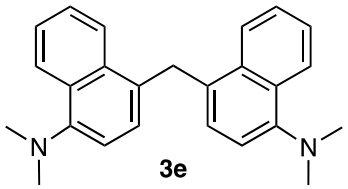

Reaction time 24 h; Eluent = hexane/EtOAc (10:1); 37.7 mg (0.133 mmol, 53% yield); White solid; mp 81–82 °C; $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 2.24 (s, 6H), 2.90 (s, 12H), 3.74 (s, 2H), 6.52 (dd, $J$ = 2.7, 8.3 Hz, 2H), 6.61 (d, $J$ = 2.7 Hz, 2H), 6.77 (d, $J$ = 8.5 Hz, 2H); $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ 20.3, 34.9, 41.1, 110.8, 115.0, 127.8, 130.0, 137.2, 149.3; IR (KBr) 2982, 2965, 2941, 2916, 2884, 2878, 2841, 2795, 1614, 1566, 1508, 1479, 1445, 1346, 1331, 1290, 1227, 1196, 1186, 1109, 1096, 1059, 1011, 966, 843, 818, 800, 777, 702 cm$^{-1}$; HRMS (FAB) calcd for $C_{19}H_{26}N_2$ 282.2096, found 282.2095 ($M^+$).

**4,4'-Methylenebis(3-bromo-*N*,*N*-dimethylaniline) (3d).**



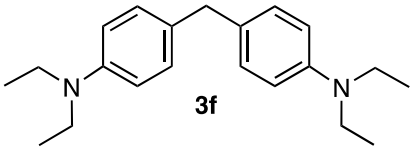

Reaction time 24 h; Eluent = hexane/EtOAc (10:1); 51.9 mg (0.126 mmol, 50% yield); White solid; mp 96–97 °C; $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 2.91 (s, 12H), 4.00 (s, 2H), 6.58 (dd, $J$ = 2.6, 8.5 Hz, 2H), 6.85 (d, $J$ = 8.6 Hz, 2H), 6.94 (d, $J$ = 2.6 Hz, 2H); $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ 39.9, 40.6, 111.9, 116.3, 125.7, 127.2, 130.8, 150.1; IR (KBr) 3071, 2990, 2886, 2880, 2851, 2803, 1609, 1545, 1506, 1441, 1427, 1362, 1356, 1329, 1229, 1173, 1132, 1065, 1020, 959, 845, 826, 820, 806, 791, 739, 696, 685, 669 cm$^{-1}$; HRMS (FAB) calcd for $C_{17}H_{20}N_2{}^{79}Br^{81}Br$ 411.9973, found 411.9977 ($M^+$).

**4,4'-Methylenebis[1-(dimethylamino)naphthalene] (3e).**



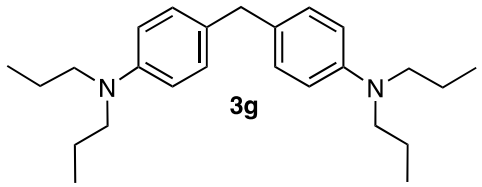

Reaction time 72 h; Eluent = hexane/$CHCl_3$ (3:1); 46.4 mg (0.131 mmol, 52% yield); White solid; mp 181–182 °C; $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 2.88 (s, 12H), 4.75 (s, 2H), 6.95 (d, $J$ = 7.7 Hz, 2H), 6.99 (d, $J$ = 7.7 Hz, 2H), 7.45–7.53 (m, 4H), 8.03 (d, $J$ = 8.7 Hz, 2H), 8.33 (d, $J$ = 8.1 Hz, 2H); $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ 35.4, 45.5, 114.0, 124.6, 124.9, 125.0, 126.0, 127.1, 129.2, 131.1, 133.5, 149.9; IR (KBr) 3067, 3044, 2992, 2980, 2938, 2859, 2825, 2785, 1582, 1512, 1476, 1462, 1452, 1423, 1391, 1308, 1206, 1184, 1144, 1055, 1043, 995, 847, 831, 772 cm$^{-1}$; HRMS (FAB) calcd for $C_{25}H_{26}N_2$ 354.2096, found 354.2096 ($M^+$).

**4,4'-Methylenebis(*N*,*N*-diethylaniline) (3f).**



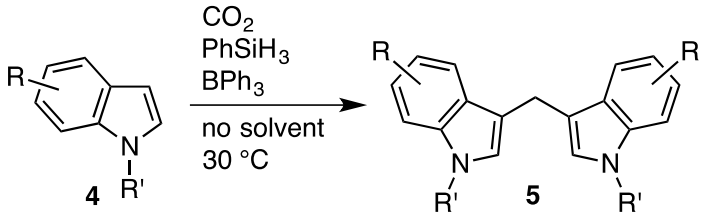

Reaction time 24 h; Eluent = hexane/EtOAc (10:1); 35.8 mg (0.115 mmol, 46% yield); Colorless oil; $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 1.13 (t, $J$ = 7.0 Hz, 12H), 3.31 (q, $J$ = 7.1 Hz, 8H), 3.77 (s, 2H), 6.62 (d, $J$ = 8.8 Hz, 4H), 7.03 (d, $J$ = 8.6 Hz, 4H); $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ 12.7, 39.9, 44.6, 112.3, 129.3, 129.7, 146.2; IR (neat) 3094, 3073, 3030, 3009, 2970, 2930, 2893, 2870, 2835, 1614, 1566, 1520, 1516, 1466, 1447, 1431, 1395, 1373, 1356, 1263, 1196, 1152, 1134, 1094, 1076, 1028, 1013, 999, 799, 739, 698, 509 cm$^{-1}$; HRMS (FAB) calcd for $C_{21}H_{30}N_2$ 310.2409, found 310.2408 ($M^+$).

**4,4'-Methylenebis(*N*,*N*-propylaniline) (3g).**




50 °C, 72 h; Eluent = hexane/EtOAc (20:1); 10.3 mg (0.0281 mmol, 11% yield); Colorless oil; $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 0.90 (t, $J$ = 7.4 Hz, 12H), 1.53–1.62 (m, 8H), 3.18 (t, $J$ = 7.6 Hz, 8H), 3.76 (s, 2H), 6.56 (d, $J$ = 8.7 Hz, 4H), 7.01 (d, $J$ = 8.7 Hz, 4H); $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ 11.6, 20.6, 39.9, 53.2, 112.0, 128.9, 129.6, 146.6.

**(b) Synthesis of diindolylmethanes 5.**

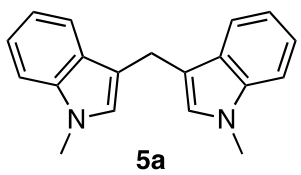



**General procedure for liquid indoles (4a, 4c, 4e, 4f, 4j–l).** In a glovebox (purge type) under $N_2$ atmosphere, $BPh_3$ (48.4 mg, 0.20 mmol, 10 mol% based on $PhSiH_3$) was put in a 30 mL Schlenk flask, and the flask was taken out from the glovebox. After the flask was evacuated and filled with $CO_2$ (1 atm, balloon, ca. 1.6 L), indole **4** (1.0 mmol) and $PhSiH_3$ (250 μL, 2.0 mmol, stored over molecular sieves 3A) were added in this order via syringes, and the mixture was stirred at 30 °C for reaction time. Purification by column chromatography on basic alumina (short column, $CHCl_3$) and silica gel (eluent shown below) gave **5**.

**General procedure for solid indoles (4b, 4d, 4g–i).** In a glovebox (purge type) under $N_2$ atmosphere, $BPh_3$ (48.4 mg, 0.20 mmol, 10 mol% based on $PhSiH_3$) and indole **4** (1.0 mmol) were put in a 30 mL Schlenk flask, and the flask was taken out from the glovebox. After the flask was evacuated and filled with $CO_2$ (1 atm, balloon, ca. 1.6 L), $PhSiH_3$ (250 μL, 2.0 mmol, stored over molecular sieves 3A) was added via a syringe, and the mixture was stirred at 30 °C for reaction time. Purification by column chromatography on basic alumina (short column, $CHCl_3$) and silica gel (eluent shown below) gave **5**.

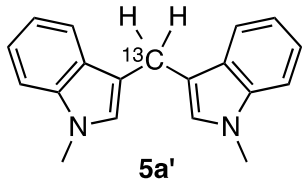
**Product characterizations.** Products **5a**,[S6] **5b**,[S6] **5c**,[S6] **5d**,[S6] **5e**,[S7] **5f**,[S7] **5g**,[S7] **5h**,[S7] **5j**,[S7] **5k**,[S6] and **8a**[S8] were characterized according to the literature.

**3,3'-Methylenebis(1-methylindole) (5a).**




Reaction time 24 h; Eluent = hexane/$CHCl_3$ (2:1); 101 mg (0.369 mmol, 74% yield); White solid; mp 96–99 °C; $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 3.71 (s, 6H), 4.22 (s, 2H), 6.80 (s, 2H), 7.07–7.11 (m, 2H), 7.20–7.25 (m, 2H), 7.30 (d, $J$ = 8.2 Hz, 2H), 7.63 (d, $J$ = 8.0 Hz, 2H); $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ 21.0, 32.7, 109.2, 114.4, 118.7, 119.4, 121.5, 127.1, 128.0, 137.3; IR (KBr) 3117, 3083, 3051, 3024, 2932, 2909, 2886, 2824, 1616, 1555, 1474, 1420, 1373, 1350, 1327, 1292, 1254, 1238, 1200, 1188, 1153, 1126, 1065, 1053, 1011, 930, 845, 829, 810, 799, 783, 741, 691, 598, 579, 559 cm$^{-1}$; HRMS (FAB) calcd for $C_{19}H_{18}N_2$ 274.1470, found 274.1470 ($M^+$).

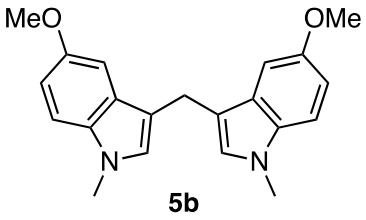
**3,3'-Methylenebis(1-methylindole) labeled with the $^{13}C$ atom (5a').**



**5a'**

Reaction time 24 h; Eluent = hexane/$CHCl_3$ (2:1); 7.6 mg (0.028 mmol, 6% yield); White solid; mp 91–92 °C; $^1H$ NMR ($CDCl_3$, 400 MHz) $\delta$ 3.71 (s, 6H), 4.22 (d, $^1J_{CH}$ = 126.4 Hz, 2H), 6.80 (s, 2H), 7.09 (t, $J$ = 7.4 Hz, 2H), 7.23 (t, $J$ = 7.5 Hz, 2H), 7.30 (d, $J$ = 8.2 Hz, 2H), 7.63 (d, $J$ = 7.8 Hz, 2H); $^{13}C$ NMR ($CDCl_3$, 100 MHz) $\delta$ 21.0, 32.7, 109.2, 114.5 (d, $J$ = 48.5 Hz), 118.7, 119.4, 121.5, 127.1 (d, $J$ = 5.3 Hz); HRMS (FAB) calcd for $^{12}C_{18}{}^{13}CH_{18}N_2$ 275.1504, found 275.1504 ($M^+$).

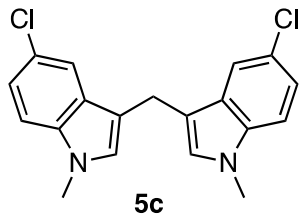
**3,3'-Methylenebis(5-methoxy-1-methylindole) (5b).**



**5b**

Reaction time 24 h; Eluent = hexane/$CHCl_3$ (3:2); 98.9 mg (0.296 mmol, 59%); Slightly brown solid; mp 132–133 °C; $^1H$ NMR ($CDCl_3$, 400 MHz) $\delta$ 3.68 (s, 6H), 3.82 (s, 6H), 4.14 (s, 2H), 6.76 (s, 2H), 6.89 (dd, $J$ = 2.4, 8.8 Hz, 2H), 7.07 (d, $J$ = 2.4 Hz, 2H), 7.19 (d, $J$ = 8.8 Hz, 2H); $^{13}C$ NMR ($CDCl_3$, 100 MHz) $\delta$ 21.1, 32.8, 56.1, 101.3, 110.0, 111.7, 113.8, 127.8, 128.3, 132.7, 153.7; IR (KBr) 3105, 3059, 3001, 2954, 2904, 2832, 2798, 1847, 1667, 1620, 1578, 1539, 1493, 1450, 1423, 1381, 1350, 1315, 1300, 1285, 1261, 1246, 1227, 1177, 1150, 1134, 1057, 1030, 918, 899, 887, 837, 814, 795, 775, 760, 710, 698, 667, 633, 621, 606 $cm^{-1}$; HRMS (FAB) calcd for $C_{21}H_{22}N_2O_2$ 334.1681, found 334.1681 ($M^+$).

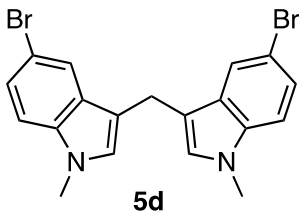
**3,3'-Methylenebis(5-chloro-1-methylindole) (5c).**



**5c**

Reaction time 48 h; Eluent = hexane/$CHCl_3$ (2:1); 95.4 mg (0.278 mmol, 56% yield); White solid; mp 123–125 °C; $^1H$ NMR ($CDCl_3$, 400 MHz) $\delta$ 3.71 (s, 6H), 4.11 (s, 2H), 6.80 (s, 2H), 7.14–7.21 (m, 4H), 7.54 (d, $J$ = 1.9 Hz, 2H); $^{13}C$ NMR ($CDCl_3$, 100 MHz) $\delta$ 20.9, 32.9, 110.4, 113.7, 118.8, 121.9, 124.7, 128.4, 128.9, 135.8; IR (KBr) 3063, 2909, 2824, 1562, 1543, 1477, 1423, 1377, 1342, 1296, 1277, 1242, 1227, 1200, 1138, 1080, 1049, 1015, 868, 860, 829, 814, 799, 787, 772, 756, 694, 648, 610, 575 $cm^{-1}$; HRMS (FAB) calcd for $C_{19}H_{16}N_2{}^{35}Cl_2$ 342.0691, found 342.0691 ($M^+$).

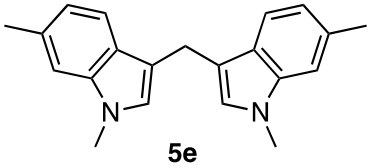
**3,3'-Methylenebis(5-bromo-1-methylindole) (5d).**



**5d**

Reaction time 24 h; Eluent = hexane/$CHCl_3$ (2:1); 145 mg (0.336 mmol, 67% yield); Pink solid; mp 58–63 °C; $^1H$ NMR ($CDCl_3$, 400 MHz) $\delta$ 3.70 (s, 6H), 4.10 (s, 2H), 6.78 (s, 2H), 7.16 (d, $J$ = 8.7 Hz, 2H), 7.29 (dd, $J$ = 1.8, 8.7 Hz, 2H), 7.70 (d, $J$ = 1.8 Hz, 2H); $^{13}C$ NMR ($CDCl_3$, 100 MHz) $\delta$ 20.8, 32.8, 110.8, 112.2, 113.6, 121.8, 124.4, 128.2, 129.5, 135.9; IR (KBr) 3071, 3061, 2905, 2824, 1717, 1611, 1560, 1476, 1443, 1422, 1373, 1292, 1275, 1244, 1202, 1144, 1072, 1045, 1015, 868, 860, 812, 795, 789, 771, 754, 692, 640, 608, 604, 596, 567 $cm^{-1}$; HRMS (FAB) calcd for $C_{19}H_{16}N_2{}^{79}Br^{81}Br$ 431.9660, found 431.9664 ($M^+$).

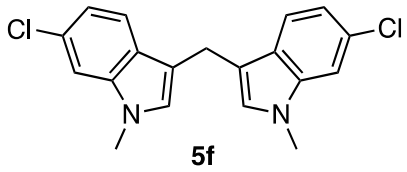
**3,3'-Methylenebis(1,6-dimethylindole) (5e).**



**5e**

Reaction time 3 h; Eluent = hexane/$CHCl_3$ (2:1); 84.3 mg (0.279 mmol, 56% yield); Orange solid; mp 105–109 °C; $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 2.52 (s, 6H), 3.68 (s, 6H), 4.19 (s, 2H), 6.73 (s, 2H), 6.94 (dd, $J$ = 1.1, 8.1 Hz, 2H), 7.11 (s, 2H), 7.52 (d, $J$ = 8.0 Hz, 2H); $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ 21.1, 22.0, 32.6, 109.2, 114.4, 119.1, 120.4, 126.0, 126.5, 131.3, 137.7; IR (KBr) 3076, 3021, 2901, 2886, 1622, 1553, 1476, 1445, 1422, 1368, 1325, 1317, 1250, 1238, 1175, 1134, 1111, 1053, 853, 843, 802, 604, 592, 569 cm$^{-1}$; HRMS (FAB) calcd for $C_{21}H_{22}N_2$ 302.1783, found 302.1783 ($M^+$).

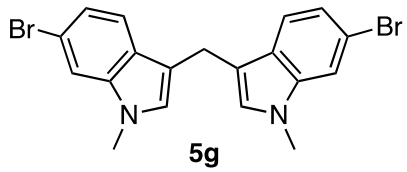
**3,3'-Methylenebis(6-chloro-1-methylindole) (5f).**



**5f**

Reaction time 24 h; Eluent = hexane/$CHCl_3$ (3:1); 102 mg (0.297 mmol, 60% yield); Pink solid; mp 44–52 °C; $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 3.68 (s, 6H), 4.14 (s, 2H), 6.76 (s, 2H), 7.04 (dd, $J$ = 1.8, 8.3 Hz, 2H), 7.28 (d, $J$ = 1.2 Hz, 2H), 7.47 (d, $J$ = 8.4 Hz, 2H); $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ 21.0, 32.8, 109.4, 114.4, 119.5, 120.2, 126.5, 127.7, 127.8, 137.7; IR (KBr) 3115, 3069, 3055, 2934, 2913, 2901, 2884, 2837, 2818, 1715, 1661, 1611, 1476, 1456, 1420, 1366, 1325, 1231, 1198, 1130, 1065, 849, 804, 743, 637, 596 cm$^{-1}$; HRMS (FAB) calcd for $C_{19}H_{16}N_2{}^{35}Cl_2$ 342.0691, found 342.0691 ($M^+$).

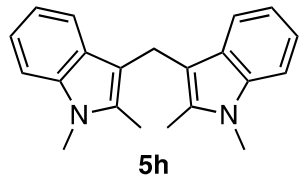
**3,3'-Methylenebis(6-bromo-1-methylindole) (5g).**



**5g**

Reaction time 24 h; Eluent = hexane/$CHCl_3$ (3:1); 114 mg (0.264 mmol, 53% yield); Pink solid; mp 161–164 °C; $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 3.67 (s, 6H), 4.14 (s, 2H), 6.74 (s, 2H), 7.16 (dd, $J$ = 1.8, 8.3 Hz, 2H), 7.42 (d, $J$ = 8.4 Hz, 2H), 7.44 (d, $J$ = 1.6 Hz, 2H); $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ 20.9, 32.8, 112.4, 114.4, 115.4, 120.6, 122.0, 126.8, 127.6, 138.1; IR (KBr) 3061, 2934, 2893, 2831, 2816, 1609, 1545, 1477, 1450, 1429, 1420, 1368, 1323, 1308, 1240, 1200, 1132, 1061, 1053, 935, 930, 831, 799, 704, 590 cm$^{-1}$; HRMS (FAB) calcd for $C_{19}H_{16}N_2{}^{79}Br^{81}Br$ 431.9660, found 431.9664 ($M^+$).

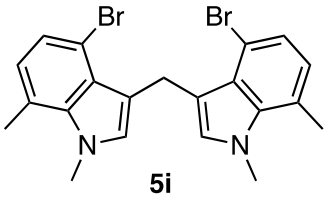
**3,3'-Methylenebis(1,2-dimethylindole) (5h).**



**5h**

Reaction time 3 h; Eluent = hexane/$CHCl_3$ (2:1); 109 mg (0.360 mmol, 72% yield); White solid; mp 160–162 °C; $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 2.38 (s, 6H), 3.65 (s, 6H), 4.15 (s, 2H), 6.95–6.99 (m, 2H), 7.08–7.12 (m, 2H), 7.22 (d, $J$ = 8.2 Hz 2H), 7.43 (d, $J$ = 7.8 Hz, 2H); $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ 10.5, 20.0, 29.5, 108.4, 110.5, 118.5, 118.6, 120.3, 128.2, 132.8, 136.6; IR (KBr) 3046, 2934, 2911, 2893, 2843, 1611, 1562, 1472, 1447, 1433, 1408, 1366, 1331, 1252, 1215, 1186, 1177, 1146, 1128, 1013, 733 cm$^{-1}$; HRMS (FAB) calcd for $C_{21}H_{22}N_2$ 302.1783, found 302.1783 ($M^+$).

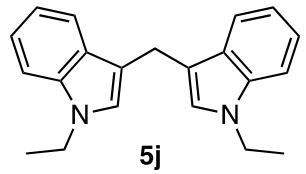
**3,3'-Methylenebis(4-bromo-1,7-dimethylindole) (5i).**



**5i**

Reaction time 36 h; Eluent = hexane/$CHCl_3$ (2:1); 161 mg (0.350 mmol, 70% yield); White solid; mp 211–215 °C; $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 2.70 (s, 6H), 3.94 (s, 6H), 4.73 (s, 2H), 6.53 (s, 2H), 6.71 (d, $J$ = 7.7 Hz, 2H), 7.10 (d, $J$ = 7.6 Hz, 2H); $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ 19.7, 24.0, 36.9, 112.6, 115.9, 120.6, 123.5, 124.9, 126.5, 131.3, 137.2; IR (KBr) 3017, 2959, 2926, 2866, 1595, 1551, 1483, 1449, 1395, 1375, 1331, 1304, 1269, 1223, 1144, 1125, 1096, 1051, 1032, 1001, 922, 827, 820, 799, 787, 610 cm$^{-1}$; HRMS (FAB) calcd for $C_{21}H_{20}N_2{}^{79}Br^{81}Br$ 459.9973, found 459.9972 ($M^+$).

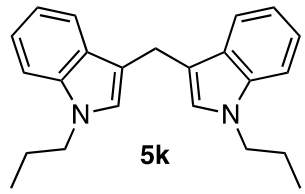
**3,3'-Methylenebis(1-ethylindole) (5j).**



**5j**

50 °C, 6 h; Eluent = hexane/$CHCl_3$ (3:1); 74.5 mg (0.246 mmol, 49% yield); Red oil; $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 1.41 (t, $J$ = 7.3 Hz, 6H), 4.10 (q, $J$ = 7.3 Hz, 4H), 4.23 (s, 2H), 6.86 (s, 2H), 7.06–7.10 (m, 2H), 7.19–7.23 (m, 2H), 7.32 (d, $J$ = 8.3 Hz, 2H), 7.62 (d, $J$ = 8.1 Hz, 2H); $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ 15.7, 21.2, 40.8, 109.3, 114.5, 118.6, 119.6, 121.4, 125.4, 128.2, 136.3; IR (neat) 3111, 3049, 2974, 2932, 2880, 2832, 1726, 1661, 1614, 1551, 1481, 1470, 1447, 1396, 1371, 1354, 1333, 1294, 1275, 1231, 1192, 1153, 1134, 1074, 1013, 939, 922, 841, 826, 789, 777, 737 cm$^{-1}$; HRMS (FAB) calcd for $C_{21}H_{22}N_2$ 302.1783, found 302.1783 ($M^+$).

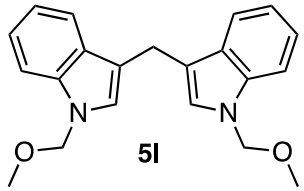
**3,3'-Methylenebis(1-propylindole) (5k).**



**5k**

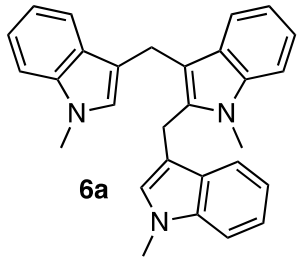
50 °C, 4 h; Eluent = hexane/$CHCl_3$ (3:1); 99.7 mg (0.302 mmol, 60% yield); Red oil; $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 0.91 (t, $J$ = 7.4 Hz, 6H), 1.82 (sext, $J$ = 7.3 Hz, 4H), 4.01 (t, $J$ = 7.1 Hz, 4H), 4.24 (s, 2H), 6.85 (s, 2H), 7.07 (t, $J$ = 7.4 Hz, 2H), 7.18–7.22 (m, 2H), 7.33 (d, $J$ = 8.2 Hz, 2H), 7.62 (d, $J$ = 7.8 Hz, 2H); $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ 11.7, 21.2, 23.7, 48.0, 109.4, 114.2, 118.6, 119.6, 121.3, 126.3, 128.2, 136.6; IR (neat) 3049, 2963, 2932, 2874, 2833, 1661, 1612, 1551, 1479, 1468, 1393, 1356, 1331, 1215, 1192, 1155, 1136, 1078, 1013, 895, 841, 826, 802, 773, 737, 561 cm$^{-1}$; HRMS (FAB) calcd for $C_{23}H_{26}N_2$ 330.2096, found 330.2096 ($M^+$).

**3,3'-Methylenebis[1-(methoxymethyl)indole] (5l).**



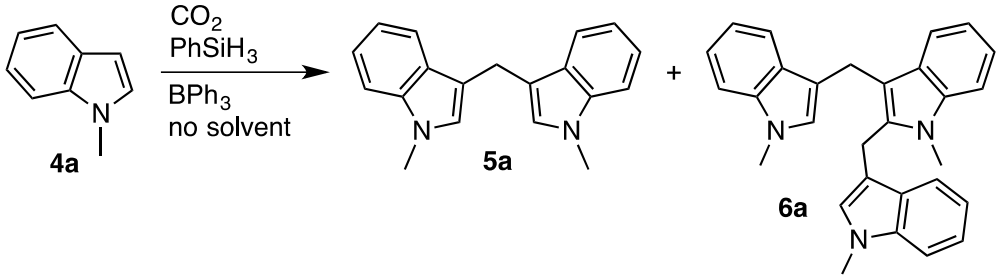

50 °C, 24 h; Eluent = hexane/$CHCl_3$ (3:1); 109 mg (0.327 mmol, 65% yield); Pink solid; mp 58–59 °C; $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 3.22 (s, 6H), 4.22 (s, 2H), 5.38 (s, 4H), 6.94 (s, 2H), 7.13 (t, $J$ = 6.9 Hz, 2H), 7.25 (t, $J$ = 7.0 Hz, 2H), 7.47 (d, $J$ = 8.2 Hz, 2H), 7.61 (d, $J$ = 8.0 Hz, 2H); $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ 21.2, 55.9, 77.3, 109.9, 115.5, 119.6, 119.8, 122.3, 126.3, 128.9, 137.0; IR (KBr) 3082, 3044, 2990, 2943, 2884, 2822, 1614, 1560, 1479, 1464, 1439, 1329, 1231, 1190, 1177, 1153, 1130, 1115, 1090, 1047, 1032, 1013, 908, 793, 785, 750, 737, 700, 646 cm$^{-1}$; HRMS (FAB) calcd for $C_{21}H_{22}N_2O_2$ 334.1681, found 334.1681 ($M^+$).

**1-Methyl-3-{1-methyl-2-[(1-methylindol-3-yl)methyl]indol-3-yl}methylindole (6a).**



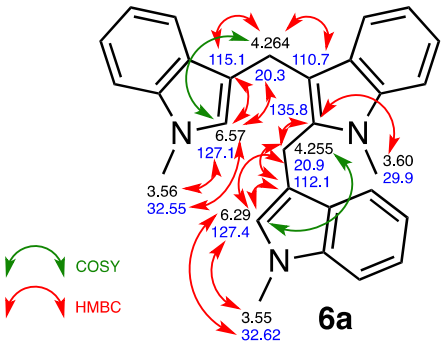

Obtained as a byproduct in the synthesis of **5a**. Orange solid; mp 81–87 °C; $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 3.55 (s, 3H), 3.56 (s, 3H), 3.60 (s, 3H), 4.255 (s, 2H), 4.264 (s, 2H), 6.29 (s, 1H), 6.57 (s, 1H), 7.01–7.12 (m, 3H), 7.16–7.31 (m, 6H), 7.57–7.62 (m, 3H); $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ 20.3, 20.9, 29.9, 32.55, 32.62, 108.8, 109.1, 109.3, 110.7, 112.1, 115.1, 118.6, 118.80, 118.83, 119.0, 119.1, 119.3, 120.8, 121.4, 121.7, 127.1, 127.3, 127.4, 127.9, 128.2, 135.8, 137.0, 137.17, 137.19; IR (KBr) 3049, 2928, 2911, 2899, 2895, 2880, 1614, 1481, 1472, 1445, 1431, 1423, 1369, 1348, 1327, 1236, 1153, 1130, 1117, 1011, 907, 739 cm$^{-1}$; HRMS (FAB) calcd for $C_{29}H_{27}N_3$ 417.2205, found 417.2205 ($M^+$).

**Table S1.** Temperature effect on the formation of **5a** and **6a**.[a]

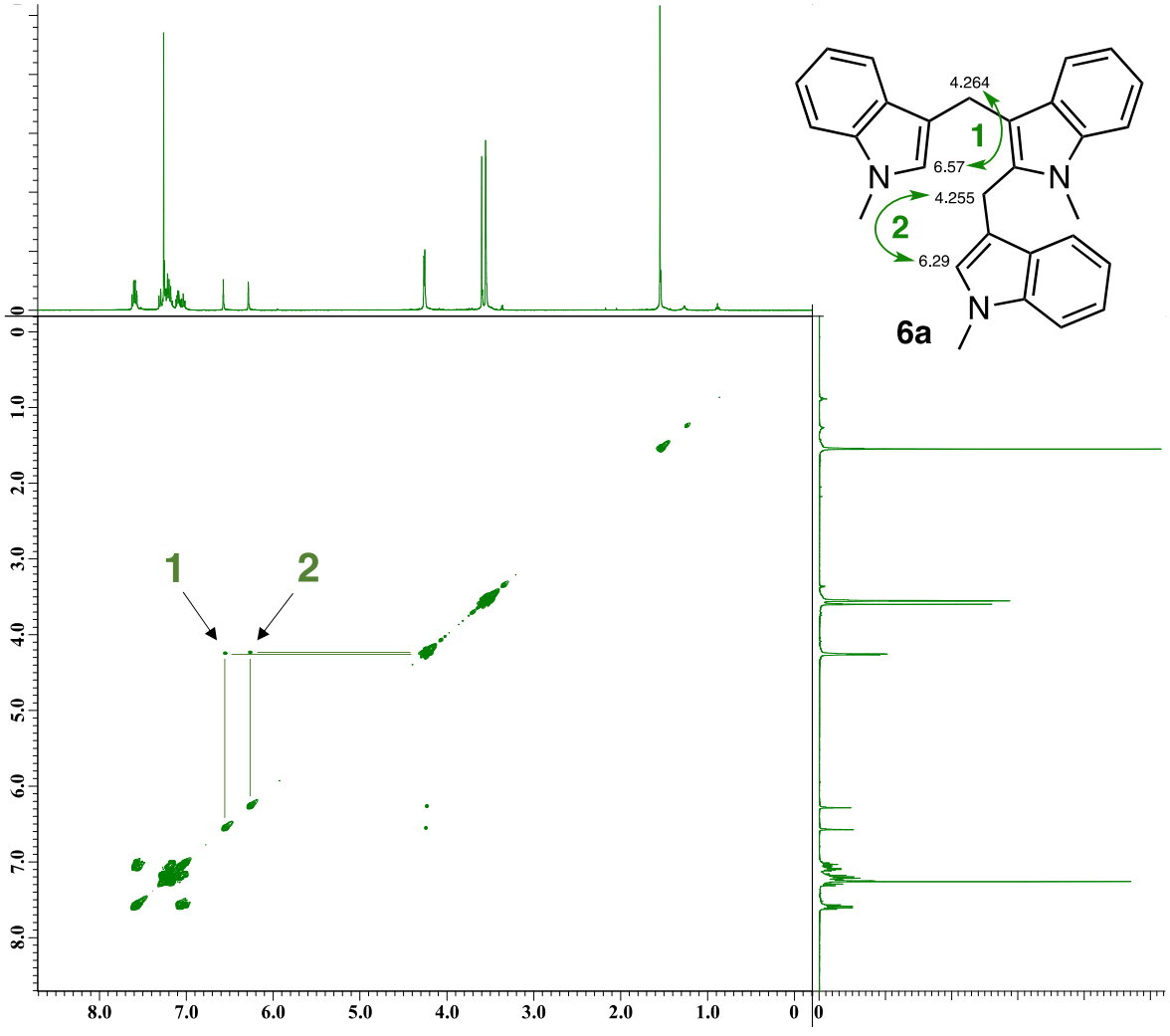



| entry | $T$ (°C) | **4a** (% yield)[b] | **5a** (% yield)[b] | **6a** (% yield)[b] |
|---|---|---|---|---|
| 1 | 10 | 93 | 0 | 0 |
| 2 | 20 | 24 | 77 | trace |
| 3 | 30 | 0 | 62 | 32 |
| 4 | 40 | 0 | 82 | 15 |
| 5 | 60 | 14 | 71 | 6 |

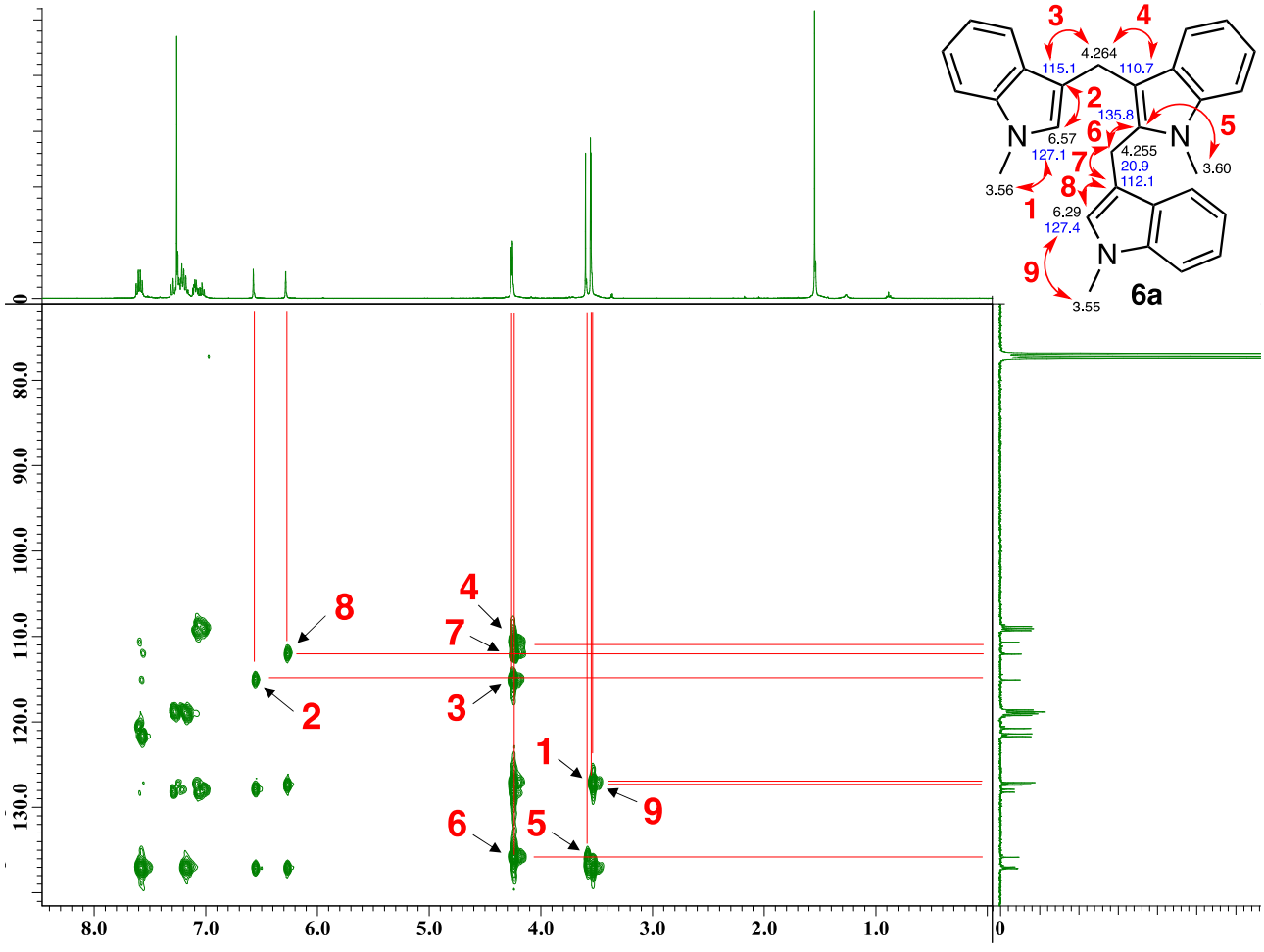
[a] Reaction conditions: **4a** (1.0 mmol), $PhSiH_3$ (2.0 mmol), $BPh_3$ (10 mol% based on $PhSiH_3$), $CO_2$ (1 atm, balloon), 24 h. [b] Determined by NMR using mesitylene as an internal standard.




Correlations observed in 2D NMR spectra of **6a** are summarized above, where the chemical shifts of $^{1}H$ and $^{13}C$ NMR spectra are indicated in black and blue, respectively. Typical spectra are given below.

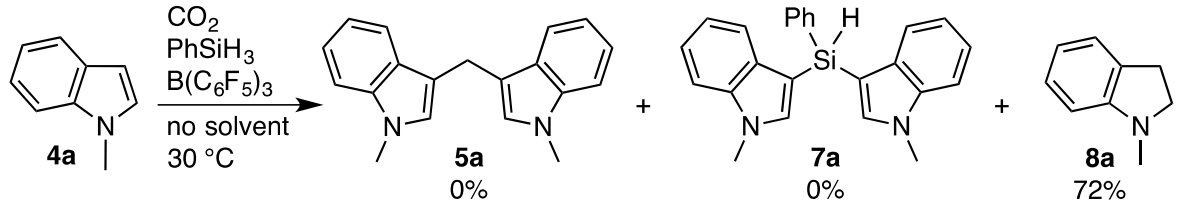



COSY spectrum of **6a** in $CDCl_3$.




HMBC spectrum of **6a** in $CDCl_3$.

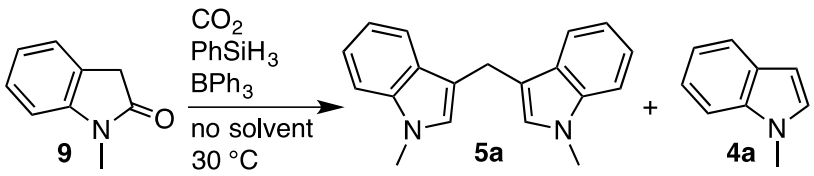
**Control experiment with $B(C_6F_5)_3$.**




Control experiments using $B(C_6F_5)_3$ instead of $BPh_3$ were conducted under the standard reaction conditions to give **8a** after chromatographic purification on silica gel (hexane/$CHCl_3$ (2:1)).

**1-Methylindoline (8a).** Reaction time 24 h; 95.9 mg (0.720 mmol, 72% yield); Slightly purple oil; $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 2.77 (s, 3H), 2.95 (t, $J$ = 8.1 Hz, 2H), 3.30 (t, $J$ = 8.1 Hz, 2H), 6.50 (d, $J$ = 8.1 Hz, 1H), 6.68 (t, $J$ = 7.4 Hz, 1H), 7.07–7.11 (m, 2H); $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ 28.9, 36.4, 56.3, 107.4, 117.9, 124.4, 127.4, 130.4, 153.5; IR (neat) 3048, 3024, 2947, 2918, 2849, 2805, 1611, 1505, 1493, 1470, 1462, 1454, 1377, 1329, 1302, 1273, 1217, 1198, 1169, 1153, 1117, 1082, 1020, 989, 866, 745, 714 cm$^{-1}$; MS (EI) calcd for $C_9H_{11}N$ 133, found 133 ($M^+$).

**Cascade synthesis of 5a from lactam 9.**




< Under the standard conditions >

The reaction was conducted at 30 °C for 24 h according to the above general procedure but using lactam **9** as a substrate. Chromatographic purification on basic alumina (short column, $CHCl_3$) and silica gel (hexane/$CHCl_3$ (2:1)) afforded **5a** (83 mg, 0.30 mmol, 61% yield) and **4a** (24 mg, 0.18 mmol, 18% yield).

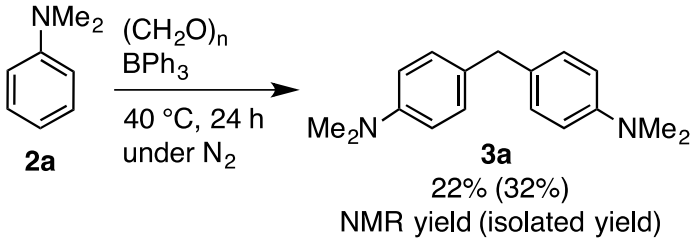
In contrast, a control reaction under $N_2$ (without $CO_2$) gave only **4a** (122 mg, 0.931 mmol, 93% yield).

< Under slightly modified conditions >

The same reaction using **9** in $CO_2$ was also performed under slightly modified conditions; the amount of $PhSiH_3$ was increased to 300 μL (2.4 mmol), and the reaction temperature was set to 35 °C. As a result, **5a** (101 mg, 0.369 mmol, 74% yield) and **4a** (21 mg, 0.16 mmol, 16% yield) were isolated.

**(c) Control experiments with paraformaldehyde.**

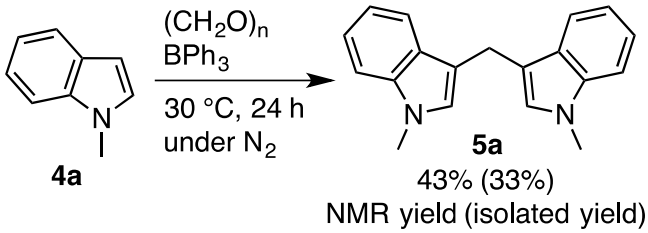
**(c-1) $BPh_3$-catalyzed synthesis of 3a with paraformaldehyde.**




**Scheme S1.** A control reaction with formaldehyde.

In a glovebox (purge type) under $N_2$ atmosphere, $BPh_3$ (48.8 mg, 0.20 mmol, 10 mol% based on the formaldehyde equivalent) and paraformaldehyde (60.3 mg, 2.0 mmol based on the formaldehyde equivalent) were put in a 30 mL Schlenk flask, and the flask was taken out from the glovebox. After the flask was evacuated and filled with $N_2$ (balloon), **2a** (63 µL, 0.50 mmol) was added via a syringe. The mixture was stirred at 40 °C for 24 h to give **3a** in 22% yield (NMR yield determined by using mesitylene as the internal standard). Purification by column chromatography on silica gel (hexane/EtOAc (9:1)) afforded **3a** (20.6 mg, 0.0810 mmol, 32% yield).

**(c-2) $BPh_3$-catalyzed synthesis of 5a with paraformaldehyde.**




**Scheme S2.** A control reaction with formaldehyde.

In a glovebox (purge type) under $N_2$ atmosphere, $BPh_3$ (48.4 mg, 0.20 mmol, 10 mol% based on the formaldehyde equivalent) and paraformaldehyde (60.8 mg, 2.0 mmol based on the formaldehyde equivalent) were put in a 30 mL Schlenk flask, and the flask was taken out from the glovebox. After the flask was evacuated and filled with $N_2$ (balloon), **4a** (125 µL, 1.0 mmol) was added via a syringe. The mixture was stirred at 30 °C for 24 h to give **5a** in 43% yield (NMR yield determined by using mesitylene as the internal standard). Purification by column chromatography on basic alumina (short column, $CHCl_3$) and silica gel (hexane/$CHCl_3$ (2:1)) afforded **5a** (45.2 mg, 0.165 mmol, 33% yield).

**[D] References.**


(S1) W.-D. Li, D.-Y. Zhu, G. Li, J. Chen and J.-B. Xia, *Adv. Synth. Catal.*, 2019, **361**, 5098–5104.

(S2) Z. Yang, B. Yu, H. Zhang, Y. Zhao, Y. Chen, Z. Ma, G. Ji, X. Gao, B. Han and Z. Liu, *ACS Catal.*, 2016, **6**, 1268–1273.

(S3) S. Das, F. D. Bobbink, G. Laurenczy and P. J. Dyson, *Angew. Chem., Int. Ed.*, 2014, **53**, 12876–12879.

(S4) L. Zhang, C. Peng, D. Zhao, Y. Wang, H.-J. Fu, Q. Shen and J.-X. Li, *Chem. Commun.*, 2012, **48**, 5928–5930.

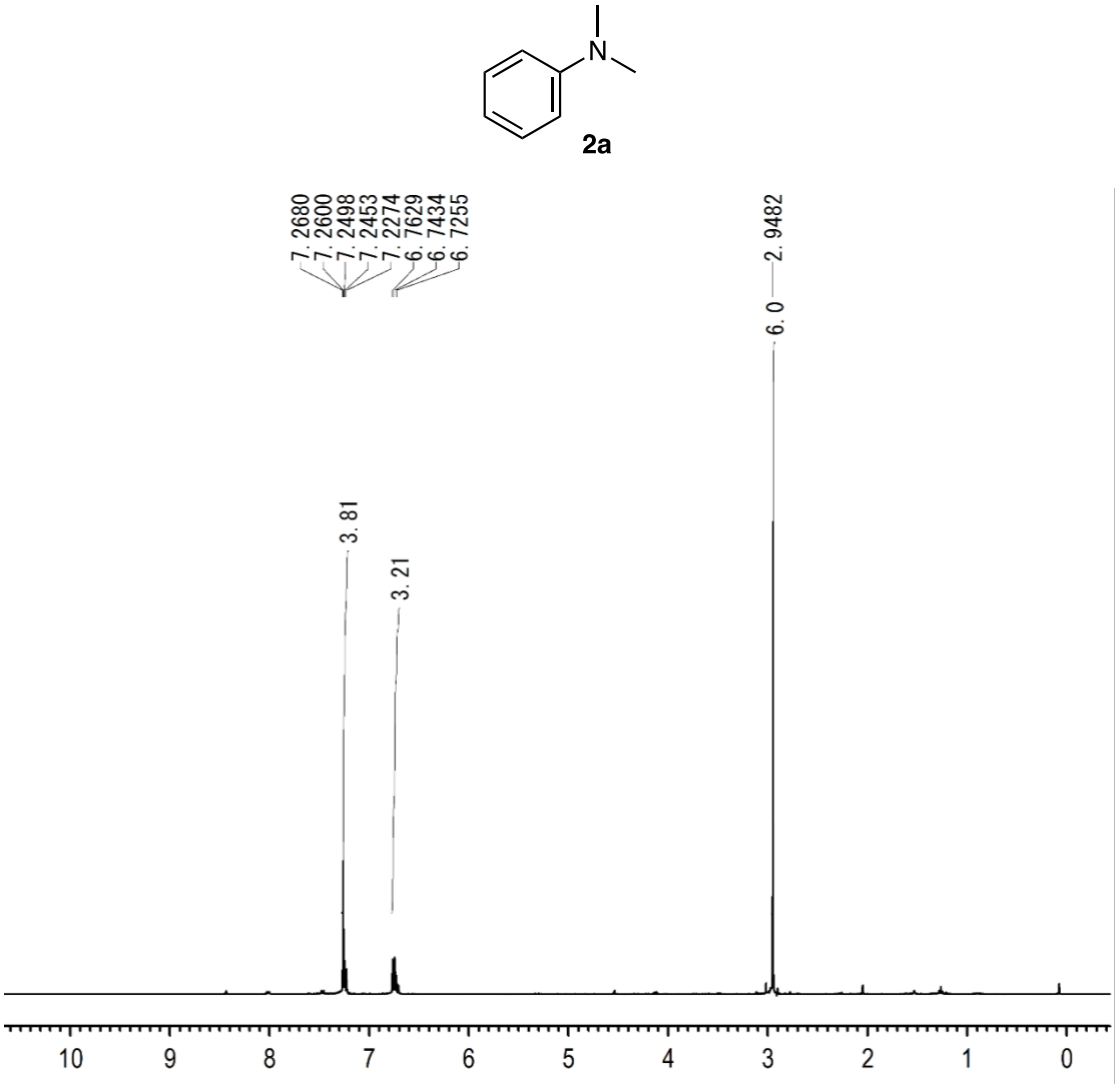
(S5) Y. Wang, R. Duan, Y. Wu, X. Li and C. Deng, *ChemistrySelect*, 2021, **6**, 6097–6101.

(S6) K. Takaishi, H. Kosugi, R. Nishimura, Y. Yamada and T. Ema, *Chem. Commun.*, 2021, **57**, 8083–8086.

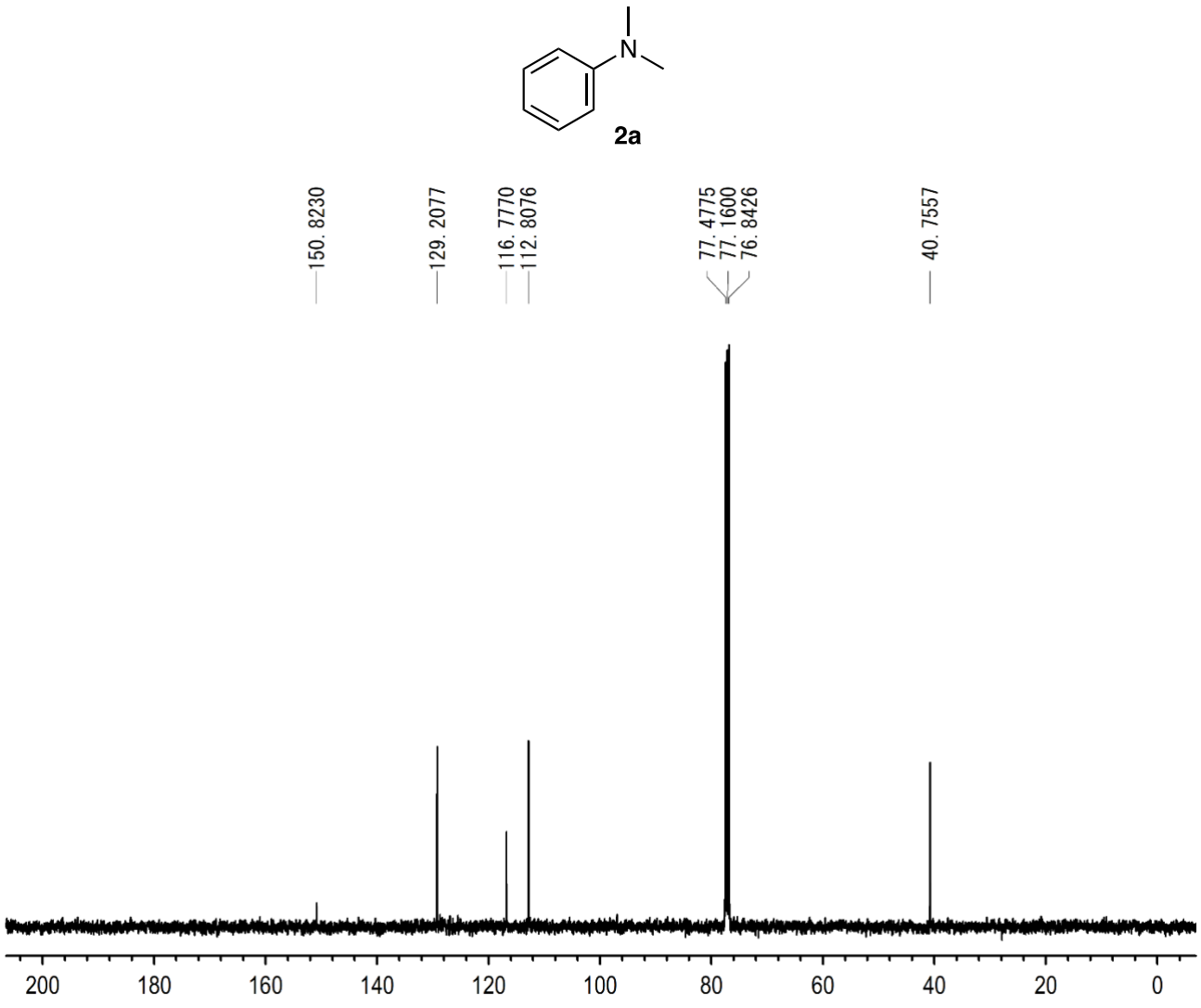
(S7) C. Qiao, X.-F. Liu, H.-C. Fu, H.-P. Yang, Z.-B. Zhang and L.-N. He, *Chem. Asian J.*, 2018, **13**, 2664–2670.

(S8) A. Kulkarni, W. Zhou and B. Török, *Org. Lett.*, 2011, **13**, 5124–5127.

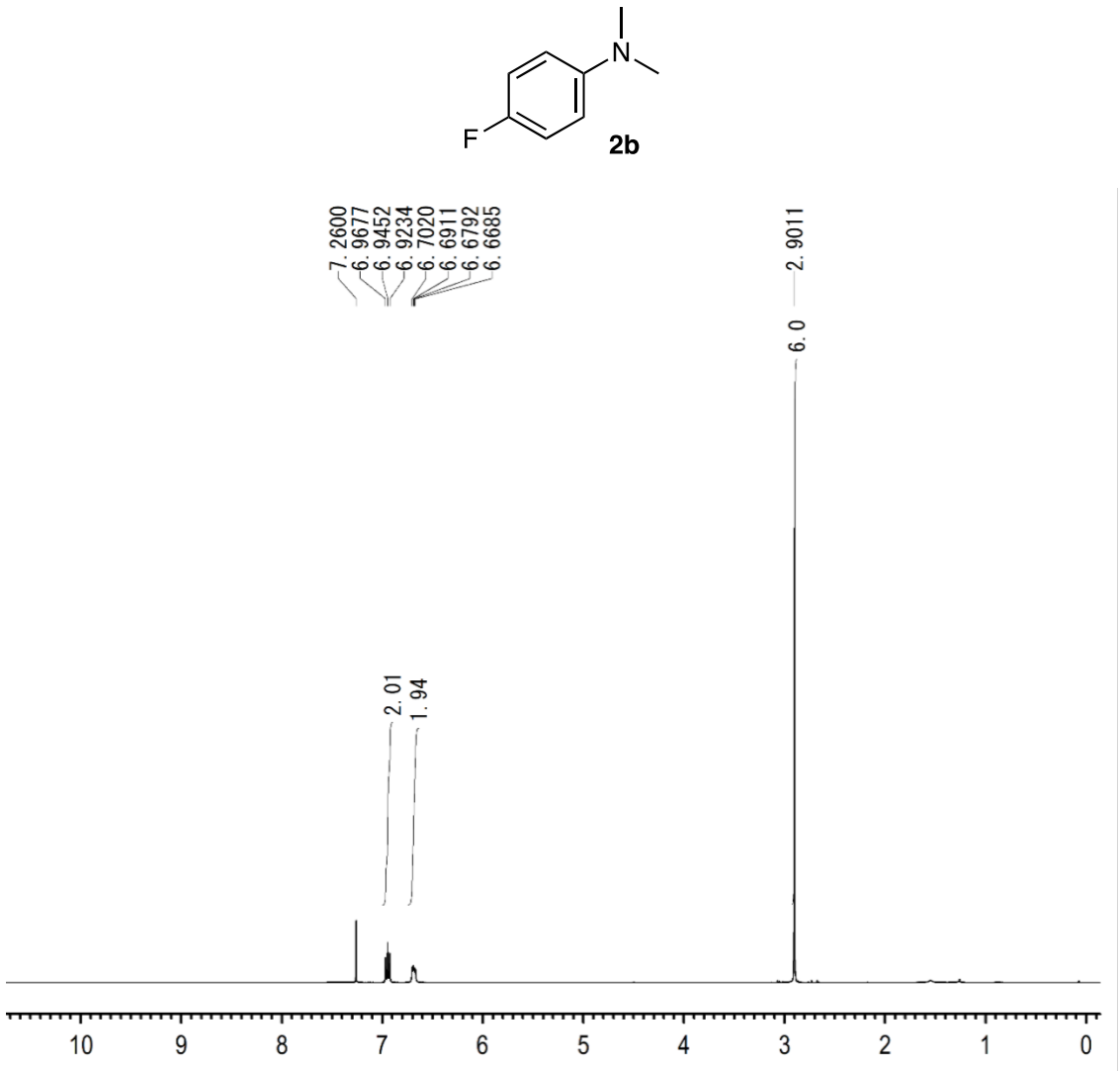
**[E] $^{1}$H and $^{13}$C NMR spectra.**



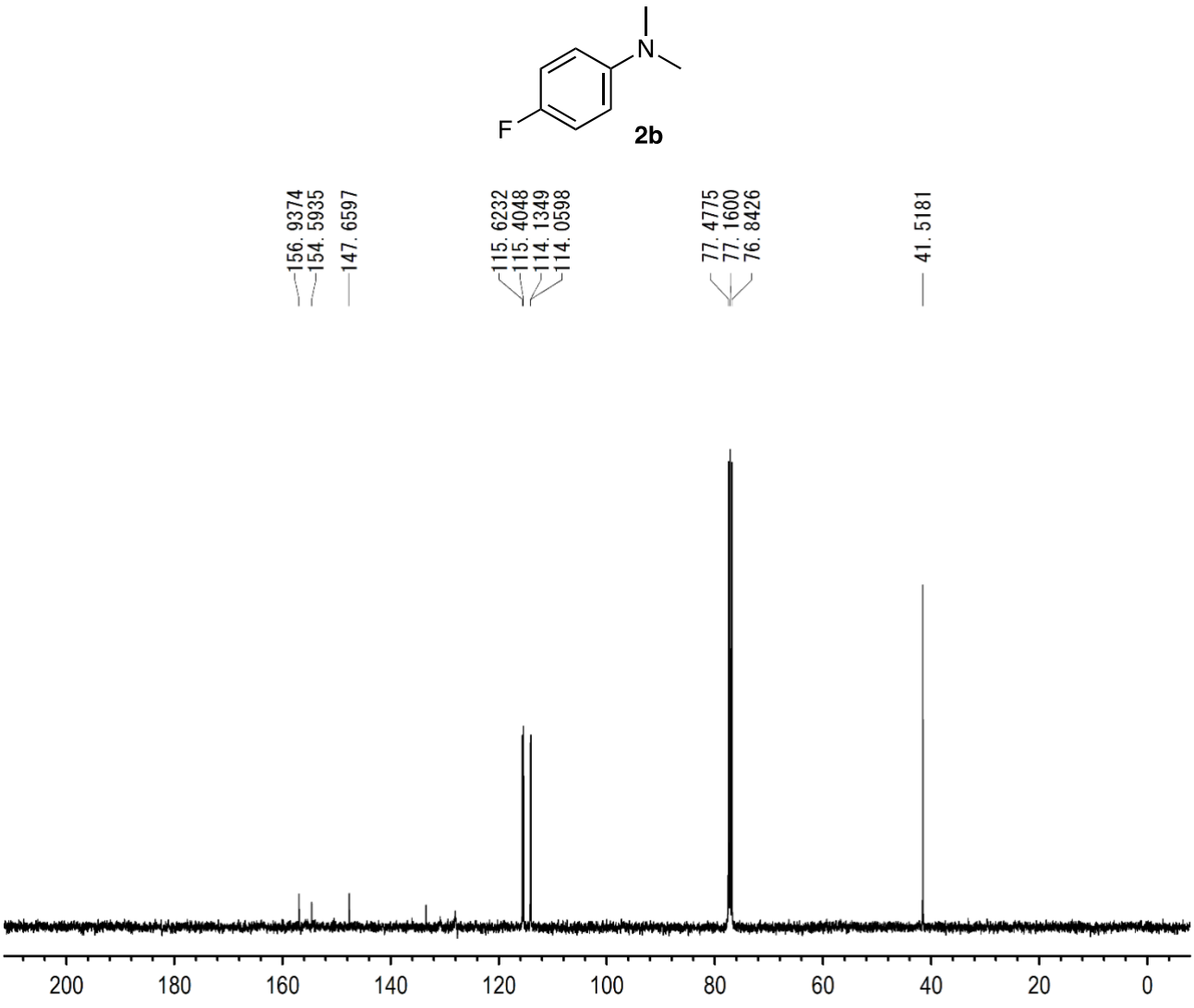

400 MHz $^{1}$H NMR spectrum of **2a** in $CDCl_3$.



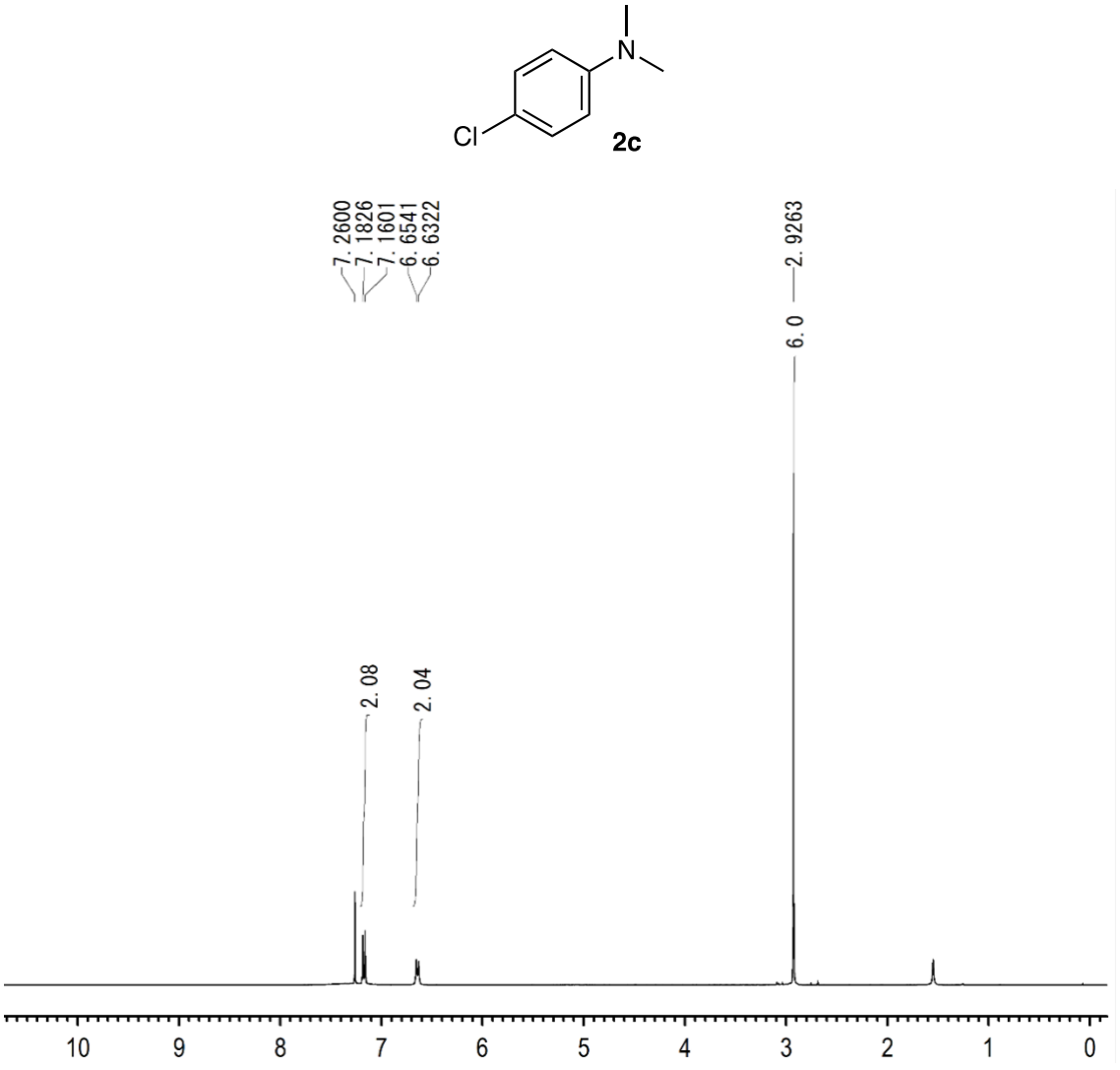

100 MHz $^{13}C$ NMR spectrum of **2a** in $CDCl_3$.



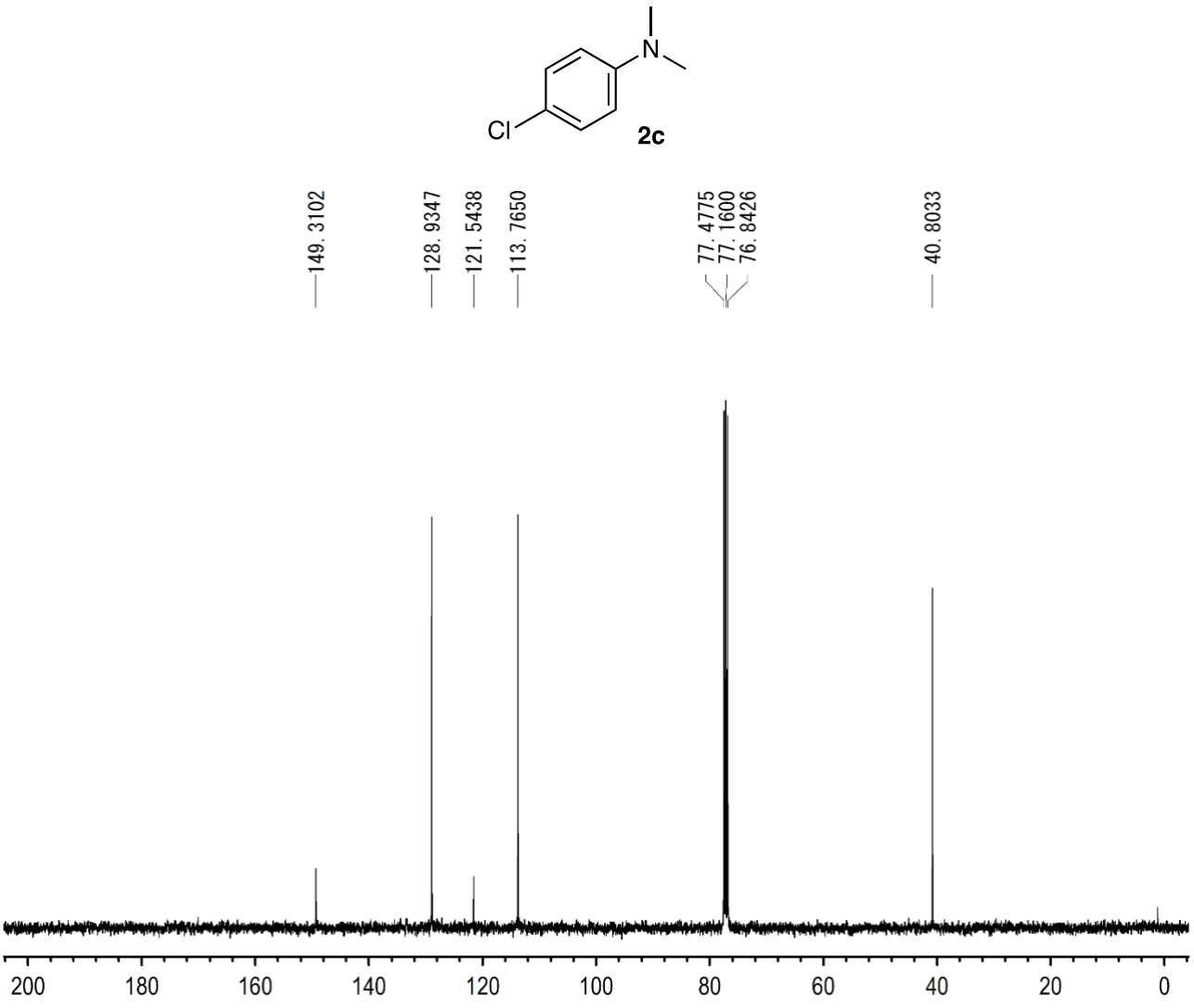

400 MHz $^{1}$H NMR spectrum of **2b** in $CDCl_3$.



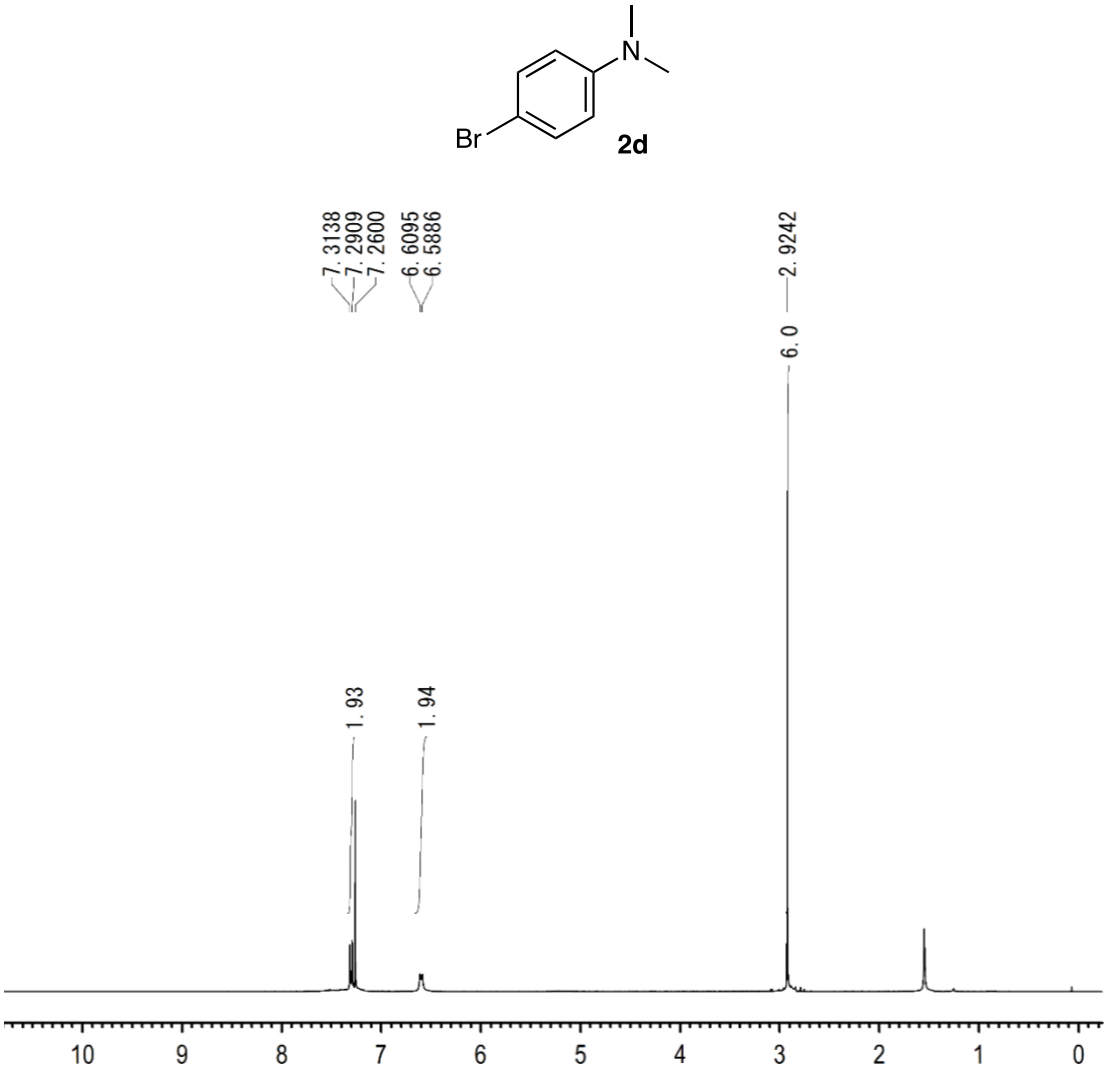

100 MHz $^{13}C$ NMR spectrum of **2b** in $CDCl_3$.



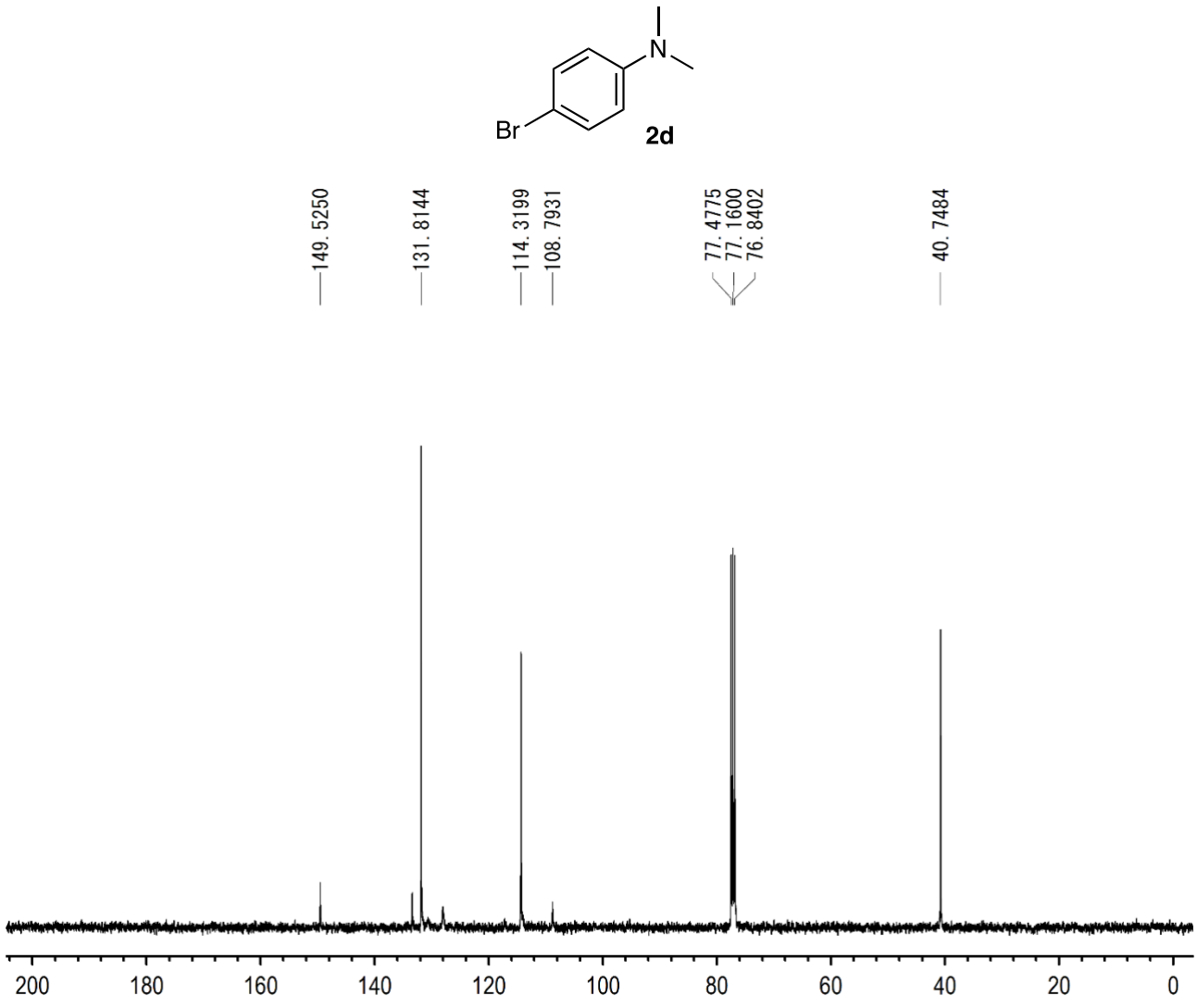

400 MHz $^{1}$H NMR spectrum of **2c** in $CDCl_3$.



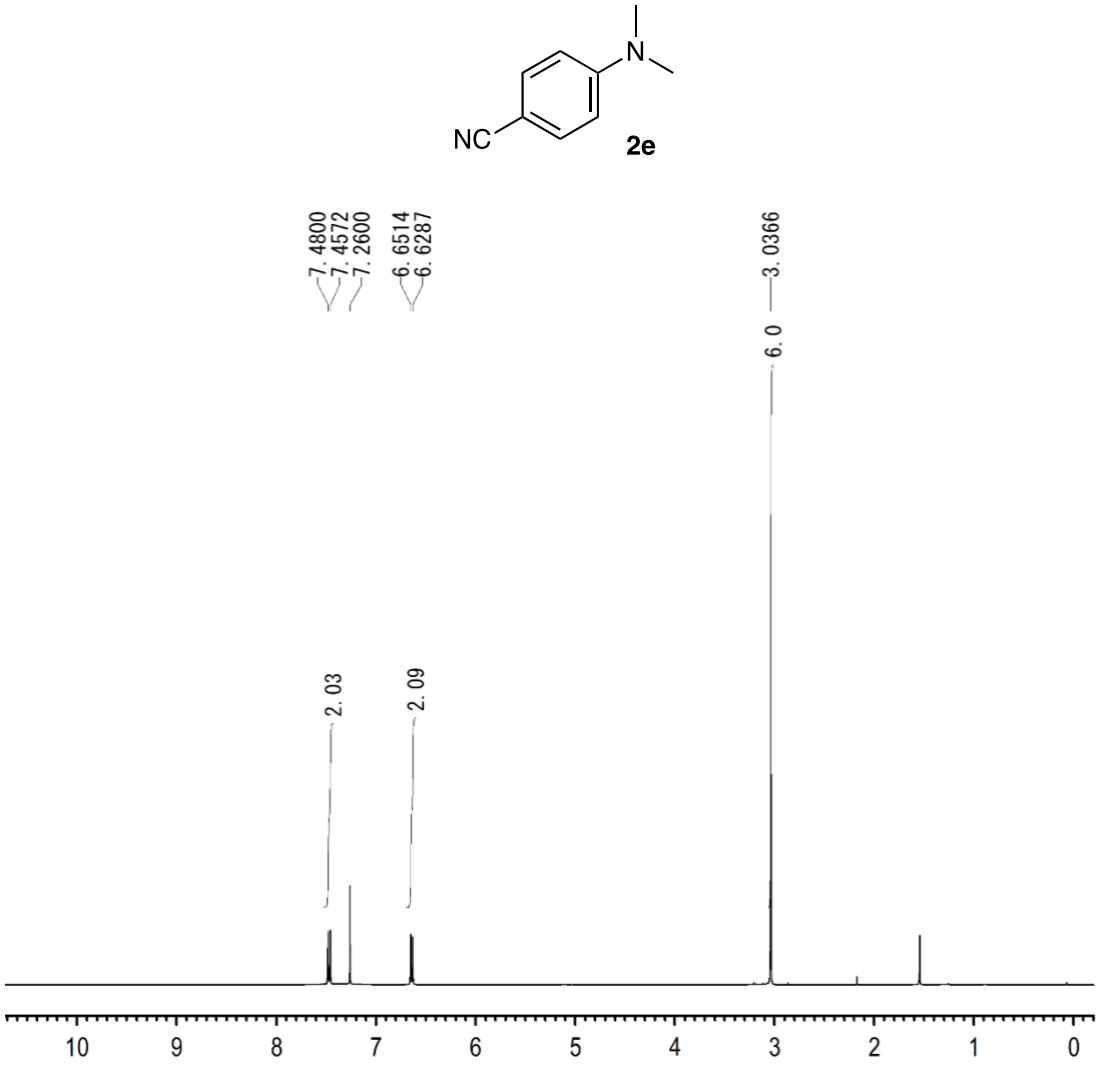

100 MHz $^{13}C$ NMR spectrum of **2c** in $CDCl_3$.



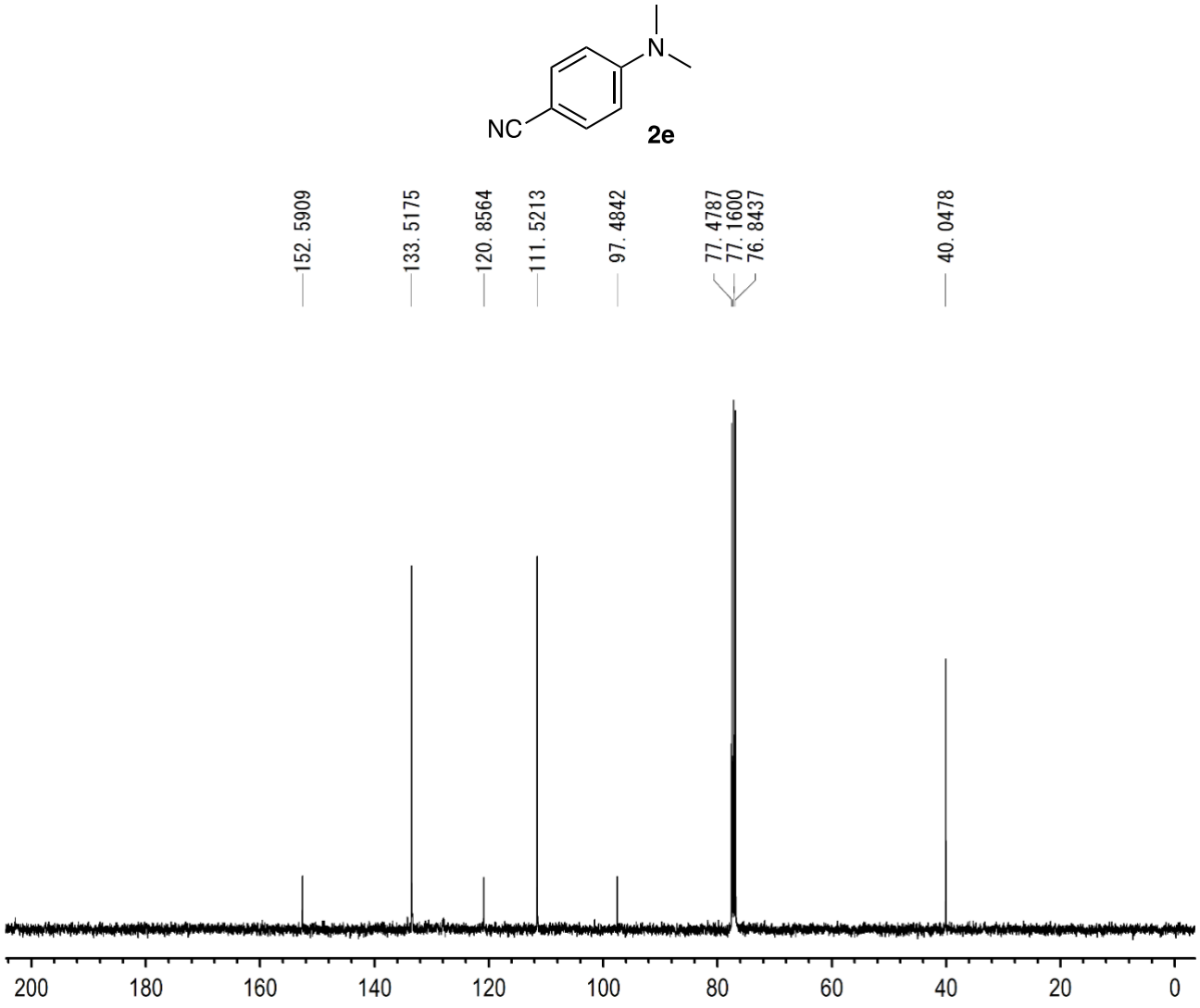

400 MHz $^{1}$H NMR spectrum of **2d** in $CDCl_3$.



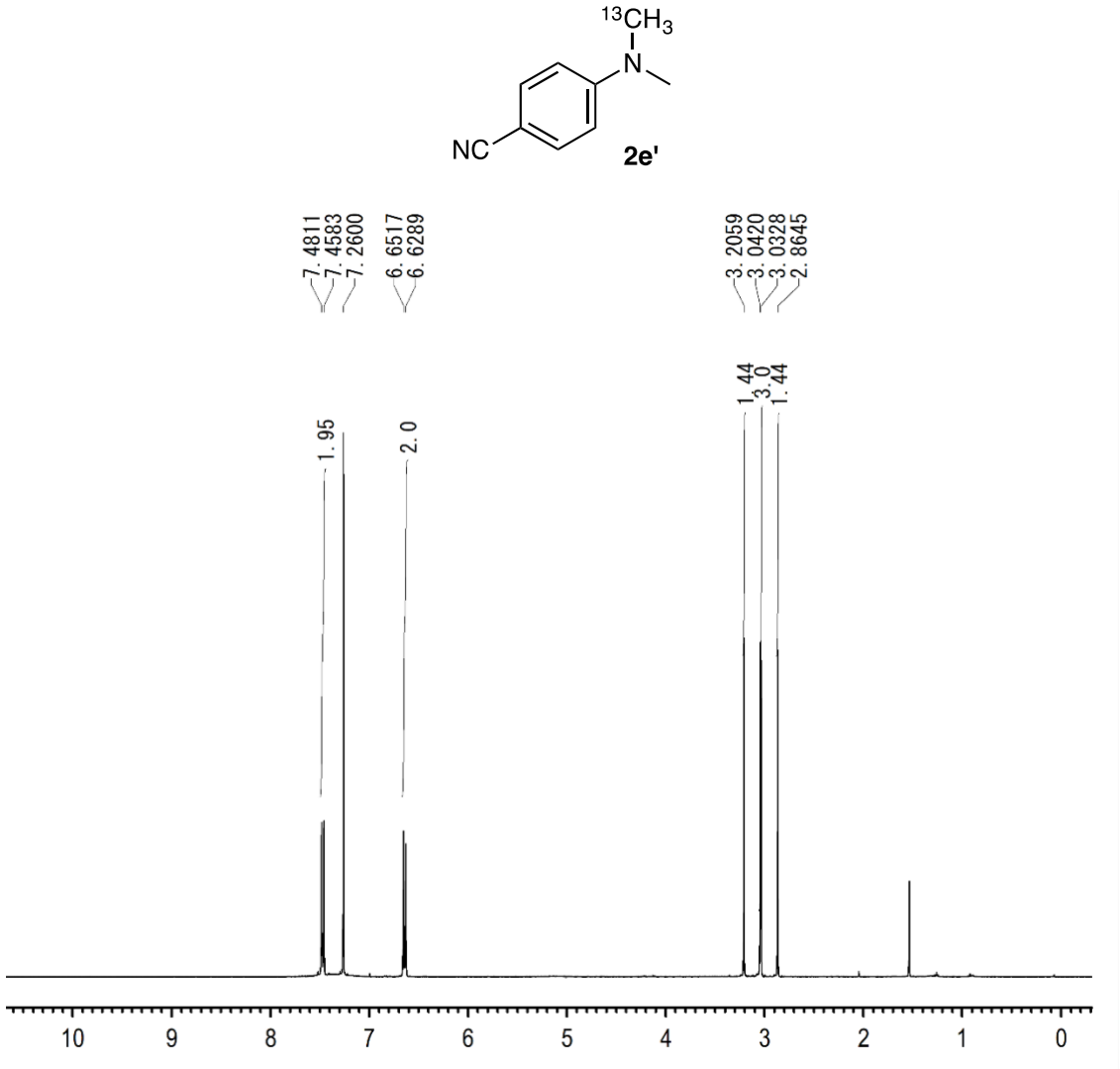

100 MHz $^{13}C$ NMR spectrum of **2d** in $CDCl_3$.



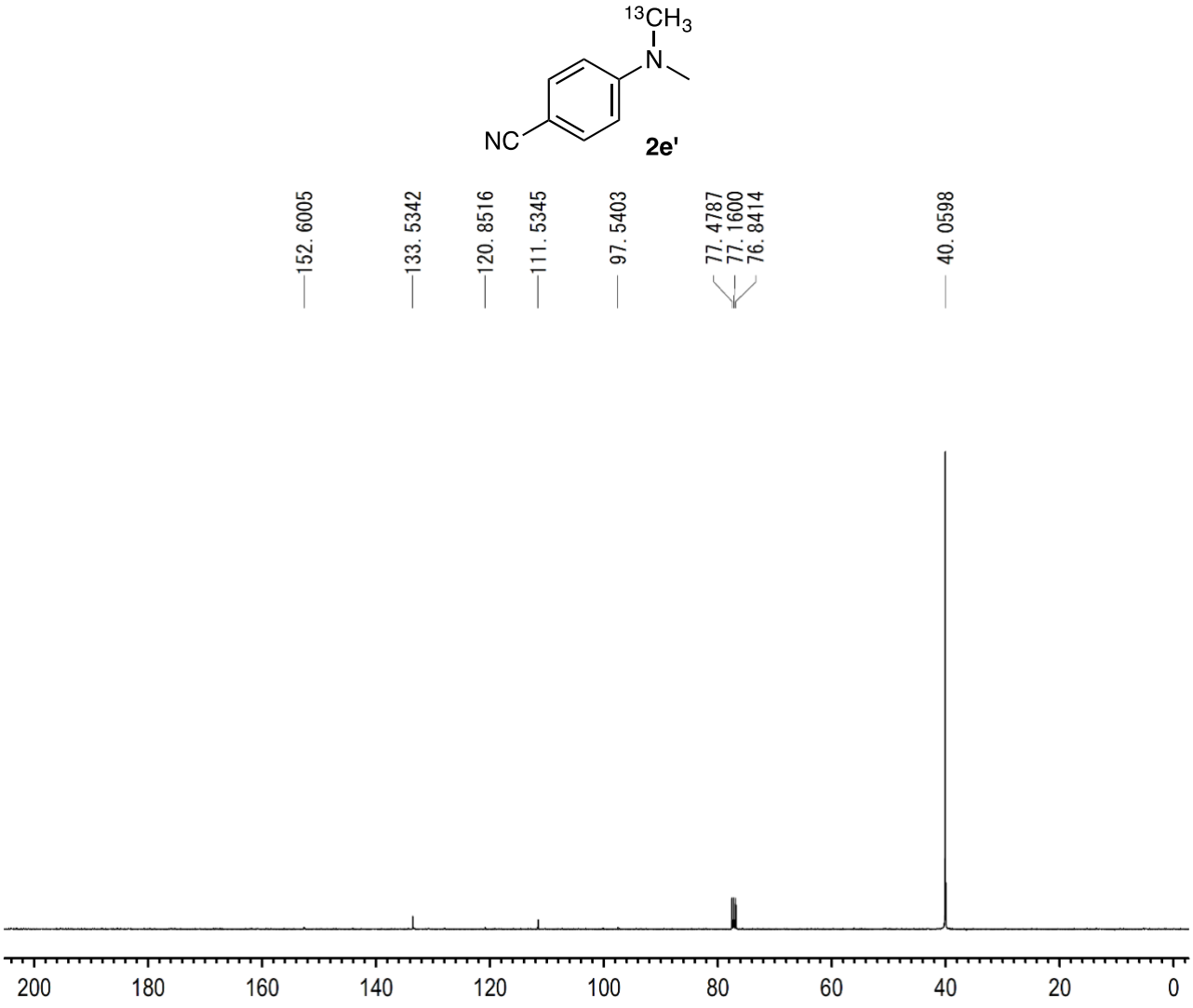

400 MHz $^{1}$H NMR spectrum of **2e** in $CDCl_3$.



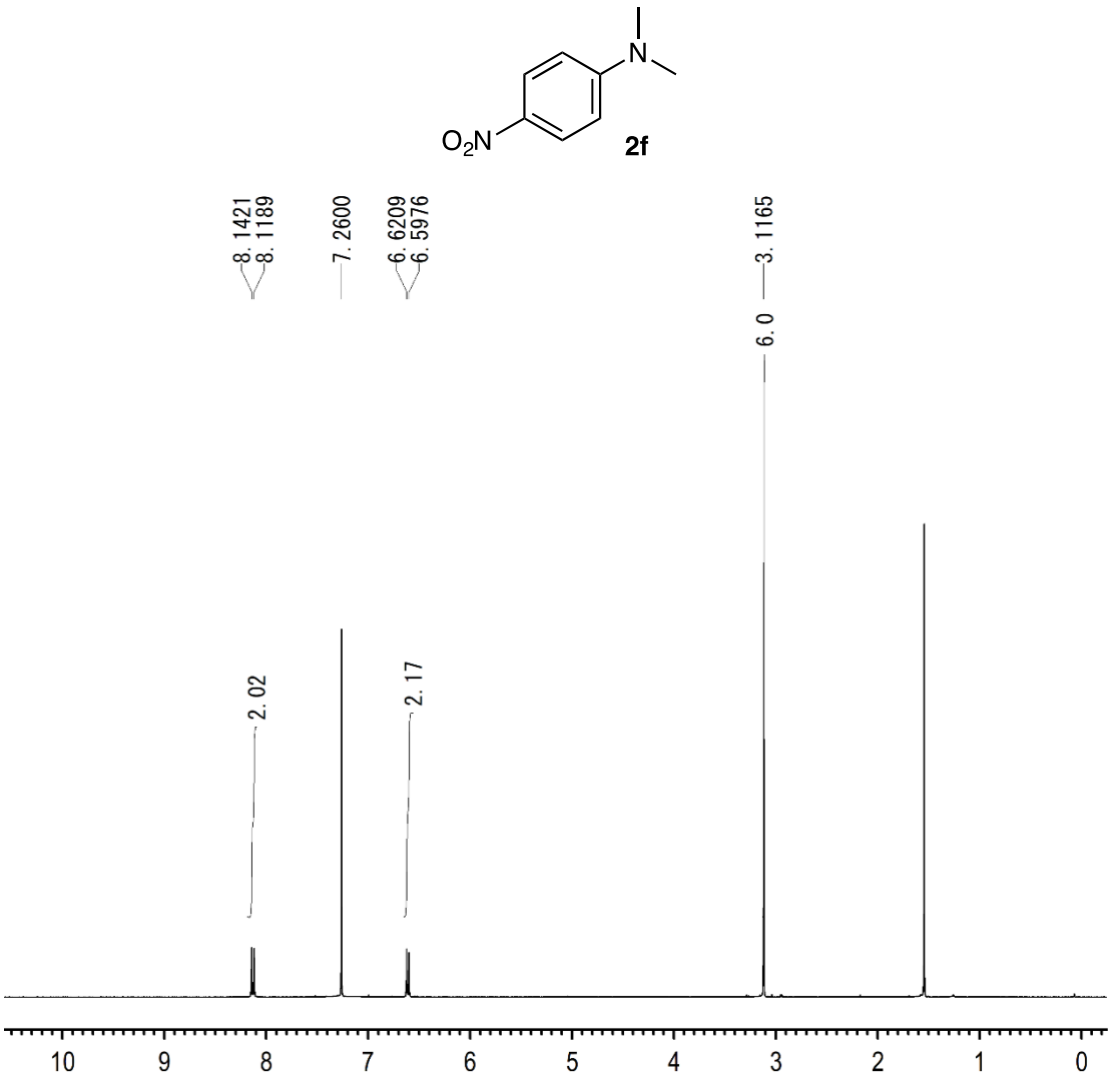

100 MHz $^{13}C$ NMR spectrum of **2e** in $CDCl_3$.



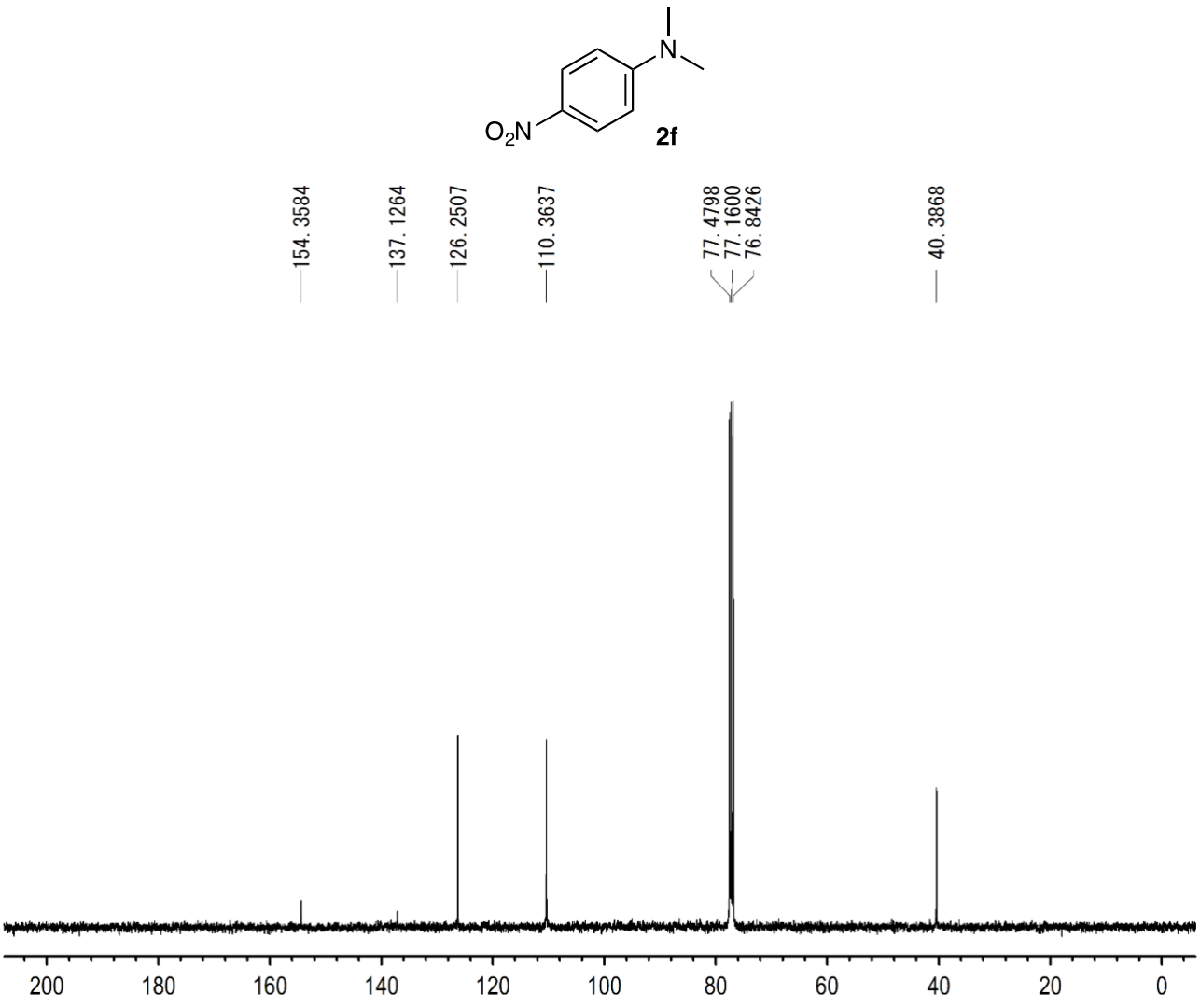

400 MHz $^{1}$H NMR spectrum of **2e'** in $CDCl_3$.



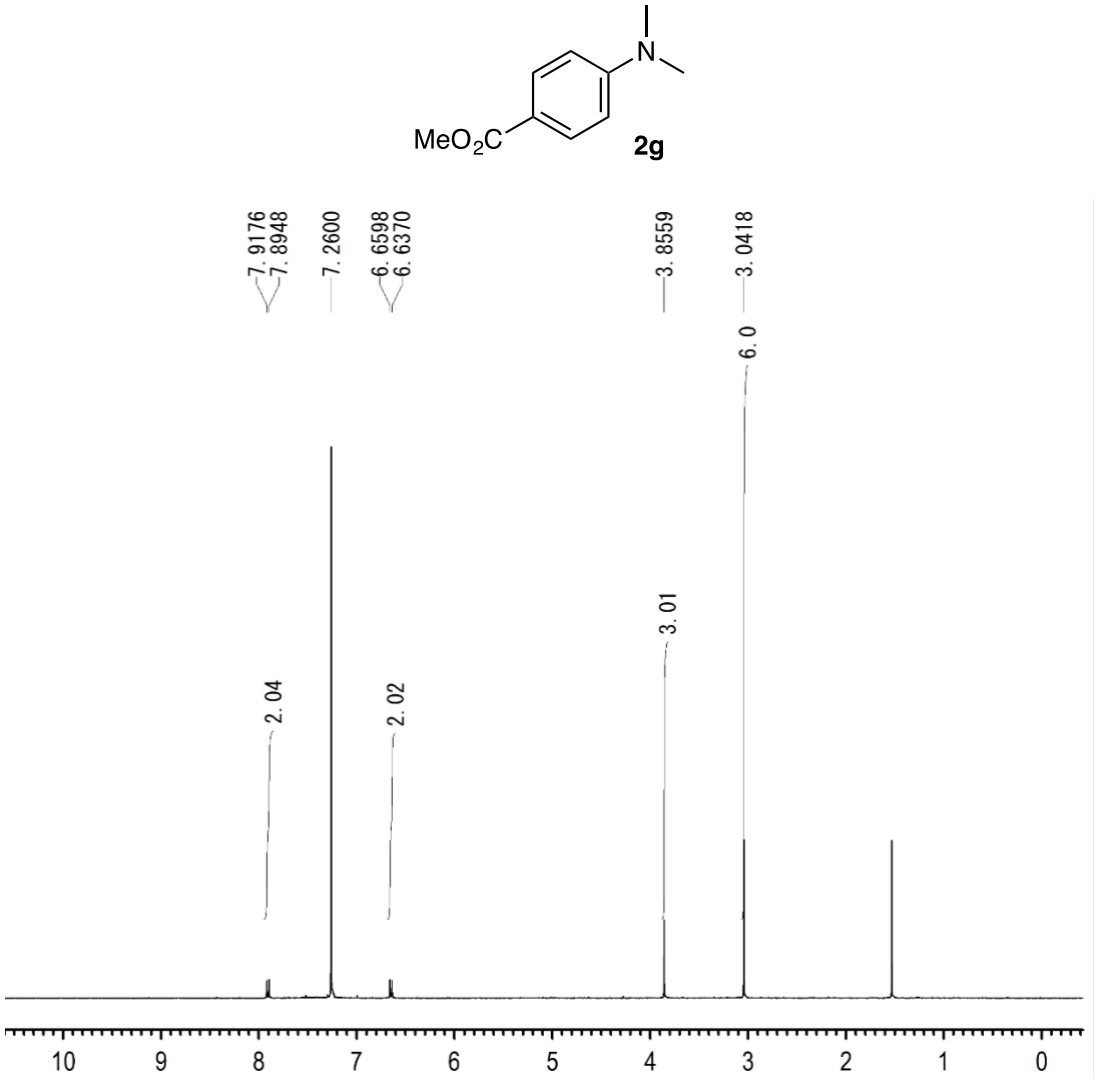

100 MHz $^{13}C$ NMR spectrum of **2e'** in $CDCl_3$.



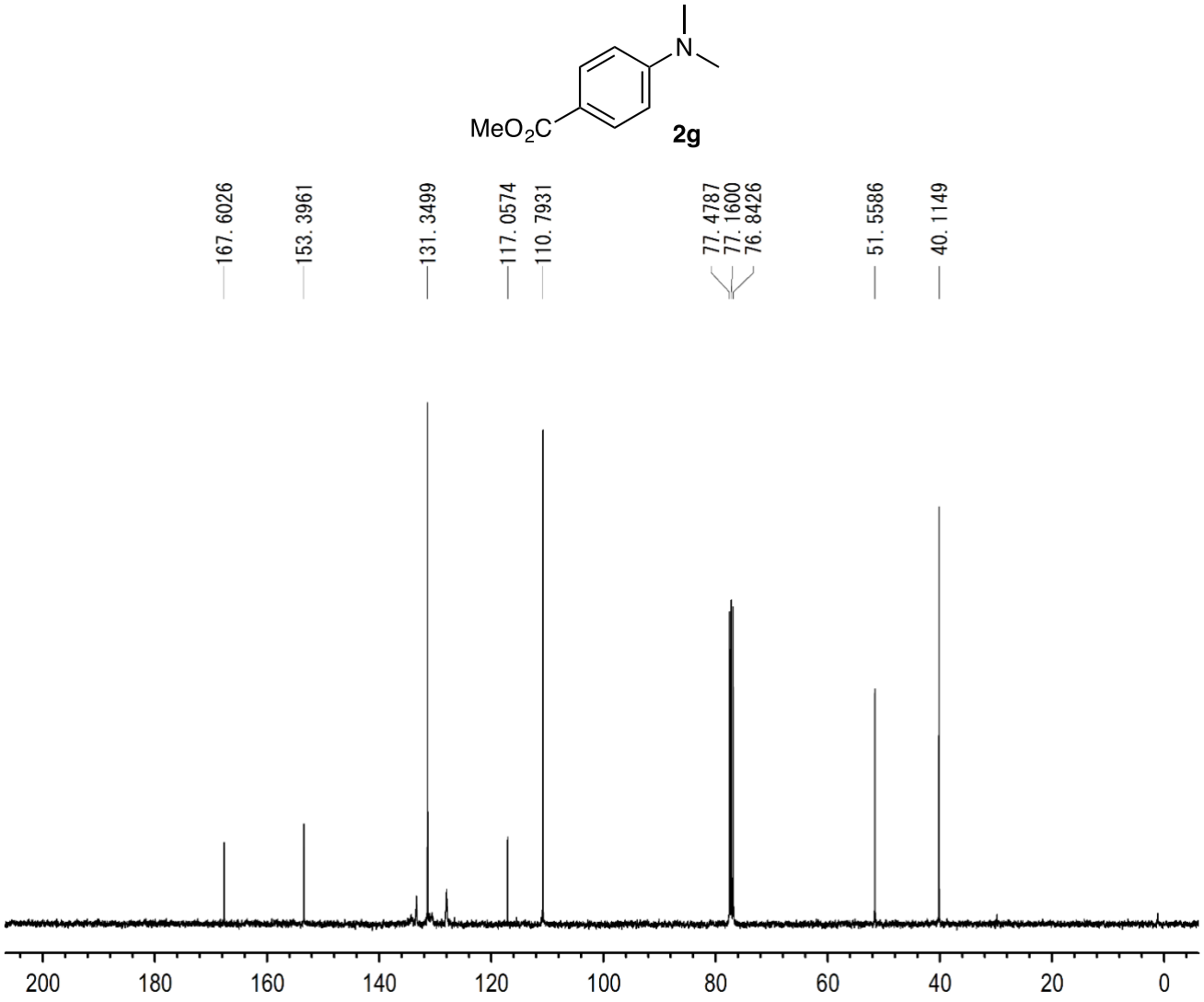

400 MHz $^{1}$H NMR spectrum of **2f** in $CDCl_3$.



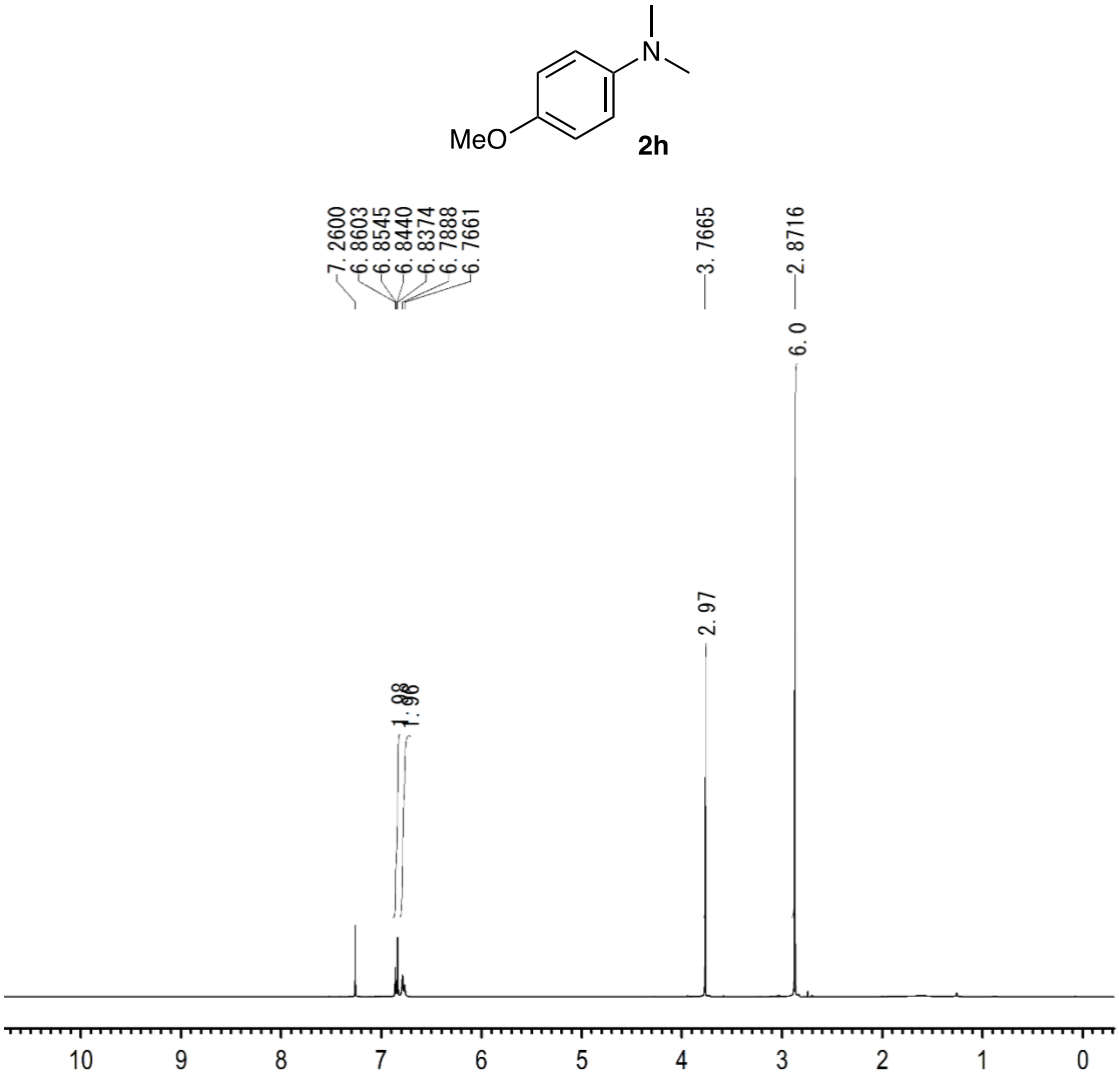

100 MHz $^{13}C$ NMR spectrum of **2f** in $CDCl_3$.



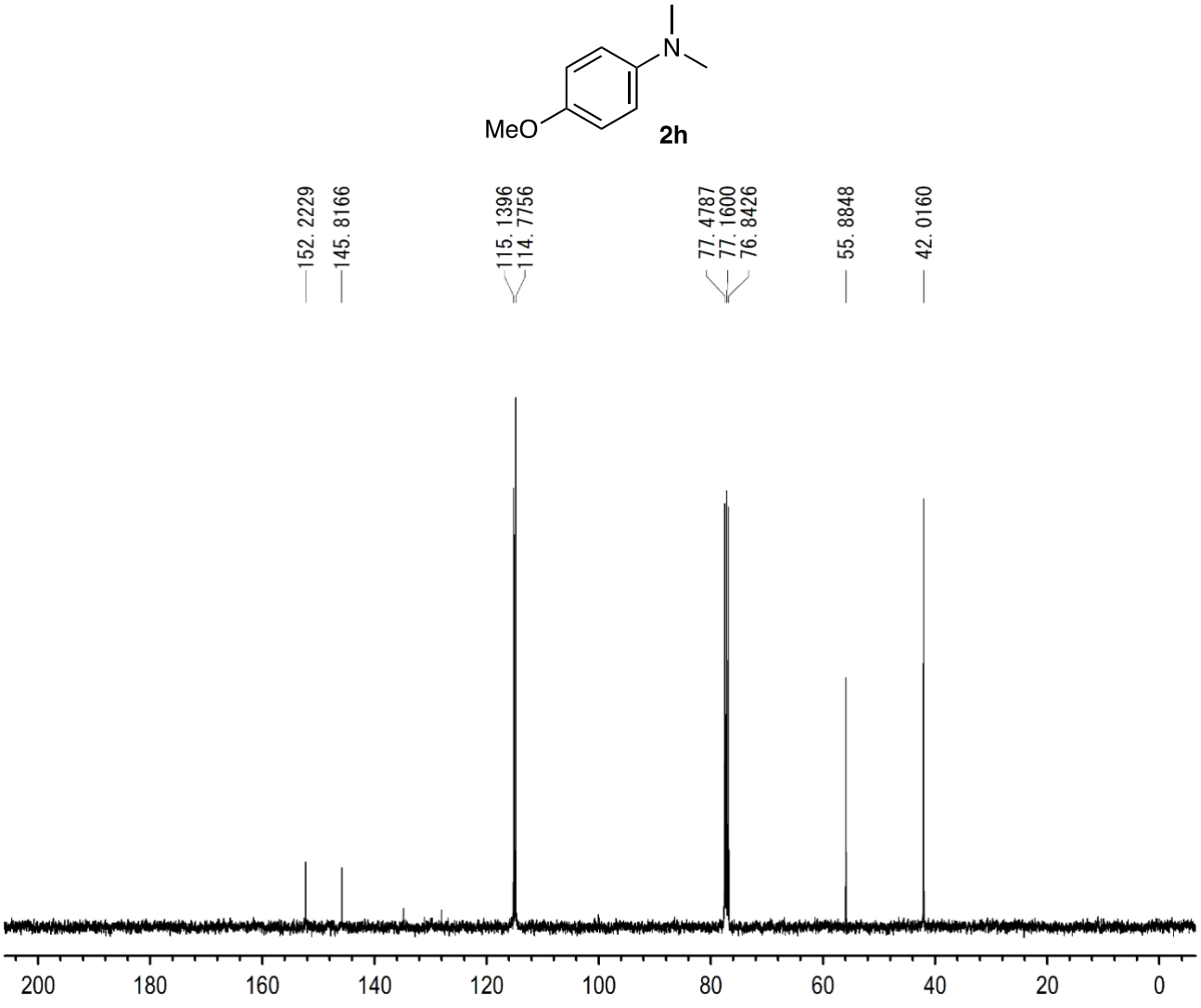

400 MHz $^{1}$H NMR spectrum of **2g** in $CDCl_3$.



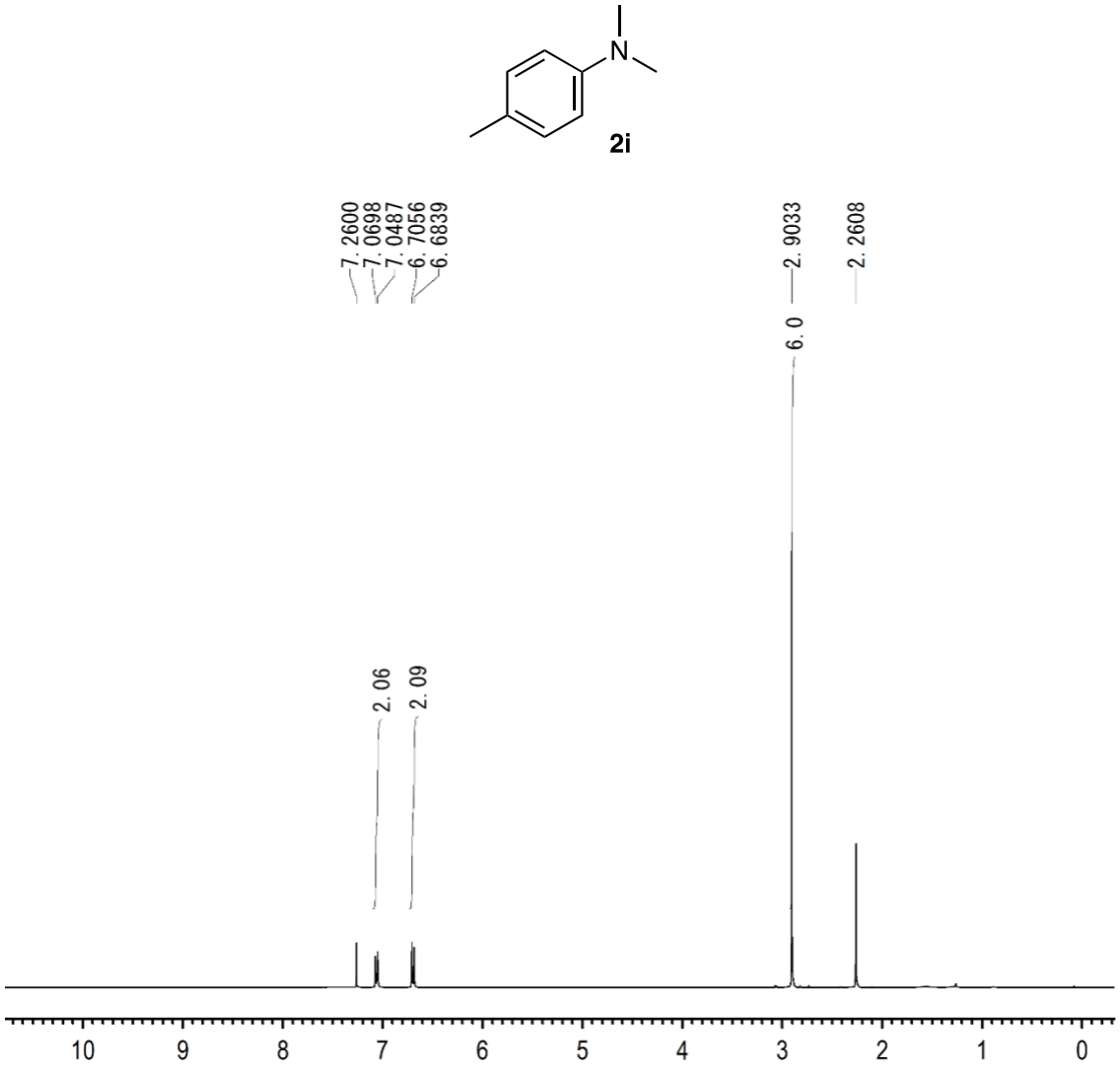

100 MHz $^{13}C$ NMR spectrum of **2g** in $CDCl_3$.



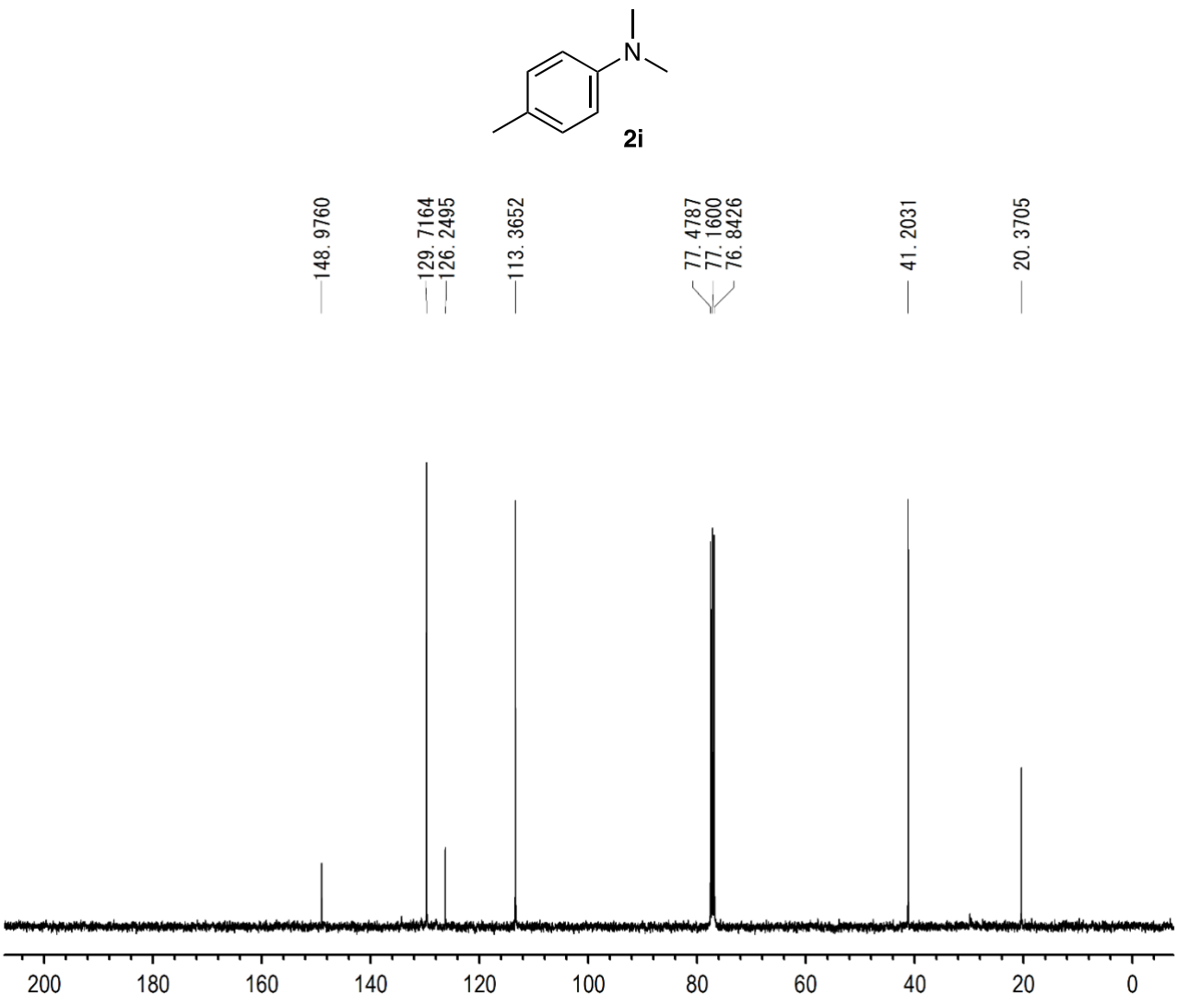

400 MHz $^{1}$H NMR spectrum of **2h** in $CDCl_3$.



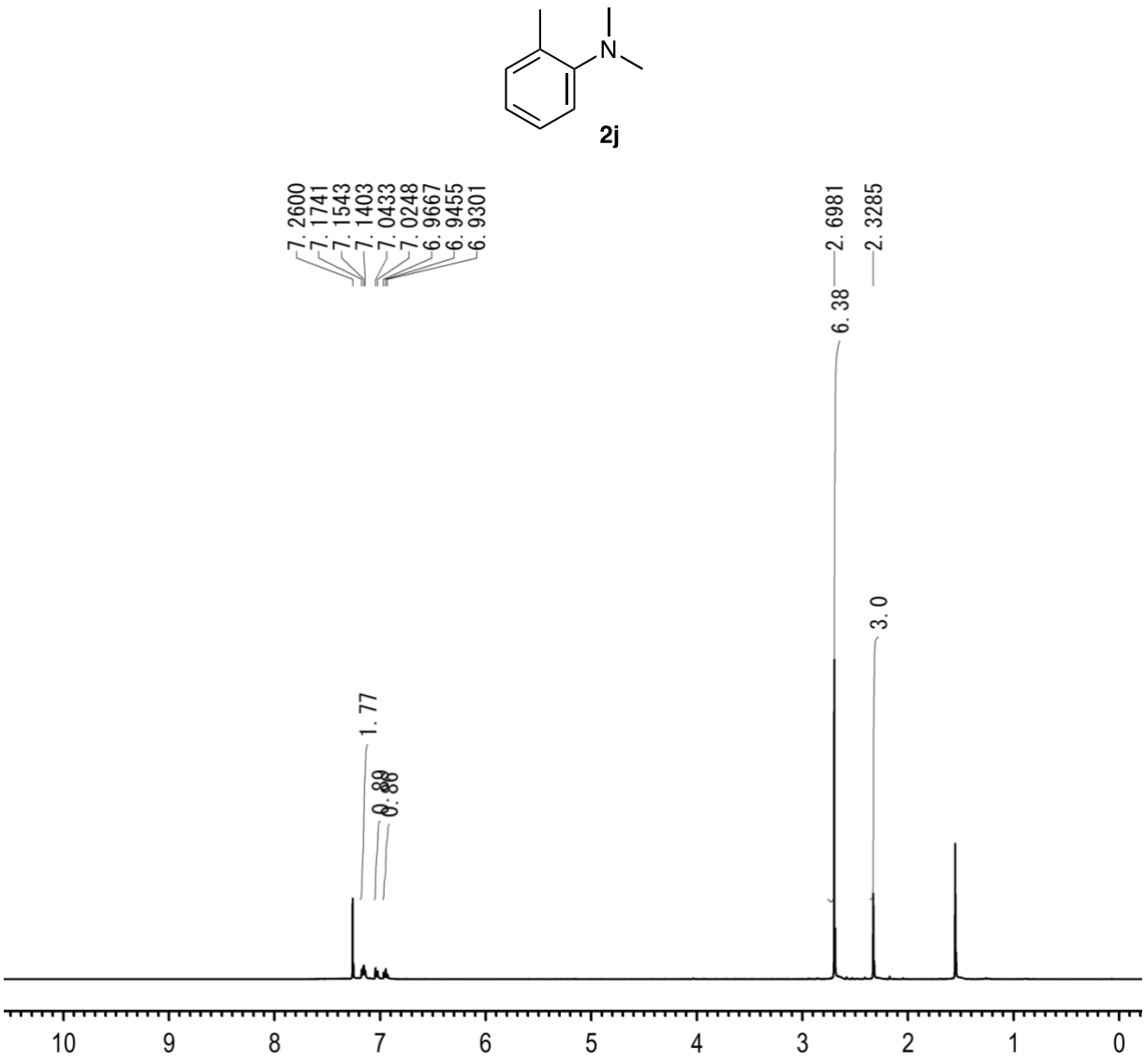

100 MHz $^{13}C$ NMR spectrum of **2h** in $CDCl_3$.



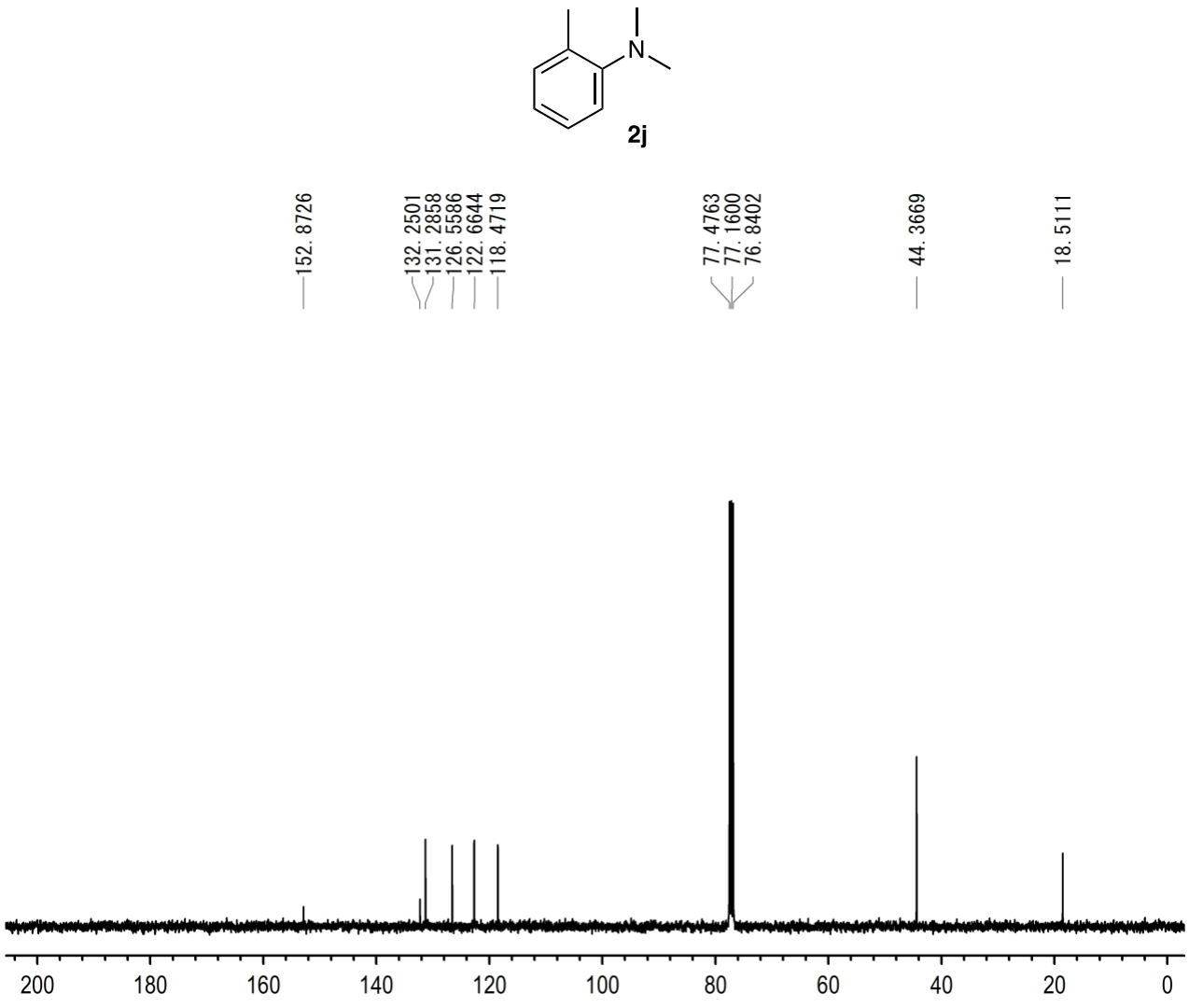

400 MHz $^{1}$H NMR spectrum of **2i** in $CDCl_3$.



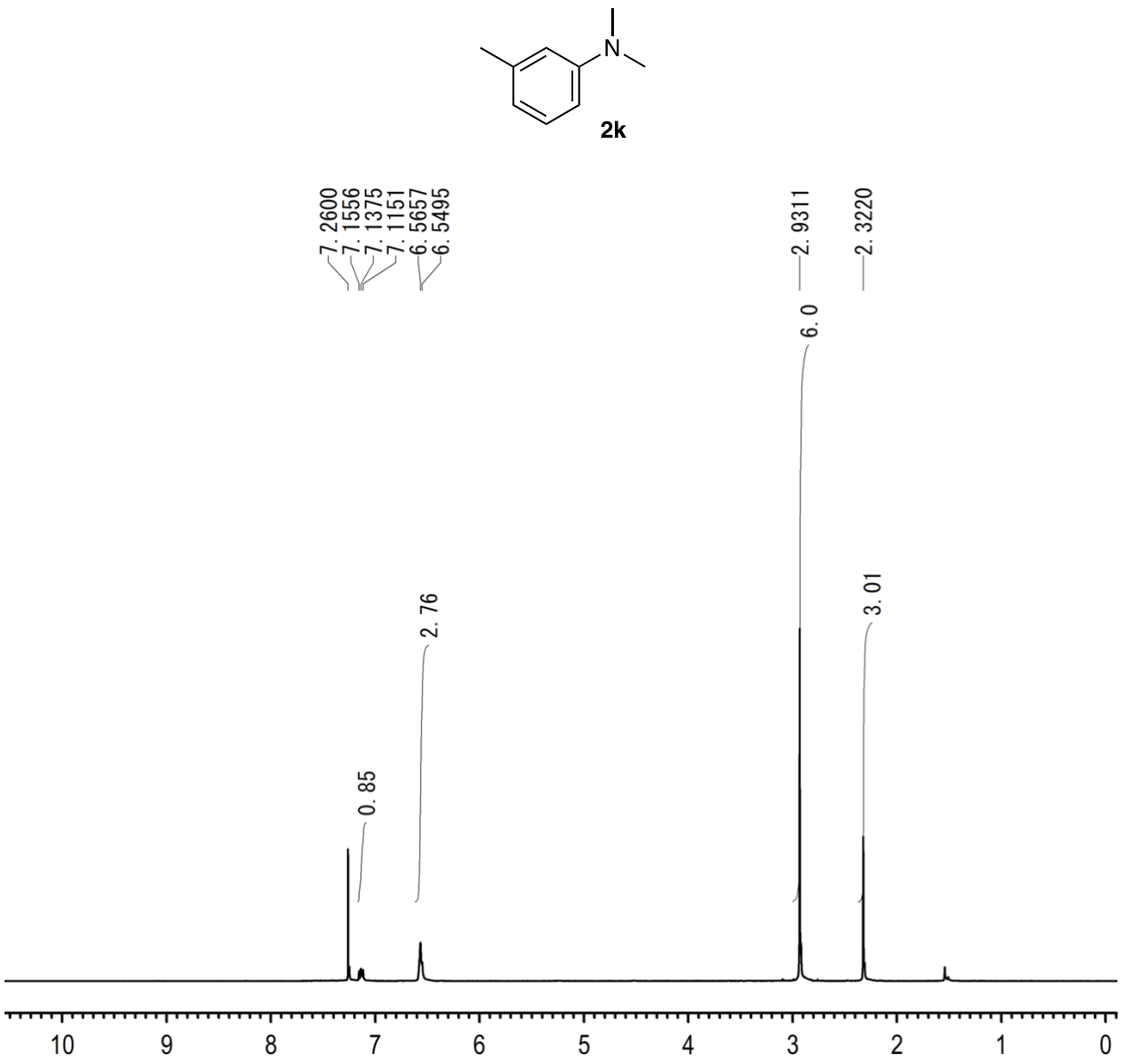

100 MHz $^{13}C$ NMR spectrum of **2i** in $CDCl_3$.



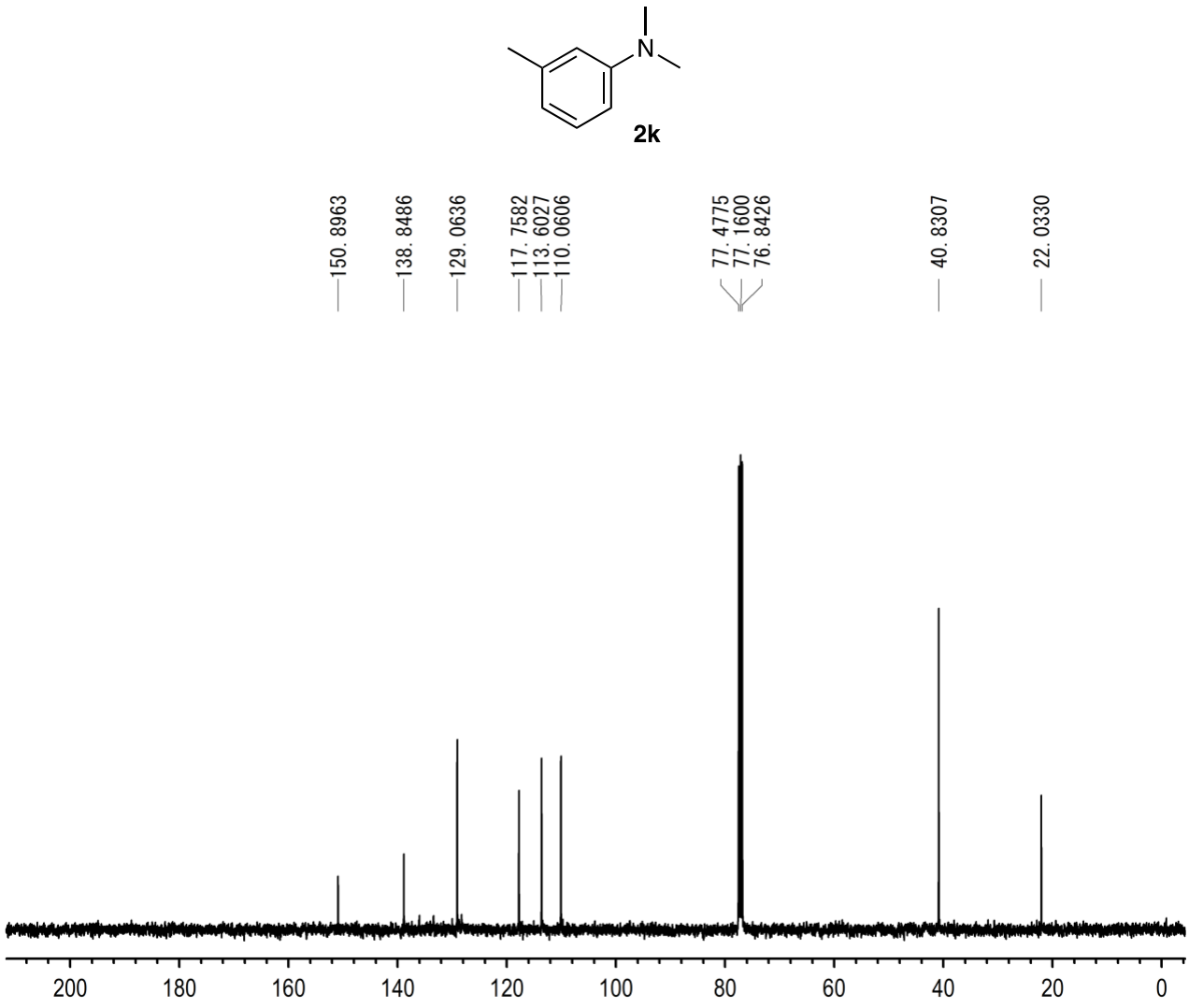

400 MHz $^{1}$H NMR spectrum of **2j** in $CDCl_3$.



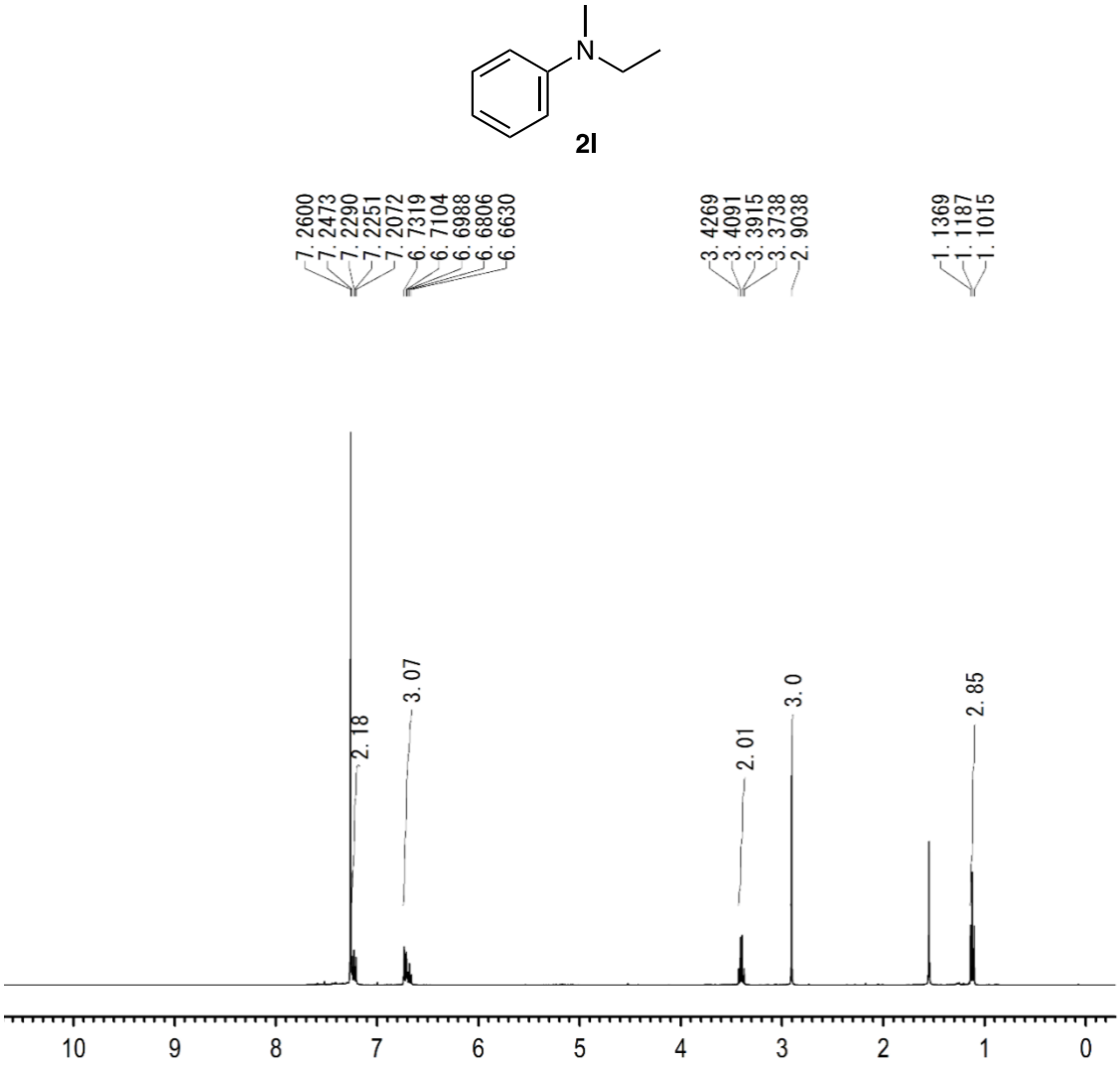

100 MHz $^{13}C$ NMR spectrum of **2j** in $CDCl_3$.



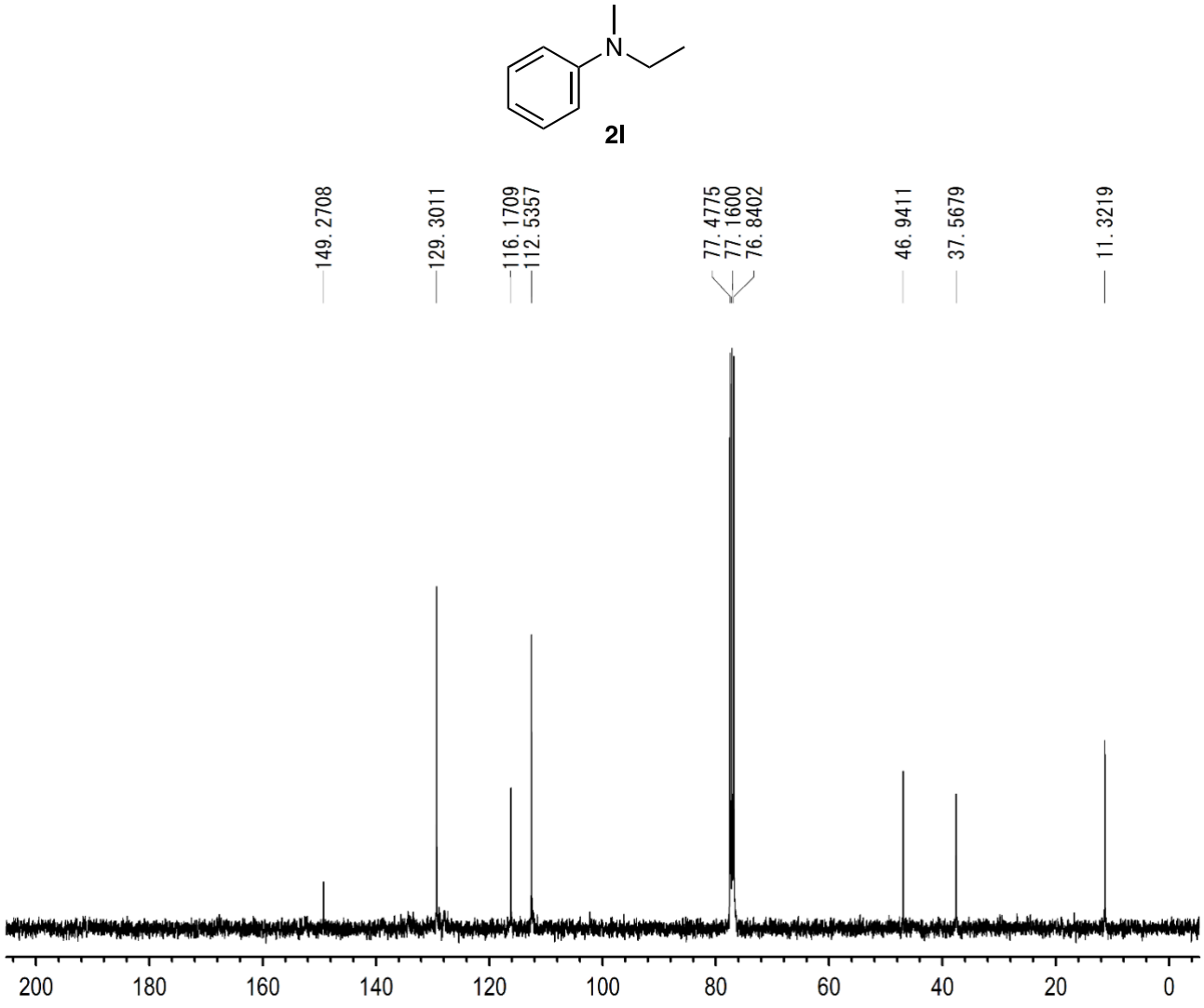

400 MHz $^{1}$H NMR spectrum of **2k** in $CDCl_3$.



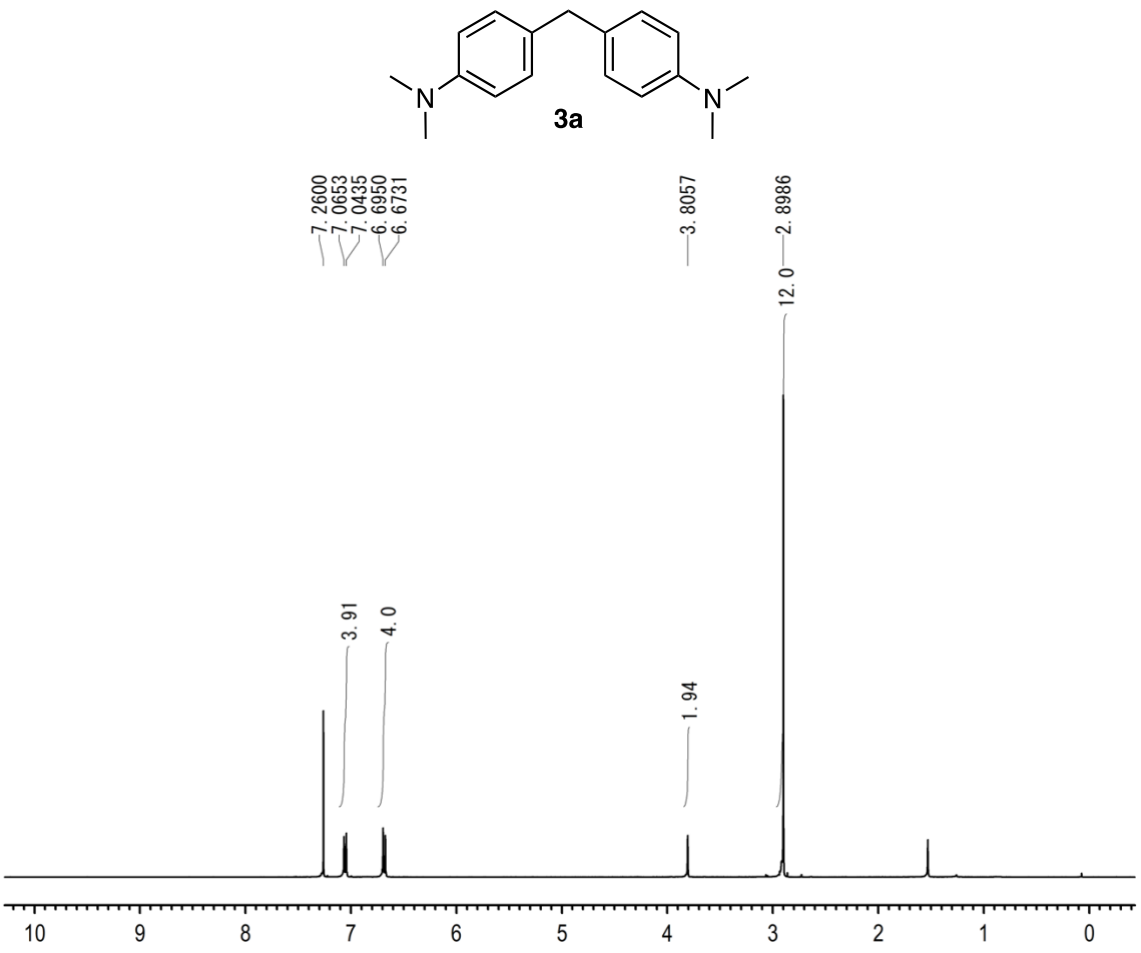

100 MHz $^{13}C$ NMR spectrum of **2k** in $CDCl_3$.



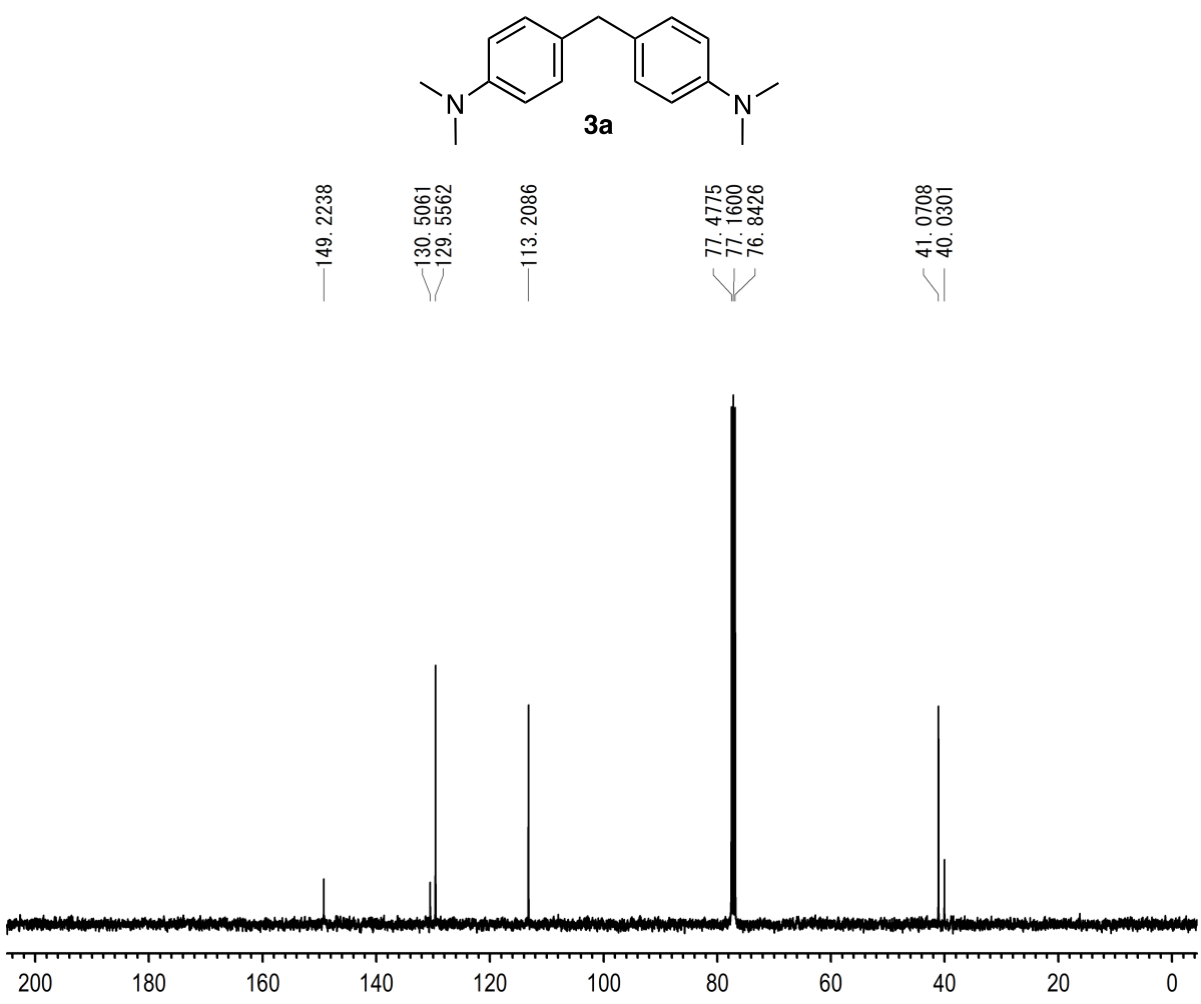

400 MHz $^{1}$H NMR spectrum of **2l** in $CDCl_3$.



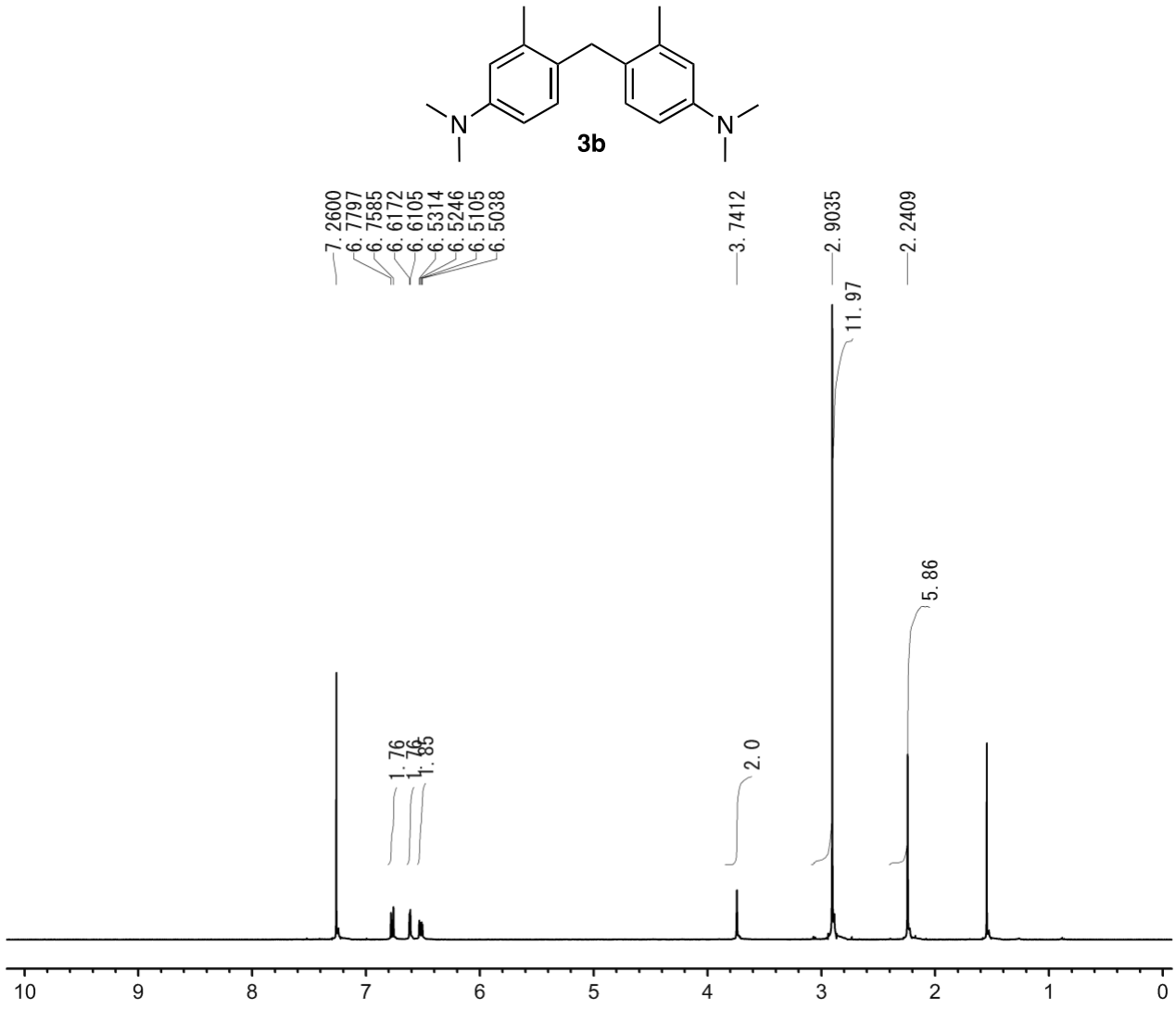

100 MHz $^{13}C$ NMR spectrum of **2l** in $CDCl_3$.



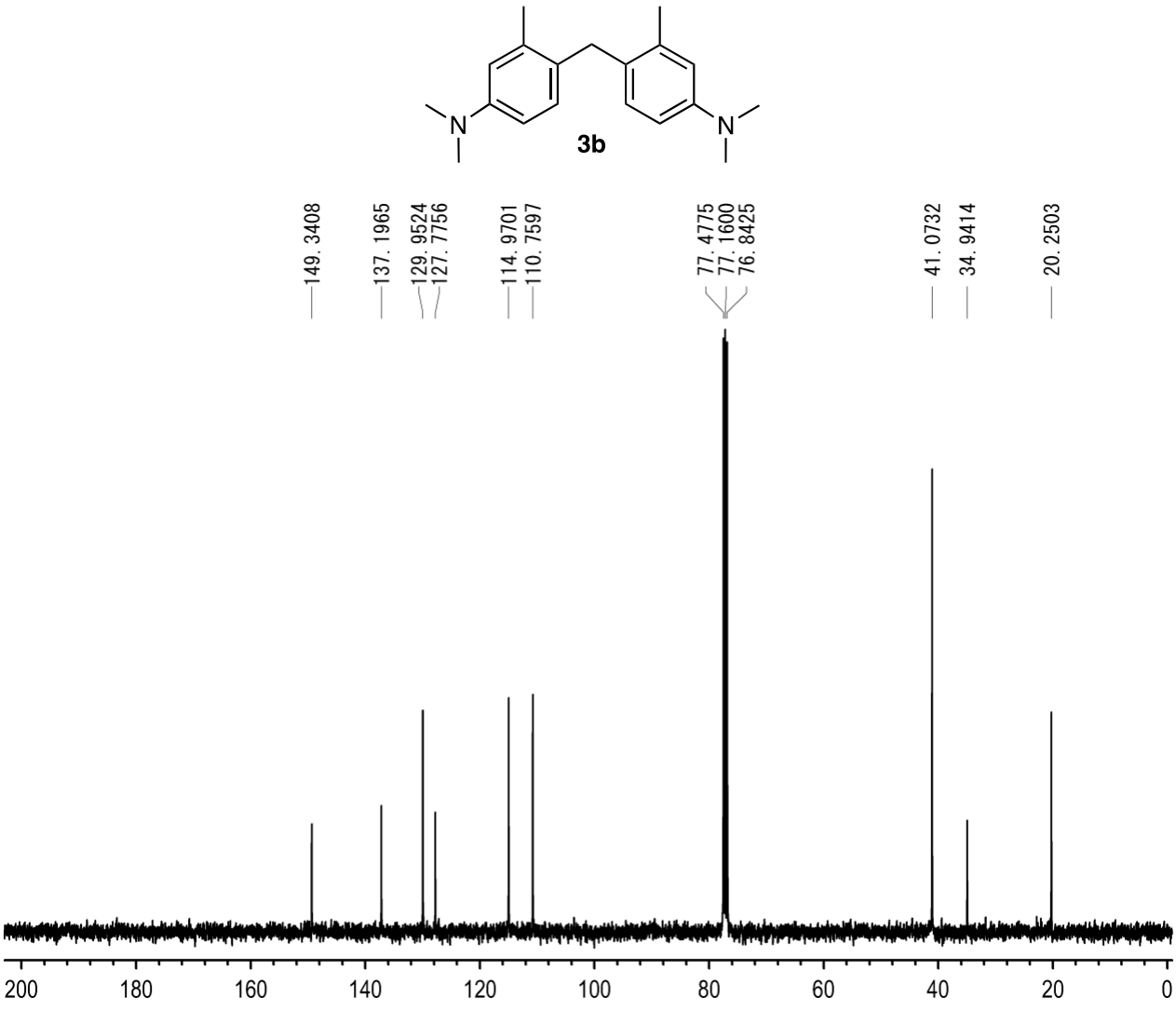

400 MHz $^{1}$H NMR spectrum of **3a** in $CDCl_3$.



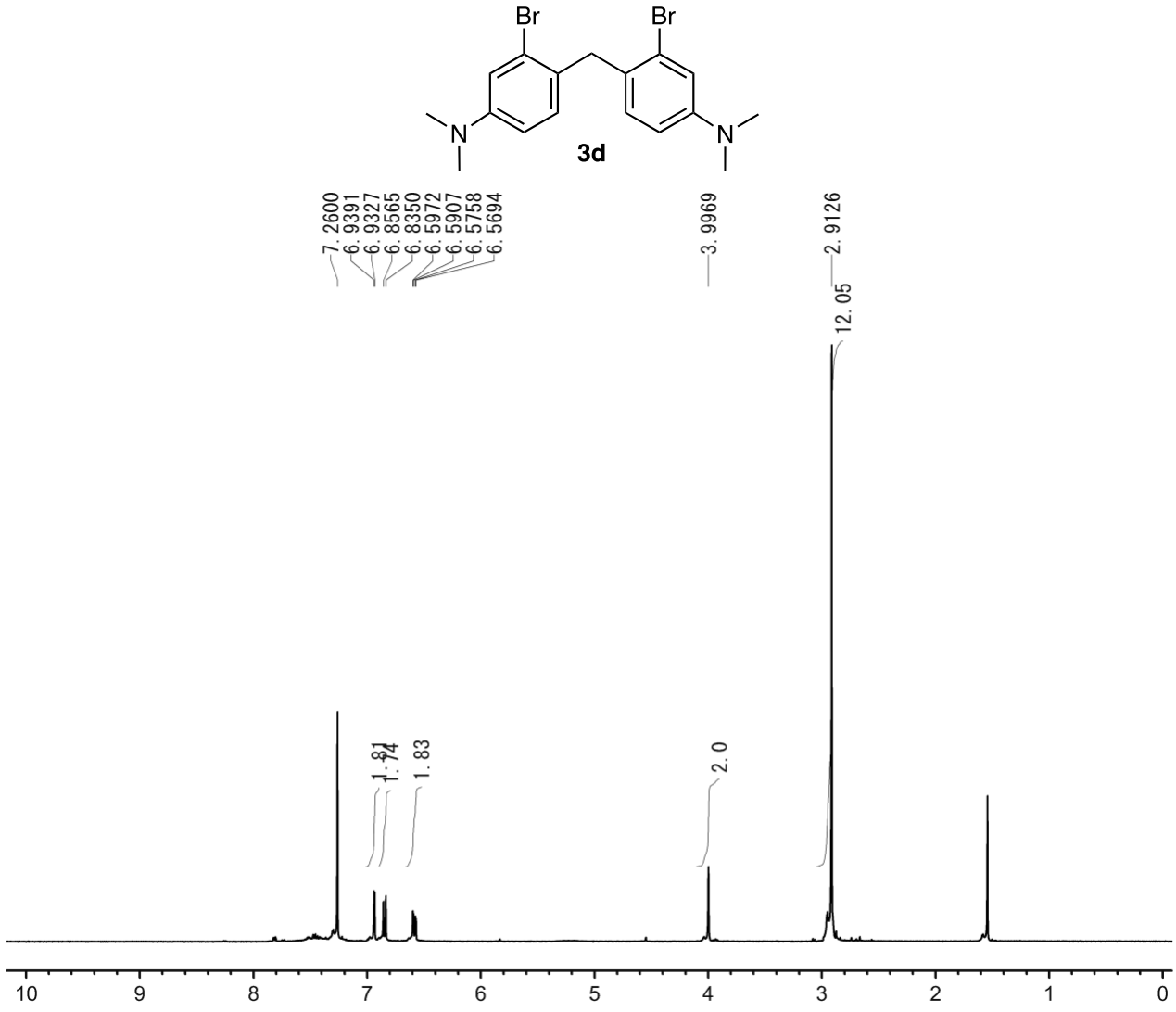

100 MHz $^{13}C$ NMR spectrum of **3a** in $CDCl_3$.



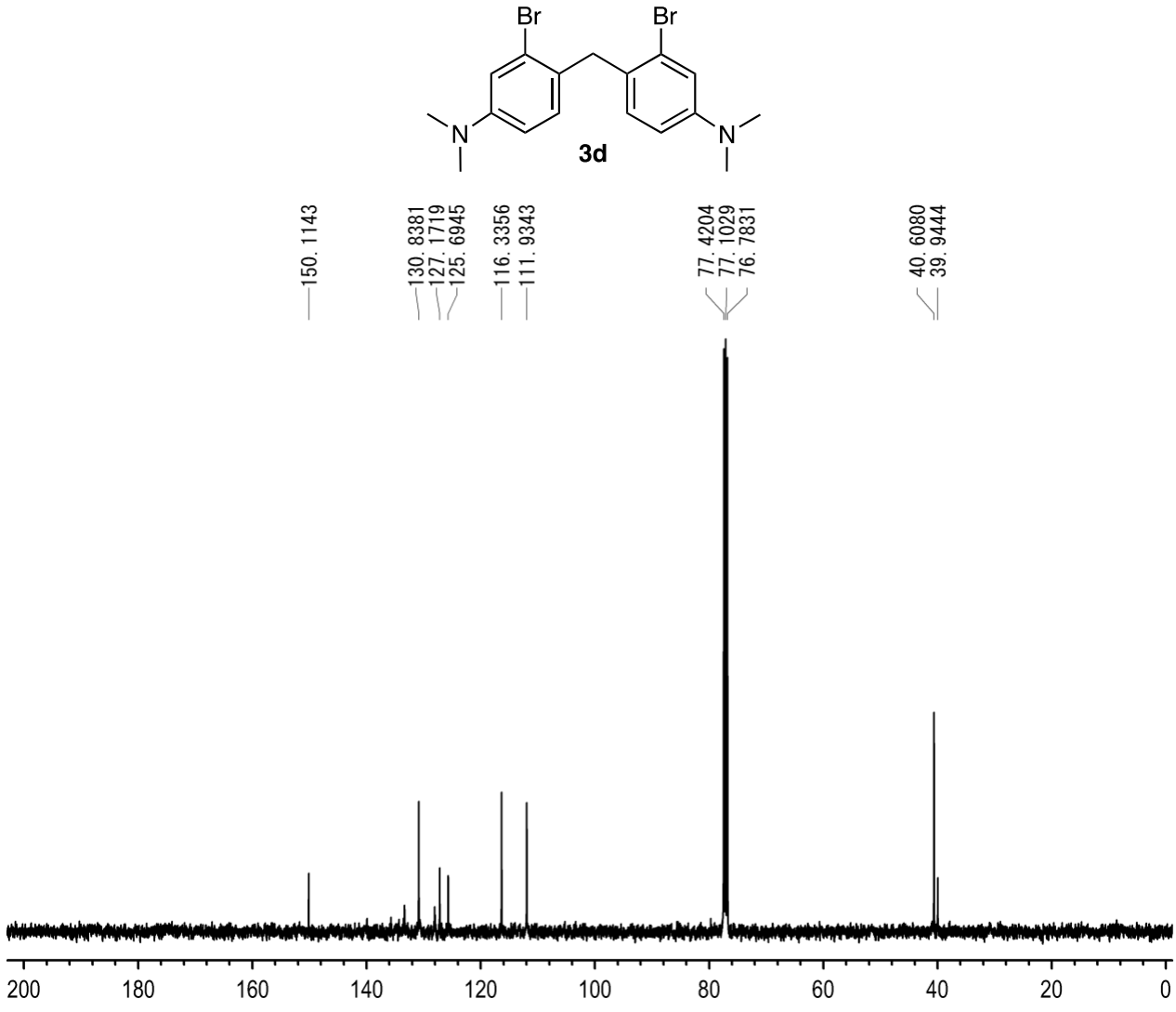

400 MHz $^{1}$H NMR spectrum of **3b** in $CDCl_3$.



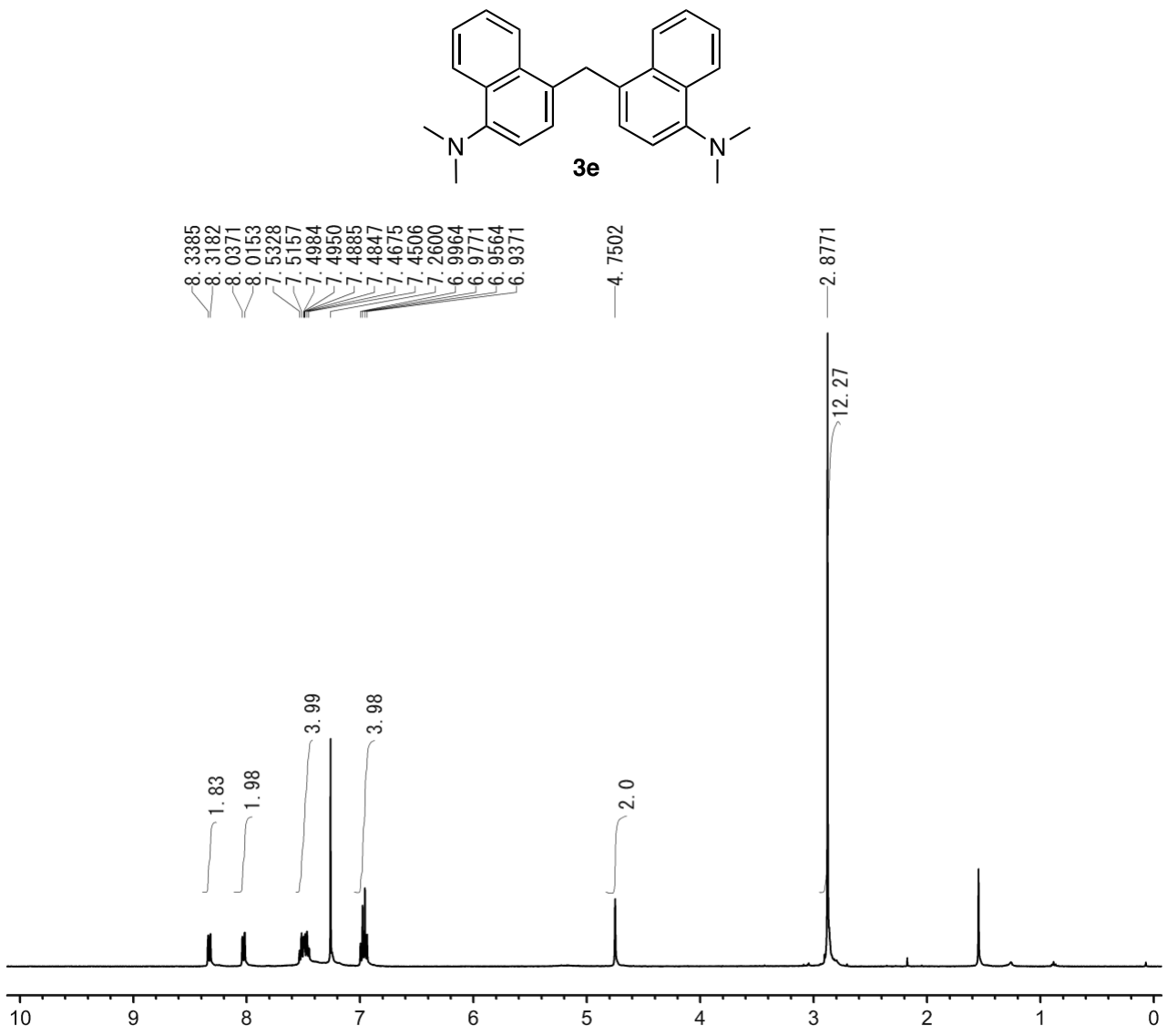

100 MHz $^{13}C$ NMR spectrum of **3b** in $CDCl_3$.



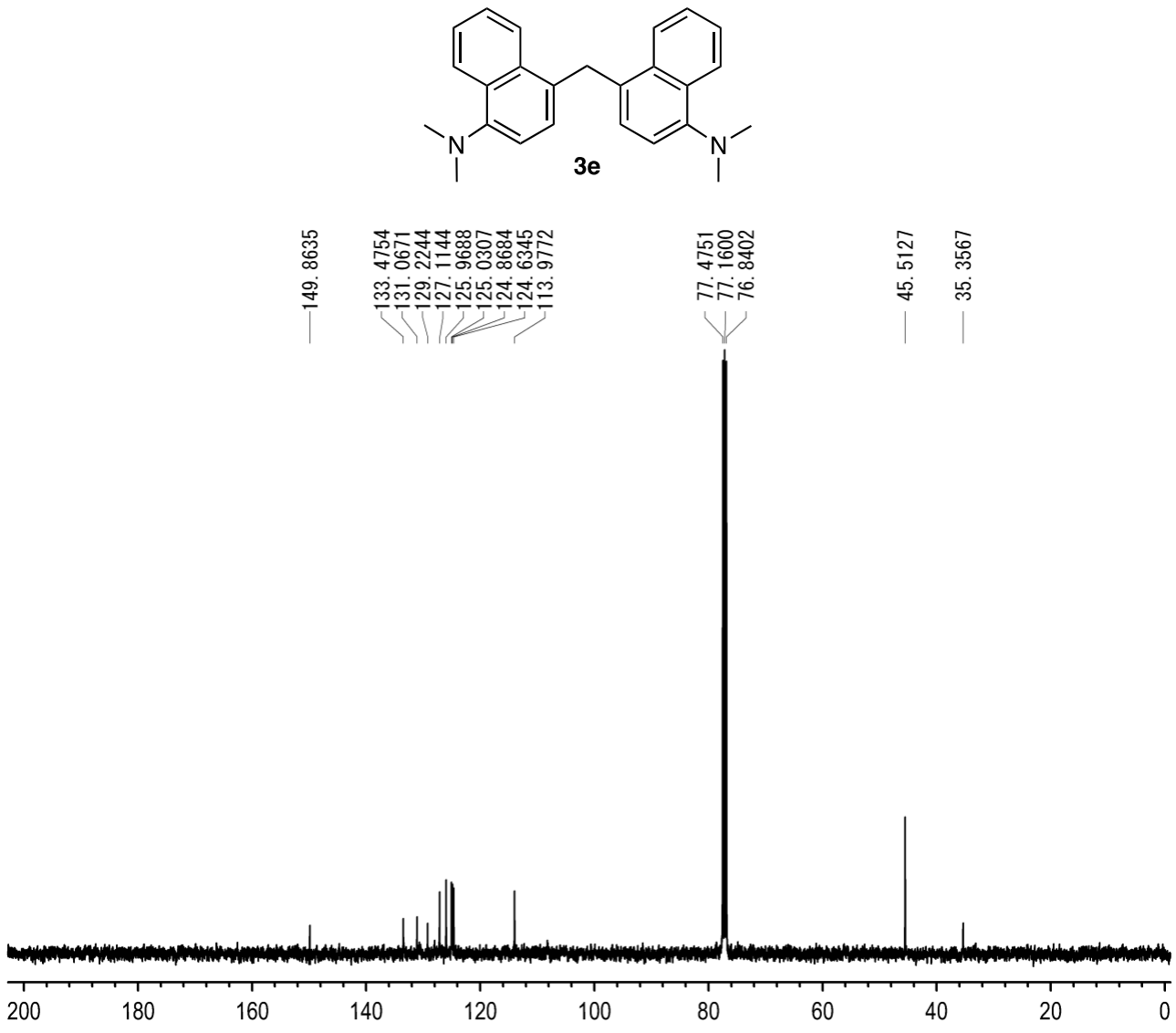

400 MHz $^{1}$H NMR spectrum of **3d** in $CDCl_3$.



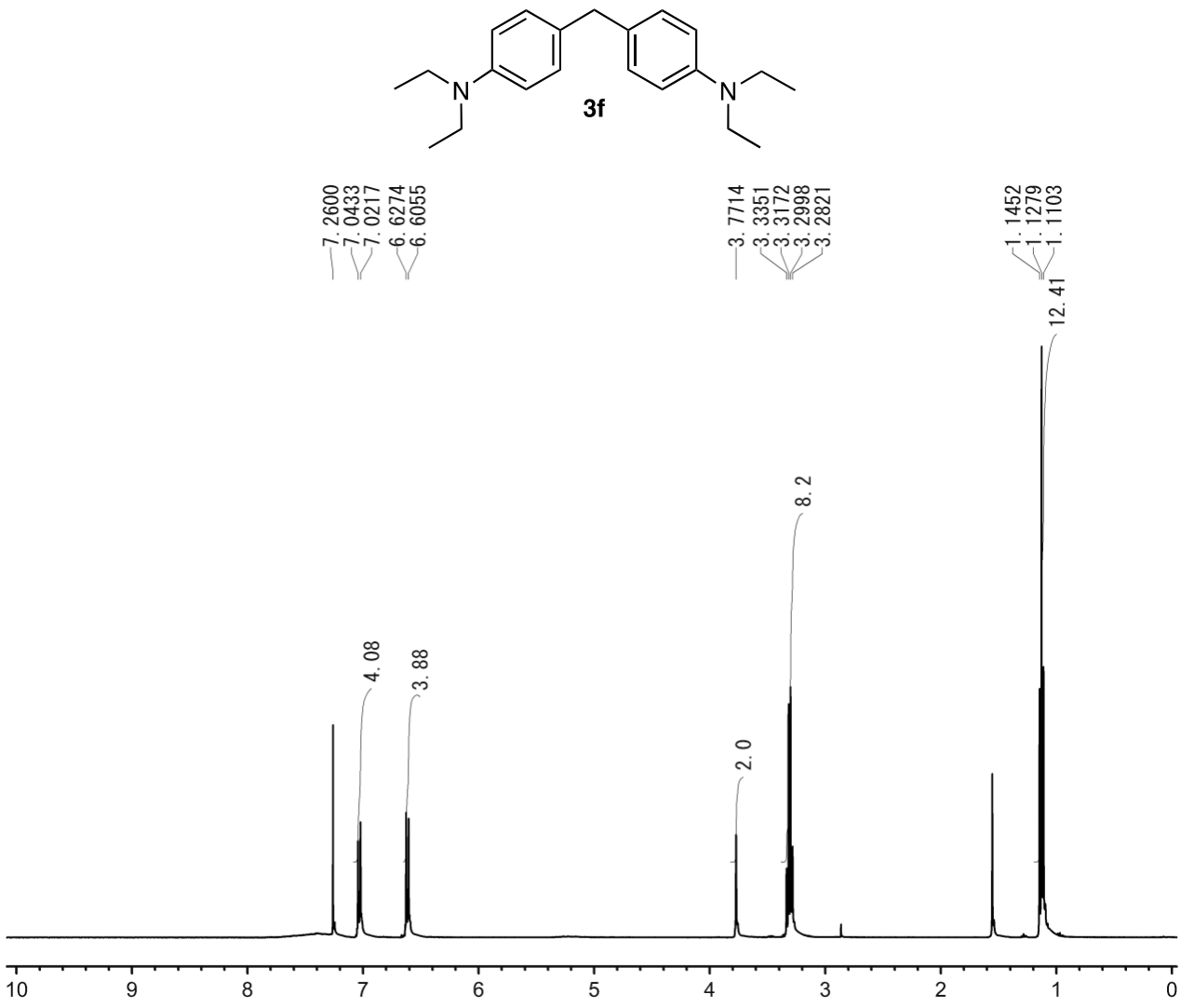

100 MHz $^{13}C$ NMR spectrum of **3d** in $CDCl_3$.



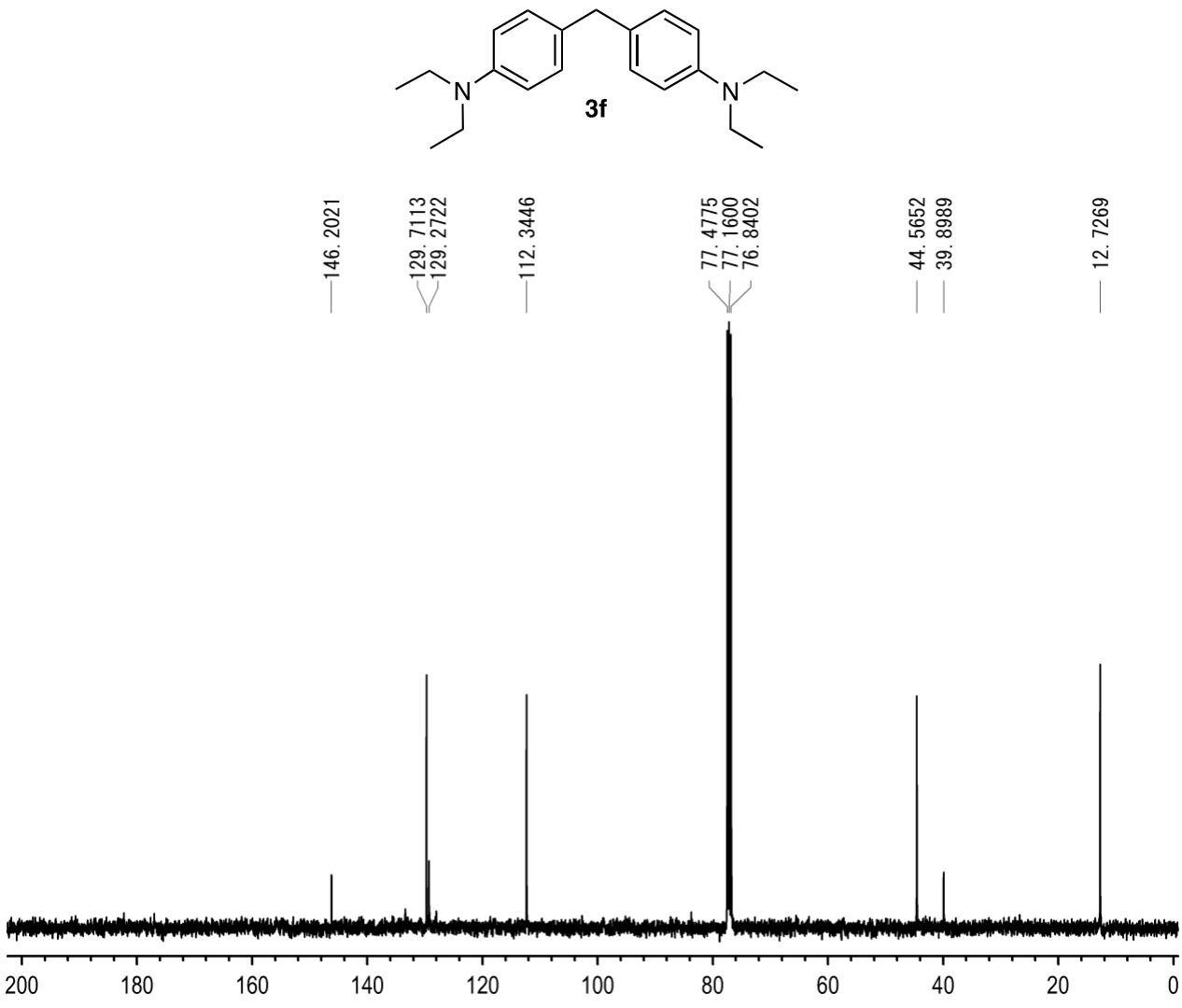

400 MHz $^{1}$H NMR spectrum of **3e** in $CDCl_3$.



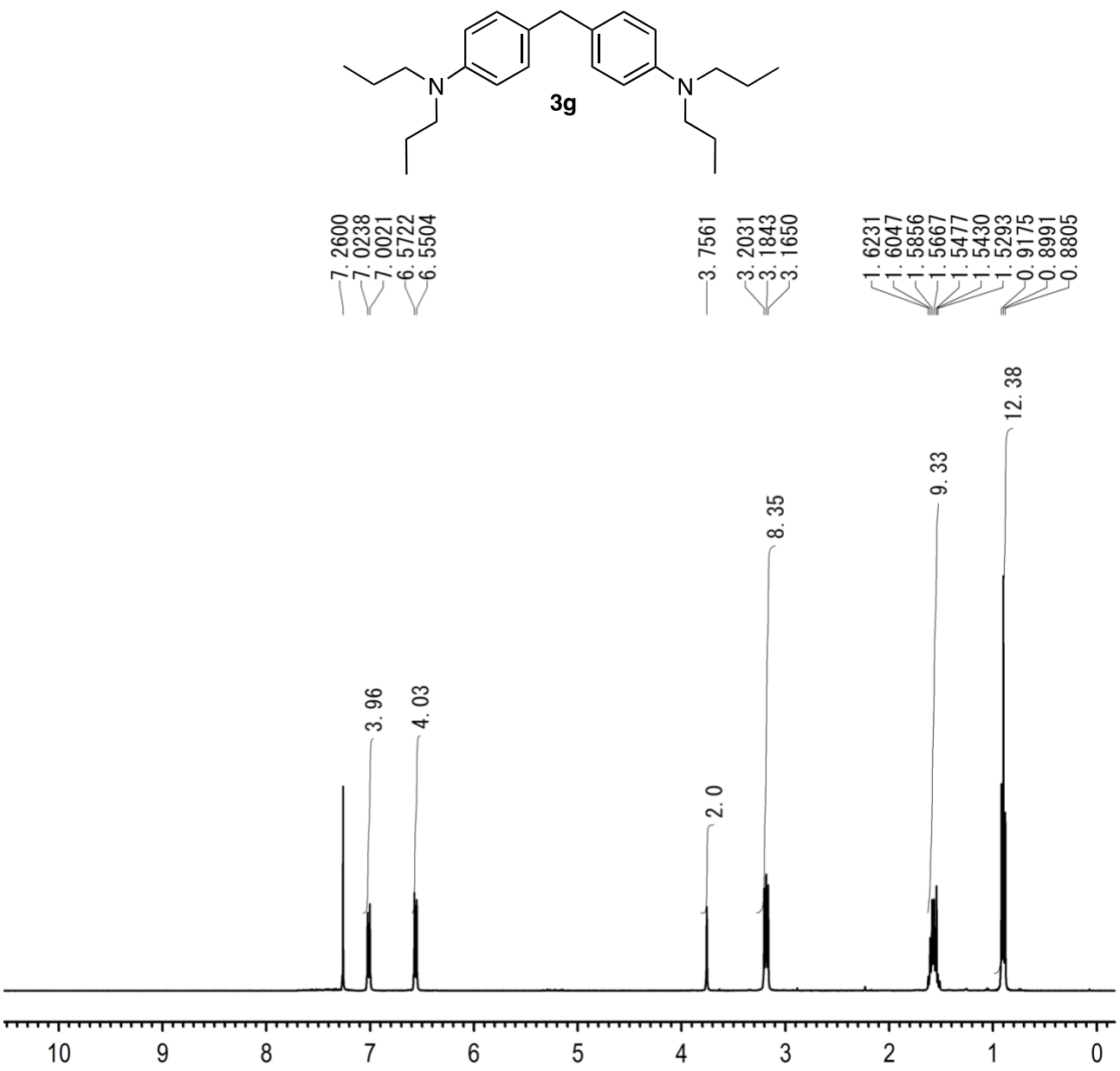

100 MHz $^{13}C$ NMR spectrum of **3e** in $CDCl_3$.



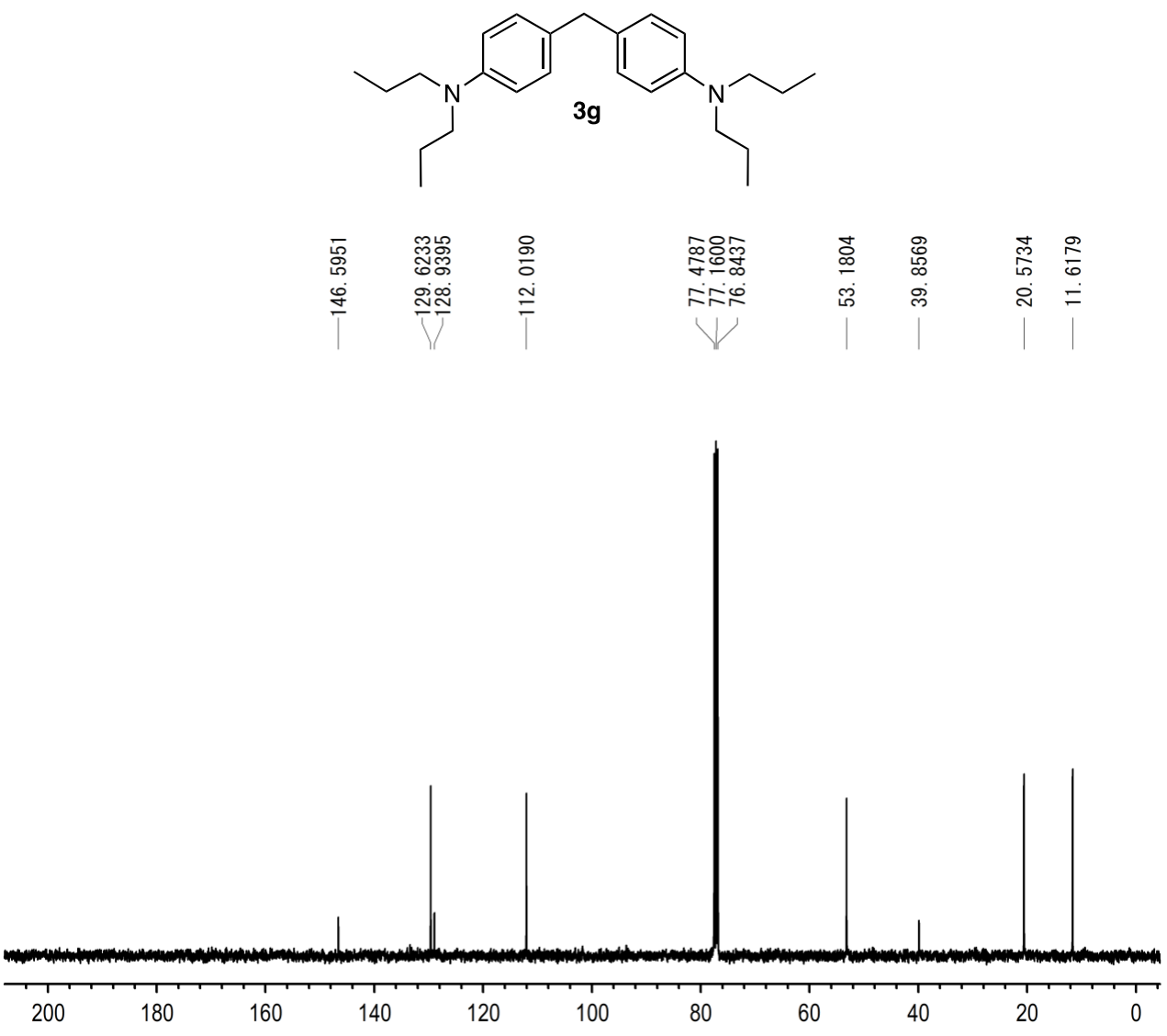

400 MHz $^{1}$H NMR spectrum of **3f** in $CDCl_3$.



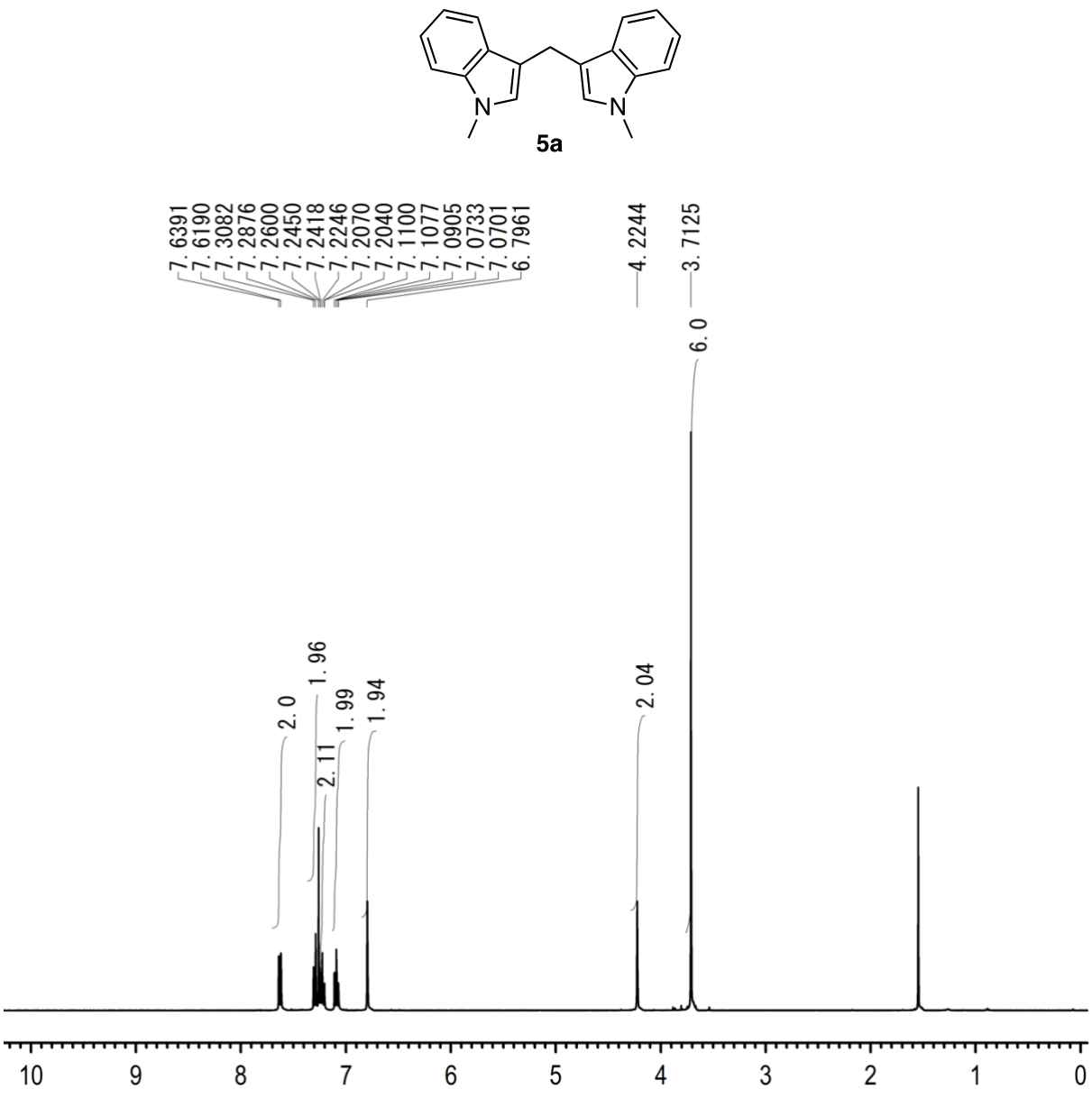

100 MHz $^{13}C$ NMR spectrum of **3f** in $CDCl_3$.



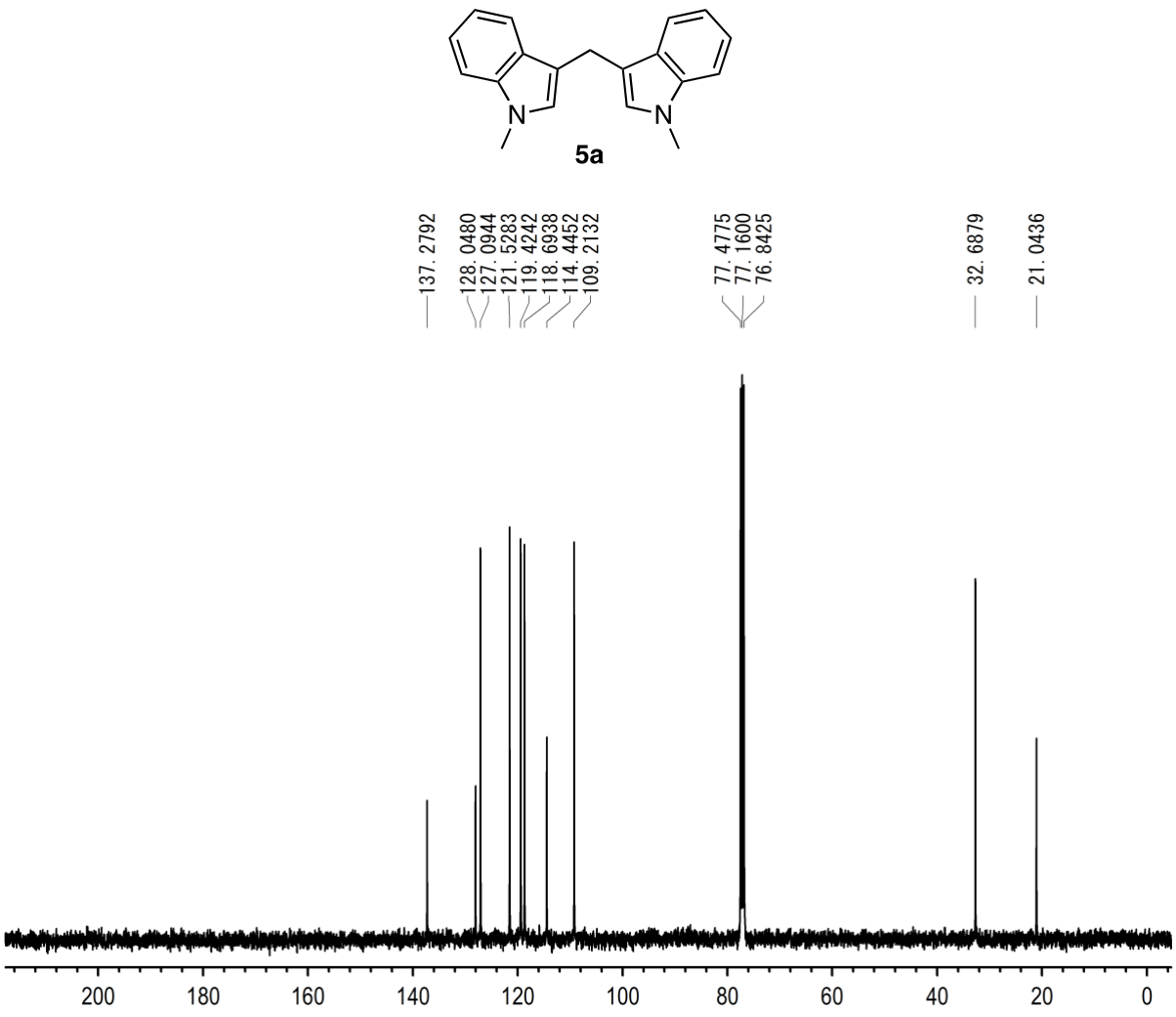

400 MHz $^{1}$H NMR spectrum of **3g** in $CDCl_3$.



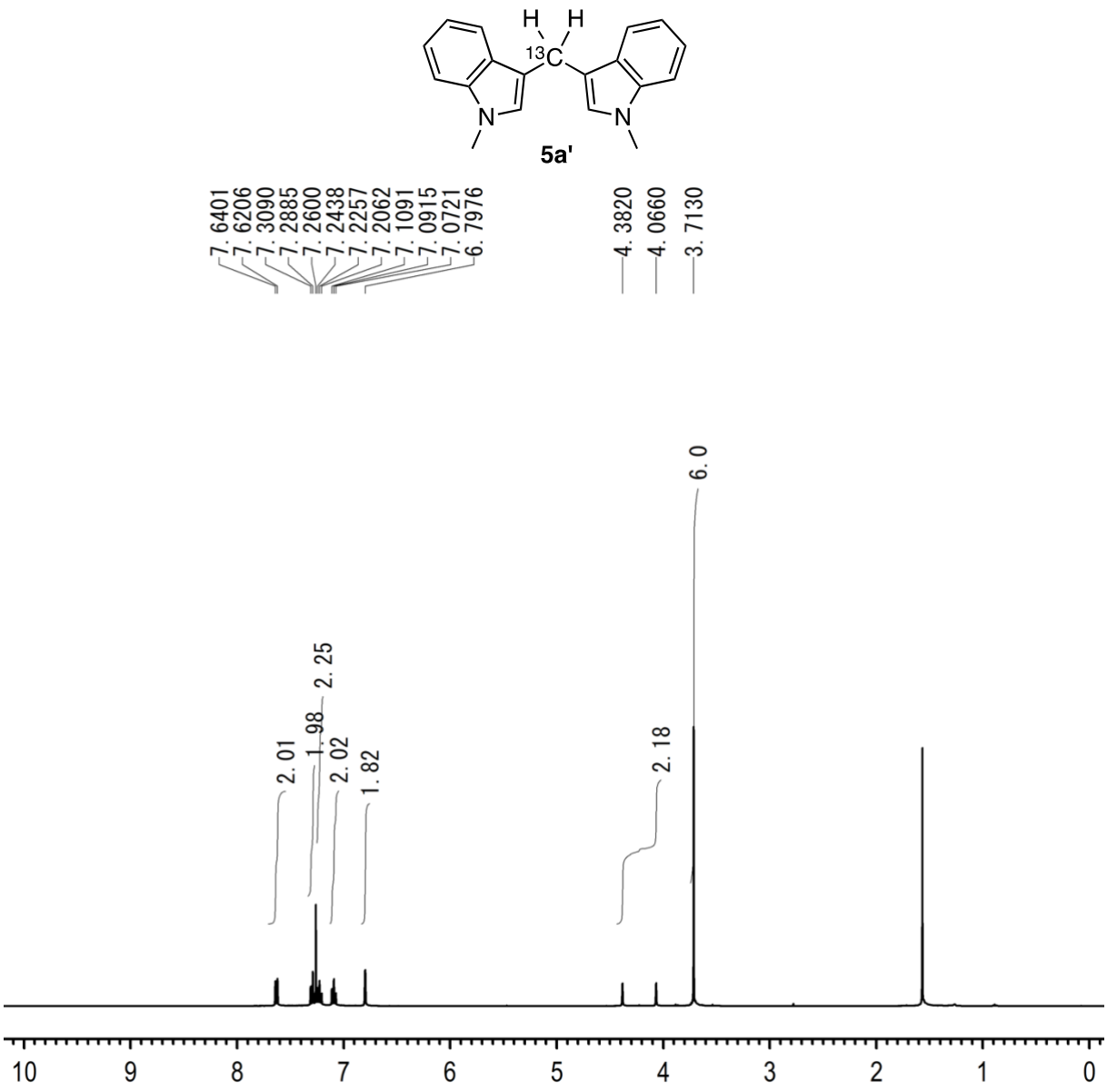

100 MHz $^{13}C$ NMR spectrum of **3g** in $CDCl_3$.



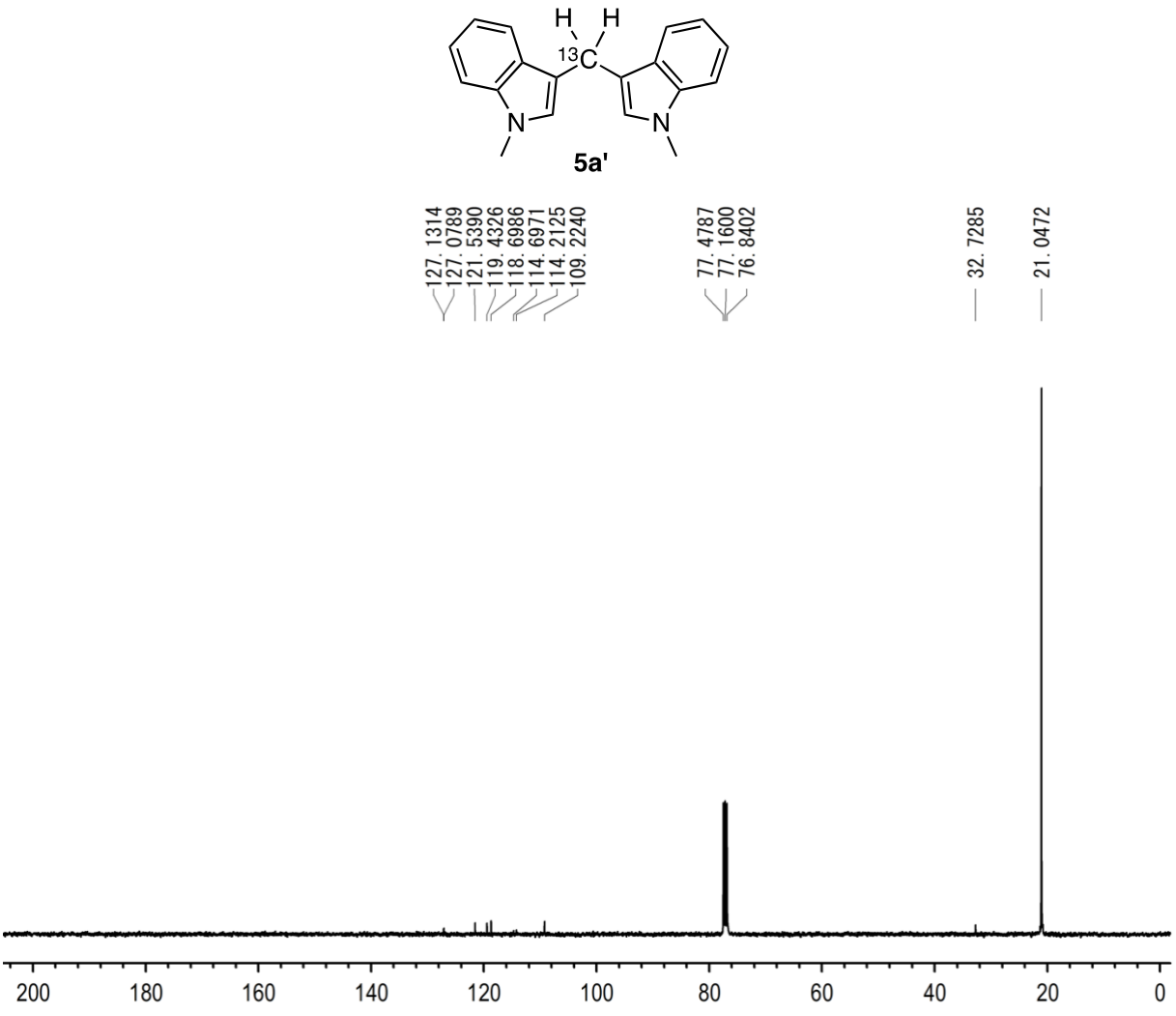

400 MHz $^{1}$H NMR spectrum of **5a** in $CDCl_3$.



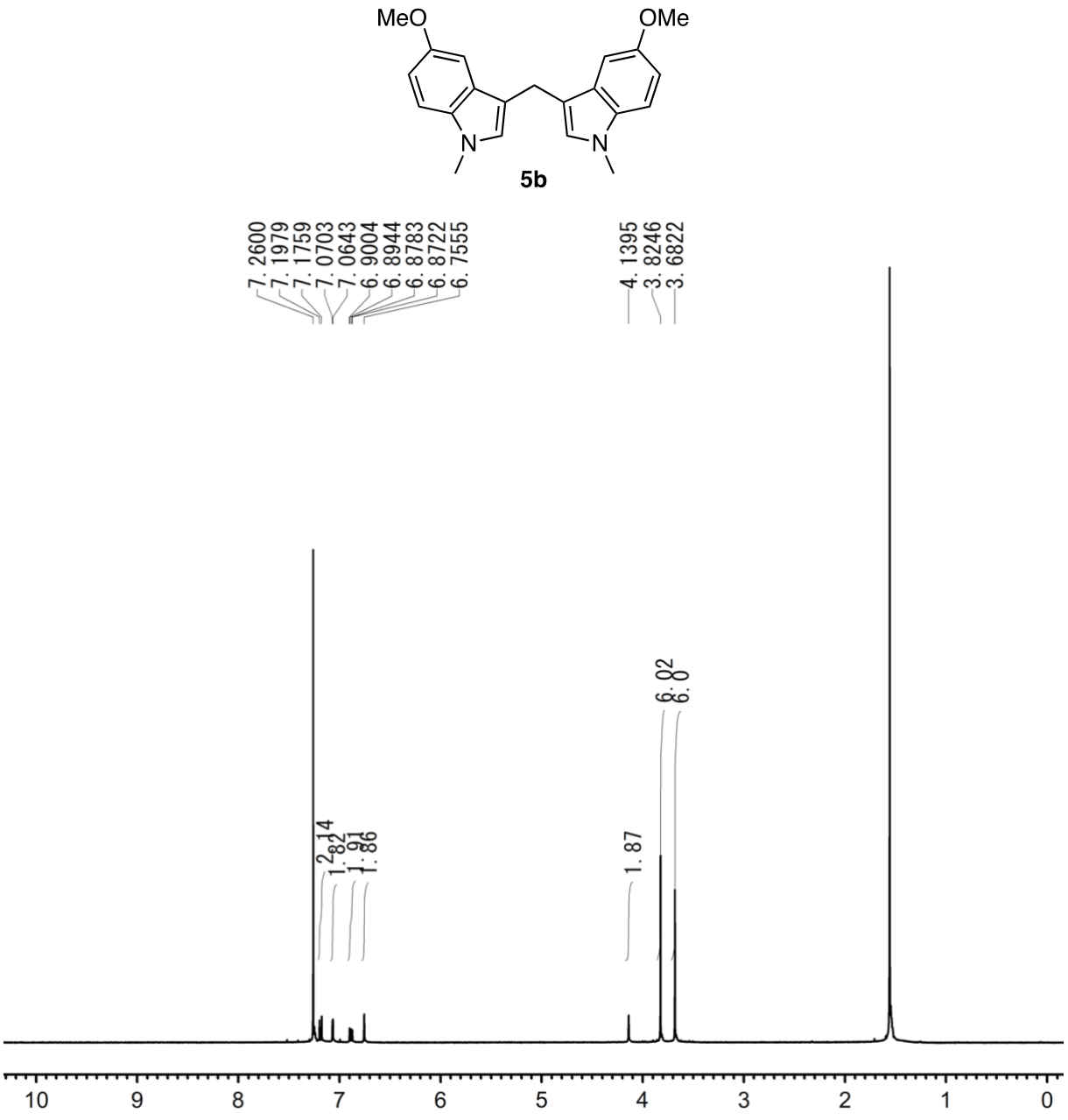

100 MHz $^{13}C$ NMR spectrum of **5a** in $CDCl_3$.



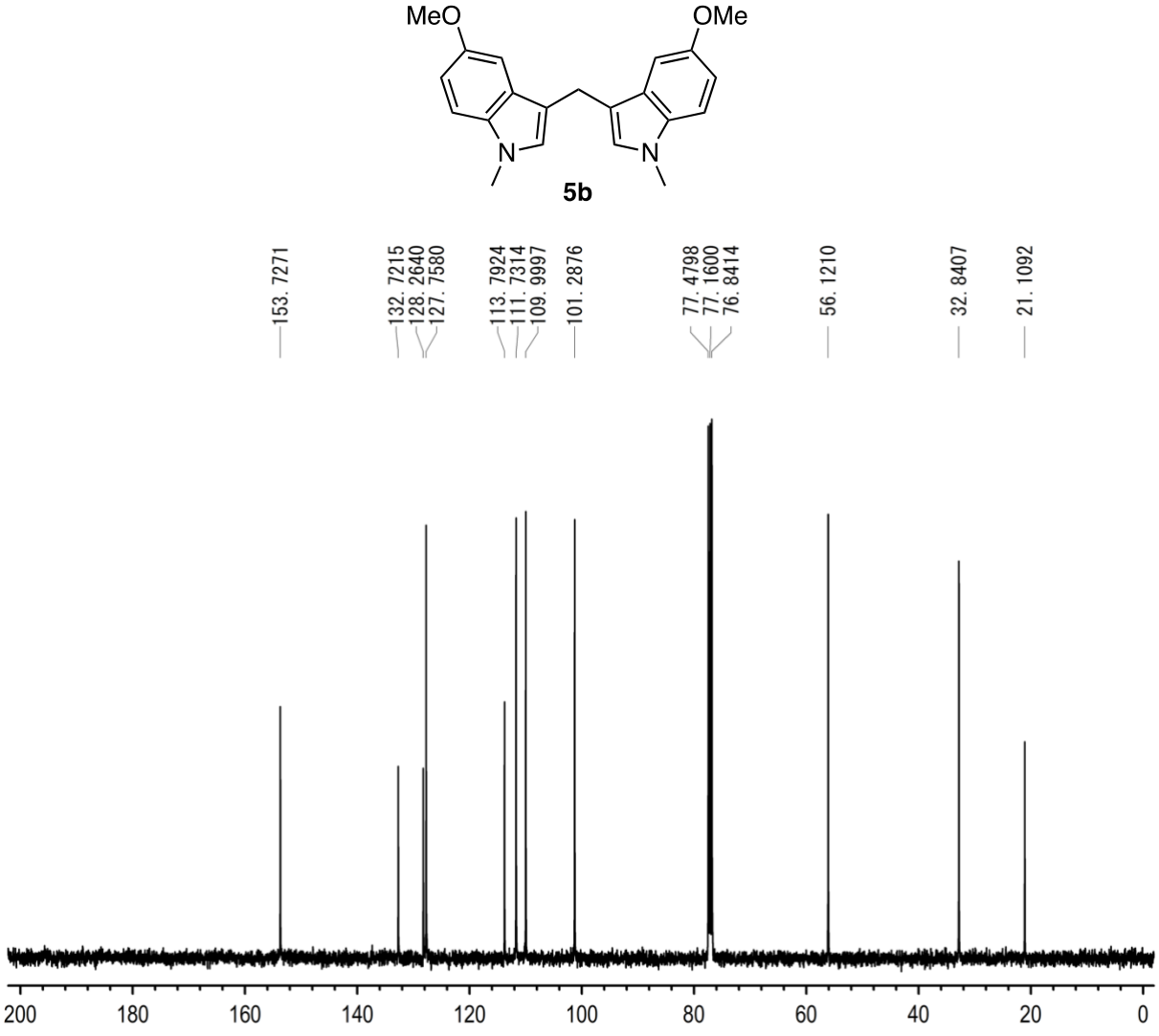

400 MHz $^{1}$H NMR spectrum of **5a'** in $CDCl_3$.



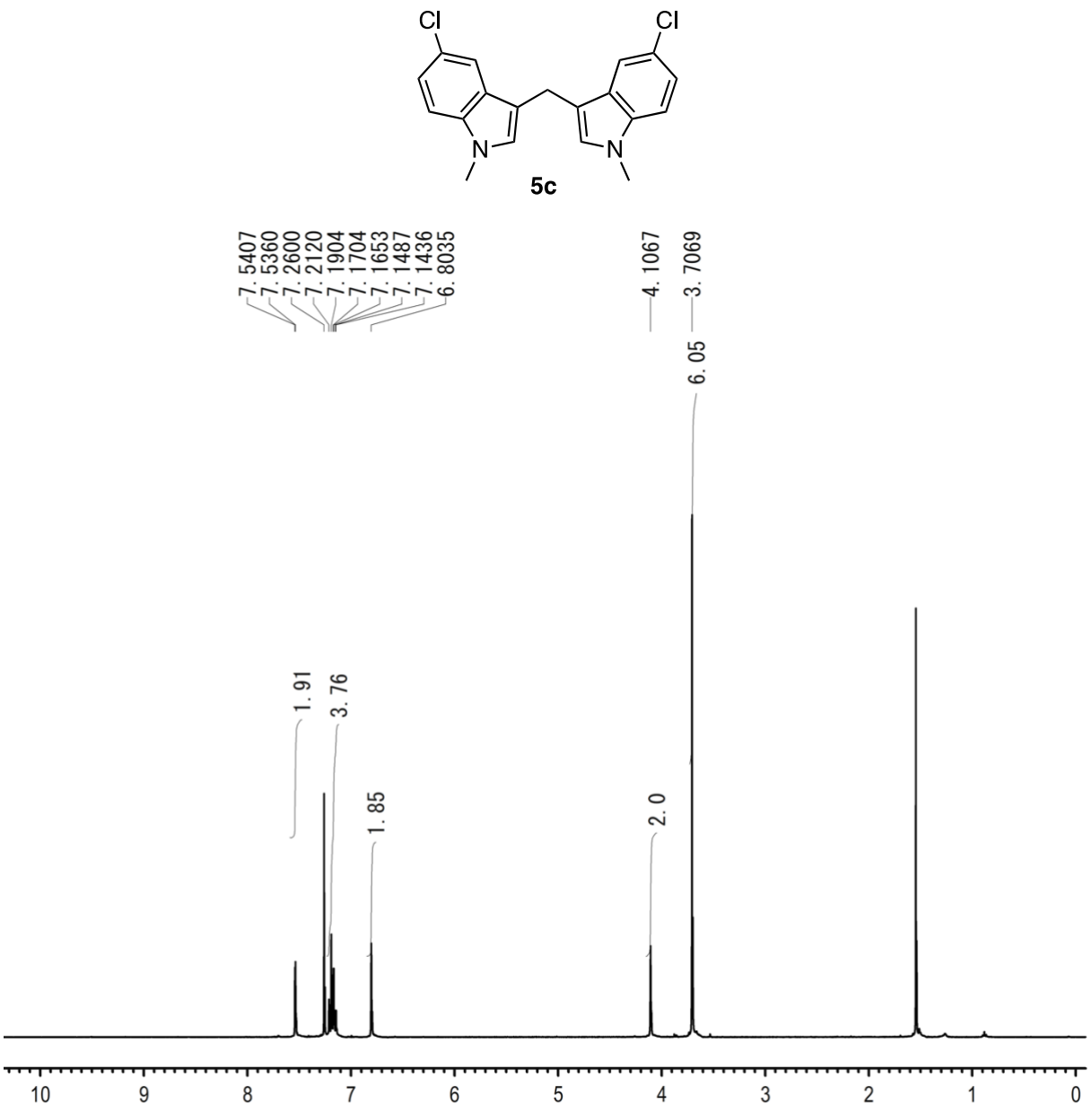

100 MHz $^{13}C$ NMR spectrum of **5a'** in $CDCl_3$.



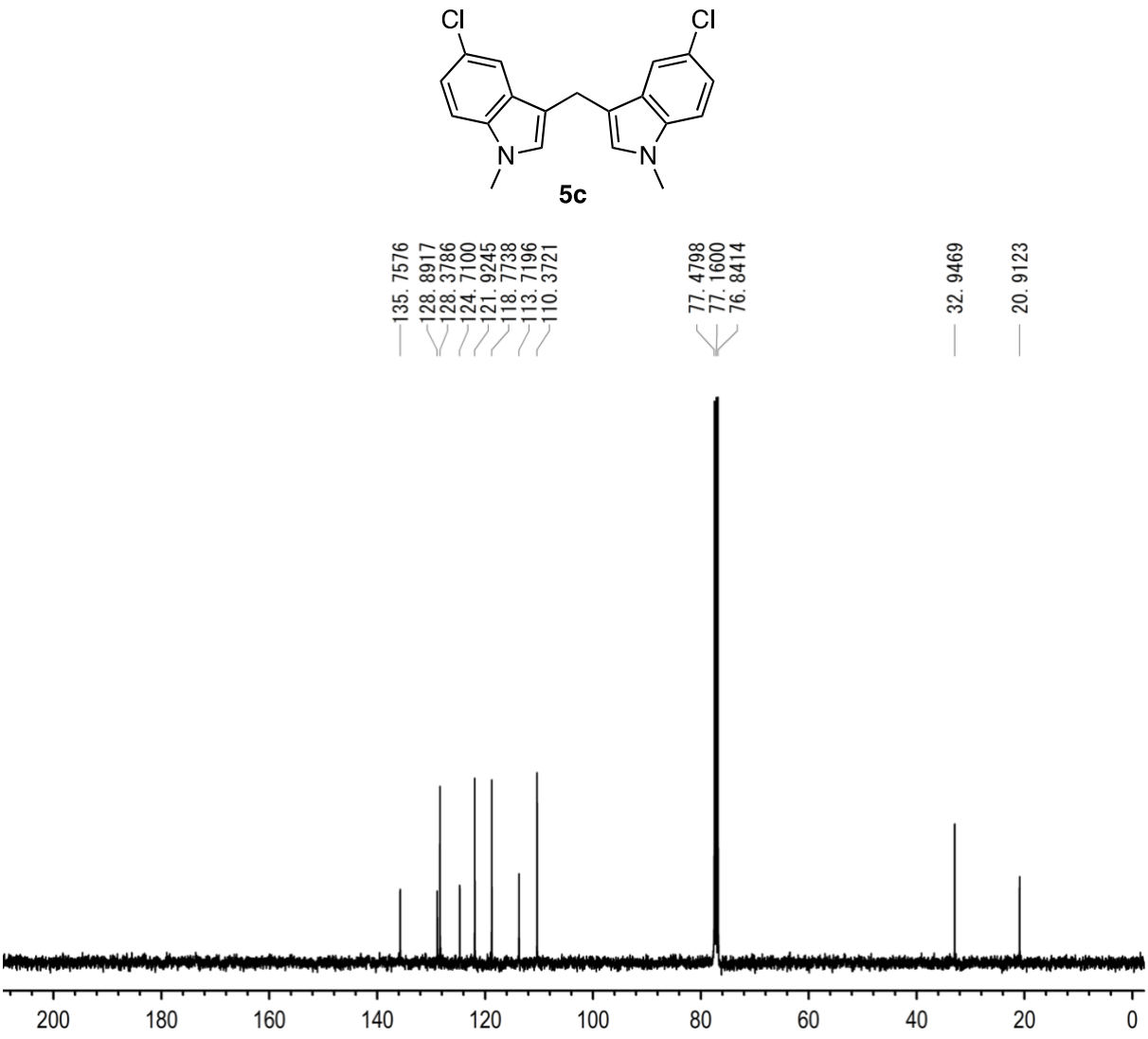

400 MHz $^{1}$H NMR spectrum of **5b** in $CDCl_3$.



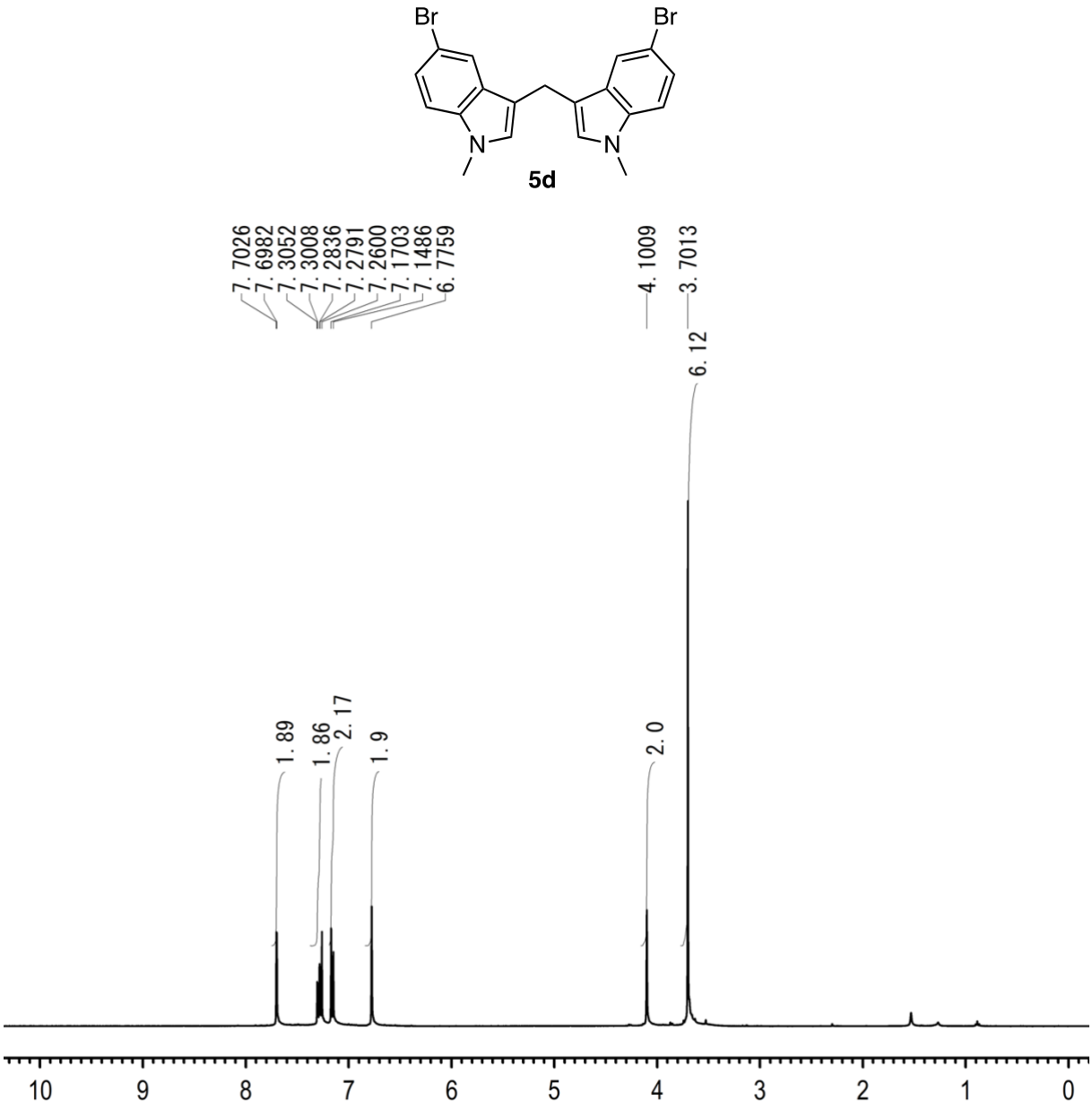

100 MHz $^{13}C$ NMR spectrum of **5b** in $CDCl_3$.



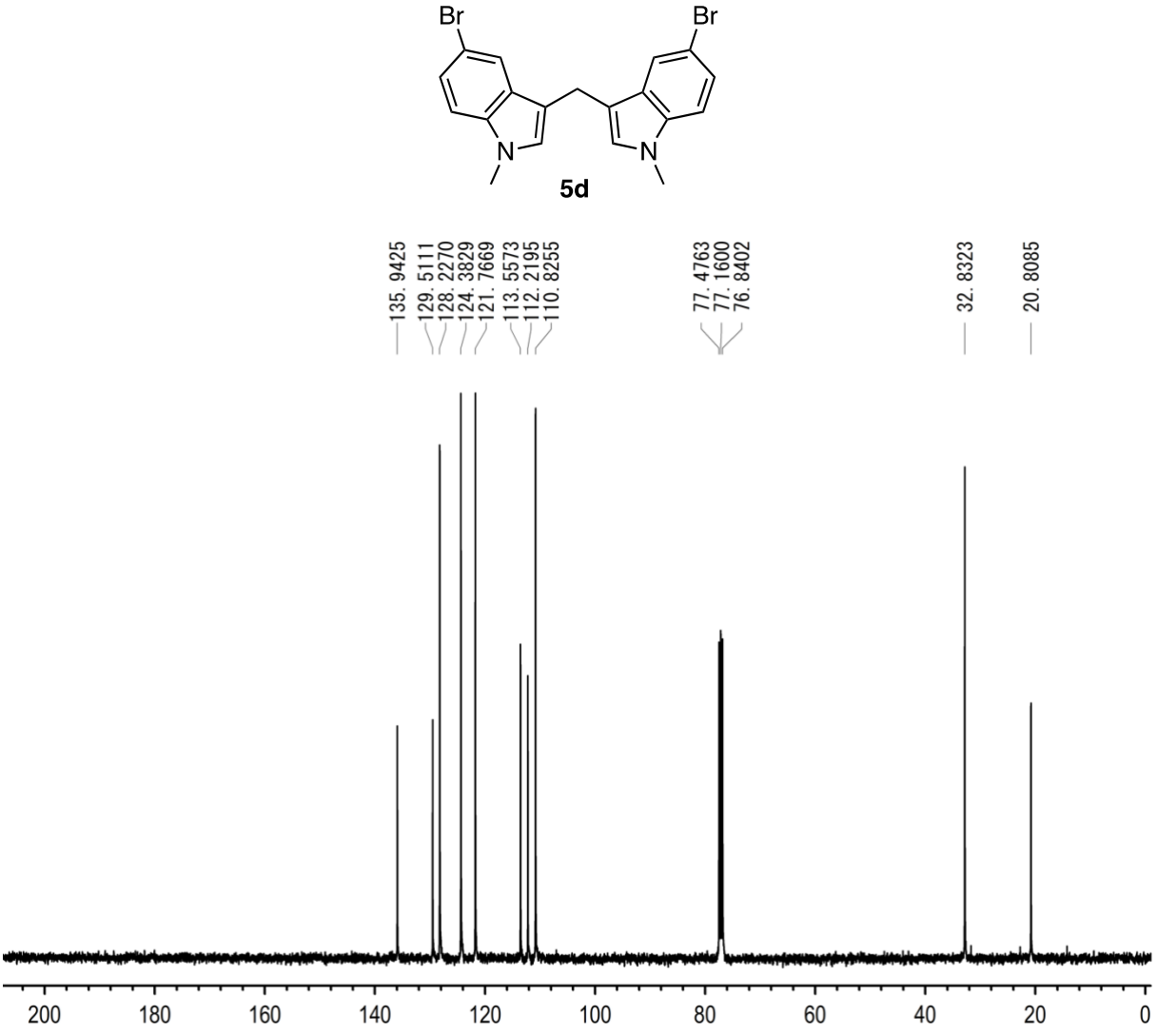

400 MHz $^{1}$H NMR spectrum of **5c** in $CDCl_3$.



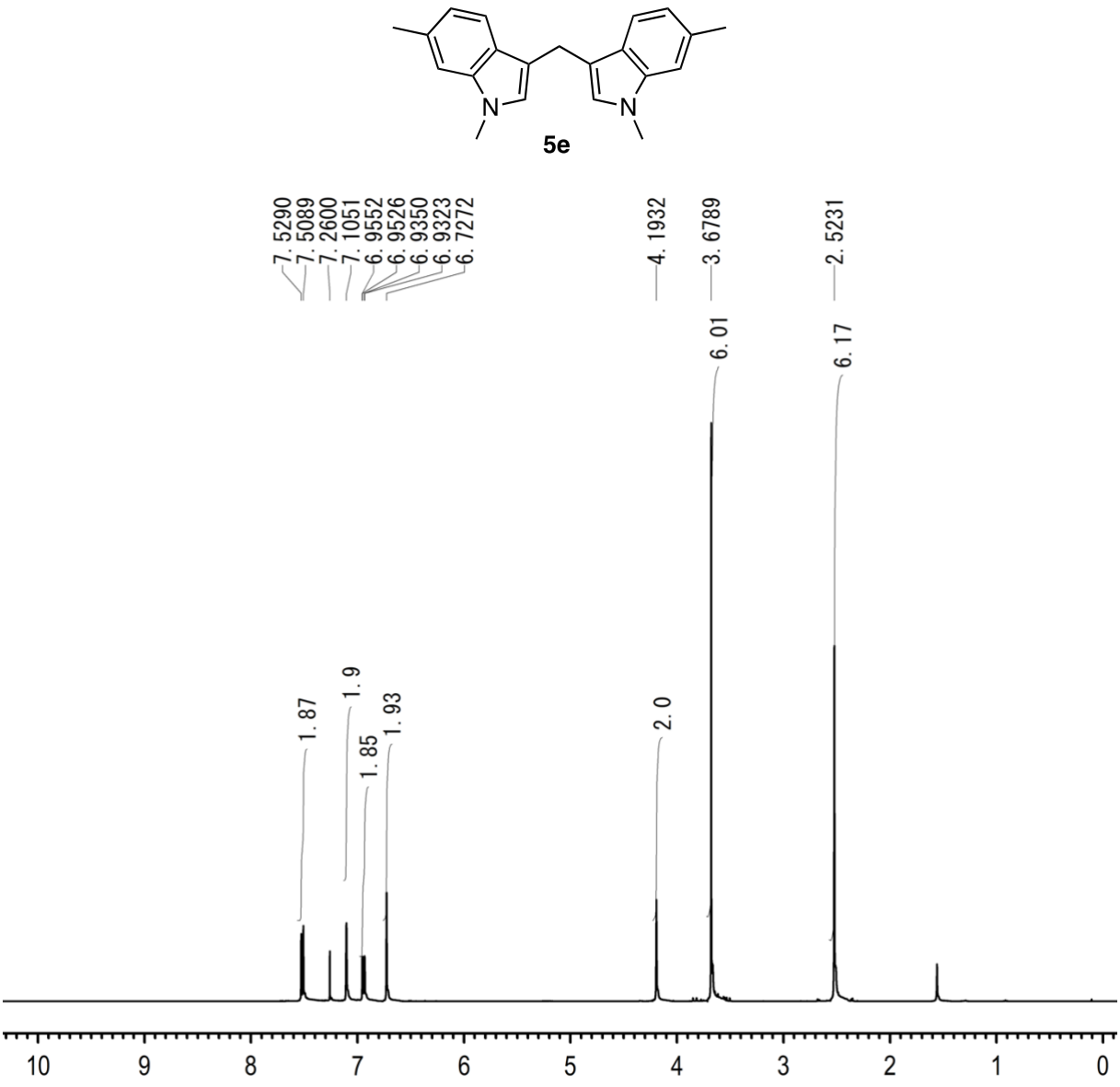

100 MHz $^{13}C$ NMR spectrum of **5c** in $CDCl_3$.



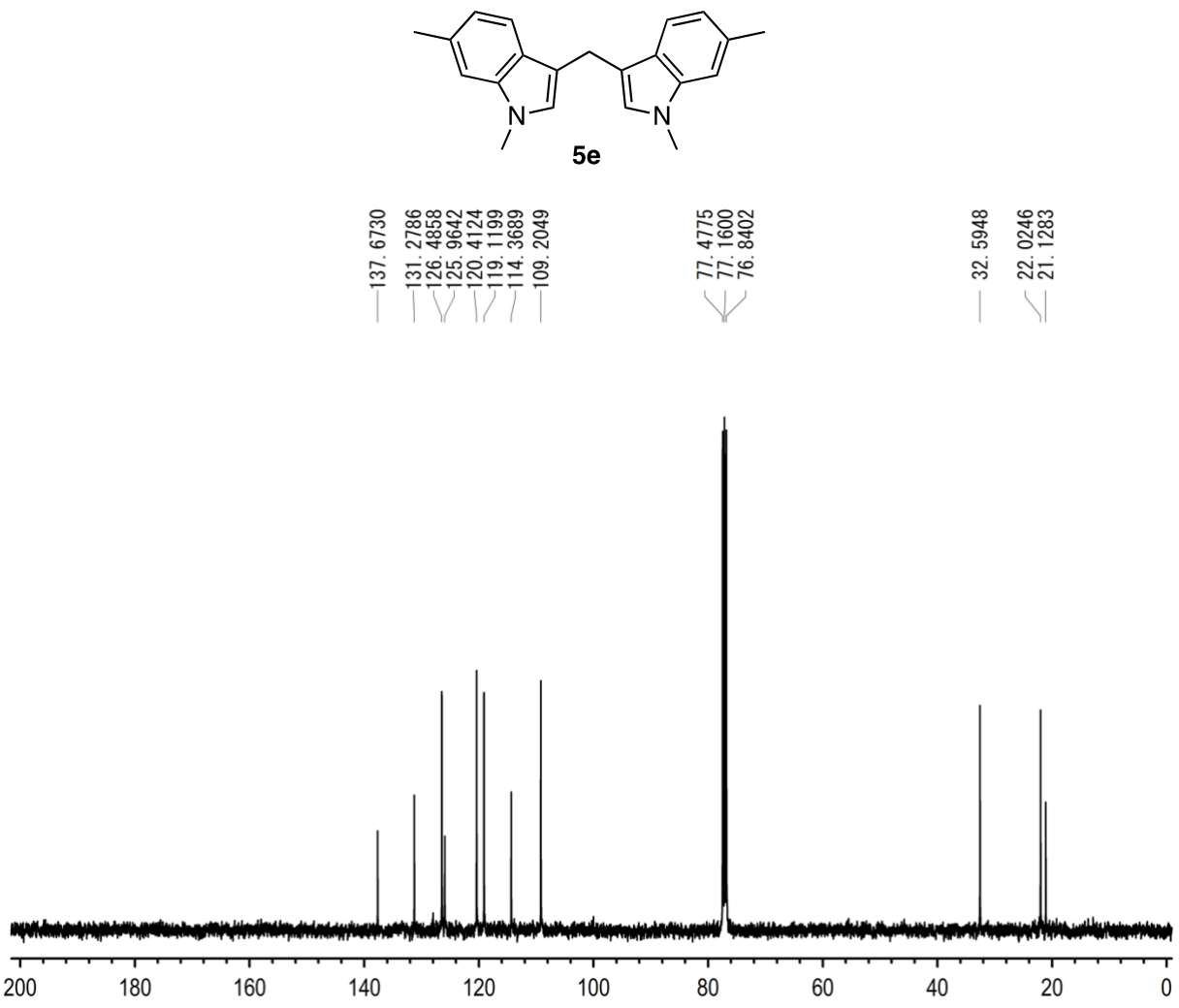

400 MHz $^{1}$H NMR spectrum of **5d** in $CDCl_3$.



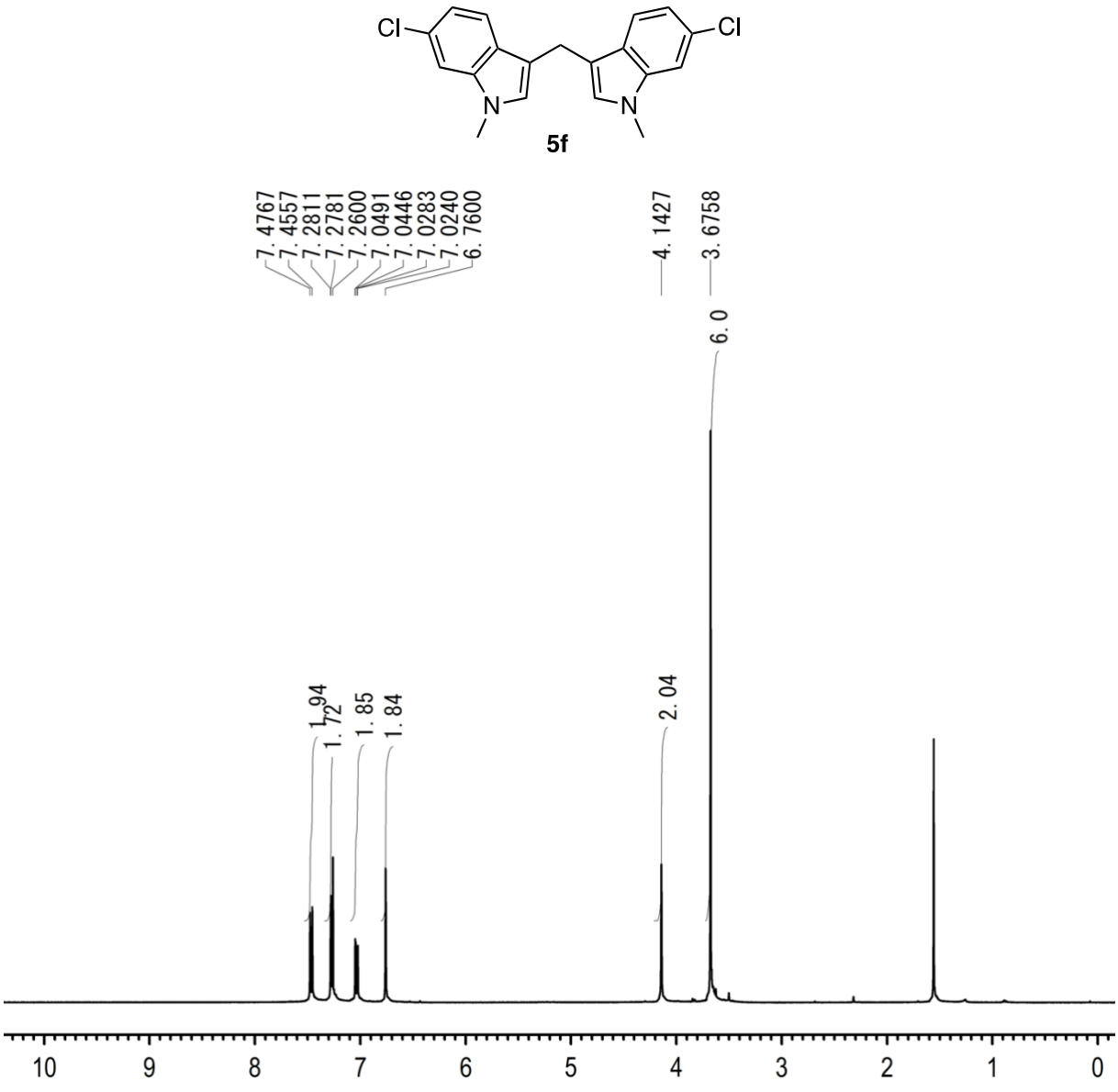

100 MHz $^{13}C$ NMR spectrum of **5d** in $CDCl_3$.



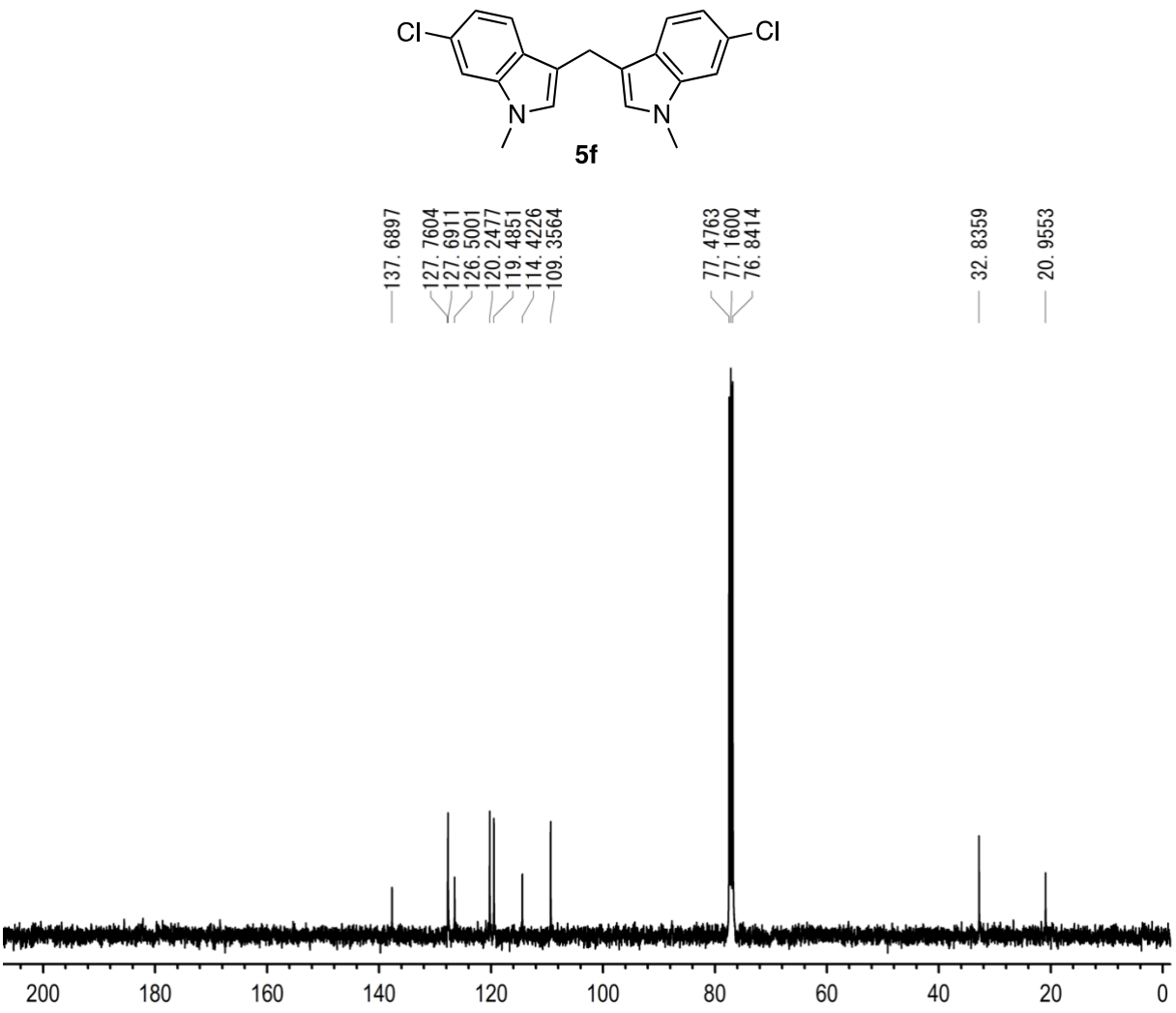

400 MHz $^{1}$H NMR spectrum of **5e** in $CDCl_3$.



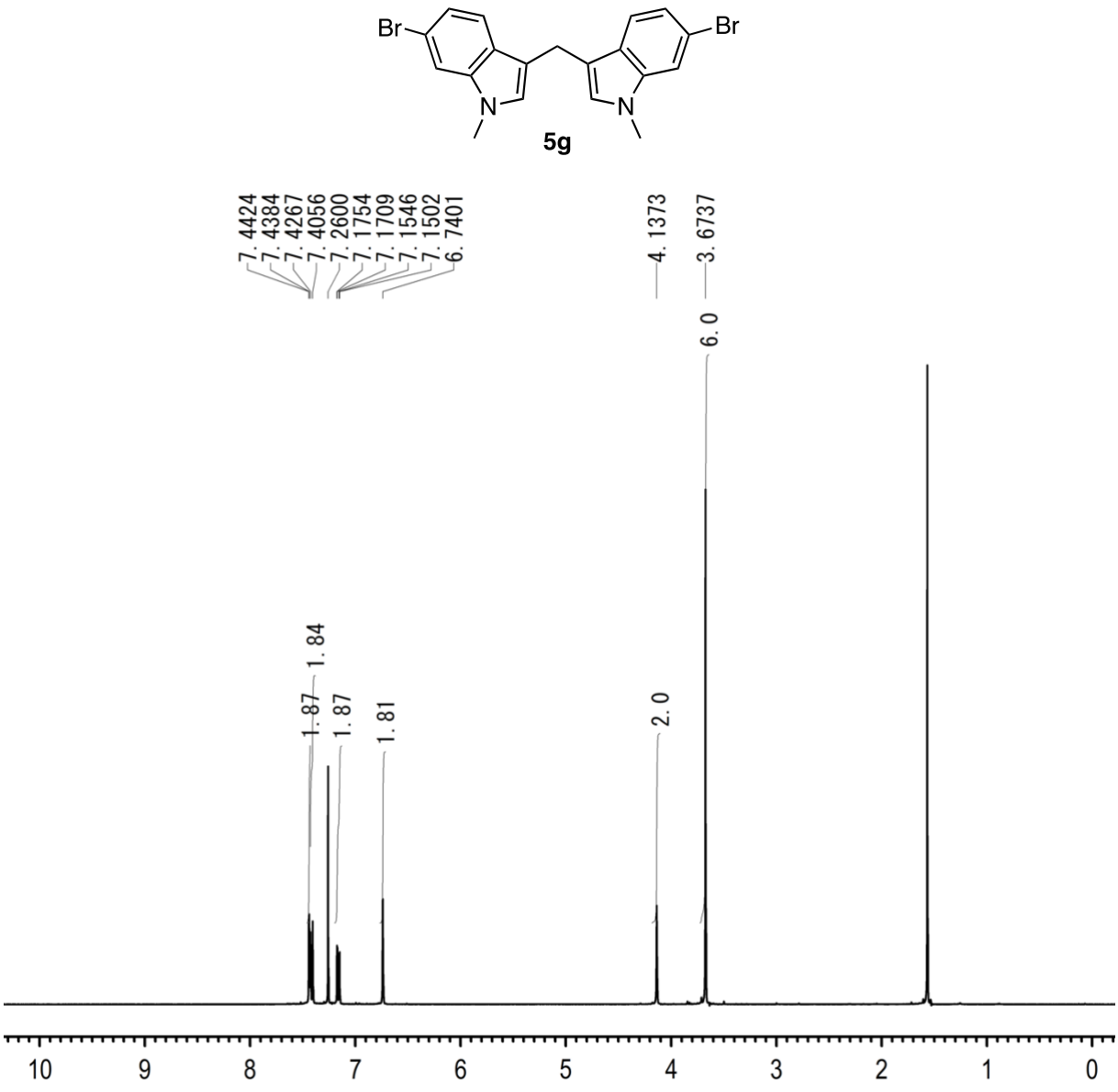

100 MHz $^{13}C$ NMR spectrum of **5e** in $CDCl_3$.



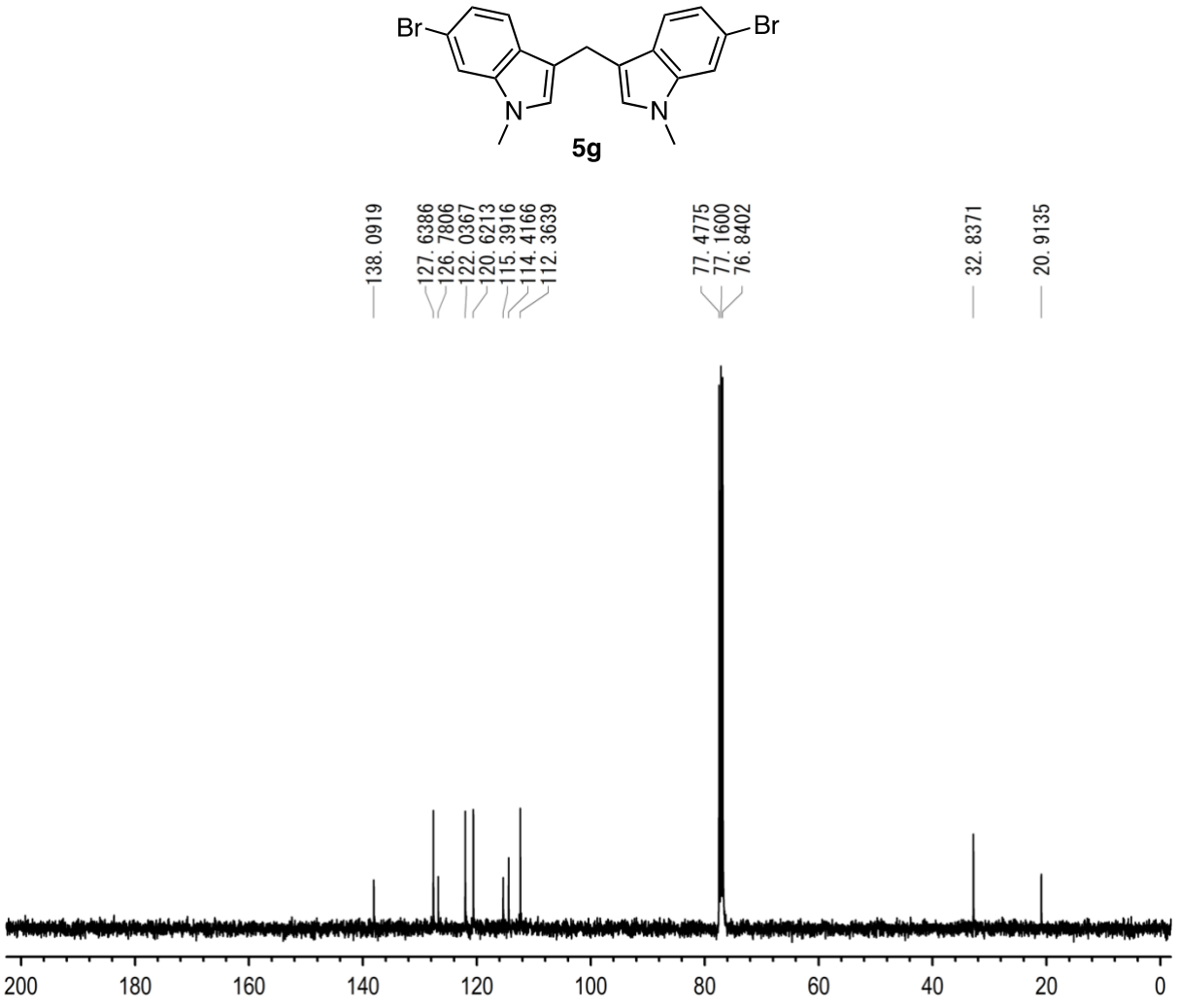

400 MHz $^{1}$H NMR spectrum of **5f** in $CDCl_3$.



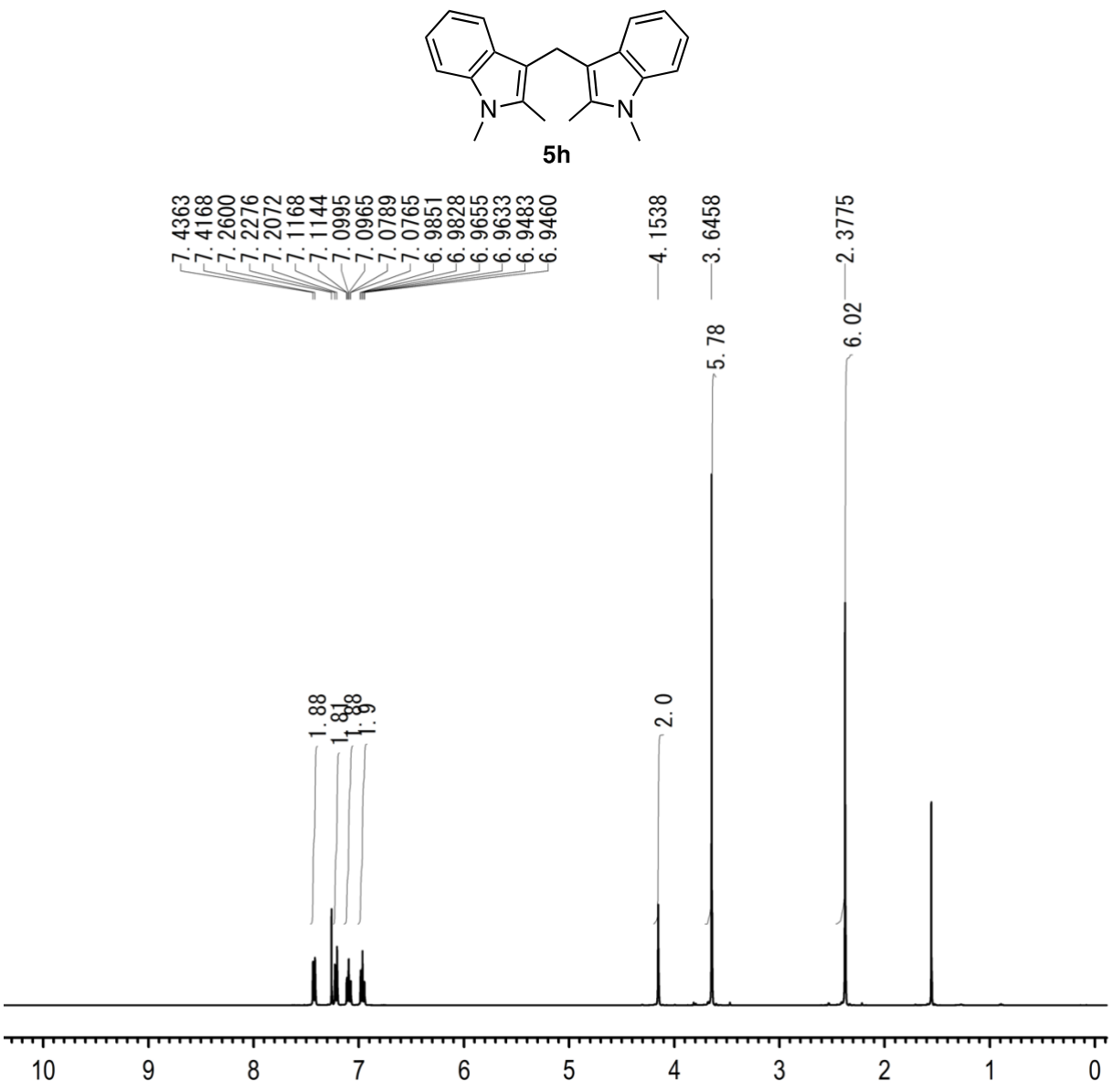

100 MHz $^{13}C$ NMR spectrum of **5f** in $CDCl_3$.



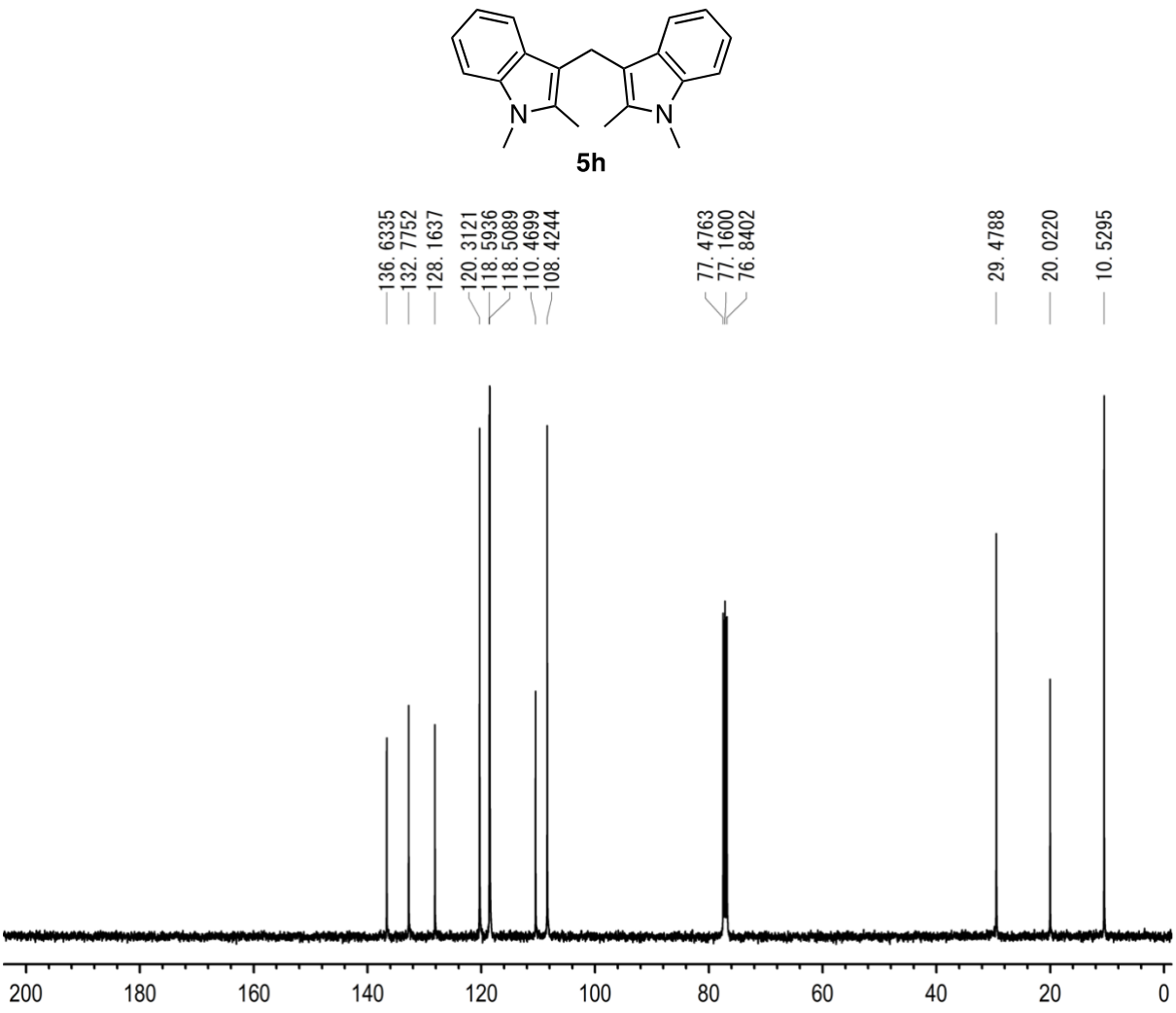

400 MHz $^{1}$H NMR spectrum of **5g** in $CDCl_3$.



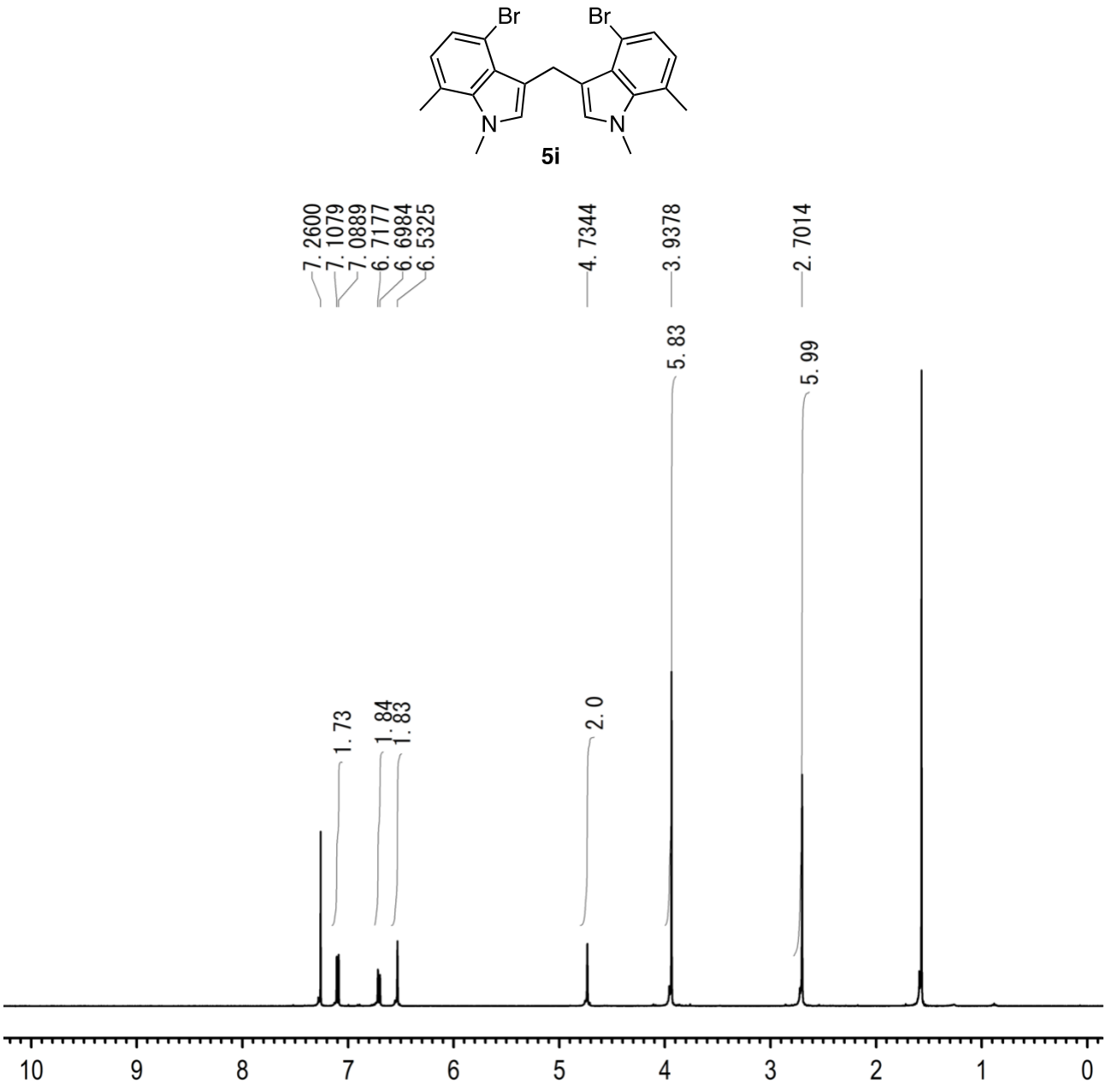

100 MHz $^{13}C$ NMR spectrum of **5g** in $CDCl_3$.



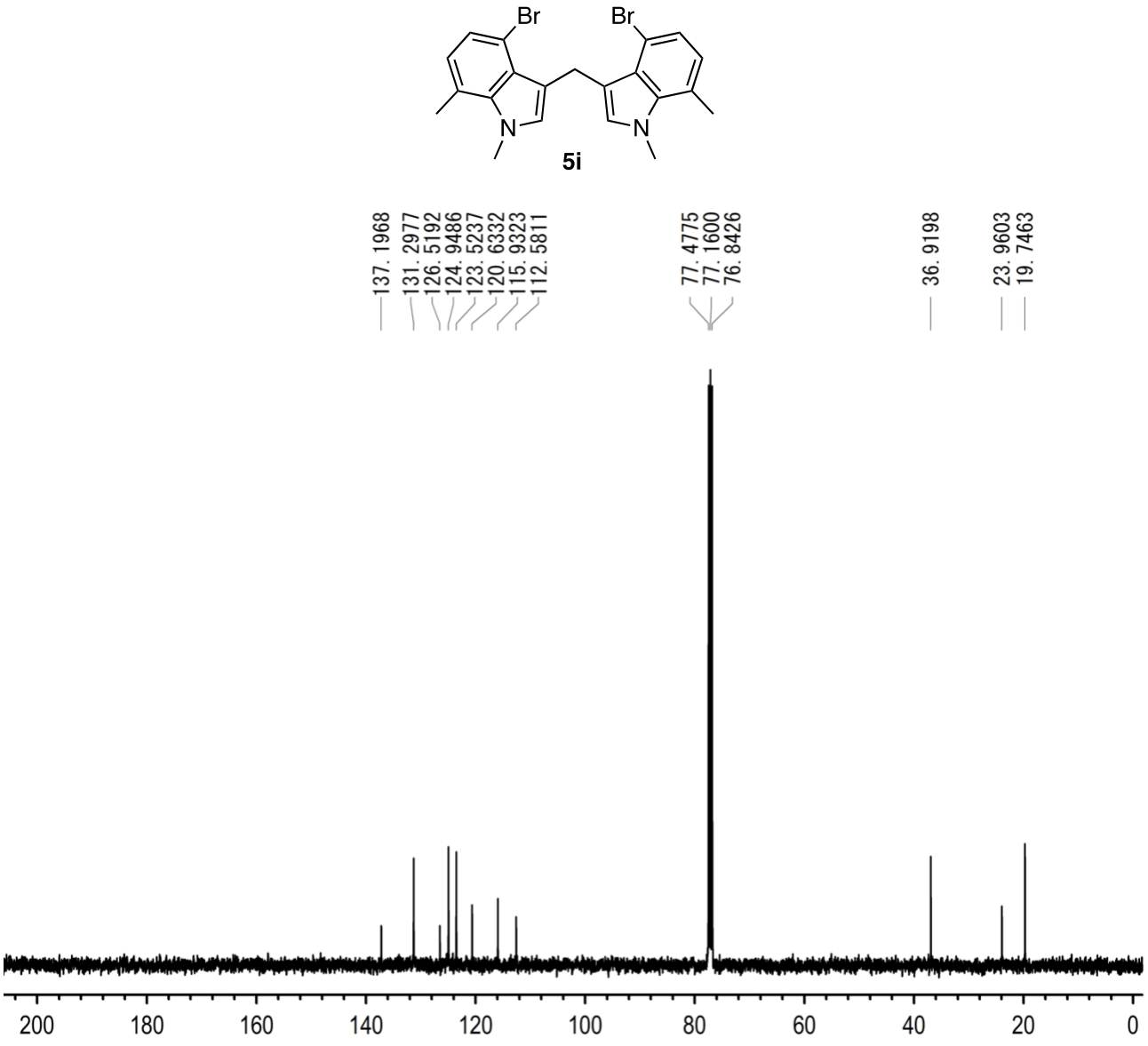

400 MHz $^{1}$H NMR spectrum of **5h** in $CDCl_3$.



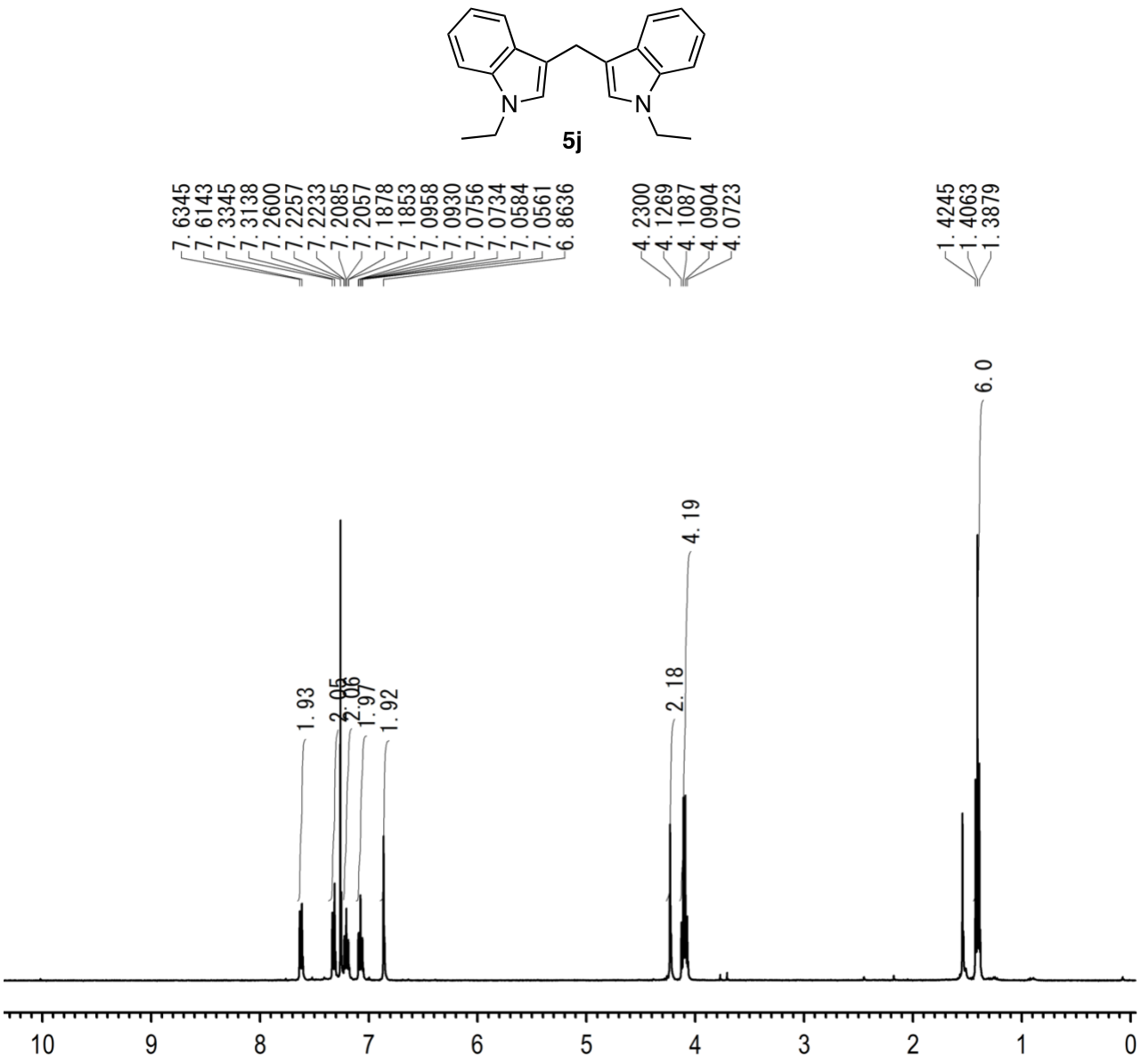

100 MHz $^{13}C$ NMR spectrum of **5h** in $CDCl_3$.



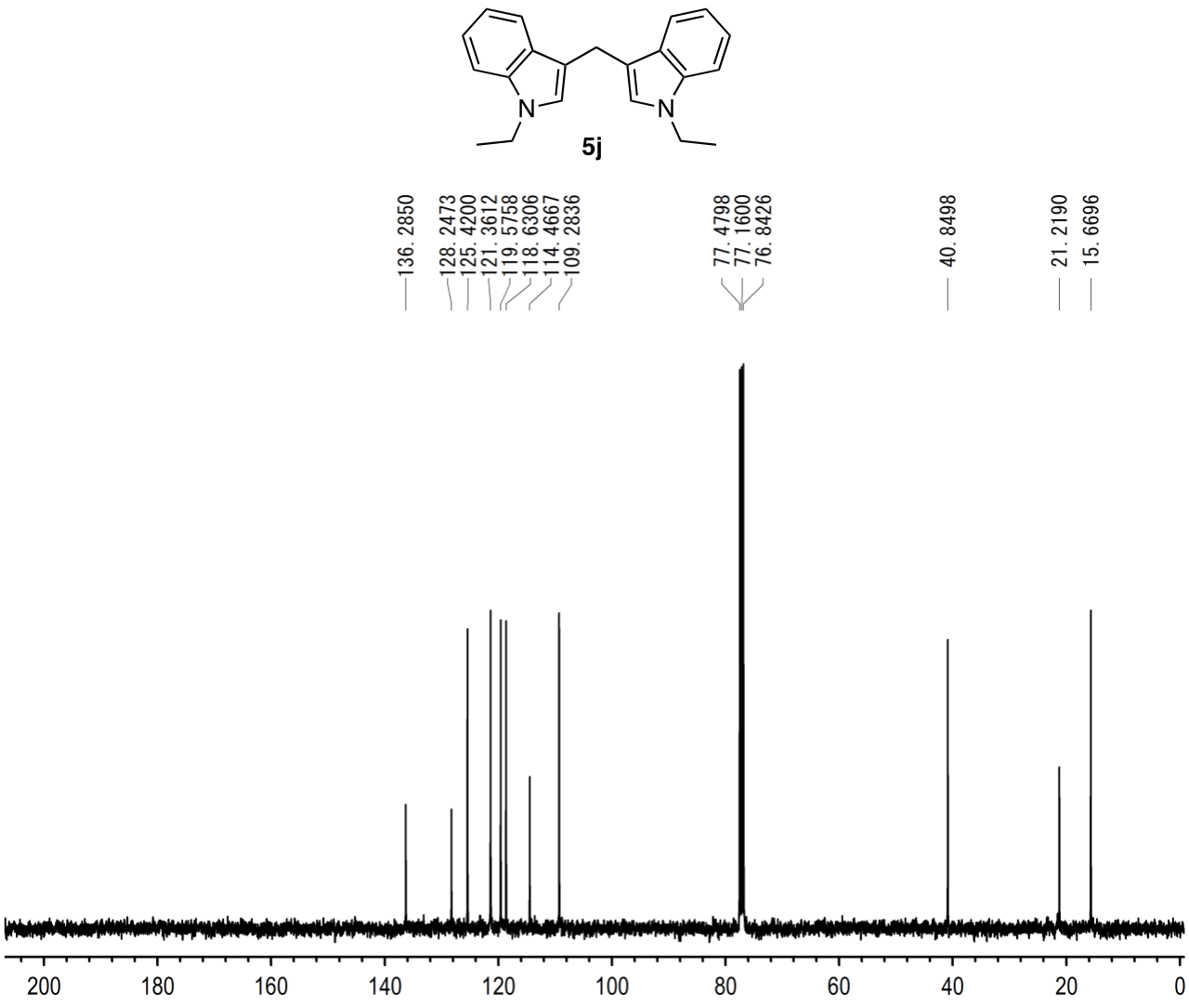

400 MHz $^{1}$H NMR spectrum of **5i** in $CDCl_3$.



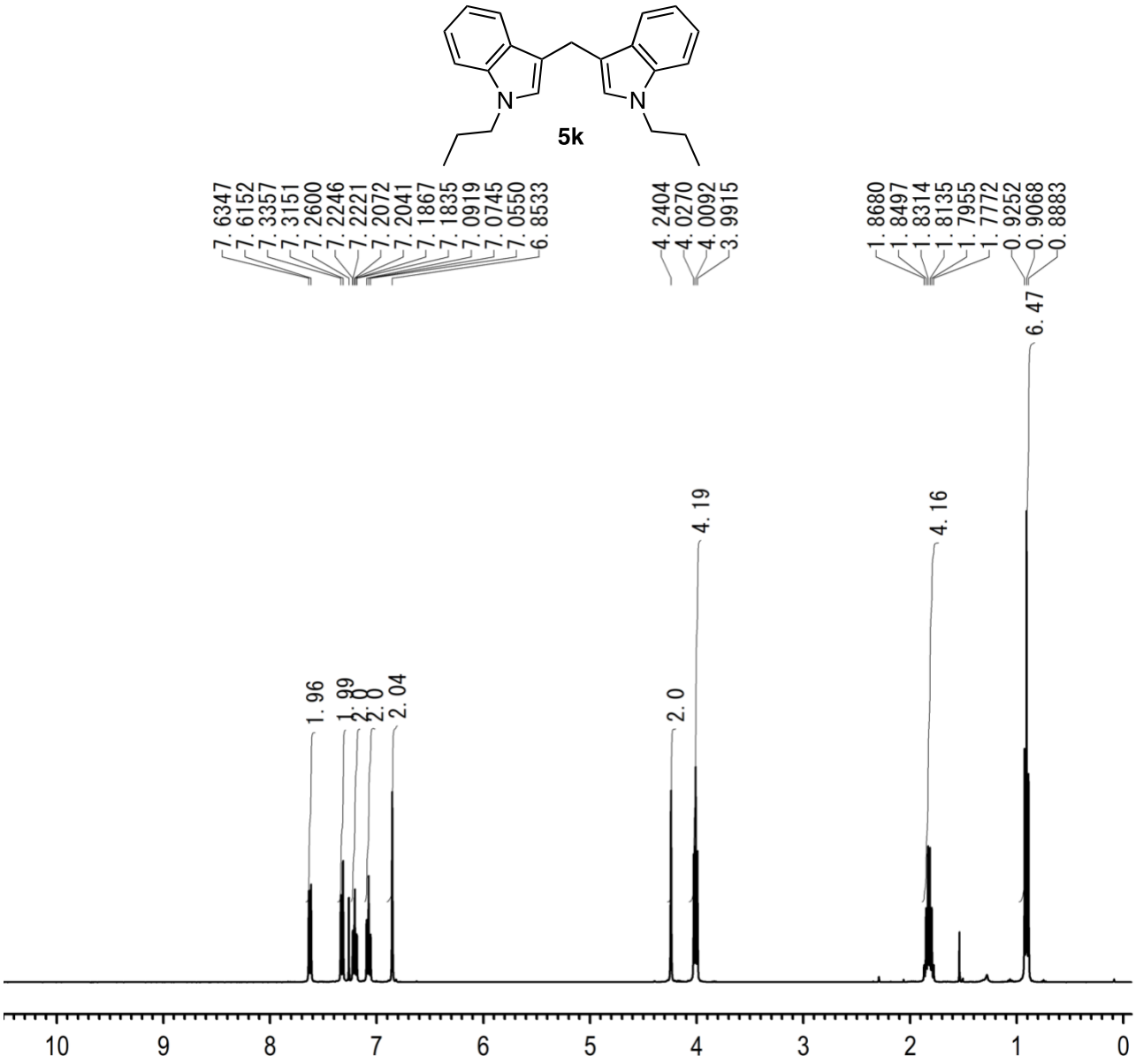

100 MHz $^{13}C$ NMR spectrum of **5i** in $CDCl_3$.



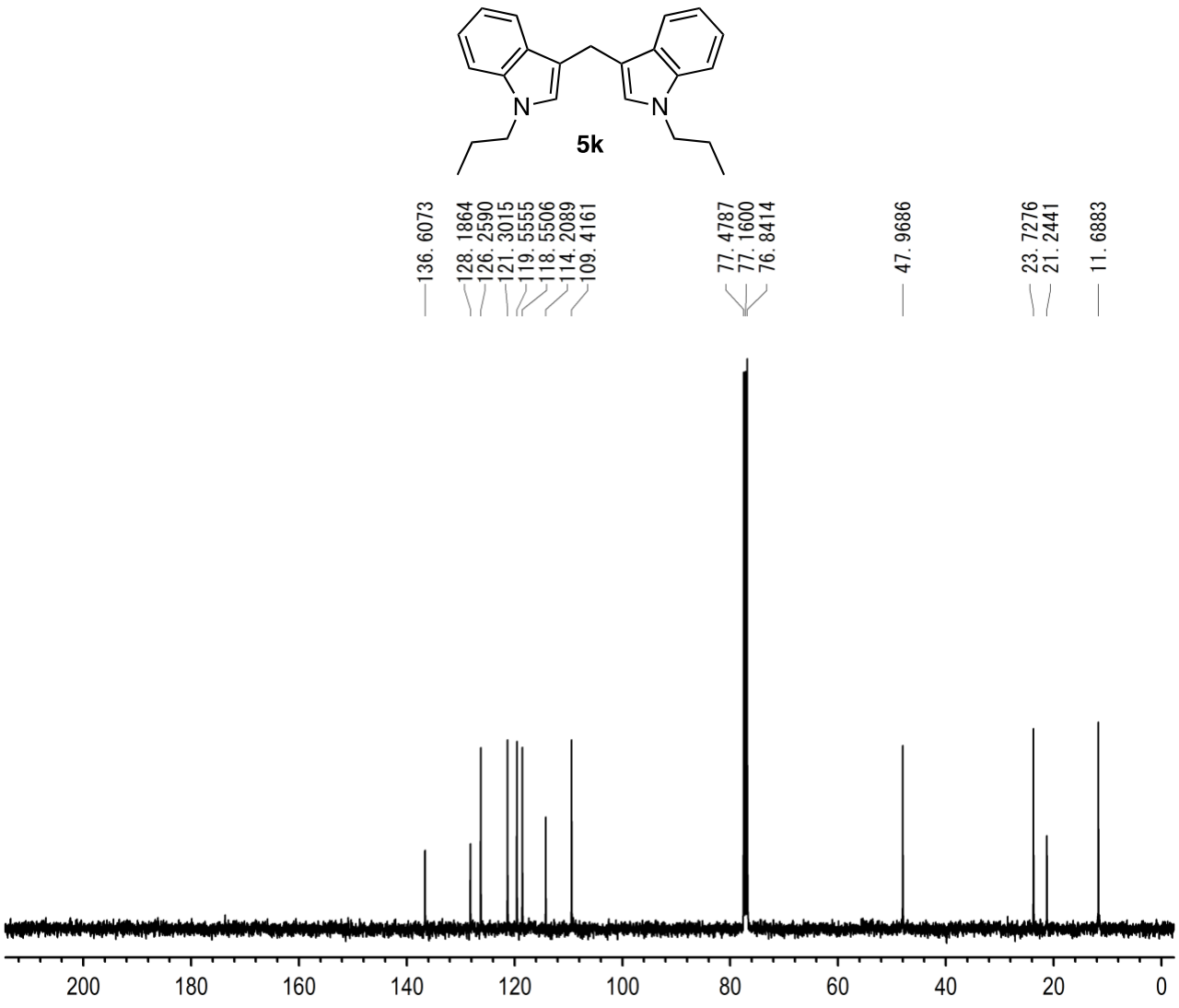

400 MHz $^{1}$H NMR spectrum of **5j** in $CDCl_3$.



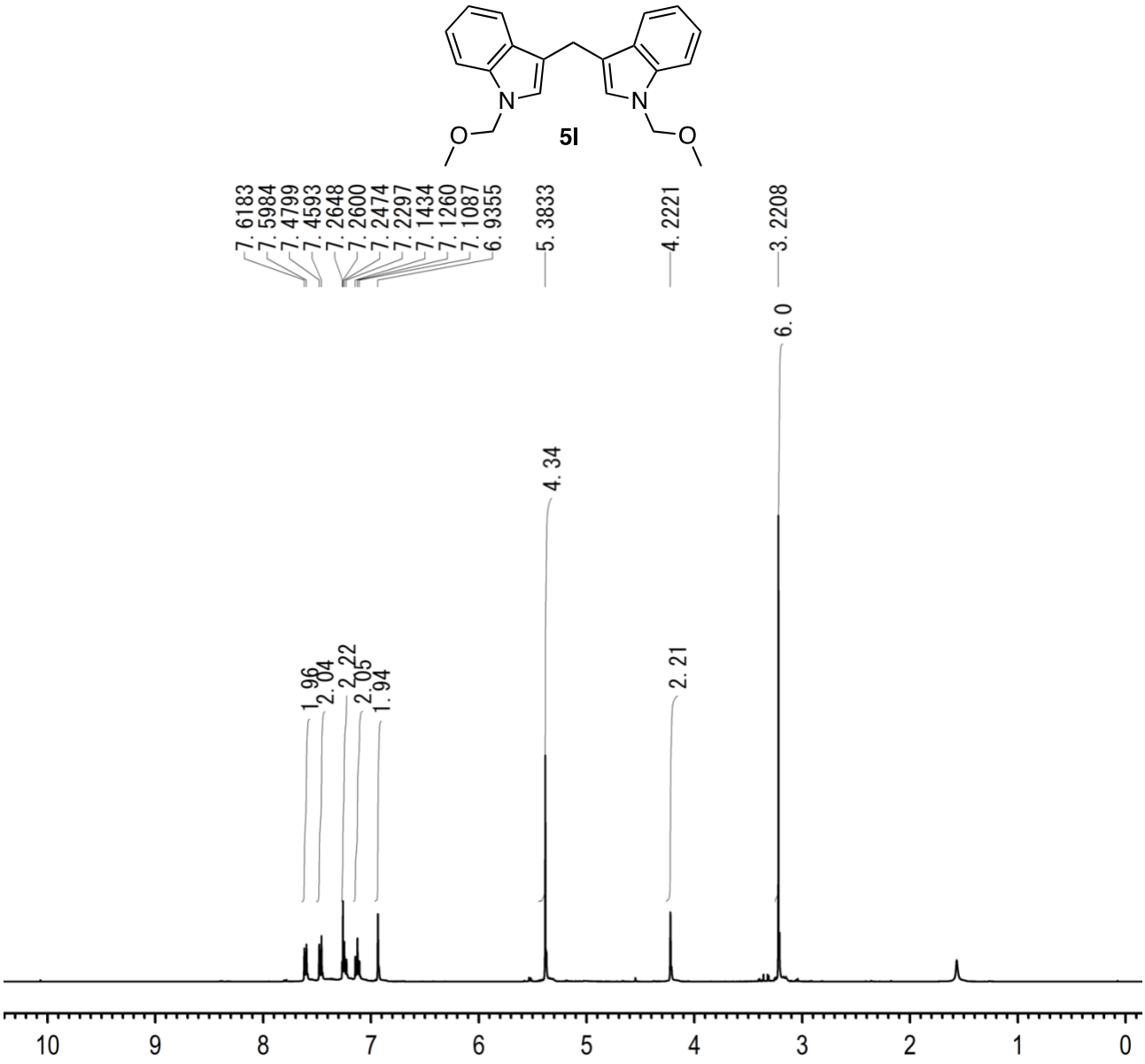

100 MHz $^{13}C$ NMR spectrum of **5j** in $CDCl_3$.



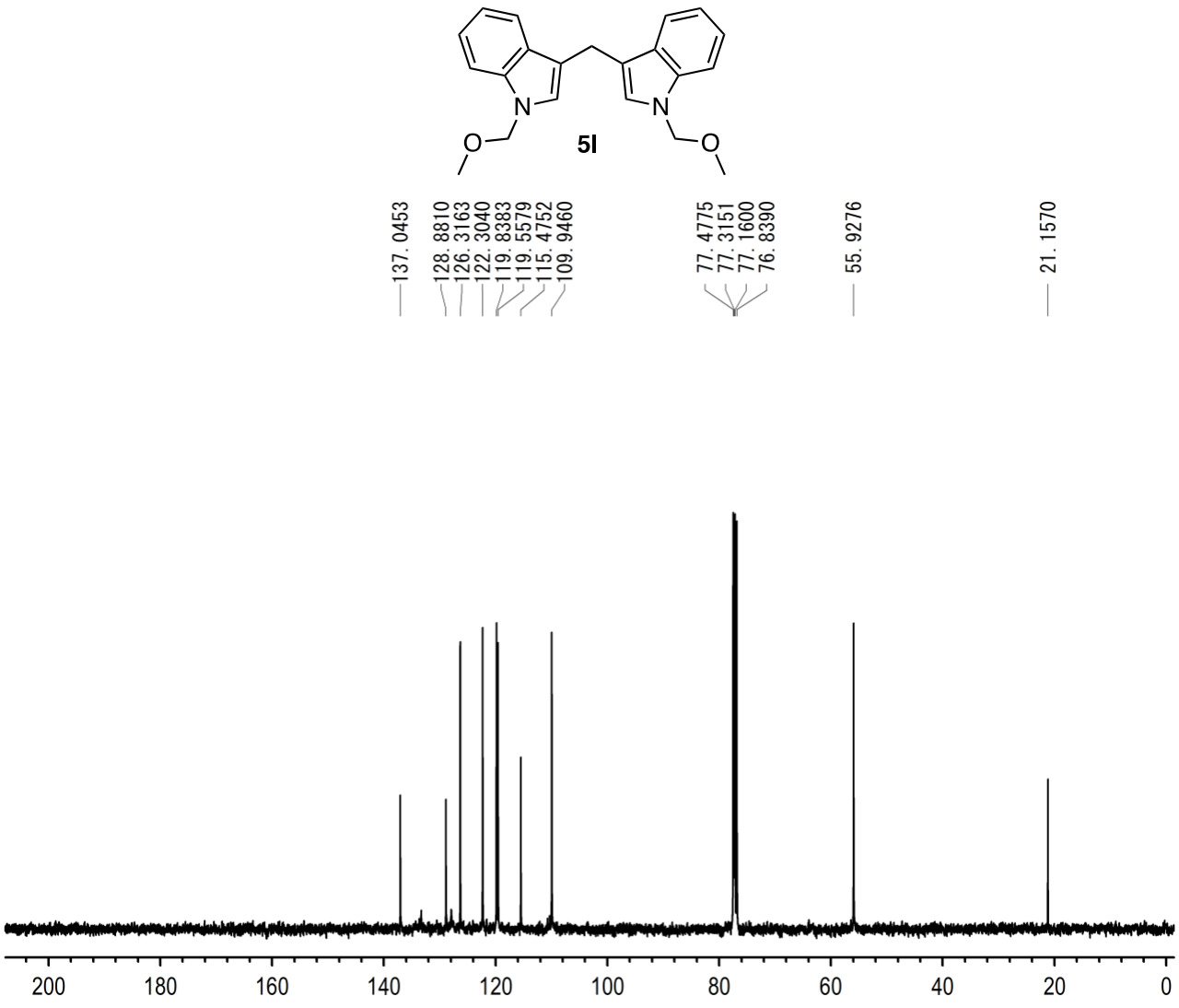

400 MHz $^{1}$H NMR spectrum of **5k** in $CDCl_3$.



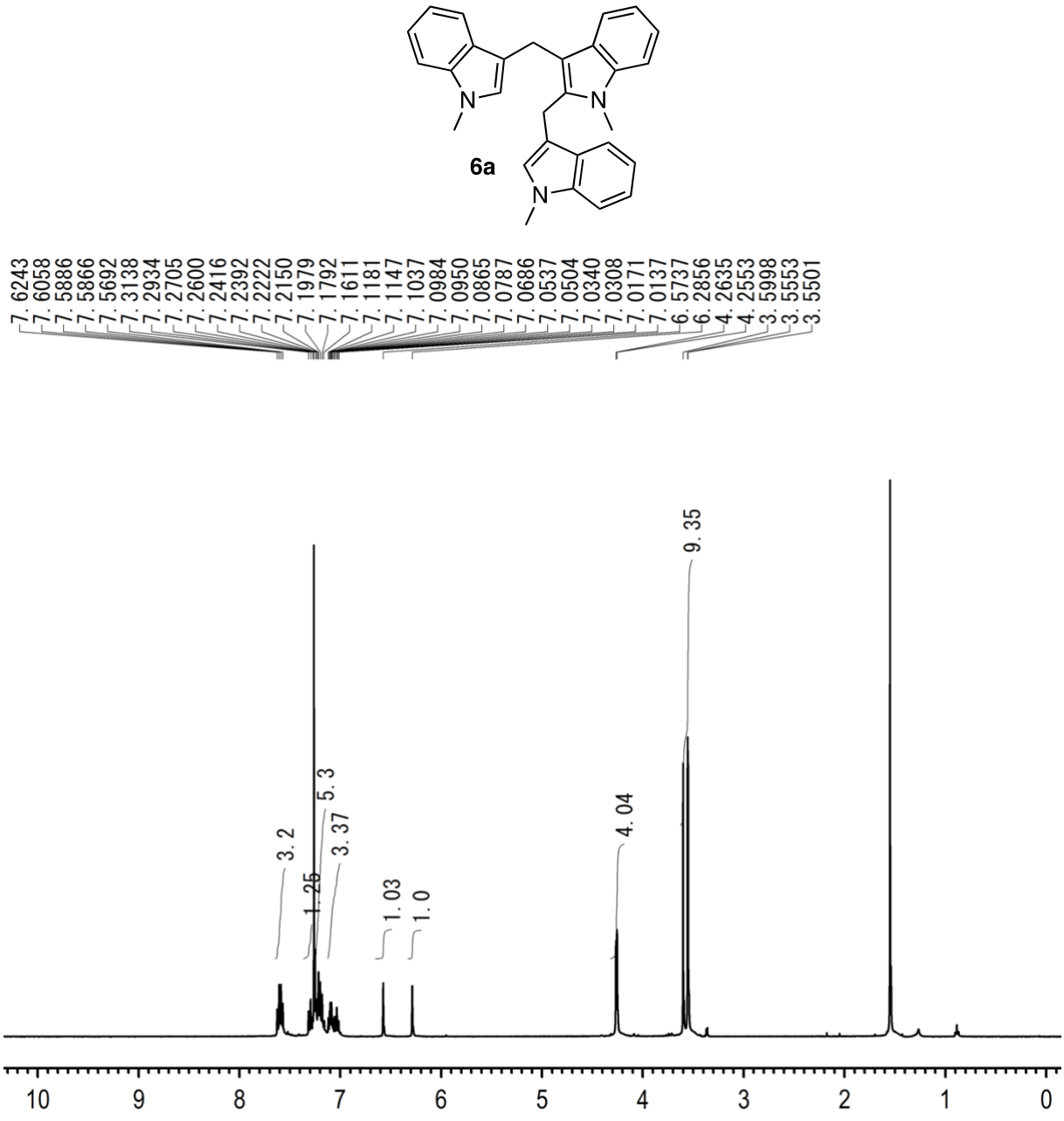

100 MHz $^{13}C$ NMR spectrum of **5k** in $CDCl_3$.



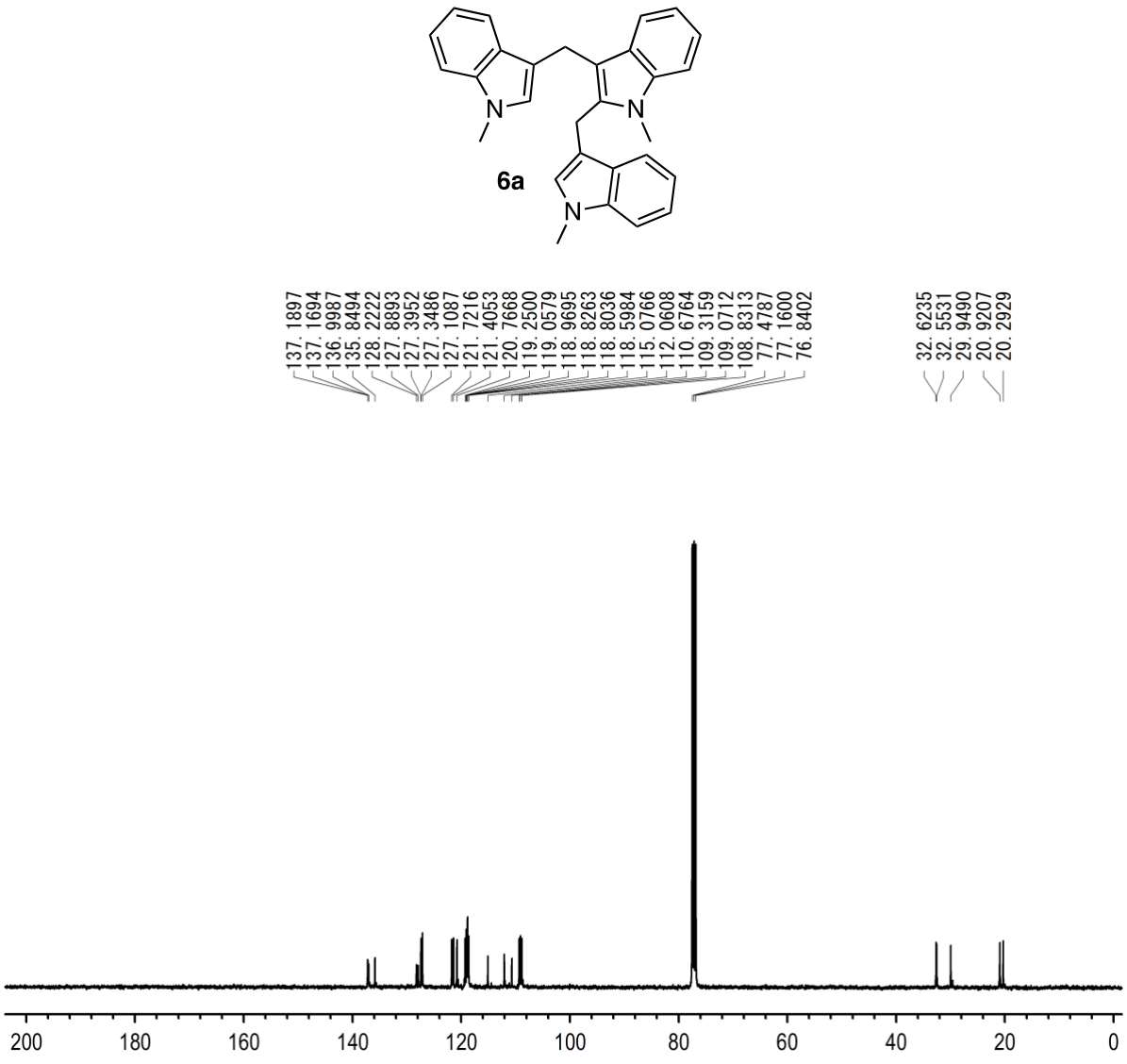

400 MHz $^{1}$H NMR spectrum of **5l** in $CDCl_3$.



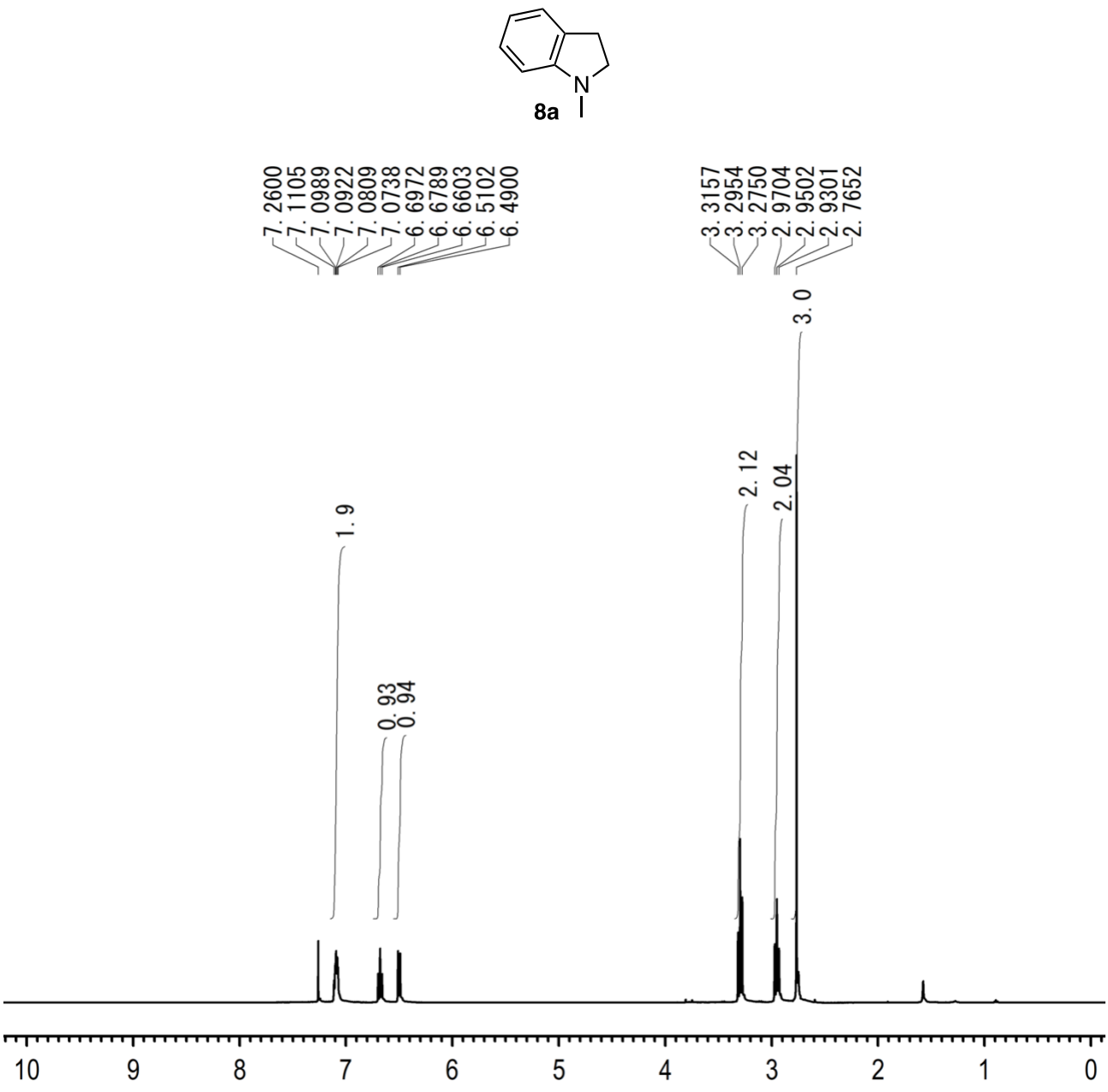

100 MHz $^{13}C$ NMR spectrum of **5l** in $CDCl_3$.



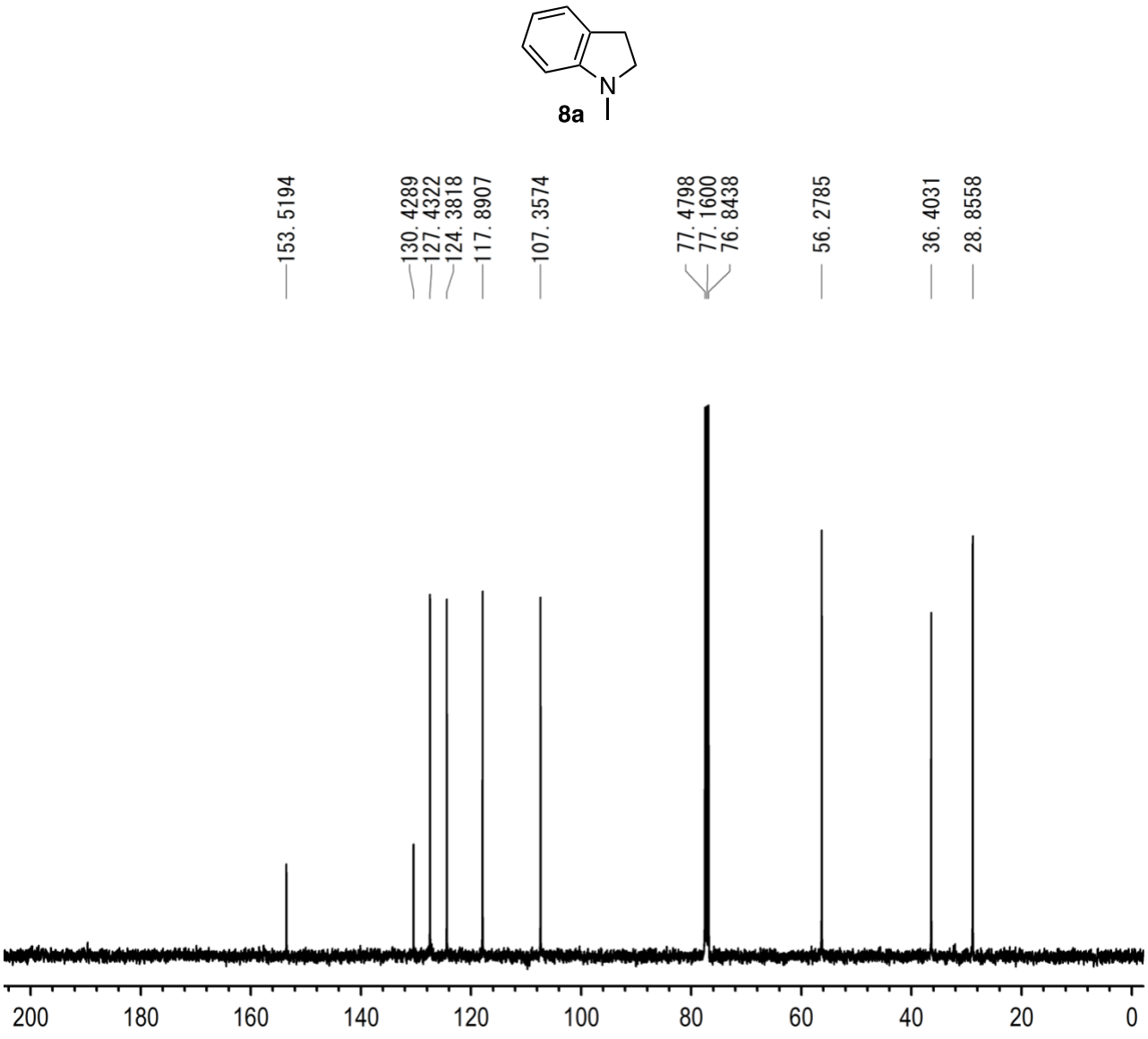

400 MHz $^{1}$H NMR spectrum of **6a** in $CDCl_3$.




100 MHz $^{13}C$ NMR spectrum of **6a** in $CDCl_3$.




400 MHz $^{1}$H NMR spectrum of **8a** in $CDCl_3$.




100 MHz $^{13}C$ NMR spectrum of **8a** in $CDCl_3$.