Supporting Information

Palladium-Catalyzed Cyclocoupling of 2-Halobiaryls with Isocyanides via the Cleavage of Carbon-Hydrogen

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CONTENTS

I. General Information.

^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ with tetramethylsilane as an internal standard. Data are reported as follows: chemical shift in ppm (δ), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet), coupling constant (Hz), and integration. Infrared spectra (IR) were are reported in reciprocal centimeters with the following relative intensities: s (strong), m (medium), or w (weak). Mass spectra were obtained with ionization voltages of 70 eV.

II. Materials.

$Pd(OAc)_2$ was purchased from Wako Chemicals and used as received. Cesium pivalate was prepared by the reaction of cesium carbonate and pivalic acid[1]. Halides **1a**, **1b**, **1d**, and **15a** and isocyanides **2g**, **2h**, and **2i** were commercially available and used as received. Triflates **1c** (CAS [17763-65-4]), **16b** (CAS [24764-60-1]), **17** (CAS [4877-77-4]), **19** (CAS [120537-57-7]), **21** (CAS [137058-15-2]) were prepared by the treatment of the corresponding phenols or carbonyl compounds with Tf_2O and a base. Halides **1e** (CAS [154542-81-1]), **1f** (CAS [74447-76-0]), **1g** (CAS [255838-15-1]), **1h** (CAS [89900-97-0]), **1i** (CAS [198205-81-1]), **1j** (482377-55-9), **1k** (CAS [146534-36-3]), **1l** (CAS [154407-16-6]), **1m** (CAS [690260-40-3]), **1n** (CAS [74447-77-1]), **1o** (CAS [251320-87-3]), **5** (CAS [69907-27-3]), **7** (CAS [154407-13-3]), **9** (CAS [20608-83-7]), **11** (CAS [82080-39-5]), and **13** (CAS [101681-34-9]) were prepared by Suzuki-Miyaura cross-coupling reaction of 1-bromo-2-iodobenzene with the corresponding aryl boronic acids. Isocyanides **2a** (CAS [2008-61-9]), **2b** (CAS [2769-71-3]), **2c** (CAS [2980-92-9]), and **2d** (CAS [69847-28-5]) were known and prepared by the dehydration of the corresponding formamides by following a literature procedure[2]. Iodide **23** was prepared by the reported method.[3]

III. Synthesis of Isocyanide.

4-Methyl-2,6-di(4-tolyl)phenyl isocyanide (2e). To a flame-dried two-necked flask, 2,6-dibromo-4-methylaniline (8.7 g, 33 mmol), phenylboronic acid (10 g, 72 mmol), aqueous solution of K_2CO_3 (2M, 56 mL) and DME (70 mL) were added under gentle stream of nitrogen, and the mixture was stirred for 30 min at r.t. under N_2 atmosphere. To the stirred mixture, $PdCl_2(PPh_3)_2$ (913 mg, 1.3 mmol) was added at r.t., and the mixture was stirred for overnight at 80°C under N_2. The reaction mixture was then cooled to room temperature, diluted with diethyl ether. The organic layer was washed with brine and dried over $MgSO_4$. After removing the volatiles in vacuo, the residue was subjected to column chromatography on silica gel (hexane/EtOAc = 10/1) to afford 4-methy-2,6-di(4-tolyl)aniline (8.2 g, 40 %). Subsequent formylation and the dehydration[2] afforded the title compound. The compound was purified by recrystalization from $CHCl_3$/hexane (52 % over all yield).

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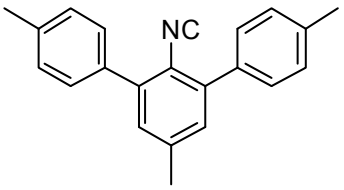
1 Campo, M. A.; Larock, R. C. *Org. Lett.* **2000**, *2*, 3675.
2 Hoogenboom, B. E.; Oldenziel, O. H.; van Leusen, A. M. *Org. Synth., Coll. Vol. VI* **1988**, 987.
3 Zhou, C.; Dubrovsky, A. V.; Larock, R. C. *J. Org. Chem.* **2006**, *71*, 1626.

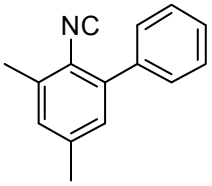
White solid. Mp= 141 °C. R_f = 0.43 (hexane/EtOAc = 4/1). ^{1}H NMR ($CDCl_3$) δ: 2.41 (brs, 9H), 7.12 (s, 2H), 7.26-7.29 (m, 4H), 7.41-7.44 (m, 4H). ^{13}C NMR ($CDCl_3$) δ: 21.2, 21.3, 128.9, 129.1, 129.9, 134.8, 138.0, 139.2, 139.7, 168.0. IR (KBr):3018 w, 2920 w, 2117 m, 1597 w, 1552 m, 1437 w, 1398 w, 1377 w, 1309 w, 1188 w, 1022 w, 870 m, 810 s, 758 w, 729 m, 579 w, 552 w, 515 m. MS, *m/z* (relative intensity, %): 298 (M^+, 23), 297 (M^+-1, 100), 296 (54), 295 (10), 283 (10), 282 (44), 281 (15), 280 (12), 141 (13), 140 (10), 134 (14). Exact Mass Calcd for $C_{22}H_{19}N$: 297.1517. Found: 297.1509.



2e

2-Isocyano-3,5-dimethyl-1,1'-biphenyl (2f). To a flame-dried two-necked flask, 2-bromo-4,6-dimethylaniline (5.0 g, 25 mmol), phenylboronic acid (3.7 g, 30 mmol), aqueous solution of K_2CO_3 (2M, 56 mL) and DME (40 mL) were added under gentle stream of nitrogen, and the mixture was stirred for 30 min at r.t. under N_2 atmosphere. To stirred mixture, $PdCl_2(PPh_3)_2$ (351 mg, 0.5 mmol) was added at r.t., and the mixture was stirred for overnight at 80°C under N_2. The reaction mixture was then cooled to room temperature, diluted with diethyl ether. The organic layer was washed with brine and dried over $MgSO_4$. After removing the volatiles in vacuo, the residue was subjected to column chromatography on silica gel to afford 3,5-dimethylbiphenyl-2-amine (4.6 g, 93 %). Subsequent formylation and the dehydration[2] afforded the title compound.

Colorless oil. *Rf* = 0.4 (hexane/EtOAc = 4/1).^{1}H NMR ($CDCl_3$) δ: 2.36 (s, 3H), 2.45 (s, 3H), 7.06 (d, *J* = 0.8 Hz, 8.9 Hz, 2H), 7.38-7.50 (m, 5H). ^{13}C NMR ($CDCl_3$) δ:19.2, 21.2, 128.0, 128.3, 128.5, 128.9, 129.9, 135.5, 137.6, 138.7, 139.1, 167.6. IR (neat): 3033 m, 2951 m, 2922 m, 2116 s, 1755 w, 1603 s, 1577 m, 1496 m, 1470 s, 1446 s, 1381 m, 1281 w, 1201 m, 1159 w, 1109 w, 1076 m, 1034 m, 918 w, 862 s, 771 s, 711 s, 700 s, 648 w, 611 m, 584 m, 559 w, 530 w, 486 w. MS, *m/z* (relative intensity, %): 208 (M^+, 16), 207 (M^+-1, 100), 206 (66), 204 (10), 193 (10), 192 (64), 191 (19), 190 (18), 179 (14), 178 (15), 165 (25), 102 (24), 96 (12), 89 (15), 88 (12), 77 (15), 76 (17), 63 (12), 51 (14). Exact Mass Calcd for $C_{15}H_{13}N$: 207.1048. Found:207.1041.



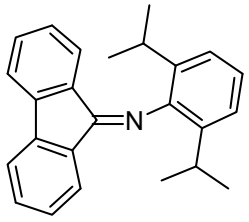
2f

IV. General Procedure for the Palladium-Catalyzed Cyclocoupling of 2-Halobiaryls.

To a flame-dried 10 mL two-necked flask, 2-halobiaryl (0.25 mmol), isocyanide (0.3 mmol), $Pd(OAc)_2$ (0.0125 mmol), PPh_3 (0.025 mmol), CsOPiv (0.3 mmol), and DMF (2 mL) were added under a gentle stream of nitrogen. The mixture was stirred at 100°C for 5 h under N_2 atmosphere. The reaction mixture was then cooled to room temperature, diluted with diethyl ether and washed with brine. The organic layer was dried ($MgSO_4$). After removing the volatiles in vacuo, the residue was subjected to column chromatography on silica gel to afford the desired product.

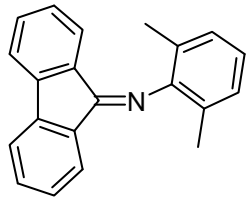
V. Spectroscopic Data of Products

***N*-(9*H*-Fluoren-9-ylidene)-2,6-diisopropylaniline (3aa).** Yellow solid. Mp = 101-102°C. *Rf* = 0.43 (hexane/EtOAc = 4/1). ^{1}H NMR ($CDCl_3$) δ: 0.94 (d, *J* = 7.0 Hz, 6H), 1.17 (d, *J* = 6.5 Hz, 6H), 2.82-2.92 (m, 2H), 6.41 (d, *J* = 7.6 Hz, 1H), 6.89 (td, *J* = 7.8 Hz, 0.8 Hz, 1H), 7.18-7.50 (m, 6H), 7.58 (t, *J* = 8.4 Hz, 2H), 8.03 (d, *J* = 7.3 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ: 23.2, 23.3, 28.4, 119.5, 120.0, 123.1, 123.2, 123.9, 126.4, 127.8, 128.3, 131.57, 131.64, 135.2, 137.2, 141.8, 143.0, 147.0, 162.9. IR (KBr): 3060 m, 2962 s, 2868 m, 2360 w, 1651 s, 1606 m, 1450 s, 1382 m, 1361 m, 1328 m, 1306 s, 1253 m, 1190 m, 1144 m, 1103 m, 1059 w, 1043 w, 941 m, 908 m, 795 m, 771 m, 734 s, 656 m, 434 w. MS, *m/z* (relative intensity, %): 340 (M^+, 28), 339 (M^+-1, 100), 325 (14), 324 (54), 310 (20), 309 (70), 294 (24), 282 (27), 281 (26), 280 (40), 279 (12), 278 (21), 267 (16), 175 (13), 174 (89), 165 (46), 161 (25), 147 (13), 146 (46), 139 (11), 132 (50), 117 (11), 115 (10), 77 (10). Exact Mass Calcd for $C_{25}H_{25}N$: 339.1987. Found: 339.1991.



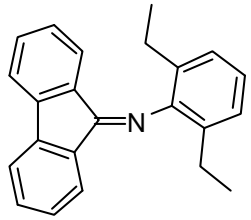
3aa

***N*-(9*H*-Fluoren-9-ylidene)-2,6-dimethylaniline (3ab).** (CAS [75838-45-8]) ^{1}H NMR ($CDCl_3$) δ: 2.05 (s, 6H), 6.47 (d, *J* = 7.8 Hz, 1H), 6.91-7.13 (m, 4H), 7.31-7.51 (m, 3H), 7.60 (t, *J* = 6.8 Hz, 2H), 8.05 (d, *J* = 7.3 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ: 18.0, 119.7, 120.1, 123.4, 123.6, 125.2, 125.6, 128.2, 128.4, 128.5, 131.88, 131.91 131.97, 132.04, 137.1, 141.9, 143.1, 163.2. Exact Mass Calcd for $C_{21}H_{17}N$: 283.1361. Found: 283.1355.



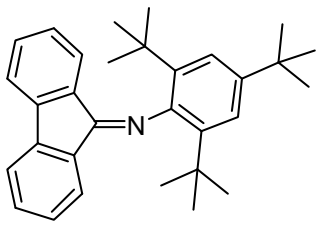
3ab

2,6-Diethyl-*N*-(9*H*-fluoren-9-ylidene)aniline (3ac). Yellow oil. *Rf* = 0.6 (hexane/EtOAc = 4/1). ^{1}H NMR ($CDCl_3$) δ: 1.06 (t, *J* = 7.6 Hz, 6H), 2.29-2.52 (m, 4H), 6.45 (d, *J* = 7.8 Hz, 1H), 6.92 (t, *J* = 7.6 Hz, 1H), 7.10-7.18 (m, 3H), 7.29-7.41 (m, 2H), 7,48 (t, *J* = 7.3 Hz, 1H), 7.60 (t, *J* = 7.8 Hz, 2H), 8.03 (d, *J* = 7.0 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ: 13.7, 24.6, 119.6, 120.0, 123.2, 123.7, 126.0, 126.2, 128.2, 128.4, 130.7, 131.7, 131.8, 131.9, 137.3, 141.9, 143.1, 148.2, 162.9. IR (neat): 3060 w, 2966 m, 2931 m, 2871 m, 2360 w, 2341 w, 1718 w, 1650 s, 1606 m, 1591 m, 1450 s, 1373 w, 1306 m, 1261 w, 1192 w, 1144 w, 1103 m, 943 m, 873 w, 843 w, 795 m, 773 m, 758 m, 735 s, 656 m. MS, *m*/*z* (relative intensity, %): 312 (M^+, 26), 311 (M^+-1, 100), 310 (43), 296 (27), 295 (12), 282 (18), 281 (13), 280 (24), 278 (15), 268 (18), 267 (55), 266 (16), 165 (18), 146 (81), 133 (13), 118 (31). Exact Mass Calcd for $C_{23}H_{21}N$: 311.1674. Found: 311.1678.



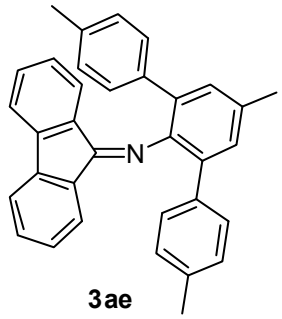
3ac

2,4,6-Tri-tert-butyl-*N*-(9*H*-fluoren-9-ylidene)aniline (3ad). Yellow solid. Mp = 173 °C. *Rf* = 0.54 (hexane/EtOAc = 4/1). ^{1}H NMR ($CDCl_3$) δ: 1.20 (s, 18H), 1.41 (s, 9H), 5.63 (d, *J* = 6.8 Hz, 1H), 6.80-6.82 (m, 1H), 7.24-7.57 (m, 7H), 8.04 (d, *J* = 6.2 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ: 31.1, 31.9, 34.8, 36.1, 119.6, 119.8, 121.89, 121.93, 123.37, 123.43, 123.5, 126.8, 127.7, 128.3, 131.0, 131.4, 136.4, 144.6, 148.3, 150.6, 163.3. IR (KBr): 2964 s, 2904 m, 2868 m, 2360 m, 2339 m, 1639 m, 1599 m, 1477 m, 1448 m, 1421 m, 1392 m, 1362 m, 1306 w, 1263 w, 1217 m, 1196 w, 1149 w, 1117 w, 1103 w, 943 w, 908 w, 891 w, 877 w, 794 m. 735 s, 669 m, 644w. MS, *m*/*z* (relative intensity, %): 424(M^+, 15), 423 (M^+-1, 45), 409 (32), 408 (100), 230 (27), 165 (11), 57 (31). Exact Mass Calcd for $C_{31}H_{37}N$: 423.2926. Found: 423.2929.



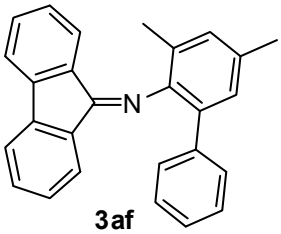
3ad

***N*-(9*H*-Fluoren-9-ylidene)-4-methyl-2,6-di(4-tolyl)aniline (3ae).** Yellow solid. Mp = 211°C. *Rf* = 0.46 (hexane/EtOAc = 4/1). ^{1}H NMR ($CDCl_3$) δ: 2.08 (s, 6H), 2.39 (s, 3H), 6.63 (d, *J* = 7.6 Hz, 1H), 6.82-6.89 (m, 5H), 7.11-7.27 (m, 11H), 7.66 (d, *J* = 6.8 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ: 20.98, 21.00, 119.2, 119.7, 122.9, 126.0, 127.9, 128.0, 128.3, 129.1, 130.4, 131.0, 131.1, 131.3, 132.3, 133.5, 135.9, 137.0, 137.2, 141.6, 142.9, 144.6, 163.5. IR (KBr): 3043 w, 3019 m, 2916 m, 2859 w, 2359 w, 1651 s, 1601 m, 1512 m, 1448 m, 1304 m, 1207 w, 1182 w, 1138 w, 1101 m, 1038 w, 1020 w, 941 m, 872 w, 839 w, 822 m, 806 m, 791 m, 748 m, 723 s, 654 m, 553 m, 517 m. MS, *m*/*z* (relative intensity, %): 450 (M^+, 35), 449 (M^+-1, 100), 448 (46), 434 (42), 284 (49), 165 (28). Exact Mass Calcd for $C_{34}H_{27}N$: 449.2143. Found: 449.2141.



3ae

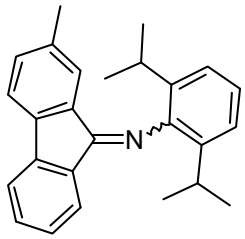
***N*-(9*H*-Fluoren-9-ylidene)-3,5-dimethylbiphenyl-2-amine (3af).** Yellow oil. *Rf* = 0.57 (hexane/EtOAc = 4/1). ^{1}H NMR ($CDCl_3$) δ: 2.05 (s, 3H), 2.42 (s, 3H), 6.64 (d , *J* = 7.6 Hz, 1H), 6.97 (td, *J* = 7.6 Hz, 0.5 Hz, 1H), 7.04-7.52 (m, 12H), 7.88 (br, 1H). ^{13}C NMR ($CDCl_3$) δ: 18.2, 20.9, 119.4, 119.9, 123.1, 125.5, 125.8, 126.3, 127.6, 128.2, 128.3, 129.0, 129.2, 130.3, 130.6, 131.5, 131.6, 132.2, 133.1, 137.2, 140.0, 141.7, 143.1, 145.4, 163.4. IR (neat): 3057 w, 2968 w, 2860 w, 2360 s, 2341 m, 1716 m, 1653 m, 1604 m, 1469 m, 1450 m, 1306 m, 1194 w, 1142 w, 1111 w, 1034 w, 984 w, 943 w, 917 w, 862 w, 795 w, 781 w, 734 s, 700 m, 669 w, 654 w. MS, *m*/*z* (relative intensity, %): 359 (M^+-1, 100), 58 (89), 165 (52). Exact Mass Calcd for $C_{27}H_{21}N$: 359.1674. Found: 359.1670



3af

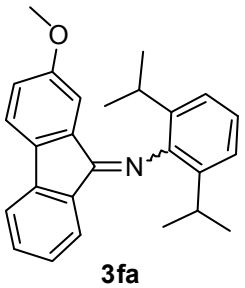
2,6-Diisopropyl-N-(2-methyl-9H-fluoren-9-ylidene)aniline (3ea). The title compound was obtained as a mixture of geometric isomers with respect to a C=N bond in a ratio of 64:36. Yellow oil. *Rf* = 0.60 (hexane/EtOAc = 4/1). ^{1}H NMR ($CDCl_3$) δ: 0.94 (d, *J* = 6.8 Hz, 6H), 1.17 (d, 7.0 Hz, 6H), 2.04 (s, 1.1H, minor), 2.46 (s, 1.9H, major), 2.82-2.92 (m, 2H), 6.18 (s, 0.3H, minor), 6.37 (d, *J* = 7.8 Hz, 0.6 H, major),

6.86 (t, J = 7.3 Hz, 0.6H, major), 7.10-7.58 (m, 7.4H), 7.85 (s, 0.6H, major), 8.00 (d, J = 7.0 Hz, 0.3H, minor). ^{13}C NMR ($CDCl_3$) δ: 21.4, 21.5, 23.1, 23.3, 28.3, 119.3, 119.5, 119.8, 123.1, 123.16, 123.22, 123.3, 123.8, 123.9, 126.5, 127.35, 127.43, 127.9, 131.6, 131.7, 131.9, 132.1, 132.27, 132.28, 132.34, 135.38, 135.41, 137.5, 137.7, 138.5, 139.4, 140.6, 142.2, 143.4, 147.2. 163.3, 163.5. IR (neat): 3060 w, 2962 s, 2927 m, 2867 m, 1718 w, 1649 s, 1603 m, 1487 m, 1458 s, 1437 m, 1383 w, 1362 w, 1327 w, 1300 m, 1176 w, 860 w, 827 w, 766 m, 739 m. MS, *m*/*z* (relative intensity, %): 354 (M^+, 29), 353 (M^+-1, 100), 338 (54), 323 (72), 296 (23), 295 (21), 294 (34), 179 (31), 174 (87), 161 (22), 146 (33), 132 (44). Exact Mass Calcd for $C_{26}H_{27}N$:353.2143. Found: 353.2137.



3ea

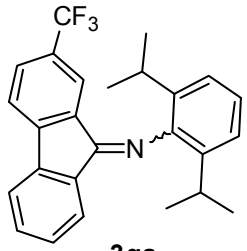
2,6-Diisopropyl-*N*-(2-methoxy-9*H*-fluoren-9-ylidene)aniline (3fa). The title compound was obtained as a mixture of geometric isomers with respect to a C=N bond in a ratio of 56:44. Yellow oil. *Rf* = 0.54 (hexane/EtOAc = 4/1). ^{1}H NMR ($CDCl_3$) δ: 0.93-0.98 (m, 6H), 1.18 (d, J = 7.0 Hz, 6H), 2.78-2.93 (m, 2H), 3.40 (s, 1.0H, minor), 3.93 (s, 1.3H, major), 5.93 (d, J = 2.1 Hz, 0.4H, minor), 6.35 (d, J = 8.1 Hz, 0.6H, major), 6.44-8.29 (m, 9H). ^{13}C NMR ($CDCl_3$) δ: 23.1, 23.3, 28.3, 55.0, 55.8, 107.7, 111.4, 118.2, 118.3, 118.9, 119.3, 119.8, 120.2, 120.7, 120.8, 123.1, 123.3, 123.4, 123.5, 124.1, 124.3, 126.5, 126.67, 126.72, 127.2, 129.1, 131.8, 131.9, 132.1, 133.2, 134.8, 135.2, 135.4, 135.9, 137.2, 142.3, 143.5, 159.4, 160.6. IR (neat): 3060 m, 2962 s, 2931 m, 2868 m, 2359 w, 1649 s, 1603 m, 1489 m, 1460 s, 1435 s, 1383 m, 1363 m, 1329 m, 1302 s, 1277 m, 1257 m, 1171 m, 1128 m, 1041 m, 972 w, 937 w, 862 m, 831 m, 768 m, 739 s. MS, *m*/*z* (relative intensity, %): 370 (M^+, 28), 369 (M^+-1, 100), 354 (49), 339 (68), 312 (21), 310 (21), 195 (20), 174 (81), 161 (21), 152 (12), 146 (28), 132 (40). Exact Mass Calcd for $C_{26}H_{27}NO$: 369.2093. Found: 369.2086.



3fa

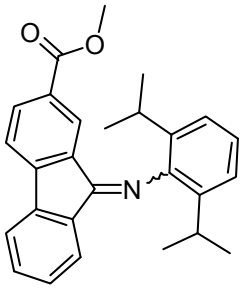
2,6-Diisopropyl-N-(2-(trifluoromethyl)-9H-fluoren-9-ylidene)aniline (3ga). The title compound

was obtained as a mixture of geometric isomers with respect to a C=N bond in a ratio of 67:33. Yellow solid. Mp = 145-146 °C. *Rf* = 0.43 (hexane/EtOAc = 4/1). ^{1}H NMR ($CDCl_3$) δ: 0.82-0.86 (m, 6H), 1.08-1.10 (m, 6H), 2.70-2.80 (m, 2H), 6.37 (d, *J* = 7.6 Hz, 0.6H, major), 6.47 (s, 0.3H, minor), 6.91(t, *J* = 7.6 Hz, 0.6H, major), 7.13-7.15 (m, 3H), 7.24-7.31 (m, 1H), 7.24-7.51 (m, 1H), 7.56-7.69 (m, 2H), 8.04 (d, *J* = 7.0 Hz, 0.3H, minor), 8.22 (s, 0.6H, major). ^{13}C NMR ($CDCl_3$) δ: 23.1, 23.2, 28.4, 119.9, 120.16, 120.22, 120.4, 120.8, 121.1, 122.2, 122.3, 123.1, 123.4, 123.5, 124.4, 124.7, 125.8, 126.2, 126.7, 128.3, 128.4, 128.57, 128.64, 128.70, 128.74, 120.1, 129.6, 130.1, 130.3, 130.8, 131.8, 132.06, 132.11, 132.7, 135.1, 135.2, 135.6, 137.6, 137.7, 140.6, 141.7, 145.0, 146.2, 146.5, 146.7, 161.9, 161.8. IR (KBr): 3064 w, 2964 m, 2929 w, 2870 w, 1738 w, 1651 m, 1620 m, 1462 m, 1434 m, 1361 m, 1329 s, 1271 m, 1169 m, 1128 s, 1057 m, 916 w, 841 w, 768 w, 739 m. MS, *m*/*z* (relative intensity, %): 398 (M^+, 28), 407 (M^+-1, 100), 393 (17), 392 (55), 378 (18), 377 (60), 362 (28),350 (35), 349 (23), 348 (39), 346 (12), 335 (20), 233 (36), 175 (14), 174 (98), 161 (27), 146 (49), 144 (11), 132 (43), 118 (12), 117 (18), 115 (12), 91 (12). Exact Mass Calcd for $C_{26}H_{24}F_3N$: 407.1861. Found: 407.1859.



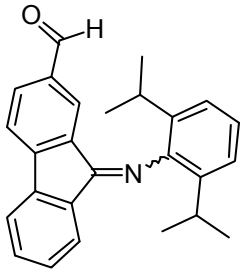
3ga

Methyl 9-(2,6-diisopropylphenylimino)-9*H*-fluorene-2-carboxylate (3ha). The title compound was obtained as a mixture of geometric isomers with respect to a C=N bond in a ratio of 71:29. Yellow solid. Mp = 145-146°C. *Rf* = 0.46 (hexane/EtOAc = 4/1). ^{1}H NMR ($CDCl_3$) δ: 0.93 (d, *J* = 7.0 Hz, 6H), 1.17 (d, *J* = 6.8 Hz, 6H), 2.80-2.90 (m, 2H), 3.77 (s, 1H, minor), 3.98 (s, 2H, major), 6.45 (d, *J* = 7.6 Hz, 0.7H, major), 6.96-7.72 (m, 7.3H), 8.02-8.09 (m, 0.6H, minor), 8.23 (d, *J* = 7.8 Hz, 0.7H, major), 8.68 (s, 0.7H, major). ^{13}C NMR ($CDCl_3$) δ: 23.07, 23.14, 23.2, 28.4, 52.0, 52.2, 119.5, 119.8, 120.5, 120.9, 123.3, 123.4, 123.9, 124.2, 124.3, 124.4, 126.6, 127.8, 129.0, 129.5, 129.6, 130.2, 131.6, 131.9, 132.0, 132.4, 133.3, 133.4, 135.2, 135.3, 137.3, 138.0, 140.8, 142.0, 146.0, 146.8, 147.1, 149.8, 162,2, 162.3, 166.1, 166.7. IR (KBr): 2960 m, 2925 m, 2866 w, 2362 w, 1712 s, 1664 m, 1618 m, 1462 2, 1435 m, 1292 m, 1265 s, 1219 m, 1147 w, 1117 w, 1095 w, 945 w, 854 w, 795 w, 752 m, 656 w. MS, *m*/*z* (relative intensity, %): 398 (M^+, 30), 397 (M^+-1, 100), 382 (52), 368 (19), 367 (64), 338 (23), 174 (96), 161 (27), 146 (43), 132 (35). Exact Mass Calcd for $C_{27}H_{27}NO_2$: 397.2042. Found: 397.2037.



3ha

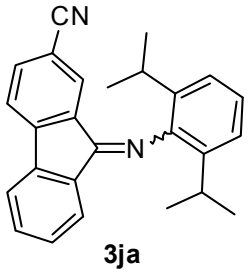
9-(2,6-Diisopropylphenylimino)-9*H*-fluorene-2-carbaldehyde (3ia). The title compound was obtained as a mixture of geometric isomers with respect to a C=N bond in a ratio of 65:35. Yellow solid. Mp =145-146°C. *Rf* = 0.34 (hexane/EtOAc = 4/1). ^{1}H NMR ($CDCl_3$) δ: 0.91-0.96 (m, 6H), 1.18 (d, *J* = 6.8 Hz, 6H), 2.78-2.88 (m, 2H), 6.48 (d, *J* = 7.8 Hz, 0.6H, major), 6.75 (s, 0.3H, minor), 7.03 (t, *J* = 7.6 Hz, 0.6H, major), 7.22-8.12 (m, 7.6H), 8,53 (s, 0.6H, major), 9.57 (s, 0.3H, minor), 10.12 (s, 0.6H, major). ^{13}C NMR ($CDCl_3$) δ: 23.16, 23.20, 28.5, 120.0, 120.5, 120.7, 121.2, 123.3, 123.4, 124.2, 124.6, 124.7, 126.5, 128.5, 129.4, 129.9, 131.9, 132.0, 132.4, 132.5, 132.9, 135.0, 135.1, 135.8, 136.6, 137.8, 138.1, 140.5, 141.6, 146.5, 146.6, 147.2, 148.5, 161.7, 161.8, 190.6, 191.2. IR (KBr): 3402 m, 2960 s, 2927 m, 2868 m, 2360 m, 1701 s, 1647 m, 1612 s, 1462 m, 1435 m, 1358 m, 1171 m, 1107 m, 980 w, 910 w, 837 m, 768 m, 741 s. MS, *m/z* (relative intensity, %): 368 (M^+, 28), 367 (M^+-1, 100), 352 (57), 337 (64), 322 (20), 308 (23), 280 (21), 174 (93), 161 (24), 146 (45), 132 (36). Exact Mass Calcd for $C_{26}H_{25}NO$: 367.1936. Found: 367.1943.



3ia

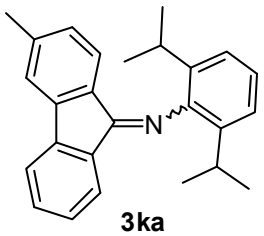
9-(2,6-Diisopropylphenylimino)-9*H*-fluorene-2-carbonitrile (3ja). The title compound was obtained as a mixture of geometric isomers with respect to a C=N bond in a ratio of 66:34. Yellow oil. *Rf* = 0.46 (hexane/EtOAc = 4/1). ^{1}H NMR ($CDCl_3$) δ: 0.94 (d, *J* = 6.8 Hz, 6H), 1.17 (d, *J* = 6.8 Hz, 6H), 2.73-2.83 (m, 2H), 6.47 (d, *J* = 7.3 Hz, 0.7H, major), 6.56 (s, 0.3H, minor), 7.04 (t, *J* = 7.6 Hz, 0.7H, major), 7.22-7.81 (m, 7.3H), 8.10 (d, *J* = 7.3 Hz, 0.3H, minor), 8.30 (s, 0.7H, major). ^{13}C NMR ($CDCl_3$) δ: 23.1, 23.2, 28.5, 28.7, 111.1, 111.7, 118.8, 120.2, 120.7(2C), 120.7, 121.1, 123.2, 123.4, 123.56, 123.6, 124.4, 125.0, 126.6, 126.7, 129.4, 129.6, 130.1, 130.2, 131.9, 132.2, 134. 9 , 134.9, 135.7, 137,4, 137.7, 141.2, 145.6, 146.0, 146.4, 146.8, 161.0, 161.2. IR (neat): 3062 w, 2962 s, 2927 m, 2867 m, 2359 m, 2339 m, 2227 m, 1649 m, 1612 m, 1456 m, 1435 m, 1383 m, 1362 m, 1327 w, 1257 w, 1159 w, 1113 m, 935 w, 910 w, 841 m, 791 m,

768 m, 739 m, 507 w. MS, *m*/*z* (relative intensity, %): 365 (M^+, 28), 364 (M^+-1, 94), 349 (66), 334 (59), 319 (29), 307 (41), 306 (22), 305 (41), 292 (21), 174 (100), 161 (28), 146 (50), 132 (43). Exact Mass Calcd for $C_{26}H_{24}N_2$: 364.1939. Found: 364.1942.

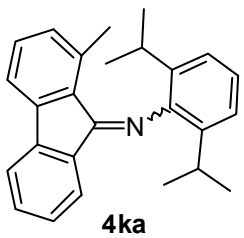


3ja

2,6-Diisopropyl-*N*-(3-methyl-9H-fluoren-9-ylidene)aniline (3ka). The cyclocoupling of **1k** under the standard conditions afforded a mixture of **3ka** and **4ka** in 88% yield in a ratio of 17:1. The major product **3ka** was obtained as a mixture of geometric isomers with respect to a C=N bond in a ratio of 59:41. Yellow solid. Mp=145-146°C. *Rf* = 0.6 (hexane/EtOAc = 4/1). ^{1}H NMR ($CDCl_3$) δ: 0.94 (d, *J* = 6.8 Hz, 6H), 1.16 (d, *J* = 6.8 Hz, 6H), 2.33 (s, 1.8H, major), 2.48 (s, 1.2H, minor), 2.82-2.92 (m, 2H), 6.27 (d, *J* = 7.8 Hz, 0.6H, major), 6.37 (d, *J* = 7.8 Hz, 0.4H, minor), 6.71 (d, *J* = 7.6 Hz, 0.6H, major), 6.89 (t. *J* = 7.3 Hz, 0.4H, minor), 7.19-7.61 (m, 7H), 7.92 (d, *J* = 7.6 Hz, 0.4H, minor), 8.02 (d, *J* = 7.0 Hz, 0.6H, major). ^{13}C NMR ($CDCl_3$) δ: 20.6, 20.8, 23.0, 23.2, 28.3, 120.1, 120.8, 122.1, 123.0, 123.1, 123.2, 123.3, 123.8, 124.1, 124.3, 126.4, 127.2, 127.6, 127.7, 128.0, 131.6, 131.7, 131.9, 132.0, 132.08, 132.14, 132.9, 133.3, 134.3, 134.4, 135.2, 137.7, 139.7, 141.1, 142.8, 144.2, 147.2, 162.9, 163.0. IR (KBr): 3059 w, 2960 s, 2924 m, 2866 m, 2360 m, 2341 m, 1707 w, 1643 m, 1610 m, 1452 m, 1432 m, 1381 w, 1360 w, 1327 m, 1304 m, 1257 m, 1190 w, 1113 m, 939 m, 831 m, 800 m, 766 m, 739 s, 656 m, 542 w. MS, *m*/*z* (relative intensity, %): 354 (M^+, 30), 353 (M^+-1, 100), 338 (50), 324 (21), 323 (71), 296 (20), 295 (22), 294 (33), 179 (33), 178 (21), 174 (88), (33), 132 (54). Exact Mass Calcd for $C_{26}H_{27}N$: 353.2143. Found: 353.2146.



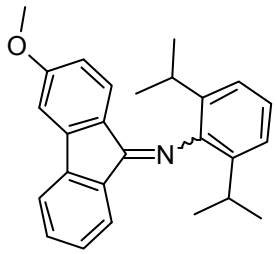
3ka



4ka

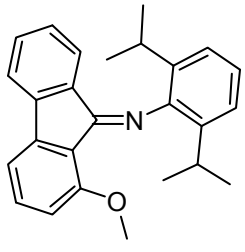
2,6-Diisopropyl-*N*-(3-methoxy-9*H*-fluoren-9-ylidene)aniline (3la). Compound **3la** was obtained by the cyclocoupling of **1n** as a mixture of geometric isomers with respect to a C=N bond in a ratio of 67:33. Yellow oil. *Rf* = 0.45 (hexane/EtOAc = 4/1). ^{1}H NMR ($CDCl_3$) δ: 0.91-0.95 (m, 6H), 1.16 (d, *J* = 6.8 Hz, 6H), 2.82-2.92 (m, 2H), 3.81 (s, 2H, major), 3.92 (s, 1H, minor), 6.23-6.41 (m, 1.7H), 6.87-6.92 (m. 0.7H,

major), 7.07-7.59 (m, 6.6H), 7.99 (br, 1H). ^{13}C NMR ($CDCl_3$) δ: 23.05, 23.09, 23.27, 23.33, 28.3, 55.4, 55.7, 105.7, 106.2, 112.4, 113.4, 119.5, 119.9, 122.3, 123.0, 123.2, 123.9, 124.02, 124.05, 124.3, 124.57, 124.64, 124.9, 126.4, 128.1, 128.4, 128.5, 128.6, 128.7, 131.4, 131.5, 132.7, 135.7, 138.3, 141.4, 142.5, 143.9, 145.5, 147.2, 162.3, 162.6. IR (neat): 3060 w, 2960 s, 2868 m, 2360 s, 2341 s, 1651 m, 1612 s, 1491 m, 1458 m, 1360 m, 1311 m, 1236 m, 1217 m, 1174 w, 1111 w, 1032 m, 941 w, 870 w, 766 m, 739 m, 658 m. MS, *m*/*z* (relative intensity, %): 370 (M^+, 28), 369 (M^+-1, 100), 354 (35), 340 (20), 339 (74), 195 (43), 174 (90), 146 (21), 132 (66). Exact Mass Calcd for $C_{26}H_{27}NO$: 369.2093. Found: 369.2086.



3la

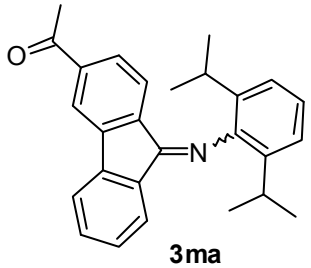
2,6-Diisopropyl-*N*-(1-methoxy-9*H*-fluoren-9-ylidene)aniline (4la). The cyclocoupling of **1l** under the standard conditions afforded a mixture of **3la** and **4la** in 97% yield in a ratio of 2.1:1. Compound **4la** was obtained by the purification using GPC. Yellow oil. *Rf* = 0.39 (hexane/EtOAc = 4/1). ^{1}H NMR ($CDCl_3$) δ: 0.91 (d, *J* = 6.6 Hz, 6H), 1.19 (d, *J* = 6.8 Hz, 6H), 2.86-2.96 (m, 2H), 4.03 (s, 3H), 6.32 (d, *J* = 7.6 Hz, 1H), 6.86-7.30 (m, 7H), 7.45 (t, *J* = 7.8 Hz, 1H), 7.57 (d, *J* = 7.3 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ: 23.0, 23.5, 28.3, 56.2, 108.1, 112.2, 112.7, 119.9, 123.3, 123.6, 123.7, 126.6, 128.0, 131.1, 132.0, 133.1, 134.9, 136.3, 143.2, 144.3, 158.7. IR (neat): 2960 m, 2868 w, 2360 s, 2339 s, 1641 m, 1593 s, 1489 m, 1456 m, 1435 m, 1382 w, 1302 w, 1265 m, 1186 w, 1126 m, 1018 w, 937 w, 802 w, 758 m, 669 w. MS, *m*/*z* (relative intensity, %): 370 (M^+, 18), 369 (M^+-1, 62), 354 (20), 340 (10), 339 (36), 326 (22), 312 (11), 311 (10), 310 (11), 296 (11), 280 (11), 195 (18), 176 (25), 175 (13), 174 (100), 146 (18), 132 (30). Exact Mass Calcd for $C_{26}H_{27}NO$: 369.2093. Found:369.2097.



4la

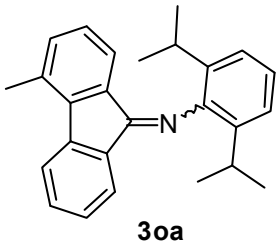
1-(9-(2,6-Diisopropylphenylimino)-9*H*-fluoren-3-yl)ethanone (3ma). The title compound was obtained as a mixture of geometric isomers with respect to a C=N bond in a ratio of 53:47. Yellow solid. Mp = 144-145 °C. *Rf* = 0.44 (hexane/EtOAc = 4/1). ^{1}H NMR ($CDCl_3$) δ: 0.92-0.96 (m, 6H), 1.17 (d, *J*=

6.8 Hz, 6H), 2.59 (s, 1.4H, minor), 2.71 (s, 1.6H, major), 2.78-2.88 (m, 2H), 6.42-6.48 (m, 1H), 6.94-7.00 (m. 0.5H), 7.22-7.26 (m, 3H), 7.35-7.58 (m, 2H), 7.68-7.74 (m, 1H), 7.99-8.01 (m, 0.5H), 8.08-8.23 (m, 2H). ^{13}C NMR ($CDCl_3$) δ: 23.00, 23.02, 23.1, 23.2, 26.8, 27.0, 28.39, 28.41, 119.1, 119.3, 120.2, 120.6, 123.3, 123.4, 123.5, 124.4, 126.3, 126.6, 128.56, 128.61, 128.61, 129.07, 131.8, 132.2, 132.3, 135.0, 135.2, 135.27, 135.29, 137.2, 139.4, 139.9, 141.0, 141.1, 142.28, 142.33, 143.7, 146.6, 162.48, 162.50, 197.4, 197.7 IR (KBr): 3060 w, 2962 m, 2925 m, 2866 m, 2362 w, 1684 s, 1660 s, 1587 m, 1466 m, 1446 m, 1417 s, 1382 w, 1358 m, 1296 m, 1277 m, 1238 m, 1196 m, 1144 w, 1113 w, 939m, 904 w, 849 m, 791 w, 661 m, 615 w. MS, *m*/*z* (relative intensity, %): 382 (M^+, 30), 381 (M^+-1, 100), 366 (48), 351 (60), 322 (20), 174 (83), 161 (23), 146 (38), 132 (34). Exact Mass Calcd for C_{27}H27NO: 381.2093. Found: 381.2092.



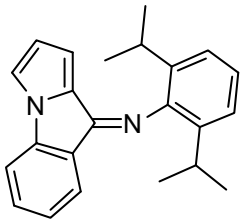
3ma

2,6-Diisopropyl-*N*-(4-methyl-9*H*-fluoren-9-ylidene)aniline (3oa). The title compound was obtained as a mixture of geometric isomers with respect to a C=N bond in a ratio of 55:45. Yellow solid. Mp =167-168 °C. *Rf* = 0.60 (hexane/EtOAc = 4/1). ^{1}H NMR ($CDCl_3$) δ: 0.94 (d, *J* = 6.8 Hz, 6H), 1.16 (d, *J* = 6.6 Hz, 6H), 2.62 (s, 1.5H, minor), 2.65 (s, 1.5 H, major), 2.81-2.91 (m, 2H), 6.34 (d, *J* = 7.6 Hz, 0.5H, minor), 6.48 (d, *J* = 7.6 Hz, 0.5H. major), 6.78-6.93 (m, 1H), 7.07-7.52 (m, 6H), 7.74 (t, *J* = 7.6 Hz, 1H), 7.94 (br, 0.5H, major), 8.08 (d, *J*= 7.0 Hz, 0.5H, minor). ^{13}C NMR ($CDCl_3$) δ: 20.6, 20.8, 22.6, 23.0, 23.2, 23.6, 28.3, 28.5, 120.1, 120.8, 122.1, 123.0, 123.1, 123.2, 123.3, 123.8, 124.1, 124.3, 125.7, 126.4, 127.2, 127.6, 127.7, 128.0, 131.7, 131.9, 132.0, 132.1, 132.9, 133.3, 134.3, 134.4, 135.2, 135.6, 137.7, 139.7, 141.1, 142.8, 144.2, 147.1, 163.00, 163.04. IR (KBr): 3074 w, 2958 m, 2866 w, 2360 w, 2341 w, 1712 w, 1647 m, 1587 w, 1452 m, 1431 m, 1381 w, 1360 w, 1329 w, 1306 w, 1113 w, 1095 w, 960 w, 800 m, 768 w, 752 m, 733 s, 663 w. MS, *m*/*z* (relative intensity, %): 354 (M^+, 28), 353 (M^+-1, 100), 339 (21), 338 (74), 323 (49), 294 (28), 179 (37), 174 (91), 161 (20), 146 (30), 132 (49). Exact Mass Calcd for $C_{26}H_{27}N$: 353.2143. Found: 353.2152.



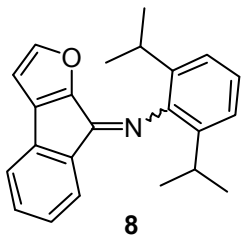
3oa

2,6-Diisopropyl-*N*-(9*H*-pyrrolo[1,2-a]indol-9-ylidene)aniline (6). Yellow solid. Mp =158 °C. *Rf* = 0.40 (hexane/EtOAc = 4/1). ^{1}H NMR ($CDCl_3$) δ: 0.99 (d, *J* = 7.0 Hz, 6H), 1.16 (d, *J* = 6.6 Hz, 6H), 2.84-2.94 (m, 2H), 5.24 (d, *J* = 2.8 Hz, 1H), 6.05 (t, *J* = 2.8 Hz, 1H), 6.95 (s, 1H), 7.14-7.25 (m, 5H), 7.45 (t, *J* = 7.6 Hz, 1H), 7.97 (br, 1H). ^{13}C NMR ($CDCl_3$) δ: 23.47, 23.53, 28.2, 110.0, 112.4, 114.7, 115.3, 123.3, 123.5, 123.7, 124.2, 124.7, 129.2, 131.7, 136.56, 136.62, 142.3, 154.4. IR (KBr): 3086 w, 2958 m, 2866 m, 2360 m, 1635 s, 1616 m, 1525 w, 1479 s, 1396 m, 1381 w, 1311 m, 1238 m, 1178 m, 1078 m, 1020 w, 930 w, 800 w, 752 s, 723 m. MS, *m*/*z* (relative intensity, %): 329 (M^+, 24), 328 (M^+-1, 100), 327 (21), 313 (46), 298 (39), 285 (20), 270 (20), 174 (31), 154 (56), 132 (39), Exact Mass Calcd for $C_{23}H_{24}N_2$: 328.1939. Found: 328.1932.



6

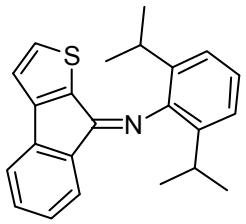
***N*-(8*H*-indeno[2,1-b]furan-8-ylidene)-2,6-diisopropylaniline (8).** The title compound was obtained as a mixture of geometric isomers with respect to a C=N bond in a ratio of 84:16. Yellow oil. *Rf* = 0.49 (hexane/EtOAc = 4/1). ^{1}H NMR ($CDCl_3$) δ: 0.98 (d, *J* = 7.0 Hz, 6H), 1.17 (d, *J* = 6.6 Hz, 6H), 2.84-2.96 (m. 2H), 6.13 (d, *J* = 7.3 Hz, 0.2H, minor), 6.47 (d, *J* = 1.6 Hz, 0.8H, major), 6.59 (s, 0.2H, minor), 6.73 (br, 0.2H, minor), 7.10-7.37 (m, 6.6H), 7.59 (s, 0.2H, minor), 7.82 (d, *J* = 7.0 Hz, 0.8H, major). ^{13}C NMR ($CDCl_3$) δ: 23.1, 23.2, 23.3, 23.4, 28.1, 28.2, 105.8, 106.2, 119.7, 119.8, 122.8, 123.1, 123.5, 124.0, 124.3, 126.5, 126.7, 127.1, 131.06, 131.15, 132.7, 135.0, 135.6, 135.7, 136.9, 137.6, 137.9, 139.7, 146.0, 146.9, 149.8, 150.4, 152.4, 152.5, 152.7, 156.1. IR (neat): 3060 w, 2962 s, 28868 m, 1657 s, 1612 s, 1589 m, 1485 m, 1458 m, 1419 m, 1383 w, 1362 w, 1327w, 1255 m, 1159 m, 1111 m, 1159 m, 970 m, 920 m, 893 m, 798 m, 750 s, 592 w. MS, *m*/*z* (relative intensity, %): 330 (M^+, 10), 329 (M^+-1, 37), 328 (10), 315 (25), 314 (100), 312 (10), 296 (23), 286 (12), 271 (14), 270 (15), 254 (12), 174 (14), 127 (12), 115 (11). Exact Mass Calcd for $C_{23}H_{23}NO$: 329.1780. Found: 329.1776.



8

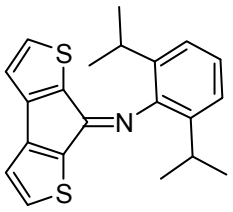
***N*-(8*H*-indeno[2,1-b]thiophen-8-ylidene)-2,6-diisopropylaniline (10).** Yellow solid. Mp = 140-141 °C. *Rf* = 0.6 (hexane/EtOAc = 4/1). ^{1}H NMR ($CDCl_3$) δ: 1.00 (d, *J* = 6.8 Hz, 6H), 1.15 (d, *J* = 7.0

Hz, 6H), 2.79-2.89 (m, 2H), 7.06 (d, *J* = 5.1 Hz, 1H), 7.21-7.39 (m, 7H), 7.95 (d, *J* = 7.3 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ: 23.1, 23.4, 28.4, 118.7, 119.3, 123.0, 123.7, 124.6, 126.8, 131.2, 132.0, 135.94, 135.96, 136.3, 136.3, 139.1, 140.0, 153.1. IR (KBr): 3051 w, 2958 m, 2864 m, 1637 s, 1606 m, 1483 m, 1454 m, 1415 m, 1381 w, 1323 w, 1294 w, 1255 w, 1144 m, 1101 w, 895 m, 796 m, 762 m, 735 s. MS, *m*/*z* (relative intensity, %): 346(M^+, 19), 345 (M^+-1, 72), 331 (24), 330 (100), 315 (32), 312 (29), 296 (36), 285 (28), 174 (35), 171 (25), 132 (26). Exact Mass Calcd for $C_{26}H_{19}N$: 345.1551. Found: 345.1574.



10

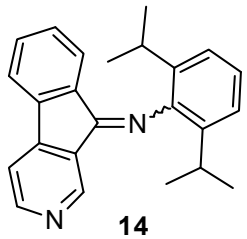
***N*-(7*H*-Cyclopenta[1,2-b;4,3-b']dithiophen-7-ylidene)-2,6-diisopropylaniline (12).** Yellow solid. Mp = 136-137°C. *Rf* = 0.51 (hexane/EtOAc = 4/1). ^{1}H NMR ($CDCl_3$) δ: 1.04 (d , *J* = 6.8 Hz, 6H), 1.16 (d, *J* = 6.8 H, 6H), 2.83-2.93 (m, 2H), 6.84 (d, *J* = 4.6 Hz, 1H), 7.00 (d, *J* = 4.6 Hz, 1H), 7.12-7.26 (m, 4H), 7.45 (d, *J* = 4.6 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ: 23.2, 23.4, 28.4, 118.3, 119.2, 123.8, 124.8, 130.8, 132.1, 134.1, 136.2, 138.9, 147.2, 147.8, 148.0, 156.2. IR (KBr): 3087 w, 2958 s, 2866 m, 1633 s, 1587 w, 1504 m, 1462 m, 1415 m, 1381 w, 1325 w, 1252 m, 1165 m, 1088 m, 937 w, 843 s, 789 m, 746 s, 677 m. MS, *m*/*z* (relative intensity, %): 352 (M^+, 15), 351 (M^+-1, 55), 337 (25), 336 (100), 321 (27), 292 (32), 174 (20). Exact Mass Calcd for $C_{21}H_{21}NS_2$: 351.1115. Found: 351.1122.



12

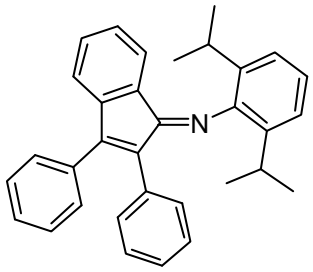
***N*-(9*H*-indeno[2,1-c]pyridin-9-ylidene)-2,6-diisopropylaniline (14).** The title compound was obtained as a mixture of geometric isomers with respect to a C=N bond in a ratio of 50:50. Yellow oil. *Rf* = 0.51 (hexane/EtOAc = 1/1).^{1}H NMR ($CDCl_3$) δ: 0.92-0.96 (m, 6H), 1.16-1.19 (m, 6H), 2.77-2.87 (m, 2H), 6.48 (d, *J* = 7.6 H, 0.5H), 7.09 (t, *J* = 7.6 H, 0.5H), 7.22-7.24 (m, 3H), 7.41 (t, *J* = 8.1 H, 0.5H), 7.54-7.76 (m, 2.5H), 7.73-7.76 (m, 1 H), 8.11-8.14 (m, 0.5H), 7.56 (d, *J* = 4.9 H, 0.5H), 8.77 (d, *J* = 5.4 H, 0.5H) 9.24 (s, 0.5 H). ^{13}C NMR ($CDCl_3$) δ:23.0, 23.05, 23.14, 27.2, 28.36, 28.37, 114.6, 115.1, 121.2, 121.7, 123.4, 123.5. 123.6, 124.4, 124.8, 126.7, 126.8, 130.4, 130.8, 131.7, 132.0, 132.1, 135.08, 135.12, 137.3, 139.5, 140.5, 144.4, 146.7, 146.8, 147.1, 149.3, 150.2, 152.4, 152.5, 161.8, 162.2. IR (neat): 3062 m, 2962 s, 2929 s,

2868 s, 1651 s, 1597 s, 1568 s, 1452 s, 1433 s, 1383 m, 1362 m, 1315 m, 1255 m, 1182 m, 1161 m, 1105 w, 1092 m, 1059 w, 1041 w, 937 s, 908 m, 839 m, 798 m, 774 m, 742 s, 646 w, 623 m, 571 w, 455 w, 434 m. MS, *m*/*z* (relative intensity, %): 341 (M^+, 24), 340 (M^+-1, 100), 326 (16), 325 (60), 311 (16), 310 (61), 295 (29), 283 (36), 282 (22), 281 (32), 280 (10), 279 (13), 268 (15), 181 (11), 180 (29), 174 (63), 167 (16), 166 (25), 146 (26), 132 (21), 117 (12), 115 (11), 91 (11), 77 (12). Exact Mass Calcd for $C_{24}H_{24}N_2$: 340.1939. Found: 340.1941.



14

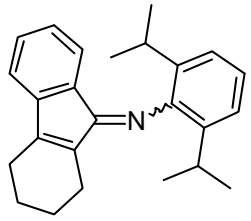
***N*-(2,3-Diphenyl-1*H*-inden-1-ylidene)-2,6-diisopropylaniline (16).** Yellow solid. Mp = 147-148 °C. *Rf* = 0.63 (hexane/EtOAc = 4/1). ^{1}H NMR ($CDCl_3$) δ: 1.02 (d, *J* = 7.0 Hz, 6H), 1.14 (d, *J* = 7.0 Hz, 6H), 2.79-290 (m, 2H), 6.34 (d, *J* = 7.3 Hz, 1H), 6.85-6.91 (m, 1H), 7.12-7.40 (m, 15H). ^{13}C NMR ($CDCl_3$) δ: 23.1, 23.2, 28.4, 120.5, 123.1, 123.8, 125.2, 127.1, 127.3, 127.6, 128.2, 128.4, 128.7, 129.2, 130.7, 131.0, 132.9, 133.6, 134.5, 136.3, 144.7, 147.7, 148.3, 166.5. IR (KBr): 3060 m, 2958 s, 2925 m, 2866 m, 2360 w, 1631 s, 1589 m, 1456 m, 1439 m, 1379 w, 1358 m, 1326 m, 1252 w, 1196 m, 1176 m, 1092 m, 1029.8 w, 787 m, 771 m, 754 m, 700 s. MS, *m*/*z* (relative intensity, %): 442 (M^+, 36), 441 (M^+-1, 100), 440 (12), 427 (27), 426 (79), 364 (18), 265 (17), 252 (10), 174 (34), 132 (11), 91 (10). Exact Mass Calcd for $C_{33}H_{31}N$: 441.2457. Found: 441.2459.



16

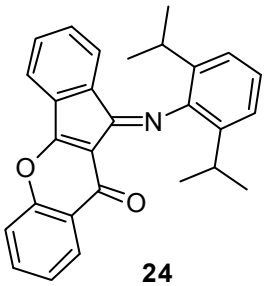
***N*-(3,4-Dihydro-1*H*-fluoren-9(2*H*)-ylidene)-2,6-diisopropylaniline (22).** The title compound was obtained as a mixture of geometric isomers with respect to a C=N bond in a ratio of ca. 5:1. Yellow oil. *Rf* = 0.63 (hexane/EtOAc = 4/1). ^{1}H NMR ($CDCl_3$) δ: 0.95 (d, *J* = 6.8 Hz, 6H), 1.09-1.17 (m, 6H), 1.88 (br, 3H), 2.47-4.57 (m, 3H), 2.79-2.85 (m, 2H), 6.09 (d, *J* = 7.3 Hz, 1H), 6.74 (t, *J* = 7.6 Hz, 1H), 6.96 (d, *J* = 7.3 Hz, 1H), 7.09-7.16 (m, 4H). ^{13}C NMR ($CDCl_3$) δ: 21.0, 21.6, 22.3, 22.40, 22.43, 22.6, 22.8, 22.9, 23.3, 23.4,

28.18, 28.25, 116.0, 117.7, 117.8, 122.5, 123.0, 123.2, 123.3, 123.4, 123.7, 124.5, 124.6, 126.3, 126.9, 129.6, 130.4, 130.5, 130.6, 130.78, 130.83, 131.1,135.4, 135.9, 143.7, 145.2, 147.3, 148.1, 155.2, 155.5, 166.8, 167.1. IR (KBr): 2962 s, 2931 m, 2870 m, 1674 m, 1643 m, 1599 w, 1460 s, 1435 m, 1257 w, 912 m, 766 m, 735 m. MS, *m*/*z* (relative intensity, %): 344 (M^+, 16), 343 (M^+-1, 55), 329 (27), 328 (100), 314 (11), 313 (11), 286 (10), 272 (10), 256 (10), 174 (27), 162 (19), 115 (12). Exact Mass Calcd for $C_{25}H_{29}N$:343.2300. Found: 343.2291.



22

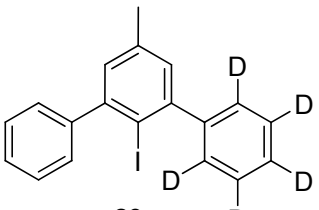
11-((2,6-Diisopropylphenyl)imino)indeno[1,2-b]chromen-10(11*H*)-one (24). Yellow solid. Mp = 165-166 °C. *Rf* = 0.29 (hexane/EtOAc = 4/1). ^{1}H NMR ($CDCl_3$) δ: 0.89 (d, *J* = 7.0 Hz, 6H), 1.19 (d, *J* = 7.0 Hz, 6H), 2.87-2.95 (m, 2H), 6.32 (d, *J* = 7.6 Hz, 1H), 7.15-7.27(m, 4H), 7,41-7.53 (m, 2H), 7.63-7.77 (m, 3H) 8.45 (d, *J* = 7.0 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ: 23.1, 23.5, 28.3, 113.4, 118.1, 120.6, 123.2, 124.2, 125.9, 126.4, 127.0, 130.0, 130.1, 131.2, 132.1, 133.4, 134.4, 135.0, 147.4, 155.5, 158.9, 171.9, 172.5. IR (KBr): 2962 m, 2927 m, 2868 w, 2237 w, 1670 s, 1620 m, 1587 w, 1552 m, 1477 s, 1462 s, 1429 s, 1327 w, 1284 w, 1203 w, 1105 w, 935 w, 910 m, 854 m, 760 s, 731 s, 712 m, 646 w. MS, *m*/*z* (relative intensity, %): 407 (M^+-1, 27), 393 (29), 392 (100), 234 (24). Exact Mass Calcd for $C_{28}H_{25}NO_2$:407.1885. Found: 407.1885.



24

VI. Experiment for Intramolecular Kinetic Isotope Effect (eq 1).

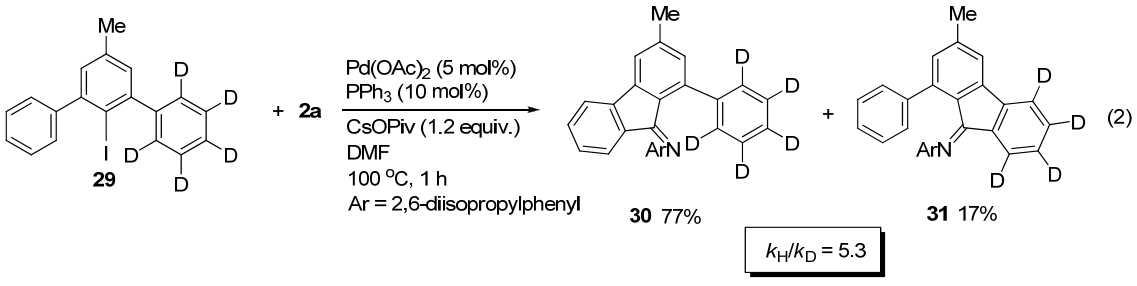
Synthesis of 4-methyl-2-pentadeuteriophenyl-6-phenyl-1-iodobenzene (29). 4-Methyl-2-pentadeuterio phenyl-6-phenylaniline (CAS 1174572-61-2, 1.30 g, 4.9 mmol)[4] was suspended in aqueous solution of HCl (6M, 50 mL). To this suspension, an aqueous solution (5 mL) of $NaNO_2$ (370 mg, 5.4 mmol) was added dropwise at 0 °C, and the mixture was stirred at 0 °C for 1 h. Then, an aqueous solution (13 mL) of KI (4.15 g, 25 mmol) was added dropwise at 0 °C, and the mixture was stirred at r.t. overnight. The mixture was extracted with Et_2O (10 mL x 3). The organic layer was washed with aqueous solution of $Na_2S_2O_5$ (10 mL x 2) and brine (10 mL x 1) and dried over $MgSO_4$. After removing the volatiles in vacuo, the residue was purified by column chromatography on silica gel (hexane:EtOAc = 20/1) to afford the title compound. White solid. Mp = 98 °C. *Rf* = 0.69 (hexane/EtOAc = 4/1). ^{1}H NMR ($CDCl_3$) δ: 2.35 (s, 3H), 7.10 (s, 2H), 7.35-7.43 (m, 5H),. ^{13}C NMR ($CDCl_3$) δ:20.7, 99.5, 127.4, 127.8, 129.4, 129.6, 137.4, 145.6, 147.7, 147.8. IR (KBr):3028 w, 2920 w, 2264 w, 1558 w, 1493 m, 1442 m, 1396 m, 1383 m, 1313 w, 1178 w, 1070 w, 1028 m, 1005 m, 866 m, 839 m, 818 w, 789 w, 760 s, 733 w, 700 s, 654 w, 607 m, 584 m, 567 m, 540 s, 478 s,424 w. MS, *m*/*z* (relative intensity, %): 249 (14), 248 (60), 246 (14), 245 (12), 244 (15), 243 (18), 234 (20), 233 (100), 232 (38), 231 (32), 230 (24), 229 (10), 188 (16), 170 (17), 169 (13), 166 (12), 165 (19), 123 (14), 122 (21), 121 (11), 117 (11), 116 (28), 114 (11), 110 (16), 109 (12), 103 (16), 96 (14), 95 (11). Exact Mass Calcd for $C_{19}H_{10}D_5I$: 375.0532. Found: 375.0533.

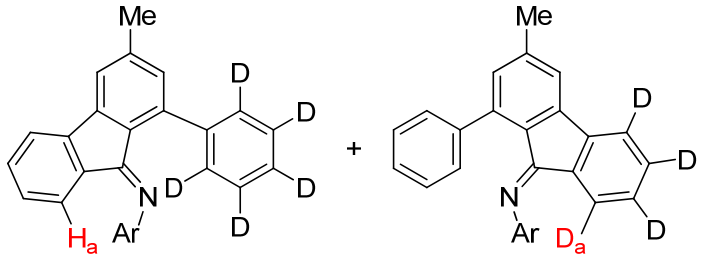


29

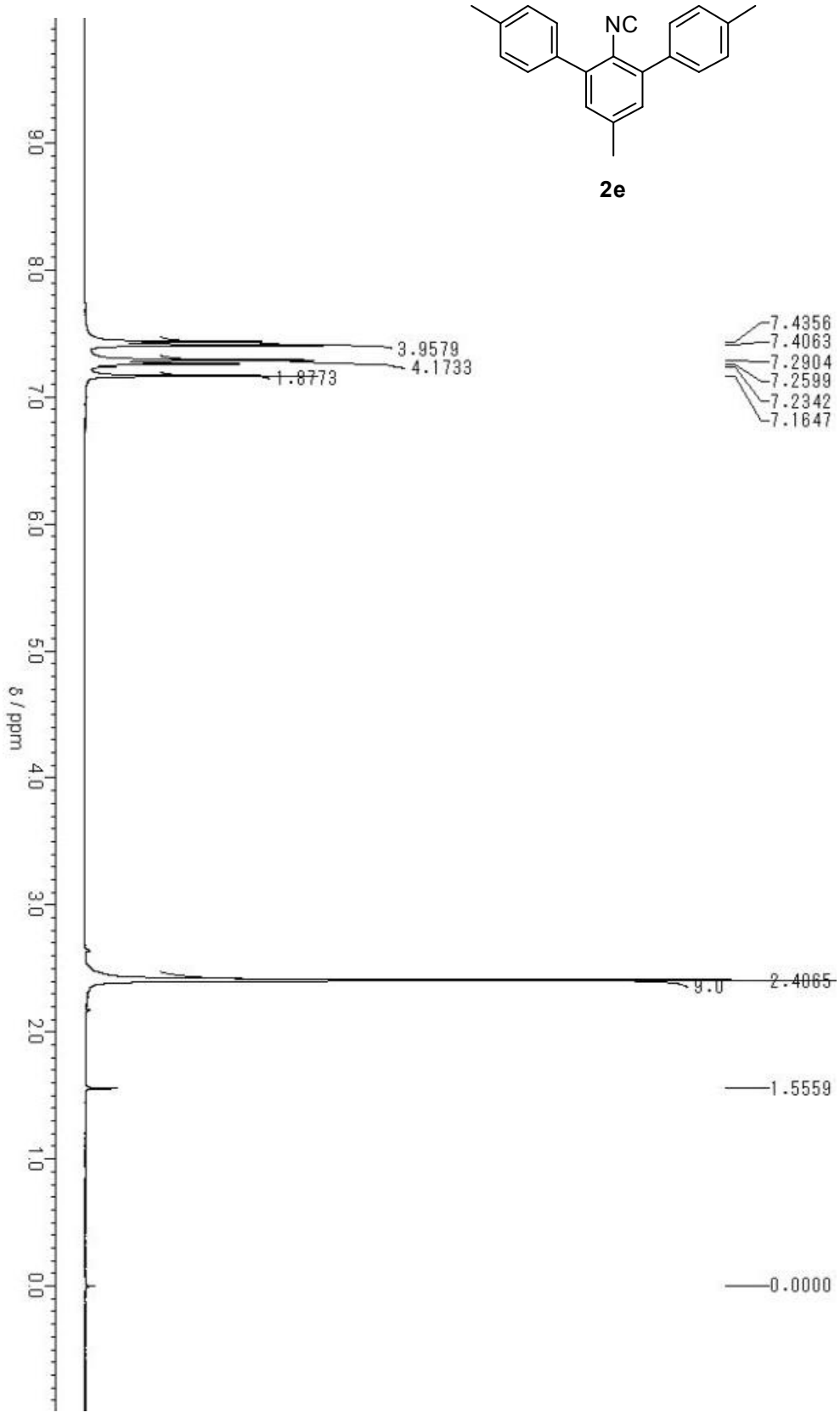
Pd-Catalyzed Cyclocoupling of 29 with 2a. The general procedure was followed using **29** as a substrate. Silica gel column chromatography (hexane:EtOAc = 20:1) of the crude reaction mixture afforded a mixture of **30** and **31** as a yellow solid (100 mg). Based on the ^{1}H-^{1}H COSY and NOESY measurements, the resonance appeared at 6.28 ppm was assigned to H_a (D_a). The ratio of **30** and **31** was determined by the integration value of H_a (D_a) appeared at 6.28 ppm (0.805H when the intergration value of the methine group was adjusted as 2.0H). Based on the ^{1}H NMR spectra of the corresponding non-deuterated compound, the relative integration value of H_a was determined to be 0.959H when the integration value of the methine groups (2.60 ppm) was adjusted as 2.0H. Thus, the deuterium content at this position was estimated to be (0.959-0.805)/0.959 = 0.160. The k_H/k_D was estimated to be (1-0.160)/0.160 = 5.3.

[4] Stokes, B. J.; Richert, K. J.; Driver, T. G. *J. Org. Chem.* **2009**, *74*, 6442.





2,6-Diisopropyl-*N*-(3-methyl-1-pentadeuteriophenyl-9*H*-fluoren-9-ylidene)aniline (30) and 2,6-diisopropyl-*N*-(1,2,3,4-tetradeuterio-6-methyl-8-phenyl-9*H*-fluoren-9-ylidene)aniline (31). Yellow solid. *Rf* = 0.66 (hexane:EtOAc = 4/1). ^{1}H NMR ($CDCl_3$) δ: 0.86 (d, *J*= 7.0 Hz, 12H), 2.40 (s, 3H), 2.55-2.63 (m, 2H), 6.29 (d, *J*= 7.8 Hz, 1H), 6.79 (d, *J*= 7.8 Hz, 1H), 6.97-7.03 (m, 4H), 7.15-7.42 (m, 3H),7.53 (d, *J*= 7.6 Hz, 1H).^{13}C NMR ($CDCl_3$) δ: 21.7, 22.3, 23.0, 28.3, 119.4, 110.6, 122.9, 123.0, 126.1, 126.9, 127.2, 127.9, 129.1, 130.4, 131.3, 132.0, 132.9, 134.2, 139.7, 141.2, 142.4, 143.0, 147.5, 161.9. IR (KBr):3057 w, 2960 s, 2866 m, 2476 w, 2266 w, 1637 s, 1610 s, 1583 s, 1460 m, 1431 s, 1398 w, 1381 w, 1360 m, 1329 w, 1292 m, 1252 m, 1184 m, 1161 m, 1111 m, 935 m, 899 w, 854 m, 795 m, 762 s, 741 s, 715 w, 698 w, 660 m, 528 s, 453w, 318 w. MS, *m*/*z* (relative intensity, %): 435 (28), 434 (90), 433 (42), 432 (58), 420 (12), 419 (36), 404 (28), 403 (12), 391 (14), 376 (12), 375 (20), 374 (18), 373 (10), 359 (11), 275 (11), 260 (38), 259 (12), 175 (16), 174 (100), 161 (10), 146 (12), 132 (37). Exact Mass Calcd for $C_{25}H_{25}N$: 433.2708, 434.2770. Found: 433.2694, 434.2767.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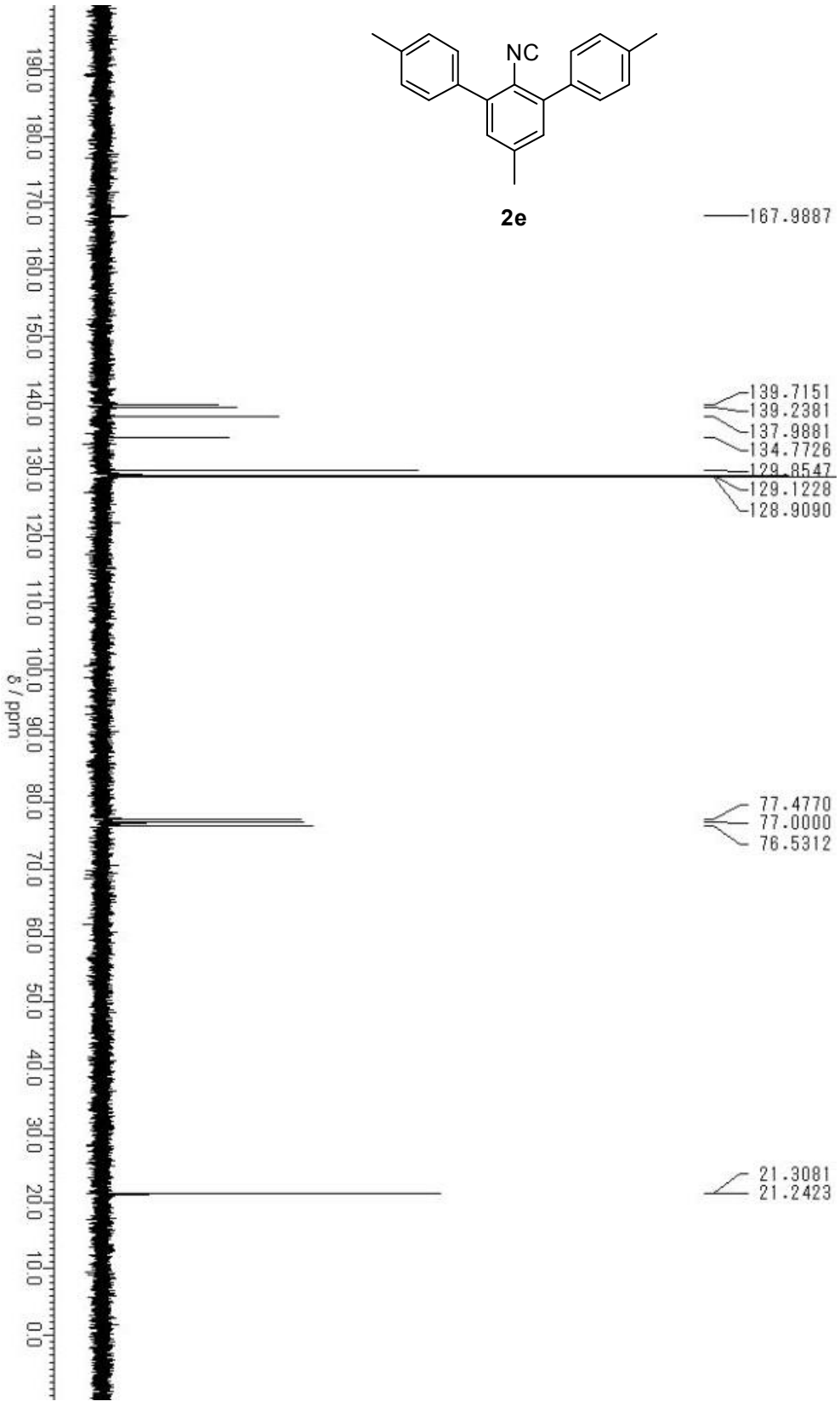
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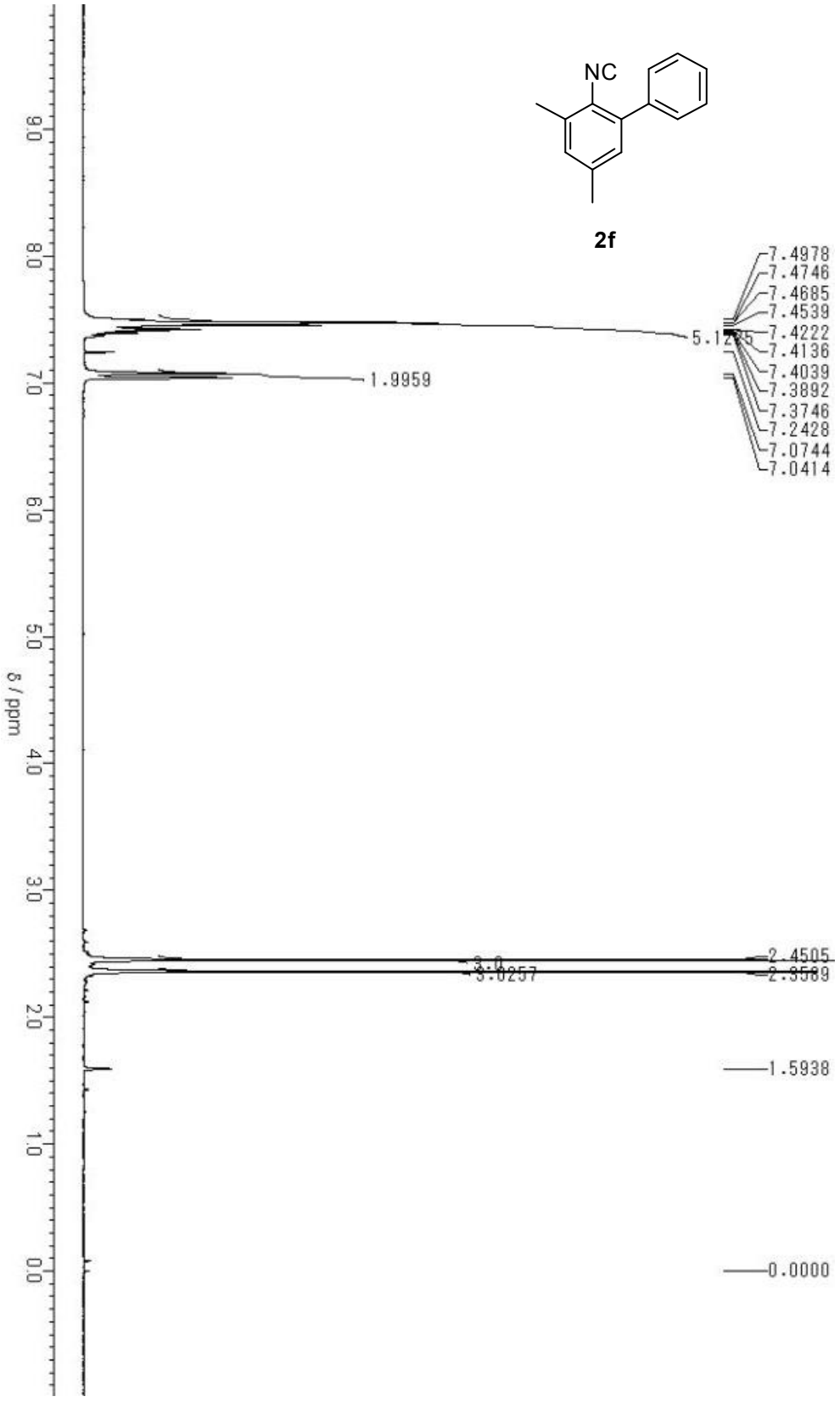
δ / ppm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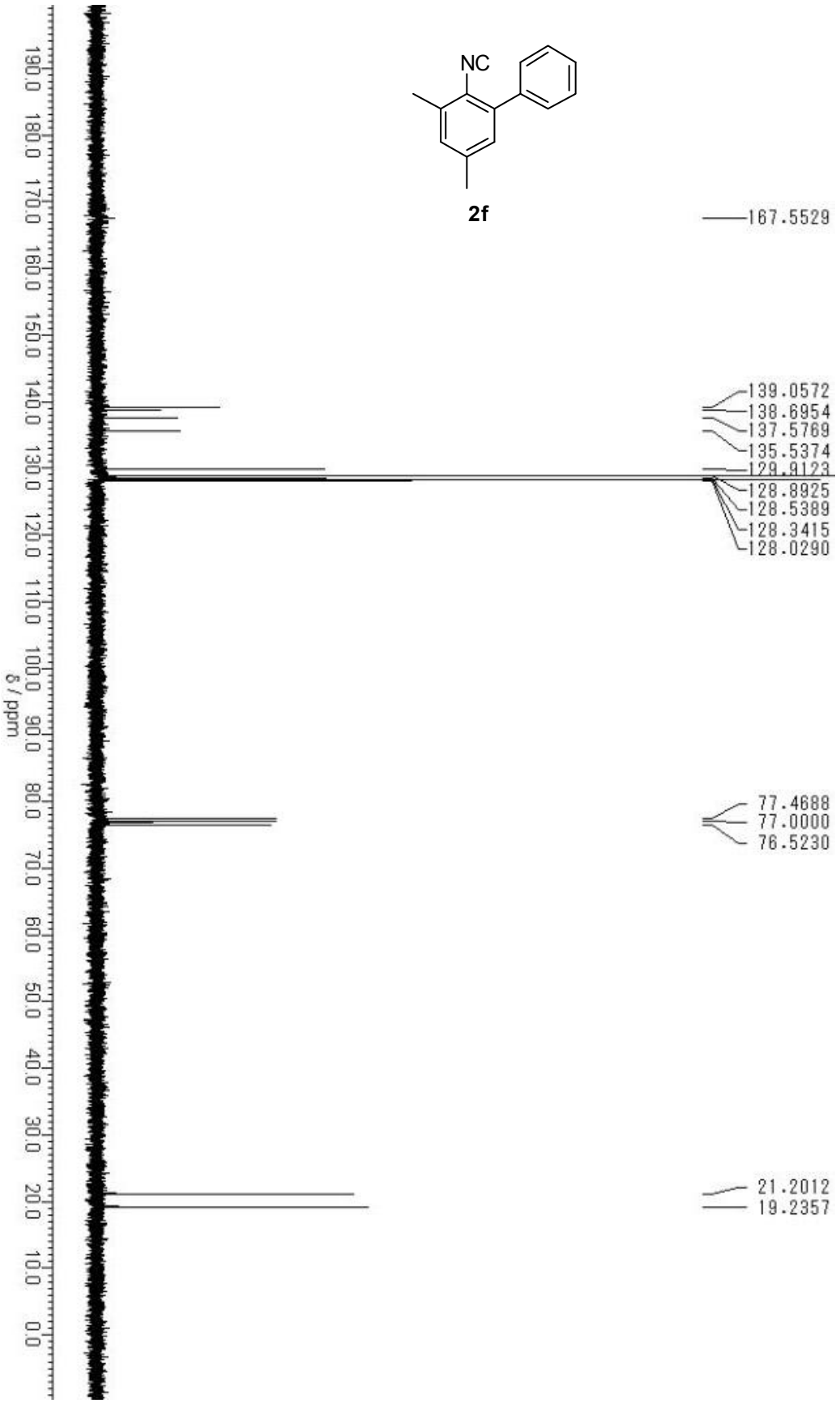
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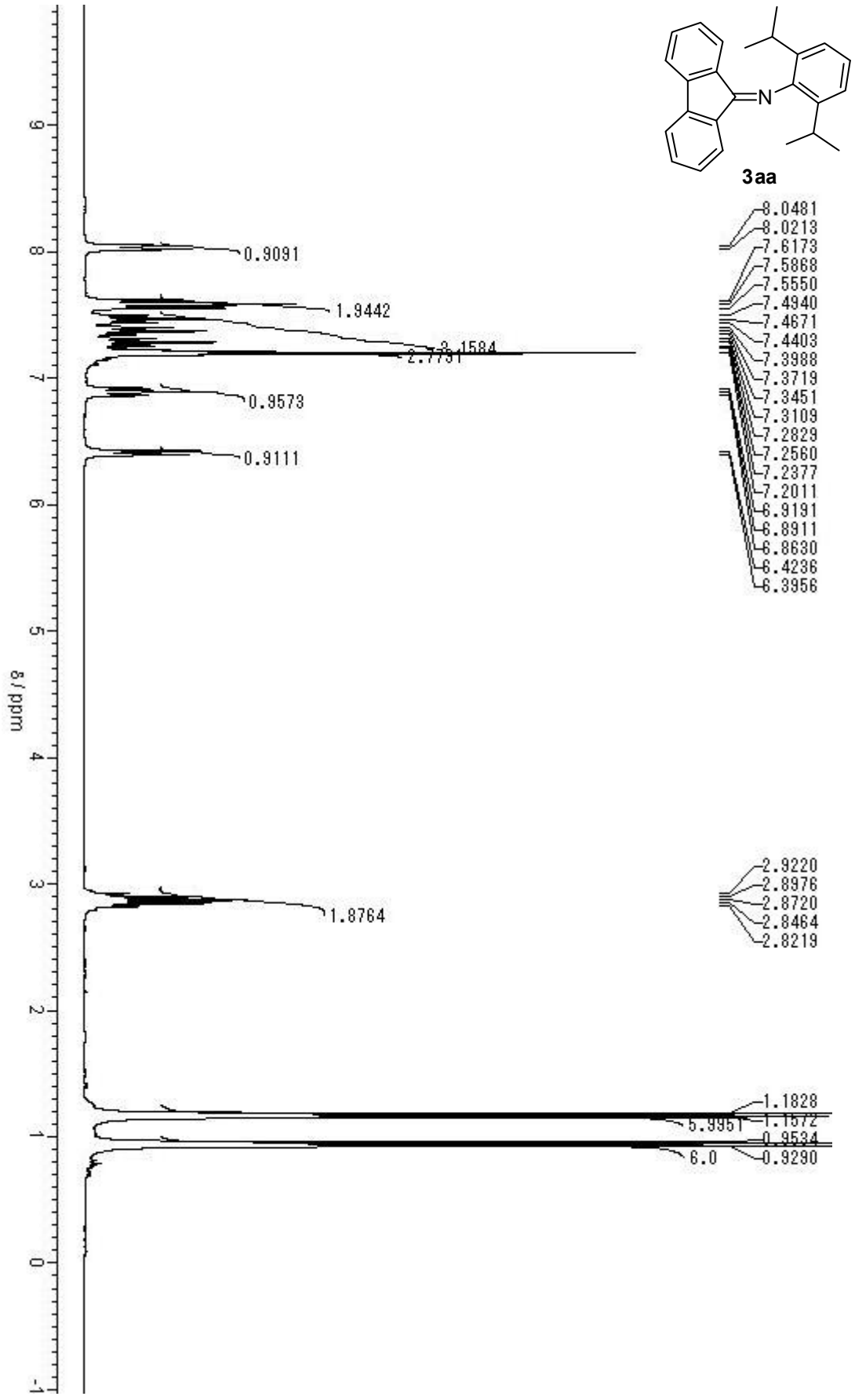
δ / ppm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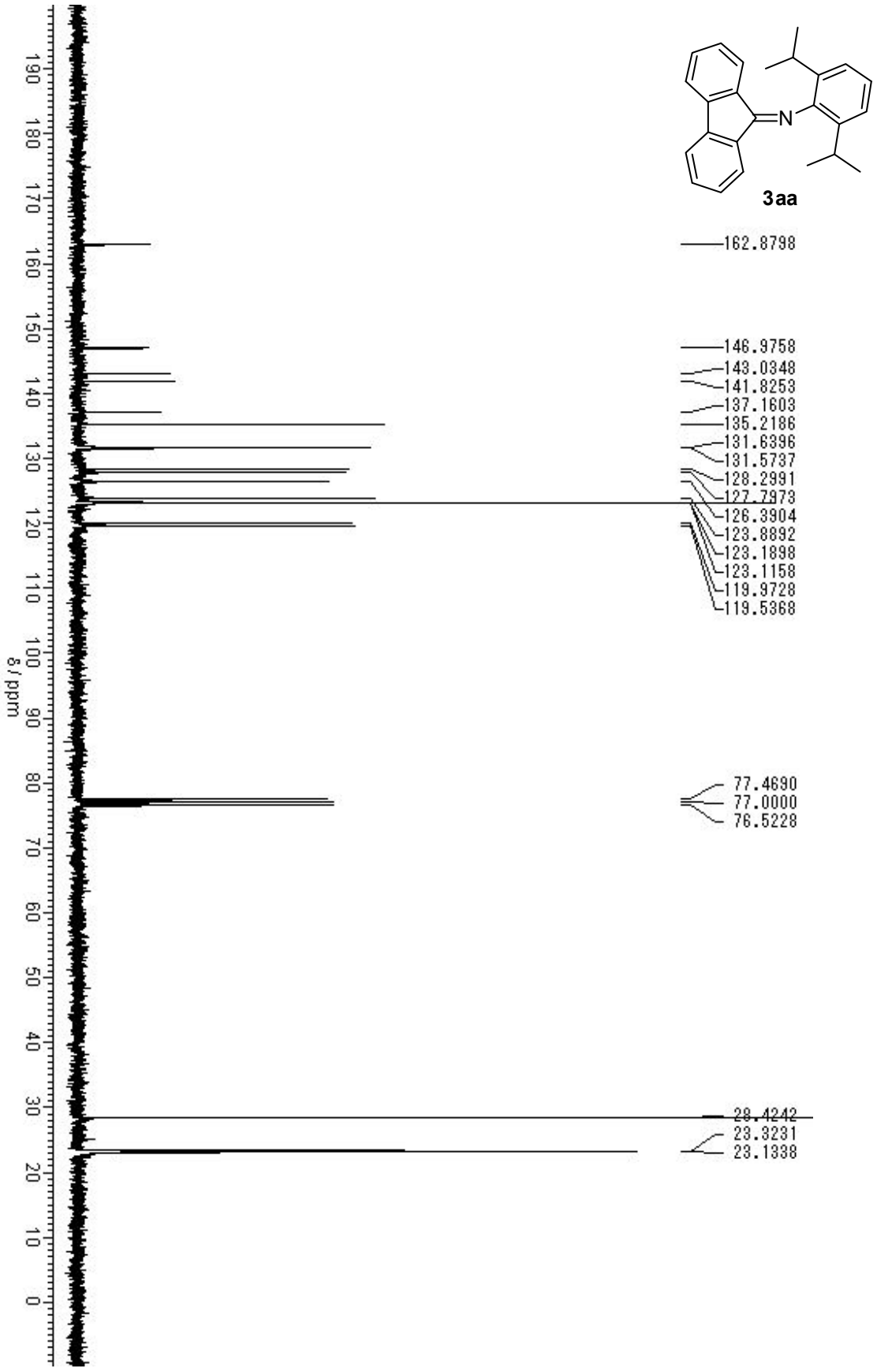
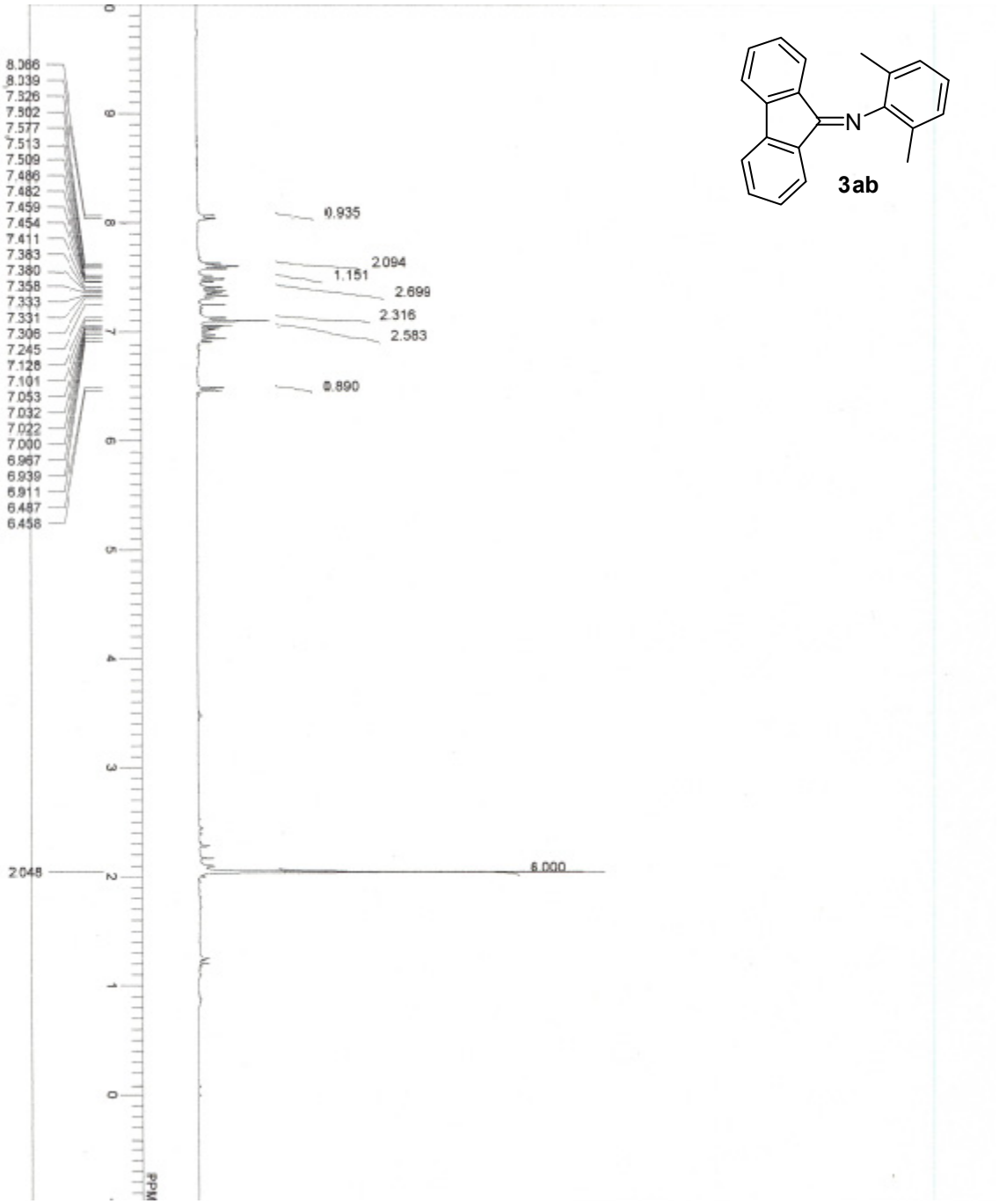
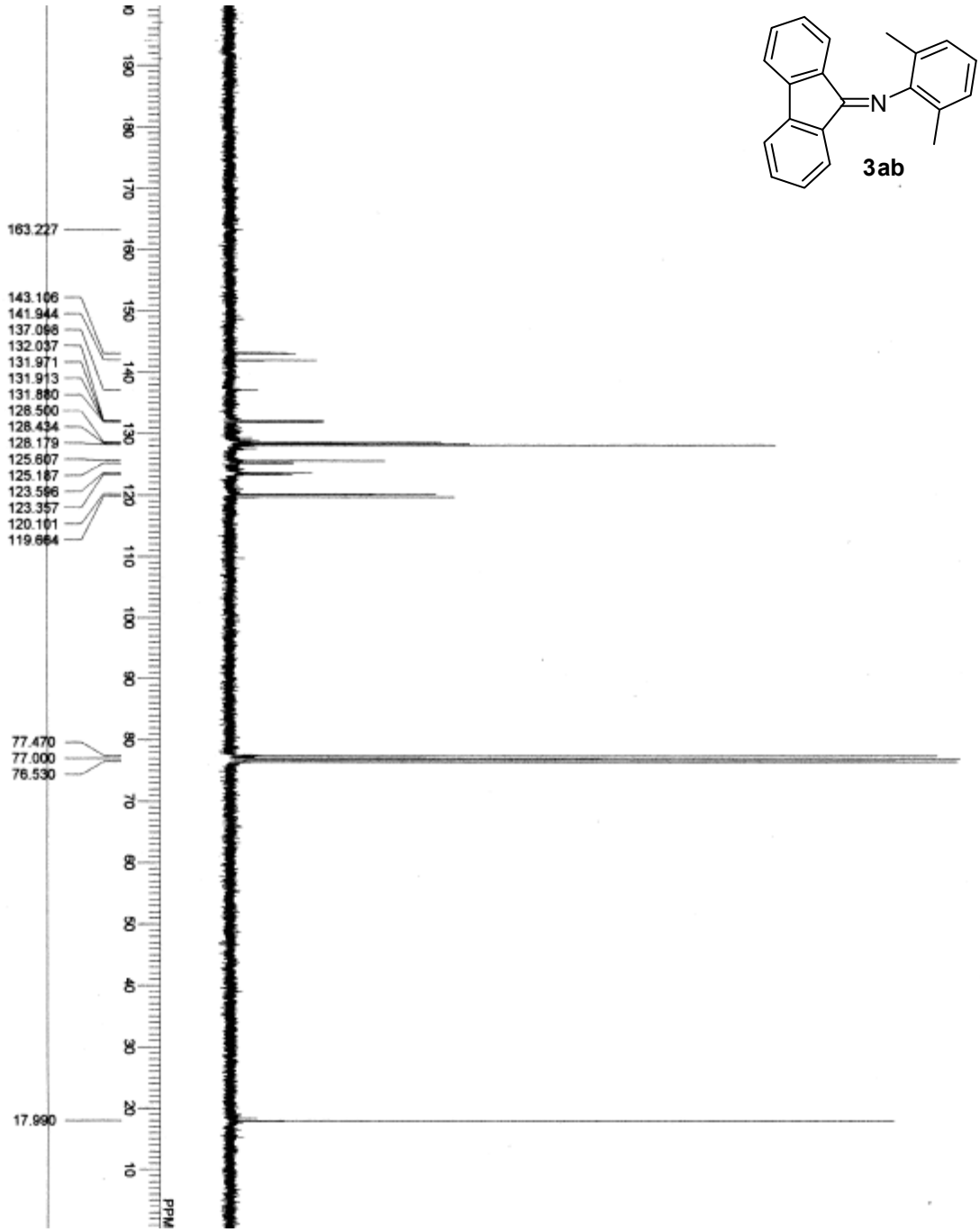
1.1828
1.1572
0.9534
0.9290
5.9951
6.0
δ / ppm


3aa
162.8798
146.9758
143.0348
141.8253
137.1603
135.2186
131.6396
131.5737
128.2991
127.7973
126.3904
123.8892
123.1898
123.1158
119.9728
119.5368
77.4690
77.0000
76.5228
28.4242
23.3231
23.1338
δ / ppm


8.066
8.039
7.826
7.802
7.577
7.513
7.509
7.486
7.482
7.459
7.454
7.411
7.383
7.380
7.358
7.333
7.331
7.306
7.245
7.128
7.101
7.053
7.032
7.022
7.000
6.967
6.939
6.911
6.487
6.458
0.935
2.094
1.151
2.699
2.316
2.583
0.890
2.048
6.000
N
3ab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141.944
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131.880
128.500
128.434
128.179
125.607
125.187
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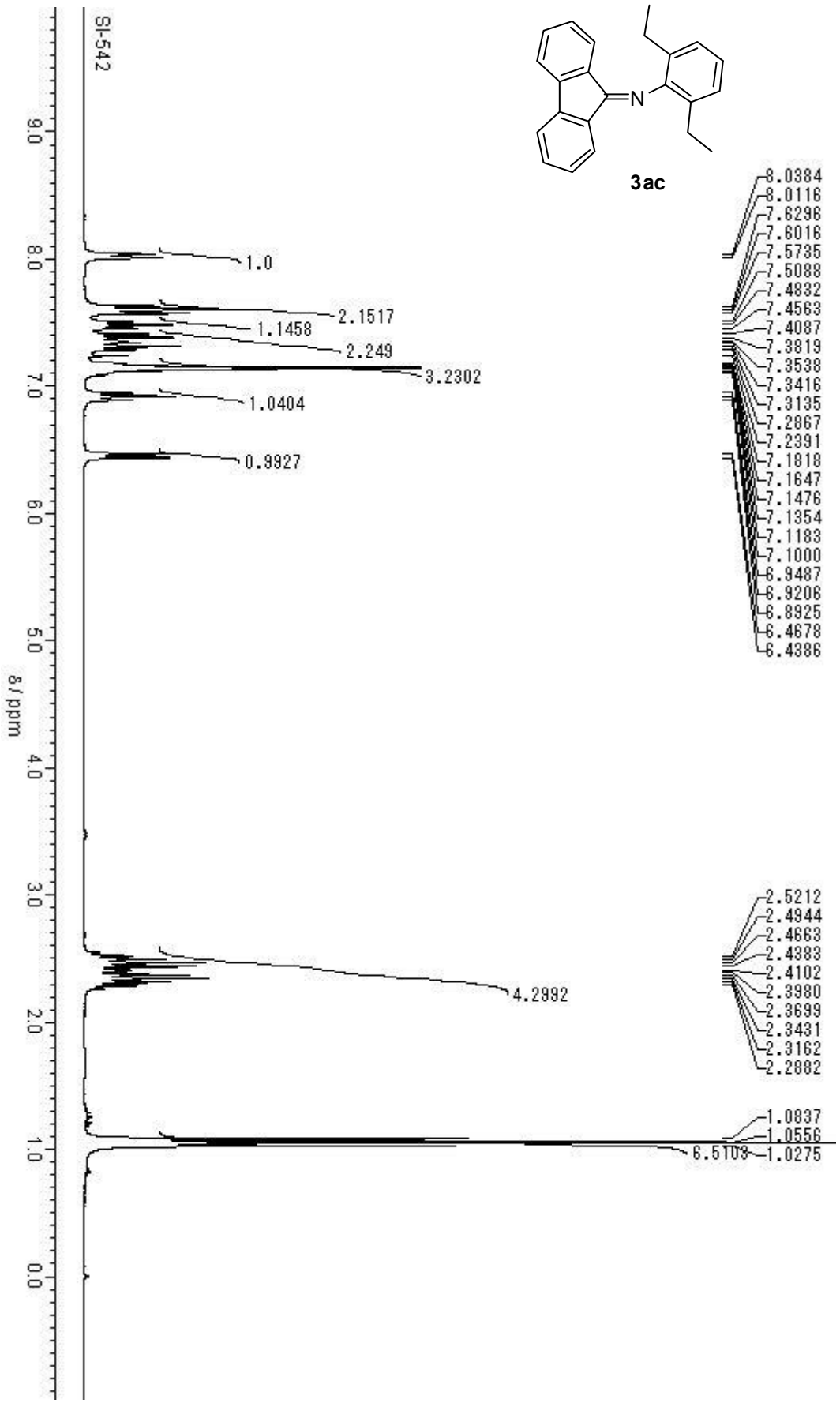
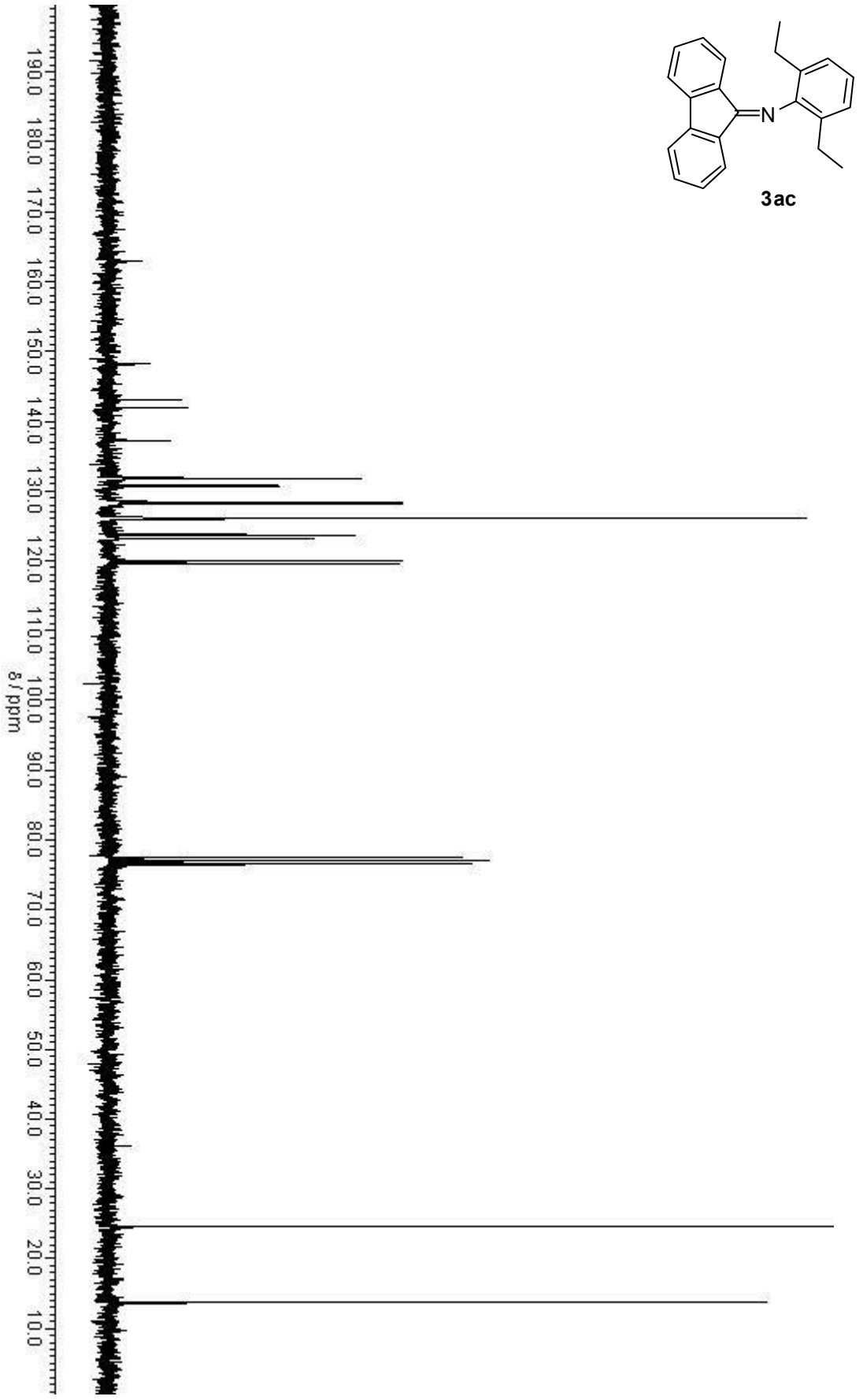
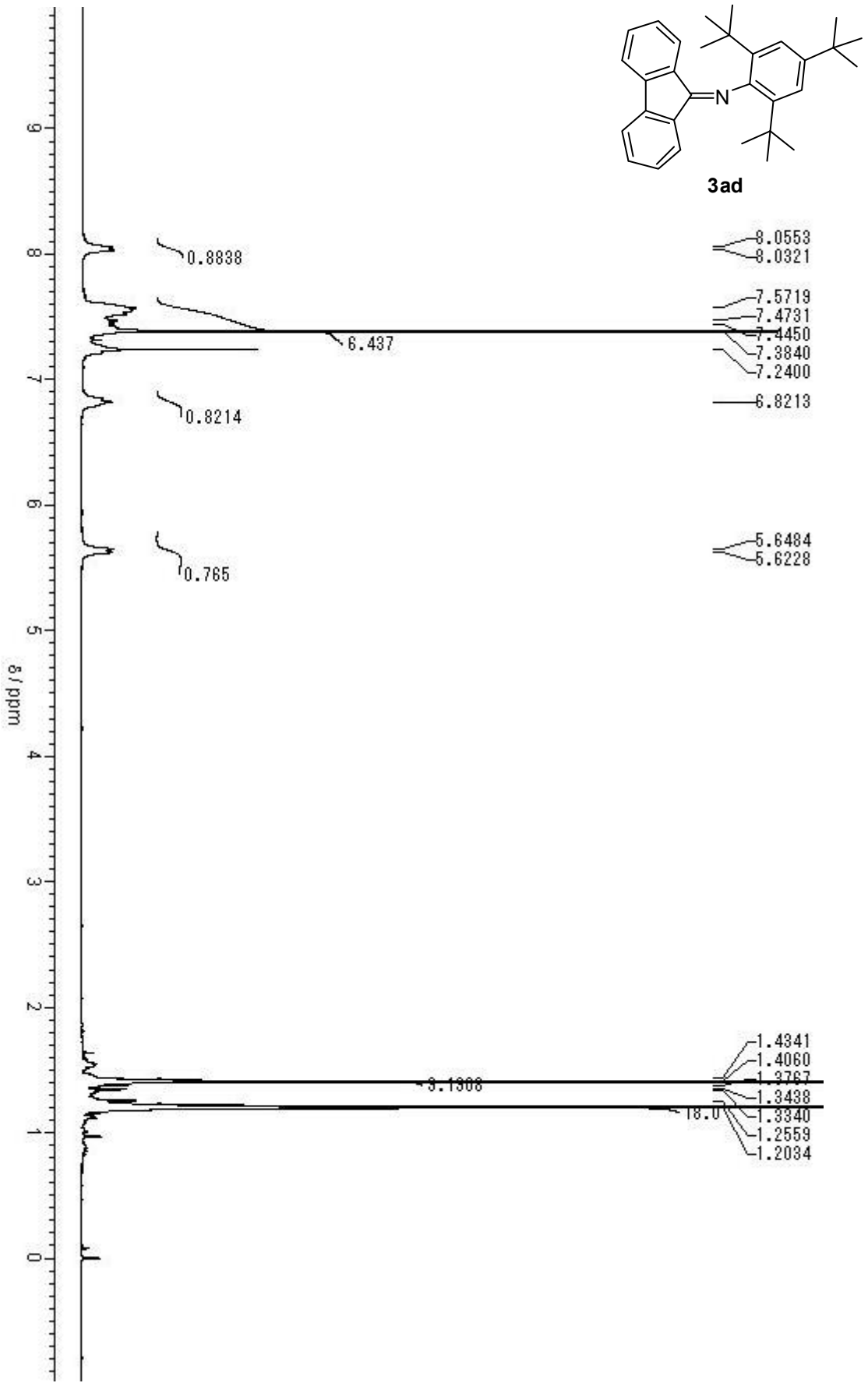
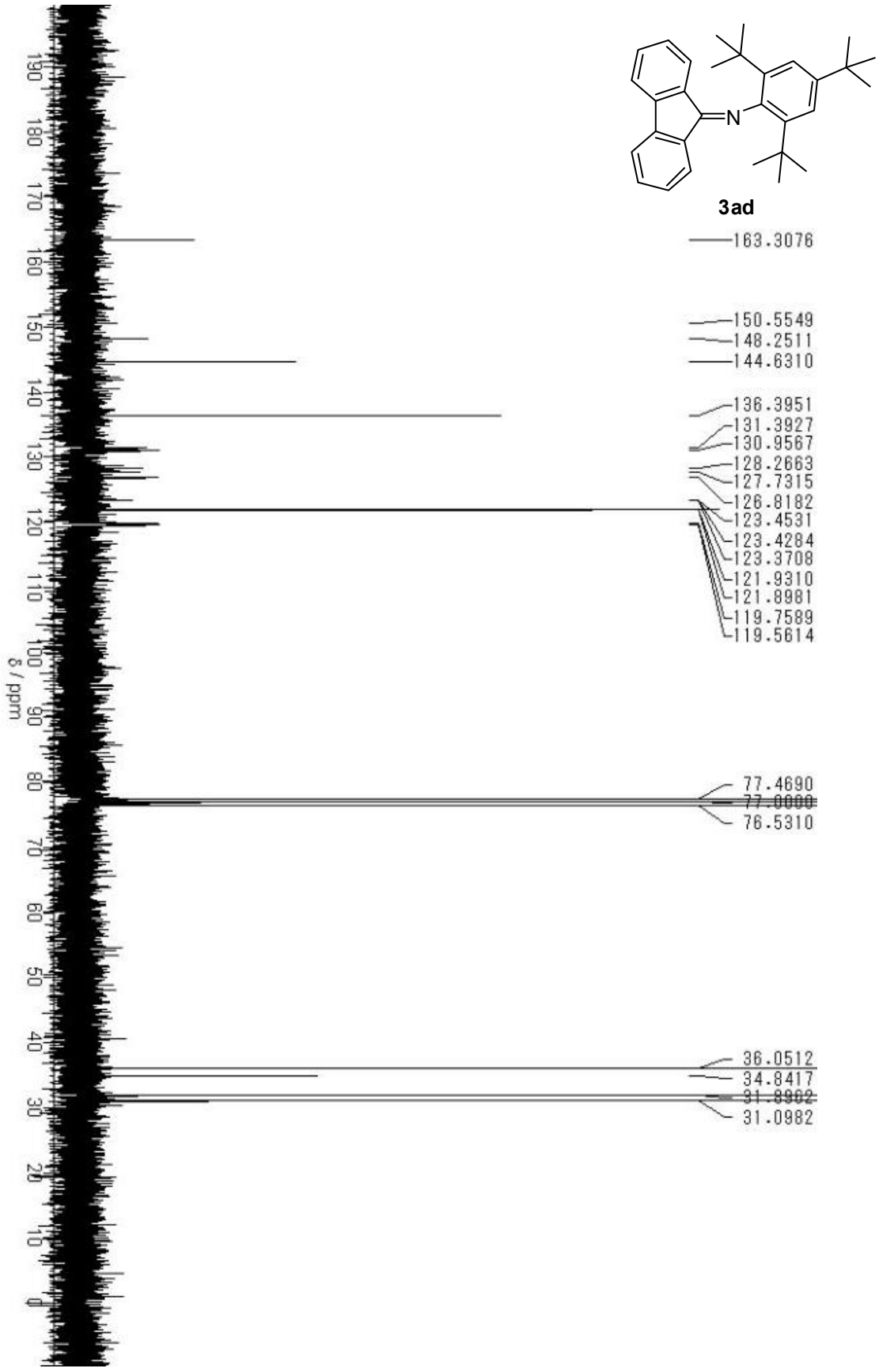
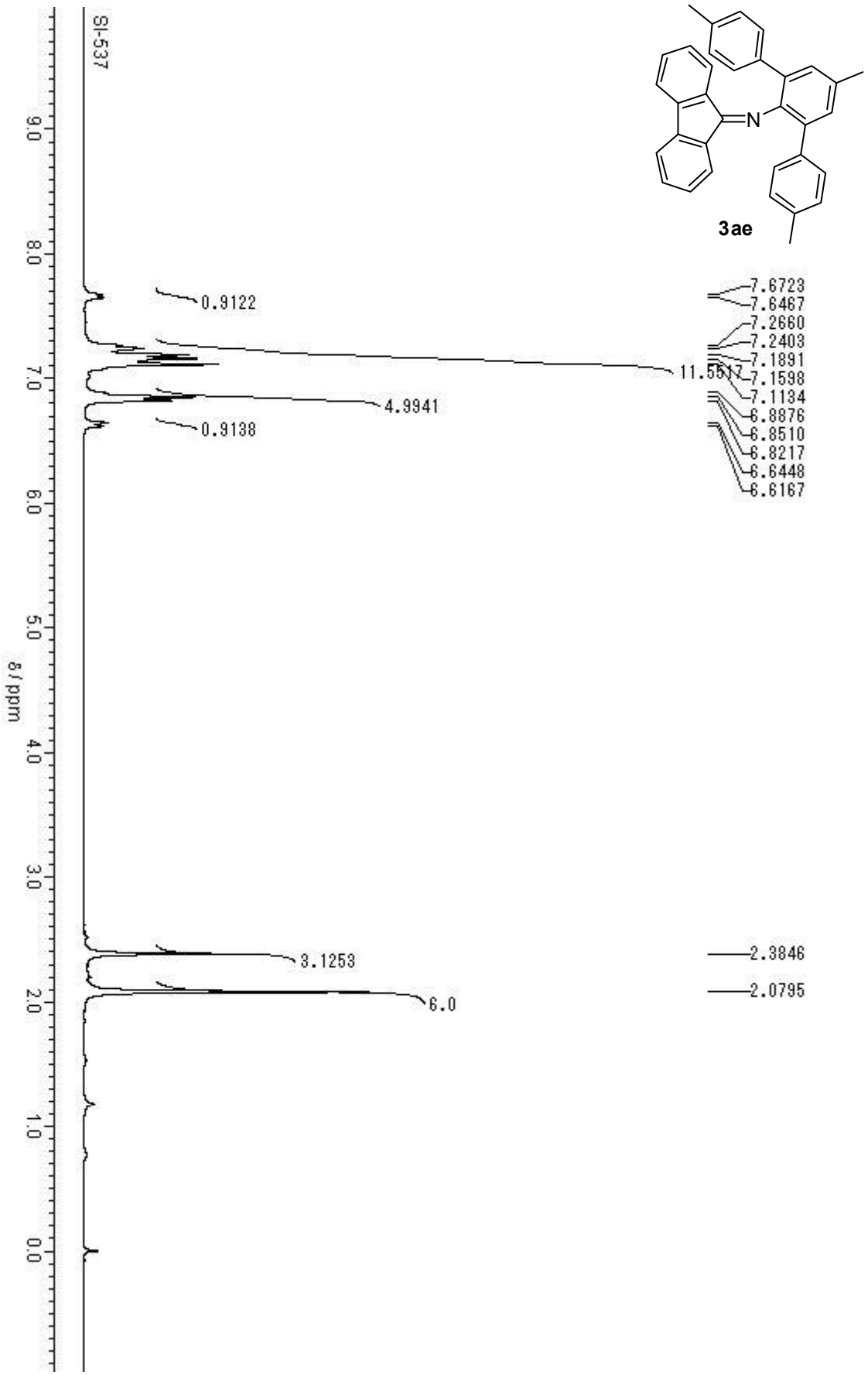
123.357
120.101
119.664
77.470
77.000
76.530
17.990
PPM
N
3ab

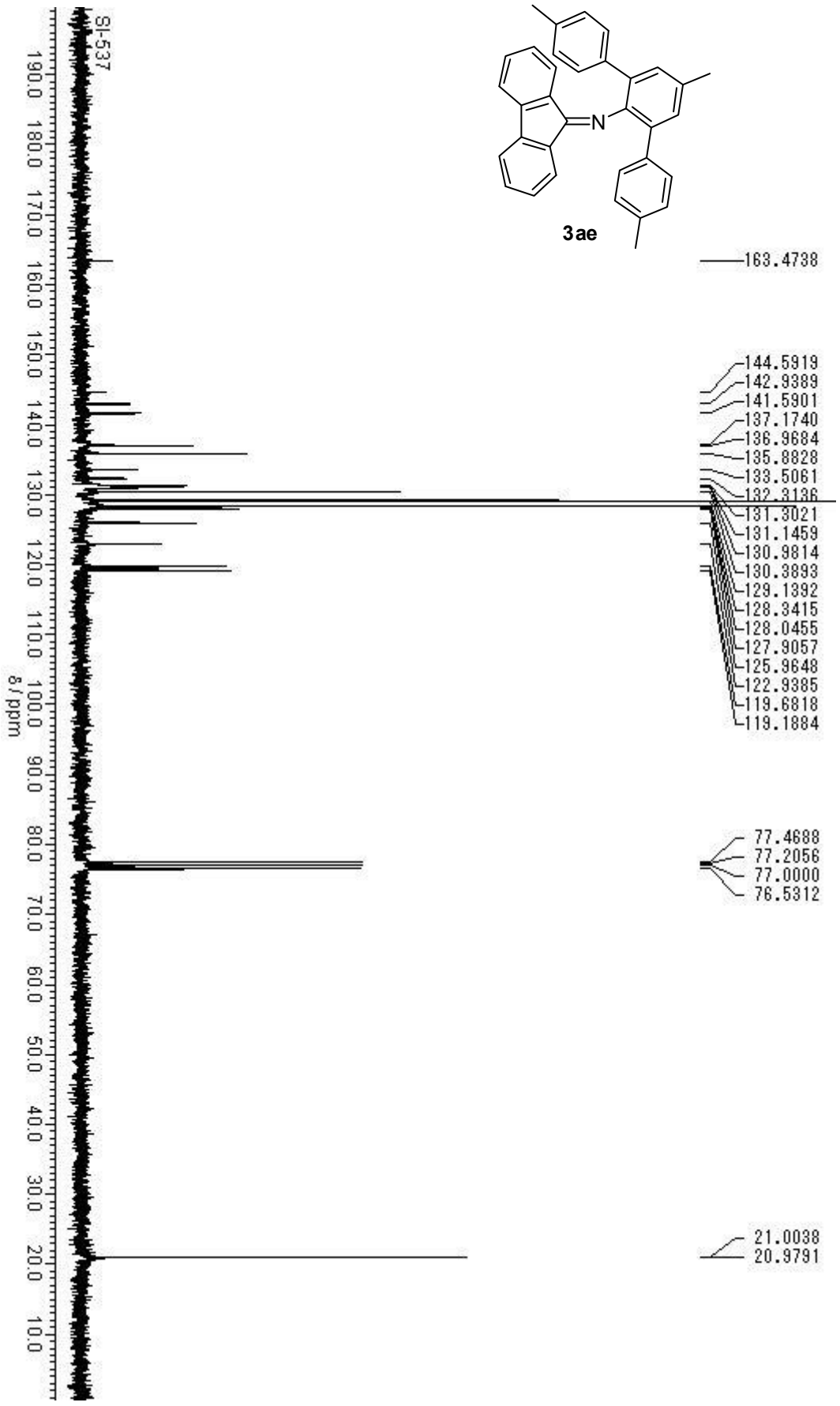

SI-542
3ac
8.0384
8.0116
7.6296
7.6016
7.5735
7.5088
7.4832
7.4563
7.4087
7.3819
7.3538
7.3416
7.3135
7.2867
7.2391
7.1818
7.1647
7.1476
7.1354
7.1183
7.1000
6.9487
6.9206
6.8925
6.4678
6.4386
2.5212
2.4944
2.4663
2.4383
2.4102
2.3980
2.3699
2.3431
2.3162
2.2882
1.0837
1.0556
1.0275
1.0
2.1517
1.1458
2.249
3.2302
1.0404
0.9927
4.2992
6.5103
δ / ppm

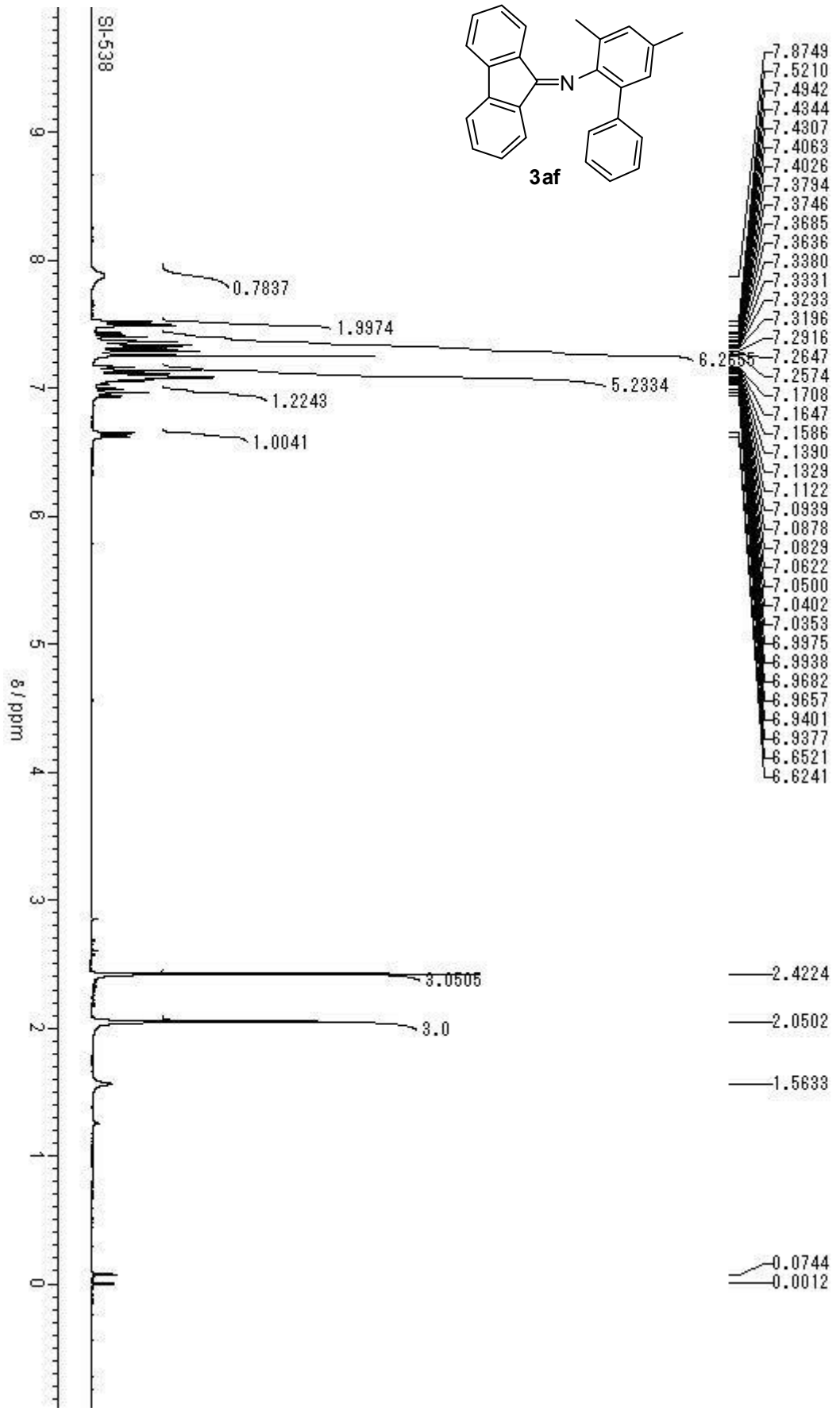

N
3ac
190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0
δ / ppm

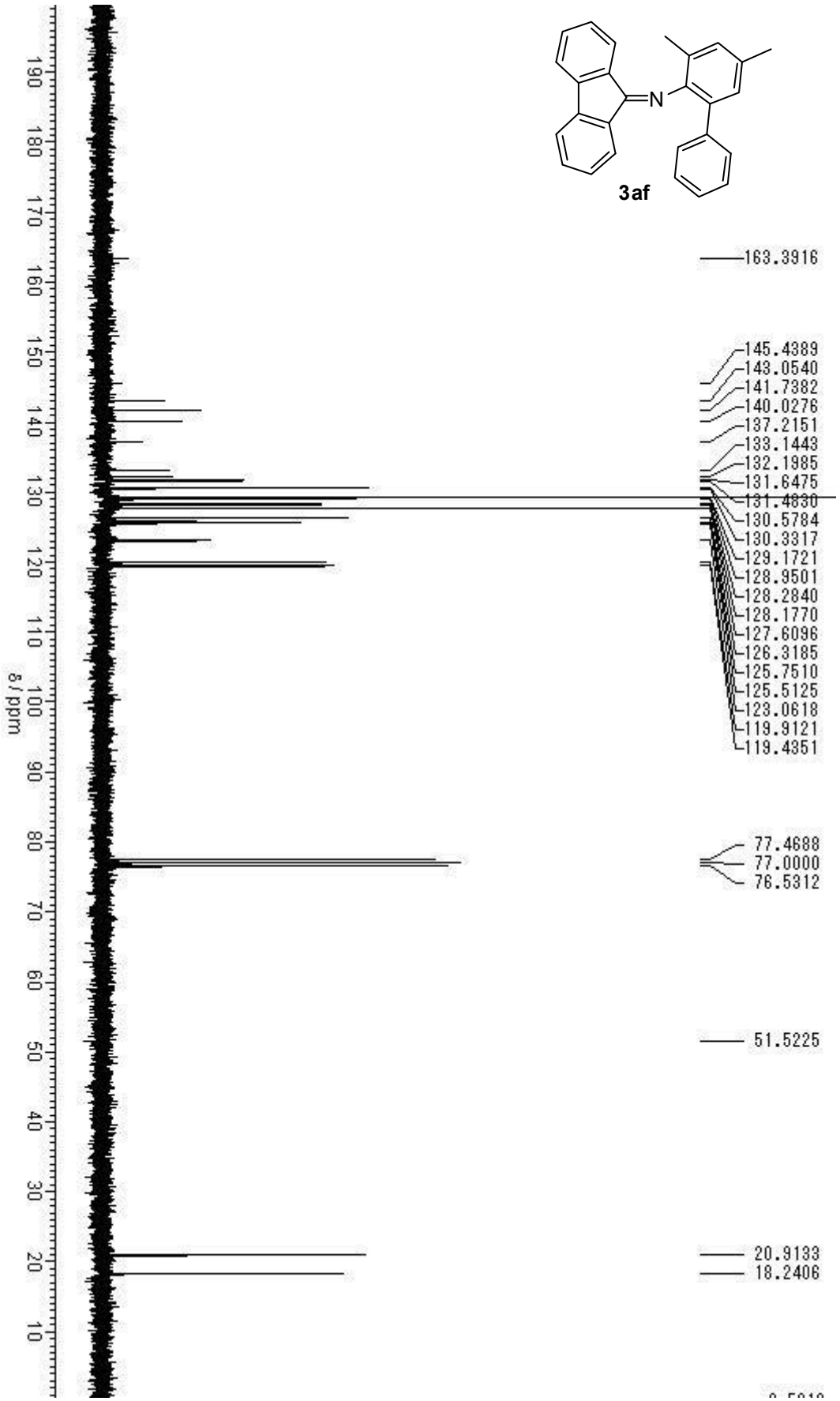

N
3ad
8.0553
8.0321
7.5719
7.4731
7.4450
7.3840
7.2400
6.8213
5.6484
5.6228
1.4341
1.4060
1.3767
1.3438
1.3340
1.2559
1.2034
0.8838
6.437
0.8214
0.765
3.1308
18.0
f1 / ppm


3ad
163.3076
150.5549
148.2511
144.6310
136.3951
131.3927
130.9567
128.2663
127.7315
126.8182
123.4531
123.4284
123.3708
121.9310
121.8981
119.7589
119.5614
77.4690
77.0000
76.5310
36.0512
34.8417
31.8982
31.0982
δ / ppm


SI-537
3ae
N
0.9122
11.5517
4.9941
0.9138
3.1253
6.0
7.6723
7.6467
7.2660
7.2403
7.1891
7.1598
7.1134
6.8876
6.8510
6.8217
6.6448
6.6167
2.3846
2.0795
δ / ppm


SI-537
3ae
N
163.4738
144.5919
142.9389
141.5901
137.1740
136.9684
135.8828
133.5061
132.3136
131.3021
131.1459
130.9814
130.3893
129.1392
128.3415
128.0455
127.9057
125.9648
122.9385
119.6818
119.1884
77.4688
77.2056
77.0000
76.5312
21.0038
20.9791
δ / ppm


SI-538
3af
N
7.8749
7.5210
7.4942
7.4344
7.4307
7.4063
7.4026
7.3794
7.3746
7.3685
7.3636
7.3380
7.3331
7.3233
7.3196
7.2916
7.2647
7.2574
7.1708
7.1647
7.1586
7.1390
7.1329
7.1122
7.0939
7.0878
7.0829
7.0622
7.0500
7.0402
7.0353
6.9975
6.9938
6.9682
6.9657
6.9401
6.9377
6.6521
6.6241
0.7837
1.9974
6.2655
5.2334
1.2243
1.0041
3.0505
3.0
2.4224
2.0502
1.5633
0.0744
0.0012
ppm


3af
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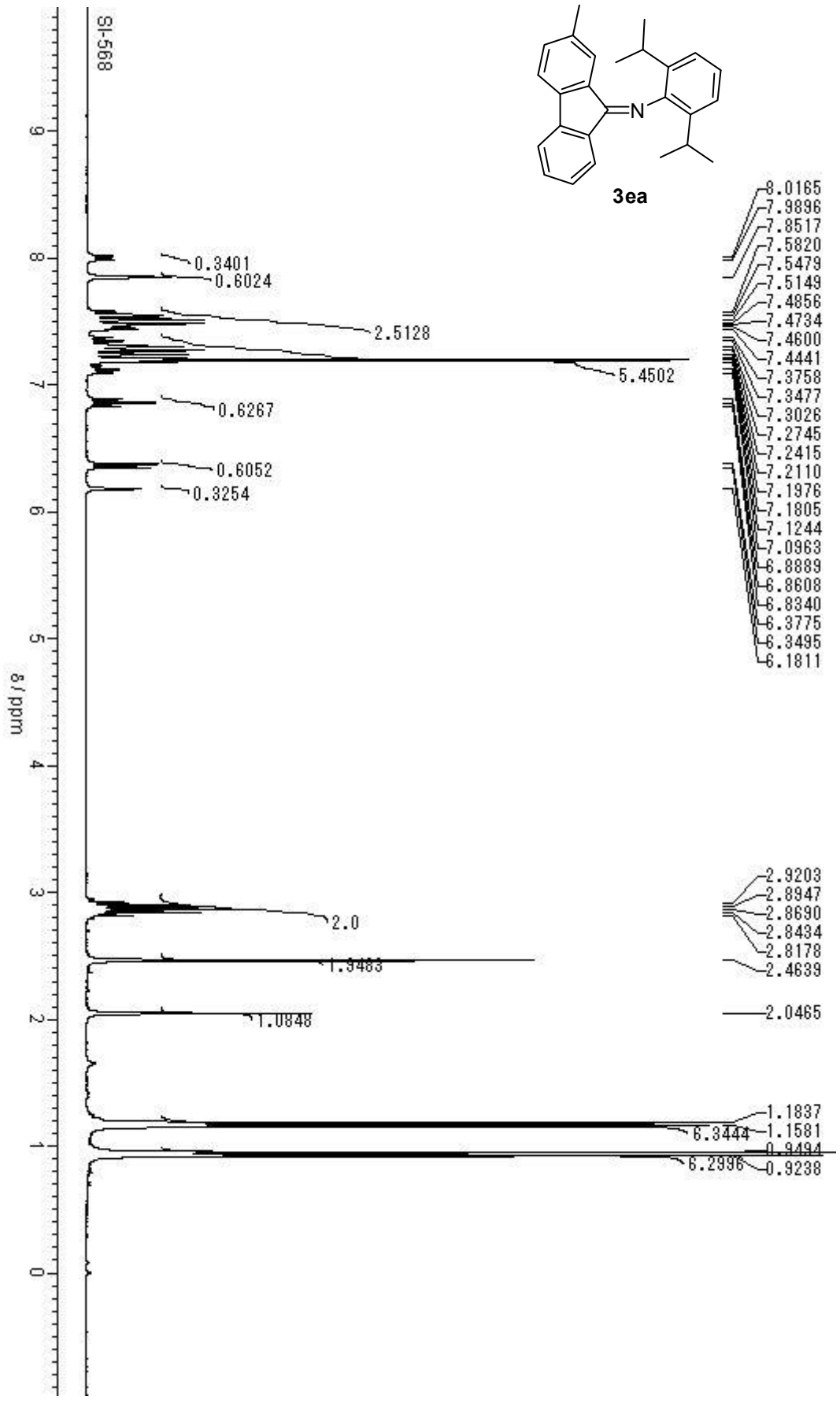
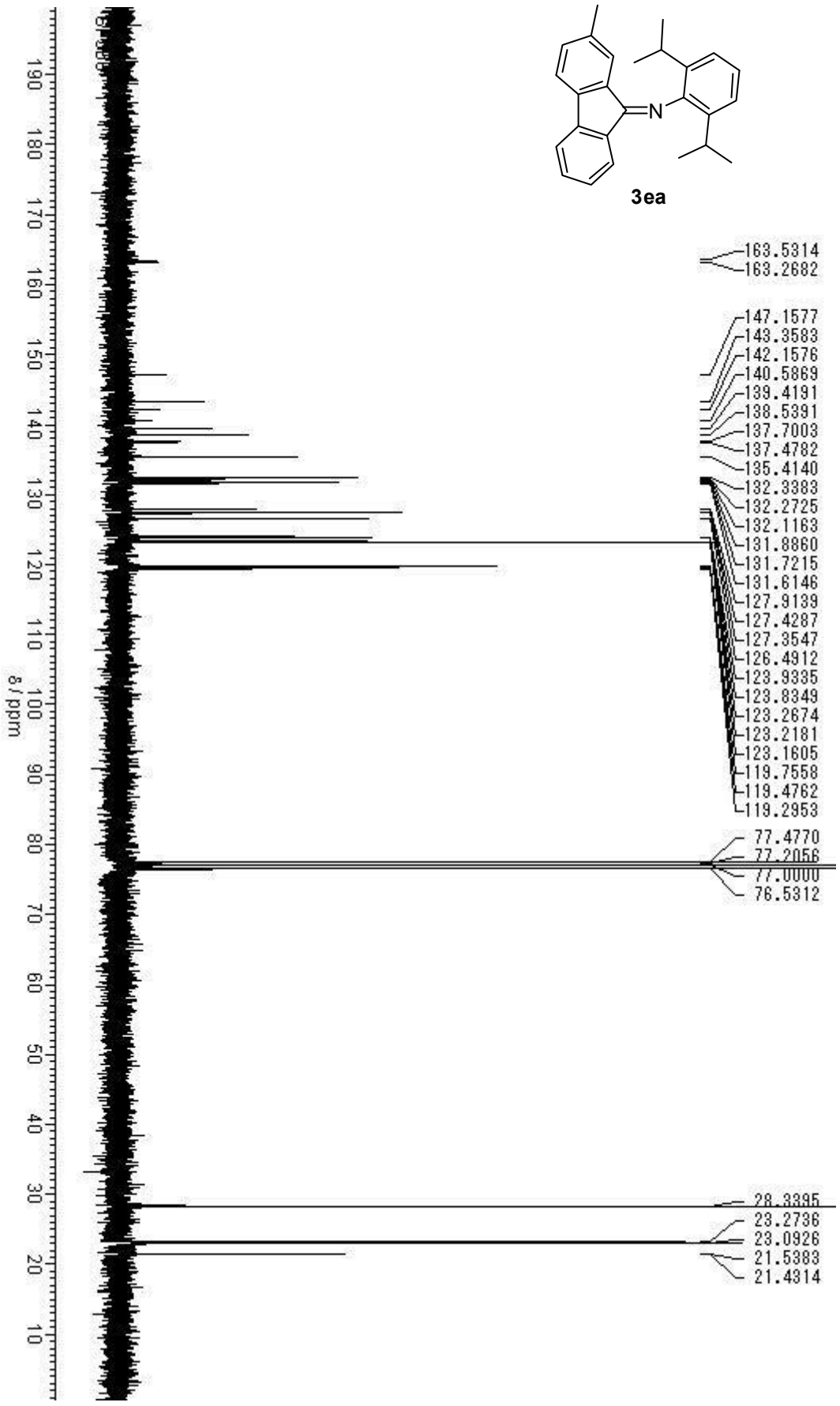
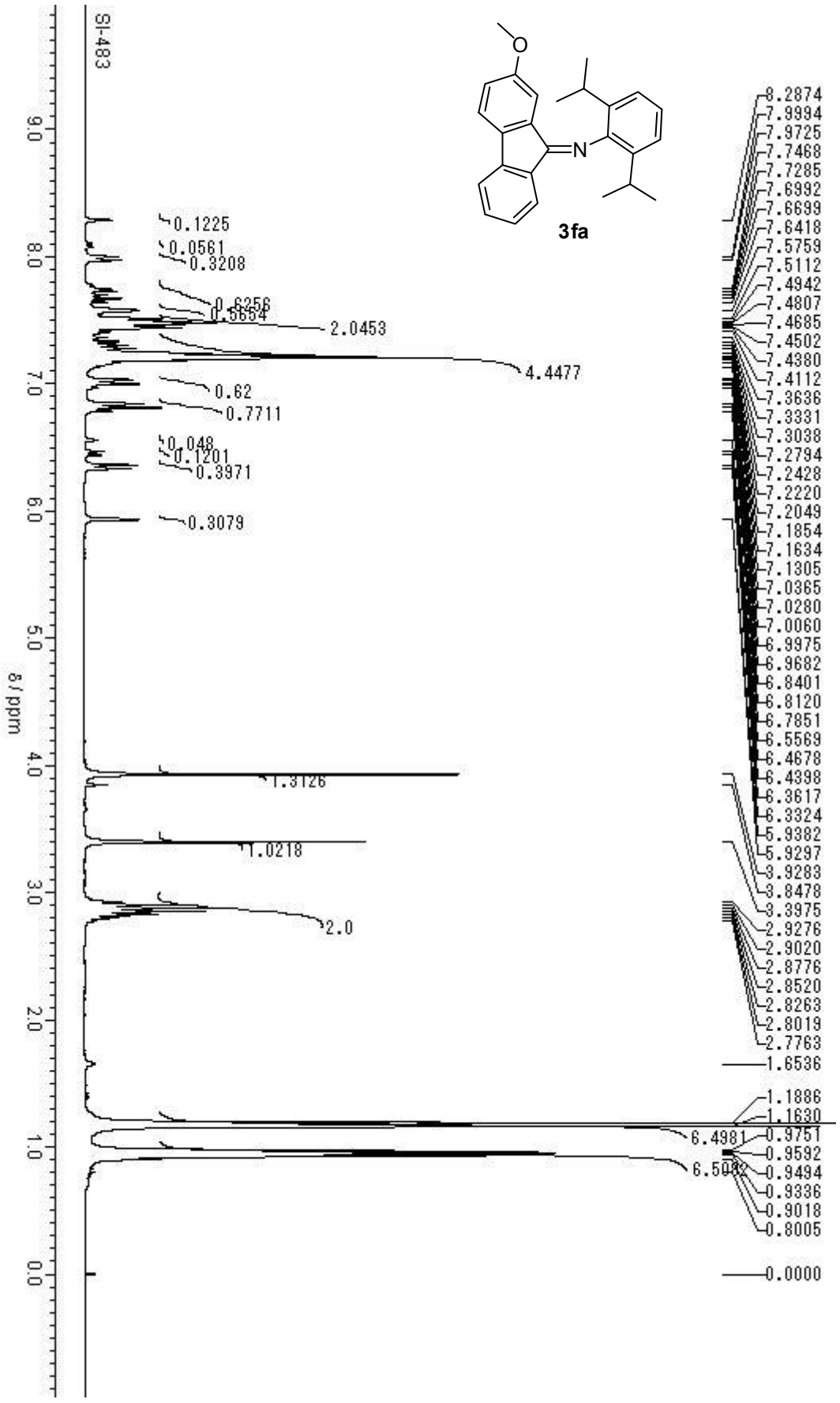
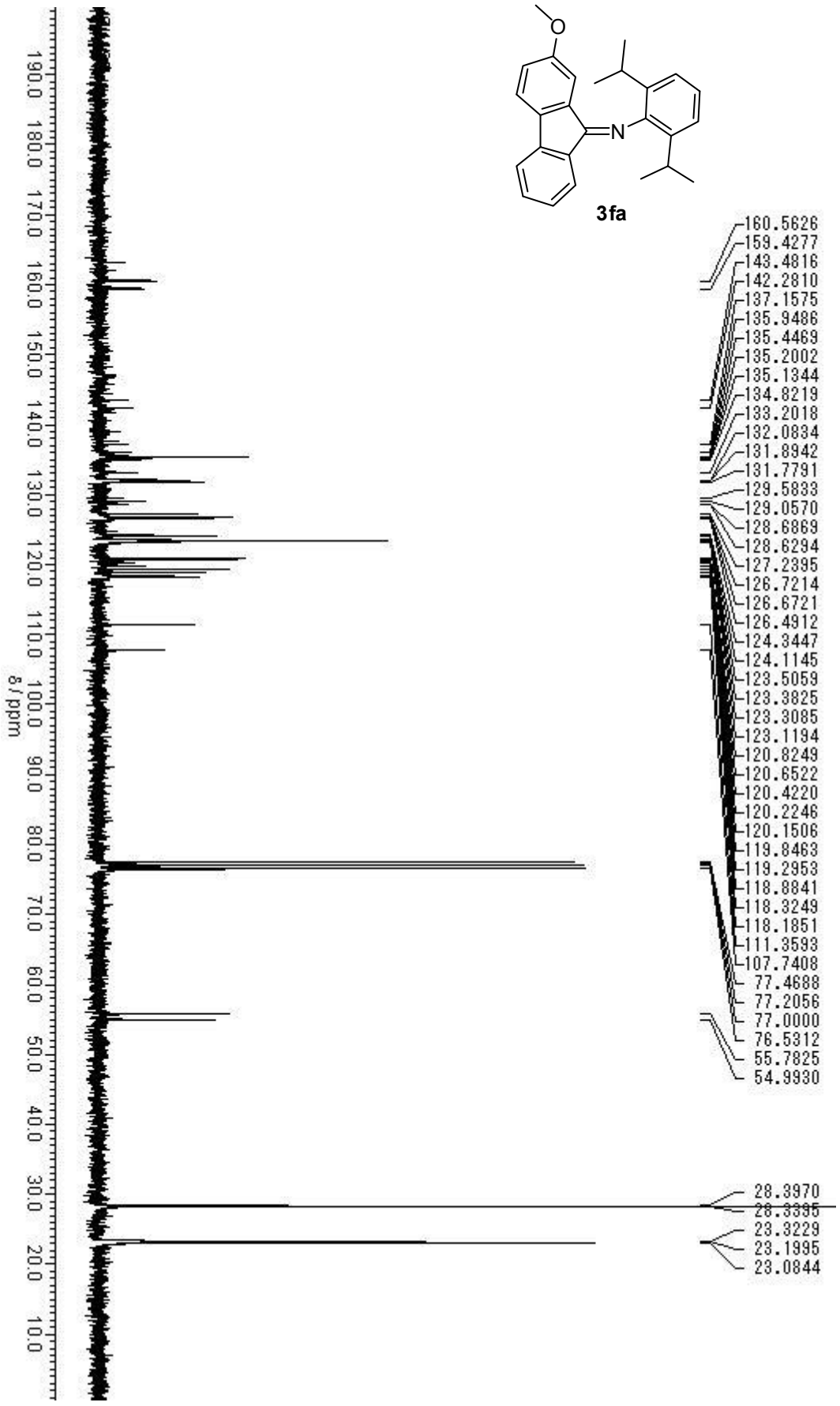
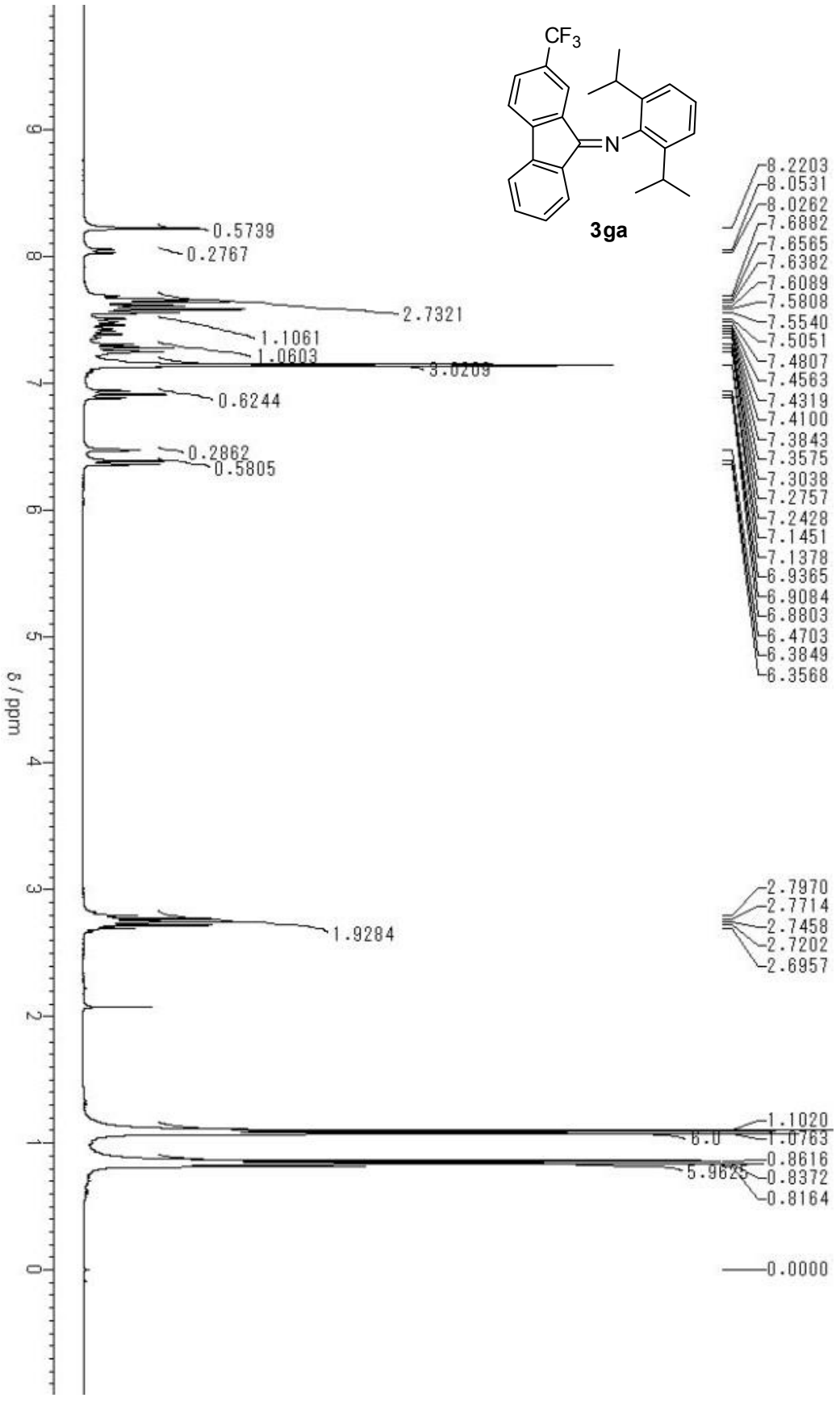
141.7382
140.0276
137.2151
133.1443
132.1985
131.6475
131.4830
130.5784
130.3317
129.1721
128.9501
128.2840
128.1770
127.6096
126.3185
125.7510
125.5125
123.0618
119.9121
119.4351
77.4688
77.0000
76.5312
51.5225
20.9133
18.2406
δ / ppm

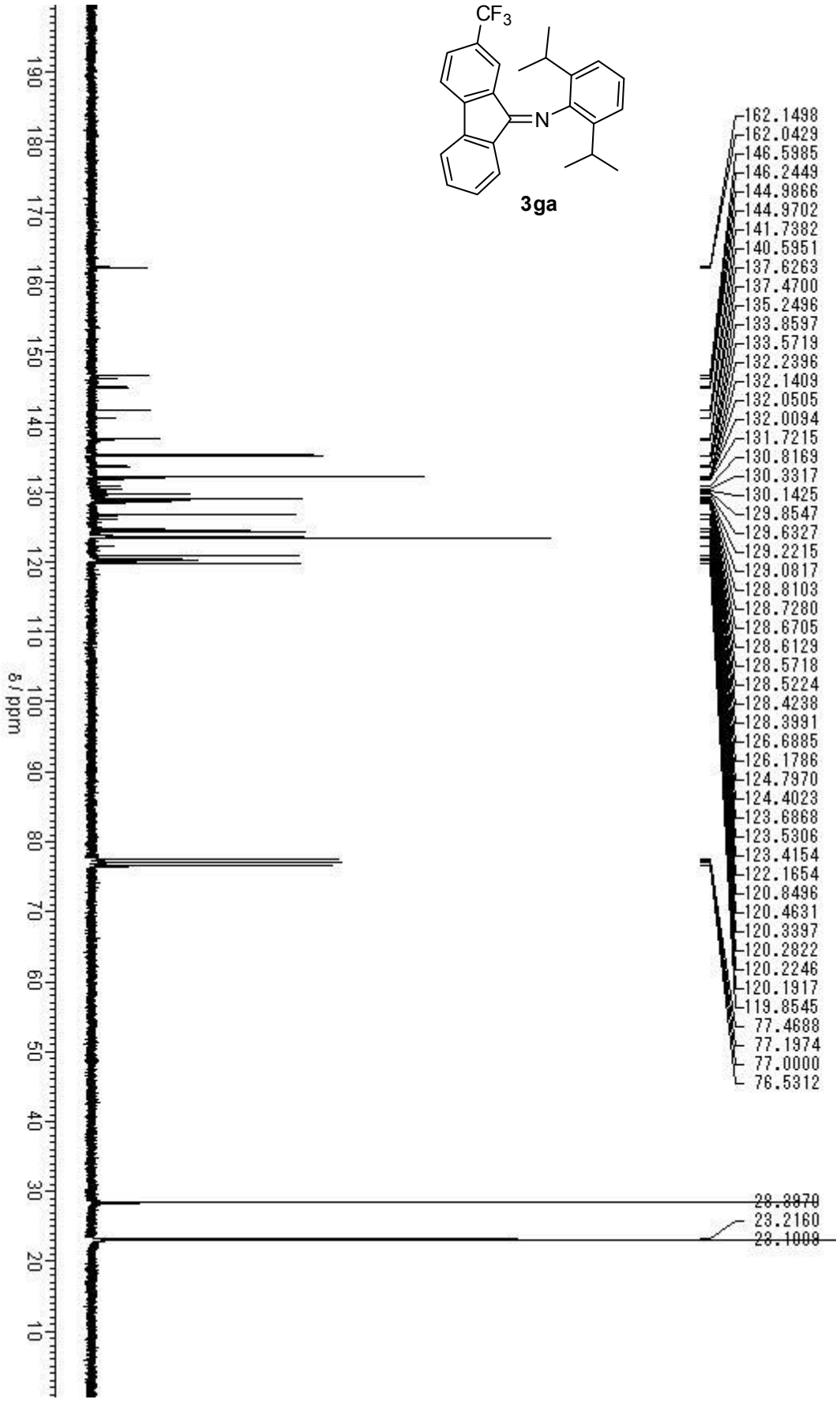

SI-568
3ea
N
8.0165
7.9896
7.8517
7.5820
7.5479
7.5149
7.4856
7.4734
7.4600
7.4441
7.3758
7.3477
7.3026
7.2745
7.2415
7.2110
7.1976
7.1805
7.1244
7.0963
6.8889
6.8608
6.8340
6.3775
6.3495
6.1811
0.3401
0.6024
2.5128
5.4502
0.6267
0.6052
0.3254
2.9203
2.8947
2.8690
2.8434
2.8178
2.4639
2.0465
2.0
1.9483
1.0848
1.1837
6.3444
1.1581
0.9494
6.2996
0.9238
f1 / ppm

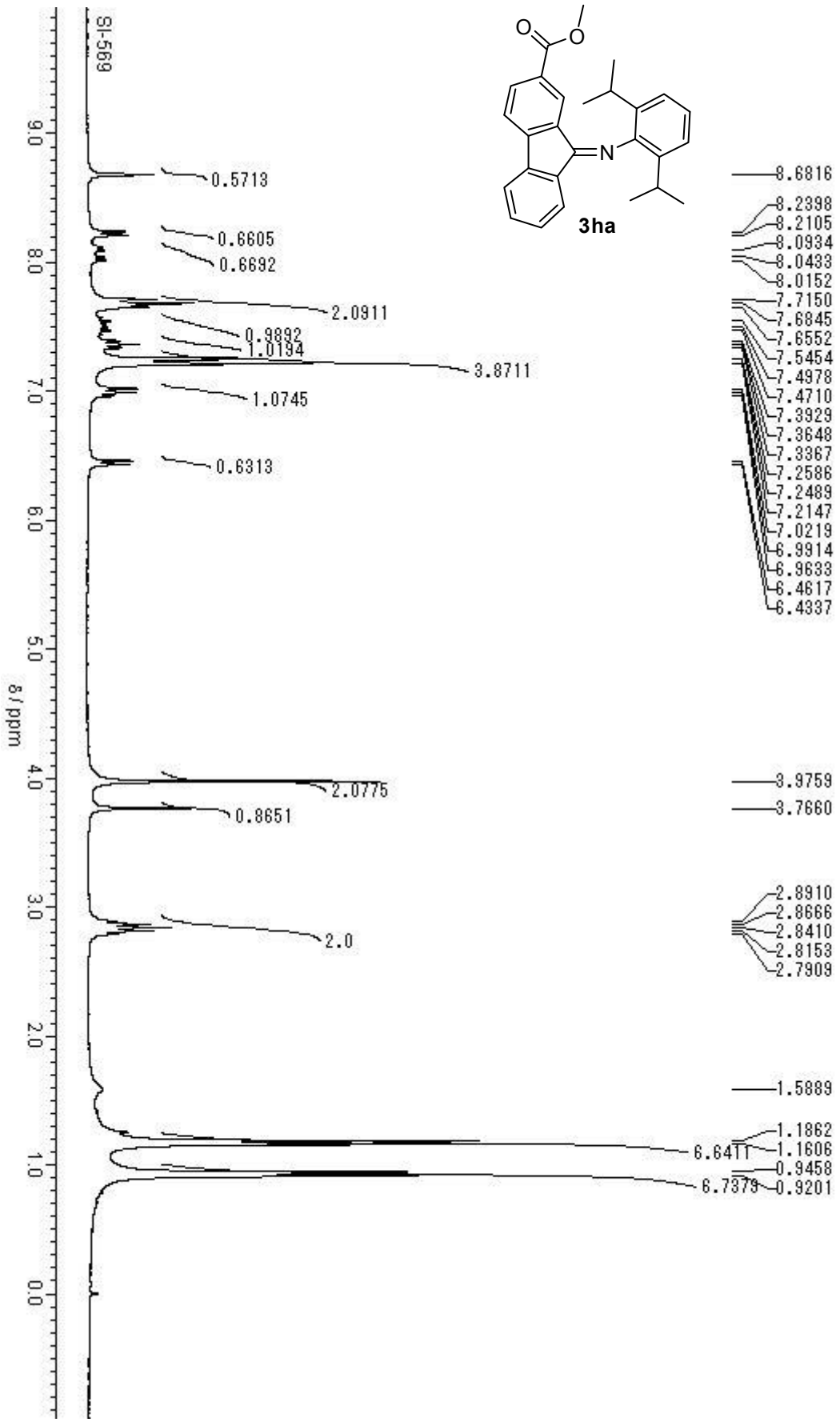

N
3ea
163.5314
163.2682
147.1577
143.3583
142.1576
140.5869
139.4191
138.5391
137.7003
137.4782
135.4140
132.3383
132.2725
132.1163
131.8860
131.7215
131.6146
127.9139
127.4287
127.3547
126.4912
123.9335
123.8349
123.2674
123.2181
123.1605
119.7558
119.4762
119.2953
77.4770
77.2056
77.0000
76.5312
28.3395
23.2736
23.0926
21.5383
21.4314
δ / ppm

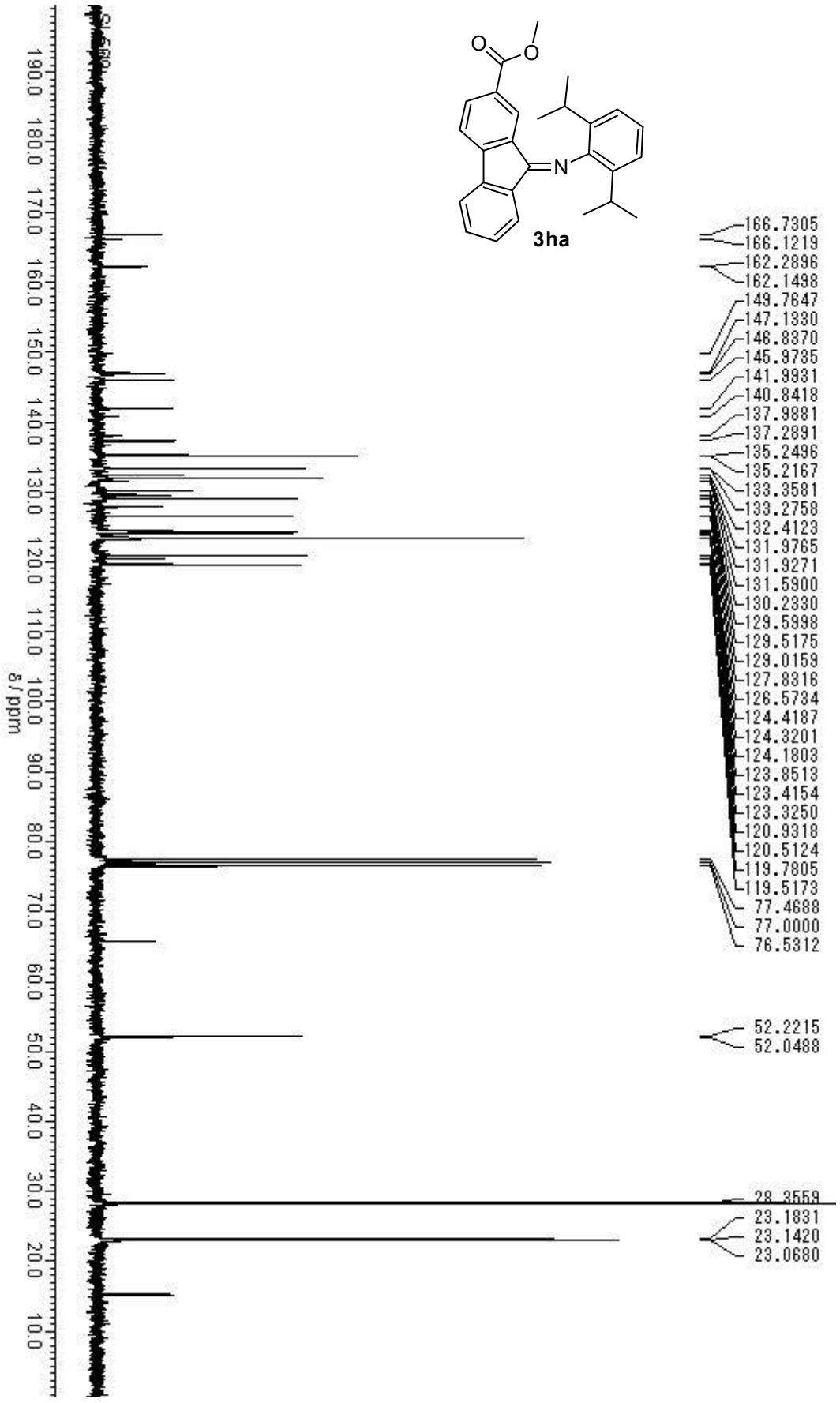

SI-483
O
N
3fa
δ / ppm
0.1225
0.0561
0.3208
2.0453
4.4477
0.62
0.7711
0.048
0.1201
0.3971
0.3079
1.3126
1.0218
2.0
6.4981
8.2874
7.9994
7.9725
7.7468
7.7285
7.6992
7.6699
7.6418
7.5759
7.5112
7.4942
7.4807
7.4685
7.4502
7.4380
7.4112
7.3636
7.3331
7.3038
7.2794
7.2428
7.2220
7.2049
7.1854
7.1634
7.1305
7.0365
7.0280
7.0060
6.9975
6.9682
6.8401
6.8120
6.7851
6.5569
6.4678
6.4398
6.3617
6.3324
5.9382
5.9297
3.9283
3.8478
3.3975
2.9276
2.9020
2.8776
2.8520
2.8263
2.8019
2.7763
1.6536
1.1886
1.1630
0.9751
0.9592
0.9494
0.9336
0.9018
0.8005
0.0000

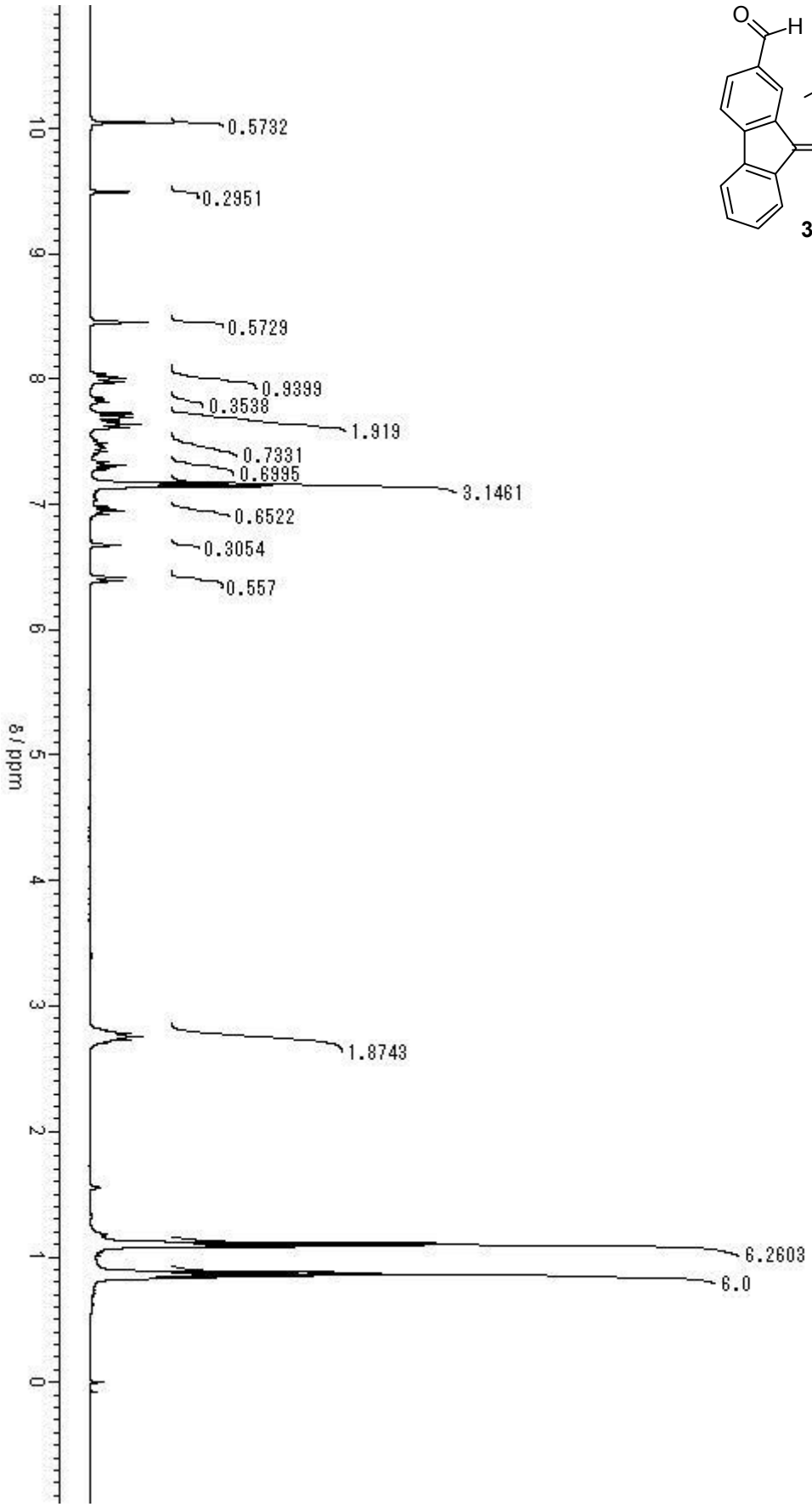

O
N
3fa
160.5626
159.4277
143.4816
142.2810
137.1575
135.9486
135.4469
135.2002
135.1344
134.8219
133.2018
132.0834
131.8942
131.7791
129.5833
129.0570
128.6869
128.6294
127.2395
126.7214
126.6721
126.4912
124.3447
124.1145
123.5059
123.3825
123.3085
123.1194
120.8249
120.6522
120.4220
120.2246
120.1506
119.8463
119.2953
118.8841
118.3249
118.1851
111.3593
107.7408
77.4688
77.2056
77.0000
76.5312
55.7825
54.9930
28.3970
28.3395
23.3229
23.1995
23.0844
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
δ / ppm

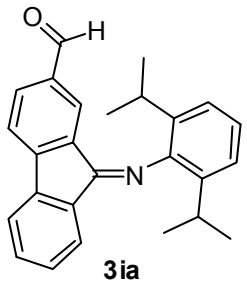

CF3
N
3ga
δ / ppm
0.5739
0.2767
2.7321
1.1061
1.0603
3.0209
0.6244
0.2862
0.5805
1.9284
1.1020
6.0
1.0763
0.8616
5.9625
0.8372
0.8164
0.0000
8.2203
8.0531
8.0262
7.6882
7.6565
7.6382
7.6089
7.5808
7.5540
7.5051
7.4807
7.4563
7.4319
7.4100
7.3843
7.3575
7.3038
7.2757
7.2428
7.1451
7.1378
6.9365
6.9084
6.8803
6.4703
6.3849
6.3568
2.7970
2.7714
2.7458
2.7202
2.6957


CF3
N
3ga
162.1498
162.0429
146.5985
146.2449
144.9866
144.9702
141.7382
140.5951
137.6263
137.4700
135.2496
133.8597
133.5719
132.2396
132.1409
132.0505
132.0094
131.7215
130.8169
130.3317
130.1425
129.8547
129.6327
129.2215
129.0817
128.8103
128.7280
128.6705
128.6129
128.5718
128.5224
128.4238
128.3991
126.6885
126.1786
124.7970
124.4023
123.6868
123.5306
123.4154
122.1654
120.8496
120.4631
120.3397
120.2822
120.2246
120.1917
119.8545
77.4688
77.1974
77.0000
76.5312
28.8870
23.2160
23.1008
δ / ppm

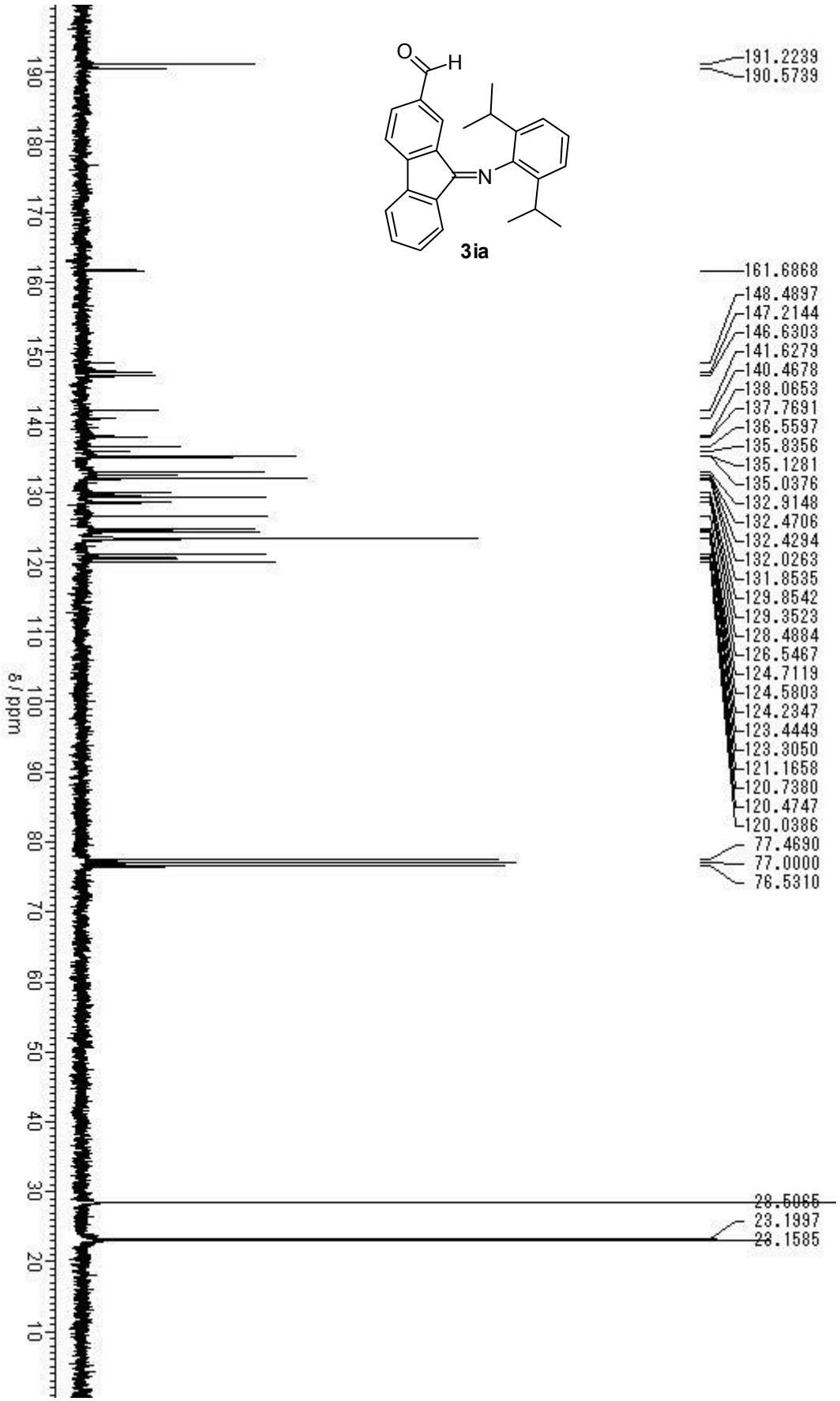

SI-569
3ha
δ / ppm
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
0.5713
0.6605
0.6692
2.0911
0.9892
1.0194
3.8711
1.0745
0.6313
2.0775
0.8651
2.0
6.6411
6.7379
1.5889
1.1862
1.1606
0.9458
0.9201
3.9759
3.7660
2.8910
2.8666
2.8410
2.8153
2.7909
8.6816
8.2398
8.2105
8.0934
8.0433
8.0152
7.7150
7.6845
7.6552
7.5454
7.4978
7.4710
7.3929
7.3648
7.3367
7.2586
7.2489
7.2147
7.0219
6.9914
6.9633
6.4617
6.4337


O
O
N
3ha
166.7305
166.1219
162.2896
162.1498
149.7647
147.1330
146.8370
145.9735
141.9931
140.8418
137.9881
137.2891
135.2496
135.2167
133.3581
133.2758
132.4123
131.9765
131.9271
131.5900
130.2330
129.5998
129.5175
129.0159
127.8316
126.5734
124.4187
124.3201
124.1803
123.8513
123.4154
123.3250
120.9318
120.5124
119.7805
119.5173
77.4688
77.0000
76.5312
52.2215
52.0488
28.3559
23.1831
23.1420
23.0680
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
δ / ppm


0.5732
0.2951
0.5729
0.9399
0.3538
1.919
0.7331
0.6995
3.1461
0.6522
0.3054
0.557
1.8743
6.2603
6.0
δ / ppm


O
H
N

3ia


O
H
N
3ia
δ / ppm
191.2239
190.5739
161.6868
148.4897
147.2144
146.6303
141.6279
140.4678
138.0653
137.7691
136.5597
135.8356
135.1281
135.0376
132.9148
132.4706
132.4294
132.0263
131.8535
129.8542
129.3523
128.4884
126.5467
124.7119
124.5803
124.2347
123.4449
123.3050
121.1658
120.7380
120.4747
120.0386
77.4690
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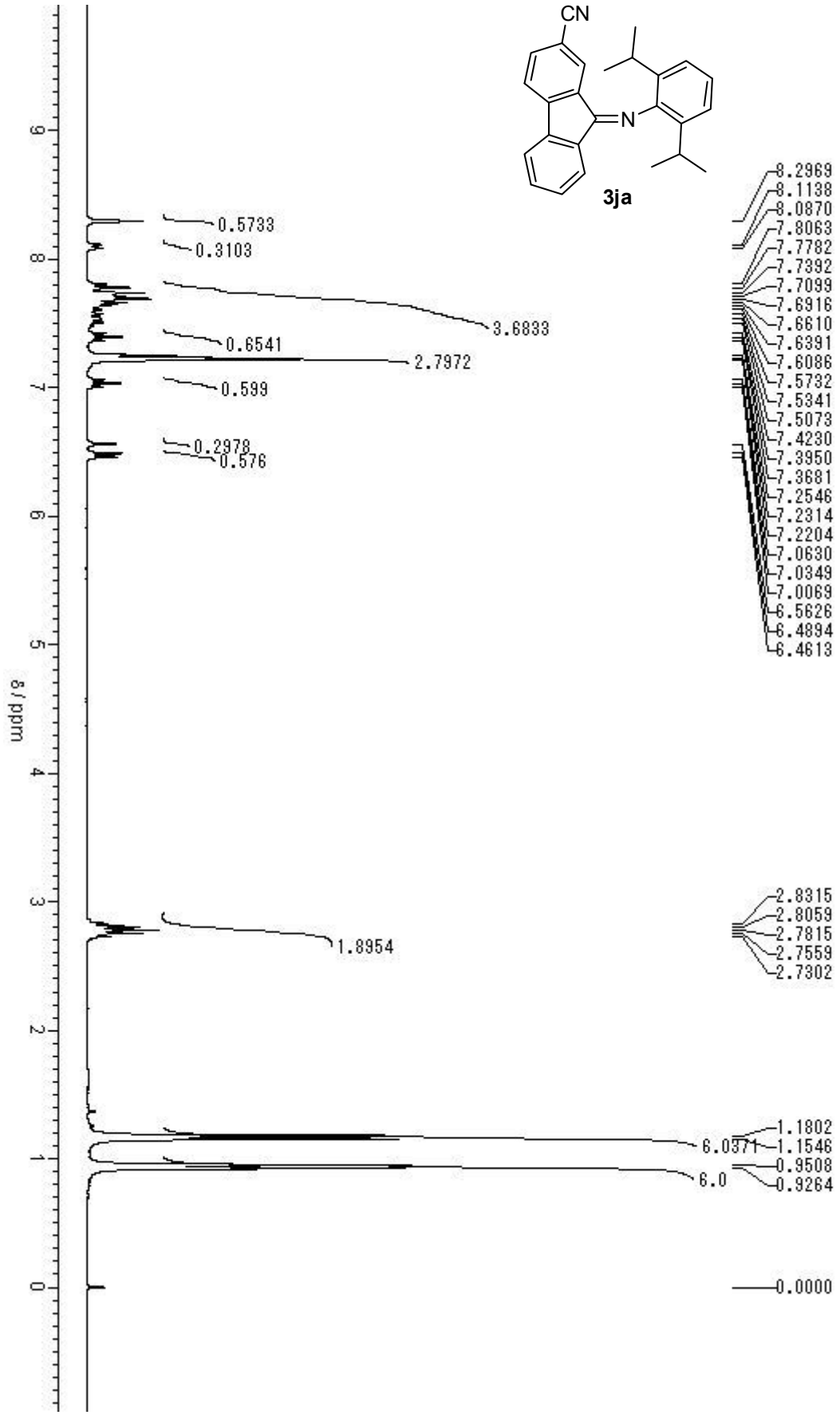
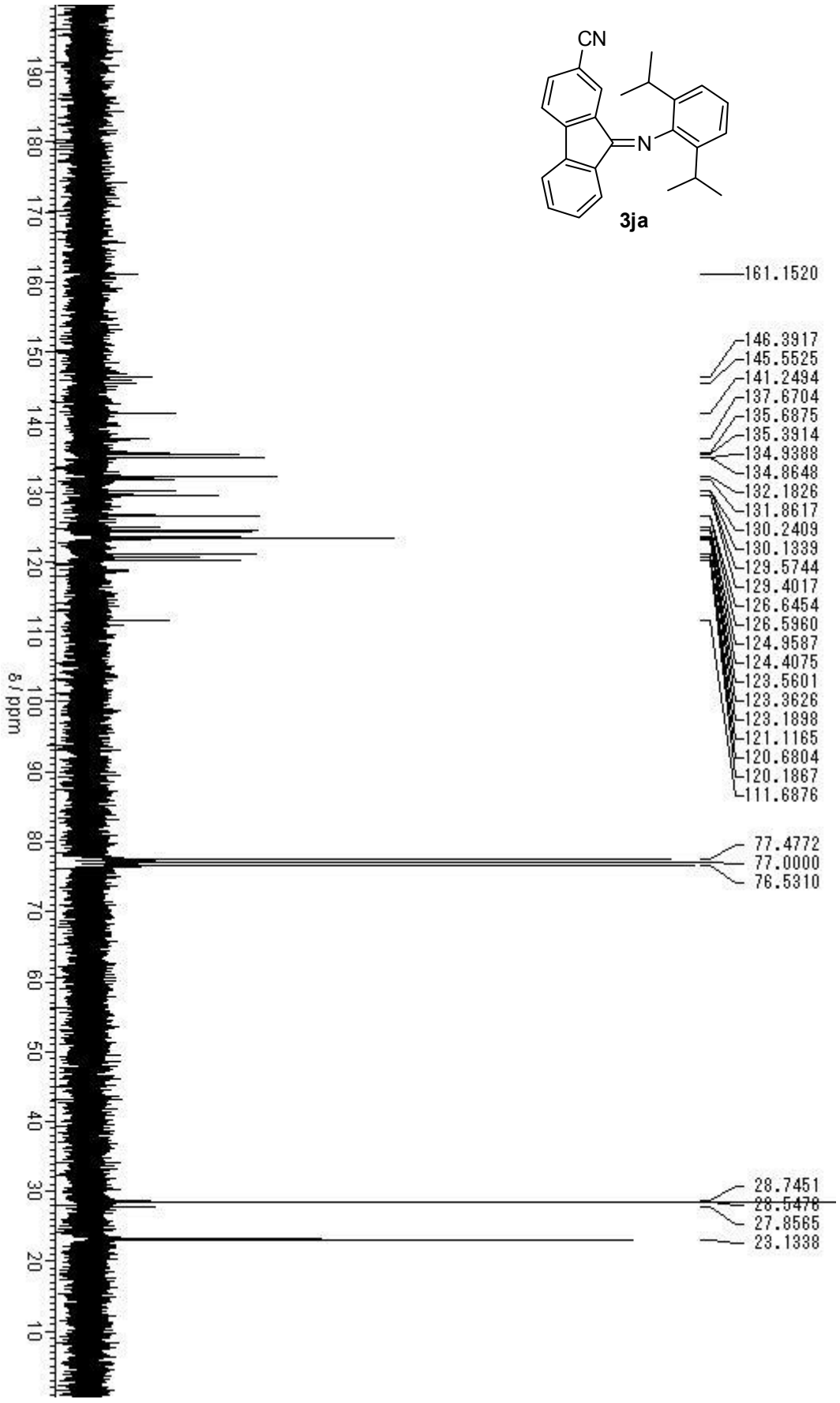
76.5310
28.5065
23.1997
23.1585


CN
N
3ja
δ / ppm
0.5733
0.3103
3.6833
0.6541
2.7972
0.599
0.2978
0.576
1.8954
6.0371
6.0
0.0000
8.2969
8.1138
8.0870
7.8063
7.7782
7.7392
7.7099
7.6916
7.6610
7.6391
7.6086
7.5732
7.5341
7.5073
7.4230
7.3950
7.3681
7.2546
7.2314
7.2204
7.0630
7.0349
7.0069
6.5626
6.4894
6.4613
2.8315
2.8059
2.7815
2.7559
2.7302
1.1802
1.1546
0.9508
0.9264


CN
N
3ja
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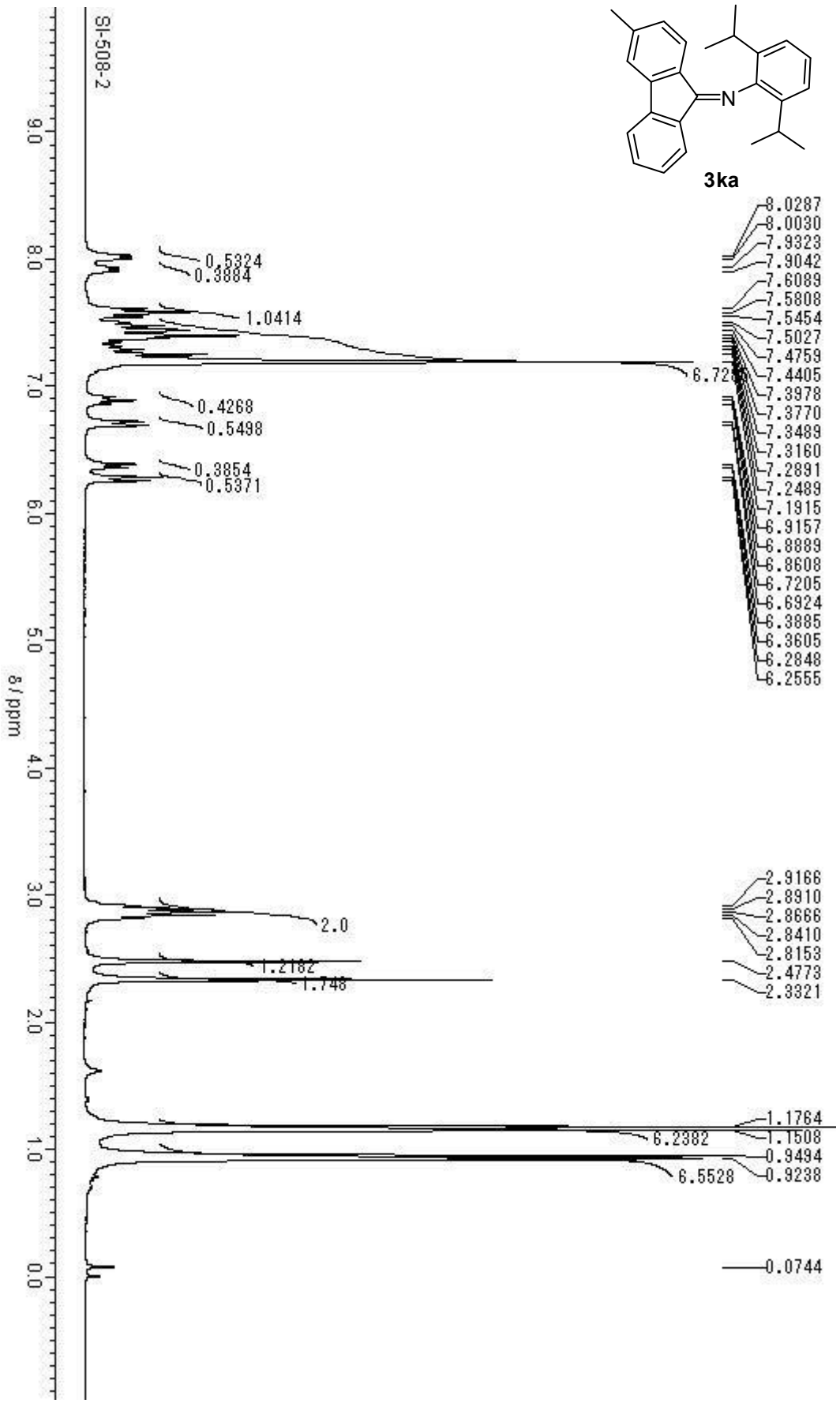
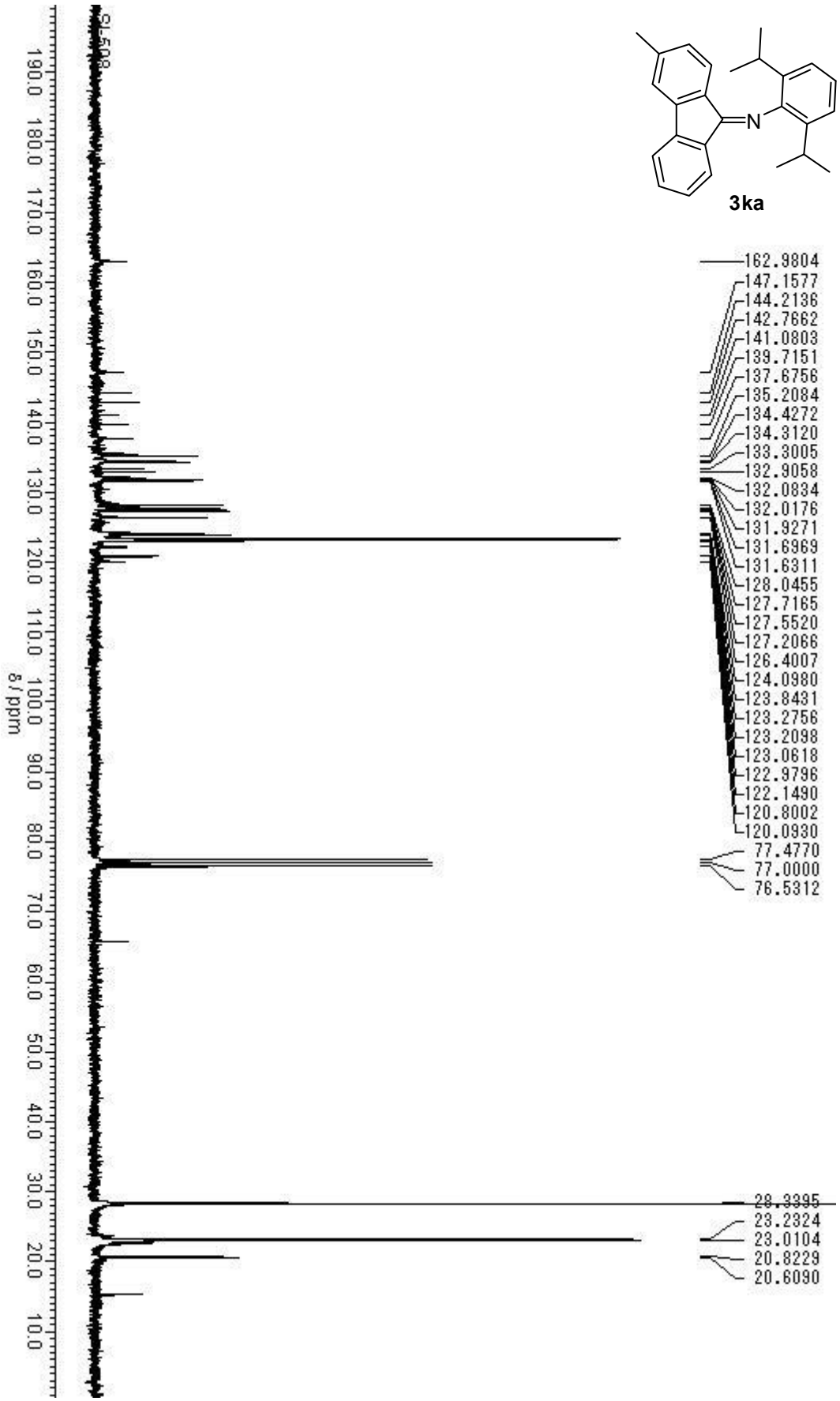
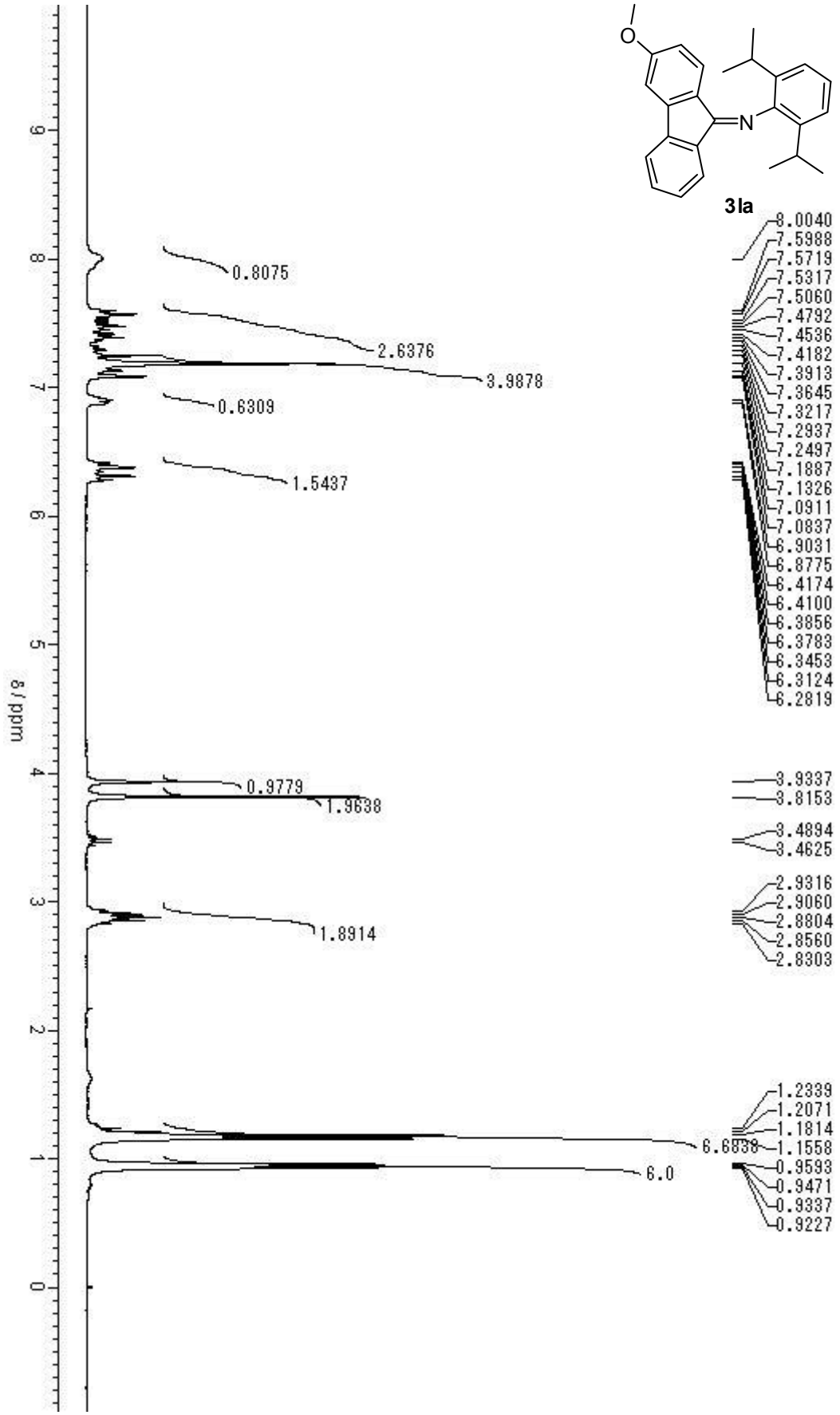
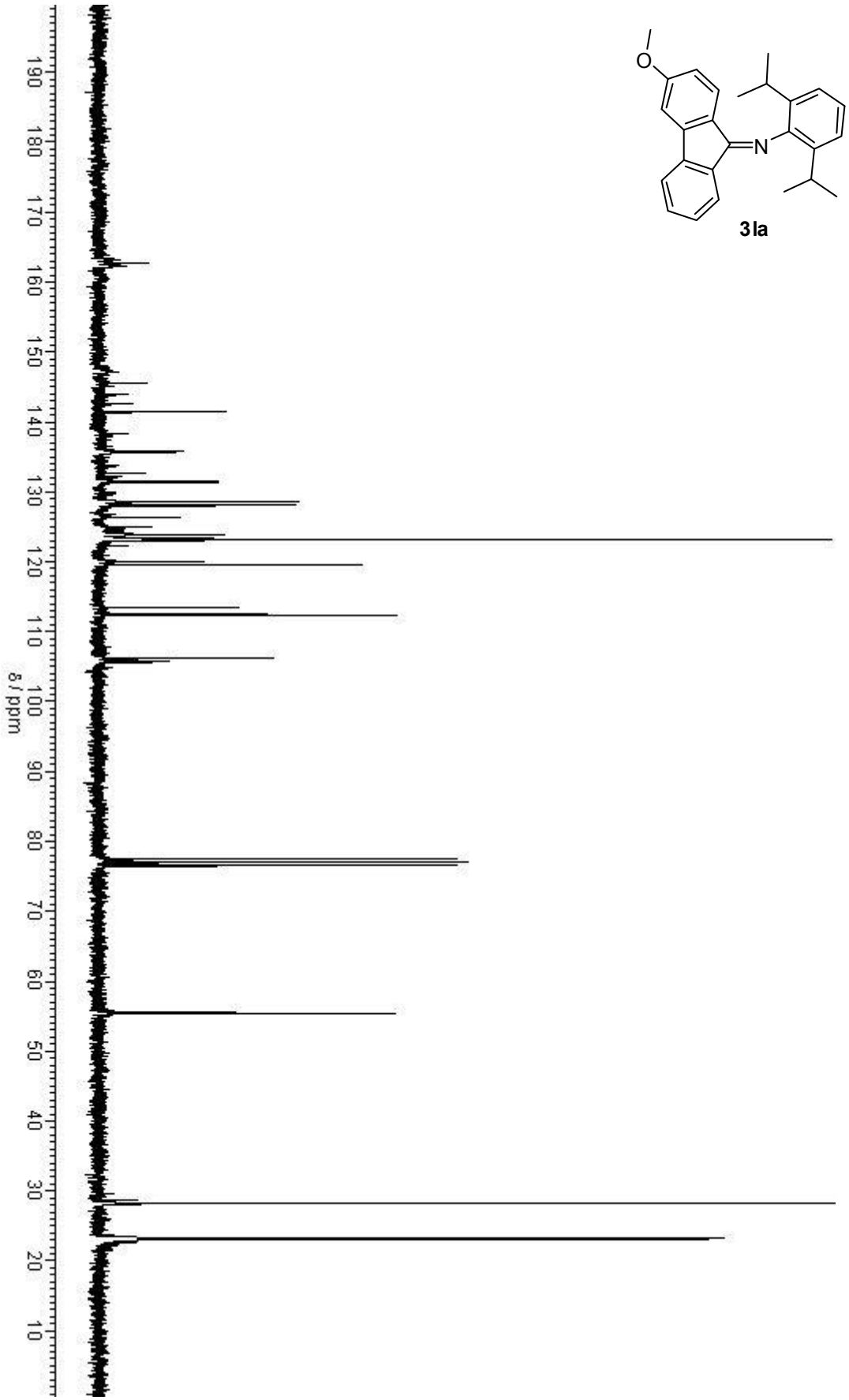
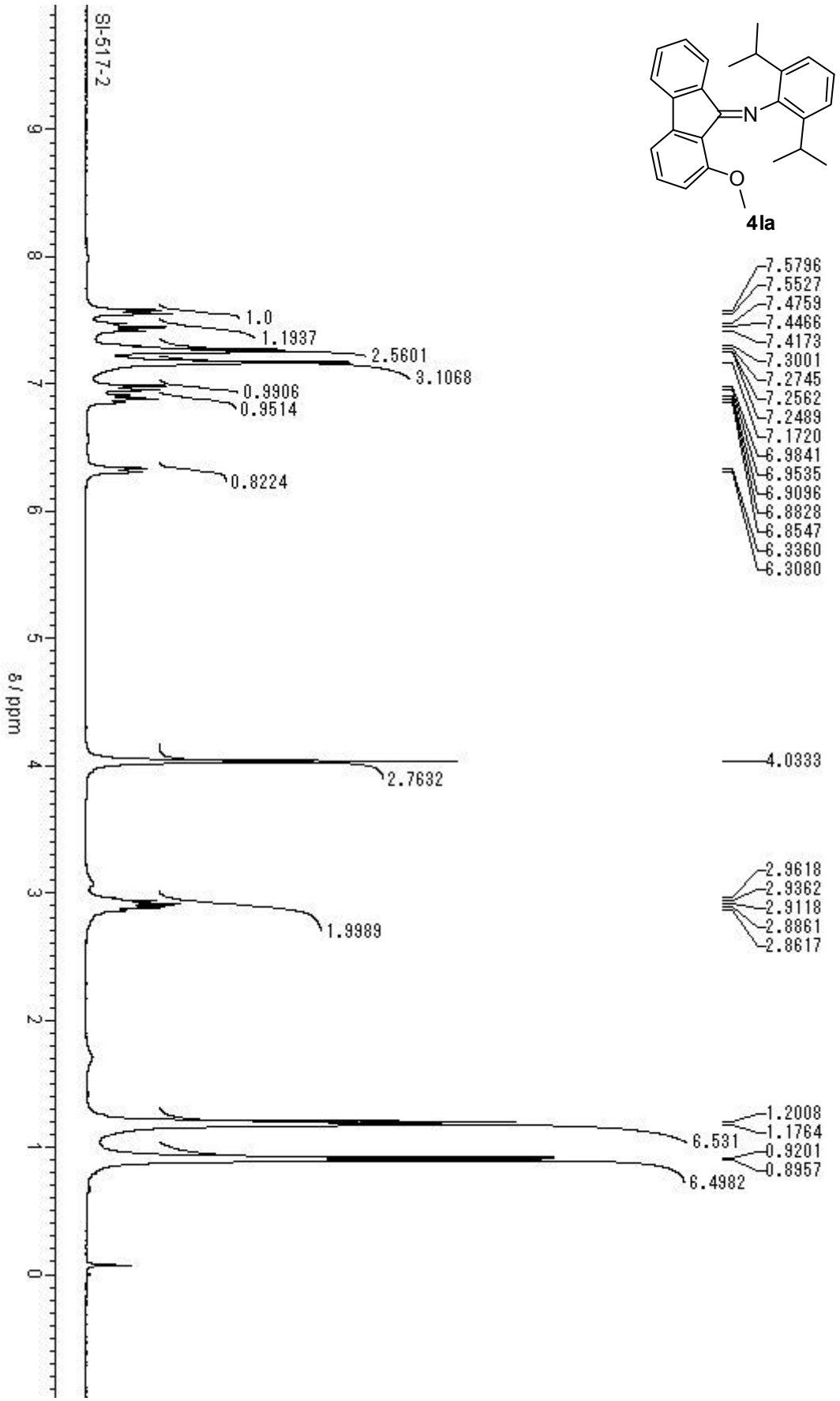
146.3917
145.5525
141.2494
137.6704
135.6875
135.3914
134.9388
134.8648
132.1826
131.8617
130.2409
130.1339
129.5744
129.4017
126.6454
126.5960
124.9587
124.4075
123.5601
123.3626
123.1898
121.1165
120.6804
120.1867
111.6876
77.4772
77.0000
76.5310
28.7451
28.5478
27.8565
23.1338
δ / ppm


SI-508-2
3ka
N
8.0287
8.0030
7.9323
7.9042
7.6089
7.5808
7.5454
7.5027
7.4759
7.4405
7.3978
7.3770
7.3489
7.3160
7.2891
7.2489
7.1915
6.9157
6.8889
6.8608
6.7205
6.6924
6.3885
6.3605
6.2848
6.2555
0.5324
0.3884
1.0414
0.4268
0.5498
0.3854
0.5371
2.0
1.2162
1.748
2.9166
2.8910
2.8666
2.8410
2.8153
2.4773
2.3321
1.1764
6.2382
1.1508
0.9494
6.5528
0.9238
0.0744
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
δ / ppm

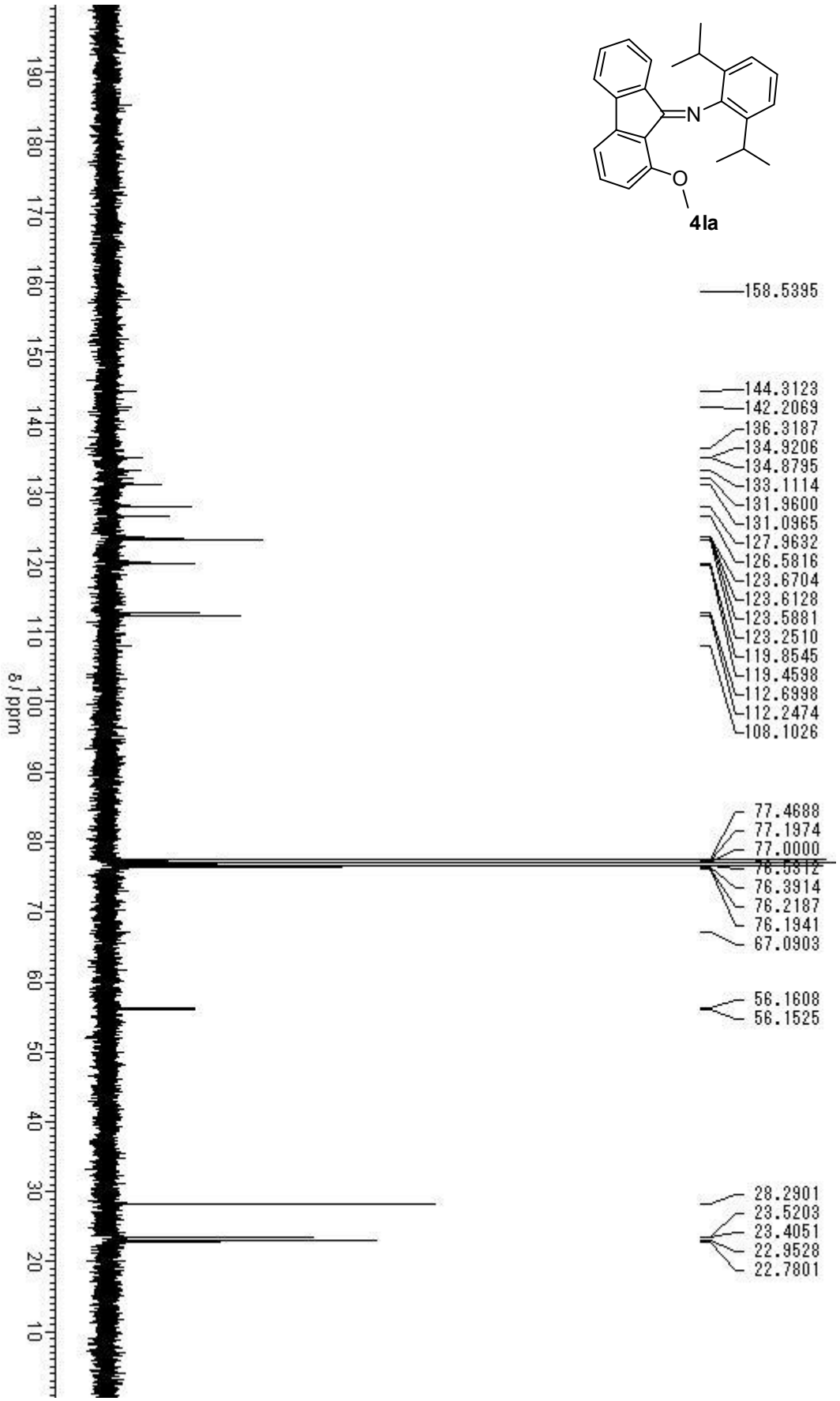

SL-508
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
δ / ppm
N
3ka
162.9804
147.1577
144.2136
142.7662
141.0803
139.7151
137.6756
135.2084
134.4272
134.3120
133.3005
132.9058
132.0834
132.0176
131.9271
131.6969
131.6311
128.0455
127.7165
127.5520
127.2066
126.4007
124.0980
123.8431
123.2756
123.2098
123.0618
122.9796
122.1490
120.8002
120.0930
77.4770
77.0000
76.5312
28.3395
23.2324
23.0104
20.8229
20.6090

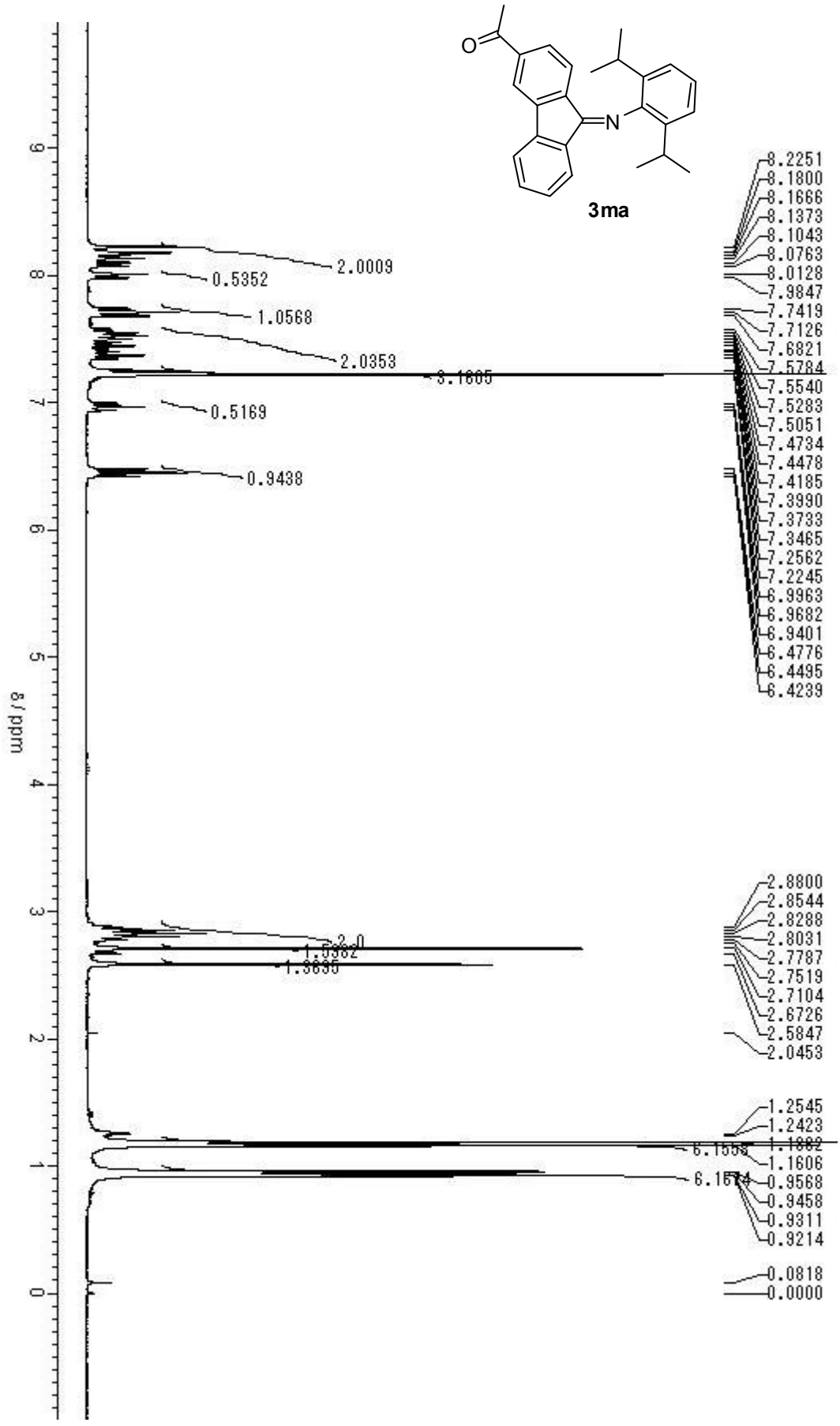

O
N
3la
8.0040
7.5988
7.5719
7.5317
7.5060
7.4792
7.4536
7.4182
7.3913
7.3645
7.3217
7.2937
7.2497
7.1887
7.1326
7.0911
7.0837
6.9031
6.8775
6.4174
6.4100
6.3856
6.3783
6.3453
6.3124
6.2819
3.9337
3.8153
3.4894
3.4625
2.9316
2.9060
2.8804
2.8560
2.8303
1.2339
1.2071
1.1814
1.1558
0.9593
0.9471
0.9337
0.9227
0.8075
2.6376
3.9878
0.6309
1.5437
0.9779
1.9638
1.8914
6.6838
6.0
f2 / ppm

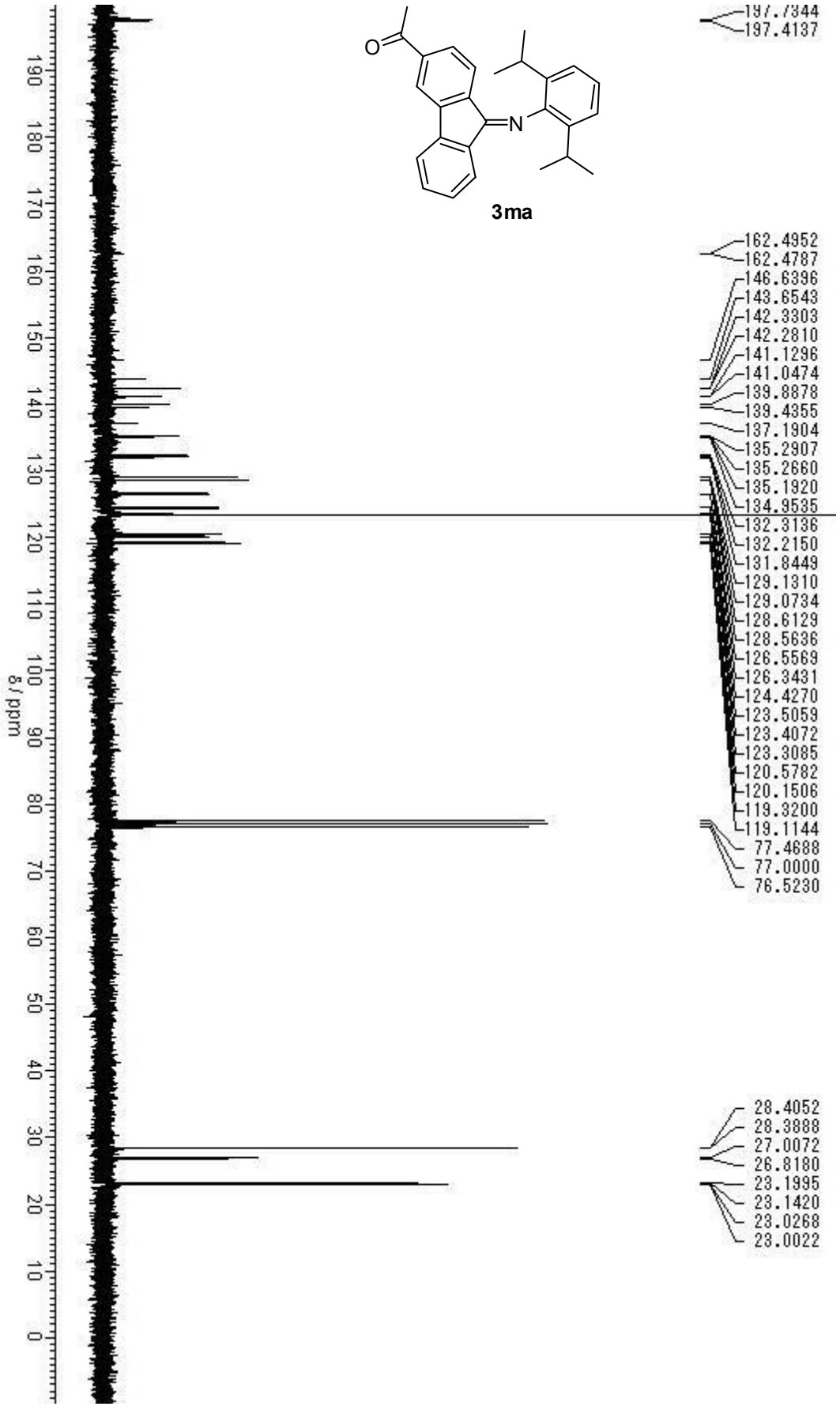

O
N
3la
δ / ppm
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

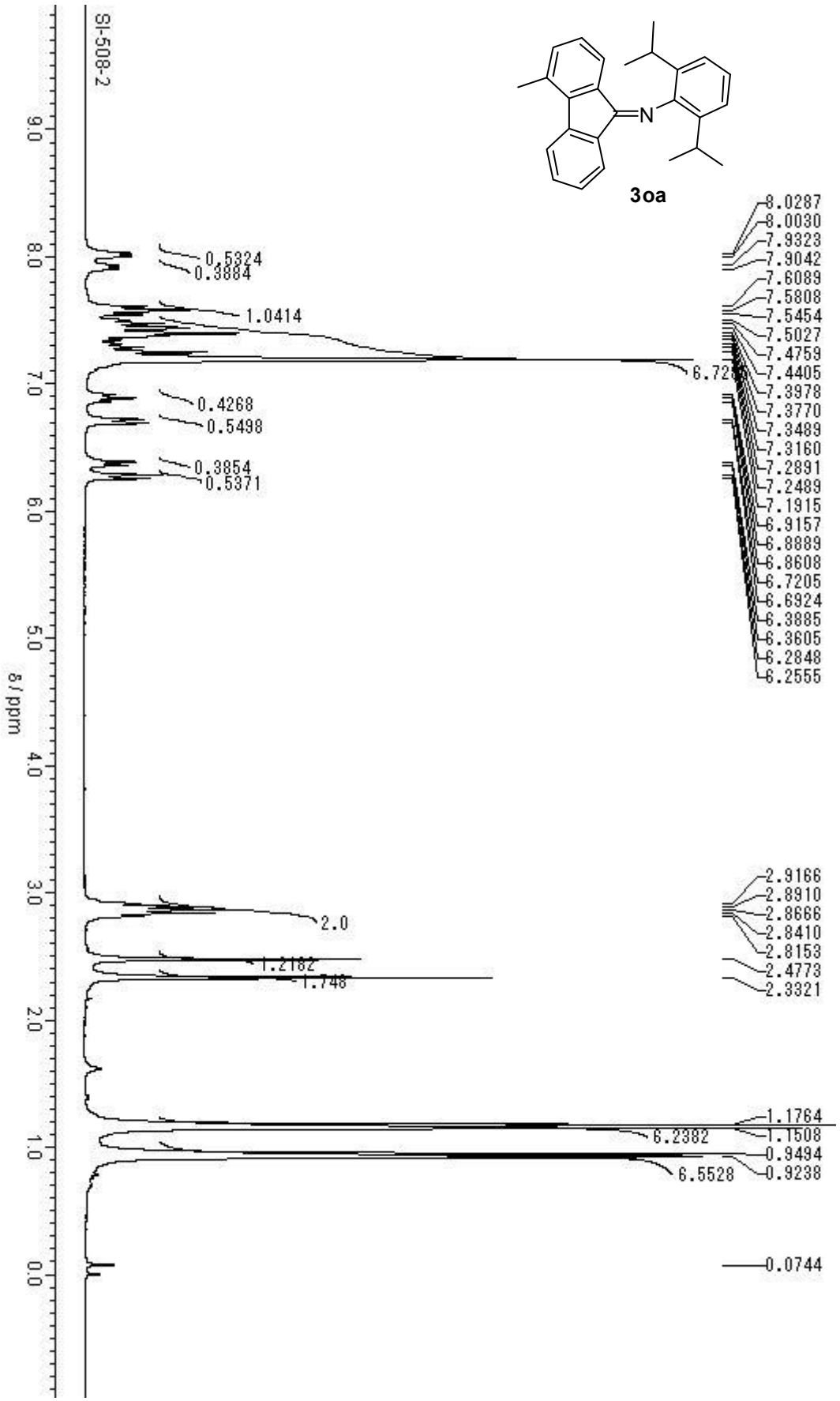

SI-517-2
f1 (ppm)
1.0
1.1937
2.5601
3.1068
0.9906
0.9514
0.8224
2.7632
1.9989
6.531
6.4982
7.5796
7.5527
7.4759
7.4466
7.4173
7.3001
7.2745
7.2562
7.2489
7.1720
6.9841
6.9535
6.9096
6.8828
6.8547
6.3360
6.3080
4.0333
2.9618
2.9362
2.9118
2.8861
2.8617
1.2008
1.1764
0.9201
0.8957
N
O

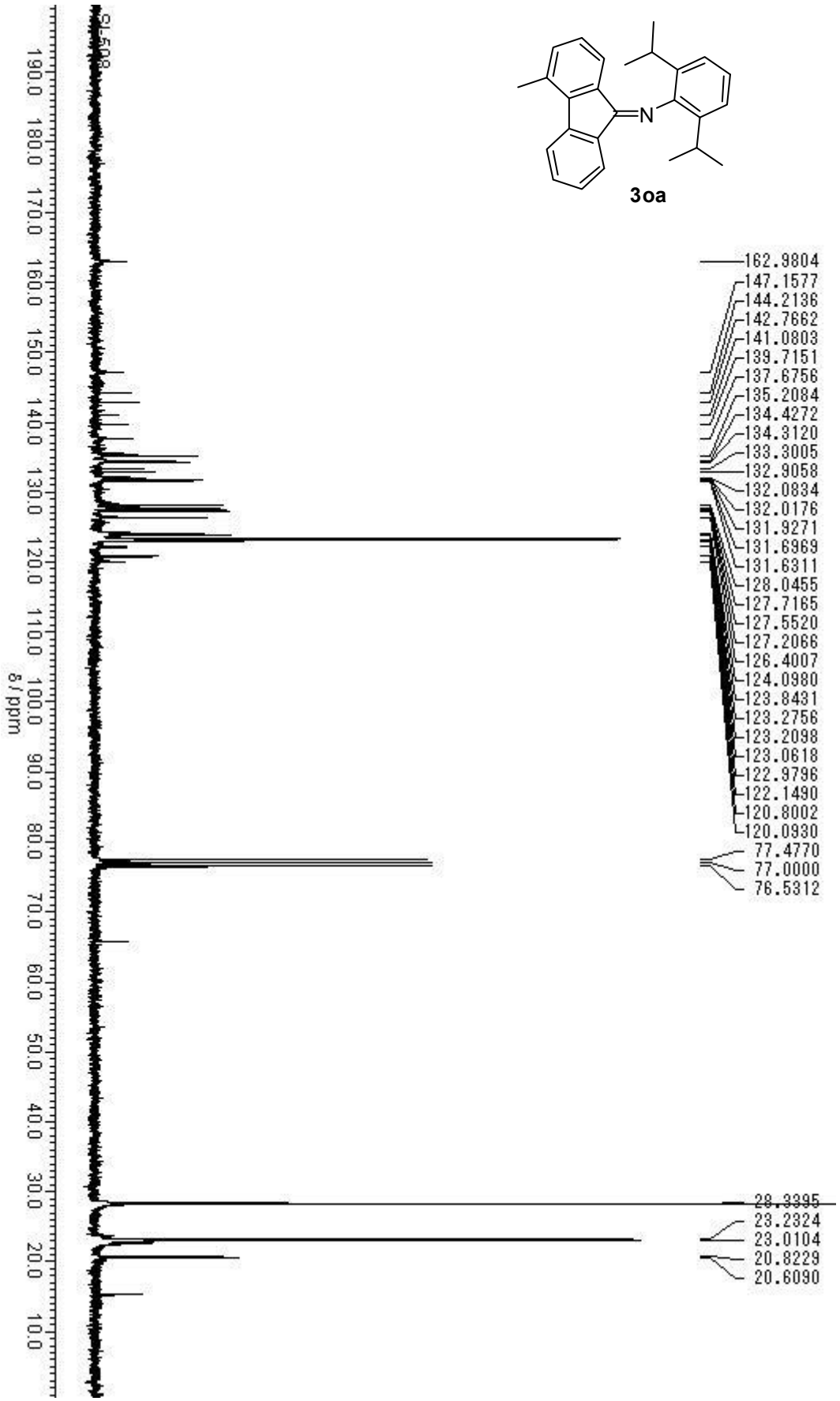
4la


N
O
4la
158.5395
144.3123
142.2069
136.3187
134.9206
134.8795
133.1114
131.9600
131.0965
127.9632
126.5816
123.6704
123.6128
123.5881
123.2510
119.8545
119.4598
112.6998
112.2474
108.1026
77.4688
77.1974
77.0000
76.3914
76.2187
76.1941
67.0903
56.1608
56.1525
28.2901
23.5203
23.4051
22.9528
22.7801
δ / ppm


O
N
3ma
8.2251
8.1800
8.1666
8.1373
8.1043
8.0763
8.0128
7.9847
7.7419
7.7126
7.6821
7.5784
7.5540
7.5283
7.5051
7.4734
7.4478
7.4185
7.3990
7.3733
7.3465
7.2562
7.2245
6.9963
6.9682
6.9401
6.4776
6.4495
6.4239
2.0009
0.5352
1.0568
2.0353
3.1605
0.5169
0.9438
2.8800
2.8544
2.8288
2.8031
2.7787
2.7519
2.7104
2.6726
2.5847
2.0453
1.2545
1.2423
1.1882
1.1606
0.9568
0.9458
0.9311
0.9214
0.0818
0.0000
f1 (ppm)

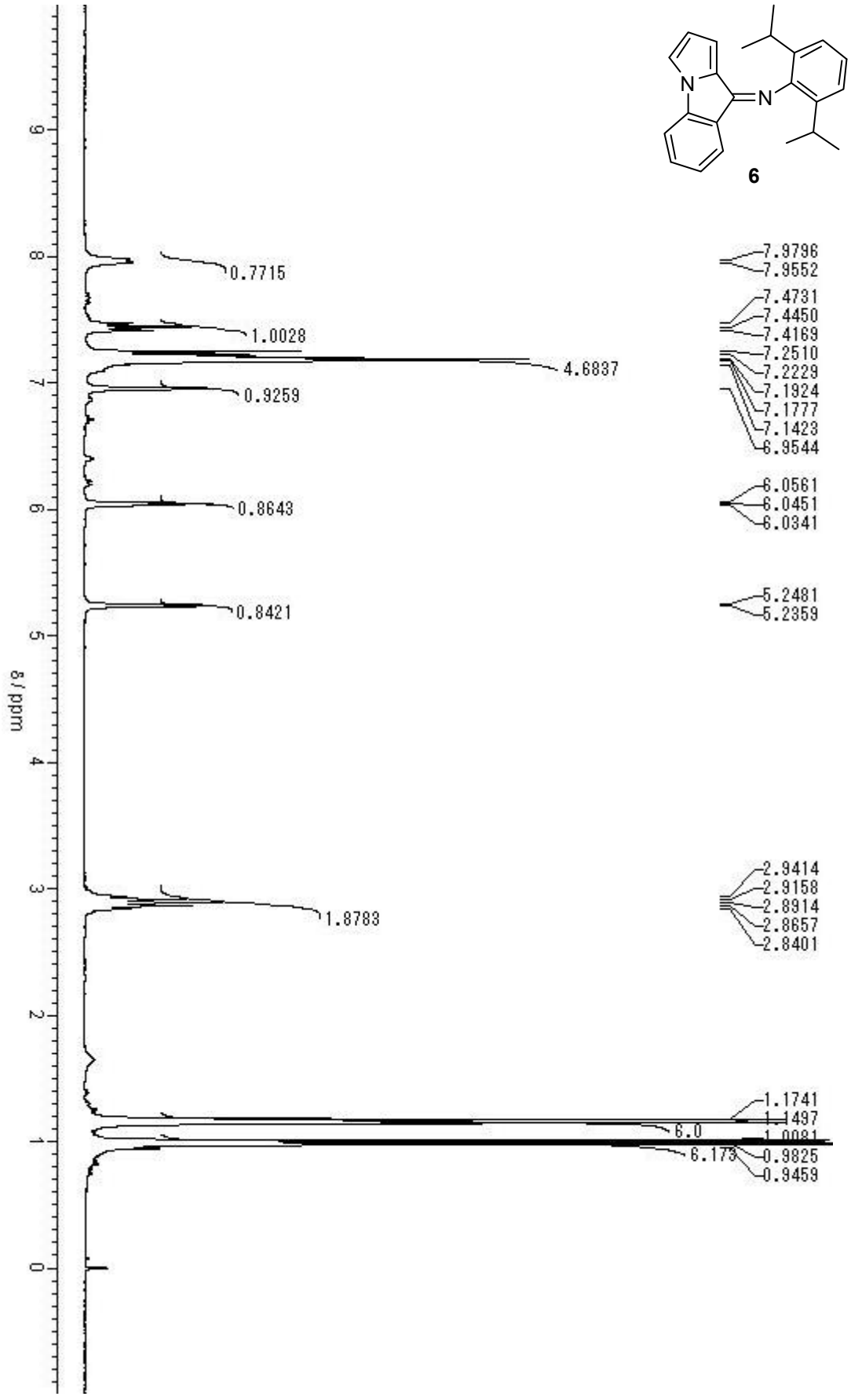

O
N
3ma
197.7844
197.4137
162.4952
162.4787
146.6396
143.6543
142.3303
142.2810
141.1296
141.0474
139.8878
139.4355
137.1904
135.2907
135.2660
135.1920
134.9535
132.3136
132.2150
131.8449
129.1310
129.0734
128.6129
128.5636
126.5569
126.3431
124.4270
123.5059
123.4072
123.3085
120.5782
120.1506
119.3200
119.1144
77.4688
77.0000
76.5230
28.4052
28.3888
27.0072
26.8180
23.1995
23.1420
23.0268
23.0022
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
δ / ppm

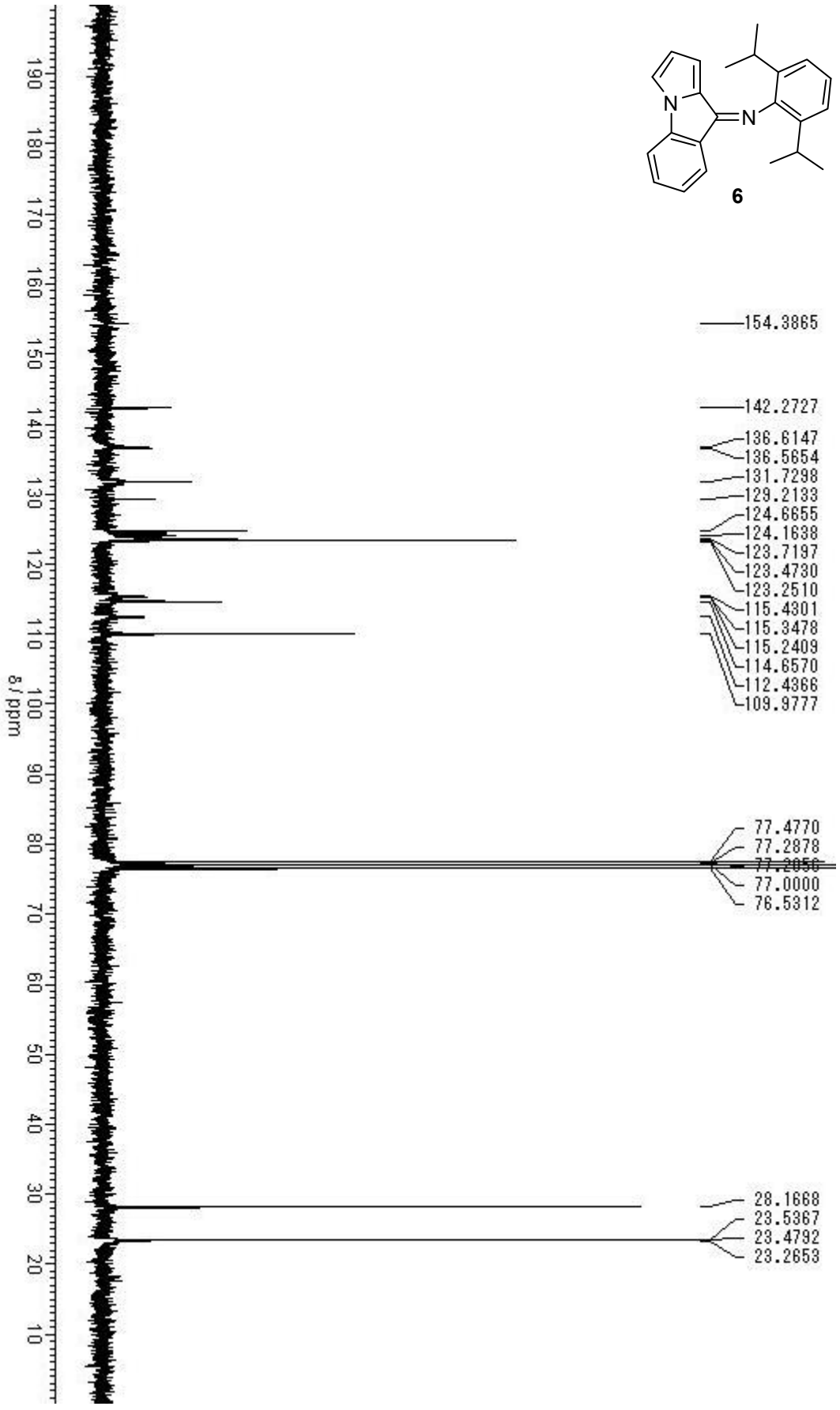

SI-508-2
3oa
N
δ / ppm
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
8.0287
8.0030
7.9323
7.9042
7.6089
7.5808
7.5454
7.5027
7.4759
7.4405
7.3978
7.3770
7.3489
7.3160
7.2891
7.2489
7.1915
6.9157
6.8889
6.8608
6.7205
6.6924
6.3885
6.3605
6.2848
6.2555
0.5324
0.3884
1.0414
0.4268
0.5498
0.3854
0.5371
2.0
1.2162
1.748
2.9166
2.8910
2.8666
2.8410
2.8153
2.4773
2.3321
1.1764
6.2382
1.1508
0.9494
6.5528
0.9238
0.0744

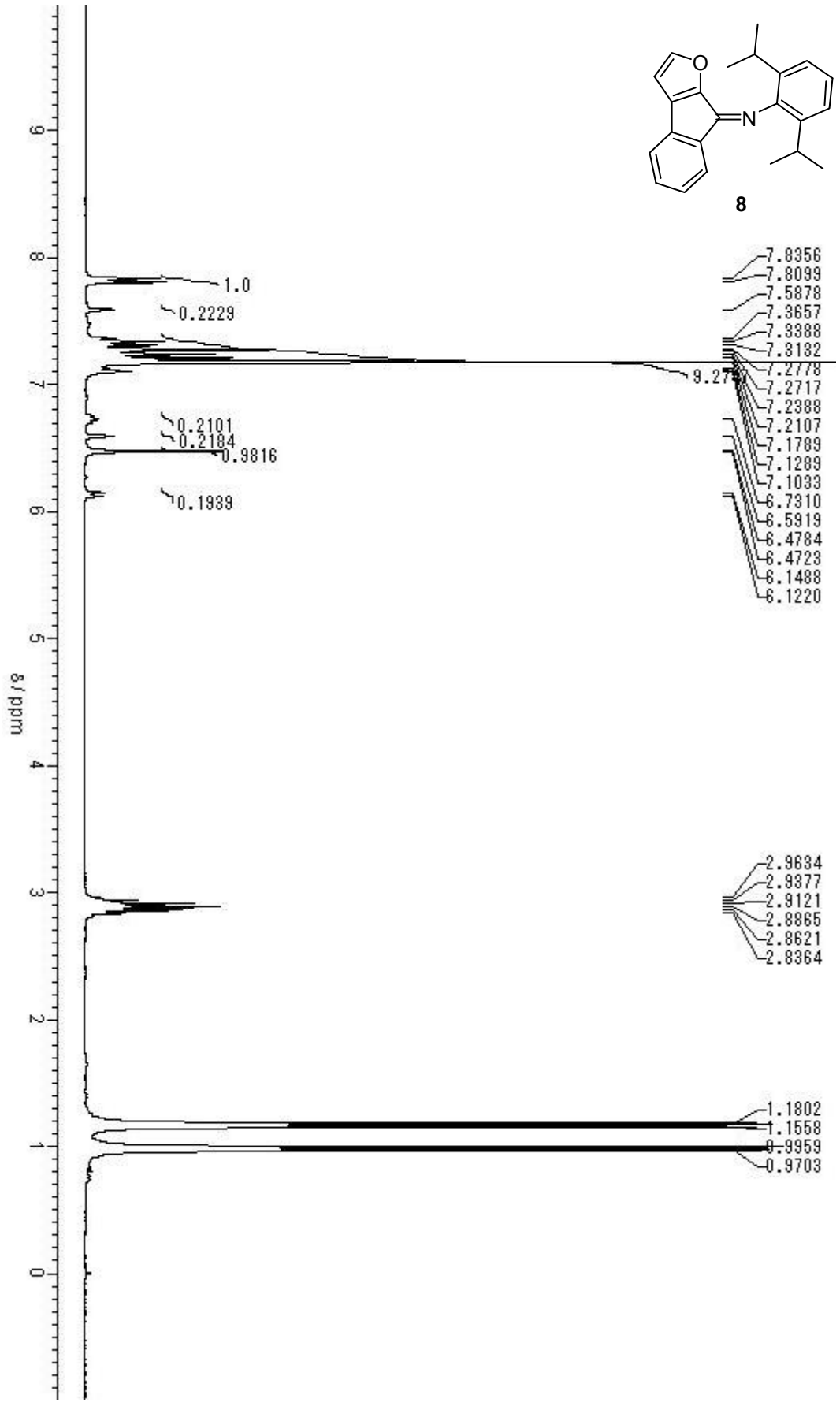

SL-508
δ f ppm
162.9804
147.1577
144.2136
142.7662
141.0803
139.7151
137.6756
135.2084
134.4272
134.3120
133.3005
132.9058
132.0834
132.0176
131.9271
131.6969
131.6311
128.0455
127.7165
127.5520
127.2066
126.4007
124.0980
123.8431
123.2756
123.2098
123.0618
122.9796
122.1490
120.8002
120.0930
77.4770
77.0000
76.5312
28.3395
23.2324
23.0104
20.8229
20.6090

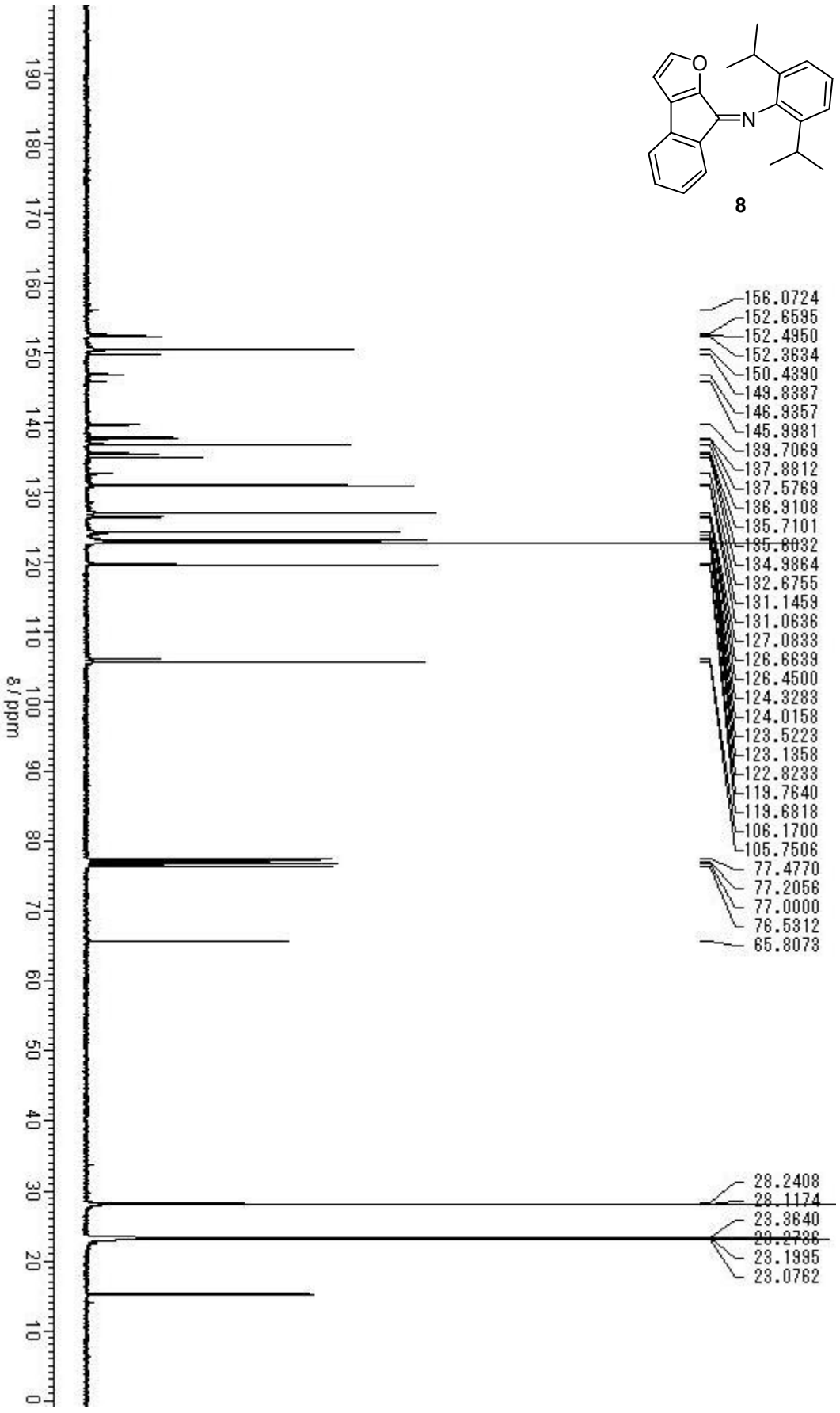
N

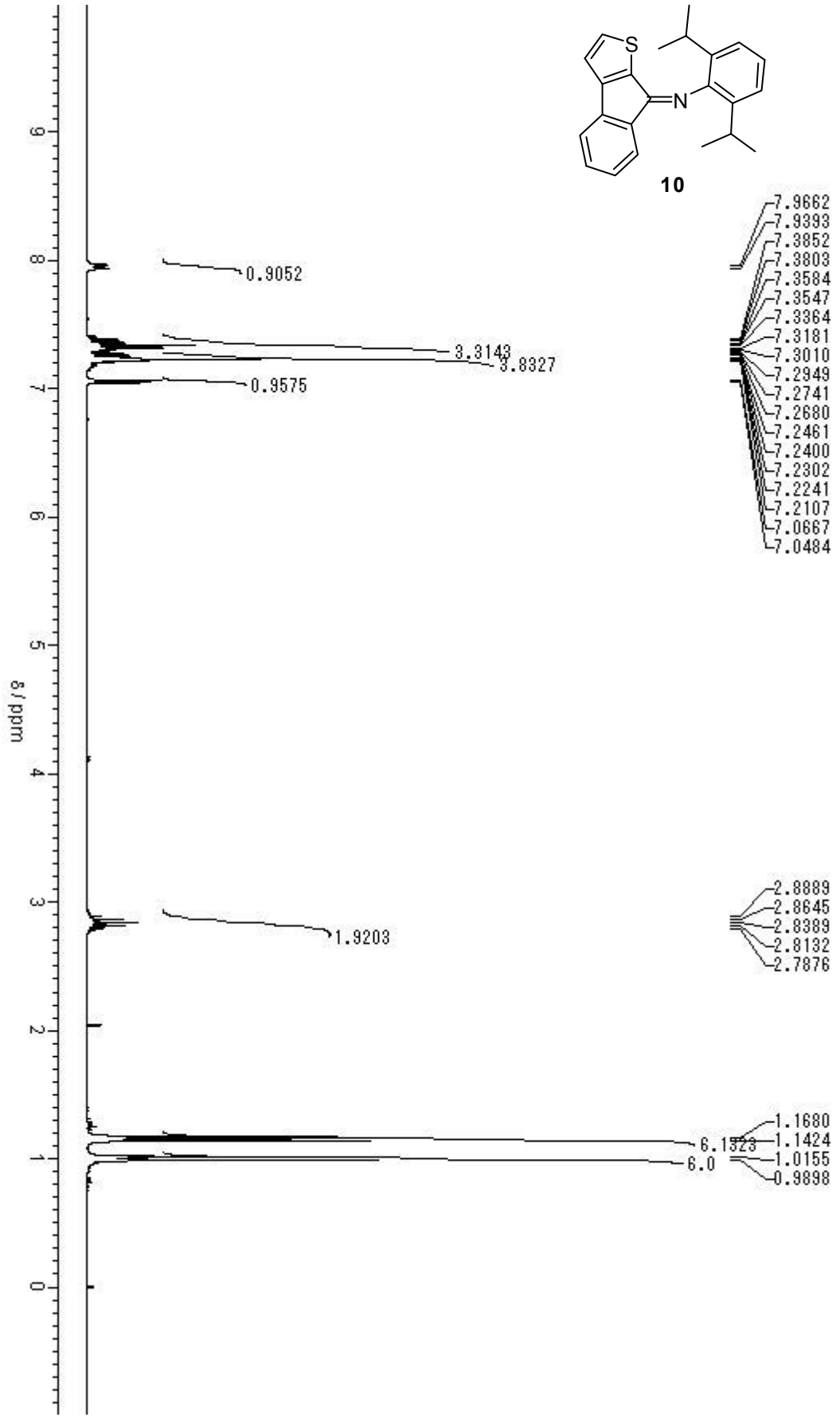
3oa

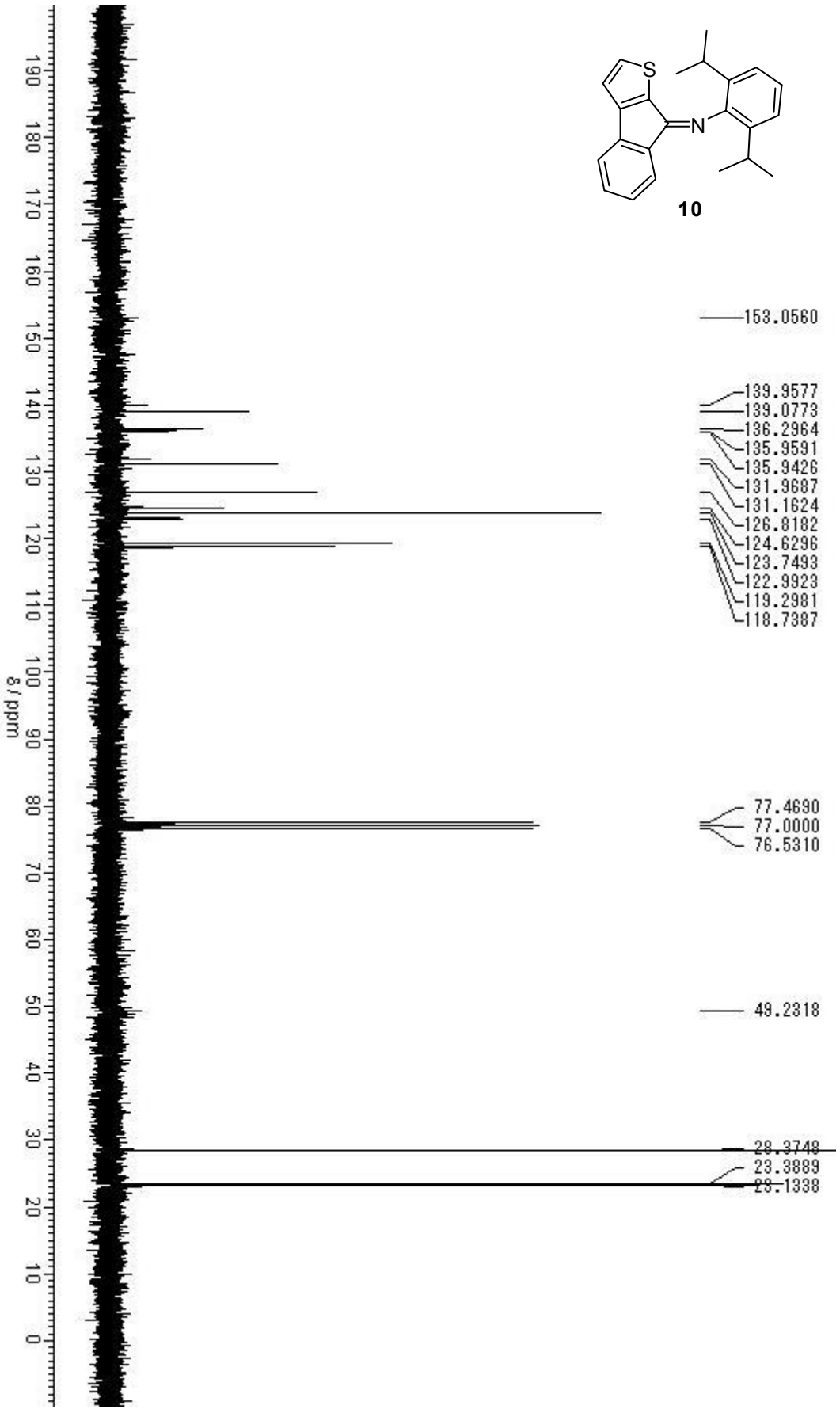

6
7.9796
7.9552
7.4731
7.4450
7.4169
7.2510
7.2229
7.1924
7.1777
7.1423
6.9544
6.0561
6.0451
6.0341
5.2481
5.2359
2.9414
2.9158
2.8914
2.8657
2.8401
1.1741
1.1497
1.0081
0.9825
0.9459
0.7715
1.0028
4.6837
0.9259
0.8643
0.8421
1.8783
6.0
6.173
f1 / ppm

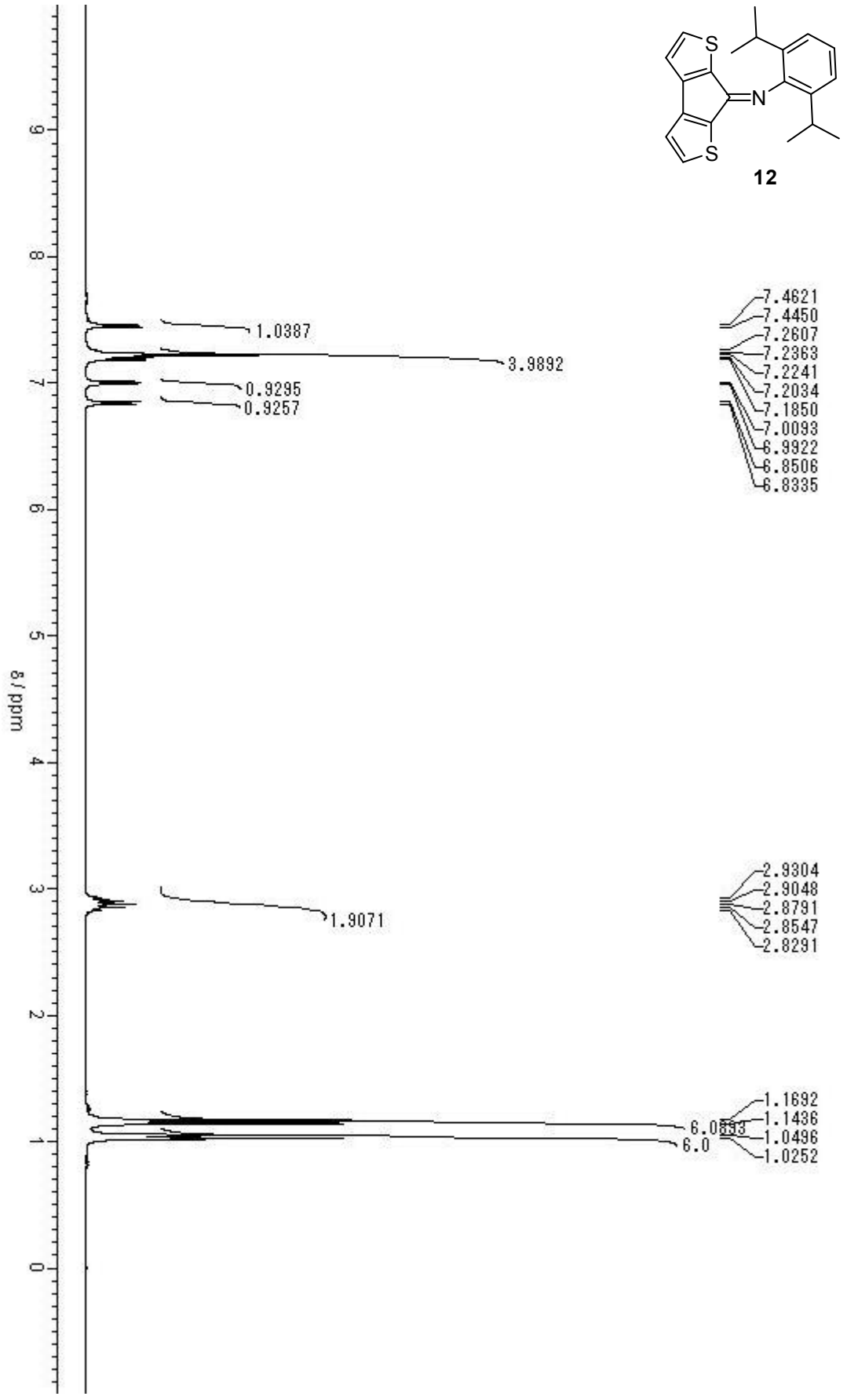

N
N
6
154.3865
142.2727
136.6147
136.5654
131.7298
129.2133
124.6655
124.1638
123.7197
123.4730
123.2510
115.4301
115.3478
115.2409
114.6570
112.4366
109.9777
77.4770
77.2878
77.2056
77.0000
76.5312
28.1668
23.5367
23.4792
23.2653
f1 / ppm

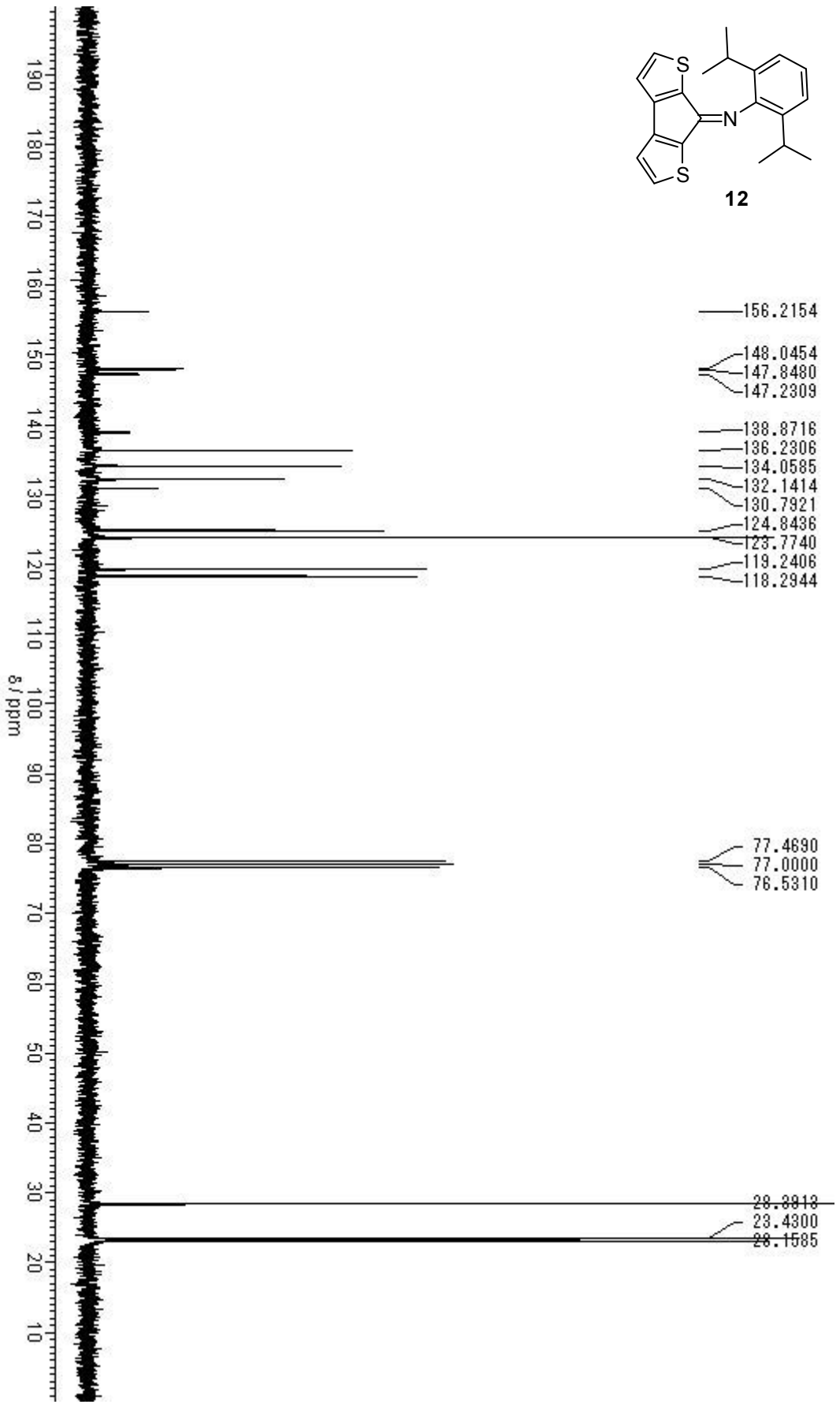

8
7.8356
7.8099
7.5878
7.3657
7.3388
7.3132
7.2778
7.2717
7.2388
7.2107
7.1789
7.1289
7.1033
6.7310
6.5919
6.4784
6.4723
6.1488
6.1220
2.9634
2.9377
2.9121
2.8865
2.8621
2.8364
1.1802
1.1558
0.9959
0.9703
1.0
0.2229
0.2101
0.2184
0.9816
0.1939
f1 (ppm)

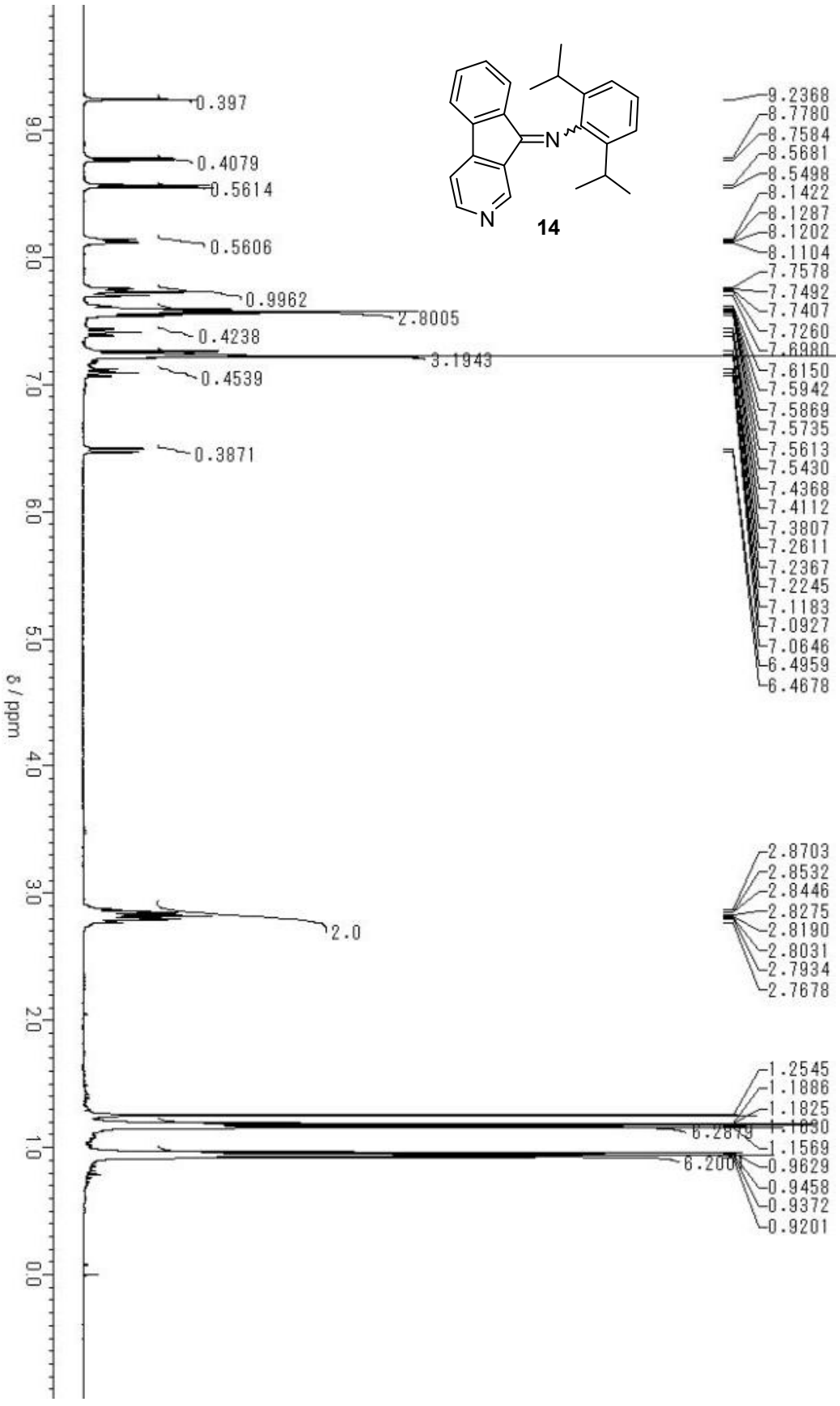

O
N
8
156.0724
152.6595
152.4950
152.3634
150.4390
149.8387
146.9357
145.9981
139.7069
137.8812
137.5769
136.9108
135.7101
135.6032
134.9864
132.6755
131.1459
131.0636
127.0833
126.6639
126.4500
124.3283
124.0158
123.5223
123.1358
122.8233
119.7640
119.6818
106.1700
105.7506
77.4770
77.2056
77.0000
76.5312
65.8073
28.2408
28.1174
23.3640
23.2736
23.1995
23.0762
δ / ppm

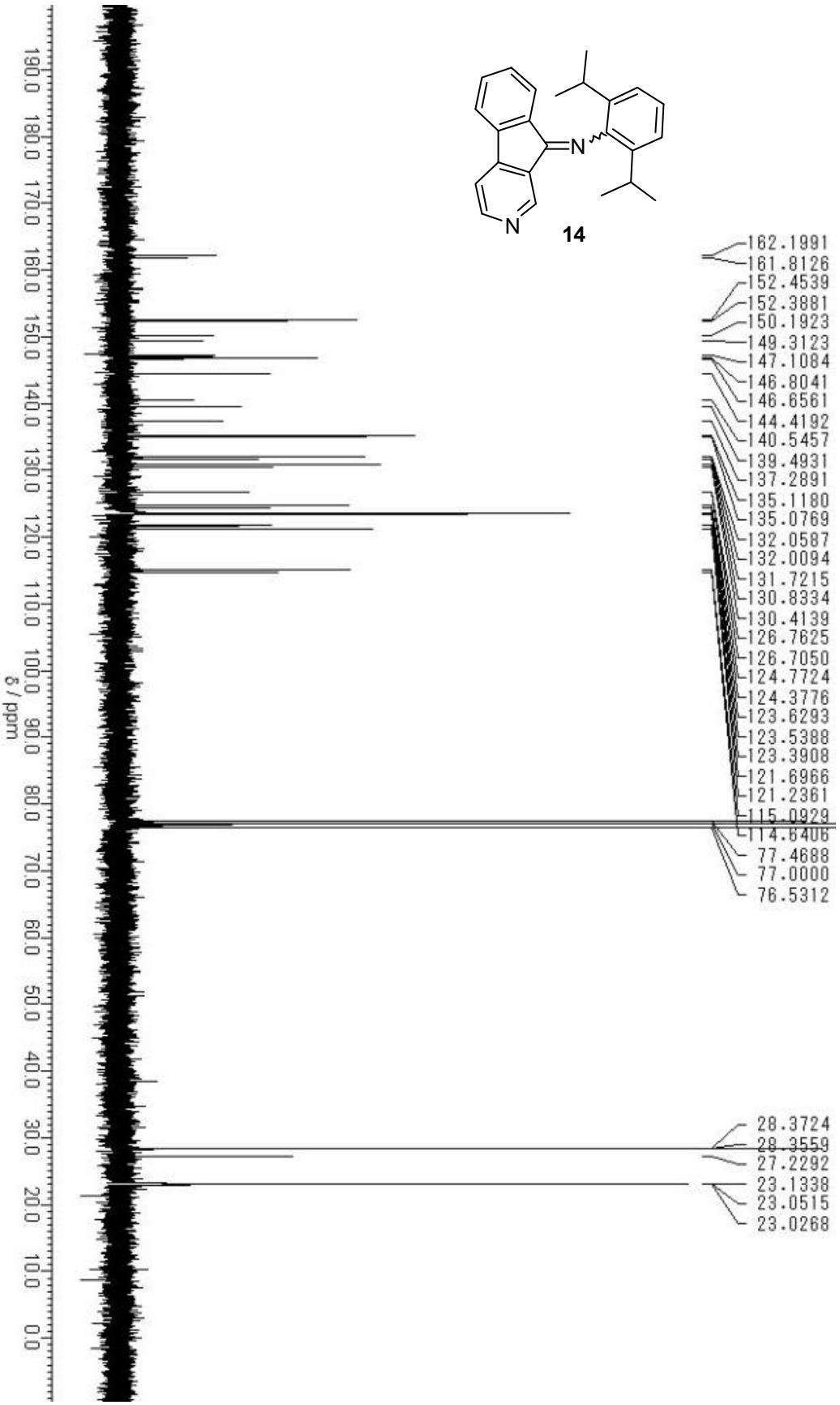

S
N
10
7.9662
7.9393
7.3852
7.3803
7.3584
7.3547
7.3364
7.3181
7.3010
7.2949
7.2741
7.2680
7.2461
7.2400
7.2302
7.2241
7.2107
7.0667
7.0484
0.9052
3.3143
3.8327
0.9575
1.9203
2.8889
2.8645
2.8389
2.8132
2.7876
1.1680
6.1523
1.1424
6.0
1.0155
0.9898
f1 / ppm

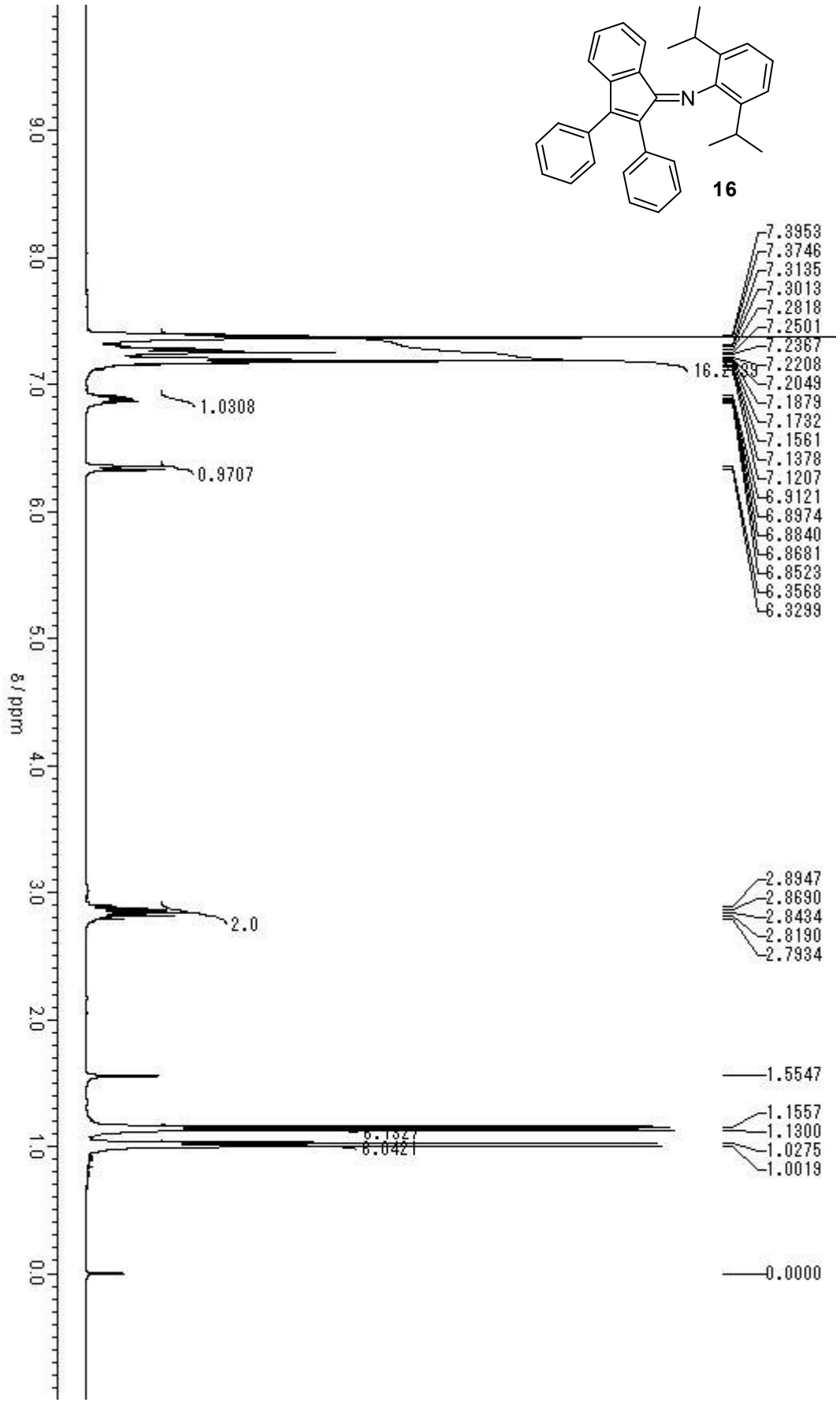

S
N
10
153.0560
139.9577
139.0773
136.2964
135.9591
135.9426
131.9687
131.1624
126.8182
124.6296
123.7493
122.9923
119.2981
118.7387
77.4690
77.0000
76.5310
49.2318
28.3748
23.3889
23.1338
f1 / ppm

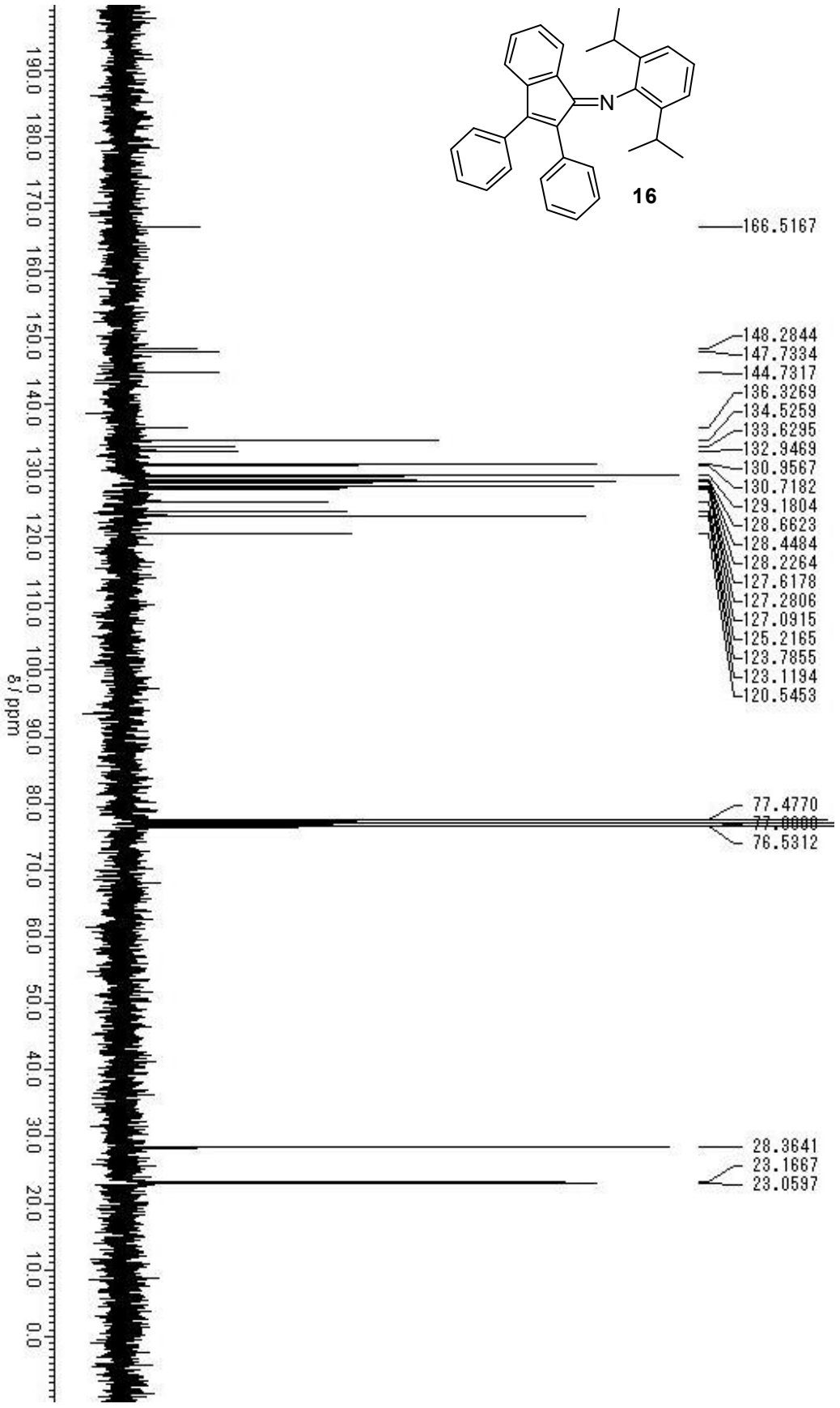

S
N
S
12
7.4621
7.4450
7.2607
7.2363
7.2241
7.2034
7.1850
7.0093
6.9922
6.8506
6.8335
1.0387
3.9892
0.9295
0.9257
1.9071
2.9304
2.9048
2.8791
2.8547
2.8291
1.1692
1.1436
1.0496
1.0252
6.0
f1 / ppm

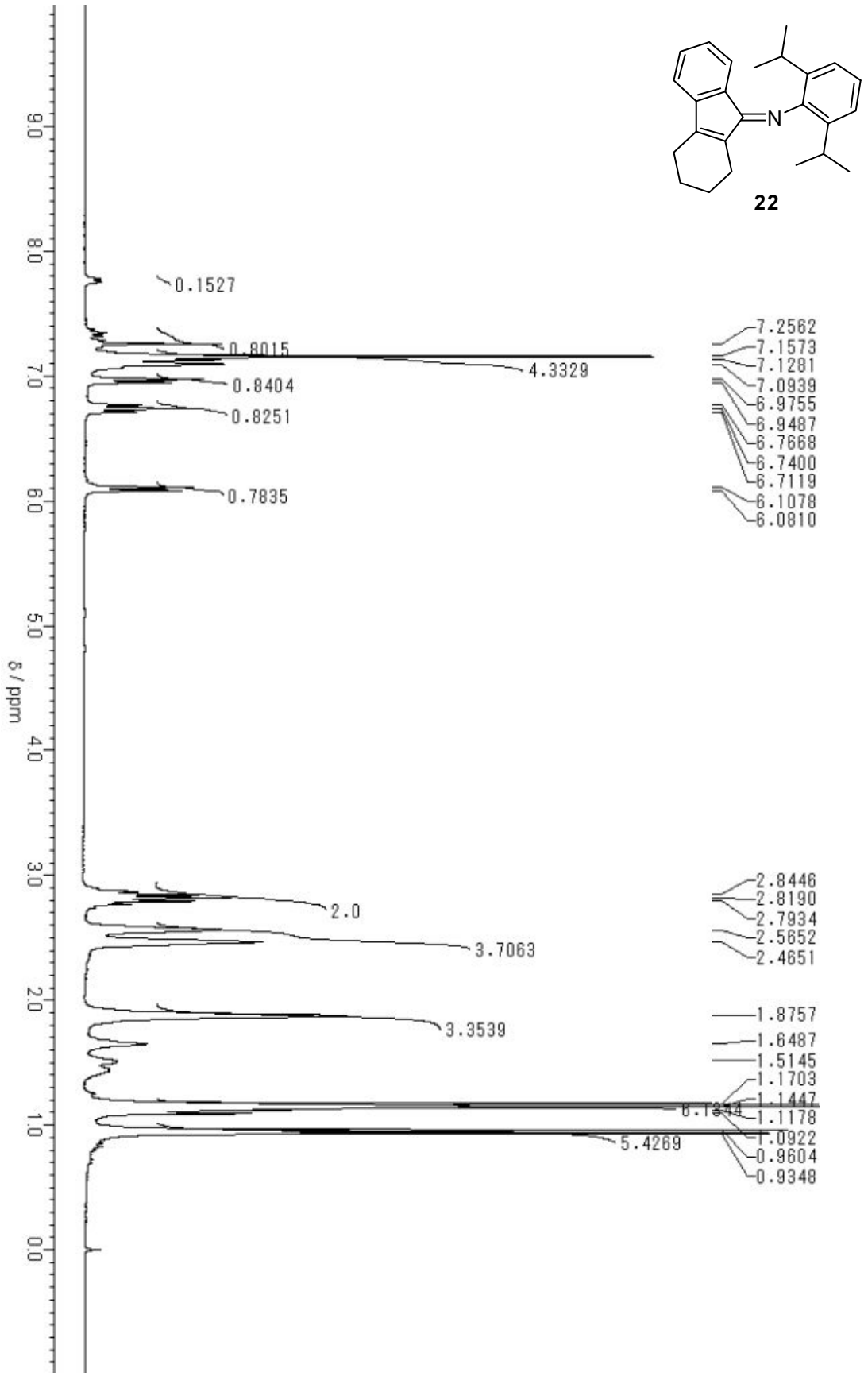

S
N
S
12
156.2154
148.0454
147.8480
147.2309
138.8716
136.2306
134.0585
132.1414
130.7921
124.8436
123.7740
119.2406
118.2944
77.4690
77.0000
76.5310
28.8913
23.4300
28.1585
δ / ppm

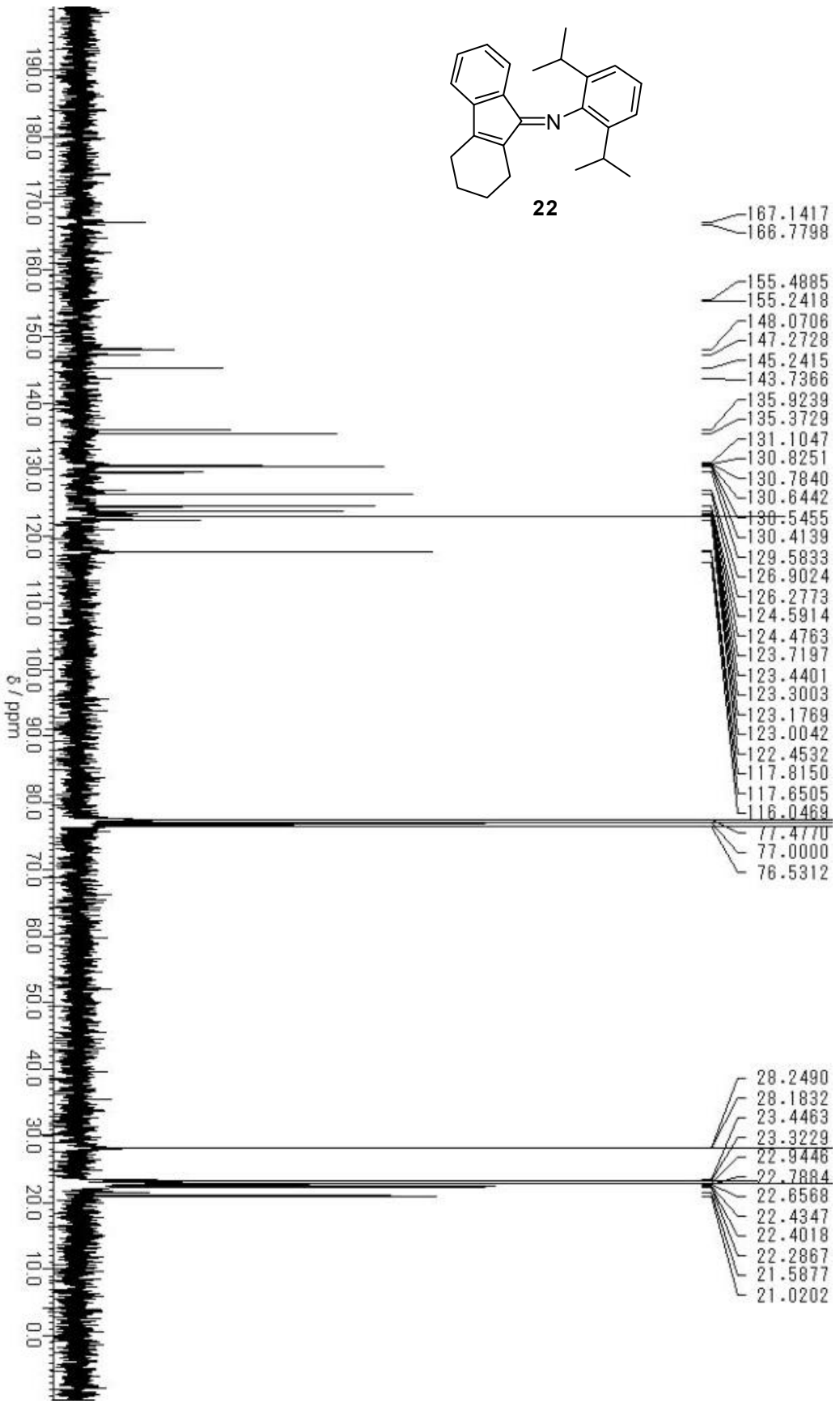

14
δ / ppm
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
0.397
0.4079
0.5614
0.5606
0.9962
2.8005
0.4238
3.1943
0.4539
0.3871
2.0
9.2368
8.7780
8.7584
8.5681
8.5498
8.1422
8.1287
8.1202
8.1104
7.7578
7.7492
7.7407
7.7260
7.6980
7.6150
7.5942
7.5869
7.5735
7.5613
7.5430
7.4368
7.4112
7.3807
7.2611
7.2367
7.2245
7.1183
7.0927
7.0646
6.4959
6.4678
2.8703
2.8532
2.8446
2.8275
2.8190
2.8031
2.7934
2.7678
1.2545
1.1886
1.1825
1.1569
0.9629
0.9458
0.9372
0.9201

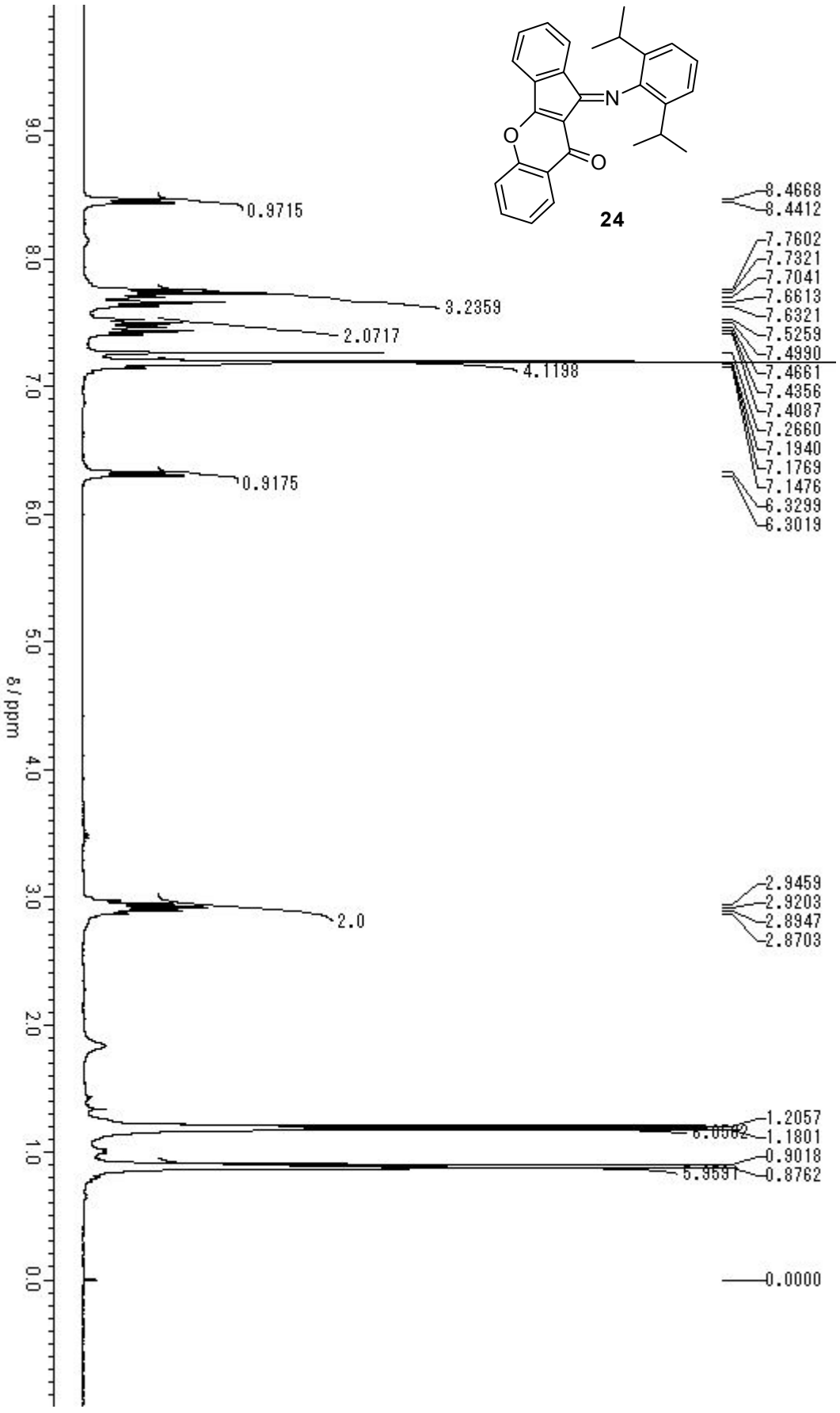

N
N
14
δ / ppm
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
162.1991
161.8126
152.4539
152.3881
150.1923
149.3123
147.1084
146.8041
146.6561
144.4192
140.5457
139.4931
137.2891
135.1180
135.0769
132.0587
132.0094
131.7215
130.8334
130.4139
126.7625
126.7050
124.7724
124.3776
123.6293
123.5388
123.3908
121.6966
121.2361
115.0929
114.6406
77.4688
77.0000
76.5312
28.3724
28.3559
27.2292
23.1338
23.0515
23.0268

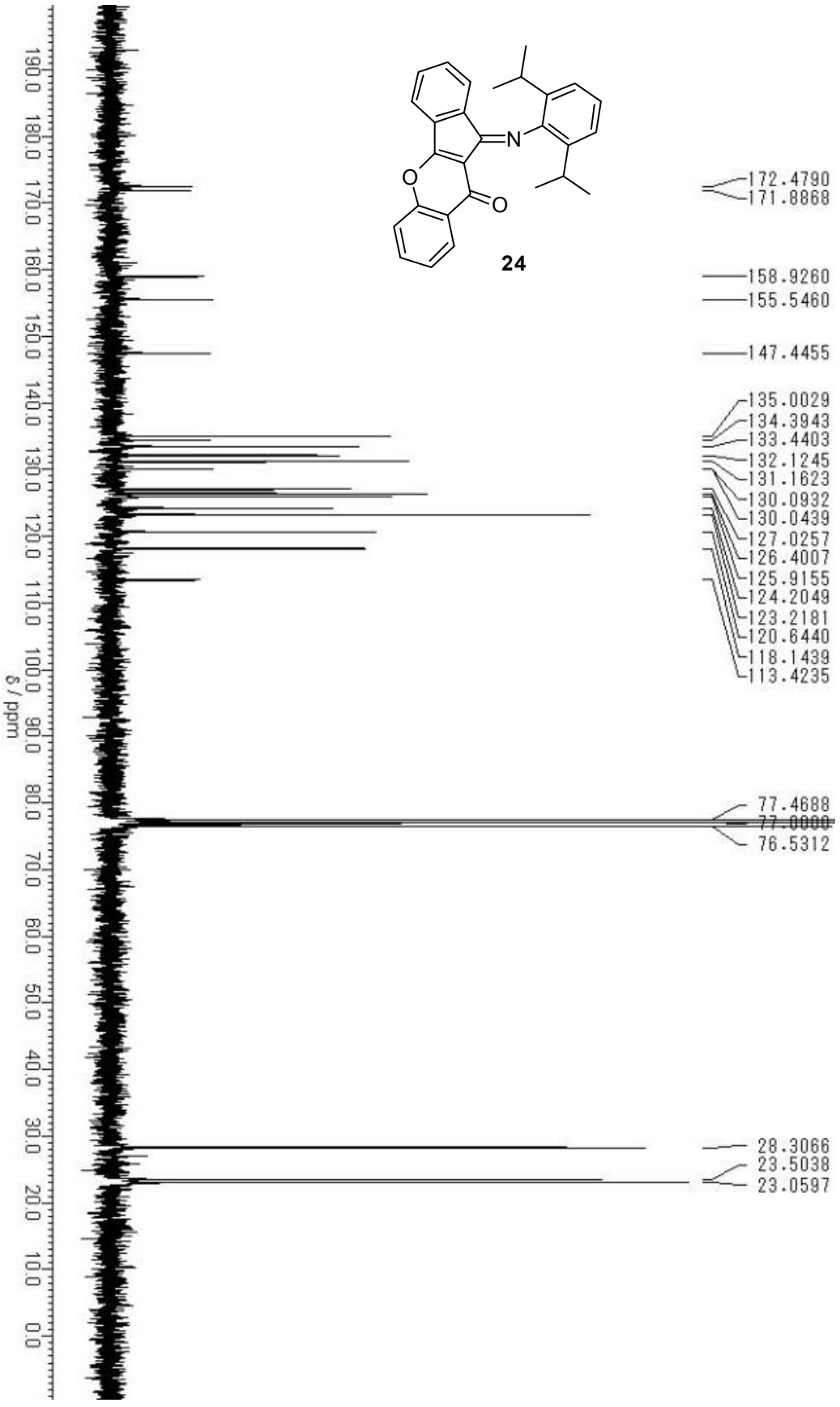

N
16
7.3953
7.3746
7.3135
7.3013
7.2818
7.2501
7.2367
7.2208
7.2049
7.1879
7.1732
7.1561
7.1378
7.1207
6.9121
6.8974
6.8840
6.8681
6.8523
6.3568
6.3299
16.
1.0308
0.9707
2.0
2.8947
2.8690
2.8434
2.8190
2.7934
1.5547
1.1557
1.1300
1.0275
1.0019
0.0000
δ / ppm

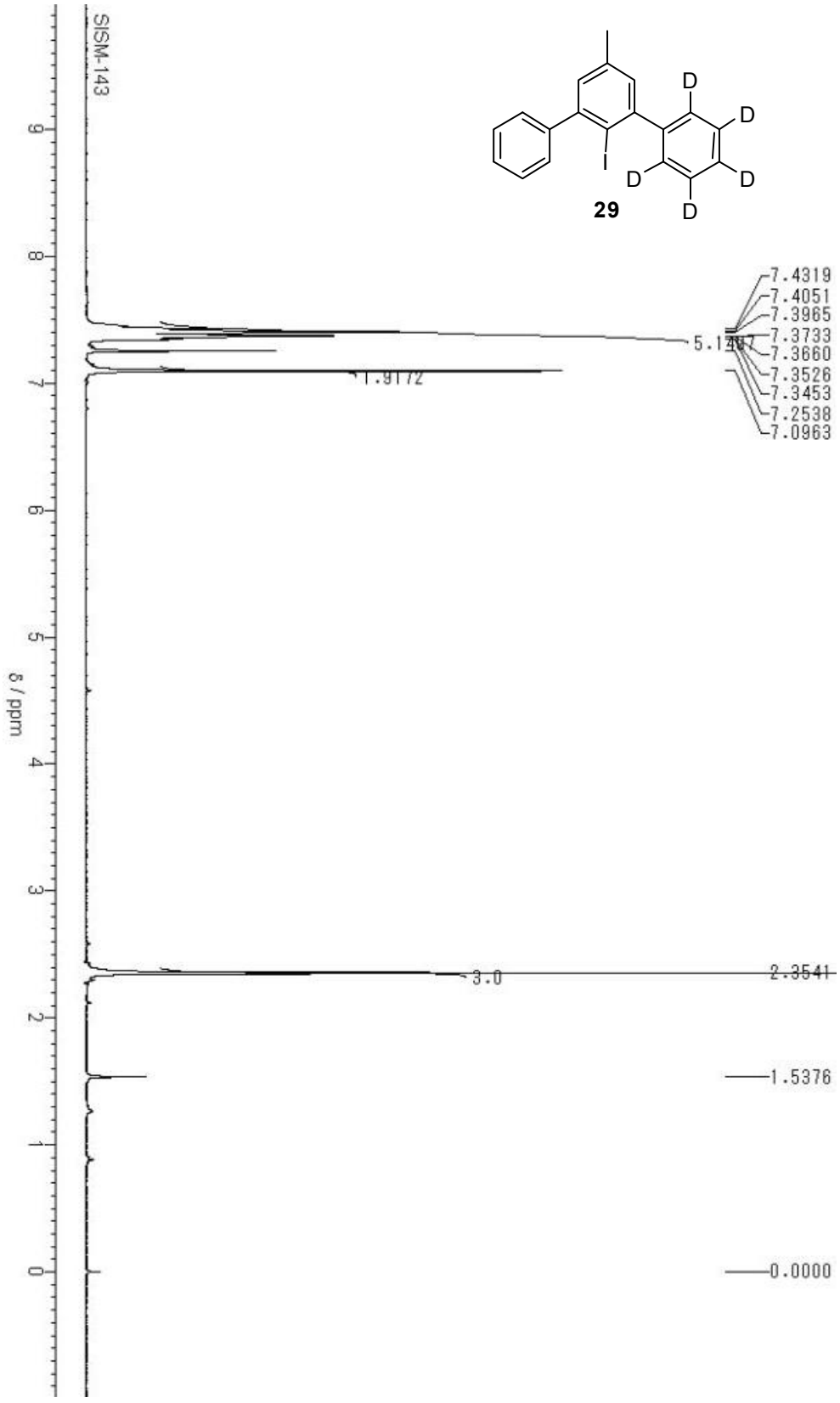

N
16
166.5167
148.2844
147.7334
144.7317
136.3269
134.5259
133.6295
132.9469
130.9567
130.7182
129.1804
128.6623
128.4484
128.2264
127.6178
127.2806
127.0915
125.2165
123.7855
123.1194
120.5453
77.4770
77.0000
76.5312
28.3641
23.1667
23.0597
δ / ppm

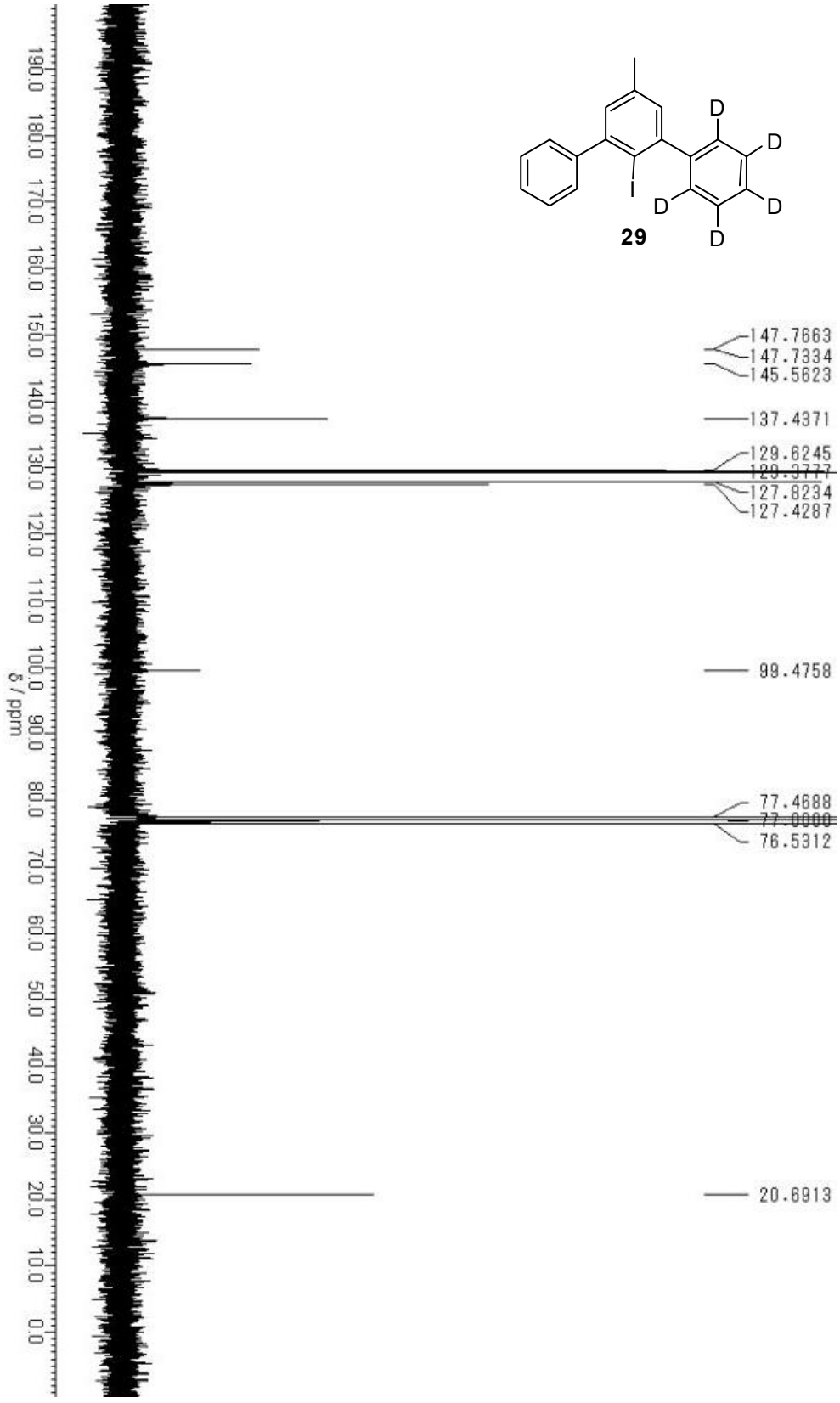

N
22
δ / ppm
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
0.1527
0.8015
4.3329
0.8404
0.8251
0.7835
2.0
3.7063
3.3539
5.4269
7.2562
7.1573
7.1281
7.0939
6.9755
6.9487
6.7668
6.7400
6.7119
6.1078
6.0810
2.8446
2.8190
2.7934
2.5652
2.4651
1.8757
1.6487
1.5145
1.1703
1.1178
1.0922
0.9604
0.9348

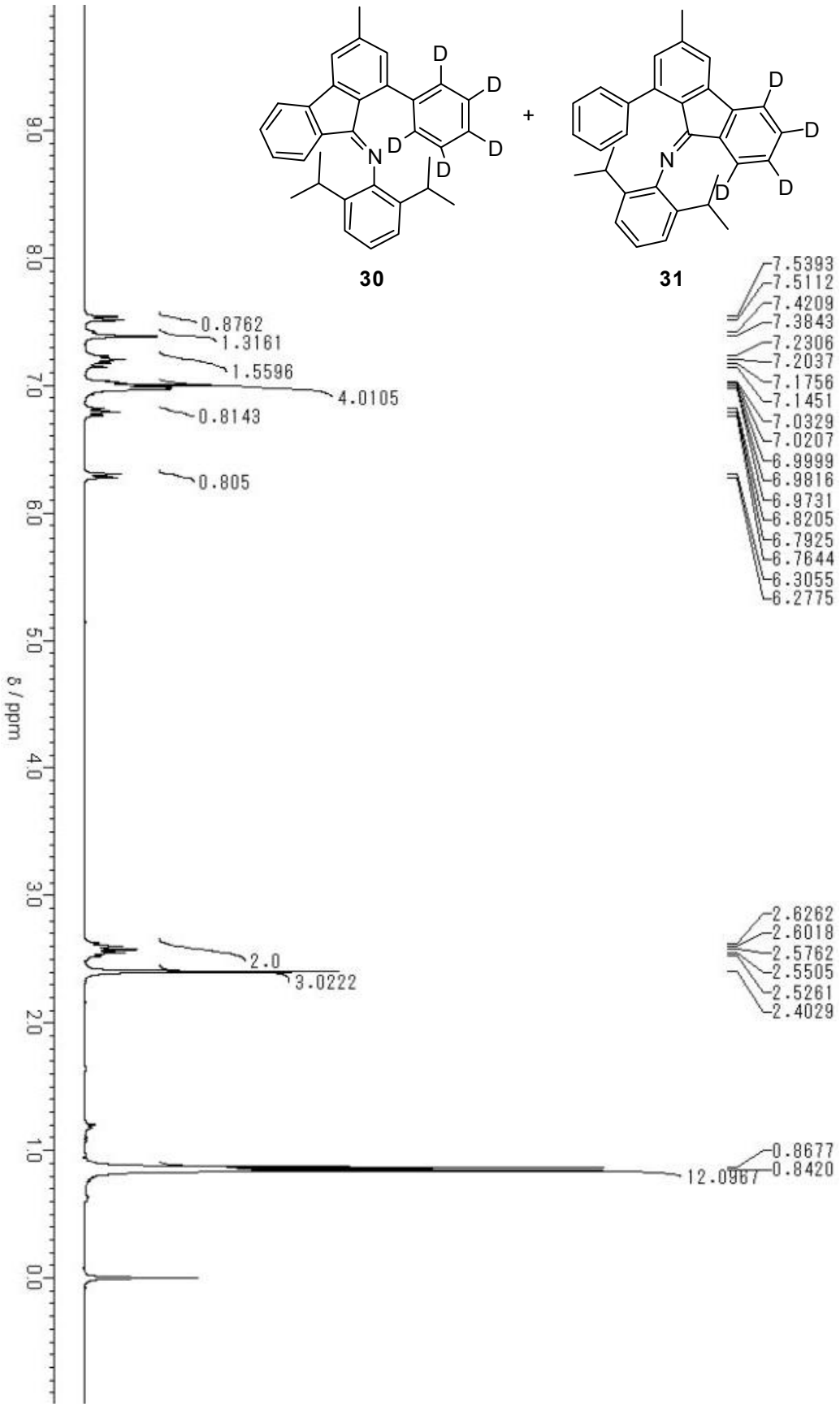

N
22
167.1417
166.7798
155.4885
155.2418
148.0706
147.2728
145.2415
143.7366
135.9239
135.3729
131.1047
130.8251
130.7840
130.6442
130.5455
130.4139
129.5833
126.9024
126.2773
124.5914
124.4763
123.7197
123.4401
123.3003
123.1769
123.0042
122.4532
117.8150
117.6505
116.0469
77.4770
77.0000
76.5312
28.2490
28.1832
23.4463
23.3229
22.9446
22.7884
22.6568
22.4347
22.4018
22.2867
21.5877
21.0202
δ / ppm

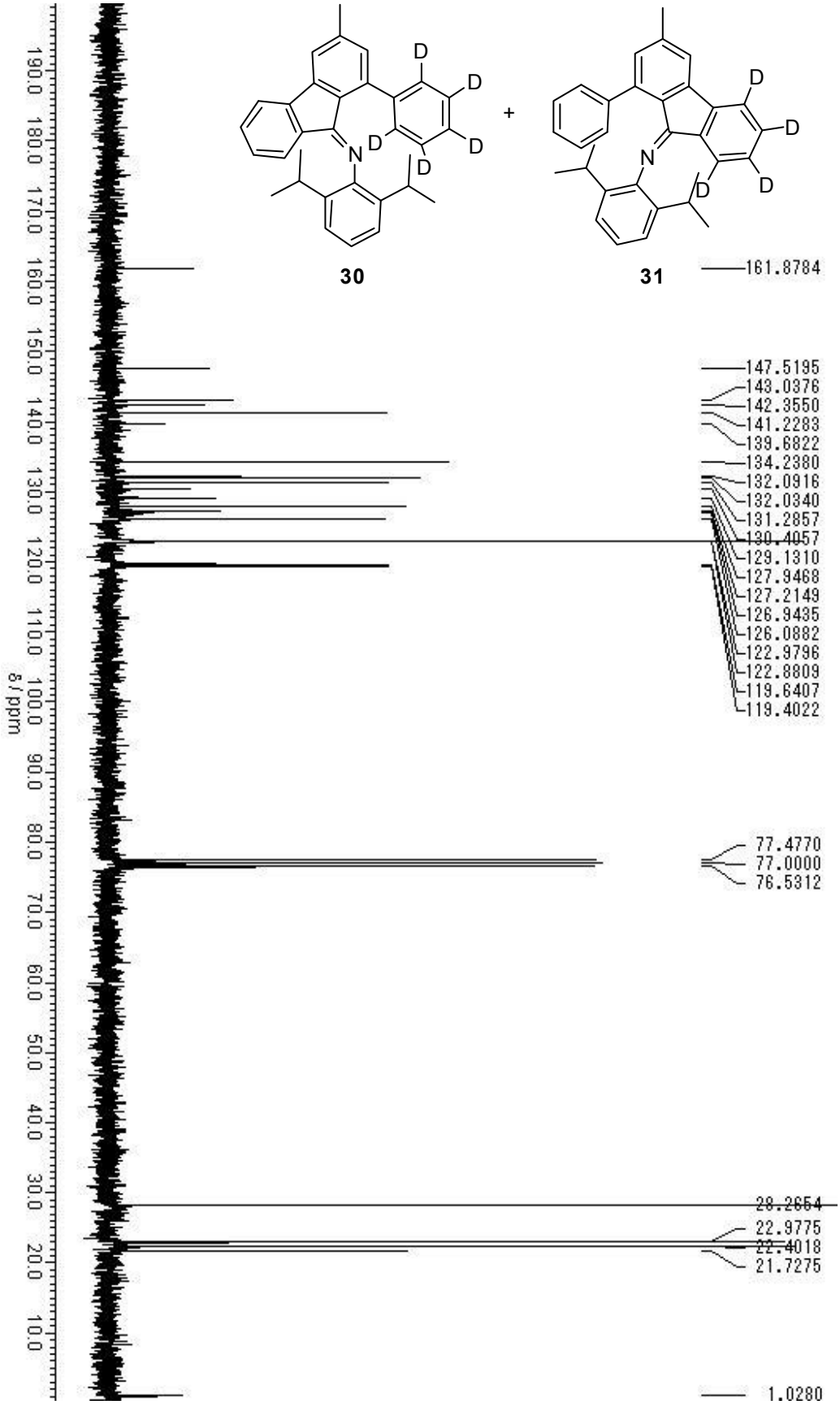

24
8.4668
8.4412
7.7602
7.7321
7.7041
7.6613
7.6321
7.5259
7.4990
7.4661
7.4356
7.4087
7.2660
7.1940
7.1769
7.1476
6.3299
6.3019
2.9459
2.9203
2.8947
2.8703
1.2057
1.1801
0.9018
0.8762
0.0000
0.9715
3.2359
2.0717
4.1198
0.9175
2.0
δ / ppm

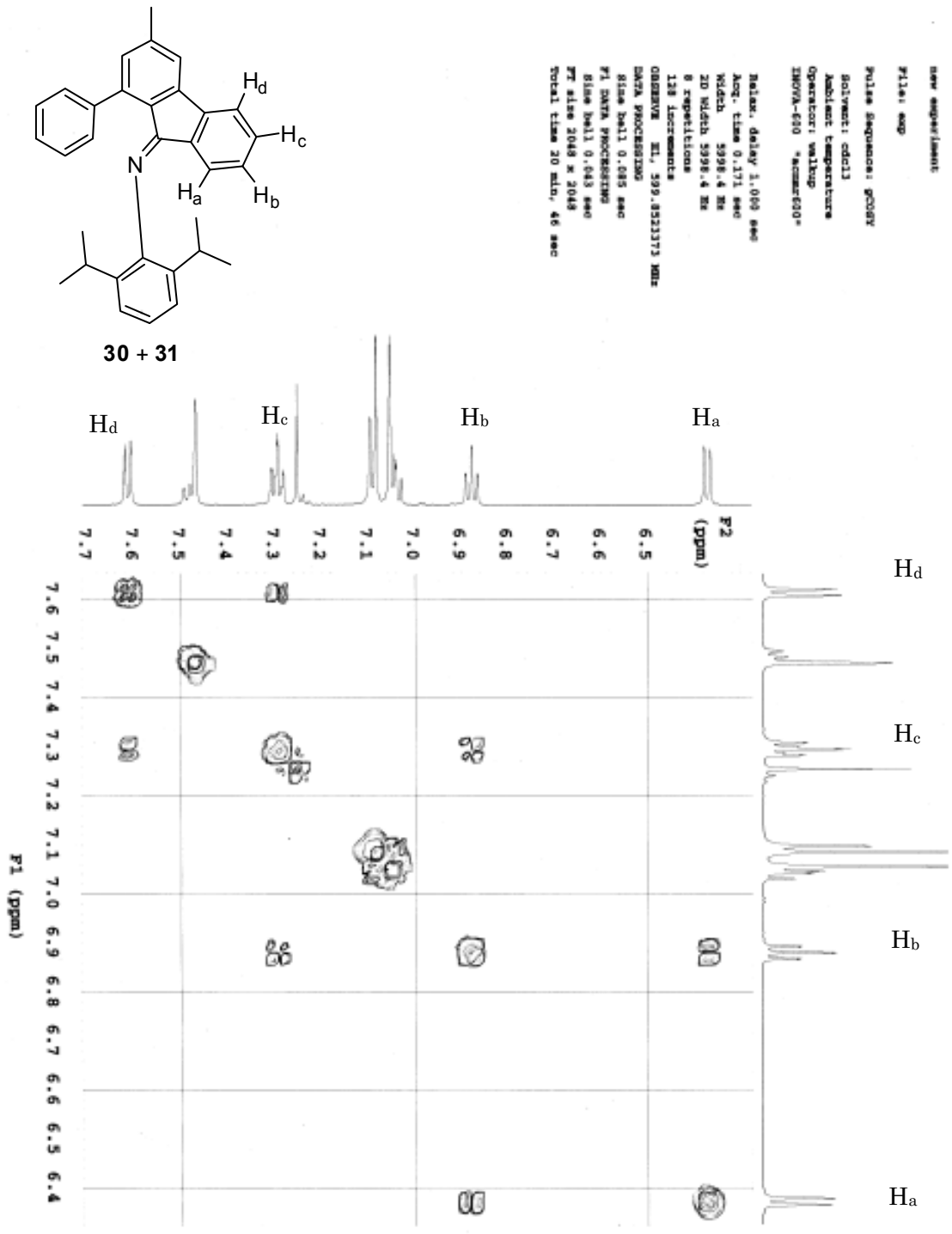

O
N
O
24
172.4790
171.8868
158.9260
155.5460
147.4455
135.0029
134.3943
133.4403
132.1245
131.1623
130.0932
130.0439
127.0257
126.4007
125.9155
124.2049
123.2181
120.6440
118.1439
113.4235
77.4688
77.0000
76.5312
28.3066
23.5038
23.0597
δ / ppm

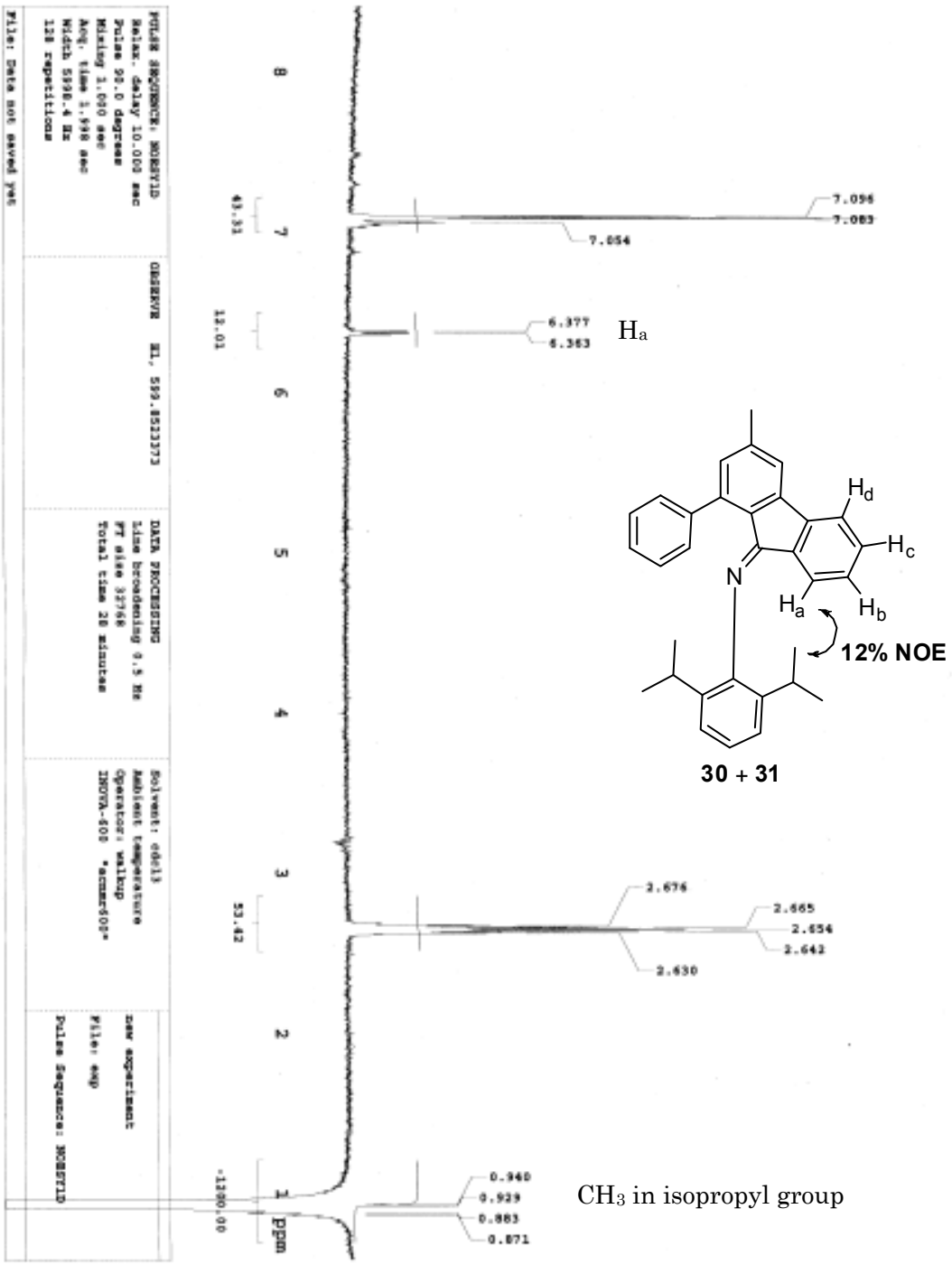

SISM-143
D
D
D
D
D
I
29
7.4319
7.4051
7.3965
7.3733
7.3660
7.3526
7.3453
7.2538
7.0963
1.9172
3.0
2.3541
1.5376
0.0000
δ / ppm


D
D
D
D
D
I
29
147.7663
147.7334
145.5623
137.4371
129.6245
129.3777
127.8234
127.4287
99.4758
77.4688
77.0000
76.5312
20.6913
δ / ppm


D
D
D
D
D
N
+
D
D
D
D
D
N
30
31
7.5393
7.5112
7.4209
7.3843
7.2306
7.2037
7.1756
7.1451
7.0329
7.0207
6.9999
6.9816
6.9731
6.8205
6.7925
6.7644
6.3055
6.2775
0.8762
1.3161
1.5596
4.0105
0.8143
0.805
2.6262
2.6018
2.5762
2.5505
2.5261
2.4029
2.0
3.0222
0.8677
12.0967
0.8420
δ / ppm
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0


D
D
D
D
D
N
30
+
D
D
D
D
D
N
31
161.8784
147.5195
143.0376
142.3550
141.2283
139.6822
134.2380
132.0916
132.0340
131.2857
130.4057
129.1310
127.9468
127.2149
126.9435
126.0882
122.9796
122.8809
119.6407
119.4022
77.4770
77.0000
76.5312
28.2654
22.9775
22.4018
21.7275
1.0280
ppm
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0


Hd
Hc
N
Ha
Hb
30 + 31
Hd
Hc
Hb
Ha
F2 (ppm)
F1 (ppm)
Hd
Hc
Hb
Ha


7.096
7.083
7.054
6.377
6.363
Ha
2.676
2.665
2.654
2.643
2.630
0.940
0.929
0.883
0.871
ppm
Hd
Hc
N
Ha
Hb
12% NOE
30 + 31
CH3 in isopropyl group