Supplementary Material (ESI) for Chemical Communications

Supporting Information

Rhodium-Catalysed Anomalous Dimerization of Styrenes Involving the Cleavage of the ortho C–H Bond

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Contents

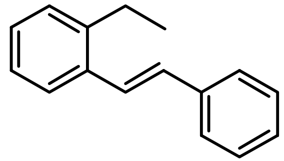
General Information. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL JMN-270 spectrometer or JEOL JMTC-400/54/ss spectrometer in $CDCl_3$ with tetramethylsilane as an internal standard. Data are reported as follows: chemical shift in ppm (δ), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet), coupling constant (Hz), and integration. Infrared spectra (IR) were obtained on a Horiba FT-700 spectrometer; absorptions are reported in reciprocal centimeters with the following relative intensities: s (strong), m (medium), or w (weak). Mass spectra were obtained on a Shimadzu GCMS-QP 5000 or GCMS-QP 2010 instrument with ionization voltages of 70 eV. Elemental analyses were performed by the Elemental Analysis Section of Osaka University. High resolution mass spectra (HRMS) were obtained on a

JEOL JMS-DX303. Column chromatography was performed with SiO_2 (Merck SilicaGel 60 (230-400 mesh)).

Materials. 1,4-Dioxane was distilled over Na-benzophenone. $[RhCl(cod)]_2$ and ^tBuOH were purchased from Wako Chemicals and used as received. Na_2CO_3 was purchased from Nakarai tesque and used as received. All styrene derivatives used in this study are commercially available, unless otherwise noted. 9-(4-Vinyl-phenyl)-anthracene [35244-03-2] was synthesized from 9-bromoanthracene (TCI) and 4-vinylphenylboronic acid (TCI) under Suzuki-Miyaura conditions.

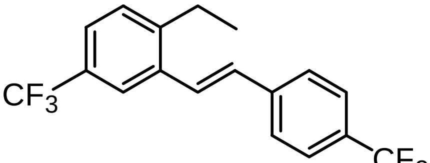
General Procedure for the Rh-Catalyzed Dimerization of Styrene Derivatives. To a oven-dried 10 mL pressure-screw-capped vial, $[RhCl(cod)]_2$ (49.3 mg, 0.1 mmol), ^tBuOH (14.8 mg, 0.20 mmol), Na_2CO_3 (42.4 mg, 0.40 mmol), substrate (1.0 mmol) and 1,4-dioxane (0.5 mL) were added under a gentle stream of nitrogen. The cap was fastened quickly and the mixture was stirred for 20 h at 160 °C. After removing the volatiles *in vacuo*, the residue was subjected to column chromatography on silica gel to afford the desired product. The product was further purified using either bulb-to-bulb distillation or GPC.

1-Ethyl-2-styrylbenzene (3). Rf 0.29 (hexane). Light yellow liquid. ^1H NMR ($CDCl_3$, 270.05 MHz) δ 1.26 (t, *J* = 7.6 Hz, 3H), 2.81 (q, *J* = 7.6 Hz, 2H), 7.02 (d, *J* = 16.2 Hz, 1H), 7.23-7.31 (m, 3H), 7.36-7.47 (m, 4H), 7.53-7.64 (m, 3H); ^{13}C NMR ($CDCl_3$, 67.80 MHz) δ 15.27, 26.33, 125.47, 126.01, 126.06, 126.34, 127.36, 127.58, 128.49, 128.61, 129.90, 135.52, 137.52, 141.73; IR (neat) 3080 m, 3058 s, 3025 s, 2966 s, 2931 m, 2873 m, 1945 w, 1874 w, 1803 w, 1598 m, 1577 w, 1494 s, 1450 s, 1375 w, 1327 w, 1265 w, 1221 w, 1180 w, 1159 w, 1072 w, 1055 w, 1030 w, 960 s, 910 w, 835 w, 760 s, 692 s, 579 w, 550 w, 532 m; MS *m/z* (relative intensity, %) 209 (14), 208 (79), 194 (10), 193 (60), 179 (32), 178 (46), 130 (35), 129 (15), 117 (41), 116 (14), 115 (100), 91 (48), 89 (19), 83 (10), 77 (13), 76 (10), 51 (10). HRMS Calcd for $C_{16}H_{16}$: 208.1252; Found: 208.1248.



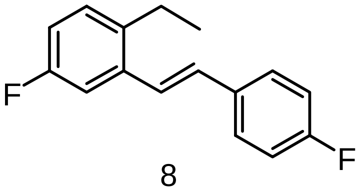
3

1-Ethyl-4-methyl-2-[2-(4-trifluoromethylphenyl)vinyl]benzene (6). Rf 0.34 (hexane). Light yellow liquid. ^{1}H NMR ($CDCl_3$, 270.05 MHz) δ 1.27 (t, *J* = 7.6 Hz, 3H), 2.84 (q, *J* = 7.6 Hz, 2H), 7.08 (d, *J* = 15.9 Hz, 1H), 7.29 (d, *J* = 5.9 Hz, 1H), 7.35-7.51 (m, 2H), 7.64 (s, 4H), 7.83 (s, 1H); ^{13}C NMR ($CDCl_3$, 67.80 MHz) δ 15.04, 26.46, 118.21 (q, *J* = 8.3 Hz), 122.21 (q, *J* = 8.3 Hz), 122.66 (q, *J* = 3.9 Hz), 124.69 (q, *J* = 3.3 Hz), 125.67 (q, *J* = 3.9 Hz), 126.21 (q, *J* = 8.9 Hz), 126.81, 127.37, 128.36 (q, *J* = 45.2 Hz), 128.74 (q, *J* = 32.3 Hz), 129.74 (q, *J* = 32.3 Hz), 135.78, 140.52, 145.88; IR (neat) 3043 w, 2973 w, 2938 w, 2881 w, 2360 w, 1915 w, 1616 m, 1577 w, 1469 w, 1456 w, 1417 w, 1327 s, 1255 m, 1220 w, 1165 s, 1124 s, 1068 s, 1068 w, 966 w, 953 w, 924 w, 904 w, 866 w, 835 w, 823 m, 752 w, 735 w, 661 w, 619 w, 596 w, 519 w, 415 w; MS *m/z* (relative intensity, %) 345 (20), 344 (100), 330 (12), 329 (66), 325 (22), 315 (10), 314 (17), 295 (10), 275 (43), 260 (28), 259 (11), 246 (13), 198 (30), 197 (10), 191 (10), 185 (36), 183 (43), 165 (26), 159 (33), 133 (10), 129 (28), 128 (11), 127 (10), 116 (14), 115 (17), 109 (17), 91 (11). HRMS Calcd for $C_{18}H_{14}F_6$: 344.1000; Found: 344.0997.



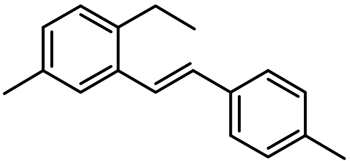
6

1-Ethyl-4-fluoro-2-[2-(4-fluorophenyl)vinyl]benzene (8). Rf 0.34 (hexane). Colorless liquid. ^{1}H NMR ($CDCl_3$, 270.05 MHz) δ 1.22 (t, *J* = 7.6 Hz, 3H), 2.74 (q, *J* = 7.6 Hz, 2H), 6.87-6.97 (m, 2H), 7.02-7.29 (m, 5H), 7.45-7.50 (m, 2H); ^{13}C NMR ($CDCl_3$, 67.80 MHz) δ 15.54, 25.81, 111.81 (d, *J* = 21.8 Hz), 114.39 (d, *J* = 21.2 Hz), 115.66 (d, *J* = 21.8 Hz), 124.97,, 128.15 (d, *J* = 8.3 Hz), 129.81, 130.20 (*J* = 8.3 Hz), 134.40 (*J* = 3.3 Hz), 137.22 (d, *J* = 7.4 Hz), 137.50 (d, *J* = 2.8 Hz), 161.41 (d, *J* = 242.5 Hz), 162.46 (d, *J* = 247.0 Hz); IR (neat) 3041 w, 2968 m, 2933 m, 2875 m, 2366 w, 2330 w, 1884 w, 1601 s, 1581 m, 1510 s, 1489 s, 1469 m, 1454 w, 1377 w, 1323 w, 1296 w, 1269 s, 1230 s, 1203 w, 1174 w, 1159 s, 1099 m, 1061 w, 1012 w, 978 m, 962 s, 881 w, 854 s, 816 s, 752 w, 712 w, 592 w, 526, m, 496 m, 453 w, 413 w; MS *m/z* (relative intensity, %) 245 (15), 244 (88), 230 (14), 229 (83), 215 (15), 214 (41), 148 (22), 135 (19), 134 (11), 133 (86), 122 (14), 110 (10), 109 (100), 107 (12), 83 (14). HRMS Calcd for $C_{16}H_{14}F_2$: 244.1064; Found: 244.1060.



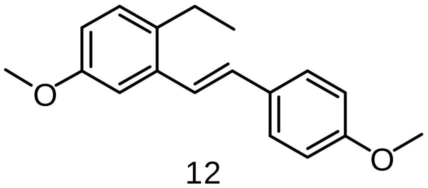
8

1-Ethyl-4-methyl-2-(2-p-tolylvinyl)benzene (10). Rf 0.29 (hexane). Colorless liquid. ^{1}H NMR ($CDCl_3$, 270.05 MHz) δ 1.15 (t, *J* = 7.6 Hz, 3H), 2.29 (s, 3H), 2.30 (s, 3H), 2.68 (q, *J* = 7.6 Hz, 2H), 6.90 (d, *J* = 16.1 Hz, 1H), 6.98-7.12 (m, 3H), 7.19-7.27 (m, 2H), 7.34-7.37 (m, 3H); ^{13}C NMR ($CDCl_3$, 67.80 MHz) δ 15.63, 21.08, 21.24, 26.09, 125.33, 126.14, 126.41, 128.38, 128.75, 129.15, 129.36, 129.70, 135.50, 135.60, 137.36, 138.93; IR (neat) 3047 m, 3022 s, 2964 s, 2924 s, 2871 m, 2731 w, 1896 w, 1606 m, 1572 w, 1514 s, 1495 m, 1452 m, 1375 m, 1325 w, 1183 w, 1161 w, 1111 m, 1061 m, 1039 m, 1020 w, 964 s, 856 m, 818 s, 806 s, 750 w, 573 w, 525 m, 415 m; MS *m/z* (relative intensity, %) 237 (20), 236 (100), 222 (15), 221 (78), 207 (15), 206 (33), 205 (10), 192 (16), 191 (14), 144 (29), 131 (23), 130 (11), 129 (90), 128 (25), 118 (13), 115 (22), 105 (50), 103 (14), 102 (14), 101 (12), 91 (23), 89 (18), 79 (10), 77 (14). HRMS Calcd for $C_{18}H_{20}$: 236.1565; Found: 236.1564.



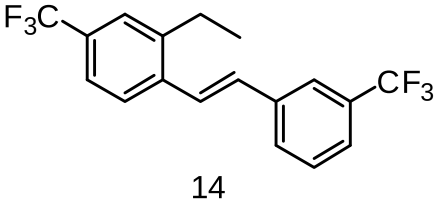
10

1-Ethyl-4-methoxy-2-[2-(4-methoxyphenyl)vinyl]benzene (12). Rf 0.46 (Ethyl acetate/ hexane = 1/5). Light yellow liquid. ^{1}H NMR ($CDCl_3$, 270.05 MHz) δ 1.19 (t, *J* = 7.6 Hz, 3H), 2.71 (q, *J* = 7.6 Hz, 2H), 3.82 (s, 6H), 6.74-6.96 (m, 4H), 7.07-7.22 (m, 2H), 7.34-7.47 (m, 3H); ^{13}C NMR ($CDCl_3$, 67.80 MHz) δ 15.75, 25.72, 55.31, 55.33, 110.48,113.09, 114.10, 124.12, 127.76, 129.66, 129.74, 130.41, 134.26, 136.93, 157.88, 159.27; IR (neat) 3032 w, 3000 w, 2960 m, 2933 m, 2871 w, 2835 w, 1604 s, 1571 w, 1512 s, 1464 m, 1442 m, 1421 w, 1284 m, 1252 s, 1211 w, 1176 m, 1113 w, 1036 m, 964 w, 843 w, 818 m, 789 w, 750 w, 704 w, 567 w, 530 w, 478 w, 434 w, 418 w; MS *m/z* (relative intensity, %) 269 (20), 268 (100), 254 (16), 253 (79), 238 (13), 165 (11), 160 (18), 145 (58), 134 (20), 121 (92), 115 (23), 91 (14). HRMS Calcd for $C_{18}H_{20}O_2$: 268.1463; Found: 268.1461.



12

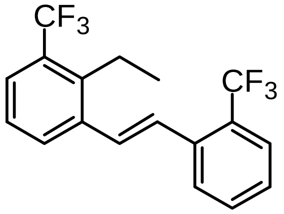
2-Ethyl-4-trifluoromethyl-1-[2-(3-trifluoromethylphenyl)vinyl]benzene (14). Rf 0.29 (hexane). Colorless liquid. ^{1}H NMR ($CDCl_3$, 270.05 MHz) δ 1.29 (t, *J* = 7.6 Hz, 3H), 2.85 (q, *J* = 7.6 Hz, 2H), 7.08 (d, *J*= 16.2 Hz, 1H), 7.39-7.57 (m, 5H), 7.66-7.77 (m, 3H); ^{13}C NMR ($CDCl_3$, 67.80 MHz) δ 15.00, 26.42, 122.18 (q, *J* = 13.4 Hz), 123.09 (q, *J* = 3.9 Hz), 123.39 (q, *J* = 3.9 Hz), 124.59 (q, *J* = 3.9 Hz), 125.58 (q, *J* = 3.9 Hz), 126.11, 126.70, 129.25 (q, *J* = 20.1 Hz), 129.25, 129.75 (q, *J* = 1.1 Hz), 129.89 (q, *J* = 32.3 Hz), 130.78, 131.25 (q, *J* = 31.8 Hz), 137.12, 138.71 (q, *J* = 1.2 Hz), 142.63; IR (neat) 3045 m, 3021 w, 2971 s, 2939 m, 2881 m, 1957 w, 1896 w, 1795 w, 1712 w, 1614 s, 1593 m, 1574 w, 1487 m, 1468 m, 1450 s, 1437 s, 1421 s, 1379 m, 1328 s, 1290 s, 1254 s, 1223 s, 1157 s, 1111 s, 1072 s, 1045 m, 997 w, 962 s, 901 s, 856 m, 825 s, 796 s, 748 w, 735 m, 696 s, 667 s, 640 w, 557 w, 528 w, 474 w; MS *m/z* (relative intensity, %) 345 (20), 344 (100), 330 (18), 329 (96), 325 (22), 315 (11), 314 (17), 289 (12), 275 (26), 260 (25), 259 (11), 246 (13), 198 (31), 191 (10), 185 (30), 183 (50), 165 (25), 159 (35), 133 (11), 129 (25), 128 (11), 116 (14), 115 (19), 109 (18). HRMS Calcd for $C_{18}H_{14}F_6$: 344.1000; Found: 344.0999.



14

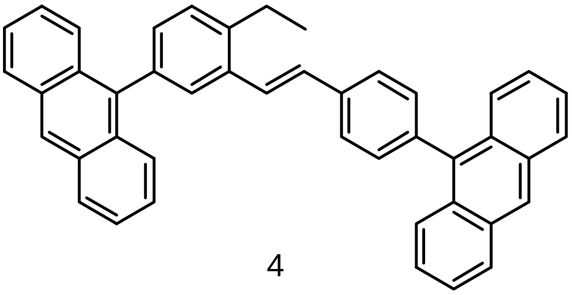
2-Ethyl-1-trifluoromethyl-3-[2-(2-trifluoromethylphenyl)vinyl]benzene (16). Rf 0.37 (hexane). Light yellow liquid. ^{1}H NMR ($CDCl_3$, 270.05 MHz) δ 1.21 (t, *J* = 7.3 Hz, 3H), 2.92 (q, *J* = 7.3 Hz, 2H), 7.29-7.42 (m, 4H), 7.54-7.75 (m, 5H); ^{13}C NMR ($CDCl_3$, 67.80 MHz) δ 15.22, 22.66 (q, *J* = 1.6 Hz), 118.45 (q, *J* = 21.8 Hz), 1122.48 (q, *J* = 21.7

Hz), 125.80 (q, *J* = 6.1 Hz), 126.00 (q, *J* = 5.6 Hz), 126.18, 126.52 (q, *J* = 21.7 Hz), 127.48(q, *J* = 17.7 Hz), 127.74 (q, *J* = 29.6 Hz), 128.13 (q, *J* = 2.2 Hz), 128.93 (q, *J* = 29.0 Hz), 129.99 (q, *J* = 39.6 Hz), 130.55 (q, *J* = 22.3 Hz), 132.04, 136.35 (q, *J* = 1.2 Hz), 137.94, 140.87 (q, *J* = 1.2 Hz); IR (neat) 3066 m, 3006 m, 2970 m, 2933 m, 2877 m, 2877 w, 2360 w, 2339 w, 1637 w, 1604 m, 1576 m, 1489 s, 1317 s, 1286 s, 1161 s, 1101 s, 1059 s, 1034 s, 962 s, 895 m, 856 w, 804 s, 762 s, 737 s, 671 m, 644 m, 604 m, 550 w, 538 m, 467 w; MS *m/z* (relative intensity, %) 345 (20), 344 (100), 330 (13), 329 (75), 309 (46), 290 (10), 289 (55), 275 (12), 269 (14), 260 (10), 240 (10), 220 (28), 185 (50), 183 (26), 165 (40), 159 (25), 145 (10), 133 (14), 129 (15), 119 (12), 116 (22), 115 (26), 110 (11), 109 (22), 69 (13). HRMS Calcd for $C_{18}H_{14}F_6$: 344.1000; Found: 344.0996.



16

(*E*)-9-(4-(5-(anthracen-9-yl)-2-ethylstyryl)phenyl)anthracene (4). Rf 0.11 (hexane). Light yellow solid. m.p.= 246-247 °C; ^{1}H NMR (CDCl$_3$, 270.05 MHz) δ 1.47 (t, *J* = 7.6 Hz, 3H), 3.04 (q, *J* = 7.6 Hz, 2H), 7.14 (d, *J* = 15.9 Hz, 1H), 7.32-7.52 (m, 12H), 7.64-7.73 (m, 5H), 7.80-7.84 (m, 3H), 8.03-8.10 (m, 4H), 8.50-8.54 (m, 2H); ^{13}C NMR (CDCl$_3$, 67.80 MHz) δ15.56, 26.45, 125.10, 125.12, 125.23, 125.36, 126.15, 126.50, 126.60, 126.75, 126.99, 128.35, 128.39, 128.88, 130.01, 130.14, 130.32, 130.74, 131.33, 131.41, 131.63, 135.66, 136.54, 136.62, 136.77, 137.02, 138.10, 141.10; IR (KBr) 3050 s, 3030 m, 2966 m, 2931 m, 2873 s, 2247 w, 1624 w, 1603 w, 1512 m, 1442 m, 1412 m, 1358 m, 1311 w, 1165 w, 1105 w, 1014 m, 966 m, 933 m, 908 s, 887 s, 844 s, 816 s, 789 m, 739 s, 727 s, 652 m, 613 m, 553 m, 523 w, 418 w; MS *m/z* (relative intensity, %) 563 (16), 562 (37), 561 (50), 560 (100), 281 (13), 280 (28), 267 (22), 265 (14); HRMS Calcd for $C_{16}H_{10}F_6$: 560.2504; Found:560.2502.



4

X-ray Crystallographic Structure Analysis. X-ray crystallography was performed on Rigaku RAXIS RAPID imaging plate diffractometer with graphite monochromated Cu Kα radiation ($\lambda = 1.54187$ Å). The data were collected at 113 K using ω scan in the 2θ range of 3.5–71.8 deg. The structure of (*E*)-9-(4-(5-(anthracen-9-yl)-2-ethylstyryl)phenyl)anthracene (**4**) was solved using the SHELXL97 program.[1] All H atoms were located at ideal positions. They were included in the refinement, but restricted to riding on the atoms to which they were bonded. Isotropic thermal factors of H atoms were held to 1.2 to 1.5 times U_{eq} of the riding atoms.

Crystal Data for (*E*)-9-(4-(5-(anthracen-9-yl)-2-ethylstyryl)phenyl)anthracene (**4**, CCDC 684849): $C_{44}H_{32}$, $M = 560.70$, yellow prism, triclinic, space group P-1 (#2), $a = 11.4861$ (2) Å, $b = 12.8423$ (2) Å, $c = 21.3357$ (4) Å, $\alpha = 96.95572$ (7)°, $\beta = 96.5045$ (7)°, $\gamma = 100.6850$ (7)°, $V = 3039.99$ (9) Å^3, $T = 113$ K, $Z = 4$, $D_c = 1.225$ g cm^{-1}, $\mu = 0.523$ cm^{-1}, crystal dimensions $0.17 \times 0.14 \times 0.10$ mm^3, 57689 reflections collected, 11498 unique ($R_{int} = 0.0956$) which were used in all calculations. $R_1 = 0.0898$, $wR_2 = 0.2162$ for $I > 2\sigma(I)$, $wR_2 = 0.2954$ for all data, $GOF = 0.972$ for all data.

Labeling study

Procedure for the Rh-catalyzed dimerization of 3,4,5-trifluorostyrene.

To a oven-dried 10 mL pressure-screw-capped vial, $[RhCl(cod)]_2$ (49.2 mg, 0.1 mmol), ^{t}BuOH (16.0 mg, 0.22 mmol), Na_2CO_3 (43.1 mg, 0.41 mmol), substrate (150.1 mg, 0.95 mmol) and 1, 4-dioxane (0.5 mL) were added under a gentle stream of nitrogen. The cap was fastened quickly and the mixture was stirred for 20 h at 160 °C. After removing the volatiles *in vacuo*, the residue was subjected to column chromatography on silica gel

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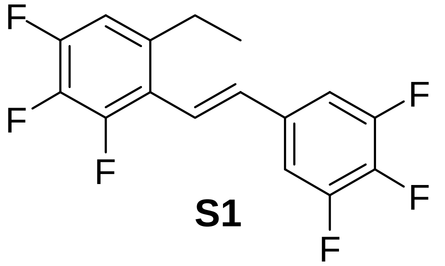
[1] Sheldrick, G.. M. *SHELXL97*, *Program for the Refinement of Crystal Structures*, University of Göttingen, Germany, 1997.

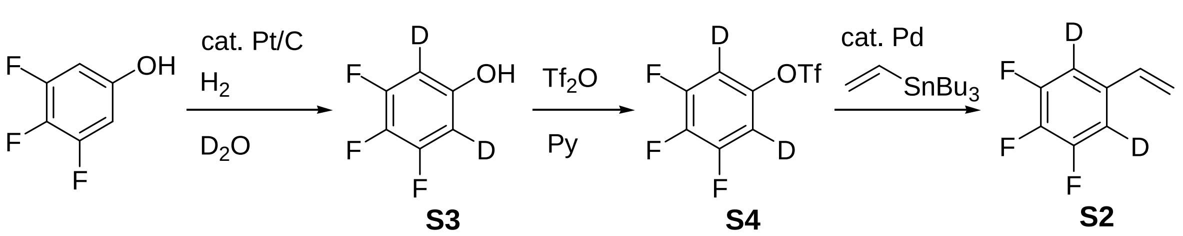
to afford **S1**(37.2 mg, 25%). The product was further purified using GPC.

1-Ethyl-3,4,5-trifluoro-2-[2-(3,4,5-trifluoro-phenyl)-vinyl]-benzene (S1). Rf 0.34(hexane). colorless solid, m.p.= 76-77 °C. ^{1}H NMR ($CDCl_3$, 270.05 MHz) δ 1.23(t, *J*= 7.6 Hz, 3H), 2.71(q, *J*= 7.6 Hz 2H), 6.81-6.89(m, 2H), 6.99(d, *J*= 16.5 Hz, 1H), 7.07-7.14(m, 2H); ^{13}C NMR ($CDCl_3$, 67.80 MHz) δ 14.74, 26.29 (t, *J*= 1.1 Hz), 110.28 (dd, *J*= 14.5, 7.3 Hz), 111.87 (dd, *J*= 17.3, 3.9 Hz), 120.07 (dd, *J*= 9.0, 4.5 Hz), 132.39 (dt, *J*= 11.1, 2.2 Hz), 133.48 (dt, *J*= 12.2, 5.0 Hz), 137.04(dt, *J*= 66.4, 15.1 Hz), 138.68 (dt, *J*= 7.32, 4.5 Hz), 140.74 (td, *J*= 71.4, 15.7 Hz), 147.98 (td, *J*= 14.5, 4.5 Hz), 149.63 (dd, *J*= 10.0, 4.5 Hz), 151.67 (dt, *J*= 4.5, 14.0 Hz), 153.31 (dd, *J*= 10.0, 4.5 Hz).;IR (neat) 2983 w, 2368 w, 2321 w, 1602 m, 1525 s, 1502 s, 1437 m, 1362 s, 1340 m, 1319 w, 1234 w, 1107 w, 1043 w, 989 w, 962 w, 910 w, 864 w, 837 w, 795 w, 700 w, 660 w, 602 w, 565 w, 534 w, 459 w,; MS *m/z* (relative intensity, %) 317 (18), 316 (100), 302 (11), 301 (68), 287 (13), 286 (26), 281 (15), 184 (16), 171 (42), 169 (64), 158 (12), 151 (25), 145 (72), 133 (11), 125 (15).; HRMS Calcd for $C_{16}H_{10}F_6$: 316.0687; Found: 316.0681.



S1

Procedure for the synthesis of 3,4,5-trifluorostyrene-2,6-d$_2$ (S2)[2]



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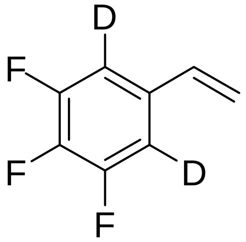
[2] (a) N. Ito, H. Esaki, T. Maesawa, E. Imamiya, T. Maegawa, H. Sajiki, *Bull. Chem. Soc. Jpn.* **2008**, *81*, 278., (b) A. L. S. Thompson, G. W. Kabalka, M. R. Akula, J. W. Hoffman, *Synthesis*, **2005**, *4*, 547., (c) A. M. Echavarren, J. K. Stille, *J. Am. Chem. Soc.* **1987**, *109*, 5478.

3,4,5-Trifluorophenol (2.0 g, 13.5 mmol) and 5% Pt/C (200 mg, 20 wt% of the substrate) in D_2O (20 mL) was stirred at 90 °C under H_2 atmosphere for 24 h. After cooling, the reaction mixture was filtered to remove the catalyst. Solvent was evaporated to give 3,4,5-trifluorophenol-2,6-d_2 (**S3**).

A mixture of 3,4,5-trifluorophenol-2,6-d_2(**S3**) and pyridine (2.1 g, 54.0 mmol) in C_2Cl_2 (13 mL) was cooled to 0 °C with ice-water bath. After the trifluoromethanesulfonic anhydrate (4.6g, 27.0 mmol) was added dropwise, the solution was allowed to warm to r.t. The reaction was complete within 10 min as shown by TLC. Et_2O (20 mL) was added to the reaction mixture, and the mixture was filtered. Solvent was evaporated very carefully and gives 3,4,5-trifluorophenyltrifluoromethanesulfonate-2,6-d_2 (**S4**). The residue was used in the next reaction without further purification.

To a solution of 3,4,5-trifluorophenyltrifluoromethanesulfonate-2,6-d_2(**S4**) in 15 mL of 1,4-dioxane were added tri-*n*-butylethenylstannane (4.7 g, 14.9 mmol), LiCl(1.7 g, 40.5 mmol), $Pd(OAc)_2$ (303.1 mg, 1.35 mmol), PPh_3(1.40g, 5.4 mmol), and a few crystals of 2,6-di-*tert*-butyl-4-methylphenol. The resulting suspension was heated to reflux (100 °C) for 17 h, cooled to r.t., and filtered to remove the insoluble salts. Solvent was evaporated and the reaction mixture was distilled under 100 °C/0.01 MPa condition to give 3.4.5-trifluorostyrene-2,6-d_2 (**S2**, 1.53 g, 65% for 3 steps).

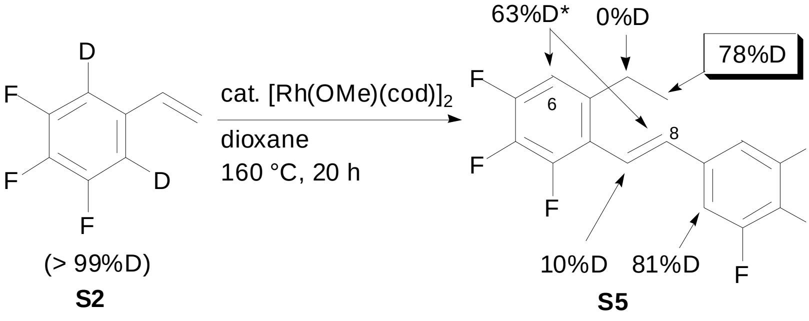
3,4,5-Trifluorostyrene-d_2(S2). Rf 0.63 (hexane). colorless liquid. ^1H NMR ($CDCl_3$, 270.05 MHz) δ 5.20-3.38 (m, 1H), 5.64-5.80 (m, 1H), 6.51-6.78 (m, 1H).; MS *m/z* (relative intensity, %) 161 (9), 160 (100), 159 (22), 158 (11), 157 (2), 141 (8), 140 (6), 139 (11), 138 (9), 134 (16), 133 (8), 121 (3), 120 (2), 121 (15), 108 (9), 107 (5), 106 (2), 100 (1), 89 (3), 88 (2), 83 (4), 82 (3), 81 (3), 80 (4), 79 (1), 76 (3), 75 (2), 65 (1), 64 (2), 63 (1), 52 (2). HRMS Calcd for $C_8H_3D_2F_3$: 160.0467; Found: 160.0470.



S2

Procedure for the Rh-Catalyzed Dimerization of 3,4,5-trifluorostyrene-2,6-d_2 (S2)

To an oven-dried 10 mL pressure-screw-capped vial, $[Rh(OMe)(cod)]_2$ (70.2 mg, 0.15 mmol), substrate (97.2 mg, 0.61 mmol) and 1,4-dioxane (0.5 mL) were added under a gentle stream of nitrogen. The cap was fastened quickly and the mixture was stirred for 24 h at 160 °C. After removing the volatiles *in vacuo*, the residue was subjected to column chromatography on silica gel to afford dimmer **S5**. ^{2}H NMR measurement of **S5** revealed that no deuterium was incorporated in to the methylene group of **S5** (see page S-30). Thus, relative deuterium content at each position of **S5** was calculated based on the relative integration values of **S5**/**S1** by using a methylene signal of the dimer (around 2.70 ppm) as a standard (Scheme S1). Because of peak-overlapping, the deuterium contents at position 6 and 8 (see Scheme S1) can be calculated only as an average of these two positions. Significant deuterium incorporation at the methyl group in **S5** agrees with our proposed mechanisms.

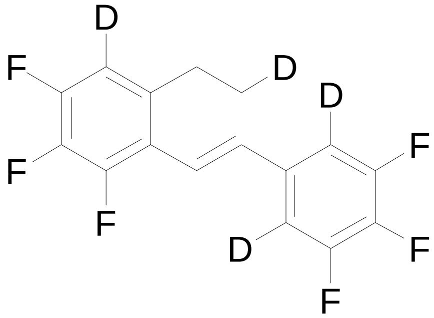


* Average of deuterium content at the indicated two positions.

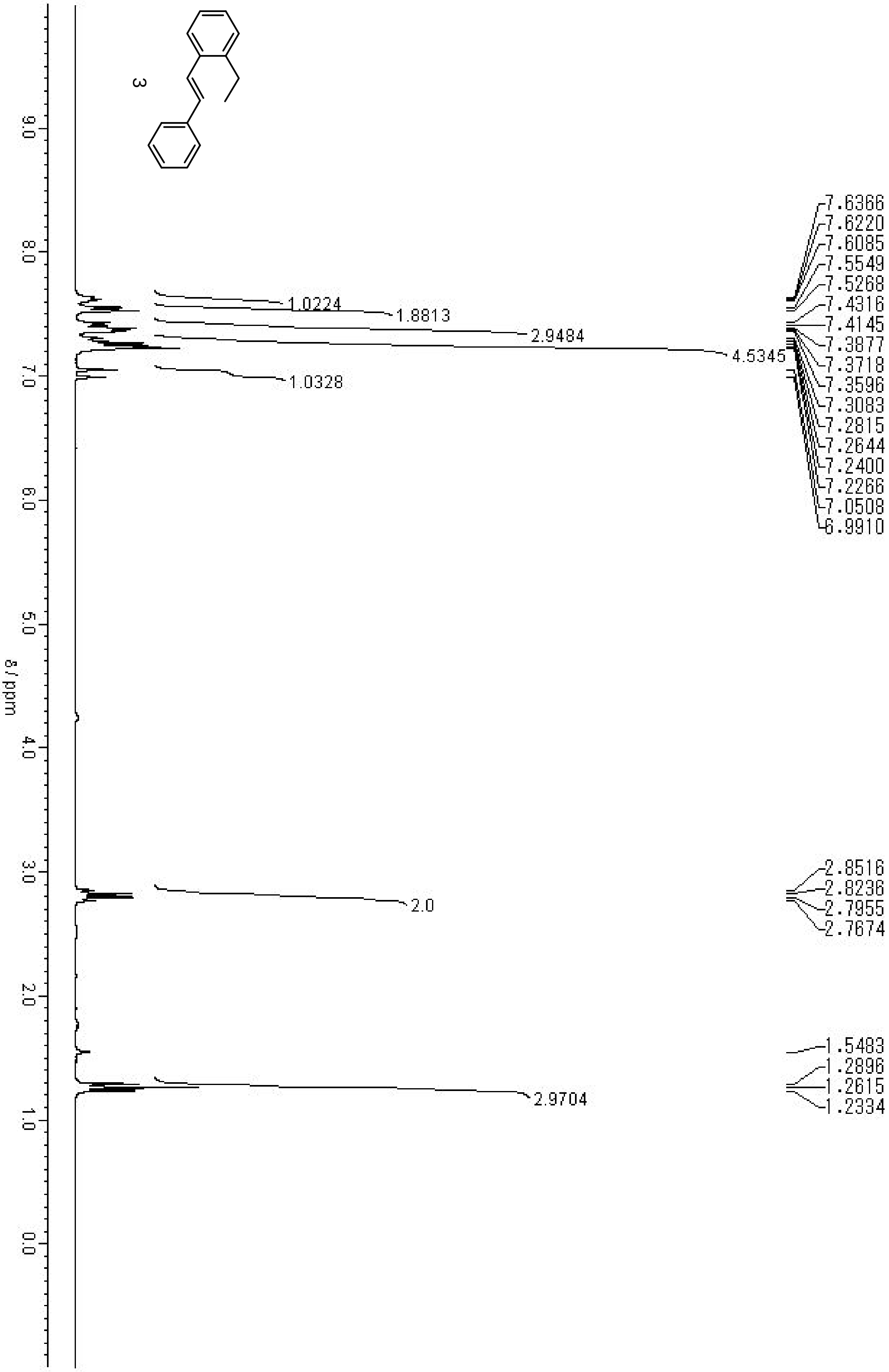
Scheme S1 Labeling study.

1-Ethyl-3,4,5-trifluoro-2-[2-(3,4,5-trifluoro-phenyl)-vinyl]-benzene-d_4 (S5)

Rf 0.37 (hexane). colorless liquid. ^{1}H NMR ($CDCl_3$, 270.05 MHz) δ 5.20-3.38 (m, 1H), 5.64-5.80 (m, 1H), 6.51-6.78 (m, 1H).; MS *m/z* (relative intensity, %) 321 (22), 320 (100), 319 (16), 305 (30), 304 (61), 303 (10), 290 (11), 289 (16), 288 (12), 284 (11), 186 (15), 174 (10), 173 (32), 172 (18), 171 (30), 170 (44), 153 (17), 152 (12), 148 (12), 146 (33), 58 (33). HRMS Calcd for $C_{16}H_6D_4F_6$: 320.0934; Found: 320.0936.



S5


3

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7.0
6.0
5.0
δ / ppm
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2.0
1.0
0.0
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1.8813
2.9484
4.5345
1.0328
2.0
2.9704
7.6366
7.6220
7.6085
7.5549
7.5268
7.4316
7.4145
7.3877
7.3718
7.3596
7.3083
7.2815
7.2644
7.2400
7.2266
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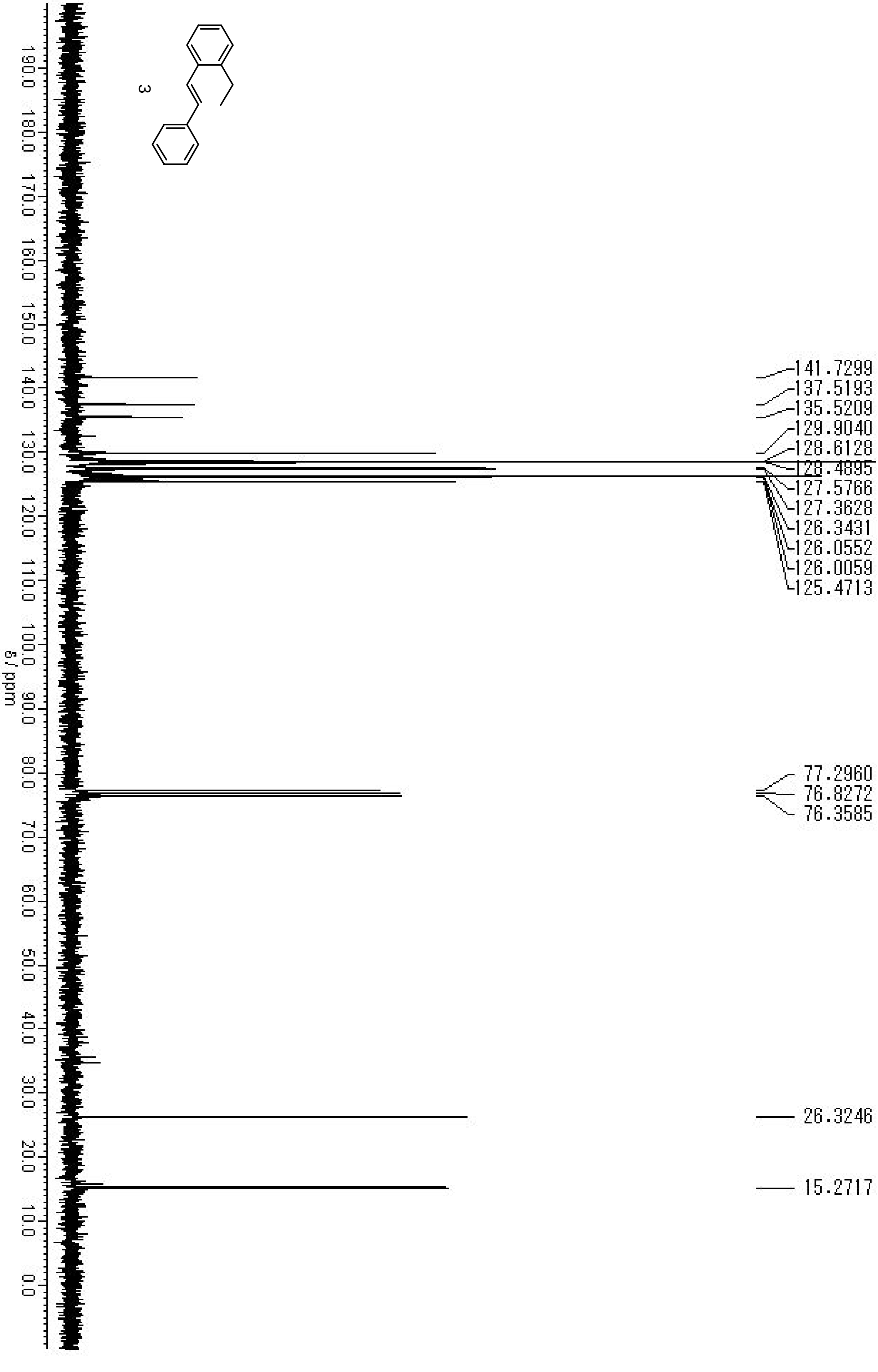
2.7674
1.5483
1.2896
1.2615
1.2334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150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
δ / ppm
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137.5193
135.5209
129.9040
128.6128
128.4895
127.5766
127.3628
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126.0552
126.0059
125.4713
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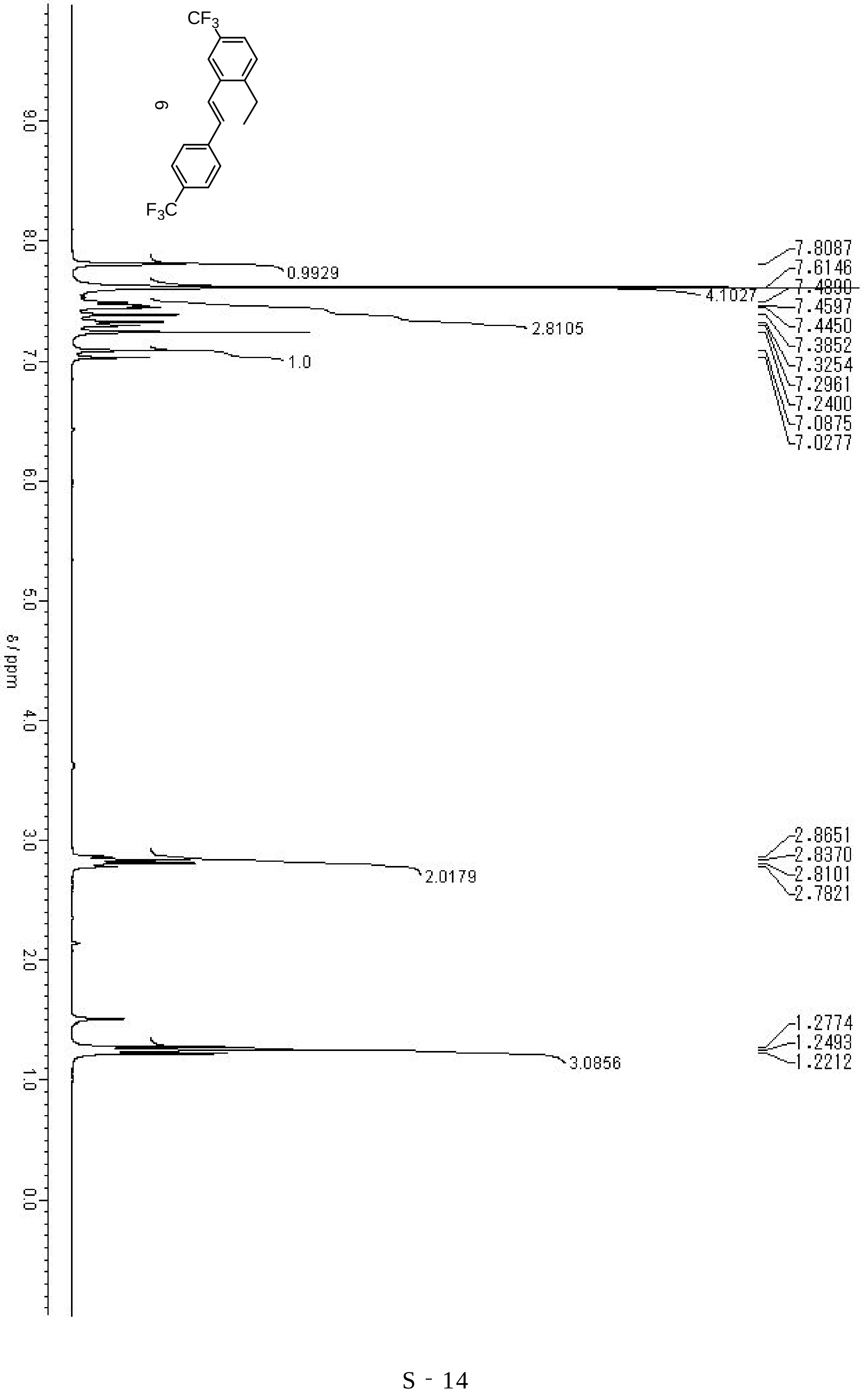
76.8272
76.3585
26.3246
15.2717



6

CF3
F3C
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7.0
6.0
5.0
4.0
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2.0
1.0
0.0
δ / ppm
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4.1027
2.8105
1.0
2.0179
3.0856
7.8087
7.6146
7.4890
7.4597
7.4450
7.3852
7.3254
7.2961
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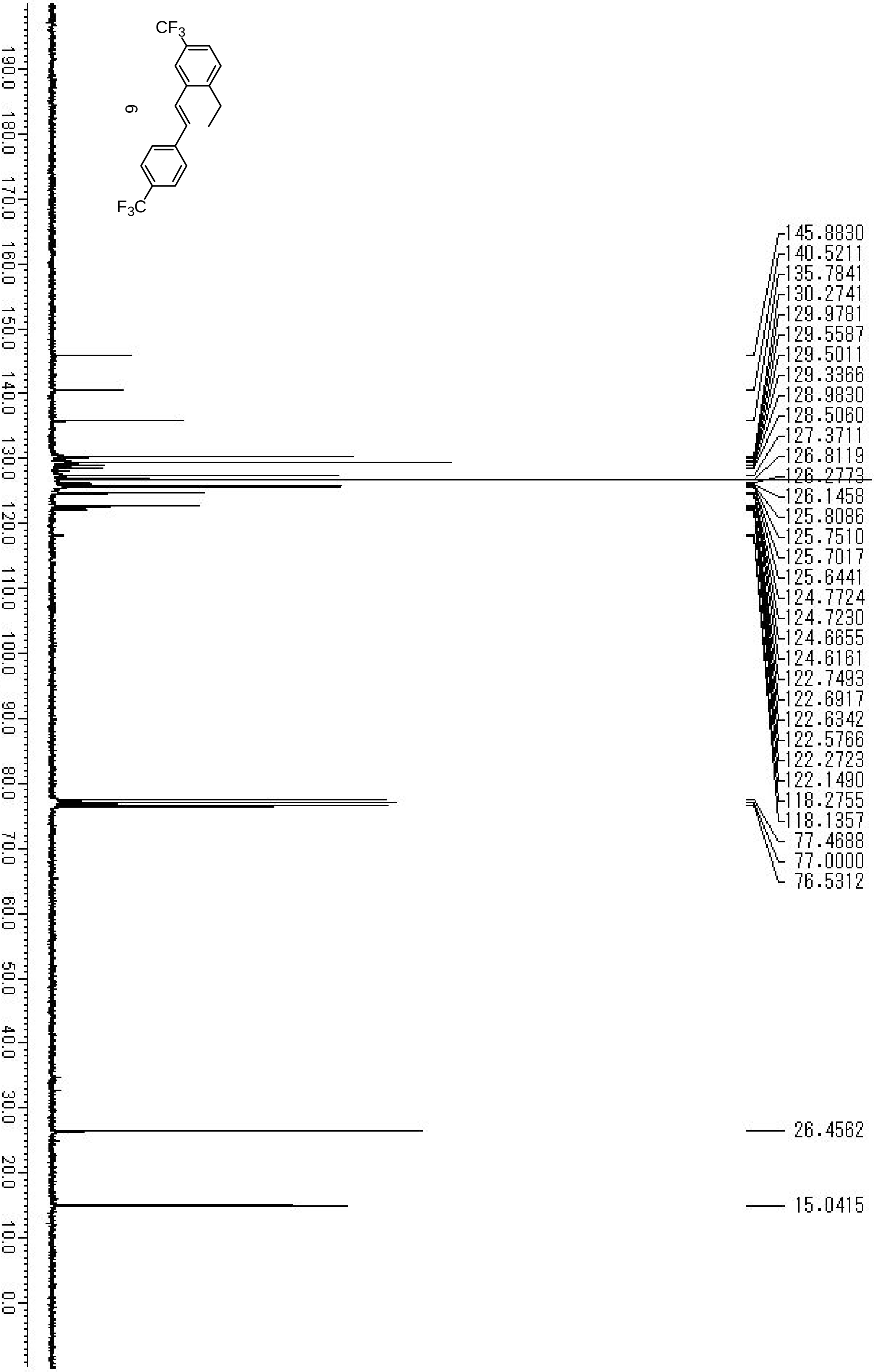
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160.0
150.0
140.0
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120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
δ / ppm
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140.5211
135.7841
130.2741
129.9781
129.5587
129.5011
129.3366
128.9830
128.5060
127.3711
126.8119
126.2773
126.1458
125.8086
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125.7017
125.6441
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124.7230
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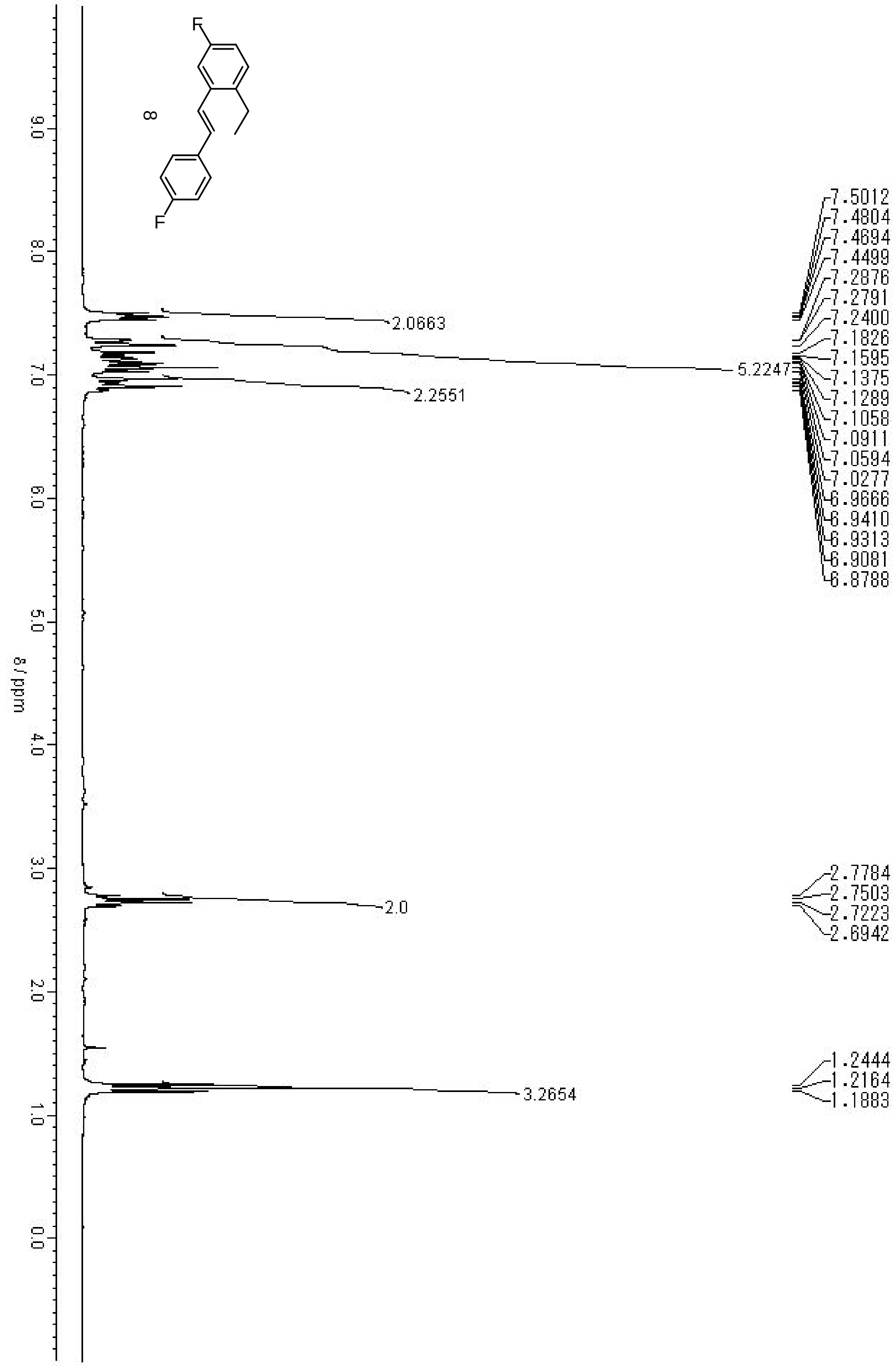

8

F
F
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6.0
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4.0
3.0
2.0
1.0
0.0
δ / ppm
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2.2551
2.0
3.2654
7.5012
7.4804
7.4694
7.4499
7.2876
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7.1826
7.1595
7.1375
7.1289
7.1058
7.0911
7.0594
7.0277
6.9666
6.9410
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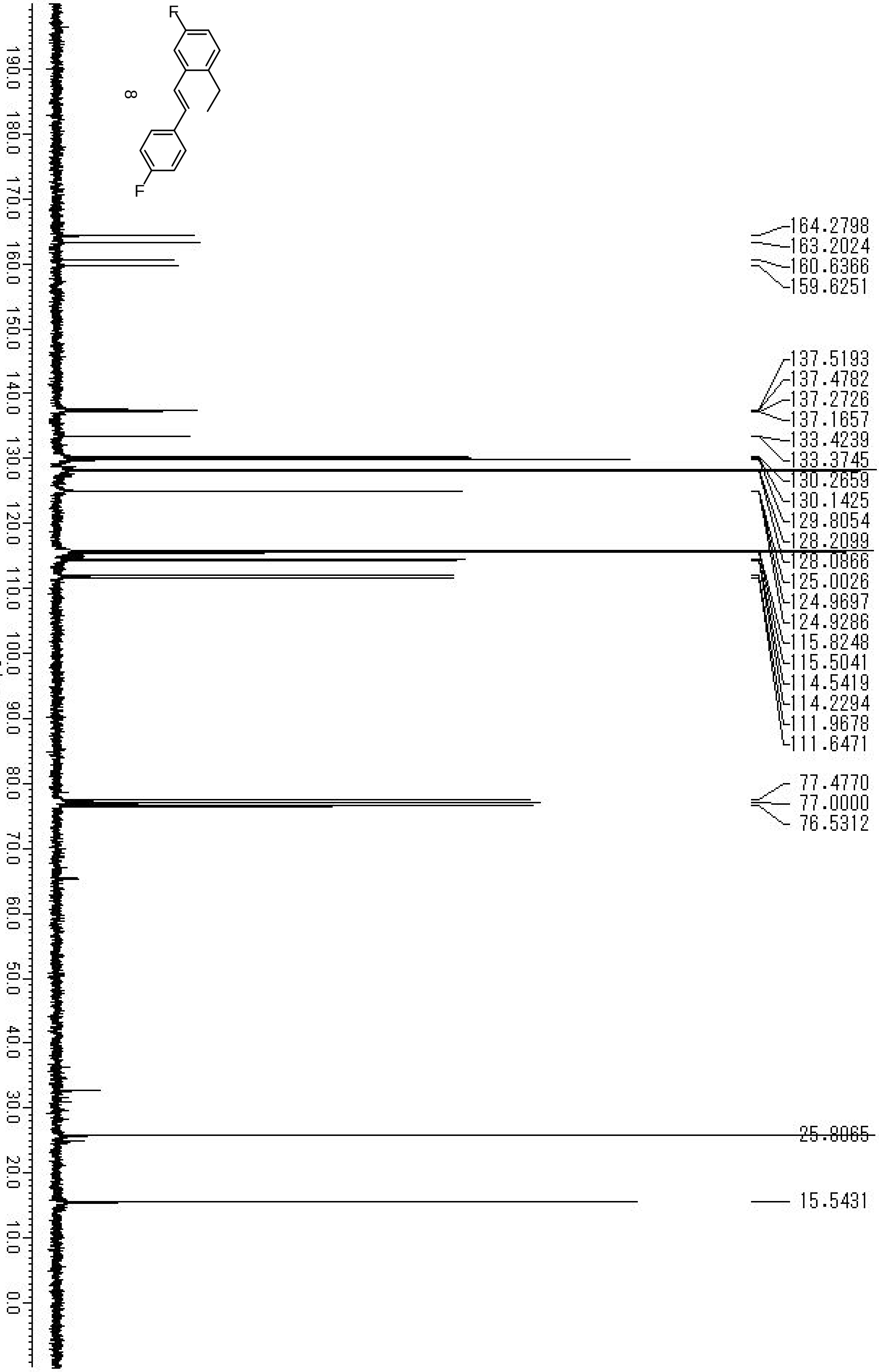
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F
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130.0
120.0
110.0
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90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
δ / ppm
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160.6366
159.6251
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137.2726
137.1657
133.4239
133.3745
130.2659
130.1425
129.8054
128.2099
128.0866
125.0026
124.9697
124.9286
115.8248
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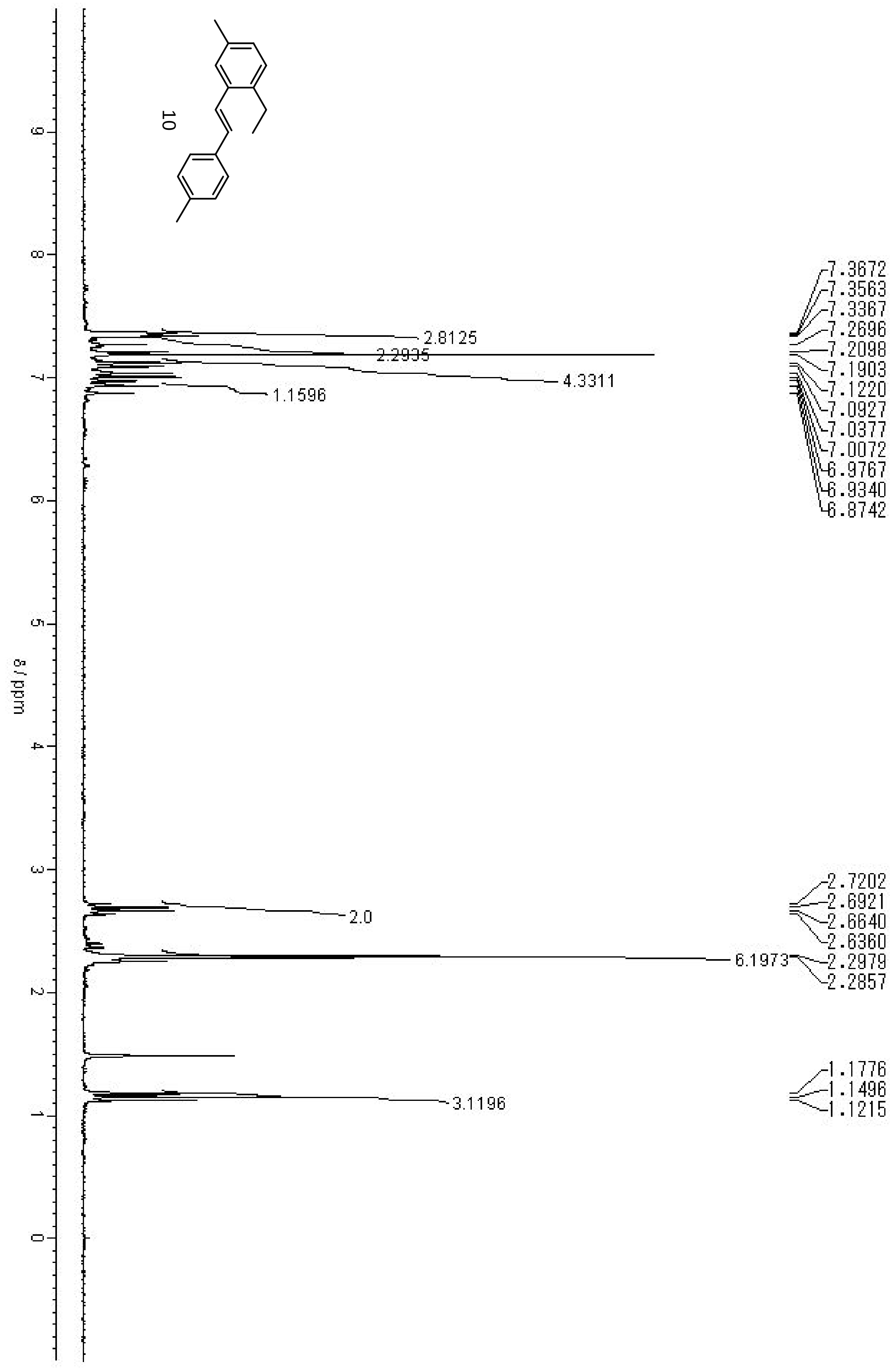
15.5431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δ / ppm
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8
7
6
5
4
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2.0
6.1973
3.1196
7.3672
7.3563
7.3367
7.2696
7.2098
7.1903
7.1220
7.0927
7.0377
7.0072
6.9767
6.9340
6.8742
2.7202
2.6921
2.6640
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1.1215

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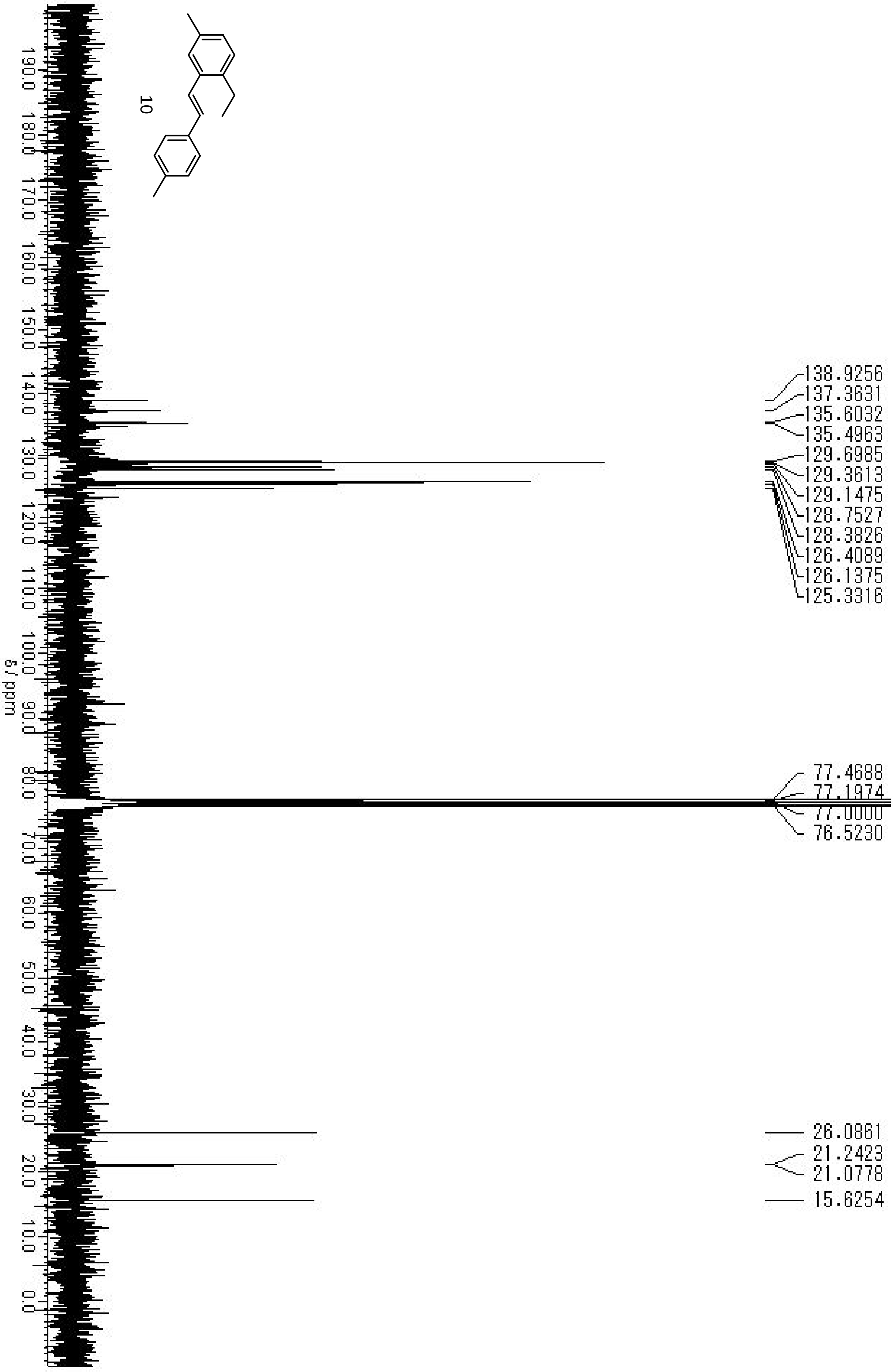
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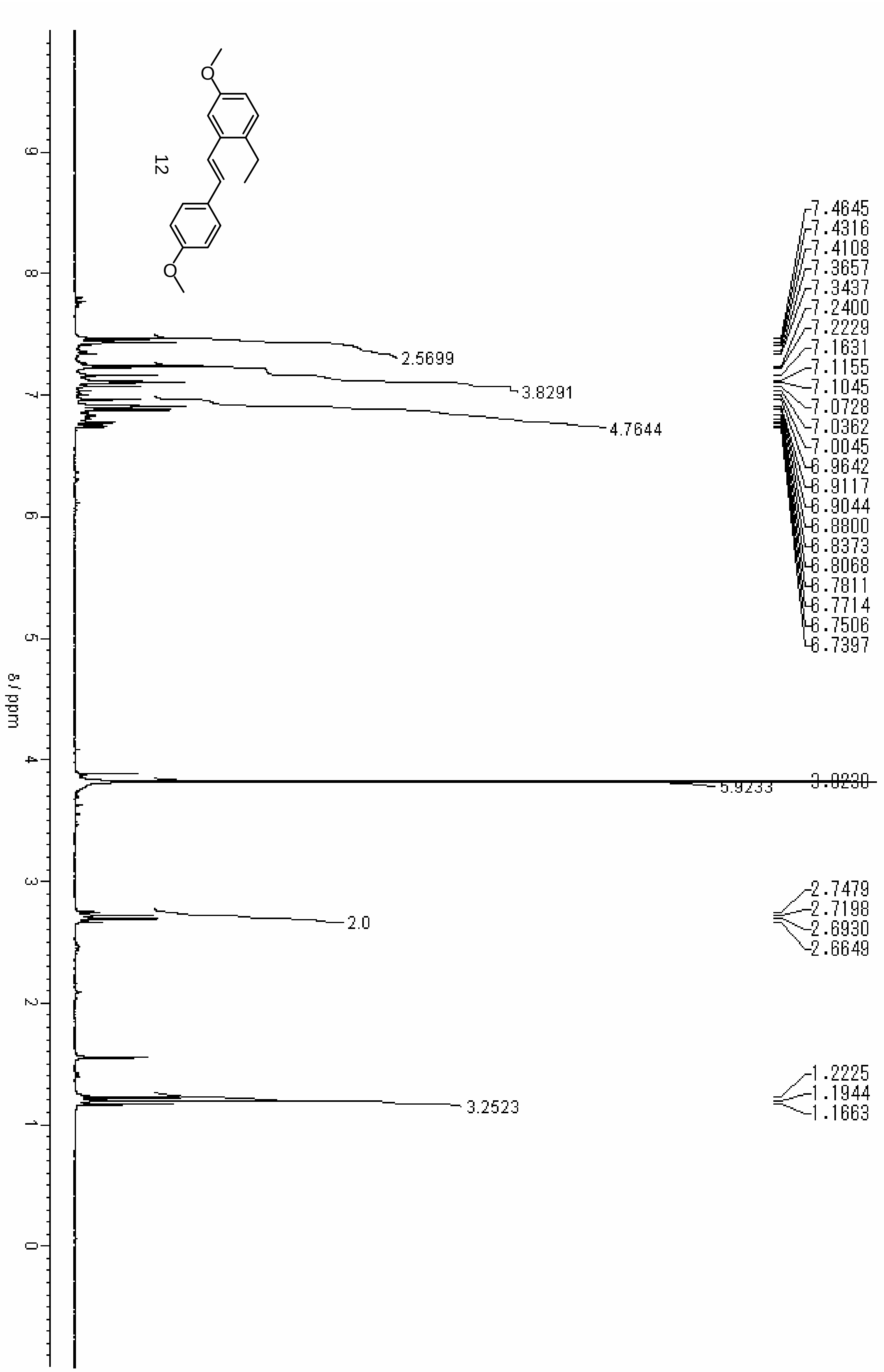
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O
δ / ppm
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8
7
6
5
4
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2
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2.0
3.2523
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7.4108
7.3657
7.3437
7.2400
7.2229
7.1631
7.1155
7.1045
7.0728
7.0362
7.0045
6.9642
6.9117
6.9044
6.8800
6.8373
6.8068
6.7811
6.7714
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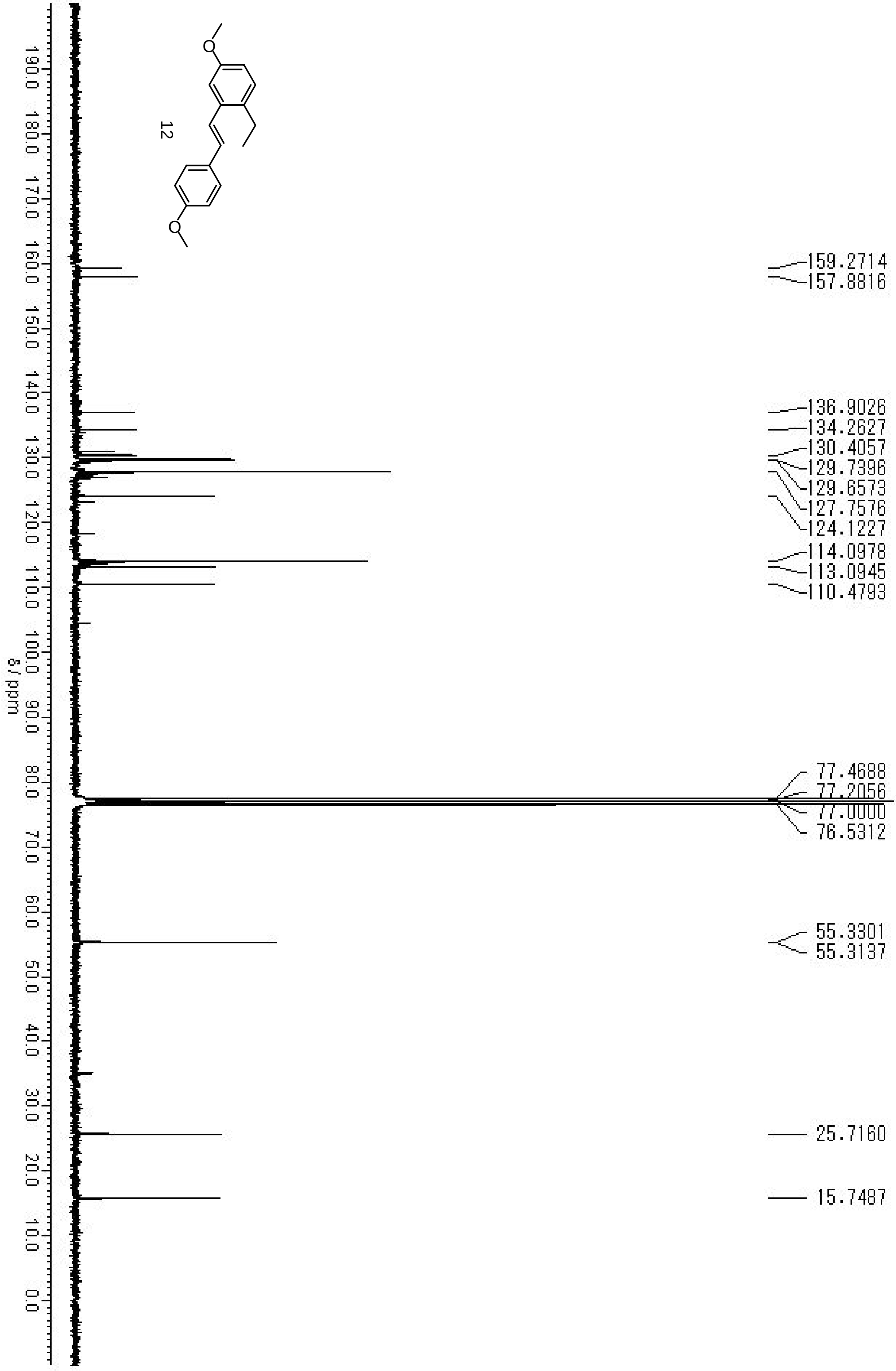

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130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
δ / ppm
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O
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136.9026
134.2627
130.4057
129.7396
129.6573
127.7576
124.1227
114.0978
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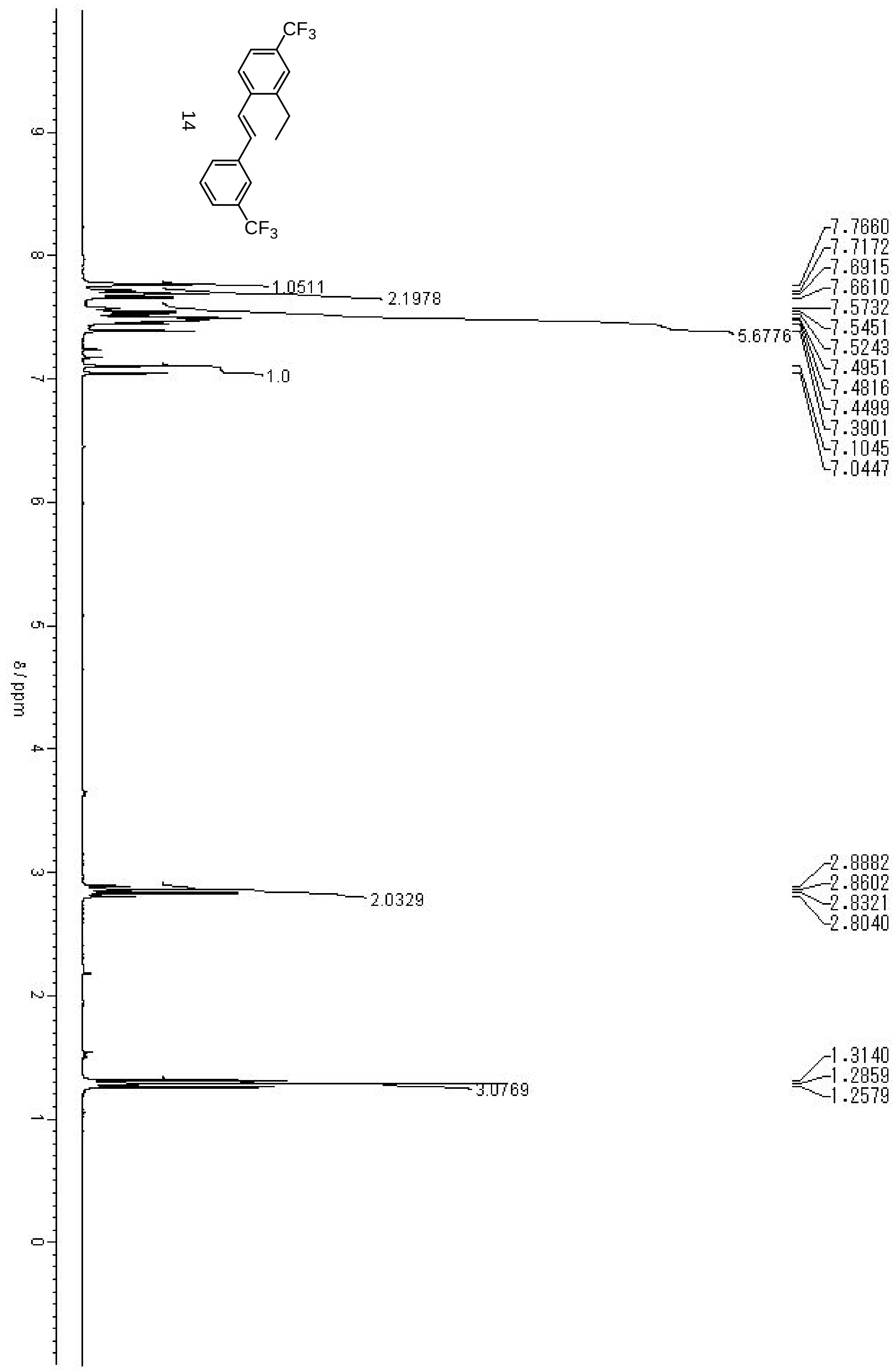
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CF3
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7
6
5
4
3
2
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0
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2.0329
3.0769
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7.7172
7.6915
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7.5732
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7.5243
7.4951
7.4816
7.4499
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7.1045
7.0447
2.8882
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1.2859
1.2579

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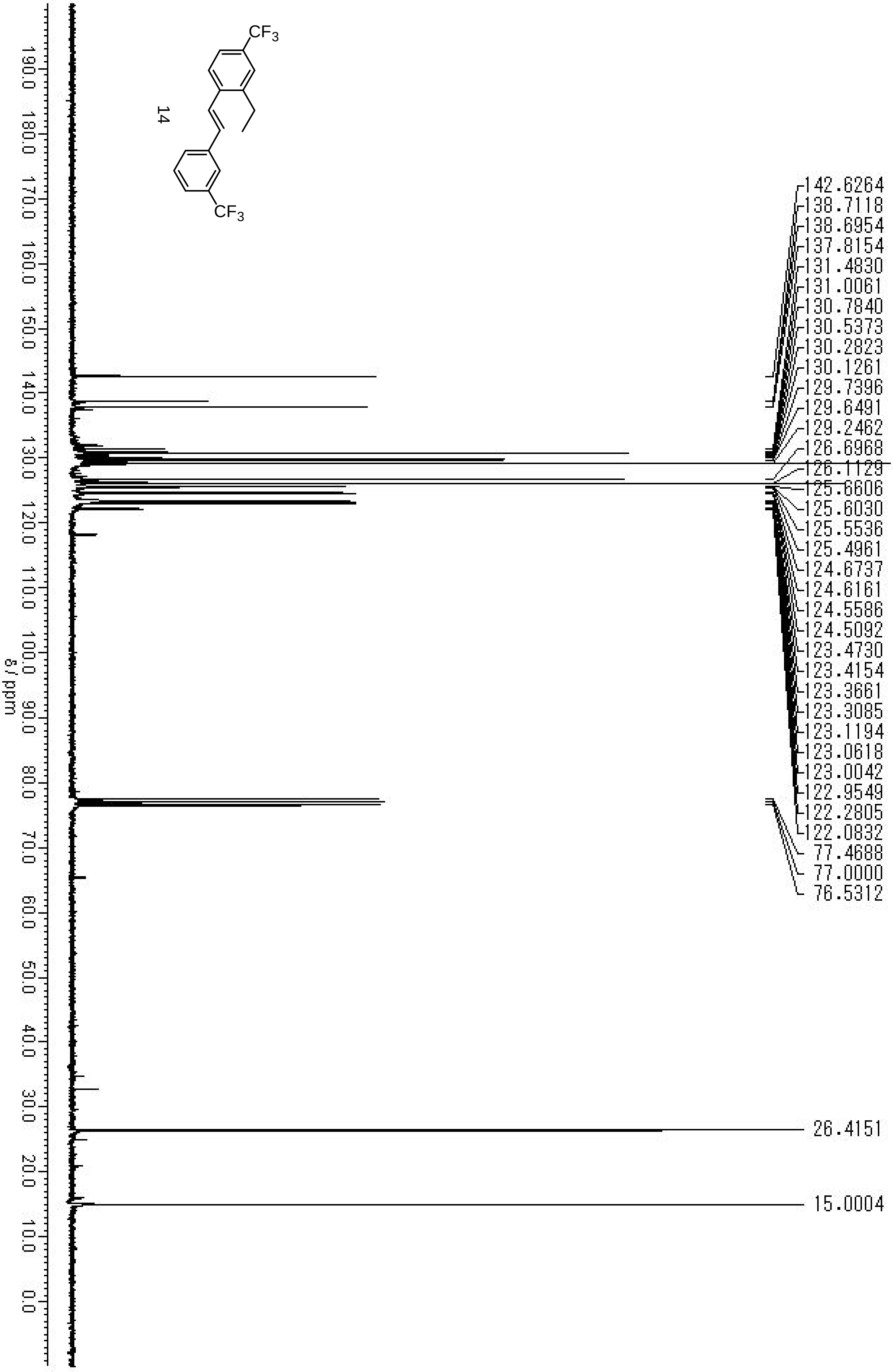
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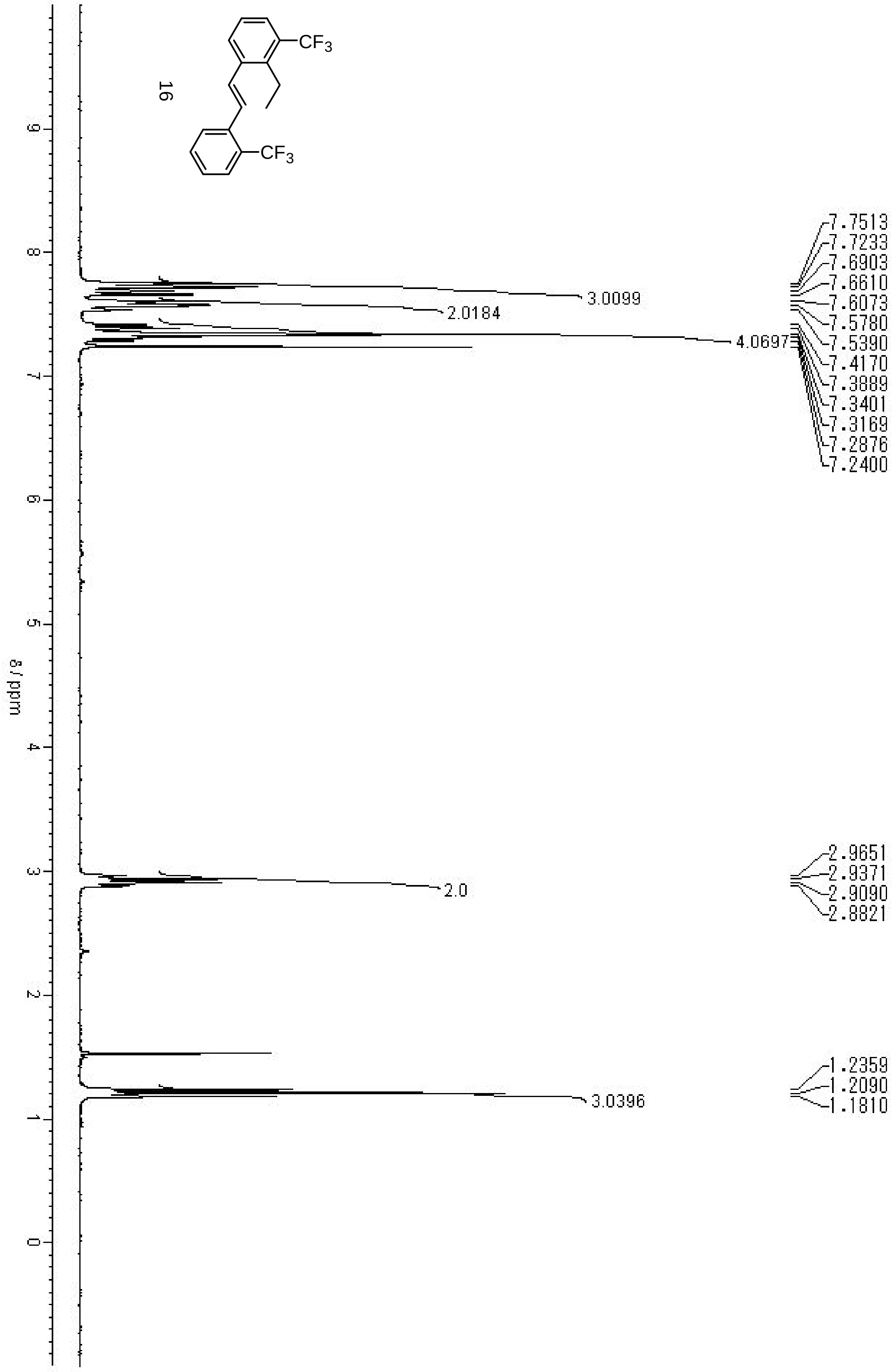
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CF3
δ / ppm
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8
7
6
5
4
3
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2.0
3.0396
7.7513
7.7233
7.6903
7.6610
7.6073
7.5780
7.5390
7.4170
7.3889
7.3401
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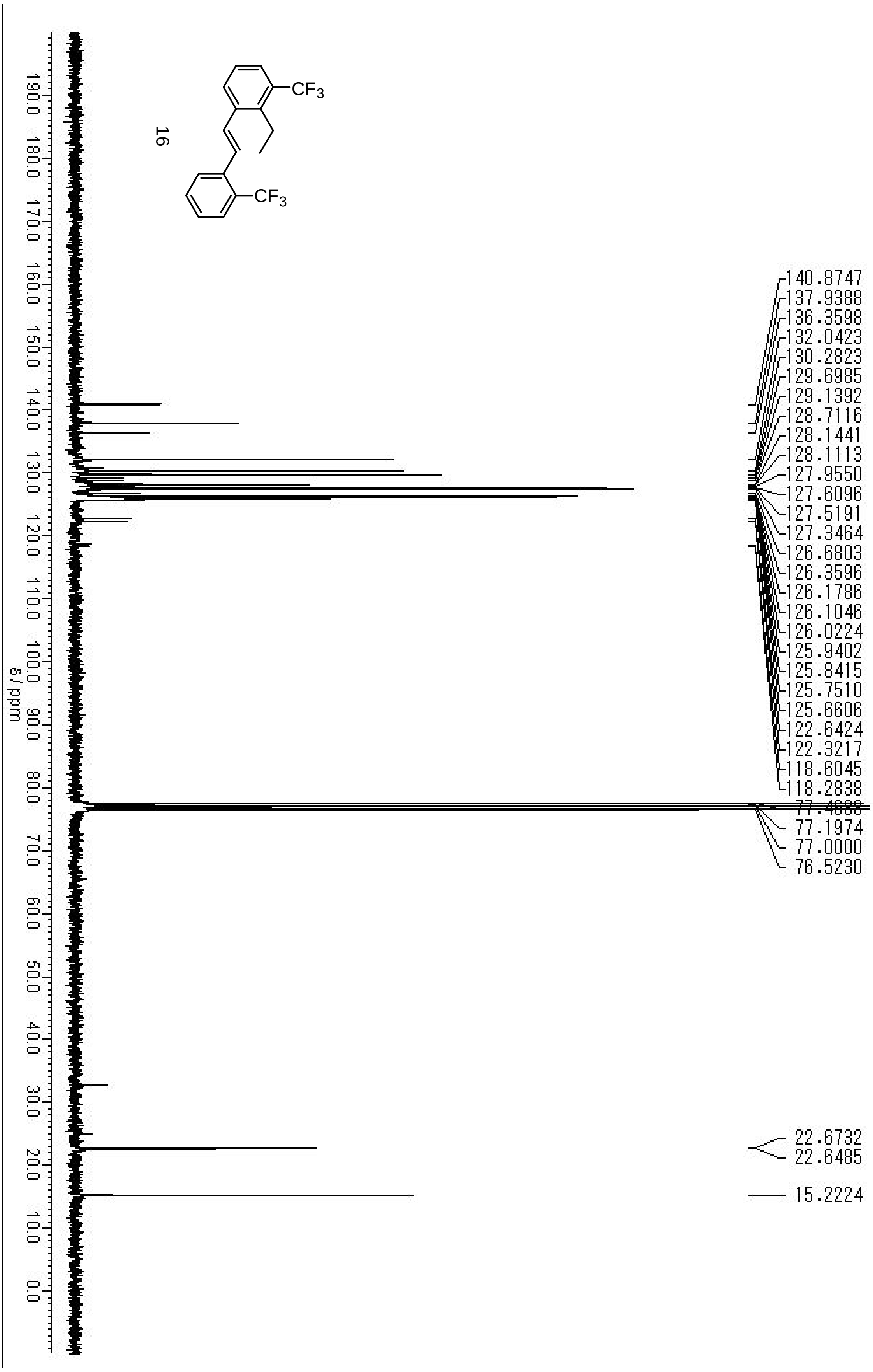
1.1810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CF3
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120.0
110.0
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90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
δ / ppm
140.8747
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136.3598
132.0423
130.2823
129.6985
129.1392
128.7116
128.1441
128.1113
127.9550
127.6096
127.5191
127.3464
126.6803
126.3596
126.1786
126.1046
126.0224
125.9402
125.8415
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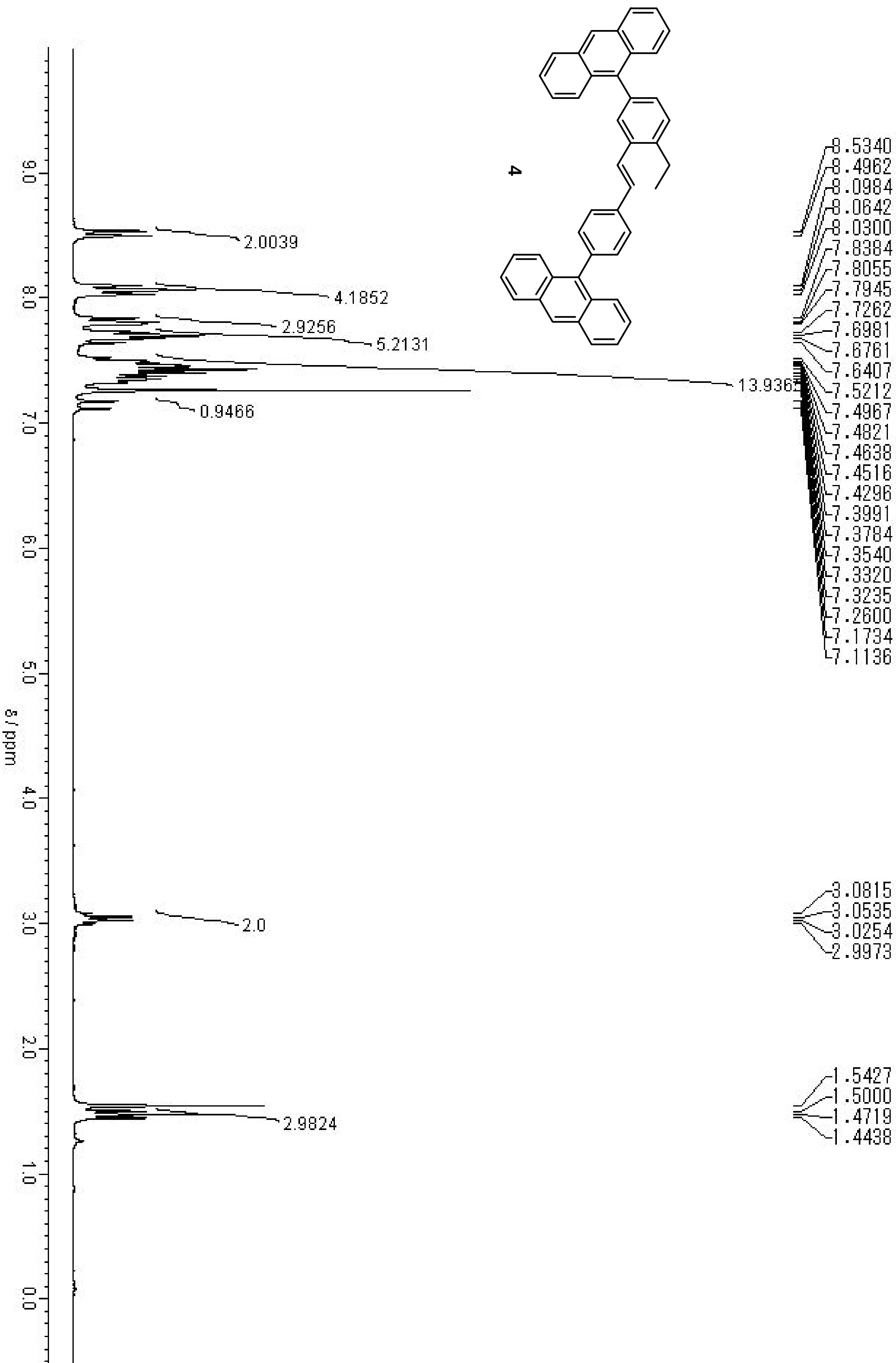
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7.6761
7.6407
7.5212
7.4967
7.4821
7.4638
7.4516
7.4296
7.3991
7.3784
7.3540
7.3320
7.3235
7.2600
7.1734
7.1136
3.0815
3.0535
3.0254
2.9973
1.5427
1.5000
1.4719
1.4438
2.0039
4.1852
2.9256
5.2131
13.936
0.9466
2.0
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4.0
3.0
2.0
1.0
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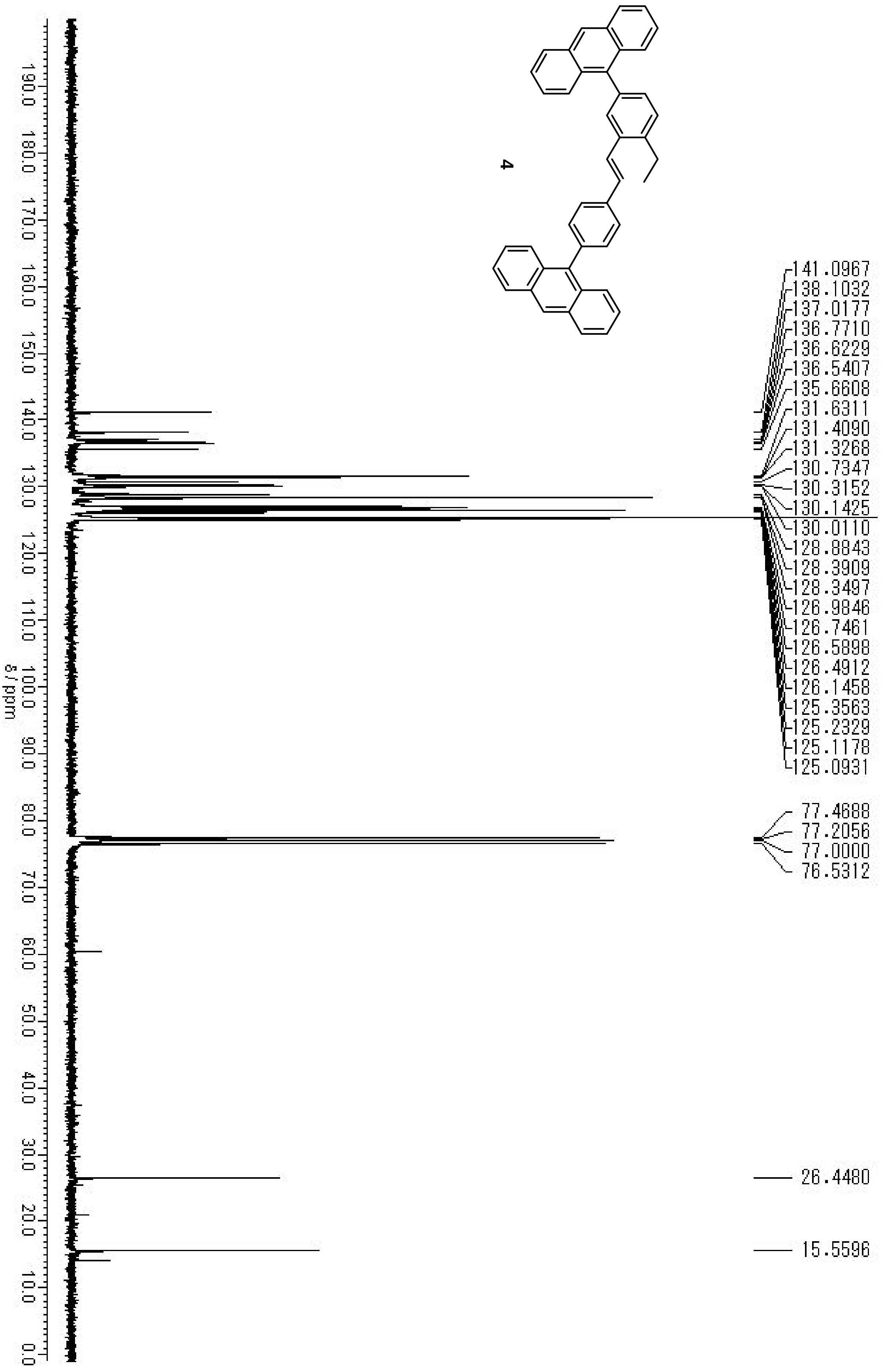
δ / ppm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100.0
δ / ppm
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80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
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136.6229
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135.6608
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131.4090
131.3268
130.7347
130.3152
130.1425
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128.8843
128.3909
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126.9846
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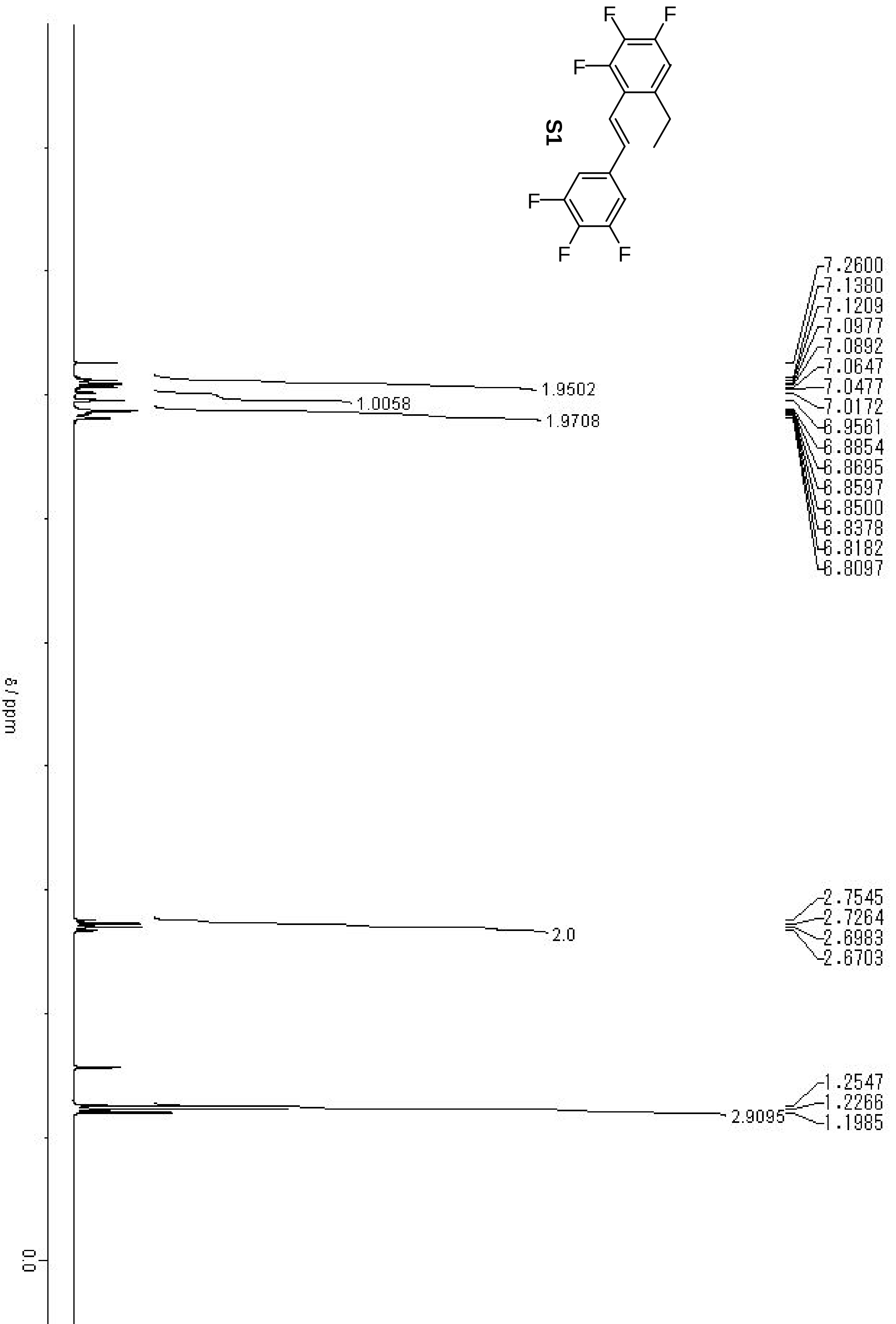

S1

F
F
F
F
F
F
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7.1380
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7.0892
7.0647
7.0477
7.0172
6.9561
6.8854
6.8695
6.8597
6.8500
6.8378
6.8182
6.8097
1.9502
1.0058
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δ / ppm
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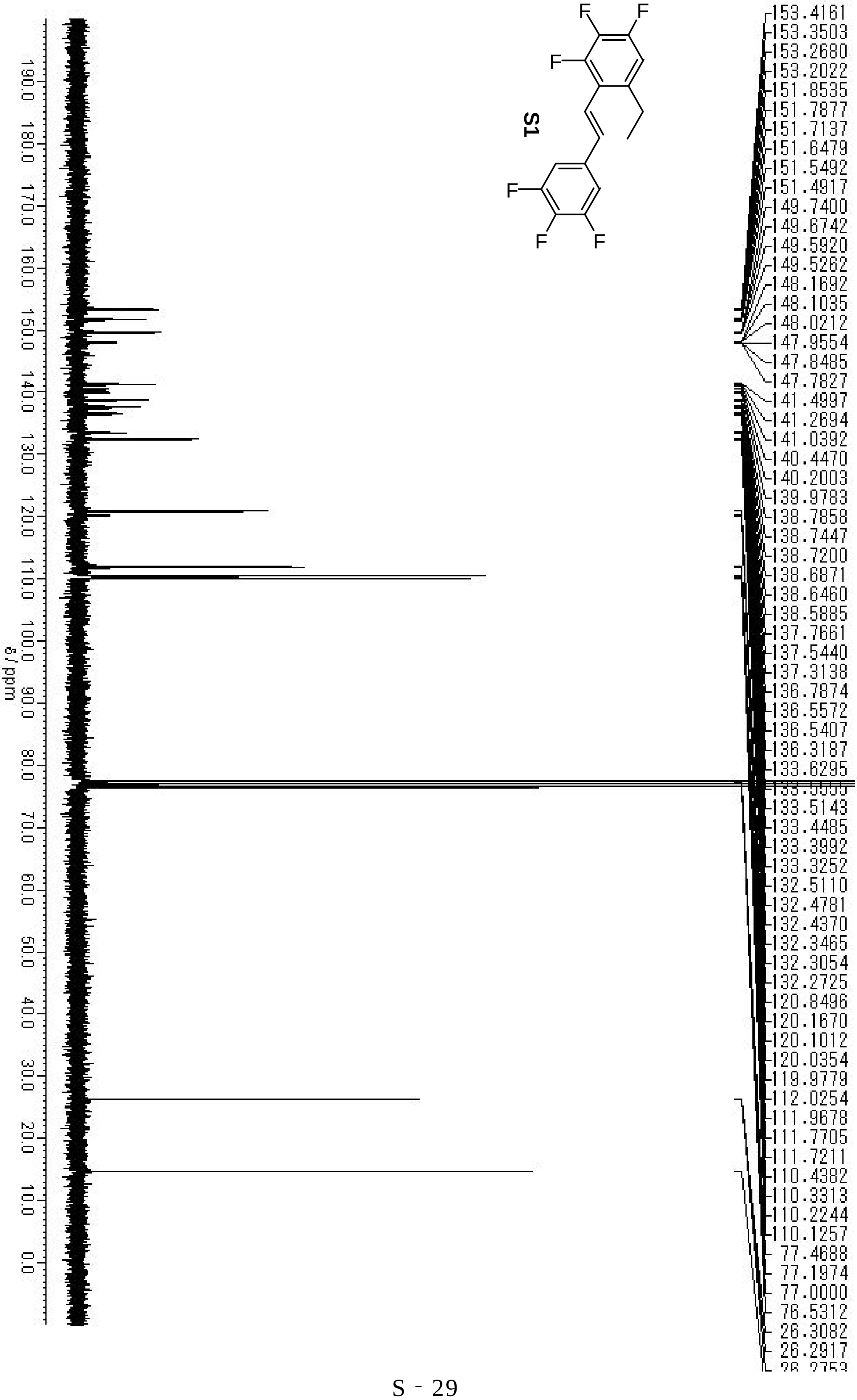

S1

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F
F
F
F
F
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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
δ / ppm
153.4161
153.3503
153.2680
153.2022
151.8535
151.7877
151.7137
151.6479
151.5492
151.4917
149.7400
149.6742
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147.8485
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132.4781
132.4370
132.3465
132.3054
132.2725
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120.1670
120.1012
120.0354
119.9779
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111.9678
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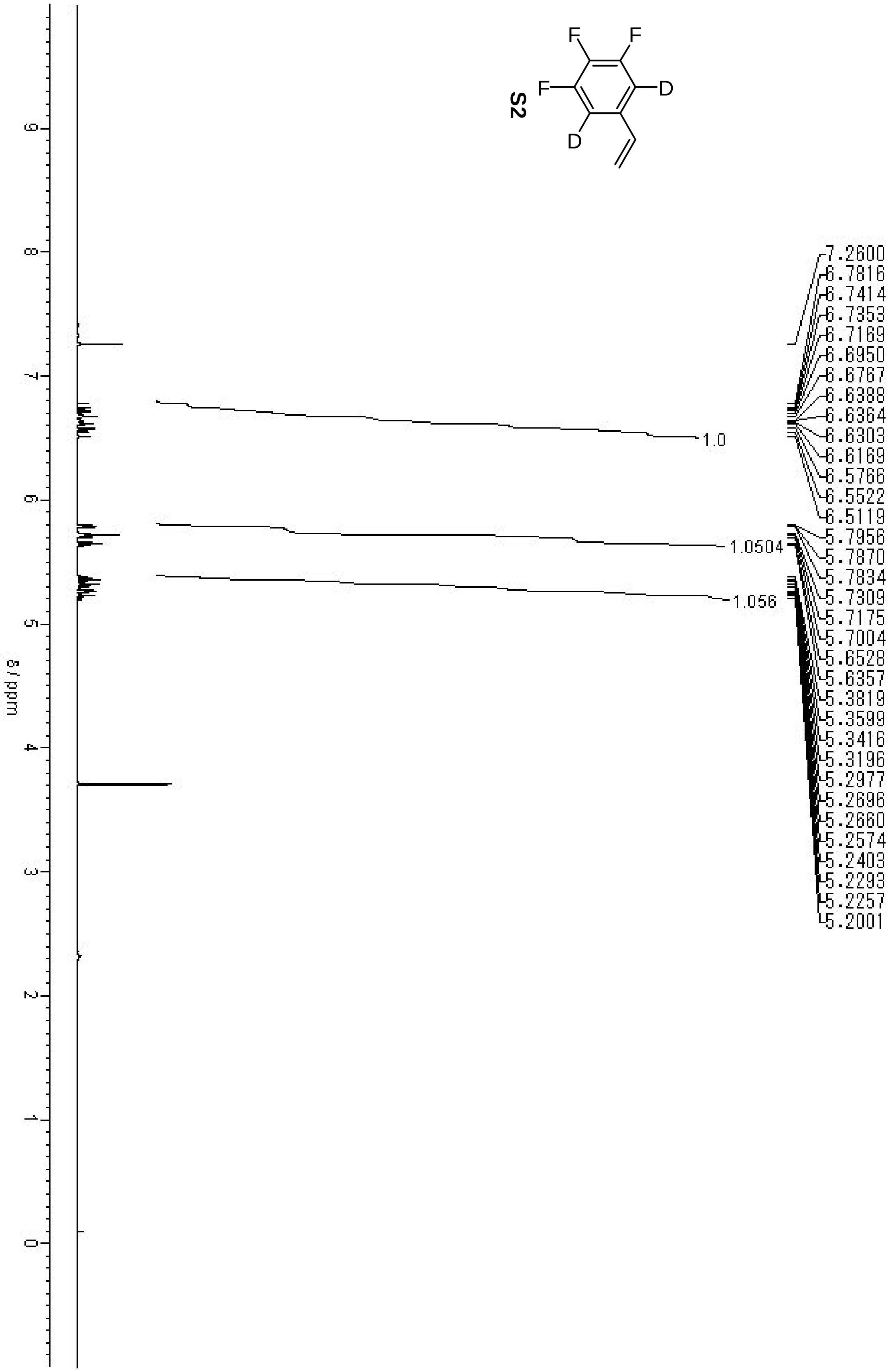
26.2917
26.2753


S2
F
F
F
D
D
9
8
7
6
5
4
3
2
1
0
δ / ppm
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1.0504
1.056
7.2600
6.7816
6.7414
6.7353
6.7169
6.6950
6.6767
6.6388
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5.7004
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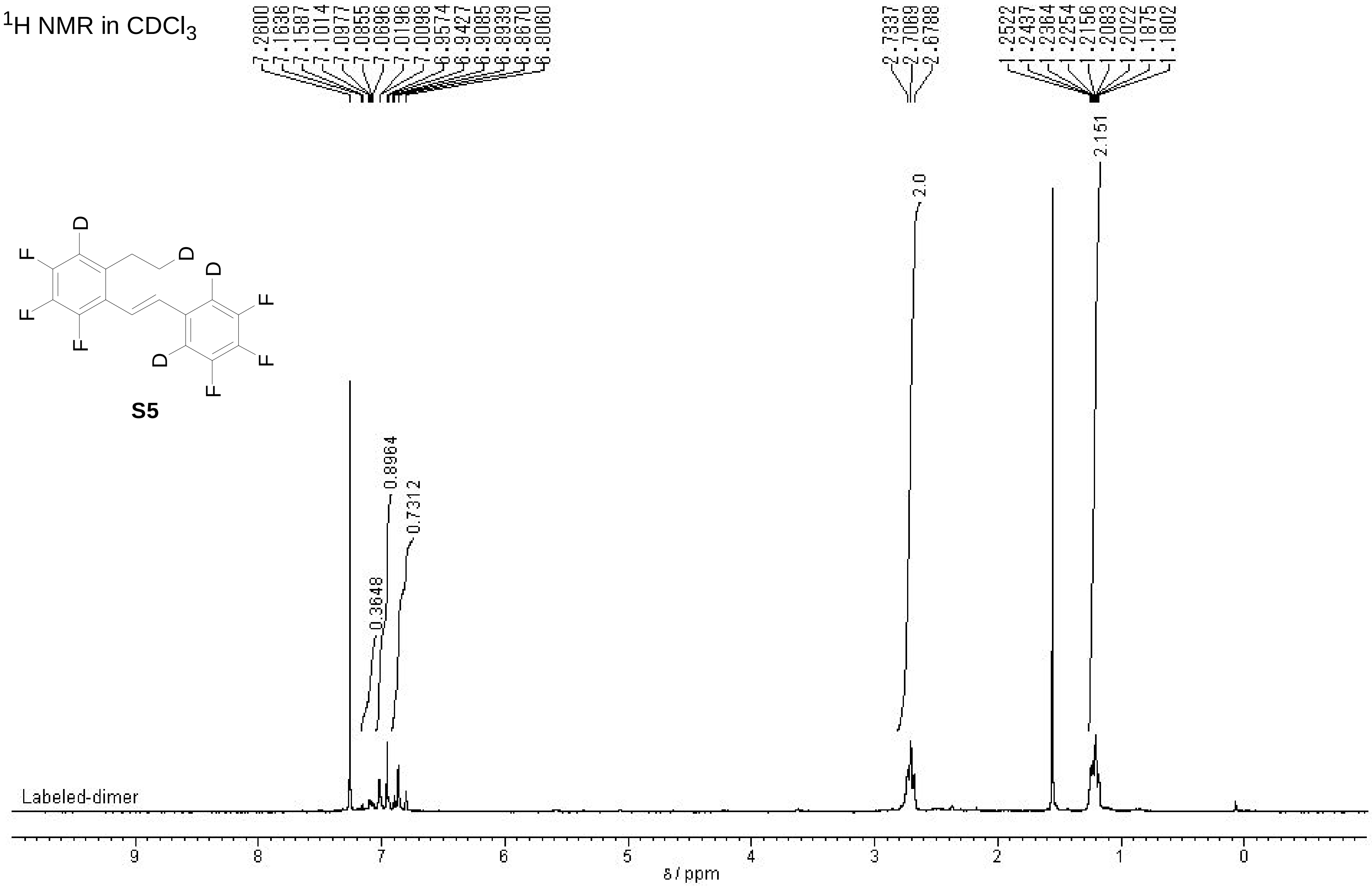
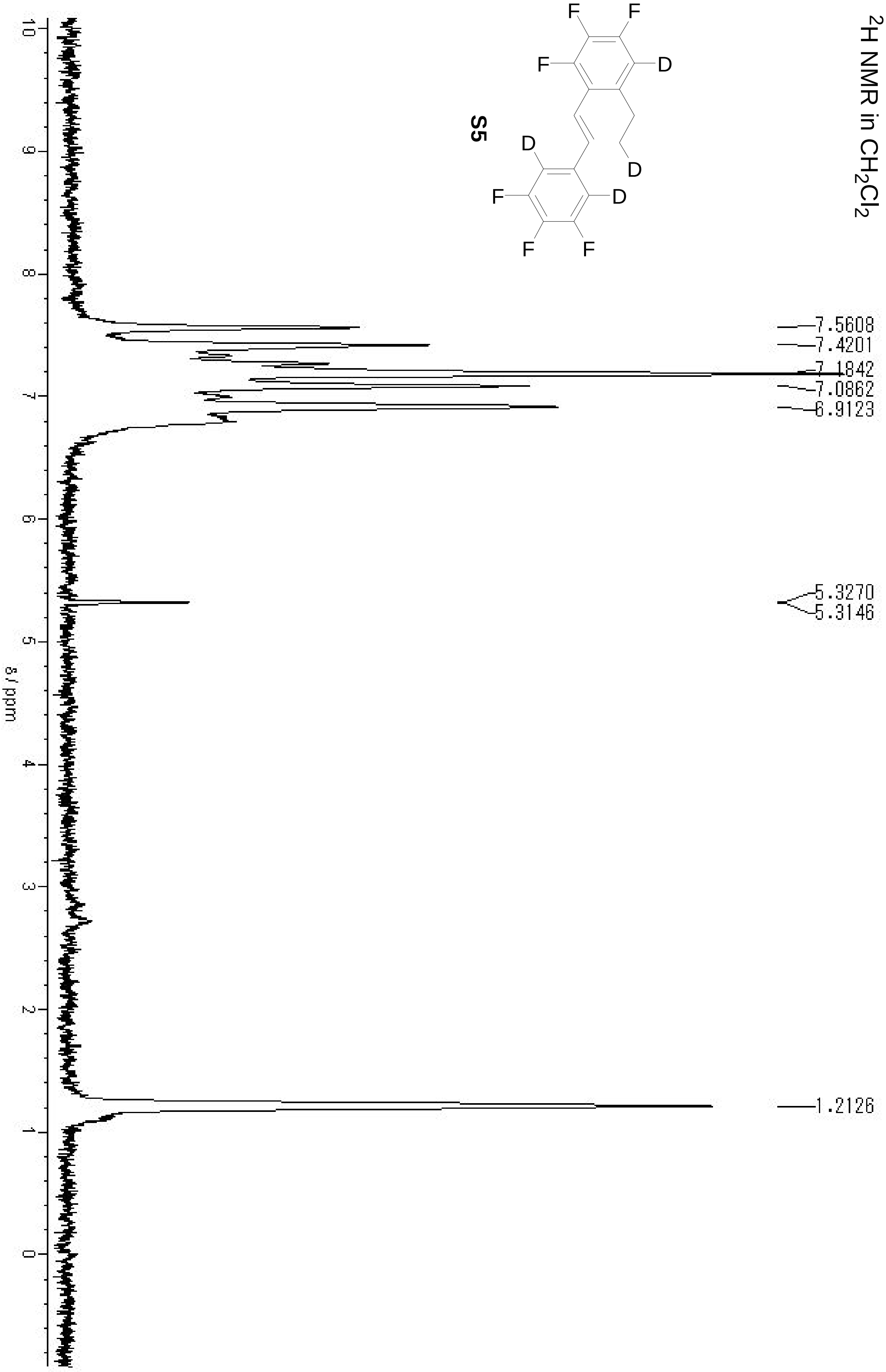
5.3819
5.3599
5.3416
5.3196
5.2977
5.2696
5.2660
5.2574
5.2403
5.2293
5.2257
5.2001

^{1}H NMR in CDCl$_3$



S5



^{2}H NMR in CH_2Cl_2

S5