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Supporting Information

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Palladium-Catalyzed, Sequential, Three Component Cross-Couplings of Aryl Halides, Alkynes and Arynes

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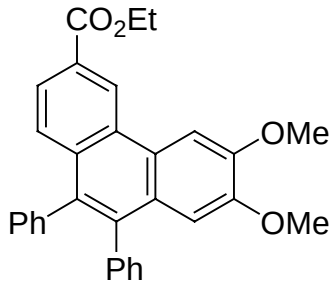
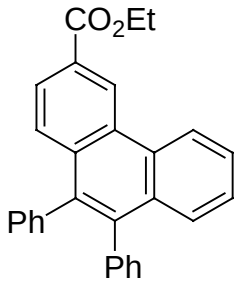
General. The ^{1}H and ^{13}C NMR spectra were recorded at 300 and 75.5 MHz or 400 and 100 MHz respectively. All melting points are uncorrected. High resolution mass spectra were recorded on a Kratos MS50TC double focusing magnetic sector mass spectrometer using EI at 70 eV. All reagents were used directly as obtained commercially unless otherwise noted. All yields reported represent an average of two independent runs. The silylaryl triflate **3b,** CsF, P(*o*-tolyl)$_3$ and acetonitrile were purchased from Sigma-Aldrich Co. Pd(dba)$_2$ was purchased from Acros Organics. The substituted silylaryl triflates **3a**, **3c**, **3d** and **3e** were prepared according to a literature procedure.[1] Unsymmetrical acetylenes **2e** and **2f** were prepared according to a literature procedure.[2]

General procedure for the palladium-catalyzed, three component cross- coupling. To a mixture of the haloarene (0.3 mmol), Pd(dba)$_2$ (0.015 mmol), TlOAc (0.36 mmol) and silylaryl triflate (0.36 mmol) in 2 mL of MeCN and 2 mL of toluene was added CsF (0.9 mmol). The reaction mixture was allowed to stir at 90 ^{o}C for 8 h. The resulting reaction mixture was washed with brine (20 mL) and extracted with CH_2Cl_2 (20 mL) twice. The combined CH_2Cl_2 fractions were dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to afford the desired product.



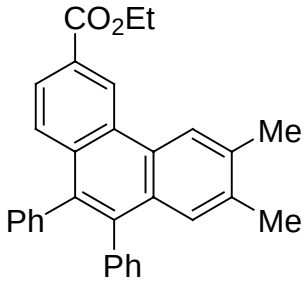
4a

Ethyl 6,7-dimethoxy-9,10-diphenylphenanthrene-3-carboxylate (4a). The indicated compound was obtained in an 86% yield as a white solid: mp 216-218 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.48 (t, J = 7.2 Hz, 3H), 3.72 (s, 3H), 4.20 (s, 3H), 4.50 (q, J = 7.2 Hz, 2H), 6.93 (s, 1H), 7.12-7.27 (m, 10H), 7.60 (d, J = 8.4 Hz, 1H), 8.02 (d, J = 8.4 Hz, 1H), 8.21 (s, 1H), 9.39 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.7, 55.8, 56.5, 61.4, 103.5, 108.3, 115.5, 124.8, 125.4, 126.8, 126.9, 127.3, 127.6, 127.9, 128.0, 128.2, 129.0, 130.9, 131.3, 134.1, 135.5, 139.1, 139.5, 139.6, 149.7, 149.8, 167.4; IR ($CDCl_3$, cm^{-1}) 3055, 2958, 2934, 2830, 1713, 1522; MS m/z 462.1836 (calcd $C_{31}H_{26}O_4$, 462.1831).



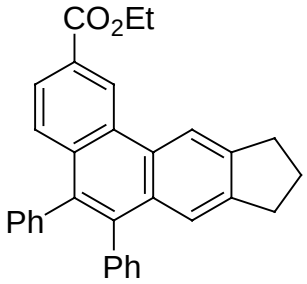
4b

Ethyl 9,10-diphenylphenanthrene-3-carboxylate (4b). The indicated compound was obtained in an 85% yield as a white solid from ethyl 4-iodobenzoate: mp 170-171 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.48 (t, J = 7.2 Hz, 3H), 4.49 (q, J = 7.2 Hz, 2H), 7.12-7.27 (m, 10H), 7.51-7.61 (m, 3H), 7.71 (t, J = 8.4 Hz, 1H), 8.08 (dd, J = 8.4, 1.2 Hz, 1H), 8.91 (d, J = 8.4 Hz, 1H), 9.54 (d, J = 1.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.7, 61.5, 115.5, 122.9, 125.1, 126.7, 126.9, 127.2, 127.4, 127.9, 128.0, 128.1, 128.2, 128.3, 129.7, 130.5, 131.0, 131.2, 132.2, 134.9, 137.1, 139.3, 139.4, 139.8, 167.2; IR ($CDCl_3$, cm^{-1}) 3056, 2980, 2929, 1715, 1263; MS m/z 402.1625 (calcd $C_{29}H_{22}O_2$, 402.1619).



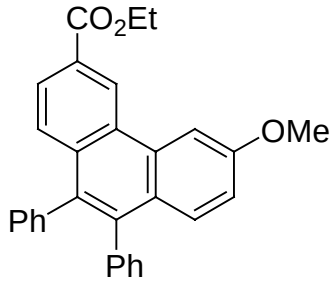
4c

Ethyl 6,7-dimethyl-9,10-diphenylphenanthrene-3-carboxylate (4c). The indicated compound was obtained in an 85% yield as a white solid: mp 209-211 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.48 (t, J = 7.2 Hz, 3H), 2.33 (s, 3H), 2.56 (s, 3H), 4.49 (q, J = 7.2 Hz, 2H), 7.10-7.26 (m, 10H), 7.30 (s, 1H), 7.56 (d, J = 8.8 Hz, 1H), 8.03 (dd, J = 8.4, 1.6 Hz, 1H), 8.65 (s, 1H), 9.49 (d, J = 1.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.7, 20.5, 20.7, 61.4, 123.3, 124.9, 126.0, 126.7, 126.8, 127.7, 127.8, 127.9, 128.0, 128.2, 128.8, 129.4, 130.7, 131.0, 131.3, 134.6, 136.2, 136.7, 136.8, 139.4, 139.5, 139.6, 167.4; IR ($CDCl_3$, cm^{-1}) 3049, 2937, 1707, 1443; MS m/z 430.1941 (calcd $C_{31}H_{26}O_2$, 430.1932).



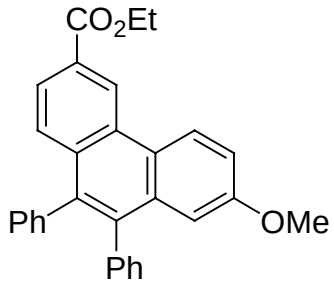
4d

Ethyl 5,6-diphenyl-9,10-dihydrocyclopenta[*b*]phenanthrene-2-carboxylate (4d). The indicated compound was obtained in an 81% yield as a white solid: mp 198-199 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.47 (t, J = 7.2 Hz, 3H), 2.16 (t, J = 7.2 Hz, 2H), 2.97 (t, J = 7.2 Hz, 2H), 3.20 (t, J = 7.2 Hz, 2H), 4.49 (q, J = 7.2 Hz, 2H), 7.11-7.25 (m, 10H), 7.37 (s, 1H), 7.56 (d, J = 8.4 Hz, 1H), 8.03 (dd, J = 8.4, 1.2 Hz, 1H), 8.76 (s, 1H), 9.51 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.8, 26.3, 33.2, 33.3, 61.4, 118.0, 123.0, 125.1, 126.0, 126.8, 127.8, 127.9, 128.0, 129.5, 129.8, 131.0, 131.3, 134.6, 136.1, 139.6, 139.9, 140.0, 144.6, 144.7, 167.3; IR ($CDCl_3$, cm^{-1}) 3056, 2959, 2938, 2856, 1711, 1441; MS m/z 442.1939 (calcd $C_{32}H_{26}O_2$, 442.1932).



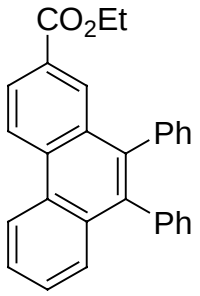
4e

Ethyl 6-methoxy-9,10-diphenylphenanthrene-3-carboxylate (4e). The indicated compound was obtained in a 40% yield as a white solid: mp 138-140 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.48 (t, J = 7.2 Hz, 3H), 4.07 (s, 3H), 4.50 (q, J = 7.2 Hz, 2H), 7.13-7.27 (m, 11H), 7.51 (d, J = 9.2 Hz, 1H), 7.60 (d, J = 8.8 Hz, 1H), 8.07 (dd, J = 8.8, 1.6 Hz, 1H), 8.26 (d, J = 2.4 Hz, 1H), 9.46 (d, J = 1.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.7, 55.9, 61.5, 104.3, 117.2, 125.2, 126.6, 126.8, 126.8, 126.9, 127.6, 127.8, 127.9, 128.2, 128.6, 129.1, 129.2, 129.9, 130.9, 131.4, 132.0, 135.4, 139.4, 139.5, 158.9, 167.3; IR ($CDCl_3$, cm^{-1}) 3056, 2957, 2931, 1712, 1521; MS m/z 432.1732 (calcd $C_{30}H_{24}O_3$, 432.1725).



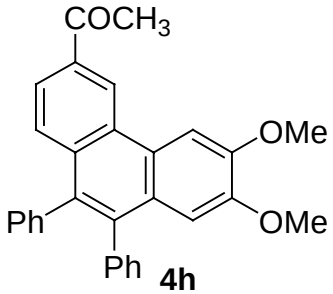
4f

Ethyl 7-methoxy-9,10-diphenylphenanthrene-3-carboxylate (4f). The indicated compound was obtained in a 40% yield as a white solid: mp 160-162 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.48 (t, J = 7.2 Hz, 3H), 3.72 (s, 3H), 4.49 (q, J = 7.2 Hz, 2H), 6.95 (d, J = 2.8 Hz, 1H), 7.12-7.27 (m, 10H), 7.36 (dd, J = 8.8, 2.8 Hz, 1H), 7.57 (d, J = 8.4 Hz, 1H), 8.02 (dd, J = 8.8, 1.6 Hz, 1H), 8.83 (d, J = 9.2 Hz, 1H), 9.43 (d, J = 1.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.7, 55.4, 61.4, 109.2, 115.5, 117.0, 124.6, 124.7, 124.8, 125.6, 126.9, 127.0, 127.9, 128.0, 128.1, 128.2, 129.8, 130.9, 131.1, 133.8, 133.9, 137.7, 139.3, 139.4, 158.8, 167.2; IR ($CDCl_3$, cm^{-1}) 3055, 2955, 2934, 1713, 1522; MS m/z 432.1732 (calcd $C_{30}H_{24}O_3$, 432.1725).



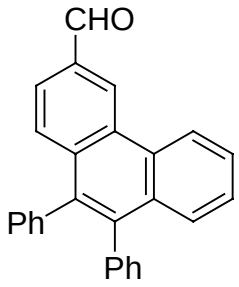
4g

Ethyl 9,10-diphenylphenanthrene-2-carboxylate (4g). The indicated compound was obtained in a 76% yield as a white solid: mp 180-181 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.36 (t, J = 7.2 Hz, 3H), 4.36 (q, J = 7.2 Hz, 2H), 7.15-7.29 (m, 10H), 7.53-7.62 (m, 2H), 7.70 (t, J = 7.6 Hz, 1H), 8.28 (dd, J = 8.8, 1.6 Hz, 1H), 8.33 (d, J = 1.2 Hz, 1H), 8.82-8.86 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.5, 61.3, 122.9, 123.4, 126.4, 126.8, 126.9, 127.0, 127.9, 128.0, 128.2, 128.6, 129.6, 130.3, 131.1, 131.2, 131.7, 133.0, 133.2, 137.9, 138.2, 138.9, 139.4, 166.9; IR ($CDCl_3$, cm^{-1}) 3056, 3025, 2980, 1715, 1259; MS m/z 402.1625 (calcd $C_{29}H_{22}O_2$, 402.1619).



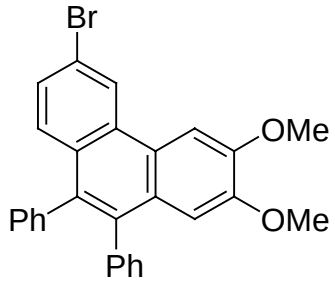
4h

1-(6,7-Dimethoxy-9,10-diphenylphenanthren-3-yl)ethanone (4h). The indicated compound was obtained in a 91% yield as a white solid: mp 206-208 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.76 (s, 3H), 3.71 (s, 3H), 4.19 (s, 3H), 6.92 (s, 1H), 7.11-7.26 (m, 10H), 7.60 (d, J = 8.4 Hz, 1H), 7.91 (dd, J = 8.8, 0.8 Hz, 1H), 8.19 (s, 1H), 9.28 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.3, 55.8, 56.5, 103.4, 108.4, 123.1, 124.8, 125.7, 126.8, 127.0, 127.4, 127.9, 128.0, 128.4, 129.1, 130.8, 131.3, 134.2, 134.3, 135.4, 139.4, 139.4, 139.5, 149.7, 149.9, 198.7; IR ($CDCl_3$, cm^{-1}) 3056, 2990, 2940, 2832, 1672, 1510; MS m/z 432.1732 (calcd $C_{30}H_{24}O_3$, 432.1725).



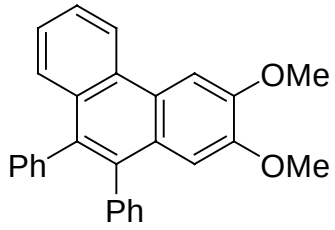
4i

9,10-Diphenylphenanthrene-3-carbaldehyde (4i). The indicated compound was obtained in a 91% yield as a white solid: mp 213-215 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13-7.28 (m, 10H), 7.54-7.77 (m, 4H), 7.95 (dd, J = 8.4, 1.2 Hz, 1H), 8.91 (d, J = 8.0 Hz, 1H), 9.30 (s, 1H), 10.28 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 115.5, 122.8, 125.3, 127.0, 127.1, 127.5, 127.7, 127.9, 128.0, 128.4, 129.0, 130.0, 130.4, 130.9, 131.1, 132.3, 134.0, 136.1, 137.2, 139.0, 139.1, 140.9, 192.7; IR ($CDCl_3$, cm^{-1}) 3055, 2826, 1696, 1605; MS m/z 358.1363 (calcd $C_{27}H_{18}O$, 358.1357).



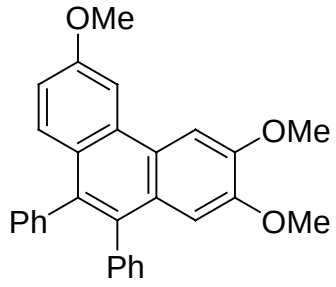
4j

6-Bromo-2,3-dimethoxy-9,10-diphenylphenanthrene (4j). The indicated compound was obtained in a 78% yield as a white solid: mp 210-211 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.72 (s, 3H), 4.17 (s, 3H), 6.91 (s, 1H), 7.11-7.26 (m, 10H), 7.41 (d, J = 9.2 Hz, 1H), 7.49 (dd, J = 8.8, 1.6 Hz, 1H), 7.99 (s, 1H), 8.74 (d, J = 1.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.8, 56.4, 103.2, 108.2, 120.7, 123.9, 124.9, 126.8, 126.9, 127.6, 127.8, 127.9, 128.9, 129.9, 130.0, 130.9, 131.1, 131.3, 135.4, 137.2, 139.4, 139.7, 149.6, 149.8; IR ($CDCl_3$, cm^{-1}) 3056, 2999, 2956, 2825, 1521, 1261; MS m/z 468.0732 (calcd $C_{28}H_{21}BrO_2$, 468.0725).



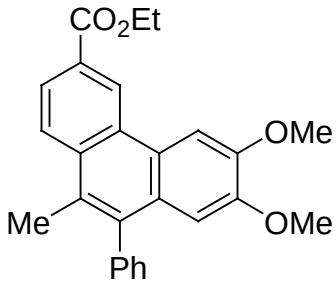
4k

2,3-Dimethoxy-9,10-diphenylphenanthrene (4k). The indicated compound was obtained in a 75% yield as a white solid: mp 228-229 °C (lit.[3] 228-229 °C); the ^{1}H and ^{13}C NMR spectra match the literature data;[3] MS m/z 390.1624 (calcd $C_{28}H_{22}O_2$, 390.1619).



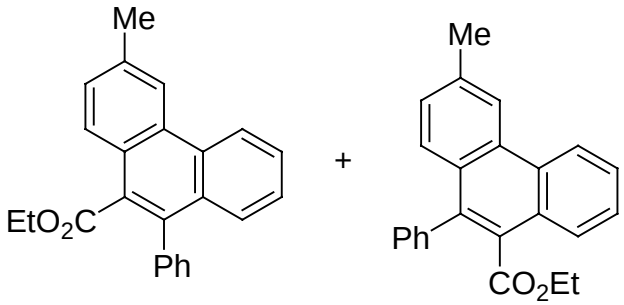
4l

2,3,6-Trimethoxy-9,10-diphenylphenanthrene (4l). The indicated compound was obtained in a 49% yield as a white solid: mp 180-181 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.71 (s, 3H), 4.03 (s, 3H), 4.15 (s, 3H), 6.91 (s, 1H), 7.09 (dd, J = 8.8, 2.4 Hz, 1H), 7.13-7.26 (m, 10H), 7.48 (d, J = 9.2 Hz, 1H), 7.99 (d, J = 2.4 Hz, 1H), 8.01 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.8, 55.8, 56.4, 103.5, 104.3, 108.2, 115.2, 124.2, 126.2, 126.5, 126.6, 127.6, 127.7, 127.8, 129.8, 130.9, 131.3, 131.4, 134.5, 135.7, 140.0, 140.1, 149.1, 149.4, 158.2; IR ($CDCl_3$, cm^{-1}) 3054, 2998, 2932, 2831, 1614, 1507, 1260; MS m/z 420.1731 (calcd $C_{29}H_{24}O_3$, 420.1725).



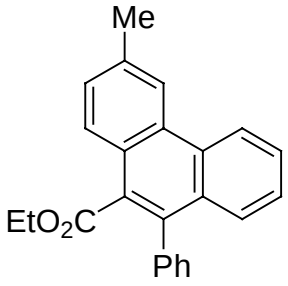
4m

Ethyl 6,7-dimethoxy-10-methyl-9-phenylphenanthrene-3-carboxylate (4m). The indicated compound was obtained in a 56% yield as a white solid: mp 150-151 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.50 (t, J = 7.2 Hz, 3H), 2.44 (s, 3H), 3.69 (s, 3H), 4.15 (s, 3H), 4.52 (q, J = 7.2 Hz, 2H), 6.73 (s, 1H), 7.30-7.32 (m, 2H), 7.46-7.55 (m, 3H), 8.12-8.21 (m, 3H), 9.33 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.7, 17.5, 55.8, 56.4, 61.4, 103.4, 108.1, 124.6, 125.1, 125.5, 125.7, 127.4, 127.5, 127.8, 128.0, 128.9, 129.1, 130.2, 134.3, 139.1, 140.7, 149.2, 149.4, 167.4; IR ($CDCl_3$, cm^{-1}) 3056, 2935, 2830, 1712, 1522, 1256; MS m/z 400.1681 (calcd $C_{26}H_{24}O_4$, 400.1674).



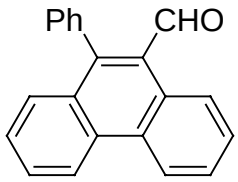
4o (6:1) **4n**

Ethyl 6-methyl-10-phenylphenanthrene-9-carboxylate (4o) and ethyl 3-methyl- 10-phenylphenanthrene-9-carboxylate (4n). The indicated compounds were obtained as a mixture in a 6:1 ratio in an 80% yield as a white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.95-0.99 (m, 3.5H), 2.62 (s, 0.5H), 2.65 (s, 3H), 4.11 (q, J = 7.2 Hz, 2.4H), 7.43-7.52 (m, 8H), 7.62-7.70 (m, 2.5H), 7.84 (d, J = 8.0 Hz, 1H), 8.55 (s, 1 H), 8.75 (d, J = 8.4 Hz, 1H).



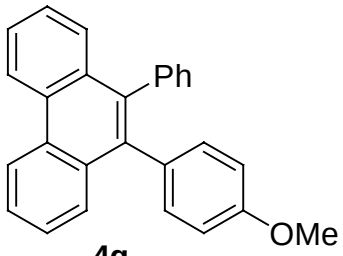
4o

Ethyl 6-methyl-10-phenylphenanthrene-9-carboxylate (4o). The indicated compound was obtained in a 68% yield as a white solid by crystallizing the above mixture of **4o** and **4n**: mp 144-146 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.95 (t, J = 7.2 Hz, 3H), 2.63 (s, 3H), 4.10 (q, J = 7.2 Hz, 2H), 7.42-7.50 (m, 7H), 7.60-7.67 (m, 2H), 7.82 (d, J = 8.4 Hz, 1H), 8.53 (s, 1H), 8.74 (d, J = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0, 22.4, 61.3, 122.8, 122.9, 125.9, 126.9, 127.4, 127.9, 128.1, 128.3, 129.3, 130.2, 130.5, 130.6, 130.7, 131.2, 135.7, 137.1, 138.5, 169.6; IR ($CDCl_3$, cm^{-1}) 3059, 3000, 2977, 2954, 2929, 1718, 1445, 1227; MS m/z 340.1468 (calcd $C_{24}H_{20}O_2$, 340.1463).



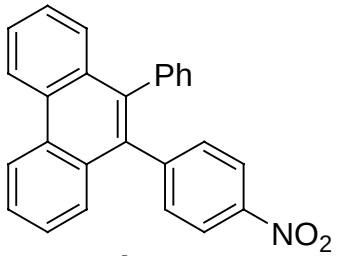
4p

10-Phenylphenanthrene-9-carbaldehyde (4p). The indicated compound was obtained in an 81% yield as a white solid: mp 124-126 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.59 (m, 7H), 7.70-7.76 (m, 3H), 7.74 (d, J = 9.2 Hz, 2H), 9.28-9.30 (m, 1H), 10.12 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 122.7, 123.0, 126.9, 127.2, 127.6, 128.1, 128.3, 128.5, 128.6, 128.9, 129.8, 130.4, 131.1, 131.2, 132.8, 136.4, 148.9, 195.5; IR ($CDCl_3$, cm^{-1}) 3062, 2868, 2765, 1679, 1369; MS m/z 282.1045 (calcd $C_{21}H_{14}O$, 282.1044).



4q

9-(4-Methoxyphenyl)-10-phenylphenanthrene (4q). The indicated compound was obtained in a 79% yield as a white solid: mp 217-218 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.76 (s, 3H), 6.76 (dt, J = 8.8, 2.4 Hz, 2H), 7.03-7.26 (m, 7H), 7.44-7.66 (m, 6H), 8.79 (d, J = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.4, 113.3, 122.7, 126.5, 126.6, 126.7, 126.8, 127.9, 128.0, 128.1, 130.1, 130.2, 131.2, 132.0, 132.2, 132.3, 132.5, 137.1, 137.7, 140.0, 158.2; IR ($CDCl_3$, cm^{-1}) 3056, 2986, 2831, 1613, 1507; MS m/z 360.1518 (calcd $C_{27}H_{20}O$, 360.1514).



4s

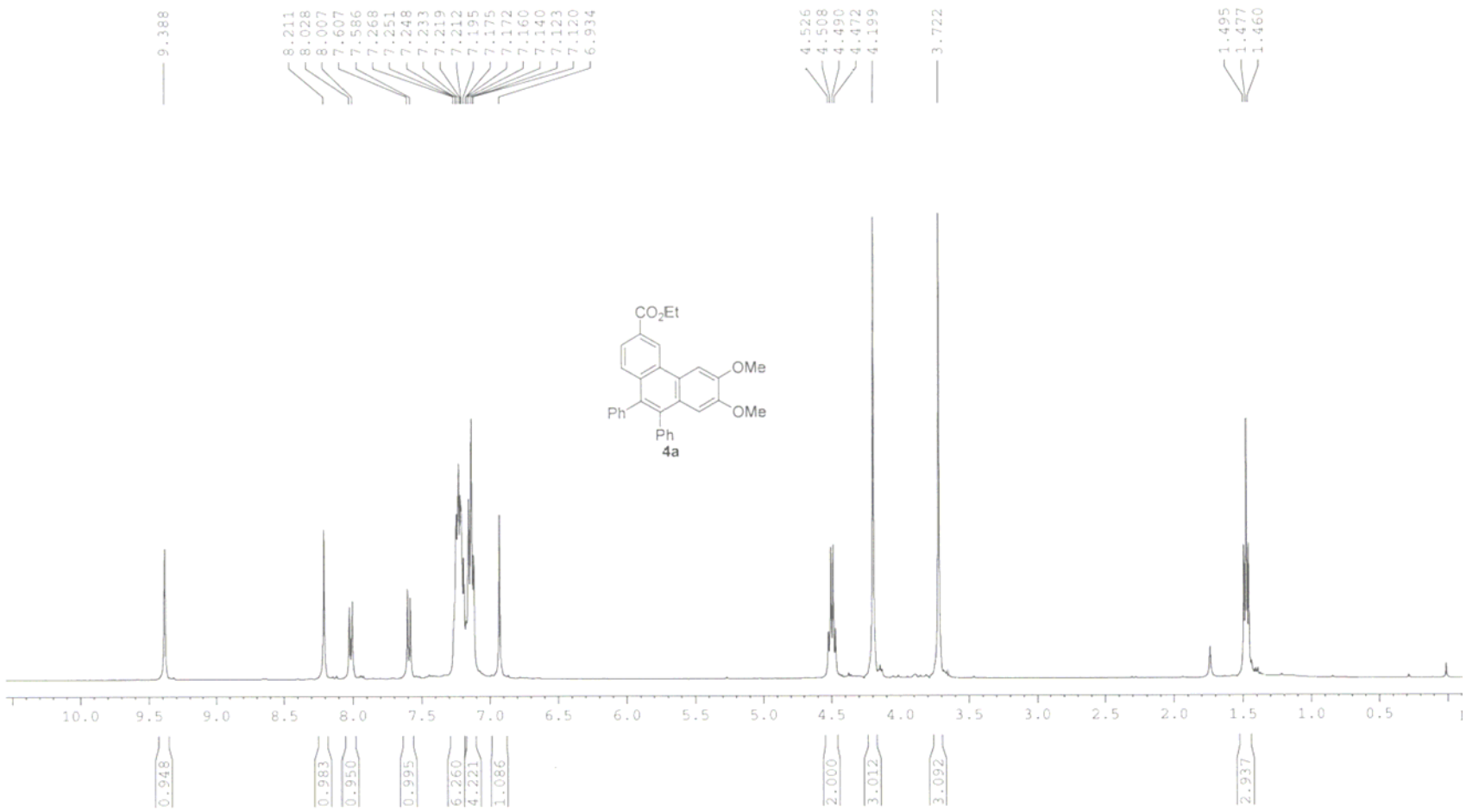
9-(4-Nitrophenyl)-10-phenylphenanthrene (4s). The indicated compound was obtained in an 89% yield as a white solid: mp 234-235 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10-7.12 (m, 2H), 7.21-7.41 (m, 6H), 7.49-7.58 (m, 3H), 7.67-7.72 (m, 2H), 8.10 (dd, J = 7.2, 2.0 Hz, 2H), 8.80-8.84 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 122.8, 123.0, 123.2, 127.1, 127.2, 127.2, 127.2, 127.3, 127.4, 128.2, 128.2, 130.3, 130.4, 130.9, 131.0, 131.7, 132.3, 135.1, 137.8, 138.9, 146.7, 147.4; IR ($CDCl_3$, cm^{-1}) 3053, 2985, 1600, 1517, 1263; MS m/z 375.1267 (calcd $C_{26}H_{17}NO_2$, 375.1259).

References

[1] H. Yoshida, J. Ikadai, M. Shudo, J. Ohshita, A. Kunai, *J. Am. Chem. Soc*. **2003**, *125*, 6638.

[2] Y. Liang, Y.-X. Xie, J.-H. Li, *J. Org. Chem.* **2006**, *71*, 379.

[3] Z. Liu, X. Zhang, R. C. Larock, *J. Am. Chem. Soc*. **2005**, *127*, 15716.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OMe
OMe
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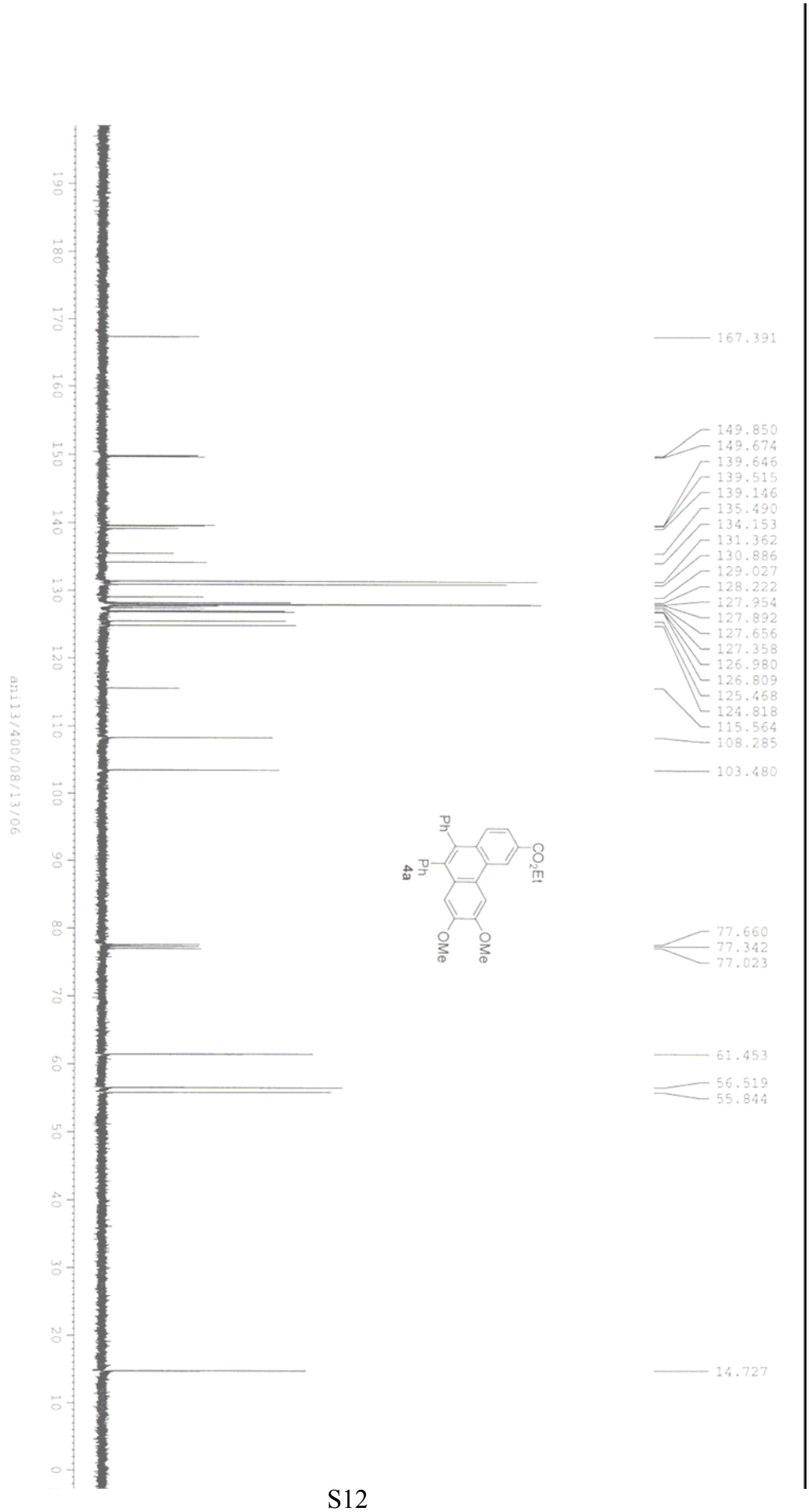
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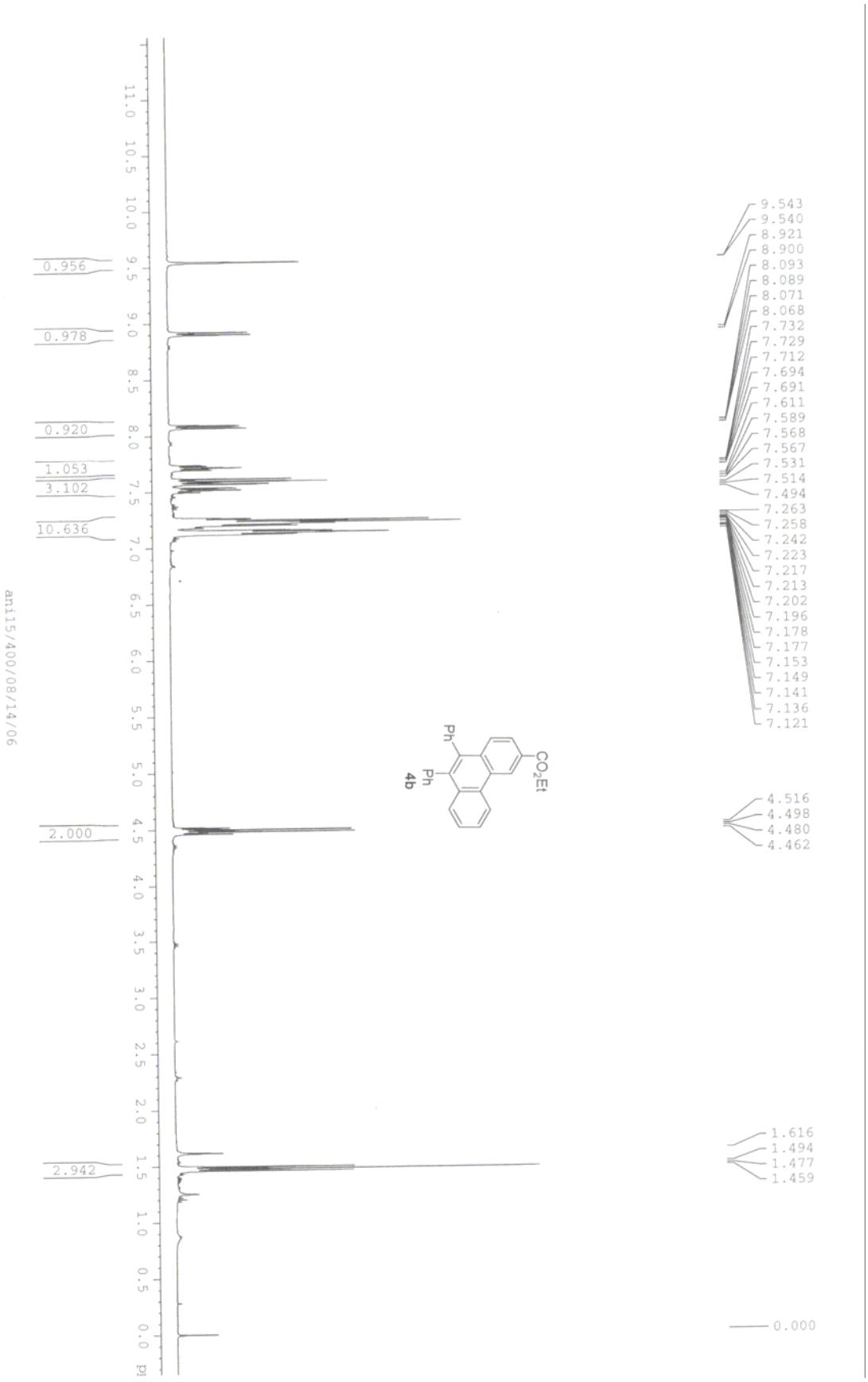
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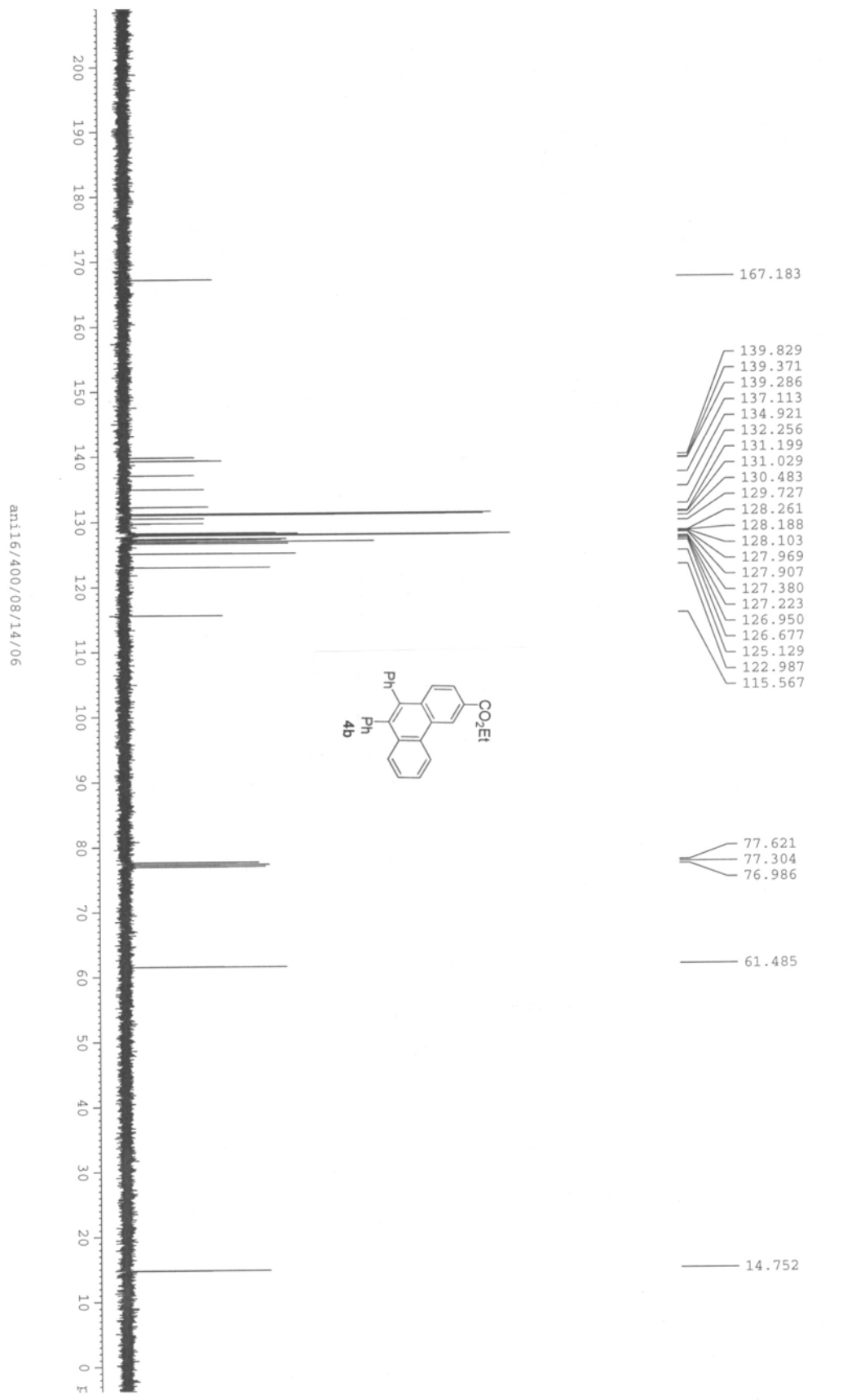
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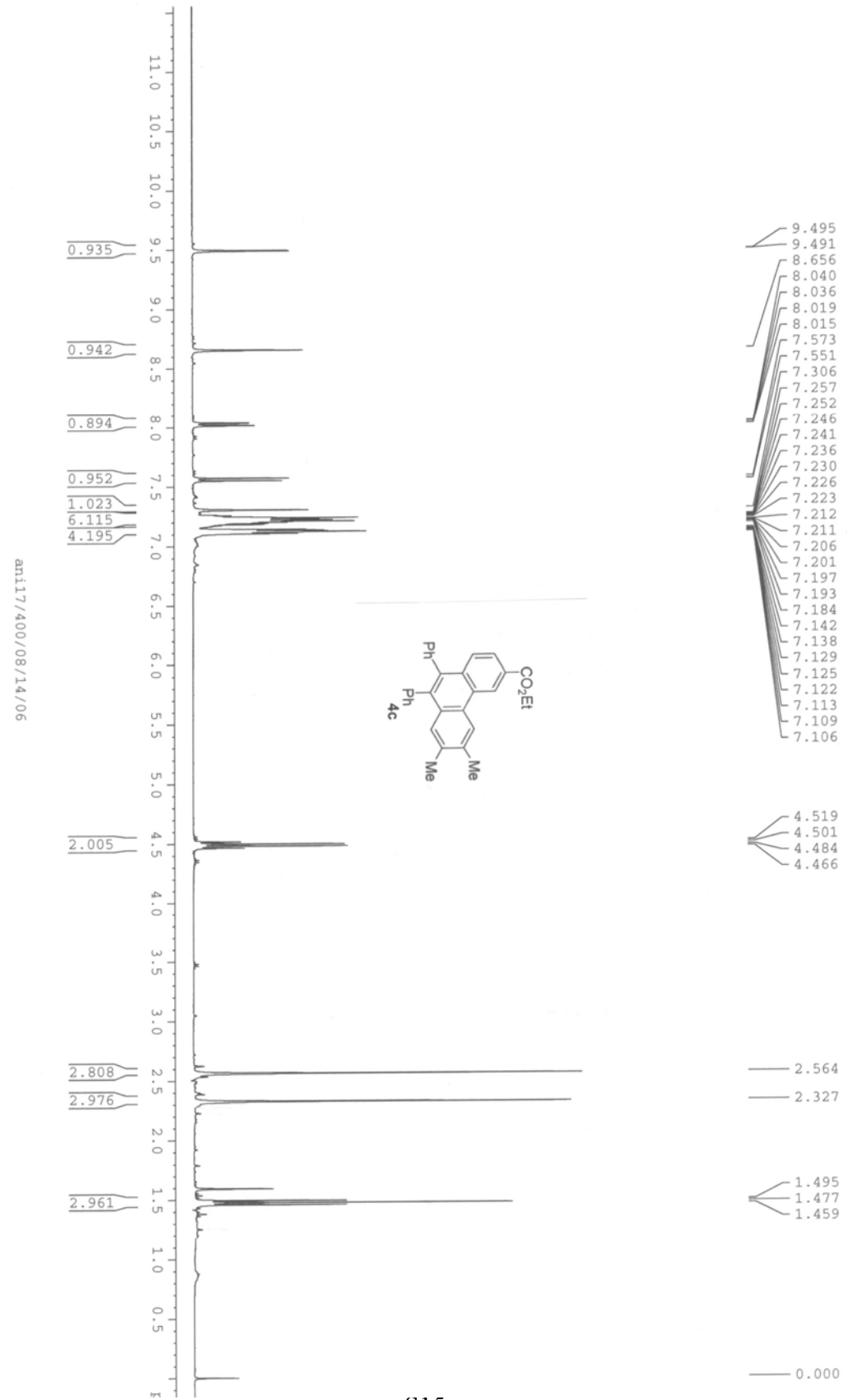
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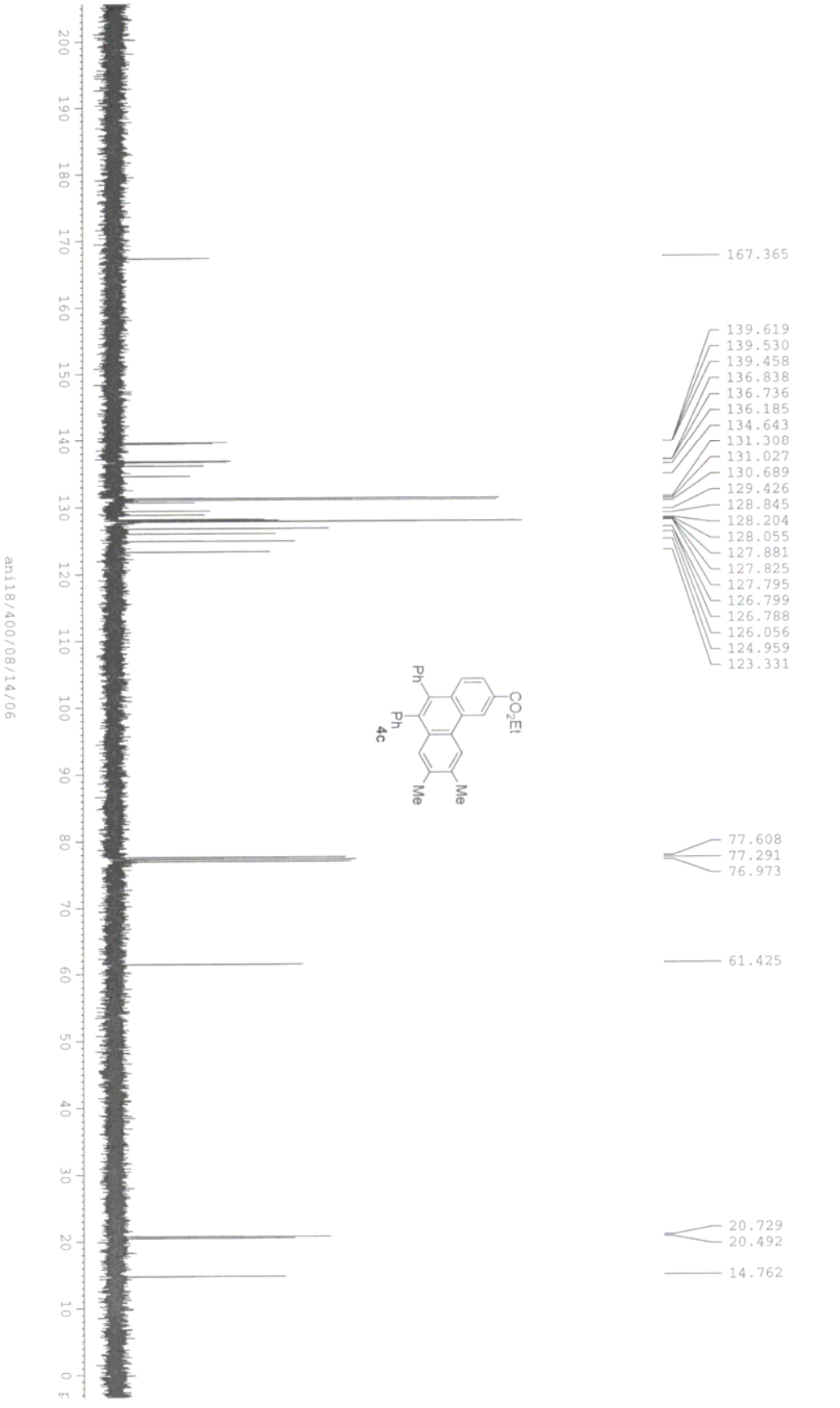
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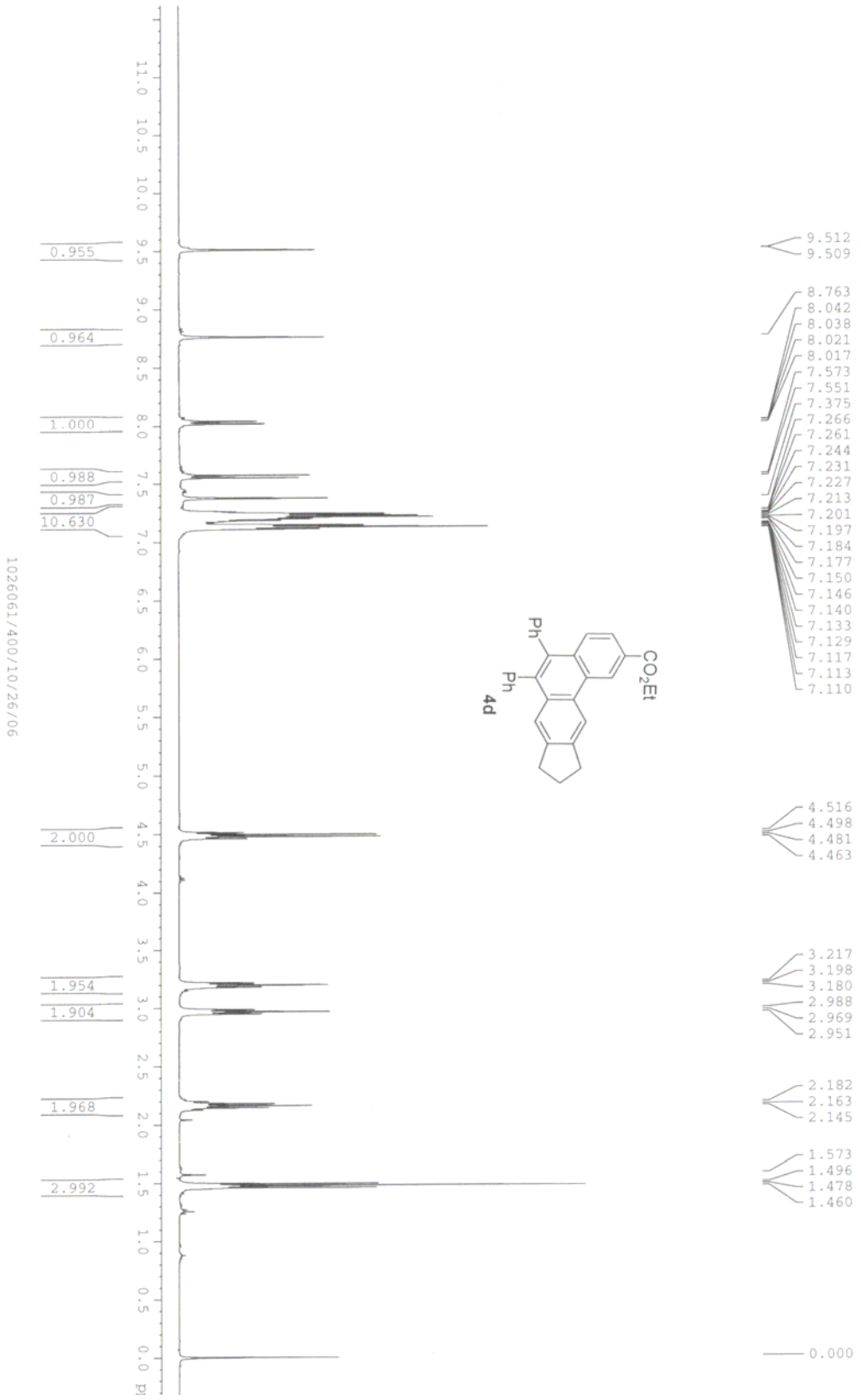
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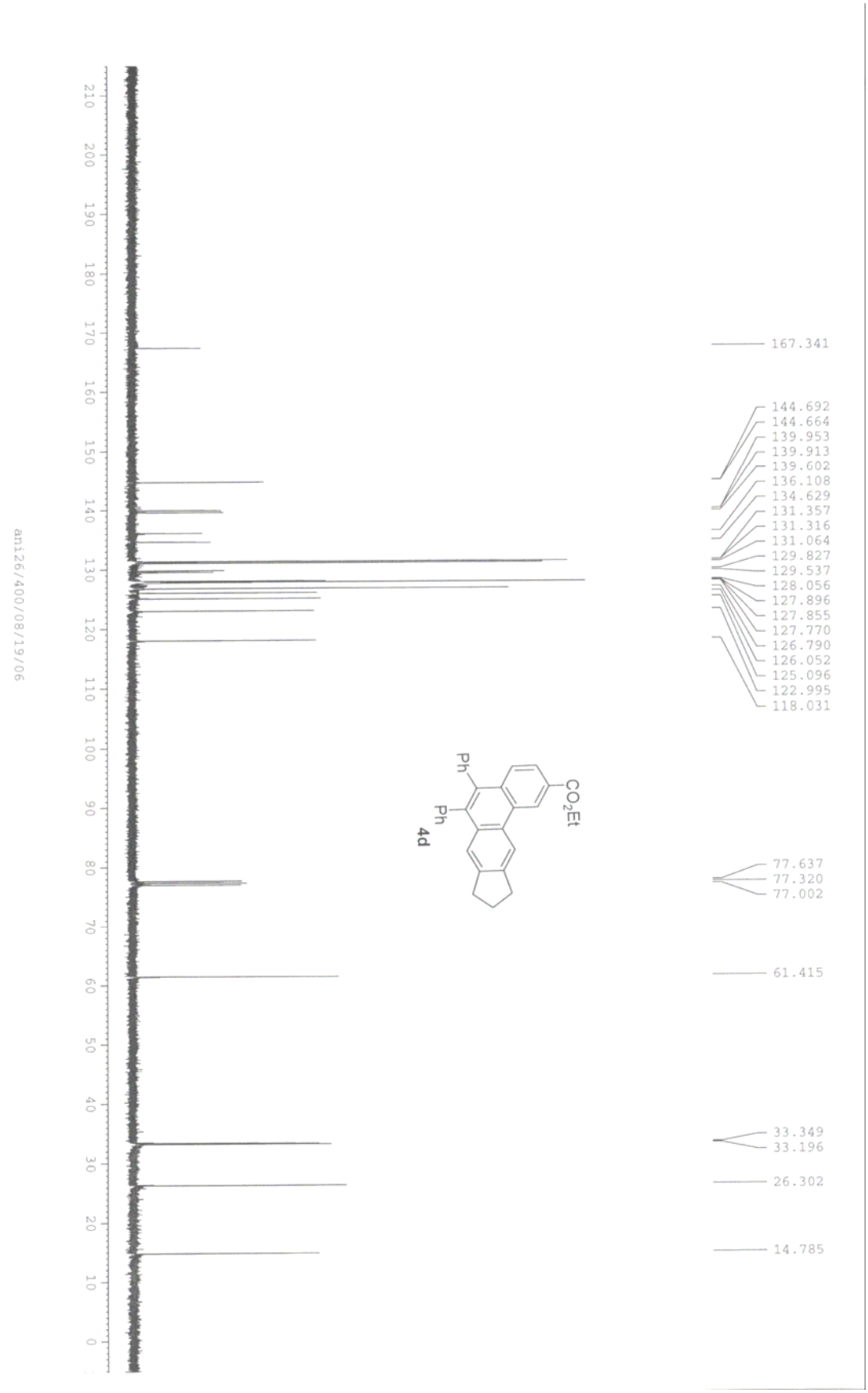
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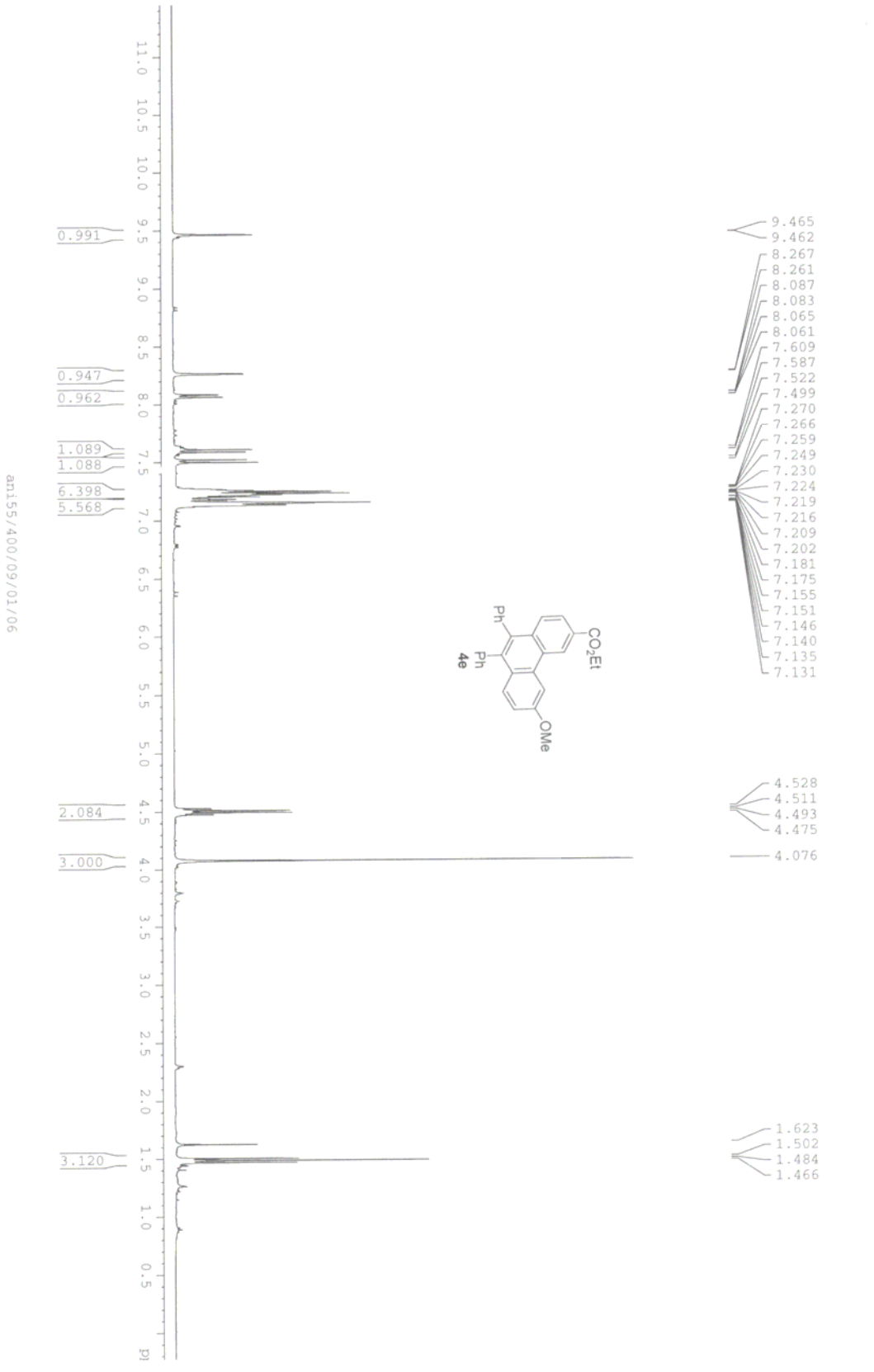
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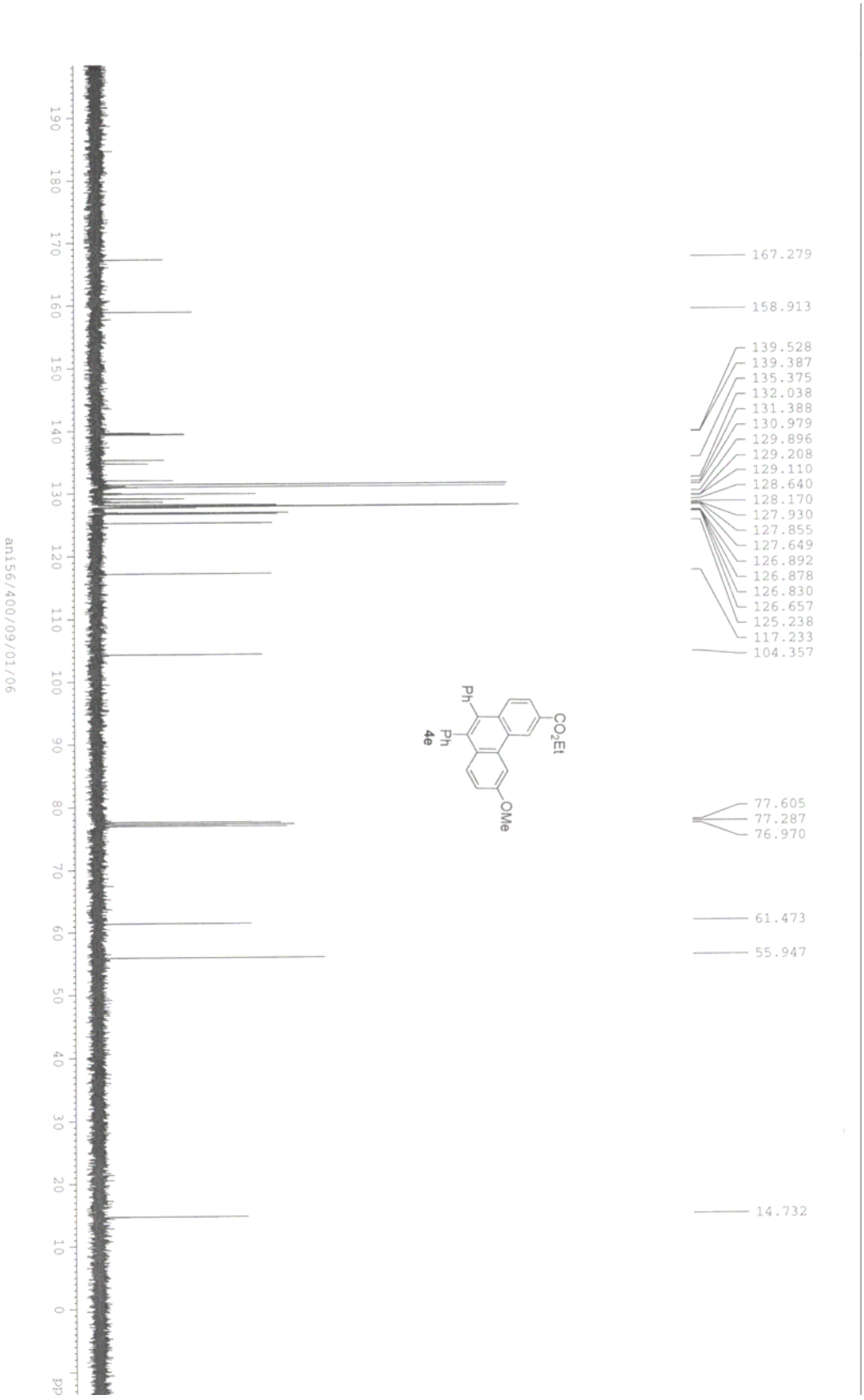
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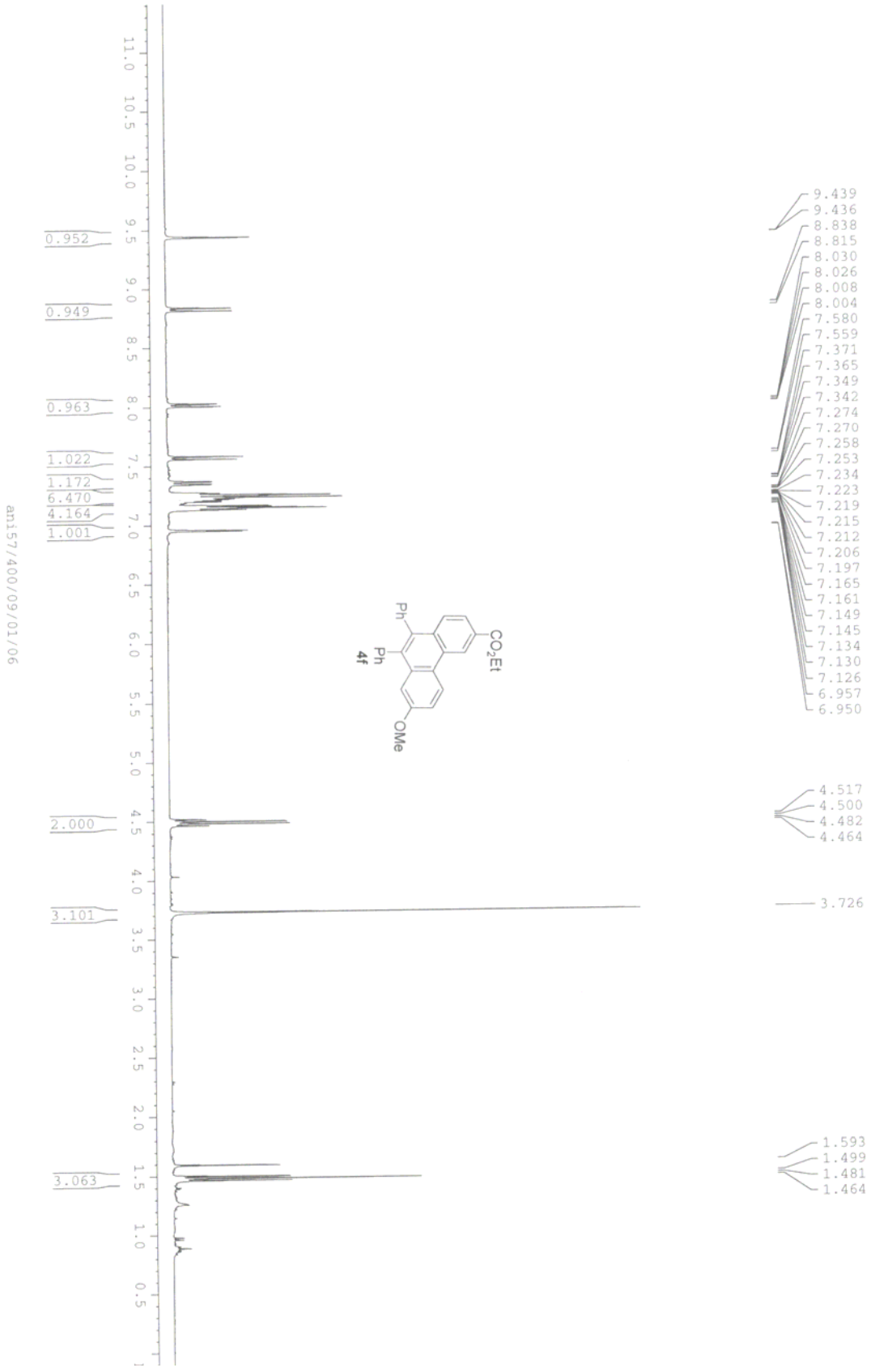
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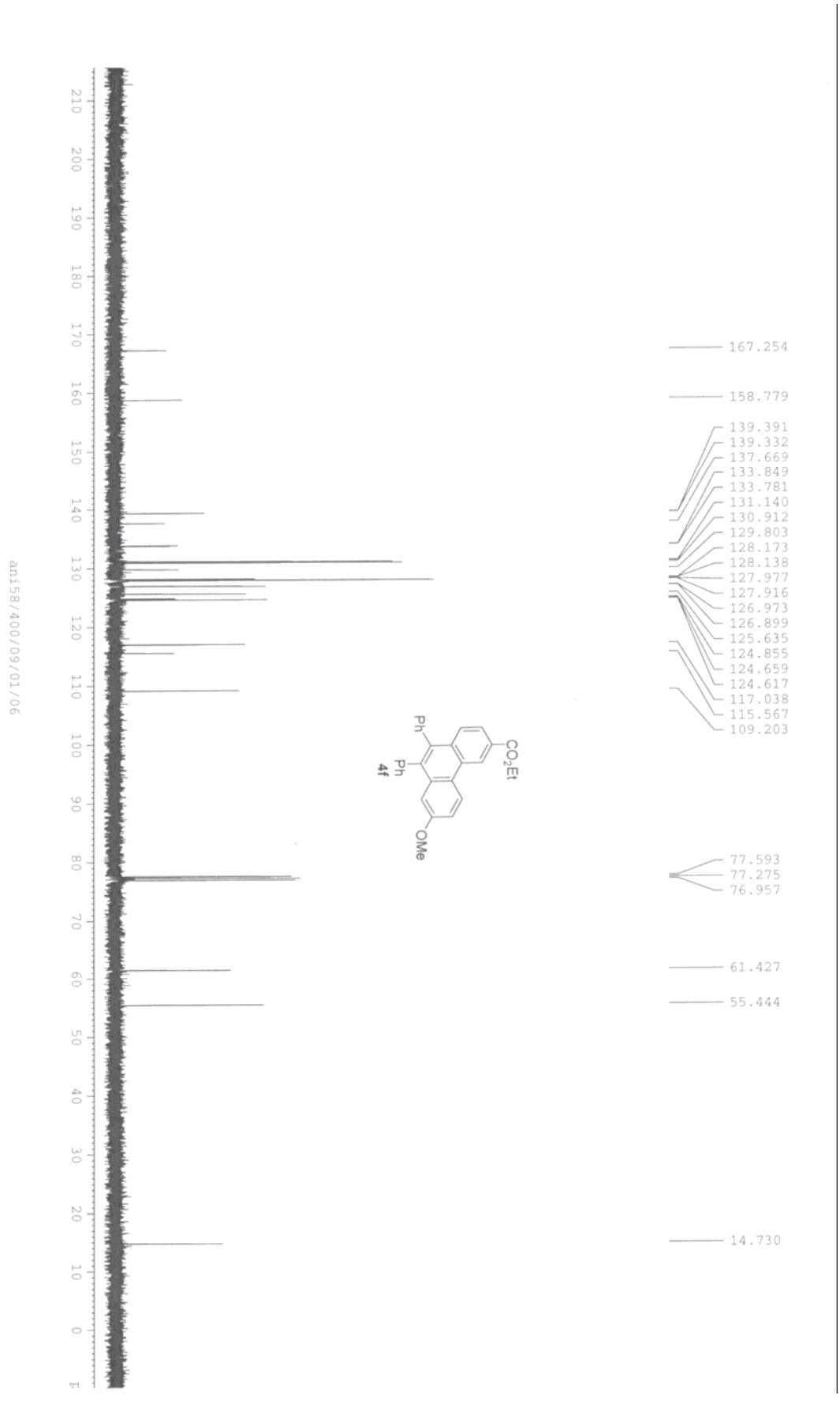
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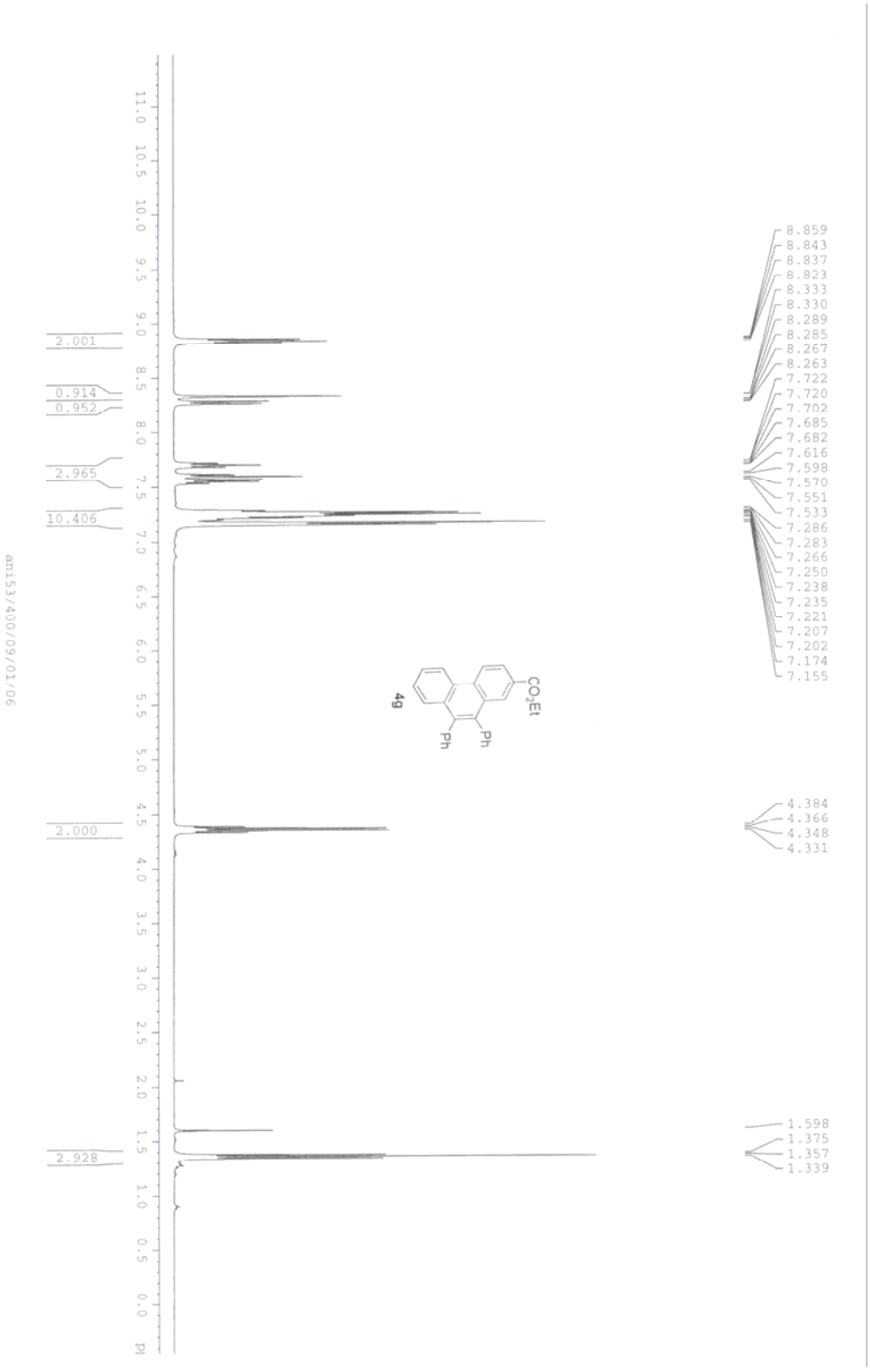
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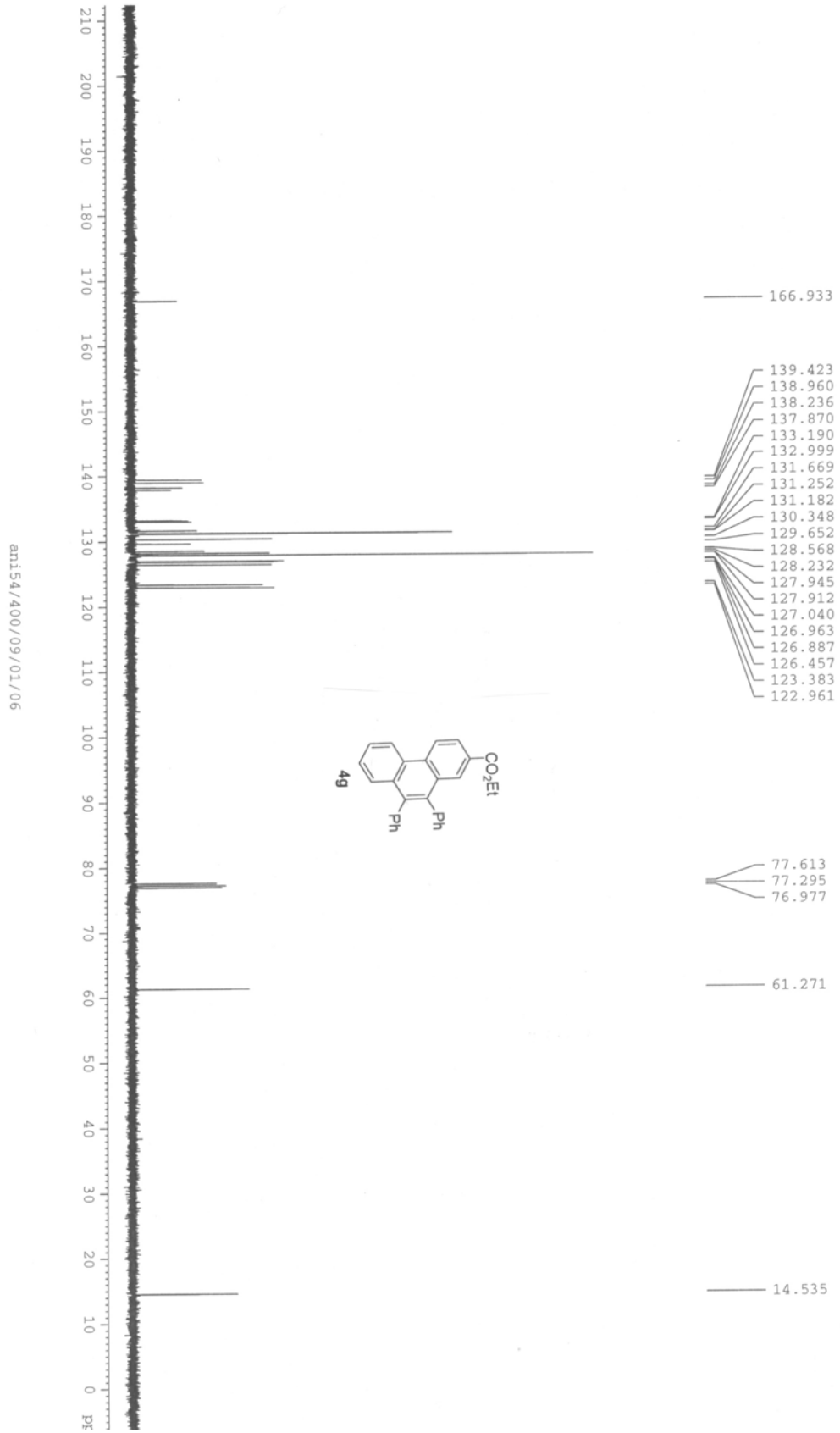
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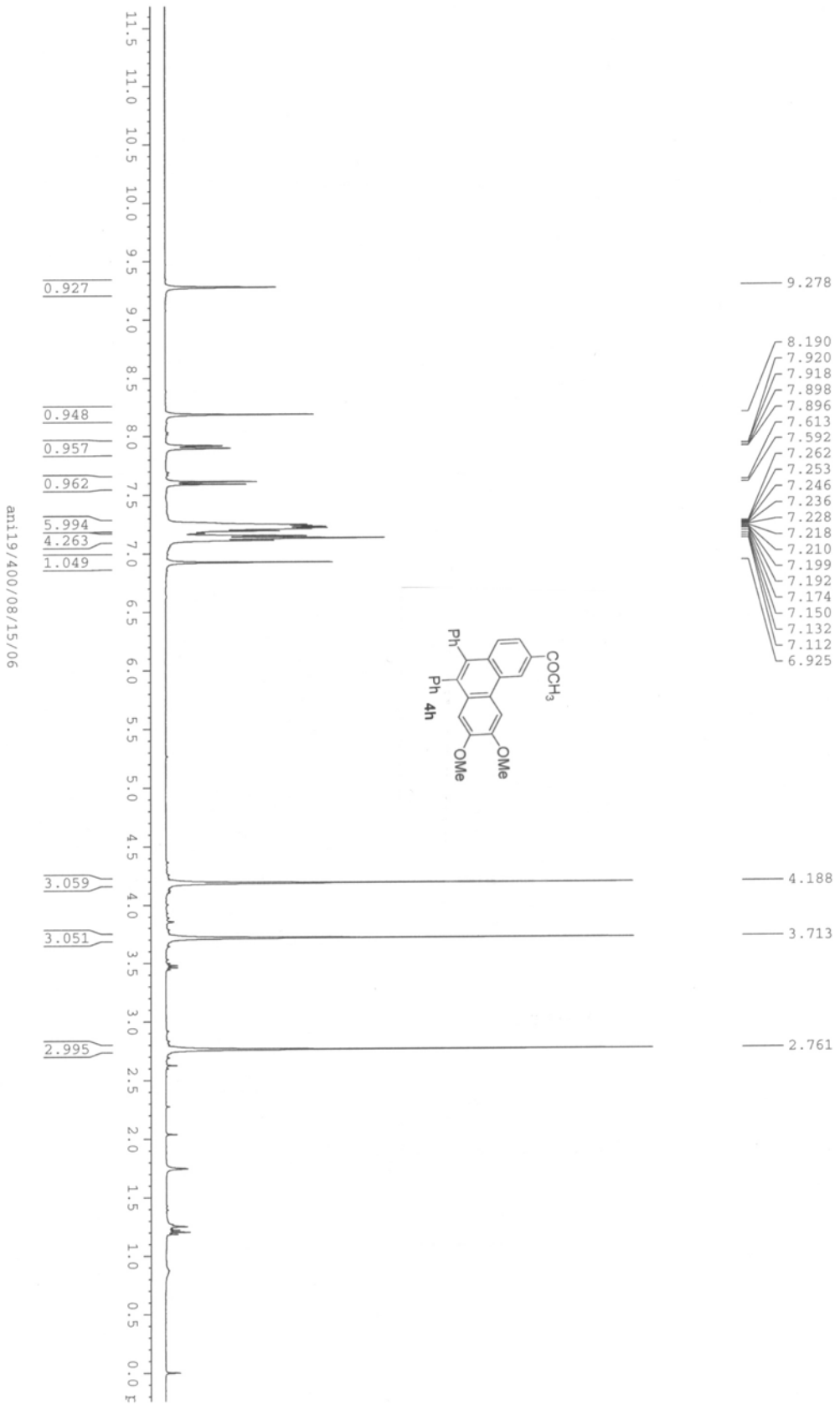
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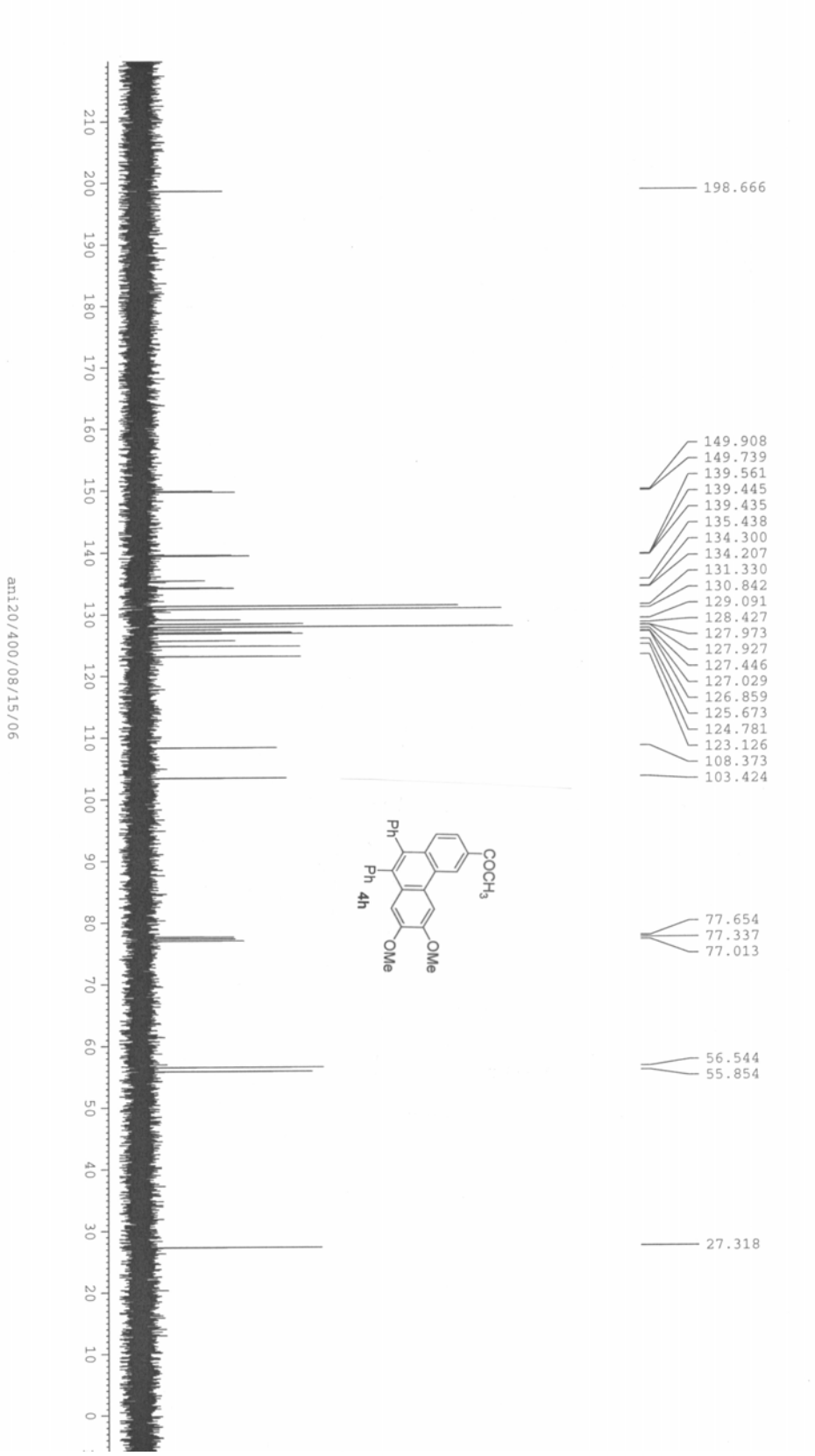
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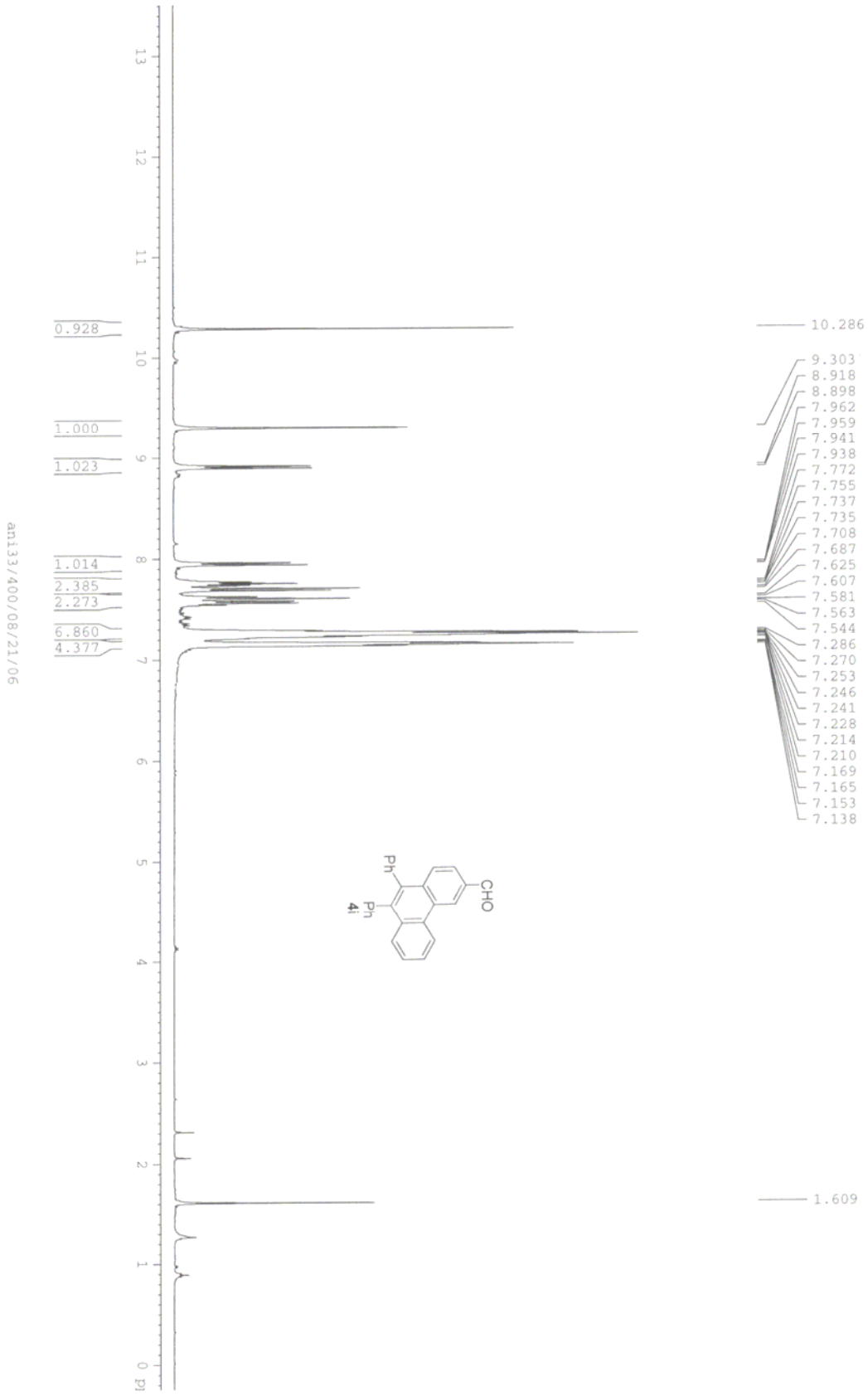
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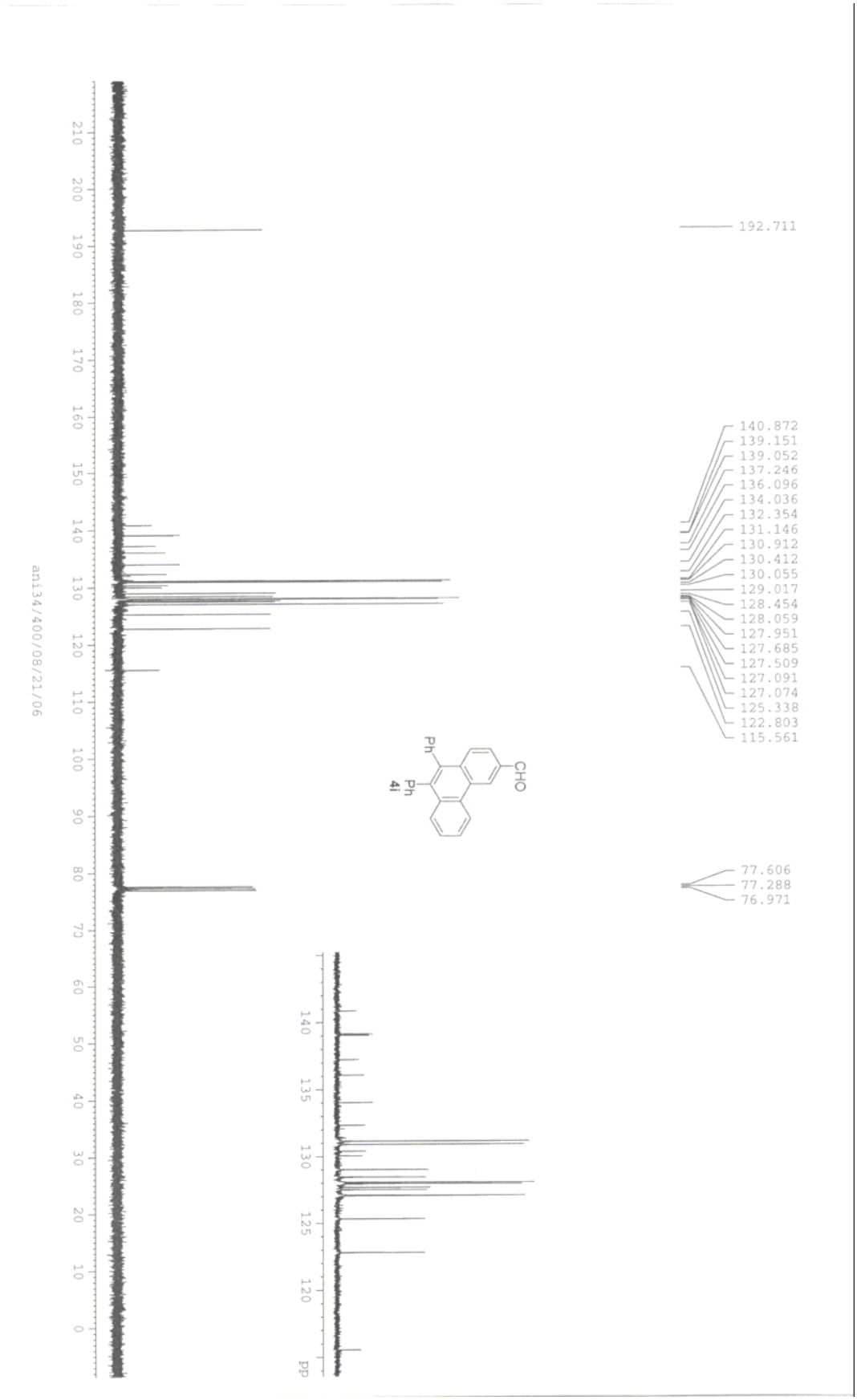
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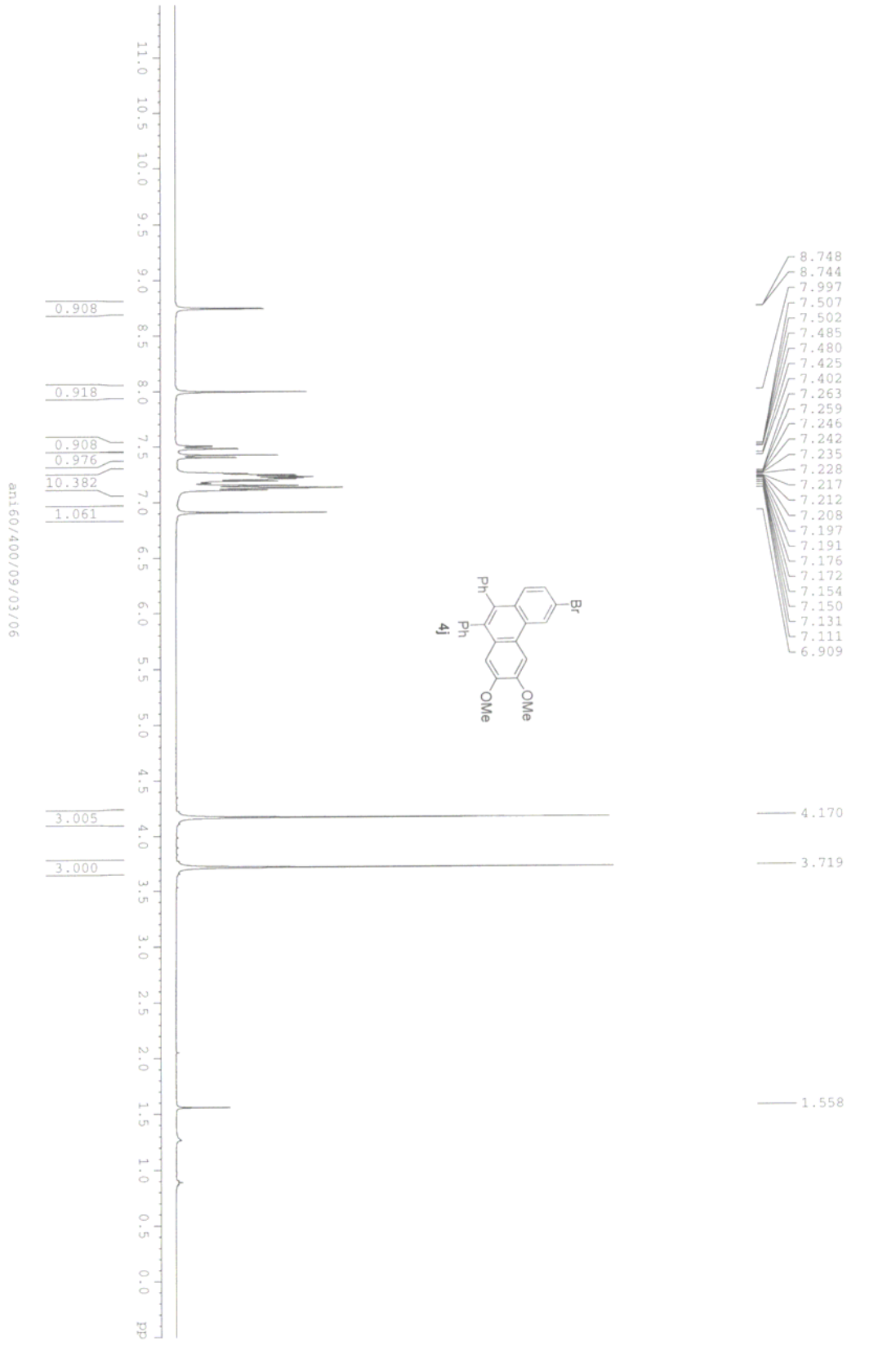
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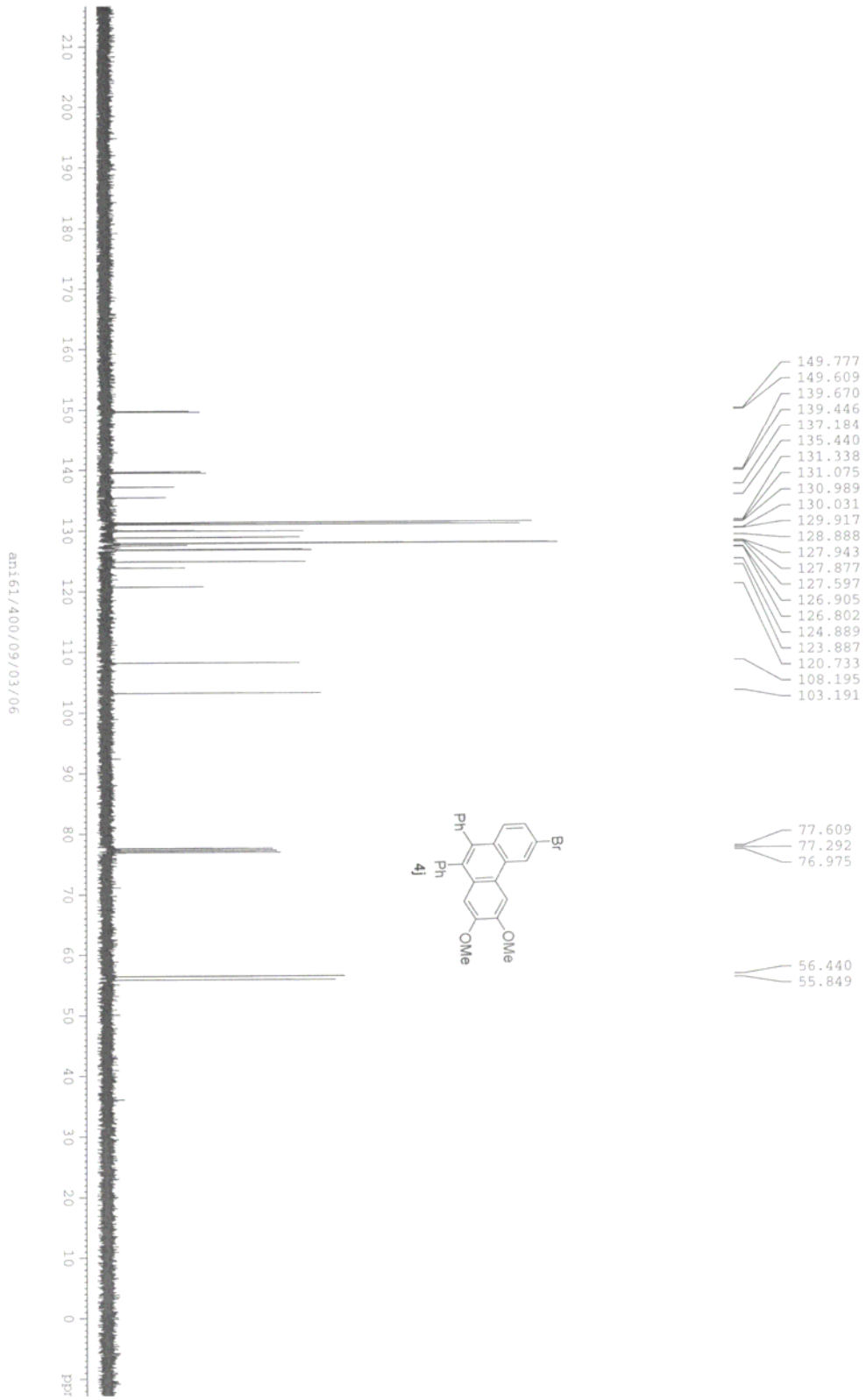
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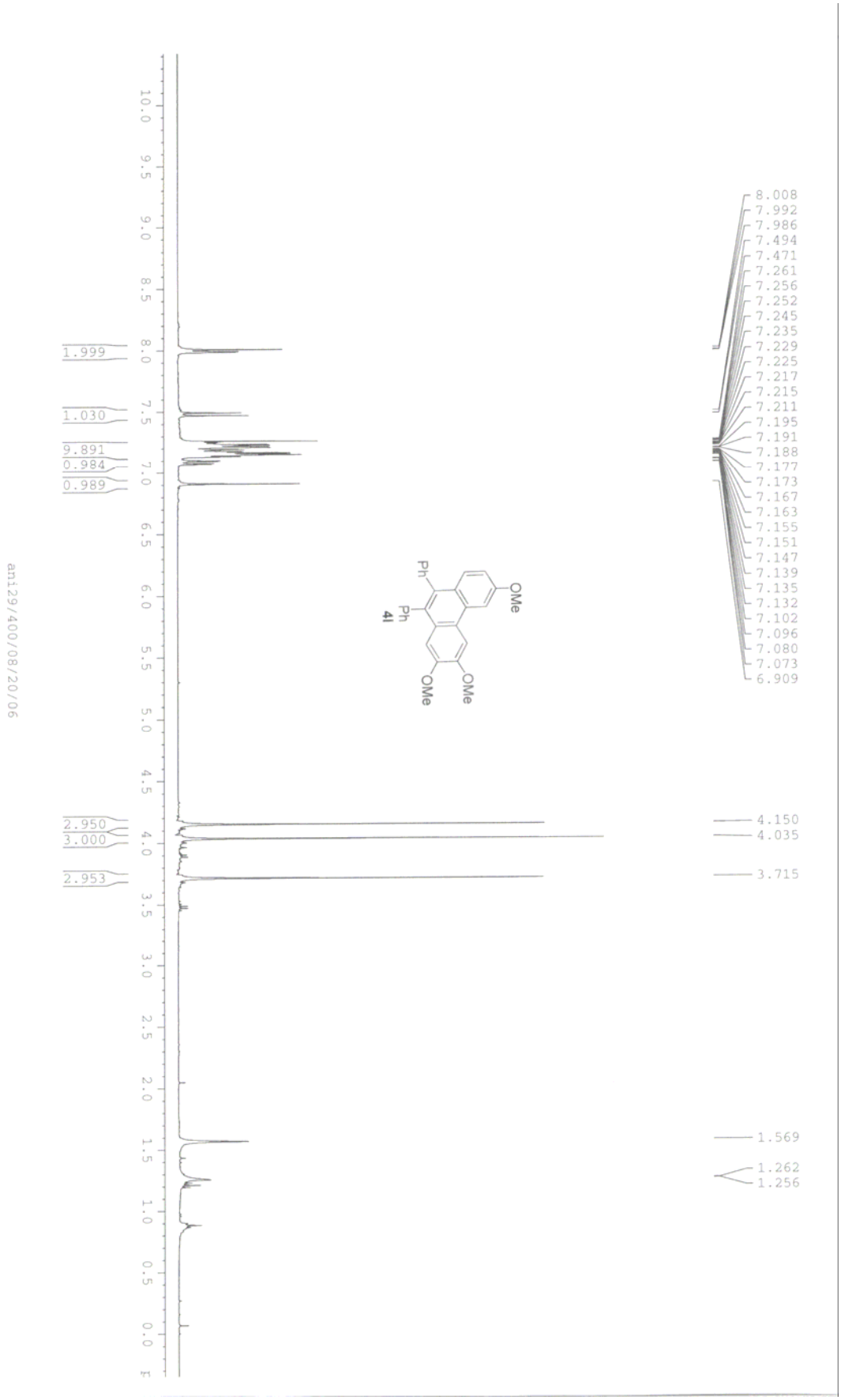
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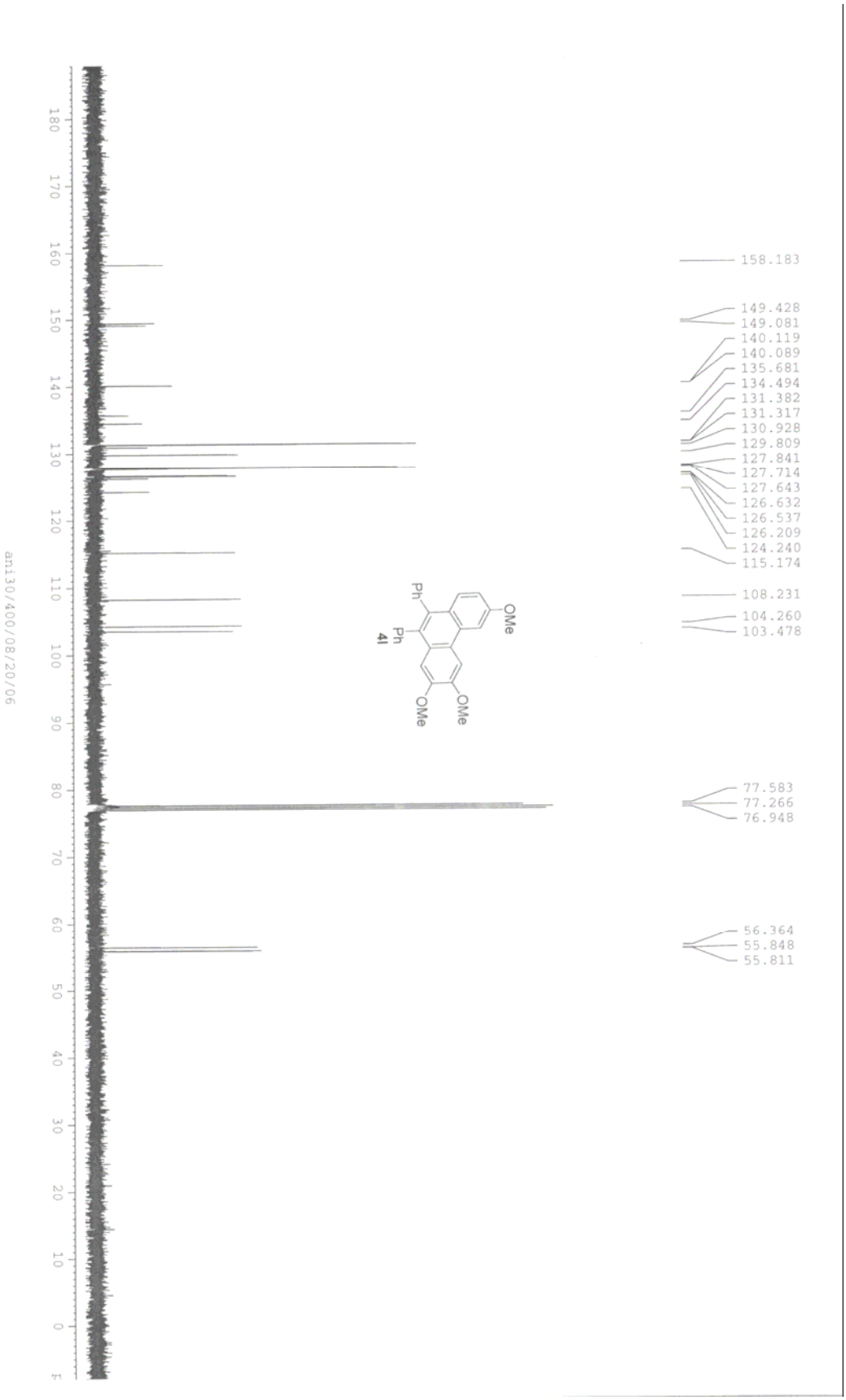
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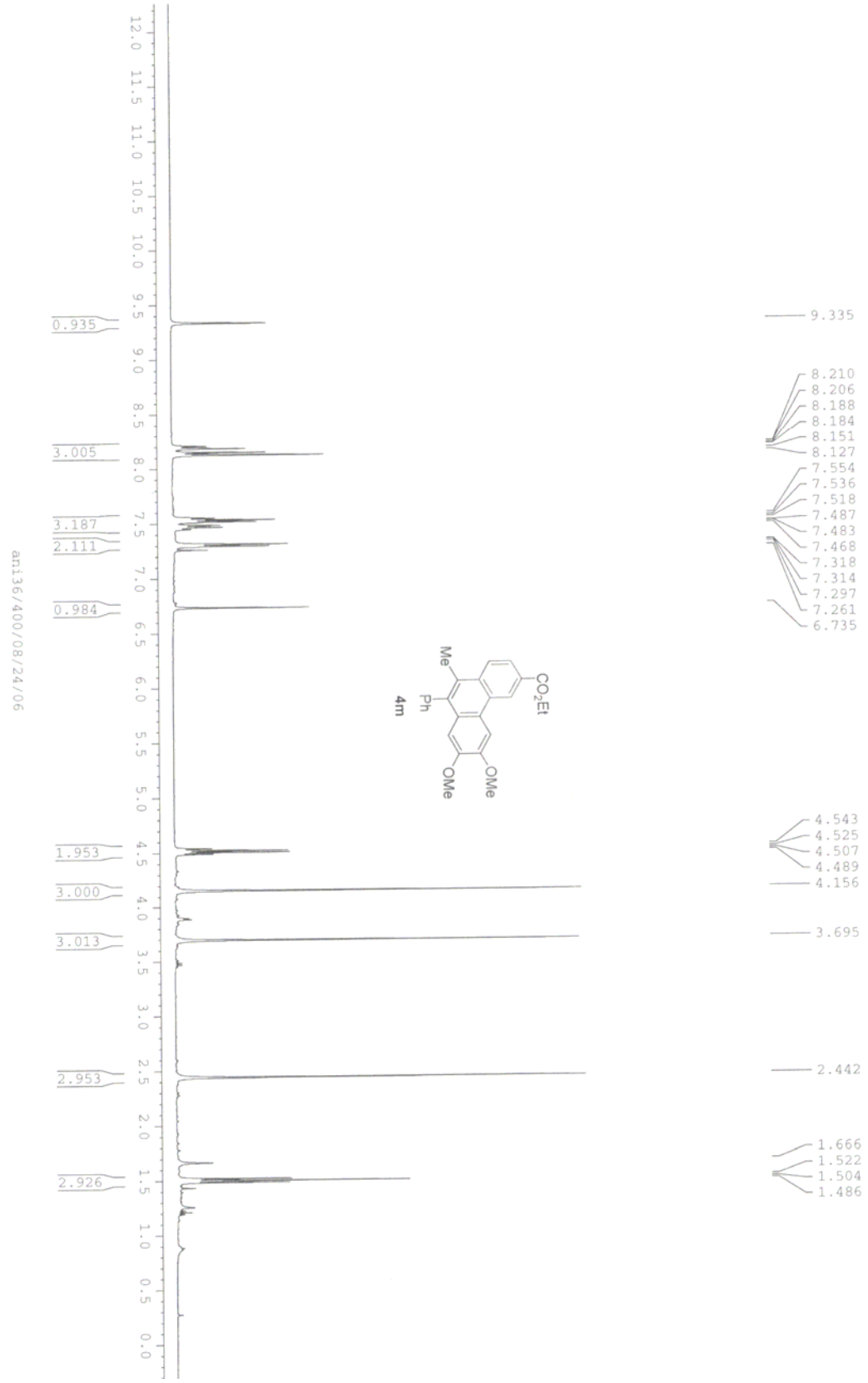
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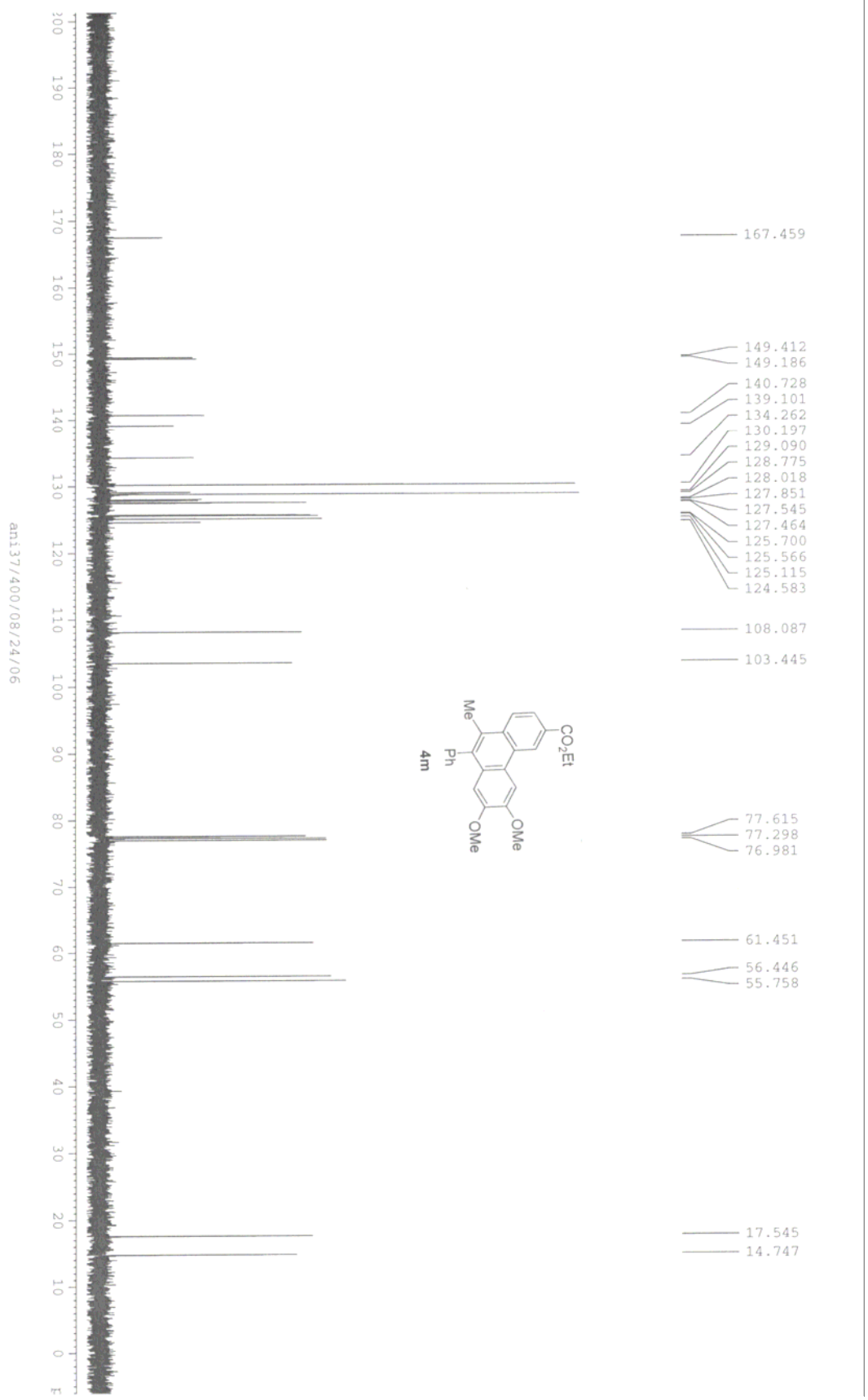
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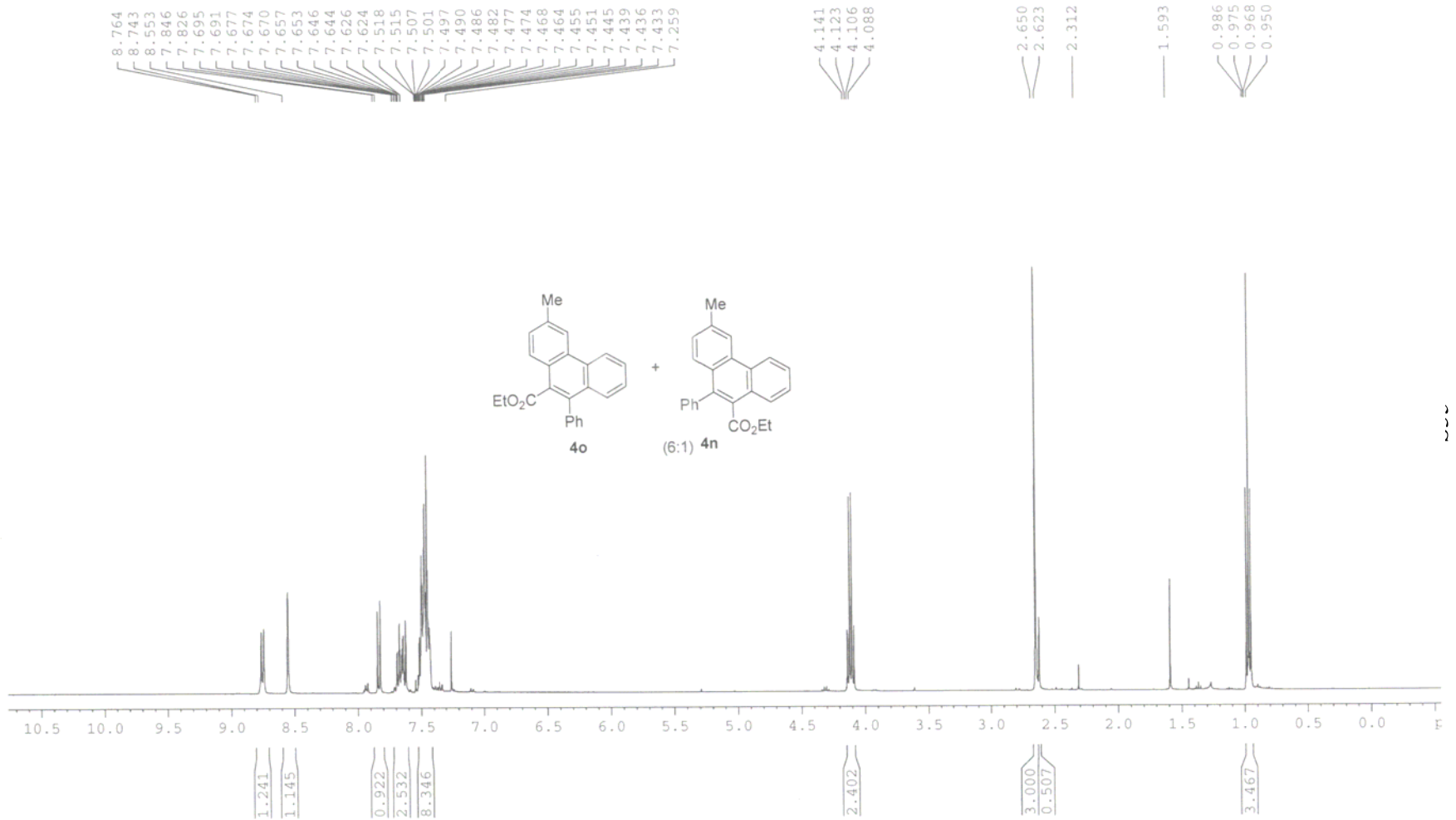
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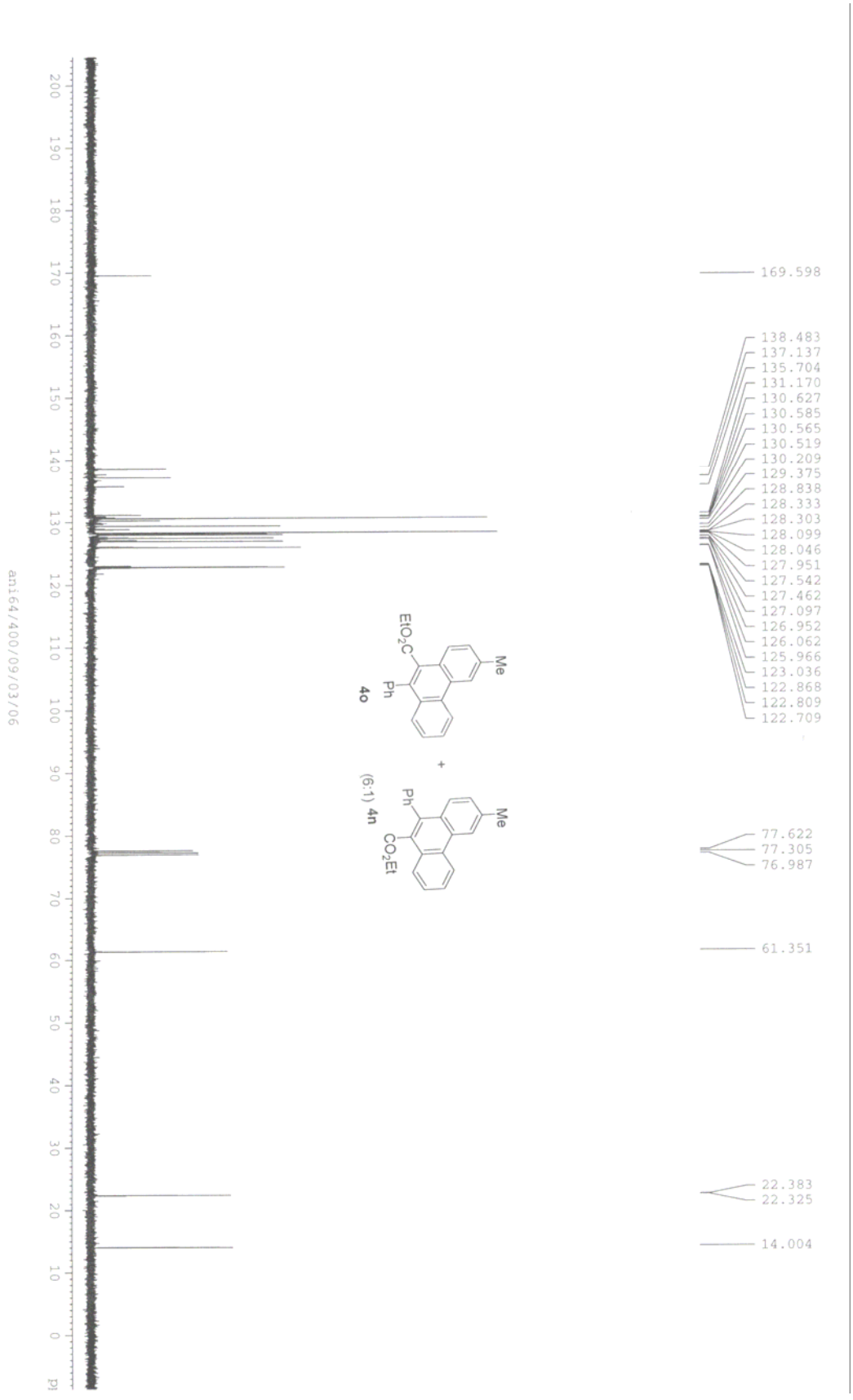
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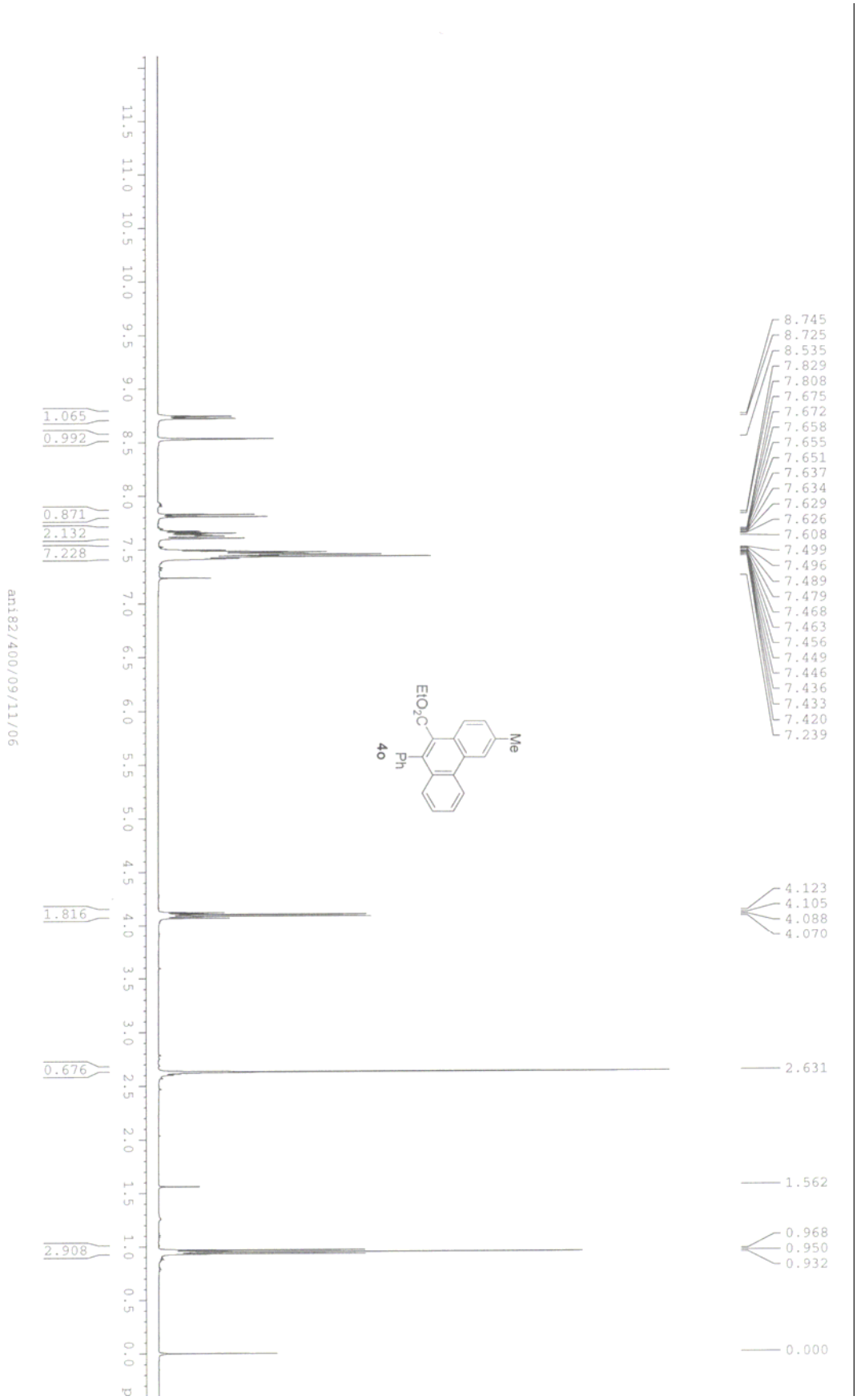
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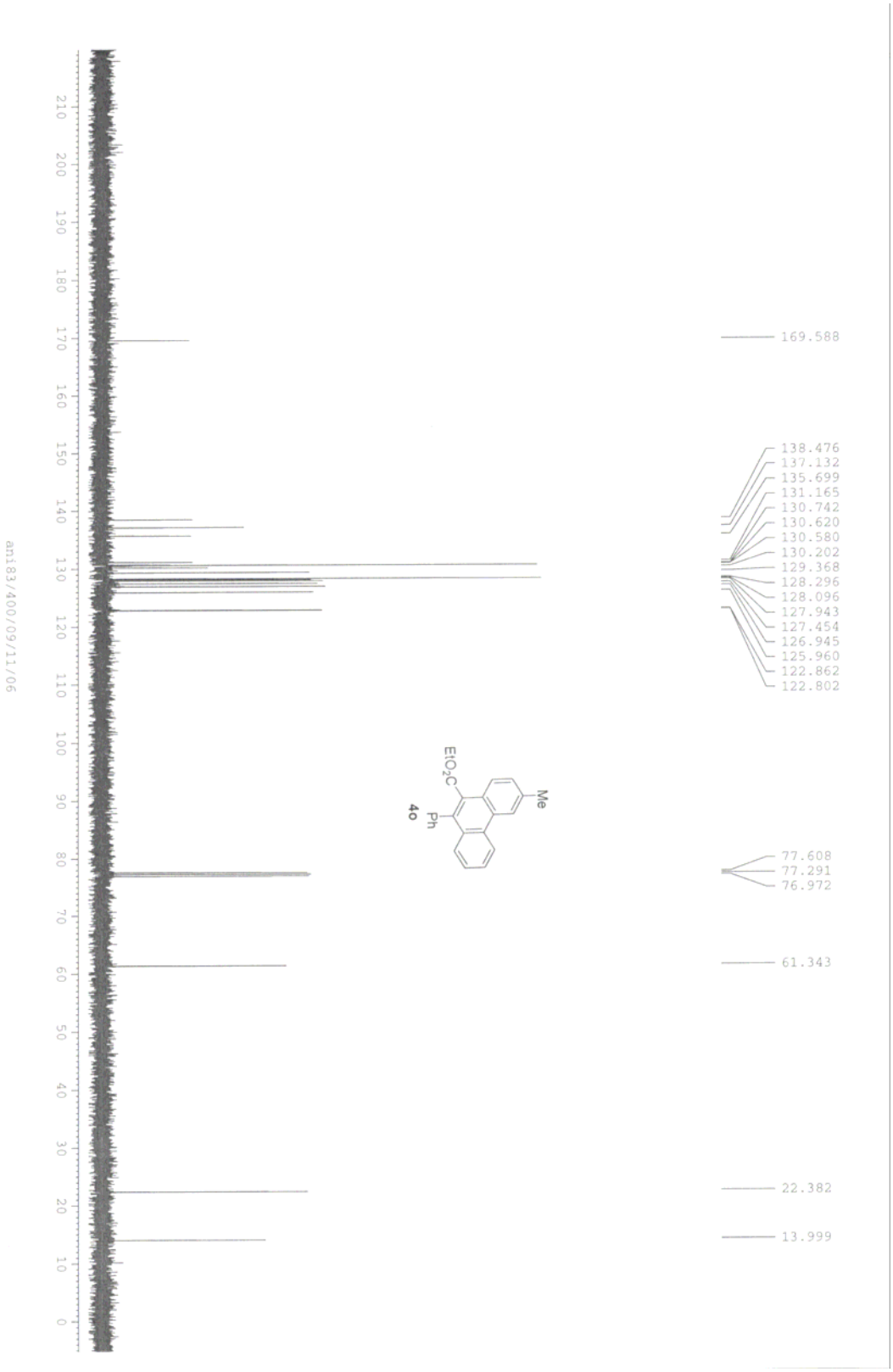
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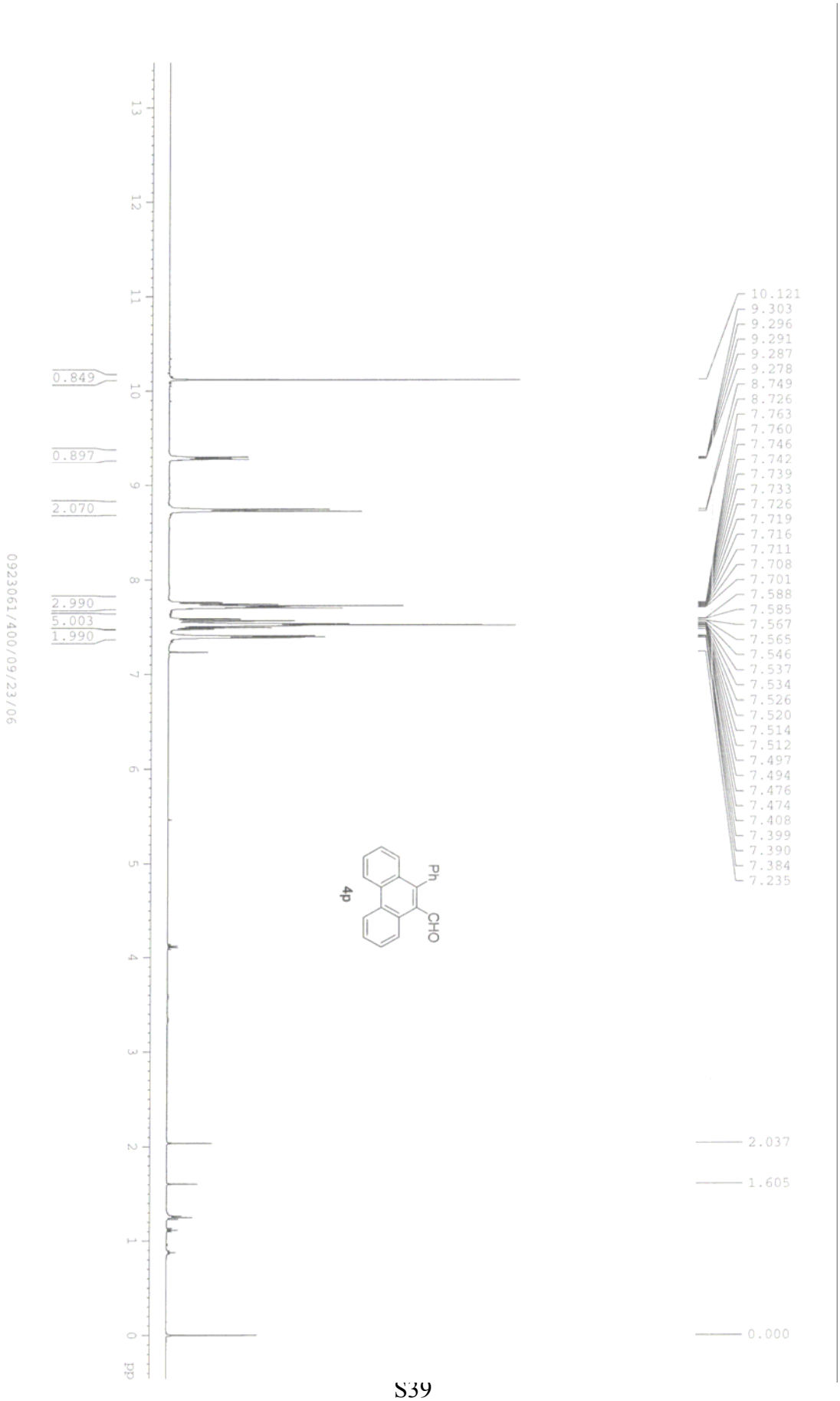
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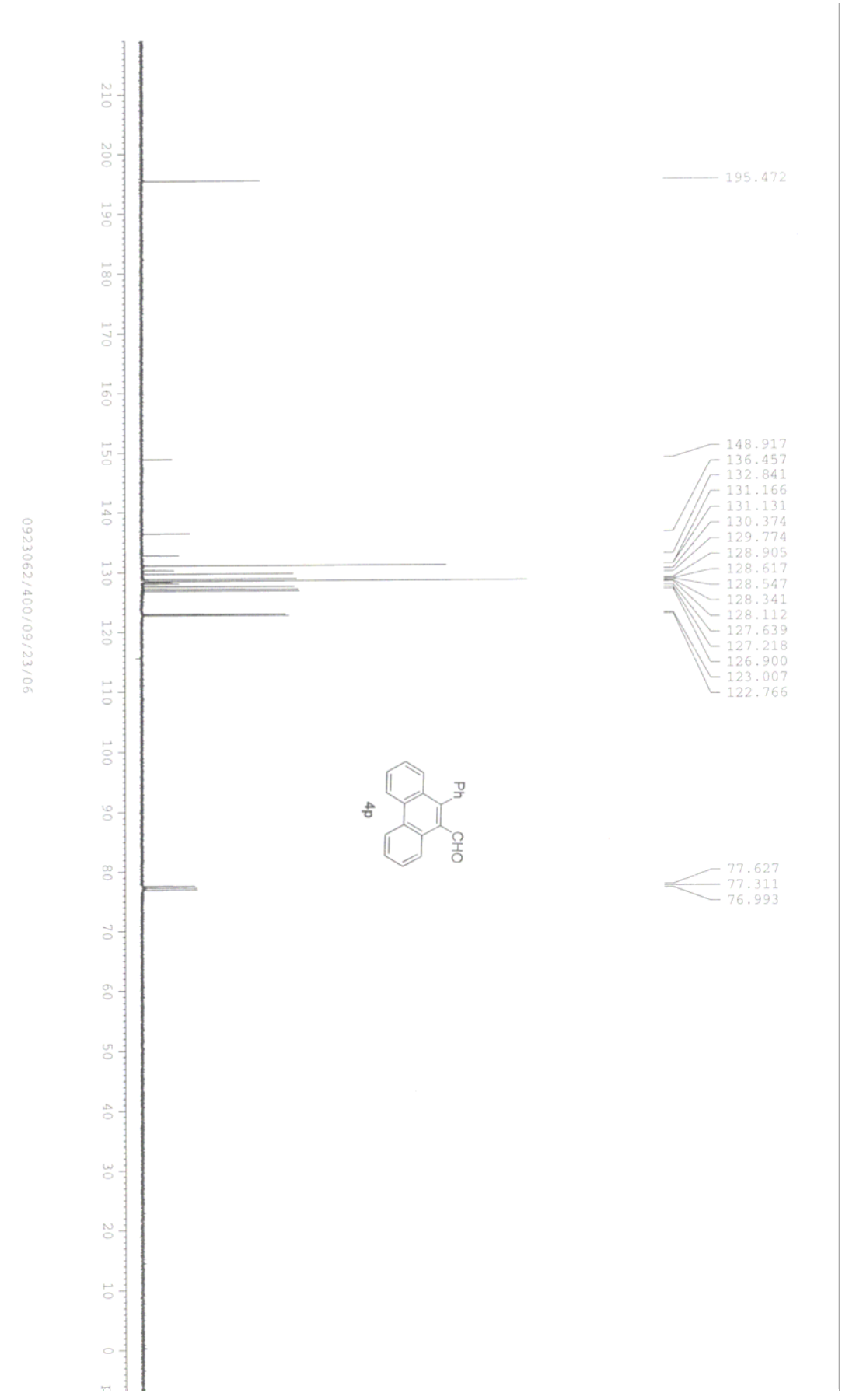
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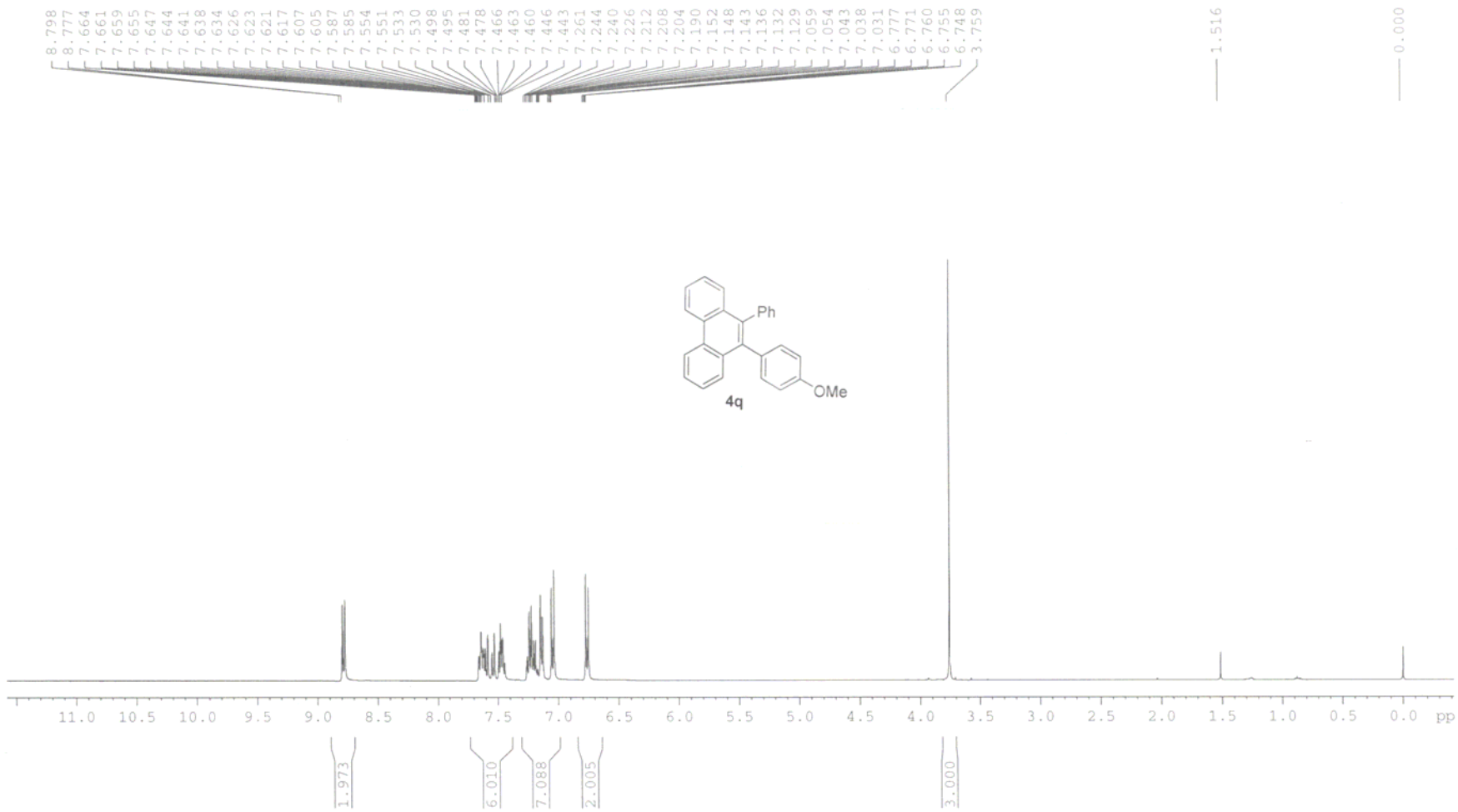
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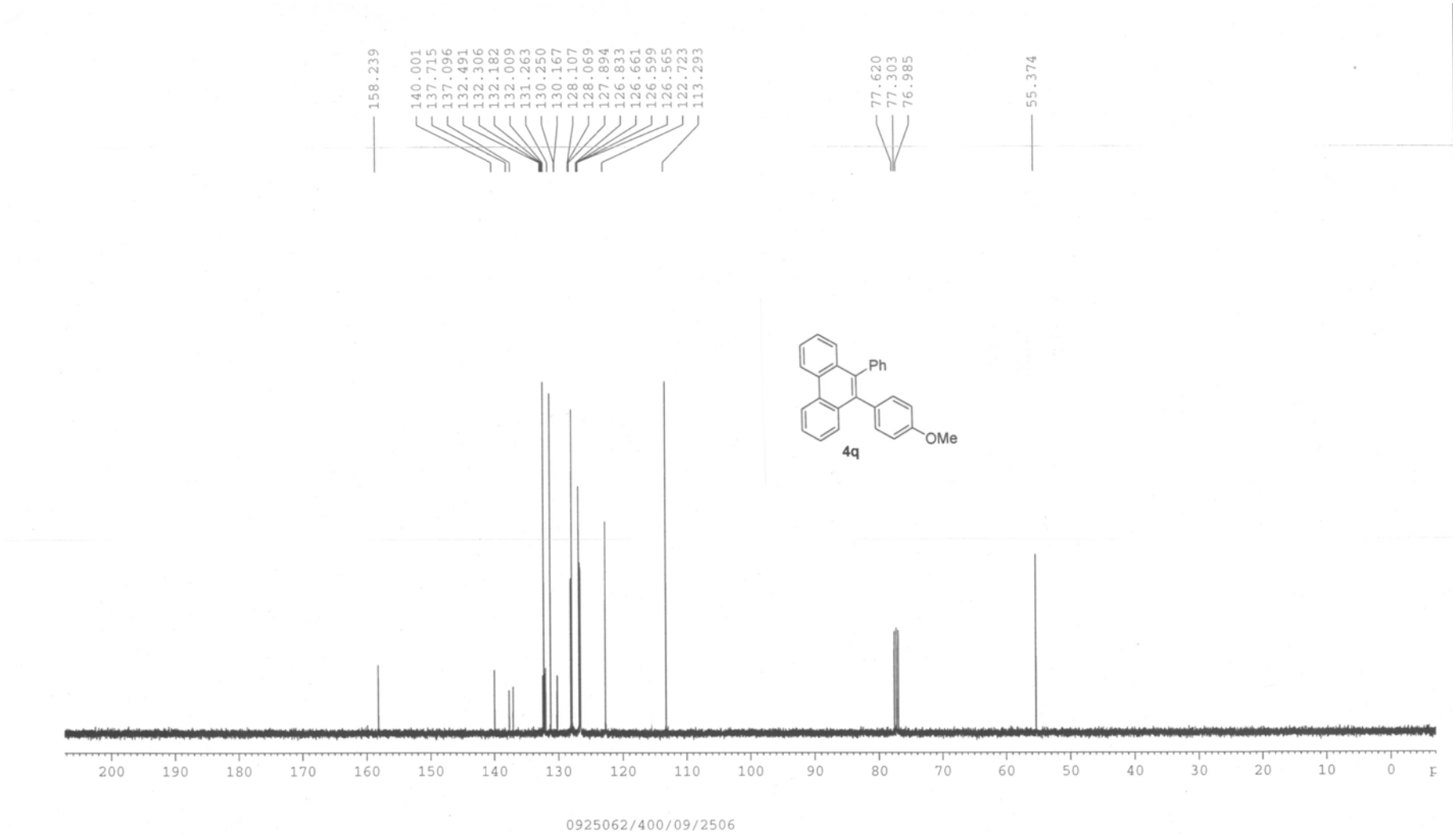
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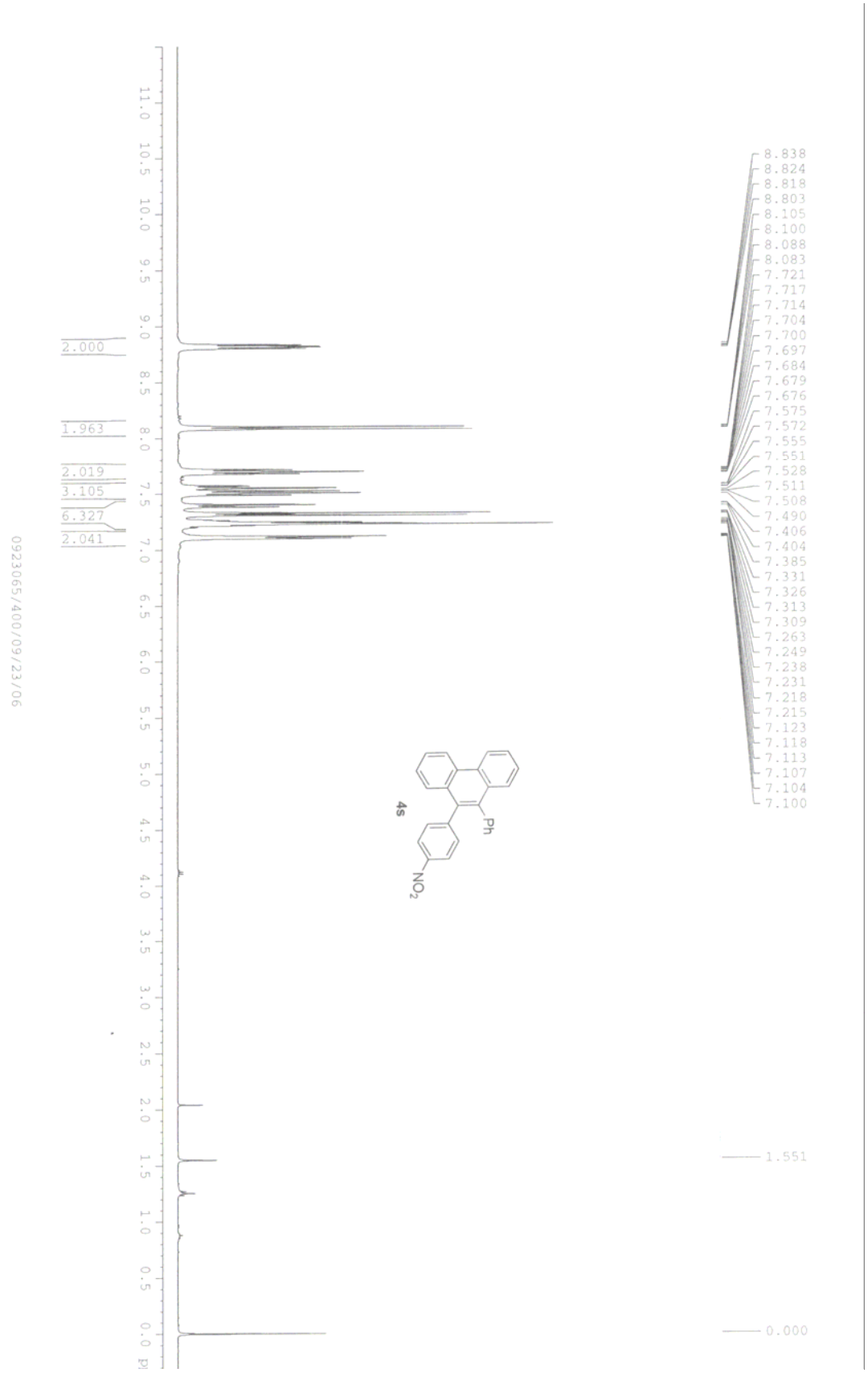
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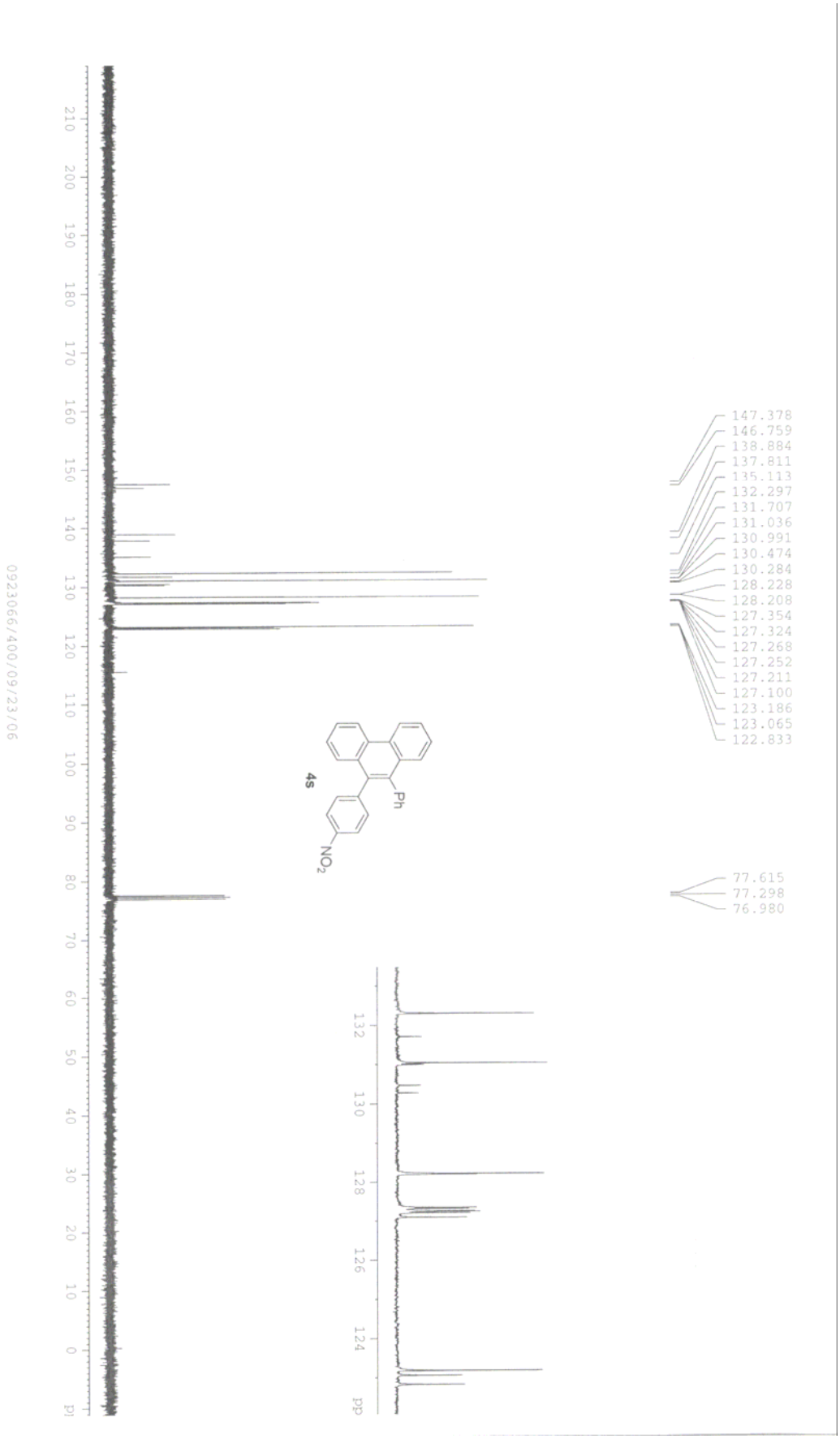
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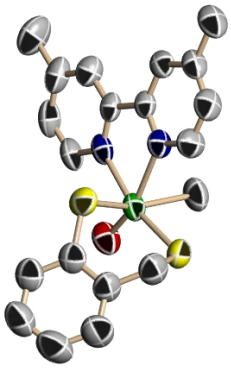

IOWA STATE UNIVERSITY

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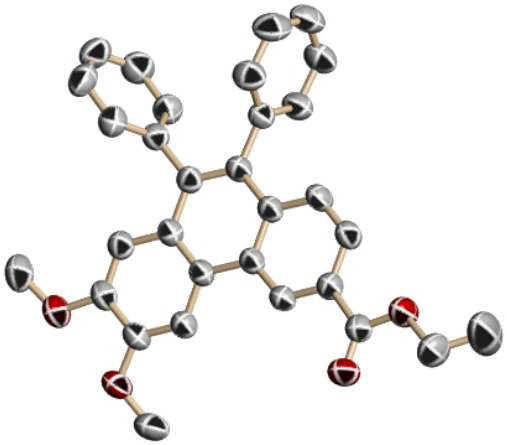
Single Crystal X-Ray Structure determination.

LAR13



August 24, 2006

Crystallographic Experimental Section

Data Collection

A colorless perfectly shaped transparent prismatic crystal was selected under ambient conditions. The crystal was mounted and centered in the X-ray beam by using a video camera.

The crystal evaluation and data collection were performed at room temperature on a Bruker CCD-1000 diffractometer with Mo K_α (λ = 0.71073 Å) radiation and the detector to crystal distance of 5.03 cm.

The initial cell constants were obtained from three series of ω scans at different starting angles. Each series consisted of 30 frames collected at intervals of 0.3º in a 10º range about ω with the exposure time of 20 seconds per frame. The obtained reflections were successfully indexed by an automated indexing routine built in the SMART program. The final cell constants were calculated from a set of strong reflections from the actual data collection.

The data were collected using the full sphere routine by collecting four sets of frames with 0.3º scans in ω with an exposure time 20 sec per frame. This dataset was corrected for Lorentz and polarization effects. The absorption correction was based on fitting a function to the empirical transmission surface as sampled by multiple equivalent measurements [1] using SADABS software [2].

Structure Solution and Refinement

The systematic absences in the diffraction data were consistent for the space groups $P1$ and $P\bar{1}$ [2]. The *E*-statistics strongly suggested the centrosymmetric space group $P\bar{1}$ yielded chemically reasonable and computationally stable results of refinement. The position of almost all non-hydrogen atoms were found by direct methods. The remaining atoms were located in an alternating series of least-squares cycles and difference Fourier maps. All non-hydrogen atoms were refined in full-matrix anisotropic approximation. All hydrogen atoms were placed in the structure factor calculation at idealized positions and were allowed to ride on the neighboring atoms with relative isotropic displacement coefficients.

The ORTEP diagram was drawn at 50% probability level. H-atoms were omitted for clarity. The resulting CIF file has been tested with PLATON [3] software. The results and comments have been included to output package (Platon_Lar13.doc).

I would strongly recommend collecting data for “light atoms” organic substances at low temperature, because this dramatically improves the quality of data. Please, if you willing to apply low temperature for you sample in future, just mark the relevant box on a submission form.

All publications arising from this report MUST either

1) include Dr. Arkady Ellern as a coauthor

OR

2) acknowledge Dr. Arkady Ellern and the Molecular Structure Laboratory of Iowa State University.

References

[1] Blessing, R.H. *Acta Cryst*. **1995**, *A51*, 33-38.

[2] All software and sources of the scattering factors are contained in the SHELXTL (version 5.1) program library (G. Sheldrick, Bruker Analytical X-Ray Systems, Madison, WI).

[3] A.L.Spek, J.Appl.Cryst. 36, 7-13.

Table 1. Crystal data and structure refinement for Lar13.

Identification code	lar13	
Empirical formula	C31 H26 O4	
Formula weight	462.52	
Temperature	298(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 9.6500(12) Å	α= 91.798(2)°.
	b = 10.7406(13) Å	β= 94.629(2)°.
	c = 13.0021(16) Å	γ = 114.503(2)°.
Volume	1219.1(3) $Å^3$	
Z	2	
Density (calculated)	1.260 Mg/m^3	
Absorption coefficient	0.082 mm^{-1}	
F(000)	488	
Crystal size	0.40 x 0.30 x 0.30 mm^3	
Theta range for data collection	1.58 to 28.31°.	
Index ranges	-12<=h<=12, -13<=k<=14, -17<=l<=16	
Reflections collected	11409	
Independent reflections	5661 [R(int) = 0.0459]	
Completeness to theta = 25.00°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1 and 0.76	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5661 / 0 / 319	
Goodness-of-fit on F^2	1.042	
Final R indices [I>2sigma(I)]	R1 = 0.0544, wR2 = 0.1477	
R indices (all data)	R1 = 0.0819, wR2 = 0.1684	
Largest diff. peak and hole	0.388 and -0.327 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for Lar13. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	12364(2)	8169(2)	2682(1)	46(1)
C(2)	11186(2)	7411(2)	1954(1)	44(1)
C(3)	10389(2)	5975(2)	1976(1)	39(1)
C(4)	9131(2)	5177(2)	1202(1)	39(1)
C(5)	8503(2)	5781(2)	473(1)	42(1)
C(6)	7291(2)	5015(2)	-245(1)	43(1)
C(7)	6678(2)	5759(2)	-964(1)	46(1)
C(8)	4795(3)	5550(2)	-2326(2)	74(1)
C(9)	3930(6)	4622(4)	-3149(3)	173(2)
C(10)	6667(2)	3578(2)	-262(1)	50(1)
C(11)	7245(2)	2960(2)	438(1)	48(1)
C(12)	8482(2)	3725(2)	1192(1)	40(1)
C(13)	9037(2)	3059(2)	1963(1)	40(1)
C(14)	8394(2)	1526(2)	1875(1)	41(1)
C(15)	8880(2)	885(2)	1138(2)	54(1)
C(16)	8300(3)	-523(2)	1010(2)	64(1)
C(17)	7239(2)	-1311(2)	1619(2)	66(1)
C(18)	6739(3)	-706(2)	2355(2)	71(1)
C(19)	7307(2)	714(2)	2480(2)	58(1)
C(20)	10133(2)	3823(2)	2746(1)	40(1)
C(21)	10600(2)	3116(2)	3588(1)	42(1)
C(22)	11346(2)	2286(2)	3389(2)	50(1)
C(23)	11690(2)	1577(2)	4163(2)	62(1)
C(24)	11311(3)	1694(2)	5144(2)	66(1)
C(25)	10571(2)	2512(2)	5355(2)	63(1)
C(26)	10223(2)	3219(2)	4586(1)	53(1)
C(27)	10849(2)	5305(2)	2754(1)	40(1)
C(28)	12056(2)	6115(2)	3520(1)	45(1)
C(29)	12776(2)	7507(2)	3499(1)	47(1)
C(30)	14288(3)	7825(3)	5110(2)	74(1)
C(31)	13008(3)	10214(2)	1817(2)	78(1)

O(1)	13211(2)	9548(1)	2705(1)	60(1)
O(2)	13913(2)	8375(1)	4211(1)	65(1)
O(3)	7173(2)	6987(1)	-962(1)	67(1)
O(4)	5507(2)	4916(1)	-1617(1)	64(1)

Table 3. Bond lengths [Å] and angles [°] for Lar13.

C(1)-O(1)	1.361(2)	C(10)-C(11)	1.358(2)	C(22)-C(23)	1.380(3)
C(1)-C(2)	1.365(2)	C(10)-H(10)	0.9300	C(22)-H(22)	0.9300
C(1)-C(29)	1.416(3)	C(11)-C(12)	1.417(2)	C(23)-C(24)	1.372(3)
C(2)-C(3)	1.412(2)	C(11)-H(11)	0.9300	C(23)-H(23)	0.9300
C(2)-H(2)	0.9300	C(12)-C(13)	1.442(2)	C(24)-C(25)	1.376(3)
C(3)-C(27)	1.406(2)	C(13)-C(20)	1.371(2)	C(24)-H(24)	0.9300
C(3)-C(4)	1.451(2)	C(13)-C(14)	1.497(2)	C(25)-C(26)	1.376(3)
C(4)-C(5)	1.400(2)	C(14)-C(19)	1.378(3)	C(25)-H(25)	0.9300
C(4)-C(12)	1.418(2)	C(14)-C(15)	1.382(2)	C(26)-H(26)	0.9300
C(5)-C(6)	1.376(2)	C(15)-C(16)	1.377(3)	C(27)-C(28)	1.422(2)
C(5)-H(5)	0.9300	C(15)-H(15)	0.9300	C(28)-C(29)	1.365(2)
C(6)-C(10)	1.403(2)	C(16)-C(17)	1.359(3)	C(28)-H(28)	0.9300
C(6)-C(7)	1.487(2)	C(16)-H(16)	0.9300	C(29)-O(2)	1.365(2)
C(7)-O(3)	1.203(2)	C(17)-C(18)	1.367(3)	C(30)-O(2)	1.413(3)
C(7)-O(4)	1.329(2)	C(17)-H(17)	0.9300	C(30)-H(30A)	0.9600
C(8)-C(9)	1.391(4)	C(18)-C(19)	1.389(3)	C(30)-H(30B)	0.9600
C(8)-O(4)	1.452(2)	C(18)-H(18)	0.9300	C(30)-H(30C)	0.9600
C(8)-H(8A)	0.9700	C(19)-H(19)	0.9300	C(31)-O(1)	1.420(3)
C(8)-H(8B)	0.9700	C(20)-C(27)	1.448(2)	C(31)-H(31A)	0.9600
C(9)-H(9A)	0.9600	C(20)-C(21)	1.495(2)	C(31)-H(31B)	0.9600
C(9)-H(9B)	0.9600	C(21)-C(22)	1.389(2)	C(31)-H(31C)	0.9600
C(9)-H(9C)	0.9600	C(21)-C(26)	1.389(2)		

O(1)-C(1)-C(2)	125.54(17)	C(3)-C(2)-H(2)	119.1	C(5)-C(4)-C(3)	122.67(14)
O(1)-C(1)-C(29)	115.17(15)	C(27)-C(3)-C(2)	119.00(14)	C(12)-C(4)-C(3)	119.10(15)
C(2)-C(1)-C(29)	119.29(16)	C(27)-C(3)-C(4)	119.52(14)	C(6)-C(5)-C(4)	122.19(15)
C(1)-C(2)-C(3)	121.80(16)	C(2)-C(3)-C(4)	121.47(15)	C(6)-C(5)-H(5)	118.9
C(1)-C(2)-H(2)	119.1	C(5)-C(4)-C(12)	118.21(14)	C(4)-C(5)-H(5)	118.9

C(5)-C(6)-C(10)	119.39(16)	C(17)-C(16)-C(15)	120.1(2)	C(29)-C(28)-C(27)	121.40(16)
C(5)-C(6)-C(7)	117.95(15)	C(17)-C(16)-H(16)	119.9	C(29)-C(28)-H(28)	119.3
C(10)-C(6)-C(7)	122.65(15)	C(15)-C(16)-H(16)	119.9	C(27)-C(28)-H(28)	119.3
O(3)-C(7)-O(4)	122.95(17)	C(16)-C(17)-C(18)	119.94(19)	C(28)-C(29)-O(2)	125.85(17)
O(3)-C(7)-C(6)	124.36(16)	C(16)-C(17)-H(17)	120.0	C(28)-C(29)-C(1)	119.99(15)
O(4)-C(7)-C(6)	112.69(15)	C(18)-C(17)-H(17)	120.0	O(2)-C(29)-C(1)	114.16(15)
C(9)-C(8)-O(4)	110.4(2)	C(17)-C(18)-C(19)	120.2(2)	O(2)-C(30)-H(30A)	109.5
C(9)-C(8)-H(8A)	109.6	C(17)-C(18)-H(18)	119.9	O(2)-C(30)-H(30B)	109.5
O(4)-C(8)-H(8A)	109.6	C(19)-C(18)-H(18)	119.9	H(30A)-C(30)-H(30B)	109.5
C(9)-C(8)-H(8B)	109.6	C(14)-C(19)-C(18)	120.43(19)	O(2)-C(30)-H(30C)	109.5
O(4)-C(8)-H(8B)	109.6	C(14)-C(19)-H(19)	119.8	H(30A)-C(30)-H(30C)	109.5
H(8A)-C(8)-H(8B)	108.1	C(18)-C(19)-H(19)	119.8	H(30B)-C(30)-H(30C)	109.5
C(8)-C(9)-H(9A)	109.5	C(13)-C(20)-C(27)	120.43(15)	O(1)-C(31)-H(31A)	109.5
C(8)-C(9)-H(9B)	109.5	C(13)-C(20)-C(21)	119.63(15)	O(1)-C(31)-H(31B)	109.5
H(9A)-C(9)-H(9B)	109.5	C(27)-C(20)-C(21)	119.94(14)	H(31A)-C(31)-H(31B)	109.5
C(8)-C(9)-H(9C)	109.5	C(22)-C(21)-C(26)	118.12(17)	O(1)-C(31)-H(31C)	109.5
H(9A)-C(9)-H(9C)	109.5	C(22)-C(21)-C(20)	121.42(15)	H(31A)-C(31)-H(31C)	109.5
H(9B)-C(9)-H(9C)	109.5	C(26)-C(21)-C(20)	120.38(15)	H(31B)-C(31)-H(31C)	109.5
C(11)-C(10)-C(6)	119.89(15)	C(23)-C(22)-C(21)	120.69(18)	C(1)-O(1)-C(31)	116.85(15)
C(11)-C(10)-H(10)	120.1	C(23)-C(22)-H(22)	119.7	C(29)-O(2)-C(30)	118.10(16)
C(6)-C(10)-H(10)	120.1	C(21)-C(22)-H(22)	119.7	C(7)-O(4)-C(8)	116.66(15)
C(10)-C(11)-C(12)	121.84(15)	C(24)-C(23)-C(22)	120.34(19)		
C(10)-C(11)-H(11)	119.1	C(24)-C(23)-H(23)	119.8		
C(12)-C(11)-H(11)	119.1	C(22)-C(23)-H(23)	119.8		
C(11)-C(12)-C(4)	118.47(15)	C(23)-C(24)-C(25)	119.75(19)		
C(11)-C(12)-C(13)	121.34(15)	C(23)-C(24)-H(24)	120.1		
C(4)-C(12)-C(13)	120.14(14)	C(25)-C(24)-H(24)	120.1		
C(20)-C(13)-C(12)	120.35(14)	C(26)-C(25)-C(24)	120.2(2)		
C(20)-C(13)-C(14)	121.52(15)	C(26)-C(25)-H(25)	119.9		
C(12)-C(13)-C(14)	118.12(14)	C(24)-C(25)-H(25)	119.9		
C(19)-C(14)-C(15)	118.08(16)	C(25)-C(26)-C(21)	120.93(18)		
C(19)-C(14)-C(13)	122.99(16)	C(25)-C(26)-H(26)	119.5		
C(15)-C(14)-C(13)	118.91(16)	C(21)-C(26)-H(26)	119.5		
C(16)-C(15)-C(14)	121.21(19)	C(3)-C(27)-C(28)	118.38(15)		
C(16)-C(15)-H(15)	119.4	C(3)-C(27)-C(20)	120.08(14)		
C(14)-C(15)-H(15)	119.4	C(28)-C(27)-C(20)	121.51(15)		

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for Lar13. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	45(1)	36(1)	51(1)	-4(1)	2(1)	13(1)
C(2)	48(1)	39(1)	44(1)	-1(1)	-1(1)	18(1)
C(3)	41(1)	36(1)	39(1)	-2(1)	3(1)	16(1)
C(4)	41(1)	35(1)	39(1)	-1(1)	2(1)	16(1)
C(5)	46(1)	33(1)	44(1)	1(1)	2(1)	14(1)
C(6)	47(1)	41(1)	42(1)	2(1)	1(1)	19(1)
C(7)	48(1)	43(1)	44(1)	2(1)	-1(1)	17(1)
C(8)	83(2)	72(1)	69(1)	9(1)	-20(1)	39(1)
C(9)	269(6)	101(2)	125(3)	-21(2)	-122(3)	82(3)
C(10)	52(1)	40(1)	50(1)	-4(1)	-12(1)	15(1)
C(11)	52(1)	34(1)	52(1)	-4(1)	-8(1)	15(1)
C(12)	44(1)	36(1)	41(1)	-1(1)	1(1)	17(1)
C(13)	45(1)	35(1)	42(1)	0(1)	3(1)	17(1)
C(14)	43(1)	36(1)	43(1)	2(1)	-4(1)	16(1)
C(15)	66(1)	40(1)	56(1)	1(1)	11(1)	20(1)
C(16)	78(1)	42(1)	71(1)	-5(1)	4(1)	27(1)
C(17)	64(1)	37(1)	88(2)	2(1)	-10(1)	16(1)
C(18)	58(1)	54(1)	89(2)	25(1)	14(1)	11(1)
C(19)	57(1)	53(1)	64(1)	6(1)	14(1)	21(1)
C(20)	43(1)	40(1)	39(1)	0(1)	3(1)	19(1)
C(21)	40(1)	39(1)	43(1)	2(1)	0(1)	14(1)
C(22)	51(1)	52(1)	51(1)	3(1)	1(1)	26(1)
C(23)	62(1)	59(1)	71(1)	5(1)	-8(1)	33(1)
C(24)	67(1)	65(1)	60(1)	17(1)	-12(1)	24(1)
C(25)	65(1)	75(1)	43(1)	12(1)	2(1)	22(1)
C(26)	55(1)	58(1)	46(1)	2(1)	4(1)	24(1)
C(27)	40(1)	39(1)	39(1)	-2(1)	2(1)	17(1)
C(28)	45(1)	46(1)	42(1)	0(1)	-2(1)	19(1)
C(29)	42(1)	45(1)	47(1)	-6(1)	-2(1)	12(1)
C(30)	71(1)	78(2)	60(1)	-9(1)	-22(1)	24(1)
C(31)	92(2)	38(1)	85(2)	8(1)	-10(1)	12(1)

O(1)	62(1)	35(1)	66(1)	-2(1)	-8(1)	9(1)
O(2)	60(1)	53(1)	61(1)	-6(1)	-19(1)	7(1)
O(3)	76(1)	44(1)	71(1)	8(1)	-17(1)	19(1)
O(4)	69(1)	49(1)	65(1)	1(1)	-25(1)	23(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^{-3}) for Lar13.

	x	y	z	U(eq)
H(2)	10901	7852	1428	53
H(5)	8918	6733	474	50
H(8A)	4141	5856	-1961	89
H(8B)	5580	6345	-2586	89
H(9A)	4593	4380	-3544	259
H(9B)	3407	5032	-3583	259
H(9C)	3193	3812	-2888	259
H(10)	5859	3051	-751	60
H(11)	6817	2007	422	58
H(15)	9613	1415	721	65
H(16)	8635	-935	505	77
H(17)	6854	-2262	1534	79
H(18)	6016	-1246	2774	85
H(19)	6951	1120	2976	70
H(22)	11616	2206	2728	60
H(23)	12181	1018	4018	75
H(24)	11553	1222	5665	79
H(25)	10305	2588	6018	76
H(26)	9728	3774	4737	64
H(28)	12361	5687	4046	54
H(30A)	13375	7320	5430	111
H(30B)	14993	8558	5585	111
H(30C)	14751	7224	4925	111
H(31A)	13170	9774	1214	117

H(31B)	13730	11160	1892	117
H(31C)	11986	10161	1745	117