Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

Regioselective C-H bond functionalizations of acridines using organozinc reagents

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Contents

I. General Information

^{1}H NMR and ^{13}C NMR spectra were recorded on a JEOL JMN-270, JEOL ECS-400 or JEOL ECP-400 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, sept = septet, br = broad and m = multiplet), coupling constant (Hz), integration, and interpretation. Peak assignments were made with the aid of DEPT and COSY method. Infrared spectra (IR) were obtained on a Horiba FT-720 spectrometer. Mass spectra were obtained on a Shimadzu GCMS-QP 5000 or GCMS-QP 2010 instrument with ionization voltages of 70 eV. Melting points were determined on a Yamato melting point apparatus and are uncorrected. Elemental analyses and high resolution mass spectra (HRMS) were performed by the Elemental Analysis Section of Osaka University. Flash column chromatography was performed with SiO_2 (Silicycle Silica Flash F60 (230-400 mesh)). All catalytic reactions were carried out in 10 mL sample vials with a Teflon-sealed screw cap in a glovebox filled with N_2.

II. Materials

Unless otherwise noted, all reagents were obtained from commercial suppliers and used as received. $Ni(cod)_2$ was purchased from Strem Chemicals. Toluene, Ph_2Zn (**2**), $Cu(OTf)_2$, $Pd(OAc)_2$, $K_3[Fe(CN)_6]$, and $ZnCl_2$ were purchased from Wako Pure Chemical Industries. Acridine was purchased from Sigma-Aldrich and used after recrystallization. PCy_3, $FeCl_3$, $^{i}Pr_2Zn$ (1M toluene solution), and Grignard reagents used in this study were purchased from Sigma-Aldrich Co. $InCl_3$, $P^{t}Bu_3$, $P^{i}Pr_3$, PMe_3, IMes·HCl, IPr·HCl, SIPr·HCl, and $NaO^{t}Bu$ were purchased from Tokyo Kasei Kogyo Co., Ltd. KOH was purchased from Nacalai Tesque. CH_2Cl_2 was purchased from Kishida Chemical Co.,Ltd. $(2\text{-Tolyl})_2Zn$ was prepared by a Charette's method.[1]

III. Synthesis of Starting Materials

A general procedure for the preparation of 2,7-diarylacridine. To a oven-dried three-necked 100 mL flask, 2,6-dibromoacridine[2] (505.5 mg, 1.5 mmol), arylboronic acid (4.0 mmol), $Pd(PPh_3)_4$ (115.6 mg, 0.067 mmol) and Na_2CO_3 (635.9 mg, 6.0 mmol) were added. DME (40 mL) and H_2O (10 mL) were then added, and the mixture was refluxed for 15-20 h. The solution was diluted with CH_2Cl_2 (100 mL). The separated organic layer was washed with water (100 mL), dried over $MgSO_4$, filtered and concentrated under reduced pressure. The resultant reddish-brown solid was purified by chromatography on silica gel (hexane/EtOAc = 10:1 to 5:1) to furnish 2,7-diarylacridine as a yellow solid (70-90%).

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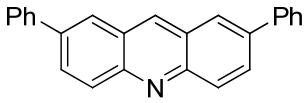
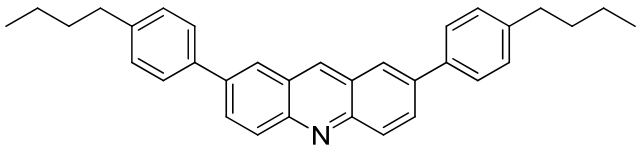
[1] A. Cote', A. B. Charette, *J. Am. Chem. Soc.* **2008**, *130*, 2771.
[2] M. Vlassa, I. A. Silberg, R. Custelceanu, M. Culea, *Synth. Commun.* **1995**, 3493.

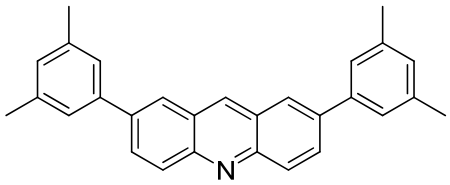
2,7-Diphenylacridine. Rf 0.31 (hexane: EtOAc= 5:1). Pale yellow solid (mp = 184-185 ˚C). ^{1}H NMR ($CDCl_3$, 399.78 MHz) δ 7.40-7.44 (m, 2H), 7.50-7.54 (m, 4H), 7.77-7.79 (m, 4H), 8.06-8.09 (m, 2H), 8.17 (s, 2H), 8.31 (d, *J* = 9.2 Hz, 2H), 8.82 (s, 1H); ^{13}C NMR ($CDCl_3$, 100.53 MHz) δ 125.32, 127.00, 127.35, 127.84, 129.00, 129.85, 130.52, 136.30, 138.30, 140.12, 148.42; IR (neat) 3433 w, 3051 w, 1564 w, 1498 w, 1477 w, 1450 m, 1408 w, 1157 w, 1076 w, 1036 w, 922 m, 833 s, 752 s, 694 s, 621 w; MS *m/z* (relative intensity, %) 332 (28), 331 (100), 330 (16), 166 (15). HRMS Calcd for $C_{25}H_{17}N$: 331.1360; Found: 331.1361.



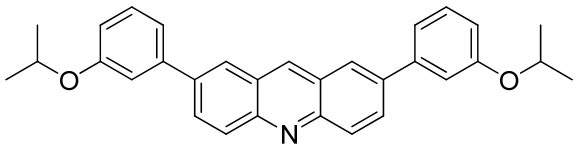
2,7-Bis(4-butylphenyl)acridine. Rf 0.31 (hexane: EtOAc = 5:1). Greenish solid (mp = 169-170 ˚C). ^{1}H NMR ($CDCl_3$, 399.78 MHz) δ 0.95 (t, *J* = 7.6 Hz, 6H), 1.34-1.44 (m, 4H), 1.60-1.68 (m, 4H), 2.65 (t, *J* = 7.6 Hz, 4H), 7.27 (d, *J* = 8.0 Hz, 4H), 7.62 (d, *J* = 7.6 Hz, 4H), 7.97-8.03 (m, 4H), 8.24 (d, *J* = 9.2 Hz, 2H), 8.63 (s, 1H); ^{13}C NMR ($CDCl_3$, 100.53 MHz) δ 13.94, 22.36, 33.54, 35.26, 124.68, 126.92, 127.06, 128.98, 129.65, 130.23, 135.83, 137.28, 137.96, 142.62, 148.18; IR (KBr) 3026 w, 2958 s, 2922 s, 2854 m, 1558 w, 1513 m, 1485 w, 1412 w, 1375 w, 1157 w, 920 m, 820 s, 775 m; MS *m/z* (relative intensity, %) 444 (36), 443 (100), 401 (14), 400 (42), 357 (20), 179 (18). HRMS Calcd for $C_{33}H_{33}N$: 443.2613; Found: 443.2610.



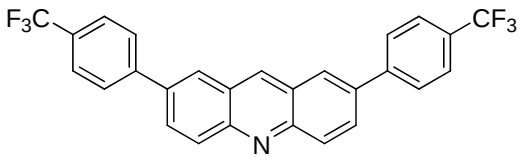
2,7-Bis(3,5-dimethylphenyl)acridine. Rf 0.31 (hexane: EtOAc = 5:1). Pale yellow solid (mp = 169-170 ˚C). ^{1}H NMR ($CDCl_3$, 399.78 MHz) δ 2.43 (s, 12H), 7.06 (s, 2H), 7.39 (s, 4H), 8.05 (dd, *J* = 2.0, 8.8 Hz, 2H), 8.14 (d, *J* = 2.0 Hz, 2H), 8.29 (d, *J* = 9.2 Hz, 2H), 8.79 (s, 1H); ^{13}C NMR ($CDCl_3$, 100.53 MHz) δ 21.44, 125.14, 125.26, 126.99, 129.47, 129.56, 130.69, 136.18, 138.49, 138.52, 140.10, 148.26; IR (neat) 3016 m, 2914 s, 2858 m, 2185 w, 1631 w, 1599 s, 1570 s, 1508 m, 1442 s, 1375 m, 1345 m, 1155 m, 1038 m, 922 s, 854 m, 827 s, 800 m, 752 s, 696 s, 663 m, 640 s; MS *m/z* (relative intensity, %) 388 (31), 387 (100). HRMS Calcd for $C_{29}H_{25}N$: 387.1987; Found: 387.1985.



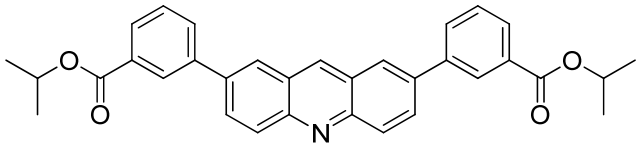
2,7-Bis(3-isopropoxyphenyl)acridine. Rf 0.26 (hexane: EtOAc = 5:1). Yellow solid (mp = 132-133 ˚C). ^{1}H NMR ($CDCl_3$, 399.78 MHz) δ 1.41 (d, *J* = 6.0 Hz, 12H), 4.68 (sept, *J* = 6.0 Hz, 2H), 6.95 (dd, *J* = 2.0, 7.6 Hz, 2H), 7.30-7.34 (m, 4H), 7.41 (t, *J* = 8.0 Hz, 2H), 8.05 (dd, *J* = 2.4, 9.2 Hz, 2H), 8.16 (d, *J* = 2.0 Hz, 2H), 8.29 (d, *J* = 8.8 Hz, 2H), 8.80 (s, 1H); ^{13}C NMR ($CDCl_3$, 100.53 MHz) δ 22.10, 69.98, 114.98, 115.17, 119.62, 125.34, 126.95, 129.76, 129.99, 130.50, 136.29, 138.19, 141.62, 148.47, 158.38; IR (KBr) 3055 w, 2973 s, 2927 m, 1934 w, 1749 w, 1603 s, 1572 s, 1489 m, 1450 s, 1404 m, 1377 m, 1335 m, 1282 s, 1196 s, 1115 s, 1038 w, 997 m, 974 m, 926 m, 876 m, 833 s, 777 s, 696 m, 652 m, 617 w; MS *m/z* (relative intensity, %) 448 (20), 447 (59), 364 (27), 363 (100), 334 (15), 182 (19). HRMS Calcd for C16H16: 447.2198; Found: 447.2207.



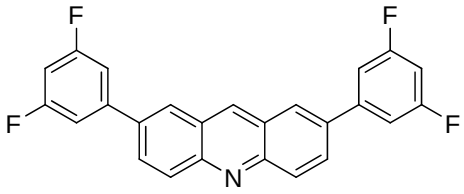
2,7-Bis(4-(trifluoromethyl)phenyl)acridine. Rf 0.29 (hexane: EtOAc = 5:1). Greenish solid (mp = >200 ˚C). ^{1}H NMR ($CDCl_3$, 399.78 MHz) δ 7.78 (d, *J* = 8.4 Hz, 4H), 7.88 (d, *J* = 8.4 Hz, 4H), 8.07 (dd, *J* = 1.6, 9.2 Hz, 2H), 8.21 (d, *J* = 1.2 Hz, 2H), 8.35 (d, *J* = 9.2 Hz, 2H), 8.88 (s, 1H); ^{13}C NMR ($CDCl_3$, 100.53 MHz) δ 125.96, 125.98 (d, *J* = 3.8 Hz), 126.17, 126.87, 127.66, 129.91 (q, *J* = 32.6 Hz), 130.24, 130.38, 136.83, 137.06, 143.54, 148.83; IR (neat) 3076 w, 1929 w, 1614 w, 1566 w, 1487 w, 1435 w, 1412 w, 1389 w, 1331 s, 1277 w, 1194 m, 1176 m, 1138 s, 1074 s, 1013 m, 920 w, 860 w, 825 s, 781 w, 741 w, 708 w, 644 w, 625 w; MS *m/z* (relative intensity, %) 468 (29), 467 (100), 466 (10), 233 (11). HRMS Calcd for $C_{27}H_{15}F_6N$: 467.1109; Found: 467.1106.



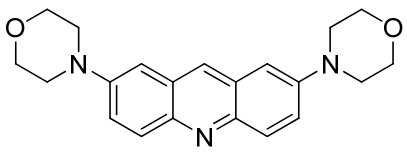
Isopropyl 3,3'-(acridine-2,7-diyl)dibenzoate. Rf 0.09 (hexane: EtOAc = 5:1) Yellow solid (mp = 129-130 ˚C). ^{1}H NMR ($CDCl_3$, 399.78 MHz) δ 1.43 (d, *J* = 6.4 Hz, 12H), 5.33 (sept, *J* = 6.4 Hz, 2H), 7.60 (t, *J* = 7.6 Hz, 2H), 7.97 (d, *J* = 6.4 Hz, 2H), 8.09-8.13 (m, 4H), 8.26 (s, 2H), 8.35 (d, *J* = 4.4 Hz, 2H), 8.46 (s, 2H), 8.91 (s, 1H); ^{13}C NMR ($CDCl_3$, 100.53 MHz) δ 21.99, 68.70, 125.74, 126.96, 128.38, 128.85, 129.03, 130.13, 130.35, 131.49, 131.70, 136.59, 137.45, 140.29, 148.62, 165.93; IR (neat) 2976 s, 2935w, 1709 s, 1604 w, 1570 w, 1512 w, 1473 w, 1448 m, 1427 m, 1373 m, 1352 m, 1282 s, 1234 s, 1178 m, 1169 m, 1105 s, 1036 m, 916 m, 870 w, 839 m, 821 m, 781 w, 756 s, 688 w, 621 w; MS *m/z* (relative intensity, %) 504 (36), 503 (100), 461 (12), 444 (11), 420 (15), 419 (50), 328 (10). HRMS Calcd for $C_{33}H_{29}NO_4$: 503.2097; Found: 503.2100.



2,7-Bis(3,5-difluorophenyl)acridine. Rf 0.31 (hexane: EtOAc = 5:1). Pale yellow solid. (mp = 196-197 ˚C). ^{1}H NMR ($CDCl_3$, 399.78 MHz) δ 6.85-6.91 (m, 2H), 7.28-7.33 (m, 4H), 8.01 (dd, *J* = 1.6, 8.8 Hz, 2H), 8.18 (d, *J* = 1.2 Hz, 2H), 8.33 (d, *J* = 9.2 Hz, 2H), 8.87 (s, 1H); ^{13}C NMR ($CDCl_3$, 100.53 MHz) δ 103.20 (t, *J* = 25.8 Hz), 110.237 (d, *J* = 11.7 Hz), 110.243 (d, *J* = 25.8 Hz), 126.4 (d, *J* = 77.6 Hz), 130.69 (d, *J* = 50.8 Hz), 136.25, 136.93, 143.32 (t, *J* = 9.6 Hz), 148.93, 162.22 (d, *J* = 12.5 Hz), 164.69 (d, *J* = 13.4 Hz); IR (neat) 3068 m, 2962 w, 1621 s, 1591 s, 1508 m, 1466 m, 1435 s, 1402 m, 1333 s, 1282 m, 1261 m, 1184 m, 1119 s, 1059 m, 1026 s, 987 s, 914 m, 845 s, 822 s, 805 s, 765 m, 744 s, 679 m, 638 m; MS *m/z* (relative intensity, %) 404 (27), 403 (100), 402 (15), 202 (13). HRMS Calcd for $C_{25}H_{13}F_4N$: 403.0984; Found: 403.0982.

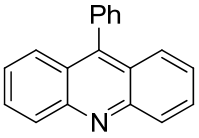


2,7-Dimorpholinoacridine. To an oven-dried 10 mL vial, 2,7-dibromoacridine[1] (337 mg, 1.0 mmol), morpholine (261 mg, 3.0 mmol), $Pd(dba)_2$ (57.5 mg, 0.10 mmol), 2-dicyclohexylphosphino-2',4',6'-triisopropylbiphenyl (100 mg, 2.1 mmol), Cs_2CO_3 (488.7 mg, 1.5 mmol) and ^{t}BuOH (5 mL) were added under N_2. The reaction was stirred at 120 ˚C for 20 h under N_2. After cooling to rt, the reaction mixture was then filtered thrugh a Celite pad, and the filitrate was concentrated under reduced pressure to give a reddish-brown oil. Chromatography on silica gel (hexane/ EtOAc = 5:1 to 1:1) furnished 2,7-dimorpholylacridine as a greenish solid (227 mg, 65%).
Rf 0.09 (hexane: EtOAc= 5:1). Dark-red solid (mp = 130-131 ˚C). ^{1}H NMR ($CDCl_3$, 399.78 MHz) δ 3.29-3.32 (m, 8H), 3.91-3.94 (m, 8H), 7.03-7.05 (m, 2H), 7.50-7.54 (m, 2H), 8.07 (d, *J* = 9.6 Hz, 2H), 8.33 (s, 1H); ^{13}C NMR ($CDCl_3$, 100.53 MHz) δ 49.37, 66.78, 107.05, 123.57, 128.13, 129.98, 131.05, 144.14, 148.30; IR (KBr) 2960 m, 2854 m, 2825 m, 1612 s, 1576 m, 1493 w, 1452 m, 1377 m, 1265 m, 1220 s, 1119 s, 1068 w, 1045 m, 970 w, 908 m, 823 m, 754 w, 638 w; MS *m/z* (relative intensity, %) 350 (24), 349 (100), 291 (22), 233 (29), 177 (14), 116 (13). HRMS Calcd for $C_{21}H_{23}N_2O_2$: 349.1790; Found: 349.1793.

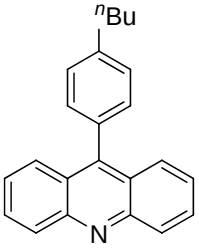


General procedure for the preparation of 9-arylacridines. To an oven-dried three-necked 100 mL flask, 9-chloroacridine (641.0 mg, 3.0 mmol), arylboronic acid (4.0 mmol), $Pd(OAc)_2$ (28 mg, 0.125 mmol), PCy_3 (70 mg, 0.25 mmol), K_3PO_4 (1.3 g, 6.0 mmol) were added. Toluene (40 mL) and H_2O (10 mL) were then added, and the reaction mixture was refluxed for 15-20 h. The solution was dissolved in 100 mL of CH_2Cl_2. The separated organic layer was washed water (100 mL), dried over $MgSO_4$, filtered and concentrated under reduced pressure. The resultant solid was purified by chromatography on silica gel (hexane/ EtOAc = 20:1 to 10:1) to furnish 9-diarylacridine (90->99%).

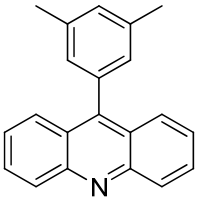
9-Phenylacridine (3). Rf 0.31 (hexane: EtOAc= 5:1). White solid (mp = 160-161 ˚C). ^{1}H NMR ($CDCl_3$, 399.78 MHz) δ 7.39-7.44 (m 4H), 7.55-7.62 (m, 3H), 7.70 (d, *J* = 8.8 Hz, 2H), 7.74-7.79 (m, 2H), 8.29 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100.53 MHz) δ 125.07, 125.56, 126.82, 128.31, 128.39, 129.46, 129.97, 130.38, 135.86, 147.25, 148.65; IR (KBr) 3055 m, 1623 m, 1606 m, 1554 m, 1539 m, 1510 s, 1476 m, 1437 m, 1412 s, 1356 m, 1174 m, 1155 m, 1134 m, 1070 m, 1011 m, 856 m, 758 s, 706 s, 648 m, 607 s; MS *m/z* (relative intensity, %) 256 (20), 255 (100), 254 (72), 253 (13), 127 (12), 126 (10). HRMS Calcd for $C_{19}H_{13}N$: 255.1048; Found: 255.1046.



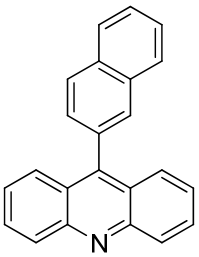
9-(4-Butylphenyl)acridine. Rf 0.31 (hexane: EtOAc = 5:1). Pale yellow solid (mp = 139-140 ˚C). ^{1}H NMR ($CDCl_3$, 399.78 MHz) δ 1.01 (t, *J* = 7.6 Hz, 3H), 1.42-1.52 (m, 2H), 1.71-1.78 (m, 2H), 2.77 (t, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 8.4 Hz, 2H), 7.39-7.43 (m, 4H), 7.74-7.78 (m, 4H), 8.29 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100.53 MHz) δ 14.01, 22.46, 33.58, 33.51, 125.23, 125.44, 126.99, 128.39, 129.32, 129.99, 130.30, 132.88, 143.14, 147.74, 148.56; IR (neat) 3033 m, 2956 m, 2923 s, 2848 m, 1625 w, 1608 w, 1554 m, 1540 m, 1512 m, 1458 m, 1435 m, 1412 m, 1358 w, 1182 w, 1112 w, 1014 m, 866 m, 823 m, 756 s, 655 m, 611 m; MS *m/z* (relative intensity, %) 312 (25), 311 (100), 269 (12), 268 (51), 267 (19), 266 (15), 254 (15). HRMS Calcd for $C_{23}H_{21}N$: 311.1674; Found: 311.1677.



9-(3,5-Dimethylphenyl)acridine. Rf 0.34 (hexane: EtOAc = 5:1). Yellow solid (mp = 182-183 ˚C). ^{1}H NMR ($CDCl_3$, 399.78 MHz) δ 2.42 (s, 6H), 7.04 (s, 2H), 7.19 (s, 1H), 7.39-7.43 (m, 2H), 7.74-7.77 (m, 4H), 8.30 (d, *J* = 9.6 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100.53 MHz) δ 21.31, 125.10, 125.40, 127.05, 128.05, 129.18, 129.86, 130.02, 135.62, 137.89, 148.04, 148.42; IR (KBr) 3051 m, 3001 m, 2943 m, 2914 m, 2857 m, 1929 w, 1815 w, 1716 w, 1626 w, 1601 m, 1556 m, 1541 m, 1512 m, 1481 m, 1460 m, 1433 m, 1412 m, 1365 m, 1259 m, 1132 m, 1038 m, 1009 m, 870 m, 839 m, 752 s, 706 s, 638 m, 617 m; MS *m/z* (relative intensity, %) 284 (23), 283 (100), 282 (15), 268 (44), 267 (14), 266 (13), 134 (20). HRMS Calcd for $C_{21}H_{17}N$: 283.1361; Found: 283.1363.

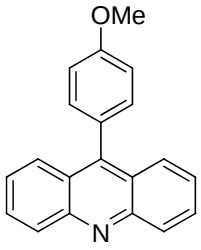


9-(Naphthalen-2-yl)acridine. Rf 0.26 (hexane: EtOAc = 5:1). Yellow solid (mp = >200 ˚C). ^{1}H NMR ($CDCl_3$, 399.78 MHz) δ 7.40 (m, 2H), 7.56 (dd, *J* = 1.6, 8.0 Hz, 1H), 7.59-7.66 (m, 2H), 7.73-7.82 (m, 4H), 7.91-7.95 (m, 2H), 8.01-8.03 (m, 1H), 8.08 (d, *J* = 8.8 Hz, 1H), 8.36 (d, *J* = 9.2 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100.53 MHz) δ 125.28, 125.79, 126.80, 126.84, 126.95 (two overlapping peaks), 127.92, 128.14 (three overlapping peaks), 129.21, 129.67, 130.31, 133.02, 133.24, 147.66, 148.34; IR (KBr)3055 w, 1603 w, 1543 m, 1512 m, 1483 w, 1460 w, 1435 m, 1414 m, 1350 w, 1159 m, 1120 m, 897 w, 868 m, 822 m, 754 s, 667 w, 644 w, 602 w; MS *m/z* (relative intensity, %) 306 (24), 305 (100), 304 (70), 303(16), 302 (12), 153 (13), 152 (21), 151 (14). HRMS Calcd for $C_{23}H_{15}N$: 305.1204; Found: 305.1200.

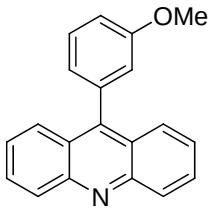


9-(4-Methoxyphenyl)acridine Rf 0.17 (hexane: EtOAc = 5:1). White solid (mp = 186-187 ˚C). ^{1}H NMR ($CDCl_3$, 399.78 MHz) δ 3.96 (s, 3H), 7.13-7.16 (m, 2H), 7.36-7.45 (m, 4H), 7.75-7.79 (m, 4H), 8.26-8.28 (m, 2H); ^{13}C NMR ($CDCl_3$, 100.53 MHz) δ 55.40, 113.90, 125.46 (two overlapping peaks), 126.94, 127.90, 129.55, 129.92, 131.71, 147.19, 148.80, 159.65; IR (KBr)3053 w, 3024 w, 2960 w, 2931 w, 2904 w, 2835 w, 1604 m, 1564 w, 1541 w, 1512 s, 1460 m, 1438 m, 1414 m, 1356 w, 1288

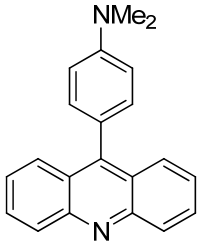
m, 1246 s, 1173 m, 1140 w, 1103 m, 1022 m, 822 m, 760 s, 725 w, 661 w, 606 m; MS *m/z* (relative intensity, %) 286 (22), 285 (100), 242 (16), 241(33), 240 (19). HRMS Calcd for $C_{20}H_{15}NO$: 285.1154; Found: 285.1155.



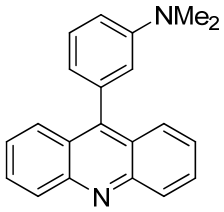
9-(3-Methoxyphenyl)acridine. Rf 0.17 (hexane: EtOAc = 5:1). Yellow solid (mp = 183-184 ˚C). ^{1}H NMR ($CDCl_3$, 399.78 MHz) δ 3.85 (s, 3H), 6.98-7.03 (m, 2H), 7.10-7.12 (m, 1H), 7.40-7.44 (m, 2H), 7.50 (t, *J* = 8.0 Hz, 1H), 7.73-7.79 (m, 4H), 8.29 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100.53 MHz) δ 55.31, 113.89, 115.86, 122.79, 124.99, 125.58, 126.86, 129.43, 129.50, 129.99, 137.21, 147.07, 148.61, 159.48; IR (KBr) 3047 m, 3006 m, 2958 m, 2931 m, 2906 m, 2883 m, 1936 w, 1747 w, 1626 w, 1593 s, 1554 m, 1541 m, 1514 m, 1458 s, 1423 s, 1356 m, 1321 m, 1282 m, 1254 s, 1174 m, 1153 m, 1136 m, 1082 w, 1036 s, 10121 m, 966 s, 899 m, 864 m, 788 s, 754 s, 704 s, 650 m; MS *m/z* (relative intensity, %) 286 (22), 285 (100), 270 (20), 254 (19), 242 (14), 241 (29), 240 (19), 121 (13). HRMS Calcd for $C_{20}H_{15}NO$: 285.1154; Found: 285.1152.



4-(Acridin-9-yl)-*N*,*N*-dimethylaniline. Rf 0.14 (hexane: EtOAc = 5:1). Pale orange solid (mp = >200 ˚C). ^{1}H NMR ($CDCl_3$, 399.78 MHz) δ 3.11 (s, 6H), 6.92-6.96 (m, 2H), 7.32-7.36 (m, 2H), 7.41-7.45 (m, 2H), 7.75-7.79 (m, 2H), 7.89 (d, *J* = 8.4 Hz, 2H), 8.29 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100.53 MHz) δ 40.45, 111.86, 122.95, 125.23, 125.62, 127.36, 129.16, 130.03, 131.60, 148.57 (2C), 150.33; IR (KBr) 2367 s, 1774 m, 1714 m, 1701 m, 1682 m, 1651 m, 1608 s, 1558 m, 1541 s, 1523 m, 1456 m, 1415 m, 1360 m, 1317 m, 1234 m, 1206 m, 1182 m, 1068 m, 813 m, 760 m; MS *m/z* (relative intensity, %) 299 (23), 298 (100), 297 (33), 149 (12). HRMS Calcd for $C_{21}H_{18}N_2$: 298.1470; Found: 298.1473.



3-(Acridin-9-yl)-*N*,*N*-dimethylaniline. Rf 0.14 (hexane: EtOAc = 5:1). Pale orange solid (mp = 152-153 ˚C). ^{1}H NMR ($CDCl_3$, 399.78 MHz) δ 2.97 (s, 6H), 6.76-6.78 (m, 2H), 6.90 (dd, *J* = 2.8, 8.0 Hz, 1H), 7.38-7.42 (m, 3H), 7.73-7.77 (m, 2H), 7.82 (d, *J* = 8.4 Hz, 2H), 8.29 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100.53 MHz) δ 40.41, 112.01, 114.21, 118.57, 125.12, 125.31, 127.21, 128.97, 129.20, 129.95, 136.56, 148.53, 148.58, 150.16.; IR (KBr) 3054 m, 2971 m, 2879 m, 2844 m, 2796 m, 1599 s, 1568 s, 1487 s, 1458 m, 1432 s, 1414 s, 1360 s, 1338 s, 1288 m, 1222 s, 1176 m, 1149 m, 1124 m, 1062 m, 1002 s, 931 m, 890 m, 864 m, 852 m, 775 s, 750 s, 703 s, 650 m; MS *m/z* (relative intensity, %) 299 (23), 298 (100), 297 (46), 254(26), 253 (12). HRMS Calcd for $C_{21}H_{18}N_2$: 298.1470; Found: 298.1471.

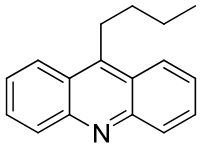


9-Butylacridine.[3] To a oven-dried three-necked 100 mL flask, acridine (1.0 g, 5.6 mmol) was dissolved in THF (10 mL), and the solution was cooled to 0 ˚C. To the solution, ^{n}BuLi (1.6 M in hexane, 4.0 mL, 6.4 mmol) was added dropwise at 0 ˚C, then allowed to room temperature and stirred for 1 h. The reaction was quenched with MeOH (5 mL) and then the reaction was filtered through a Celite pad, and washed with Et_2O. The filtrate was concentrated under reduced pressure to afford a yellow oil. The yellow oil was dissolved in CH_2Cl_2 (50 mL) and H_2O (9 mL). $K_3[Fe(CN)_6]$ (5.1 g, 16 mmol) and KOH (2.5 g, 45 mmol) were then added, and the mixture was stirred at room temperature for 20 h. Chromatography on silica gel (hexane/ EtOAc = 10:1 to 5:1) furnished 9-butylacridine as a yellow solid (745 mg, 57%)

Rf 0.31 (hexane: EtOAc = 5:1) Greenish yellow solid (mp = 143-144 ˚C). ^{1}H NMR ($CDCl_3$, 399.78 MHz) δ 0.98 (t, *J* = 7.2 Hz, 3H), 1.50-1.59 (m, 2H), 1.72-1.79 (m, 2H), 3.53 (t, *J* = 7.6 Hz, 2H), 7.48-7.52 (m, 2H), 7.71-7.75 (m, 2H), 8.18-8.23 (m, 4H); ^{13}C NMR ($CDCl_3$, 100.53 MHz) δ 13.87,

[3] E. Hayashi, S. Ohsumi and T. Maeda, *Yakugaku Zasshi*, **1959**, **7**, 969.

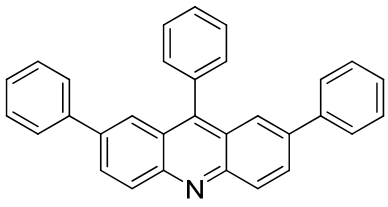
23.24, 27.27, 33.35, 124.23, 124.72, 125.32, 129.57, 130.19, 147.05, 148.50; IR (KBr)3053 m, 2956 s, 2923 s, 2861 s, 1944 w, 1915 w, 1801 w, 1712 w, 1622 m, 1606 m, 1550 m, 1514 s, 1489 m, 1458 s, 1437 m, 1410 m, 1379 m, 1342 m, 1298 w, 1143 m, 1097 m, 1011 w, 951 w, 862 w, 839 w, 744 s, 642 m; MS *m/z* (relative intensity, %) 236 (17), 235 (88), 193 (28), 192 (100), 191 (21). HRMS Calcd for $C_{17}H_{17}N$: 2351361; Found: 235.1362.



IV. Typical Procedures

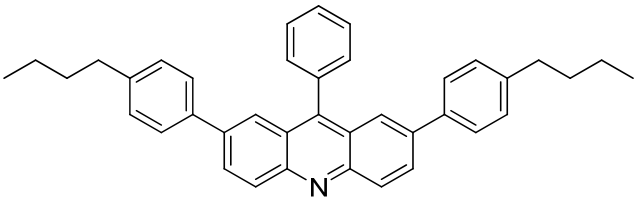
Typical procedure for the C-9 arylation reaction of acridines (Table 2). To an oven-dried 10 mL vial, $[RhCl(cod)]_2$ (12.4 mg, 0.025 mmol), PCy_3 (14.0 mg, 0.05 mmol), acridine (**1**, 44.8 mg, 0.25 mmol), Ph_2Zn (**2**, 219.6 mg, 1.0 mmol), toluene (2.0 mL) were added in a glove-box. The reaction was stirred at 160 ˚C for 20 h. After removing the volatiles *in vacuo*, chromatography on silica gel (hexane/EtOAc = 10:1 to 5:1) furnished 9-phenylacridine (**3**, 51.5 mg, 81%) as a white solid.
^{1}H NMR ($CDCl_3$, 399.78 MHz) δ 7.39-7.44 (m 4H), 7.55-7.62 (m, 3H), 7.70 (d, *J* = 8.8 Hz, 2H), 7.74-7.79 (m, 2H), 8.29 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100.53 MHz) δ 125.07, 125.56, 126.82, 128.31, 128.39, 129.46, 129.97, 130.38, 135.86, 147.25, 148.65. HRMS Calcd for $C_{19}H_{13}N$: 255.1048; Found: 255.1046.

2,7,9-Triphenylacridine. Rf 0.26 (hexane: EtOAc = 5:1). Yellow solid (mp = >200 ˚C). ^{1}H NMR ($CDCl_3$, 399.78 MHz) δ 7.34-7.36 (m, 2H), 7.42-7.44 (m, 4H), 7.51-7.52 (m, 2H), 7.59-7.64 (m, 7H), 7.88 (d, *J* = 1.2 Hz, 2H), 8,06 (dd, *J* = 1.6, 6.0 Hz, 2H), 8.36 (d, *J* = 6.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100.53 MHz) δ 124.08, 125.52, 127.36, 127.65, 128.53, 128.61, 128.88, 130.05, 130.18, 130.47, 135.73, 138.19, 140.41, 147.51, 148.10; IR (KBr) 3051 m, 3030 m, 1597 w, 1537 m, 1477 m, 1448 m,1332 w, 1167 w, 1147 w, 1074 w, 1030 w, 962 w, 887 w, 833 m, 760 s, 702 s, 619 m; MS *m/z* (relative intensity, %) 408 (33), 407 (100), 406 (18), 330 (10). HRMS Calcd for $C_{31}H_{21}N$: 467.1674; Found: 407.1675.

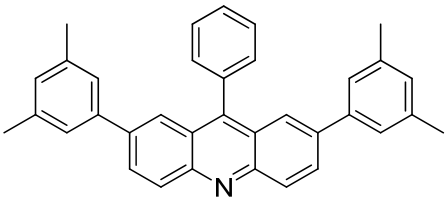


2,7-Bis(4-butylphenyl)-9-phenylacridine. Rf 0.20 (hexane: EtOAc = 5:1). Yellow solid (mp =

145-146 ˚C). ^{1}H NMR ($CDCl_3$, 399.78 MHz) δ 0.93 (t, *J* = 7.2 Hz, 6H), 1.32-1.41 (m, 4H), 1.57-1.65 (m 4H), 2.62 (t, *J* = 7.2 Hz, 4H), 7.22-7.24 (m, 4H), 7.49-7.51 (m, 6H), 7.55-7.64 (m, 3H), 7.85 (d, *J* = 2.4 Hz, 2H), 8.03 (dd, *J* = 2.0, 8.8 Hz, 2H), 8.33 (d, *J* = 9.2 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100.53 MHz) δ 13.93, 22.34, 33.55, 35.24, 123.61, 125.55, 127.17, 128.40, 128.54, 128.94, 129.95, 130.06, 130.49, 135.87, 137.73, 138.06, 142.56, 147.11, 147.98; IR (KBr) 3053 w, 3022 w, 2952 s, 2925 s, 2858 m, 1907 w, 1608 w, 1539 w, 1512 m, 1481 w, 1446 m, 1373 w, 1332 w, 1184 w, 1145 w, 1116 w, 1072 w, 1020 w, 962 w, 887 w, 823 s, 788 m, 761 w, 609 m; MS *m/z* (relative intensity, %) 520 (43), 519 (100), 477 (12), 476(31), 433 (14), 217 (34). HRMS Calcd for $C_{39}H_{37}N$: 519.2926; Found: 519.2927

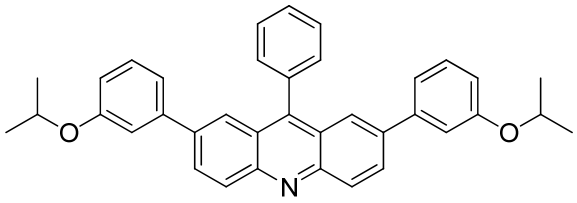


2,7-Bis(3,5-dimethylphenyl)-9-phenylacridine. Rf 0.31 (hexane: EtOAc = 5:1). Yellow solid (mp = >200 ˚C). ^{1}H NMR ($CDCl_3$, 399.78 MHz) δ 2.36 (s, 12H), 7.00 (s, 2H), 7.20 (s, 4H), 7.51-7.53 (m, 2H), 7.59-7.65 (m, 3H), 7.84 (s, 2H), 8.03 (dd, *J* = 1.6, 9.2 Hz, 2H), 8.33 (t, *J* = 9.2 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100.53 MHz) δ 21.39, 123.95, 125.34, 125.49, 128.43, 128.56, 129.29, 129.89, 130.41, 130.54, 135.85, 138.41, 138.49, 140.61, 147.26, 148.08; IR (KBr) 3055 w, 3024 w, 2916 m, 2857 w, 1599 m, 1537 m, 1444 m, 1377 w, 1335 w, 1147 w, 1074 w, 1036 w, 999 w, 852 w, 831 s, 793 w, 756 m, 702 m, 679 w, 621 w, 602 m; MS *m/z* (relative intensity, %) 463 (100). 462 (10) 358 (5) 232 (6). HRMS Calcd for $C_{35}H_{29}N$: 463.2300; Found: 463.2303.

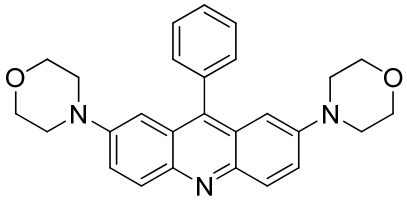


2,7-Bis(3-isopropoxyphenyl)-9-phenylacridine. Rf 0.17 (hexane: EtOAc = 5:1). Yellow solid (mp = 117-118 ˚C). ^{1}H NMR ($CDCl_3$, 399.78 MHz) δ 1.35 (d, *J* = 6.0 Hz, 12H), 4.58 (sept, *J* = 6.0 Hz, 2H), 6.87-6.89 (m, 2H), 7.11-7.15 (m, 4H), 7.32 (t, *J* = 7.6 Hz, 2H), 7.50-7.52 (m, 2H), 7.56-7.65 (m, 3H), 7.87 (d, *J* = 2.0 Hz, 2H), 8.02 (d, *J* = 2.4 Hz, 1H), 8.04 (d, *J* = 2.0 Hz, 1H), 8.34 (d, *J* = 9.2 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100.53 MHz) δ 22.01, 69.91, 114.75, 115.12, 119.66, 124.13, 128.51, 128.60, 129.86, 130.01, 130.18, 130.48, 131.37, 135.69, 138.12, 141.97, 147.47, 148.19, 158.22; IR (KBr) 3058 m, 2976 m, 2927 m, 1677 w, 1651 m, 1576 s, 1541 m, 1506 m, 1481 s, 1455 m, 1379 m,

1335 m, 1290 s, 1205 s, 1119 s, 999 w, 974 m, 950 m, 879 m, 835 m, 758 m, 700 s, 621 m; MS *m/z* (relative intensity, %) 524 (41), 523 (100), 440 (23), 439(68), 438 (15), 220 (19). HRMS Calcd for $C_{37}H_{33}NO_2$: 523.2511; Found: 523.2508.



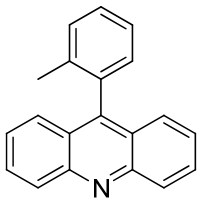
4,4'-(9-Phenylacridine-2,7-diyl)dimorpholine. Rf 0.09 (hexane: EtOAc = 5:1). Dark orange solid (mp = >200 ˚C). ^{1}H NMR ($CDCl_3$, 399.78 MHz) δ 3.11-3.13 (m, 8H), 3.82-3.84 (m, 8H), 6.70 (d, *J* = 2.8 Hz, 2H), 7.42-7.44 (m, 2H), 7.50-7.64 (m, 5H), 8.14 (d, *J* = 9.6 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100.53 MHz) δ 49.06, 66.71, 105.74, 123.09, 126.51, 128.09, 128.70, 130.07, 130.18, 136.74, 141.91, 143.64, 148.14; IR (KBr) 2960 m, 2889 m, 2852 m, 2821 m, 2821 m, 1606 s, 1493 m, 1468 s, 1444 s, 1371 m, 1344 m, 1301 m, 1269 m, 1221 s, 1165 m, 1119 s, 1068 m, 1045 m, 999 m, 964 w, 912 s, 872 w, 825 s, 776 w, 717 m, 629 m; MS *m/z* (relative intensity, %) 425 (21), 350 (24), 303 (100), 291 (24), 233 (31), 117 (16), 116 (15). HRMS Calcd for $C_{27}H_{27}N_3O_2$: 425.2103; Found: 425.2101.



9-(2-Tolyl)acridine. $(2\text{-Tolyl})_2Zn$ prepapred from 2-TolMgBr and $Zn(OMe)_2$ was used in place of Ph_2Zn.[1] Thus, to an oven-dried 10 mL Schlenk tube, $Zn(OMe)_2$ (308.7 mg, 2.5 mmol) and Et_2O were added, and the mixture was cooled to 0 °C. To the mixture, 2-tolylMgBr (2.0 M Et_2O solution, 2.44 mL, 4.88 mmol) was added dropwise at 0 °C, and the mixture was stirred for 1 h. The resulting mixture was allowed to warm to room temperature and stirred for extra 15 h. The mixture was filtrated through a Celite pad under an N_2 atmosphere. The filtrate was concentrated in vacuo, affording $(2\text{-tolyl})_2Zn$ as a white solid.

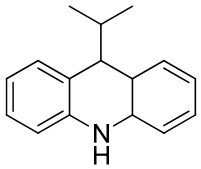
To an oven-dried 10 mL vial, $[RhCl(cod)]_2$ (7.4 mg, 0.015 mmol), PCy_3 (8.4 mg, 0.03 mmol), acridine (26.9 mg, 0.15 mmol), $(2\text{-Tolyl})_2Zn$ (148.6 mg, 0.6 mmol), toluene (1.5 mL) were added in a glove-box. The reaction was stirred at 160 ˚C for 20 h. After removing the volatiles *in vacuo*, chromatography on silica gel (hexane/EtOAc = 10:1 to 5:1) furnished 9-(2-tolyl)acridine (22.0 mg, 54%) as a pale yellow solid. Rf 0.34 (hexane: EtOAc= 5:1). Yellow solid (mp = 157-158

˚C). ^{1}H NMR ($CDCl_3$, 399.78 MHz) δ 1.88 (s, 3H), 7.24 (d, *J* = 8.0 Hz, 1H), 7.38-7.51 (m, 6H), 7.54 (d, *J* = 8.4 Hz, 1H), 7.76-7.80 (m, 2H), 8.30 (d, *J* = 9.2 Hz, 2H); ^{13}C NMR ($CDCl_3$, 150.83 MHz) δ 19.73, 125.10, 125.72, 125.83, 126.57, 1228.60, 129.66, 130.06, 130.19, 130.20, 135.48, 136.92, 147.02, 148.82; IR (KBr) 3045 w, 2910 w, 1649 w, 1614 w, 1554 m, 1541 m, 1512 s, 1479 m, 1458 m, 1435 m, 1412 m, 1313 w, 1132 w, 1110 w, 1014 w, 862 w, 820 m, 754 s, 723 m, 648 w, 606 m; MS *m/z* (relative intensity, %) 270 (21), 269 (100), 268 (63), 267 (24), 266 (13), 254 (18), 134 (15). HRMS Calcd for $C_{20}H_{15}N$: 269.1204; Found: 269.1201.

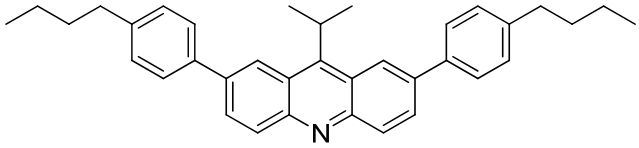


Typical procedure for the formal C-9 alkylation of acridine (Table 3). To an oven-dried 10 mL vial, acridine (44.8 mg, 0.25 mmol), $^{i}Pr_2Zn$ (**4**, 1.0 M in toluene, 0.5 mL, 0.5 mmol), toluene (0.5 mL) were added in a glove-box. The reaction was stirred at 70 ˚C for 20 h under N_2. The reaction was quenched by adding MeOH (1 mL), and the resulting solution was then filtered through a silica gel pad using EtOAc. The filtrate was concentrated *in vacuo* to afford crude 9-isopropyl-9,10-dihydroacridine (**5**). The crude mixture was dissolved in toluene (or CH_2Cl_2, 5 mL), and $K_3[Fe(CN)_6]$ (231 mg, 0.7 mmol), KOH (115.5 mg, 2.1 mmol) and H_2O (0.4 mL) were added, and the solution was stirred at room temperature for 20 h under air. After $MgSO_4$ was added, and the reaction mixture was filtered using CH_2Cl_2. After removing the volatiles *in vacuo*, chromatography on silica gel (hexane/EtOAc = 10:1 to 5:1) furnished 9-isopropylacridine (**11**) as a yellow oil (53.1 mg, 96%).

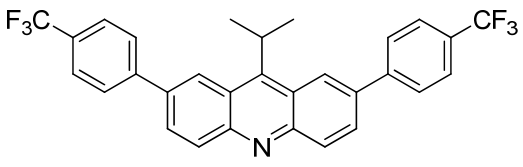
9-Isopropyl-9,10-dihydroacridine. (5) Rf 0.66 (hexane: EtOAc = 5:1). White solid (mp = 143-144 ˚C). ^{1}H NMR ($CDCl_3$, 399.78 MHz) δ 0.77 (d, *J* = 6.8 Hz, 6H), 1.83 (septet, *J* = 6.8 Hz, 1H), 3.73 (d, *J* = 5.6 Hz, 1H), 5.94 (s, 1H), 6.69 (d, *J* = 8.0 Hz, 2H), 6.87-6.91 (m, 2H), 7.08-7.20 (m, 4H); ^{13}C NMR ($CDCl_3$, 100.53 MHz) δ 19.27, 37.37, 48.84, 113.26, 120.23, 122.79, 126.74, 129.58, 140.30; IR (KBr) 3379 s, 3041 w, 2956 s, 2921 m, 2870 m, 1604 m, 1579 m, 1483 s, 1456 s, 1417 m, 1381 m, 1365 m, 1306 s, 1296 s, 1159 w, 1130 m, 1034 w, 928 w, 867 m, 858 w, 752 s, 717 m, 677 w, 638 w. This compound was easily oxidized to 9-isopropylacridine under the conditions to measure GC/MS and HRMS. MS *m/z* (relative intensity, %) 223 (4), 181 (14), 180 (100). HRMS Calcd for $C_{16}H_{19}N$: 225.1517; Found: 223.1357.



2,7-Bis(4-butylphenyl)-9-isopropylacridine (6). Rf 0.31 (hexane: EtOAc = 5:1). Orange solid (mp = 121-122 ˚C). ^{1}H NMR ($CDCl_3$, 399.78 MHz) δ 0.96 (t, *J* = 7.2 Hz, 6H), 1.36-1.45 (m, 4H), 1.60-1.70 (m 4H), 1.82 (t, *J* = 7.2 Hz, 6H), 2.68 (t, *J* = 7.6 Hz, 4H), 4.62 (sept, *J* = 7.2 Hz, 1H), 7.33 (d, *J* = 8.4 Hz, 4H), 7.68 (d, *J* = 8.4 Hz, 4H), 8.01 (dd, *J* = 2.0, 9.2 Hz, 2H), 8.31 (d, *J* = 8.8 Hz, 2H), 8.58 (s, 2H); ^{13}C NMR ($CDCl_3$, 100.53 MHz) δ 13.96, 22.37, 22.92, 28.44, 33.60, 35.29, 122.04, 124.88, 127.26, 129.07, 129.61, 130.96, 137.59, 138.17, 142.61, 148.00, 151.86; IR (KBr) 2960 m, 2927 s, 2854 m, 1606 w, 1543 w, 1512 m, 1483 m, 1454 m, 1406 w, 1375 w, 1331 w, 1184 w, 1159 w, 1095 w, 1016 w, 991 w, 955 w, 822 s, 788 m, 679 w, 619 w; MS *m/z* (relative intensity, %) 486 (38), 485 (100), 470 (15), 200 (21). HRMS Calcd for $C_{36}H_{39}N$: 485.3083; Found: 485.3085.

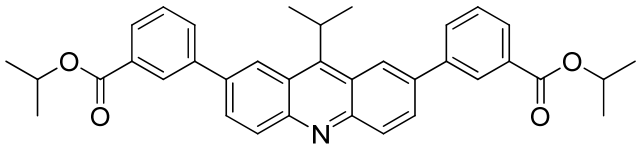


9-Isopropyl-2,7-bis(4-(trifluoromethyl)phenyl)acridine (7). Rf 0.14 (hexane: EtOAc = 5:1). Yellow solid (mp >200 ˚C). ^{1}H NMR ($CDCl_3$, 399.78 MHz) δ 1.85 (d, *J* = 7.2 Hz, 6H), 4.64 (sept, *J* = 7.2 Hz, 1H), 7.80 (d, *J* = 8.0 Hz, 4H), 7.88 (d, *J* = 8.4 Hz, 4H), 8.02 (dd, *J* = 2.0, 8.8 Hz, 2H), 8.35 (d, *J* = 9.2 Hz, 2H), 8.64 (s, 2H); ^{13}C NMR ($CDCl_3$, 100.53 MHz) δ 23.11, 28.57, 122.85, 123.23, 124.79, 125.56, 125.99 (d, *J* = 3.8 Hz), 127.77, 129.34, 129.80 (q, *J* = 32.6 Hz), 131.76, 136.49, 144.37, 148.75, 152.80; IR (KBr) 2968 w, 2935 w, 1614 m, 1541 w, 1518 w, 1460 w, 1398 w, 1325 s, 1271 w, 1165 s, 1120 s, 1166 s, 1012 m, 953 w, 852 m, 829 s, 794 w, 609 w; MS *m/z* (relative intensity, %) 510 (33), 509 (100), 495 (23), 494 (71), 492 (12), 348 (11). HRMS Calcd for $C_{30}H_{21}F_6N$: 509.1578; Found: 509.1576.

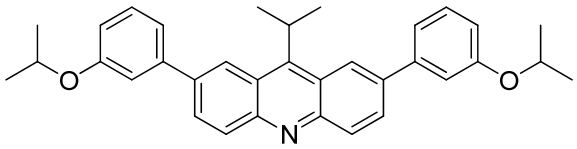


Isopropyl 3,3'-(9-isopropylacridine-2,7-diyl)dibenzoate (8). Rf 0.11 (hexane: EtOAc = 5:1). Pale yellow solid (mp = 121-122 ˚C). ^{1}H NMR ($CDCl_3$, 399.78 MHz) δ 1.43 (d, *J* = 6.0 Hz, 12H), 1.87 (d, *J* = 7.2 Hz, 6H), 4.66 (septet, *J* = 7.2 Hz, 1H), , 5.33 (septet, *J* = 6.0 Hz, 2H), 7.61 (t, *J* = 8.0 Hz,

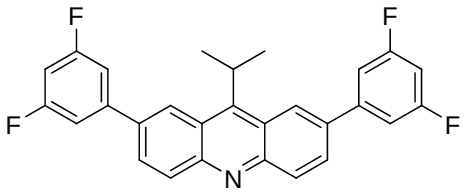
2H),7.95-7.97 (m, 2H), 8.06-8.12 (m, 4H), 8.36 (d, *J* = 8.8 Hz, 2H), 8.47 (t, *J* = 2.0 Hz, 2H), 8.66 (s, 2H); ^{13}C NMR ($CDCl_3$, 100.53 MHz) δ 21.95, 23.03, 28.49, 68.66, 122.80, 124.82, 128.50, 128.68, 129.02, 129.47, 131.44, 131.59, 131.67, 136.87, 141.07, 148.45, 152.52, 165.91; IR (neat)2979 m, 2933 m, 2875 w, 1712 s, 1648 m, 1577 w, 1510 m, 1460 m, 1423 m, 1373 m, 1294 s, 1242 s, 1174 m, 1109 s, 1047 w, 924 w, 837 m, 818 m, 756 m, 696 w; MS *m/z* (relative intensity, %) 546 (39), 545 (100), 446 (19). HRMS Calcd for $C_{36}H_{35}NO_4$: 545.2566; Found: 545.2561.



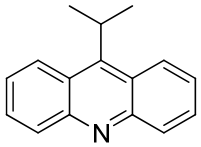
2,7-Bis(3-isopropoxyphenyl)-9-isopropylacridine (9). Rf 0.11 (hexane: EtOAc = 5:1). Orange solid (mp= 87-88 ˚C). ^{1}H NMR ($CDCl_3$, 599.85 MHz) δ 1.41 (d, *J* = 6.0 Hz, 12H), 1.84 (d, *J* = 7.2 Hz, 6H), 4.60-4.70 (m, 3H), 6.95 (dd, *J* = 1.8, 7.2 Hz, 2H), 7.30-7.34 (m, 4H), 7.42 (t, *J* = 7.8 Hz, 2H), 8.02 (dd, *J* = 1.8, 9.0 Hz, 2H), 8.32 (d, *J* = 9.0 Hz, 2H), 8.61 (s, 2H); ^{13}C NMR ($CDCl_3$, 150.83 MHz) δ 22.06, 22.97, 28.43, 69.95, 114.58, 115.41, 119.71, 122.17, 124.79, 129.63, 129.98, 131.06, 137.55, 142.41, 148.27, 152.18, 158.34; IR (KBr) 3062 m, 2974 s, 2929 m, 2873 m, 1600 s, 1576 s, 1541 m, 1479 m, 1454 s, 1377 m, 1329 m, 1286 s, 1200 s, 1115 s, 997 m, 966 m, 945 m, 872 m, 833 s, 779 s, 754 m, 698 m; MS *m/z* (relative intensity, %) 490 (37), 489 (100), 405 (15), 203 (11). HRMS Calcd for $C_{34}H_{35}NO_2$: 489.2668; Found: 489.2664.



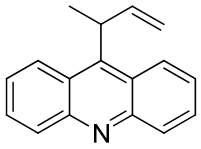
2,7-Bis(3,5-difluorophenyl)-9-isopropylacridine (10). Rf 0.20 (hexane: EtOAc = 5:1). Pale yellow oil. ^{1}H NMR ($CDCl_3$, 399.78 MHz) δ 1.86 (d, *J* = 4.8 Hz, 6H), 4.62 (sept, *J* = 4.8 Hz, 1H), 6.87-6.90 (m, 2H), 7.27-7.7.30 (m, 4H), 7.96 (dd, *J* = 1.6, 6.4 Hz, 2H), 8.32 (d, *J* = 6.0 Hz, 2H), 8.59 (s, 2H); ^{13}C NMR ($CDCl_3$, 150.85 MHz) δ 23.17, 28.58, 103.07 (t, *J* = 25.5 Hz), 110.33 (dd, *J* = 5.0, 20.5 Hz), 122.45, 124.70, 129.04, 131.84, 135.67, 144.15 (t, *J* = 9.5 Hz), 148.85, 153.00, 163.46 (dd, *J* = 13.3, 248.60 Hz); IR (neat) 3014 m, 2958 m, 2927 m, 2871 m, 1747 w, 1622 s, 1591 s, 1541 m, 1506 m, 1468 m, 1446 s, 1402 m, 1326 m, 1267 w, 1242 w, 1188 m, 1119 s, 1061 w, 989 s, 924 w, 877 m, 825 s, 785 w, 667 m, 613 w; MS *m/z* (relative intensity, %) 446 (30), 445 (100), 431 (22), 430 (73), 428 (15), 316 (13). HRMS Calcd for $C_{28}H_{19}F_4N$: 445.1454; Found: 445.1457.



9-Isopropylacridine (11). Rf 0.31 (hexane: EtOAc = 5:1). Yellow oil. ^{1}H NMR ($CDCl_3$, 399.78 MHz) δ 1.73 (d, *J* = 7.2 Hz, 6H), 4.50 (septet, *J* = 7.2 Hz, 1H), 7.49-7.51 (m, 2H), 7.71-7.75 (m, 2H), 8.26 (d, *J* = 8.4 Hz, 2H), 8.42 (d, *J* = 9.2 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100.53MHz) δ 22.68, 28.33, 124.44, 124.95 (two overlapping peaks), 129.38, 130.54, 148.76, 152.09; IR (neat) 3045 w, 2989 m, 2964 m, 2931 m, 2875 w, 1623 w, 1608 w, 1550 m, 1518 m, 1458 m, 1406 w, 1367 w, 1340 w, 1211 w, 1184 w, 1145 w, 1092 w, 1014 w, 989 w, 922 w, 866 w, 847 w, 758 s, 652 m, 614 w; MS *m/z* (relative intensity, %) 222 (13), 221 (77), 207 (16), 296 (100), 205 (17), 204 (46), 102 (22). HRMS Calcd for $C_{16}H_{15}N$: 221.1204; Found: 221.1206.

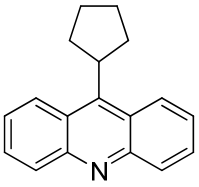


9-(But-3-en-2-yl)acridine (12). Rf 0.29 (hexane: EtOAc = 5:1). Orange solid (mp = 164-165 ˚C). ^{1}H NMR ($CDCl_3$, 399.78 MHz) δ 1.79 (d, *J* = 7.2 Hz, 3H), 5.00-5.07 (m, 1H), 5.24-5.29 (m, 2H), 6.38-6.45 (m, 1H), 7.48-7.53 (m, 2H), 7.73-7.77 (m, 2H), 8.25 (d, *J* = 9.2 Hz, 2H), 8.40 (d, *J* = 9.2 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100.53 MHz) δ 19.27, 36.10, 114.26, 124.61, 125.01, 125.21, 129.59, 130.46, 142.27, 148.85, 149.16; IR (neat) 3566 w, 3082 w, 3047 w, 2970 m, 2927 m, 2854 w, 2368 w, 1680 w, 1631 m, 1547 m, 1520 m, 1458 m, 1408 w, 1373 w, 1147 w, 1105 w, 1038 w, 1012 w, 914 w, 756 s, 646 w, 604 w; MS *m/z* (relative intensity, %) 234 (12), 233 (63), 232 (16), 219 (18), 218 (100), 217 (88), 216 (27), 204 (20), 109 (21). HRMS Calcd for $C_{17}H_{15}N$: 233.1204; Found: 233.1202.



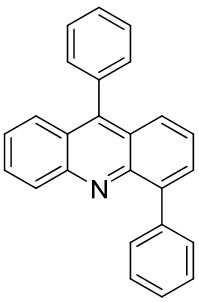
9-Cyclopentylacridine (13). Rf 0.29 (hexane: EtOAc = 5:1). Brown solid (mp = 179-180 ˚C). ^{1}H NMR ($CDCl_3$, 399.78 MHz) δ 1.95-2.05 (m, 2H), 2.19-2.42 (m, 6H), 4.50-4.60 (m, 1H), 7.48-7.52 (m, 2H), 7.72-7.76 (m, 2H), 8.27 (d, *J* = 8.4 Hz, 2H), 8.34 (d, *J* = 8.6 Hz, 2H),; ^{13}C NMR ($CDCl_3$, 100.53 MHz) δ 27.84, 34.31, 39.47, 124.68, 124.86, 124.96, 129.63, 130.33, 148.34, 151.02; IR

(KBr) 3095 m, 2989 m, 1866 w, 1752 m, 1700 w, 1633 s, 1599 s, 1556 s, 1529 s, 1473 s, 1344 m, 1261 m, 1182 m, 1159 m, 1024 m, 935 m, 818 m, 754 s, 707 w, 673 m, 629 w; MS *m/z* (relative intensity, %) 248 (14), 247 (70), 246 (19), 218 (24), 217 (30), 216 (14), 204 (30), 180 (26), 179 (100). HRMS Calcd for $C_{19}H_{19}N$: 247.1361; Found: 247.1358.



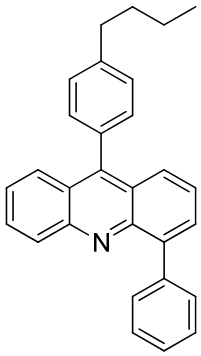
Typical procedure for the C-4 arylation reaction of acridines (Table 5). To an oven-dried 10 mL vial, $Ni(cod)_2$ (13.6 mg, 0.050 mmol), SIPr·HCl (42.7 mg, 0.10 mmol), NaO^tBu (48.1 mg, 0.50 mmol), and toluene (1 mL) were added, and the solution was then stirred for a few minutes until the color of the catalyst mixture changed to orange-dark brown. 9-Phenylacridine (63.8 mg, 0.25 mmol), Ph_2Zn (219.6 mg, 1.0 mmol), toluene (1.0 mL) were then added. All operations were conducted in a glove-box. The reaction was stirred at 160 ˚C for 20 h. After removing the volatiles *in vacuo*, chromatography on silica gel (hexane/EtOAc = 50:1) furnished 4,9-diphenylacridine as a white solid (56.3 mg, 68%).

4,9-Diphenylacridine (15). Rf 0.69 (hexane). White solid (mp = 173-174 ˚C). ^{1}H NMR ($CDCl_3$, 399.78 MHz) δ 7.38-7.42 (m, 1H), 7.45-7.49 (m, 4H), 7.53-7.71 (m, 8H), 7.79 (d, *J* = 6.8 Hz, 1H), 7.91 (d, *J* = 7.6 Hz, 2H), 7.91 (d, *J* = 7.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100.53 MHz) δ 124.78, 125.31, 125.45, 125.75, 126.55, 126.57, 127.27, 127.83, 128.23, 128.43, 129.34, 130.29, 130.48, 130.58, 131.13, 136.39, 139.80, 140.55, 146.68, 146.87, 148.44; IR (KBr) 3057 m, 3032 m, 1743 m, 1684 m, 1648 m, 1624 m, 1599 m, 1560 m, 1541 m, 1522 m, 1458 m, 1419 m, 1068 w, 1028 w, 864 w, 825 w, 758 s, 698 s, 669 w, 611 m.; MS *m/z* (relative intensity, %) 332 (15), 331 (57), 330 (100), 329 (10), 328 (29), 165 (11), 164 (12). HRMS Calcd for $C_{25}H_{17}N$: 331.1361; Found: 331.1360.

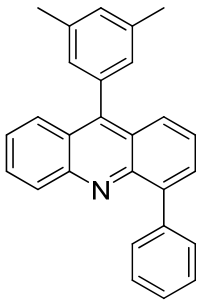


9-(4-Butylphenyl)-4-phenylacridine. Rf 0.66 (hexane: EtOAc = 5:1). Yellow solid (mp = 157-158 ˚C). ^{1}H NMR ($CDCl_3$, 399.78 MHz) δ 1.01 (t, *J* = 7.6 Hz, 3H), 1.43-1.52 (m, 2H), 1.71-1.79 (m, 2H),

2.78 (t, *J* = 7.2 Hz, 2H), 7.34-7.46 (m, 7H), 7.51-7.55 (m, 2H), 7.65-7.77 (m, 4H), 7.90 (d, *J* = 7.2 Hz, 2H), 8.20 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100.53 MHz) δ 14.04, 22.50, 33.62, 35.54, 124.91, 125.14, 125.58 (two overlapping peaks), 126.70 (two overlapping peaks), 133.43, 127.21, 127.79, 128.39, 129.28, 130.24, 130.38, 130.50, 131.11, 139.86, 140.46, 142.98, 146.67, 147.17, 148.44; IR (KBr) 3057 w, 3030 w, 2956 m, 2925 m, 2854 m, 1619 w, 1599 w, 1518 m, 1458 m, 1417 m, 1379 w, 1354 w, 1179 w, 1132 w, 1117 w, 1064 w, 1018 w, 869 w, 829 w, 754 s, 694 m, 671 w, 642 w, 613 m; MS *m/z* (relative intensity, %) 388 (19), 387 (72), 386 (100), 343 (25), 341 (13). HRMS Calcd for $C_{29}H_{25}N$: 387.1987; Found: 387.1981.

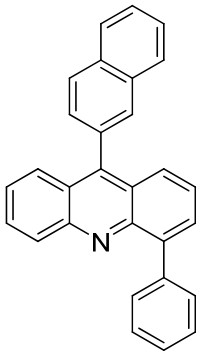


9-(3,5-Dimethylphenyl)-4-phenylacridine. Rf 0.63 (hexane: EtOAc = 5:1). Pale yellow solid (mp = 128-129 ˚C). ^{1}H NMR ($CDCl_3$, 399.78 MHz) δ 2.44 (s, 6H), 7.07 (s, 2H), 7.20 (s, 1H), 7.38-7.40 (m, 1H), 7.44-7.47 (m, 2H), 7.52-7.55 (m, 2H), 7.67-7.71 (m, 2H), 7.73 (dd, *J* = 0.9, 6.0 Hz, 1H), 7.78 (dd, *J* = 1.2, 4.8 Hz, 1H), 7.90-7.92 (m, 2H), 8.20 (d, *J* = 5.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100.53 MHz) δ 21.42, 124.85, 125.15, 125.53, 125.59, 126.82, 126.83, 127.26, 127.84, 128.24, 129.31, 129.80, 130.28, 130.54, 131.16, 136.26, 137.95, 139.88, 140.47, 146.69, 147.45, 148.47; IR (KBr) 3059 w, 3032 w, 3006 m, 2918 w, 2858 w, 1599 m, 1541 w, 1522 m, 1483 w, 1456 m, 1410 m, 1219 m, 1200 w, 1180 w, 1134 w, q032 w, 1016 w, 858 w, 841 w, 754 s, 700 s, 665 m, 631 m; MS *m/z* (relative intensity, %) 360 (14), 359 (62), 358 (100), 171(11), 164 (11). HRMS Calcd for $C_{27}H_{21}N$: 359.1674; Found: 359.1680.

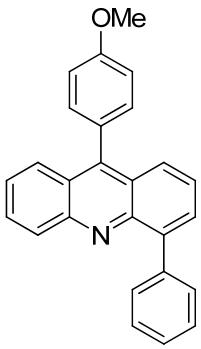


9-(Naphthalen-2-yl)-4-phenylacridine. Rf 0.60 (hexane: EtOAc = 5:1). Yellow solid (mp =

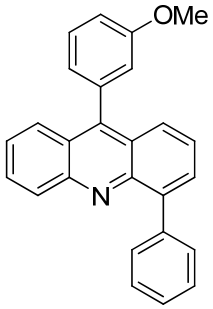
188-189 ˚C). ^{1}H NMR ($CDCl_3$, 399.78 MHz) δ 7.36-7.40 (m, 1H), 7.42-7.49 (m, 2H), 7.54-7.63 (m, 5H), 7.68-7.73 (m, 3H), 7.80 (dd, *J* = 1.6, 7.2 Hz, 1H), 7.91-7.96 (m, 4H), 8.01-8.03 (m, 1H), 8.08 (d, *J* = 8.8 Hz, 1H), 8.23-8.25 (m, 1H); ^{13}C NMR ($CDCl_3$, 150.85 MHz) δ 124.93, 125.41, 125.61, 125.84, 126.61, 126.63, 126.68, 126.76, 127.29, 127.84, 127.93, 128.08, 128.16, 128.35, 129.37, 129.69, 130.31, 130.63, 131.14, 132.98, 133.08, 133.86, 139.78, 140.59, 146.70, 146.74, 148.46; IR (neat) 3055 w, 2374 w, 2314 w, 1600 w, 1541 w, 1522 w, 1485 w, 1458 w, 1417 w, 1213 w, 1180 w, 1140 w, 901 w, 864 w, 823 w, 756 s, 698 m, 669 w, 640 w; MS *m/z* (relative intensity, %) 382 (18), 381 (70), 380 (100), 379 (14), 378 (32), 190 (15), 189 (19), 188 (11). HRMS Calcd for $C_{29}H_{19}N$: 381.1517; Found: 381.1521.



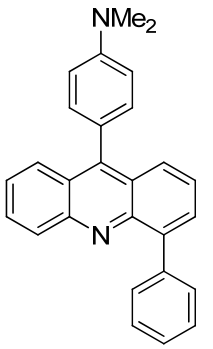
9-(4-Methoxyphenyl)-4-phenylacridine. Rf 0.57 (hexane: EtOAc = 5:1). White solid (mp = 159-160 ˚C). ^{1}H NMR ($CDCl_3$, 399.78 MHz) δ 3.93 (s, 3H), 7.11-7.14 (m, 2H), 7.36-7.40 (m, 3H), 7.43-7.47 (m, 2H), 7.51-7.55 (m, 2H), 7.65-7.78 (m, 4H), 7.89-7.91 (m, 2H), 8.19 (d, *J* = 8.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100.53 MHz) δ 55.38, 113.87, 125.08, 125.17, 125.62, 125.77, 126.62, 126.64, 127.22, 127.79, 128.33, 129.259, 130.23, 130.55, 131.11, 131.73, 139.83, 140.50, 146.69, 146.78, 148.46, 159.56; IR (KBr) 1604 m, 1540 w, 1513 m, 1458 m, 1419 m, 1288 w, 1245 m, 1174 m, 1103 w, 1028 m, 868 w, 831 m, 759 s, 700 m, 67 w.; MS *m/z* (relative intensity, %) 362 (15), 361 (67), 360 (100), 316 (24), 315 (13), 158 (12). HRMS Calcd for $C_{26}H_{19}NO$: 361.1467; Found: 361.1478.



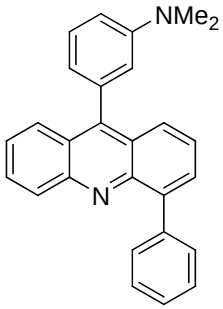
9-(3-Methoxyphenyl)-4-phenylacridine. Rf 0.54 (hexane: EtOAc = 5:1). White solid (mp = 128-129 ˚C). ^{1}H NMR ($CDCl_3$, 399.78 MHz) δ 3.85 (s, 3H), 7.00-7.05 (m, 2H), 7.09-7.12 (m, 1H), 7.37-7.55 (m, 6H), 7.66-7.79 (m, 4H), 7.89-7.91 (m, 2H), 8.20 (d, *J* = 8.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100.53 MHz) δ 55.33, 113.87, 115.92, 122.89, 124.65, 125.31 (two overlapping peaks), 125.75, 126.54, 126.57, 127.24, 127.80, 129.32, 129.50, 130.27, 130.53, 131.10, 137.73, 139.78, 140.50, 146.64 (two overlapping peaks), 148.40, 159.53; IR (KBr) 3060 w, 2958 w, 2931 w, 2831 w, 1591 m, 1541 m, 1519 m, 1458 m, 1421 m, 1355 w, 1313 w, 1267 w, 1242 m, 1174 w, 1134 w, 1039 m, 910 w, 885 w, 862 w, 754 s, 700 s, 667 w; MS *m/z* (relative intensity, %) 362 (16), 361 (68), 360 (100), 344 (18), 316 (15), 315 (14), 158 (11). HRMS Calcd for $C_{26}H_{19}NO$: 361.1467; Found: 361.1466.



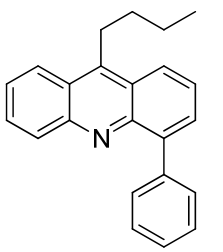
***N,N*-Dimethyl-4-(4-phenylacridin-9-yl)aniline.** Rf 0.49 (hexane: EtOAc = 5:1). Greenish solid (mp = 196-197 ˚C). ^{1}H NMR ($CDCl_3$, 399.78 MHz) δ 3.09 (s, 6H), 6.92-6.95 (m, 2H), 7.33-7.41 (m, 3H), 7.43-7.47 (m, 2H), 7.52-7.56 (m, 2H), 7.65-7.69 (m, 1H), 7.77 (dd, *J* = 1.2. 6.8 Hz, 1H), 7.83 (d, *J* = 8.8 Hz, 1H), 7.87 (dd, *J* = 1.2, 8.8 Hz, 1H), 7.90 (s, 1H), 7.92 (d, *J* = 1.2 Hz, 1H), 8.19 (d, *J* = 8.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100.53 MHz) δ 40.47, 111.89, 123.57, 124.86, 125.29, 125.31, 125.98, 127.02 (two overlapping peaks), 127.14, 127.78, 129.16, 130.18, 130.51, 131.12, 131.58, 139.99, 140.40, 146.77, 147.78, 148.57, 150.21; IR (KBr) 2889 w, 2804 w, 1608 s, 1523 s, 1479 m, 1456 m, 1419 m, 1356 m, 1227 w, 1205 w, 1171 m, 1065 m, 818 m, 760 s, 731 m, 698 m, 671 w, 634 m, 611 m; MS *m/z* (relative intensity, %) 375 (18), 374 (72), 373 (100), 357 (29), 328 (13), 187 (11), 186 (24), 164 (13). HRMS Calcd for $C_{27}H_{22}N_2$: 374.1783; Found: 374.1779.



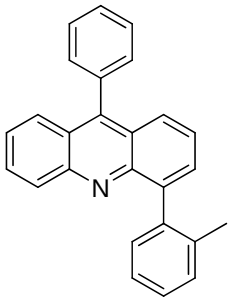
***N,N*-Dimethyl-3-(4-phenylacridin-9-yl)aniline.** Rf 0.46 (hexane: EtOAc = 5:1). Yellow oil. ^{1}H NMR ($CDCl_3$,270.05 MHz) δ 2.99 (s, 6H), 6.79-6.82 (m, 2H), 6.92 (dd, *J* = 2.4, 8.4 Hz, 1H), 7.37-7.41 (m, 1H), 7.43-7.47 (m, 3H), 7.52-7.56 (m, 2H), 7.66-7.70 (m, 1H), 7.77-7.83 (m, 3H), 7.90-7.92 (m, 2H), 8.20 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100.53 MHz) δ 40.50, 111.96, 114.40, 118.74, 124.83, 125.05, 125.49 (two overlapping peaks), 126.97 (two overlapping peaks), 127.20, 127.80, 129.01, 129.29, 130.26, 130.41, 131.11, 137.14, 139.90, 140.38, 146.64, 148.07, 148.43, 150.25; IR (neat) 3057 w, 3030 w, 2850 w, 2802 w, 1682 w, 1599 s, 1574 m, 1541 m, 1522 m, 1491 m, 1458 m, 1427 m, 1362 m, 1342 w, 1228 w, 1178 w, 1134 w, 1061 w, 1005 m, 908 w, 874 w, 854 w, 760 s, 733 m, 700 s, 671 w, 644 w, 617 w; MS *m/z* (relative intensity, %) 375 (19), 374 (73), 373 (100), 357 (26), 328 (17), 187 (10), 186 (23), 164 (13). HRMS Calcd for $C_{27}H_{22}N_2$: 374.1783; Found: 374.1778.



9-Butyl-4-phenylacridine. Rf 0.60 (hexane: EtOAc = 5:1). Yellow-green oil. ^{1}H NMR ($CDCl_3$, 399.78 MHz) δ 1.03 (t, *J* = 7.6 Hz, 3H), 1.58-1.65 (m, 2H), 1.80-1.87 (m, 2H), 3.63 (t, *J* = 8.0 Hz, 2H), 7.42-7.45 (m, 1H), 7.49-7.54 (m, 3H), 7.57-7.61 (m, 1H), 7.66-7.70 (m, 1H), 7.78 (dd, *J* = 0.8, 6.8 Hz, 1H), 7.85-7.87 (m, 2H), 8.15 (d, *J* = 9.2 Hz, 1H), 8.24 (t, *J* = 9.6 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100.53 MHz) δ 14.01, 23.41, 27.63, 33.51, 123.95, 124.07, 124.47, 125.15, 125.18, 125.63, 127.15, 127.73, 129.04, 130.06, 131.12, 131.38, 139.98, 141.23, 146.57, 146.60, 148.31; IR (KBr) 3059 w, 3030 w, 2954 m, 2925 m, 2862 m, 2362 w, 2339 w, 1620 w, 1601 w, 1549 w, 1523 m, 1491 m, 1460 m, 1418 w, 1292 w, 1180 w, 1140 w, 1103 w, 1072 w, 1020 w, 958 w, 904 w, 754 s, 698 m, 642 w, 600 w; MS *m/z* (relative intensity, %) 312 (16), 311 (66), 310 (100), 268 (30), 267 (44), 266 (12), 65 (10), 256 (21), 254 (12). HRMS Calcd for $C_{23}H_{21}N$: 311.1674; Found: 311.1667.



9-Phenyl-4-(2-tolyl)acridine. Rf 0.57 (hexane: EtOAc = 5:1). Yellow-green oil. ^{1}H NMR ($CDCl_3$, 399.78 MHz) δ 2.14 (s, 3H), 7.34-7.42 (m, 5H), 7.45-7.47 (m, 3H), 7.58-7.67 (m, 6H), 7.72 (dd, *J* = 1.2, 8.4 Hz, 1H), 8.12 (t, *J* = 9.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100.53 MHz) δ 20.80, 124.76, 125.13, 125.16, 125.31, 125.65, 126.52, 126.56, 127.35, 128.23, 128.41, 129.26, 129.59, 130.53 (two overlapping peaks), 130.60, 130.66, 136.38, 137.68, 140.48, 141.61, 146.82, 147.14, 148.52; IR (KBr) 3059 w, 3020 w, 2954 w, 2929 w, 1622 w, 1601 w, 1562 w, 1541 w, 1522 m, 1458 m, 1419 m, 1257 w, 1176 w, 1138 w, 1093 w, 1072 w, 1053 w, 1030 w, 908 m, 868 w, 827 w, 756 s, 733 s, 702 s, 671 w, 646 w, 615 m; MS *m/z* (relative intensity, %) 346 (20), 345 (82), 344 (100), 343 (13), 342 (13), 341 (11), 331 (17), 330 (61), 328 (19), 171 (11), 165 (15), 164 (18). HRMS Calcd for $C_{26}H_{19}N$: 345.1517; Found: 345.1519.



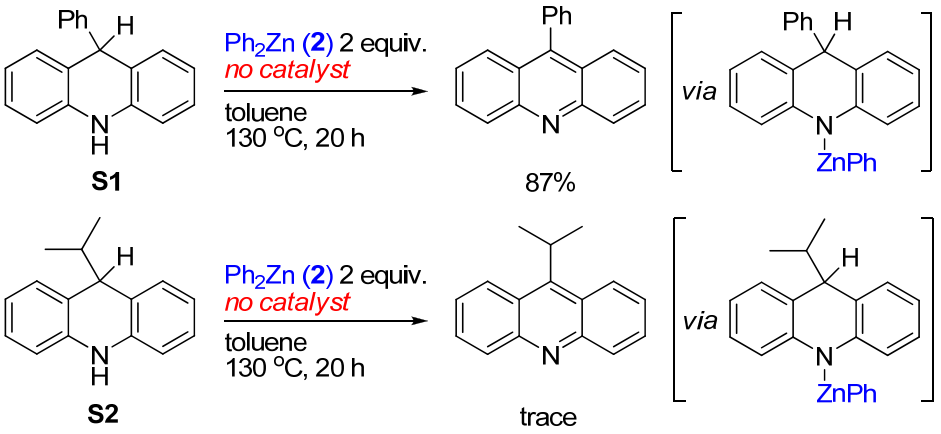
V. Mechanistic Studies

As shown in the paper, in the arylation of acridines, 9- or 4-arylated acridines were obtained as products, while in the alkylation 9-alkyl-9,10-dihydroacridines, not the aromatized product, were obtained. To collect information regarding these contrasting results, the following investigations were conducted.

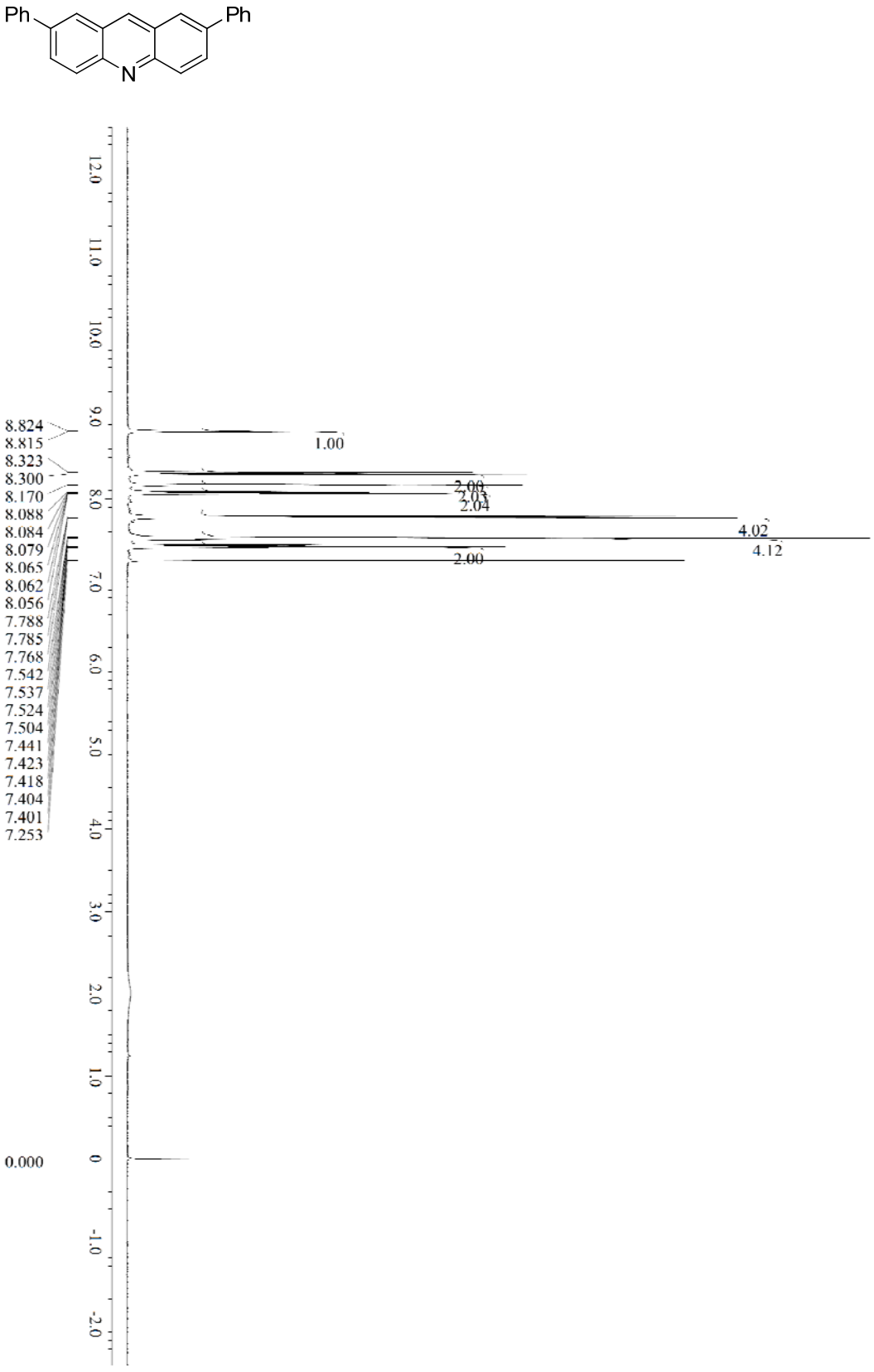
S1 (64.3 mg, 0.25 mmol) or **S2** (55.8 mg, 0.25 mmol) in toluene (2 mL) were treated with 2 equivalents of **2** (109.8 mg, 0.5 mmol) in the absence of the catalyst, and each reaction vessels were stirred at 130 °C for 20 h. As a result, **S1** was aromatized to afford 9-phenylacridine in 87% yield,[4] while **S2** was recovered quantitatively

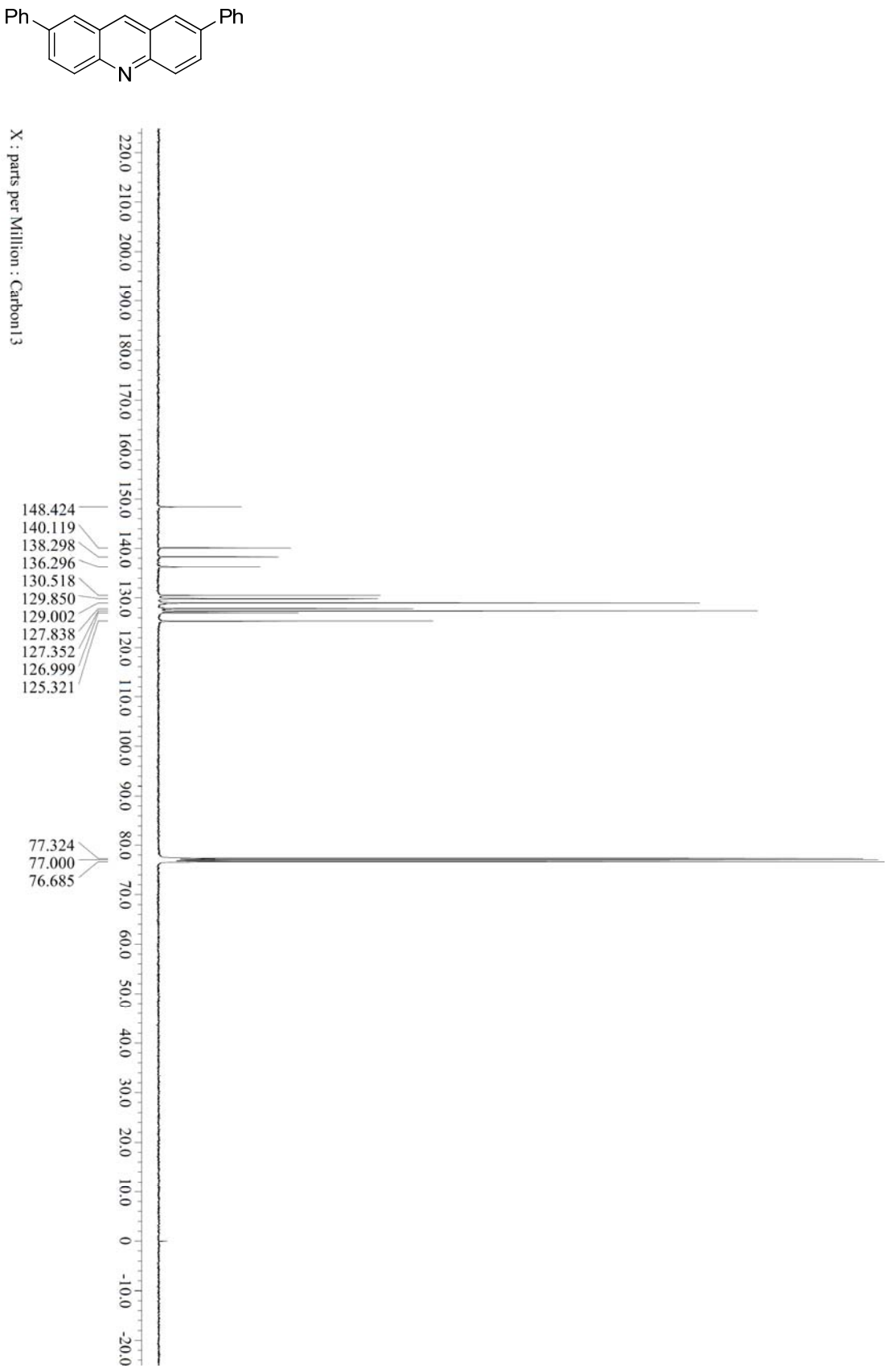
.

[4] Similar aromatization induced by Ph_2Zn was observed with 2-aryl-1,2-dihydroquinolines: M. Tobisu, I. Hyodo, N. Chatani, *J. Am. Chem. Soc.* **2009**, *131*, 12070.



This result shows that those contrasting results were due to the stability of **S2** toward aromatization induced by organozinc reagents.




Ph
Ph
N
X : parts per Million : Carbon13
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129.002
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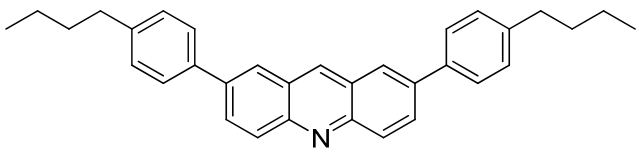
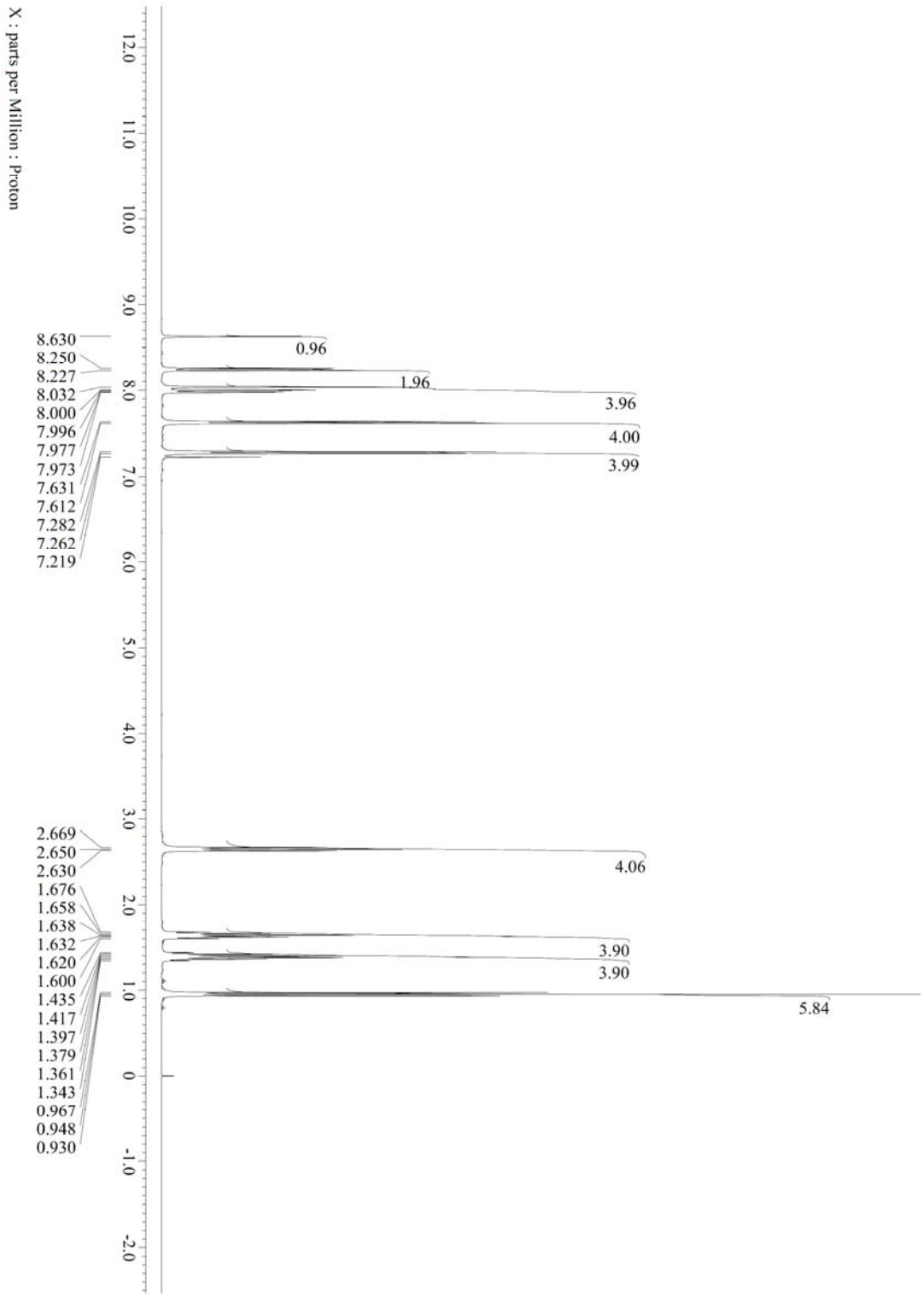
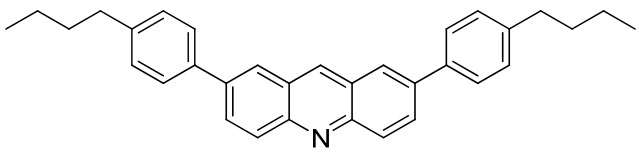
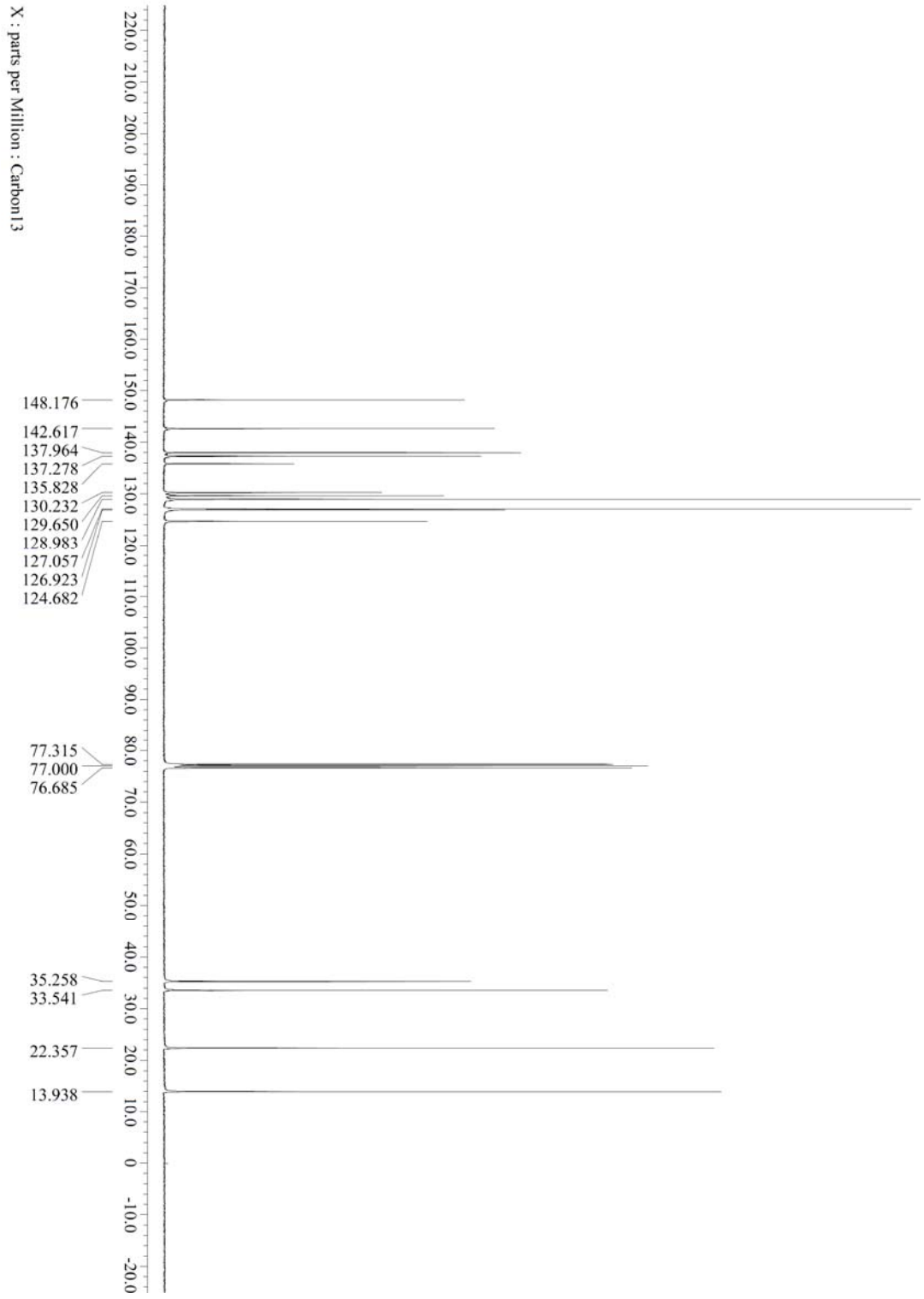
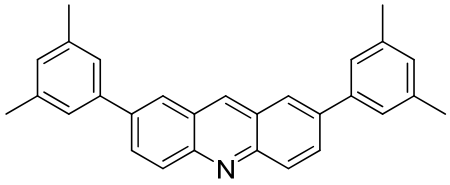
77.000
76.685

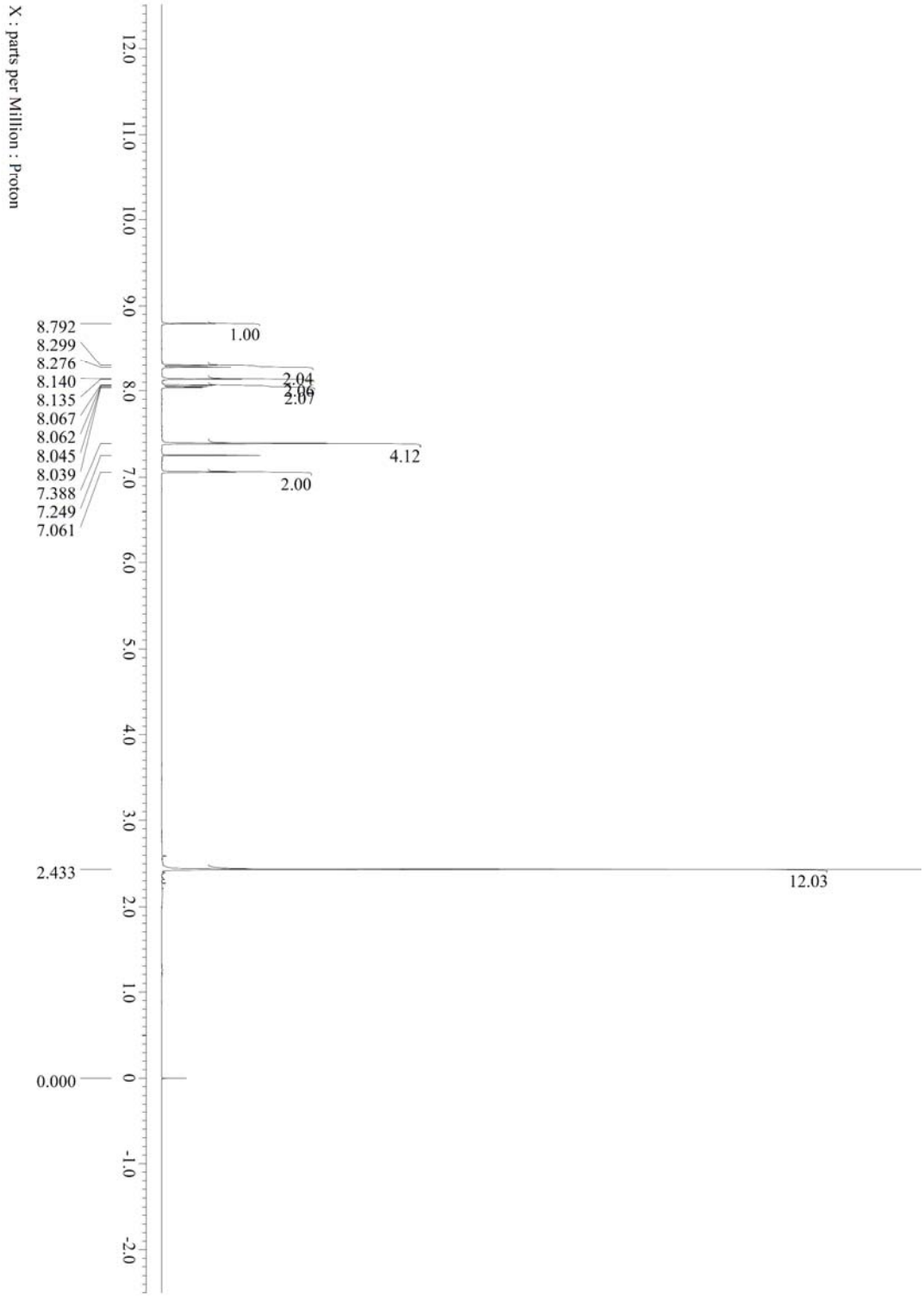









N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1.0
0
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-2.0
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8.276
8.140
8.135
8.067
8.062
8.045
8.039
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1.00
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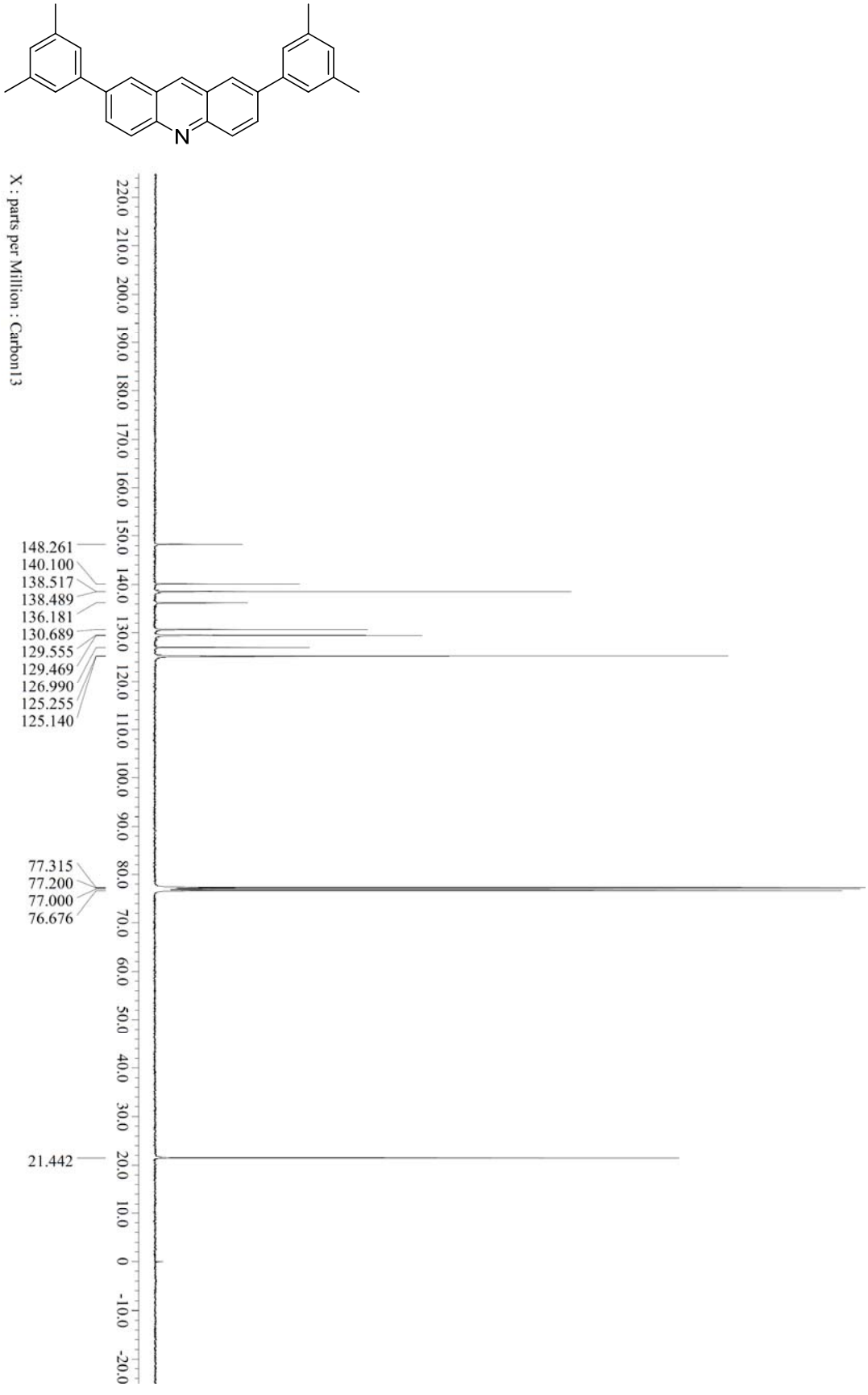
2.06
2.07
4.12
2.00
12.03


N
X : parts per Million : Carbon13
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148.261
140.100
138.517
138.489
136.181
130.689
129.555
129.469
126.990
125.255
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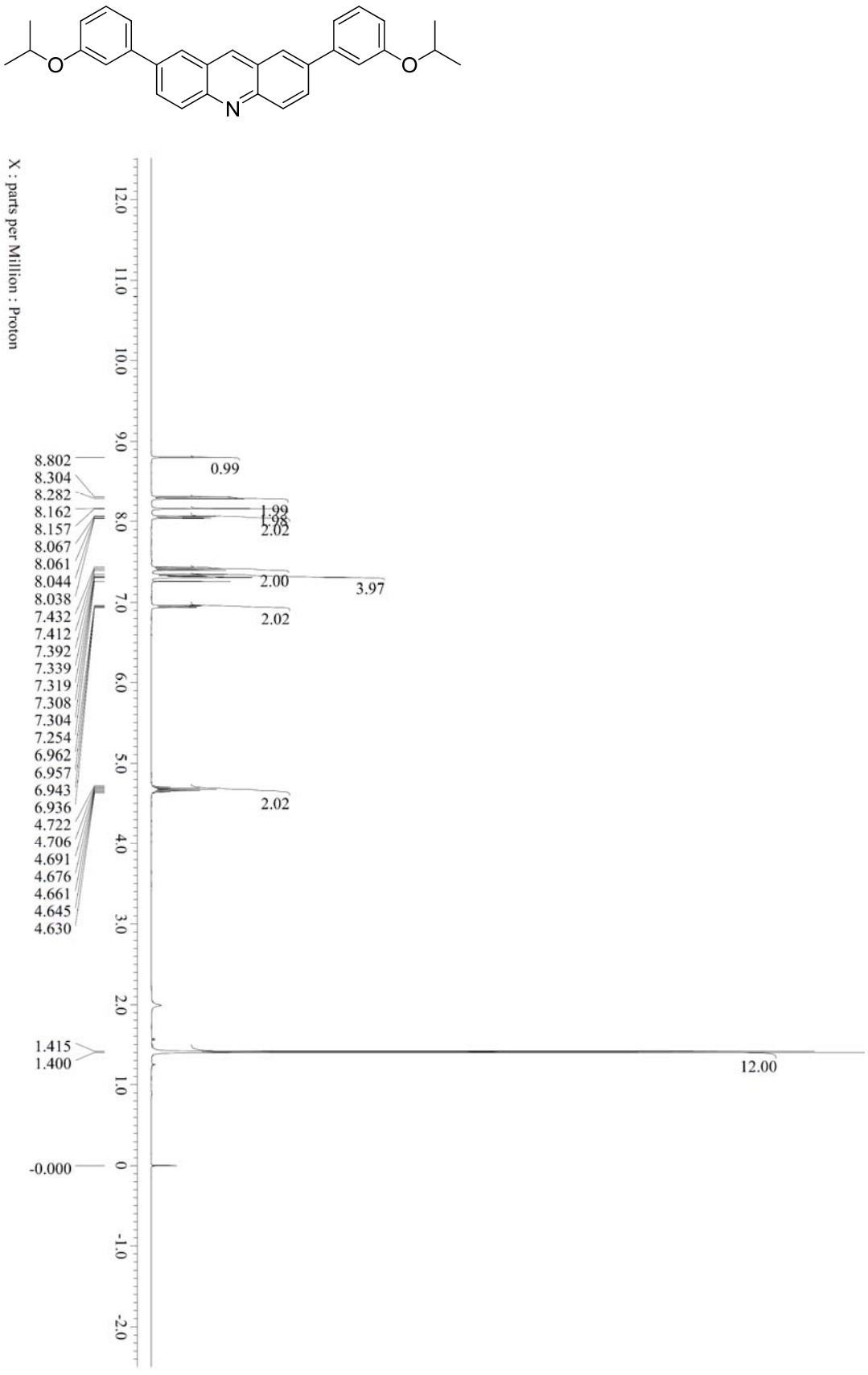
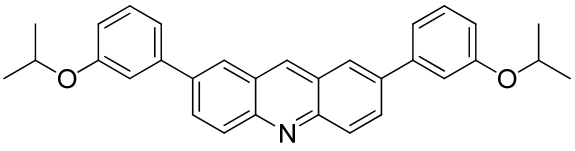
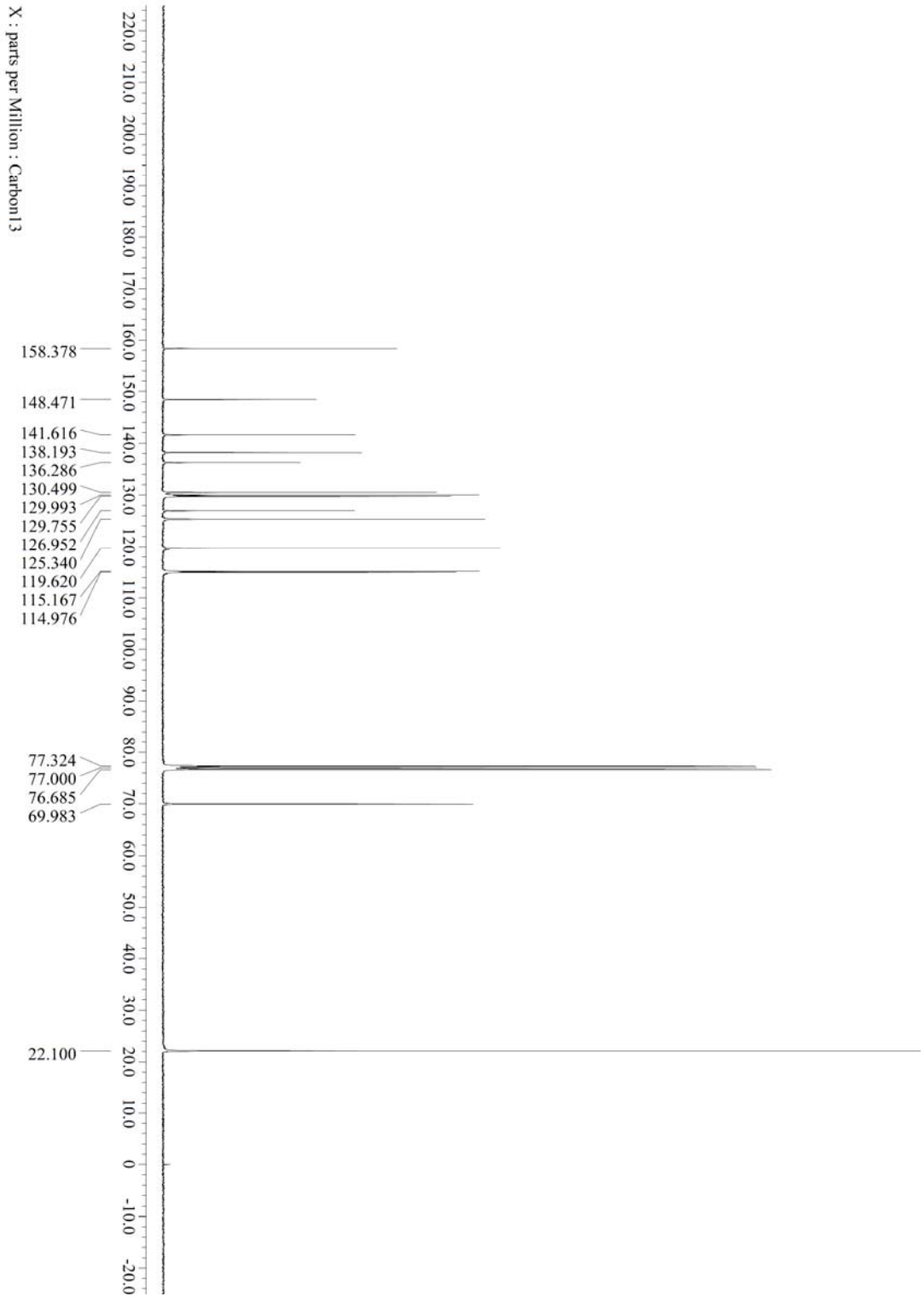
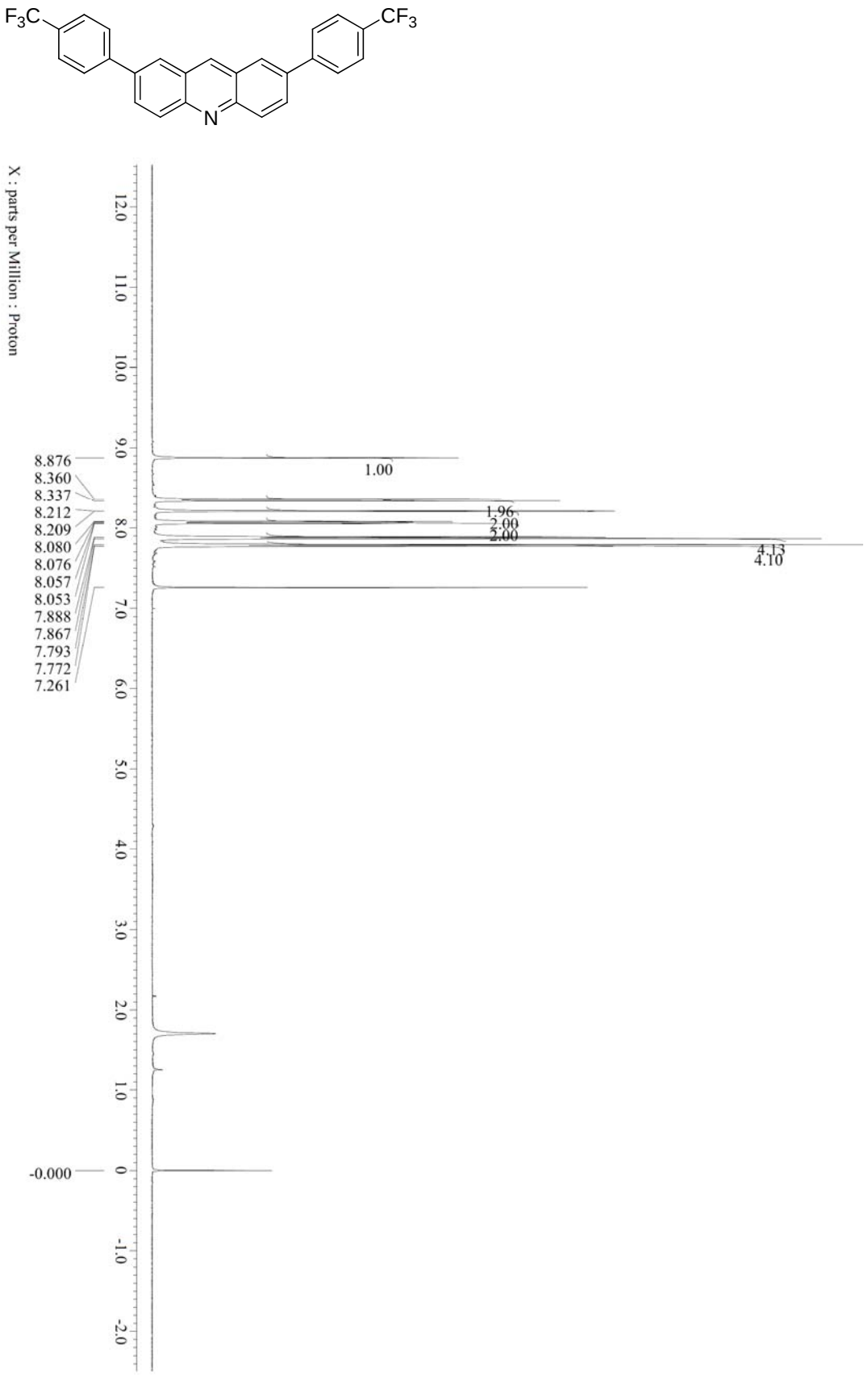
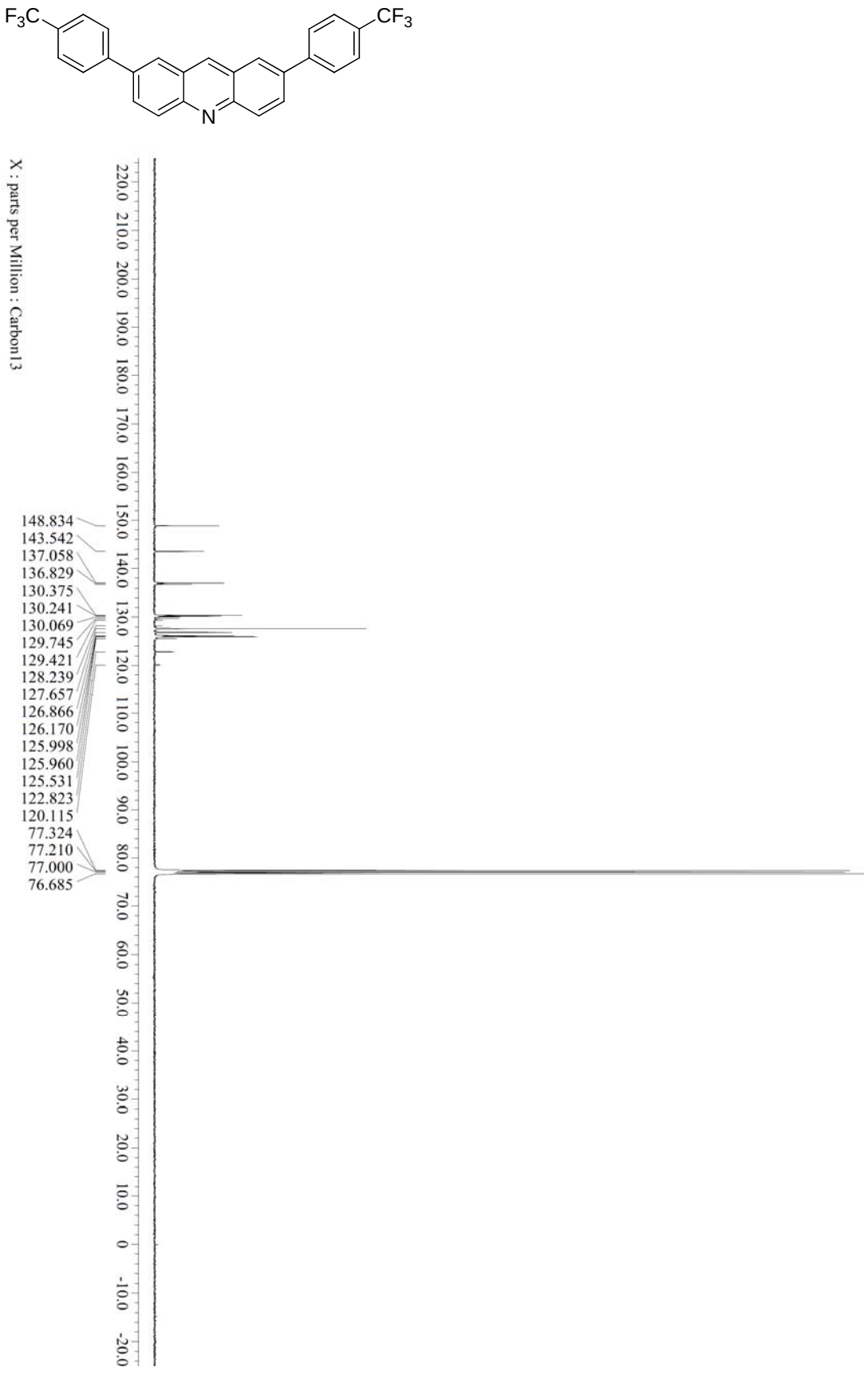
77.000
76.676
21.442

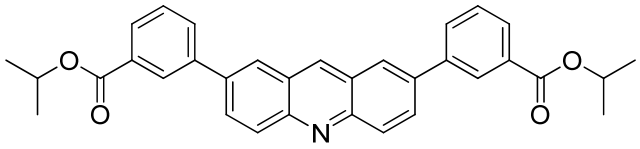


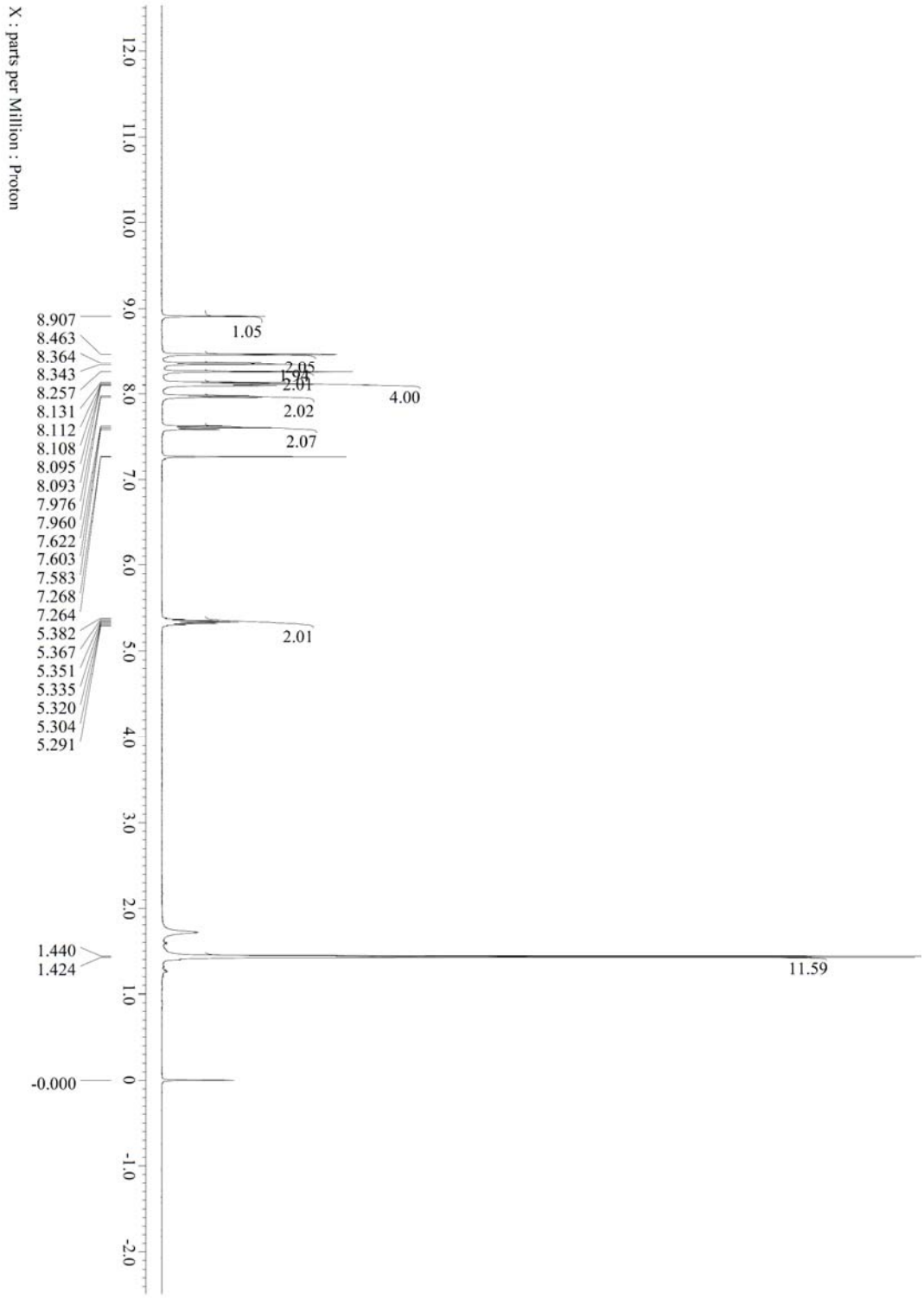


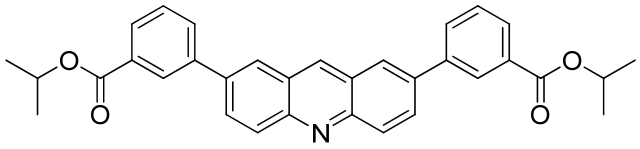


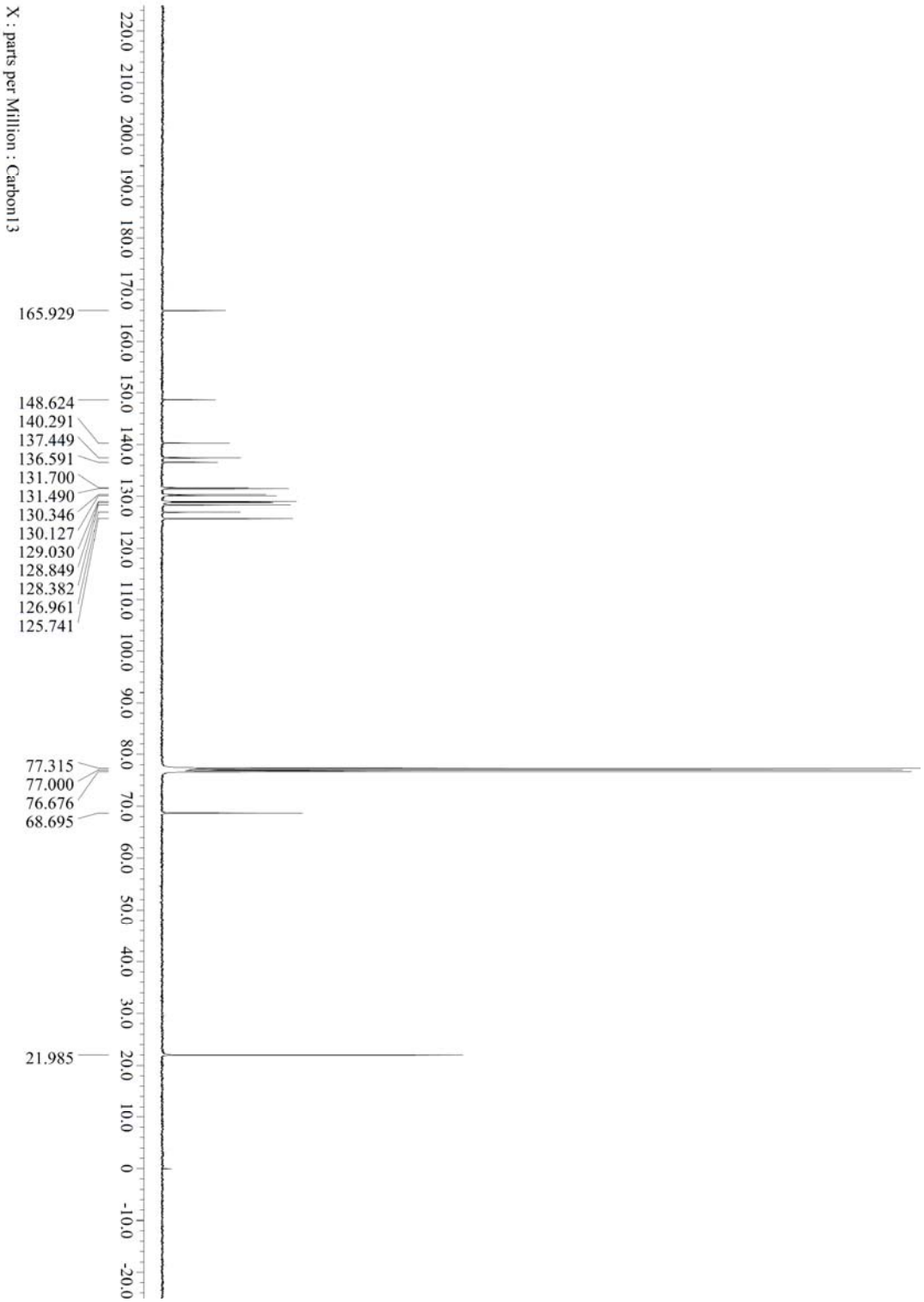


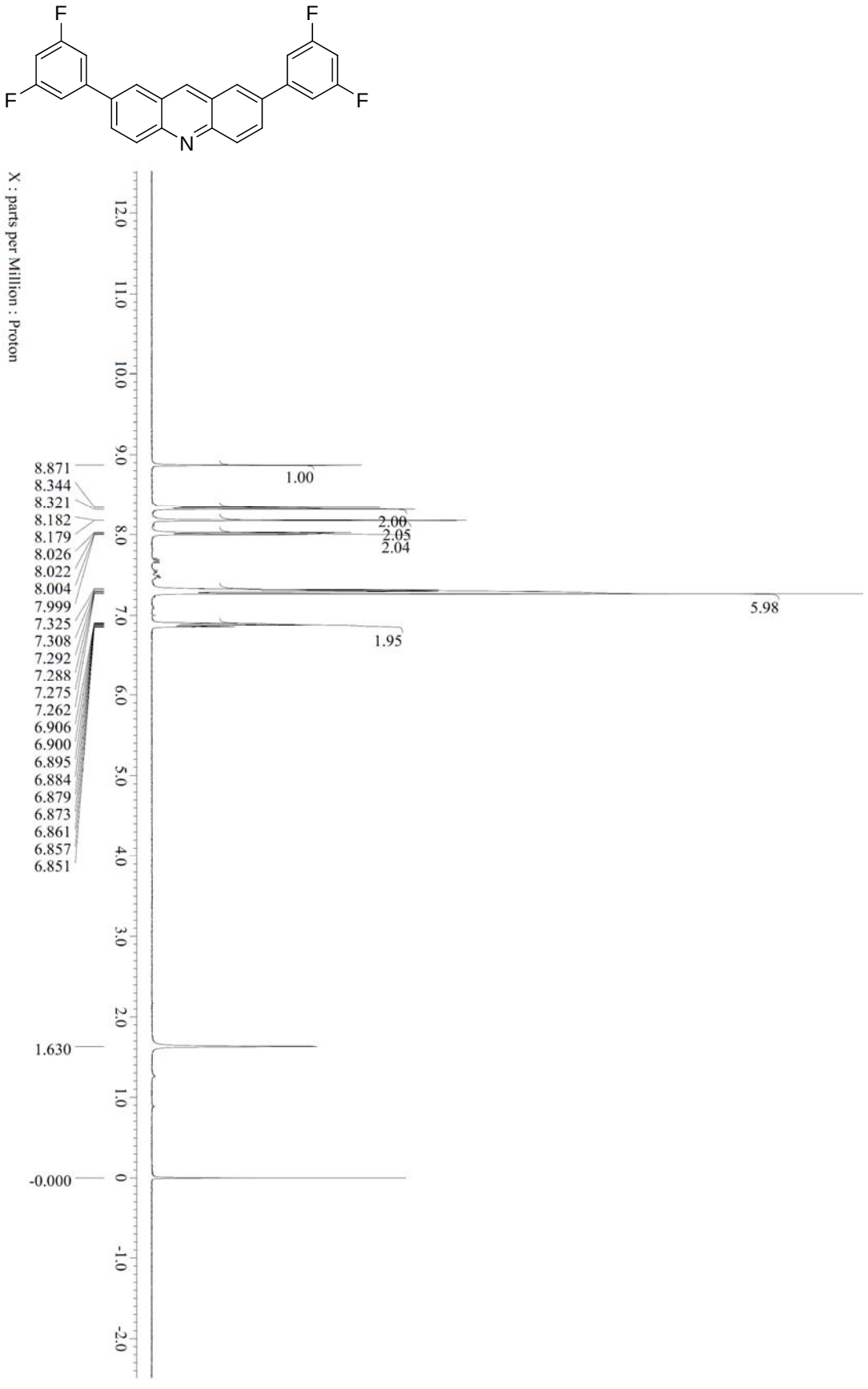


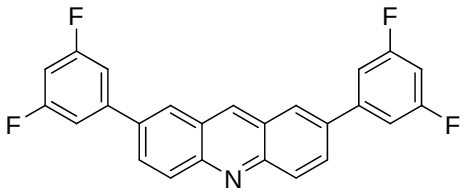


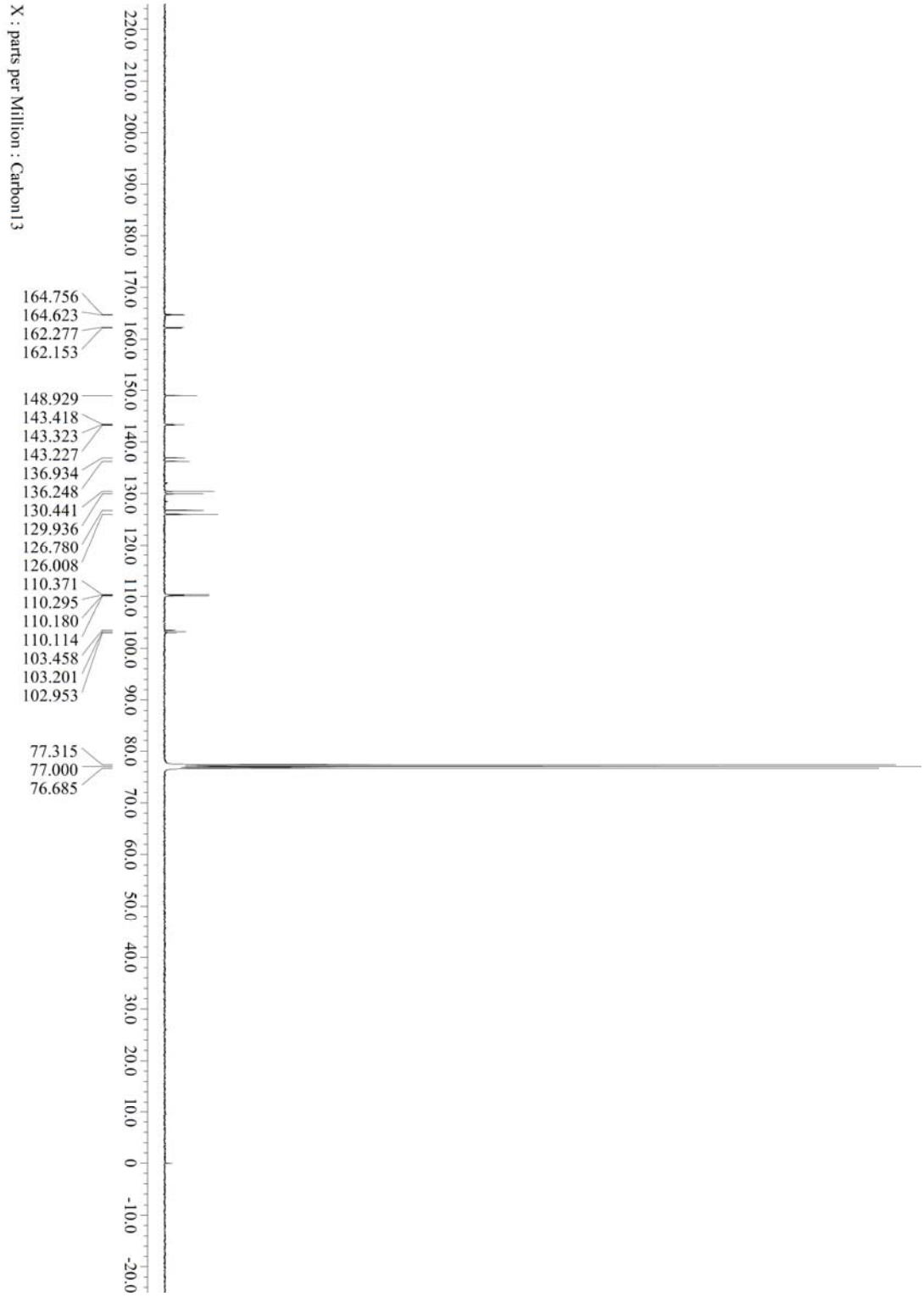


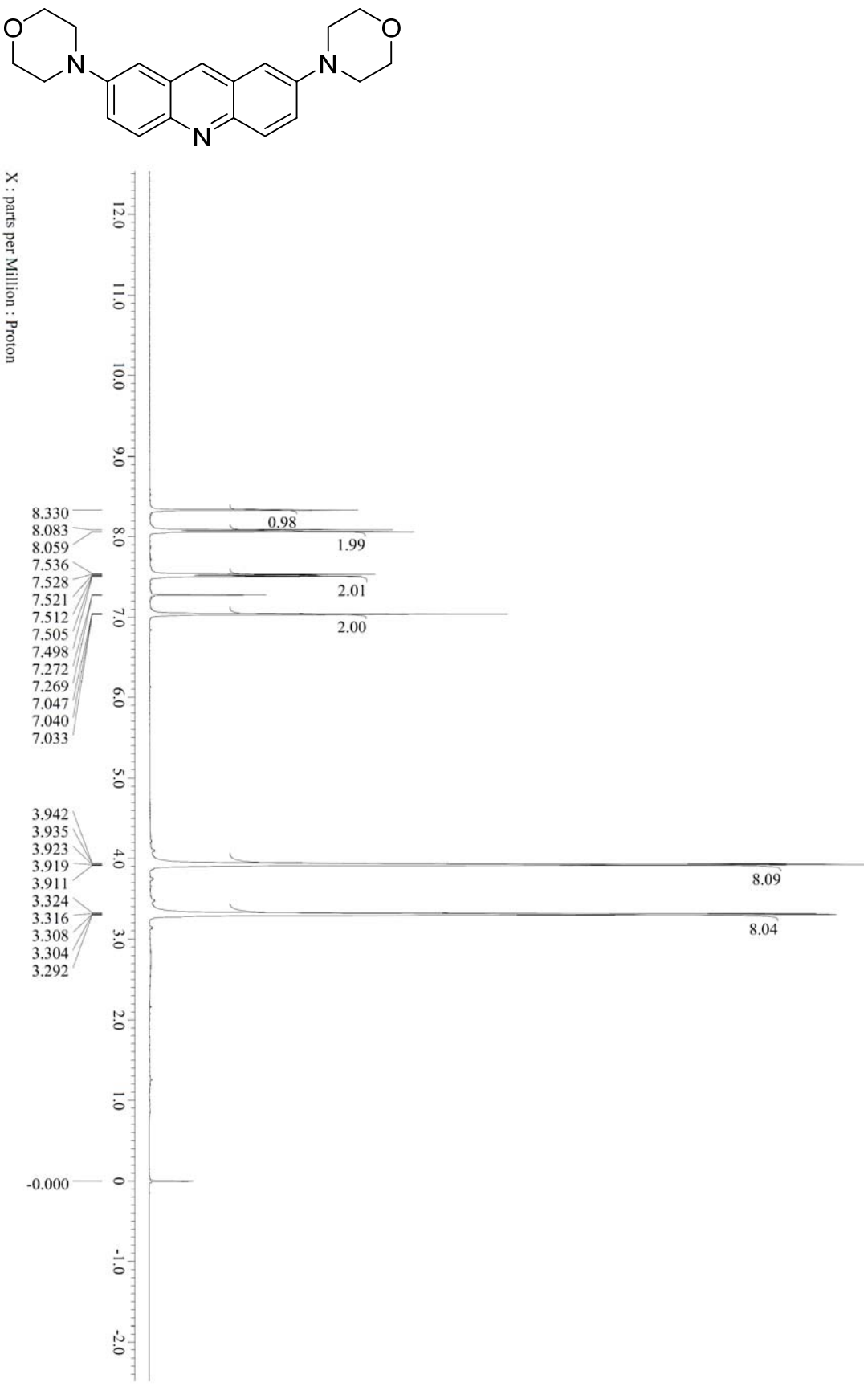


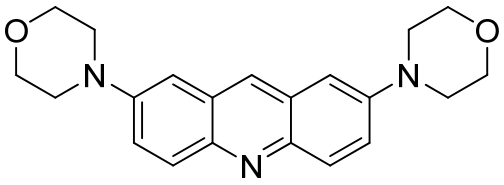


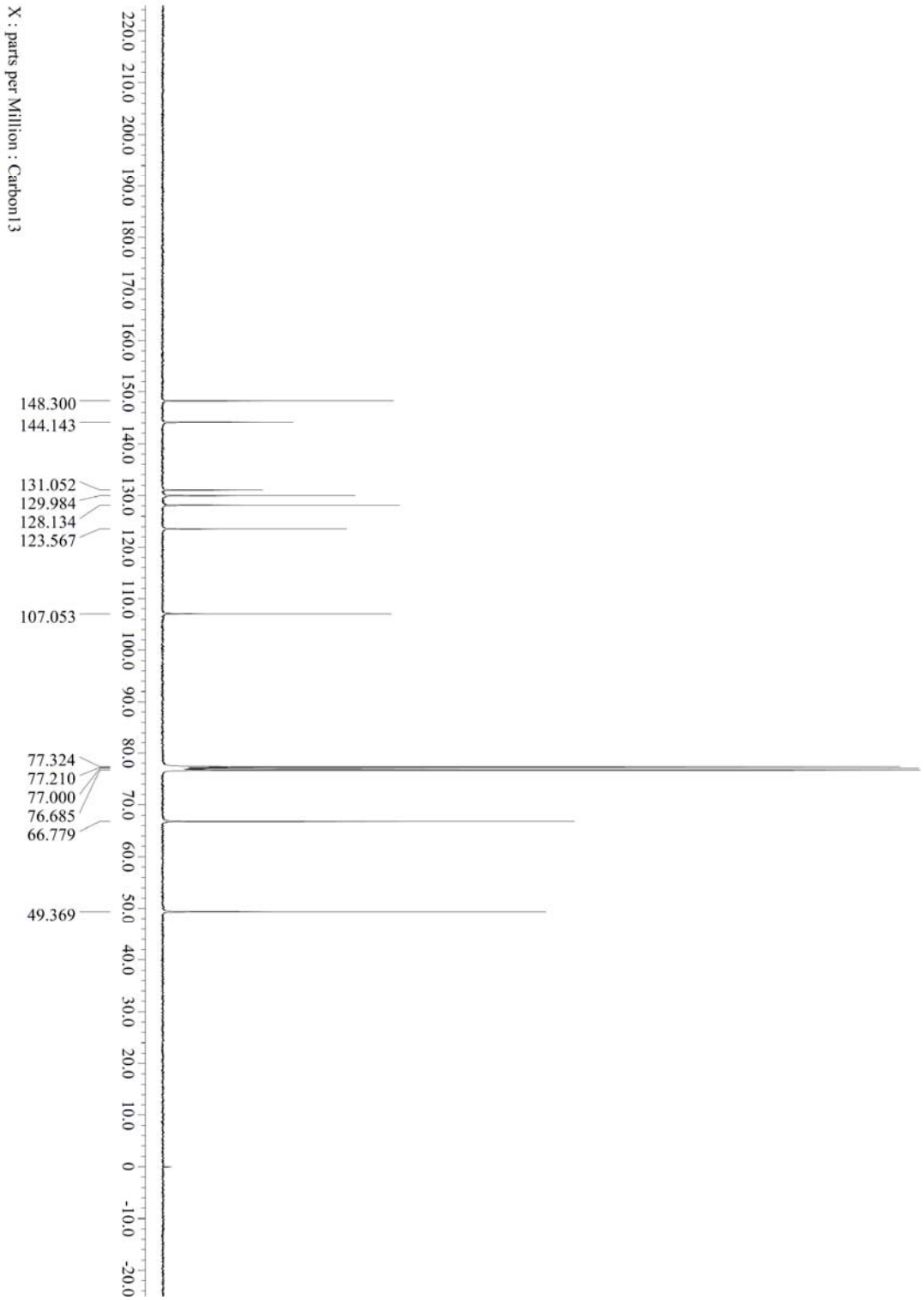


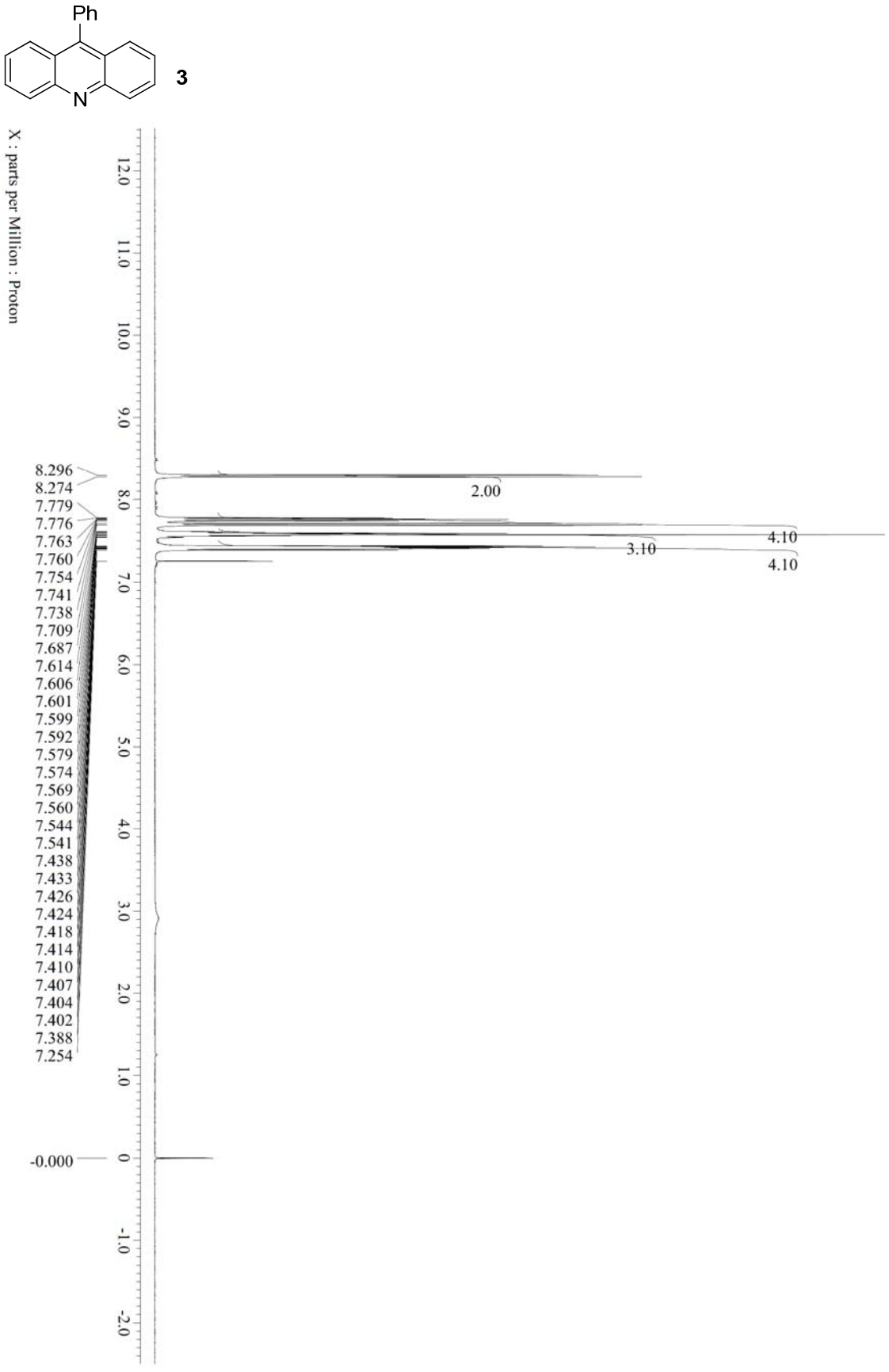


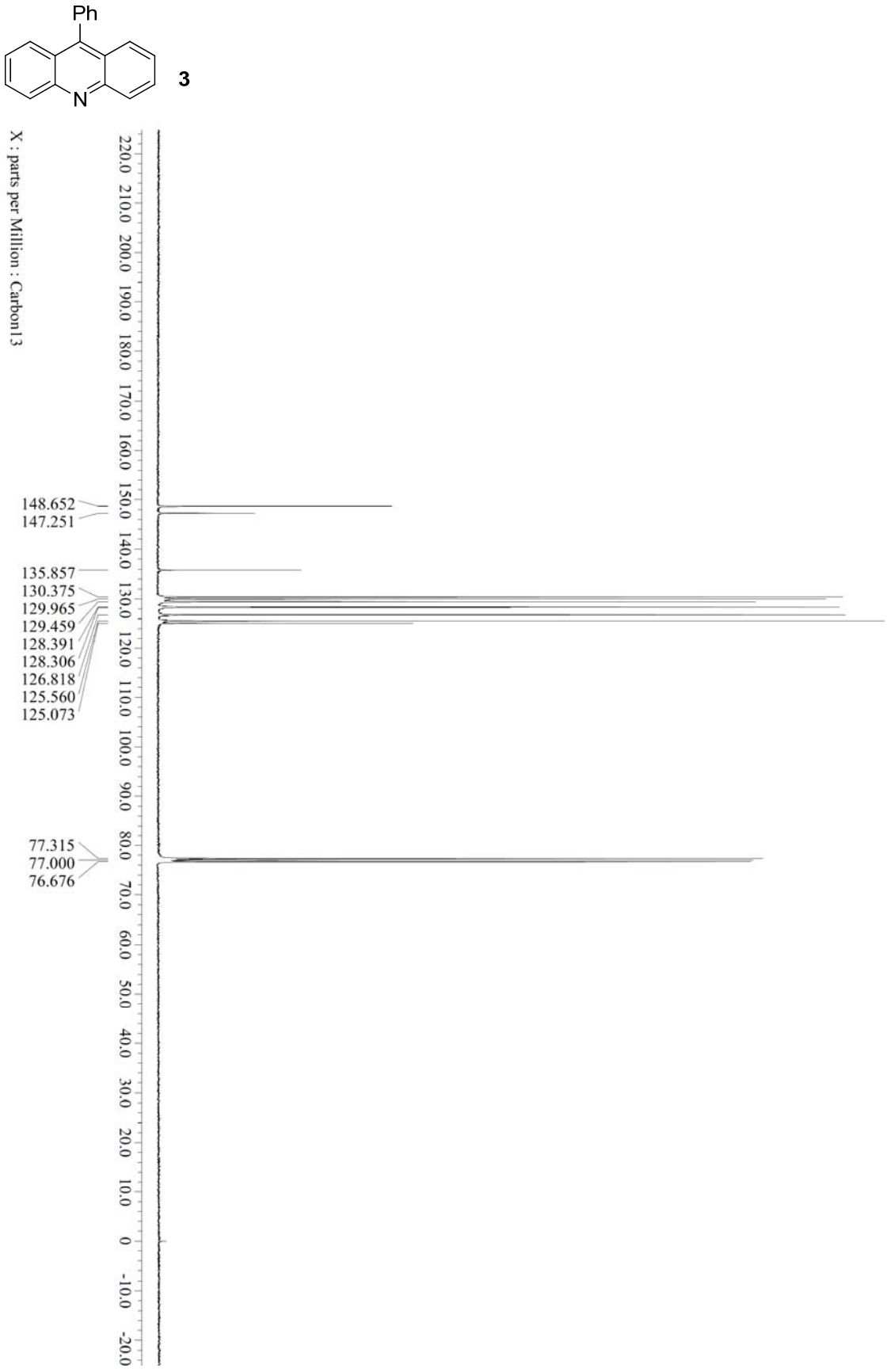











Ph
N
3
X : parts per Million : Carbon13
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
148.652
147.251
135.857
130.375
129.965
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128.391
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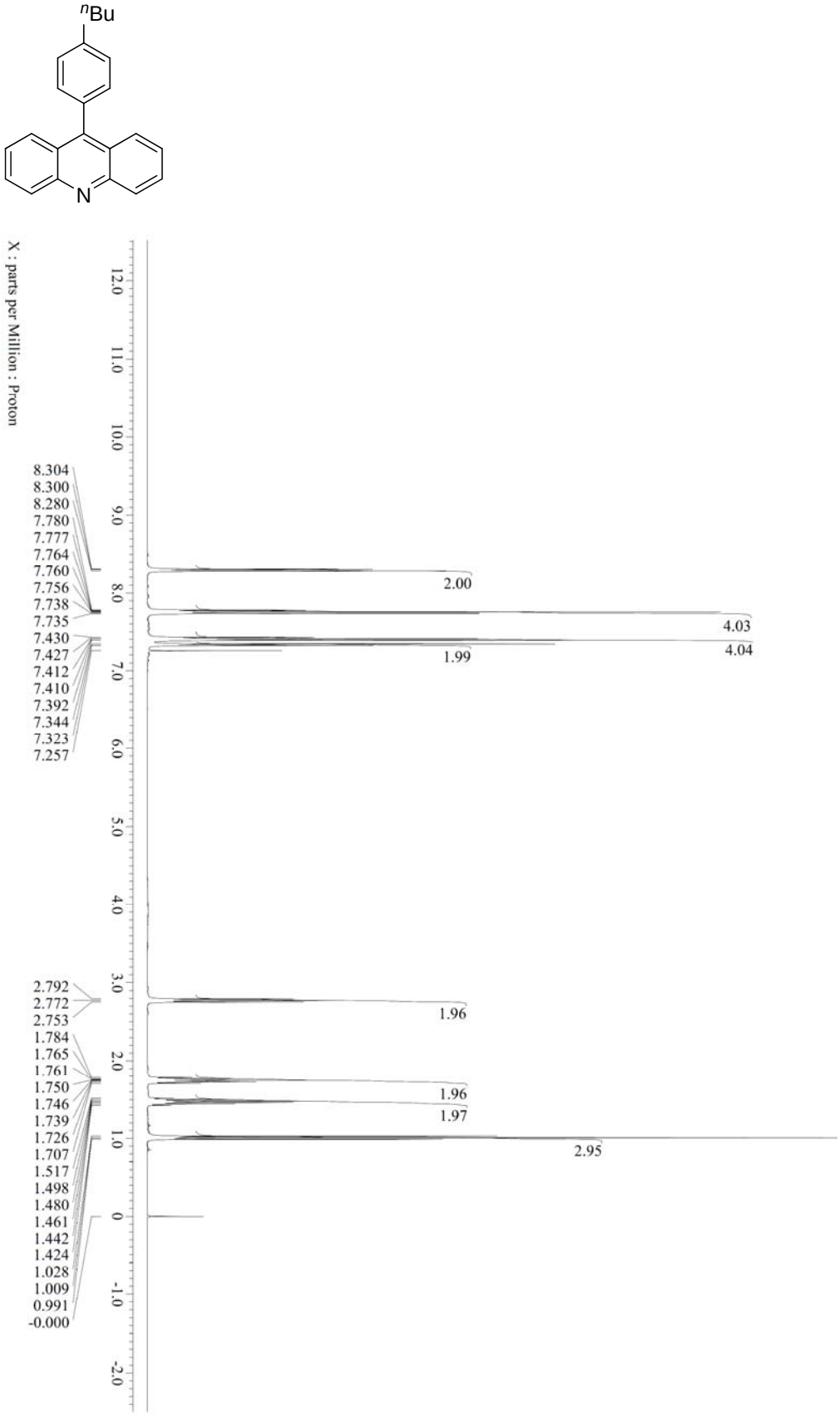
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3.0
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1.0
0
-1.0
-2.0
8.304
8.300
8.280
7.780
7.777
7.764
7.760
7.756
7.738
7.735
7.430
7.427
7.412
7.410
7.392
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7.323
7.257
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2.772
2.753
1.784
1.765
1.761
1.750
1.746
1.739
1.726
1.707
1.517
1.498
1.480
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1.424
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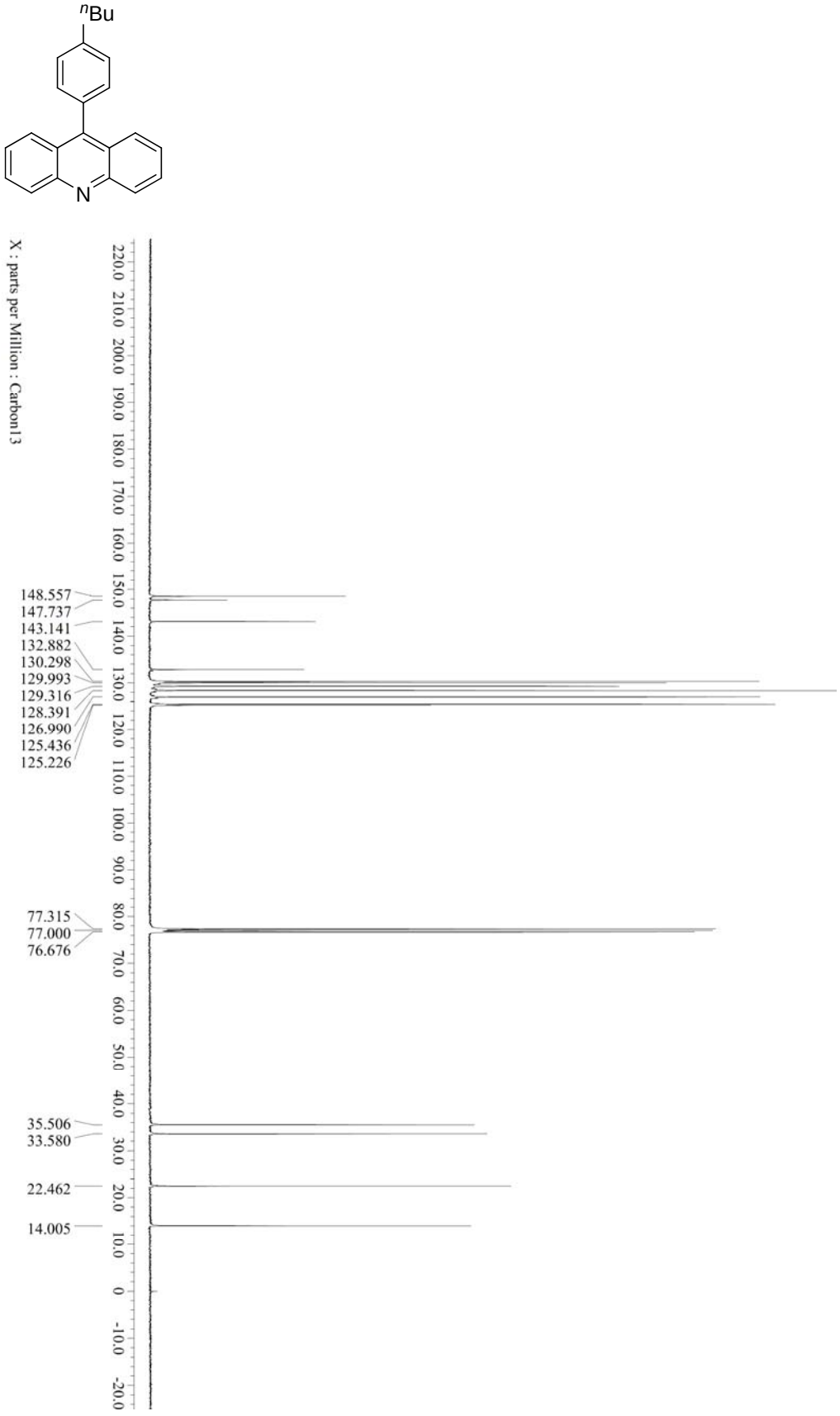

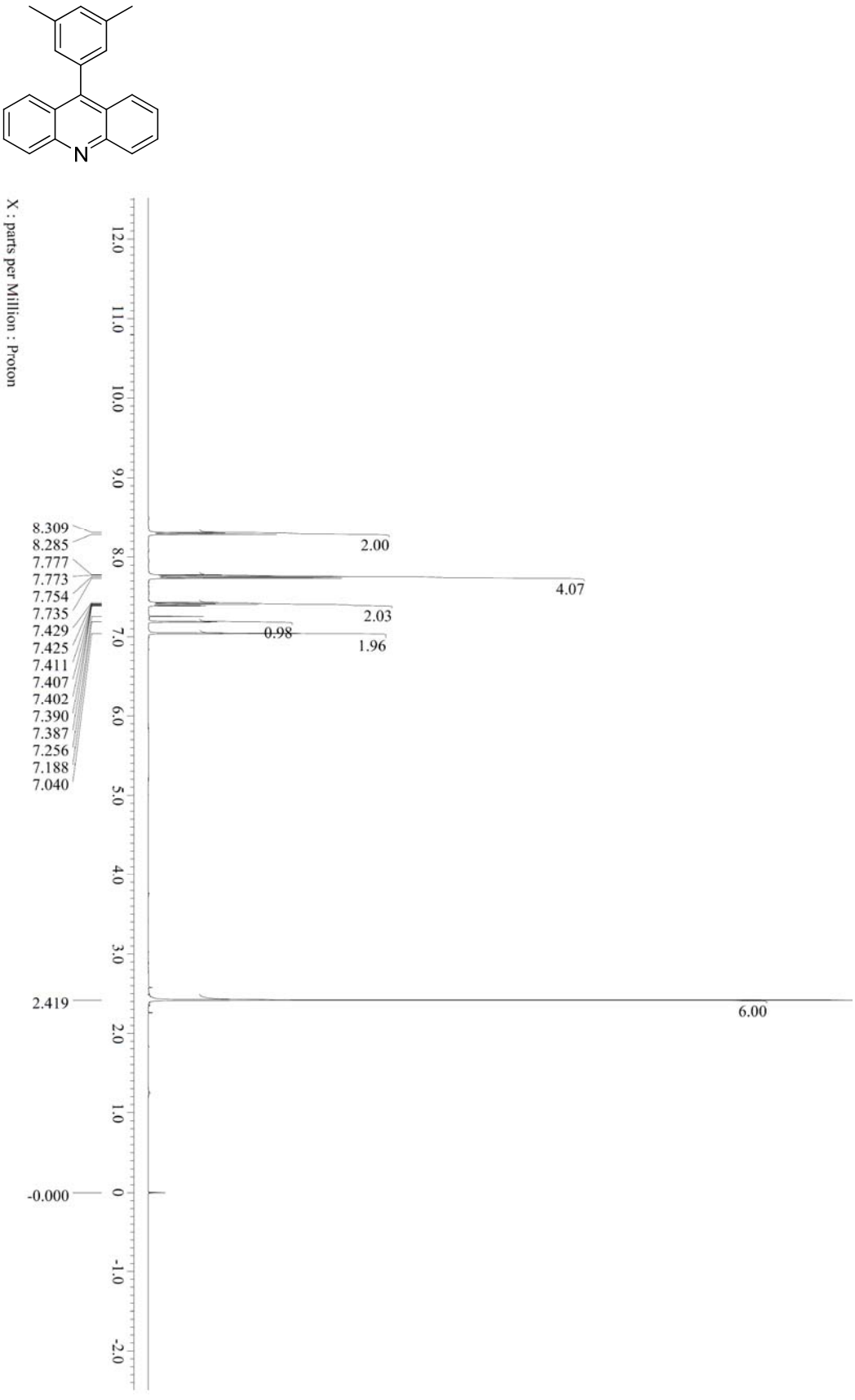
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-2.0
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7.754
7.735
7.429
7.425
7.411
7.407
7.402
7.390
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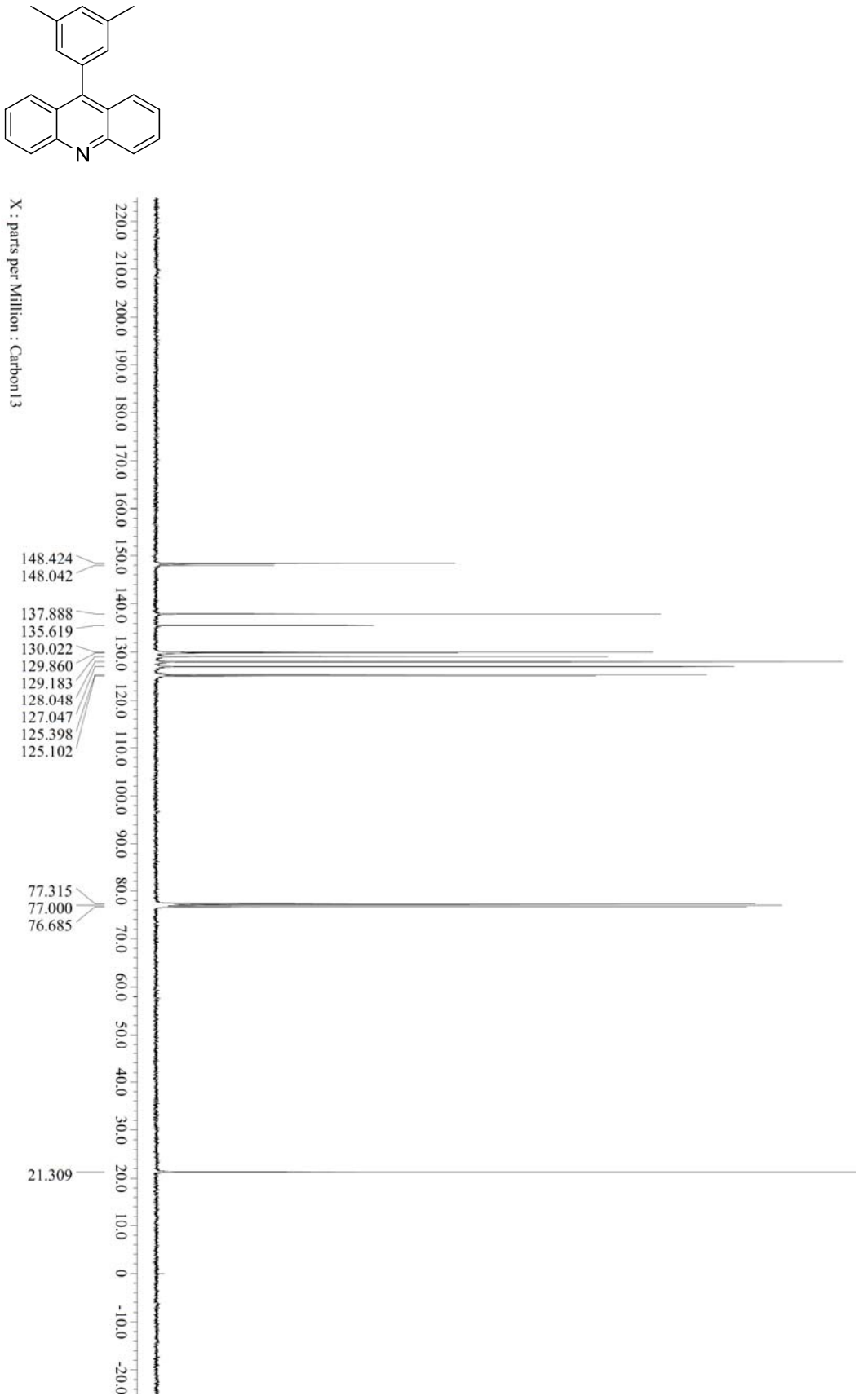
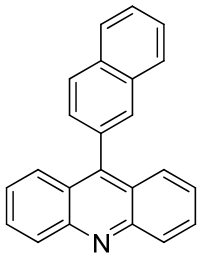
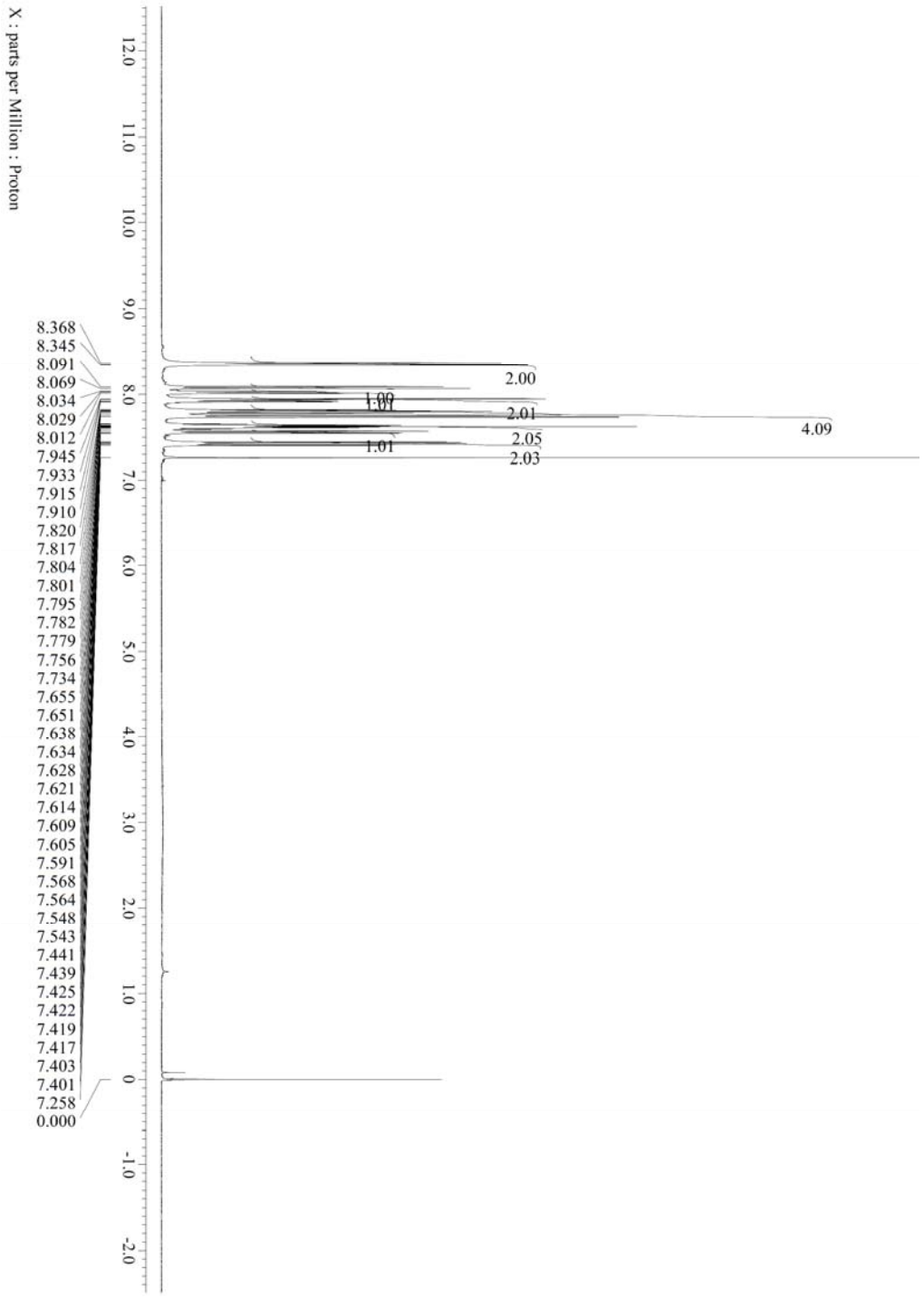
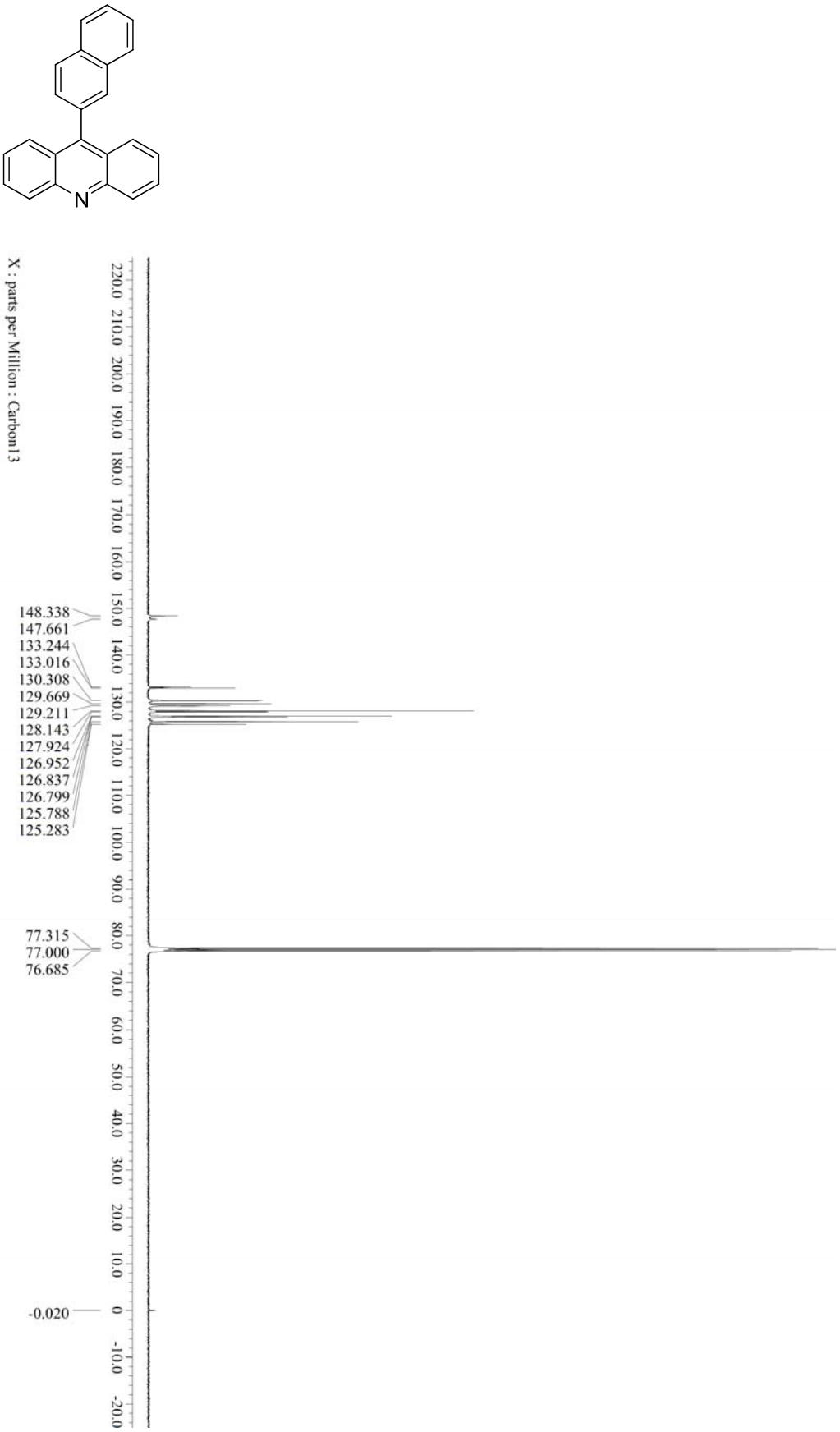
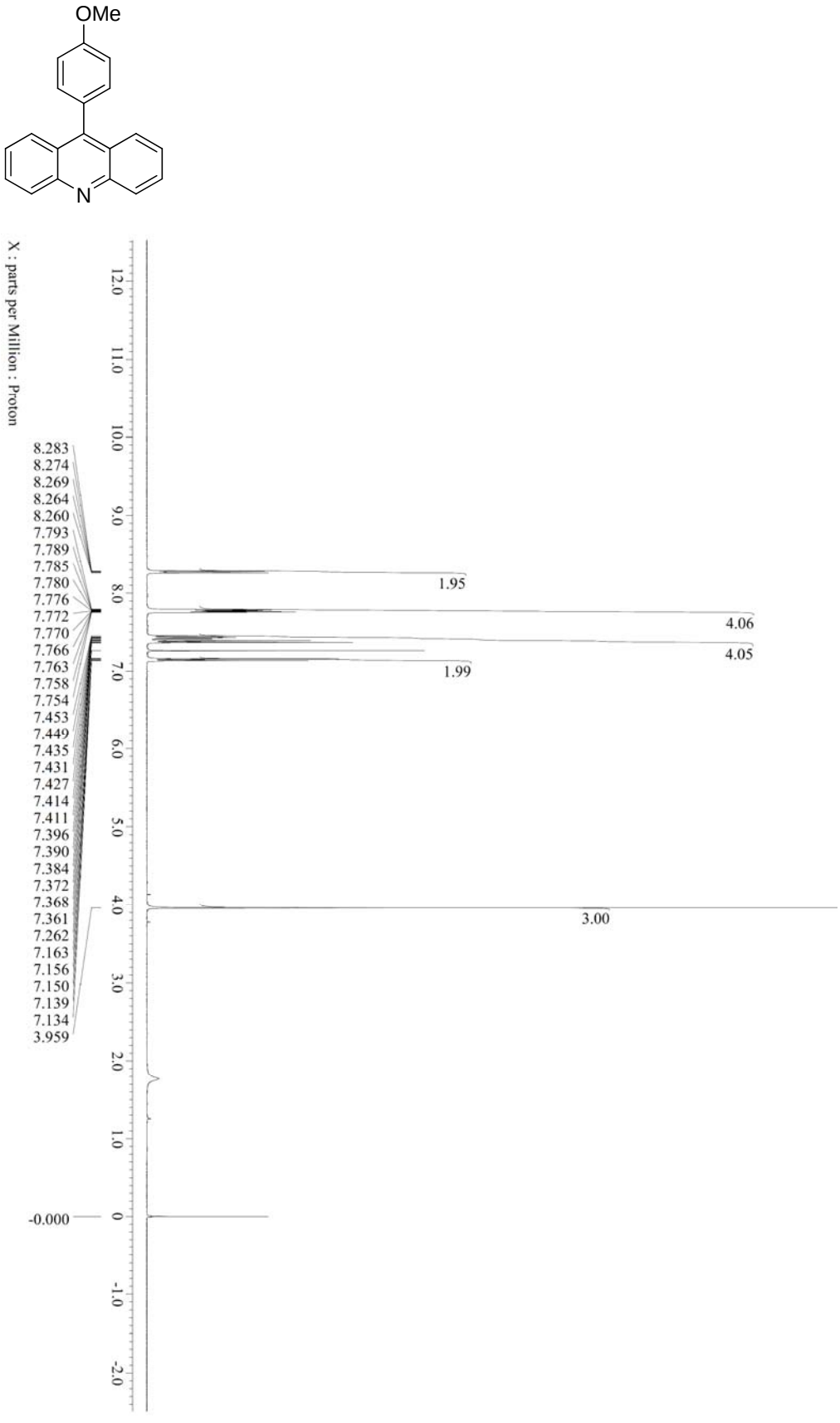
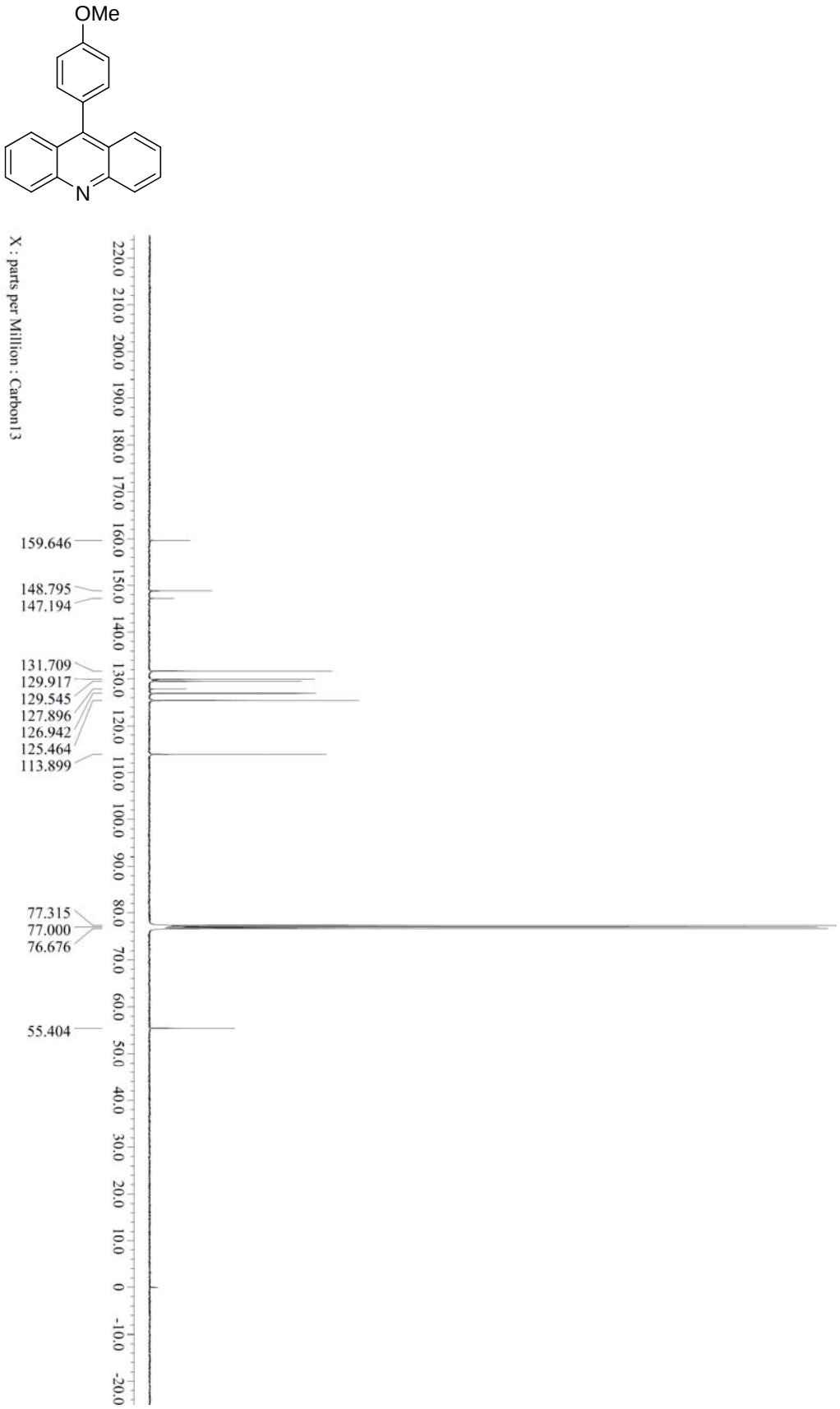


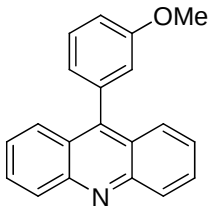


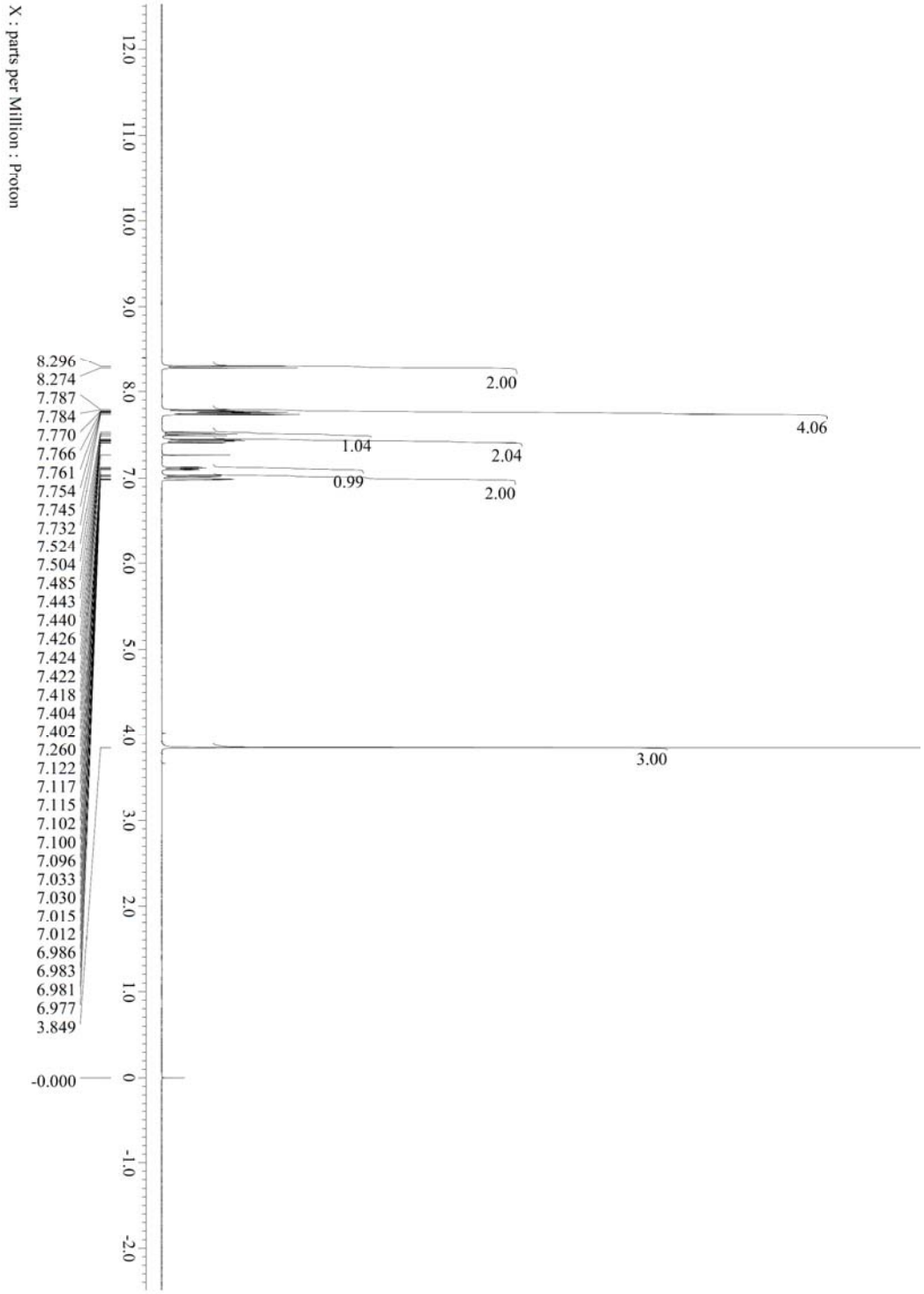









OMe
N


X : parts per Million : Proton
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4.0
3.0
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0
-1.0
-2.0
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8.274
7.787
7.784
7.770
7.766
7.761
7.754
7.745
7.732
7.524
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7.485
7.443
7.440
7.426
7.424
7.422
7.418
7.404
7.402
7.260
7.122
7.117
7.115
7.102
7.100
7.096
7.033
7.030
7.015
7.012
6.986
6.983
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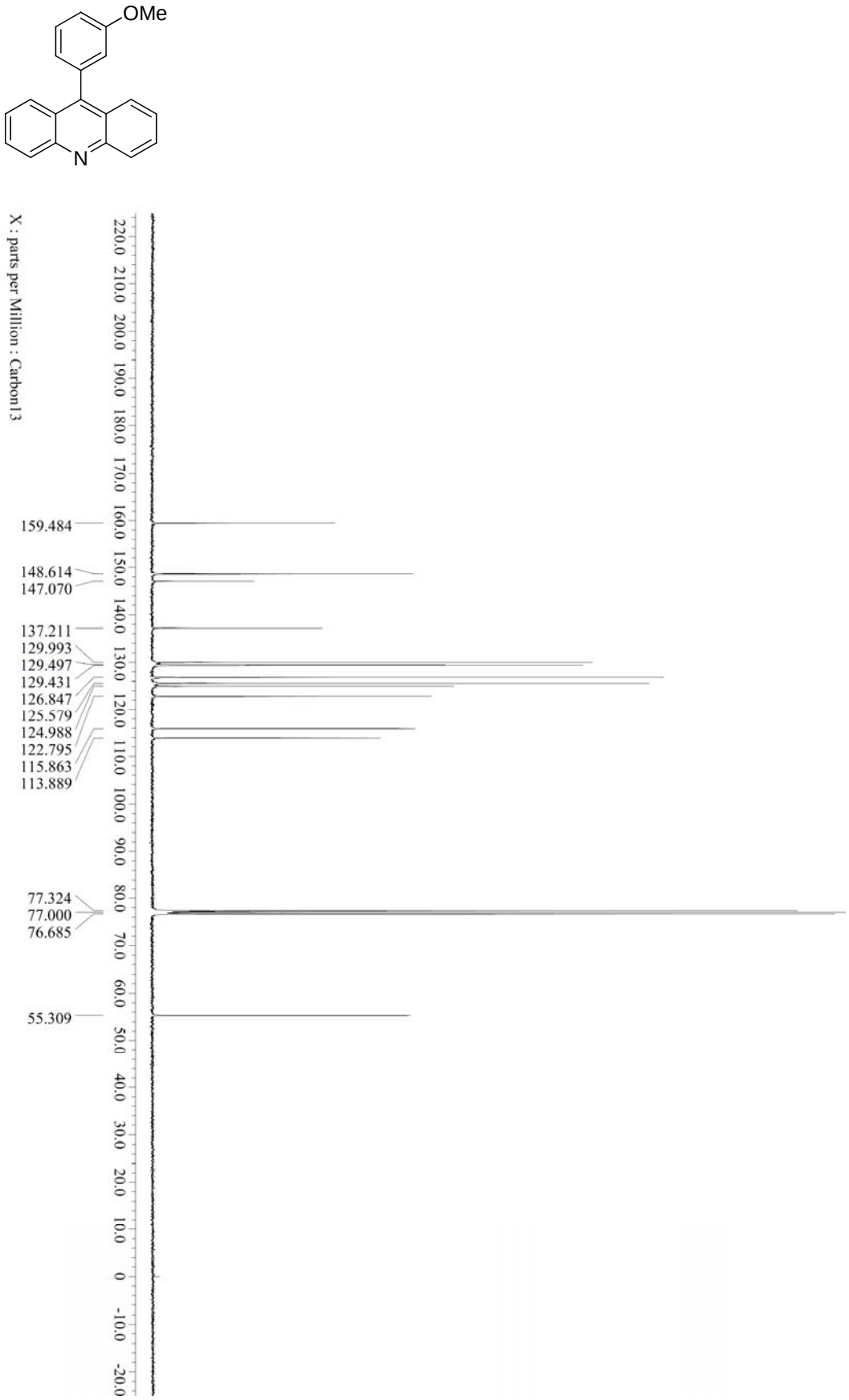
2.00
3.00


OMe
N
X : parts per Million : Carbon13
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
159.484
148.614
147.070
137.211
129.993
129.497
129.431
126.847
125.579
124.988
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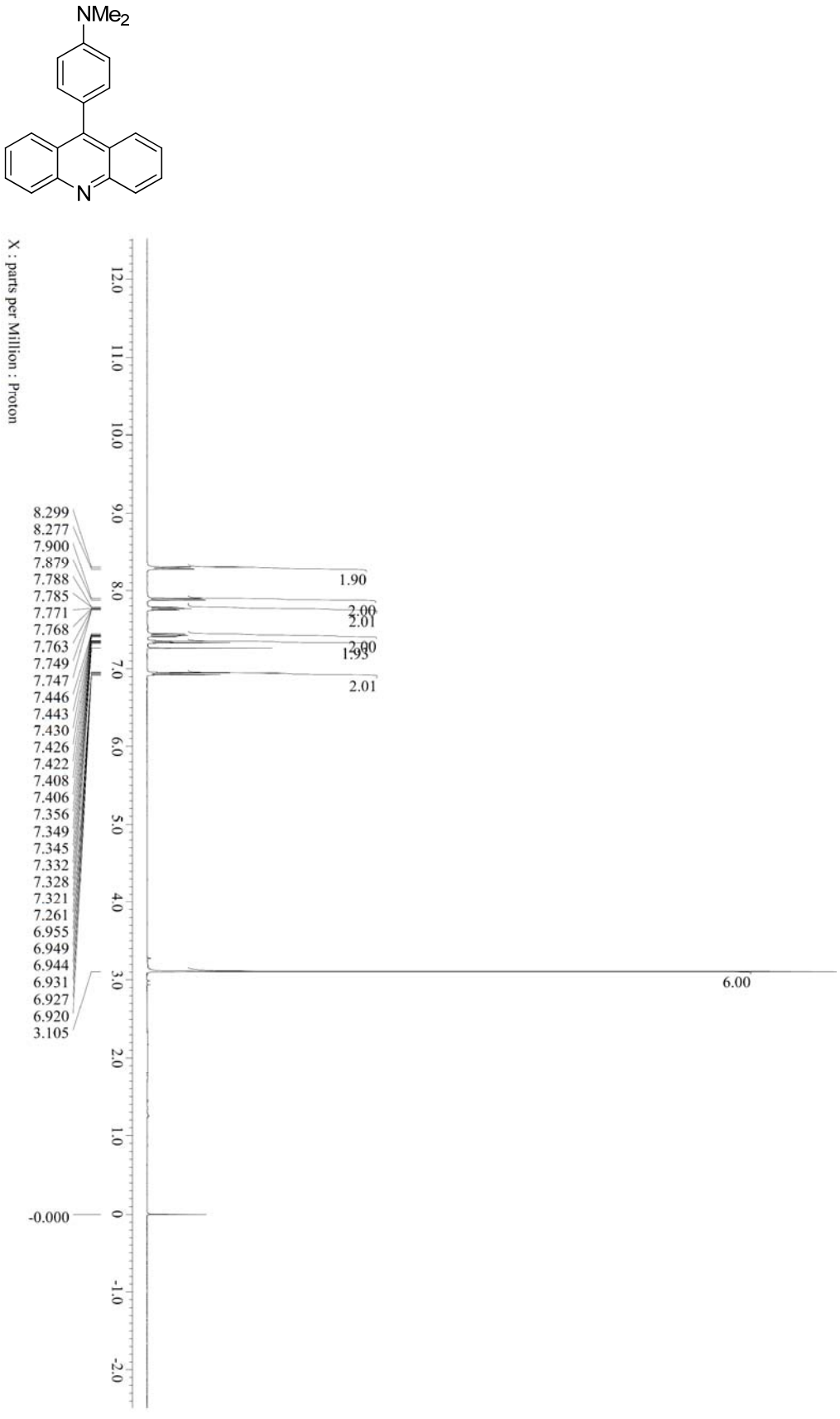
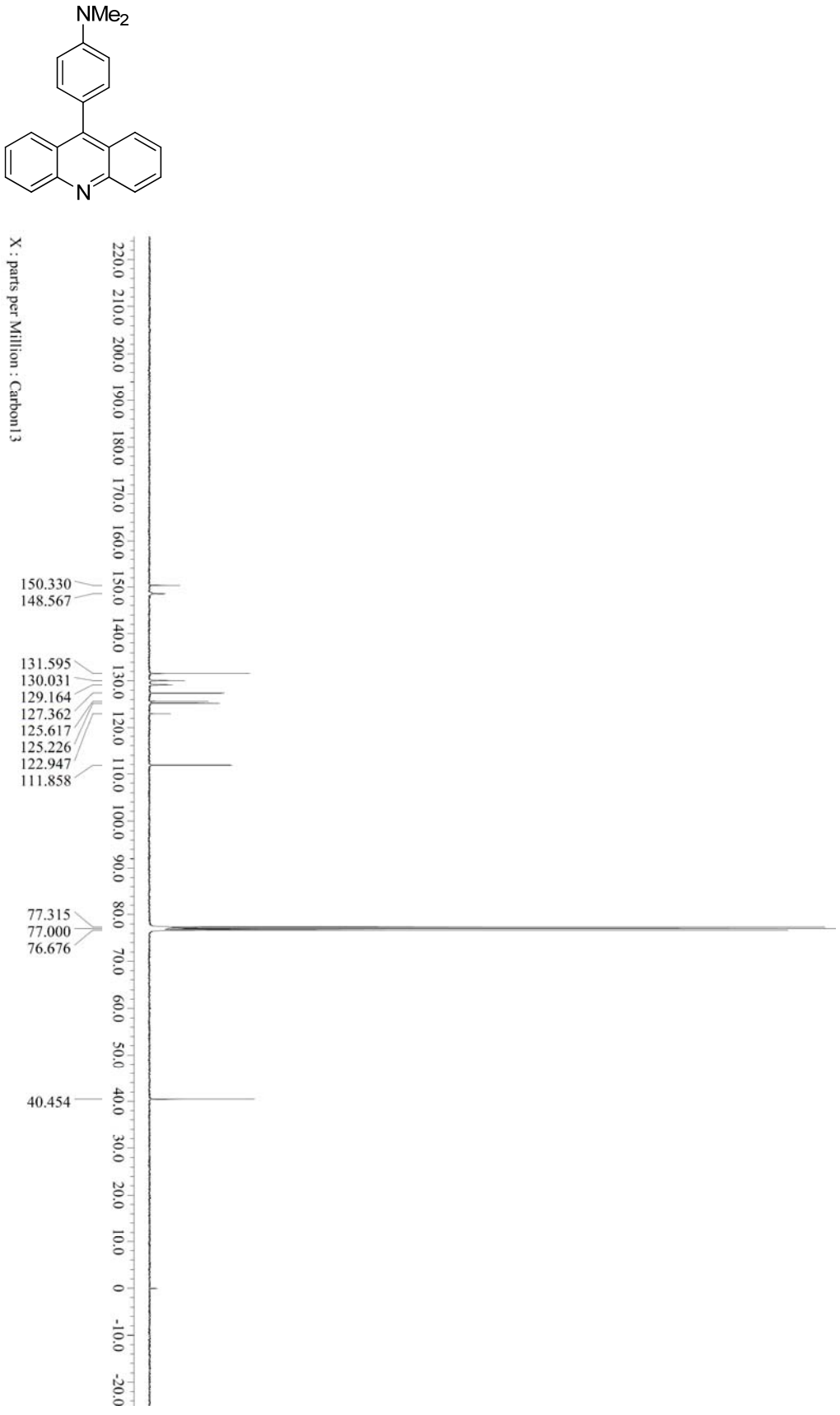
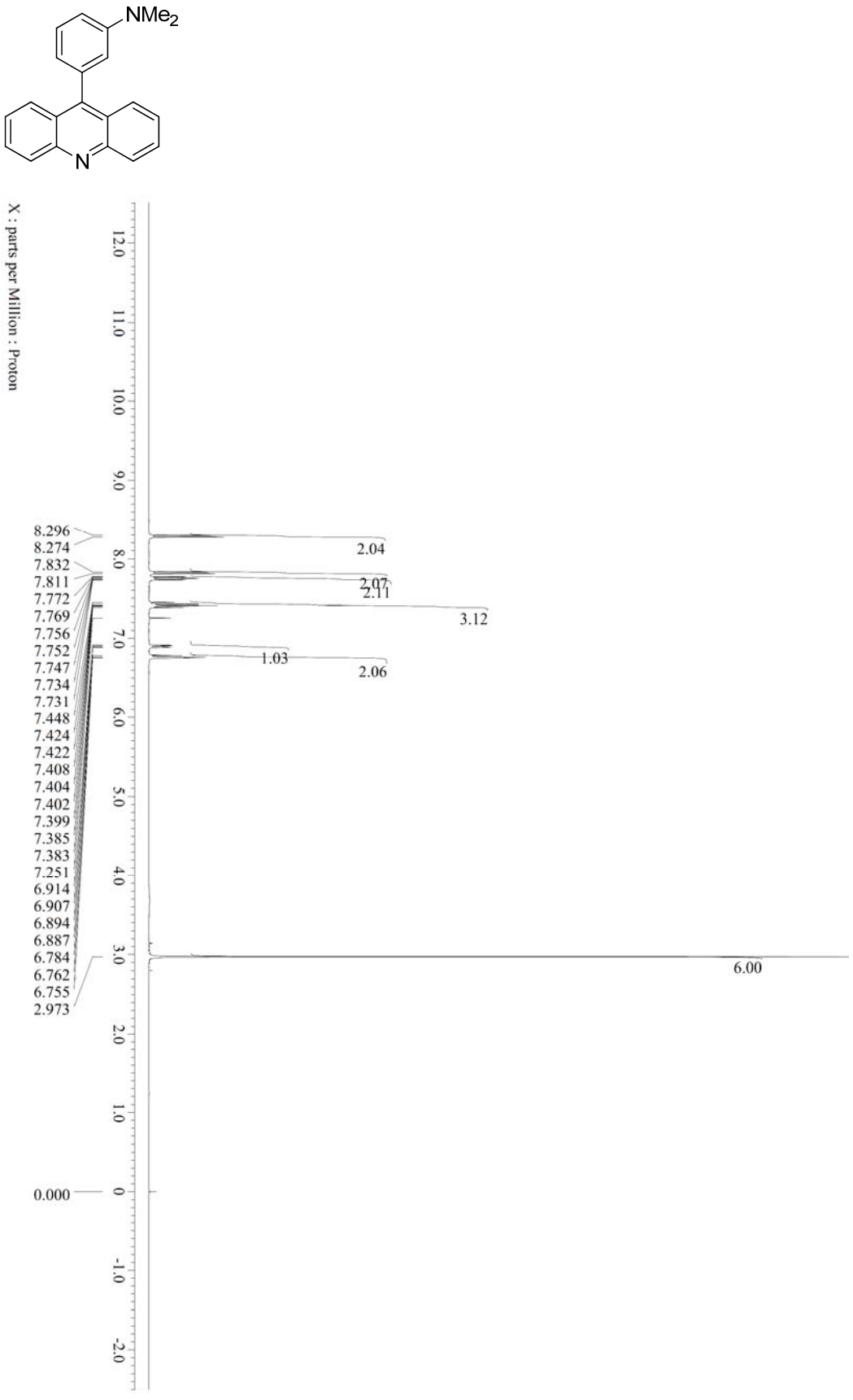
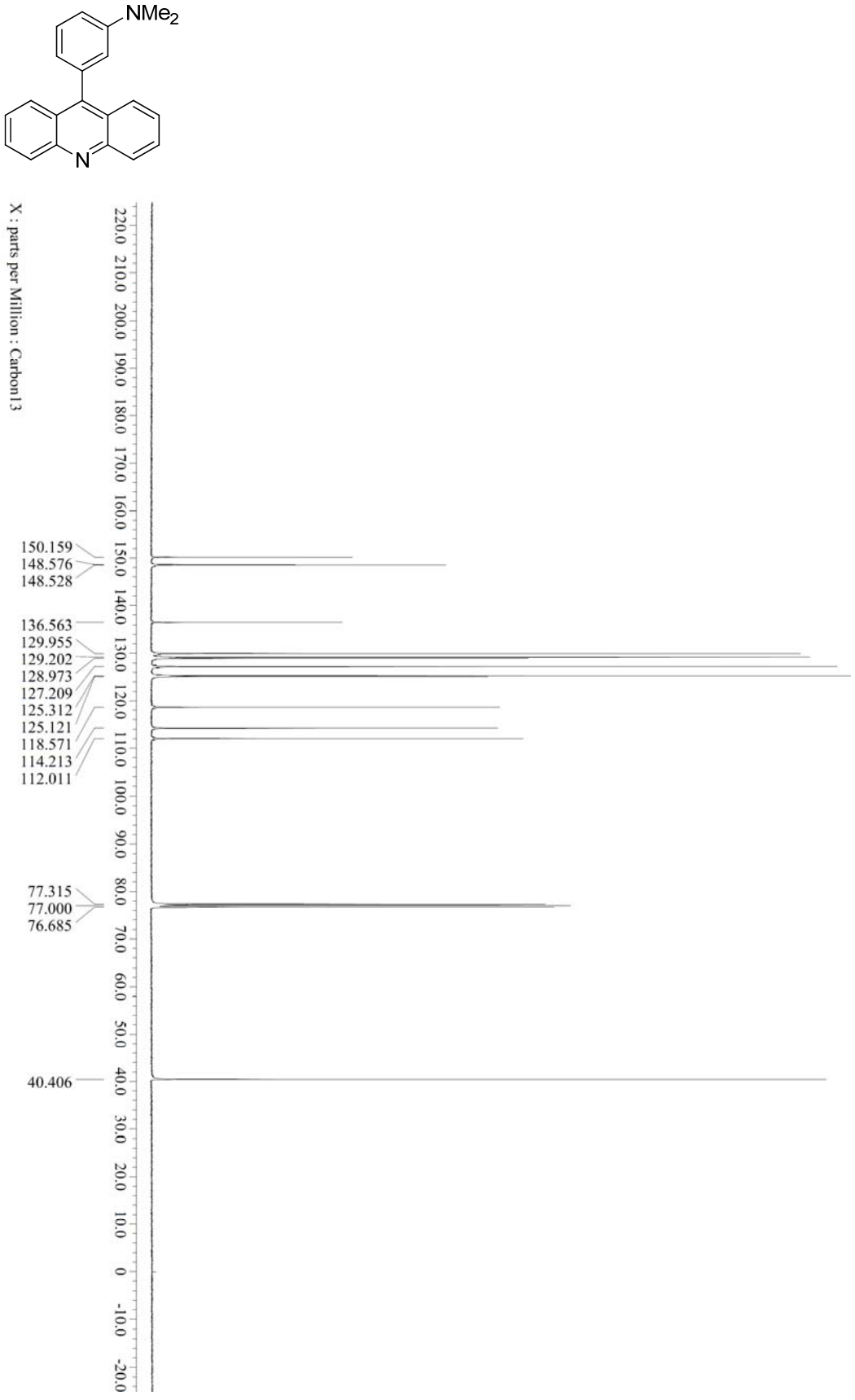
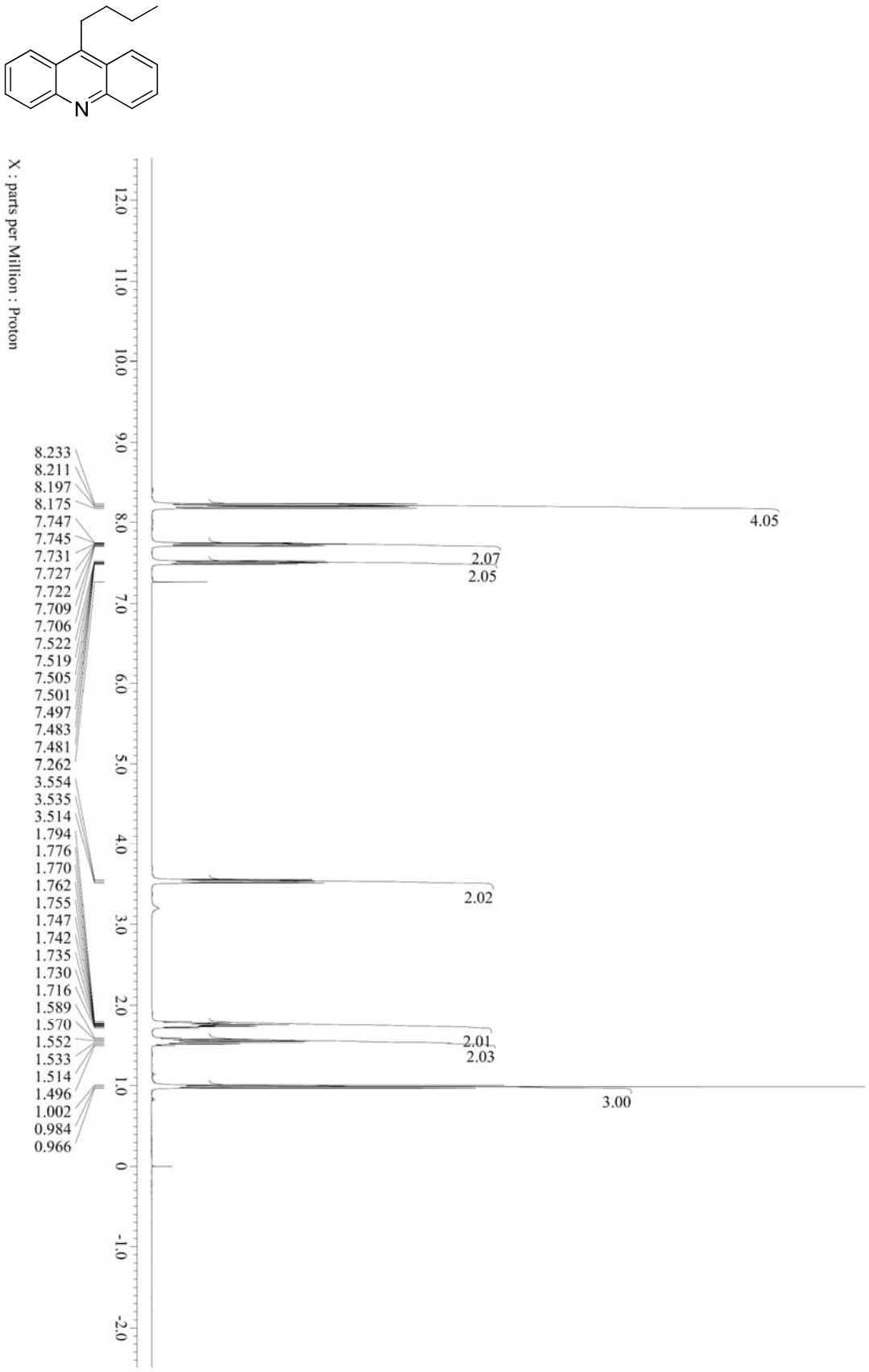
76.685
55.309

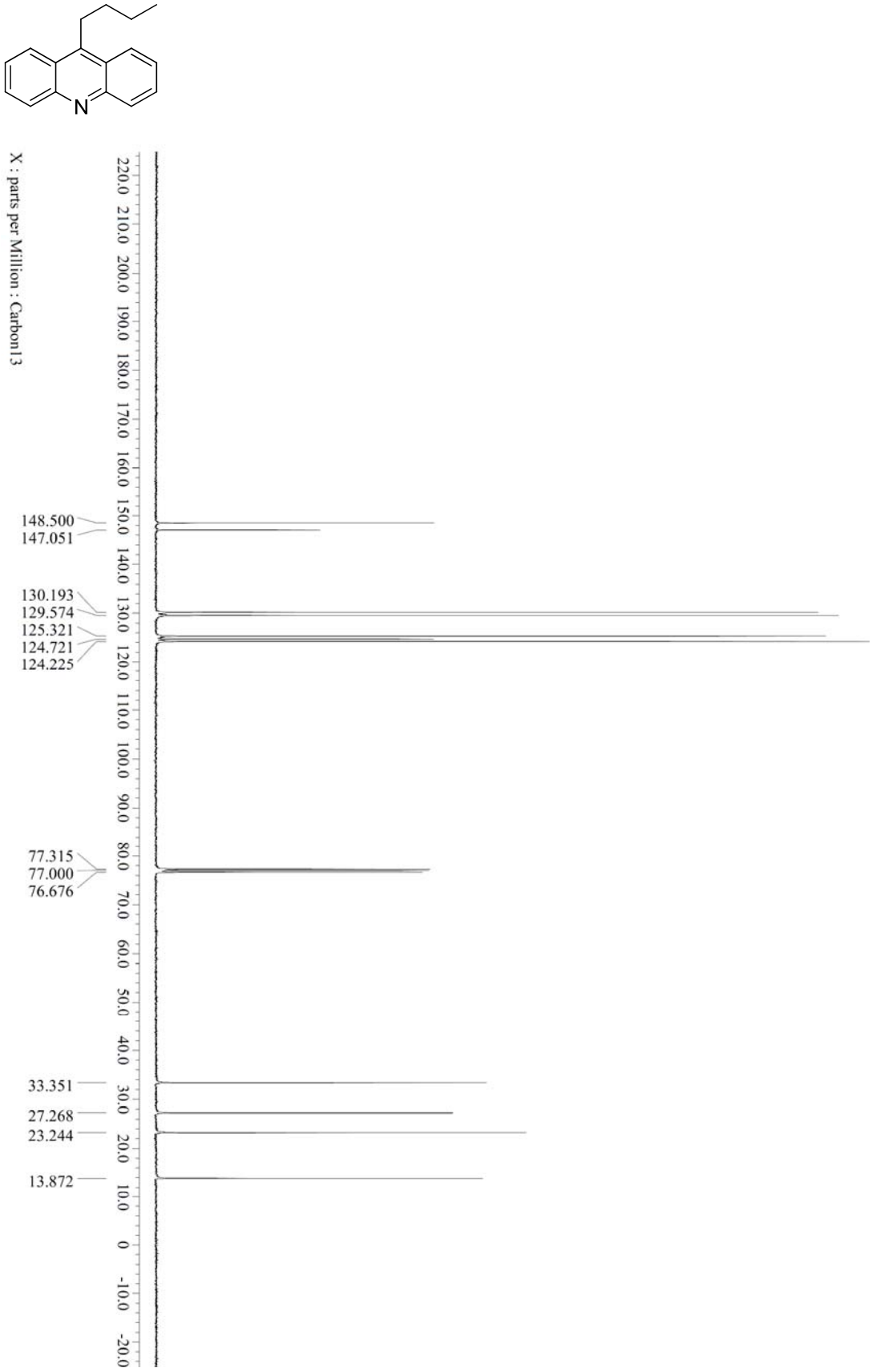











N
X : parts per Million : Carbon13
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
148.500
147.051
130.193
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124.721
124.225
77.315
77.000
76.676
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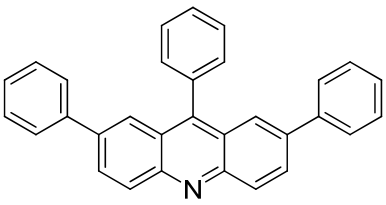
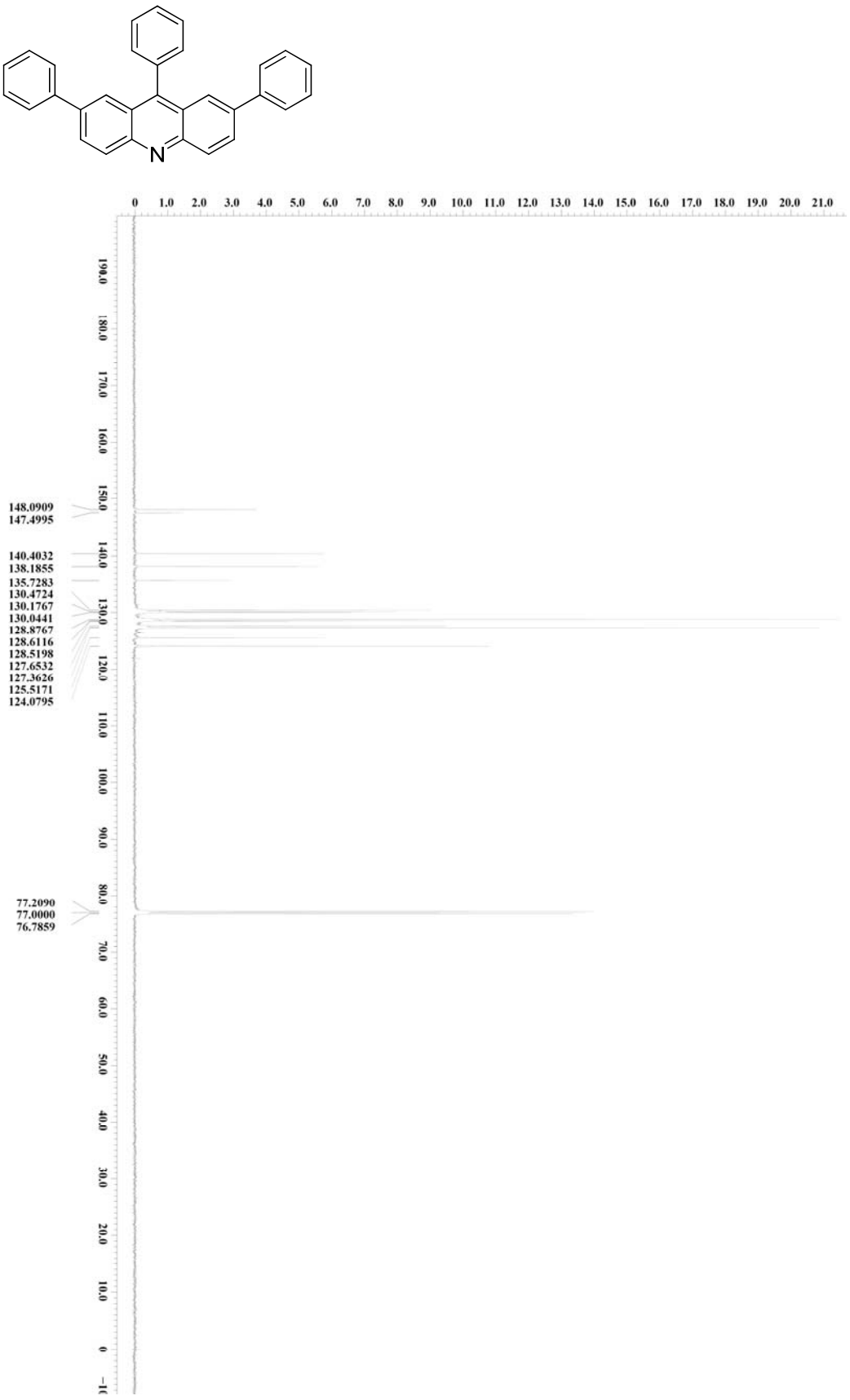
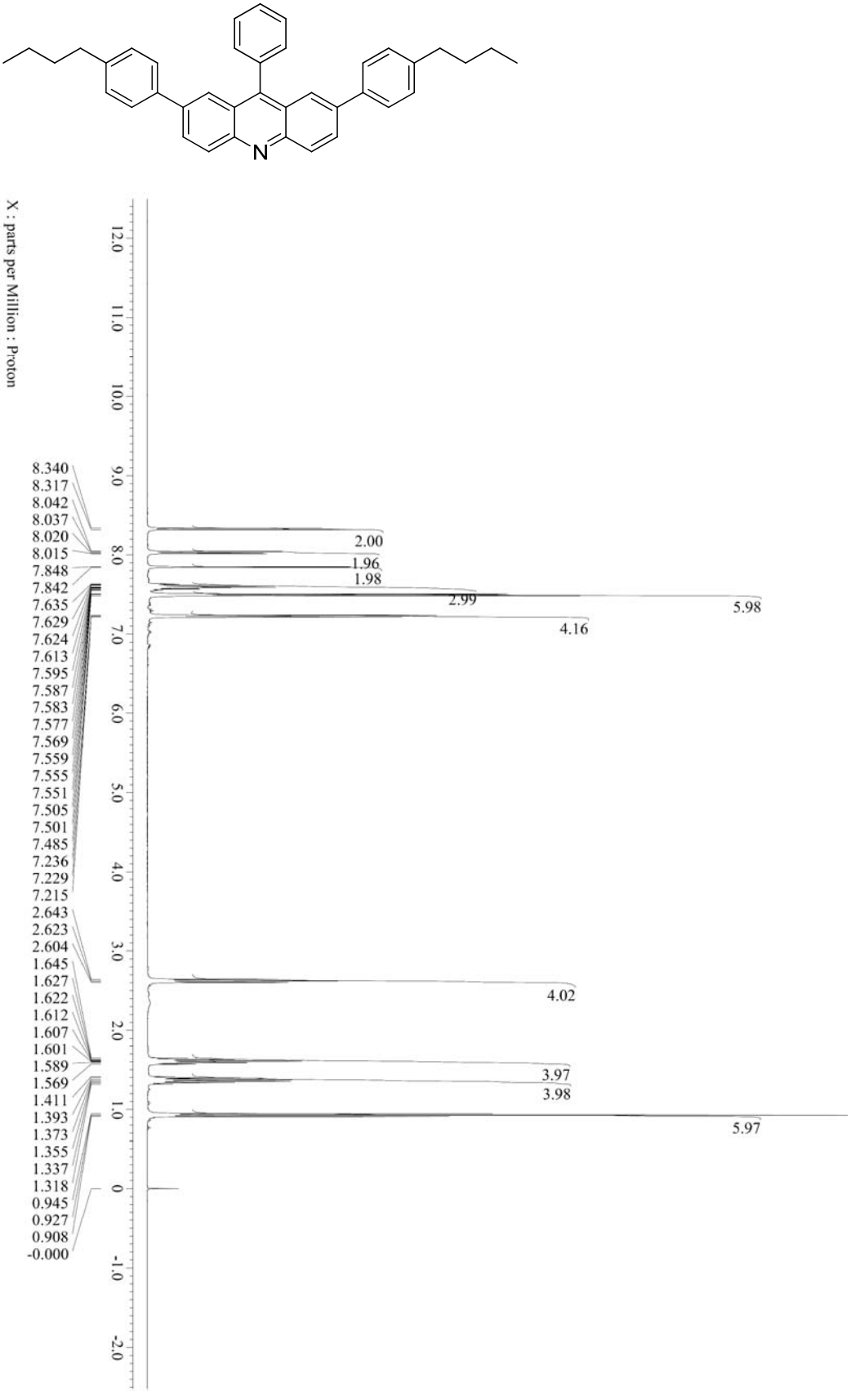
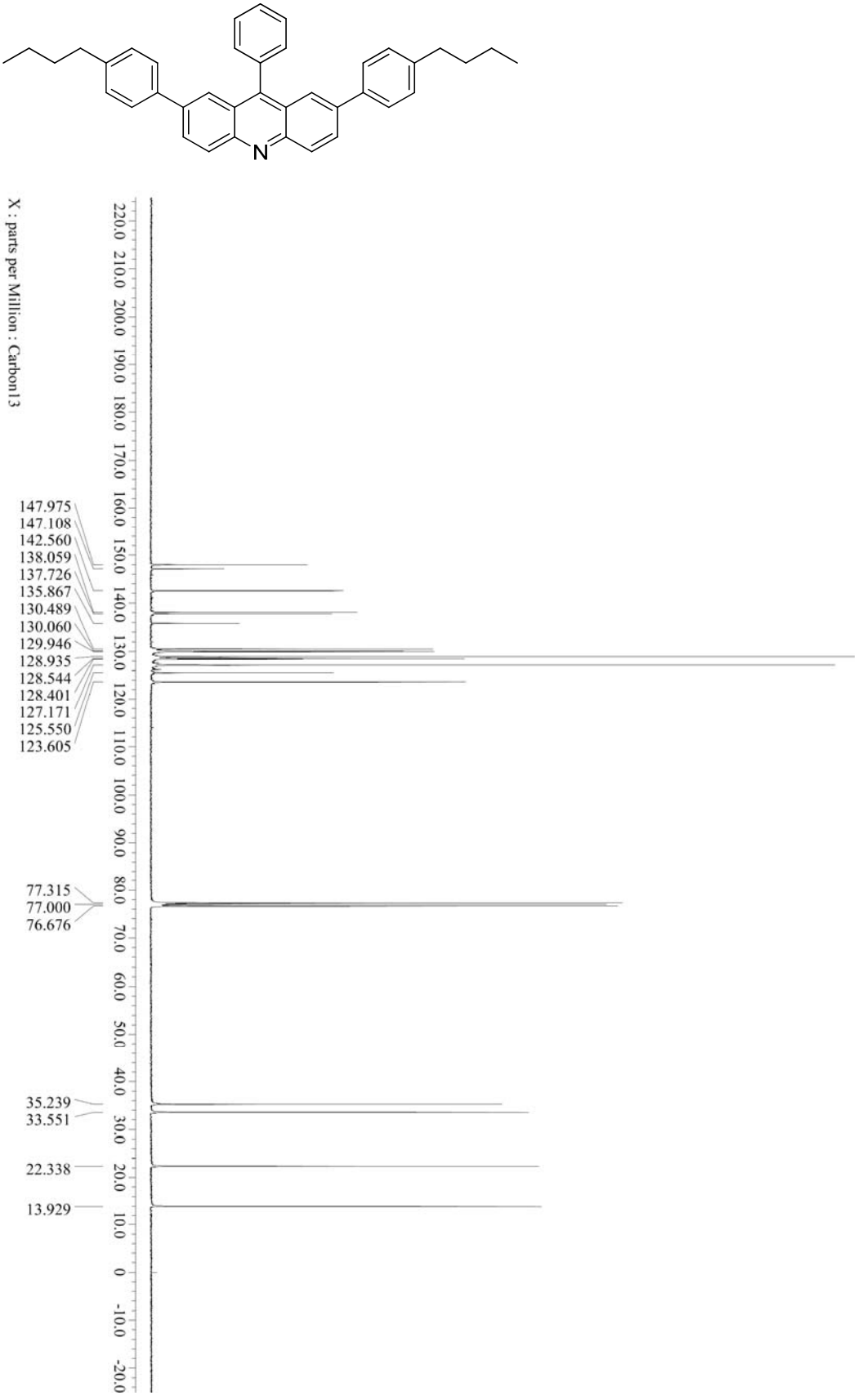
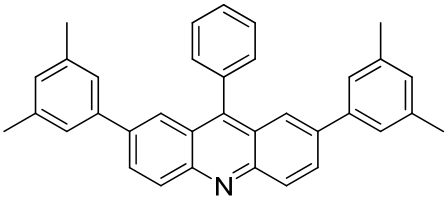
13.872

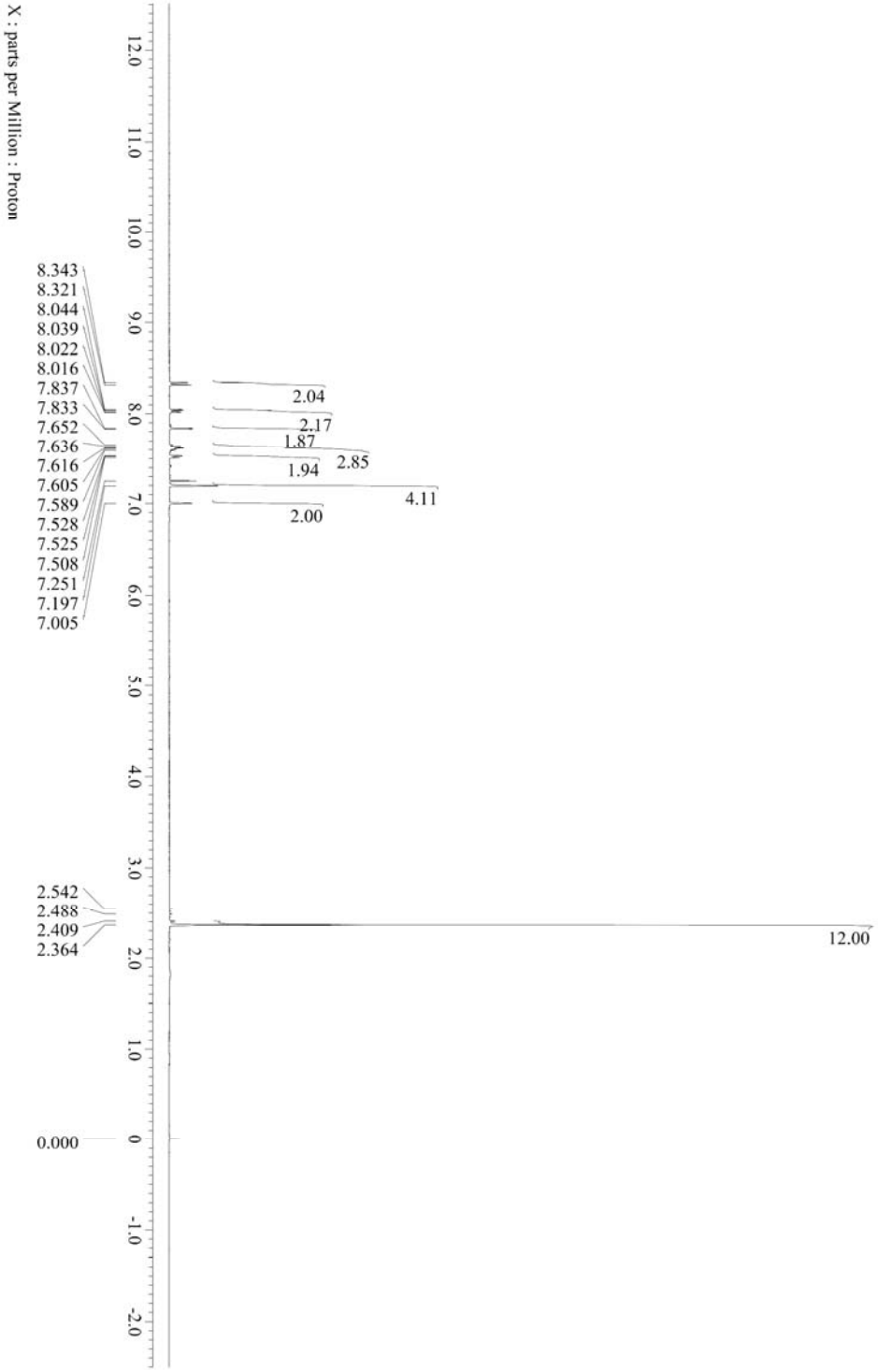


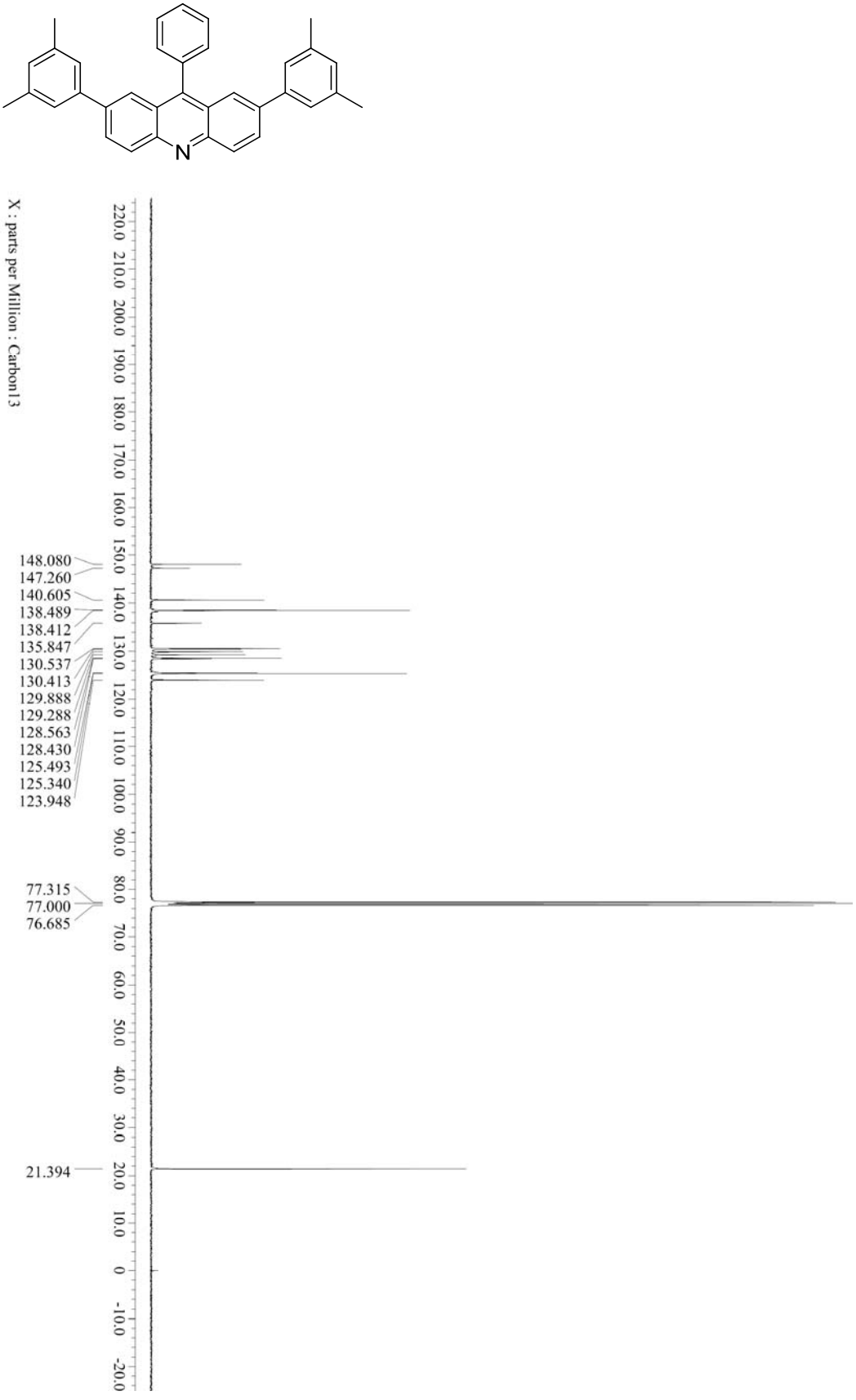


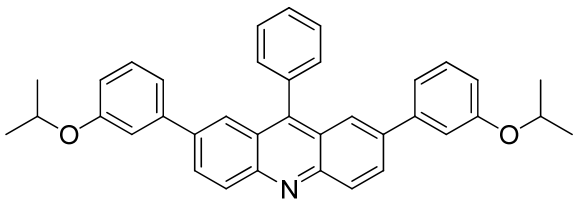


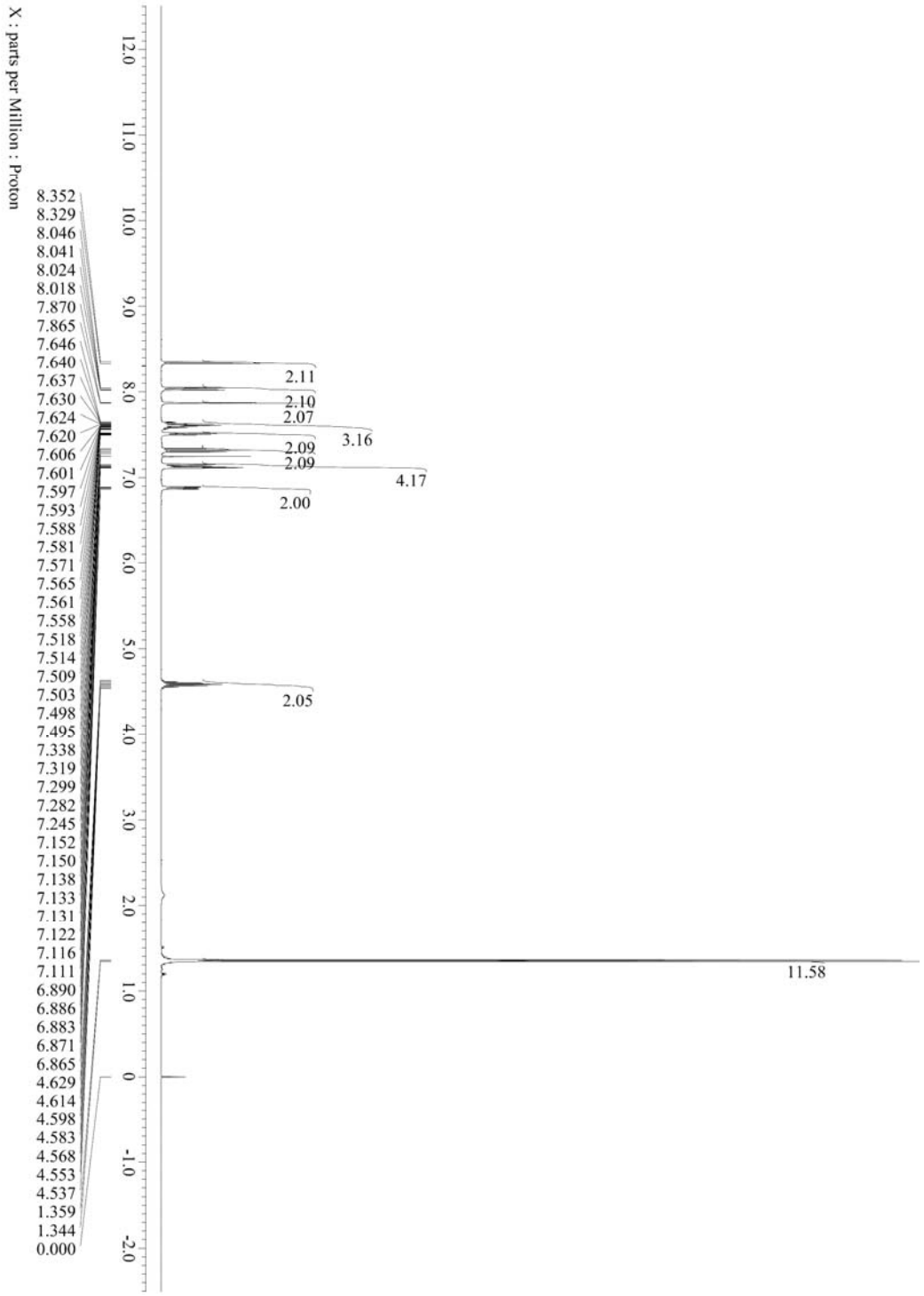


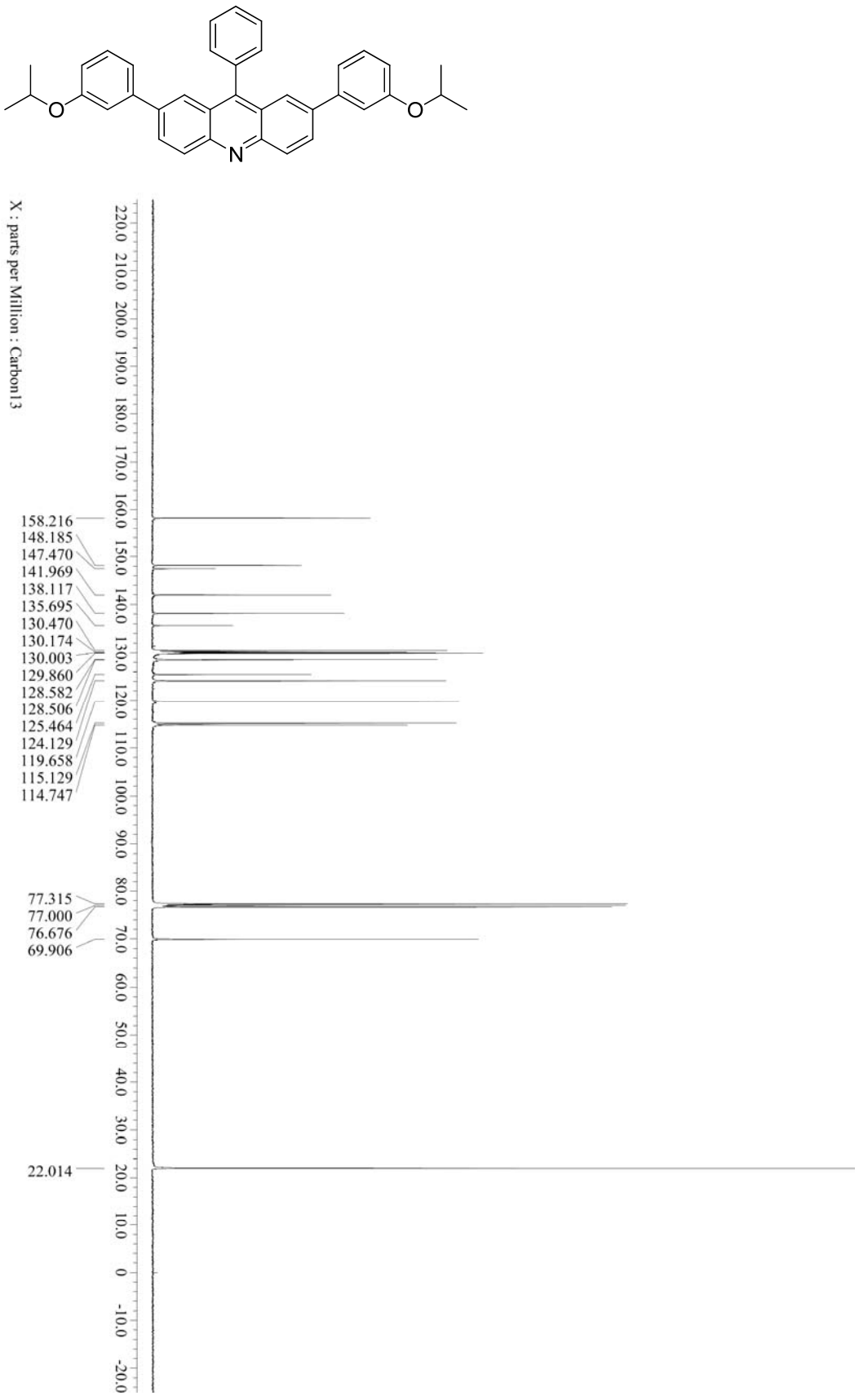


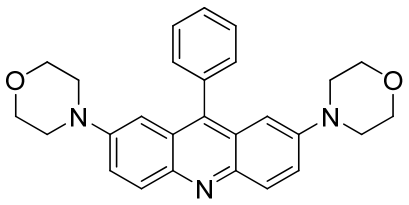


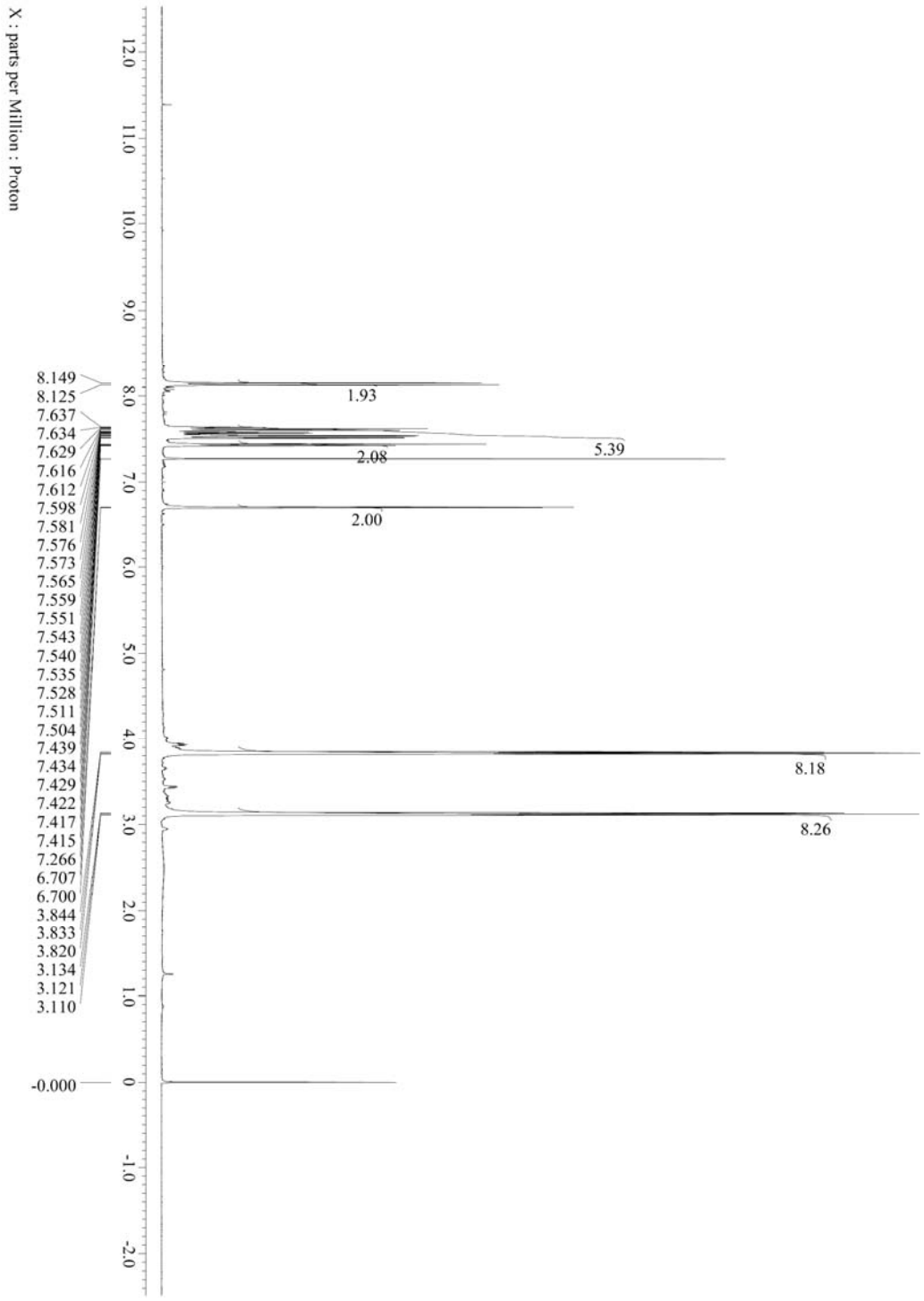


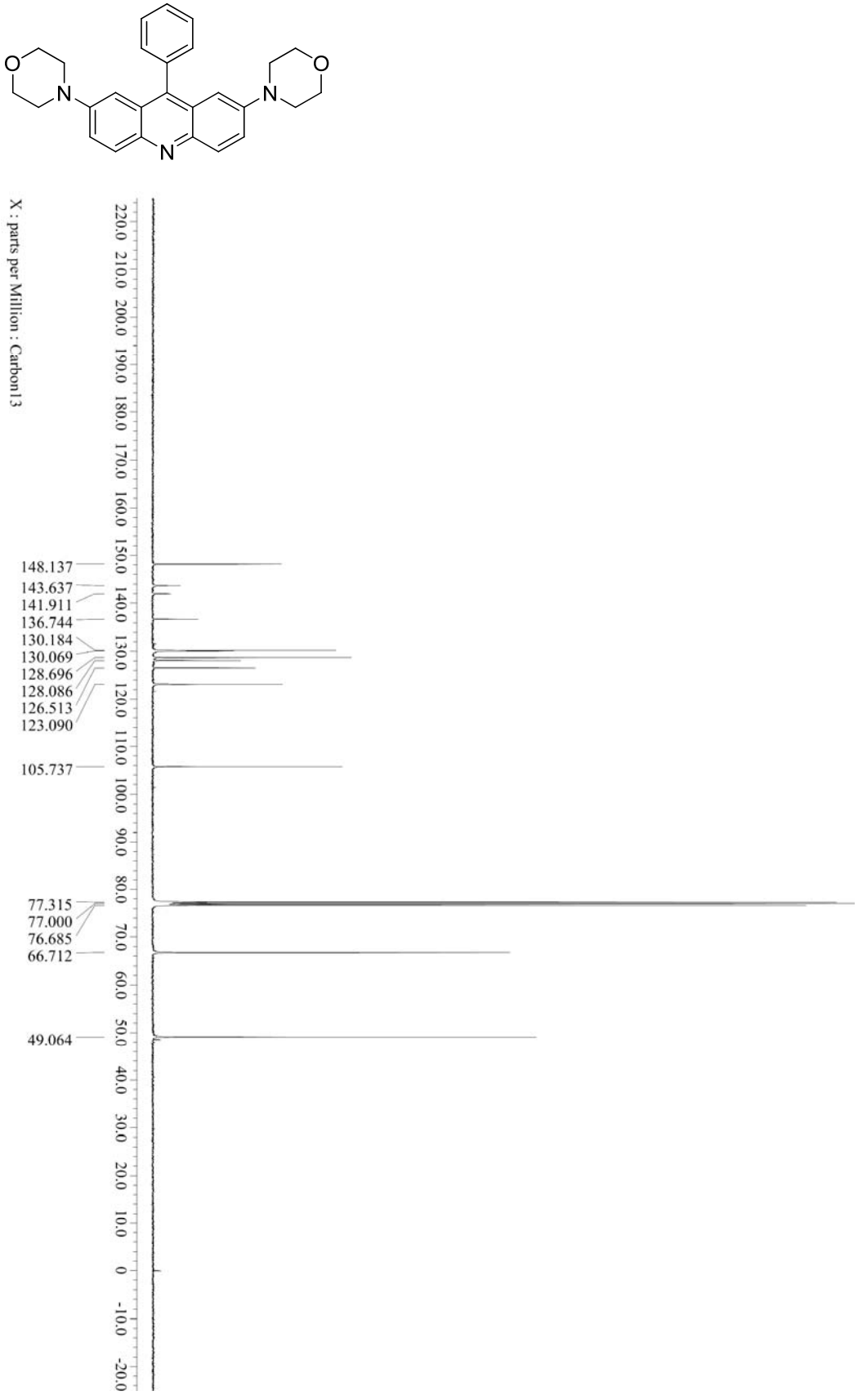


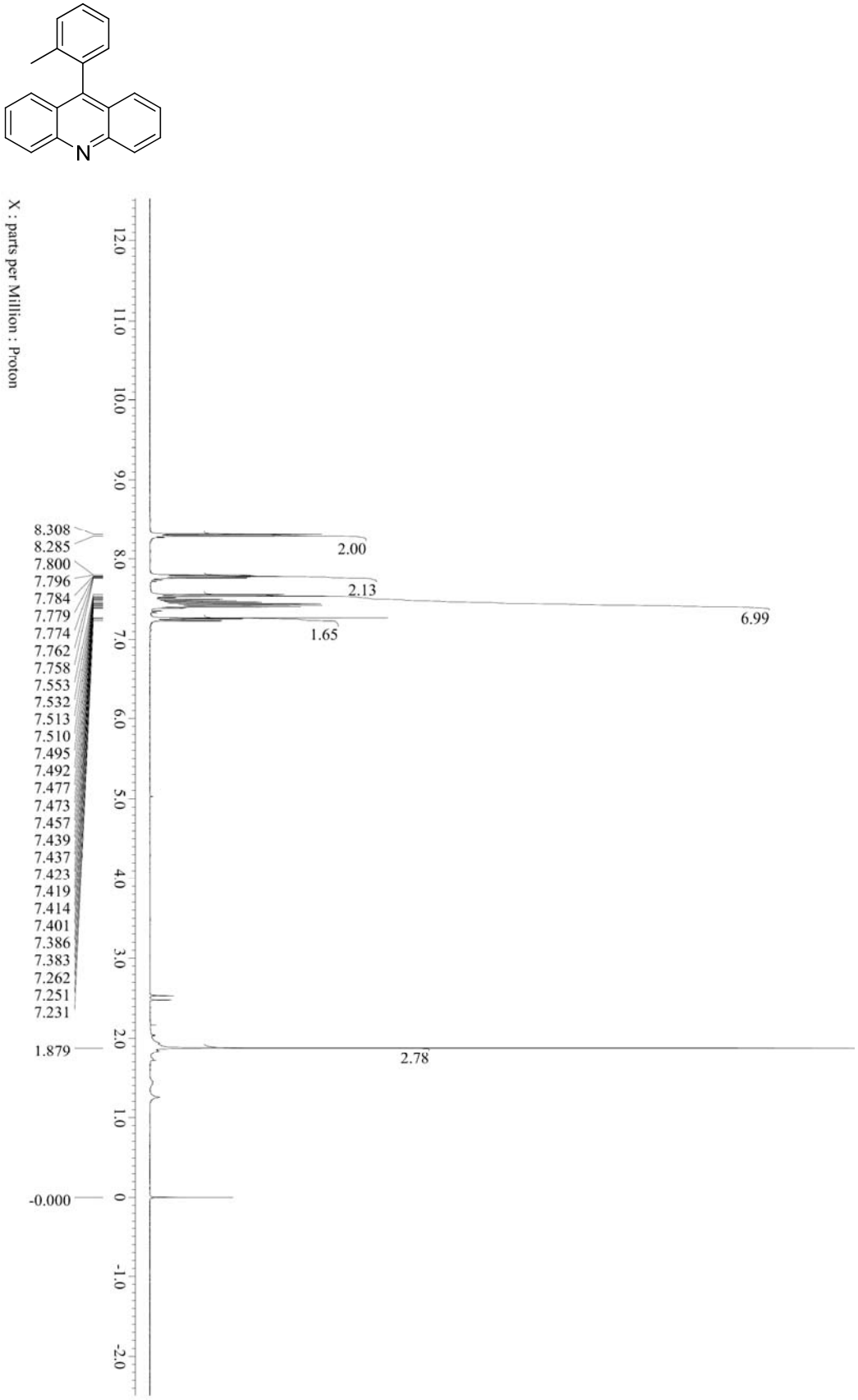


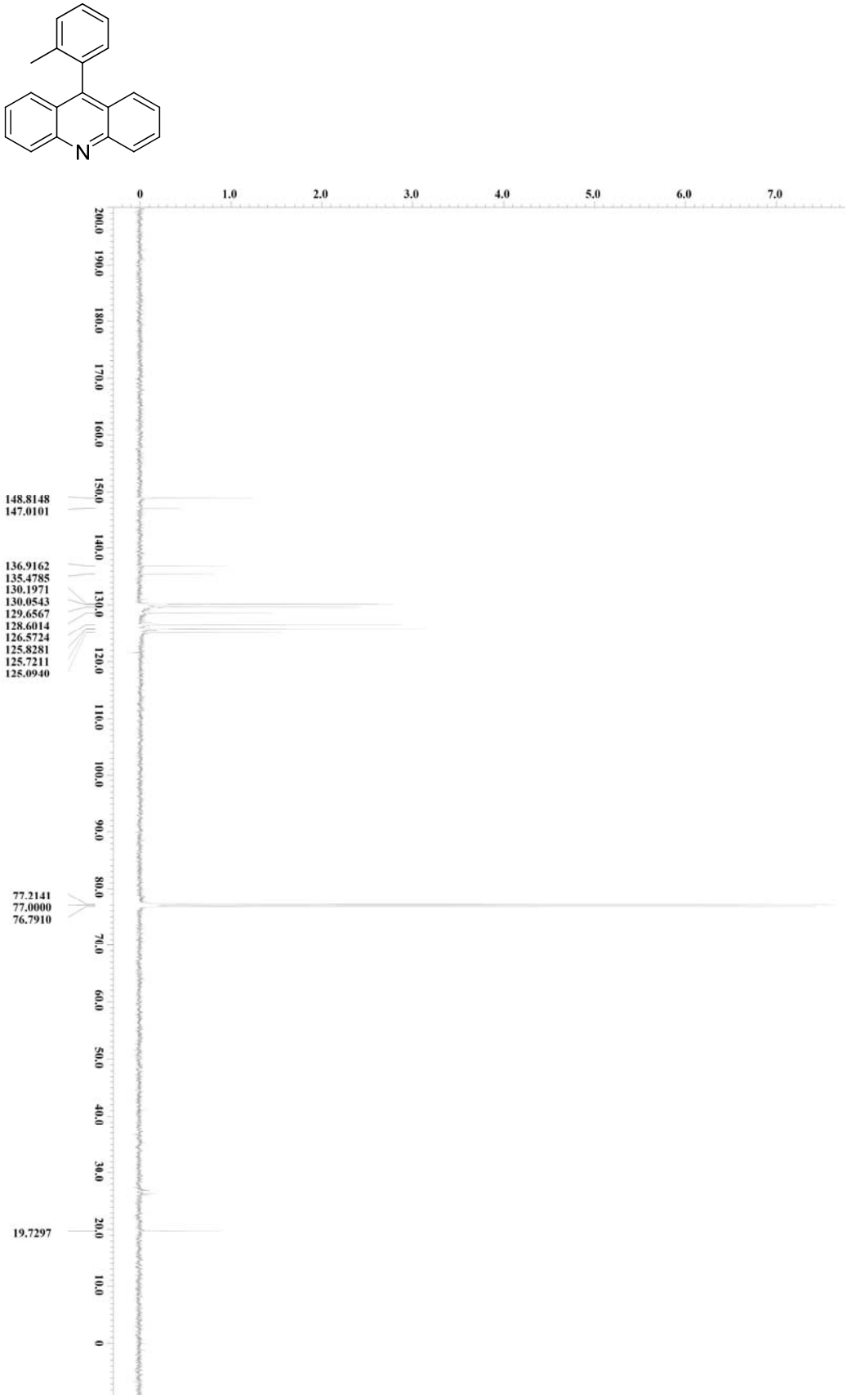


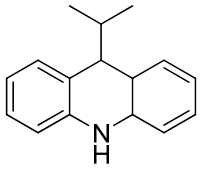












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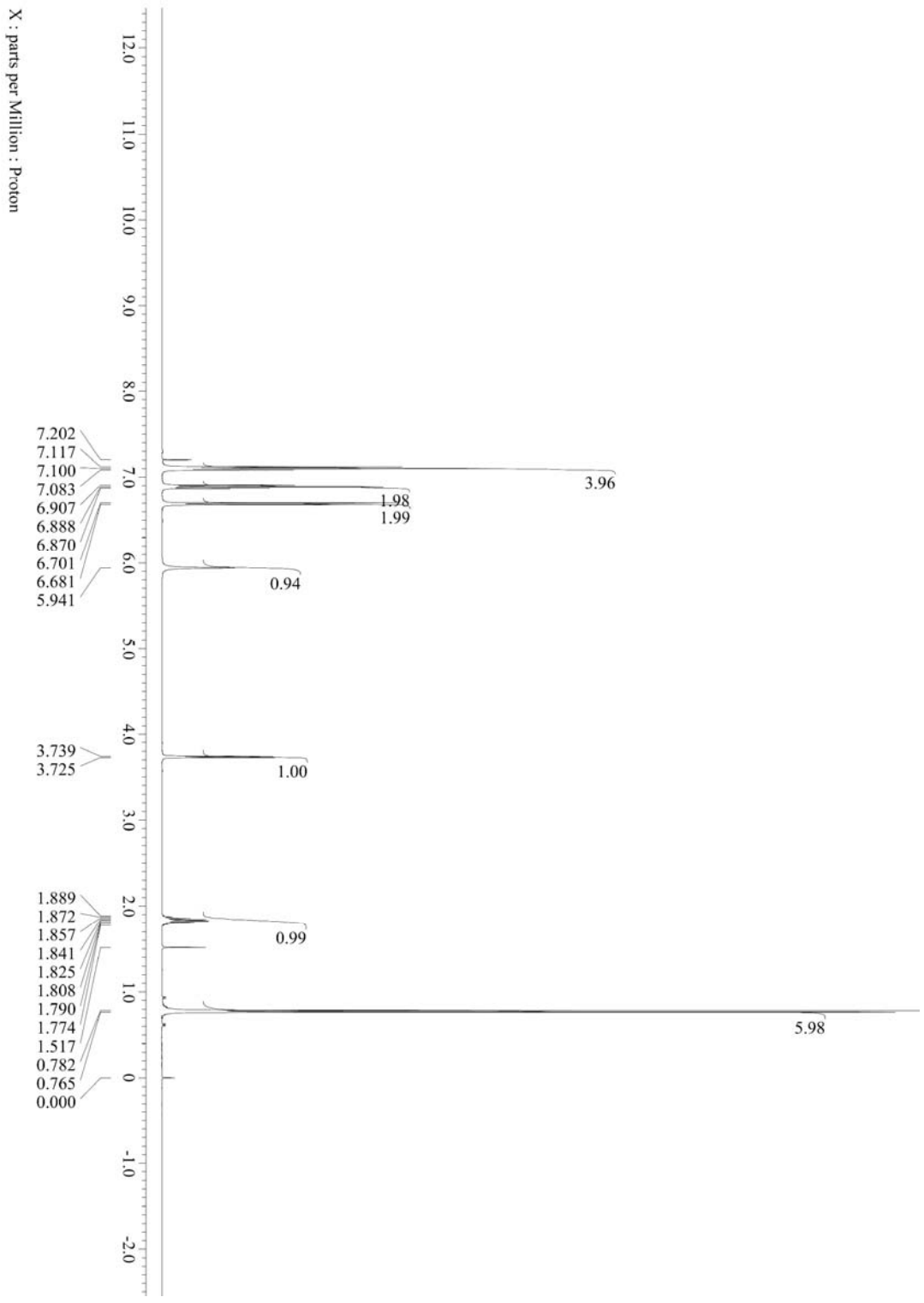
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4.0
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1.0
0
-1.0
-2.0
7.202
7.117
7.100
7.083
6.907
6.888
6.870
6.701
6.681
5.941
3.96
1.98
1.99
0.94
3.739
3.725
1.00
1.889
1.872
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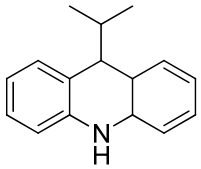
5.98



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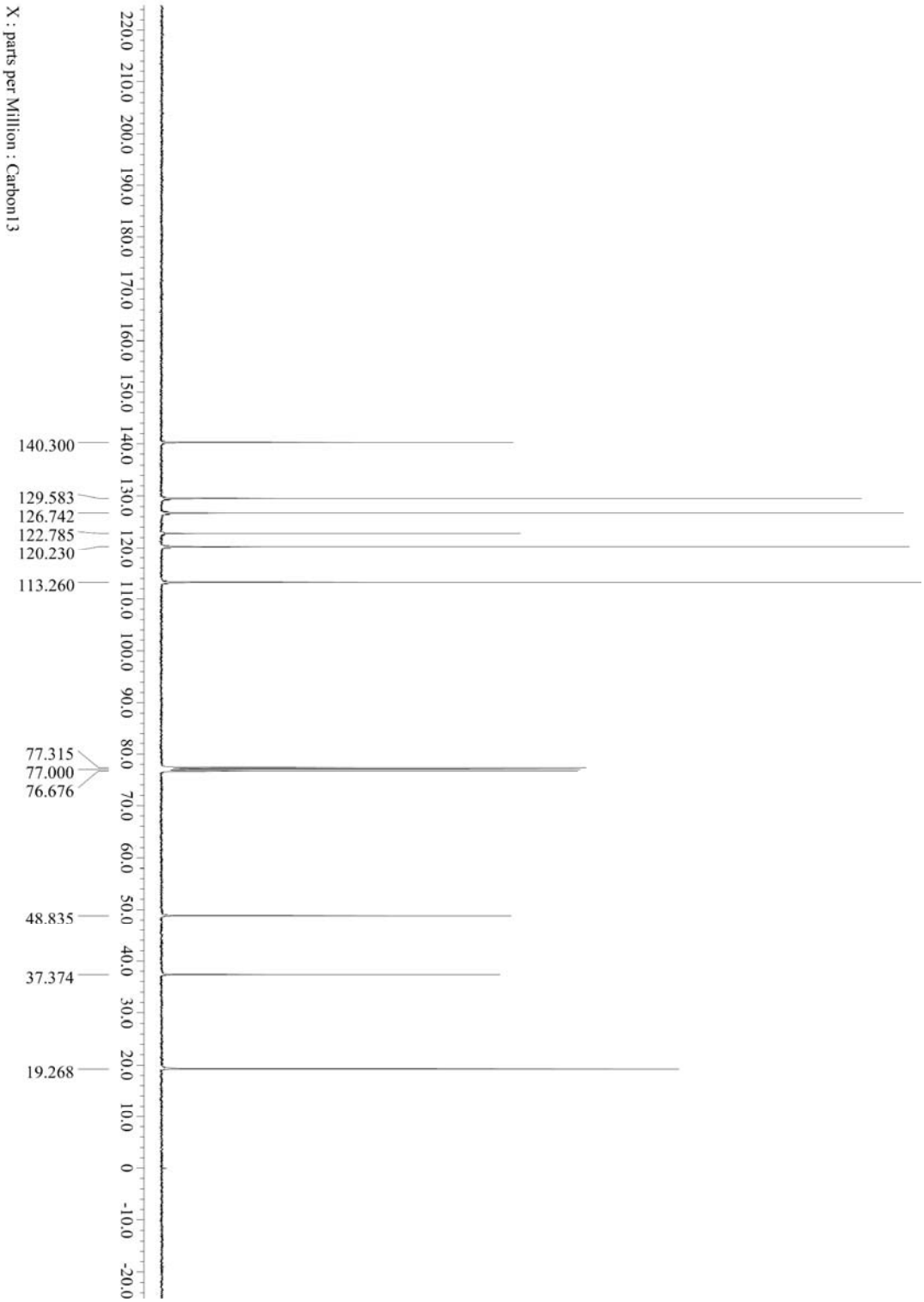
X : parts per Million : Carbon13
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140.300
129.583
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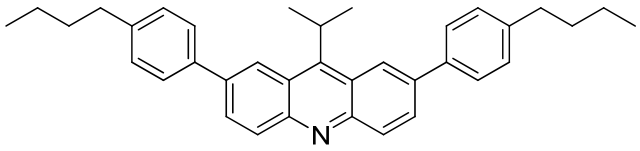
122.785
120.230
113.260
77.315
77.000
76.676
48.835
37.374
19.268



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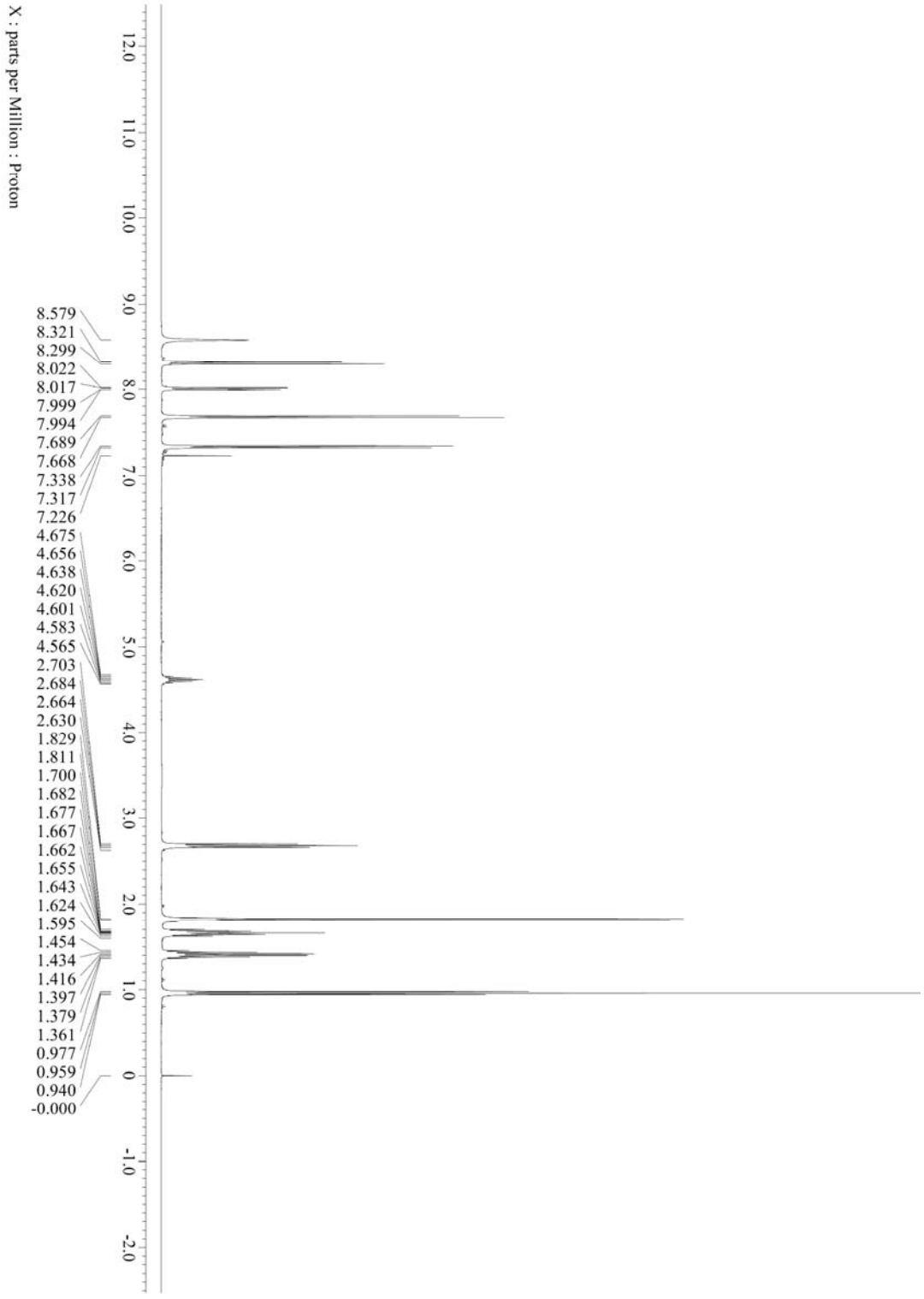
X : parts per Million : Proton
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4.0
3.0
2.0
1.0
0
-1.0
-2.0
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8.321
8.299
8.022
8.017
7.999
7.994
7.689
7.668
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7.317
7.226
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4.656
4.638
4.620
4.601
4.583
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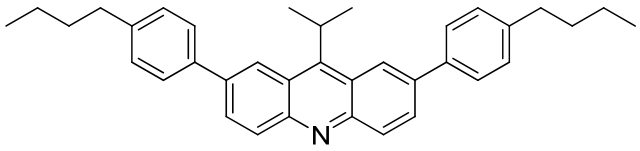

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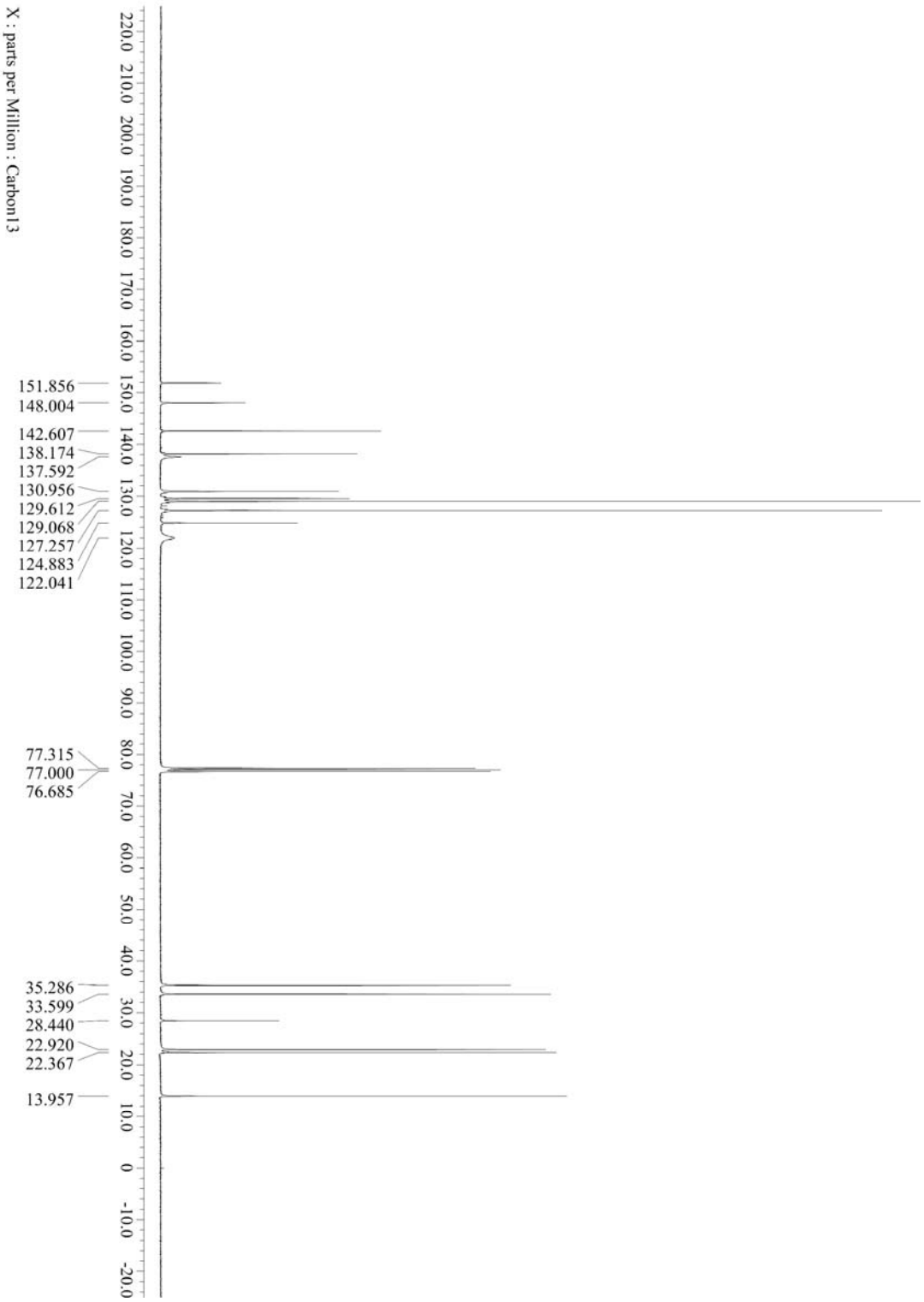
X : parts per Million : Carbon13
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142.607
138.174
137.592
130.956
129.612
129.068
127.257
124.883
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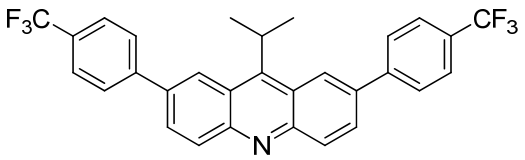
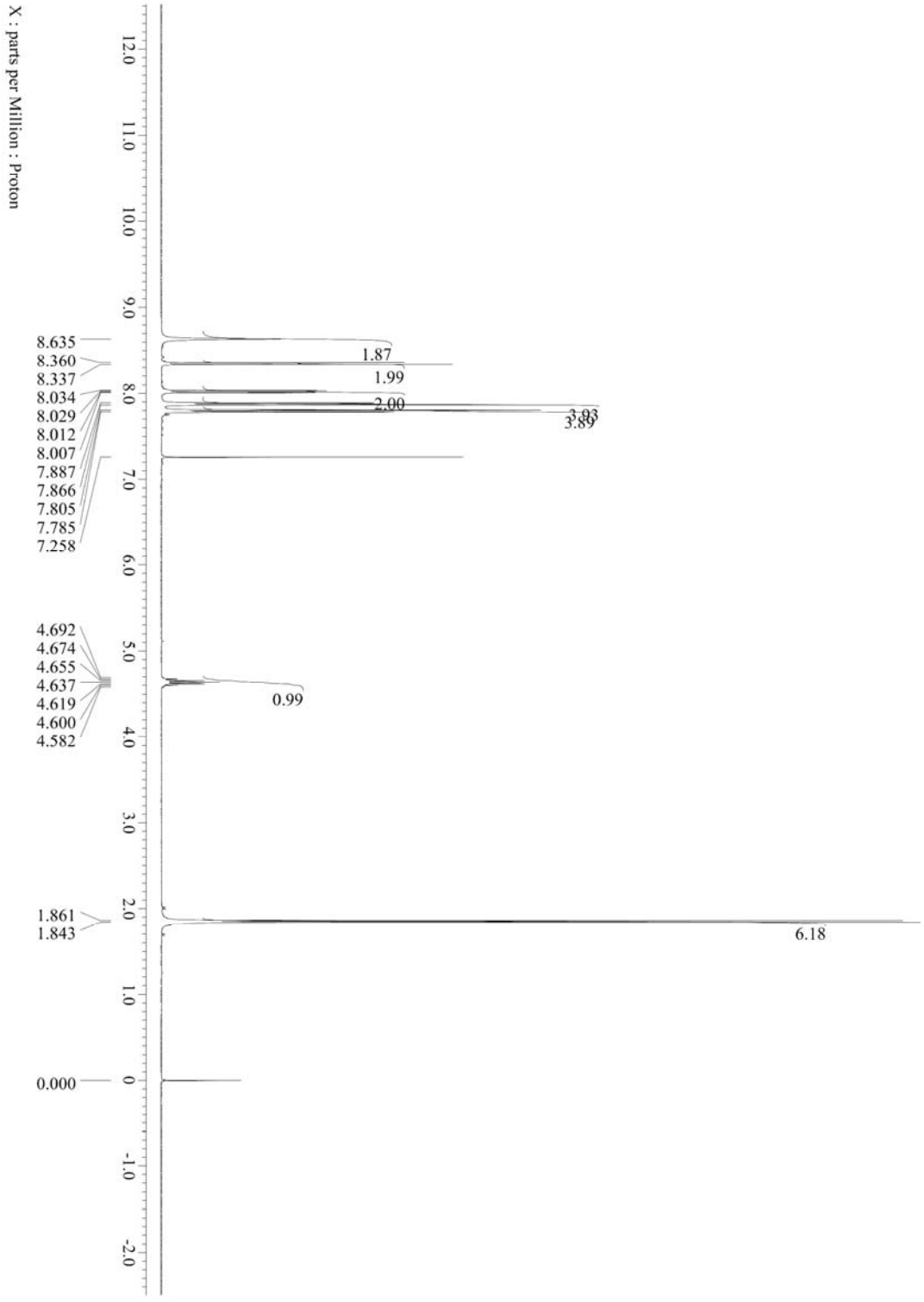
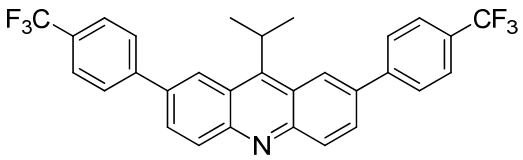
22.920
22.367
13.957

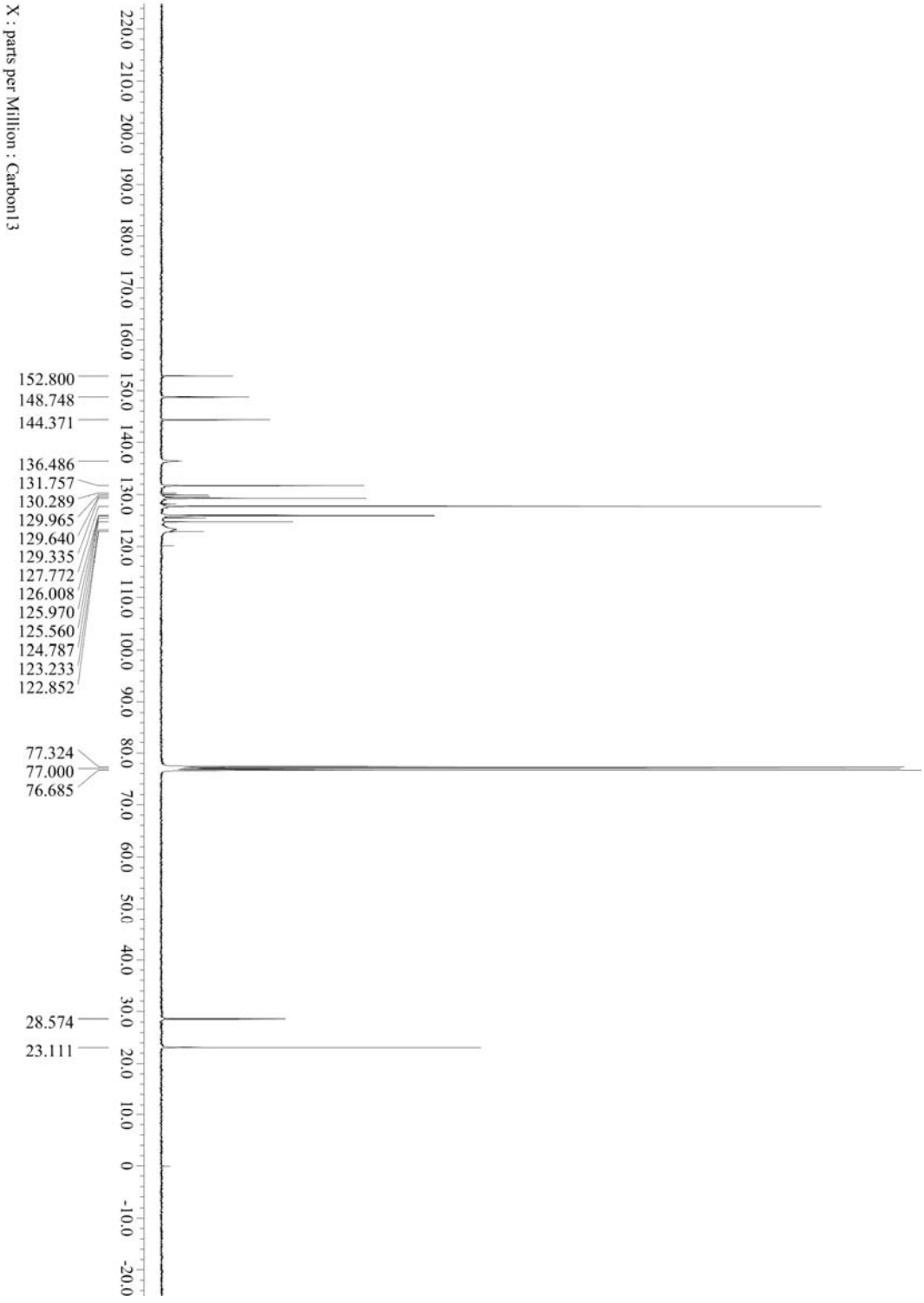


7




F3C
CF3
N

7


X : parts per Million : Carbon13
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152.800
148.748
144.371
136.486
131.757
130.289
129.965
129.640
129.335
127.772
126.008
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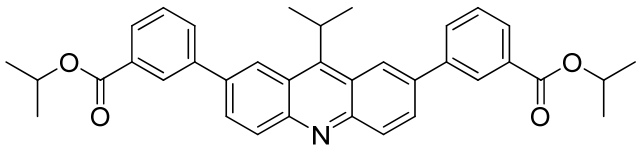
125.560
124.787
123.233
122.852
77.324
77.000
76.685
28.574
23.111



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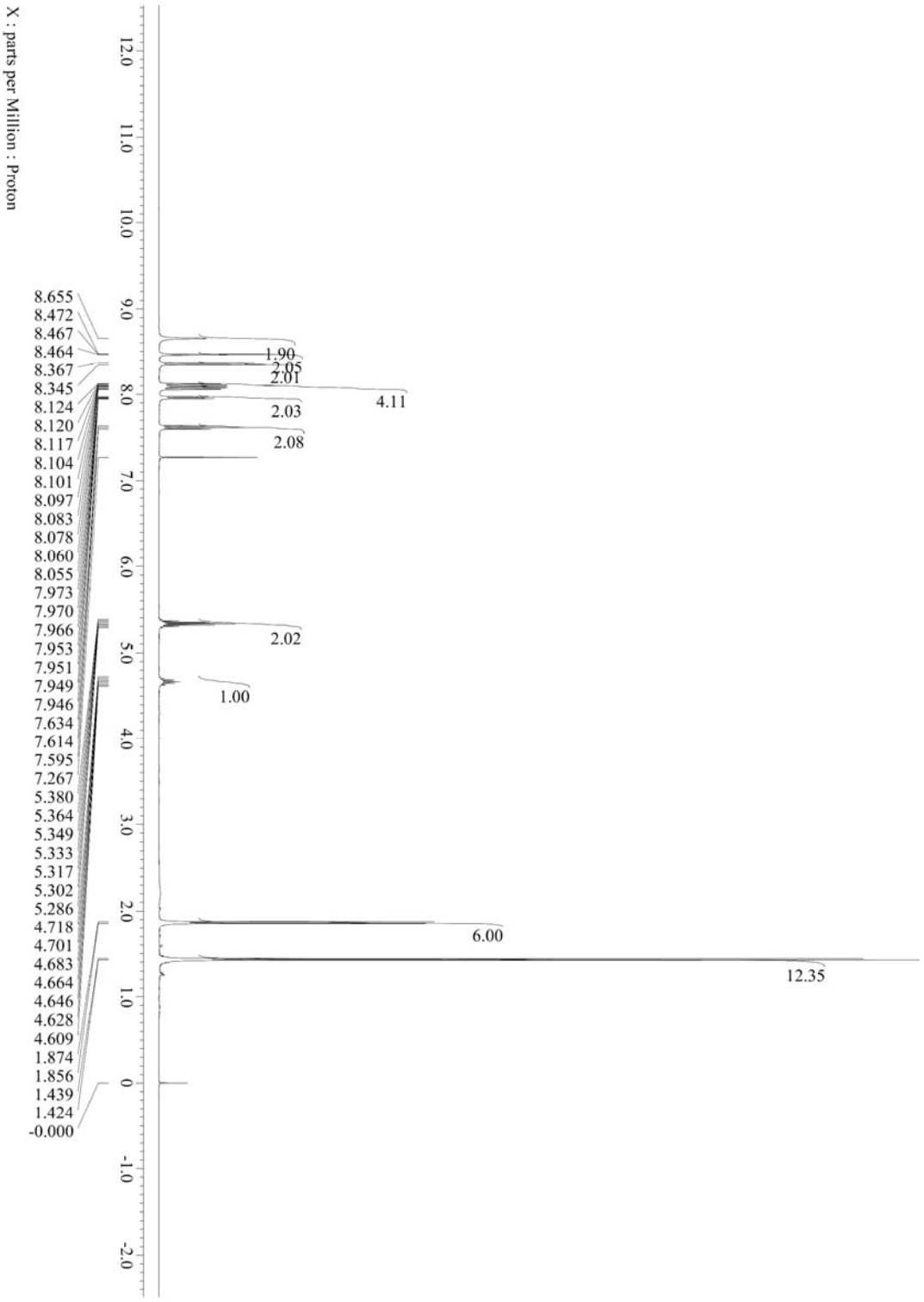

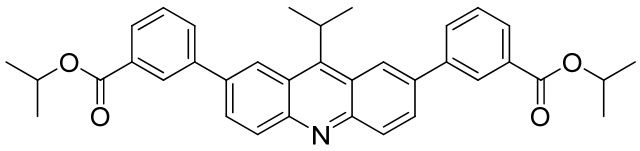

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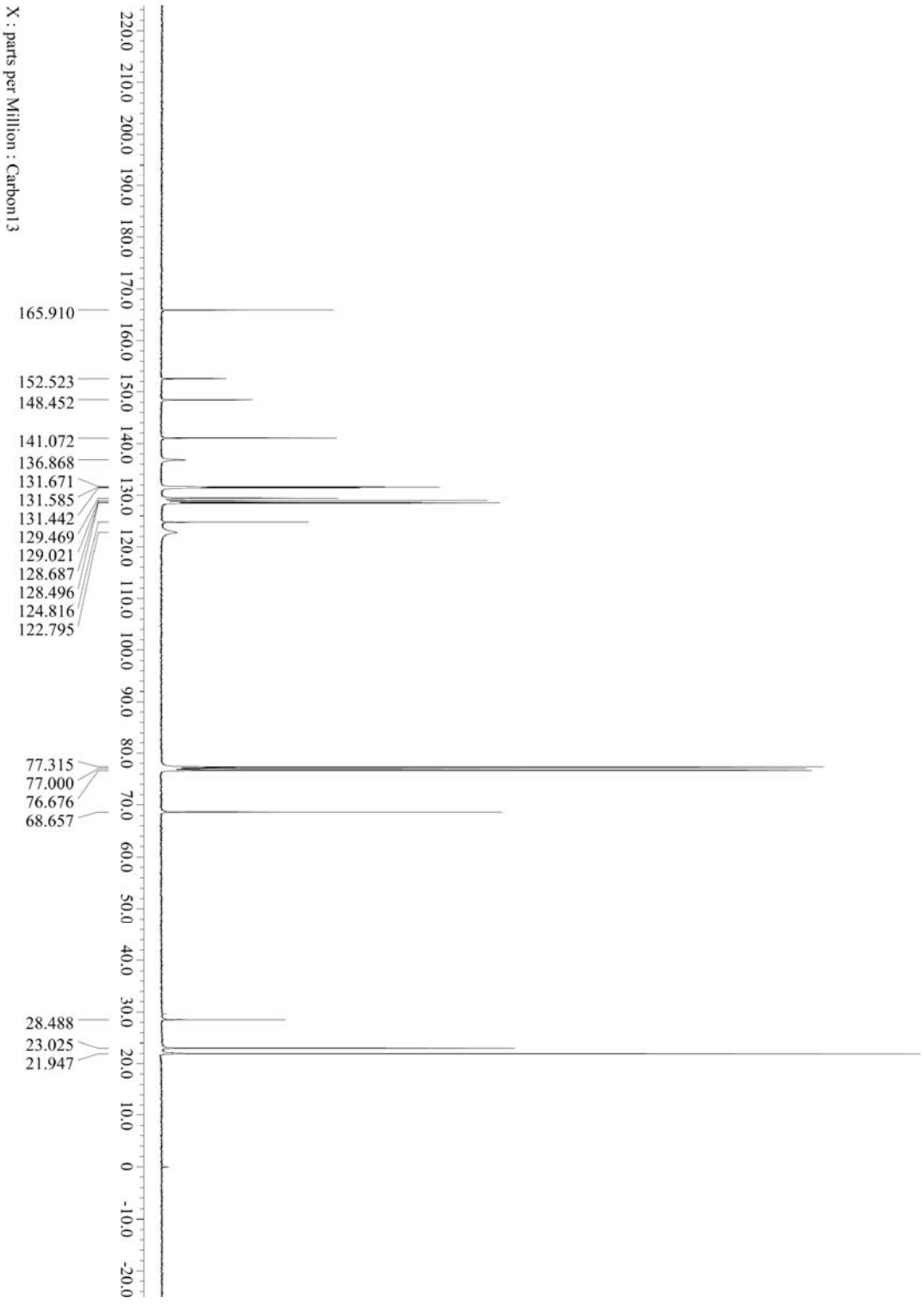
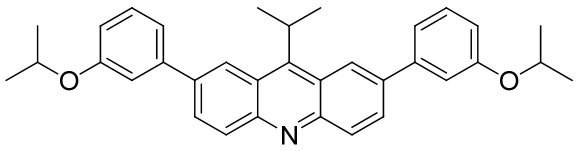

X : parts per Million : Carbon13
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
165.910
152.523
148.452
141.072
136.868
131.671
131.585
131.442
129.469
129.021
128.687
128.496
124.816
122.795
77.315
77.000
76.676
68.657
28.488
23.025
21.947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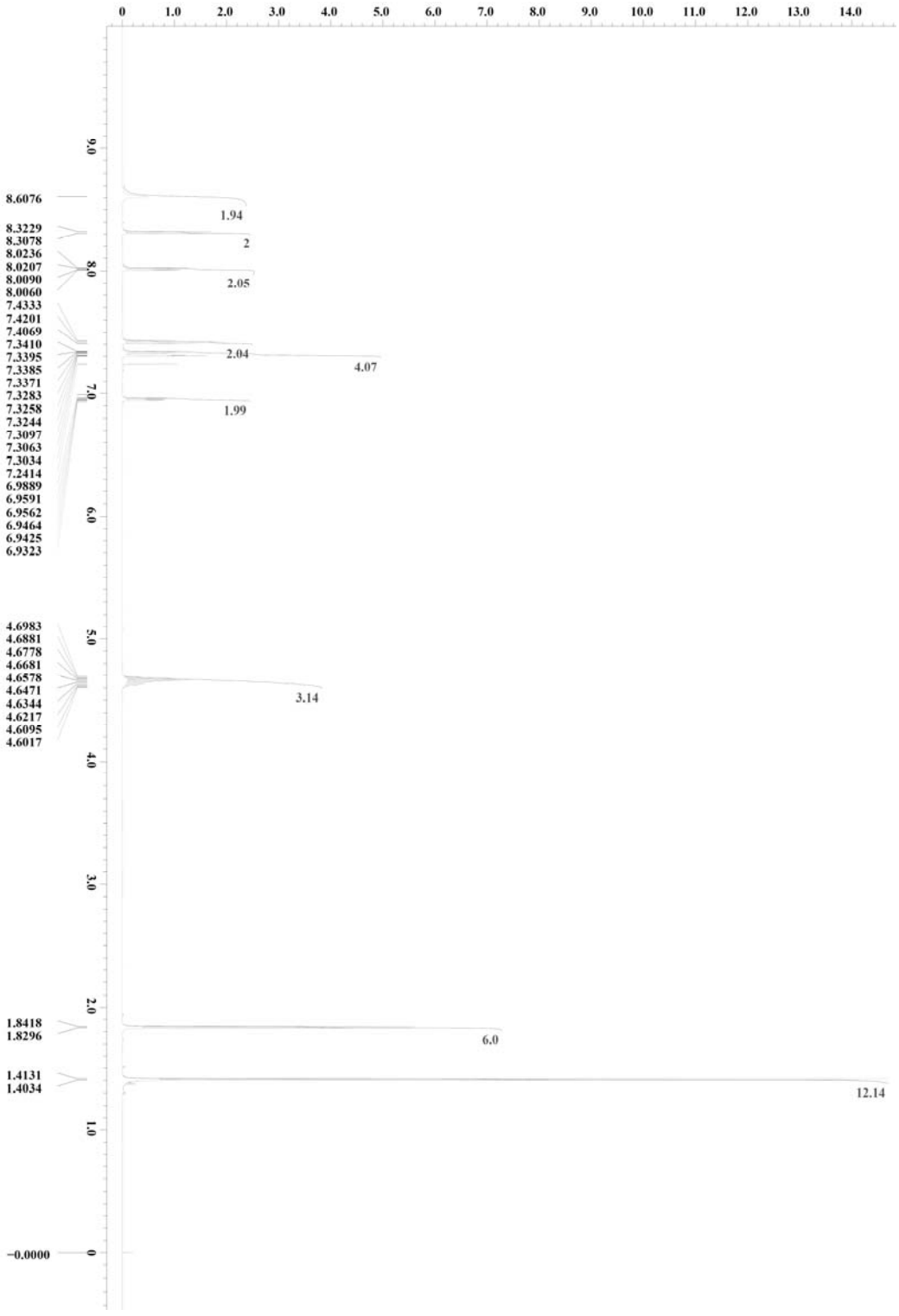
N
O

9


0 1.0 2.0 3.0 4.0 5.0 6.0 7.0 8.0 9.0 10.0 11.0 12.0 13.0 14.0
8.6076
8.3229
8.3078
8.0236
8.0207
8.0090
8.0060
7.4333
7.4201
7.4069
7.3410
7.3395
7.3385
7.3371
7.3283
7.3258
7.3244
7.3097
7.3063
7.3034
7.2414
6.9889
6.9591
6.9562
6.9464
6.9425
6.9323
4.6983
4.6881
4.6778
4.6681
4.6578
4.6471
4.6344
4.6217
4.6095
4.6017
1.8418
1.8296
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−0.0000
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2
2.05
2.04
4.07
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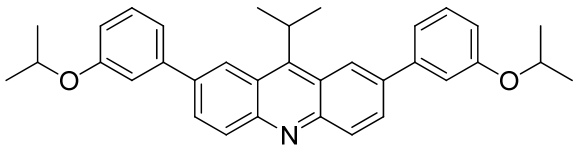
3.14
6.0
12.14



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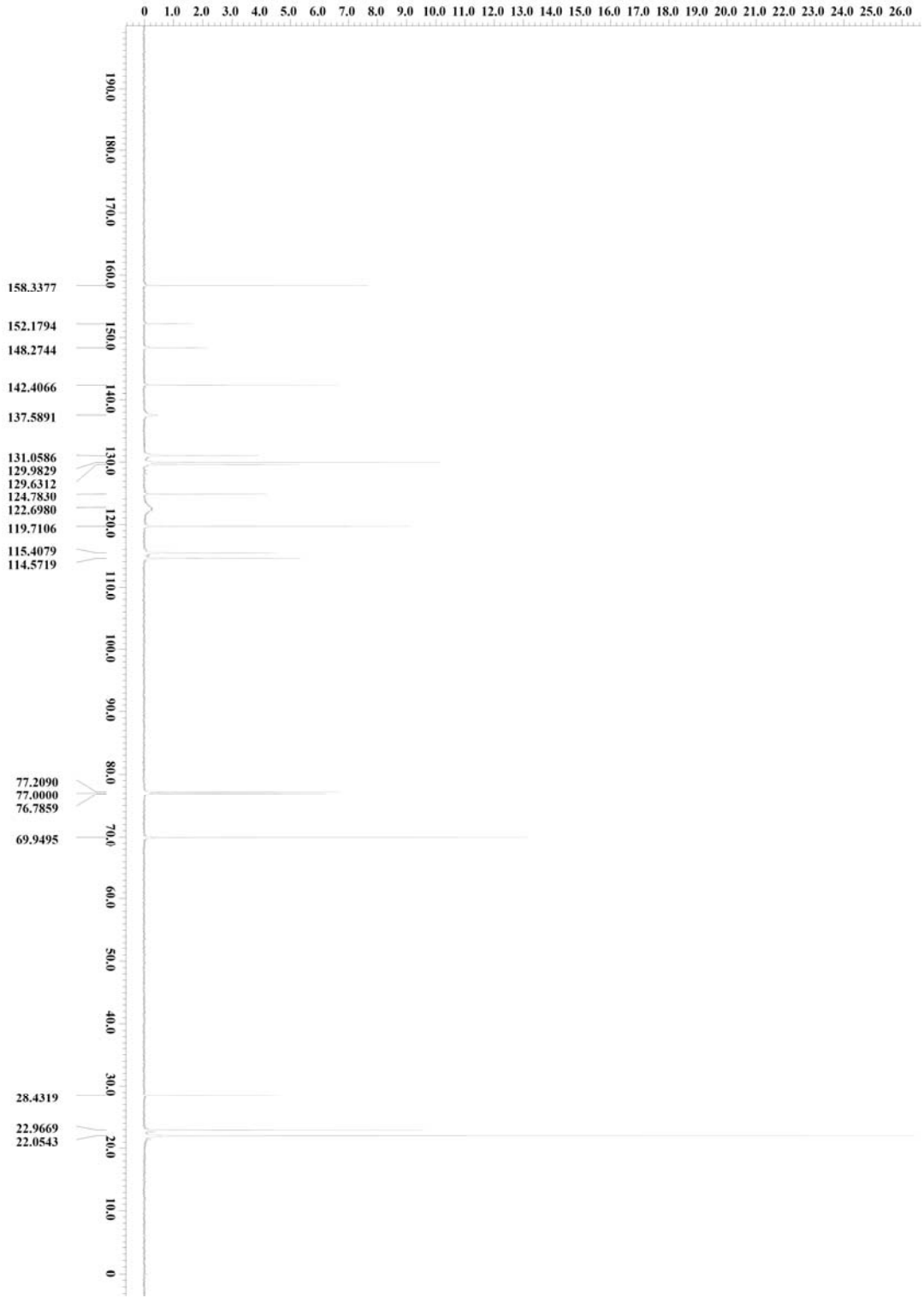

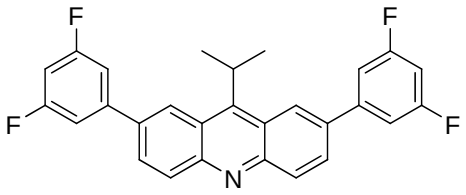

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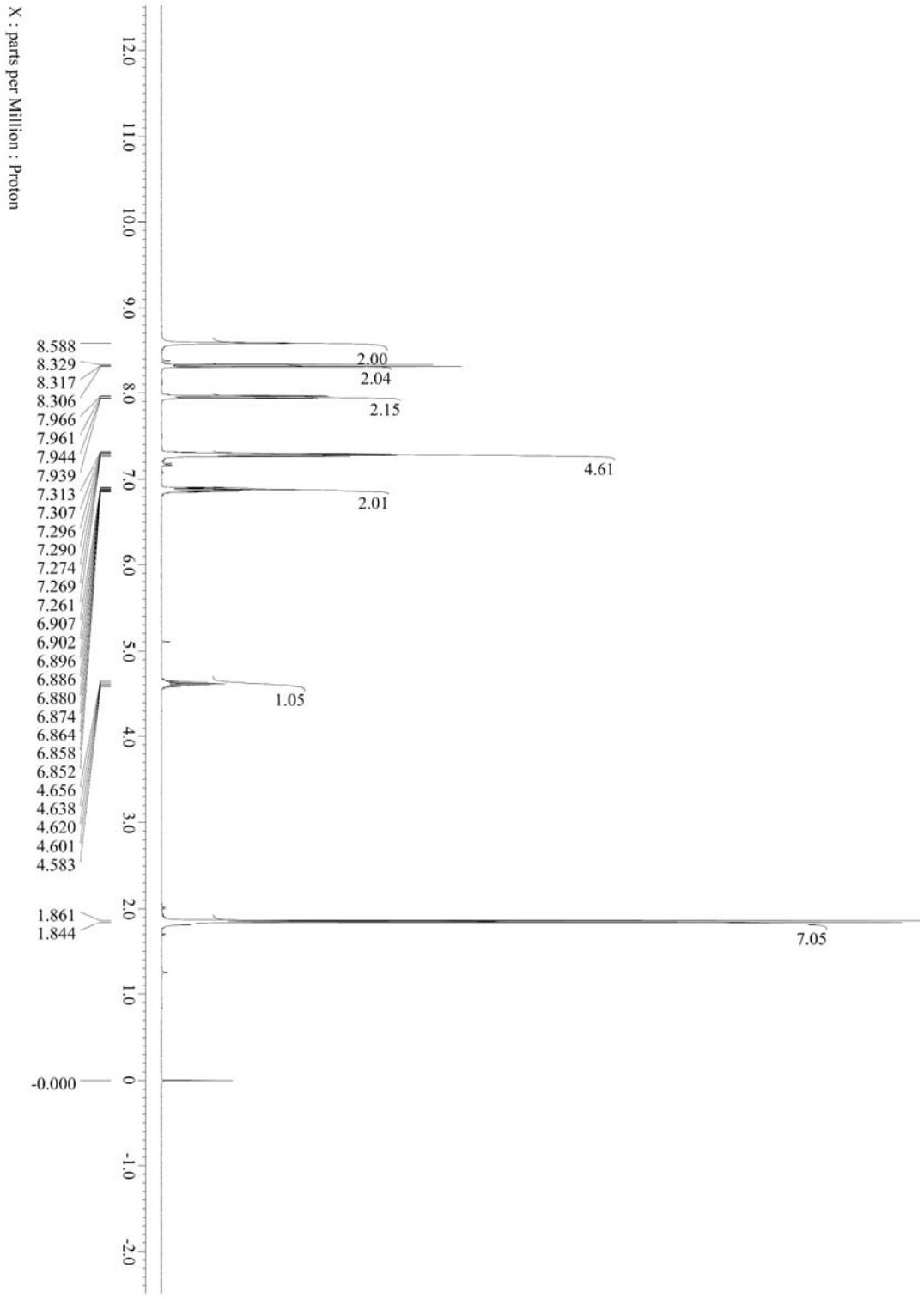

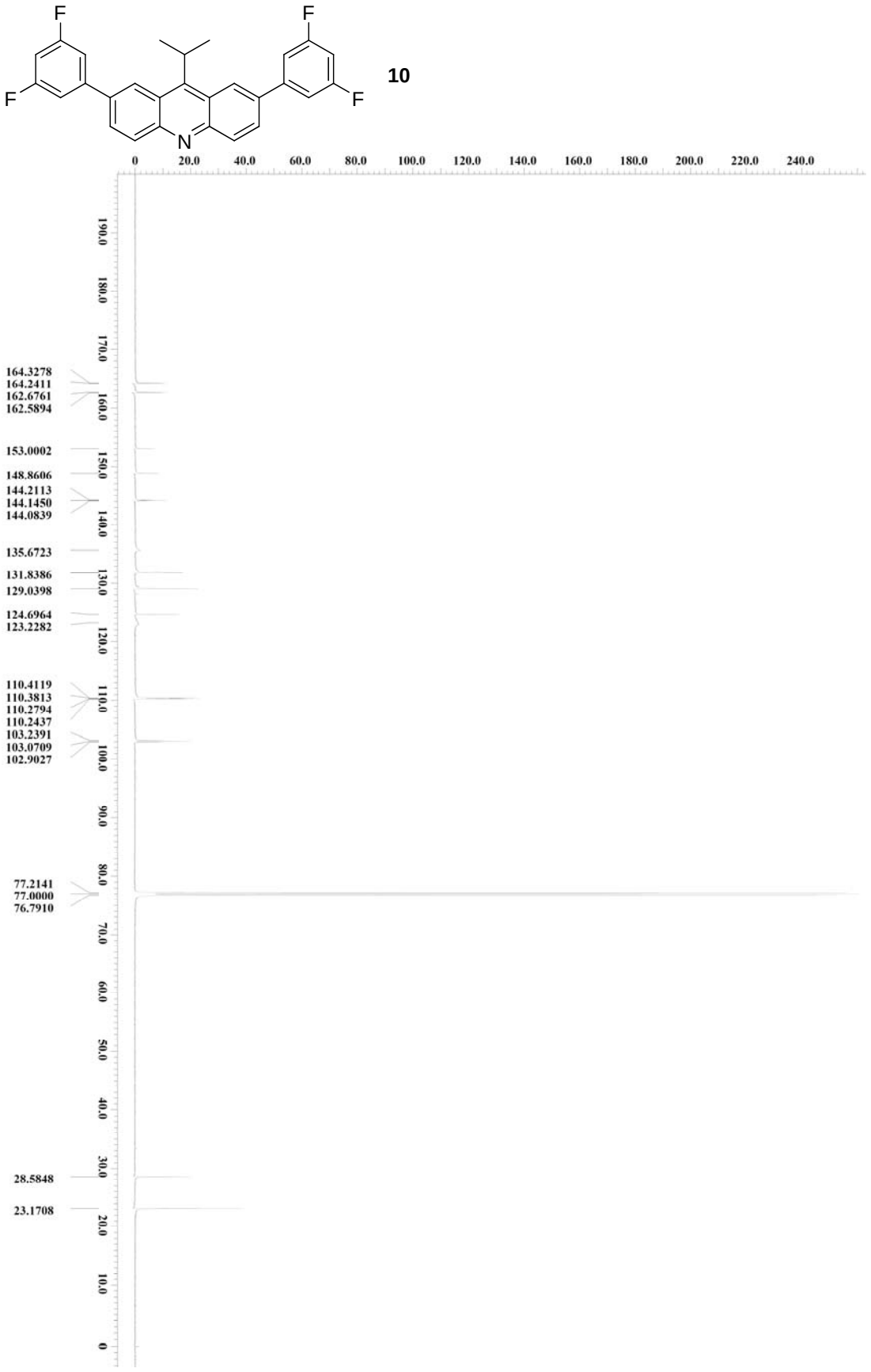

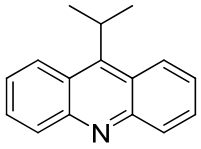
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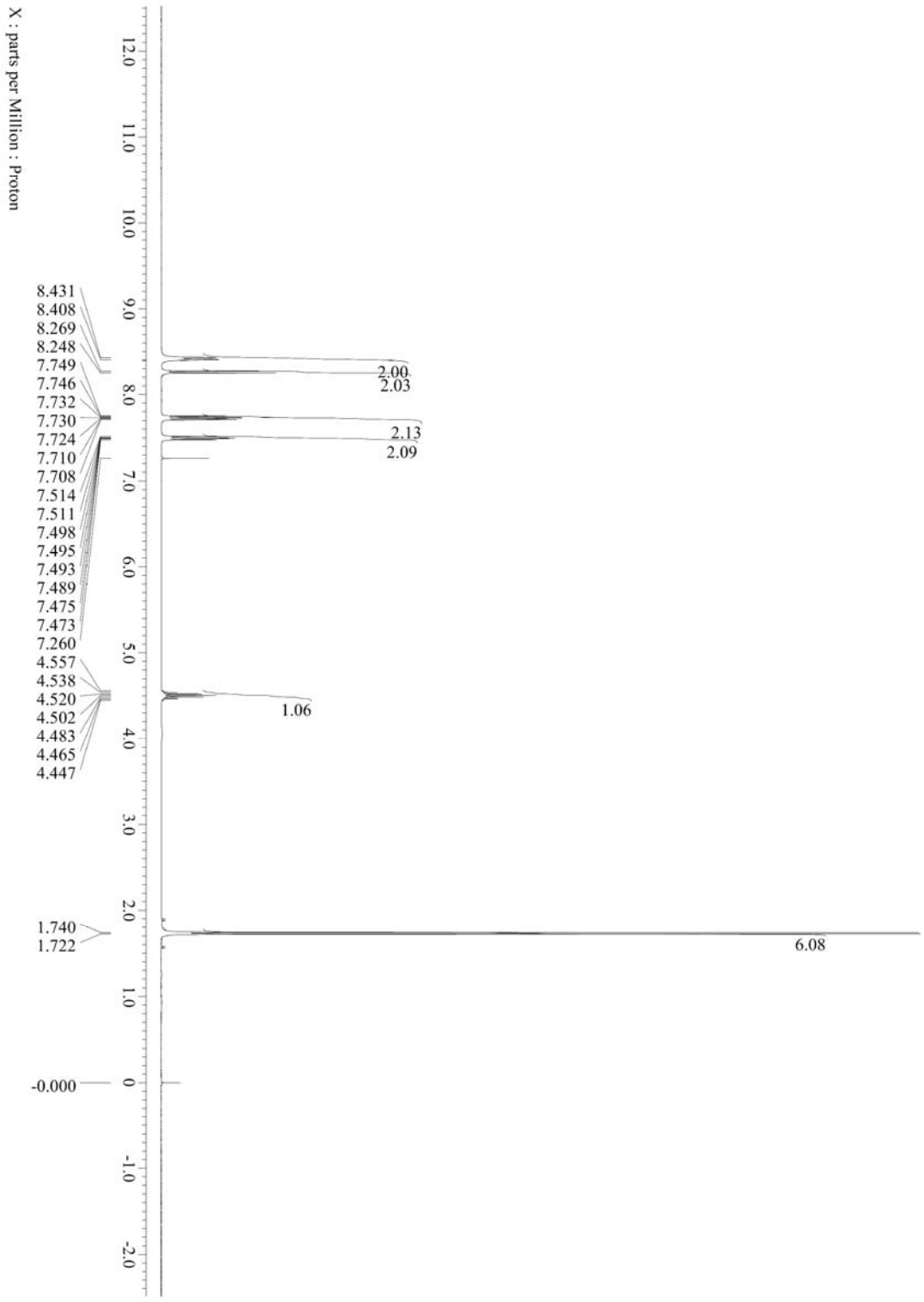
11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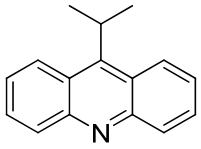
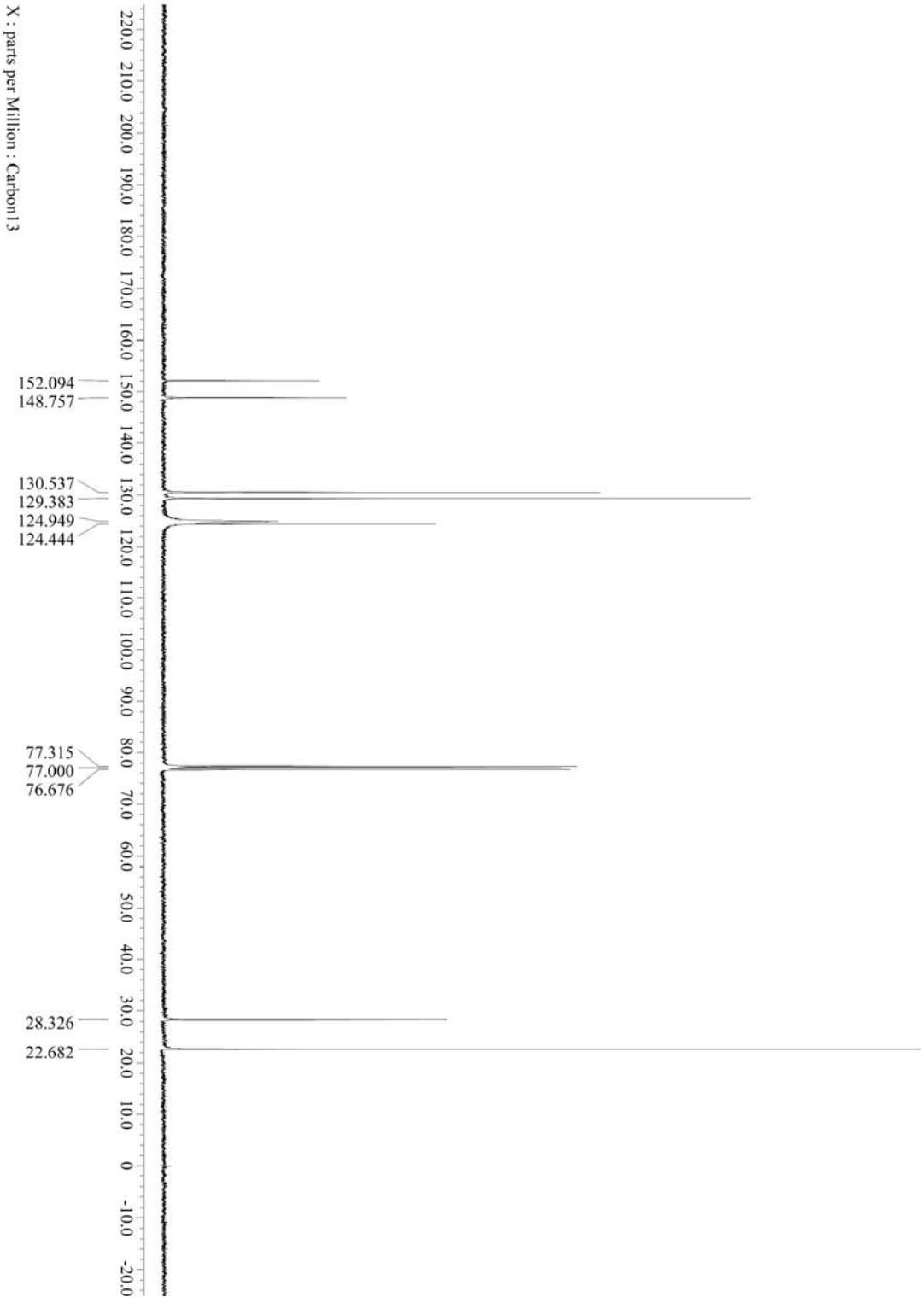
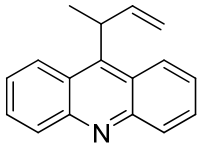
8.408
8.269
8.248
7.749
7.746
7.732
7.730
7.724
7.710
7.708
7.514
7.511
7.498
7.495
7.493
7.489
7.475
7.473
7.260
4.557
4.538
4.520
4.502
4.483
4.465
4.447
1.740
1.722
-0.000
2.00
2.03
2.13
2.09
1.06
6.08
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
-2.0



11


X : parts per Million : Carbon13
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
152.094
148.757
130.537
129.383
124.949
124.444
77.315
77.000
76.676
28.326
22.682



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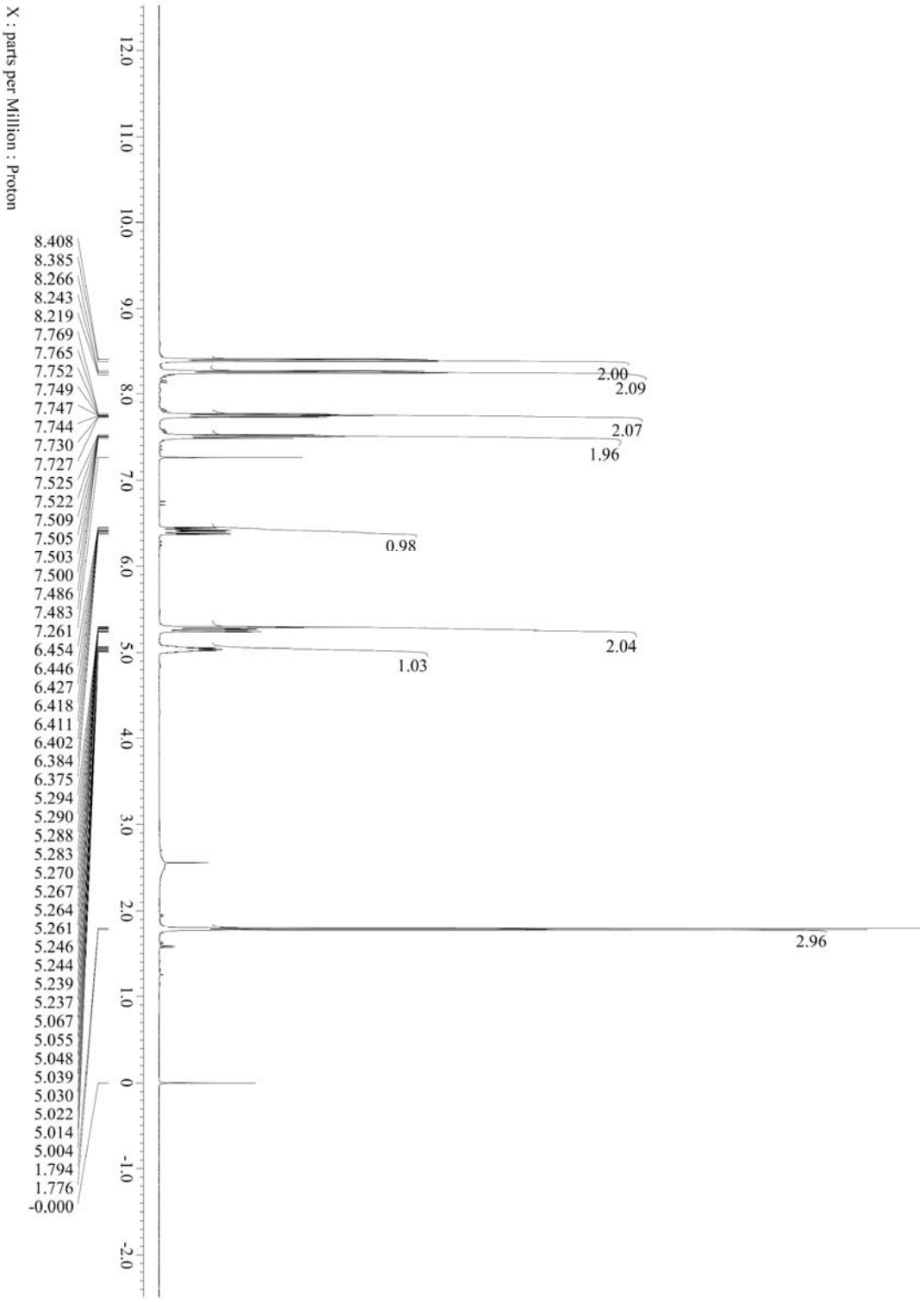
X : parts per Million : Proton
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8.266
8.243
8.219
7.769
7.765
7.752
7.749
7.747
7.744
7.730
7.727
7.525
7.522
7.509
7.505
7.503
7.500
7.486
7.483
7.261
6.454
6.446
6.427
6.418
6.411
6.402
6.384
6.375
5.294
5.290
5.288
5.283
5.270
5.267
5.264
5.261
5.246
5.244
5.239
5.237
5.067
5.055
5.048
5.039
5.030
5.022
5.014
5.004
1.794
1.776
-0.000
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
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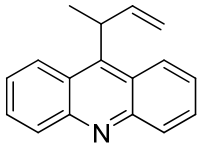
-2.0
2.00
2.09
2.07
1.96
0.98
2.04
1.03
2.96



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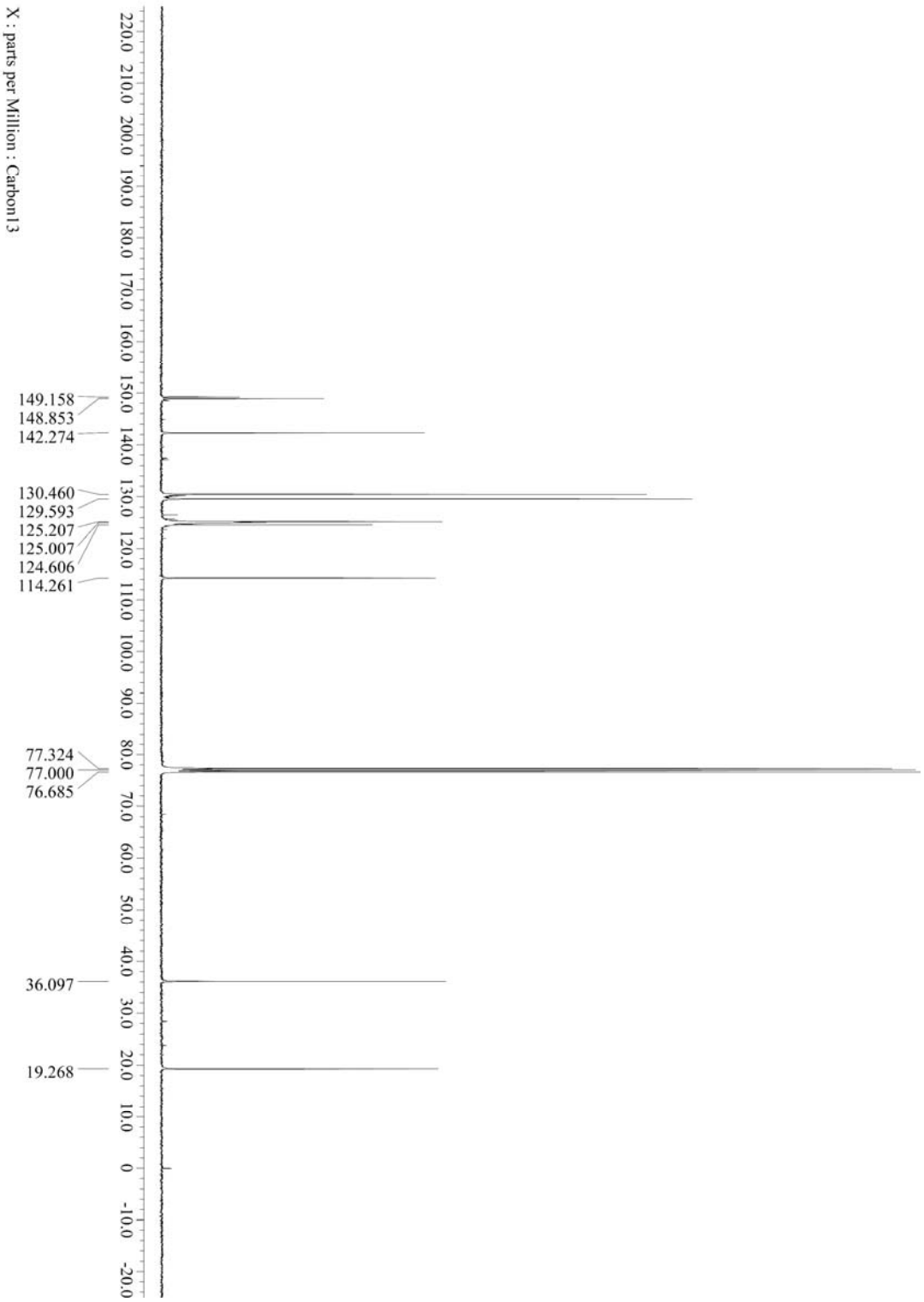
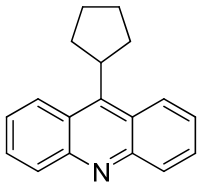
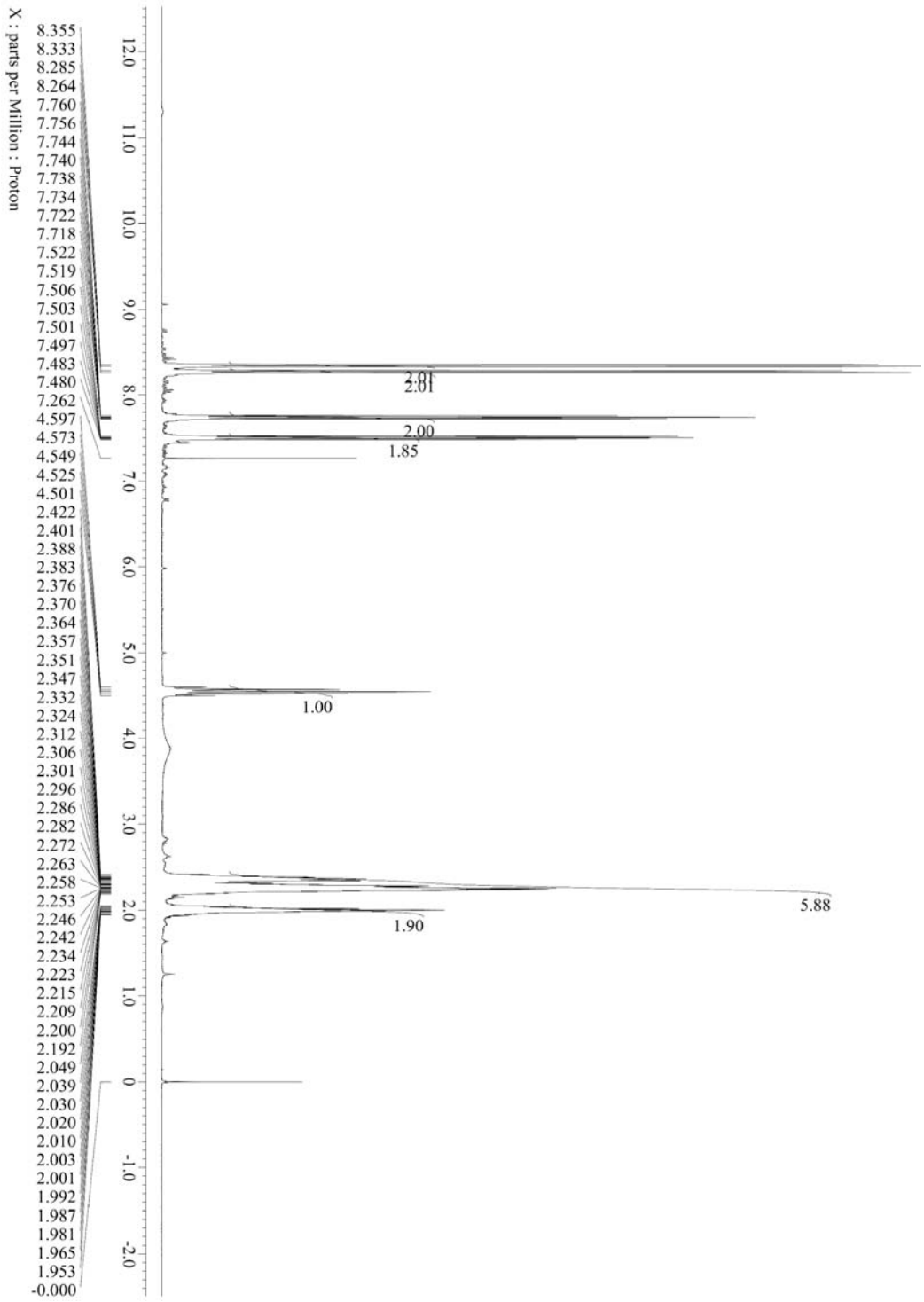

X : parts per Million : Carbon13
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
149.158
148.853
142.274
130.460
129.593
125.207
125.007
124.606
114.261
77.324
77.000
76.685
36.097
19.268



13


X : parts per Million : Proton
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8.264
7.760
7.756
7.744
7.740
7.738
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7.722
7.718
7.522
7.519
7.506
7.503
7.501
7.497
7.483
7.480
7.262
4.597
4.573
4.549
4.525
4.501
2.422
2.401
2.388
2.383
2.376
2.370
2.364
2.357
2.351
2.347
2.332
2.324
2.312
2.306
2.301
2.296
2.286
2.282
2.272
2.263
2.258
2.253
2.246
2.242
2.234
2.223
2.215
2.209
2.200
2.192
2.049
2.039
2.030
2.020
2.010
2.003
2.001
1.992
1.987
1.981
1.965
1.953
-0.000
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
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2.01
2.00
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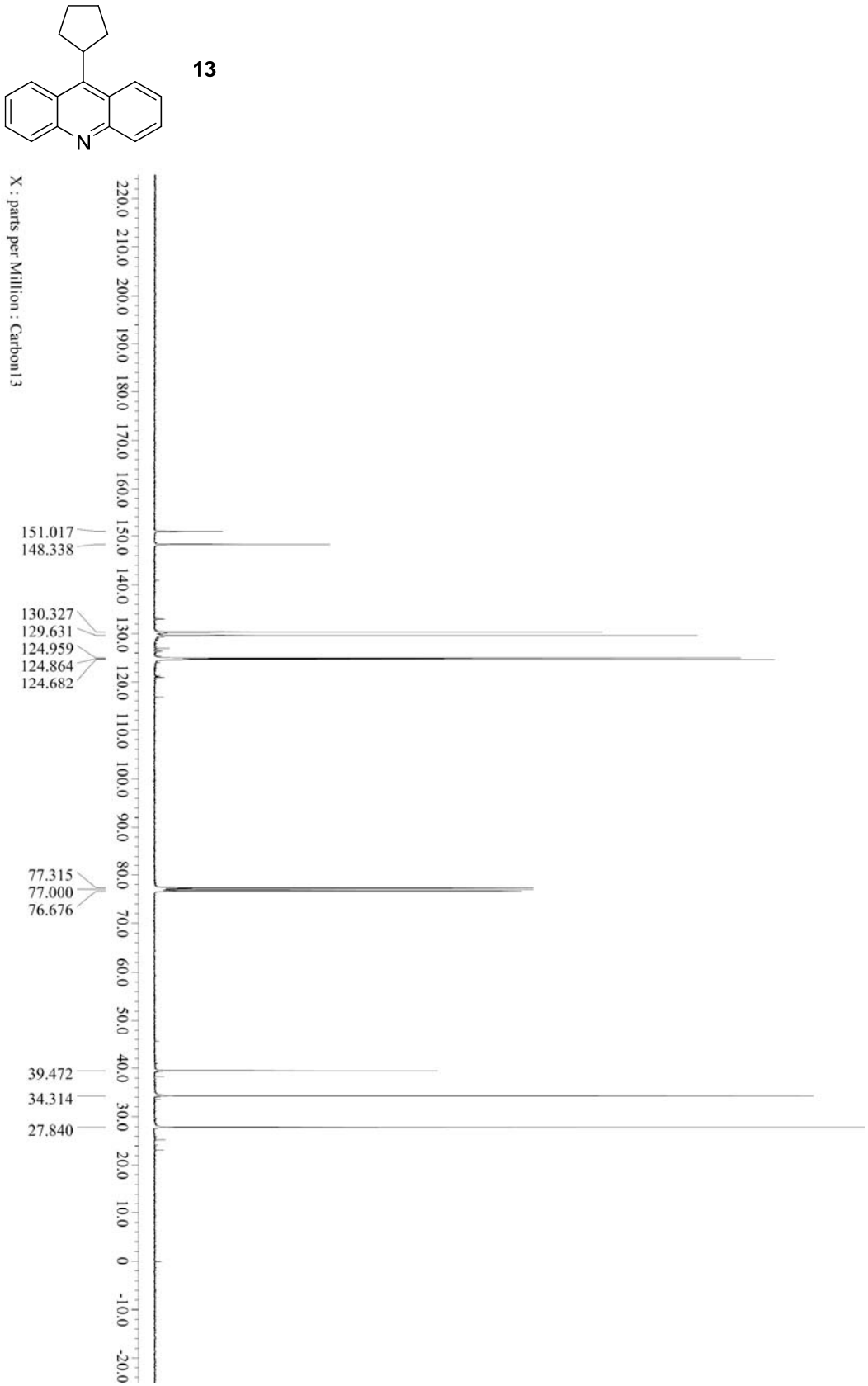
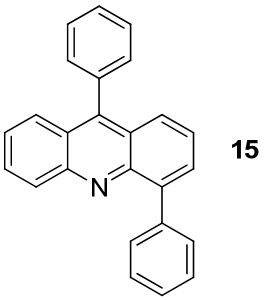
1.00
5.88
1.90





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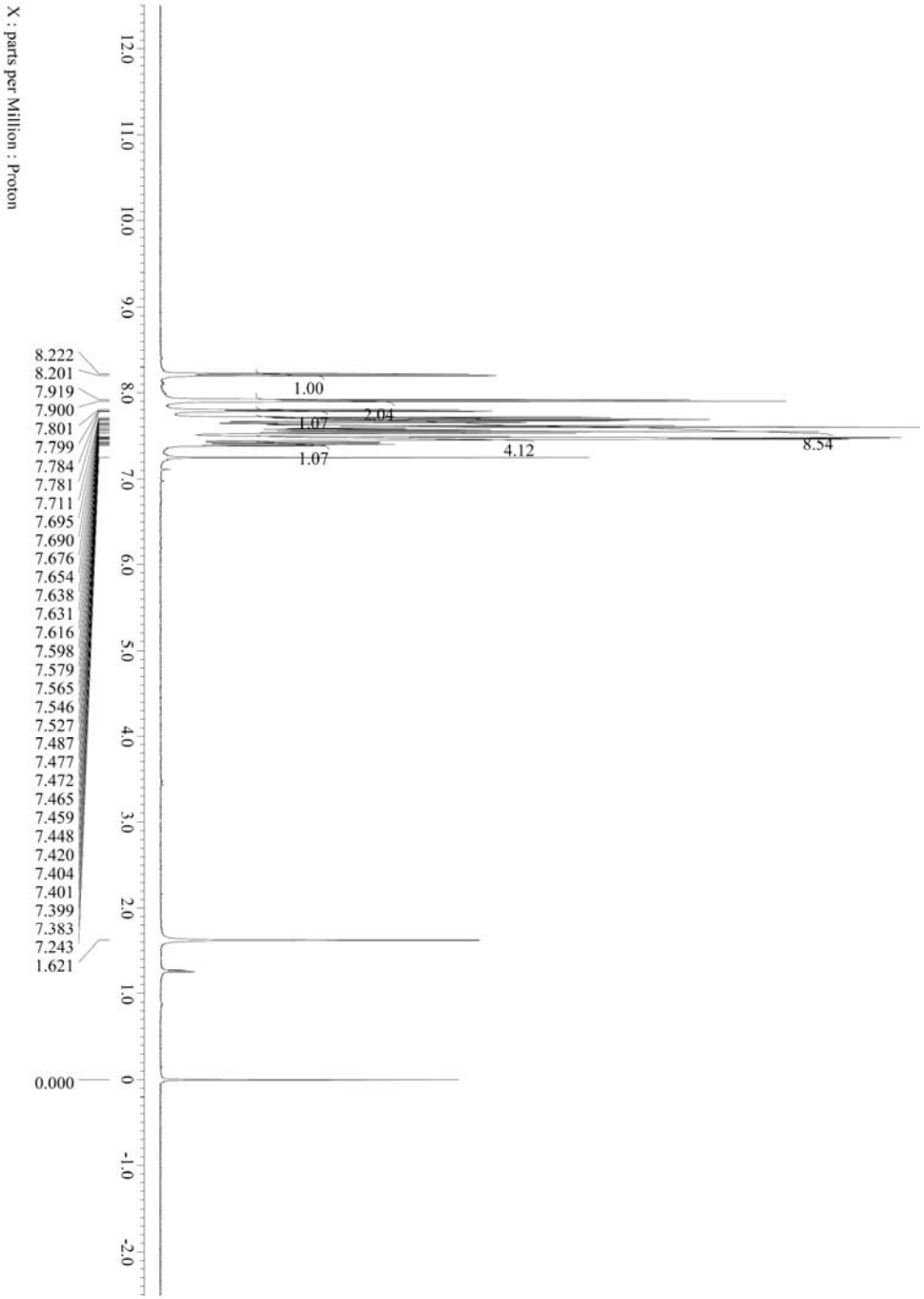
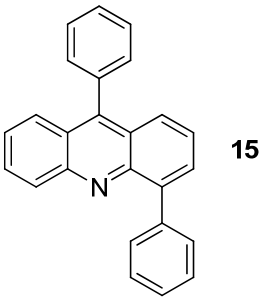
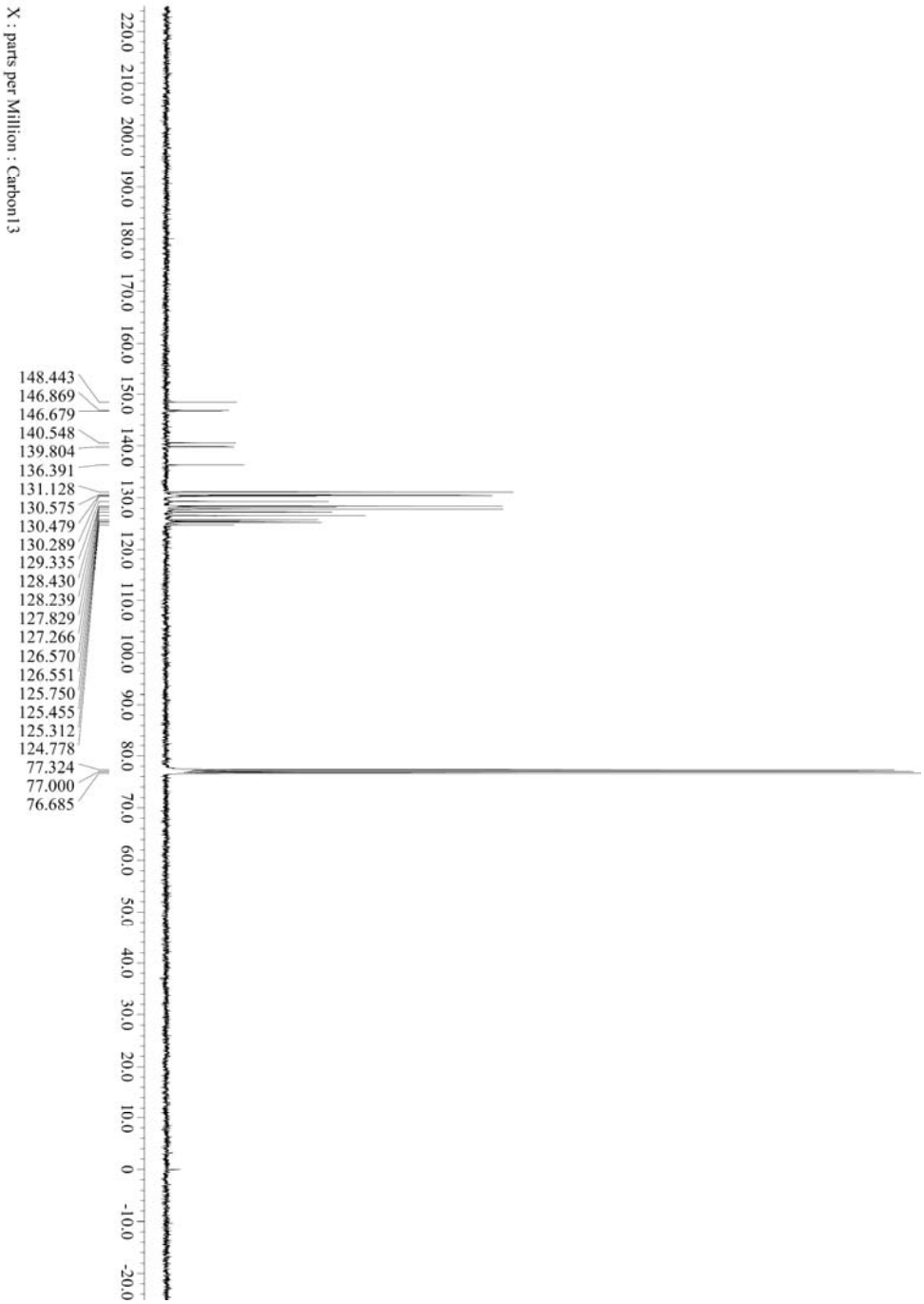

X : parts per Million : Proton
8.222
8.201
7.919
7.900
7.801
7.799
7.784
7.781
7.711
7.695
7.690
7.676
7.654
7.638
7.631
7.616
7.598
7.579
7.565
7.546
7.527
7.487
7.477
7.472
7.465
7.459
7.448
7.420
7.404
7.401
7.399
7.383
7.243
1.621
0.000
1.00
1.07
2.04
1.07
4.12
8.54


N

15


X : parts per Million : Carbon13
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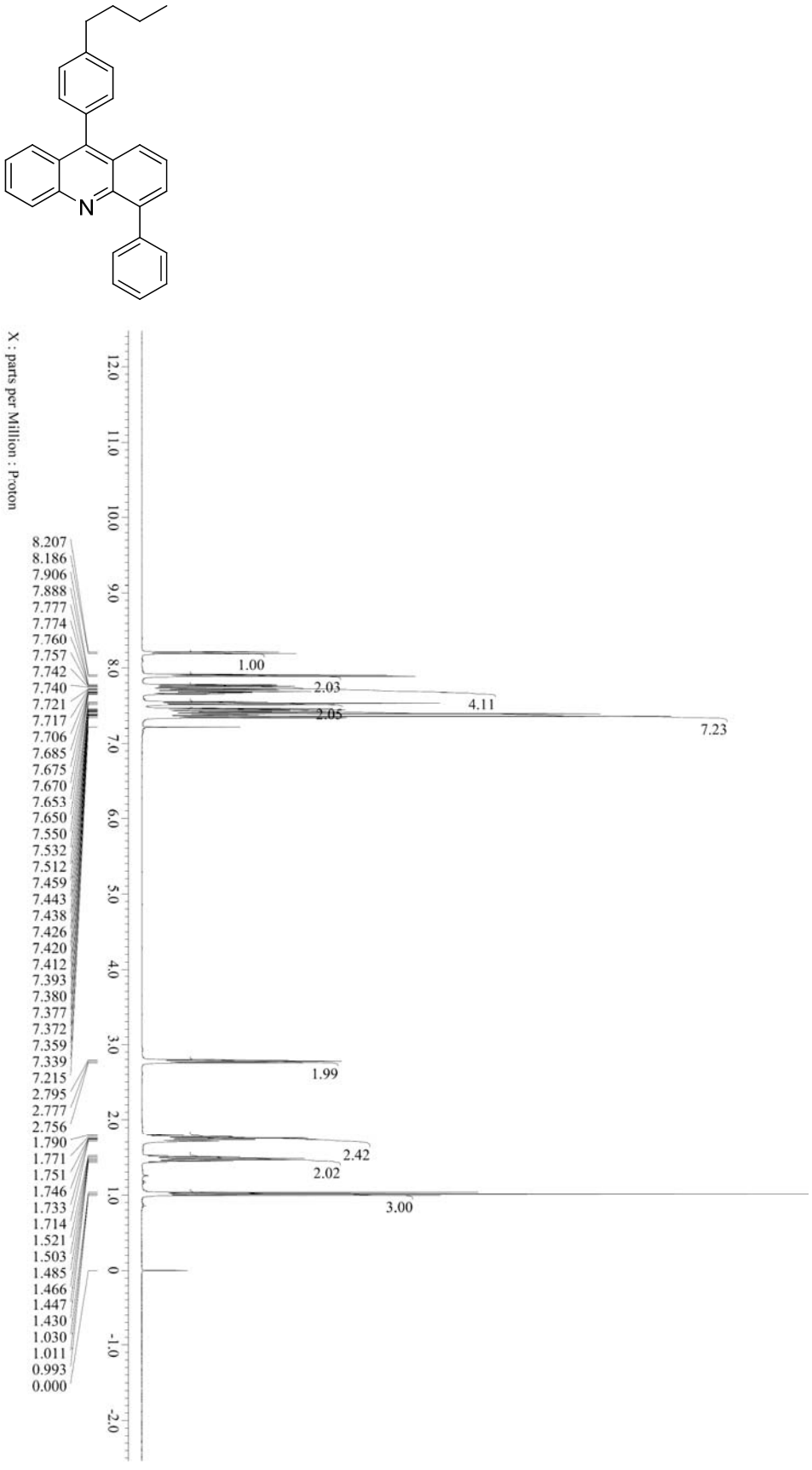
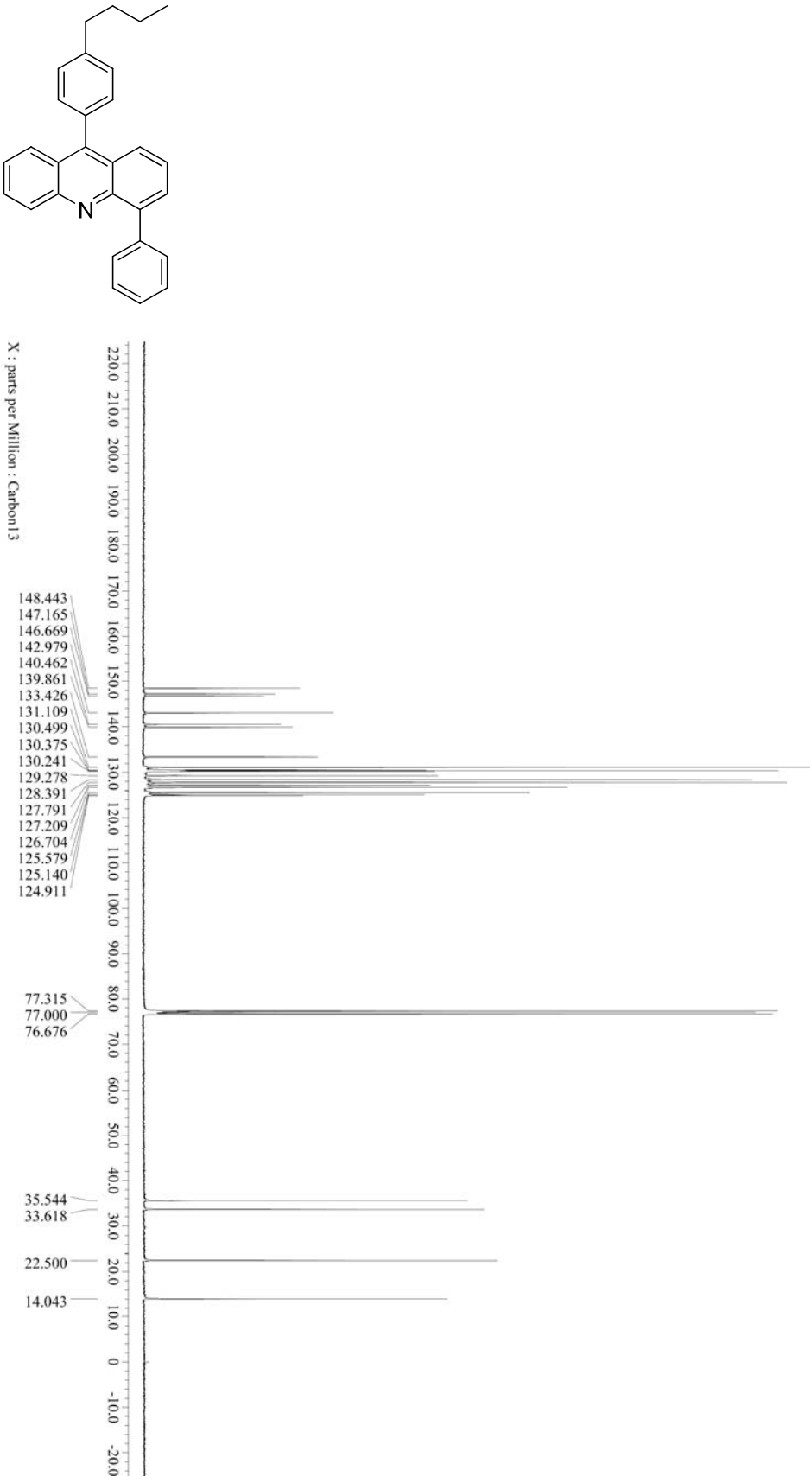
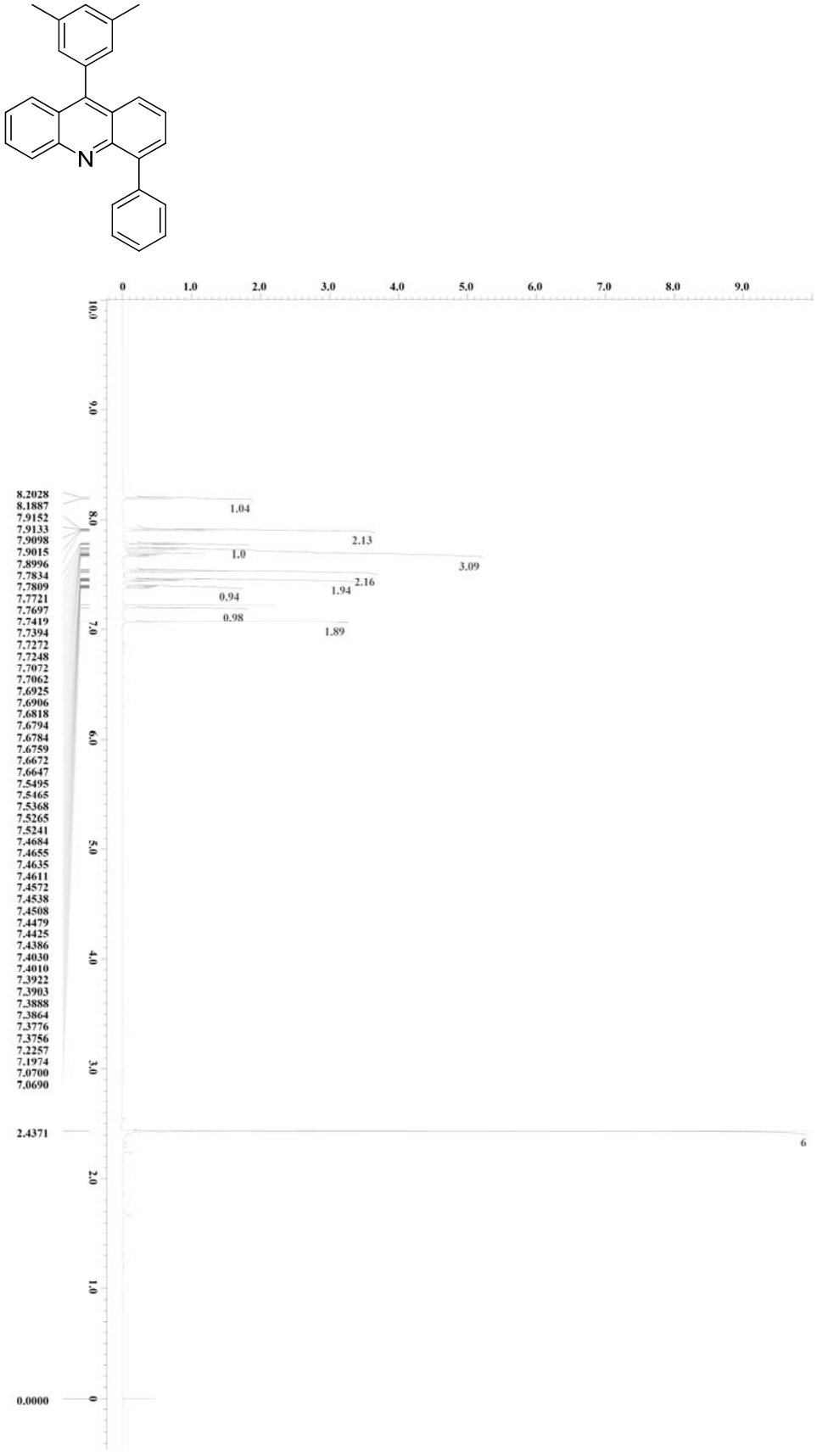
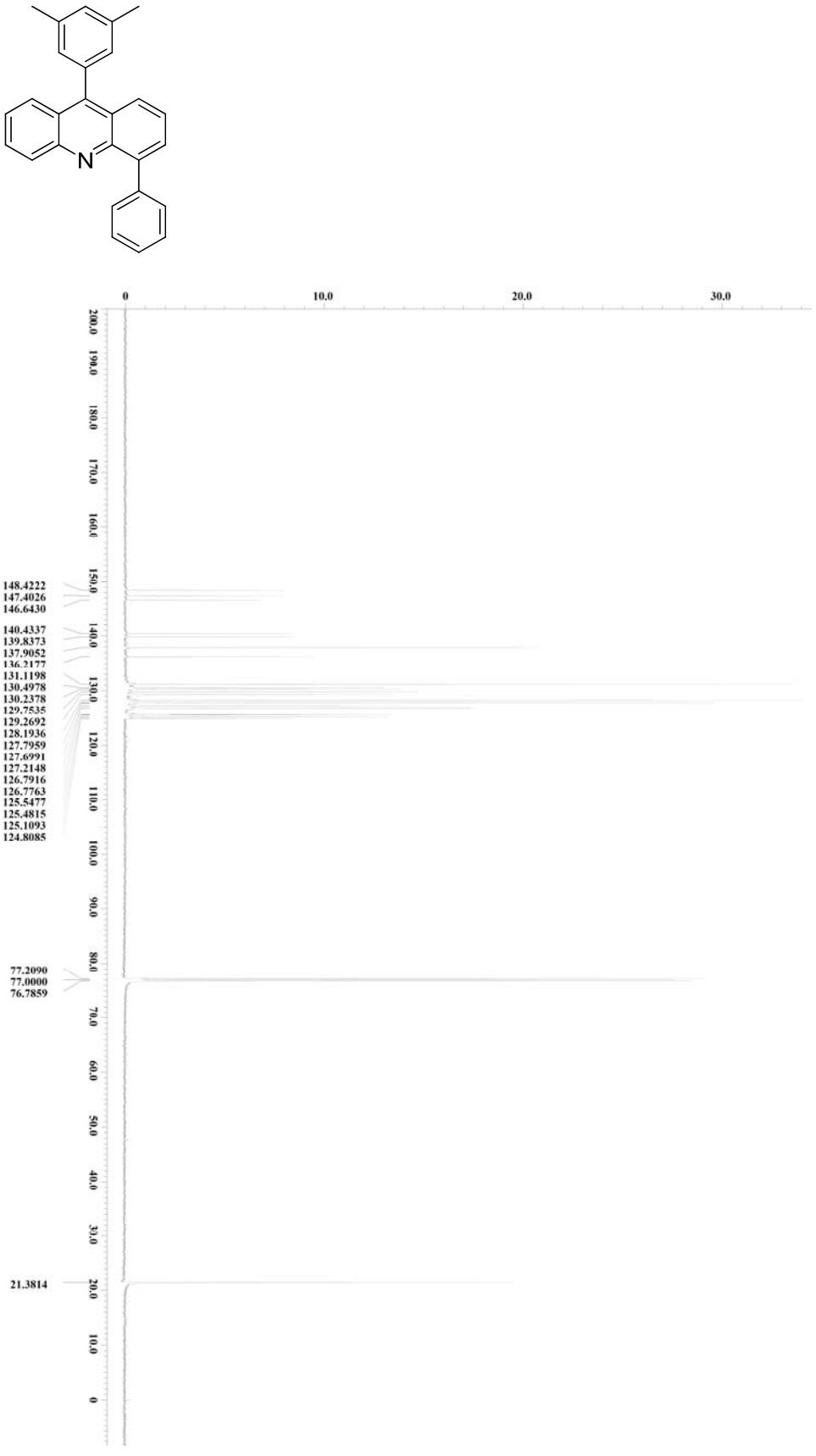
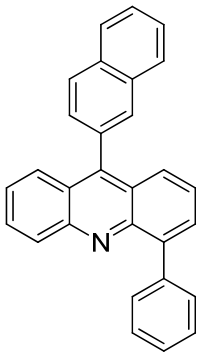
146.679
140.548
139.804
136.391
131.128
130.575
130.479
130.289
129.335
128.430
128.239
127.829
127.266
126.570
126.551
125.750
125.455
125.312
124.778
77.324
77.000
76.685
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0

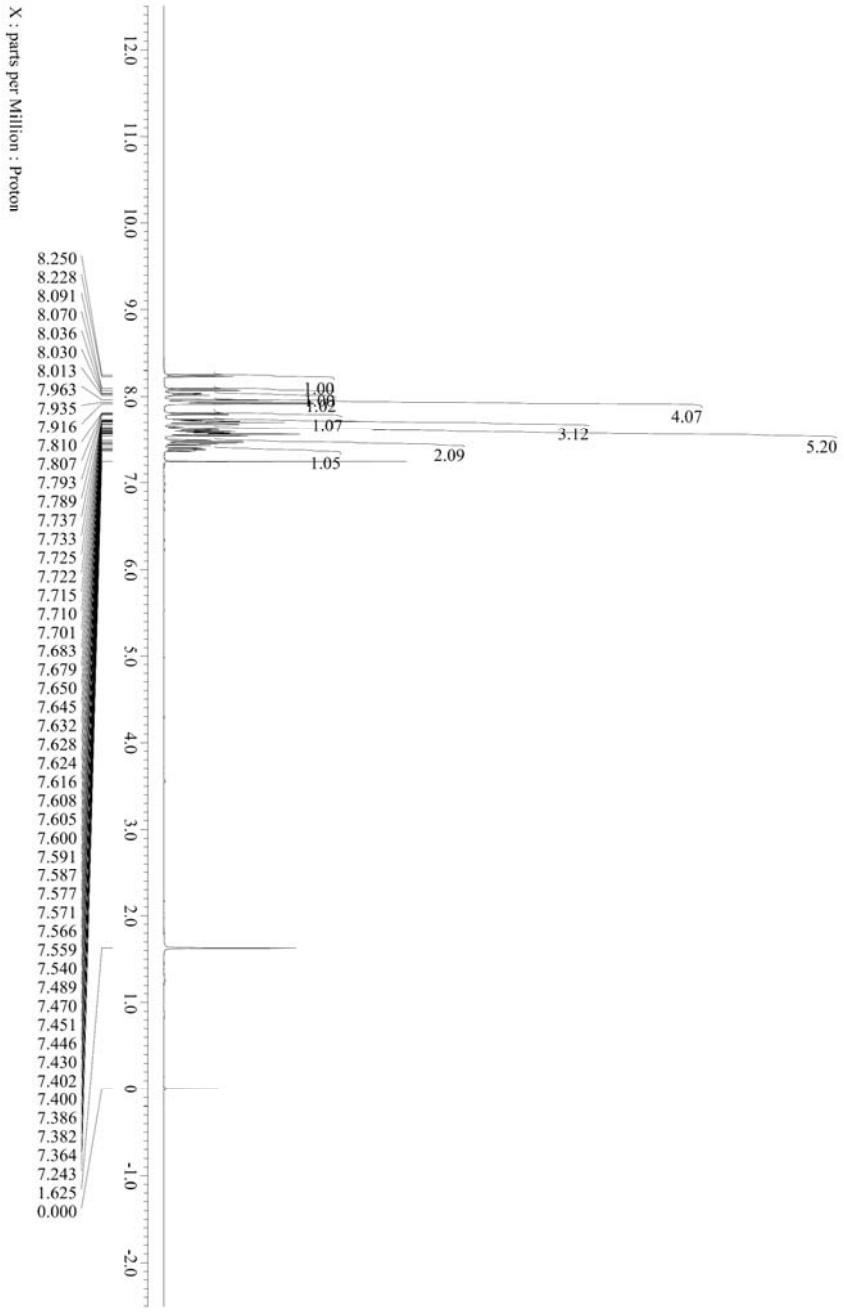


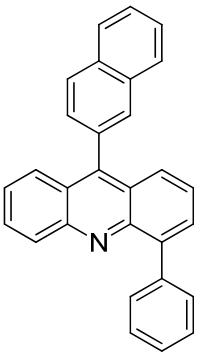


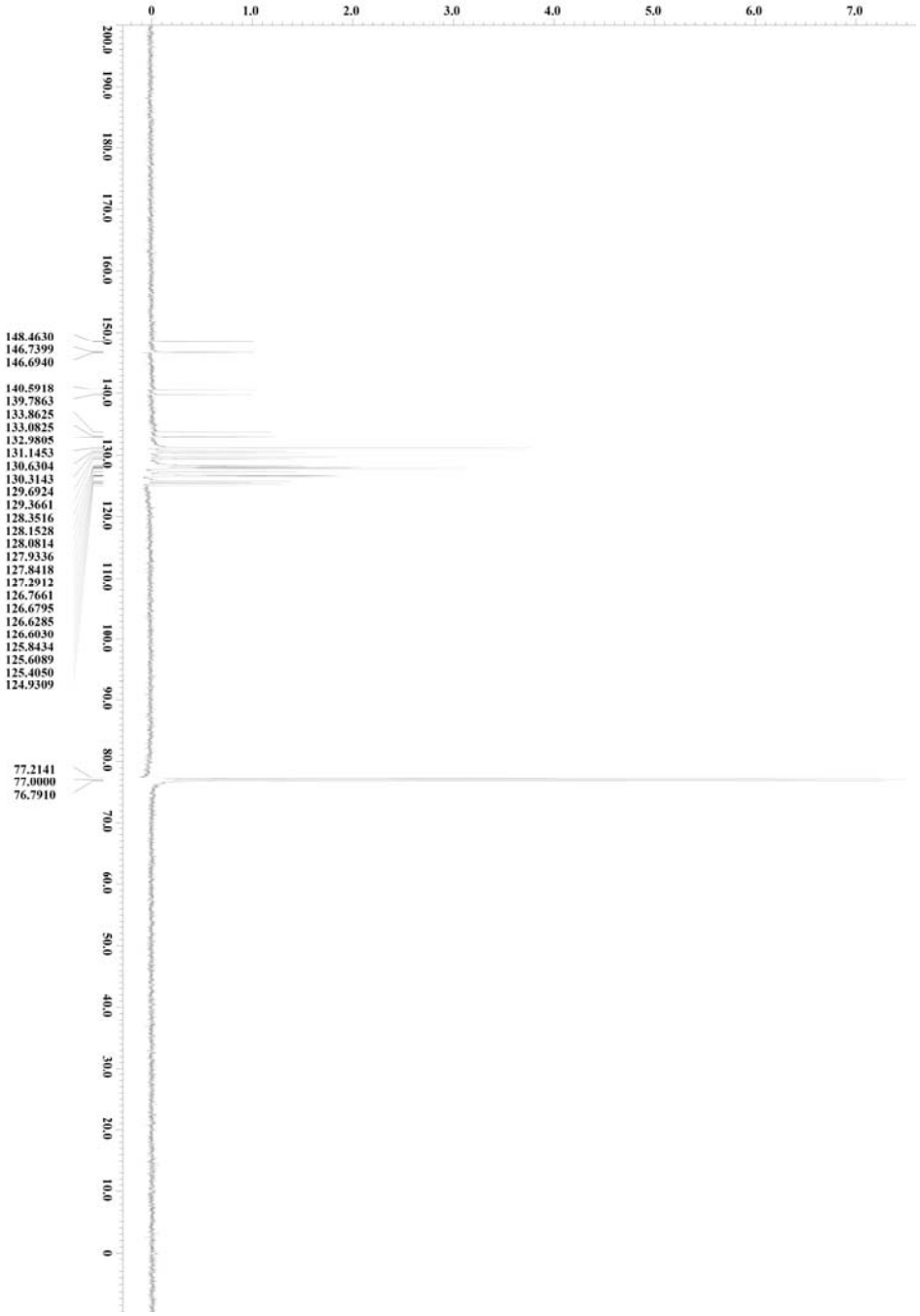


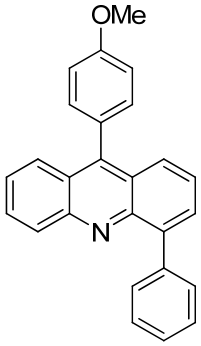


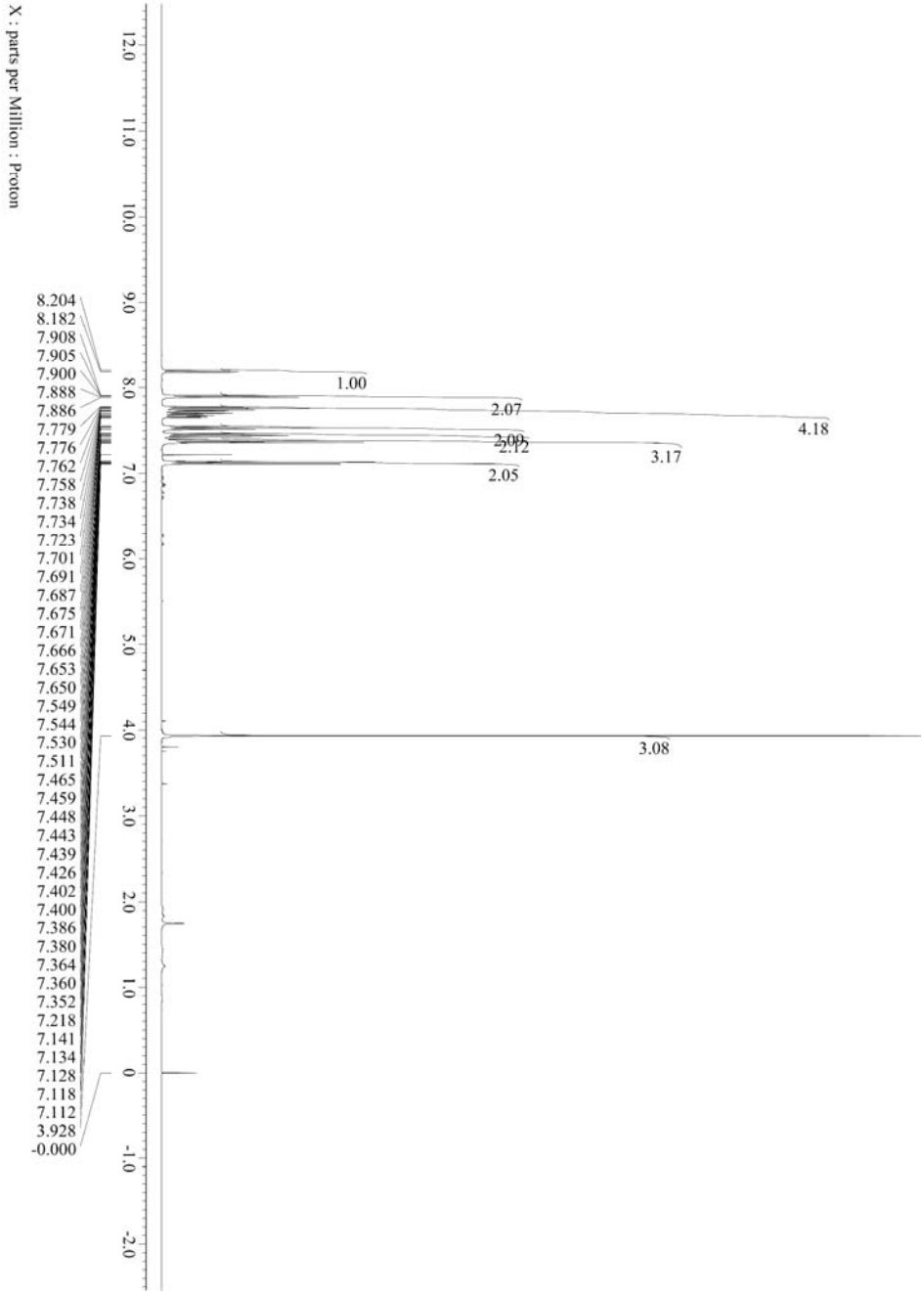


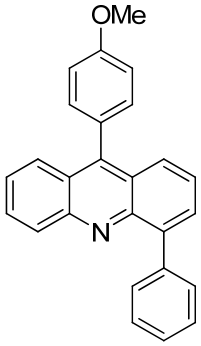


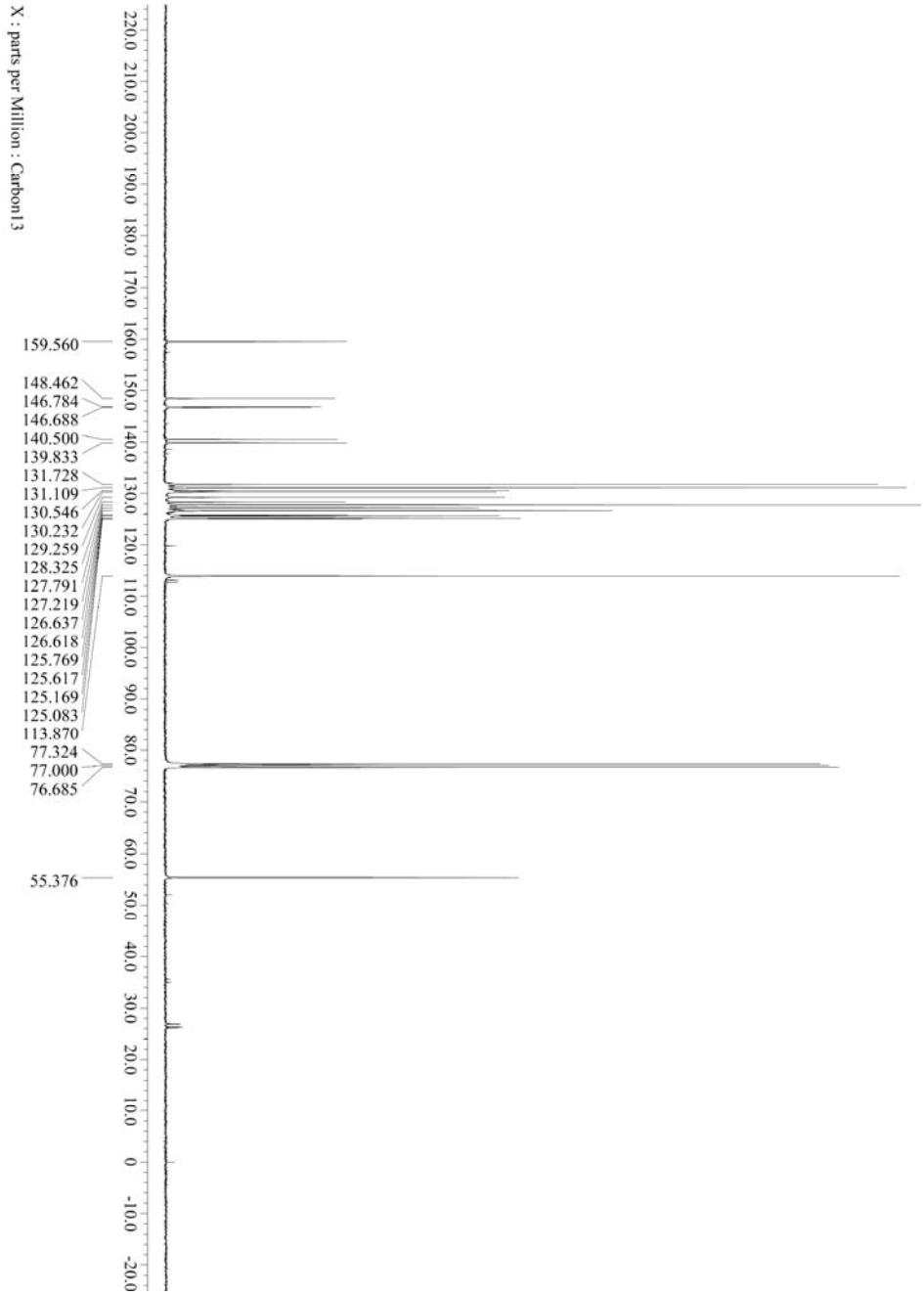


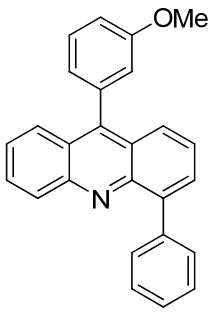


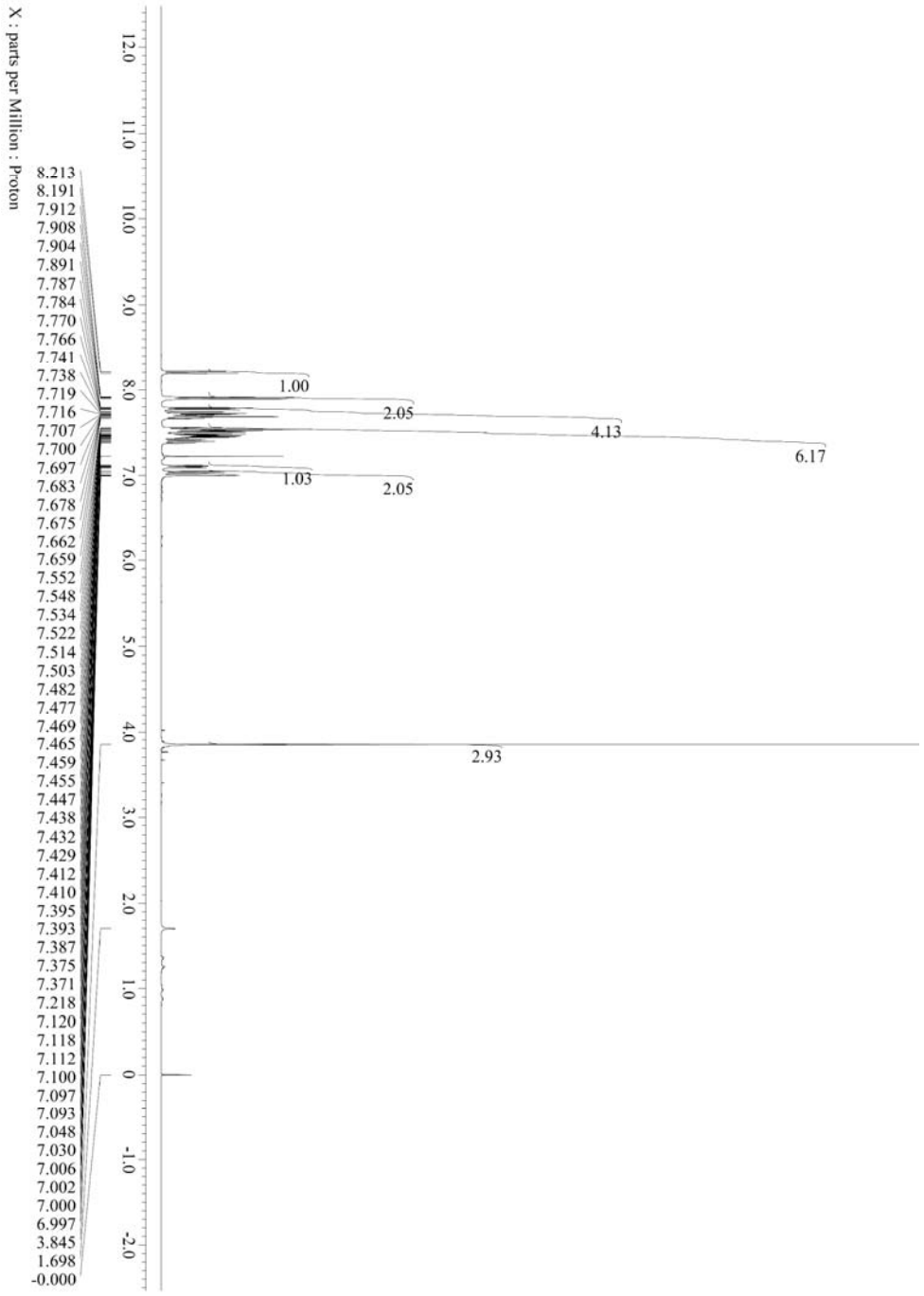


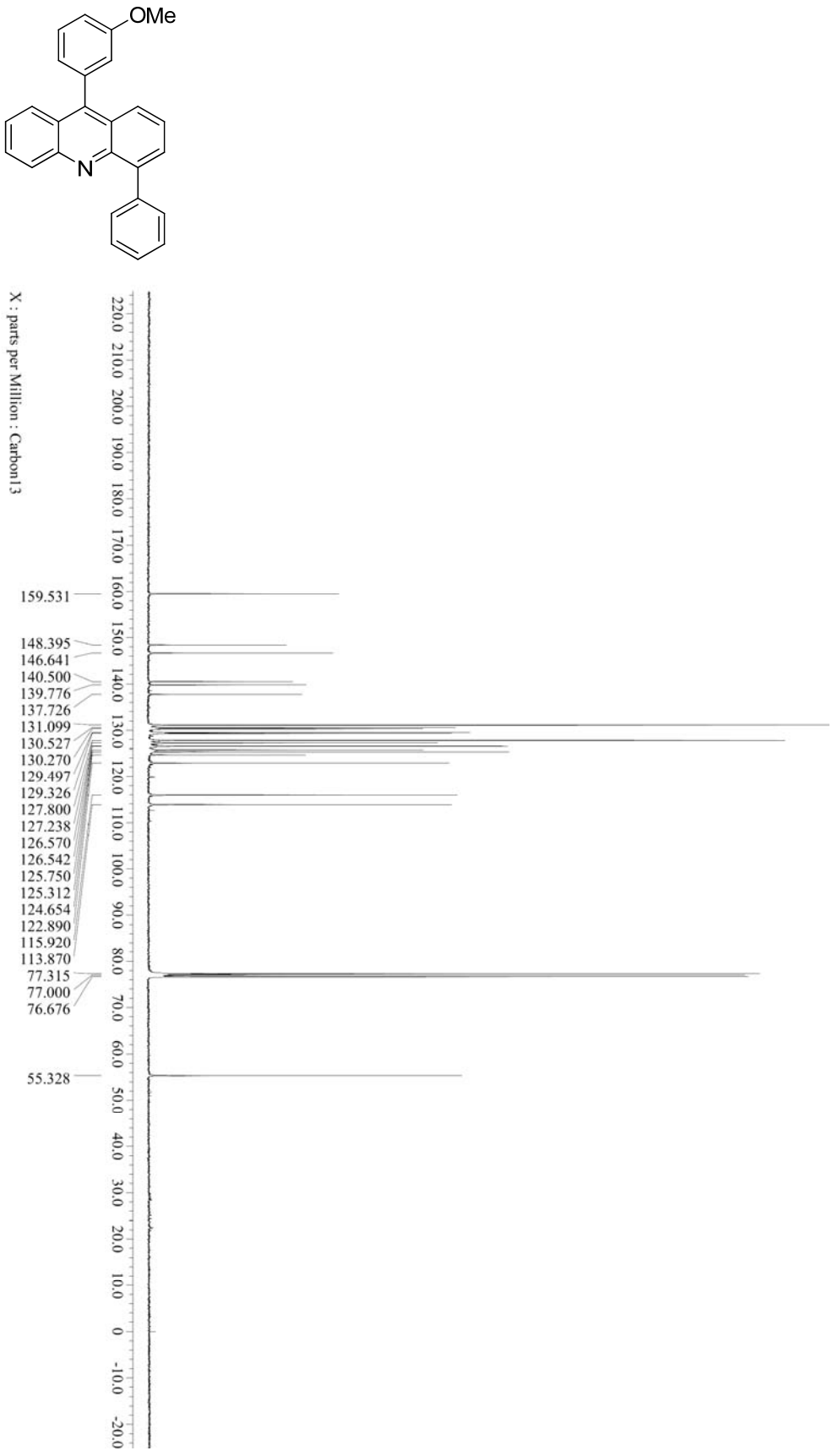


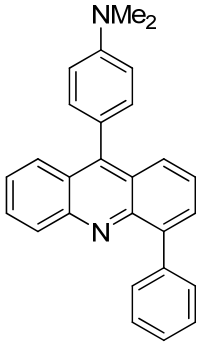


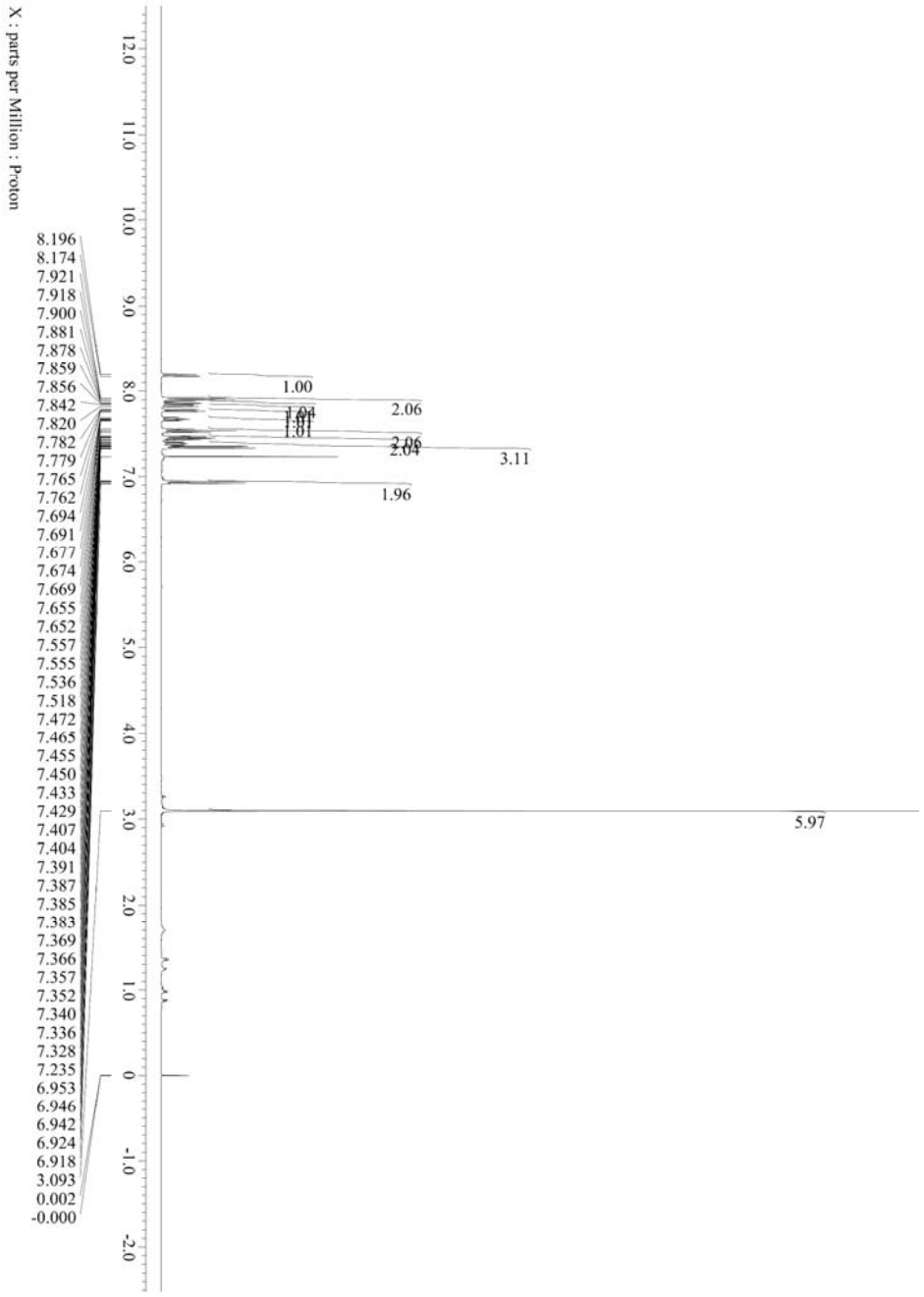


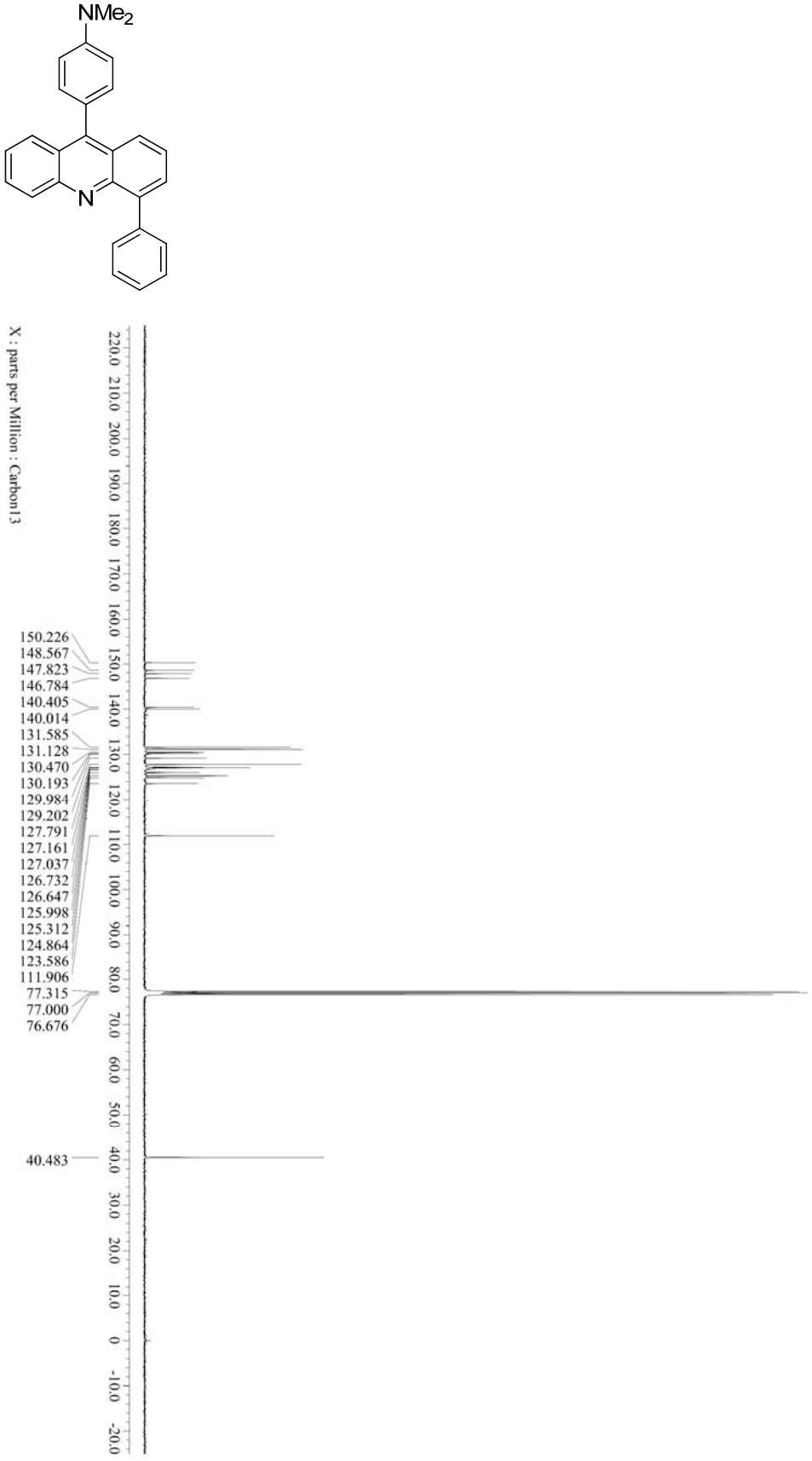


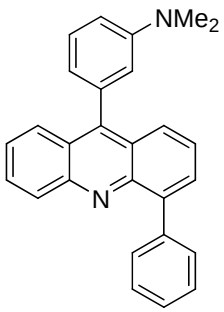








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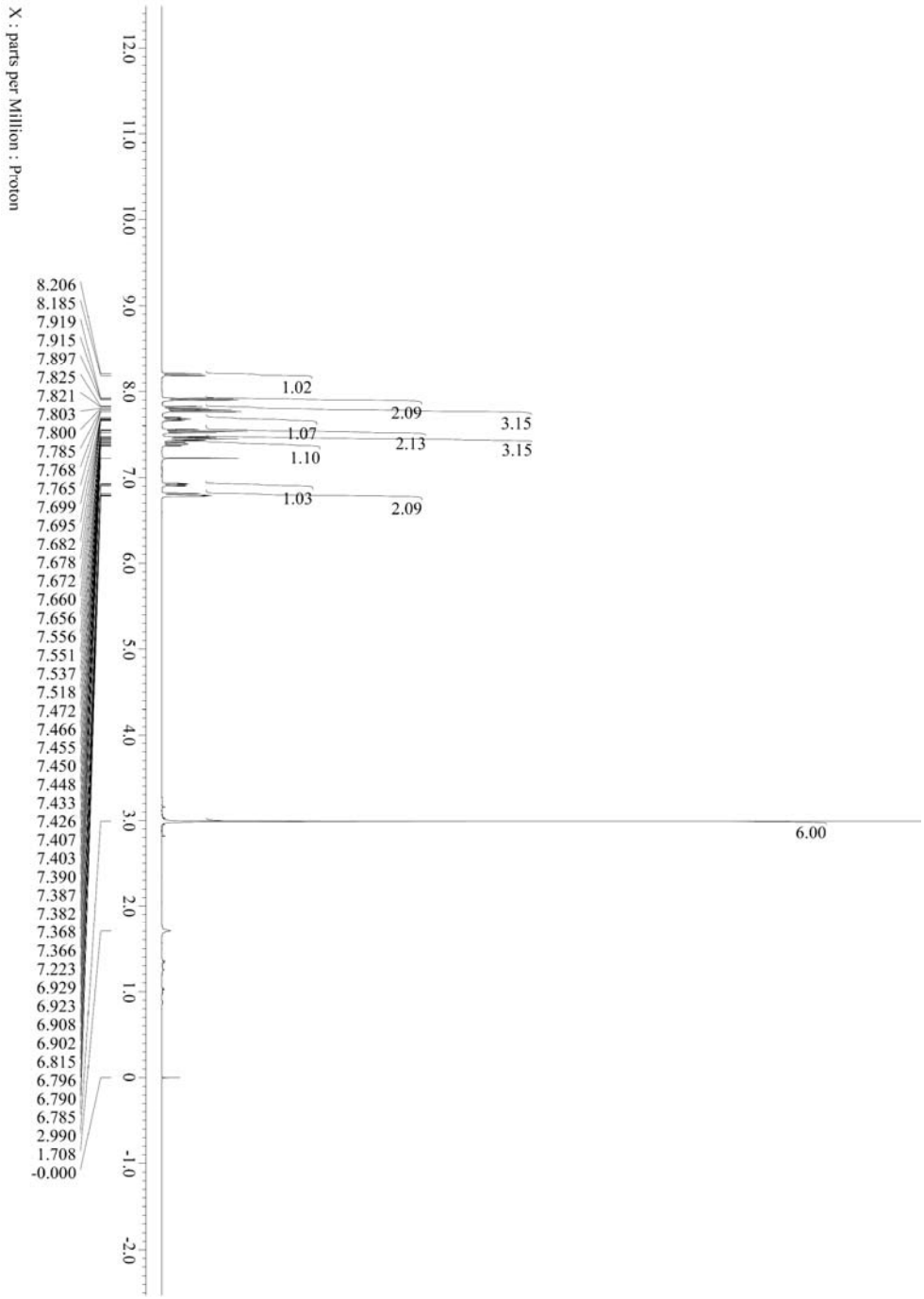
X : parts per Million : Proton
8.206
8.185
7.919
7.915
7.897
7.825
7.821
7.803
7.800
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7.765
7.699
7.695
7.682
7.678
7.672
7.660
7.656
7.556
7.551
7.537
7.518
7.472
7.466
7.455
7.450
7.448
7.433
7.426
7.407
7.403
7.390
7.387
7.382
7.368
7.366
7.223
6.929
6.923
6.908
6.902
6.815
6.796
6.790
6.785
2.990
1.708
-0.000
1.02
2.09
3.15
1.07
2.13
3.15
1.10
1.03
2.09
6.00
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
-2.0