Supporting Information

Carborane functionalized pyrroles and porphyrins via the Suzuki cross-coupling reaction

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Instrumentation and Materials

All reactions were monitored by TLC using 0.25 mm silica gel plates with or without UV indicator (60F-254). Silica gel Sorbent Technologies 32-63 μm was used for flash column chromatography. ^{1}H- and ^{13}C-NMR were obtained on either a DPX-250 or an ARX-300 Bruker spectrometer. Chemical shifts (δ) are given in ppm relative to $CDCl_3$ (7.26 ppm, ^{1}H) or CD_2Cl_2 (5.32 ppm, ^{1}H), unless otherwise indicated. Electronic absorption spectra were measured on a Perkin Elmer Lambda 35 UV-Vis spectrophotometer. MALDI-TOF mass spectra were obtained on an Applied Biosystems QSTAR XL, using positive method with dithranol as matrix unless otherwise indicated. Exact mass was obtained from ESI-TOF under negative or positive mode. The isotope peaks were matched with calculated patterns. Only the most abundant peaks are listed below (see the copy of spectra for isotope peaks). Unless otherwise noted, materials obtained from commercial suppliers were used without further purification.

General coupling procedure (9 as an example): A 50 mL shlenk reaction tube was charged with H_2TPPBr_4 (18.6 mg, 1 eq), $Pd(PPh_3)_4$ (4.6 mg, 0.2 eq), boronic acid **8** (58.4 mg, 10 eq), and anhydrous K_2CO_3 (55.2 mg, 20 eq). Anhydrous toluene (10 mL) was added via syringe. The mixture was degassed using the freeze-pump-thaw method three consecutive times. The reaction was then heated to 90 ºC for three days. The resulting mixture was purified by silica gel flash chromatography using $CHCl_3$ for elution.

Characterization data for new compounds:

Compound 2: ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.85 (2H, d, J = 7.76 Hz), 7.23 (2H, d, J = 7.81 Hz), 3.49 (2H, s), 2.19 (3H, s), 1.5-3.5 (10H, br), 1.41 (12H, s). ^{13}C-NMR (75 MHz, $CDCl_3$) δ 139.5, 136.6, 131.3, 85.6, 79.0, 78.3, 42.9, 26.5, 25.3. HRMS (ESI) $[M-C_2H(CH_3)_4]^-$: 291.2535, calcd. for $C_{10}H_{20}B_{11}O_2$: 291.2565.

Compound 3: ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.50 (2H, d, J = 8.19 Hz), 7.13 (2H, d, J = 8.31), 7.10 (1H, m), 6.82 (1H, m), 6.61 (1H, m), 3.45 (2H, s), 2.16 (3H, s), 1.5-3.5 (10H, br), 1.41 (3H, s), 1.11 (18H, m). MALDI-TOF $[M+H]^+$: 470.745, calcd. for $C_{23}H_{44}B_{10}NSi$: 470.782. HRMS (ESI) $[M + Na]^+$: 492.4086, calcd. for $C_{23}H_{43}B_{10}NSiNa$: 492.4078.

Compound 4: ^{1}H-NMR (250 MHz, CD_2Cl_2) δ 8.43 (1H, br), 7.53 (2H, d, J = 8.19 Hz), 7.15 (2H, d, J = 8.31), 7.14 (1H, m), 6.84 (1H, m), 6.53 (1H, m), 3.48 (2H, s), 2.18 (3H, s), 1.5-3.5 (10H, br), ^{13}C-NMR (75 MHz, CD_2Cl_2) δ 136.1, 132.5, 131.0, 125.4, 124.4, 119.4, 115.2, 106.6, 78.8, 75.7, 41.2, 23.9. MALDI-TOF $[M+H]^+$: 314.367, calcd. for $C_{14}H_{24}B_{10}N$: 314.442. HRMS (ESI) $[M-H]^-$: 312.2721, Calcd. for $C_{14}H_{22}B_{10}N$: 312.2721.

Compound 6: ^{1}H-NMR (250 MHz, $CDCl_3$) δ 7.67 (2H, d, J = 8.09 Hz), 6.92 (2H, d, J = 8.07 Hz), 3.39 (2H, s), 2.15 (3H, s), 1.5-3.5 (10H, br). ^{13}C-NMR (75 MHz, $CDCl_3$) δ

138.2, 134.9, 132.6, 94.3, 76.8, 74.8, 41.1, 24.1. HRMS (ESI) $[M-H]^-$: 373.1487, calcd. for $C_{10}H_8B_{10}I$: 373.1462.

Compound 8: ^{1}H-NMR (300 MHz, DMSO-d^6) δ 8.06 (2H, s), 7.74 (2H, d, J = 7.75), 7.21 (2H, d, J = 7.86), 3.32 (2H, s), 2.21 (3H, s), 1.5-3.5 (10H, br). ^{13}C-NMR (75 MHz, DMSO-d^6) δ 137.2, 134.1, 129.5, 78.9, 76.4, 75.2, 40.5, 22.9. HRMS (ESI) $[M-H]^-$: 291.2566, calcd. for $C_{10}H_{20}B_{11}O_2$: 291.2565.

Compound 9: ^{1}H-NMR (250 MHz, CD_2Cl_2 with 0.1 % TFA) δ 8.30 (8H, br), 8.24 (4H, s), 7.67-7.70 (12H, m), 6.71-6.74 (16H, m), 3.20-3.22 (8H, m), 2.05 (12H, s), 1.5-3.5 (40H, br). MS (MALDI-TOF) $[M^+]$: 1600.24 calcd. for $C_{84}H_{102}B_{40}N_4$: 1600.18. HRMS (ESI) $[M + H]^+$: 1601.2177, calcd. for $C_{84}H_{103}B_{40}N_4$: 1601.2214. UV-vis (CH_2Cl_2 with 1% NEt_3) λ_{max} (nm): 433 (log ε 5.41), 527 (4.25), 600 (3.79), 670 (3.54).

Compound 10: ^{1}H-NMR (250 MHz, CD_2Cl_2) δ 8.69-8.72 (2H, m), 8.56-8.58 (2H, m), 8.47-8.49 (1H, m), 8.25-8.29 (2H, m), 7.68-7.80 (8H, m), 7.23-7.39 (12H, m), 6.96-6.99 (2H, d, J = 8.21), 6.87-6.91 (4H, m), 6.66-6.69 (4H, d, J = 7.03), 3.39 (2H,s), 3.17 (4H, s), 2.21 (3H, s), 2.14 (6H, s), 1.5-3.5 (30H, br), -2.38 (2H, br). MS (MALDI-TOF) $[M^+]$: 1353.62, calcd. for $C_{74}H_{84}B_{30}N_4$: 1353.82. HRMS (ESI) $[M + H]^+$: 1354.9814, calcd. for $C_{74}H_{85}B_{30}N_4$: 1354.9795. UV-vis (CH_2Cl_2 with 1% NEt_3) λ_{max} (nm): 431 (log ε 5.51), 526 (4.41), 555 (sh, 4.18), 597 (4.05), 657 (3.72).

Compound 11: ^{1}H-NMR (250 MHz, CD_2Cl_2) δ 7.76 (8H, m), 7.24-7.32 (12H, m), 6.55-6.84 (32H, m), 3.18-3.34 (16H, m), 2.11-2.21 (24H, m), 1.5-3.5 (80H, br). MS (MALDI-TOF) $[M+H]^+$: 2643.807, calcd. for $C_{124}H_{173}B_{80}N_4Ni$: 2643.174. UV-vis ($CH_2Cl_2$) λ_{max} (nm): 441 (log ε 5.11), 556 (4.04), 597 (3.93).

Mass spectra for all new compounds:

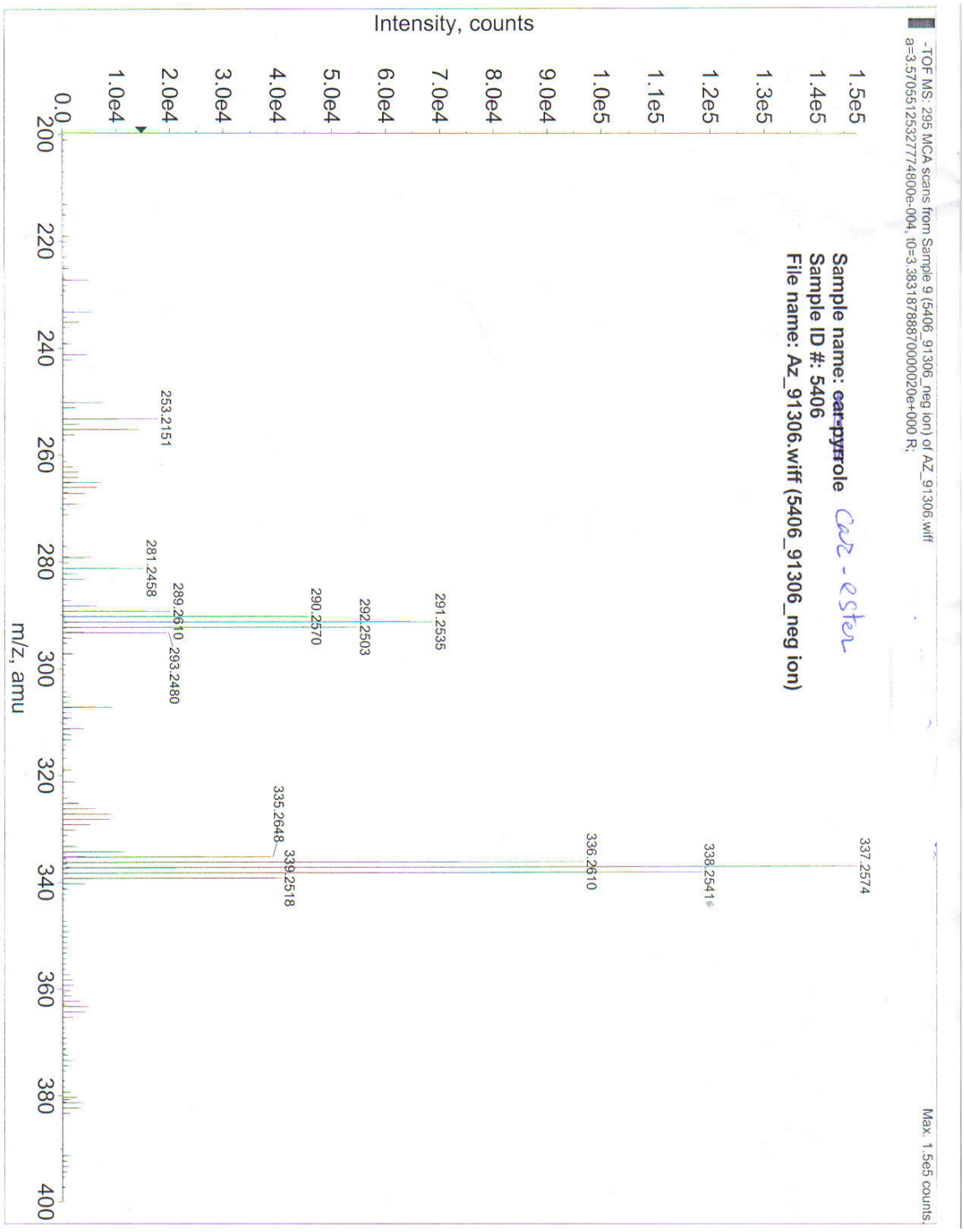

Figure 1: HRMS (ESI) for compound **2**.

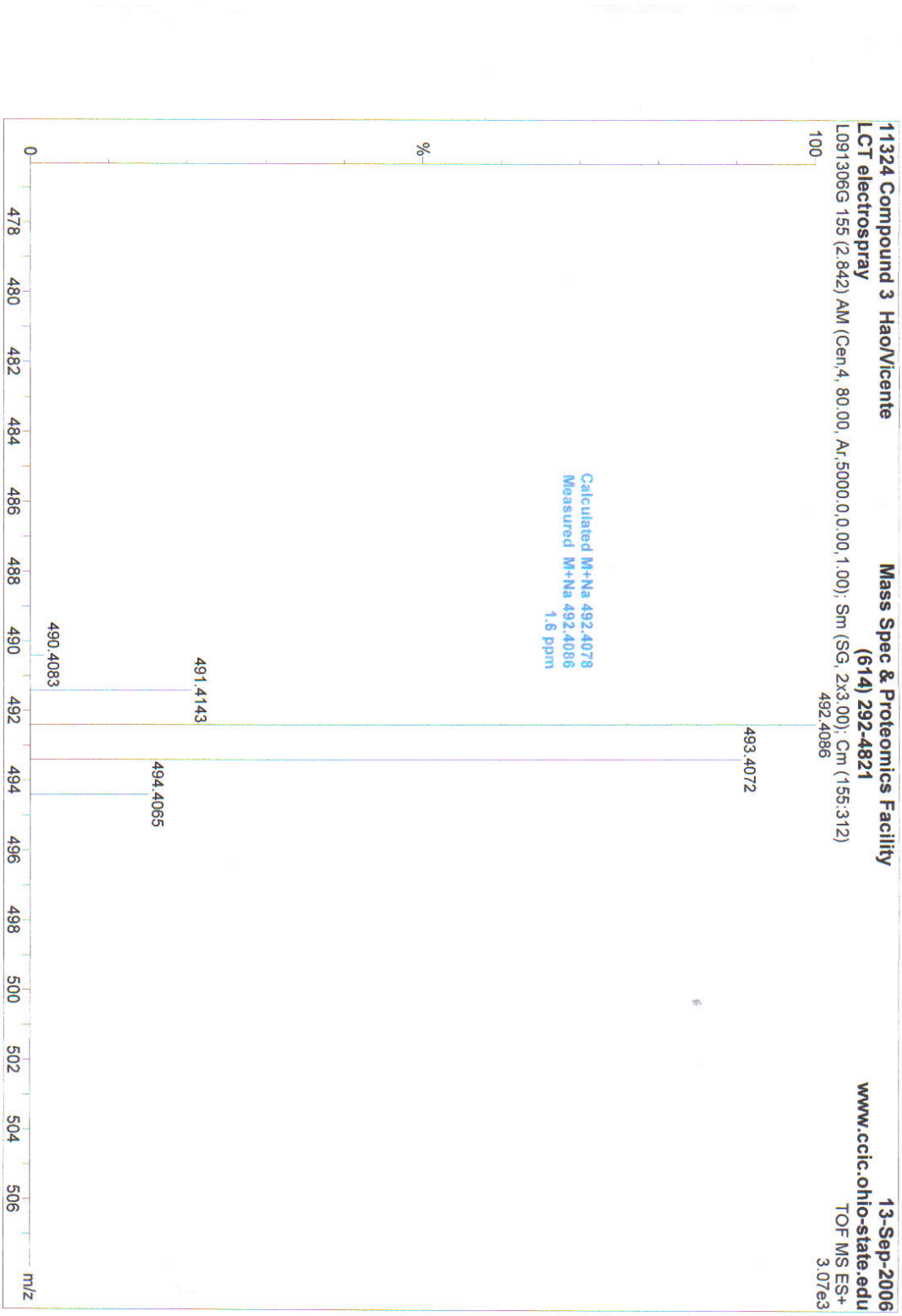

Figure 2: HRMS (ESI) for compound **3**.

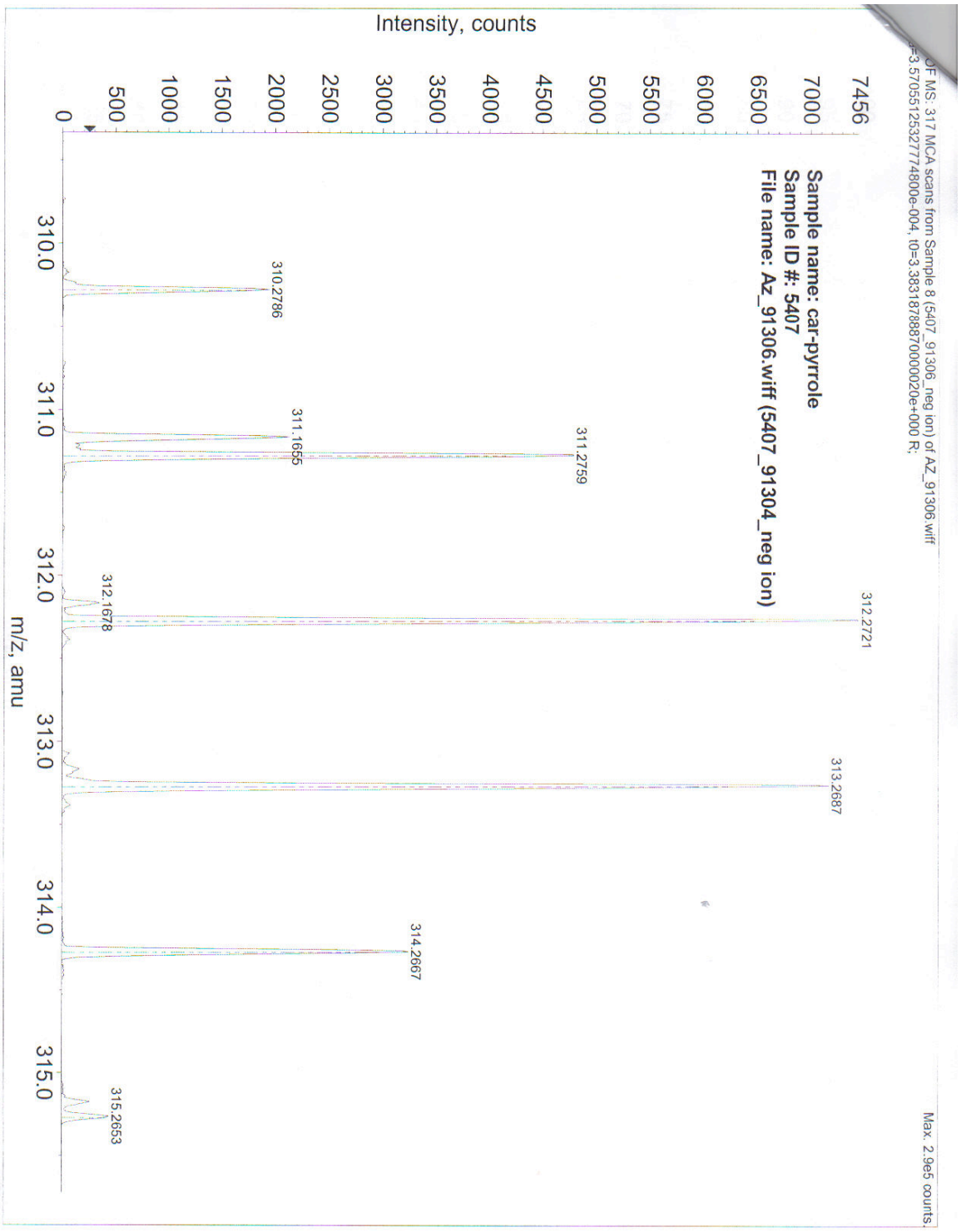

Figure 3: HRMS (ESI) for compound **4**.

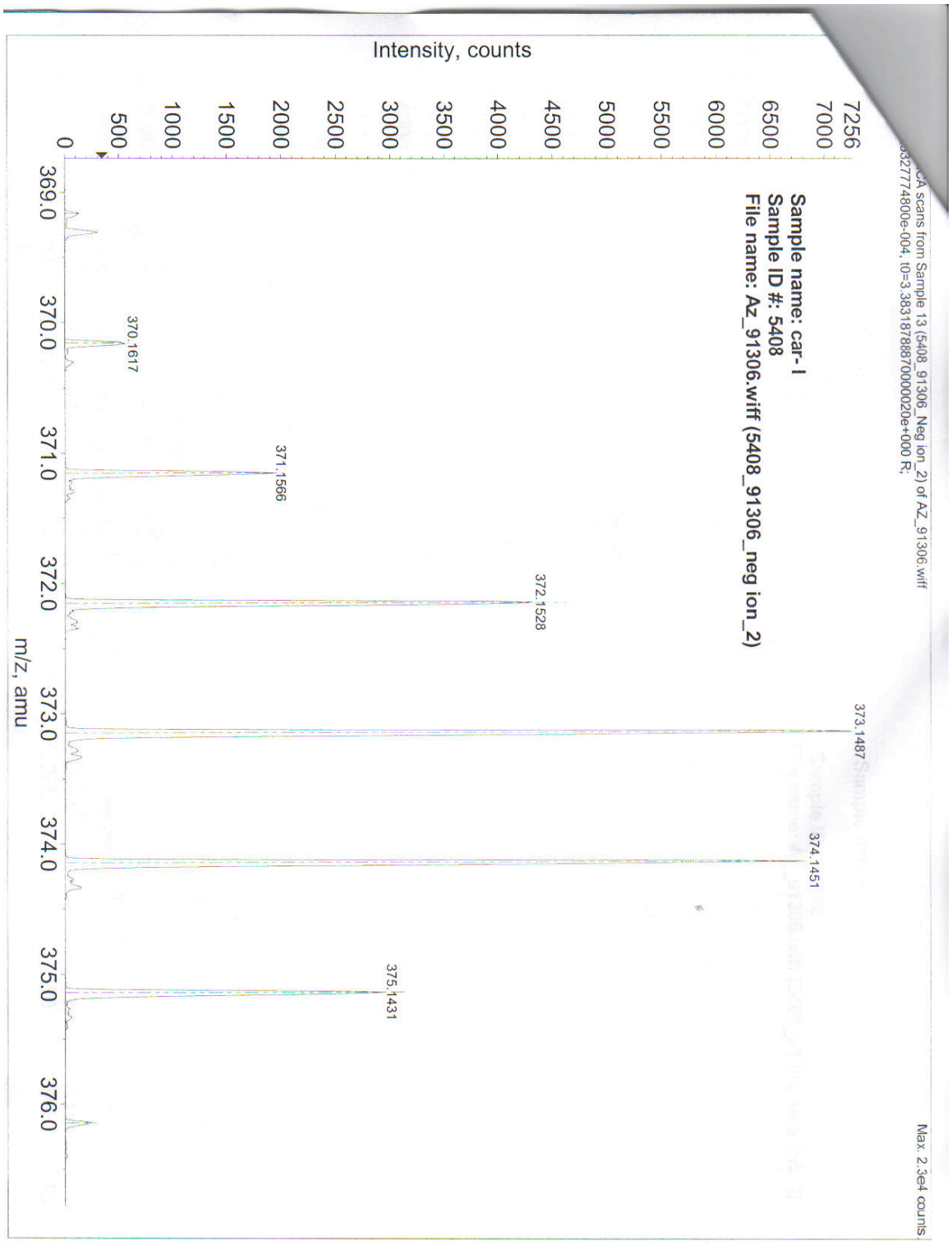

Figure 4: HRMS (ESI) for compound **6**.

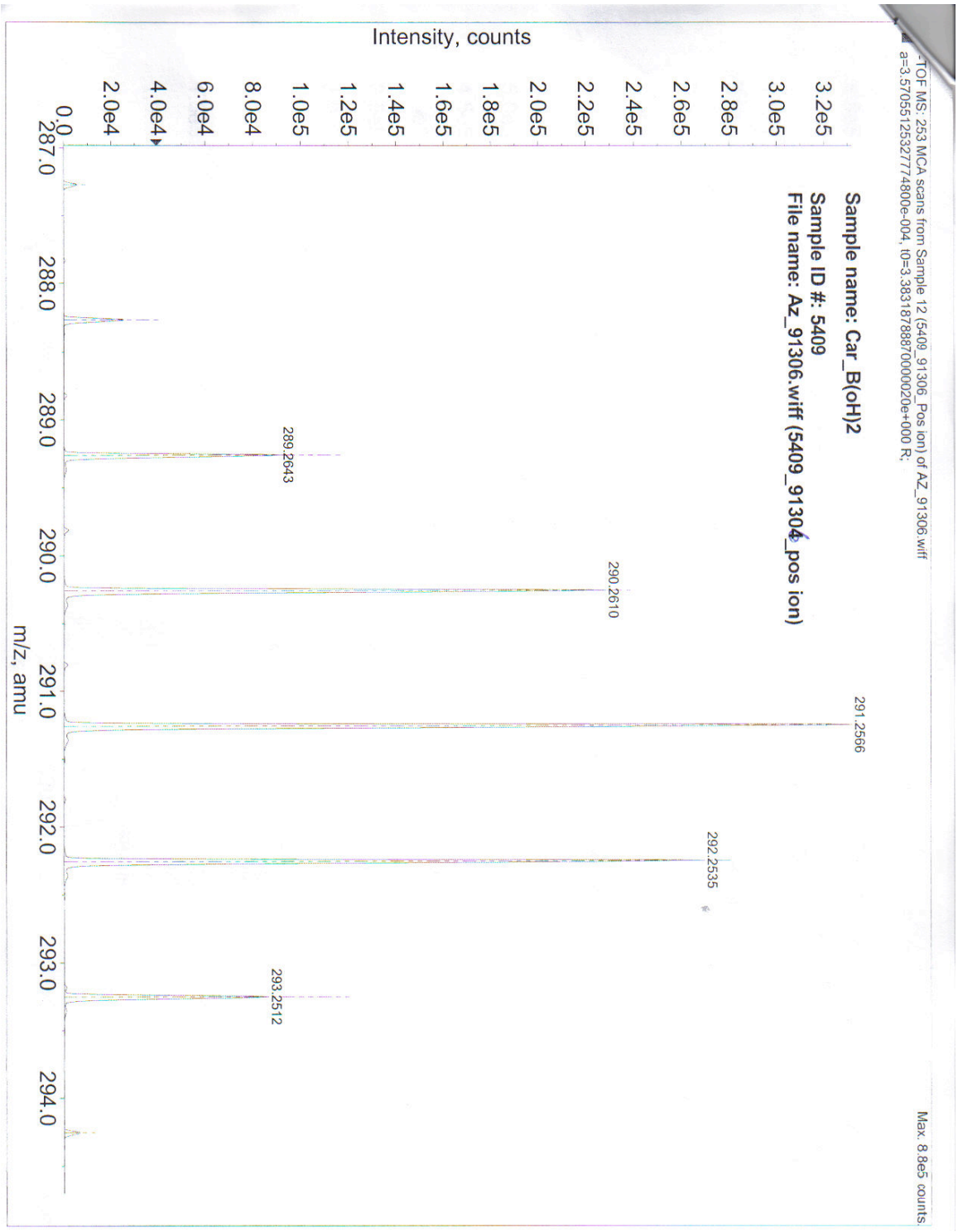

Figure 5: HRMS (ESI) for compound **8**.

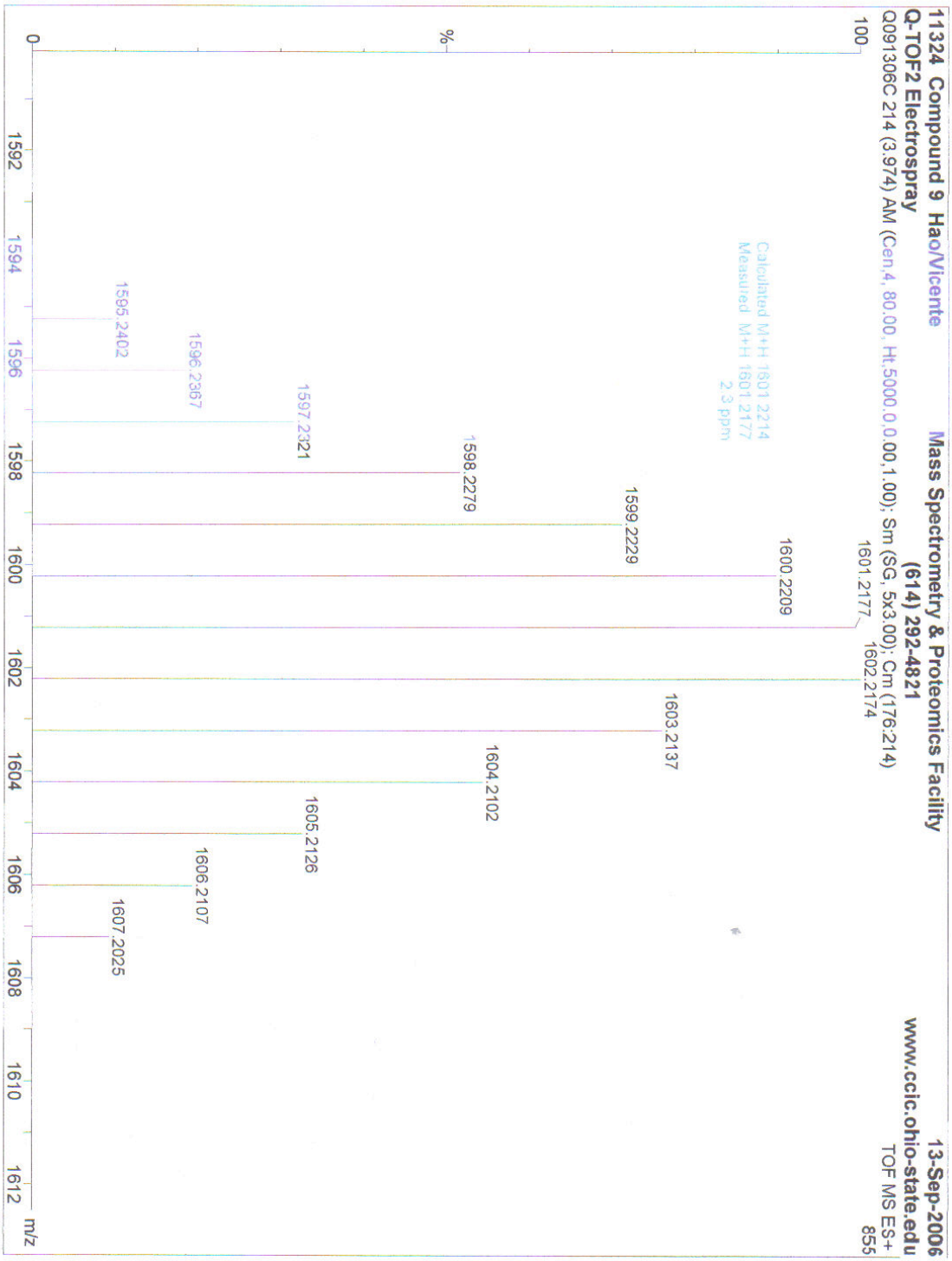

Figure 6: HRMS (ESI) for compound **9**.

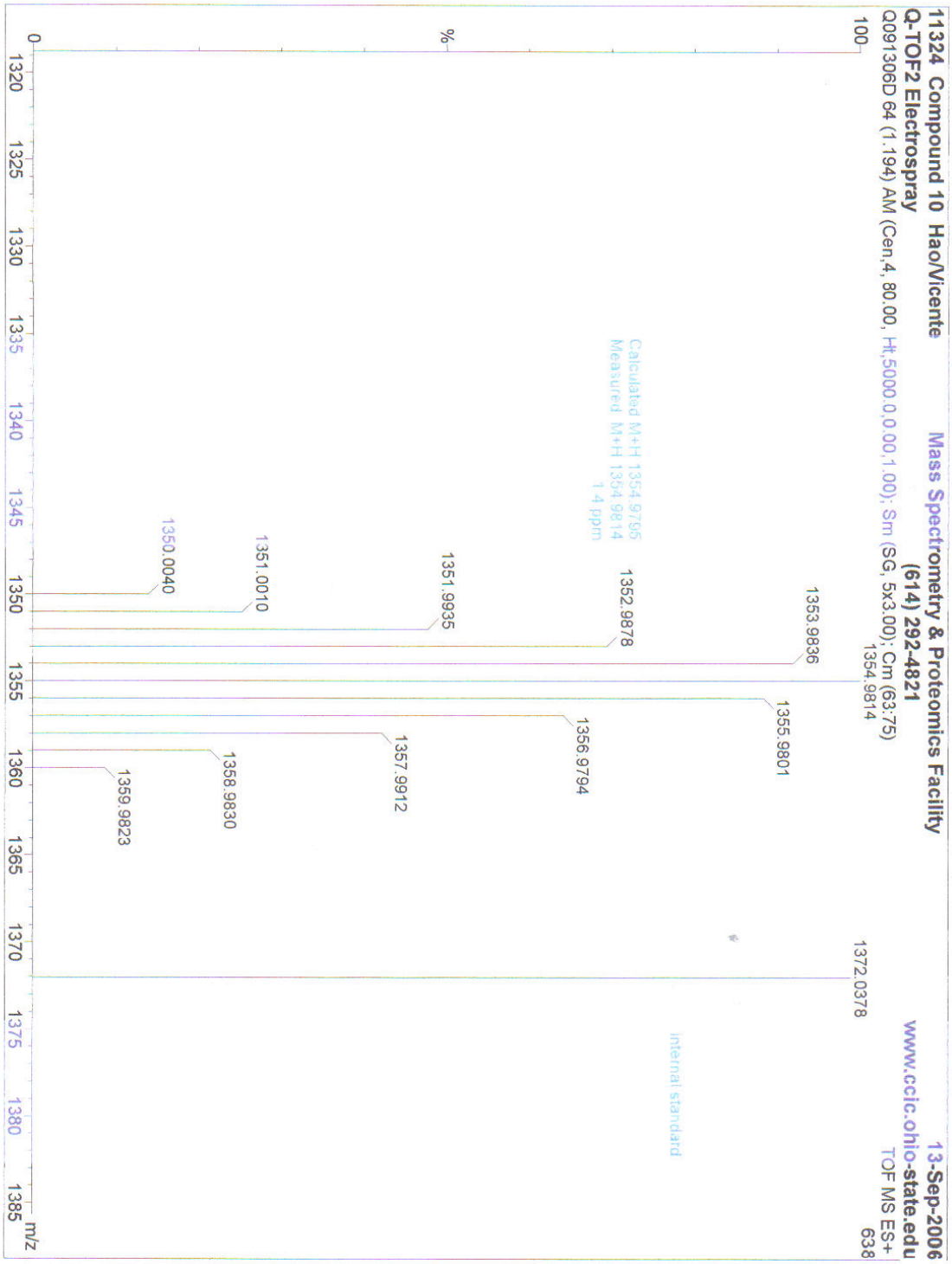

Figure 7: HRMS (ESI) for compound **10**.

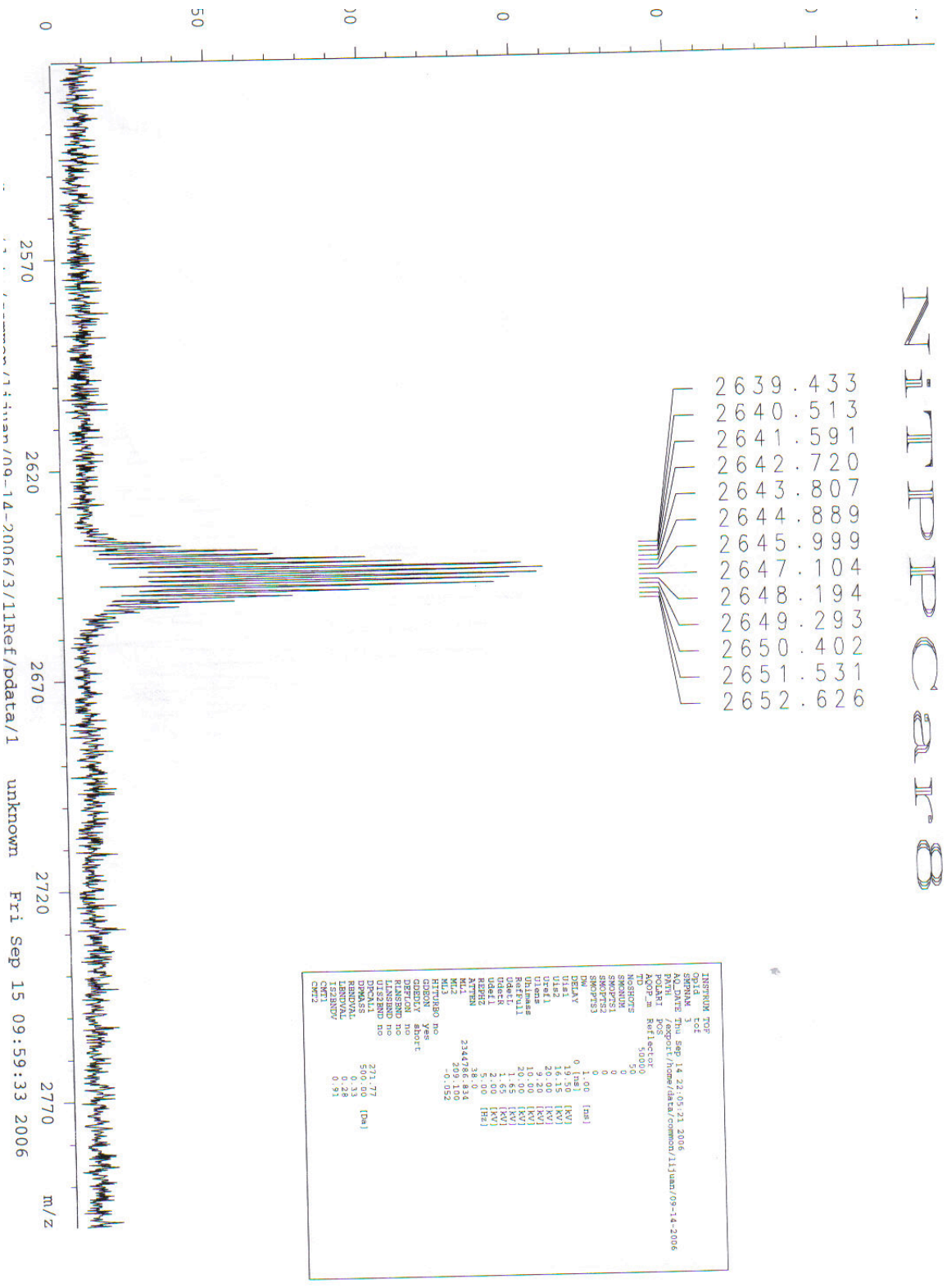

Figure 6: MALDI-TOF for compound **11**.