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Supporting Information

for

Unravelling a trichloroacetic acid-catalyzed cascade access to benzo[*f*]chromeno[2,3-*h*]quinoxalinoporphyrins

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Characterization data, ^1H and ^{13}C NMR spectra of newly prepared porphyrin products

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Characterization data of copper(II) benzo[*f*]chromeno[2,3-*h*]quinoxalino-porphyrins 3–8

Copper(II) benzo[*f*]chromeno[2,3-*h*]quinoxalinoporphyrin 3, Ar = 4-$CH_3C_6H_4$, **R** = C_6H_5

Purple solid; yield: 65%; mp >300°C; IR ($CHCl_3$) ν_{max}: 755, 796, 1003, 1039, 1179, 1210, 1344, 1450, 1507, 1597, 1659, 2872, 2957, 3021 cm^{-1}; UV λ_{max} ($\varepsilon \times 10^{-4}$, M^{-1} cm^{-1}): 408 (21.6), 445 (25.6), 562 (3.7), 604 (1.6) nm; ESI-HRMS (m/z) calcd for $C_{73}H_{55}N_6O_2Cu$: 1110.3677 $[M + H]^+$; found 1110.3607.

Copper(II) benzo[*f*]chromeno[2,3-*h*]quinoxalinoporphyrin 4, Ar = 4-$CH_3C_6H_4$, **R =** 4-$OCH_3C_6H_4$

Purple solid; yield: 67%; mp >300°C; IR ($CHCl_3$) ν_{max}: 758, 797, 1004, 1039, 1112, 1179, 1211, 1244, 1345, 1456, 1509, 1606, 1660, 2857, 2923, 3020 cm^{-1}; UV λ_{max} ($\varepsilon \times 10^{-4}$, M^{-1} cm^{-1}): 409 (23.2), 445 (27.6), 562 (4.4), 602 (2.2) nm; ESI-HRMS (m/z) calcd for $C_{74}H_{57}N_6O_3Cu$: 1140.3783 $[M + H]^+$; found 1140.3784.

Copper(II) benzo[*f*]chromeno[2,3-*h*]quinoxalinoporphyrin 5, Ar = 4-$CH_3C_6H_4$, **R =** 4-$NO_2C_6H_4$

Purple solid; yield: 65%; mp >300°C; IR ($CHCl_3$) ν_{max}: 763, 798, 1004, 1181, 1213, 1345, 1458, 1518, 1661, 1744, 2323, 2365, 2854, 2923, 3021 cm^{-1}; UV λ_{max} ($\varepsilon \times 10^{-4}$, M^{-1} cm^{-1}): 410 (24.6), 447 (23.3), 564 (4.4), 603 (2.4) nm; ESI-HRMS (m/z) calcd for $C_{73}H_{54}N_7O_4Cu$: 1155.3528 $[M + H]^+$; found 1155.3525.

Copper(II) benzo[*f*]chromeno[2,3-*h*]quinoxalinoporphyrin 6, Ar = 4-$CH_3C_6H_4$, **R** = 4-BrC_6H_4

Purple solid; yield: 61%; mp >300°C; IR ($CHCl_3$) ν_{max}: 753, 796, 1004, 1178, 1211, 1259, 1344, 1455, 1511, 1656, 2858, 2921, 2958, 3018 cm^{-1}; UV λ_{max} ($\varepsilon \times 10^{-4}$, M^{-1} cm^{-1}): 418 (19.3), 444 (13.3), 564 (2.0), 602 (0.6) nm; ESI-HRMS (m/z) calcd for $C_{73}H_{54}BrN_6O_2Cu$: 1188.2782 $[M + H]^+$; found 1188.2777.

Copper(II) benzo[*f*]chromeno[2,3-*h*]quinoxalinoporphyrin 7, Ar = C_6H_5, **R =** C_6H_5

Purple solid; yield: 68%; mp >300°C; IR ($CHCl_3$) ν_{max}: 700, 750, 796, 1003, 1071, 1212, 1344, 1448, 1514, 1596, 1656, 2957, 3020 cm^{-1}; UV λ_{max} ($\varepsilon \times 10^{-4}$, M^{-1} cm^{-1}): 422 (29.9), 443 (19.9) 561 (3.4), 601 (1.7) nm; ESI-HRMS (m/z) calcd for $C_{69}H_{47}N_6O_2Cu$: 1054.3051 $[M + H]^+$; found 1054.3062.

Copper(II) benzo[*f*]chromeno[2,3-*h*]quinoxalinoporphyrin 8, Ar = C_6H_5, **R =** 4-BrC_6H_4
Purple solid; yield: 66%; mp >300°C; IR ($CHCl_3$) ν_{max}: 759, 797, 1005, 1179, 1211, 1344, 1453, 1510, 1659, 2852, 2921, 3021 cm^{-1}; UV λ_{max} ($\varepsilon \times 10^{-4}$, M^{-1} cm^{-1}): 421 (18.0), 445 (17.6), 562 (2.8), 600 (1.5) nm; ESI-HRMS (m/z) calcd for $C_{69}H_{46}N_6O_2BrCu$: 1132.2156 $[M + H]^+$; found 1132.2150.

Characterization data of free-base benzo[*f*]chromeno[2,3-*h*]quinoxalino-porphyrins 9–13

Free-base benzo[*f*]chromeno[2,3-*h*]quinoxalinoporphyrin 9, Ar = 4-$CH_3C_6H_4$, **R** = C_6H_5
Purple solid; yield: 80%; mp >300°C; IR ($CHCl_3$) ν_{max}: 669, 751, 795, 970, 1031, 1154, 1209, 1301, 1347, 1460, 1509, 1598, 1656, 2850, 2917, 3018, 3346 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: -2.56 (s, 2H, internal NH), 1.17(s, 3H, CH_3), 1.57 (s, 3H, CH_3), 2.47(dd, *J* = 16.02 Hz, 2H, CH_2), 2.71-2.72 (m, 6H, CH_3), 2.82 (s, 2H, CH_2), 2.86 (s, 3H, CH_3), 2.94 (s, 3H, CH_3), 5.79 (s, 1H, CH), 6.82 (t, *J* = 7.63 Hz, 1H, ArH), 6.93 (t, *J* = 7.63 Hz, 2H, ArH), 7.16 (d, *J* = 7.63 Hz, 2H, ArH), 7.54-7.84 (m, 11H, *meso*-ArH, ArH), 8.00-8.22 (m, 7H, *meso*-ArH), 8.40 (d, *J* = 7.63 Hz, 1H, ArH), 8.63 (d, *J* = 7.63 Hz, 1H, ArH), 8.75 (s, 2H, *β*-pyrrolic H), 8.91-8.98 (m, 4H, *β*-pyrrolic H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ_C: 14.13, 21.53, 21.74, 21.90, 27.25, 32.16, 32.37, 41.41, 51.28, 115.48, 117.08, 117.98, 118.17, 121.23, 121.47, 125.73, 125.76, 127.41, 127.49, 127.53, 127.75, 127.88, 128.10, 128.14, 128.36, 128.58, 128.76, 131.56, 133.90, 134.12, 134.18, 134.40, 134.48, 134.57, 137.24, 137.28, 137.45, 137.48, 138.10, 138.20, 138.36, 138.61, 138.75, 138.87, 139.05, 139.48, 139.63, 140.33, 144.79, 145.51, 146.71, 149.98, 151.76, 154.89, 155.11, 164.12, 196.25 ppm; UV λ_{max} ($\varepsilon \times 10^{-4}$, M^{-1} cm^{-1}): 441 (28.9), 529 (2.7), 568 (0.3), 600 (1.3), 642 (0.1) nm; λ_{Em} ($CHCl_3$; λ_{Ex} 420 nm): 668, 730 nm; ESI-HRMS (m/z) calcd for $C_{73}H_{57}N_6O_2$: 1049.4538 $[M + H]^+$; found 1049.4558.

Free-base benzo[*f*]chromeno[2,3-*h*]quinoxalinoporphyrin 10, Ar = 4-$CH_3C_6H_4$, **R** = 4-$OCH_3C_6H_4$
Purple solid; yield: 78%; mp >300°C; IR ($CHCl_3$) ν_{max}: 755 796, 972, 1039, 1170, 1210, 1302, 1372, 1463, 1509, 1606, 1658, 2592, 2679, 2858, 2922, 3018, 3348 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: -2.36 (s, 2H, internal NH), 1.33 (s, 3H, CH_3), 1.41 (s, 3H, CH_3), 2.63 (dd, *J* = 16.02, Hz, 2H, CH_2), 2.85-2.86 (m, 6H, CH_3), 2.97 (s, 2H, CH_2), 3.05 (s, 3H, CH_3), 3.08 (s, 3H, CH_3), 3.64 (s, 3H, OCH_3), 5.91 (s, 1H, CH), 6.65 (d, *J* = 9.16, Hz, 2H, ArH), 7.28 (s, 1H, ArH), 7.69-7.76 (m, 4H, *meso*-ArH, ArH), 7.83-7.96 (m, 6H, *meso*-ArH), 8.07-8.10 (m, 1H, *meso*-ArH), 8.20-8.39 (m, 8H, *meso*-ArH), 8.55 (d, *J* = 7.63 Hz, 1H, ArH), 8.78 (d, *J* = 8.39, Hz, 1H, ArH), 8.92 (s, 2H, *β*-pyrrolic H), 9.09-9.15 (m, 4H, *β*-pyrrolic H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$)

δ_C: 14.13, 21.51, 21.72, 21.93, 27.25, 31.44, 32.37, 41.38, 51.29, 54.83, 112.77, 115.58, 117.11, 118.16, 118.20, 121.21, 121.24, 121.48, 125.75, 125.77, 127.50, 127.52, 127.74, 127.90, 128.12, 128.16, 128.59, 128.74, 129.39, 131.52, 133.93, 134.13, 134.45, 134.56, 135.24, 137.23, 137.32, 137.44, 137.47, 138.11, 138.22, 138.42, 138.67, 138.75, 138.86, 139.00, 139.50, 139.62, 140.36, 144.80, 145.58, 146.52, 149.97, 151.76, 154.90, 155.13, 157.45, 163.85, 196.31 ppm; UV λ_{max} ($\varepsilon \times 10^{-4}$, M^{-1} cm^{-1}): 441 (53.0), 529 (4.4), 570 (0.5), 600 (2.0), 640 (0.1) nm; λ_{Em} ($CHCl_3$; λ_{Ex} 440 nm): 672, 728 nm; ESI-HRMS (m/z) calcd for $C_{74}H_{59}N_6O_3$: 1079.4643 $[M + H]^+$; found 1079.4649.

Free-base benzo[*f*]chromeno[2,3-*h*]quinoxalinoporphyrin 11, Ar = 4-$CH_3C_6H_4$, **R =** 4-$NO_2C_6H_4$

Purple solid; yield: 70%; mp >300°C; IR ($CHCl_3$) ν_{max}: 722, 761, 797, 971, 1040, 1162, 1211, 1304, 1345, 1464, 1518, 1599, 1661, 2854, 2923, 3023, 3348 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: -2.55 (s, 2H, internal NH), 1.14 (s, 3H, CH_3), 1.56 (s, 3H, CH_3), 2.48 (dd, *J* = 16.02, 2H, CH_2), 2.71-2.72 (m, 6H, CH_3), 2.85 (s, 2H, CH_2), 2.88 (s, 3H, CH_3), 2.93 (s, 3H, CH_3), 5.87 (s, 1H, CH), 7.29-7.31 (m, 2H, ArH), 7.57-7.92 (m, 14H, *meso*-ArH, ArH), 8.07-8.22 (m, 6H, *meso*-ArH), 8.42 (d, *J* = 7.63 Hz, 1H, ArH), 8.64 (d, *J* = 7.63 Hz, 1H, ArH), 8.74 (s, 2H, *β*-pyrrolic H), 8.89-8.95 (m, 4H, *β*-pyrrolic H) ppm; UV λ_{max} ($\varepsilon \times 10^{-4}$, M^{-1} cm^{-1}): 441 (21.8), 530 (3.8), 569 (0.4), 600 (2.6), 638 (0.1) nm; λ_{Em} ($CHCl_3$; λ_{Ex} 430 nm): 672, 730 nm; ESI-HRMS (m/z) calcd for $C_{73}H_{56}N_7O_4$: 1094.4388 $[M + H]^+$; found 1094.4395.

Free-base benzo[*f*]chromeno[2,3-*h*]quinoxalinoporphyrin 12, Ar = 4-$CH_3C_6H_4$, **R** = 4-BrC_6H_4

Purple solid; yield: 77%; mp >300°C; IR ($CHCl_3$) ν_{max}:755, 796, 971, 1041, 1156, 1209, 1302, 1368, 1472, 1510, 1600, 1659, 2860, 2920, 2956, 3020, 3345 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: -2.54 (s, 2H, internal NH), 1.16 (s, 3H, CH_3), 1.27 (s, 3H, CH_3), 2.48 (dd, *J* = 16.02, 2H, CH_2), 2.72 (s, 6H, CH_3), 2.83 (s, 2H, CH_2), 2.89 (s, 3H, CH_3), 2.94 (s, 3H, CH_3), 5.76 (s, 1H, CH), 7.02-7.07 (m, 4H, ArH), 7.58-7.88 (m, 10H, *meso*-ArH, ArH), 8.04-8.24 (m, 7H, *meso*-ArH), 8.35-8.41 (m, 2H, ArH), 8.64 (d, *J* = 8.39 Hz, 1H, ArH), 8.75-8.77 (m, 2H, *β*-pyrrolic H), 8.90-8.97 (m, 4H, *β*-pyrrolic H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ_C: 21.53. 21.74, 21.89, 27.21, 29.79, 31.97, 32.38, 41.37, 51.21, 114.95, 117.10, 117.33, 118.05, 119.65, 121.27, 121.56, 125.58, 125.81, 127.51, 127.54, 127.76, 127.94, 128.09, 128.21, 128.60, 128.85, 130.30, 130.46, 131.64, 133.95, 134.18, 134.54, 137.26, 137.29, 137.48, 137.51, 138.13, 138.26, 138.43, 138.46, 138.70, 138.83, 139.03, 139.48, 139.63, 140.34, 143.87, 144.61, 145.27, 146.60, 150.07, 151.68, 154.94, 155.19, 164.16, 196.22 ppm; UV λ_{max} ($\varepsilon \times 10^{-4}$, M^{-1}

cm^{-1}): 441 (25.0), 529 (2.2), 568 (0.3), 600 (1.1), 639 (0.1) nm; λ_{Em} ($CHCl_3$; λ_{Ex} 440 nm): 671, 730 nm; ESI-HRMS (m/z) calcd for $C_{73}H_{56}N_6O_2Br$: 1127.3643 [M + H]$^+$; found 1127.3647.

Free-base benzo[*f*]chromeno[2,3-*h*]quinoxalinoporphyrin 13, Ar = C_6H_5, **R =** C_6H_5 Purple solid; yield: 76%; mp >300°C IR ($CHCl_3$) ν_{max}: 750, 798, 968, 1158, 1207, 1347, 1440, 1596, 1657, 2882, 2960, 3022, 3058, 3344 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: -2.56 (s, 2H, internal NH), 1.19 (s, 3H, CH_3), 1.28 (s, 3H, CH_3), 2.51 (dd, J_1 = 16.78 Hz and J_2 = 16.02 Hz, 2H, CH_2), 2.83 (s, 2H, CH_2), 5.77 (s, 1H, CH), 6.84-6.87 (m, 1H, *meso*-ArH), 6.96 (t, J = 7.63 Hz, 2H, ArH), 7.19 (d, J = 8.39 Hz, 2H, ArH), 7.74-7.94 (m, 11H, *meso*-ArH), 8.01-8.05 (m, 2H, ArH), 8.10-8.22 (m, 4H, *meso*-ArH), 8.29-8.34 (m, 4H, *meso*-ArH), 8.40 (d, J = 7.63 Hz, 1H, ArH), 8.47-8.49 (m, 1H, ArH), 8.58 (d, J = 8.39 Hz, 1H, ArH), 8.75 (s, 2H, β-pyrrolic H), 8.92-8.96 (m, 4H, β-pyrrolic H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ_C: 27.20, 29.90, 31.76, 32.41, 41.40, 51.30, 115.56, 117.13, 117.92, 118.24, 121.20, 121.28, 121.53, 125.71, 125.82, 125.87, 126.79, 127.12, 127.24, 127.39, 127.43, 127.56, 127.84, 127.97, 128.25, 128.65, 128.86, 129.29, 131.43, 134.04, 134.22, 134.45, 134.57, 134.92, 135.01, 137.24, 138.04, 138.09, 138.71, 139.52, 140.10, 141.76, 141.89, 142.52, 144.59, 144.78, 145.52, 147.03, 150.08, 151.85, 154.84, 155.03, 164.67, 196.76 ppm; UV λ_{max} ($\varepsilon \times 10^{-4}$, M^{-1} cm^{-1}): 439 (37.9), 527 (3.8), 567 (0.5), 597 (1.9), 637 (0.1) nm; λ_{Em} ($CHCl_3$; λ_{Ex} 435 nm): 668, 726 nm; ESI-HRMS (m/z) calcd for $C_{69}H_{49}N_6O_2$: 993.3912 [M + H]$^+$; found 993.3905.

Characterization data of zinc(II) benzo[*f*]chromeno[2,3-*h*]quinoxalino-porphyrins 14–16

Zinc(II) benzo[*f*]chromeno[2,3-*h*]quinoxalinoporphyrin 14, Ar = 4-$CH_3C_6H_4$, **R** = C_6H_5 Purple solid; yield: 78%; mp >300°C; IR ($CHCl_3$) ν_{max}: 758, 796, 1000, 1039, 1175, 1212, 1303, 1340, 1371, 1406, 1450, 1505, 1605, 1653, 2859, 2922, 3021 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 1.18 (s, 6H, CH_3), 2.47(dd, J = 15.26 Hz, 2H, CH_2), 2.72 (s, 6H, CH_3), 2.83 (s, 2H, CH_2), 2.86 (s, 3H, CH_3), 2.94 (s, 3H, CH_3), 5.86 (s, 1H, CH), 6.84 (t, J = 6.87 Hz, 1H, ArH), 6.94 (d, J = 7.63 Hz, 2H, ArH), 7.16 (d, J = 7.63 Hz, 2H, ArH), 7.53-7.58 (m, 4H, *meso*-ArH), 7.64 (t, J = 6.10 Hz, 2H, ArH), 7.73-7.79 (m, 4H, *meso*-ArH), 7.99-8.09 (m, 4H, *meso*-ArH), 8.16 (t, J = 6.87 Hz, 3H, *meso*-ArH), 8.26 (d, J = 6.87 Hz, 1H, *meso*-ArH), 8.37 (d, J = 7.63 Hz, 1H, ArH), 8.63 (d, J = 7.63 Hz, 1H, ArH), 8.81 (d, J = 4.58 Hz, 1H, β-pyrrolic H), 8.88 (s, 2H, β-pyrrolic H), 8.92-8.97 (m, 3H, β-pyrrolic H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ_C: 21.53, 21.75, 21.94, 27.25, 29.83, 32.15, 32.37, 41.40, 51.28, 115.55, 117.56, 117.92, 118.79, 121.25, 122.99, 123.28, 125.78, 125.96, 127.33, 127.42, 127.62, 127.66, 127.83, 127.94, 128.39, 128.90, 131.33, 131.46, 131.54, 132.02, 132.17, 133.48, 133.76, 134.17, 134.29, 134.47, 136.89, 137.19, 137.21, 137.67, 138.24, 139.00, 139.11, 139.61, 139.63, 140.31, 140.61, 141.04, 144.75, 146.94, 147.81, 149.15, 149.20, 149.79, 149.86, 149.99, 152.36, 153.07, 164.20, 196.26 ppm; UV λ_{max} ($\varepsilon \times 10^{-4}$, M^{-1} cm^{-1}): 450 (19.0), 574 (2.8), 615 (1.2) nm; λ_{Em} ($CHCl_3$; λ_{Ex} 430 nm): 632, 675 nm; ESI-HRMS (m/z) calcd for $C_{73}H_{55}N_6O_2Zn$: 1111.3672 $[M + H]^+$; found 1111.3694.

Zinc(II) benzo[*f*]chromeno[2,3-*h*]quinoxalinoporphyrin 15, Ar = 4-$CH_3C_6H_4$, **R** = 4-$OCH_3C_6H_4$

Purple solid; yield: 80%; mp >300°C; IR ($CHCl_3$) ν_{max}: 759, 796, 1001, 1039, 1175, 1213, 1340, 1371, 1454, 1509, 1607, 1651, 2858, 2923, 3019 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ_H: 1.16 (s, 3H, CH_3), 1.25 (s, 3H, CH_3), 2.45 (dd, *J* = 15.26, 2H, CH_2), 2.71 (s, 6H, CH_3), 2.81 (s, 2H, CH_2), 2.86 (s, 3H, CH_3), 2.93 (s, 3H, CH_3), 3.46 (s, 3H, OCH_3), 5.77 (s, 1H, CH), 6.46 (d, *J* = 9.16 Hz, 2H, ArH), 7.07 (d, *J* = 8.39 Hz, 2H, ArH), 7.52-7.63 (m, 6H, *meso*-ArH, ArH), 7.73-7.82 (m, 3H, *meso*-ArH), 7.96-8.19 (m, 8H, *meso*-ArH), 8.28 (d, *J* = 8.39 Hz, 1H, ArH), 8.38 (d, *J* = 7.63 Hz, 1H, ArH), 8.65 (d, *J* = 8.39 Hz, 1H, ArH), 8.81 (d, *J* = 4.58 Hz, 1H, *β*-pyrrolic H), 8.86 (s, 2H, *β*-pyrrolic H), 8.91-8.95 (m, 3H, *β*-pyrrolic H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ_C: 21.53, 21.73, 21.91, 27.24, 29.84, 31.39, 32.36, 41.36, 51.24, 54.82, 112.74, 115.63, 117.53, 118.11, 118.71, 121.15, 122.95, 123.22, 125.73, 125.88, 127.32, 127.49, 127.59, 127.63, 127.84, 127.88, 128.80, 129.37, 131.32, 131.34, 131.43, 131.52, 131.97, 132.15, 133.45, 133.78, 134.17, 134.23, 134.31, 134.56, 136.83, 137.15, 137.18, 137.23, 137.64, 138.25, 139.06, 139.08, 139.62, 140.30, 140.60, 141.00, 146.68, 147.78, 149.11, 149.17, 149.77, 149.82, 149.95, 152.34, 153.03, 157.40, 163.92, 196.33 ppm; UV λ_{max} ($\varepsilon \times 10^{-4}$, M^{-1} cm^{-1}): 428 (18.5), 451 (19.0), 574 (2.8), 618 (1.2) nm; λ_{Em} ($CHCl_3$; λ_{Ex} 435 nm): 625, 677 nm; ESI-HRMS (m/z) calcd for $C_{74}H_{57}N_6O_3Zn$: 1141.3778 $[M + H]^+$; found 1141.3775.

Zinc(II) benzo[*f*]chromeno[2,3-*h*]quinoxalinoporphyrin 16, Ar = C_6H_5, **R =** C_6H_5

Purple solid; yield: 80%; mp >300°C; IR ($CHCl_3$) ν_{max}: 698, 750, 795, 831, 999, 1069, 1173, 1211, 1338, 1444, 1483, 1597, 1652, 2852, 2920, 2954, 3020, 3056 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ_H: 1.24 (s, 3H, methyl H), 1.19 (s, 3H, methyl H), 2.48 (dd, *J* = 16.78, 2H, CH_2), 2.84 (s, 2H, CH_2), 5.81(s, 1H, CH), 6.85 (t, *J* = 7.63 Hz, 1H, ArH), 6.96 (t, *J* = 7.63 Hz, 2H, ArH), 7.19 (d, *J* = 7.63 Hz, 2H, ArH), 7.73-7.84 (m, 10H, *meso*-ArH), 7.91-7.96 (m, 2H, *meso*-ArH), 8.01 (t, *J* = 7.63 Hz, 1H, ArH), 8.08-8.22 (m, 5H, *meso*-ArH), 8.26-8.30 (m, 3H, *meso*-ArH), 8.39 (d, *J* = 7.63 Hz, 2H, ArH), 8.61 (d, *J* = 7.63 Hz, 1H, ArH), 8.86-8.88 (m, 4H, *β*-pyrrolic H), 8.92-8.95 (m, 2H, *β*-pyrrolic H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ_C: 27.18, 31.75, 32.40, 41.38, 51.26, 115.61, 117.60, 117.84, 118.83, 121.21, 122.99, 123.26, 125.75, 125.89, 125.99, 126.58, 126.97, 127.01, 127.12, 127.28, 127.47, 127.55, 127.60, 128.28, 129.00, 131.32, 131.43, 131.54, 131.63, 132.06, 132.13, 132.24, 133.59, 133.88, 134.09, 134.21, 134.31, 134.47, 137.63, 139.06, 140.55, 141.02, 141.86, 142.54, 143.28, 144.54, 147.19, 147.87, 149.11, 149.77, 149.89, 152.37, 152.82, 164.70, 196.77 ppm; UV λ_{max} ($\varepsilon \times 10^{-4}$, M^{-1} cm^{-1}): 449 (15.4), 572 (2.4), 613 (1.0) nm; λ_{Em} ($CHCl_3$; λ_{Ex} 440 nm): 623, 678 nm; ESI-HRMS (m/z) calcd for $C_{69}H_{47}N_6O_2Zn$: 1055.3046 [M + H]$^+$; found 1055.3046.

Characterization data of copper(II) benzo[*f*]quinoxalinoporphyrin 17, Ar = 4-$CH_3C_6H_4$ Purple solid; yield: 67%; mp >300°C; IR ($CHCl_3$) ν_{max}: 796, 1004, 1183, 1222, 1346, 1453, 1511, 1604, 1689, 2856, 2923, 3023 cm^{-1}; UV λ_{max} ($\varepsilon \times 10^{-4}$, M^{-1} cm^{-1}): 441 (13.8), 559 (3.0), 600 (1.4) nm; ESI-HRMS (m/z) calcd for $C_{58}H_{41}CuN_6O$: 900.2632 [M + H]$^+$; found 900.2635.

^{1}H and ^{13}C NMR spectra of free-base and zinc(II) porphyrins 9–16

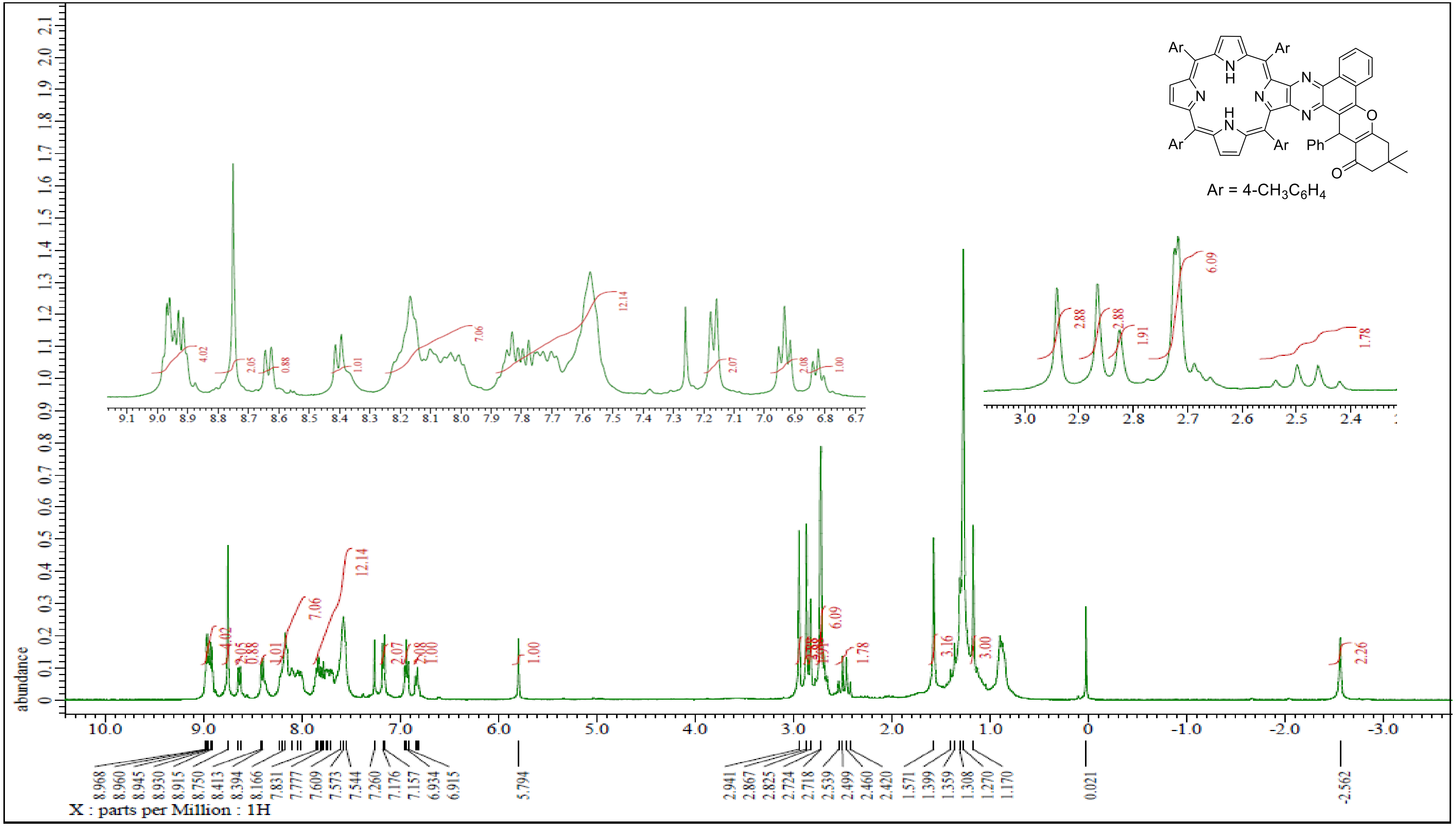

Figure 1. ^{1}H NMR spectrum of porphyrin **9** in $CDCl_3$.

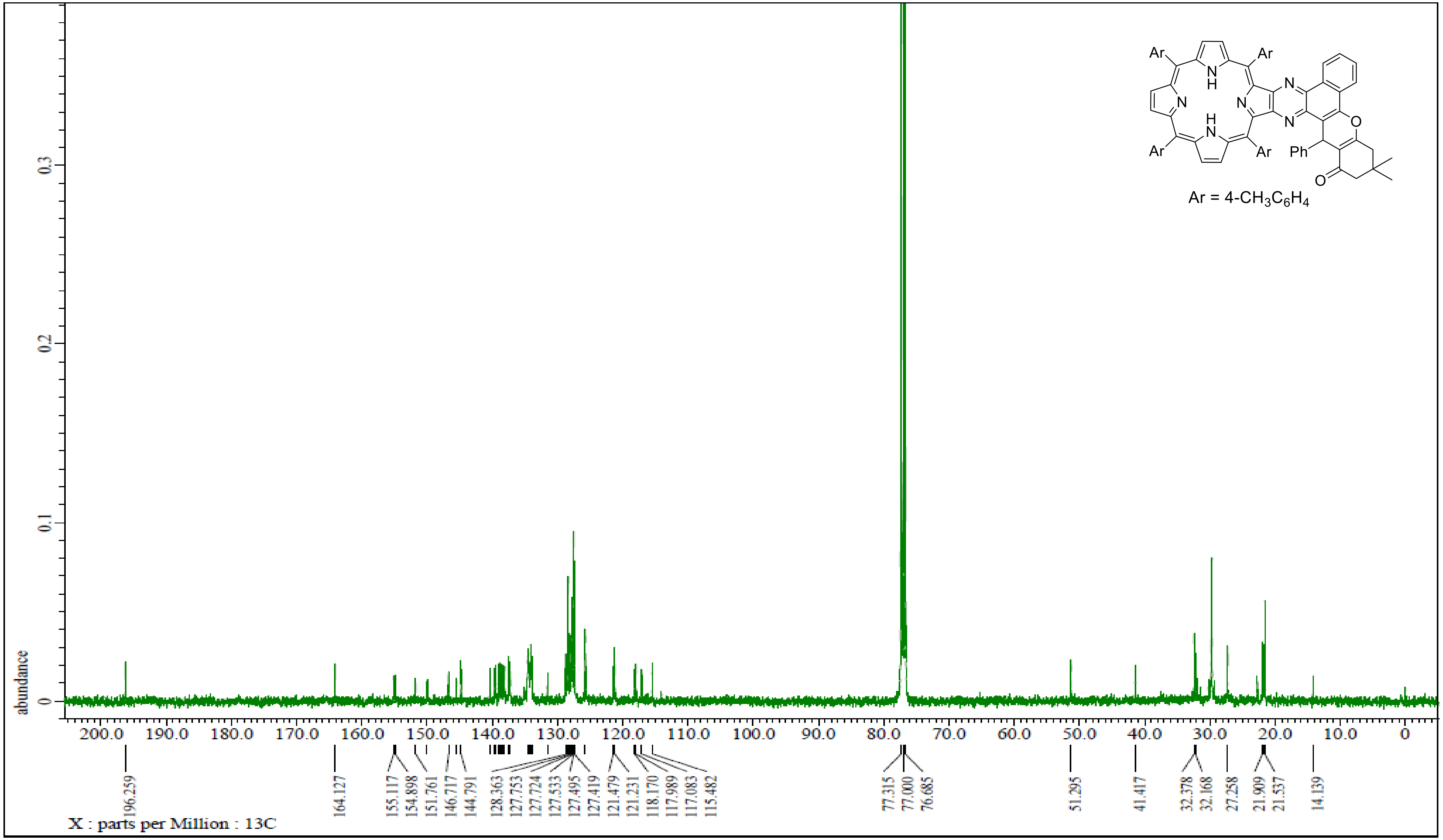

Figure 2. ^{13}C NMR spectrum of porphyrin **9** in $CDCl_3$.

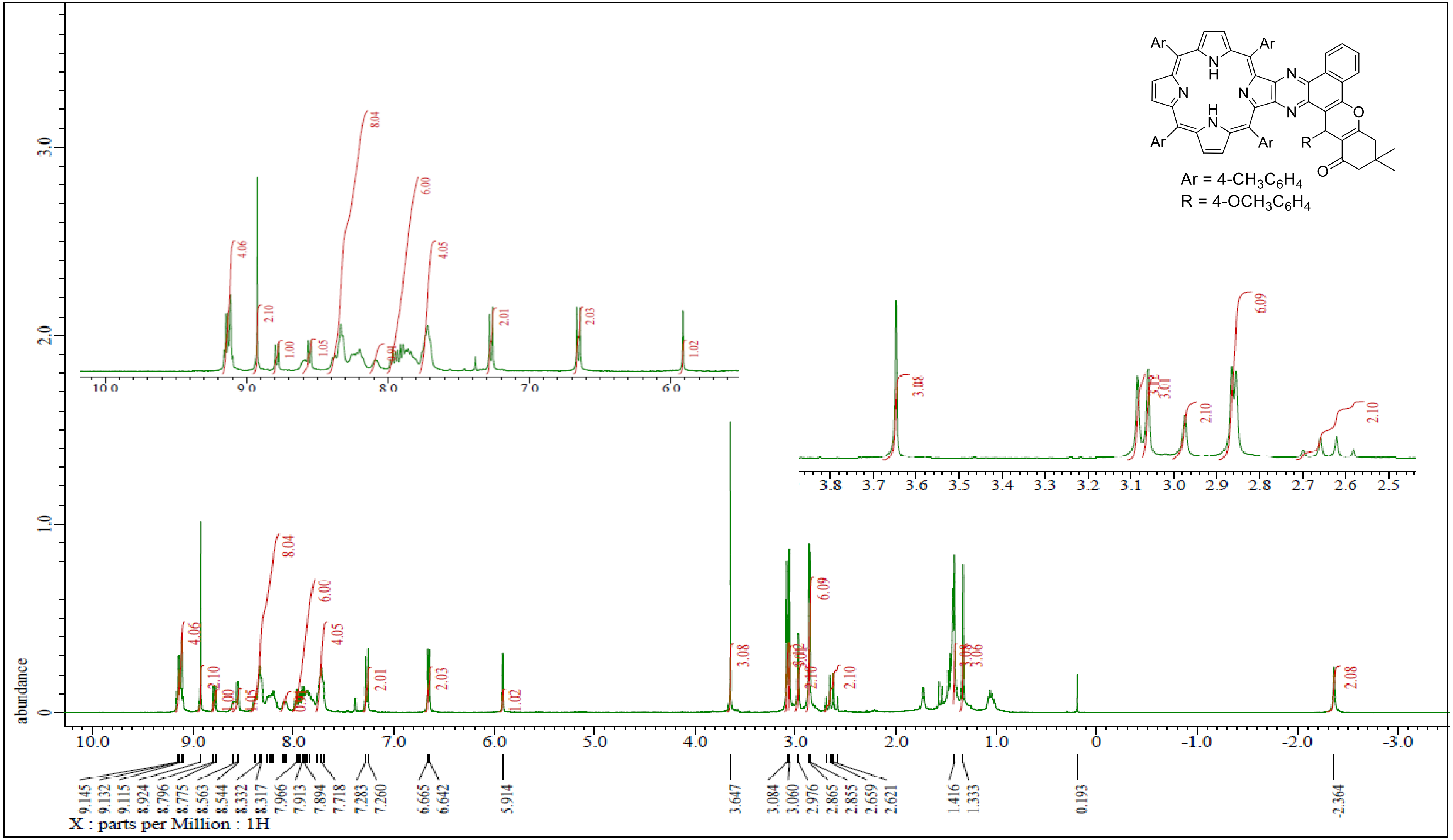

Figure 3. ^{1}H NMR spectrum of porphyrin **10** in $CDCl_3$.

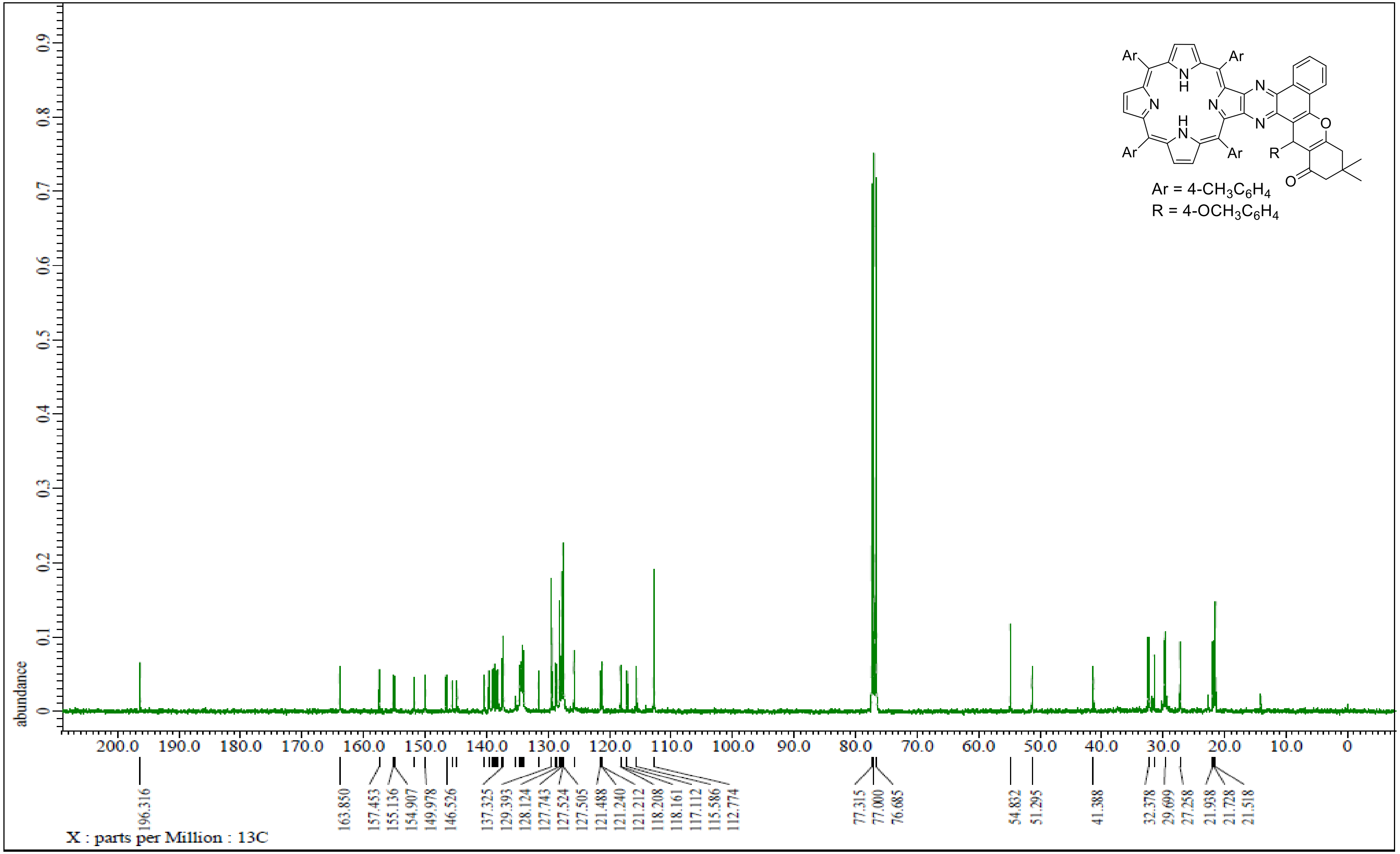

Figure 4. ^{13}C NMR spectrum of porphyrin **10** in $CDCl_3$.

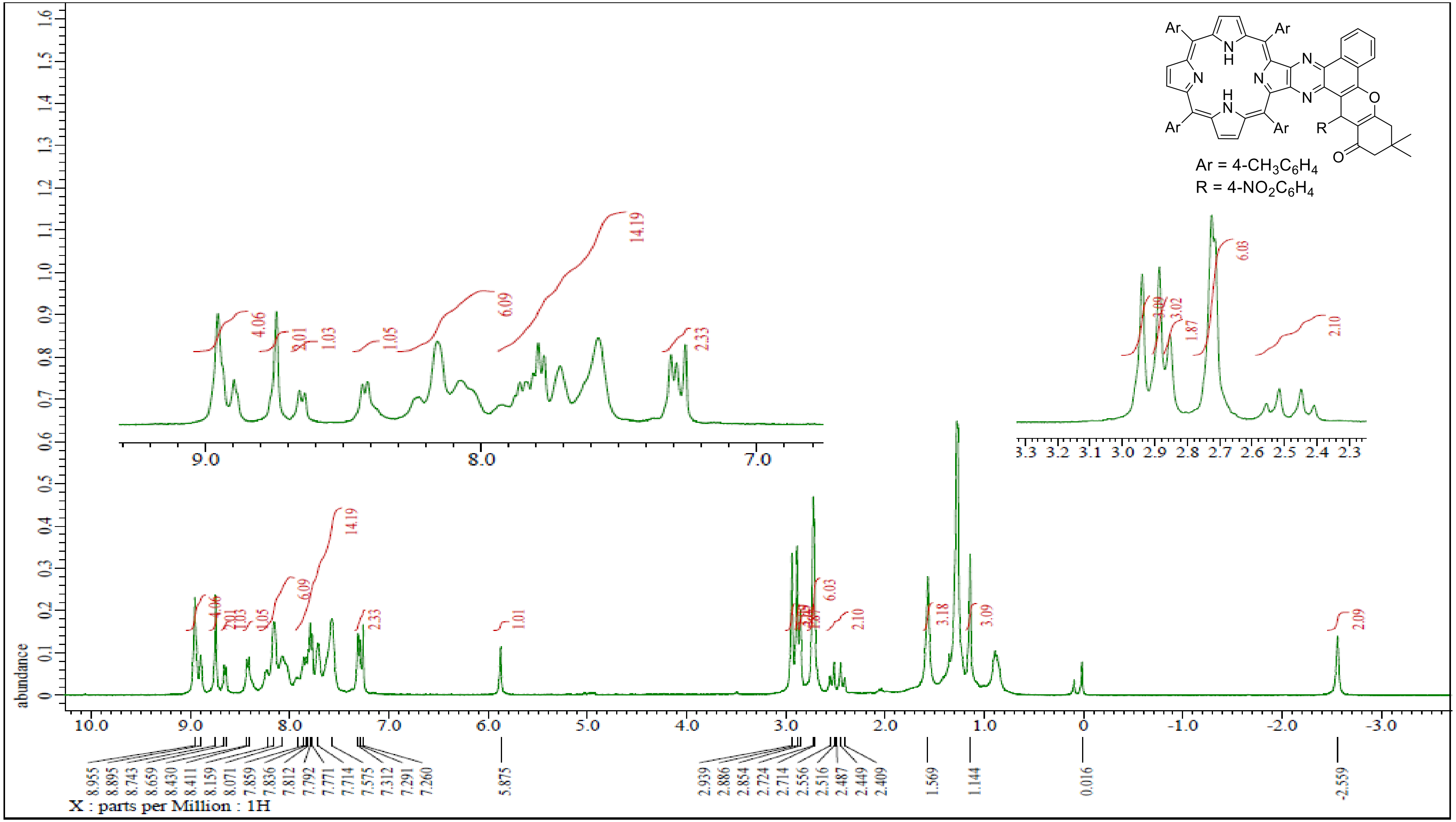

Figure 5. ^{1}H NMR spectrum of porphyrin **11** in $CDCl_3$.

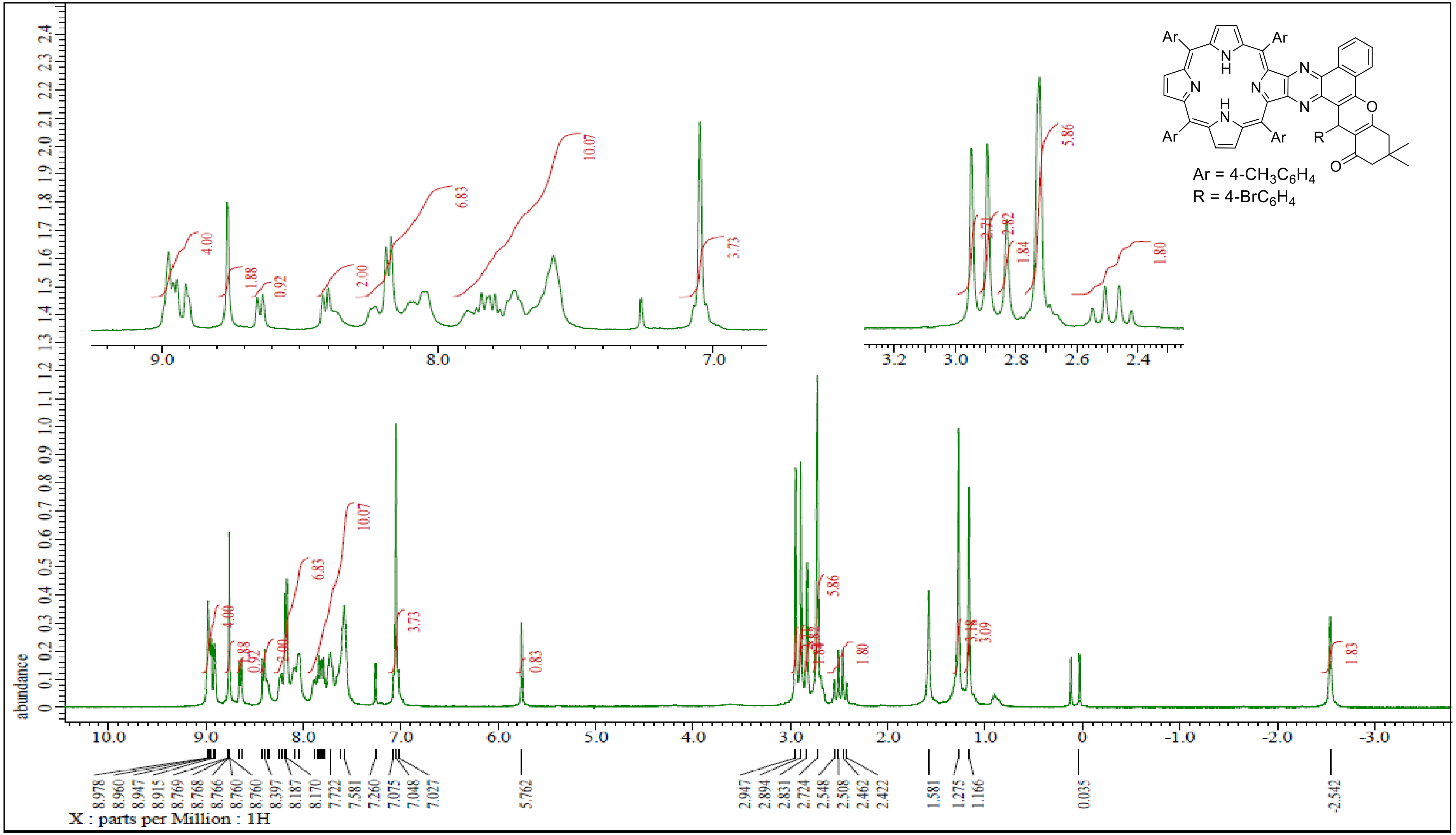

Figure 6. ^{1}H NMR spectrum of porphyrin **12** in $CDCl_3$.

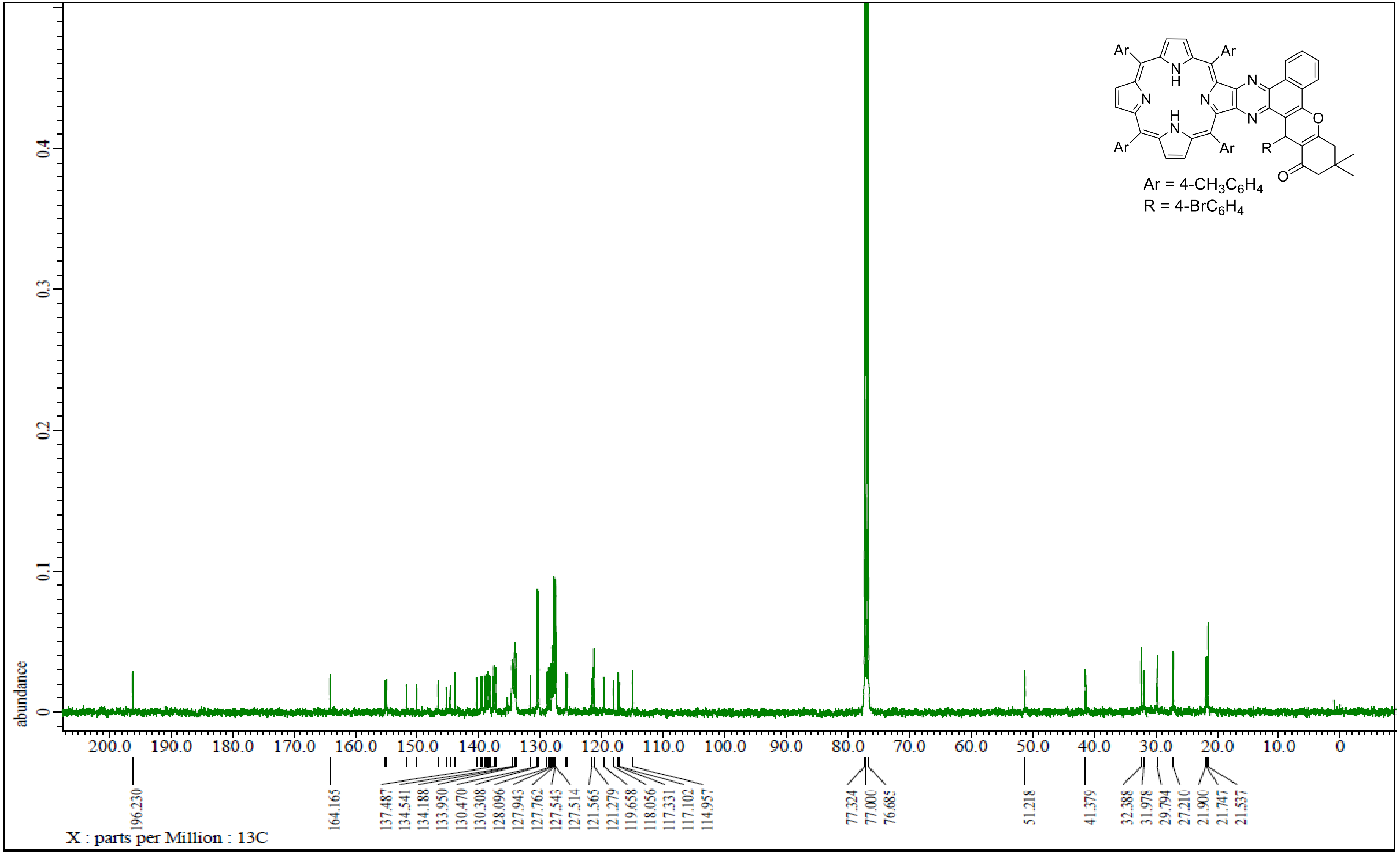

Figure 7. ^{13}C NMR spectrum of porphyrin **12** in $CDCl_3$.

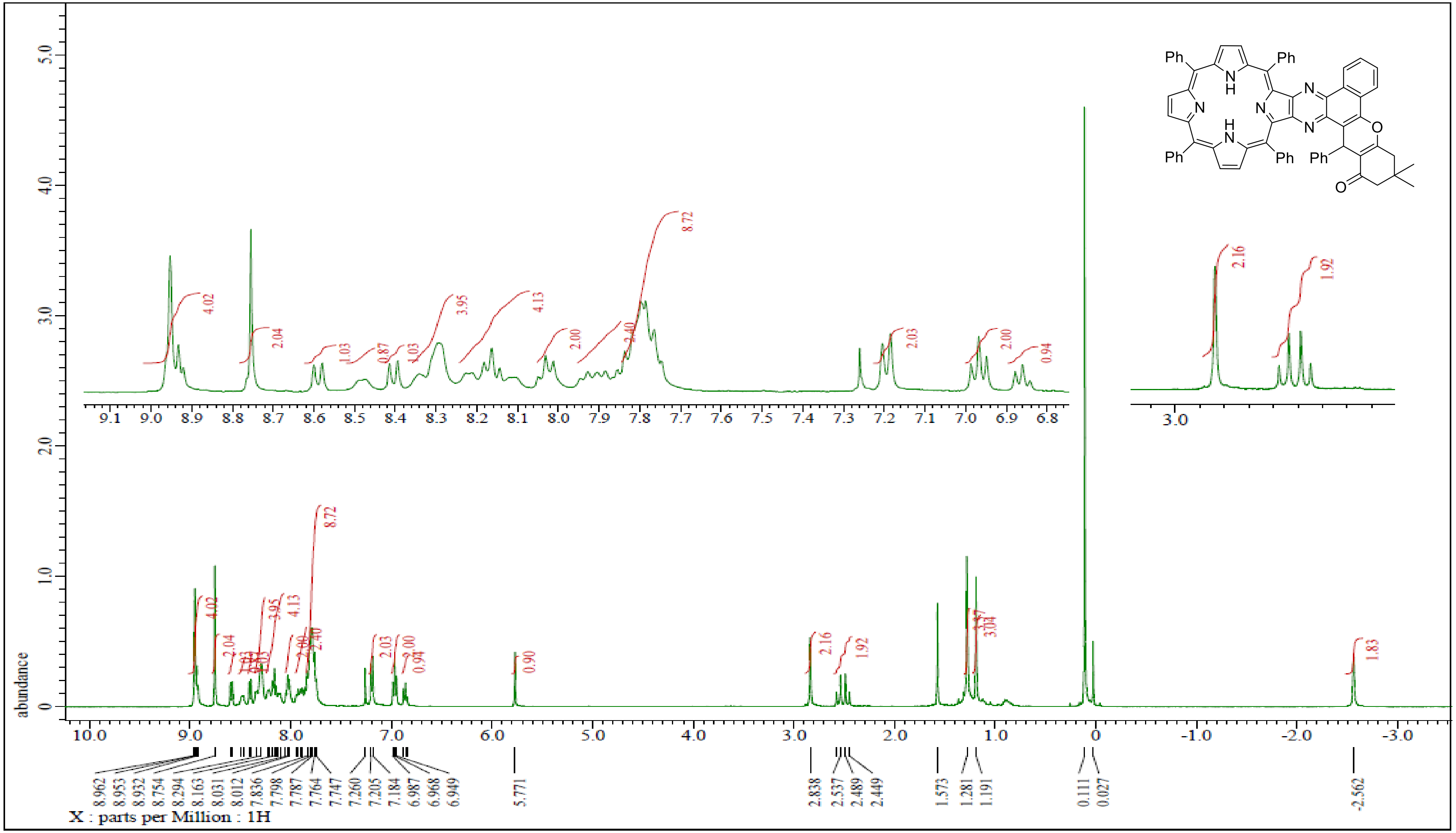

Figure 8. ^{1}H NMR spectrum of porphyrin **13** in $CDCl_3$.

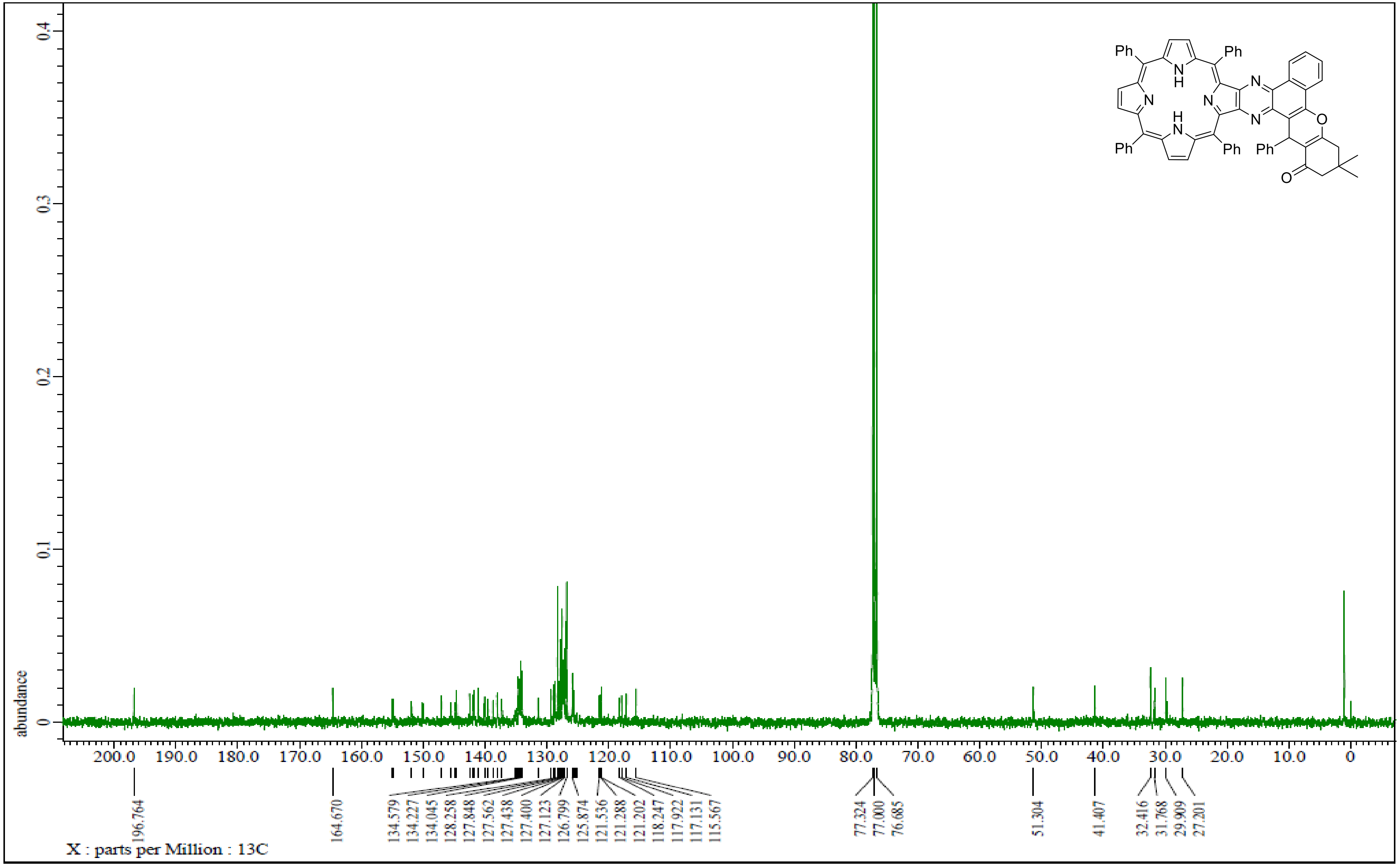

Figure 9. ^{13}C NMR spectrum of porphyrin **13** in $CDCl_3$.

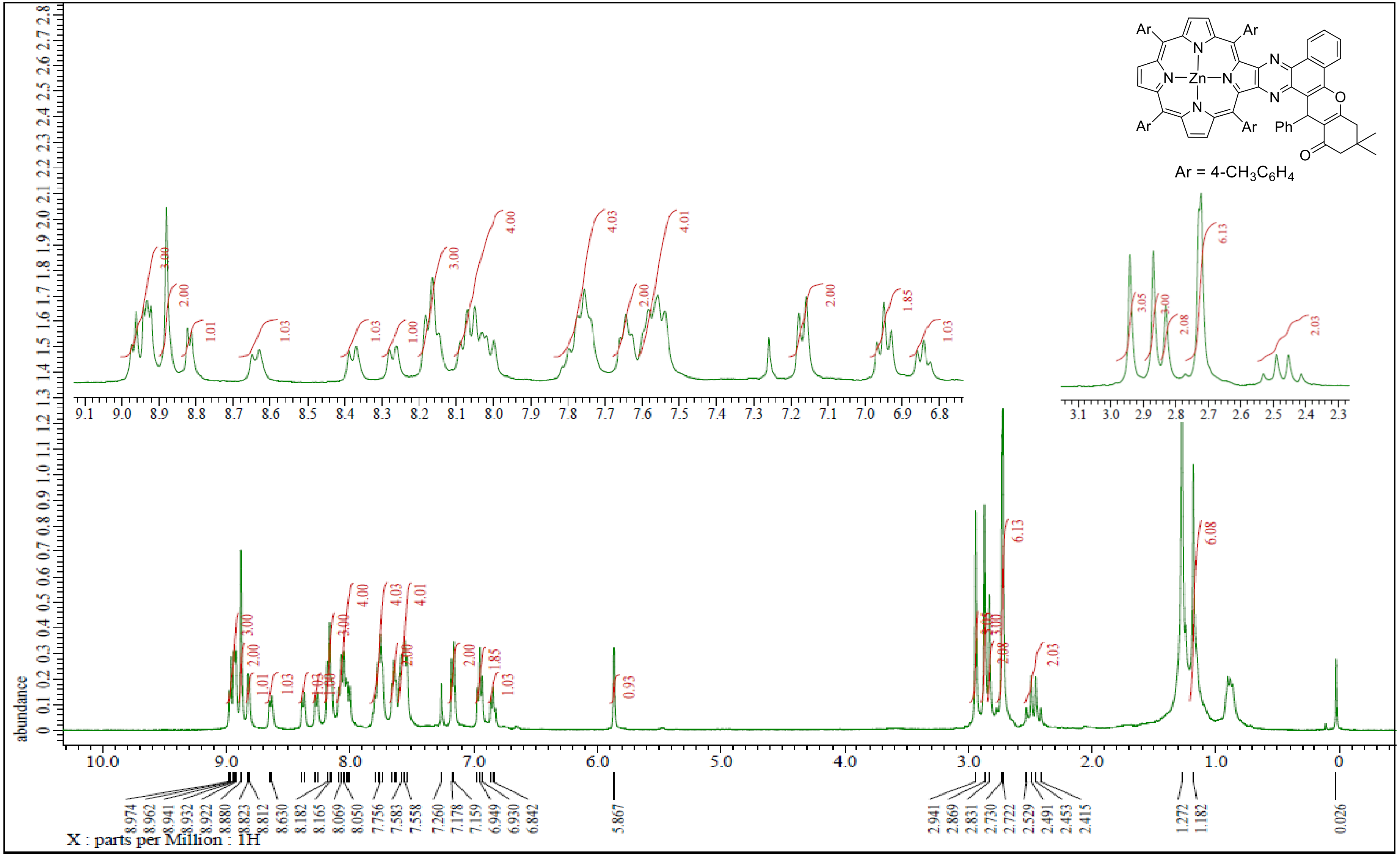

Figure 10. [1]H NMR spectrum of porphyrin **14** in $CDCl_3$.

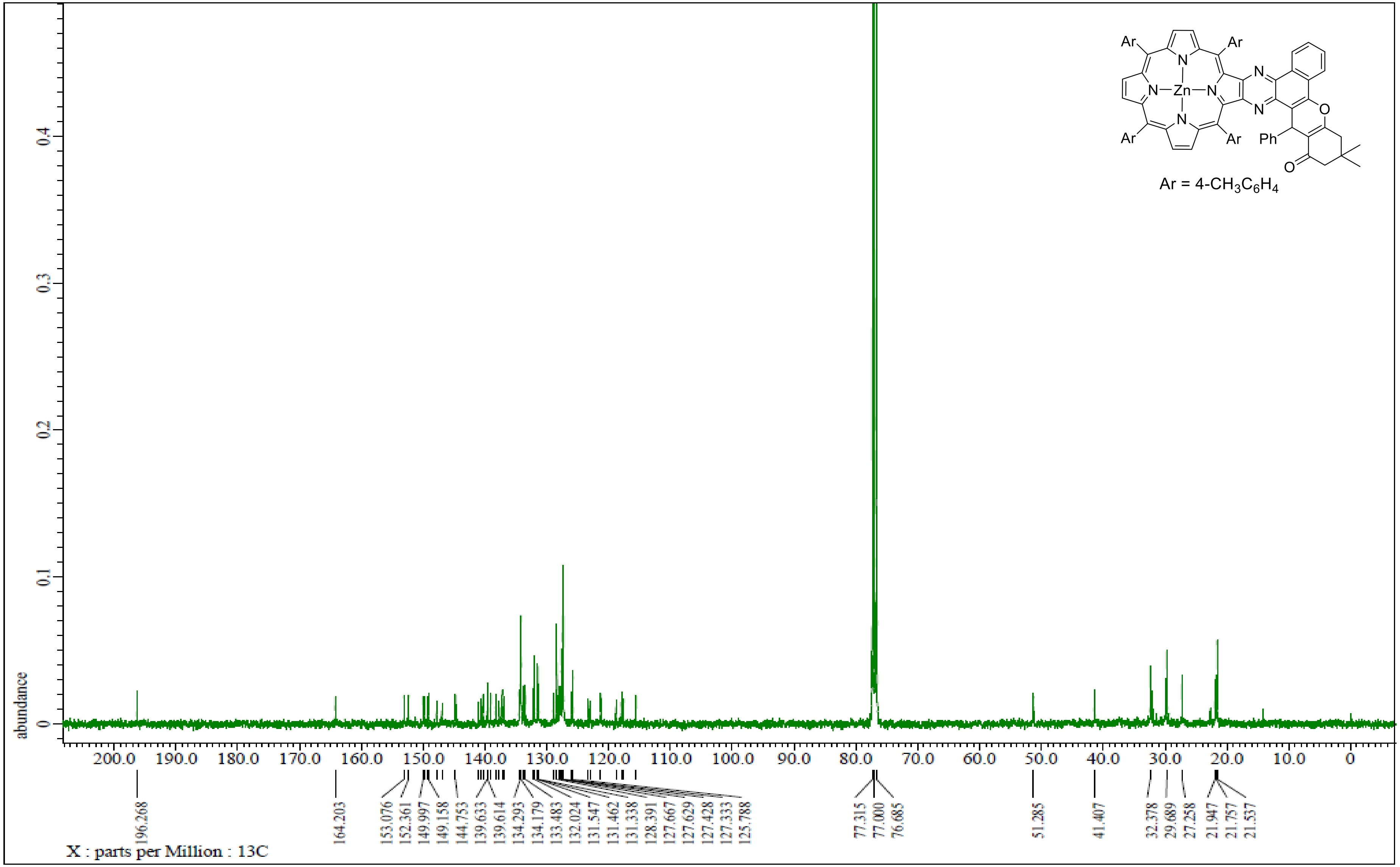

Figure 11. ^{13}C NMR spectrum of porphyrin **14** in $CDCl_3$.

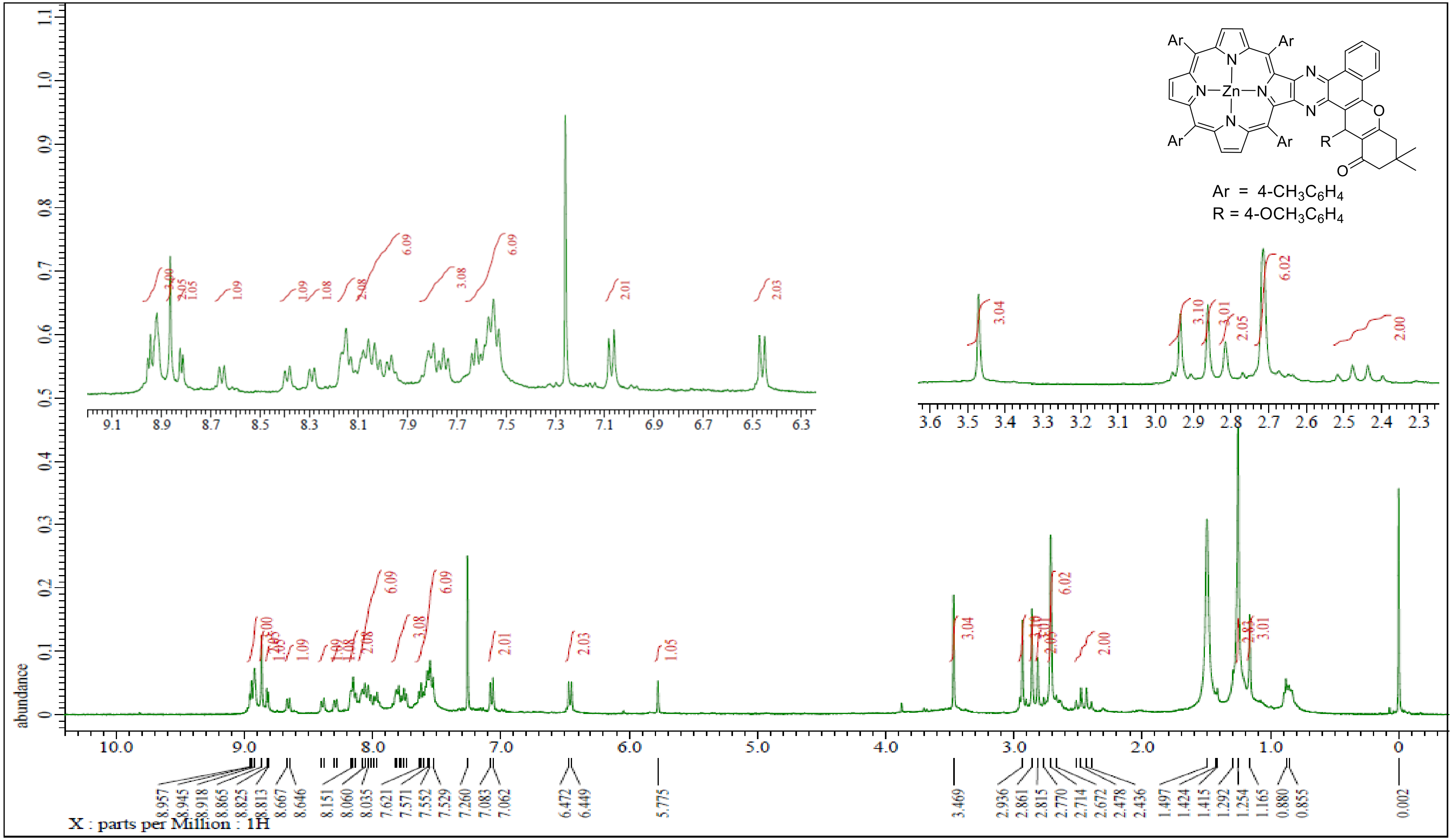

Figure 12. ^{1}H NMR spectrum of porphyrin **15** in $CDCl_3$.

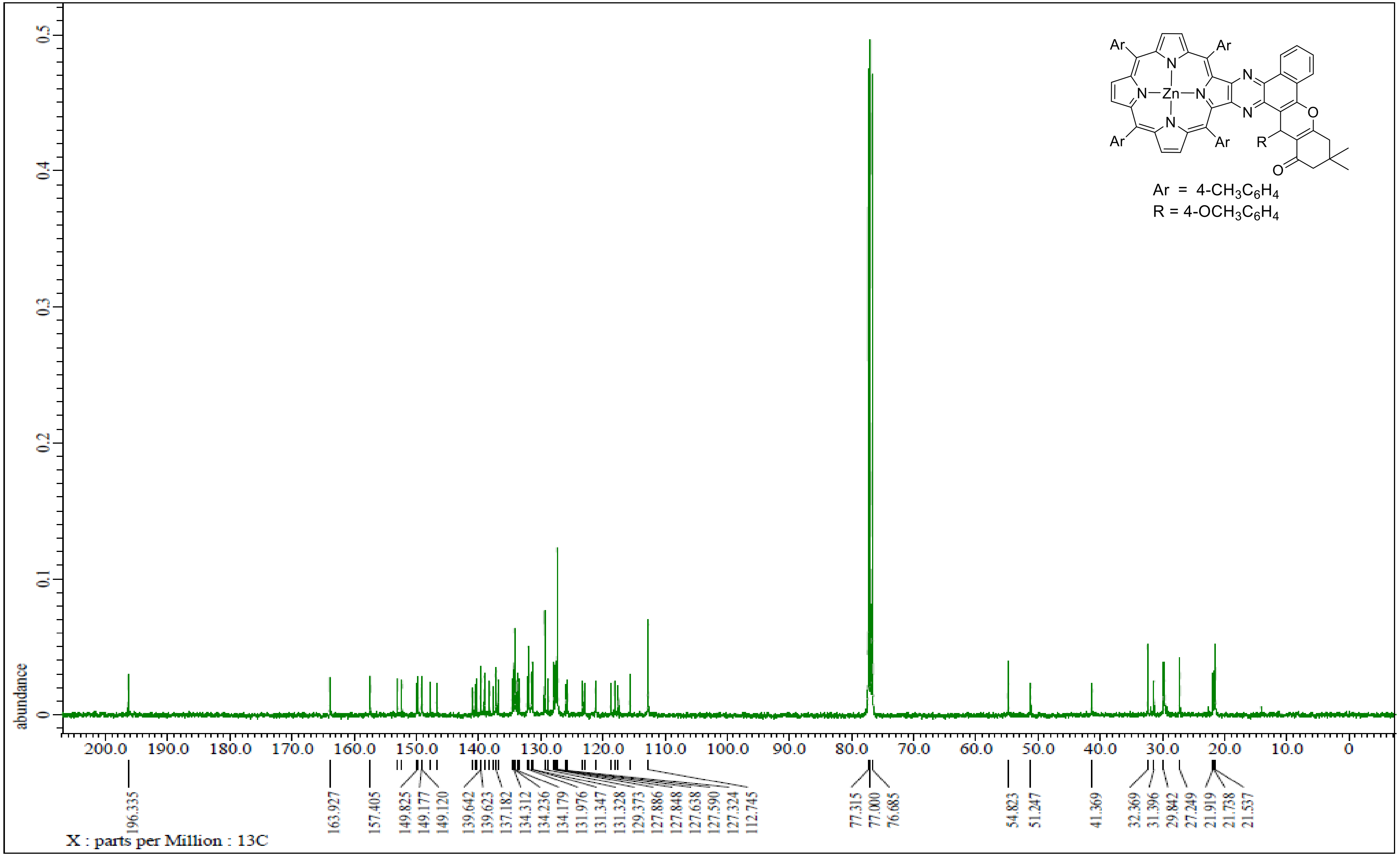

Figure 13. ^{13}C NMR spectrum of porphyrin **15** in $CDCl_3$.

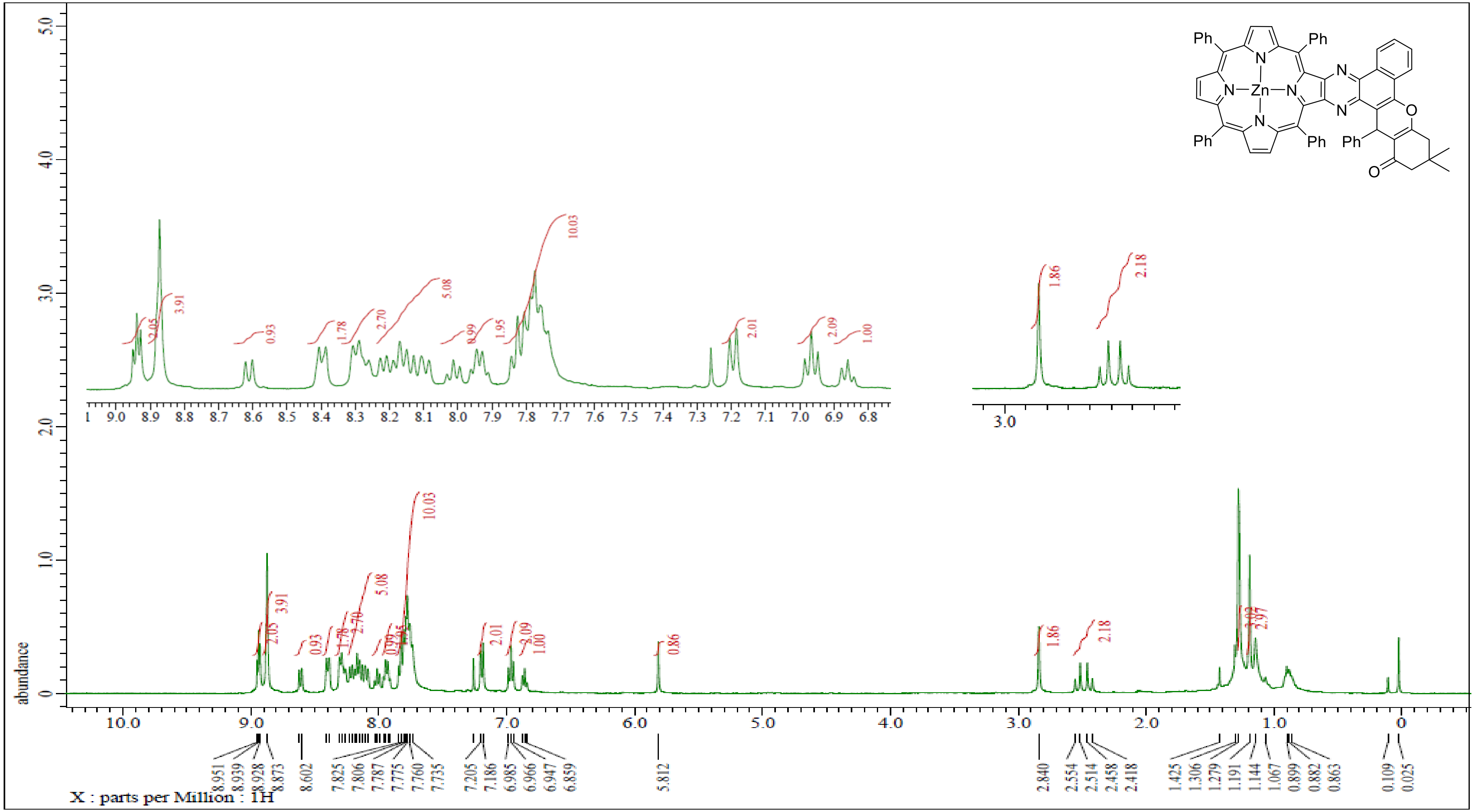

Figure 14. ^{1}H NMR spectrum of porphyrin **16** in $CDCl_3$.

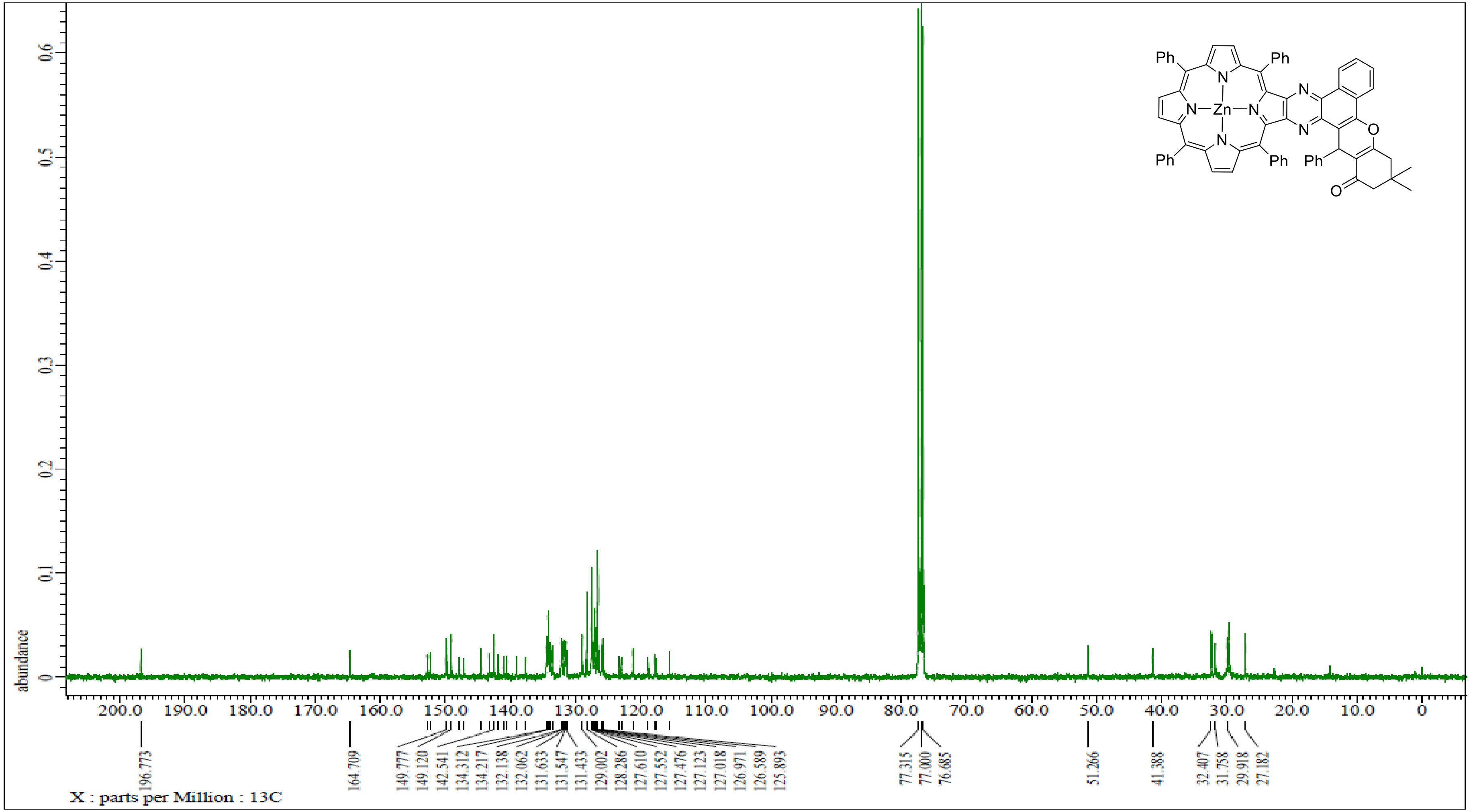

Figure 15. ^{13}C NMR spectrum of porphyrin **16** in $CDCl_3$.