Supporting Information

Au(I)-Catalyzed and Iodine-Mediated Cyclization of Enynylpyrazoles to Provide Pyrazolo[1,5-*a*]pyridines

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Table of Contents

Data of compounds 2

(Z)-5-(But-1-en-3-yn-1-yl)-3-phenyl-1H-pyrazole (2a)

brown liquid; R_f = 0.52 (*n*-hexane/ethyl acetate = 5/1 as eluent); ^{1}H NMR ($CDCl_3$, 500 MHz) : δ 11.43 (s, 1H), 7.78 (d, *J* = 7.5 Hz, 2H), 7.42 (t, *J* = 7.5 2H), 7.34 (t, *J* = 1H), 6.89 (s, 1H), 6.74 (d, *J* = 12.0 Hz, 1H), 5.70 (dd, *J* = 12.0, 2.0 Hz, 1H), 3.55 (d, *J* = 2.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) : δ 150.4 142.5, 132.1, 128.7(2C), 128.5, 128.1, 125.6, 106.1, 104.2, 86.5, 82.1; MS (EI) 194 (M^+, 100), 193 (M^+-H^+, 27), 167 (10); HRMS (EI) calcd. for $C_{13}H_{10}N_2$ 194.0844, found 194.0847.

5-((Z)-Dec-1-en-3-ynyl)-3-phenyl-1H-pyrazole (2b)

brown liquid; R_f = 0.48 (*n*-hexane/ethyl acetate = 5/1 as eluent); ^{1}H NMR ($CDCl_3$, 500 MHz) : δ 7.80 (d, *J* = 7.0 Hz, 2H), 7.42 (t, *J* = 8.0 Hz, 2H), 7.33 (t, *J* = 7.5 Hz, 1H), 6.73 (s, 1H), 6.56 (d, *J* = 11.5 Hz, 1H), 5.73 (dt, *J* = 11.5, 2.5 Hz, 1H), 2.50 (td, *J* = 7.5, 2.5 Hz, 2H), 1.66 (m, *J* = 7.5 Hz, 2H), 1.46 (m, *J* = 7.5Hz, 1H), 1.32-1.36 (m, 4H), 0.91 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125MHz) : δ 151.1, 142.2, 132.7, 128.6(2C), 127.9, 125.6(2C), 124.6, 108.1, 103.6, 99.7, 79.3, 31.3, 28.7, 28.6, 22.5, 19.9, 14.0; MS (EI) 278 (M^+, 47), 221 (89), 208 (100), 77 (46); HRMS (EI) calcd. for $C_{19}H_{22}N_2$ 278.1783, found 278.1784.

(Z)-5-(Oct-1-en-3-yn-1-yl)-3-phenyl-1H-pyrazole (2c)

brown liquid; R_f = 0.52 (*n*-hexane/ethyl acetate = 5/1 as eluent); ^{1}H NMR ($CDCl_3$, 500MHz)：δ 7.80 (d, *J* = 7 Hz, 2H), 7.42 (t, *J* = 7.5 Hz, 2H), 7.33 (t, *J* = 7.5 Hz, 2H), 6.75 (S, 1H), 6.56 (d, *J* = 11.5 Hz, 1H), 5.73(dt, *J* = 11.5, 2.5 Hz, 1H), 2.50 (td, *J* = 11.5, 2.5 Hz, 2H), 1.65 (m, 2H), 1.50 (m, 2H), 0.97 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125MHz)：151.0, 142.3, 132.7, 128.6(2C), 127.9, 125.6(2C), 124.6, 108.1, 103.6, 99.6, 79.3, 30.6, 22.1, 19.5, 13.5; MS (EI) 250 (M^+, 100), 221 (39), 207 (100), 77 (28); HRMS (EI) calcd. for $C_{17}H_{18}N_2$ 250.1470, found 250.1469.

5-((Z)-Non-1-en-3-ynyl)-3-phenyl-1H-pyrazole (2d)

brown liquid; R_f = 0.50 (*n*-hexane/ethyl acetate = 5/1 as eluent); ^{1}H NMR ($CDCl_3$, 500 MHz) : δ 7.80(d, *J* = 7.0 Hz, 2H), 7.42(t, *J* = 7.5 Hz, 2H), 7.33(t, *J* = 7.5 Hz), 6.72(s, 1H), 6.56(d, *J* = 11.5 Hz,1H), 5.73 (dt, *J* = 11.5, 2.5 Hz, 1H), 2.50(td, *J* = 7.2 Hz, 2H), 1.67(m, 2H), 1.48-1.34(m, 4H), 0.93(t, *J* = 7 Hz, 3H); ^{13}C NMR ($CDCl_3$. 125MHz) : δ 151.1, 142.1, 132.8, 128.6(2C), 127.9, 125.6(2C), 124.5, 108.1, 103.7,

99.7, 79.3, 31.2, 28.3, 22.1, 19.9, 13.9; MS (EI) 264 (M^+, 65), 221 (88), 208 (100), 77 (45); HRMS (EI) calcd. For $C_{18}H_{20}N_2$ 264.1626, found 264.1624.

5-((Z)-6-Methylhept-1-en-3-ynyl)-3-phenyl-1H-pyrazole (2e)

brown liquid; R_f = 0.47 (*n*-hexane/ethyl acetate = 5/1 as eluent); ^{1}H NMR ($CDCl_3$, 500 MHz) : δ 7.80 (d, *J* = 7.5 Hz, 2H), 7.42 (t, *J* = 7.5 Hz, 2H), 7.33 (t, *J* = 7.5 Hz, 1H), 6.72 (s, 1H), 6.57 (d, *J* = 11.5 Hz, 1H), 5.74 (td, *J* = 11.5, 2.5 Hz, 1H), 2.41(dd, *J* = 6.5, 2.5 Hz, 2H), 1.97(m, *J* = 7.0Hz, 1H), 1.07 (d, *J* = 6.5 Hz, 6H) ; ^{13}C NMR ($CDCl_3$, 125MHz) : δ 151.2, 142.1, 132.8, 128.6(2C), 127.9, 125.6(2C), 124.5, 108.1, 103.7, 98.7, 80.2, 29.0, 28.2, 22.1; MS (EI) 250 (M^+, 80), 207 (72), 104 (72), 77 (85); HRMS (EI) calcd. for $C_{17}H_{18}N_2$ 250.1470, found 250.1469.

5-((Z)-5,5-Dimethylhex-1-en-3-ynyl)-3-phenyl-1H-pyrazole (2f)

brown liquid; R_f = 0.50 (*n*-hexane/ethyl acetate = 5/1 as eluent); ^{1}H NMR ($CDCl_3$, 500 MHz) : δ 7.79 (d, *J* = 7.0 Hz, 2H), 7.41 (t, *J* = 7.5 Hz, 2H), 7.33 (t, *J* = 7 Hz, 1H), 6.78 (s, 1H), 6.56 (d, *J* = 11.5 Hz, 1H), 5.72 (d, *J* = 11.5 Hz, 1H), 1.39 (s, 9H) ; ^{13}C NMR ($CDCl_3$, 125MHz) : δ 151.0, 142.4, 132.7, 128.6(2C), 127.9, 125.6(2C), 124.6, 108.1, 107.3, 103.6, 78.1, 30.7(3C), 28.6; MS (EI) 250 (M^+, 80), 207 (72), 104 (72), 77 (85); HRMS (EI) calcd. for $C_{17}H_{18}N_2$ 250.1470, found 250.1469.

3-Phenyl-5-((Z)-4-phenylbut-1-en-3-ynyl)-1H-pyrazole (2g)

brown liquid; R_f = 0.46 (*n*-hexane/ethyl acetate = 5/1 as eluent); ^{1}H NMR ($CDCl_3$, 500 MHz) : δ 7.80 (d, *J* = 7.0 Hz, 2H), 7.37-7.56 (m, 7H), 7.33 (t, *J* = 7.5 Hz, 1H), 6.86 (s, 1H), 6.72 (d, *J* =11.5 Hz, 1H), 5.97(d, *J* = 11.5 Hz, 1H) ; ^{13}C NMR ($CDCl_3$, 125MHz) : δ 151.0, 142.4, 132.5, 131.5(2C), 129.1, 128.7(2C), 128.6(2C), 128.0, 125.6(2C), 122.2, 107.4, 104.2, 97.5, 87.6; MS (EI) 270(M^+, 100), 269(M^+-H^+, 100); HRMS (EI) calcd. for $C_{19}H_{14}N_2$ 270.1157, found 270.1158.

(Z)-3-Phenyl-5-(4-(o-tolyl)but-1-en-3-yn-1-yl)-1H-pyrazole (2h)

Yellow solid; m.p.: 110-112 ^{o}C; R_f = 0.45 (*n*-hexane/ethyl acetate = 5/1 as eluent); ^{1}H NMR ($CDCl_3$, 500MHz)：δ 7.80 (d, *J* = 7 Hz, 2H), 7.53 (d, *J* = 7.5 Hz, 1H), 7.42 (t, *J* = 7.5 Hz, 2H), 7.35-7.20 (m, 4H), 6.90 (s, 1H), 6.70 (d, *J* = 11.5 Hz, 1H), 6.02 (d, *J* = 11.5 Hz, 1H), 2.54 (s, 3H); ^{13}C NMR ($CDCl_3$, 125MHz)：150.8, 142.7, 140.1, 132.4, 132.1, 129.7, 129.1, 128.7(2C), 128.0, 125.8, 125.6(2C), 125.5, 122.1, 107.6, 104.0, 96.7, 91.2, 20.9; MS (EI) 284 (M^+, 100), 283 ($M^+ - H^+$, 100), 269(88); HRMS (EI) calcd. for $C_{20}H_{16}N_2$ 284.1313, found 284.1310.

3-Phenyl-5-((Z)-4-m-tolylbut-1-en-3-ynyl)-1H-pyrazole (2i)

Yellow solid; m.p.: 82-84 °C; R_f = 0.43 (*n*-hexane/ethyl acetate = 5/1 as eluent); ^{1}H NMR ($CDCl_3$, 500 MHz) : δ 7.80 (d, *J* = 7 Hz, 2H), 7.42 (t, *J* = 7.5 Hz, 2H), 7.38-7.28 (m, 4H), 7.21(d, *J* = 8Hz, 1H), 6.87 (s, 1H), 6.70 (d, *J* = 11.5 Hz, 1H), 5.96(d, *J* = 11.5 Hz, 1H), 2.38 (s, 3H) ; ^{13}C NMR ($CDCl_3$, 125MHz) : δ 151.0, 138.3, 132.5, 132.0, 131.0, 128.7(2C), 128.6, 128.5, 128.0, 125.7, 125.6(2C), 122.0, 107.9, 104.1, 97.8, 87.3, 21.2; MS (EI) 284 (M^+, 100), 283 ($M^+ - H^+$, 76); HRMS (EI) calcd. for $C_{20}H_{16}N_2$ 284.1313, found 284.1310.

3-Phenyl-5-((Z)-4-p-tolylbut-1-en-3-ynyl)-1H-pyrazole (2j)

Yellow solid; m.p.: 124-126 °C; R_f = 0.45 (*n*-hexane/ethyl acetate = 5/1 as eluent); ^{1}H NMR ($CDCl_3$, 500 MHz) : δ 7.80 (d, *J* = 7.0 Hz, 2H), 7.45-7.32 (m, 5H), 7.20 (d, *J* = 8.0 Hz, 2H), 6.84 (s,1H), 6.68 (d, *J* = 11.5Hz, 1H), 5.95 (d, *J* = 11.5 Hz, 1H), 2.39(s, 3H) ; ^{13}C NMR ($CDCl_3$, 125MHz) : δ 151.0, 139.4, 132.5, 131.4(2C), 129.4(2C), 128.7(2C), 128.0, 125.6(2C), 125.4, 119.1, 107.6, 97.9, 87.1, 21.5; MS (EI) 284 (M^+, 100), 283($M^+ - H^+$, 88); HRMS (EI) calcd. for $C_{20}H_{16}N_2$ 284.1313, found 284.1310.

5-((Z)-4-(2-Methoxyphenyl)but-1-en-3-ynyl)-3-phenyl-1H-pyrazole (2k)

beige solid; m.p.: 114-116 ℃; R_f = 0.41 (*n*-hexane/ethyl acetate = 5/1 as eluent); ^{1}H NMR ($CDCl_3$, 500 MHz) : δ 7.88 (d, *J* = 7.5Hz, 2H), 7.46-7.30 (m, 5H), 7.02-6.97 (m, 2H), 6.70 (d, *J* = 11.5 Hz, 1H), 6.64 (s, 1H), 5.92 (d, *J* = 11.5 Hz, 1H), 4.30 (s, 3H) ; ^{13}C NMR ($CDCl_3$, 125MHz) : δ 160.4, 151.2, 141.0, 133.4, 132.4, 130.5, 128.5(2C), 127.6, 125.6(2C), 125.4, 120.8, 111.7, 110.4, 106.2, 104.5, 94.2, 92.9, 56.6; MS (EI) 300 (M^+, 100), 283 (63), 269 (98); HRMS (EI) calcd. for $C_{20}H_{16}ON_2$ 300.1263, found 300.1265.

5-((Z)-4-(3-Methoxyphenyl)but-1-en-3-ynyl)-3-phenyl-1H-pyrazole (2l)

beige solid; m.p.: 70-72 °C; R_f = 0.43 (*n*-hexane/ethyl acetate = 5/1 as eluent); ^{1}H NMR ($CDCl_3$, 500 MHz) : δ 7.79 (d, *J* = 7 Hz, 2H), 7.42 (t, *J* = 7.5Hz, 2H), 7.35-7.28 (m, 2H), 7.15 (d, *J* = 7.5 Hz, 1H), 7.06 (s, 1H), 6.95 (dd, *J* = 8.5, 7.0 Hz, 1H), 6.93 (s, 1H), 6.72(d, *J* = 11.5 Hz, 1H), 5.95 (d, *J* = 11.5 Hz, 1H), 3.83 (s, 3H) ; ^{13}C NMR ($CDCl_3$, 125MHz) : δ 159.4, 150.6, 142.8, 132.3, 129.6, 128.7(2C), 128.0, 126.2, 125.6(2C), 124.1, 123.3, 116.2, 115.6, 107.4, 104.0, 97.4, 87.4, 55.3; MS (EI) 300 (M^+, 100), 299 ($M^+ - H^+$, 63); HRMS (EI) calcd. for $C_{20}H_{16}ON_2$ 300.1263, found 300.1265.

5-((Z)-4-(4-Methoxyphenyl)but-1-en-3-ynyl)-3-phenyl-1H-pyrazole (2m)

beige solid; m.p.: 128-130 ^{o}C; R_f = 0.42 (*n*-hexane/ethyl acetate = 5/1 as eluent); ^{1}H NMR ($CDCl_3$, 500 MHz) : δ 7.49 (d, *J* = 9.0 Hz, 2H), 7.42 (t, *J* = 8.0 Hz, 2H), 7.34 (t, *J* = 7.5 Hz, 1H), 6.92 (d. *J* = 8.5 Hz, 2H), 6.83 (s, 1H), 6.67 (d, *J* = 11.5 Hz, 1H), 5.95(d, *J* = 11.5 Hz, 1H), 3.85 (s, 3H) ; ^{13}C NMR ($CDCl_3$, 125MHz) : δ 160.2, 151.0, 142.5, 133.1 (2C), 132.6, 128.9, 128.7 (2C), 128.0, 125.6(2C), 125.0, 114.3(2C), 107.7, 104.0, 97.8, 86.6, 55.3; MS (EI) 300 (M^+, 100), 299 (M^+−H^+, 74); HRMS (EI) calcd. for $C_{20}H_{16}ON_2$ 300.1263, found 300.1265.

5-((Z)-4-(4-Nitrophenyl)but-1-en-3-ynyl)-3-phenyl-1H-pyrazole (2n)

orange solid; m.p.: 123-125 ^{o}C; R_f = 0.38 (*n*-hexane/ethyl acetate = 5/1 as eluent); ^{1}H NMR ($CDCl_3$, 500 MHz) : δ 8.25 (d, *J* = 8.5 Hz, 2H), 7.75 (d, *J* = 7.0 Hz, 2H), 7.68 (d, *J* = 8.5 Hz, 2H), 7.44 (t, *J* = 7.5 Hz, 2H), 7.37 (t, *J* = 7.0 Hz, 1H), 6.97 (s, 1H), 6.84 (d, *J* = 11.5 Hz, 1H), 5.98 (d, *J* = 11.5 Hz, 1H) ; ^{13}C NMR ($CDCl_3$, 125MHz) : δ 147.3, 132.2(2C), 129.2, 129.0, 128.9(2C), 128.3, 125.6(2C), 123.8(2C), 123.6, 106.5, 104.3, 94.9, 92.5; MS (EI) 315 (M^+, 100), 314 (M^+−H^+, 65); HRMS (EI) calcd. for $C_{19}H_{13}O_2N_3$ 315.1008, found 315.1010.

4-((Z)-4-(3-Phenyl-1H-pyrazol-5-yl)but-3-en-1-ynyl)benzonitrile (2o)

yellow solid; m.p.: 141-142 ^{o}C; R_f = 0.41 (*n*-hexane/ethyl acetate = 5/1 as eluent); ^{1}H NMR ($CDCl_3$, 500 MHz) : δ 7.75 (d, *J* = 7.5 Hz, 2H), 7.67 (d, *J* = 8.5 Hz, 2H), 7.61 (d, *J* = 8.5 Hz, 2H), 7.43 (t, *J* = 8.0 Hz, 2H), 7.36 (t, *J* = 7.5 Hz, 1H), 6.96 (s, 1H), 6.82 (d, *J* = 12.0 Hz, 1H), 6.96 (s, 1H), 6.82 (d, *J* = 12.0 Hz, 1H), 5.97 (d, *J* = 12.0 Hz, 1H) ; ^{13}C NMR ($CDCl_3$. 50MHz) : δ 150.2, 143.2, 132.2(2C), 132.0(2C), 128.8(2C), 128.3, 128.2, 127.3, 125.6(2C), 118.2, 112.2, 106.6, 104.2, 95.2, 91.7; MS (EI) 295 (M^+, 100), 294 (M^+−H^+, 35); HRMS (EI) calcd. for $C_{20}H_{13}N_3$ 295.1109, found 295.1106.

(Z)-5-(4-(2-(Methylthio)phenyl)but-1-en-3-yn-1-yl)-3-phenyl-1H-pyrazole (2p)

yellow solid; m.p.: 142-144 ^{o}C; R_f = 0.47 (*n*-hexane/ethyl acetate = 5/1 as eluent); ^{1}H NMR ($CDCl_3$, 500MHz)：δ 7.84 (d, *J* = 6.8 Hz, 2H), 7.49 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.43-7.28 (m, 6H), 7.17 (td, *J* = 7.6, 1.6 Hz, 1H), 6.82 (s, 1H), 6.60 (d, *J* = 11.6 Hz, 1H), 5.99 (d, *J* = 11.6 Hz, 1H), 2.61 (s, 3H); ^{13}C NMR ($CDCl_3$, 125MHz)：140.9, 132.7, 129.4, 128.6(2C), 127.8, 126.1, 125.8, 125.7(2C), 125.6, 125.5, 125.2, 121.7, 106.5, 104.5, 95.4, 93.3, 16.2; MS (EI) 316 (M^+, 68), 269(100); HRMS (EI) calcd. for $C_{20}H_{16}SN_2$ 316.1034, found 316.1032.

(Z)-5-(Dec-1-en-3-yn-1-yl)-3-(4-methoxyphenyl)-1H-pyrazole (2q)

brown solid; m.p.: 49-52 ^{o}C; R_f = 0.52 (*n*-hexane/ethyl acetate = 5/1 as eluent); ^{1}H NMR ($CDCl_3$, 500 MHz) : δ 7.70 (d, *J* = 9.0 Hz, 2H), 6.93 (dt, J = 9.0, 3.0 Hz, 2H), 6.74 (s, 1H), 6.55 (d, *J* = 11.5 Hz, 1H), 5.70 (dt, *J* = 11.5, 2.5 Hz, 1H), 3.83 (s, 3H), 2.48 (td, *J* = 7.0, 2.5 Hz, 2H), 1.64 (m, *J* = 7.0 Hz, 2H), 1.44 (m, *J* = 7.0 Hz, 2H), 1.35-1.30 (m, 4H), 0.90 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125MHz) : δ 159.4, 150.4, 142.7, 126.8(2C), 125.3, 125.0, 114.0(2C), 108.1, 102.9, 99.5, 79.3, 55.2, 31.2, 28.7, 28.5, 22.4, 19.8, 13.9; MS (EI) 308 (M^+, 100), 251 (48), 238 (50); HRMS (EI) calcd. for $C_{20}H_{24}ON_2$ 308.1889, found 308.1892.

(Z)-3-(4-Methoxyphenyl)-5-(4-phenylbut-1-en-3-yn-1-yl)-1H-pyrazole (2r)

beige solid; m.p.: 138-140 ^{o}C; R_f = 0.44 (*n*-hexane/ethyl acetate = 5/1 as eluent); ^{1}H NMR ($CDCl_3$, 500 MHz) : δ 7.70 (d, *J* = 9.0 Hz, 2H), 7.55-7.53 (m, 2H), 7.38 (m, 3H), 6.94 (d, *J* = 9.0 Hz, 2H), 6.88 (s, 1H), 6.70 (d, *J* = 11.5 Hz, 1H), 5.94 (d, *J* = 11.5 Hz, 1H), 3.84 (s, 3H); ^{13}C NMR ($CDCl_3$, 125MHz) : δ 159.5, 150.2, 143.2, 131.5(2C), 128.9, 128.5(2C), 126.9(2C), 126.4, 124.9, 122.4, 114.1(2C), 107.4, 103.3, 97.3, 87.7, 55.2; MS (EI) 300 (M^+, 100), 285 (16); HRMS (EI) calcd. for $C_{20}H_{16}ON_2$ 300.1263, found 300.1263.

(Z)-3-(4-Methoxyphenyl)-5-(4-(4-methoxyphenyl)but-1-en-3-yn-1-yl)-1H-pyrazol e (2s)

beige solid; m.p.: 161-163 ^{o}C; R_f = 0.45 (*n*-hexane/ethyl acetate = 5/1 as eluent); ^{1}H NMR ($CDCl_3$, 500 MHz) : δ 7.72 (d, *J* = 9.0 Hz, 2H), 7.48 (d, *J* = 8.5 Hz, 2H), 6.95 (d, *J* = 8.5 Hz, 2H), 6.91 (d, *J* = 9.0 Hz, 2H), 6.78 (s, 1H), 6.65 (d, *J* = 11.5 Hz, 1H), 5.93 (d, *J* = 11.5 Hz, 1H), 3.84 (s, 6H); ^{13}C NMR ($CDCl_3$, 125MHz) : δ 160.2, 159.5, 150.6, 142.7, 133.0(2C), 126.8(2C), 125.3, 114.4, 114.2(2C), 1141.(2C), 114.0, 107.6, 103.4, 97.7, 86.6, 55.3, 55.2; MS (EI) 330 (M^+, 100), 308 (23), 238 (22); HRMS (EI) calcd. for $C_{21}H_{18}O_2N_2$ 330.1368, found 330.1371.

4-((Z)-4-(3-(4-Methoxyphenyl)-1H-pyrazol-5-yl)but-3-en-1-ynyl)benzonitrile (2t)

orange solid; m.p.: 141-143 ^{o}C; R_f = 0.34 (*n*-hexane/ethyl acetate = 5/1 as eluent); ^{1}H NMR ($CDCl_3$, 500 MHz) : δ 7.80 (d, *J* = 7.5 Hz, 2H), 7.45-7.41 (m, 4H), 7.34 (t, *J* = 7.5 Hz, 1H), 7.20 (d, *J* = 8.5 Hz, 2H), 6.84 (s, 1H), 6.69 (d, *J* = 11.5 Hz, 1H), 5.95 (d, *J* = 11.5 Hz, 1H), 2.39 (s, 3H) ; ^{13}C NMR ($CDCl_3$, 125MHz) : δ 139.4, 132.5, 131.4(2C), 129.4(2C), 128.0, 125.6(2C), 125.4, 119.1, 107.6, 104.1, 97.9, 87.1, 21.5; MS (EI) 325 (M^+, 100), 324 (M^+-H^+, 66); HRMS (EI) calcd. for $C_{21}H_{15}ON_3$ 325.1215,

found 325.1214.

5-((Z)-Dec-1-en-3-ynyl)-3-(4-(trifluoromethyl)phenyl)-1H-pyrazole (2u)

yellow solid; m.p.: 76-78 ^{o}C; R_f = 0.48 (*n*-hexane/ethyl acetate = 5/1 as eluent); ^{1}H NMR ($CDCl_3$, 500 MHz) : δ 7.92 (d, *J* = 8.0 Hz, 2H), 7.67 (d, *J* = 8.0 Hz, 2H), 6.71 (s, 1H), 6.56 (d, *J* = 11.5 Hz, 1H), 5.76 (dt, *J* = 11.5, 2.5 Hz, 2H), 1.69-1.32 (m, 8H), 0.91(t, *J* = 6.5 Hz, 3H) ; ^{13}C NMR ($CDCl_3$, 125MHz) : δ 150.31, 141.89, 136.4, 129.7 (q, J_{C-F} = 31.8 Hz), 125.7(2C), 125.6(q, J_{C-F} = 4.5 Hz, 2C), 125.3, 123.9, 108.5, 104.0, 100.2, 79.3, 31.2, 28.7, 28.5, 22.5, 19.9, 14.0; MS (EI) 346 (M^+, 400), 289 (65), 276(100); HRMS (EI) calcd. for $C_{20}H_{21}N_2F_3$ 346.1657, found 346.1657.

(Z)-5-(But-1-en-3-yn-1-yl)-3-(4-fluorophenyl)-1H-pyrazole (2v)

brown liquid; R_f = 0.30 (*n*-hexane/ethyl acetate = 5/1 as eluent); ^{1}H NMR ($CDCl_3$, 500 MHz) : δ 7.76 (dd, *J* = 8.0, 5.5 Hz, 2H0, 7.10 (m, 2H), 6.75 (s, 1H), 6.72 (d, *J* = 11.5 Hz, 1H), 5.72 (dd, *J* = 11.5, 2.0 Hz, 1H), 3.59 (d, *J* = 1.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125MHz) : δ 163.7 (d, *J* = 246.0 Hz), 150.3, 141.7, 128.7, 127.8, 127.3 (d, *J* = 7.3 Hz), 115.7 (d, *J* = 83.5 Hz), 106.2, 104.3, 85.5, 82.2; MS (EI) 212 (M^+, 100), 211 (M^+−H^+, 94), 185 (94), 157 (35); HRMS (EI) calcd. for $C_{13}H_9FN_2$ 212.0750, found 212.0750.

(Z)-3-Methyl-5-(non-1-en-3-yn-1-yl)-1H-pyrazole (2w)

yellow liquid; R_f = 0.48 (*n*-hexane/ethyl acetate = 5/1 as eluent); ^{1}H NMR ($CDCl_3$, 500 MHz) : δ 6.50 (d, *J* = 11.5 Hz, 1H), 6.31 (s, 1H), 5.56 (dt, *J* = 11.5, 2.5 Hz, 1H), 2.46 (td, *J* = 7.5, 2.5 Hz, 2H), 2.30 (s, 3H), 1.63 (m, *J* = 7.0 Hz, 2H), 1.46-1.32 (m, 4H), 0.92 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125MHz) : δ 146.8, 142.8, 125.6, 107.6, 105.8, 99.0, 79.3, 31.1, 28.2, 22.1, 19.8, 13.9, 12.8; MS (EI) 202 (M^+, 76), 173 (38), 159 (85), 146 (100); HRMS (EI) calcd. for $C_{13}H_{18}N_2$ 202.1470, found 202.1473.

X-ray data for

(Z)-5-(4-(2-(methylthio)phenyl)but-1-en-3-yn-1-yl)-3-phenyl-1H-pyrazole (2p)

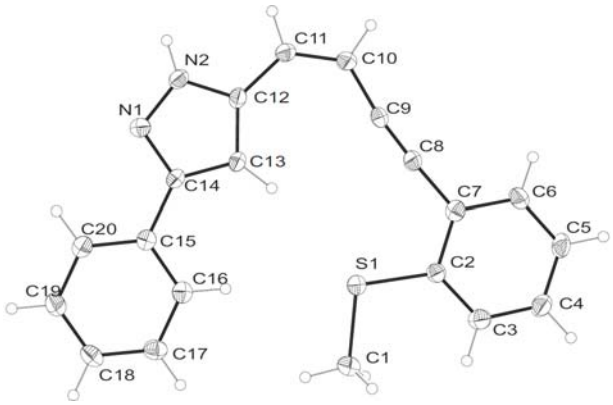


Table 1. Crystal data and structure refinement for $C_{20}H_{16}N_2S$

Identification code	9252	
Empirical formula	$C_{20}H_{16}N_2S$	
Formula weight	316.41	
Temperature	200(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C 2/c	
Unit cell dimensions	a = 26.0310(9) Å	a= 90°.
	b = 5.2668(2) Å	b= 114.261(2)°.
	c = 25.4350(11) Å	g = 90°.
Volume	3179.2(2) $Å^3$	
Z	8	

Density (calculated)	1.322 Mg/m^3
Absorption coefficient	0.204 mm^{-1}
F(000)	1328
Crystal size	0.15 x 0.12 x 0.04 mm^3
Theta range for data collection	2.92 to 25.02°.
Index ranges	-30<=h<=30, -6<=k<=6, -29<=l<=30
Reflections collected	9281
Independent reflections	2792 [R(int) = 0.1016]
Completeness to theta = 25.02°	99.5 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.057 and 0.9313
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2792 / 0 / 208
Goodness-of-fit on F^2	1.054
Final R indices [I>2sigma(I)]	R1 = 0.0664, wR2 = 0.1323
R indices (all data)	R1 = 0.1318, wR2 = 0.1602
Largest diff. peak and hole	0.293 and -0.316 $e.Å^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å ^{2}x 10^3) for $C_{20}H_{16}N_2S$.

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
S(1)	3413(1)	-336(2)	2561(1)	39(1)
N(1)	2488(1)	5197(6)	391(1)	33(1)
N(2)	2962(1)	6605(6)	590(1)	34(1)
C(1)	3049(2)	-3013(8)	2674(2)	50(1)
C(2)	4057(2)	-327(7)	3171(2)	30(1)
C(3)	4187(2)	-1931(8)	3640(2)	39(1)
C(4)	4701(2)	-1754(8)	4109(2)	42(1)
C(5)	5096(2)	7(8)	4117(2)	43(1)
C(6)	4980(2)	1616(8)	3657(2)	38(1)
C(7)	4460(2)	1480(7)	3170(2)	32(1)
C(8)	4352(2)	3167(8)	2693(2)	34(1)
C(9)	4289(2)	4622(8)	2313(2)	33(1)
C(10)	4280(2)	6487(8)	1903(2)	39(1)
C(11)	3865(2)	6980(8)	1385(2)	36(1)
C(12)	3328(2)	5732(8)	1105(2)	31(1)
C(13)	3077(2)	3651(7)	1244(2)	33(1)
C(14)	2551(2)	3387(7)	788(2)	29(1)
C(15)	2089(2)	1584(7)	699(2)	31(1)
C(16)	2156(2)	-351(7)	1095(2)	35(1)
C(17)	1720(2)	-2027(8)	1020(2)	39(1)
C(18)	1212(2)	-1815(8)	542(2)	42(1)
C(19)	1143(2)	52(8)	142(2)	43(1)
C(20)	1574(2)	1758(8)	217(2)	41(1)

Table 3. Bond lengths [Å] and angles [°] for $C_{20}H_{16}N_2S$.

S(1)-C(2)	1.756(4)
S(1)-C(1)	1.785(4)
N(1)-N(2)	1.348(4)
N(1)-C(14)	1.350(4)
N(2)-C(12)	1.345(4)
N(2)-H(2)	0.8800
C(1)-H(1A)	0.9800
C(1)-H(1B)	0.9800
C(1)-H(1C)	0.9800
C(2)-C(3)	1.385(5)
C(2)-C(7)	1.418(5)
C(3)-C(4)	1.383(5)
C(3)-H(3)	0.9500
C(4)-C(5)	1.379(6)
C(4)-H(4)	0.9500
C(5)-C(6)	1.373(5)
C(5)-H(5)	0.9500
C(6)-C(7)	1.411(5)
C(6)-H(6)	0.9500
C(7)-C(8)	1.434(5)
C(8)-C(9)	1.192(5)
C(9)-C(10)	1.424(5)
C(10)-C(11)	1.342(5)
C(10)-H(10)	0.9500
C(11)-C(12)	1.441(5)
C(11)-H(11)	0.9500
C(12)-C(13)	1.394(5)
C(13)-C(14)	1.391(5)
C(13)-H(13)	0.9500
C(14)-C(15)	1.475(5)
C(15)-C(16)	1.393(5)
C(15)-C(20)	1.398(5)
C(16)-C(17)	1.388(5)
C(16)-H(16)	0.9500

C(17)-C(18)	1.385(5)
C(17)-H(17)	0.9500
C(18)-C(19)	1.371(5)
C(18)-H(18)	0.9500
C(19)-C(20)	1.388(5)
C(19)-H(19)	0.9500
C(20)-H(20)	0.9500

C(2)-S(1)-C(1)	103.72(19)
N(2)-N(1)-C(14)	107.2(3)
C(12)-N(2)-N(1)	110.6(3)
C(12)-N(2)-H(2)	124.7
N(1)-N(2)-H(2)	124.7
S(1)-C(1)-H(1A)	109.5
S(1)-C(1)-H(1B)	109.5
H(1A)-C(1)-H(1B)	109.5
S(1)-C(1)-H(1C)	109.5
H(1A)-C(1)-H(1C)	109.5
H(1B)-C(1)-H(1C)	109.5
C(3)-C(2)-C(7)	119.5(4)
C(3)-C(2)-S(1)	124.4(3)
C(7)-C(2)-S(1)	116.1(3)
C(4)-C(3)-C(2)	120.5(4)
C(4)-C(3)-H(3)	119.7
C(2)-C(3)-H(3)	119.7
C(5)-C(4)-C(3)	120.7(4)
C(5)-C(4)-H(4)	119.7
C(3)-C(4)-H(4)	119.7
C(6)-C(5)-C(4)	120.0(4)
C(6)-C(5)-H(5)	120.0
C(4)-C(5)-H(5)	120.0
C(5)-C(6)-C(7)	120.9(4)
C(5)-C(6)-H(6)	119.6
C(7)-C(6)-H(6)	119.6
C(6)-C(7)-C(2)	118.4(4)
C(6)-C(7)-C(8)	119.7(4)
C(2)-C(7)-C(8)	121.9(4)
C(9)-C(8)-C(7)	176.7(4)

C(8)-C(9)-C(10)	172.9(4)
C(11)-C(10)-C(9)	128.1(4)
C(11)-C(10)-H(10)	116.0
C(9)-C(10)-H(10)	116.0
C(10)-C(11)-C(12)	128.4(4)
C(10)-C(11)-H(11)	115.8
C(12)-C(11)-H(11)	115.8
N(2)-C(12)-C(13)	107.3(3)
N(2)-C(12)-C(11)	118.7(3)
C(13)-C(12)-C(11)	134.0(3)
C(14)-C(13)-C(12)	105.7(3)
C(14)-C(13)-H(13)	127.1
C(12)-C(13)-H(13)	127.1
N(1)-C(14)-C(13)	109.2(3)
N(1)-C(14)-C(15)	119.9(3)
C(13)-C(14)-C(15)	130.9(3)
C(16)-C(15)-C(20)	118.2(4)
C(16)-C(15)-C(14)	120.4(4)
C(20)-C(15)-C(14)	121.4(4)
C(17)-C(16)-C(15)	120.8(4)
C(17)-C(16)-H(16)	119.6
C(15)-C(16)-H(16)	119.6
C(18)-C(17)-C(16)	120.1(4)
C(18)-C(17)-H(17)	120.0
C(16)-C(17)-H(17)	120.0
C(19)-C(18)-C(17)	119.7(4)
C(19)-C(18)-H(18)	120.1
C(17)-C(18)-H(18)	120.1
C(18)-C(19)-C(20)	120.6(4)
C(18)-C(19)-H(19)	119.7
C(20)-C(19)-H(19)	119.7
C(19)-C(20)-C(15)	120.5(4)
C(19)-C(20)-H(20)	119.8
C(15)-C(20)-H(20)	119.8

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for $C_{20}H_{16}N_2S$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S(1)	30(1)	44(1)	38(1)	10(1)	7(1)	-2(1)
N(1)	35(2)	32(2)	36(2)	2(2)	16(2)	0(2)
N(2)	35(2)	37(2)	31(2)	9(2)	15(2)	2(2)
C(1)	43(3)	47(3)	52(3)	9(2)	12(2)	-14(2)
C(2)	27(2)	32(2)	32(2)	1(2)	13(2)	1(2)
C(3)	37(3)	36(3)	45(3)	5(2)	19(2)	2(2)
C(4)	39(3)	49(3)	35(2)	12(2)	13(2)	4(2)
C(5)	30(2)	54(3)	36(2)	10(2)	3(2)	8(2)
C(6)	27(2)	42(3)	41(2)	0(2)	9(2)	-4(2)
C(7)	30(2)	34(2)	33(2)	2(2)	14(2)	6(2)
C(8)	23(2)	42(3)	34(2)	5(2)	8(2)	0(2)
C(9)	21(2)	39(3)	34(2)	2(2)	6(2)	-1(2)
C(10)	28(2)	43(3)	43(3)	10(2)	13(2)	-5(2)
C(11)	34(3)	38(3)	37(2)	10(2)	15(2)	-2(2)
C(12)	27(2)	39(3)	26(2)	5(2)	10(2)	5(2)
C(13)	30(2)	36(2)	28(2)	8(2)	8(2)	3(2)
C(14)	33(2)	27(2)	27(2)	4(2)	12(2)	4(2)
C(15)	32(2)	32(2)	30(2)	-1(2)	14(2)	3(2)
C(16)	36(2)	34(2)	33(2)	-3(2)	14(2)	1(2)
C(17)	45(3)	34(3)	42(3)	-3(2)	22(2)	-6(2)
C(18)	34(3)	45(3)	45(3)	-9(2)	14(2)	-11(2)
C(19)	35(2)	46(3)	41(2)	-4(2)	8(2)	-6(2)
C(20)	42(3)	40(3)	35(2)	6(2)	11(2)	0(2)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for $C_{20}H_{16}N_2S$.

	x	y	z	U(eq)
H(2)	3024	7914	409	41
H(1A)	2679	-3167	2350	75
H(1B)	3000	-2785	3033	75
H(1C)	3269	-4556	2700	75
H(3)	3920	-3162	3639	46
H(4)	4783	-2857	4429	51
H(5)	5449	106	4440	52
H(6)	5252	2838	3668	46
H(10)	4608	7509	2011	46
H(11)	3935	8328	1175	43
H(13)	3233	2625	1580	39
H(16)	2506	-525	1421	42
H(17)	1770	-3321	1297	47
H(18)	913	-2958	491	51
H(19)	797	179	-189	52
H(20)	1519	3053	-61	49

X-ray data for

(Z)-5-(4-(2-(methylthio)phenyl)but-1-en-3-yn-1-yl)-3-phenyl-1H-pyrazole (6i)

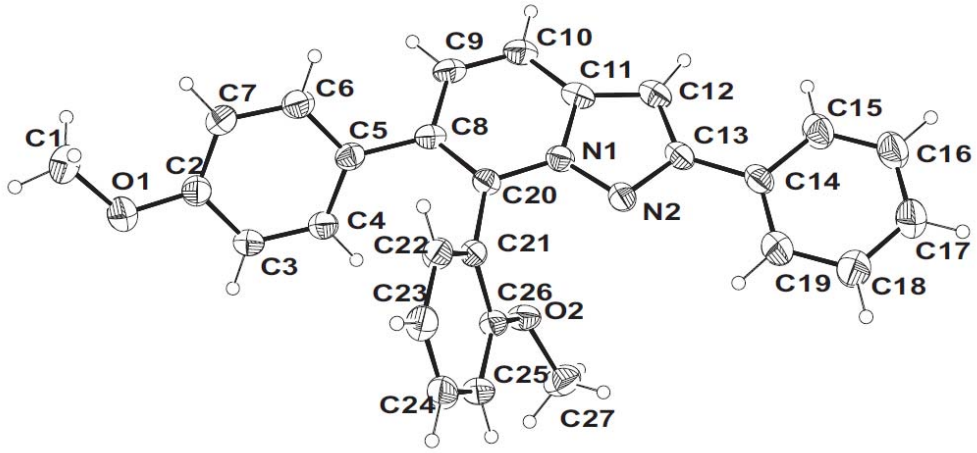


Table 1. Crystal data and structure refinement for $C_{27}H_{22}N_2O_2$

Identification code	ch13402	
Empirical formula	$C_{27}H_{22}N_2O_2$	
Formula weight	406.47	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21	
Unit cell dimensions	a = 11.123(5) Å	= 90°.
	b = 7.632(4) Å	= 90.390(10)°.
	c = 12.700(5) Å	= 90°.
Volume	1078.0(8) $Å^3$	

Z	2
Density (calculated)	1.252 Mg/m^3
Absorption coefficient	0.079 mm^{-1}
F(000)	428
Crystal size	0.76 x 0.51 x 0.36 mm^3
Theta range for data collection	1.60 to 25.02°.
Index ranges	-12<=h<=13, -4<=k<=9, -15<=l<=15
Reflections collected	6366
Independent reflections	2970 [R(int) = 0.0437]
Completeness to theta = 25.02°	99.6 %
Absorption correction	multi-scan
Max. and min. transmission	0.9719 and 0.9421
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2970 / 1 / 280
Goodness-of-fit on F^2	0.789
Final R indices [I>2sigma(I)]	R1 = 0.0534, wR2 = 0.1428
R indices (all data)	R1 = 0.0847, wR2 = 0.1896
Absolute structure parameter	-5(3)
Largest diff. peak and hole	0.231 and -0.308 $e.Å^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for ch13402.

U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	5228(5)	-2762(11)	-698(4)	86(2)
C(2)	3965(4)	-2531(7)	836(3)	53(1)
C(3)	2813(4)	-2265(6)	1232(3)	51(1)
C(4)	2653(4)	-2060(6)	2297(3)	47(1)
C(5)	3623(4)	-2105(6)	3006(3)	45(1)
C(6)	4751(4)	-2416(7)	2601(4)	55(1)
C(7)	4941(4)	-2612(8)	1531(4)	58(1)
C(8)	3451(4)	-1947(6)	4163(3)	45(1)
C(9)	3928(4)	-3300(6)	4838(4)	52(1)
C(10)	3755(4)	-3268(6)	5895(4)	55(1)
C(11)	3123(4)	-1879(6)	6351(3)	49(1)
C(12)	2787(4)	-1357(7)	7360(3)	55(1)
C(13)	2194(4)	238(7)	7242(3)	48(1)
C(14)	1685(4)	1372(7)	8081(3)	50(1)
C(15)	1921(5)	1008(8)	9142(3)	63(1)
C(16)	1508(5)	2090(9)	9926(4)	73(2)
C(17)	833(5)	3532(11)	9681(4)	81(2)
C(18)	555(6)	3889(11)	8649(4)	94(2)
C(19)	974(6)	2789(9)	7852(4)	82(2)
C(20)	2816(4)	-575(6)	4596(3)	41(1)
C(21)	2288(4)	889(6)	3979(3)	42(1)
C(22)	3031(4)	2068(6)	3438(3)	51(1)
C(23)	2556(5)	3401(6)	2838(3)	55(1)
C(24)	1326(5)	3585(7)	2759(3)	58(1)
C(25)	562(4)	2449(6)	3283(3)	53(1)
C(26)	1028(4)	1105(6)	3894(3)	44(1)
C(27)	-889(4)	302(8)	4599(4)	70(2)
N(1)	2688(3)	-553(5)	5689(3)	44(1)
N(2)	2116(3)	748(5)	6222(3)	47(1)

O(1)	4043(3)	-2665(7)	-242(2)	76(1)
O(2)	349(3)	-125(4)	4413(2)	53(1)

Table 3. Bond lengths [Å] and angles [°] for ch13402.

C(1)-O(1)	1.445(6)
C(1)-H(1A)	0.9600
C(1)-H(1B)	0.9600
C(1)-H(1C)	0.9600
C(2)-O(1)	1.377(5)
C(2)-C(3)	1.394(6)
C(2)-C(7)	1.396(7)
C(3)-C(4)	1.374(6)
C(3)-H(3)	0.9300
C(4)-C(5)	1.401(6)
C(4)-H(4)	0.9300
C(5)-C(6)	1.379(6)
C(5)-C(8)	1.488(6)
C(6)-C(7)	1.385(6)
C(6)-H(6)	0.9300
C(7)-H(7)	0.9300
C(8)-C(20)	1.380(6)
C(8)-C(9)	1.441(6)
C(9)-C(10)	1.357(6)
C(9)-H(9)	0.9300
C(10)-C(11)	1.400(7)
C(10)-H(10)	0.9300
C(11)-C(12)	1.395(6)
C(11)-N(1)	1.401(5)
C(12)-C(13)	1.392(7)
C(12)-H(12)	0.9300
C(13)-N(2)	1.355(5)
C(13)-C(14)	1.488(6)
C(14)-C(19)	1.370(8)
C(14)-C(15)	1.399(6)
C(15)-C(16)	1.375(8)
C(15)-H(15)	0.9300

C(16)-C(17)	1.367(9)
C(16)-H(16)	0.9300
C(17)-C(18)	1.372(8)
C(17)-H(17)	0.9300
C(18)-C(19)	1.397(8)
C(18)-H(18)	0.9300
C(19)-H(19)	0.9300
C(20)-N(1)	1.397(5)
C(20)-C(21)	1.483(6)
C(21)-C(22)	1.405(6)
C(21)-C(26)	1.415(6)
C(22)-C(23)	1.374(7)
C(22)-H(22)	0.9300
C(23)-C(24)	1.378(7)
C(23)-H(23)	0.9300
C(24)-C(25)	1.387(7)
C(24)-H(24)	0.9300
C(25)-C(26)	1.385(6)
C(25)-H(25)	0.9300
C(26)-O(2)	1.376(5)
C(27)-O(2)	1.436(5)
C(27)-H(27A)	0.9600
C(27)-H(27B)	0.9600
C(27)-H(27C)	0.9600
N(1)-N(2)	1.362(5)

O(1)-C(1)-H(1A)	109.5
O(1)-C(1)-H(1B)	109.5
H(1A)-C(1)-H(1B)	109.5
O(1)-C(1)-H(1C)	109.5
H(1A)-C(1)-H(1C)	109.5
H(1B)-C(1)-H(1C)	109.5
O(1)-C(2)-C(3)	115.8(4)
O(1)-C(2)-C(7)	124.8(4)
C(3)-C(2)-C(7)	119.4(4)
C(4)-C(3)-C(2)	119.8(4)
C(4)-C(3)-H(3)	120.1
C(2)-C(3)-H(3)	120.1

C(3)-C(4)-C(5)	121.7(4)
C(3)-C(4)-H(4)	119.2
C(5)-C(4)-H(4)	119.2
C(6)-C(5)-C(4)	117.6(4)
C(6)-C(5)-C(8)	120.3(4)
C(4)-C(5)-C(8)	121.9(4)
C(5)-C(6)-C(7)	122.0(4)
C(5)-C(6)-H(6)	119.0
C(7)-C(6)-H(6)	119.0
C(6)-C(7)-C(2)	119.5(4)
C(6)-C(7)-H(7)	120.3
C(2)-C(7)-H(7)	120.3
C(20)-C(8)-C(9)	119.6(4)
C(20)-C(8)-C(5)	121.7(4)
C(9)-C(8)-C(5)	118.7(4)
C(10)-C(9)-C(8)	121.4(4)
C(10)-C(9)-H(9)	119.3
C(8)-C(9)-H(9)	119.3
C(9)-C(10)-C(11)	119.9(4)
C(9)-C(10)-H(10)	120.1
C(11)-C(10)-H(10)	120.1
C(12)-C(11)-N(1)	104.6(4)
C(12)-C(11)-C(10)	137.3(4)
N(1)-C(11)-C(10)	118.1(4)
C(11)-C(12)-C(13)	106.3(4)
C(11)-C(12)-H(12)	126.9
C(13)-C(12)-H(12)	126.9
N(2)-C(13)-C(12)	112.4(4)
N(2)-C(13)-C(14)	119.7(4)
C(12)-C(13)-C(14)	127.9(4)
C(19)-C(14)-C(15)	117.8(5)
C(19)-C(14)-C(13)	122.0(4)
C(15)-C(14)-C(13)	120.3(5)
C(16)-C(15)-C(14)	121.1(5)
C(16)-C(15)-H(15)	119.5
C(14)-C(15)-H(15)	119.5
C(17)-C(16)-C(15)	120.3(5)
C(17)-C(16)-H(16)	119.9

C(15)-C(16)-H(16)	119.9
C(16)-C(17)-C(18)	119.8(6)
C(16)-C(17)-H(17)	120.1
C(18)-C(17)-H(17)	120.1
C(17)-C(18)-C(19)	119.9(6)
C(17)-C(18)-H(18)	120.1
C(19)-C(18)-H(18)	120.1
C(14)-C(19)-C(18)	121.0(5)
C(14)-C(19)-H(19)	119.5
C(18)-C(19)-H(19)	119.5
C(8)-C(20)-N(1)	117.5(4)
C(8)-C(20)-C(21)	124.3(3)
N(1)-C(20)-C(21)	118.2(3)
C(22)-C(21)-C(26)	118.3(4)
C(22)-C(21)-C(20)	120.6(4)
C(26)-C(21)-C(20)	121.1(4)
C(23)-C(22)-C(21)	121.4(4)
C(23)-C(22)-H(22)	119.3
C(21)-C(22)-H(22)	119.3
C(24)-C(23)-C(22)	119.6(4)
C(24)-C(23)-H(23)	120.2
C(22)-C(23)-H(23)	120.2
C(23)-C(24)-C(25)	120.8(4)
C(23)-C(24)-H(24)	119.6
C(25)-C(24)-H(24)	119.6
C(26)-C(25)-C(24)	120.3(4)
C(26)-C(25)-H(25)	119.9
C(24)-C(25)-H(25)	119.9
O(2)-C(26)-C(25)	124.7(4)
O(2)-C(26)-C(21)	115.5(4)
C(25)-C(26)-C(21)	119.7(4)
O(2)-C(27)-H(27A)	109.5
O(2)-C(27)-H(27B)	109.5
H(27A)-C(27)-H(27B)	109.5
O(2)-C(27)-H(27C)	109.5
H(27A)-C(27)-H(27C)	109.5
H(27B)-C(27)-H(27C)	109.5
N(2)-N(1)-C(20)	123.7(3)

N(2)-N(1)-C(11)	112.9(3)
C(20)-N(1)-C(11)	123.4(4)
C(13)-N(2)-N(1)	103.8(4)
C(2)-O(1)-C(1)	117.8(4)
C(26)-O(2)-C(27)	117.0(4)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$)for ch13402.
The anisotropic displacement factor exponent takes the form: $-2\ ^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

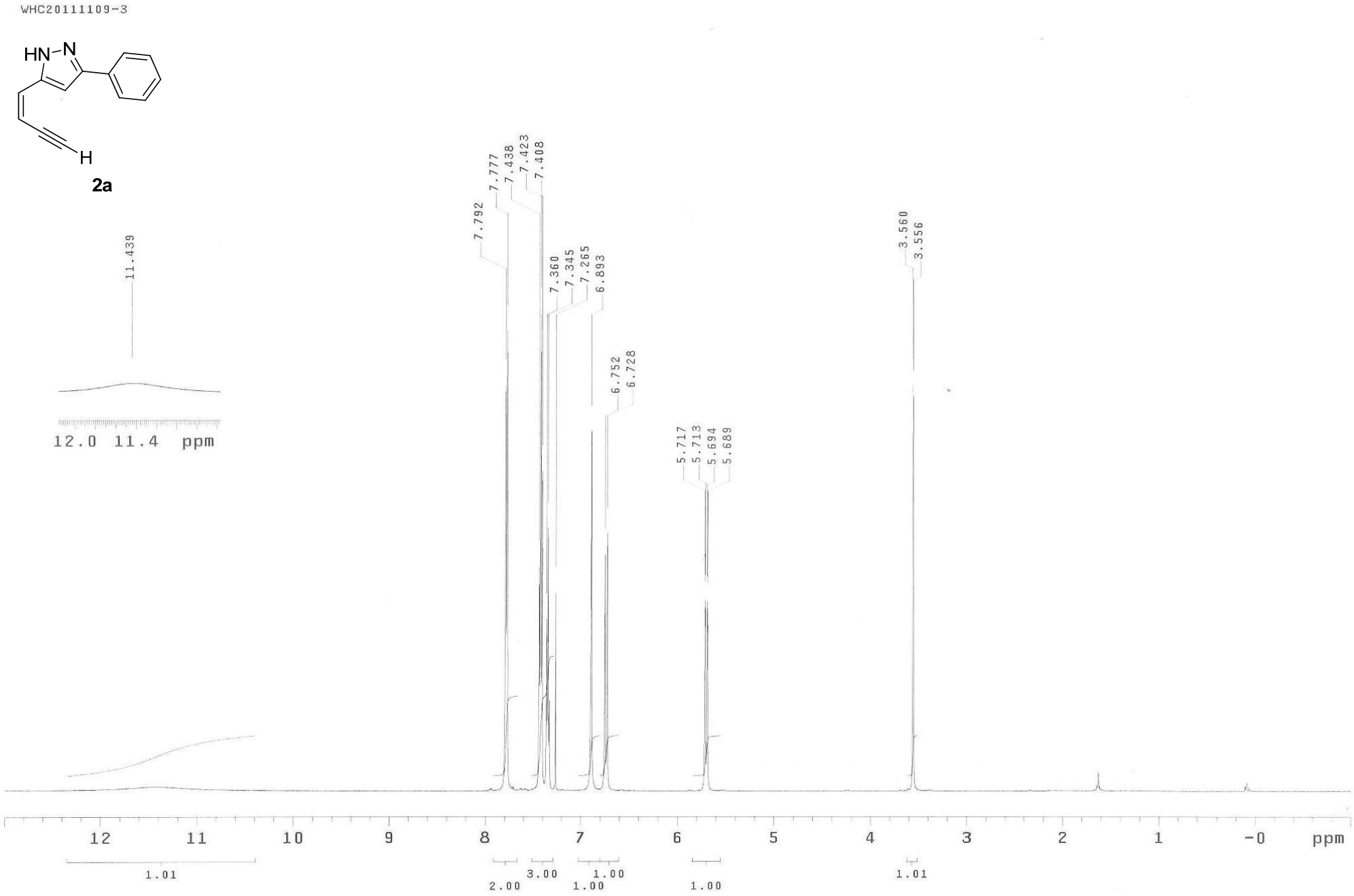
	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	79(4)	116(5)	64(3)	0(4)	20(3)	21(4)
C(2)	61(3)	51(3)	48(3)	3(2)	4(2)	9(2)
C(3)	49(2)	53(3)	51(2)	4(2)	-5(2)	10(2)
C(4)	44(2)	47(3)	50(2)	3(2)	0(2)	3(2)
C(5)	45(2)	38(2)	52(2)	-3(2)	0(2)	5(2)
C(6)	49(3)	53(3)	61(3)	-6(2)	-6(2)	7(2)
C(7)	49(3)	68(3)	59(3)	-6(3)	2(2)	10(2)
C(8)	39(2)	43(2)	55(2)	2(2)	-8(2)	5(2)
C(9)	44(2)	48(3)	65(3)	2(2)	-9(2)	11(2)
C(10)	52(3)	50(3)	62(3)	8(2)	-13(2)	8(2)
C(11)	46(2)	50(3)	52(2)	11(2)	-12(2)	-4(2)
C(12)	55(3)	62(3)	47(2)	12(2)	-10(2)	-3(2)
C(13)	45(2)	61(3)	38(2)	7(2)	-5(2)	-6(2)
C(14)	43(2)	70(3)	38(2)	2(2)	-6(2)	-7(2)
C(15)	67(3)	76(4)	47(3)	6(3)	5(2)	-5(3)
C(16)	74(4)	101(5)	45(3)	-1(3)	4(2)	-1(4)
C(17)	82(4)	106(5)	53(3)	-12(3)	7(3)	9(4)
C(18)	118(5)	100(5)	63(3)	-2(4)	2(3)	46(5)
C(19)	99(4)	96(5)	49(3)	-1(3)	-6(3)	32(4)
C(20)	43(2)	40(2)	41(2)	0(2)	-6(2)	0(2)
C(21)	47(2)	40(2)	39(2)	-2(2)	-2(2)	7(2)
C(22)	52(3)	50(3)	51(2)	-1(2)	5(2)	3(2)
C(23)	71(3)	40(2)	55(3)	6(2)	11(2)	3(2)

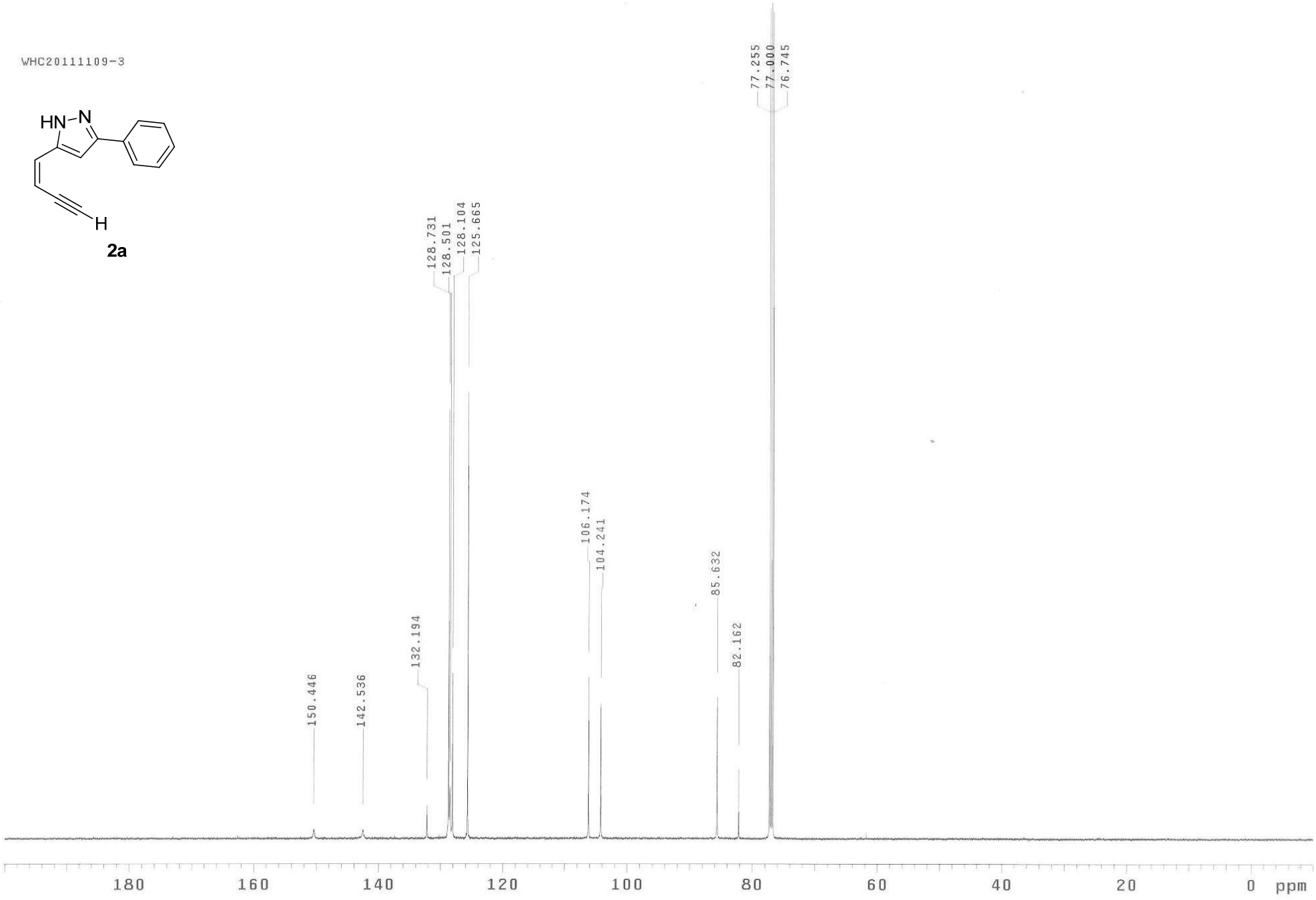
C(24)	81(4)	48(3)	46(2)	9(2)	4(2)	14(3)
C(25)	56(3)	49(3)	55(2)	5(2)	-5(2)	14(2)
C(26)	47(2)	41(2)	44(2)	0(2)	-3(2)	8(2)
C(27)	54(3)	74(4)	83(4)	16(3)	13(3)	10(3)
N(1)	46(2)	42(2)	43(2)	1(2)	-6(2)	4(2)
N(2)	52(2)	49(2)	40(2)	-2(2)	-3(2)	2(2)
O(1)	70(2)	108(3)	50(2)	6(2)	6(2)	11(2)
O(2)	46(2)	52(2)	60(2)	16(2)	-1(1)	6(1)

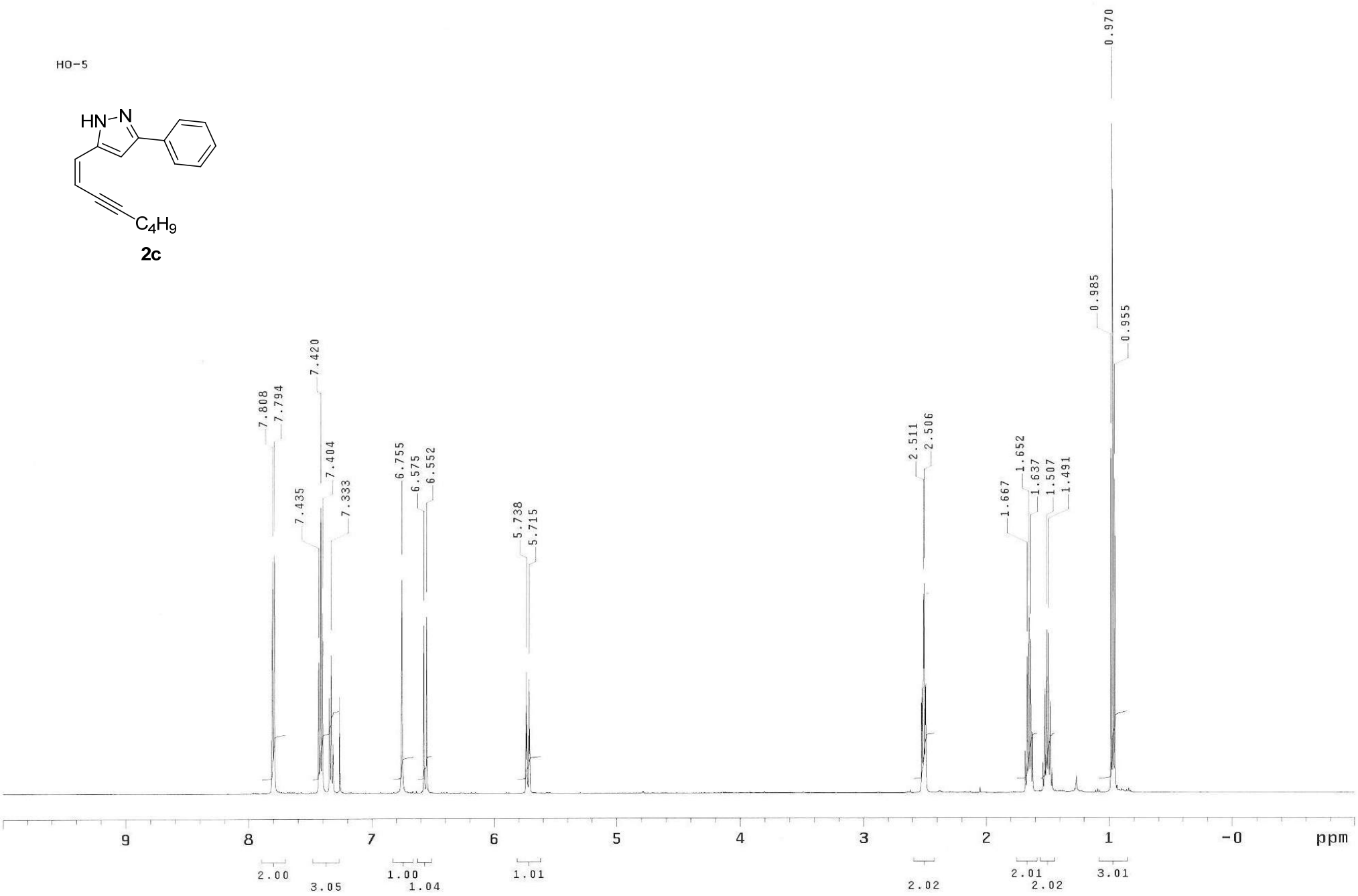
Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for ch13402.

	x	y	z	U(eq)
H(1A)	5157	-2860	-1449	129
H(1B)	5643	-3768	-424	129
H(1C)	5672	-1721	-523	129
H(3)	2155	-2227	777	61
H(4)	1881	-1888	2554	57
H(6)	5403	-2497	3061	65
H(7)	5713	-2796	1277	70
H(9)	4363	-4216	4543	62
H(10)	4056	-4167	6314	66
H(12)	2931	-1955	7987	66
H(15)	2365	17	9320	76
H(16)	1689	1840	10626	88
H(17)	562	4268	10212	97
H(18)	88	4861	8480	113
H(19)	767	3023	7155	98
H(22)	3861	1945	3487	61
H(23)	3061	4173	2487	66
H(24)	1004	4482	2349	70
H(25)	-266	2590	3223	64
H(27A)	-1270	-650	4961	106
H(27B)	-1291	499	3938	106
H(27C)	-934	1343	5022	106

^{1}H and ^{13}C NMR spectra of previously unreported compounds







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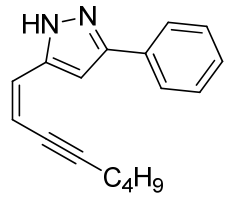

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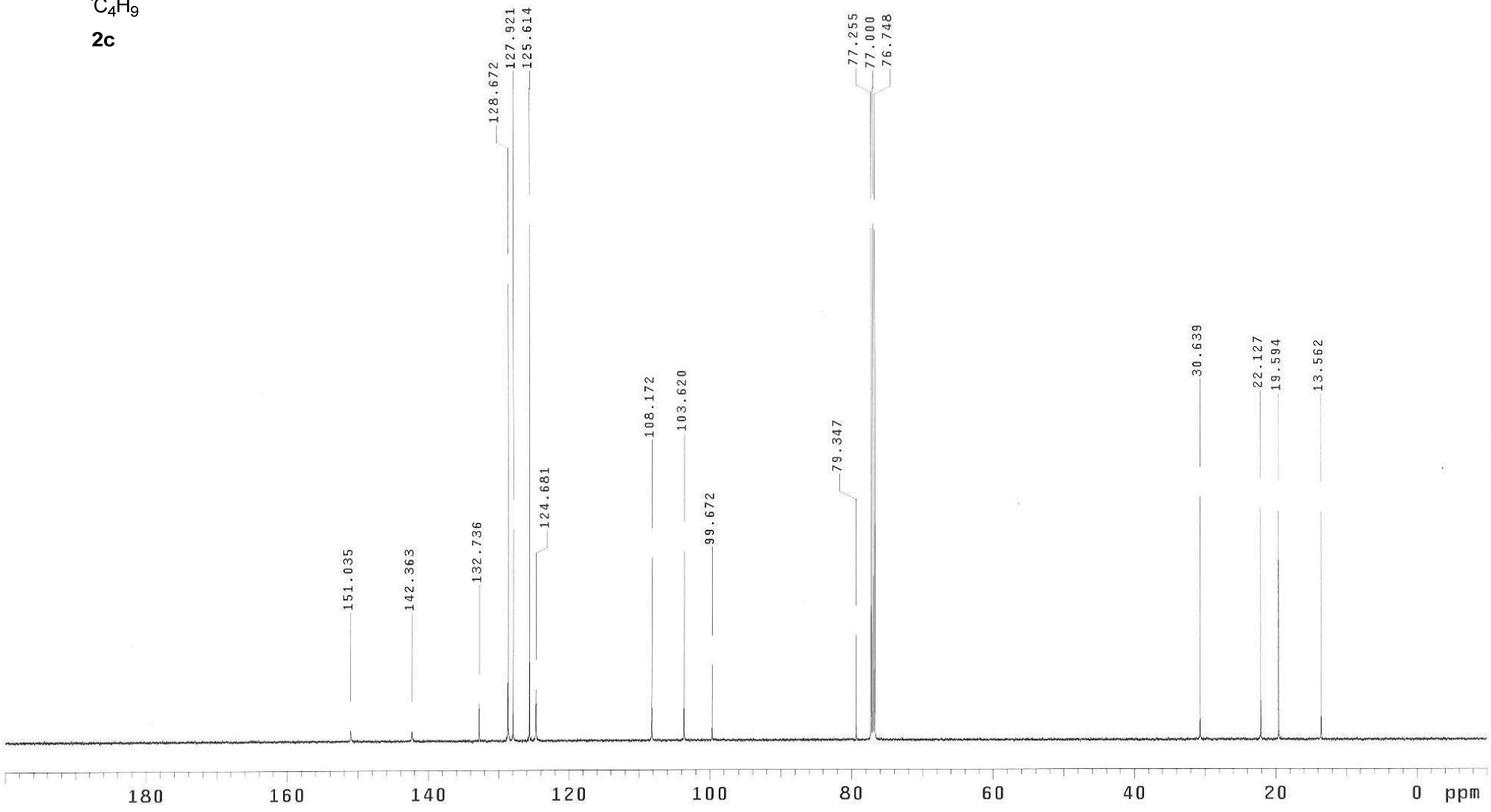

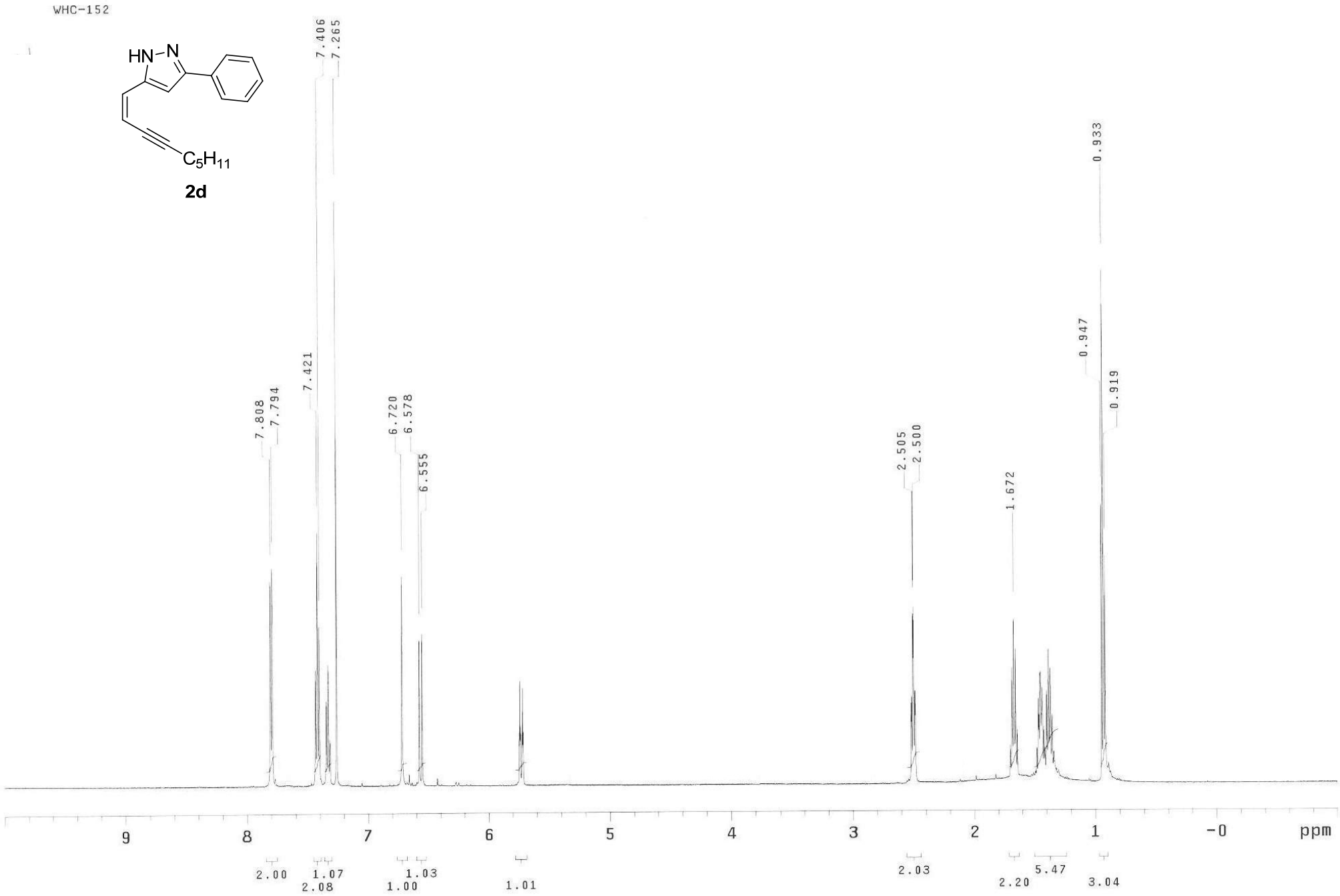

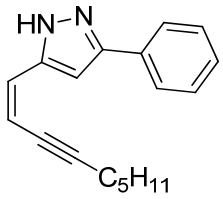

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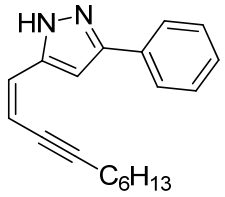

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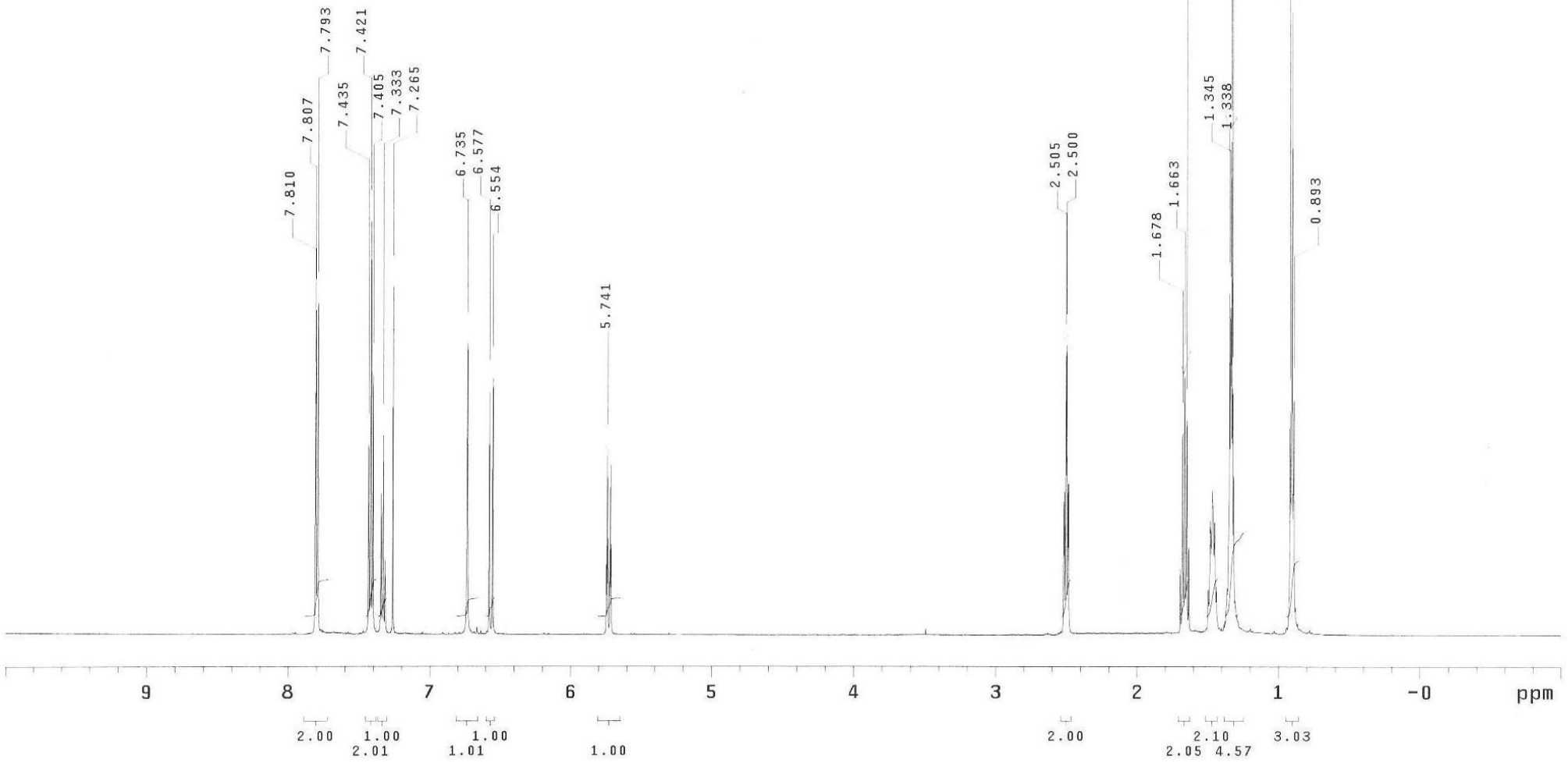

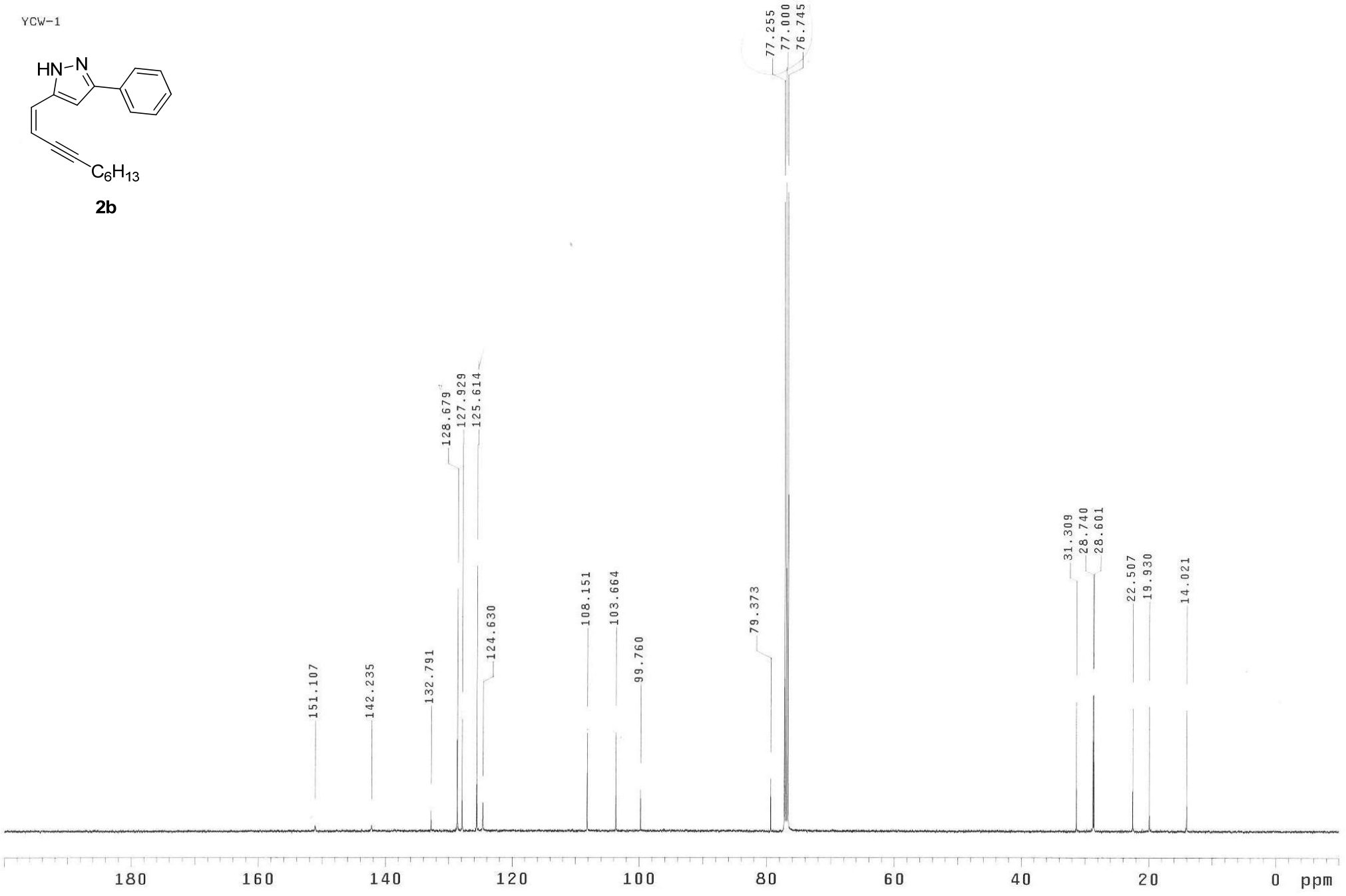

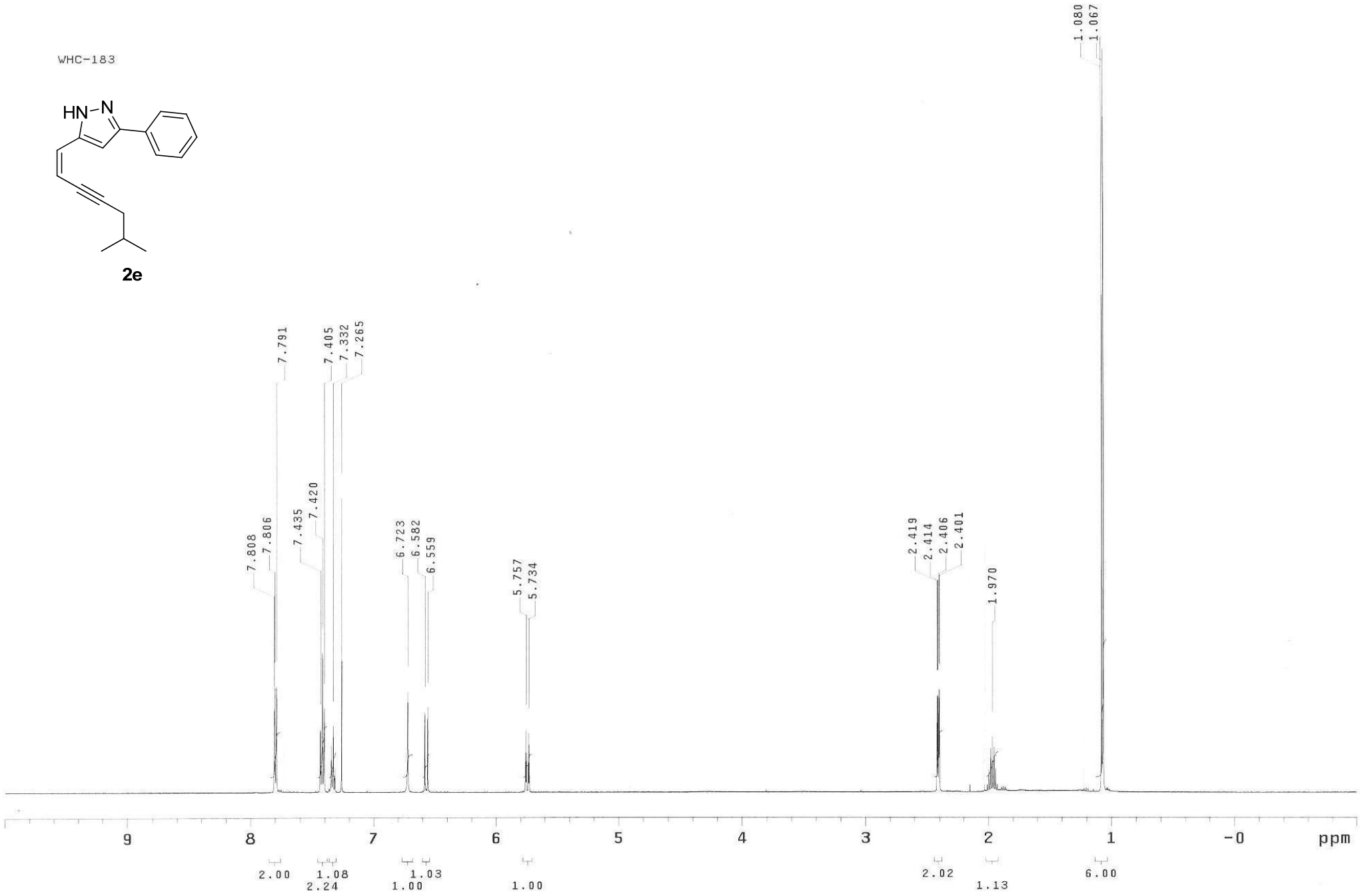

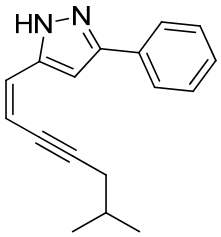

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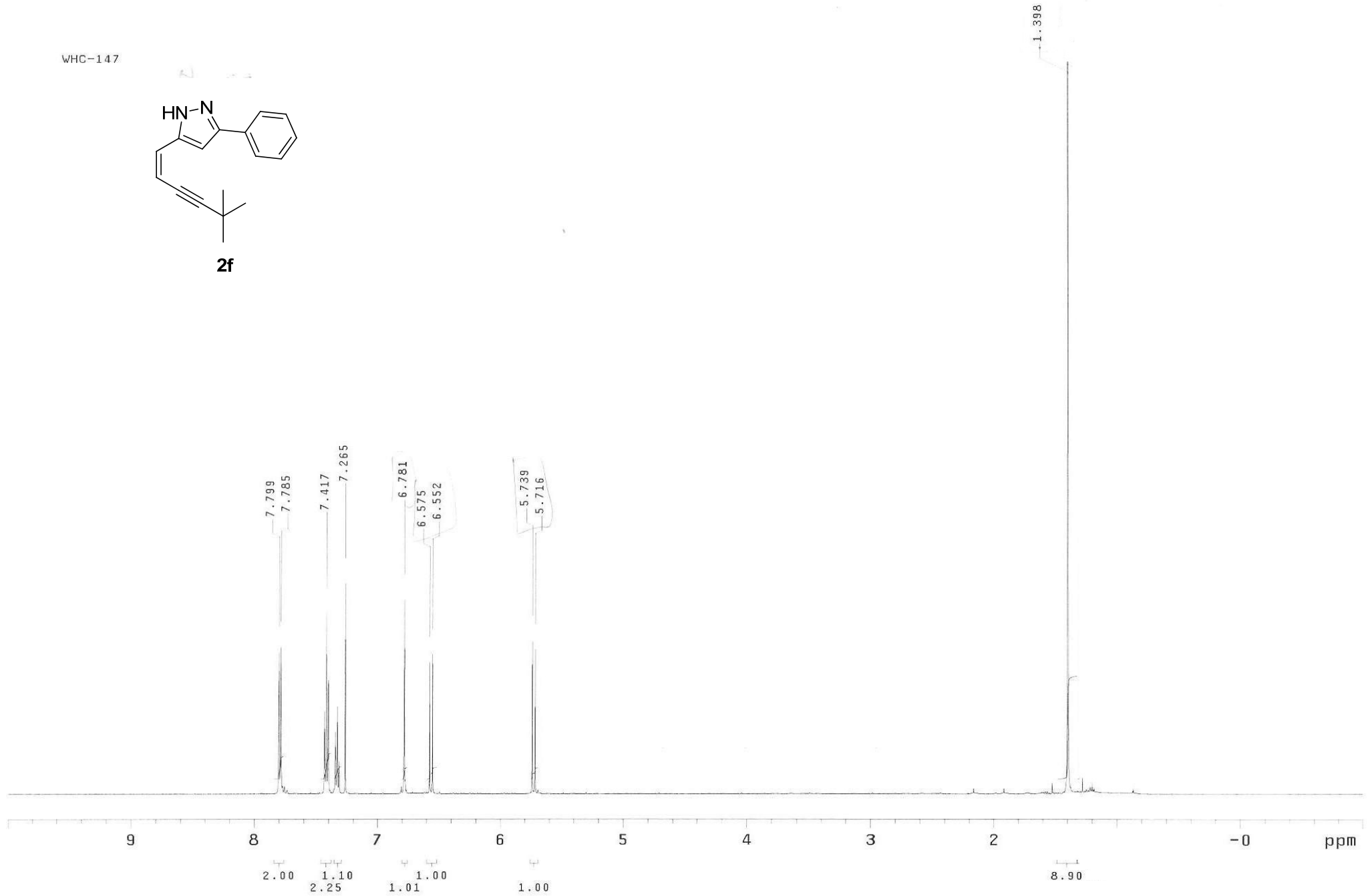

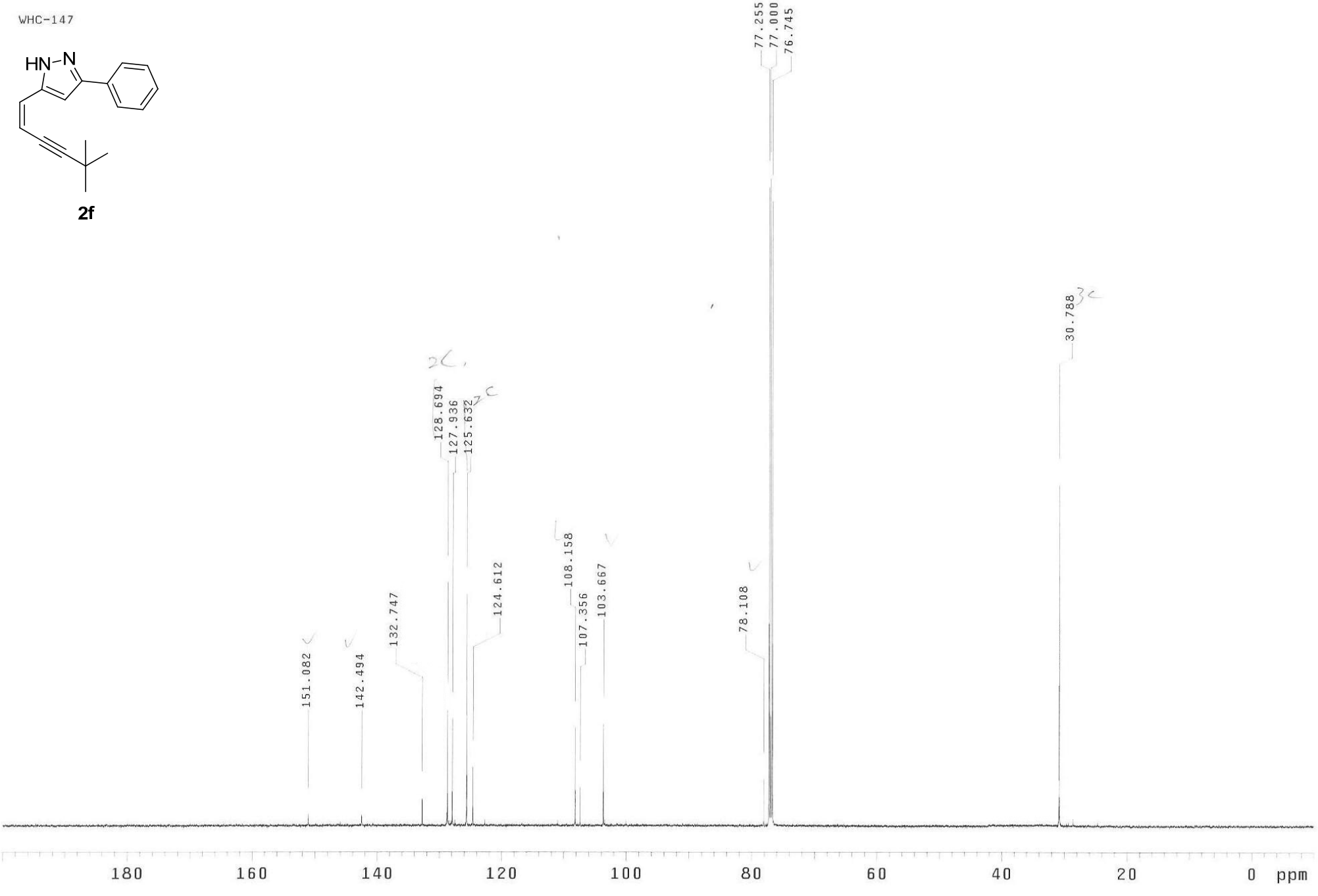

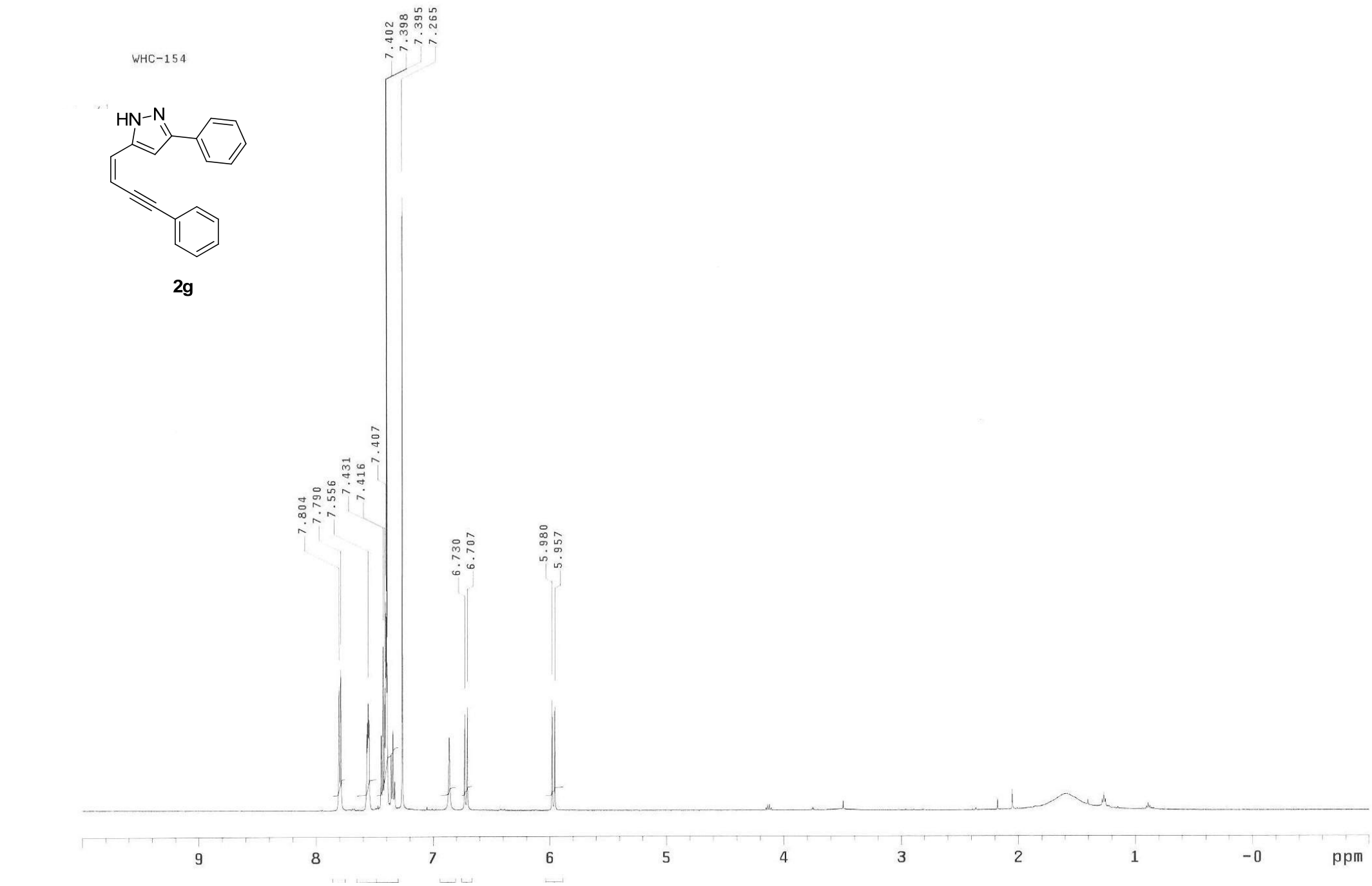

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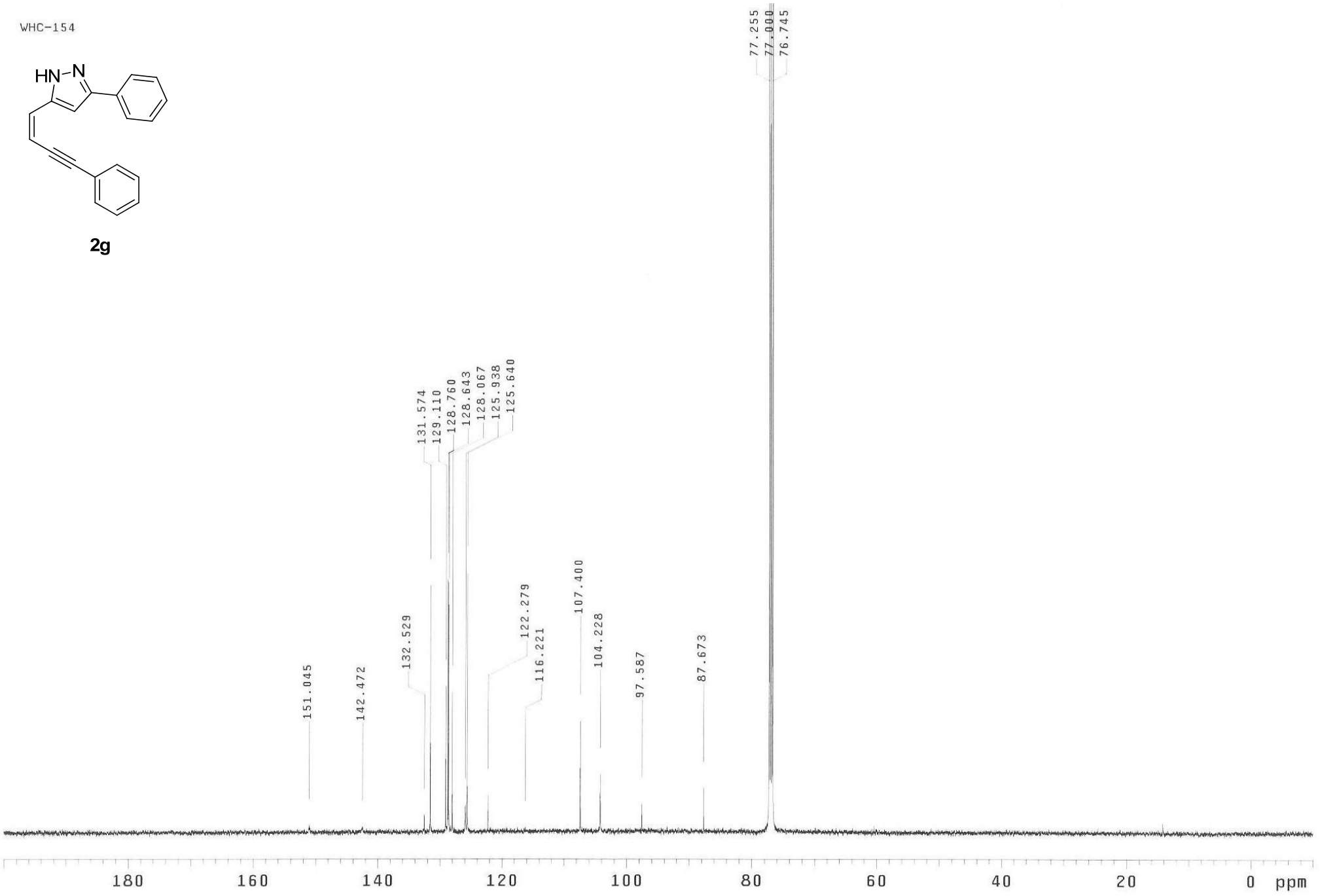

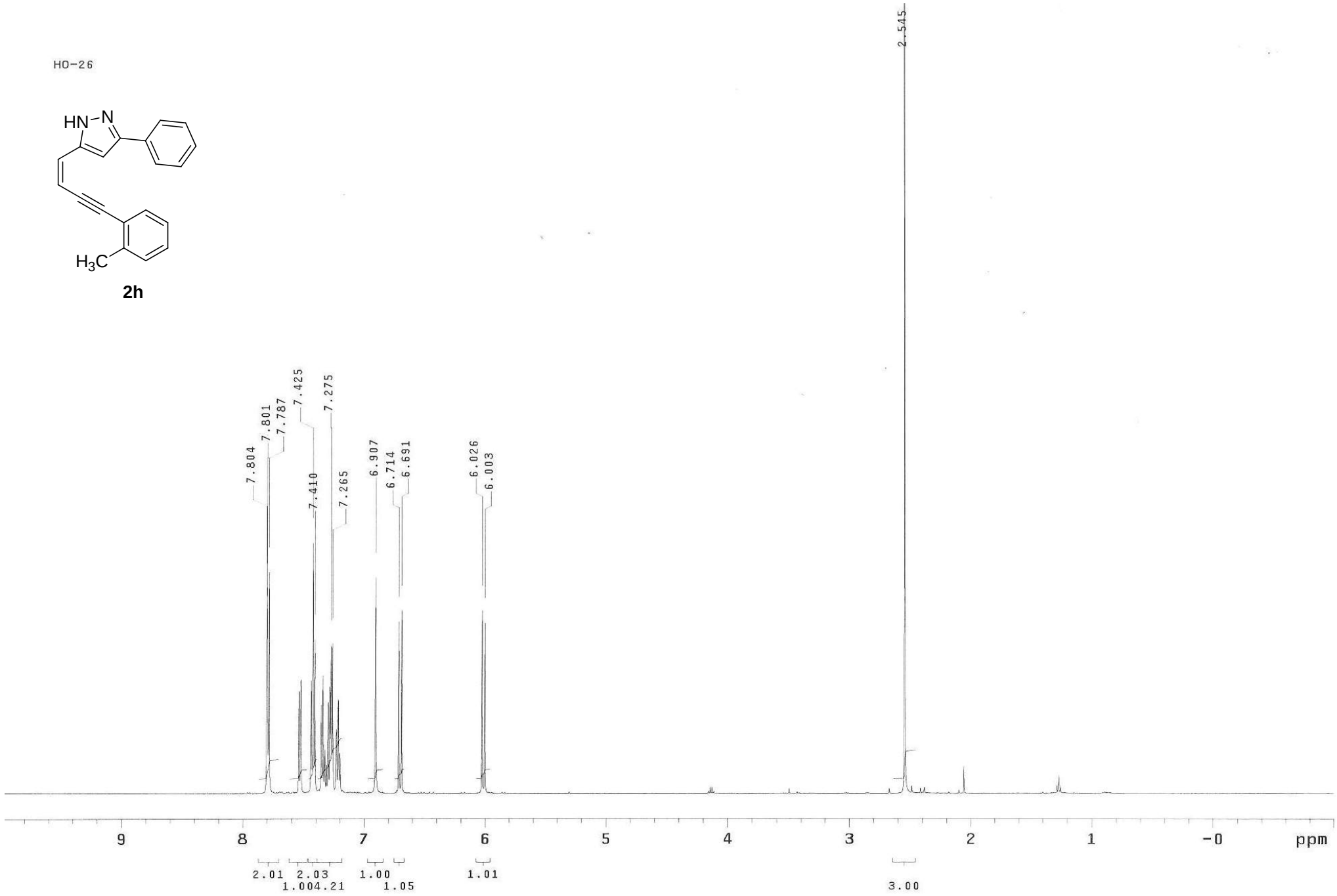

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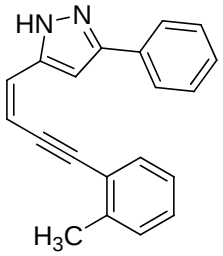

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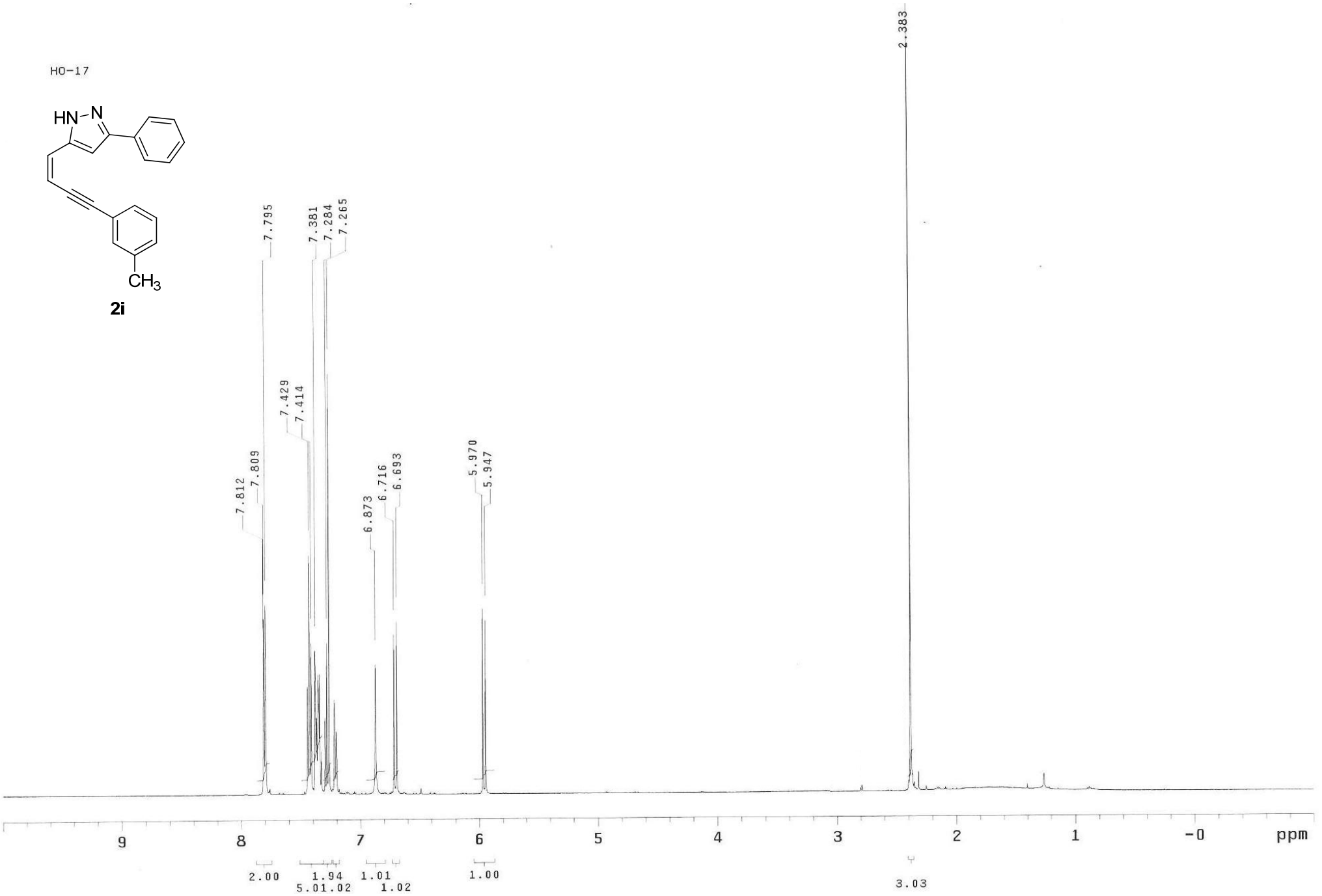

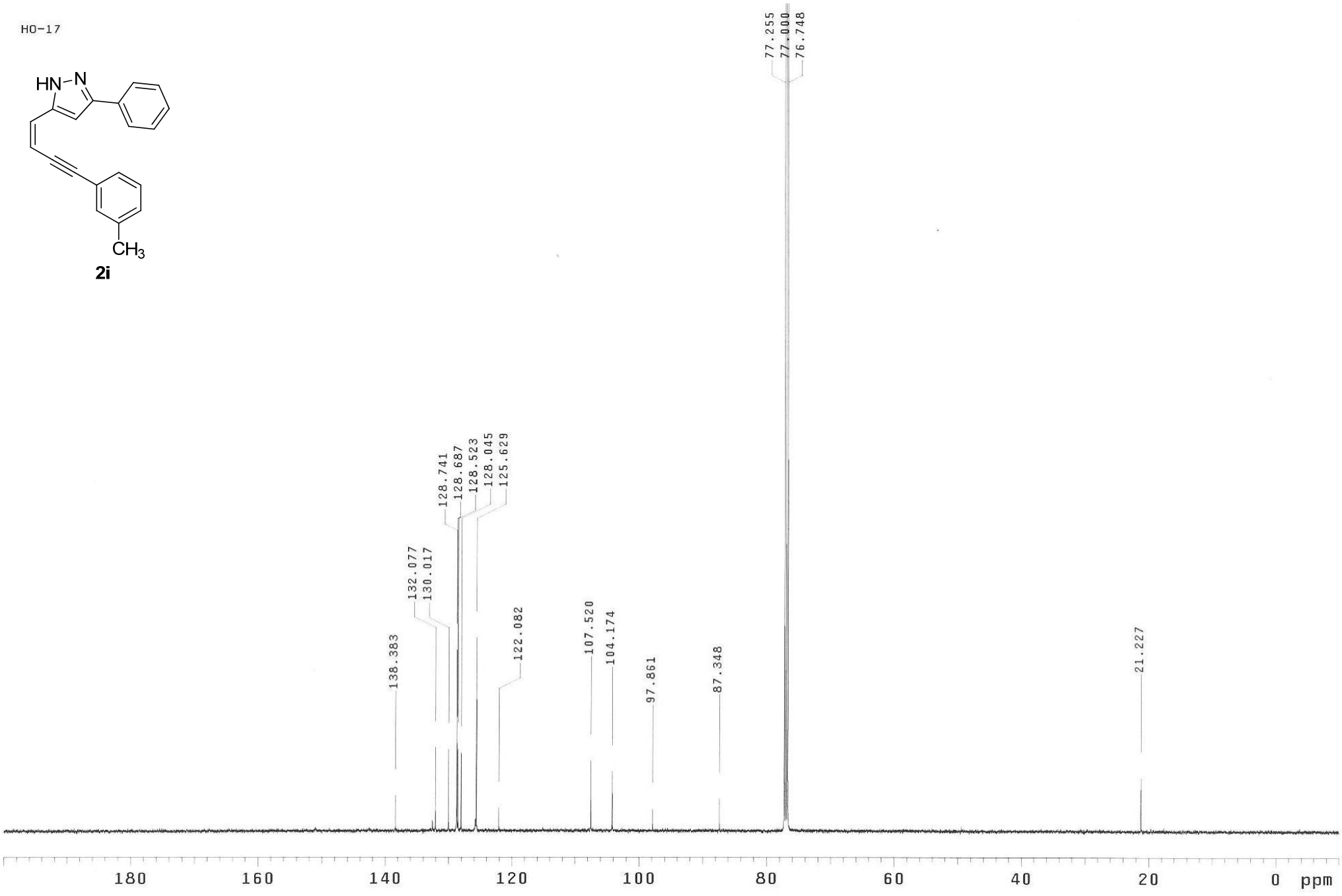

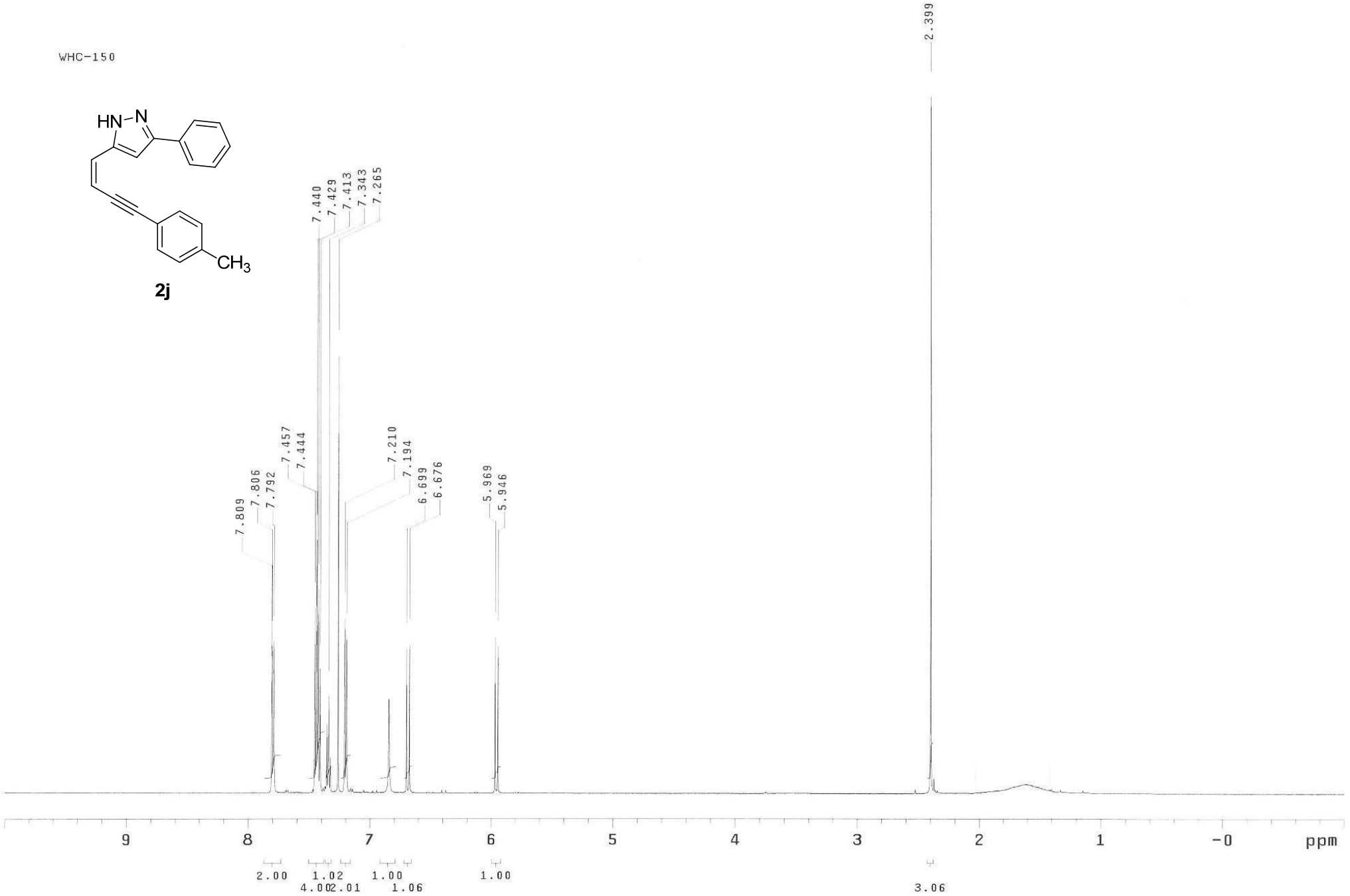

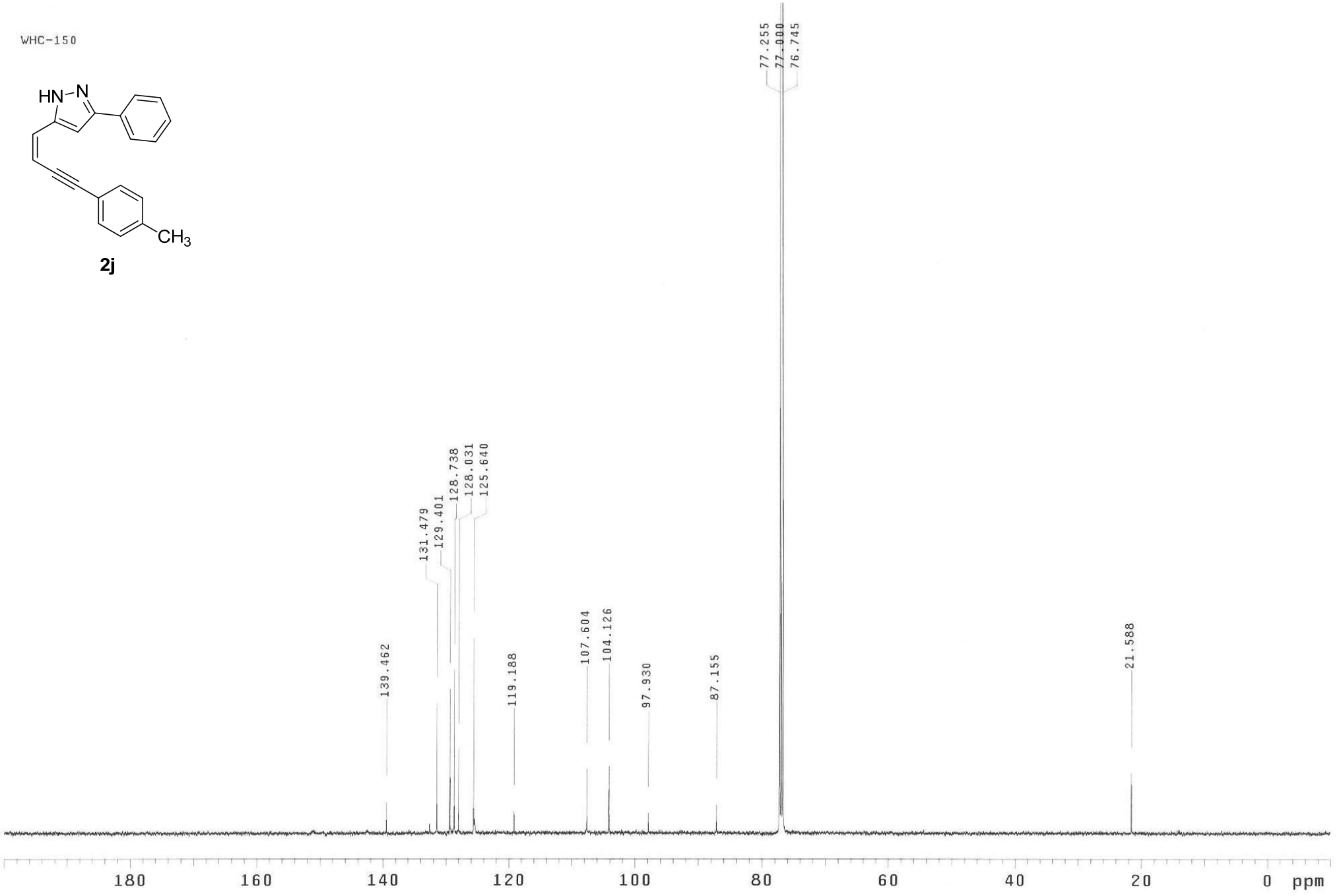

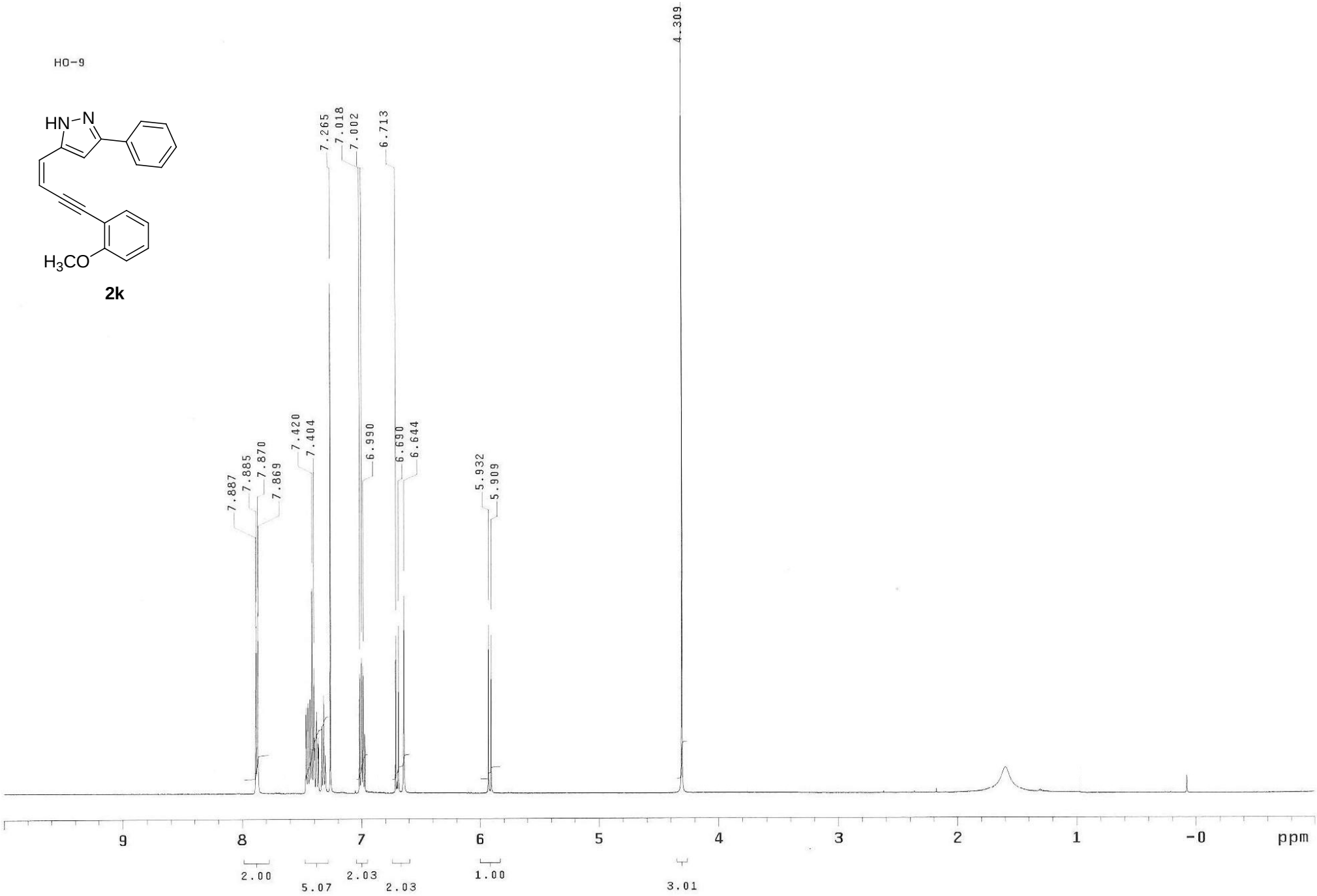

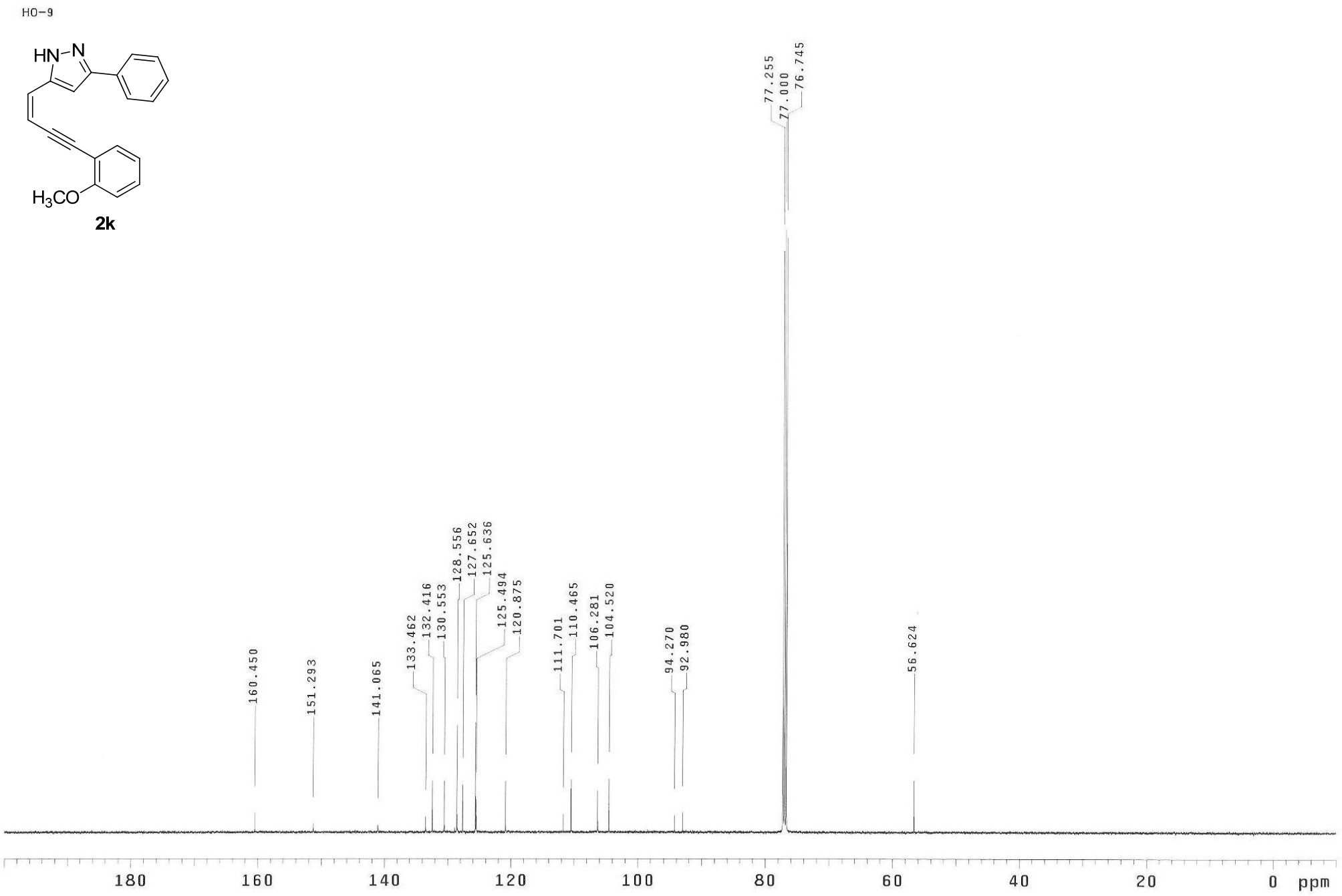

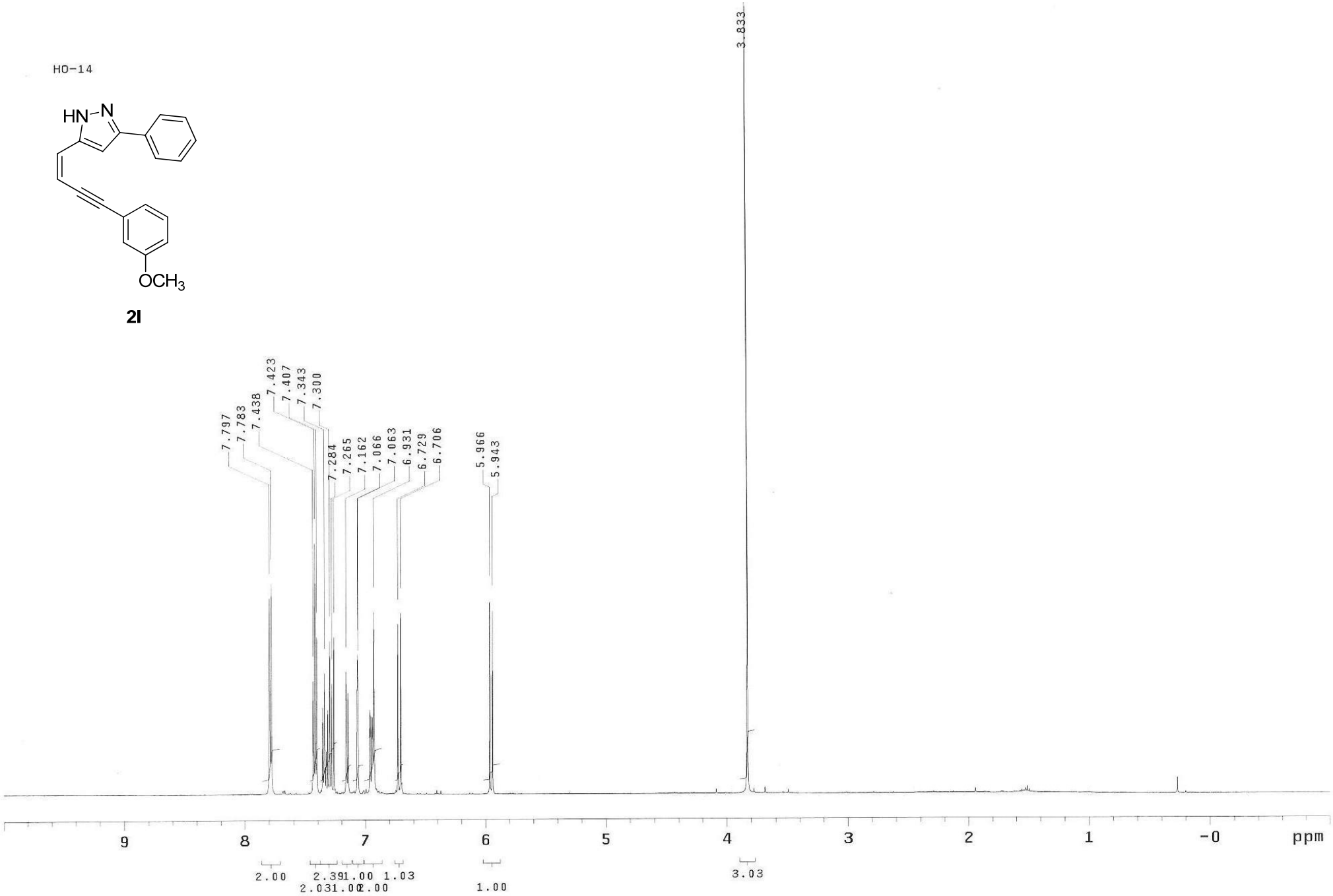

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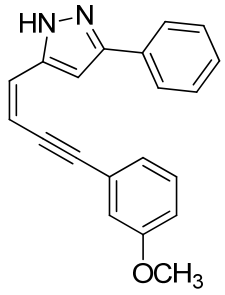

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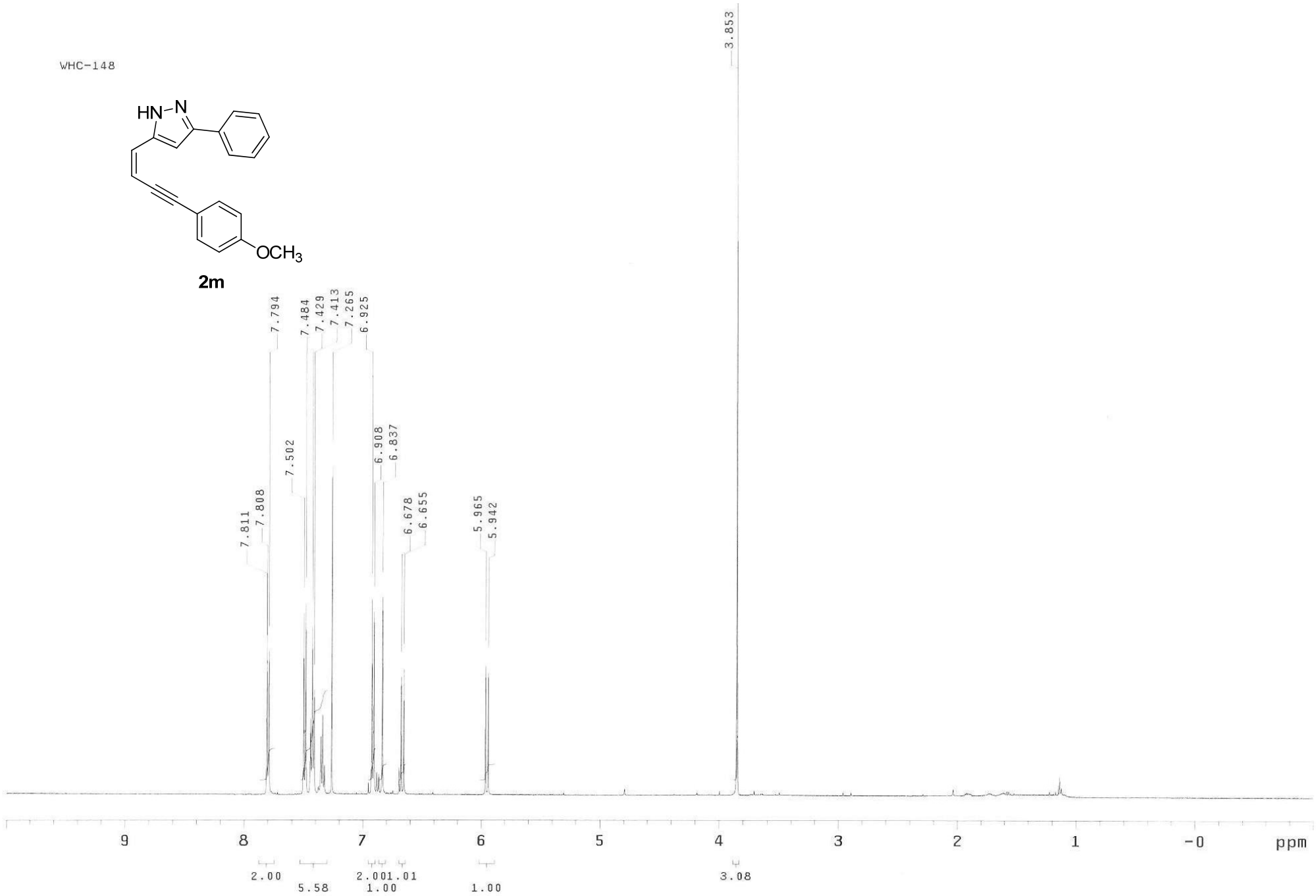

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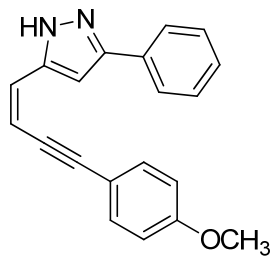

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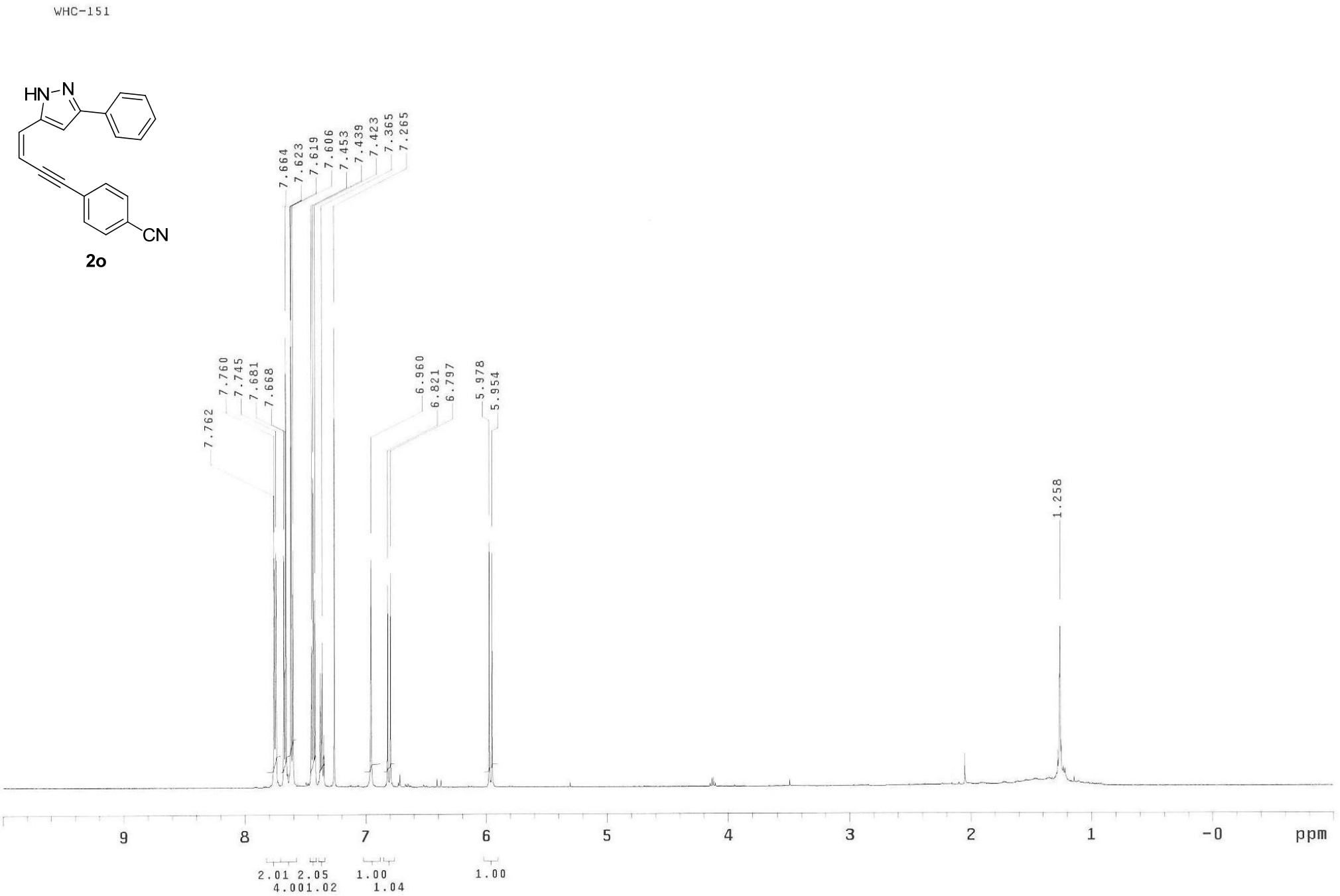

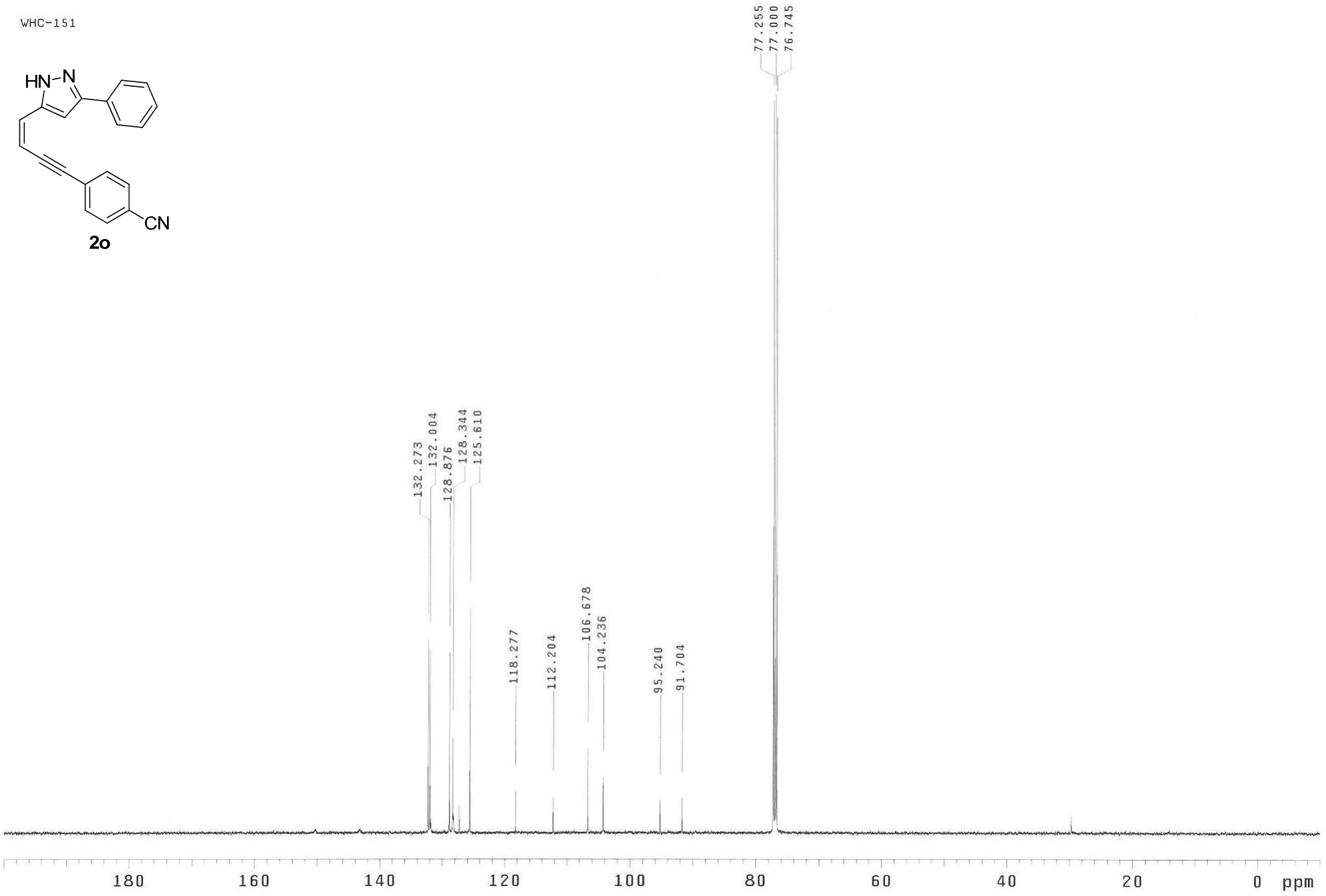

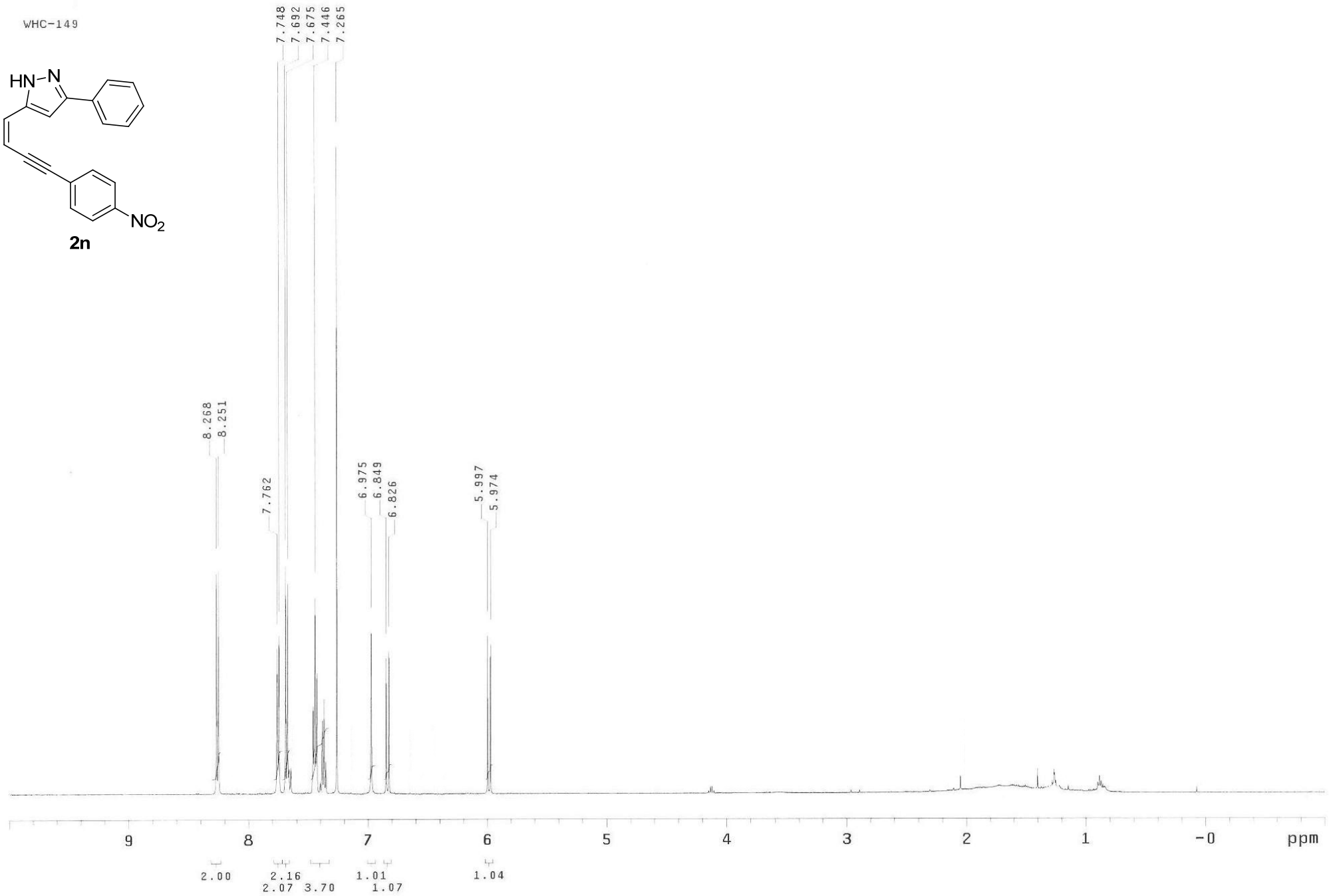

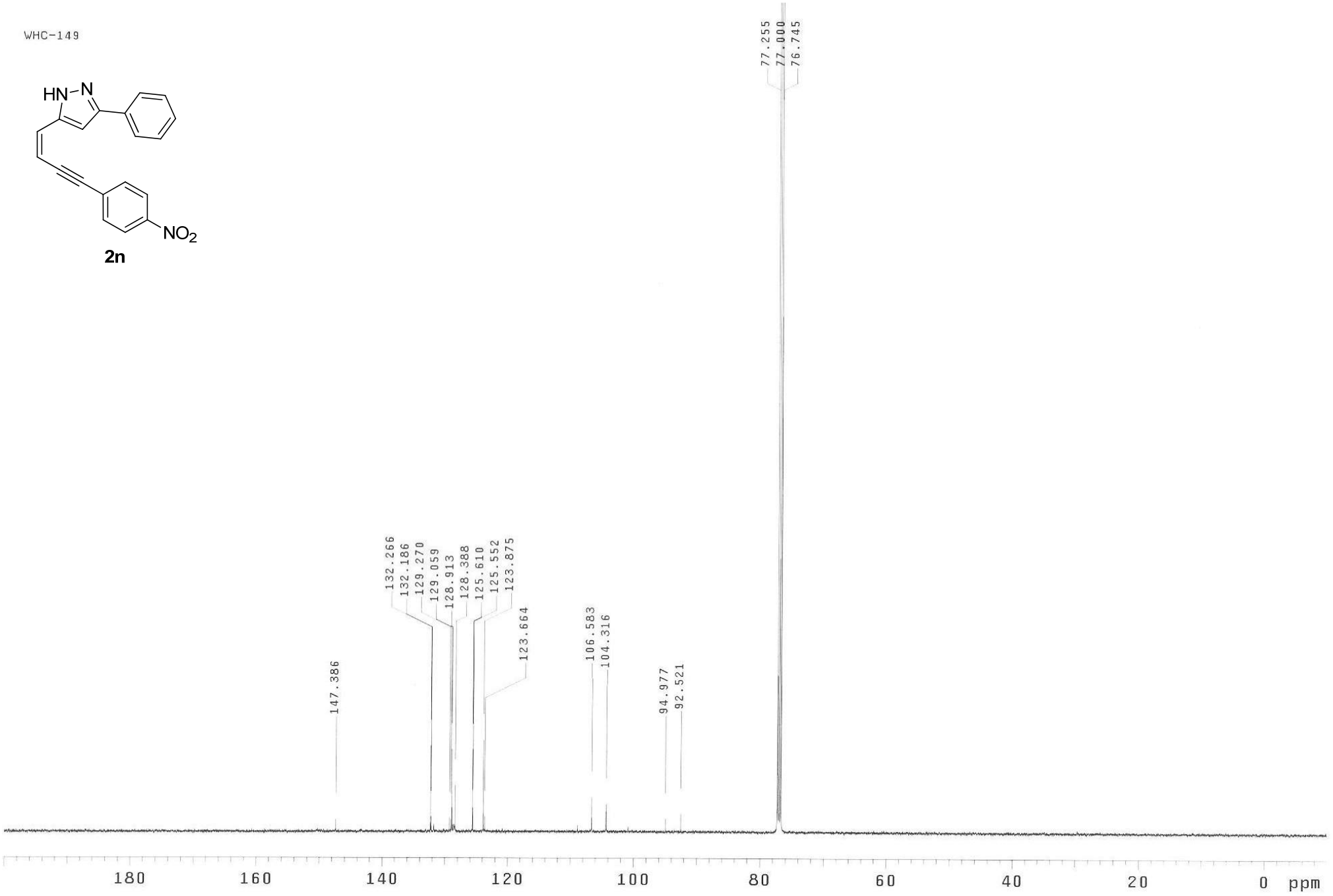

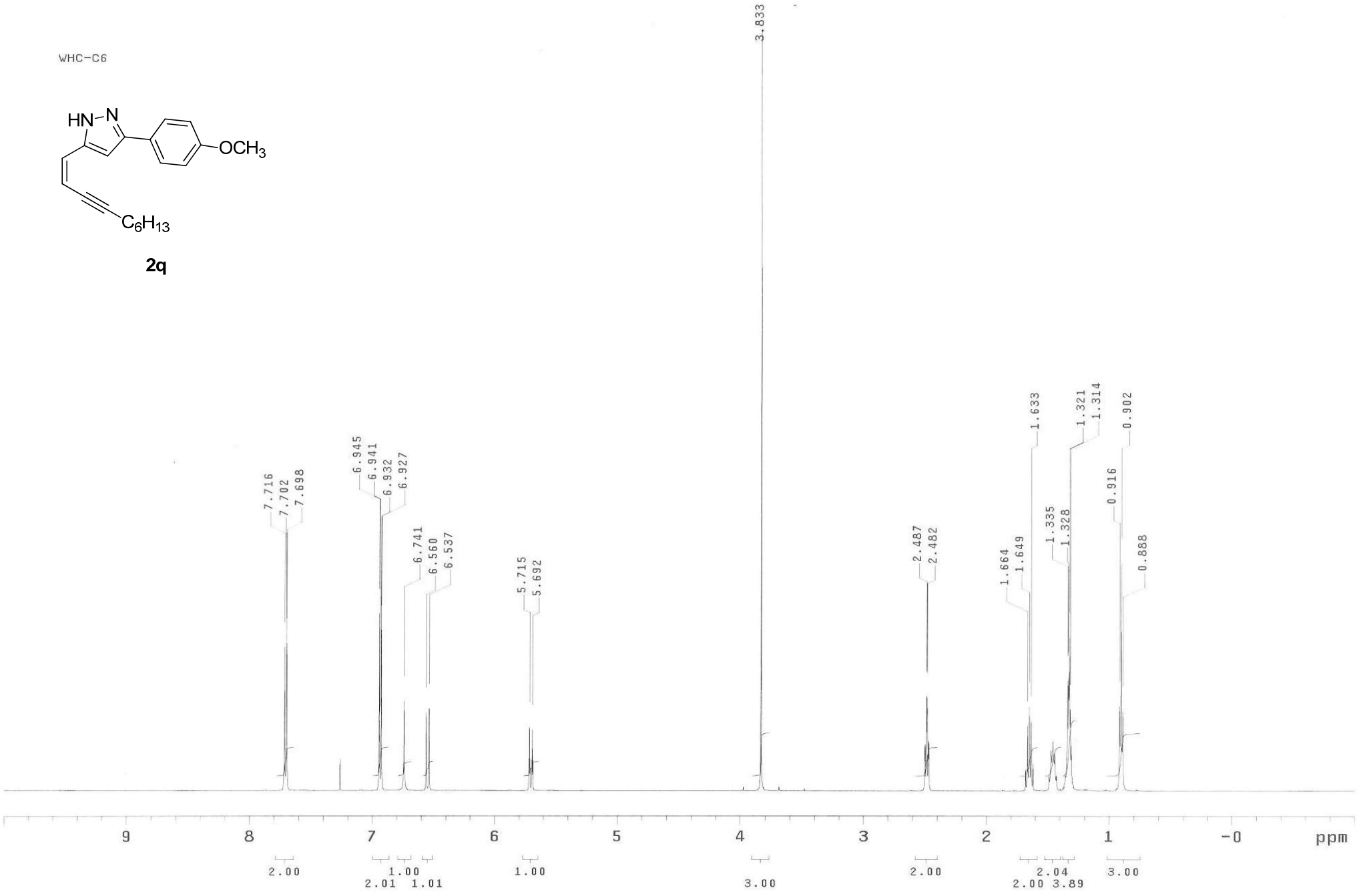

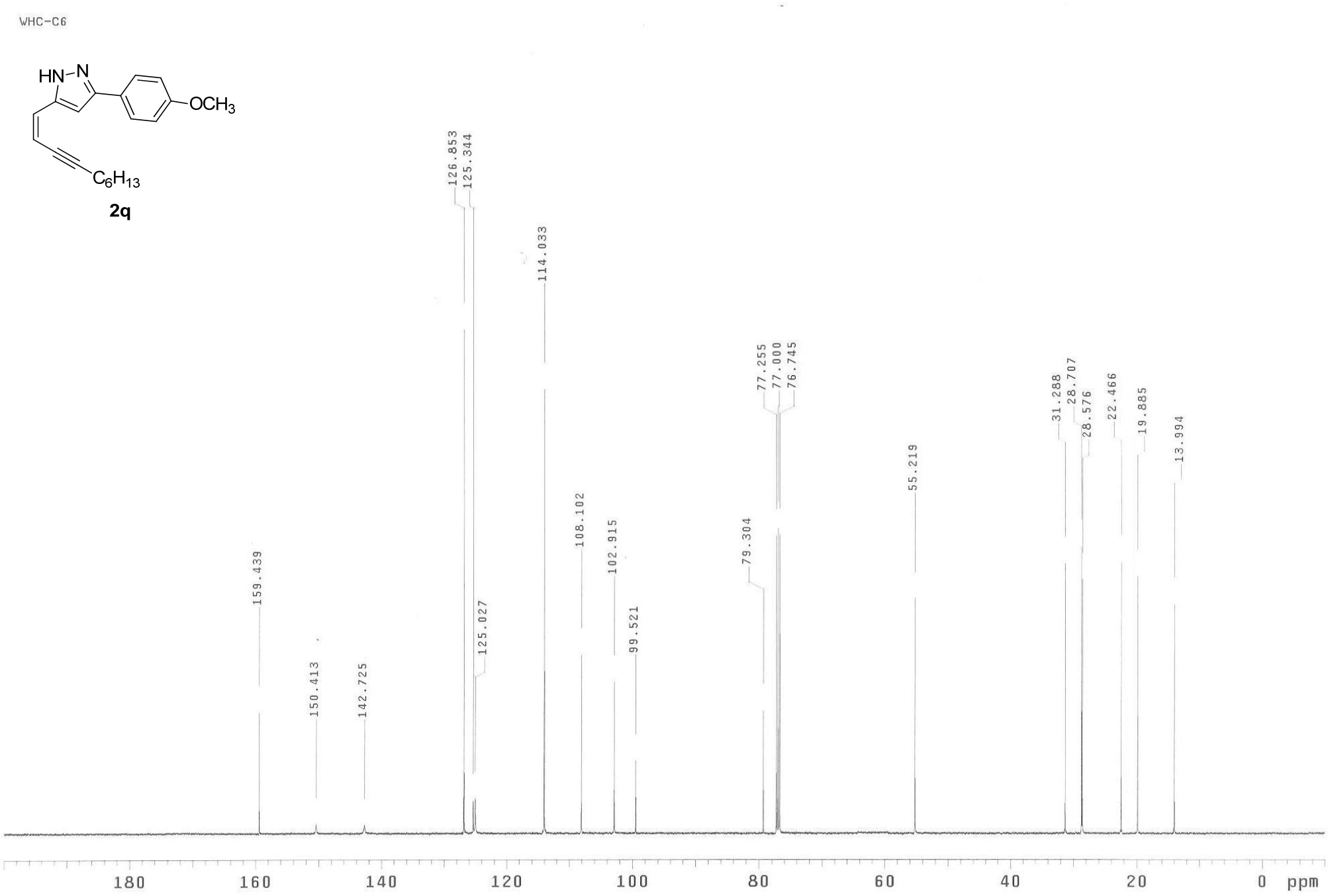

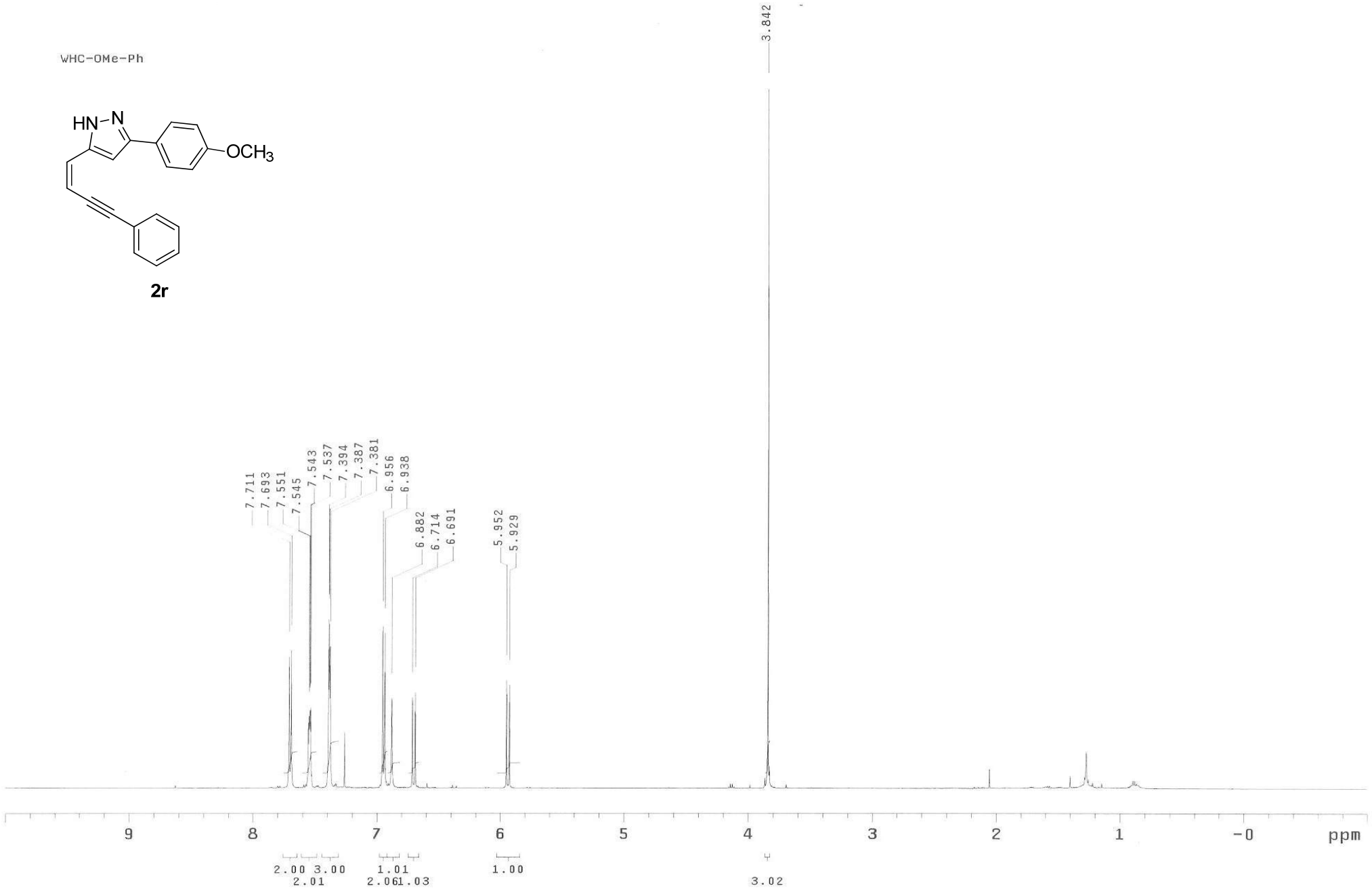

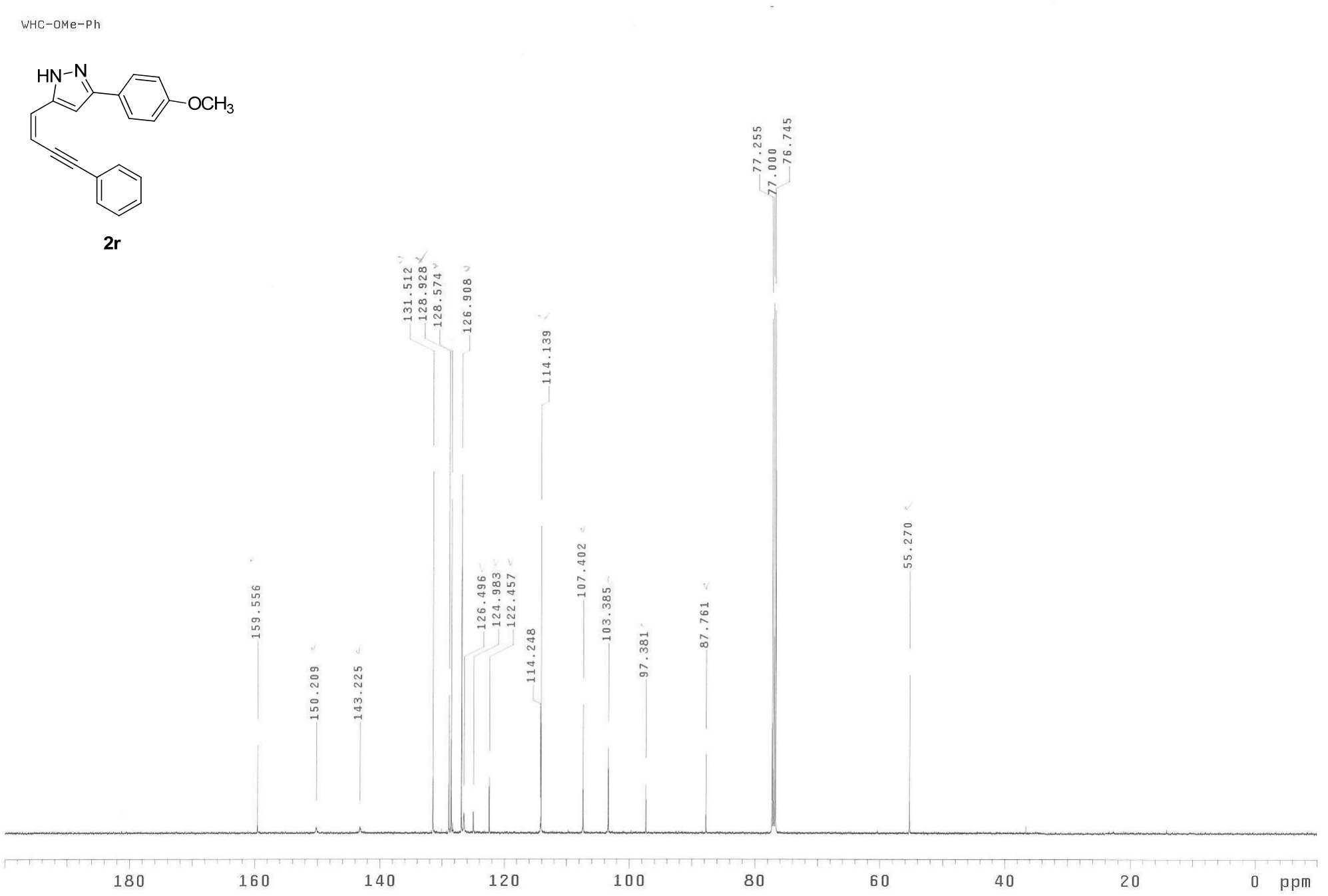

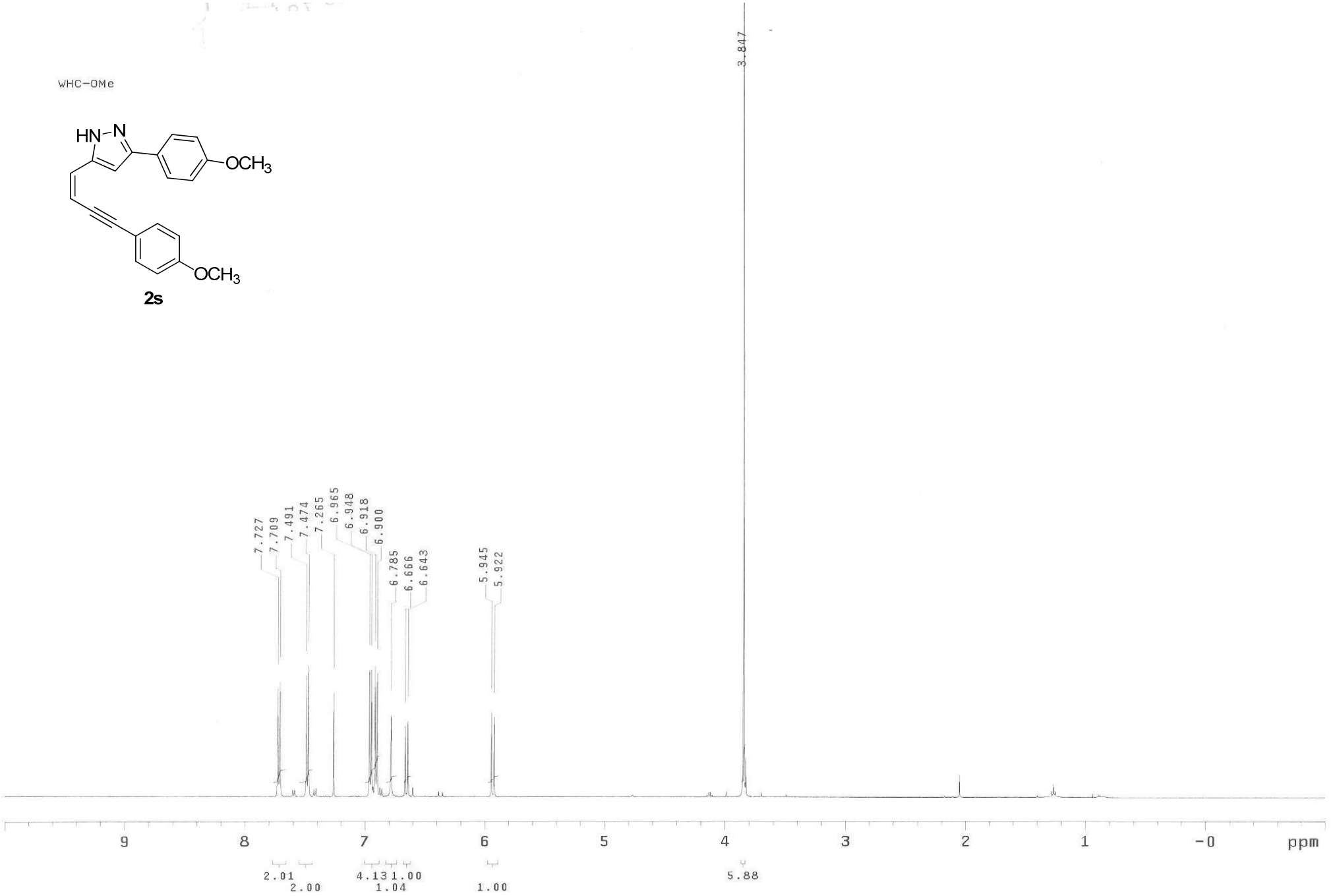

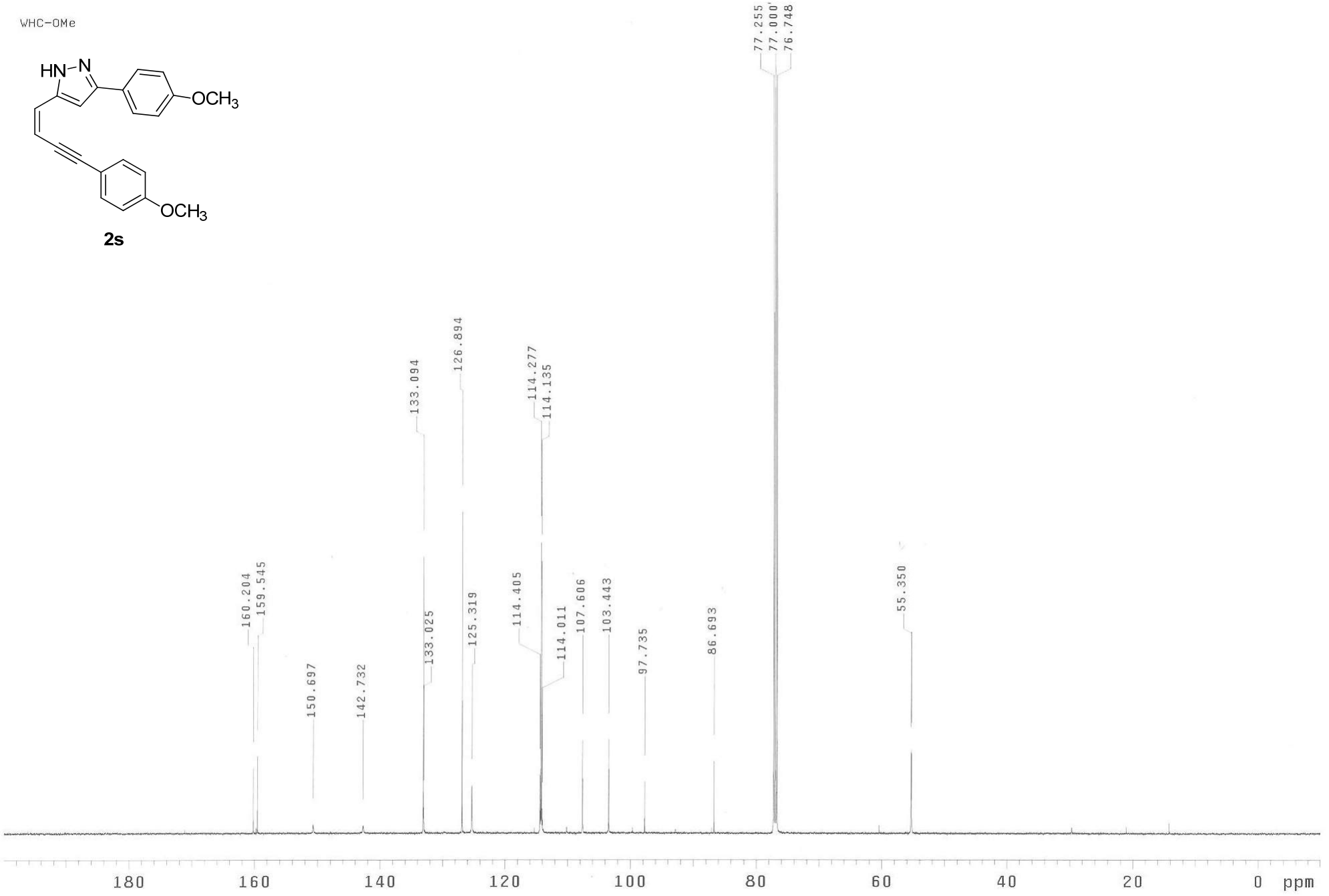

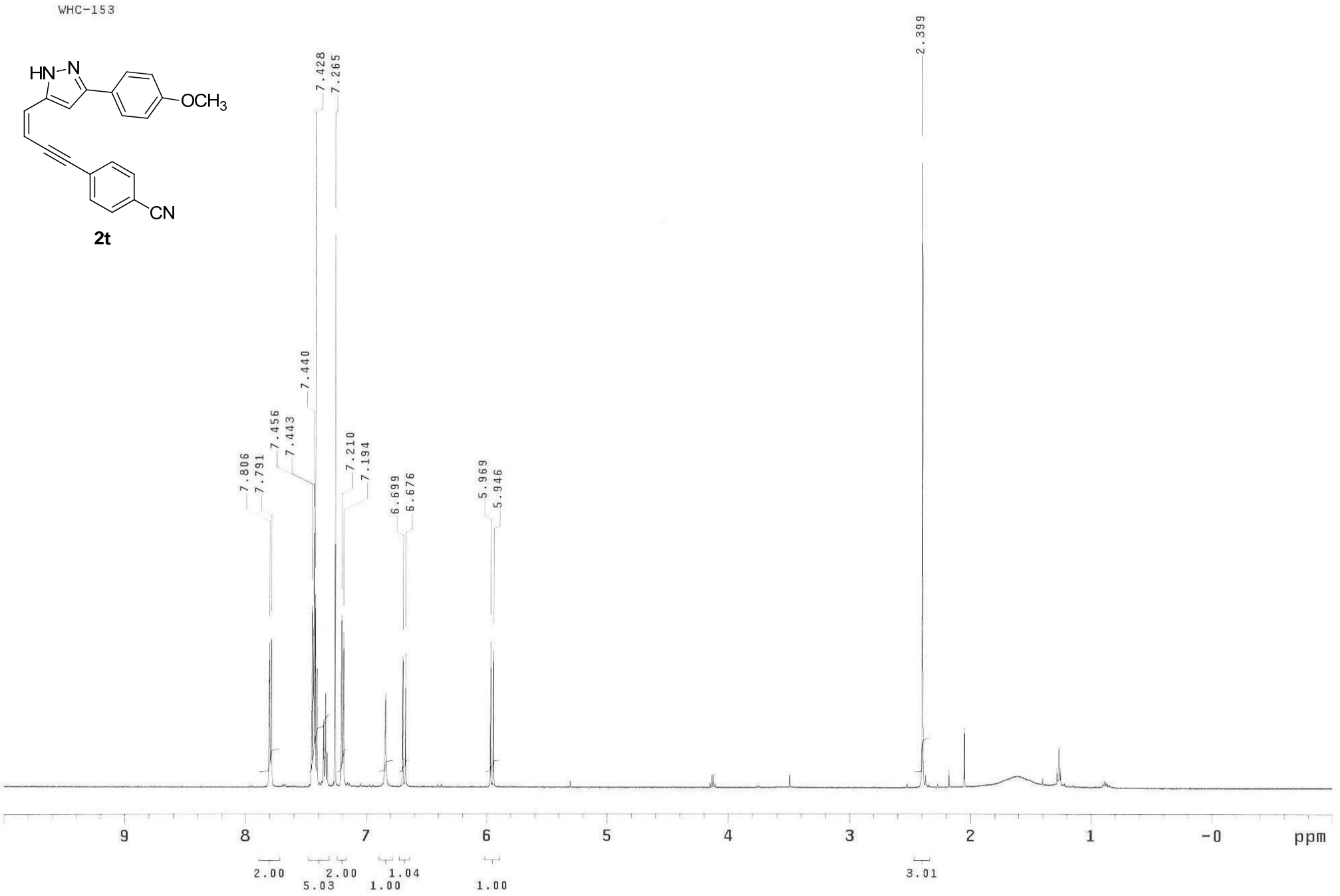

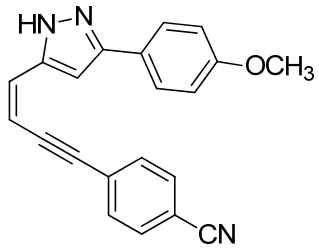

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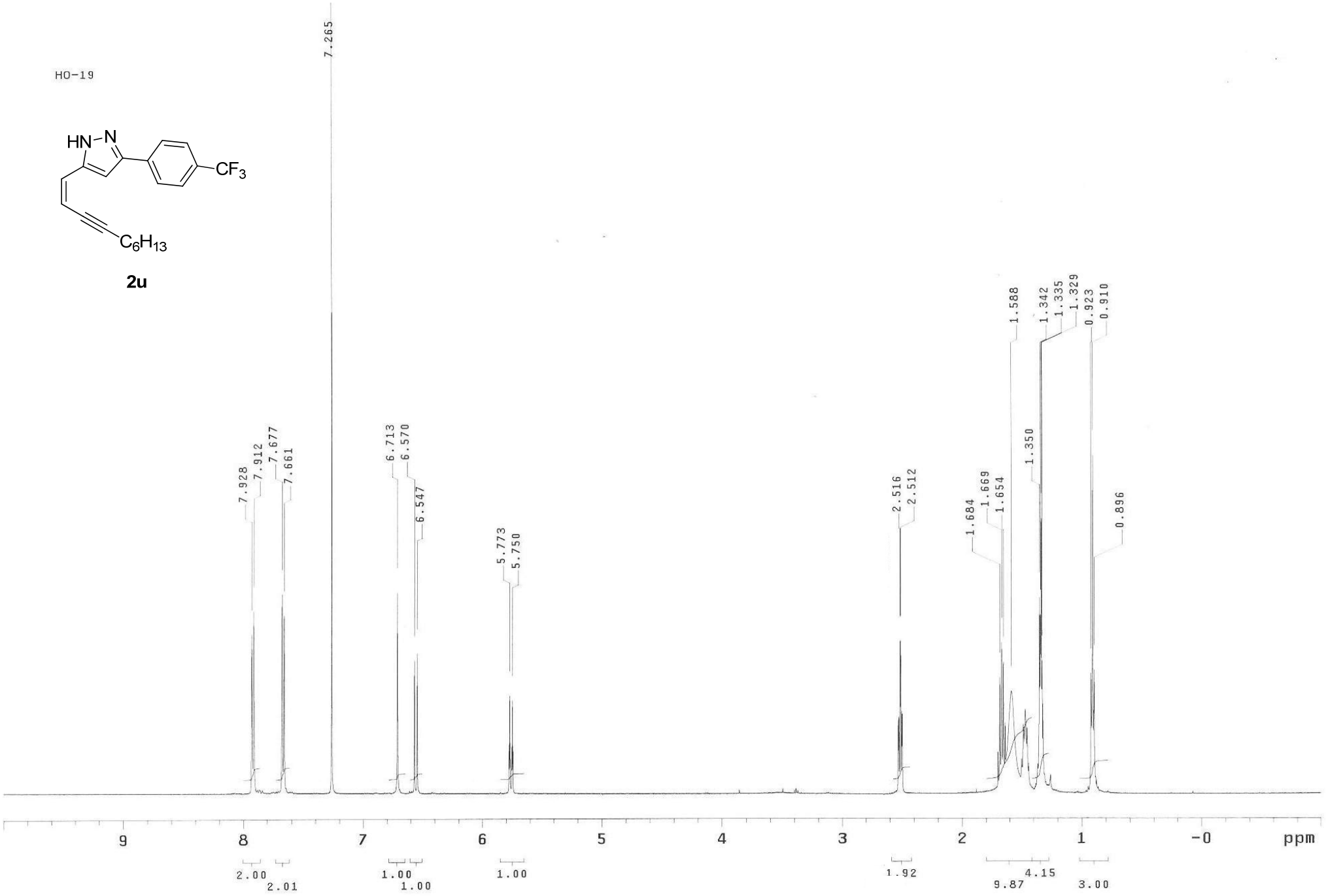
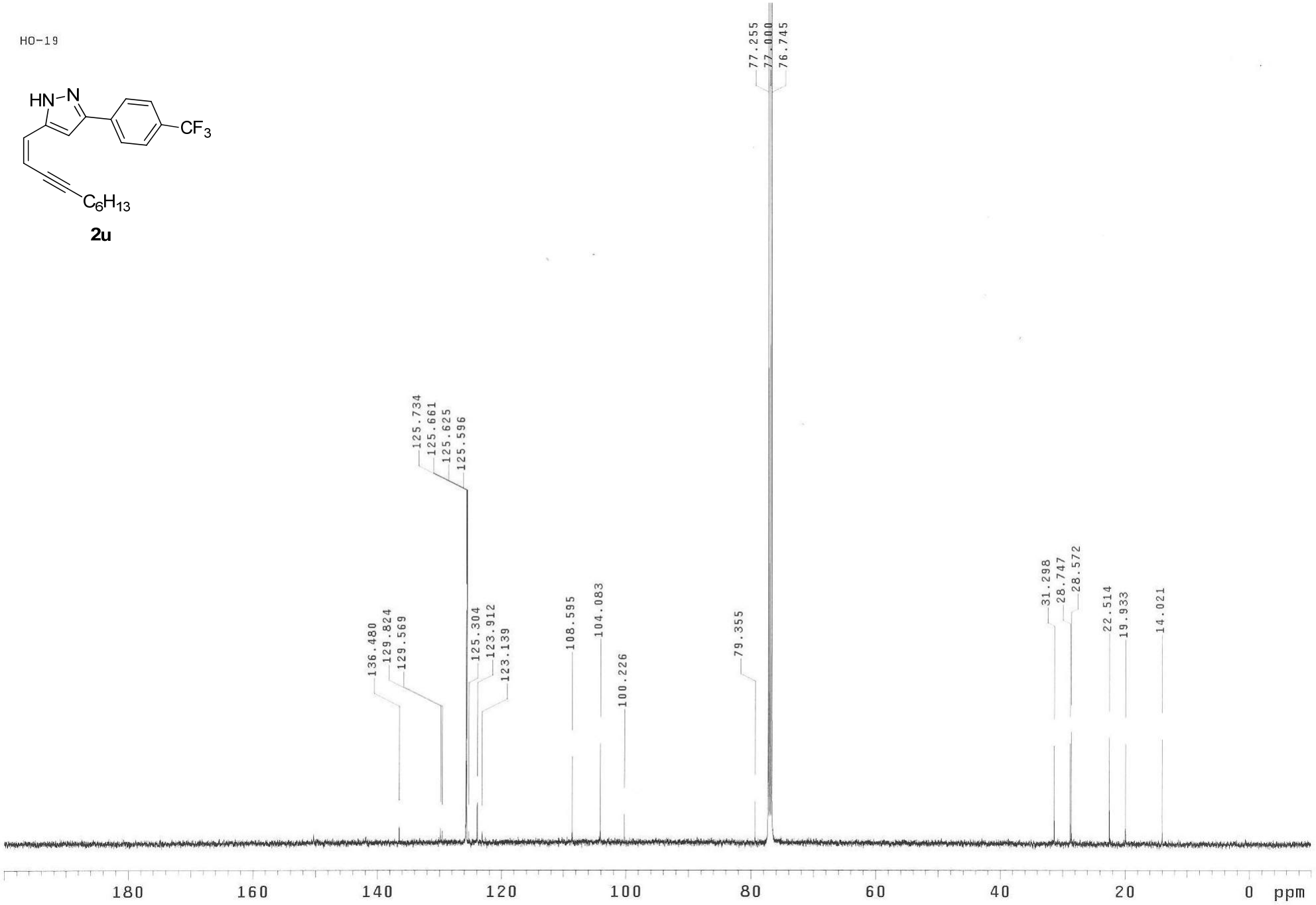
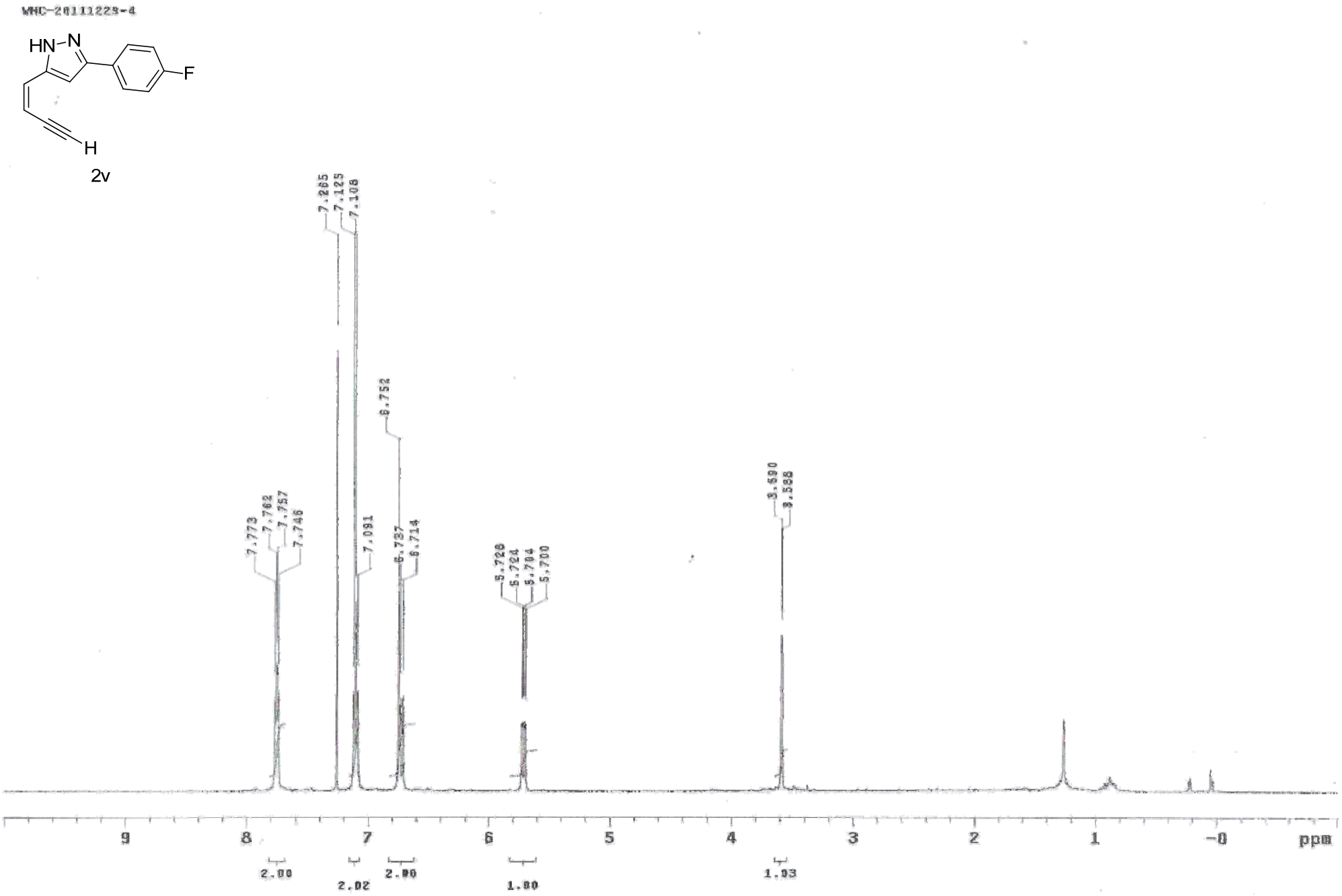
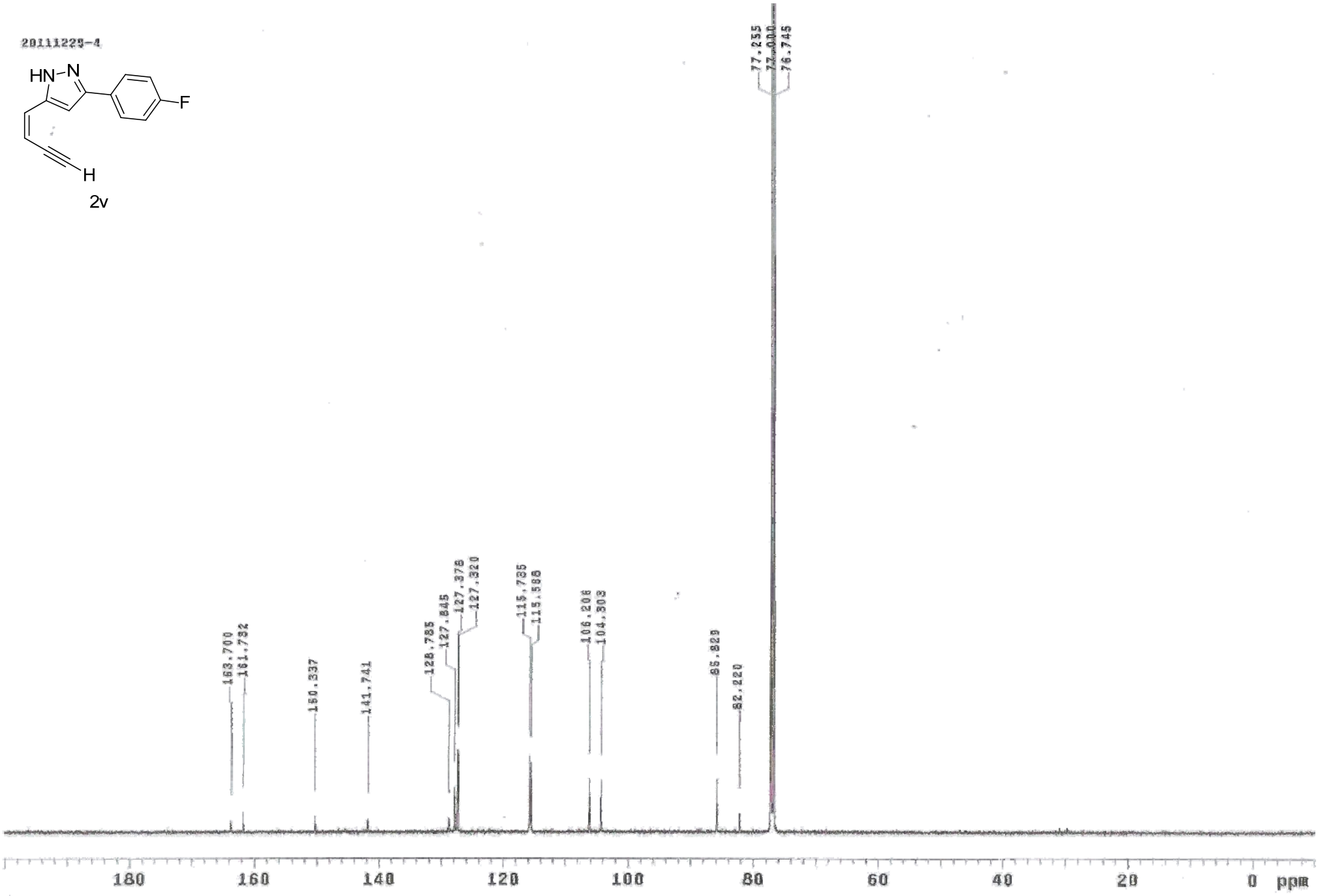
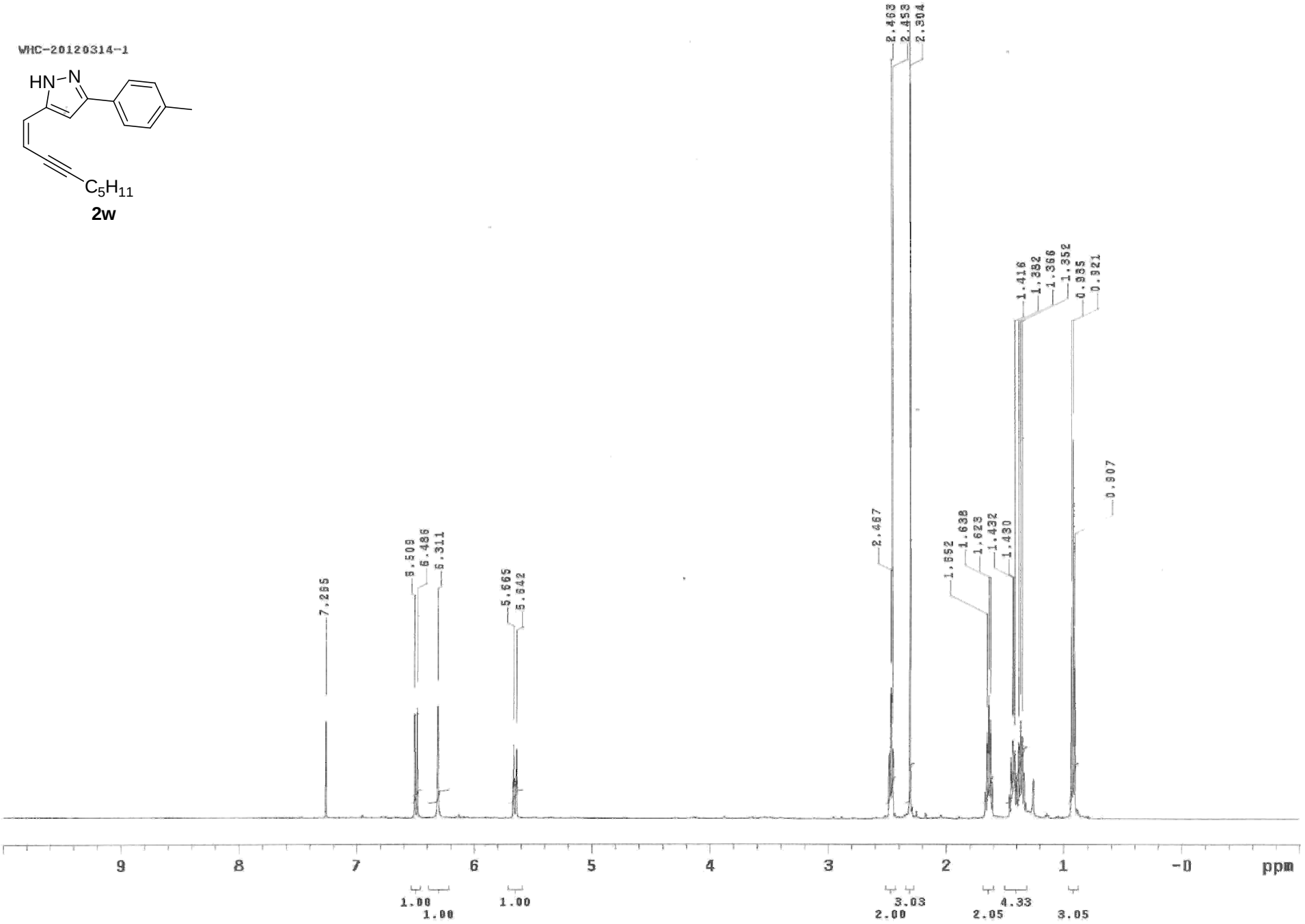
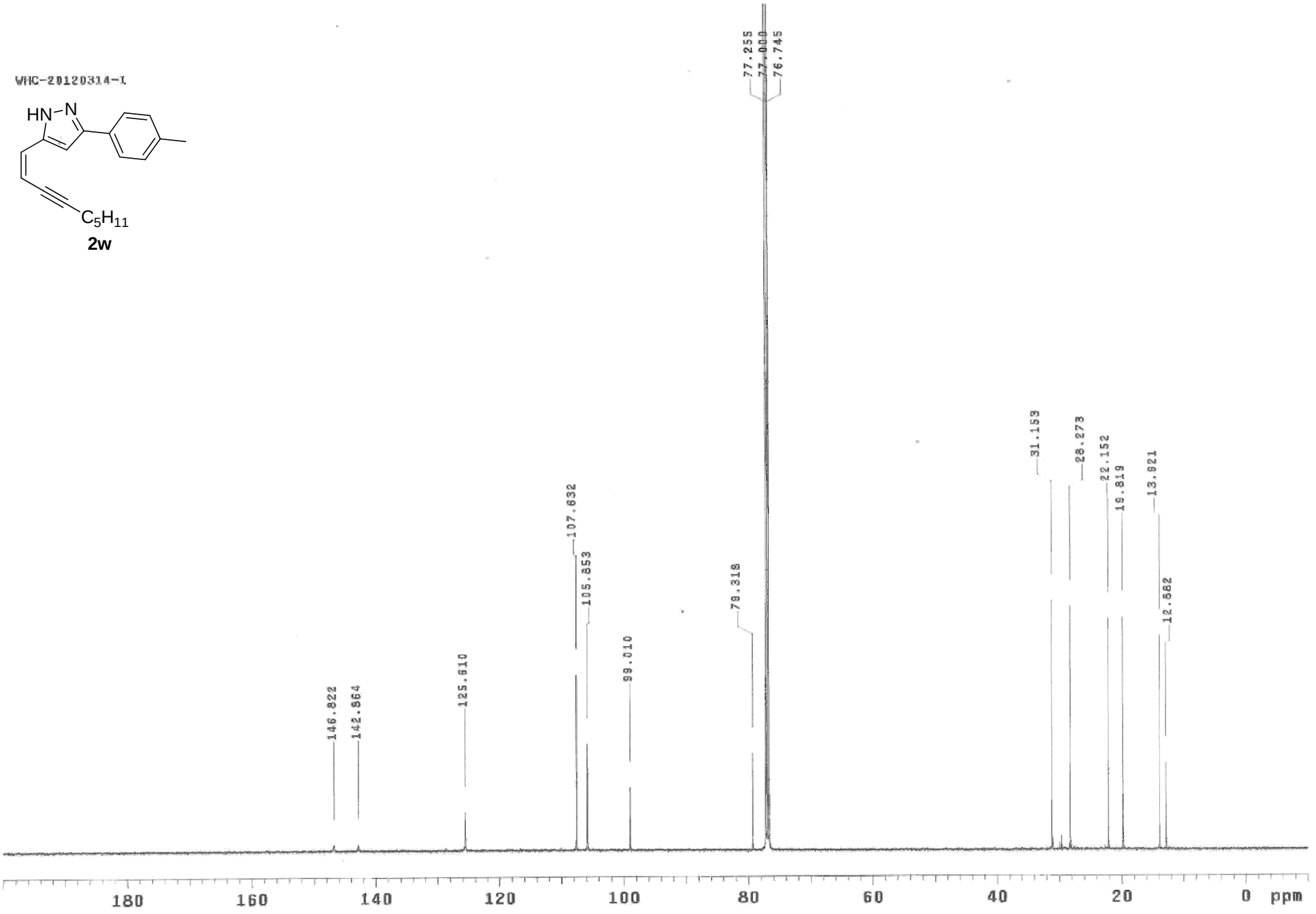


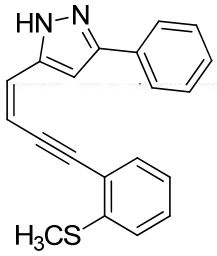








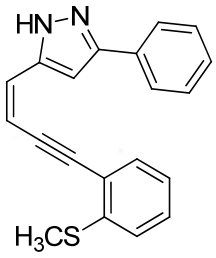




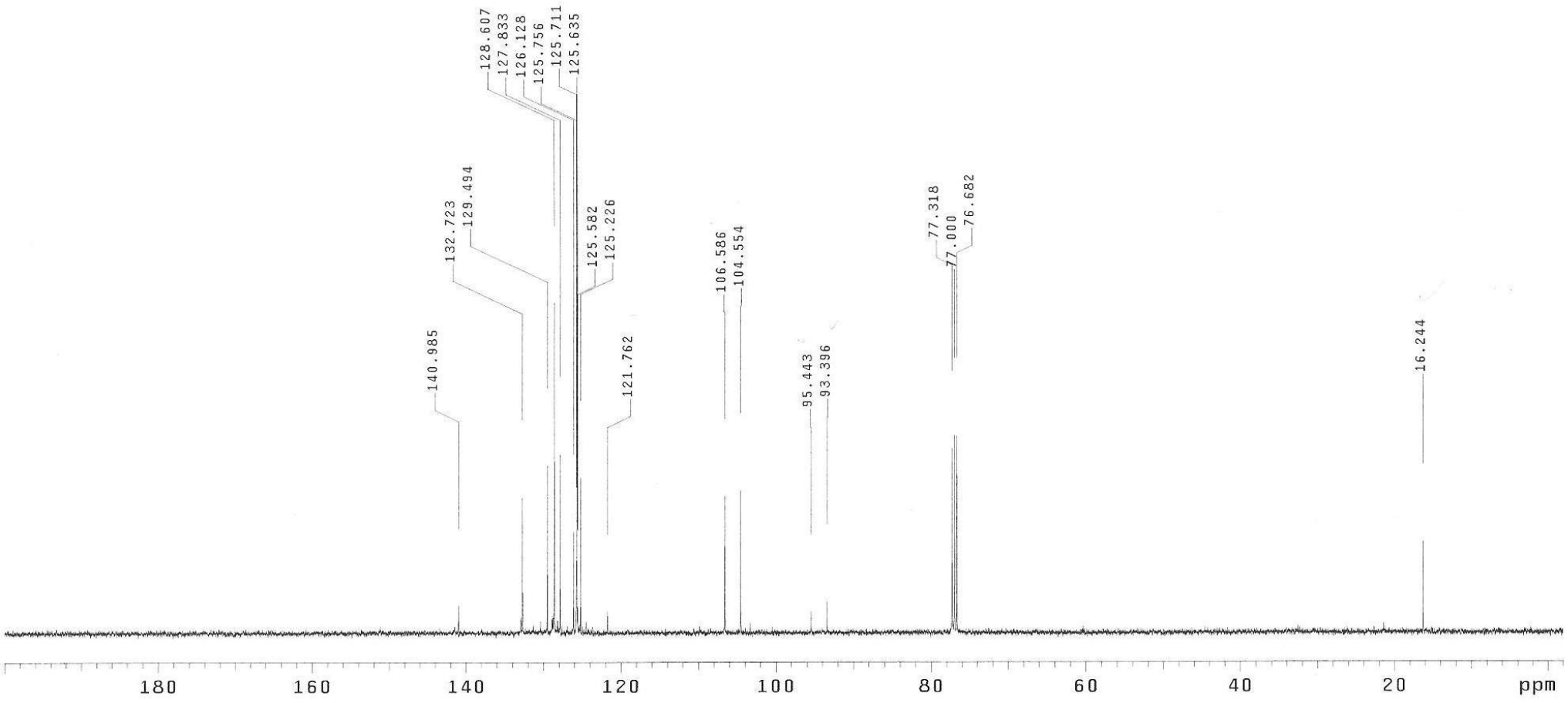
2p

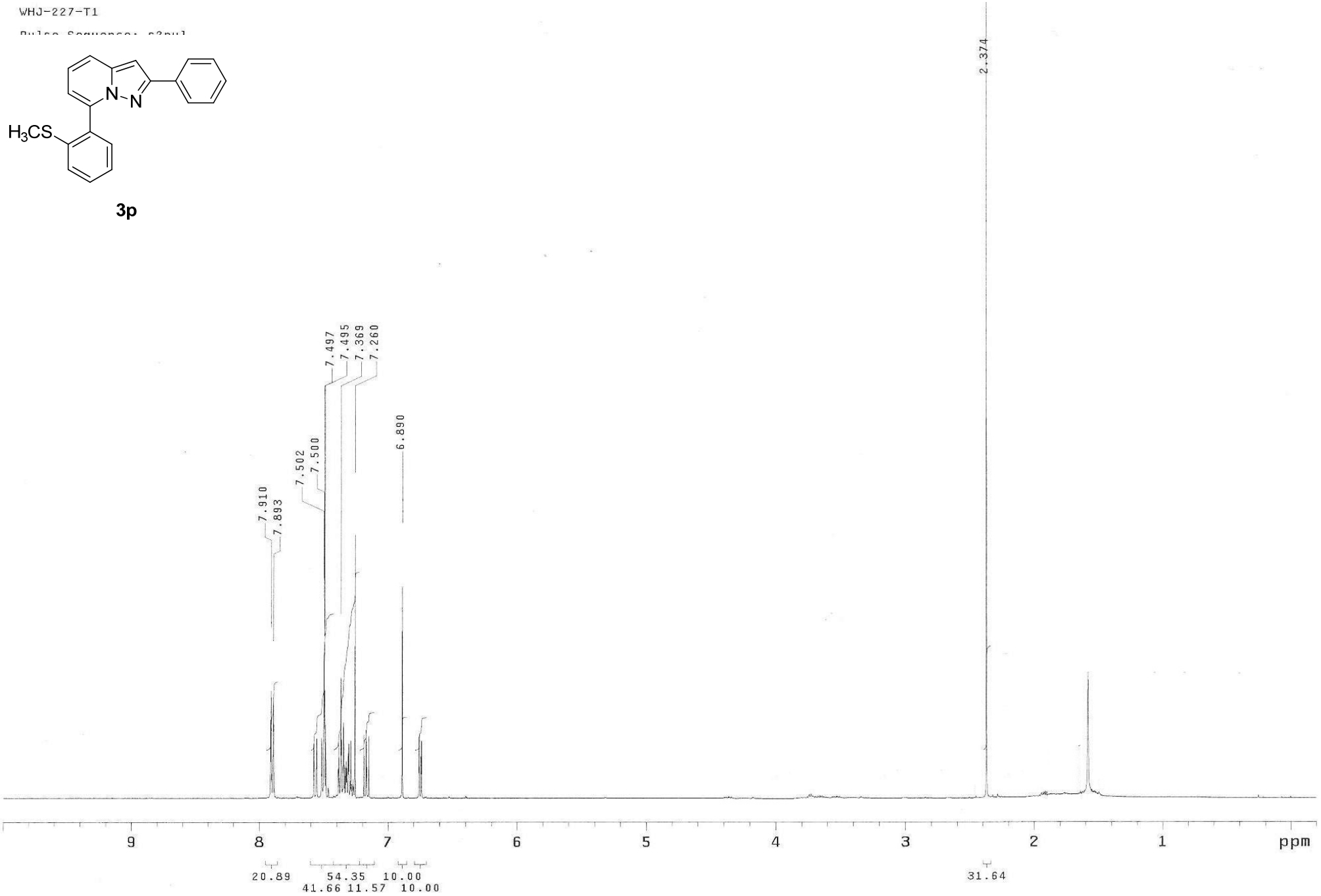
WHJ-227-T2

Pulse Sequence: s2pul



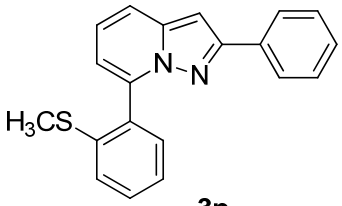
2p



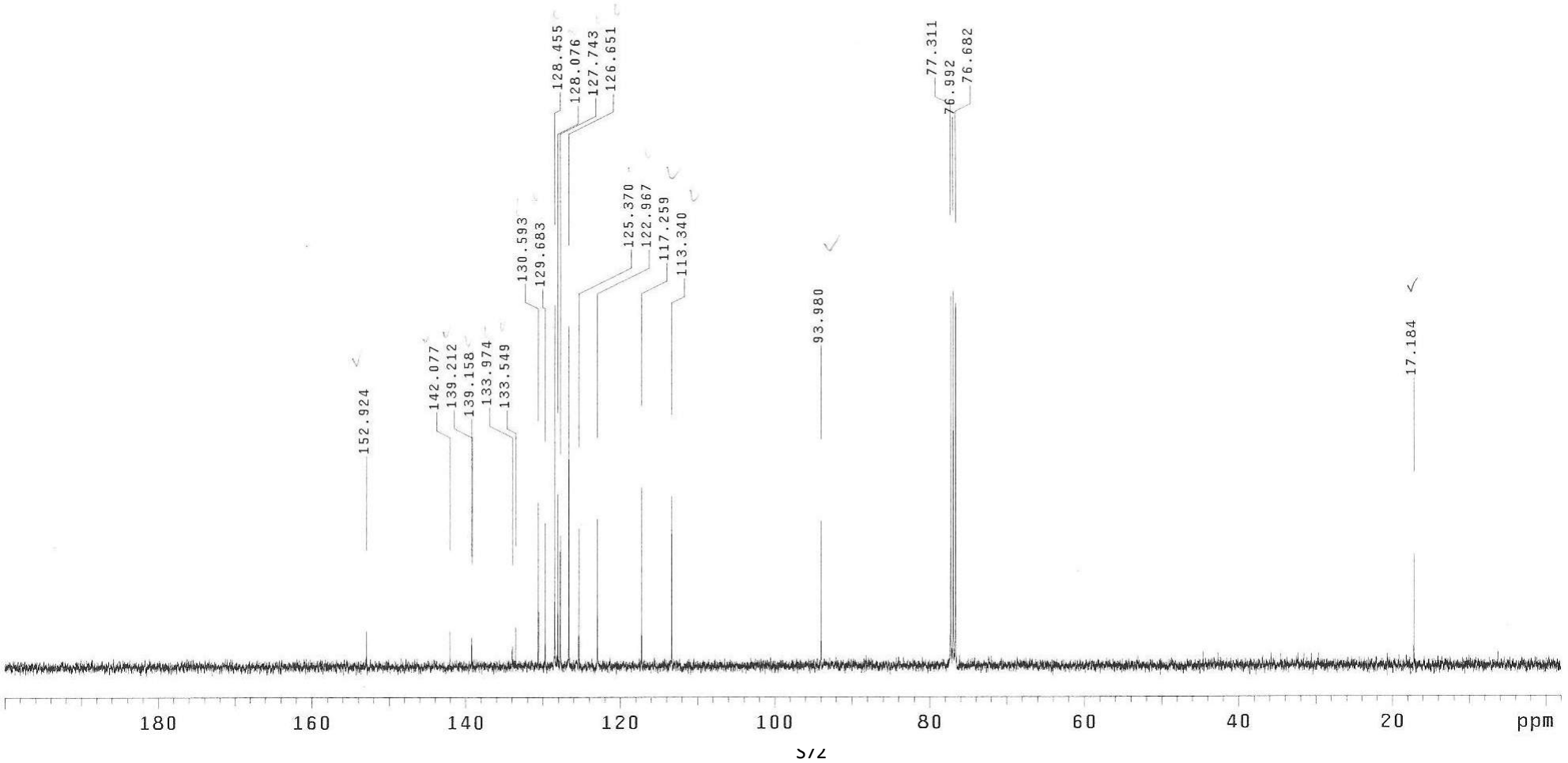


WHJ-227-T1

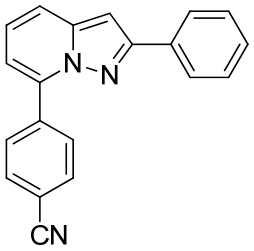
Pulse Sequence: s2pul



3p



WHC-080-T2



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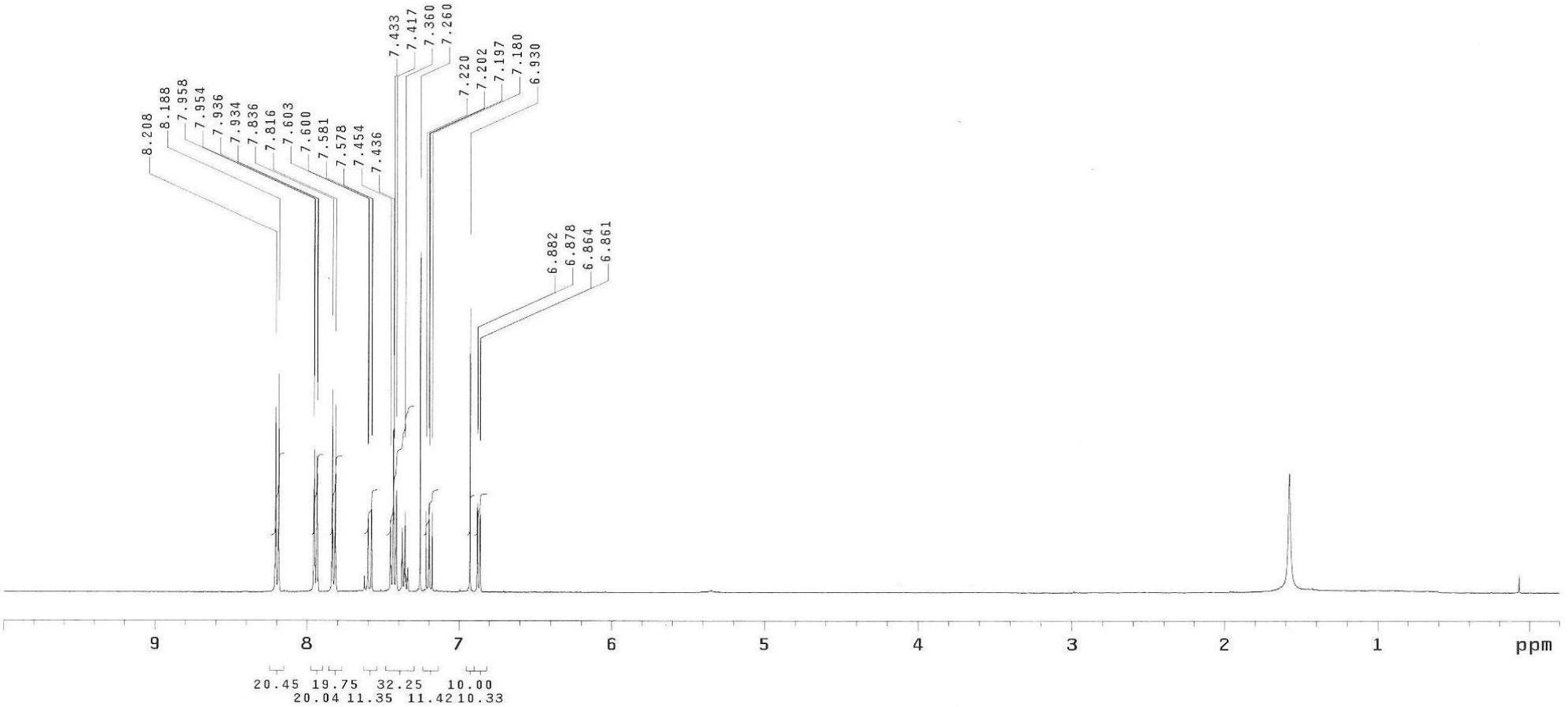
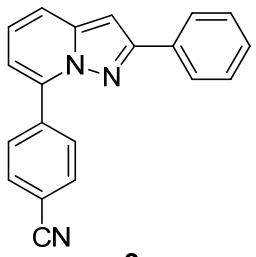
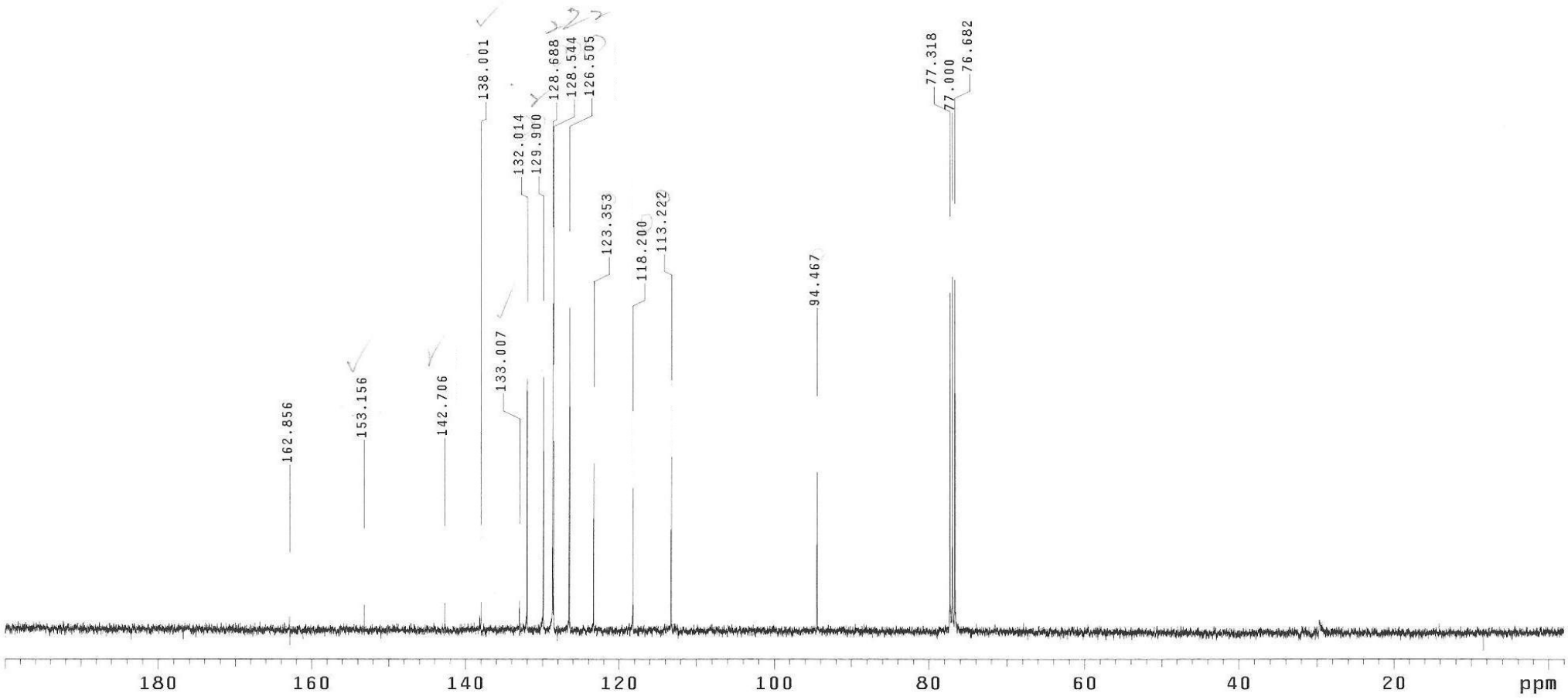
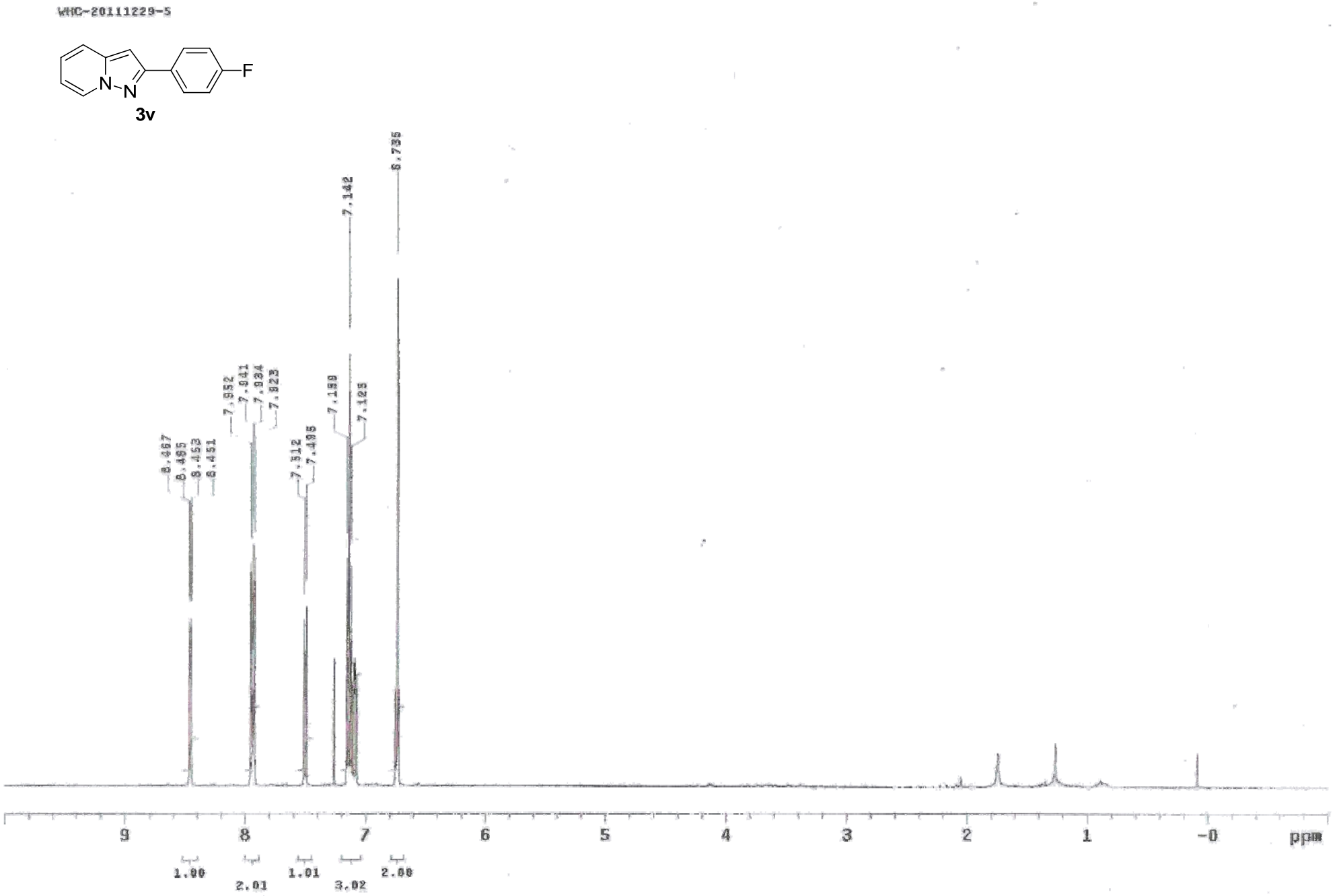


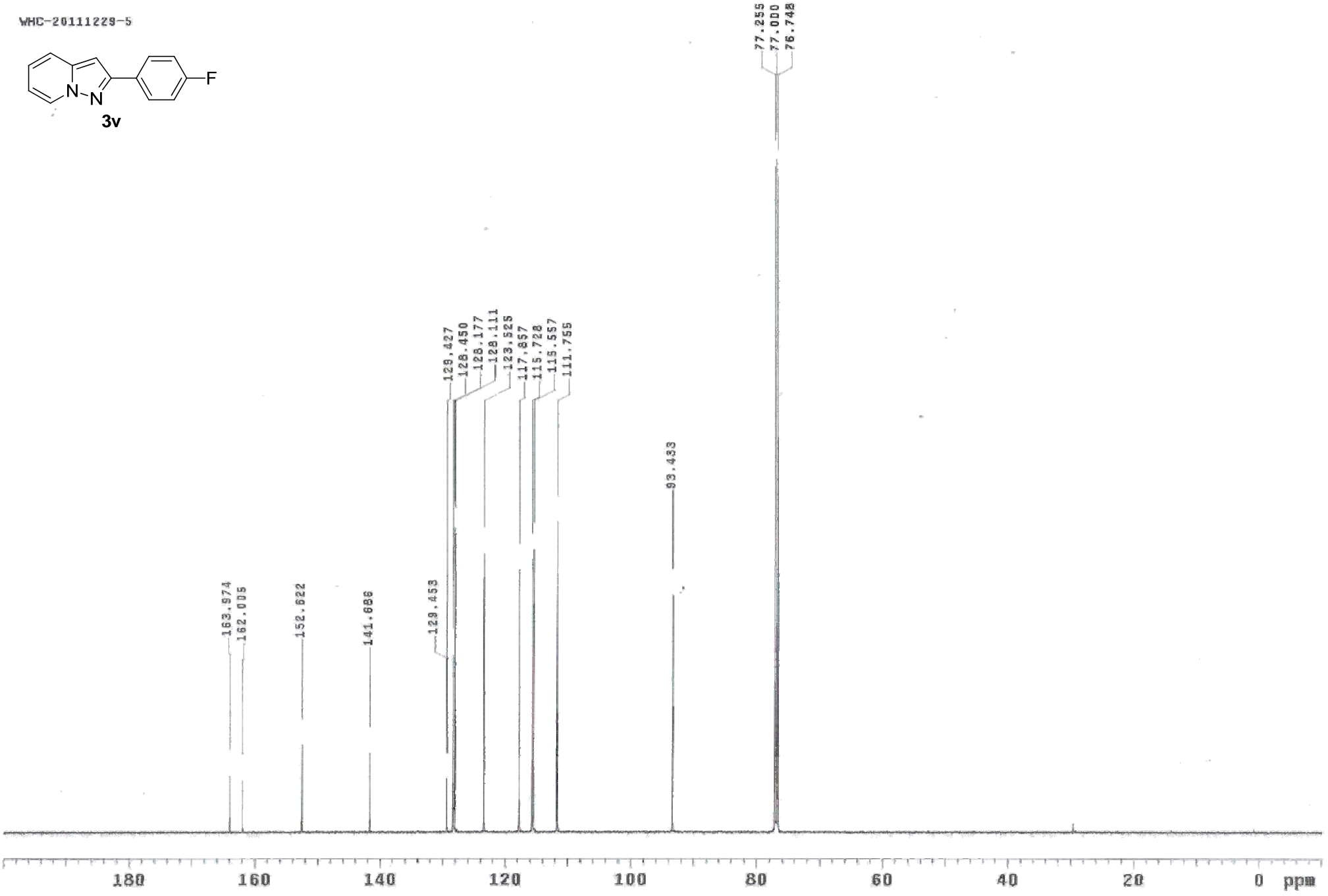
WHC-080-T2



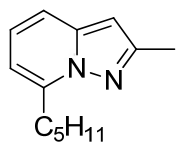
3o



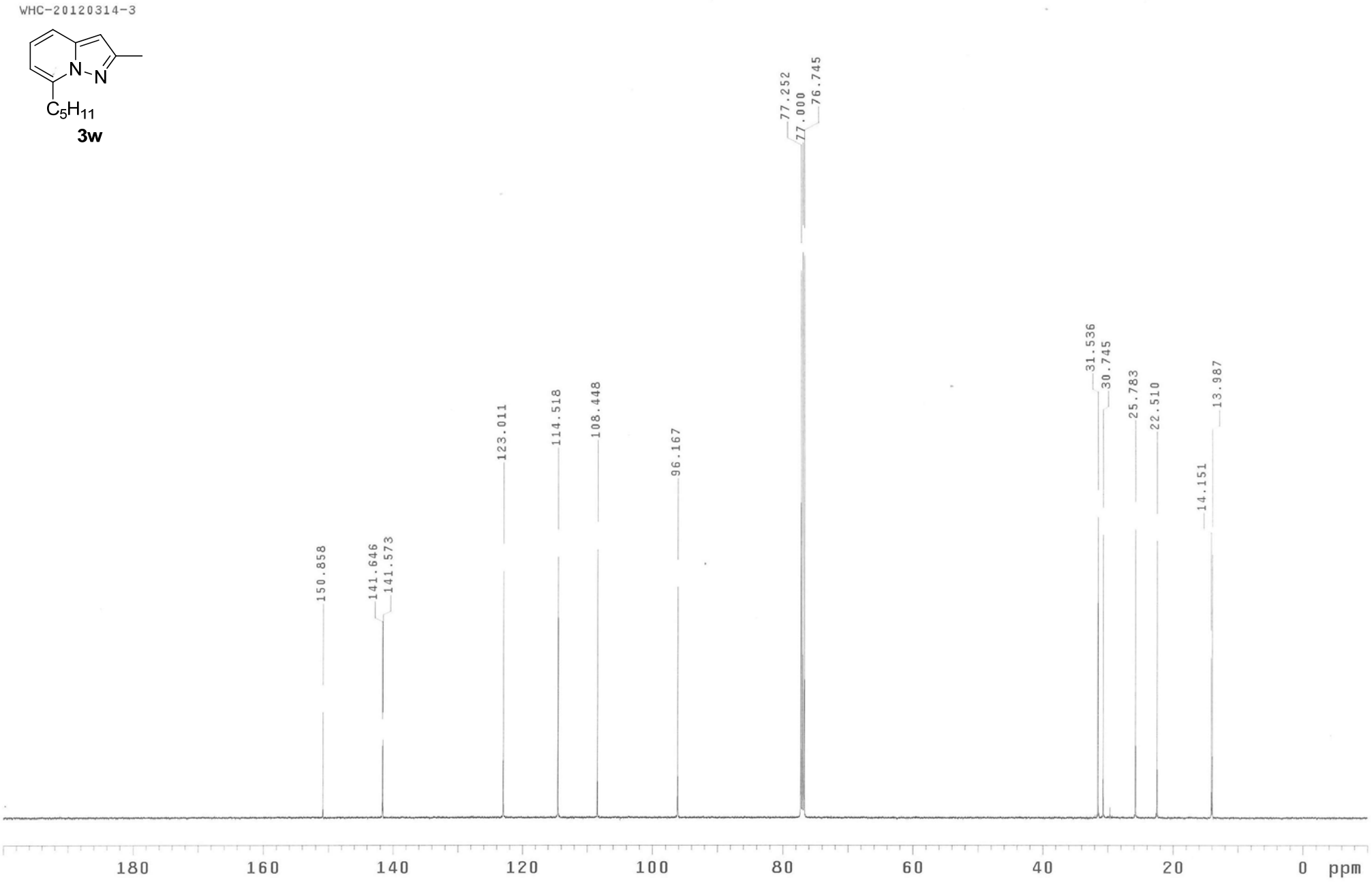


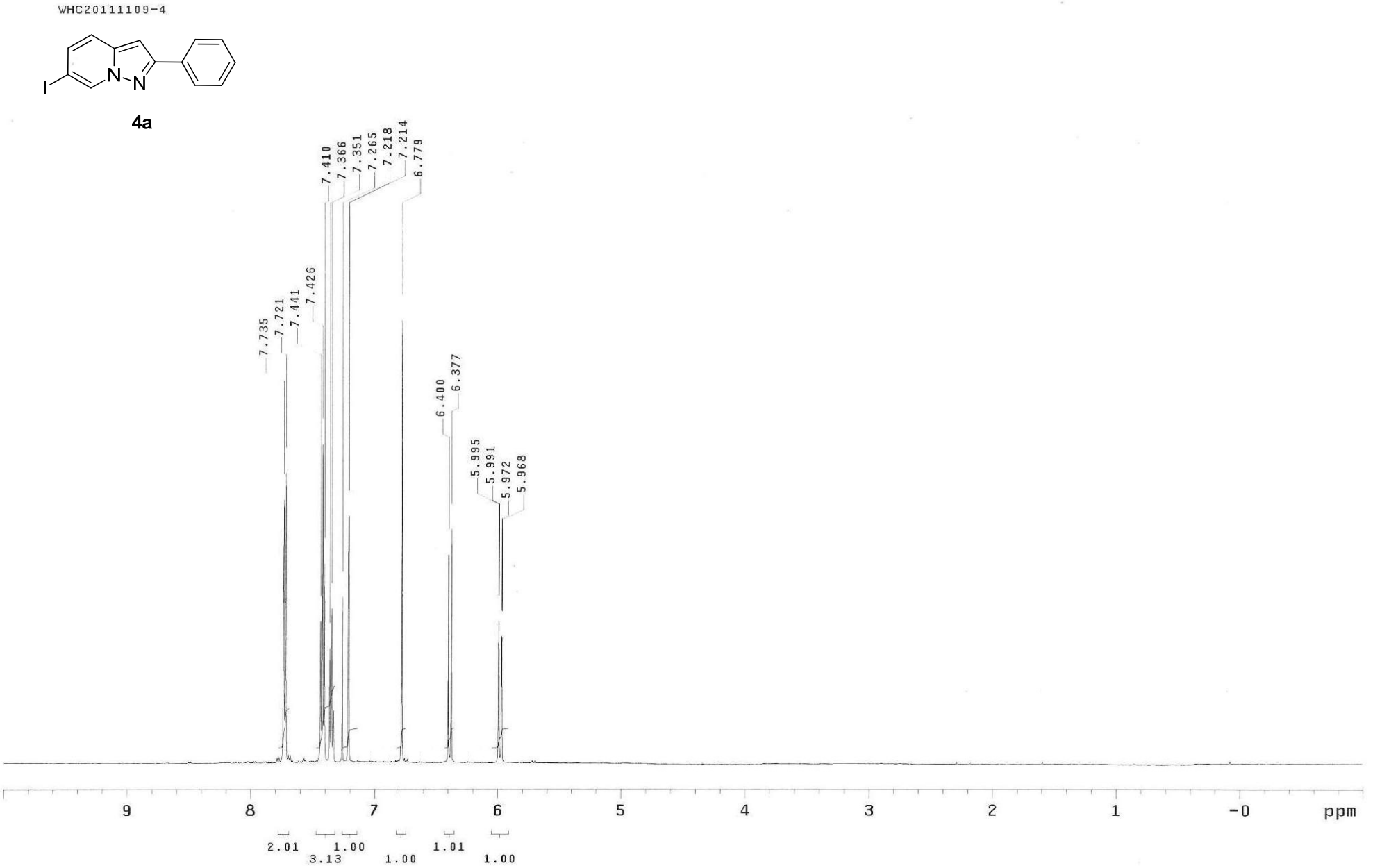


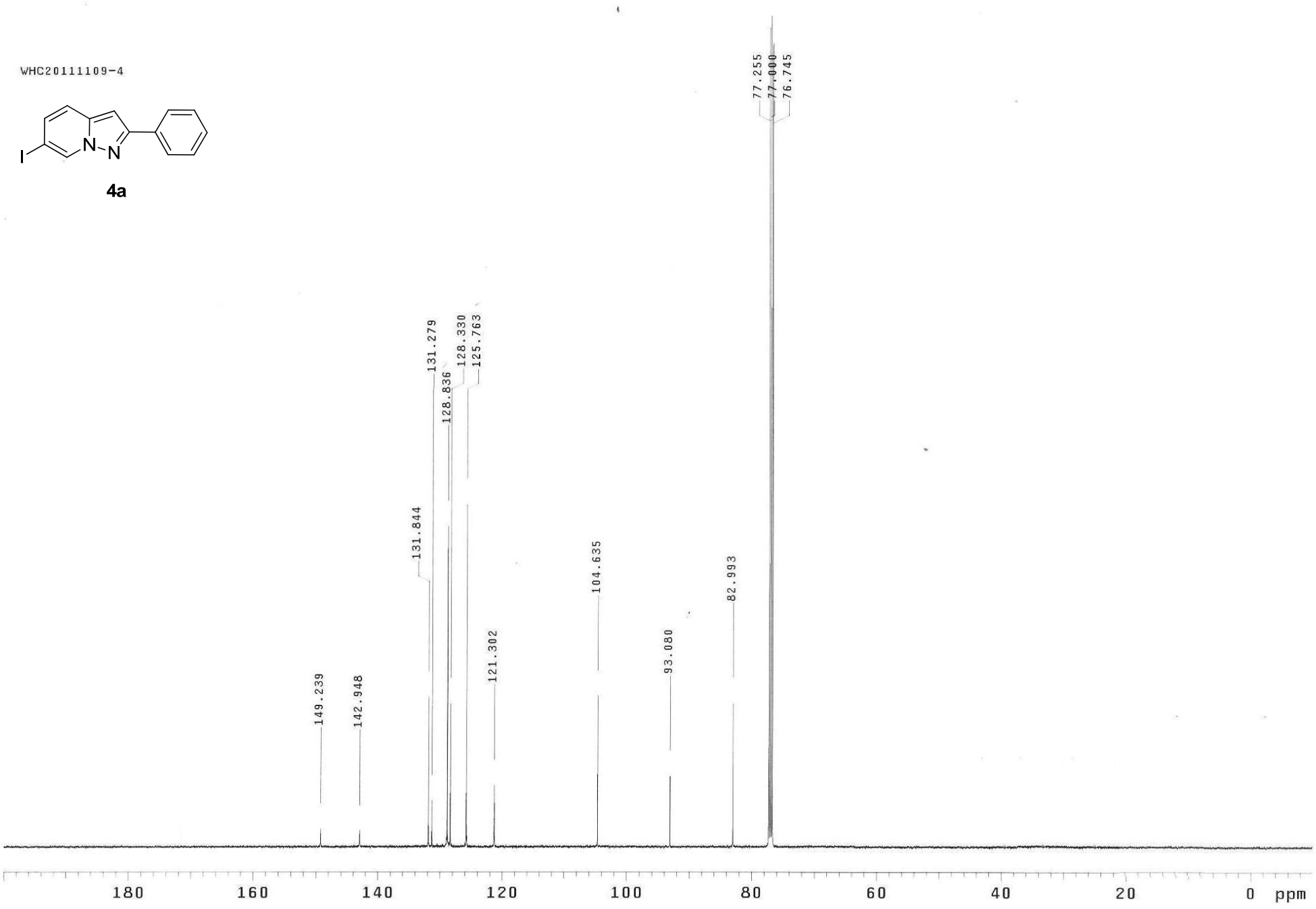
WHC-20120314-3

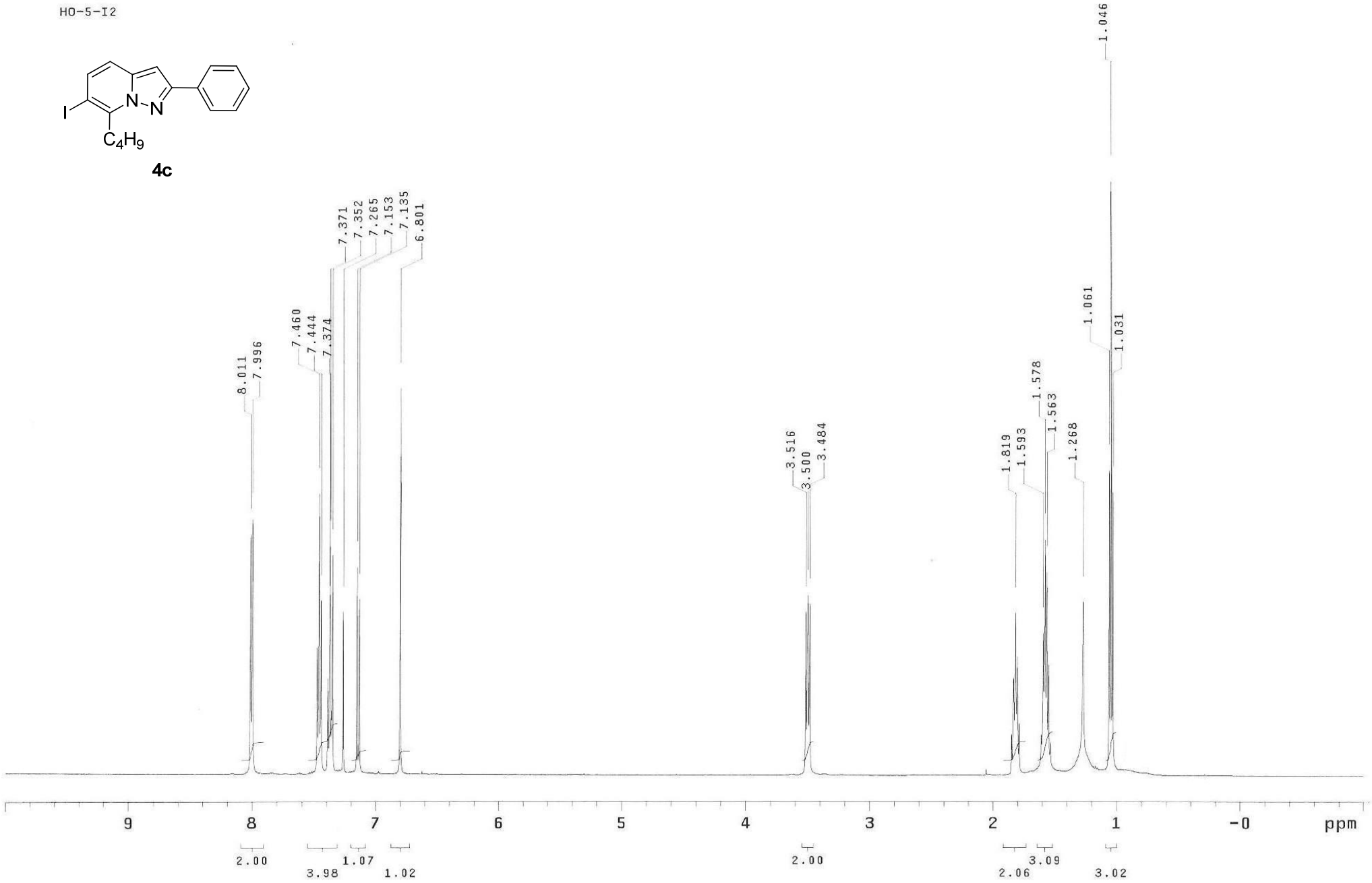


3w

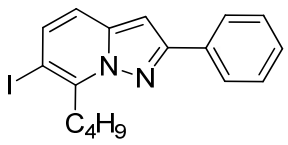








HO-5-I2



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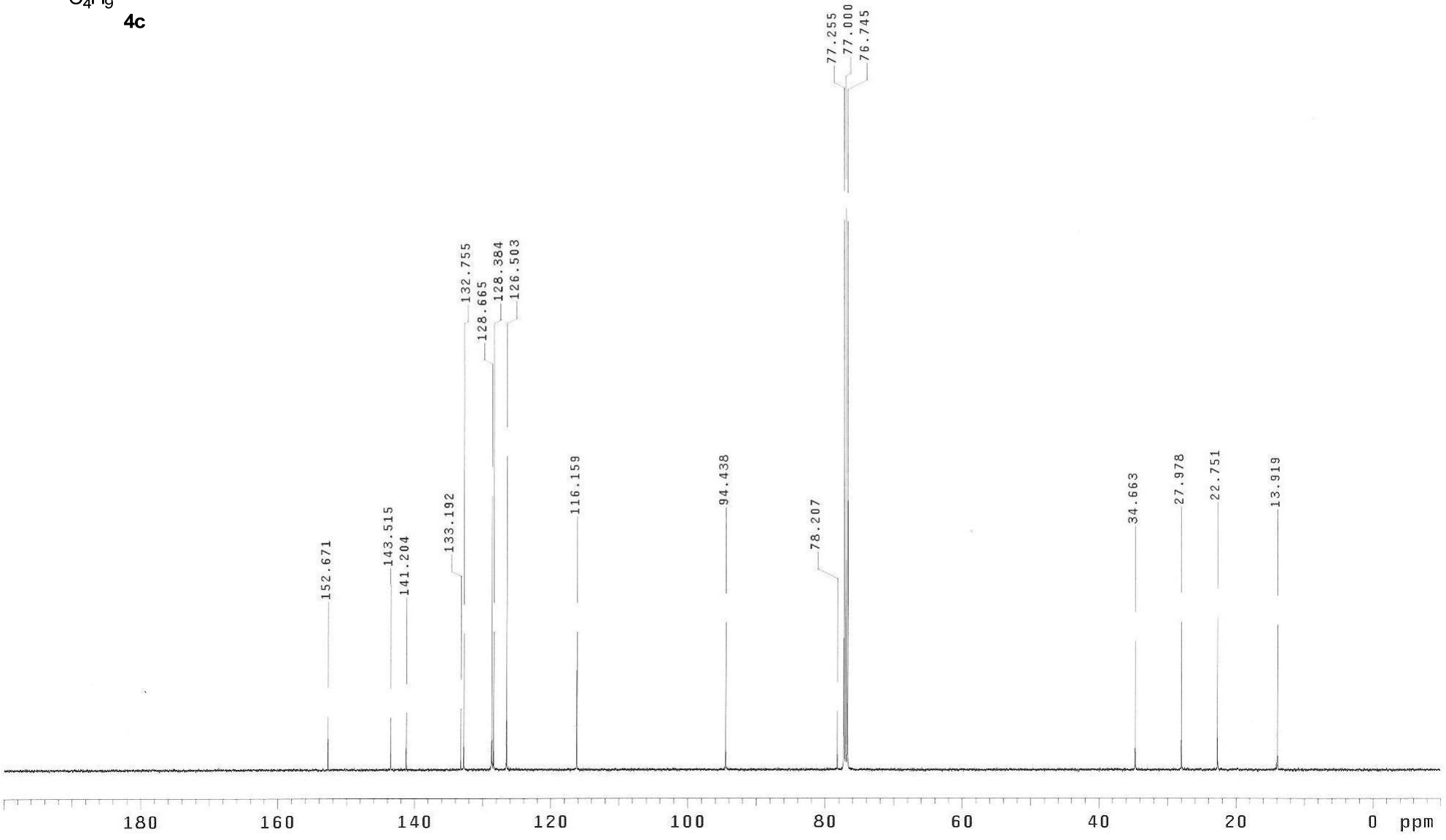
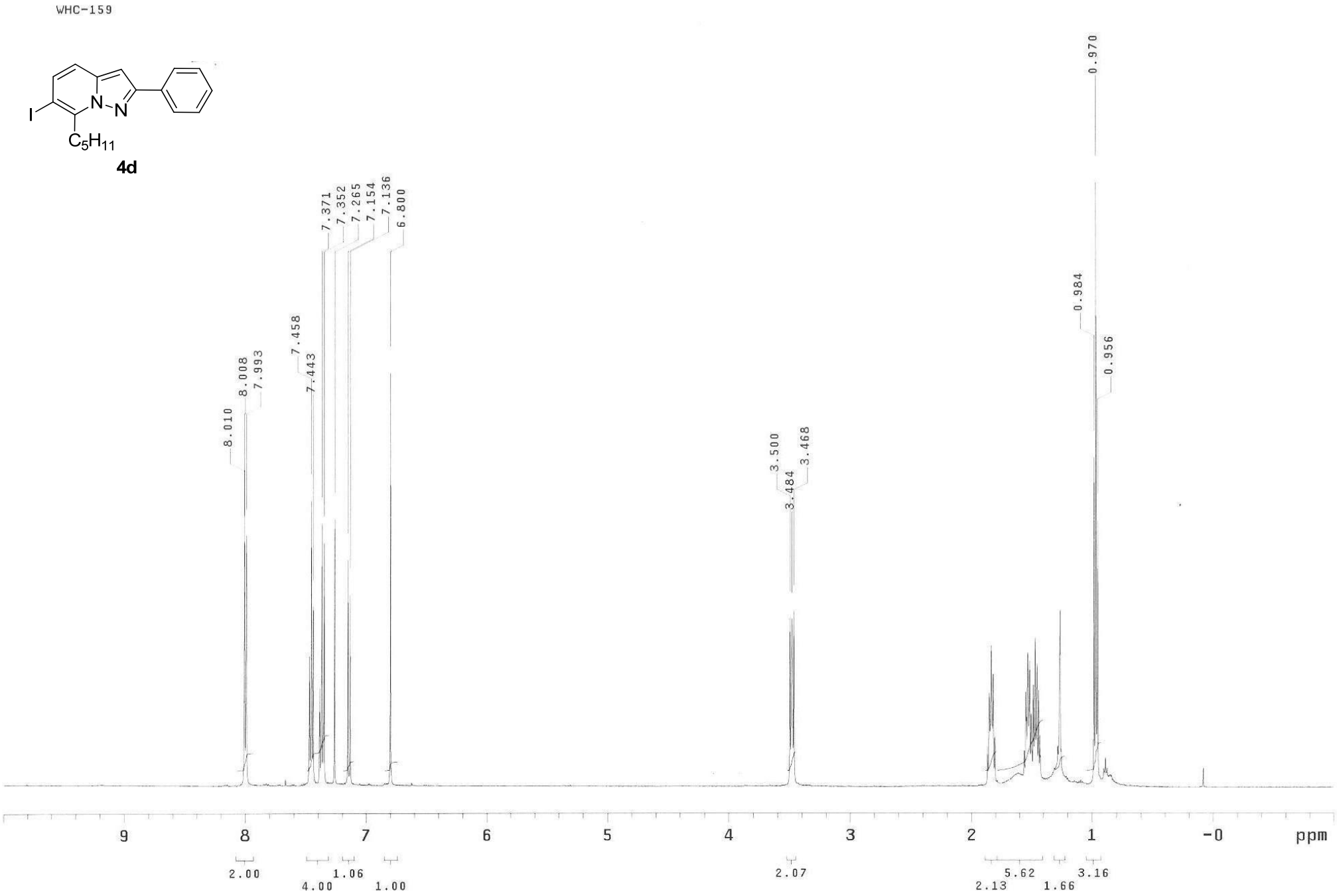
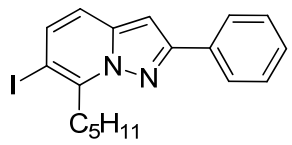




WHC-159



4d

77.255
77.000
76.745
132.755
128.665
128.381
126.507
152.686
143.551
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133.192
116.155
94.438
78.203
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120
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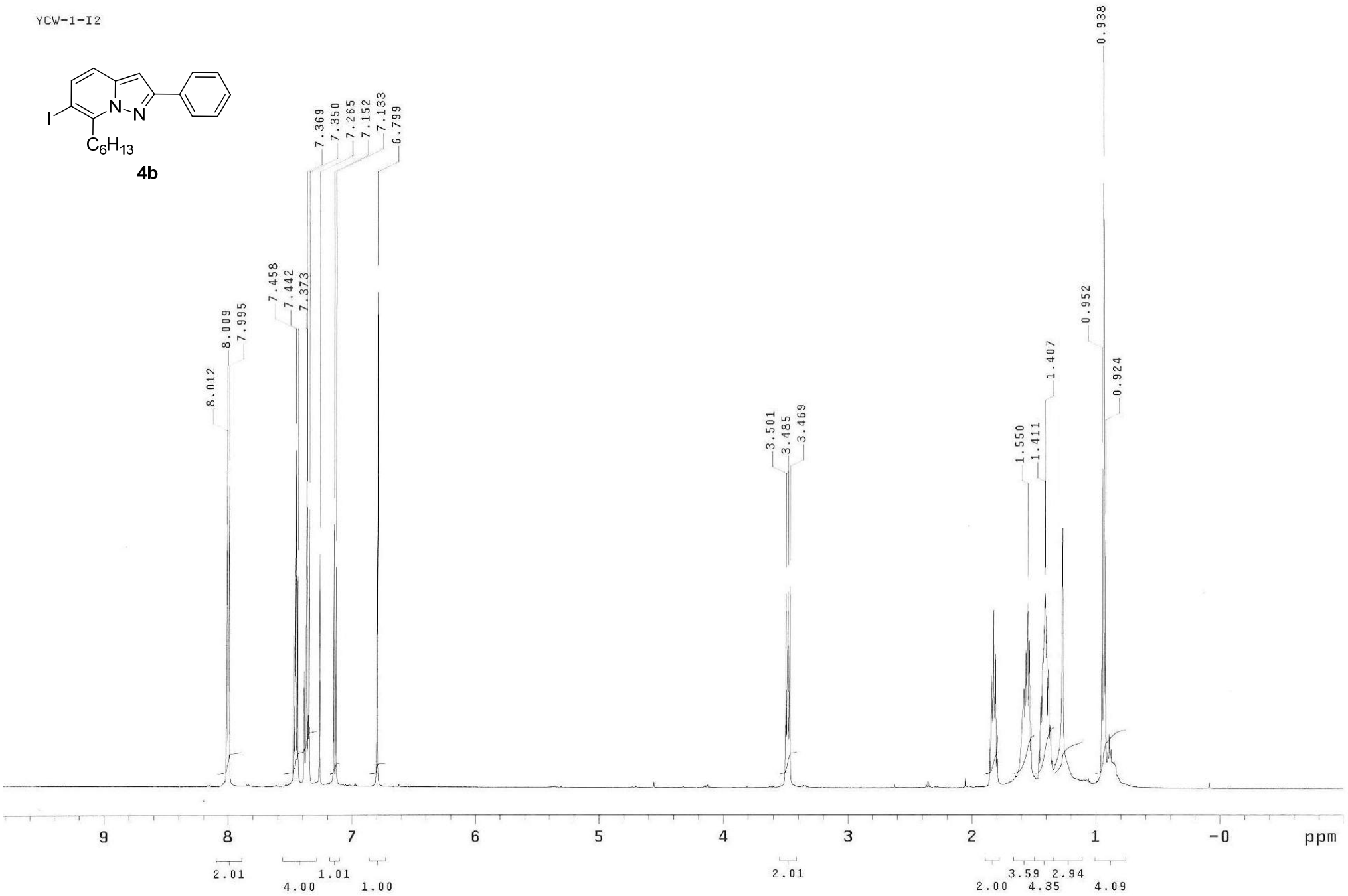
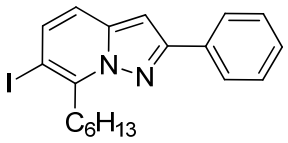
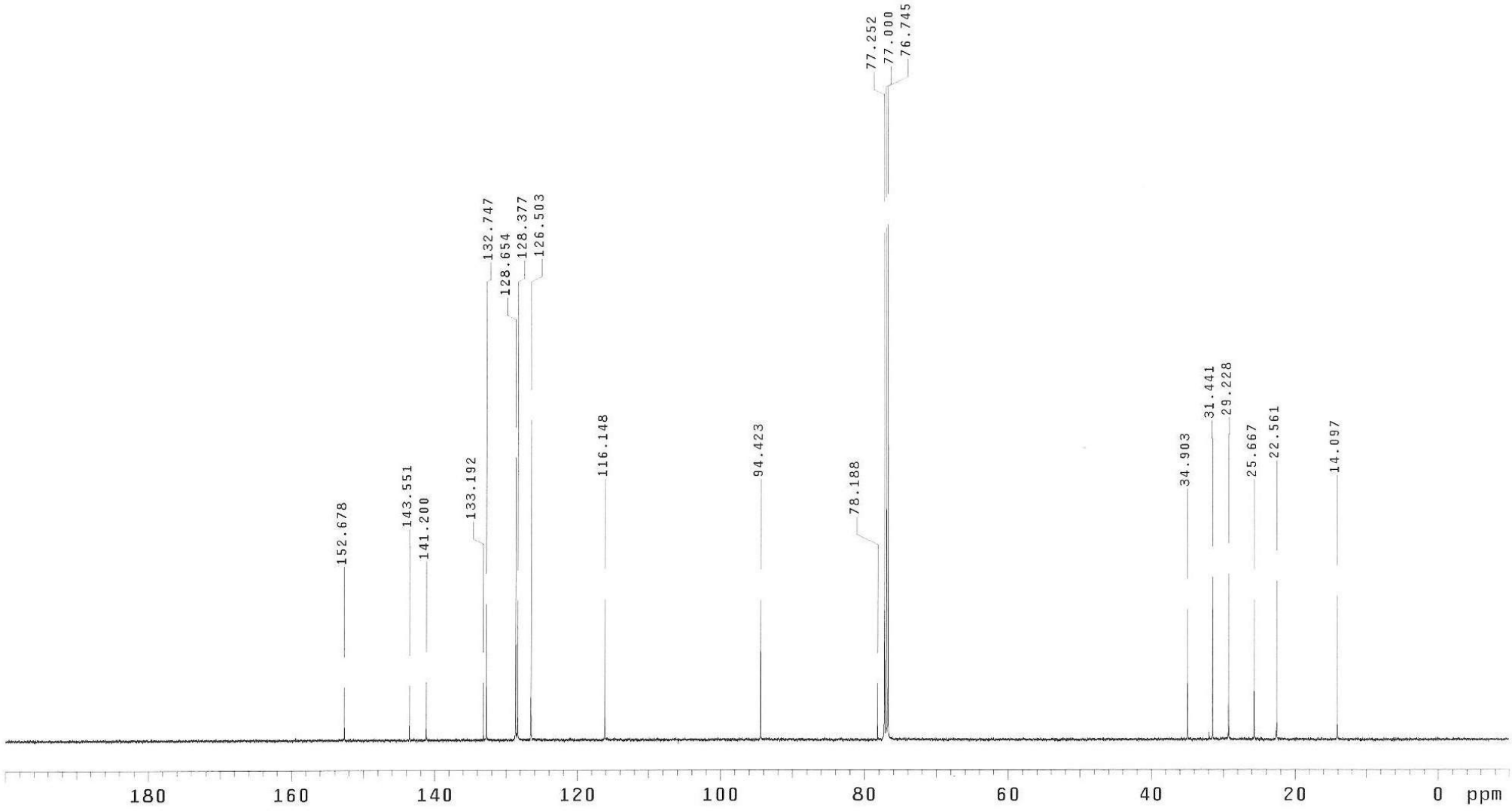
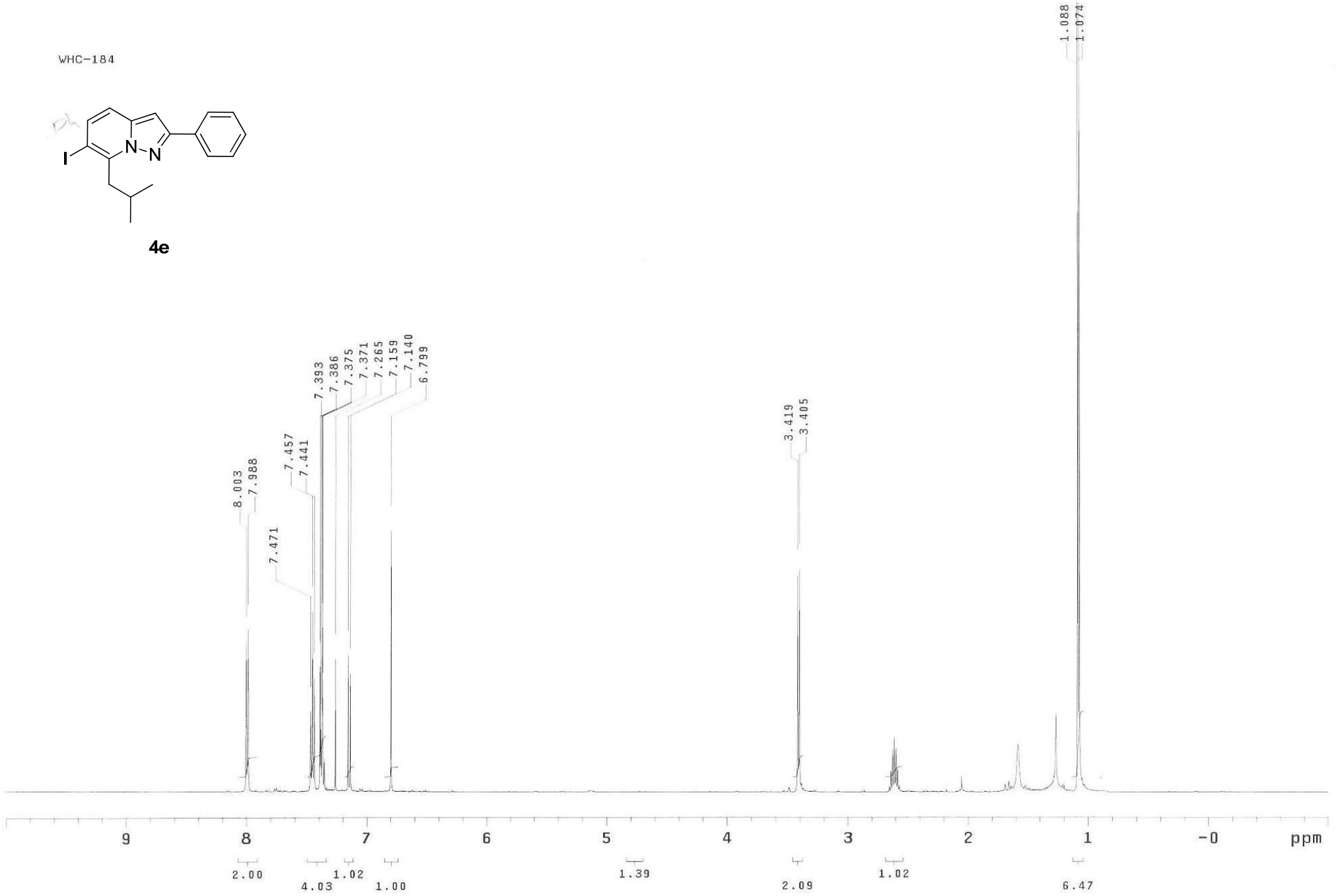


YCW-1-I2

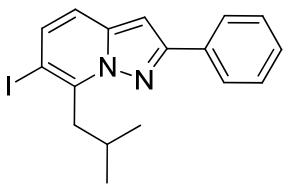


4b

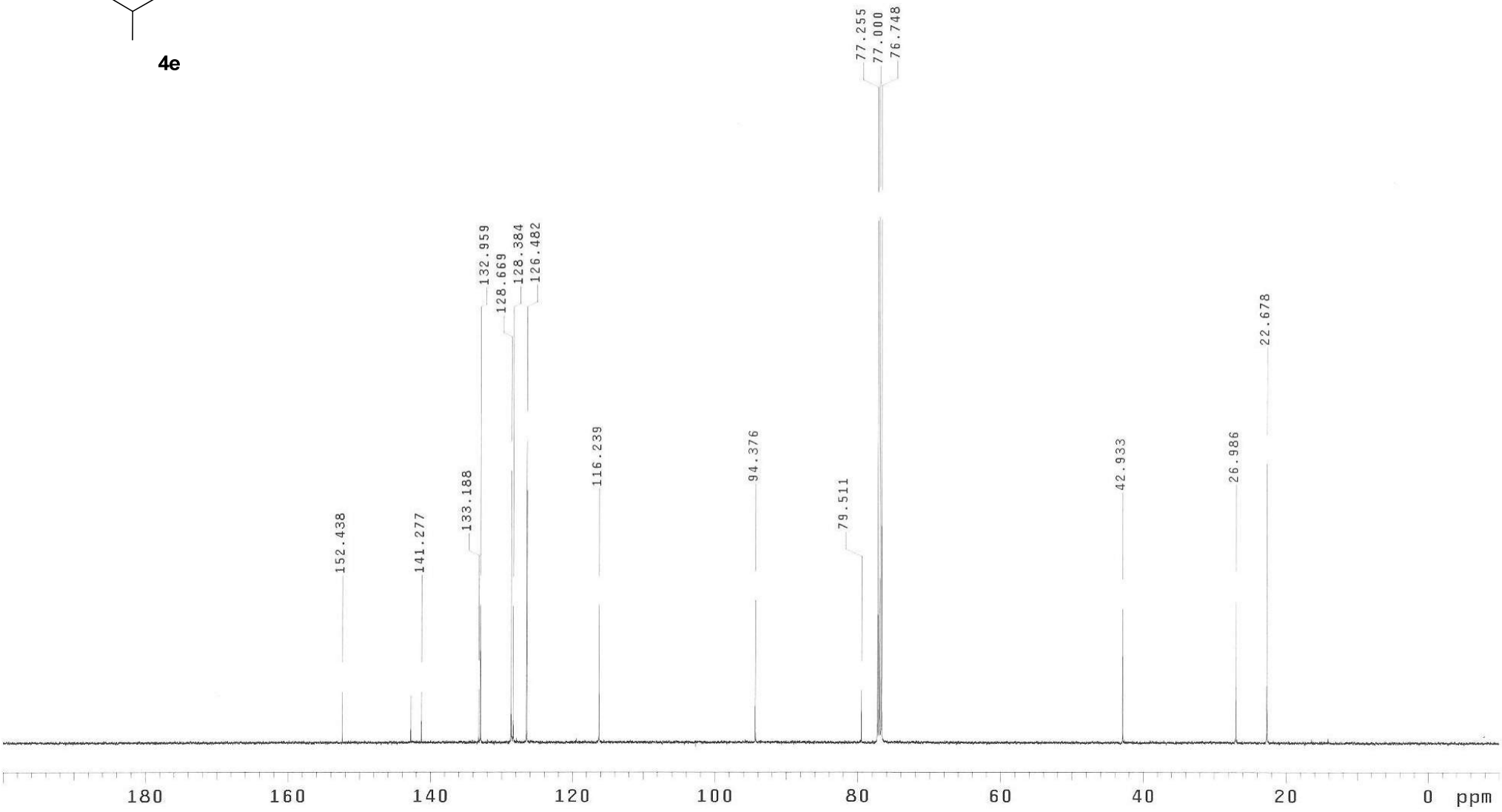


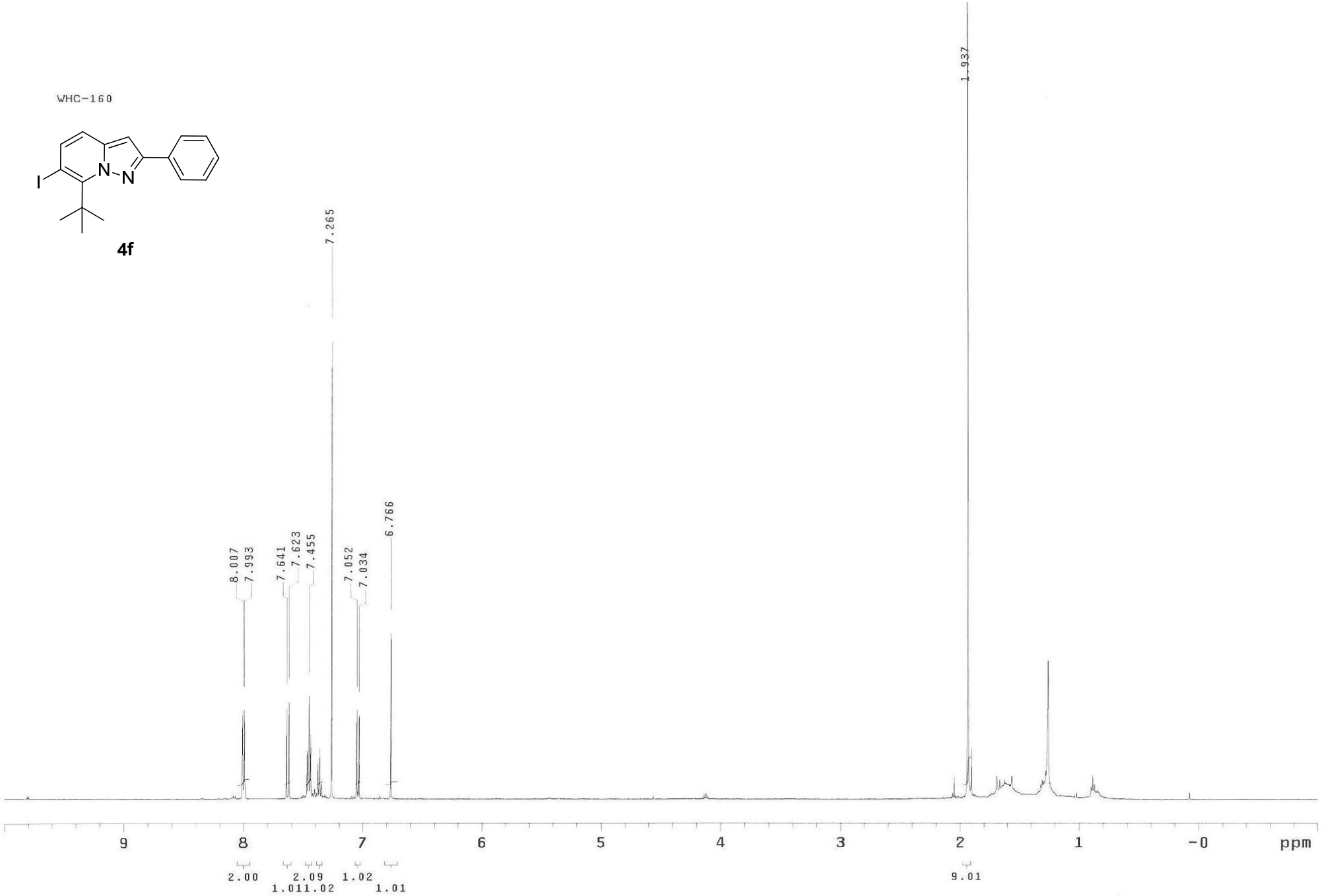


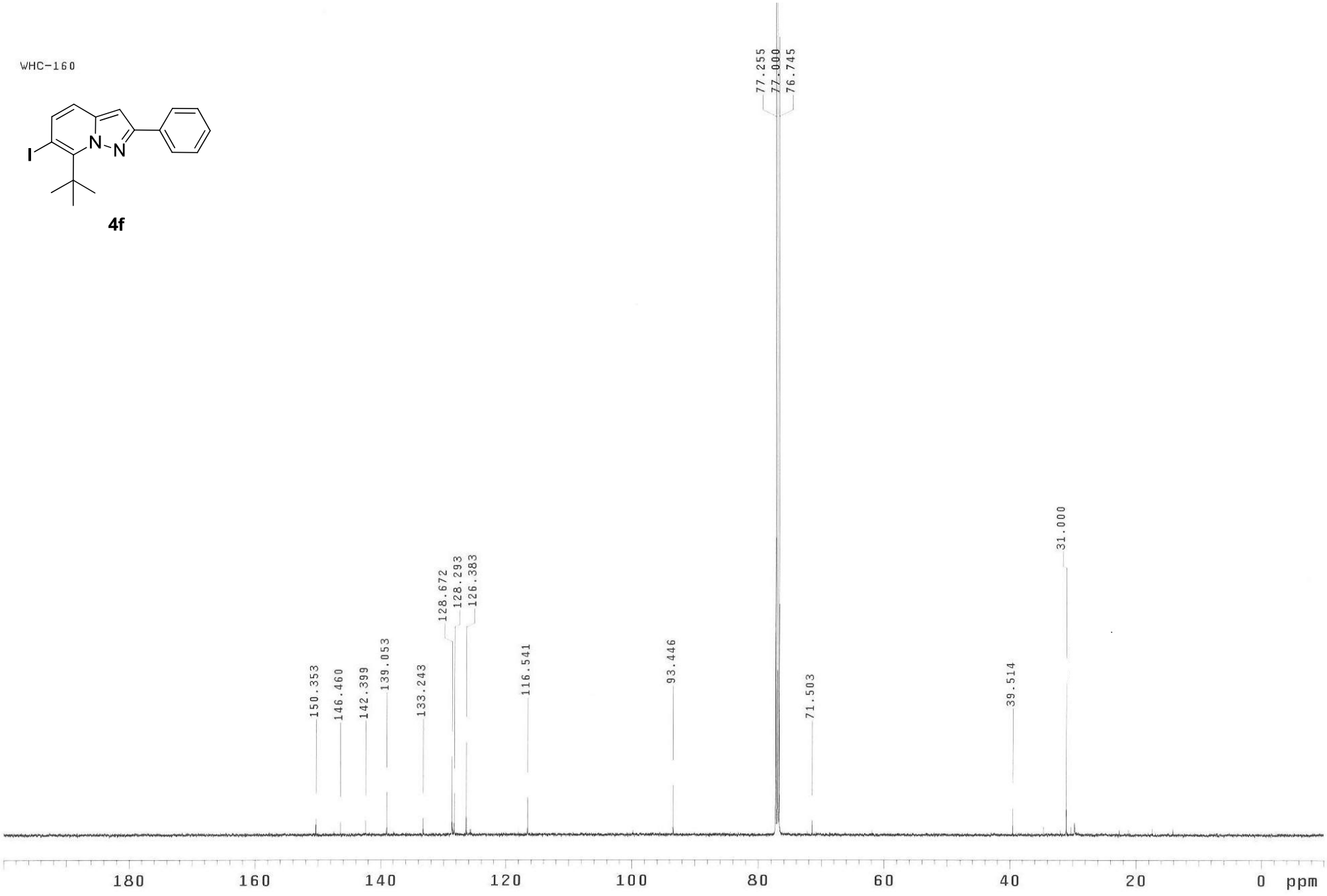
WHC-184



4e







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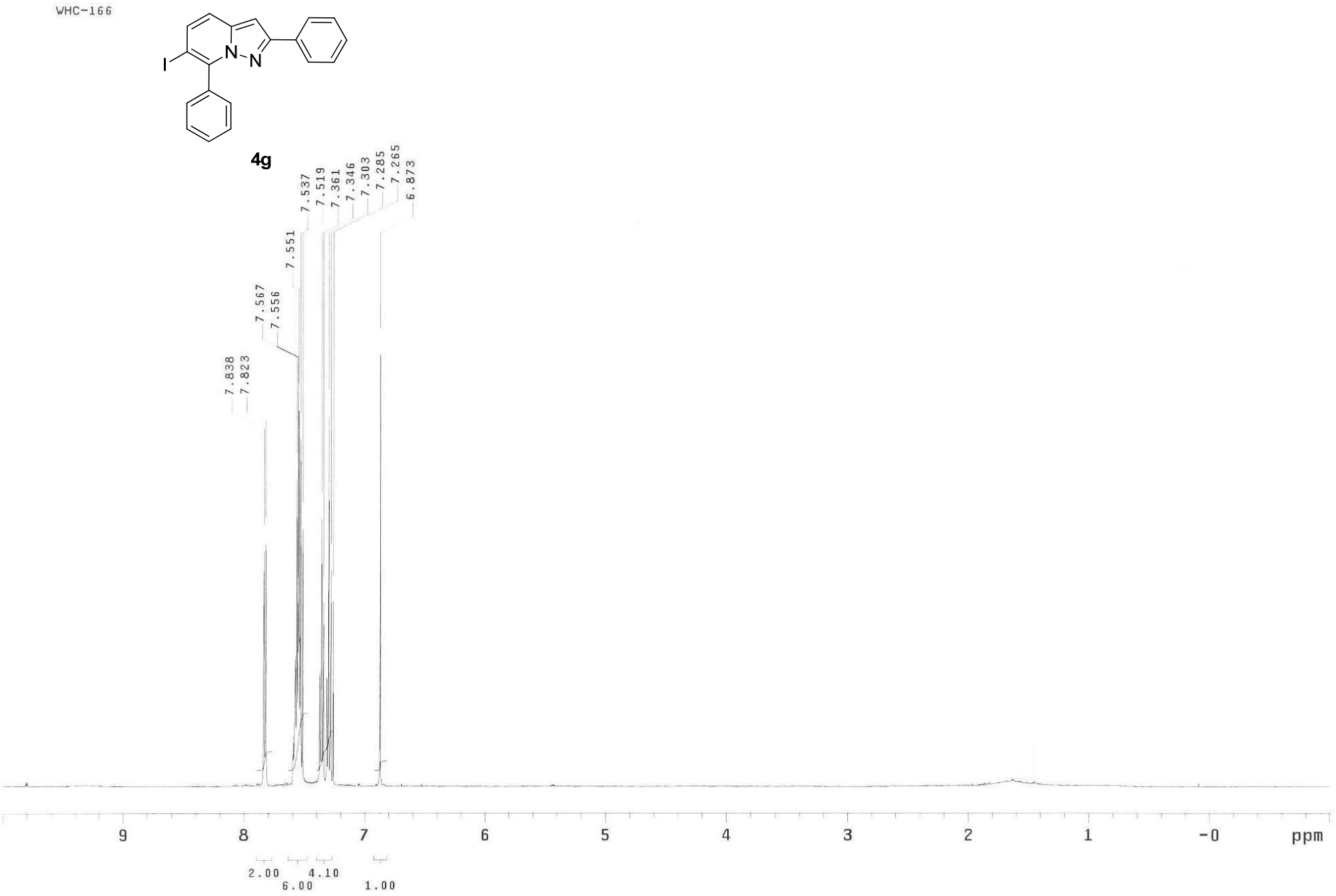
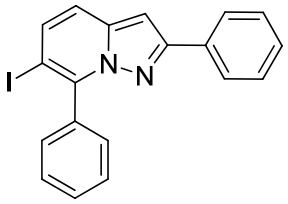
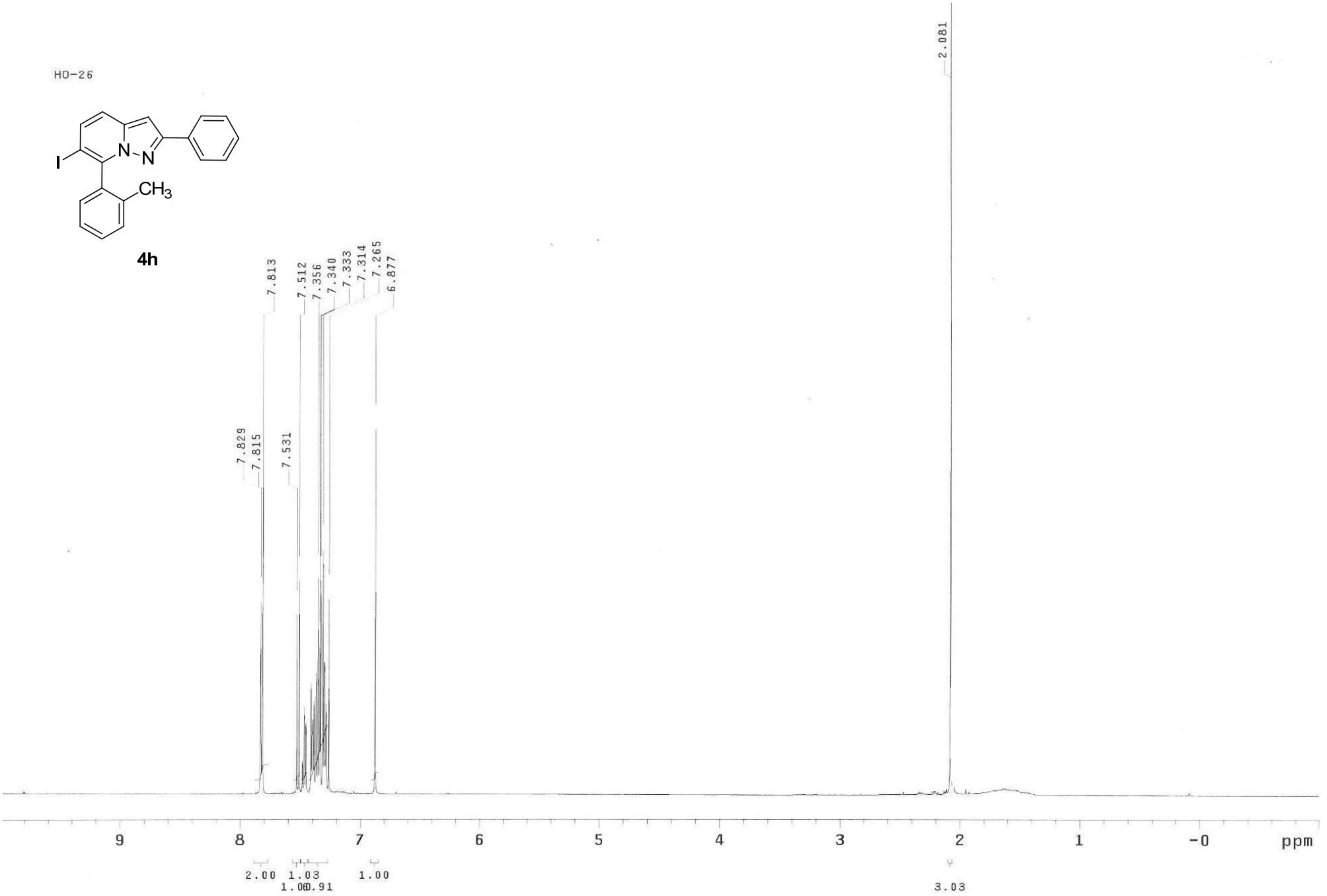


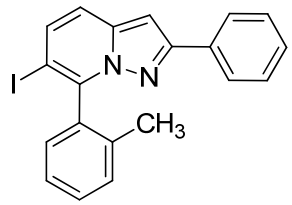
WHC-166



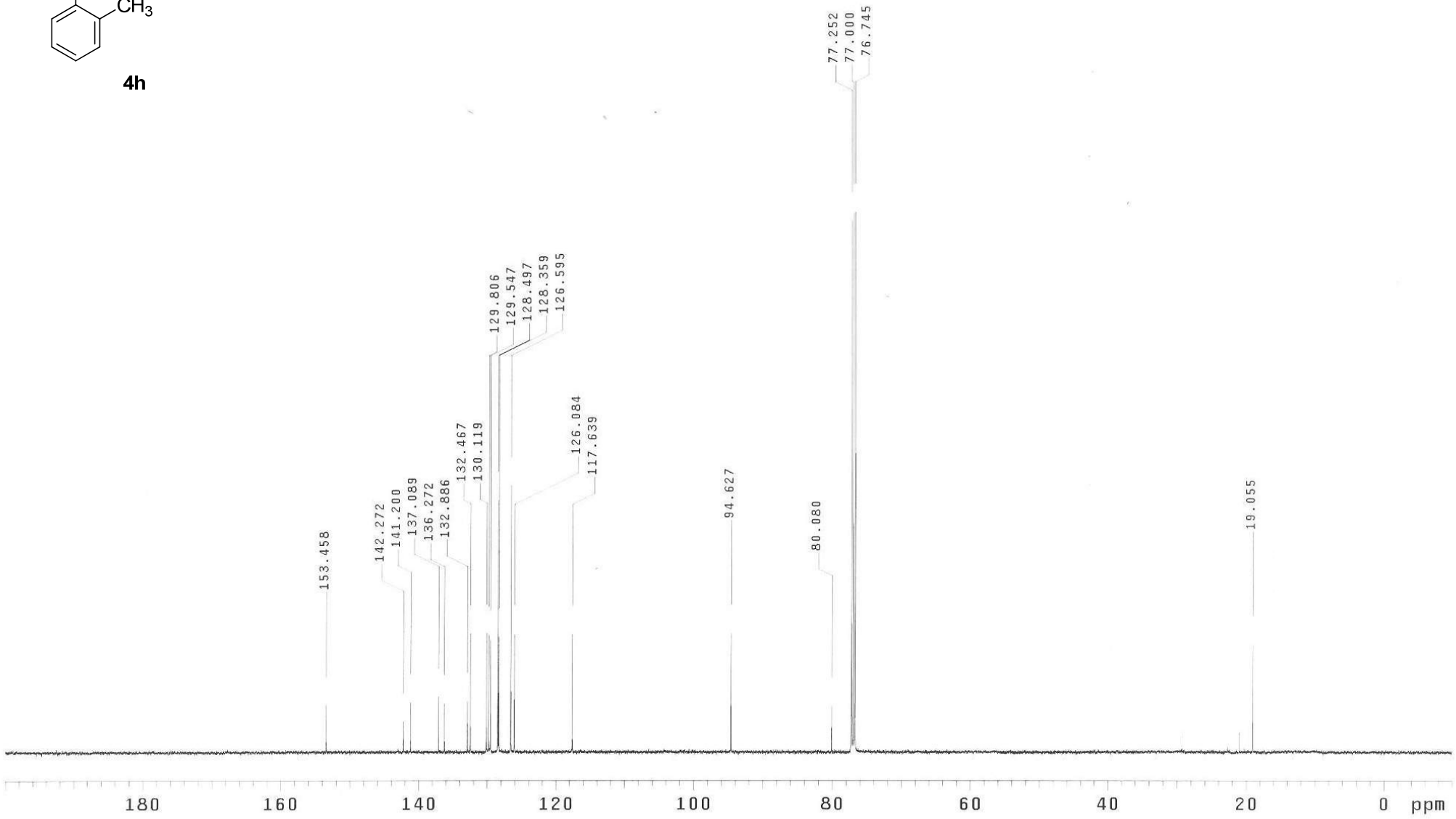
4g



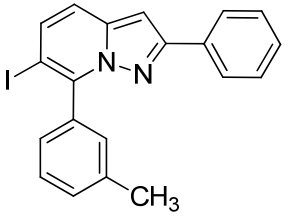
HO-26



4h

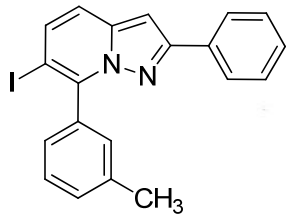


HO-17-I2

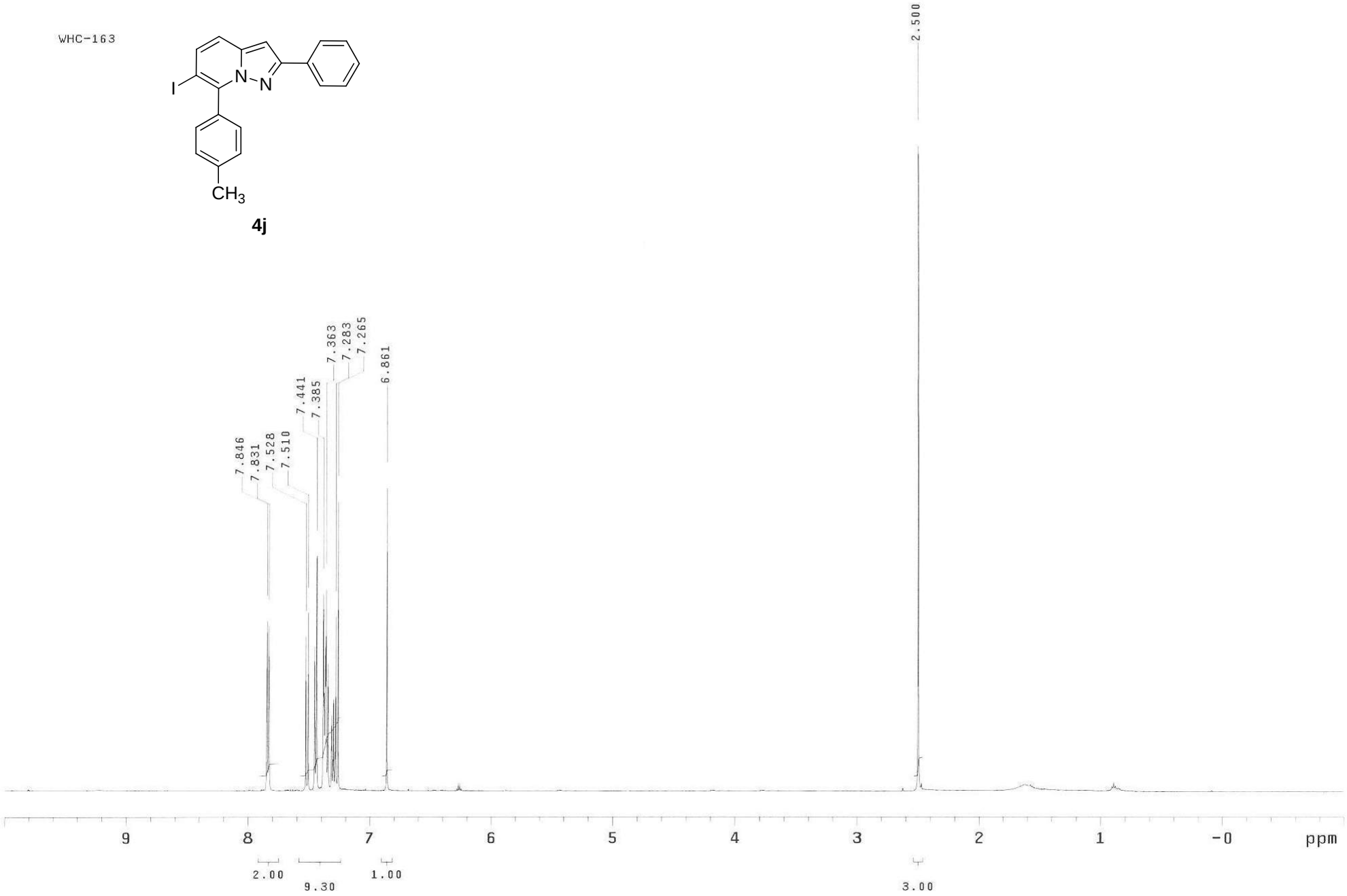


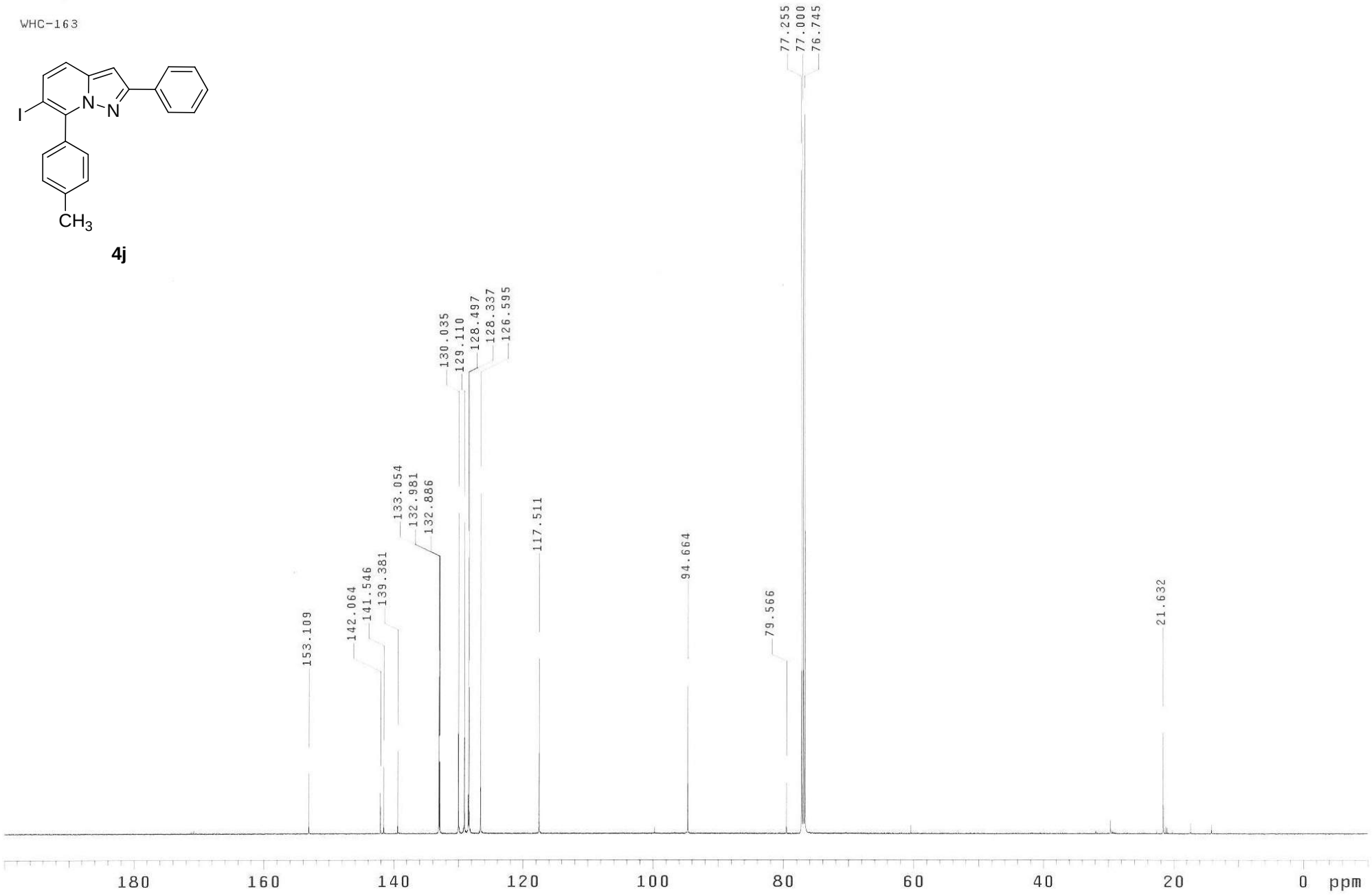
4i

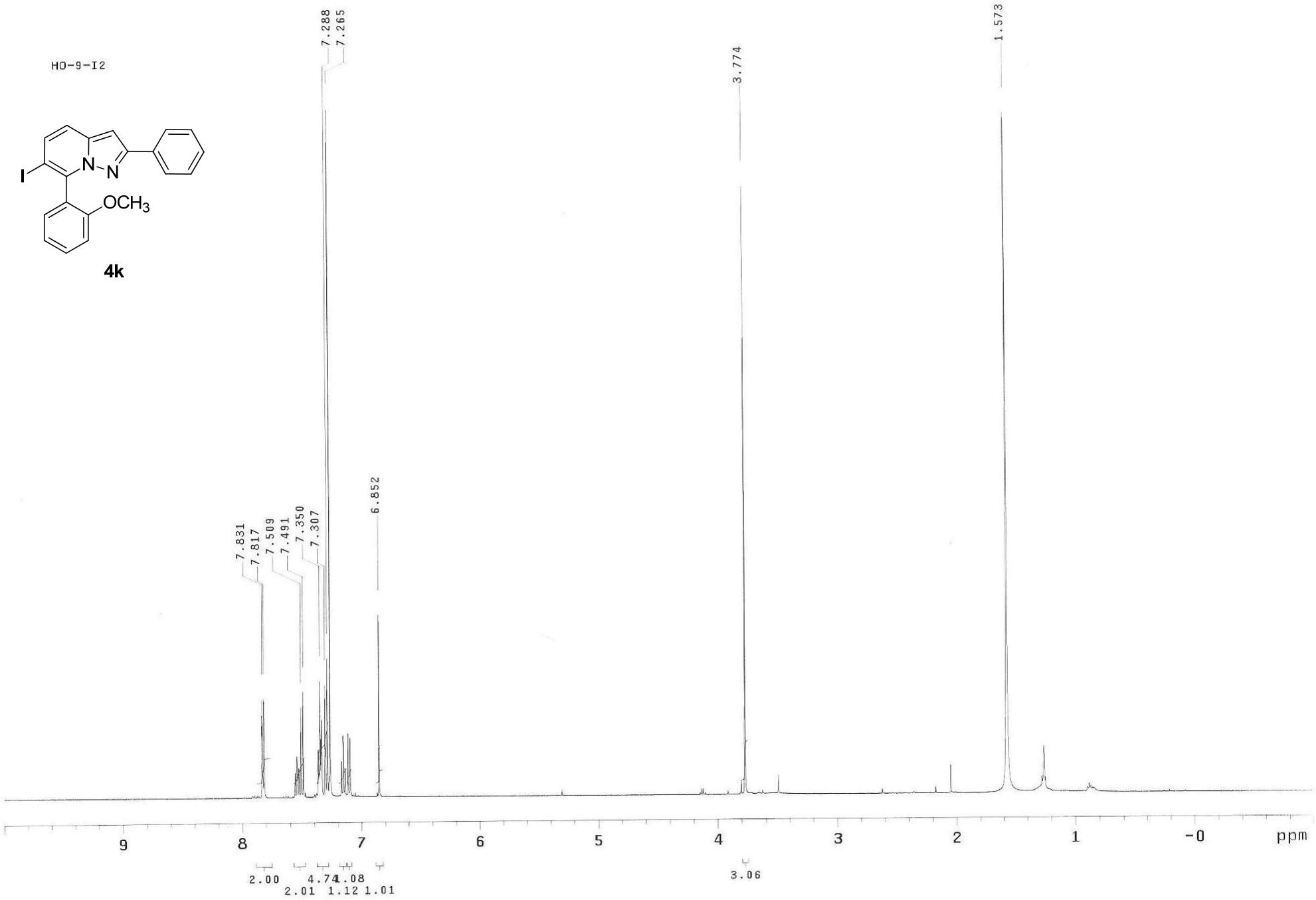
HO-17-I2

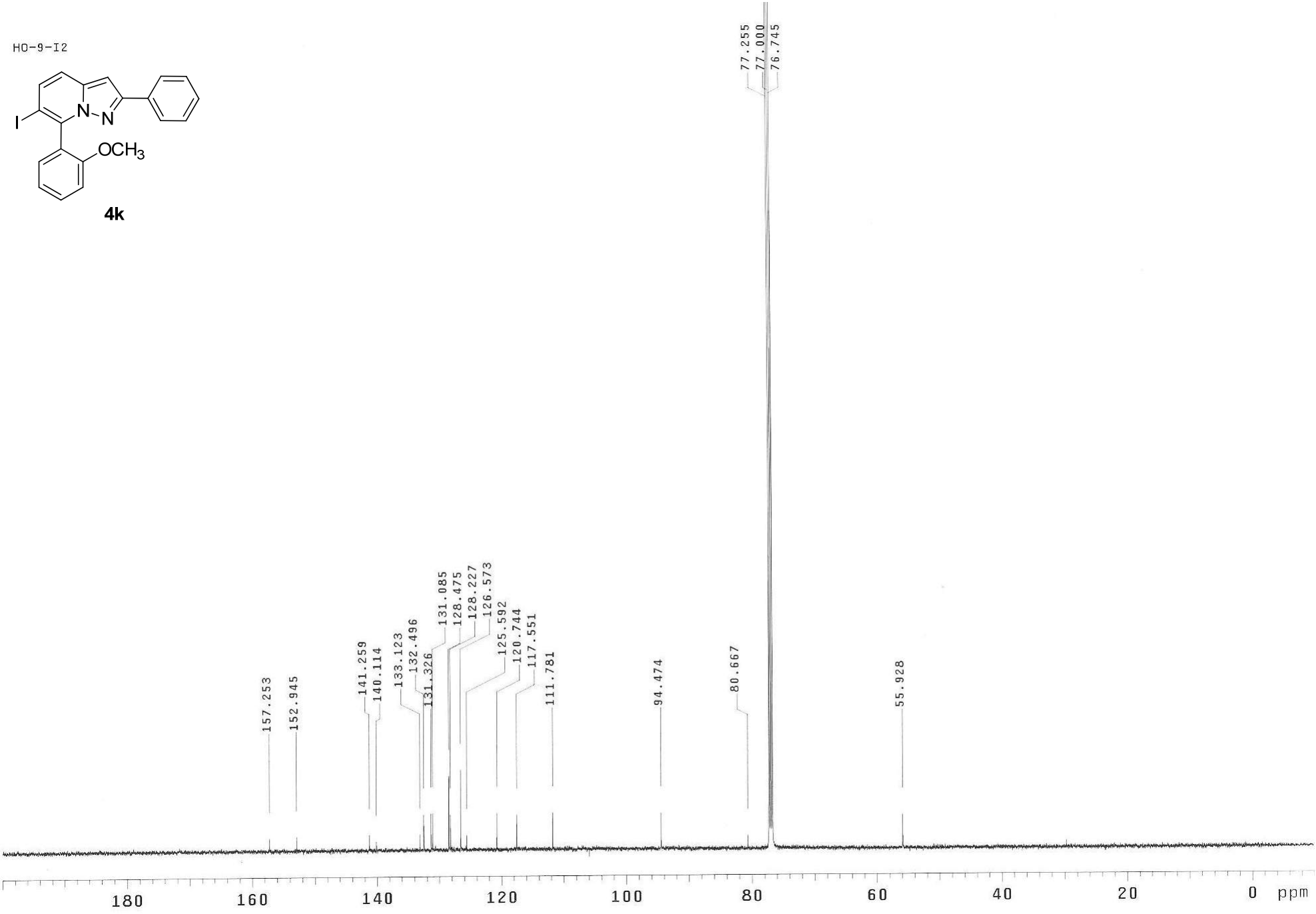


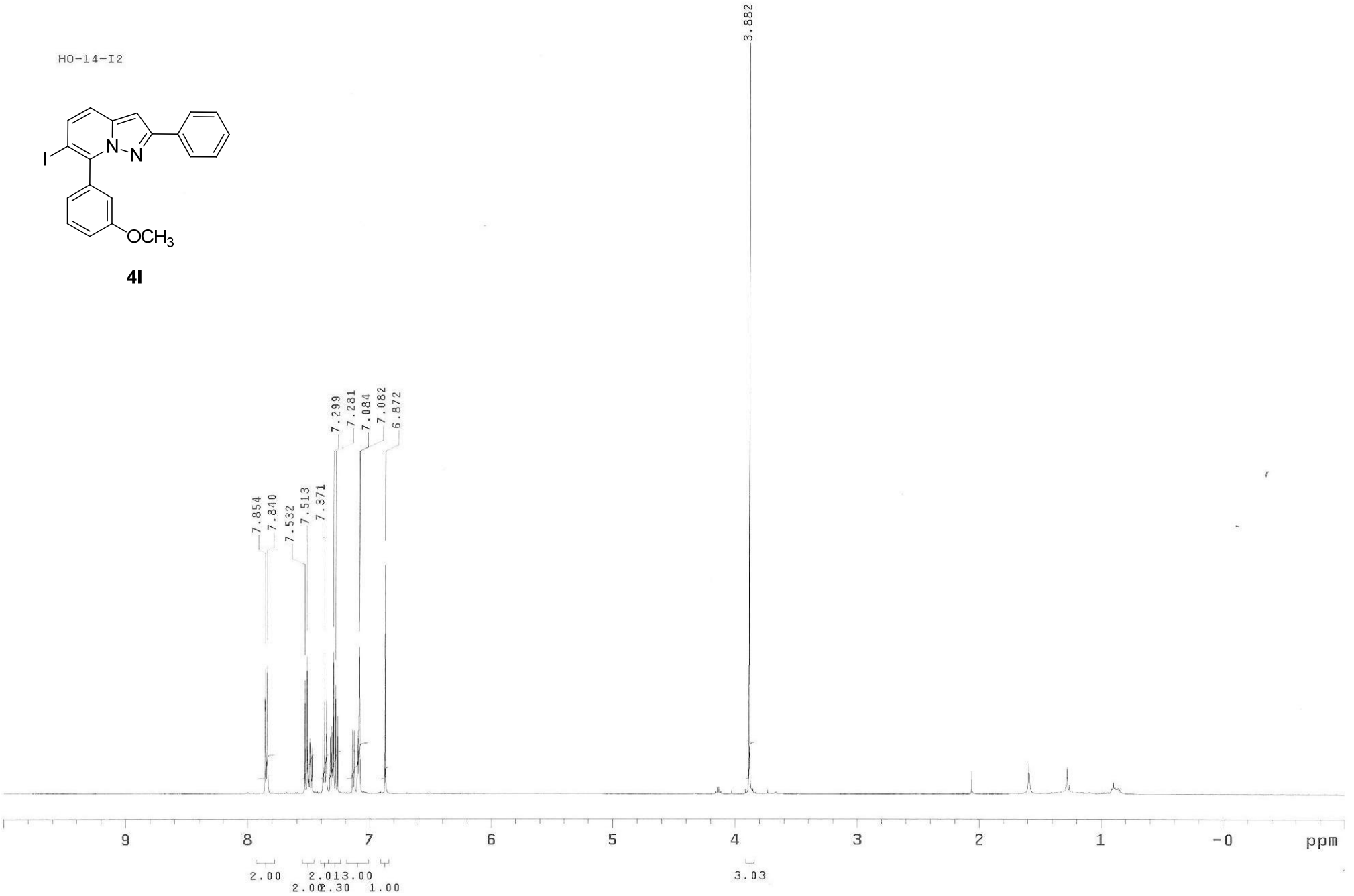
4i



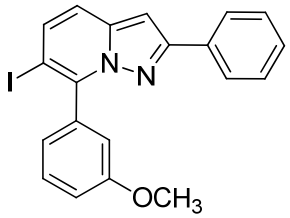




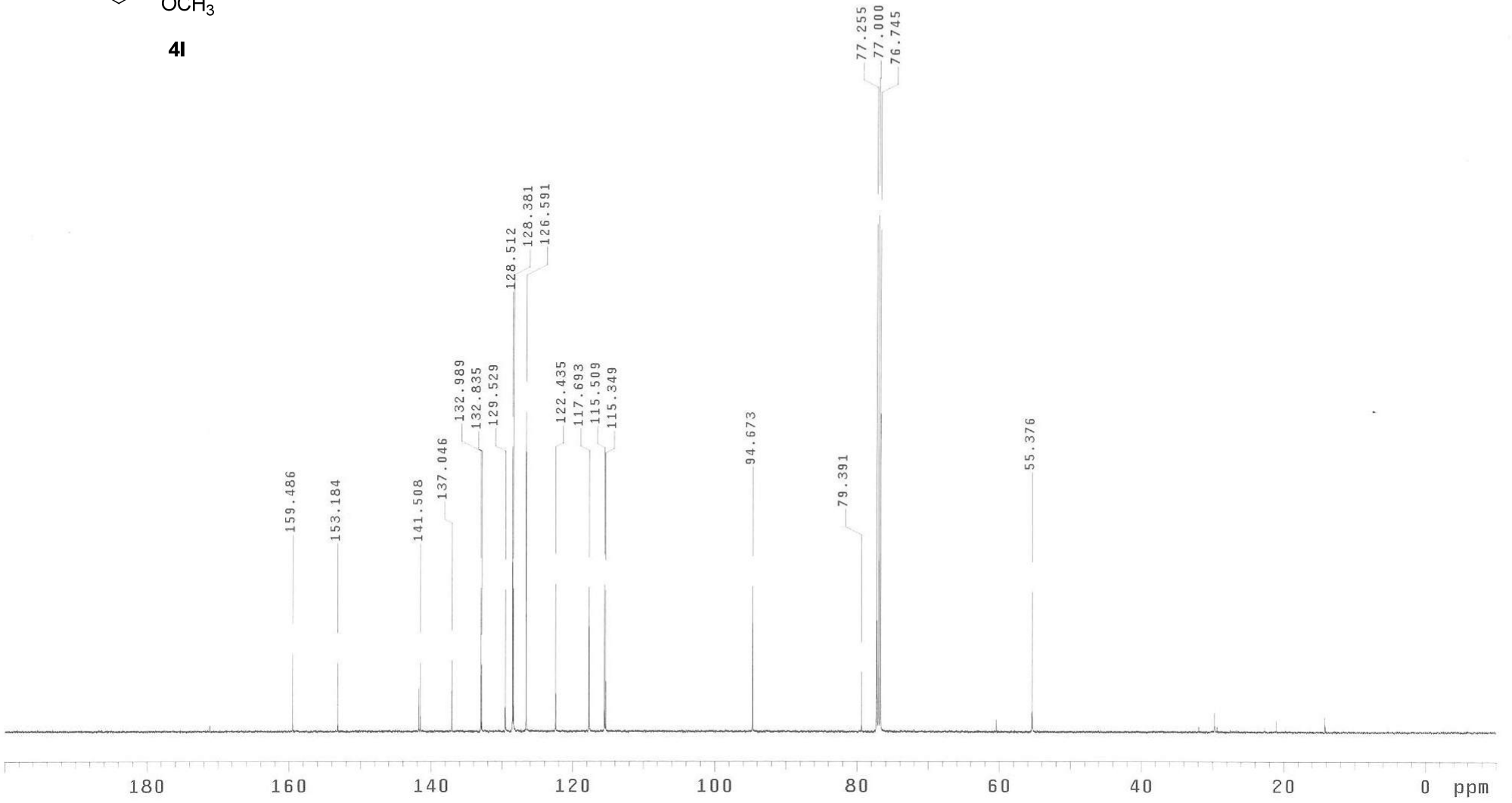


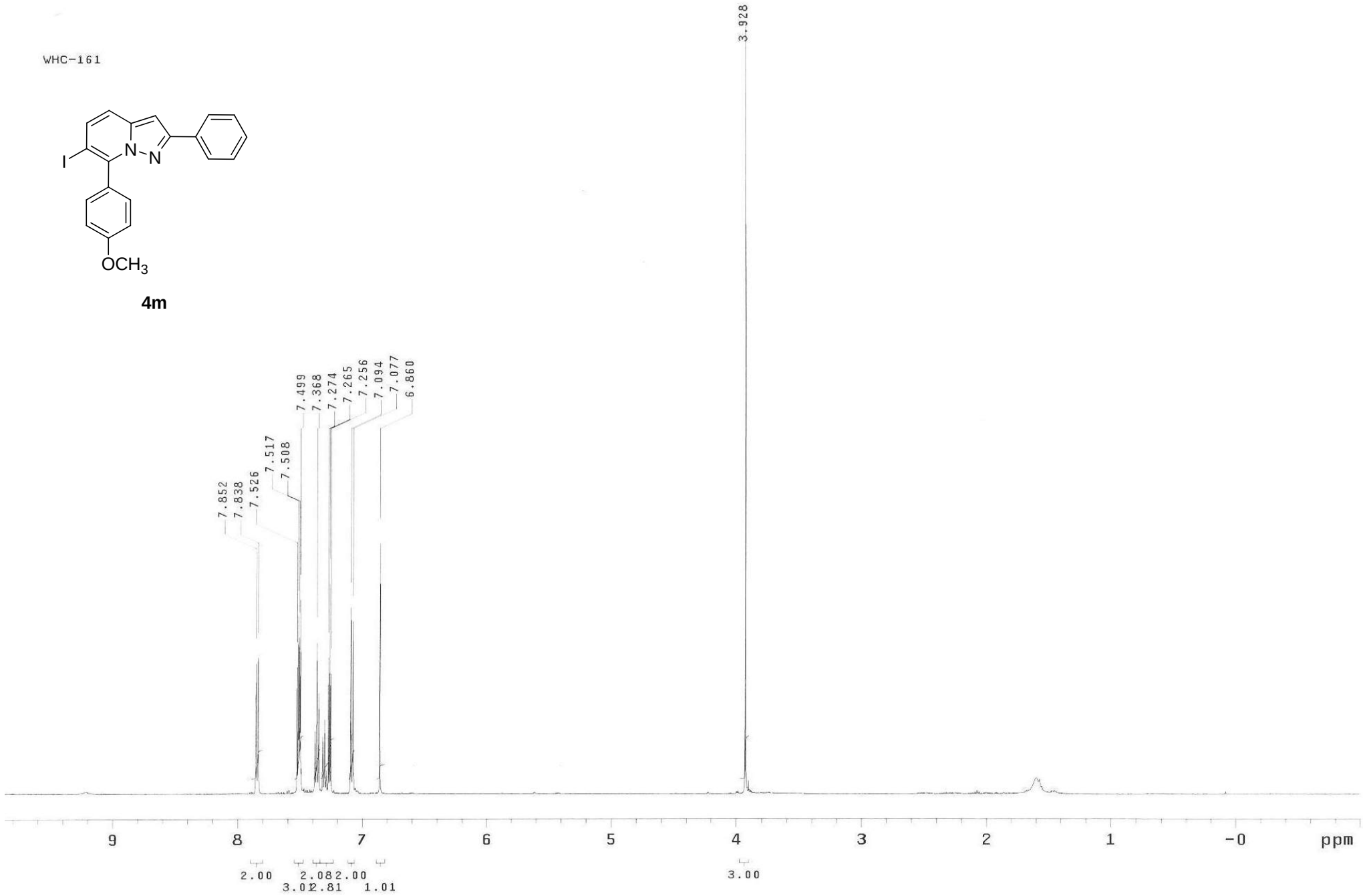


HO-14-I2



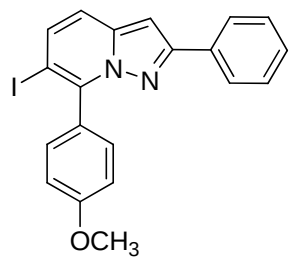
4l





4m

WHC-161



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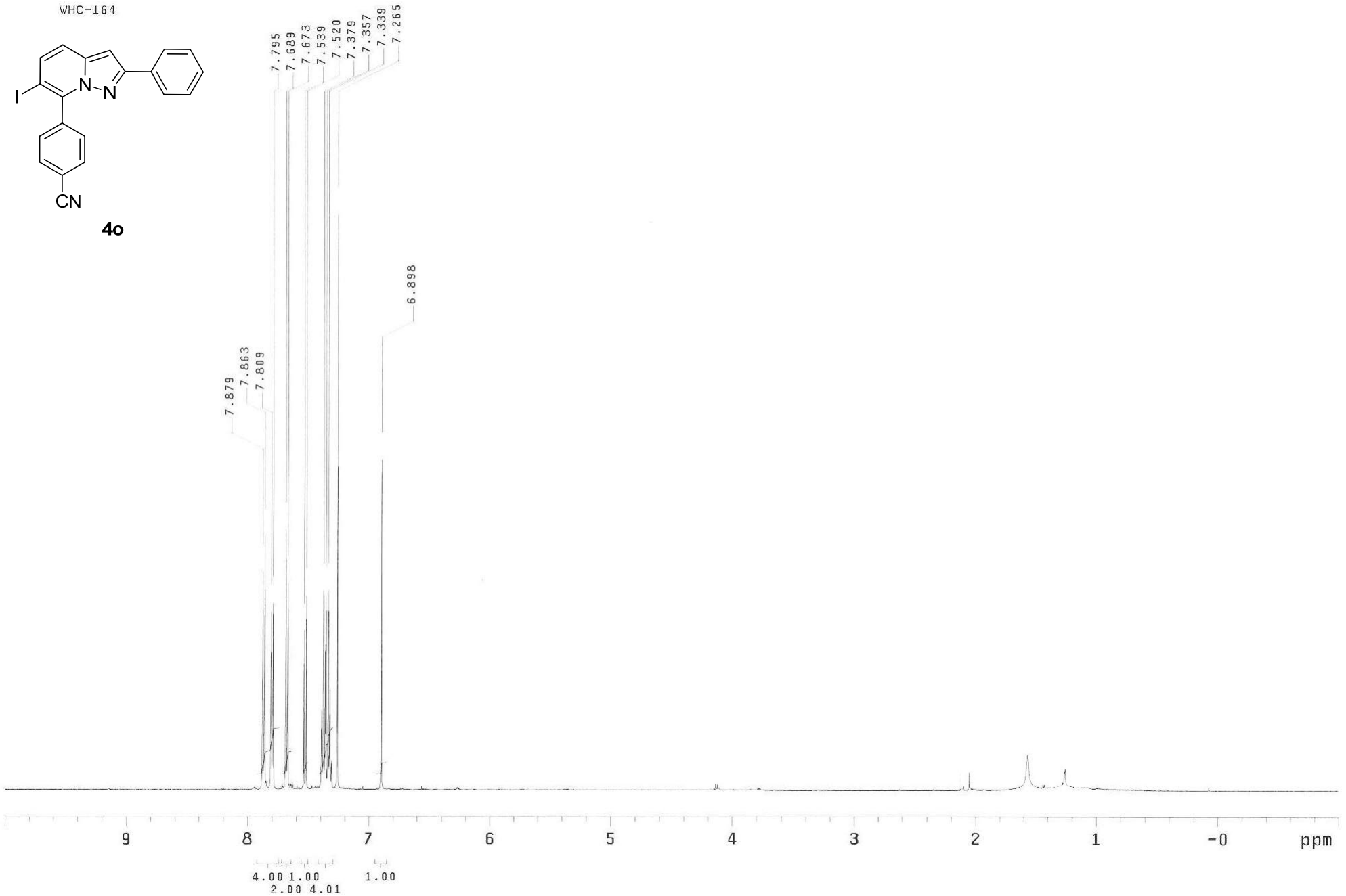

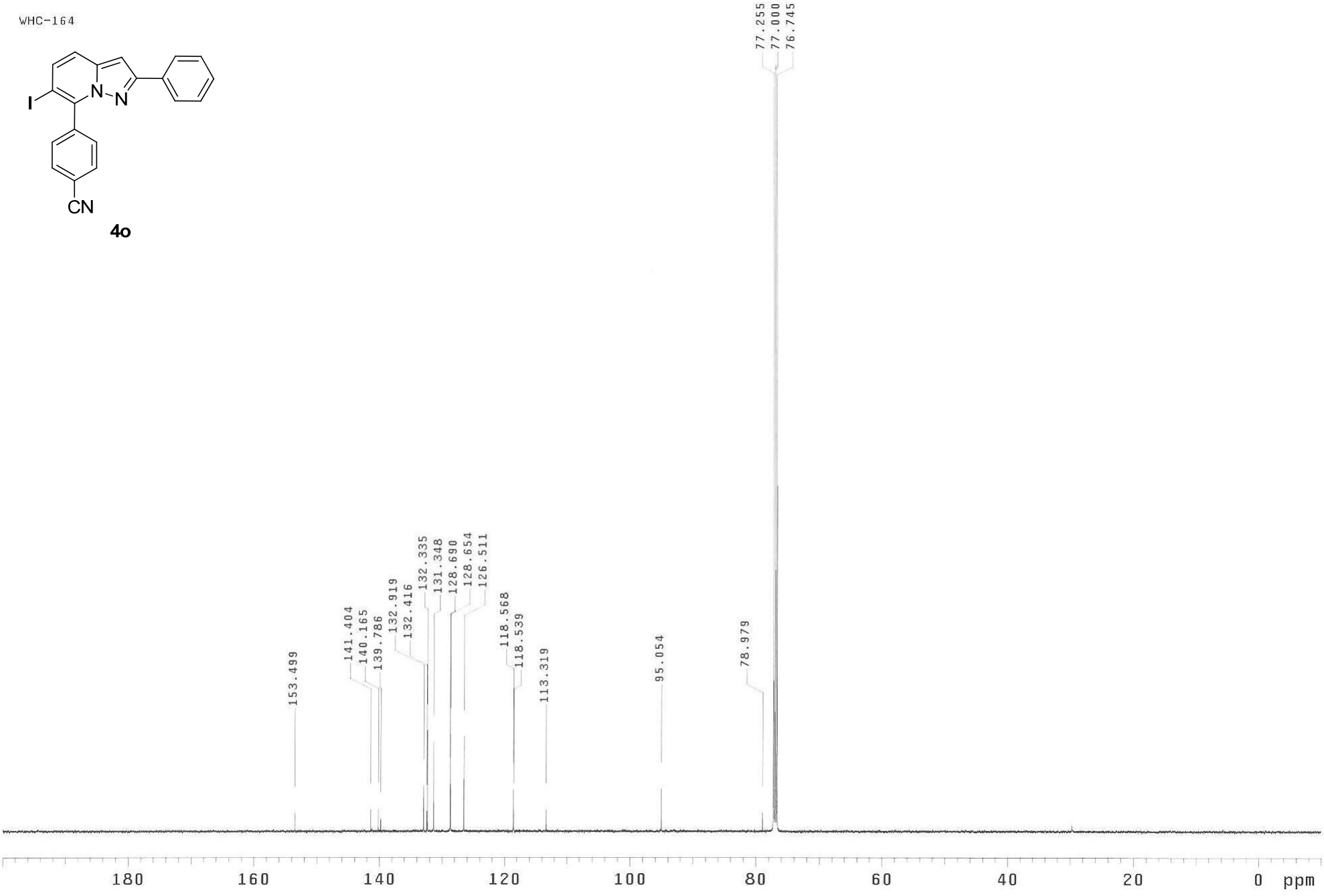

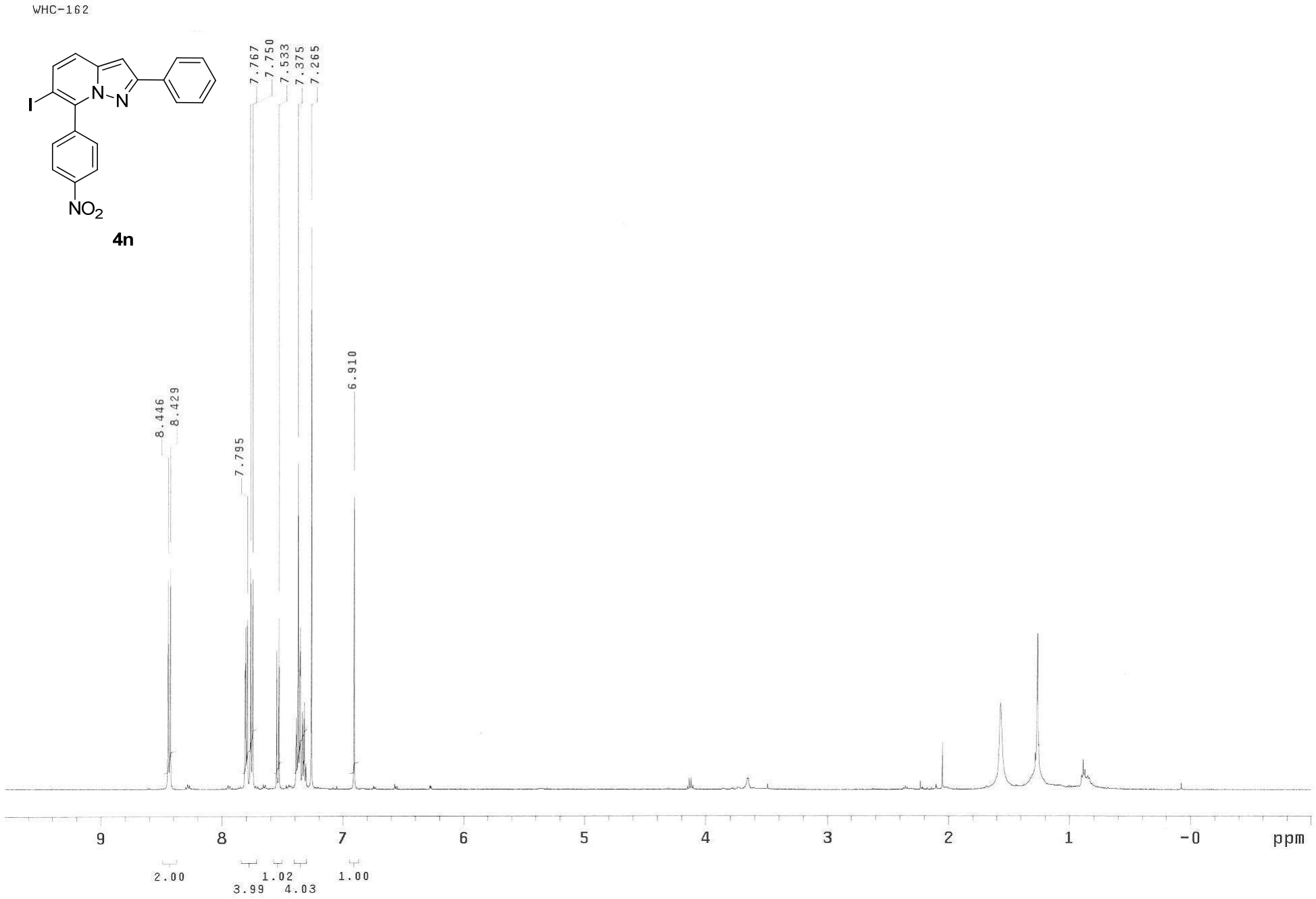

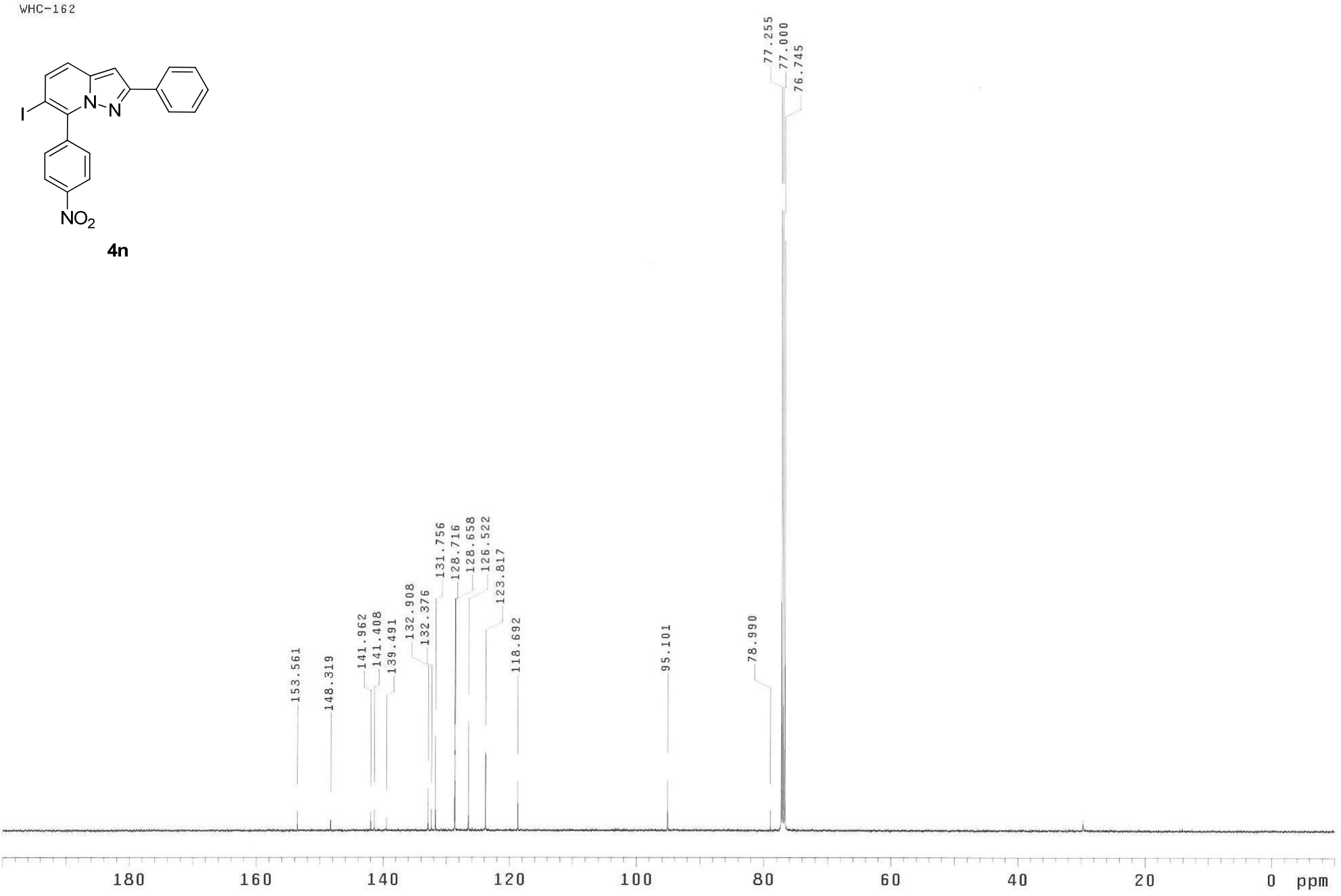

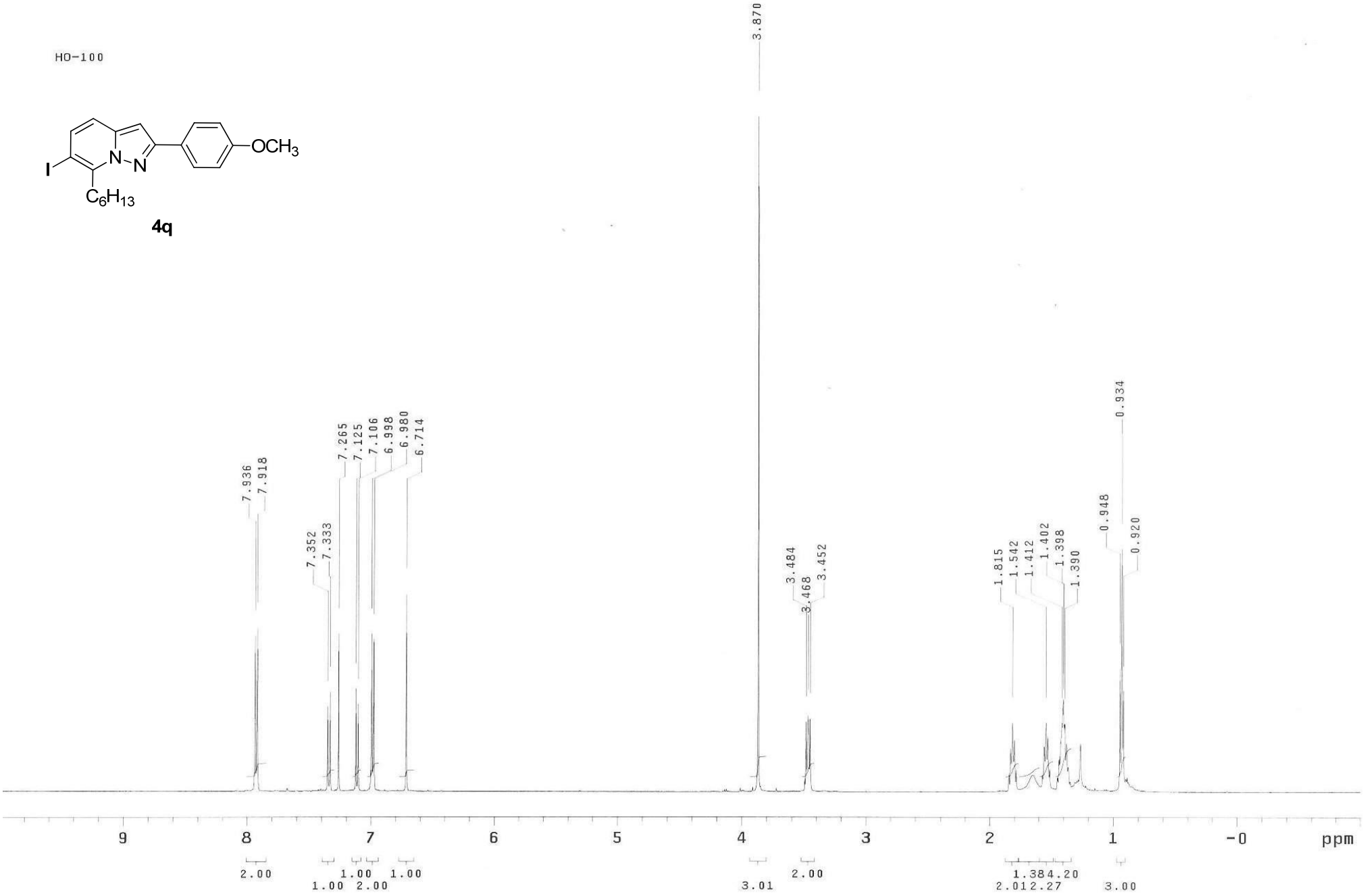

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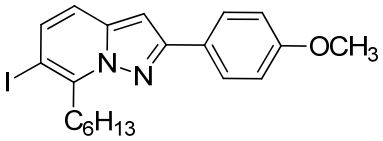

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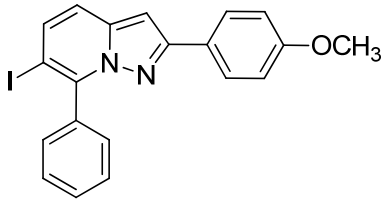

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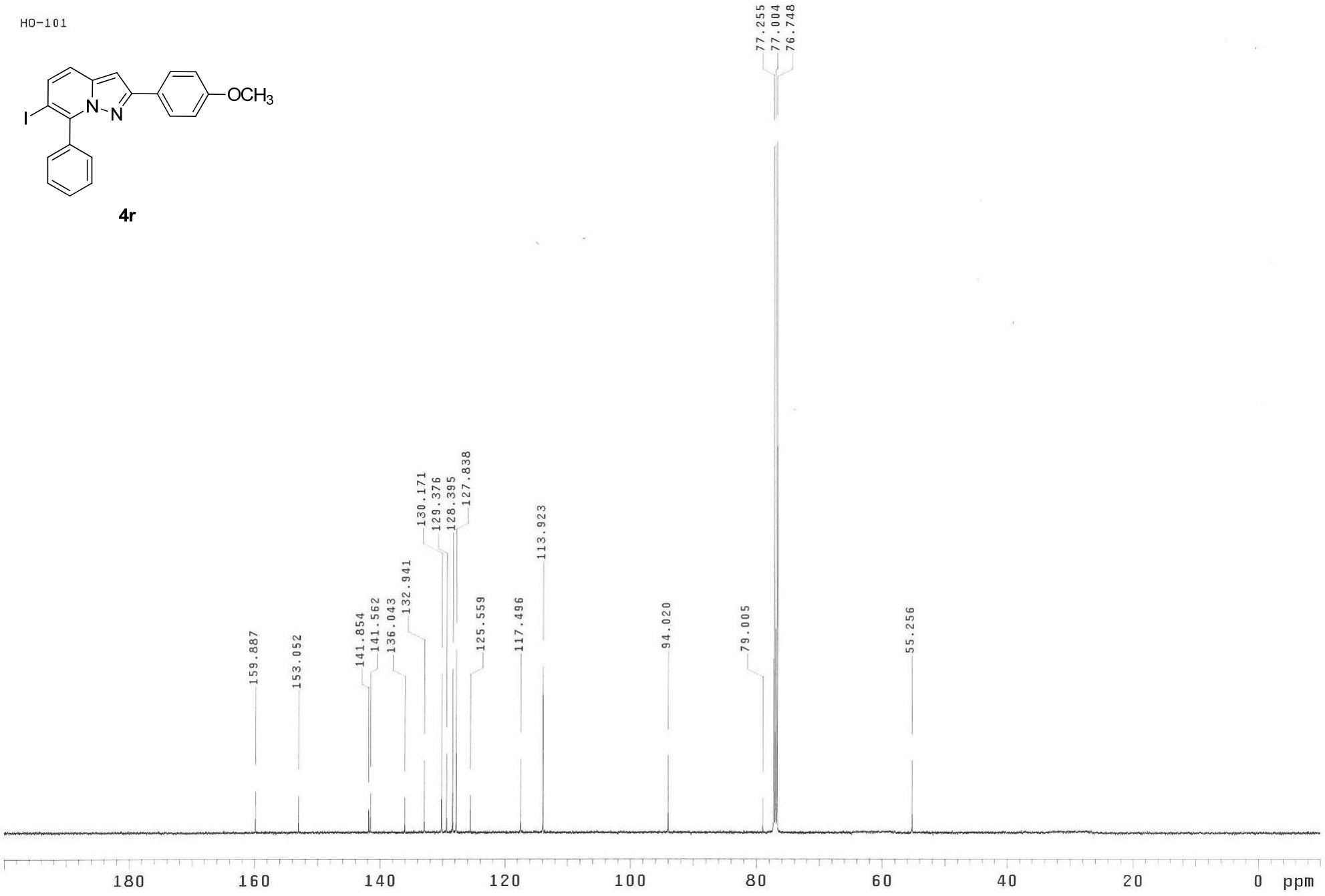

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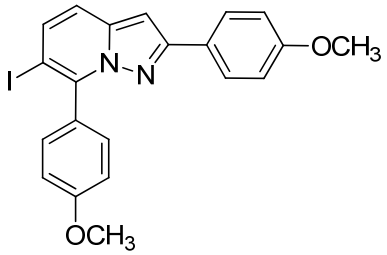

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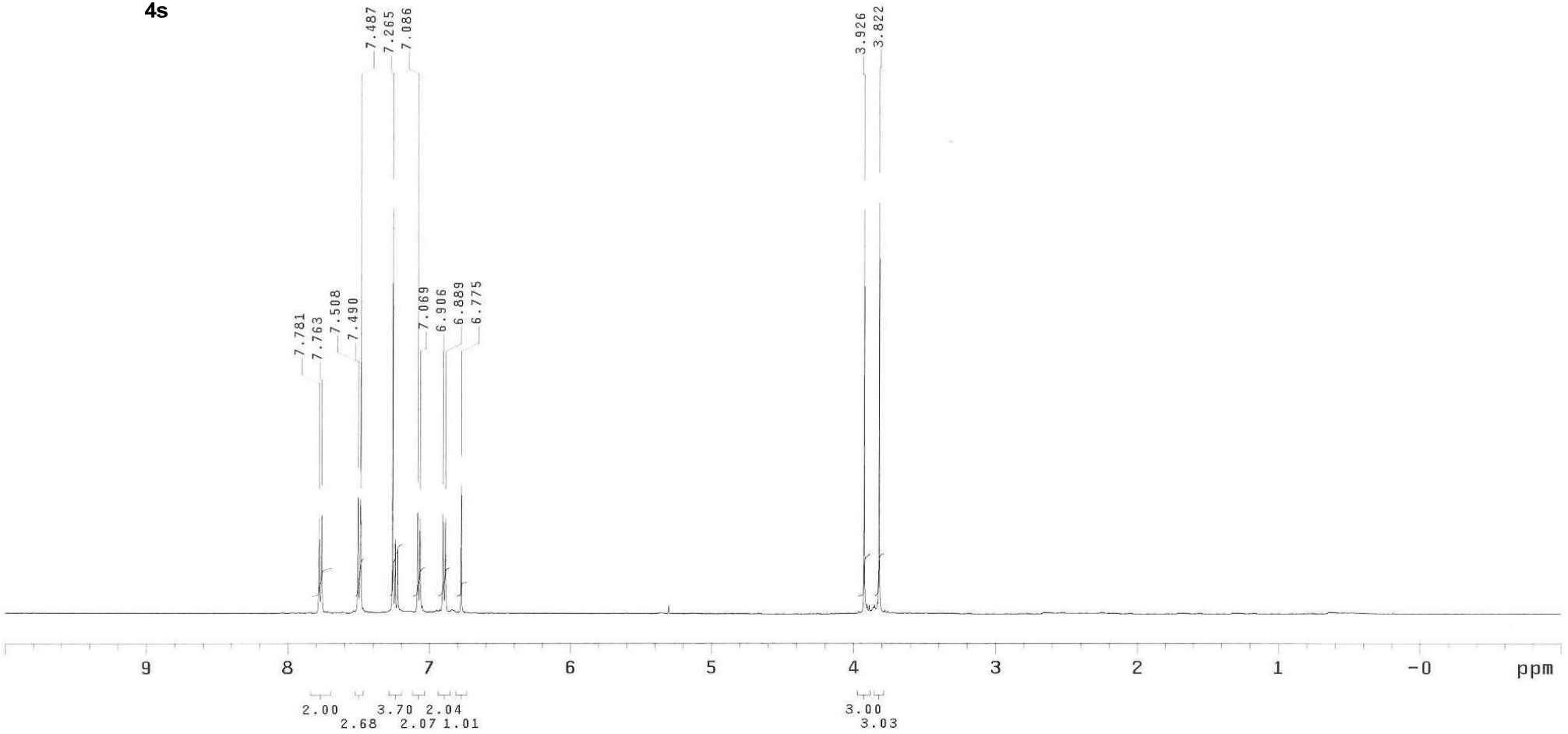
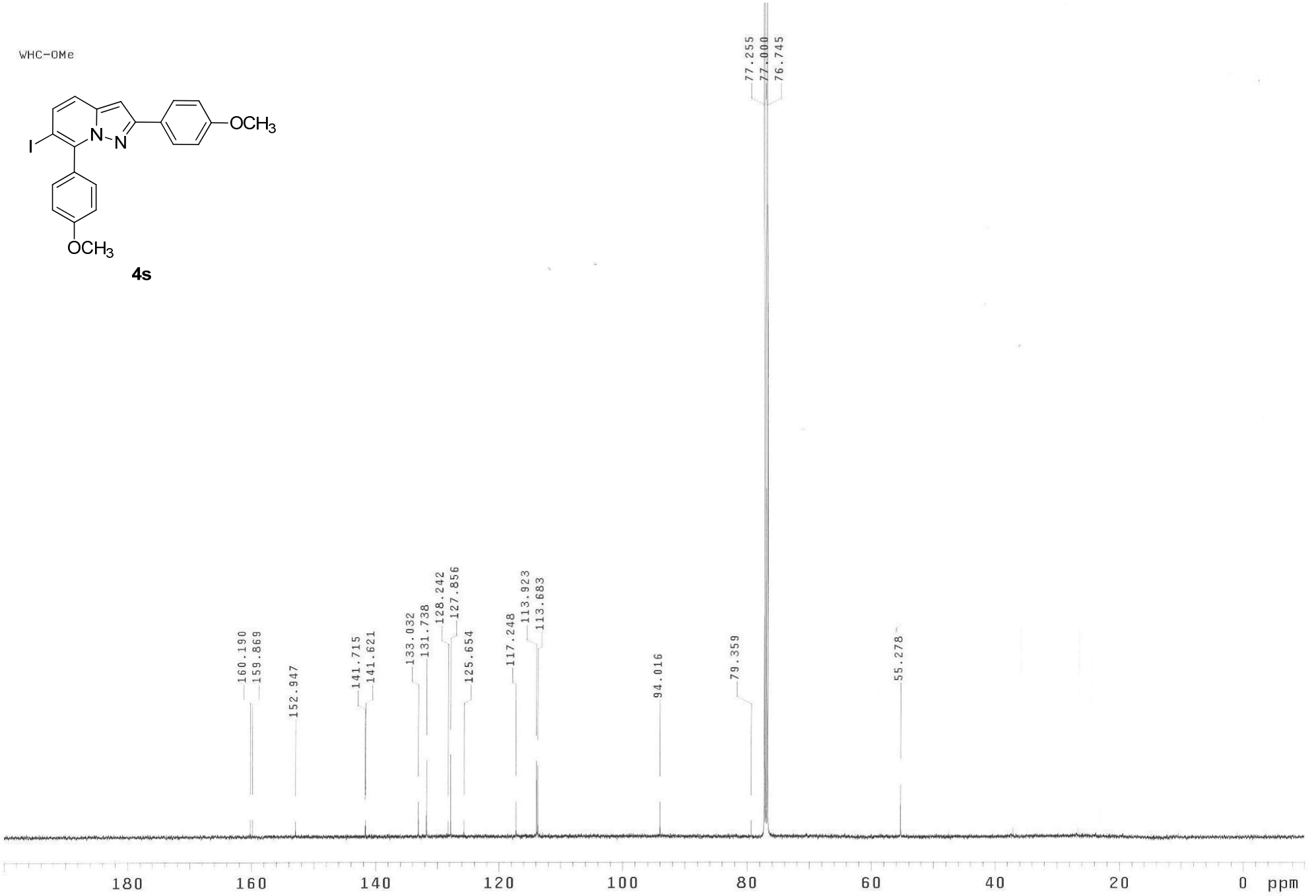
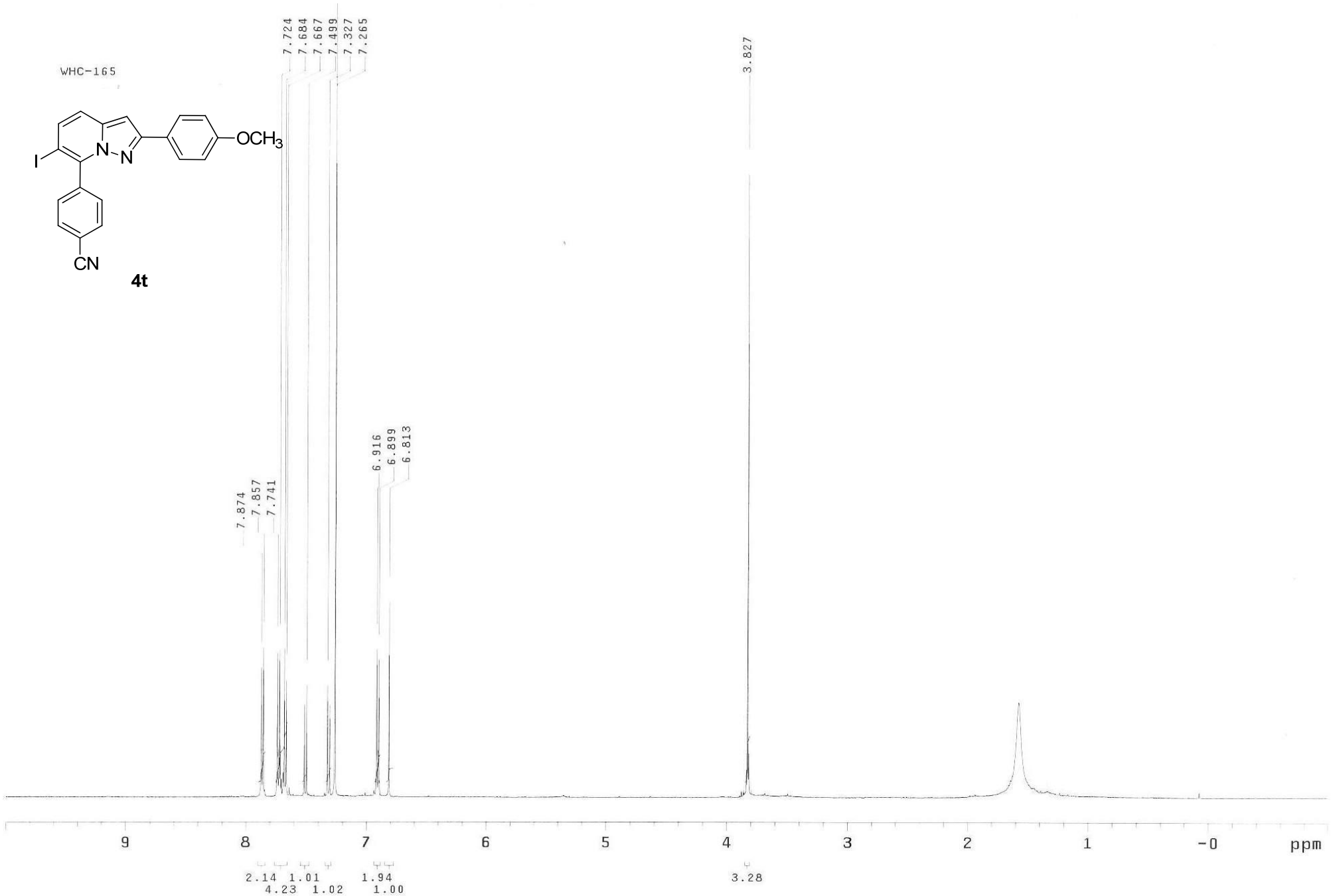
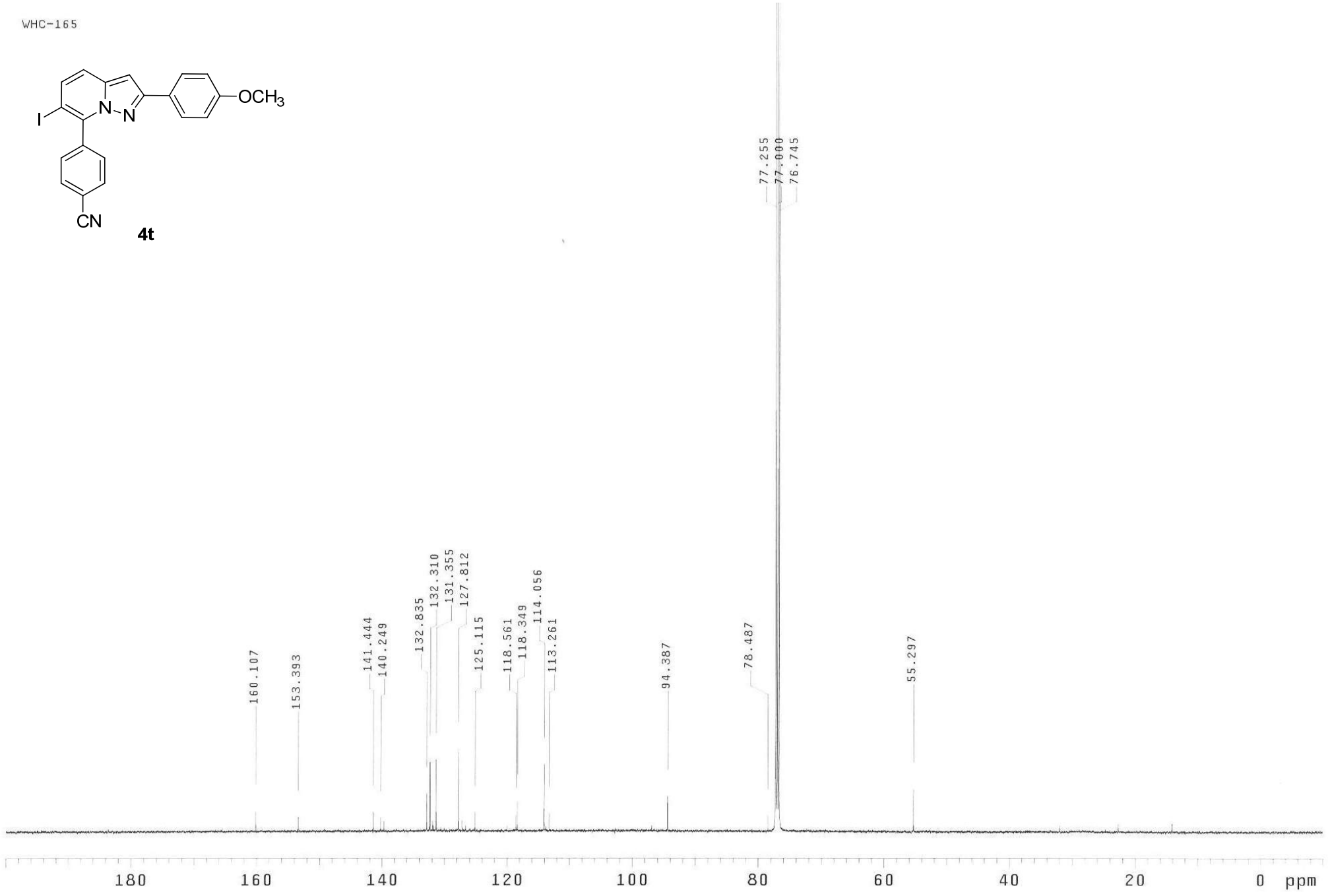
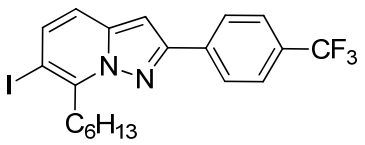








HO-19-I2



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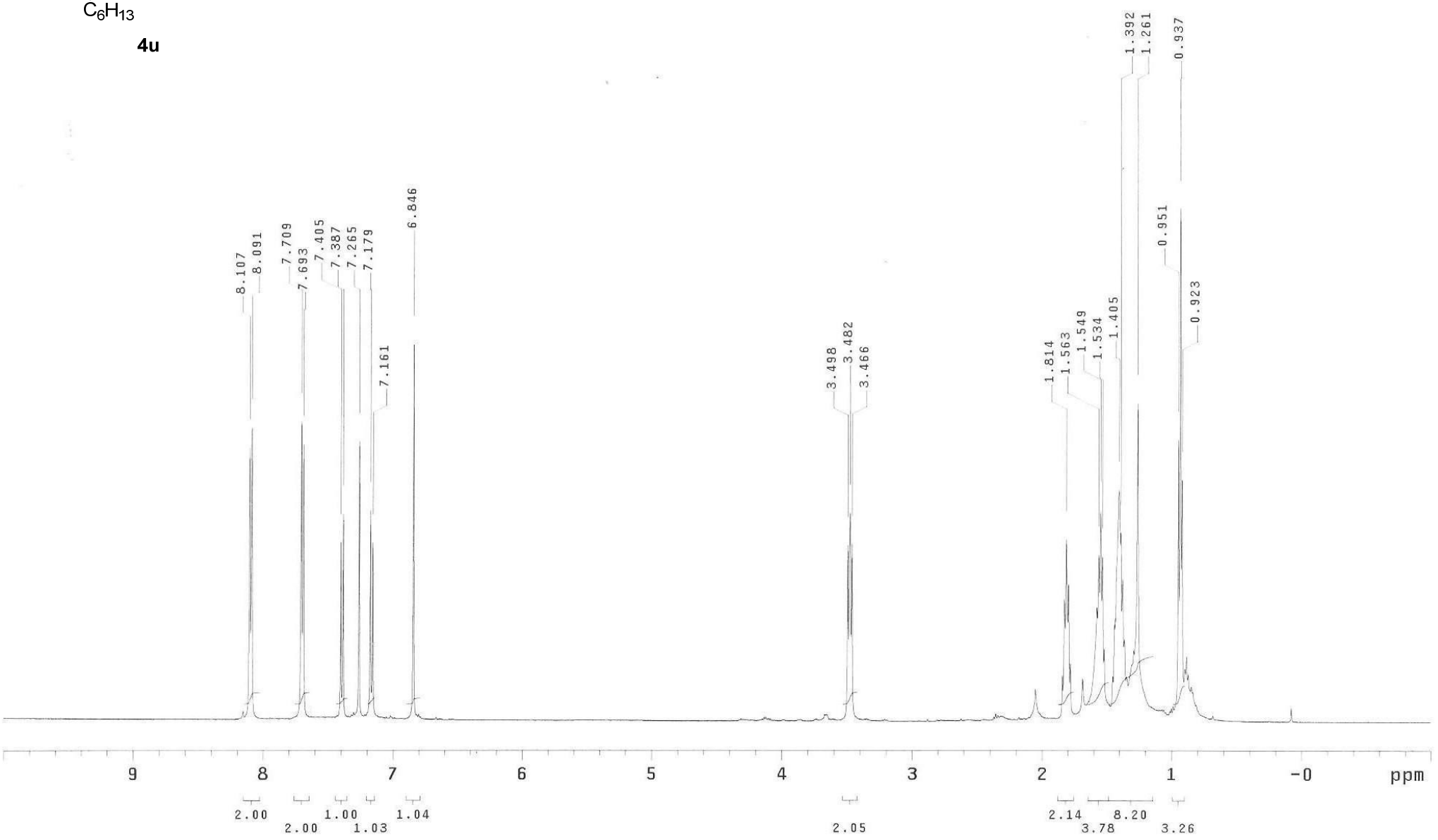

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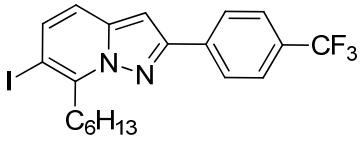
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4u

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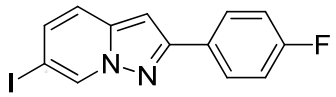

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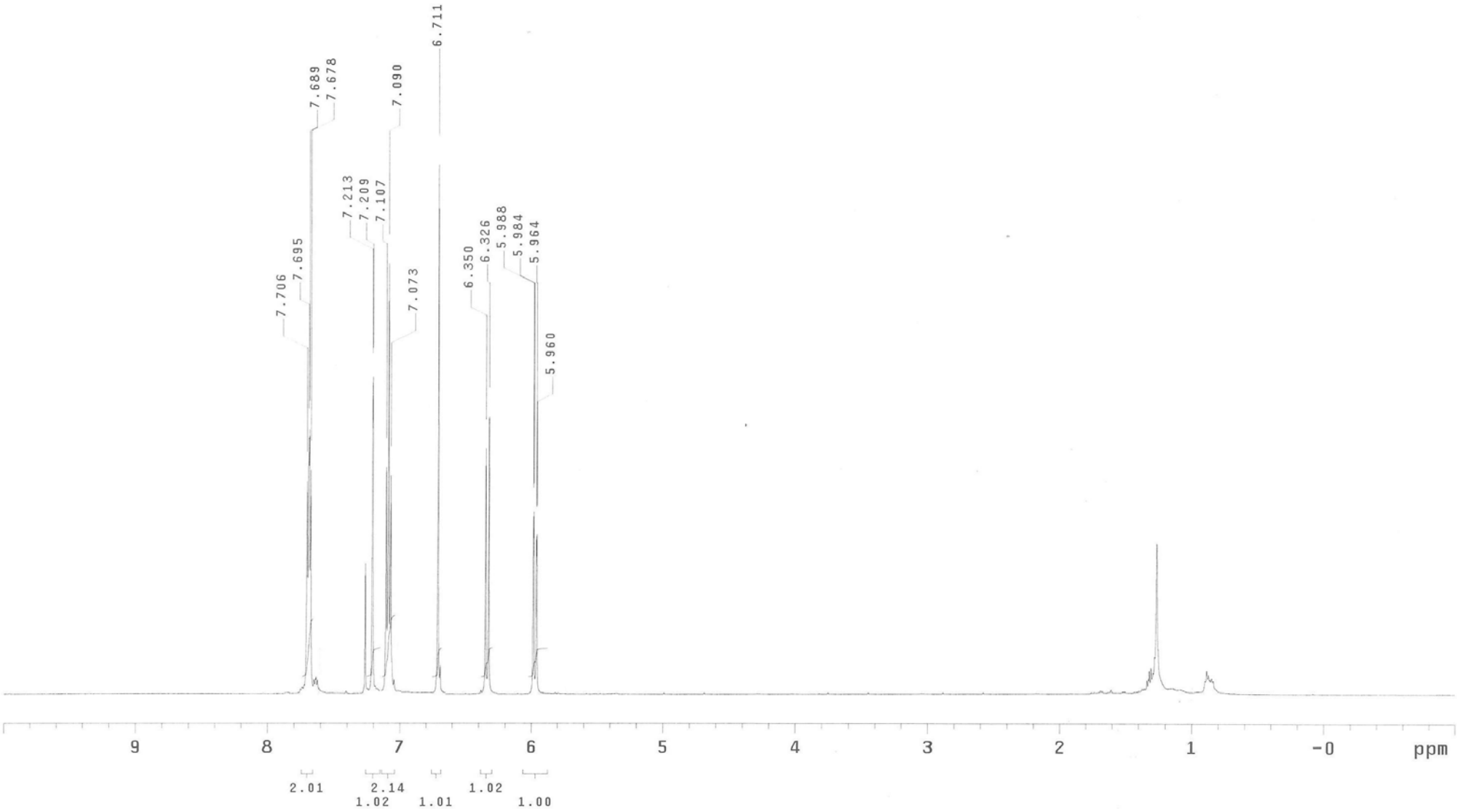

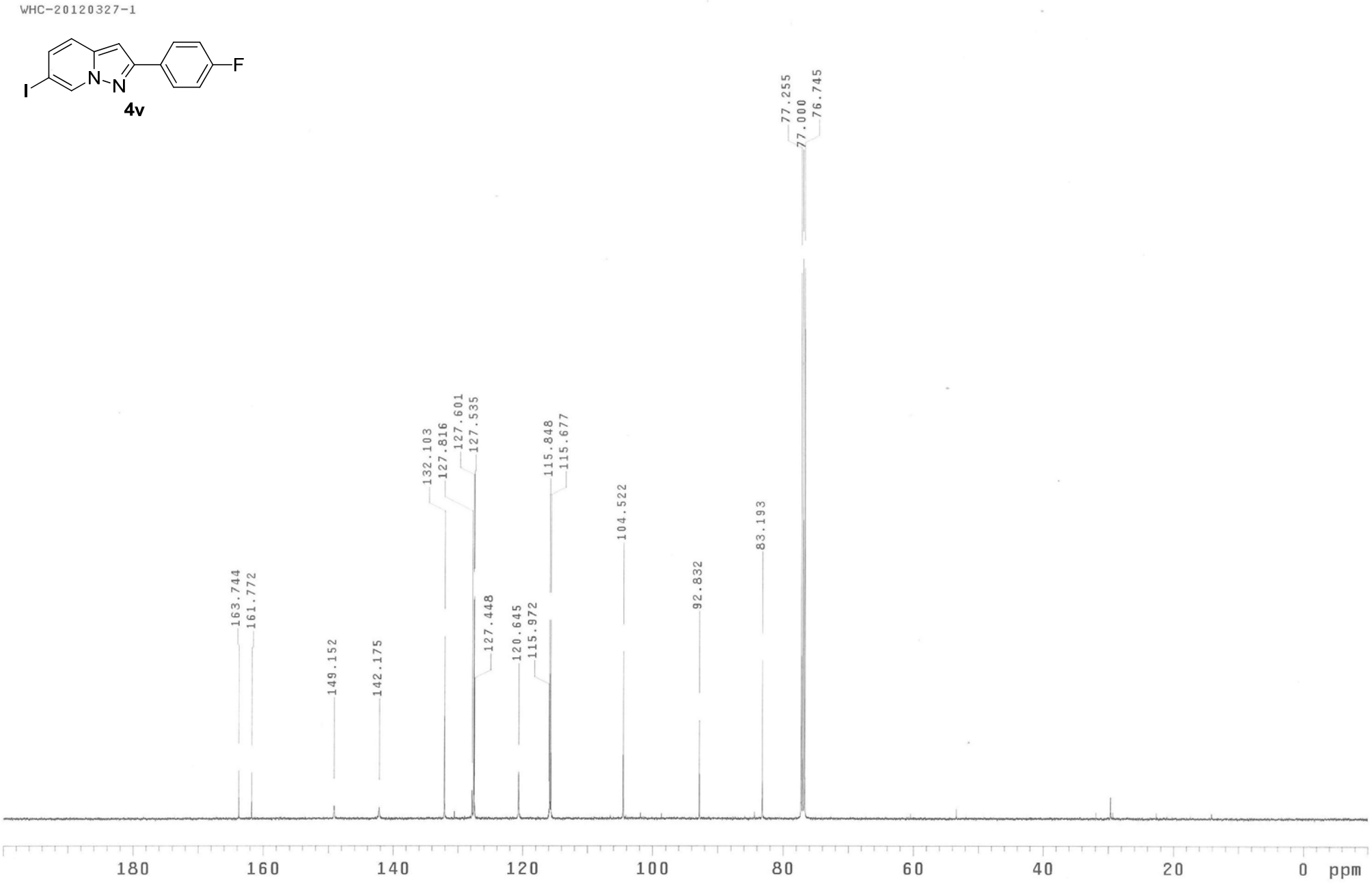

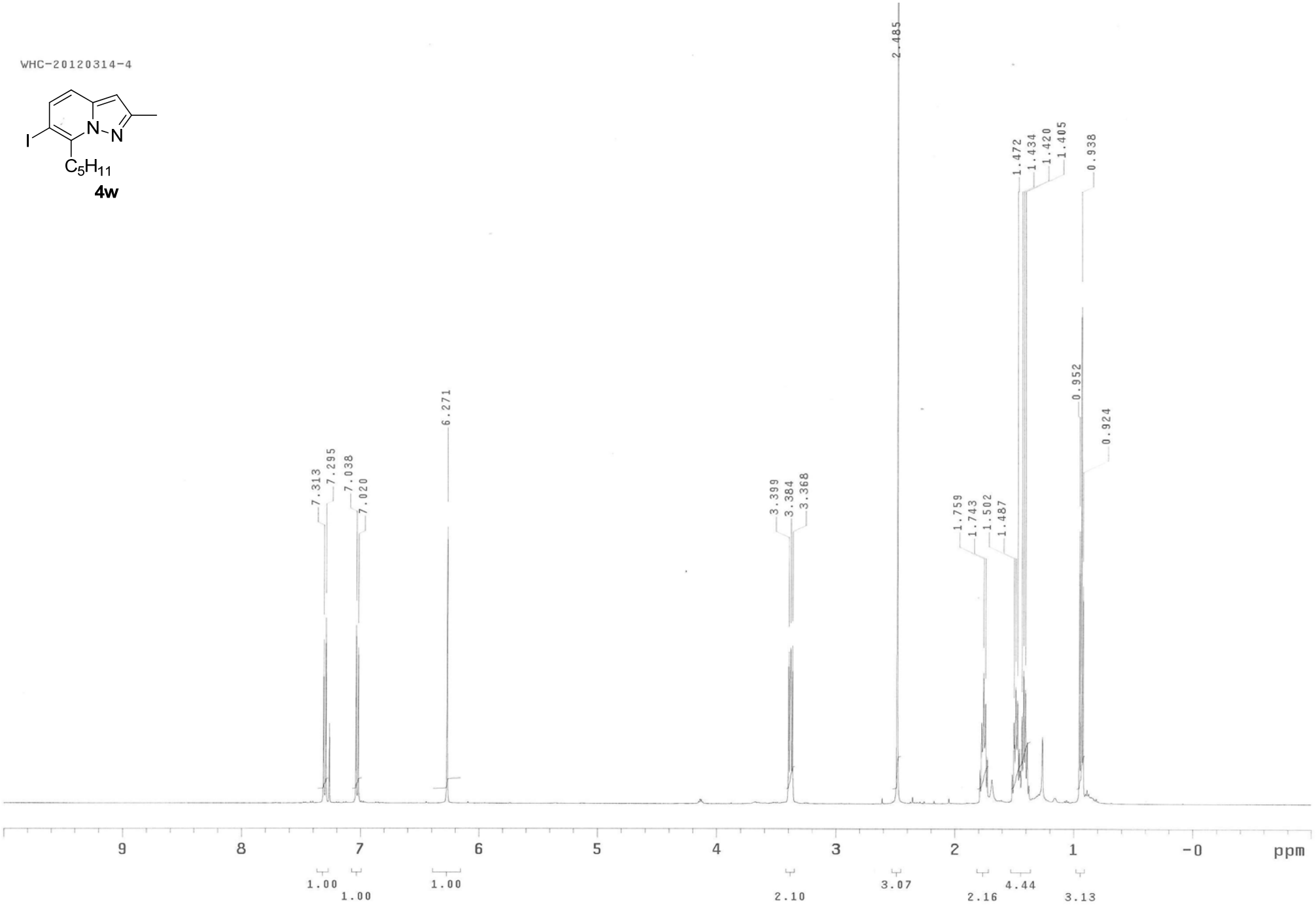

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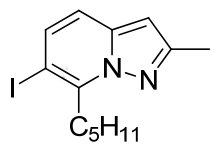

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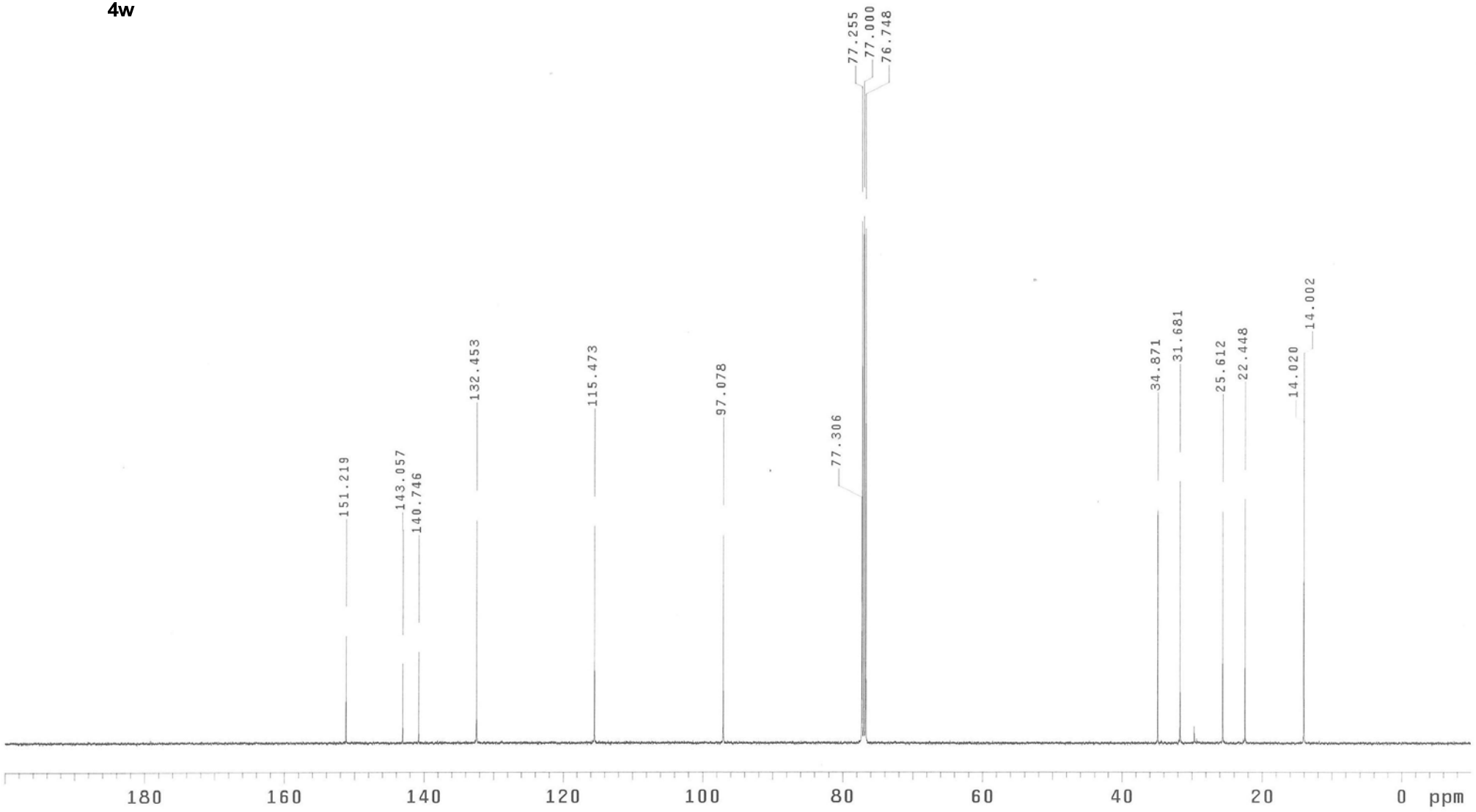

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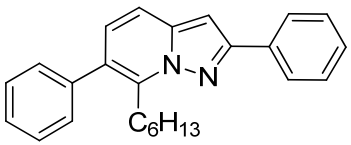

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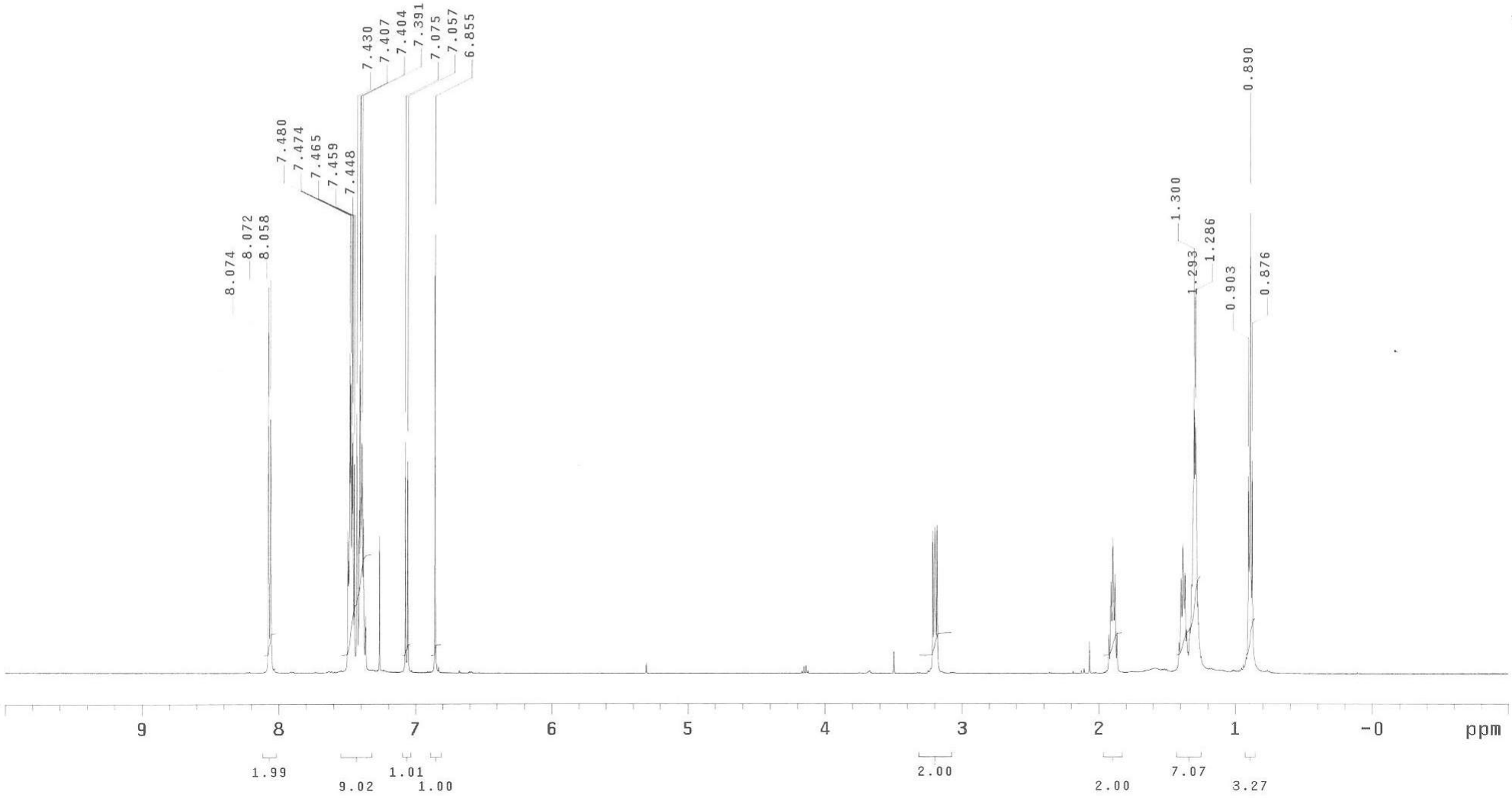

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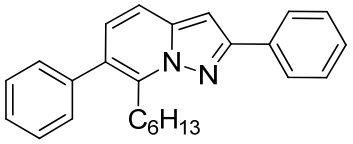

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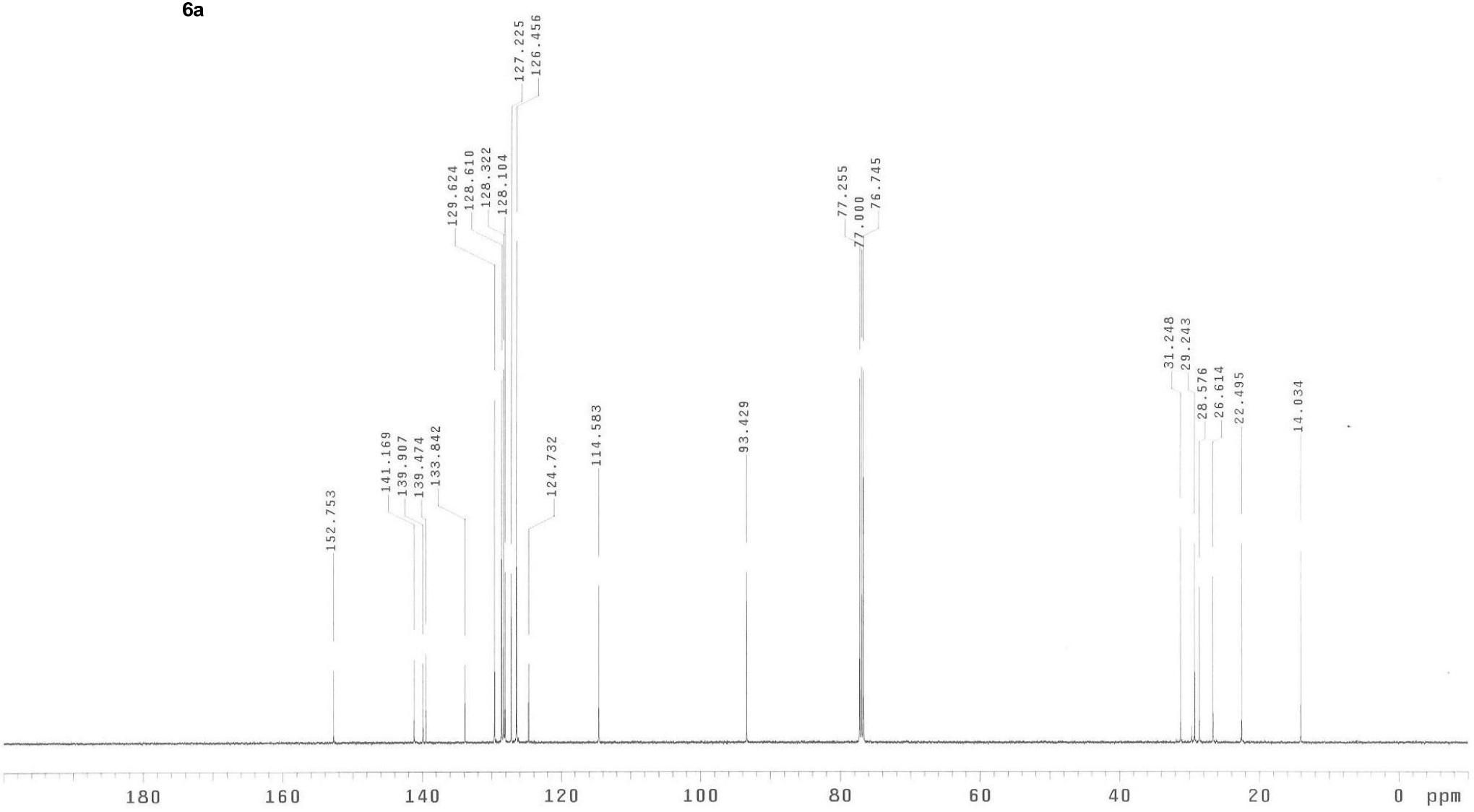

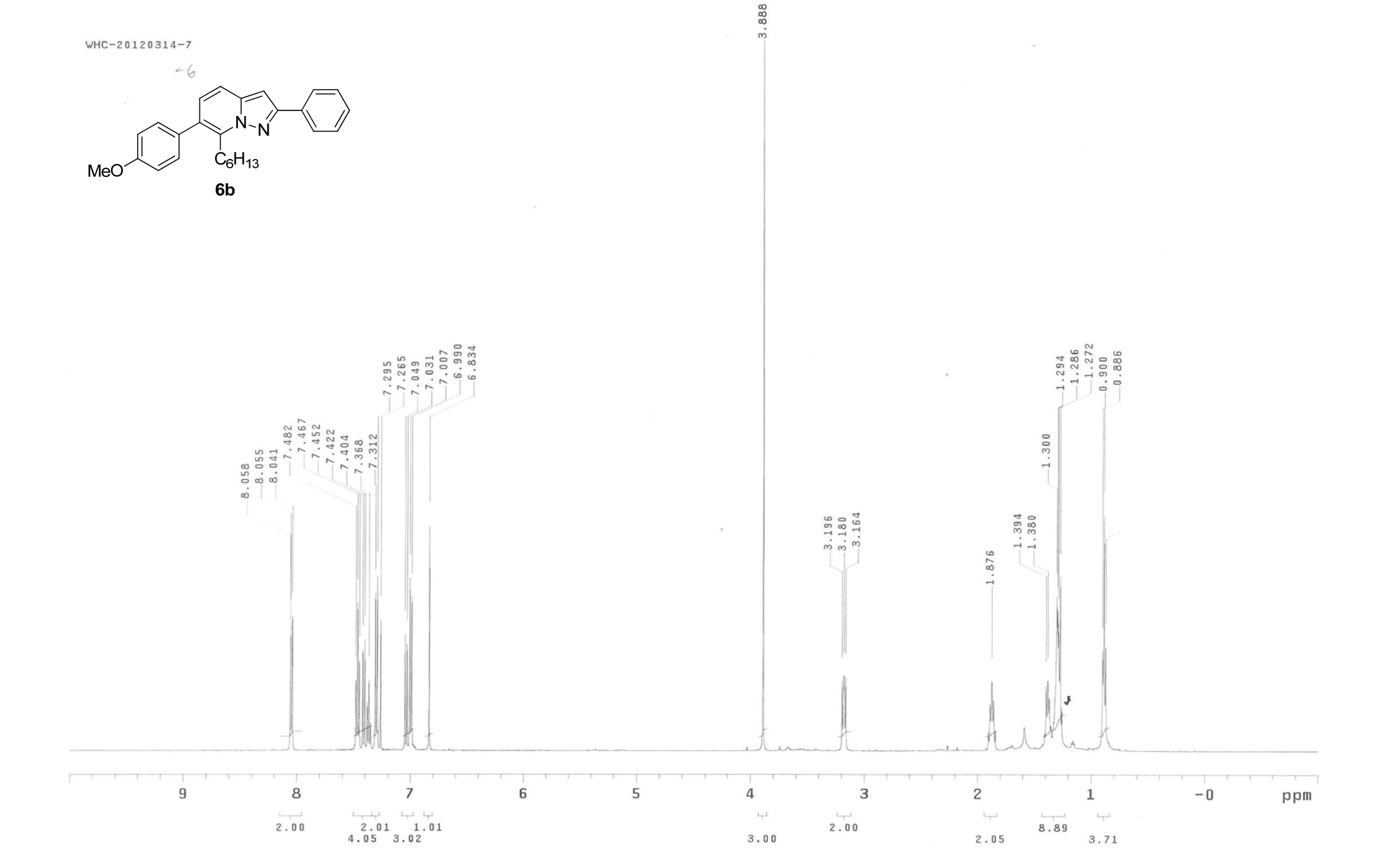

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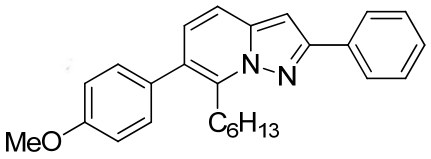

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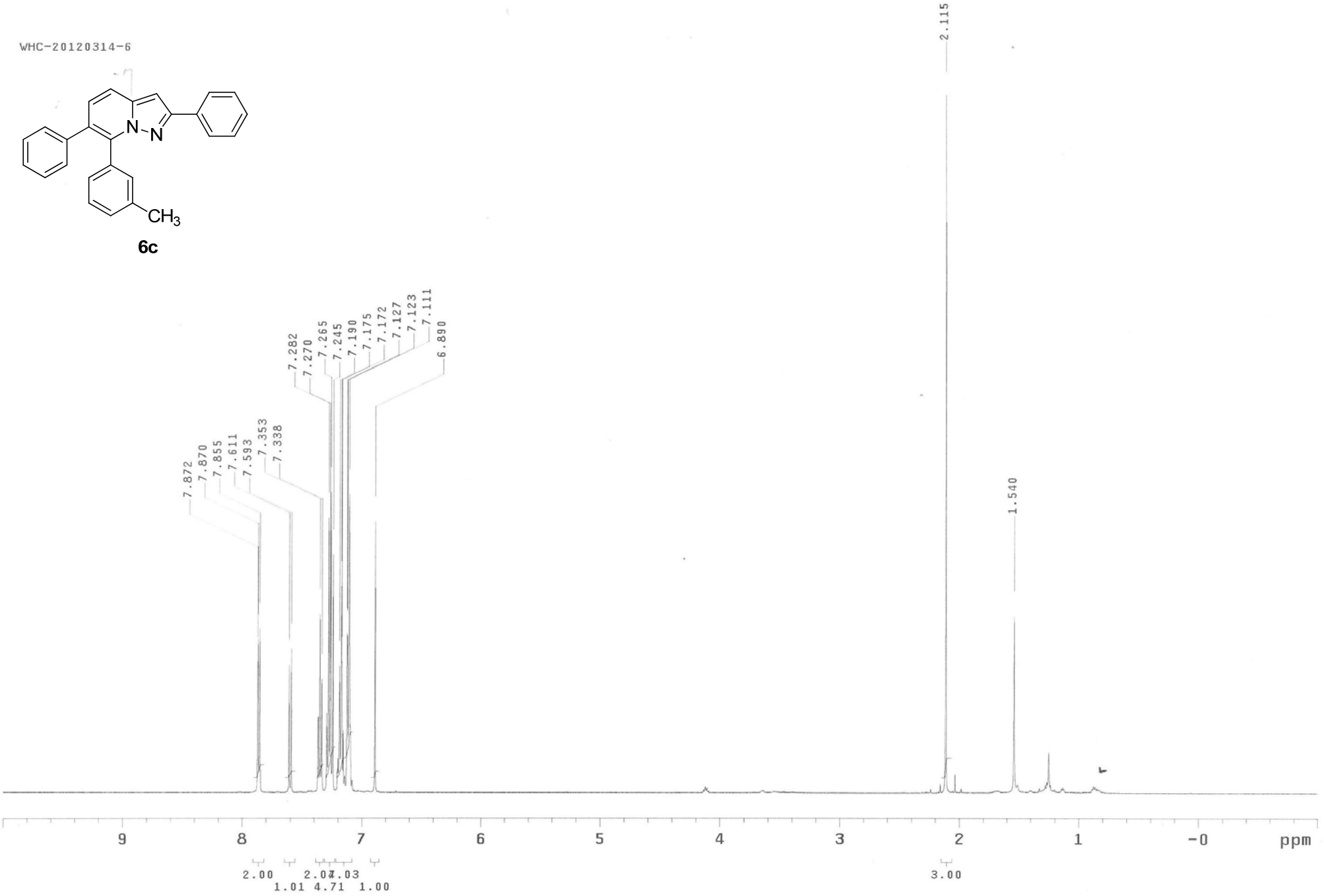

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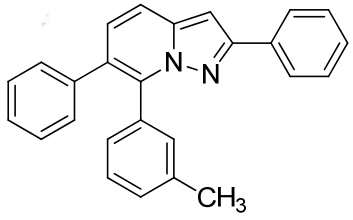

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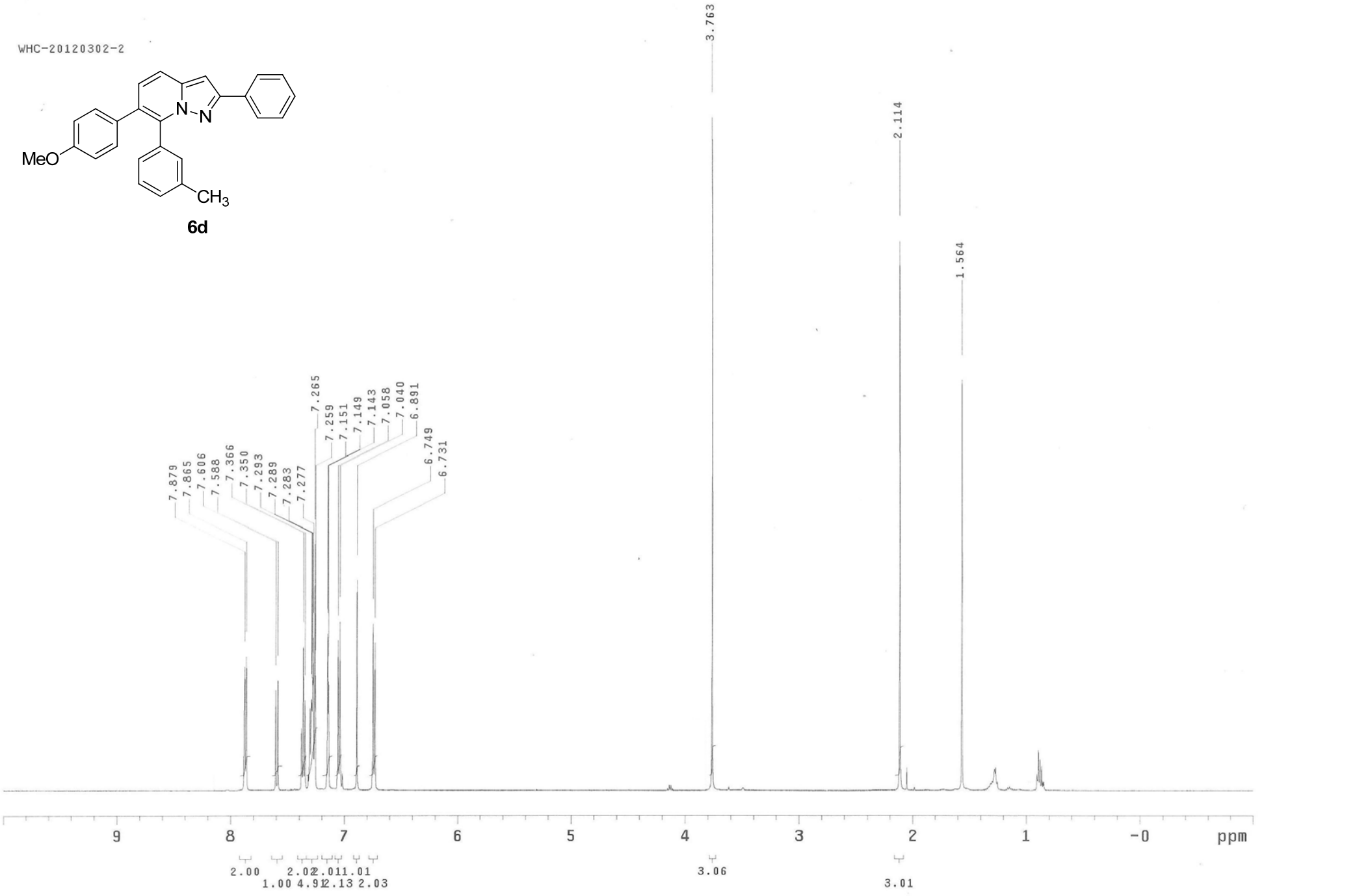
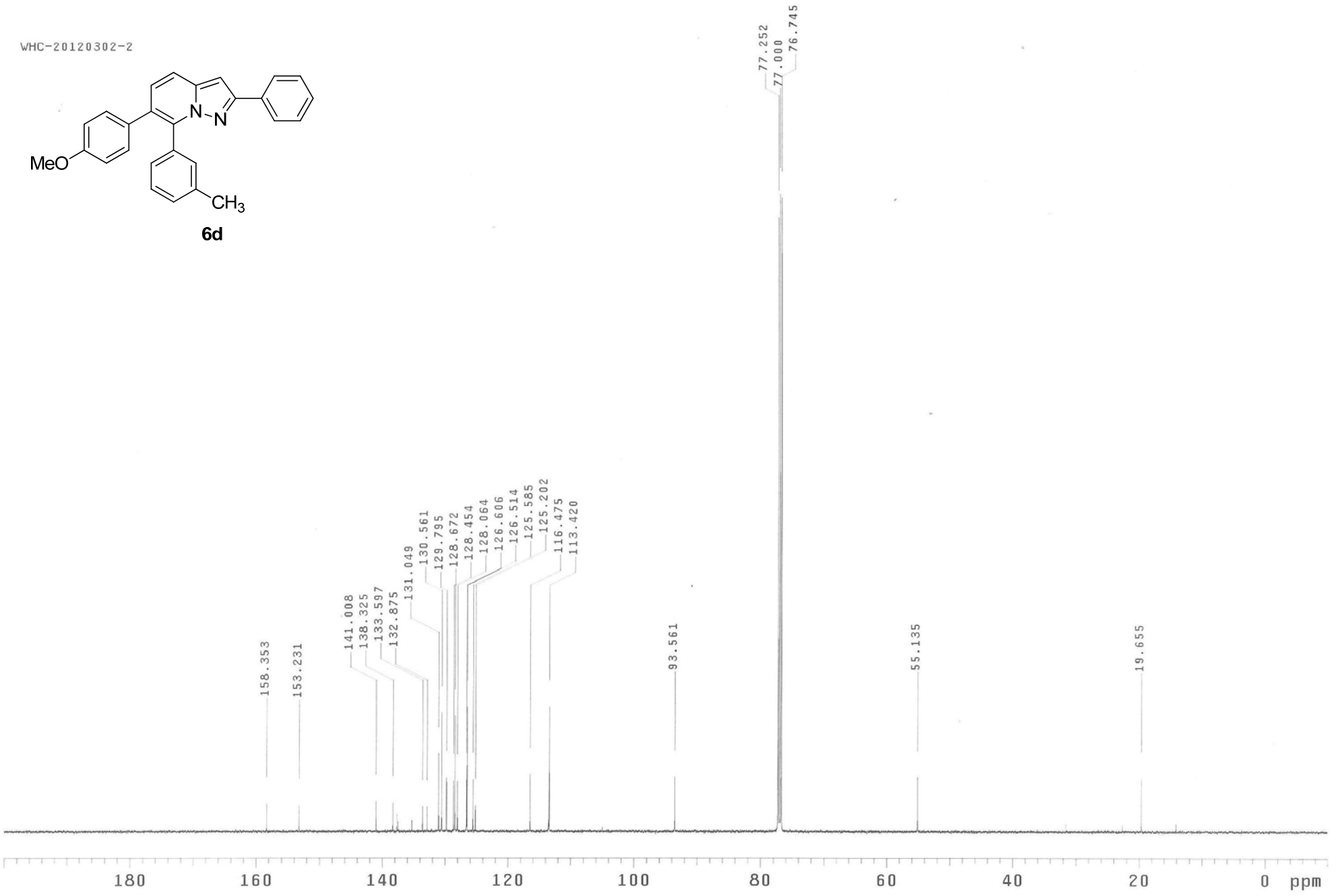
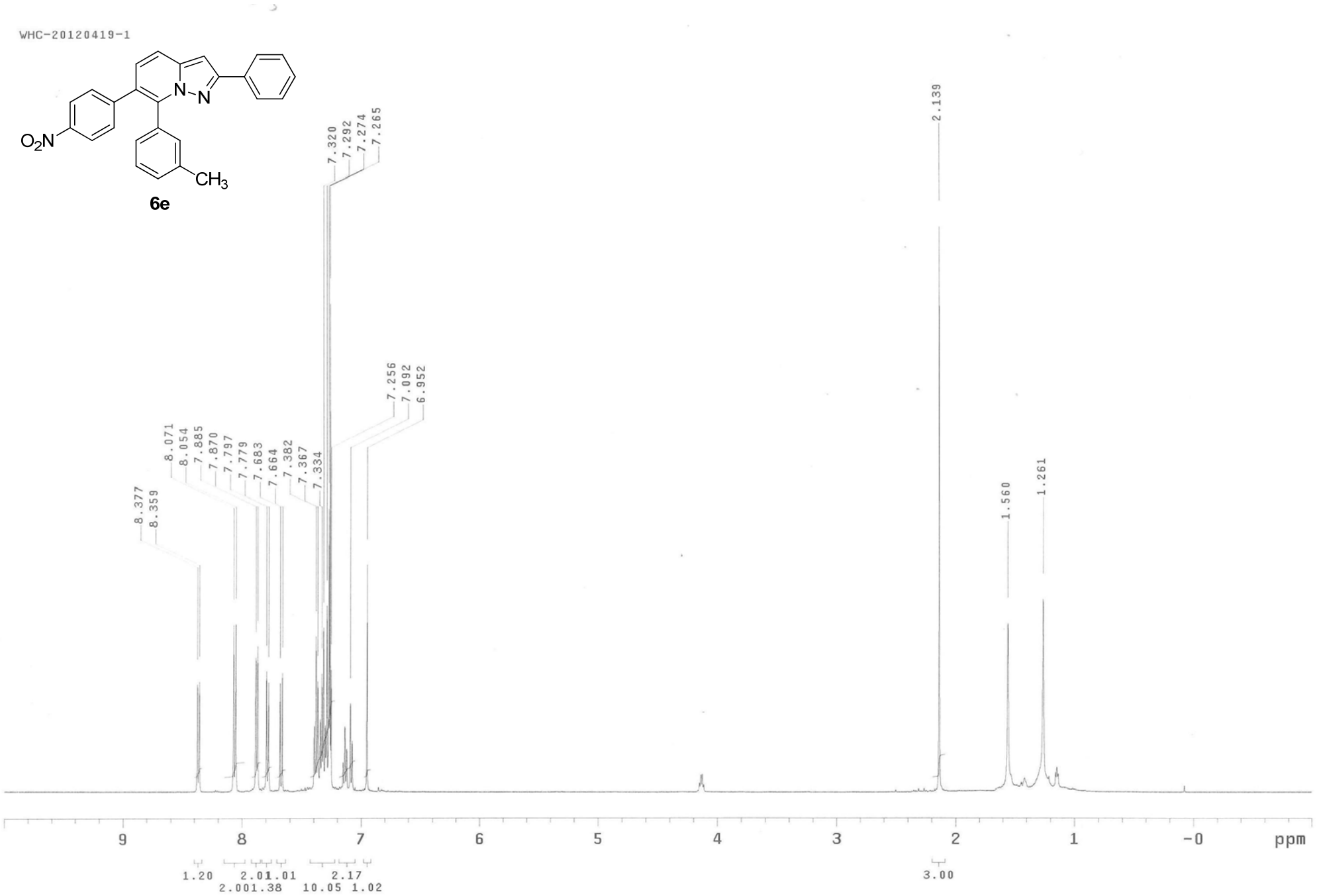
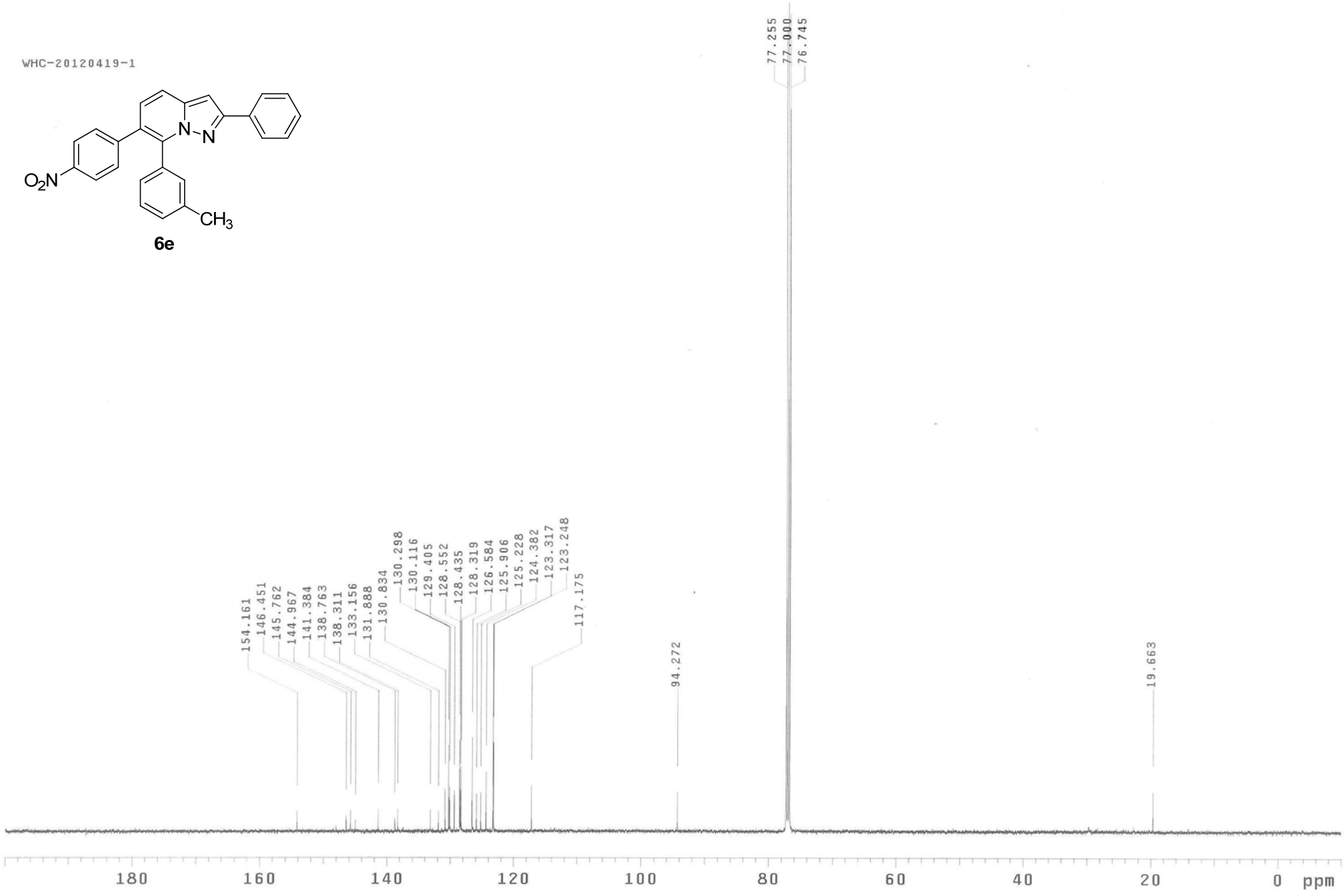
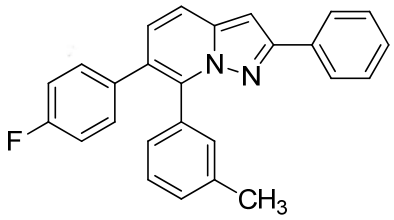








WHC-20120419-2



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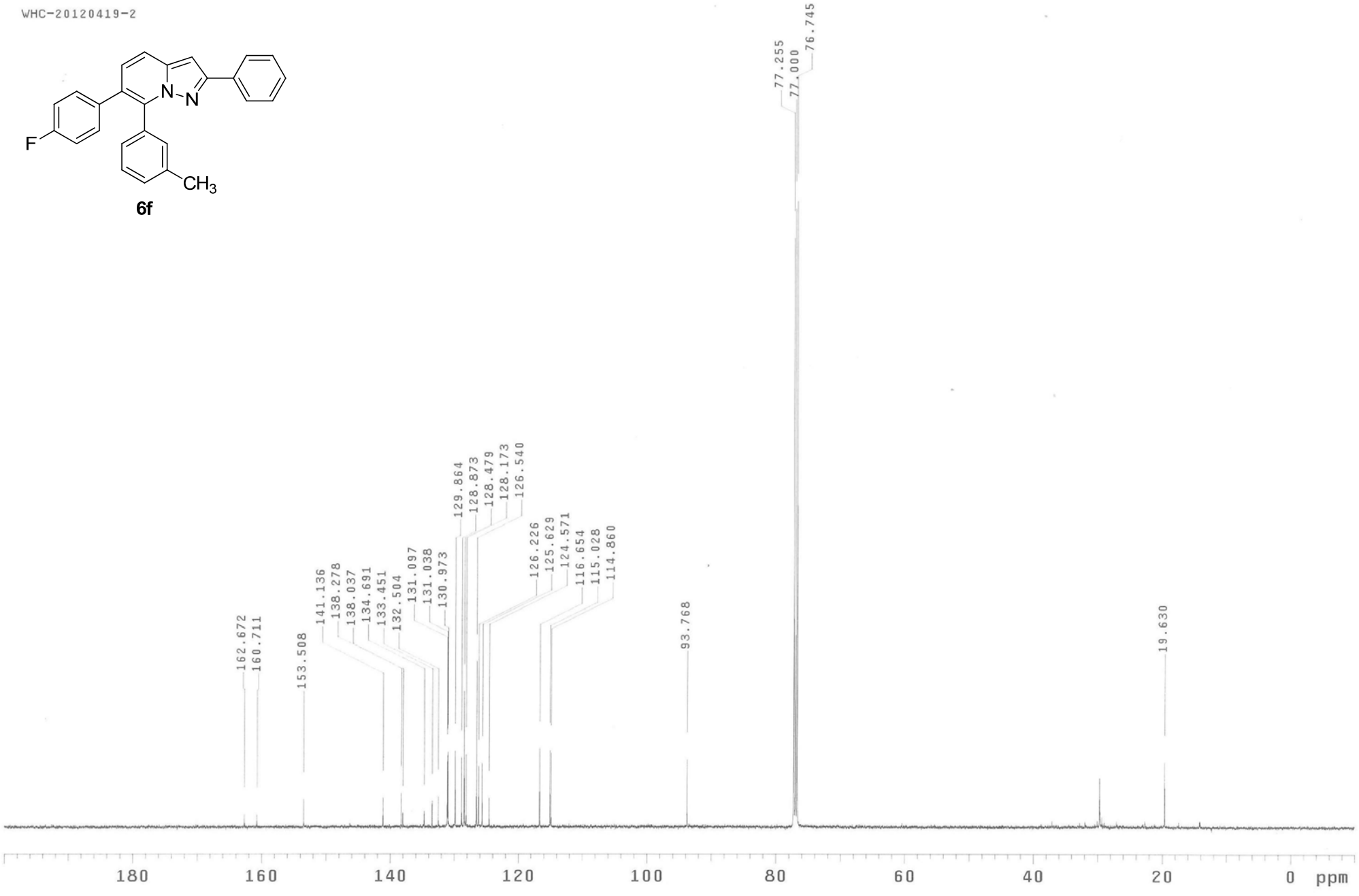

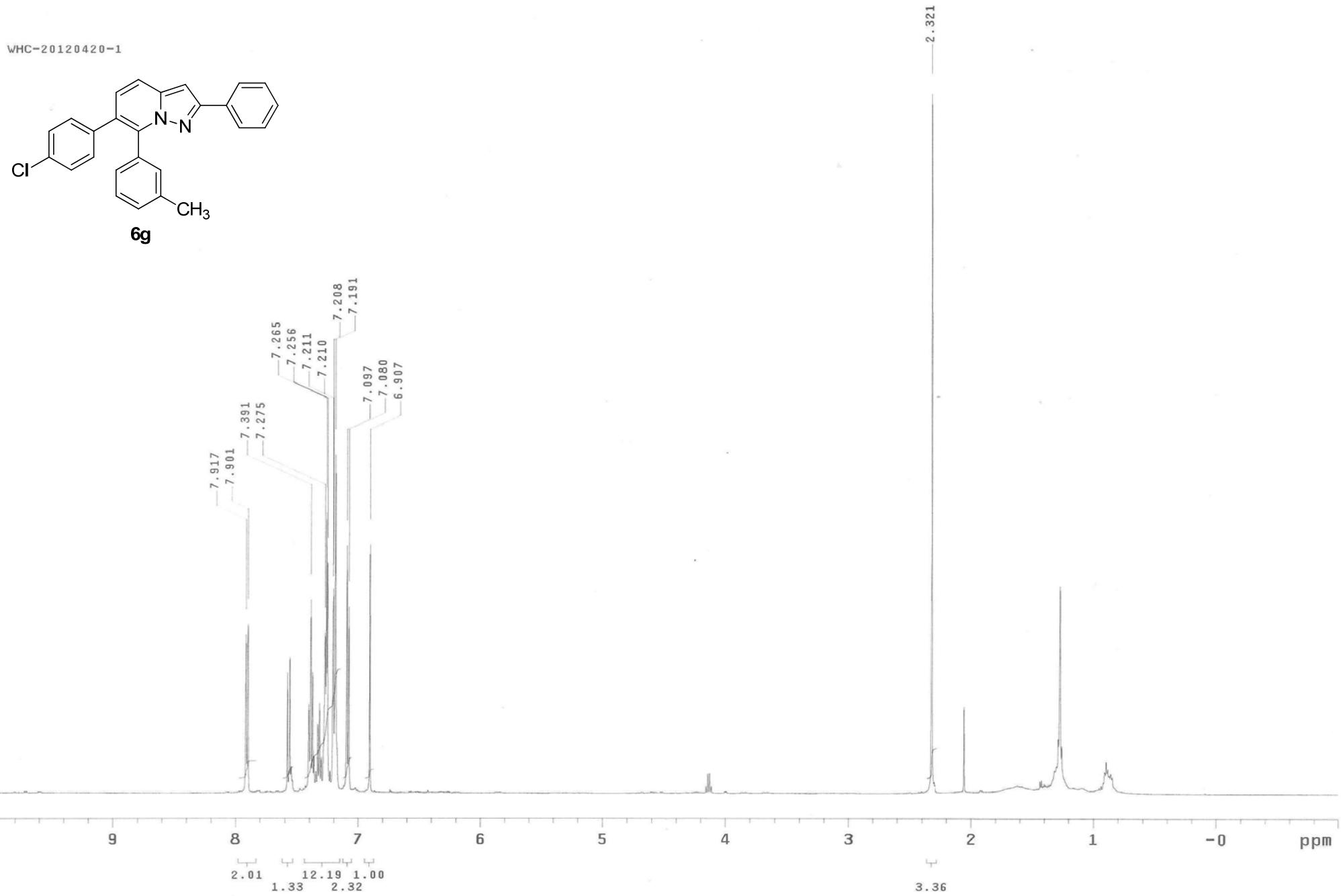

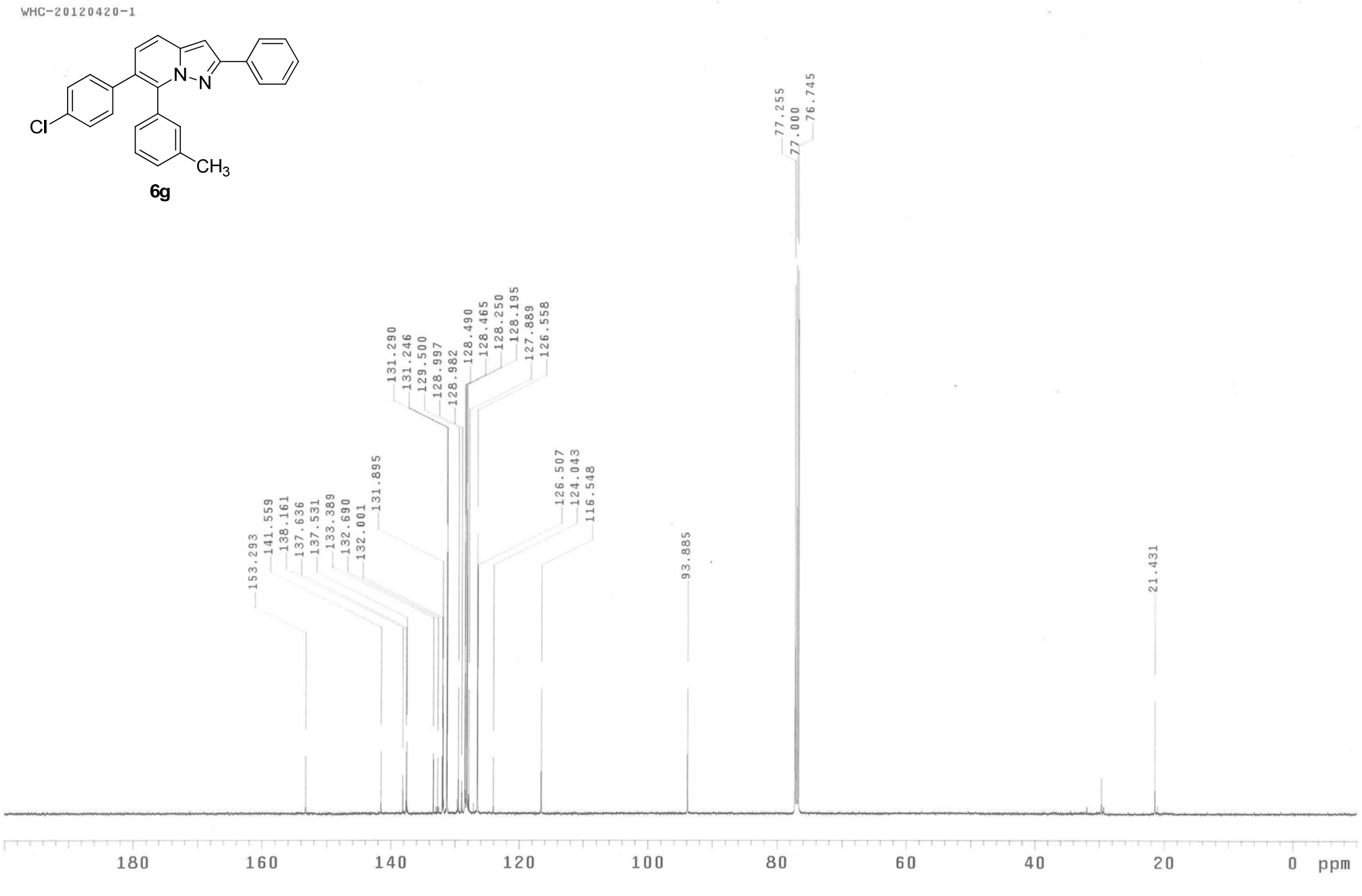

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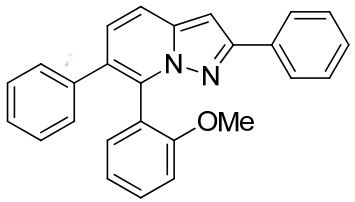

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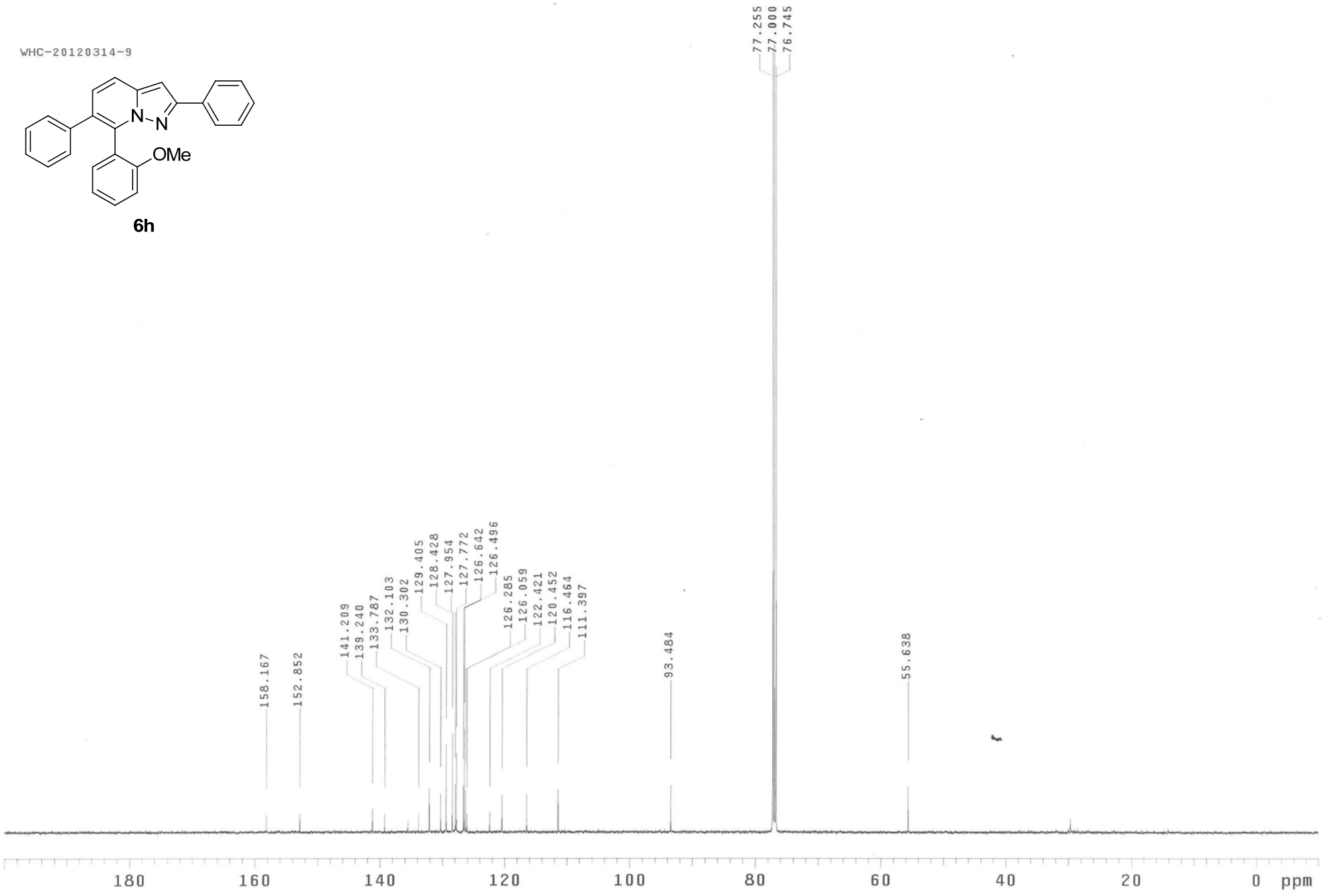

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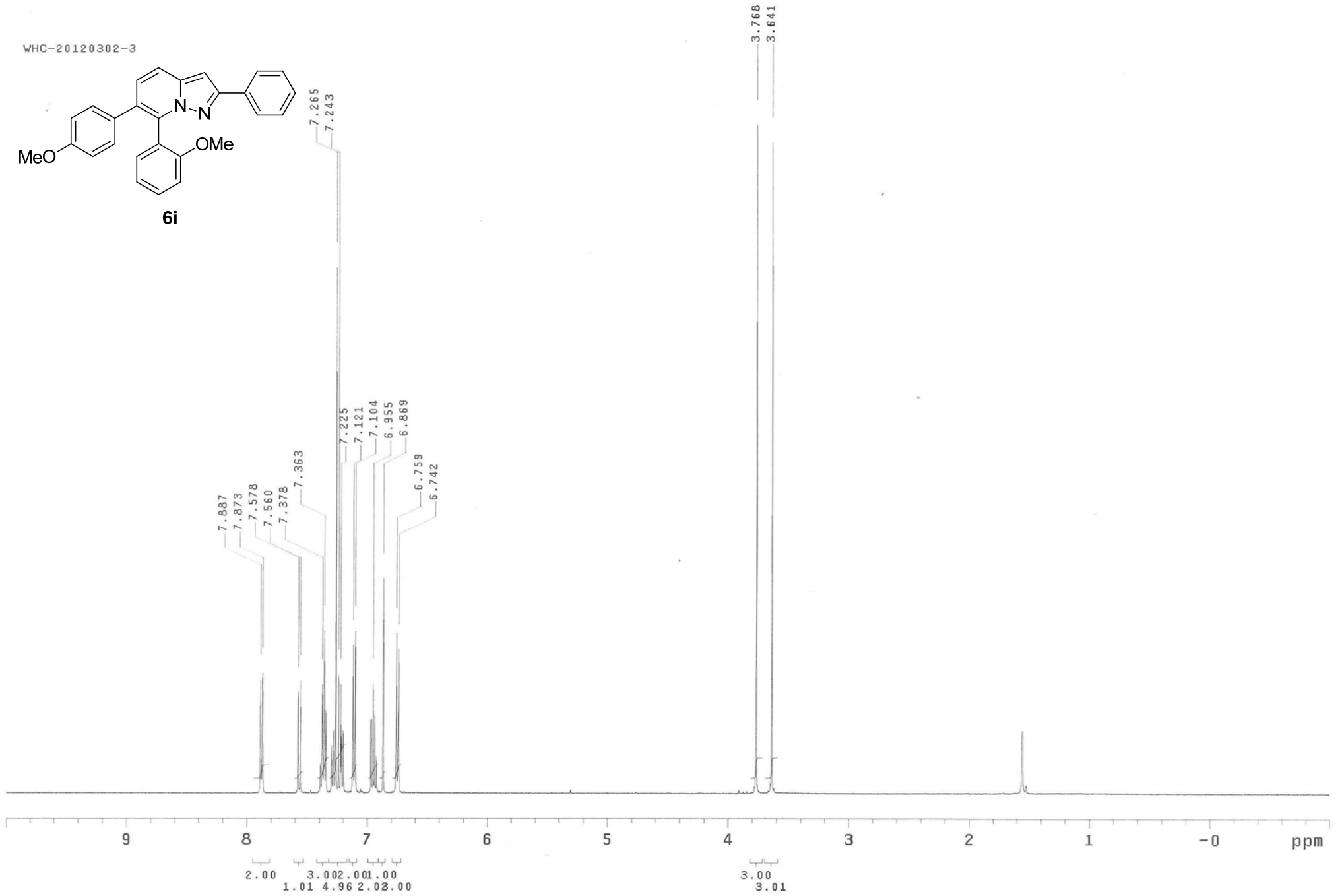
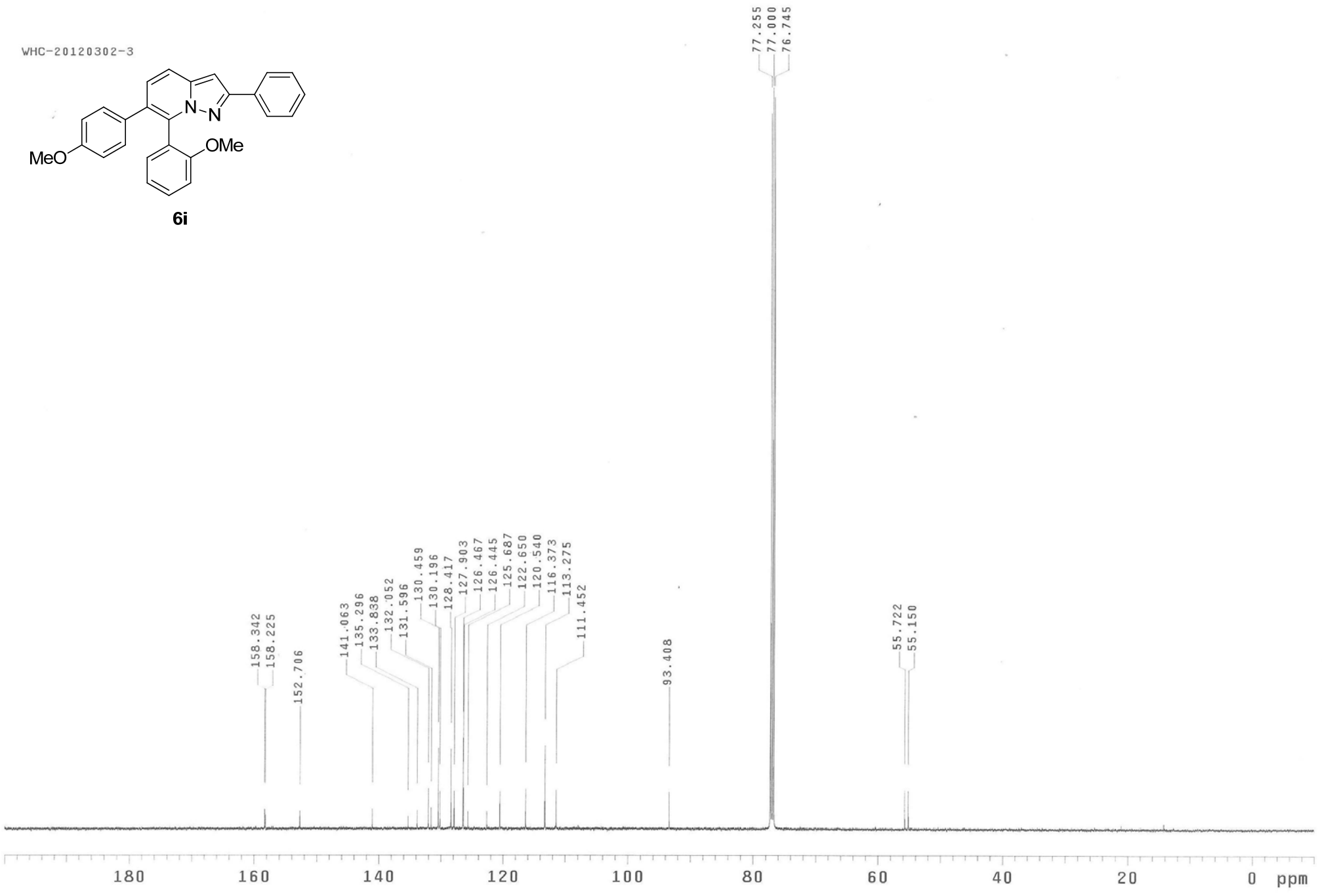
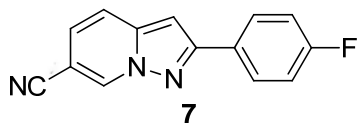




WHC-20120327-2



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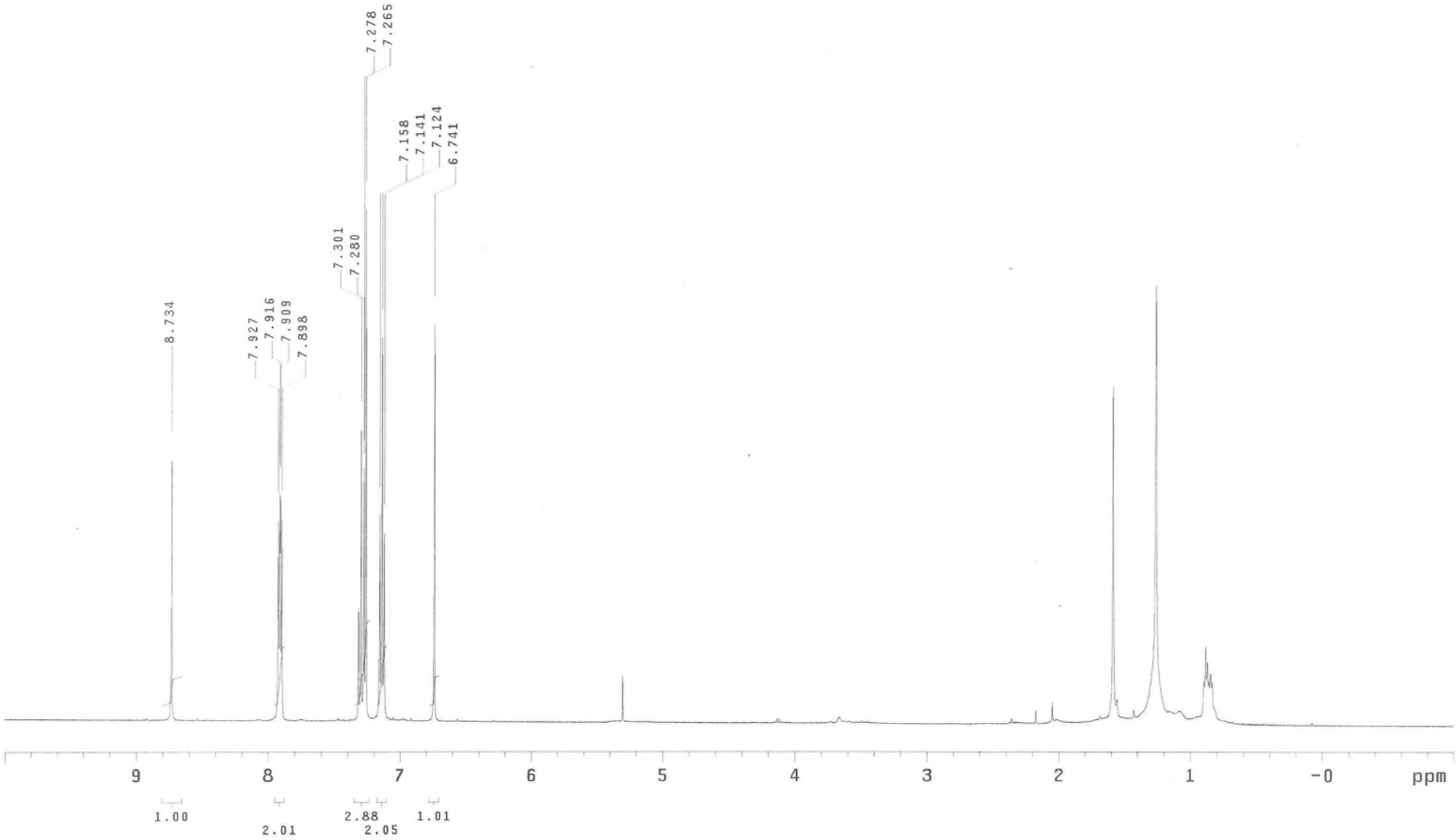

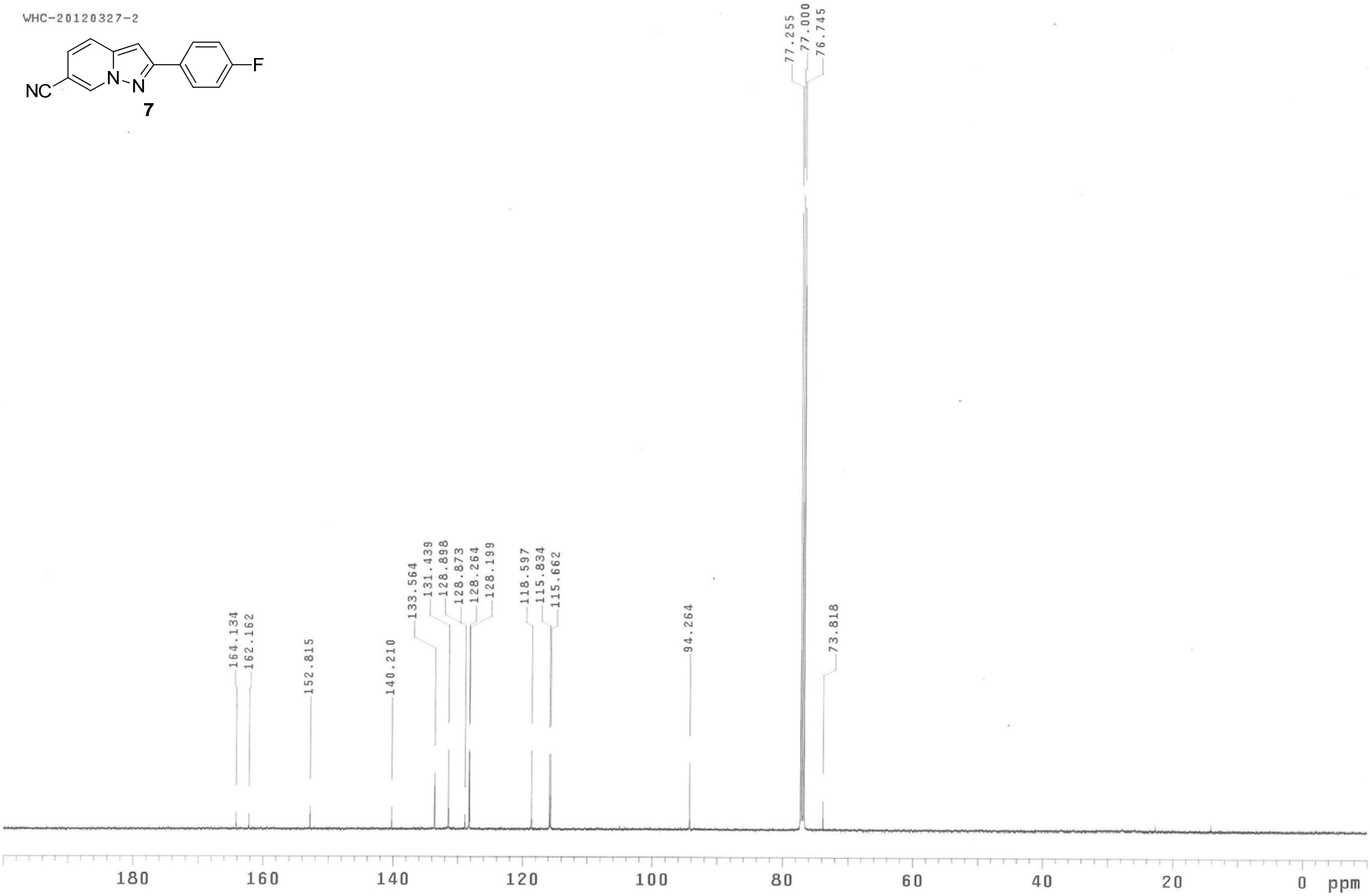

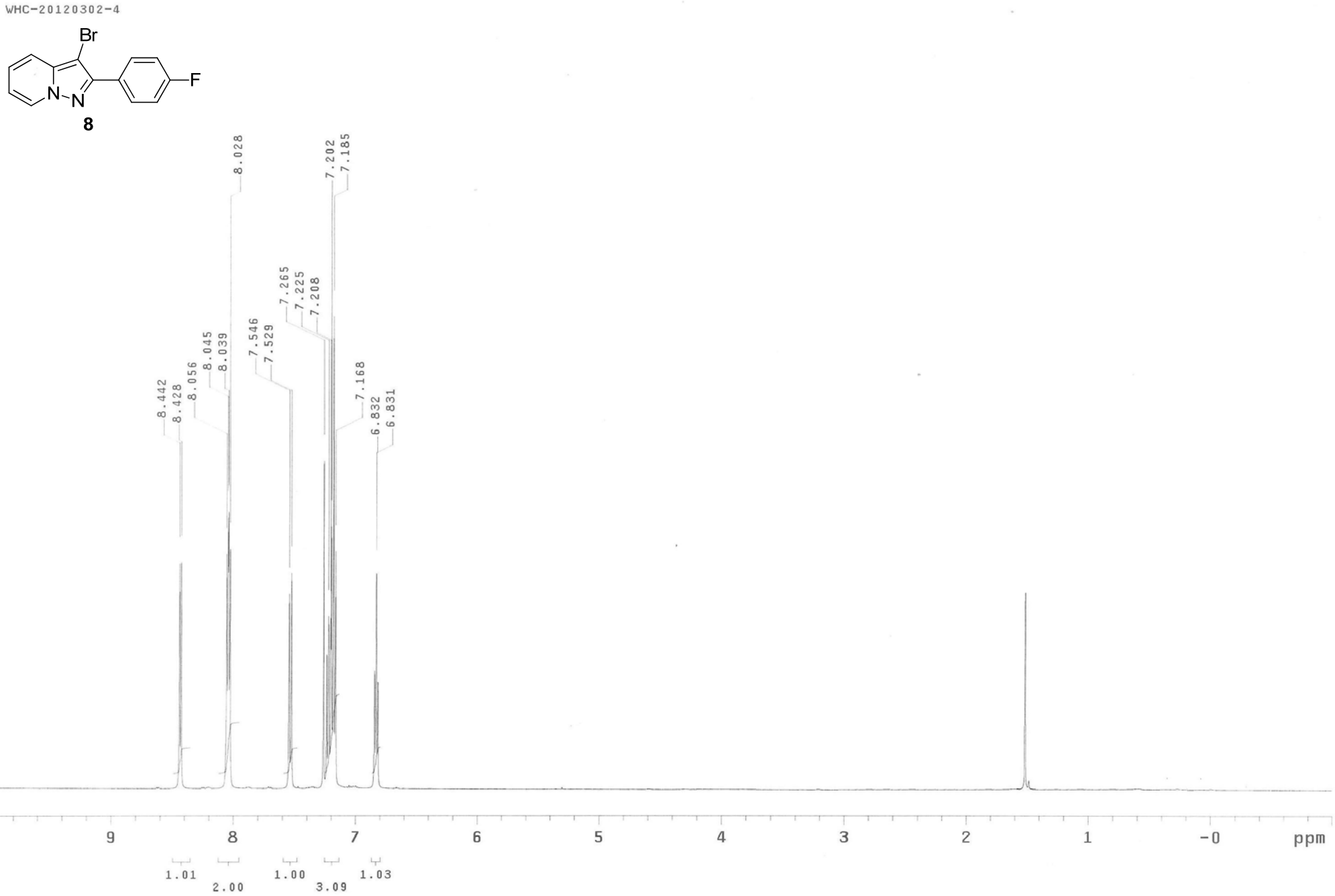

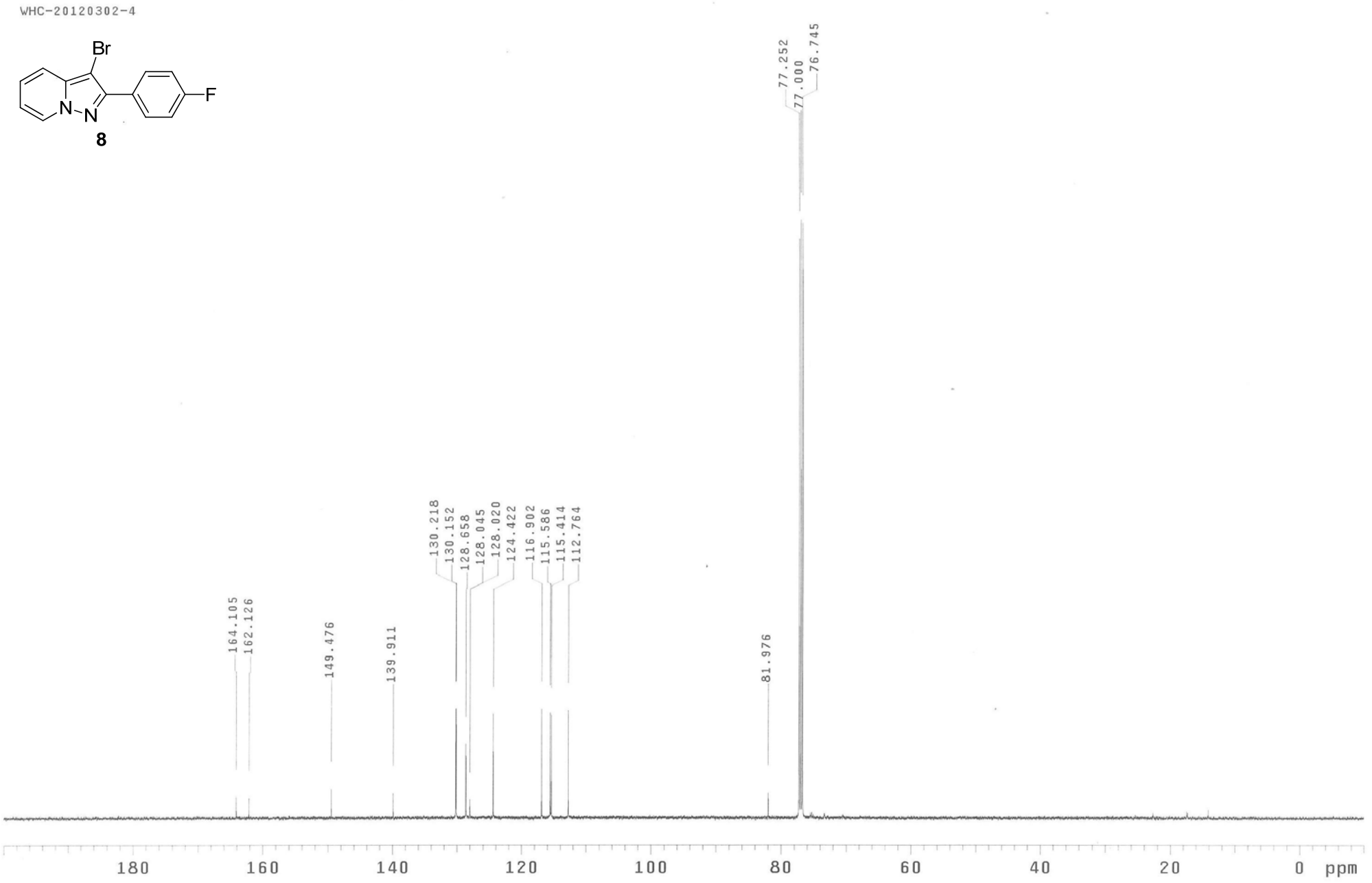

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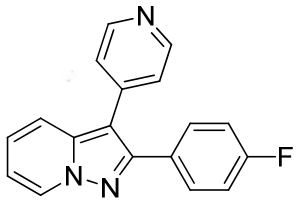

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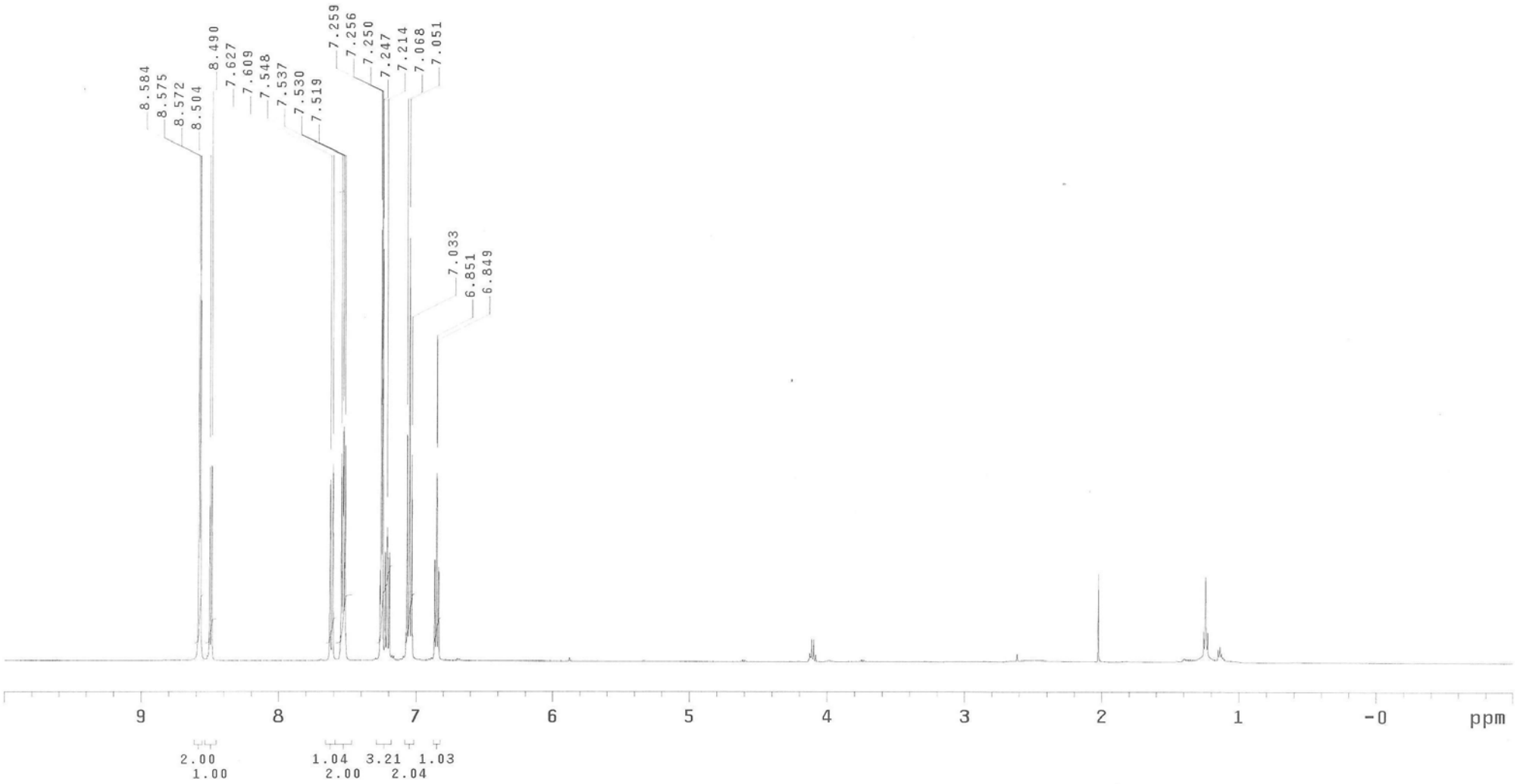

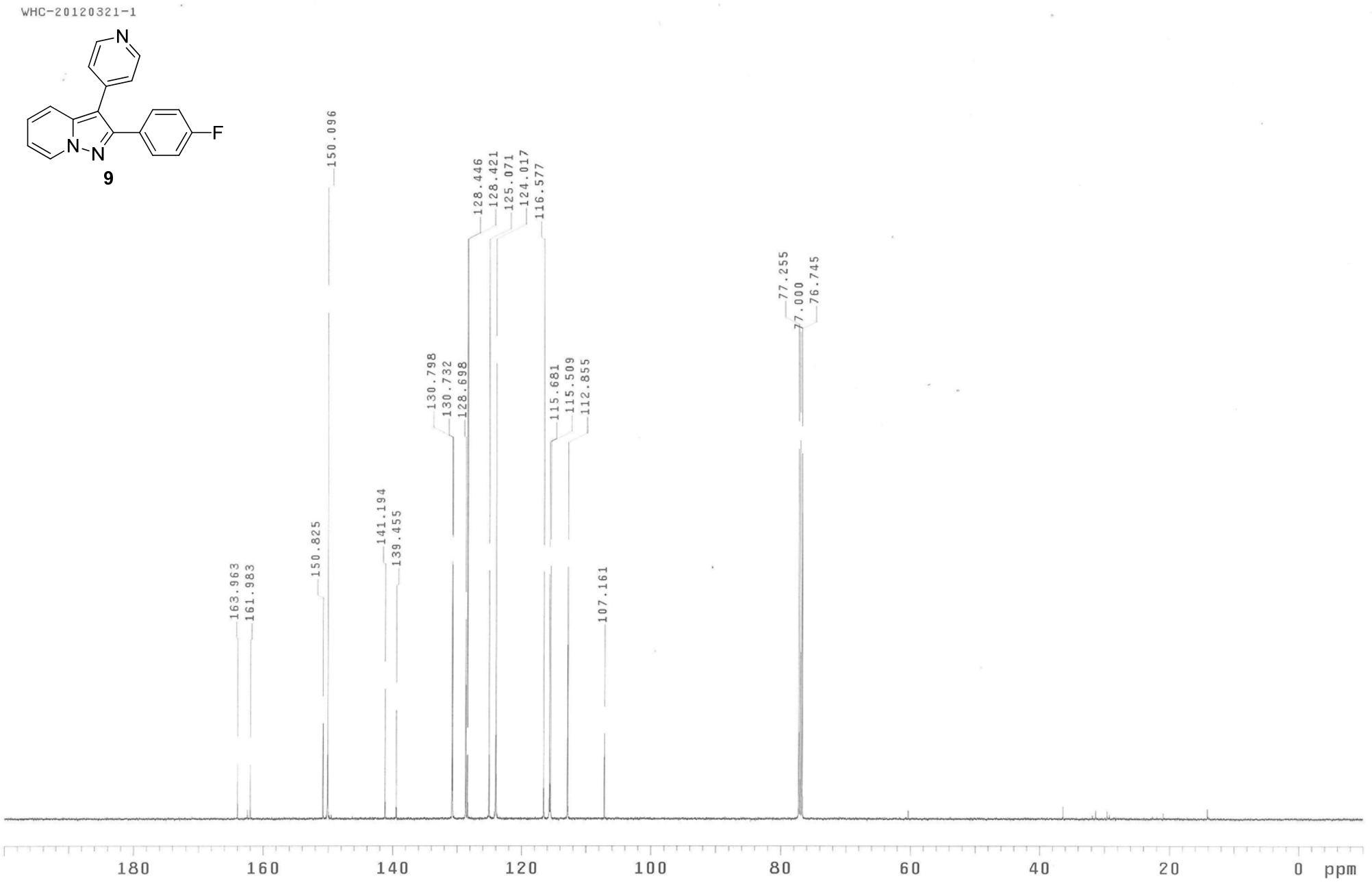
WHC-20120321-1
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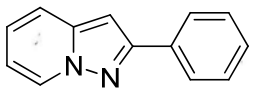
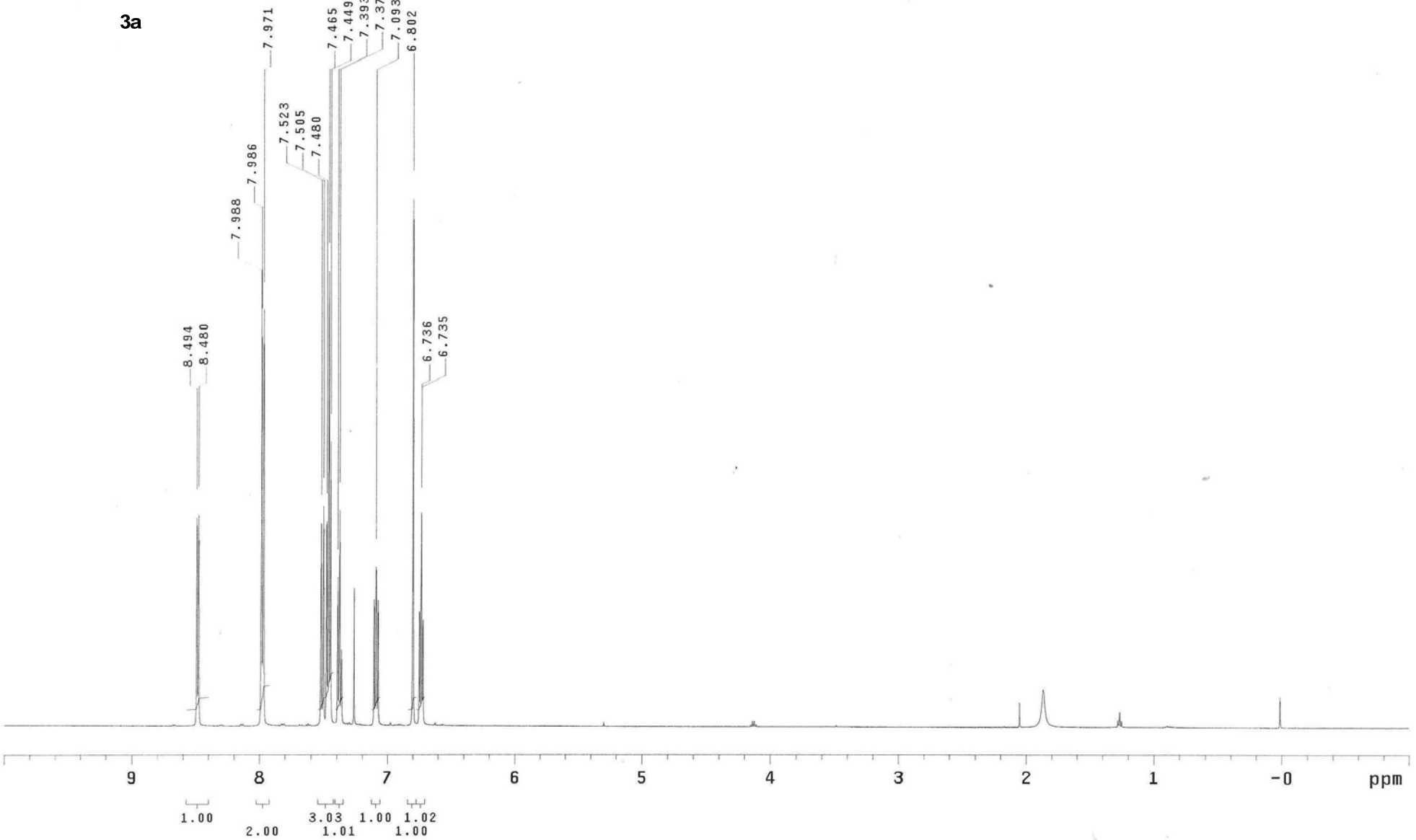
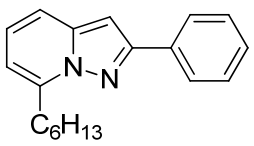
ppm

^{1}H NMR spectra of known compounds **3a-3n** and **3q-3u**.



3a





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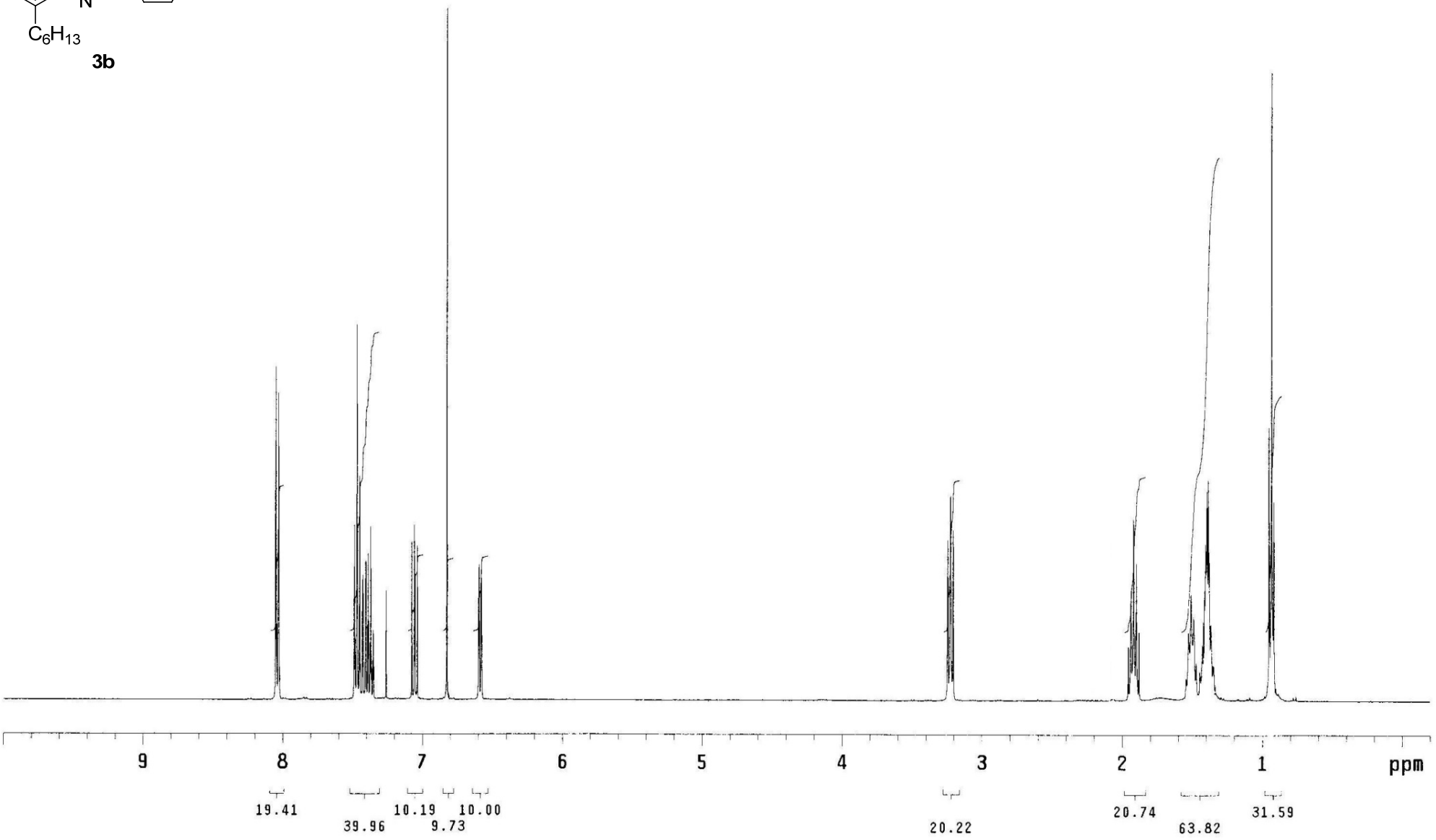
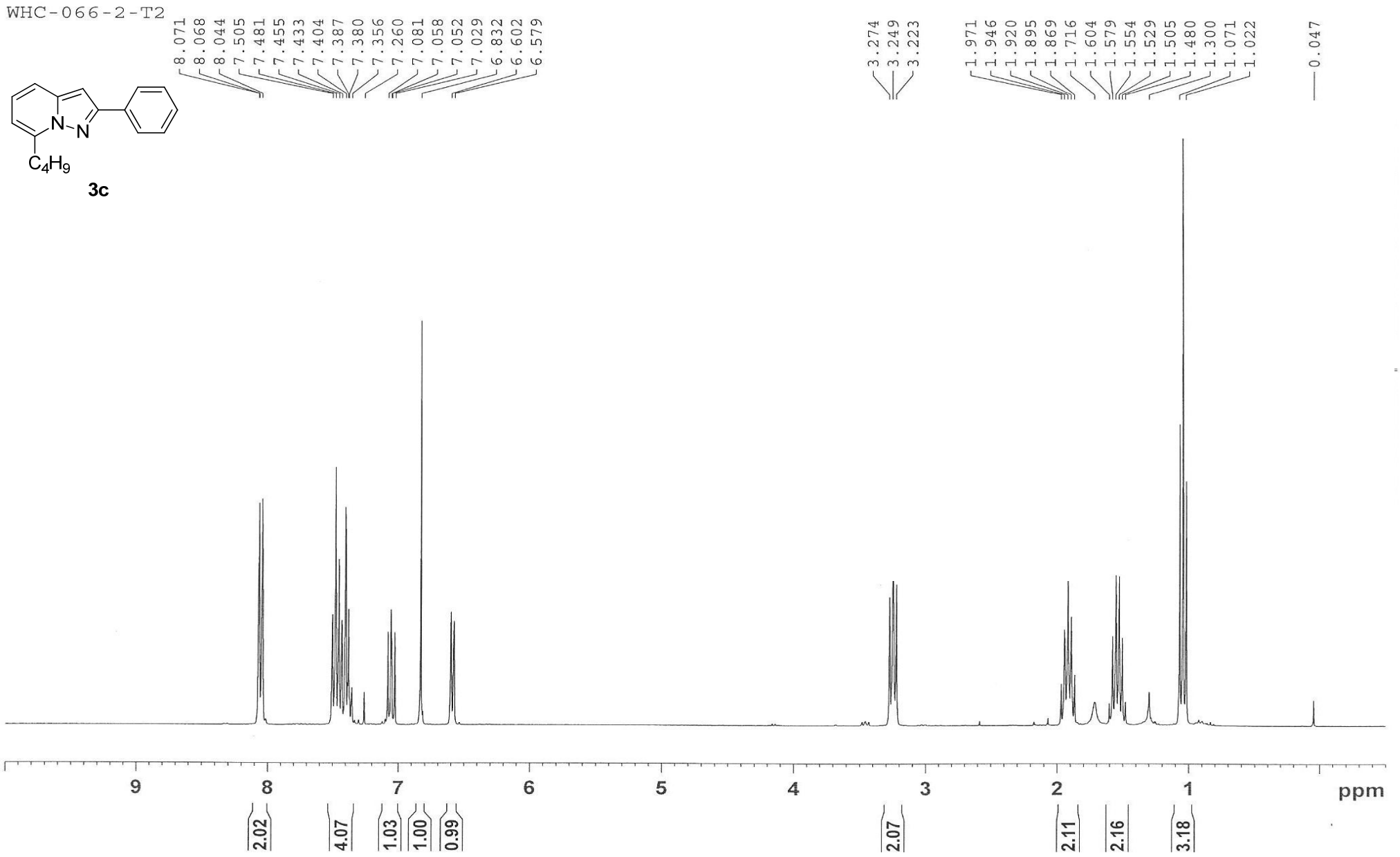
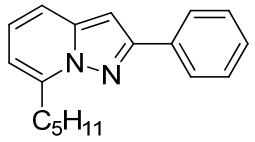
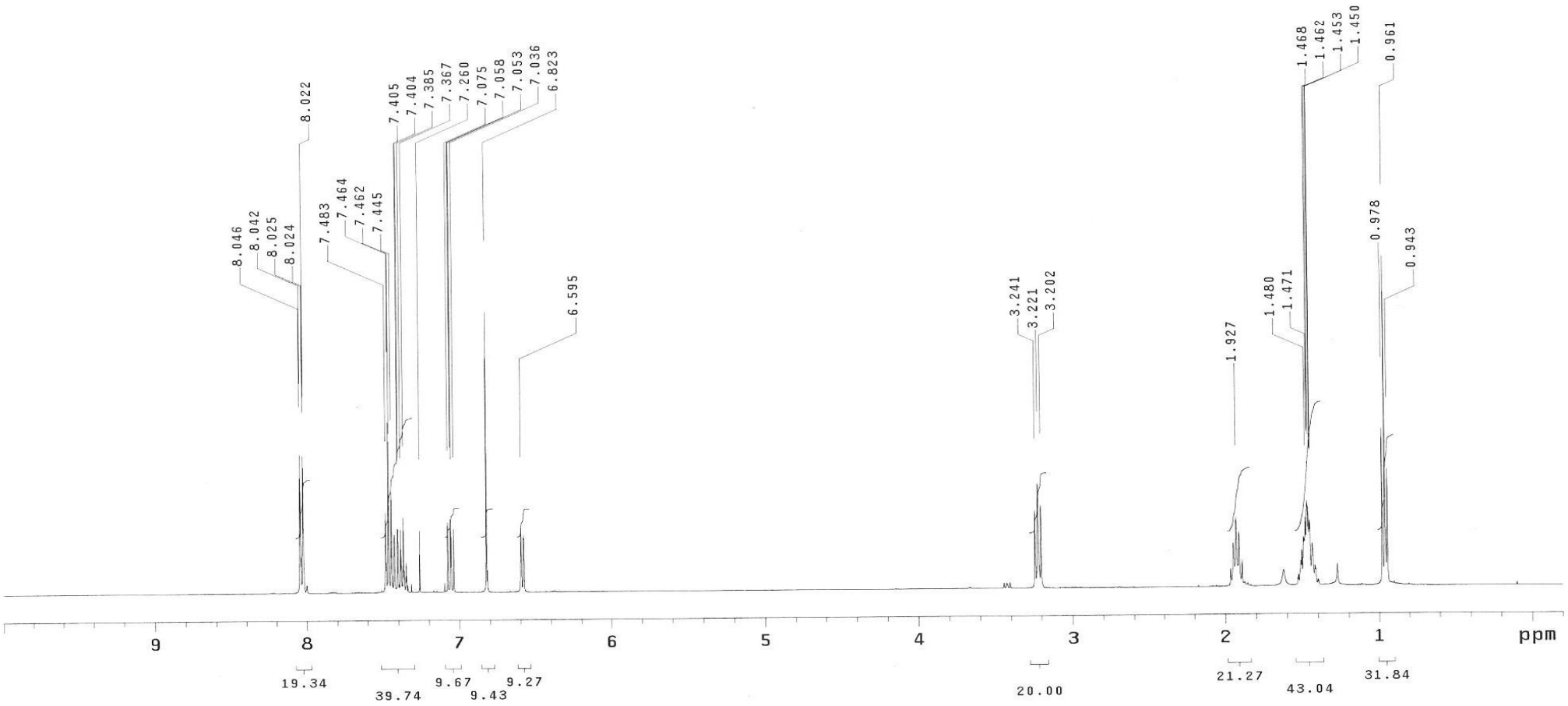
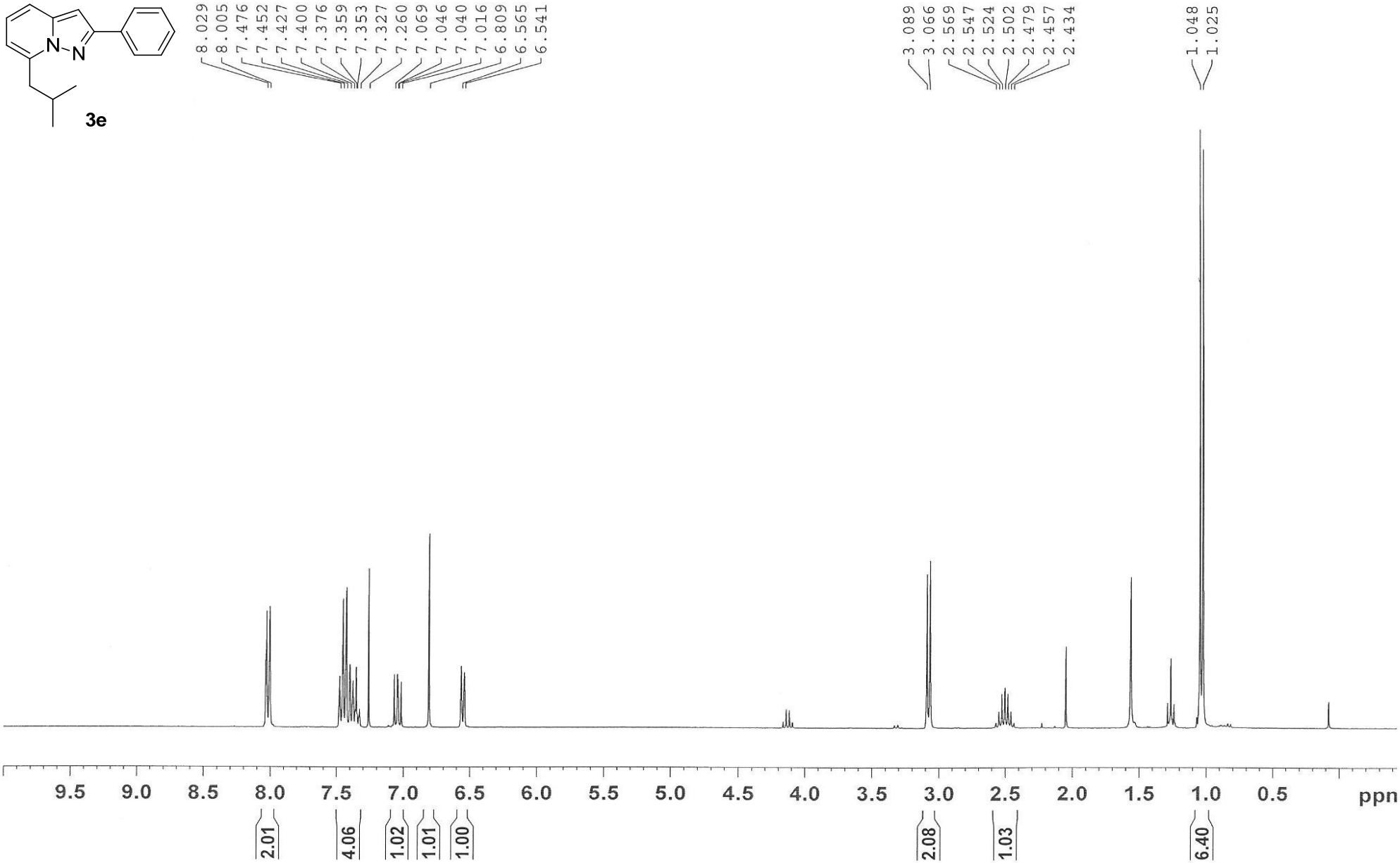


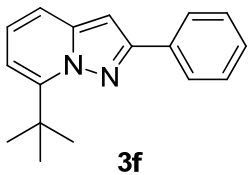




3d







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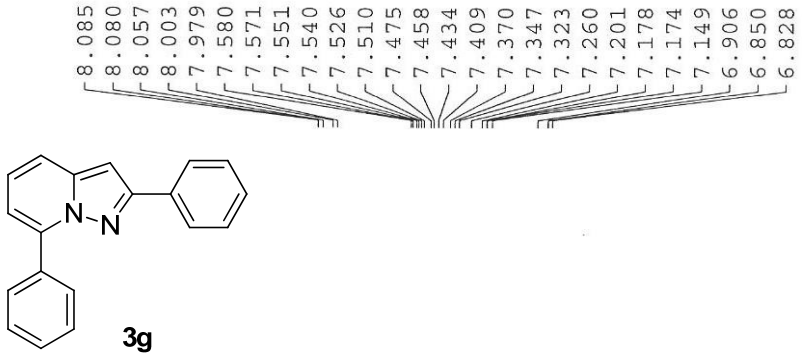

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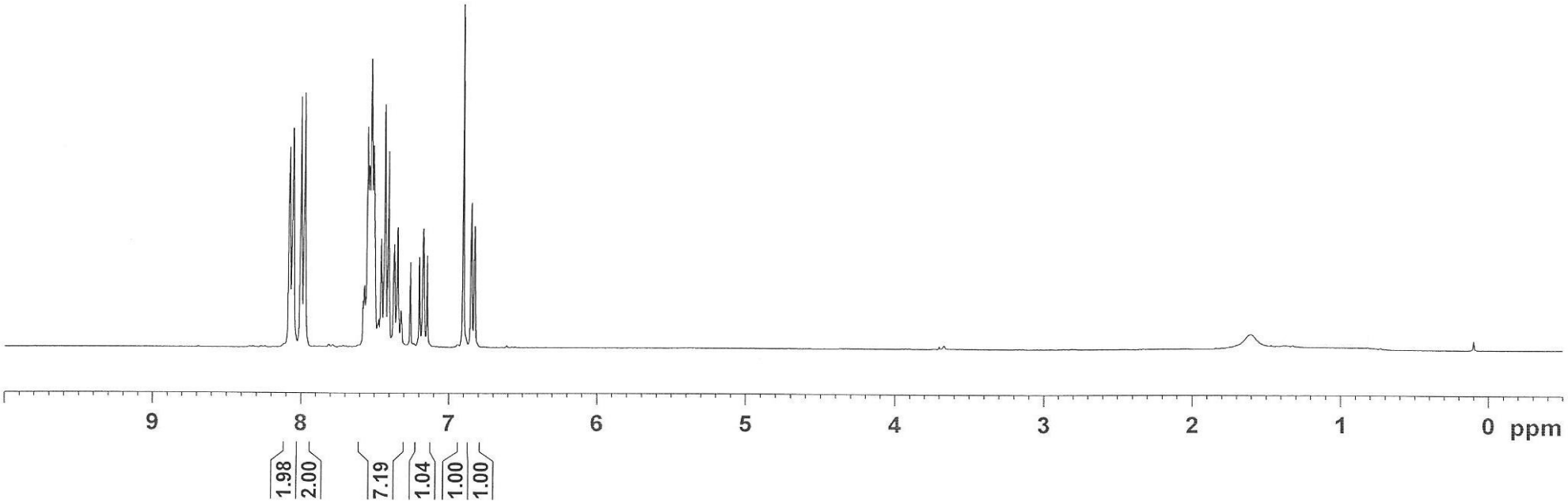

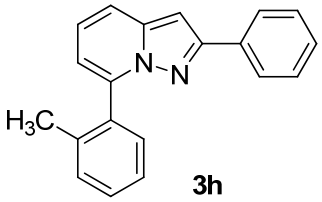

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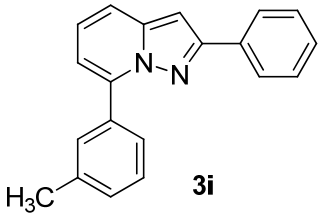
N
N
H3C

3i

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7.999
8.001
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7.350
7.265
6.895
9
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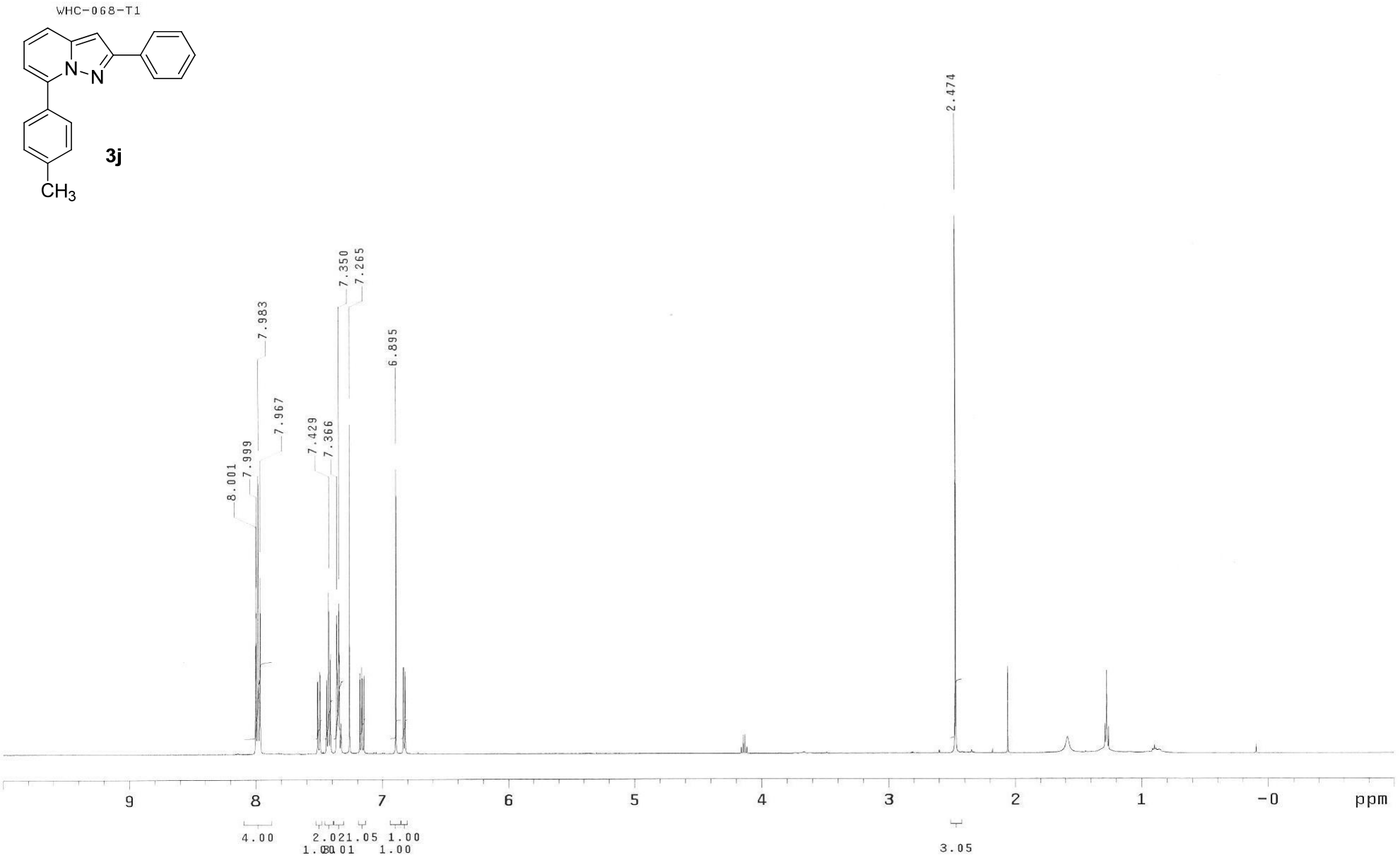

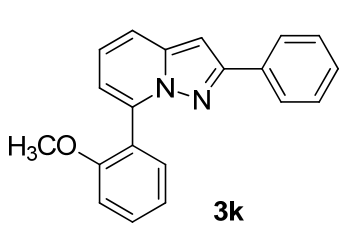

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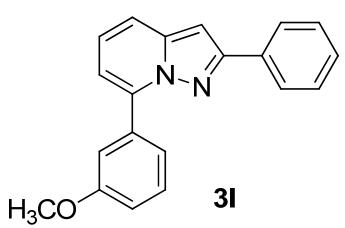

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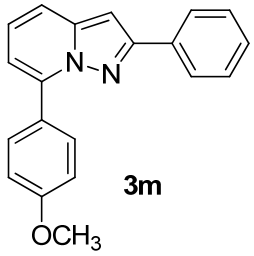

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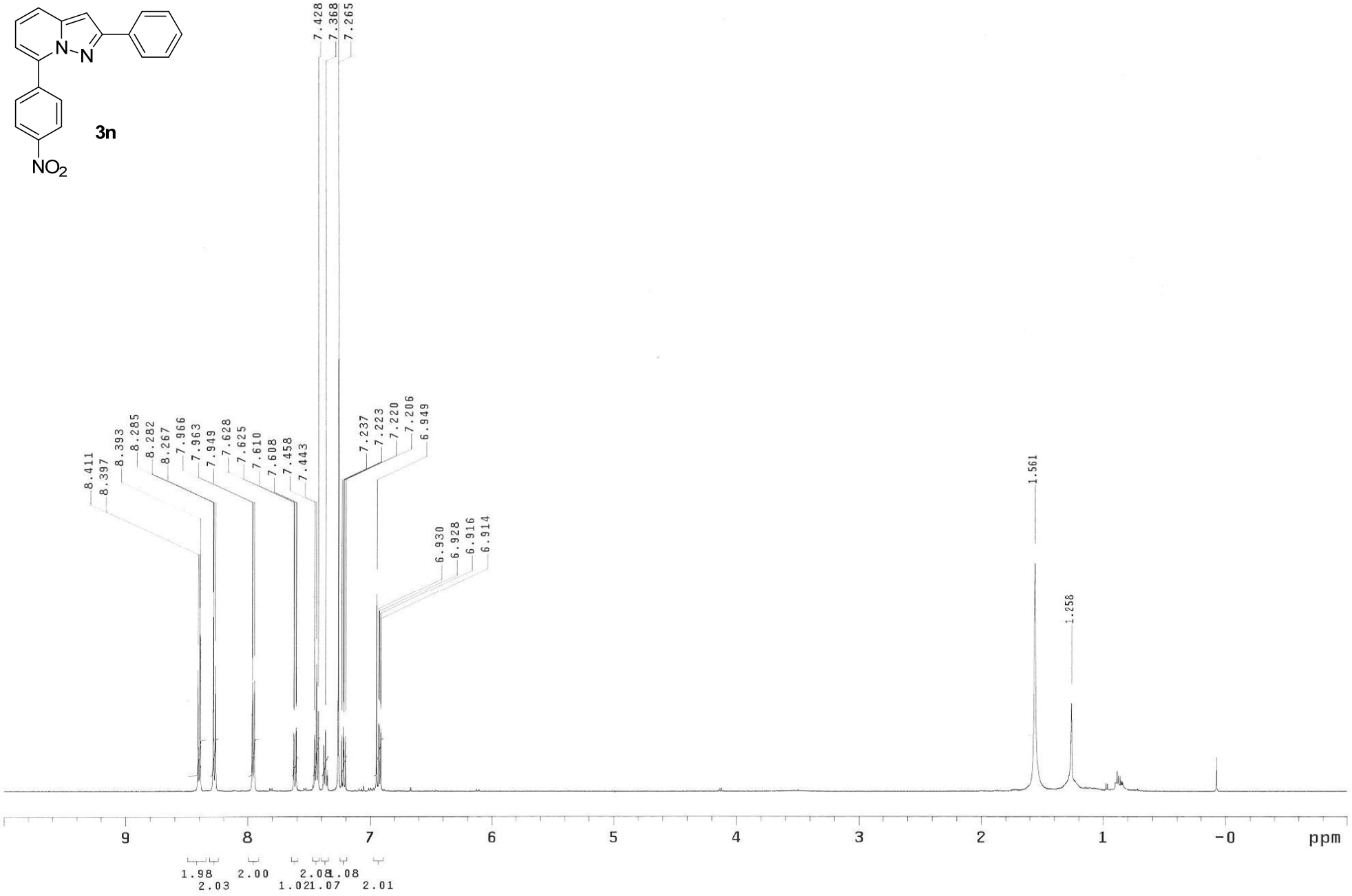

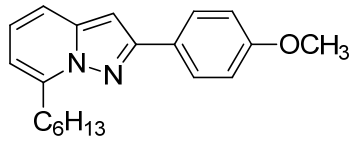

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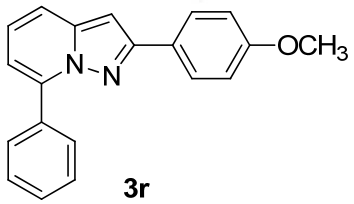

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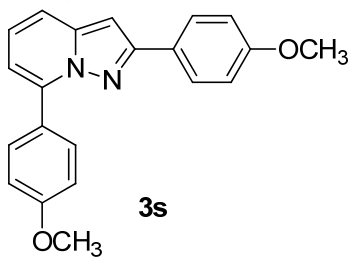

3s