Supporting Information

The Copper-Mediated Cyclization Reaction of Hydrazine with Enediynones Provides Pyrazolo[1,5-*a*]pyridines†

Hung-Chou Wu[a], Long-Chih Hwang[a] and Ming-Jung Wu[b,*]

[a]*Department of Medicinal and Applied Chemistry, Kaohsiung Medical University, Kaohsiung, Taiwan*

[b]*Department of Chemistry, National Sun Yat-sen University, Kaohsiung, Taiwan*

Fax: 886-7-5253909; E-mail: mijuwu@faculty.nsysu.edu.tw

Table of Contents

P. S1.	General procedures
P. S2-20.	Data of compound **1a-r** and **8a-r**.
P. S15-17.	X-ray data for **8j**
P. S20-24.	X-ray data for **9a** and **9e**
P. S24.	References
P. S25-113.	Spectra data of compounds

General procedure for the synthesis of enediynones (1)

Manganese dioxide (15 mmol) was added to solution of enediynols (**6**) (1 mmo) in CH_2Cl_2 (10 ml). The reaction mixture was stirred at room temperature for 2 h. The solution was filtered through $MgSO_4$ and silica gel on cotton plug and washed with dichloromethane. After removal of solvent, the residue was purified by column chromatography to give the products.

General procedure for the synthesis of vinyl chlorides (4)

Terminal alkynes (**3**) (5 mmol), *cis*-1,2dichloroethylene (**2**) (7.5mmol), $Pd(PPh_3)_4$ (5 mol %), CuI (5 mol %), and *n*-$BuNH_2$ (10 mmol) in ether (10 mL) were stirred at room temperature for 2 h. The saturated aqueous solutions of NH_4Cl and Na_2CO_3 were added subsequently into the reaction mixture and extracted with ethyl acetate. The combined organic extracts were dried over anhydrous $MgSO_4$. After filtration and removal of solvent, the residue was purified by column chromatography to give the products.

General procedure for the synthesis of pyrazolo[1,5-*a*]pyridines (8)

Hydrazine monohydrate (0.3 mmol) was added to a solution of enediyneones (0.15 mmol) in CH_3CN (5 ml). The reaction mixture was stirred at 60 ^oC for 1 h, copper-(I) chloride (0.15 mmol) was then added to the reaction mixture and stirred for an additional 30 h at refluxing temperature under nitrogen. After cooling to room temperature, the solution was filtered through $MgSO_4$ and silica gel on cotton plug and washed with ethyl acetate. After removal of solvent, the residue was purified by column chromatography to give the products.

Data of compounds 4

Compounds 4a~4f, 4j, and 4l, see references [1]~[5].

(Z)-1-(4-chlorobut-3-en-1-yn-1-yl)-2-methylbenzene (4g)

brown liquid; R_f = 0.72 (*n*-hexane as eluent);

^{1}H NMR ($CDCl_3$, 300 MHz) : δ 7.46 (d, *J* = 7.5 Hz, 1H), 7.13-7.25 (m, 3H), 6.45 (d, *J* = 7.5 Hz, 1H), 6.13 (d, *J* = 7.2 Hz, 1H), 2.5 (s, 3H) ppm; HRMS (EI) calcd. for $C_{11}H_9Cl$ 176.0393, found 176.0395.

(Z)-1-(4-chlorobut-3-en-1-yn-1-yl)-3-methylbenzene (4h)

brown liquid; R_f = 0.68 (*n*-hexane as eluent);

^{1}H NMR ($CDCl_3$, 500 MHz) : δ 7.15-7.36 (m, 4H), 6.43 (d, *J* = 7.5 Hz, 1H), 6.09 (d, *J* = 7.5 Hz, 1H), 2.35 (s, 3H); ^{13}C NMR ($CDCl_3$. 125MHz) : δ 138.1, 132.9, 132.2, 130.1, 129.6, 128.7, 123.2, 123.1, 122.5, 112.1, 21.2 ppm; HRMS (EI) calcd. for $C_{11}H_9Cl$ 176.0393, found 176.0395.

(Z)-1-(4-chlorobut-3-en-1-yn-1-yl)-3-methoxybenzene (4k)

brown liquid; R_f = 0.67 (*n*-hexane as eluent);

^{1}H NMR ($CDCl_3$, 500 MHz) : δ 7.24 (d, *J* = 8.0 Hz, 1H), 7.10 (d, *J* = 7.5 Hz, 1H), 7.02 (s, 1H), 6.91 (dd, *J* = 8.0, 2.5 Hz, 1H), 6.45 (d, *J* = 7.5 Hz, 1H), 6.09 (d, *J* = 7.5 Hz, 1H), 3.82 (s, 3H); ^{13}C NMR ($CDCl_3$. 125MHz) : δ 159.3, 129.4, 128.4, 124.3, 123.6, 116.3, 115.4, 112.0, 97.2, 83.0, 55.3 ppm; HRMS (EI) calcd. for $C_{11}H_9ClO$ 192.0342, found 192.0344.

Data of compounds 6

(Z)-1-Phenyltrideca-4-en-2,6-diyn-1-ol (6a)

brown liquid; R_f = 0.52 (*n*-hexane/ethyl acetate = 10/1 as eluent);

^{1}H NMR ($CDCl_3$, 500 MHz) : δ 7.62 (d, J = 7.0 Hz, 2H), 7.32-7.40 (m, 3H), 5.88 (td,

J = 10.5, 2.0 Hz, 1H), 5.82 (dd, J = 11.0, 2.0 Hz, 1H), 5.65 (s, 1H), 2.53 (s, 1H), 2.38 (td, J = 7.0, 2.0 Hz, 2H), 1.54 (m, J = 7.0 Hz, 2H), 123-1.43 (m, 6H), 0.89 (t, J = 7.0 Hz, 3H) ; ^{13}C NMR ($CDCl_3$. 125MHz) : δ 140.39, 128.48(2C), 128.29, 126.78(2C), 121.38, 117.34, 99.55, 95.13, 84.15, 78.06, 65.06, 31.26, 28.54, 28.52, 22.47, 19.74, 14.01 ppm; HRMS (EI) calcd. for $C_{19}H_{22}O$ 266.1671, found 266.1672.

(Z)-1-Phenylundeca-4-en-2,6-diyn-1-ol (6b)

brown liquid; R_f = 0.53 (*n*-hexane/ethyl acetate = 10/1 as eluent);

^{1}H NMR ($CDCl_3$, 500 MHz) : δ 7.62 (d, J = 7.5 Hz, 2H), 7.32-7.40 (m, 3H), 5.87 (dt, J = 11.0, 2.0 Hz, 1H), 5.82 (dd, J = 11.0, 2.0 Hz, 1H), 5.65 (s, 1H), 2.59 (s, 1H), 2.39, (td, J = 7.0, 2.0 Hz, 2H), 1.40-1.56 (m, 4H), 0.90 (t, J = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$. 125MHz) : δ 140.38, 128.47(2C), 128.26, 126.76(2C), 121.33, 117.37, 99.43, 95.15, 84.11, 78.09, 65.03, 30.55, 21.88, 19.38, 13.51 ppm; HRMS (EI) calcd. for $C_{17}H_{18}O$ 238.1358, found 238.11360.

(Z)-1-phenyldodeca-4-en-2,6-diyn-1-ol (6c)

brown liquid; R_f = 0.58 (*n*-hexane/ethyl acetate = 10/1 as eluent);

^{1}H NMR ($CDCl_3$, 200 MHz) : δ 7.34-7.63 (m, 5H), 5.77-5.91 (m, 2H), 5.65 (d, J = 5.8 Hz, 1H), 2.38 (td, J = 7.0, 1.6 Hz, 2H), 2.28 (s,1H), 1.22-1.62 (m, 6H), 0.88 (t, J = 6.8 Hz, 3H) ppm; HRMS (EI) calcd. for $C_{18}H_{20}O$ 252.1514, found 252.1512.

(Z)-9-Methyl-1-phenyldeca-4-en-2,6-diyn-1-ol (6d)

brown liquid; R_f = 0.56 (*n*-hexane/ethyl acetate = 10/1 as eluent);

^{1}H NMR ($CDCl_3$, 200 MHz) : δ 7.59 (dd, *J* = 8.0, 2.2 Hz, 2H), 7.41-7.35 (m, 3H), 5.87-5.84 (m, 2H), 5.65 (s, 1H), 2.28 (dd, *J* = 6.6, 1.8 Hz, 2H), 1.83 (m, 1H), 0.98 (d, *J* = 7.0 Hz, 6H) ; ^{13}C NMR ($CDCl_3$. 50MHz) : δ 143.8, 129.0 (2C), 127.7, 127.2 (2C),

122.1, 118.9, 92.8, 91.1, 84.9, 79.8, 31.8, 28.5, 22.0 (2C) ppm; HRMS (EI) calcd. for $C_{17}H_{18}O$ 238.1358, found 238.1360.

(Z)-8,8-Dimethyl-1-phenylnona-4-en-2,6-diyn-1-ol (6e)

brown liquid; R_f = 0.57 (*n*-hexane/ethyl acetate = 10/1 as eluent);

^{1}H NMR ($CDCl_3$, 300 MHz) : δ 7.60 (d, *J* = 6.6 Hz, 2H), 7.32-7.41 (m, 3H), 5.78-5.89 (m, 2H), 5.66 (d, J = 5.7 Hz, 1H), 2.29 (d, J = 6.3 Hz, 1H), 1.24 (s, 9H) ; ^{13}C NMR ($CDCl_3$. 50MHz) : δ 144.8, 129.0 (2C), 127.6, 127.1 (2C), 118.5, 105.9, 91.1, 84.9, 77.9, 61.8, 31.2 (3C), 28.6 ppm; HRMS (EI) calcd. for $C_{17}H_{18}O$ 238.1358, found 238.1359.

(Z)-1,7-Diphenylhepta-4-en-2,6-diyn-1-ol (6f)

brown liquid; R_f = 0.52 (*n*-hexane/ethyl acetate = 10/1 as eluent);

^{1}H NMR ($CDCl_3$, 200 MHz) : δ 7.67-7.29 (m, 10H), 6.11 (d, *J* = 10.8 Hz, 1H), 5.95 (dd, *J* = 10.6, 1.4 Hz, 1H), 2.04 (s,1H) ; ^{13}C NMR ($CDCl_3$. 50MHz) : δ 132.3 (2C), 129.0 (2C), 128.5, 128.4 (2C), 127.1 (2C), 122.6, 121.1, 118.9, 94.7, 93.1, 91.1, 84.9, 61.8 ppm; HRMS (EI) calcd. for $C_{19}H_{14}O$ 258.1045, found 258.1048.

(Z)-1-phenyl-7-o-tolylhepta-4-en-2,6-diyn-1-ol (6g)

brown liquid; R_f = 0.51 (*n*-hexane/ethyl acetate = 10/1 as eluent);

^{1}H NMR ($CDCl_3$, 400 MHz) : δ 7.61-7.10 (m, 9H), 6.14 (d, *J* = 10.8 Hz, 1H), 5.92 (dd, *J* = 10.8, 1.6 Hz, 1H), 5.68 (d, *J* = Hz, 1H), 2.40 (s, 3H); ^{13}C NMR ($CDCl_3$, 100MHz) : δ140.4, 140.2, 132.1, 129.4, 128.7, 128.6 (2C), 128.4, 126.7 (2C), 125.5, 122.5, 120.7, 118.1, 96.4, 96.3, 90.6, 84.2, 65.2, 20.7 ppm; HRMS (EI) calcd. for $C_{20}H_{16}O$ 272.1201, found 272.1203.

(Z)-1-phenyl-7-m-tolylhepta-4-en-2,6-diyn-1-ol (6h)

brown liquid; R_f = 0.52 (*n*-hexane/ethyl acetate = 10/1 as eluent);

^{1}H NMR ($CDCl_3$, 400 MHz) : δ 7.66-7.13 (m, 9H), 6.10 (d, *J* = 10.8 Hz, 1H), 5.94 (dd, *J* = 10.8, 2 Hz, 1H), 5.70 (s, 1H), 2.30 (s, 3H); ^{13}C NMR ($CDCl_3$, 100MHz) : δ140.3, 137.9, 132.3, 129.6, 128.9, 1128.6 (2C), 128.3, 128.2, 126.7 (2C), 122.5, 120.7, 118.4, 97.7, 96.3, 86.4, 84.1, 65.2, 21.1 ppm; HRMS (EI) calcd. for $C_{20}H_{16}O$ 272.1201, found 272.1202.

(Z)-7-(2-methoxyphenyl)-1-phenylhepta-4-en-2,6-diyn-1-ol (6j)

brown liquid; R_f = 0.53 (*n*-hexane/ethyl acetate = 10/1 as eluent);

^{1}H NMR ($CDCl_3$, 500 MHz) : δ 7.63 (dd, J = 7.5, 2.5 Hz, 2H), 7.29-7.36 (m, 4H), 6.87-6.91 (m, 2H), 6.17 (d, J = 10.5 Hz, 1H), 5.93 (dd, J = 11.0, 2.0 Hz, 1H), 5.69 (d, J = 3.0 Hz, 1H), 3.83 (S, 1H), 2.58 (d, J = 5.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125MHz) : δ 159.87, 140.35, 133.99, 130.28, 128.57(2C), 128.30, 126.81(2C), 121.03, 120.60, 118.10, 112.09, 110.83, 96.49, 93.96, 90.90, 84.42, 65.16, 55.90 ppm; HRMS (EI) calcd. for $C_{20}H_{16}O_2$ 288.1150, found 288.1151.

(Z)-7-(4-methoxyphenyl)-1-phenylhepta-4-en-2,6-diyn-1-ol (6l)

brown liquid; R_f = 0.54 (*n*-hexane/ethyl acetate = 10/1 as eluent);

^{1}H NMR ($CDCl_3$, 200 MHz) : δ 7.62-7.67 (m, 2H), 7.30-7.36 (m, 2H), 6.79-6.85 (m, 2H), 6.09 (d, J = 10.6 Hz, 1H), 5.90 (dd, J = 11.0, 1.8 Hz, 1H), 5.70 (d, J = 4.6 Hz, 1H), 3.81 (S, 3H), 2.39 (d, J = 6.2 Hz, 1H) ppm; HRMS (EI) calcd. for $C_{20}H_{16}O_2$ 288.1150, found 288.1152.

(Z)-7-(4-nitrophenyl)-1-phenylhepta-4-en-2,6-diyn-1-ol (6m)

Yellow solid; m.p.: 88-90 ℃ R_f = 0.42 (*n*-hexane/ethyl acetate = 10/1 as eluent);

^{1}H NMR ($CDCl_3$, 300 MHz) : δ 8.14 (d, J = 9 Hz, 2H), 7.60-7.64 (m, 2H), 7.45 (d, J = 8.7 Hz, 3H), 7.34-7.36 (m, 3H), 6.09 (m, 2H), 5.71(d, J = 5.4 Hz, 1H), 2.34 (d, J = 4.2 Hz, 1H) ppm; HRMS (EI) calcd. for $C_{19}H_{13}NO_3$ 303.0895, found 303.0897.

(Z)-7-(4-hexylphenyl)-1-(4-methoxyphenyl)hepta-4-en-2,6-diyn-1-ol (6n)

brown liquid; R_f = 0.58 (*n*-hexane/ethyl acetate = 10/1 as eluent);

^{1}H NMR ($CDCl_3$, 300 MHz) : δ 7.54 (d, J = 8.7 Hz, 2H), 6.91 (d, J = 8.7 Hz, 2H), 5.79-5.89 (m, 2H), 5.60 (d, J = 5.4 Hz), 3.81 (S, 3H), 2.38 (td, J = 7.2, 1.8 Hz, 2H), 2.14 (d, J = 6.3 Hz, 1H), 1.23-1.55 (m, 8H), 0.87 (t, J = 6.9 Hz, 3H) ppm; HRMS (EI) calcd. for $C_{20}H_{22}O_2$ 296.1776, found 196.1777.

(Z)-1-(4-methoxyphenyl)-7-phenylhepta-4-en-2,6-diyn-1-ol (6o)

brown liquid; R_f = 0.55 (*n*-hexane/ethyl acetate = 10/1 as eluent);

^{1}H NMR ($CDCl_3$, 300 MHz) : δ 7.56 (d, J = 8.7 Hz, 2H), 7.28-7.41 (m, 5H), 6.82 (d, J = 8.7 Hz, 2H), 6.10 (d, J = 10.8, 1H), 5.96 (dd, J = 10.8, 1.5 Hz, 1H), 3.76 (S, 3H), 2.19 (d, J = 6 Hz, 1H) ppm; HRMS (EI) calcd. for $C_{20}H_{16}O_2$ 288.1150, found 288.1152.

(Z)-1,7-bis(4-methoxyphenyl)hepta-4-en-2,6-diyn-1-ol (6p)

brown liquid; R_f = 0.53 (*n*-hexane/ethyl acetate = 10/1 as eluent);

^{1}H NMR ($CDCl_3$, 300 MHz) : δ 7.56 (d, J = 6.9 Hz, 2H), 7.32 (d, J = 6.3, 2H), 6.83 (m, 4H), 6.08 (d, J = 10.8 Hz, 1H), 5.90 (dd, J = 10.8, 1.8 Hz, 1H), 5.64 (d, J = 5.7 Hz, 1H), 3.81 (s, 3H), 3.77 (s, 3H), 2.24 (d, J = 6.3 Hz, 1H) ppm; HRMS (EI) calcd. for $C_{2}{}_{\cdot}H_{18}O_3$ 318.1256, found 318.1257.

(Z)-4-(7-hydroxy-7-(4-methoxyphenyl)hepta-3-en-1,5-diyn-1-yl)benzonitrile (6q)

brown liquid; R_f = 0.50 (*n*-hexane/ethyl acetate = 10/1 as eluent);

^{1}H NMR ($CDCl_3$, 300 MHz) : δ 7.50-7.55 (m, 4H), 7.39 (d, J = 8.4 Hz, 2H), 6.84 (d, J = 8.7 Hz, 2H), 6.02-6.11 (m, 2H), 5.64 (d, J = 5.7 Hz, 1H), 3.79 (s, 3H), 2.23 (d, J = 5.4 Hz, 1H) ppm; HRMS (EI) calcd. for $C_{20}H_{21}F_3O$ 334.1544, found 334.1546.

Data of compounds 1

(Z)-1-Phenyltrideca-4-en-2,6-diyn-1-one (1a)

brown liquid; R_f = 0.62 (*n*-hexane/ethyl acetate = 20/1 as eluent); ^{1}H NMR ($CDCl_3$, 400 MHz) : δ 8.23 (*J* = 7.8Hz, 2H), 7.66-7.43 (m, 3H), 6.21 (dt, *J* = 10.6, 2.2 Hz, 1H), 5.98 (d, *J* = 10.6 Hz, 1H), 2.48 (td, *J* = 6.8, 2.2 Hz, 2H), 1.66-1.20 (m, 8H), 0.85 (t, *J* = 6.6 Hz, 3H) ; ^{13}C NMR ($CDCl_3$, 100MHz) : δ 177.9, 135.2, 134.7, 129.9 (2C), 128.5 (2C), 122.8, 117.3, 109.1, 93.8, 89.9, 30.9, 30.2, 28.1, 26.3, 22.2, 14.1 ppm; HRMS (EI) calcd. for $C_{19}H_{20}O$ 264.1514, found 264.1516.

(Z)-1-Phenylundeca-4-en-2,6-diyn-1-one (1b)

brown liquid; R_f = 0.64 (*n*-hexane/ethyl acetate = 20/1 as eluent); ^{1}H NMR ($CDCl_3$, 400 MHz) : δ 8.24 (d, *J* = 7.8 Hz, 2H), 7.61 (t, *J* = 7.2Hz, 2H), 7.47 (t, *J* = 7.0Hz, 1H), 6.19 (dt, *J* = 10.6, 2.2 Hz, 1H), 5.98 (d, *J* = 10.6, 1H), 2.47 (td, *J* = 8.8, 1.8 Hz, 2H), 1.65-1.37 (m, 4H), 0.87 (t, *J* = 6.8 Hz, 3H) ; ^{13}C NMR ($CDCl_3$, 100MHz) : δ 177.5, 135.1, 134.6, 129.7 (2C), 128.4 (2C), 126.8, 115.6, 109.3, 93.8, 89.9, 31.2, 21.5, 18.9, 14.8 ppm; HRMS (EI) calcd. for $C_{17}H_{16}O$ 236.1201, found 236.1200.

(Z)-9-Methyl-1-phenyldeca-4-en-2,6-diyn-1-one (1d)

Yellow green liquid; R_f = 0.66 (*n*-hexane/ethyl acetate = 20/1 as eluent); ^{1}H NMR ($CDCl_3$, 400 MHz) : δ 8.24 (d, *J* = 7.8 Hz, 2H), 7.61 (t, *J* = 7.2 Hz, 2H), 7.47 (t, *J* = 7.0 Hz, 1H), 6.18 (dt, *J* = 10.6, 2.2 Hz, 1H), 5.98 (d, *J* = 10.6 Hz, 1H), 2.36 (dd, *J* =

8.8, 2.2 Hz, 2H), 1.87 (m, J = 6.6 Hz, 1H), 0.98 (d, J = 6.6 Hz, 6H) ; ^{13}C NMR ($CDCl_3$, 100MHz) : δ 177.8, 136.7, 134.6, 129.8 (2C), 128.5 (2C), 126.8, 115.7, 102.1, 92.1, 90.1, 79.1, 29.1, 28.1, 22.0 (2C) ppm; HRMS (EI) cacld. for 236.1201, found 236.1200; Chemical Formula: $C_{17}H_{16}O$

(Z)-8,8-Dimethyl-1-phenylnona-4-en-2,6-diyn-1-one (1e)

brown liquid; R_f = 0.62 (*n*-hexane/ethyl acetate = 20/1 as eluent); ^{1}H NMR ($CDCl_3$, 400 MHz) : δ 8.23 (d, J = 7.4Hz, 2H), 7.61-7.47 (m, 3H), 6.17 (d, J = 10.6 Hz, 1H), 5.98 (d, J = 10.6 Hz, 1H), 1.30 (s, 9H) ; ^{13}C NMR ($CDCl_3$, 100MHz) : δ 177.6, 135.1, 134.6, 129.7 (2C), 128.4 (2C), 124.3, 115.5, 103.9, 93.8, 89.9, 78.9, 31.2 (3C), 28.6ppm; HRMS (EI) calcd. for $C_{17}H_{16}O$ 236.1201, found 236.1199.

(Z)-1,7-Diphenylhepta-4-en-2,6-diyn-1-one (1f)

brown liquid; R_f = 0.55 (*n*-hexane/ethyl acetate = 20/1 as eluent); ^{1}H NMR ($CDCl_3$, 400 MHz) : δ 8.25 (d, J = 7.8 Hz, 2H), 7.55-7.30 (m, 8H), 6.42 (d, J = 10.6 Hz, 1H), 6.12 (d, J = 10.6 Hz, 1H) ; ^{13}C NMR ($CDCl_3$, 100MHz) : δ 177.9, 135.6, 134.1, 130.1 (2C), 129.7 (2C), 129.3 (2C), 128.2 (2C), 127.8, 124.5, 117.3, 112.5, 109.7, 93.8 ppm; HRMS (EI) calcd. for $C_{19}H_{12}O$ 256.0888, found 256.0891.

(Z)-1-phenyl-7-o-tolylhepta-4-en-2,6-diyn-1-one (1g)

brown liquid; R_f = 0.54 (*n*-hexane/ethyl acetate = 20/1 as eluent); ^{1}H NMR ($CDCl_3$, 400 MHz) : δ 8.23 (d, J = 7.2 Hz, 2H), 7.54-7.22 (m, 7H), 6.46 (d, J = 10.8 Hz, 1H), 6.13 (d, J = 10.8 Hz, 1H), 2.43 (s, 3H) ; ^{13}C NMR ($CDCl_3$, 100MHz) : δ177.7, 140.8, 136.6, 134.0, 132.3, 129.7 (2C), 129.6, 129.3, 128.6, 128.5 (2C), 125.6, 116.2, 99.5, 92.9, 91.0, 90.3, 20.7 ppm; HRMS (EI) calcd. for $C_{12}H_{14}O$ 270.1045, found 270.1046.

(Z)-1-phenyl-7-m-tolylhepta-4-en-2,6-diyn-1-one (1h)

brown liquid; R_f = 0.58 (*n*-hexane/ethyl acetate = 20/1 as eluent); ^{1}H NMR ($CDCl_3$, 400 MHz) : δ 8.29 (d, *J* = 7.2 Hz, 2H), 7.55 (t, J = 7.2 Hz, 1H), 7.36-7.18 (m, 6H), 6.42 (d, J = 10.8 Hz, 1H), 6.13 (d, J = 10.8 Hz, 1H), 2.30 (s, 3H) ; ^{13}C NMR ($CDCl_3$, 100MHz) : δ 177.7, 138.1, 136.7, 134.0, 132.4, 130.2, 129.7 (2C), 129.0, 128.6, 128.5 (2C), 128.3, 126.3, 116.6, 100.9, 92.9, 89.7, 86.4, 21.1 ppm; HRMS (EI) calcd. for $C_{12}H_{14}O$ 270.1045, found 270.1043.

(Z)-1-phenyl-7-(p-tolyl)hepta-4-en-2,6-diyn-1-one (1i)

brown solid; m.p.: 46-48 ℃ R_f = 0.62 (*n*-hexane/ethyl acetate = 20/1 as eluent); ^{1}H NMR ($CDCl_3$, 400 MHz) : δ 8.27 (d, *J* = 7.2 Hz, 2H), 7.56 (t, *J* = 7.2Hz, 1H), 7.47-7.34 (m, 4H), 6.86 (d, *J* = 8.4 Hz, 2H), 6.40 (d, *J* = 10.8 Hz, 1H), 6.06 (d, *J* = 10.8 Hz, 1H), 3.82 (s, 3H); ^{13}C NMR ($CDCl_3$, 100MHz) : δ 177.7, 160.4, 136.7, 133.9, 133.5 (2C), 129.6 (2C), 129.4, 128.7, 129.5 (2C), 126.6, 115.6, 114.1 (2C), 101.2, 92.8, 90.1, 86.0, 55.3ppm; HRMS (EI) calcd. for $C_{20}H_{14}O_2$ 286.0994, found 286.0991.

(Z)-7-(2-methoxyphenyl)-1-phenylhepta-4-en-2,6-diyn-1-one (1j)

brown solid; m.p.: 40-42 ℃ R_f = 0.56 (*n*-hexane/ethyl acetate = 20/1 as eluent); ^{1}H NMR ($CDCl_3$, 400 MHz) : δ 8.28 (d, *J* = 7.2 Hz, 2H), 7.53-7.27 (m, 5H), 6.90 (d, *J* = 8.4 Hz, 1H), 6.96 (td, *J* = 7.4, 0.8 Hz, 1H), 6.50 (d, J = 10.6 Hz, 1H), 6.13 (d, J = 10.8 Hz, 1H), 3.77 (s, 3H) ; ^{13}C NMR ($CDCl_3$, 100MHz) : δ 177.8, 160.2, 136.7, 133.9, 130.9, 129.8 (2C), 128.4 (2C), 127.8, 126.5, 120.5, 116.2, 111.4, 110.6, 97.2, 91.3, 90.7, 90.0, 55.6 ppm; HRMS (EI) calcd. for $C_{20}H_{14}O_2$ 286.0994, found 286.0992.

(Z)-7-(3-methoxyphenyl)-1-phenylhepta-4-en-2,6-diyn-1-one (1k)

brown solid; m.p.: 48-50 ℃ R_f = 0.52 (*n*-hexane/ethyl acetate = 20/1 as eluent); ^{1}H

NMR ($CDCl_3$, 500 MHz) : δ 8.27 (dd, *J* = 8.5, 1.5 Hz, 2H), 7.55 (t, *J* = 7.5Hz, 1H), 7.35 (t, *J* = 7.5Hz, 2H),7.28-7.24 (m, 2H), 7.13 (dt, *J* = 7.5, 1 Hz, 1H), 7.05 (dd, *J* = 2.5, 1.5 Hz, 2H), 6.94 (ddd, *J* = 8, 2.5, 1 Hz, 1H), 6.41 (d, *J* = 10.5, 1H), 6.13 (d, *J* = 10.5, 1H), 3.75 (s, 3H); ^{13}C NMR ($CDCl_3$, 125MHz) : δ 177.7, 159.3, 136.7, 134.0, 129.7 (2C), 129.5, 128.6 (2C), 126.1, 124.4, 123.1, 117.0, 116.4, 116.2, 100.5, 93.0, 89.6, 86.5, 55.2 ppm; HRMS (EI) calcd. for $C_{20}H_{14}O_2$ 286.0994, found 286.0991.

(Z)-7-(4-methoxyphenyl)-1-phenylhepta-4-en-2,6-diyn-1-one (1l)

brown solid; m.p.: 46-48 ℃ R_f = 0.56 (*n*-hexane/ethyl acetate = 20/1 as eluent); ^1H NMR ($CDCl_3$, 400 MHz) : δ 8.27 (d, J = 7.2 Hz, 2H), 7.56 (t, J = 7.2 Hz, 1H), 7.34-7.47 (m, 5H), 6.86 (d, J = 8.4 Hz, 2H), 6.40 (d, J = 10.8 Hz, 1H), 6.06 (d, J = 10.8 Hz, 1H), 3.82 (s, 3H); ^{13}C NMR ($CDCl_3$, 100MHz) : δ 177.8, 160.5, 136.7, 133.9, 133.5(2C), 129.6(2C), 129.4, 128.5(2C), 126.6, 115.6, 114.1(2C), 101.2, 92.8, 90.1, 86.7, 55.3 ppm; HRMS (EI) calcd. for $C_{20}H_{14}O_2$ 286.0994, found 286.0992.

(Z)-7-(4-nitrophenyl)-1-phenylhepta-4-en-2,6-diyn-1-one (1m)

yellow solid; m.p.: 68-70 ℃ R_f = 0.48 (*n*-hexane/ethyl acetate = 20/1 as eluent); ^1H NMR ($CDCl_3$, 500 MHz) : δ 8.20-8.24 (m, 4H), 7.59-7.67 (m, 3H), 7.41 (t, J = 7.5 Hz, 2H), 6.43 (d, J = 10.5 Hz, 1H), 6.24 (d, J = 10.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125MHz) : δ 177.5, 147.6, 136.6, 134.3, 132.7(2C), 129.6(2C), 128.9, 128.6(2C), 124.9, 123.7(2C), 119.1, 97.5, 93.7, 90.9, 88.8 ppm; HRMS (EI) calcd. for $C_{19}H_{11}NO_3$ 301.0379, found 301.0380.

(Z)-1-(4-methoxyphenyl)trideca-4-en-2,6-diyn-1-one (1n)

brown liquid; R_f = 0.58 (*n*-hexane/ethyl acetate = 20/1 as eluent); ^1H NMR ($CDCl_3$, 500 MHz) : δ 8.22 (d, J = 9 Hz, 2H), 6.94 (d, J = 9 Hz, 2H), 6.14 (dt, J = 10.5, 2.5 Hz,

1H), 5.98 (d, J = 11 Hz, 1H), 3.88 (s,3H), 2.46 (td, J = 7.0, 2.0 Hz, 2H0, 1.58 (m, J = 7.5 Hz, 2H), 1.23-1.43 (m, 6H), 0.85 (t, J = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125MHz) : δ 176.4, 164.3, 132.2(2C), 130.3, 126.3, 115.9, 113.7(2C), 102.7, 92.1, 89.3, 78.3, 55.5, 31.3, 28.6, 28.4, 22.4, 19.9, 13.9 ppm; HRMS (EI) calcd. for $C_{20}H_{22}O_2$ 294.1620, found 294.1621.

(Z)-1-(4-methoxyphenyl)-7-phenylhepta-4-en-2,6-diyn-1-one (1o)

brown liquid; R_f = 0.55 (*n*-hexane/ethyl acetate = 20/1 as eluent); ^{1}H NMR ($CDCl_3$, 300 MHz) : δ 8.24 (d, J = 9.0 Hz, 2H), 7.32-7.55 (m, 5H), 6.76 (d, J = 9.0 Hz, 1H), 6.39 (d, J = 10.5 Hz, 1H), 6.13 (d, J = 10.8 Hz, 1H), 3.80 (s, 3H) ppm; HRMS (EI) calcd. for $C_{20}H_{14}O_2$ 286.0994, found 286.0992.

(Z)-1,7-bis(4-methoxyphenyl)hepta-4-en-2,6-diyn-1-one (1p)

orange liquid; R_f = 0.48 (*n*-hexane/ethyl acetate = 20/1 as eluent); ^{1}H NMR ($CDCl_3$, 500 MHz) : δ 8.24 (d, *J* = 9 Hz, 2H), 7.48 (d, *J* = 9 Hz, 2H), 6.88 (d, *J* = 9 Hz, 2H), 6.79 (d, *J* = 9 Hz, 2H), 6.38 (d, *J* = 10.5 Hz, 1H), 6.07 (d, *J* = 10.5 Hz, 1H), 3.83 (s, 3H), 3.82 (s, 1H); ^{13}C NMR ($CDCl_3$, 125MHz) : δ176.4, 164.3, 160.4, 133.6 (2C), 132.1 (2C), 130.2, 126.1, 116.1, 114.4, 114.1 (2C), 113.8 (2C), 100.7, 93.0, 89.3, 86.1, 55.4, 55.3ppm; HRMS (EI) calcd. for $C_{21}H_{16}O_3$ 316.1099, found 316.1099

(Z)-4-(7-(4-methoxyphenyl)-7-oxohepta-3-en-1,5-diynyl)benzonitrile (1q)

Yellow solid; m.p.: 56-58 ℃ R_f = 0.62 (*n*-hexane/ethyl acetate = 20/1 as eluent); ^{1}H NMR ($CDCl_3$, 500 MHz) : δ 8.18 (d, *J* = 9 Hz, 2H), 7.64-7.59 (m, 4H), 6.83 (d, *J* = 9 Hz, 2H), 6.38 (d, *J* = 10.5 Hz, 1H), 6.20 (d, *J* = 10.5 Hz, 1H), 3.85 (s, 3H); ^{13}C NMR ($CDCl_3$, 125MHz) : δ176.1, 164.5, 132.4 (2C), 132.1 (2C), 132.0 (2C), 130.0, 127.1, 124.5, 119.0, 118.2, 113.8 (2C), 112.4, 97.6, 93.8, 90.4, 88.2, 55.5 ppm; HRMS (EI)

calcd. for $C_{21}H_{13}NO_2$ 311.0946, found 311.0946.

(Z)-1-(4-(trifluoromethyl)phenyl)trideca-4-en-2,6-diyn-1-one (1r)

brown liquid; R_f = 0.57 (*n*-hexane/ethyl acetate = 20/1 as eluent); ^{1}H NMR ($CDCl_3$, 500 MHz) : δ8.37 (d, *J* = 8 Hz, 2H), 7.75 (d, *J* = 8 Hz, 2H), 6.23 (dt, *J* = 11, 2.5 Hz), 6.01 (d, *J* = 11Hz), 2.47 (td, *J* = 7.5, 2.5 Hz, 2H), 1.59 (quintet, *J* = 7.5 Hz, 2H), 1.40 (quintet, *J* = 7.5 Hz, 2H), 1.26 (m, 4H), 0.85 (t, *J* = 7 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125MHz) : δ176.4, 139.3, 130.0 (2C), 127.8, 125.5 (quartet, *J* = 3.6 Hz), 115.3, 103.7, 91.5, 91.4, 78.3, 31.2, 28.6, 28.4, 22.4, 20.0, 13.9 ppm; HRMS (EI) calcd. for $C_{20}H_{19}F_3O$ 332.1388, found 332.1391.

Data of compound 8a-8r

7-Hexyl-2-phenylpyrazolo[1,5-a]pyridine (8a)

brown liquid; R_f = 0.69 (*n*-hexane/ethyl acetate = 10/1 as eluent); ^{1}H NMR ($CDCl_3$, 400 MHz) : δ 8.03 (dt, *J* = 7.2, 1.2 Hz, 2H), 7.48-7.35 (m, 4H), 7.05 (dd, *J* = 9.2, 7.0 Hz, 1H), 6.28 (s, 1H), 6.58 (dt, *J* = 6.8, 0.8 Hz, 1H), 3.22 (t, *J* = 7.6 Hz, 2H), 1.92 (m, 2H), 1.52-1.25 (m, 8H), 0.93 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$. 50MHz) : δ 152.6, 128.6 (2C), 128.1, 126.5 (3C), 123.3, 115.3, 109.6, 93.6, 31.6, 30.9, 29.6, 29.1, 26.1, 22.6, 14.8; ^{13}C NMR ($CDCl_3$, 100MHz) : δ 152.5, 142.2, 133.7, 128.6 (2C), 128.1, 126.5 (2C), 123.2, 115.2, 109.5, 31.6, 30.9, 29.1, 26.1, 22.5, 14.0 ppm; HRMS (EI) calcd. for $C_{19}H_{22}N_2$ 278.1783, found 278.1780.

7-Butyl-2-phenylpyrazolo[1,5-a]pyridine (8b)

brown liquid; R_f = 0.67 (*n*-hexane/ethyl acetate = 10/1 as eluent); ^{1}H NMR ($CDCl_3$, 400 MHz) : δ 8.11 (dt, *J* = 8.4, 1.8 Hz, 2H), 7.53-7.36 (m, 4H), 7.16 (dd, *J* = 9.0, 7.0 Hz, 1H), 6.80 (s, 1H), 6.65 (dt, *J* = 6.8, 0.8 Hz, 1H), 3.20 (t, *J* = 7.6 Hz, 2H), 1.90 (m,

J = 7.2 Hz, 2H), 1.60 (m, *J* = 7.0 Hz, 2H), 1.02 (t, *J* = 7.4Hz, 3H) ; ^{13}C NMR ($CDCl_3$, 100MHz) : δ 152.5, 142.2, 142.0 133.7, 128.6 (2C), 128.1, 126.5 (2C), 122.1, 116.5, 109.5, 93.4, 31.5, 31.4, 22.3, 14.1 ppm; HRMS (EI) calcd. for $C_{17}H_{18}N_2$ 250.1470, found 250.1469.

7-pentyl-2-phenylpyrazolo[1,5-a]pyridine (8c)

brown liquid; R_f = 0.61 (*n*-hexane/ethyl acetate = 10/1 as eluent); ^{1}H NMR ($CDCl_3$, 400 MHz) : δ 8.04 (dt, *J* = 7.2, 1.6 Hz, 2H), 7.48-7.34 (m, 4H), 7.07 (dd, *J* = 8.8, 6.8 Hz, 1H), 6.82 (s, 1H), 6.59 (dt, *J* = 6.8, 0.8 Hz, 1H) 3.24 (t, *J* = 8 Hz, 2H), 1.96 (q, *J* = 7.6 Hz, 2H), 1.50 (m, 4H), 0.97 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100MHz) : δ 152.5, 142.2, 142.0, 133.7, 128.6 (2C), 128,1, 126.5 (2C), 123.2, 115.2, 109.5, 93.6, 31.6, 30.9, 25.8, 22.4, 14.0 ppm; HRMS (EI) calcd. for $C_{18}H_{20}N_2$ 264.1626, found 264.1629.

7-Isobutyl-2-phenylpyrazolo[1,5-a]pyridine (8d)

brown liquid; R_f = 0.58 (*n*-hexane/ethyl acetate = 10/1 as eluent); ^{1}H NMR ($CDCl_3$, 400 MHz) : δ 8.02 (dt, *J* = 6.8, 1.6 Hz, 2H), 7.49-7.30 (m, 4H), 7.05 (dd, *J* = 8.8, 6.8 Hz, 1H), 6.81 (s, 1H), 6.55 (dt, *J* = 7.0, 0.8 Hz, 1H), 3.08 (d, *J* = 7.0 Hz, 2H), 2.50 (m, *J* = 6.8 Hz, 1H), 1.03 (d, *J* = 6.6 Hz, 6H) ; ^{13}C NMR ($CDCl_3$, 100MHz) : δ 152.4, 142.1, 141.1, 128.6 (2C), 128.1, 126.5 (2C), 123.1, 115.4, 110.9, 93.5, 40.4, 25.3, 22.7 (2C) ppm; HRMS (EI) calcd. for $C_{17}H_{18}N_2$ 250.1470, found 250.1469.

7-tert-butyl-2-phenylpyrazolo[1,5-a]pyridine (8e)

brown liquid; R_f = 0.60 (*n*-hexane/ethyl acetate = 10/1 as eluent); ^{1}H NMR ($CDCl_3$, 400 MHz) : δ 8.03 (dt, *J* = 6.8, 1.6 Hz, 2H), 7.47-7.33 (m, 4H), 7.04 (dd, *J* = 8.8, 6.8 Hz, 1H), 6.80 (s,1H), 6.65 (dd, *J* = 7.2, 1.2 Hz, 1H), 1.68 (s, 9H) ; ^{13}C NMR ($CDCl_3$,

100MHz) : δ 152.5, 142.2, 141.1, 133.7, 128.6 (2C), 128.1, 126.5 (2C), 122.1, 115.6, 109.5, 93.5, 31.7, 30.3 (3C) ppm; HRMS (EI) calcd. for $C_{17}H_{18}N_2$ 250.1470, found 250.1467.

2,7-Diphenylpyrazolo[1,5-a]pyridine (8f)

brown liquid; R_f = 0.52 (*n*-hexane/ethyl acetate = 10/1 as eluent); ^{1}H NMR ($CDCl_3$, 400 MHz) : δ 8.10-8.02 (m, 4H), 7.56-7.35 (m, 7H), 7.18 (dd, *J* = 8.8, 7.0 Hz, 1H), 6.91 (s, 1H), 6.84 (dd, *J* = 7.0, 1.6 Hz, 1H) ; ^{13}C NMR ($CDCl_3$, 100MHz) : δ 152.7, 142.7, 140.2, 133.6, 133.4, 129.3 (2C), 129.2, 128.5 (2C), 128.2, 128.1 (2C), 126.5 (2C), 123.4, 116.7, 112.4, 93.8 ppm; HRMS (EI) calcd. for $C_{19}H_{14}N_2$ 270.1157, found 270.1158.

2-phenyl-7-o-tolylpyrazolo[1,5-a]pyridine (8g)

brown liquid; R_f = 0.48 (*n*-hexane/ethyl acetate = 10/1 as eluent); ^{1}H NMR ($CDCl_3$, 400 MHz) : δ 7.90 (dt, *J* = 8.8, 1.6 Hz, 2H), 7.55 (dd, *J* = 8.8, 12. Hz, 1H), 7.45-7.28 (m, 7H), 7.17 (dd, *J* = 8.8, 6.8 Hz, 1H), 6.88 (S, 1H), 6.67 (dd, *J* = 6.4, 1.2 Hz, 1H), 2.19 (S, 3H) ; ^{13}C NMR ($CDCl_3$, 100MHz) : δ 153.1, 142.1, 140.9, 138.1, 133.9, 133.4, 130.0, 129.1, 128.4 (2C), 128.1, 126.5 (2C), 125.6, 123.1, 116.8, 112.9, 93.7, 19.8 ppm; HRMS (EI) calcd. for $C_{20}H_{16}N_2$ 284.1313, found 284.1311.

2-phenyl-7-m-tolylpyrazolo[1,5-a]pyridine (8h)

brown liquid; R_f = 0.43 (*n*-hexane/ethyl acetate = 10/1 as eluent); ^{1}H NMR ($CDCl_3$, 400 MHz) : δ 7.58 (dt, *J* = 8.8, 1.2 Hz, 2H), 6.96-6.54 (m, 10H), 6.10 (S, 1H), 2.14 (S, 3H) ; ^{13}C NMR ($CDCl_3$, 100MHz) : δ 155.4, 147.1, 136.9, 133.8, 131.5, 128.6, 128.2, 128.1, 127.7, 127.4 (2C), 126.8, 126.6 (2C), 105.1, 101.2, 92.5, 21.1 ppm; HRMS (EI) calcd. for $C_{20}H_{16}N_2$ 284.1313, found 284.1314.

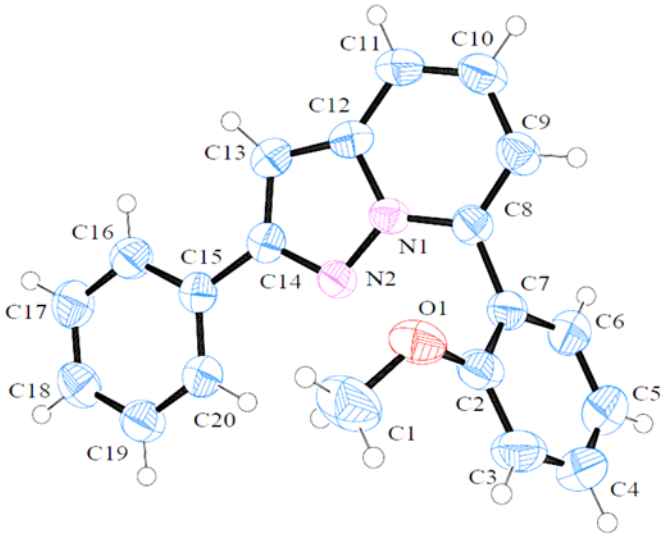
2-phenyl-7-p-tolylpyrazolo[1,5-a]pyridine(8i)

brown liquid; R_f = 0.43 (*n*-hexane/ethyl acetate = 10/1 as eluent); ^{1}H NMR ($CDCl_3$, 500 MHz) : δ 8.00-7.96 (m, 4H), 7.51 (dd, *J* = 8.5, 1 Hz, 1H), 7.44 (t, *J* = 7.5 Hz, 2H), 7.36-7.33 (m, 3H), 7.18 (dd, *J* = 8.5, 7 Hz, 1H), 6.89 (s, 1H), 6.83 (dd, *J* = 7, 1.5 Hz, 1H) 2.47 (s, 3H); ^{13}C NMR ($CDCl_3$, 125MHz) : δ 152.7, 142.7, 140.4, 139.3, 133.5, 130.7, 129.2 (2C), 128.8 (2C), 128.5 (2C), 126.5 (2C), 123.5, 116.4, 112.1, 93.7 pmm; HRMS (EI) calcd. for $C_{20}H_{16}N_2$ 284.1313, found 284.1311.

7-(2-methoxyphenyl)-2-phenylpyrazolo[1,5-a]pyridine (8j)

White solid; m.p.: 165-167℃; R_f = 0.50 (*n*-hexane/ethyl acetate = 10/1 as eluent); ^{1}H NMR ($CDCl_3$, 400 MHz) : δ 7.91 (dt, *J* = 6.8, 1.6 Hz, 2H), 7.57-7.47 (m, 3H), 7.39-7.27 (m, 3H), 7.17-7.08 (m, 3H), 6.86 (S, 1H), 6.76 (dd, *J* = 6.8, 1.2 Hz, 1H), 3.79 (S, 3H) ; ^{13}C NMR ($CDCl_3$, 100MHz) : δ 157.8, 142.1, 131.2, 130.6, 128.4 (2C), 128.0, 126.5 (2C), 123.0, 120.5, 116.8, 113.2, 111.6, 93.6, 55.8 ppm; HRMS (EI) calcd. for $C_{20}H_{16}N_2O$ 300.1263, found 300.1263.

X-ray Crystal Data for ***8j*** :



Empirical formula	$C_{20}H_{16}N_2O$

Formula weight	300.35
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	C 2/c
Unit cell dimensions	a = 23.0916(13) Å = 90°.
	b = 7.3204(4) Å = 97.320(3)°.
	c = 38.0041(18) Å = 90°.
Volume	6371.8(6) $Å^3$
Z	16
Density (calculated)	1.252 Mg/m^3
Absorption coefficient	0.078 mm^{-1}
F(000)	2528
Crystal size	0.29 x 0.24 x 0.11 mm^3
Theta range for data collection	1.78 to 25.02°.
Index ranges	-27<=h<=24, -8<=k<=8, -43<=l<=45
Reflections collected	21286
Independent reflections	5605 [R(int) = 0.0350]
Completeness to theta = 25.02°	99.5 %
Absorption correction	multi-scan
Max. and min. transmission	0.9914 and 0.9777
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5605 / 0 / 415
Goodness-of-fit on F^2	1.041
Final R indices [I>2sigma(I)]	R1 = 0.0454, wR2 = 0.1279

R indices (all data)	R1 = 0.0688, wR2 = 0.1535
Largest diff. peak and hole	0.174 and -0.303 e.Å^{-3}

Crystallographic data for the structure have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC **XXXXXX**. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [e-mail: data_request@ccdc.cam.ac.uk, or fax: +44-1223-336033].

7-(3-methoxyphenyl)-2-phenylpyrazolo[1,5-a]pyridine(8k)

yellow solid; m.p.: 180-182℃; R_f = 0.48 (*n*-hexane/ethyl acetate = 10/1 as eluent); ^{1}H NMR ($CDCl_3$, 500 MHz) : δ 8.00 (d, *J* = 7.5 Hz, 2H), 7.72 (s, 1H), 7.60 (d, *J* = 8 Hz, 1H), 7.53 (dd, *J* = 8 Hz, 1H), 7.46 (m, 3H), 7.36 (t, *J* = 7.5 Hz, 1H), 7.18 (dd, *J* = 8.5, 7 Hz, 1H), 7.07 (dd, *J* = 8, 2.5 Hz, 1H), 6.90 (s, 1H), 6.87 (dd, *J* = 6.5, 1 Hz, 1H) 3.91 (s, 3H); ^{13}C NMR ($CDCl_3$, 125MHz) : δ 159.2, 152.7, 142.7, 140.0, 134.8, 133.4, 129.2, 128.5 (2C), 128.2, 126.5 (2C), 123.4, 121.7, 116.8, 115.3,114.6, 112.4, 93.8, 55.3 ppm; HRMS (EI) calcd. for $C_{20}H_{16}N_2O$ 300.1263, found 300.1261.

7-(4-methoxyphenyl)-2-phenylpyrazolo[1,5-a]pyridine (8l)

brown liquid; R_f = 0.51 (*n*-hexane/ethyl acetate = 10/1 as eluent); ^{1}H NMR ($CDCl_3$, 400 MHz) : δ 8.05 (dt, *J* = 8.8, 2.0 Hz, 2H), 7.98-7.35 (m, 4H), 7.15 (dd, *J* = 8.8, 6.8 Hz, 2H), 6.88 (s, 1H), 6.80 (dd, *J* = 6.8, 1.2 Hz, 1H), 3.90 (s, 3H) ; ^{13}C NMR ($CDCl_3$, 100MHz) : δ 160.3, 152.6, 142.8, 104.1, 133.4, 130.7 (2C), 128.5 (2C), 128.3, 128.1, 126.5 (2C), 123.6, 116.1, 113.5 (2C), 111.7, 93.7, 55.3 ppm; HRMS (EI) calcd. for $C_{20}H_{16}N_2O$ 300.1263, found 300.1262.

7-(4-nitrophenyl)-2-phenylpyrazolo[1,5-a]pyridine (8m)

orange solid; m.p.: 155-158℃; R_f = 0.32 (*n*-hexane/ethyl acetate = 10/1 as eluent); ^{1}H NMR ($CDCl_3$, 500 MHz) : δ 8.41 (d, *J* = 9 Hz, 2H), 8.28 (d, *J* = 9 Hz, 2H), 7.96 (d, *J* = 7 Hz, 2H), 7.62 (dd, *J* = 9, 1.5 Hz, 1H), 7.45 (t, *J* = 7.5 Hz, 2H), 7.38 (t, *J* = 7.5 Hz, 1H), 7.23 (dd, *J* = 8.5, 7 Hz, 1H), 6.94 (s, 1H), 6.93 (dd, *J* = 7 Hz, 1, 1H) ; ^{13}C NMR ($CDCl_3$, 125MHz) : δ 153.2, 148.0, 142.7, 139.8, 137.8, 132.9, 130.2 (2C), 128.7 (2C), 128.5, 126.5 (2C), 123.4 (2C), 123.3, 118.4, 113.4, 94.5 ; HRMS (EI) calcd. for $C_{19}H_{13}N_3O_2$ 315.1008, found 315.1010.

7-hexyl-2-(4-methoxyphenyl)pyrazolo[1,5-a]pyridine (8n)

brown liquid; R_f = 0.56 (*n*-hexane/ethyl acetate = 10/1 as eluent); ^{1}H NMR ($CDCl_3$, 500 MHz) : δ7.97 (d, *J* = 9 Hz, 2H), 7.39 (d, *J* = 8.5 Hz, 1H), 7.05 (dd, *J* = 8.5, 7 Hz, 1H), 7.00 (d, *J* = 9 Hz, 2H), 6.73 (s, 1H), 6.56 (d, *J* = 7 Hz, 1H), 3.86 (s, 3H), 3.22(t, *J* = 7.5 Hz, 2H), 1.94 (q, *J* = 7.5 Hz, 2H), 1.53 (q, *J* = 7 Hz, 2H), 1.43 (m, 4H), 0.94 (t, *J* = 7 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125MHz) : δ 159.6,152.4, 142.1, 142.0, 127.7 (2C), 126.5, 123.1, 115.0, 114.0 (2C), 109.2, 92.9, 55.2, 31.6, 30.9, 29.1, 26.1, 22.5, 14.0; HRMS (EI) calcd. for $C_{20}H_{24}N_2O$ 308.1889, found 308.1889.

2-(4-methoxyphenyl)-7-phenylpyrazolo[1,5-a]pyridine (8o)

brown solid; m.p.: 158-160℃; R_f = 0.52 (*n*-hexane/ethyl acetate = 10/1 as eluent); ^{1}H NMR ($CDCl_3$, 500 MHz) : δ8.07 (d, *J* = 7 Hz, 2H), 7.92 (d, *J* = 8.5 Hz, 1H), 7.56-7.48 (m, 4H), 7.16 (dd, *J* = 9, 7 Hz, 1H), 6.97 (d, *J* = 9 Hz, 2H), 6.82 (s, 1H), 6.56 (dd, *J* = 7, 1 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125MHz) : δ159.7, 152.6, 142.7, 140.2, 133.7, 129.3 (2C), 129.2 (2C), 128.1 (2C), 127.7 (2C), 126.2, 123.4, 116.5, 113.9, 112.1, 93.2, 55.2 ppm; HRMS (EI) calcd. for $C_{20}H_{16}N_2O$ 300.1263, found 300.1265.

2,7-bis(4-methoxyphenyl)pyrazolo[1,5-a]pyridine (8p)

green solid; m.p.: 170-172℃; R_f = 0.54 (*n*-hexane/ethyl acetate = 10/1 as eluent) ; ^{1}H NMR ($CDCl_3$, 500 MHz) : δ 8.05 (d, *J* = 9 Hz, 2H), 7.92 (d, *J* = 9 Hz, 2H), 7.47 (dd, *J* = 9, 1.5 Hz, 1H), 7.15 (dd, *J* = 9, 7 Hz, 1H), 7.07 (d, *J* = 8.5 Hz, 2H), 6.97 (d, *J* = 8.5 Hz, 2H), 6.80 (s, 1H), 6.78 (dd, *J* = 7, 1.5 Hz, 1H), 3.91 (s, 1H), 3.85 (s, 1H); ^{13}C NMR ($CDCl_3$, 125MHz) : δ 160.3, 159.7, 152.5, 142.8, 140.0, 130.7 (2C), 127,7 (2C), 126.2, 126.1, 123.5, 115.9, 113.9(2C), 113.5(2C), 111.4, 93.1, 55.3, 55.2ppm; HRMS (EI) calcd. for $C_{21}H_{18}N_2O_2$ 330.1368, found 330.1368.

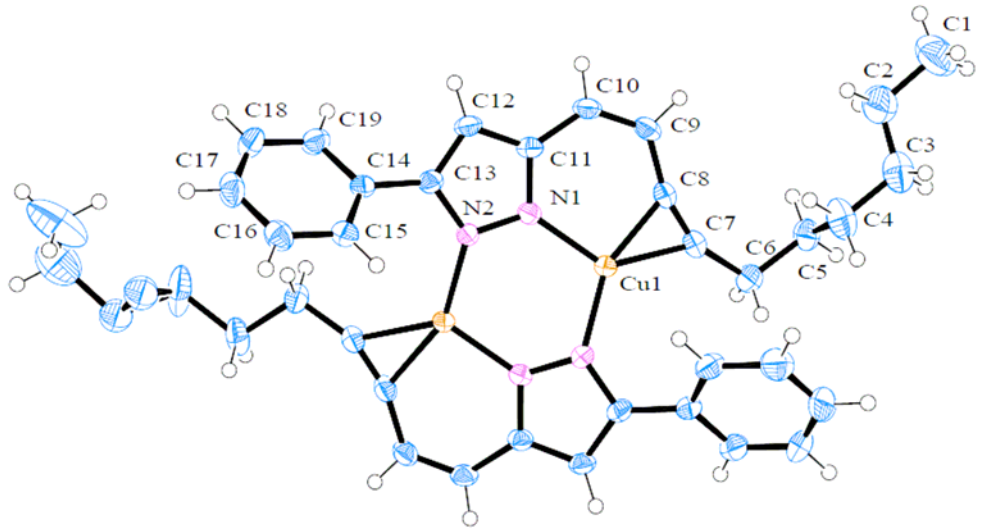
4-(2-(4-methoxyphenyl)pyrazolo[1,5-a]pyridin-7-yl)benzonitrile (8q)

yellow solid; m.p.: 154-156℃; R_f = 0.42 *n*-hexane/ethyl acetate = 10/1 as eluent); ^{1}H NMR ($CDCl_3$, 500 MHz) : δ 8.20 (d, *J* = 8.5 Hz, 2H), 7.88 (d, *J* = 8.5 Hz, 2H), 7.82 (d, *J* = 8.5 Hz, 2H), 7.56 (dd, *J* = 9, 1 Hz, 1H), 7.19 (dd, *J* = 8.5, 7 Hz, 1H), 6.97 (d, *J* = 8.5 Hz, 2H), 6.85-6.83 (2H), 3.59 (s, 3H); ^{13}C NMR ($CDCl_3$, 125MHz) : δ 159.9, 153.0, 142.7, 138.0, 131.9(2C), 129.8 (2C), 127.7 (2C), 125.7, 123.2, 118.6, 117.9, 114.0 (2C), 112.9, 112.6, 93.7, 55.3; HRMS (EI) calcd. for $C_{21}H_{15}N_3O$ 325.1215, found 325.1212.

7-hexyl-2-(4-(trifluoromethyl)phenyl)pyrazolo[1,5-a]pyridine (8r)

brown liquid; R_f = 0.51 *n*-hexane/ethyl acetate = 10/1 as eluent); ^{1}H NMR ($CDCl_3$, 500 MHz) : δ8.13 (d, *J* = 8 Hz, 2H), 7.71 (d, *J* = 8 Hz, 2H), 7.44 (d, *J* = 9 Hz, 1H), 7.10 (dd, *J* = 9, 7 Hz, 1H), 6.86 (s, 1H), 6.63 (d, *J* = 6.5 Hz, 1H), 3.22 (t, *J* = 8 Hz, 2H), 1.90 (quintet, *J* = 7.5 Hz, 2H), 1.50 (quintet, *J* = 7 Hz, 2H), 1.38, (m, 4H), 0.93 (t, *J* = 7 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125MHz) : δ 150.9, 142.3, 142.1, 137.2, 129.9 (quartet, J_{C-F} = 64.5 Hz, 2C), 124.3 (quartet, J_{C-F} = 270.1 Hz), 126.6 (2C), 125.5 (quartet, J_{C-F} = 4.1 Hz), 123.6, 115.5, 110.1, 94.1, 31.5, 30.9, 29.1, 26.1, 22.5, 14.0 ppm; HRMS (EI) calcd. for $C_{20}H_{21}F_3N_2$ 346.1657, found 346.1658.

X-ray Crystal Data for ***9a*** :

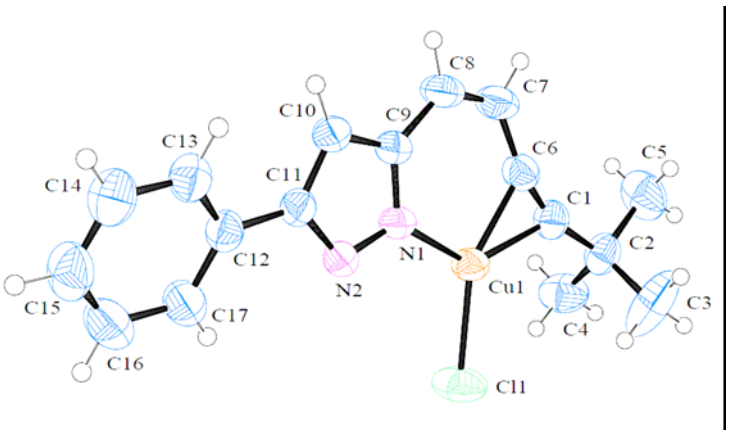


Empirical formula	$C_{38}H_{42}Cu_2N_4$	
Formula weight	681.84	
Temperature	200(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/a	
Unit cell dimensions	a = 14.2593(3) Å	= 90°.
	b = 12.1166(3) Å	= 101.7380(10)°
	c = 19.4748(5) Å	= 90°.
Volume	3294.38(14) $Å^3$	
Z	4	
Density (calculated)	1.375 Mg/m^3	

Absorption coefficient	1.324 mm^{-1}
F(000)	1424
Crystal size	0.6 x 0.5 x 0.25 mm^3
Theta range for data collection	2.14 to 25.35°.
Index ranges	-17<=h<=17, -13<=k<=14, -18<=l<=23
Reflections collected	19908
Independent reflections	5936 [R(int) = 0.0637]
Completeness to theta = 25.35°	98.3 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.635 and 0.4947
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5936 / 0 / 397
Goodness-of-fit on F^2	1.037
Final R indices [I>2sigma(I)]	R1 = 0.0432, wR2 = 0.1097
R indices (all data)	R1 = 0.0580, wR2 = 0.1192
Largest diff. peak and hole	0.733 and -0.582 e.$Å^{-3}$

Crystallographic data for the structure have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC **XXXXXX**. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [e-mail: data_request@ccdc.cam.ac.uk, or fax: +44-1223-336033].

*X-ray Crystal Data for **9e*** :



Empirical formula	$C_{17}H_{19}ClCuN_2O$
Formula weight	366.33
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P -1
Unit cell dimensions	a = 9.3101(2) Å = 69.3330(10)
	b = 9.2508(3) Å = 84.4530(10)
	c = 11.2420(4) Å = 76.7640(10)
Volume	881.72(5) $Å^3$
Z	2
Density (calculated)	1.380 Mg/m^3
Absorption coefficient	1.392 mm^{-1}
F(000)	378
Crystal size	0.6 x 0.42 x 0.15 mm^3
Theta range for data collection	2.25 to 25.05
Index ranges	-11<=h<=11, -10<=k<=11, -13<=l<=13
Reflections collected	6959
Independent reflections	3083 [R(int) = 0.0495]
Completeness to theta = 25.05?	99.1 %

Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7228 and 0.5248
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3083 / 0 / 196
Goodness-of-fit on F^2	1.038
Final R indices [I>2sigma(I)]	R1 = 0.0799, wR2 = 0.1958
R indices (all data)	R1 = 0.0866, wR2 = 0.2017
Largest diff. peak and hole	2.787 and -3.062 e.Å $^{-3}$

Crystallographic data for the structure have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC **XXXXXX**. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [e-mail: data_request@ccdc.cam.ac.uk, or fax: +44-1223-336033].

Reference

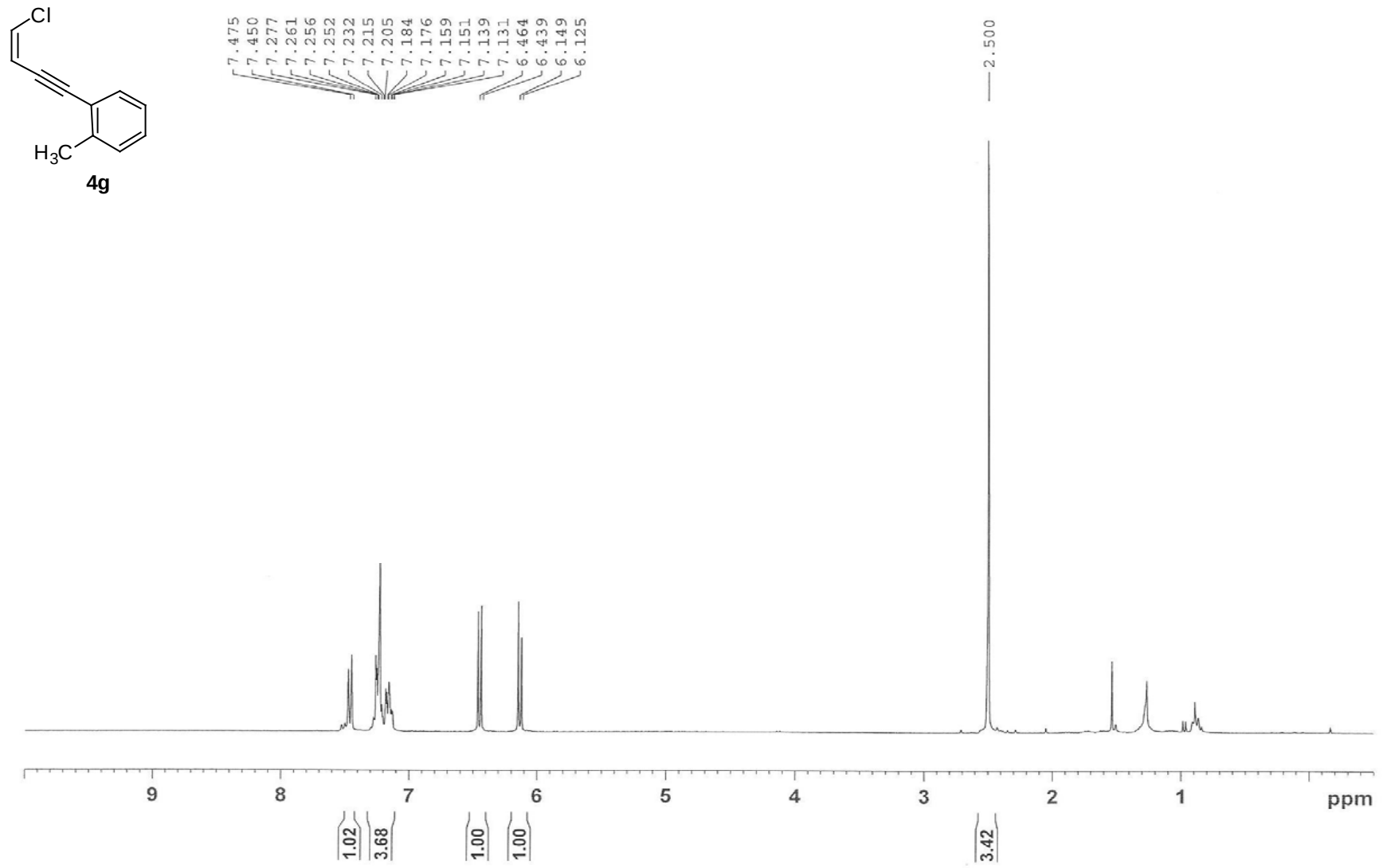
[1]. C. Y. Lee, C. F. Lin, J. L. Lee, C. C. Chiu, W. D. Lu, M. J. Wu, *J. Org. Chem*. **2004**, *69*, 2106-2110.

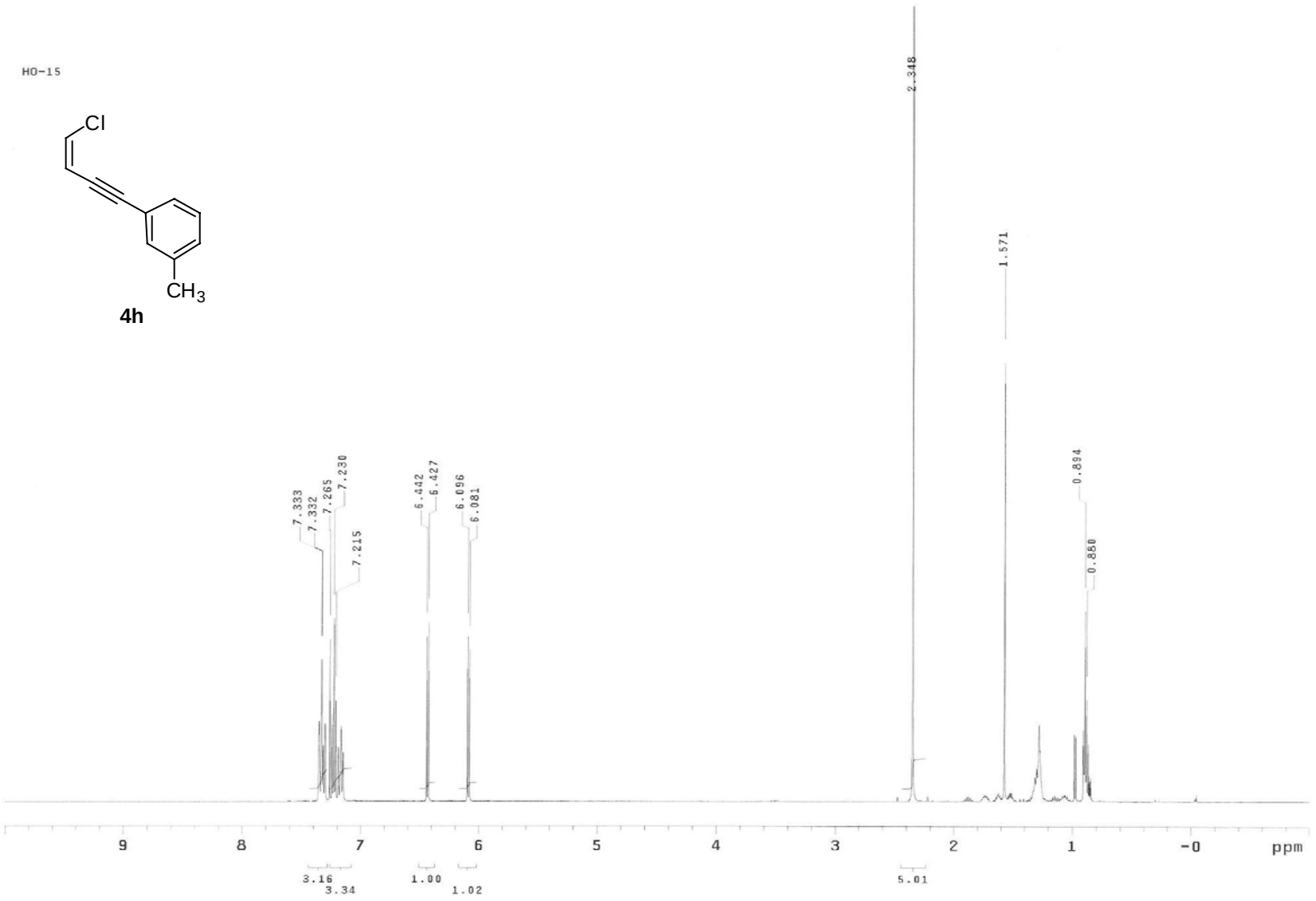
[2]. O. Loreau, A. Maret, J. M. Chardigny, J. L. Sebedio, J. P. Noel, Chemistry and physics of lipids **2001** *110*, 57-67.

[3]. C. Kosinski, A. Hirsch, FW Heine- mann, F. Hampel, *Eur*. *J*. *Org. Chem*. **2001**, *20,* 3879-3890.

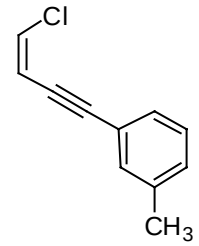
[4]. A. Tikad, A. Hamze, O. Provot, J. D. Brion, M. Alami, *Eur*. *J*. *Org. Chem*. **2010**, *4,* 725-731.

[5]. O. Provot, A. Giraud, J. F. Peyrat, M. Alami, J. D. Brion, *Tetrahedron Lett.* **2005**, *46*, 8547-8550.

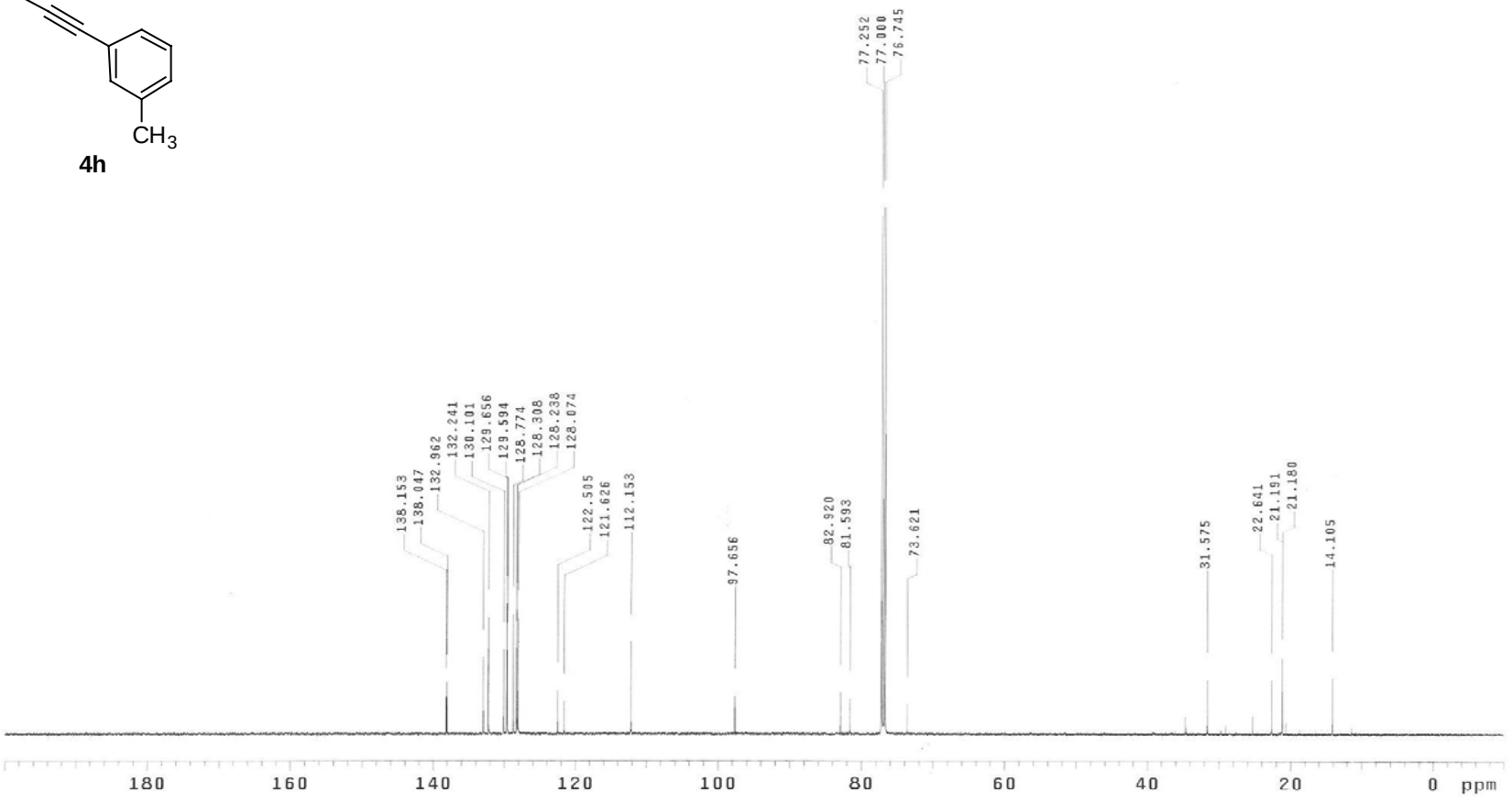

Cl
H3C
4g
7.475
7.450
7.277
7.261
7.256
7.252
7.232
7.215
7.205
7.184
7.176
7.159
7.151
7.139
7.131
6.464
6.439
6.149
6.125
2.500
9
8
7
6
5
4
3
2
1
ppm
1.02
3.68
1.00
1.00
3.42

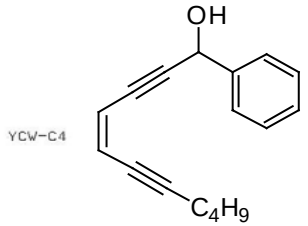

HO-15
Cl
CH3
4h
2.348
1.571
0.894
0.880
7.333
7.332
7.265
7.230
7.215
6.442
6.427
6.096
6.081
9
8
7
6
5
4
3
2
1
-0
ppm
3.16
3.34
1.00
1.02
5.01

HO-15

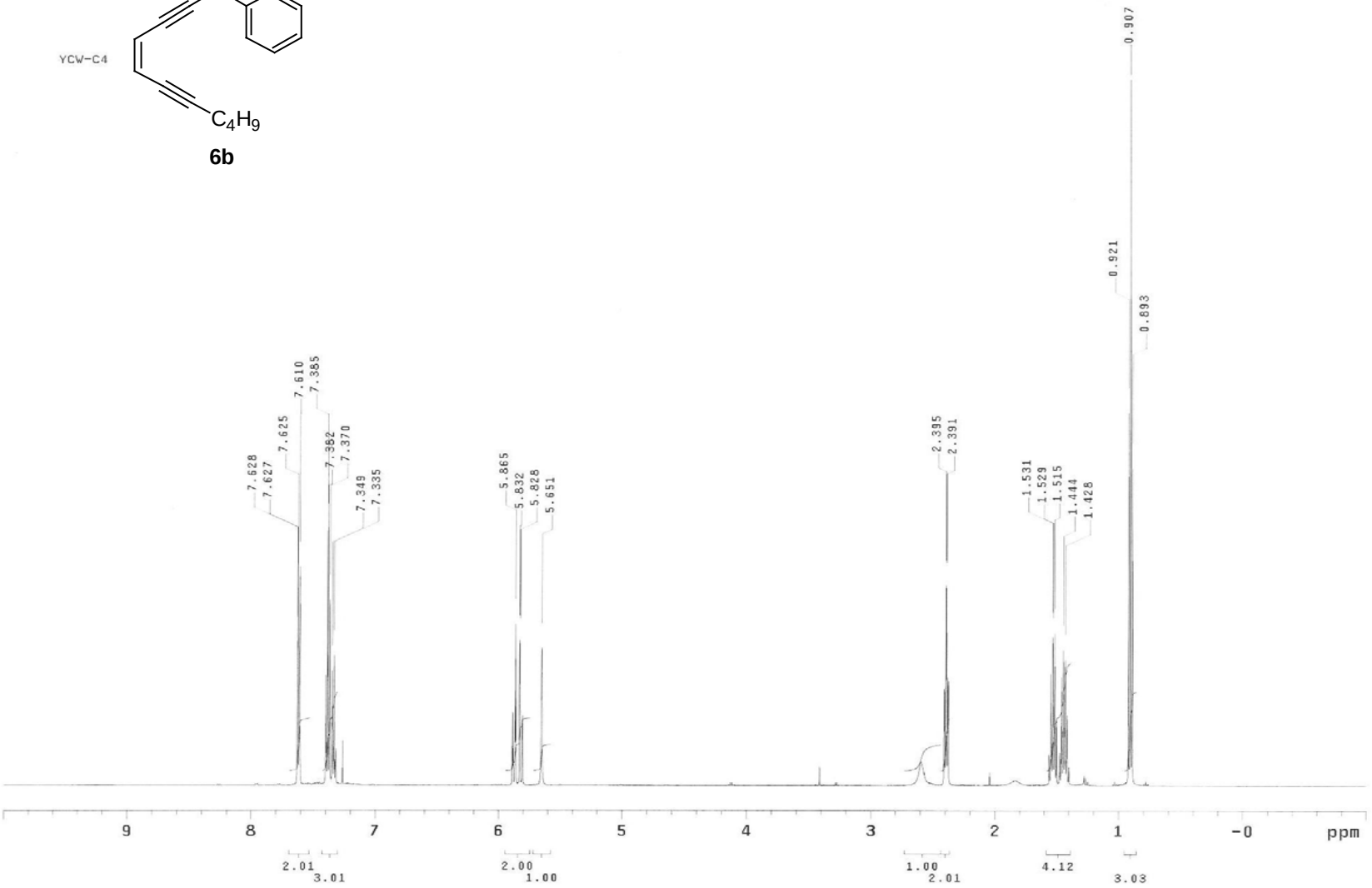

Cl
CH3

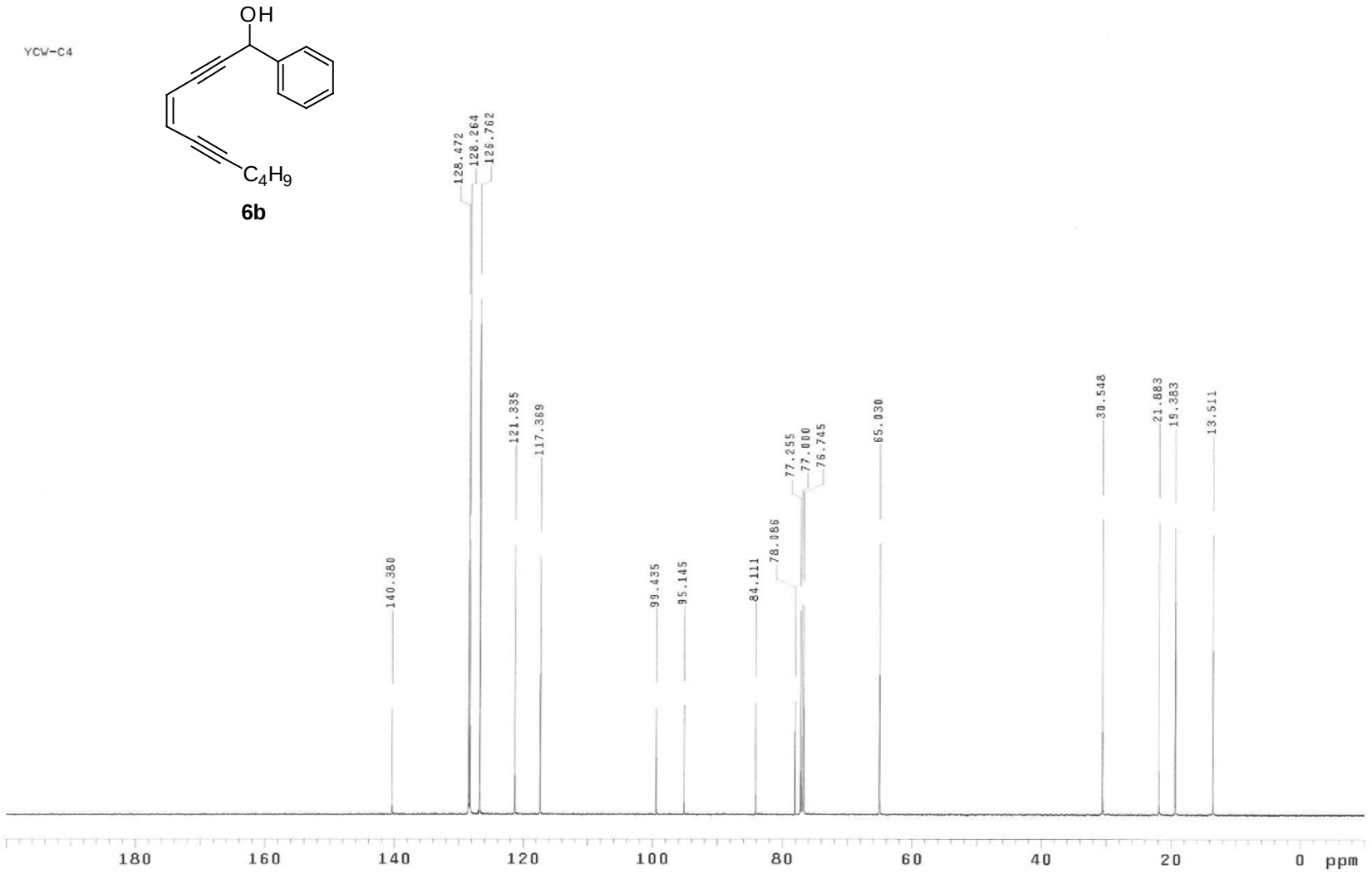
4h

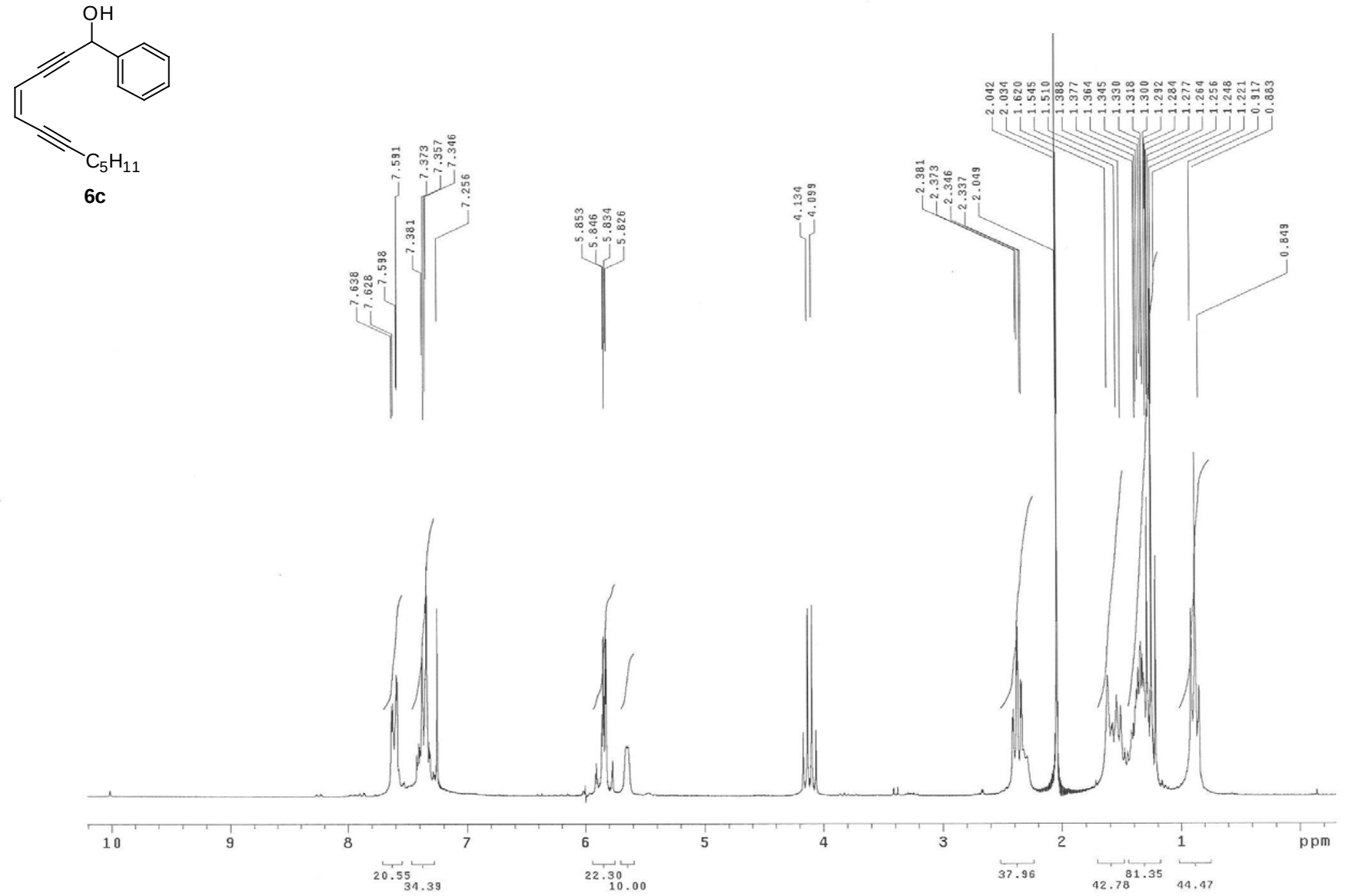

138.153
138.047
132.962
132.241
130.101
129.656
129.594
128.774
128.308
128.238
128.074
122.505
121.626
112.153
97.656
82.520
81.593
77.252
77.000
76.745
73.621
31.575
22.641
21.191
21.180
14.105
180
160
140
120
100
80
60
40
20
0
ppm


OH
YCW-C4
C_4H_9

6b

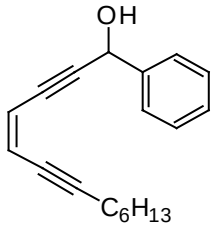

0.907
0.921
0.893
7.610
7.385
7.628
7.627
7.625
7.382
7.370
7.349
7.335
5.865
5.832
5.828
5.651
2.395
2.391
1.531
1.529
1.515
1.444
1.428
9
8
7
6
5
4
3
2
1
-0
ppm
2.01
3.01
2.00
1.00
1.00
2.01
4.12
3.03


YCW-C4
OH
C_4H_9
6b
128.472
128.264
126.762
121.335
117.369
140.380
99.435
95.145
84.111
78.086
77.255
77.000
76.745
65.030
30.548
21.883
19.383
13.511
180
160
140
120
100
80
60
40
20
0
ppm

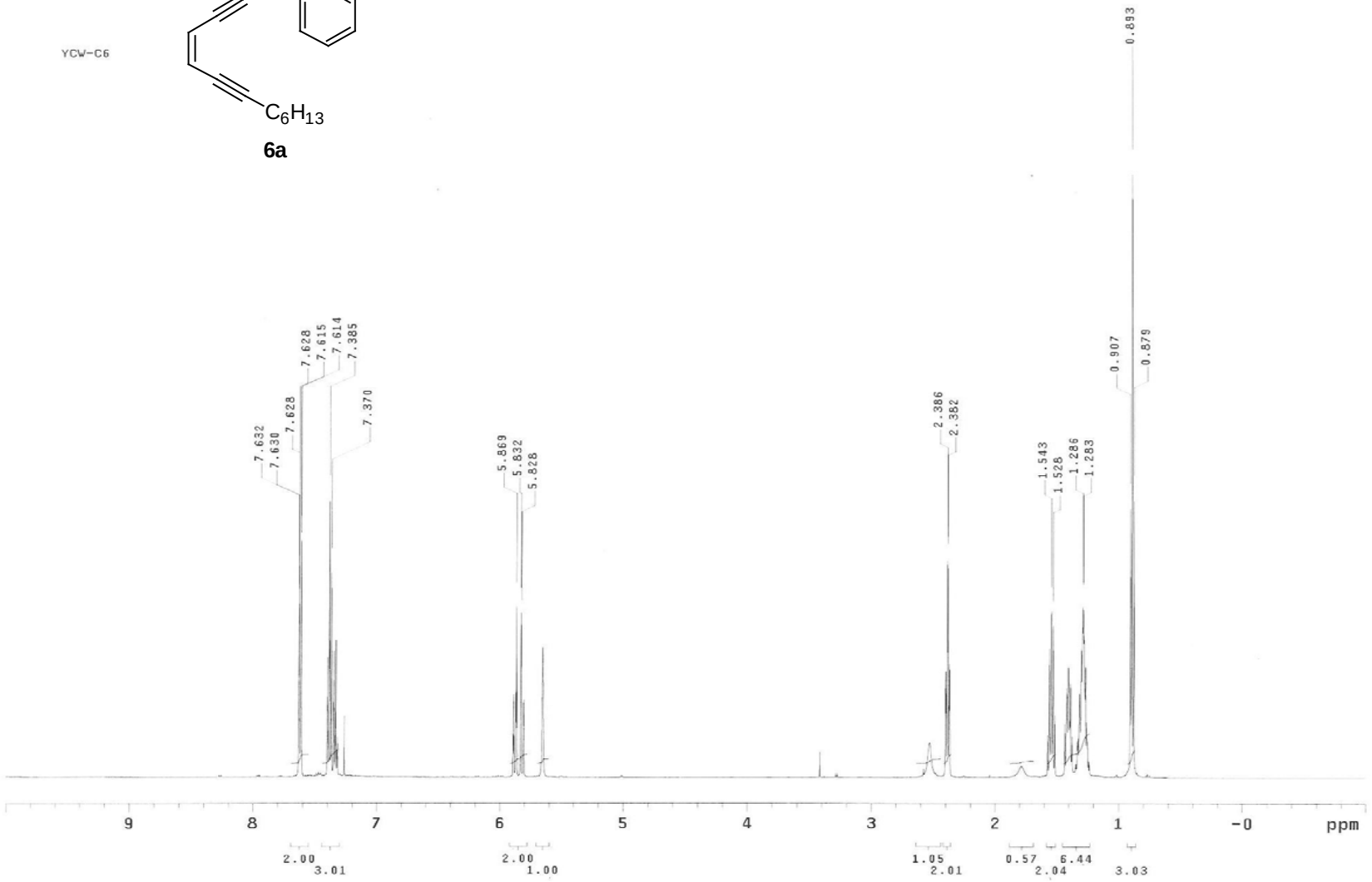

OH
C_5H_{11}
7.638
7.628
7.598
7.591
7.381
7.373
7.357
7.346
7.256
5.853
5.846
5.834
5.826
4.134
4.099
2.381
2.373
2.346
2.337
2.049
2.042
2.034
1.620
1.545
1.510
1.388
1.377
1.364
1.345
1.330
1.318
1.300
1.292
1.284
1.277
1.264
1.256
1.248
1.221
0.917
0.883
0.849
10
9
8
7
6
5
4
3
2
1
ppm
20.55
34.39
22.30
10.00
37.96
42.78
81.35
44.47

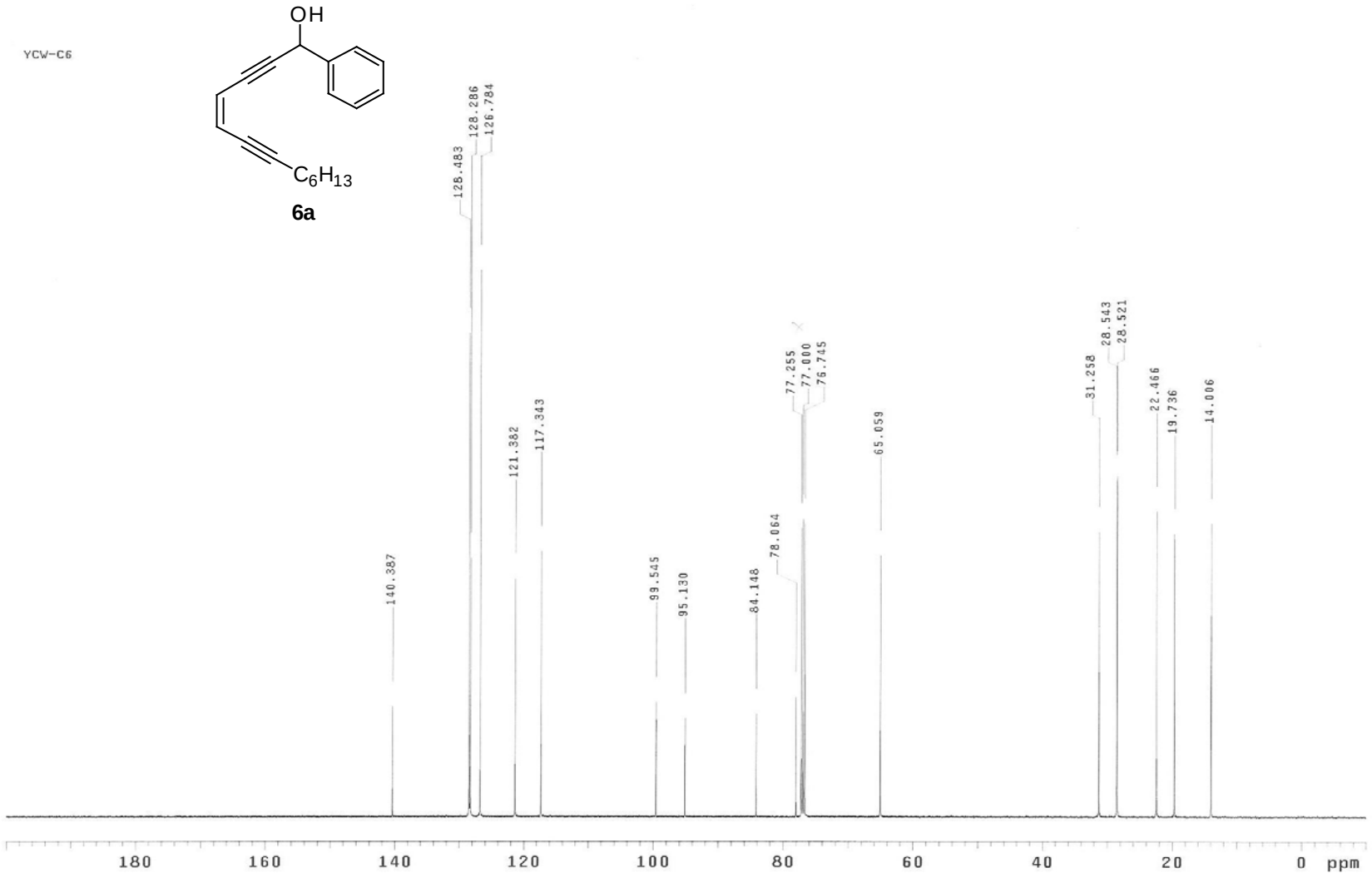
6c

YCW-C6


OH
C_6H_{13}

6a

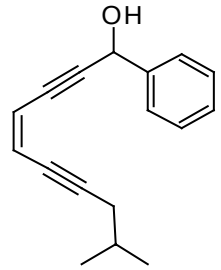

0.893
0.907
0.879
7.632
7.630
7.628
7.628
7.615
7.614
7.385
7.370
5.869
5.832
5.828
2.386
2.382
1.543
1.528
1.286
1.283
9
8
7
6
5
4
3
2
1
-0
ppm
2.00
3.01
2.00
1.00
1.05
2.01
0.57
2.04
6.44
3.03


YCW-C6
OH
C_6H_{13}
6a
140.387
128.483
128.286
126.784
121.382
117.343
99.545
95.130
84.148
78.064
77.255
77.000
76.745
65.059
31.258
28.543
28.521
22.466
19.736
14.006
180
160
140
120
100
80
60
40
20
0 ppm

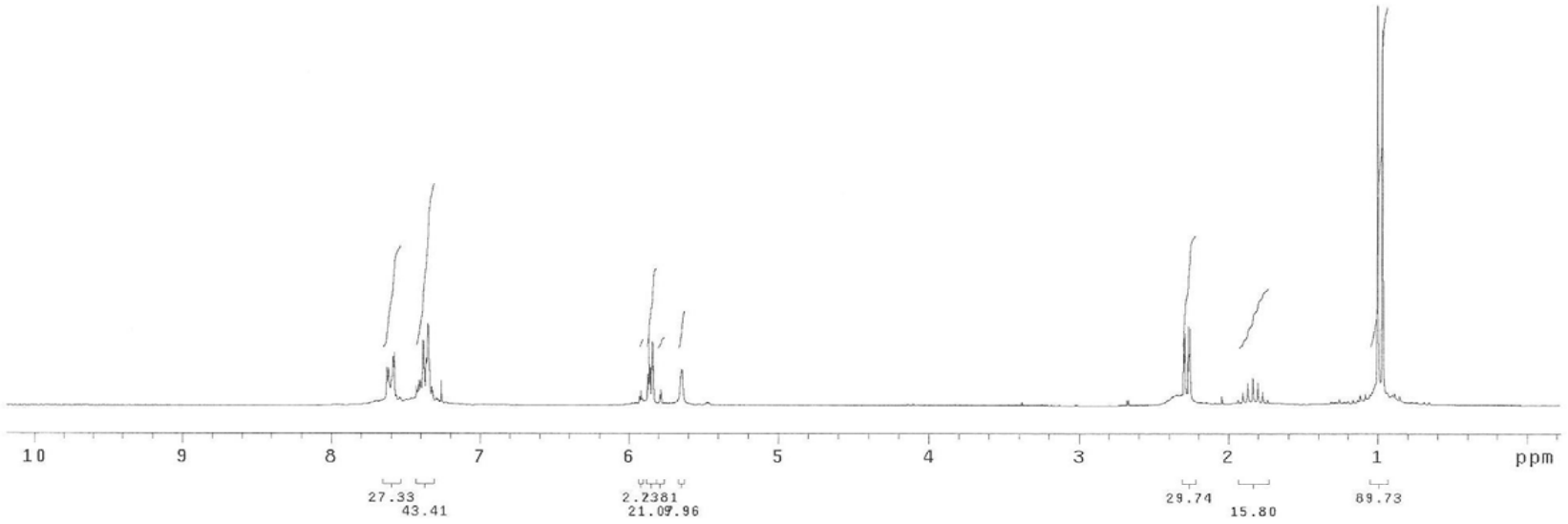
WHJ-124-T2

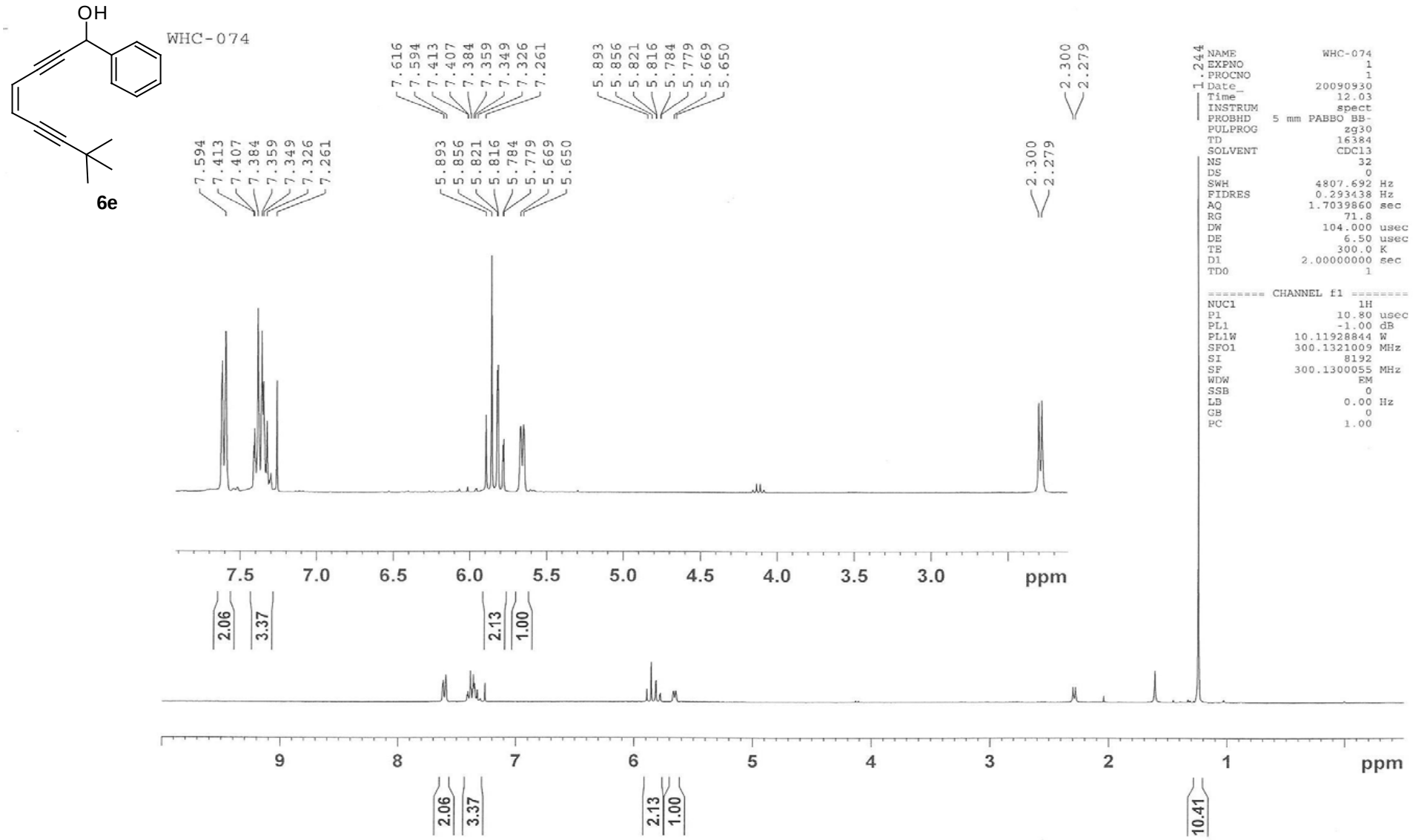
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
GEMINI-200 "gemini200"

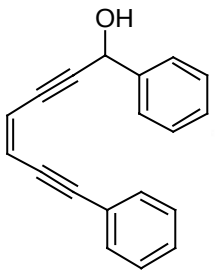
Pulse 42.0 degrees
Acq. time 1.994 sec
Width 3000.3 Hz
72 repetitions
OBSERVE H1, 199.9750736 MHz
DATA PROCESSING
FT size 16384
Total time 2 hr, 51 sec



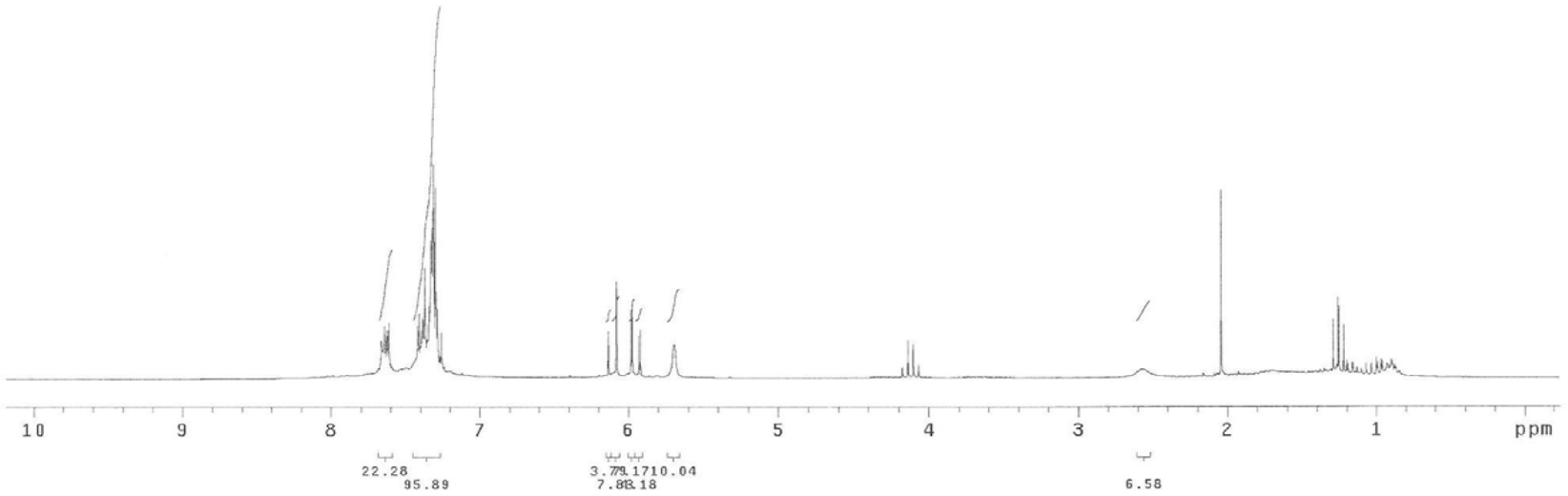
6d



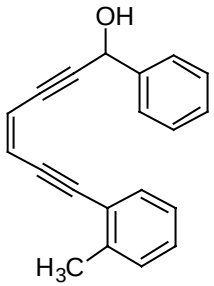

OH
WHC-074
6e
7.616
7.594
7.413
7.407
7.384
7.359
7.349
7.326
7.261
5.893
5.856
5.821
5.816
5.784
5.779
5.669
5.650
2.300
2.279
1.244
NAME WHC-074
EXPNO 1
PROCNO 1
Date_ 20090930
Time 12.03
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 16384
SOLVENT CDCl3
NS 32
DS 0
SWH 4807.692 Hz
FIDRES 0.293438 Hz
AQ 1.7039860 sec
RG 71.8
DW 104.000 usec
DE 6.50 usec
TE 300.0 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 10.80 usec
PL1 -1.00 dB
PL1W 10.11928844 W
SFO1 300.1321009 MHz
SI 8192
SF 300.1300055 MHz
WDW EM
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
ppm
2.06
3.37
2.13
1.00
9
8
7
6
5
4
3
2
1
ppm
2.06
3.37
2.13
1.00
10.41



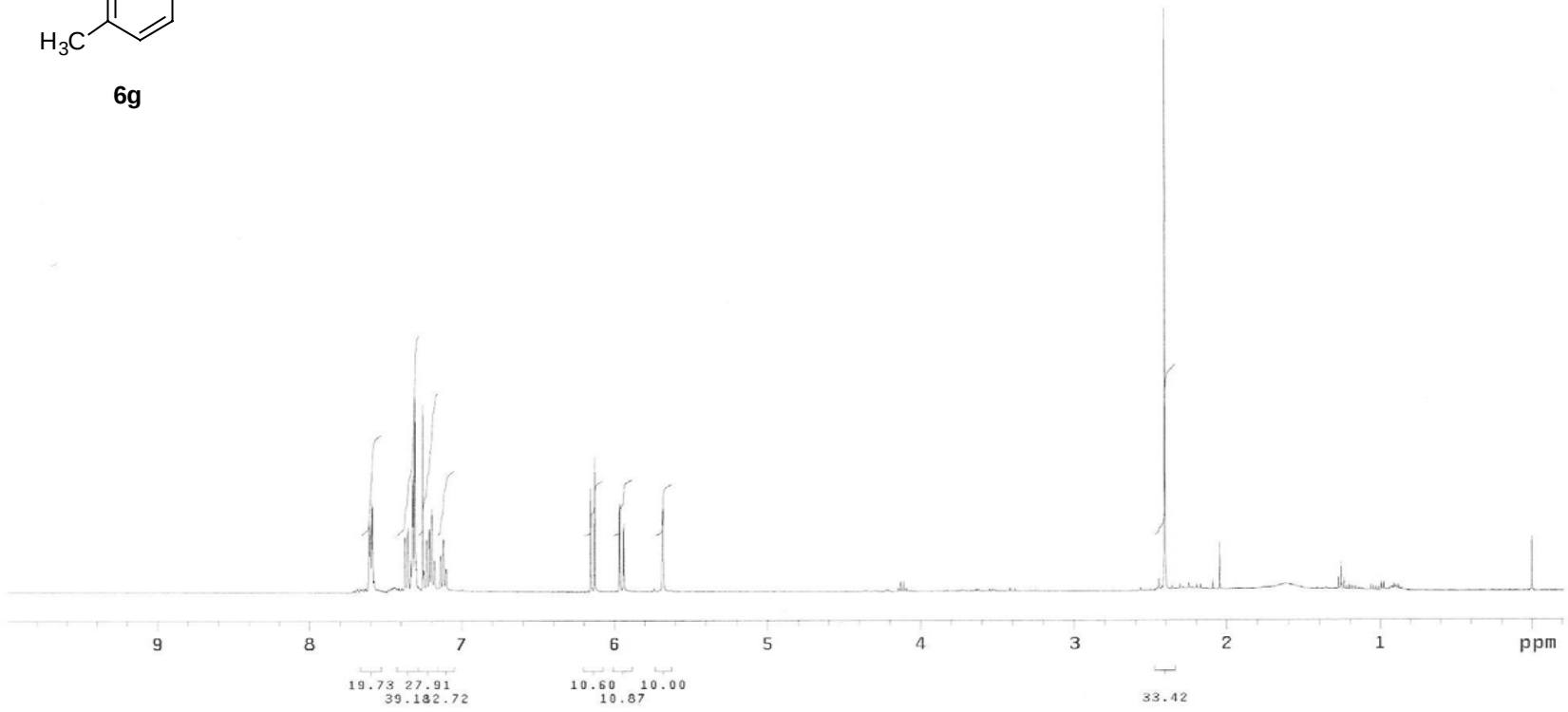
6g



WHJ-210

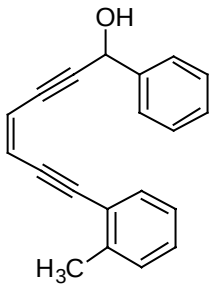


6g

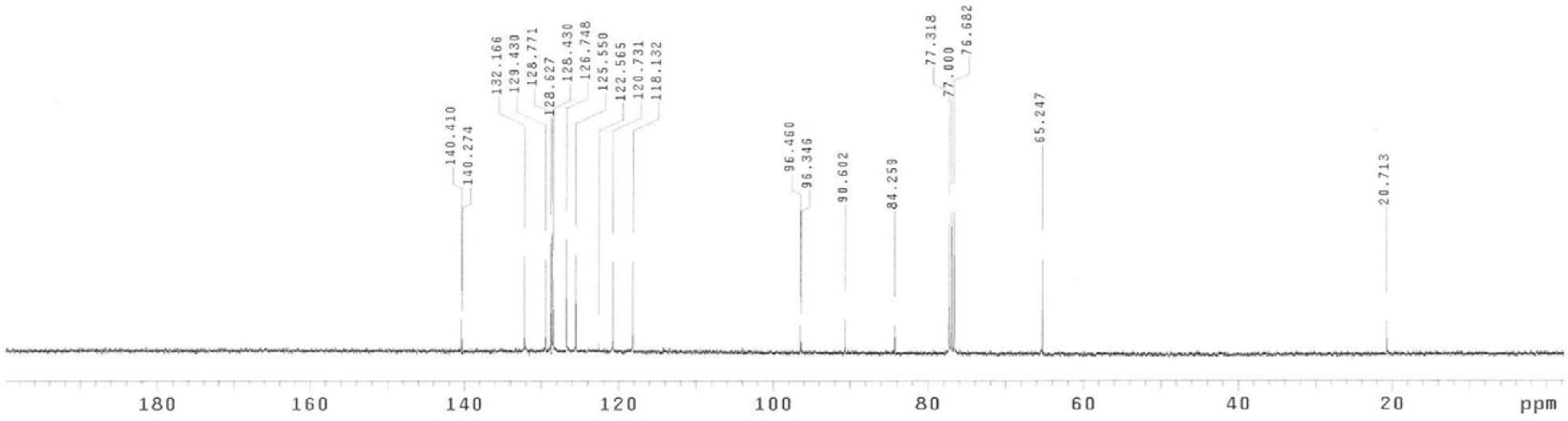


WHJ-210

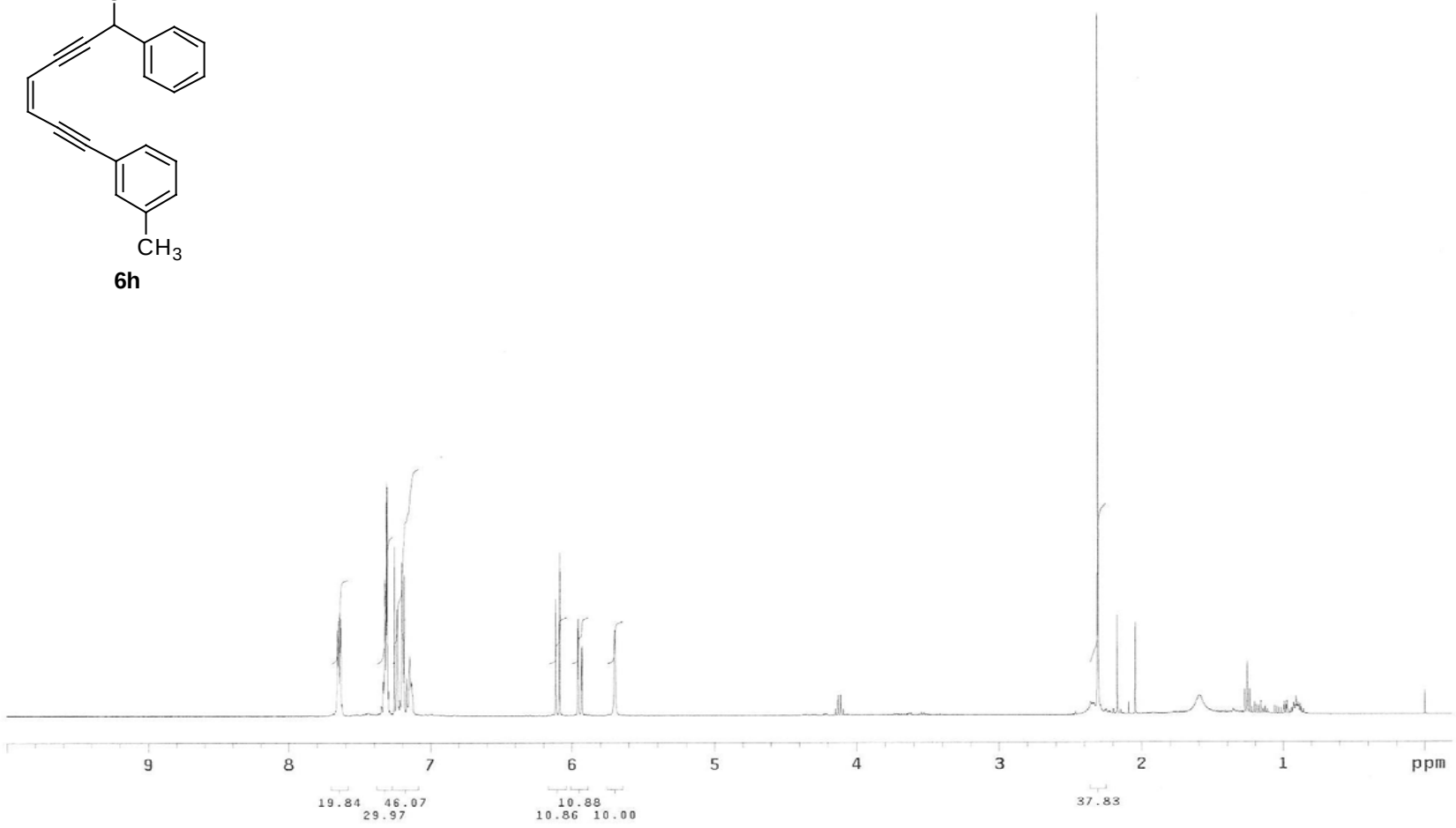
Mercury-400BB "Mercuryplus400"
Date: Mar 5 2008
Solvent: CDCl3
Ambient temperature
Total 1392 repetitions

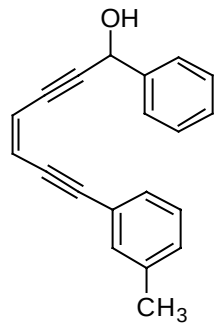


6g

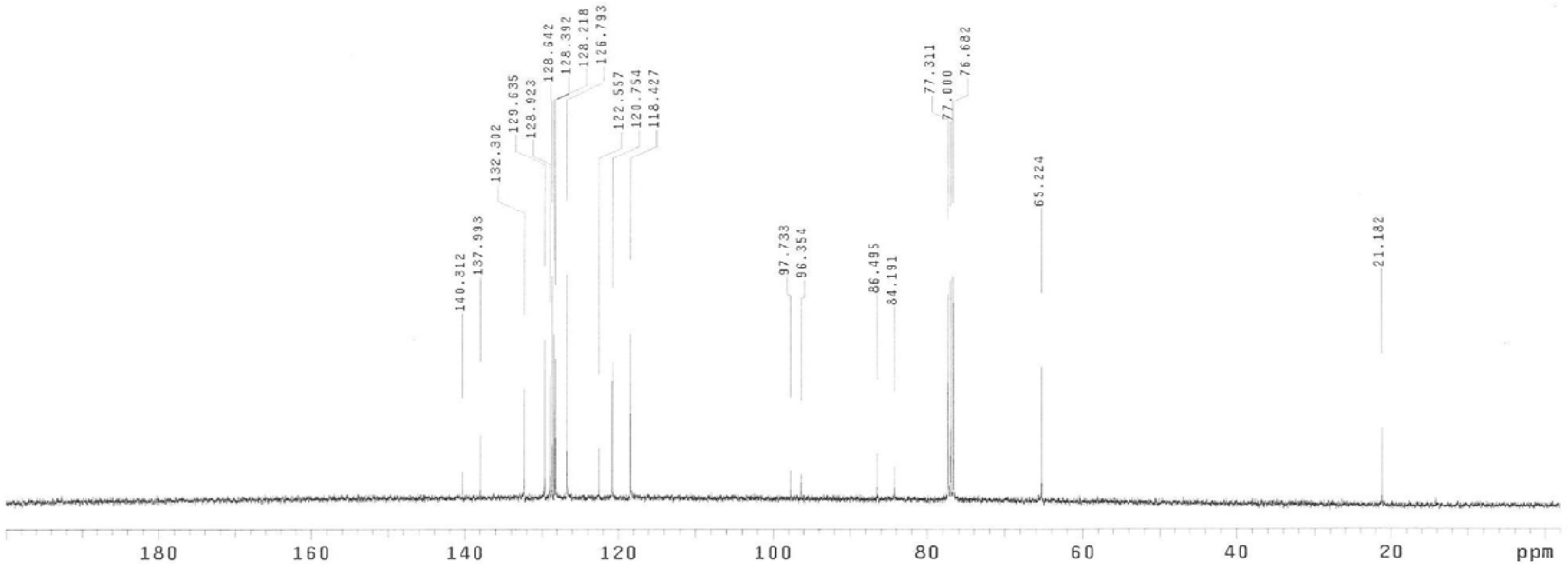


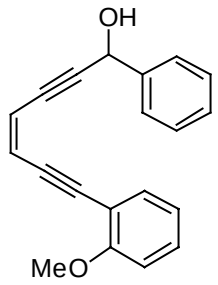
6h



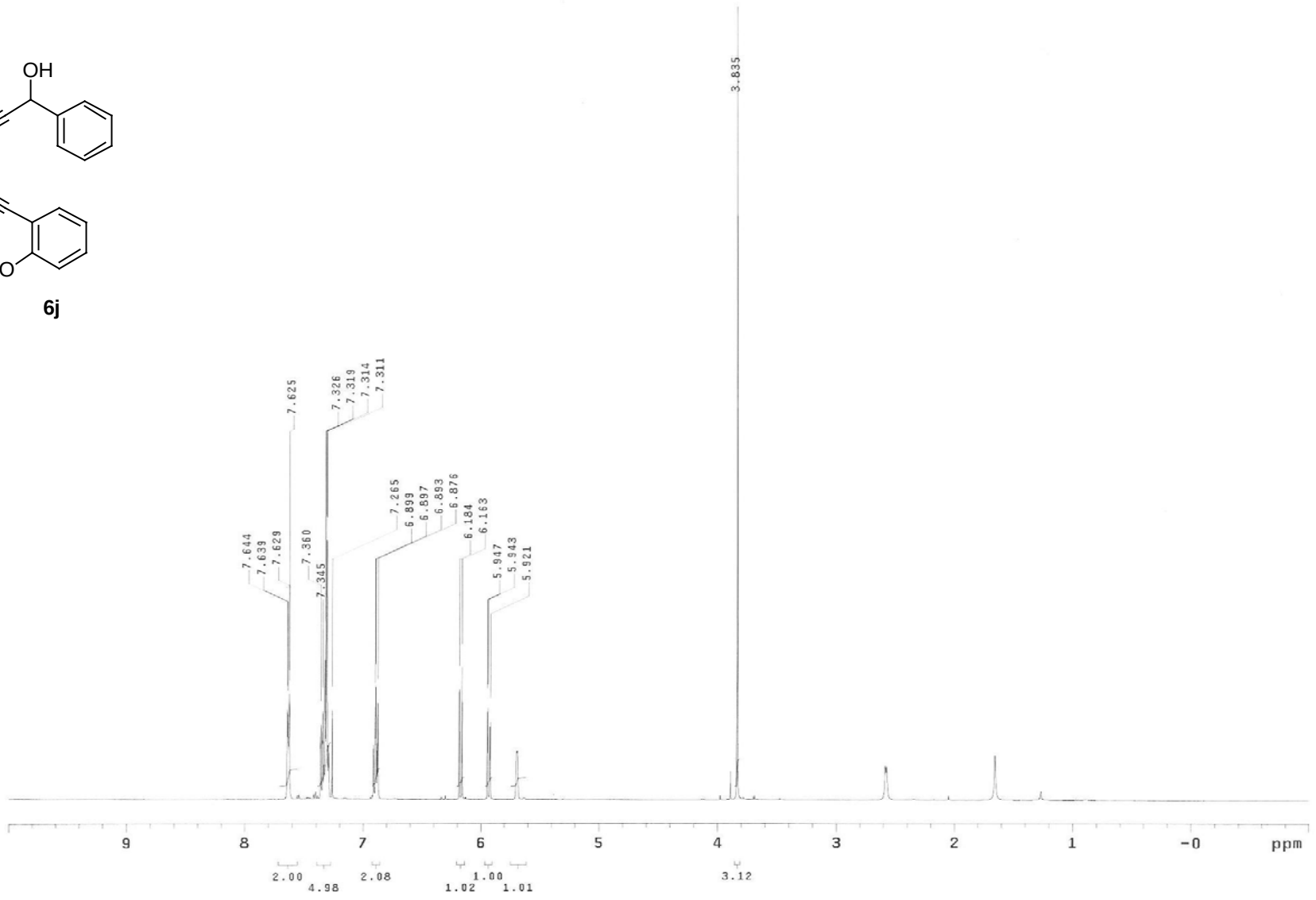

OH
CH3

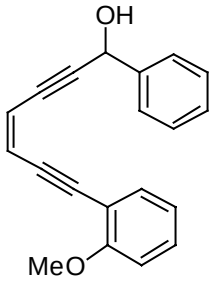
6h


140.312
137.993
132.302
129.635
128.923
128.642
128.392
128.218
126.793
122.557
120.754
118.427
97.733
96.354
86.495
84.191
77.311
77.000
76.682
65.224
21.182
180
160
140
120
100
80
60
40
20
ppm

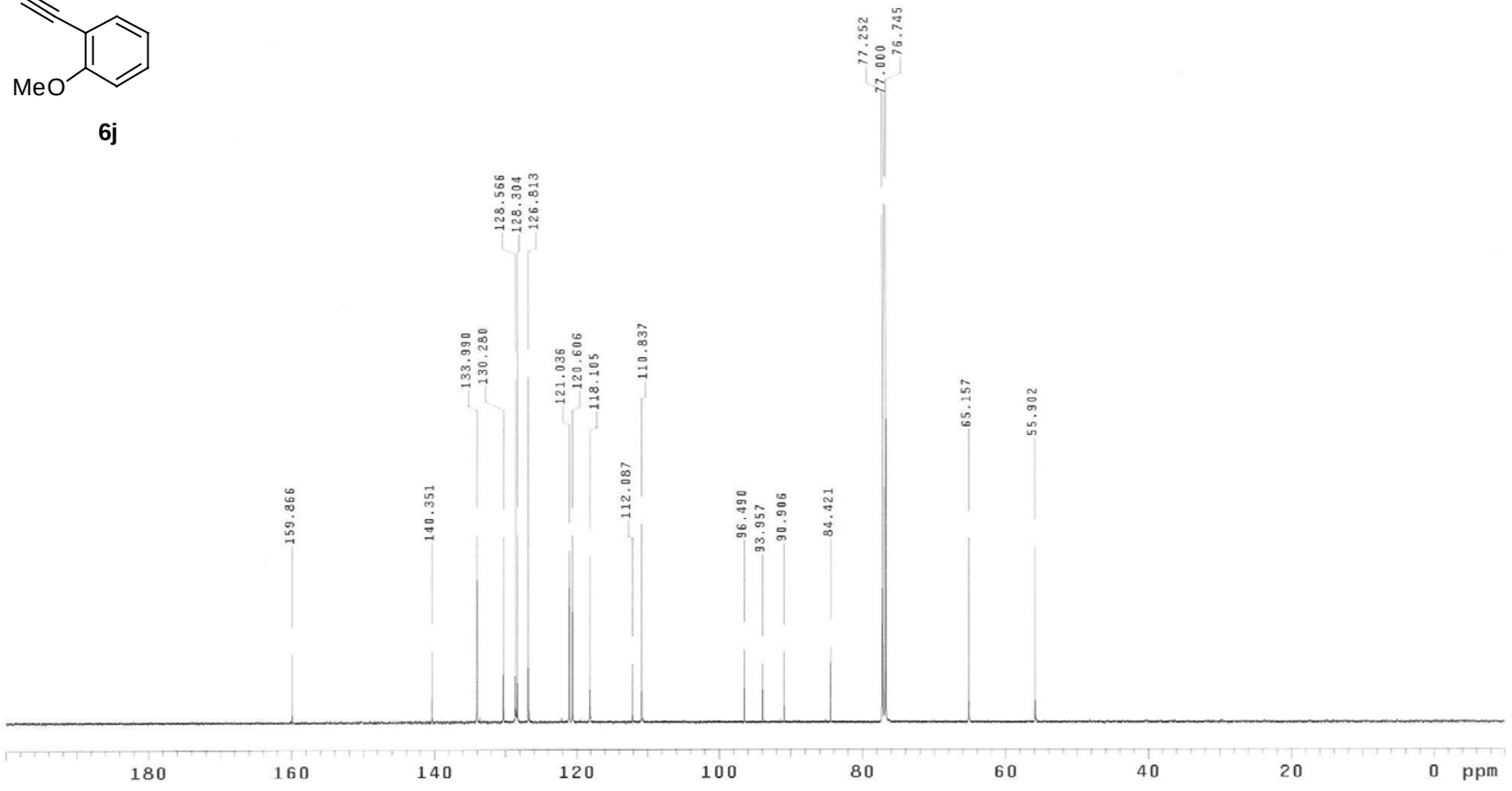

OH
MeO

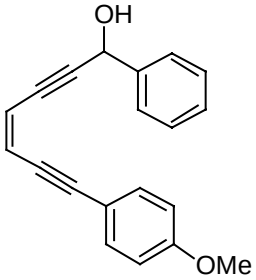
6j


3.835
7.644
7.639
7.629
7.625
7.360
7.345
7.326
7.319
7.314
7.311
7.265
6.899
6.897
6.893
6.876
6.184
6.163
5.947
5.943
5.921
9
8
7
6
5
4
3
2
1
-0
ppm
2.00
4.98
2.08
1.02
1.00
1.01
3.12

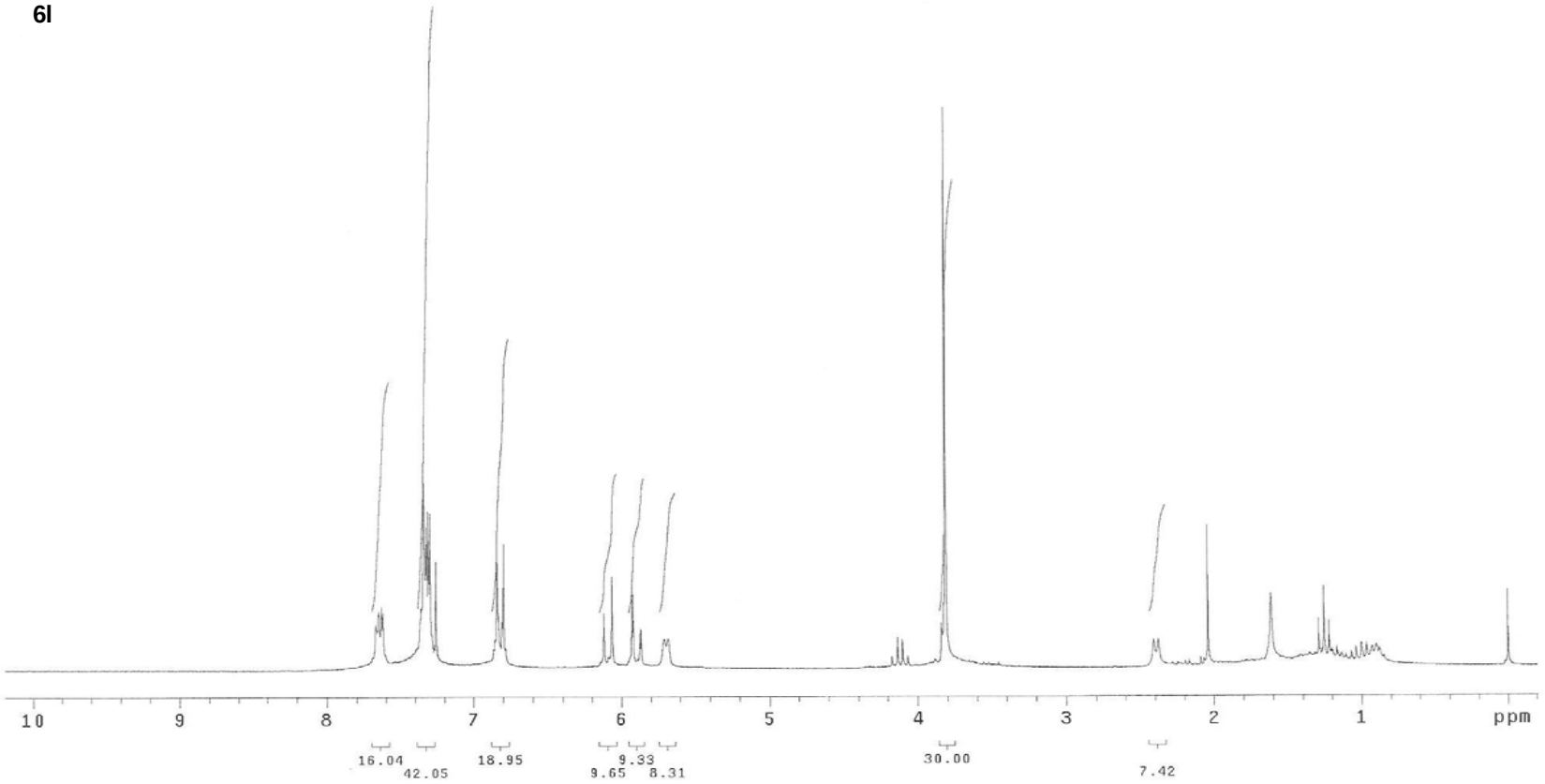

OH
MeO

6j


159.866
140.351
133.990
130.280
128.566
128.304
126.813
121.036
120.606
118.105
112.087
110.837
96.490
93.957
90.906
84.421
77.252
77.000
76.745
65.157
55.902
180
160
140
120
100
80
60
40
20
0 ppm



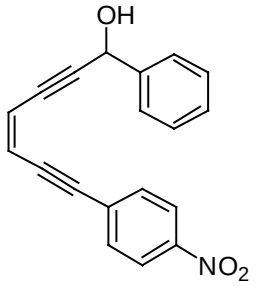
6l



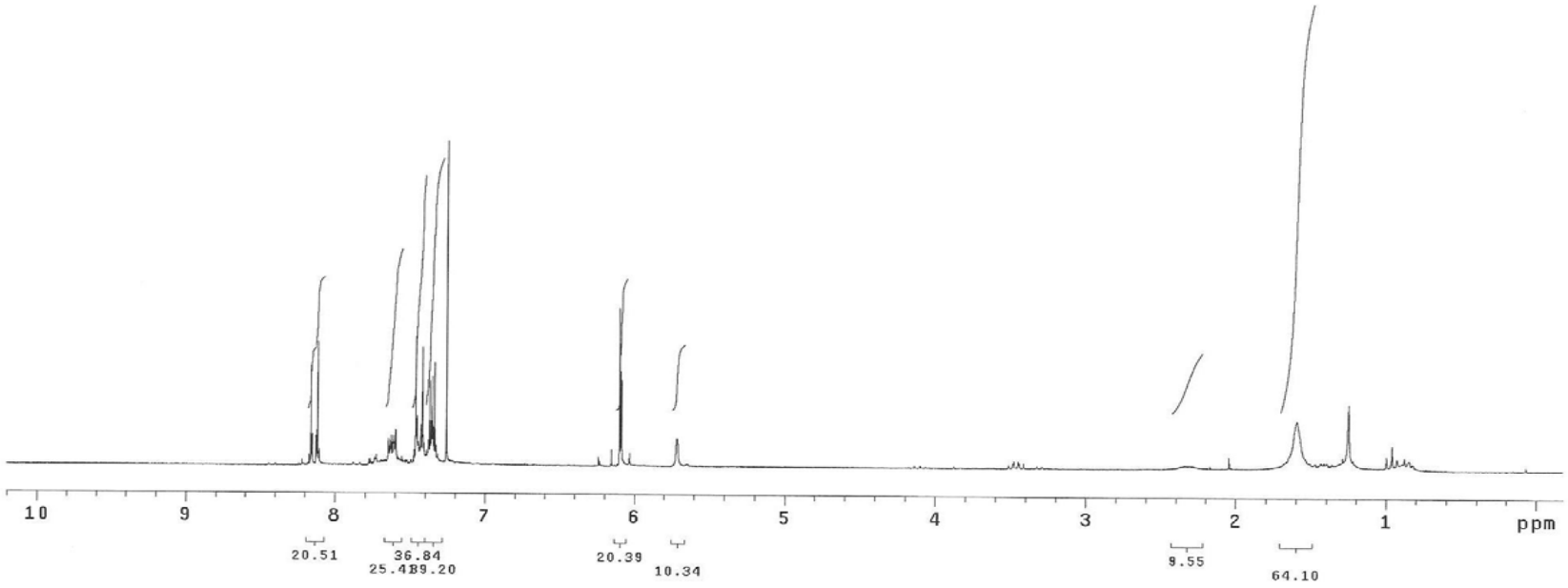
WHJ-140-P4

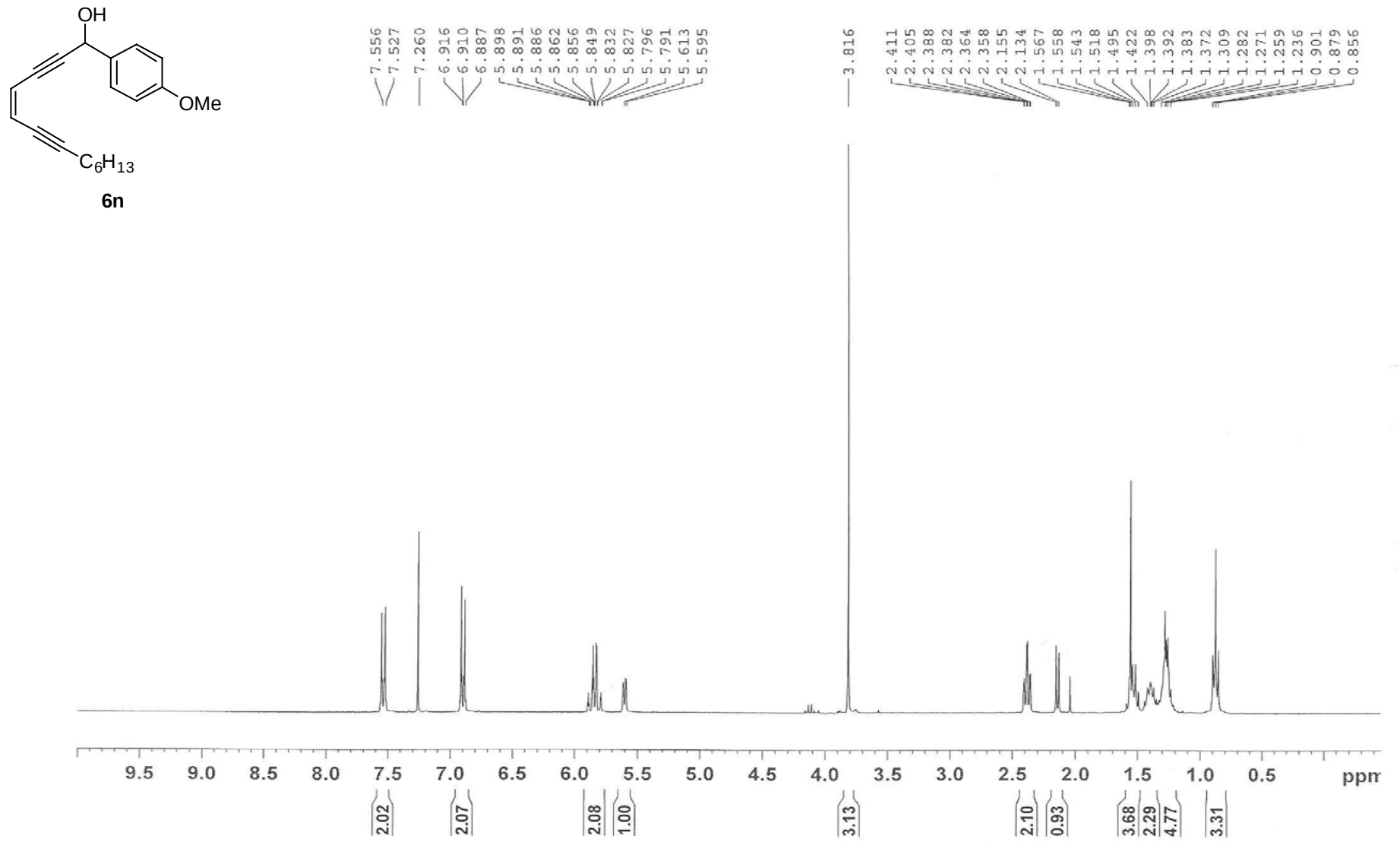
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
GEMINI-200 "oxford200"

Pulse 44.0 degrees
Acq. time 3.002 sec
Width 3000.3 Hz
136 repetitions
OBSERVE H1, 199.9678376 MHz
DATA PROCESSING
FT size 32768
Total time 2 hr, 50 min, 36 sec

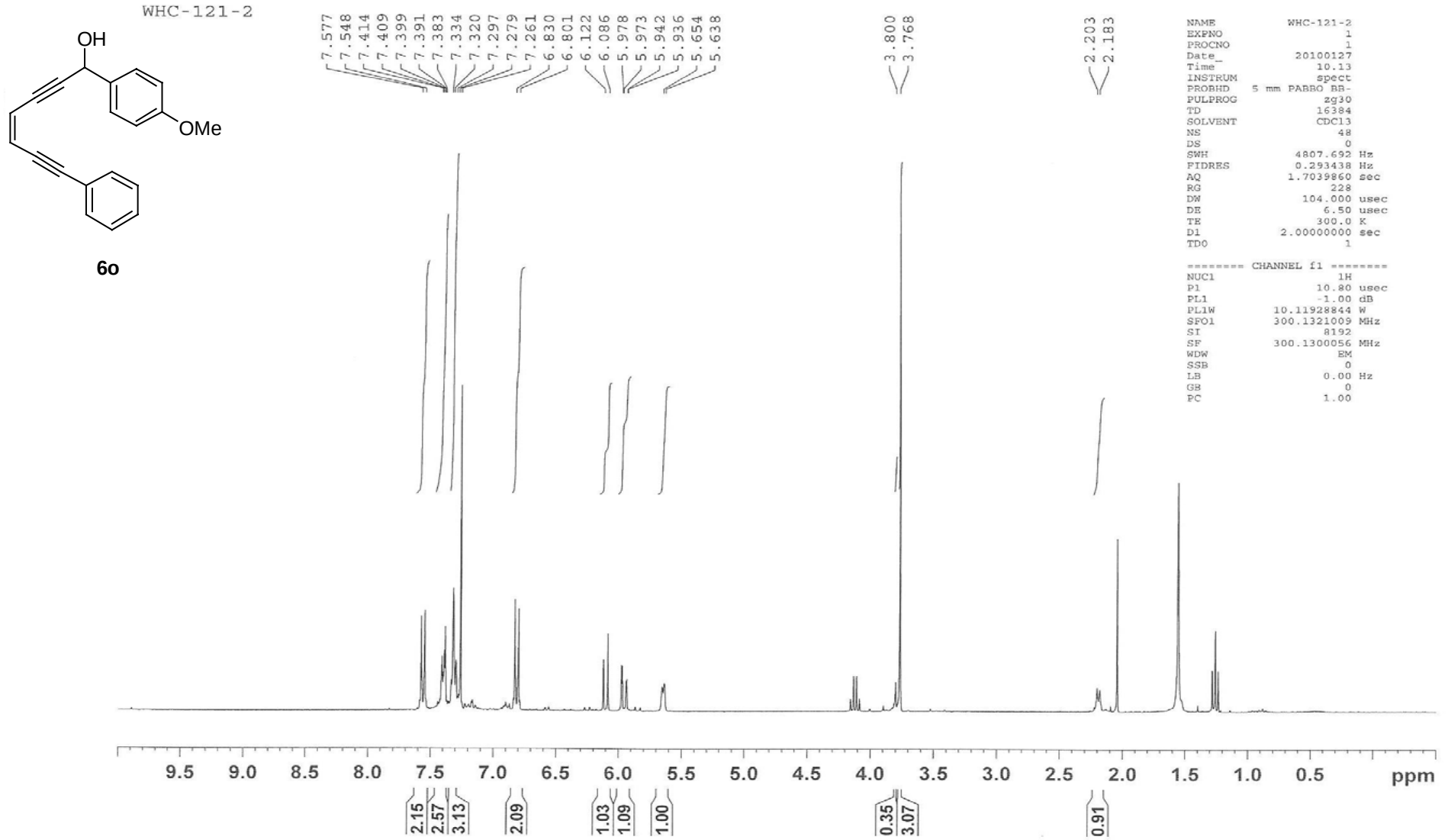


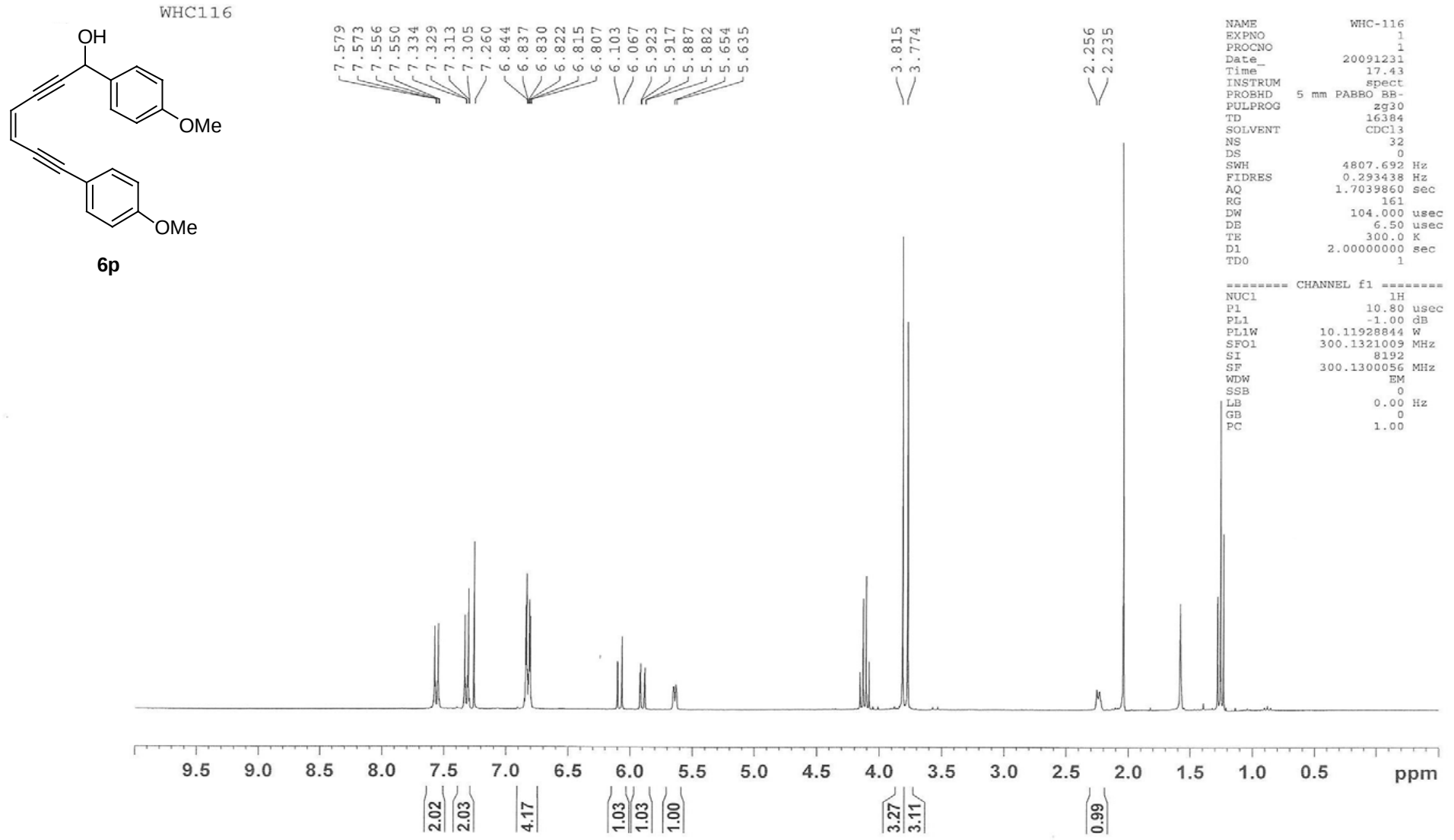
6m

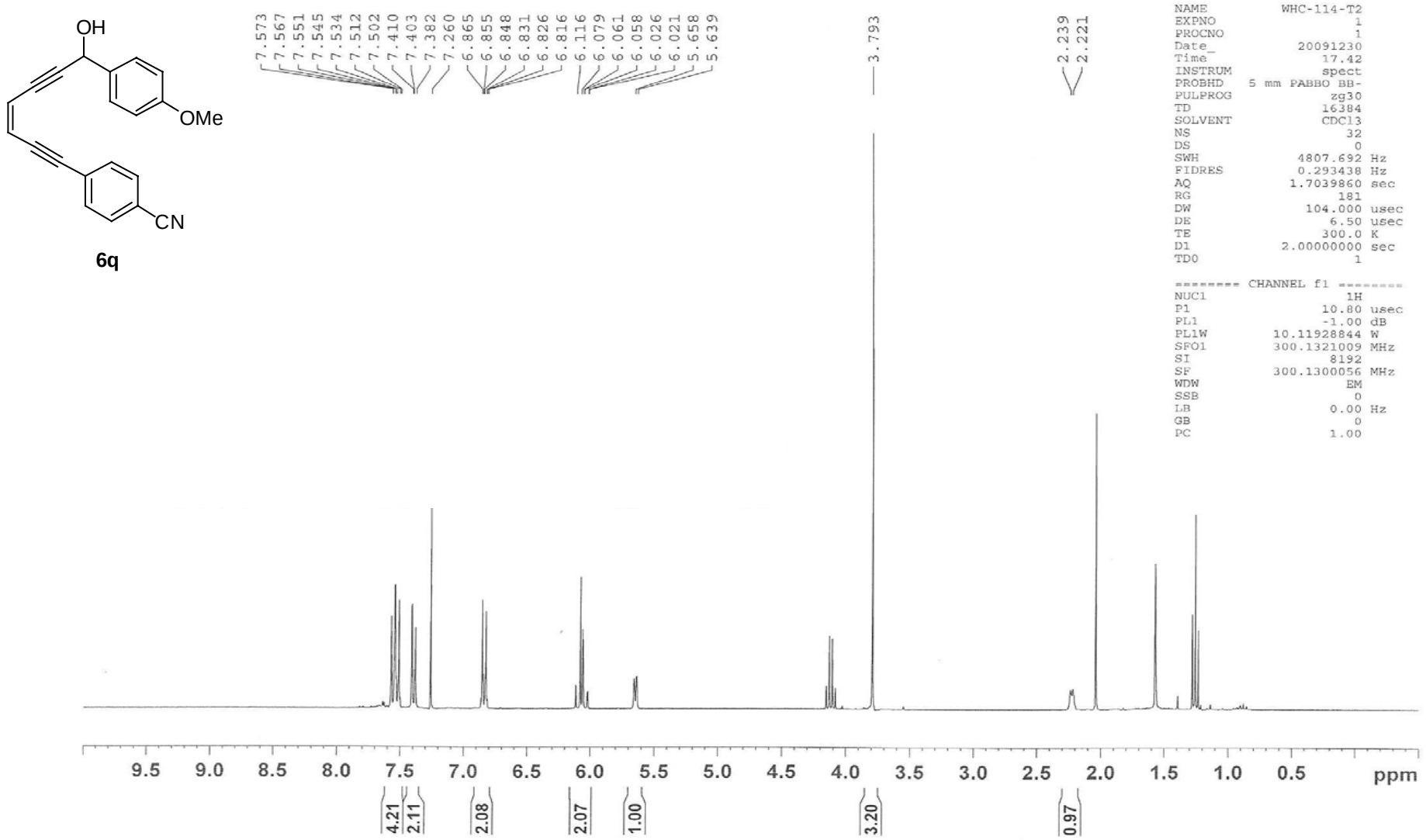


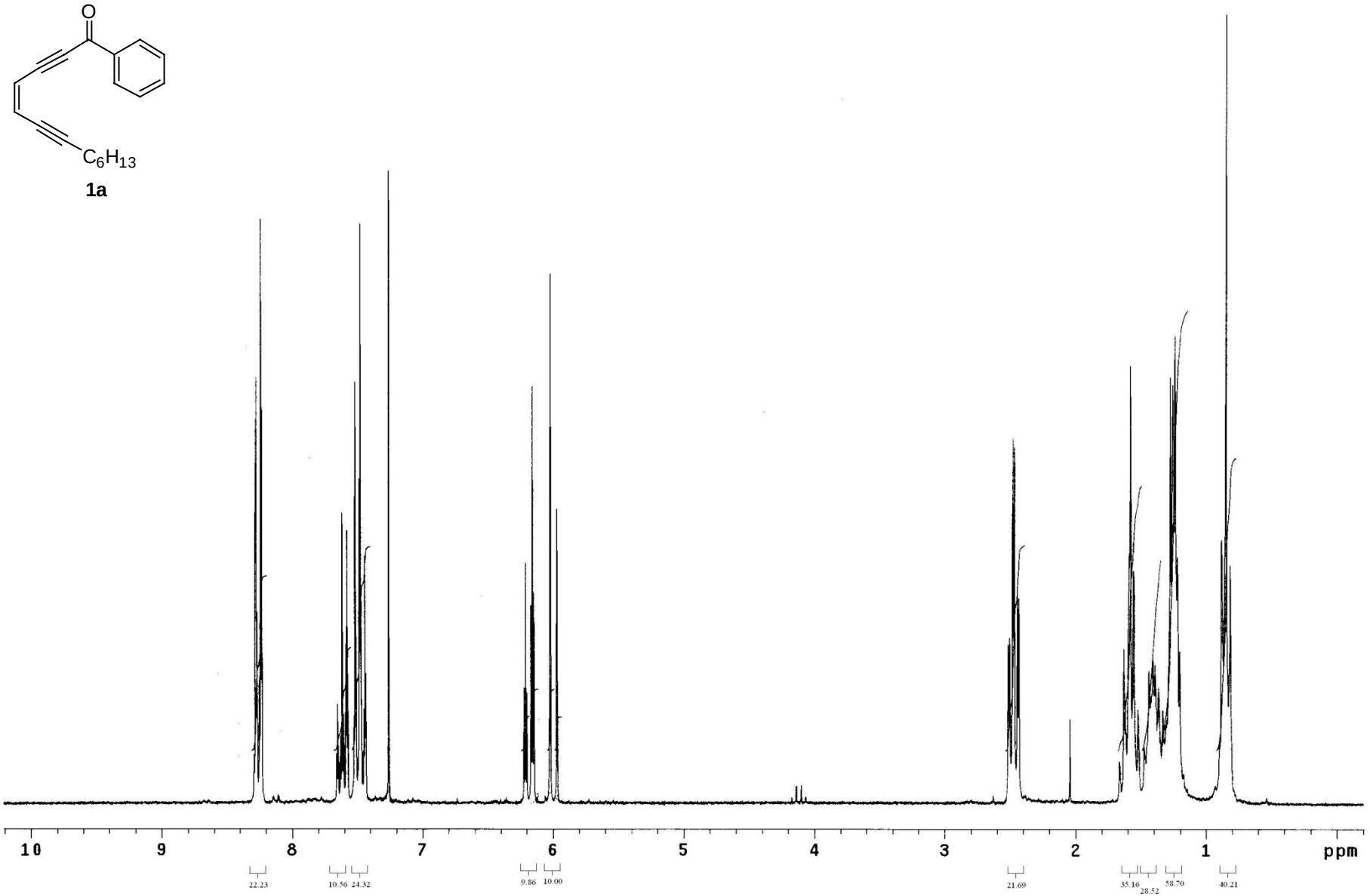

OH
OMe
C_6H_{13}
7.556
7.527
7.260
6.916
6.910
6.887
5.898
5.891
5.886
5.862
5.856
5.849
5.832
5.827
5.796
5.791
5.613
5.595
3.816
2.411
2.405
2.388
2.382
2.364
2.358
2.155
2.134
1.567
1.558
1.543
1.518
1.495
1.422
1.398
1.392
1.383
1.372
1.309
1.282
1.271
1.259
1.236
0.901
0.879
0.856
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.02
2.07
2.08
1.00
3.13
2.10
0.93
3.68
2.29
4.77
3.31

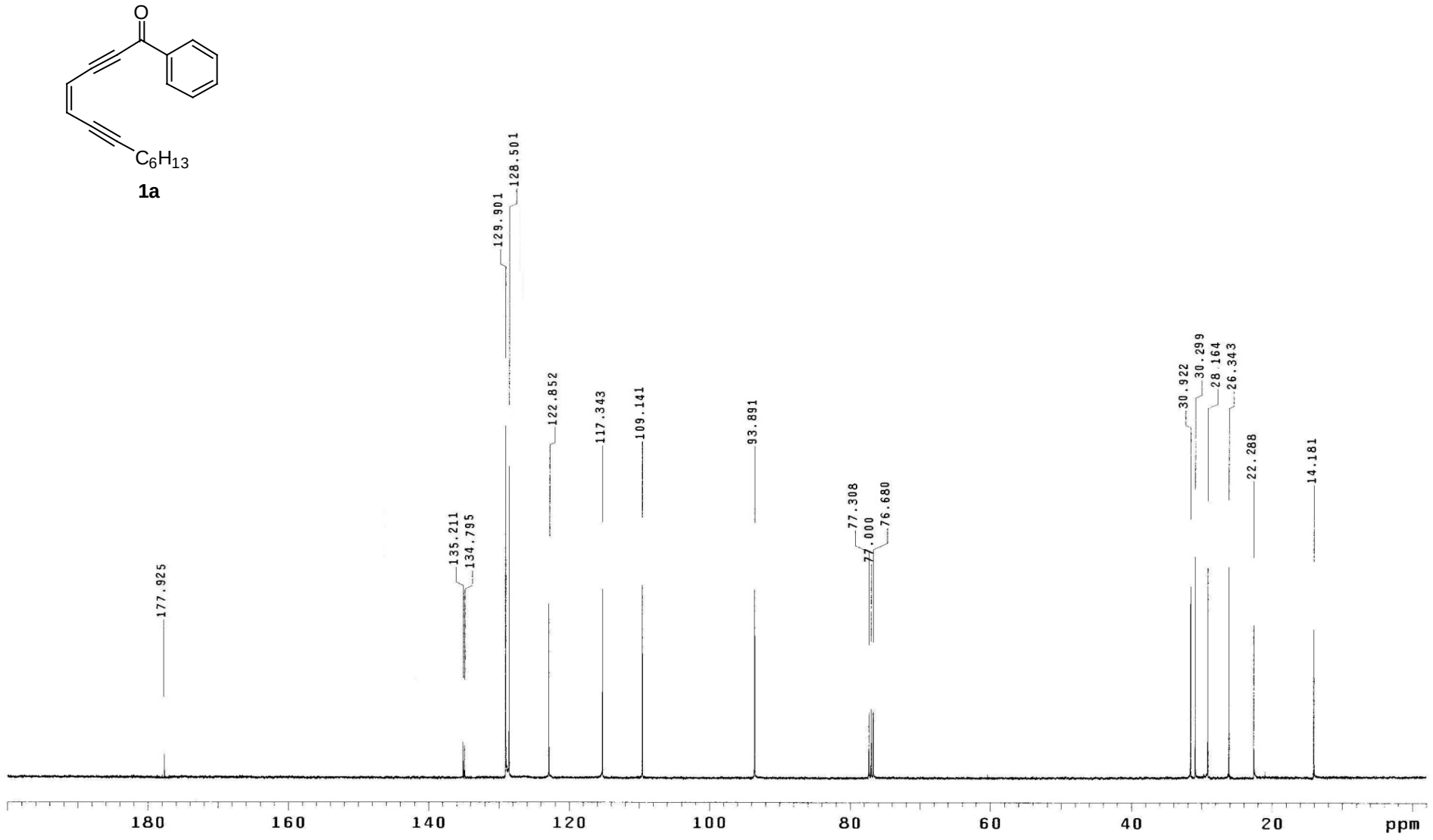
6n

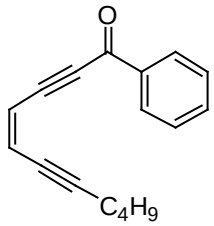

WHC-121-2
OH
OMe
6o
7.577
7.548
7.414
7.409
7.399
7.391
7.383
7.334
7.320
7.297
7.279
7.261
6.830
6.801
6.122
6.086
5.978
5.973
5.942
5.936
5.654
5.638
3.800
3.768
2.203
2.183
NAME WHC-121-2
EXPNO 1
PROCNO 1
Date_ 20100127
Time 10.13
INSTRUM spect
PROBHD 5 mm PABBO BR-
PULPROG zg30
TD 16384
SOLVENT CDCl3
NS 48
DS 0
SWH 4807.692 Hz
FIDRES 0.293438 Hz
AQ 1.7039860 sec
RG 228
DW 104.000 usec
DE 6.50 usec
TE 300.0 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 10.80 usec
PL1 -1.00 dB
PL1W 10.11928844 W
SFO1 300.1321009 MHz
SI 8192
SF 300.1300056 MHz
WDW EM
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.15
2.57
3.13
2.09
1.03
1.09
1.00
0.35
3.07
0.91


WHC116
OH
OMe
OMe
6p
7.579
7.573
7.556
7.550
7.334
7.329
7.313
7.305
7.260
6.844
6.837
6.830
6.822
6.815
6.807
6.103
6.067
5.923
5.917
5.887
5.882
5.654
5.635
3.815
3.774
2.256
2.235
NAME WHC-116
EXPNO 1
PROCNO 1
Date_ 20091231
Time 17.43
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 16384
SOLVENT CDCl3
NS 32
DS 0
SWH 4807.692 Hz
FIDRES 0.293438 Hz
AQ 1.7039860 sec
RG 161
DW 104.000 usec
DE 6.50 usec
TE 300.0 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 10.80 usec
PL1 -1.00 dB
PL1W 10.11928844 W
SFO1 300.1321009 MHz
SI 8192
SF 300.1300056 MHz
WDW EM
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.02
2.03
4.17
1.03
1.03
1.00
3.27
3.11
0.99

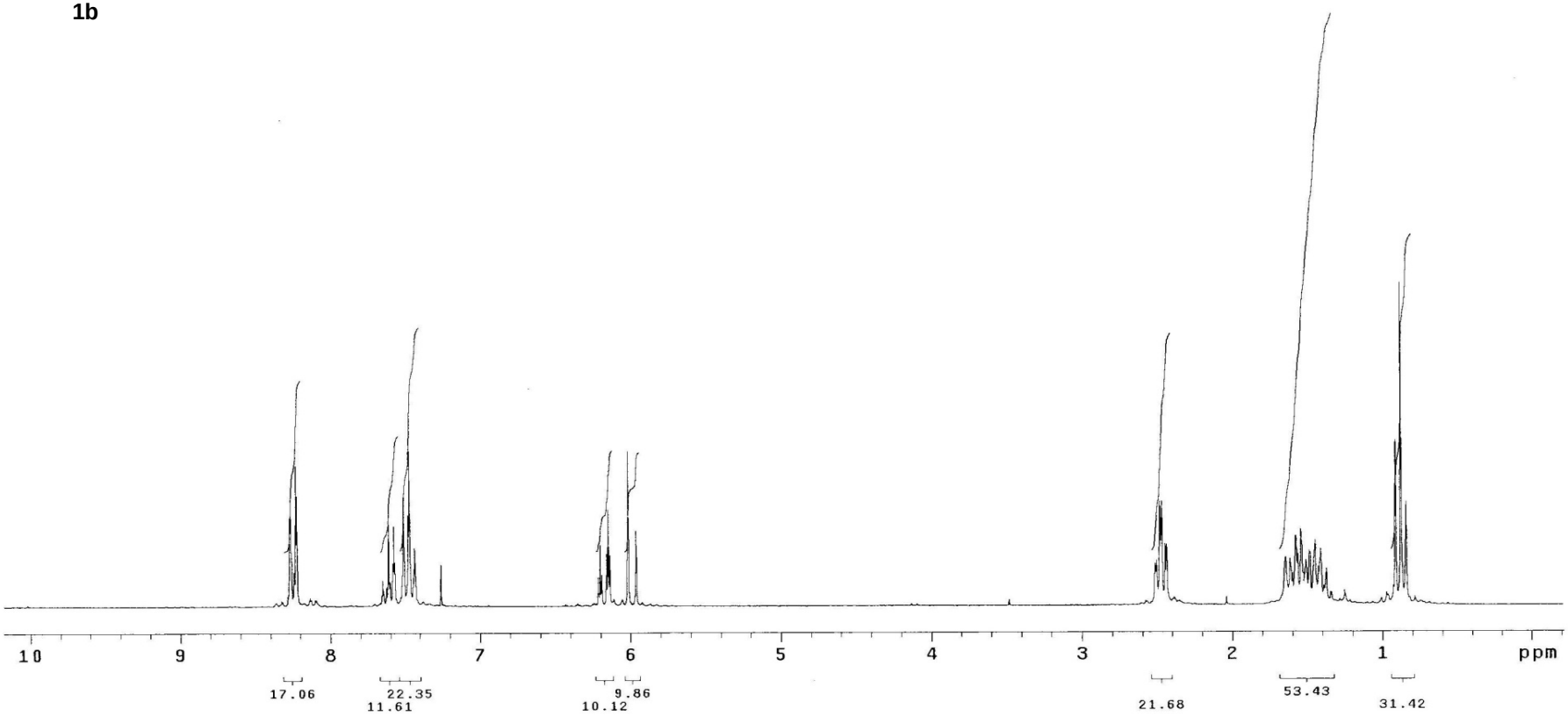

OH
OMe
CN
6q
7.573
7.567
7.551
7.545
7.534
7.512
7.502
7.410
7.403
7.382
7.260
6.865
6.855
6.848
6.831
6.826
6.816
6.116
6.079
6.061
6.058
6.026
6.021
5.658
5.639
3.793
2.239
2.221
NAME WHC-114-T2
EXPNO 1
PROCNO 1
Date_ 20091230
Time 17.42
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 16384
SOLVENT CDCl3
NS 32
DS 0
SWH 4807.692 Hz
FIDRES 0.293438 Hz
AQ 1.7039860 sec
RG 181
DW 104.000 usec
DE 6.50 usec
TE 300.0 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 10.80 usec
PL1 -1.00 dB
PL1W 10.11928844 W
SFO1 300.1321009 MHz
SI 8192
SF 300.1300056 MHz
WDW EM
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
4.21
2.11
2.08
2.07
1.00
3.20
0.97

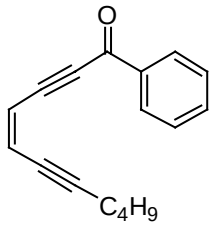

O
C6H13
1a
10
9
8
7
6
5
4
3
2
1
ppm
22.23
10.56
24.32
9.86
10.00
21.69
35.16
28.52
58.70
40.21


O
C6H13
1a
177.925
135.211
134.795
129.901
128.501
122.852
117.343
109.141
93.891
77.308
77.000
76.680
30.922
30.299
28.164
26.343
22.288
14.181
180
160
140
120
100
80
60
40
20
ppm

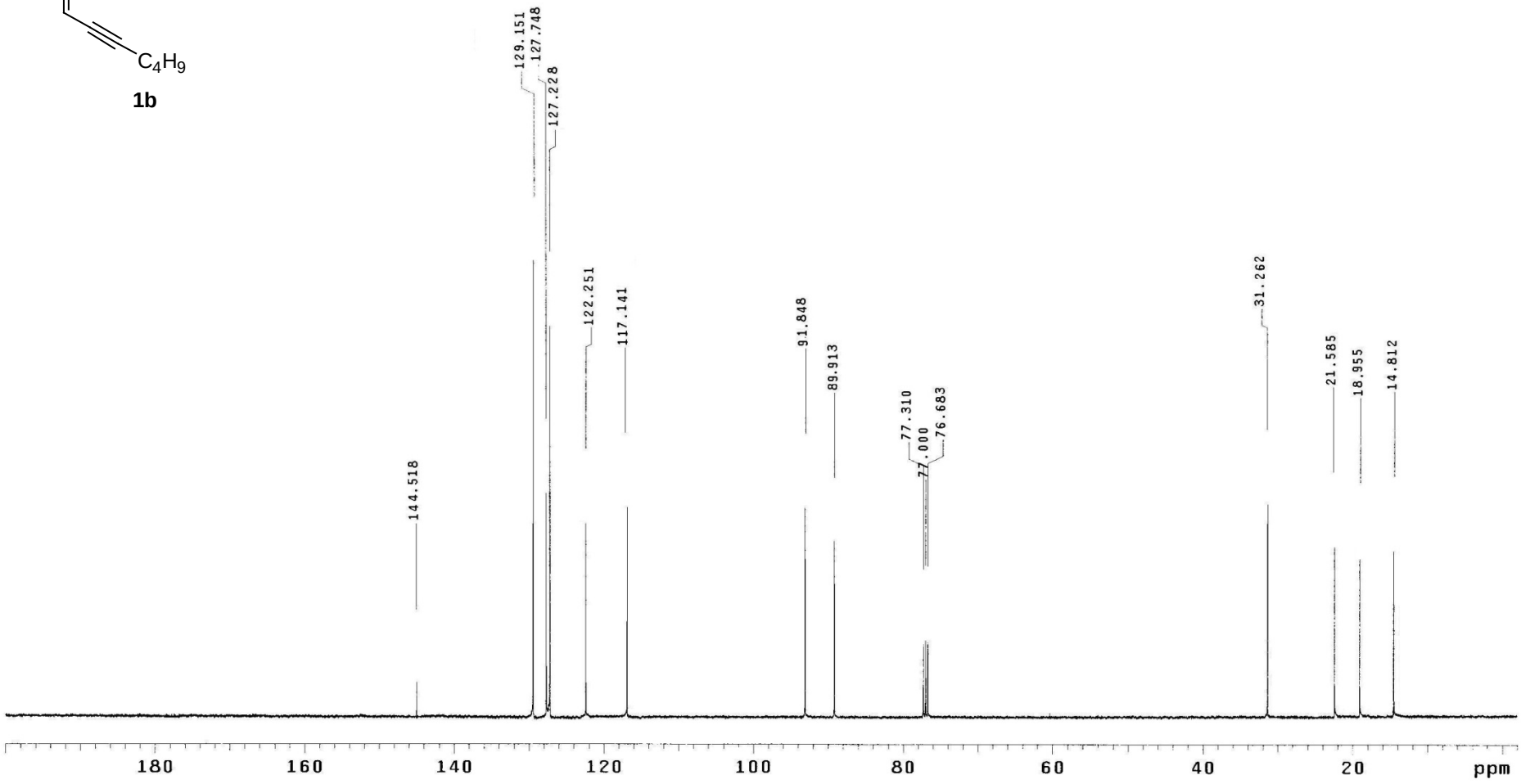

O
C4H9

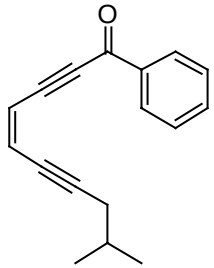
1b


10
9
8
7
6
5
4
3
2
1
ppm
17.06
22.35
11.61
9.86
10.12
21.68
53.43
31.42

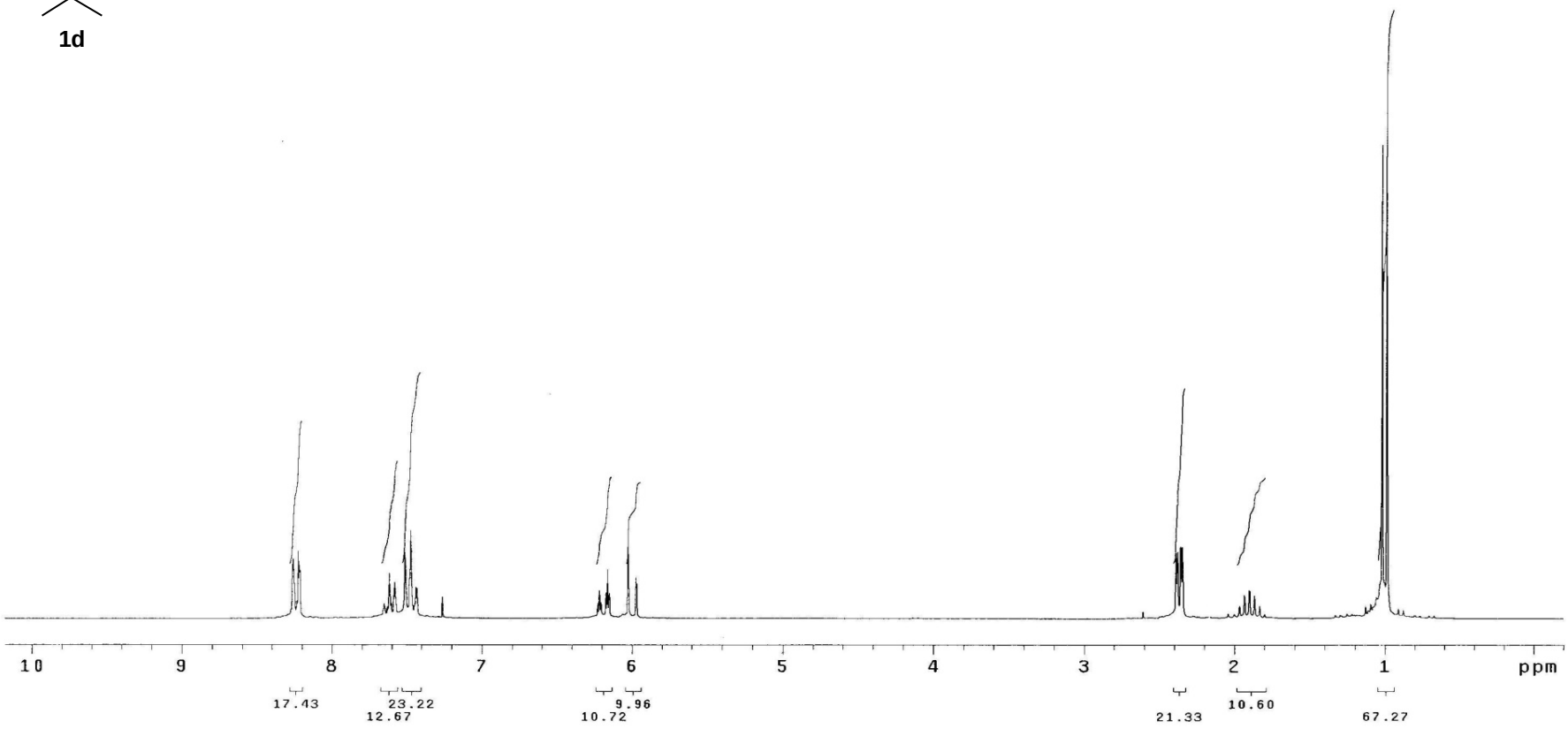

O
C4H9

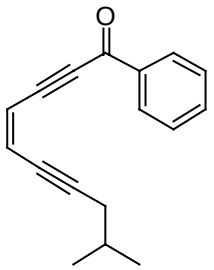
1b


129.151
127.748
127.228
122.251
117.141
91.848
89.913
77.310
77.000
76.683
144.518
31.262
21.585
18.955
14.812
180
160
140
120
100
80
60
40
20
ppm

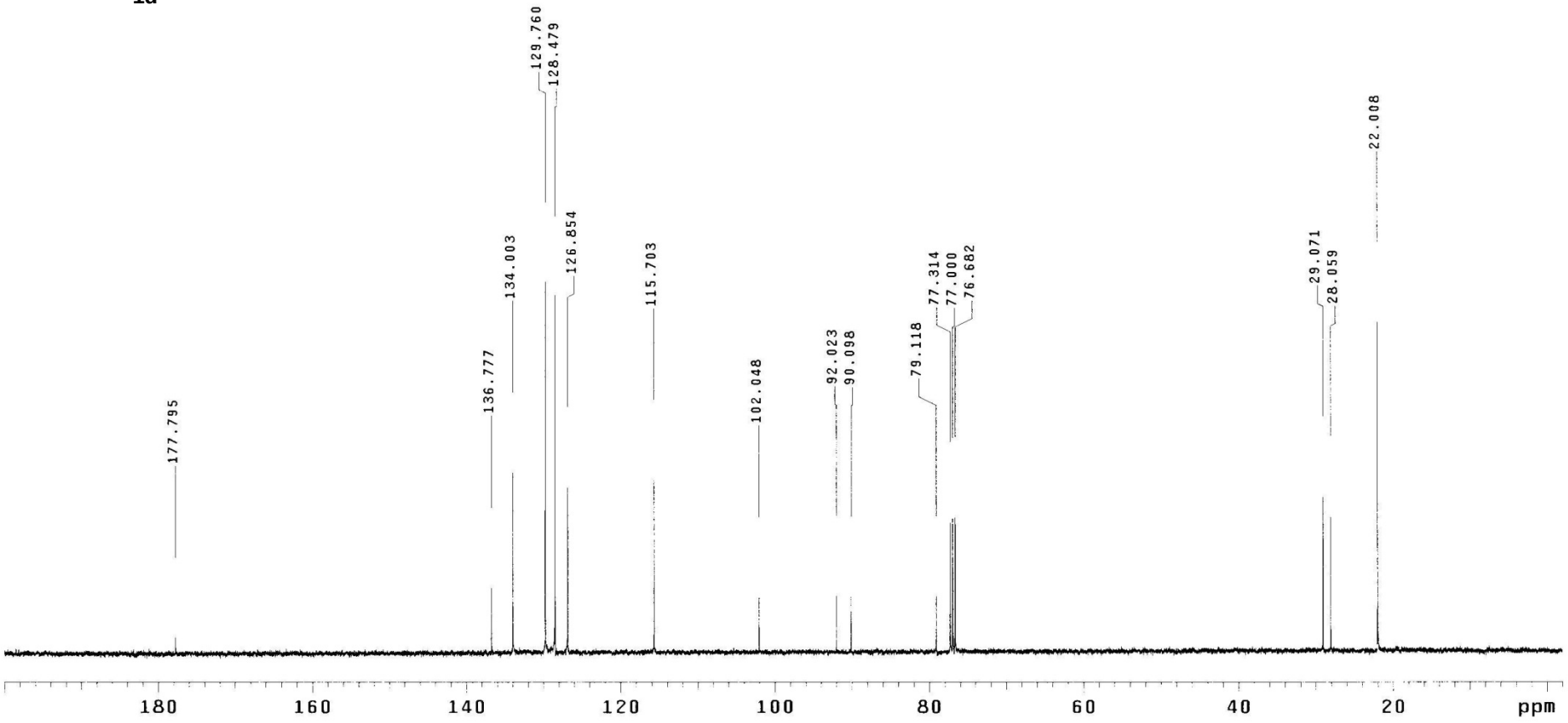


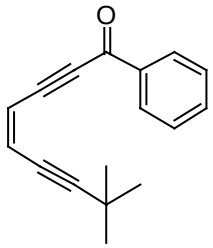
1d



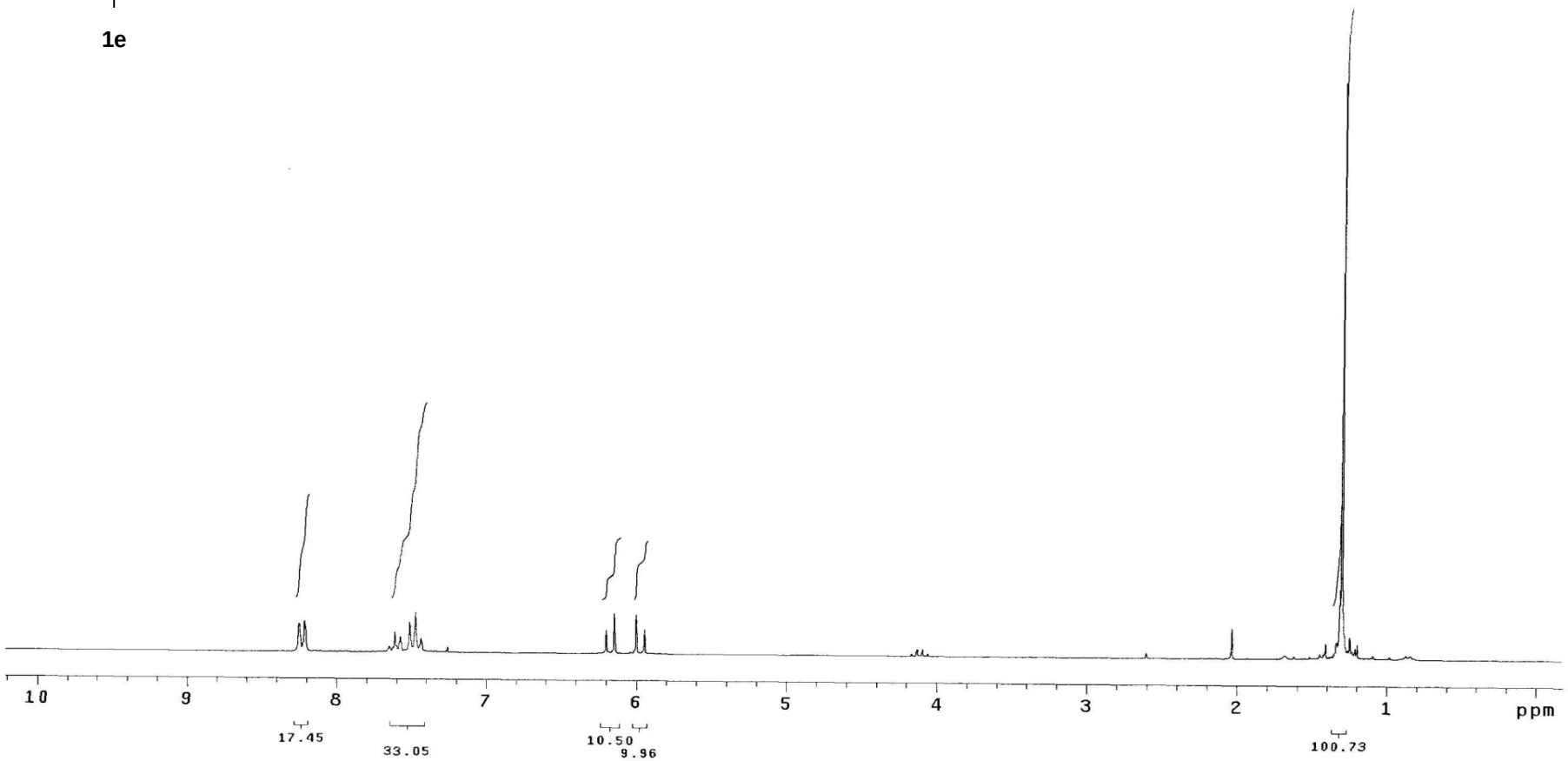


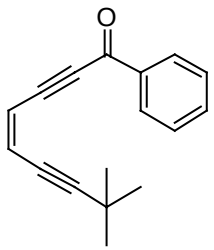
1d


177.795
136.777
134.003
129.760
128.479
126.854
115.703
102.048
92.023
90.098
79.118
77.314
77.000
76.682
29.071
28.059
22.008
180
160
140
120
100
80
60
40
20
ppm

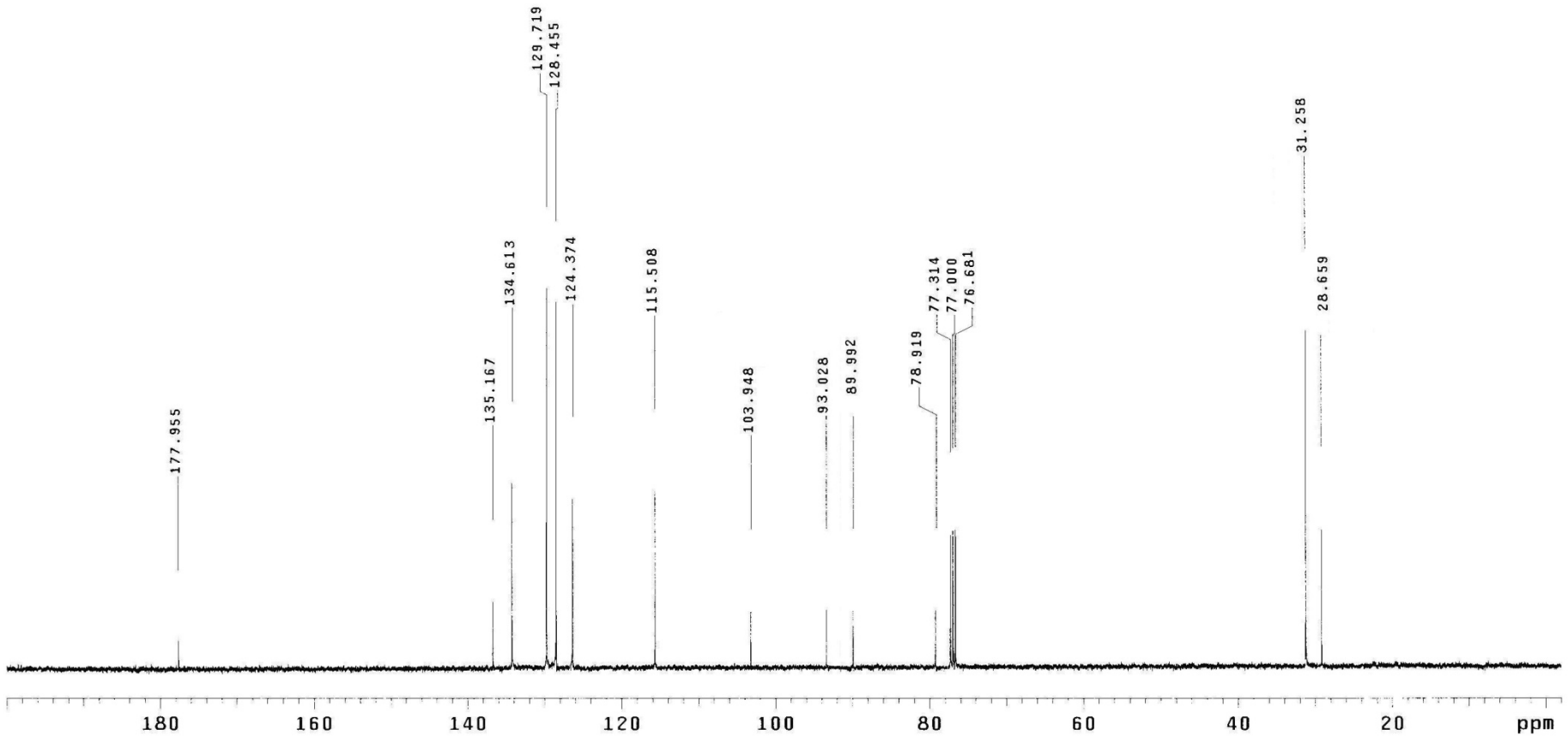


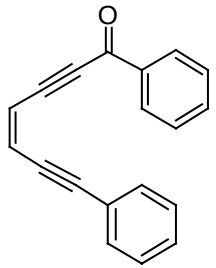
1e



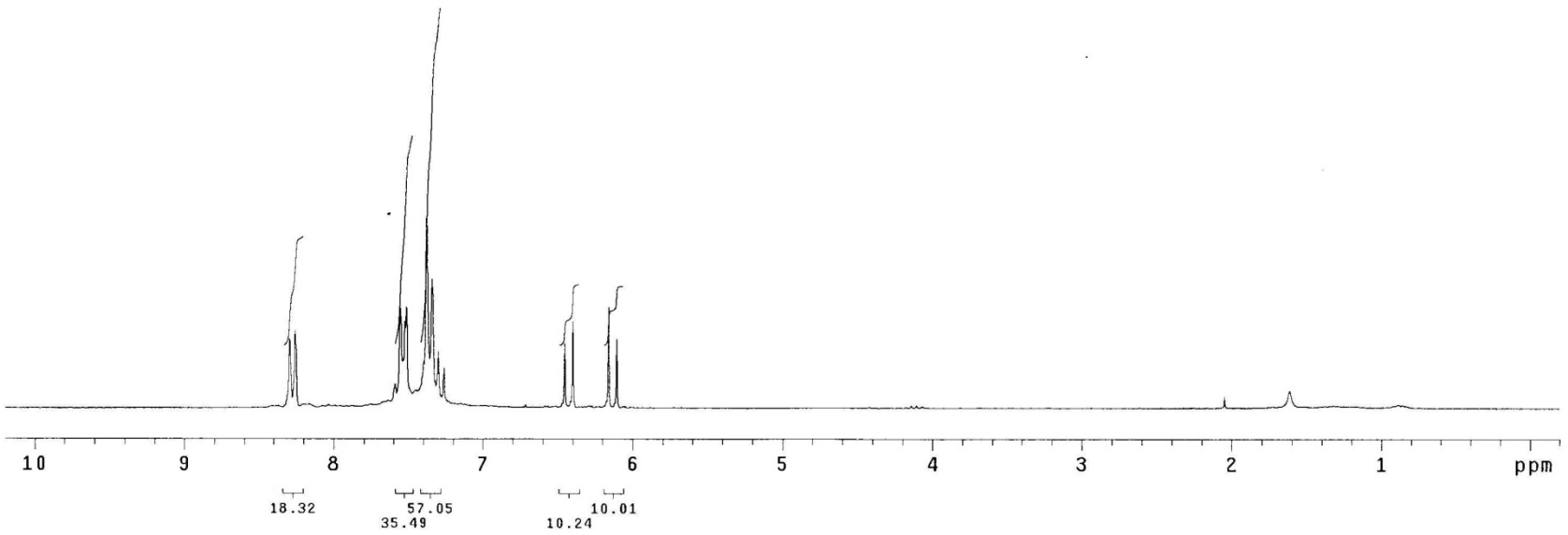


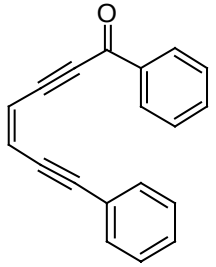
1e


177.955
135.167
134.613
129.719
128.455
124.374
115.508
103.948
93.028
89.992
78.919
77.314
77.000
76.681
31.258
28.659
180
160
140
120
100
80
60
40
20
ppm

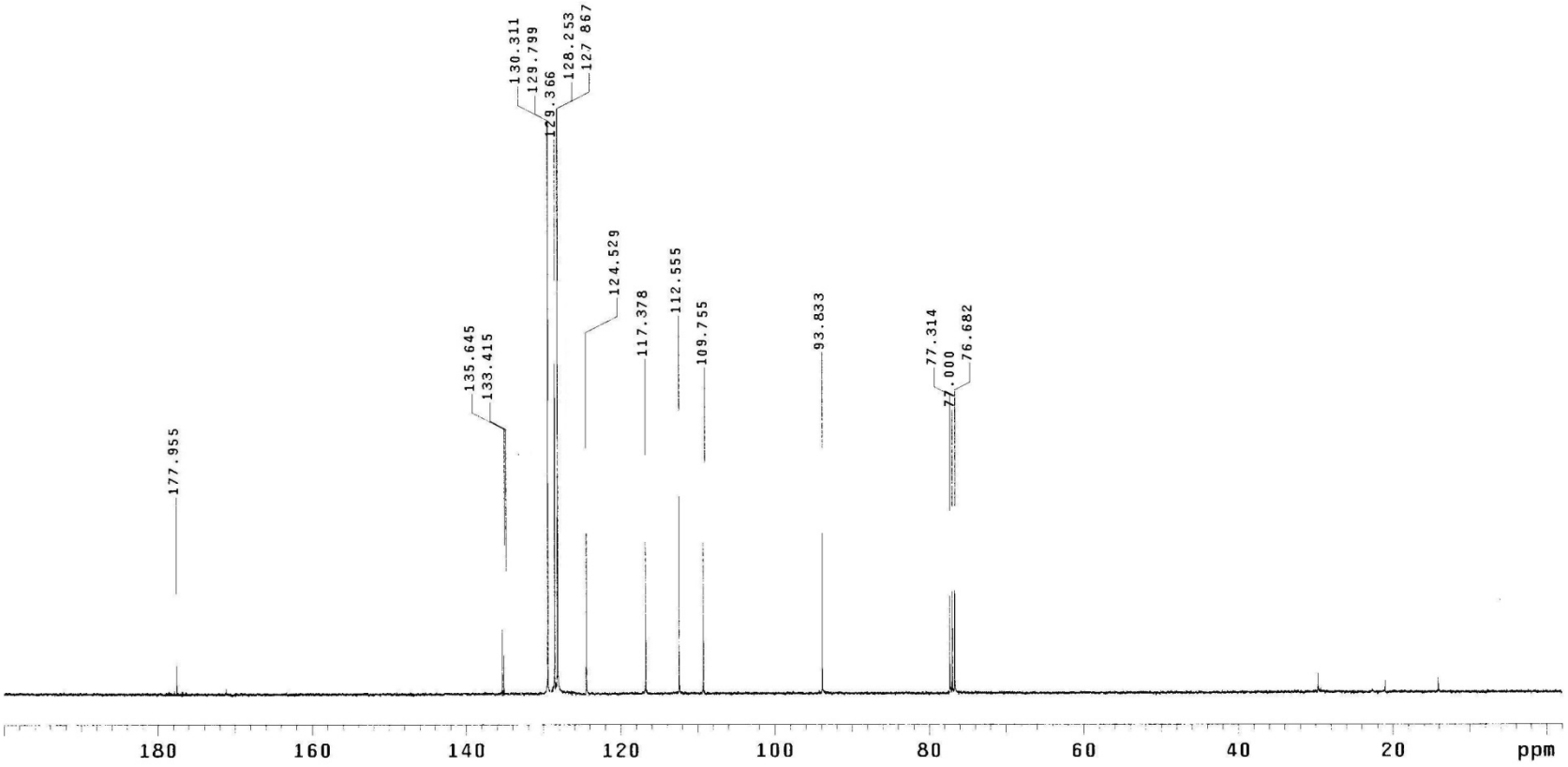


1f





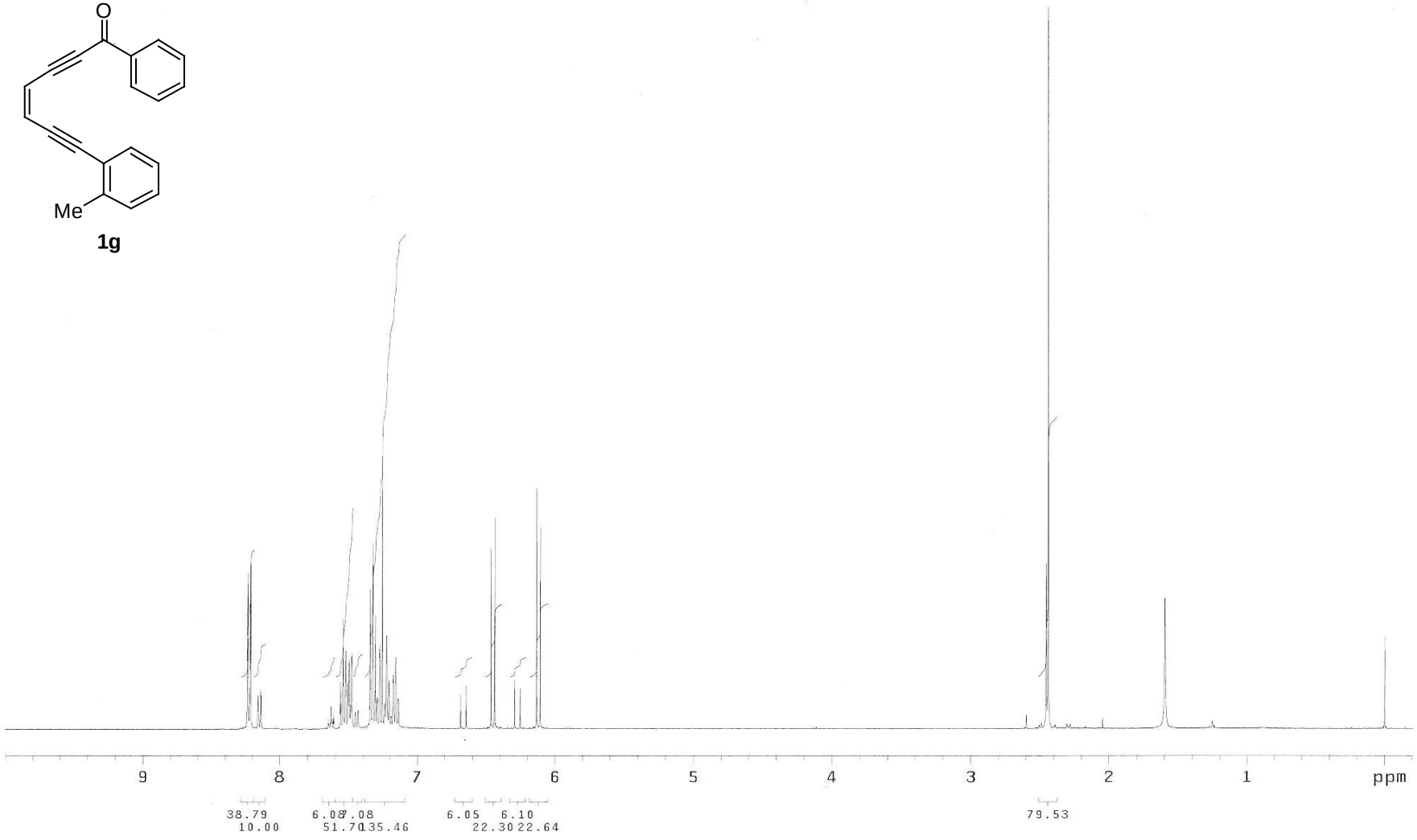
1f


177.955
135.645
133.415
130.311
129.799
129.366
128.253
127.867
124.529
117.378
112.555
109.755
93.833
77.314
77.000
76.682
180
160
140
120
100
80
60
40
20
ppm

WHJ-217

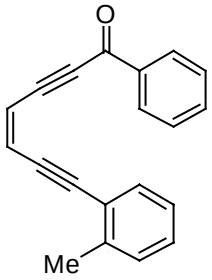
Mercury-400BB "Mercuryplus400"
Date: Mar 31 2008
Solvent: CDCl3
Ambient temperature
Total 48 repetitions

1g

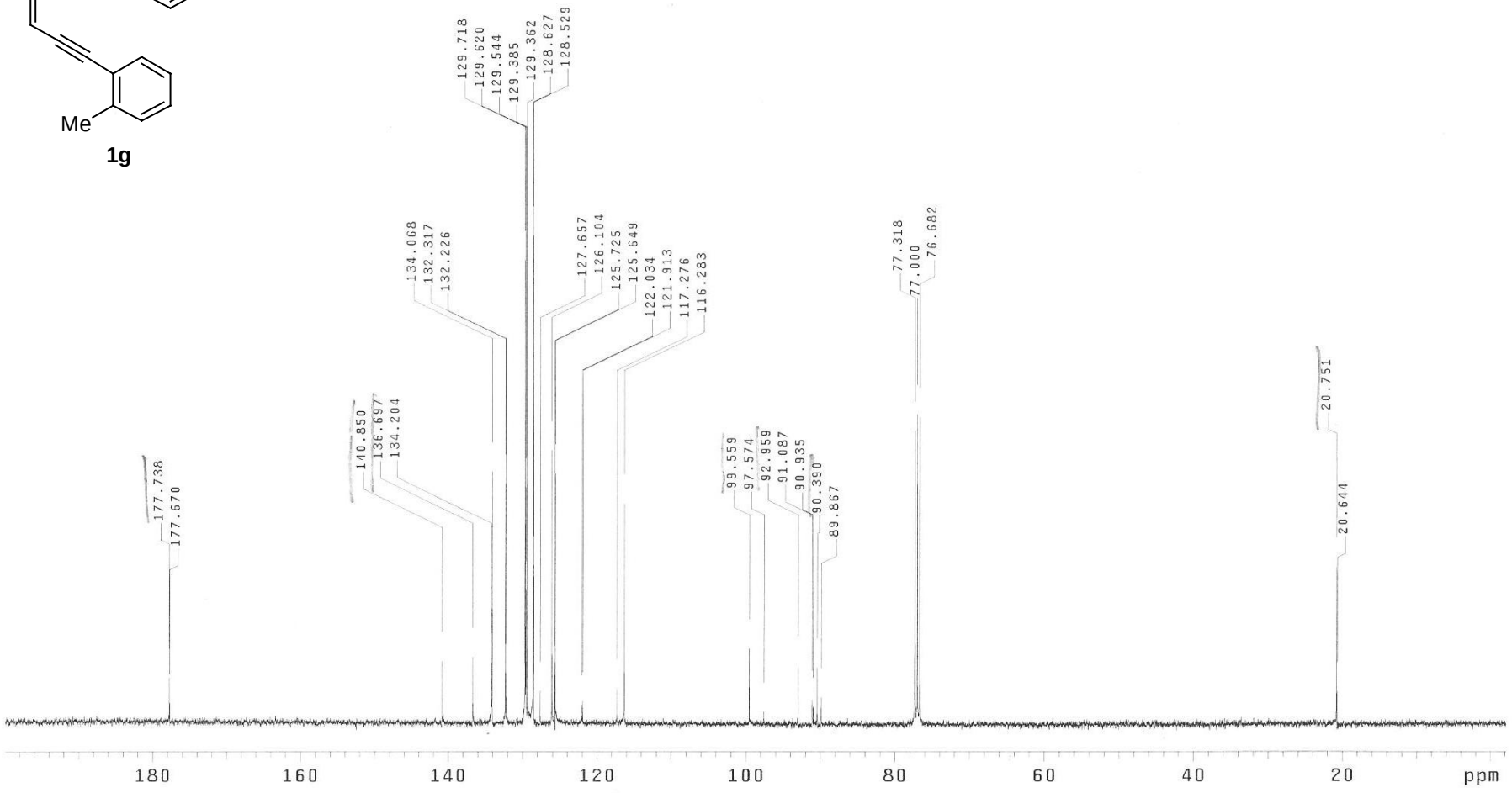


WHJ-217

Mercury-400BB "Mercuryplus400"
Date: Mar 31 2008
Solvent: CDCl3
Ambient temperature
Total 3744 repetitions

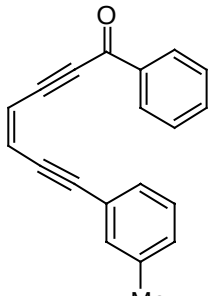


1g

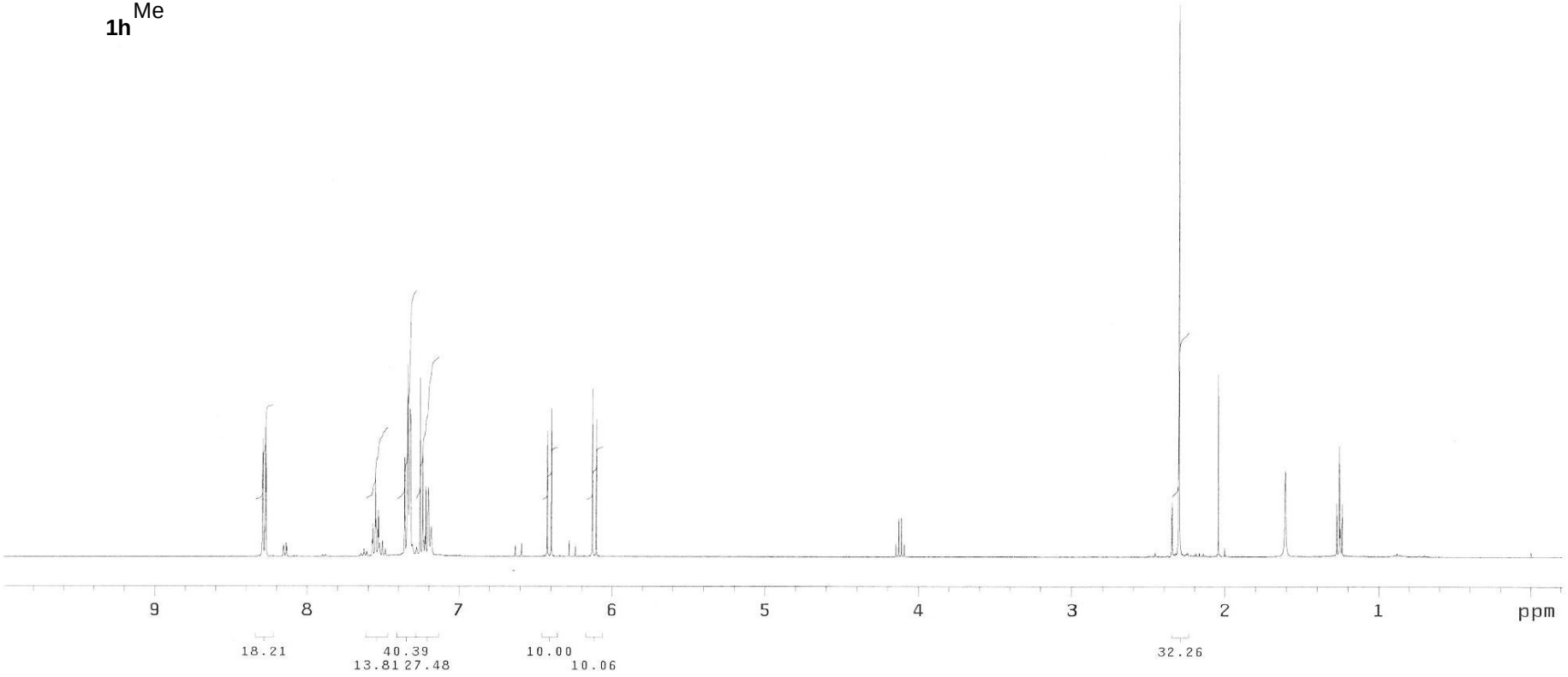


WHJ-214

Mercury-400BB "Mercuryplus400"
Date: Mar 27 2008
Solvent: CDCl3
Ambient temperature
Total 36 repetitions

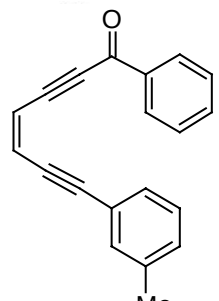


1h

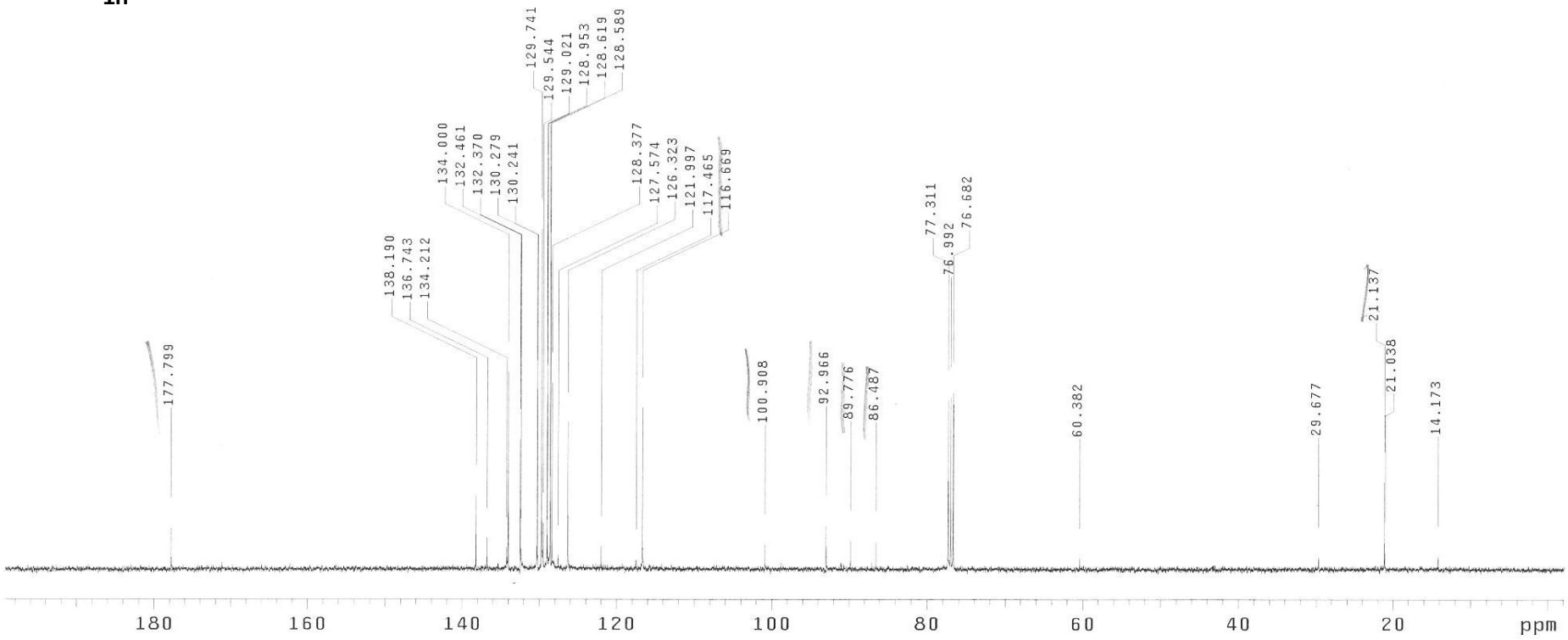


WHJ-214

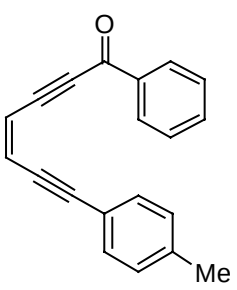
Mercury-400BB "Mercuryplus400"
Date: Mar 27 2008
Solvent: CDCl3
Ambient temperature
Total 1568 repetitions



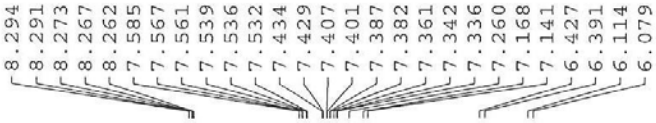
1h



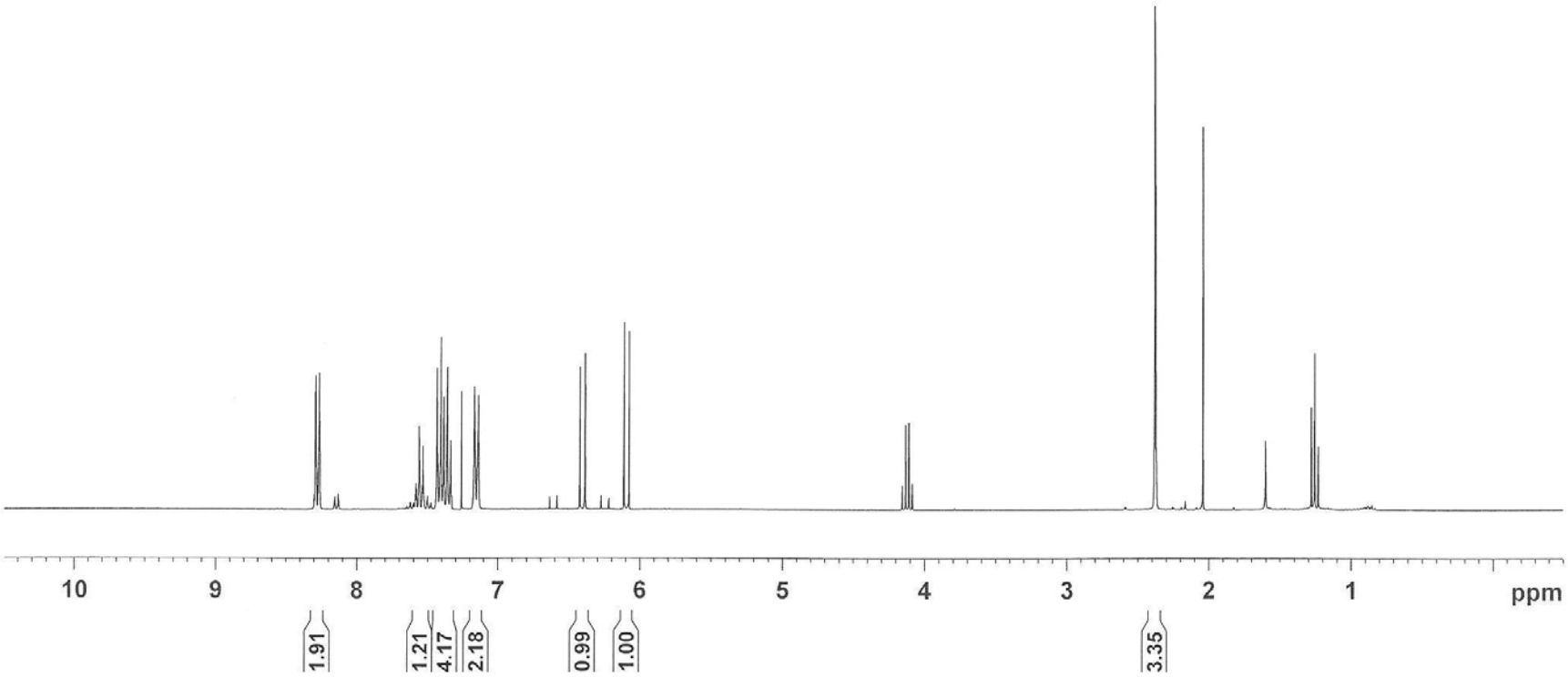
WHC-034-2


O
Me

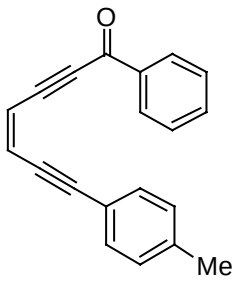
1i


8.294
8.291
8.273
8.267
8.262
7.585
7.567
7.561
7.539
7.536
7.532
7.434
7.429
7.407
7.401
7.387
7.382
7.361
7.342
7.336
7.260
7.168
7.141
6.427
6.391
6.114
6.079

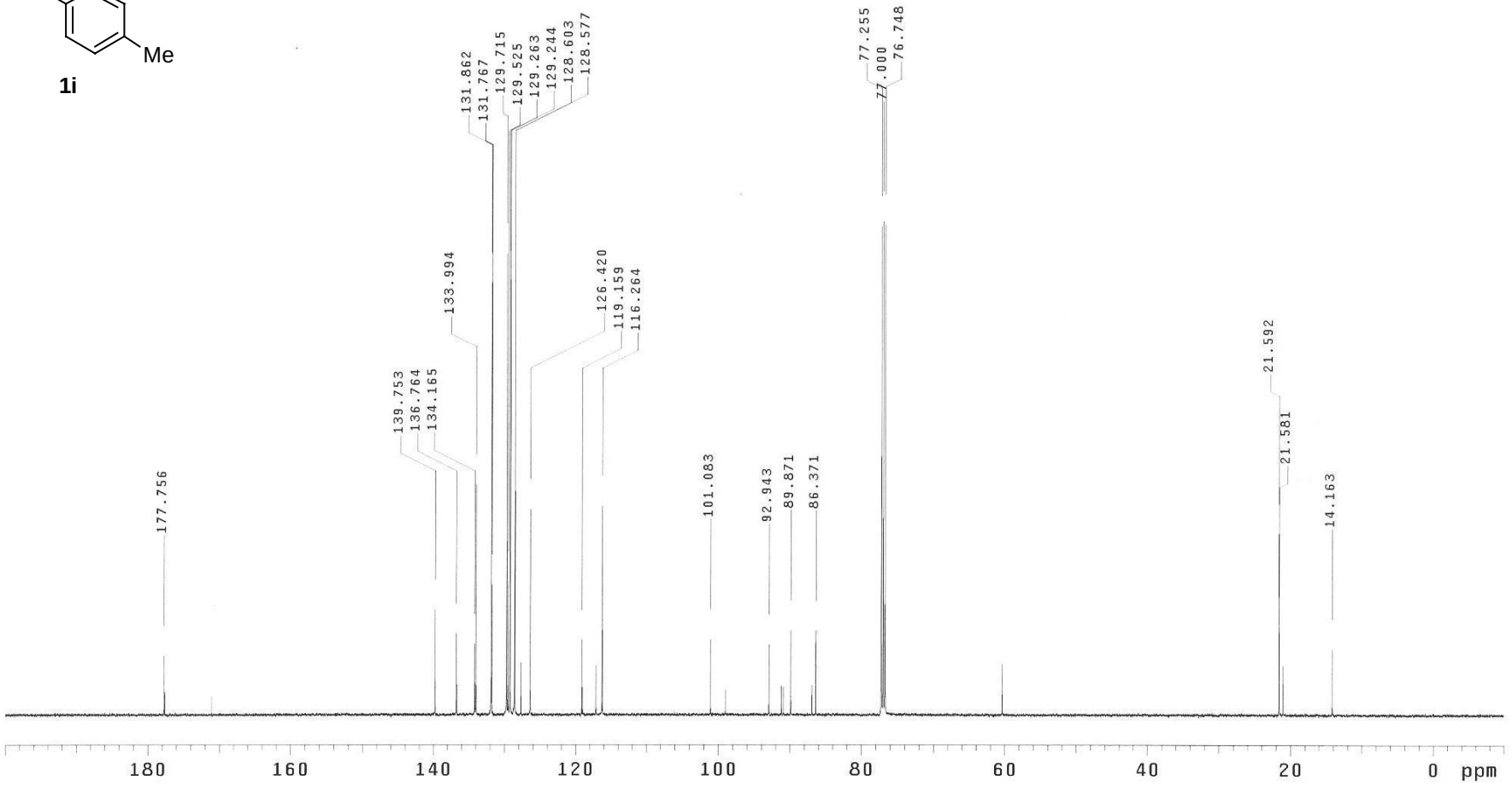
2.381


10
9
8
7
6
5
4
3
2
1
ppm
1.91
1.21
4.17
2.18
0.99
1.00
3.35

WHC-034-2


O
Me

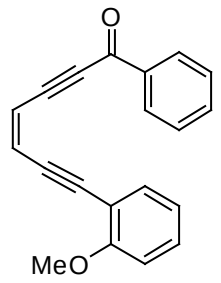
1i


177.756
139.753
136.764
134.165
133.994
131.862
131.767
129.715
129.525
129.263
129.244
128.603
128.577
126.420
119.159
116.264
101.083
92.943
89.871
86.371
77.255
77.000
76.748
21.592
21.581
14.163
180
160
140
120
100
80
60
40
20
0
ppm

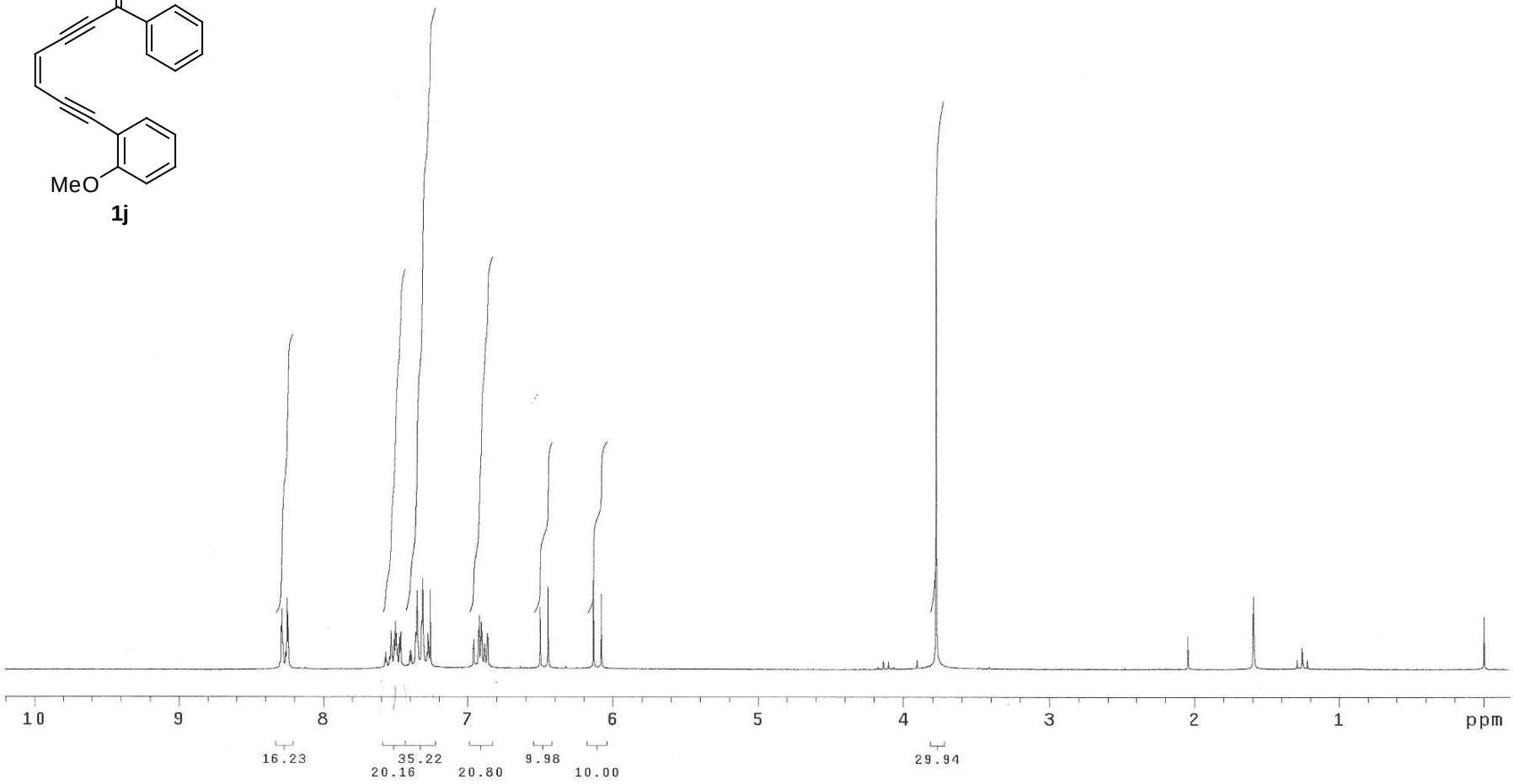
WHJ-213

Solvent: CDCl3
Ambient temperature
GEMINI-200 "oxford200"

Pulse 44.0 degrees
Acq. time 3.002 sec
Width 3000.3 Hz
40 repetitions
OBSERVE H1, 199.9678378 MHz
DATA PROCESSING
FT size 32768
Total time 2 hr, 50 min, 36 sec

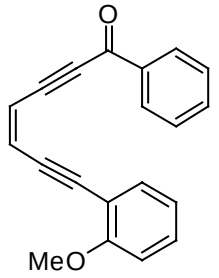


1j

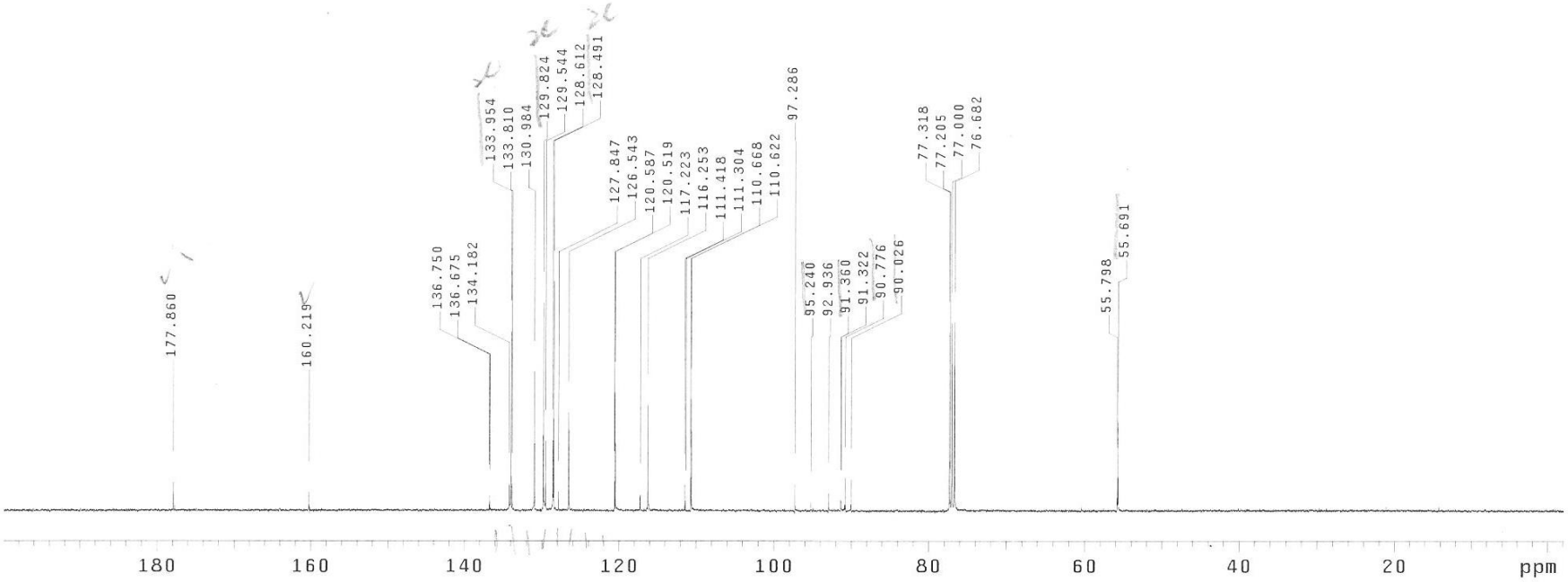


WHJ-213

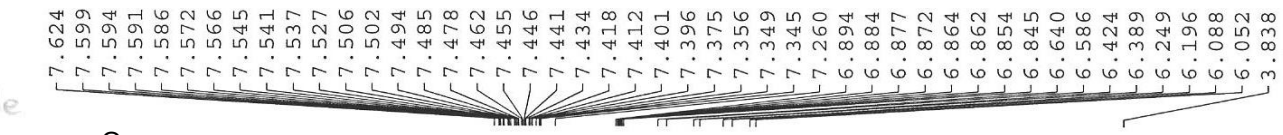
Mercury-400BB "Mercuryplus400"
Date: Mar 27 2008
Solvent: CDCl3
Ambient temperature
Total 7104 repetitions

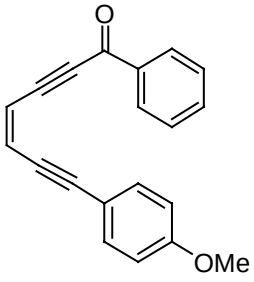


1j

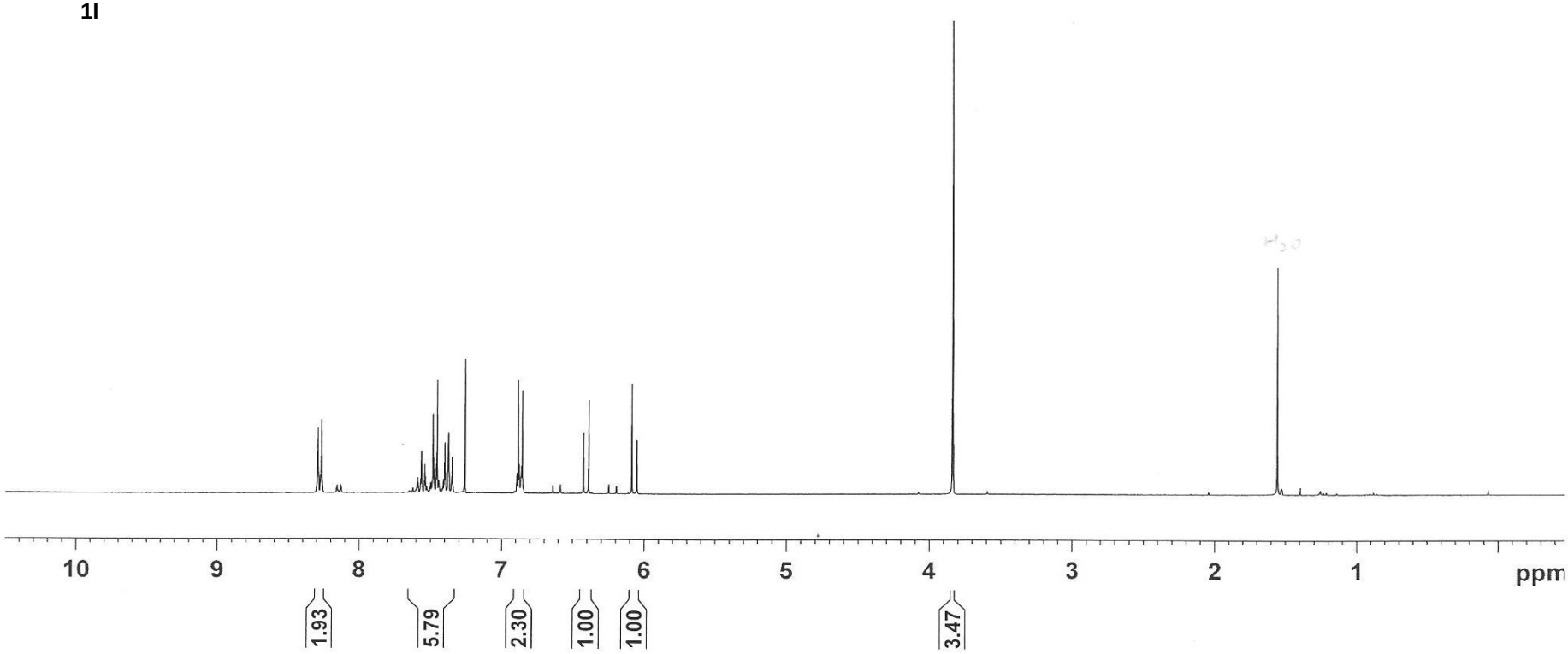


WHC-040

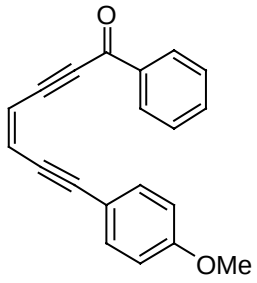

7.624
7.599
7.594
7.591
7.586
7.572
7.566
7.545
7.541
7.537
7.527
7.506
7.502
7.494
7.485
7.478
7.462
7.455
7.446
7.441
7.434
7.418
7.412
7.401
7.396
7.375
7.356
7.349
7.345
7.260
6.894
6.884
6.877
6.872
6.864
6.862
6.854
6.845
6.640
6.586
6.424
6.389
6.249
6.196
6.088
6.052
3.838
1.559


O
OMe

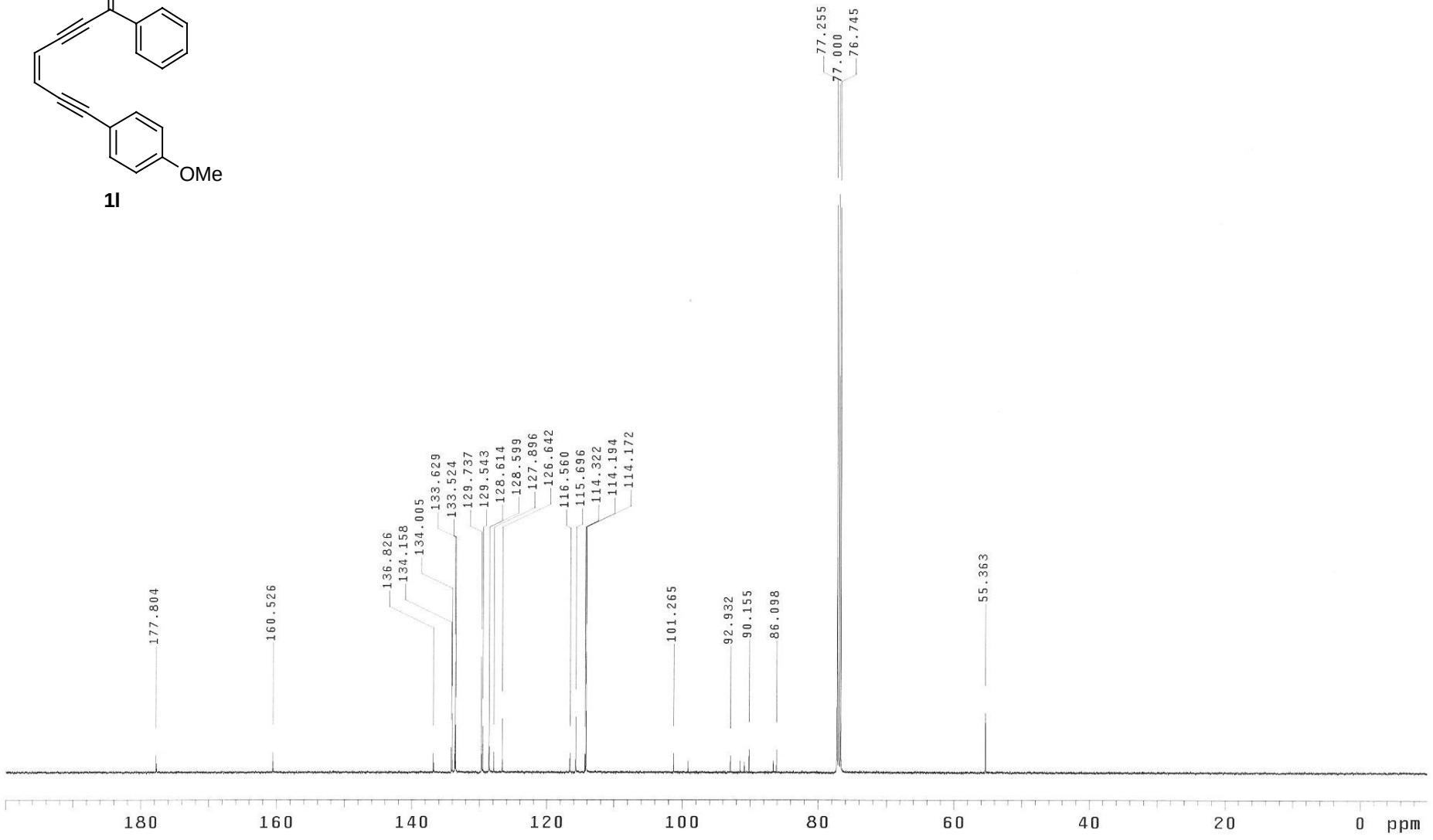
1l

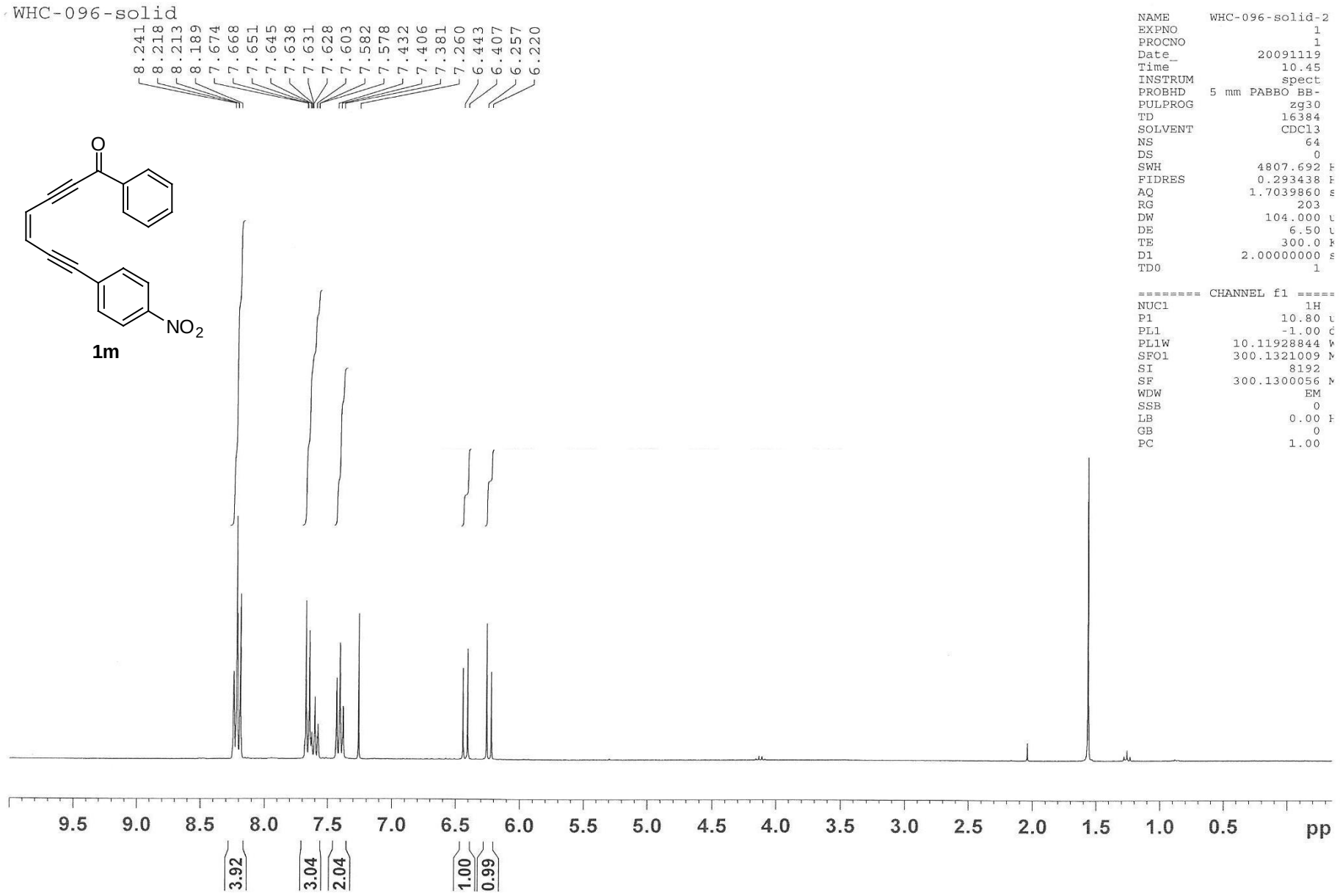

10
9
8
7
6
5
4
3
2
1
ppm
1.93
5.79
2.30
1.00
1.00
3.47

WHC-040

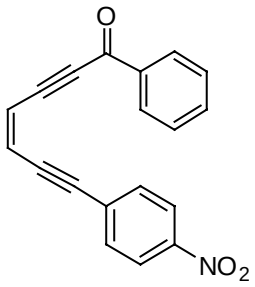

O
OMe

1l

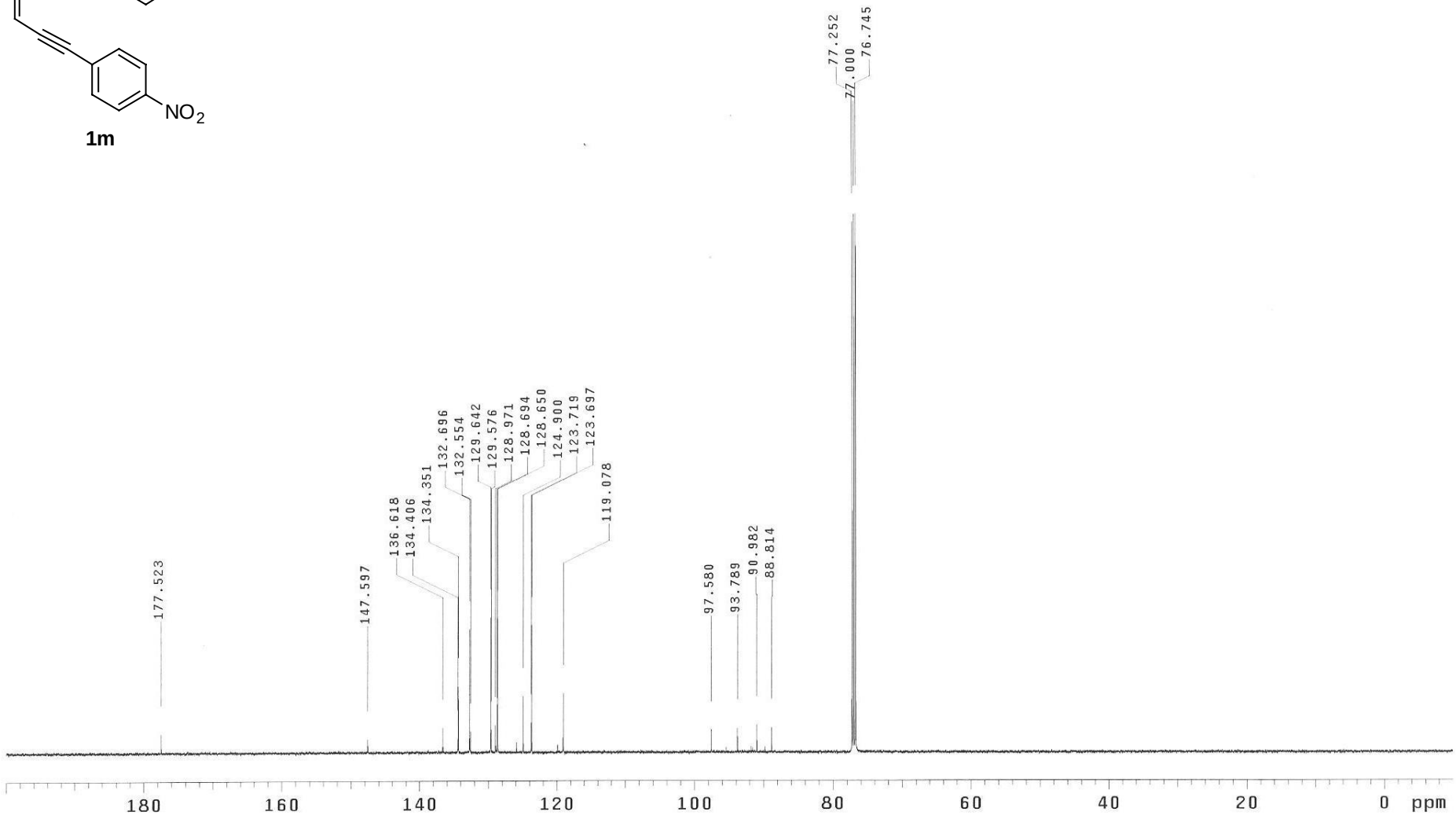

77.255
77.000
76.745
177.804
160.526
136.826
134.158
134.005
133.629
133.524
129.737
129.543
128.614
128.599
127.896
126.642
116.560
115.696
114.322
114.194
114.172
101.265
92.932
90.155
86.098
55.363
180
160
140
120
100
80
60
40
20
0
ppm

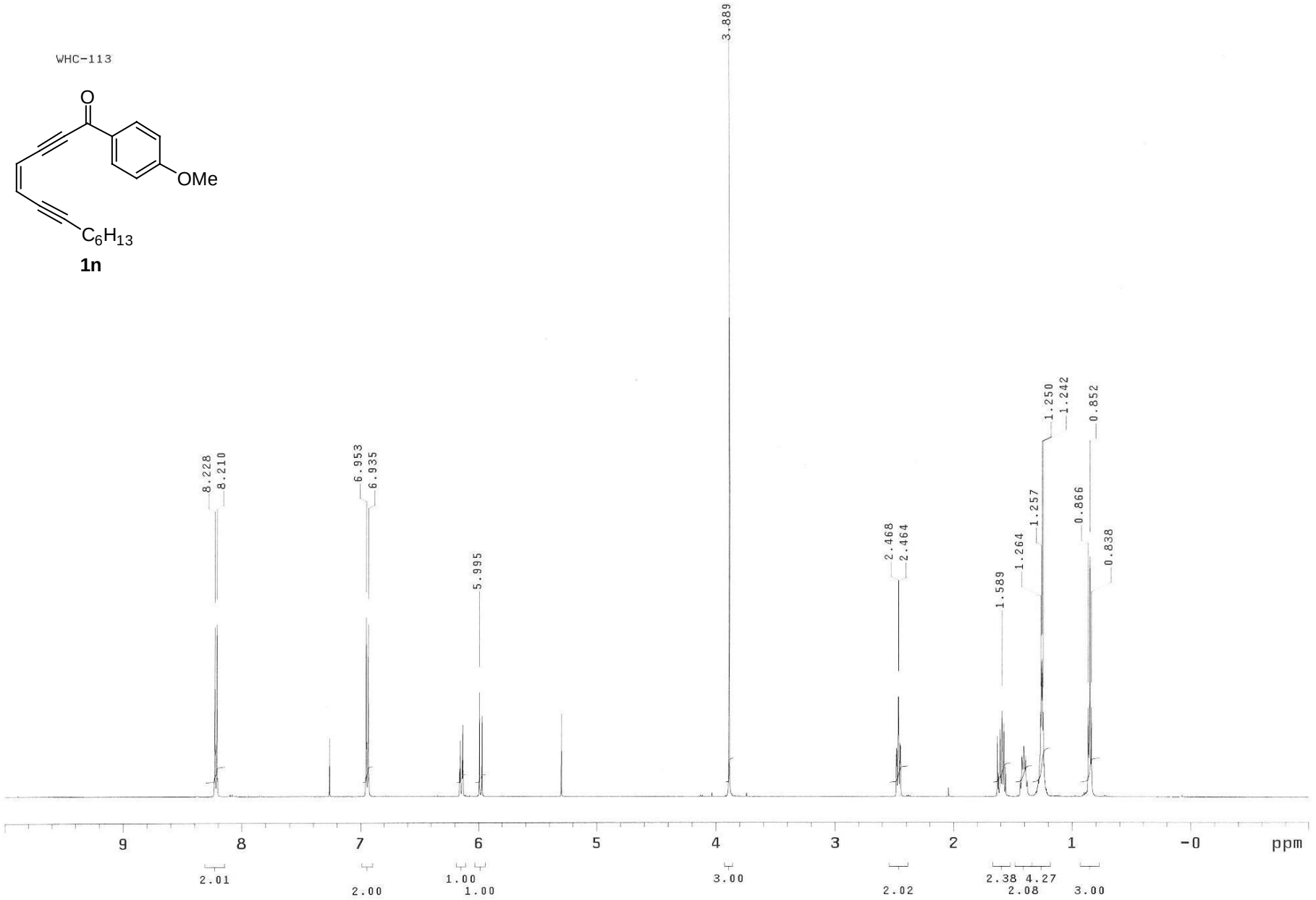

WHC-096-solid
8.241
8.218
8.213
8.189
7.674
7.668
7.651
7.645
7.638
7.631
7.628
7.603
7.582
7.578
7.432
7.406
7.381
7.260
6.443
6.407
6.257
6.220
O
NO2
1m
NAME WHC-096-solid-2
EXPNO 1
PROCNO 1
Date_ 20091119
Time 10.45
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 16384
SOLVENT CDCl3
NS 64
DS 0
SWH 4807.692
FIDRES 0.293438
AQ 1.7039860
RG 203
DW 104.000
DE 6.50
TE 300.0
D1 2.00000000
TD0 1
======== CHANNEL f1 =====
NUC1 1H
P1 10.80
PL1 -1.00
PL1W 10.11928844
SFO1 300.1321009
SI 8192
SF 300.1300056
WDW EM
SSB 0
LB 0.00
GB 0
PC 1.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 pp
3.92
3.04
2.04
1.00
0.99

WHC-096


O
NO2

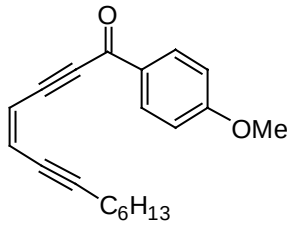
1m


77.252
77.000
76.745
132.696
132.554
129.642
129.576
128.971
128.694
128.650
124.900
123.719
123.697
119.078
136.618
134.406
134.351
177.523
147.597
97.580
93.789
90.982
88.814
180
160
140
120
100
80
60
40
20
0
ppm

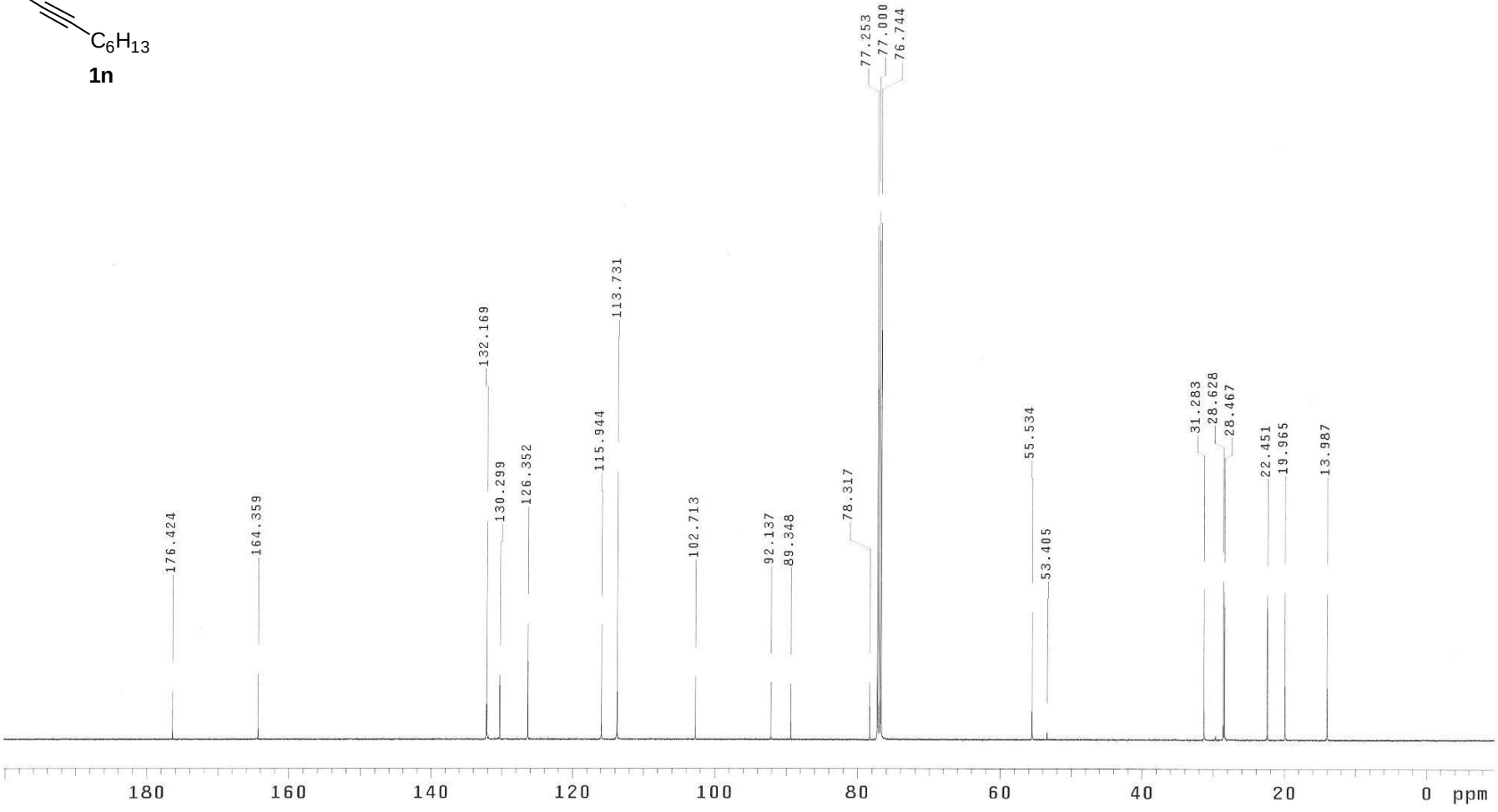

WHC-113
O
OMe
C_6H_{13}
3.889
8.228
8.210
6.953
6.935
5.995
2.468
2.464
1.589
1.264
1.257
1.250
1.242
0.866
0.852
0.838
9
8
7
6
5
4
3
2
1
-0
ppm
2.01
2.00
1.00
1.00
3.00
2.02
2.38
4.27
2.08
3.00

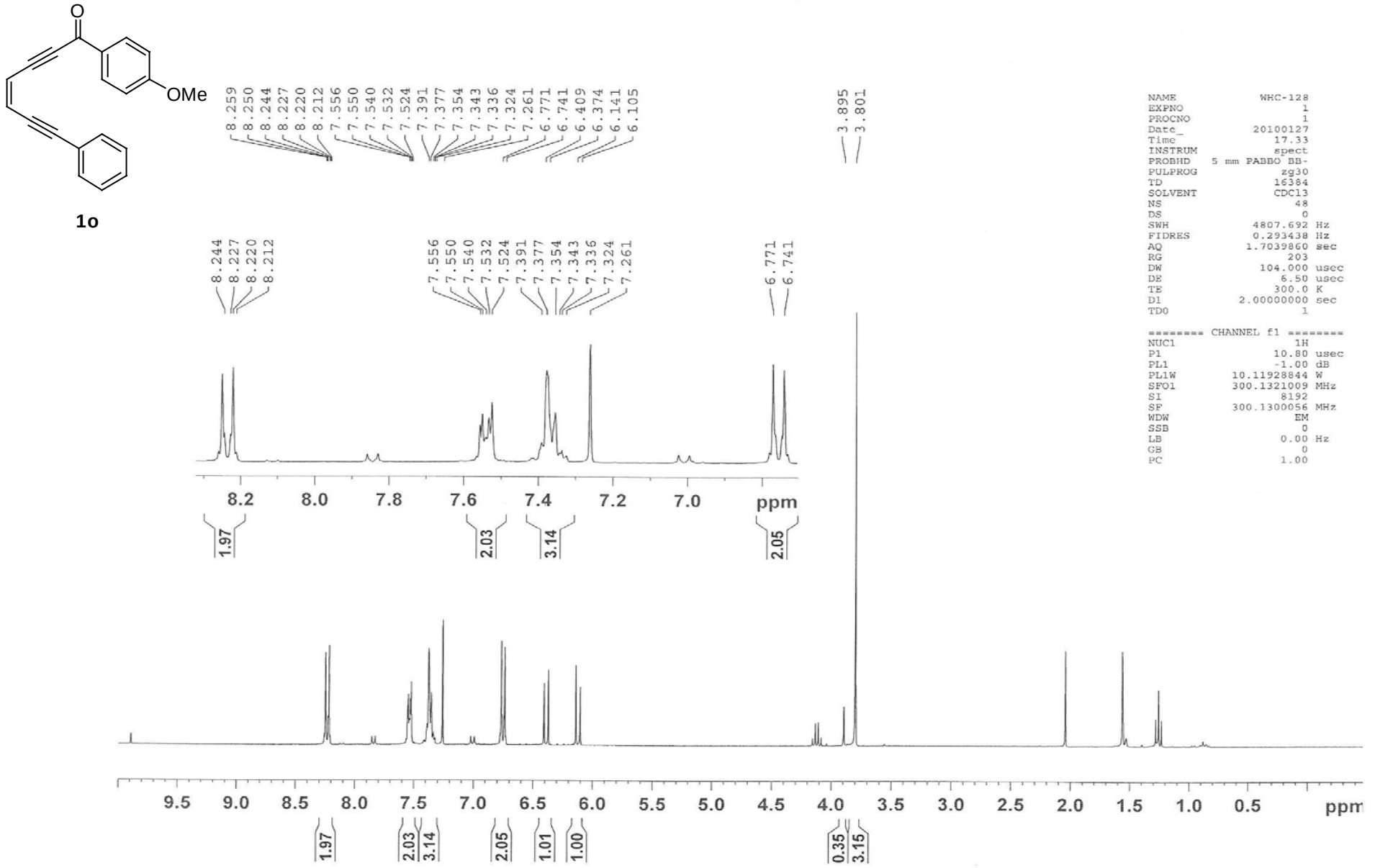
1n

WHC-113


O
OMe
C_6H_{13}

1n

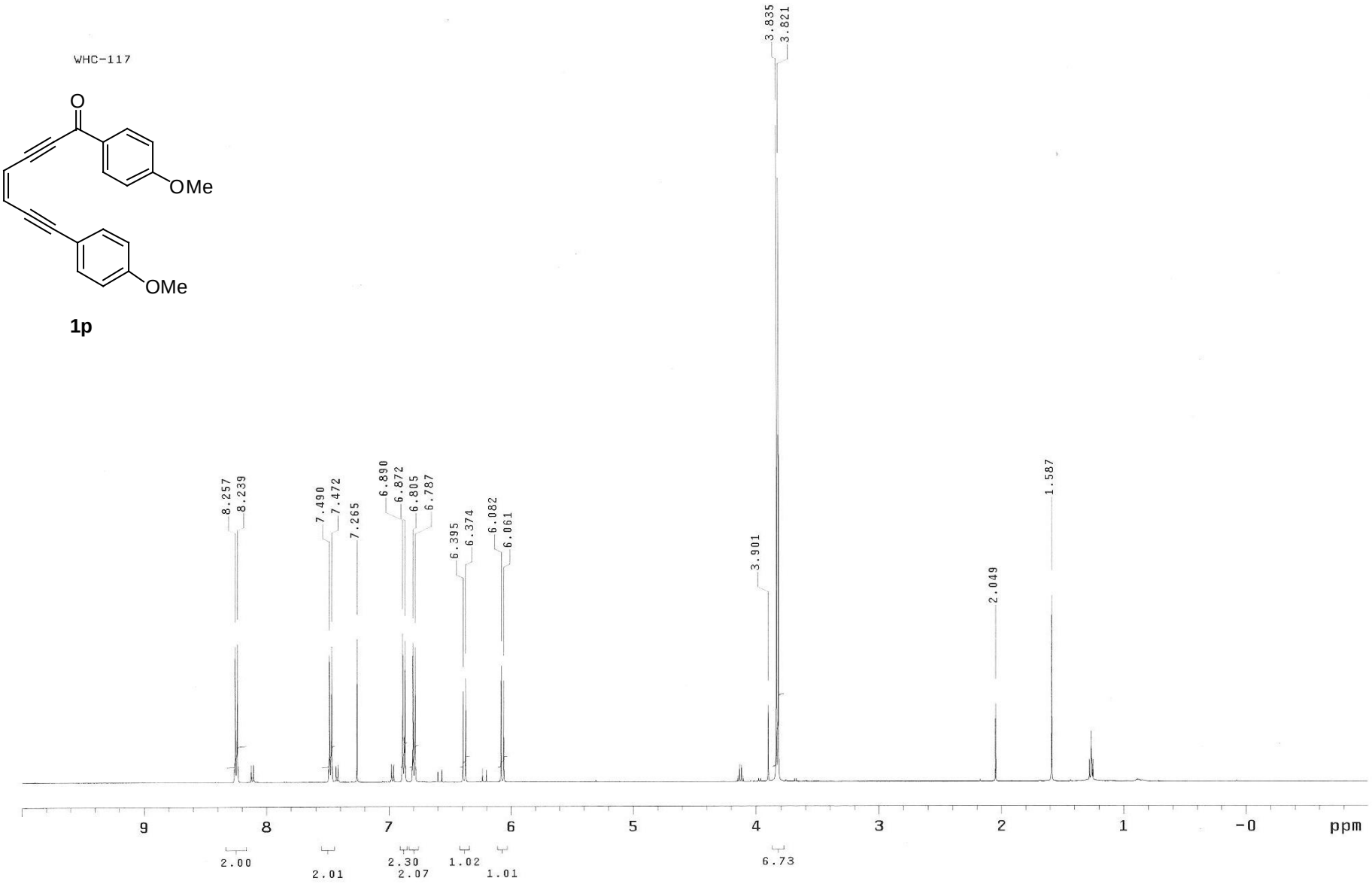

77.253
77.000
76.744
132.169
130.299
126.352
115.944
113.731
102.713
92.137
89.348
78.317
55.534
53.405
31.283
28.628
28.467
22.451
19.965
13.987
176.424
164.359
180
160
140
120
100
80
60
40
20
0 ppm


O
OMe
1o
8.259
8.250
8.244
8.227
8.220
8.212
7.556
7.550
7.540
7.532
7.524
7.391
7.377
7.354
7.343
7.336
7.324
7.261
6.771
6.741
6.409
6.374
6.141
6.105
3.895
3.801
NAME WHC-128
EXPNO 1
PROCNO 1
Date_ 20100127
Time 17.33
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 16384
SOLVENT CDCl3
NS 48
DS 0
SWH 4807.692 Hz
FIDRES 0.293438 Hz
AQ 1.7039860 sec
RG 203
DW 104.000 usec
DE 6.50 usec
TE 300.0 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 10.80 usec
PL1 -1.00 dB
PL1W 10.11928844 W
SFO1 300.1321009 MHz
SI 8192
SF 300.1300056 MHz
WDW EM
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
8.2
8.0
7.8
7.6
7.4
7.2
7.0
ppm
1.97
2.03
3.14
2.05
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.97
2.03
3.14
2.05
1.01
1.00
0.35
3.15

WHC-117

O
OMe
OMe

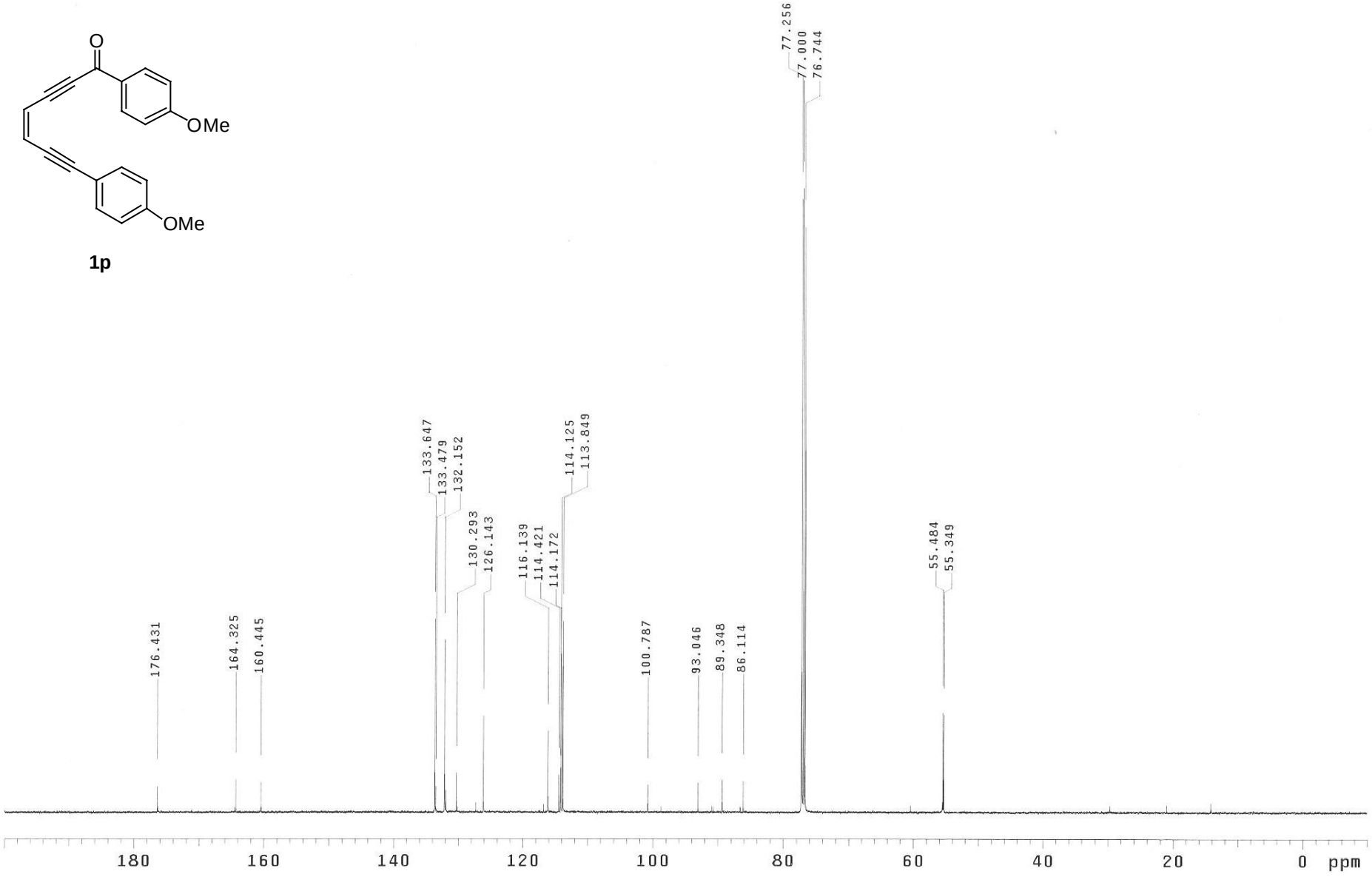
1p


3.835
3.821
8.257
8.239
7.490
7.472
7.265
6.890
6.872
6.805
6.787
6.395
6.374
6.082
6.061
3.901
2.049
1.587
9
8
7
6
5
4
3
2
1
-0
ppm
2.00
2.01
2.30
2.07
1.02
1.01
6.73

WHC-117

O
OMe
OMe

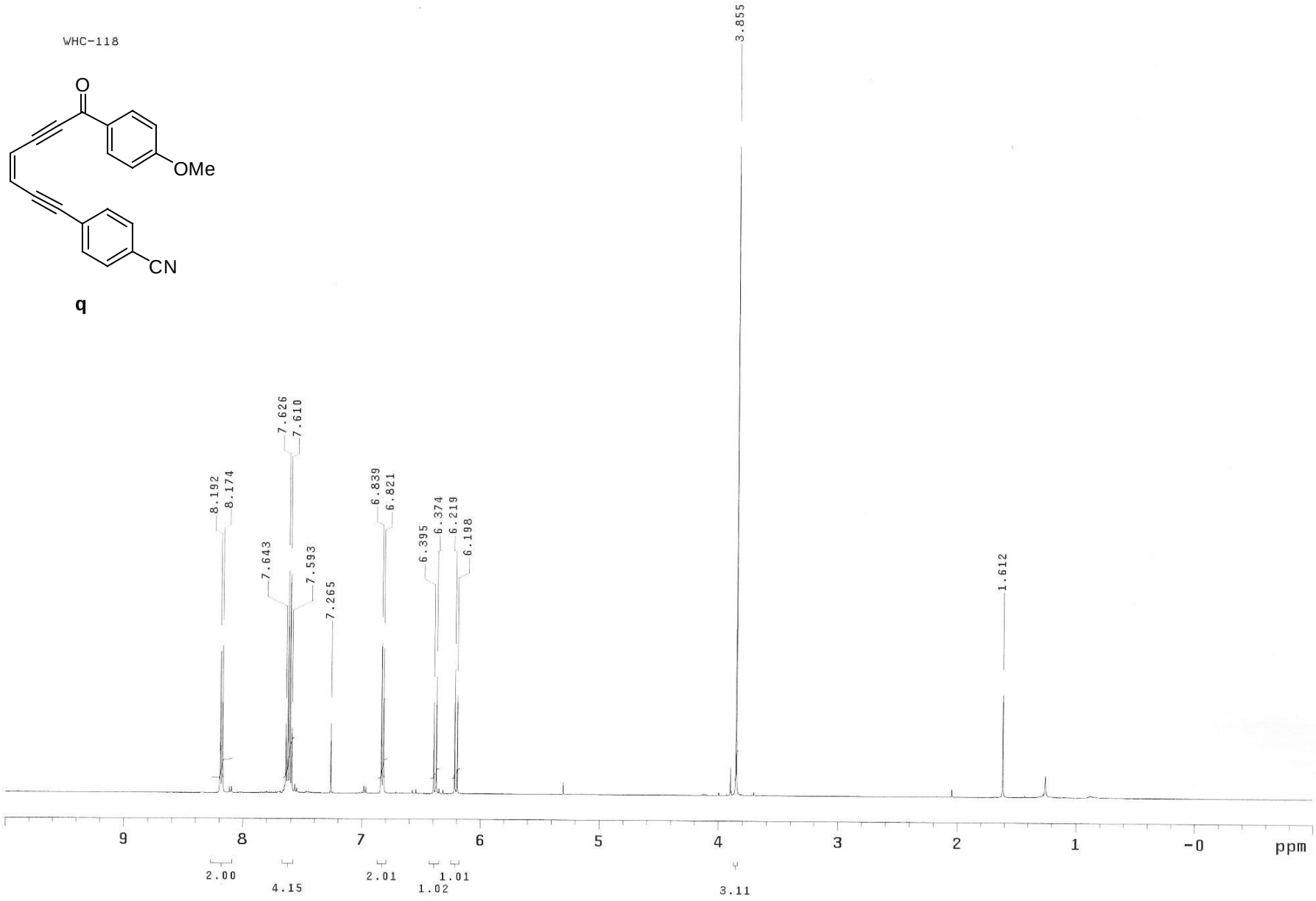
1p


77.256
77.000
76.744
133.647
133.479
132.152
130.293
126.143
116.139
114.421
114.172
114.125
113.849
176.431
164.325
160.445
100.787
93.046
89.348
86.114
55.484
55.349
180
160
140
120
100
80
60
40
20
0
ppm

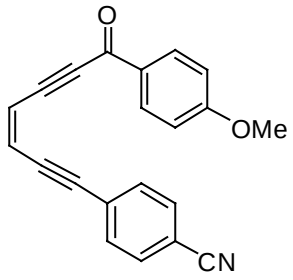
WHC-118

O
OMe
CN

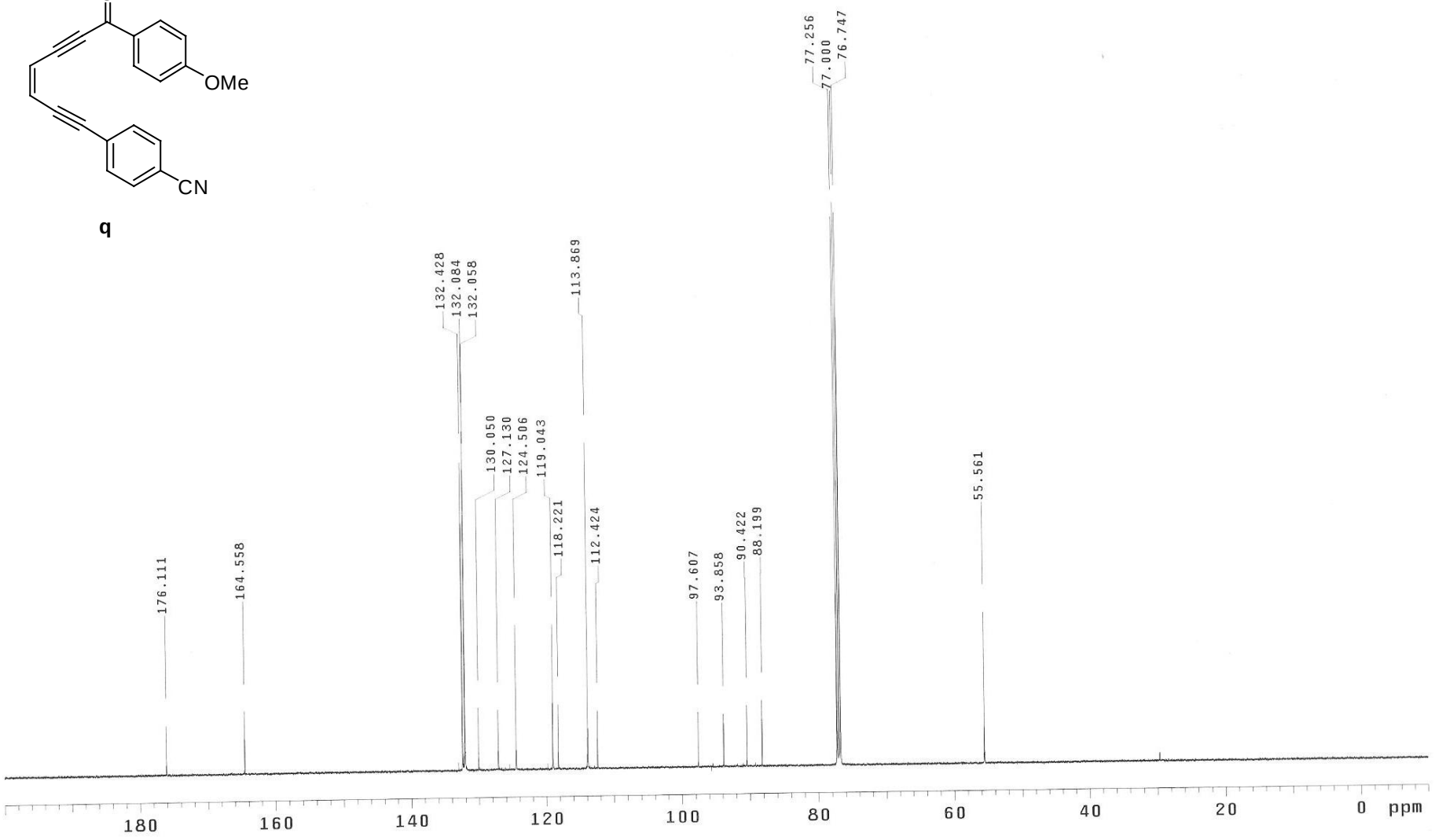
q

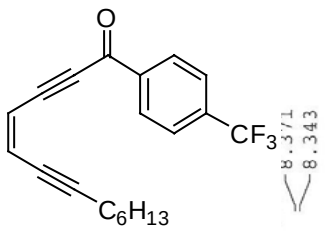

3.855
8.192
8.174
7.643
7.626
7.610
7.593
7.265
6.839
6.821
6.395
6.374
6.219
6.198
1.612
9
8
7
6
5
4
3
2
1
-0
ppm
2.00
4.15
2.01
1.02
1.01
3.11

WHC-118

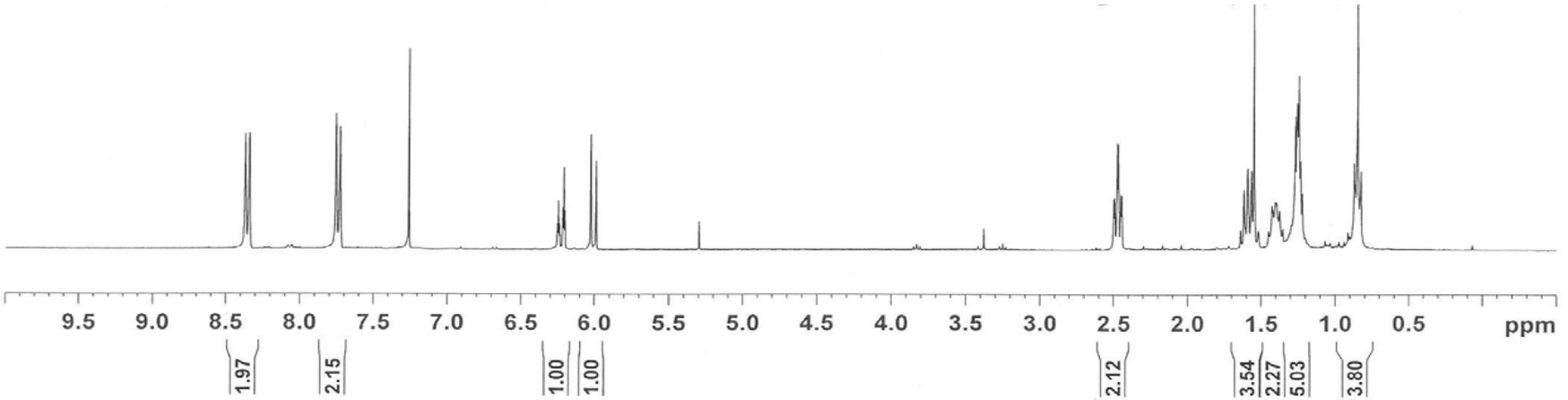

O
OMe
CN

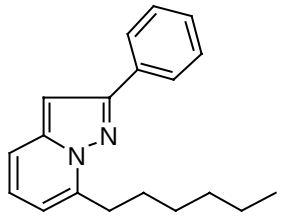
q


176.111
164.558
132.428
132.084
132.058
130.050
127.130
124.506
119.043
118.221
113.869
112.424
97.607
93.858
90.422
88.199
77.256
77.000
76.747
55.561
180
160
140
120
100
80
60
40
20
0
ppm

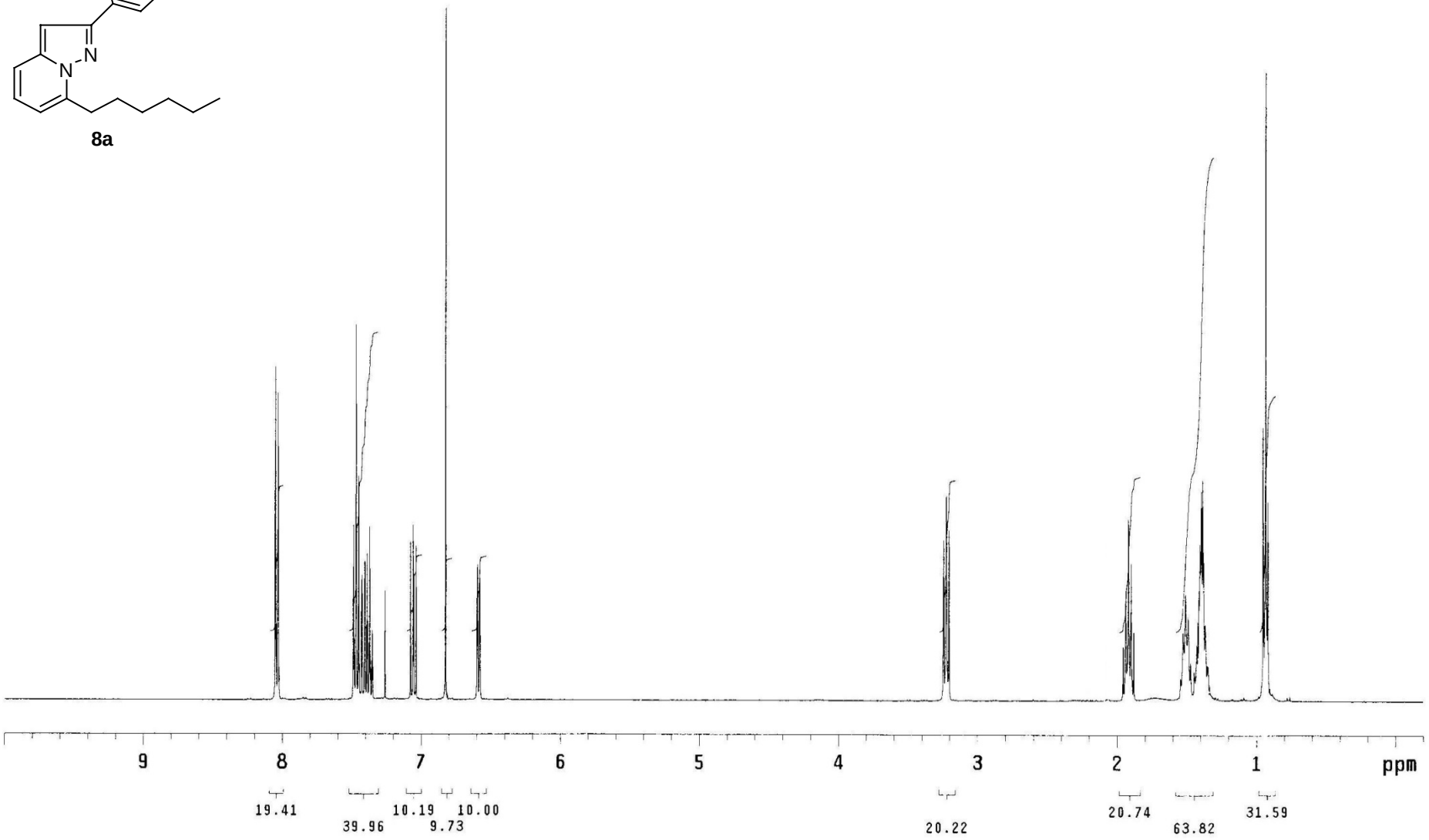

O
CF3
C6H13

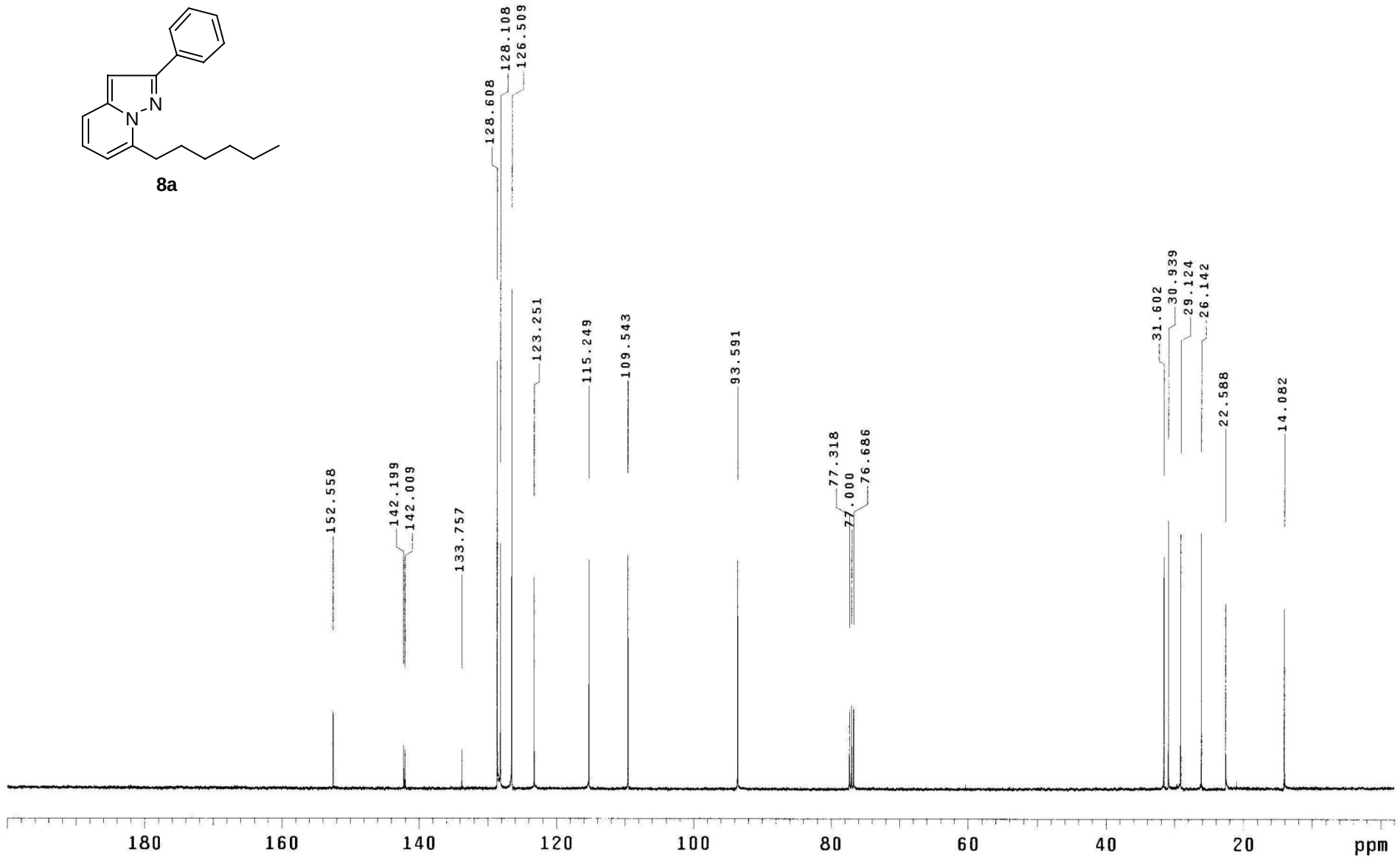
1r

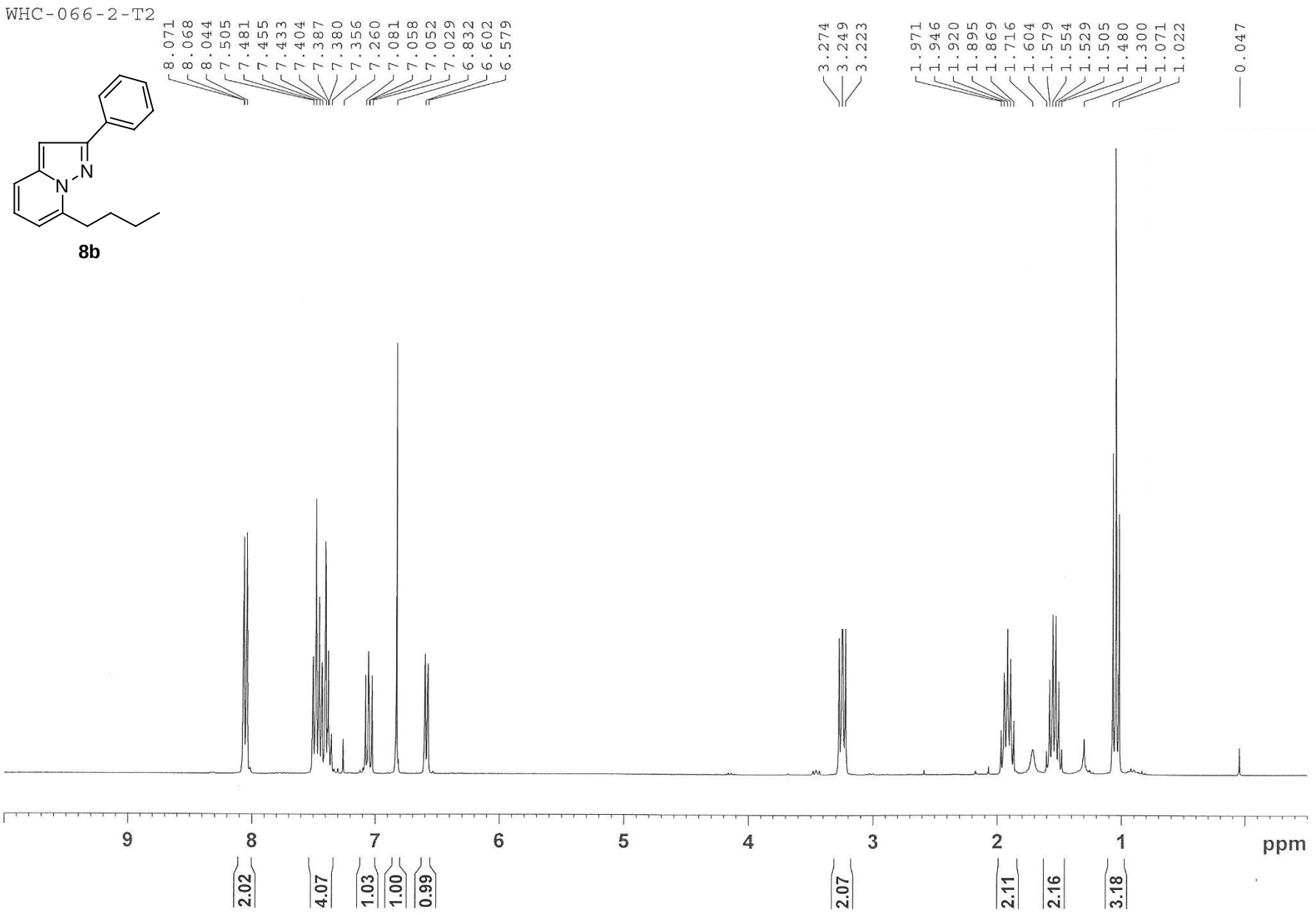

9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.97
2.15
1.00
1.00
2.12
3.54
2.27
5.03
3.80



8a

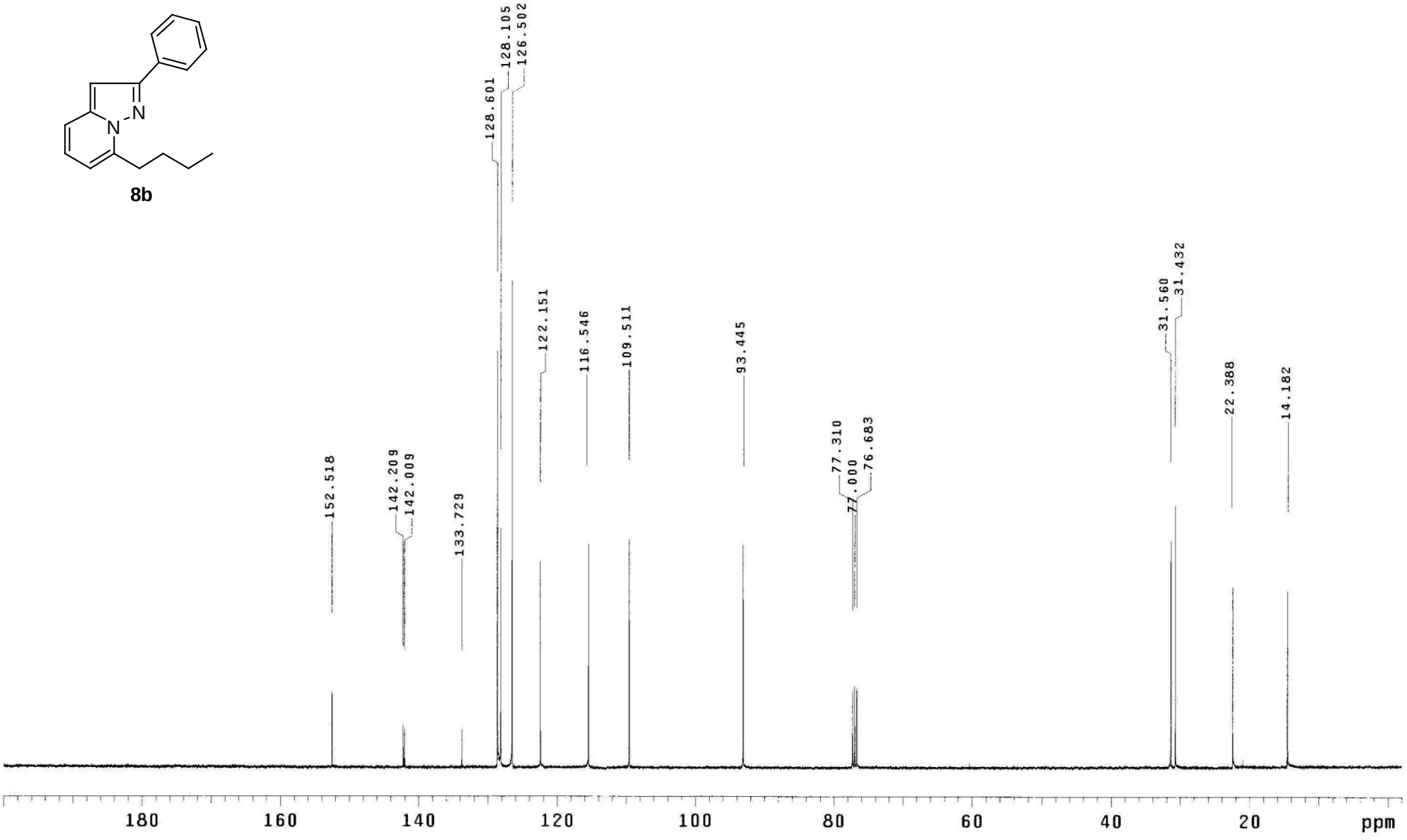



8a
152.558
142.199
142.009
133.757
128.608
128.108
126.509
123.251
115.249
109.543
93.591
77.318
77.000
76.686
31.602
30.939
29.124
26.142
22.588
14.082
180
160
140
120
100
80
60
40
20
ppm


WHC-066-2-T2
8.071
8.068
8.044
7.505
7.481
7.455
7.433
7.404
7.387
7.380
7.356
7.260
7.081
7.058
7.052
7.029
6.832
6.602
6.579
3.274
3.249
3.223
1.971
1.946
1.920
1.895
1.869
1.716
1.604
1.579
1.554
1.529
1.505
1.480
1.300
1.071
1.022
0.047
N
N
9
8
7
6
5
4
3
2
1
ppm
2.02
4.07
1.03
1.00
0.99
2.07
2.11
2.16
3.18

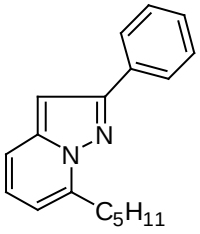
8b

8b

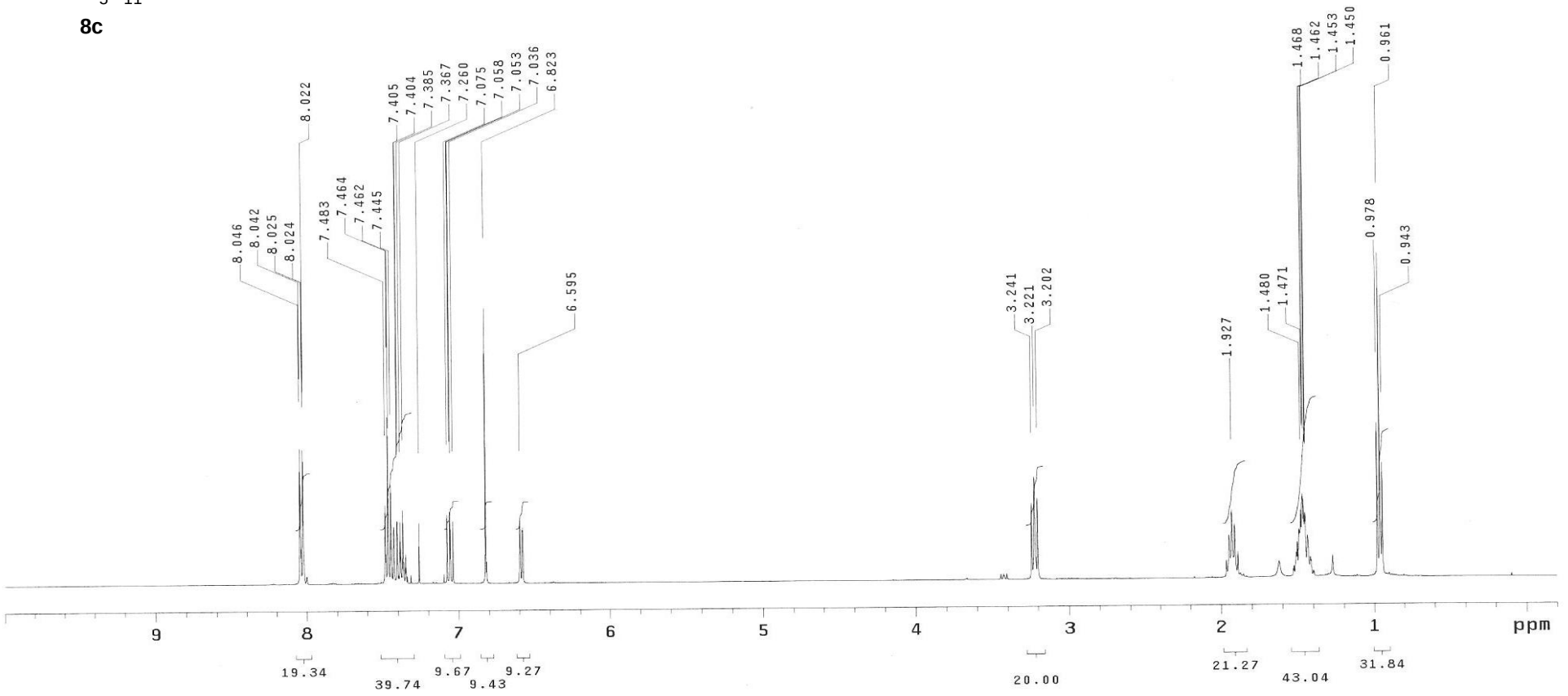

152.518
142.209
142.009
133.729
128.601
128.105
126.502
122.151
116.546
109.511
93.445
77.310
77.000
76.683
31.560
31.432
22.388
14.182
180
160
140
120
100
80
60
40
20
ppm

WHC-055-T2

Mercury-400BB "Mercuryplus400"
Date: Nov 6 2009
Solvent: CDCl3
Ambient temperature
Total 32 repetitions

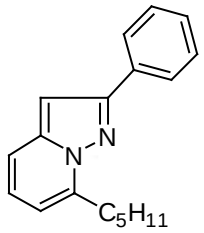


8c

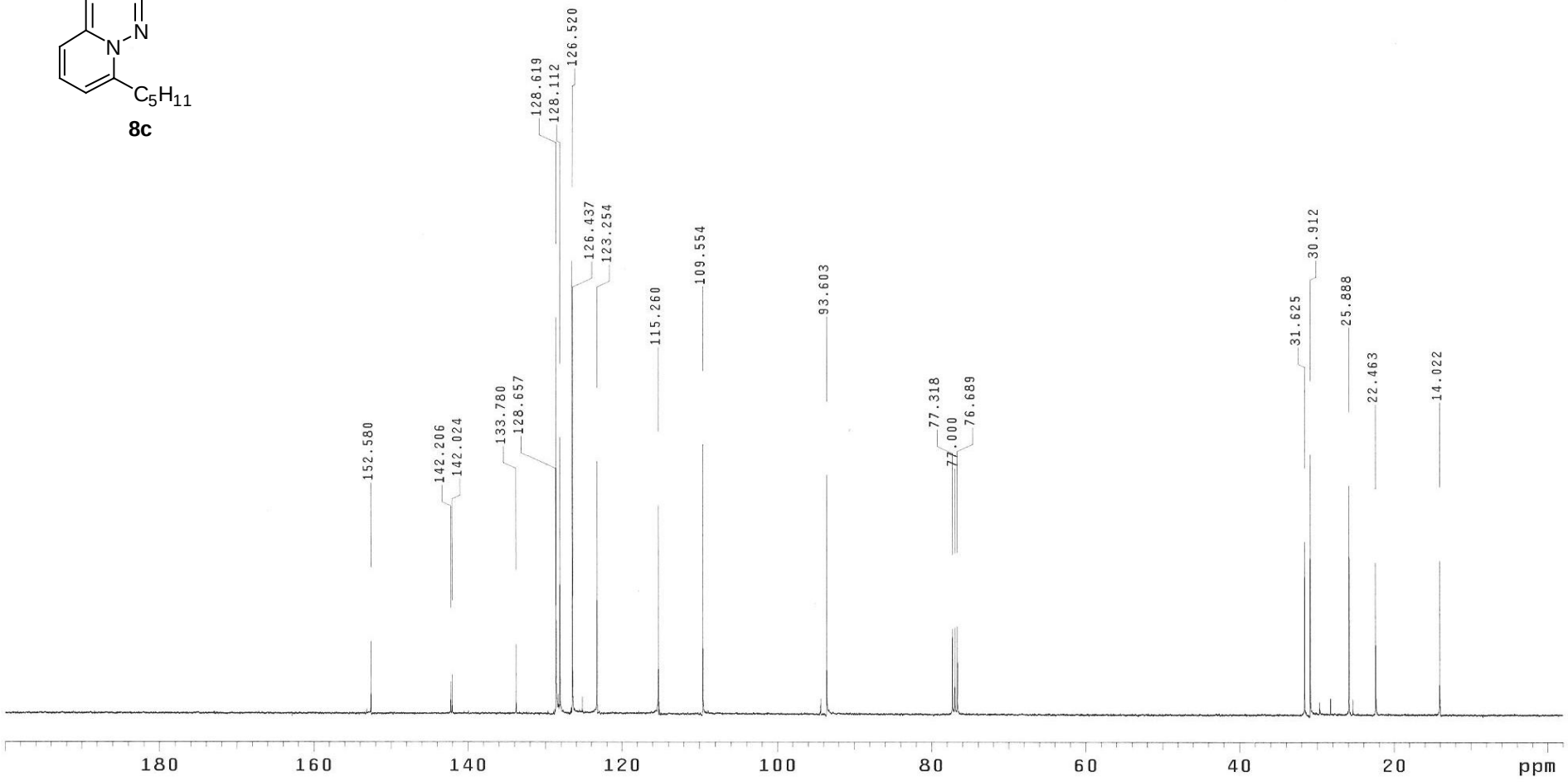


WHC-055-T2

Mercury-400BB "Mercuryplus400"
Date: Nov 6 2009
Solvent: CDCl3
Ambient temperature
Total 7232 repetitions



8c



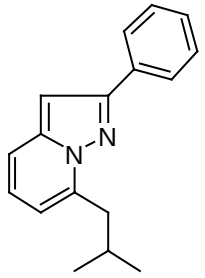
WHC-082-2

NAME	WHC-082-2
EXPNO	1
PROCNO	1
Date_	20091020
Time	14.20
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	16384
SOLVENT	CDCl3
NS	32
DS	0
SWH	4807.692 Hz
FIDRES	0.293438 Hz
AQ	1.7039860 sec
RG	161
DW	104.000 use
DE	6.50 use
TE	300.0 K
D1	2.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	10.80 use
PL1	-1.00 dB
PL1W	10.11928844 W
SFO1	300.1321009 MHz
SI	8192
SF	300.1300056 MHz
WDW	EM
SSB	0
LB	0.00 Hz
GB	0
PC	1.00

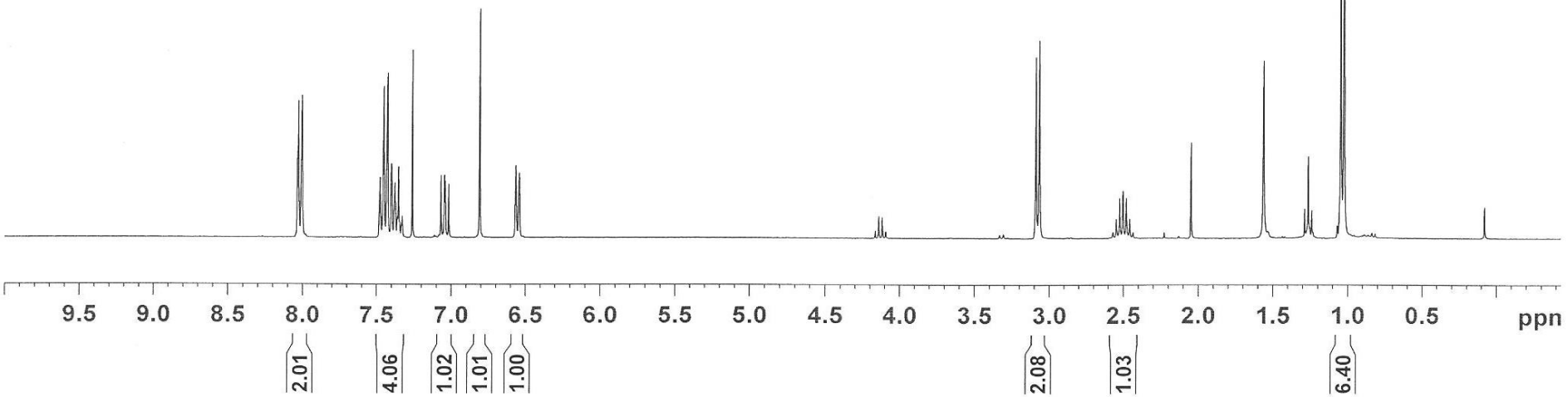
8.029 8.005 7.476 7.452 7.427 7.400 7.376 7.359 7.353 7.327 7.260 7.069 7.046 7.040 7.016 6.809 6.565 6.541

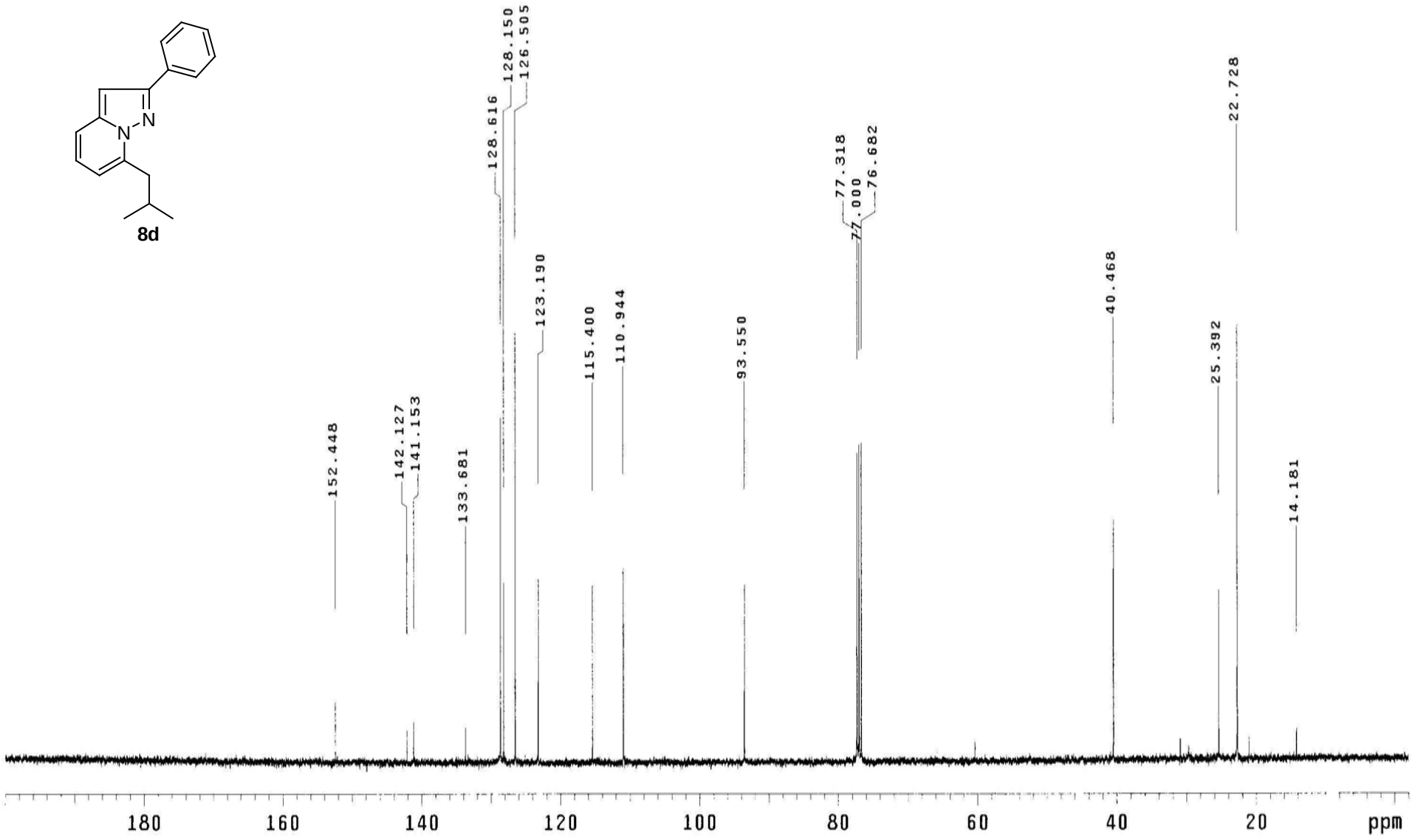
3.089 3.066 2.569 2.547 2.524 2.502 2.479 2.457 2.434

1.048 1.025



8d




8d
152.448
142.127
141.153
133.681
128.616
128.150
126.505
123.190
115.400
110.944
93.550
77.318
77.000
76.682
40.468
25.392
22.728
14.181
180
160
140
120
100
80
60
40
20
ppm

WHC-081-2-liquid

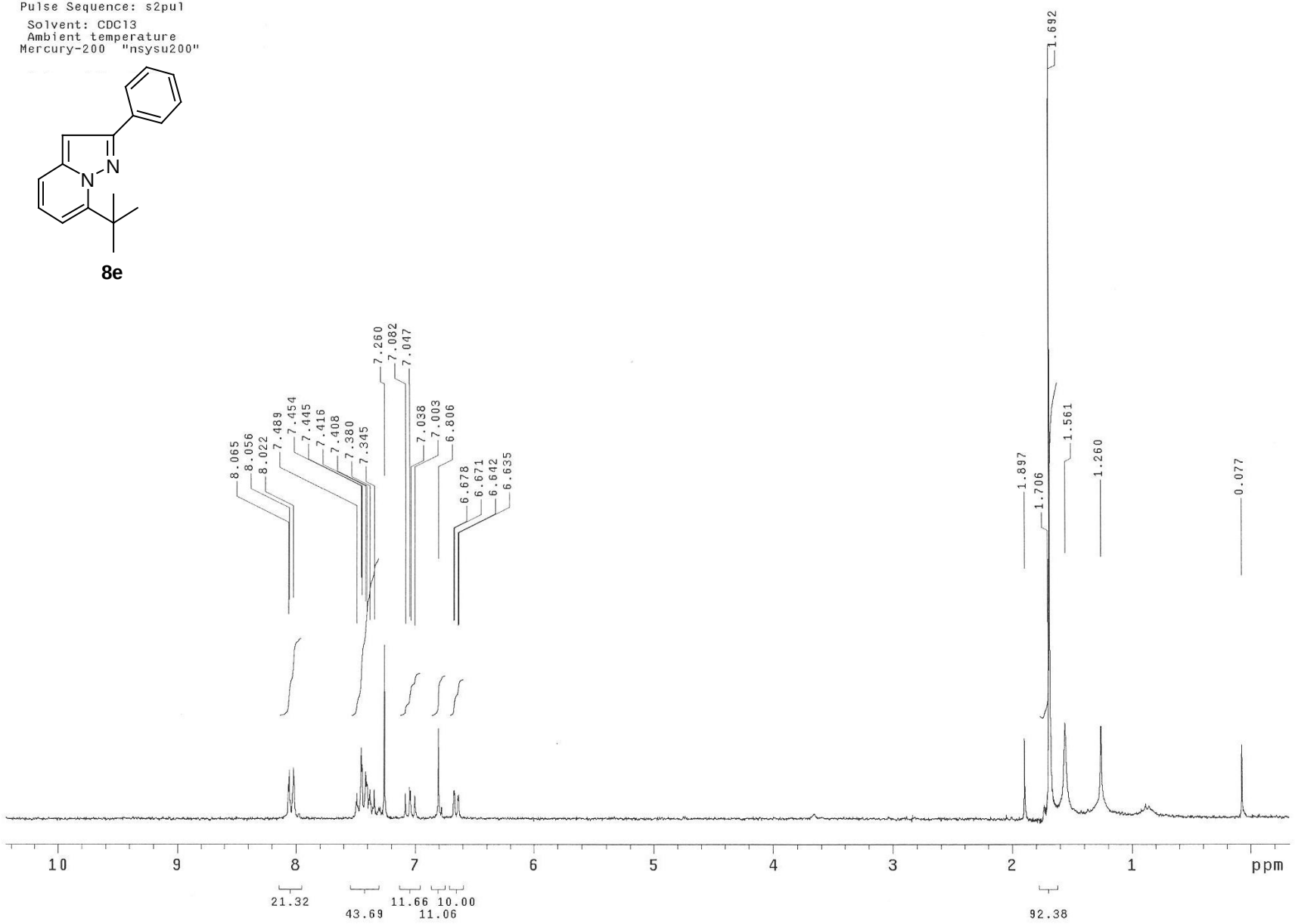
Pulse Sequence: s2pul

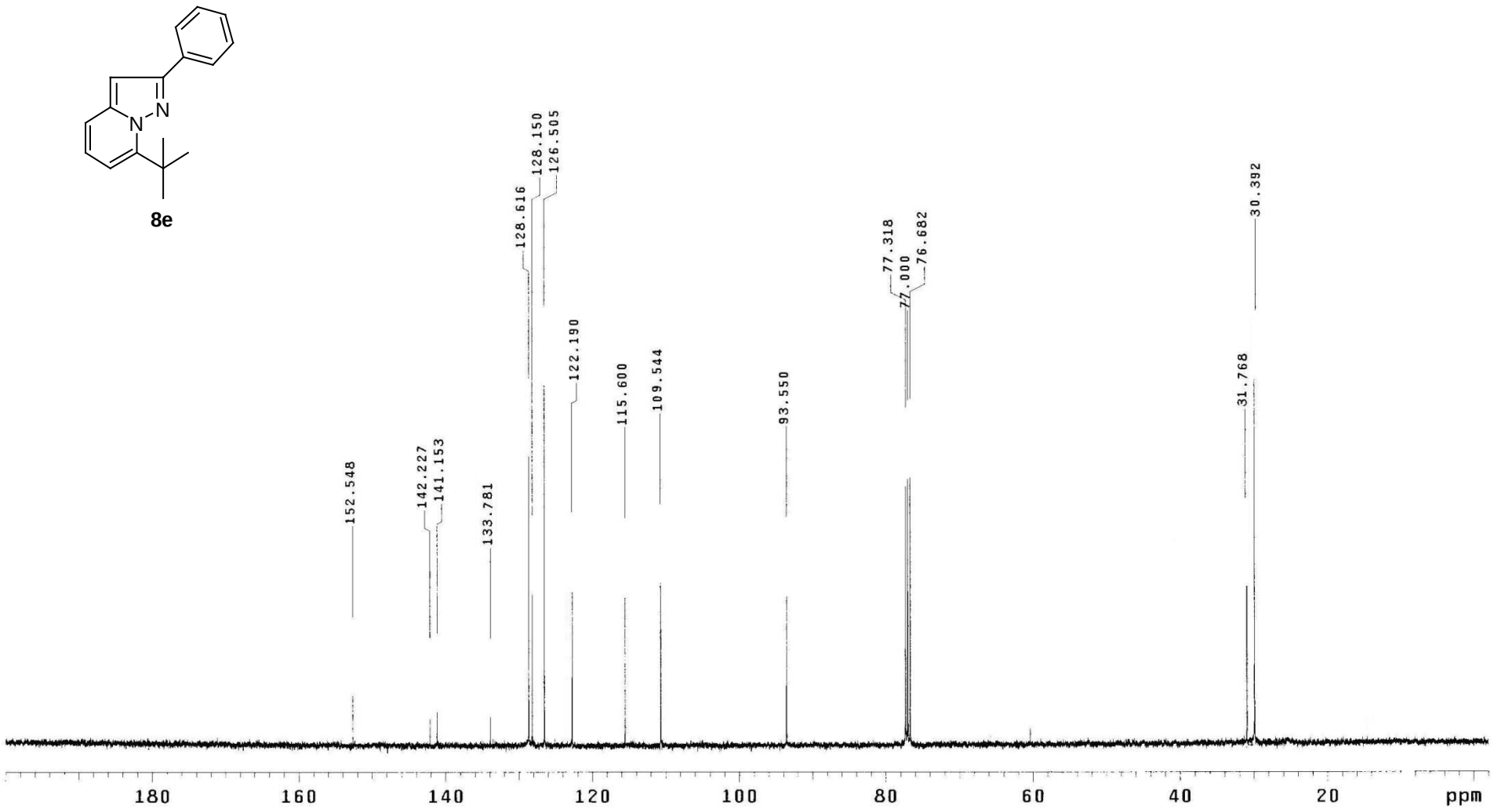
Solvent: CDCl3

Ambient temperature

Mercury-200 "nsysu200"

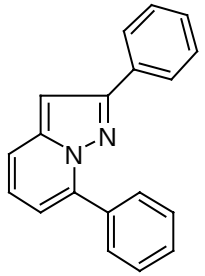
8e



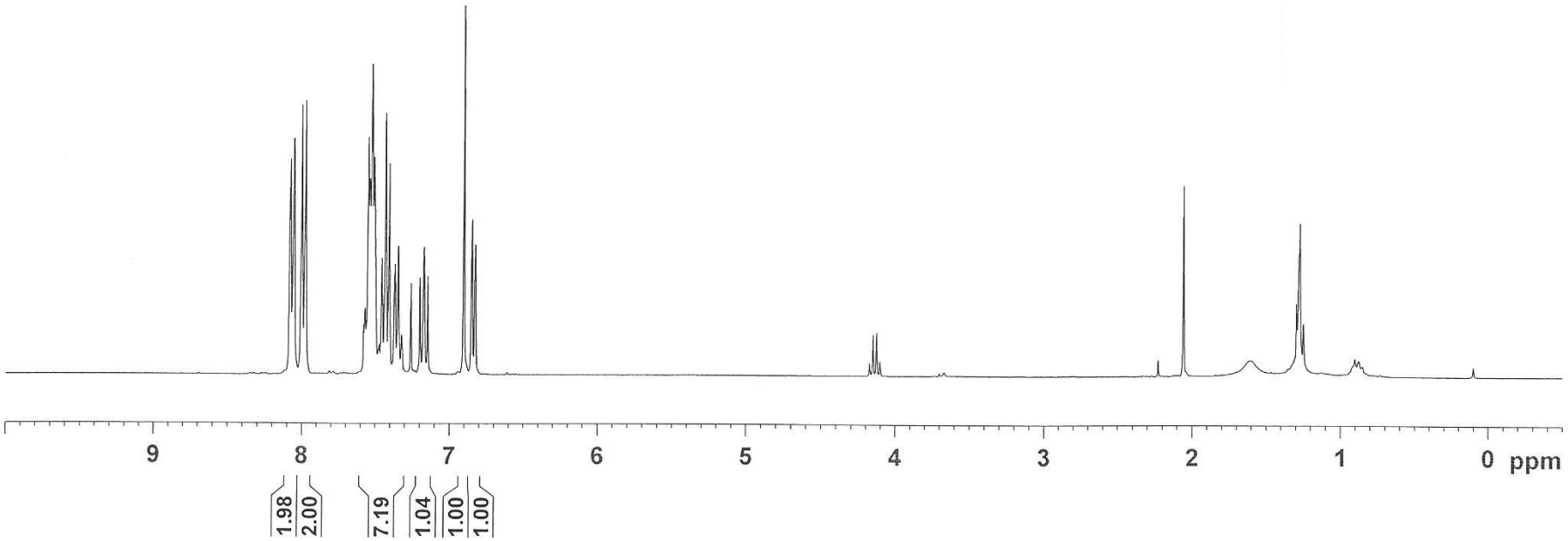

8e
152.548
142.227
141.153
133.781
128.616
128.150
126.505
122.190
115.600
109.544
93.550
77.318
77.000
76.682
31.768
30.392
180
160
140
120
100
80
60
40
20
ppm

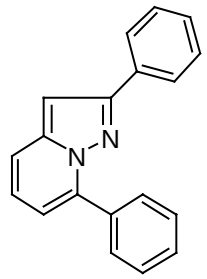
WHC-090

8.085
8.080
8.057
8.003
7.979
7.580
7.571
7.551
7.540
7.526
7.510
7.475
7.458
7.434
7.409
7.370
7.347
7.323
7.260
7.201
7.178
7.174
7.149
6.906
6.850
6.828

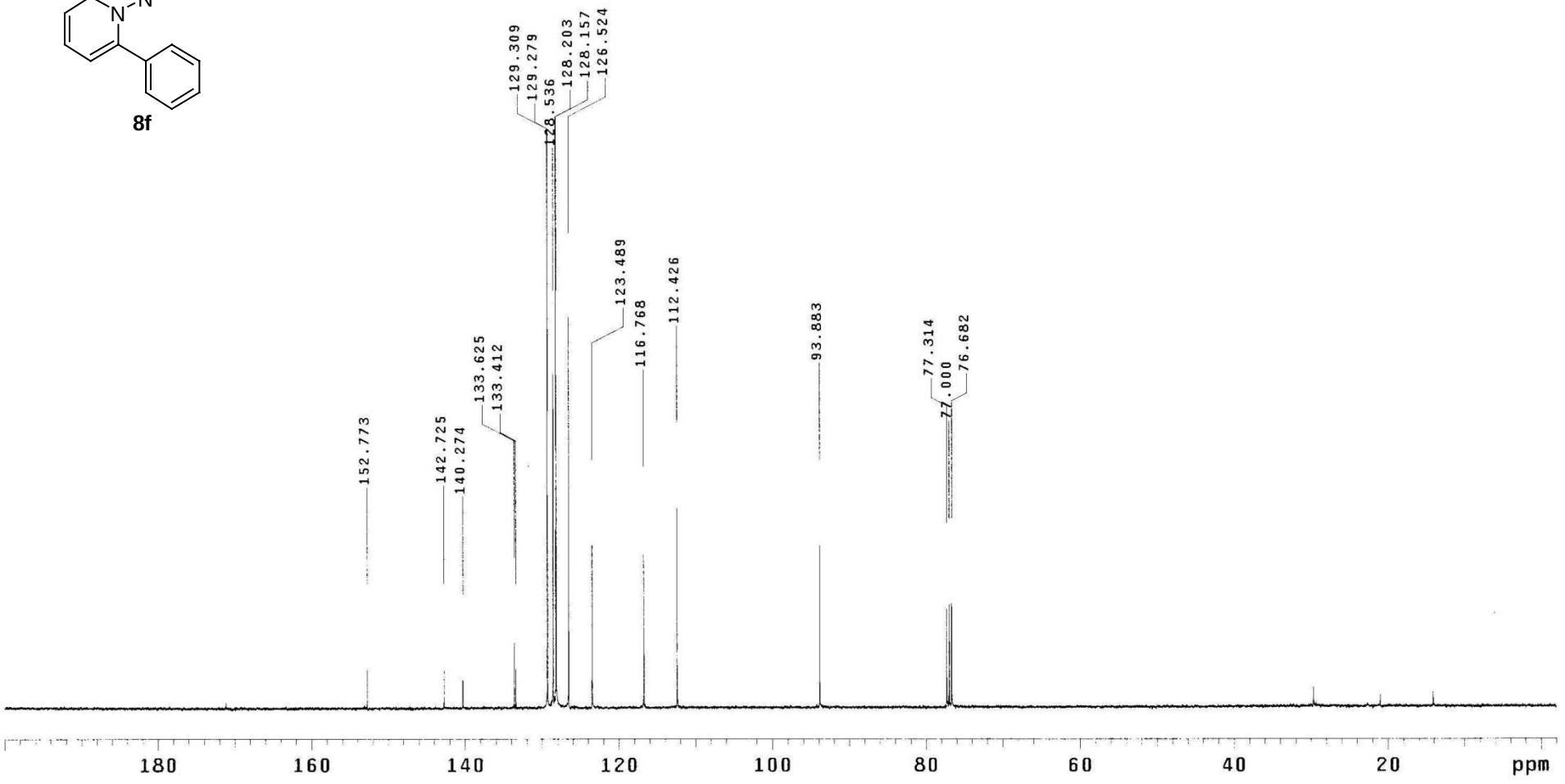


8f



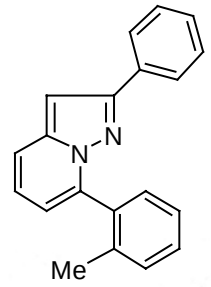


8f

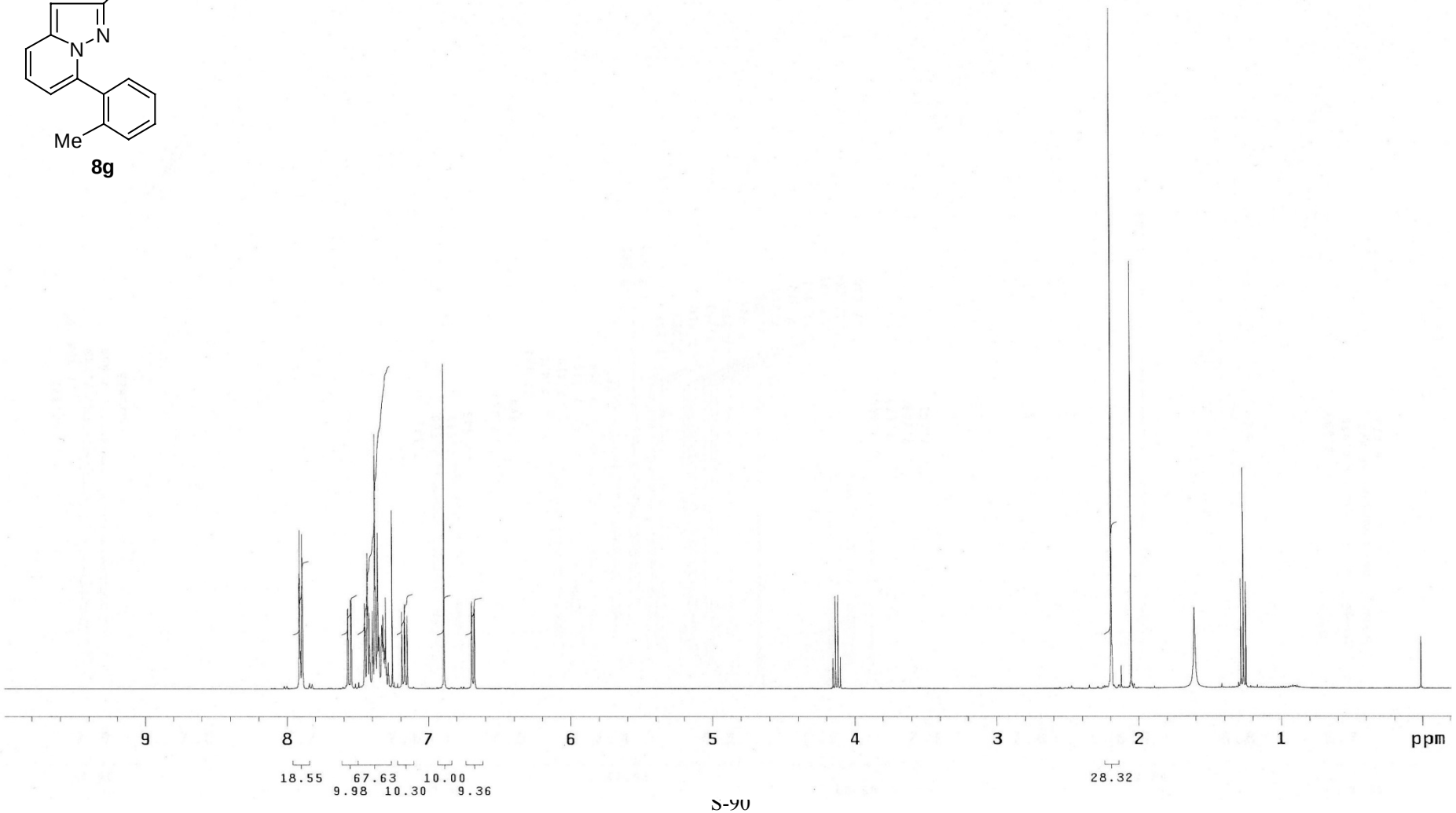

129.309
129.279
128.536
128.203
128.157
126.524
123.489
116.768
112.426
93.883
77.314
77.000
76.682
152.773
142.725
140.274
133.625
133.412
180
160
140
120
100
80
60
40
20
ppm

WHJ-218

Mercury-400BB "Mercuryplus400"
Date: Mar 31 2008
Solvent: CDCl3
Ambient temperature
Total 36 repetitions

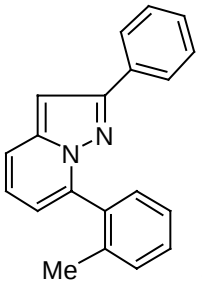


8g

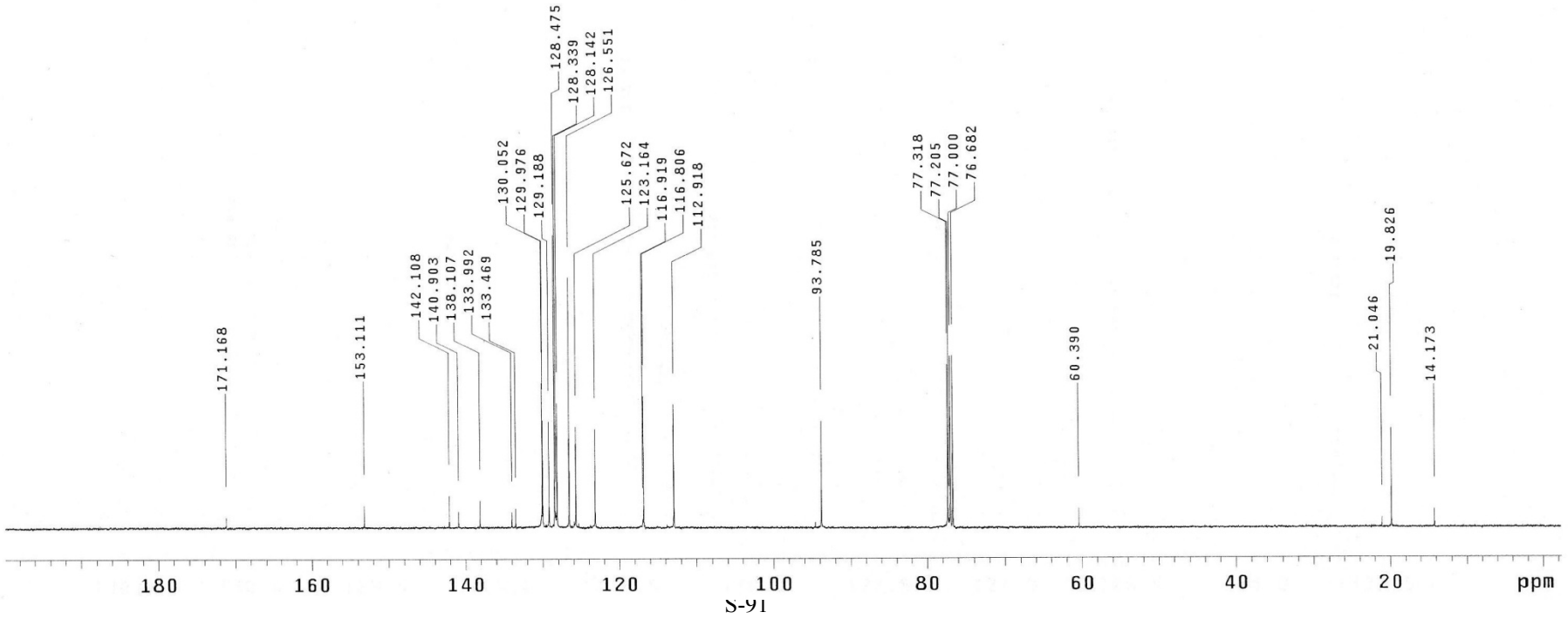


WHJ-218

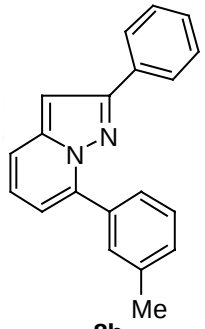
Mercury-400BB "Mercuryplus400"
Date: Mar 31 2008
Solvent: CDCl3
Ambient temperature
Total 7680 repetitions



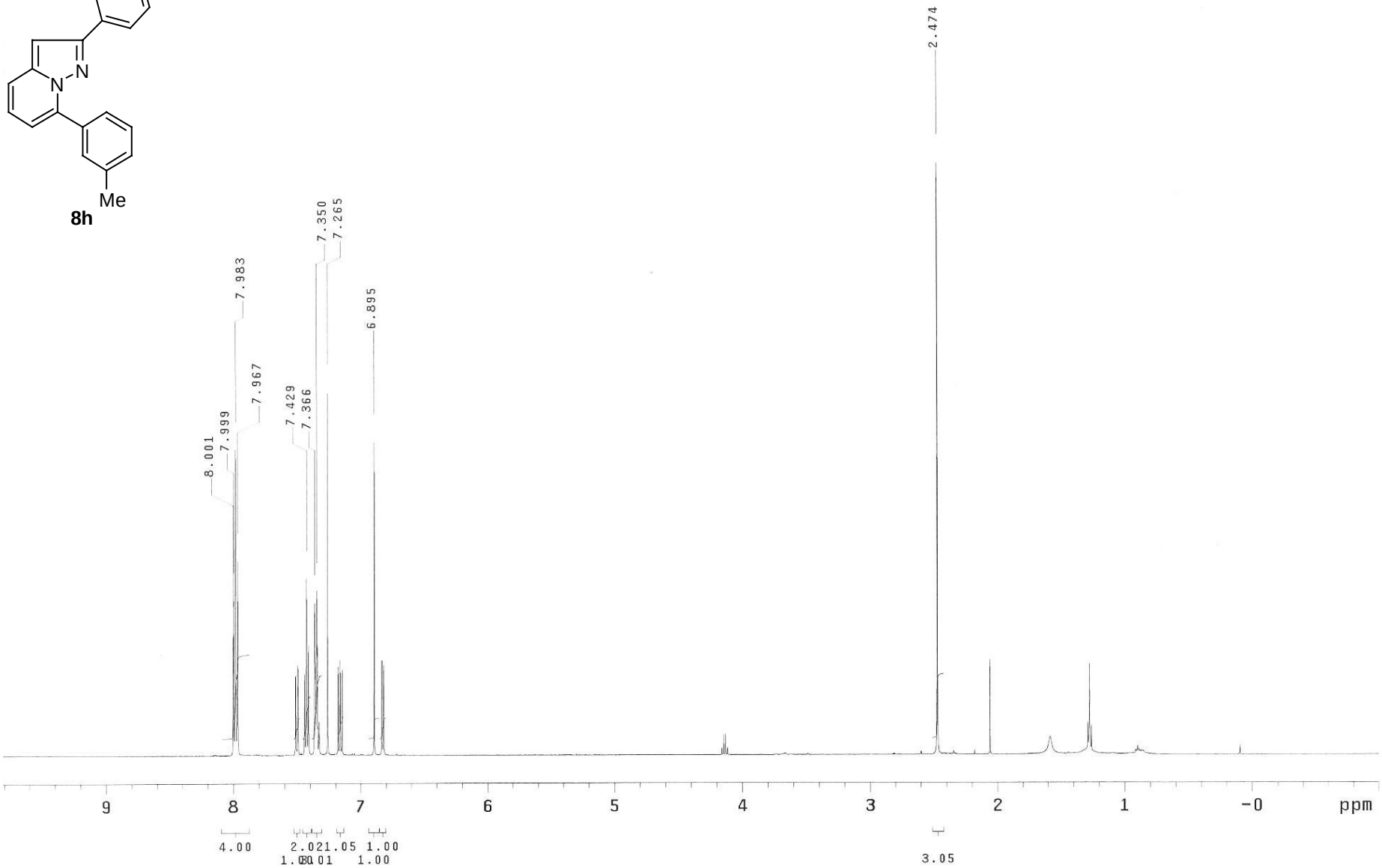
8g



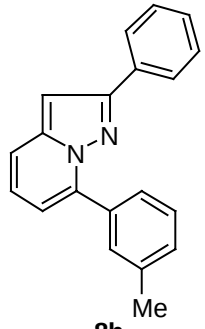
WHC-068-T1


N
N
Me

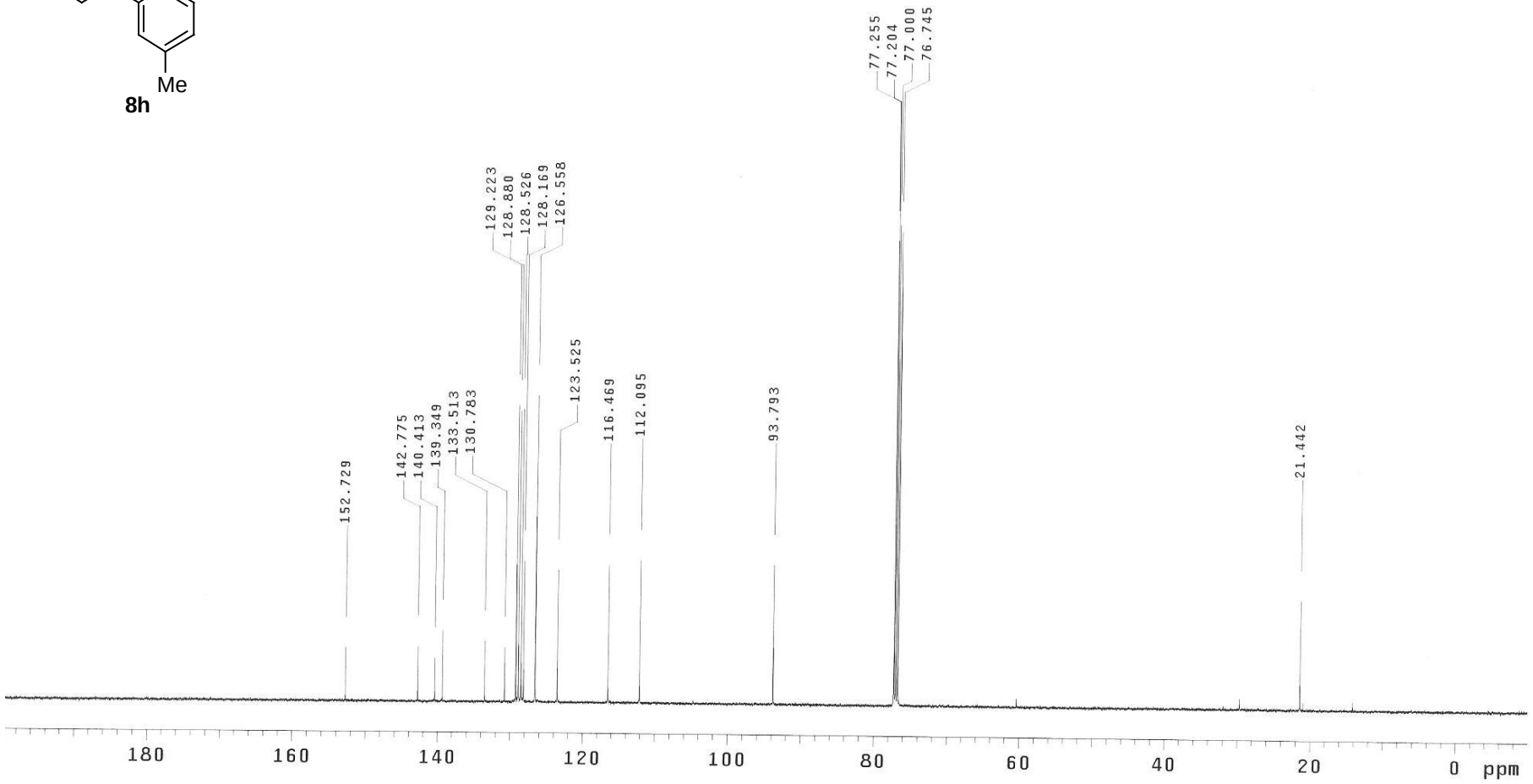
8h


8.001
7.999
7.983
7.967
7.429
7.366
7.350
7.265
6.895
2.474
9
8
7
6
5
4
3
2
1
-0
ppm
4.00
2.02
1.05
1.00
3.05

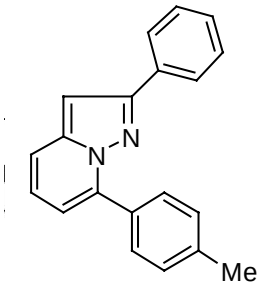
WHC-068-T1


N
N
Me

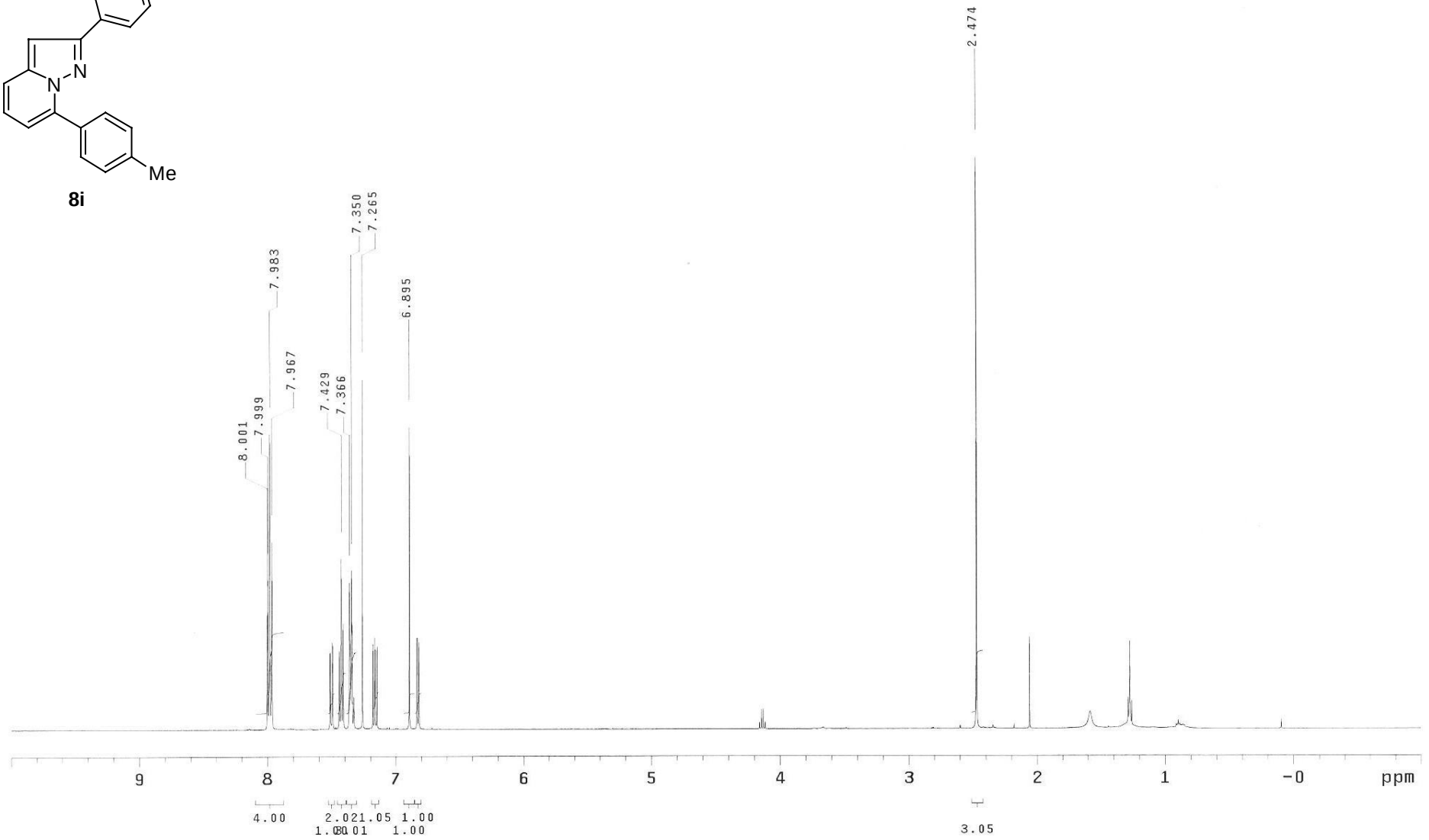
8h


152.729
142.775
140.413
139.349
133.513
130.783
129.223
128.880
128.526
128.169
126.558
123.525
116.469
112.095
93.793
77.255
77.204
77.000
76.745
21.442
180
160
140
120
100
80
60
40
20
0 ppm

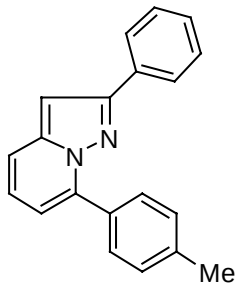
WHC-068-T1


N
N
Me

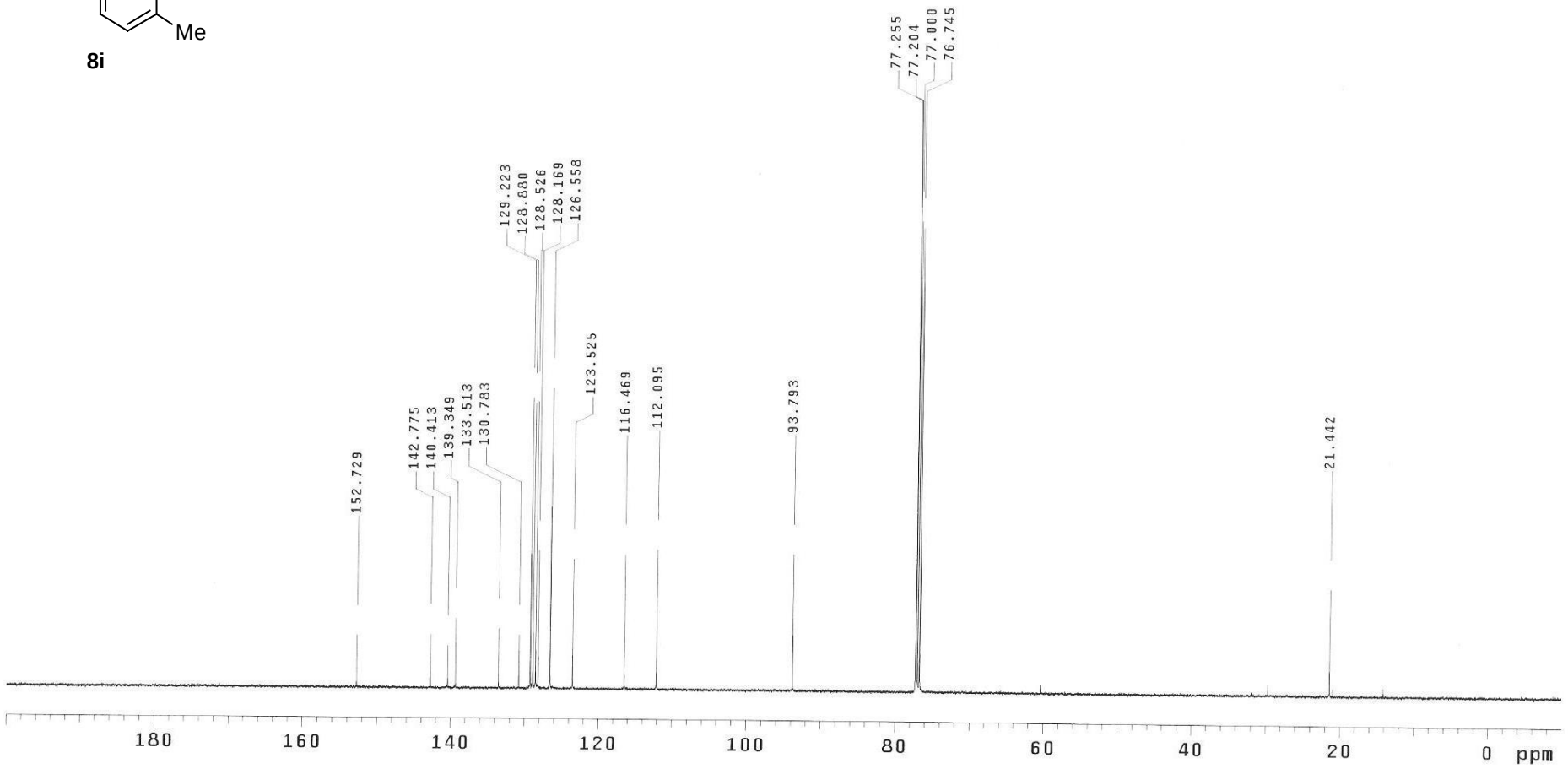
8i


8.001
7.999
7.983
7.967
7.429
7.366
7.350
7.265
6.895
2.474
9
8
7
6
5
4
3
2
1
-0
ppm
4.00
2.02
1.05
1.00
1.00
3.05

WHC-068-T1


N
N
Me

8i

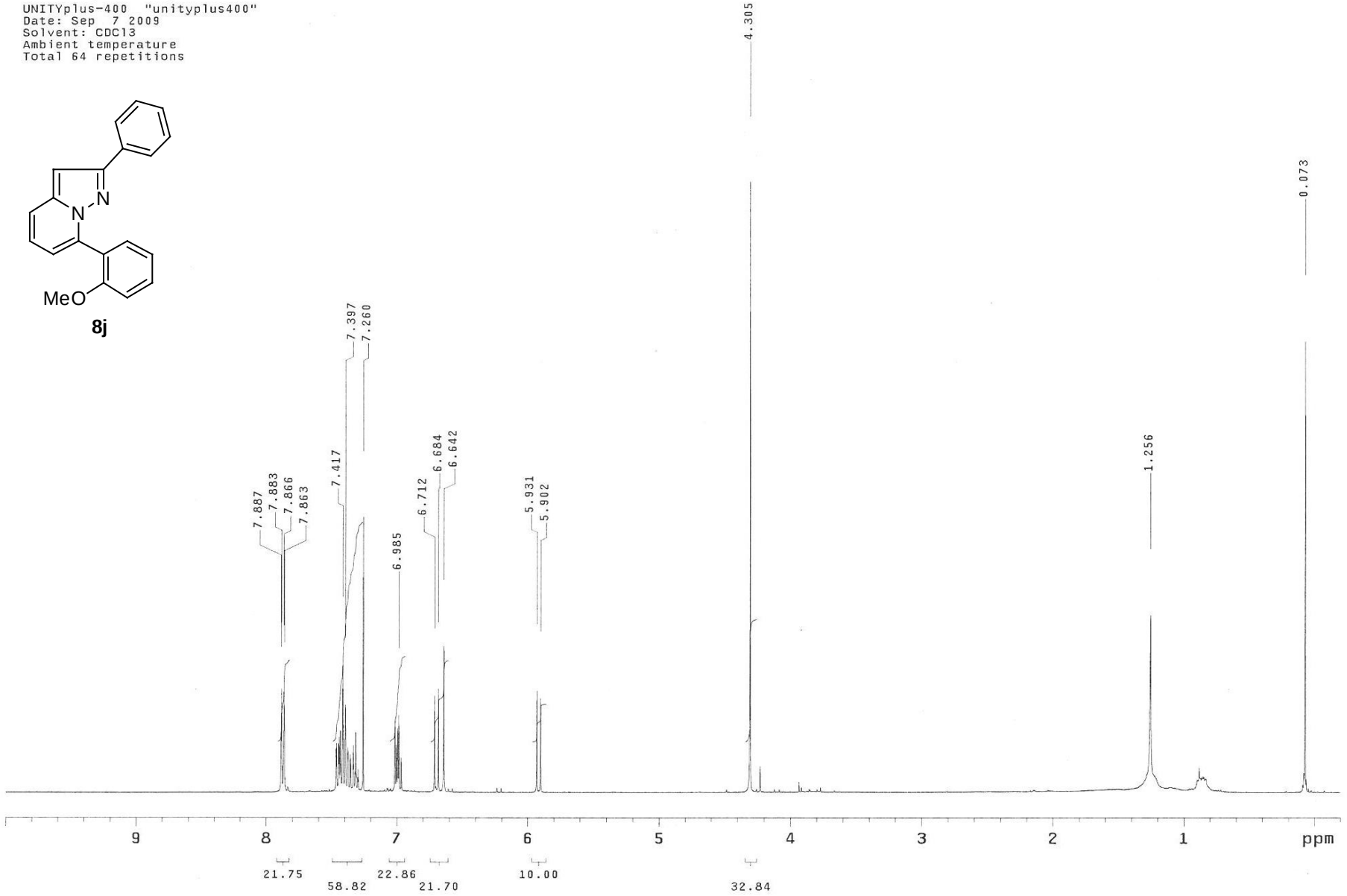

152.729
142.775
140.413
139.349
133.513
130.783
129.223
128.880
128.526
128.169
126.558
123.525
116.469
112.095
93.793
77.255
77.204
77.000
76.745
21.442
180
160
140
120
100
80
60
40
20
0
ppm

WHC-054-T2

Pulse Sequence: s2pul

UNITYplus-400 "unityplus400"
Date: Sep 7 2009
Solvent: CDCl3
Ambient temperature
Total 64 repetitions

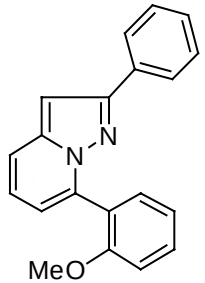
8j



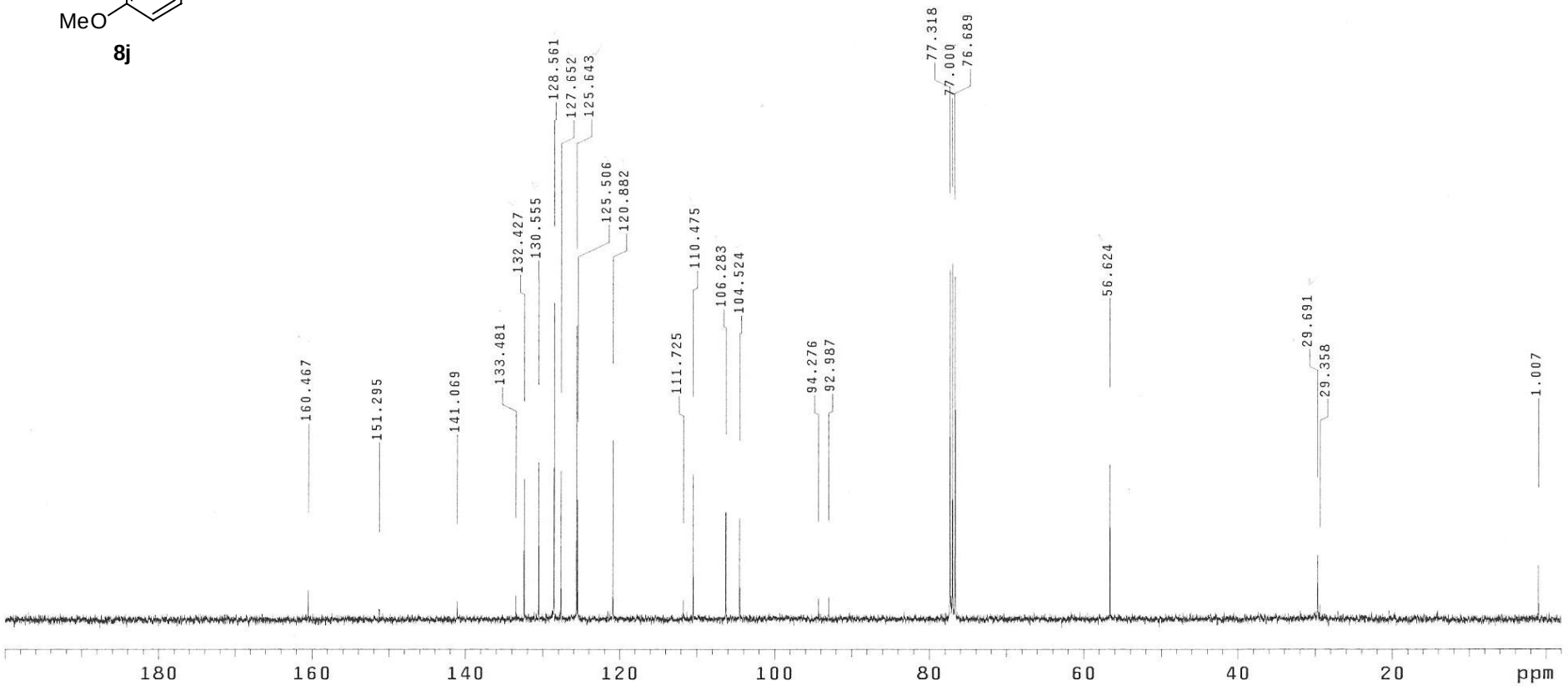
WHC-054-T2

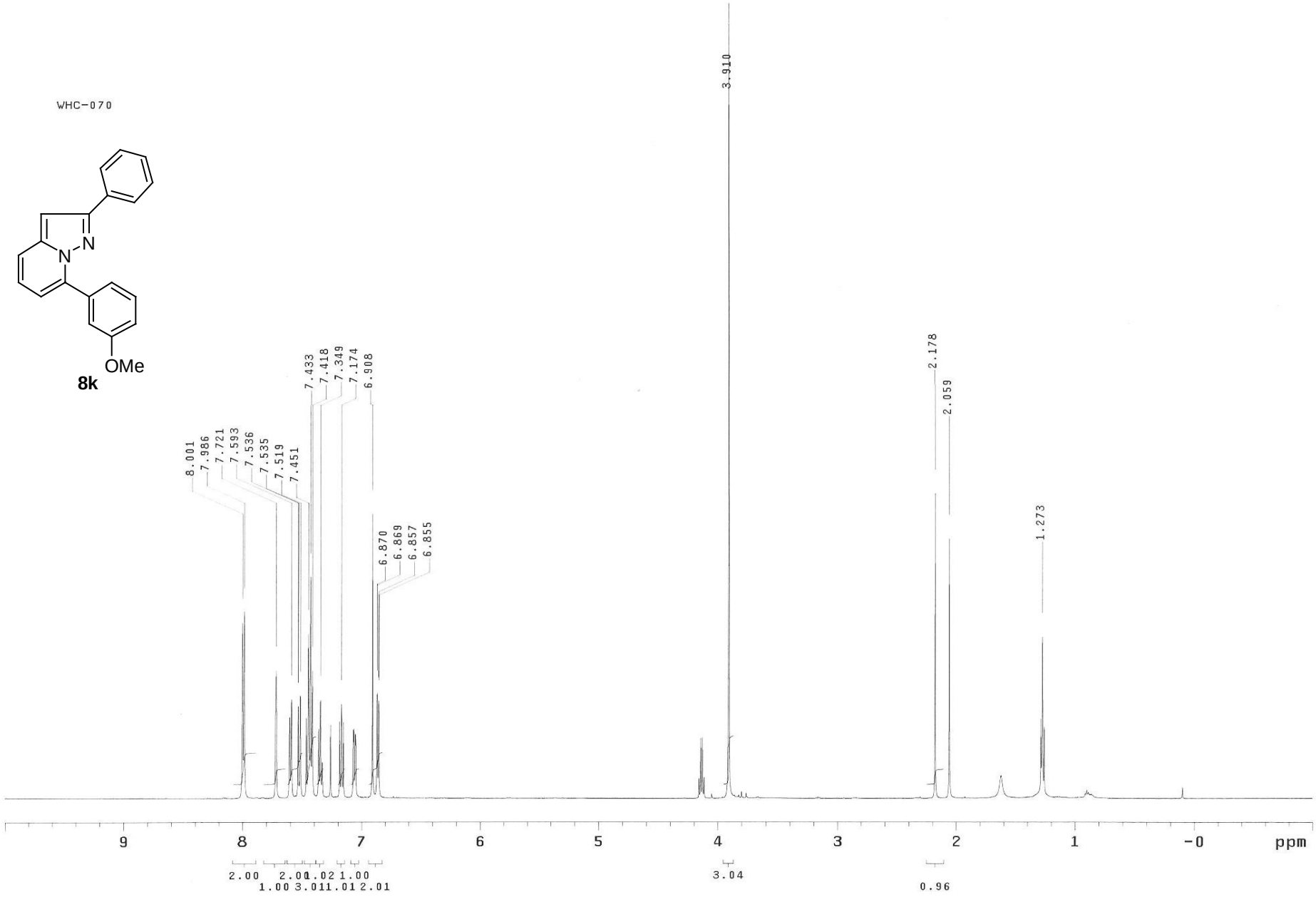
Pulse Sequence: s2pul

UNITYplus-400 "unityplus400"
Date: Sep 7 2009
Solvent: CDCl3
Ambient temperature
Total 10144 repetitions

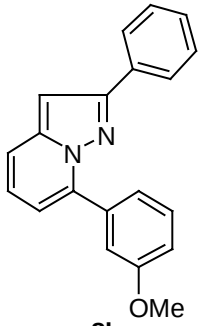


8j

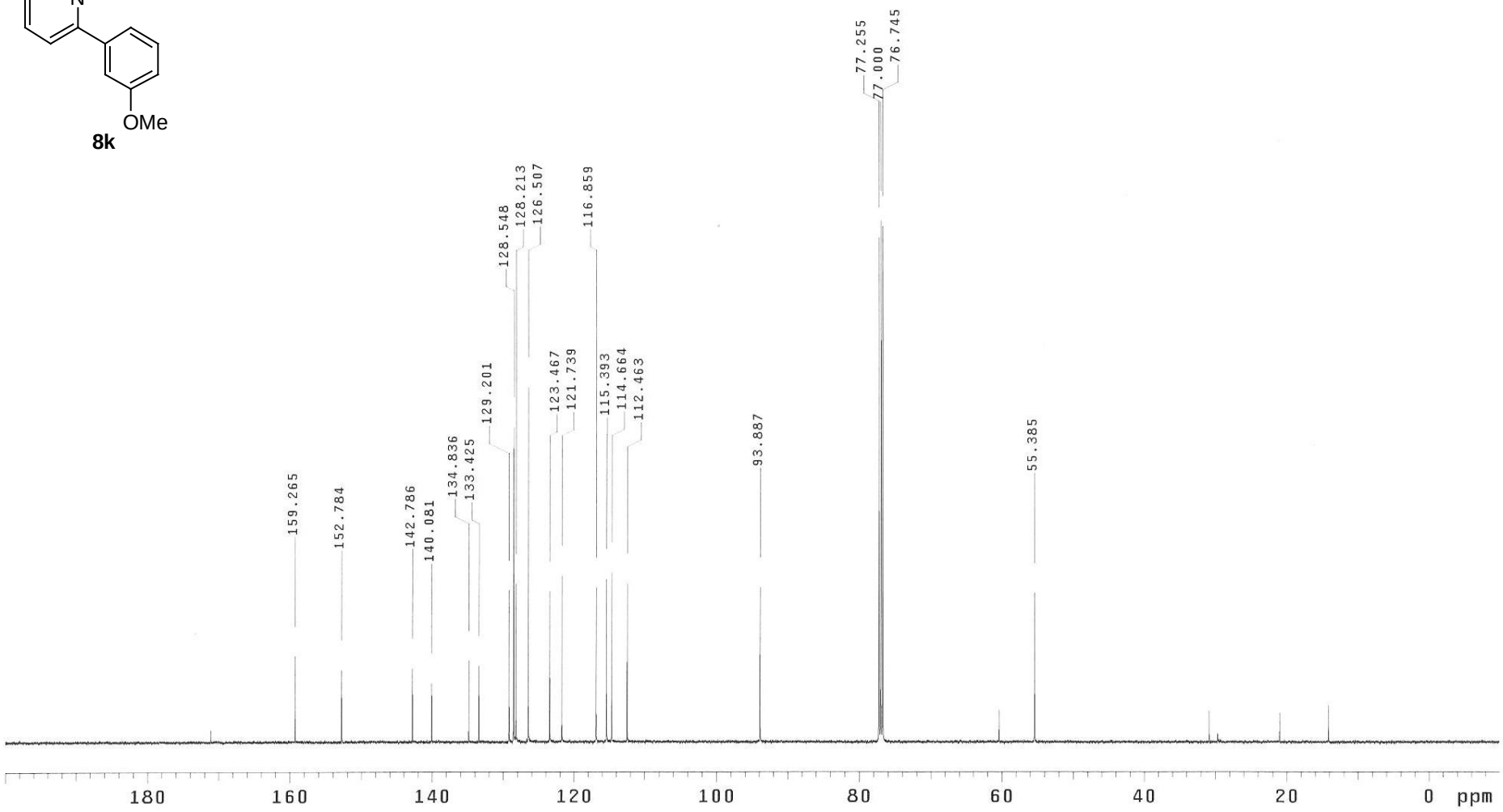



WHC-070
OMe
8k
8.001
7.986
7.721
7.593
7.536
7.535
7.519
7.451
7.433
7.418
7.349
7.174
6.908
6.870
6.869
6.857
6.855
3.910
2.178
2.059
1.273
9
8
7
6
5
4
3
2
1
-0
ppm
2.00
2.00
1.02
1.00
1.00
3.01
1.01
2.01
3.04
0.96

WHC-070


N
N
OMe

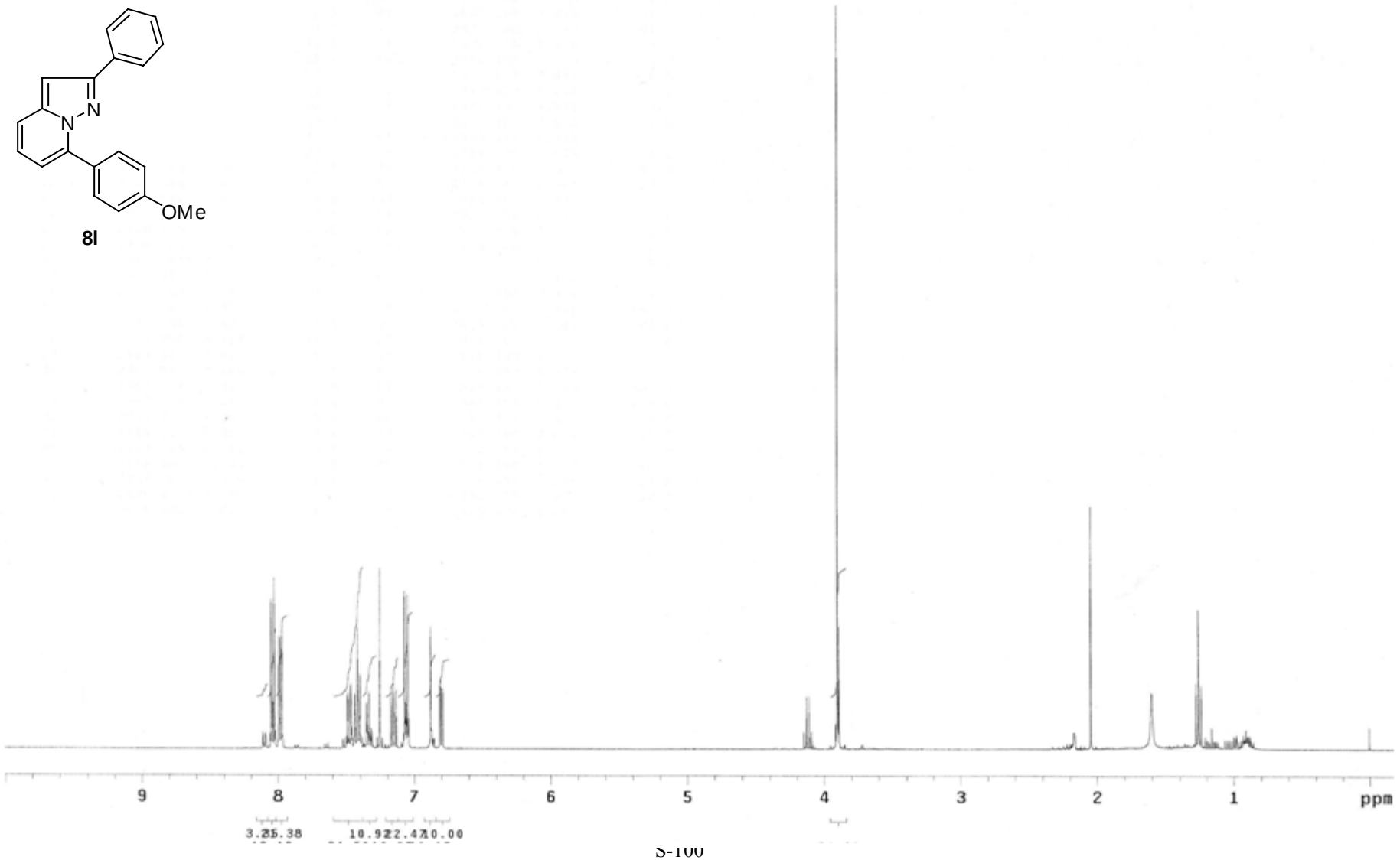
8k


159.265
152.784
142.786
140.081
134.836
133.425
129.201
128.548
128.213
126.507
123.467
121.739
116.859
115.393
114.664
112.463
93.887
77.255
77.000
76.745
55.385
180
160
140
120
100
80
60
40
20
0
ppm

VHJ-221

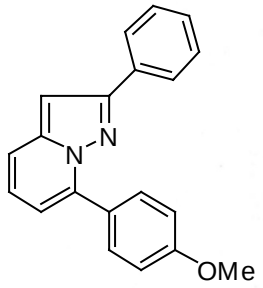
Mercury-400BB "Mercuryplus400"
Date: Apr 17 2008
Solvent: CDCl3
Ambient temperature
Total 48 repetitions

8l

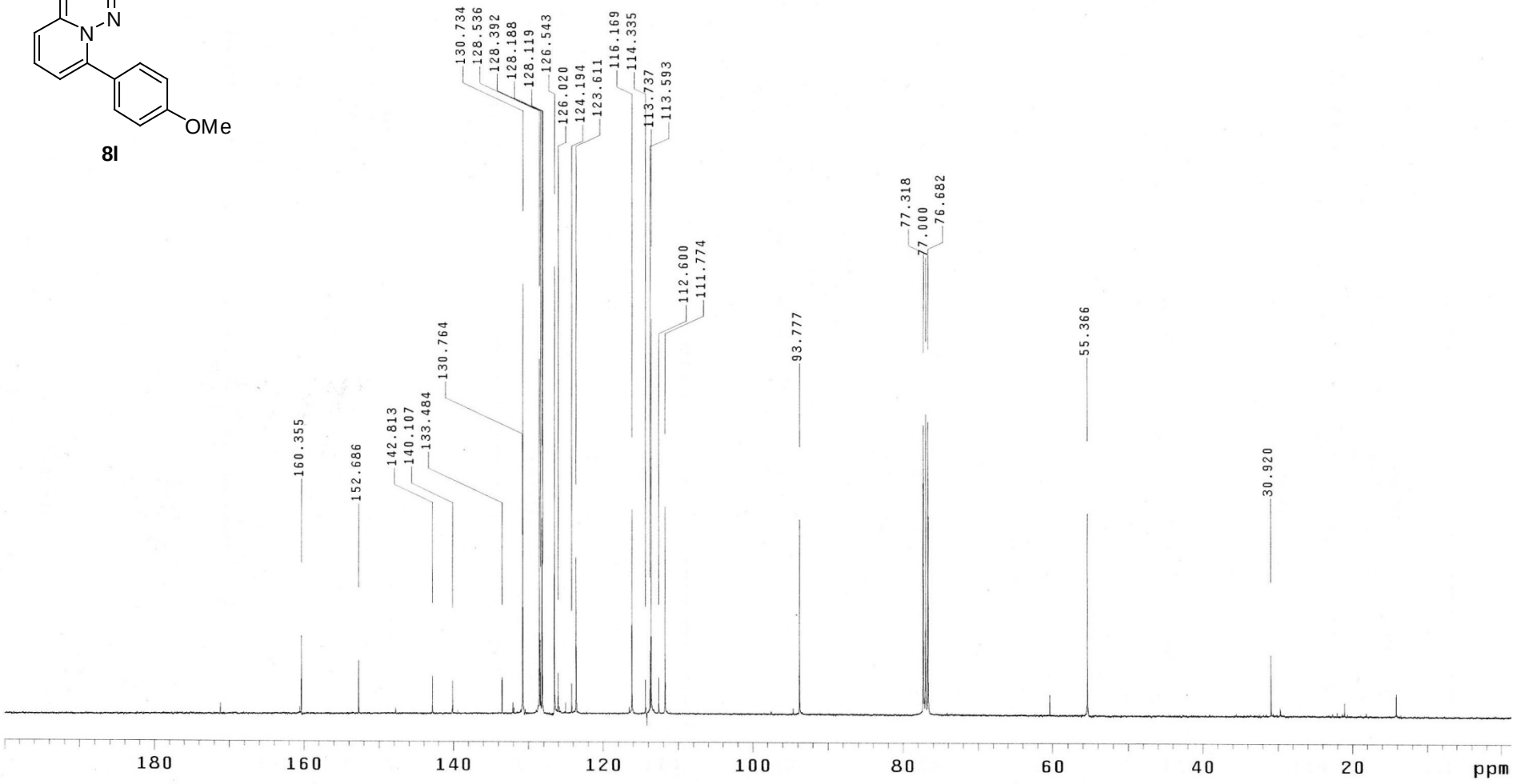


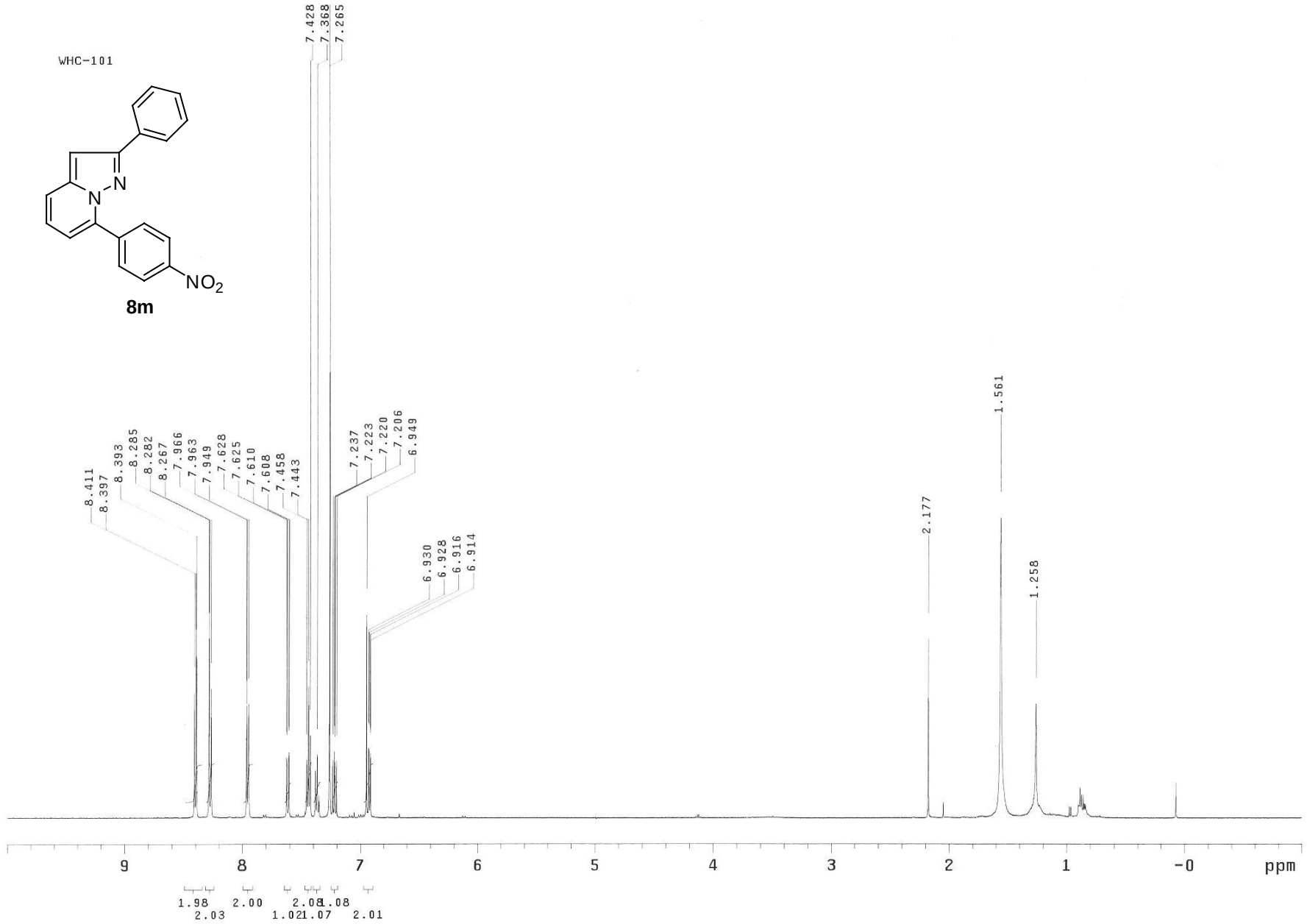
WHJ-221

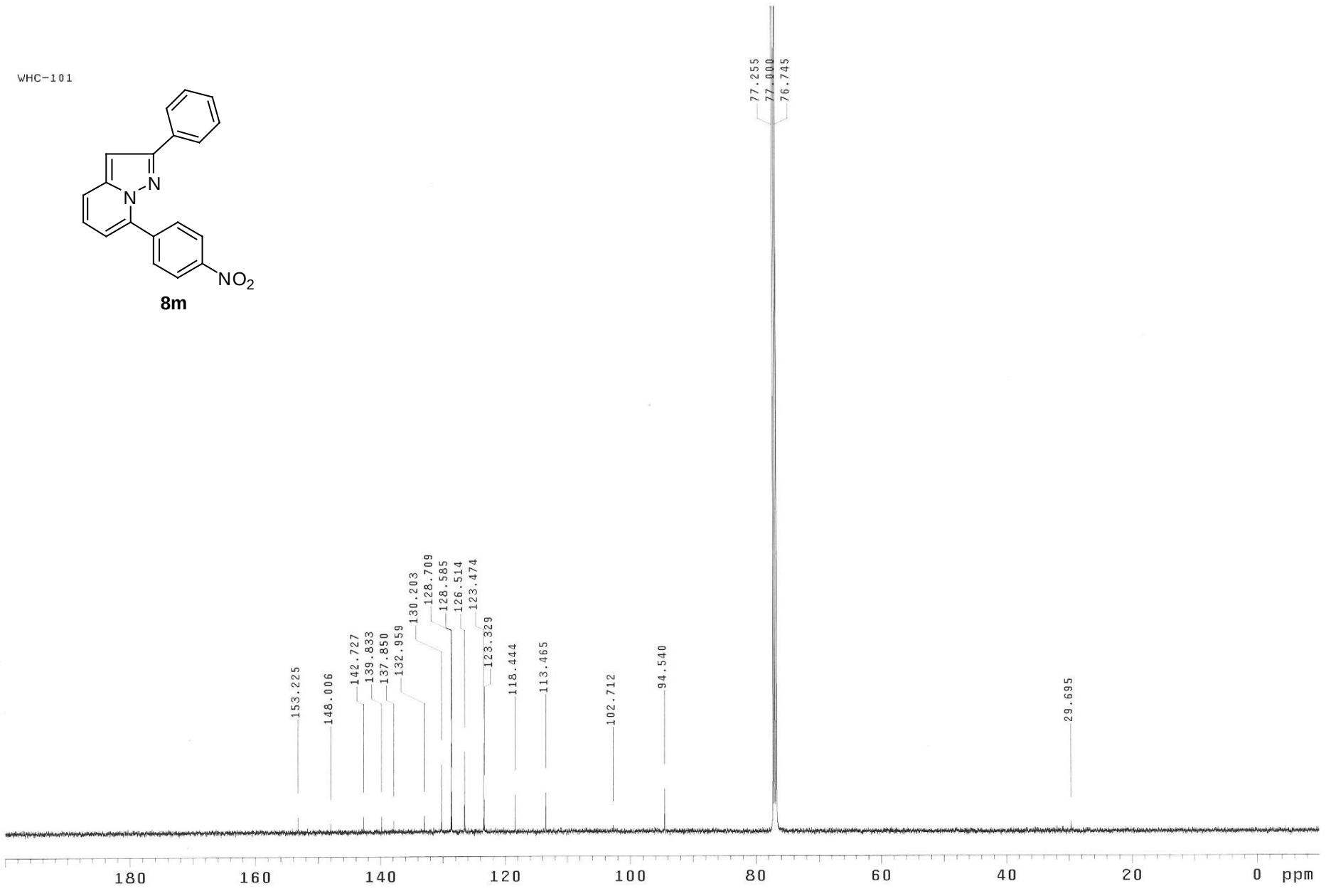
Mercury-400BB "Mercuryplus400"
Date: Apr 17 2008
Solvent: CDCl3
Ambient temperature
Total 32000 repetitions



8l



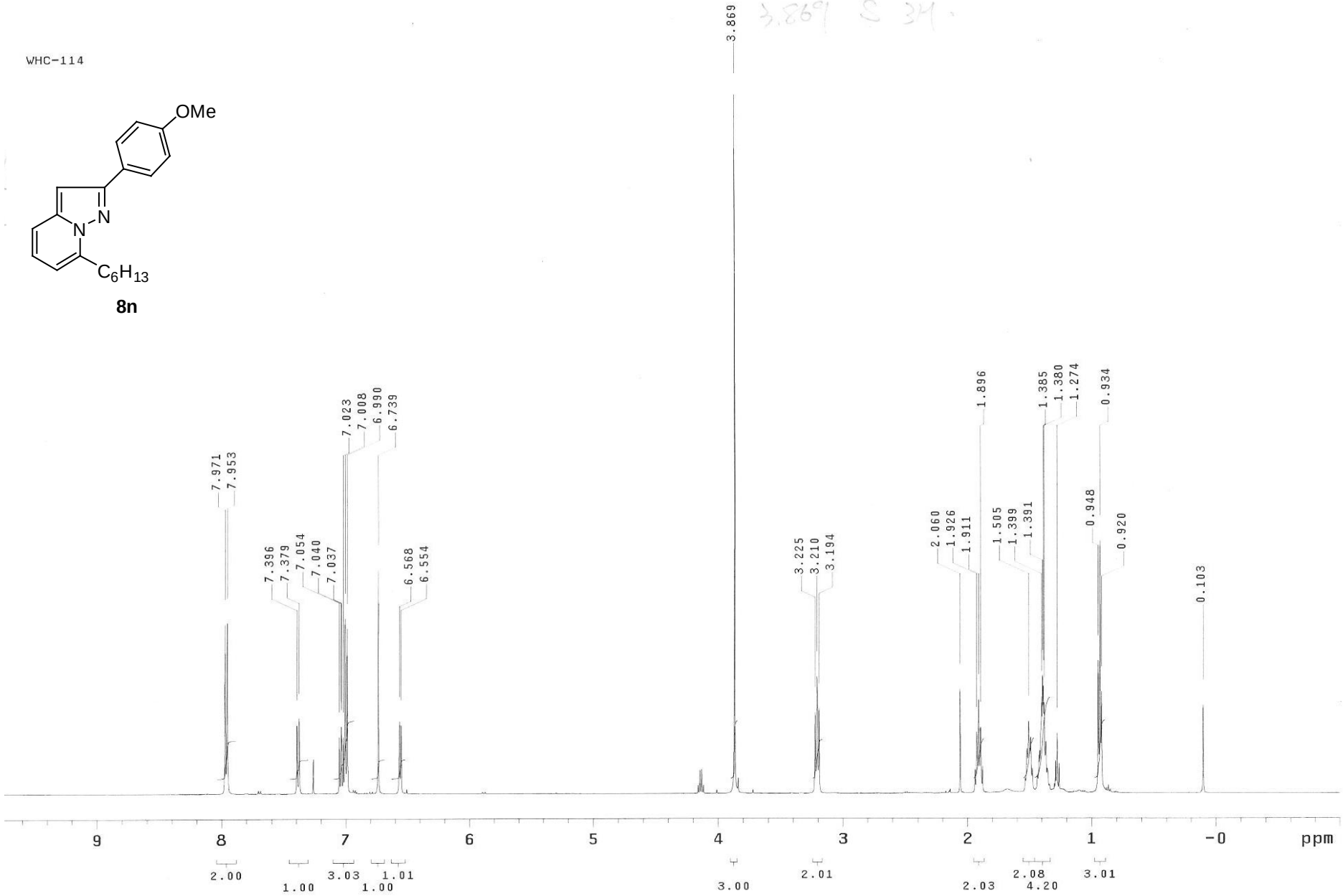

WHC-101
8m
7.428
7.368
7.265
8.411
8.397
8.393
8.285
8.282
8.267
7.966
7.963
7.949
7.628
7.625
7.610
7.608
7.458
7.443
7.237
7.223
7.220
7.206
6.949
6.930
6.928
6.916
6.914
2.177
1.561
1.258
9
8
7
6
5
4
3
2
1
-0
ppm
1.98
2.03
2.00
2.08
1.02
1.08
1.07
2.01


WHC-101
N
N
NO2
8m
77.255
77.000
76.745
153.225
148.006
142.727
139.833
137.850
132.959
130.203
128.709
128.585
126.514
123.474
123.329
118.444
113.465
102.712
94.540
29.695
180
160
140
120
100
80
60
40
20
0
ppm

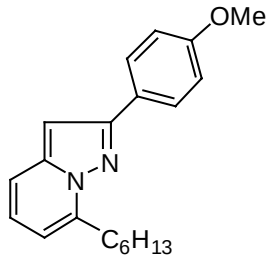
WHC-114

OMe
N
N
C_6H_{13}

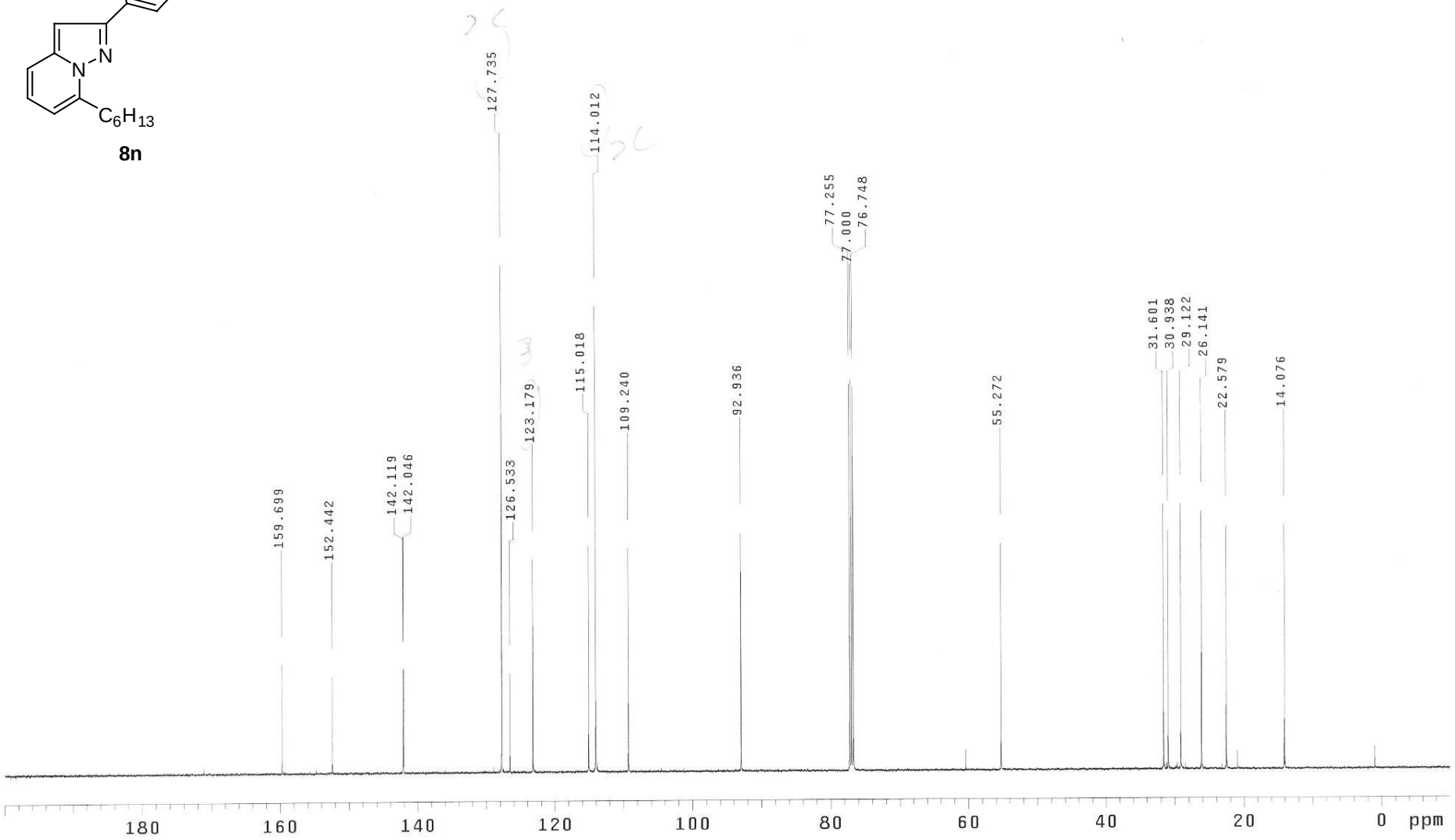
8n

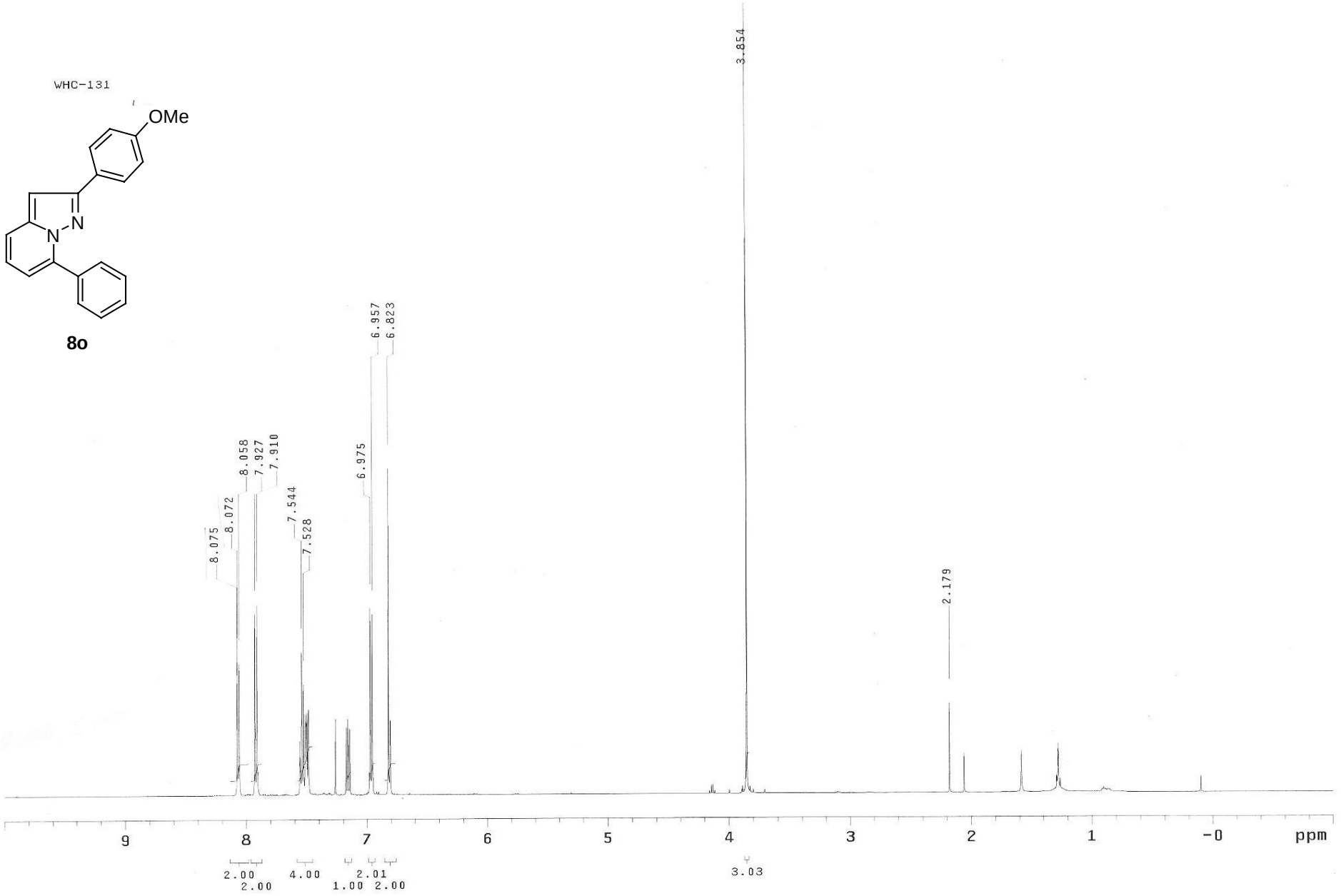

3.869
7.971
7.953
7.396
7.379
7.054
7.040
7.037
7.023
7.008
6.990
6.739
6.568
6.554
3.225
3.210
3.194
2.060
1.926
1.911
1.896
1.505
1.399
1.391
1.385
1.380
1.274
0.948
0.934
0.920
0.103
9
8
7
6
5
4
3
2
1
-0
ppm
2.00
1.00
3.03
1.00
1.01
3.00
2.01
2.03
2.08
4.20
3.01

WHC-114

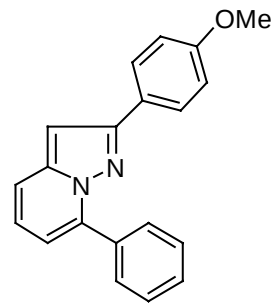

OMe
N
N
C_6H_{13}

8n

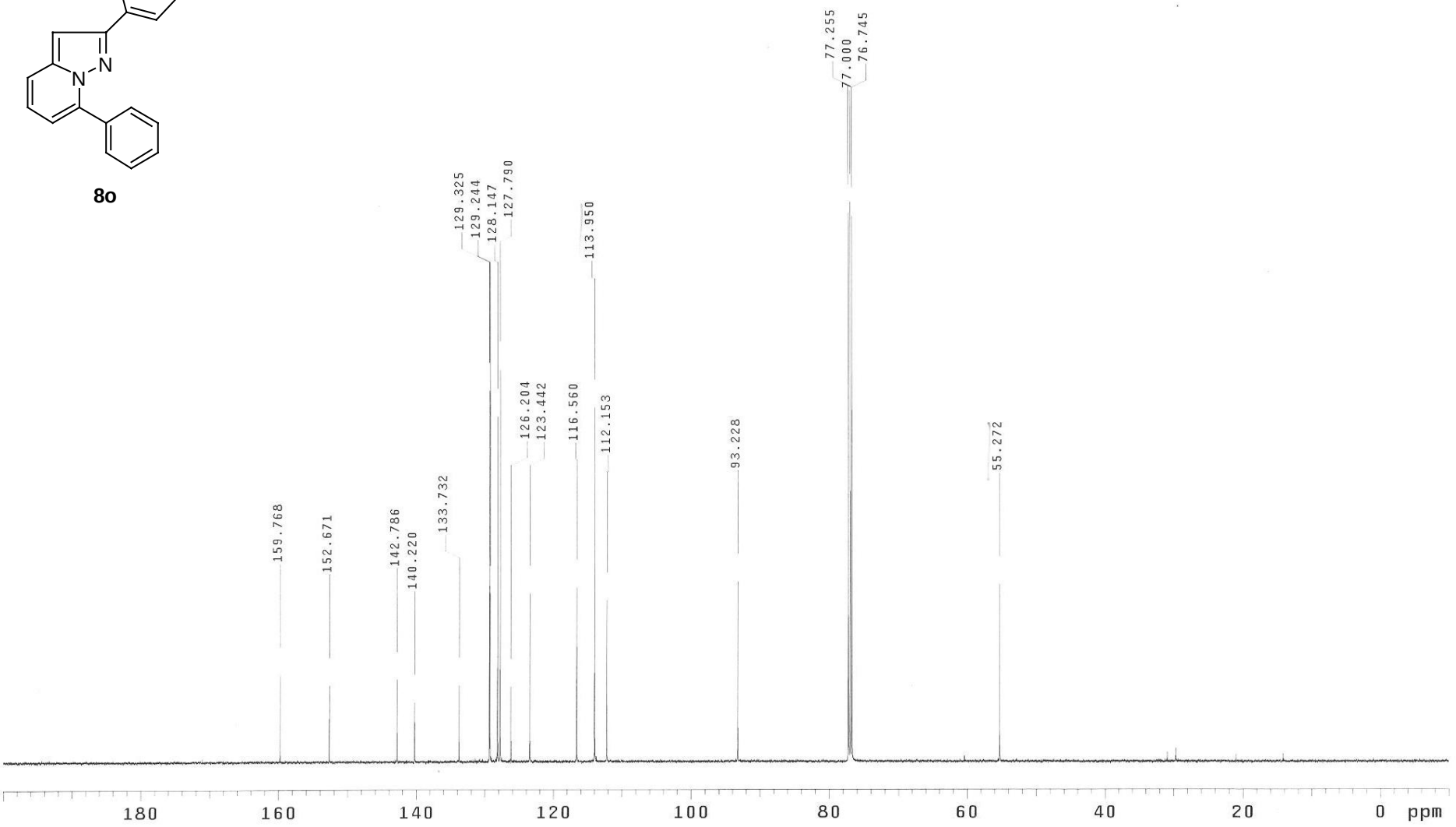

159.699
152.442
142.119
142.046
127.735
126.533
123.179
115.018
114.012
109.240
92.936
77.255
77.000
76.748
55.272
31.601
30.938
29.122
26.141
22.579
14.076
180
160
140
120
100
80
60
40
20
0
ppm

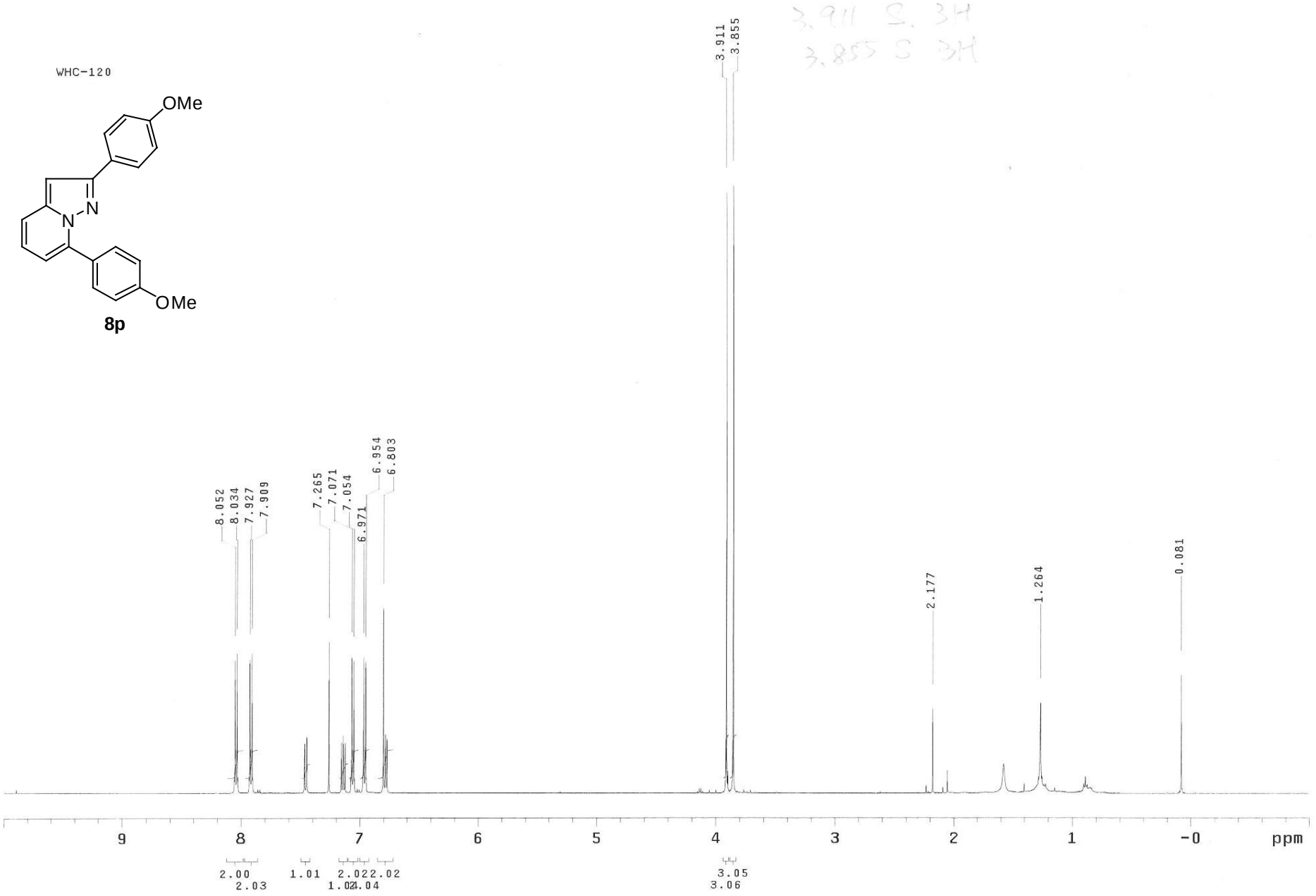

WHC-131
OMe
N
N
8o
3.854
6.957
6.823
8.058
7.927
7.910
6.975
7.544
8.075
8.072
7.528
2.179
9
8
7
6
5
4
3
2
1
-0
ppm
2.00
2.00
4.00
2.01
1.00
2.00
3.03

WHC-131


OMe
N
N

8o

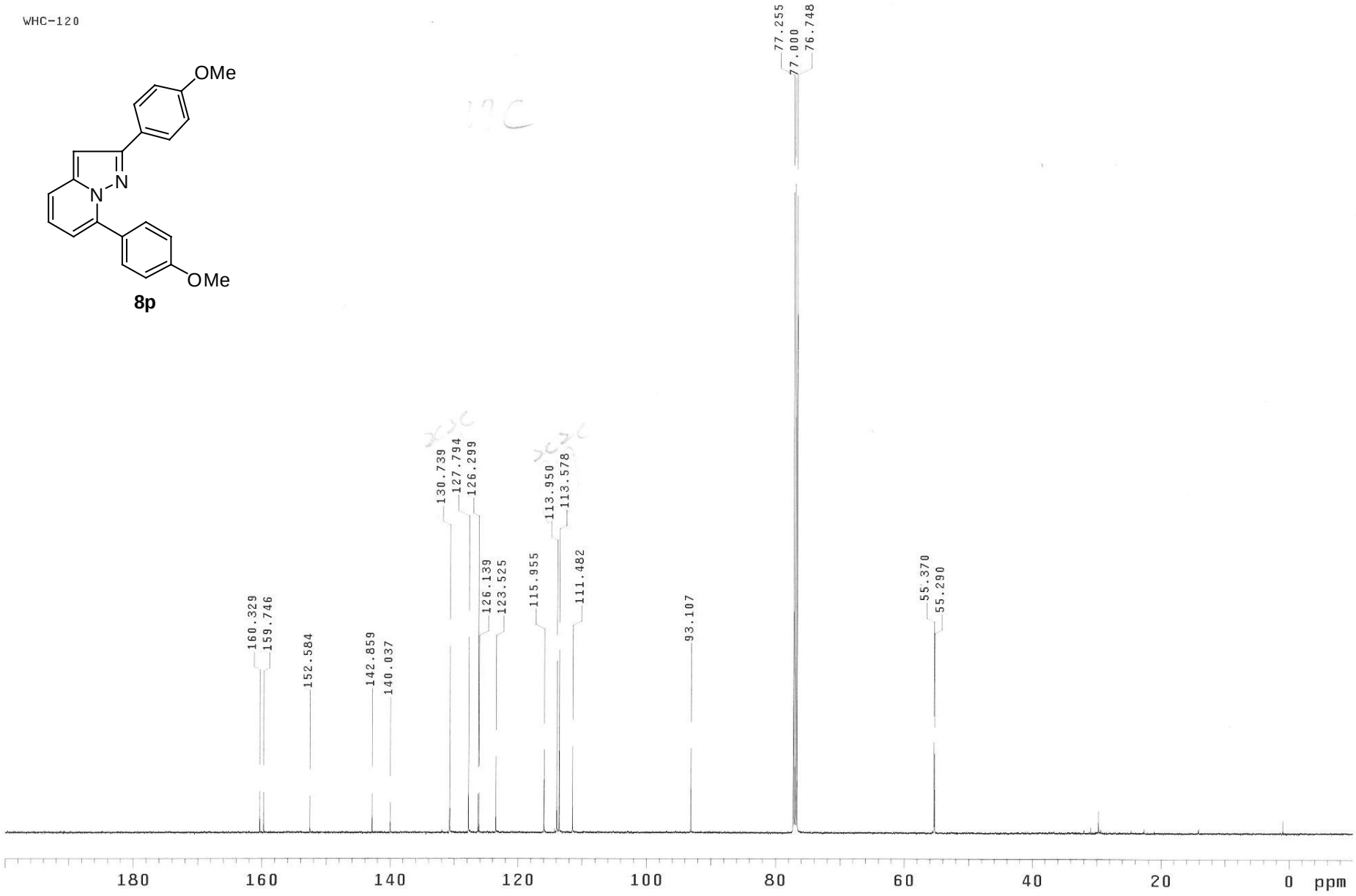

159.768
152.671
142.786
140.220
133.732
129.325
129.244
128.147
127.790
126.204
123.442
116.560
113.950
112.153
93.228
77.255
77.000
76.745
55.272
180
160
140
120
100
80
60
40
20
0
ppm

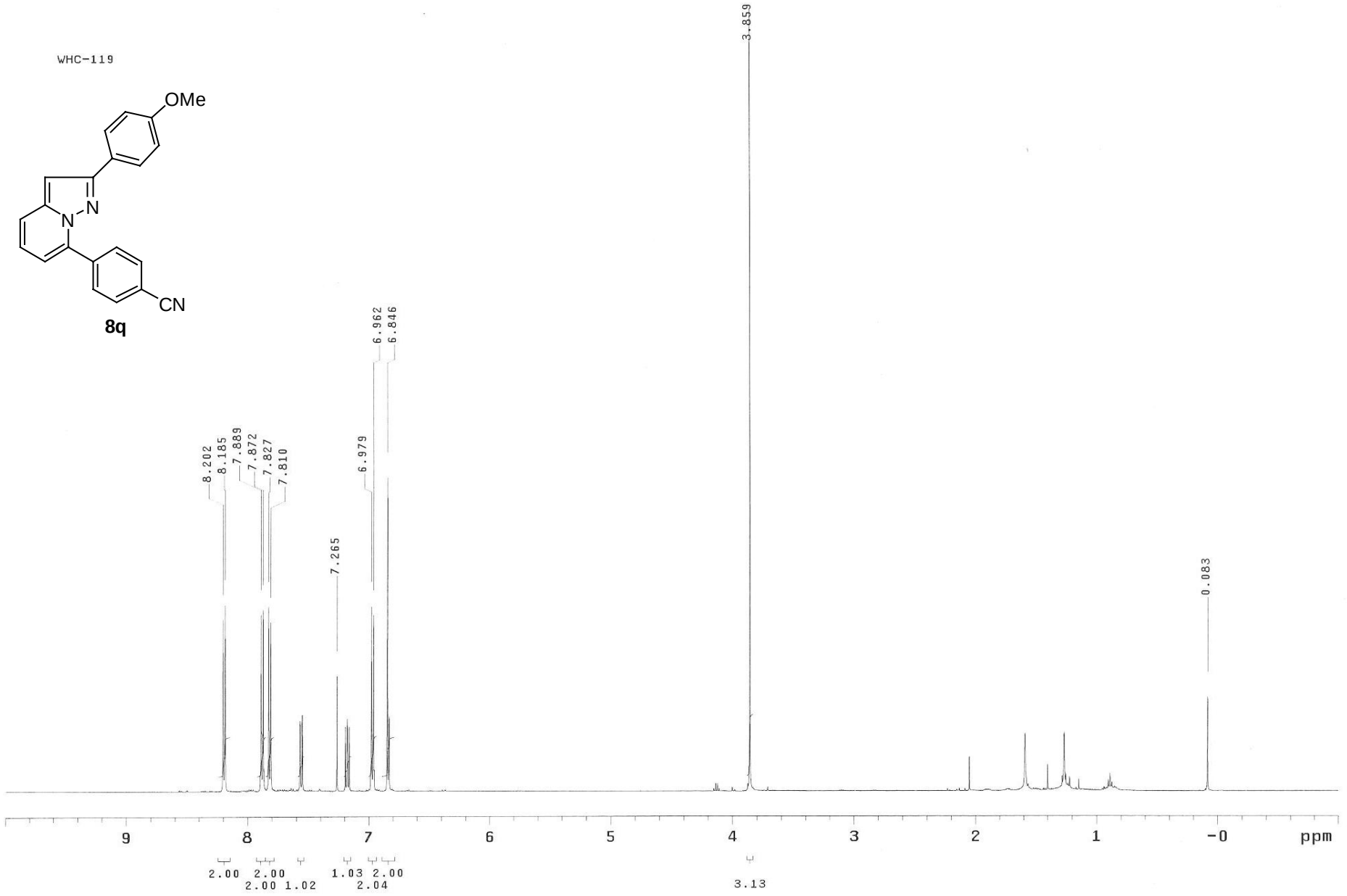

WHC-120
OMe
N
N
OMe
8p
3.911
3.855
8.052
8.034
7.927
7.909
7.265
7.071
7.054
6.971
6.954
6.803
2.177
1.264
0.081
9
8
7
6
5
4
3
2
1
-0
ppm
2.00
2.03
1.01
2.02
1.02
2.04
2.02
3.05
3.06

WHC-120

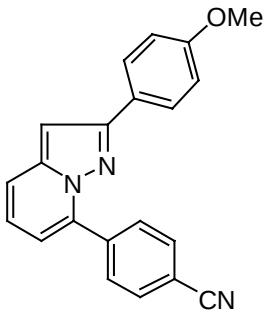
OMe
N
N
OMe

8p

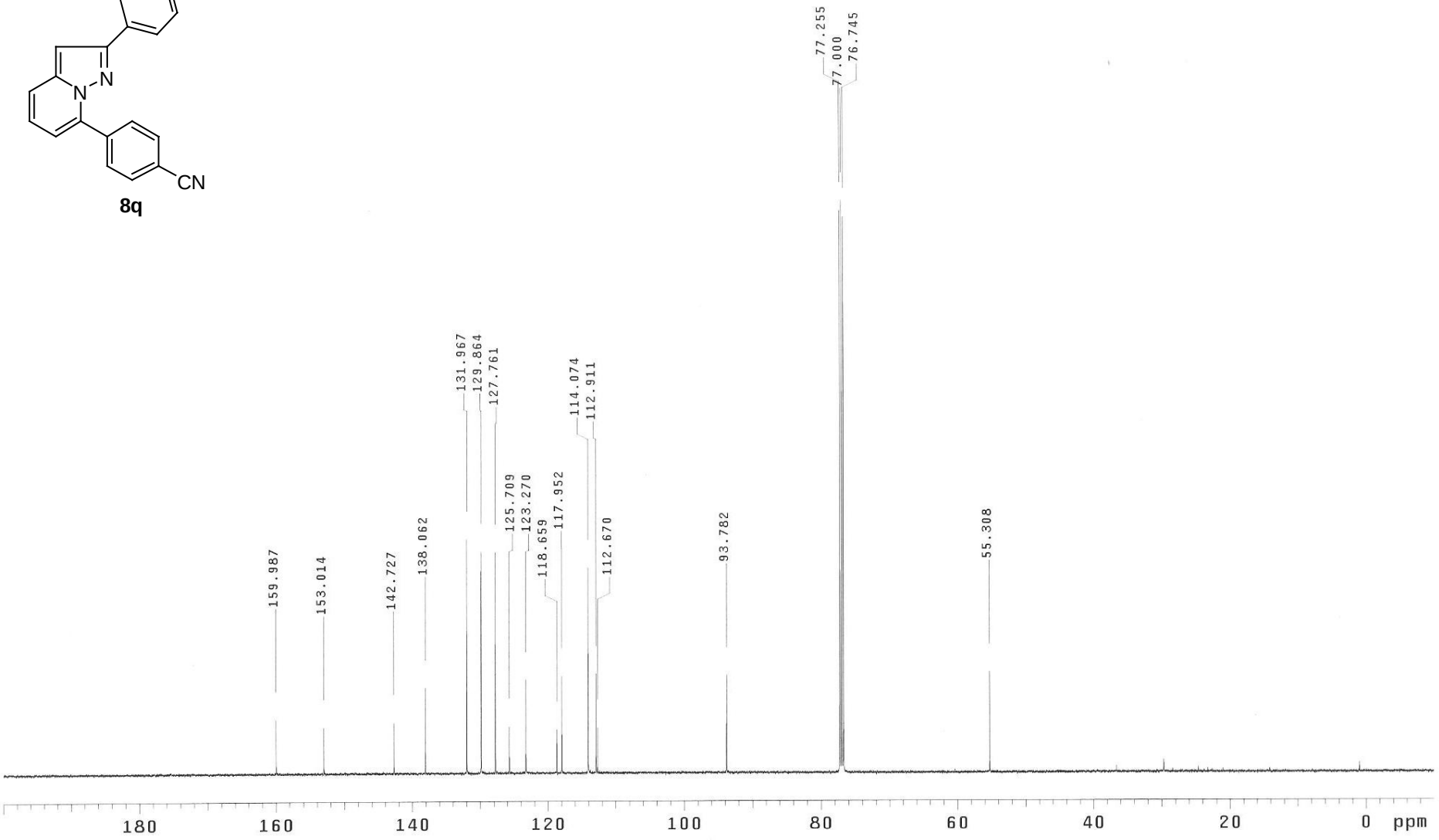

77.255
77.000
76.748
160.329
159.746
152.584
142.859
140.037
130.739
127.794
126.299
126.139
123.525
115.955
113.950
113.578
111.482
93.107
55.370
55.290
180
160
140
120
100
80
60
40
20
0
ppm


WHC-119
OMe
N
N
CN
8q
3.859
6.962
6.846
8.202
8.185
7.889
7.872
7.827
7.810
6.979
7.265
0.083
9
8
7
6
5
4
3
2
1
-0
ppm
2.00
2.00
2.00
1.02
1.03
2.00
2.04
3.13

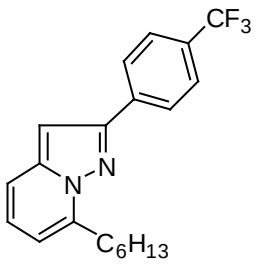
WHC-119


OMe
N
N
CN

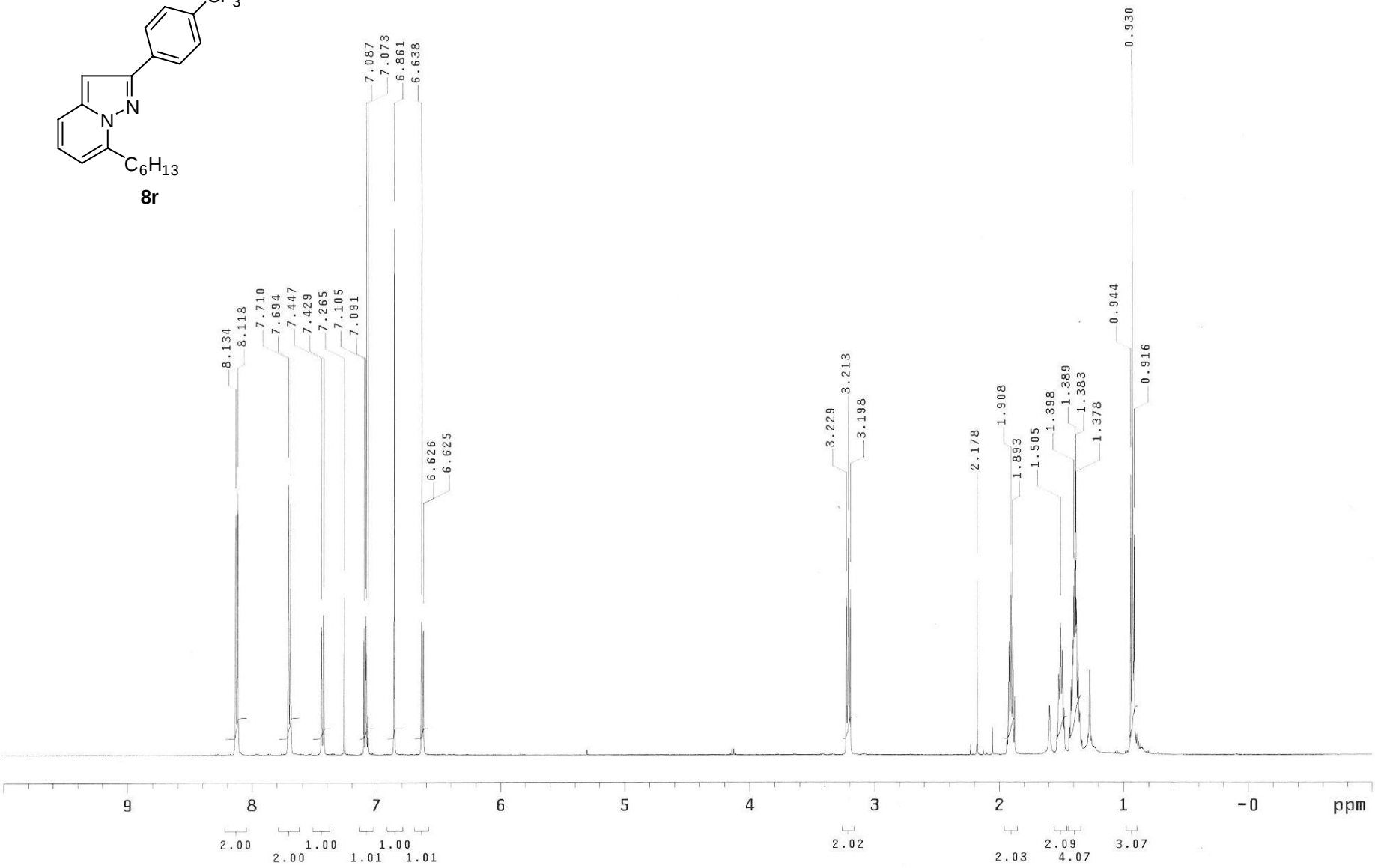
8q


77.255
77.000
76.745
131.967
129.864
127.761
125.709
123.270
118.659
117.952
114.074
112.911
112.670
159.987
153.014
142.727
138.062
93.782
55.308
180
160
140
120
100
80
60
40
20
0
ppm

WHC-132T2


CF3
N
N
C6H13

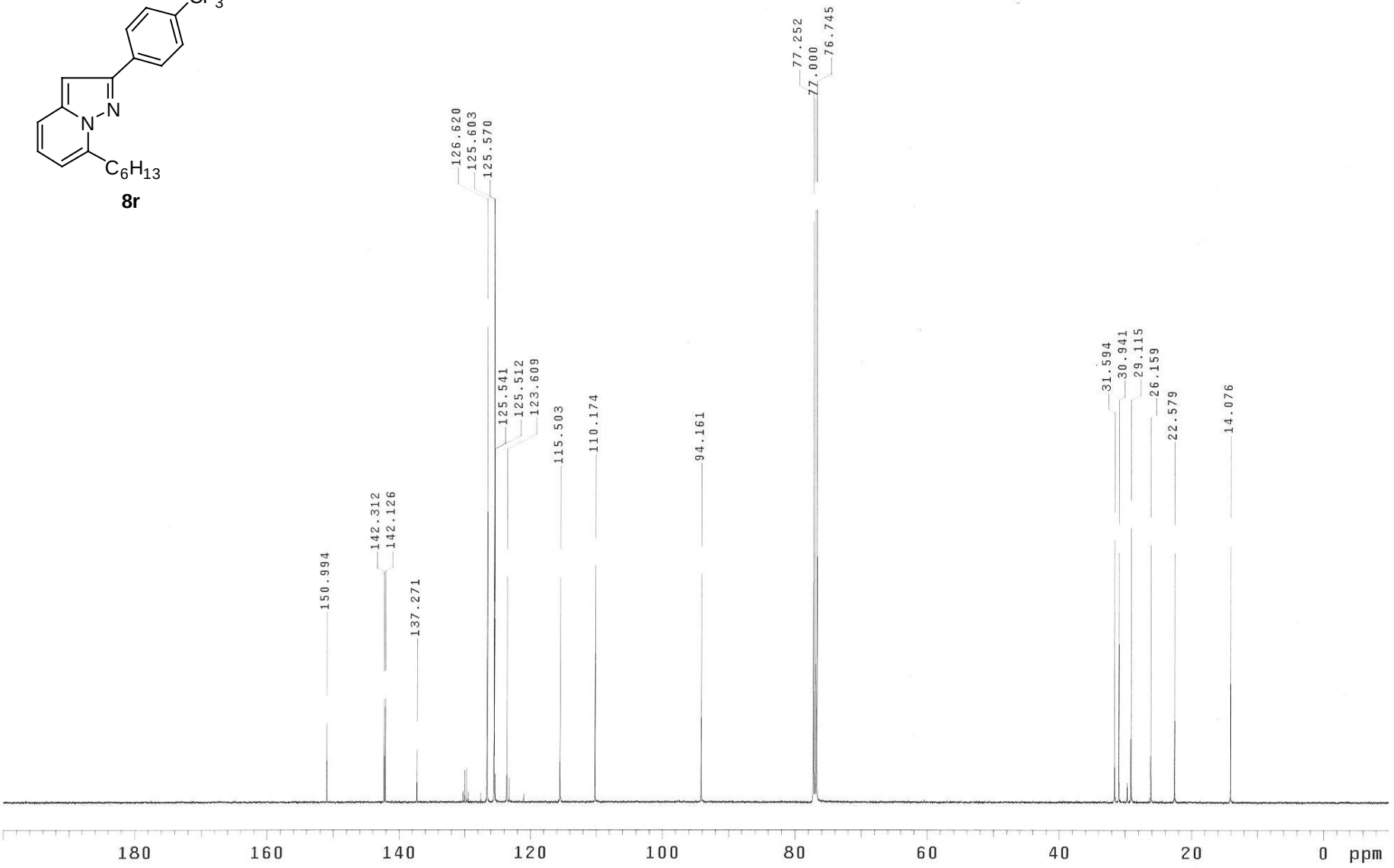
8r


8.134
8.118
7.710
7.694
7.447
7.429
7.265
7.105
7.091
7.087
7.073
6.861
6.638
6.626
6.625
3.229
3.213
3.198
2.178
1.908
1.893
1.505
1.398
1.389
1.383
1.378
0.944
0.930
0.916
9
8
7
6
5
4
3
2
1
-0
ppm
2.00
2.00
1.00
1.01
1.00
1.01
2.02
2.03
2.09
4.07
3.07

WHC-132T2

CF3
N
N
C6H13

8r


150.994
142.312
142.126
137.271
126.620
125.603
125.570
125.541
125.512
123.609
115.503
110.174
94.161
77.252
77.000
76.745
31.594
30.941
29.115
26.159
22.579
14.076
180
160
140
120
100
80
60
40
20
0
ppm