Recyclable Glucose-Derived Palladium(0) Nanoparticles as in situ-Formed Catalysts for Cross-Coupling Reactions in Aqueous Media

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Supporting Information

Contents

I. General Experimental Information

Unless otherwise indicated, all commercially available reagents and solvents were used directly from the supplier without further purification. Solvents used for column chromatography were of technical grade. For purification procedures using column chromatography, silica gel (60-120) mesh was used. Thin layer chromatography was carried out using Merck Kieselgel silica gel 60 F254 plates (0.2 mm) and visualization was achieved using UV light followed by dipping in a potassium permanganate solution and heating. All reactions were performed in Biotage 5 mL microwave vials with Teflon coated caps.

II. Instrumentation

Melting Point – The melting points were recorded on a Stuart Scientific SMP3 melting point apparatus and are uncorrected.

NMR – ^{1}H NMR and ^{13}C NMR were recorded on a Bruker AV400 (400 MHz) spectrometer, Bruker AV(III)400 (400 MHz) spectrometer, Bruker DPX400 (400 MHz) spectrometer or JOEL EX270 (270 MHz) spectrometer at ambient temperature using $CDCl_3$ (7.26 ppm), DMSO-d^6 (2.50 ppm), $(CD_3)_2CO$ (2.05 ppm) or CD_3OD (3.31 ppm) as the solvent. Chemical shift values are expressed as parts per million (ppm) and *J* values are in Hertz. Splitting patterns are indicated as s: singlet, d: doublet, t: triplet, q: quartet or combination there of, br.s broad singlet or m: multiplet.

FTIR – Solution IR spectra were recorded on a Perkin Elmer 1600 series FTIR-spectrophotometer.

Mass Spectrometry – Mass spectra were determined using a Bruker MicroTOF mass spectrometer.

pH meter – The pH measurements were recorded on a Philip Harris digital pH meter using a pH = 7 standard buffer.

Transmission Electron Microscopy (TEM) – TEM analysis was performed using a JEOL2100F field-emission gun microscope operating at 200 kV and equipped with a Gatan Orius camera. The Pd(0) nanoparticles were dispersed in water using an ultrasound bath and a suspension (3.5 μL) was deposited onto a holey carbon grid (Agar Scientific), which had previously been exposed to a low temperature O_2/Ar plasma for five seconds in a Fischione Model 1020 Plasma Cleaner to make them hydrophilic. TEM image simulations was carried out using spherical aberration coefficient (*Cs*) = 1 mm. TEM-EDS was performed in scanning TEM mode using a prototype Oxford Instruments XMAX 100 TLE, on loan from Oxford Instruments.

Nanoparticle Tracking Analysis (NTA) – NTA was performed with a Nanosight LM10-HS instrument equipped with an electron multiplication charge coupled device camera mounted on an optical microscope system to track light scattered by particles that are present in a focused (80 μm) beam generated by a single mode laser diode with a 60 mW blue laser illumination (405 nm). The solution containing the palladium(0) nanoparticles in a concentration of between 10^7 and 10^9 particles/mL was injected in a sample chamber of 0.5 mL size from which a volume of 120x80x20 microns was visualized under the microscope. The sample concentration was adjusted to ensure statistically significant number of particles under analysis. The Brownian motion of the nanoparticles was tracked at 30 frames/s. NTA 2.2 software was used to evaluate the mean square displacements of each visible particle (calibration 166 nm/pixel) and from the Strokes-Einstein equation the particle sizes were determined. All experiments were performed without filtering to ensure measurement of all particles.[1]

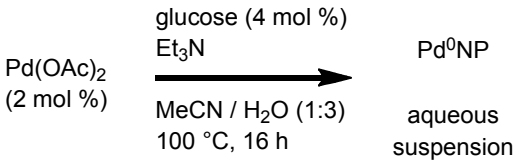
Dynamic Light Scattering (DLS) – DLS experiments were preformed on a Malvern Zetasizer ZS equipped with a He-Ne (633 nm, 5 mW) laser and an Avalanche photodiode detector at an angle of 173°. All DLS data were processed using a Dispersion Technology Software (Malvern Instruments). All experiments were performed without filtering to ensure measurement of all particles.[2]

X-ray Photoelectron Spectroscopy (XPS) – XPS spectra were recorded on the Kratos AXIS ULTRA with a mono-chromated Al kα X-ray source (1486.6eV) operated at 15mA emission current and 12kV anode potential – 180W. Hybrid (magnet/electrostatic) optics (300 x 700 μm aperture), hemispherical analyzer, multichannel plate and delay line detector (DLD) with a take-off angle of 90° and an acceptance angle of 30°. All scans were acquired under charge neutralization conditions using a low energy electron gun within the field of magnetic lens. Survey scans were taken with a pass energy of 80 eV and high resolution scans with a pass energy of 20 eV. Data analysis is carried out using CASAXPS software with Kratos sensitivity factors to determine atomic % values from the peak areas.

Scanning Ion Occlusion Sensing (SIOS) – SIOS measurements were carried out on a qNano instrument (Izon Science Ltd., Christchurch, NZ). A standard electrolyte buffer (SEB) of 0.1 M KCl, 10 mM Tris buffer, 0.01% Triton X-100, and 3 mM EDTA, pH 8.0, filtered through a 0.22 μm filter was used in all experiments. The membrane was wetted prior to sampling by applying a voltage (typically 0.3 V) and manually stretching the pore open (typically with a jaw stretch of 5 mm). Once a stable background current achieved, the fluid in the top half of the cell was replaced with a solution of the palladium(0) nanoparticles in the SEB (30–70 μL). The magnitude and duration of changes in the current signal were collected at a sampling frequency of 50 kHz. The instrument was calibrated using a solution of polystyrene particles (3000 series, 100 nm) in SEB.[3]

III. Palladium nanoparticle formation and characterization

1a. Synthesis of sugar derived palladium(0) nanoparticles



A stirred solution of $Pd(OAc)_2$ (10 mg, 0.044 mmol), glucose (16 mg, 0.088 mmol) and triethylamine (0.4 mL, 2.8 mmol) in acetonitrile / water (1:3, 4 mL) was heated to 100 °C for 16 h in a sealed vial. The mixture was cooled and centrifuged for 5 mins and the majority of solvent was removed. Water (2 mL) was added and the mixture was centrifuged for 5 mins and the majority of solvent was removed (repeated 2x). The particles were isolated as an aqueous suspension, which was directly used for nanoparticle characterization.

1b. Solid state analysis of palladium(0) nanoparticles

Transmission Electron Microscopy (TEM), Energy-dispersive X-ray spectroscopy (EDX) and X-ray Photoelectron Spectroscopy (XPS) analysis were conducted on the sugar derived palladium(0) nanoparticles. An aqueous suspension of the nanoparticles was deposited on the requisite supports (see, Instrumentation section) for direct analysis of the solid samples. The results of the various techniques are discussed in Supplemental Figures 1-3.

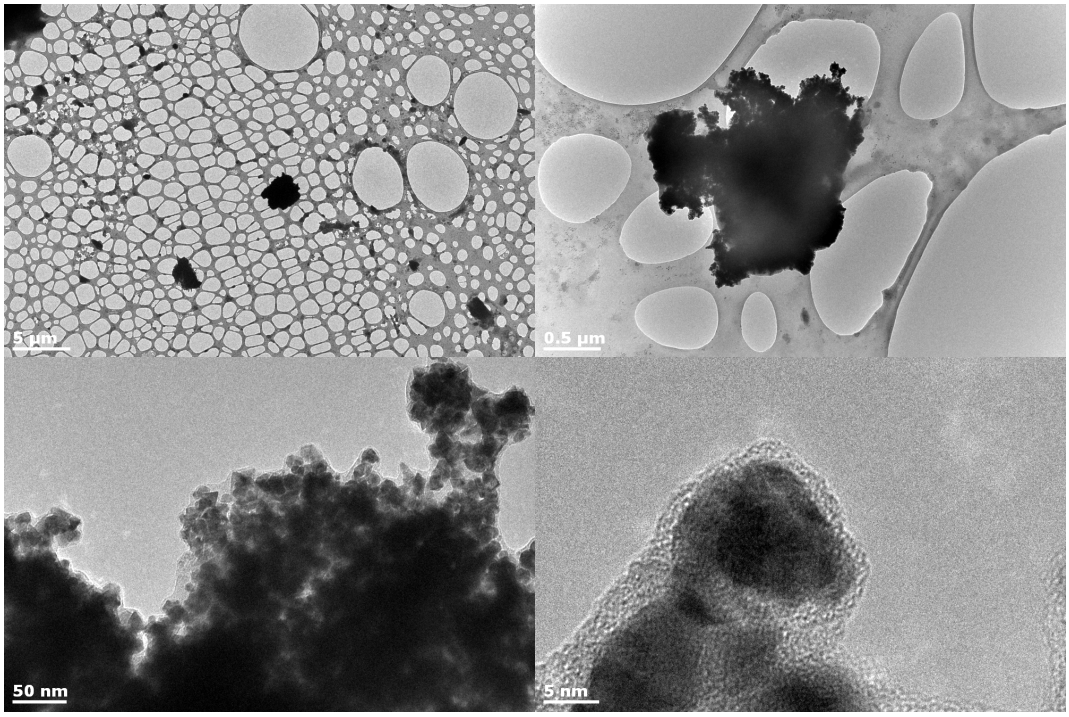
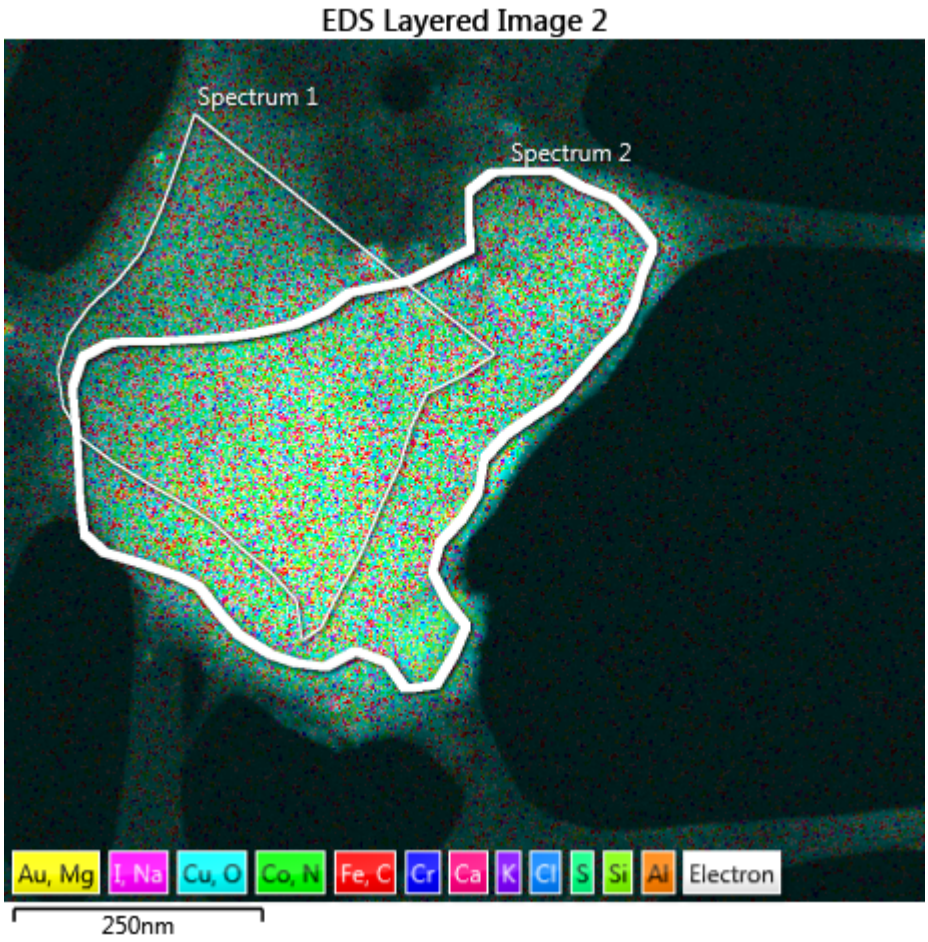
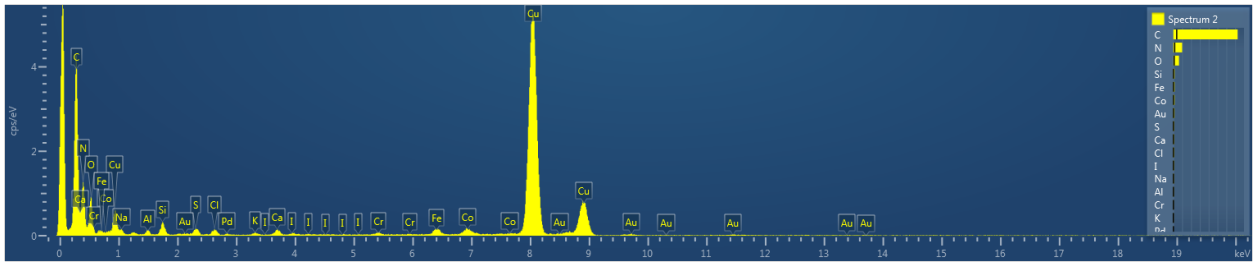


Figure SF1a | Representative TEM images of sugar-derived palladium(0) nanoparticle. The images show the aggregation of the nanoparticles as well as the stabilizing role of the sugar residues. High magnification imaging shows that individual nanoparticles are in the range of 5 – 20 nm and exist in a variety of different conformations and morphologies (spheres, prisms, etc.). The existence of crystalline planes indicates that some of the species are semi-crystalline. Importantly, the lighter amorphous materials at the periphery of the nanoparticles most likely contain the sugar residue.





Spectrum 2	Wt%	Wt% Sigma
C	72.81	3.78
N	10.02	1.50
O	6.42	0.98
Na	0.61	0.11
Al	0.52	0.09
Si	1.43	0.21
S	0.85	0.13
Cl	0.79	0.12
K	0.30	0.06
Ca	0.81	0.13
Cr	0.41	0.08
Fe	1.43	0.22
Co	1.41	0.22
Pd	0.24	0.13

I	0.69	0.17
Au	1.26	0.28
Total	100.00	

Figure SF1b | Representative EDS-TEM images of sugar-derived palladium(0) nanoparticle. The image shows that the surface of the palladium nanoparticle has carbon and oxygen species on it. Importantly, the method is able to quantify the amount of carbon and oxygen on the surface. Copper has been deconvolved for the analysis, due to stray Cu signal from the supporting TEM grid. Cr, Fe and Co signals may also originate from the structure of the TEM itself.

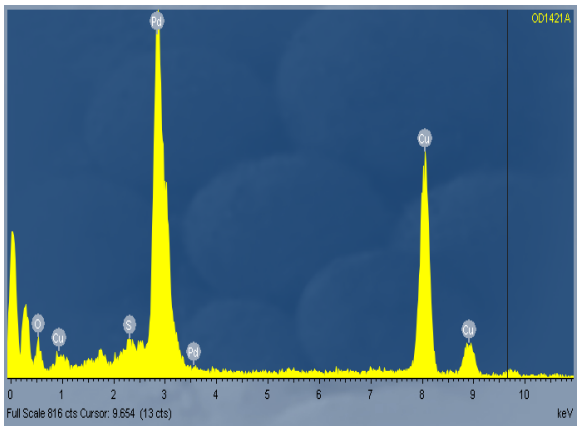
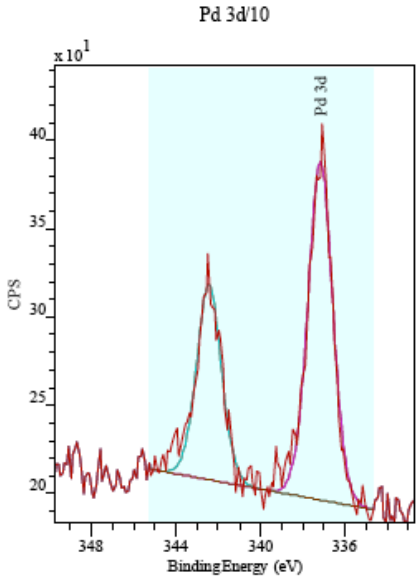


Figure SF2 | EDX spectrum of sugar-derived palladium(0) nanoparticle. The Energy-dispersive X-ray spectrum confirms the presence of palladium in the sample. The Cu signal is attributed to the use of a Cu mesh support grid.



Element	Orbital	At%
C	1s	42.3
N	1s	4.9
Pd	3d	51.2
Si	2p	1.7

Figure SF3 | XPS data of sugar-derived palladium(0) nanoparticle. The X-ray photoelectron spectrum indicates that the palladium present in the sample is in the Pd(0) oxidation state.

1c. Solution state analysis of palladium(0) nanoparticles.

Analysis of the sugar-derived palladium(0) nanoparticles was carried out on solution phase samples in order to access the size the degree of aggregation of the nanoparticles in aqueous solutions. Thus, dynamic light scattering (DLS), Nanoparticle Tracking Analysis (NTA) and Scanning Ion Occlusion Sensing (SIOS) were conducted on suspensions of the nanoparticles as described in the instrumentation section. It should be noted that these three solution phase techniques differ significantly in the way that they determine the size of the nanoparticles in solution. DLS uses the changes in the intensity of scattered light caused by the Brownian motion of the particles to determine their size distribution through the use of the Stokes Einstein equation. A hard spherical model has been used for the calculations. In contrast, NTA directly observes each nanoparticle to give an indirect measure of the size of each particle that is tracked. Again, the Brownian motion of the particles was used to determine their size distribution through the use of the Stokes Einstein equation. Finally, SIOS detects and characterizes individual molecules by nanopore resistive pulse sensing. Importantly, the qNano instrument that was used in our study allows for the rapid tuning of the pore size to allow for improved signal. The results of the various techniques are discussed in Supplemental Figures 4-6.

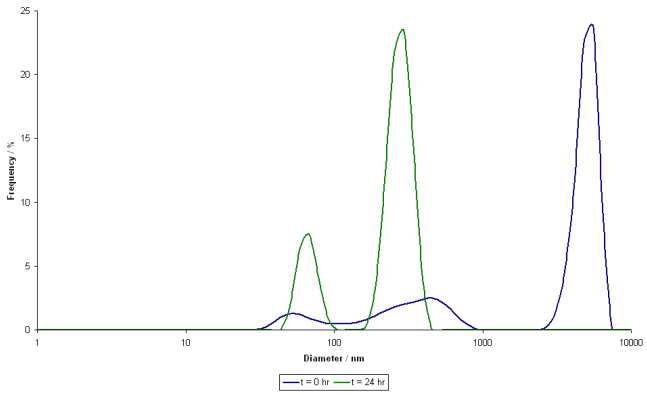


Figure SF4 | DLS data of sugar-derived palladium(0) nanoparticle. The dynamic light scattering spectrum suggests that numerous (semi-)stable particulate species are present in solution and that the nanoparticles aggregate in aqueous media. At t = 0 h the suspension was trimodal with the following size distribution of: 61.6 ± 19.2 nm, 372.8 ± 164.7 nm, 5032 ± 836 nm. After the suspension was allowed to stand for 24 h (t = 24 h) the distribution was bimodal with the following size distribution: 66.7±10.0 nm, 281.2±50.3 nm, as the 5 µm feature had precipitated from solution.

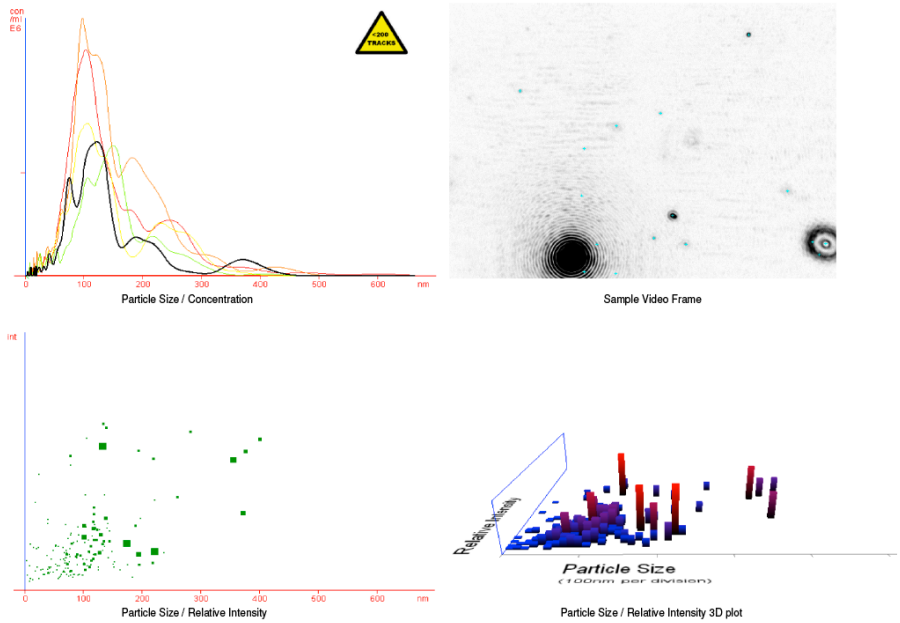


Figure SF5 | NTA data of sugar-derived palladium(0) nanoparticle. The nanoparticle tracking analysis data indicates that the aqueous suspension of nanoparticles aggregate with the following distribution: mean (151 nm), mode (122 nm) and SD (86 nm).

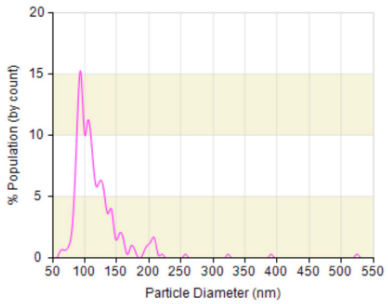
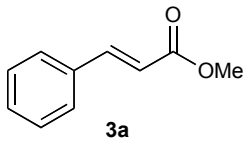


Figure SF6 | SIOS data of sugar-derived palladium(0) nanoparticle. The scanning ion occlusion sensing spectrum indicates that the nanoparticles aggregate in the SEB buffer. The mean (180 nm), median (75 nm) and mode (70 nm) of the filtered (1 µM) suspension were calculated and suggest that the nanoparticles aggregate in the aqueous buffer

IV. Preparation of styrene derivatives 3

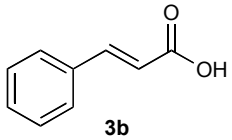
(*E*)-Methyl Cinnamate (3a)



3a

To a stirred solution of $Pd(OAc)_2$ (3.5 mg, 0.016 mmol) and glucose (5.0 mg, 0.032 mmol) in acetonitrile / water (1:3, 4 mL) at rt were added triethylamine (0.14 mL, 1.0 mmol), 4-iodobenzene (87 µL, 0.78 mmol) and methyl acrylate (87 µL, 0.97 mmol). The vial was sealed and the resultant mixture was heated at 100 °C for 16 h. The mixture was cooled to rt and water (10 mL) and dichloromethane (10 mL) were added. The combined organic extracts were dried over Na_2SO_4 and the solvent was removed under reduced pressure. The crude residue was purified by flash column chromatography on silica gel (petrol / EtOAc, 15:1) to give (*E*)-methyl cinnamate (**3a**, 112 mg, 97 %) as a white solid. mp: 34–35 °C (lit.[4] 34–34.5); ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.69 (d, *J* = 16.0 Hz, 1H), 7.63–7.47 (m, 2H), 7.47–7.29 (m, 3H), 6.44 (d, *J* = 16.0 Hz, 1H), 3.80 (s, 3H); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 167.6, 145.0, 134.5, 130.4, 129.0, 128.2, 117.9, 51.8; IR ($CHCl_3$): 3021, 1712, 1604, 1497, 1455, 1361, 954 cm^{-1}; HRMS (*m/z*): [M] calcd. for $C_{10}H_{10}O_2Na$, 185.0578; found 185.0579.

(*E*)-3-Phenyl-2*E*-propenoic Acid (3b)



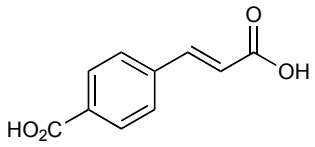
3b

Method 1: To a stirred solution of $Pd(OAc)_2$ (3.5 mg, 0.016 mmol) and glucose (5.0 mg, 0.032 mmol) in acetonitrile / water (1:3, 4 mL) at rt were added triethylamine (0.14 mL, 1.0 mmol), iodobenzene (87 µL, 0.78 mmol) and acrylic acid (66 µL, 0.97 mmol). The vial was sealed and the resultant mixture was heated at 100 °C for 16 h. The mixture was cooled to rt and water (10 mL) and dichloromethane (10 mL) were added. The combined organic extracts were dried over Na_2SO_4 and the solvent was removed under reduced pressure. The crude residue was washed with diethyl ether to give (*E*)-3-phenyl-2*E*-propenoic acid (**3b**, 115 mg, 100%) as white crystals.

Method 2: To a stirred solution of $Pd(OAc)_2$ (3.5 mg, 0.016 mmol) and sodium erythorbate (6.3 mg, 0.032 mmol) in acetonitrile / water (1:3, 4 mL) at rt were added triethylamine (0.14 mL, 1.0 mmol), iodobenzene (87 µL, 0.78 mmol) and acrylic acid (66 µL, 0.97 mmol). The vial was sealed and the resultant mixture was heated at 100 °C for 16 h. The mixture was cooled to rt and water (10 mL) and dichloromethane (10 mL) were added. The combined organic extracts were dried over Na_2SO_4 and the solvent was removed under reduced pressure. The crude residue was washed with diethyl ether to give (*E*)-3-phenyl-2*E*-propenoic acid (**3b**, 100 mg, 87%) as white crystals.

mp: 132–133 °C (lit.[5] 133 °C); ^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ 7.71-7.66 (m, 4H), 7.45-7.43 (m, 2H), 6.54 (d, *J* = 16.0 Hz, 1H); ^{13}C NMR (125 MHz, $(CD_3)_2CO$) δ 167.8, 135.5, 131.1, 129.8, 129.0, 119.3; IR ($CHCl_3$): 3525, 3085, 3002, 1717, 1692, 1635, 1497, 1451, 1416, 1284, 981 cm^{-1}; HRMS (*m/z*) [M] calcd. for $C_9H_8O_2Na$, 171.0423; found, 171.0417.

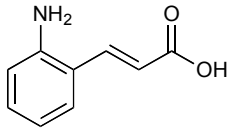
(*E*)-4-(2-Carboxyvinyl)benzoic Acid (3c)



3c

To a stirred solution of $Pd(OAc)_2$ (3.5 mg, 0.016 mmol) and glucose (5.0 mg, 0.032 mmol) in acetonitrile / water (1:3, 4 mL) at rt were added triethylamine (0.14 mL, 1.0 mmol), 4-iodobenzoic acid (193 mg, 0.78 mmol) and acrylic acid (66 μL, 0.97 mmol). The vial was sealed and the mixture heated at 100 °C for 16 h. The mixture was cooled to rt and water (10 mL) and dichloromethane (10 mL) were added. The combined organic extracts were dried over Na_2SO_4 and the solvent was removed under reduced pressure to give (*E*)-4-(2-carboxyvinyl)benzoic acid (**3c**, 149 mg, 100%) as a white powder. mp: 353–355 °C (lit.[6] 352 °C); ^{1}H NMR (270 MHz, DMSO-D^6): δ 7.95 (d, *J* = 8.3 Hz, 2H), 7.81 (d, *J* = 8.3 Hz, 2H), 7.64 (d, *J* = 16.1 Hz, 1H), 6.64 (d, *J* = 16.1 Hz, 1H); ^{13}C NMR (67.5 MHz, DMSO-D^6): δ 167.3, 167.3, 143.1, 138.9, 132.4, 130.2, 128.8, 122.1; IR ($CHCl_3$): 2361, 2342, 1602 cm^{-1}; HRMS (*m/z*) [M] calcd. for $C_{10}H_8O_4$ Na, 215.0315; found, 215.0332.

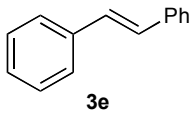
(*E*)-3-(2-Aminophenyl)acrylic Acid (3d)



3d

To a stirred solution of $Pd(OAc)_2$ (3.5 mg, 0.016 mmol) and glucose (5.0 mg, 0.032 mmol) in acetonitrile / water (1:3, 4 mL) at rt were added triethylamine (0.14 mL, 1.0 mmol), 2-iodoaniline (170 mg, 0.78 mmol) and acrylic acid (66 μL, 0.97 mmol). The vial was sealed and the mixture was heated at 100 °C for 16 h. The mixture was cooled to rt and water (10 mL) and dichloromethane (10 mL) were added. The combined organic extracts were dried over Na_2SO_4 and the solvent was removed under reduced pressure. The crude residue was purified by flash column chromatography on silica gel (petrol / EtOAc, 9:1) to give (*E*)-3-(2-aminophenyl) acrylic acid (**3d**, 0.72 mmol, 118 mg, 93%) as a yellow solid. mp: 158–159 °C (lit.[7] 157–158 °C); ^{1}H NMR (270 MHz, $CDCl_3$): δ 7.93 (d, *J* = 15.8 Hz, 1H), 7.43 (dd, *J* = 8.0, 1.2 Hz, 1H), 6.80 (t, *J* = 6.8 Hz, 2H), 6.73 (dd, *J* = 8.0, 1.2 Hz, 1H), 6.39 (d, *J* = 15.8 Hz, 1H); ^{13}C NMR (67.5 MHz, CD_3OD): δ 171.2, 148.6, 142.5, 132.5, 128.6, 120.8, 119.3, 118.2, 117.9; IR ($CHCl_3$): 2927, 2856, 2364, 2339, 1717, 1687, 1621, 1491, 1460, 1253, 1161, 1126, 982 cm^{-1}; HRMS (*m/z*) [M] calcd. for $C_9H_{10}NO_2$, 164.0706; found, 164.0713.

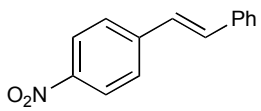
(*E*)-stilbene (3e)



3e

To a stirred solution of $Pd(OAc)_2$ (3.5 mg, 0.016 mmol) and glucose (5.0 mg, 0.032 mmol) in acetonitrile / water (1:3, 4 mL) at rt were added triethylamine (0.14 mL, 1.0 mmol), styrene (111 μL, 0.97 mmol) and iodobenzene (87 μL, 0.78 mmol). The vial was sealed and the mixture was heated to 100 °C for 16 h. The mixture was cooled and water (10 mL) and ether (10 mL) were added. The combined organic extracts were dried over Na_2SO_4 and the solvent was removed under reduced pressure. The crude residue was purified by flash column chromatography on silica gel (petrol / EtOAc, 9:1) to give (*E*)-stilbene (**3e**, 126 mg, 90%) as a white crystalline solid. mp: 122–124 °C (lit.[8] 121–122 °C); ^{1}H NMR (270 MHz, $CDCl_3$): δ 7.53 (d, *J* = 7.2 Hz, 4H), 7.37 (t, *J* = 7.2 Hz, 4H), 7.27 (t, *J* = 7.2 Hz, 2H), 7.13 (s, 2H); ^{13}C NMR; (67.5 MHz, $CDCl_3$) δ 137.3, 128.7, 127.6, 126.5; IR ($CHCl_3$): 3011, 1609, 1452, 961, 527 cm^{-1}; HRMS (*m/z*) [M] calcd. for $C_{14}H_{12}$, 180.0939; found 180.0939.

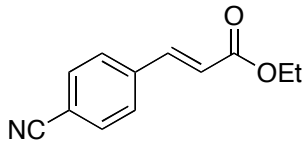
(*E*)-4-Nitrostilbene (3f)



3f

To a stirred solution of $Pd(OAc)_2$ (3.5 mg, 0.016 mmol) and glucose (5.0 mg, 0.032 mmol) in acetonitrile / water (1:3, 4 mL) at rt were added triethylamine (0.14 mL, 1.0 mmol), styrene (87 µL 0.78 mmol) and 4-iodonitrobenzene (193 mg, 0.78 mmol). The vial was sealed and the mixture was heated to 100 °C for 16 h. The mixture was cooled and water (10 mL) and ether (10 mL) were added. The combined organic extracts were dried over Na_2SO_4 and the solvent was removed under reduced pressure. The crude residue was purified by flash column chromatography on silica gel (petrol / EtOAc, 30:1) to give (*E*)-4-nitrostilbene (**3f**, 175 mg, 94%) as a yellow solid. mp: 153–154 °C (lit.[9] 153–154 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.23 (d, *J* = 12.0 Hz, 2H), 7.65 (d, 8.9 Hz, 2H), 7.58-7.55 (m, 2H), 7.43-7.31 (m, 4H), 7.18-7.14 (m, 1H); ^{13}C NMR (67.5 MHz, $CDCl_3$): δ 146.7, 143.8, 136.2, 133.3, 128.9, 128.8, 127.0, 126.8, 126.2, 124.1; IR ($CHCl_3$): 1594, 1518, 1343, 1111, 966, 955, 851 cm^{-1}; HRMS (*m/z*) [M] calcd. for $C_{14}H_{11}NO_2$, 225.0790; found 225.0784.

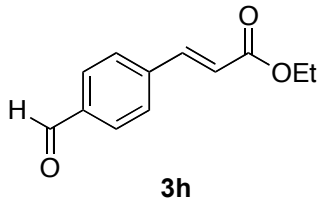
Ethyl (*E*)-3-(4-cyanophenyl)acrylate (3g)



3g

To a stirred solution of $Pd(OAc)_2$ (3.5 mg, 0.016 mmol) and glucose (5.0 mg, 0.032 mmol) in acetonitrile / water (1:3, 4 mL) at rt were added triethylamine (0.14 mL, 1.0 mmol), 4-iodobenzonitrile (178 mg, 0.78 mmol) and ethyl acrylate (106 µL, 0.97 mmol). The vial was then sealed and the mixture heated at 100 °C for 16 h. The mixture was cooled and water (10 mL) and CH_2Cl_2 (10 mL) were added. The combined organic extracts were dried over Na_2SO_4 and the solvent was removed under reduced pressure. The crude residue was purified by flash column chromatography on silica gel (hexane / EtOAc, 9:1) to give ethyl (*E*)-3-(4-cyanophenyl)acrylate (**3g**, 37 mg, 23%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ7.69 – 7.59 (m, 5H), 6.51 (d, J = 16.0 Hz, 1H), 4.28 (q, J = 7.0, 7.19 Hz, 2H), 1.34 (t, J = 7.2 Hz, 3H); ^{13}C NMR (400MHz, $CDCl_3$): δ166.1, 142.1, 138.8, 132.7, 128.4, 121.9, 118.4, 113.3, 61.0, 14.3; IR (neat): 2989, 2921, 2226, 1705, 1637 cm^{-1}. HRMS (*m/z*) $[M+H]^+$ calcd. for $C_{12}H_{12}NO_2$, 202.0863; found, 202.0861.

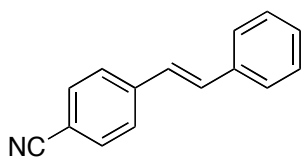
Ethyl (*E*)-3-(4-formylphenyl)acrylate (3h)



3h

To a stirred solution of $Pd(OAc)_2$ (2.47 mg, 0.011 mmol) and glucose (3.96 mg, 0.022 mmol) in acetonitrile / water (1:3, 2.86 mL) at rt were added triethylamine (0.10 mL, 0.72 mmol), 4-iodobenzaldehyde (130 mg, 0.56 mmol) and ethyl acrylate (76 µL, 0.70 mmol). The vial was then sealed and the mixture heated at 100 °C for 16 h. The mixture was cooled and water (10 mL) and CH_2Cl_2 (10 mL) were added. The combined organic extracts were dried over Na_2SO_4 and the solvent was removed under reduced pressure. The crude residue was purified by flash column chromatography on silica gel (hexane / EtOAc, 9:1) to give ethyl (*E*)-3-(4-formylphenyl)acrylate (**3h**, 75 mg, 47%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ10.01 (s, 1H), 7.89 (d, J = 8.12 Hz, 2H), 7.68 (m, 3H), 6.54 (d, J = 16.0 Hz, 1H), 4.27 (q, J = 7.1, 7.2 Hz, 2H), 1.33 (t, J = 7.1 Hz, 3H); ^{13}C NMR (400MHz, $CDCl_3$): δ191.5, 166.4, 142.8, 140.1, 137.1, 130.2, 128.5, 121.5, 60.8, 14.3; IR (neat): 2980, 2847, 1693, 1633, 1602 cm^{-1}. HRMS (*m/z*) $[M+H]^+$ calcd. for $C_{12}H_{13}O_3$, 205.0859; found, 205.0862.

(*E*)-4-styrylbenzonitrile (3i)



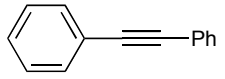
3i

To a stirred solution of $Pd(OAc)_2$ (3.5 mg, 0.016 mmol) and glucose (5.0 mg, 0.032 mmol) in acetonitrile / water (1:3, 4 mL) at rt were added triethylamine (0.14 mL, 1.0 mmol), 4-iodobenzonitrile (178 mg, 0.78 mmol) and styrene (112 µL,

0.97 mmol). The vial was then sealed and the mixture heated at 100 °C for 16 h. The mixture was cooled and water (10 mL) and CH_2Cl_2 (10 mL) were added. The combined organic extracts were dried over Na_2SO_4 and the solvent was removed under reduced pressure. The crude residue was purified by flash column chromatography on silica gel (hexane / EtOAc, 9:1) to give (*E*)-3-(2,6-dimethylphenyl)acrylic acid (**3i**, 58 mg, 36%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ7.62 (d, J = 8.4 Hz, 2H), 7.57 (d, J = 8.8 Hz, 2H), 7.54 (d, J = 7.5 Hz, 2H), 7.40 (t, J = 7.7 Hz, 2H), 7.33 (t, J = 7.3 Hz, 1H), 7.21 (d, J = 16.4 Hz, 1H), 7.08 (d, J = 16.4 Hz, 1H); ^{13}C NMR (400MHz, $CDCl_3$): δ141.8, 136.3, 132.5, 132.4, 128.9, 128.7, 127.0, 126.9, 126.7, 119.1, 110.6; IR (neat): 3022, 2224, 1600 cm^{-1}. HRMS (m/z) [M+H]+ calcd. for $C_{15}H_{12}N$, 206.0964; found, 206.0973

V. Preparation of acetylene derivatives 6

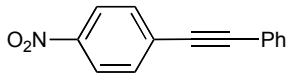
Diphenyl Acetylene (6a)



6a

To a stirred solution of $Pd(OAc)_2$ (3.5 mg, 0.016 mmol) and glucose (5.0 mg, 0.032 mmol) in acetonitrile / water (1:3, 4 mL) at rt were added triethylamine (0.14 mL, 1.0 mmol), phenyl acetylene (85 μL, 0.78 mmol) and iodobenzene (87 μl, 0.777 mmol). The vial was sealed and the mixture was heated to 100 °C for 16 h. The mixture was cooled and water (10 mL) and ether (10 mL) were added. The combined organic extracts were dried over Na_2SO_4 and the solvent was removed under reduced pressure. The crude residue was purified by flash column chromatography on silica gel (petrol / EtOAc, 9:1) to give diphenyl acetylene (**6a**, 130 mg, 95 %) as a brown solid. mp: 56–58 °C (lit.[10] 57 °C); ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.60–7.47 (m, 2H), 7.38–7.30 (m, 3H); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 131.6, 128.4, 128.3, 123.3, 89.4; IR ($CHCl_3$): 3071, 3004, 2922, 1599, 1494, 1432, 1073, 1033, 920 cm^{-1}; HRMS (*m/z*) [M] calcd. for $C_{14}H_{10}$, 178.0783; found 178.0775.

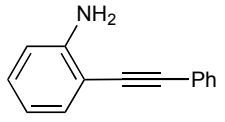
(*E*)-1-Nitro-4-(2-phenyl-1-ethynl)benzene (6b)



6b

To a stirred solution of $Pd(OAc)_2$ (3.5 mg, 0.016 mmol) and glucose (5.0 mg, 0.032 mmol) in acetonitrile / water (1:3, 4 mL) at rt were added triethylamine (0.14 mL, 1.0 mmol), phenylacetylene (85 μL, 0.78 mmol) and 4-iodonitrobenzene (193 mg, 0.78 mmol). The vial was sealed and the mixture was heated to 100 °C for 16 h. The mixture was cooled and water (10 mL) and ether (10 mL) were added. The combined organic extracts were dried over Na_2SO_4 and the solvent was removed under reduced pressure. The crude residue was purified by flash column chromatography on silica gel (petrol / EtOAc, 9:1) to give (*E*)-1-nitro-4-(2-phenyl-1-ethynl)benzene (**6b**, 172 mg, 60%) as a yellow solid. mp: 119–121 °C (lit.[11] 119–121 °C); ^{1}H NMR (400 MHz, CD_3OD): δ 8.28 (d, *J* = 8.0, 2H), 7.76 (d, *J* = 8.0, 2H), 7.60–7.58 (m, 2H), 7.45–7.42 (m, 3H); ^{13}C NMR (125 MHz, CD_3OD): δ 147.1, 132.0, 131.4, 129.2, 129.0, 128.3, 123.3, 122.0, 93.7, 86.9; IR ($CHCl_3$): 2219, 1597, 1520, 1345, 1107, 863; HRMS (*m/z*) [M] calcd. for $C_{14}H_9NO_2$, 223.0633; found 223.0630.

(*E*)-2-phenylethynylaniline (6c)

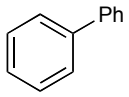


6c

To a stirred solution of $Pd(OAc)_2$ (3.5 mg, 0.016 mmol) and glucose (5.0 mg, 0.032 mmol) in acetonitrile / water (1:3, 4 mL) at rt were added triethylamine (0.14 mL, 1.0 mmol), phenylacetylene (85 μL, 0.78 mmol) and 2-iodoaniline (170 mg, 0.78 mmol). The vial was sealed and the mixture was heated to 100 °C for 16 h. The mixture was cooled and water (10 mL) and ether (10 mL) were added. The combined organic extracts were dried over Na_2SO_4 and the solvent was removed under reduced pressure. The crude residue was purified by flash column chromatography on silica gel (petrol / EtOAc, 30:1) to give (*E*)-2-phenylethynylaniline (**6c**, 64 mg, 44%) as a yellow solid. mp: 86–87 °C (lit.[12] 85–87 °C); ^{1}H NMR (270 MHz, $CDCl_3$): δ 7.59–7.51 (m, 2H), 7.43–7.33 (m, 4H), 7.16 (td, *J* = 7.5, 1.5, 1H), 6.79–6.68 (m, 2H), 4.40 (br.s 2H); ^{13}C NMR (67.5 MHz, $CDCl_3$): δ_c 147.8, 132.1, 131.4, 129.7, 128.3, 128.2, 123.3, 117.9, 114.3, 94.6, 85.8; IR ($CHCl_3$): 2219, 1597, 1520, 1345, 1107, 863 cm^{-1}; HRMS (*m/z*) [M] calcd. for $C_{14}H_{11}N$, 193.0892; found 193.0897

VI. Preparation of biphenyl derivatives 7 and Boscalid (8)

Biphenyl (7a)



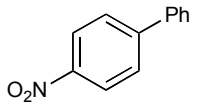
7a

Method 1: To a stirred solution of $Pd(OAc)_2$ (3.5 mg, 0.016 mmol) and glucose (14 mg, 0.077 mmol) in DMF / water (10:1, 4 mL) at rt were added caesium carbonate (510 mg, 1.55 mmol), iodobenzene (87 µL, 0.78 mmol) and phenylboronic acid (140 mg, 1.17 mmol). The vial was sealed and the mixture was heated to 100 °C for 16 h. The mixture was cooled and water (10 mL) and ether (10 mL) were added. The combined organic extracts were dried over Na_2SO_4 and the solvent was removed under reduced pressure. The crude residue was purified by flash column chromatography on silica gel (petrol / EtOAc, 30:1) to give biphenyl (**7a**, 120 mg, 98%) as a white crystalline solid.

Method 2: To a stirred solution of $Pd(OAc)_2$ (3.5 mg, 0.016 mmol) and glucose (14 mg mg, 0.077 mmol) in DMF / water (10:1, 4 mL) at rt were added caesium carbonate (510 mg, 1.55 mmol), bromobenzene (82 µL, 0.78 mmol) and phenylboronic acid (140 mg, 1.17 mmol). The vial was sealed and the mixture was heated to 100 °C for 16 h. The mixture was cooled and water (10 mL) and ether (10 mL) were added. The combined organic extracts were dried over Na_2SO_4 and the solvent was removed under reduced pressure. The crude residue was purified by flash column chromatography on silica gel (petrol / EtOAc, 30:1) to give biphenyl (**7a**, 120 mg, 98%) as a white crystalline solid.

mp: 70–72 °C (lit.[13] 70–72 °C); ^{1}H NMR (270 MHz, $CDCl_3$): δ 7.75–7.67 (m, 4H), 7.61–7.50 (m, 4H), 7.50–7.41 (m, 2H); ^{13}C NMR (67.5 MHz, $CDCl_3$): 141.2, 128.7, 127.2, 127.1; IR ($CHCl_3$): 3066, 1597, 1485, 907 cm^{-1}; HRMS (*m/z*) $[M]^+$ calcd. for $C_{12}H_{10}$, 154.0783; found 154.0772.

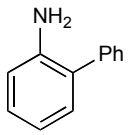
4-Nitrobiphenyl (7b)



7b

To a stirred solution of $Pd(OAc)_2$ (3.5 mg, 0.016 mmol) and glucose (14 mg, 0.077 mmol) in DMF / water (10:1, 4 mL) at rt were added caesium carbonate (510 mg, 1.55 mmol), 1-iodo-4-nitrobenzene (190 mg, 0.78 mmol) and phenylboronic acid (140 mg, 1.17 mmol). The vial was sealed and the mixture was heated to 100 °C for 16 h. The mixture was cooled and water (10 mL) and ether (10 mL) were added. The combined organic extracts were dried over Na_2SO_4 and the solvent was removed under reduced pressure. The crude residue was purified by flash column chromatography on silica gel (petrol / EtOAc, 15:1) to give 4-nitrobiphenyl (**7b**, 140 mg, 94%) as an orange crystalline solid. mp: 98–100 °C (lit.[14] 100–102 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.33 (d, J = 8.0 Hz, 2H), 7.77 (d, J = 8.0 Hz, 2H), 7.67–7.64 (m, 2H), 7.55–7.47 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): 147.6, 138.8, 132.1, 129.1, 128.9, 127.8, 127.4, 124.1; IR ($CHCl_3$): 3066, 1597, 1519, 1347, 855 cm^{-1}; HRMS (*m/z*) [M] calcd. for $C_{10}H_{10}N_1O_2$, 200.0712; found 200.0710.

Biphenyl-2-amine (7c)

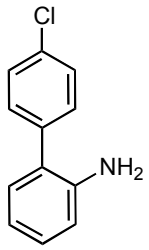


7c

To a stirred solution of $Pd(OAc)_2$ (3.5 mg, 0.016 mmol) and glucose (14 mg, 0.077 mmol) in DMF / water (10:1, 4 mL) at rt were added caesium carbonate (510 mg, 1.55 mmol), iodoaniline (170 mg, 0.78 mmol), phenylboronic acid (140 mg, 1.17 mmol). The vial was sealed and the mixture was heated to 100 °C for 16 h. The mixture was cooled and water (10 mL) and ether (10 mL) were added. The combined organic extracts were dried over Na_2SO_4 and the solvent was removed under reduced pressure. The crude residue was purified by flash column chromatography on silica gel (petrol / EtOAc, 6:1) to give biphenyl-2-amine (**7c**, 66 mg, 65%) as a brown oil. ^{1}H NMR (270 MHz, $CDCl_3$): δ 7.51–7.45 (m, 4H), 7.42–7.33 (m, 1H), 7.20–7.13 (m, 1H), 6.86–6.83 (m, 2H), 6.81 (s, 2H), 6.79 (d, 1H, J = 8.0 Hz); ^{13}C NMR (67.5

MHz, $CDCl_3$): δ 148.7, 139.5, 130.4, 129.0, 128.8, 128.7, 127.2, 127.1, 118.6 115.5; IR ($CHCl_3$): 3394, 3011, 1617, 1501, 1158 cm^{-1}; HRMS (*m/z*) [M] calcd. for $C_{12}H_{12}N_1$, 170.0970; found 170.0978.

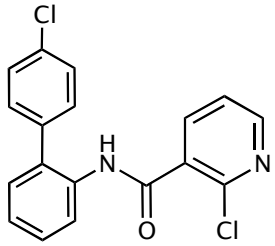
4-Chloro-biphenyl-2-amine (7d)[15]



7d

To a stirred solution of $Pd(OAc)_2$ (3.5 mg, 0.016 mmol) and glucose (14 mg, 0.077 mmol) in DMF / water (10:1, 4 mL) at rt were added caesium carbonate (510 mg, 1.55 mmol), iodoaniline (170 mg, 0.78 mmol) and 4-chloro-phenylboronic acid (180 mg, 1.17 mmol). The vial was sealed and the mixture was heated to 100 °C for 16 h. The mixture was cooled and water (10 mL) and ether (10 mL) were added. The combined organic extracts were dried over Na_2SO_4 and the solvent was removed under reduced pressure. The crude residue was purified by flash column chromatography on silica gel (petrol / EtOAc, 8:1) to give 4-chloro-biphenyl-2-amine (**7d**, 130 mg, 88%) as a cream oil. ^1H NMR (270 MHz, $CDCl_3$); δ 7.43–7.38 (m, 2H), 7.21–7.14 (m, 2H), 7.13–7.06 (m, 1H), 6.89–6.82 (m, 1H), 6.82–6.74 (m, 2H), 3.75 (s, 2H); ^{13}C NMR (67.9 MHz, $CDCl_3$); 143.8, 133.5, 131.5, 130.9, 129.4, 129.3, 128.7, 126.8, 119.2, 116.2; IR ($CHCl_3$) 1045, 1617, 1731, 2985, 3394 cm^{-1}; HRMS (ESI) m/z Calcd for $C_{12}H_{11}ClN$, 204.0580. Found 204.0780.

2-Chloro-*N*-(4'-chloro-[1,1'-biphenyl]-2-yl) Nicotinamide (8)



Boscalid (**8**)

To a stirred solution of 4-chloro-biphenyl-2-amine (**7d**, 90 mg, 0.44 mmol) in dichloromethane (2.0 mL) at rt were added 2-chloronicotoyl chloride (80 mg g, 0.45 mmol), triethylamine (0.12 mL, 0.88 mmol) and 4-dimethylaminopyridine (5 mg, 0.04 mmol). The resulting mixture was stirred at rt for 14 h. Dichloromethane (10 mL) and water (10 mL) were added. The combined organic extracts were dried over Na_2SO_4 and the solvent was removed under reduced pressure. The crude residue was purified by flash column chromatography on silica gel (petrol / EtOAc, 6:1) to afford 2-chloro-*N*-(4'-chloro-[1,1'-biphenyl]-2-yl) nicotinamide (**8**, 104 mg, 81%) as a white solid. mp 138–140 °C (lit.[15] 142–144 °C); ^1H NMR (270 MHz, $CDCl_3$) δ 8.37–8.34 (m, 1H), 8.23 (bs, 1H), 8.06–8.02 (m, 2H), 7.47–7.40 (m, 2H), 7.39–7.37 (m, 2H), 7.33–7.31 (m, 2H), 7.30–7.29 (m, 1H), 7.28–7.23 (m, 1H); ^{13}C NMR (67.9 MHz, $CDCl_3$) 162.1, 150.6, 146.1, 139.0, 135.8, 133.77, 133.70, 132.0, 130.6, 130.2, 129.7, 128.7, 128.5, 128.3, 122.3, 121.9; IR ($CHCl_3$) (cm^{-1}) 1522, 1561, 1581, 1610, 1674, 3008, 3402; HRMS (ESI) m/z Calcd for $C_{18}H_{13}N_2Cl_2O$, 343.0405, found 343.0394.

VI. Molecular Efficiency Calculations

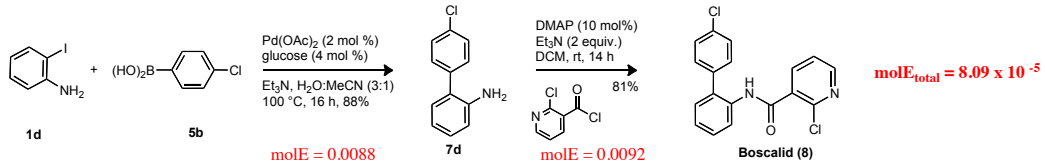
Molar efficiency calculations were calculated using the method of Watson *et al.*[16] in which:

molar efficiency (Mol. E%) = [moles product / moles starting material + additives + catalysts + solvents] x 100

The Mol. E% was calculated for each step of the process and the total molar efficiency ($molE_{total}$) is the multiplication of these values.

Molar Efficiency Calculations

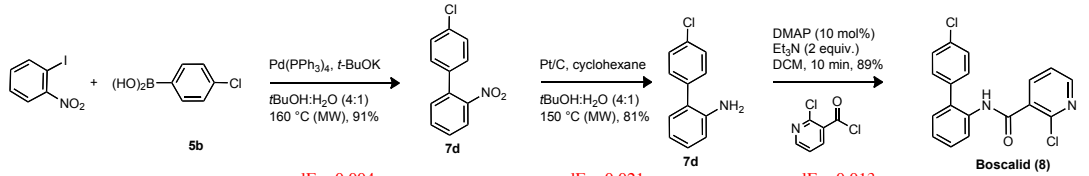
This work



molE = 0.0088 molE = 0.0092

$molE_{total}$ = 8.09 x 10 $^{-5}$

Kappe *et al.* [17]



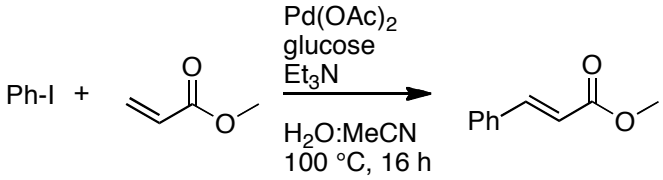
molE = 0.004 molE = 0.021 molE = 0.013

$molE_{total}$ = 1.09 x 10 $^{-6}$

Thus, the approach presented in this report amounts to a nearly two-fold increase in molar efficiency.

VIII. Reaction Optimization and Substrate Scope Studies

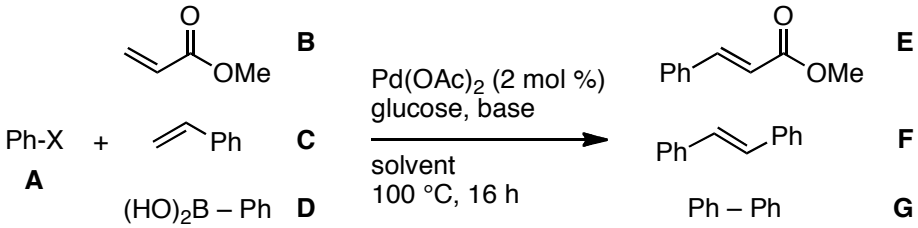
Table S1. Development of the sugar-derived PdNP-catalysed cross-coupling reaction, solvent effects and reaction times



Entry	Solvent	Pd (mol %)	Glucose (mol %)	Et_3N (equiv.)	Temp. (°C)	Time (h)	Yield[b] (%)
1	MeCN / Water (1:3)	2	4	1.3	100	16	97
2	DMF	2	4	1.3	100	16	97
3	THF / H_2O (1:3)	2	4	1.3	100	16	13
4	Water	2	4	1.3	100	16	4
5	MeCN / Water (1:3)	2	4	1.3	100	0	0
6	MeCN / Water (1:3)	2	4	1.3	100	1	22
7	MeCN / Water (1:3)	2	4	1.3	100	5	30
8	MeCN / Water (1:3)	2	4	1.3	100	8	58

[a] Reaction conditions: 1-iodo-4-nitrobenzene (0.78 mmol, 1 equiv.), phenylboronic acid (1.16 mmol, 1.5 equiv.), base (1.56 mmol, 2 equiv.). [b] Isolated yields. [c] A dichloromethane stock solution was employed to load the $Pd(OAc)_2$ catalyst, with the dichloromethane removed *in vacuo* prior to the addition of other substrates.

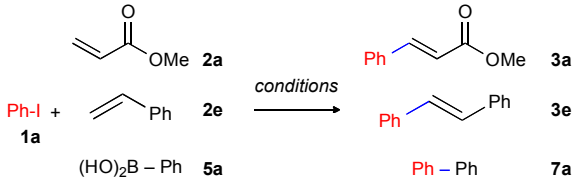
Table S2. Development of the sugar-derived PdNP-catalysed cross-coupling reactions and substrate evaluation



Entry	X	S.M.	Solvent	Glucose (mol %)	Base (equiv.)	Product	Yield[b] (%)
1	I	**B**	MeCN / Water (1:3)	4	Et_3N (1.3)	**E**	97
2	Br	**B**	MeCN / Water (1:3)	4	Et_3N (1.3)	**E**	8
3	Cl	**B**	MeCN / Water (1:3)	4	Et_3N (1.3)	**E**	2
4	I	**C**	MeCN / Water (1:3)	4	Et_3N (1.3)	**F**	90
5	Br	**C**	MeCN / Water (1:3)	4	Et_3N (1.3)	**F**	5
6	I	**D**	DMF / Water (10:1)	10	Cs_2CO_3 (2.0)	**G**	98
7	Br	**D**	DMF / Water (10:1)	10	Cs_2CO_3 (2.0)	**G**	98
8	Cl	**D**	DMF / Water (10:1)	10	Cs_2CO_3 (2.0)	**G**	0

[a] Reaction conditions: 1-iodo-4-nitrobenzene (0.78 mmol, 1 equiv.), phenylboronic acid (1.16 mmol, 1.5 equiv.), base (1.56 mmol, 2 equiv.). [b] Isolated yields. [c] A dichloromethane stock solution was employed to load the $Pd(OAc)_2$ catalyst, with the dichloromethane removed *in vacuo* prior to the addition of other substrates.

Table S3. Comparison of recyclable Pd-catalysed cross-coupling reactions using bio-derived supports and derivatives



Entry	Pd Catalyst Formation / Isolation time[a] / processes[b]	Pd Catalyst (mol %)	Cross-Coupling Conditions	Product	Yield (%)	Ref.
1	31 h / 12 steps	0.1	Et_3N, 80 °C, 6 h	**3a**	93	[17]
2	76 h / 10 steps	0.1	PS-TEA[c], CH_3CN:H_2O, 130 ºC, 2 h	**3a**	74	[18]
3	80.5 h / 9 steps	1.0	K_2CO_3, H_2O, 100 °C, 2 h	**3e**	99	[19]
4	18.5 h / 7 steps	10	NaOAc, MeCN:H_2O, 100 ºC, 16 h	**3e**	87	[20]
5	336 h / 19 steps	0.01	K_3PO_4, H_2O:EtOH, 80 °C, 18 h	**7a**	89	[21]
6	88.5 h / 9 steps	0.9	K_2CO_3, MeOH, 100 °C, 22 h[c]	**7a**	86	[22]
7	224.5 h / 10 steps	0.5	K_2CO_3, H_2O:EtOH, 60 °C, 0.25 h	**7a**	99	[23]
8	51 h / 8 steps	0.5	K_2CO_3, xylene, 143 °C, 1 h	**7a**	85	[24]
9	30 h / 11 steps	0.2	K_2CO_3, H_2O:DMF, 90 °C, 1.5 h	**7a**	95	[25]

[a] Times were approximated from published experimental conditions and do not include work-up or isolation procedures for which no times were reported.

[b] The number of processes was calculated based on the sum of the chemical transformation(s), isolation(s) and purification(s).

[c] Chlorobenzene was used

VII. References

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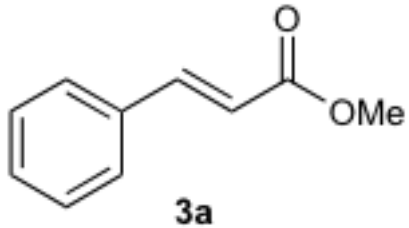
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3a

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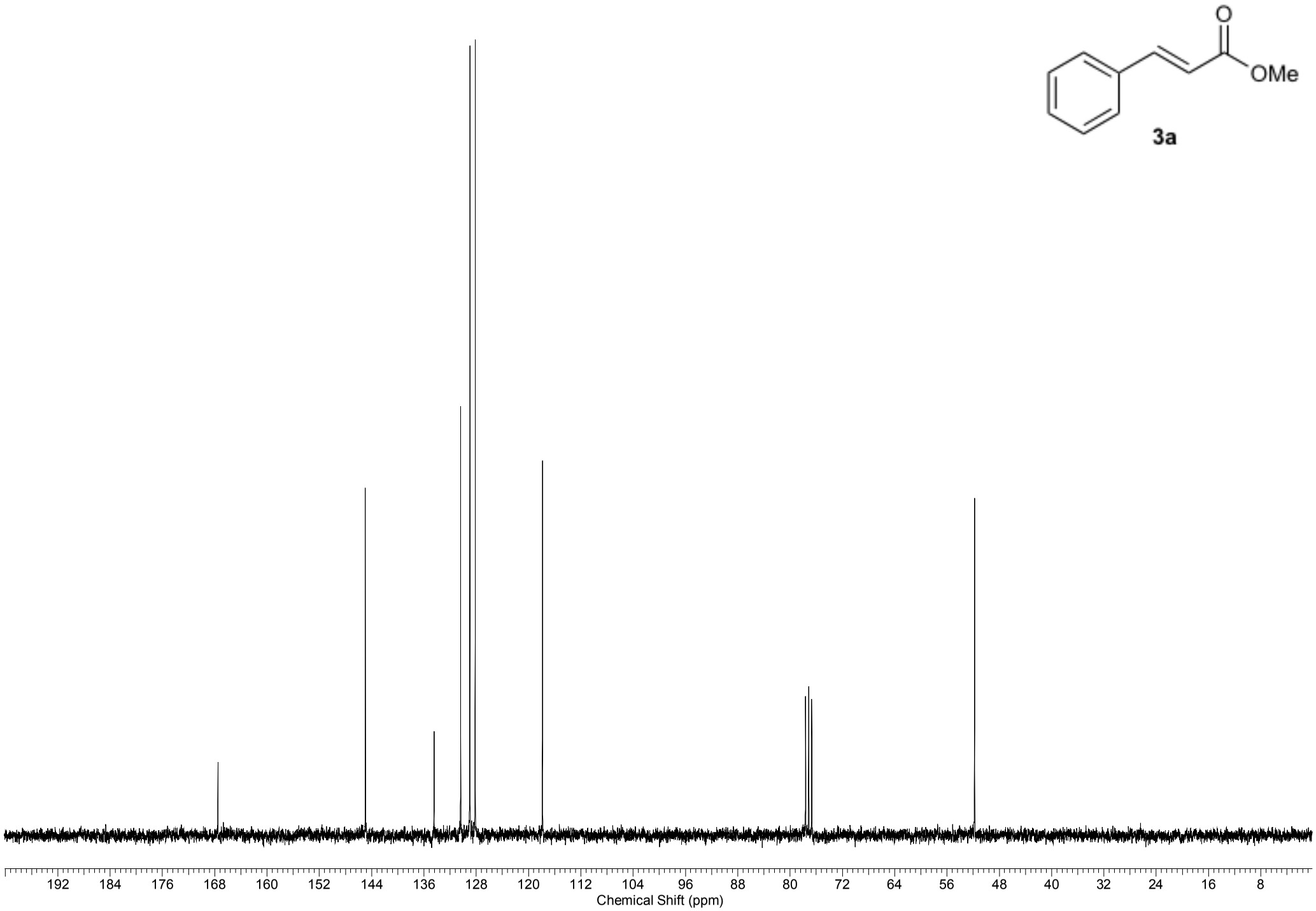
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3a
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152
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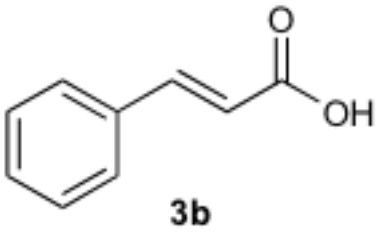
48
40
32
24
16
8
Chemical Shift (ppm)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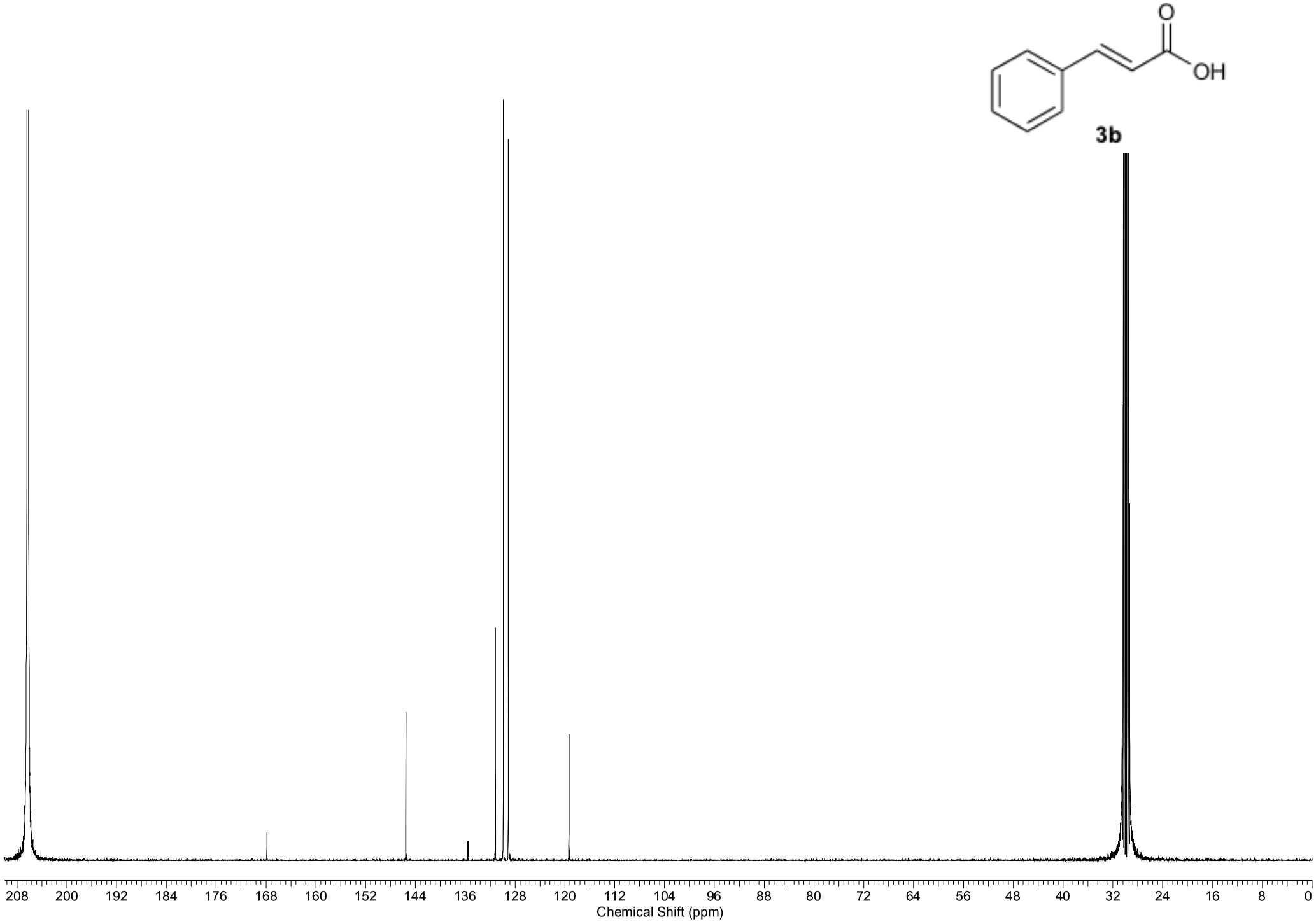
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3b
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40
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24
16
8
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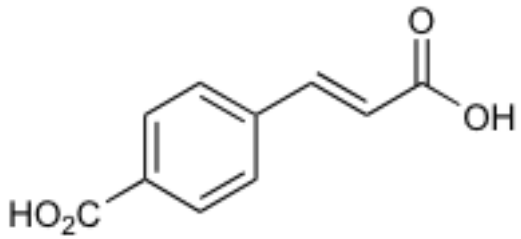
Chemical Shift (ppm)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HO2C

3c

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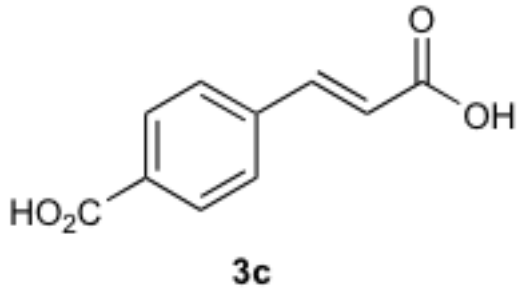
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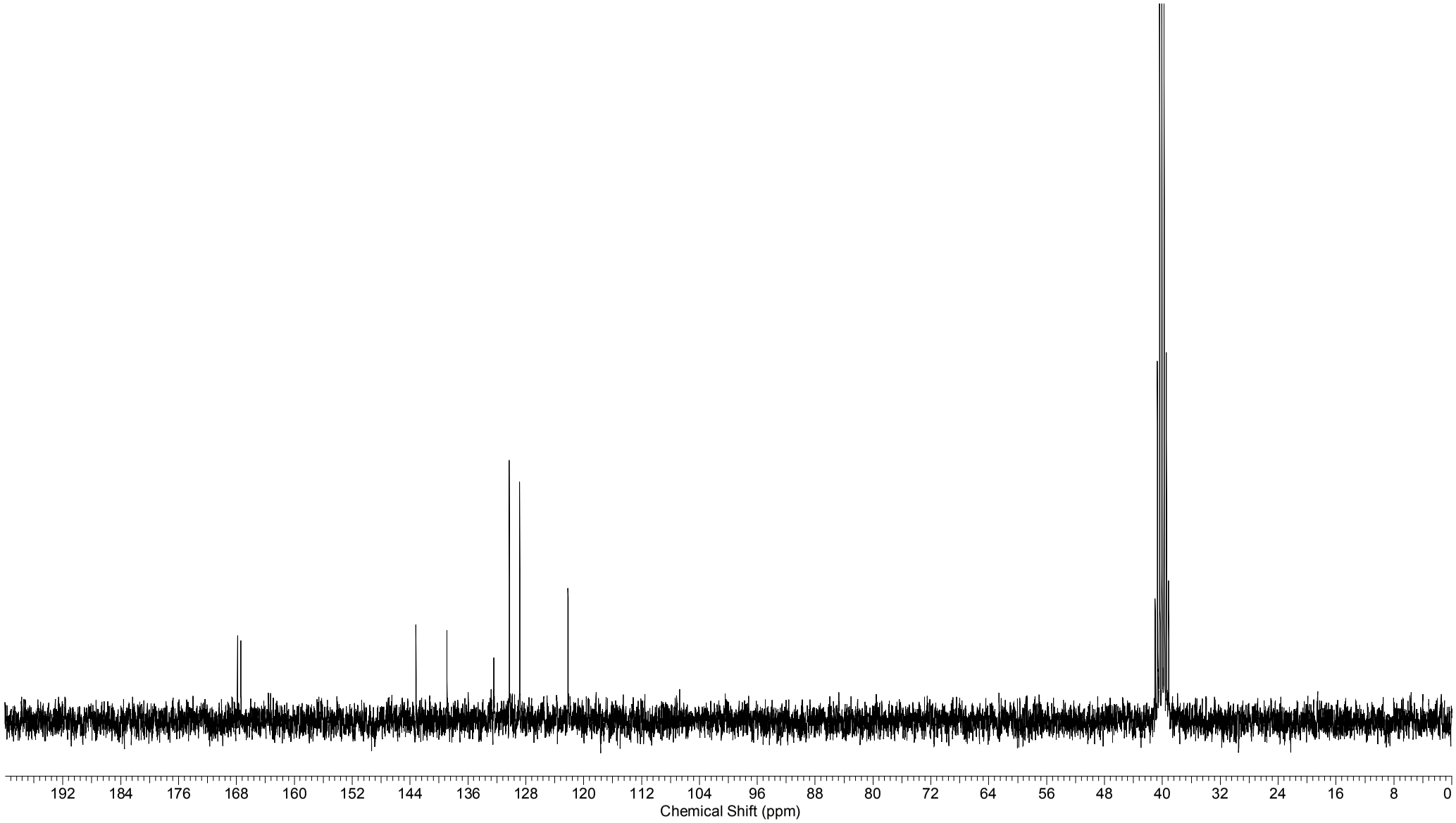
HO2C

3c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32
24
16
8
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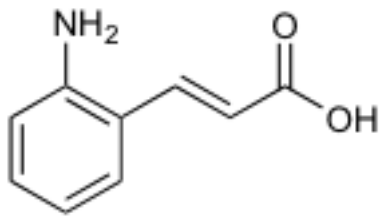
Chemical Shift (ppm)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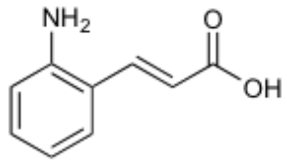

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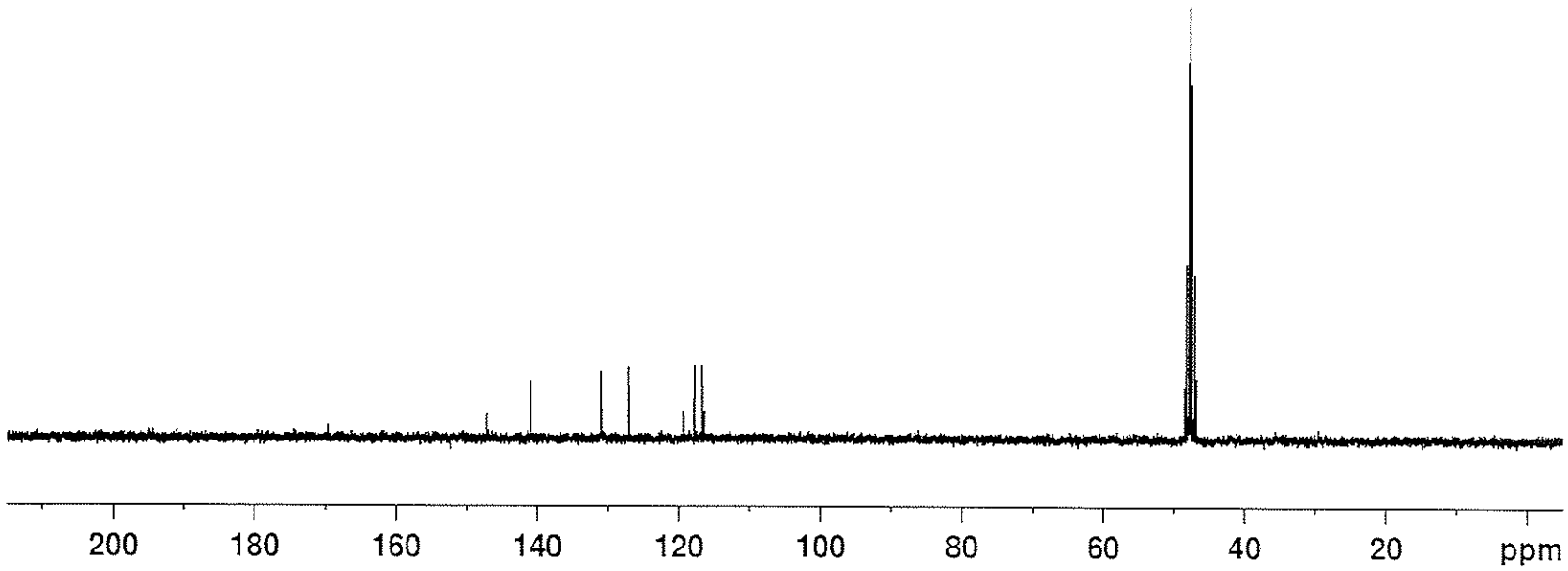

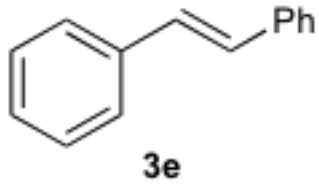
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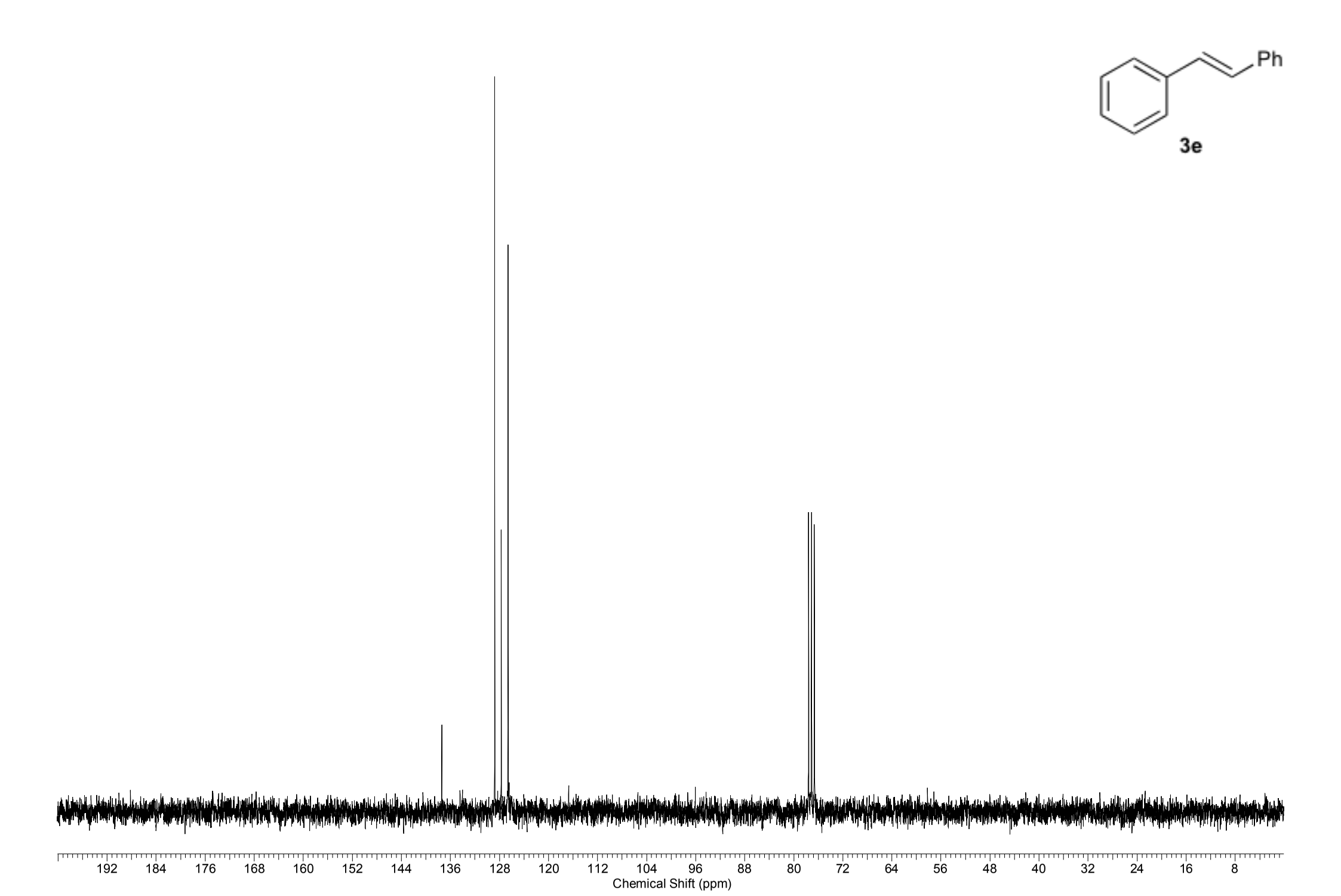
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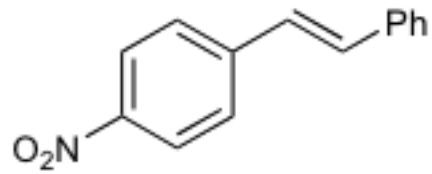
40
32
24
16
8
Chemical Shift (ppm)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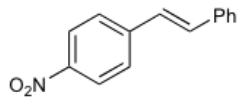
2.5
Chemical Shift (ppm)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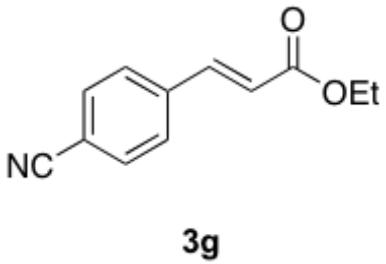

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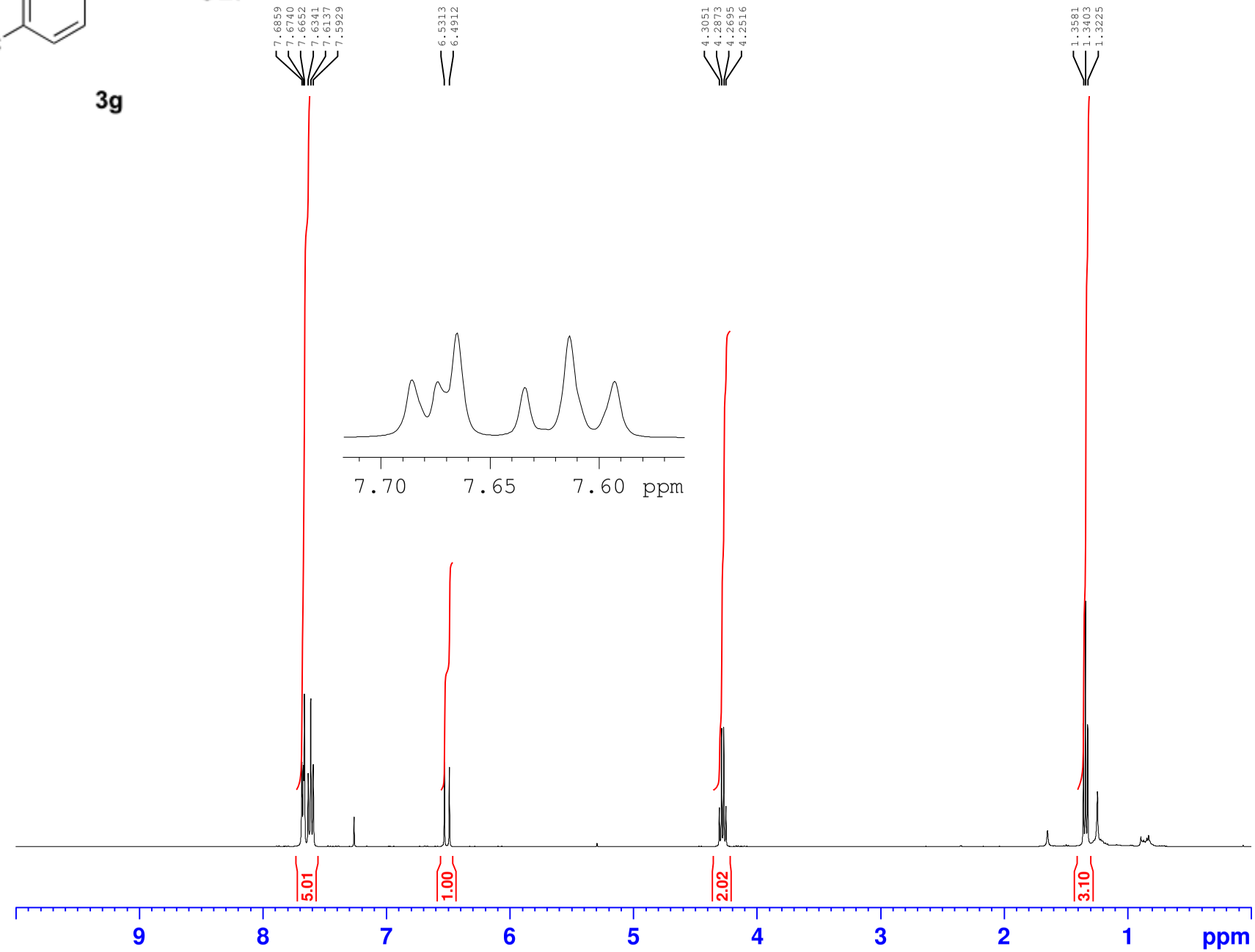


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TE                293.7 K
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TD0                    1

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F2 - Processing parameters
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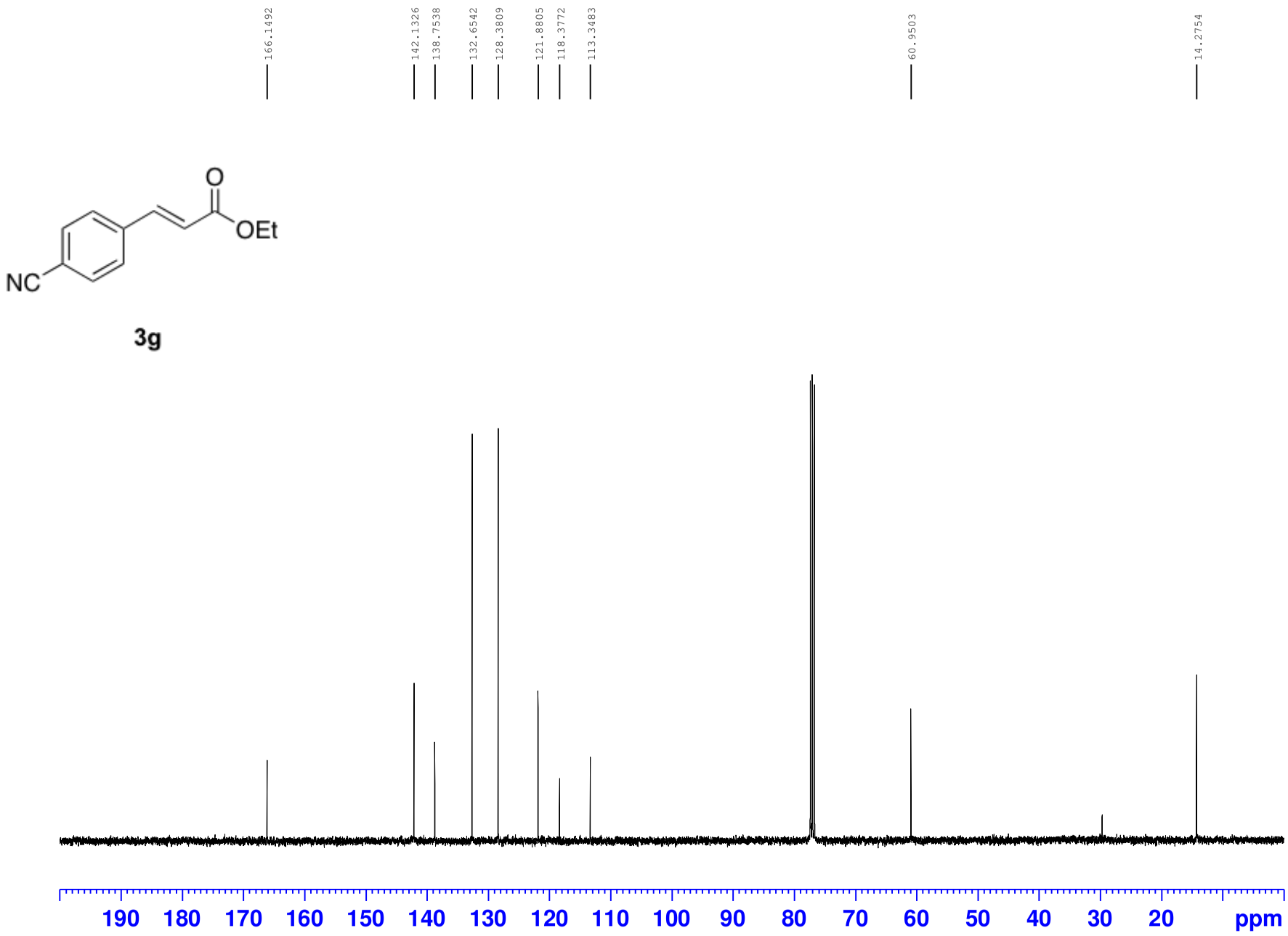

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PLW13         0.14229999 W

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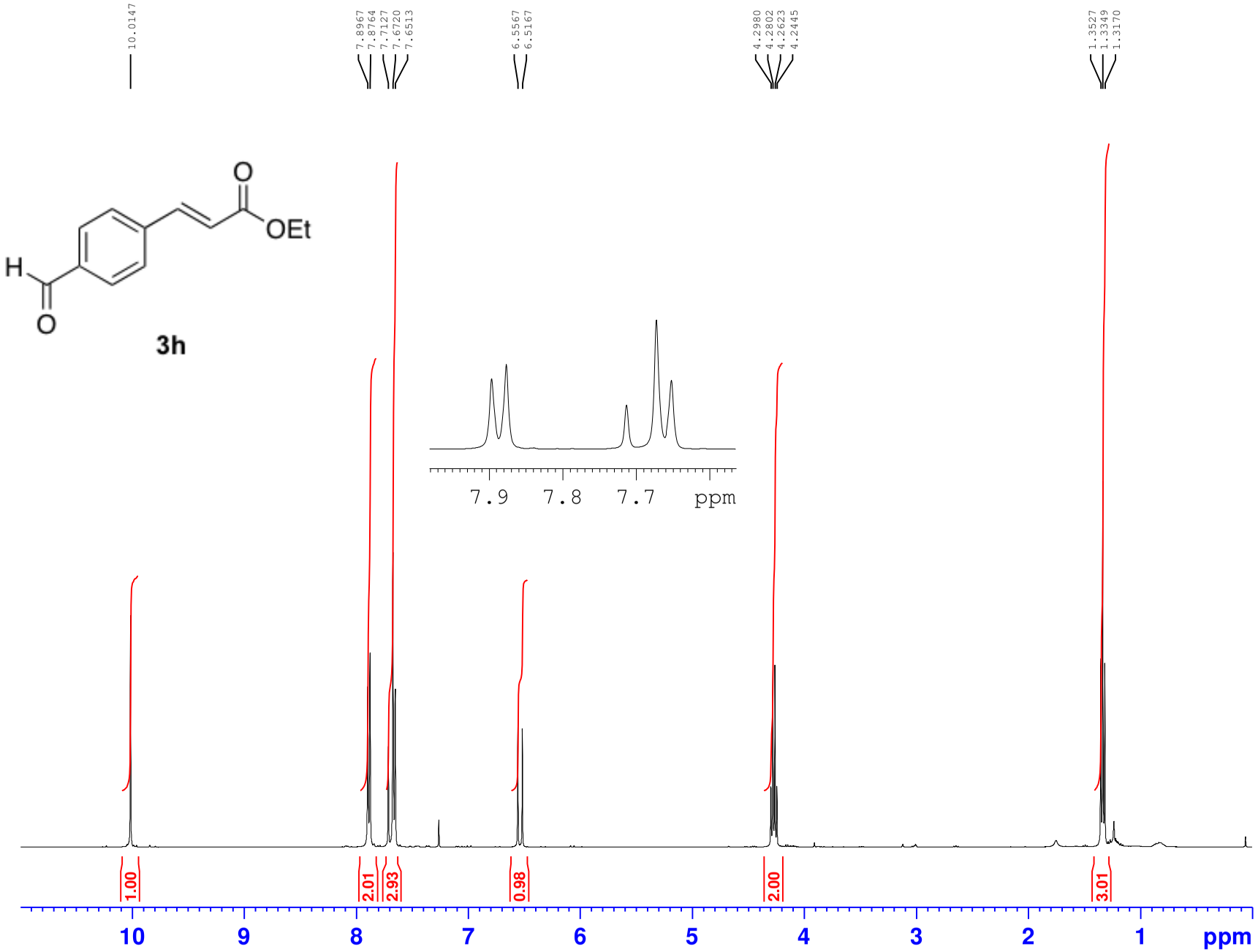

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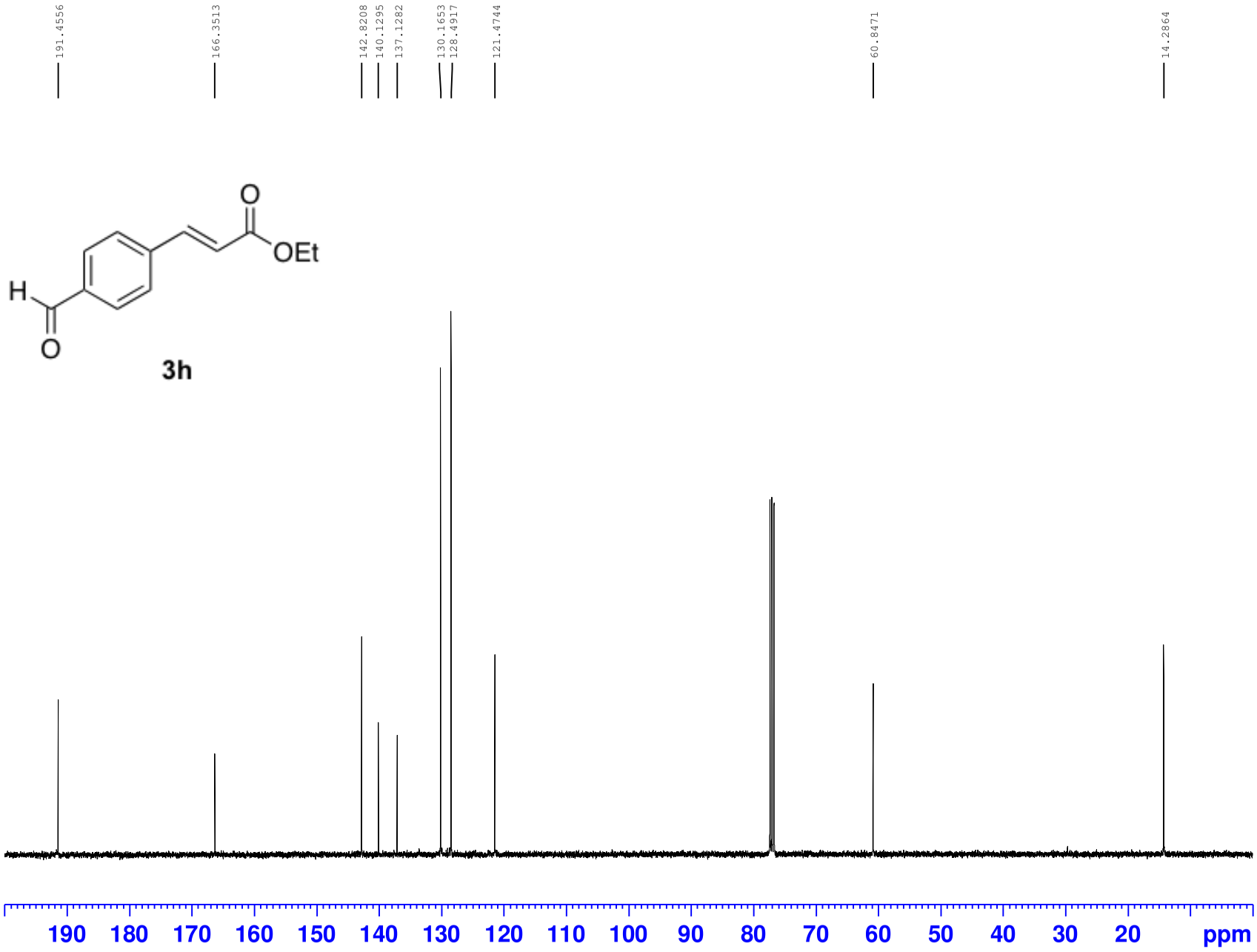

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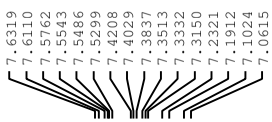

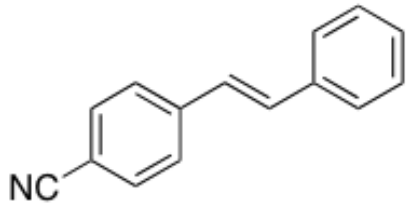

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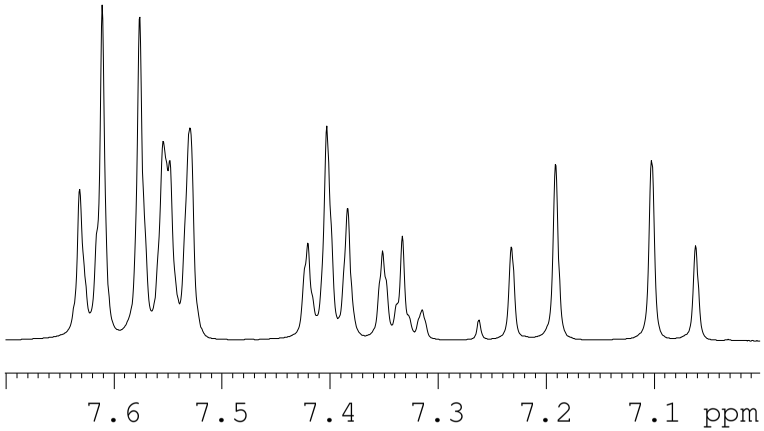

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TE                     293.9 K
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PC                      1.50
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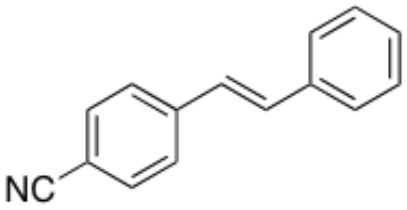
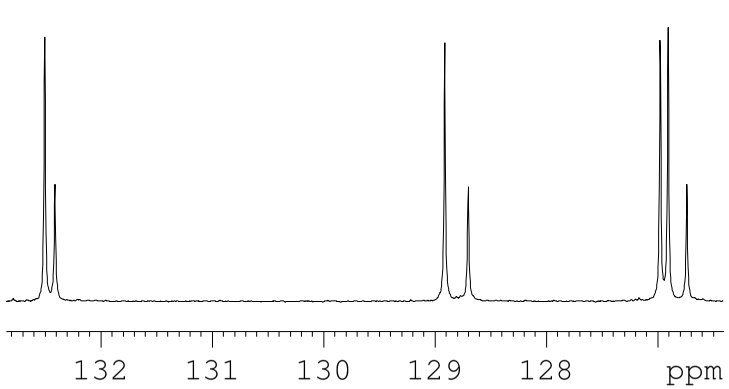


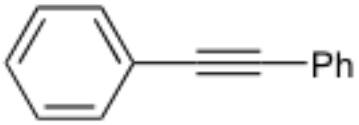
3i

141.8392
136.3091
132.5030
132.4116
128.9078
128.6969
126.9714
126.9000
126.7323
119.1033
110.5587

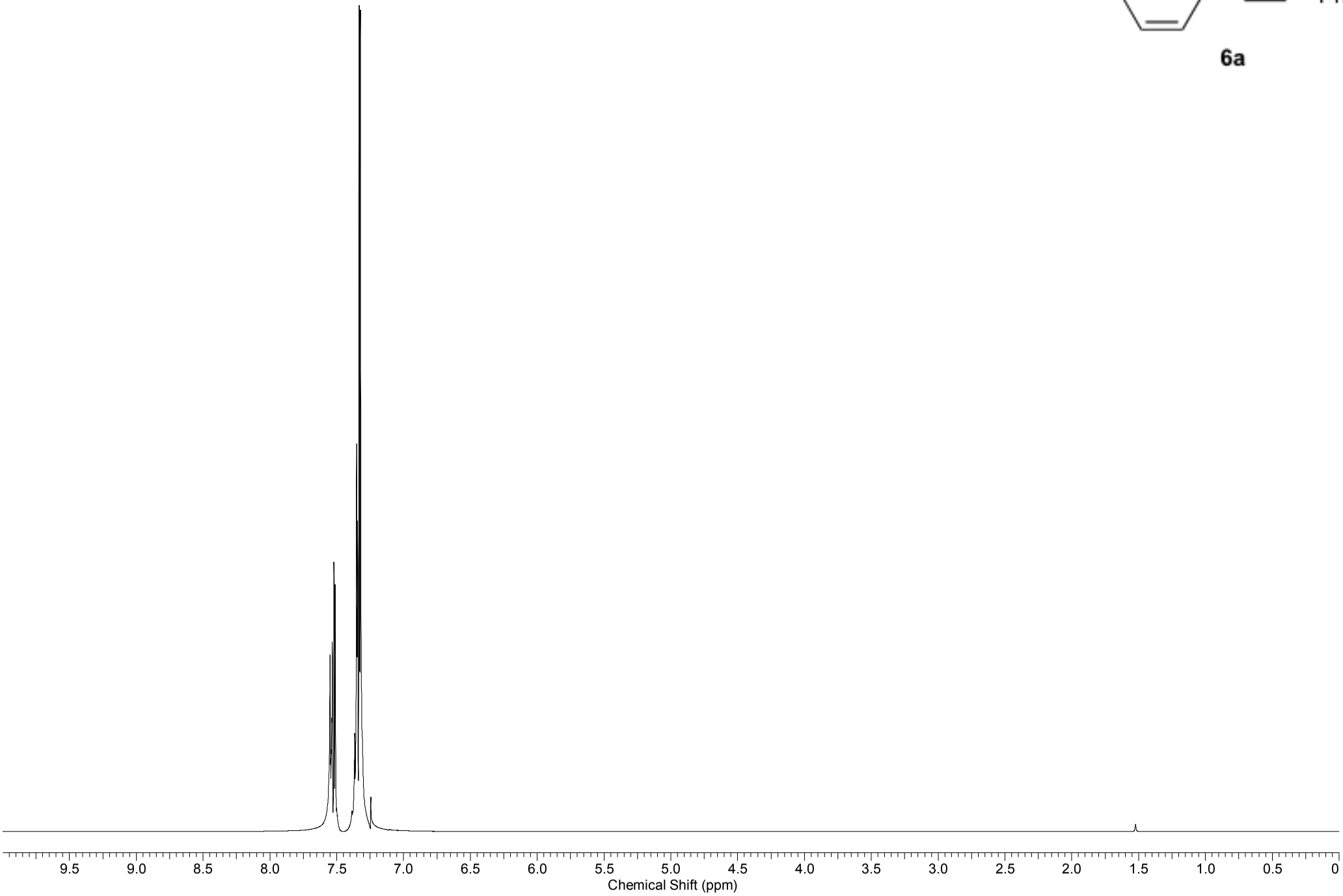


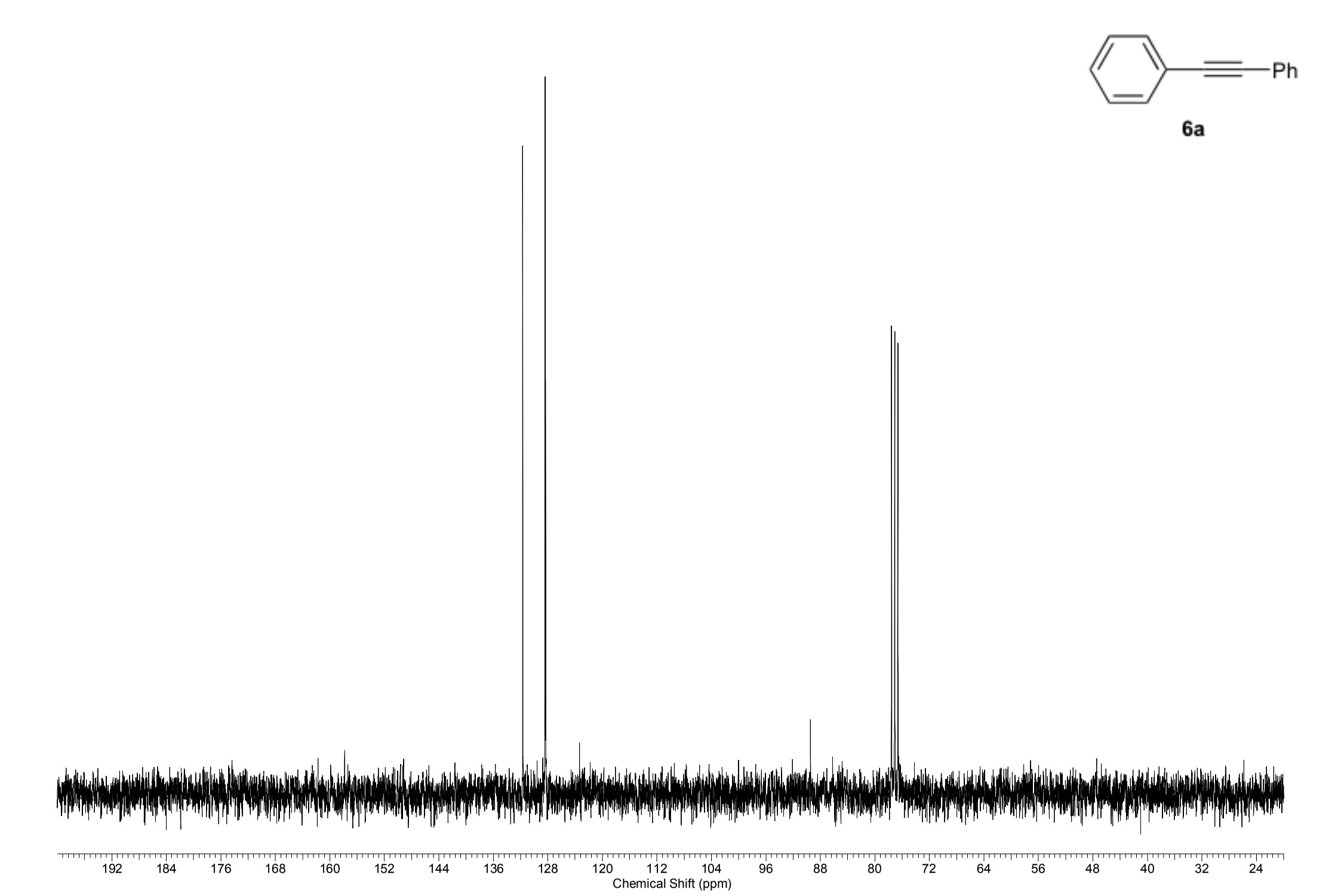
University of HUDDERSFIELD

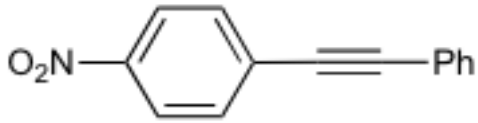
```
Current Data Parameters
NAME            TW 1-009
EXPNO                 11
PROCNO                 1

F2 - Acquisition Parameters
Date_           20151119
Time                2.23
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   256
DS                     4
SWH            24038.461 Hz
FIDRES          0.366798 Hz
AQ             1.3631488 sec
RG                181.72
DW                20.800 usec
DE                 8.18 usec
TE                294.3 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1          100.6228303 MHz
NUC1                 13C
P1                  9.00 usec
PLW1          77.00000000 W

======== CHANNEL f2 ========
SFO2          400.1316005 MHz
NUC2                 1H
CPDPRG[2          waltz16
PCPD2               90.00 usec
PLW2          24.00000000 W
PLW12          0.17567000 W
PLW13          0.14229999 W

F2 - Processing parameters
SI                 65536
SF            100.6127690 MHz
WDW                  EM
SSB       0
LB                1.00 Hz
GB        0
PC                1.40
```


Ph

6a

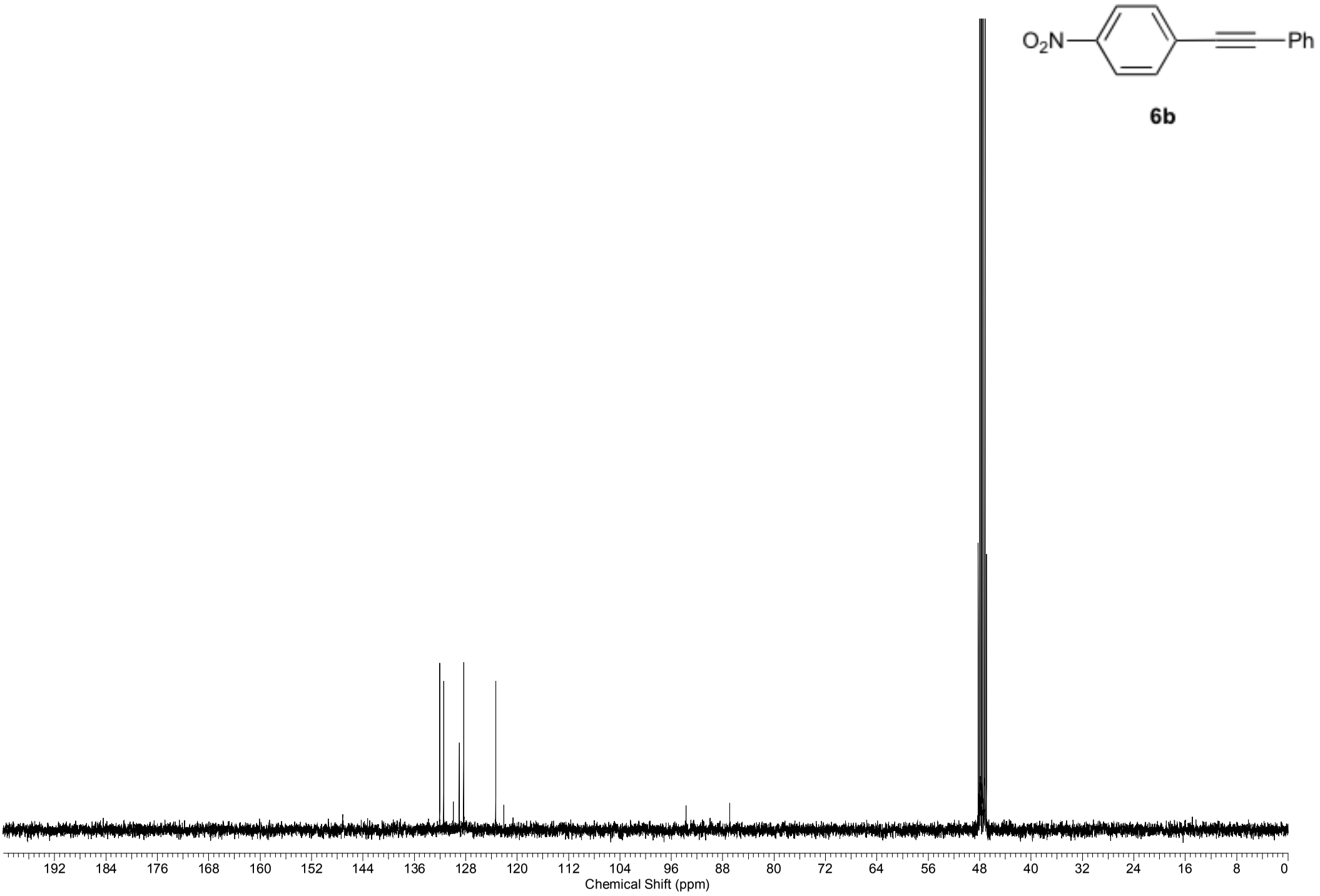

9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

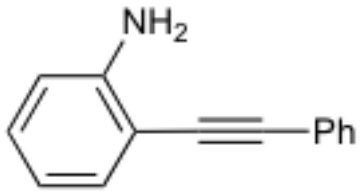

Ph
6a
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
Chemical Shift (ppm)


O2N
Ph

6b

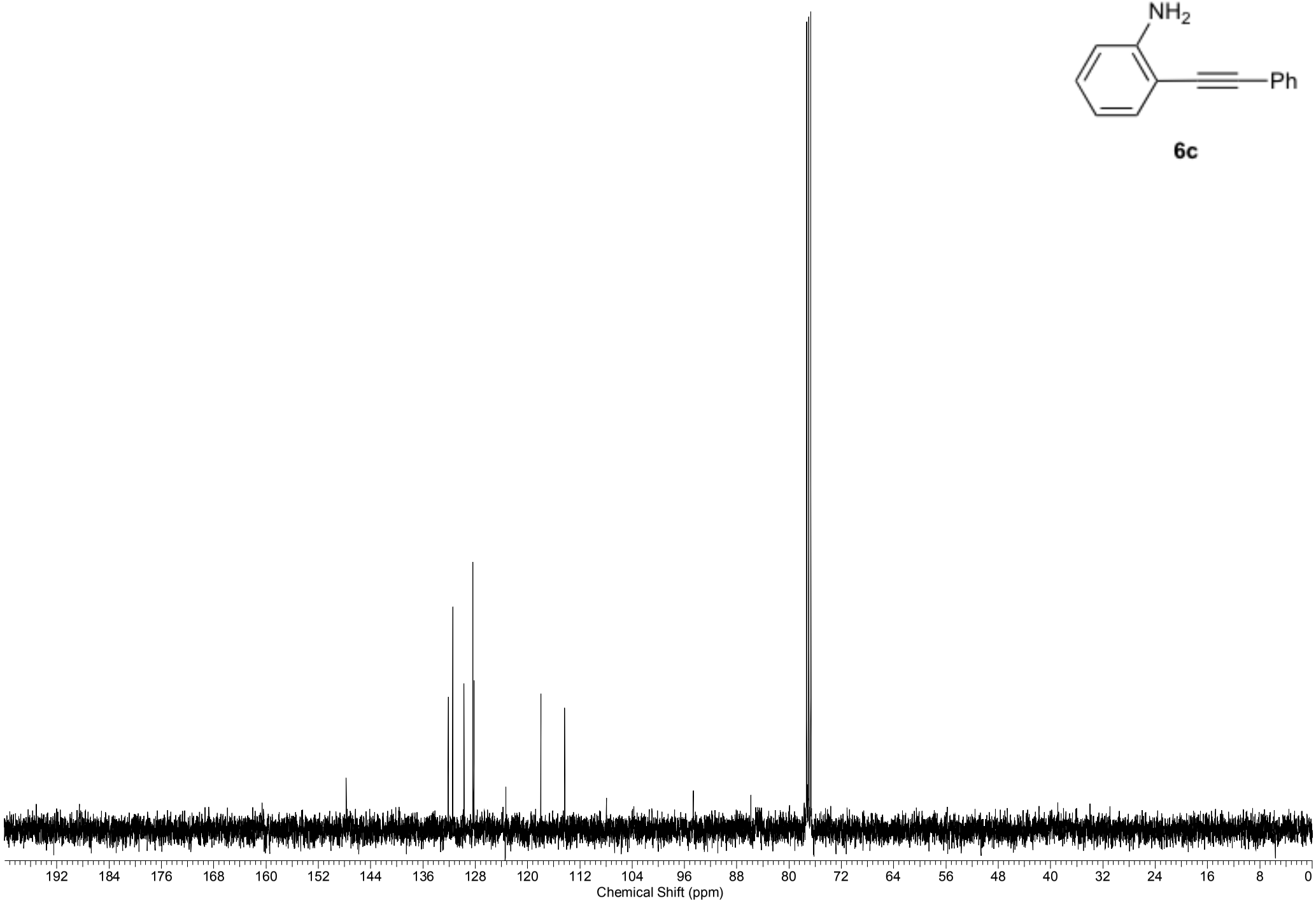
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

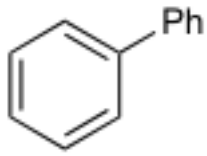

O2N
Ph
6b
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)


NH2
Ph

6c

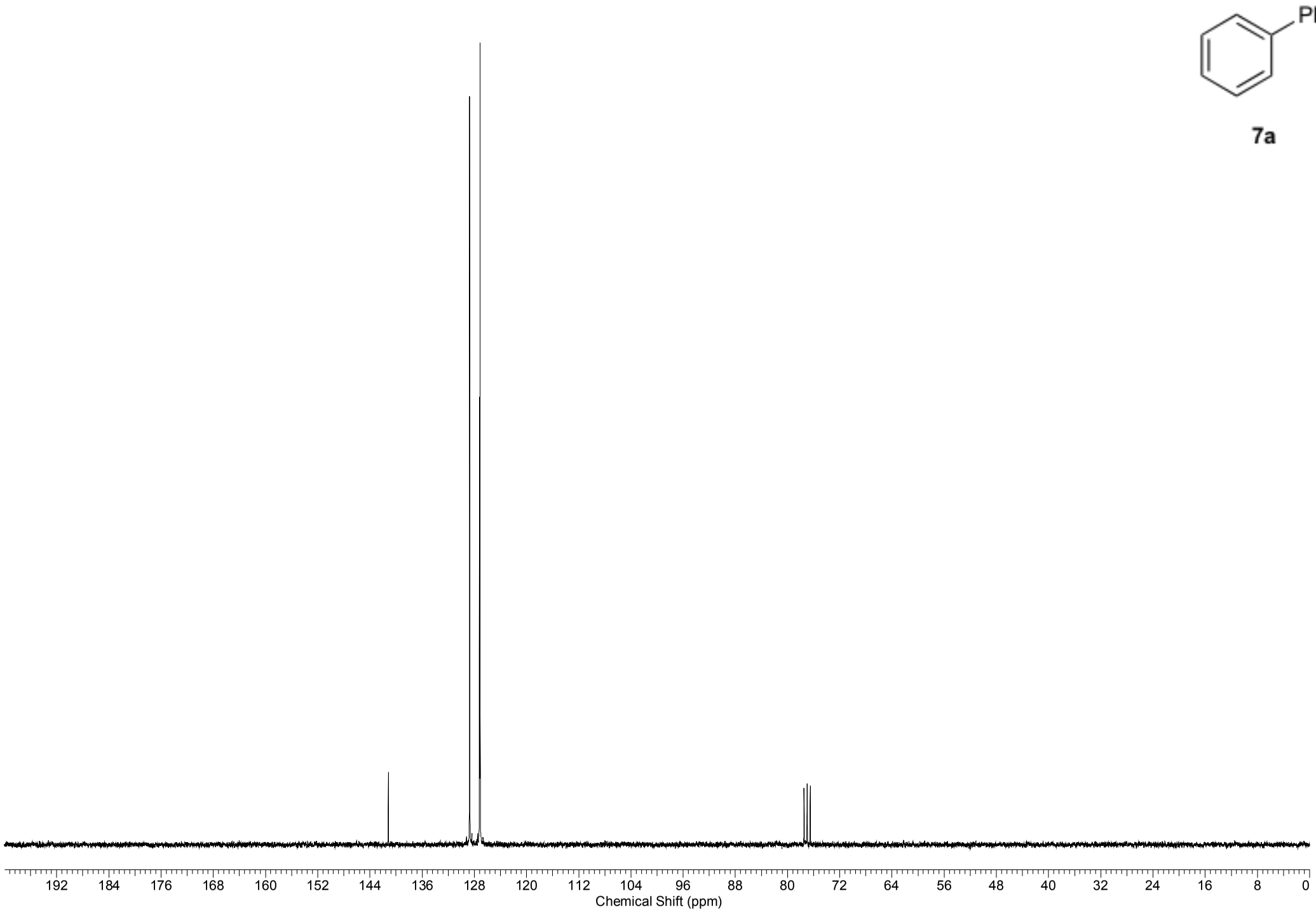
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

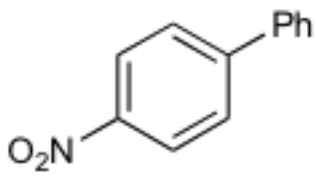

NH2
Ph
6c
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)


Ph

7a

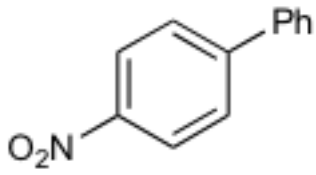
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)


Ph
7a
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)


Ph
O2N

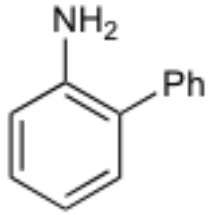
7b

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
Chemical Shift (ppm)


Ph
O2N

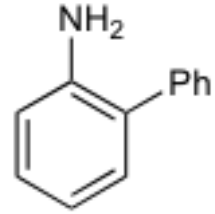
7b

192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)


NH2
Ph

7c

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
Chemical Shift (ppm)

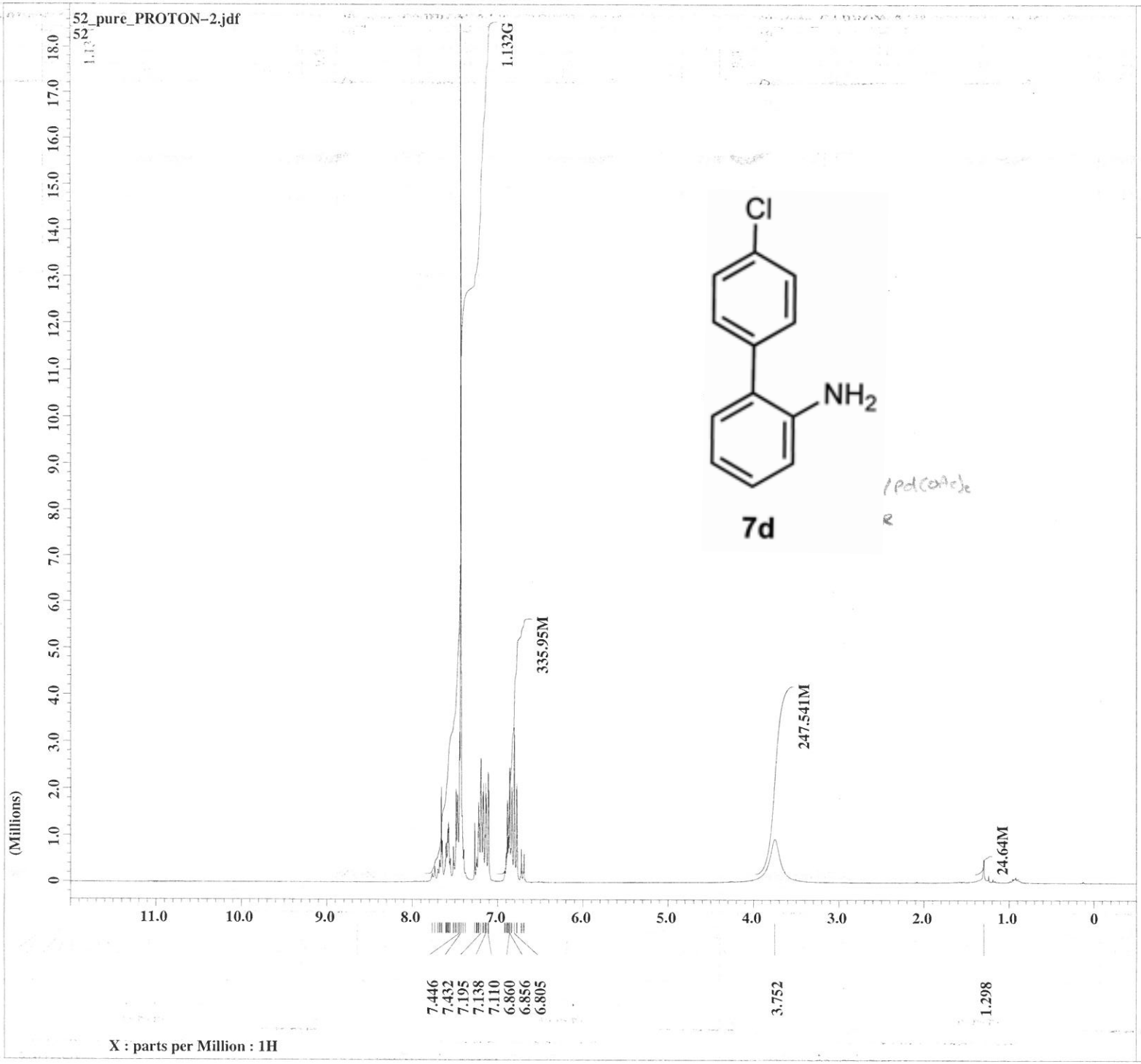


7c

192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24

Chemical Shift (ppm)

(52) Final



7d

1Pd(OAc)2

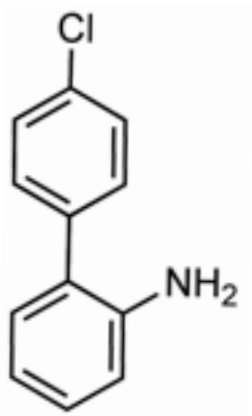
R

JEOL

Filename	= 52_pure_PROTON-2.jdf
Author	= delta
Experiment	= single_pulse.exp
Sample_id	= jcamp/r_smi/52_pure
Solvent	= CHLOROFORM-D
Creation_time	= 24-FEB-2012 15:06:01
Revision_time	= 24-FEB-2012 15:01:28
Current_time	= 24-FEB-2012 15:01:28
Content	= 52
Data_format	= 1D COMPLEX
Dim_size	= 29491
Dim_title	= 1H
Dim_units	= [ppm]
Dimensions	= X
Site	= EX 270
Spectrometer	= DELTA_NMR
Field_strength	= 6.345446[T] (270[MHz]
X_acq_duration	= 3.6306944[s]
X_domain	= 1H
X_freq	= 270.16608844[MHz]
X_offset	= 5[ppm]
X_points	= 16384
X_prescans	= 0
X_resolution	= 0.27542941[Hz]
X_sweep	= 4.51263538[kHz]
Clipped	= FALSE
Mod_return	= 1
Scans	= 16
Total_scans	= 16
X_90_width	= 9.8[us]
X_acq_time	= 3.6306944[s]
X_angle	= 45[deg]
X_pulse	= 4.9[us]
Initial_wait	= 1[s]
Phase_preset	= 3[us]
Recvr_gain	= 19
Relaxation_delay	= 1[s]
Temp_get	= 21.1[dC]
Unblank_time	= 2[us]

(52) final

52_pure_CARBON-2.jdf
52



7d

(Millions)

10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0

190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0

130.567
130.453
129.101
128.948
128.337
118.916
115.868

77.630
77.164
76.691

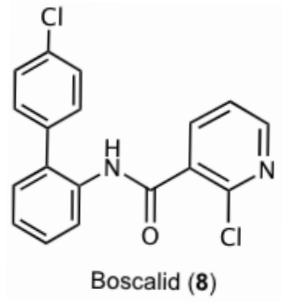
X : parts per Million : 13C

JEOL

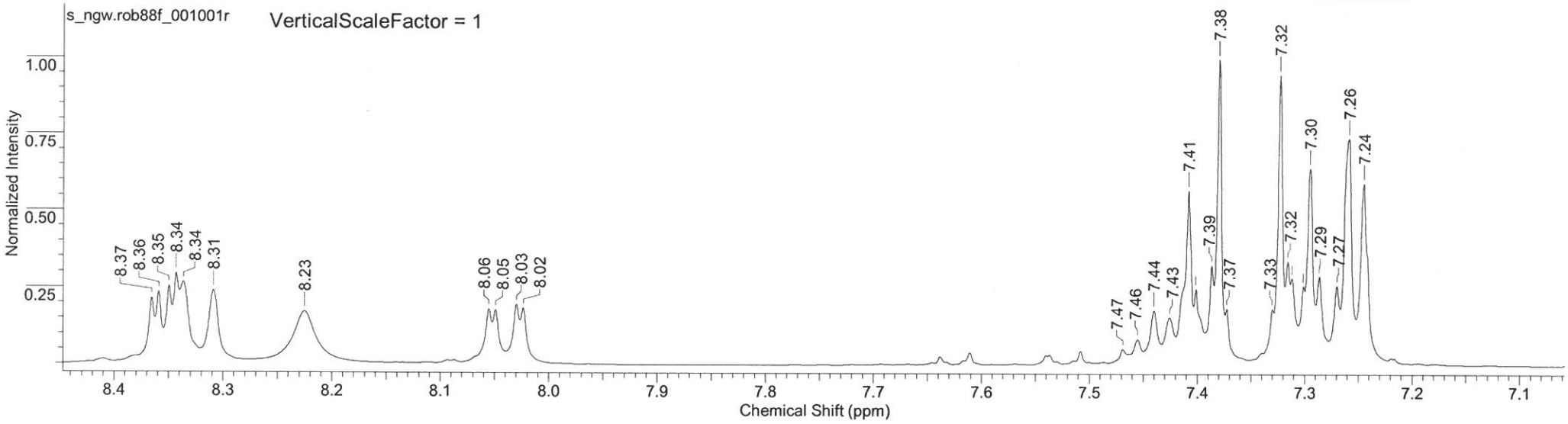
Filename	= 52_pure_CARBON-2.jdf
Author	= delta
Experiment	= single_pulse_dec
Sample_id	= jcamp/r_smi/52_pure
Solvent	= CHLOROFORM-D
Creation_time	= 24-FEB-2012 15:11:00
Revision_time	= 24-FEB-2012 15:06:26
Current_time	= 24-FEB-2012 15:06:26
Content	= 52
Data_format	= 1D COMPLEX
Dim_size	= 32768
Dim_title	= 13C
Dim_units	= [ppm]
Dimensions	= X
Site	= EX 270
Spectrometer	= DELTA_NMR
Field_strength	= 6.345446[T] (270[MHz]
X_acq_duration	= 0.9633792[s]
X_domain	= 13C
X_freq	= 67.93330993[MHz]
X_offset	= 100[ppm]
X_points	= 16384
X_prescans	= 0
X_resolution	= 1.03801286[Hz]
X_sweep	= 17.00680272[kHz]
Irr_domain	= 1H
Irr_freq	= 270.16608844[MHz]
Irr_offset	= 5[ppm]
Clipped	= FALSE
Mod_return	= 4
Scans	= 128
Total_scans	= 128
X_90_width	= 10[us]
X_acq_time	= 0.9633792[s]
X_angle	= 45[deg]
X_pulse	= 5[us]
Initial_wait	= 1[s]
Phase_preset	= 3[us]
Recvr_gain	= 30
Relaxation_delay	= 1[s]
Temp_get	= 21.9[dC]
Unblank_time	= 2[us]

Formula $C_{18}H_{12}Cl_2N_2O$	**FW**	343.2067	

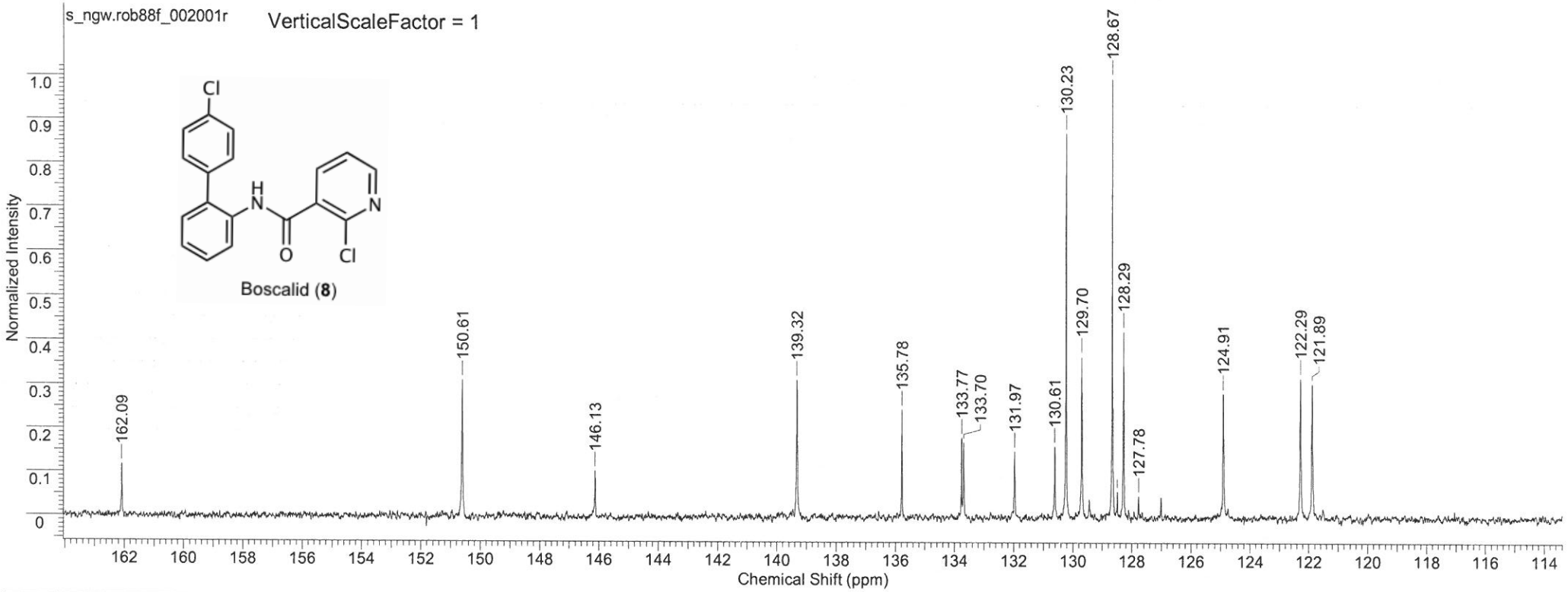
Acquisition Time (sec)	5.3084	**Comment**	Slot No. 40 Sample ID rob88f SupervisorID jcamp Lab Phone No. 14190 UserID s_ngw				
Date	27 Apr 2012 13:46:08			**Date Stamp**	27 Apr 2012 13:46:08		
File Name	\\brukdpx300\nmr_data\s_ngw\nmr\s_ngw.rob88f\1\pdata\1\1r			**Frequency (MHz)**	300.13	**Nucleus**	1H
Number of Transients	16	**Origin**	dpx300	**Original Points Count**	32768	**Owner**	nmruser
Points Count	65536	**Pulse Sequence**	zg30	**Receiver Gain**	64.00	**SW(cyclical) (Hz)**	6172.84
Solvent	CHLOROFORM-d	**Spectrum Offset (Hz)**	1848.2770	**Spectrum Type**	STANDARD	**Sweep Width (Hz)**	6172.75
Temperature (degree C)	25.000						



Boscalid (**8**)



Acquisition Time (sec)	0.8700	***Comment***	Slot No. 40 Sample ID rob88f SupervisorID jcamp Lab Phone No. 14190 UserID s_ngw				
Date	27 Apr 2012 13:52:32			***Date Stamp***	27 Apr 2012 13:52:32		
File Name	\\brukdpx300\nmr_data\s_ngw\nmr\s_ngw.rob88f\2\pdata\1\1r			***Frequency (MHz)***	75.47	***Nucleus***	13C
Number of Transients	128	***Origin***	dpx300	***Original Points Count***	16384	***Owner***	nmruser
Points Count	32768	***Pulse Sequence***	zgpg30	***Receiver Gain***	1448.20	***SW(cyclical) (Hz)***	18832.39
Solvent	CHLOROFORM-d	***Spectrum Offset (Hz)***	8259.0322	***Spectrum Type***	STANDARD	***Sweep Width (Hz)***	18831.82
Temperature (degree C)	25.000						



No.	(ppm)	(Hz)	Height
1	121.89	9198.4	0.3073
2	122.29	9228.9	0.3203
3	124.91	9426.6	0.2856
4	127.78	9643.2	0.0502
5	128.29	9681.7	0.4256
6	128.50	9697.3	0.0598
7	128.67	9710.5	1.0000
8	129.70	9788.1	0.3685
9	130.23	9828.3	0.8752
10	130.61	9857.0	0.1630
11	131.97	9959.3	0.1522