Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information

Relative Rates of Alkylation for B-Substituted Triarylphosphines: An ortho-Boron Group Enhances Reactivity on Phosphorus

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General Information

Reaction setup and reagent synthesis: All reactions were carried out under a nitrogen atmosphere in flame-dried glassware using standard Schlenk techniques unless otherwise stated. All other reagents were purchased from commercial sources and were used without purification unless otherwise noted. Triarylphosphines **1-5** have been previously reported in the literature[1-5] and fully matched previous characterization. Triarylphosphine**s 6, 7, and 8** are commercially available and were used without further purification. Benzyltriphenylphosphonium bromide is commercially available. Salts **1a-8a** have not been previously reported and characterization is provided below.

Solvents: Toluene was purified using a GlassContour solvent purification system purchased from Pure Process Technologies. Deuterated chloroform was purchased from Cambridge Isotope Laboratories and used without further purification but was stored over activated 4 Å molecular sieves (beads).

Chromatography: Analytical thin layer chromatography (TLC) was performed on SiliaPlate glass backed silica gel plates (250 μm thickness, 60 Å, F-254 indicator) purchased from Silicycle and visualized using ultraviolet light (254 and 200 nm) and stained with $KMNO_4$, *p*-anisaldehyde, cerium molybdate, ceric ammonium nitrate, vanillin, or ninhydrin made following reported recipes.[6] Flash column chromatography was performed with SiliaFlash silica gel 60 Å, 230–400 mesh (40–63 μm) purchased from Silicycle according to the literature procedure.[7]

Melting points: All melting points were measured on powdered solids using a Mel-Temp II capillary melting point device and are uncorrected unless otherwise stated.

Nuclear Magnetic Resonance Characterization: ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AV Neo-600 (equipped with a CryoQNP probe) or Bruker AV III-600 MHz spectrometer (150 MHz for ^{13}C NMR) for characterization. ^{1}H NMR spectra for kinetic studies were recorded on a Bruker AV III-500 spectrometer. ^{31}P NMR spectra were recorded on a Bruker AV Neo-600 (equipped with a CryoQNP probe) spectrometer (243 MHz for ^{31}P NMR) for characterization and a Bruker AV III NanoBay-400 for kinetic studies (162 MHz for ^{31}P NMR). ^{11}B spectra were recorded on a Bruker AV III NanoBay-400 (128 MHz for ^{11}B NMR) in borosilicate NMR tubes at high sample concentrations (~50-70 mg in 500 µL solvent). All spectra were recorded in deuterated chloroform ($CDCl_3$) with residual chloroform (δ = 7.26 ppm for ^{1}H NMR and 77.16 for ^{13}C NMR) as the internal standard and are reported in parts per million (ppm). Abbreviations for the signal couplings are as follows: s, singlet; d, doublet; t, triplet; q, quartet; quin, quintet; sex, sextet; sept; septet; and m, multiplet. Coupling constants were taken from the spectra directly and are uncorrected. Phosphorus-Carbon coupling constants are reported with corresponding bond distances.[8] Yields refer to isolated yields of compounds estimated to be ≥ 95% pure as determined by ^{1}H NMR analysis unless otherwise noted.

Infrared Spectroscopy Characterization: Infrared (IR) spectra were collected on a Thermo Scientific Nicolet iS 5 FT-IR. Compounds were analyzed as solids on the diamond surface. Spectra are reported in frequency of absorption in cm^{-1}. Only selected references are reported.

Mass spectrometry: High-resolution mass spectra (HRMS) determinations were performed by the mass spectrometry core at the University of North Carolina at Chapel Hill. Samples were analyzed with a Q Exactive HF-X (ThermoFisher, Bremen, Germany) mass spectrometer for APCI and ESI.

General procedures for synthesis of starting materials

A. General procedure for the synthesis of phosphonium salts 2a-2l:

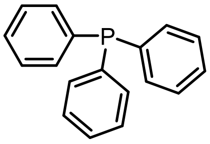
Triarylphosphine (1.00 equiv) toluene (0.10 M) and a stir bar were added to a 50 mL two-necked round bottom fitted with a water-cooled reflux condenser. Benzyl bromide (1.6 equiv) was added, and the solution was heated and allowed to reflux overnight. The reaction was cooled to room temperature and the solid was filtered, washed with dry toluene (3 x 10.0 mL) and dried under vacuum.

B. General procedure for ^{1}H NMR Studies

To an oven-dried, one dram vial was added the triarylphosphine (7.0 mmol) and deuterated chloroform (0.450 mL). This solution was added to a clean, oven-dried NMR tube. To a second oven-dried, one dram vial was added mesitylene (65 µL) and deuterated chloroform (1.0 mL). An aliquot (0.150 mL, 1.00 equiv) of the mesitylene stock solution was added to the NMR tube. To a third oven-dried, one dram vial was added benzyl bromide (83 µL) and deuterated chloroform (1.0 mL). This was set aside until the ^{1}H NMR experiment was set up.

An initial ^{1}H NMR was taken on the NMR tube containing the triarylphosphine, mesitylene, and deuterated chloroform on a 500 MHz NMR instrument. The internal temperature of the NMR instrument was 23 °C. After confirming the shifts for the starting materials, an aliquot (0.100 mL, 1.00 equiv) of the benzyl bromide solution was added directly to the NMR tube, and a stopwatch was simultaneously started. The NMR tube was returned to the instrument, and a fixed ^{1}H NMR interval experiment was set up. Each timepoint was collected as a *new ^{1}H NMR experiment* and is the average of 8 scans (35 second total) with a 10 second delay between experiments. A total of 60 time points were collected. In the tables and graphs that follow, the ^{1}H NMR yields are reported at 45 second intervals. To account for the time between addition of the benzyl bromide solution and the first ^{1}H NMR experiment, the first time point is the time shown on the stopwatch after the first ^{1}H NMR experiment was acquired. The second time point is 45 seconds after the first time point, and every subsequent time point is 45 seconds apart. After full acquisition of the experiments, yields of the phosphonium salts at each time point were determined relative to the 1.00 equiv of mesitylene added to the NMR tube. Graphs of ^{1}H NMR yield versus time were then generated. For the ^{31}P NMR studies, the same fixed interval experiment was set up, but at 50 second intervals (average of 16 scans, 40 seconds total, and a 10 second delay). Triphenylphosphine oxide was used as the internal standard.

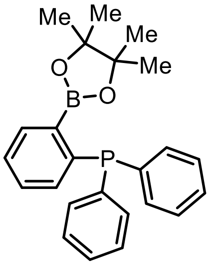
Characterization data for triphenylphosphine and phosphine compounds 1-8



Triphenylphosphine

^{1}H NMR (600 MHz, CDCl$_3$) δ 7.36-7.30 (m, 15 H).

^{31}P NMR (243 MHz, CDCl$_3$) δ -5.5

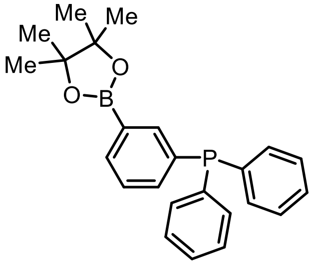


1

Diphenyl[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-phenyl]-phosphine

^{1}H NMR (600 MHz, CDCl$_3$) δ 7.81 (dt, *J* = 6.8, 2.5 Hz, 1H), 7.32-7.29 (m, 10H), 7.28-7.26 (m, 2H), 6.79-6.75 (m, 1H), 1.09 (s, 1H). All shifts are in agreement with the literature values.[1]

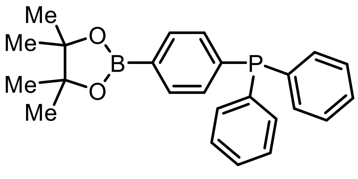
^{31}P NMR (243 MHz, CDCl$_3$) δ -4.2



2

Diphenyl[3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-phenyl]-phosphine

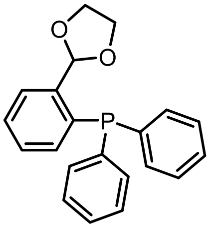
^{1}H NMR (600 MHz, CDCl$_3$) δ 7.99 (d, 1H), 7.79 (dt, *J* = 7.3, 1.3 Hz, 1H), 7.34-7.28 (m, 11H), 7.25-7.23 (m, 1H), 1.32 (s, 12H). All shifts are in agreement with the literature.[2]



3

Diphenyl[4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-phenyl]-phosphine

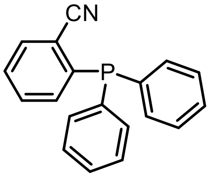
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.76-7.74 (m, 2H), 7.35-7.28 (m, 12H), 1.33 (s, 12H). All shifts are in agreement with the literature.[3]



4

Diphenyl[2-(1,3-dioxolan-2-yl)-phenyl]-phosphine

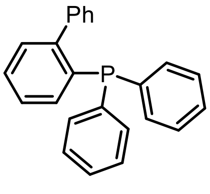
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.70 (dd, *J* = 7.9, 4.0 Hz, 1H), 7.40 (t, *J* = 7.5 Hz, 1 H), 7.34-7.30 (m, 6H), 7.28-7.24 (m, 6H), 6.95 (dd, *J* = 7.9, 4.5 Hz, 1H), 6.43 (d, *J* = 4.9 Hz, 1H), 4.11-4.08 (m, 2H), 3.98-3.94 (m, 2H). All shifts are in agreement with the literature.[4]



5

Diphenyl[2-cyano-phenyl]-phosphine

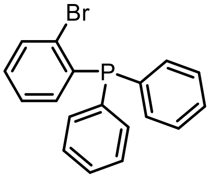
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.73-7.69 (m, 1H), 7.48 (td, *J* = 7.6, 1.5 Hz, 1 H), 7.42 (dd, *J* = 7.5, 1.4 Hz, 1H), 7.40-7.34 (m, 6H), 7.33-7.27 (m, 4H), 7.06-7.01 (m, 1H). All shifts are in agreement with the literature.[5]



6

Diphenyl-1-biphenyl-phosphine

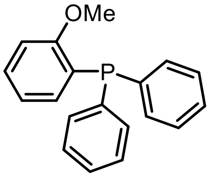
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40 (td, *J* = 7.5, 1.3 Hz, 1H), 7.34-7.24 (m, 11H), 7.25-7.17 (m, 6H), 7.06 (ddd, *J* = 7.8, 3.9, 1.2 Hz, 1H).



7

Diphenyl[2-bromo-phenyl]-phosphine

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.61 (m, 1H), 7.40-7.34 (m, 6H), 7.30-7.26 (m, 4H), 7.22-7.17 (m, 2H), 6.76-6.73 (m, 1H).

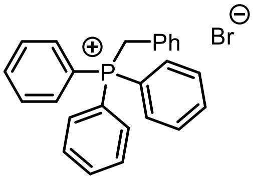


8

Diphenyl[2-methoxy-phenyl]-phosphine

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36-7.30 (m, 7H), 7.30-7.26 (m, 4H), 6.90 (ddd, *J* = 8.2, 4.7, 1.0 Hz, 1H), 6.87 (t, *J* = 7.4 Hz, 1H), 6.69-6.66 (m, 1H), 3.75 (s, 3H).

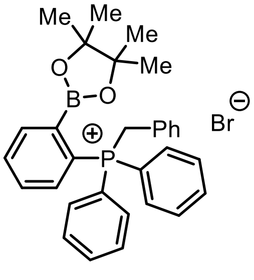
Characterization data for $BnPPh_3Br$ and phosphonium salts 1a-8a



Benzyltriphenylphosphonium bromide

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.80-7.70 (m, 9H), 7.66-7.60 (m, 6H), 7.24-7.20 (m, 1H), 7.16-7.06 (m, 4H), 5.41 (d, *J* = 14.3 Hz, 2H).

^{31}P NMR (243 MHz, $CDCl_3$) δ 23.2



1a

Benzyldiphenyl[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-phenyl]-phosphonium bromide

Following General Procedure A, **1a** was obtained as a white solid. **Isolated yield**: 186 mg, 56%, 594 µmol scale.

m.p. 273-275 °C

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.28 (ddd, J = 7.5, 4.2, 1.4 Hz, 1H), 7.81–7.77 (m, 1H), 7.76-7.68 (m, 6H), 7.63-7.56 (m, 5H), 7.49 (dd, J = 14.3, 7.8 Hz, 1H), 7.23-7.19 (m, 1H), 7.17-7.12 (m, 4H), 5.62 (d, J = 15.6 Hz, 2H), 1.03 (s, 12H).

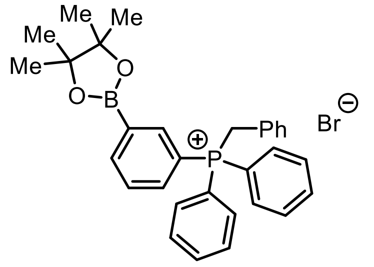
^{13}C NMR (151 MHz, $CDCl_3$) δ 139.2 (d, $^{3}J_{\text{C-P}}$ = 13.6 Hz, $\mathrm{CH_{arom}}$), 137.4 (d, $^{3}J_{\text{C-P}}$ = 11.4 Hz, $\mathrm{CH_{arom}}$), 134.4 (d, $^{4}J_{\text{C-P}}$ = 3.3 Hz, $\mathrm{CH_{arom}}$), 134.3 (d, $^{2}J_{\text{C-P}}$ = 9.8 Hz, $\mathrm{CH_{arom}}$), 133.8 (d, $^{4}J_{\text{C-P}}$ = 3.3 Hz, $\mathrm{CH_{arom}}$), 132.2 (d, $^{3}J_{\text{C-P}}$ = 12.5 Hz, $\mathrm{CH_{arom}}$), 131.4 (d, $^{2}J_{\text{C-P}}$ = 6.0 Hz, $\mathrm{CH_{arom}}$), 130.1 (d, $^{3}J_{\text{C-P}}$ = 12.5 Hz, $\mathrm{CH_{arom}}$), 128.9 (d, $^{5}J_{\text{C-P}}$ = 2.7 Hz, $\mathrm{CH_{arom}}$), 128.5 (d, $^{2}J_{\text{C-P}}$ = 8.7 Hz, $\mathrm{CH_{arom}}$), 128.3 (d, $^{4}J_{\text{C-P}}$ = 3.8 Hz, $\mathrm{CH_{arom}}$), 123.1 (d, $^{1}J_{\text{C-P}}$ = 81.7 Hz, $\mathrm{CH_{arom}}$), 120.6 (d, $^{1}J_{\text{C-P}}$ = 85.5 Hz, $\mathrm{CH_{arom}}$), 85.5 (s, C), 31.5 (d, $^{1}J_{\text{C-P}}$ = 45.2 Hz, $\mathrm{CH_{2\text{-}benzylic}}$), 24.6 (s, CH_3).

^{31}P NMR (243 MHz, $CDCl_3$) δ 24.8

^{11}B NMR (128 MHz, $CDCl_3$) δ 31.0

IR (ATR) 2976, 2358, 1716, 1437, 1110, 854, 515 cm^{-1}.

HRMS-APCI (*m/z*) calc'd for $C_{31}H_{33}BO_2P^+$ $[M]^+$: 479.2306, found 479.2311. Br^- is not observed as it is not covalently bonded.



2a

Benzyldiphenyl[3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-phenyl]-phosphonium bromide

Following General Procedure A, **2a** was obtained as a white solid. **Isolated yield**: 196 mg, 48%, 725 µmol scale.

m.p. 243-245 °C

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.18-8.16 (m, 1H), 7.93-7.88 (m, 1H), 7.80-7.74 (m, 7H), 7.68-7.61 (m, 5H), 7.23-7.19 (m, 1H), 7.13 (t, J = 7.5 Hz, 2H), 7.09-7.06 (m, 2H), 5.36 (d, J = 14.3 Hz, 2H) 1.31 (s, 12H).

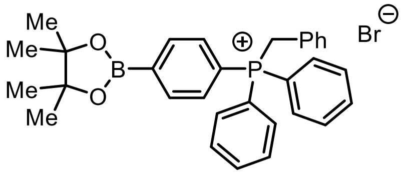
^{13}C NMR (151 MHz, $CDCl_3$) δ 141.3 (d, $^5J_{C\text{-}P} = 2.7$ Hz, CH_{arom}), 139.5 (d, $^2J_{C\text{-}P} = 8.7$ Hz, CH_{arom}), 137.2 (d, $^3J_{C\text{-}P} = 10.4$ Hz, CH_{arom}), 135.1 (d, $^4J_{C\text{-}P} = 3.3$ Hz, CH_{arom}), 134.6 (d, $^2J_{C\text{-}P} = 9.8$ Hz, CH_{arom}), 131.7 (d, $^2J_{C\text{-}P} = 6.0$ Hz, CH_{arom}), 130.3 (d, $^3J_{C\text{-}P} = 12.5$ Hz, CH_{arom}), 129.8 (d, $^3J_{C\text{-}P} = 12.0$ Hz, CH_{arom}), 129.0 (d, $^4J_{C\text{-}P} = 3.3$ Hz, CH_{arom}), 128.5 (d, $^4J_{C\text{-}P} = 3.8$ Hz, CH_{arom}), 127.2 (d, $^2J_{C\text{-}P} = 8.7$ Hz, CH_{arom}), 117.9 (d, $^1J_{C\text{-}P} = 85.6$ Hz, CH_{arom}) 117.1 (d, $^1J_{C\text{-}P} = 84.5$ Hz, CH_{arom}), 84.8 (s, C), 31.1 (d, $^1J_{C\text{-}P} = 47.4$ Hz, $CH_{2\text{-benzylic}}$), 25.0 (s, CH_3).

^{31}P NMR (243 MHz, $CDCl_3$) δ 23.1

^{11}B NMR (128 MHz, $CDCl_3$) δ 29.2

IR (ATR) 2977, 2357, 1718, 1356, 1111, 697, 509 cm^{-1}.

HRMS-APCI (*m/z*) calc'd for $C_{31}H_{33}BO_2P^+$ $[M]^+$: 479.2306, found 479.2307. Br^- is not observed as it is not covalently bonded.



3a

Benzyldiphenyl[4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-phenyl]-phosphonium bromide

Following General Procedure A, **3a** was obtained as a white solid. **Isolated yield**: 156 mg, 55%, 505 μmol scale.

m.p. 276-278 °C

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.00 (dd, $J = 8.2, 3.6$ Hz, 2H), 7.78-7.73 (m, 6H), 7.64-7.59 (m, 6H), 7.23-7.20 (m, 1H), 7.14-7.09 (m, 4H), 5.43 (d, $J = 14.3$ Hz, 2H), 1.35 (s, 12H).

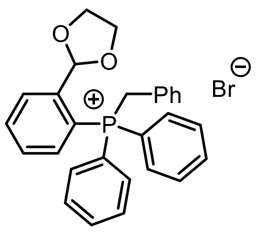
^{13}C NMR (151 MHz, $CDCl_3$) δ 135.9 (d, $^3J_{C\text{-}P} = 12.0$ Hz, CH_{arom}), 135.1 (d, $^5J_{C\text{-}P} = 2.7$ Hz, CH_{arom}), 134.6 (d, $^3J_{C\text{-}P} = 9.8$ Hz, CH_{arom}), 133.4 (d, $^2J_{C\text{-}P} = 9.3$ Hz, CH_{arom}), 131.7 (d, $^2J_{C\text{-}P} = 6.0$ Hz, CH_{arom}), 130.3 (d, $^3J_{C\text{-}P} = 12.5$ Hz, CH_{arom}), 129.0 (d, $^4J_{C\text{-}P} = 3.3$ Hz, CH_{arom}), 128.5 (d, $^4J_{C\text{-}P} = 3.8$ Hz, CH_{arom}), 127.1 (d, $^2J_{C\text{-}P} = 8.7$ Hz, CH_{arom}), 120.4 (d, $^1J_{C\text{-}P} = 84.5$ Hz, CH_{arom}), 117.9 (d, $^1J_{C\text{-}P} = 85.5$ Hz, CH_{arom}), 84.9 (s, C), 30.9 (d, $^1J_{C\text{-}P} = 46.9$ Hz, $CH_{2\text{-benzylic}}$), 25.0 (s, CH_3).

^{31}P NMR (243 MHz, $CDCl_3$) δ 23.1

^{11}B NMR (128 MHz, $CDCl_3$) δ 32.3

IR (ATR) 2976, 2362, 1601, 1359, 1078, 719, 514 cm^{-1}.

HRMS-APCI (*m/z*) calc'd for $C_{31}H_{33}BO_2P^+$ $[M]^+$: 479.2306, found 479.2308. Br^- is not observed as it is not covalently bonded.



4a

Benzyldiphenyl[2-(1,3-dioxolan-2-yl)-phenyl]-phosphonium bromide

Following General Procedure A, **4a** was obtained as a white solid. **Isolated yield**: 153 mg, 66%, 460 μmol scale.

m.p. 258-260 °C

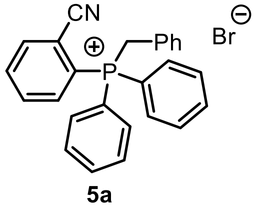
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.98 (ddd, J = 7.9, 5.0, 1.3 Hz, 1H), 7.84 (tt, J = 7.6, 1.6 Hz, 1H), 7.73-7.65 (m, 7H), 7.61-7.56 (m, 5H), 7.23-7.19 (m, 1H), 7.13-7.09 (m, 2H), 7.05-7.02 (m, 2H), 5.57 (s, 1H), 5.45 (d, J = 14.4 Hz, 2H), 3.84-3.73 (m, 4H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 143.3 (d, $^2J_{C\text{-}P}$ = 7.1 Hz, CH_{arom}), 136.9 (d, $^2J_{C\text{-}P}$ = 9.3 Hz, CH_{arom}), 135.3 (d, $^5J_{C\text{-}P}$ = 2.7 Hz, CH_{arom}), 134.6 (d, $^4J_{C\text{-}P}$ = 3.3 Hz, CH_{arom}), 134.1 (d, $^3J_{C\text{-}P}$ = 9.8 Hz, CH_{arom}), 131.6 (d, $^2J_{C\text{-}P}$ = 6.0 Hz, CH_{arom}), 130.3 (d, $^3J_{C\text{-}P}$ = 12.5 Hz, CH_{arom}), 130.0 (d, $^3J_{C\text{-}P}$ = 12.5 Hz, CH_{arom}), 129.5 (d, $^3J_{C\text{-}P}$ = 10.3 Hz, CH_{arom}), 128.9 (d, $^4J_{C\text{-}P}$ = 3.3 Hz, CH_{arom}), 128.5 (d, $^4J_{C\text{-}P}$ = 3.8 Hz, CH_{arom}), 127.8 (d, $^2J_{C\text{-}P}$ = 8.7 Hz, CH_{arom}), 119.6 (d, $^1J_{C\text{-}P}$ = 86.1 Hz, CH_{arom}), 116.8 (d, $^1J_{C\text{-}P}$ = 81.7 Hz, CH_{arom}), 100.3 (s, CH) 65.3 (s, CH_2) 32.4 (d, $^1J_{C\text{-}P}$ = 46.9 Hz, $CH_{2\text{-benzylic}}$).

^{31}P NMR (243 MHz, $CDCl_3$) δ 23.9

IR (ATR) 2891, 2357, 1586, 1437, 1103, 696, 515 cm^{-1}.

HRMS-APCI (*m/z*) calc'd for $C_{28}H_{26}O_2P^+$ $[M]^+$: 425.1665, found 425.1663. Br is not observed as it is not covalently bonded.



5a

Benzyldiphenyl[2-cyano-phenyl]-phosphonium bromide

Following General Procedure A, **5a** was obtained as a white solid. **Isolated yield**: 63.4 mg, 41%, 335 μmol scale.

m.p. 250-252 °C

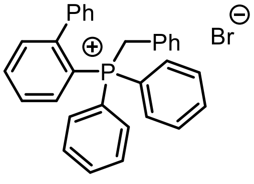
^{1}H NMR (600 MHz, $CDCl_3$) δ 9.1 (dd, *J* = 13.4, 7.8 Hz, 1H), 8.15-8.09 (m, 1H), 7.92-7.89 (m, 2H), 7.84-7.78 (m, 6H), 7.66-7.61 (m, 4H), 7.24-7.20 (m, 1H), 7.10 (t, *J* = 7.4 Hz, 2H), 6.97-6.93 (m, 2H), 5.67 (d, *J* = 14.8 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 138.4 (d, $^3J_{C\text{-}P}$ = 9.2 Hz, CH_{arom}), 136.4 (d, $^2J_{C\text{-}P}$ = 7.9 Hz, CH_{arom}), 135.6 (d, $^4J_{C\text{-}P}$ = 3.1 Hz, CH_{arom}), 135.2 (d, $^3J_{C\text{-}P}$ = 11.8 Hz, CH_{arom}), 135.1 (d, $^5J_{C\text{-}P}$ = 2.7 Hz, CH_{arom}), 134.8 (d, $^3J_{C\text{-}P}$ = 9.9 Hz, CH_{arom}), 131.7 (d, $^2J_{C\text{-}P}$ = 5.8 Hz, CH_{arom}), 130.3 (d, $^3J_{C\text{-}P}$ = 13.0 Hz, CH_{arom}), 129.0 (d, $^4J_{C\text{-}P}$ = 3.4 Hz, CH_{arom}), 128.8 (d, $^4J_{C\text{-}P}$ = 4.3 Hz, CH_{arom}), 126.3 (d, $^2J_{C\text{-}P}$ = 8.1 Hz, CH_{arom}), 122.2 (d, $^1J_{C\text{-}P}$ = 82.2 Hz, CH_{arom}), 116.0 (s, CN), 115.8 (d, $^1J_{C\text{-}P}$ = 86.1 Hz, CH_{arom}), 115.7 (d, $^2J_{C\text{-}P}$ = 4.8 Hz, CH_{arom}), 31.9 (d, $^1J_{C\text{-}P}$ = 46.3 Hz, $CH_{2\text{-benzylic}}$).

^{31}P NMR (243 MHz, $CDCl_3$) δ 22.0

IR (ATR) 3005, 2853, 2226, 1455, 1109, 690, 505 cm^{-1}.

HRMS-APCI (*m/z*) calc'd for $C_{26}H_{21}NP^+$ $[M]^+$: 378.1406, found 378.1401. Br^- is not observed as it is not covalently bonded.



6a

Benzyldiphenyl-1-biphenyl-phosphonium bromide

Following General Procedure A, **6a** was obtained as a white solid. **Isolated yield**: 287 mg, 70%, 800 µmol scale.

m.p. 297-299 °C

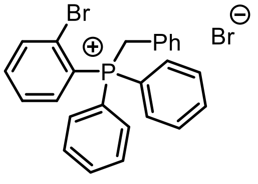
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.22 (dd, *J* = 13.9, 8.0 Hz, 1H), 7.88-7.83 (m, 1H), 7.80-7.55 (m, 1 H), 7.70-7.65 (m, 2H), 7.51-7.45 (m, 5H), 7.41-7.35 (m, 4H), 7.24-7.20 (m, 1H), 7.17-7.13 (m, 1 H), 7.03 (t, *J* = 7.8 Hz, 4H), 6.82-6.78 (m, 2H), 6.77-6.74 (m, 2H), 4.77 (d, *J* = 14.5 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 148.2 (d, $^2J_{C\text{-}P}$ = 8.8 Hz, CH_{arom}), 138.9 (d, $^4J_{C\text{-}P}$ = 3.8 Hz, CH_{arom}), 136.4 (d, $^3J_{C\text{-}P}$ = 10.4 Hz, CH_{arom}), 135.1 (d, $^5J_{C\text{-}P}$ = 2.8 Hz, CH_{arom}), 134.5 (d, $^4J_{C\text{-}P}$ = 3.1 Hz, CH_{arom}), 134.2 (d, $^3J_{C\text{-}P}$ = 9.7 Hz, CH_{arom}), 133.8 (d, $^3J_{C\text{-}P}$ = 10.3 Hz, CH_{arom}), 131.5 (d, $^2J_{C\text{-}P}$ = 5.7 Hz, CH_{arom}), 129.8 (d, $^3J_{C\text{-}P}$ = 12.6 Hz, CH_{arom}), 129.4 (s, CH_{arom}), 129.2 (d, $^3J_{C\text{-}P}$ = 12.1 Hz, CH_{arom}), 128.8 (m, 2 CH_{arom}), 128.5 (s, CH_{arom}), 128.4 (d, $^4J_{C\text{-}P}$ = 3.8 Hz, CH_{arom}), 127.5 (d, $^2J_{C\text{-}P}$ = 8.1 Hz, CH_{arom}), 118.9 (d, $^1J_{C\text{-}P}$ = 85.9 Hz, CH_{arom}), 117.5 (d, $^1J_{C\text{-}P}$ = 83.7 Hz, CH_{arom}), 31.4 (d, $^1J_{C\text{-}P}$ = 46.9 Hz, $CH_{2\text{-benzylic}}$).

^{31}P NMR (243 MHz, CDCl$_3$) δ 22.6

IR (ATR) 3053, 2861, 2358, 1438, 1110, 782, 504 cm^{-1}.

HRMS-APCI (*m/z*) calc'd for $C_{31}H_{22}P^+$ [M]$^+$: 429.1767, found 429.1760. Br$^-$ is not observed as it is not covalently bonded.



7a

Benzyldiphenyl[2-bromo-phenyl]-phosphonium bromide

Following General Procedure A, **7a** was obtained as a white solid. **Isolated yield**: 103 mg, 40%, 500 μmol scale.

m.p. 276-278 °C

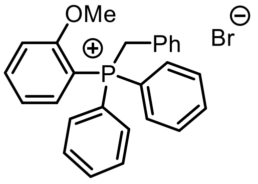
^{1}H NMR (600 MHz, CDCl$_3$) δ 8.26 (dd, *J* = 10.3, 7.8 Hz, 1H), 7.85 (dd, *J* = 8.1, 4.6 Hz, 1H), 7.80-7.74 (m, 5H), 7.63-7.58 (m, 4H), 7.25-7.22 (m, 1H), 7.13 (t, *J* = 7.5 Hz, 2H), 7.00-6.96 (m, 2H), 5.54 (d, *J* = 14.6 Hz, 2H).

^{13}C NMR (151 MHz, CDCl$_3$) δ 139.2 (d, $^2J_{C\text{-}P}$ = 9.8 Hz, CH$_{arom}$), 136.8 (d, $^5J_{C\text{-}P}$ = 2.7 Hz, CH$_{arom}$), 136.2 (d, $^2J_{C\text{-}P}$ = 7.6 Hz, CH$_{arom}$), 135.0 (d, $^3J_{C\text{-}P}$ = 3.3 Hz, CH$_{arom}$), 134.6 (d, $^3J_{C\text{-}P}$ = 9.8 Hz, CH$_{arom}$), 131.6 (d, $^2J_{C\text{-}P}$ = 6.0 Hz, CH$_{arom}$), 130.1 (d, $^3J_{C\text{-}P}$ = 13.1 Hz, CH$_{arom}$), 129.7 (d, $^3J_{C\text{-}P}$ = 11.4 Hz, CH$_{arom}$), 129.0 (d, $^4J_{C\text{-}P}$ = 3.0 Hz, CH$_{arom}$), 128.7 (d, $^4J_{C\text{-}P}$ = 4.4 Hz, CH$_{arom}$), 127.6 (d, $^2J_{C\text{-}P}$ = 4.90 Hz, CH$_{arom}$), 127.1 (d, $^3J_{C\text{-}P}$ = 10.9 Hz, CH$_{arom}$), 119.5 (d, $^1J_{C\text{-}P}$ = 90.5 Hz, CH$_{arom}$), 116.7 (d, $^1J_{C\text{-}P}$ = 87.2 Hz, CH$_{arom}$), 31.9 (d, $^1J_{C\text{-}P}$ = 46.9 Hz, CH$_{2\text{-benzylic}}$).

^{31}P NMR (243 MHz, CDCl$_3$) δ 24.0

IR (ATR) 3382, 2857, 2358, 1437, 1110, 697, 582 cm^{-1}.

HRMS-APCI (*m/z*) calc'd for $C_{25}H_{21}BrP^+$ [M]$^+$: 431.0559, found 431.0560. Br$^-$ is not observed as it is not covalently bonded.



8a

Benzyldiphenyl[2-methoxy-phenyl]-phosphonium bromide

Following General Procedure A, **8a** was obtained as a white solid. **Isolated yield**: 257 mg, 81%, 684 μmol scale.

m.p. 226-228 °C

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.85-7.81 (m, 1H), 7.75-7.71 (m, 2H), 7.61-7.53 (m, 8H), 7.41 (ddd, J = 14.0, 7.8, 1.6 Hz, 1H), 7.25-7.19 (m, 3H), 7.16 (t, J = 7.5 Hz, 2H), 7.07-7.03 (m, 2H), 5.23 (dd, J = 15.1 Hz, 2H), 3.81 (s, 3H).

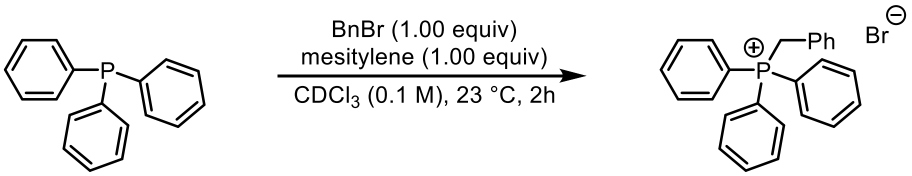
^{13}C NMR (151 MHz, $CDCl_3$) δ 162.1 (d, $^{4}J_{C\text{-}P}$ = 2.3 Hz, CH_{arom}), 138.1 (d, $^{5}J_{C\text{-}P}$ = 2.3 Hz, CH_{arom}), 136.5 (d, $^{2}J_{C\text{-}P}$ = 7.7 Hz, CH_{arom}), 134.7 (d, $^{4}J_{C\text{-}P}$ = 3.0 Hz, CH_{arom}), 134.2 (d, $^{3}J_{C\text{-}P}$ = 9.8 Hz, CH_{arom}), 131.4 (d, $^{2}J_{C\text{-}P}$ = 5.9 Hz, CH_{arom}), 129.9 (d, $^{3}J_{C\text{-}P}$ = 12.6 Hz, CH_{arom}), 129.0 (d, $^{4}J_{C\text{-}P}$ = 3.3 Hz, CH_{arom}), 128.5 (d, $^{4}J_{C\text{-}P}$ = 3.9 Hz, CH_{arom}), 127.9 (d, $^{3}J_{C\text{-}P}$ = 8.7 Hz, CH_{arom}), 122.9 (d, $^{3}J_{C\text{-}P}$ = 12.2 Hz, CH_{arom}), 117.8 (d, $^{1}J_{C\text{-}P}$ = 87.5 Hz, CH_{arom}), 112.9 (d, $^{2}J_{C\text{-}P}$ = 6.5 Hz, CH_{arom}), 105.8 (d, $^{1}J_{C\text{-}P}$ = 88.1 Hz, CH_{arom}), 56.6 (s, CH_3), 31.0 (d, $^{1}J_{C\text{-}P}$ = 48.0 Hz, $CH_{2\text{-benzylic}}$).

^{31}P NMR (243 MHz, $CDCl_3$) δ 21.7

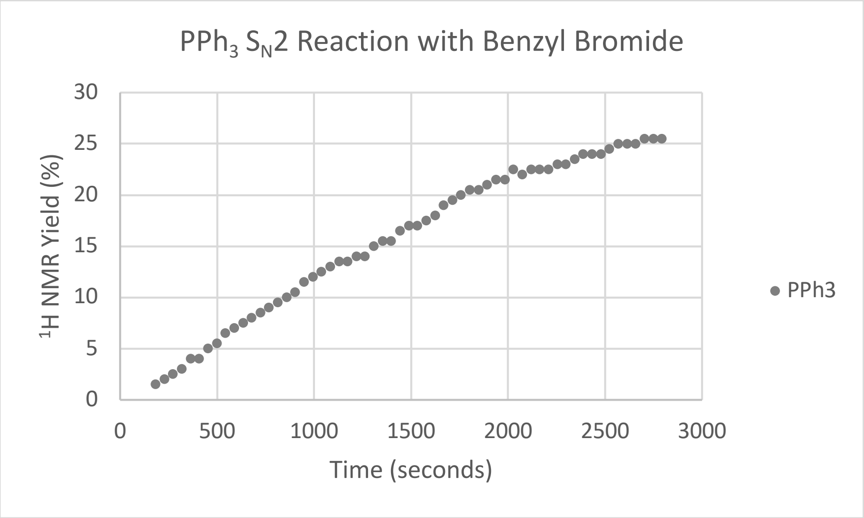
IR (ATR) 2855, 2358, 1714, 1435, 1110, 692, 498 cm^{-1}.

HRMS-APCI (*m/z*) calc'd for $C_{26}H_{24}OP^{+}$ $[M]^{+}$: 383.1558, found 383.1552. Br^{-} is not observed as it is not covalently bonded.

Kinetic Data Plotted in Microsoft Excel:

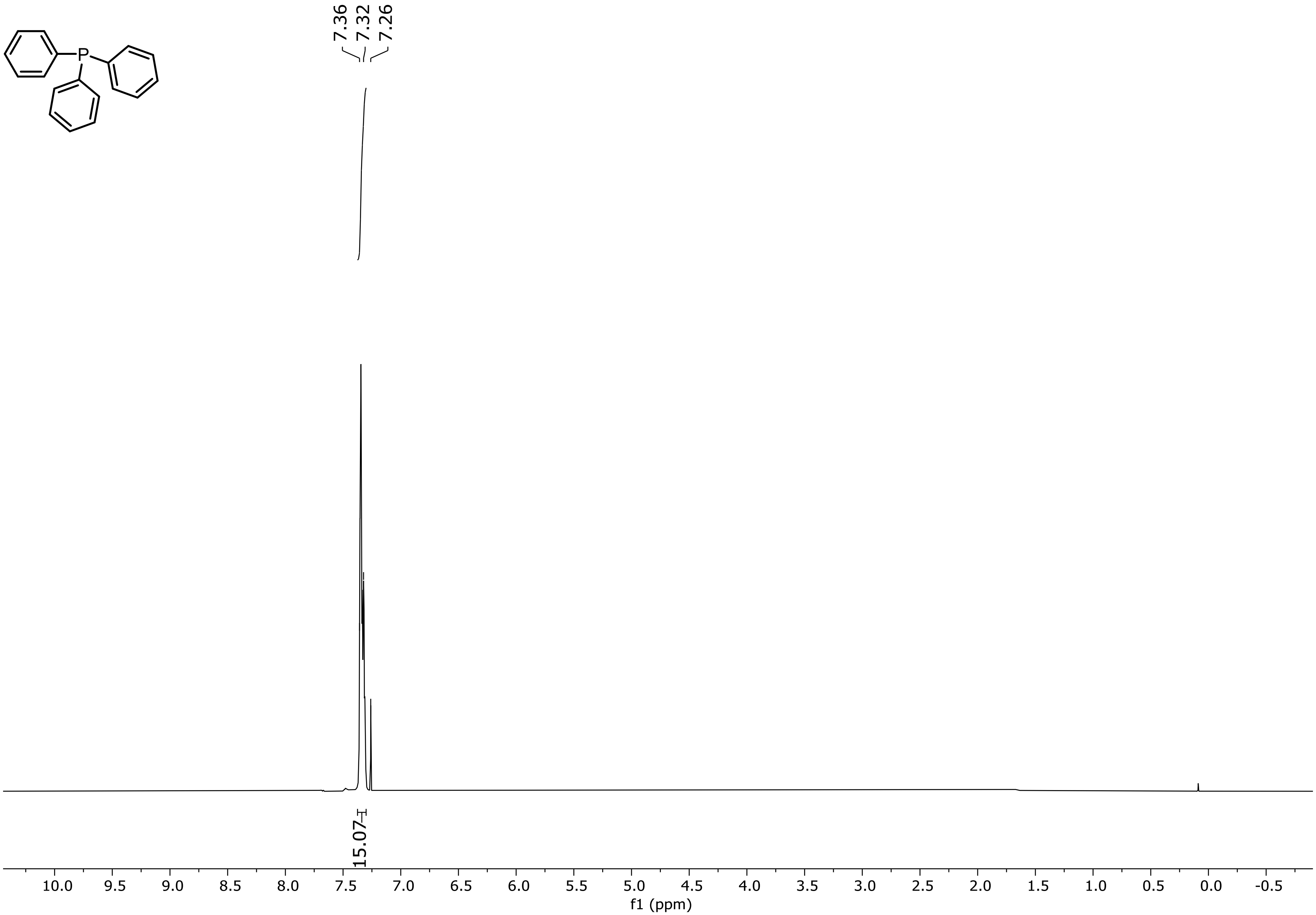


Scheme S1. Reaction of PPh_3 with benzyl bromide.



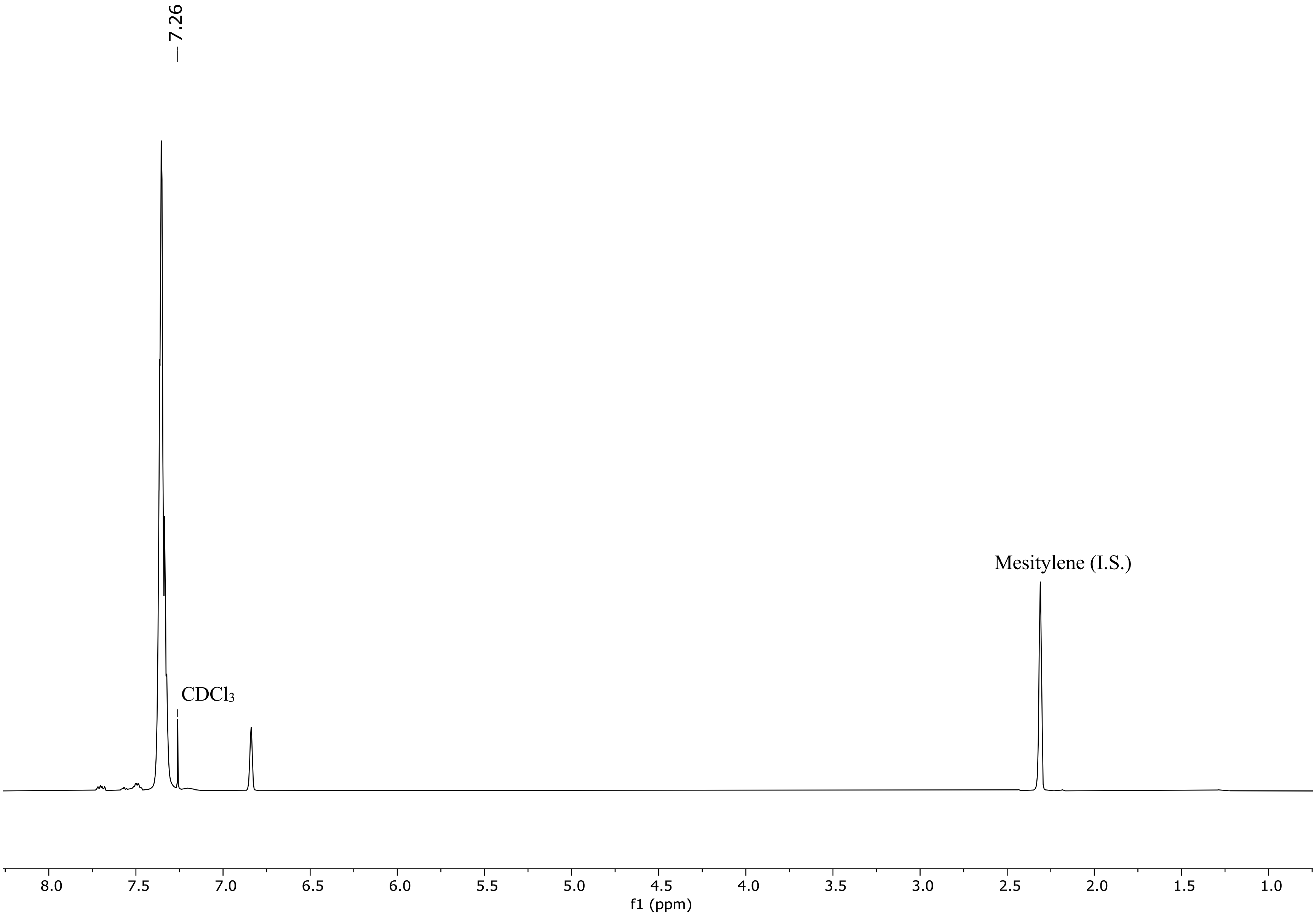
Time	NMR Yield	Time	NMR Yield	Time	NMR Yield
183	1.5	1083	13	1983	21.5
228	2	1128	13.5	2028	22.5
273	2.5	1173	13.5	2073	22
318	3	1218	14	2118	22.5
363	4	1263	14	2163	22.5
408	4	1308	15	2208	22.5
453	5	1353	15.5	2253	23
498	5.5	1398	15.5	2298	23
543	6.5	1443	16.5	2343	23.5
588	7	1488	17	2388	24
633	7.5	1533	17	2433	24
678	8	1578	17.5	2478	24
723	8.5	1623	18	2523	24.5
768	9	1668	19	2568	25
813	9.5	1713	19.5	2613	25
858	10	1758	20	2658	25
903	10.5	1803	20.5	2703	25.5
948	11.5	1848	20.5	2748	25.5
993	12	1893	21	2793	25.5
1038	12.5	1938	21.5		

NMR #1. Triphenylphosphine ^{1}H NMR.



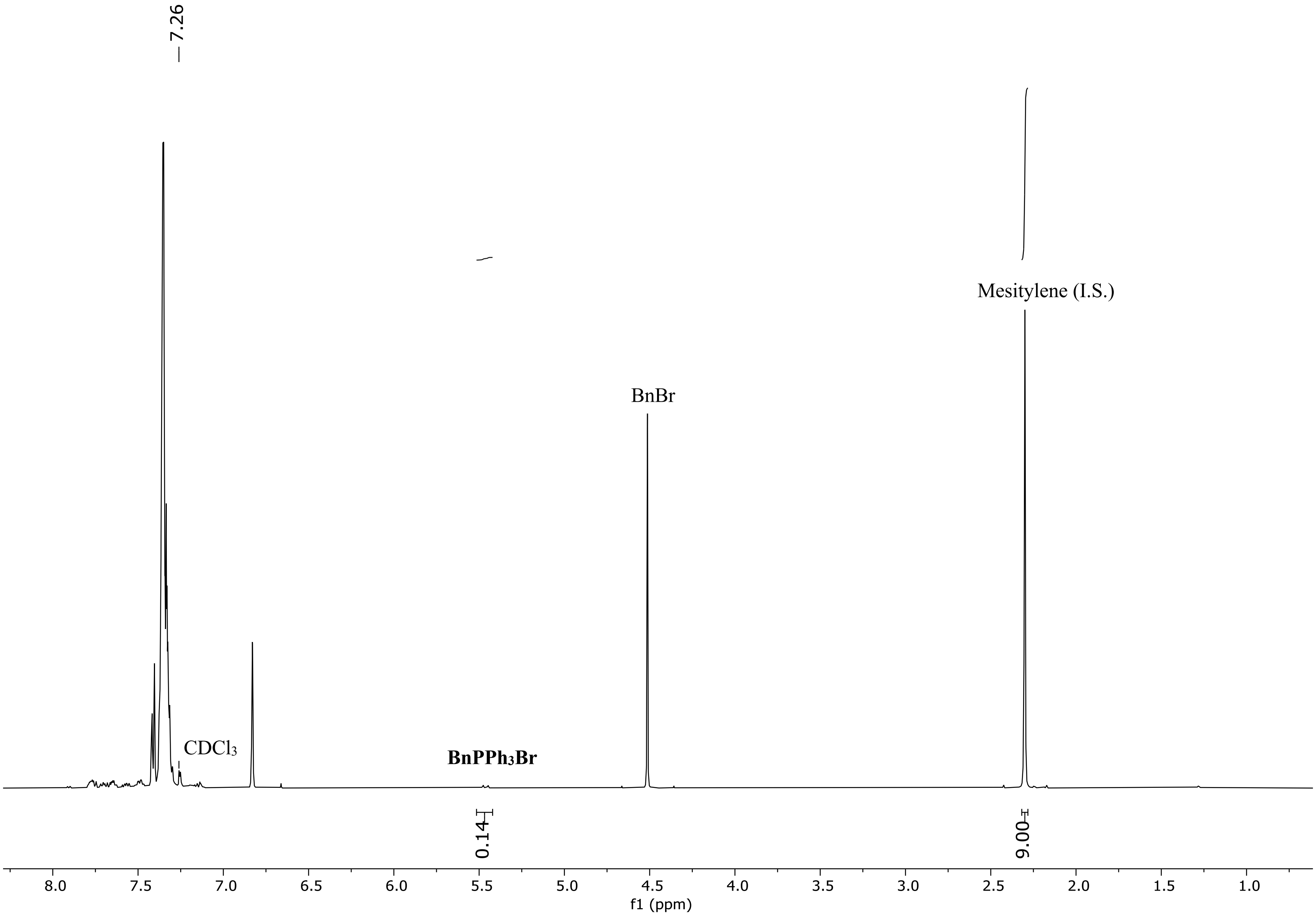
^{1}H NMR ($CDCl_3$, 600 MHz)

NMR #2. Triphenylphosphine and mesitylene initial ^{1}H NMR before addition of benzyl bromide.



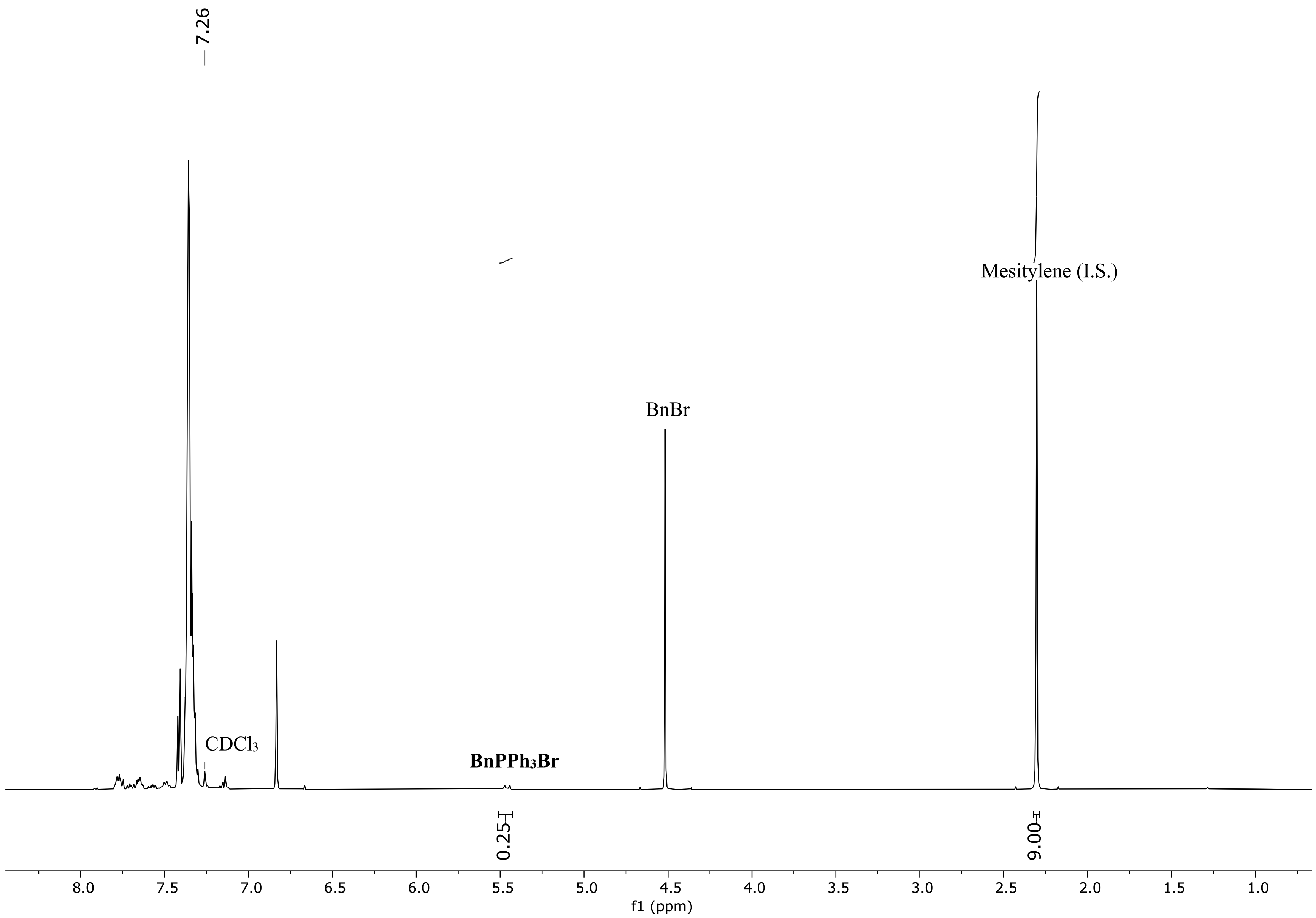
^{1}H NMR (CDCl$_3$, 500 MHz)

NMR #3. Time = 588 seconds for triphenylphosphine reaction with benzyl bromide (^{1}H NMR Yield = 14%, Actual yield = 7%).



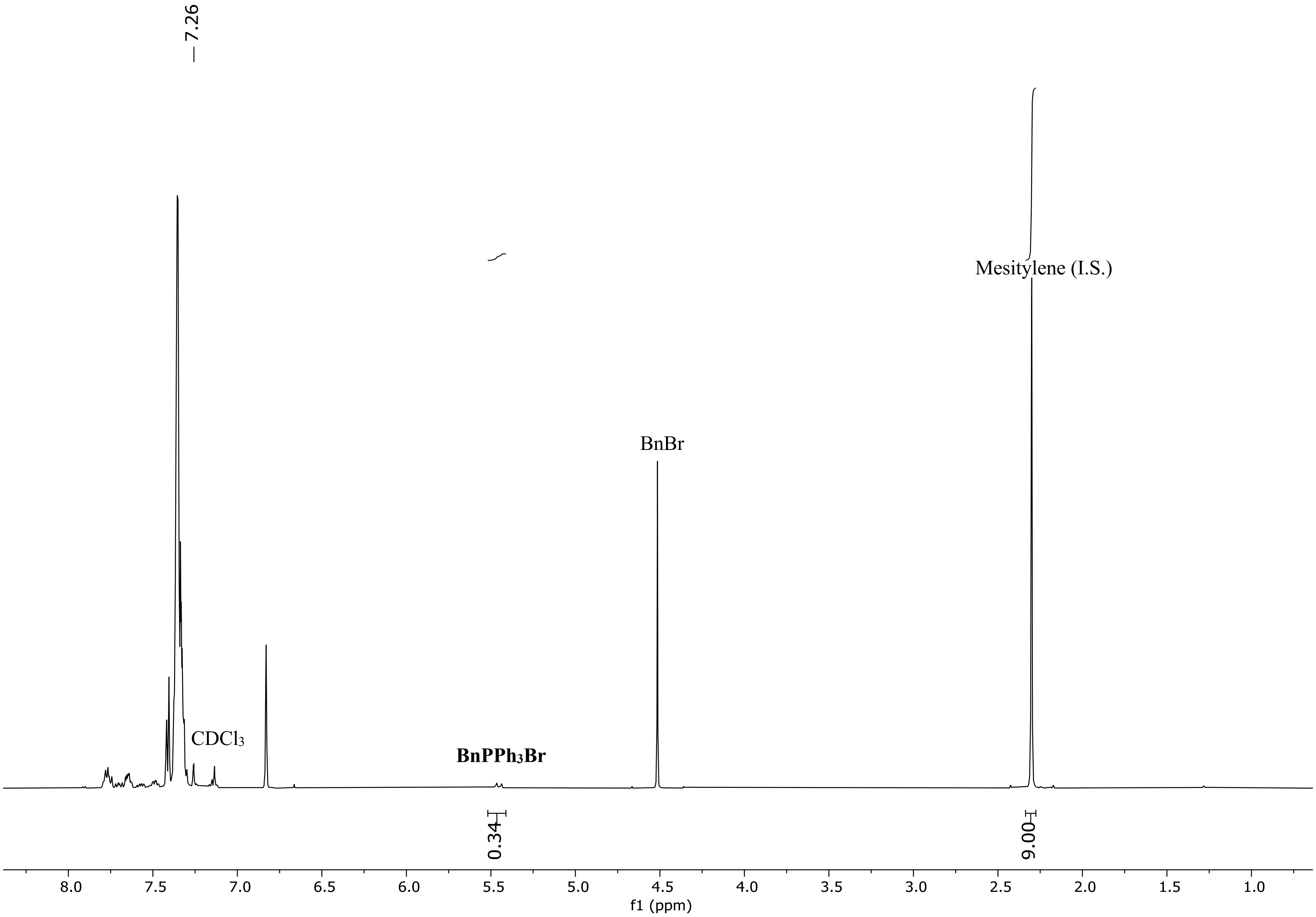
^{1}H NMR (CDCl$_3$, 500 MHz)

NMR #4. Time = 1038 seconds for triphenylphosphine reaction with benzyl bromide (^{1}H NMR Yield = 25%, Actual yield = 12.5%).



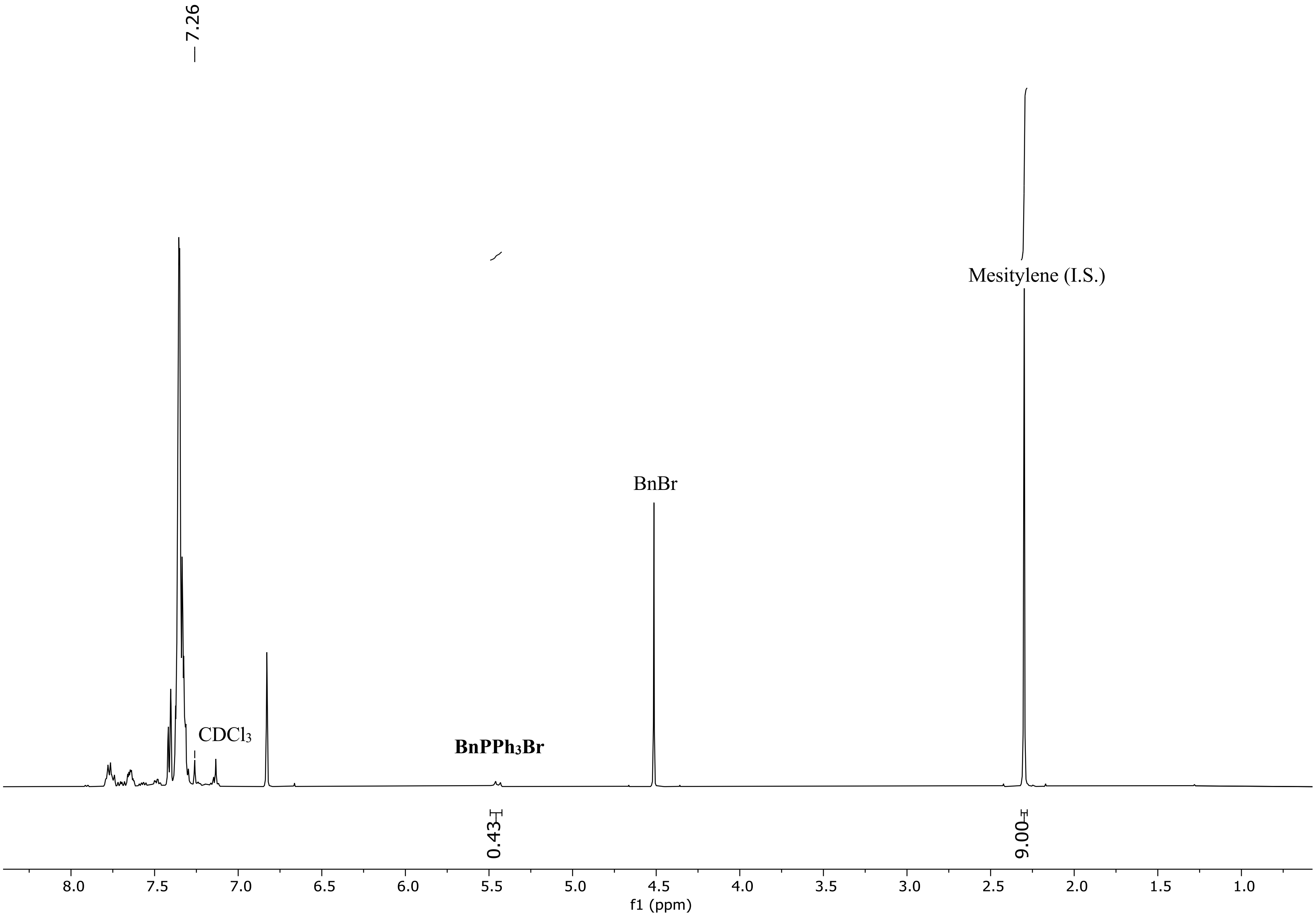
^{1}H NMR ($CDCl_3$, 500 MHz)

NMR #5. Time = 1488 seconds for triphenylphosphine reaction with benzyl bromide (^{1}H NMR Yield = 34%, Actual yield = 17%).



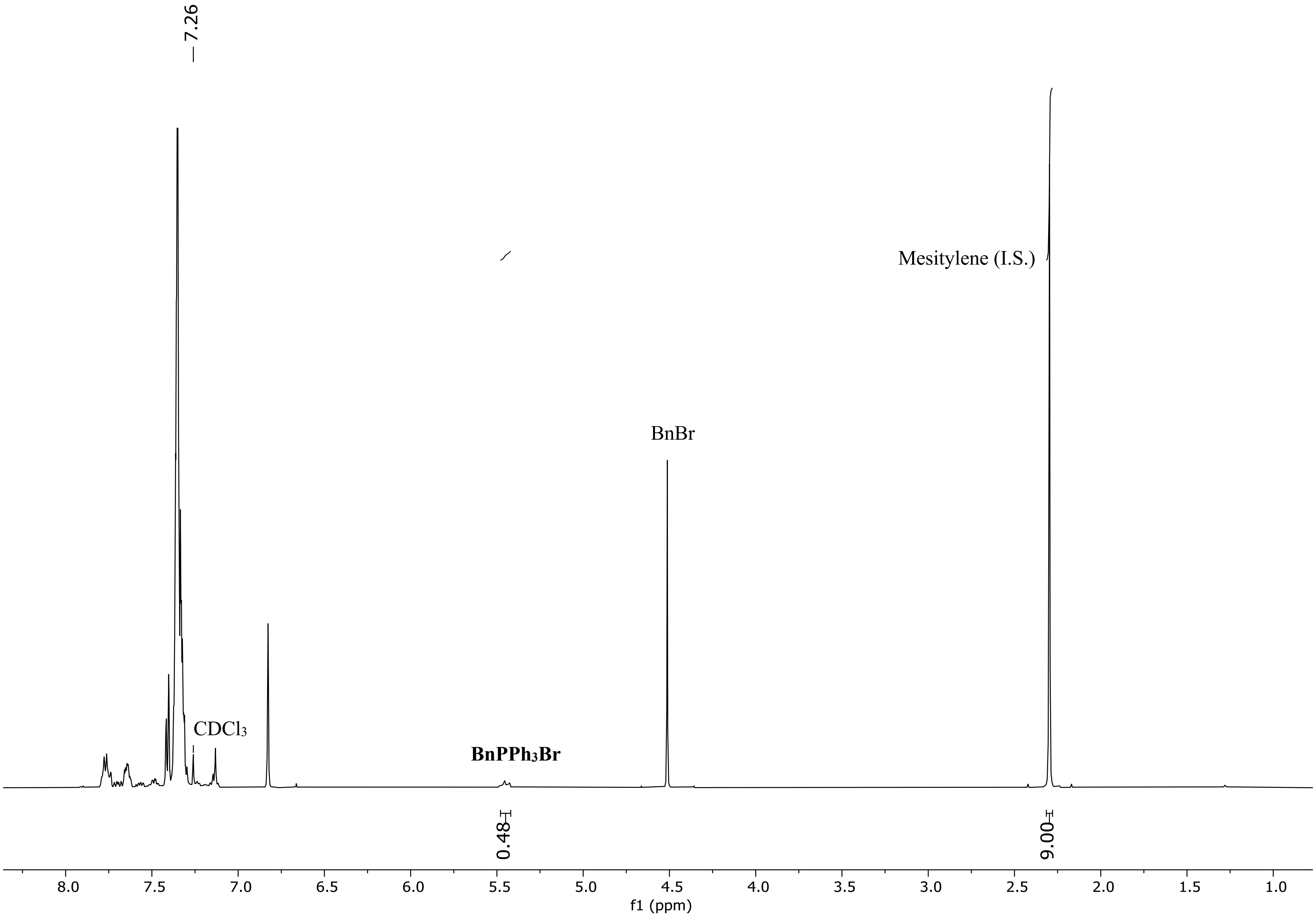
^{1}H NMR (CDCl$_3$, 500 MHz)

NMR #6. Time = 1938 seconds for triphenylphosphine reaction with benzyl bromide (^{1}H NMR Yield = 43%, Actual yield = 21.5%).



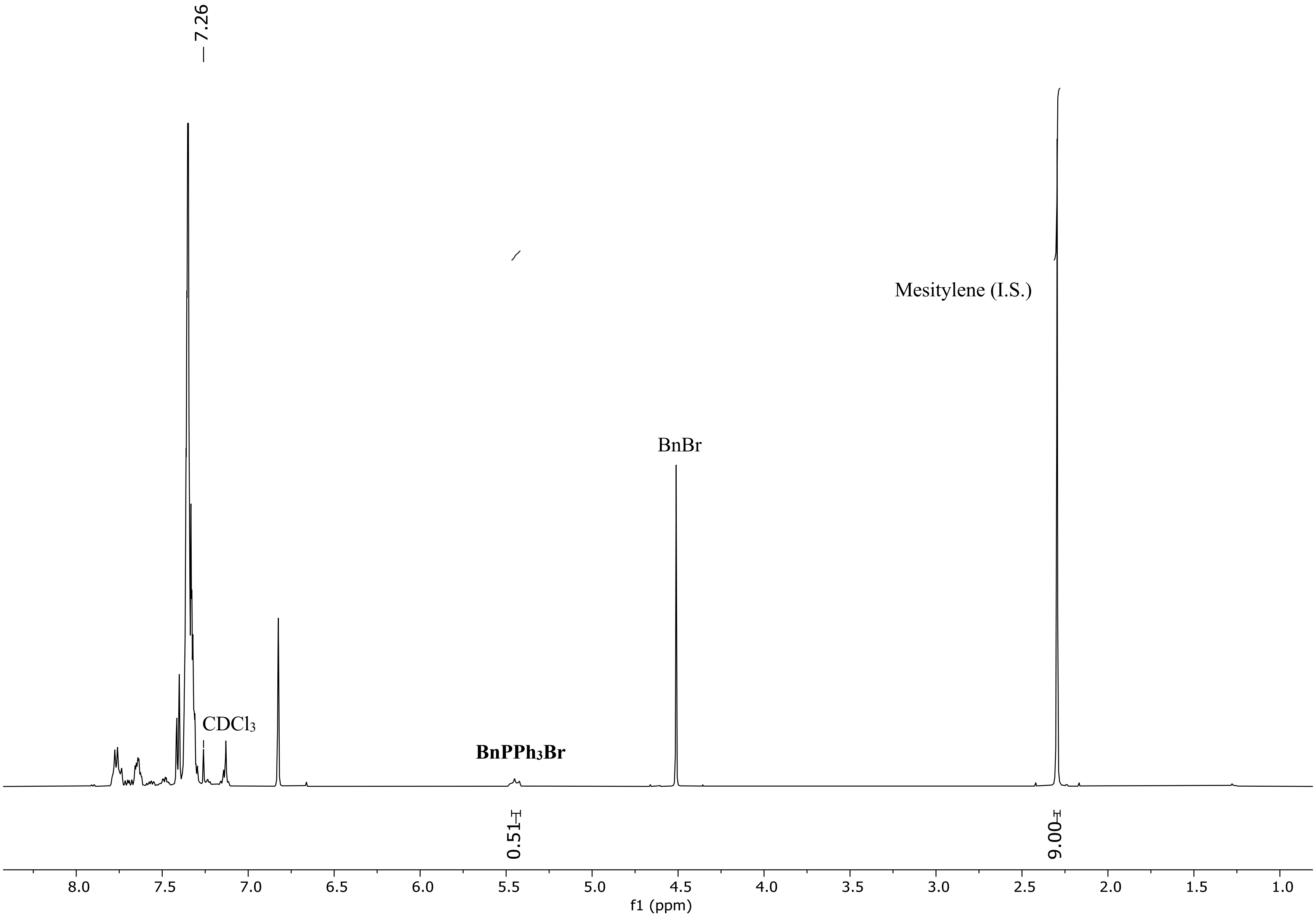
^{1}H NMR (CDCl$_3$, 500 MHz)

NMR #7. Time = 2388 seconds for triphenylphosphine reaction with benzyl bromide (^{1}H NMR Yield = 48%, Actual yield = 24%).



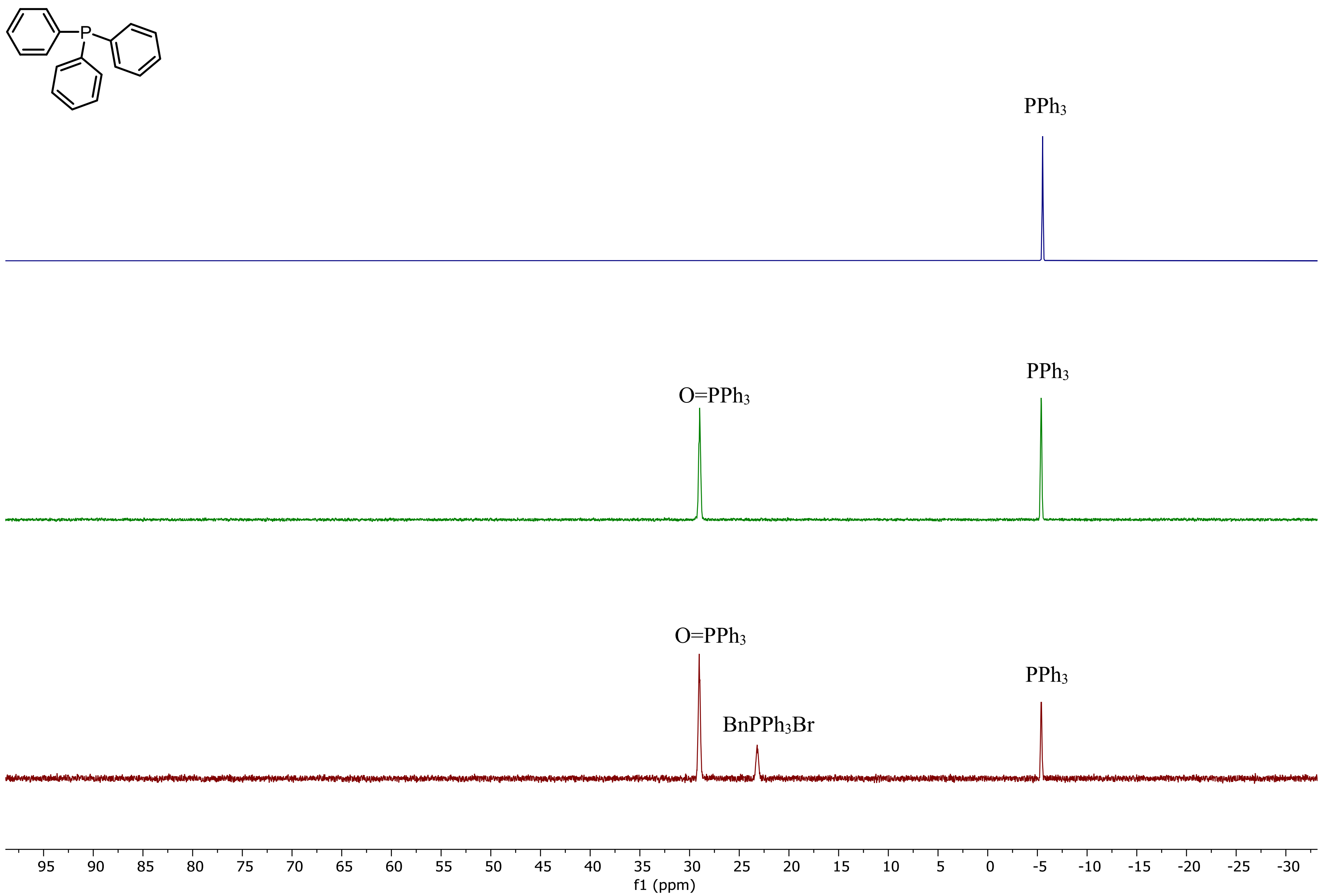
^{1}H NMR (CDCl$_3$, 500 MHz)

NMR #8. Time = 2793 seconds for triphenylphosphine reaction with benzyl bromide (^{1}H NMR Yield = 53%, Actual yield = 21.5%).

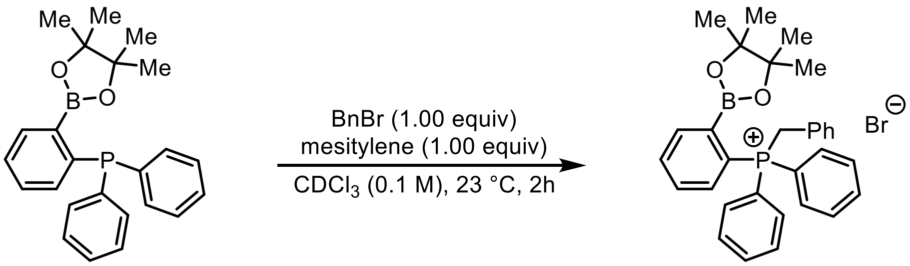


^{1}H NMR (CDCl$_3$, 500 MHz)

NMR #9. ^{31}P NMR spectra of PPh_3, PPh_3 and $OPPh_3$ before addition of benzyl bromide, and final time point of reaction (2750 seconds).

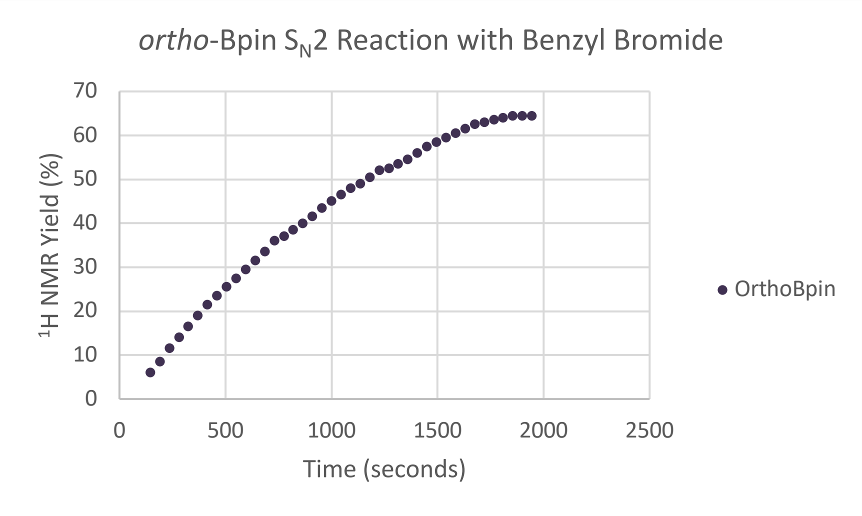


^{31}P NMR ($CDCl_3$, 162 MHz)



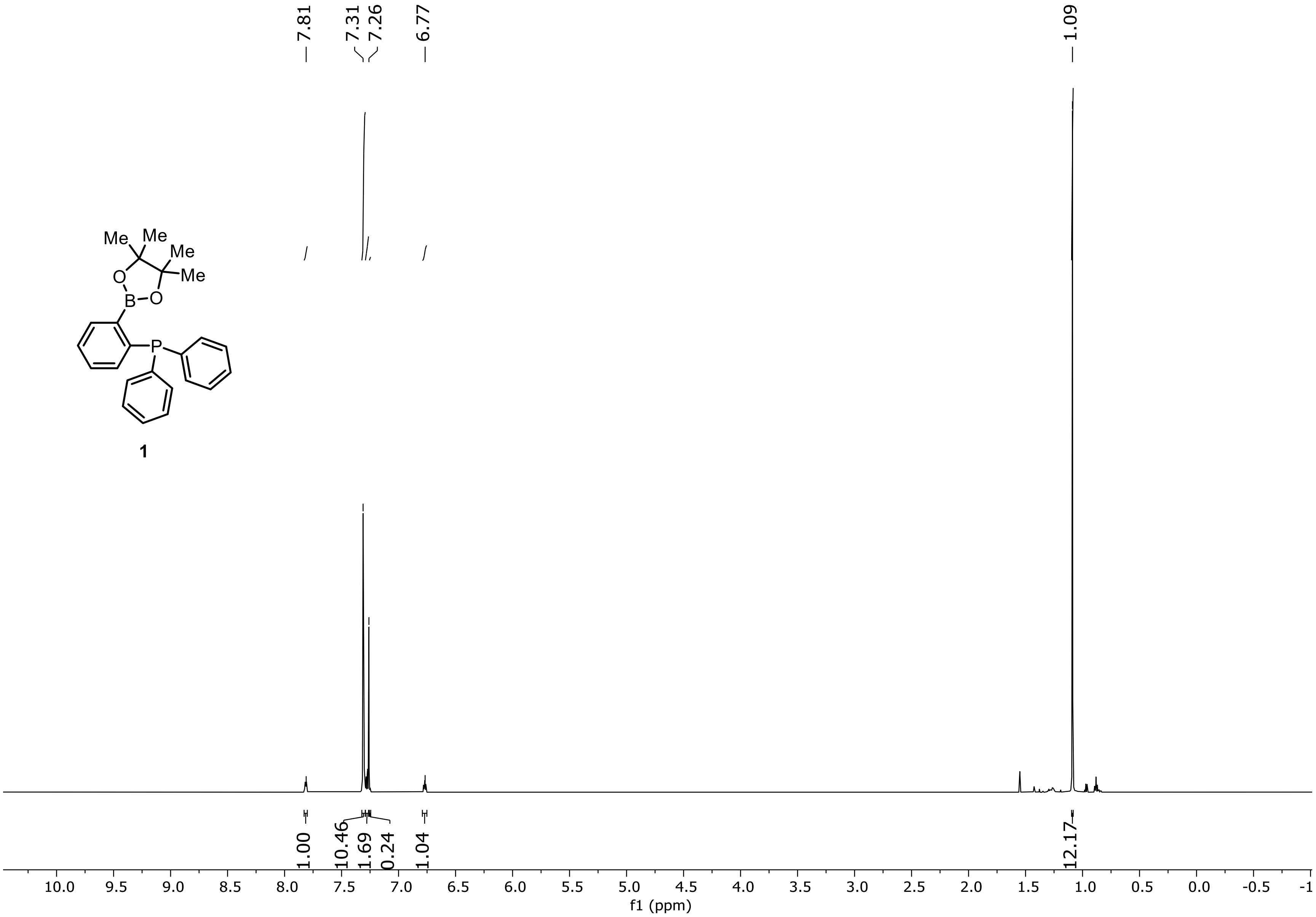
1 **1a**

Scheme S2. Reaction of *ortho*-Bpin with benzyl bromide.



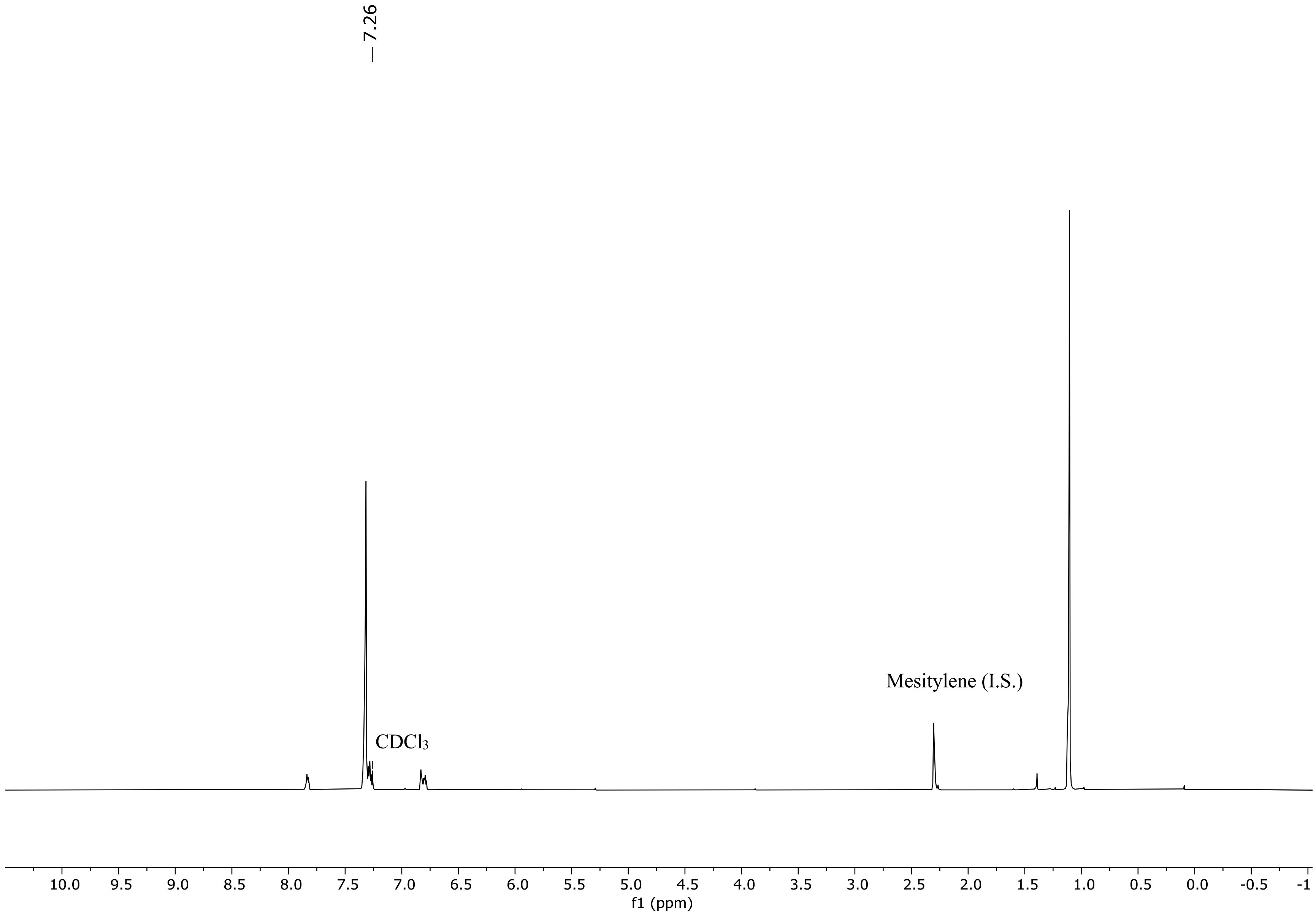
Time	NMR Yield	Time	NMR Yield
145	6	1090	48
190	8.5	1135	49
235	11.5	1180	50.5
280	14	1225	52
325	16.5	1270	52.5
370	19	1315	53.5
415	21.5	1360	54.5
460	23.5	1405	56
505	25.5	1450	57.5
550	27.5	1495	58.5
595	29.5	1540	59.5
640	31.5	1585	60.5
685	33.5	1630	61.5
730	36	1675	62.5
775	37	1720	63
820	38.5	1765	63.5
865	40	1810	64
910	41.5	1855	64.5
955	43.5	1900	64.5
1000	45	1945	64.5
1045	46.5		

NMR #1. Phosphine **1** ^{1}H NMR.



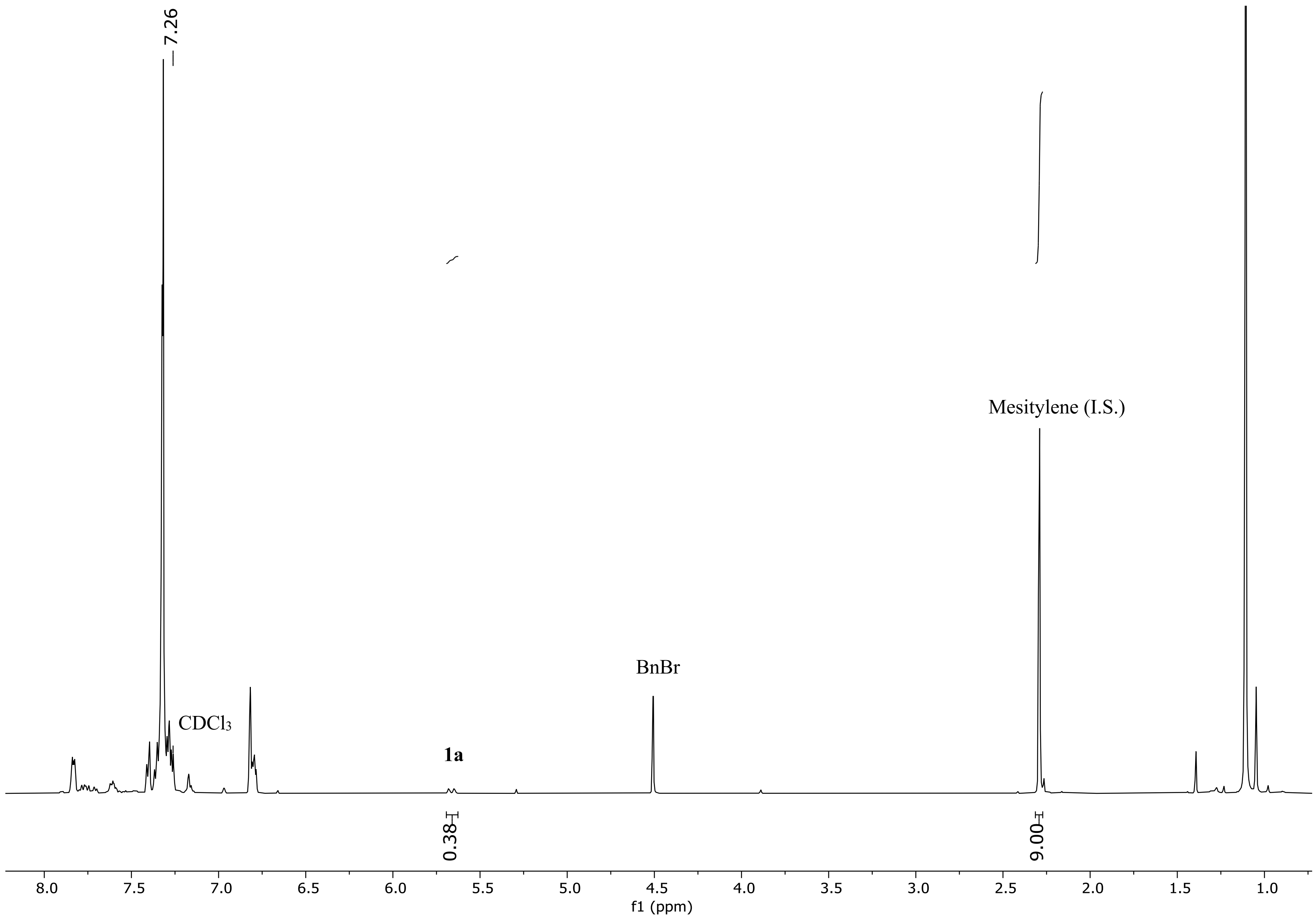
^{1}H NMR ($CDCl_3$, 600 MHz)

NMR #2. Phosphine **1** and mesitylene initial ^{1}H NMR before addition of benzyl bromide.



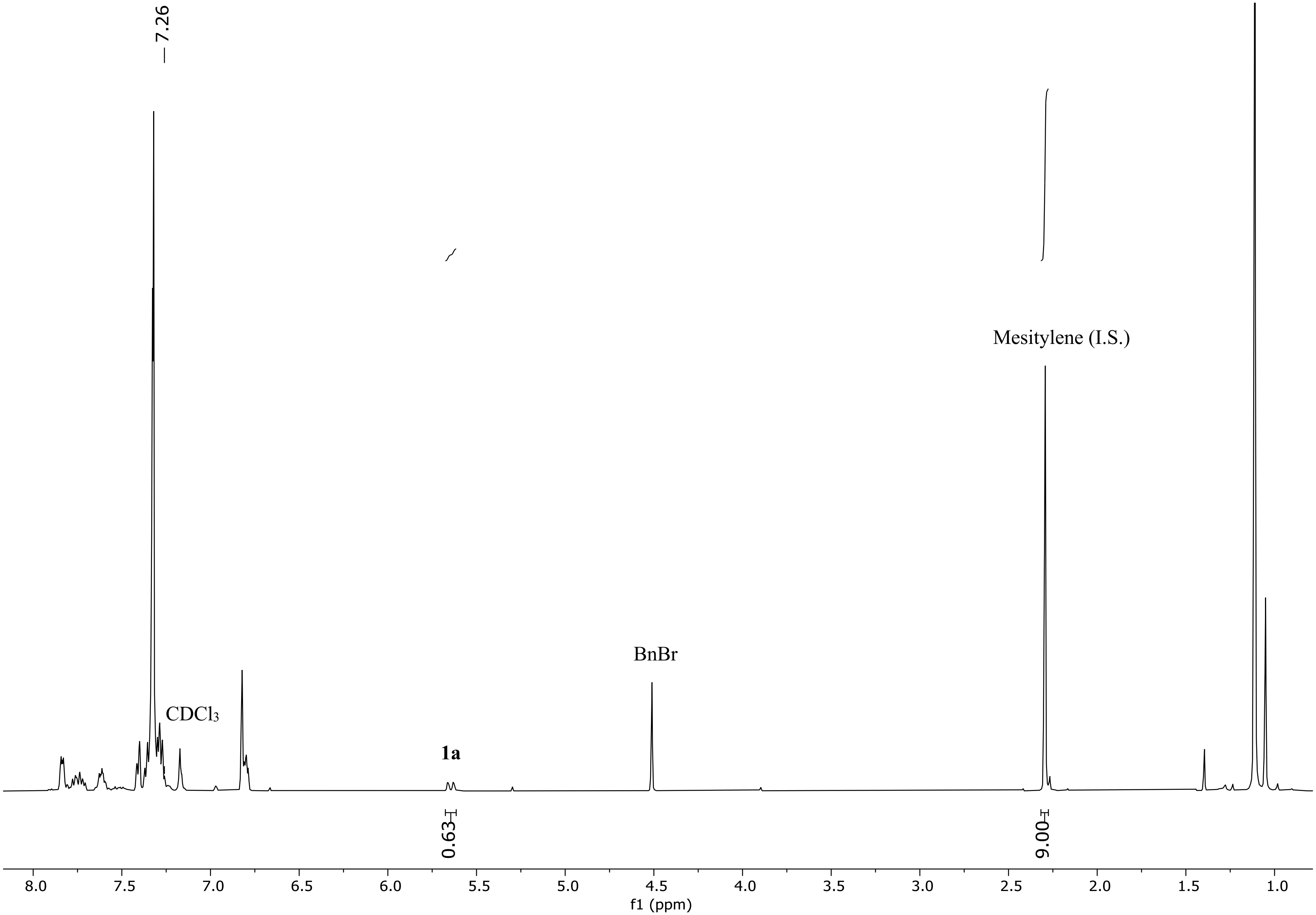
^{1}H NMR (CDCl$_3$, 500 MHz)

NMR #3. Time = 370 seconds for Phosphine **1** reaction with benzyl bromide (^{1}H NMR Yield = 38%, Actual yield = 19%).



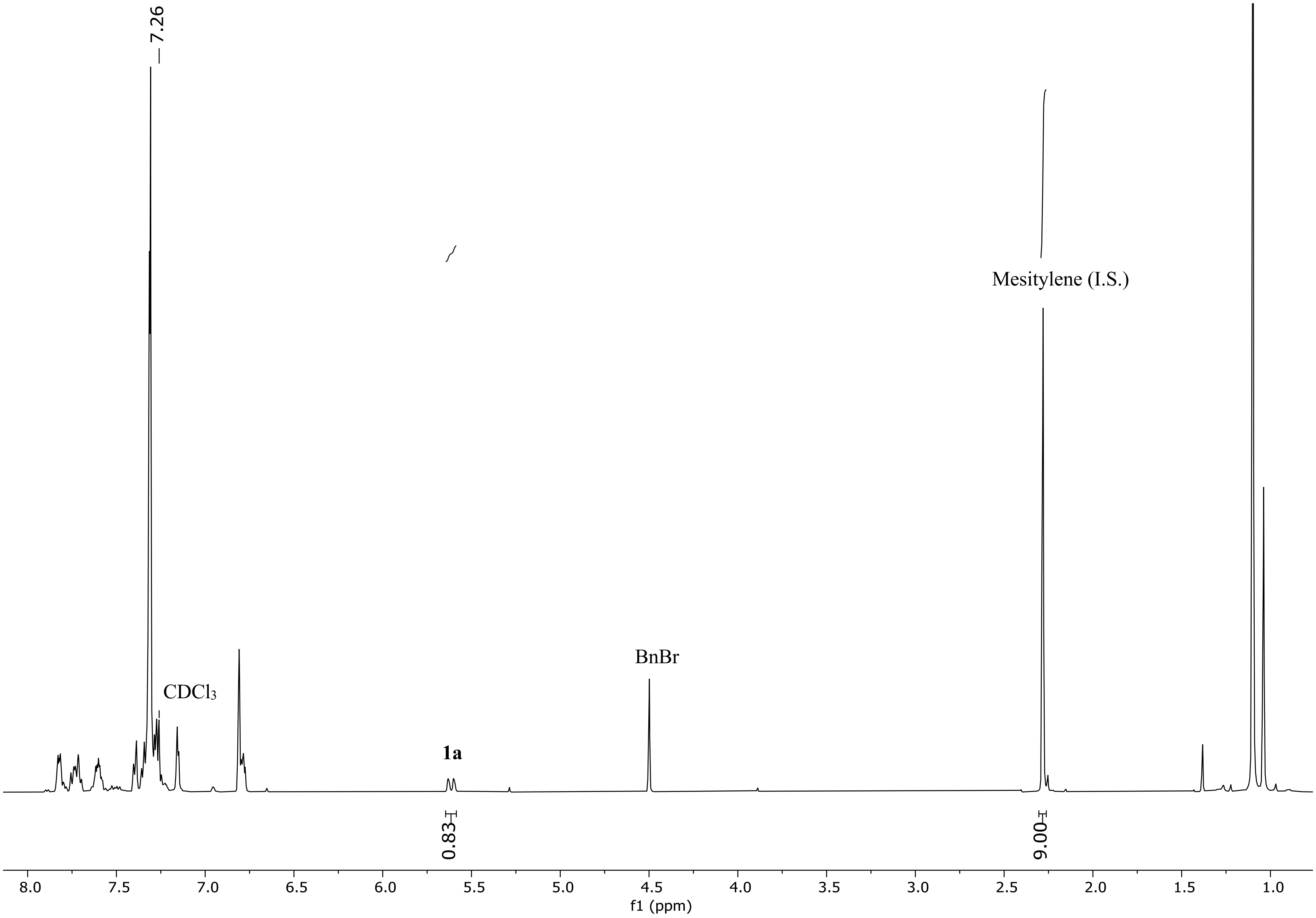
^{1}H NMR (CDCl$_3$, 500 MHz)

NMR #4. Time = 640 seconds for Phosphine **1** reaction with benzyl bromide (^{1}H NMR Yield = 63%, Actual yield = 31.5%).



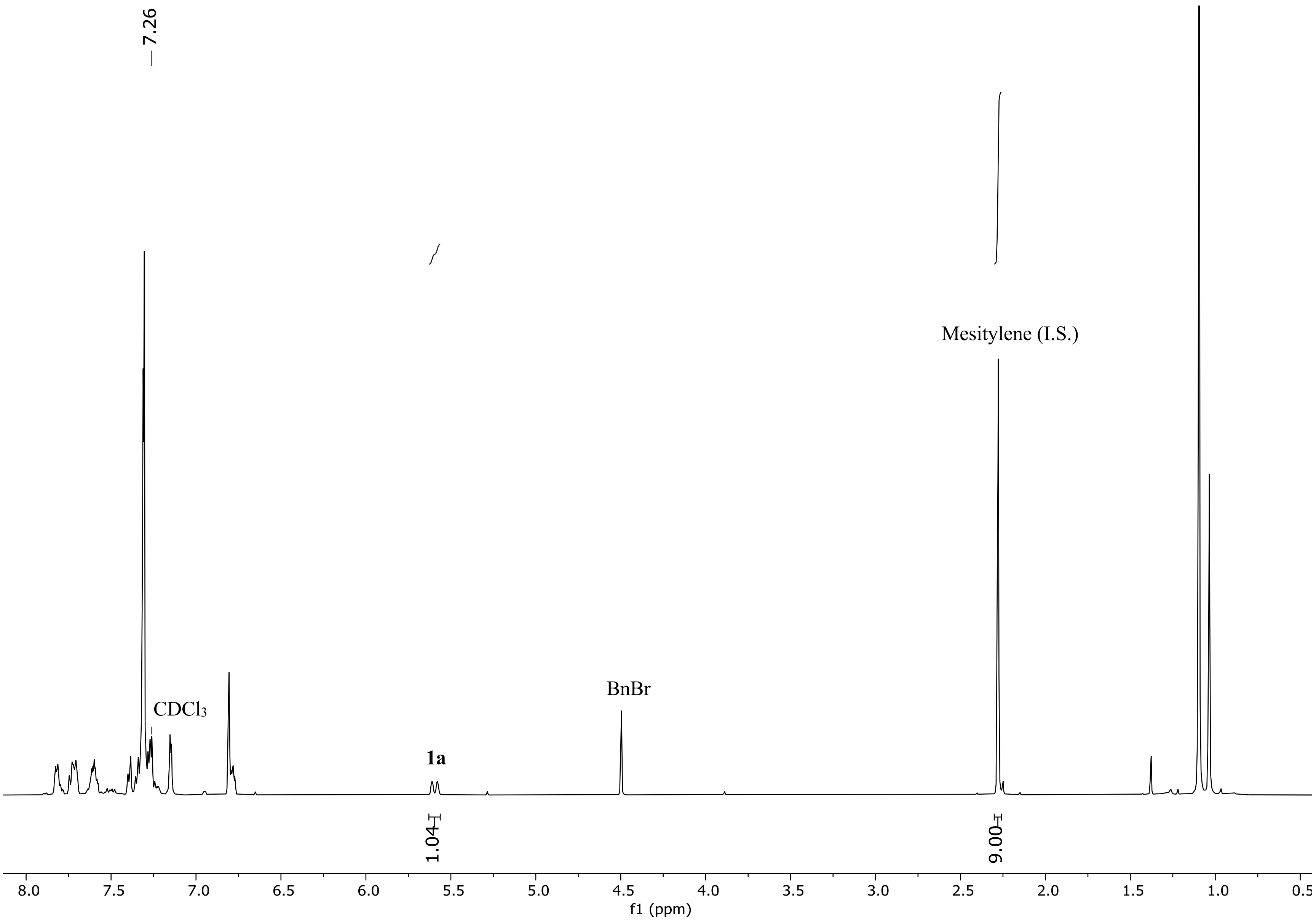
^{1}H NMR (CDCl$_3$, 500 MHz)

NMR #5. Time = 910 seconds for Phosphine **1** reaction with benzyl bromide (^{1}H NMR Yield = 83%, Actual yield = 41.5%).



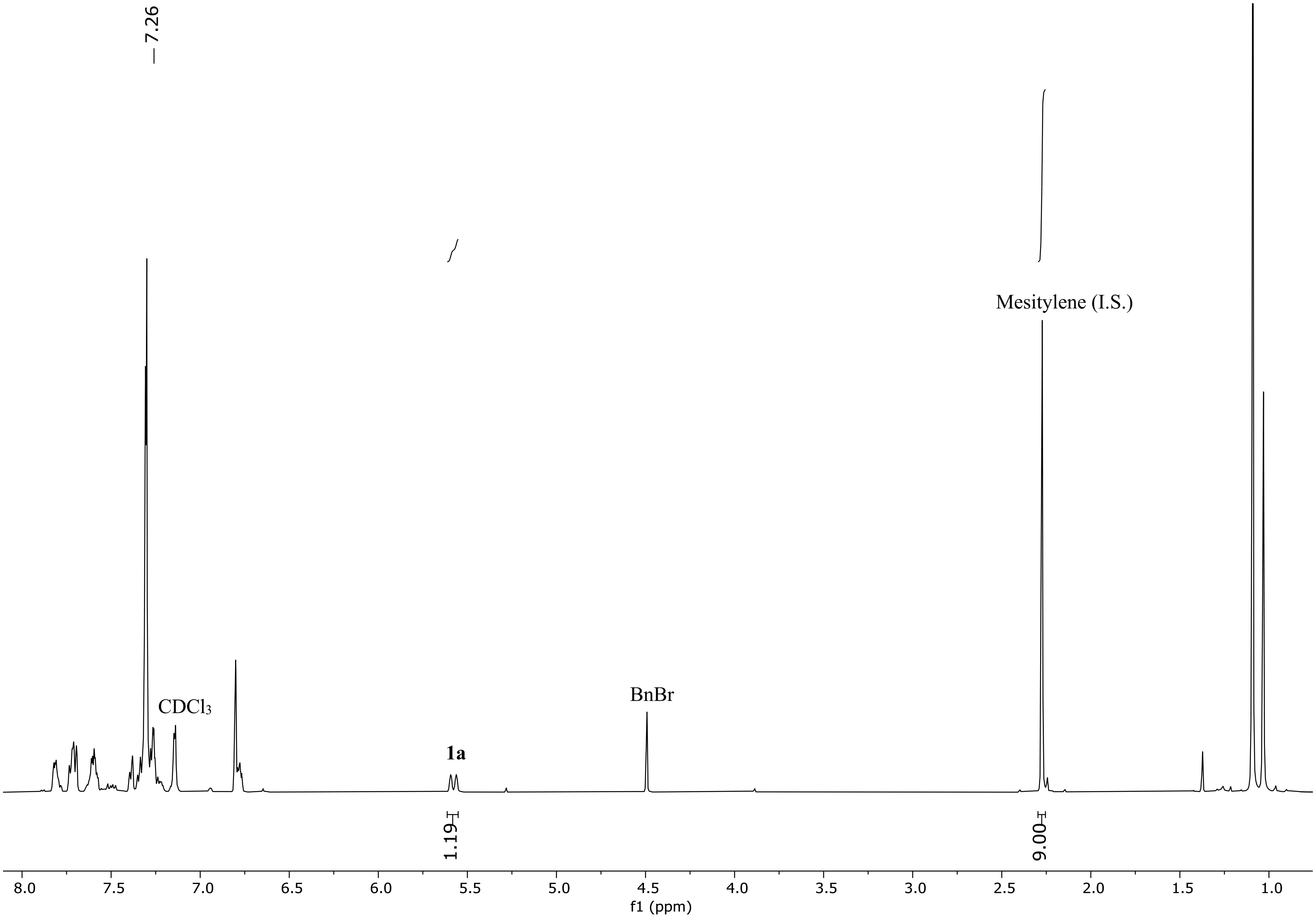
^{1}H NMR (CDCl$_3$, 500 MHz)

NMR #6. Time = 1225 seconds for Phosphine **1** reaction with benzyl bromide (^{1}H NMR Yield = 104%, Actual yield = 52%).



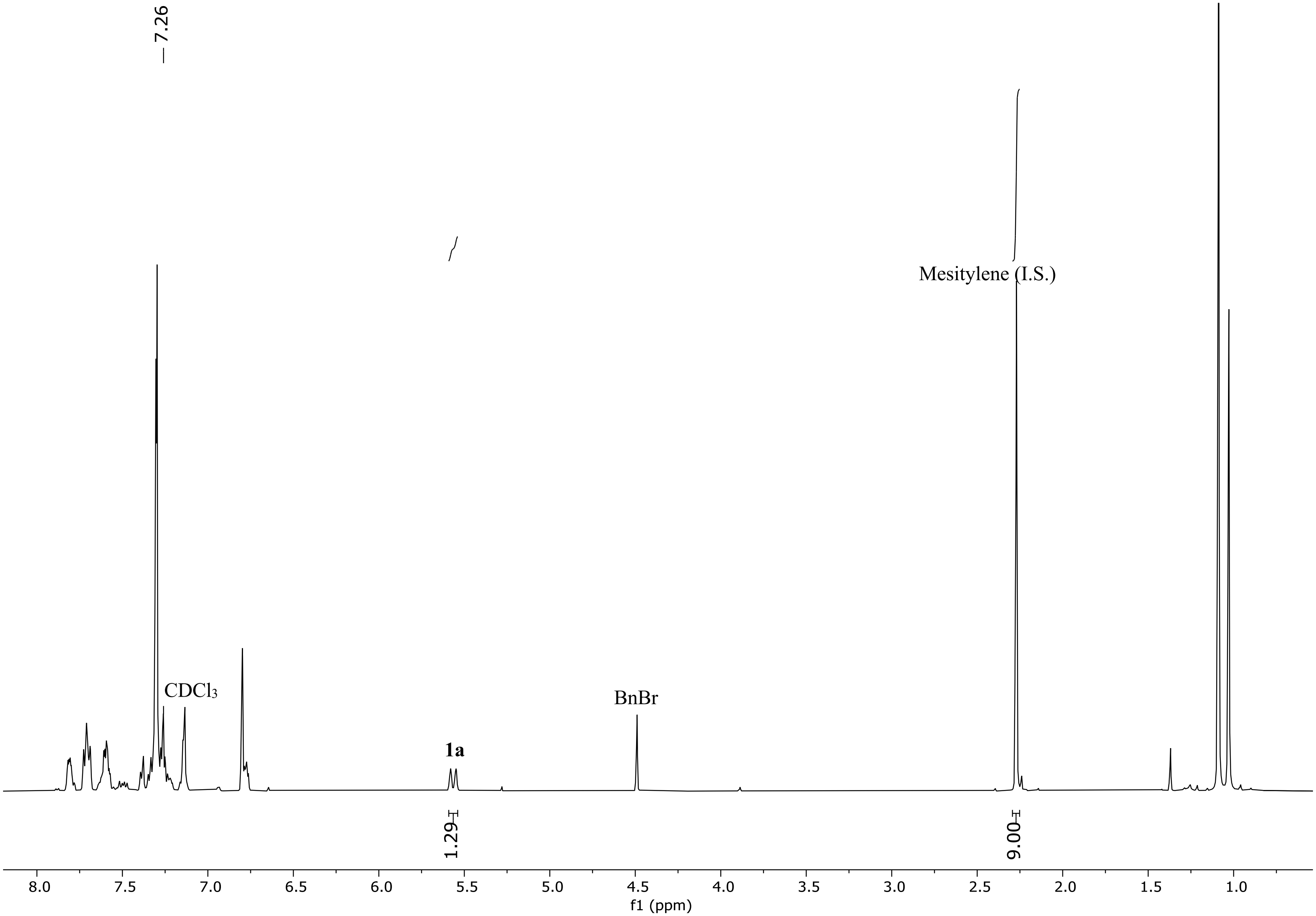
^{1}H NMR (CDCl$_3$, 500 MHz)

NMR #7. Time = 1540 seconds for Phosphine **1** reaction with benzyl bromide (^{1}H NMR Yield = 119%, Actual yield = 59.5%).



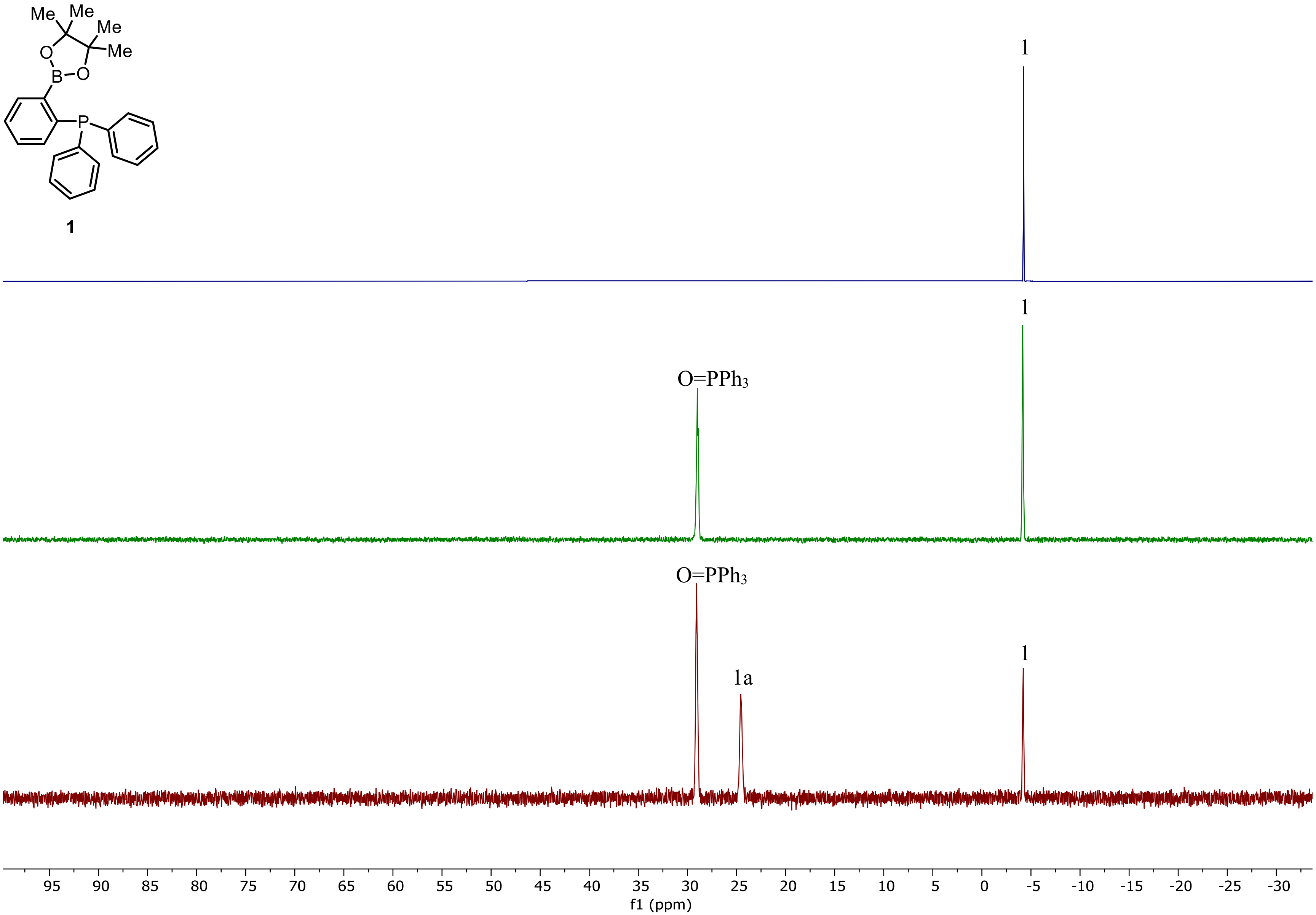
^{1}H NMR (CDCl$_3$, 500 MHz)

NMR #8. Time = 1855 seconds for Phosphine **1** reaction with benzyl bromide (^{1}H NMR Yield = 129%, Actual yield = 64.5%).

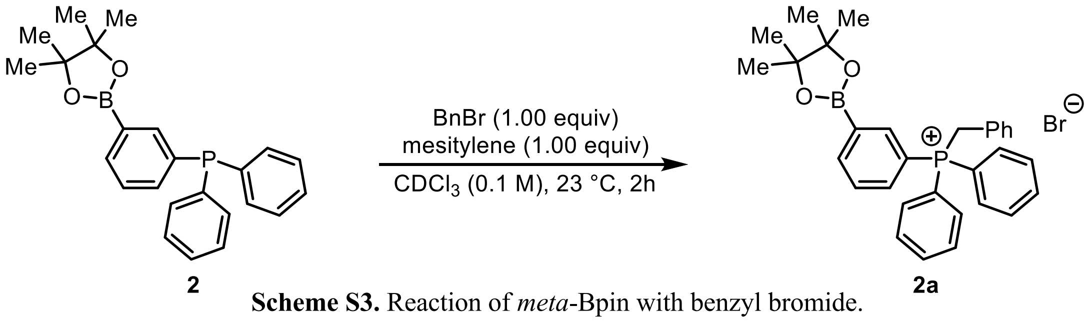


^{1}H NMR (CDCl$_3$, 500 MHz)

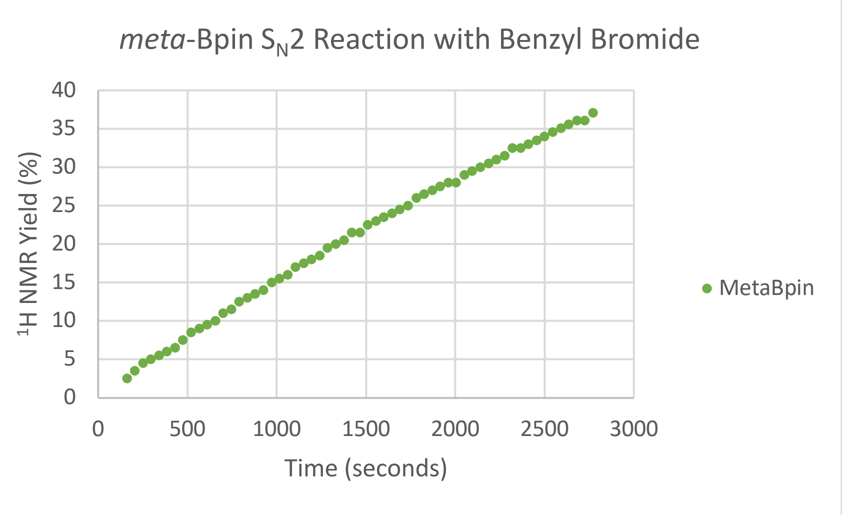
NMR #9. ^{31}P NMR spectra of **1**, **1** and OPPh$_3$ before addition of benzyl bromide, and final time point for reaction (1945 seconds).



^{31}P NMR (CDCl$_3$, 162 MHz)

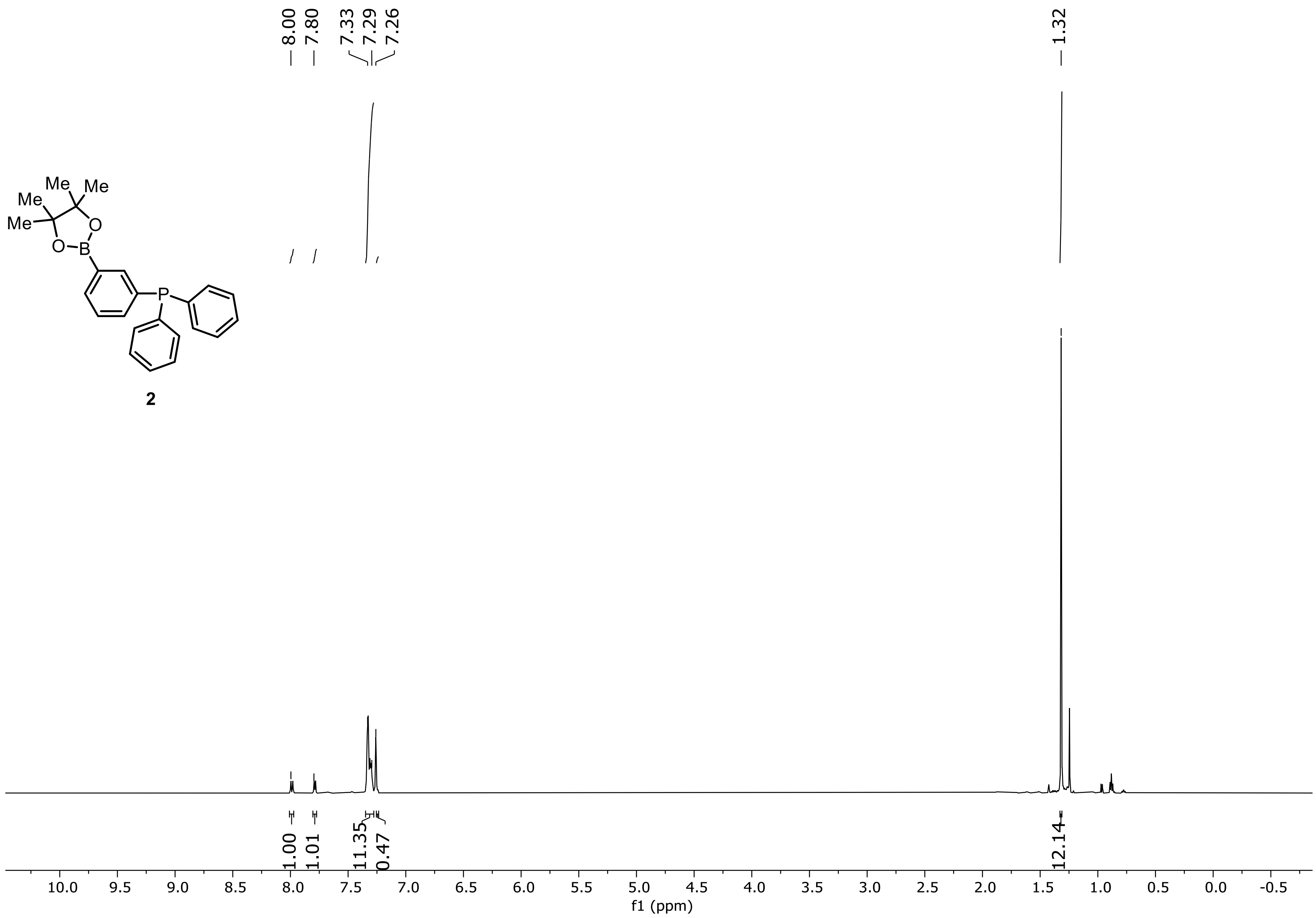


Scheme S3. Reaction of *meta*-Bpin with benzyl bromide.



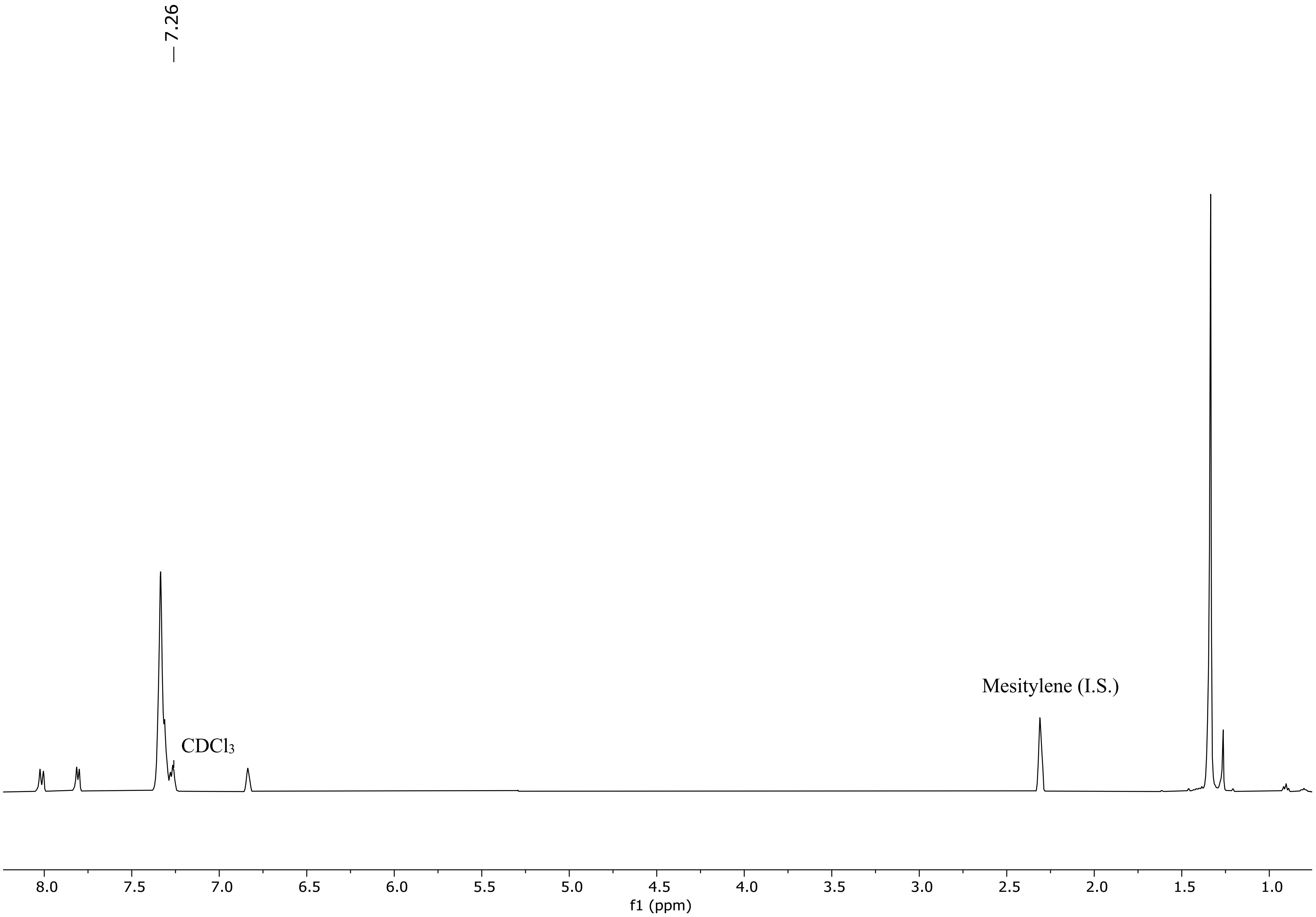
Time	NMR Yield	Time	NMR Yield	Time	NMR Yield
161	2.5	1061	16	1961	28
206	3.5	1106	17	2006	28
251	4.5	1151	17.5	2051	29
296	5	1196	18	2096	29.5
341	5.5	1241	18.5	2141	30
386	6	1286	19.5	2186	30.5
431	6.5	1331	20	2231	31
476	7.5	1376	20.5	2276	31.5
521	8.5	1421	21.5	2321	32.5
566	9	1466	21.5	2366	32.5
611	9.5	1511	22.5	2411	33
656	10	1556	23	2456	33.5
701	11	1601	23.5	2501	34
746	11.5	1646	24	2546	34.5
791	12.5	1691	24.5	2591	35
836	13	1736	25	2636	35.5
881	13.5	1781	26	2681	36
926	14	1826	26.5	2726	36
971	15	1871	27	2771	37
1016	15.5	1916	27.5		

NMR #1. Phosphine **2** ^{1}H NMR.



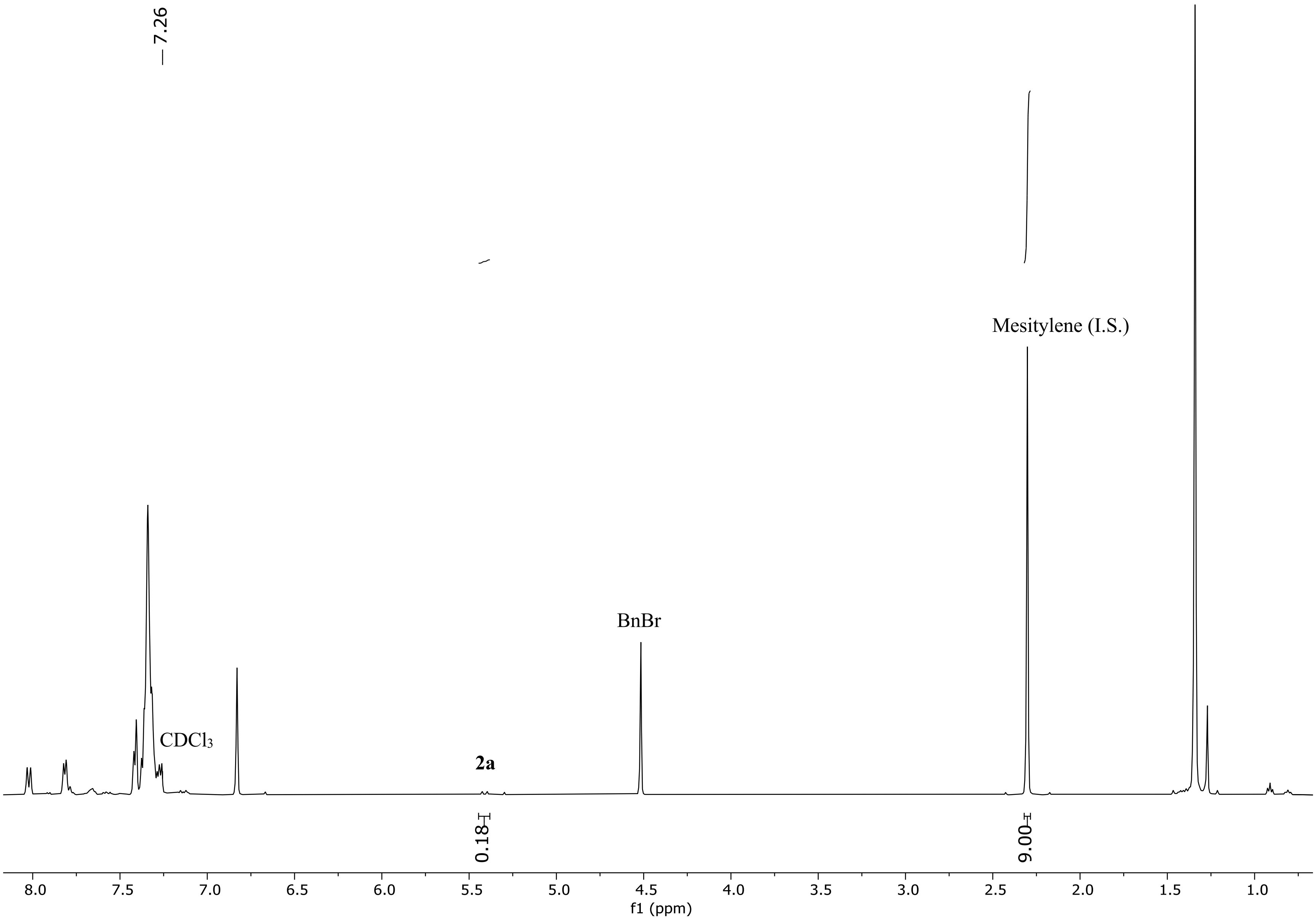
^{1}H NMR (CDCl$_3$, 600 MHz)

NMR #2. Phosphine **2** and mesitylene initial ^{1}H NMR before addition of benzyl bromide.



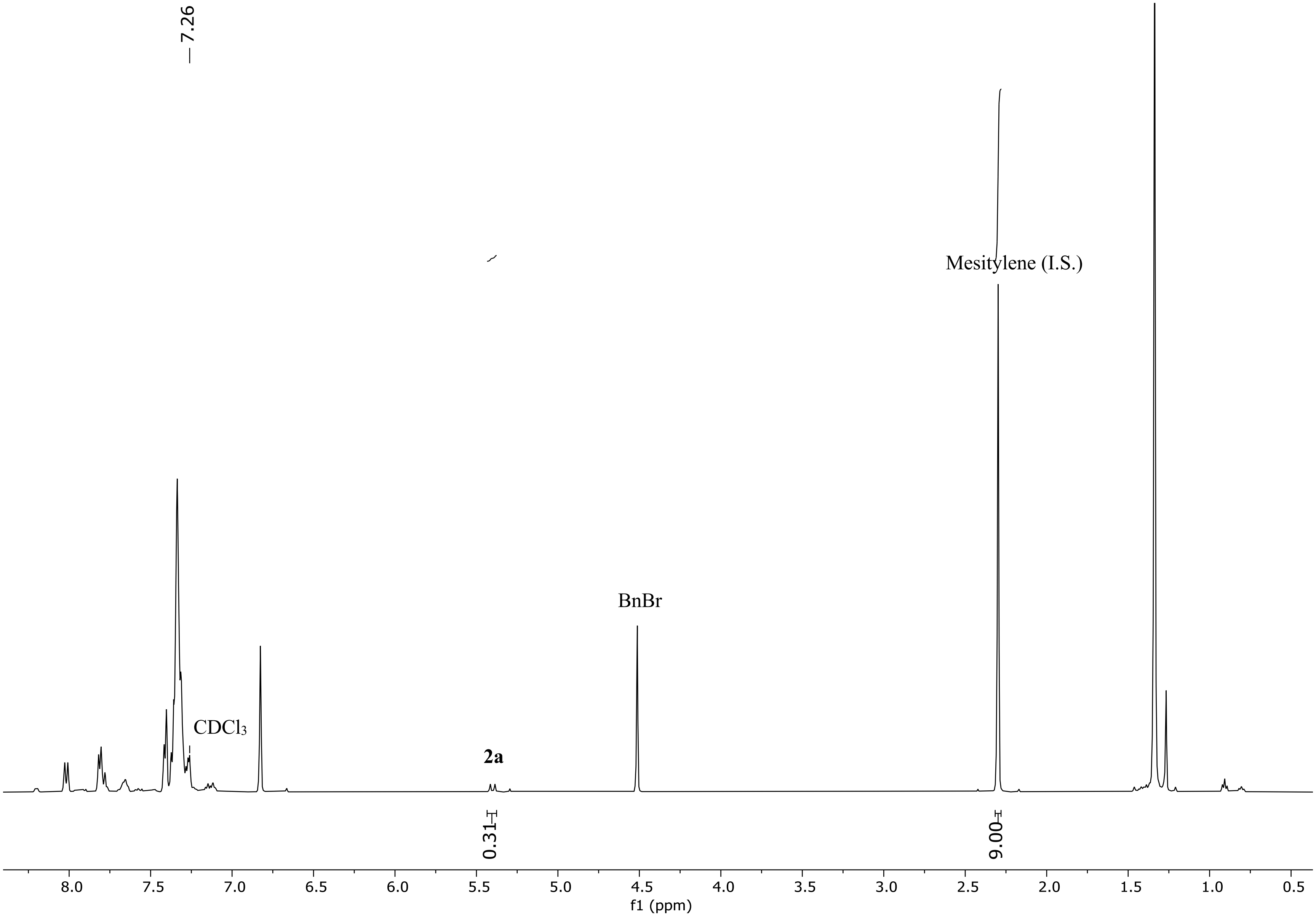
^{1}H NMR (CDCl$_3$, 500 MHz)

NMR #3. Time = 566 seconds for Phosphine **2** reaction with benzyl bromide (^{1}H NMR Yield = 18%, Actual yield = 9%).



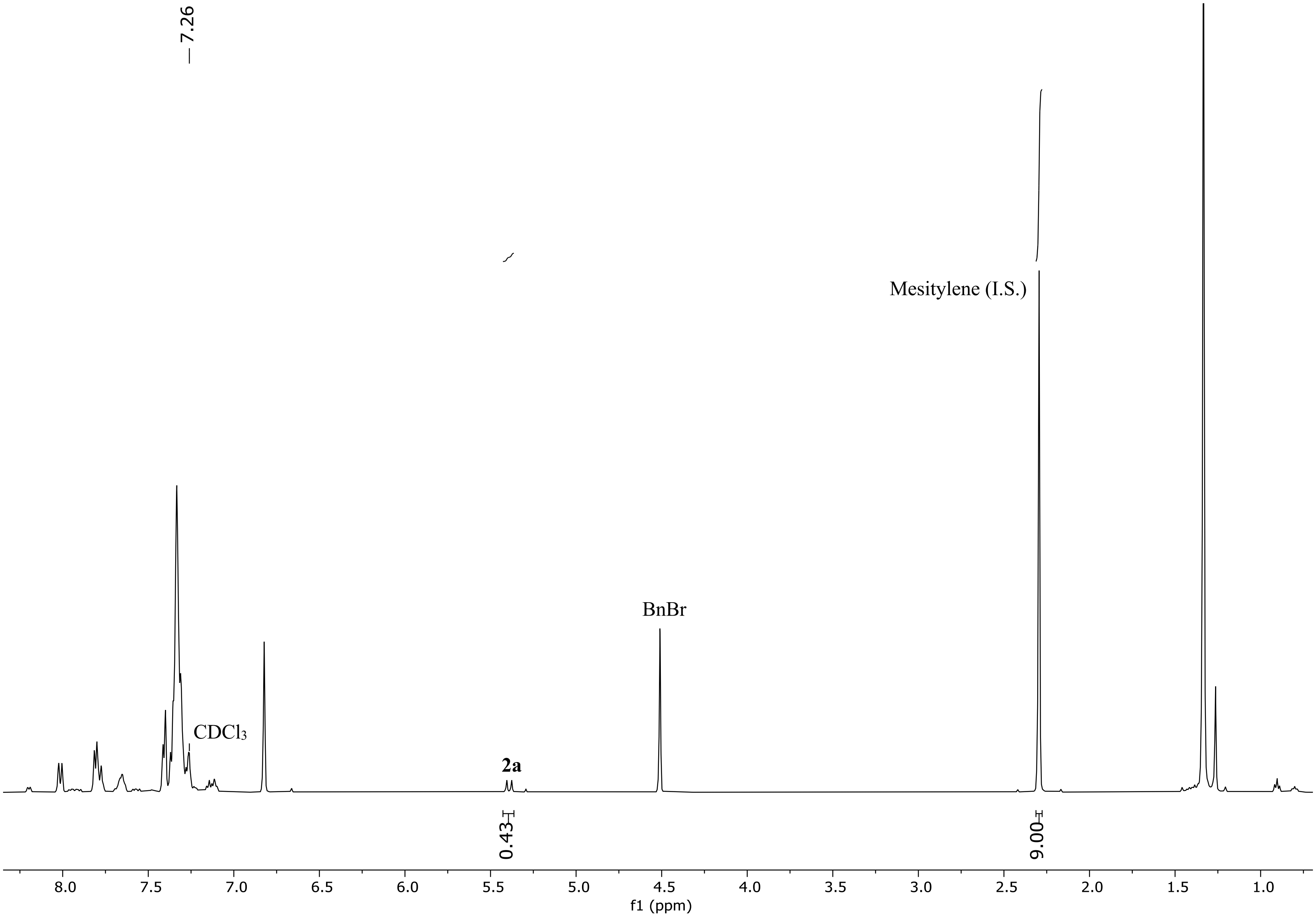
^{1}H NMR (CDCl$_3$, 500 MHz)

NMR #4. Time = 1016 seconds for Phosphine **2** reaction with benzyl bromide (^{1}H NMR Yield = 31%, Actual yield = 15.5%).



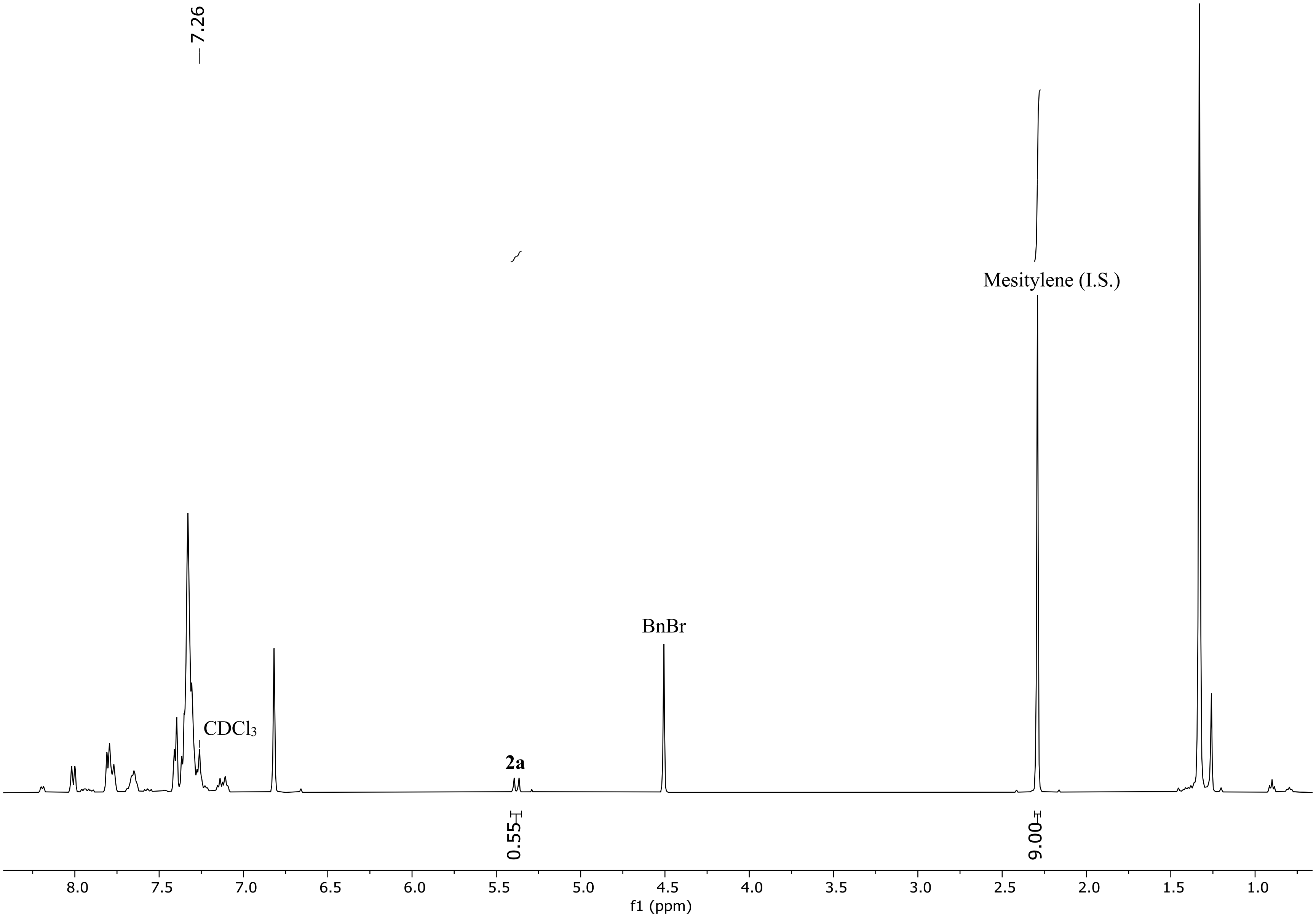
^{1}H NMR (CDCl$_3$, 500 MHz)

NMR #5. Time = 1466 seconds for Phosphine **2** reaction with benzyl bromide (^{1}H NMR Yield = 43%, Actual yield = 21.5%).



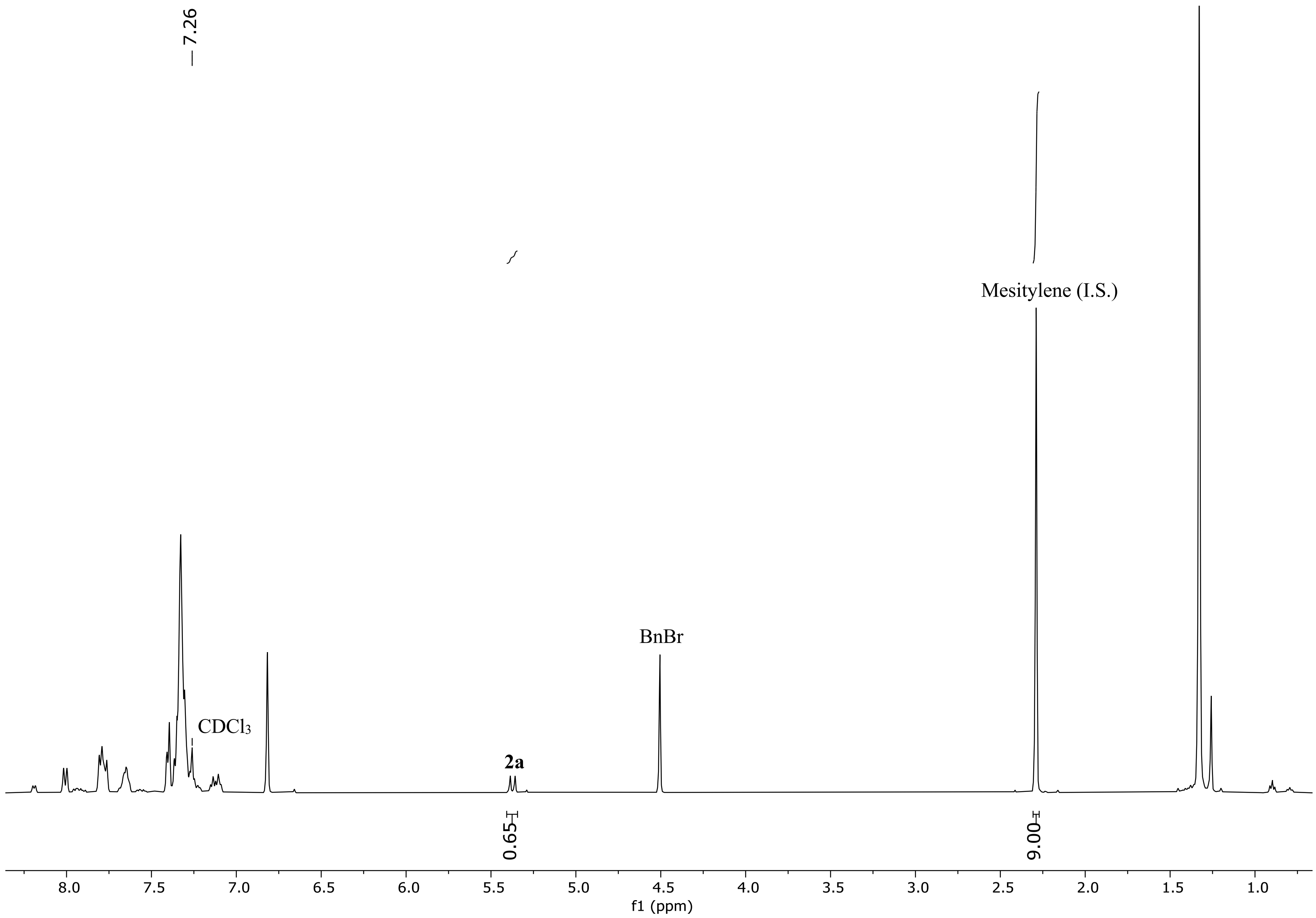
^{1}H NMR ($CDCl_3$, 500 MHz)

NMR #6. Time = 1916 seconds for Phosphine **2** reaction with benzyl bromide (^{1}H NMR Yield = 55%, Actual yield = 27.5%).



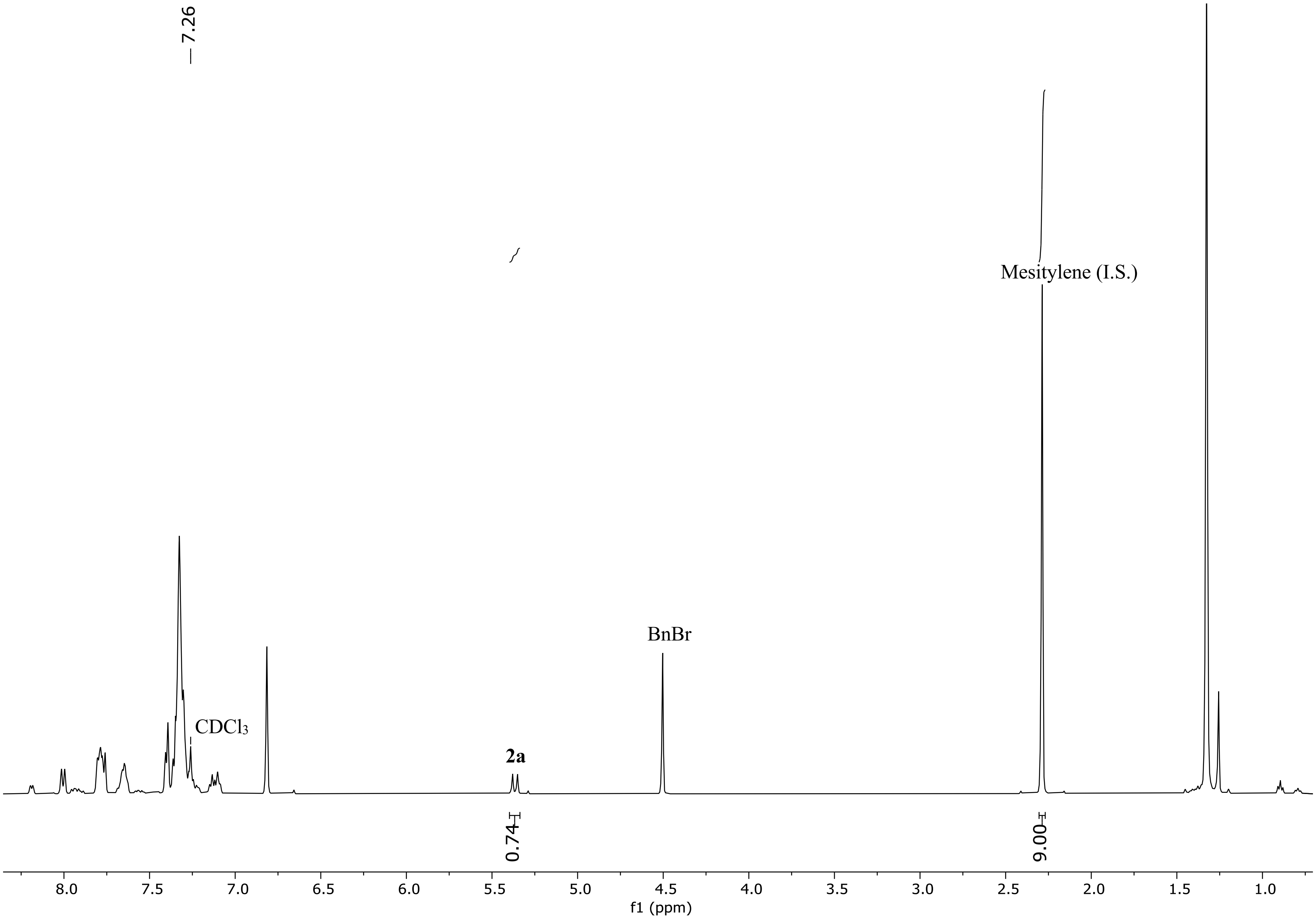
^{1}H NMR ($CDCl_3$, 500 MHz)

NMR #7. Time = 2366 seconds for Phosphine **2** reaction with benzyl bromide (^{1}H NMR Yield = 65%, Actual yield = 32.5%).

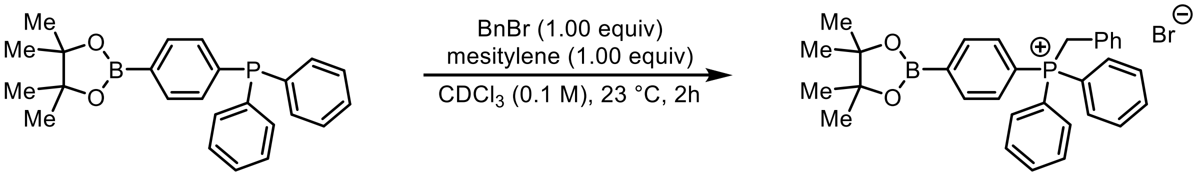


^{1}H NMR (CDCl$_3$, 500 MHz)

NMR #8. Time = 2771 seconds for Phosphine **2** reaction with benzyl bromide (^{1}H NMR Yield = 74%, Actual yield = 37%).

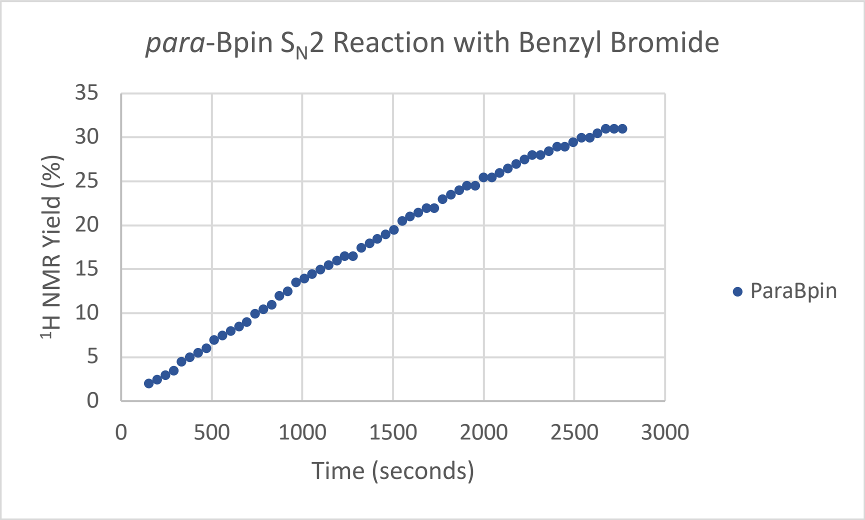


^{1}H NMR ($CDCl_3$, 500 MHz)



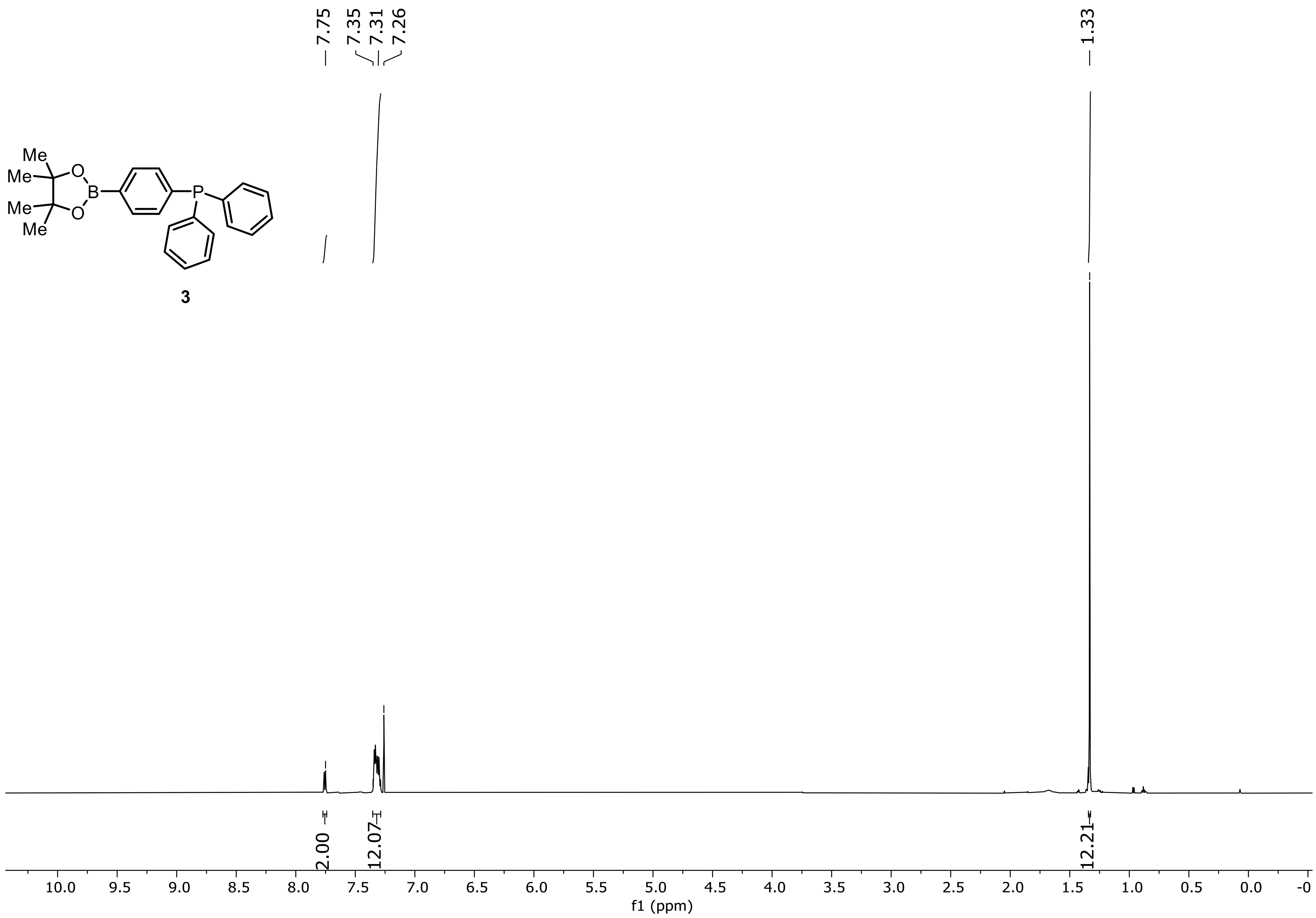
3 **3a**

Scheme S4. Reaction of *para*-Bpin with benzyl bromide.



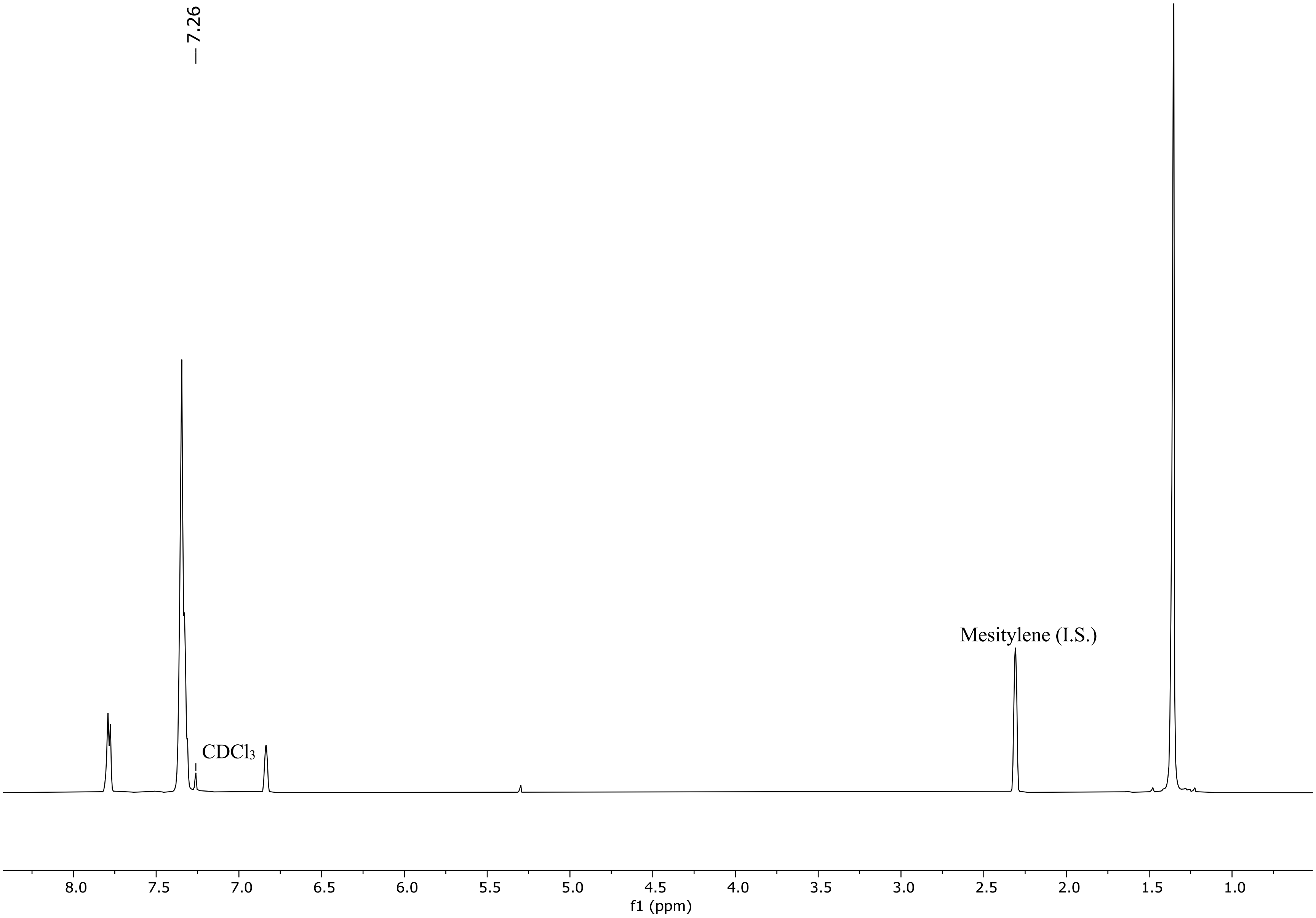
Time	NMR Yield	Time	NMR Yield	Time	NMR Yield
154	2	1054	14.5	1954	24.5
199	2.5	1099	15	1999	25.5
244	3	1144	15.5	2044	25.5
289	3.5	1189	16	2089	26
334	4.5	1234	16.5	2134	26.5
379	5	1279	16.5	2179	27
424	5.5	1324	17.5	2224	27.5
469	6	1369	18	2269	28
514	7	1414	18.5	2314	28
559	7.5	1459	19	2359	28.5
604	8	1504	19.5	2404	29
649	8.5	1549	20.5	2449	29
694	9	1594	21	2494	29.5
739	10	1639	21.5	2539	30
784	10.5	1684	22	2584	30
829	11	1729	22	2629	30.5
874	12	1774	23	2674	31
919	12.5	1819	23.5	2719	31
964	13.5	1864	24	2764	31
1009	14	1909	24.5		

NMR #1. Phosphine **3** ^{1}H NMR.



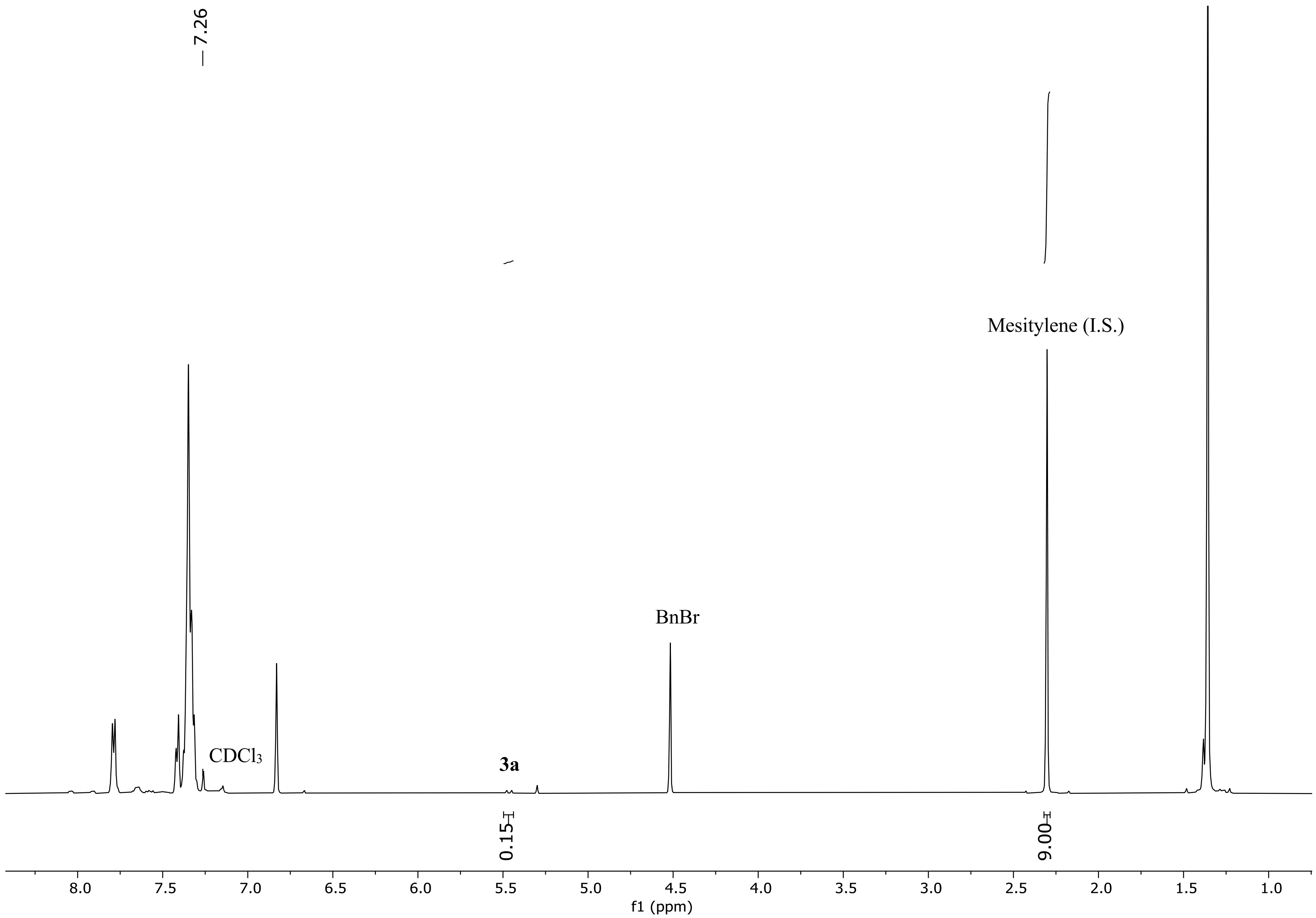
^{1}H NMR (CDCl$_3$, 600 MHz)

NMR #2. Phosphine **3** and mesitylene initial ^{1}H NMR before addition of benzyl bromide.



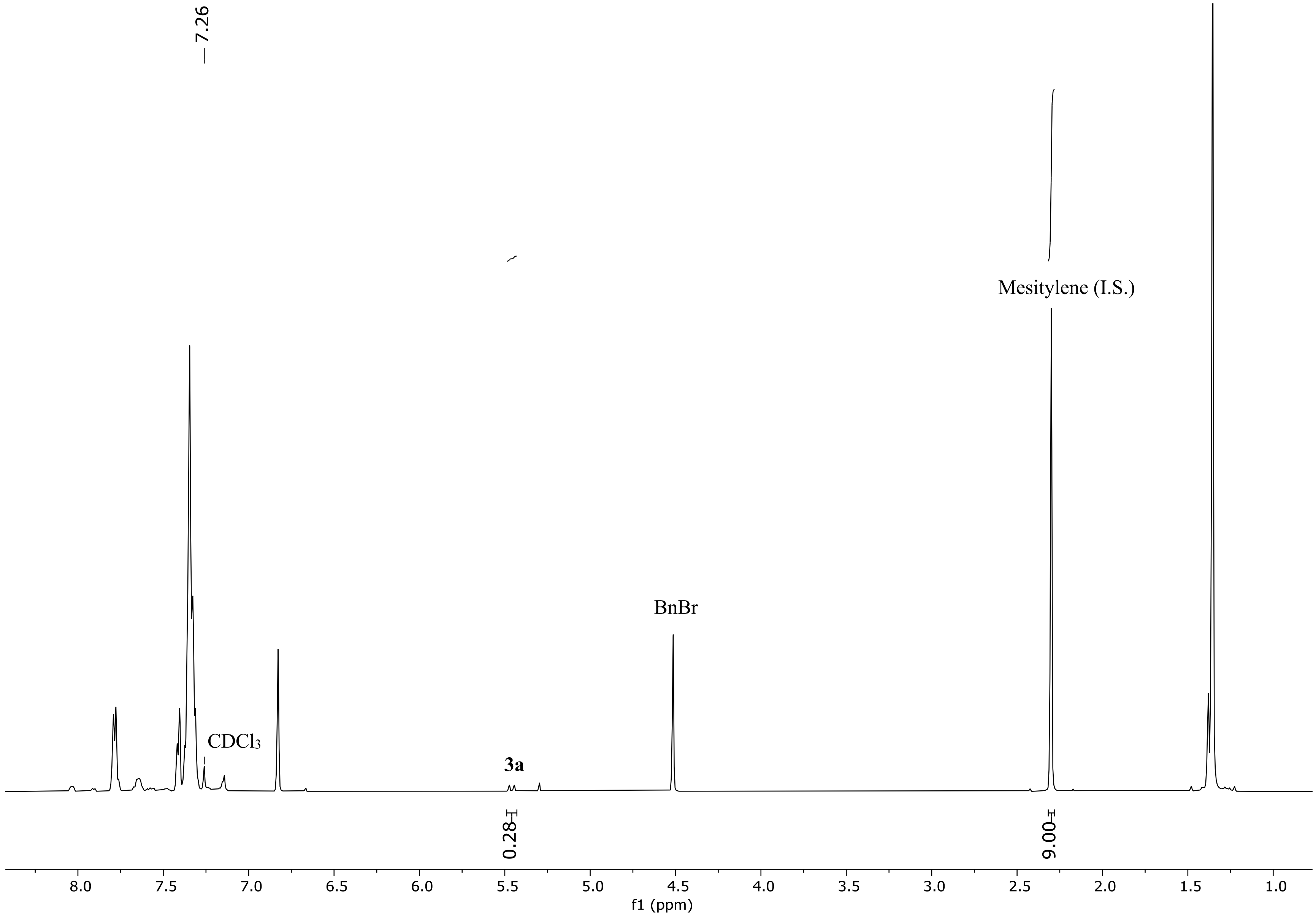
^{1}H NMR ($CDCl_3$, 500 MHz)

NMR #3. Time = 559 seconds for Phosphine **3** reaction with benzyl bromide (^{1}H NMR Yield = 15%, Actual yield = 7.5%).



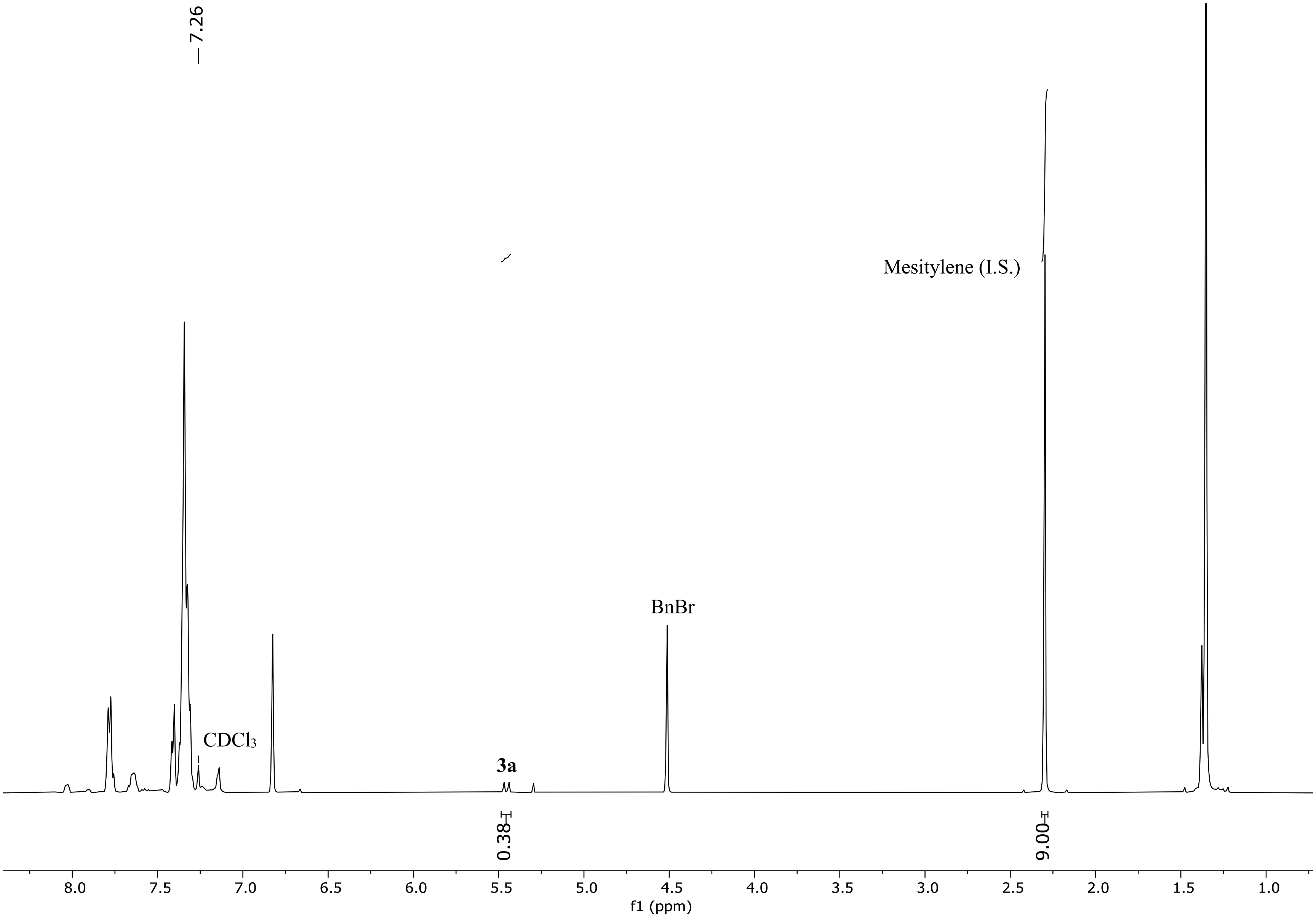
^{1}H NMR (CDCl$_3$, 500 MHz)

NMR #4. Time = 1009 seconds for Phosphine **3** reaction with benzyl bromide (^{1}H NMR Yield = 28%, Actual yield = 14%).



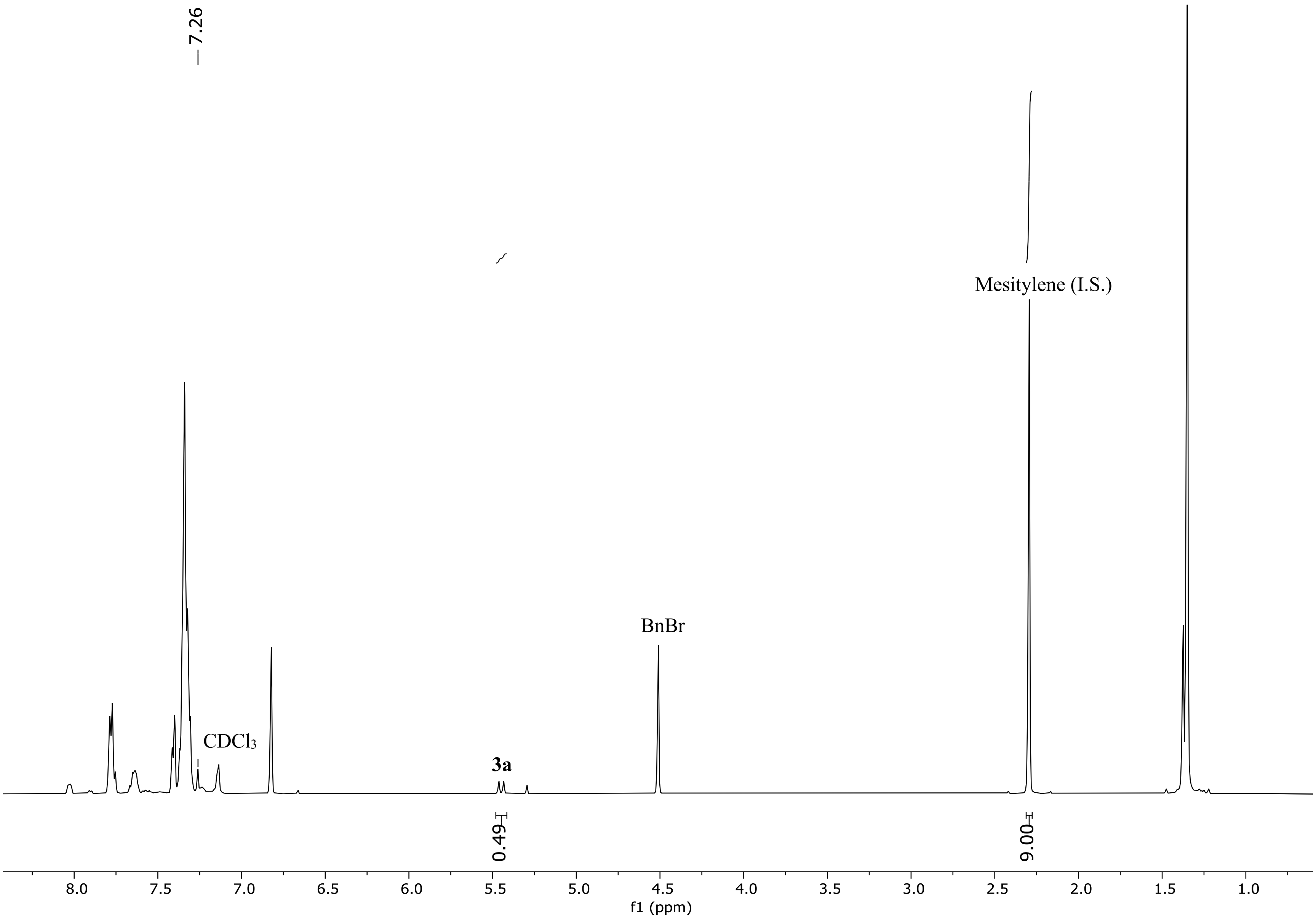
^{1}H NMR (CDCl$_3$, 500 MHz)

NMR #5. Time = 1459 seconds for Phosphine **3** reaction with benzyl bromide (^{1}H NMR Yield = 38%, Actual yield = 19%).



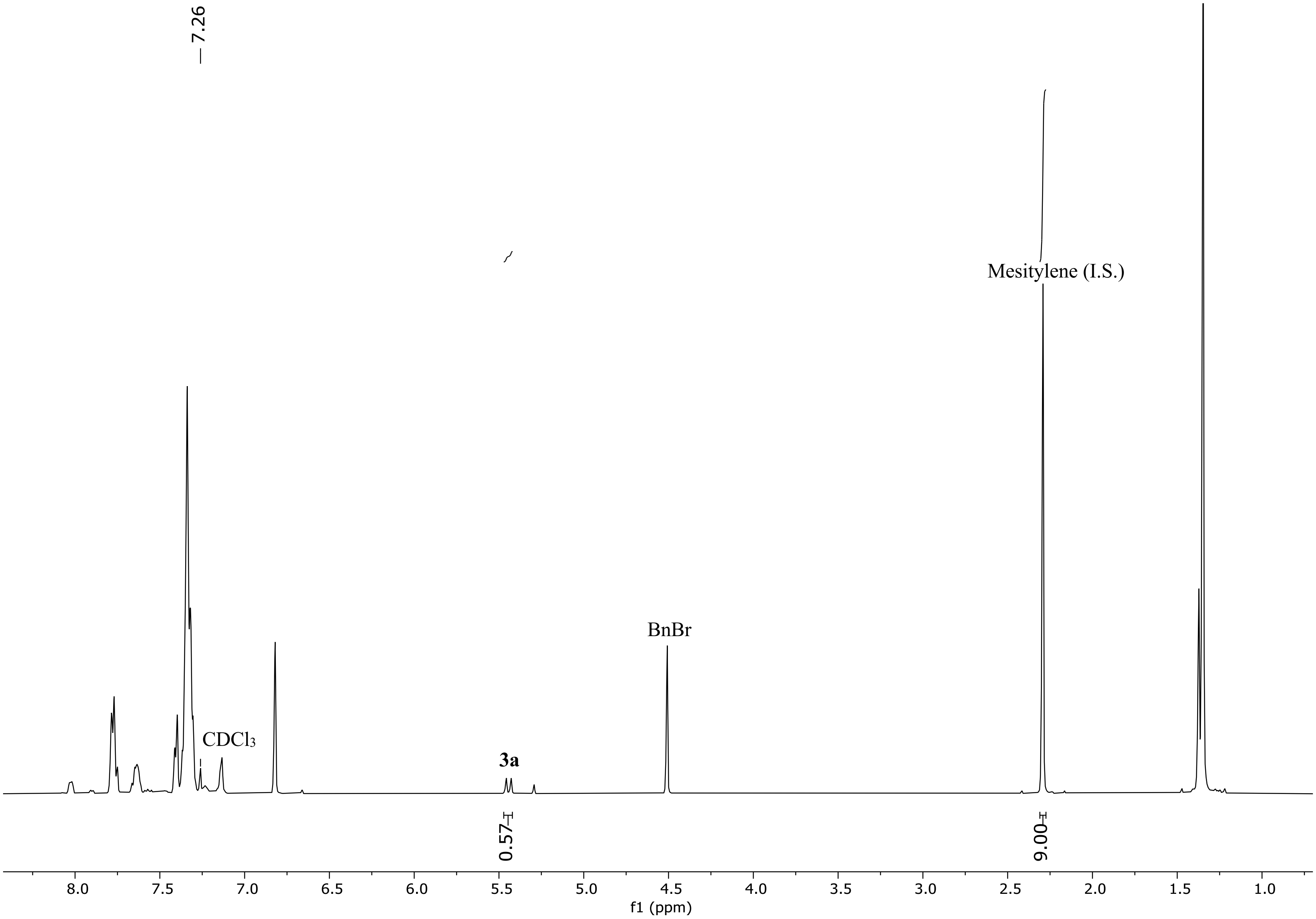
^{1}H NMR ($CDCl_3$, 500 MHz)

NMR #6. Time = 1909 seconds for Phosphine **3** reaction with benzyl bromide (^{1}H NMR Yield = 49%, Actual yield = 24.5%).



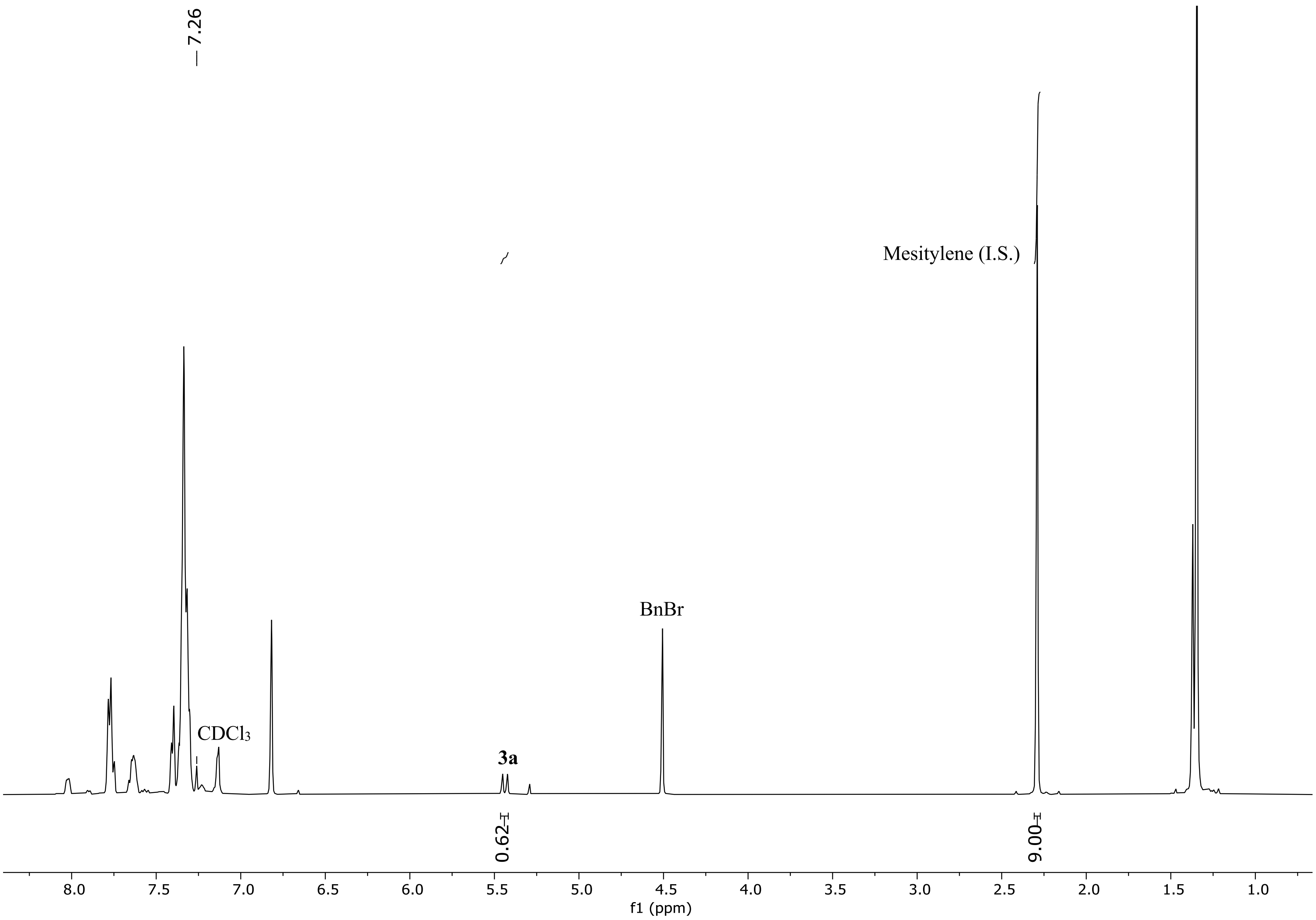
^{1}H NMR ($CDCl_3$, 500 MHz)

NMR #7. Time = 2359 seconds for Phosphine **3** reaction with benzyl bromide (^{1}H NMR Yield = 57%, Actual yield = 28.5%).

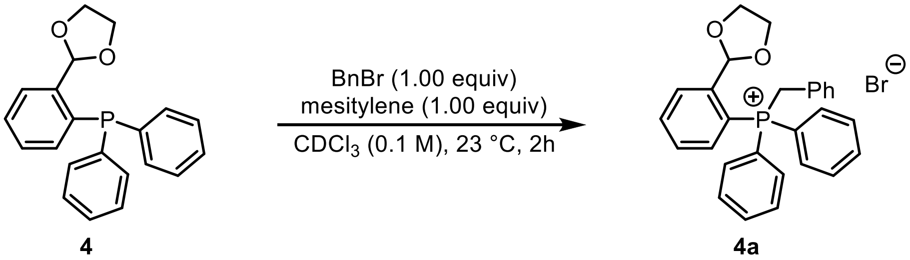


^{1}H NMR (CDCl$_3$, 500 MHz)

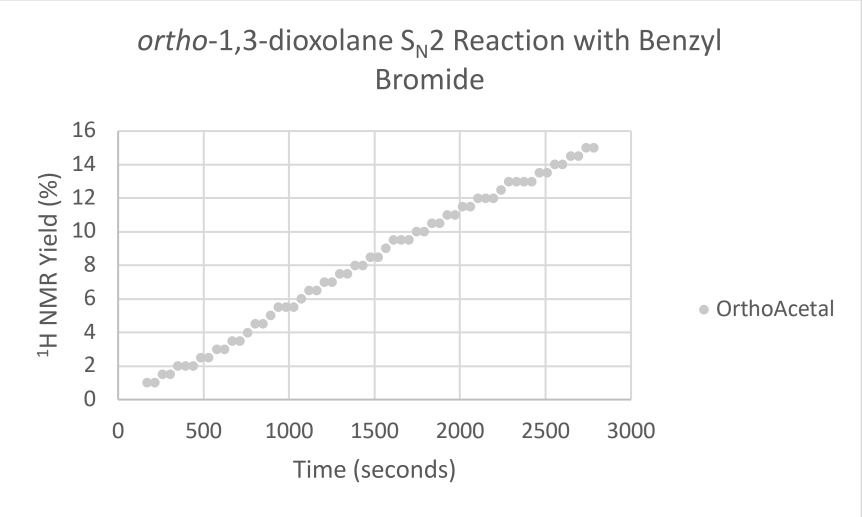
NMR #8. Time = 2764 seconds for Phosphine **3** reaction with benzyl bromide (^{1}H NMR Yield = 62%, Actual yield = 31%).



^{1}H NMR (CDCl$_3$, 500 MHz)

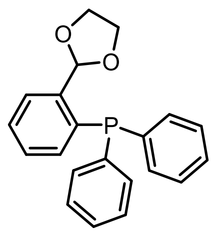


Scheme S10. Reaction of *ortho*- 1,3-dioxolane with benzyl

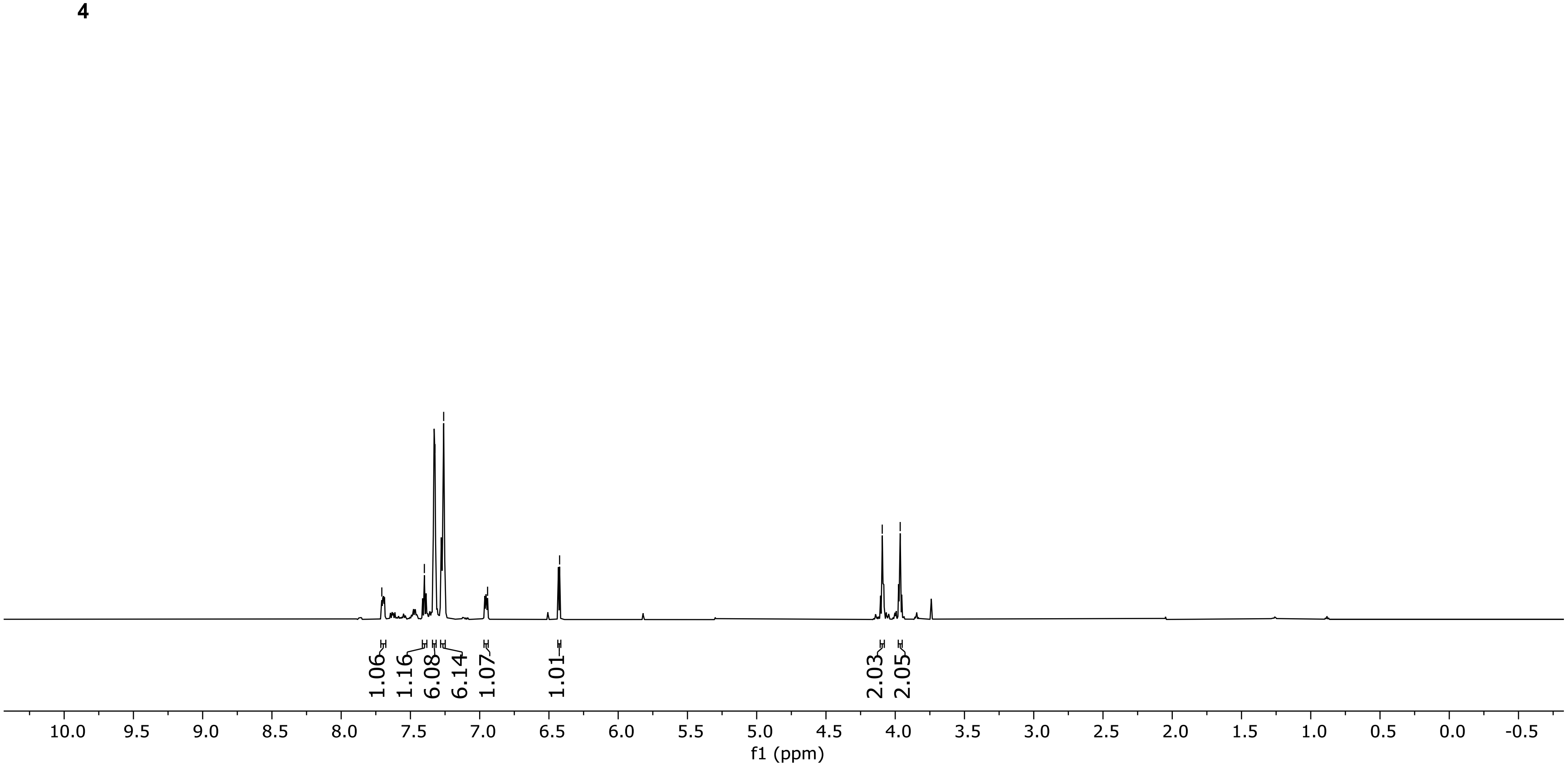


Time	NMR Yield	Time	NMR Yield	Time	NMR Yield
171	1	1071	6	1971	11
216	1	1116	6.5	2016	11.5
261	1.5	1161	6.5	2061	11.5
306	1.5	1206	7	2106	12
351	2	1251	7	2151	12
396	2	1296	7.5	2196	12
441	2	1341	7.5	2241	12.5
486	2.5	1386	8	2286	13
531	2.5	1431	8	2331	13
576	3	1476	8.5	2376	13
621	3	1521	8.5	2421	13
666	3.5	1566	9	2466	13.5
711	3.5	1611	9.5	2511	13.5
756	4	1656	9.5	2556	14
801	4.5	1701	9.5	2601	14
846	4.5	1746	10	2646	14.5
891	5	1791	10	2691	14.5
936	5.5	1836	10.5	2736	15
981	5.5	1881	10.5	2781	15
1026	5.5	1926	11		

NMR #1. Phosphine **4** ^{1}H NMR.

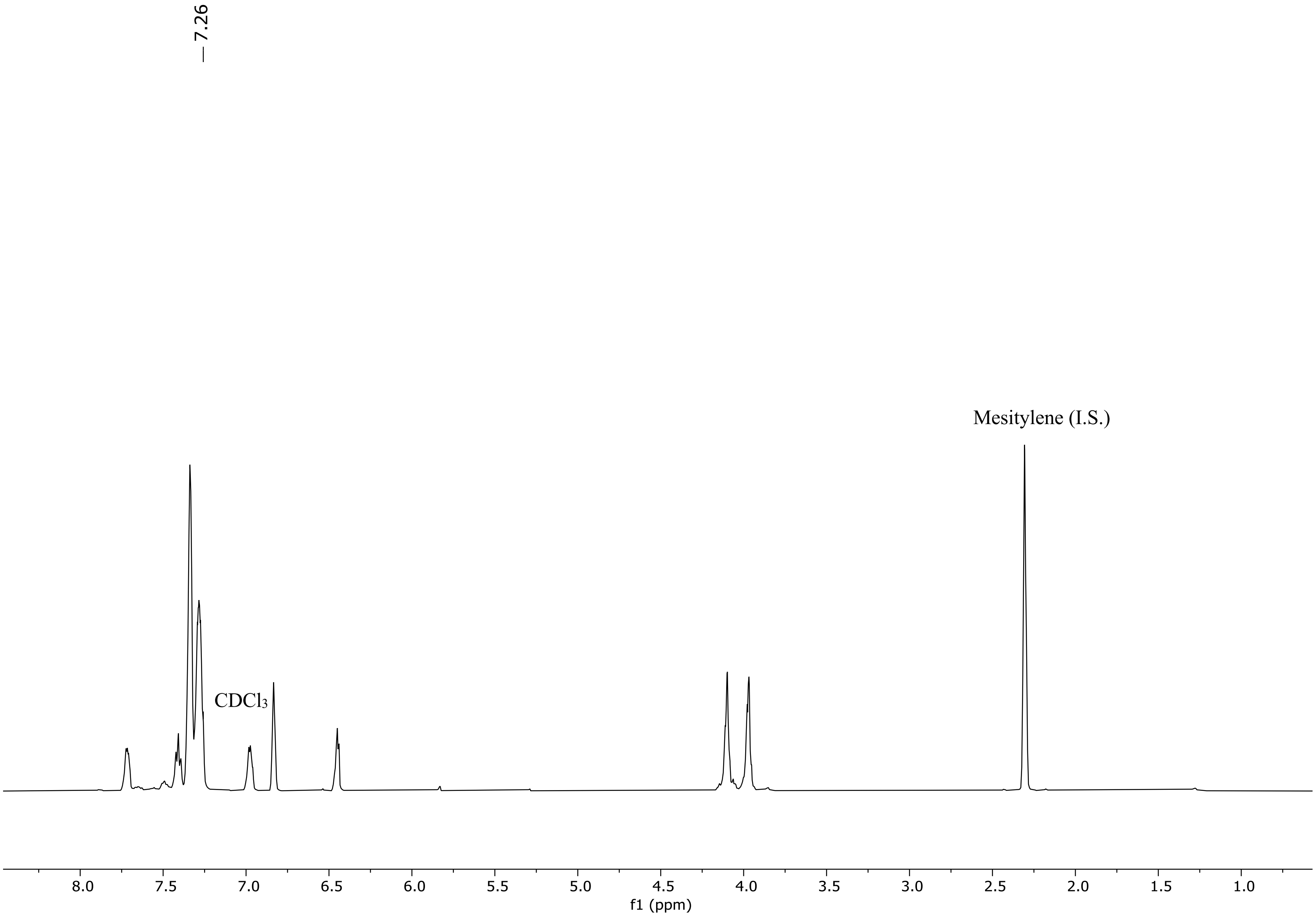


4



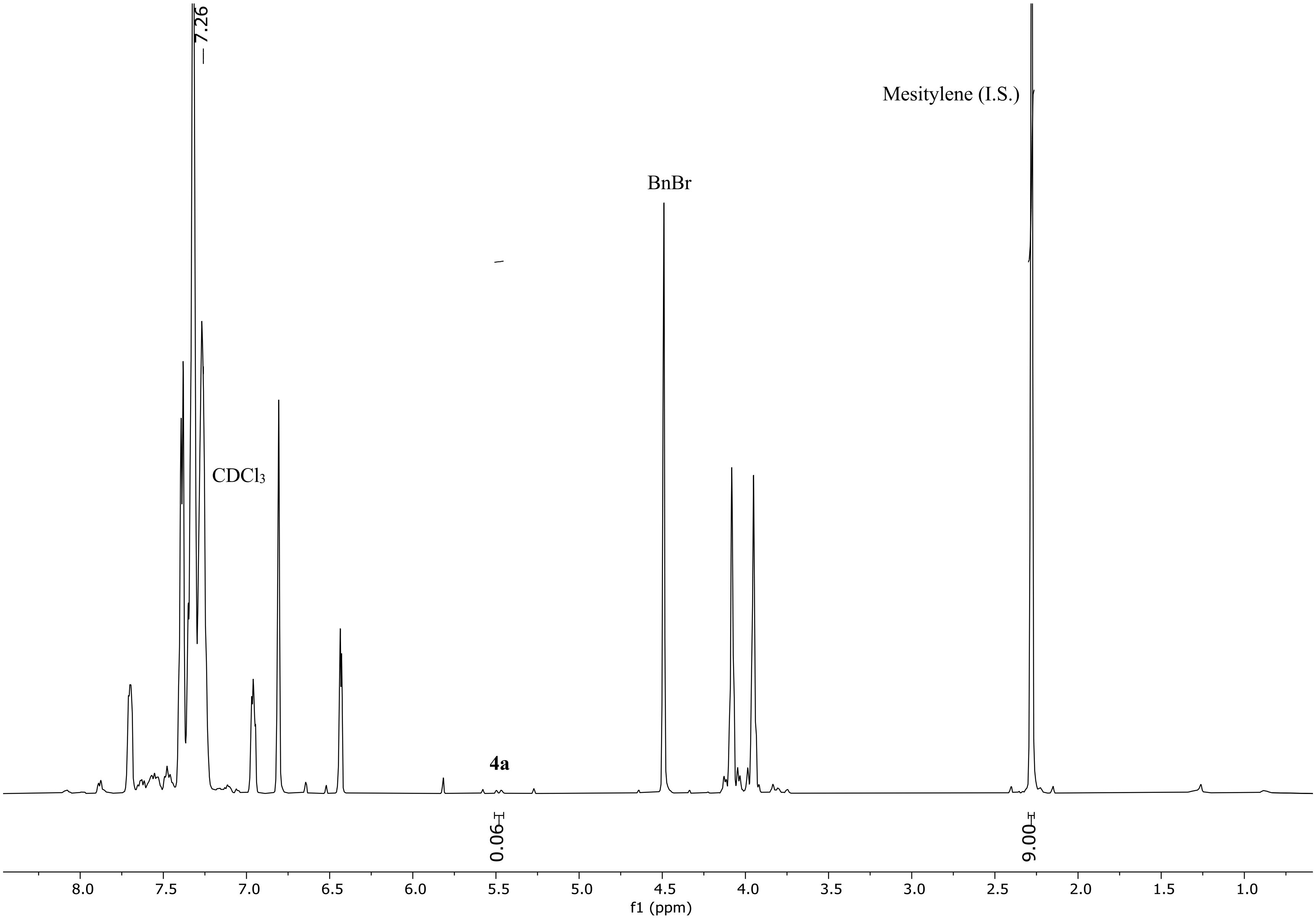
^{1}H NMR (CDCl$_3$, 600 MHz)

NMR #2. Phosphine **4** and mesitylene initial ^{1}H NMR before addition of benzyl bromide.



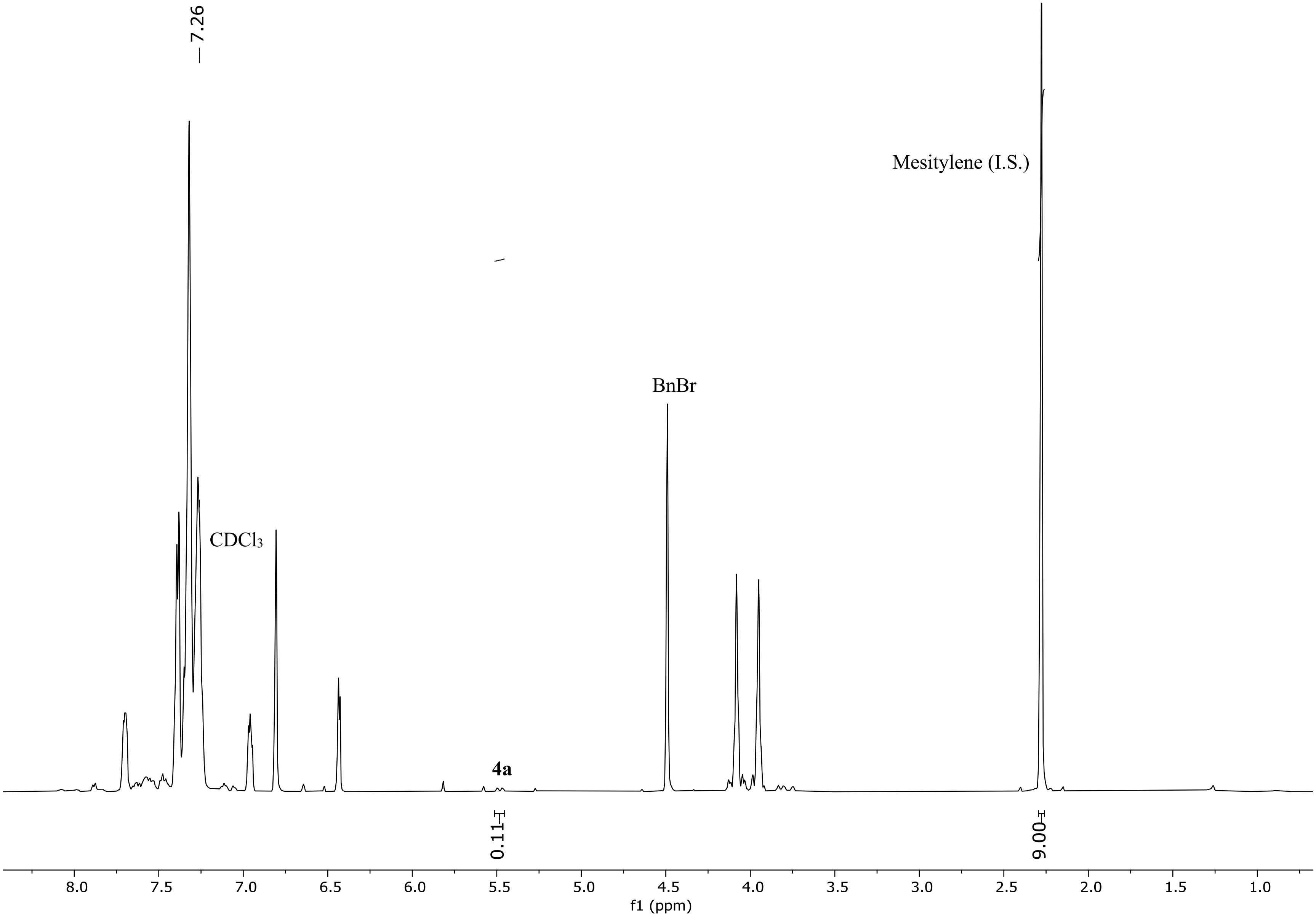
^{1}H NMR (CDCl$_3$, 500 MHz)

NMR #3. Time = 576 seconds for Phosphine **4** reaction with benzyl bromide (^{1}H NMR Yield = 6%, Actual yield = 3%).



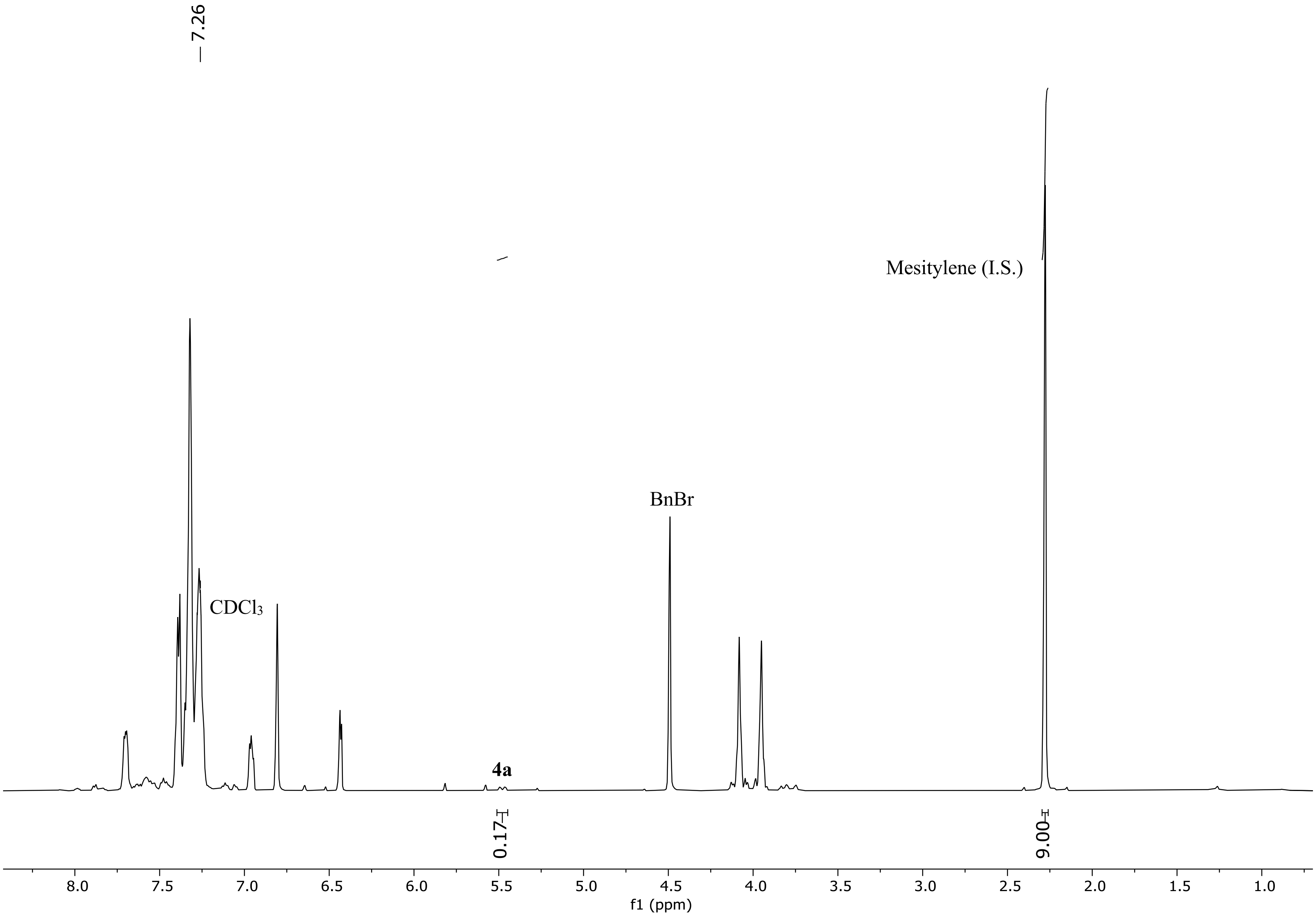
^{1}H NMR (CDCl$_3$, 500 MHz)

NMR #4. Time = 1026 seconds for Phosphine **4** reaction with benzyl bromide (^{1}H NMR Yield = 11%, Actual yield = 5.5%).



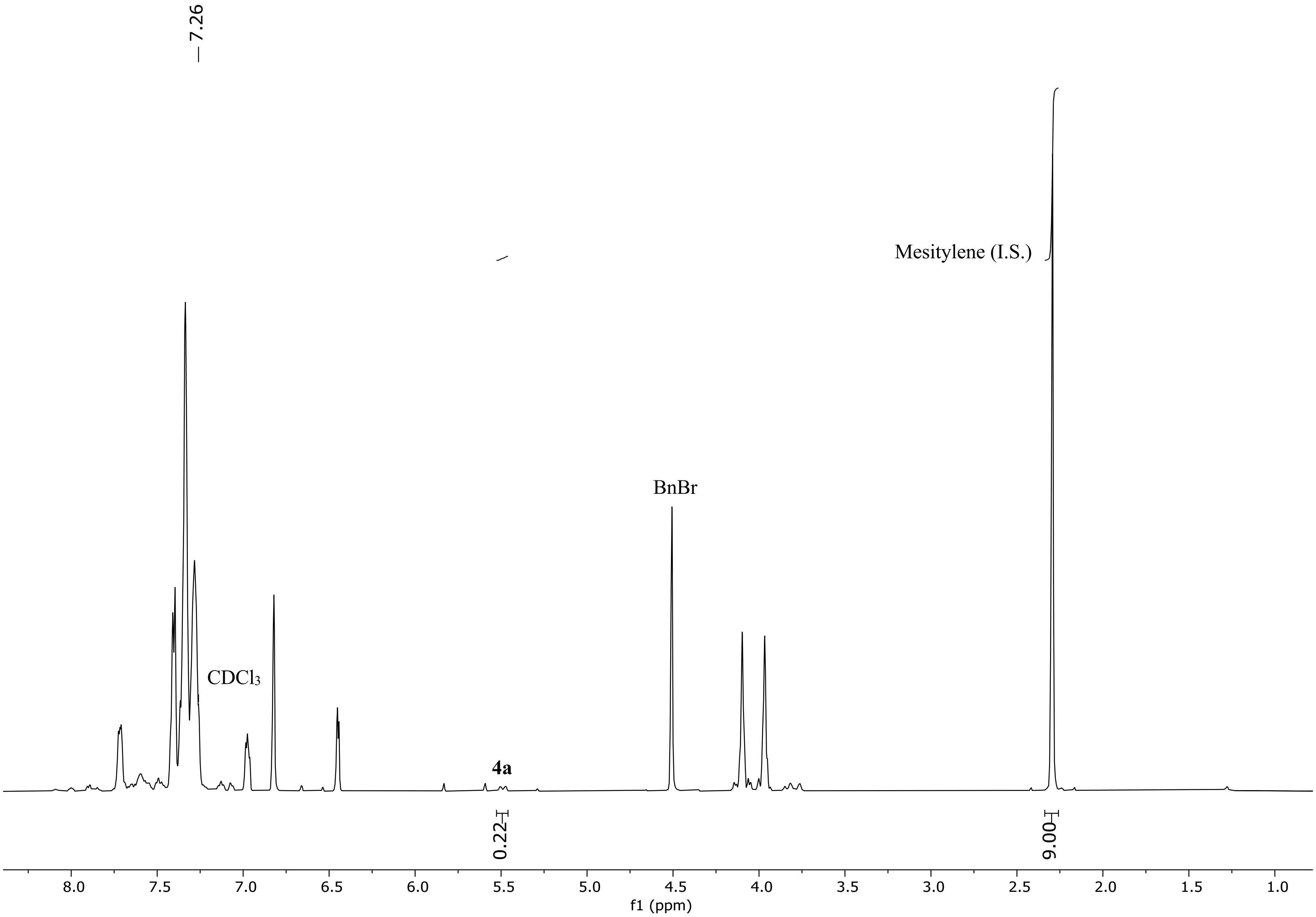
^{1}H NMR (CDCl$_3$, 500 MHz)

NMR #5. Time = 1476 seconds for Phosphine **4** reaction with benzyl bromide (^{1}H NMR Yield = 17%, Actual yield = 8.5%).



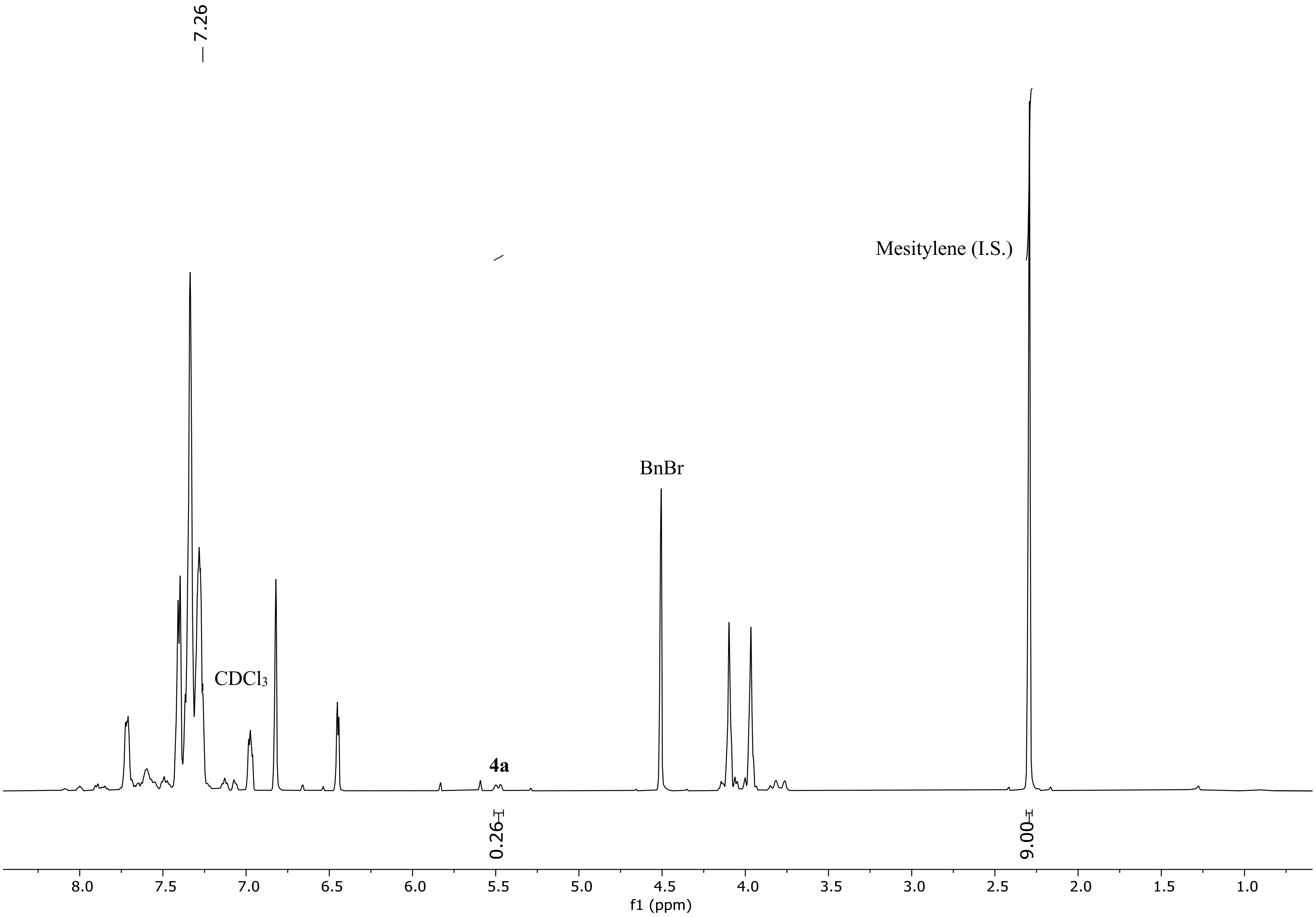
^{1}H NMR ($CDCl_3$, 500 MHz)

NMR #6. Time = 1926 seconds for Phosphine **4** reaction with benzyl bromide (^{1}H NMR Yield = 22%, Actual yield = 11%).



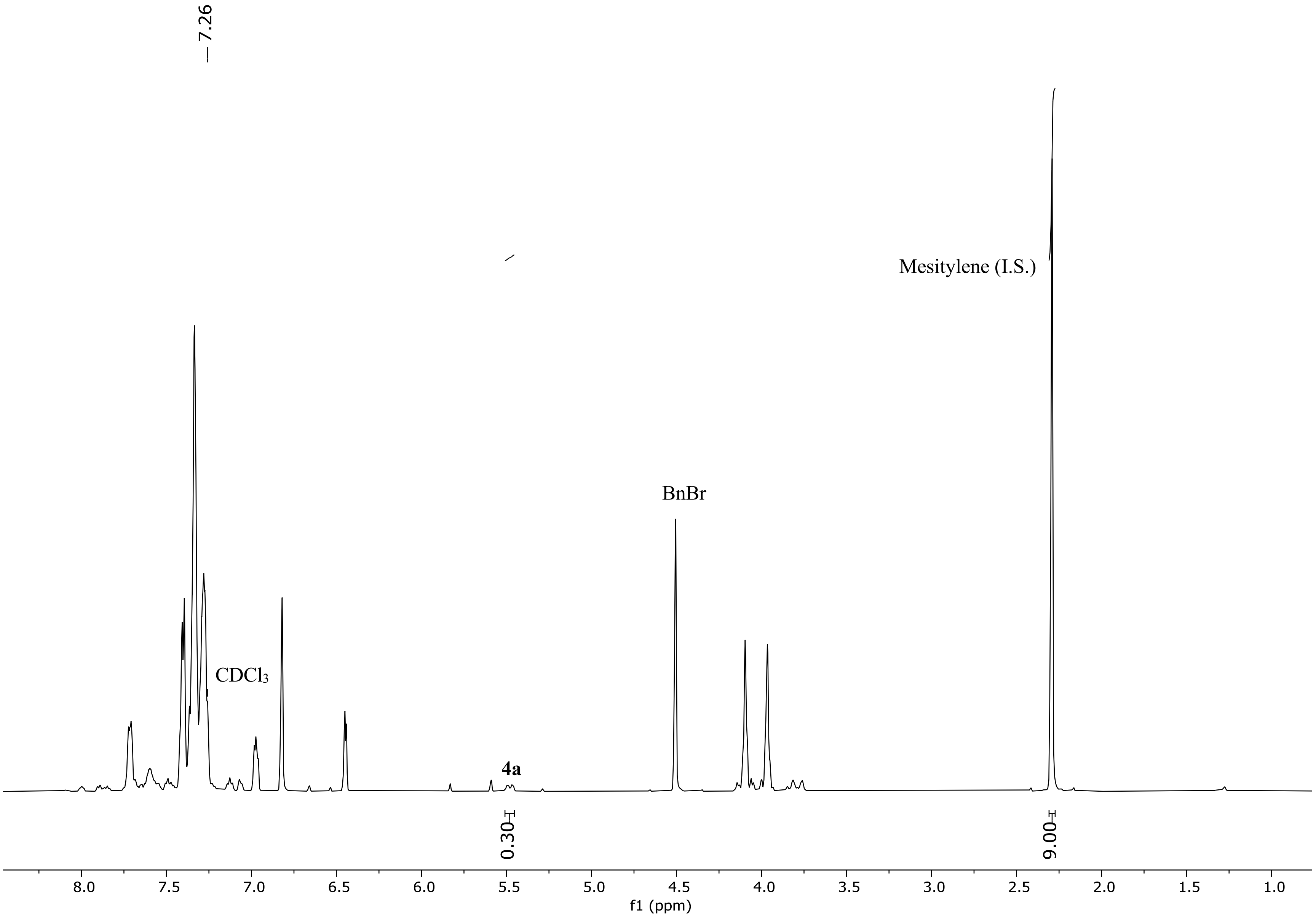
^{1}H NMR (CDCl$_3$, 500 MHz)

NMR #7. Time = 2376 seconds for Phosphine **4** reaction with benzyl bromide (^{1}H NMR Yield = 26%, Actual yield = 13%).

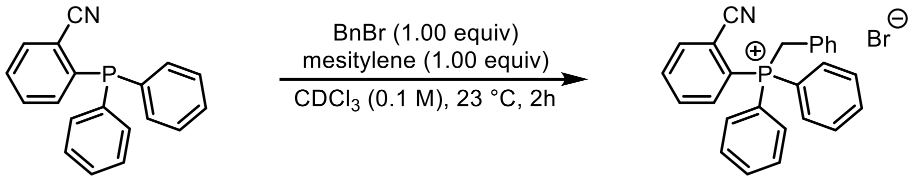


^{1}H NMR (CDCl$_3$, 500 MHz)

NMR #8. Time = 2781 seconds for Phosphine **4** reaction with benzyl bromide (^{1}H NMR Yield = 30%, Actual yield = 15%).

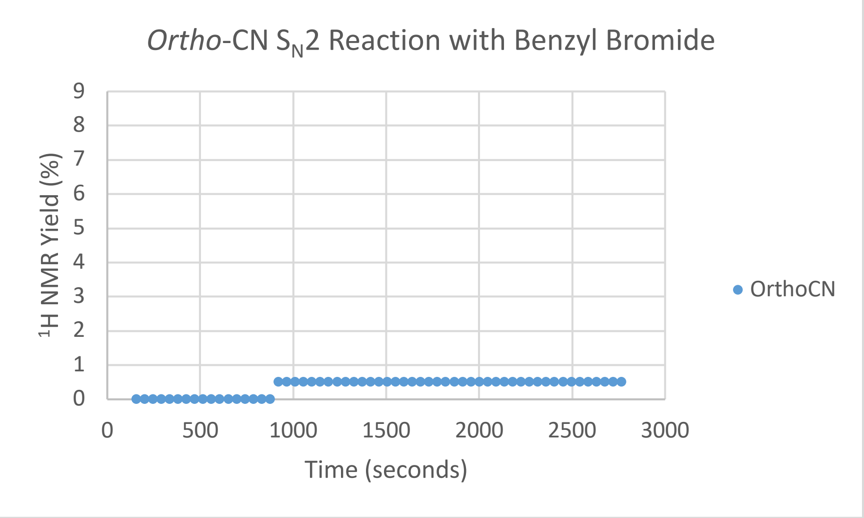


^{1}H NMR (CDCl$_3$, 500 MHz)



5 **5a**

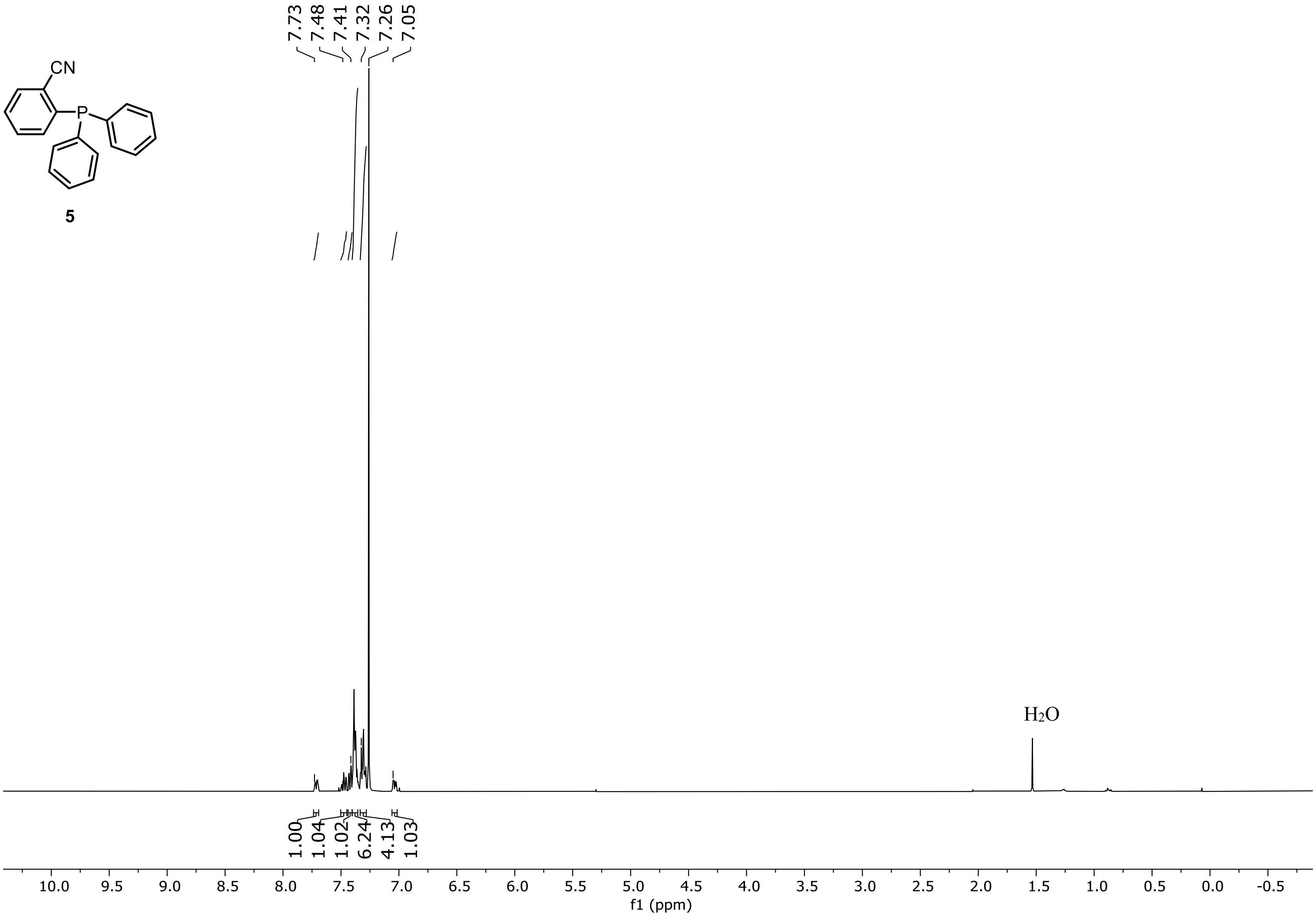
Scheme S9. Reaction of *ortho*-CN with benzyl bromide.



Time	NMR Yield	Time	NMR Yield	Time	NMR Yield
155	0	1055	0.5	1955	0.5
200	0	1100	0.5	2000	0.5
245	0	1145	0.5	2045	0.5
290	0	1190	0.5	2090	0.5
335	0	1235	0.5	2135	0.5
380	0	1280	0.5	2180	0.5
425	0	1325	0.5	2225	0.5
470	0	1370	0.5	2270	0.5
515	0	1415	0.5	2315	0.5
560	0	1460	0.5	2360	0.5
605	0	1505	0.5	2405	0.5
650	0	1550	0.5	2450	0.5
695	0	1595	0.5	2495	0.5
740	0	1640	0.5	2540	0.5
785	0	1685	0.5	2585	0.5
830	0	1730	0.5	2630	0.5
875	0	1775	0.5	2675	0.5
920	0.5	1820	0.5	2720	0.5
965	0.5	1865	0.5	2765	0.5
1010	0.5	1910	0.5		

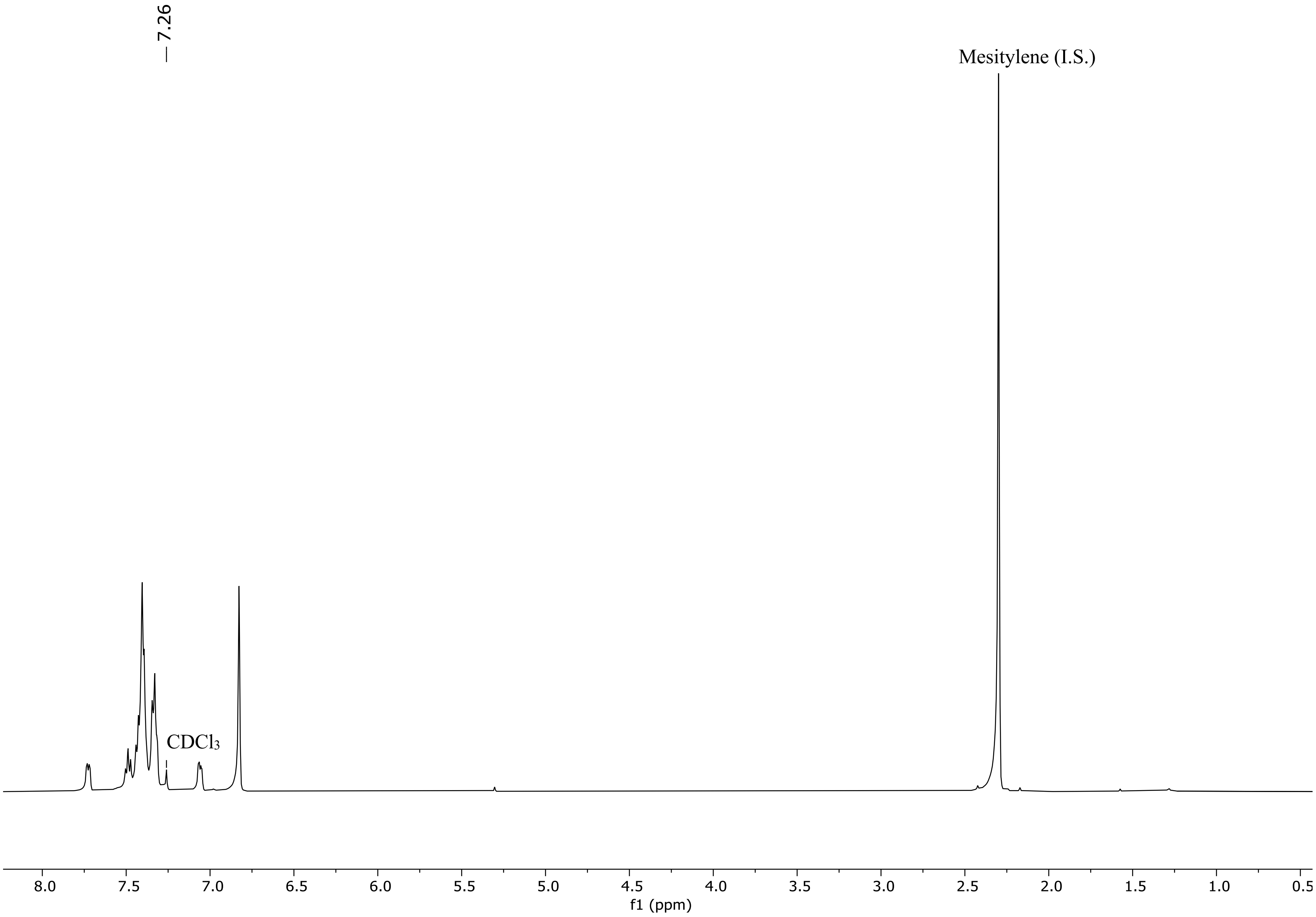
NMR #1. Phosphine **5** ^{1}H NMR.

5



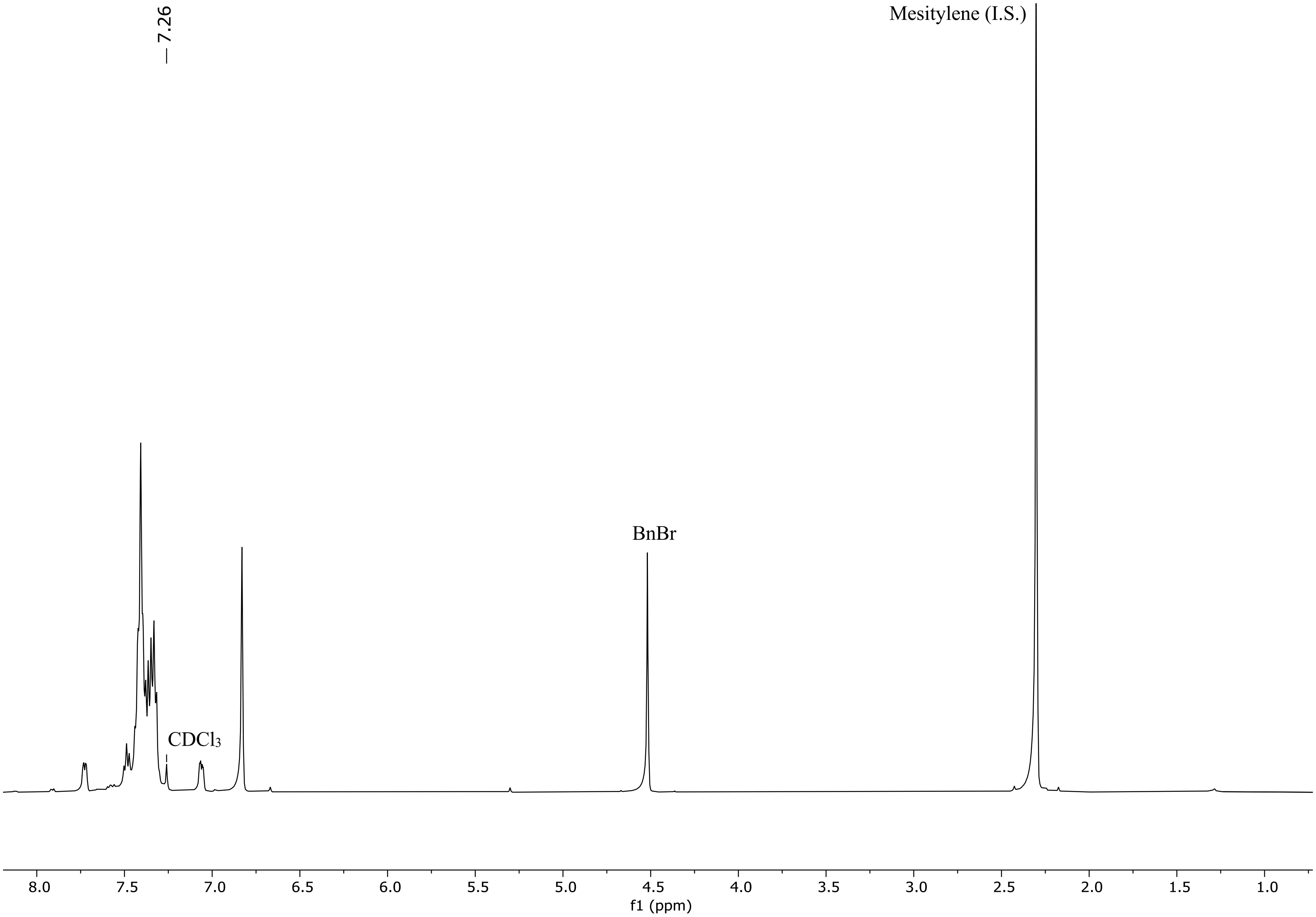
^{1}H NMR ($CDCl_3$, 600 MHz)

NMR #2. Phosphine **5** and mesitylene initial ^{1}H NMR before addition of benzyl bromide.



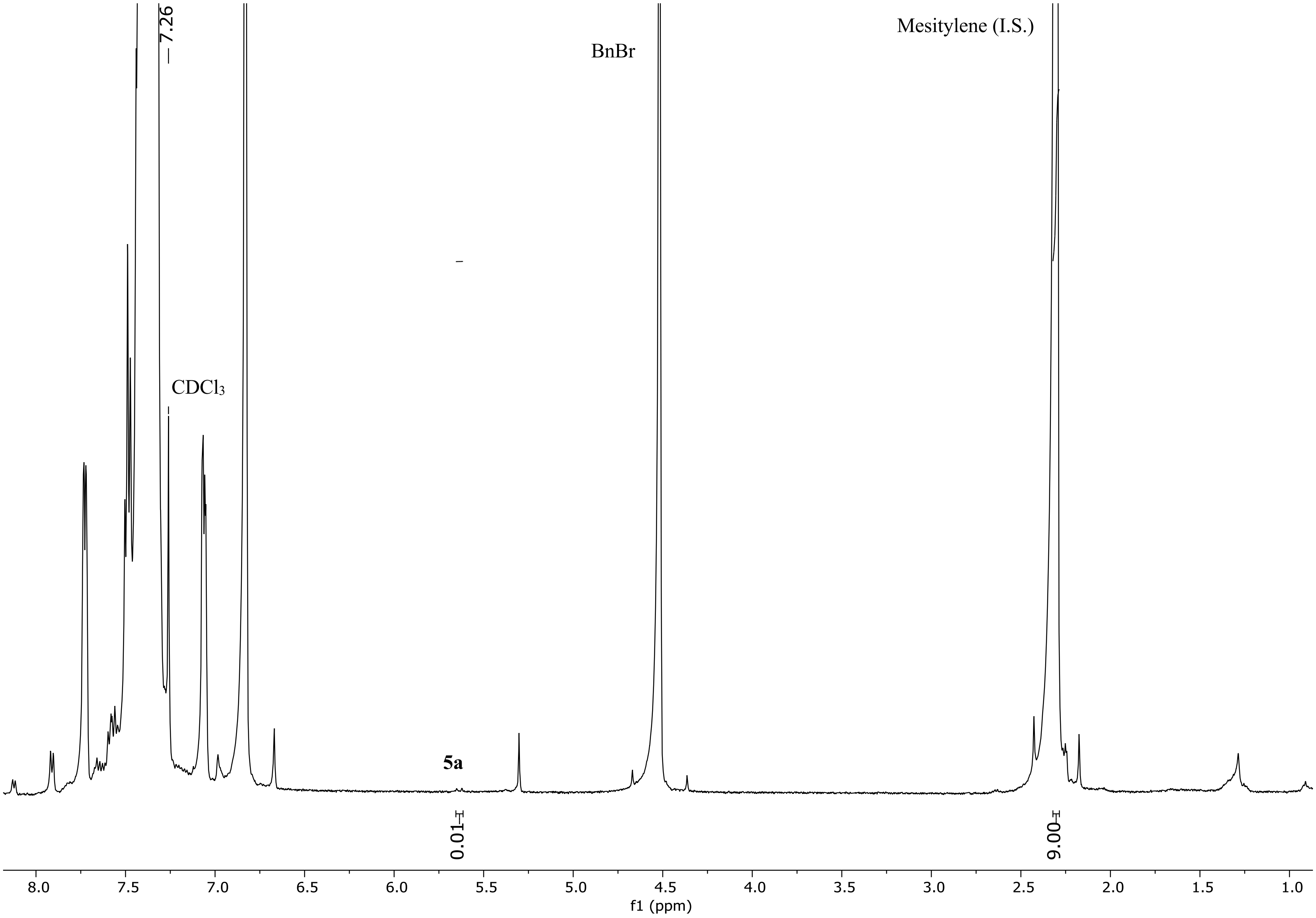
^{1}H NMR (CDCl$_3$, 500 MHz)

NMR #3. Time = 560 seconds for Phosphine **5** reaction with benzyl bromide (^{1}H NMR Yield = 0%, Actual yield = 0%).



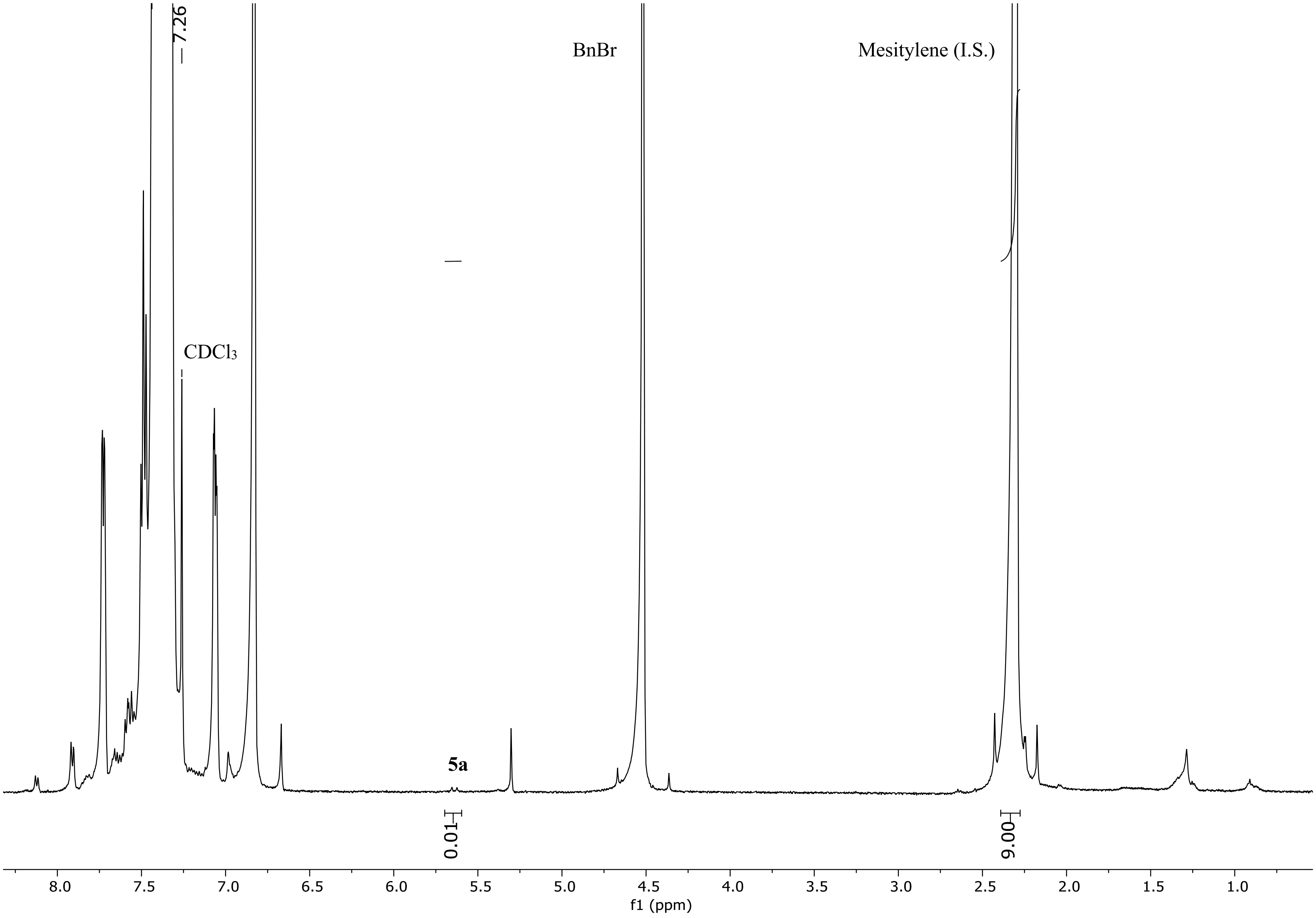
^{1}H NMR (CDCl$_3$, 500 MHz)

NMR #4. Time = 965 seconds for Phosphine **5** reaction with benzyl bromide (^{1}H NMR Yield = 1%, Actual yield = 0.5%).



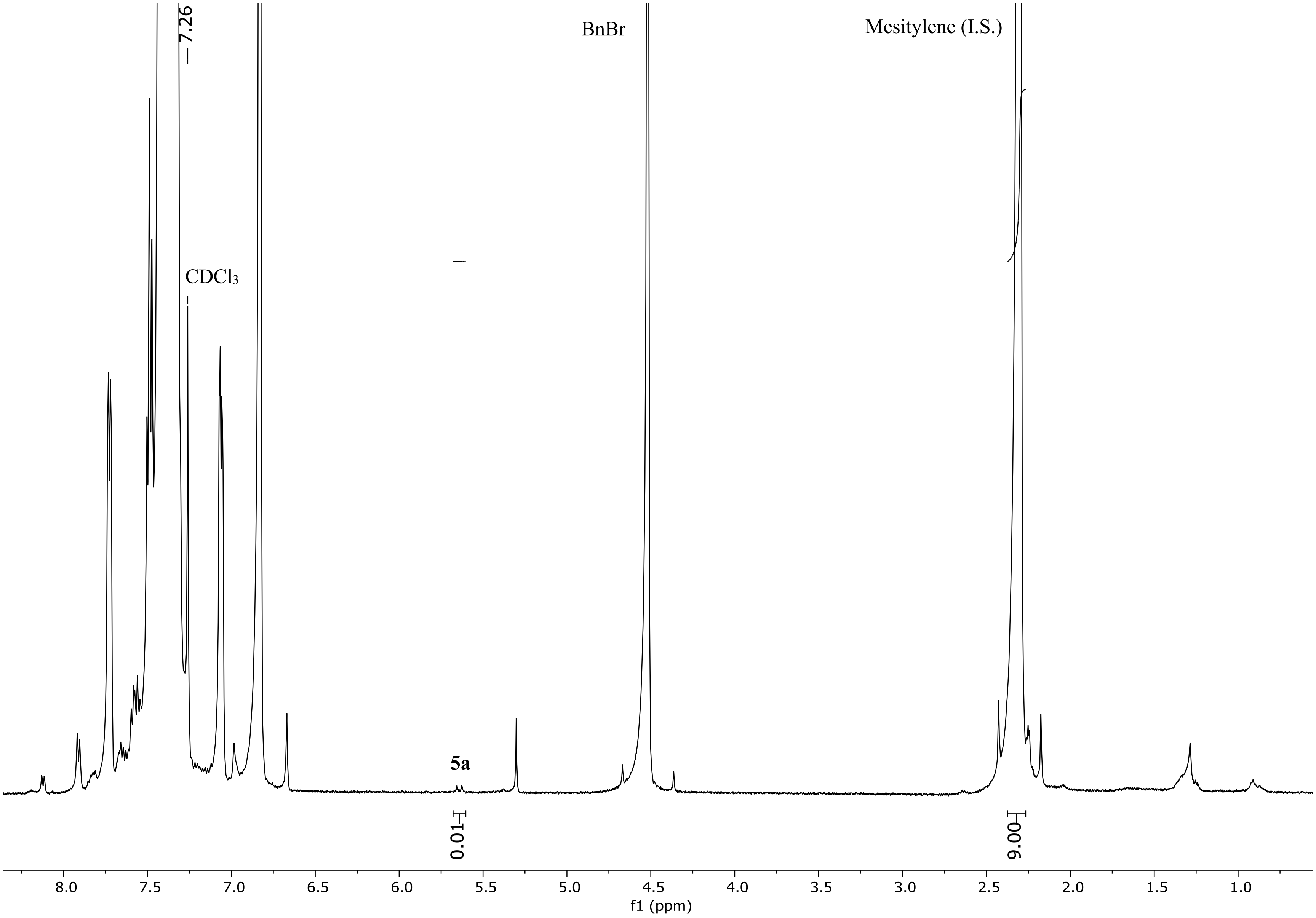
^{1}H NMR (CDCl$_3$, 500 MHz)

NMR #5. Time = 1550 seconds for Phosphine **5** reaction with benzyl bromide (^{1}H NMR Yield = 1%, Actual yield = 0.5%).

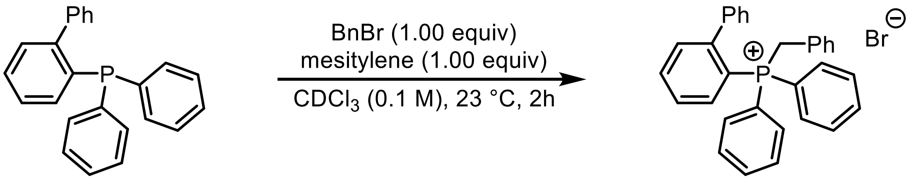


^{1}H NMR (CDCl$_3$, 500 MHz)

NMR #6. Time = 2000 seconds for Phosphine **5** reaction with benzyl bromide (^{1}H NMR Yield = 1%, Actual yield = 0.5%).

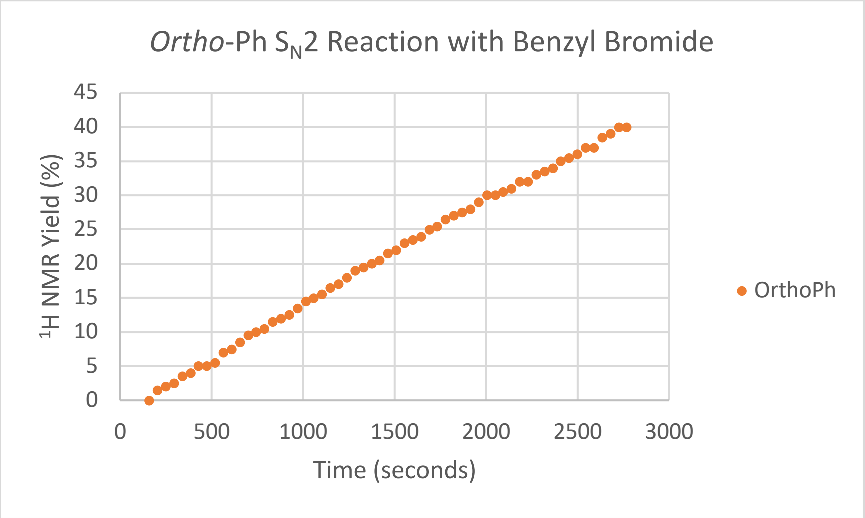


^{1}H NMR ($CDCl_3$, 500 MHz)



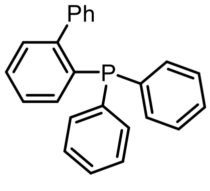
6 **6a**

Scheme S8. Reaction of *ortho*-Ph with benzyl bromide.

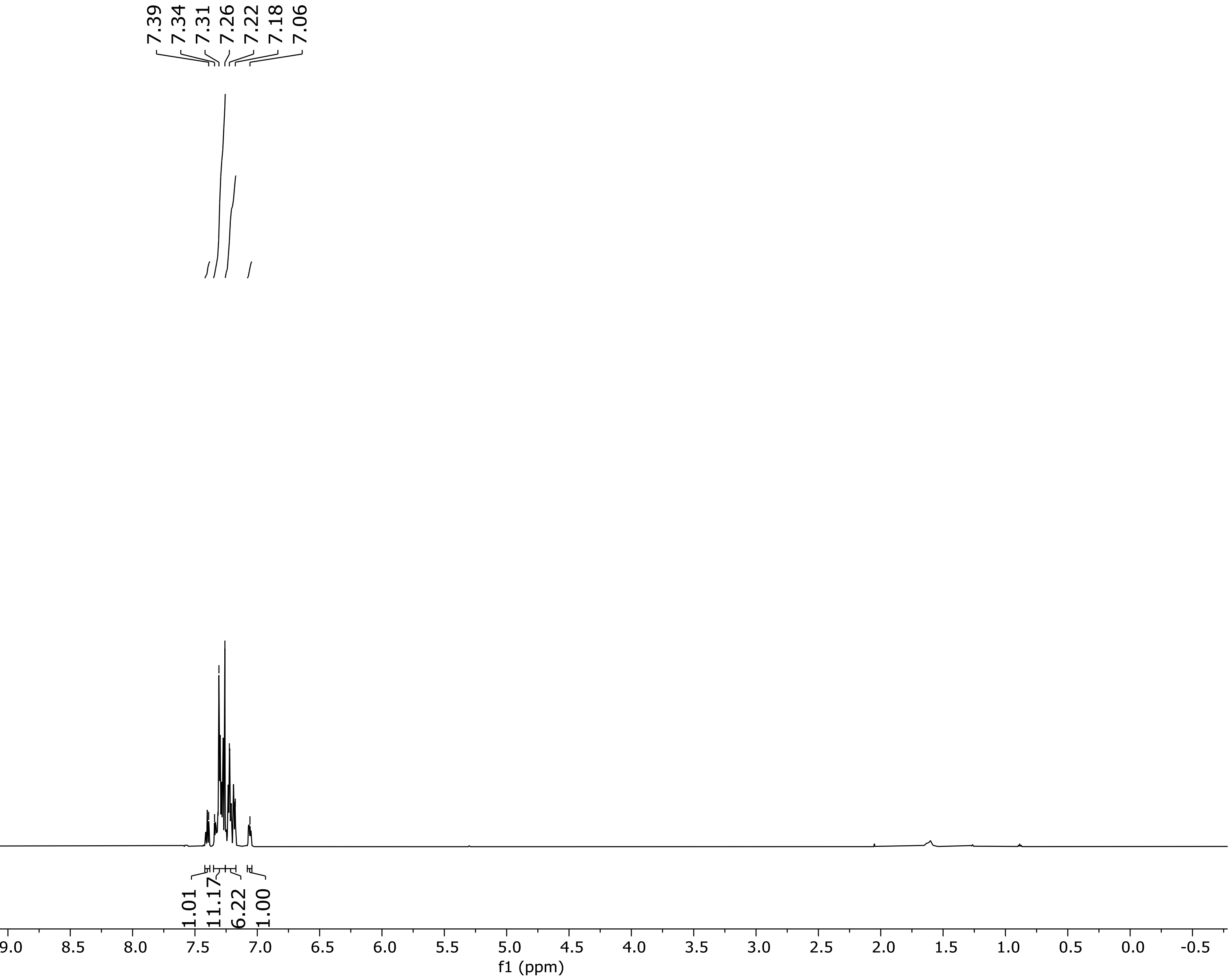


Time	NMR Yield	Time	NMR Yield	Time	NMR Yield
159	0	1059	15	1959	29
204	1.5	1104	15.5	2004	30
249	2	1149	16.5	2049	30
294	2.5	1194	17	2094	30.5
339	3.5	1239	18	2139	31
384	4	1284	19	2184	32
429	5	1329	19.5	2229	32
474	5	1374	20	2274	33
519	5.5	1419	20.5	2319	33.5
564	7	1464	21.5	2364	34
609	7.5	1509	22	2409	35
654	8.5	1554	23	2454	35.5
699	9.5	1599	23.5	2499	36
744	10	1644	24	2544	37
789	10.5	1689	25	2589	37
834	11.5	1734	25.5	2634	38.5
879	12	1779	26.5	2679	39
924	12.5	1824	27	2724	40
969	13.5	1869	27.5	2769	40
1014	14.5	1914	28		

NMR #1. Phosphine **6** ^{1}H NMR.

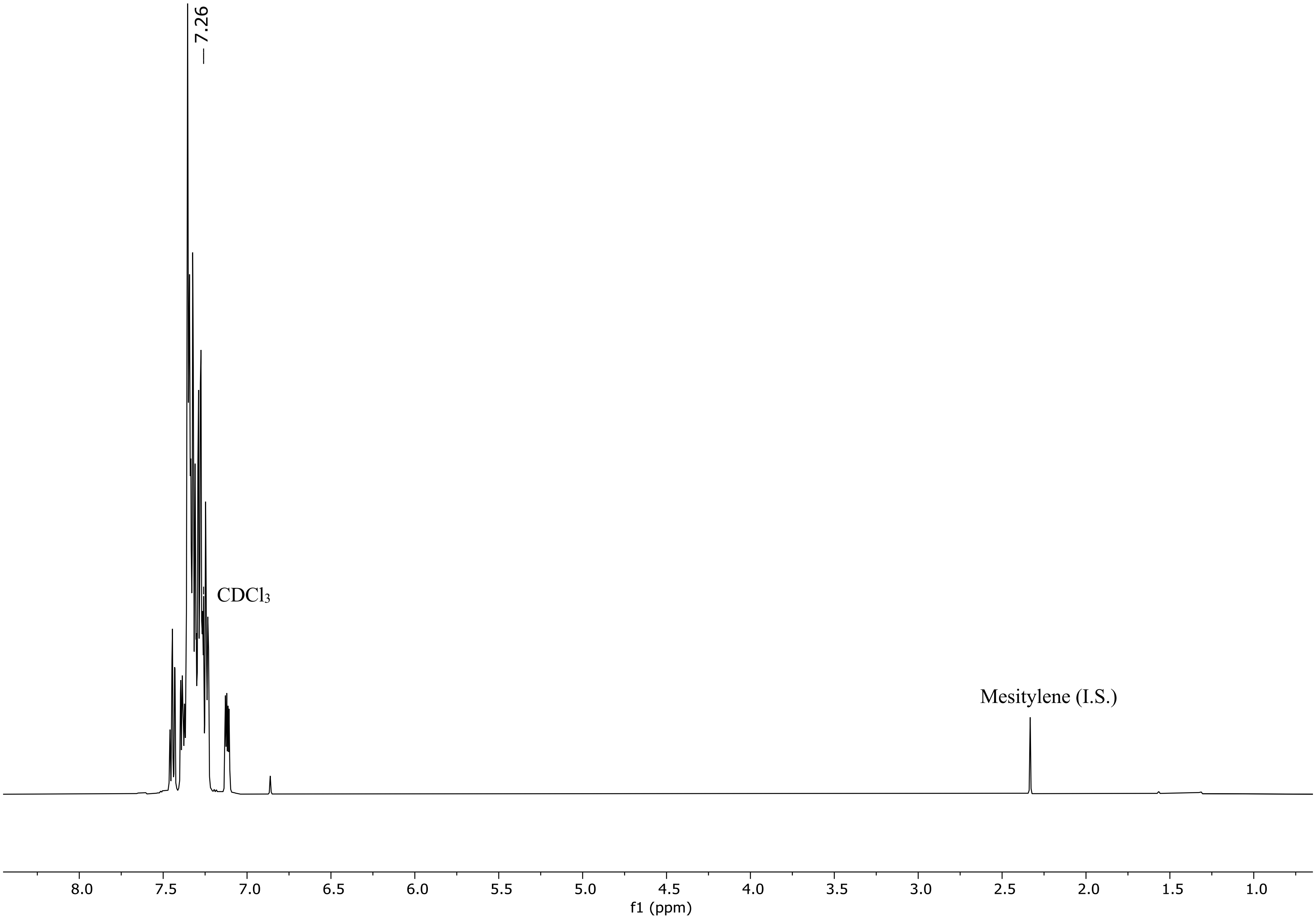


6



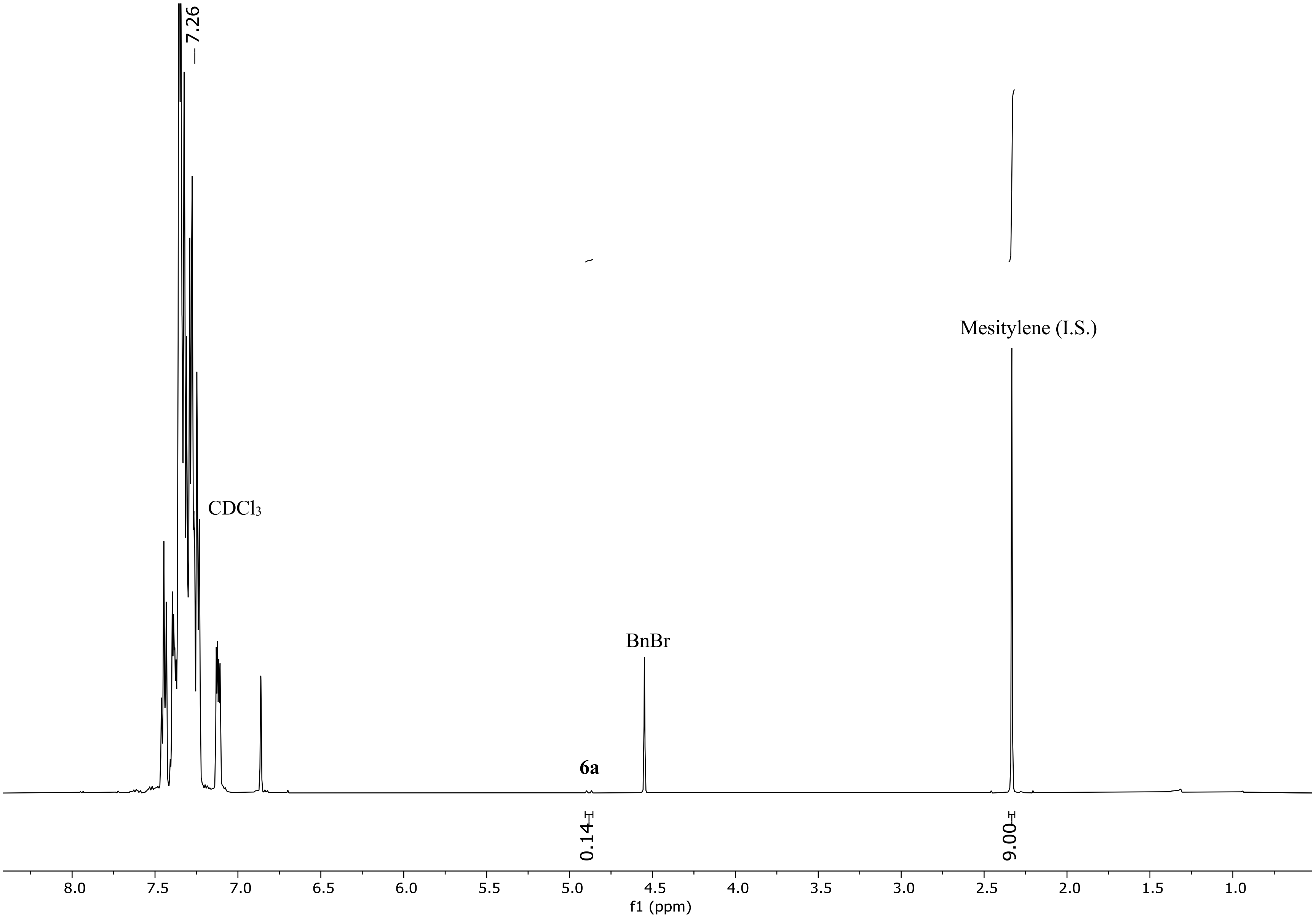
^{1}H NMR (CDCl$_3$, 600 MHz)

NMR #2. Phosphine **6** and mesitylene initial ^{1}H NMR before addition of benzyl bromide.



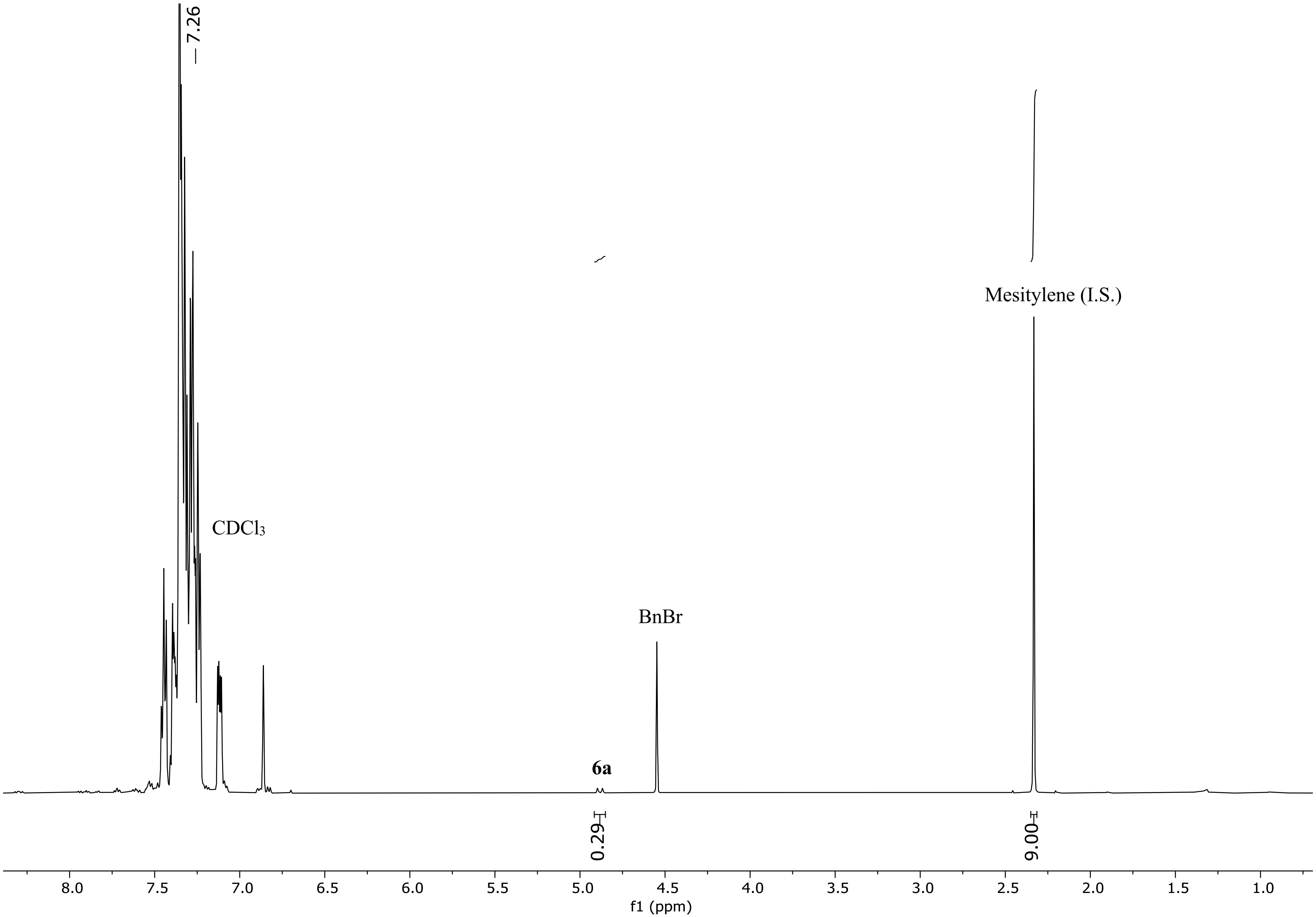
^{1}H NMR (CDCl$_3$, 500 MHz)

NMR #3. Time = 564 seconds for Phosphine **6** reaction with benzyl bromide (^{1}H NMR Yield = 14%, Actual yield = 7%).



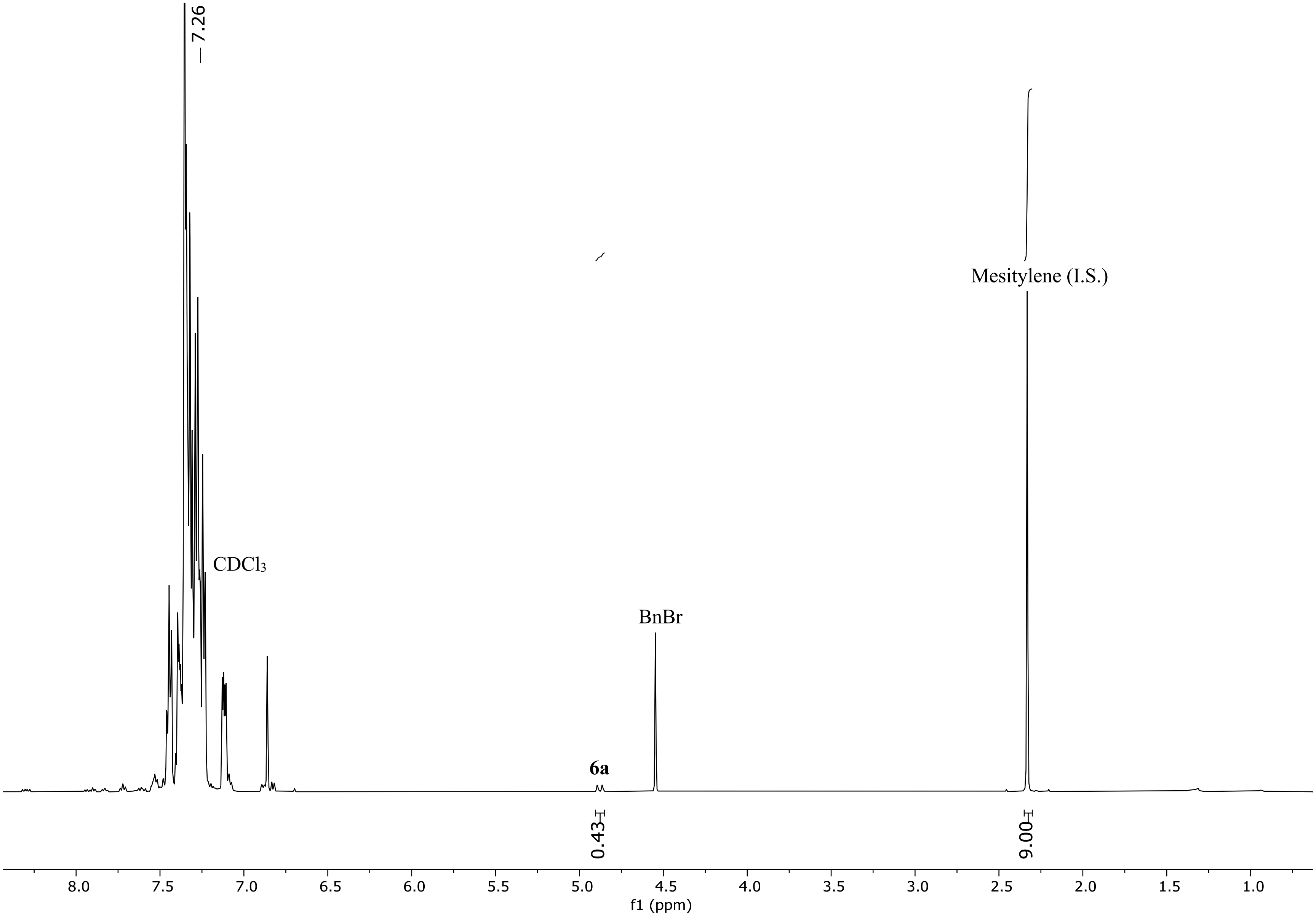
^{1}H NMR ($CDCl_3$, 500 MHz)

NMR #4. Time = 1014 seconds for Phosphine **6** reaction with benzyl bromide (^{1}H NMR Yield = 29%, Actual yield = 14.5%).



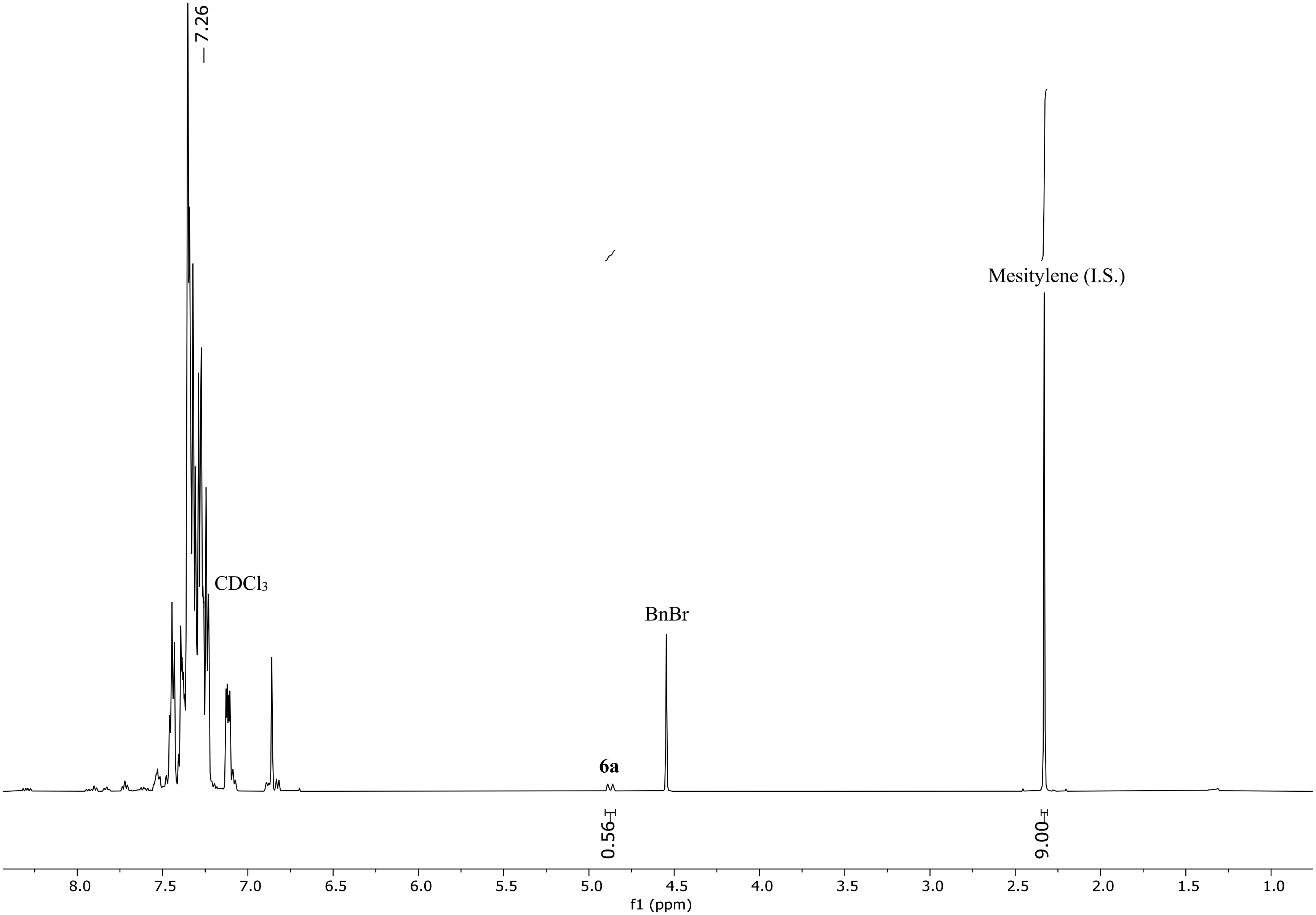
^{1}H NMR (CDCl$_3$, 500 MHz)

NMR #5. Time = 1464 seconds for Phosphine **6** reaction with benzyl bromide (^{1}H NMR Yield = 43%, Actual yield = 21.5%).



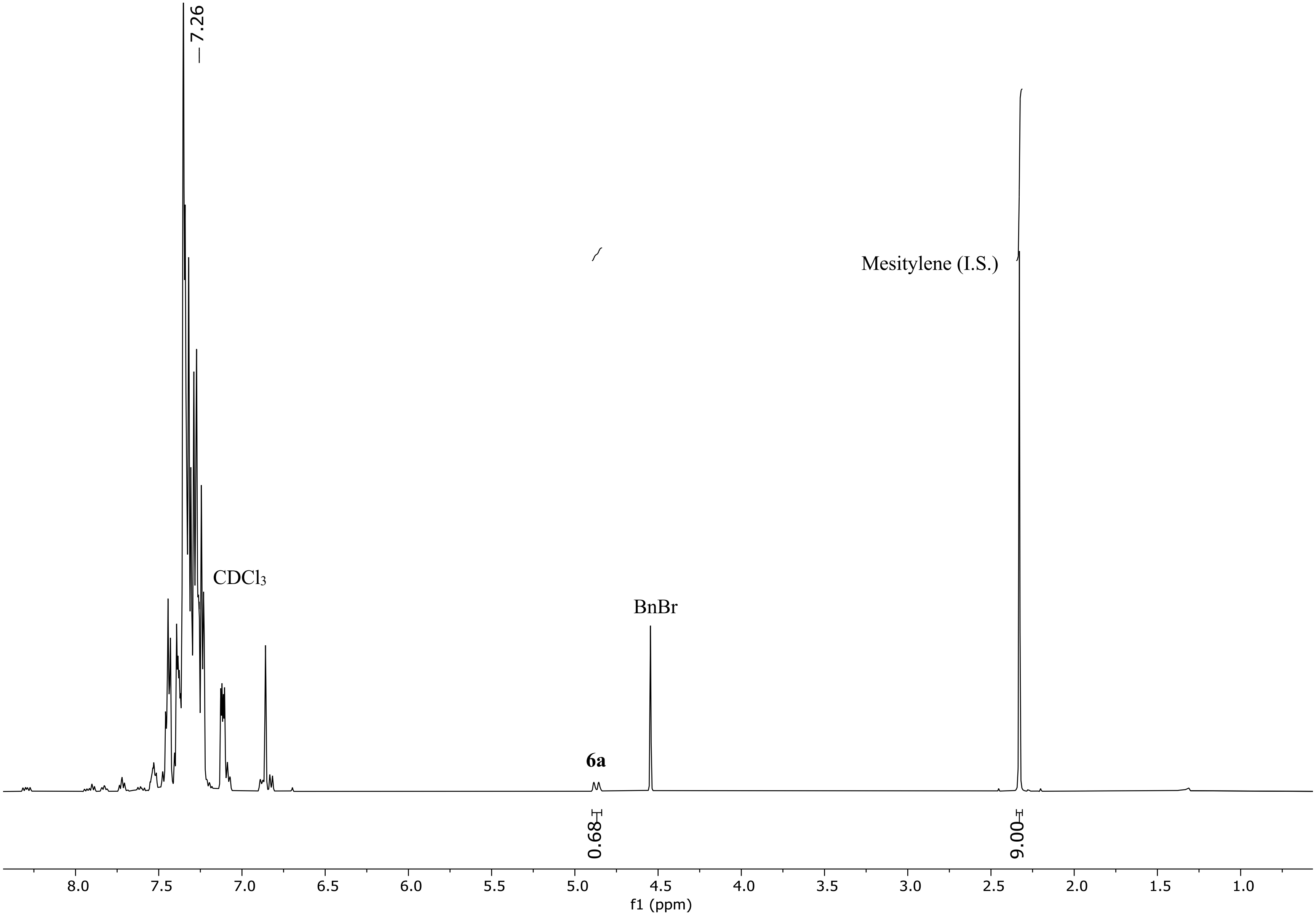
^{1}H NMR (CDCl$_3$, 500 MHz)

NMR #6. Time = 1914 seconds for Phosphine **6** reaction with benzyl bromide (^{1}H NMR Yield = 56%, Actual yield = 28%).



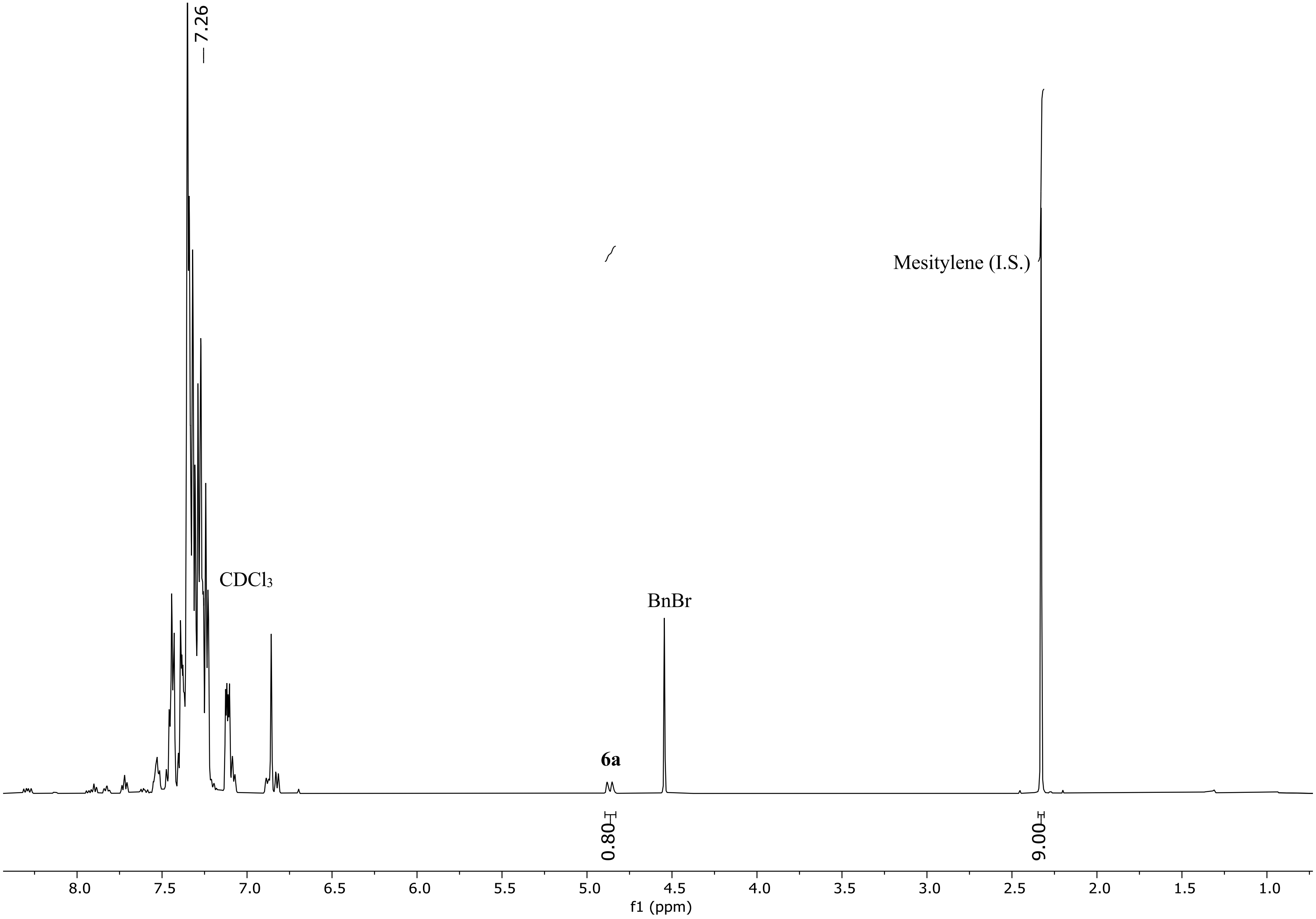
^{1}H NMR ($CDCl_3$, 500 MHz)

NMR #7. Time = 2364 seconds for Phosphine **6** reaction with benzyl bromide (^{1}H NMR Yield = 68%, Actual yield = 34%).

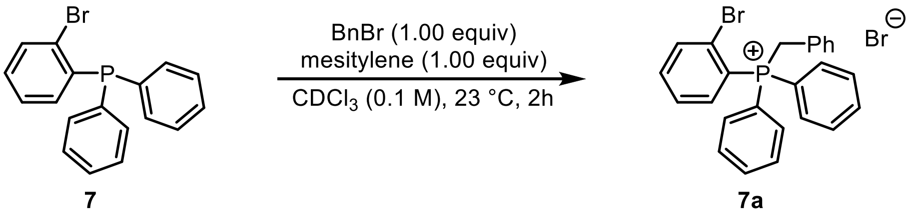


^{1}H NMR ($CDCl_3$, 500 MHz)

NMR #8. Time = 2769 seconds for Phosphine **6** reaction with benzyl bromide (^{1}H NMR Yield = 80%, Actual yield = 40%).



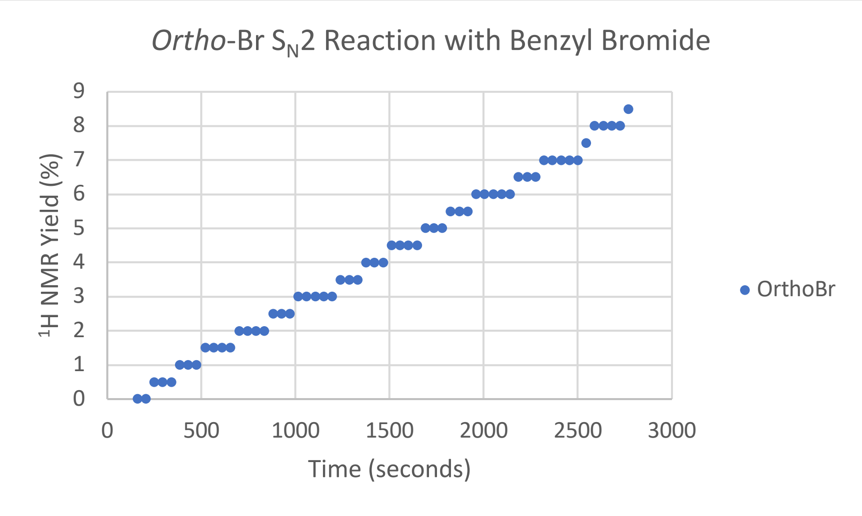
^{1}H NMR (CDCl$_3$, 500 MHz)



7

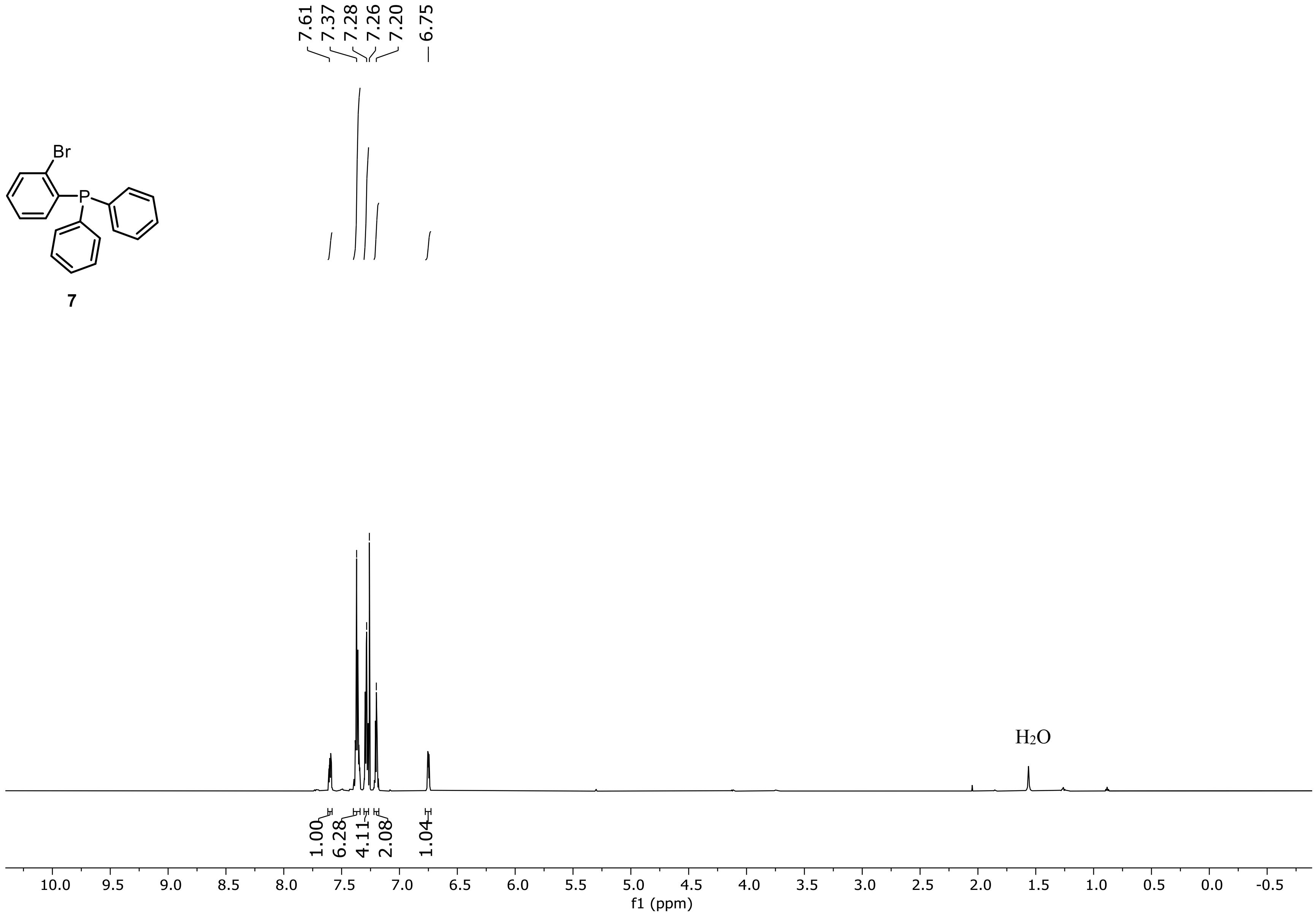
7a

Scheme S7. Reaction of *ortho*-Br with benzyl bromide.



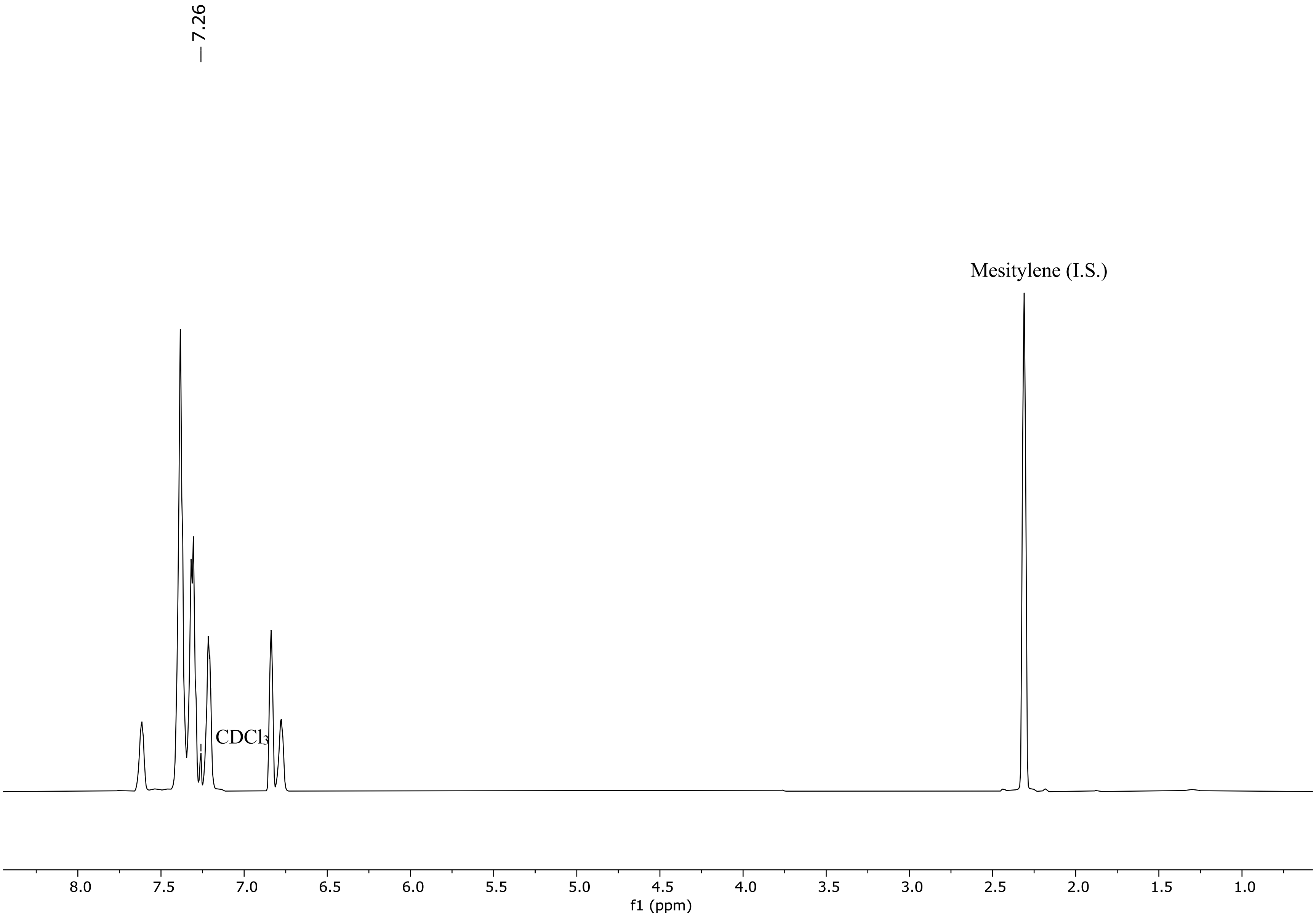
Time	NMR Yield	Time	NMR Yield	Time	NMR Yield
160	0	1060	3	1960	6
205	0	1105	3	2005	6
250	0.5	1150	3	2050	6
295	0.5	1195	3	2095	6
340	0.5	1240	3.5	2140	6
385	1	1285	3.5	2185	6.5
430	1	1330	3.5	2230	6.5
475	1	1375	4	2275	6.5
520	1.5	1420	4	2320	7
565	1.5	1465	4	2365	7
610	1.5	1510	4.5	2410	7
655	1.5	1555	4.5	2455	7
700	2	1600	4.5	2500	7
745	2	1645	4.5	2545	7.5
790	2	1690	5	2590	8
835	2	1735	5	2635	8
880	2.5	1780	5	2680	8
925	2.5	1825	5.5	2725	8
970	2.5	1870	5.5	2770	8.5
1015	3	1915	5.5		

NMR #1. Phosphine **7** ^{1}H NMR.



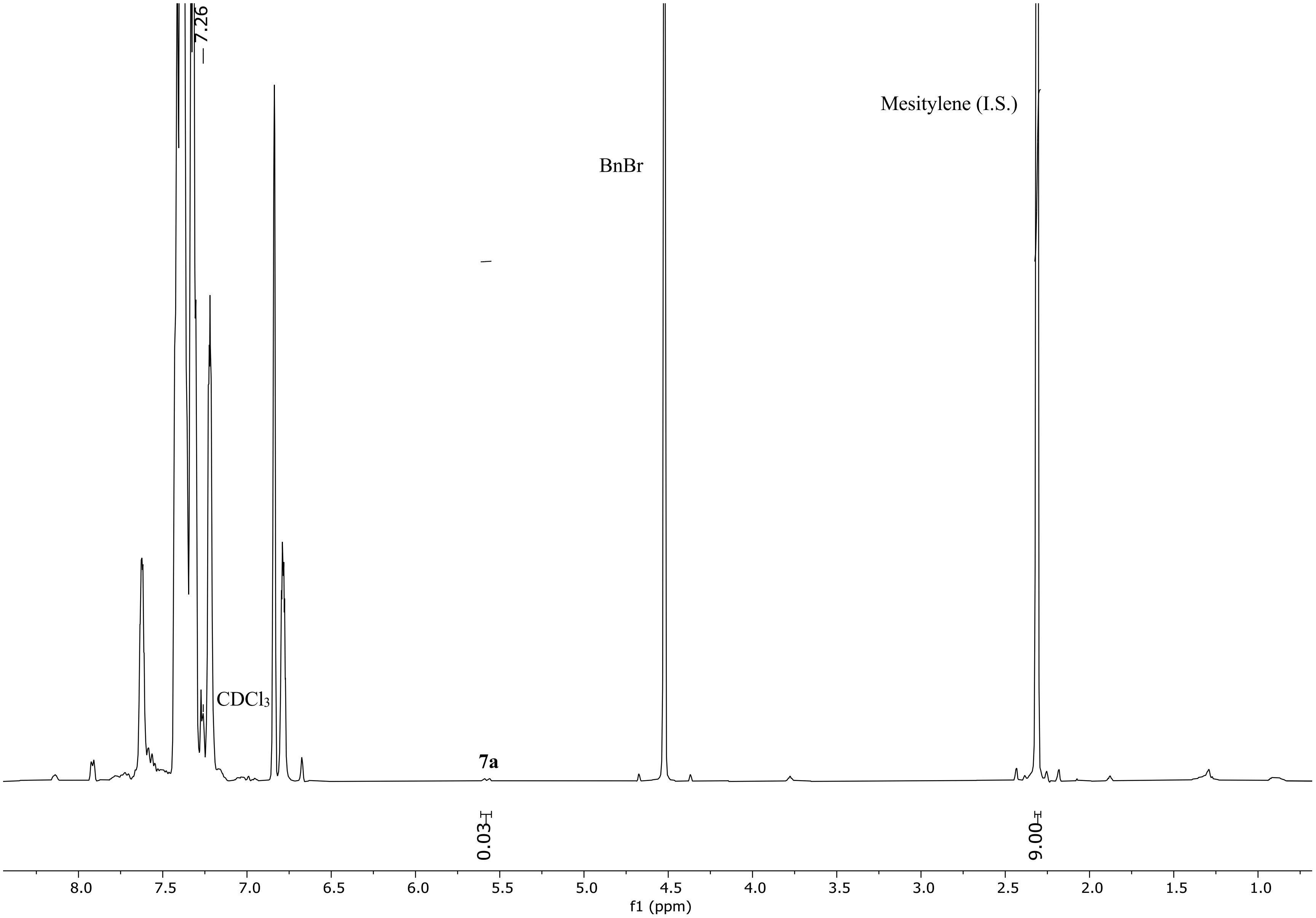
^{1}H NMR ($CDCl_3$, 600 MHz)

NMR #2. Phosphine **7** and mesitylene initial ^{1}H NMR before addition of benzyl bromide.



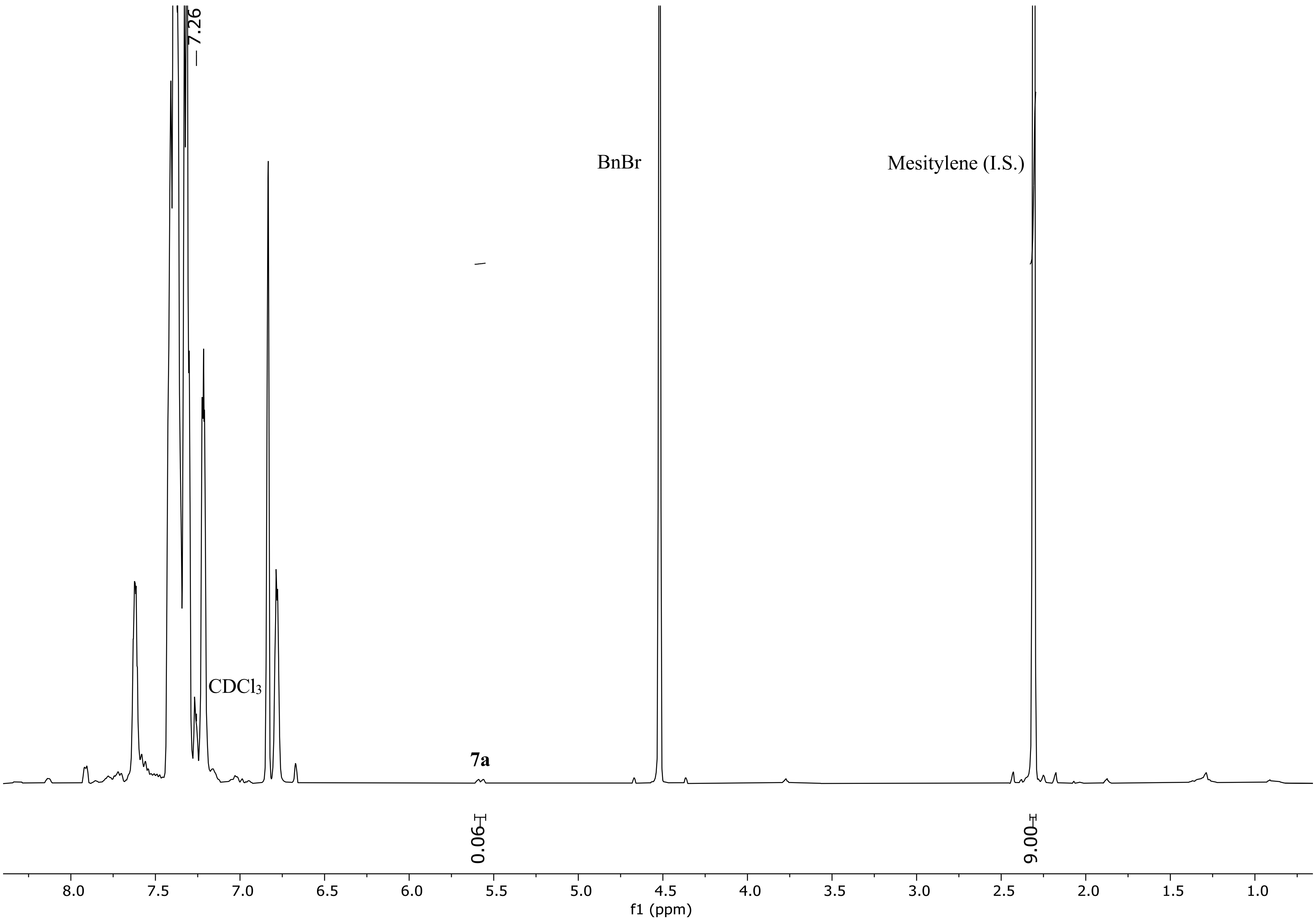
^{1}H NMR (CDCl$_3$, 500 MHz)

NMR #3. Time = 565 seconds for Phosphine **7** reaction with benzyl bromide (^{1}H NMR Yield = 3%, Actual yield = 1.5%).



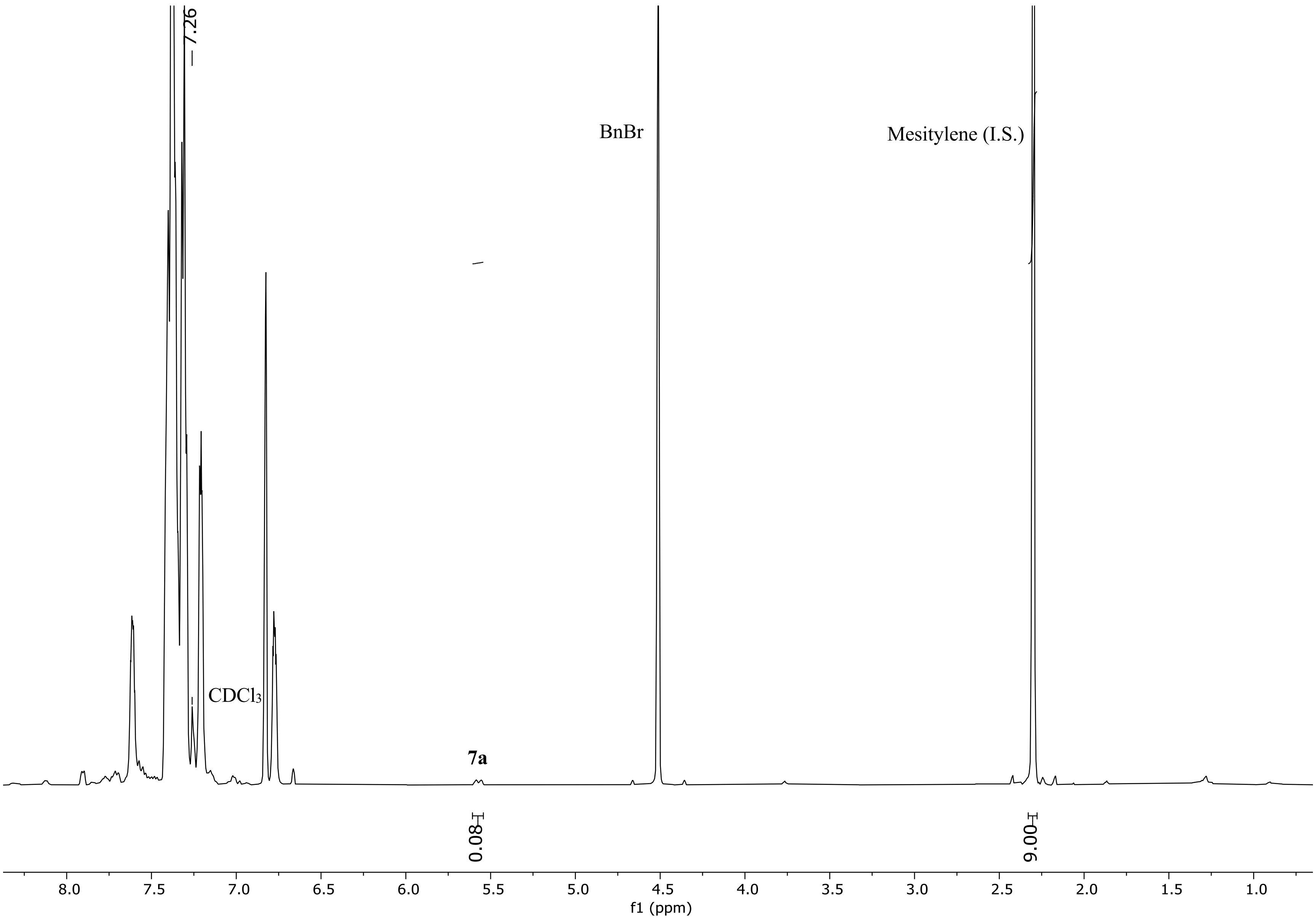
^{1}H NMR (CDCl$_3$, 500 MHz)

NMR #4. Time = 1015 seconds for Phosphine **7** reaction with benzyl bromide (^{1}H NMR Yield = 6%, Actual yield = 3%).



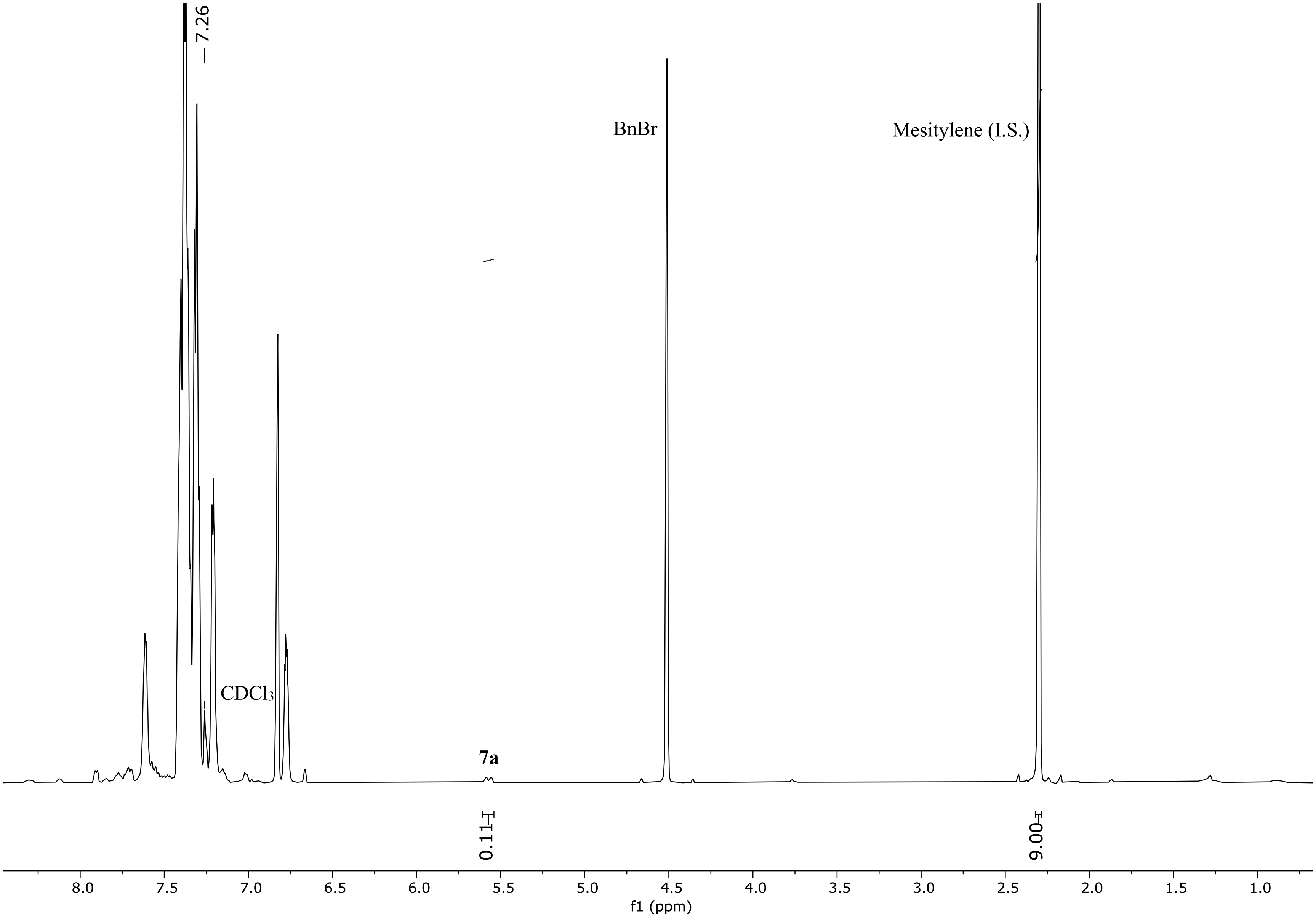
^{1}H NMR ($CDCl_3$, 500 MHz)

NMR #5. Time = 1465 seconds for Phosphine **7** reaction with benzyl bromide (^{1}H NMR Yield = 8%, Actual yield = 4%).



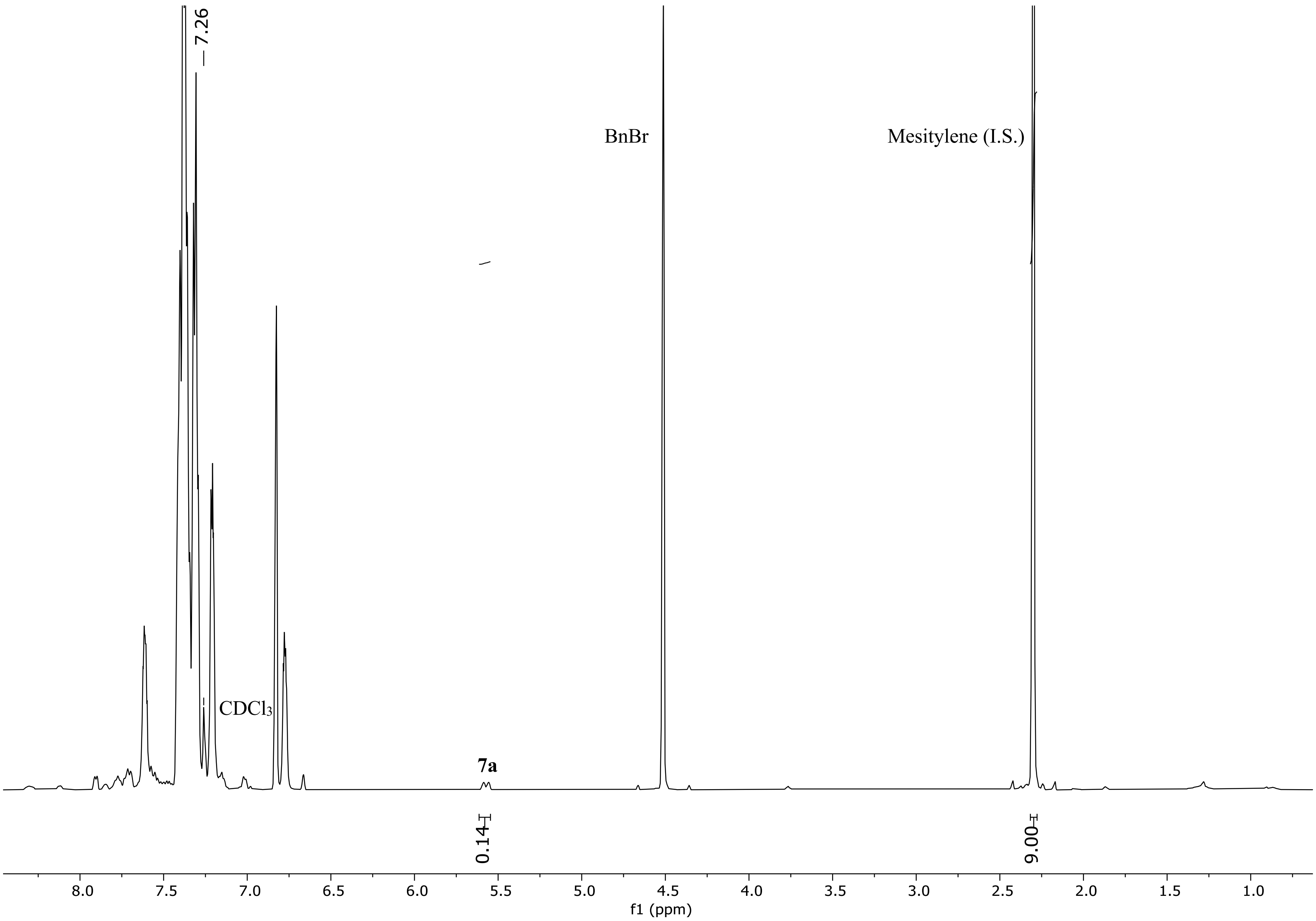
^{1}H NMR (CDCl$_3$, 500 MHz)

NMR #6. Time = 1915 seconds for Phosphine **7** reaction with benzyl bromide (^{1}H NMR Yield = 11%, Actual yield = 5.5%).



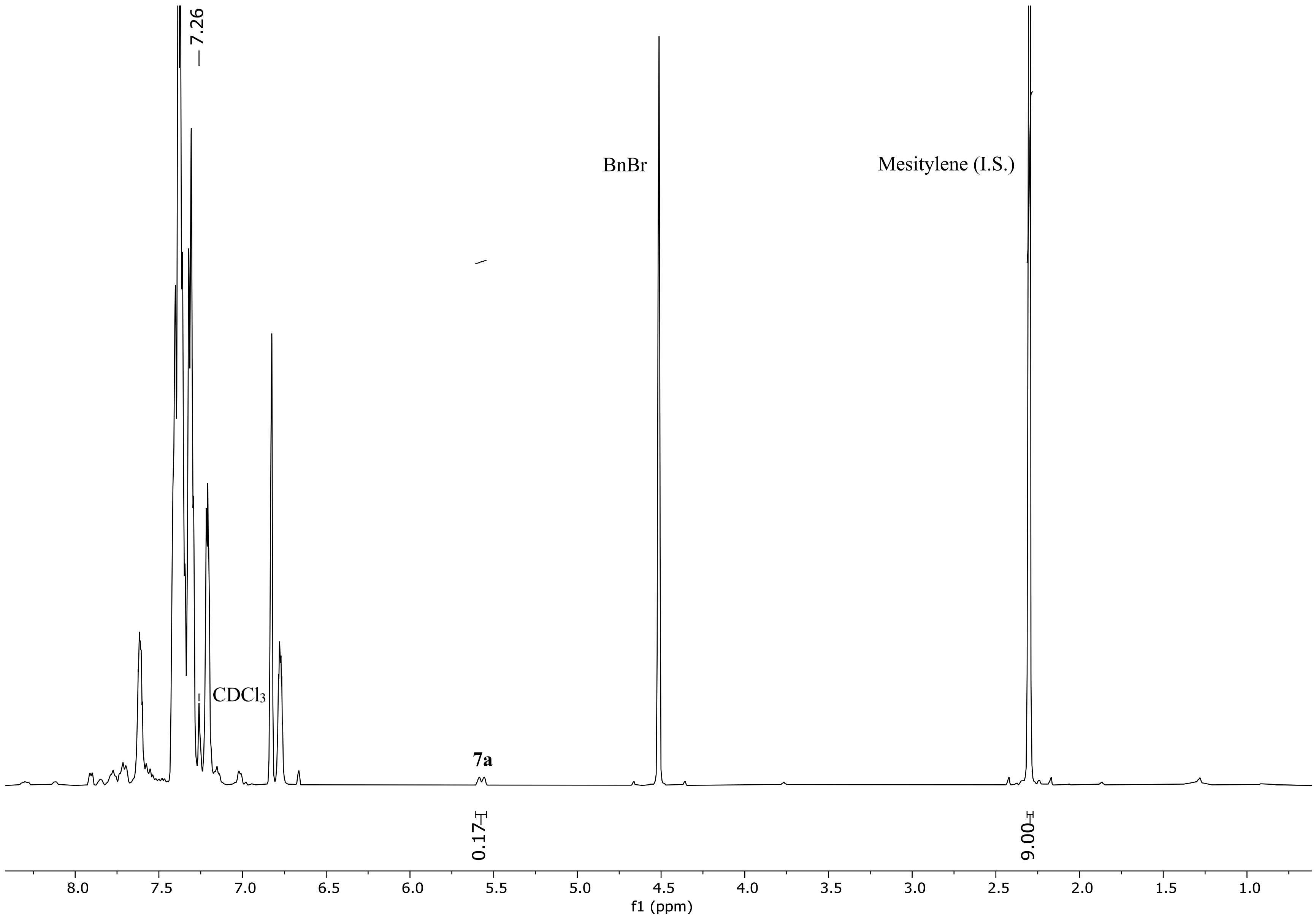
^{1}H NMR (CDCl$_3$, 500 MHz)

NMR #7. Time = 2365 seconds for Phosphine **7** reaction with benzyl bromide (^{1}H NMR Yield = 14%, Actual yield = 7%).

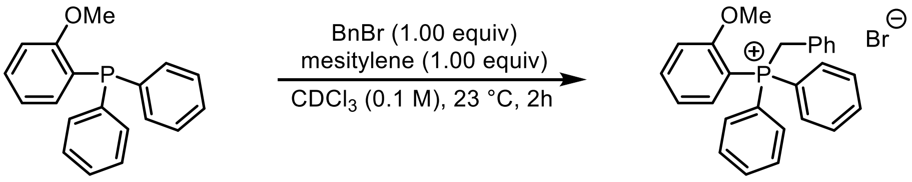


^{1}H NMR ($CDCl_3$, 500 MHz)

NMR #8. Time = 2770 seconds for Phosphine **7** reaction with benzyl bromide (^{1}H NMR Yield = 17%, Actual yield = 8.5%).

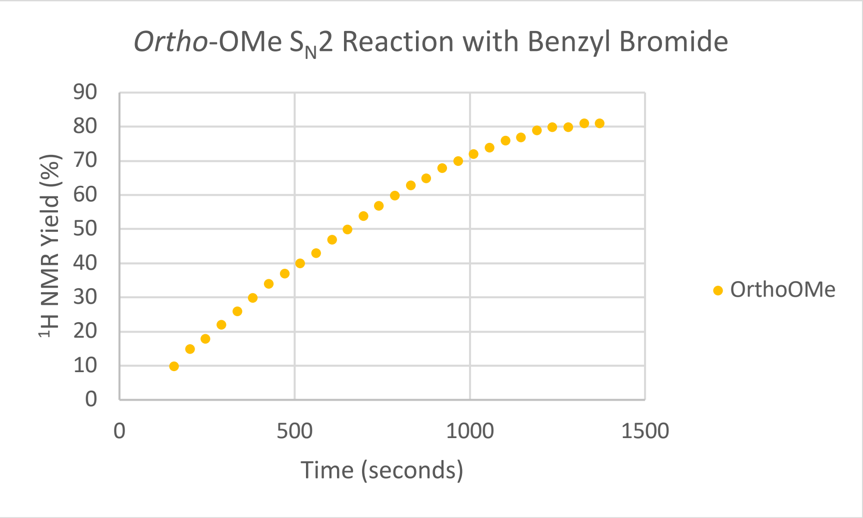


^{1}H NMR ($CDCl_3$, 500 MHz)



8 **8a**

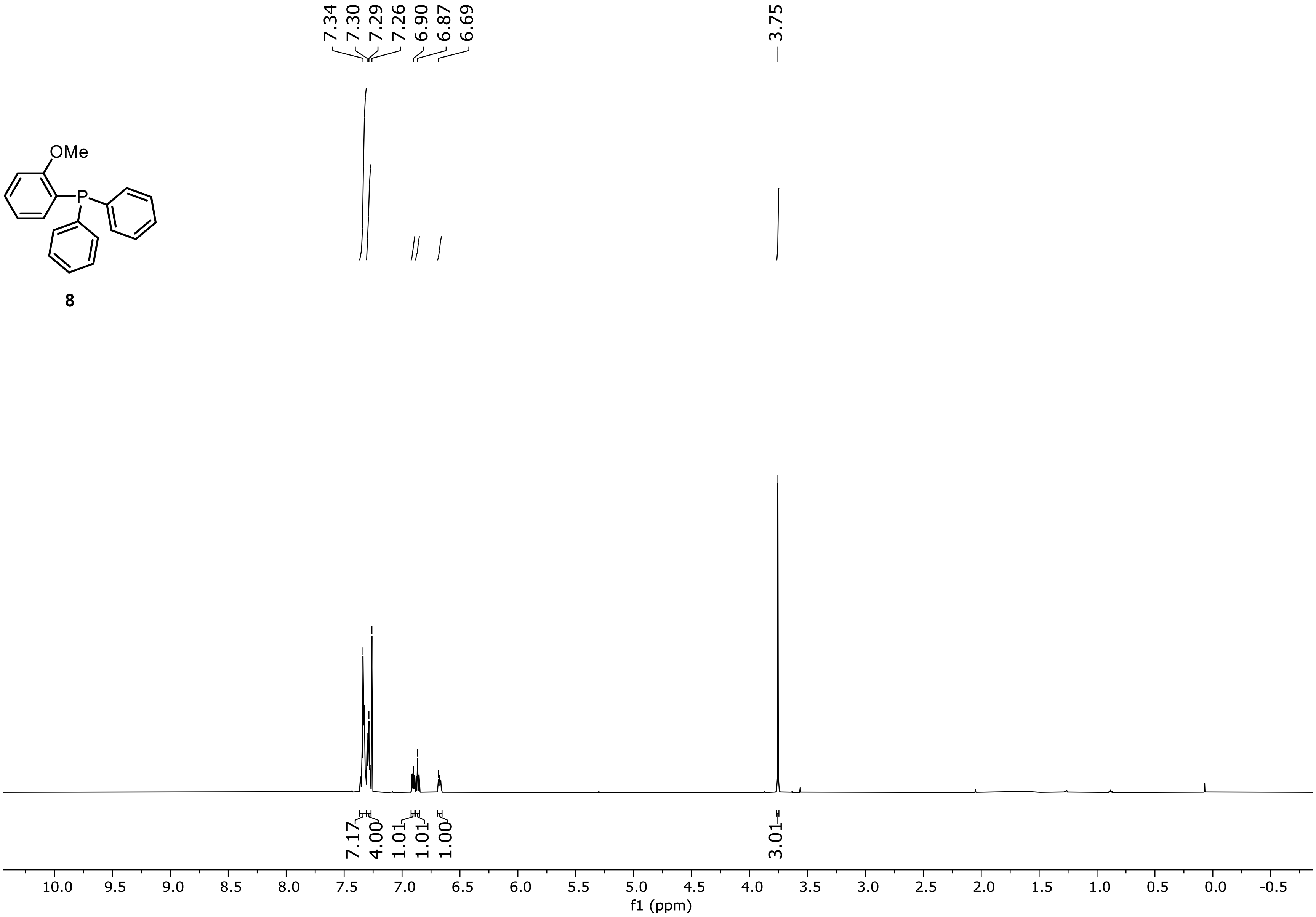
Scheme S9. Reaction of *ortho*-OMe with benzyl bromide.



Time	NMR Yield	Time	NMR Yield
156	10	786	60
201	15	831	63
246	18	876	65
291	22	921	68
336	26	966	70
381	30	1011	72
426	34	1056	74
471	37	1101	76
516	40	1146	77
561	43	1191	79
606	47	1236	80
651	50	1281	80
696	54	1326	81
741	57	1371	81

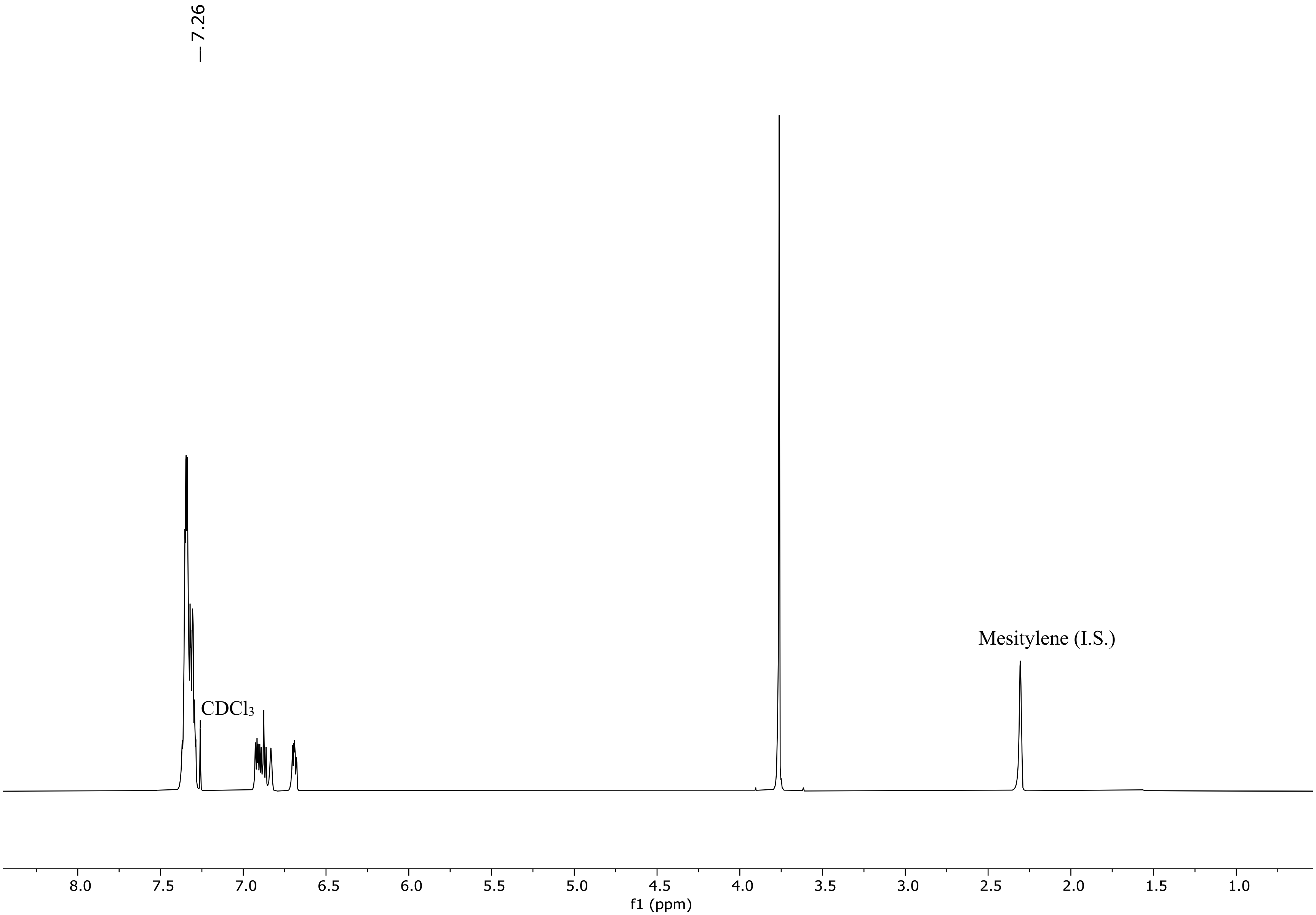
NMR #1. Phosphine **8** ^{1}H NMR.

8



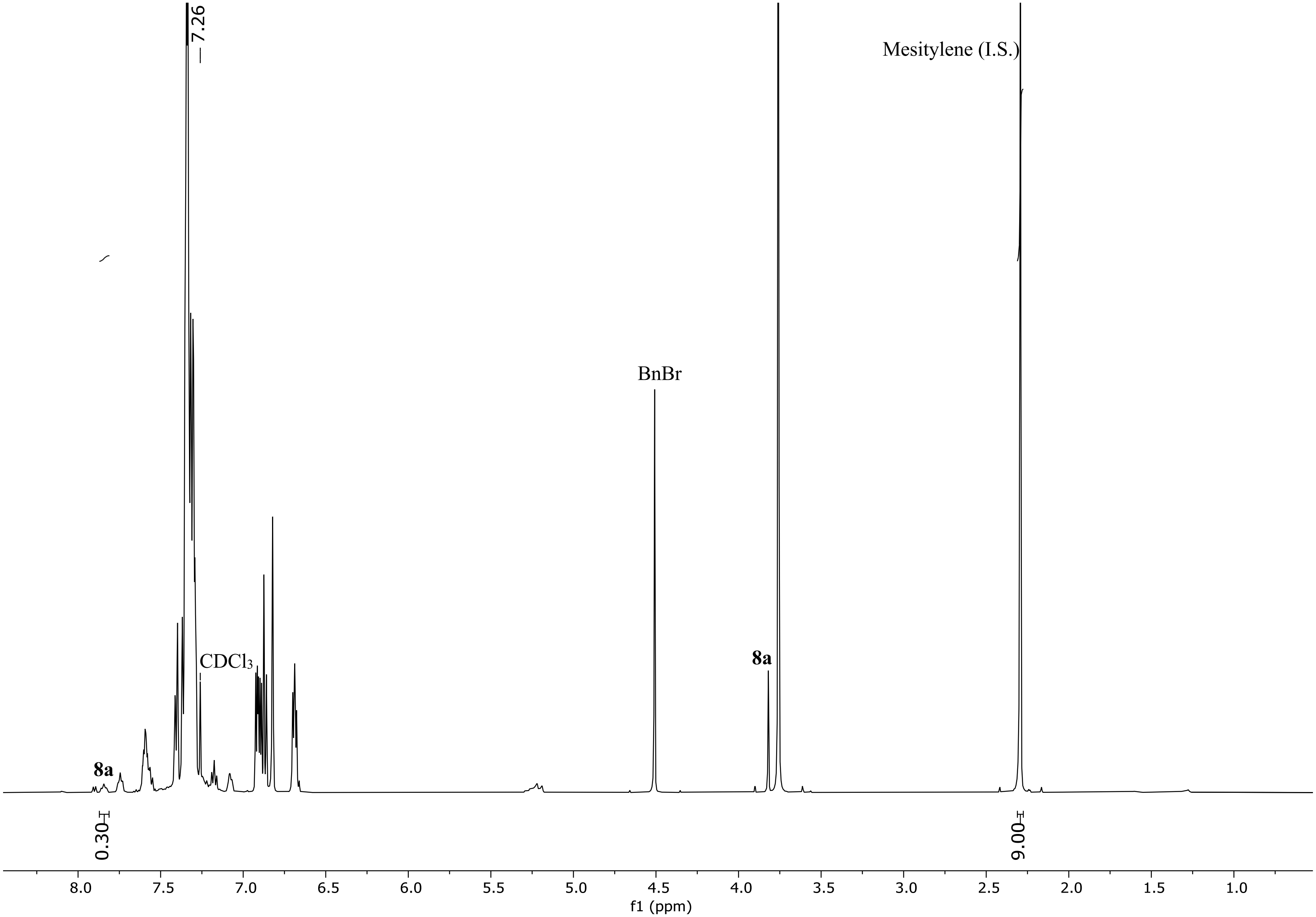
^{1}H NMR (CDCl$_3$, 600 MHz)

NMR #2. Phosphine **8** and mesitylene initial ^{1}H NMR before addition of benzyl bromide.



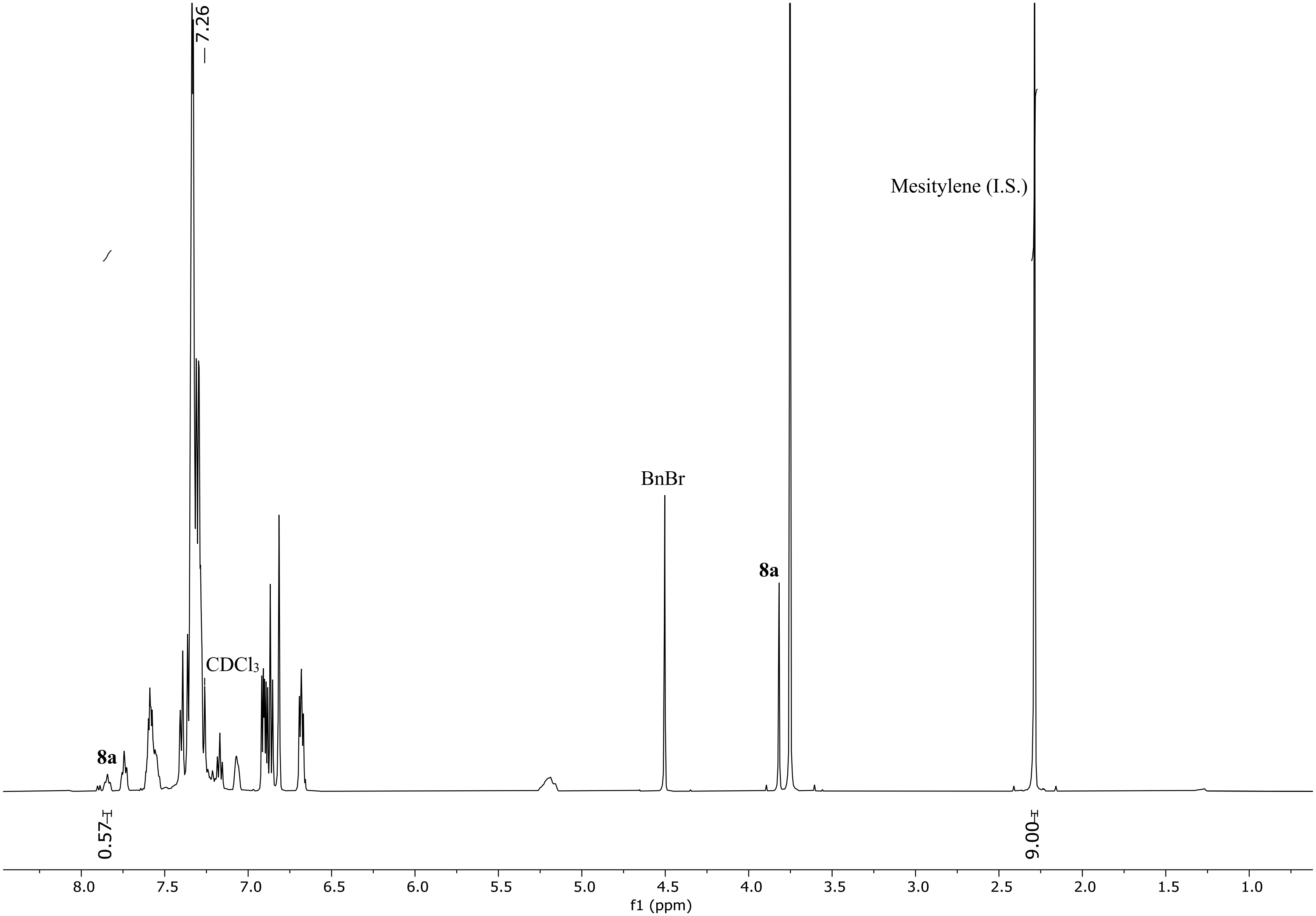
^{1}H NMR (CDCl$_3$, 500 MHz)

NMR #3. Time = 381 seconds for Phosphine **8** reaction with benzyl bromide (^{1}H NMR Yield = 30%).



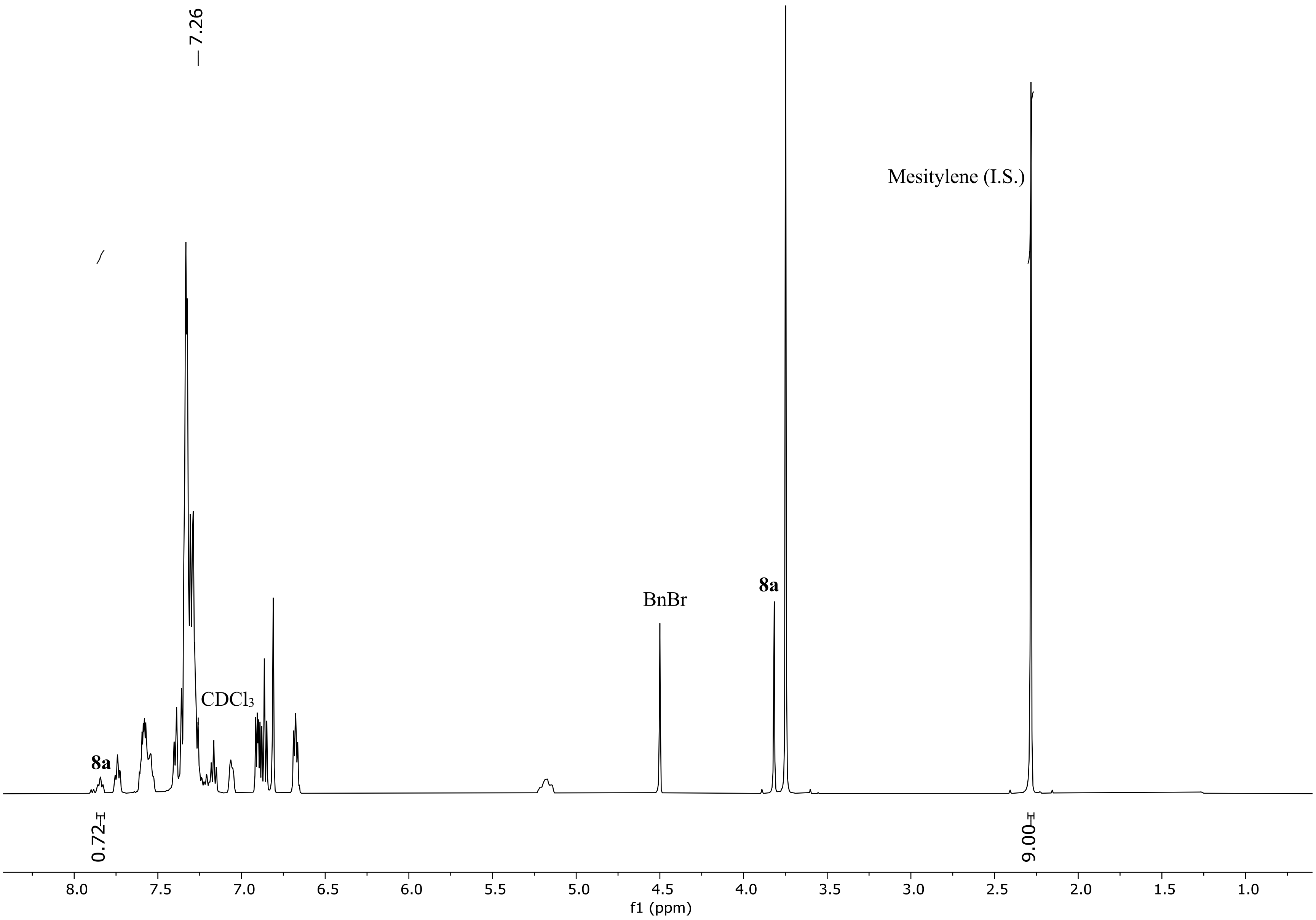
^{1}H NMR (CDCl$_3$, 500 MHz)

NMR #4. Time = 741 seconds for Phosphine **8** reaction with benzyl bromide (^{1}H NMR Yield = 57%).



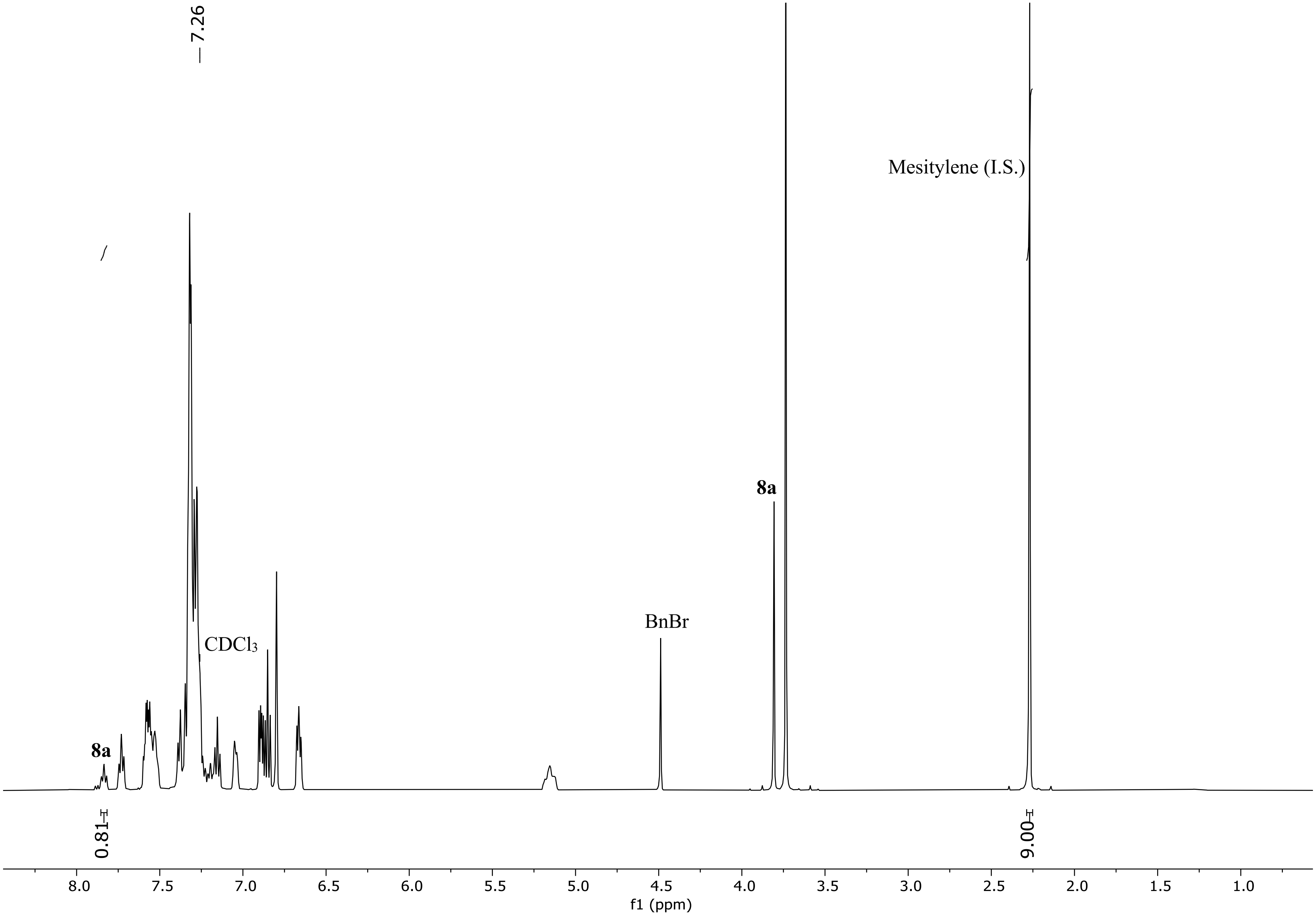
^{1}H NMR (CDCl$_3$, 500 MHz)

NMR #5. Time = 1011 seconds for Phosphine **8** reaction with benzyl bromide (^{1}H NMR Yield = 72%).



^{1}H NMR ($CDCl_3$, 500 MHz)

NMR #6. Time = 1371 seconds for Phosphine **8** reaction with benzyl bromide (^{1}H NMR Yield = 81%).



^{1}H NMR (CDCl$_3$, 500 MHz)

Quantum Chemical Calculations:

Computational Methodology and Details:

To appreciate the reactivity difference between the two systems, we performed density functional theory (DFT) calculations. All computations were carried out with Gaussian 16 package version C01[9] with tight self-consistent-field convergence and ultrafine integration grids. The DFT B3LYP[10,11] approximate functional was employed with B, C and H elements using Pople's 6-311G(d) basis set and O and P using 6-311+G(d) basis set in the $CHCl_3$ solvent with CPCM as the implicit solvent model.[12,13] The optimized transition state (TS) structures are shown in Fig. S1. The EPS surface of the Bpin TS is shown in Fig. S2 and its HOMO and LUMO surfaces are in Fig. S3. The barrier height in terms of the Gibbs free energy difference $\Delta G^{\neq}$ between the TS and reactant for the H and Bpin systems is 19.8 and 18.2 kcal/mol, respectively. In terms of enthalpy difference, it is 13.8 and 12.9 kcal/mol, respectively. In terms of the total energy difference, it is 14.4 and 13.5 kcal/mol, respectively. These results are consistent with our experimental finding.

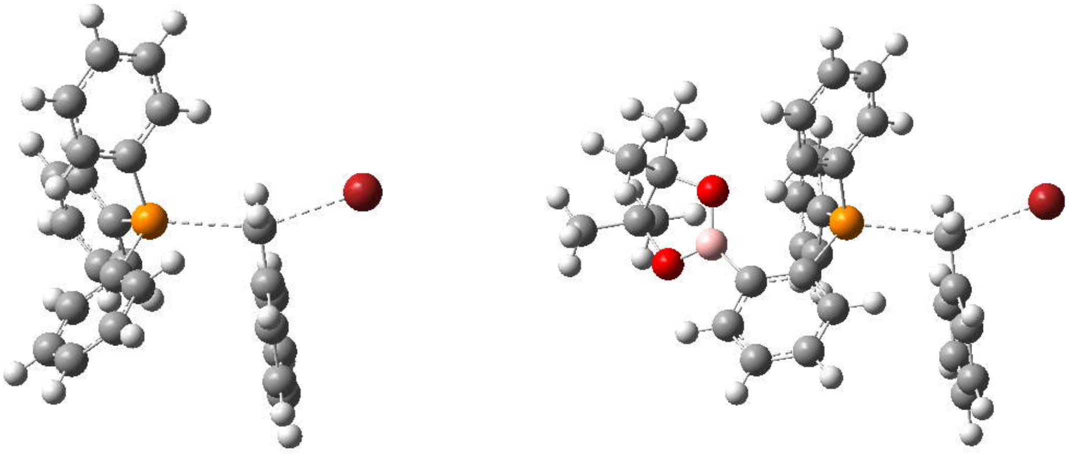


Figure S1. The optimized transition state structures for the two systems.

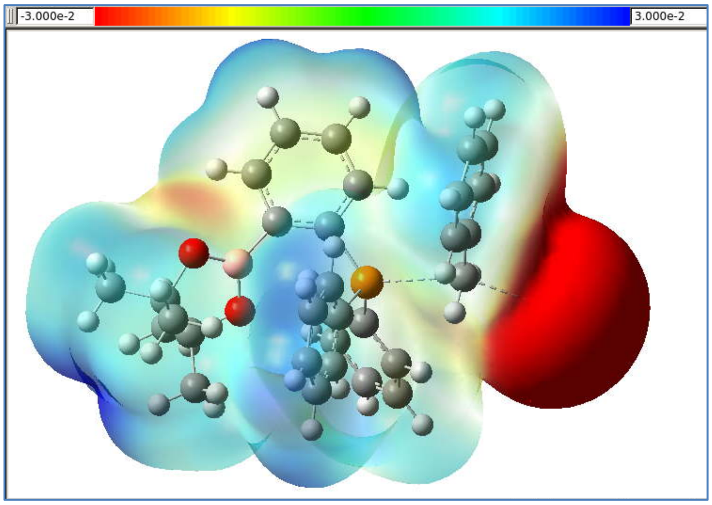
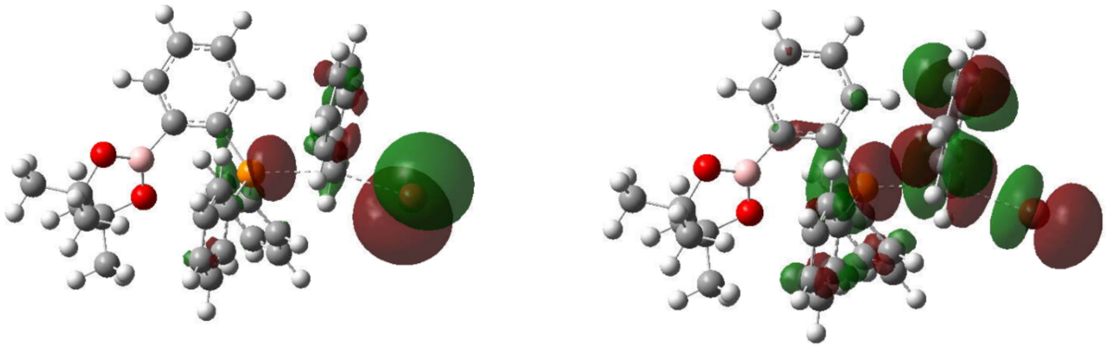


Figure S2. The electrostatic potential contour map on the von der Waals surface for the transition state structure of the Bpin system.



(a) (b)

Figure S3. Frontier molecular orbitals of the transition state structure for the Bpin system: (a) highest occupied molecular orbital (HOMO) and (b) lowest unoccupied molecular orbital (LUMO).

To understand the nature of interactions for the Bpin system, we performed NPA (natural population analysis).[14] Using the second-order perturbation theory, we obtained that the total interaction due to the hyperconjugation effect between the Bpin group with the P motif in the TS structure is 6.1 kcal/mol, suggesting that this additional stability attributes to the lower barrier height for the Bpin system.

To further understand the origin of the barrier height difference in the above two systems, we applied two total energy decomposition approaches in DFT available in the literature,[15,16] where the total energy difference ΔE can be decomposed into kinetic ΔT_S, exchange-correlation ΔExc and electrostatic ΔEe contributions

$$\Delta E = \Delta Ts + \Delta Exc + \Delta Ee. \tag{S1}$$

Alternatively, ΔE can be partitioned using steric effect ΔEs, electrostatic interaction ΔEe, and quantum effect due to the exchange-correlation interactions ΔEq

$$\Delta E = \Delta Ee + \Delta Es + \Delta Eq. \tag{S2}$$

Table S1 exhibits the results from these two partition approaches. As can be seen from the Table, the difference between H and Bpin systems in total energy difference (ΔΔE = 0.93 kcal/mol) dominantly comes from the electrostatic interaction (ΔΔEe = 7.54 kcal/mol). Surprisingly, steric hindrance (ΔΔEs) also contributed positively to the ΔΔE with ΔΔEs = 2.49 kcal/mol. This is likely due to the favorable electrostatic and steric interaction from the Bpin and O atoms.

Table S1. The decomposition analysis of the total energy difference for the two systems. Units in kcal/mol.

	ΔE	ΔTs	ΔExc	ΔEe	ΔEs	ΔEq
H	14.40	-44.41	13.49	45.32	-9.52	-21.40
Bpin	13.47	-37.27	12.95	37.78	-12.01	-12.30
Difference	0.93	-7.14	0.54	7.54	2.49	-9.10

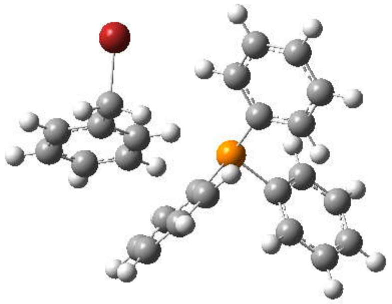
Table S2. The reaction barrier height in terms of the total energy difference ΔE, *enthalpy difference* ΔH, *and Gibbs free energy difference* ΔG *for the two systems. Units in kcal/mol.*

	ΔE	ΔH	ΔG
H	14.40	13.80	19.82
Bpin	13.47	12.87	18.24
Difference	0.93	0.93	1.58

Cartesian Coordinates:

1. The optimized reactant (molecular complex) of PPh_3 in substitution reaction with BnBr

Total Energy = -3881.64556516 a.u.
Enthalpy = -3881.227192 a.u.
Gibbs Free Energy = -3881.324133 a.u.

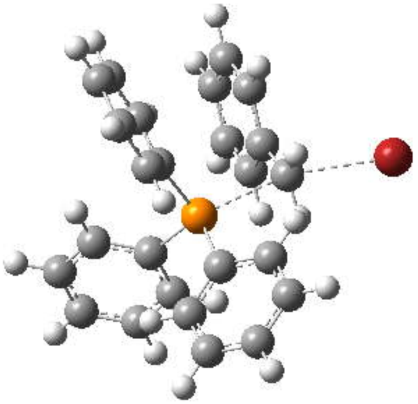


Br	2.57597	16.70805	9.00133
P	5.93278	12.60531	9.08794
C	6.71792	11.38873	7.93058
C	7.09589	10.08759	8.28554
C	7.65889	9.22943	7.34070
C	7.85782	9.66018	6.03028
C	7.48444	10.95346	5.66444
C	6.91071	11.80603	6.60463
C	5.44327	11.54351	10.52625
C	6.22986	11.34152	11.66735
C	5.76727	10.54724	12.71687
C	4.51592	9.93869	12.63931
C	3.72268	10.13335	11.50853
C	4.17909	10.93681	10.46636
C	7.39014	13.54506	9.74174
C	7.13182	14.79463	10.32499
C	8.16919	15.57093	10.83719
C	9.48554	15.11755	10.75737
C	9.75643	13.88367	10.16785
C	8.71685	13.10130	9.66569
C	2.15768	14.72950	9.12737

C	1.22225	14.28534	8.05742
C	-0.16235	14.30415	8.26801
C	-1.03513	13.86952	7.27425
C	-0.53413	13.41076	6.05588
C	0.84327	13.38674	5.83675
C	1.71562	13.82128	6.83111
H	7.94448	8.22353	7.63190
H	8.29610	8.99124	5.29684
H	7.62954	11.29490	4.64452
H	6.60758	12.80513	6.30470
H	7.20728	11.80485	11.74131
H	6.38878	10.40298	13.59498
H	4.15803	9.32110	13.45662
H	2.74400	9.66893	11.44243
H	3.54531	11.09599	9.59864
H	6.11232	15.16586	10.37484
H	7.95030	16.53388	11.28726
H	10.29584	15.72515	11.14692
H	10.77911	13.52649	10.09913
H	8.94287	12.14276	9.21184
H	1.74730	14.62209	10.12685
H	3.13533	14.25964	9.06610
H	-0.55610	14.65969	9.21540
H	-2.10549	13.88578	7.45095
H	-1.21405	13.07093	5.28164
H	1.23794	13.02599	4.89269
H	2.78715	13.80090	6.65790
H	6.95112	9.73926	9.30208

2. The optimized transition state structure of PPh_3 in substitution reaction with BnBr

Total Energy = -3881.62261799 a.u.
Enthalpy = -3881.205203 a.u.
Gibbs Free Energy = -3881.292543 a.u.

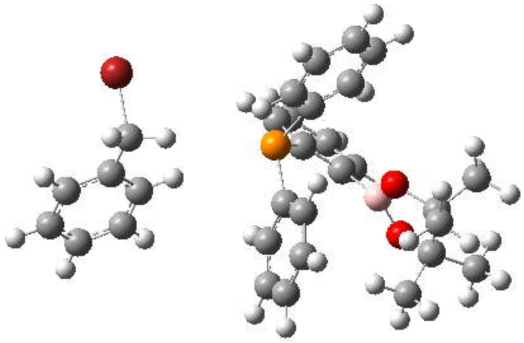


Br	2.53000	17.03700	8.24500
P	5.46500	12.86600	9.25400
C	6.02700	11.74000	7.91500
C	6.07500	10.34700	8.04800
C	6.48500	9.55100	6.97800
C	6.85300	10.13500	5.76800
C	6.80800	11.52300	5.62700
C	6.39100	12.31900	6.68900
C	4.96300	11.78700	10.65200
C	5.67000	11.73800	11.86000
C	5.20900	10.95100	12.91400
C	4.04000	10.20400	12.77600
C	3.32700	10.25100	11.57800
C	3.77900	11.04200	10.52500
C	6.98500	13.73500	9.81400
C	6.83900	14.96200	10.47700
C	7.95800	15.66200	10.92200
C	9.23600	15.15000	10.69900
C	9.39100	13.93400	10.03300
C	8.27300	13.22800	9.59300
C	3.61300	14.64900	8.52200
C	2.62200	13.79900	7.89200
C	1.55100	13.28000	8.64100
C	0.59600	12.47200	8.03700
C	0.69500	12.16800	6.67800
C	1.75300	12.67900	5.92300
C	2.70900	13.48900	6.52300
H	6.52100	8.47300	7.09600
H	7.17200	9.51400	4.93800
H	7.09200	11.98500	4.68700
H	6.35900	13.39700	6.56200
H	6.58200	12.31100	11.98200
H	5.76800	10.92000	13.84300
H	3.68500	9.59200	13.59800
H	2.41500	9.67600	11.46400
H	3.20800	11.07600	9.60300
H	5.85200	15.37800	10.64800
H	7.83100	16.61000	11.43300
H	10.10800	15.69800	11.03900
H	10.38300	13.53300	9.85600
H	8.40600	12.28500	9.07500
H	3.55300	14.87500	9.57100
H	4.41700	15.08400	7.95700
H	1.46900	13.52400	9.69500
H	-0.22900	12.08100	8.62300
H	-0.05300	11.53900	6.20700

H	1.82800	12.44800	4.86600
H	3.52400	13.89300	5.93300
H	5.79900	9.87800	8.98500

3. The optimized reactant (molecular complex) of *1* in substitution reaction with BnBr

Total Energy = -4292.42331516 a.u.
Enthalpy = -4291.823515 a.u.
Gibbs Free Energy = -4291.940227 a.u.

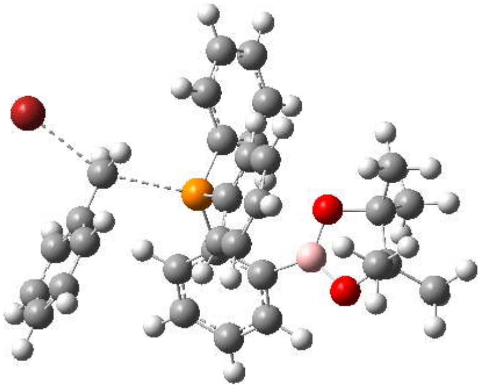


Br	3.23929	16.54066	6.81112
P	5.94555	12.90968	9.46774
O	7.42924	8.34242	9.23081
O	8.17600	10.17266	10.37322
C	6.51865	11.88170	8.02801
C	7.06215	10.57238	8.03380
C	7.30696	9.95914	6.79009
C	7.07388	10.60639	5.57918
C	6.56416	11.89944	5.58324
C	6.27430	12.51516	6.79902
C	5.26190	11.70468	10.69532
C	5.60917	11.69723	12.05138
C	4.91075	10.90322	12.96100
C	3.85938	10.09546	12.53158
C	3.50877	10.08816	11.18131
C	4.19504	10.89279	10.27538
C	7.47677	13.60480	10.23330
C	7.30997	14.59062	11.22014
C	8.41046	15.23333	11.78243
C	9.69816	14.92652	11.34323
C	9.87431	13.97093	10.34415
C	8.77427	13.31166	9.79629
C	2.51024	15.16412	8.10744
C	1.46016	14.31129	7.48498
C	0.10958	14.67415	7.56209
C	-0.87372	13.86672	6.99672

C	-0.51876	12.68543	6.34539
C	0.82349	12.31434	6.26419
C	1.80620	13.12202	6.83025
C	7.92382	7.81660	10.50391
C	8.78281	9.02328	11.05037
C	8.70887	6.53980	10.22194
C	6.69512	7.50053	11.35944
C	10.24765	8.98401	10.60397
C	8.70228	9.24507	12.55621
B	7.52001	9.71384	9.26421
H	7.70453	8.94979	6.77673
H	7.28618	10.10042	4.64288
H	6.37197	12.42217	4.65193
H	5.83825	13.50929	6.79478
H	6.43199	12.30785	12.40438
H	5.19527	10.91415	14.00859
H	3.31776	9.47822	13.24082
H	2.69265	9.46313	10.83299
H	3.89256	10.89085	9.23226
H	6.31137	14.86544	11.54760
H	8.26009	15.98510	12.55064
H	10.55618	15.43595	11.76967
H	10.87232	13.73219	9.99010
H	8.93109	12.56367	9.02923
H	2.13936	15.76629	8.93130
H	3.39432	14.61017	8.41163
H	-0.17104	15.59255	8.06887
H	-1.91671	14.15738	7.06651
H	-1.28488	12.05552	5.90548
H	1.10438	11.39407	5.76280
H	2.84982	12.83003	6.76483
H	9.15306	6.14552	11.13958
H	9.50510	6.70097	9.49550
H	8.03688	5.77681	9.82274
H	6.97910	7.05529	12.31568
H	6.09802	8.39172	11.55684
H	6.06526	6.78399	10.82756
H	10.72565	9.92994	10.86647
H	10.79588	8.17909	11.09819
H	10.33940	8.85018	9.52407
H	9.30336	10.11440	12.83214
H	9.09846	8.38078	13.09575
H	7.68024	9.42258	12.88739

4. The optimized transition state structure of *1* in substitution reaction with BnBr

Total Energy = -4292.40185713 a.u.
Enthalpy = -4291.803004 a.u.
Gibbs Free Energy = -4291.911158 a.u.



Br	2.39900	16.83600	9.23400
P	5.56000	12.72600	9.16200
O	7.28700	8.28300	9.40800
O	7.82900	10.29500	10.34300
C	6.13400	11.60200	7.81700
C	6.72900	10.32400	7.97000
C	6.99000	9.58800	6.80100
C	6.72100	10.08700	5.52800
C	6.16500	11.35400	5.39200
C	5.86100	12.09300	6.53200
C	4.90100	11.68100	10.51700
C	5.18100	11.92500	11.86700
C	4.51600	11.21500	12.86500
C	3.56600	10.25100	12.53000
C	3.28300	9.99900	11.18800
C	3.93700	10.71300	10.18800
C	7.01800	13.65300	9.77900
C	6.80500	14.73800	10.64500
C	7.87400	15.52200	11.07300
C	9.16500	15.25100	10.62200
C	9.38100	14.19200	9.74300
C	8.31800	13.39600	9.32400
C	3.62100	14.55000	8.77300
C	2.67900	13.87800	7.90300
C	1.69200	13.03100	8.43900
C	0.78300	12.39200	7.60600
C	0.84000	12.59100	6.22500
C	1.81000	13.43500	5.68000
C	2.72200	14.07300	6.51000
C	7.79700	7.95600	10.74200

C	8.52800	9.29300	11.15500
C	8.70200	6.73500	10.62300
C	6.58000	7.62800	11.61000
C	9.99800	9.34400	10.73000
C	8.39500	9.67500	12.62400
B	7.24700	9.64900	9.28800
H	7.43100	8.60200	6.89600
H	6.94500	9.48800	4.65200
H	5.95000	11.76200	4.41000
H	5.39500	13.06500	6.41900
H	5.92600	12.66100	12.14600
H	4.74700	11.41400	13.90600
H	3.05000	9.70000	13.30900
H	2.54700	9.24900	10.91700
H	3.69700	10.51300	9.14900
H	5.80500	14.98500	10.98700
H	7.69200	16.35200	11.74800
H	9.99500	15.86900	10.94700
H	10.38200	13.98000	9.38200
H	8.50300	12.57200	8.64700
H	3.55000	14.43900	9.84000
H	4.40000	15.17700	8.37700
H	1.64000	12.88500	9.51300
H	0.02500	11.74200	8.03000
H	0.12600	12.09600	5.57600
H	1.84800	13.59800	4.60800
H	3.46300	14.74400	6.08800
H	9.15500	6.49200	11.58800
H	9.49900	6.88500	9.89600
H	8.11300	5.87100	10.30500
H	6.87800	7.32200	12.61500
H	5.90100	8.47700	11.69400
H	6.03000	6.80100	11.15500
H	10.37900	10.35500	10.88600
H	10.61000	8.65700	11.31900
H	10.12400	9.09600	9.67400
H	8.90500	10.62400	12.80500
H	8.86000	8.91900	13.26300
H	7.35400	9.78900	12.92400

X-Ray Crystallographic Data for 1a:

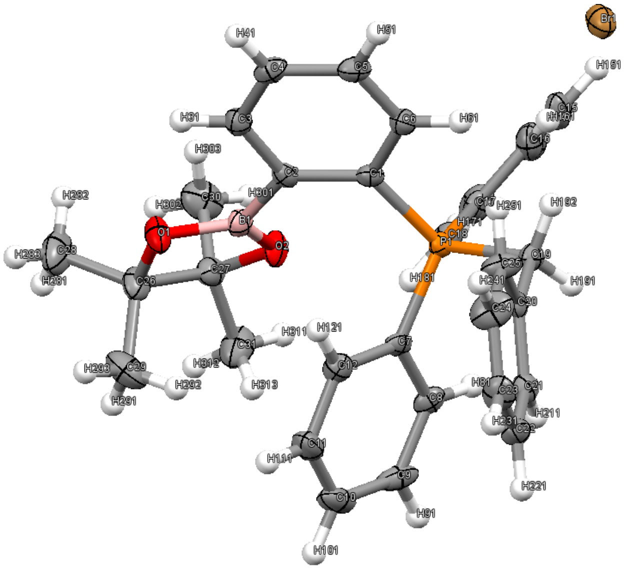


Figure 1. Molecular structure for **1a** (50% probability level shown).

X-ray quality crystals were grown by placing an uncapped 1-dram vial containing a 1.0 mL solution of compound **1a** dissolved in dry acetonitrile into a scintillation vial containing 2.0 mL of ethyl acetate and allowing vapor diffusion to occur for 48 hours. A colorless crystal (approximate dimensions 0.230 x 0.100 x 0.070 mm^3) was placed onto the tip of MiTeGen and mounted on a Bruker SMART Apex II diffractometer and measured at 150 K.

Data collection:

A preliminary set of cell constants was calculated from reflections harvested from three sets of 12 frames. These initial sets of frames were oriented such that orthogonal wedges of reciprocal space were surveyed. This produced initial orientation matrices determined from 146 reflections. The data collection was carried out using Mo Kα radiation (graphite monochromator) with a frame time of 40 seconds and a detector distance of 4.0 cm. A randomly oriented region of reciprocal space was surveyed to achieve complete data with a redundancy of 4. Sections of frames were collected with 2.00° steps in ω and ϕ scans. Data to a resolution of 0.84 Å were considered in the reduction. Final cell constants were calculated from the xyz centroids of 3644 strong reflections from the actual data collection after integration (SAINT). The intensity data were corrected for absorption (SADABS). Please refer to Table 1 for additional crystal and refinement information.

Structure solution and refinement:

The space group $P2_1/n$ was determined based on intensity statistics and systematic absences. The structure was solved using SHELXT and refined (full-matrix-least squares) using the Oxford University Crystals for Windows system. The intrinsic phasing solution provided most non-hydrogen atoms from the E-map. Full-matrix least squares / difference Fourier cycles were performed, which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were placed in ideal positions and refined as riding atoms. The final full matrix least squares refinement converged to R1 = 0.0465 and wR2 = 0.1485 (F^2, all data).

Table S1. Crystal data and structure refinement for Compound **1a**.

Empirical formula	C31 H33 B1 Br1 O2 P1	
Formula weight	559.29	
Crystal color, shape, size	colorless block, 0.230 x 0.100 x 0.070 mm^3	
Temperature	150 K	
Wavelength	0.71073 Å	
Crystal system, space group	Monoclinic, P 1 21/n 1	
Unit cell dimensions	a = 9.7302(3) Å	$\alpha = 90^\circ$.
	b = 15.9096(4) Å	$\beta = 92.761(3)^\circ$.
	c = 17.8875(7) Å	$\gamma = 90^\circ$.
Volume	2765.83(15) Å^3	
Z	4	
Density (calculated)	1.343 Mg/m^3	
Absorption coefficient	1.570 mm^{-1}	
F(000) 1160		
Data collection		
Diffractometer	Bruker Apex Kappa Duo, Bruker	
Theta range for data collection	1.714 to 25.035°.	
Index ranges	-11<=h<=11, -17<=k<=18, -21<=l<=16	
Reflections collected	21021	
Independent reflections	4879 [R(int) = 0.109]	
Observed Reflections	3270	
Completeness to theta = 25.035°	99.6 %	
Solution and Refinement		
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.90 and 0.85	
Solution	Charge-Flipping methods	
Refinement method	Full-matrix least-squares on F^2	
Weighting scheme	$w = [\sigma^2 Fo^2 + AP^2 + BP]^{-1}$, with $P = (Fo^2 + 2\,Fc^2)/3$, A = 0.070, B = 1.990	
Data / restraints / parameters	4878 / 0 / 325	
Goodness-of-fit on F^2	1.0242	
Final R indices [I>2sigma(I)]	R1 = 0.0465, wR2 = 0.1053	
R indices (all data)	R1 = 0.0863, wR2 = 0.1485	
Largest diff. peak and hole	1.05 and -0.97 e.Å^{-3}	

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for **1a**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Label	x	y	z	U(eq)
Br1	6258(1)	10082(1)	3238(1)	33
P1	5861(1)	8032(1)	5283(1)	17
O1	7660(4)	5296(2)	5217(2)	31
O2	7802(3)	6516(2)	5883(2)	26
C1	6382(4)	7459(3)	4466(3)	19
C2	6962(5)	6636(3)	4497(3)	19
C3	7236(5)	6260(3)	3815(3)	23
C4	6992(5)	6653(3)	3137(3)	25
C5	6481(5)	7467(3)	3121(3)	24
C6	6182(5)	7863(3)	3783(3)	22
C7	5023(4)	7349(3)	5916(3)	19
C8	4896(5)	7575(3)	6662(3)	24
C9	4187(5)	7048(4)	7125(3)	32
C10	3598(5)	6318(4)	6858(3)	35
C11	3677(5)	6112(3)	6112(3)	34
C12	4391(5)	6619(3)	5641(3)	25
C13	7286(4)	8599(3)	5724(3)	18
C14	7725(5)	9316(3)	5370(3)	27
C15	8813(5)	9777(3)	5700(3)	32
C16	9456(5)	9518(3)	6366(3)	33
C17	9020(5)	8809(3)	6715(3)	33
C18	7921(5)	8344(3)	6396(3)	22
C19	4575(5)	8823(3)	5016(3)	20
C20	3185(5)	8462(3)	4773(3)	18
C21	2209(5)	8300(3)	5294(3)	23
C22	922(5)	8003(3)	5068(3)	27
C23	589(5)	7851(3)	4328(3)	32
C24	1547(6)	8006(4)	3805(3)	39
C25	2837(5)	8312(3)	4026(3)	30
C26	8050(6)	5042(3)	5987(3)	29
C27	8518(5)	5883(3)	6362(3)	26
C28	9167(7)	4380(4)	5963(4)	52
C29	6769(6)	4672(4)	6306(4)	45
C30	10043(6)	6065(4)	6305(3)	43
C31	8080(7)	5999(4)	7160(3)	42
B1	7442(6)	6145(3)	5221(3)	22

Table S3. Bond lengths [Å] and angles [°] for **1a**.

P1-C1	1.815(5)	P1-C7	1.795(4)
P1-C13	1.803(5)	P1-C19	1.822(5)
O1-C26	1.468(6)	O1-B1	1.367(6)
O2-C27	1.474(6)	O2-B1	1.353(7)
C1-C2	1.427(6)	C1-C6	1.387(7)
C2-C3	1.397(7)	C2-B1	1.564(7)
C3-C4	1.376(7)	C3-H31	0.950
C4-C5	1.386(7)	C4-H41	0.950
C5-C6	1.384(7)	C5-H51	0.950
C6-H61	0.950	C7-C8	1.393(7)
C7-C12	1.393(7)	C8-C9	1.386(7)
C8-H81	0.950	C9-C10	1.372(8)
C9-H91	0.950	C10-C11	1.380(8)
C10-H101	0.950	C11-C12	1.378(7)
C11-H111	0.950	C12-H121	0.950
C13-C14	1.383(7)	C13-C18	1.385(7)
C14-C15	1.395(7)	C14-H141	0.950
C15-C16	1.382(8)	C15-H151	0.950
C16-C17	1.367(7)	C16-H161	0.950
C17-C18	1.400(7)	C17-H171	0.950
C18-H181	0.950	C19-C20	1.514(6)
C19-H191	0.950	C19-H192	0.950
C20-C21	1.386(6)	C20-C25	1.384(7)
C21-C22	1.381(7)	C21-H211	0.950
C22-C23	1.369(7)	C22-H221	0.950
C23-C24	1.374(7)	C23-H231	0.950
C24-C25	1.386(7)	C24-H241	0.950
C25-H251	0.950	C26-C27	1.555(7)
C26-C28	1.515(7)	C26-C29	1.515(7)
C27-C30	1.520(7)	C27-C31	1.521(7)
C28-H281	0.950	C28-H282	0.950
C28-H283	0.950	C29-H291	0.950
C29-H292	0.950	C29-H293	0.950
C30-H301	0.950	C30-H302	0.950
C30-H303	0.950	C31-H311	0.950
C31-H312	0.950	C31-H313	0.950
C1-P1-C7	110.9(2)	C1-P1-C13	111.4(2)
C7-P1-C13	112.9(2)	C1-P1-C19	110.6(2)

C7-P1-C19	104.9(2)	C13-P1-C19	105.9(2)
C26-O1-B1	107.5(4)	C27-O2-B1	107.8(4)
P1-C1-C2	123.7(4)	P1-C1-C6	116.4(3)
C2-C1-C6	119.9(4)	C1-C2-C3	116.8(4)
C1-C2-B1	126.3(4)	C3-C2-B1	116.7(4)
C2-C3-C4	123.0(4)	C2-C3-H31	118.3
C4-C3-H31	118.7	C3-C4-C5	119.3(5)
C3-C4-H41	120.2	C5-C4-H41	120.5
C4-C5-C6	119.9(5)	C4-C5-H51	120.1
C6-C5-H51	120.0	C1-C6-C5	121.1(4)
C1-C6-H61	119.3	C5-C6-H61	119.7
P1-C7-C8	120.8(4)	P1-C7-C12	119.2(4)
C8-C7-C12	119.7(4)	C7-C8-C9	119.0(5)
C7-C8-H81	120.4	C9-C8-H81	120.5
C8-C9-C10	121.1(5)	C8-C9-H91	119.7
C10-C9-H91	119.2	C9-C10-C11	119.8(5)
C9-C10-H101	120.0	C11-C10-H101	120.2
C10-C11-C12	120.3(5)	C10-C11-H111	119.8
C12-C11-H111	119.9	C7-C12-C11	120.0(5)
C7-C12-H121	119.7	C11-C12-H121	120.4
P1-C13-C14	117.4(4)	P1-C13-C18	122.4(4)
C14-C13-C18	120.2(4)	C13-C14-C15	119.0(5)
C13-C14-H141	120.2	C15-C14-H141	120.7
C14-C15-C16	120.7(5)	C14-C15-H151	119.5
C16-C15-H151	119.7	C15-C16-C17	120.1(5)
C15-C16-H161	119.8	C17-C16-H161	120.1
C16-C17-C18	119.9(5)	C16-C17-H171	120.3
C18-C17-H171	119.8	C17-C18-C13	120.0(5)
C17-C18-H181	120.4	C13-C18-H181	119.7
P1-C19-C20	113.9(3)	P1-C19-H191	108.4
C20-C19-H191	108.4	P1-C19-H192	108.3
C20-C19-H192	108.3	H191-C19-H192	109.5
C19-C20-C21	120.6(4)	C19-C20-C25	121.1(4)
C21-C20-C25	118.3(4)	C20-C21-C22	120.5(5)
C20-C21-H211	119.5	C22-C21-H211	120.0
C21-C22-C23	120.9(5)	C21-C22-H221	119.5
C23-C22-H221	119.6	C22-C23-C24	119.3(5)
C22-C23-H231	120.2	C24-C23-H231	120.5
C23-C24-C25	120.3(5)	C23-C24-H241	120.0
C25-C24-H241	119.6	C24-C25-C20	120.8(5)
C24-C25-H251	120.0	C20-C25-H251	119.3
O1-C26-C27	102.9(4)	O1-C26-C28	108.6(4)
C27-C26-C28	114.5(5)	O1-C26-C29	106.3(4)

C27-C26-C29	113.7(4)	C28-C26-C29	110.2(5)
C26-C27-O2	102.5(4)	C26-C27-C30	113.7(4)
O2-C27-C30	105.5(4)	C26-C27-C31	114.8(4)
O2-C27-C31	108.4(4)	C30-C27-C31	111.0(5)
C26-C28-H281	109.3	C26-C28-H282	109.0
H281-C28-H282	109.5	C26-C28-H283	110.1
H281-C28-H283	109.5	H282-C28-H283	109.5
C26-C29-H291	109.4	C26-C29-H292	109.5
H291-C29-H292	109.5	C26-C29-H293	109.5
H291-C29-H293	109.5	H292-C29-H293	109.5
C27-C30-H301	109.7	C27-C30-H302	109.5
H301-C30-H302	109.5	C27-C30-H303	109.2
H301-C30-H303	109.5	H302-C30-H303	109.5
C27-C31-H311	109.4	C27-C31-H312	109.5
H311-C31-H312	109.5	C27-C31-H313	109.4
H311-C31-H313	109.5	H312-C31-H313	109.5
C2-B1-O1	121.9(5)	C2-B1-O2	124.2(4)
O1-B1-O2	113.7(5)		

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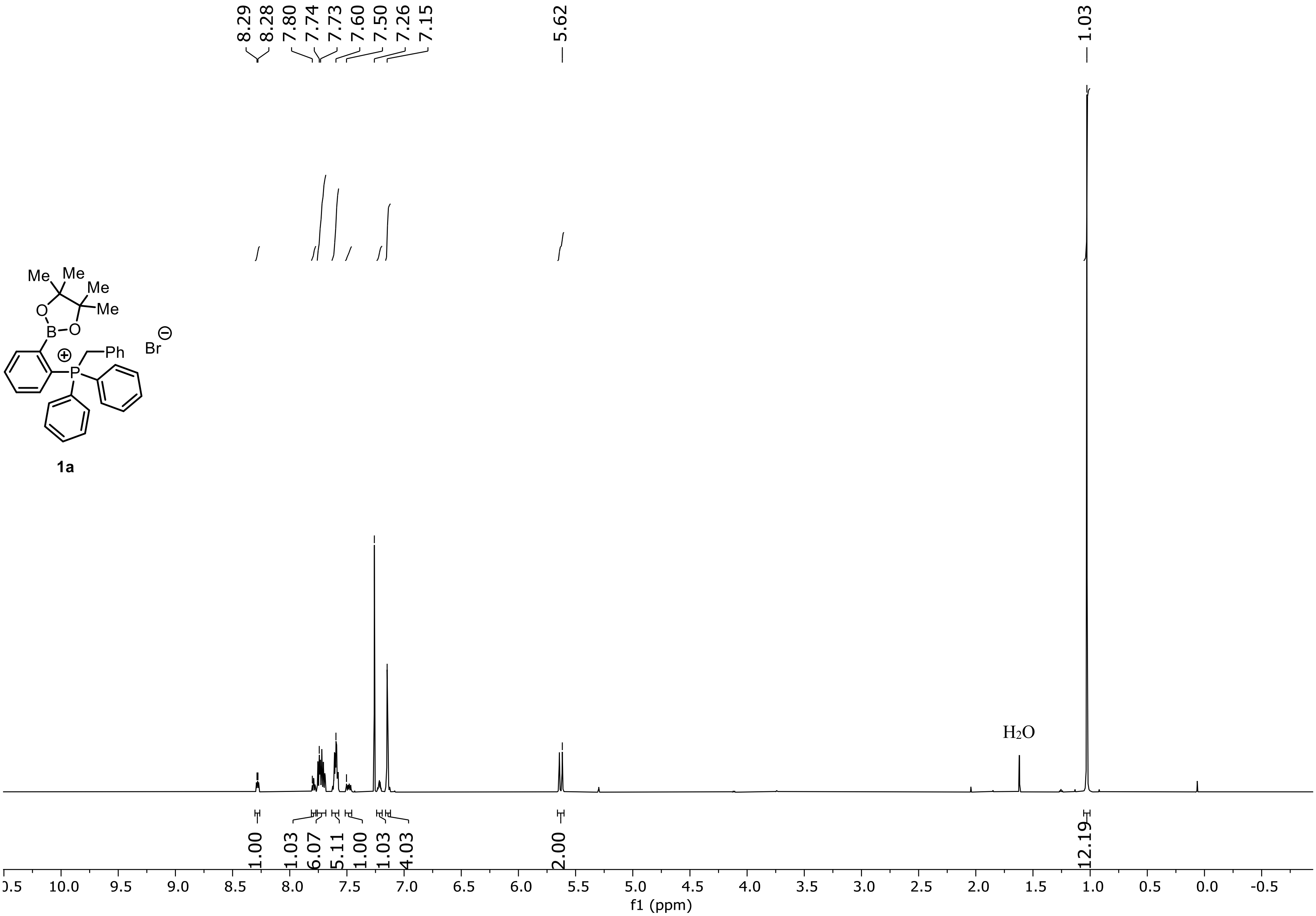
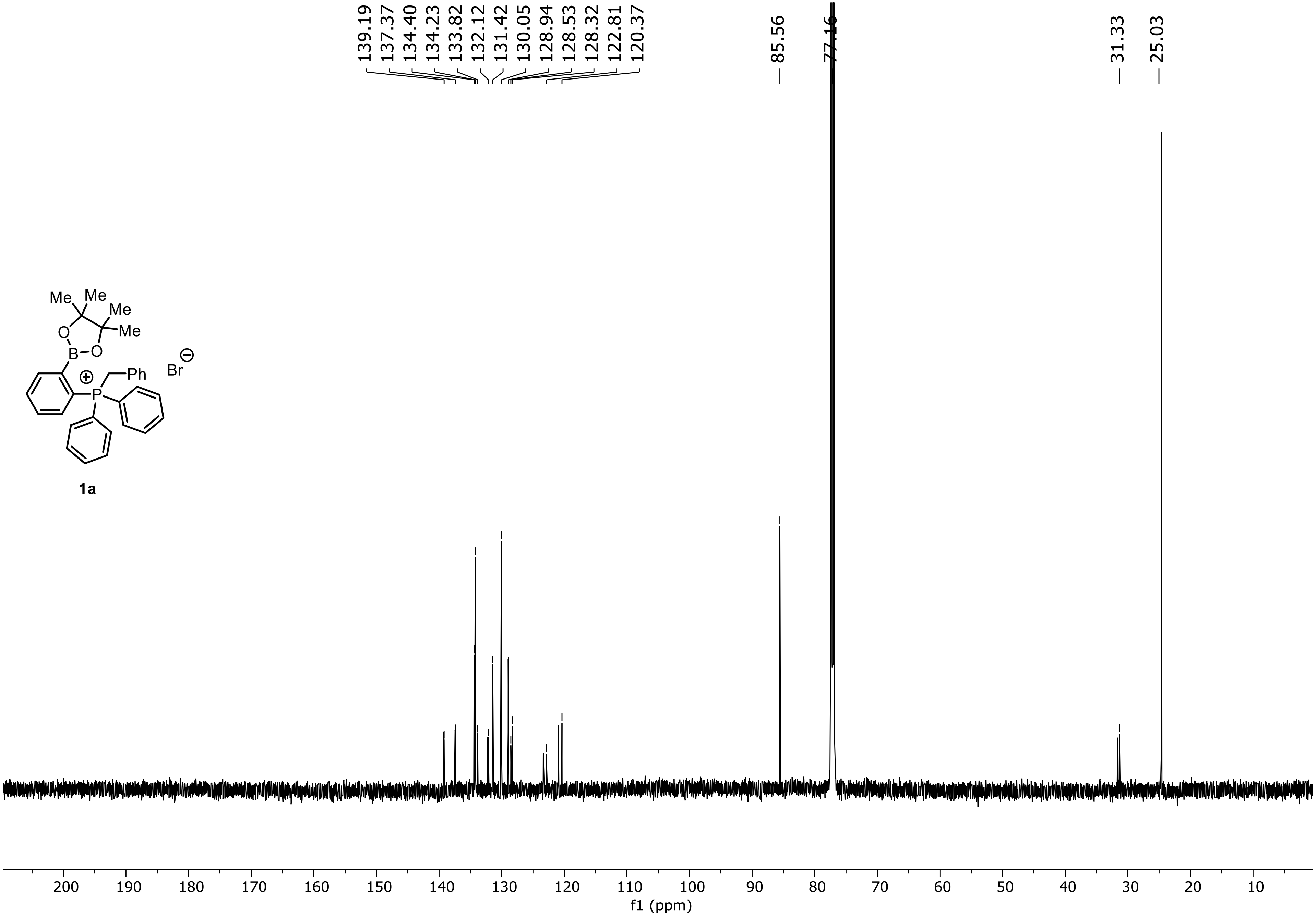
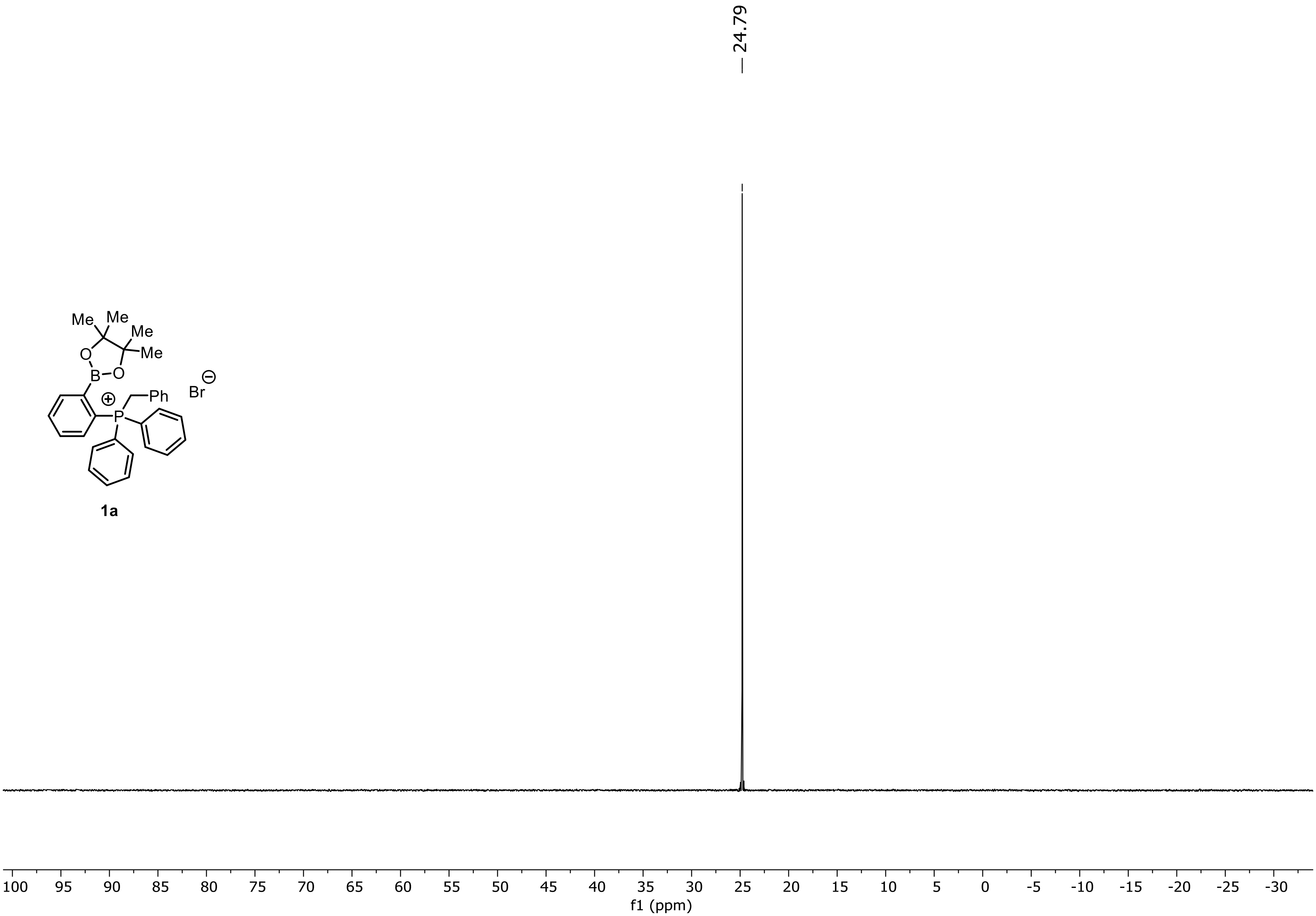
^{1}H, ^{13}C, and ^{31}P NMR Spectra



^{1}H NMR (CDCl$_3$, 600 MHz)

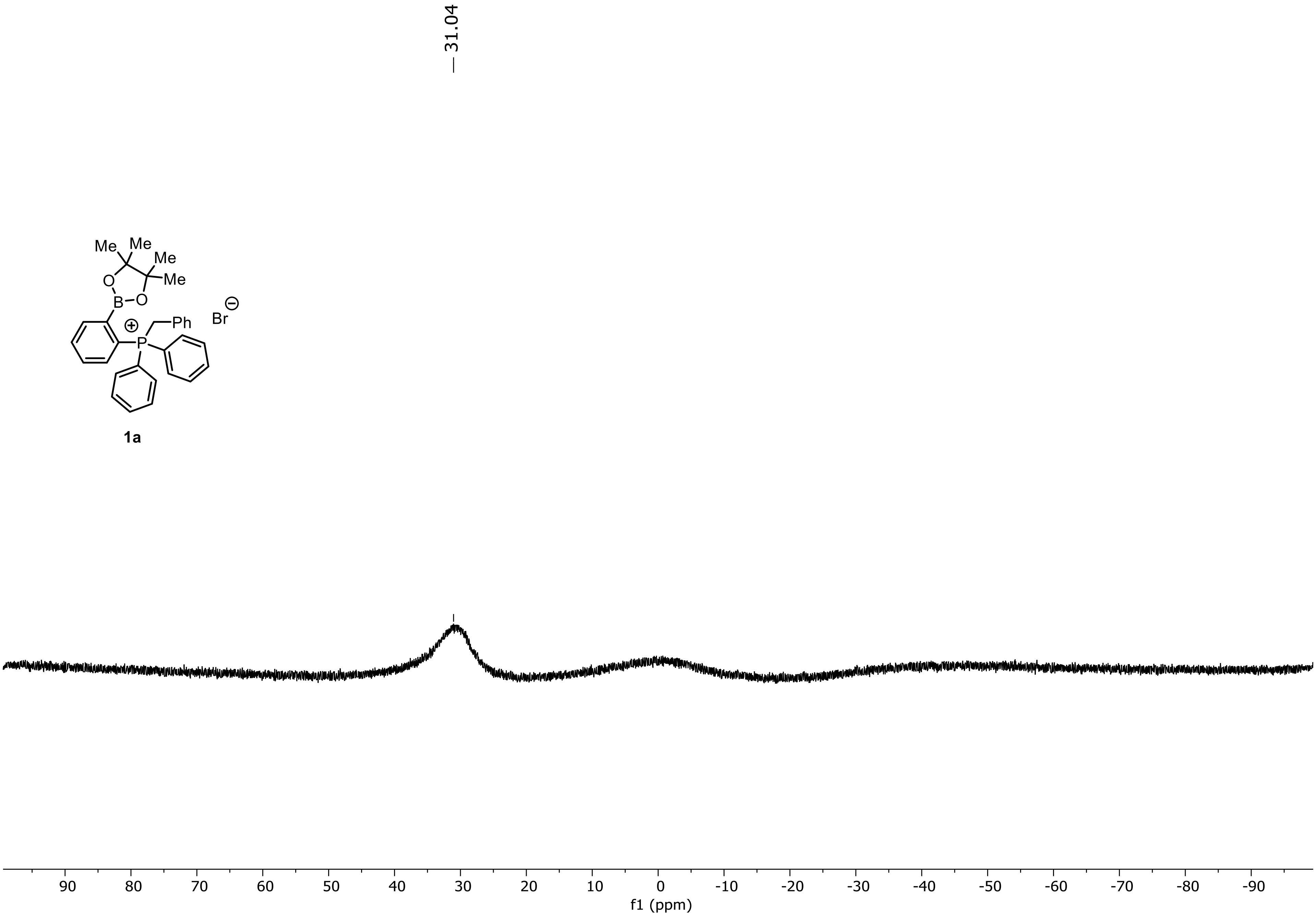


^{13}C NMR (CDCl$_3$, 151 MHz)



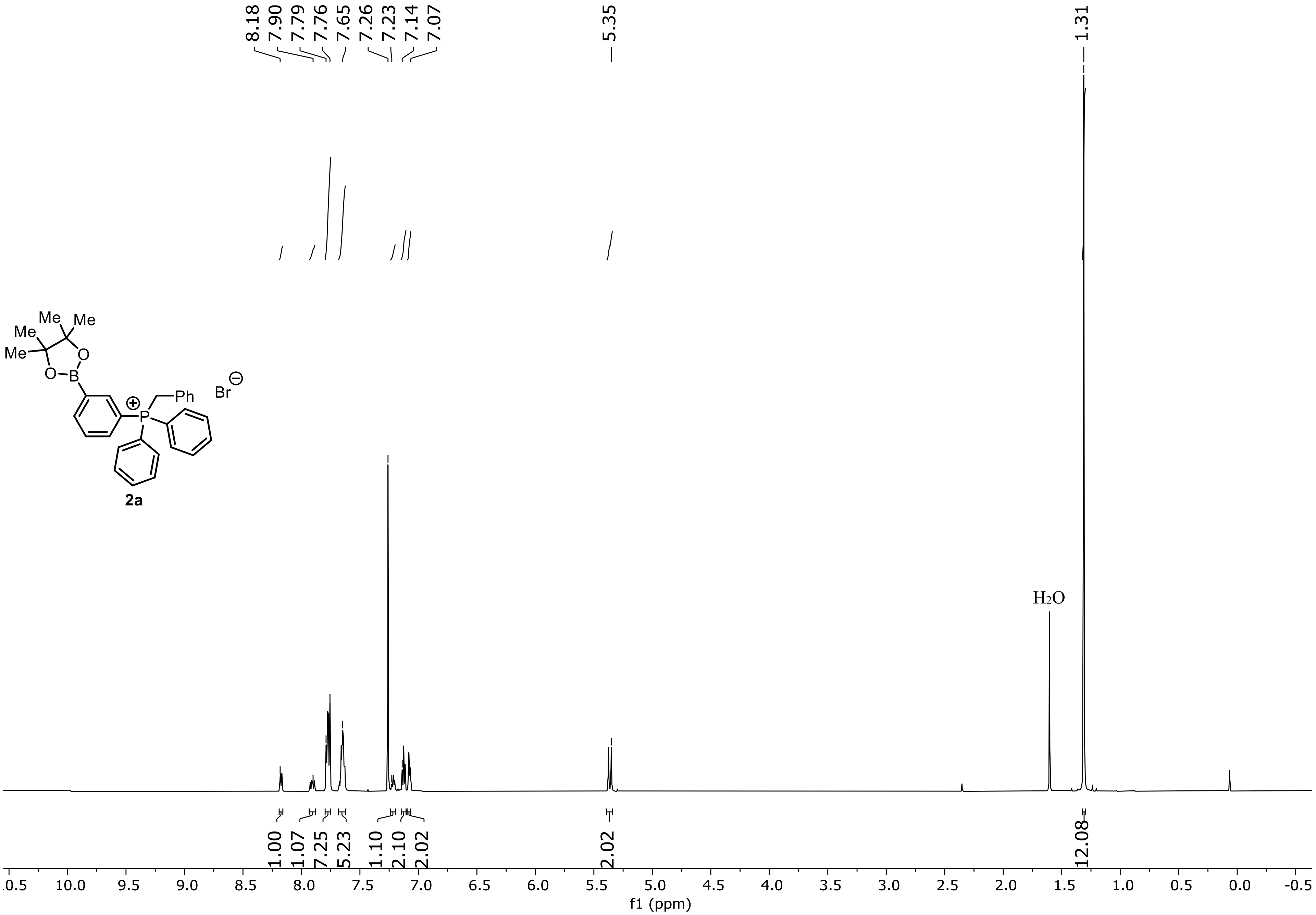
1a

^{31}P NMR (CDCl$_3$, 243 MHz)



1a

^{11}B NMR (CDCl$_3$, 128 MHz)



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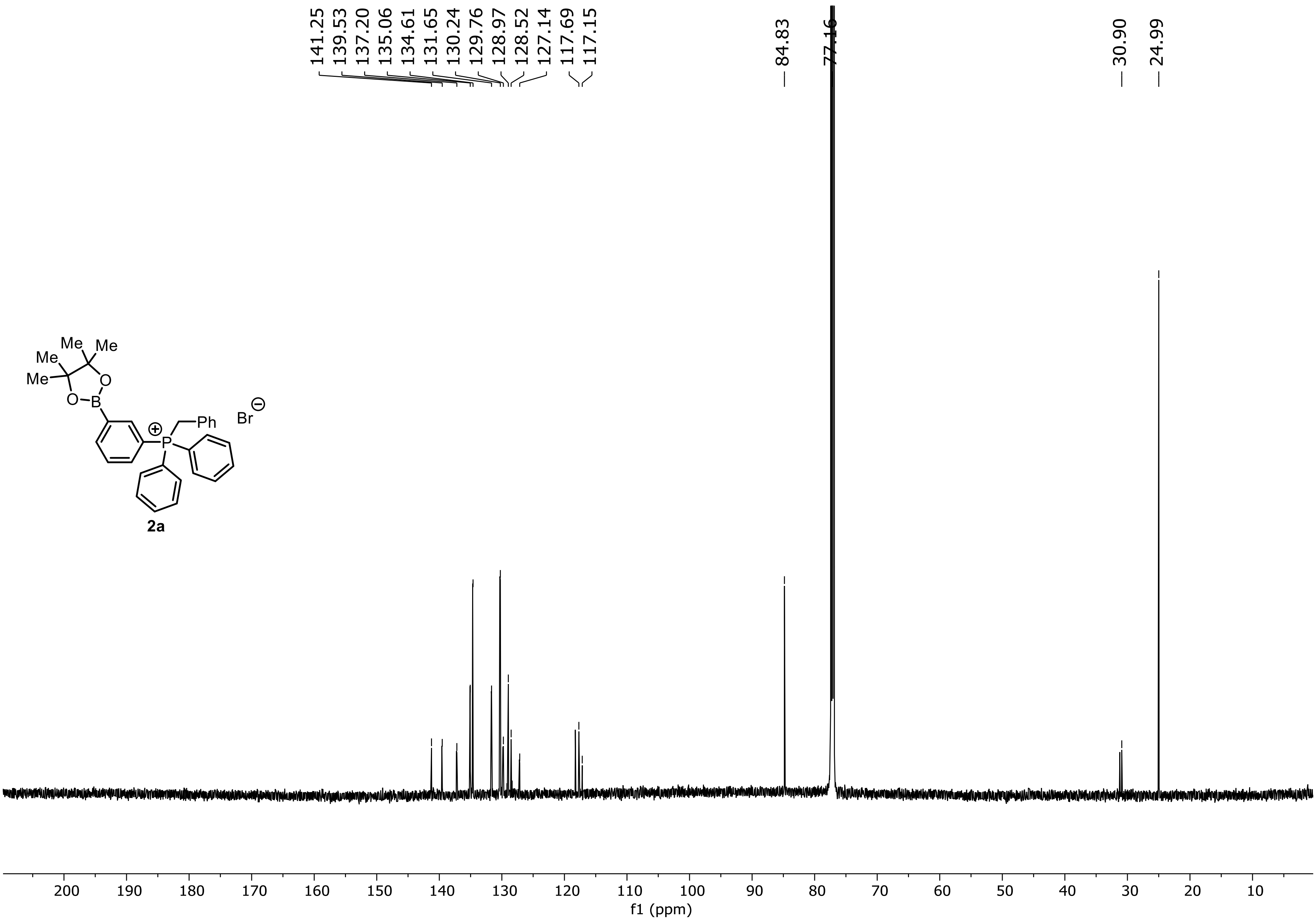

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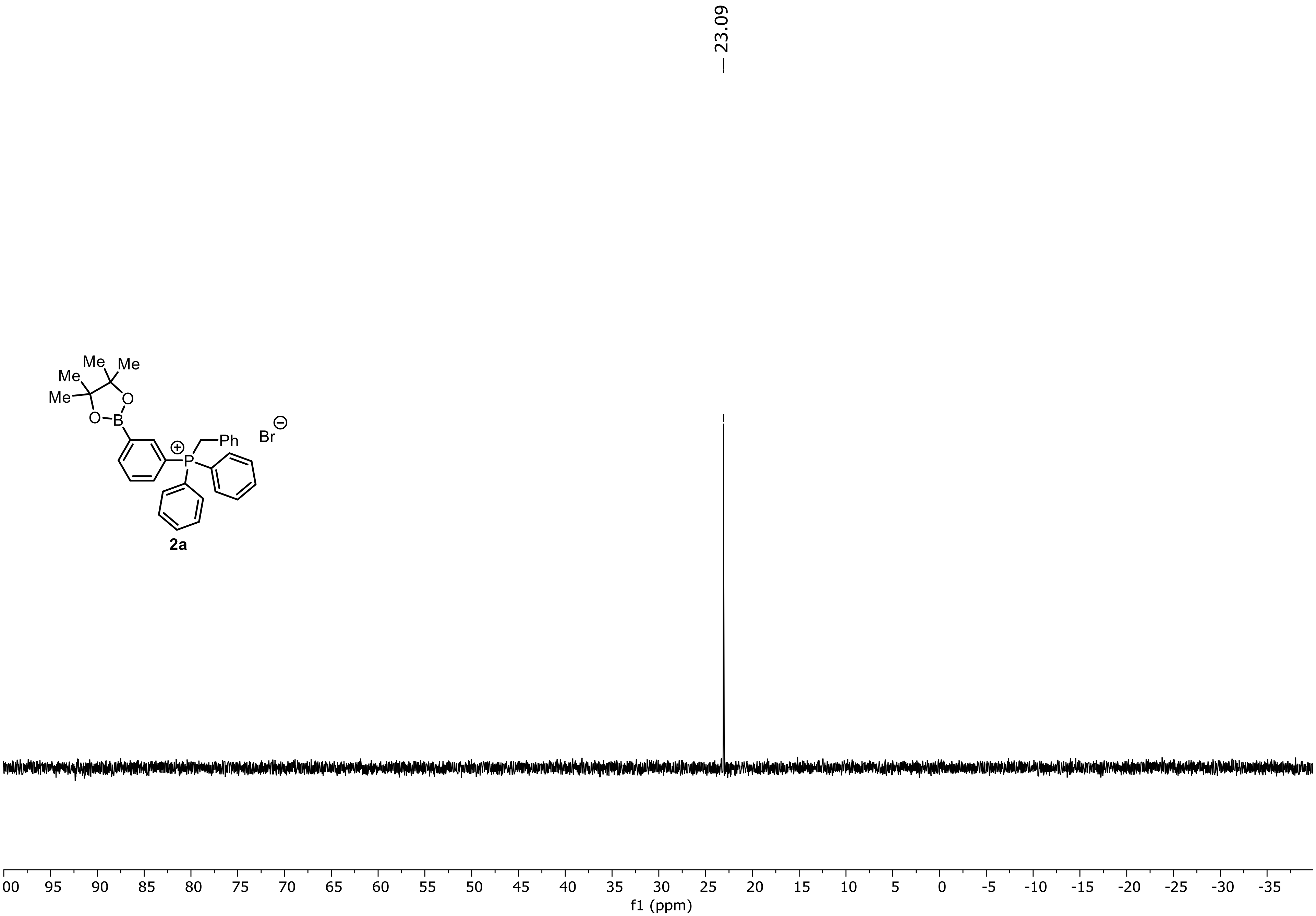

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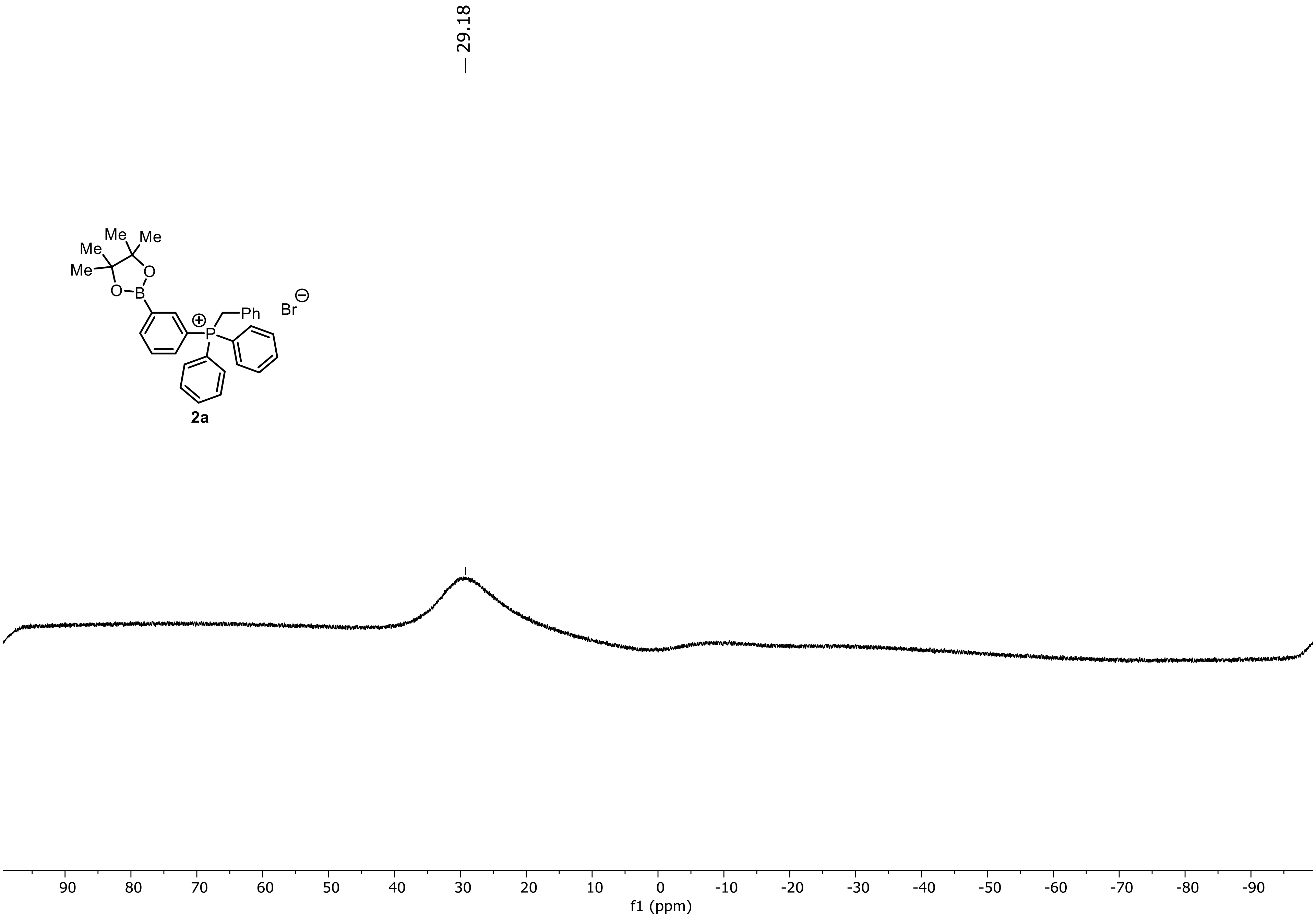

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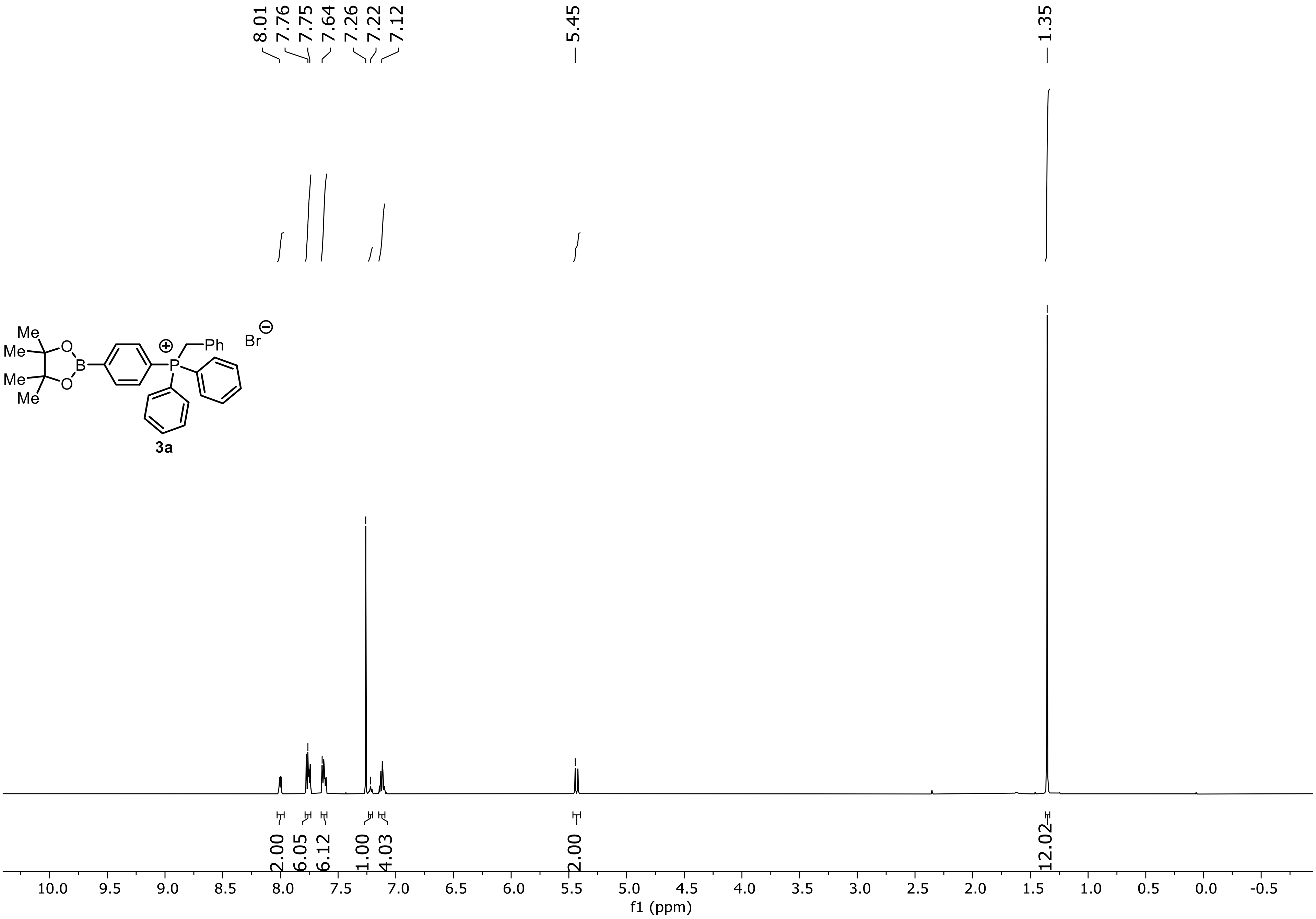

3a

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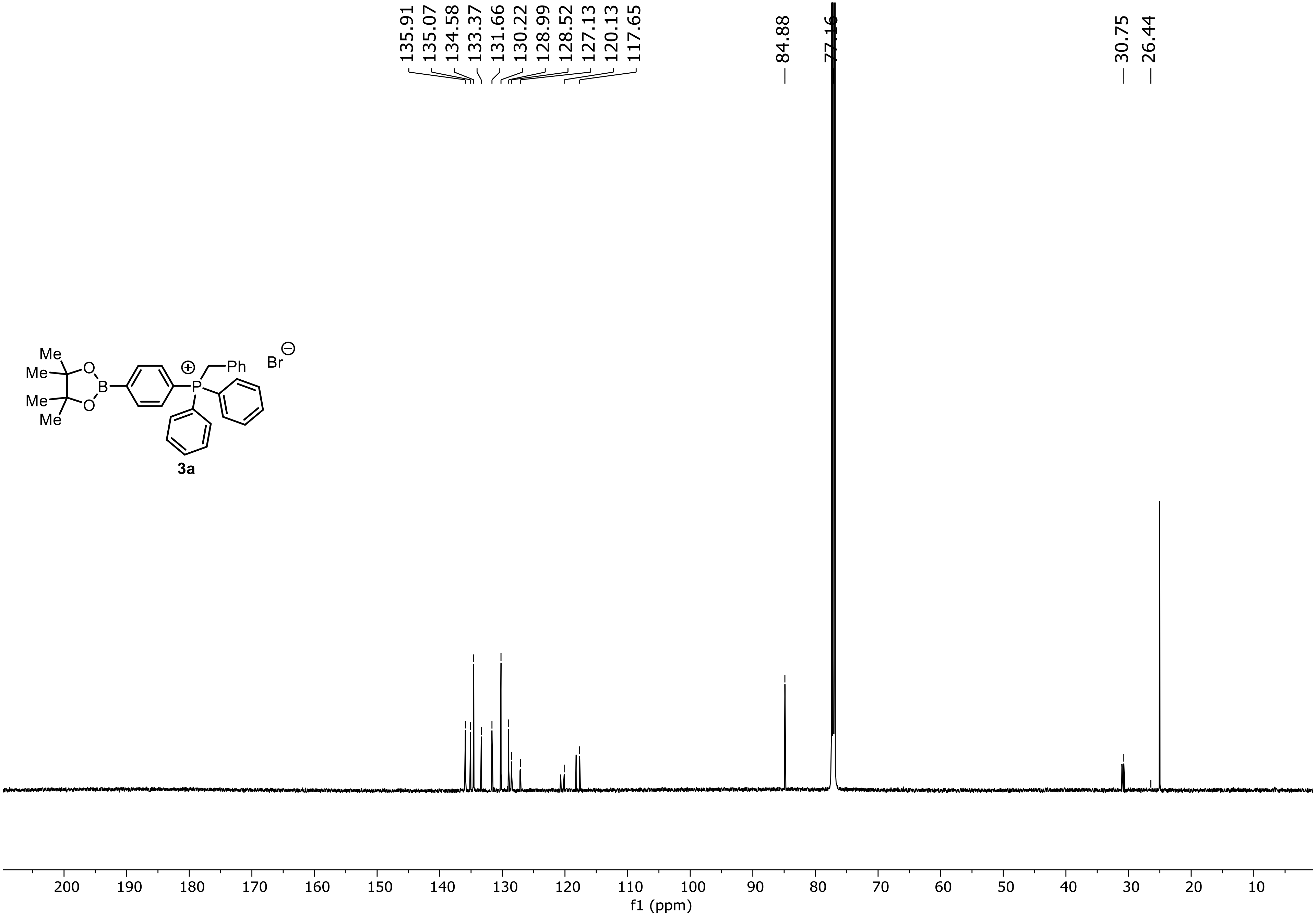

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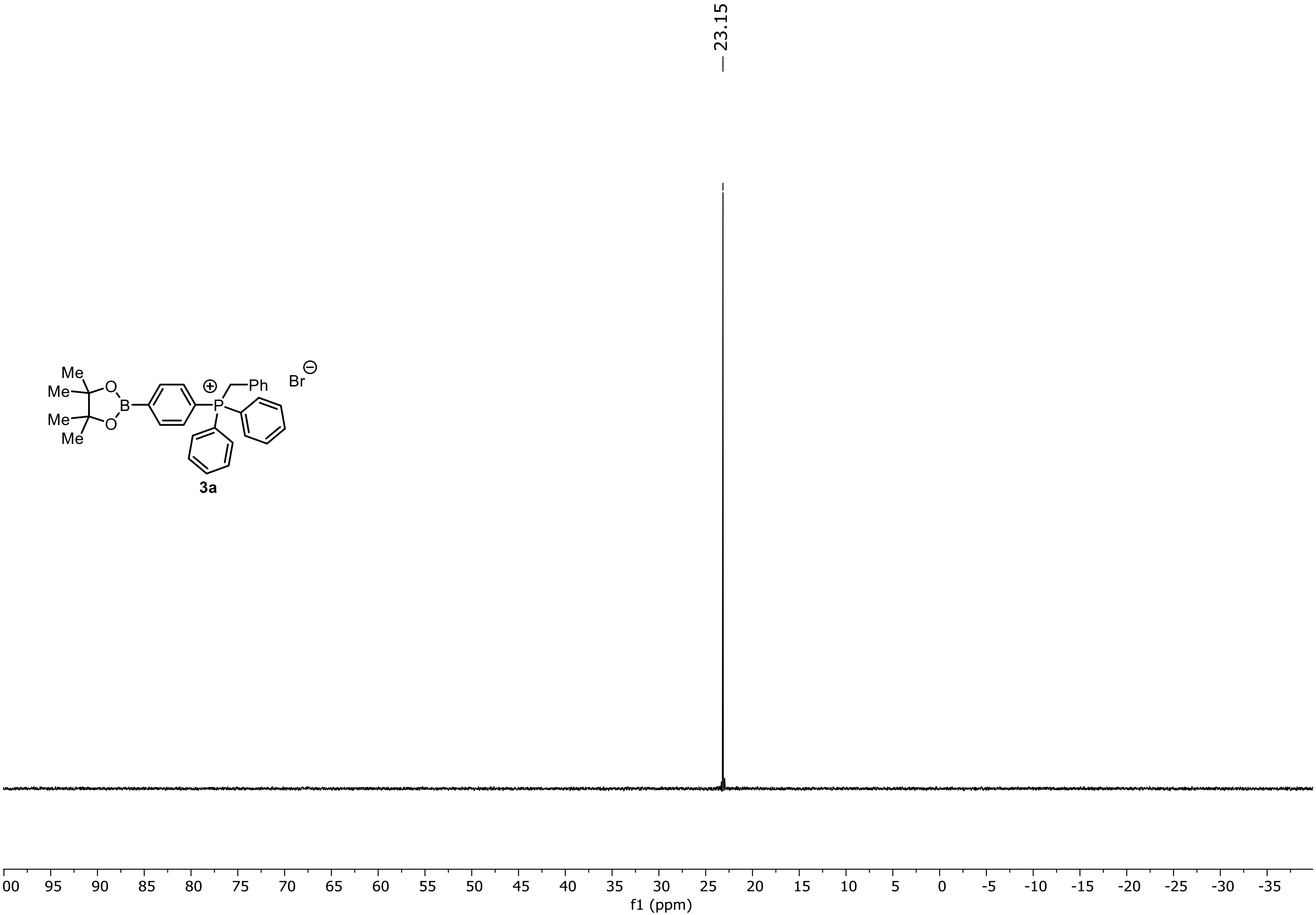

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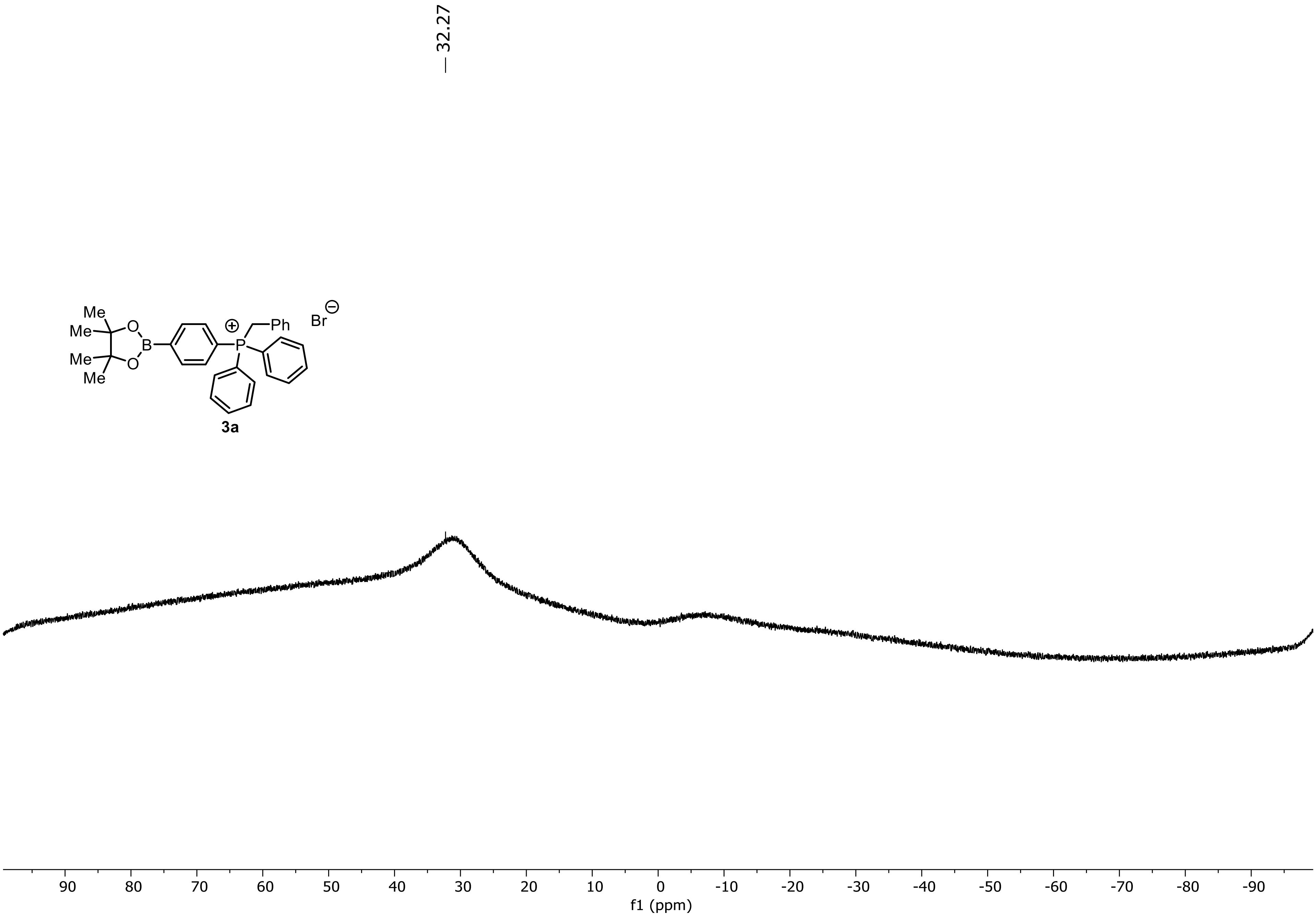

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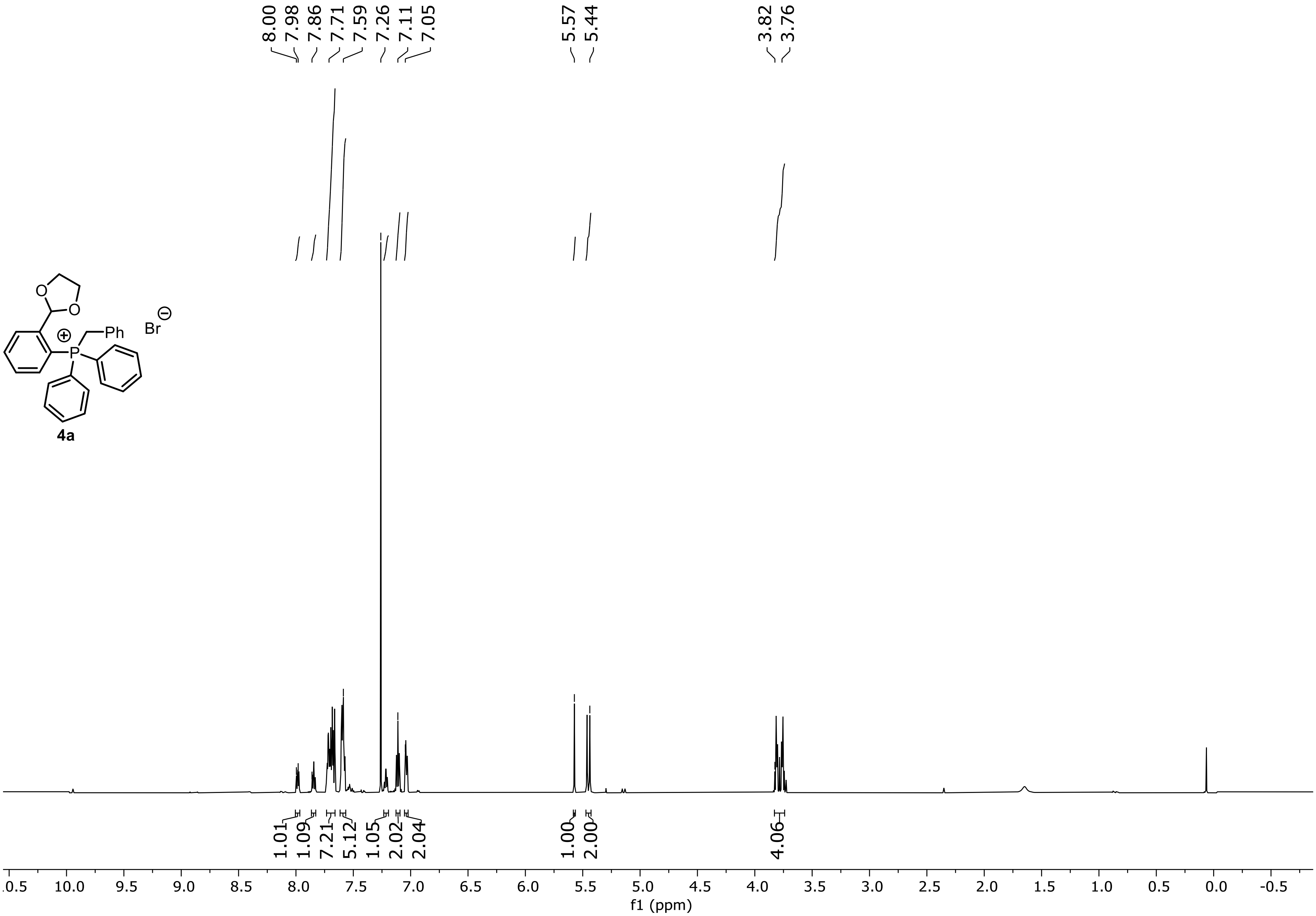

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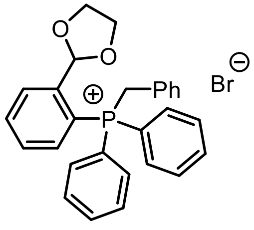

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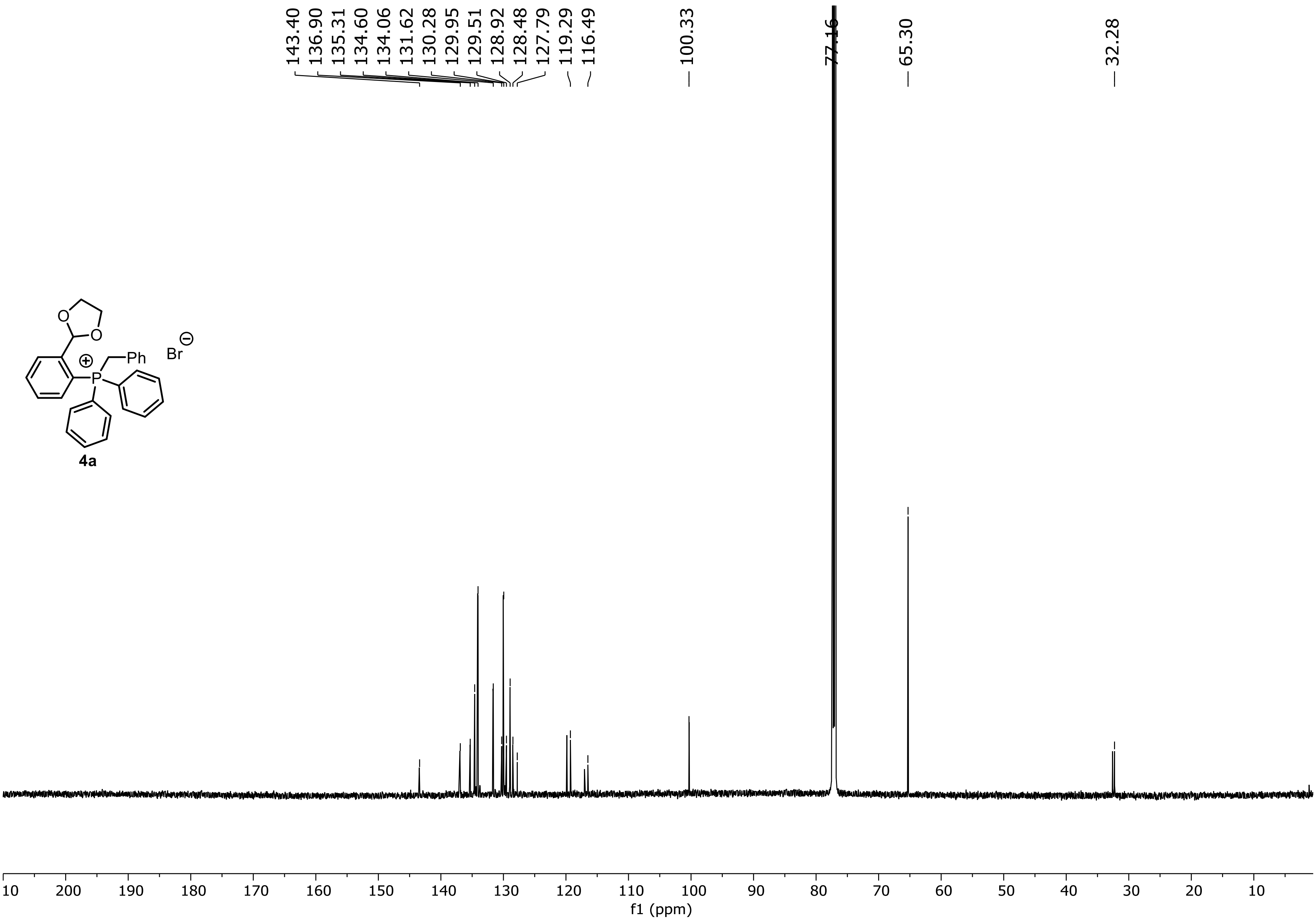

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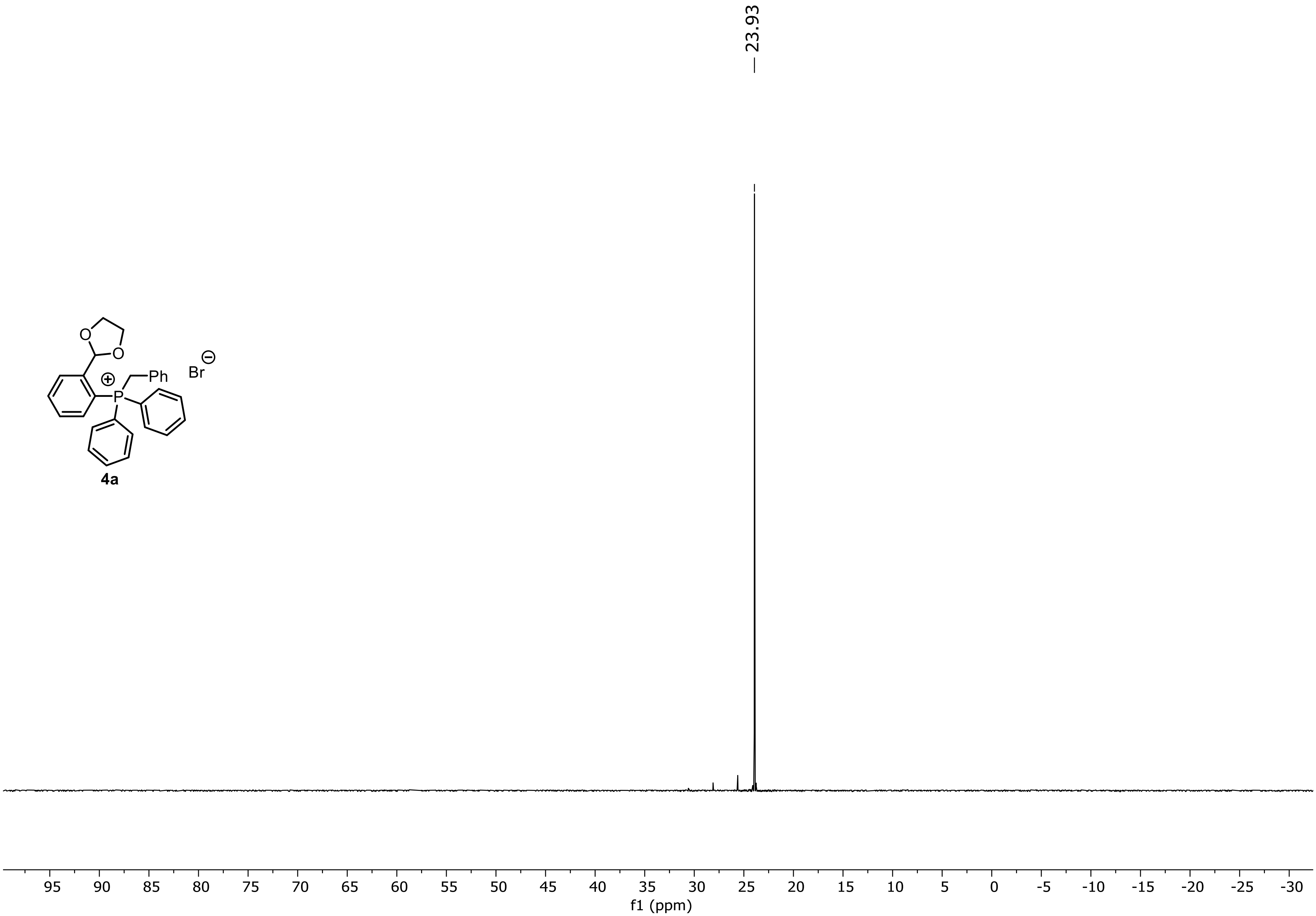

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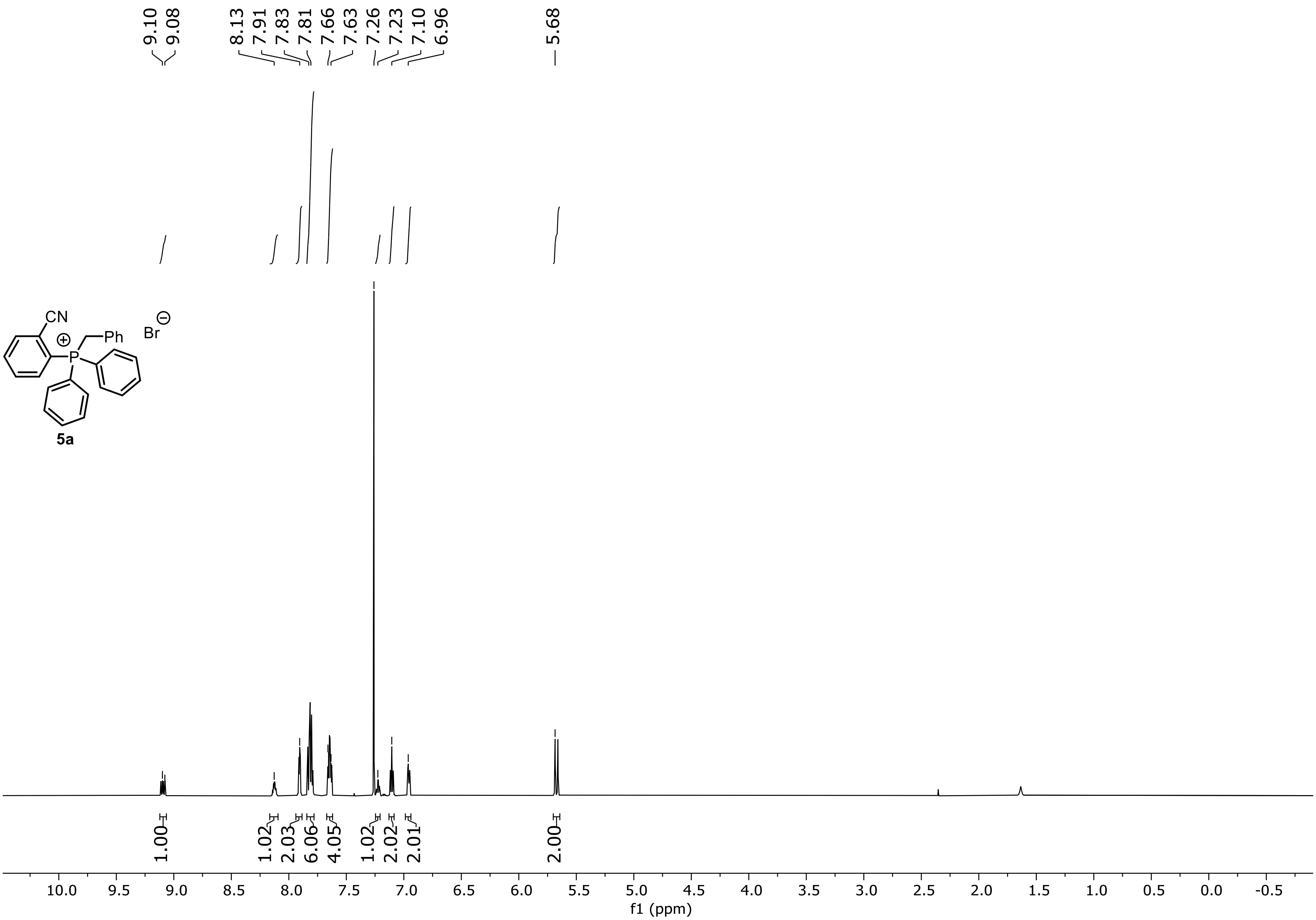

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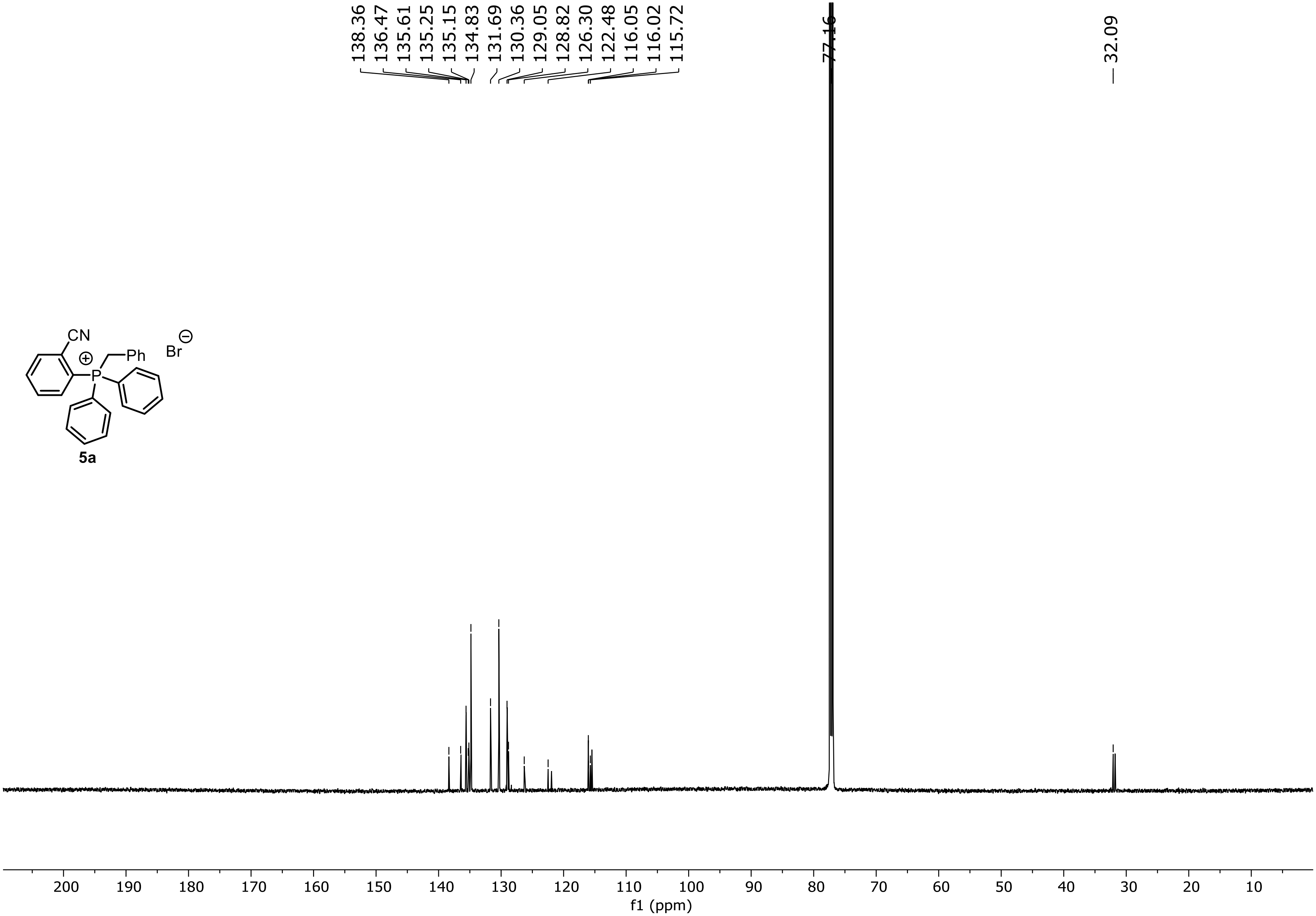

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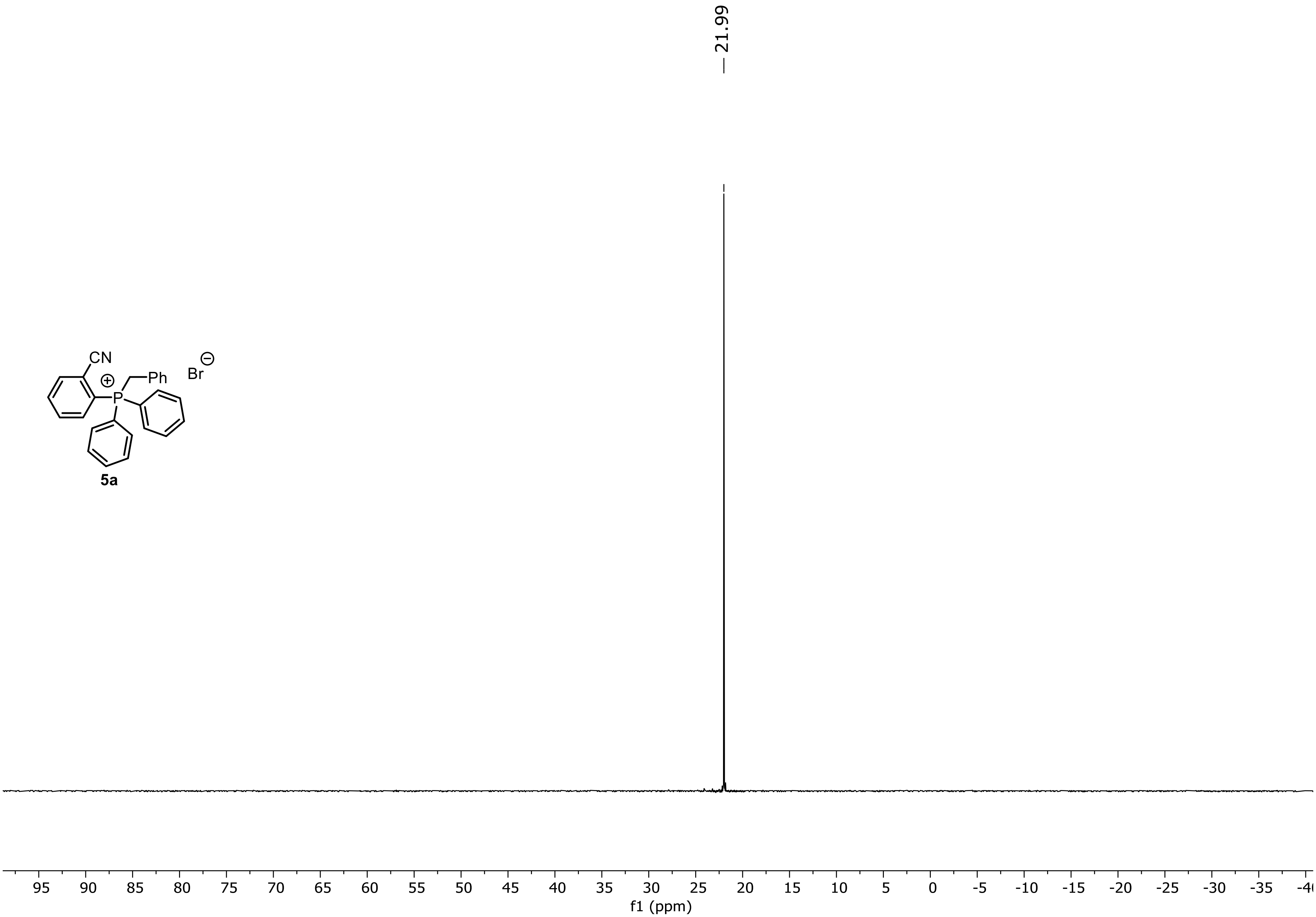
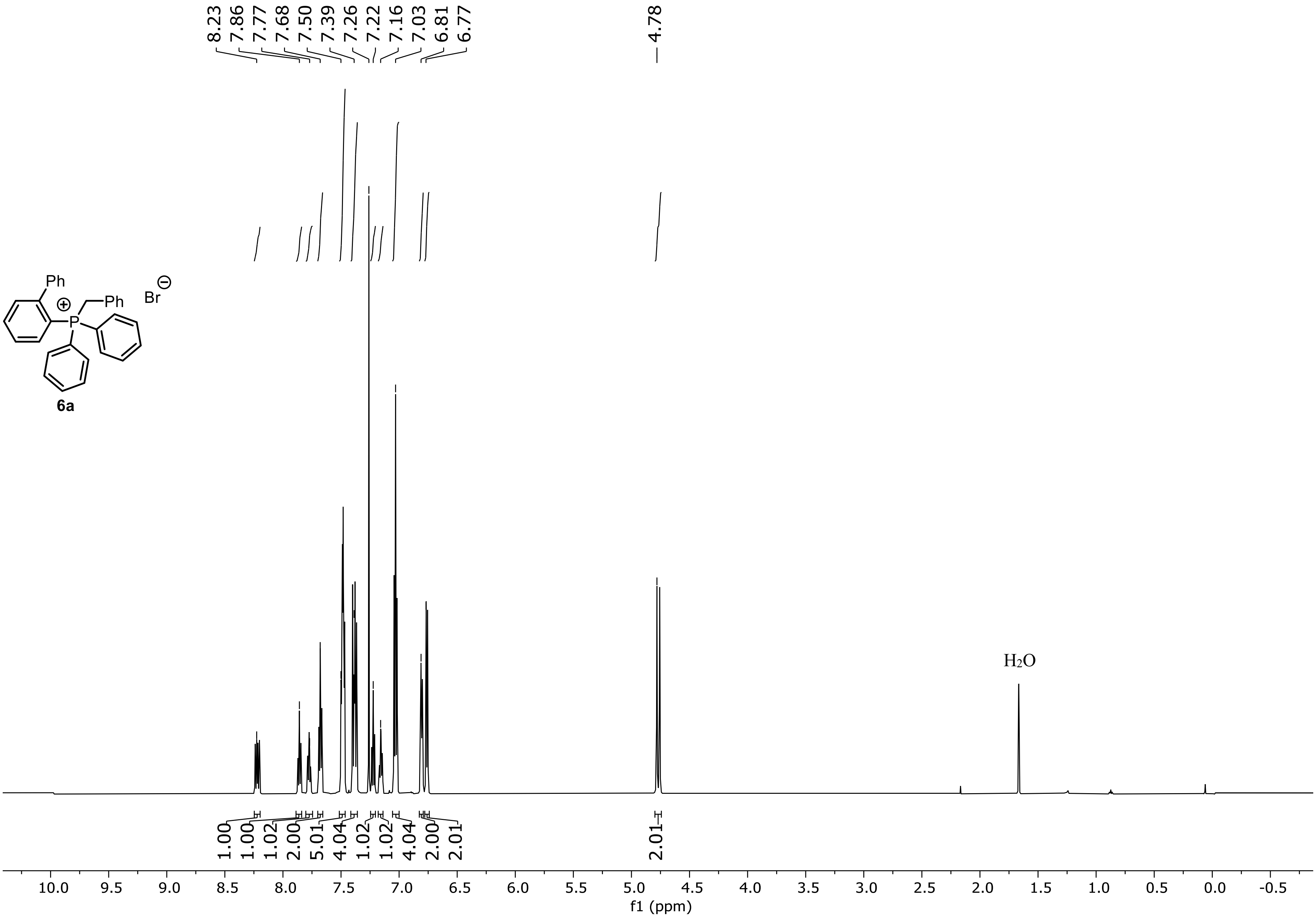


^{31}P NMR (CDCl$_3$, 243 MHz)

6a



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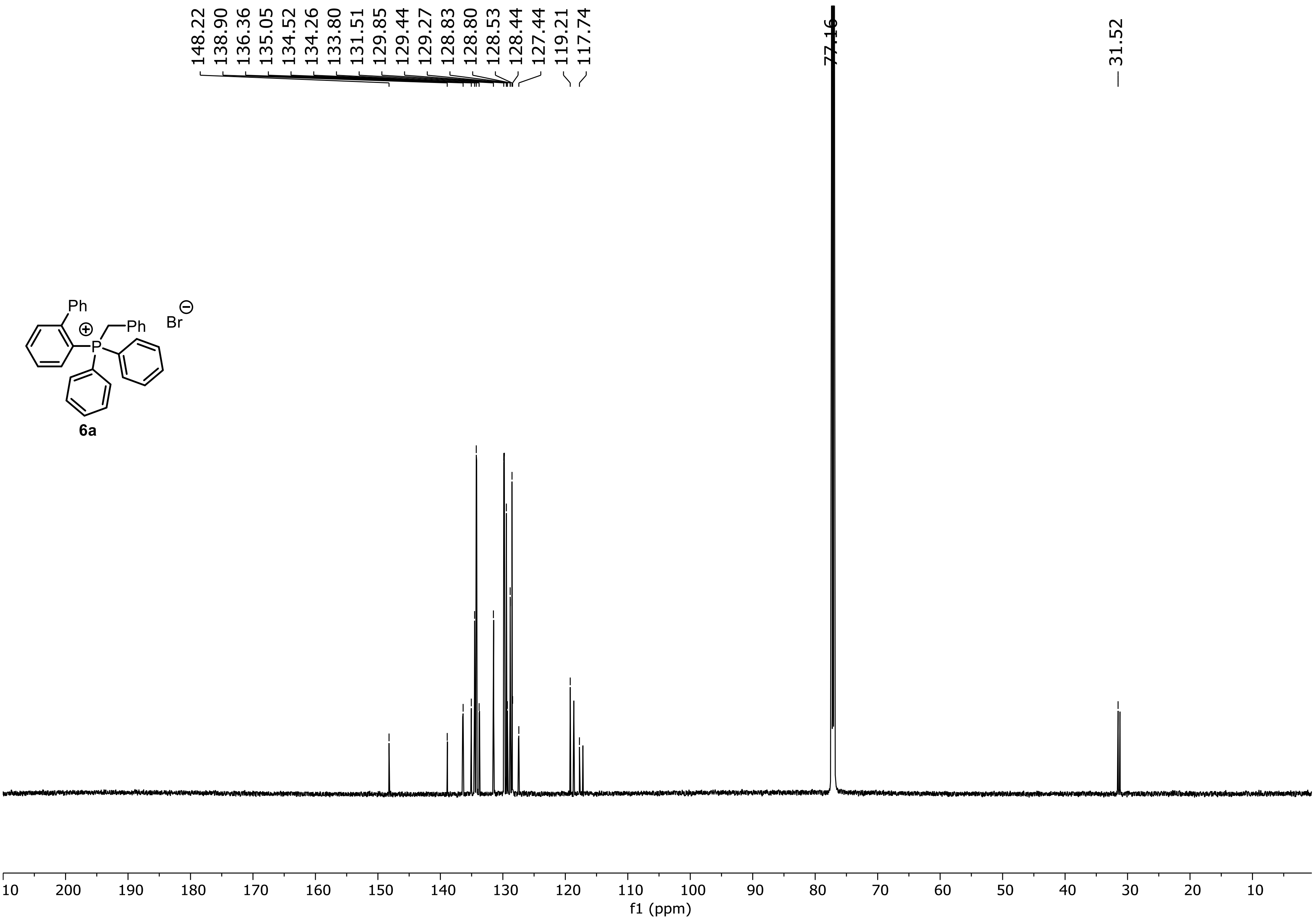

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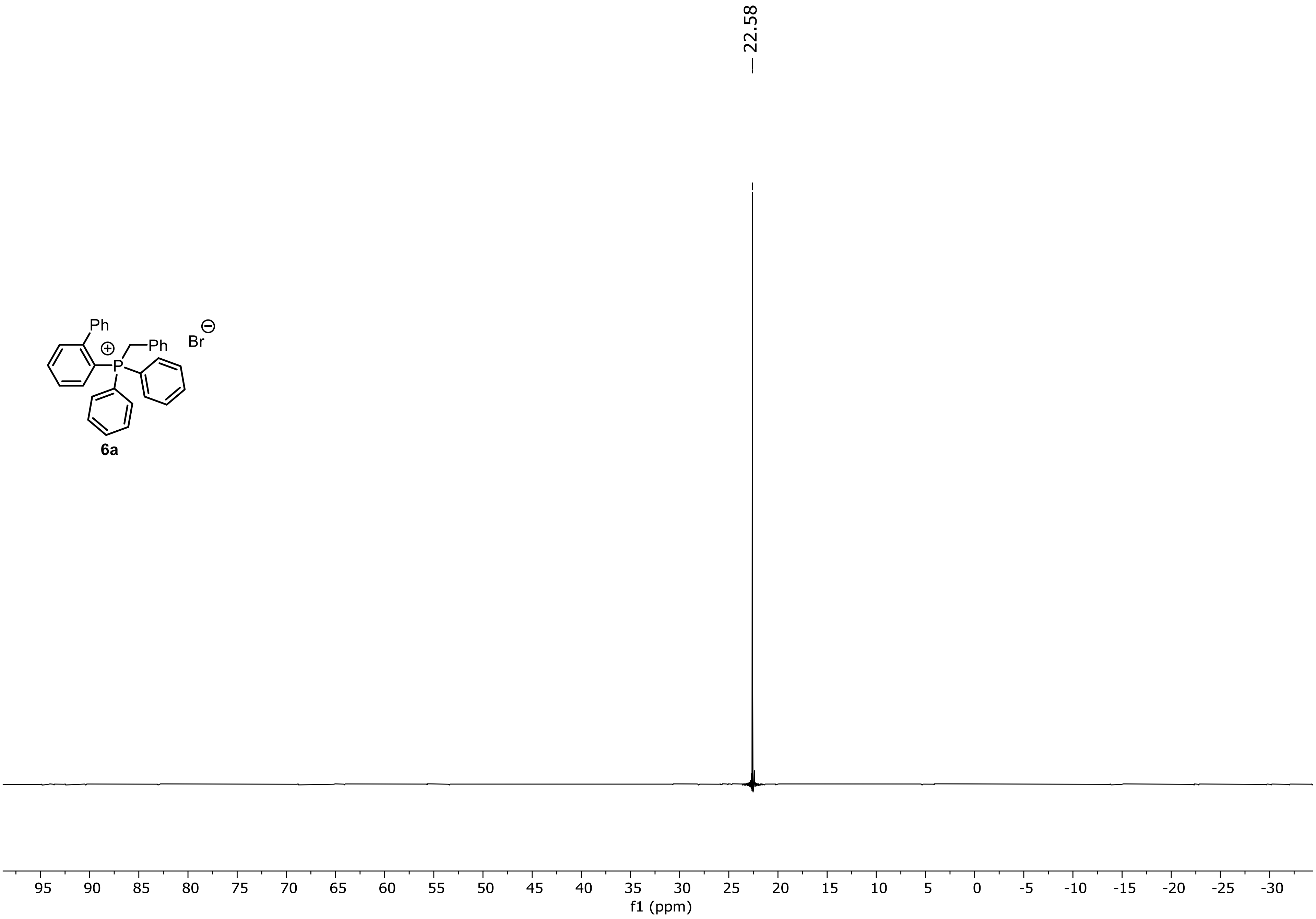

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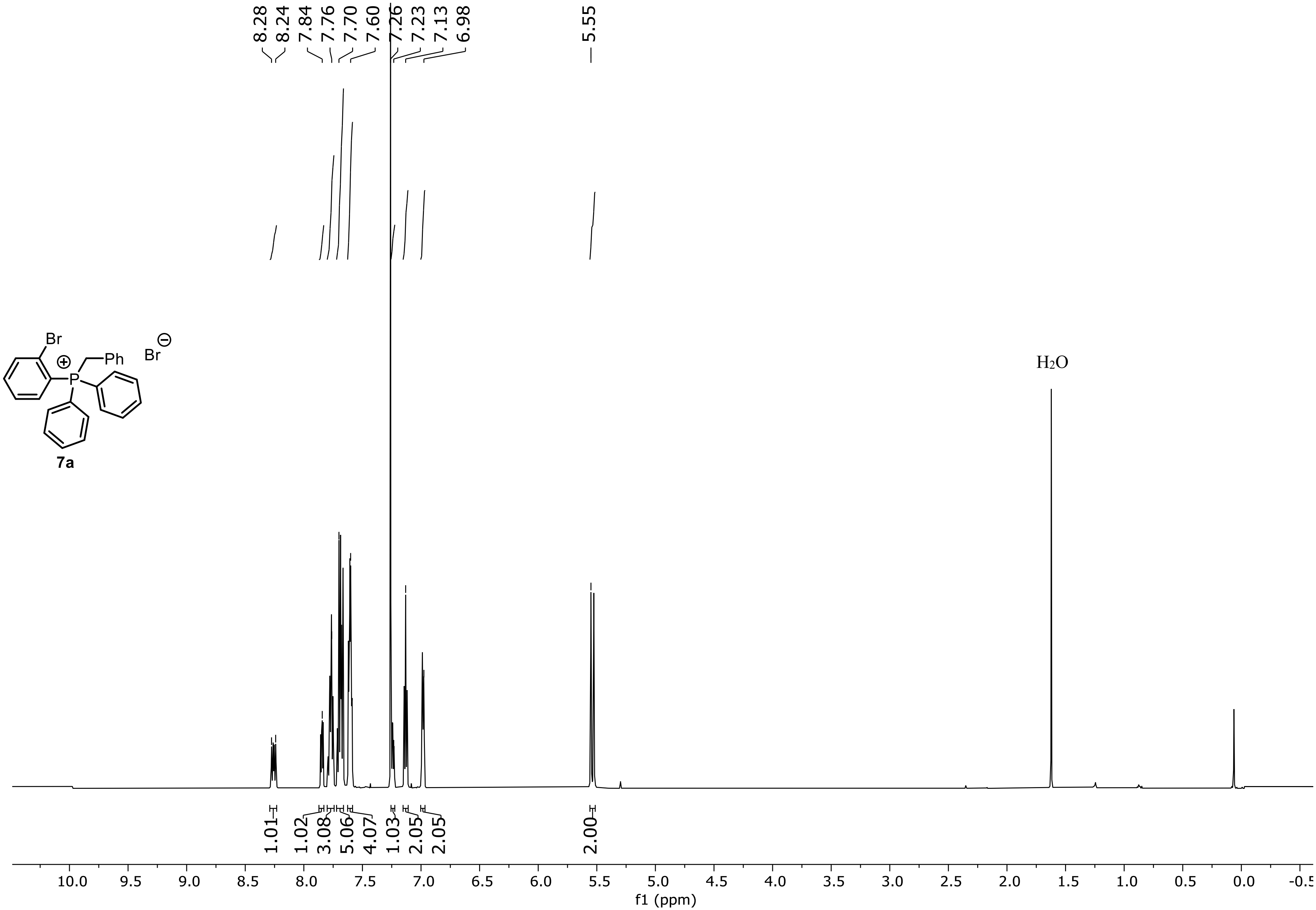

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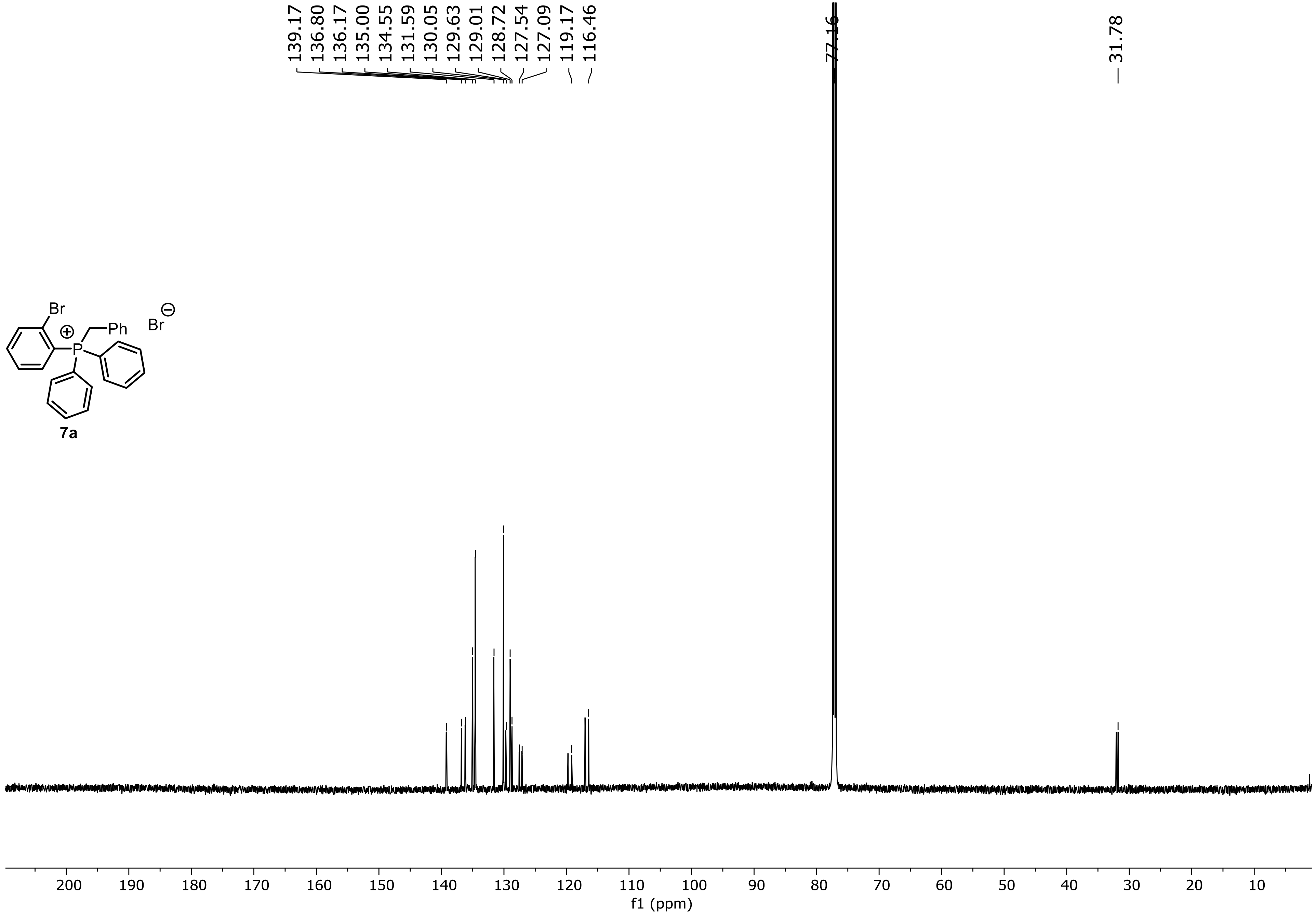
7a



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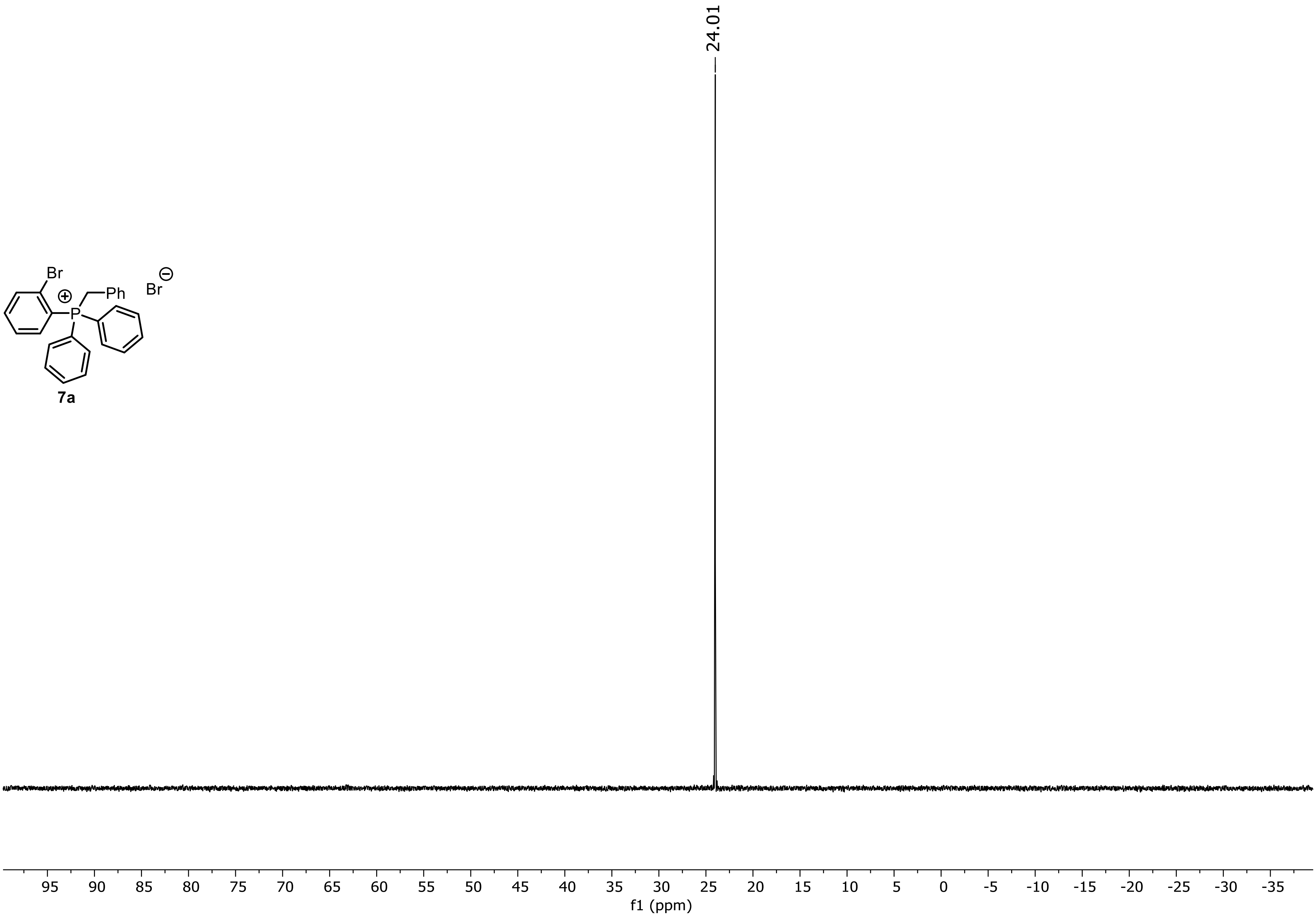

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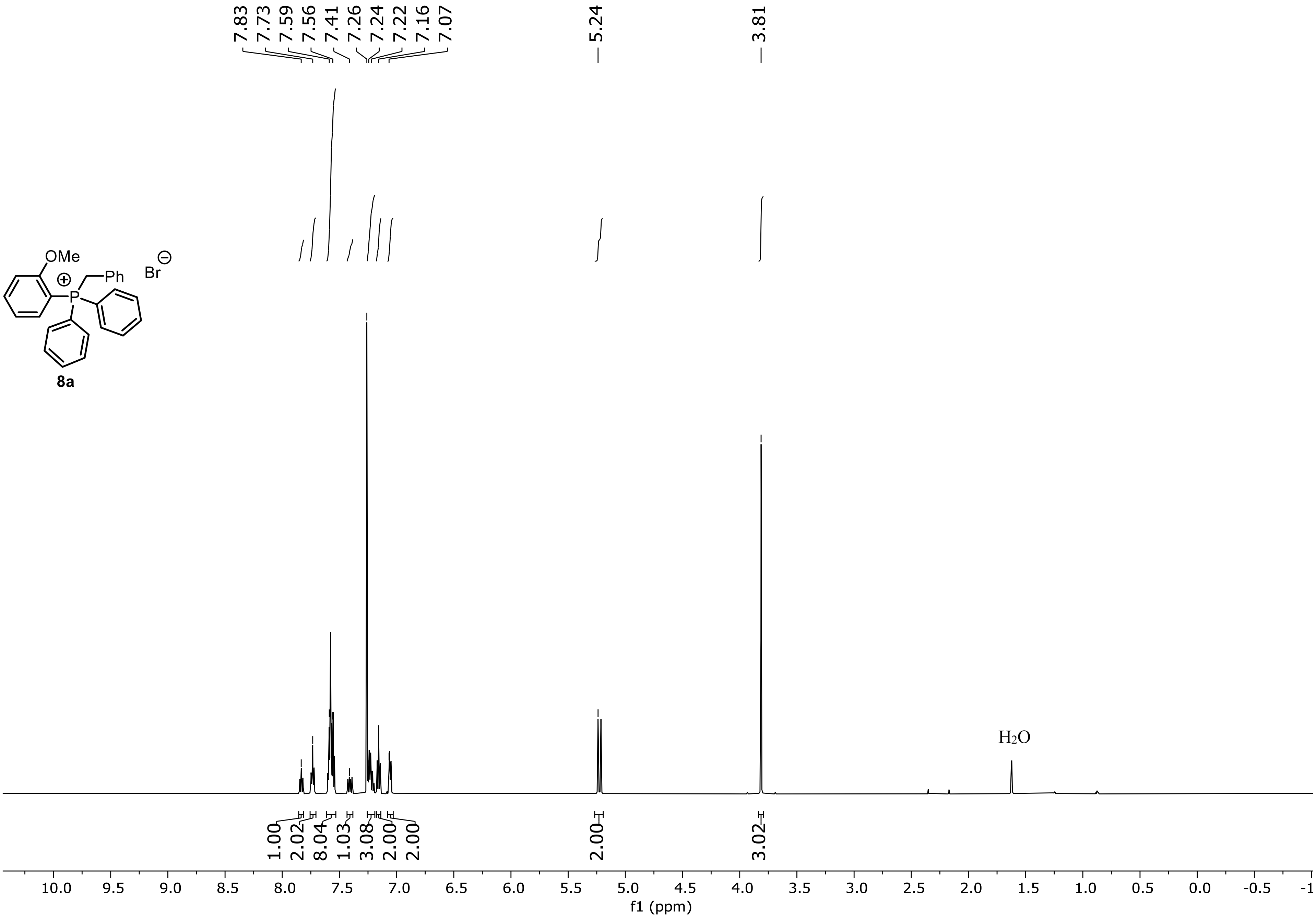

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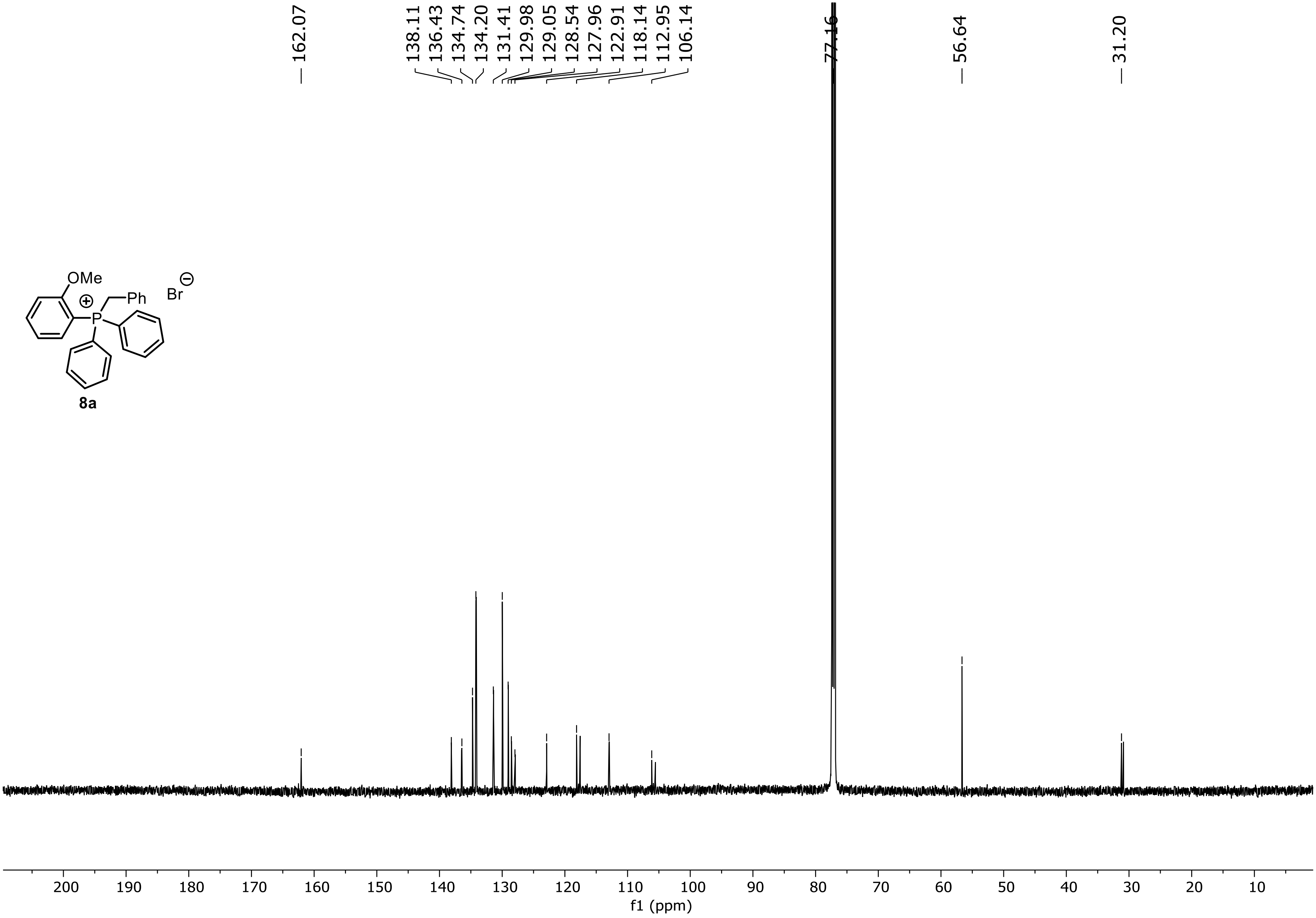

8a

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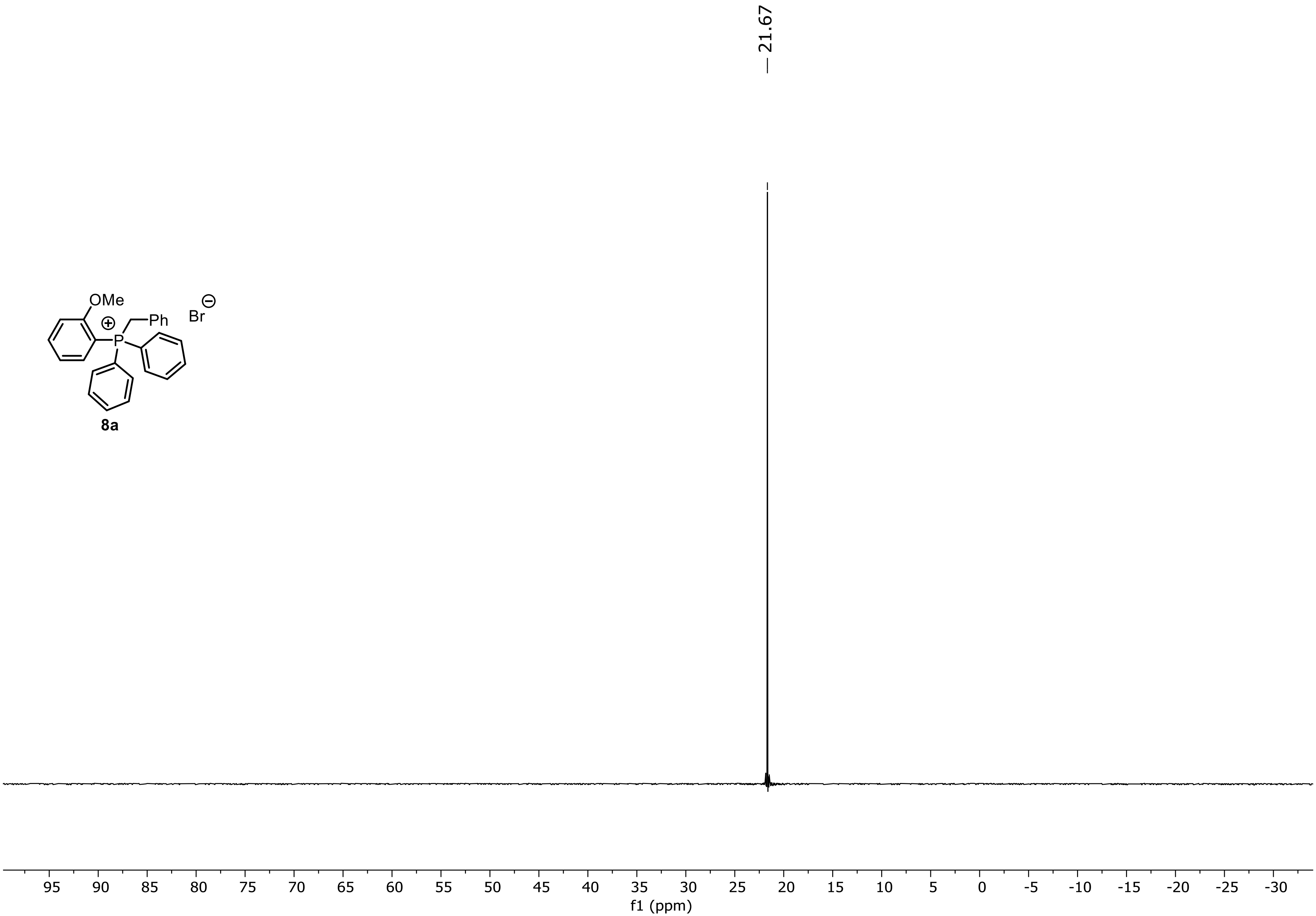
8a



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