Supplementary Materials for

Catalyst-Free Synthesis of Borylated Lactones from Esters via Electrophilic Oxyboration

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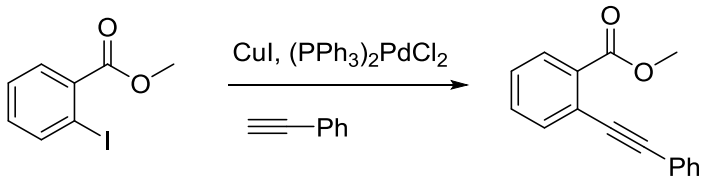
I. General Methods

All chemicals were used as received from commercial sources unless otherwise noted. Triethylamine, acetonitrile, toluene, tetrahydrofuran, and dichloromethane were purified by passage through an alumina column under argon pressure on a push-still solvent system. Toluene-d_8 was dried over CaH_2, degassed using three freeze-pump-thaw cycles, and vacuum transferred prior to use. All manipulations were conducted using standard Schlenk techniques unless otherwise specified. Analytical thin layer chromatography (TLC) was performed using Merck F_{250} plates. Plates were visualized under UV irradiation (254 nm) and/or using a basic aqueous solution of potassium permanganate. Flash chromatography was conducted using a Teledyne Isco Combiflash® Rf 200 Automated Flash Chromatography System, and Teledyne Isco Redisep® 35–70 μm silica gel. All proton and carbon nuclear magnetic resonance (^{1}H and ^{13}C NMR) spectra were recorded on a Bruker DRX-400 spectrometer, Bruker DRX-500 spectrometer outfitted with a cryoprobe, or a Bruker AVANCE-600 spectrometer. All boron nuclear magnetic resonance (^{11}B NMR) spectra were recorded on a Bruker AVANCE-600 spectrometer. All fluorine nuclear magnetic resonance (^{19}F NMR) spectra were recorded on a Bruker DRX-400. All chemical shifts (δ) are reported in parts per million (ppm) downfield of tetramethylsilane, and referenced to the residual protiated solvent peak (δ = 7.26 ppm for $CDCl_3$, δ = 2.08 ppm for d_8-toluene, δ = 2.05 ppm for d_6-acetone, or δ = 1.94 ppm for CD_3CN in ^{1}H NMR spectroscopy experiments; δ = 77.2 ppm for $CDCl_3$, δ = 29.8 ppm for d_6-acetone, δ = 20.4 ppm for d_8-toluene, or δ = 1.34 ppm for CD_3CN in ^{13}C NMR spectroscopy experiments). ^{11}B and ^{19}F NMR spectroscopy experiments are referenced to the absolute frequency of 0 ppm in the ^{1}H dimension according to the Xi scale. High-resolution mass spectrometry data were obtained at the University of California, Irvine.

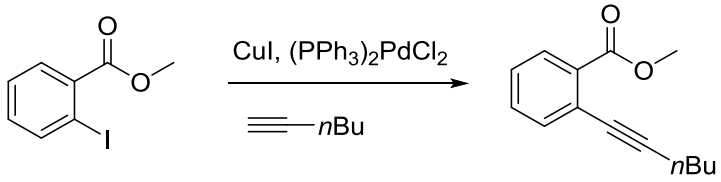
II. Synthetic Procedures

A. Preparation of Esters 1a-1p



10 **1a**

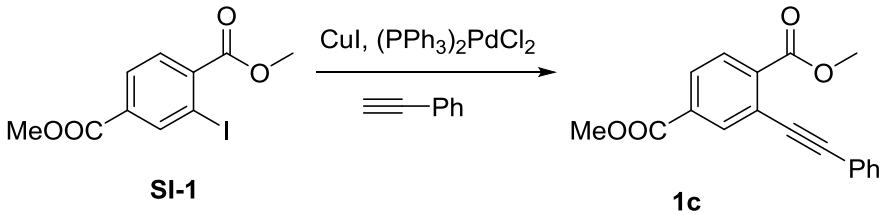
Methyl 2-(phenylethynyl)benzoate (1a). A flask was charged with compound **10** (3.0 mL, 20. mmol, 1.0 equiv), $(PPh_3)_2PdCl_2$ (0.28 g, 0.40 mmol, 0.020 equiv), and CuI (0.15 g, 0.80 mmol, 0.040 equiv). The flask was then evacuated and refilled with N_2 three times before 40 mL of acetonitrile and Et_3N (22 mL, 160 mmol, 8.0 equiv) were added. Phenylacetylene (2.4 mL, 22 mmol, 1.1 equiv) was then syringed into the reaction mixture which stirred for 18 h under dynamic N_2. At this time, analysis by TLC (5% EtOAc/hexanes) indicated full consumption of starting material. The reaction mixture was diluted with 200 mL EtOAc and washed with NH_4Cl (1 × 45 mL), water (1 × 45 mL), brine (1 × 45 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo. The resulting oily residue was purified by column chromatography using an elution gradient from 100% hexanes to 5% EtOAc/hexanes. Product-containing fractions were combined and concentrated in vacuo, and volatiles were removed at c.a. 10 mTorr for 18 h to afford **1a** as a light yellow oil (4.2 g, 88% yield). ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.98 (d, *J* = 7.6 Hz, 1H), 7.65 (d, *J* = 7.3 Hz, 1H), 7.59-7.57 (m, 2H), 7.59-7.57 (m, 1H), 7.40-7.35 (m, 4H), 3.97 (s, 3H). This spectrum is in agreement with previously reported spectral data.[1]



10 **1b**

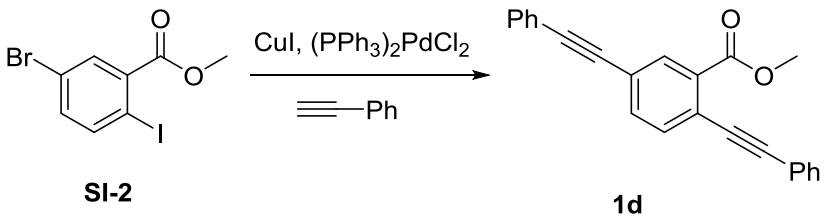
Methyl 2-(hex-1-yn-1-yl)benzoate (1b). A flask was charged with compound **10** (0.73 mL, 5.0 mmol, 1.0 equiv), $(PPh_3)_2PdCl_2$ (0.070 g, 0.10 mmol, 0.020 equiv), and CuI (0.038 g, 0.20 mmol, 0.040 equiv). The flask was then evacuated and refilled with N_2 three times before 10 mL of acetonitrile and Et_3N (5.6 mL, 40. mmol, 8.0 equiv) were added. 1-Hexyne (0.63 mL, 5.5 mmol, 1.1 equiv) was then syringed into the reaction mixture, which then stirred for 18 h under dynamic N_2. At this time, analysis by TLC (10% EtOAc/hexanes) indicated full consumption of starting material. The reaction mixture was diluted with 100 mL EtOAc and washed with NH_4Cl (1 × 25 mL), water (1 × 25 mL), brine (1 × 25 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo. The resulting oily residue was purified by column chromatography using an elution gradient from 100% hexanes to 10% EtOAc/hexanes. Product-containing fractions were combined and concentrated in vacuo, and volatiles were removed at c.a. 10 mTorr for 18 h to afford **1b** as a light yellow oil (0.80 g, 74% yield). ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.88 (d *J* = 7.9 Hz, 1H), 7.51 (d, *J* = 7.8 Hz, 1H), 7.41 (td, *J* = 7.6 Hz, 1H), 7.30 (t, *J* = 7.6 Hz, 1H), 3.91 (s, 3H),

2.48 (t, *J* = 7.1 Hz, 2H), 1.64-1.60 (m, 2H), 1.54-1.48 (m, 2H), 0.96 (t, *J* = 7.3 Hz, 3H). This spectrum is in agreement with previously reported spectral data.[2]



SI-1 **1c**

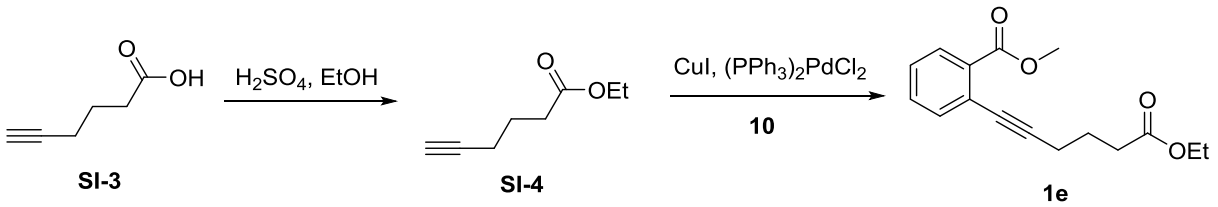
Methyl 4-acetoxy-2-(phenylethynyl)benzoate (1c). A flask was charged with $(PPh_3)_2PdCl_2$ (0.022 g, 0.030 mmol, 0.020 equiv), and CuI (0.011 g, 0.060 mmol, 0.040 equiv). The flask was then evacuated and refilled with N_2 three times before 4 mL of Et_3N were added. The reaction mixture was then sparged for 5 minutes before compound **SI-1** (0.50 g, 1.6 mmol, 1.0 equiv) was added. Phenylacetylene (0.21 mL, 1.9 mmol, 1.2 equiv) was then added via syringe, and the reaction mixture was heated to 55 ^oC in an oil bath and stirred for 16 h under dynamic N_2. At this time, analysis by TLC (20% EtOAc/hexanes) indicated full consumption of starting material. The reaction mixture was diluted with 100 mL DCM and washed with water (1 × 25 mL), brine (1 × 25 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo. The resulting oily residue was purified by column chromatography using an elution gradient from 100% hexanes to 20% EtOAc/hexanes. Product-containing fractions were combined and concentrated in vacuo, and volatiles were removed at c.a. 10 mTorr for 18 h to afford **1c** as a yellow solid (0.44 g, 95% yield). ^1H NMR ($CDCl_3$, 600 MHz): δ 8.26 (s, 1H), 8.00-7.96 (m, 2H), 7.57-7.56 (m, 2H), 7.35-7.34 (m, 3H), 3.96 (s, 3H), 3.92 (s, 3H). This spectrum is in agreement with previously reported spectral data.[2]



SI-2 **1d**

Methyl 2,5-bis(phenylethynyl)benzoate (1d) A flask was charged with $(PPh_3)_2PdCl_2$ (0.017 g, 0.24 mmol, 0.040 equiv), and CuI (0.016 g, 0.12 mmol, 0.020 equiv). The flask was then evacuated and refilled with N_2 three times before 4 mL of Et_3N were added. The reaction mixture was then sparged for 5 min before **SI-2** (2.00 g, 5.87 mmol, 1.00 equiv) was added. Phenylacetylene (0.70 mL, 6.5 mmol, 1.1 equiv) was then added via syringe, and the reaction mixture was heated to 55 ^oC in an oil bath and stirred for 16 h under dynamic N_2. At this time, analysis by TLC (5% EtOAc/hexanes) indicated full consumption of starting material. The reaction mixture was diluted with 100 mL DCM and washed with water (1 × 25 mL), brine (1 × 25 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo. The resulting oily residue was purified by column chromatography using an elution gradient from 100% hexanes to 5% EtOAc/hexanes. Product-containing fractions were combined and concentrated in vacuo, and volatiles were removed at c.a. 10 mTorr for 18 h to afford the minor product **1d** as a white solid

(0.17 g, 11% yield). ^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.15 (s, 1H), 7.60-7.54 (m, 4H), 7.38-7.36 (m, 6H), 4.0 (s, 3H). This spectrum is in agreement with previously reported spectral data.[3]



SI-3 SI-4 1e

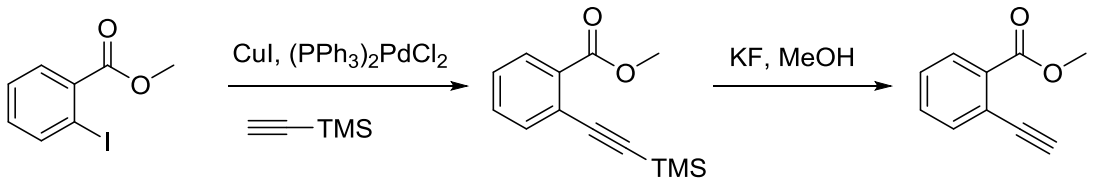
Ethyl hex-5-ynoate (SI-4) was prepared according to a literature procedure[4] in 87% yield. ^{1}H NMR ($CDCl_3$, 600 MHz) δ 4.14 (q, *J* = 7.1 Hz, 2H), 2.44 (t, *J* = 7.4 Hz, 2H), 2.27 (dt, *J* = 7.0, 2.6 Hz, 2H), 1.97 (t, *J* = 2.6 Hz, 1H), 1.85 (quin, *J* = 7.2 Hz, 1H), 1.26 (t, *J* = 7.2 Hz, 3H). This spectrum is in agreement with previously reported spectral data.

Methyl 2-(6-ethoxy-6-oxohex-1-yn-1-yl)benzoate (1e). A flask was charged with compound **10** (0.50 g, 1.8 mmol, 1.0 equiv), $(PPh_3)_2PdCl_2$ (0.038 g, 0.054 mmol, 0.030 equiv), and CuI (0.031 g, 0.16 mmol, 0.090 equiv). The flask was then evacuated and refilled with N_2 three times before 4 mL of acetonitrile and Et_3N (0.25 mL, 1.8 mmol, 8.0 equiv) were added. Compound **SI-4** (0.38 g, 2.7 mmol, 1.5 equiv) was then syringed into the reaction mixture which stirred for 18 h under dynamic N_2. At this time, analysis by TLC (10% EtOAc/hexanes) indicated full consumption of starting material. The reaction mixture was diluted with 125 mL EtOAc and washed with NH_4Cl (1 × 45 mL), water (1 × 45 mL), brine (1 × 45 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo. The resulting oily residue was purified by column chromatography using an elution gradient from 100% hexanes to 10% EtOAc/hexanes. Product-containing fractions were combined and concentrated in vacuo, and volatiles were removed at c.a. 10 mTorr for 18 h to afford **1e** as a light yellow oil (0.42 g, 80% yield).

^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.88 (d, *J* = 7.8 Hz, 1H), 7.50 (d, *J* = 7.6 Hz, 1H), 7.42 (t, *J* = 7.3 Hz, 1H), 7.31 (t, *J* = 7.3 Hz, 1H), 4.13 (q, *J* = 7.2 Hz, 2H), 3.91 (s, 3H), 2.56-2.52 (m, 4H), 1.95 (quin, *J* = 7.2 Hz, 2H), 1.25 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 173.3, 166.9, 134.3, 132.0, 131.6, 130.2, 127.4, 124.2, 94.4, 80.1, 60.4, 52.2, 33.2, 23.9, 23.5, 18.7, 14.3.

HRMS (ESI+): Calculated for $C_{16}H_{18}O_4Na$ ($[M+Na]^+$), 297.1103; found 297.1096.

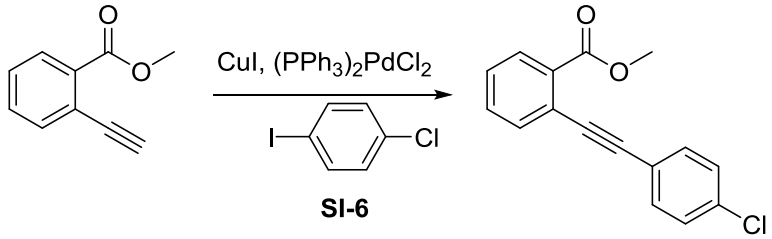


10 SI-5 1f

Methyl 2-((trimethylsilyl)ethynyl)benzoate (SI-5). A flask was charged with compound **10** (5.2 mL, 38 mmol, 1.0 equiv), $(PPh_3)_2PdCl_2$ (0.53 g, 1.5 mmol, 0.020 equiv), and CuI (0.29 g, 1.5 mmol, 0.040 equiv). The flask was then evacuated and refilled with N_2 three times before 76 mL of acetonitrile and Et_3N (40 mL, 300 mmol, 8 equiv) were added. Trimethylsilyl acetylene

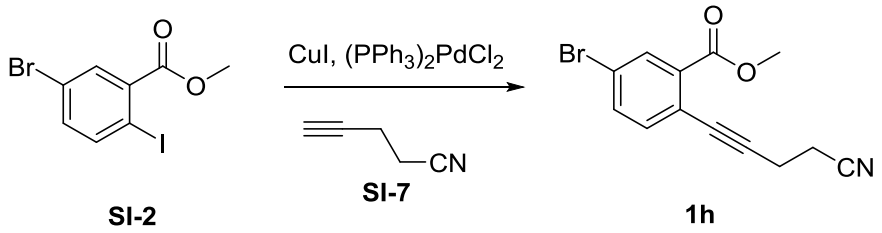
(5.9 mL, 42 mmol, 1.1 equiv) was then syringed into the reaction mixture which stirred for 18 h under dynamic N_2. At this time, analysis by TLC (5% EtOAc/hexanes) indicated full consumption of starting material. The reaction mixture was diluted with 300 mL Et_2O and washed with NH_4Cl (1 × 50 mL), water (1 × 50 mL), brine (1 × 50 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo. The resulting oily residue was purified by column chromatography using an elution gradient from 100% hexanes to 5% EtOAc/hexanes. Product-containing fractions were combined and concentrated in vacuo, and volatiles were removed at c.a. 10 mTorr for 18 h to afford **SI-5** as a yellow oil (7.0 g, 79% yield). ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.90 (app d, *J* = 7.6 Hz, 1H), 7.58 (app d, *J* = 7.5 Hz, 1H), 7.44 (td, *J* = 7.6, 0.8 Hz, 1H), 7.36 (app t, *J* = 7.6 Hz, 1H), 3.92 (s, 3H), 0.27 (s, 9H). This spectrum is in agreement with previously reported spectral data.[5]

Methyl 2-ethynylbenzoate (1f). A flask was charged with compound **SI-5** (2.9 g, 13 mmol, 1.0 equiv), 63 mL methanol, and potassium fluoride (2.6 g, 44 mmol, 3.5 equiv). The flask was then sealed with a ground glass stopper and heated to 40 °C while stirring for 3 h. At this time, analysis by TLC (10% EtOAc/hexanes) indicated full consumption of starting material. The reaction mixture was diluted with 200 mL Et_2O and washed with water (4 × 50 mL), brine (1 × 50 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo at ~10 Torr and 25 °C [warning: product is volatile], yielding **1f** as a dark yellow/red liquid (1.7 g, 84% yield). ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.94 (d, *J* = 7.8 Hz, 1H), 7.62 (d, *J* = 7.7 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 1H), 7.40 (t, *J* = 7.6 Hz, 1H), 3.93 (s, 3H), 3.40 (s, 1H). This spectrum is in agreement with previously reported spectral data.[6]



Methyl 2-((4-chlorophenyl)ethynyl)benzoate (1g). A flask was charged with compound **SI-6** (0.36 g, 1.5 mmol, 1.0 equiv), $(PPh_3)_2PdCl_2$ (0.021 g, 0.030 mmol, 0.020 equiv), and CuI (0.012 g, 0.060 mmol, 0.040 equiv). The flask was then evacuated and refilled with N_2 three times before 3 mL of acetonitrile and Et_3N (1.7 mL, 12 mmol, 8.0 equiv) were added. Compound **1f** (0.27 g, 1.7 mmol, 1.1 equiv) was then syringed into the reaction mixture which stirred for 18 h under dynamic N_2. At this time, analysis by TLC (10% EtOAc/hexanes) indicated full consumption of starting material. The reaction mixture was diluted with 150 mL Et_2O and washed with NH_4Cl (1 × 40 mL), water (1 × 40 mL), brine (1 × 40 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo. The resulting oily residue was purified by column chromatography using an elution gradient from 100% hexanes to 10% EtOAc/hexanes. Product-containing fractions were combined and concentrated in vacuo, and volatiles were removed at c.a. 10 mTorr for 18 h to afford **1g** as a light yellow liquid that solidified upon standing at room temperature (0.34 g, 84% yield). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.99 (dd, *J* = 7.9, 1.0 Hz, 1H),

7.64 (dd, *J* = 7.7, 0.9 Hz, 1H), 7.52-7.49 (m, 3H), 7.40 (td, *J* = 7.7, 1.3 Hz, 1H), 7.35-7.33 (m, 2H), 3.96 (s, 3H). This spectrum is in agreement with previously reported spectral data.[7]



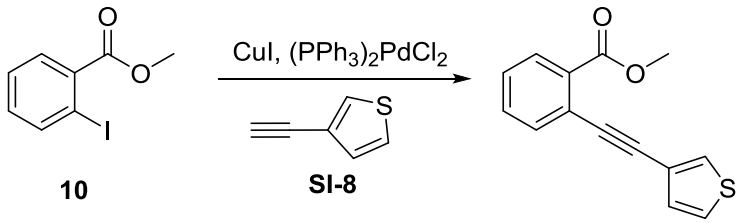
SI-2 **SI-7** **1h**

Methyl 5-bromo-2-(4-cyanobut-1-yn-1-yl)benzoate (1h). A flask was charged with compound **SI-2** (0.34 g, 1.0 mmol, 1.0 equiv), $(PPh_3)_2PdCl_2$ (0.014 g, 0.020 mmol, 0.020 equiv), and CuI (0.008 g, 0.04 mmol, 0.04 equiv). The flask was then evacuated and refilled with N_2 three times before 2 mL of acetonitrile and Et_3N (1.1 mL, 8.0 mmol, 8.0 equiv) were added. Compound **SI-7** (0.10 mL, 1.1 mmol, 1.1 equiv) was then syringed into the reaction mixture which stirred for 18 h under dynamic N_2. At this time, analysis by TLC (20% EtOAc/hexanes) indicated full consumption of starting material. The reaction mixture was diluted with 150 mL EtOAc and washed with NH_4Cl (1 × 25 mL), water (1 × 25 mL), brine (1 × 25 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo. The resulting oily residue was purified by column chromatography using an elution gradient from 100% hexanes to 20% EtOAc/hexanes. Product-containing fractions were combined and concentrated in vacuo, and volatiles were removed at c.a. 10 mTorr for 18 h to afford **1h** as a light yellow solid (0.25 g, 86% yield).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.06 (s, 1H), 7.57 (d, *J* = 8.3 Hz, 1H), 7.40 (d, *J* = 8.3 Hz, 1H), 3.92 (s, 3H), 2.84 (t, *J* = 7.2 Hz, 2H), 2.69 (t, *J* = 7.2 Hz, 2H).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 165.2, 135.7, 134.9, 133.41, 133.38, 122.3, 122.0, 118.3, 91.7, 81.0, 52.6, 17.5, 17.2.

HRMS (CI+): Calculated for $C_{13}H_{14}BrN_2O_2$ ($[M+NH_4]^+$), 309.0239; found 309.0230.



10 **SI-8** **1i**

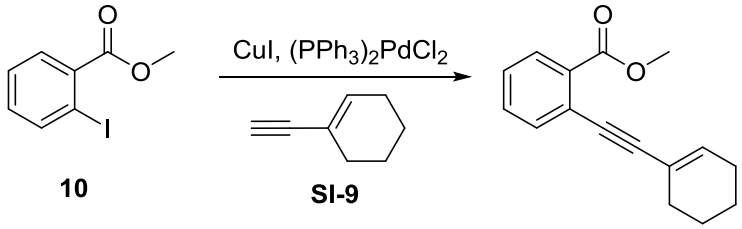
Methyl 2-(thiophen-3-ylethynyl)benzoate (1i). A flask was charged with compound **10** (0.22 mL, 1.5 mmol, 1.0 equiv), $(PPh_3)_2PdCl_2$ (0.021 g, 0.030 mmol, 0.020 equiv), and CuI (0.011 g, 0.060 mmol, 0.040 equiv). The flask was then evacuated and refilled with N_2 three times before 3 mL of acetonitrile and Et_3N (1.7 mL, 12 mmol, 8.0 equiv) were added. Compound **SI-8** (0.17 mL, 1.7 mmol, 1.1 equiv) was then syringed into the reaction mixture, which was then stirred for 18 h under dynamic N_2. At this time, analysis by TLC (20% EtOAc/hexanes) indicated full consumption of starting material. The reaction mixture was diluted with 150 mL EtOAc and

washed with NH_4Cl (1 × 25 mL), water (1 × 25 mL), brine (1 × 25 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo. The resulting oily residue was purified by column chromatography using an elution gradient from 100% hexanes to 20% EtOAc/hexanes. Product-containing fractions were combined and concentrated in vacuo, and volatiles were removed at c.a. 10 mTorr for 18 h to afford **1i** as a light yellow solid (0.37 g, 78% yield).

^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.95 (d, *J* = 7.8 Hz, 1H), 7.61 (d, *J* = 7.6 Hz, 1H), 7.58-7.56 (m, 1H), 7.45 (td, *J* = 7.6, 1.3 Hz, 1H), 7.34 (td, *J* = 7.6, 1.3 Hz, 1H), 7.29 (dd, *J* = 4.9, 3.0 Hz, 1H), 7.23 (app. d, *J* = 5.0 Hz, 1H), 3.93 (s, 3H).

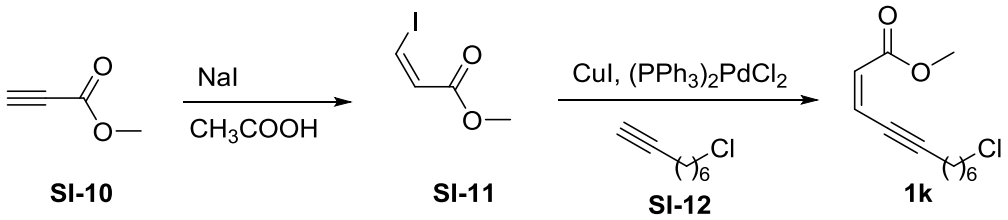
^{13}C NMR ($CDCl_3$, 125 MHz): δ 166.7, 134.0, 131.8, 131.7, 130.5, 130.0, 129.2, 127.9, 125.5, 123.8, 122.5, 89.7, 87.9, 52.2.

HRMS (CI+): Calculated for $C_{14}H_{10}SO_2$ ($[M]^+$), 242.0401; found 242.0390.



10 **SI-9** **1j**

methyl 2-(cyclohex-1-en-1-ylethynyl)benzoate (1j). A flask was charged with compound **10** (0.22 mL, 1.5 mmol, 1.0 equiv), $(PPh_3)_2PdCl_2$ (0.021 g, 0.030 mmol, 0.020 equiv), and CuI (0.011 g, 0.060 mmol, 0.040 equiv). The flask was then evacuated and refilled with N_2 three times before 3 mL of acetonitrile and Et_3N (1.7 mL, 12 mmol, 8.0 equiv) were added. Compound **SI-9** (0.20 mL, 1.7 mmol, 1.1 equiv) was then syringed into the reaction mixture which stirred for 18 h under dynamic N_2. At this time, analysis by TLC (10% EtOAc/hexanes) indicated full consumption of starting material. The reaction mixture was diluted with 150 mL Et_2O and washed with NH_4Cl (1 × 25 mL), water (1 × 25 mL), brine (1 × 25 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo. The resulting oily residue was purified by column chromatography using an elution gradient from 100% hexanes to 5% EtOAc/hexanes. Product-containing fractions were combined and concentrated in vacuo, and volatiles were removed at c.a. 10 mTorr for 18 h to afford **1j** as a yellow oil (0.35 g, 96% yield). ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.92 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.52 (dd, *J* = 7.7, 1.0 Hz, 1H), 7.43 (td, *J* = 7.6, 1.3 Hz, 1H), 7.31 (td, *J* = 7.7, 1.2 Hz, 1H), 6.28 – 6.26 (m, 1H), 3.92 (s, 3H), 2.28 – 2.25 (m, 2H), 2.18 – 2.14 (m, 2H), 1.71-1.67 (m, 2H), 1.64-1.61 (m, 2H). This spectrum is in agreement with previously reported spectral data.[8]



SI-10 **SI-11** **SI-12** **1k**

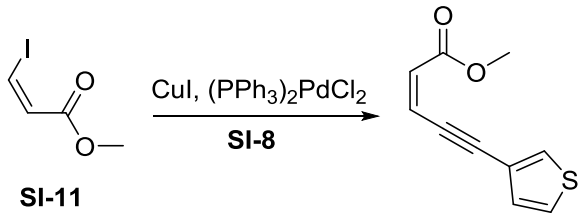
Methyl (Z)-3-iodoacrylate (SI-11) was prepared according to a literature procedure[9] in 75% yield. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.47 (d, *J* = 8.9 Hz, 1H), 6.91 (d, *J* = 9.0 Hz, 1H), 3.79 (s, 3H). This spectrum is in agreement with previously reported spectral data.

Methyl (Z)-11-chloroundec-2-en-4-ynoate (1k). This procedure was performed in a N_2-filled glove box. A 20 mL vial was charged with compound **SI-11** (0.42 g, 2.0 mmol, 1.0 equiv), $(PPh_3)_2PdCl_2$ (0.105 mg, 0.150 mmol, 0.0750 equiv), CuI (0.014 g, 0.074 mmol, 0.037 equiv), and a stir bar. 5 mL of Et_3N were added. Compound **SI-12** (0.37 mL, 2.4 mmol, 1.2 equiv) was then syringed into the reaction mixture, which was then heated to 50 °C and stirred for 18 h. At this time, analysis by TLC (10% EtOAc/hexanes) indicated full consumption of starting material. The reaction mixture was diluted with 150 mL EtOAc and washed with NH_4Cl (1 × 25 mL), water (1 × 25 mL), brine (1 × 25 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo. The resulting oily residue was purified by column chromatography using an elution gradient from 100% hexanes to 10% EtOAc/hexanes. Product-containing fractions were combined and concentrated in vacuo, and volatiles were removed at c.a. 10 mTorr for 18 h to afford **1k** as a viscous yellow oil (0.19 g, 41% yield).

^{1}H NMR ($CDCl_3$, 600 MHz): δ 6.15 (dt, *J* = 11.3, 2.3, 2.3 Hz, 1H), 6.05 (d, *J* = 11.4 Hz, 1H), 3.75 (s, 3H), 3.55 (t, *J* = 6.7, 2H), 2.47 (td, *J* = 7.0, 7.0, 2.1 Hz, 2H), 1.80 (t, *J* = 6.8 Hz, 2H), 1.61 (m, 2H), 1.47 (m, 4H).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 165.4, 127.2, 124.4, 104.2, 77.9, 51.5, 45.2, 32.6, 28.3, 28.2, 26.5, 20.1.

HRMS (CI+): Calculated for $C_{12}H_{18}ClO_2$ ($[M+H]^+$), 229.0995; found 229.0990.



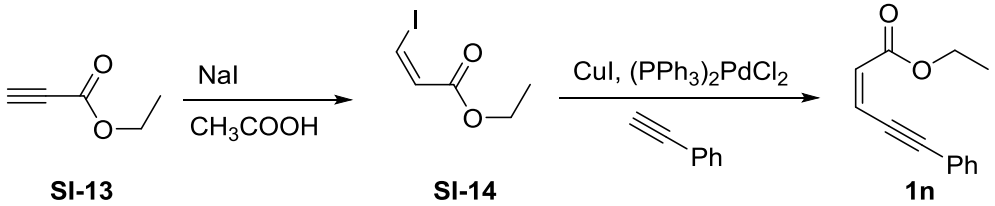
SI-11 **1m**

Methyl (Z)-5-(thiophen-3-yl)pent-2-en-4-ynoate (1m). A flask was charged with compound **SI-11** (0.500 g, 2.35 mmol, 1.00 equiv), $(PPh_3)_2PdCl_2$ (0.124 mg, 0.176 mmol, 0.0750 equiv), CuI (0.017 g, 0.087 mmol, 0.037 equiv), and a stir bar. The flask was then evacuated and refilled with N_2 three times before 5.3 mL of Et_3N was added. Compound **SI-8** (0.28 mL, 2.8 mmol, 1.2 equiv) was then syringed into the reaction mixture, which was then heated to 50 °C and stirred for 18 h. At this time, analysis by TLC (10% EtOAc/hexanes) indicated full consumption of starting material. The reaction mixture was diluted with 150 mL Et_2O and washed with NH_4Cl (1 × 25 mL), water (1 × 25 mL), brine (1 × 25 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo. The resulting oily residue was purified by column chromatography using an elution gradient from 100% hexanes to 10% EtOAc/hexanes. Product-containing fractions were combined and concentrated in vacuo, and volatiles were removed at c.a. 10 mTorr for 18 h to afford **1m** as a viscous light yellow oil (0.22 g, 48% yield).

^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.59 (d, *J* = 2.9 Hz, 1H), 7.28 (dd, *J* = 4.9, 3.1 Hz, 1H), 7.18 (d, *J* = 5.0 Hz, 1H), 6.34 (d, *J* = 11.5 Hz, 1H), 6.12 (d, *J* = 11.5 Hz, 1H), 3.78 (s, 3H).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 165.3, 130.7, 130.0, 127.5, 125.7, 123.3, 121.8, 96.8, 86.3, 51.6.

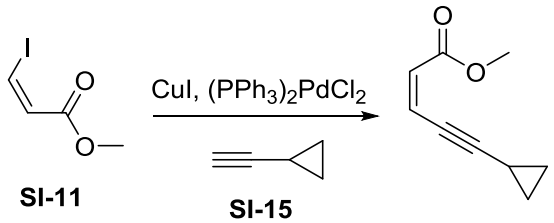
HRMS (CI+): Calculated for $C_{10}H_8SO_2$ ($[M]^+$), 192.0245; found 192.0240.



SI-13 **SI-14** **1n**

Ethyl (Z)-3-iodoacrylate (SI-14) was prepared according to a literature procedure[10] in 67% yield. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.43 (d, *J* = 8.9 Hz, 1H), 6.89 (d, *J* = 8.9 Hz, 1H), 4.25 (q, *J* = 7.1 Hz, 2H), 1.32 (t, *J* = 7.1 Hz, 3H). This spectrum is in agreement with previously reported spectral data.

Ethyl (Z)-5-phenylpent-2-en-4-ynoate (1n). A flask was charged with compound **SI-14** (0.50 g, 2.2 mmol, 1.0 equiv), $(PPh_3)_2PdCl_2$ (0.12 g, 0.17 mmol, 0.080 equiv), and CuI (0.015 g, 0.081 mmol, 0.040 equiv). The flask was then evacuated and refilled with N_2 three times before 5 mL of Et_3N was added. Phenylacetylene (0.29 mL, 2.6 mmol, 1.2 equiv) was then syringed into the reaction mixture, which was then heated to 50 °C and stirred for 18 h under dynamic N_2. At this time, analysis by TLC (10% EtOAc/hexanes) indicated full consumption of starting material. The reaction mixture was diluted with 150 mL Et_2O and washed with NH_4Cl (1 × 25 mL), water (1 × 25 mL), brine (1 × 25 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo. The resulting oily residue was purified by column chromatography using an elution gradient from 100% hexanes to 10% EtOAc/hexanes. Product-containing fractions were combined and concentrated in vacuo, and volatiles were removed at c.a. 10 mTorr for 18 h to afford **1n** as a viscous light yellow oil (0.28 g, 63% yield). ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.53 (dd, *J* = 7.4, 2.1 Hz, 1H), 7.36-7.33 (m, 3H), 4.27 (q, *J* = 7.1 Hz, 2H), 1.34 (t, *J* = 7.1 Hz, 3H). This spectrum is in agreement with previously reported spectral data.[2]



SI-11 **SI-15** **1p**

Methyl (Z)-5-cyclopropylpent-2-en-4-ynoate (1p). This procedure was performed in a N_2-filled glove box. A 20 mL vial was charged with compound **SI-11** (0.424 g, 2.00 mmol, 1.00 equiv), $(PPh_3)_2PdCl_2$ (0.112 g, 0.160 mmol, 0.0750 equiv), CuI (0.015 g, 0.080 mmol, 0.037 equiv), and a stir bar. 5 mL of Et_3N was added. Compound **SI-15** (0.20 mL, 2.4 mmol, 1.2 equiv) was then syringed into the reaction mixture, which was then heated to 50 °C and stirred for 18 h. At this time, analysis by TLC (10% EtOAc/hexanes) indicated full consumption of starting

material. The reaction mixture was diluted with 150 mL Et_2O and washed with NH_4Cl (1 × 25 mL), water (1 × 25 mL), brine (1 × 25 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo. The resulting oily residue was purified by column chromatography using an elution gradient from 100% hexanes to 10% EtOAc/hexanes. Product-containing fractions were combined and concentrated in vacuo [NOTE: product may be volatile] to afford 115 mg of **1p** as a yellow liquid in ~91% purity.

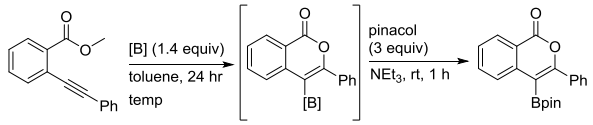
^{1}H NMR ($CDCl_3$, 600 MHz): δ 6.11 (dd, *J* = 11.4, 2.4 Hz, 1H), 6.01 (d, *J* = 11.3 Hz, 1H), 3.74 (s, 3H), 1.49 (ddt, 7.9, 5.3, 2.8, 2.8 Hz, 1H), 0.92 (m, 2H), 0.86 (m, 2H).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 165.5, 126.7, 124.5, 108.3, 73.6, 51.5, 9.7, 1.1.

HRMS (CI+): Calculated for $C_9H_{10}O_2$ ($[M]^+$), 150.0681; found 150.0677.

B. Boron Electrophile Screen

Table S1 (Table 1 in Manuscript). Boron Reagent Variation



1a 2a 3aa

Entry	Boron Electrophile [B]	Temp	Yield (%) 3aa
1	BBr_3	45 °C	0
2	BCl_3	45 °C	0
3	B-Chlorocatecholborane	45 °C	25
4	B-Chlorocatecholborane	100 °C	75
5	B-Bromocatecholborane	100°C	48

General Procedure: Entries 1 and 2

This screen was carried out in a nitrogen-filled glove box. A 4 mL vial was charged with **1a** (0.118 g, 0.500 mmol, 1.00 equiv) and 0.5 mL toluene. 0.6 mL (1.2 equiv) of a 1 M solution of either BBr_3 or BCl_3 was then added to the vial, and the vial was sealed and heated to 45 ^{o}C for 24 h. At this time, the reaction mixture was cooled down to room temperature. In a separate vial, pinacol (0.18 g, 1.5 mmol, 3.0 equiv) was dissolved in Et_3N (1.0 mL, 7.5 mmol, 15 equiv). This solution was then added to the reaction mixture. The resulting solution was then stirred for 1 h at room temperature. The solution was then concentrated in vacuo. Analysis of the resulting residue via ^{1}H NMR spectroscopy ($CDCl_3$, 600 MHz) and ^{11}B NMR Spectroscopy ($CDCl_3$, 126 MHz) confirmed that the desired product **3aa** was not produced.

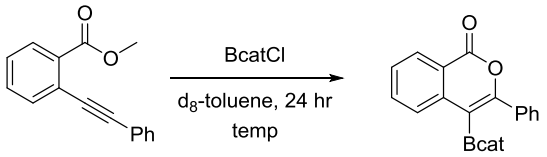
General Procedure: Entries 3-5

This screen was carried out in a nitrogen-filled glove box. A 4 mL vial was charged with **1a** (0.118 g, 0.500 mmol, 1.00 equiv) and 0.5 mL toluene. In a separate vial, *B*-chlorocatecholborane (0.70 mmol, 1.4 equiv) or *B*-bromocatecholborane (0.70 mmol, 1.4 equiv) was added. The initial reaction vial was then transferred to the boron-containing vial via pipette,

and this vial was sealed and heated to the specified temperature for 24 h. At this time, the reaction mixture was cooled down to room temperature. In a separate vial, pinacol (0.18 g, 1.5 mmol, 3.0 equiv) was dissolved in Et_3N (1.0 mL, 7.5 mmol, 15 equiv). This solution was then added to the reaction mixture. The resulting solution was then stirred for 1 h at room temperature. The solution was then concentrated in vacuo. The resulting oily residue was purified by column chromatography using an elution gradient from 100% hexanes to 15% EtOAc/hexanes. Product-containing fractions were combined and concentrated in vacuo, and volatiles were removed at c.a. 10 mTorr for 18 h to afford **3aa** as a light yellow oil, which solidified upon standing. The ^{1}H NMR spectrum for each entry was then compared to the authentic sample (see section D, product **3aa**) to establish identity.

C. Reaction Condition Optimization

Table S2. Optimization of the Oxyboration Reaction

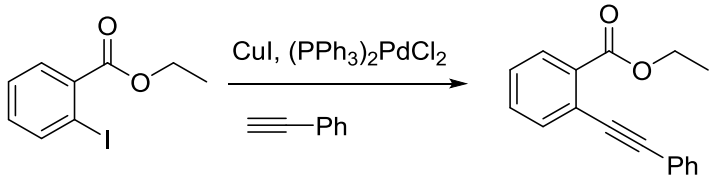


1a **2a**

Entry	Equivalents of BcatCl	Temp	2a:1a
1	**1.0 equiv**	**100 °C**	**76:24**
2	**1.2 equiv**	**100 °C**	**81:19**
3	**1.3 equiv**	**100 °C**	**87:13**
4	**1.4 equiv**	**100 °C**	**95:5**
5	**1.4 equiv**	**75 °C**	**86:14**
6	**1.4 equiv**	**45 °C**	**40:60**

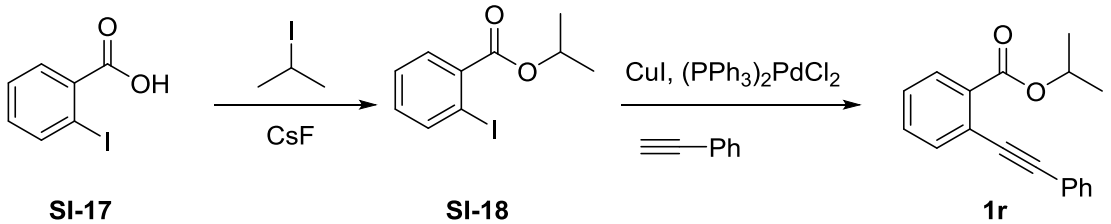
Reaction condition screening reactions were set up in a N_2-filled glovebox. **1a** (118 mg, 0.500 mmol, 1.00 equiv) was dissolved in anhydrous d_8-toluene (0.50 mL) and added to a dram vial containing *B*-chlorocatecholborane in the below amounts (1.00–1.40 equiv). After mixing thoroughly, the reaction mixture was transferred to a J. Young NMR tube, removed from the glovebox, and heated in a preheated oil bath for 24 h. The progress of the reaction was then monitored by ^{1}H and ^{11}B NMR spectroscopy, with characteristic product (**2a**) peaks at δ = 8.26 ppm in the ^{1}H NMR spectrum, and $\delta \sim 32.1$ ppm in the ^{11}B NMR spectrum in d_8-toluene.
Note: the optimized concentration was 1.0 M was the best; when higher concentrations were tested, solubility issues were encountered.

D. Synthesis of *O*-Alkyl Esters and Screen



SI-16 **1q**

Ethyl 2-(phenylethynyl)benzoate (1q). A flask was charged with compound **SI-16** (0.96 g, 3.5 mmol, 1.0 equiv), $(PPh_3)_2PdCl_2$ (0.049 g, 0.070 mmol, 0.020 equiv), and CuI (0.027 g, 0.14 mmol, 0.040 equiv). The flask was then evacuated and refilled with N_2 three times before 7 mL of acetonitrile and Et_3N (3.8 mL, 28 mmol, 8.0 equiv) were added. Phenylacetylene (0.42 mL, 3.8 mmol, 1.1 equiv) was then syringed into the reaction mixture which stirred for 18 h under dynamic N_2. At this time, analysis by TLC (10% EtOAc/hexanes) indicated full consumption of starting material. The reaction mixture was diluted with 200 mL EtOAc and washed with NH_4Cl (1 × 25 mL), water (1 × 25 mL), brine (1 × 25 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo. The resulting oily residue was purified by column chromatography using an elution gradient from 100% hexanes to 5% EtOAc/hexanes. Product-containing fractions were combined and concentrated in vacuo, and volatiles were removed at c.a. 10 mTorr for 18 h to afford **1q** as a light yellow oil (0.68 g, 78% yield). ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.99 (dd, *J* = 7.9, 0.8 Hz, 1H), 7.65 (dd, *J* = 7.7, 0.6 Hz, 1H), 7.60-7.58 (m, 2H), 7.47 (app t, *J* = 7.6 Hz, 1H), 7.38-7.34 (m, 4H), 4.44 (q, *J* = 7.2 Hz, 2H), 1.41 (t, *J* = 7.2 Hz, 3H). This spectrum is in agreement with previously reported spectral data.[12]

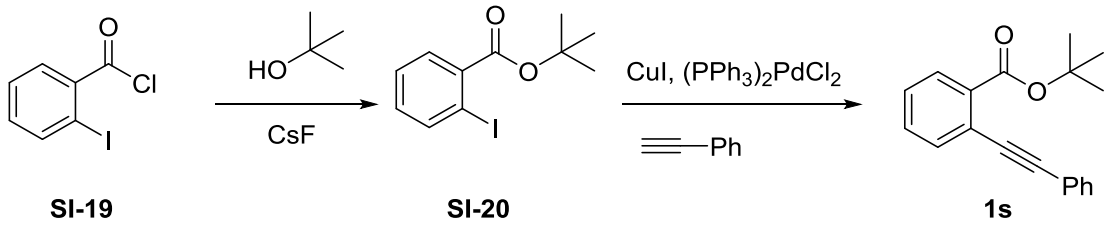


SI-17 **SI-18** **1r**

Isopropyl 2-iodobenzoate (SI-18) was prepared according to a literature procedure[13] in 56% yield. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.90 (dd, *J* = 7.9, 1.0 Hz, 1H), 7.68 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.37 (td, *J* = 7.7, 1.0 Hz, 1H), 7.10 (td, *J* = 7.9, 1.7 Hz, 1H), 5.24 (hept, *J* = 6.2 Hz, 1H), 1.39 (d, *J* = 6.2 Hz, 6H). This spectrum is in agreement with previously reported spectral data.[13]

Isopropyl 2-(phenylethynyl)benzoate (1r). A flask was charged with compound **SI-18** (0.50 g, 1.7 mmol, 1.0 equiv), $(PPh_3)_2PdCl_2$ (0.024 g, 0.034 mmol, 0.020 equiv), and CuI (0.013 g, 0.070 mmol, 0.040 equiv). The flask was then evacuated and refilled with N_2 three times before 4 mL of acetonitrile and Et_3N (1.9 mL, 14 mmol, 8.0 equiv) were added. Phenylacetylene (0.21 mL, 1.9 mmol, 1.1 equiv) was then syringed into the reaction mixture which stirred for 18 h under dynamic N_2. At this time, analysis by TLC (15% EtOAc/hexanes) indicated full consumption of starting material. The reaction mixture was diluted with 200 mL EtOAc and washed with NH_4Cl (1 × 25 mL), water (1 × 25 mL), brine (1 × 25 mL), dried over Na_2SO_4, filtered, and

concentrated in vacuo. The resulting oily residue was purified by column chromatography using an elution gradient from 100% hexanes to 5% EtOAc/hexanes. Product-containing fractions were combined and concentrated in vacuo, and volatiles were removed at c.a. 10 mTorr for 18 h to afford **1r** as a light yellow oil (0.39 g, 85% yield). ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.95 (dt, *J* = 7.9, 1.0 Hz, 1H), 7.65-7.63 (m, 1H), 7.58-7.56 (m, 2H), 7.50 (td, *J* = 7.6, 1.4 Hz, 1H), 7.39-7.34 (m, 4H), 5.30 (hept, *J* = 6.2 Hz, 1H), 1.38 (d, *J* = 6.2 Hz, 6H). This spectrum is in agreement with previously reported spectral data.[14]

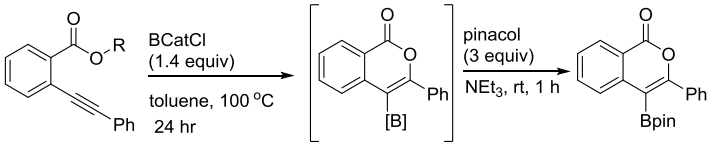


SI-19 **SI-20** **1s**

***tert*-Butyl 2-iodobenzoate (SI-20)** was prepared according to a literature procedure in 75% yield. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.94 (dd, *J* = 7.9, 1.0 Hz, 1H), 7.68 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.37 (td, *J* = 7.7, 1.0 Hz, 1H), 7.10 (td, *J* = 7.9, 1.7 Hz, 1H), 1.6 (s, 29H). This spectrum is in agreement with previously reported spectral data.[13]

***tert*-Butyl 2-(phenylethynyl)benzoate (1s)**. A flask was charged with compound **SI-20** (0.49 g, 1.6 mmol, 1.0 equiv), $(PPh_3)_2PdCl_2$ (0.022 g, 0.032 mmol, 0.020 equiv), and CuI (0.012 g, 0.064 mmol, 0.040 equiv). The flask was then evacuated and refilled with N_2 three times before 3 mL of acetonitrile and Et_3N (1.8 mL, 13 mmol, 8.0 equiv) were added. Phenylacetylene (0.20 mL, 1.8 mmol, 1.1 equiv) was then syringed into the reaction mixture which stirred for 18 h under dynamic N_2. At this time, analysis by TLC (10% EtOAc/hexanes) indicated full consumption of starting material. The reaction mixture was diluted with 200 mL EtOAc and washed with NH_4Cl (1 × 25 mL), water (1 × 25 mL), brine (1 × 25 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo. The resulting oily residue was purified by column chromatography using an elution gradient from 100% hexanes to 5% EtOAc/hexanes. Product-containing fractions were combined and concentrated in vacuo, and volatiles were removed at c.a. 10 mTorr for 18 h to afford **1s** as a light yellow oil (0.40 g, 90% yield). ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.86 (dd, *J* = 7.9, 0.8 Hz, 1H), 7.56 (dd, *J* = 7.7, 0.8 Hz, 1H), 7.51 (dd, *J* = 8.1, 1.9 Hz, 2H), 7.39 (td, *J* = 7.7, 1.3 Hz, 1H), 7.32-7.28 (m, 4H), 1.56 (s, 9H). This spectrum is in agreement with previously reported spectral data.[2]

Table S3 (Table 3 in Manuscript). Mechanistic Insight from *O*-Alkyl Group Variance of the Oxyboration Reaction



1 (1a, 1q-1s) 2 3aa

Entry	R	^{1}H NMR Yield (%) 3aa
1	Me	81
2	Et	68
3	iPr	60
4	tBu	0

General Procedure

This screen was carried out in a nitrogen-filled glove box. A 4 mL vial was charged with the desired *O*-alkyl ester (**1a**, **1q-1s**) (0.50 mmol, 1.0 equiv) and 0.5 mL toluene. In a separate vial, *B*-chlorocatecholborane (0.70 mmol, 1.4 equiv) was added. The solution in the initial reaction vial was then transferred to the boron-containing vial via pipette, and this vial was sealed and heated to 100 ^{o}C for 24 h. At this time, the reaction mixture was cooled to room temperature. In a separate vial, pinacol (0.18 g, 1.5 mmol, 3.0 equiv) was dissolved in Et_3N (1.0 mL, 7.5 mmol, 15 equiv). This solution was then added to the reaction mixture via pipette. The resulting solution was then stirred for 1 h at room temperature and then concentrated in vacuo. An ^{1}H NMR spectrum was then taken of each crude mixture in $CDCl_3$; mesitylene (50. μL, 0.36 mmol, 0.72 equiv) was added to the sample via gas tight syringe to determine the yield of the desired borylated isocoumarin **3aa**. In entry 4 (R = *t*Bu), the mesitylene was compared to characteristic peaks of the benzoic acid derivative of **1a** from an authentic sample synthesized using a known procedure.[15]

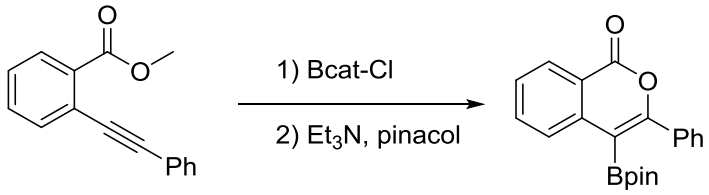
Procedure to Monitor the Formation of Isobutylene from Entry 4

A 4 mL vial was charged with compound **1s** (0.10 g, 0.37 mmol, 1.0 equiv), 1,3,5-triisopropylbenzene (30 μL, 0.12 mmol, 0.24 equiv), and 0.4 mL d_8-toluene. In a separate vial, *B*-chlorocatecholborane (0.080 g, 0.52 mmol, 1.4 equiv) was added. The solution in the initial reaction vial was then transferred to the boron-containing vial via pipette, and then this mixture was transferred to a J-young tube via pipette. The tube was heated to 100 ^{o}C. ^{1}H NMR spectra were taken at t = 3 h and 24 h to monitor isobutylene formation, as well as to confirm that catecholboronic ester **2s** did not form.

E. Synthesis and Isolation of Carboxyboration Products 3aa-3p

General Remarks

For synthetic ease, these reactions were carried out in a nitrogen-filled glovebox unless specified otherwise. *B*-Chlorocatecholborane is water-reactive and should be stored cool (0 ^{o}C or lower) in a desiccator or glovebox when not in use. The ipso C–B bond is not detected by ^{13}C NMR spectroscopy.



1a **3aa**

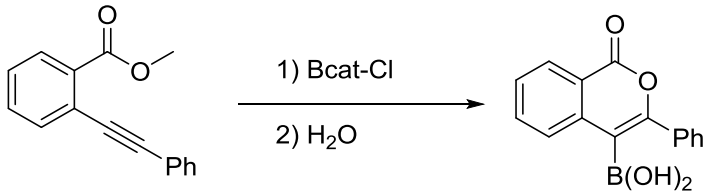
3-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1H-isochromen-1-one (3aa). A vial was charged with **1a** (0.118 g, 0.500 mmol, 1.00 equiv) and 0.5 mL toluene. A separate vial equipped with a stir bar was charged with *B*-chlorocatecholborane (0.108 g, 0.700 mmol, 1.40 equiv). The resulting homogenous solution from the first vial was then added dropwise over c.a. 2 min to the boron-containing vial, which stirred for 24 h at 100 °C. At this time, the reaction mixture was cooled to room temperature and then diluted with 0.5 mL toluene. A separate vial was then charged with pinacol (0.177 g, 1.50 mmol, 3.00 equiv) and Et_3N (1.0 mL, 7.5 mmol, 15 equiv). The reaction mixture was added dropwise over c.a. 2 min to this vial, and the resulting mixture stirred for 1 h at room temperature. The solution was concentrated in vacuo and the resulting residue was purified by column chromatography using an elution gradient from 100% hexanes to 15% EtOAc/hexanes. Product-containing fractions were combined and concentrated in vacuo, and volatiles were removed at c.a. 10 mTorr for 18 h to afford **3aa** as a yellow oil (0.13 g, 75% yield).

^{1}H NMR (toluene-d_8, 600 MHz): δ 8.32 (app dd, J = 7.9, 1.0 Hz, 1H), 7.92 (app dd, J = 7.9, 0.4 Hz, 1H), 7.52-7.50 (m, 2H), 7.27 (ddd, J = 15.3, 6.5, 1.5 Hz, 1H), 7.12-6.99 (m, 4H), 0.99 (s, 12H).

^{13}C NMR (toluene-d_8, 125 MHz): δ 161.4, 160.9, 129.1, 128.7, 128.1, 128.1, 127.8, 125.3, 124.9, 84.0, 24.7, 20.7, 20.6, 20.3, 20.1.

^{11}B NMR (toluene-d_8, 193 MHz): δ 31.5.

HRMS (ESI+): Calculated for $C_{21}H_{21}BO_4Na$ ($[M+Na]^+$), 371.1435; found 371.1434.



1a **3ab**

(1-oxo-3-phenyl-1*H*-isochromen-4-yl)Boronic acid (3ab). A vial was charged with **1a** (0.118 g, 0.500 mmol, 1.00 equiv) and 0.5 mL toluene. A separate vial equipped with a stir bar was charged with *B*-chlorocatecholborane (0.108 g, 0.700 mmol, 1.40 equiv). The resulting homogenous solution from the first vial was then added dropwise over c.a. 2 min to the boron-containing vial, which stirred for 24 h at 100 °C. At this time, the reaction mixture was cooled to room temperature and transferred to a vial containing 1 mL of water, and the resulting mixture was stirred vigorously for 18 h at room temperature. The solution was then filtered through a medium porosity fritted funnel. The solid was then rinsed with cold (~0 °C) water (3 × 3 mL).

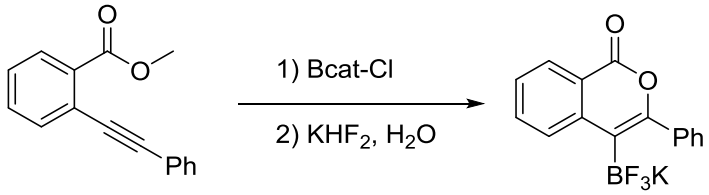
The solid was dried in vacuo c.a. 10 mTorr for 18 h to afford **3ab** as a light purple solid (0.088 g, 66% yield).

^{1}H NMR (CD_3CN, 600 MHz): δ 8.27 (dd, *J* = 7.9, 0.9 Hz, 1H), 7.81 (ddd, *J* = 15.2, 7.2, 1.4 Hz, 1H), 7.76-7.75 (m, 2H), 7.65 (app d, *J* = 7.7 Hz, 1H), (ddd, *J* = 15.2, 7.9, 0.5 Hz, 1H), 7.53-7.49 (m, 3H), 6.51 (s, 2H).

^{13}C NMR (CD_3CN, 125 MHz): δ 162.2, 155.2, 139.4, 135.0, 134.9, 129.9, 129.1, 128.7, 128.2, 127.5, 127.0, 121.0.

^{11}B NMR (CD_3CN, 193 MHz): δ 30.0.

HRMS (ESI-): Calculated for $C_{15}H_{11}BO_4Cl$ ($[M+Cl]^-$), 301.0442; found 301.0441.



1a **3ac**

3-Phenyl-4-(trifluoro-λ^4-boranyl)-1*H*-isochromen-1-one, potassium salt (3ac). A vial was charged with **1a** (0.118 g, 0.500 mmol, 1.00 equiv) and 0.5 mL toluene. A separate vial equipped with a stir bar was charged with *B*-chlorocatecholborane (0.108 g, 0.700 mmol, 1.40 equiv). The resulting homogenous solution from the first vial was then added dropwise over c.a. 2 min to the boron-containing vial, which stirred for 24 h at 100 ^{o}C. At this time, the reaction mixture was cooled to room temperature and then concentrated in vacuo. The residue was then dissolved in 1 mL of acetone and then transferred via pipette to another flask containing a solution of KHF_2 (0.137g, 1.80 mmol, 3.50 equiv) in 1.5 mL of H_2O. The resulting mixture was stirred for 1 h then concentrated in vacuo at c.a. 10 mTorr for 1 h. The product was then filtered through a medium porosity fritted funnel. The solid was then rinsed with cold (~0 ^{o}C) water (3 × 3 mL) and ether (3 x 3 mL). The solid was dried in vacuo c.a. 10 mTorr for 18 h to afford **3ac** as a white solid (0.103 g, 63% yield).

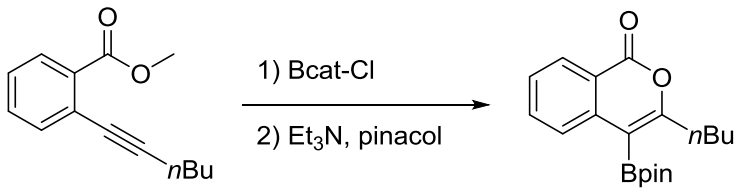
^{1}H NMR ($(CD_3)_2CO$, 600 MHz): δ 8.37 (d, *J* = 8.1 Hz, 1H), 8.16 (d, *J* = 7.7 Hz, 1H), 7.68 (d, *J* = 6.4 Hz, 2H), 7.64 (t, *J* = 7.7 Hz, 1H), 7.40 (t, *J* = 7.4 Hz, 1H), 7.31-7.30 (m, 3H).

^{13}C NMR ($(CD_3)_2CO$, 600 MHz): δ 168.5, 160.0, 148.8, 143.2, 138.2, 138.1, 135.4, 135.3, 135.2, 132.9, 131.9, 131.2, 126.3.

^{11}B NMR ($(CD_3)_2CO$, 193 MHz): δ 2.9.

^{19}F NMR ($(CD_3)_2CO$, 376 MHz): δ -131.6.

HRMS (ESI-): Calculated for $C_{15}H_9BF_3O_2$ ($[M-K]^-$), 289.0651; found 289.0640.



1b **3b**

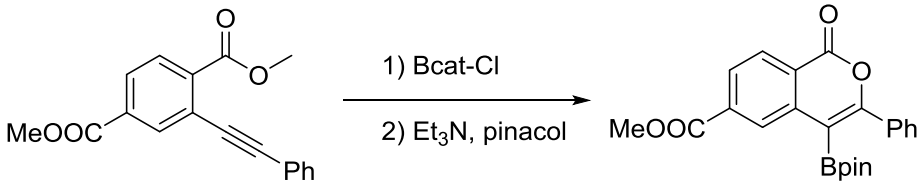
3-butyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1H-isochromen-1-one (3b). A vial was charged with **1b** (0.108 g, 0.500 mmol, 1.00 equiv) and 0.5 mL toluene. A separate vial equipped with a stir bar was charged with *B*-chlorocatecholborane (0.108 g, 0.700 mmol, 1.40 equiv). The resulting homogenous solution from the first vial was then added dropwise over c.a. 2 min to the boron-containing vial, which stirred for 24 h at 100 ^{o}C. At this time, the reaction mixture was cooled to room temperature and then diluted with 0.5 mL toluene. A separate vial was then charged with pinacol (0.177 g, 1.50 mmol, 3.00 equiv) and Et_3N (1.0 mL, 7.5 mmol, 15 equiv). The reaction mixture was added dropwise over c.a. 2 min to this vial, and the resulting mixture stirred for 1 h at room temperature. The solution was concentrated in vacuo and the resulting residue was purified by column chromatography using an elution gradient from 100% hexanes to 15% EtOAc/hexanes. Product-containing fractions were combined and concentrated in vacuo, and volatiles were removed at c.a. 10 mTorr for 18 h to afford **3b** as a yellow oil (0.16 g, 97% yield).

^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.24 (d, *J* = 9.5 Hz, 1H), 8.04 (d, *J* = 9.9 Hz, 1H), 7.65 (td, *J* = 9.5, 1.5 Hz, 1H), 7.42-7.38 (m, 1H), 2.80 (t, *J* = 9.3 Hz, 2H), 1.72-1.66 (m, 2H), 1.39-1.38 (m, 14H), 0.92 (t, *J* = 8.9 Hz, 3H).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 166.6, 162.9, 139.8, 134.7, 129.2, 127.2, 126.6, 119.9, 84.0, 33.7, 30.9, 24.9, 22.5, 13.9.

^{11}B NMR ($CDCl_3$, 193 MHz): δ 31.6.

HRMS (ESI+): Calculated for $C_{19}H_{25}BO_4K$ ($[M+K]^+$), 367.1487; found 367.1481.



1c **3c**

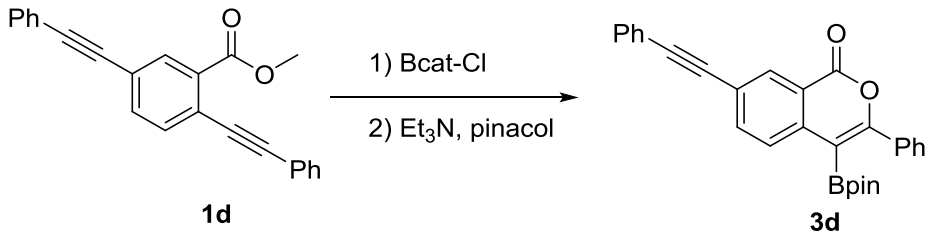
Methyl 1-oxo-3-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1H-isochromene-6-carboxylate (3c). A vial was charged with **1c** (0.147 g, 0.500 mmol, 1.00 equiv) and 0.5 mL toluene. A separate vial equipped with a stir bar was charged with *B*-chlorocatecholborane (0.108 g, 0.700 mmol, 1.40 equiv). The resulting homogenous solution from the first vial was then added dropwise over c.a. 2 min to the boron-containing vial, which stirred for 24 h at 100 ^{o}C. At this time, the reaction mixture was cooled to room temperature and then diluted with 0.5 mL toluene. A separate vial was then charged with pinacol (0.177 g, 1.50 mmol, 3.00 equiv) and Et_3N (1.0 mL, 7.5 mmol, 15 equiv). The reaction mixture was added dropwise over c.a. 2 min to this vial, and the resulting mixture stirred for 1 h at room temperature. The solution was concentrated in vacuo and the resulting residue was purified by column chromatography using an elution gradient from 100% hexanes to 20% EtOAc/hexanes. Product-containing fractions were combined and concentrated in vacuo, and volatiles were removed at c.a. 10 mTorr for 18 h to afford **3c** as a yellow solid (0.13 g, 65% yield).

^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.60 (d, *J* = 1.1 Hz, 1H), 8.40 (d, *J* = 8.2 Hz, 1H), 8.10 (dd, *J* = 8.2, 1.5 Hz, 1H), 7.71-7.70 (m, 2H), 7.49-7.43 (m, 3H), 3.99 (s, 3H), 1.35 (s, 12H).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 166.0, 161.8, 160.3, 139.7, 135.4, 134.2, 130.4, 129.9, 128.8, 128.4, 128.3, 128.1, 123.1, 84.8, 52.7, 24.8.

^{11}B NMR ($CDCl_3$, 193 MHz): δ 31.7.

HRMS (ESI+): Calculated for $C_{23}H_{23}BO_6Na$ ([M+Na]$^+$), 429.1490; found 429.1499.



1d **3d**

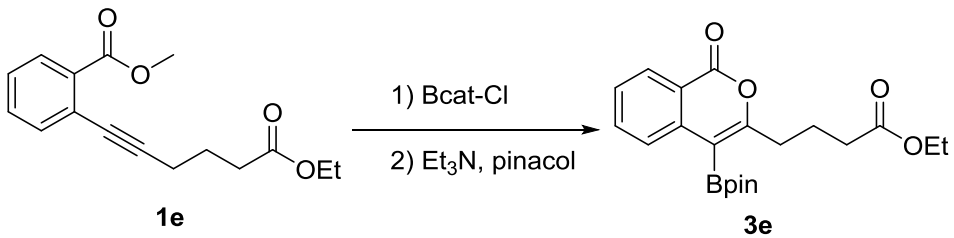
3-phenyl-7-(phenylethynyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1H-isochromen-1-one (3d). A vial was charged with **1d** (0.168 g, 0.500 mmol, 1.00 equiv) and 0.5 mL toluene. A separate vial equipped with a stir bar was charged with *B*-chlorocatecholborane (0.108 g, 0.700 mmol, 1.40 equiv). The resulting homogenous solution from the first vial was then added dropwise over c.a. 2 min to the boron-containing vial, which stirred for 24 h at 100 °C. At this time, the reaction mixture was cooled to room temperature and then diluted with 0.5 mL toluene. A separate vial was then charged with pinacol (0.177 g, 1.50 mmol, 3.00 equiv) and Et_3N (1.0 mL, 7.5 mmol, 15 equiv). The reaction mixture was added dropwise over c.a. 2 min to this vial, and the resulting mixture stirred for 1 h at room temperature. The solution was concentrated in vacuo and the resulting residue was purified by column chromatography using an elution gradient from 100% hexanes to 15% EtOAc/hexanes. Product-containing fractions were combined and concentrated in vacuo, and volatiles were removed at c.a. 10 mTorr for 18 h to afford **3d** as a yellow solid (0.15 g, 66% yield).

^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.50 (s, 1H), 7.85-7.81 (m, 2H), 7.68 (app d, *J* = 7.5 Hz, 2H), 7.56-7.54 (m, 2H), 7.47-7.45 (m, 1H), 7.43-7.41 (m, 2H), 7.38-7.35 (m, 3H), 1.29 (s, 12H).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 161.7, 160.5, 139.2, 137.3, 134.5, 132.7, 131.8.9, 130.3, 128.9, 128.8, 128.5, 128.2, 126.6, 123.1, 122.8, 120.3, 91.5, 88.3, 84.6, 24.9.

^{11}B NMR ($CDCl_3$, 193 MHz): δ 31.3.

HRMS (ESI+): Calculated for $C_{29}H_{25}BO_4Na$ ([M+Na]$^+$), 471.1749; found 471.1759.



1e **3e**

Ethyl 4-(1-oxo-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1H-isochromen-3-yl)butanoate (3e). A vial was charged with **1e** (0.064 g, 0.23 mmol, 1.0 equiv) and 0.23 mL toluene. A separate vial equipped with a stir bar was charged with *B*-chlorocatecholborane

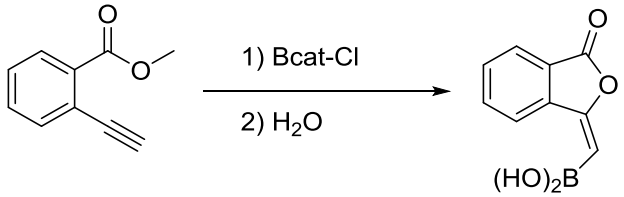
(0.050 g, 0.33 mmol, 1.4 equiv). The resulting homogenous solution from the first vial was then added dropwise over c.a. 2 min to the boron-containing vial, which stirred for 24 h at 100 °C. At this time, the reaction mixture was cooled to room temperature and then diluted with 0.23 mL toluene. A separate vial was then charged with pinacol (0.083 g, 0.70 mmol, 3.0 equiv) and Et_3N (0.50 mL, 3.8 mmol, 15 equiv). The reaction mixture was added dropwise over c.a. 2 min to this vial, and the resulting mixture stirred for 1 h at room temperature. The solution was concentrated in vacuo and the resulting residue was purified by column chromatography using an elution gradient from 100% hexanes to 20% EtOAc/hexanes. Product-containing fractions were combined and concentrated in vacuo, and volatiles were removed at c.a. 10 mTorr for 18 h to afford **3e** as a yellow solid (0.050 g, 55% yield).

^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.25 (app d, *J* = 8.0 Hz, 1H), 8.08 (app d, *J* = 8.2 Hz, 1H), 7.66 (ddd, *J* = 11.8, 5.9, 1.1 Hz, 1H), 7.42 (app t, *J* = 7.6 Hz, 1H), 4.09 (q, *J* = 7.1 Hz, 2H), 2.87 (t, *J* = 7.4 Hz, 2H), 2.36 (t, *J* = 7.6 Hz, 2H), 2.05 (tt, *J* = 14.8, 7.5 Hz, 2H), 1.38 (s, 12H), 1.22 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 173.1, 165.2, 162.7, 139.5, 134.7, 129.3, 127.5, 126.8, 120.0, 84.2, 60.4, 33.6, 33.1, 24.9, 23.7, 14.3.

^{11}B NMR ($CDCl_3$, 193 MHz): δ 31.3.

HRMS (ESI): Calculated for $C_{21}H_{27}BO_6Na$ ($[M+Na]^+$), 409.1802; found 409.1808.



1f **3f**

(E)-((3-oxoisobenzofuran-1(3H)-ylidene)methyl)boronic acid (3f). A vial was charged with **1f** (0.080 g, 0.50 mmol, 1.0 equiv) and 0.5 mL toluene. A separate vial equipped with a stir bar was charged with *B*-chlorocatecholborane (0.108 g, 0.700 mmol, 1.40 equiv). The resulting homogenous solution from the first vial was then added dropwise over c.a. 2 min to the boron-containing vial, which stirred for 20 h at 100 °C. At this time, the reaction mixture was cooled to room temperature and then transferred to a vial containing 10 mL of water, and the resulting mixture stirred vigorously for 3 h at room temperature. The solution was then filtered through a medium porosity fritted funnel. The solid was then rinsed with cold (~0 °C) water (3 × 3 mL). The solid was then dried in vacuo c.a. 10 mTorr for 18 h to afford **3f** as a white solid (0.058 g, 61% yield).

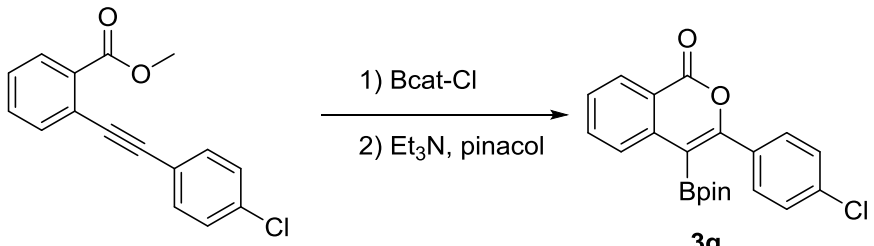
^{1}H NMR (CD_3CN, 600 MHz): δ 8.60 (d, *J* = 9.6 Hz, 1H), 7.87 (d, *J* = 9.2 Hz, 1H), 7.79 (app t, *J* = 9.2 Hz, 1H), 7.65 (app t, *J* = 9.0 Hz, 1H), 6.34 (s, 2H), 5.48 (s, 1H).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 167.5, 157.2, 139.3, 135.6, 131.8, 127.5, 125.99, 125.4, 118.3.

^{11}B NMR (CD_3CN, 193 MHz): δ 28.1.

HRMS (ESI-): Calculated for $C_9H_7BO_4Cl$ ($[M+Cl]^-$), 225.0128; found 225.0121.

HMQC was used to confirm the formation of the 5-*exo-dig* product. Because ipso B–C resonances are not detected in ^{13}C NMR, the resonance at δ = 5.48 ppm in the HMQC must be attached to an ipso B–C bond because no ^{13}C NMR signal correlates.



1g **3g**

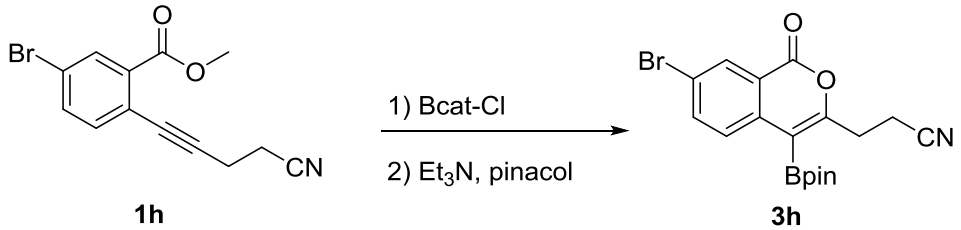
3-(4-chlorophenyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1H-isochromen-1-one (3g). A vial was charged with **1g** (0.135 g, 0.500 mmol, 1.00 equiv) and 0.5 mL toluene. A separate vial equipped with a stir bar was charged with *B*-chlorocatecholborane (0.108 g, 0.700 mmol, 1.40 equiv). The resulting homogenous solution from the first vial was then added dropwise over c.a. 2 min to the boron-containing vial, which stirred for 24 h at 100 °C. At this time, the reaction mixture was cooled to room temperature and then diluted with 0.5 mL toluene. A separate vial was then charged with pinacol (0.177 g, 1.50 mmol, 3.00 equiv) and Et_3N (1.0 mL, 7.5 mmol, 15 equiv). The reaction mixture was added dropwise over c.a. 2 min to this vial, and the resulting mixture stirred for 1 h at room temperature. The solution was concentrated in vacuo and the resulting residue was purified by column chromatography using an elution gradient from 100% hexanes to 20% EtOAc/hexanes. Product-containing fractions were combined and concentrated in vacuo, and volatiles were removed at c.a. 10 mTorr for 18 h to afford **3g** as a white solid (0.11 g, 60% yield).

^1H NMR ($CDCl_3$, 600 MHz): δ 8.34 (d, *J* = 7.9 Hz, 1H), 7.87 (d, *J* = 7.8 Hz, 1H), 7.73 (app t, *J* = 7.7 Hz, 1H), 7.64-7.62 (m, 2H), 7.52 (app t, *J* = 7.7 Hz, 1H), 7.41-7.39 (m, 2H), 1.31 (s, 12H).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 162.3, 158.8, 139.5, 136.3, 135.0, 133.2, 130.4, 129.8, 128.5, 128.3, 126.6, 120.3, 84.7, 25.0.

^{11}B NMR ($CDCl_3$, 193 MHz): δ 31.4.

HRMS (ESI+): Calculated for $C_{21}H_{20}BClO_4Na$ ($[M+Na]^+$), 405.1045; found 405.1048.



1h **3h**

3-(7-bromo-1-oxo-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1H-isochromen-3-yl)propanenitrile (3h). A vial was charged with **1h** (0.146 g, 0.500 mmol, 1.00 equiv) and 0.5 mL toluene. A separate vial equipped with a stir bar was charged with *B*-chlorocatecholborane (0.108 g, 0.700 mmol, 1.40 equiv). The resulting homogenous solution from the first vial was

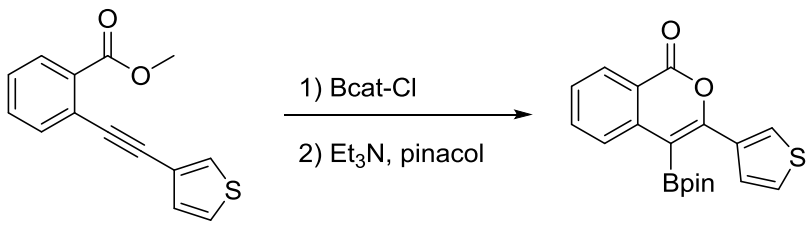
then added dropwise over c.a. 2 min to the boron-containing vial, which stirred for 24 h at 100 ^{o}C. At this time, the reaction mixture was cooled to room temperature and then diluted with 0.5 mL toluene. A separate vial was then charged with pinacol (0.177 g, 1.50 mmol, 3.00 equiv) and Et_3N (1.0 mL, 7.5 mmol, 15 equiv). The reaction mixture was added dropwise over c.a. 2 min to this vial, and the resulting mixture stirred for 1 h at room temperature. The solution was concentrated in vacuo and the resulting residue was purified by column chromatography using an elution gradient from 100% hexanes to 25% EtOAc/hexanes. Product-containing fractions were combined and concentrated in vacuo, and volatiles were removed at c.a. 10 mTorr for 18 h to afford **3h** as a white solid (0.079 g, 39% yield).

^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.37 (d, *J* = 2.2 Hz, 1H), 8.18 (d, *J* = 8.7 Hz, 1H), 7.78 (dd, *J* = 8.7, 2.2 Hz, 1H), 3.26 (t, *J* = 7.4 Hz, 2H), 2.76 (t, *J* = 7.4 Hz, 2H), 1.40 (s, 12H).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 162.3, 160.7, 138.1, 137.7, 131.8, 129.4, 121.8, 121.8, 118.3, 84.6, 29.7, 25.0, 16.2.

^{11}B NMR ($CDCl_3$, 193 MHz): δ 30.6.

HRMS (ESI+): Calculated for $C_{18}H_{19}BBrNO_4Na$ ($[M+Na]^+$), 426.0492; found 426.0486.



1i **3i**

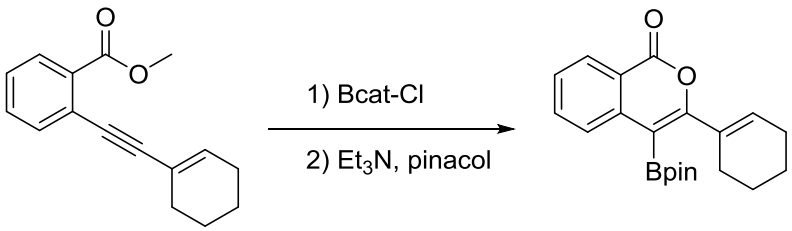
4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(thiophen-3-yl)-1H-isochromen-1-one (3i). A vial was charged with **1i** (0.177 g, 0.500 mmol, 1.00 equiv) and 0.5 mL toluene. A separate vial equipped with a stir bar was charged with *B*-chlorocatecholborane (0.108 g, 0.700 mmol, 1.40 equiv). The resulting homogenous solution from the first vial was then added dropwise over c.a. 2 min to the boron-containing vial, which stirred for 24 h at 100 ^{o}C. At this time, the reaction mixture was cooled to room temperature and then diluted with 0.5 mL toluene. A separate vial was then charged with pinacol (0.177 g, 1.50 mmol, 3.00 equiv) and Et_3N (1.0 mL, 7.5 mmol, 15 equiv). The reaction mixture was added dropwise over c.a. 2 min to this vial, and the resulting mixture stirred for 1 h at room temperature. The solution was concentrated in vacuo and the resulting residue was purified by column chromatography using an elution gradient from 100% hexanes to 20% EtOAc/hexanes. Product-containing fractions were combined and concentrated in vacuo, and volatiles were removed at c.a. 10 mTorr for 18 h to afford **3i** as a white solid (0.13 g, 71% yield).

^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.31 (app d, *J* = 7.9 Hz, 1H), 7.78-7.76 (m, 1H), 7.74 (dd, *J* = 8.0, 0.3 Hz, 1H), 7.69 (ddd, *J* = 7.6, 7.6, 1.3 Hz, 1H), 7.46 (ddd, *J* = 7.6, 7.6, 1.1 Hz, 1H), 7.43-7.42 (m, 1H), 7.35-7.33 (m, 1H), 1.34 (s, 12H).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 162.3, 154.5, 139.6, 135.9, 134.8, 129.7, 127.9, 127.7, 127.2, 126.4, 125.8, 120.2, 84.7, 25.1.

^{11}B NMR ($CDCl_3$, 193 MHz): δ 31.8.

HRMS (ESI+): Calculated for $C_{21}H_{19}BO_4SNa$ ([M+Na]$^+$), 377.0999; found 377.0995.



1j **3j**

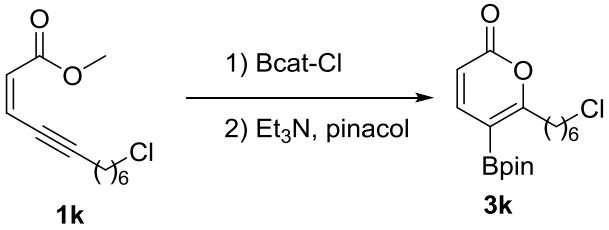
3-(cyclohex-1-en-1-yl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1H-isochromen-1-one (3j). A vial was charged with **1j** (0.120 g, 0.500 mmol, 1.00 equiv) and 0.5 mL toluene. A separate vial equipped with a stir bar was charged with *B*-chlorocatecholborane (0.108 g, 0.700 mmol, 1.40 equiv). The resulting homogenous solution from the first vial was then added dropwise over c.a. 2 min to the boron-containing vial, which stirred for 24 h at 100 ^{o}C. At this time, the reaction mixture was cooled to room temperature and then diluted with 0.5 mL toluene. A separate vial was then charged with pinacol (0.177 g, 1.50 mmol, 3.00 equiv) and Et_3N (1.0 mL, 7.5 mmol, 15 equiv). The reaction mixture was added dropwise over c.a. 2 min to this vial, and the resulting mixture stirred for 1 h at room temperature. The solution was concentrated in vacuo and the resulting residue was purified by column chromatography using an elution gradient from 100% hexanes to 20% EtOAc/hexanes. Product-containing fractions were combined and concentrated in vacuo, and volatiles were removed at c.a. 10 mTorr for 18 h to afford **3j** as a yellow oil (0.14 g, 77% yield).

^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.25 (app d, *J* = 7.8 Hz, 1H), 7.72 (app d, *J* = 8.0 Hz, 1H), 7.64 (app td, *J* = 7.6, 1.2 Hz, 1H), 7.41 (app td, *J* = 7.6, 1.0 Hz, 1H), 2.41-2.39 (m, 2H), 7.43-7.42 (m, 2H), 2.14-2.12 (m, 2H), 1.74-1.70 (m, 2H), 1.65-1.61 (m, 2H), 1.35 (s, 12H).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 163.0, 162.7, 139.8, 134.6, 134.6, 132.0, 129.5, 127.5, 126.2, 120.2, 84.2, 26.3, 25.5, 25.0, 22.2, 21.7.

^{11}B NMR ($CDCl_3$, 193 MHz): δ 31.3.

HRMS (ESI+): Calculated for $C_{21}H_{25}BO_4Na$ ([M+Na]$^+$), 375.1747; found 375.1744.



1k **3k**

6-(6-chlorohexyl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2H-pyran-2-one (3k). A vial was charged with **1k** (0.179 g, 0.780 mmol, 1.00 equiv) and 0.8 mL toluene. A separate vial equipped with a stir bar was charged with *B*-chlorocatecholborane (0.170 g, 1.10 mmol, 1.40 equiv). The resulting homogenous solution from the first vial was then added dropwise over c.a. 2 min to the boron-containing vial, which stirred for 24 h at 100 ^{o}C. At this time, the reaction mixture was cooled to room temperature and then diluted with 0.8 mL toluene. A separate vial

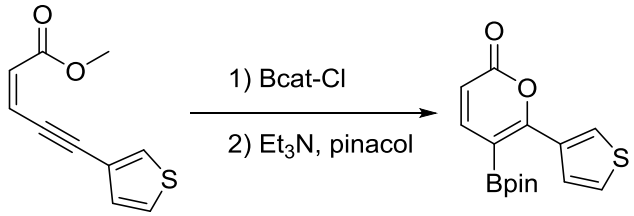
was then charged with pinacol (0.272 g, 2.30 mmol, 3.00 equiv) and Et_3N (1.6 mL, 12 mmol, 15 equiv). This mixture was added to the reaction mixture dropwise over c.a. 2 min to this vial, and the resulting mixture stirred for 1 h at room temperature. The solution was concentrated in vacuo and the resulting residue was purified by column chromatography using an elution gradient from 100% hexanes to 15% EtOAc/hexanes. Product-containing fractions were combined and concentrated in vacuo, and volatiles were removed at c.a. 10 mTorr for 18 h to afford **3k** as a yellow oil that solidified upon standing (0.11 g, 41% yield).

^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.51 (d, *J* = 9.4 Hz, 1H), 6.07 (d, *J* = 9.4 Hz, 1H), 3.48 (t, *J* = 6.7 Hz, 2H), 2.78 (t, *J* = 7.6 Hz, 2H), 1.72 (M, 2H), 1.64 (quin, *J* = 7.6, 2H), 1.42 (t, *J* = 7.8 Hz, 2H), 1.32 (quin, *J* = 7.5 Hz, 2H), 1.26 (S, 12H).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 163.0, 162.7, 139.8, 134.6, 134.6, 132.0, 129.5, 127.5, 126.2, 120.2, 84.2, 26.3, 25.5, 25.0, 22.2, 21.7.

^{11}B NMR ($CDCl_3$, 193 MHz): δ 30.2.

HRMS (ESI+): Calculated for $C_{17}H_{26}ClBO_4$ ($[M]^+$), 340.1616; found 340.1609.



1m **3m**

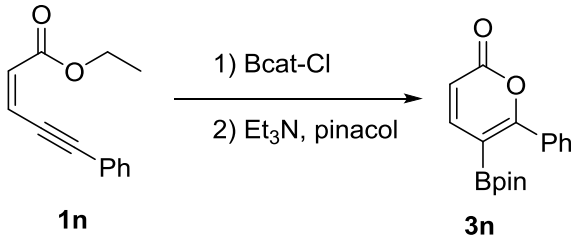
5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-6-(thiophen-3-yl)-2H-pyran-2-one (3m). A vial was charged with **1m** (0.096 g, 0.50 mmol, 1.0 equiv) and 0.5 mL toluene. A separate vial equipped with a stir bar was charged with *B*-chlorocatecholborane (0.108 g, 0.500 mmol, 1.40 equiv). The resulting homogenous solution from the first vial was then added dropwise over c.a. 2 min to the boron-containing vial, which stirred for 21 h at 100 °C. At this time, the reaction mixture was cooled to room temperature and then diluted with 0.5 mL toluene. A separate vial was then charged with pinacol (0.177 g, 1.50 mmol, 3.00 equiv) and Et_3N (1.0 mL, 7.5 mmol, 15 equiv). This mixture was added to the reaction mixture dropwise over c.a. 2 min to this vial, and the resulting mixture stirred for 1 h at room temperature. The solution was concentrated in vacuo and the resulting residue was purified by column chromatography using an elution gradient from 100% hexanes to 20% EtOAc/hexanes. Product-containing fractions were combined and concentrated in vacuo, and volatiles were removed at c.a. 10 mTorr for 18 h to afford **3m** as a yellow oil that solidified upon standing (0.090 g, 59% yield).

^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.07 (d, *J* = 2.1 Hz, 1H), 7.66 (d, *J* = 9.4 Hz, 1H), 7.56 (d, *J* = 5.0 Hz, 1H), 7.28 (dd, *J* = 5.1, 3.0 Hz, 1H), 6.20 (d, *J* = 9.4 Hz, 1H), 1.29 (s, 12H).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 164.1, 161.7, 149.6, 134.6, 129.6, 128.1, 125.1, 112.6, 84.6, 24.8.

^{11}B NMR ($CDCl_3$, 193 MHz): δ 30.3.

HRMS (ESI+): Calculated for $C_{15}H_{17}BO_4SNa$ ($[M+Na]^+$), 327.0841; found 327.0834.



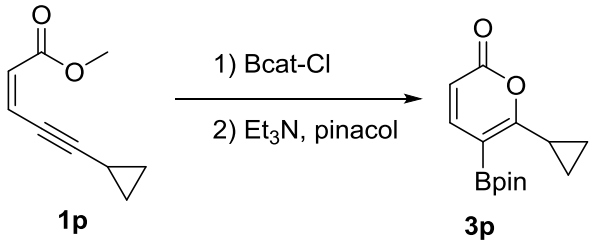
6-phenyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2H-pyran-2-one (3n). A vial was charged with **1n** (0.070 g, 0.35 mmol, 1.0 equiv) and 0.4 mL of toluene. A separate vial equipped with a stir bar was charged with *B*-chlorocatecholborane (0.075 g, 0.49 mmol, 1.4 equiv). The resulting homogenous solution from the first vial was then added dropwise over c.a. 2 min to the boron-containing vial, which stirred for 24 h at 100 °C. At this time, the reaction mixture was cooled to room temperature and then diluted with 0.4 mL toluene. A separate vial was then charged with pinacol (0.124 g, 1.05 mmol, 3.00 equiv) and Et_3N (0.70 mL, 5.3 mmol, 15 equiv). This mixture was added to the reaction mixture dropwise over c.a. 2 min to this vial, and the resulting mixture stirred for 1 h at room temperature. The solution was concentrated in vacuo and the resulting residue was purified by column chromatography using an elution gradient from 100% hexanes to 25% EtOAc/hexanes. Product-containing fractions were combined and concentrated in vacuo, and volatiles were removed at c.a. 10 mTorr for 18 h to afford **3n** as a yellow crystalline solid (0.049 g, 47% yield).

^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.65–7.63 (m, 3H), 7.47 (app t, *J* = 7.4 Hz, 1H), 7.39 (app t, *J* = 7.7 Hz, 2H), 6.27 (d, *J* = 9.3 Hz, 1H), 1.25 (s, 12H).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 169.6, 162.1, 148.9, 133.3, 131.0, 129.5, 127.9, 113.0, 84.5, 24.7.

^{11}B NMR ($CDCl_3$, 193 MHz): δ 30.8.

HRMS (ESI+): Calculated for $C_{17}H_{19}BO_4Na$ ($[M+Na]^+$), 321.1277; found 321.1283.



6-cyclopropyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2H-pyran-2-one (3p). A vial was charged with **1p** (0.100 g, 0.670 mmol, 1.00 equiv) and 0.7 mL toluene. A separate vial equipped with a stir bar was charged with *B*-chlorocatecholborane (0.144 g, 0.930 mmol, 1.40 equiv). The resulting homogenous solution from the first vial was then added dropwise over c.a. 2 min to the boron-containing vial, which stirred for 24 h at 100 °C. At this time, the reaction mixture was cooled to room temperature and then diluted with 0.7 mL toluene. A separate vial was then charged with pinacol (0.237 g, 2.01 mmol, 3.00 equiv) and Et_3N (1.4 mL, 10. mmol, 15 equiv). This mixture was added to the reaction mixture dropwise over c.a. 2 min to this vial, and the resulting mixture stirred for 1 h at room temperature. The solution was concentrated in vacuo

and the resulting residue was purified by column chromatography using an elution gradient from 100% hexanes to 15% EtOAc/hexanes. Product-containing fractions were combined and concentrated in vacuo, and volatiles were removed at c.a. 10 mTorr for 18 h to afford **3p** as a yellow solid (0.098 g, 56% yield).

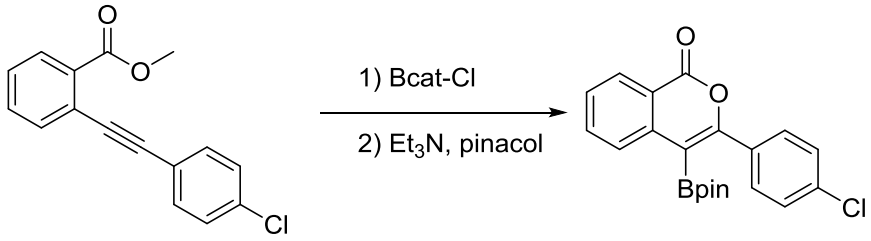
^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.52 (d, *J* = 9.2 Hz, 1H), 6.00 (d, *J* = 9.4 Hz, 1H), 2.73 (m, 1H), 1.28 (s, 12H), 1.21 (m, 2H), 0.99 (m, 2H).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 176.3, 162.1, 149.3, 110.4, 84.1, 24.9, 13.9, 10.2.

^{11}B NMR ($CDCl_3$, 193 MHz): δ 30.9.

HRMS (CI) Calculated for $C_{14}H_{19}BO_4$ ($[M]^+$), 262.1379; found 262.1368.

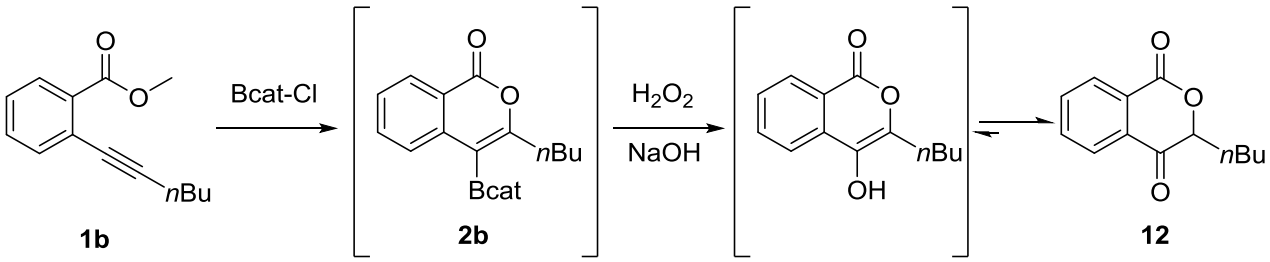
F. Multigram Scale Preparation of 3g



1g **3g**

In a nitrogen-filled glove box, a Schlenk bomb was charged with a solution of **1g** (2.50 g, 9.23 mmol, 1.00 equiv) in 4.6 mL toluene via pipette. A solution of *B*-chlorocatecholborane (1.99 g, 12.9 mmol, 1.40 equiv) in 4.6 mL toluene was then added via pipette. The Schlenk bomb was then sealed, brought outside of the glove box, and cooled to -78 ^{o}C using an isopropanol/dry ice bath. The headspace in the Schlenk bomb was then removed under reduced pressure (c.a. 10 mTorr for 10 sec) before resealing. The solution was then stirred under static vacuum for 24 h at 100 ^{o}C in an oil bath. At this time, the reaction mixture was cooled to room temperature and returned to the glove box. A solution of pinacol (3.27 g, 27.7 mmol, 3.00 equiv) and Et_3N (19.2 mL, 139 mmol, 15.0 equiv) was then added to the reaction mixture over 5 min and the resulting solution was stirred for 1.5 h at room temperature. The contents of the Schlenk bomb were then filtered over a bed of celite and rinsed with toluene (3 × 20 mL), and the filtrate was concentrated in vacuo. The resulting residue was purified by column chromatography using an elution gradient from 100% hexanes to 15% EtOAc/hexanes. Product-containing fractions were combined and concentrated in vacuo, and volatiles were removed at c.a. 10 mTorr for 18 h to afford **3g** as an off-white solid (2.5 g, 71% yield). Spectral data were identical to those previously obtained for this compound (see page S20).

G. Synthesis of 12



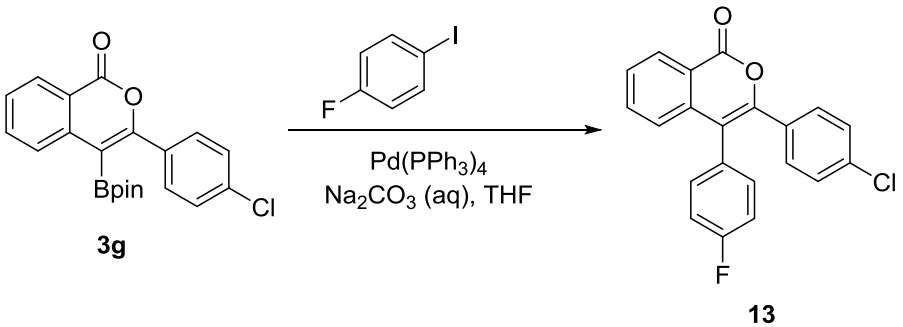
3-butylisochromane-1,4-dione (4). The initial oxyboration step was performed in a N_2-filled glove box. A vial was charged with **1b** (0.108 g, 0.500 mmol, 1.00 equiv) and 0.5 mL toluene. A separate vial equipped with a stir bar was charged with *B*-chlorocatecholborane (0.108 g, 0.700 mmol, 1.40 equiv). The resulting homogenous solution from the first vial was then added dropwise over c.a. 2 min to the boron-containing vial, which stirred for 24 h at 100 ^{o}C. The reaction mixture was then cooled to room temperature and taken out of the glovebox before 1 mL of methanol, NaOH (0.30 mL of a 3.0 M solution, 0.80 mmol, 1.6 equiv) and H_2O_2 (82 μL of a 30 wt% solution, 0.80 mmol, 1.6 equiv) were added. The reaction mixture was stirred for 2 h, then diluted with 100 mL EtOAc and washed with NH_4Cl (1 × 20 mL), water (1 × 20 mL), brine (1 × 20 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by column chromatography using an elution gradient from 100% hexanes to 30% EtOAc/hexanes. Product-containing fractions were combined and concentrated in vacuo, and volatiles were removed at c.a. 10 mTorr for 18 h to afford **12** as a yellow oil. (0.12 g, 56% yield).

^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.27 (m, 1H), 8.06 (dd, *J* = 7.6, 1.0 Hz, 1H), 7.87-7.81 (m, 2H), 5.09 (dd, *J* = 7.5. 4.7 Hz, 1H), 2.06-1.99 (m, 2H), 1.49-1.44 (m, 2H), 1.39-1.30 (m, 2H), 0.89 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 192.7, 162.0, 135.7, 134.7, 131.6, 130.7, 128.3, 126.0, 84.6, 33.8, 26.7, 22.4, 13.9.

HRMS (ESI+): Calculated for $C_{13}H_{18}NO_3$ ($[M+NH_4]^+$), 236.1287; found 236.1281.

H. Suzuki Cross-Coupling of 3g to Generate 13



3-(4-chlorophenyl)-4-(4-fluorophenyl)-1H-isochromen-1-one (13). This procedure was performed in a N_2-filled glove box. A 20 mL vial was charged with $Pd(PPh_3)_4$ (21 mg, 0.020 mmol, 0.030 equiv), THF (4.0 mL), 4-fluoroiodobenzene (69 μL, 0.60 mmol, 1.0 equiv), **3g** (0.229 g, 0.599 mmol, 2.00 equiv), sodium carbonate (1.2 mL of a 2.0 M aqueous solution, 2.3

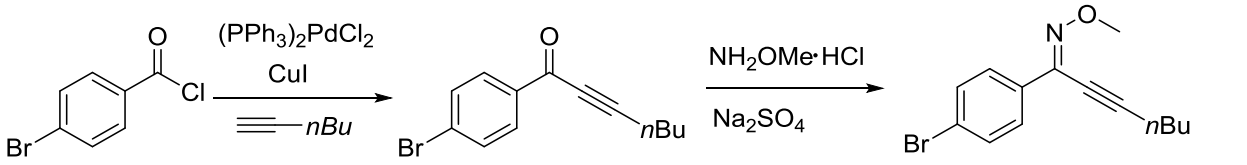
mmol), and a stir bar. The vial was then quickly sealed and brought out of the glove box. The vial was then heated to 75 °C for 17 h. At this time, TLC (80:20 hex:EtOAc) indicated complete consumption of starting material. The reaction mixture was cooled to room temperature, then diluted with 100 mL EtOAc and washed with water (2 × 20 mL), brine (1 × 20 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by column chromatography using an elution gradient from 100% hexanes to 20% EtOAc/hexanes. Product-containing fractions were combined and concentrated in vacuo, and volatiles were removed at c.a. 10 mTorr for 18 h to afford **13** as a yellow solid (0.12 g, 58% yield).

^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.43 (d, *J* = 7.8 Hz, 1H), 7.70 (t, *J* = 7.6 Hz, 1H), 7.58 (t, *J* = 7.5 Hz, 1H), 7.29-7.16 (m, 9H).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 163.7, 162.0, 161.8, 150.2, 138.6, 135.3, 135.0, 133.0, 132.97, 130.6, 129.9, 128.6, 128.4, 125.3, 120.6, 116.7, 116.5.

HRMS (ESI+): Calculated for $C_{21}H_{12}ClFO_2Na$ ($[M+Na]^+$), 373.0407; found 373.0414.

I. Synthesis of Borylated Isoxazole Product 15



SI-21 **SI-22** **14**

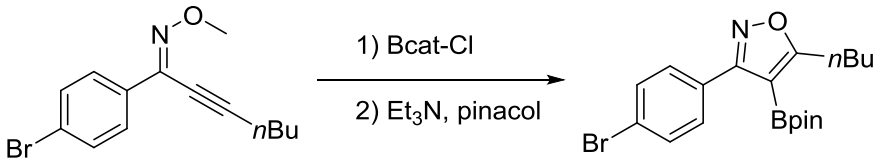
1-(4-bromophenyl)hept-2-yn-1-one (SI-22) was prepared according to a literature procedure[16] in 86% yield. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.99 (d, *J* = 8.5 Hz, 2H), 7.62 (d, *J* = 8.5 Hz, 2H), 2.50 (t, *J* = 7.1 Hz, 2H), 1.66 (quin, *J* = 7.3 Hz, 2H), 1.50 (sxt, *J* = 7.4 Hz, 2H), 0.97 (t, *J* = 7.3 Hz, 3H). This spectrum is in agreement with previously reported spectral data.[17]

(Z)-1-(4-bromophenyl)hept-2-yn-1-one *O*-methyl oxime (14) was prepared according to a modified literature procedure.[18] A round-bottom flask was charged with $H_2NOMe·HCl$ (0.38 g, 4.5 mmol, 2.0 equiv), Na_2SO_4 (0.64 g, 4.5 mmol, 2.0 equiv), and a stir bar. The solids were suspended in 8 mL of MeOH. Pyridine (0.68 mL, 8.4 mmol, 3.7 equiv) and then ketone **SI-23** (0.60 g, 2.3 mmol, 1.0 equiv) were consecutively added. The reaction was stirred at 25 °C for 23 h without special precautions for oxygen or moisture. The reaction was then quenched with 30 mL DI water and extracted with EtOAc (3 × 60 mL). The combined organic layers were washed with brine (30 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by column chromatography using an elution gradient from 100% hexanes to 40% DCM/hexanes. Product-containing fractions were combined and concentrated in vacuo to afford **14** as light yellow oil (0.27 g, 41% isolated yield).

^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.70 (d, *J* = 8.5 Hz, 2H), 7.49 (d, *J* = 8.5 Hz, 2H), 4.07 (s, 3H), 2.54 (t, *J* = 7.2 Hz, 2H), 1.65 (quin, *J* = 7.3 Hz, 2H), 1.51-1.47 (m, 2H), 0.96 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 139.4, 133.0, 131.6, 128.1, 123.9, 104.6, 71.2, 63.2, 30.5, 22.2, 19.6, 13.7.

HRMS (ESI+): Calculated for $C_{14}H_{17}NBrO$ ($[M+H]^+$), 294.0493; found 294.0493.



14 **15**

3-(4-bromophenyl)-5-butyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)isoxazole (15). A vial was charged with **14** (0.147 g, 0.500 mmol, 1.00 equiv) and 0.5 mL d_8-toluene [Note: the deuterated toluene was used to monitor this unoptimized reaction by ^{1}H and ^{11}B NMR spectroscopy]. A separate vial was charged with *B*-chlorocatecholborane (0.108 g, 0.700 mmol, 1.40 equiv). The resulting homogenous solution from the first vial was then added dropwise over c.a. 2 min to the boron-containing vial, which was then transferred to a J-Young tube via pipette. The tube was then heated to 100 ^{o}C for 48 h, and subsequently to 110 ^{o}C for 48 h. A separate vial was then charged with pinacol (0.177 g, 1.50 mmol, 3.00 equiv) and Et_3N (1.0 mL, 7.5 mmol, 15 equiv). The reaction mixture was added dropwise over c.a. 2 min to this vial, and the resulting mixture stirred for 1 h at room temperature. The solution was concentrated in vacuo and purified by column chromatography using an elution gradient from 100% hexanes to 40% DCM/hexanes. Product-containing fractions were combined and concentrated in vacuo, and volatiles were removed at c.a. 10 mTorr for 18 h to afford **15** as an off-white solid (0.072 g, 35% yield).

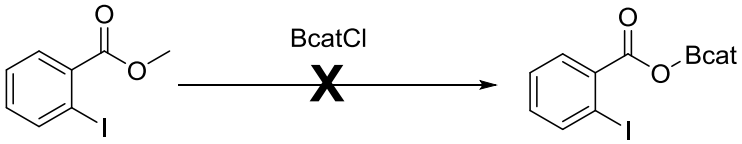
^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.72 (d, *J* = 8.4 Hz, 2H), 7.53 (d, *J* = 8.4 Hz, 2H), 3.01 (t, *J* = 7.6 Hz, 2H), 1.71 (quin, *J* = 7.5 Hz, 2H), 1.41-1.37 (m, 2H), 1.29 (s, 12H), 0.94 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 183.3, 165.2, 131.3, 130.7, 129.2, 123.8, 83.8, 30.6, 27.0, 24.8, 22.3, 13.8.

^{11}B NMR ($CDCl_3$, 193 MHz): δ 29.9.

HRMS (ESI+): Calculated for $C_{19}H_{25}NBBrO_3$ ($[M]^+$), 405.1115; found 405.1107.

J. Procedure for ^{1}H NMR observation of the rate of demethylation of methyl 2-iodobenzoate 10



10 **11**

This procedure was performed in a N_2-filled glove box. A 4 mL vial was charged with *B*-chlorocatecholborane (0.108 g, 0.700 mmol, 1.40 equiv) and 0.5 mL of d_8-toluene. To this vial was sequentially added **10** (75 μL, 0.50 mmol, 1.0 equiv) and 1,3,5-triisopropylbenzene (40. μL, 0.17 mmol, 0.33 equiv) via syringe. The contents of this vial were then transferred to a J-young tube, which was sealed, and then removed from the glove box. Single scan ^{1}H and ^{11}B NMR spectra were taken at time points *t* = 0 h, 18 h, and 24 h. The resonances corresponding to **10**

were compared to the internal standard to determine the percent of **10** remaining at t = 24 h (>95% **10** remaining at 24 h).

III. References

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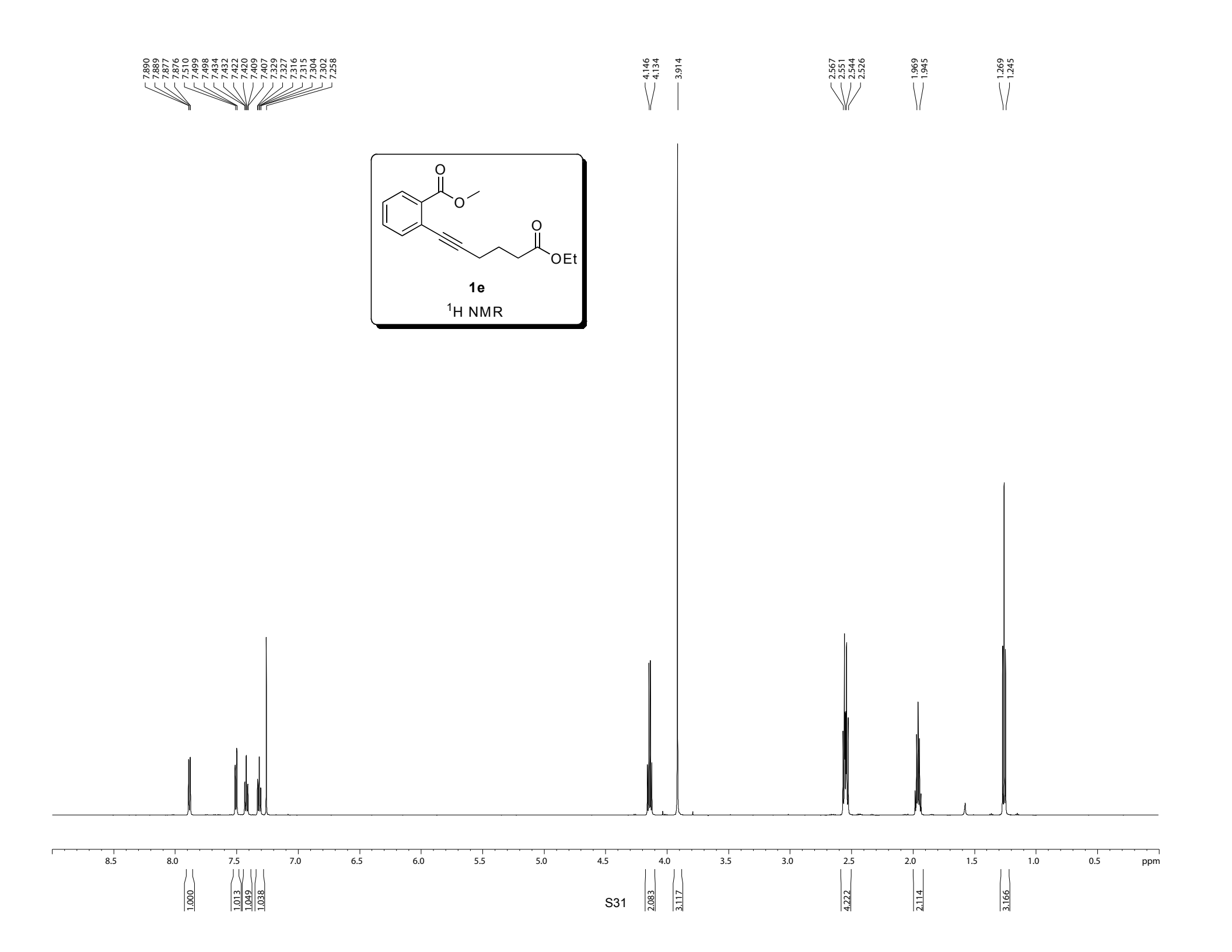
IV. NMR Spectra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7.889
7.877
7.876
7.510
7.499
7.498
7.434
7.432
7.422
7.420
7.409
7.407
7.329
7.327
7.316
7.315
7.304
7.302
7.258
4.146
4.134
3.914
2.567
2.551
2.544
2.526
1.969
1.945
1.269
1.245
O
O
O
OEt
1e
1H NMR
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
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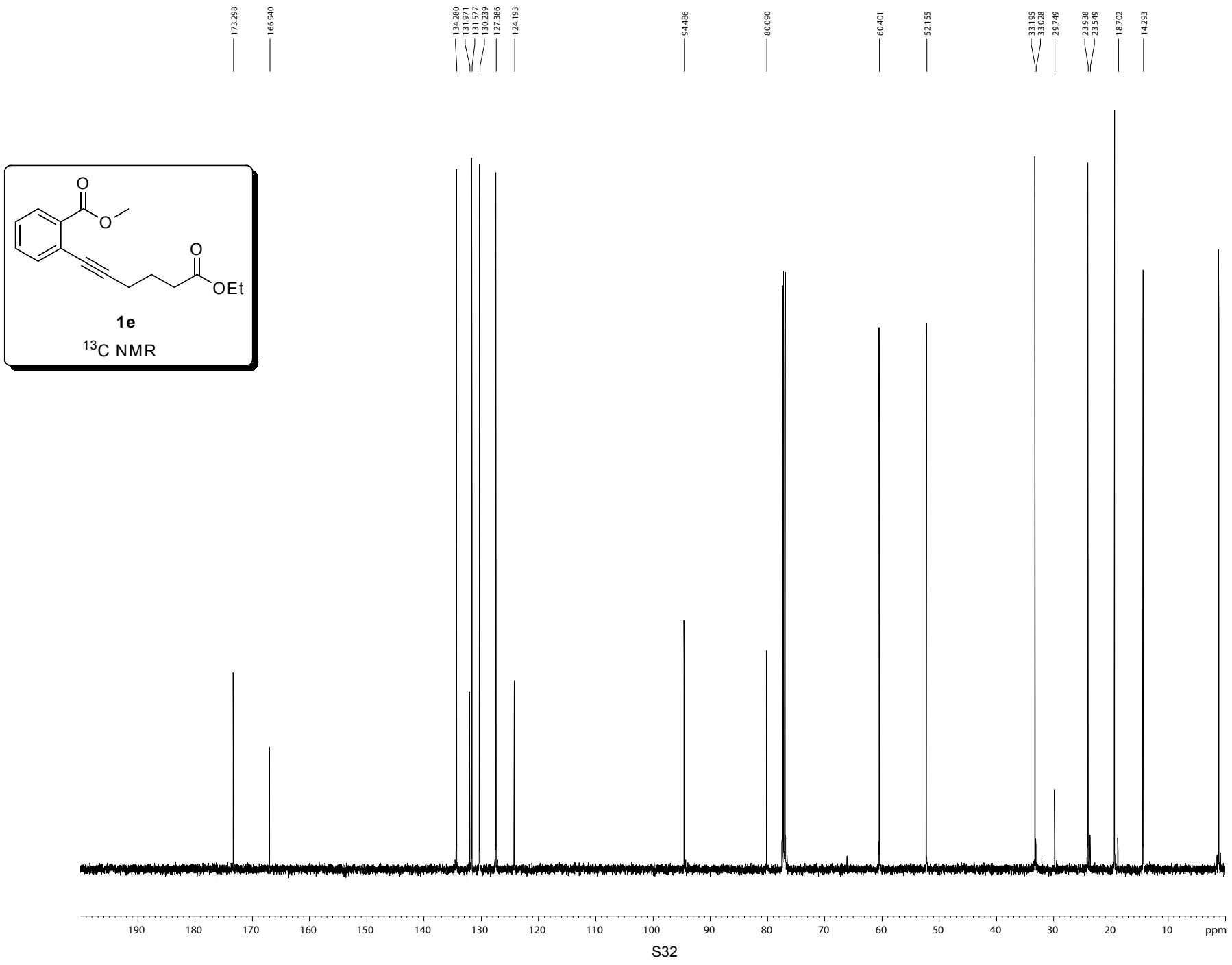
1.013
1.049
1.038
2.083
3.117
4.222
2.114
3.166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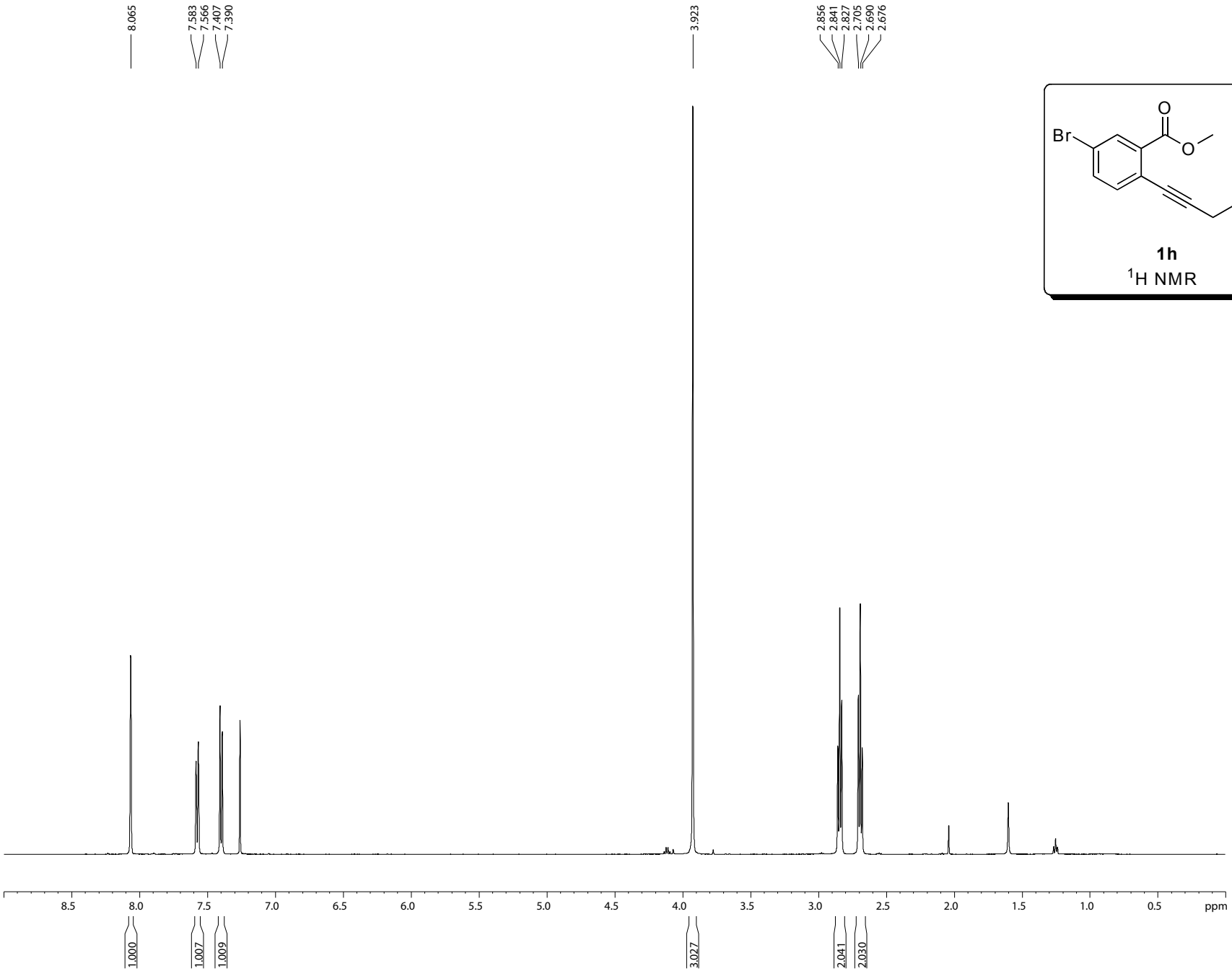
134.280
131.971
131.577
130.239
127.386
124.193
94.486
80.090
60.401
52.155
33.195
33.028
29.749
23.938
23.549
18.702
14.293
O
O
O
OEt
1e
13C NMR
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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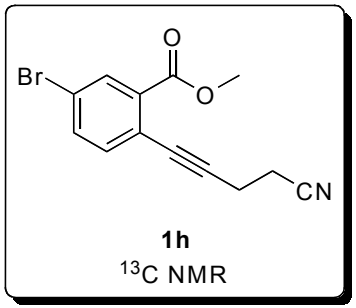
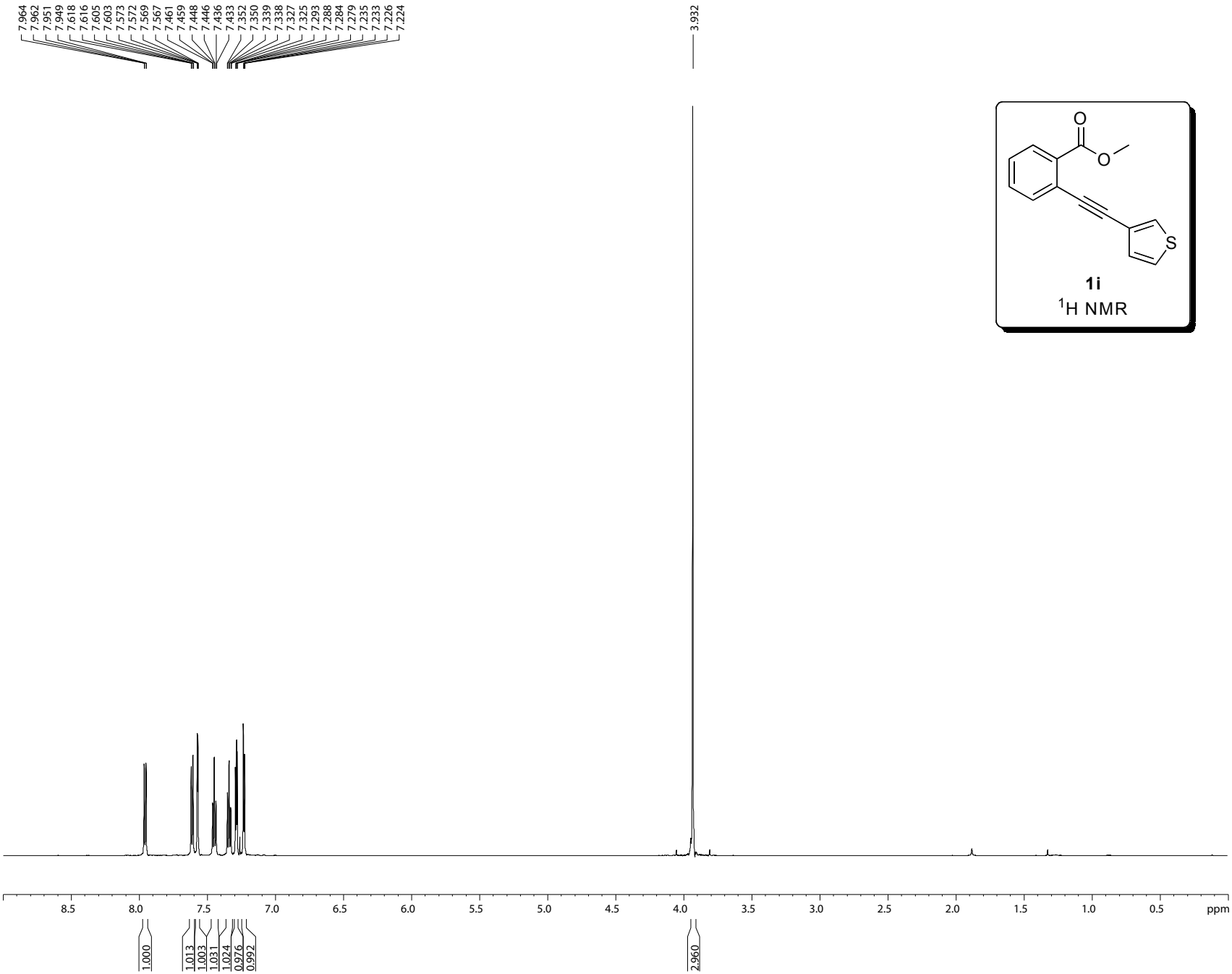
7.583
7.566
7.407
7.390
3.923
2.856
2.841
2.827
2.705
2.690
2.676
Br
O
O
CN
1h
1H NMR
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.000
1.007
1.009
3.027
2.041
2.030


O
Br
O
CN

1h

^{13}C NMR

165.200
135.710
134.858
133.383
122.257
122.028
118.278
91.694
81.009
52.561
17.463
17.175
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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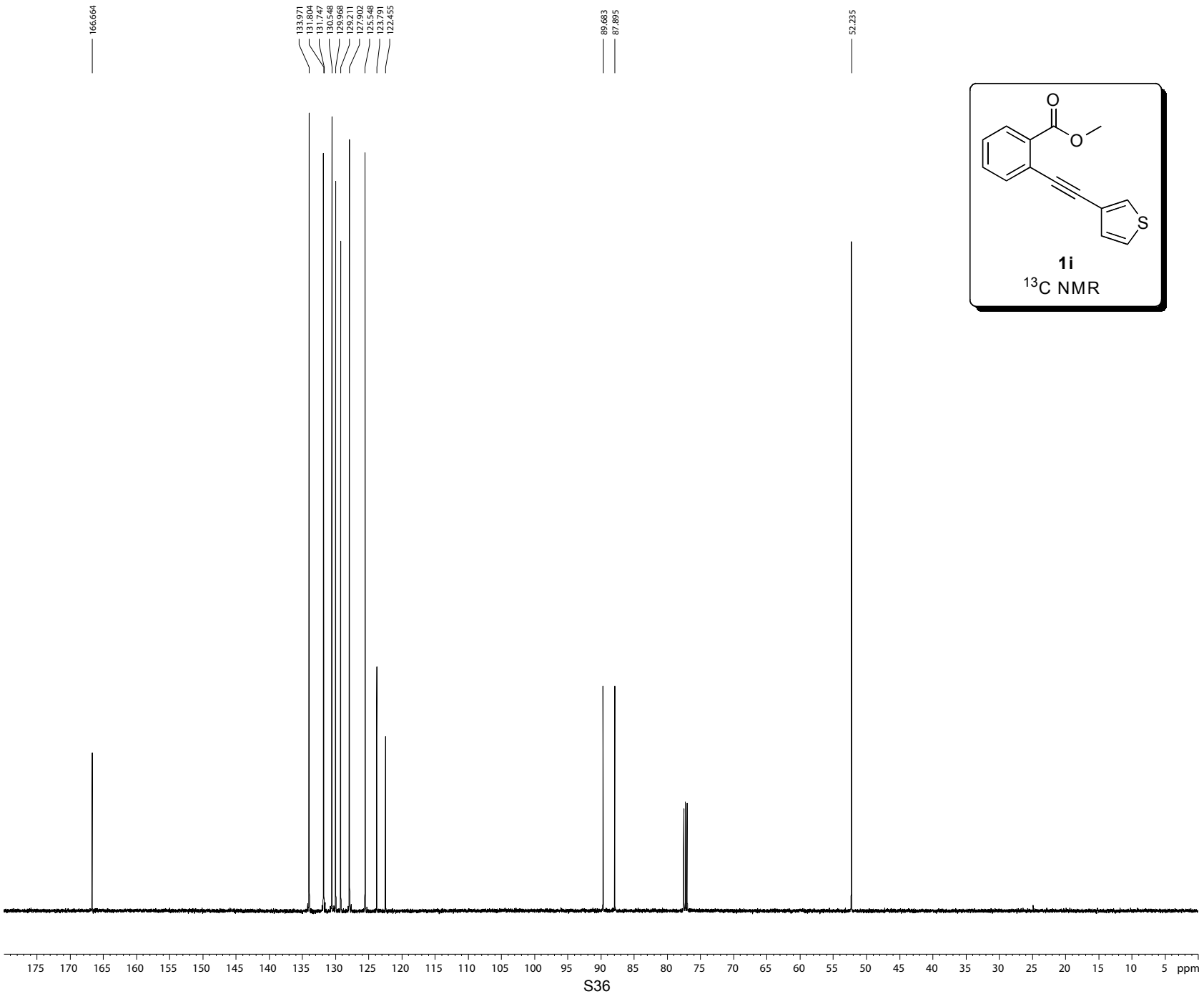
7.962
7.951
7.949
7.618
7.616
7.605
7.603
7.573
7.572
7.569
7.567
7.461
7.459
7.448
7.446
7.436
7.433
7.352
7.350
7.339
7.338
7.327
7.325
7.293
7.288
7.284
7.279
7.235
7.233
7.226
7.224
3.932
O
O
S
1i
1H NMR
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.000
1.013
1.003
1.031
1.024
0.976
0.992
2.960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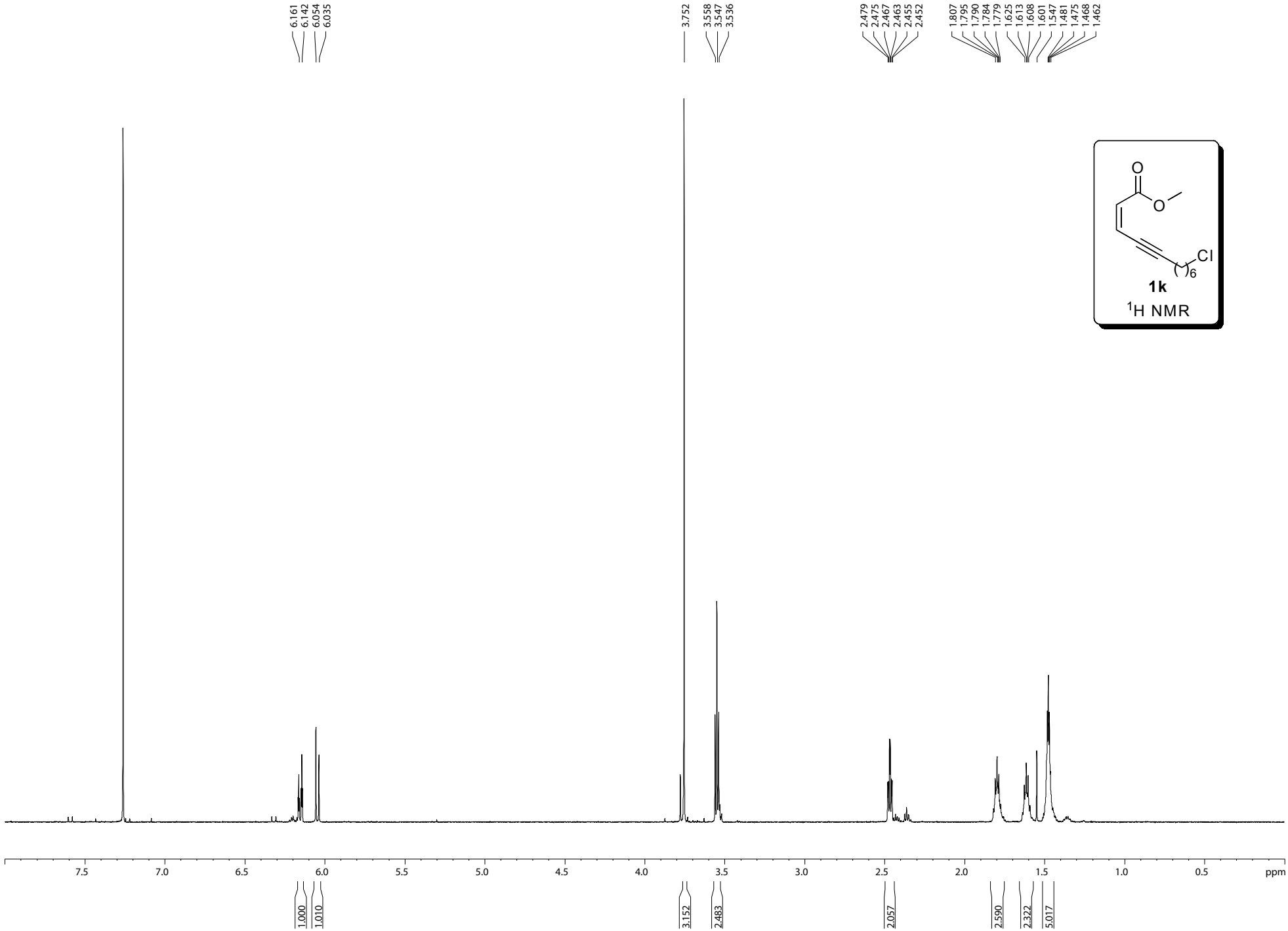
133.971
131.804
131.747
130.548
129.968
129.211
127.902
125.548
123.791
122.455
89.683
87.895
52.235
O
O
S
1i
13C NMR
175 170 165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 ppm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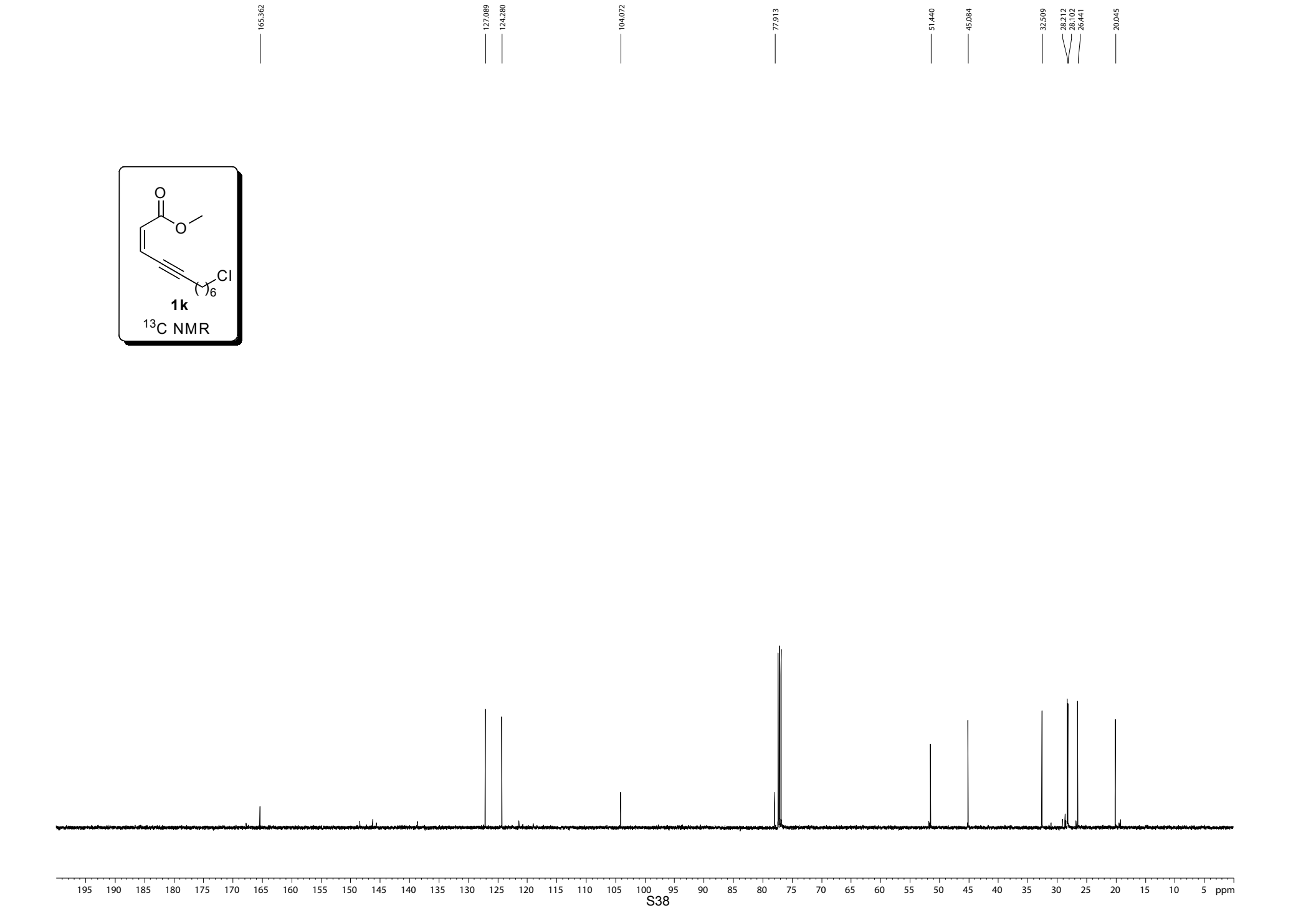
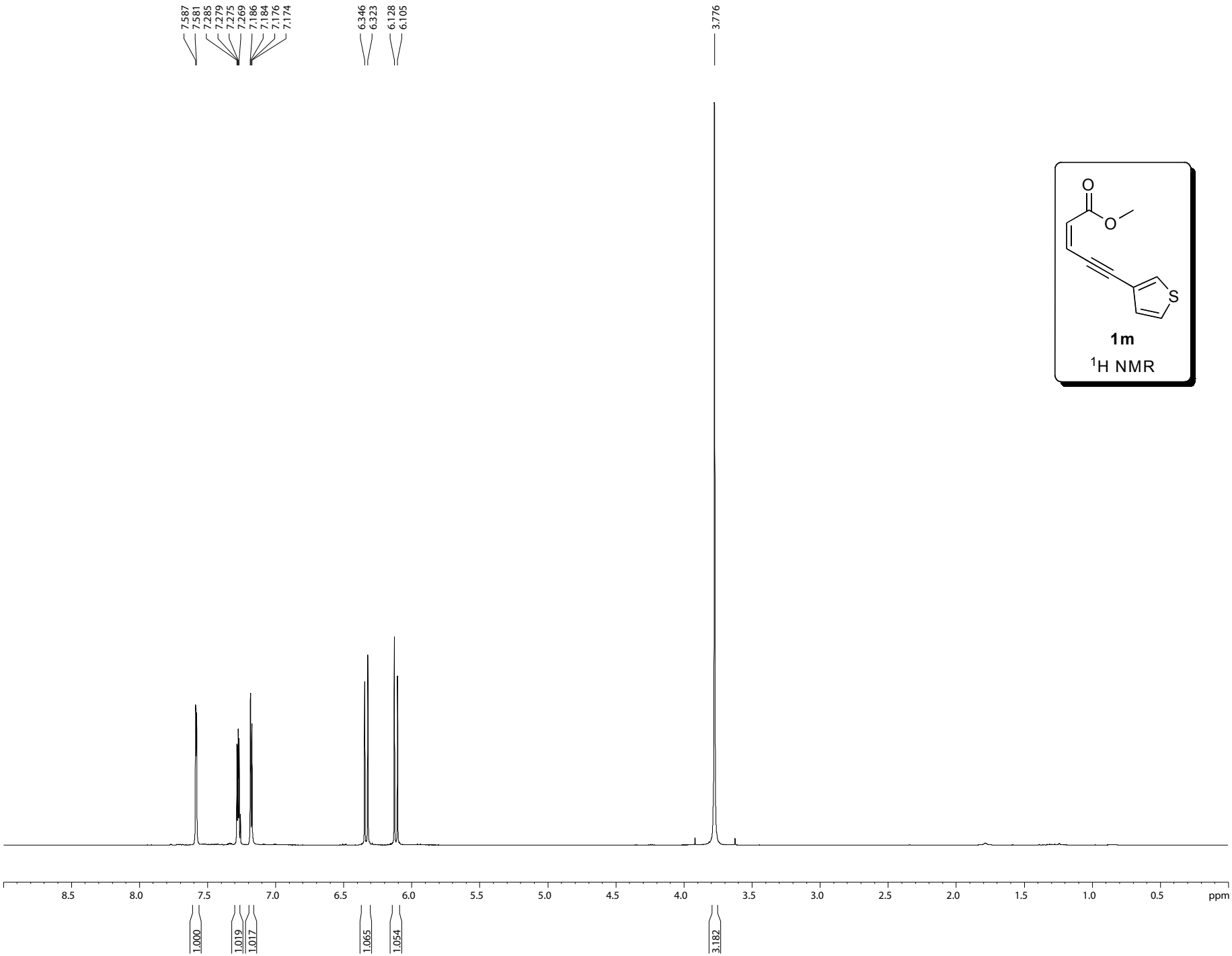
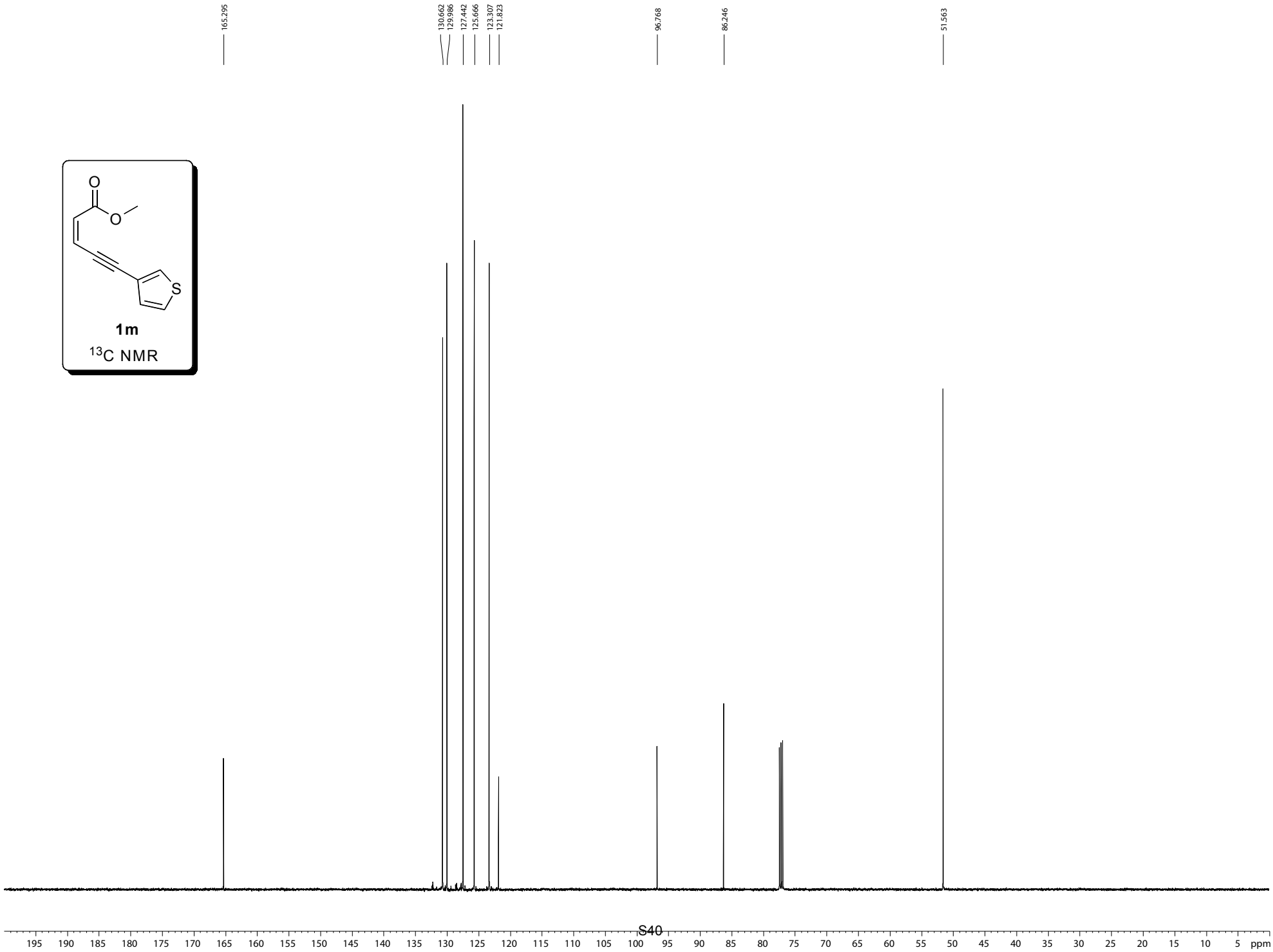
6.142
6.054
6.035
3.752
3.558
3.547
3.536
2.479
2.475
2.467
2.463
2.455
2.452
1.807
1.795
1.790
1.784
1.779
1.625
1.613
1.608
1.601
1.547
1.481
1.475
1.468
1.462
O
O
Cl
6
1k
1H NMR
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.000
1.010
3.152
2.483
2.057
2.590
2.322
5.017


165.362
127.089
124.280
104.072
77.913
51.440
45.084
32.509
28.212
28.102
26.441
20.045
O
O
Cl
6
1k
13C NMR
195 190 185 180 175 170 165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 ppm


7.587
7.581
7.285
7.279
7.275
7.269
7.186
7.184
7.176
7.174
6.346
6.323
6.128
6.105
3.776
O
O
S
1m
1H NMR
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.000
1.019
1.017
1.065
1.054
3.182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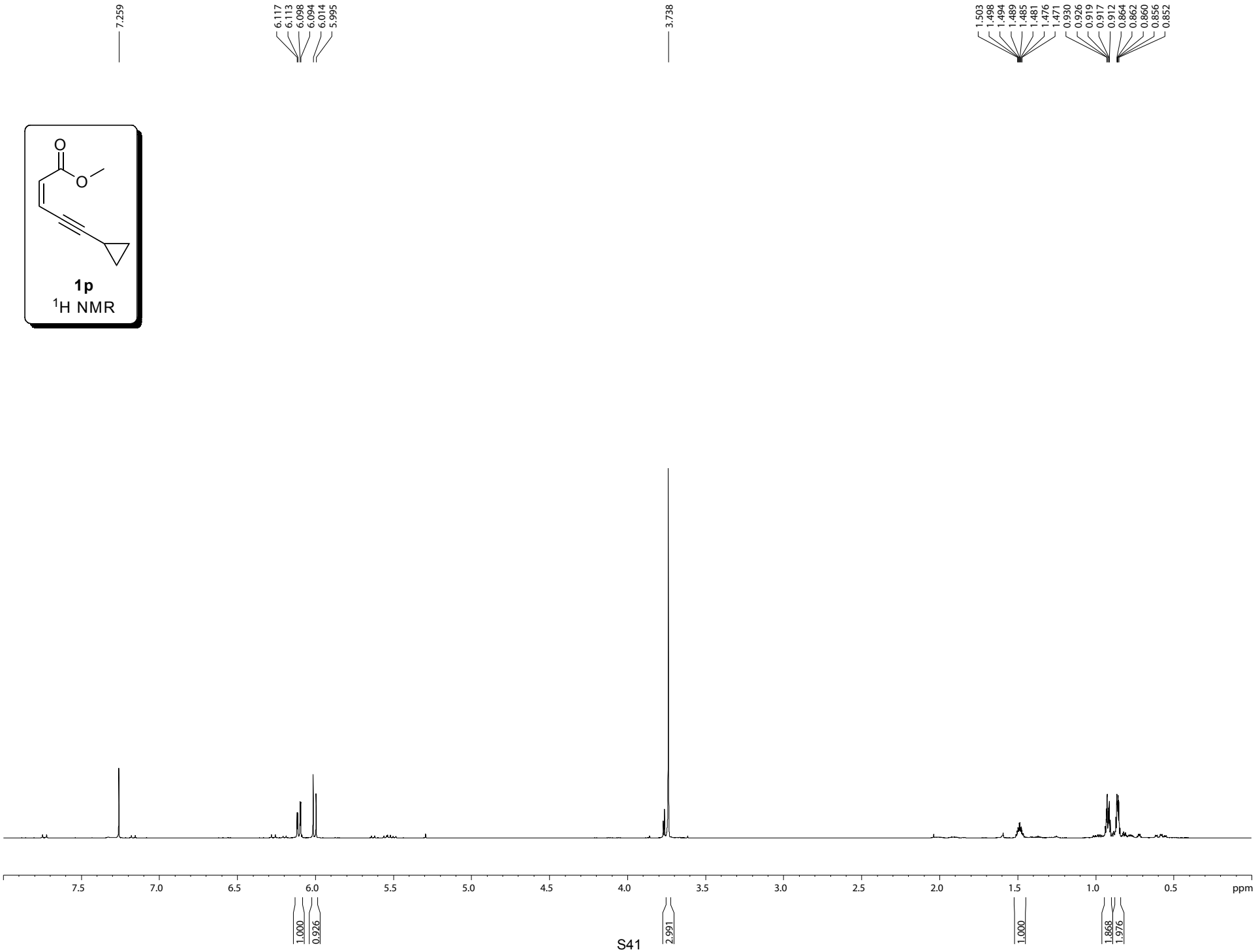
130.662
129.986
127.442
125.666
123.307
121.823
96.768
86.246
51.563
O
O
S
1m
13C NMR
195 190 185 180 175 170 165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 ppm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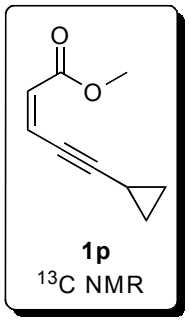
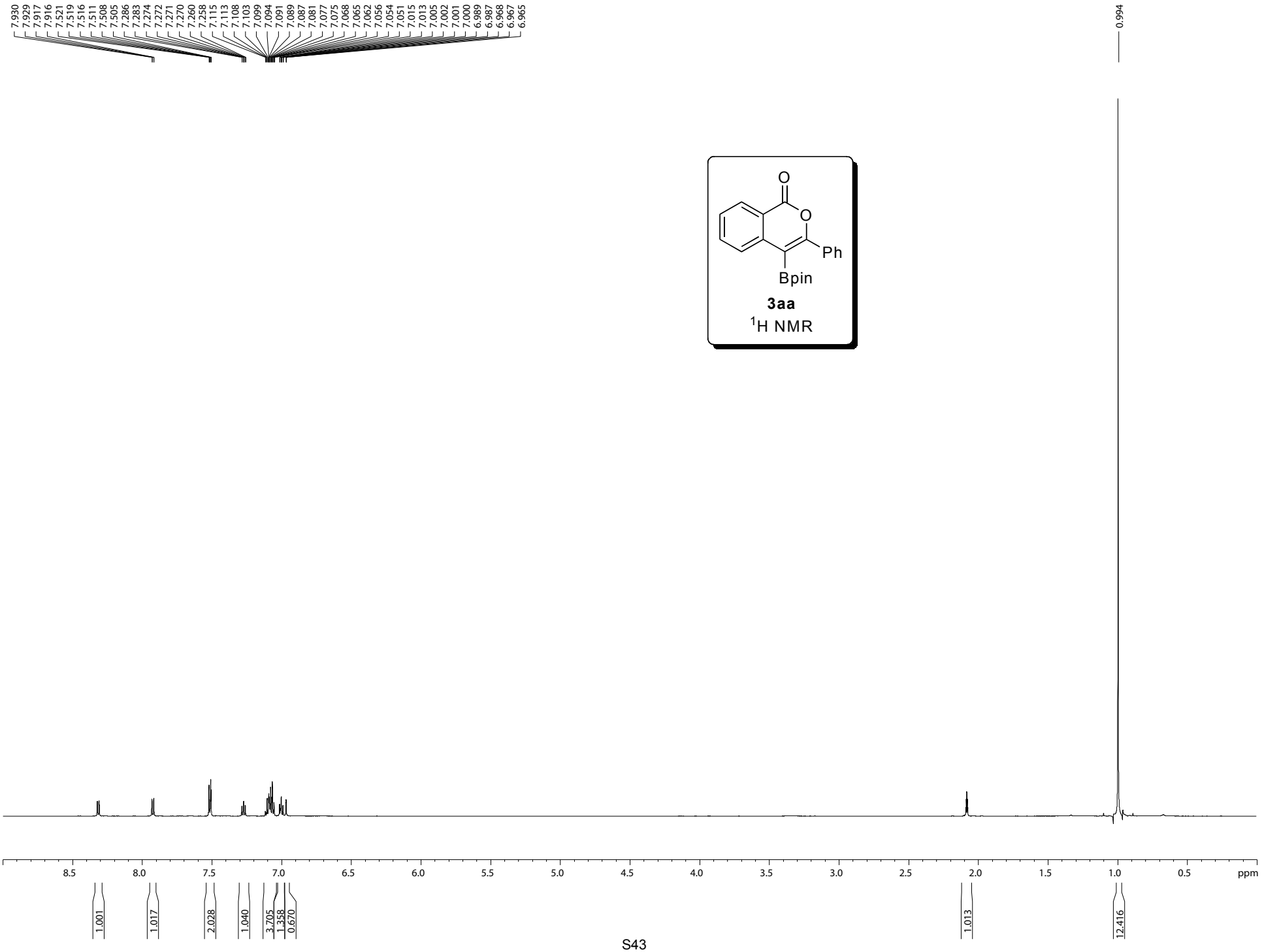
6.117
6.113
6.098
6.094
6.014
5.995
3.738
1.503
1.498
1.494
1.489
1.485
1.481
1.476
1.471
0.930
0.926
0.919
0.917
0.912
0.864
0.862
0.860
0.856
0.852
O
O
1p
1H NMR
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.000
0.926
2.991
1.000
1.868
1.976


O
O

1p
^{13}C NMR

165.453
126.588
124.383
108.219
73.520
51.375
9.592
0.984
175 170 165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 ppm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7.929
7.917
7.916
7.521
7.519
7.516
7.511
7.508
7.505
7.286
7.283
7.274
7.272
7.271
7.270
7.260
7.258
7.115
7.113
7.108
7.103
7.099
7.094
7.091
7.089
7.087
7.081
7.077
7.075
7.068
7.065
7.062
7.056
7.054
7.051
7.015
7.013
7.005
7.002
7.001
7.000
6.989
6.987
6.968
6.967
6.965
0.994
O
O
Ph
Bpin
3aa
1H NMR
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
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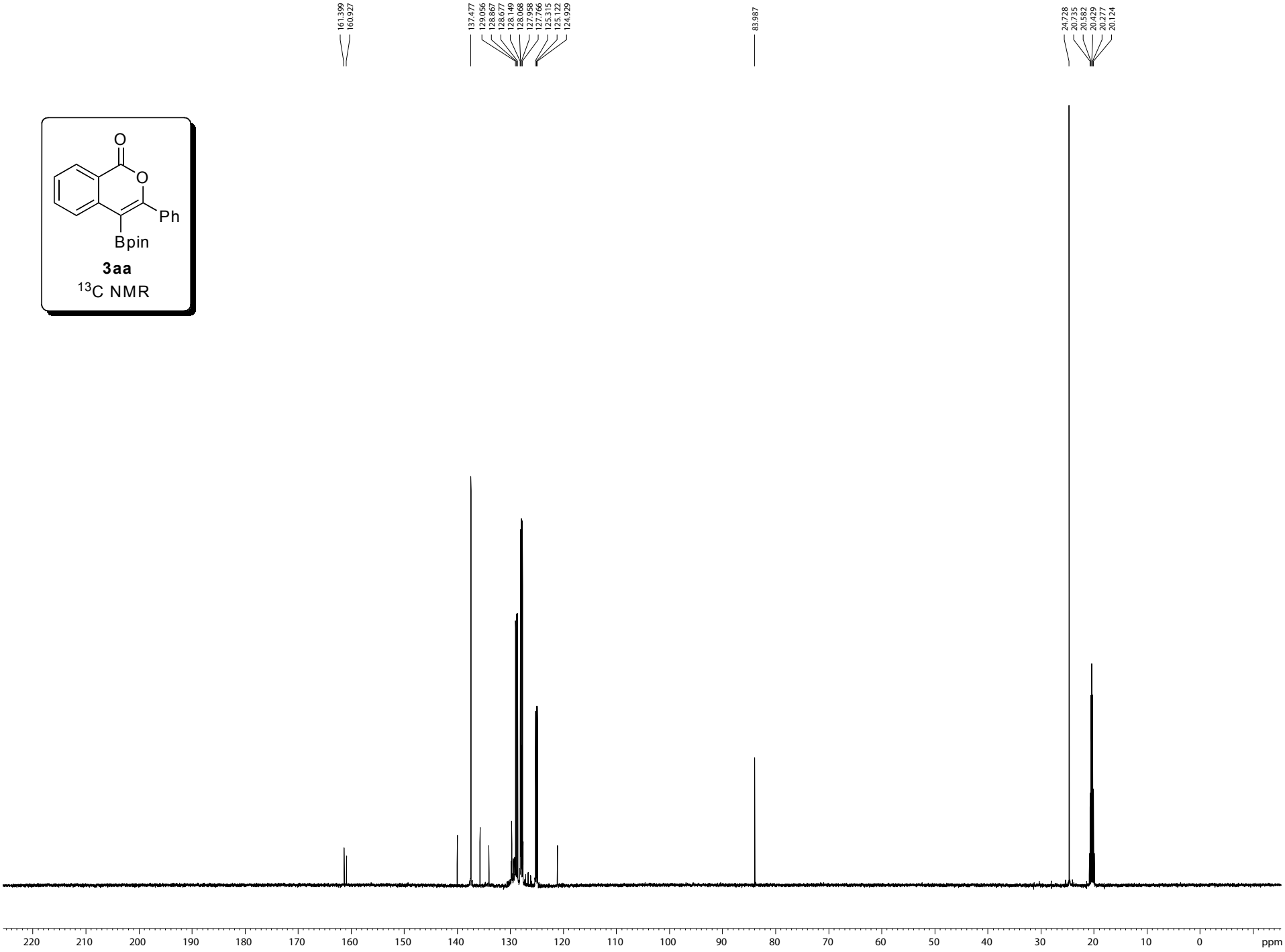
1.017
2.028
1.040
3.705
1.358
0.670
1.013
12.416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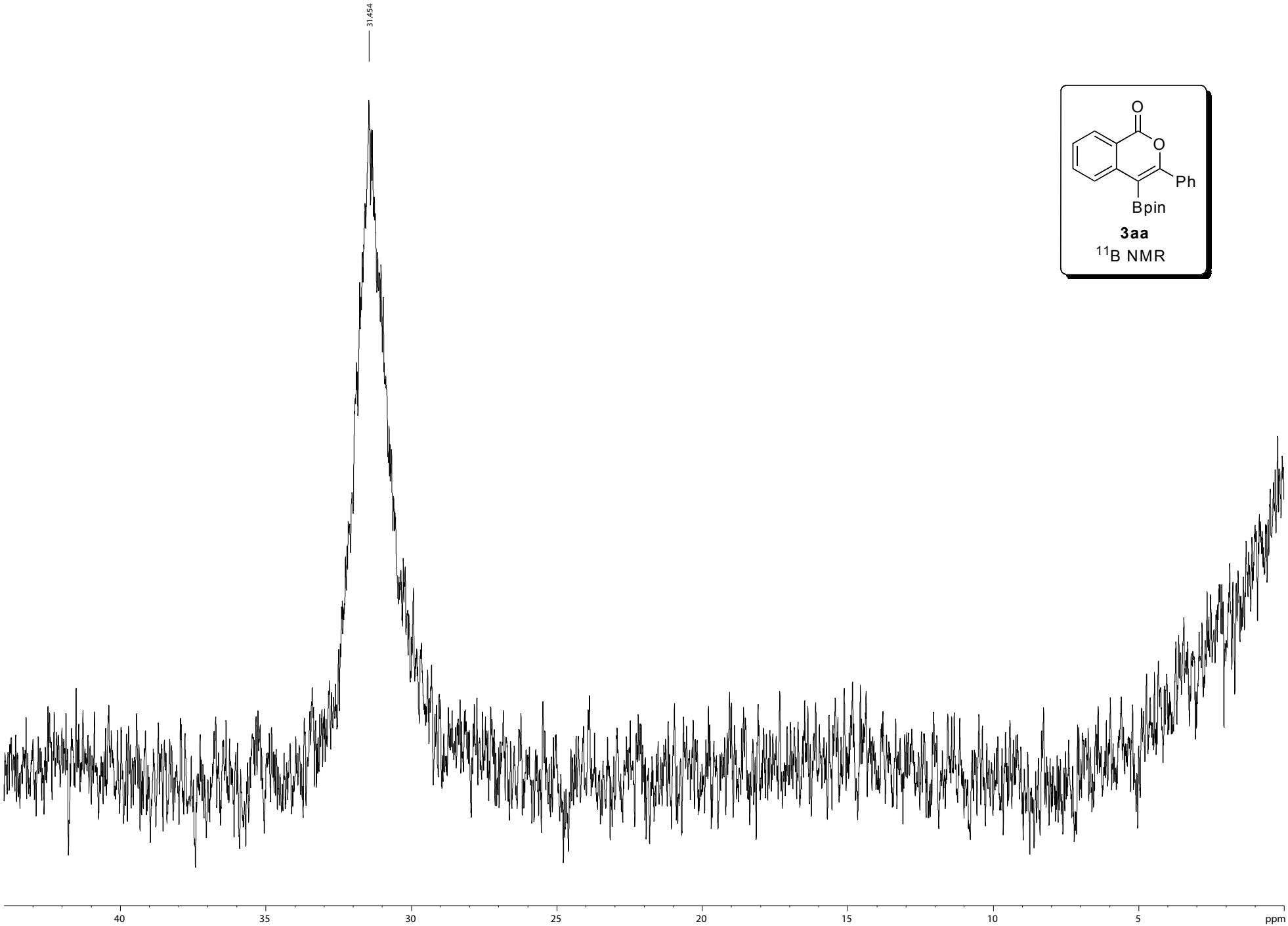
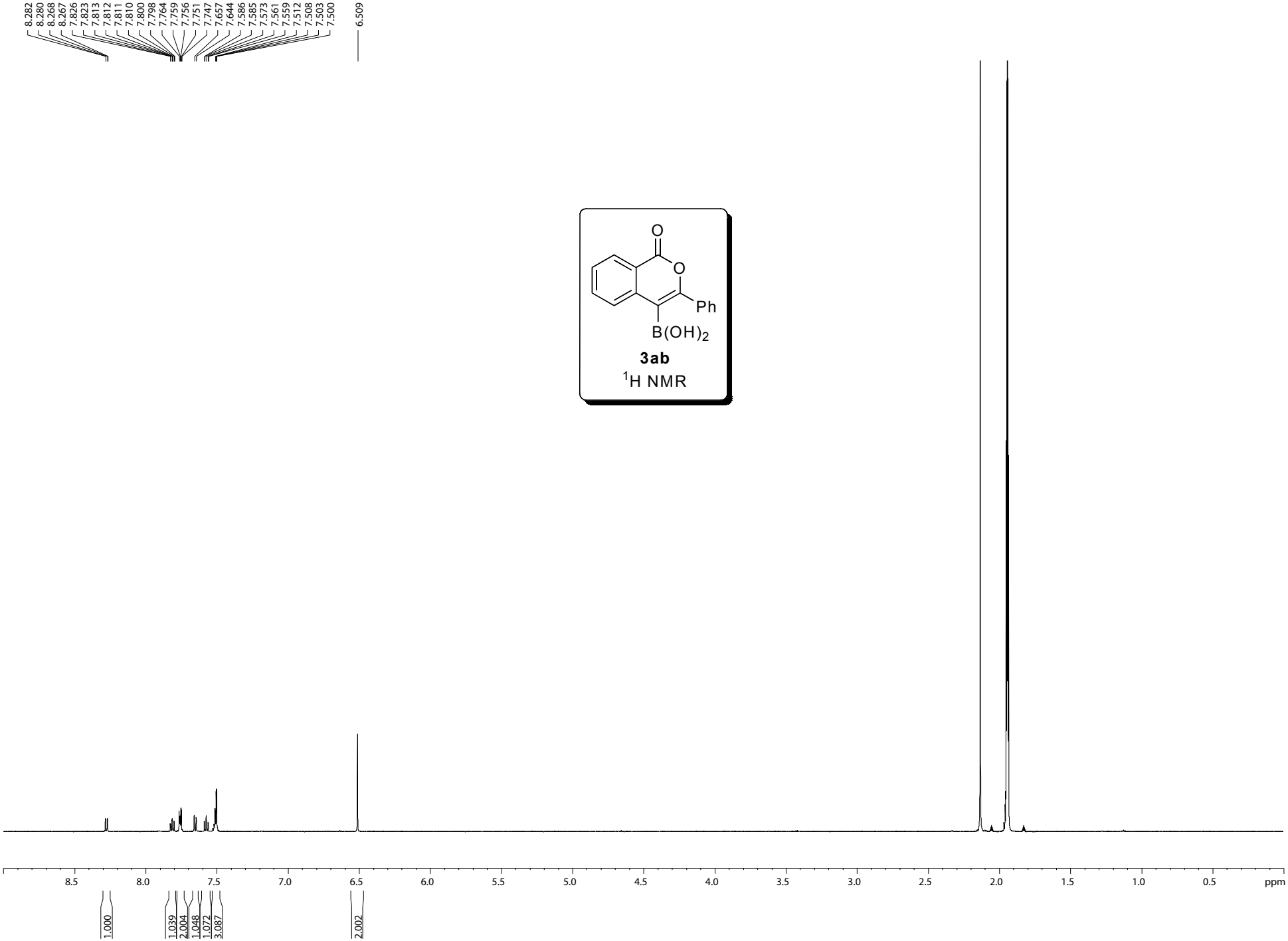
137.477
129.056
128.867
128.677
128.149
128.068
127.958
127.766
125.315
125.122
124.929
83.987
24.728
20.735
20.582
20.429
20.277
20.124
O
O
Ph
Bpin
3aa
13C NMR
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


31.454
O
O
Ph
Bpin
3aa
11B NMR
40
35
30
25
20
15
10
5
ppm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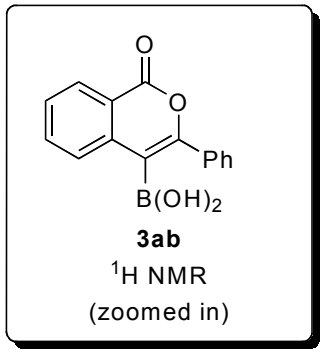
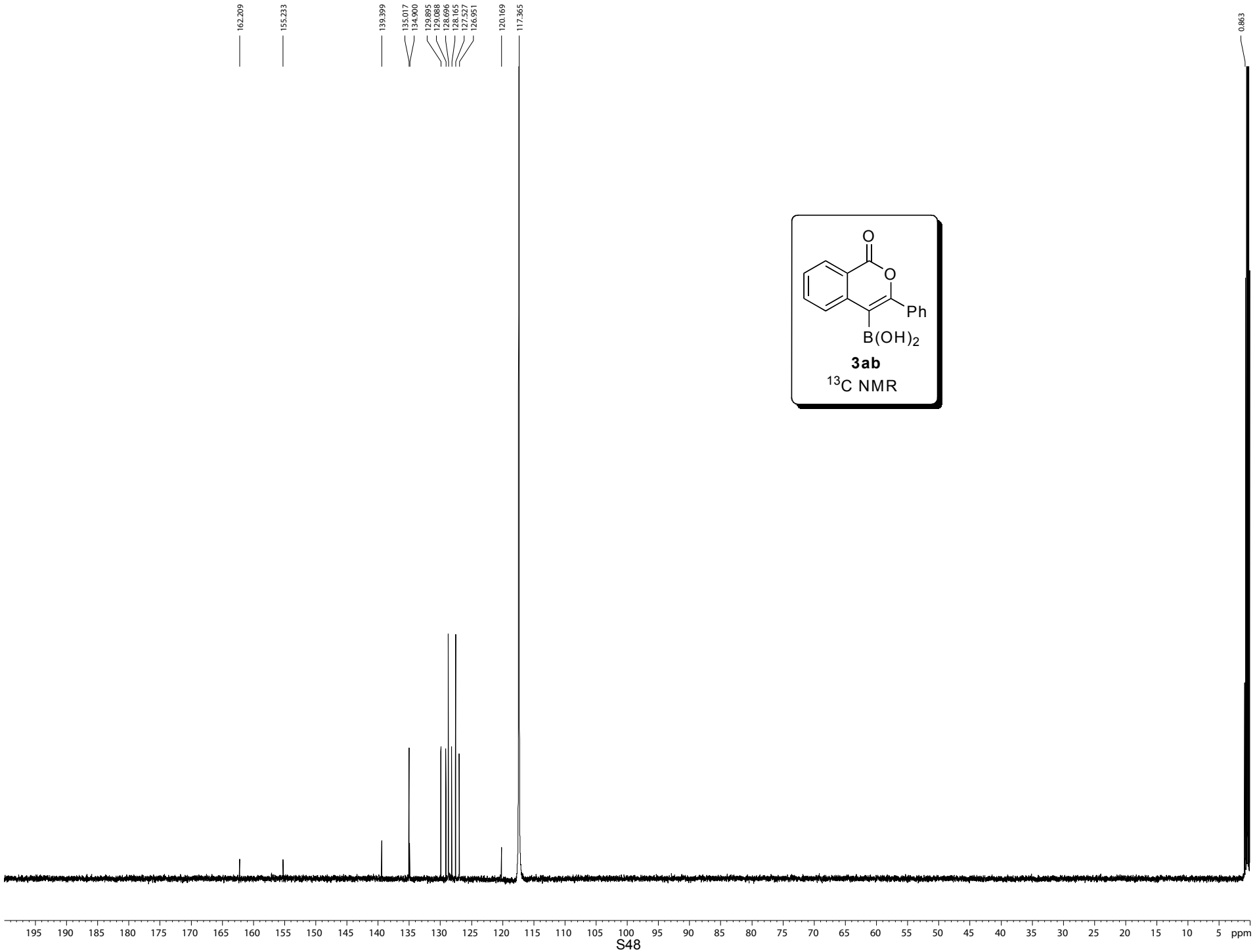
8.280
8.268
8.267
7.826
7.823
7.813
7.812
7.811
7.810
7.800
7.798
7.764
7.759
7.756
7.751
7.747
7.657
7.644
7.586
7.585
7.573
7.561
7.559
7.512
7.508
7.503
7.500
6.509
O
O
Ph
B(OH)2
3ab
1H NMR
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.000
1.039
2.004
1.048
1.072
3.087
2.002

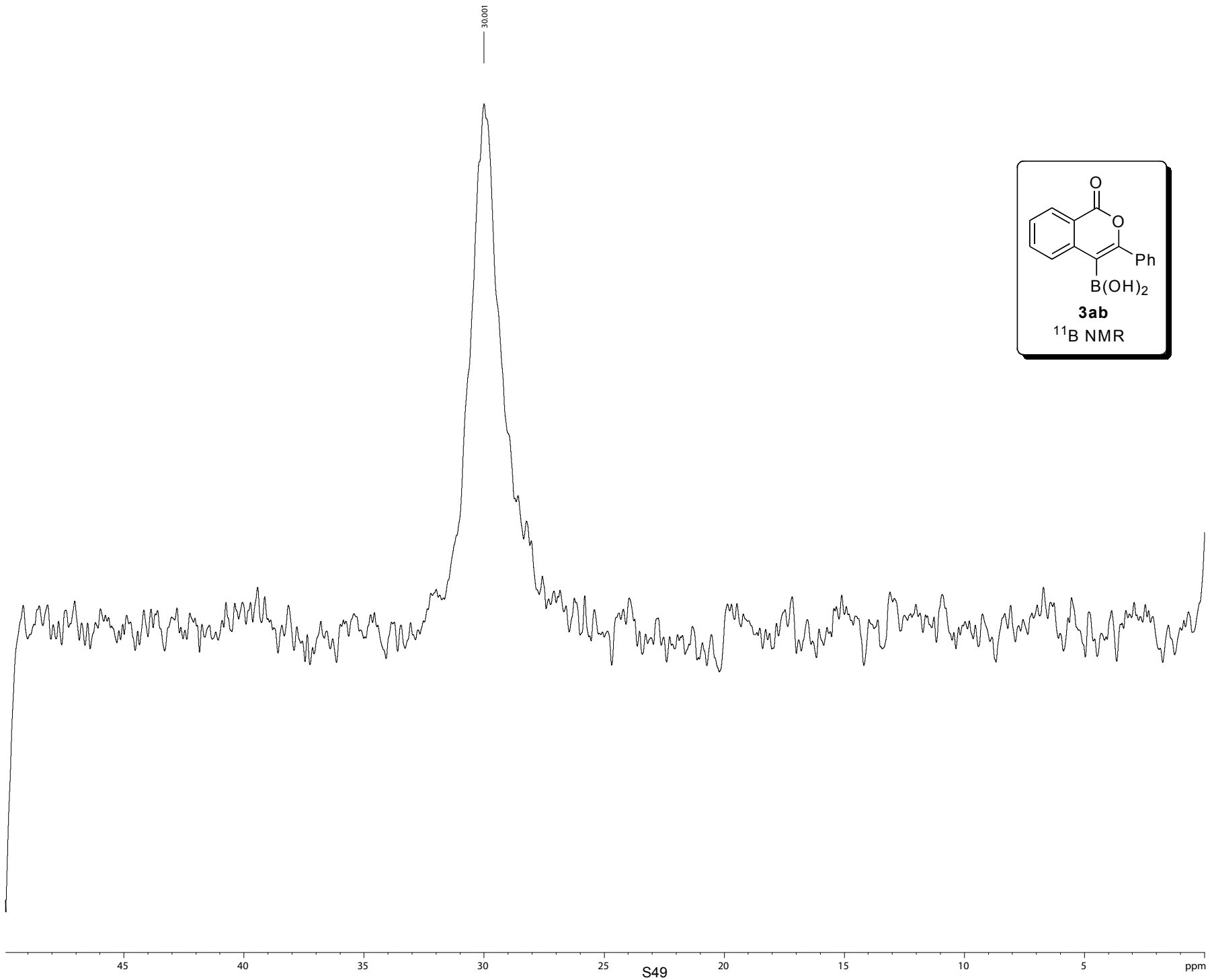


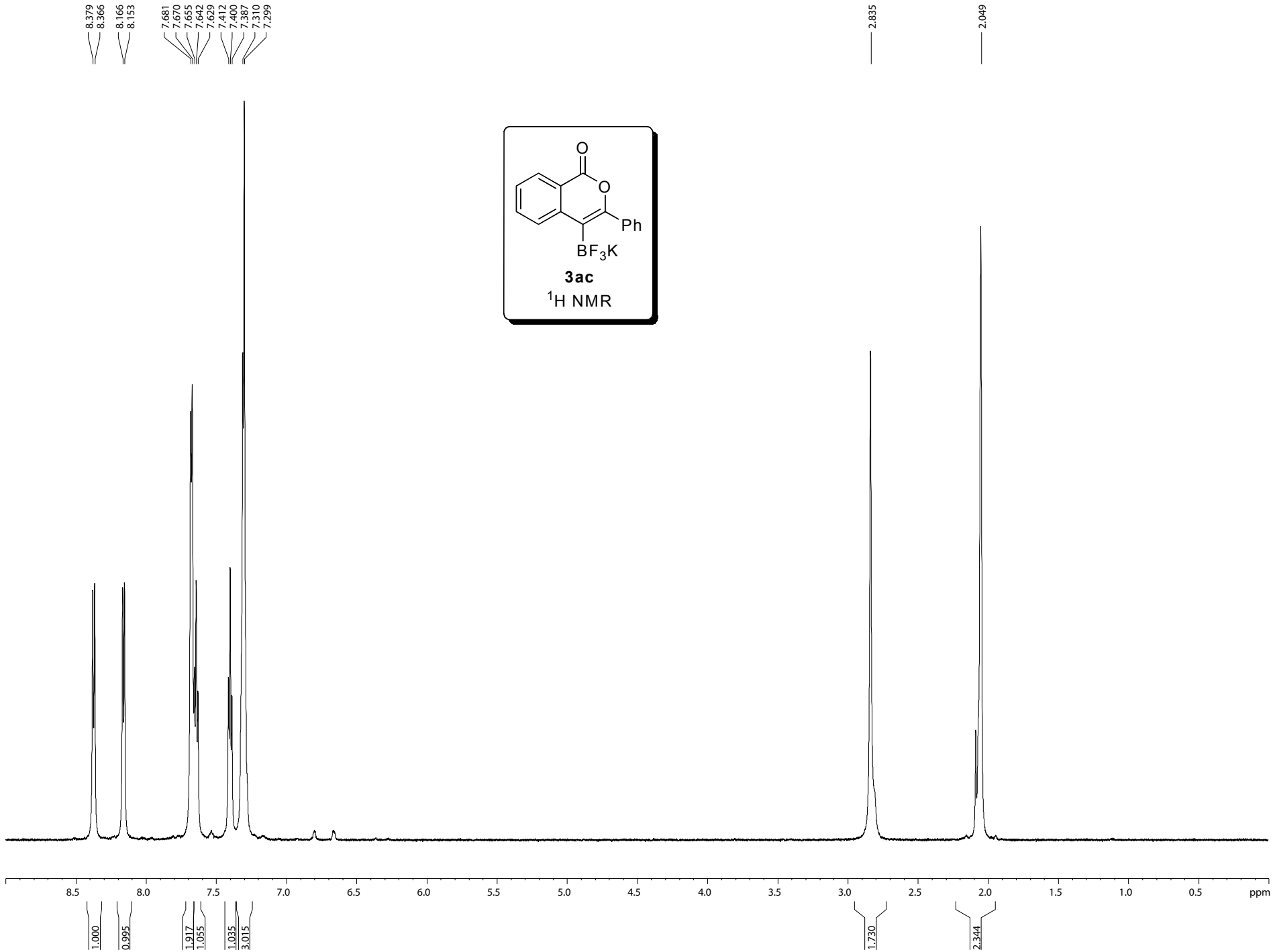
3ab

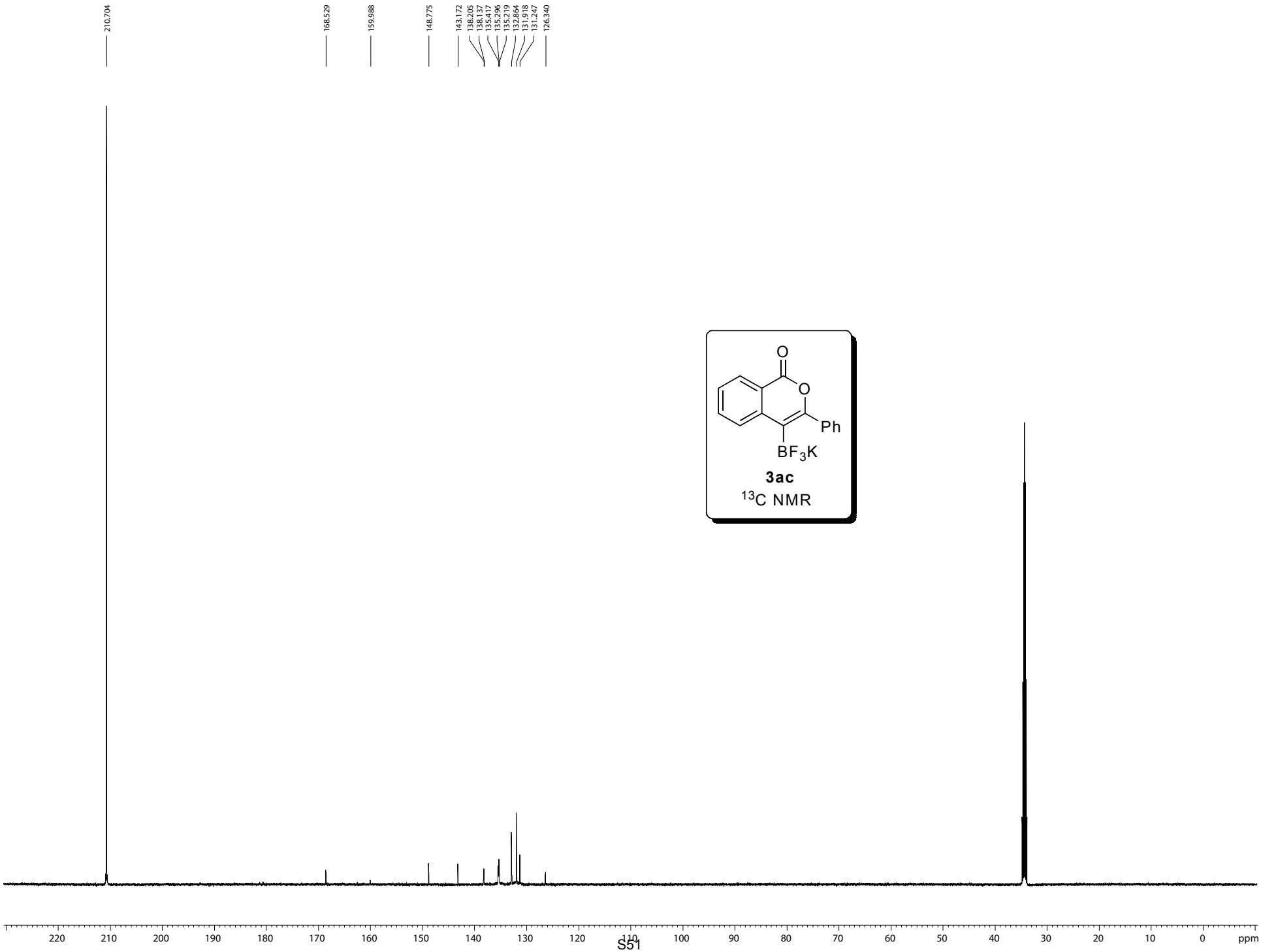
^{1}H NMR

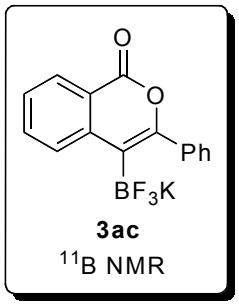
(zoomed in)


162.209
155.233
139.399
135.017
134.900
129.895
129.088
128.696
128.165
127.527
126.951
120.169
117.365
0.863
O
O
Ph
B(OH)2
3ab
13C NMR
195 190 185 180 175 170 165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 ppm


30.001
O
O
Ph
B(OH)2
3ab
11B NMR
45
40
35
30
25
20
15
10
5
ppm


8.379
8.366
8.166
8.153
7.681
7.670
7.655
7.642
7.629
7.412
7.400
7.387
7.310
7.299
2.835
2.049
O
O
Ph
BF3K
3ac
1H NMR
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.000
0.995
1.917
1.055
1.035
3.015
1.730
2.344

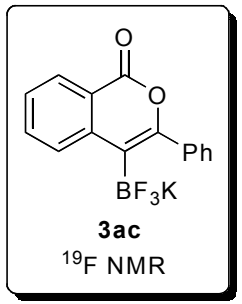

210.704
168.529
159.988
148.775
143.172
138.205
138.137
135.417
135.296
135.219
132.864
131.918
131.247
126.340
O
O
Ph
BF3K
3ac
13C NMR
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


O
O
Ph
BF_3K

3ac

^{11}B NMR

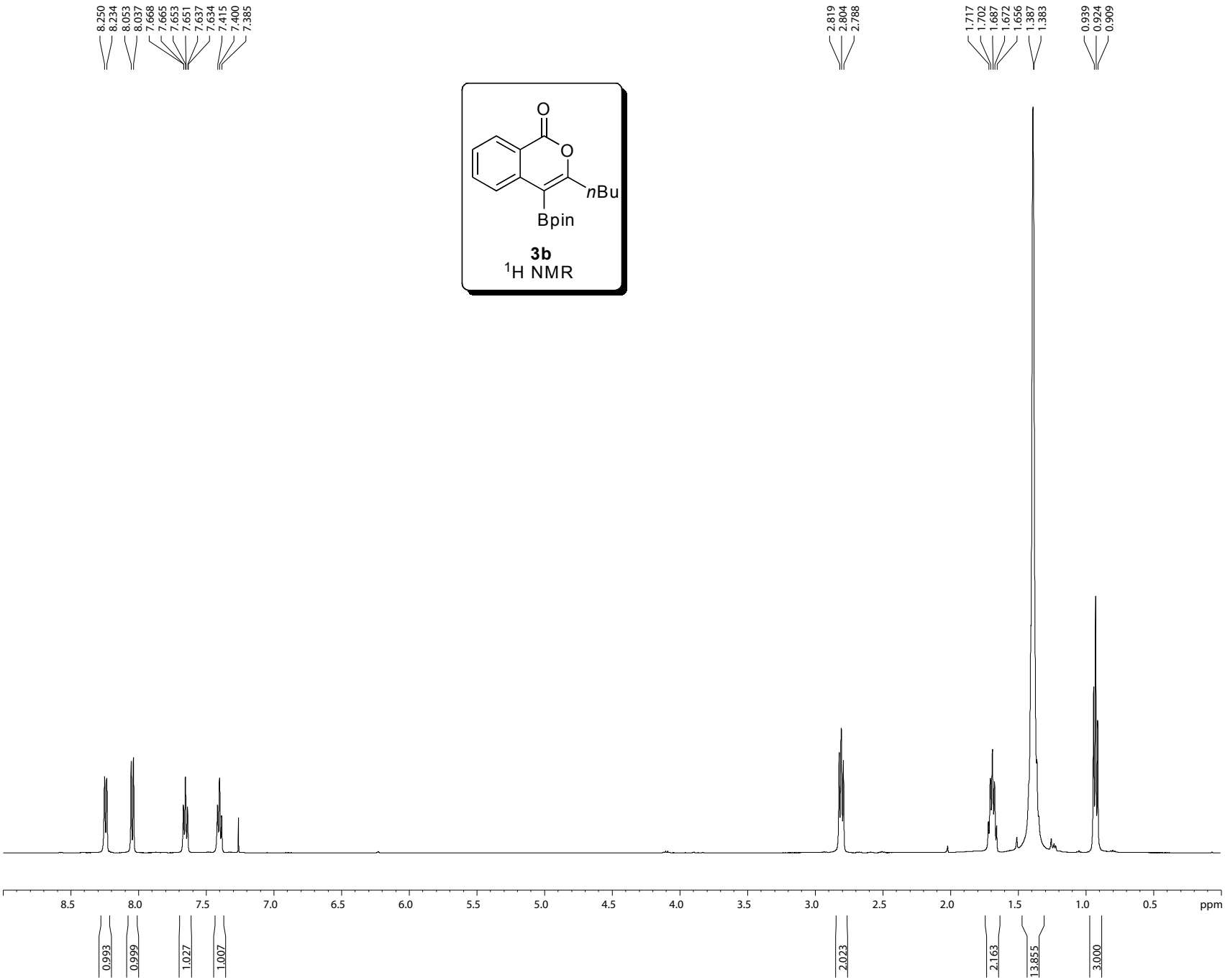
2.910
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
ppm

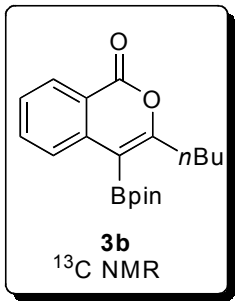

O
O
Ph
BF_3K

3ac

^{19}F NMR

-131.629
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
ppm

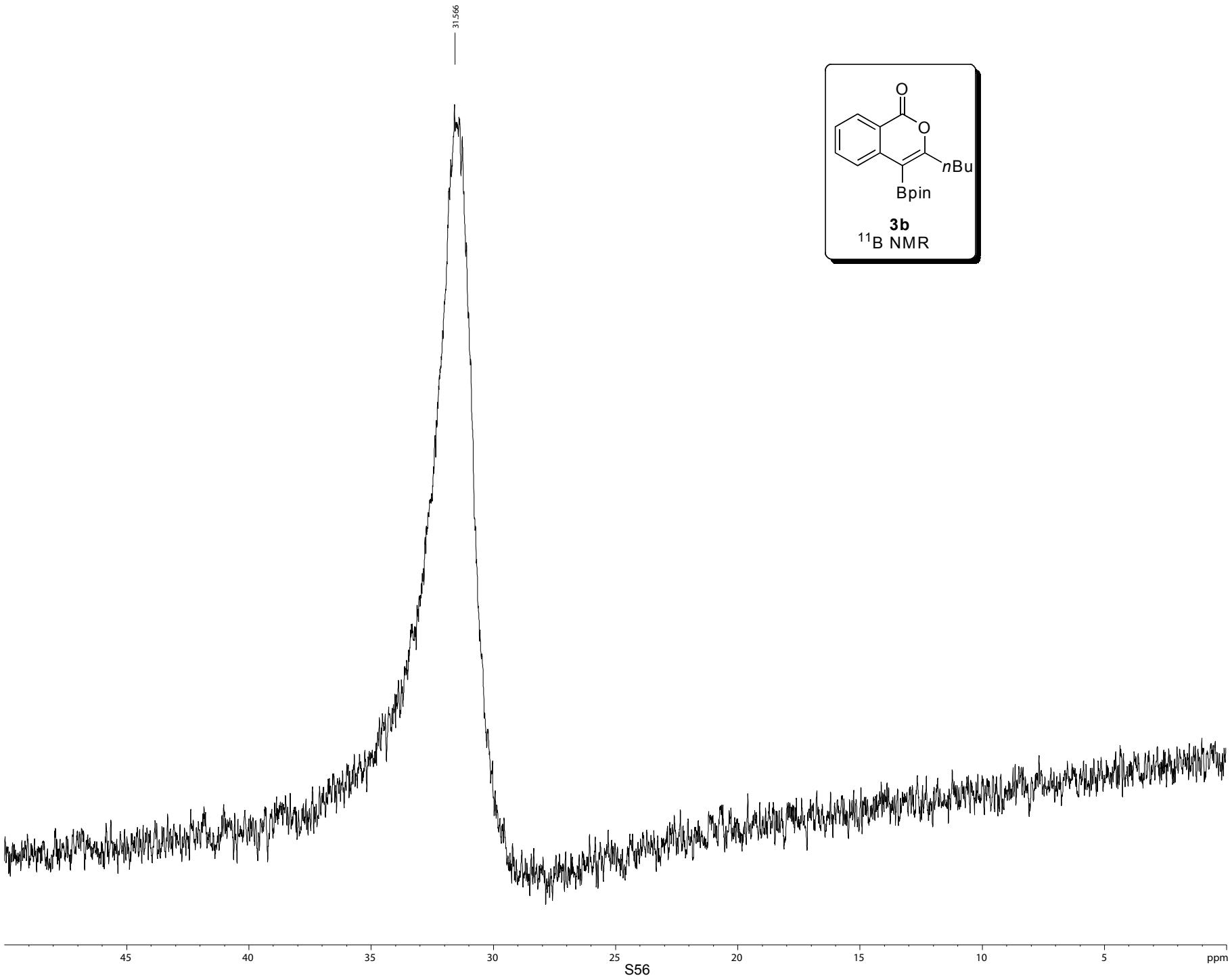

8.250
8.234
8.053
8.037
7.668
7.665
7.653
7.651
7.637
7.634
7.415
7.400
7.385
2.819
2.804
2.788
1.717
1.702
1.687
1.672
1.656
1.387
1.383
0.939
0.924
0.909
O
O
nBu
Bpin
3b
1H NMR
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
0.993
0.999
1.027
1.007
2.023
2.163
13.855
3.000



3b
^{13}C NMR

166.609
162.925
139.769
134.665
129.241
127.225
126.633
119.929
84.036
77.391
77.136
76.882
33.665
30.900
24.914
22.489
13.876

220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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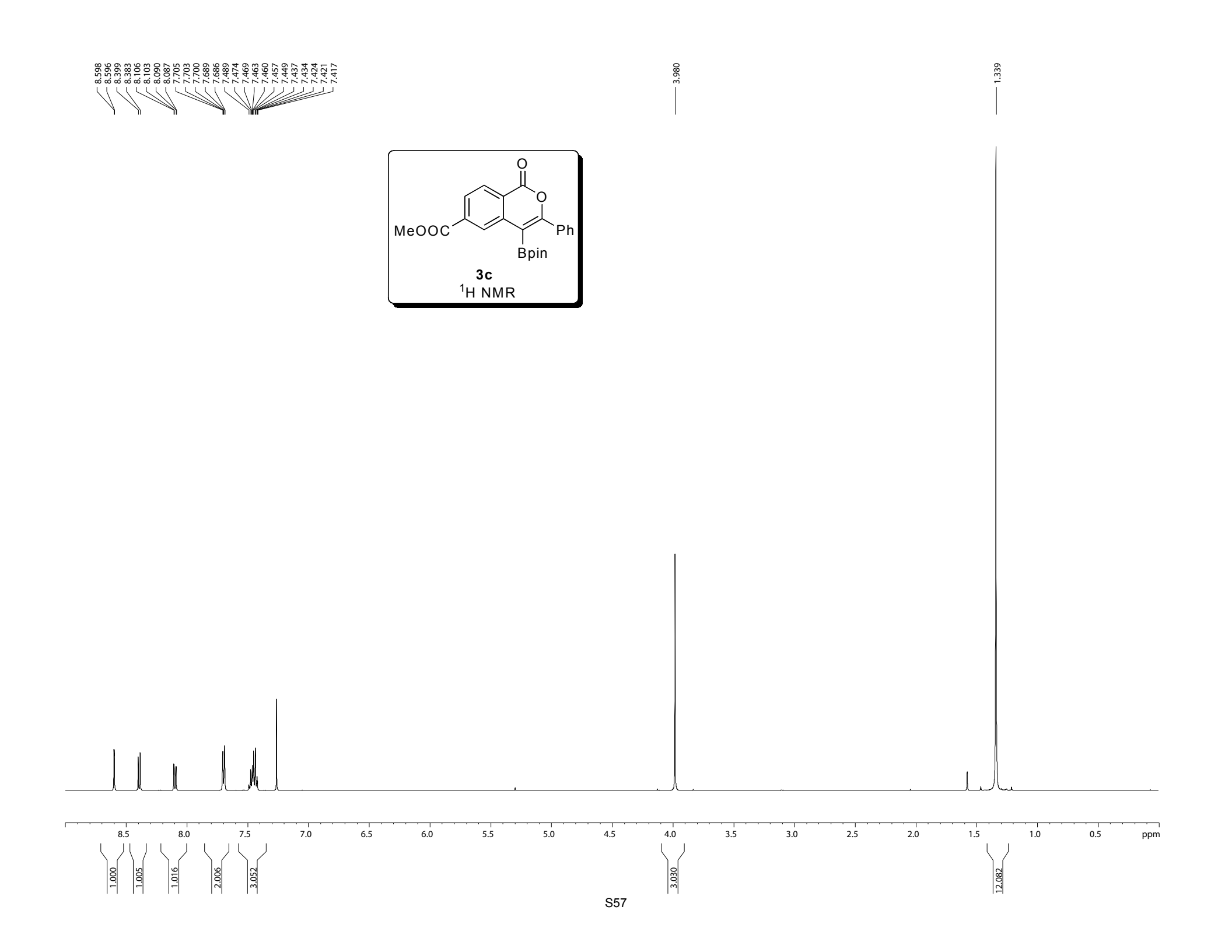
O
nBu
Bpin
3b
11B NMR
45
40
35
30
25
20
15
10
5
ppm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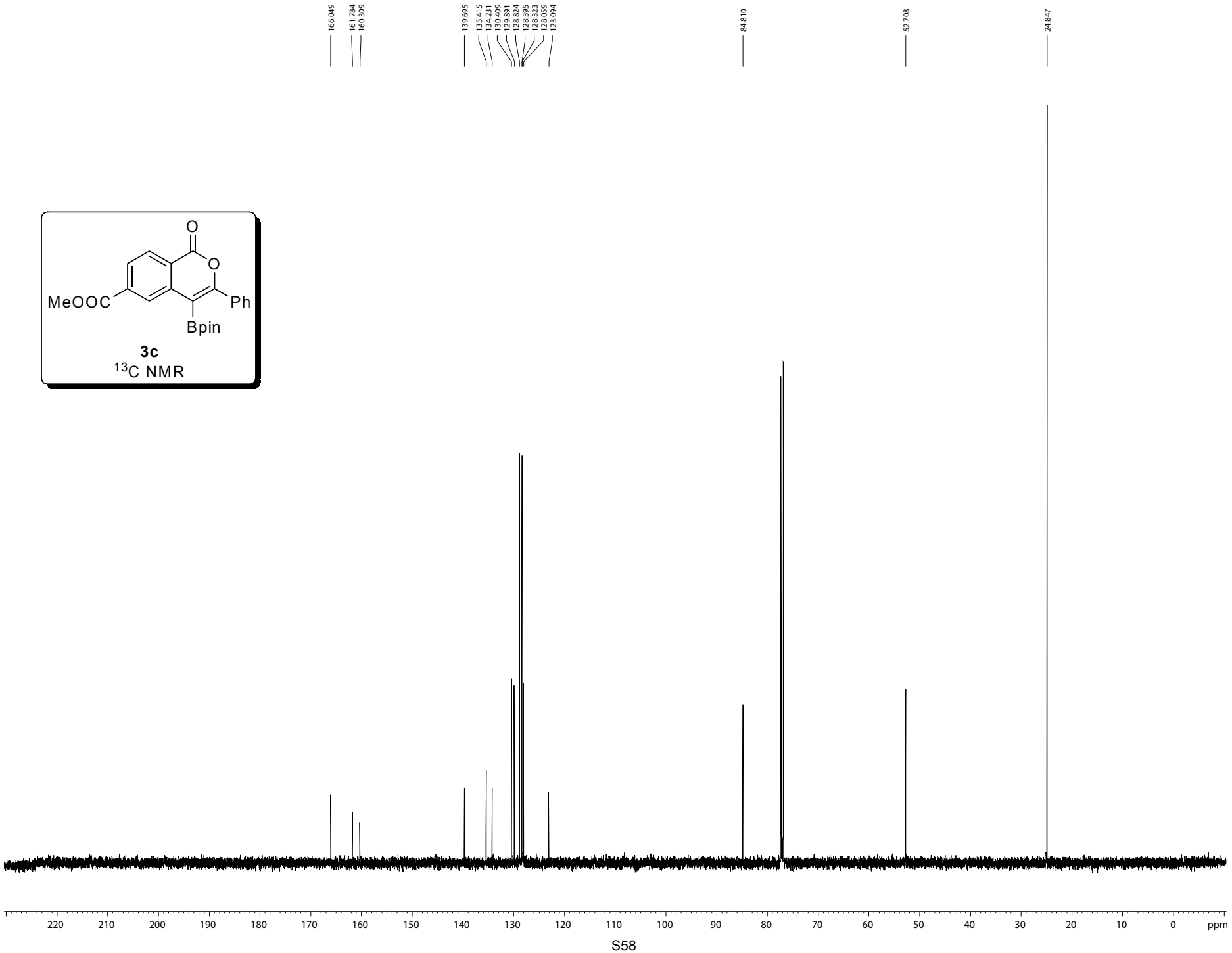
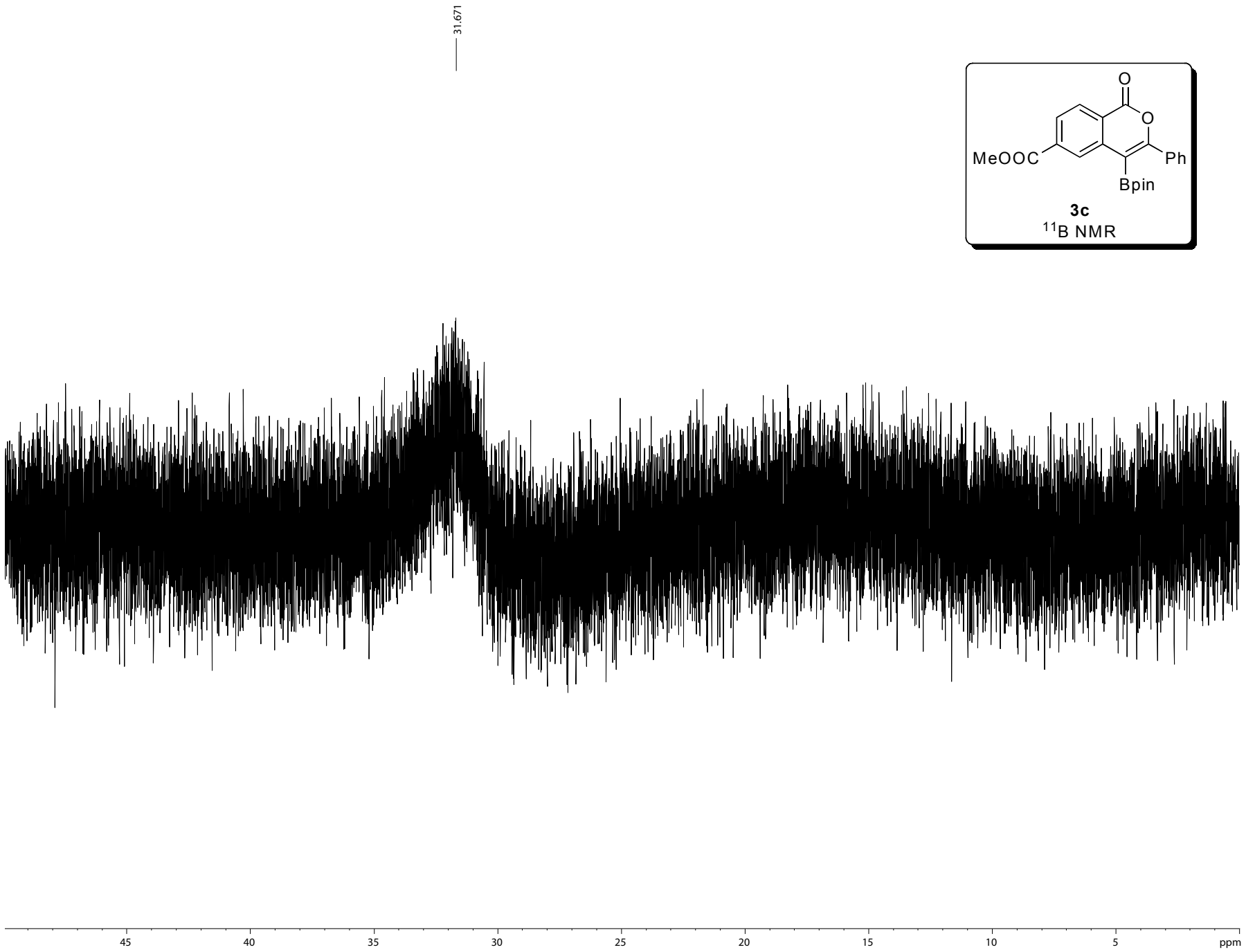
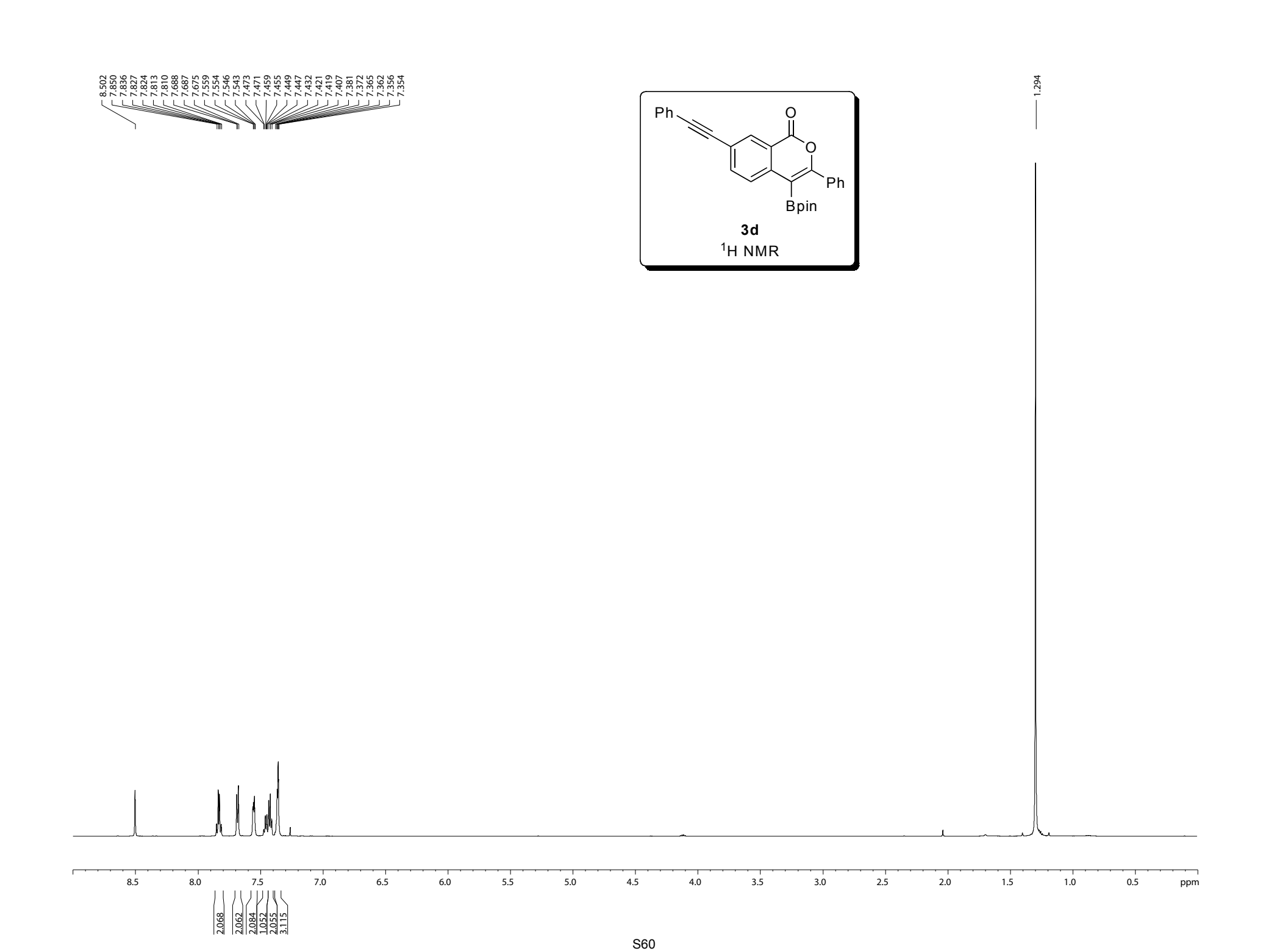
8.596
8.399
8.383
8.106
8.103
8.090
8.087
7.705
7.703
7.700
7.689
7.686
7.489
7.474
7.469
7.463
7.460
7.457
7.449
7.437
7.434
7.424
7.421
7.417
3.980
1.339
O
O
MeOOC
Ph
Bpin
3c
1H NMR
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.000
1.005
1.016
2.006
3.052
3.030
12.082


166.049
161.784
160.309
139.695
135.415
134.231
130.409
129.891
128.824
128.395
128.323
128.059
123.094
84.810
52.708
24.847
O
O
MeOOC
Ph
Bpin
3c
13C NMR
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


31.671
O
O
MeOOC
Ph
Bpin
3c
11B NMR
45
40
35
30
25
20
15
10
5
ppm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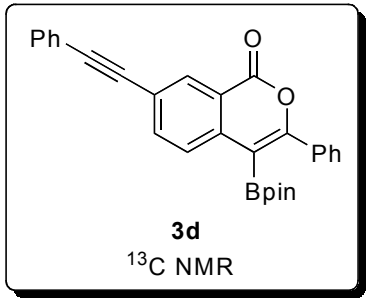
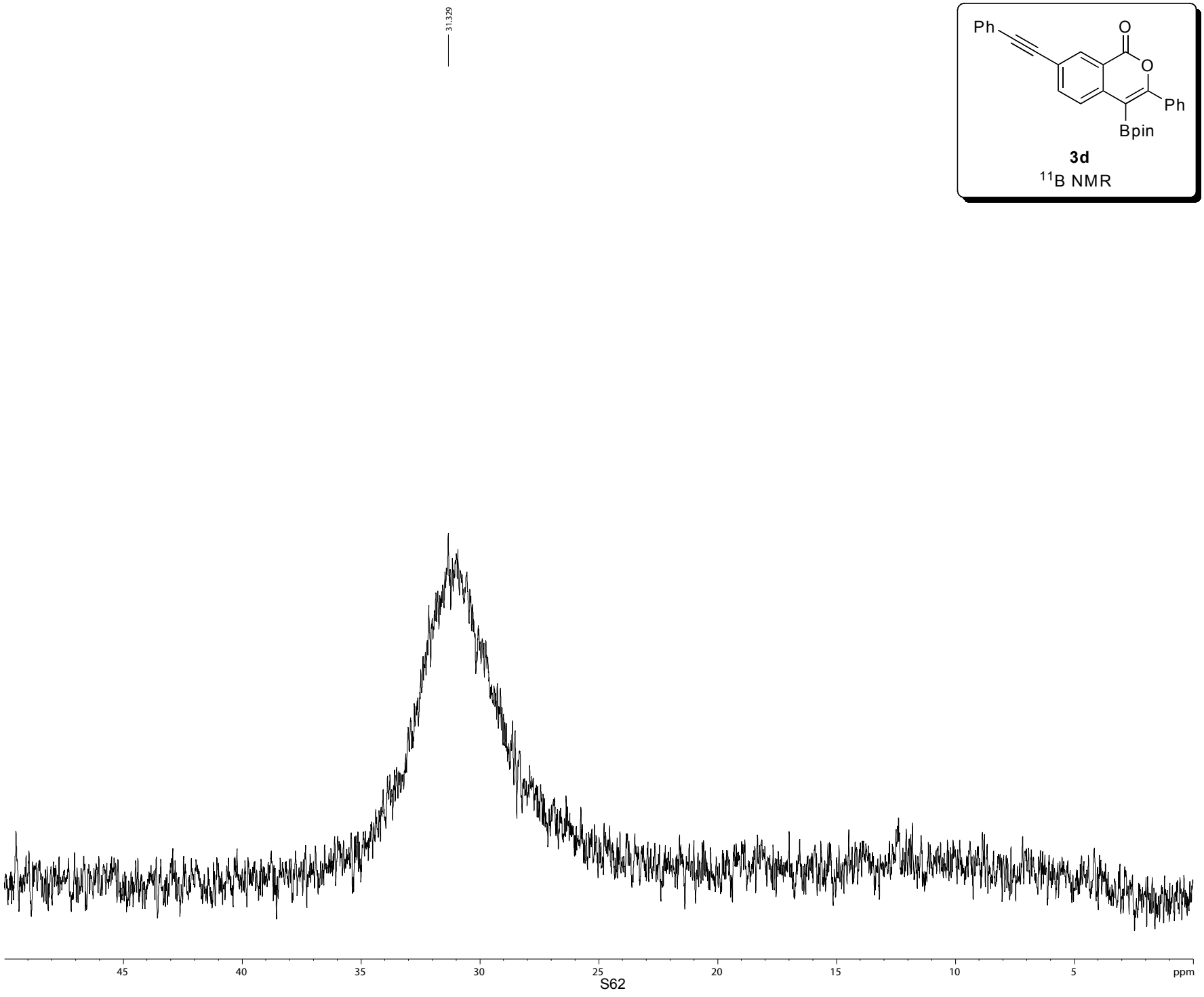
7.850
7.836
7.827
7.824
7.813
7.810
7.688
7.687
7.675
7.559
7.554
7.546
7.543
7.473
7.471
7.459
7.455
7.449
7.447
7.432
7.421
7.419
7.407
7.381
7.372
7.365
7.362
7.356
7.354
Ph
O
O
Ph
Bpin
3d
1H NMR
1.294
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.068
2.062
2.084
1.052
2.055
3.115

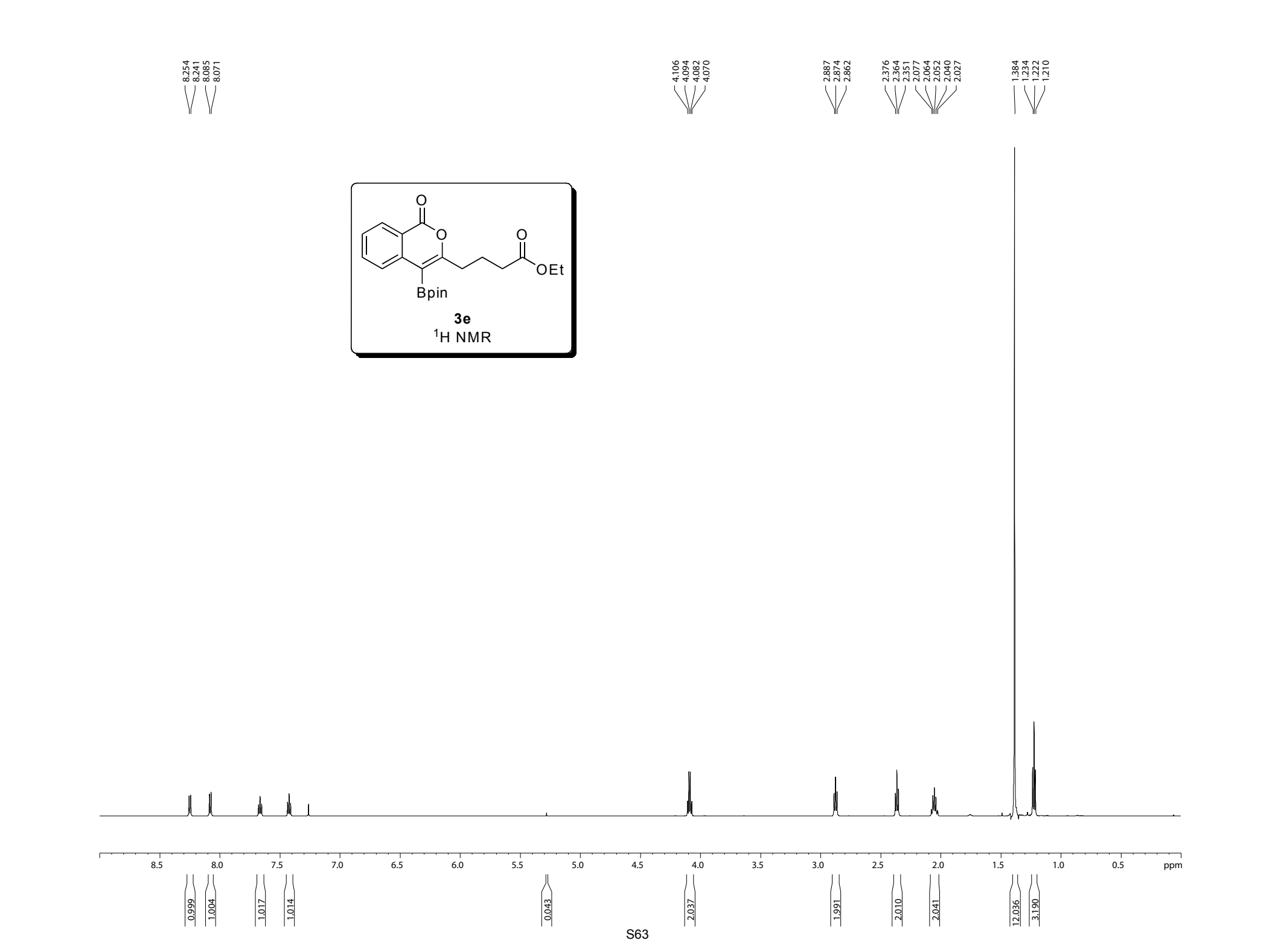

Ph
O
O
Ph
Bpin

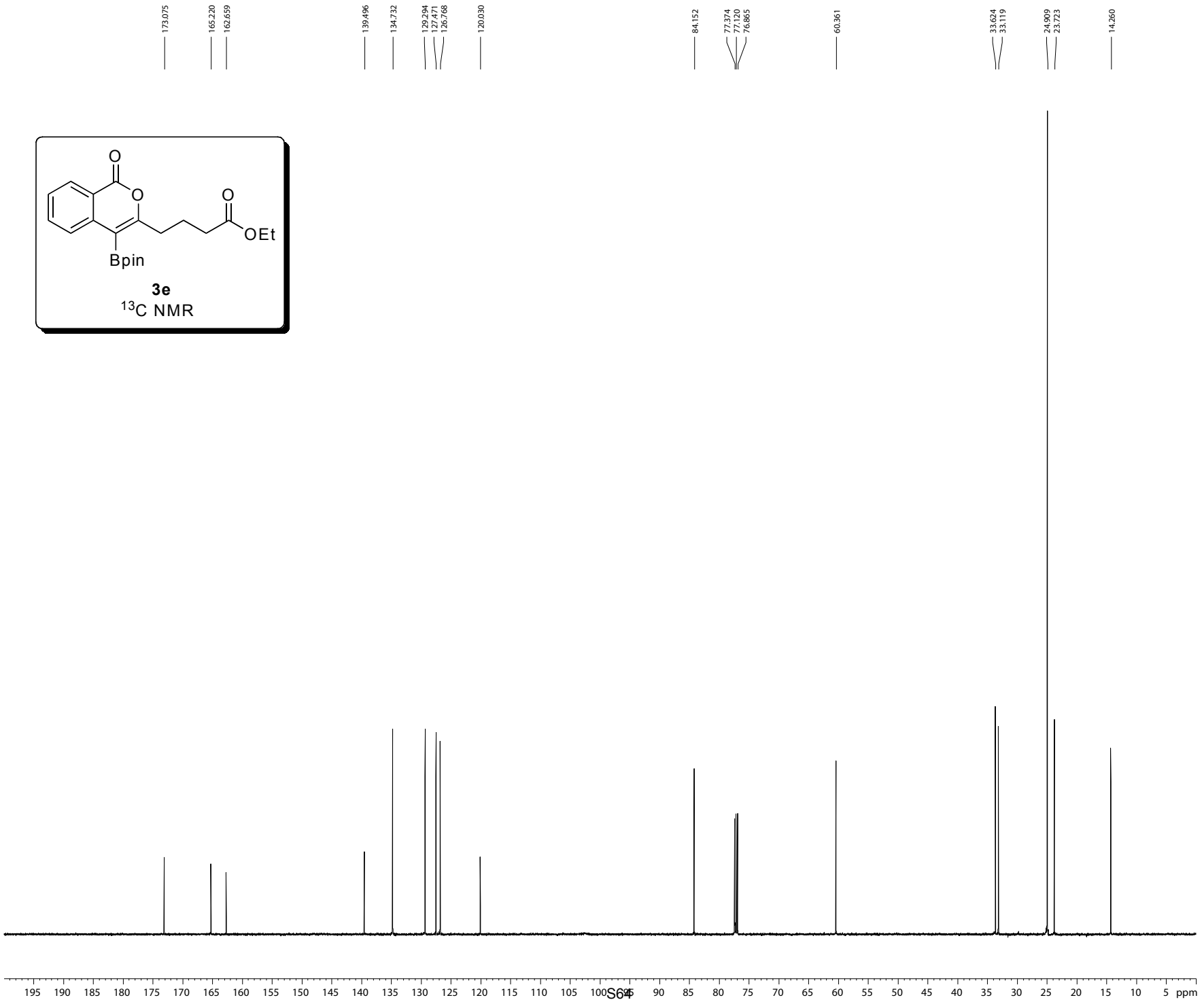
3d

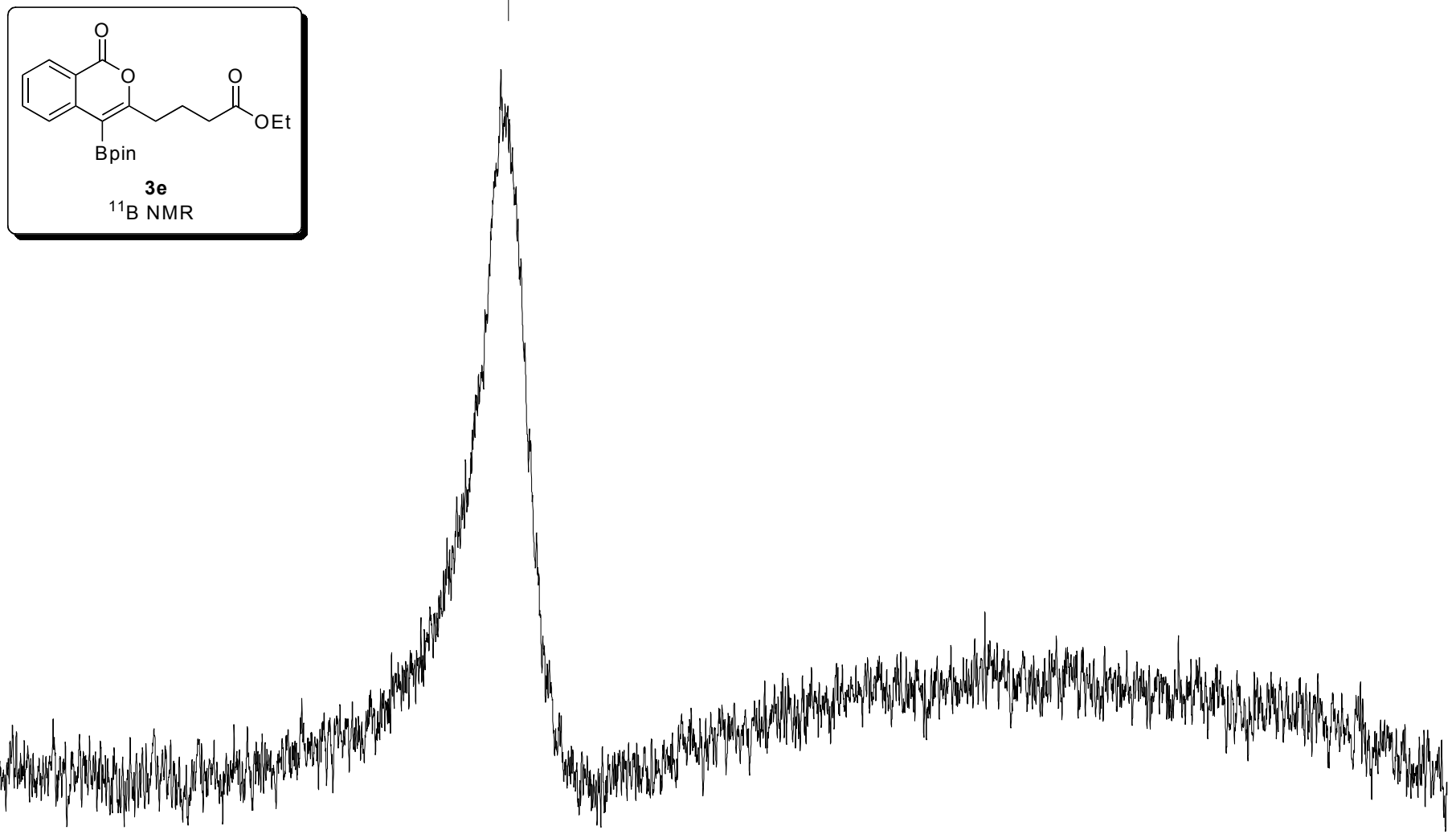
^{13}C NMR

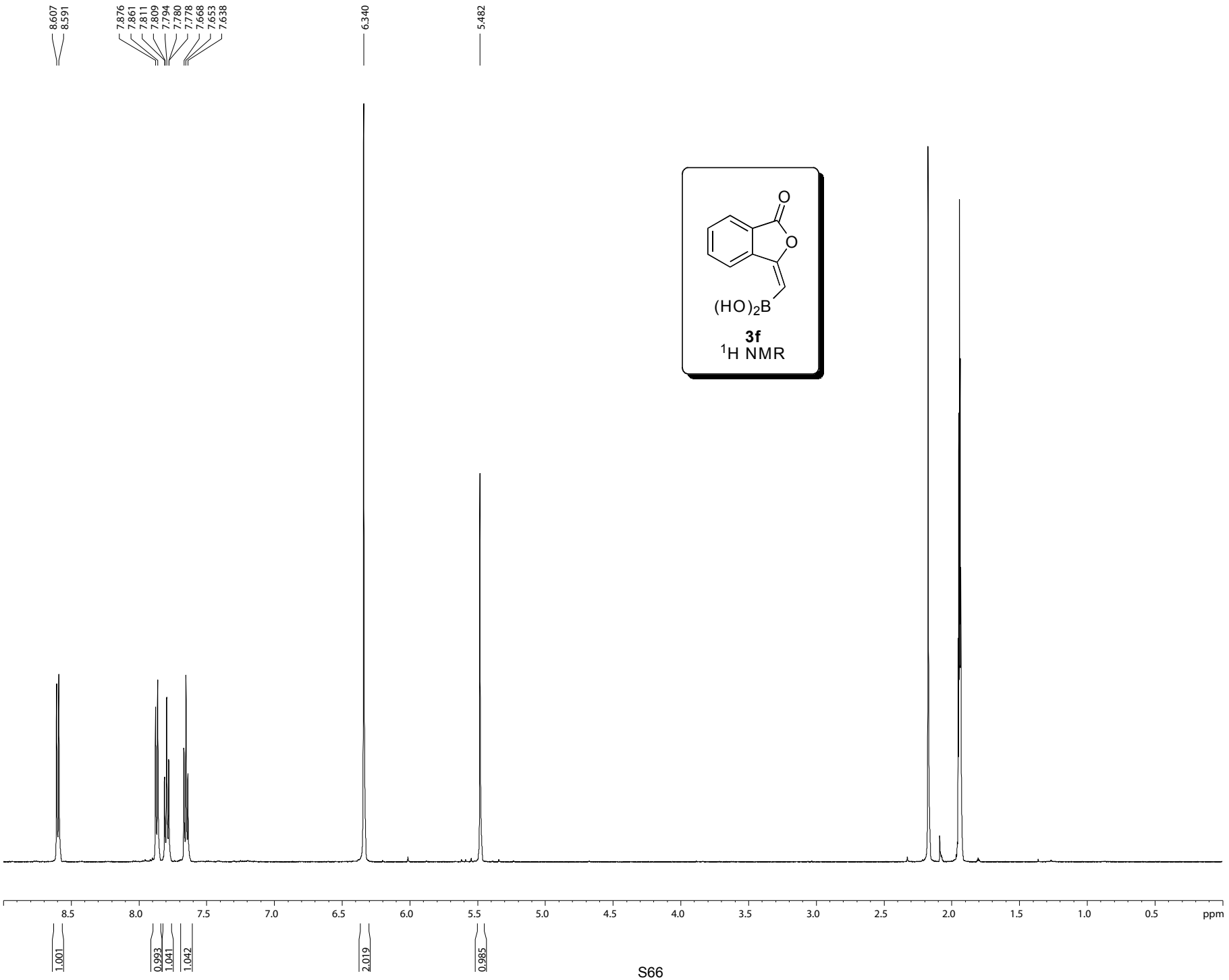
161.724
160.541
139.151
137.265
134.485
132.741
131.774
130.333
128.940
128.753
128.509
128.241
126.621
123.107
122.786
120.284
91.509
88.280
84.639
24.911
195 190 185 180 175 170 165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 ppm

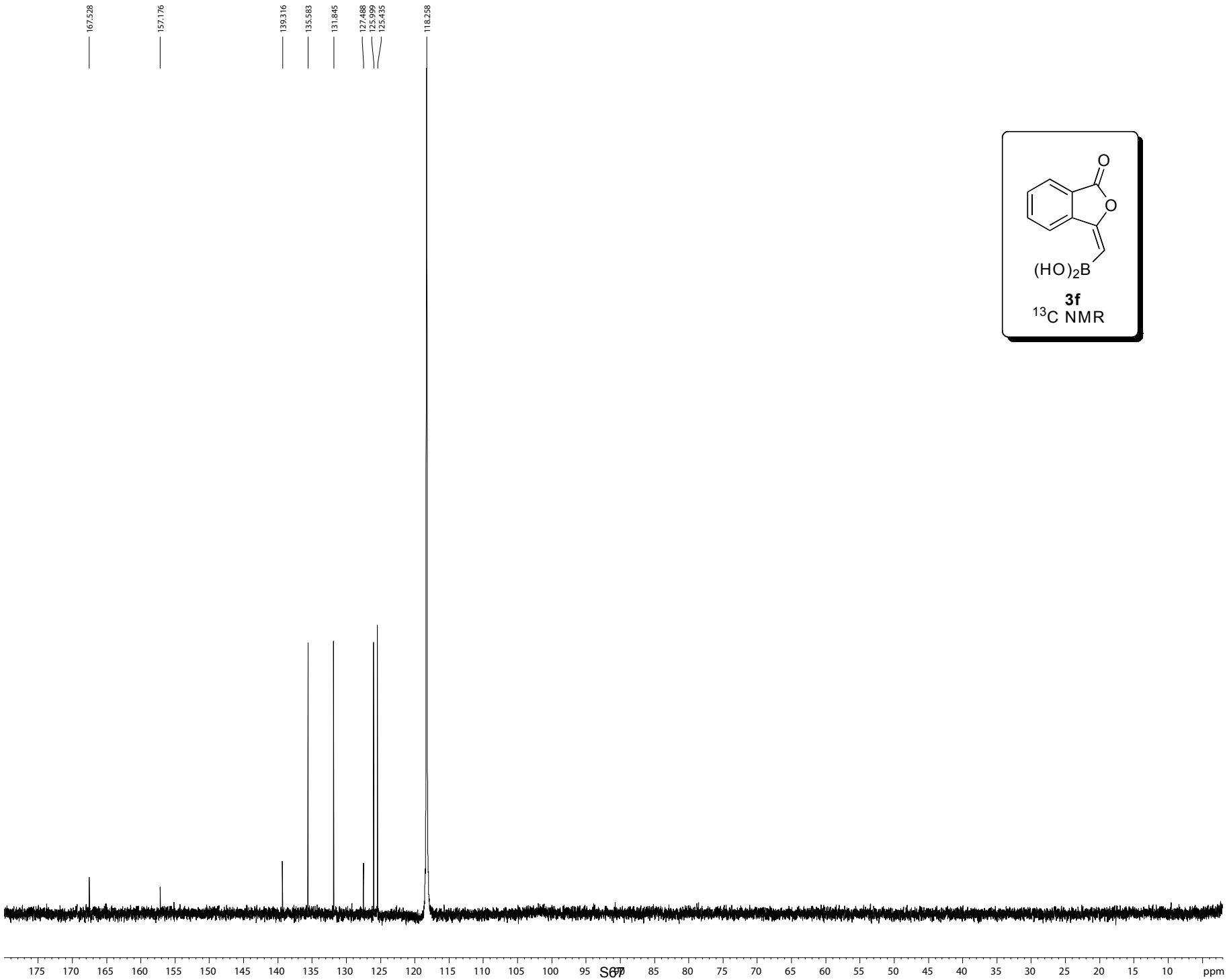

31.329
Ph
O
O
Ph
Bpin
3d
11B NMR
45
40
35
30
25
20
15
10
5
ppm

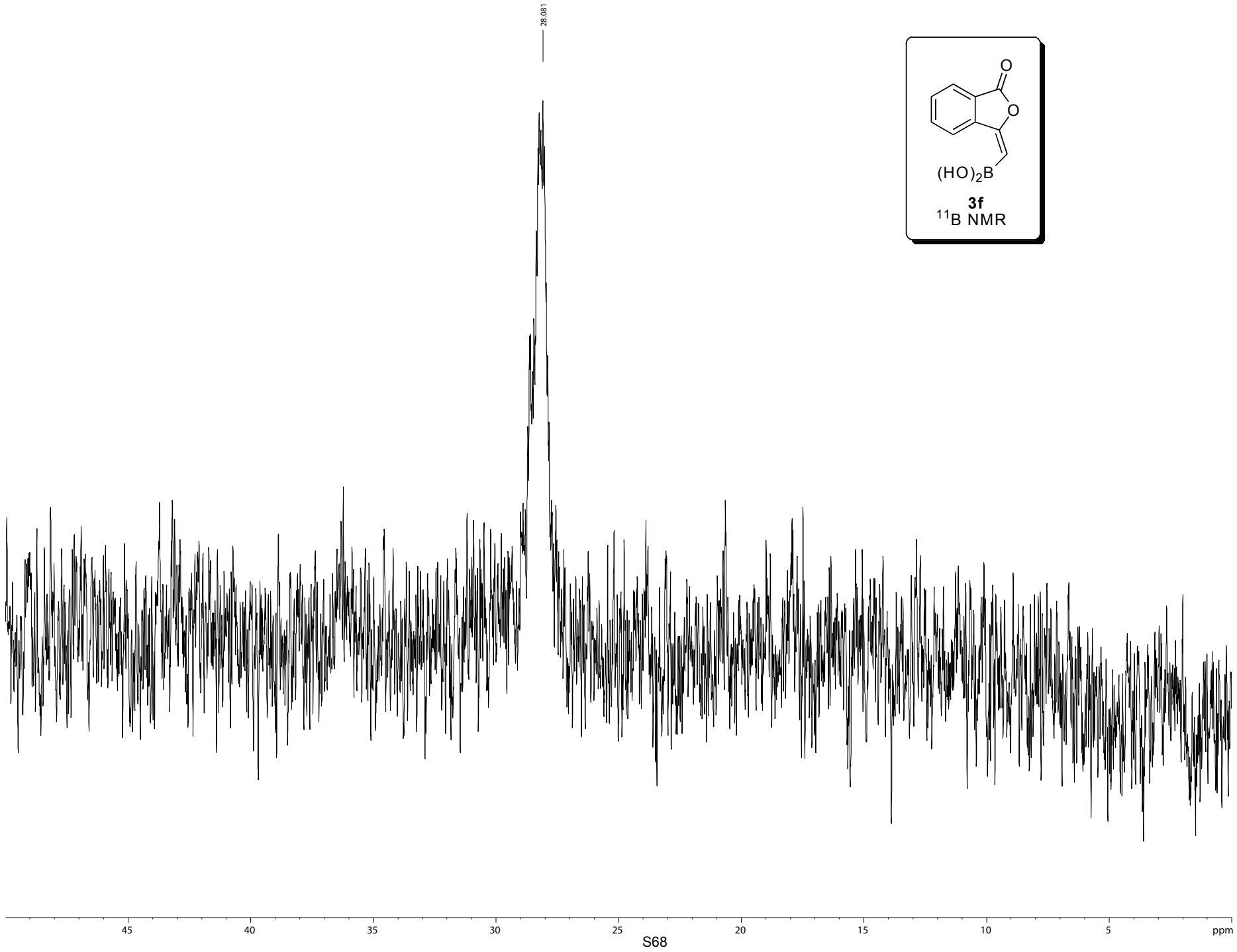

8.254
8.241
8.085
8.071
4.106
4.094
4.082
4.070
2.887
2.874
2.862
2.376
2.364
2.351
2.077
2.064
2.052
2.040
2.027
1.384
1.234
1.222
1.210
O
O
O
OEt
Bpin
3e
1H NMR
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
0.999
1.004
1.017
1.014
0.043
2.037
1.991
2.010
2.041
12.036
3.190

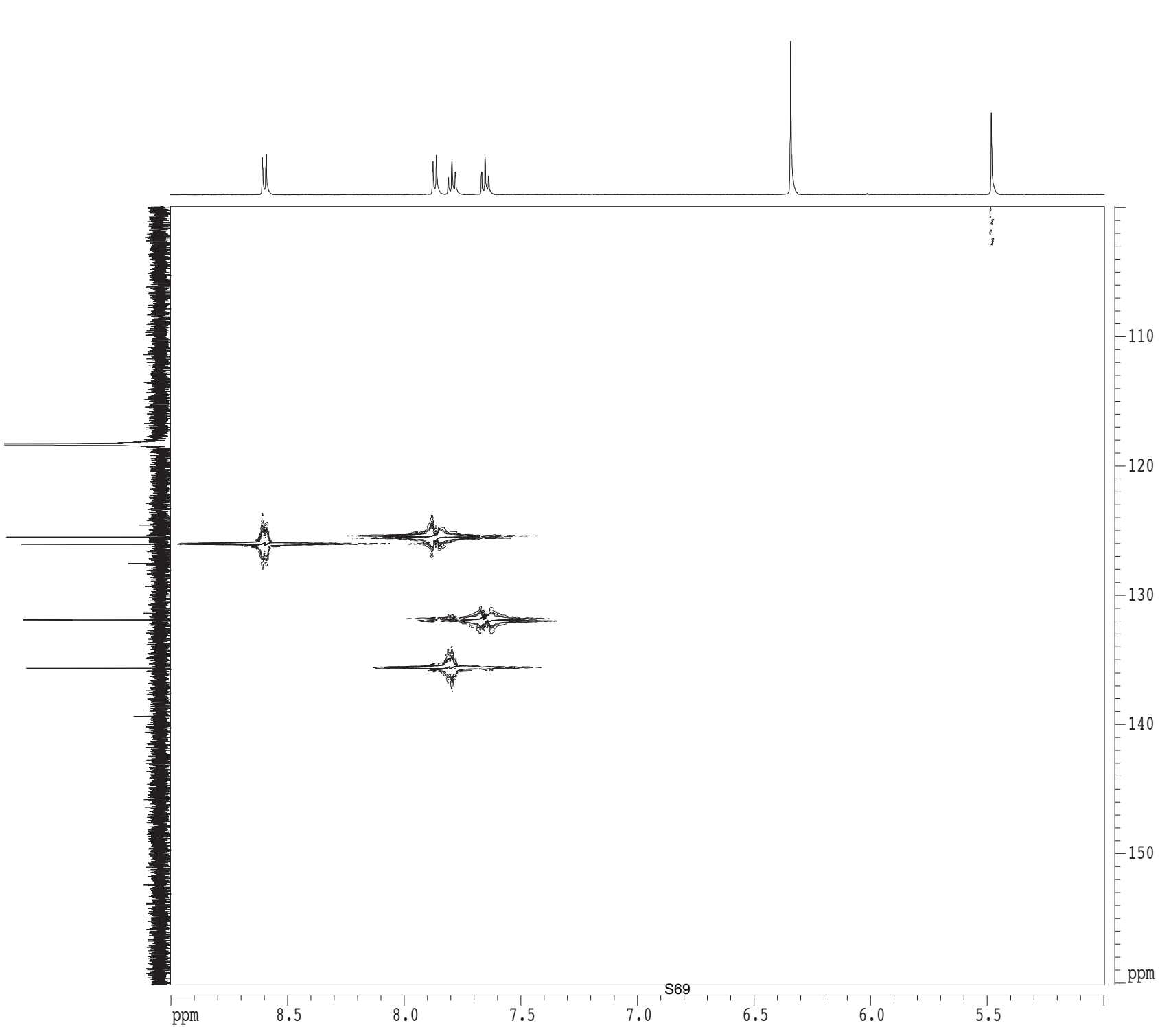

173.075
165.220
162.659
139.496
134.732
129.294
127.471
126.768
120.030
84.152
77.374
77.120
76.865
60.361
33.624
33.119
24.909
23.723
14.260
O
O
O
OEt
Bpin
3e
13C NMR
195 190 185 180 175 170 165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 ppm

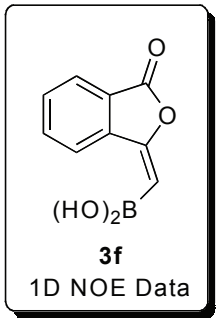

31.308
O
O
O
OEt
Bpin
3e
11B NMR
45
40
35
30
25
20
15
10
5
ppm


8.607
8.591
7.876
7.861
7.811
7.809
7.794
7.780
7.778
7.668
7.653
7.638
6.340
5.482
O
O
(HO)2B
3f
1H NMR
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.001
0.993
1.041
1.042
2.019
0.985

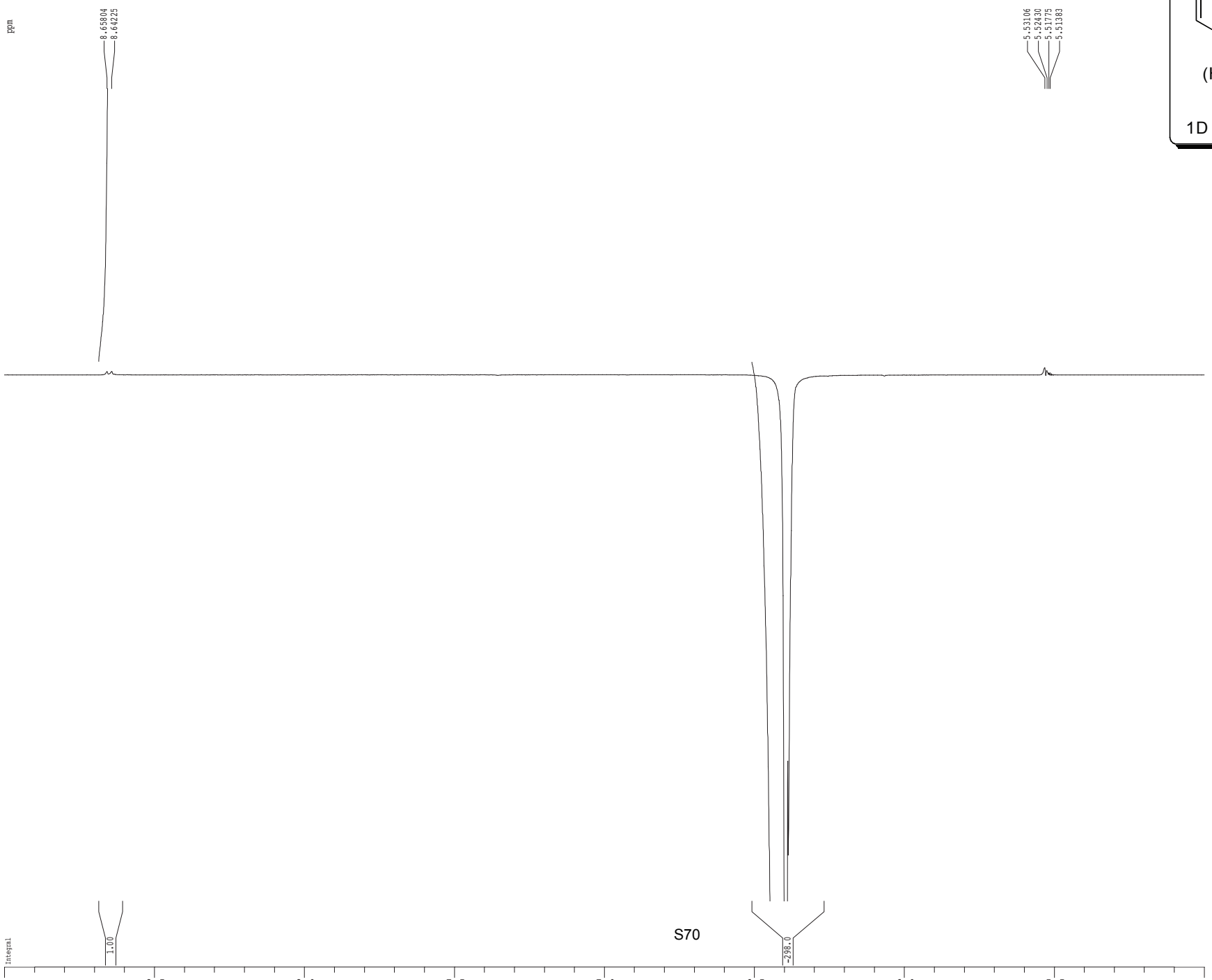

167.528
157.176
139.316
135.583
131.845
127.488
125.999
125.435
118.258
O
O
(HO)2B
3f
13C NMR
175 170 165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 ppm

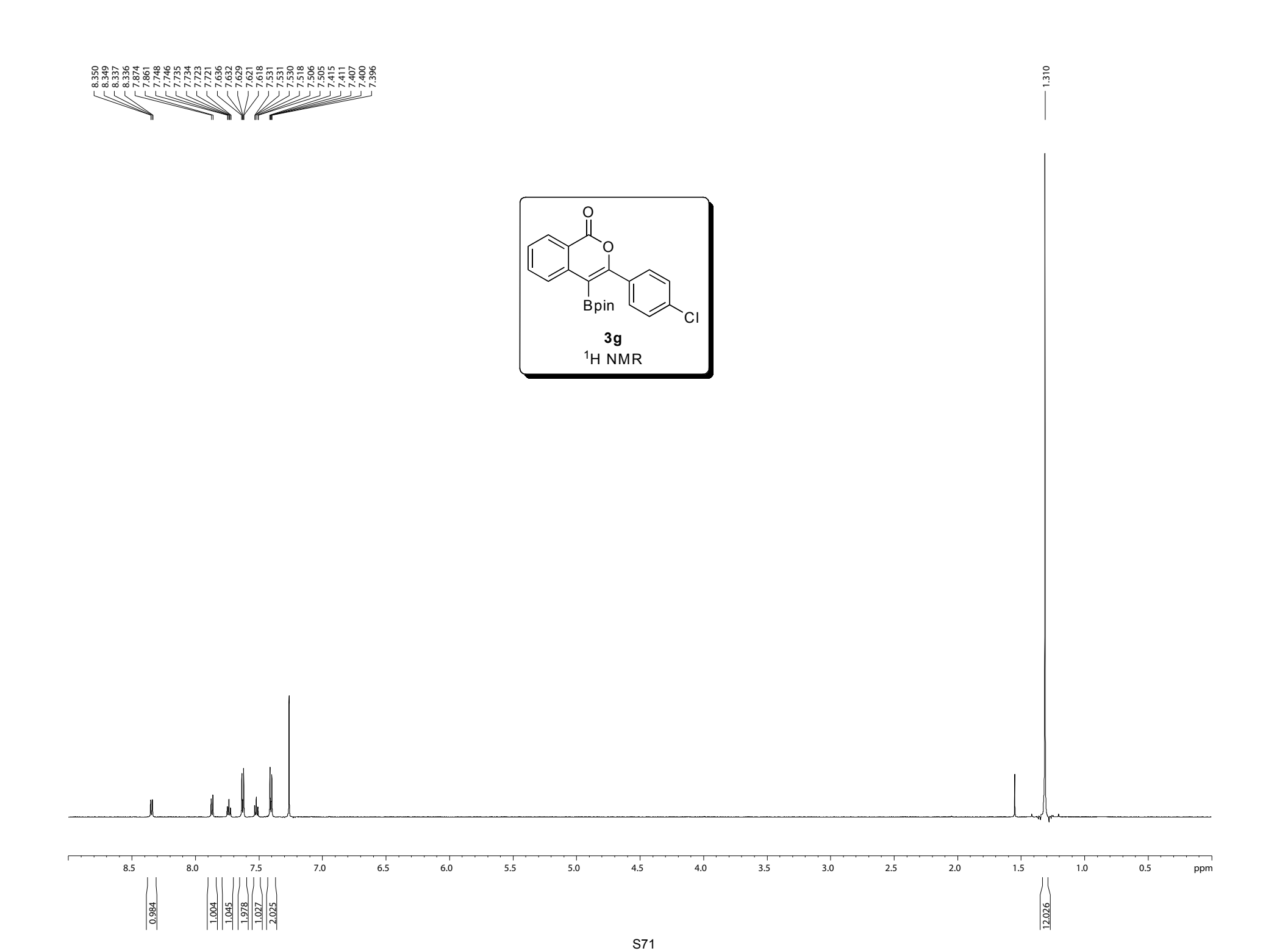

28.081
O
O
(HO)2B
3f
11B NMR
45
40
35
30
25
20
15
10
5
ppm


O
O
(HO)2B
3f
1H/13C HMQC
110
120
130
140
150
ppm
ppm
8.5
8.0
7.5
7.0
6.5
6.0
5.5



3f
1D NOE Data

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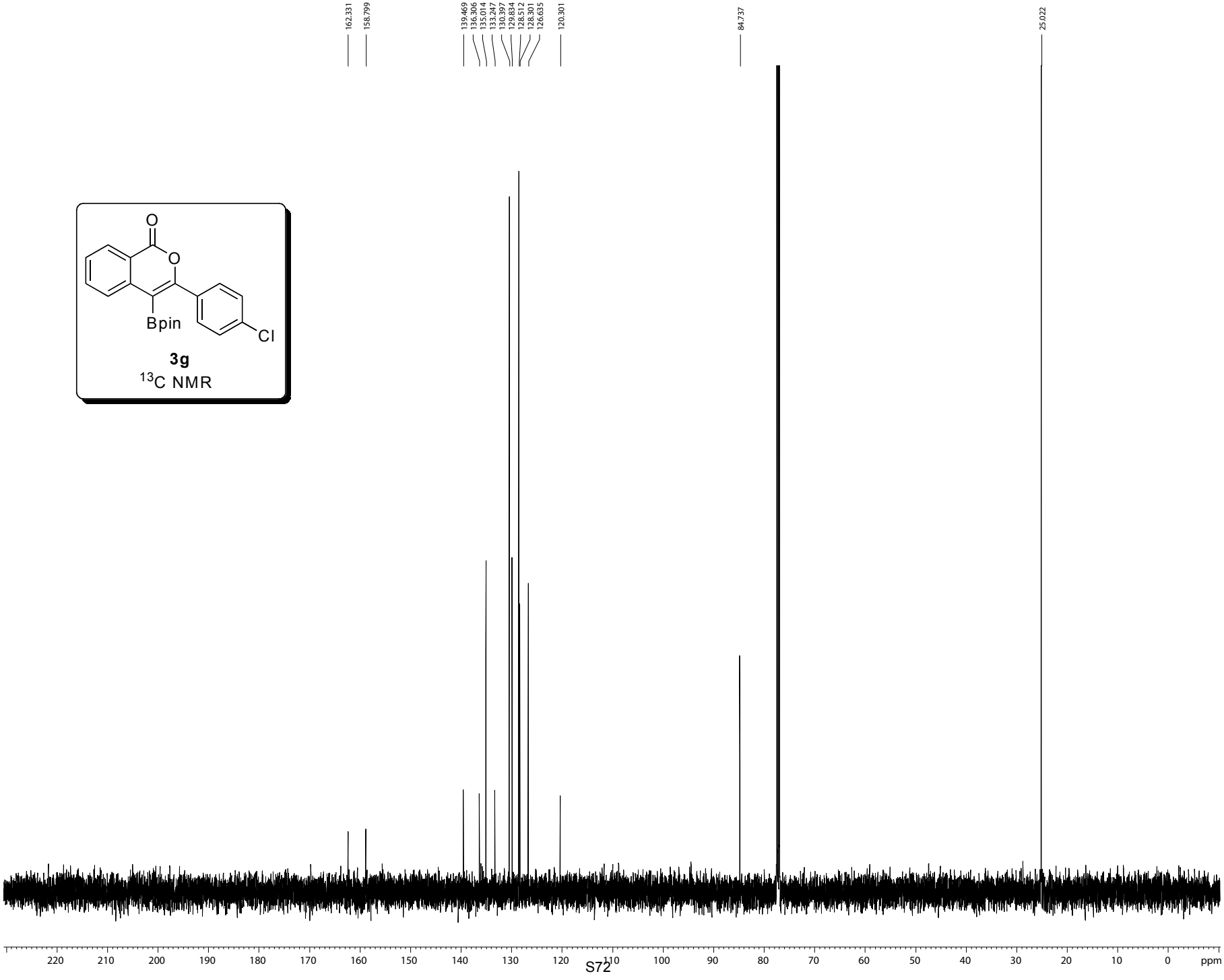
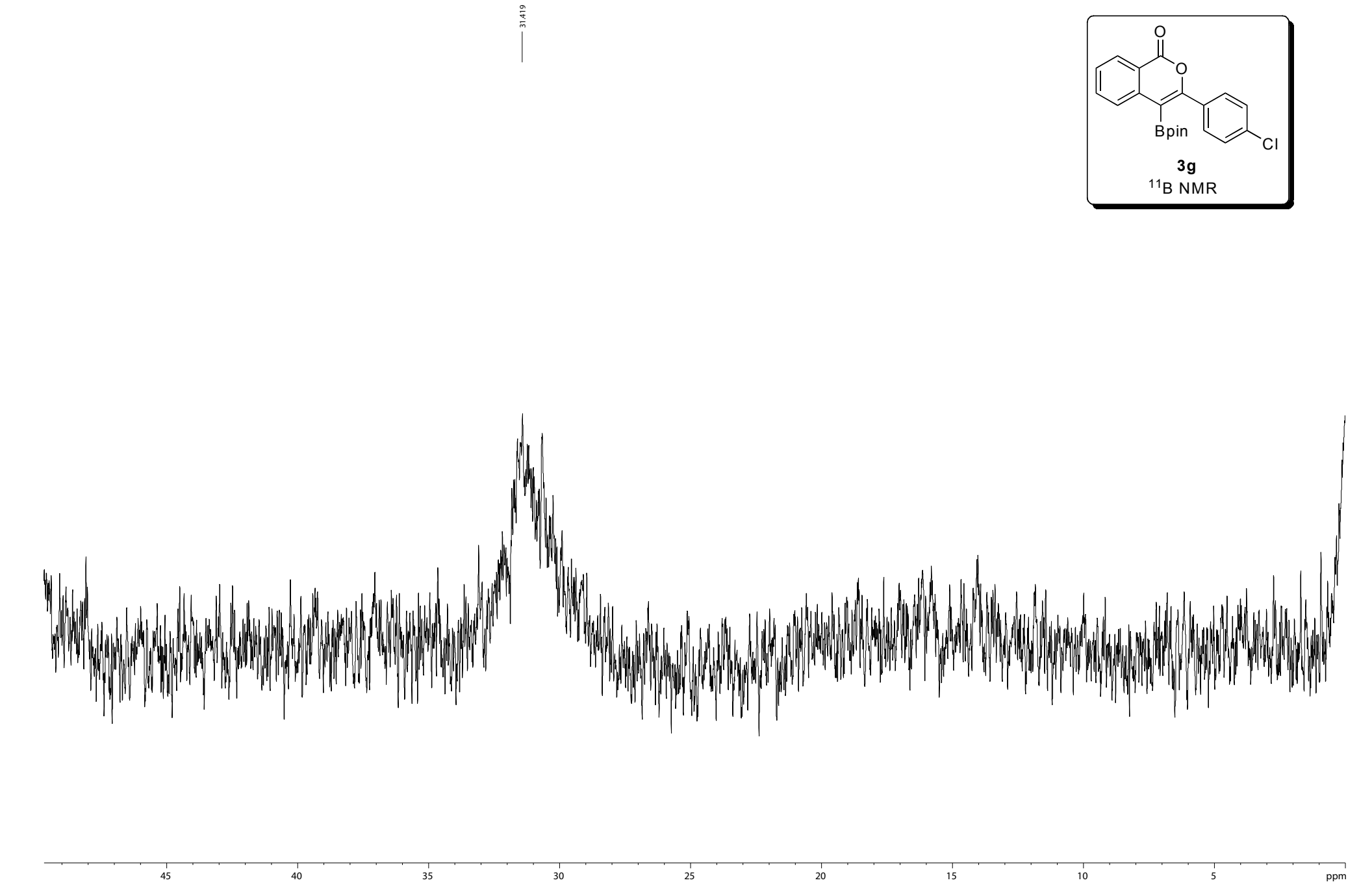
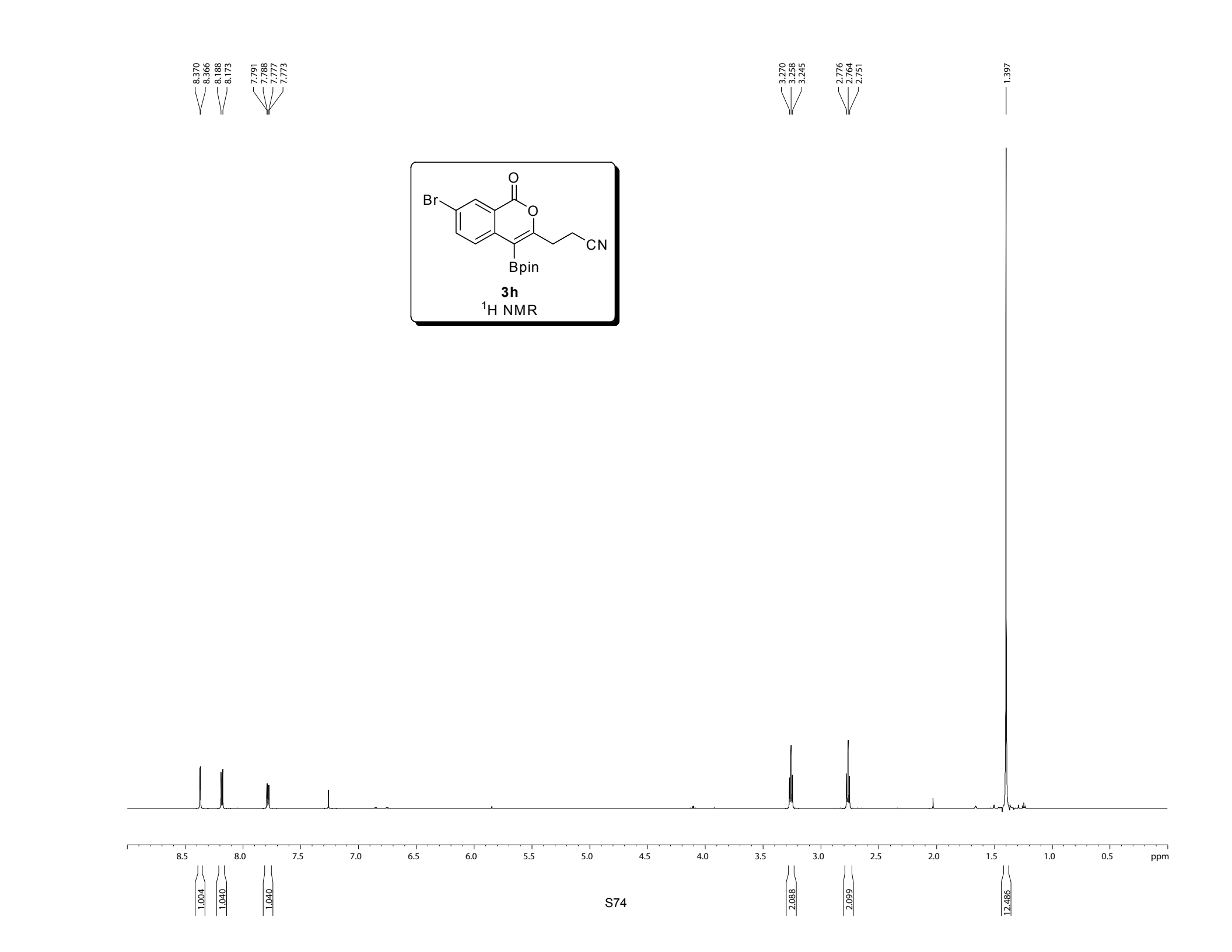
8.349
8.337
8.336
7.874
7.861
7.748
7.746
7.735
7.734
7.723
7.721
7.636
7.632
7.629
7.621
7.618
7.531
7.531
7.530
7.518
7.506
7.505
7.415
7.411
7.407
7.400
7.396
1.310
O
O
Bpin
Cl
3g
1H NMR
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
0.984
1.004
1.045
1.978
1.027
2.025
12.026


162.331
158.799
139.469
136.306
135.014
133.247
130.397
129.834
128.512
128.301
126.635
120.301
84.737
25.022
O
O
Bpin
Cl
3g
13C NMR
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


31.419
O
O
Bpin
Cl
3g
11B NMR
45
40
35
30
25
20
15
10
5
ppm


8.370
8.366
8.188
8.173
7.791
7.788
7.777
7.773
3.270
3.258
3.245
2.776
2.764
2.751
1.397
Br
O
O
CN
Bpin
3h
1H NMR
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
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1.040
1.040
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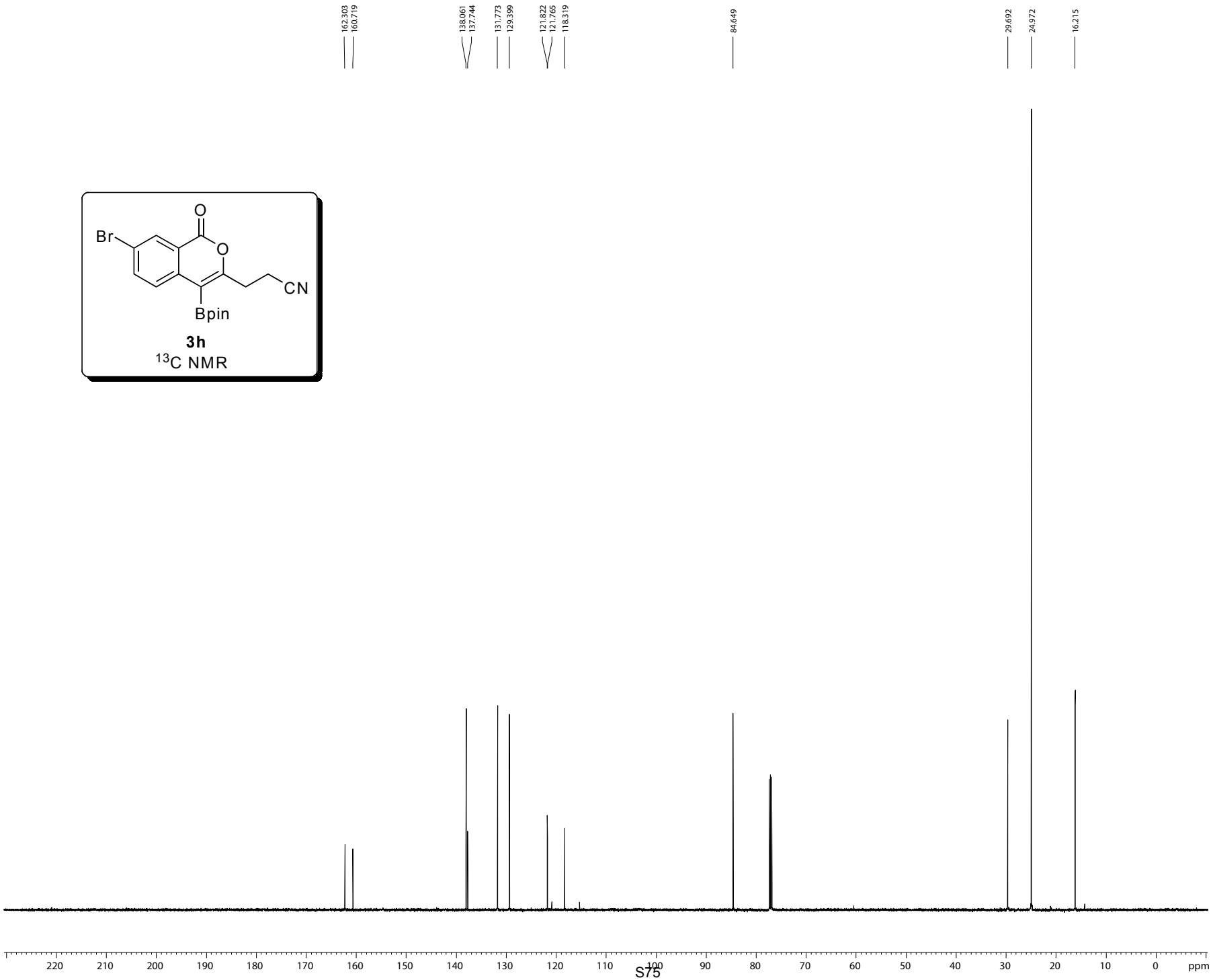
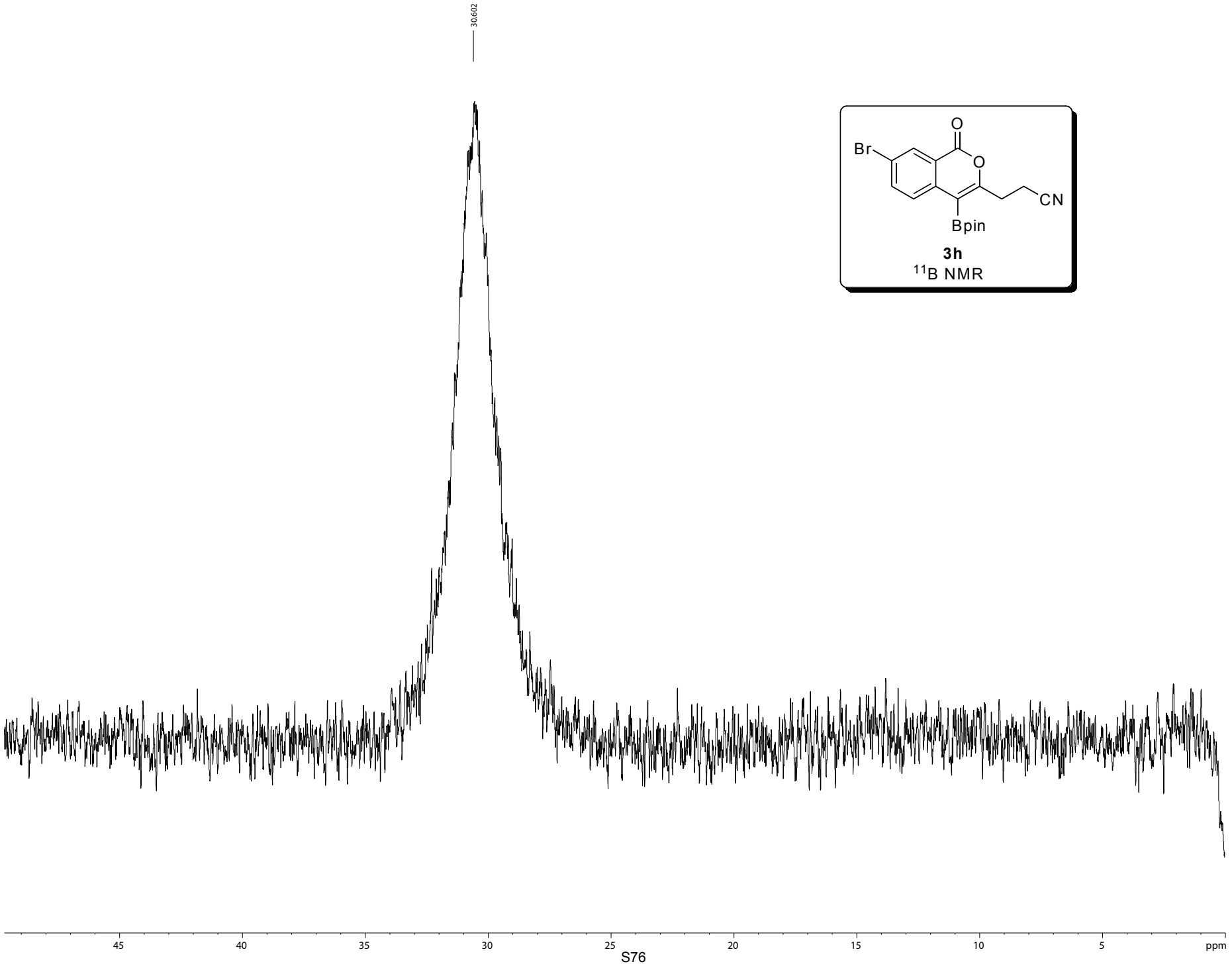
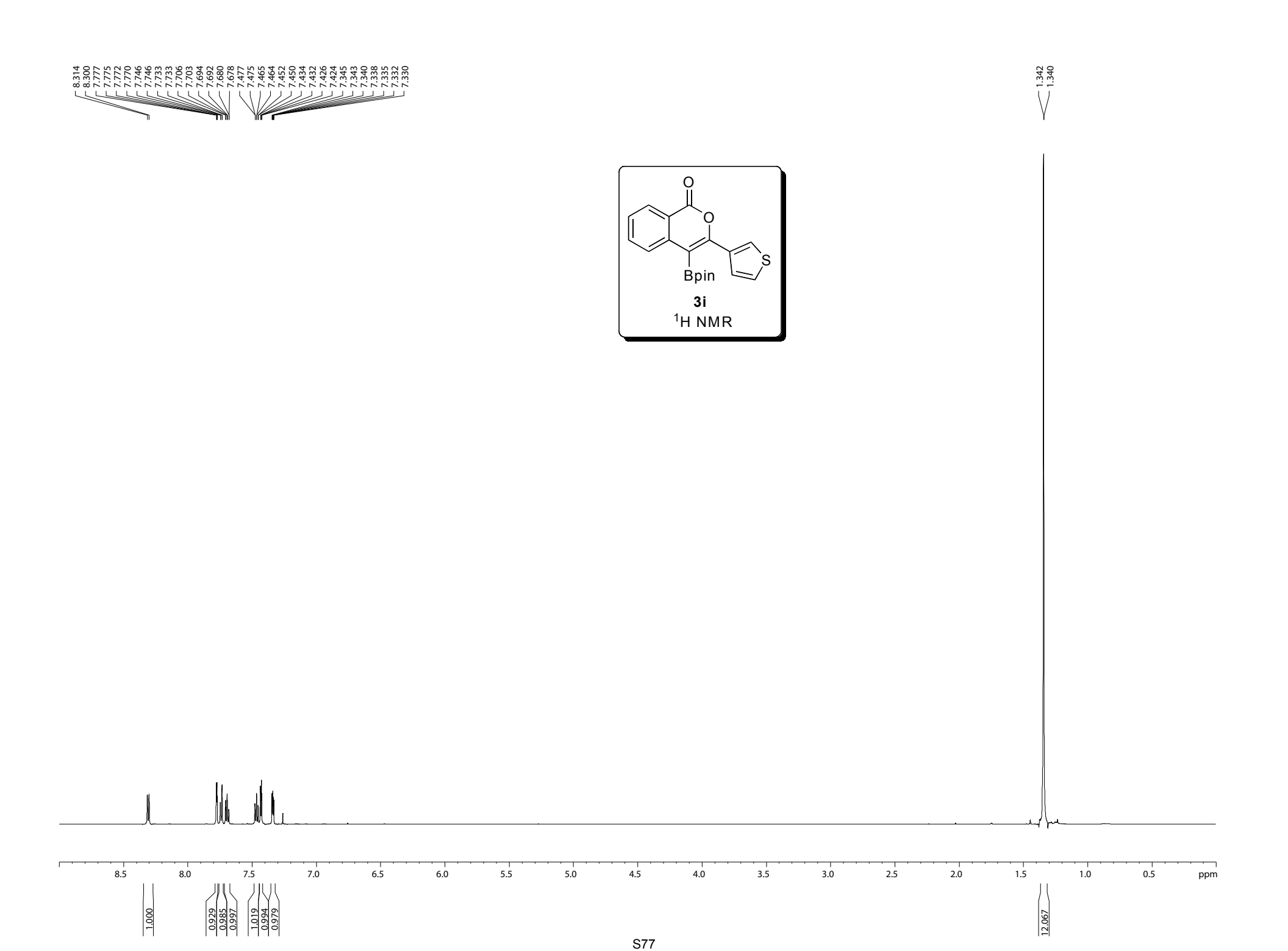
2.099
12.486


162.303
160.719
138.061
137.744
131.773
129.399
121.822
121.765
118.319
84.649
29.692
24.972
16.215
Br
O
O
CN
Bpin
3h
13C NMR
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


30.602
Br
O
O
CN
Bpin
3h
11B NMR
45
40
35
30
25
20
15
10
5
ppm


8.314
8.300
7.777
7.775
7.772
7.770
7.746
7.746
7.733
7.733
7.706
7.703
7.694
7.692
7.680
7.678
7.477
7.475
7.465
7.464
7.452
7.450
7.434
7.432
7.426
7.424
7.345
7.343
7.340
7.338
7.335
7.332
7.330
1.342
1.340
O
O
S
Bpin
3i
1H NMR
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.000
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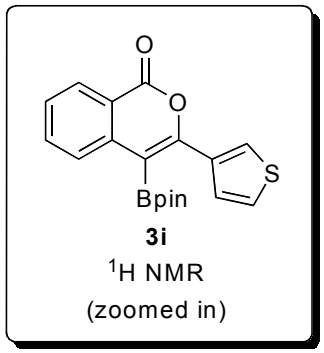
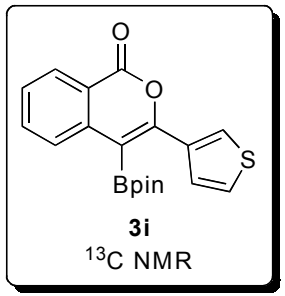
0.985
0.997
1.019
0.994
0.979
12.067



3i

^{1}H NMR

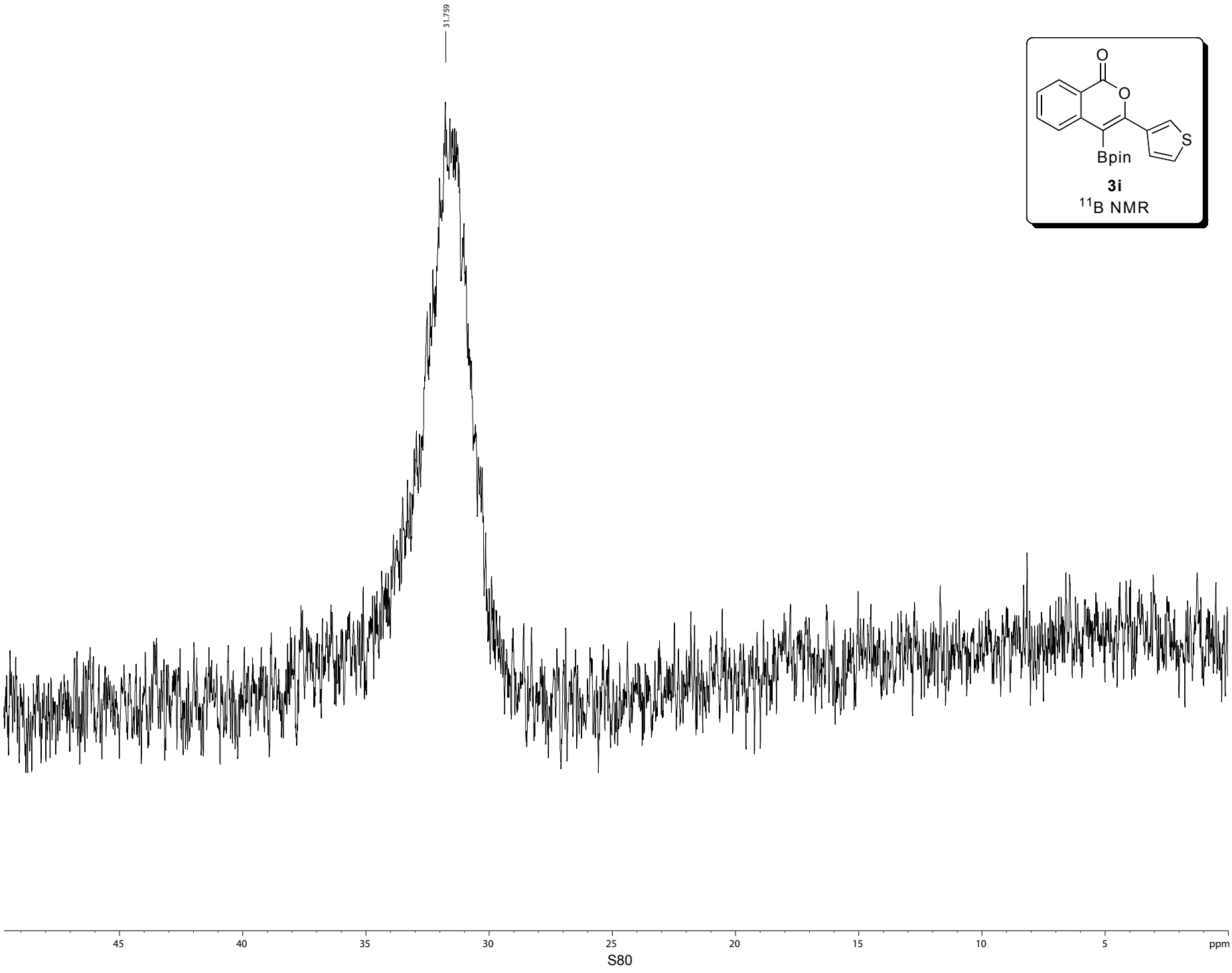
(zoomed in)

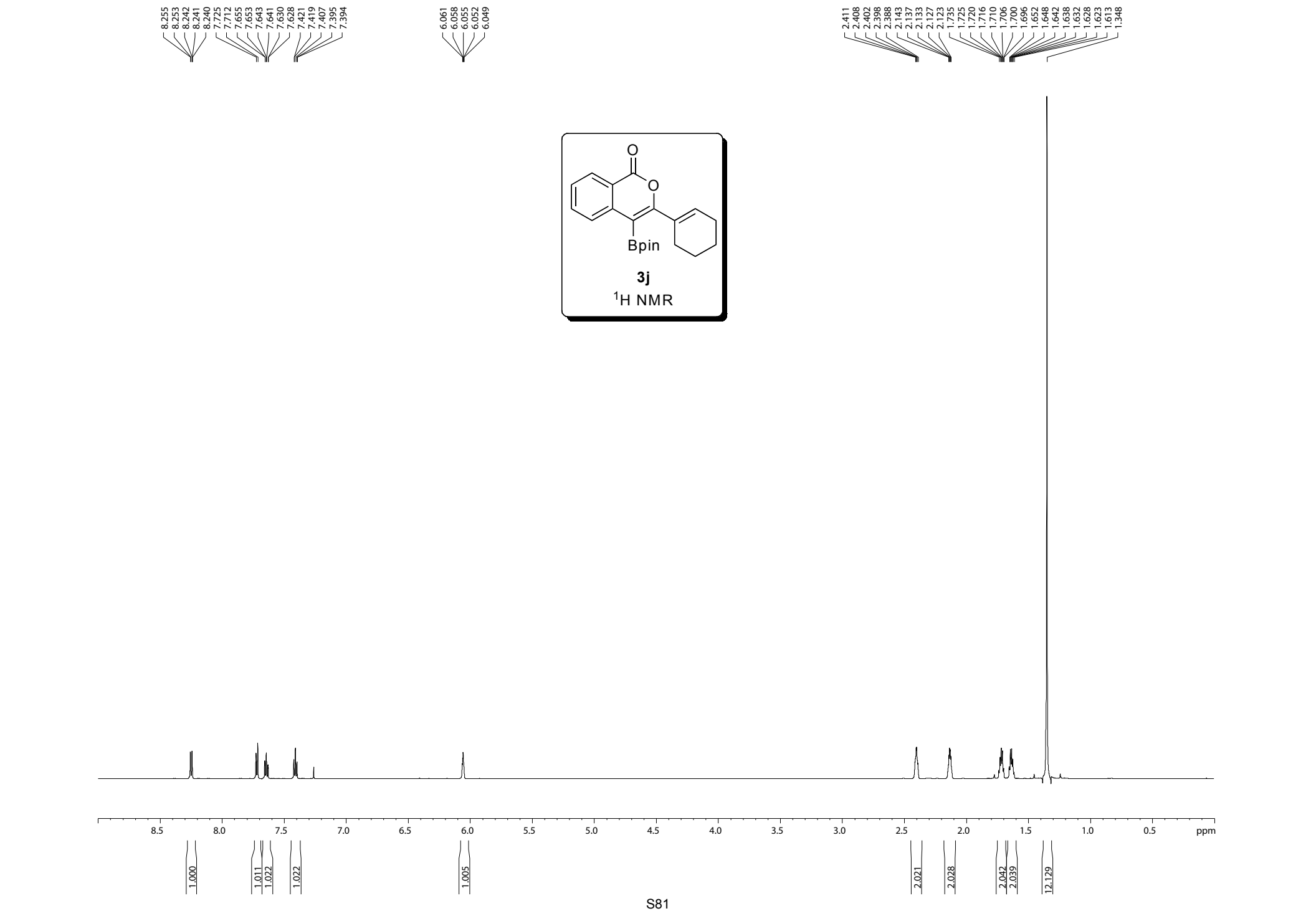

O
O
S
Bpin

3i

^{13}C NMR

162.309
154.542
139.620
135.891
134.837
129.684
127.900
127.713
127.183
126.372
125.759
120.235
84.699
25.082
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


31.759
O
O
S
Bpin
3i
11B NMR
45
40
35
30
25
20
15
10
5
ppm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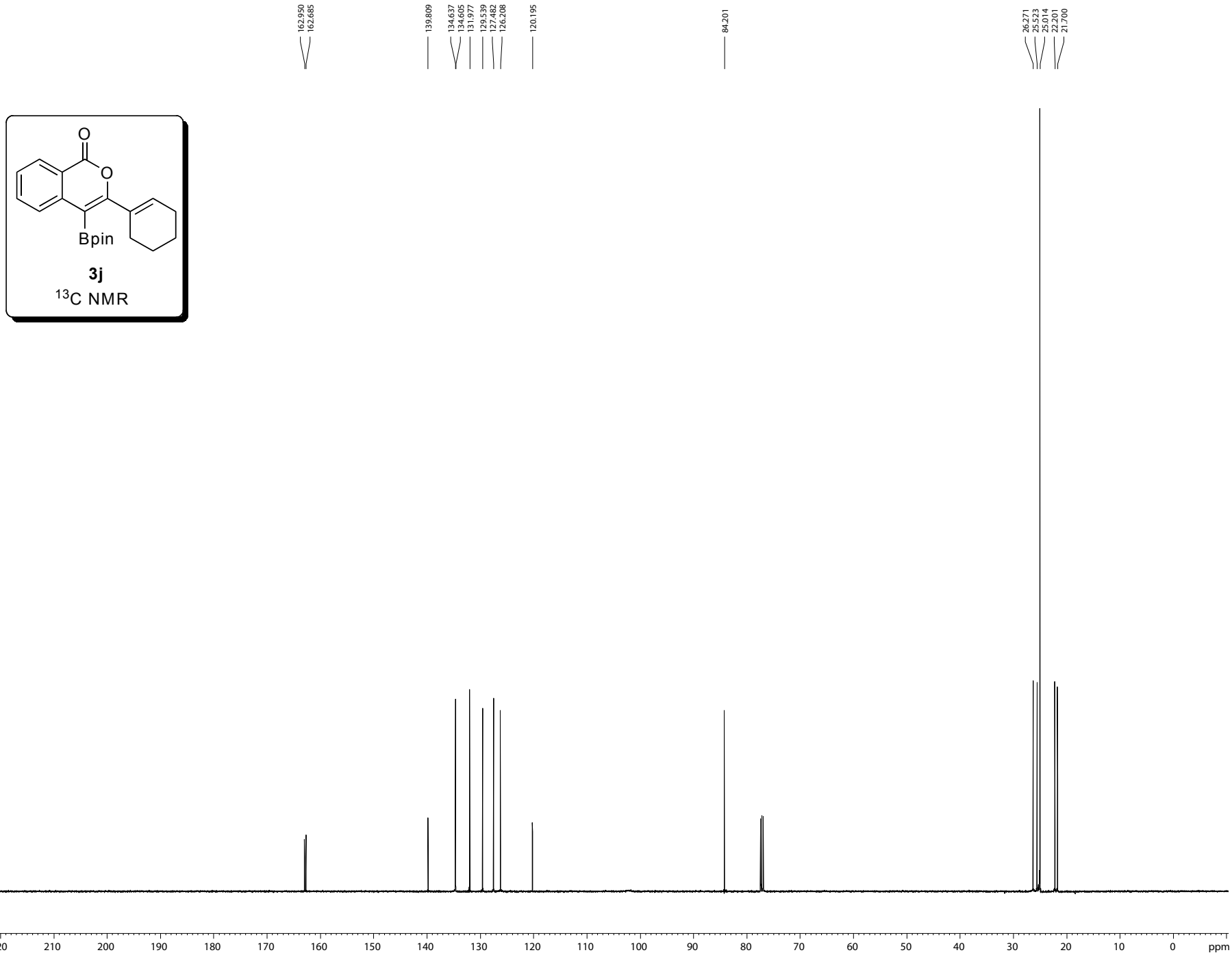
8.253
8.242
8.241
8.240
7.725
7.712
7.655
7.653
7.643
7.641
7.630
7.628
7.421
7.419
7.407
7.395
7.394
6.061
6.058
6.055
6.052
6.049
2.411
2.408
2.402
2.398
2.388
2.143
2.137
2.133
2.127
2.123
1.735
1.725
1.720
1.716
1.710
1.706
1.700
1.696
1.652
1.648
1.642
1.638
1.632
1.628
1.623
1.613
1.348
O
O
Bpin
3j
1H NMR
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.000
1.011
1.022
1.022
1.005
2.021
2.028
2.042
2.039
12.129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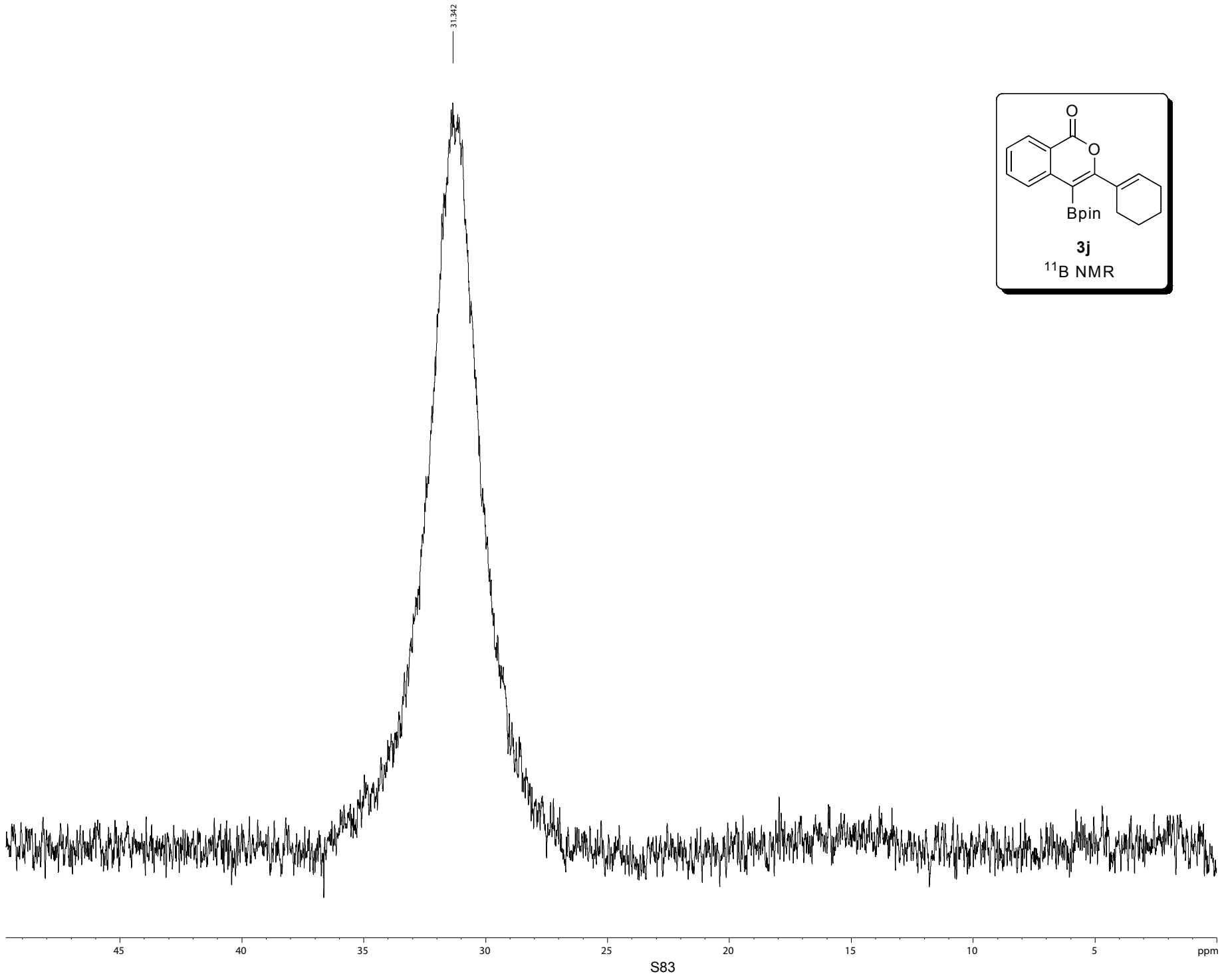
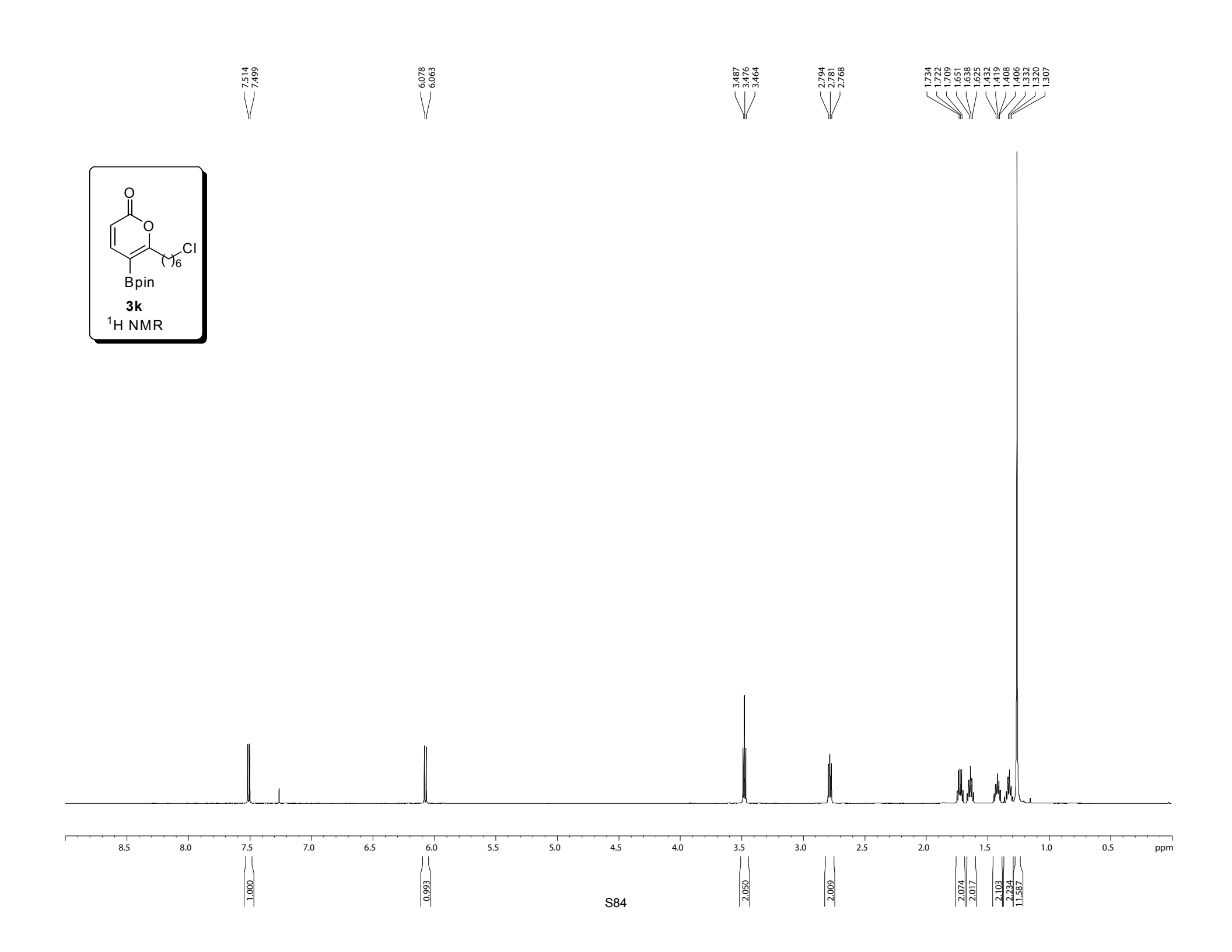
162.685
139.809
134.637
134.605
131.977
129.539
127.482
126.208
120.195
84.201
26.271
25.523
25.014
22.201
21.700
O
O
Bpin
3j
13C NMR
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


31.342
O
O
Bpin
3j
11B NMR
45
40
35
30
25
20
15
10
5
ppm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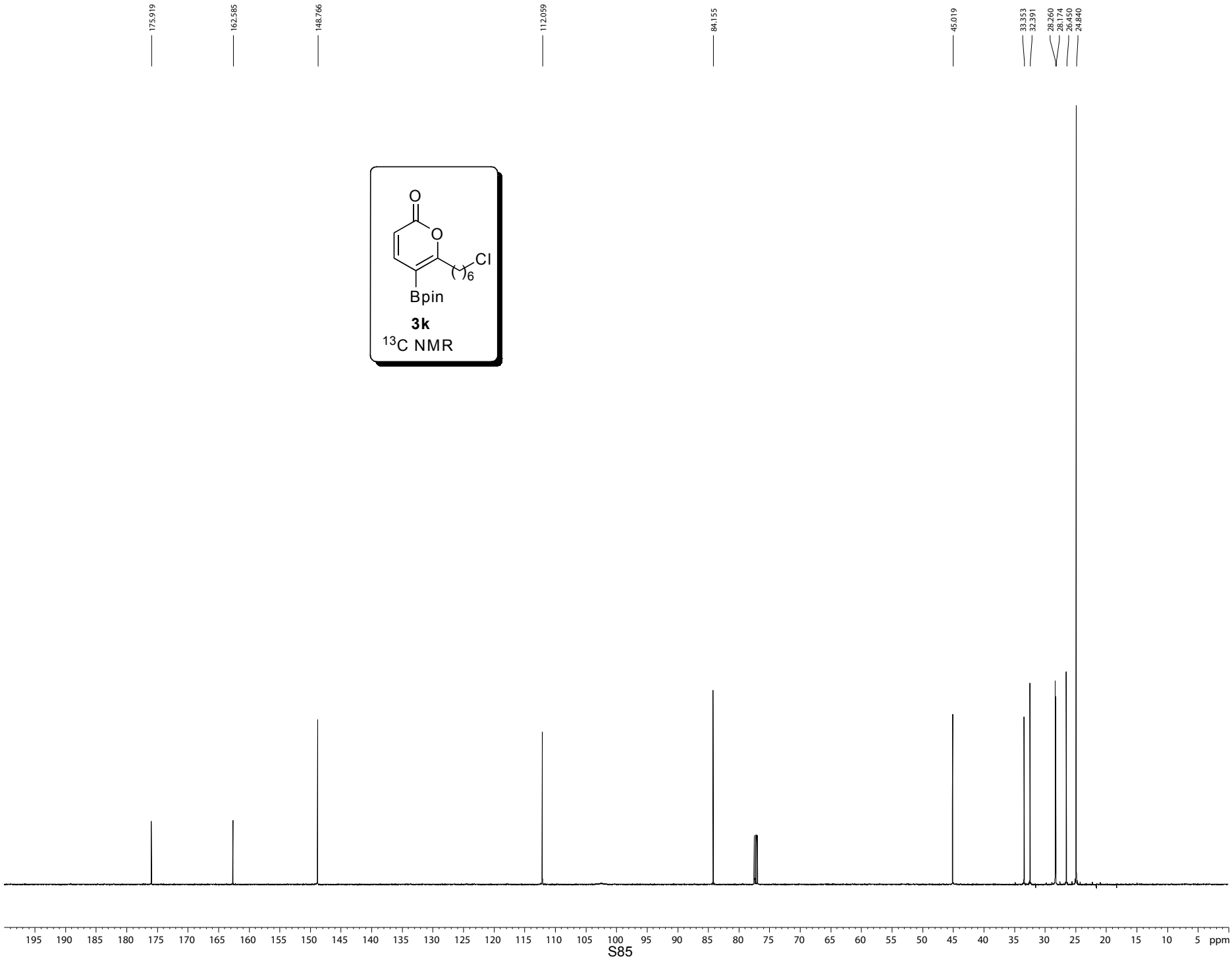
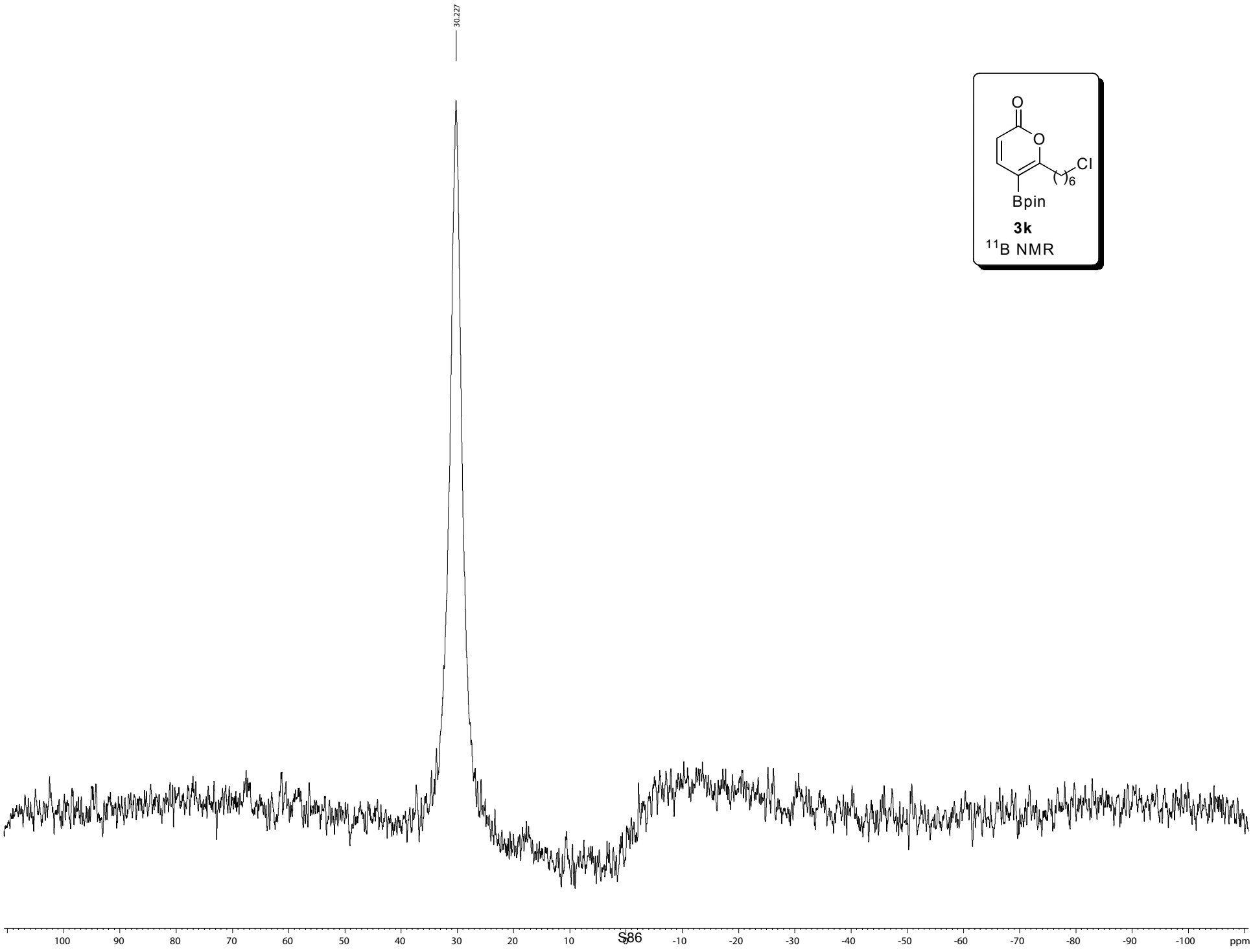
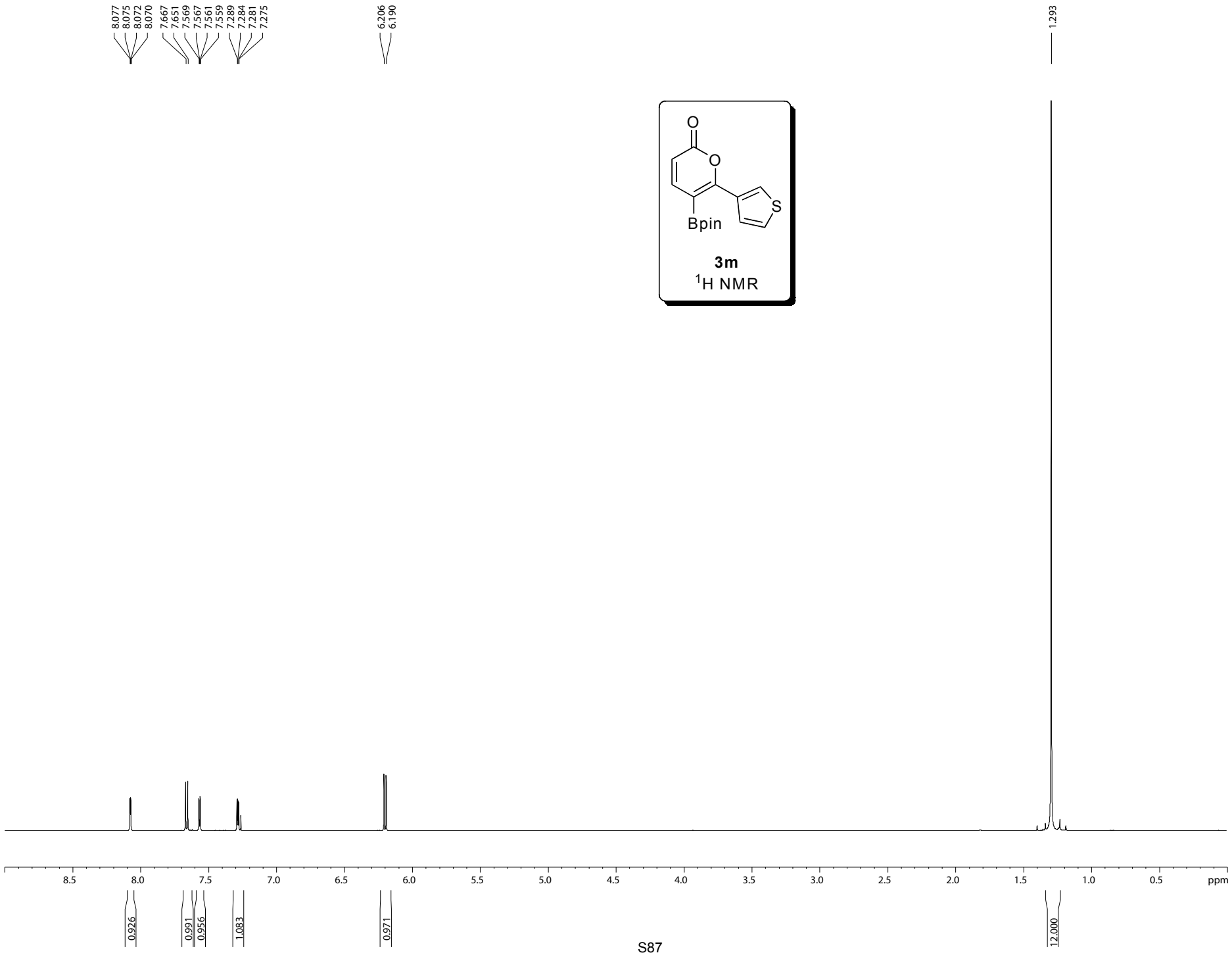
7.499
6.078
6.063
3.487
3.476
3.464
2.794
2.781
2.768
1.734
1.722
1.709
1.651
1.638
1.625
1.432
1.419
1.408
1.406
1.332
1.320
1.307
O
O
Cl
6
Bpin
3k
1H NMR
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.000
0.993
2.050
2.009
2.074
2.017
2.103
2.234
11.587


175.919
162.585
148.766
112.059
84.155
45.019
33.353
32.391
28.260
28.174
26.450
24.840
O
O
Cl
6
Bpin
3k
13C NMR
195 190 185 180 175 170 165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 ppm


30.227
O
O
Cl
6
Bpin
3k
11B NMR
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
ppm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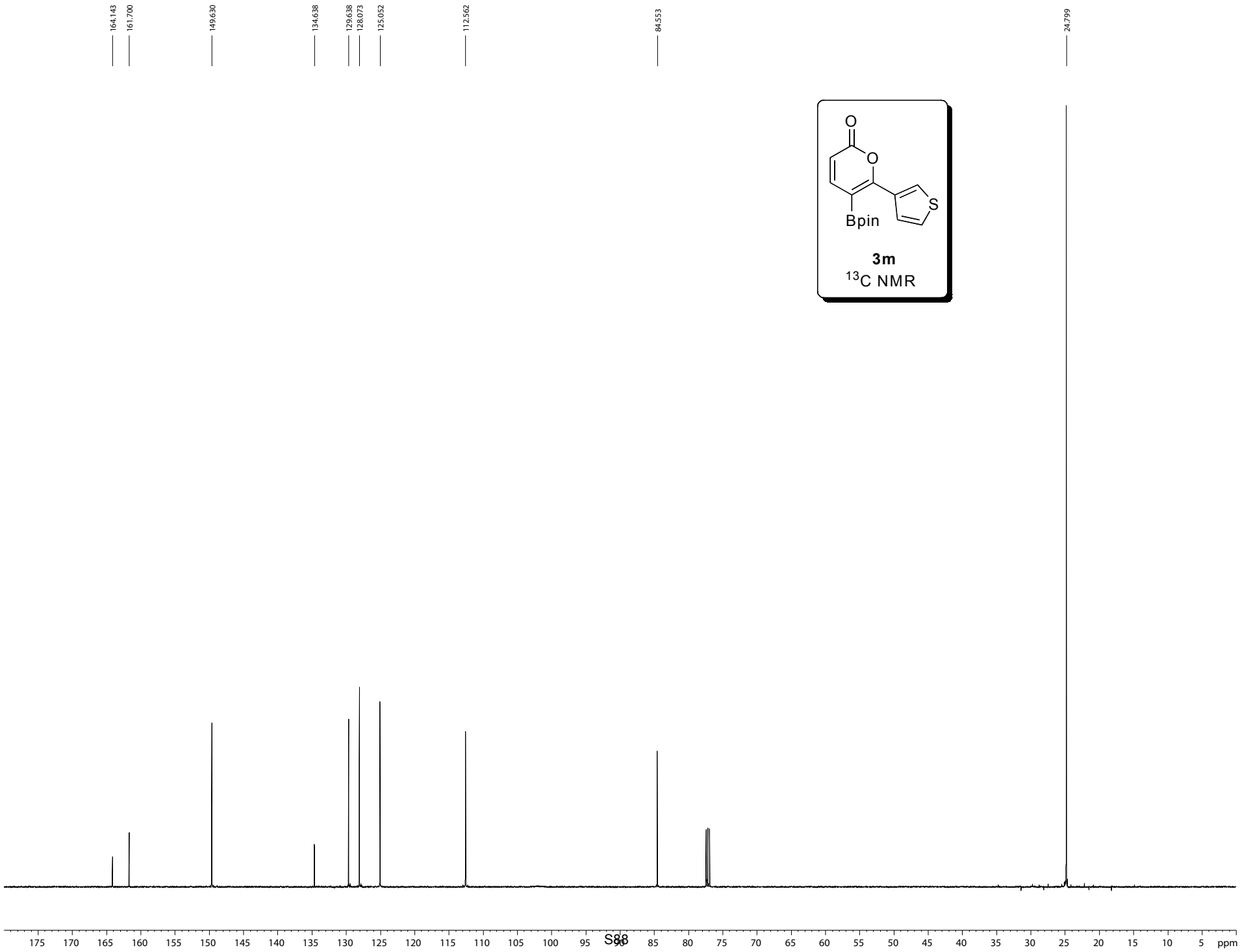
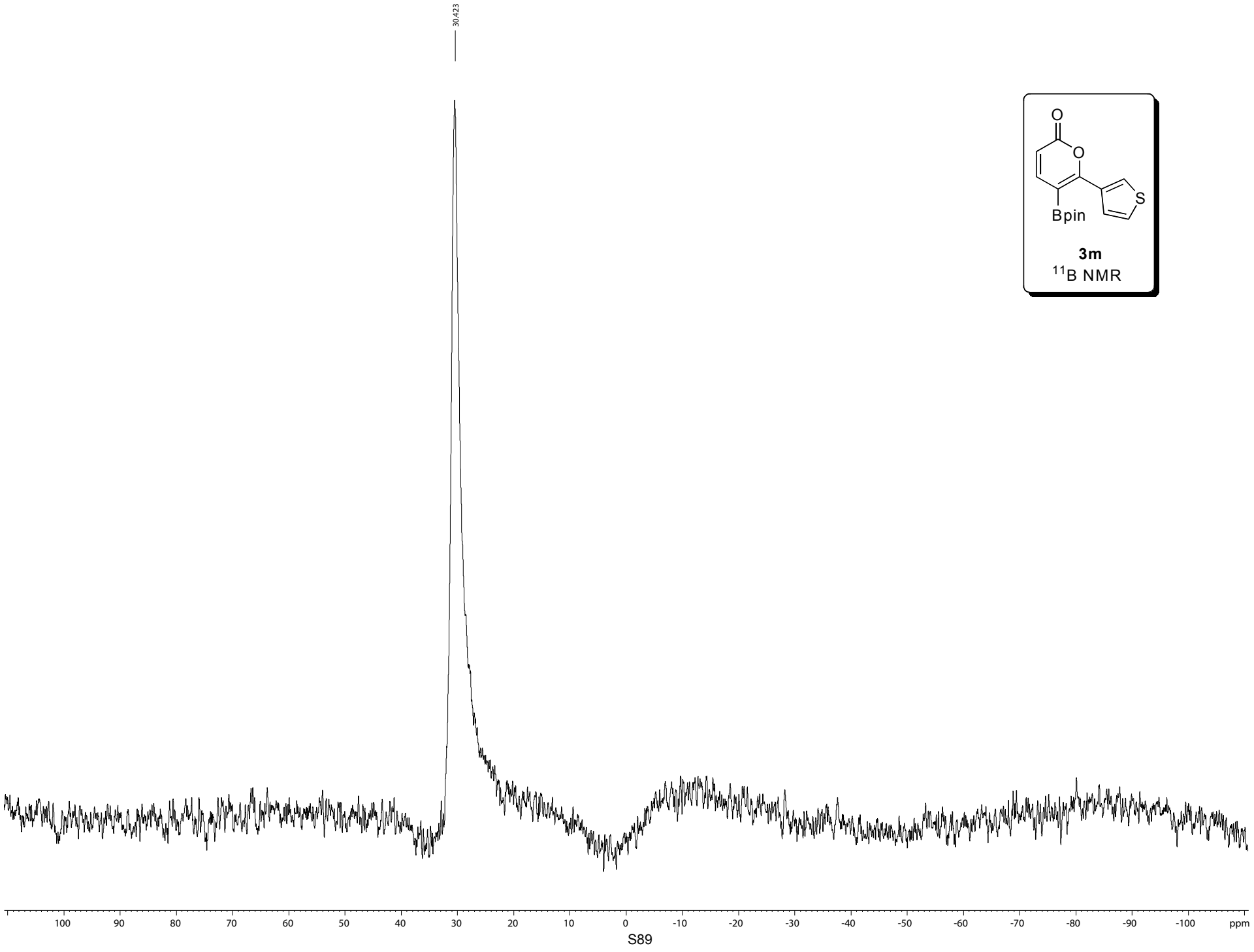
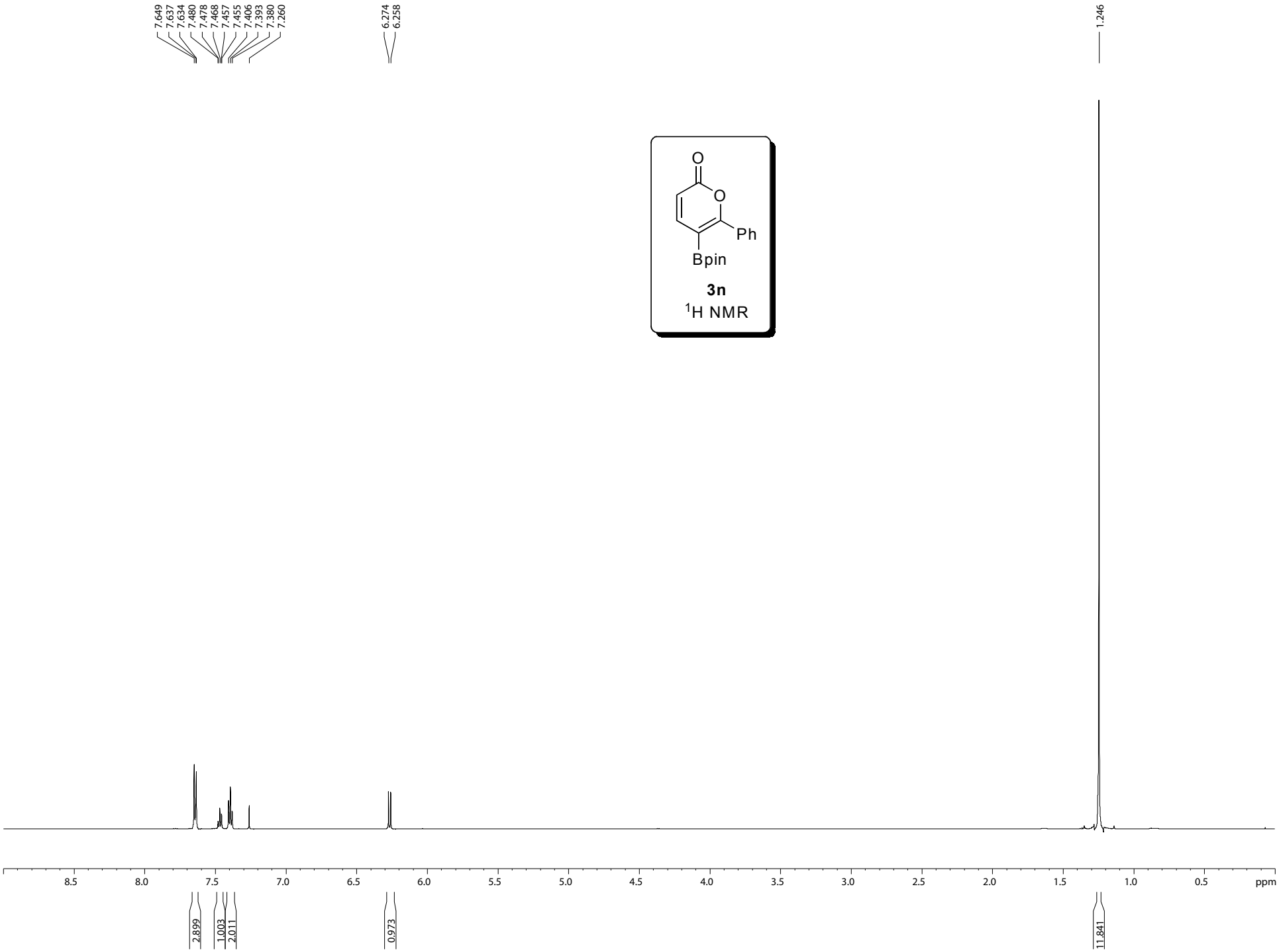
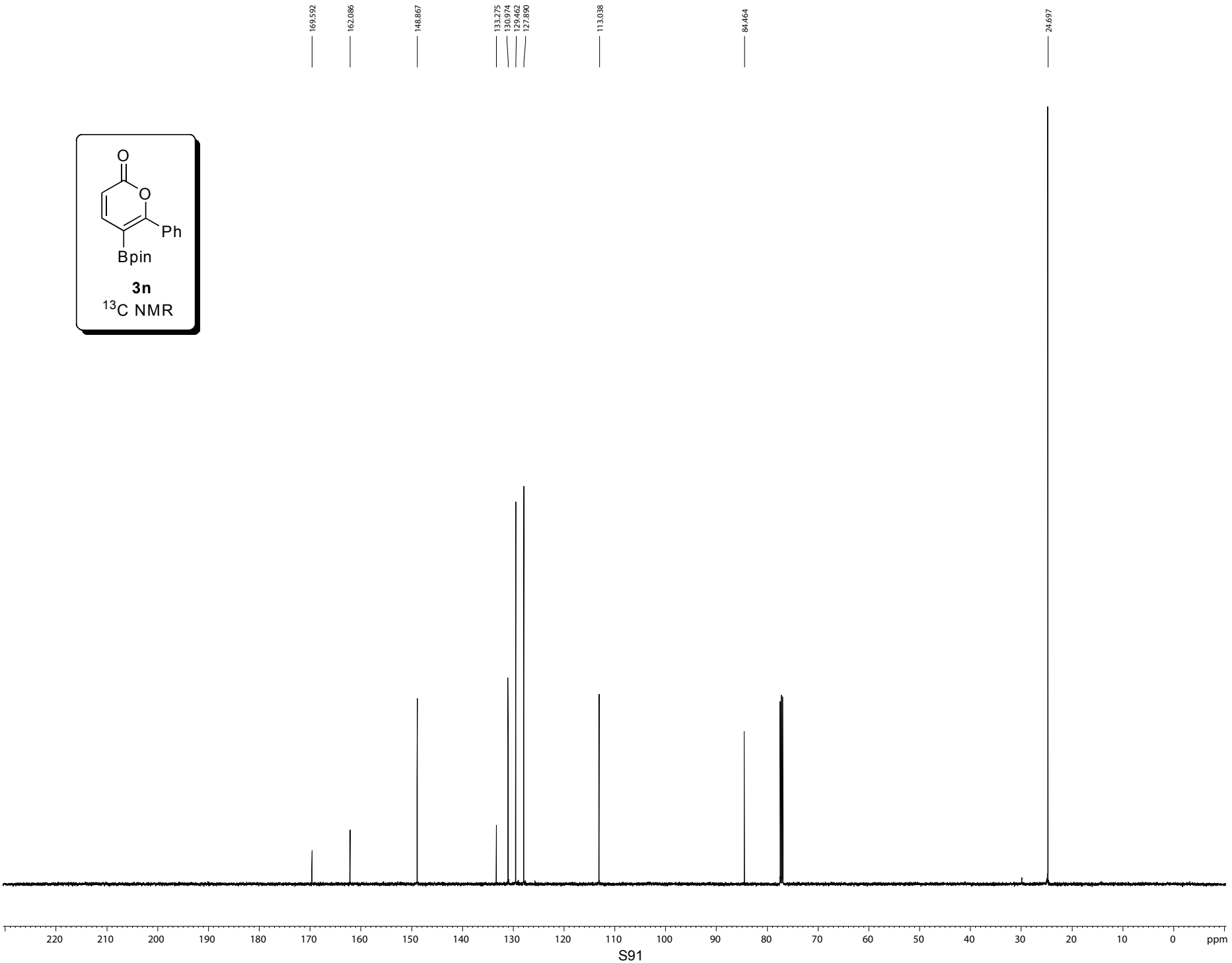
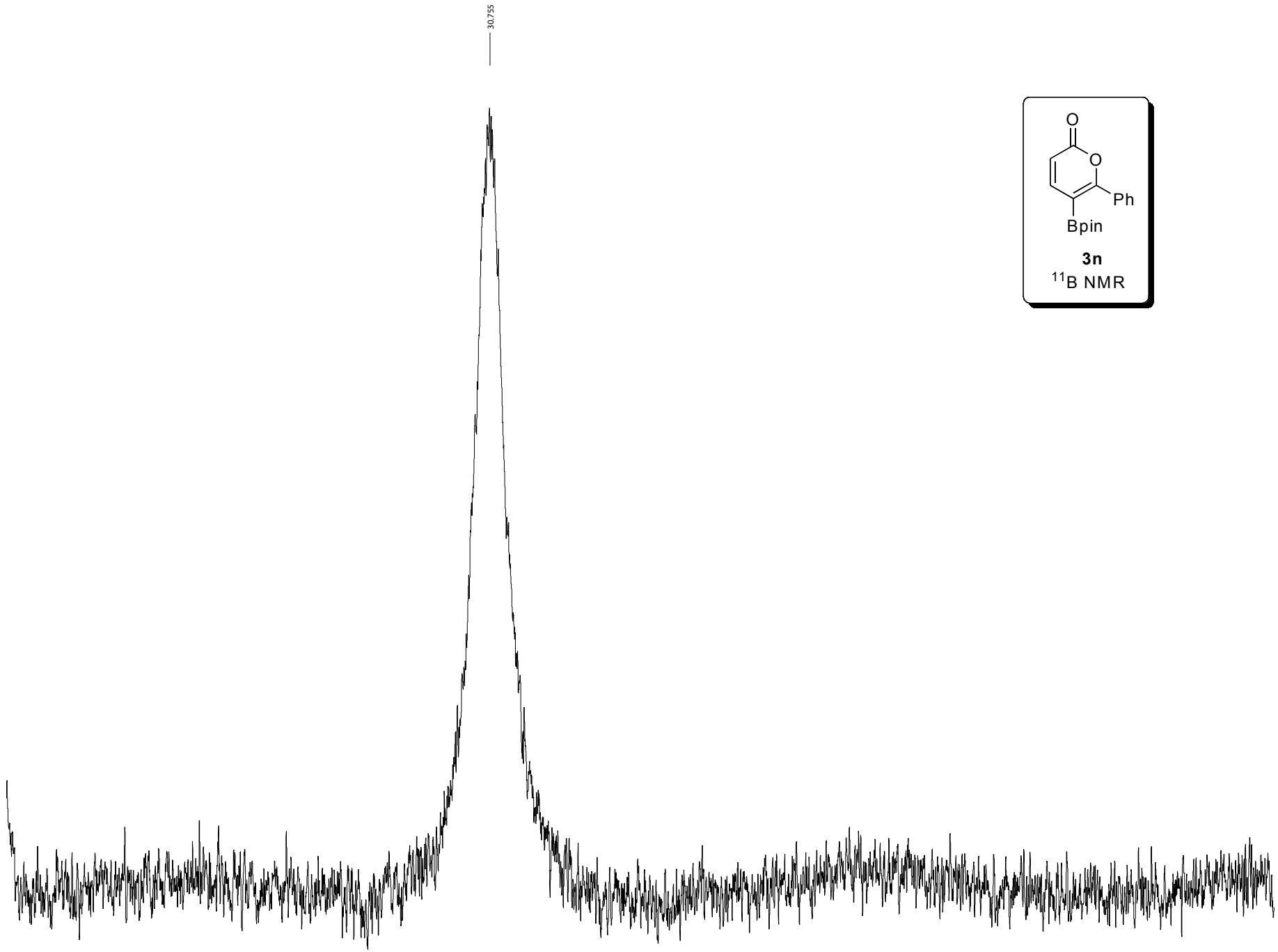
8.075
8.072
8.070
7.667
7.651
7.569
7.567
7.561
7.559
7.289
7.284
7.281
7.275
6.206
6.190
1.293
O
O
S
Bpin
3m
1H NMR
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
0.926
0.991
0.956
1.083
0.971
12.000

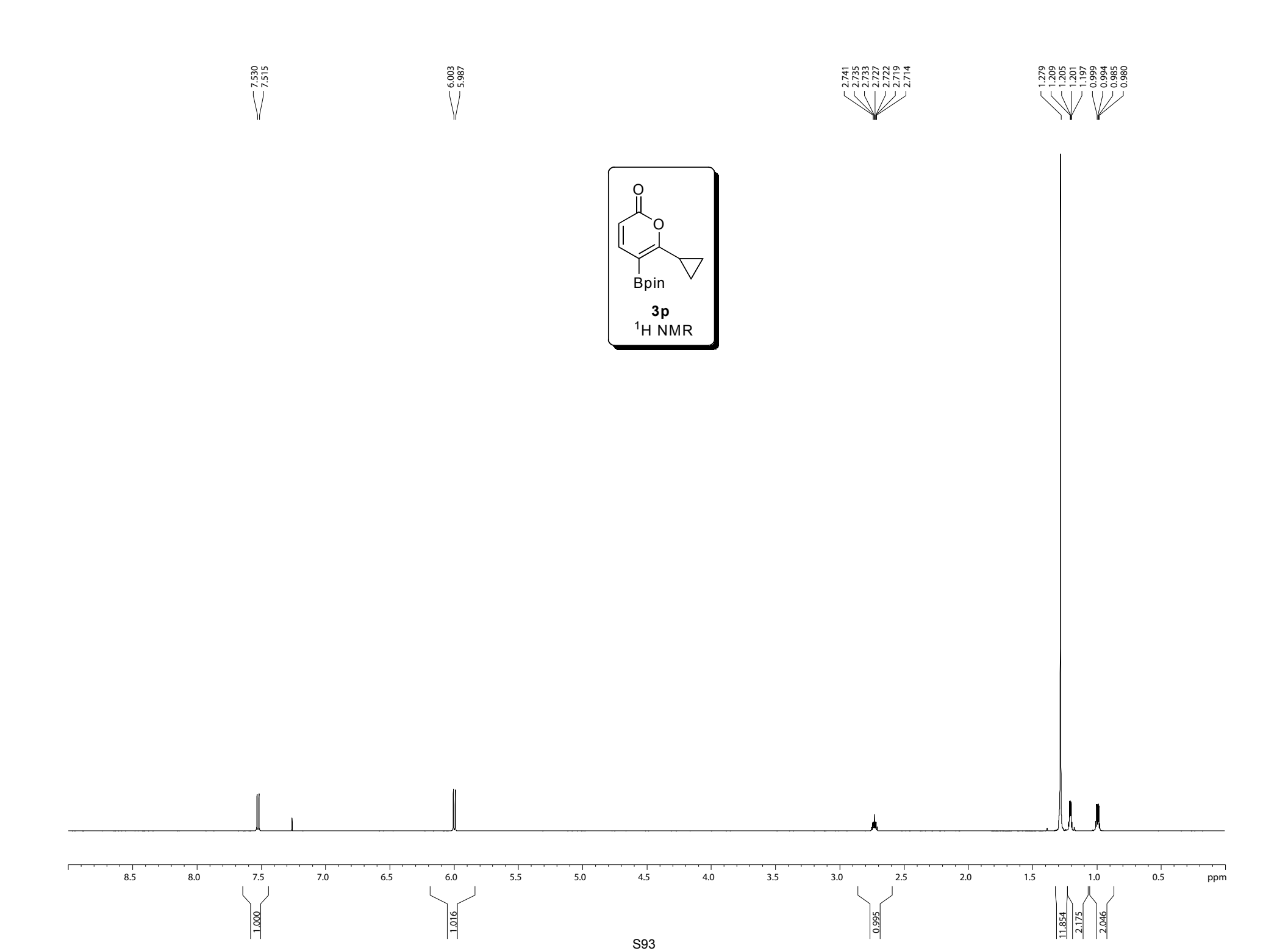

164.143
161.700
149.630
134.638
129.638
128.073
125.052
112.562
84.553
24.799
O
O
S
Bpin
3m
13C NMR
175 170 165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 ppm

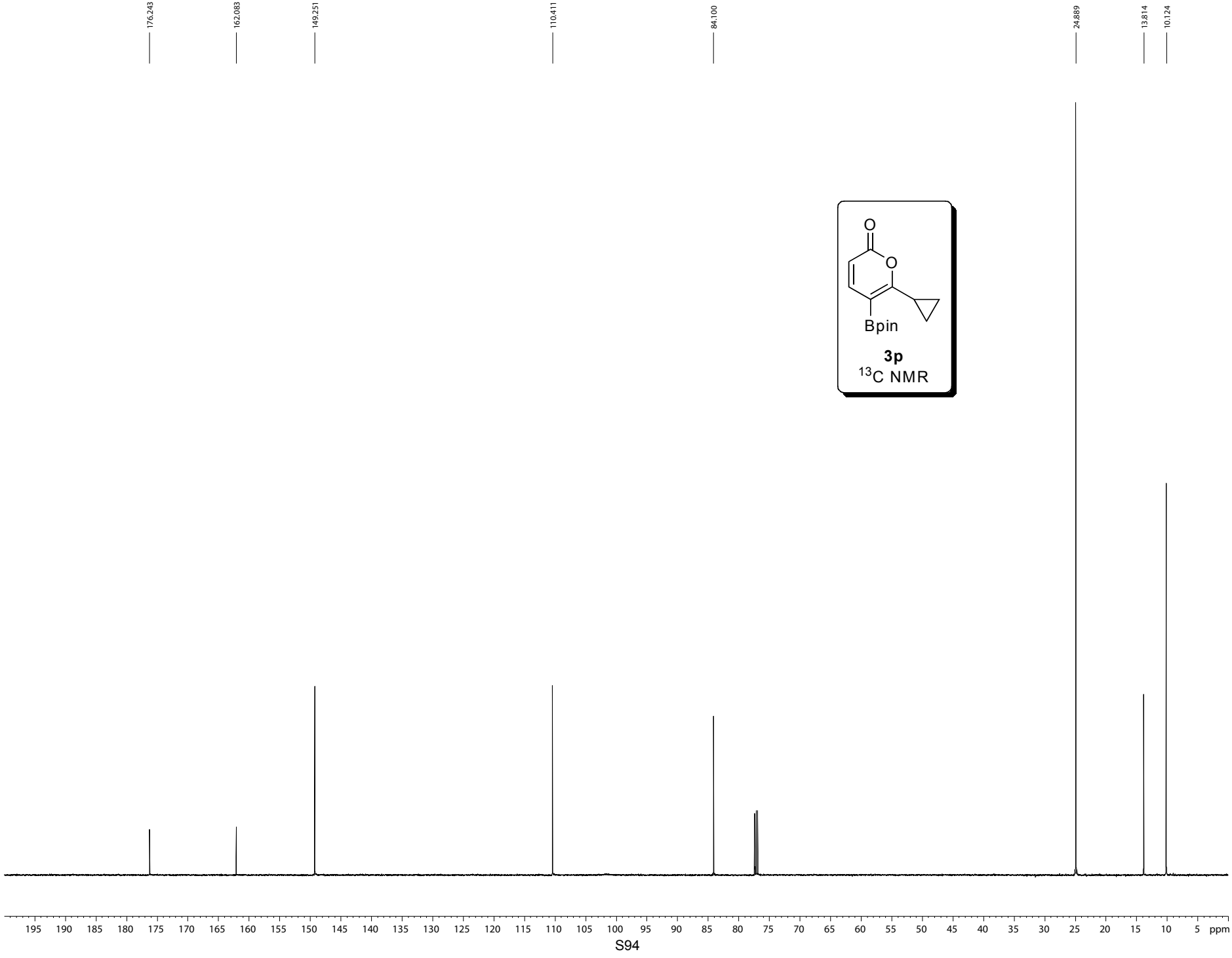

30.423
O
O
S
Bpin
3m
11B NMR
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
ppm

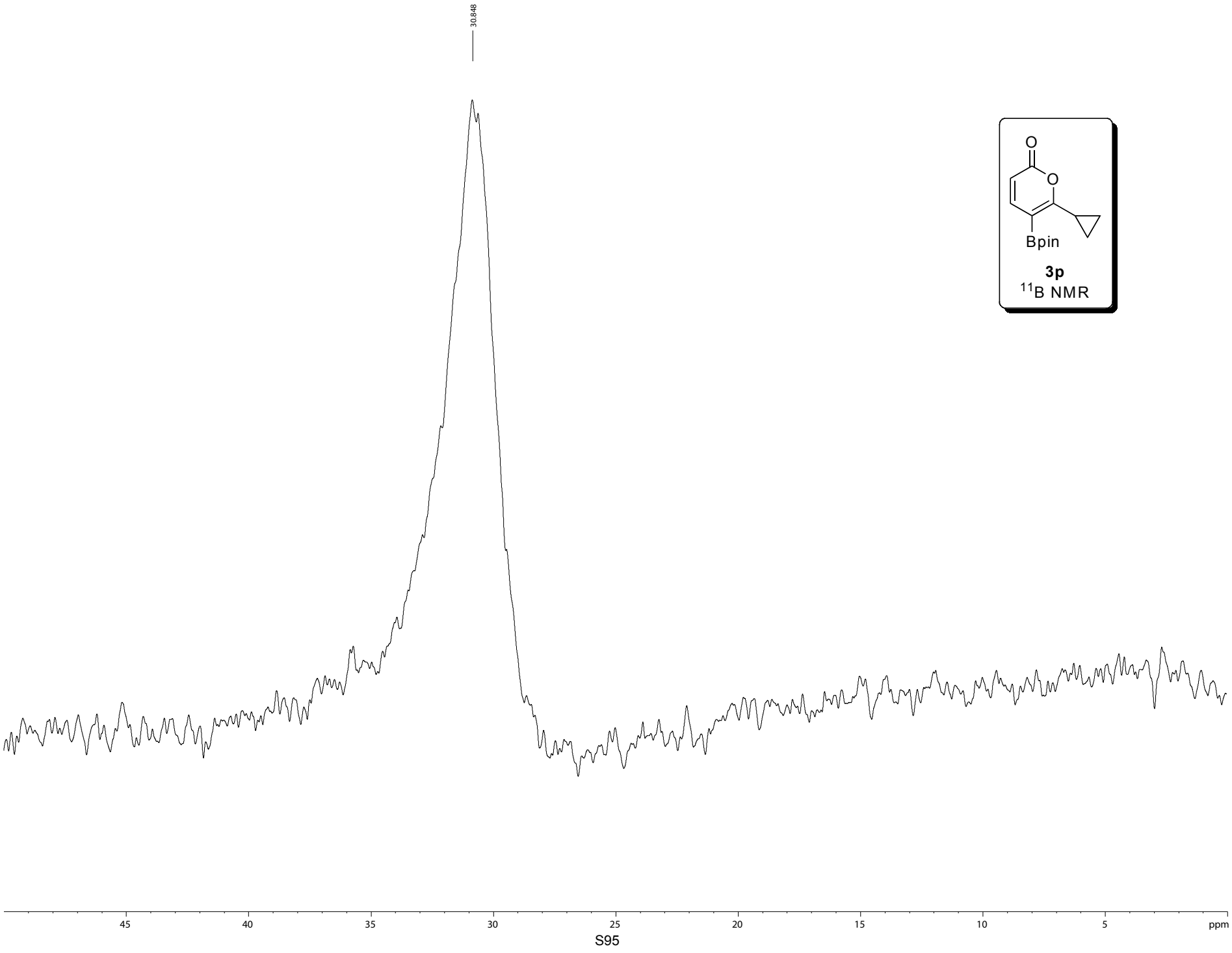

7.649
7.637
7.634
7.480
7.478
7.468
7.457
7.455
7.406
7.393
7.380
7.260
6.274
6.258
1.246
O
O
Ph
Bpin
3n
1H NMR
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.899
1.003
2.011
0.973
11.841

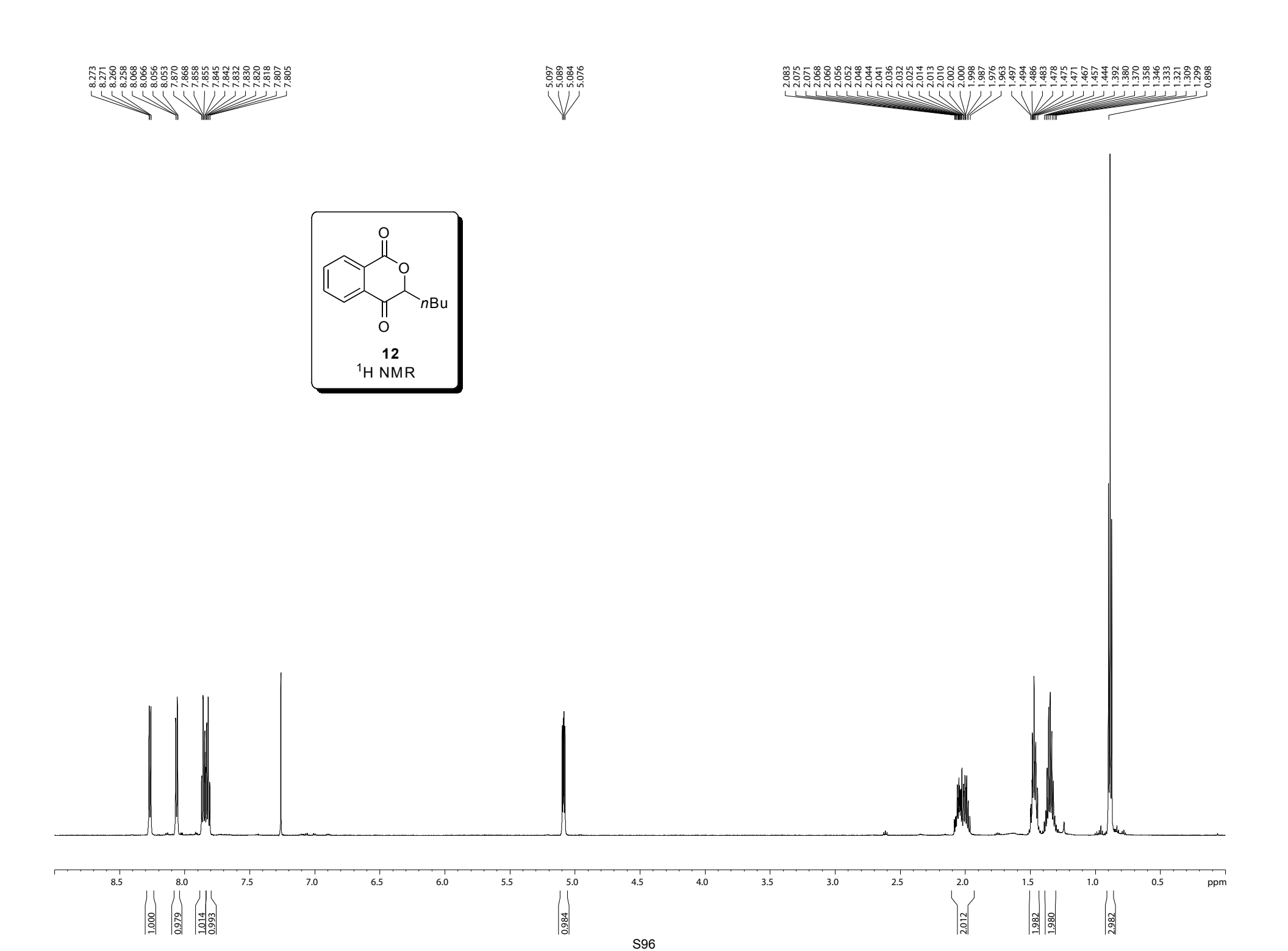

169.592
162.086
148.867
133.275
130.974
129.462
127.890
113.038
84.464
24.697
O
O
Ph
Bpin
3n
13C NMR
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

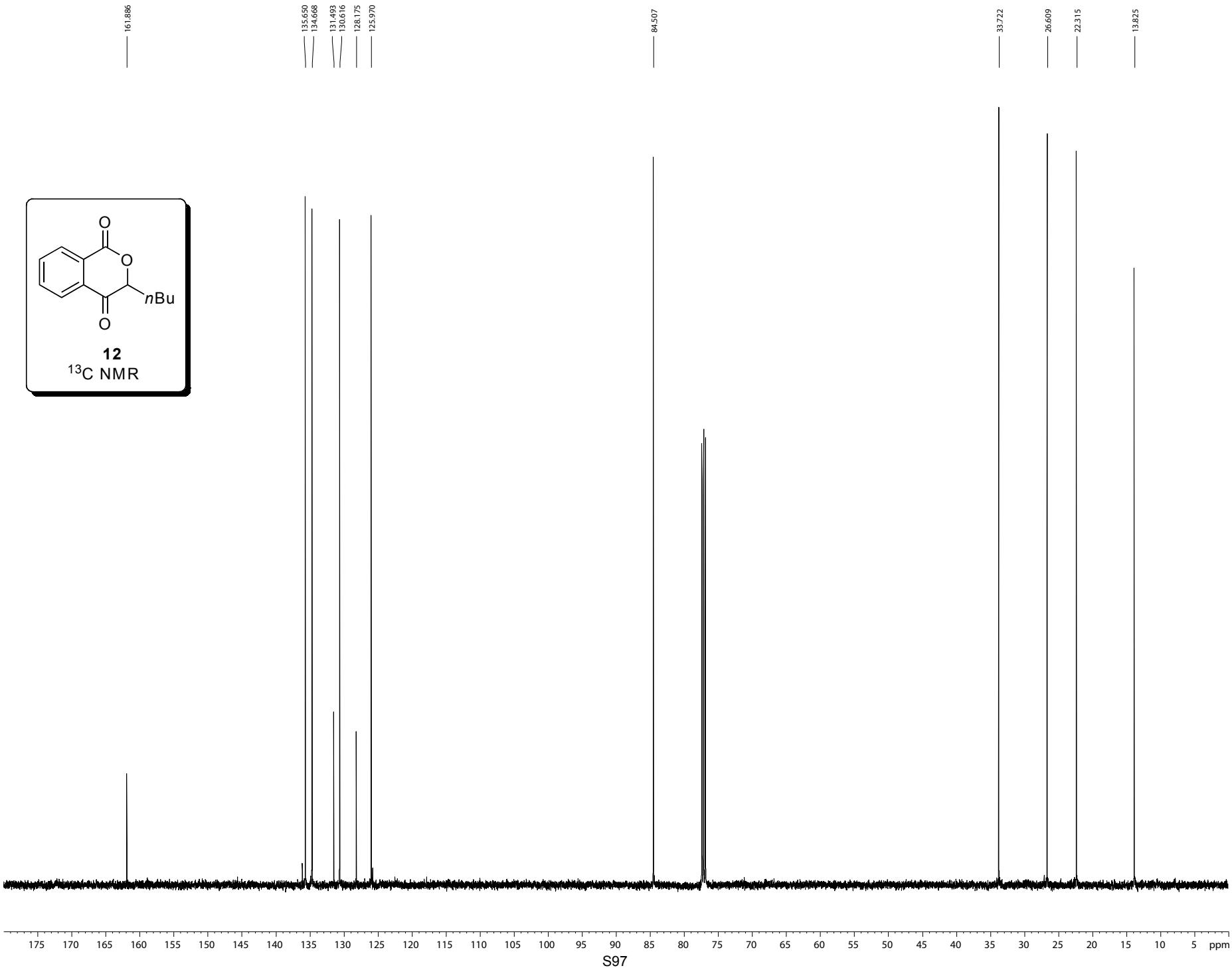

30.755
O
O
Ph
Bpin
3n
11B NMR
45
40
35
30
25
20
15
10
5
ppm

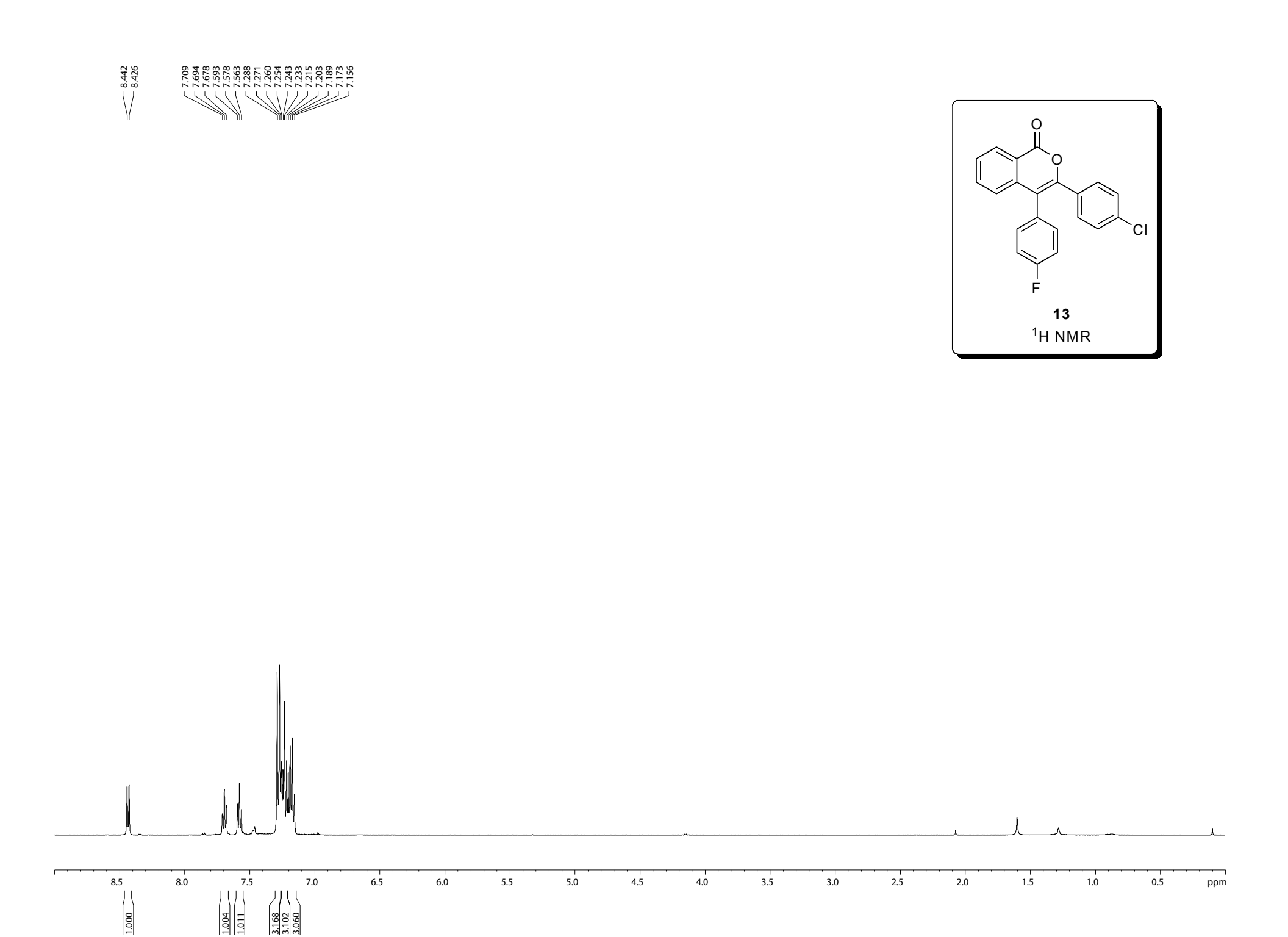

7.530
7.515
6.003
5.987
2.741
2.735
2.733
2.727
2.722
2.719
2.714
1.279
1.209
1.205
1.201
1.197
0.999
0.994
0.985
0.980
O
O
Bpin
3p
1H NMR
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.000
1.016
0.995
11.854
2.175
2.046

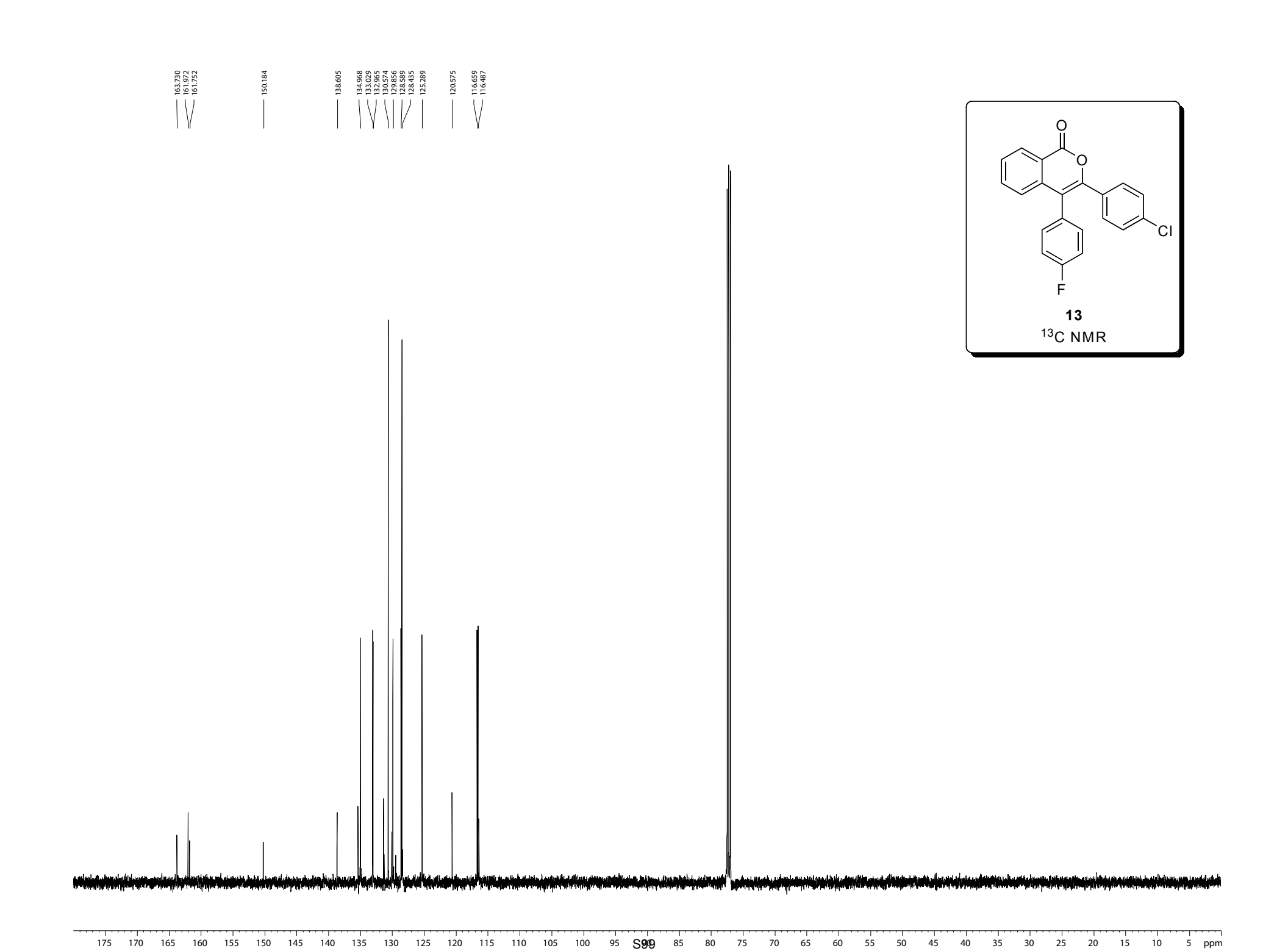

176.243
162.083
149.251
110.411
84.100
24.889
13.814
10.124
O
O
Bpin
3p
13C NMR
195 190 185 180 175 170 165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 ppm

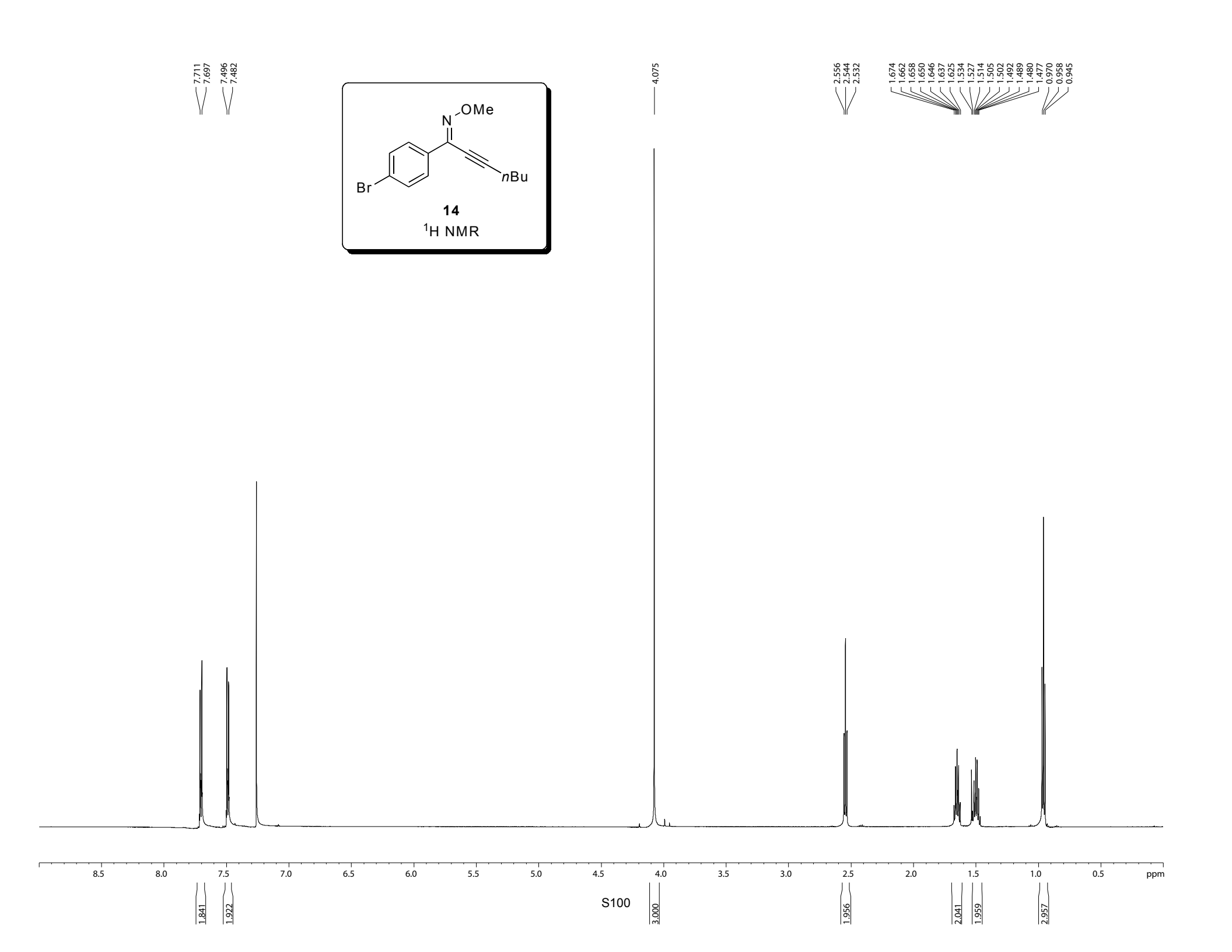

30.848
O
O
Bpin
3p
11B NMR
45
40
35
30
25
20
15
10
5
ppm


8.273
8.271
8.260
8.258
8.068
8.066
8.056
8.053
7.870
7.868
7.858
7.855
7.845
7.842
7.832
7.830
7.820
7.818
7.807
7.805
5.097
5.089
5.084
5.076
2.083
2.075
2.071
2.068
2.060
2.056
2.052
2.048
2.044
2.041
2.036
2.032
2.025
2.014
2.013
2.010
2.002
2.000
1.998
1.987
1.976
1.963
1.497
1.494
1.486
1.483
1.478
1.475
1.471
1.467
1.457
1.444
1.392
1.380
1.370
1.358
1.346
1.333
1.321
1.309
1.299
0.898
O
O
O
nBu
12
1H NMR
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.000
0.979
1.014
0.993
0.984
2.012
1.982
1.980
2.982


161.886
135.650
134.668
131.493
130.616
128.175
125.970
84.507
33.722
26.609
22.315
13.825
O
O
O
nBu
12
13C NMR
175 170 165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 ppm


8.442
8.426
7.709
7.694
7.678
7.593
7.578
7.563
7.288
7.271
7.260
7.254
7.243
7.233
7.215
7.203
7.189
7.173
7.156
O
O
Cl
F
13
1H NMR
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.000
1.004
1.011
3.168
3.102
3.060


163.730
161.972
161.752
150.184
138.605
134.968
133.029
132.965
130.574
129.836
128.589
128.435
125.289
120.575
116.659
116.487
O
O
Cl
F
13
13C NMR
175 170 165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 ppm


7.711
7.697
7.496
7.482
4.075
2.556
2.544
2.532
1.674
1.662
1.658
1.650
1.646
1.637
1.625
1.534
1.527
1.514
1.505
1.502
1.492
1.489
1.480
1.477
0.970
0.958
0.945
N
OMe
Br
nBu
14
1H NMR
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
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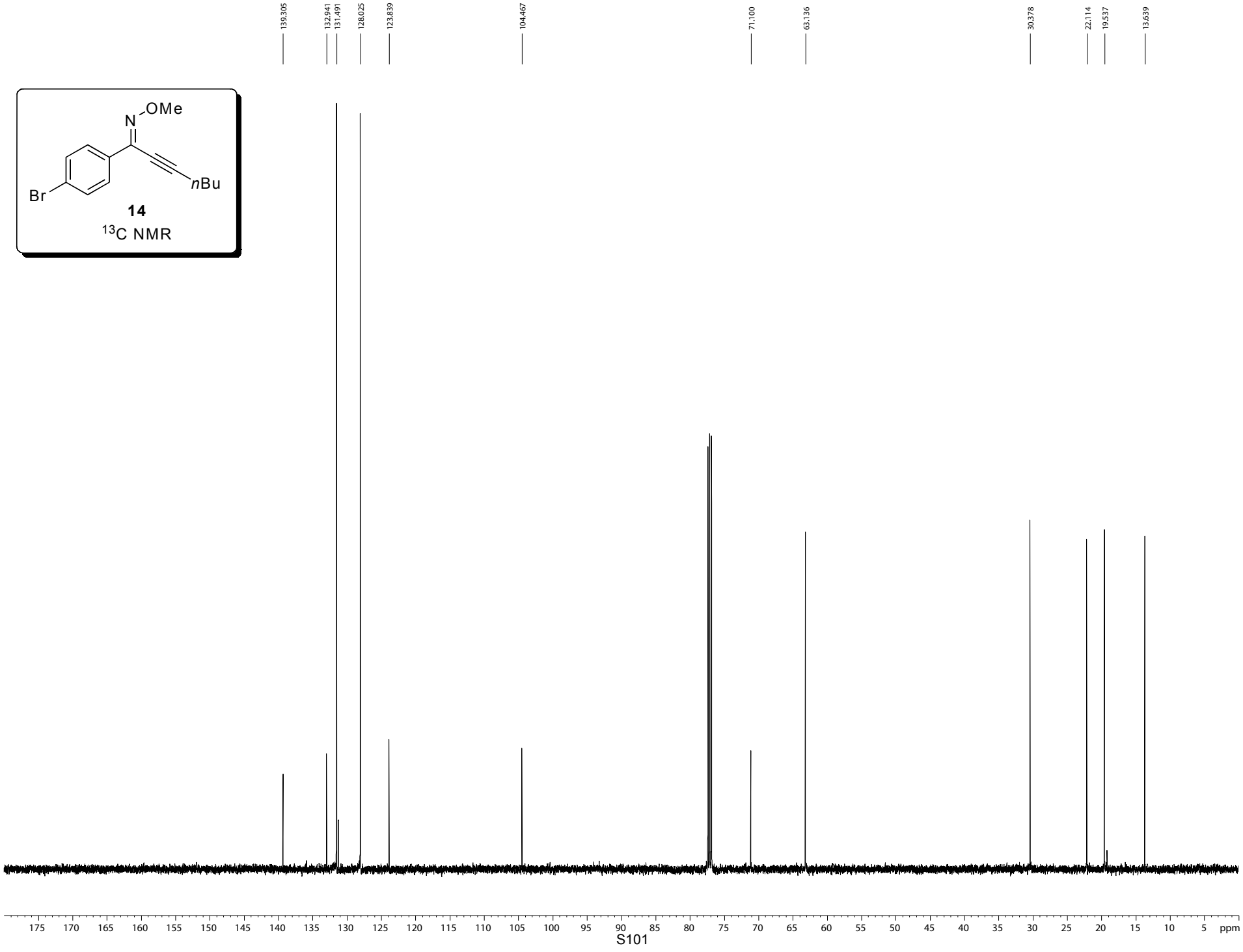
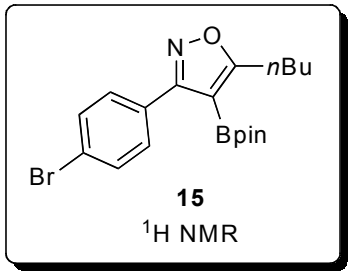
1.922
3.000
1.956
2.041
1.959
2.957

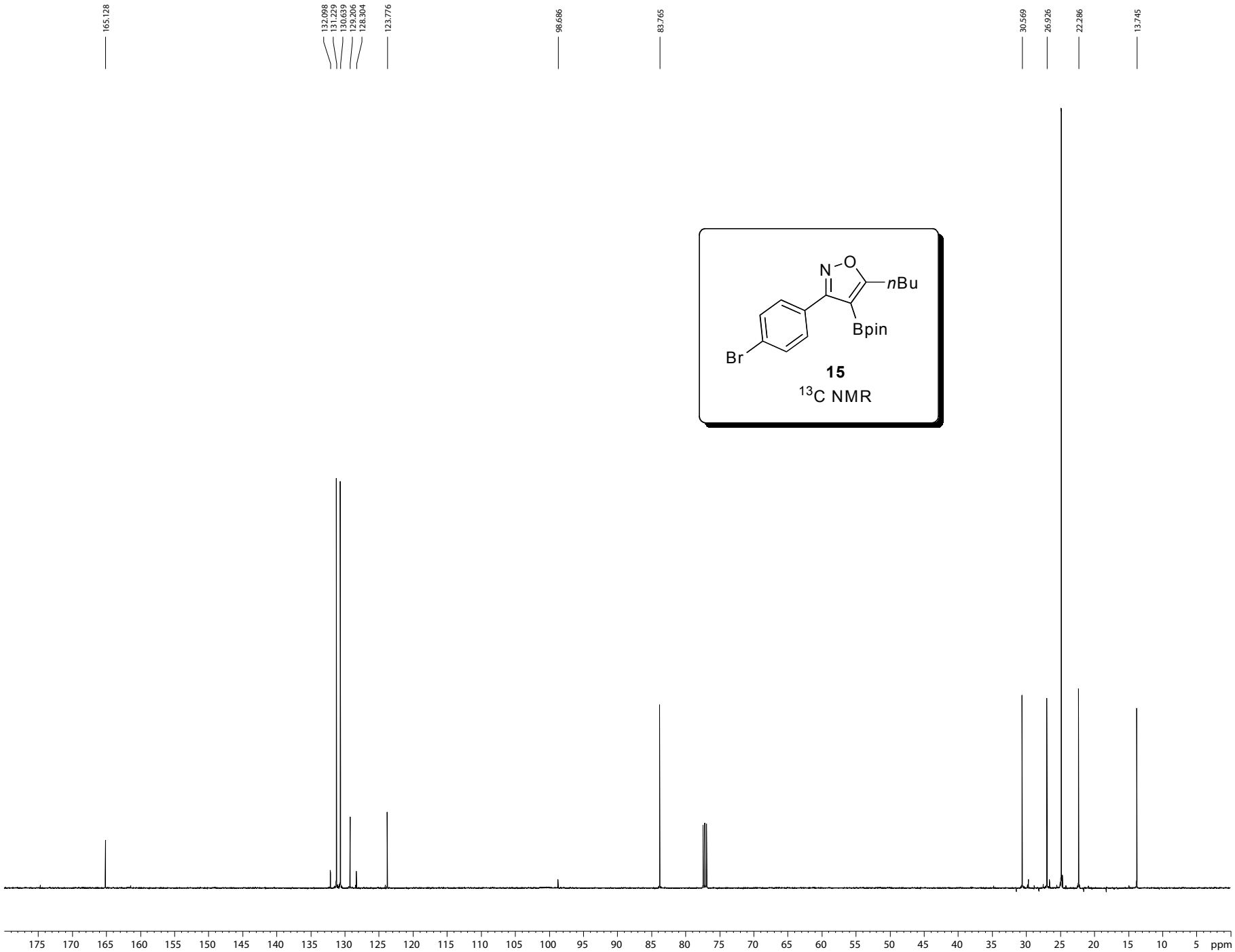

139.305
132.941
131.491
128.025
123.839
104.467
71.100
63.136
30.378
22.114
19.537
13.639
N
OMe
Br
nBu
14
13C NMR
175 170 165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 ppm

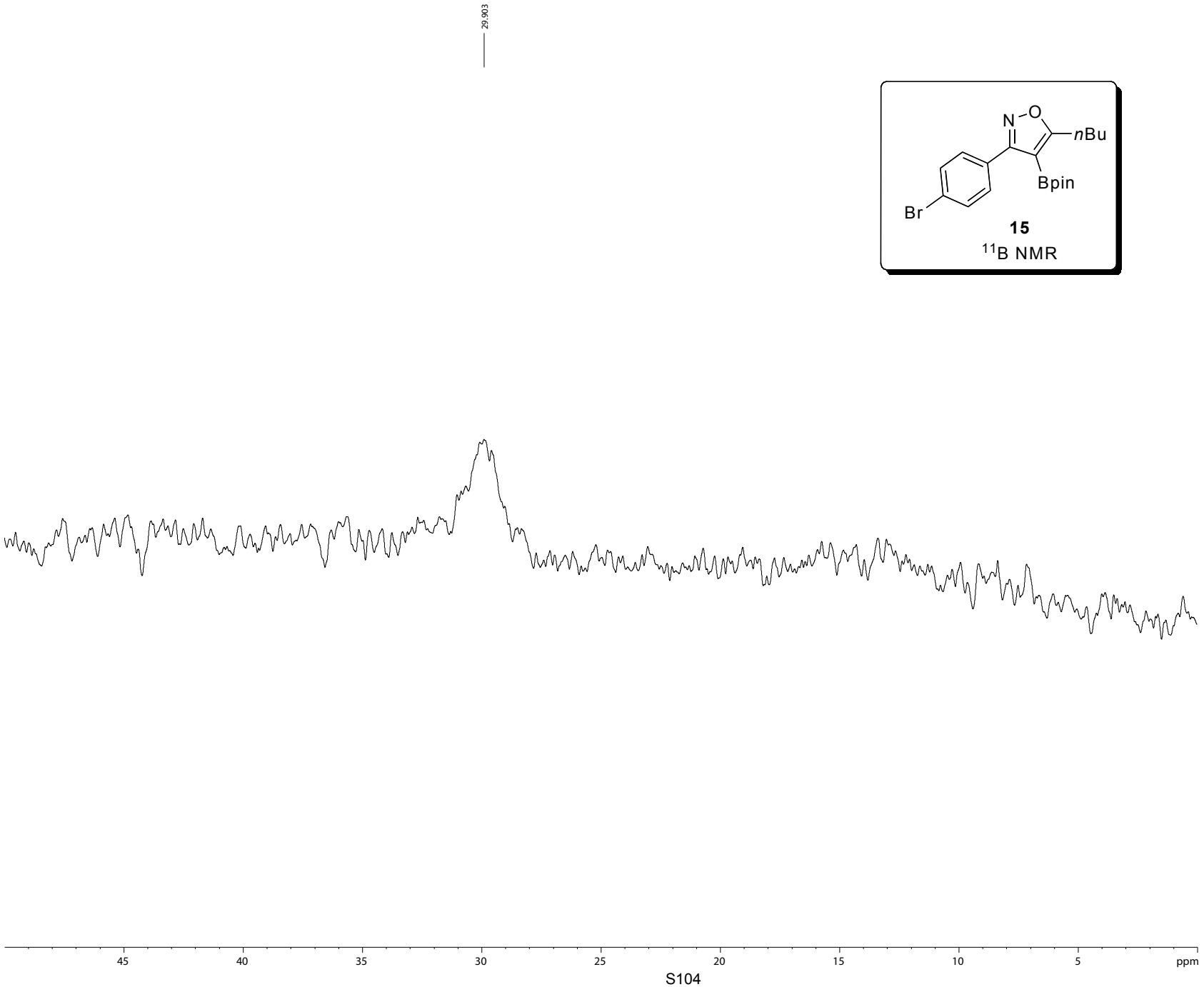

N
O
nBu
Bpin
Br

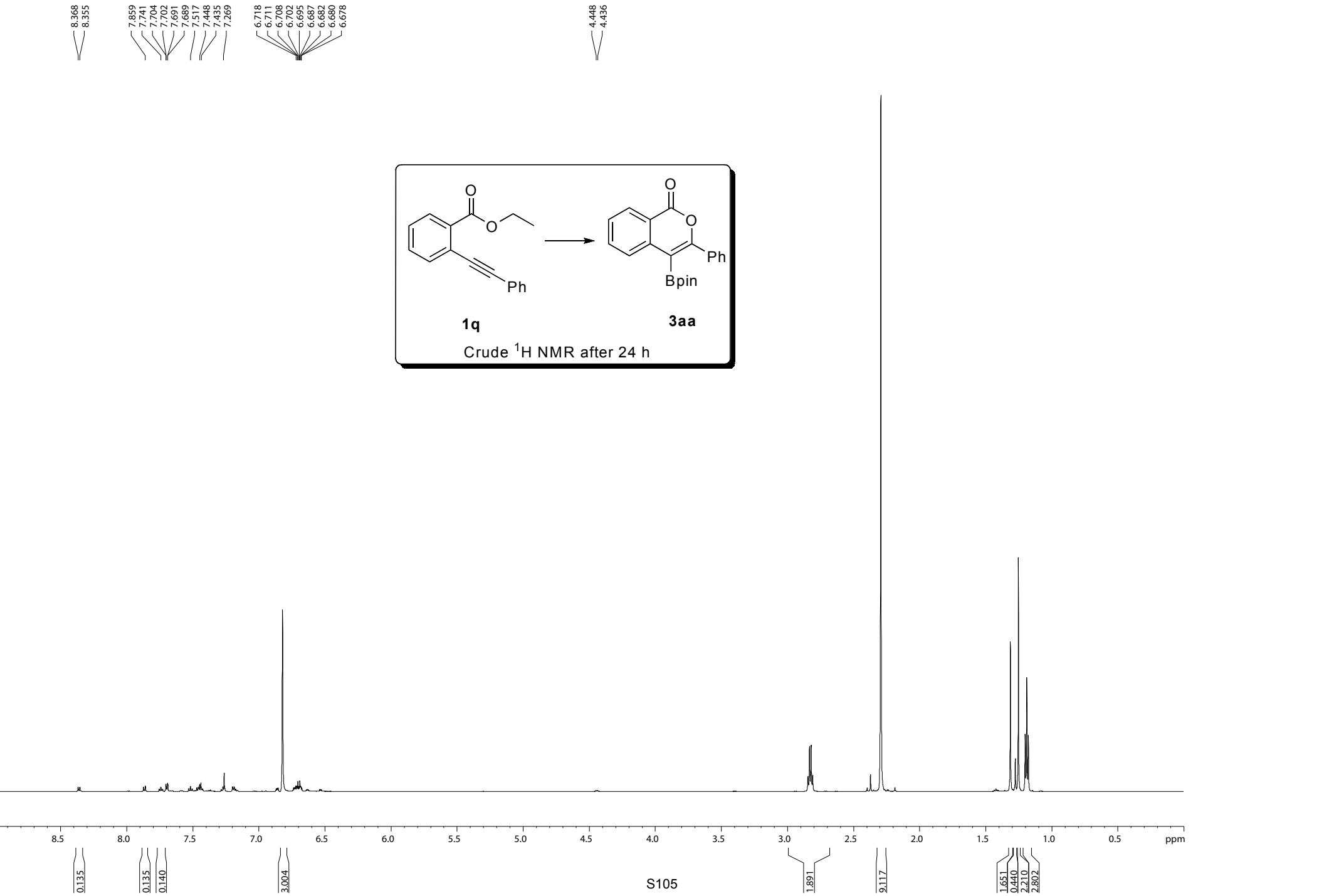
15

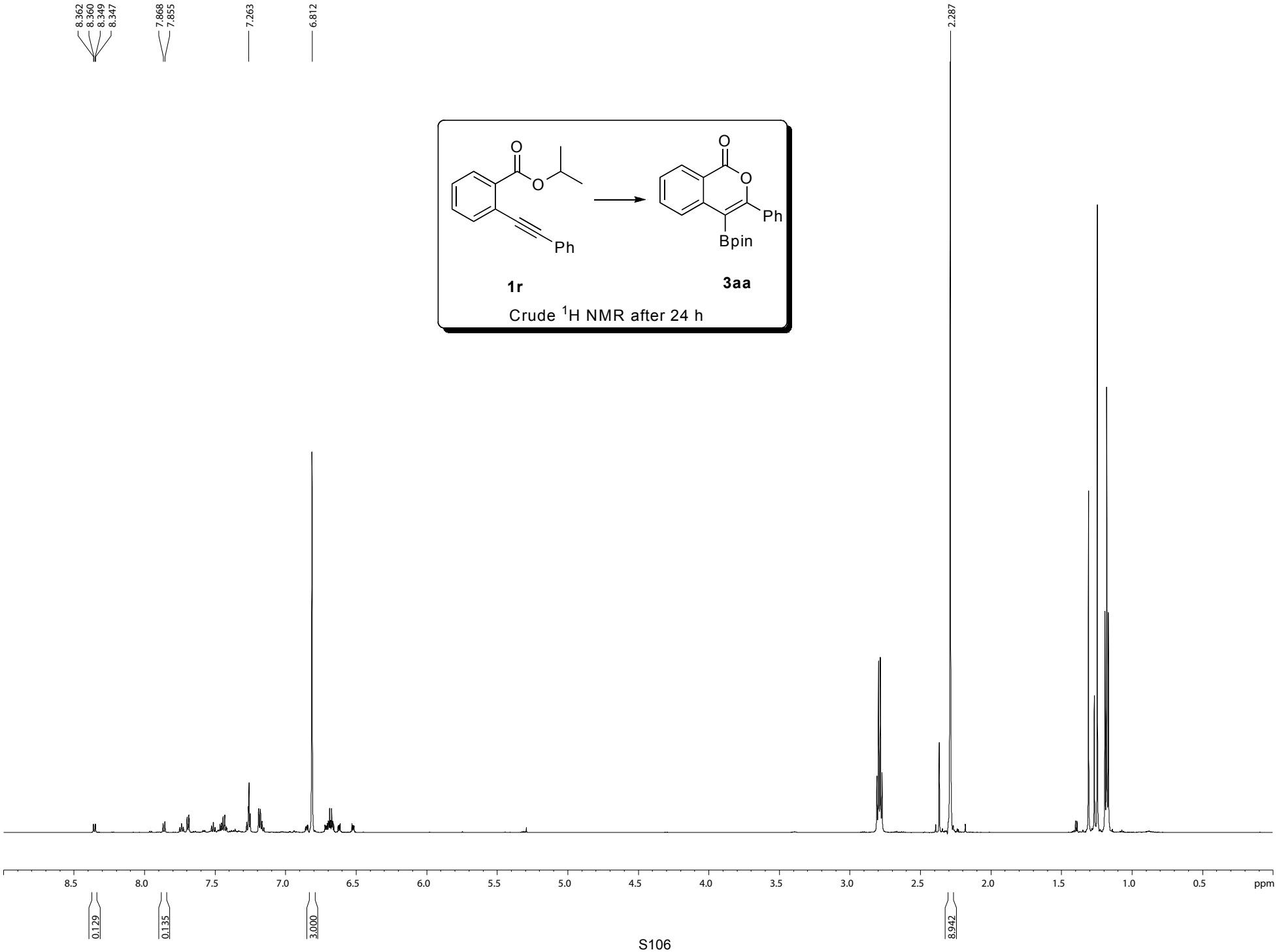
^{1}H NMR

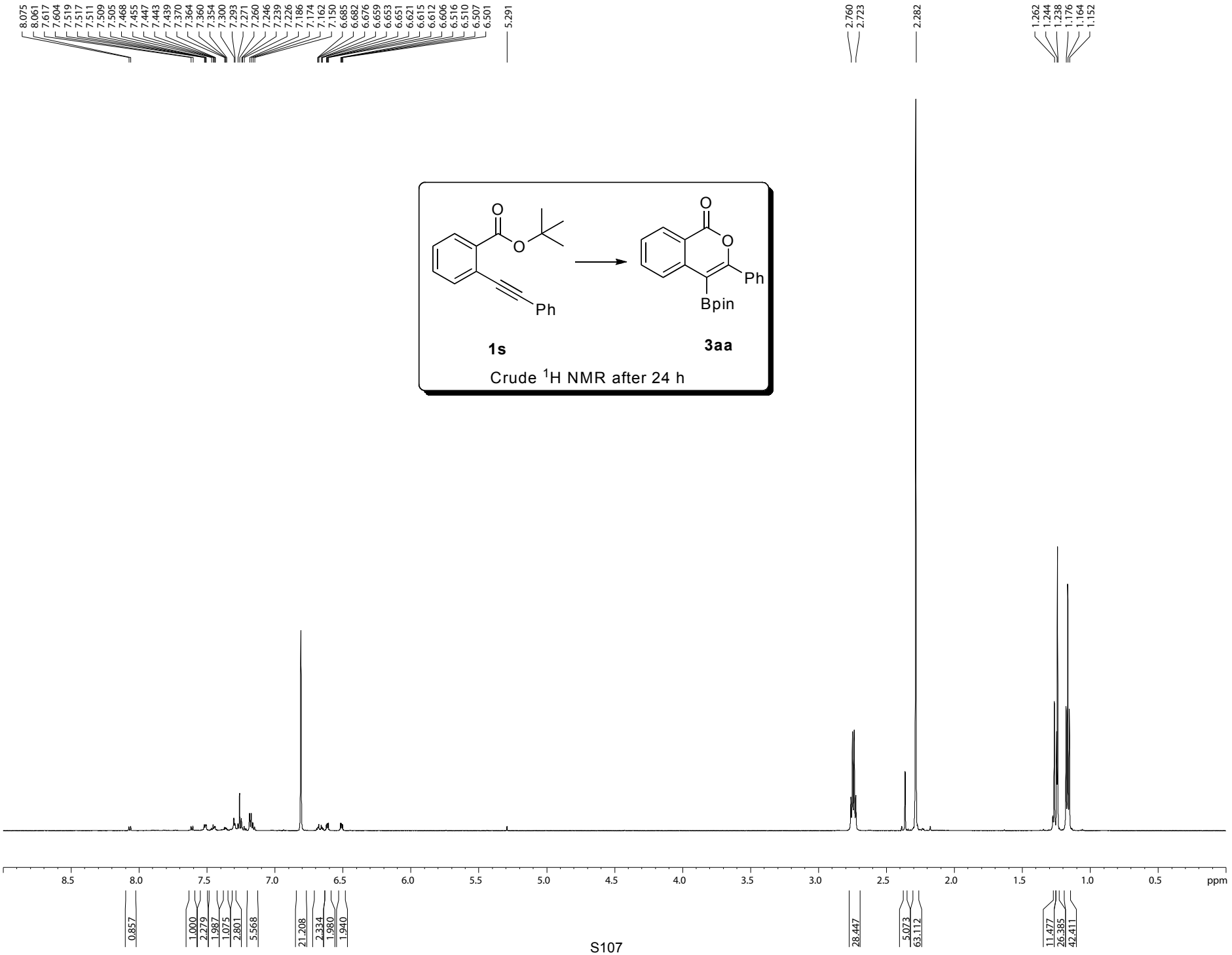
7.725
7.708
7.540
7.523
3.021
3.005
2.990
1.730
1.715
1.700
1.290
0.959
0.944
0.930
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.000
1.029
1.002
1.063
1.140
5.797
1.580

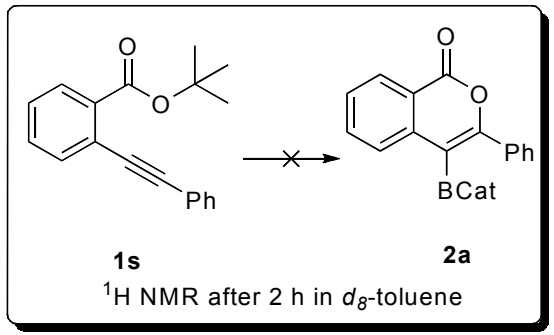

165.128
132.098
131.229
130.639
129.206
128.304
123.776
98.686
83.765
30.569
26.926
22.286
13.745
N
O
nBu
Bpin
Br
15
13C NMR
175 170 165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 ppm


29.903
N
O
nBu
Bpin
Br
15
11B NMR
45
40
35
30
25
20
15
10
5
ppm


8.368
8.355
7.859
7.741
7.704
7.702
7.691
7.689
7.517
7.448
7.435
7.269
6.718
6.711
6.708
6.702
6.695
6.687
6.682
6.680
6.678
4.448
4.436
O
O
Ph
O
O
Ph
Bpin
1q
3aa
Crude 1H NMR after 24 h
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
0.135
0.135
0.140
3.004
1.891
9.117
1.651
0.440
2.210
2.802

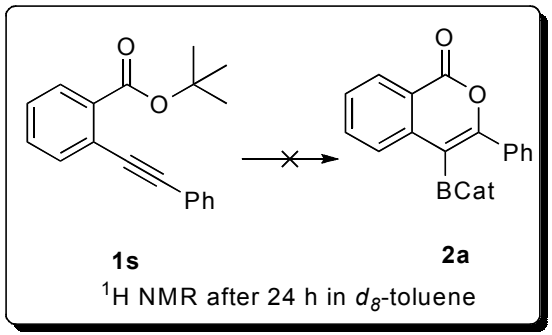

8.362
8.360
8.349
8.347
7.868
7.855
7.263
6.812
2.287
O
O
Ph
O
O
Ph
Bpin
1r
3aa
Crude ^{1}H NMR after 24 h
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
0.129
0.135
3.000
8.942


8.075
8.061
7.617
7.604
7.519
7.517
7.511
7.509
7.505
7.468
7.455
7.447
7.443
7.439
7.370
7.364
7.360
7.354
7.300
7.293
7.271
7.260
7.246
7.239
7.226
7.186
7.174
7.162
7.150
6.685
6.682
6.676
6.659
6.653
6.651
6.621
6.615
6.612
6.606
6.516
6.510
6.507
6.501
5.291
2.760
2.723
2.282
1.262
1.244
1.238
1.176
1.164
1.152
O
O
Ph
1s
O
O
Ph
Bpin
3aa
Crude ^{1}H NMR after 24 h
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
0.857
1.000
2.279
1.987
1.075
2.801
5.568
21.208
2.334
1.980
1.940
28.447
5.073
63.112
11.477
26.385
42.411



1s **2a**

^{1}H NMR after 2 h in d_8-toluene



1s **2a**

^{1}H NMR after 24 h in d_8-toluene