Supplementary Information for

Alkoxyboration: Ring-Closing Addition of B–O σ Bonds Across Alkynes

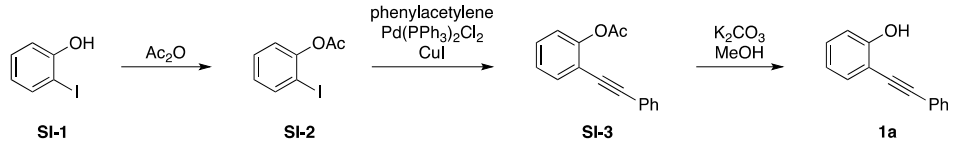
Joshua J. Hirner, Darius J. Faizi and Suzanne A. Blum*
Department of Chemistry, University of California, Irvine, California 92697-2025
Email: blums@uci.edu

I. General Methods

All chemicals were used as received from commercial sources unless otherwise noted. Sodium trifluoroacetate was dried at 130 °C at 10 mTorr for 18 h before use. Toluene and dichloromethane were purified by passage through an alumina column under argon pressure on a push-still solvent system. Anhydrous dimethylsulfoxide was obtained by stirring over activity I alumina 18 h under N_2 atmosphere, decanting the liquid, and distilling the liquid at 10 Torr over CaH_2. Acetone was dried by distillation over anhydrous $CaSO_4$ under N_2 atmosphere. 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 in a glovebox under nitrogen atmosphere or 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 = 2.50 ppm for d_6-DMSO, or δ = 1.94 ppm for CD_3CN in ^{1}H NMR spectroscopy experiments; δ = 77.16 ppm for $CDCl_3$, δ = 39.52 ppm for d_6-DMSO, 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. Low- and high-resolution mass spectrometry data were obtained at the University of California, Irvine.

II. Synthetic Procedures

A. Preparation of 2-alkynyl phenol substrates 1a–2j



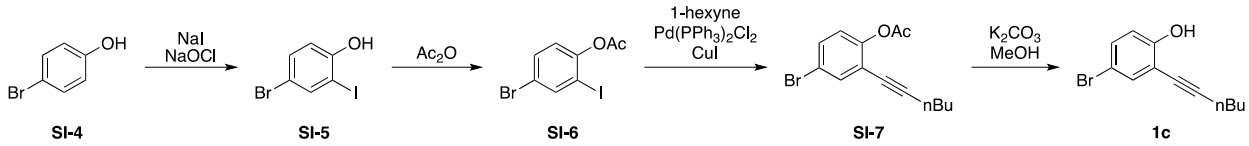
SI-1 SI-2 SI-3 1a

2-Iodophenyl acetate (SI-2). A solution of **SI-1** (6.72 g, 30.5 mmol, 1.00 equiv) and 4-dimethylaminopyridine (DMAP, 190 mg, 1.5 mmol, 5.0 mol %) was prepared in Et_3N (6.4 mL, 46 mmol, 1.5 equiv) and DCM (60 mL). Acetic anhydride (3.46 mL, 36.6 mmol, 1.20 equiv) was added dropwise. [Note: slight exotherm.] The reaction mixture stirred at 25 °C vented to air with a needle for 3 h. At this time, analysis by TLC (10% EtOAc/hexanes) indicated full conversion to a single new product. To the reaction mixture was added 50 mL water, and the resulting biphasic mixture was separated. The aqueous layer was extracted with DCM (3 × 25 mL), and then the combined organic layers were washed with brine (1 × 50 mL). The organic layer was then dried over Na_2SO_4, filtered, and concentrated in vacuo to a colorless oil, which solidified to a white solid upon standing. The resulting solid was crushed to a powder, and volatiles were removed at c.a. 10 mTorr for 2.5 h to afford **SI-2** as a white powder (7.27 g, 91% yield). ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.84 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.38 (td, *J* = 7.2, 1.3 Hz, 1H), 7.11 (dd, *J* = 8.0, 1.4 Hz, 1H), 6.99 (td, *J* = 7.6, 1.3 Hz, 1H), 2.38 (s, 3H). This spectrum is in agreement with previously reported spectral data.[1]

2-(Phenylethynyl)phenyl acetate (SI-3). A 100-mL Schlenk tube was charged with Et_3N (20 mL) and sparged with N_2 for 20 min. Compound **SI-2** (2.62 g, 10.0 mmol, 1.00 equiv), $Pd(PPh_3)_2Cl_2$ (120 mg, 0.20 mmol, 2.0 mol %), and CuI (95 mg, 0.50 mmol, 5.0 mol %) were added under positive N_2 pressure, then neat phenylacetylene (1.20 mL, 11.0 mmol, 1.10 equiv) was added. The reaction mixture was heated at 45 °C for 19 h, at which time analysis by TLC (5% EtOAc/hexanes) indicated complete consumption of the aryl iodide. The reaction mixture was cooled to 25 °C and diluted with 75 mL Et_2O. The resulting mixture was washed with saturated aqueous NH_4Cl (4 × 25 mL) and brine (2 × 25 mL). The organic layer was dried over Na_2SO_4, filtered, and concentrated in vacuo to a dark brown oil. The oily residue was purified by column chromatography using an elution gradient from 5% EtOAc/hexanes to 10% EtOAc/hexanes. Volatiles were removed at c.a. 10 mTorr and 25 °C for 18 h to afford **SI-3** as a brown oil (2.50 g, quant.). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.59 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.52–7.50 (m, 2H), 7.39–7.35 (m, 4), 7.25 (td, *J* = 7.6, 1.3 Hz, 1H), 7.14 (dd, *J* = 8.0, 1.4 Hz, 1H), 2.38 (s, 3H). This spectrum is in agreement with previously reported spectral data.[1]

2-(Phenylethynyl)phenol (1a). A suspension of K_2CO_3 (2.00 g, 14.5 mmol, 2.05 equiv) in MeOH (100 mL) and THF (90 mL) was cooled to 0 °C in an ice bath. A solution of **SI-3** (1.69 g, 7.16 mmol, 1.00 equiv) in THF (10 mL) was added dropwise over 2 min. The resulting heterogeneous mixture was stirred vigorously at 0 °C vented to air with a needle for 1.5 h, at which time analysis by TLC (20% EtOAc/hexanes) revealed complete consumption of **SI-3**. The cold reaction mixture was decanted into 200 mL DCM and washed with saturated aqueous

NH_4Cl (1 × 100 mL). The organic layer was then dried over Na_2SO_4, filtered, and concentrated in vacuo to a brown solid residue, which was purified by silica gel chromatography using an elution gradient from 100% hexanes to 10% EtOAc/hexanes. Removal of volatiles at c.a. 10 mTorr and 50 °C for 18 h to afforded **1a** as a golden solid (970 mg, 70% yield). ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.57–7.55 (m, 2H), 7.44 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.40–7.39 (m, 3H), 7.30–7.27 (m, 1H), 7.00 (dd, *J* = 8.3, 0.8 Hz, 1H), 6.93 (td, *J* = 7.5, 1.0 Hz, 1H), 5.83 (s, 1H). This spectrum is in agreement with previously reported spectral data.[2]



4-Bromo-2-iodophenol (SI-5) was prepared according to a literature procedure[3] in 66% yield. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.78 (d, *J* = 2.3 Hz, 1H), 7.35 (dd, *J* = 8.6, 2.3 Hz, 1H), 6.89 (d, *J* = 8.2 Hz, 1H), 5.25 (br s, 1H). This spectrum is in agreement with previously reported spectral data.

4-Bromo-2-iodophenyl acetate (SI-6). A solution of **SI-5** (1.79 g, 6.00 mmol, 1.00 equiv) and 4-dimethylaminopyridine (DMAP, 40. mg, 0.30 mmol, 5.0 mol %) in Et_3N (1.0 mL, 7.2 mmol, 1.2 equiv) and DCM (12 mL) was cooled to 0 °C in an ice bath. Acetic anhydride (680 µL, 7.2 mmol, 1.2 equiv) was added dropwise over c.a. 1 min, and then the cooling bath was removed. The reaction mixture was stirred at 25 °C while vented to air with a needle for 1 h. At this time, analysis by TLC (10% EtOAc/hexanes) indicated full conversion to a single new product. The reaction mixture was washed with water (3 × 3 mL) and brine (3 × 3 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo to a colorless oil, which solidified to a white solid upon standing. The resulting solid was crushed to a powder, and volatiles were removed at c.a. 10 mTorr for 2.5 h to afford **SI-6** as a white powder (1.90 g, 93% yield).

TLC (10% EtOAc/hexanes): R_f = 0.52, visualized by UV absorbance and $KMnO_4$ stain.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.97 (d, *J* = 2.3 Hz, 1H), 7.49 (dd, *J* = 8.6, 2.3 Hz, 1H), 6.98 (d, *J* = 8.6 Hz, 1H), 2.37 (s, 3H).

^{13}C NMR ($CDCl_3$, 125 MHz): 168.5, 150.6, 141.5, 132.6, 124.5, 119.9, 91.6, 21.3.

HRMS (GC/ESI): Calculated for $C_8H_{10}BrINO_2$ ($[M+NH_4]^+$), 357.8940; found 357.8942.

4-Bromo-2-(hex-1-yn-1-yl)phenyl acetate (SI-7). A 100-mL Schlenk tube was charged with 25 mL THF, Et_3N (3.9 mL, 28 mmol, 4.1 equiv), and a stirbar. The combined solvents were sparged with N_2 for 25 min. Compound **SI-6** (2.34 g, 6.86 mmol, 1.00 equiv), $Pd(PPh_3)_2Cl_2$ (96 mg, 0.14 mmol, 2.0 mol %), and CuI (65 mg, 0.34 mmol, 5.0 mol %) were added under postive N_2 flow, followed by 1-hexyne (2.4 mL, 21 mmol, 3.0 equiv). The resulting dark brown solution was stirred at 25 °C for 15 h, at which time analysis by TLC (10% EtOAc/hexanes) suggested full consumption of the starting aryl iodide. [Note: The aryl iodide starting material overlaps the desired Sonogashira product in this solvent system, but the reaction progress can be judged through differential staining by $KMnO_4$ solution.] The reaction mixture was diluted with 75 mL

EtOAc and washed with saturated aqueous NH_4Cl (3 × 20 mL), water (1 × 20 mL), and brine (3 × 20 mL). The organic layer was dried over Na_2SO_4, filtered, and concentrated in vacuo to a brown oil. Purification by column chromatography using an elution gradient (100% hexanes to 20% EtOAc/hexanes) followed by removal of volatiles at c.a. 10 Torr for 1 h afforded the desired product as a yellow-brown oil (1.91 g, 95% yield).

TLC (10% EtOAc/hexanes): $R_f = 0.52$, visualized by UV absorbance and $KMnO_4$ stain.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.58 (d, J = 2.3 Hz, 1H), 7.40 (dd, J = 8.6 Hz, 2.3 Hz, 1H), 6.94 (d, J = 8.6 Hz, 1H), 2.43 (t, J = 7.0 Hz, 2H), 2.32 (s, 3H), 1.58 (m, 2H), 1.47 (app sextet, J = 7.3 Hz, 2H), 0.95 (t, J = 7.4 Hz, 3H).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 168.8, 150.7, 135.8, 131.7, 123.8, 120.3, 118.8, 97.2, 74.5, 30.7, 22.0, 20.9, 19.3, 13.7.

HRMS (GC/EI): Calculated for $C_{14}H_{19}BrO_2N$ ($[M+NH_4]^+$), 312.0599; found 312.0600.

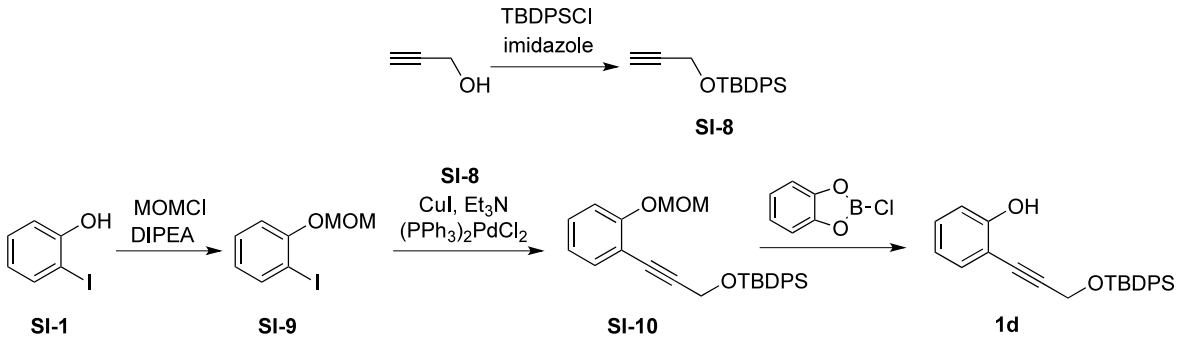
4-Bromo-2-(hex-1-yn-1-yl)phenol (1c). A stirring suspension of K_2CO_3 (1.78 g, 12.9 mmol, 2.00 equiv) in 45 mL MeOH and 35 mL THF was cooled to 0 °C in an ice bath. To the vigorously stirring cold suspension was added solution of acetate **SI-7** (1.90 g, 6.44 mmol, 1.00 equiv) in 10 mL THF dropwise over c.a. 2 min. The reaction mixture was stirred at 0 °C for 30 min, at which time analysis by TLC (10% EtOAc/hexanes) revealed full consumption of the acetate starting material. The reaction mixture was diluted with 100 mL EtOAc, then washed with saturated aqueous NH_4Cl (1 × 30 mL) and brine (3 × 10 mL). The organic layer was 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. Volatiles were removed at c.a. 10 mTorr overnight with stirring to afford **1c** as a clear yellow oil (1.45 g, 89% yield).

TLC (10% EtOAc/hexanes): $R_f = 0.40$, visualized by UV absorbance.

^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.41 (d, J = 2.4 Hz, 1H), 7.29 (dd, J = 8.7 Hz, 2.5 Hz, 1H), 6.82 (d, J = 8.7 Hz, 1H), 5.76 (s, 1H), 2.49 (t, J = 7.0 Hz, 2H), 1.65–1.50 (m, 2H), 1.45 – 1.52 (m, 2H), 0.97 (t, J = 7.4 Hz, 3H).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 155.8, 133.8, 132.6, 116.2, 112.5, 111.9, 99.5, 73.5, 30.8, 22.2, 19.4, 13.7.

HRMS (GC/CI): Calculated for $C_{12}H_{13}BrO$ (M^+), 252.0150; found 252.0148.



***tert*-Butyldiphenyl(prop-2-yn-1-yloxy)silane (SI-8)** was prepared according to a literature procedure[4] in 77% yield. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.72 (d, J = 6.6 Hz, 4H), 7.33–7.49 (m, 6H), 4.32 (d, J = 2.3 Hz, 2H), 2.39 (t, J = 2.3 Hz, 1H), 1.07 (s, 9H). This spectrum is in agreement with previously reported spectral data.

1-Iodo-2-(methoxymethoxy)benzene (SI-9) was prepared according to a literature procedure[5] in 97% yield. ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.78 (dd, J = 7.8, 1.5 Hz, 1H), 7.26–7.30 (m, 1H), 7.07 (dd, J = 8.3, 1.1 Hz, 1H), 6.76 (td, J = 7.6, 1.3 Hz, 1H), 5.24 (s, 2H), 3.52 (s, 3H).This spectrum is in agreement with previously reported spectral data.

***tert*-Butyl((3-(2-(methoxymethoxy)phenyl)prop-2-yn-1-yl)oxy)diphenylsilane (SI-10)**. A flask was charged with compound **SI-9** (1.50 g, 5.67 mmol, 1.00 equiv), $(PPh_3)_2PdCl_2$ (0.20 g, 0.28 mmol, 0.050 equiv), and CuI (0.11 g, 0.57 mmol, 0.10 equiv). The flask was then evacuated and refilled with N_2 three times before Et_3N (6.3 mL, 45 mmol, 8.0 equiv) was added and stirred for 30 min. A separate flask was charged with compound **SI-8** (2.14 g, 7.28 mmol, 1.30 equiv), and then evacuated and refilled with N_2 three times before adding 11 mL MeCN. The resulting solution was then added dropwise over c.a. 4 min to the stirring 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 50 mL EtOAc and washed with NH_4Cl (1 × 15 mL), water (1 × 10 mL), brine (1 × 10 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 **SI-10** as a light yellow oil (2.18 g, 90% yield).

TLC (10% EtOAc/hexanes): R_f = 0.38, visualized by UV absorbance and $KMnO_4$ stain.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.76 (d, J = 6.7 Hz, 4H), 7.46–7.35 (m, 6H), 7.32 (d, J = 7.6 Hz, 1H), 7.28–7.21 (m, 1H), 7.10 (d, J = 8.3 Hz, 1H), 6.95 (t, J = 7.5 Hz, 1H), 5.21 (s, 2H), 4.59 (s, 2H), 3.49 (s, 3H), 1.09 (s, 9H).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 157.9, 135.8, 133.8, 133.4, 129.9, 129.7, 127.8, 121.9, 115.4, 113.8, 95.1, 91.7, 81.5, 56.4, 53.6, 26.9, 19.4.

HRMS (ESI+): Calculated for $C_{27}H_{30}O_3SiNa$ ([M+Na]$^+$), 453.1862; found 453.1844.

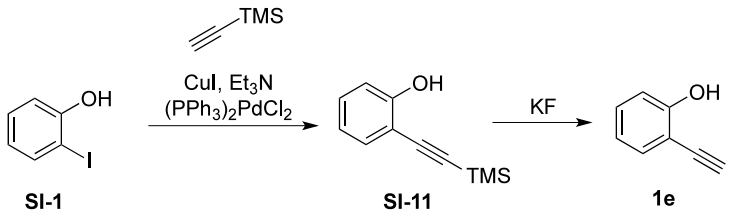
2-(3-((*tert*-Butyldiphenylsilyl)oxy)prop-1-yn-1-yl)phenol (1d). To a stirring solution of *B*-chlorocatecholborane (0.34 g, 2.2 mmol, 1.2 equiv) in 15 mL DCM was added **SI-10** (0.80 g, 1.9 mmol, 1.0 equiv) in 4 mL DCM. The reaction mixture was stirred for 4.5 h under dynamic N_2. At this time, analysis by TLC (10% EtOAc/hexanes) indicated full consumption of starting material. The reaction mixture was diluted with 50 mL DCM, and the organic layer was washed with NH_4Cl (1 × 10 mL), brine (1 × 10 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 **1d** as a light yellow oil (320 mg, 45% yield).

TLC (10% EtOAc/hexanes): R_f = 0.32, visualized by UV absorbance and $KMnO_4$ stain.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.74 (d, *J* = 6.7 Hz, 4H), 7.47–7.44 (m, 2H), 7.42–7.40 (m, 4H), 7.24 (t, *J* = 7.8 Hz, 2H), 6.91 (d, *J* = 7.9 Hz, 1H), 6.84 (t, *J* = 7.5 Hz, 1H), 5.55 (s, 1H), 4.60 (s, 2H), 1.08 (s, 9H).

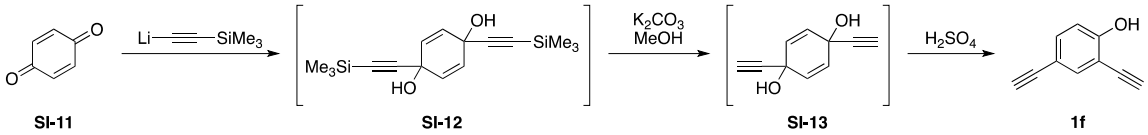
^{13}C NMR ($CDCl_3$, 125 MHz): δ 156.9, 135.8, 133.1, 132.0, 130.6, 130.1, 128.0, 120.3, 114.8, 109.2, 95.0, 79.3, 53.3, 26.8, 19.3.

HRMS (ESI+): Calculated for $C_{25}H_{26}O_2SiNa$ ([M+Na]$^+$), 409.1600; found 409.1584.



2-((Trimethylsilyl)ethynyl)phenol (SI-11) was prepared according to a literature procedure[6] in 71% yield. ^{1}H NMR ($CDCl_3$, 600MHz) δ 7.34 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.26–7.22 (m, 1H), 6.94 (d, *J* = 8.2 Hz, 1H), 6.85 (t, *J* = 6.0 Hz, 1H), 5.82 (s, 1H), 0.28 (s, 9H). This spectrum is in agreement with previously reported spectral data.

2-Ethynylphenol (1e) was prepared according to a literature procedure[6] in 82% yield. ^{1}H NMR ($CDCl_3$, 600MHz) δ 7.38 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.30–7.26 (dt, *J* = 7.8, 1.2 Hz, 1H), 6.96 (d, *J* = 8.2 Hz, 1H), 6.88 (dt, *J* = 7.5, 0.8 Hz, 1H), 5.77 (s, 1H), 3.47 (s, 1H). This spectrum is in agreement with previously reported spectral data.



1,4-Bis((trimethylsilyl)ethynyl)cyclohexa-2,5-diene-1,4-diol (SI-12). Anhydrous THF (60 mL) was cooled to -78 °C in a dry ice/isopropanol bath under a dynamic N_2 atmosphere. A solution of nBuLi (1.0 M in hexanes, 50. mL, 50. mmol, 2.2 equiv) was cannulated slowly into the reaction vessel. To the resulting stirring solution was then added trimethylsilyl acetylene (7.1 mL, 50. mmol, 2.2 equiv) dropwise over 30 min. After stirring an additional 30 min to affect complete deprotonation of the terminal alkyne, a solution of 1,4-benzoquinone (2.45 g, 22.7 mmol, 1.00 equiv) in 20. mL anhydrous THF was added dropwise over 30 min. During this addition, the reaction mixture turned from a clear, pale yellow solution to a dark, teal solution. The reaction mixture was stirred for 18 h as the cooling bath warmed gradually to 25 °C. After this time, the resulting red-brown semisolid reaction mixture was cooled to 0 °C, and 100 mL EtOAc was added with vigorous agitation to break up the solid aggregate. Saturated aqueous NH_4Cl (50 mL) was added to quench the reaction mixture, and then the pH was further adjusted to pH = 5 with c.a. 1 mL 2 N aqueous HCl. The resulting biphasic mixture was separated, and the organic layer was extracted with EtOAc (2 × 50 mL). The combined organic phases were dried over Na_2SO_4, filtered, and concentrated in vacuo to afford a tan solid. Volatiles were removed at 25 °C and c.a. 10 mTorr for 2 h to afford crude **SI-12** as a tan solid (6.08 g) in 70% purity. Crude **SI-12** was used without further purification or characterization.

1,4-Diethynylcyclohexa-2,5-diene-1,4-diol (SI-13). A suspension of K_2CO_3 (5.5 g, 40. mmol, 4.0 equiv) in MeOH (50 mL) was cooled to 0 °C in an ice bath open to air. Solid **SI-12** (3.0 g, 9.9 mmol, 1.0 equiv) was added portionwise over c.a. 1 min, and the resulting mixture was stirred vigorously at 0 °C for 1.5 h, at which time analysis by TLC (30% EtOAc/hexanes) indicated full consumption of **SI-12**. The reaction mixture was warmed to 25 °C and was decanted away from excess K_2CO_3. The resulting solution was diluted with 50 mL EtOAc and was then washed with saturated aqueous NH_4Cl (3 × 10 mL). The organic phase was dried over Na_2SO_4, filtered, and concentrated in vacuo to a tan solid containing crude **SI-13**, which was used directly in the next step without purification or characterization.

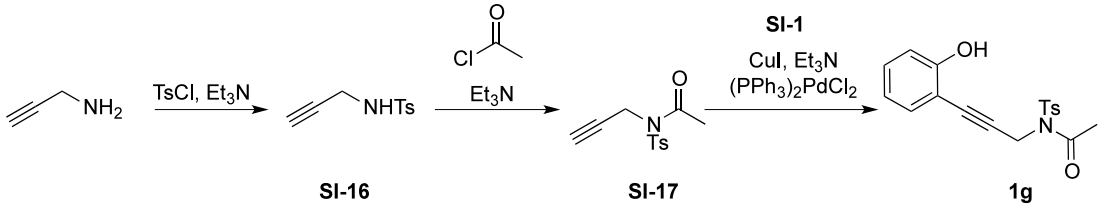
2,4-Diethynylphenol (1f) was prepared using a method adapted from Ried and Schmidt.[7] Crude **SI-13** was dissolved in 10 mL benzene, and to the resulting solution were added H_2O (10 mL) and 1 mL 1 N aqueous H_2SO_4 (1 mmol, 10 mol %). The resulting biphasic mixture was refluxed under air with vigorous stirring for 20 min. After cooling to 25 °C, the biphasic mixture was separated, and the aqueous layer was extracted with benzene (3 × 5 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated in vacuo to a brown oil, which was purified by column chromatography using an elution gradient from 100% hexanes to 20%. The purified product was dried at 25 °C and c.a. 10 mTorr for 18 h to afford **1f** as a cream-colored solid (160 mg, 12% yield over 2 steps).

TLC (20% EtOAc/hexanes): $R_f = 0.43$, visualized by $KMnO_4$ stain.

^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.33 (d, J = 7.9 Hz, 1H), 7.09 (d, J = 1.1 Hz, 1H), 7.02 (dd, J = 8.0, 1.3 Hz, 1H), 5.79 (s, 1H), 3.55 (s, 1H), 3.16 (s, 1H).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 157.1, 132.0, 124.7, 124.4, 118.5, 109.2, 86.0, 82.9, 79.2, 77.8.

HRMS (GC/ESI+): Calculated for $C_{10}H_{10}NO$ ($[M+NH_4]^+$), 160.0762; found 160.0764.



4-Ethyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide (SI-16) was prepared according to a literature procedure[8] in 91% yield. ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.77 (d, J = 8.2 Hz, 2H), 7.31 (d, J = 7.9 Hz, 2H), 4.66 (br s, 1H), 3.83 (dd, J = 6.0, 2.5 Hz, 2H), 2.43 (s, 3H), 2.10 (t, J = 2.4 Hz, 1H). This spectrum is in agreement with previously reported spectral data.

***N*-(Prop-2-yn-1-yl)-*N*-tosylacetamide (SI-17)**. A flask was charged with **SI-16** (1.29 g, 6.16 mmol, 1.00 equiv), Et_3N (2.6 mL, 19 mmol, 3.0 equiv), and 13 mL DCM before it was cooled to 0 ^{o}C in an ice bath. At this time, acetyl chloride (0.88 mL, 12 mmol, 2.0 equiv) was syringed into the stirring reaction vessel over 3 min. The ice bath was removed, and the reaction mixture was stirred for 18 h before TLC (30% EtOAc/hexanes) revealed complete consumption of starting material. The reaction was quenched with 10 mL H_2O, and the aqueous layer was extracted with DCM (2 × 10 mL). The combined organic layers were washed with brine (1 × 10 mL), and then 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 35% 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-17** as a light yellow solid (1.1 g, 72% yield). ^{1}H NMR ($CDCl_3$, 600MHz) δ 7.91 (d, J = 8.4 Hz, 2H), 7.35 (d, J = 8.2 Hz, 2H), 4.67 (d, J = 2.3 Hz, 2H), 2.45 (s, 3H), 2.33 (s, 3H), 2.28 (t, J = 2.4 Hz, 1H). This spectrum is in agreement with previously reported spectral data.[9]

***N*-(3-(2-Hydroxyphenyl)prop-2-yn-1-yl)-*N*-tosylacetamide (1g)**. A Schlenk tube was charged with **SI-1** (0.71 g, 3.2 mmol, 1.0 equiv), $(PPh_3)_2PdCl_2$ (23 mg, 0.032 mmol, 1.0 mol %), CuI (13 mg, 0.064 mmol, 2.0 mol %), and a stir bar. The tube was then evacuated and refilled with N_2 three times before the addition of Et_3N (1.8 mL, 13 mmol, 4.0 equiv) and 4 mL dioxane, and then stirred for 5 min. Compound **SI-17** (1.05 g, 4.18 mmol, 1.30 equiv) was added over positive N_2 pressure. The Schlenk tube was heated to 45 ^{o}C under dynamic N_2. After 4 h, analysis by TLC (30% EtOAc/hexanes) revealed complete consumption of starting material. To the flask was added 10 mL water, and the aqueous phase was extracted with EtOAc (2 × 30 mL). The combined organic layers were washed with brine (1 × 10 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 30% EtOAc/hexanes. Product-containing fractions

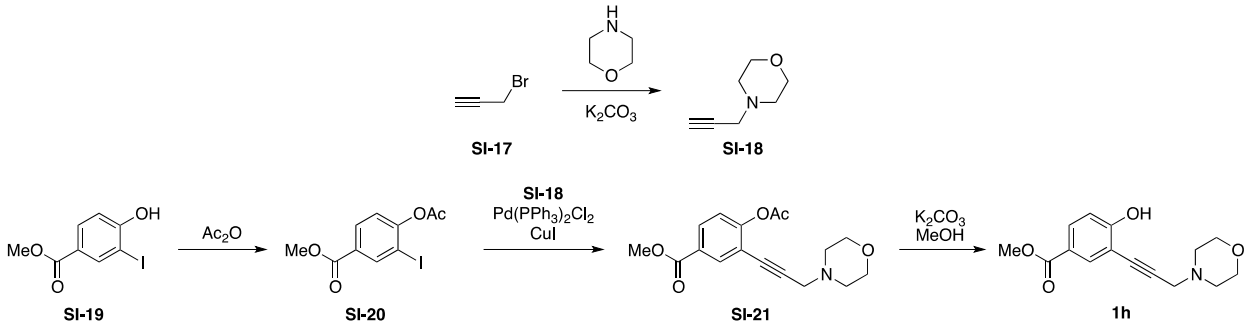
were combined and concentrated in vacuo, and volatiles were removed at c.a. 10 mTorr for 18 h to afford **1g** as a light yellow solid (0.15 g, 14% yield).

TLC (30% EtOAc/hexanes) $R_f = 0.31$, visualized by UV absorbance.

^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.88 (d, J = 8.2 Hz, 2H), 7.33 (d, J = 8.1 Hz, 2H), 7.23 (td, J = 6.7, 1.5 Hz, 2H), 6.92 (d, J = 8.1 Hz, 1H), 6.84 (t, J = 7.5 Hz, 1H), 5.92 (br. s, 1H), 4.88 (s, 2H), 2.42 (s, 3H), 2.41 (s, 3H).

^{13}C NMR (d_8-toluene, 125 MHz): δ 169.2, 158.9, 144.8, 137.1, 131.7, 131.0, 129.9, 125.4, 120.1, 115.4, 109.0, 91.9, 79.2, 36.2, 24.4, 21.0.

HRMS (ESI+): Calculated for $C_{18}H_{17}NO_4SNa$ ([M+Na]$^+$), 366.0776; found 366.0768.



4-(Prop-2-yn-1-yl)morpholine (SI-18) was prepared by adding propargyl bromide (80 wt % in toluene, 15 g solution, 100 mmol, 1.0 equiv) dropwise over 20 min to a stirring suspension of morpholine (22 mL, 250 mmol, 2.5 equiv) and K_2CO_3 (35 g, 250 mmol, 2.5 equiv) in THF (100 mL) at 25 °C. The resulting mixture was stirred vigorously for 18 h, at which point the reaction mixture was diluted with 200 mL EtOAc. The mixture was washed with water (1 × 60 mL) and brine (3 × 20 mL), then the combined aqueous layers were back extracted with DCM (1 × 20 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated in vacuo to a yellow-orange oil. Purification by Kugelrohr distillation, (250 Torr, 150 °C) afforded **SI-18** as a clear, colorless oil (9.85 g, 79% yield). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 3.74 (app t, J = 4.8 Hz, 4H), 3.29 (d, J = 2.5 Hz, 2H), 2.57 (app t, J = 4.7 Hz, 4H), 2.27 (t, J = 2.5 Hz, 1H). This spectrum is in agreement with previously reported spectral data.[10]

Methyl 4-acetoxy-3-iodobenzoate (SI-20). A solution of iodophenol **SI-19** (5.00 g, 18.0 mmol, 1.00 equiv) and 4-dimethylaminopyridine (DMAP, 110 mg, 0.90 mmol, 5.0 mol %) in Et_3N (3.0 mL, 22 mmol, 1.2 equiv) and DCM (20 mL) was cooled to 0 °C in an ice bath. Neat acetic anhydride (2.0 mL, 22 mmol, 1.2 equiv) was added dropwise over c.a. 1 min, and then the cooling bath was removed. The reaction mixture was stirred at 25 °C while vented to air with a needle for 2 h. At this time, analysis by TLC (20% EtOAc/hexanes) indicated full conversion to a single new product. The reaction mixture was washed with water (1 × 40 mL), and then the aqueous layer was back extracted with DCM (3 × 15 mL). The combined organic layers were washed with brine (3 × 3 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo to a colorless oil, which was purified by silica gel chromatography using an elution gradient from

100% hexanes to 10% EtOAc/hexanes. Volatiles were removed from the purified product at c.a. 10 mTorr for 2.5 h to afford **SI-20** as a white powder (5.41 g, 94% yield). ^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.52 (d, *J* = 1.8 Hz, 1H), 8.05 (dd, *J* = 8.4, 1.9 Hz, 1H), 7.18 (d, *J* = 8.4 Hz, 1H), 3.93 (s, 3H), 2.40 (s, 3H). This spectrum is in agreement with previously reported spectral data.[11]

Methyl 4-acetoxy-3-(3-morpholinoprop-1-yn-1-yl)benzoate (SI-21). A solution of **SI-20** (480. mg, 1.50 mmol, 1.00 equiv) in Et_3N (4 mL) was sparged with N_2 for 25 min. $PdCl_2(PPh_3)_2$ (18 mg, 0.026 mmol, 2.0 mol %) and CuI (12 mg, 0.065 mmol, 5.0 mol %) were added under positive N_2 flow, and to the resulting mixture was then added neat terminal alkyne **SI-18** (197 mg, 1.58 mmol, 1.05 equiv). The reaction mixture was then heated at 45 °C for 16 h. At this time, analysis by TLC (20% EtOAc/hexanes) indicated complete consumption of the starting aryl iodide. The reaction mixture was diluted with 10 mL DCM, then washed with water (1 × 15 mL) and brine (1 × 15 mL), and then the combined aqueous layers were back extracted with DCM (1 × 5 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated in vacuo. The resulting brown oil was purified by silica gel chromatography using an elution gradient from 100% hexanes to 100% EtOAc. Volatiles were removed from the purified product at c.a. 10 mTorr for 18 h to afford **SI-21** as a viscous, yellow-brown oil (223 mg, 55% yield) containing trace residual EtOAc.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.17 (d, *J* = 2.5 Hz, 1H), 8.00 (dd, *J* = 10.2, 2.5 Hz, 1H), 7.18 (d, *J* = 10.1 Hz, 1H), 3.92 (s, 3H), 3.77 (app t, *J* = 5.5 Hz, 4H), 3.56 (s, 2H), 2.64 (app t, *J* = 5.5 Hz, 4H), 2.37 (s, 3H).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 168.5, 165.8, 155.0, 135.0, 130.8, 128.1, 122.6, 117.6, 90.1, 80.0, 67.0, 52.5, 52.3, 48.1, 21.1.

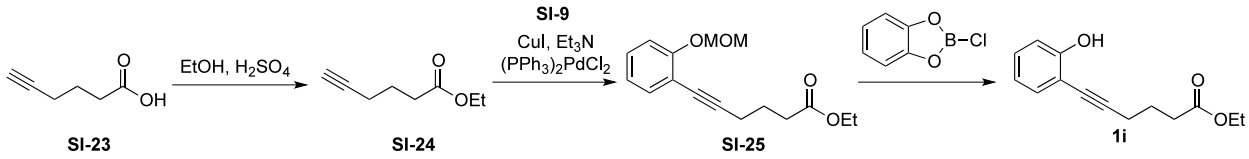
HRMS (ESI+): Calculated for $C_{17}H_{19}NO_5Na$ ($[M+Na]^+$), 340.1161; found 340.1167.

Methyl 4-hydroxy-3-(3-morpholinoprop-1-yn-1-yl)benzoate (1h). A solution of **SI-21** (1.27 g, 4.00 mmol, 1.00 equiv) in THF (30 mL) was cooled to 0 °C in an ice bath. Solid K_2CO_3 (1.1 g, 8.0 mmol, 2.0 equiv) was added followed by slow addition of MeOH (30 mL). After completion of the addition, the reaction mixture was warmed slowly to 25 °C and was stirred vigorously for 2 h. At this time, analysis by TLC (5% MeOH/$CHCl_3$) indicated complete consumption of the starting acetate. The reaction mixture was diluted with 150 mL DCM and washed with water (1 × 30 mL) and brine (1 × 30 mL). The combined aqueous layers were back-extracted with DCM (1 × 30 mL), and then the combined organic layers were dried over Na_2SO_4, filtered, and concentrated in vacuo to a pale yellow oil. The oil was purified by silica gel chromatography using an elution gradient from 100% $CHCl_3$ to 5 % MeOH/$CHCl_3$. Volatiles were removed from the purified product at c.a. 10 mTorr for 18 h to afford **1h** as a cream-colored solid (175 mg, 16% yield).

^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.07 (d, *J* = 2.1 Hz, 1H), 7.94 (d, *J* = 8.6, 2.1 Hz, 1H), 6.98 (d, *J* = 8.6 Hz, 1H), 6.27 (br s, 1H), 3.90 (s, 3H), 3.78 (app t, *J* = 4.6 Hz, 4H), 3.60 (s, 2H), 2.65 (app t, *J* = 4.5 Hz, 4H).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 166.3, 160.5, 134.2, 132.2, 122.8, 114.9, 109.6, 92.2, 79.0, 66.9, 52.6, 52.2, 48.3.

HRMS (ESI+): Calculated for $C_{15}H_{17}NO_4Na$ ([M+Na]$^+$), 298.1055; found 298.1055.



Ethyl hex-5-ynoate (SI-24) was prepared according to a literature procedure[12] in 87% yield. ^{1}H NMR ($CDCl_3$, 600MHz) 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.

Ethyl 6-(2-(methoxymethoxy)phenyl)hex-5-ynoate (SI-25). A flask was charged with **SI-9** (1.05 g, 3.98 mmol, 1.00 equiv), $(PPh_3)_2PdCl_2$ (0.14 g, 0.20 mmol, 0.050 equiv), and CuI (76 mg, 0.40 mmol, 0.10 equiv). The flask was then evacuated and refilled with N_2 three times before Et_3N (4.4 mL, 32 mmol, 8.0 equiv) and 5 mL MeCN were added, and this mixture was stirred for 30 min. Compound **SI-24** (0.98 g, 5.2 mmol, 1.30 equiv) was added dropwise by syringe over 2 min. The reaction mixture was stirred for 18 h under dynamic N_2. At this time, analysis by TLC (30% EtOAc/hexanes) indicated full consumption of starting material. The reaction mixture was diluted with 50 mL DCM, and the organic layer was washed with NH_4Cl (1 × 15 mL), water (1 × 10 mL), brine (1 × 10 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 40% 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-25** as a light yellow oil (0.97 g, 88% yield).

TLC (30% EtOAc/hexanes) R_f = 0.42, visualized by UV absorbance.

^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.37 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.22 (td, *J* = 7.8, 1.2 Hz, 1H), 7.08 (d, *J* = 8.2 Hz, 1H), 6.94 (t, *J* = 7.5 Hz, 1H), 5.24 (s, 2H), 4.14 (q, *J* = 7.0 Hz, 2H), 3.52 (s, 3H), 2.59–2.48 (m, 2H), 1.95 (quin, *J* = 7.2 Hz, 2H), 1.26 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 173.4, 157.8, 133.6, 129.1, 121.9, 115.3, 114.4, 95.1, 93.2, 77.7, 60.5, 56.4, 32.2, 24.1, 19.3, 14.4.

HRMS (ESI+): Calculated for $C_{16}H_{20}O_4Na$ ([M+Na]$^+$), 299.1259; found 299.1255.

Ethyl 6-(2-hydroxyphenyl)hex-5-ynoate (1i). A flask was charged with **SI-25** (1.6 g, 5.8 mmol, 1.0 equiv), 58 mL DCM, and a stir bar. *B*-Chlorocatecholborane (1.2 g, 7.5 mmol, 1.3 equiv) was then added, and the mixture was sparged with N_2 for 10 min. The reaction mixture stirred for 18 h under dynamic N_2. At this time, analysis by TLC (20% EtOAc/hexanes) indicated complete consumption of starting material. The reaction mixture was diluted with 100 mL DCM and washed with water (3 × 30 mL) and brine (1 × 30 mL). The organic layer was 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-

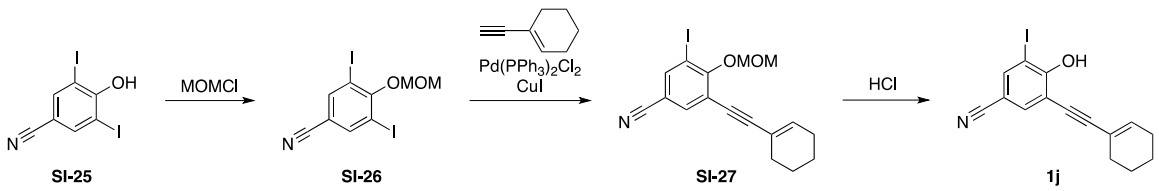
containing fractions were combined and concentrated in vacuo, and volatiles were removed at c.a. 10 mTorr for 18 h to afford **1i** as a light yellow oil (1.2 g, 87% yield).

TLC (20% EtOAc/hexanes) $R_f = 0.33$, visualized by UV absorbance.

^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.28 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.21 (t, *J* = 7.8 Hz, 1H), 6.93 (d, *J* = 8.2 Hz, 1H), 6.84 (t, *J* = 7.5 Hz, 1H), 5.99 (s, 1H), 4.16 (q, *J* = 7.2 Hz, 2H), 2.57 (t, *J* = 6.9 Hz, 2H), 2.51 (t, *J* = 7.2 Hz, 2H), 1.97 (quin, *J* = 7.0 Hz, 2H), 1.26 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 173.5, 156.9, 131.7, 129.9, 120.3, 114.7, 110.0, 96.2, 75.9, 60.8, 33.4, 23.8, 19.2, 14.4.

HRMS (CI): Calculated for $C_{14}H_{17}O_3$ ($[M+H]^+$), 233.1178; found 233.1182.



SI-25 SI-26 SI-27 1j

3,5-Diiodo-4-(methoxymethoxy)benzonitrile (SI-26). A solution of **SI-25** (742 mg, 2.00 mmol, 1.00 equiv) and *N*,*N*-diisopropylethylamine (700. µL, 4.00 mmol, 2.00 equiv) in DCM (40 mL) was cooled to 0 °C under dynamic N_2 atmosphere. Chloromethyl methyl ether (210 µL, 2.8 mmol, 1.4 equiv) was then added dropwise. The reaction mixture was stirred at 0 °C for 40 min. It was then warmed gradually to 25 °C was stirred for 15 h, at which time analysis by TLC (20% EtOAc/hexanes) indicated full consumption of the phenol starting material. The reaction mixture was diluted with 20 mL EtOAc and 10 mL H_2O. The resulting biphasic mixture was stirred vigorously for 20 min to quench unreacted MOMCl, and then the phases were separated. The organic layer was washed with H_2O (2 × 10 mL) and brine (1 × 10 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo to a pale yellow solid (780 mg, 94% yield).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.08 (s, 2H), 5.22 (s, 2H), 3.75 (s, 3H).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 161.1, 143.4, 115.4, 111.8, 100.9, 91.7, 59.2.

HRMS (GC/CI): Calculated for $C_9H_{11}I_2N_2O_2$ ($[M+NH_4]^+$), 432.8910; found 432.8896.

3-(Cyclohex-1-en-1-ylethynyl)-5-iodo-4-(methoxymethoxy)benzonitrile (SI-27). A mixture of THF (24 mL) and Et_3N (2.6 mL, 19 mmol, 5.0 equiv) was sparged with N_2 for 20 min. Solid **SI-26** (1.56 g, 3.76 mmol, 1.00 equiv), $Pd(PPh_3)_2Cl_2$ (66 mg, 0.094 mmol, 2.5 mol %), and CuI (36 mg, 0.19 mmol, 5.0 mol %) were added under positive N_2 pressure. To the resulting solution was added 1-ethynylcyclohexene (463 µL, 3.95 mmol, 1.05 equiv). The reaction mixture was stirred at 25 °C for 20 h, at which time analysis by TLC (10% EtOAc/hexanes) indicated complete consumption of **SI-26**. The reaction mixture was diluted with 100 mL EtOAc, then washed with saturated aqueous NH_4Cl (3 × 20 mL) and brine (2 × 20 mL). The organic phase was dried over Na_2SO_4, filtered, and concentrated in vacuo to an orange semisolid, which was purified using three successive silica gel chromatography columns using an elution gradient from 100% hexanes to 10% EtOAc/hexanes. Volatiles were removed at 25 °C and c.a. 10 mTorr for 18 h to afford **SI-27** as a yellow oil in 90% purity (249 mg, 17% yield).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.98 (d, J = 2.0 Hz, 1H), 7.66 (d, J = 2.0 Hz, 1H), 6.27 (m, 1H), 5.44 (s, 2H), 3.68 (s, 3H), 2.23–2.15 (m, 4H), 1.72–1.61 (m, 4H).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 161.0, 141.9, 137.7, 137.6, 120.1, 118.4, 116.6, 109.3, 99.6, 98.9, 92.5, 81.0, 58.9, 28.8, 26.0, 22.2, 21.4.

HRMS (ESI+): Calculated for $C_{17}H_{16}INO_2Na$ ($[M+Na]^+$), 416.0108; found 416.0124.

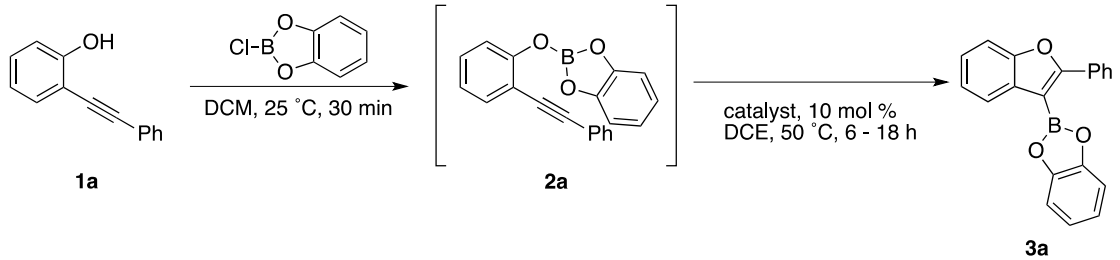
3-(Cyclohex-1-en-1-ylethynyl)-4-hydroxy-5-iodobenzonitrile (1j). To a solution of **SI-27** (91 mg, 0.23 mmol, 1.0 equiv) in 2 mL DCM at 25 °C was added $HCl{\cdot}Et_2O$ (280 μL, 1.2 equiv). The reaction mixture was stirred for 3 h, at which time analysis by TLC (10% EtOAc/hexanes) revealed complete consumption of the MOM ether starting material. The reaction mixture was diluted with 10 mL EtOAc and washed with water (3 × 2 mL) and brine (3 × 2 mL). The organic layer was dried over Na_2SO_4, filtered, and concentrated in vacuo to a pale yellow oil. The product was purified by silica gel chromatography using an elution gradient from 100% hexanes to 10% EtOAc/hexanes. Volatiles were removed at 25 °C and c.a. 10 mTorr for 18 h to afford **1j** as a white solid (45 mg, 55% yield).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.92 (d, J = 2.3 Hz, 1H), 7.60 (d, J = 2.3 Hz, 1H), 6.67 (br s, 1H), 6.35–6.32 (m, 1H), 2.24–2.16 (m, 4H), 1.74–1.62 (m, 4H).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 159.0, 142.3, 138.8, 135.3, 119.5, 117.0, 106.1, 101.1, 81.9, 78.1, 29.0, 26.0, 22.2, 21.3.

HRMS (GC/CI): Calculated for $C_{15}H_{12}INO$ (M^+), 348.9964; found 348.9967.

B. Screen of potential alkoxyboration catalysts



Boric ester 2a. A flame-dried 25-mL Schlenk tube was charged with a solution of **1a** (97.0 mg, 0.500 mmol, 1.00 equiv) in dry DCM (3 mL). To this solution was then added a solution of *B*-chlorocatecholborane (77.0 mg, 0.500 mmol, 1.00 equiv) in dry DCM (3 mL) at 25 °C. The reaction mixture was stirred for 30 min, and then the mixture was concentrated in vacuo to afford a moisture-sensitive, clear brown oil (159 mg, quant.) containing **2a**, which was used directly in the catalyst screen without further purification.

^{1}H NMR (d_8-toluene, 600 MHz): δ 7.38 (dd, J = 7.6, 1.6 Hz, 1H), 7.23–7.21 (m, 2H), 6.98 (dd, J = 10.2, 1.4 Hz, 1 H), 6.92 (td, J = 8.7, 2.9 Hz, 1H), 6.86–6.84 (m, 3H), 6.82 (dd, J = 5.8, 3.4 Hz, 2H), 6.76 (td, J = 15.1, 9.5 Hz), 6.74 (J = 5.8, 3.4 Hz, 2H).

^{11}B NMR (d_8-toluene, 193 MHz): δ 23.2 (br s).

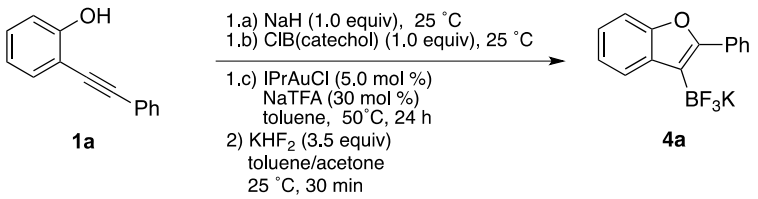
Catalyst screening reactions were set up in an N_2-filled glovebox. Catalyst (0.0040 mmol, 10. mol %) was dissolved in anhydrous 1,2-dichloroethane (400 μL) and added to a dram vial containing **2a** (13 mg, 0.040 mmol, 1.0 equiv). After mixing thoroughly, the reaction mixture was transferred to a J. Young NMR tube, removed from the glovebox, and heated in a preheated 50 °C oil bath. After heating for the indicated time, the progress of the reaction was monitored by ^{1}H and ^{11}B NMR spectroscopy.

Entry	Catalyst	Product : Starting Material Ratio (**3a**:**2a**, ^{1}H NMR)
1	None	Only **2a**
2	$Pd(PPh_3)_2Cl_2$ + 20 mol % AgOTf	Only **2a**
3	PEPPSI-IPr + 20 mol % AgOTf	Only **2a**
4	IPrAuCl + 10 mol % AgOTf	> 95:5
5	IPrAuCl	Only **2a**
6	AgOTf	Only **2a**
7	IPrAuCl + 10 mol % AgTFA	> 95:5
8	IPrCuCl + 10 mol % AgTFA	Only **2a**
9	Trifluoroacetic acid	Only **2a**
10	$InBr_3$	Only **2a**

Table SI-1. Screen of alkoxyboration catalysts for optimal conversion to **3a** by ^{1}H NMR spectroscopy.

C. Synthesis and isolation of benzofuran alkoxyboration products 4a–4j

Note: All alkoxyboration reactions were conducted in a N_2-filled glovebox due to the high moisture sensitivity of the boric ester intermediate **2**. All glassware and reagents must be rigorously dry for optimal yield. The reaction progress was monitored by removing a small aliquot of the reaction mixture from the glovebox and diluting it in 1:1 EtOAc:water. This results in rapid hydrolysis of boric ester intermediate **2** back to the phenol starting material **1**. Thus, co-spotting the reaction mixture versus phenol **1** provides a convenient method for determining whether or not intermediate **2** has been fully consumed. The addition of PPh_3 to quench the Au catalyst.[13] between the alkoxyboration step and the formation of the organotrifluoroborate or MIDA boronate was essential.



Benzofuran trifluoroborate 4a. A solution of phenol **1a** (97.0 mg, 0.500 mmol, 1.00 equiv) in 1.0 mL toluene was added to a flame-dried 10-mL Schlenk tube. To this stirring solution was added dropwise at 25 °C a suspension of NaH (69 wt % purity, 17.4 mg, 0.500 mmol, 1.00 equiv) in 0.5 mL toluene over 2 min. A suspension of NaTFA (20. mg, 0.15 mmol, 30. mol %) in 0.5 mL toluene was added next, and the resulting suspension was stirred for 15 min to affect full deprotonation.

To the resulting stirring sodium phenoxide suspension was added at 25 °C a solution of *B*-chlorocatecholborane (77.0 mg, 0.500 mmol, 1.00 equiv) in toluene (1.0 mL), using additional toluene as a rinse to ensure full transfer (2 × 0.5 mL portions). The resulting suspension was stirred vigorously for 30 min to allow for full conversion to boric ester intermediate **2a**.

Next, a suspension of IPrAuCl (16 mg, 0.025 mmol, 5.0 mol %) in toluene (0.5 mL) was added to the reaction mixture at 25 °C, using additional toluene as a rinse to aid in full transfer (1 × 0.5 mL portion). The reaction mixture was then sealed with a ground glass stopper and a PTFE sealing ring and placed in a preheated 50 °C copper shot heating bath. The final concentration of the reaction mixture was 0.1 M in **1a**.

After 24 h, analysis by TLC (20% EtOAc/hexanes) indicated full consumption of boric ester intermediate **2a**. The reaction mixture was cooled to 25 °C, and a solution of PPh_3 (13 mg, 0.050 mmol, 10 mol %) in toluene (0.5 mL) was added. The resulting suspension was stirred for 22 h at 25 °C in order to quench IPrAuTFA before proceeding.

The quenched reaction mixture was removed from the glovebox and filtered through a fiberglass filter to remove the suspended solids. The filter was then rinsed with toluene (3 × 3 mL), and the combined filtrates were concentrated in vacuo to a pale yellow powder, which was suspended in acetone (4.5 mL) and added to a stirring solution of KHF_2 (140 mg, 1.8 mmol, 3.5 equiv) in water (1.5 mL). The resulting mixture was stirred at 25 °C for 30 min, and then concentrated in vacuo to remove the solvents. To this residue was added 2 mL Et_2O and subsequently concentrated at c.a. 10 mTorr for 30 min in order to remove residual acetone. The resulting pale yellow solid residue was washed with Et_2O (4 × 2 mL) and extracted with acetone (4 × 2 mL). The combined acetone extracts were concentrated in vacuo, and the resulting residue was subjected to an additional washing/extraction cycle to yield **4a** as a white powder (113 mg, 75% yield) after removing volatiles at 25 °C and c.a. 10 mTorr for 18 h.

^{1}H NMR (d_6-DMSO, 600 MHz): δ 8.10 (d, J = 7.4 Hz, 2H), 7.88 (d, J = 7.7 Hz, 1H), 7.42 (d, J = 8.0 Hz, 1H), 7.38 (t, J = 7.6 Hz, 2H), 7.26 (t, J = 7.3 Hz, 1H), 7.13 (td, J = 6.5 Hz, 1.2 Hz, 1H), 7.08 (td, J = 7.4, 0.9 Hz, 1H).

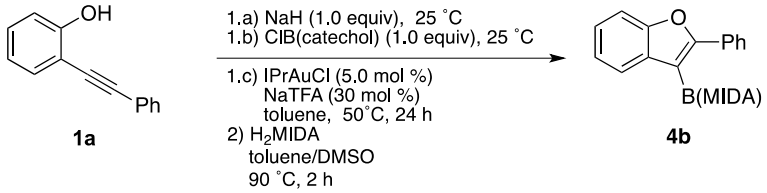
^{13}C NMR (d_6-DMSO, 125 MHz): δ 154.7 (q, $J_{C–F}$ = 4.6 Hz), 153.8, 135.4, 133.3, 127.9, 126.8, 126.7 (q, $J_{C–F}$ = 2.3 Hz), 124.1 (q, $J_{C–F}$ = 2.8 Hz), 122.7, 109.6. [Note: As with many organotrifluoroborates, the *ipso* carbon was not detected, presumably due to broadening

through coupling to the ^{11}B nucleus. The quaternary carbon at the benzofuran 2 position was also not detected.]

^{11}B NMR (d_6-DMSO, 193 MHz): δ 3.2 (br s).

^{19}F NMR (d_6-DMSO, 376 MHz): δ -131.9 (br s).

HRMS (ESI-): Calculated for $C_{14}H_9BF_3O$ ([M-K]$^-$), 261.0701; found 261.0706.



MIDA boronate 4b. A solution of phenol **1a** (97.0 mg, 0.500 mmol, 1.00 equiv) in 1.0 mL toluene was added to a flame-dried 10-mL Schlenk tube. To this stirring solution was added dropwise at 25 °C a suspension of NaH (92 wt % purity, 13.0 mg, 0.500 mmol, 1.00 equiv) in 0.5 mL toluene over 2 min. A suspension of NaTFA (20. mg, 0.15 mmol, 30 mol %) in 0.5 mL toluene was added next, and the resulting suspension was stirred for 15 min to affect full deprotonation.

To the resulting stirring sodium phenoxide suspension was added at 25 °C a solution of *B*-chlorocatecholborane (77.0 mg, 0.500 mmol, 1.00 equiv) in toluene (1.0 mL), using additional toluene as a rinse to ensure full transfer (2 × 0.5 mL portions). The resulting suspension was stirred vigorously for 30 min to allow for full conversion to boric ester intermediate **2a**.

Next, a suspension of IPrAuCl (16 mg, 0.025 mmol, 5.0 mol %) in toluene (0.5 mL) was added to the reaction mixture at 25 °C, using additional toluene as a rinse to aid in full transfer (1 × 0.5 mL portion). The reaction mixture was then sealed with a ground glass stopper and a PTFE sealing ring and placed in a preheated 50 °C copper shot heating bath. The final concentration of the reaction mixture was 0.1 M in **1a**.

After 24 h, analysis by TLC (20% EtOAc/hexanes) indicated full consumption of boric ester intermediate **2a**. The reaction mixture was cooled to 25 °C, and a solution of PPh_3 (13 mg, 0.050 mmol, 10 mol %) in toluene (0.5 mL) was added. The resulting suspension was stirred for 16 h at 25 °C in order to quench IPrAuTFA before proceeding.

Anhydrous DMSO (2.0 mL) and H_2MIDA (81 mg, 0.55 mmol, 1.1 equiv) were added to the quenched alkoxyboration reaction mixture, and the resulting suspension was stirred at 90 °C for 2h. The reaction mixture was then cooled to 25 °C and removed from the glovebox. Toluene was removed in vacuo at 25 °C and c.a. 10 Torr, then DMSO was removed by Kugelrohr distillation at c.a. 10 mTorr. The resulting semisolid residue was adsorbed onto Celite from a MeCN suspension and purified by silica gel chromatography using an elution gradient from 100% Et_2O to 100% MeCN. Removal of volatiles at 25 °C and c.a. 10 mTorr for 18 h afforded MIDA boronate **4b** as a white powder (101 mg, 58% yield). Crystals suitable for X-ray diffraction analysis were prepared by slow diffusion of Et_2O into a saturated solution of **4b** in Et_2O/acetone at 25 °C over 3 days

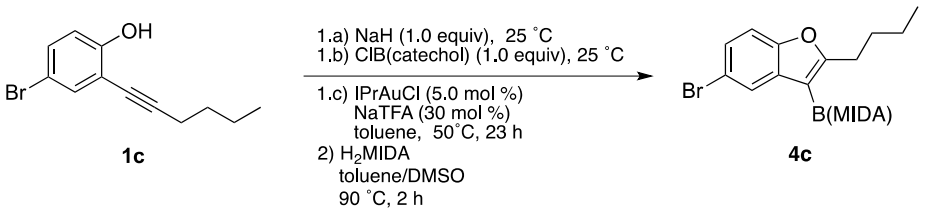
TLC (10% MeCN/ Et_2O): R_f = 0.39.

^{1}H NMR (CD_3CN, 600 MHz): δ 7.72 (dd, J = 7.8 Hz, 0.8 Hz, 1H), 7.67–7.65 (m, 2H), 7.55 (d, J = 9.7 Hz, 1H), 7.47–7.44 (m, 3H), 7.35– 7.31 (m, 1H), 7.29– 7.26 (m, 1H), 3.97 (d, J = 17.1 Hz, 2H), 3.65 (d, J = 17.1 Hz, 2H), 2.56 (s, 3H).

^{13}C NMR (CD_3CN, 125 MHz): δ 169.0, 156.0, 133.6, 133.0, 130.6, 130.2, 129.3, 125.2, 123.9, 123.5, 111.8, 63.0, 48.2. [Note: no signals were observed for the quaternary C–B *ipso* carbon or the quaternary carbon at the benzofuran 2 position.]

^{11}B NMR (CD_3CN, 193 MHz): δ 11.3 (br s).

HRMS (ESI+): Calculated for $C_{17}H_{19}BBrNO_5$ ([M+Na]$^+$), 372.1023; found 372.1016.



MIDA boronate 4c. A solution of phenol **1c** (127 mg, 0.500 mmol, 1.00 equiv) in 1.0 mL toluene was added to a flame-dried 10-mL Schlenk tube. To this stirring solution was added dropwise at 25 °C a suspension of NaH (92 wt % purity, 13.0 mg, 0.500 mmol, 1.00 equiv) in 0.5 mL toluene over 2 min. A suspension of NaTFA (20. mg, 0.15 mmol, 30 mol %) in 0.5 mL toluene was added next, and the resulting suspension was stirred for 15 min to affect full deprotonation.

To the resulting stirring sodium phenoxide suspension was added at 25 °C a solution of *B*-chlorocatecholborane (77.0 mg, 0.500 mmol, 1.00 equiv) in toluene (1.0 mL), using additional toluene as a rinse to ensure full transfer (2 × 0.5 mL portions). The resulting suspension was stirred vigorously for 30 min to allow for full conversion to boric ester intermediate **2c**.

Next, a suspension of IPrAuCl (16 mg, 0.025 mmol, 5.0 mol %) in toluene (0.5 mL) was added to the reaction mixture at 25 °C, using additional toluene as a rinse to aid in full transfer (1 × 0.5 mL portion). The reaction mixture was then sealed with a ground glass stopper and a PTFE sealing ring and placed in a preheated 50 °C copper shot heating bath. The final concentration of the reaction mixture was 0.1 M in **1c**.

After 23 h, analysis by TLC (20% EtOAc/hexanes) indicated full consumption of boric ester intermediate **2c**. The reaction mixture was cooled to 25 °C, and a solution of PPh_3 (13 mg, 0.050 mmol, 10 mol %) in toluene (0.5 mL) was added. The resulting suspension was stirred for 16 h at 25 °C in order to quench IPrAuTFA before proceeding.

Anhydrous DMSO (2.0 mL) and H_2MIDA (160 mg, 1.1 mmol, 2.2 equiv) were added to the quenched alkoxyboration reaction mixture, and the resulting suspension was stirred at 90 °C for 2h. The reaction mixture was then cooled to 25 °C and removed from the glovebox. Toluene was removed in vacuo at 25 °C and c.a. 10 Torr, then DMSO was removed by Kugelrohr distillation at c.a. 10 mTorr. The resulting semisolid residue was adsorbed onto Celite from a MeCN suspension and purified by silica gel chromatography using an elution gradient from 100% Et_2O to 100% MeCN. Removal of volatiles at 25 °C and c.a. 10 mTorr for 18 h afforded MIDA boronate **4b** as a white powder (161 mg, 79% yield).

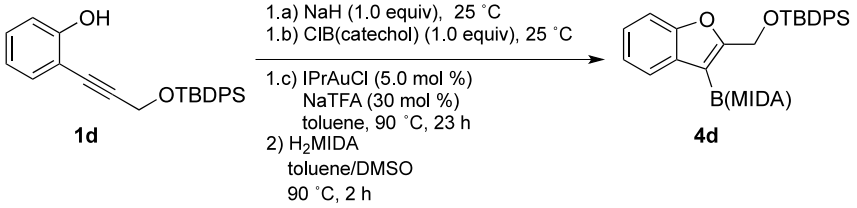
TLC (10% MeCN/ Et_2O): R_f = 0.50.

^{1}H NMR (CD_3CN, 600 MHz): δ 7.59 (dd, *J* = 1.9 Hz, 0.4 Hz, 1H), 7.37 (d, *J* = 7.4 Hz, 1H), 7.34 (dd, *J* = 8.7 Hz, 1.8 Hz, 1H), 4.12 (d, *J* = 17.2 Hz, 2H), 3.92 (d, *J* = 17.2 Hz, 2H), 2.77 (app t, *J* = 7.7 Hz, 2H), 2.66 (s, 3H), 1.70 (app quintet, *J* = 7.7 Hz, 2H), 1.38 (sextet, *J* = 7.4 Hz, 2H), 0.93 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (CD_3CN, 125 MHz): δ 169.4, 167.4, 154.6, 135.6, 126.8, 124.9, 116.1, 113.1, 63.0, 48.1, 31.6, 29.0, 23.2, 14.0. [Note: no signal was observed for the quaternary C–B *ipso* carbon.]

^{11}B NMR (CD_3CN, 193 MHz): δ 11.3 (br s).

HRMS (ESI+): Calculated for $C_{16}H_{17}BBrNO_5Na$ ([M+Na]$^+$), 430.0441; found 430.0425.



MIDA boronate 4d. A solution of phenol **1d** (85 mg, 0.22 mmol, 1.0 equiv) in 1.0 mL toluene was added to a flame-dried 10-mL Schlenk tube. To this stirring solution was added dropwise at 25 °C a suspension of NaH (92 wt % purity, 6.0 mg, 0.20 mmol, 1.0 equiv) in 0.5 mL toluene over 2 min. A suspension of NaTFA (9.0 mg, 0.070 mmol, 30 mol %) in 0.5 mL toluene was added next, and the resulting suspension was stirred for 45 min to affect full deprotonation.

To the resulting stirring sodium phenoxide suspension was added at 25 °C a solution of *B*-chlorocatecholborane (34 mg, 0.22 mmol, 1.0 equiv) in toluene (1.0 mL), using additional toluene as a rinse to ensure full transfer (2 × 0.5 mL portions). The resulting suspension was stirred vigorously for 30 min to allow for full conversion to boric ester intermediate **2d**.

Next, a suspension of IPrAuCl (7.0 mg, 0.010 mmol, 5.0 mol %) in toluene (0.5 mL) was added to the reaction mixture at 25 °C, using additional toluene as a rinse to aid in full transfer (1 × 0.5 mL portion). The reaction mixture was then sealed with a ground glass stopper and a PTFE sealing ring and placed in a preheated 50 °C copper shot heating bath. The final concentration of the reaction mixture was 0.1 M in **1d**.

After 23 h, analysis by TLC (20% EtOAc/hexanes) indicated full consumption of boric ester intermediate **2d**. The reaction mixture was cooled to 25 °C, and a solution of PPh_3 (6.0 mg, 0.020 mmol, 10 mol %) in toluene (0.5 mL) was added. The resulting suspension was stirred for 16 h at 25 °C in order to quench IPrAuTFA before proceeding.

Anhydrous DMSO (2.0 mL) and H_2MIDA (35 mg, 0.24 mmol, 1.1 equiv) were added to the quenched alkoxyboration reaction mixture, and the resulting suspension was stirred at 90 °C for 2 h. The reaction mixture was then cooled to 25 °C and removed from the glovebox. Toluene was removed in vacuo at 25 °C and c.a. 10 Torr, then DMSO was removed by Kugelrohr distillation at c.a. 10 mTorr. The resulting semisolid residue was adsorbed onto Celite from a MeCN suspension and purified by silica gel chromatography using an elution gradient from

100% Et_2O to 100% MeCN. Removal of volatiles at 25 °C and c.a. 10 mTorr for 18 h afforded MIDA boronate **4d** as a white powder (32 mg, 48% yield).

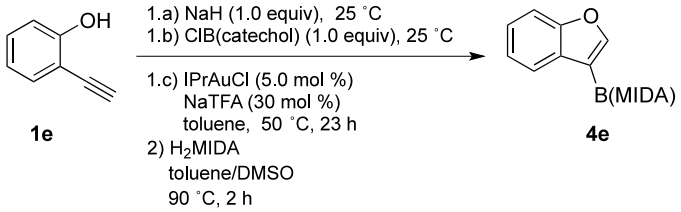
TLC (20% MeCN/Et_2O): R_f = 0.50, visualized by UV absorbance.

^{1}H NMR (CD_3CN, 600 MHz): δ 7.74 (dd, *J* = 7.8, 1.2 Hz, 4H), 7.56 (d, *J* = 7.6 Hz, 1H), 7.51–7.46 (m, 3H), 7.46–7.40 (m, 4H), 7.32 (dt, *J* = 7.2, 1.2 Hz, 1H), 7.25 (t, *J* = 7.6 Hz, 1H), 4.87 (s, 2 H), 4.24 (d, *J* = 17.2 Hz, 2H), 3.92 (d, *J* = 17.2 Hz, 2H), 2.63 (s, 3 H), 1.02 (s, 9 H)

^{13}C NMR (CD_3CN, 125 MHz): δ 169.3, 161.7, 156.0, 136.5, 133.9, 132.7, 131.0, 128.8, 125.4, 123.8, 123.1, 111.9, 62.7, 59.6, 48.3, 27.1, 19.8. [Note: no signal was observed for the quaternary C–B *ipso* carbon.]

^{11}B NMR (CD_3CN, 193 MHz): δ 11.2.

HRMS (ESI+): Calculated for $C_{30}H_{32}O_6BNSiNa$ ($[M+Na]^+$), 564.1995; found 564.1995.



MIDA boronate 4e. A solution of phenol **1e** (90. mg, 0.76 mmol, 1.0 equiv) in 1.5 mL toluene was added to a flame-dried 10-mL Schlenk tube. To this stirring solution was added dropwise at 25 °C a suspension of NaH (92 wt % purity, 20. mg, 0.76 mmol, 1.00 equiv) in 1.0 mL toluene over 2 min. A suspension of NaTFA (31 mg, 0.23 mmol, 30 mol %) in 0.5 mL toluene was added next, and the resulting suspension was stirred for 15 min to affect full deprotonation.

To the resulting stirring sodium phenoxide suspension was added at 25 °C a solution of *B*-chlorocatecholborane (120 mg, 0.76 mmol, 1.0 equiv) in toluene (1.5 mL), using additional toluene as a rinse to ensure full transfer (2 × 0.5 mL portions). The resulting suspension was stirred vigorously for 30 min to allow for full conversion to boric ester intermediate **2e**.

Next, a suspension of IPrAuCl (25 mg, 0.040 mmol, 5.0 mol %) in toluene (0.5 mL) was added to the reaction mixture at 25 °C, using additional toluene as a rinse to aid in full transfer (3 × 0.5 mL portion). The reaction mixture was then sealed with a ground glass stopper and a PTFE sealing ring and placed in a preheated 50 °C copper shot heating bath. The final concentration of the reaction mixture was 0.1 M in **1e**.

After 23 h, analysis by TLC (20% EtOAc/hexanes) indicated full consumption of boric ester intermediate **2e**. The reaction mixture was cooled to 25 °C, and a solution of PPh_3 (20. mg, 0.080 mmol, 10 mol %) in toluene (0.5 mL) was added. The resulting suspension was stirred for 16 h at 25 °C in order to quench IPrAuTFA before proceeding.

Anhydrous DMSO (2.0 mL) and H_2MIDA (124 mg, 0.84 mmol, 1.1 equiv) were added to the quenched alkoxyboration reaction mixture, and the resulting suspension was stirred at 90 °C for 2h. The reaction mixture was then cooled to 25 °C and removed from the glovebox. Toluene was removed in vacuo at 25 °C and c.a. 10 Torr, then DMSO was removed by Kugelrohr distillation at c.a. 10 mTorr. The resulting semisolid residue was adsorbed onto Celite from a MeCN

suspension and purified by silica gel chromatography using an elution gradient from 100% Et_2O to 100% MeCN. Removal of volatiles at 25 °C and c.a. 10 mTorr for 18 h afforded MIDA boronate **4e** as an off-white powder (82 mg, 40% yield).

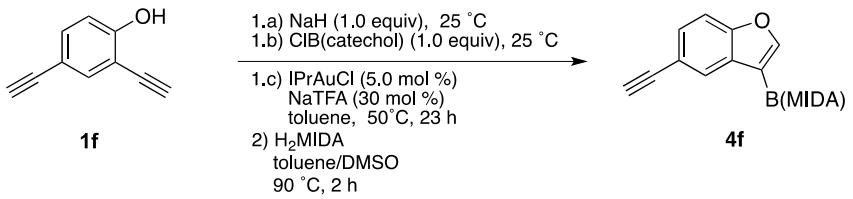
TLC (20% MeCN/Et_2O): R_f = 0.58, visualized by UV absorbance.

^{1}H NMR (CD_3CN, 600 MHz): δ 7.75 (s, 1H), 7.59 (d, *J* = 7.7 Hz, 1H), 7.55 (d, *J* = 8.1 Hz, 1H), 7.32 (t, *J* = 8.4 Hz, 1H), 7.26 (t, *J* = 9.0 Hz, 1H), 4.12 (d, *J* = 17.2 Hz, 2H), 3.95 (d, *J* = 17.2 Hz, 2H), 2.67 (s, 3H).

^{13}C NMR (CD_3CN, 125 MHz): δ 169.3, 157.0, 151.7, 131.1, 125.2, 123.9, 122.9, 112.2, 62.6, 48.1. [Note: no signal was observed for the quaternary C–B *ipso* carbon.]

^{11}B NMR (CD_3CN, 193 MHz): δ 11.2 (br s).

HRMS (ESI+): Calculated for $C_{12}H_{12}BNO_5Na$ ([M+Na]$^+$), 296.0709; found 296.0714.



MIDA boronate 4f. A solution of phenol **1f** (71.0 mg, 0.500 mmol, 1.00 equiv) in 1.0 mL toluene was added to a flame-dried 10-mL Schlenk tube. To this stirring solution was added dropwise at 25 °C a suspension of NaH (92 wt % purity, 13.0 mg, 0.500 mmol, 1.00 equiv) in 0.5 mL toluene over 2 min. A suspension of NaTFA (20. mg, 0.15 mmol, 30 mol %) in 0.5 mL toluene was added next, and the resulting suspension was stirred for 15 min to affect full deprotonation.

To the resulting stirring sodium phenoxide suspension was added at 25 °C a solution of *B*-chlorocatecholborane (77.0 mg, 0.500 mmol, 1.00 equiv) in toluene (1.0 mL), using additional toluene as a rinse to ensure full transfer (2 × 0.5 mL portions). The resulting suspension was stirred vigorously for 30 min to allow for full conversion to boric ester intermediate **2f**.

Next, a suspension of IPrAuCl (16 mg, 0.025 mmol, 5.0 mol %) in toluene (0.5 mL) was added to the reaction mixture at 25 °C, using additional toluene as a rinse to aid in full transfer (1 × 0.5 mL portion). The reaction mixture was then sealed with a ground glass stopper and a PTFE sealing ring and placed in a preheated 50 °C copper shot heating bath. The final concentration of the reaction mixture was 0.1 M in **1f**.

After 23 h, analysis by TLC (20% EtOAc/hexanes) indicated full cosumption of boric ester intermediate **2f**. The reaction mixture was cooled to 25 °C, and a solution of PPh_3 (13 mg, 0.050 mmol, 10 mol %) in toluene (0.5 mL) was added. The resulting suspension was stirred for 16 h at 25 °C in order to quench IPrAuTFA before proceeding.

Anhydrous DMSO (2.0 mL) and H_2MIDA (160 mg, 1.1 mmol, 2.2 equiv) were added to the quenched alkoxyboration reaction mixture, and the resulting suspension was stirred at 90 °C for 2h. The reaction mixture was then cooled to 25 °C and removed from the glovebox. Toluene was removed in vacuo at 25 °C and c.a. 10 Torr, then DMSO was removed by Kugelrohr distillation

at c.a. 10 mTorr. The resulting semisolid residue was adsorbed onto Celite from a MeCN suspension and purified by silica gel chromatography using an elution gradient from 100% Et_2O to 100% MeCN. Removal of volatiles at 25 °C and c.a. 10 mTorr for 18 h afforded MIDA boronate **4f** as a white powder (52 mg, 35% yield).

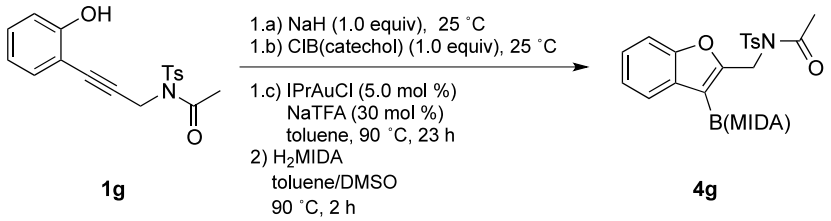
TLC (20% MeCN/ Et_2O): $R_f = 0.50$.

^{1}H NMR (CD_3CN, 600 MHz): δ 7.82 (s, 1H), 7.69 (s, 1H), 7.57 (d, J = 8.1 Hz, 1H), 7.38 (dd, J = 7.1, 1.3 Hz, 1H), 4.12 (d, J = 17.2 Hz, 2H), 3.94 (d, J = 17.2 Hz, 2H), 3.40 (s, 1H), 2.66 (s, 3H).

^{13}C NMR (CD_3CN, 125 MHz): δ 169.2, 156.4, 153.3, 132.1, 127.9, 123.1, 115.8, 84.4, 78.5, 62.6, 48.2. [Note: no signals were observed for the quaternary C–B *ipso* carbon and a second quaternary carbon.]

^{11}B NMR (CD_3CN, 193 MHz): δ 11.0 (br s).

HRMS (ESI+): Calculated for $C_{15}H_{12}BNO_5Na$ ([M+Na]$^+$), 320.0709; found 320.0713.



MIDA boronate 4g. A solution of phenol **1g** (99 mg, 0.29 mmol, 1.0 equiv) in 0.5 mL toluene was added to a flame-dried 10-mL Schlenk tube. To this stirring solution was added dropwise at 25 °C a suspension of NaH (92 wt % purity, 8.0 mg, 0.50 mmol, 1.0 equiv) in 0.5 mL toluene over 2 min. A suspension of NaTFA (9.0 mg, 0.090 mmol, 30. mol %) in 0.5 mL toluene was added next, and the resulting suspension was stirred for 15 min to affect full deprotonation.

To the resulting stirring sodium phenoxide suspension was added at 25 °C a solution of *B*-chlorocatecholborane (45 mg, 0.29 mmol, 1.0 equiv) in toluene (0.5 mL), using additional toluene as a rinse to ensure full transfer (1 × 0.3 mL portion). The resulting suspension was stirred vigorously for 30 min to allow for full conversion to boric ester intermediate **2g**.

Next, a suspension of IPrAuCl (9.0 mg, 0.010 mmol, 5.0 mol %) in toluene (0.5 mL) was added to the reaction mixture at 25 °C, using additional toluene as a rinse to aid in full transfer (1 × 0.2 mL portion). The reaction mixture was then sealed with a ground glass stopper and a PTFE sealing ring and placed in a preheated 90 °C copper shot heating bath. The final concentration of the reaction mixture was 0.1 M in **1g**.

After 23 h, analysis by TLC (20% EtOAc/hexanes) indicated full consumption of boric ester intermediate **2g**. The reaction mixture was cooled to 25 °C, and a solution of PPh_3 (8.0 mg, 0.030 mmol, 10. mol %) in toluene (0.5 mL) was added. The resulting suspension was stirred for 16 h at 25 °C in order to quench IPrAuTFA before proceeding.

Anhydrous DMSO (2.0 mL) and H_2MIDA (52 mg, 0.35 mmol, 1.1 equiv) were added to the quenched alkoxyboration reaction mixture, and the resulting suspension was stirred at 90 °C for 2h. The reaction mixture was then cooled to 25 °C and removed from the glovebox. Toluene was

removed in vacuo at 25 °C and c.a. 10 Torr, then DMSO was removed by Kugelrohr distillation at c.a. 10 mTorr. The resulting semisolid residue was adsorbed onto Celite from a MeCN suspension and purified by silica gel chromatography using an elution gradient from 100% Et_2O to 100% MeCN. Removal of volatiles at 25 °C and c.a. 10 mTorr for 18 h afforded MIDA boronate **4g** as a white powder (59 mg, 41% yield).

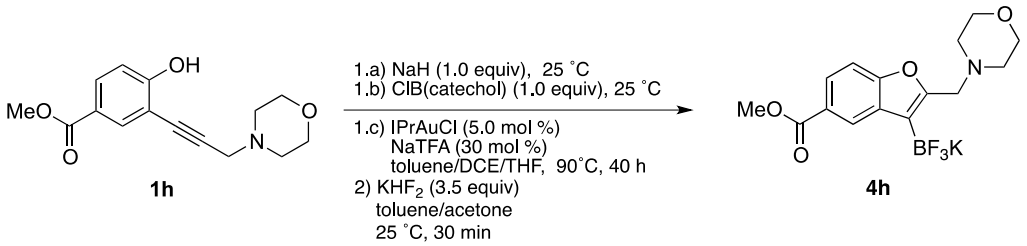
TLC (20% MeCN/Et_2O): R_f = 0.58, visualized by UV absorbance.

^{1}H NMR (CD_3CN, 600 MHz): δ 7.70 (d, *J* = 8.3 Hz, 2H), 7.47 (d, *J* = 7.6 Hz, 1H), 7.40 (d, *J* = 7.9 Hz, 1H), 7.34–7.29 (m, 3H), 7.26 (t, *J* = 7.2 Hz, 1H), 5.28 (s, 2H), 4.19 (d, *J* = 21.0 Hz, 2H), 4.12 (d, *J* = 21.0 Hz, 2H), 2.76 (s, 3H), 2.39 (s, 3H), 2.35 (s, 3H).

^{13}C NMR (CD_3CN, 125 MHz): δ 171.7, 169.6, 158.2, 155.6, 146.4, 137.2, 132.3, 130.6, 129.0, 125.4, 124.1, 122.9, 111.9, 64.0, 49.0, 44.5, 25.0, 21.6. [Note: no signal was observed for the quaternary C–B *ipso* carbon.]

^{11}B NMR (CD_3CN, 193 MHz): δ 11.3.

HRMS (ESI+): Calculated for $C_{23}H_{23}BN_2O_8SNa$ ([M+Na]$^+$), 521.1170; found 521.1153.



Benzofuran trifluoroborate 4h. A solution of phenol **1h** (138 mg, 0.500 mmol, 1.00 equiv) in 1.0 mL toluene was added to a flame-dried 10-mL Schlenk tube. To this stirring solution was added dropwise at 25 °C a suspension of NaH (92 wt % purity, 13.0 mg, 0.500 mmol, 1.00 equiv) in 0.5 mL toluene over 2 min. A suspension of NaTFA (20. mg, 0.15 mmol, 30 mol %) in 0.5 mL toluene was added next. Due to the low solubility of **1h** in toluene, dry dichloroethane (0.5 mL) and dry THF (1.0 mL) were added. The resulting suspension was stirred for 15 min to affect full deprotonation.

To the resulting stirring sodium phenoxide suspension was added at 25 °C a solution of *B*-chlorocatecholborane (77.0 mg, 0.500 mmol, 1.00 equiv) in toluene (0.5 mL), using additional toluene as a rinse to ensure full transfer (1 × 0.5 mL portions). The resulting suspension was stirred vigorously for 30 min to allow for full conversion to boric ester intermediate **2h**.

Next, a suspension of IPrAuCl (16 mg, 0.025 mmol, 5.0 mol %) in toluene (0.5 mL) was added to the reaction mixture at 25 °C, using additional toluene as a rinse to aid in full transfer (1 × 0.5 mL portion). The reaction mixture was then sealed with a ground glass stopper and a PTFE sealing ring and placed in a preheated 90 °C copper shot heating bath. The final concentration of the reaction mixture was 0.08 M in **1h**.

After 40 h, analysis by TLC (20% EtOAc/hexanes) indicated full consumption of boric ester intermediate **2h**. The reaction mixture was cooled to 25 °C, and a solution of PPh_3 (13 mg, 0.050 mmol, 10 mol %) in toluene (0.5 mL) was added. The resulting suspension was stirred for 26 h at 25 °C in order to quench IPrAuTFA before proceeding.

The quenched reaction mixture was removed from the glovebox and filtered through a fiberglass filter to remove the suspended solids. The filter was then rinsed with chloroform (3 × 3 mL), and the combined filtrates were concentrated in vacuo to a pale yellow powder, which was suspended in acetone (4.5 mL) and added to a stirring solution of KHF_2 (160 mg, 2.0 mmol 4.0 equiv) in water (1.5 mL). The resulting mixture was stirred at 25 °C for 30 min, and then concentrated in vacuo to remove the solvents. To this residue was added 2 mL Et_2O and subsequently concentrated at c.a. 10 mTorr for 30 min in order to remove residual acetone. The resulting pale yellow solid residue was washed with Et_2O (4 × 2 mL) and extracted with acetone (4 × 2 mL). The combined acetone extracts were concentrated in vacuo, and the resulting residue was subjected to an additional washing/extraction cycle to yield **4h** as a light green powder (79 mg, 42% yield) with trace residual acetone after removing volatiles at 25 °C and c.a. 10 mTorr for 18 h.

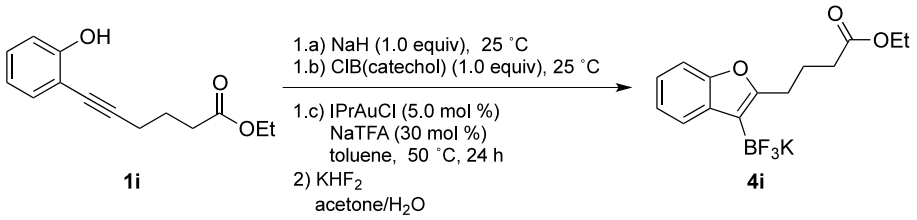
^{1}H NMR (d_6-DMSO, 600 MHz): δ 8.30 (s, 1H), 7.75 (dd, J = 9.4 Hz, 1.7 Hz, 1H), 7.44 (d, J = 8.5 Hz, 1H), 3.85, (s, 3H), 3.67 (br s, 2H), 3.54 (app t, J = 4.1 Hz, 4H), 2.44 (br s, 4H).

^{13}C NMR (d_6- DMSO, 125 MHz): δ 167.0, 157.3, 155.5 (br), 134.1, 125.2, 123.9, 122.7, 109.8, 66.2, 54.2, 53.0, 51.8. [Note: As with many organotrifluoroborates, the *ipso* carbon was not detected, presumably due to broadening through coupling to the ^{11}B nucleus.]

^{11}B NMR (d_6- DMSO, 193 MHz): δ 2.8 (br s).

^{19}F NMR (d_6-DMSO, 376 MHz): δ -133.1 (br s).

HRMS (ESI-): Calculated for $C_{15}H_{16}BF_3NO_4$ ([M-K]$^-$), 342.1127; found 342.1125.



Benzofuran trifluoroborate 4i. A solution of phenol **1i** (101 mg, 0.440 mmol, 1.00 equiv) in 0.75 mL toluene was added to a flame-dried 10-mL Schlenk tube. To this stirring solution was added dropwise at 25 °C a suspension of NaH (92 wt % purity, 11 mg, 0.44 mmol, 1.0 equiv) in 0.5 mL toluene over 2 min. A suspension of NaTFA (18 mg, 0.13 mmol, 30. mol %) in 0.5 mL toluene was added next, and the resulting suspension was stirred for 15 min to affect full deprotonation.

To the resulting stirring sodium phenoxide suspension was added at 25 °C a solution of *B*-chlorocatecholborane (67 mg, 0.44 mmol, 1.0 equiv) in toluene (0.75 mL), using additional toluene as a rinse to ensure full transfer (2 × 0.5 mL portions). The resulting suspension was stirred vigorously for 30 min to allow for full conversion to boric ester intermediate **2i**.

Next, a suspension of IPrAuCl (14 mg, 0.022 mmol, 5.0 mol %) in toluene (0.5 mL) was added to the reaction mixture at 25 °C, using additional toluene as a rinse to aid in full transfer (1 × 0.5 mL portion). The reaction mixture was then sealed with a ground glass stopper and a PTFE sealing ring and placed in a preheated 50 °C copper shot heating bath. The final concentration of the reaction mixture was 0.1 M in **1i**.

After 24 h, analysis by TLC (20% EtOAc/hexanes) indicated full consumption of boric ester intermediate **2i**. The reaction mixture was cooled to 25 °C, and a solution of PPh_3 (8.0 mg, 0.030 mmol, 10. mol %) in toluene (0.5 mL) was added. The resulting suspension stirred for 22 h at 25 °C in order to quench IPrAuTFA before proceeding.

The quenched reaction mixture was removed from the glovebox and filtered through a fiberglass filter to remove the suspended solids. The filter was then rinsed with toluene (3 × 3 mL), and the combined filtrates were concentrated in vacuo to a pale yellow powder, which was suspended in acetone (4.5 mL) and added to a stirring solution of KHF_2 (136 mg, 1.70 mmol, 3.50 equiv) in water (1.5 mL). The resulting mixture was stirred at 25 °C for 30 min, and then concentrated in vacuo to remove the solvents. To this residue was added 2 mL Et_2O and subsequently concentrated at c.a. 10 mTorr for 30 min in order to remove residual acetone. The resulting pale yellow solid residue was washed with Et_2O (4 × 2 mL) and extracted with acetone (4 × 2 mL). The combined acetone extracts were concentrated in vacuo, and the resulting residue was subjected to an additional washing/extraction cycle to yield **4i** as a white powder (102 mg, 69% yield) after removing volatiles at 25 °C and c.a. 10 mTorr for 18 h.

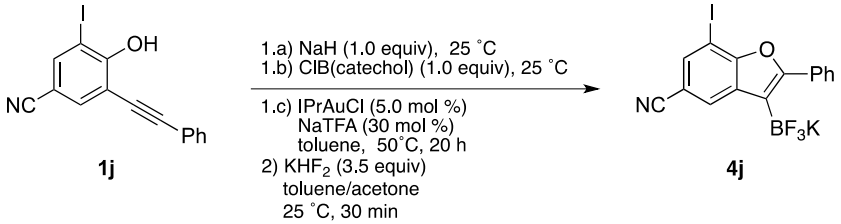
^{1}H NMR (d_6- DMSO, 600 MHz): δ 7.55 (t, J = 6.7 Hz, 1H), 7.27 (dd, J = 6.7, 1.8 Hz, 1H), 7.05–6.93 (m, 2H), 4.03 (q, J = 7.0 Hz, 2H), 2.77 (t, J = 7.3 Hz, 2H), 2.28 (t, J = 7.7 Hz, 2H), 1.85 (quin, J = 7.5 Hz, 2H), 1.16 (t, J = 7.1 Hz, 3H).

^{13}C NMR (d_6- DMSO, 125 MHz): δ 172.9, 157.3, 154.0, 134.6, 122.5, 121.3, 120.7, 109.2, 59.6, 33.1, 27.0, 24.0, 14.1.

^{11}B NMR (d_6- DMSO, 193 MHz): δ 2.9 (br s).

^{19}F NMR (d_6- DMSO, 377 MHz) δ –133.6 (m).

HRMS (ESI-): Calculated for $C_{14}H_{15}BF_3O_3$ ([M-K]$^-$), 299.1069; found 299.1063.



Benzofuran trifluoroborate 4j. A solution of phenol **1j** (41.4 mg, 0.119 mmol, 1.00 equiv) in 150 µL toluene was added to a flame-dried 10-mL Schlenk tube. To this stirring solution was added dropwise at 25 °C a suspension of NaH (92 wt % purity, 3.1 mg, 0.12 mmol, 1.0 equiv) in 150 µL toluene. A suspension of NaTFA (4.9. mg, 0.036 mmol, 30 mol %) in 150 µL toluene was added next. The resulting suspension was stirred for 15 min to affect full deprotonation.

To the resulting stirring sodium phenoxide suspension was added at 25 °C a solution of *B*-chlorocatecholborane (18.3 mg, 0.119 mmol, 1.00 equiv) in toluene (150 µL), using additional toluene as a rinse to ensure full transfer (1 × 150 µL portions). The resulting suspension was stirred vigorously for 30 min to allow for full conversion to boric ester intermediate **2j**.

Next, a suspension of IPrAuCl (16 mg, 0.025 mmol, 5.0 mol %) in toluene (150 μL) was added to the reaction mixture at 25 °C, using additional toluene as a rinse to aid in full transfer (1 × 150 μL portion). The reaction mixture was then sealed with a ground glass stopper and a PTFE sealing ring and placed in a preheated 90 °C copper shot heating bath. The final concentration of the reaction mixture was 0.1 M in **1j**.

After 20 h, analysis by TLC (10% EtOAc/hexanes) indicated full consumption of boric ester intermediate **2j**. The reaction mixture was cooled to 25 °C, and a solution of PPh_3 (3.1 mg, 0.012 mmol, 10 mol %) in toluene (0.5 mL) was added. The resulting suspension was stirred for 18 h at 25 °C in order to quench IPrAuTFA before proceeding.

The quenched reaction mixture was removed from the glovebox and filtered through a fiberglass filter to remove the suspended solids. The filter was then rinsed with chloroform (3 × 3 mL), and the combined filtrates were concentrated in vacuo to a pale yellow powder, which was suspended in acetone (1.0 mL) and added to a stirring solution of KHF_2 (37 mg, 0.48 mmol, 4.0 equiv) in water (300 μL). The resulting mixture was stirred at 25 °C for 30 min, and then concentrated in vacuo to remove the solvents. Residual water was removed azeotropically by adding 2 mL acetone and concentrating in vacuo again. To this residue was added 2 mL Et_2O and subsequently concentrated at c.a. 10 mTorr for 30 min in order to remove residual acetone. The resulting pale yellow solid residue was washed with Et_2O (4 × 2 mL) and extracted with acetone (4 × 2 mL). The combined acetone extracts were concentrated in vacuo, and the resulting residue was subjected to an additional washing/extraction cycle to yield **4j** as a light green powder (12 mg, 23% yield) with trace residual acetone after removing volatiles at 25 °C and c.a. 10 mTorr for 18 h.

^{1}H NMR (d_6-DMSO, 600 MHz): δ 8.07 (d, J = 1.4 Hz, 1H), 7.87 (d, J = 1.5 Hz, 1H), 7.59–7.57 (m, 1H), 2.56–2.53 (m, 2H), 2.23–2.20 (m, 2H), 1.69–1.65 (m, 2H), 1.62–1.58 (m, 2H).

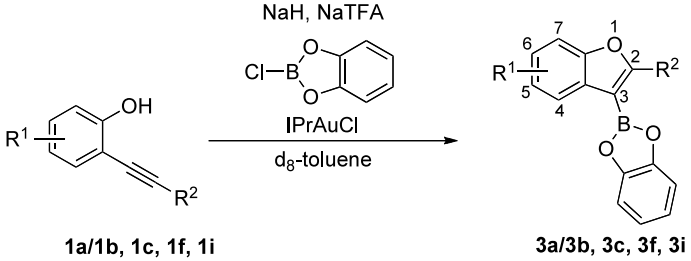
^{13}C NMR (d_6-DMSO, 125 MHz): δ. [Note: As with many organotrifluoroborates, the *ipso* carbon was not detected, presumably due to broadening through coupling to the ^{11}B nucleus. A second quaternary carbon was also not detected.]

^{11}B NMR (d_6- DMSO, 193 MHz): δ 2.8 (br s).

^{19}F NMR (d_6-DMSO, 376 MHz): δ -130.7 (br s).

HRMS (ESI-): Calculated for $C_{15}H_{11}BF_3INO$ ([M-K]$^-$), 415.9933; found 415.9916.

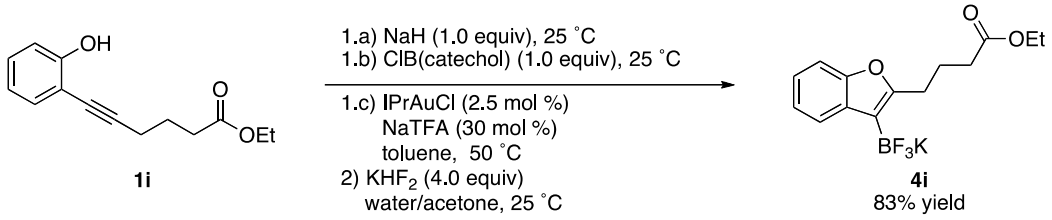
D. General procedure NMR conversions using ERETIC



A 4-mL vial was charged with a 2-substituted alkynylphenol (0.05 mmol, 1 equiv), and 0.5 mL d_8-toluene. A second 4-mL vial was charged with NaH (1.3 mg, 0.050 mmol, 1.0 equiv) and

NaTFA (2.7 mg, 0.020 mmol, 0.30 equiv). The solution containing the phenol was then added dropwise to the vial containing NaH and NaTFA, and swirled intermittently for 15 min. This cloudy mixture was then added dropwise to another 4-mL vial containing *B*-chlorocatecholborane (7.7 mg, 0.050 mmol, 1.0 equiv). This mixture was then swirled intermittently for 30 min before transferring into a new vial containing IPrAuCl (1.6 mg, 0.0030 mmol, 0.050 equiv). This mixture was then transferred into a J. Young NMR tube, which was sealed sealed and removed from the glove box. This tube was then heated to 50 ^{o}C for 18-24 h. An ^{1}H NMR was taken (600 MHz, d_8-toluene), and the signals correlating to the corresponding cyclized benzofuran boronic ester w ere compared to an external standard of mesitylene (419 mmol/L in d_8-toluene) using the ERETIC method, ensuring the acquisition parameters were identical. This general procedure was used for R^1= H, R^2=Ph (**3a, 3b**, 95%); R^1= 6-Br, R^2= Bu (**3c**, 88%); R^1= 6-CCH, R^2=H (**3f**, 42%), R^1= H, R^2= -$(CH_2)_3CO_2Et$ (**3i**, 71%).

E. Gram-scale preparation of 4i



The gram-scale alkoxyboration reaction was conducted in an N_2-filled glovebox. A flame-dried 100-mL Schlenk tube with a stirbar was charged with NaH (92 wt % purity, 123 mg, 5.13 mmol, 1.00 equiv) and NaTFA (210 mg, 1.5 mmol, 30. mol %). Anhydrous toluene (12 mL) was added. To the resulting rapidly stirring suspension was added a solution of phenol **1i** (1.30 g, 5.13 mmol, 1.00 equiv) in toluene (2 mL) at 25 °C dropwise over 5 min. Additional toluene (3 × 2 mL) was used as a rinse to aid in complete transfer. The reaction mixture was stirred at 25 °C for 30 min to affect full deprotonation.

To the resulting pale yellow suspension was added a solution of *B*-chlorocatecholborane (790. mg, 5.13 mmol, 1.00 equiv) in toluene (5 mL) dropwise over 5 min. [Note: a slight exotherm occurs.] Additional toluene (3 × 5 mL) was used as a rinse to aid in complete transfer. The reaction mixture was stirred at 25 °C for 30 min to affect full formation of boric ester intermediate **2i**.

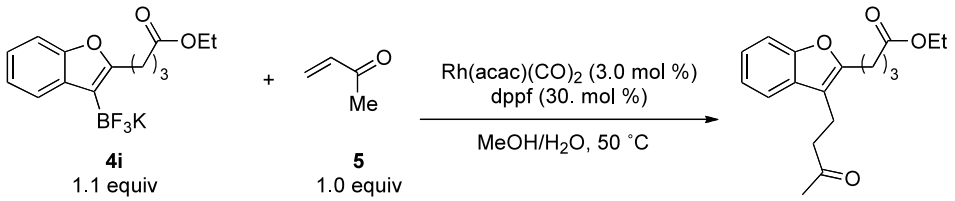
A suspension of IPrAuCl (80. mg, 0.13 mmol, 2.5 mol %) in toluene (2.5 mL) was added next, using additional toluene (3 × 2.5 mL) as a rinse to ensure full transfer. The reaction vessel was then sealed with a ground glass joint and a PTFE sealing ring and placed in a preheated 60 °C copper shot heating bath. The final concentration of the reaction mixture was 0.1 M in **1i**.

After 22 h, analysis by TLC (10% EtOAc/hexanes) indicated complete consumption of boric ester intermediate **2i**. The reaction mixture was cooled to 25 °C, and then a solution of PPh_3 (67 mg, 0.26 mmol, 5.0 mol %) in 2.5 mL toluene was added to the reaction mixture. The resulting suspension was stirred for 23 h at 25 °C in order to quench IPrAuTFA before proceeding.

The suspension containing boronic ester **3i** was removed from the glovebox and concentrated in vacuo. The resulting solid residue was extracted with toluene (3 × 15 mL), and the combined

extracts were filtered through a fiberglass filter to ensure removal of suspended solids. The filtrate was concentrated in vacuo, and the resulting residue was dissolved in acetone (45 mL) and added to a vigorously stirring solution of KHF_2 (1.6 g, 21 mmol, 4.0 equiv) in 15 mL H_2O. The reaction mixture was stirred open to air for 30 min at 25 °C before being concentrated in vacuo to remove the solvents. Residual water was removed azeotropically by adding 2 mL acetone and concentrating in vacuo again. The resulting solid residue was washed with Et_2O (15 × 30 mL) and extracted with acetone (3 × 15 mL). The combined acetone extracts were concentrated in vacuo to yield **4i** as a white powder (1.43 g, 83% yield) after removing volatiles at 25 °C and c.a. 10 mTorr for 18 h. Spectral data were identical to those previously obtained for this compound (see page S18).

F. Downstream functionalization reactions to produce 6, 8, and 10



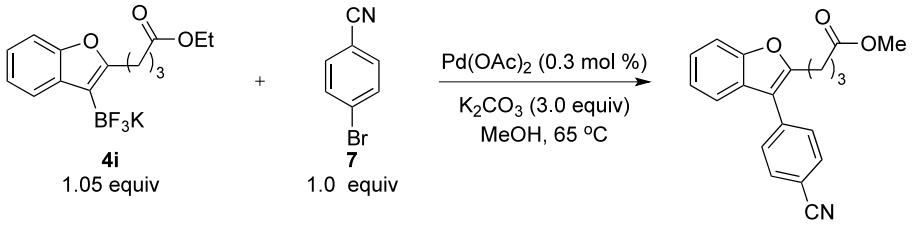
Ethyl 4-(3-(3-oxobutyl)benzofuran-2-yl)butanoate (6). The Rh-catalyzed conjugate addition of **4i** to methyl vinyl ketone was conducted using a procedure adapted from Batey.[14] A dram vial was charged with **4i** (85 mg, 0.25 mmol, 1.1 equiv) and a stirbar. The vial was pumped into an N_2-filled glovebox, where $Rh(acac)(CO)_2$ (1.9 mg, 7.1 μmol, 3.0 mol %) and dppf (40. mg, 72 μmol, 30. mol %) were added. The vial was sealed with a septum cap, removed from the glovebox, and placed under dynamic N_2 atmosphere. Methanol (2.2 mL) and water (400 μL) were added, and the resulting mixture was stirred at 25 °C for 15 min to dissolve the solids. Methyl vinyl ketone (19 μL, 0.23 mmol, 1.0 equiv) was added, and the reaction mixture was heated at 50 °C for 30 h. To the resulting heterogeneous brown mixture was added 10-mL DCM, and the resulting biphasic mixture was separated. The aqueous layer was back extracted with DCM (3 × 1 mL), and the combined organic layers were dried over Na_2SO_4, filtered, and concentrated in vacuo to a brown solid residue. Purification by silica gel chromatography using an elution gradient from 100% hexanes to 15% EtOAc/hexanes and removal of volatiles at 25 °C and c.a. 10 mTorr for 18 h afforded **6** as a clear, colorless oil (33 mg, 44% yield).

TLC (15% EtOAc/hexanes): $R_f = 0.29$.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.43 (d, J = 7.2 Hz, 1H), 7.38 (d, J = 8.4 Hz, 1H), 7.23–7.18 (m, 2H), 4.11 (q, J = 7.0 Hz, 2H), 2.88 (t, J = 7.3 Hz, 2H), 2.82 (t, J = 7.3 Hz, 2H), 2.77 (t, J = 7.3 Hz, 2H), 2.36 (t, J = 7.4 Hz, 2H), 2.13 (s, 3H), 2.05 (quin, J = 7.5 Hz, 2H), 1.25 (t, J = 7.1 Hz, 3H).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 207.9, 173.3, 154.2, 153.8, 129.1, 123.5, 122.3, 118.9, 113.8, 111.0, 60.5, 43.4, 33.6, 30.3, 25.6, 23.6, 17.6, 14.4.

HRMS (ESI+): Calculated for $C_{18}H_{22}O_4Na$ ($[M+Na]^+$), 325.1416; found 325.1420.



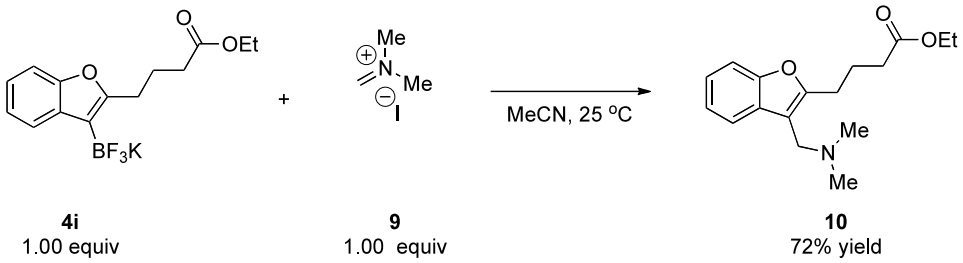
Methyl 4-(3-(4-cyanophenyl)benzofuran-2-yl)butanoate (8). A 20-mL vial was charged with **4i** (99 mg, 0.29 mmol, 1.1 equiv), K_2CO_3 (116 mg, 0.837 mmol, 3.00 equiv), and $Pd(OAc)_2$ (0.2 mg, 0.001 mmol, 0.3 mol %). The vial was then evacuated and refilled with N_2 three times. To this vial was then added 0.4 mL of MeOH that had been sparged for 10 min with N_2. In a separate flask was added 4-benzonitrile (51 mg, 0.28 mmol, 1.0 equiv), which was then evacuated and refilled with N_2 three times before adding 0.4 mL MeOH that had been sparged 10 min with N_2. This solution was then syringed into the stirring reaction vial over 1 min. The vial was then equipped with an argon balloon and heated to 65 °C. The mixture stirred for 18 h before TLC (10% EtOAc/hexanes) showed the complete consumption of starting material. The reaction mixture was diluted with 20 mL toluene, and then the organic layer was washed with H_2O (1 × 5 mL), brine (1 × 5 mL), filtered, and 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 **8** as a white solid. (41 mg, 44% yield).

TLC (10% EtOAc/hexanes) R_f = 0.20, visualized by UV absorbance.

^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.78 (d, *J* = 8.2 Hz, 2H), 7.61 (d, *J* = 8.2 Hz, 2H), 7.50 (dd, *J* = 16.3, 7.9 Hz, 2H), 7.32 (t, *J* = 7.6 Hz, 1H), 7.26 (t, *J* = 7.2 Hz, 1H), 3.61 (s, 3H), 2.93 (t, *J* = 7.5 Hz, 2H), 2.38 (t, *J* = 7.3 Hz, 2H), 2.13 (quin, *J* = 7.3 Hz, 2H).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 173.4, 155.0, 154.3, 137.8, 132.8, 129.7, 127.8, 124.5, 123.3, 119.3, 119.0, 116.4, 111.4, 110.9, 51.8, 33.2, 26.2, 23.5.

HRMS (ESI+): Calculated for $C_{20}H_{17}NO_3Na$ ($[M+Na]^+$), 342.1106; found 342.1094.



Ethyl 4-(3-((dimethylamino)methyl)benzofuran-2-yl)butanoate (10). A 10-mL Schlenk tube was charged with Eschenmoser's salt (**9**, 74.0 mg, 0.300 mmol, 1.00 equiv) and 1.0 mL anhydrous MeCN. To the resulting suspension was added a solution of organotrifluoroborate **4i** (101 mg, 0.300 mmol, 1.00 equiv) in 1.3 mL dry MeCN. The reaction mixture was stirred vigorously for 30 min at 25 °C, at which time a saturated aqueous solution of $NaHCO_3$ (1 mL) was added to quench the reaction. The resulting biphasic mixture was extracted with EtOAc (3 ×

3 mL), and the combined organic layers were washed with brine (3 × 3 mL), dried over Na_2SO_4, and concentrated in vacuo to an oily residue. Purification by column chromatography using an elution gradient from 1.5% Et_3N in hexanes to 40% EtOAc and 0.9% Et_3N in hexanes afforded **10** as a clear, pale yellow oil (63 mg, 72% yield)

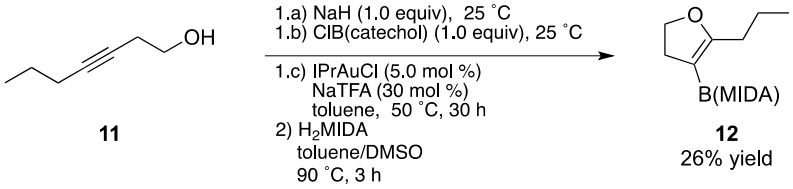
TLC (30% EtOAc + 1% Et_3N/hexanes) $R_f = 0.27$, visualized by UV absorbance.

^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.63–7.61 (m, 1H), 7.41–7.30 (m, 1H), 7.24–7.19 (m, 2H), 4.13 (q, *J* = 7.1 Hz, 2H), 3.47 (s, 2H), 2.86 (t, *J* = 7.3 Hz, 2H), 2.38 (t, *J* = 7.4 Hz, 2H), 2.26 (s, 6H), 2.09 (app quin, *J* = 7.3 Hz, 2H), 1.26 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 173.3, 155.4, 154.1, 129.7, 123.5, 122.5, 119.9, 112.6, 110.7, 60.5, 53.2, 45.6, 33.6, 25.8, 23.5, 14.4.

HRMS (ESI+): Calculated for $C_{17}H_{23}NO_3Na$ ($[M+Na]^+$), 312.1576; found 312.1570.

G. Synthesis of dihydrofuran product 12



Prior to use, **11** was dried by distilling over anhydrous K_2CO_3 (15 Torr, 80 °C) and was stored over activated 3Å molecular sieves. The alkoxyboration reaction was set up and conducted in an N_2-filled glovebox. A flame-dried 100 mL Schlenk tube with a stirbar was charged with NaH (92 wt % purity, 26.0 mg, 1.00 mmol, 1.00 equiv) and NaTFA (41 mg, 0.30 mmol, 30 mol %). Anhydrous toluene (4 mL) was added. Compound **9** (103 μL, 1.00 mmol, 1.00 equiv) was added dropwise over 1 min, and then the reaction mixture was stirred at 25 °C for 40 min to affect full deprotonation.

To the resulting suspension was added a solution of *B*-chlorocatecholborane (154 mg, 1.00 mmol, 1.00 equiv) in toluene (2 mL) dropwise over 5 min. Additional toluene (2 × 1 mL) was used as a rinse to aid in complete transfer. The reaction mixture was stirred at 25 °C for 30 min to affect full formation of the boric ester intermediate.

A suspension of IPrAuCl (31 mg, 0.050 mmol, 5.0 mol %) in toluene (1 mL) was added next, using additional toluene (2 × 0.5 mL) as a rinse to ensure full transfer. The reaction vessel was then sealed with a ground glass joint and a PTFE sealing ring and placed in a preheated 50 °C copper shot heating bath. The final concentration of the reaction mixture was 0.1 M in **11**.

Analysis by TLC (20% EtOAc/hexanes) at 23 h and 30 h indicated stalled, nearly complete consumption of the boric ester intermediate. The reaction mixture was cooled to 25 °C, and then a solution of PPh_3 (26 mg, 0.10 mmol, 10 mol %) in 1 mL toluene. The resulting suspension was stirred for 16 h at 25 °C in order to quench IPrAuTFA before proceeding.

To the quenched reaction mixture were added H_2MIDA (160 mg, 1.1 mmol, 1.1 equiv) and dry DMSO (4 mL), and the resulting suspension was stirred at 90 °C for 3 h. The reaction mixture was then cooled to 25 °C and removed from the glovebox. Toluene was removed in vacuo at 25 °C and c.a. 10 Torr, then DMSO was removed by Kugelrohr distillation at c.a. 10 mTorr. The

resulting semisolid residue was adsorbed onto Celite from a MeCN suspension and purified twice by successive silica gel chromatography using an elution gradient from 100% Et_2O to 100% MeCN. Removal of volatiles at 25 °C and c.a. 10 mTorr for 18 h afforded MIDA boronate **12** as a white powder (83 mg, 26% yield).

^{1}H NMR (CD_3CN, 600 MHz): δ 3.94 (d, J = 17.2 Hz, 2H), 3.84 (d, J = 17.2 Hz, 2H), 3.68 (t, J = 6.8 Hz, 2H), 2.86 (s, 3H), 2.38 (tt, J = 6.9, 2.3 Hz, 2H), 2.11 (tt, J = 6.9, 2.3 Hz, 2H), 1.46 (sextet, J = 7.3 Hz, 2H), 0.95 (t, J = 7.3 Hz, 3H).

^{13}C NMR (CD_3CN, 125 MHz): δ 168.3, 82.0, 78.3, 63.3, 63.1, 46.1, 23.2, 22.7, 21.1, 13.7.

^{11}B NMR (CD_3CN, 193 MHz): δ 8.8 (br s).

HRMS (ESI+): Calculated for $C_{12}H_{18}BNO_5Na$ ($[M+Na]^+$), 290.1178; found 290.1180.

III. References

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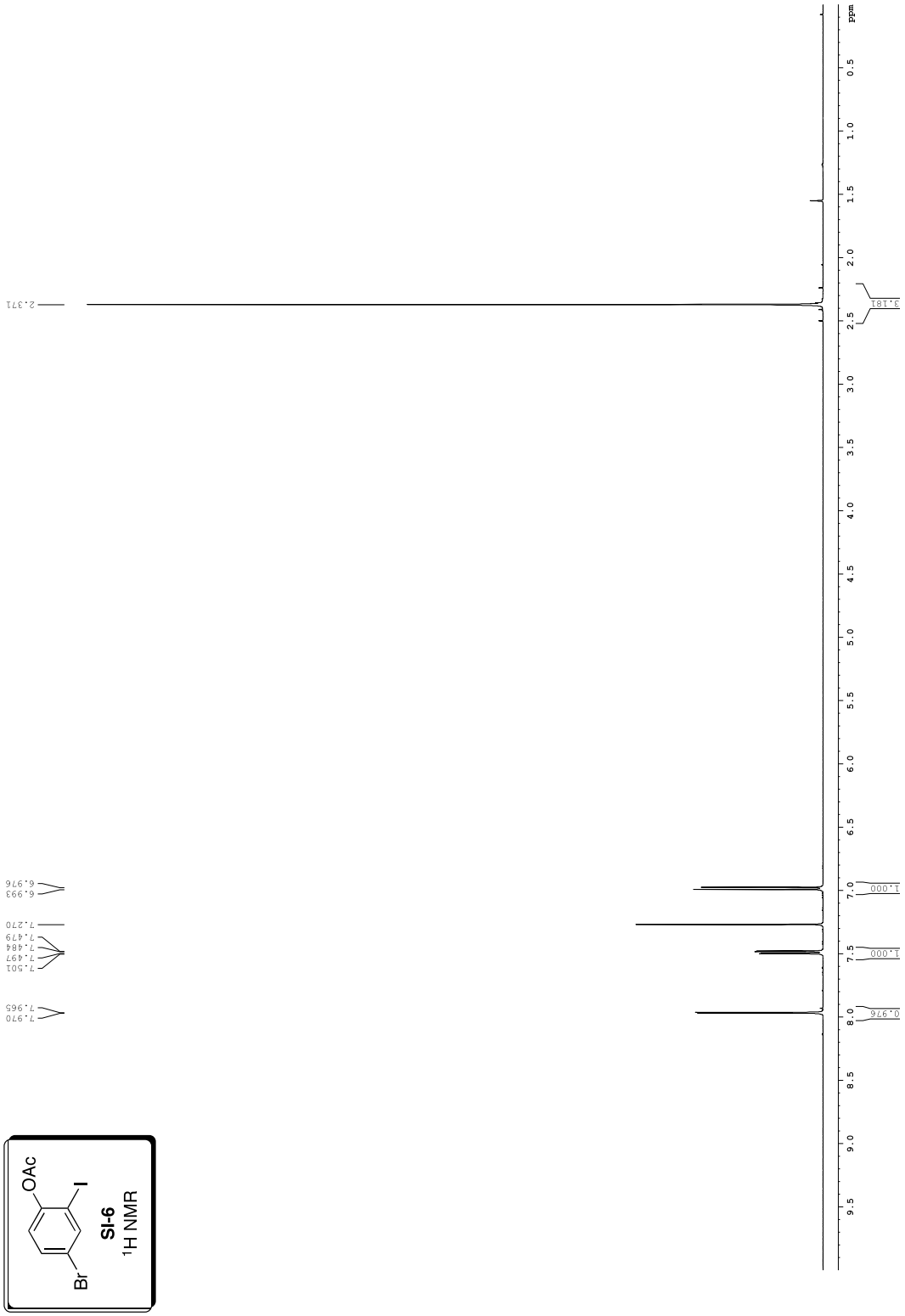
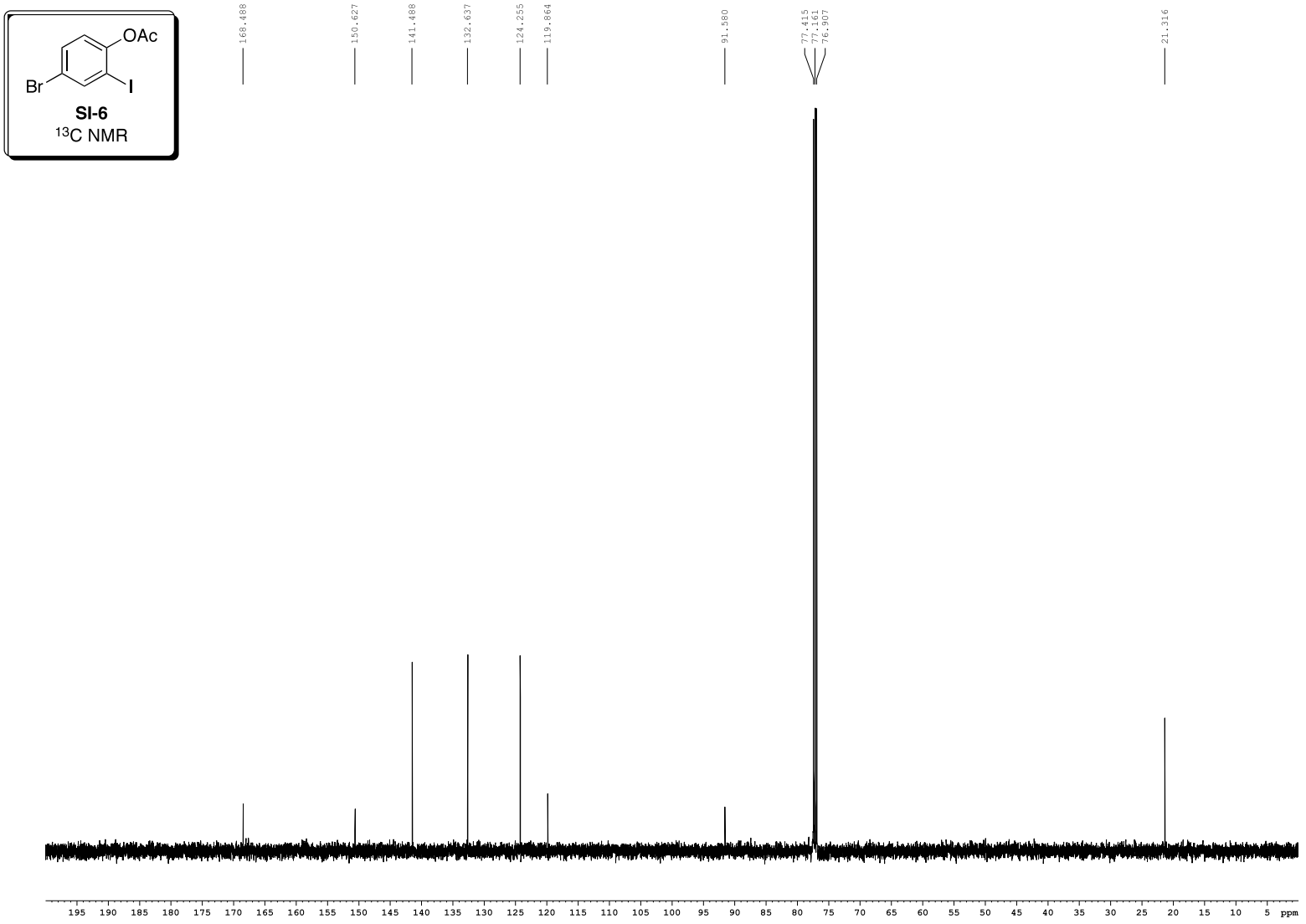
IV. NMR Spectra

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21.316
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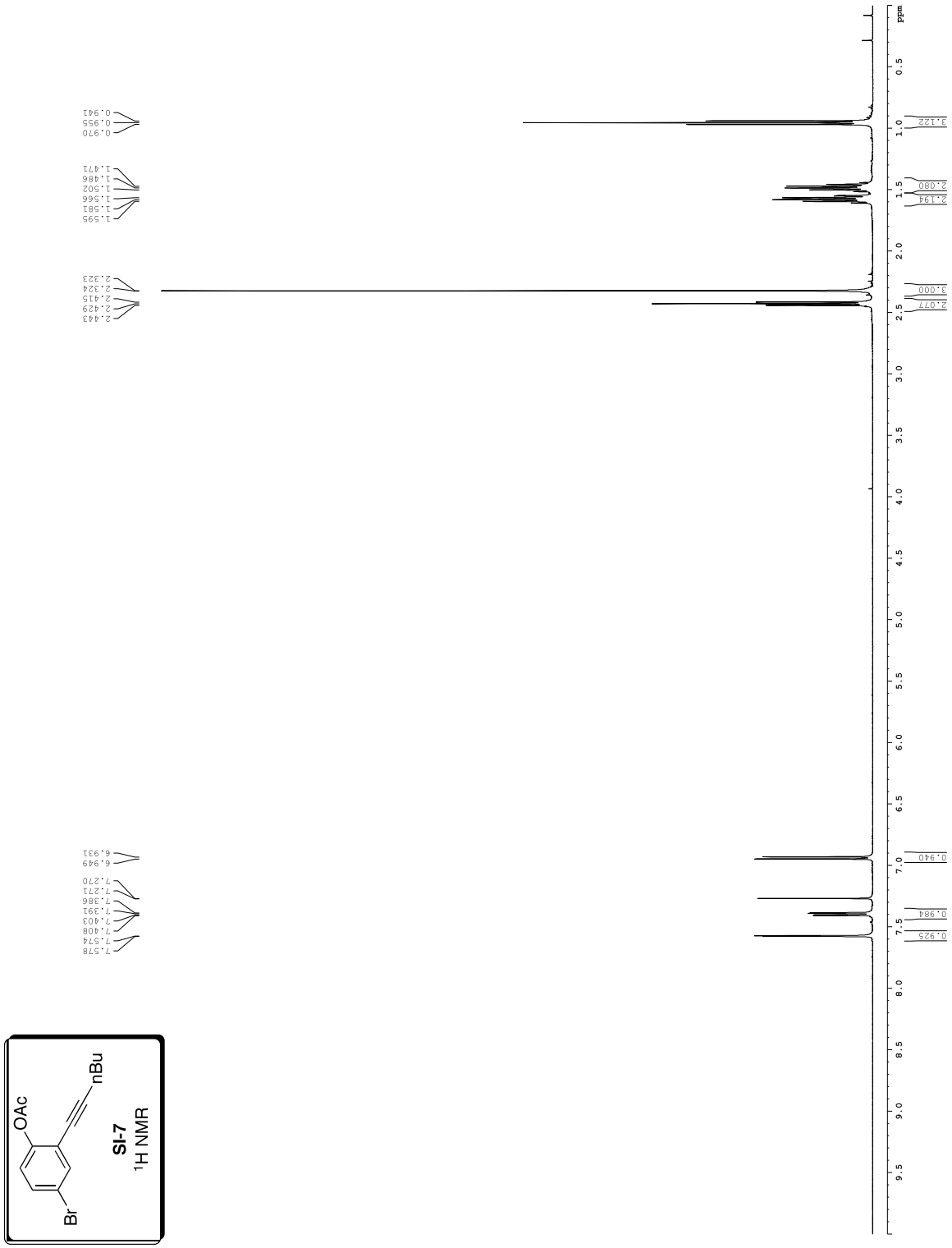
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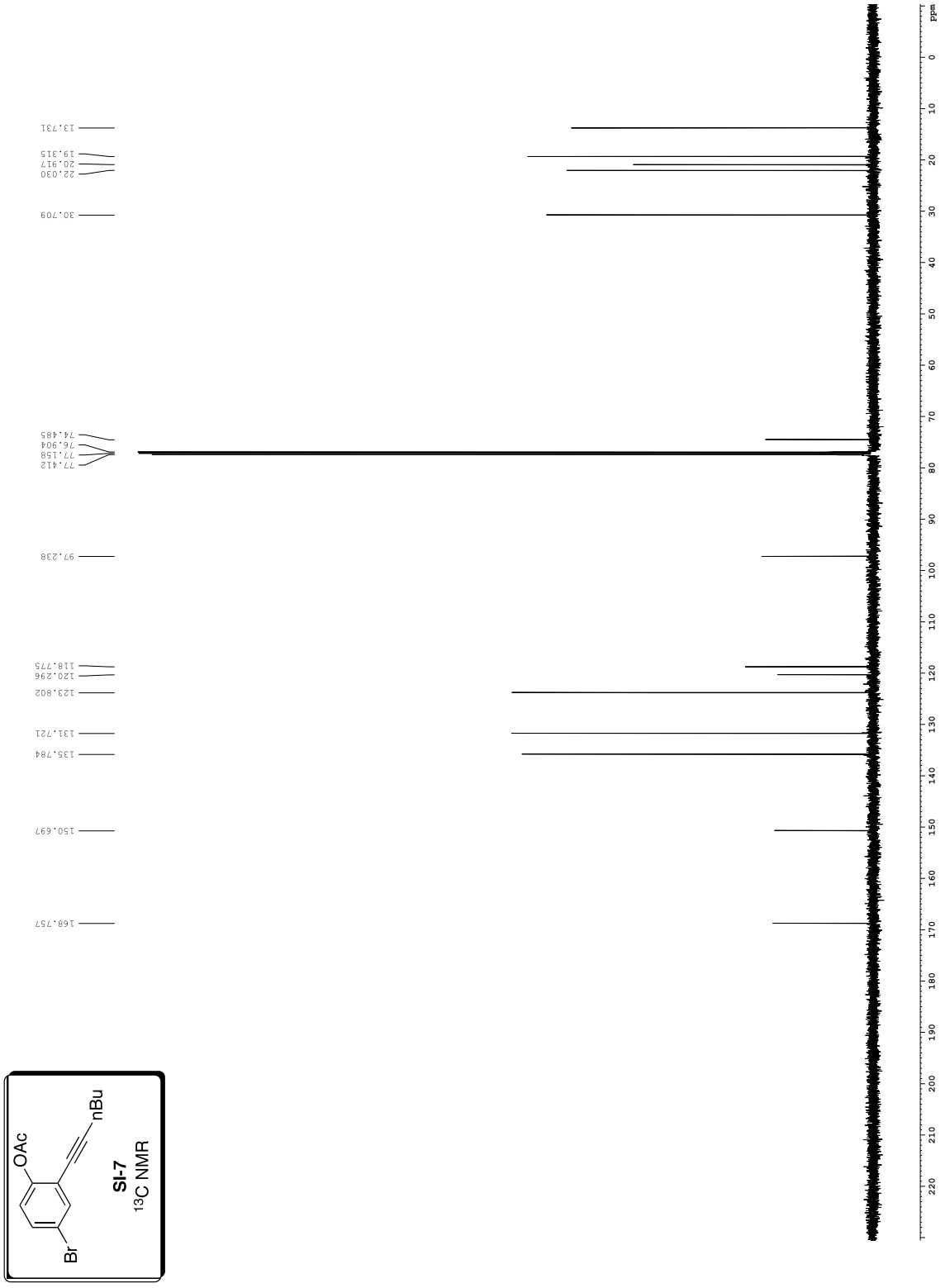
Br
SI-7
1H NMR
ppm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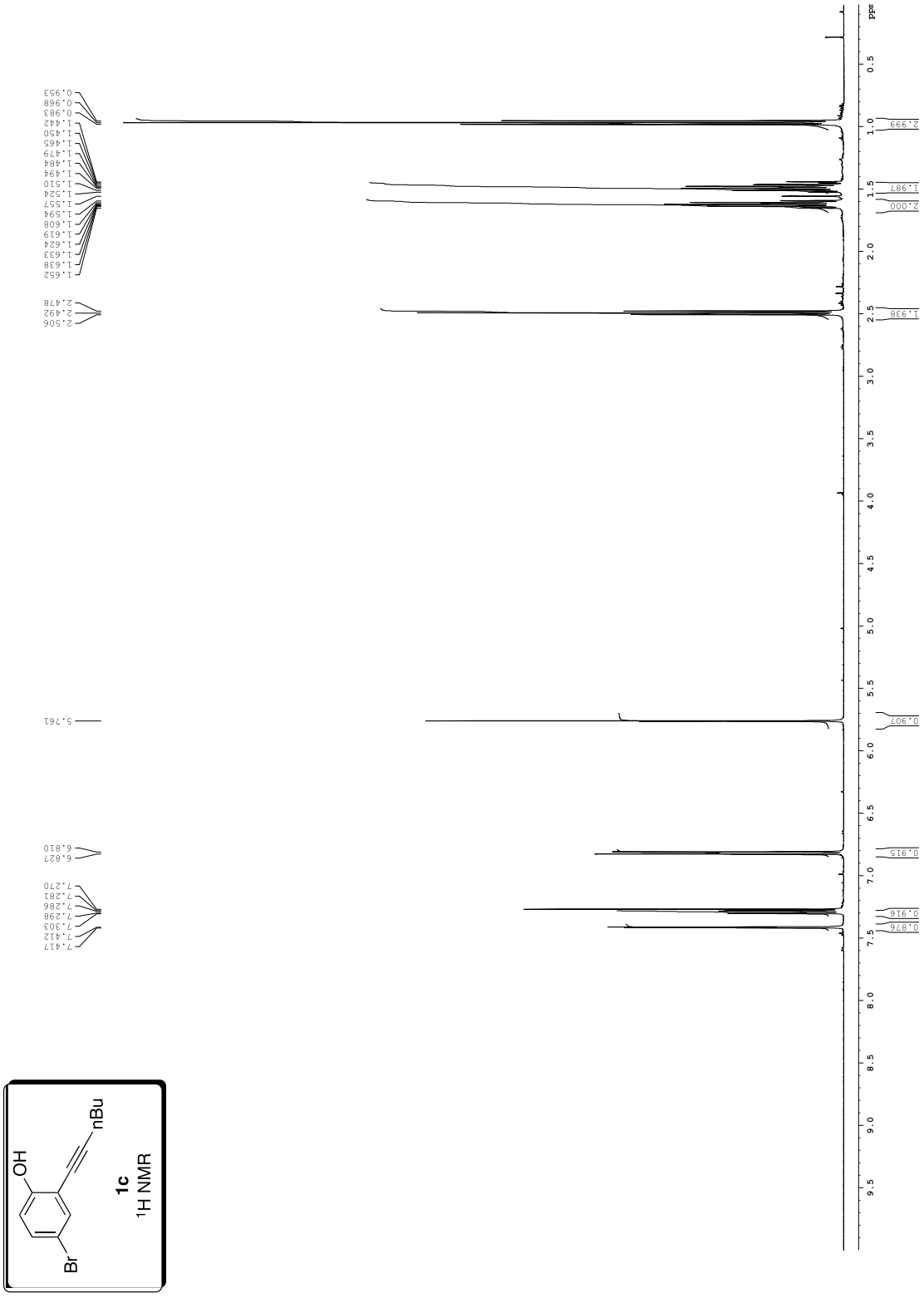
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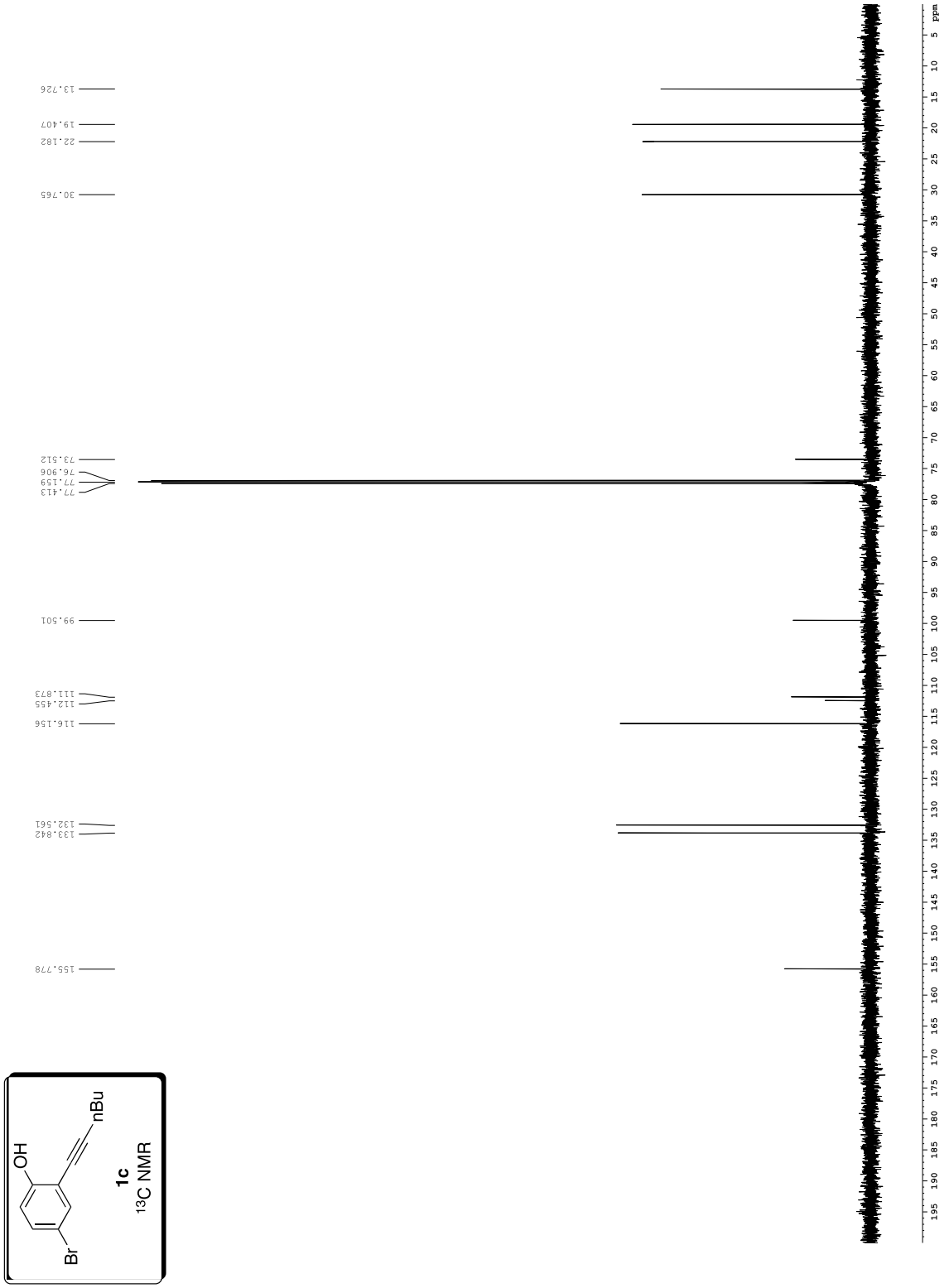
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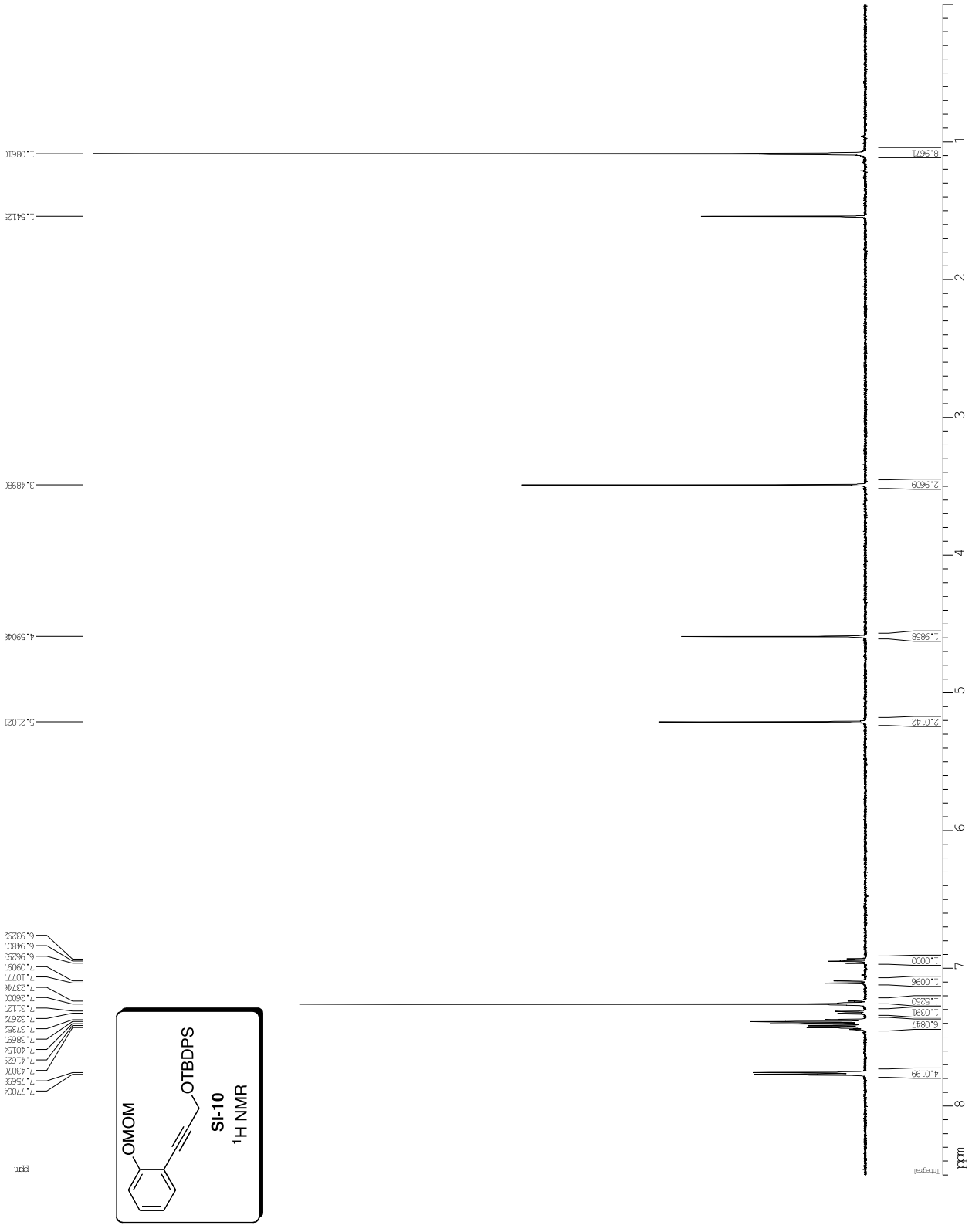
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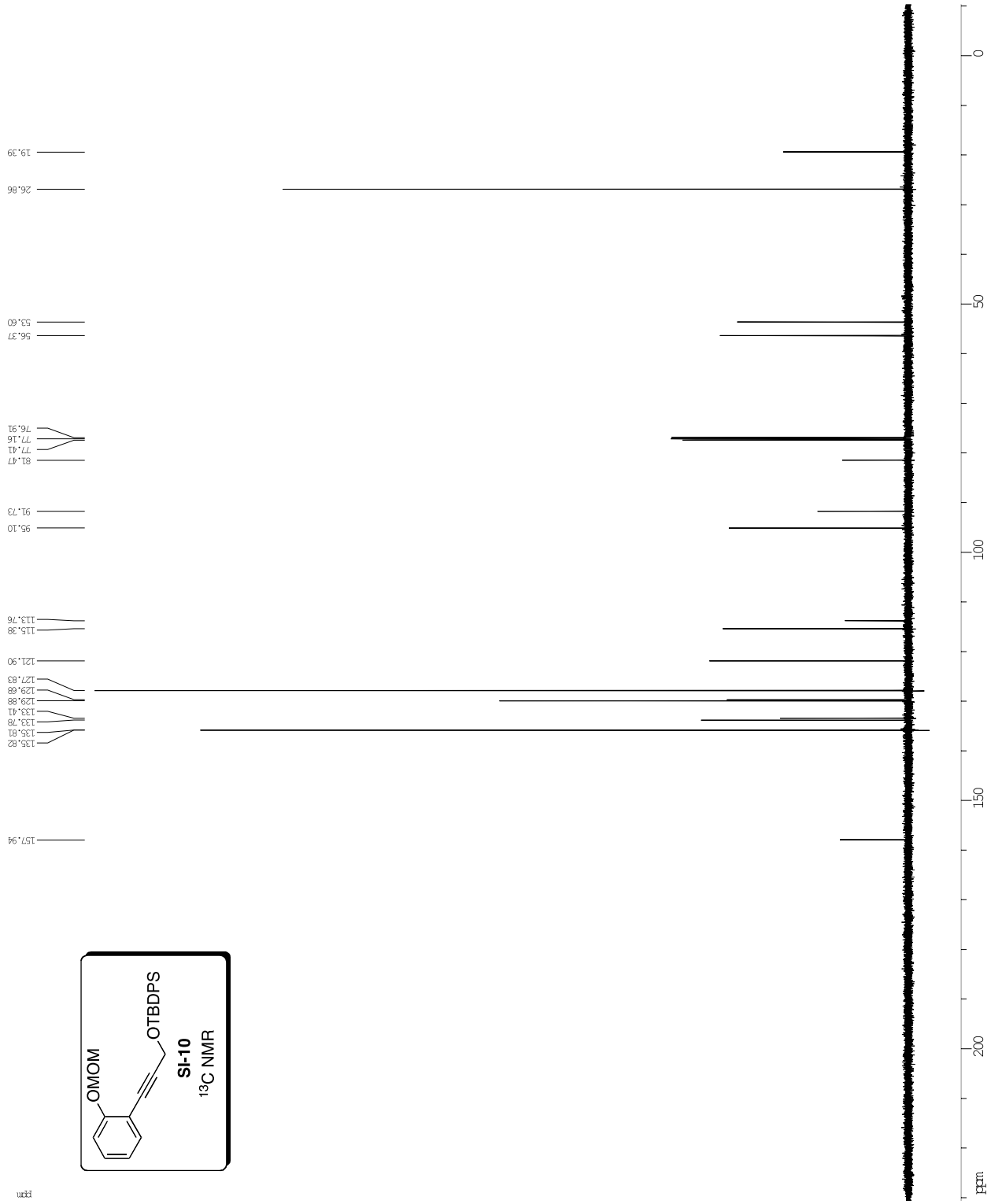
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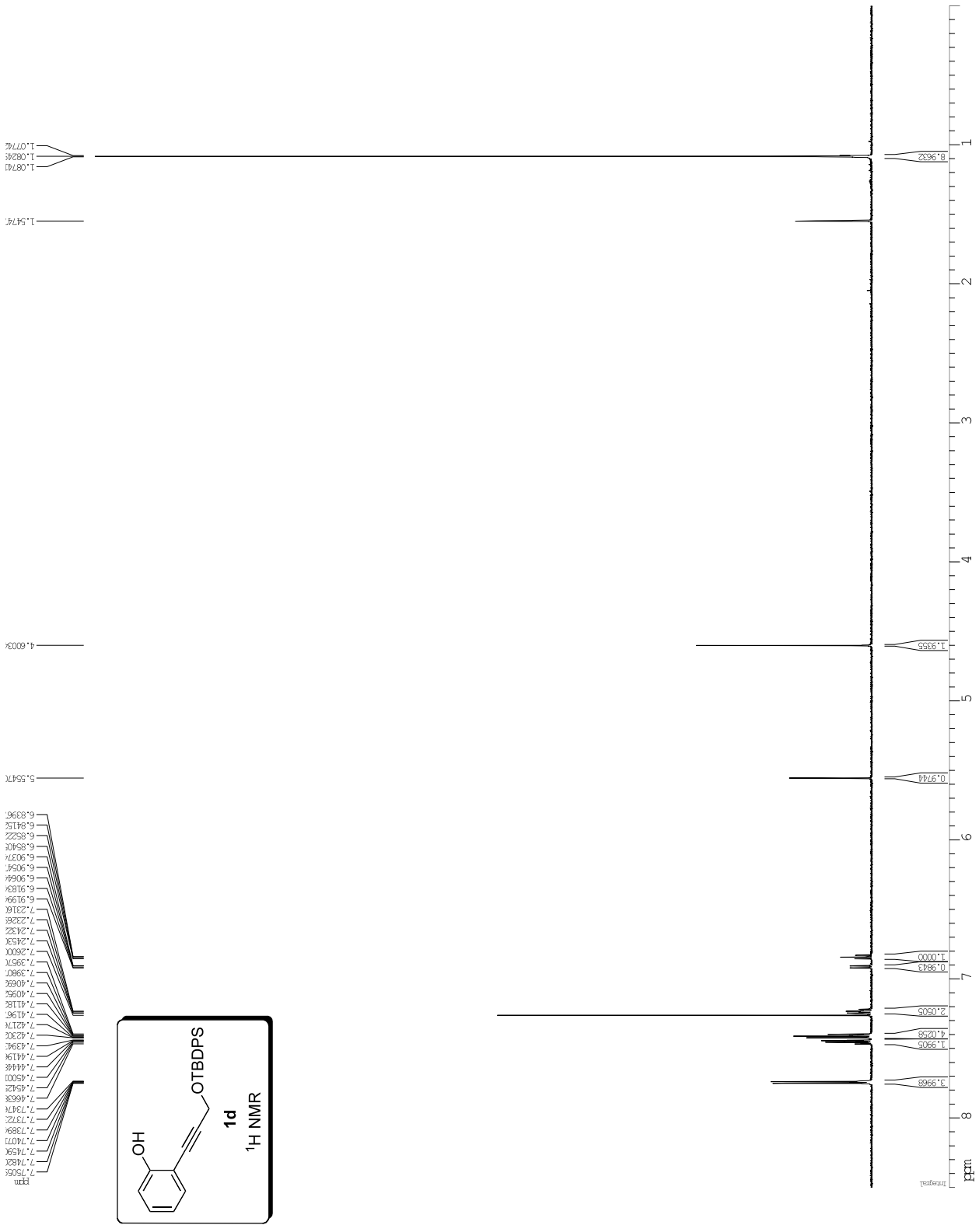
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1H NMR
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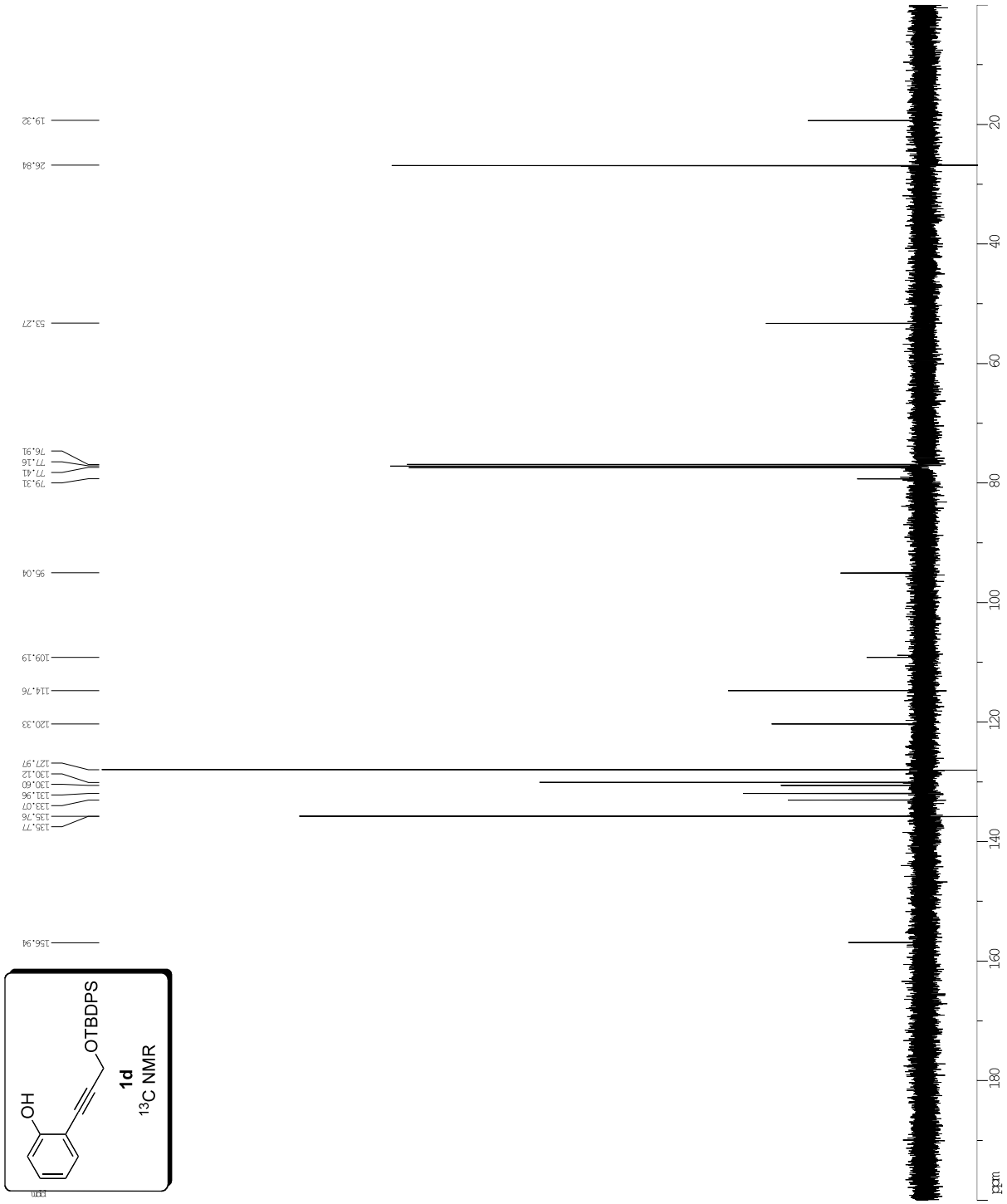
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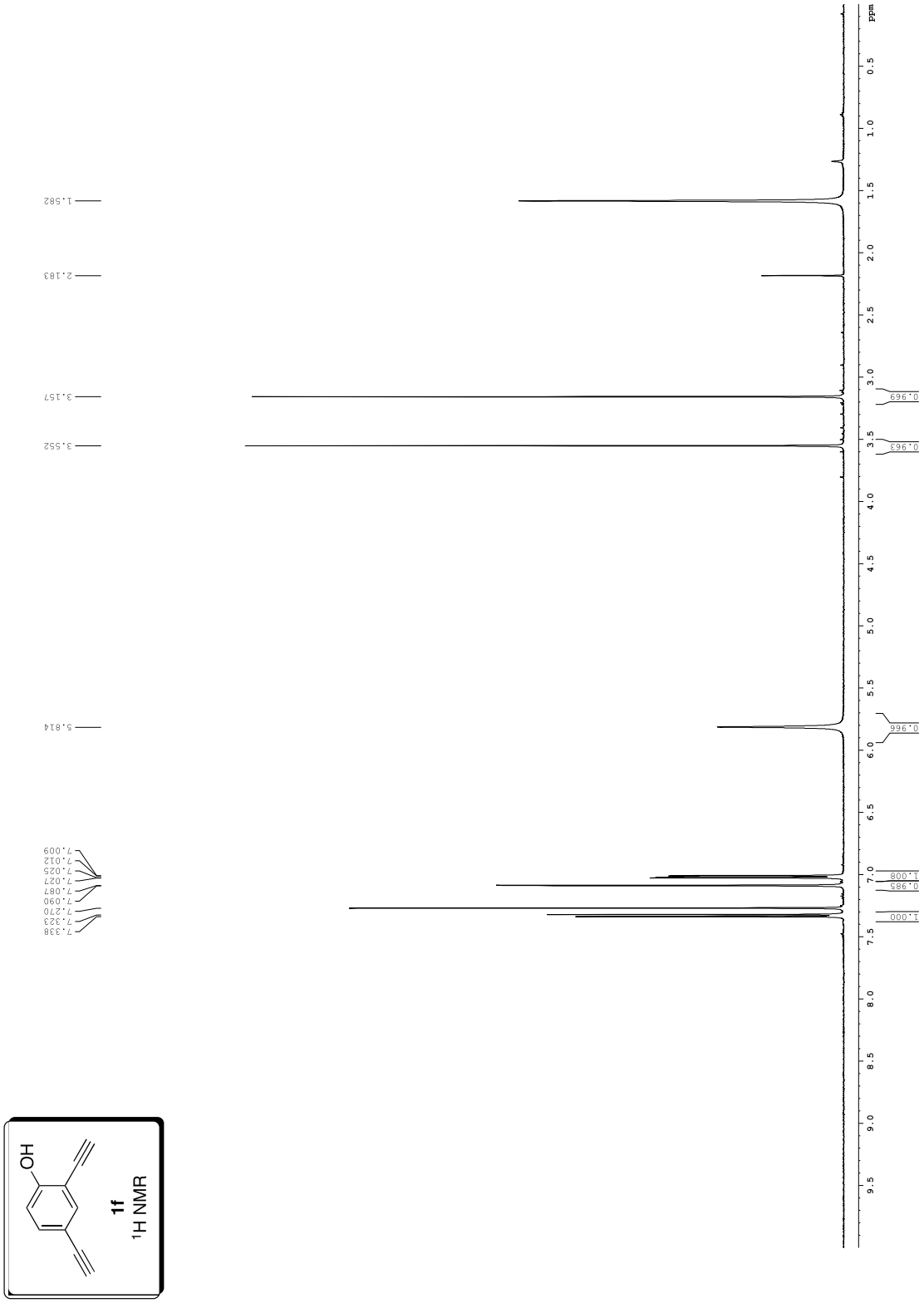
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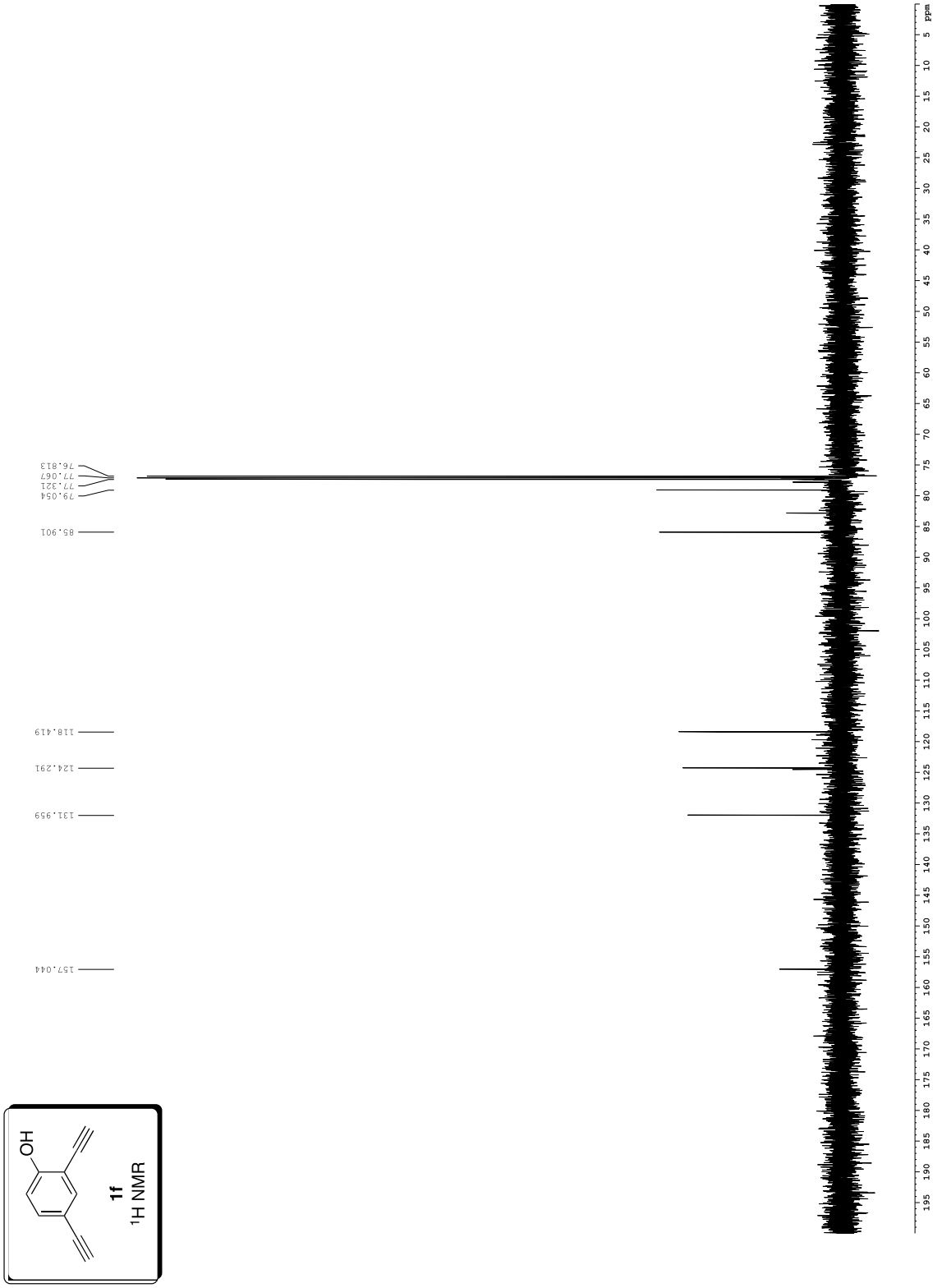
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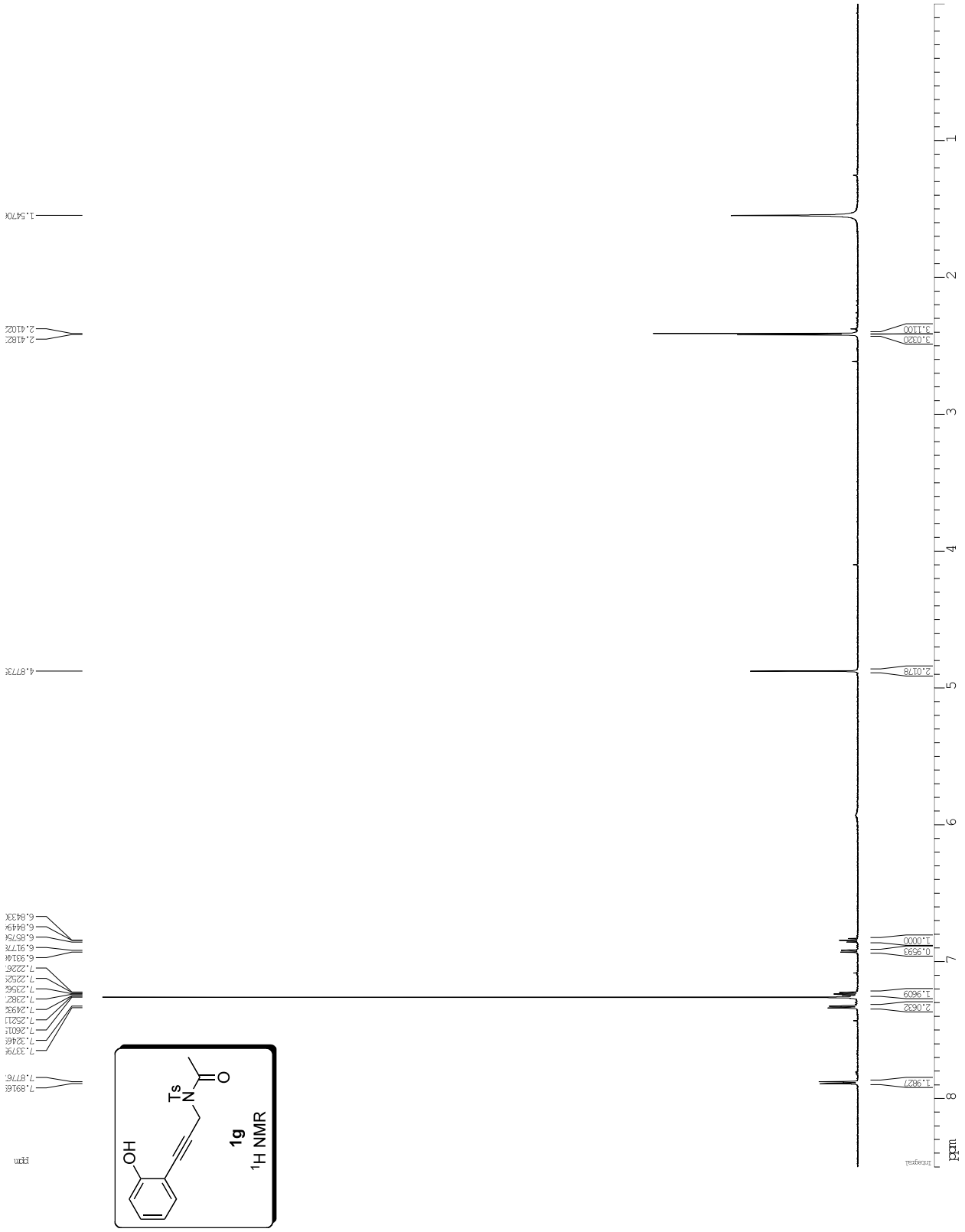
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O
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7.2601
7.2521
7.2493
7.2382
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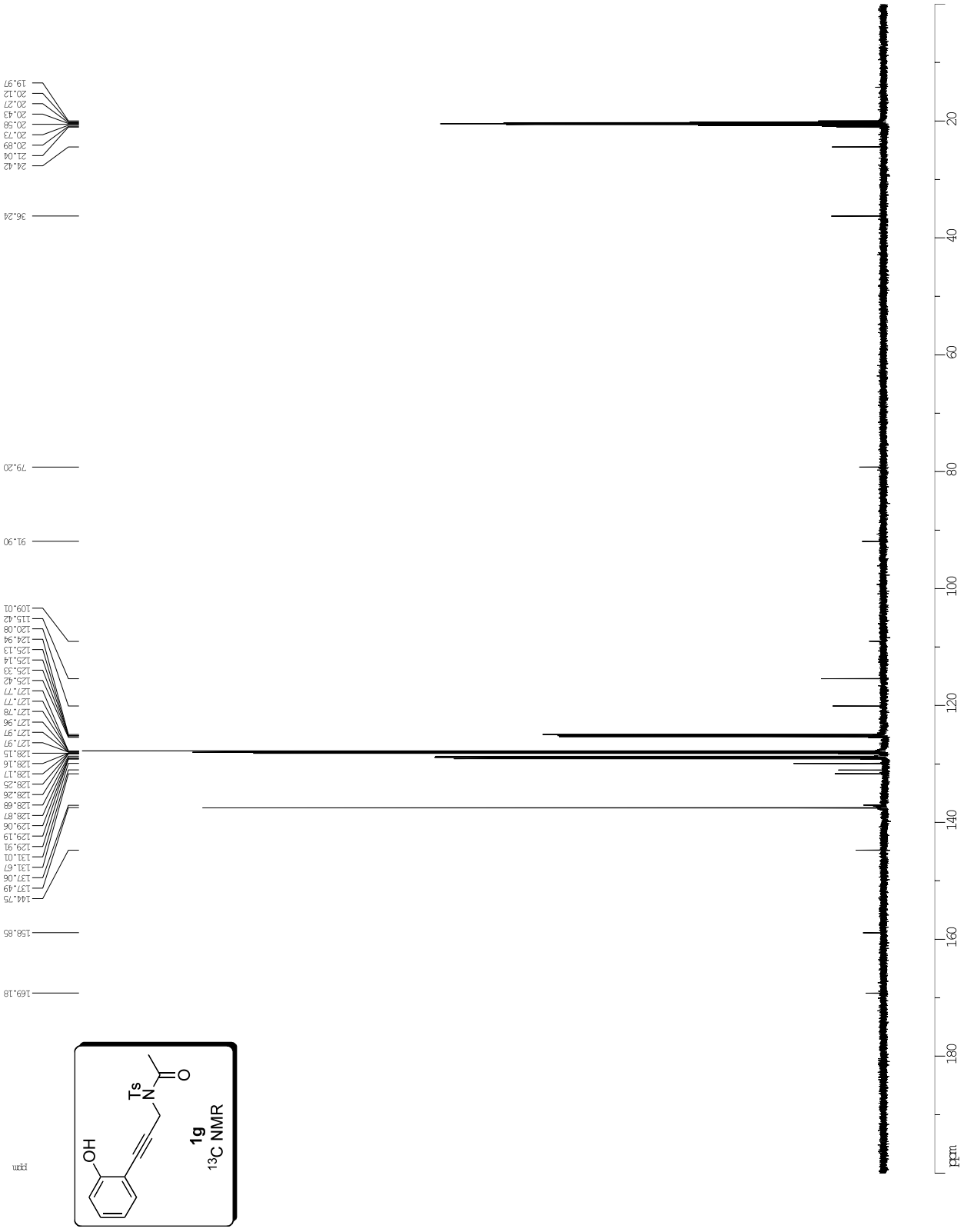
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115.42
120.08
124.94
125.13
125.14
125.33
125.42
127.77
127.77
127.78
127.96
127.97
127.97
128.15
128.16
128.17
128.25
128.26
128.68
128.87
129.06
129.19
129.91
131.01
131.67
137.06
137.49
144.75
158.85
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Ts
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O
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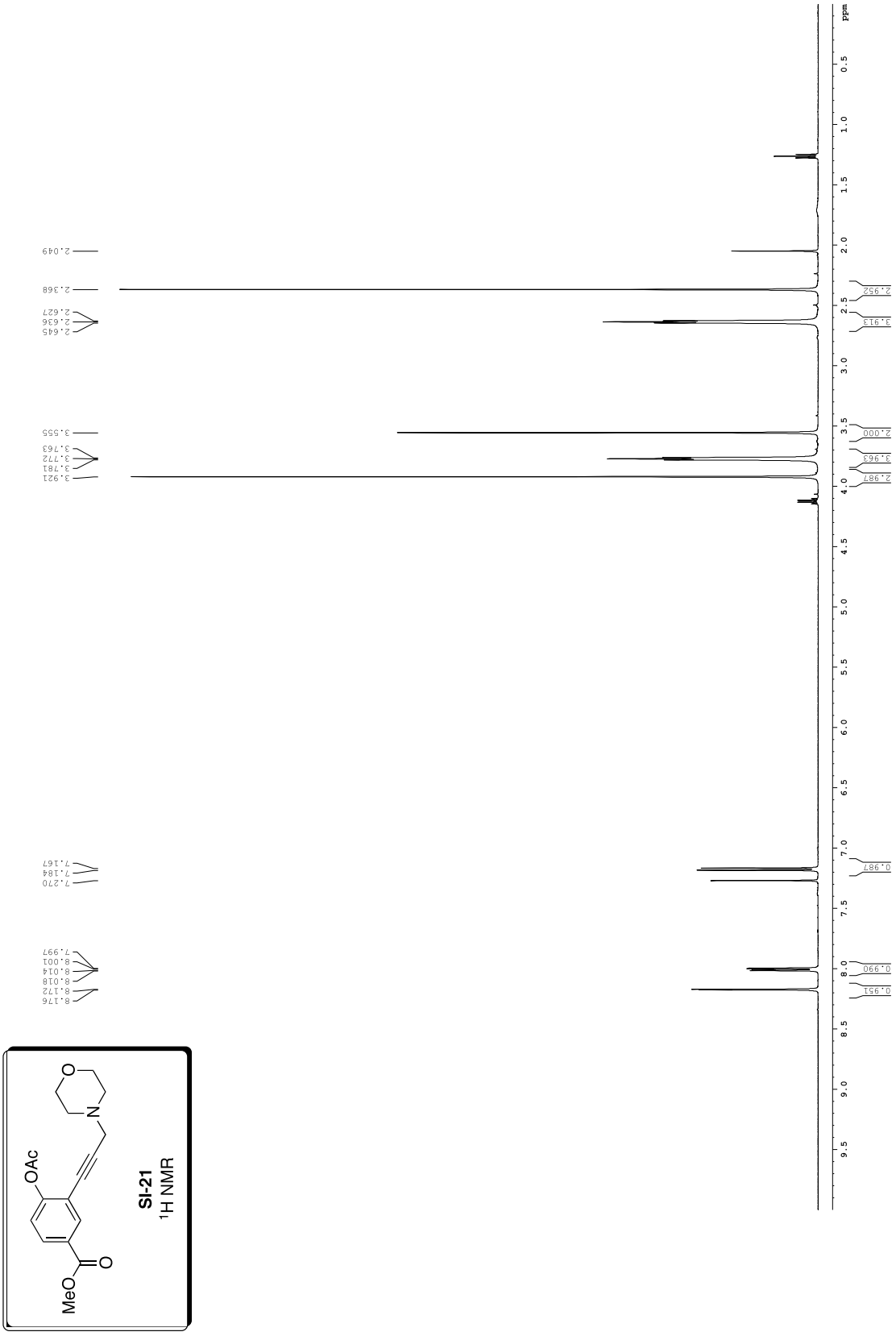
60
80
100
120
140
160
180
ppm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7.184
7.167
3.921
3.781
3.772
3.763
3.555
2.645
2.636
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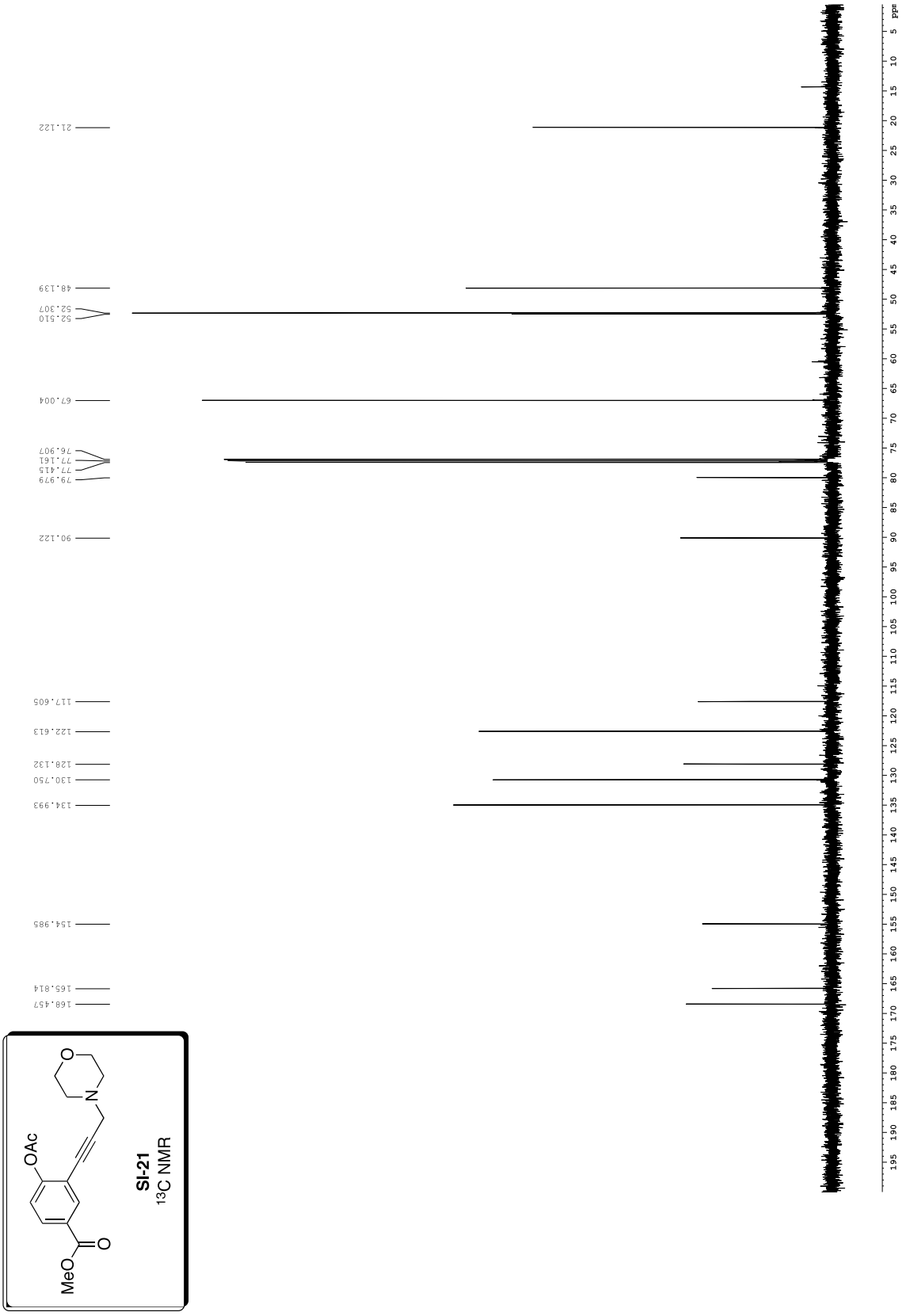
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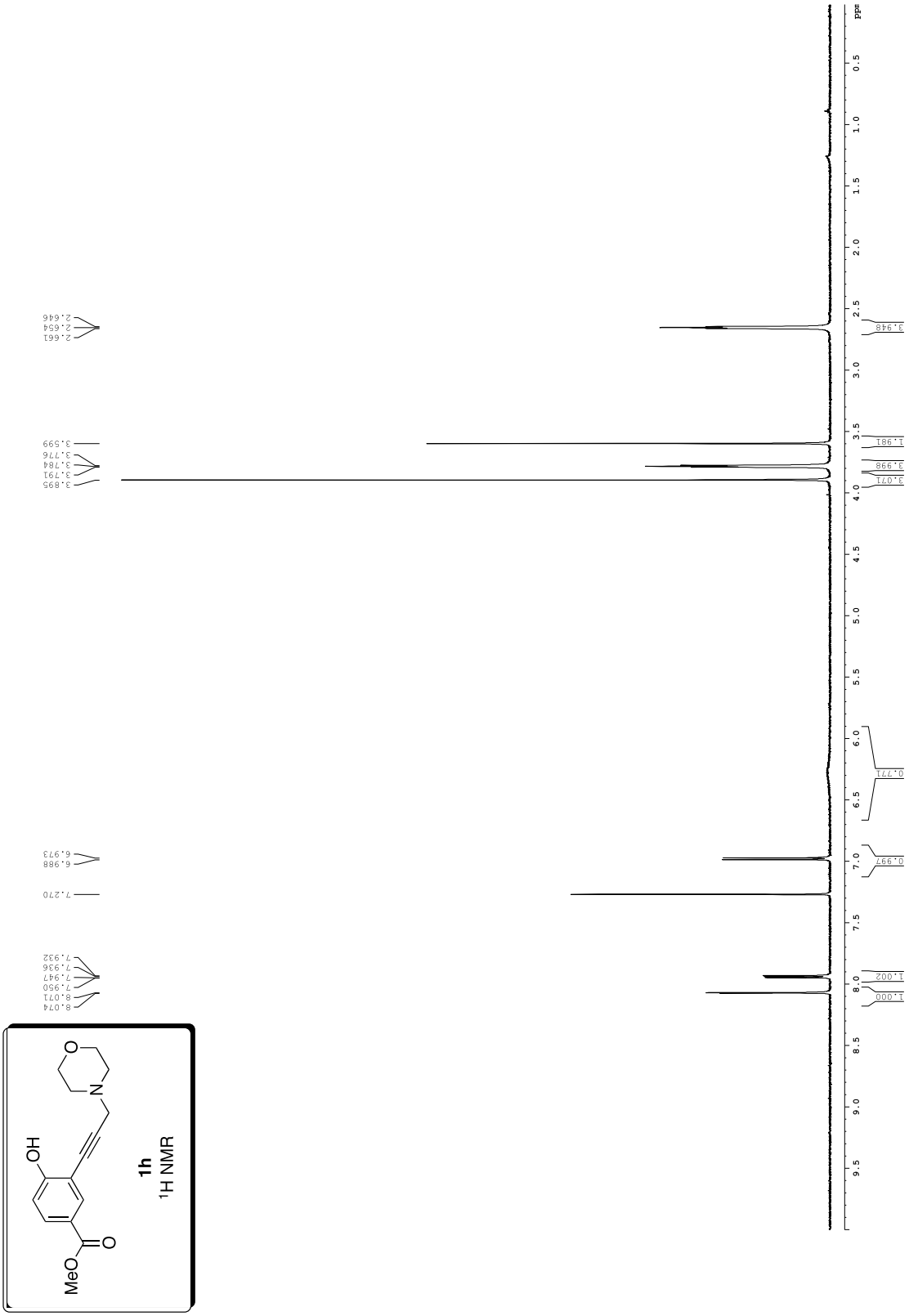
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6.988
6.973
3.895
3.791
3.784
3.776
3.599
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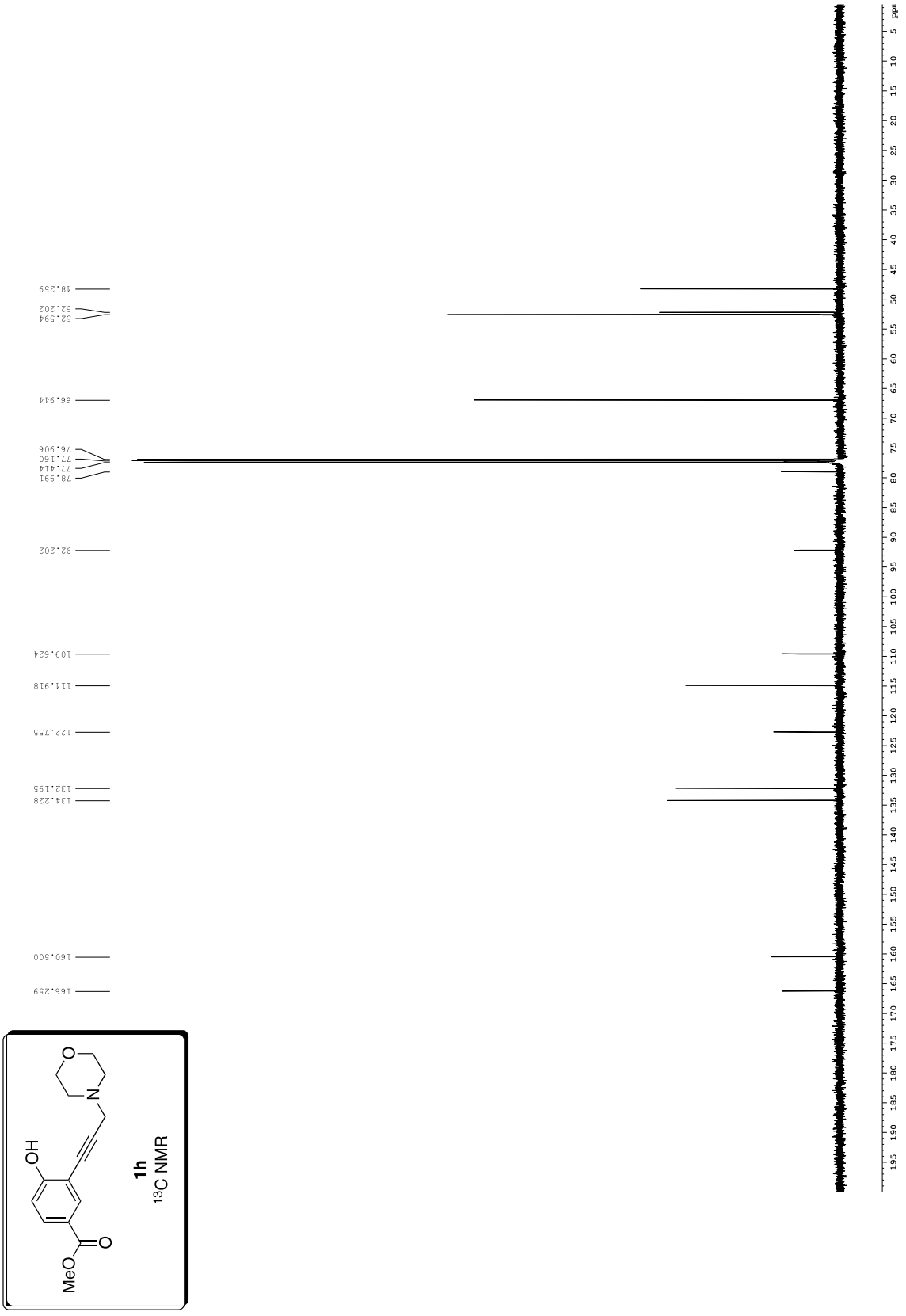
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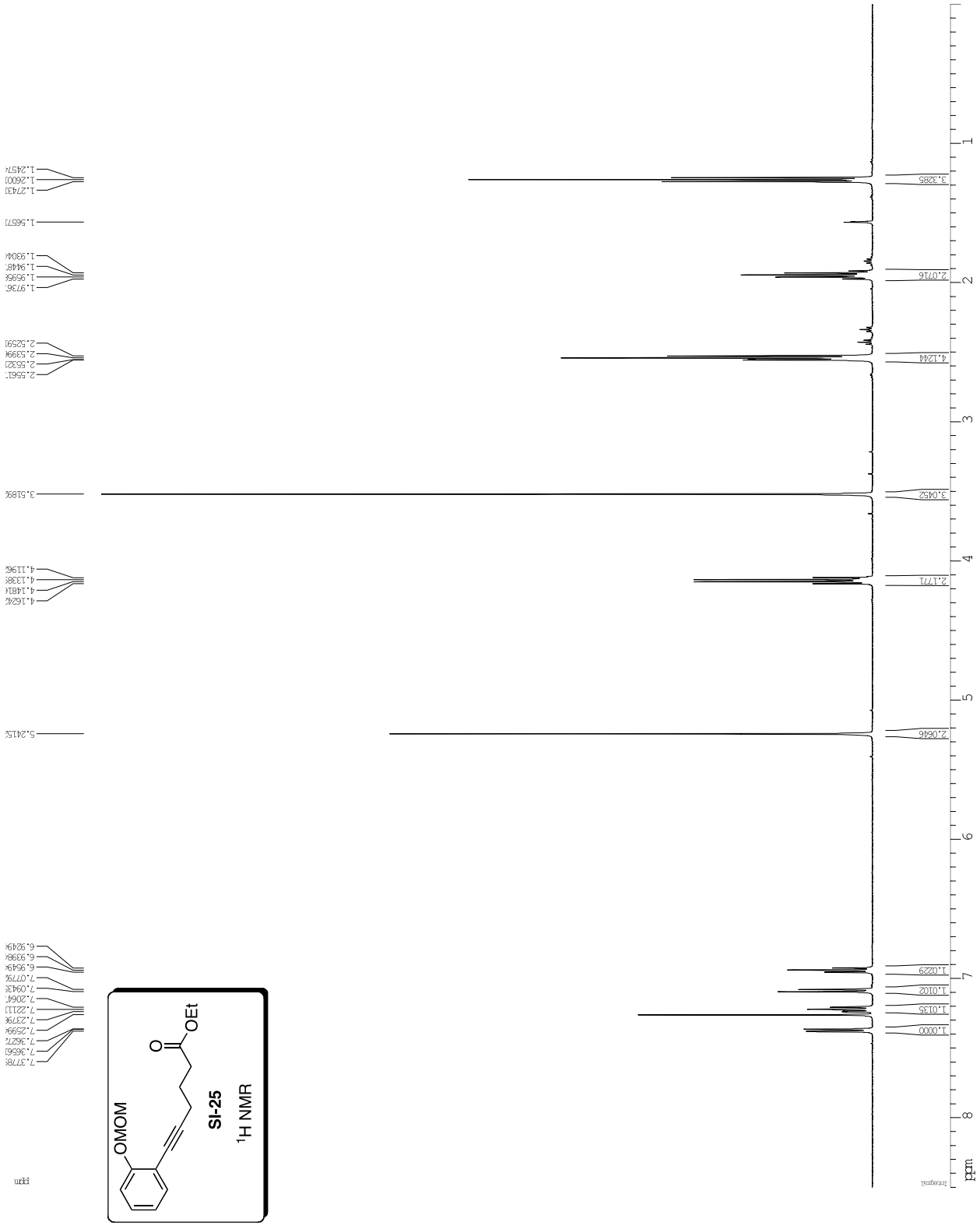
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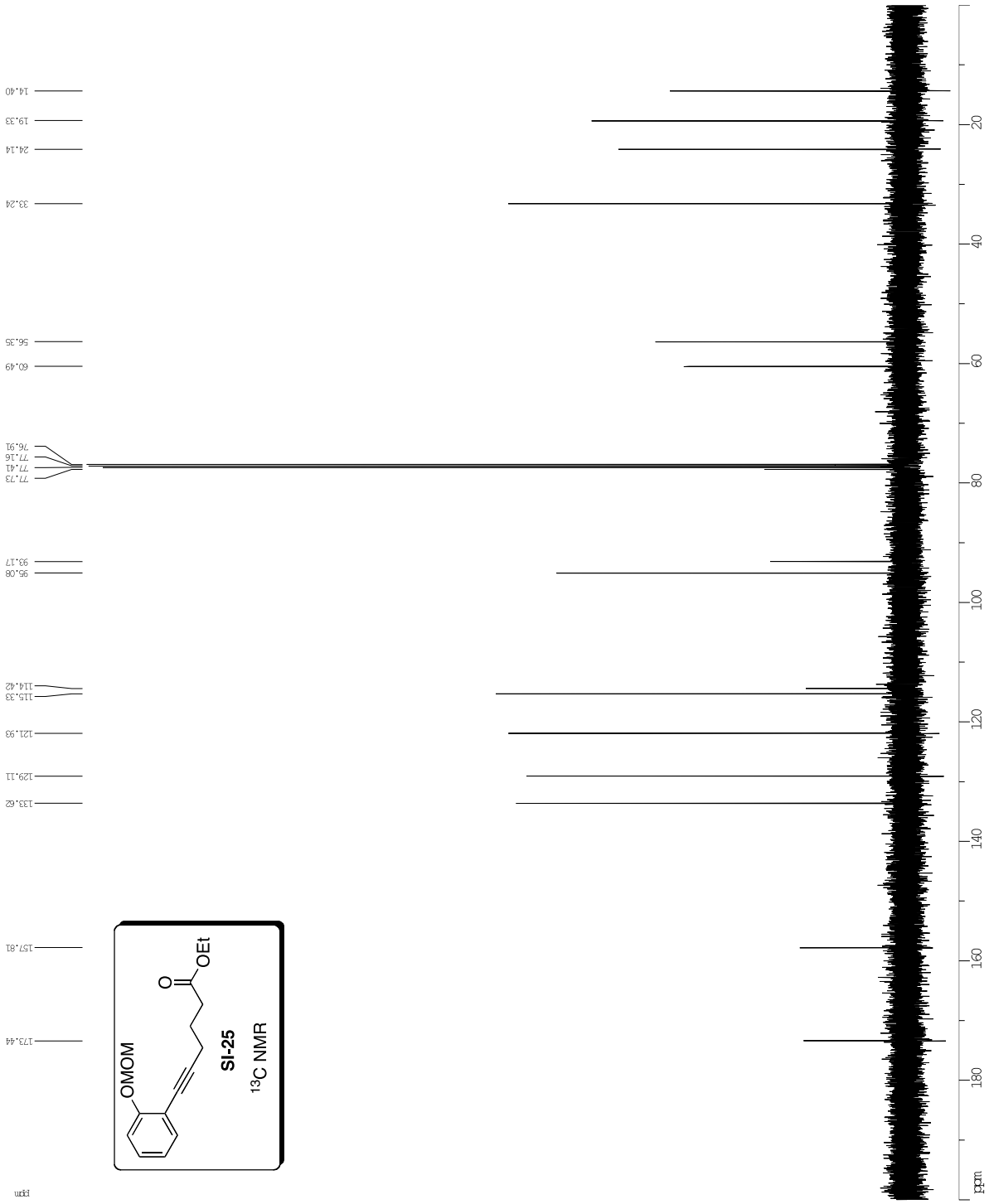
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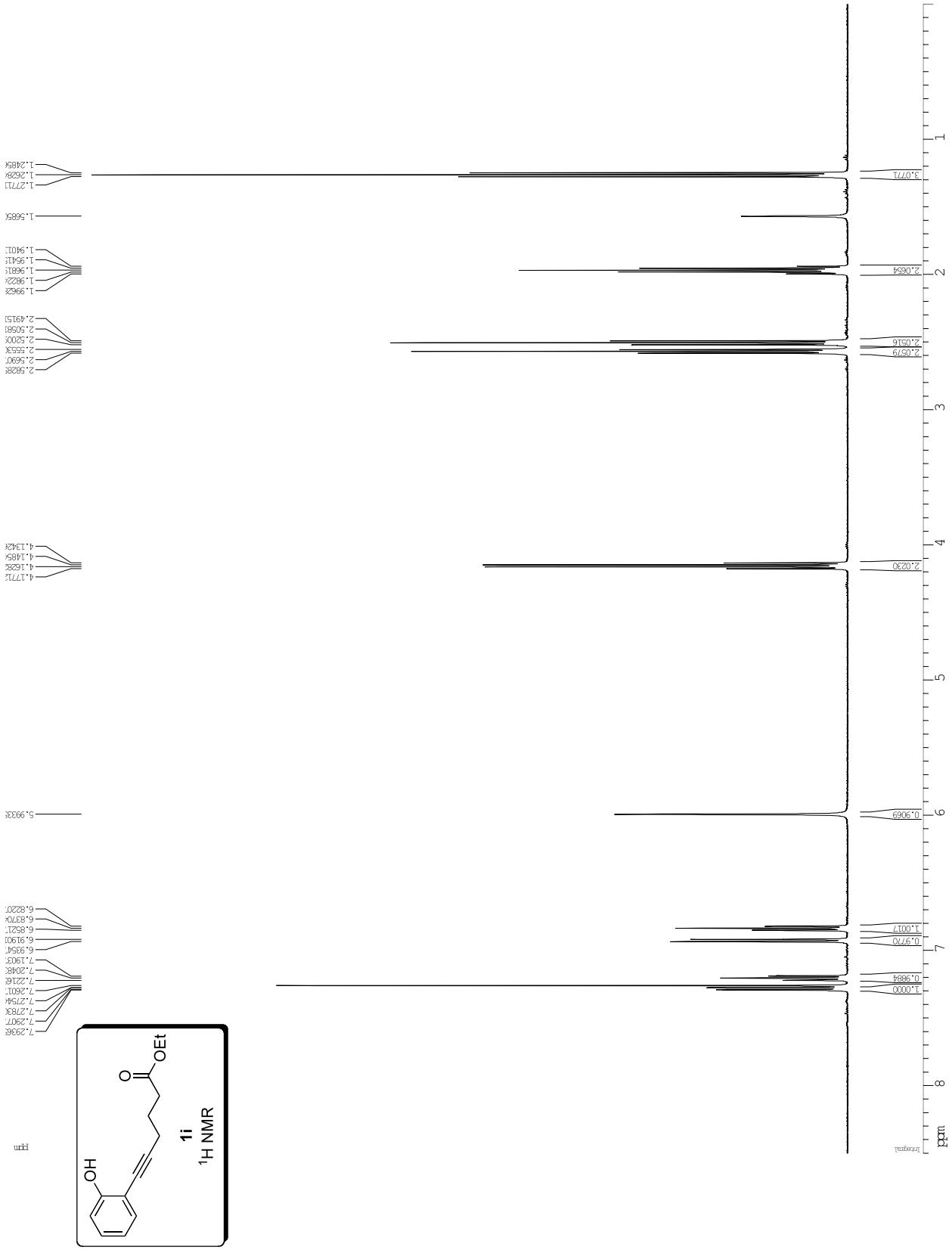
OEt
SI-25
13C NMR
ppm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2.5058
2.5200
2.5553
2.5697
2.5828
4.1342
4.1485
4.1628
4.1771
5.9933
6.8220
6.8370
6.8521
6.9190
6.9354
7.1903
7.2048
7.2216
7.2601
7.2754
7.2783
7.2907
7.2936
3.0771
2.0654
2.0516
2.0579
2.0230
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1.0017
0.9770
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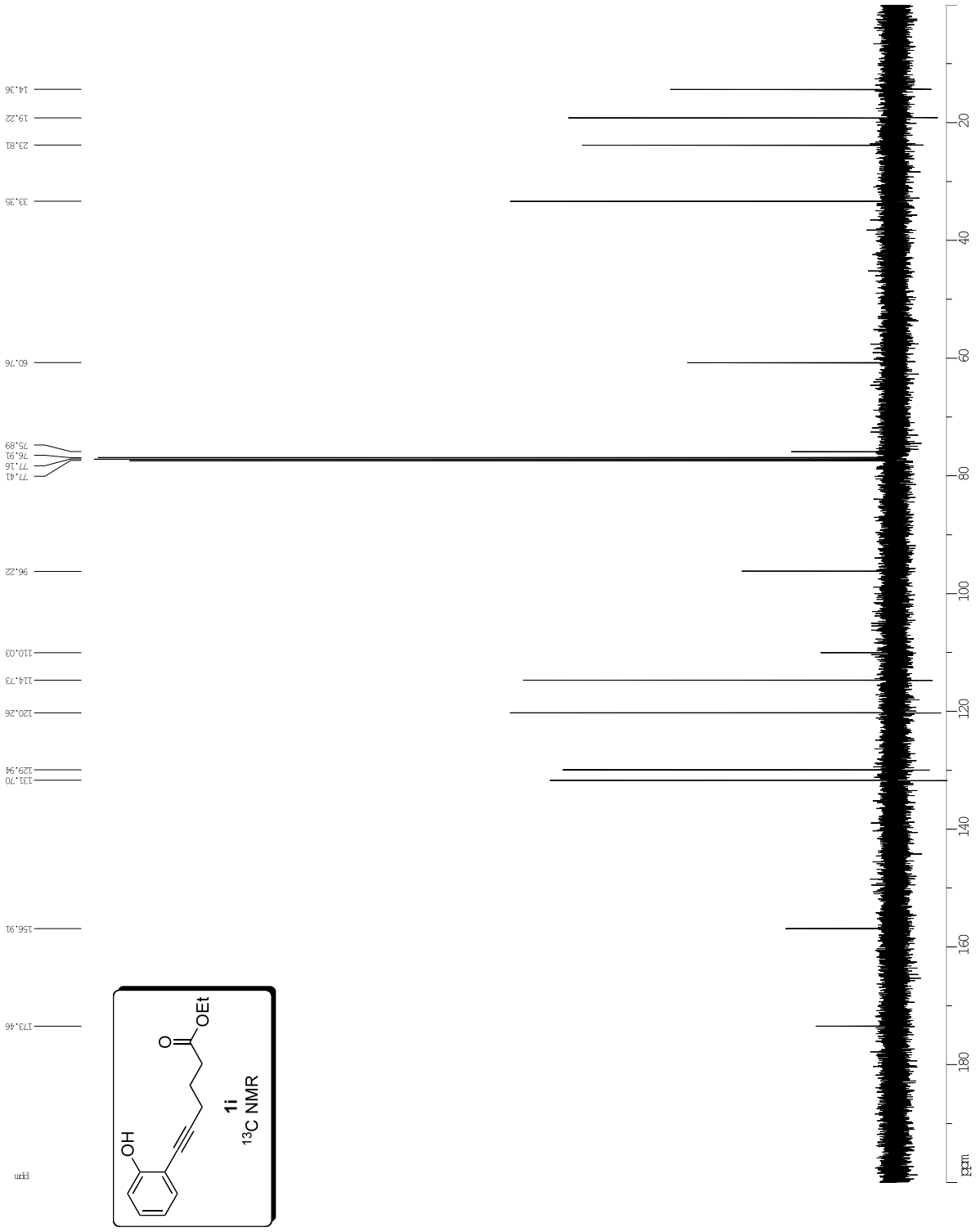
ppm
1
2
3
4
5
6
7
8
OEt
O
OH
1i
^{1}H NMR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131.70
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100
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180
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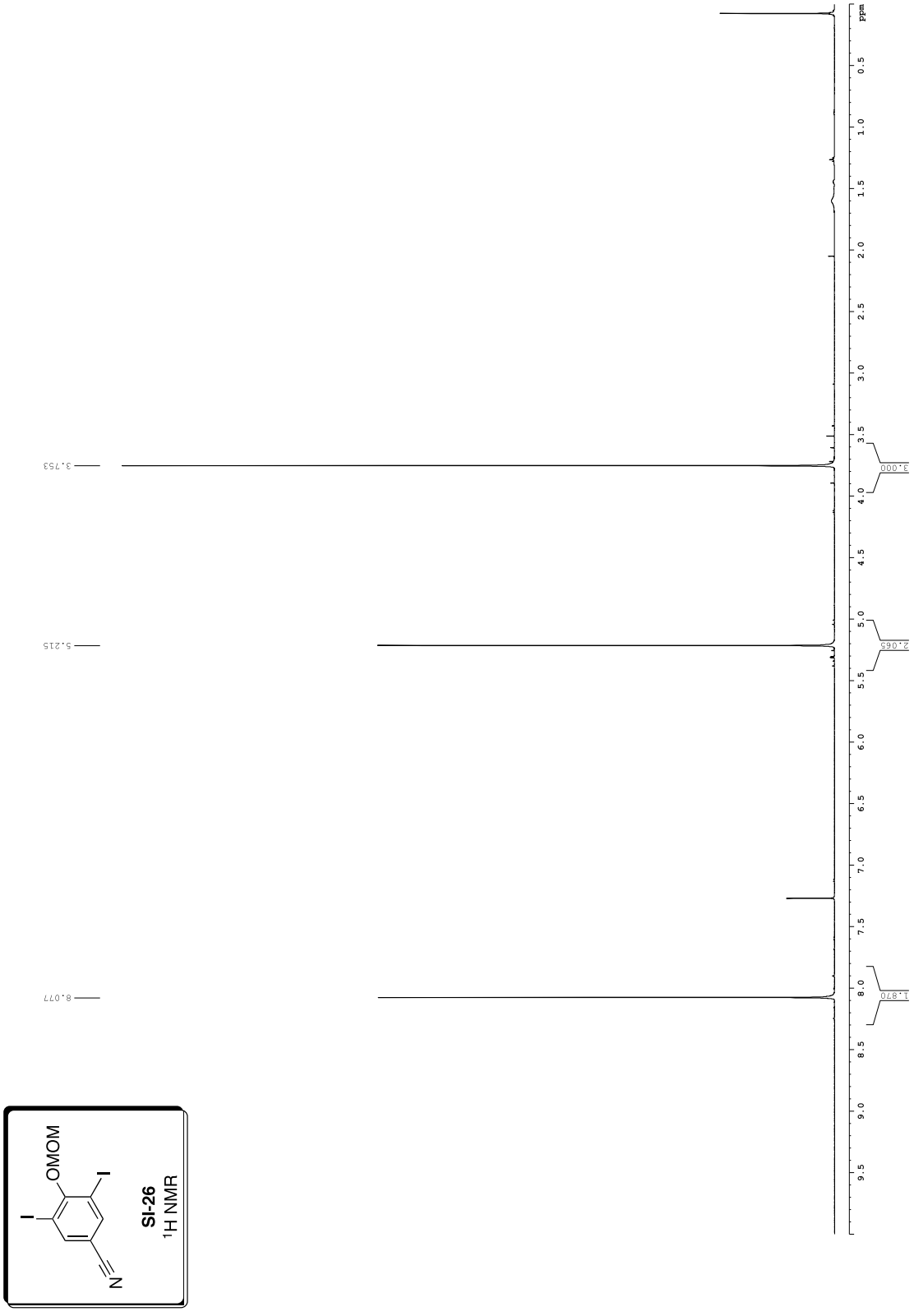
OEt
1i
13C NMR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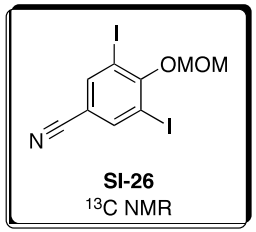
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OMOM
N
I

SI-26

^{13}C NMR

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77.160
76.906
59.242
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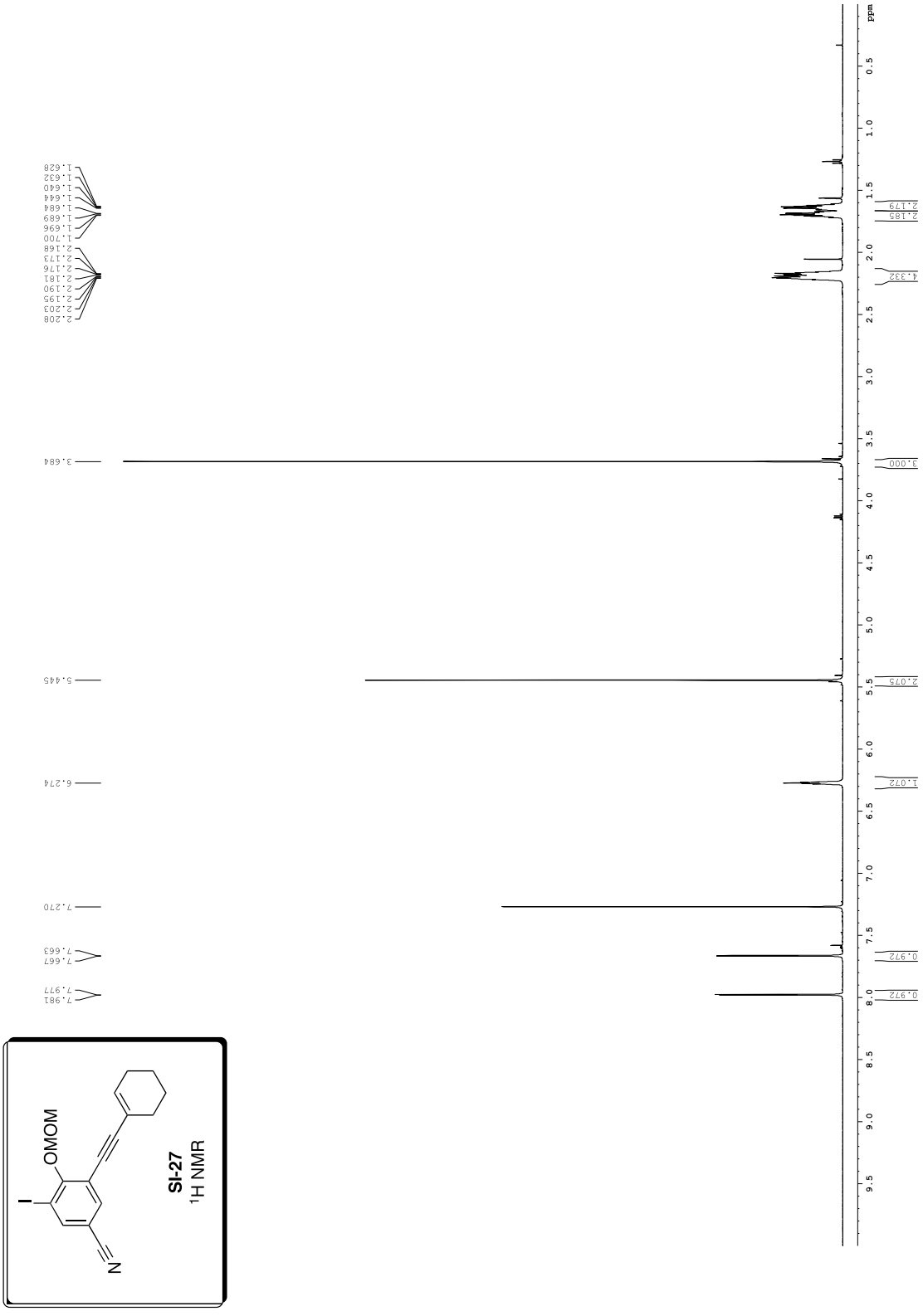
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N
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1.684
1.644
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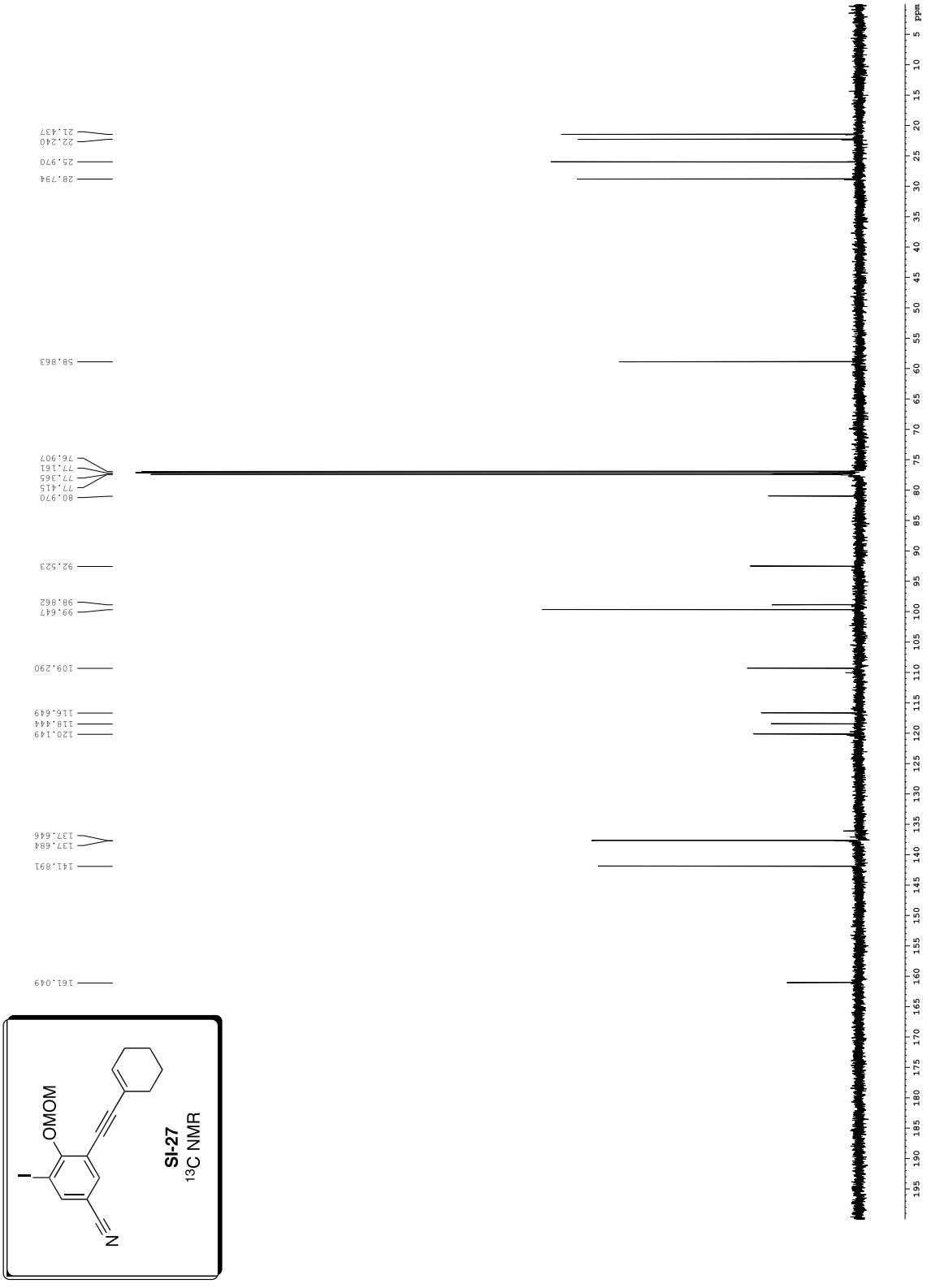
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N
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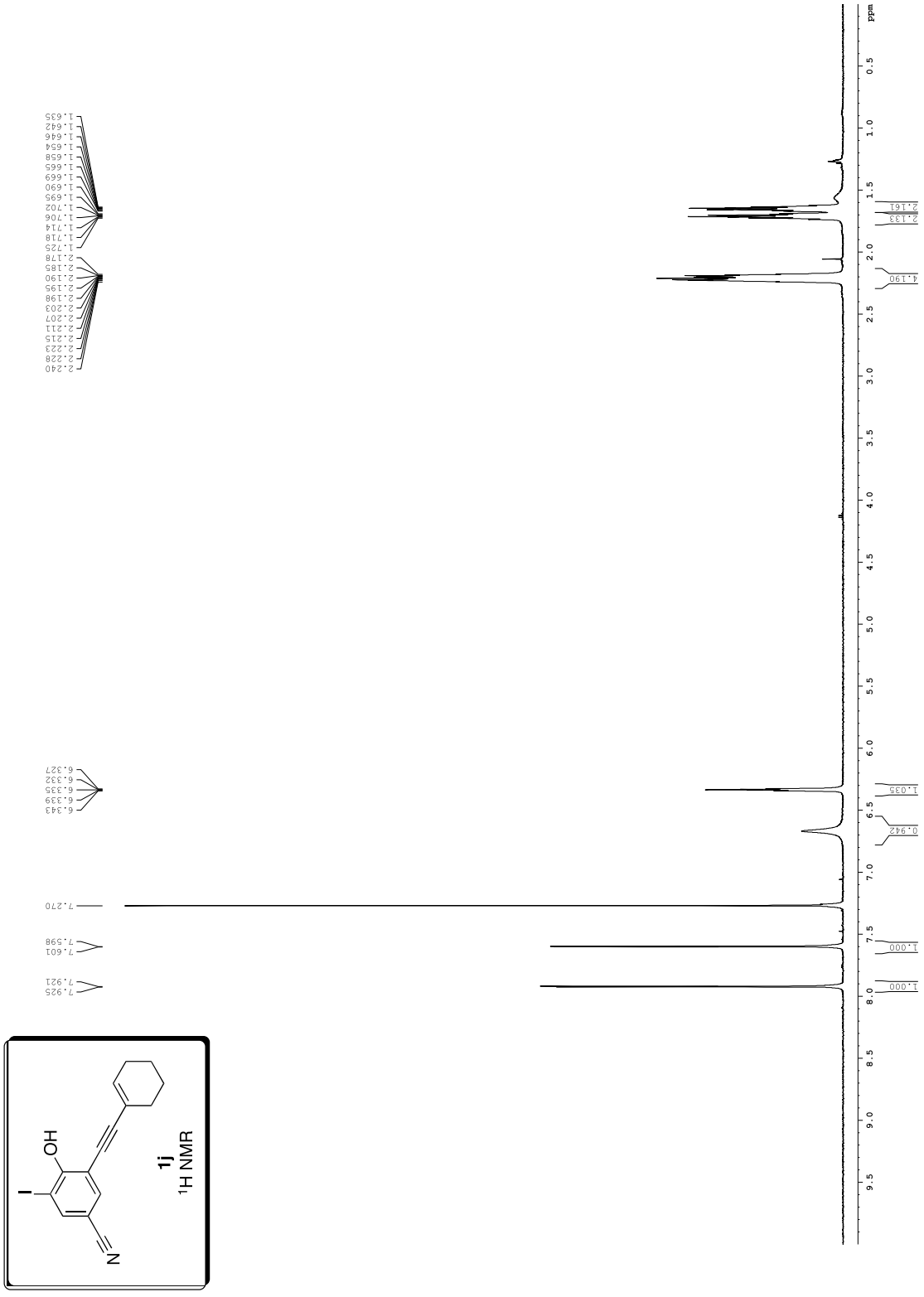
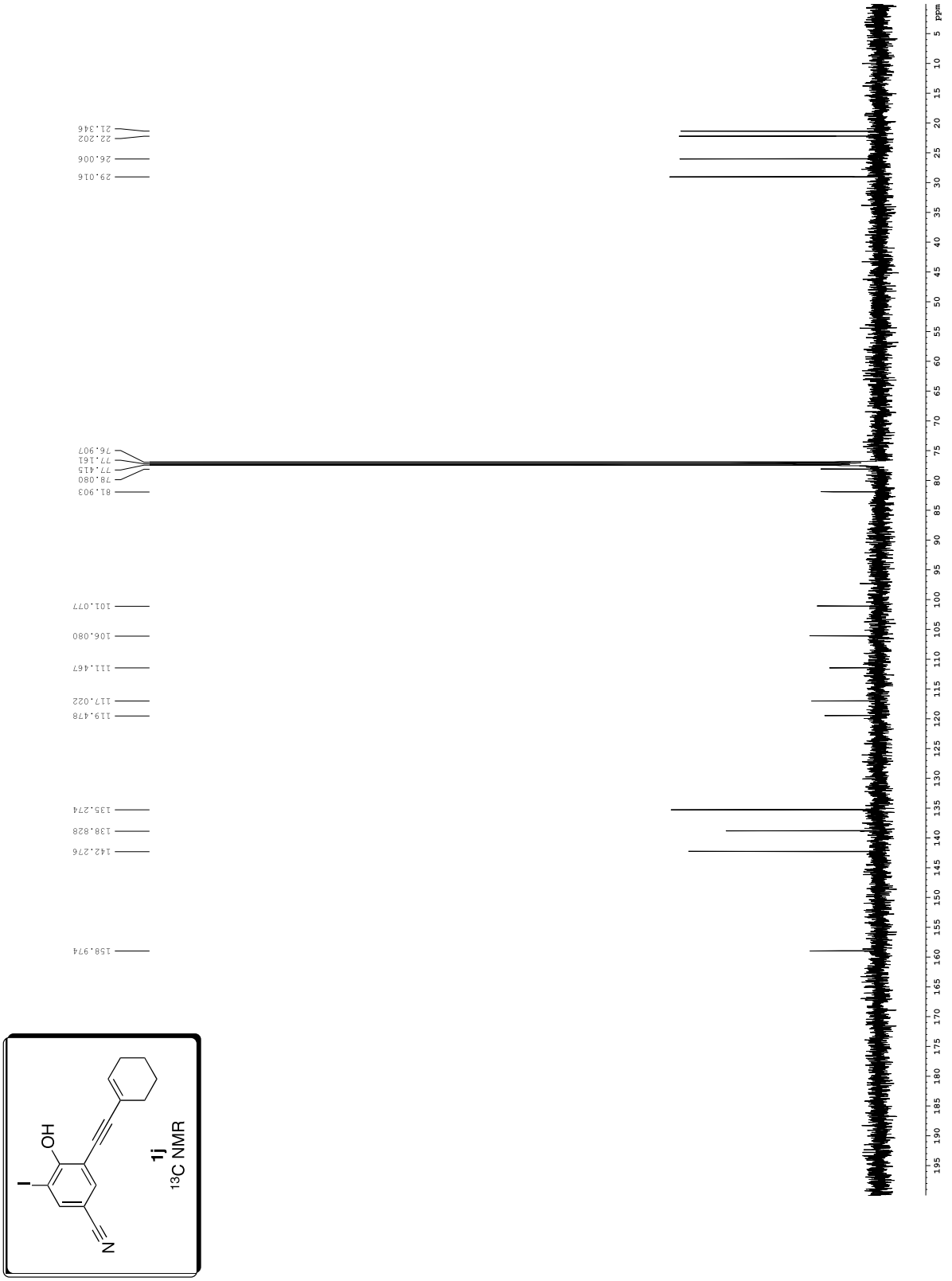

1j
^{1}H NMR
OH
I
N
ppm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119.478
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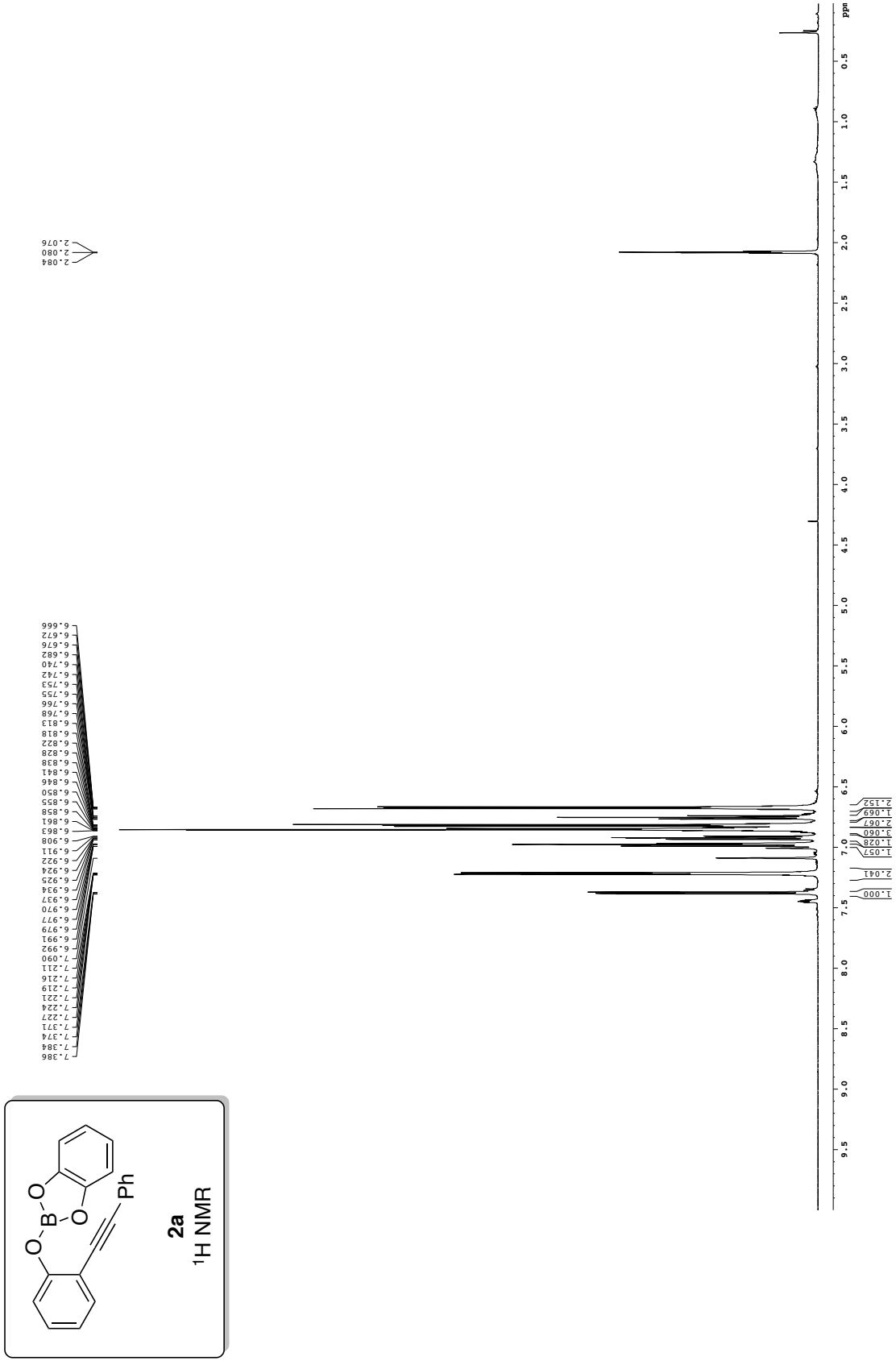
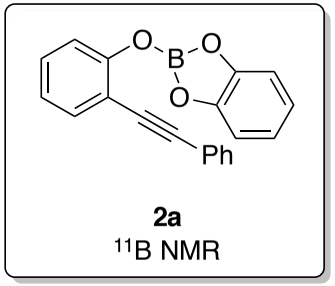
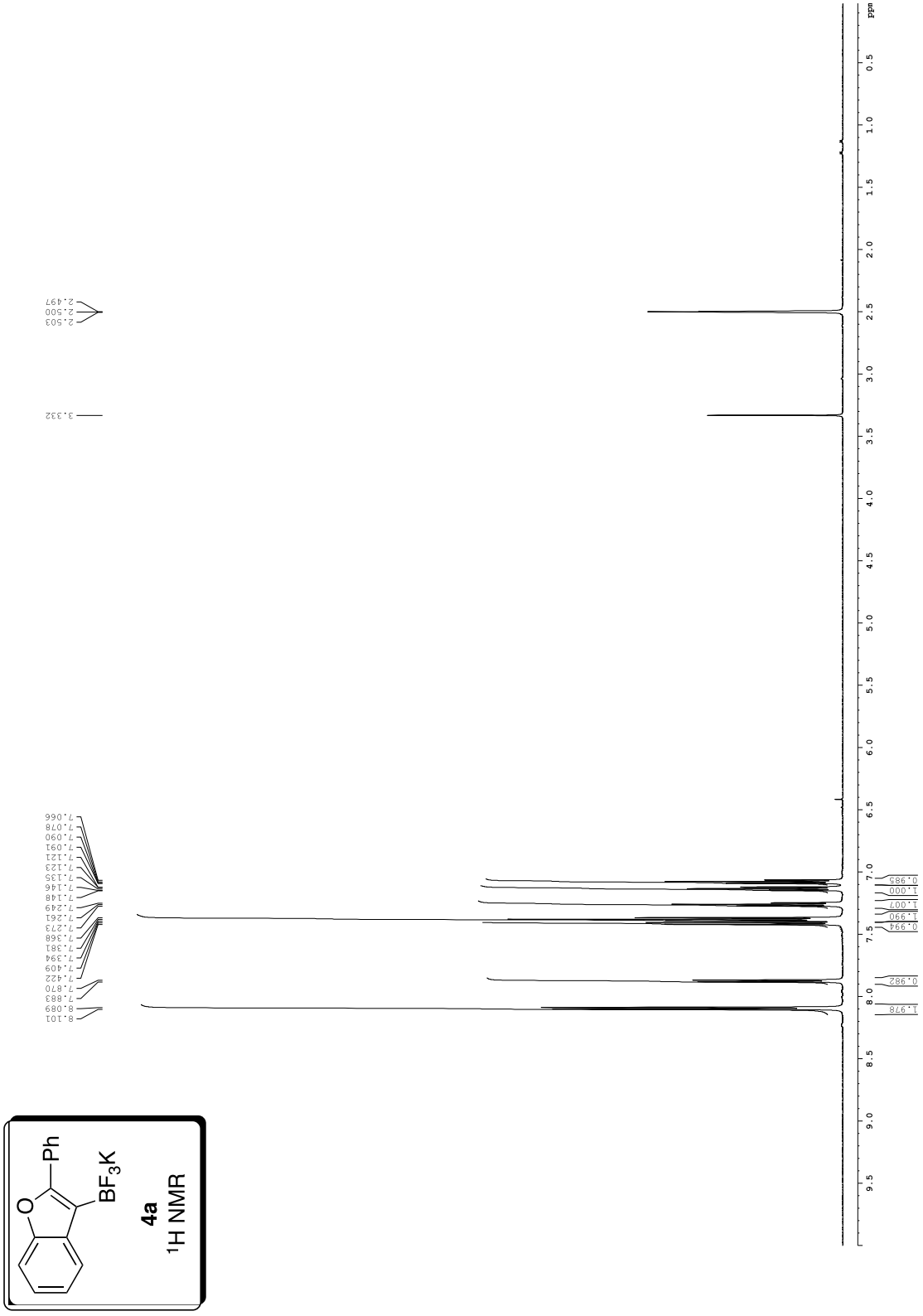
138.828
142.276
158.974
ppm
OH
I
N
1j
13C NMR

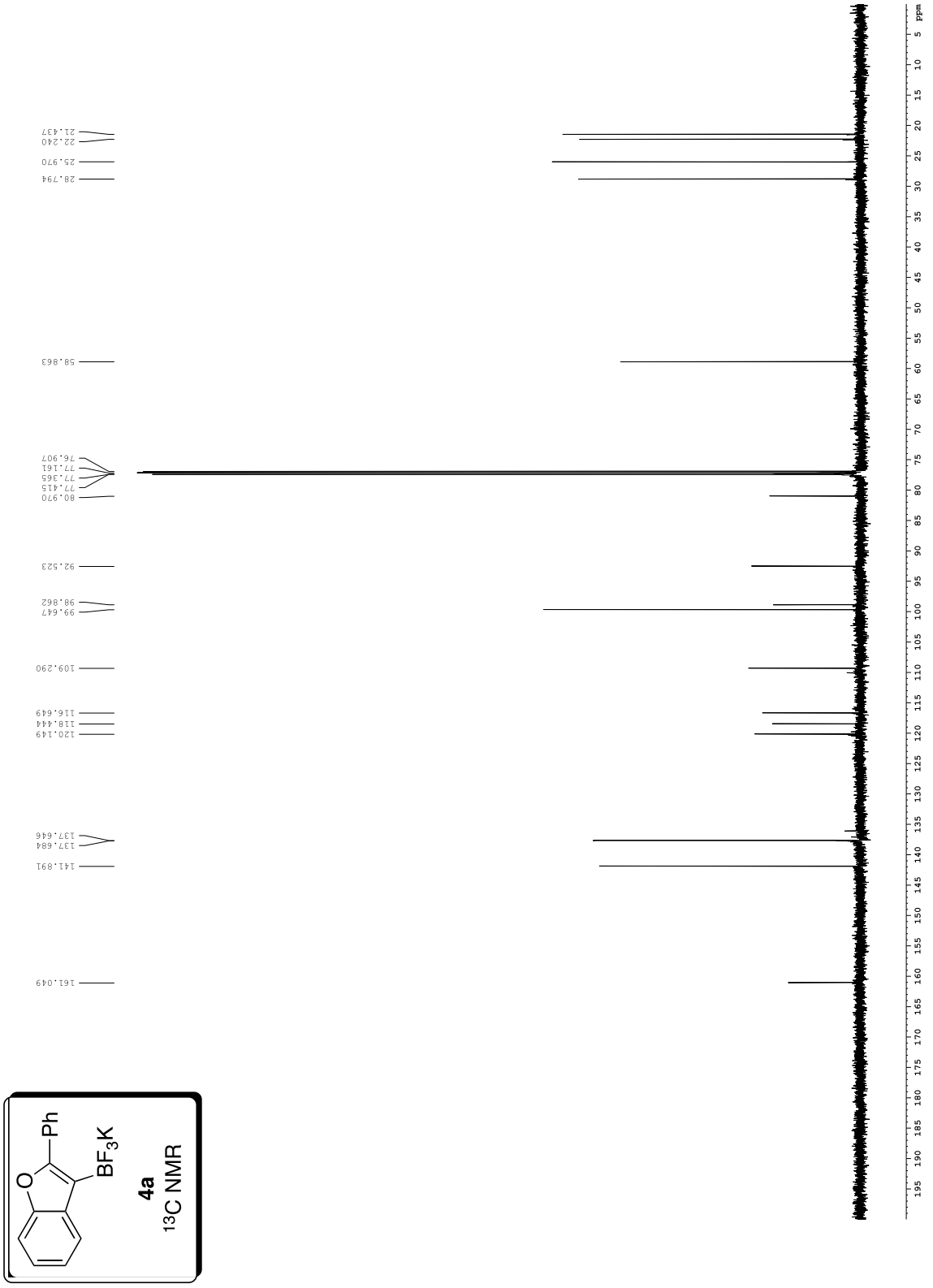

Ph
2a
1H NMR

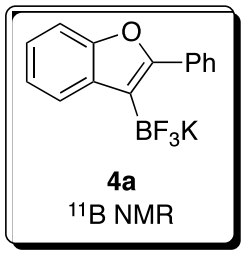


2a

^{11}B NMR


Ph
O
BF_3K
4a
^{1}H NMR
8.101
8.089
7.883
7.870
7.422
7.409
7.394
7.381
7.368
7.273
7.261
7.249
7.148
7.146
7.135
7.121
7.123
7.091
7.090
7.078
7.066
3.332
2.503
2.500
2.497
0.985
1.000
1.007
1.990
0.994
0.982
1.978
ppm

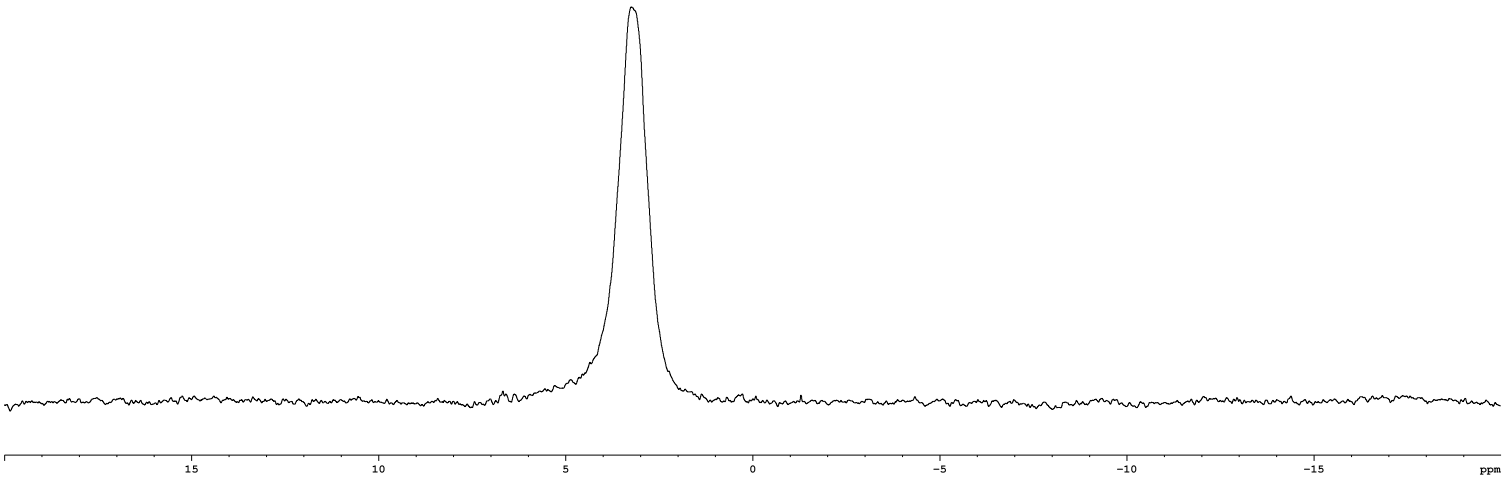

Ph
BF3K
O
4a
13C NMR
21.437
22.240
25.970
28.794
58.863
76.907
77.161
77.365
77.415
80.970
92.523
98.862
99.647
109.290
116.649
118.444
120.149
137.646
137.684
141.891
161.049
ppm

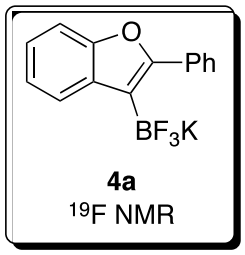


4a

^{11}B NMR

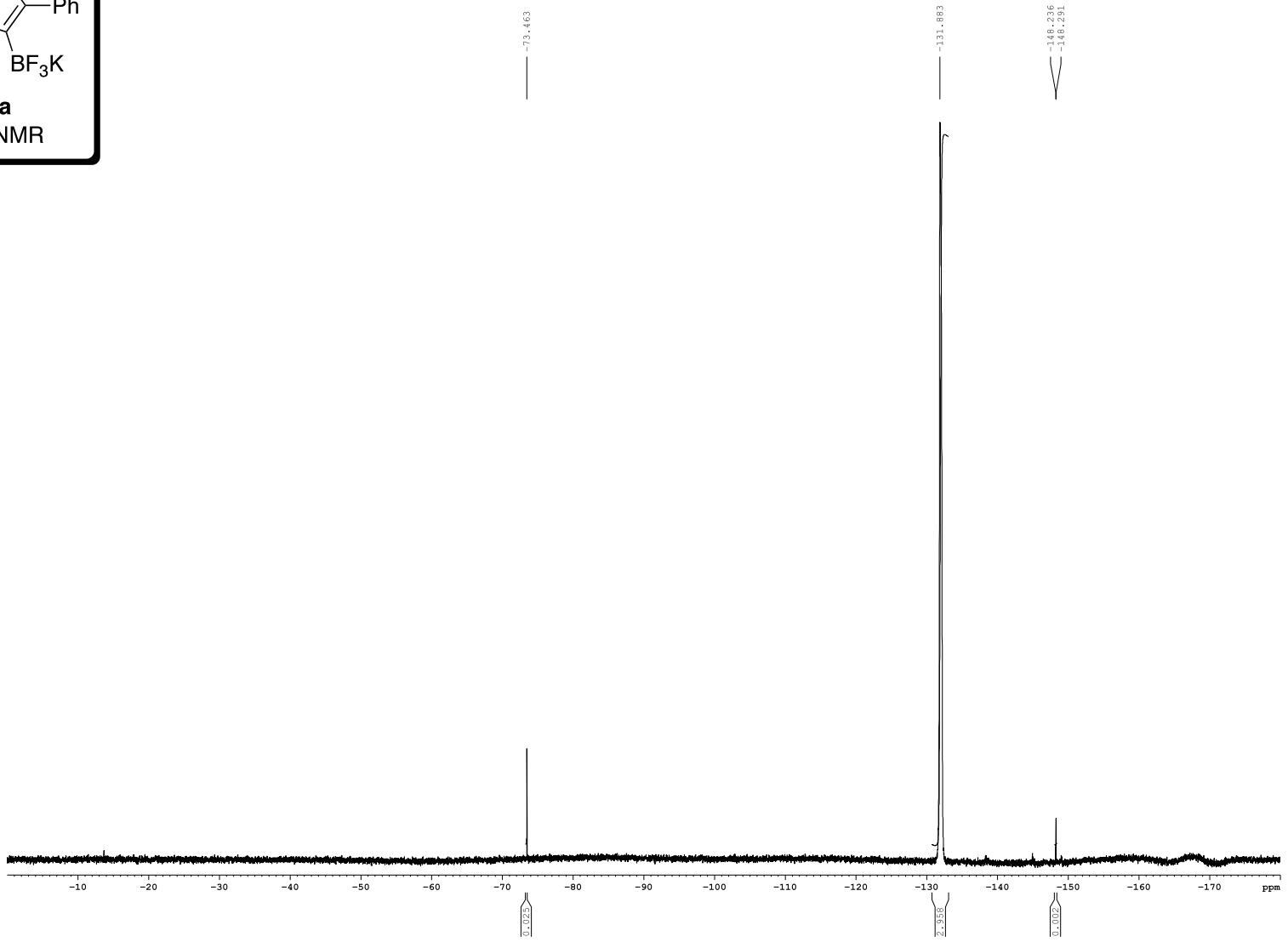
3.264

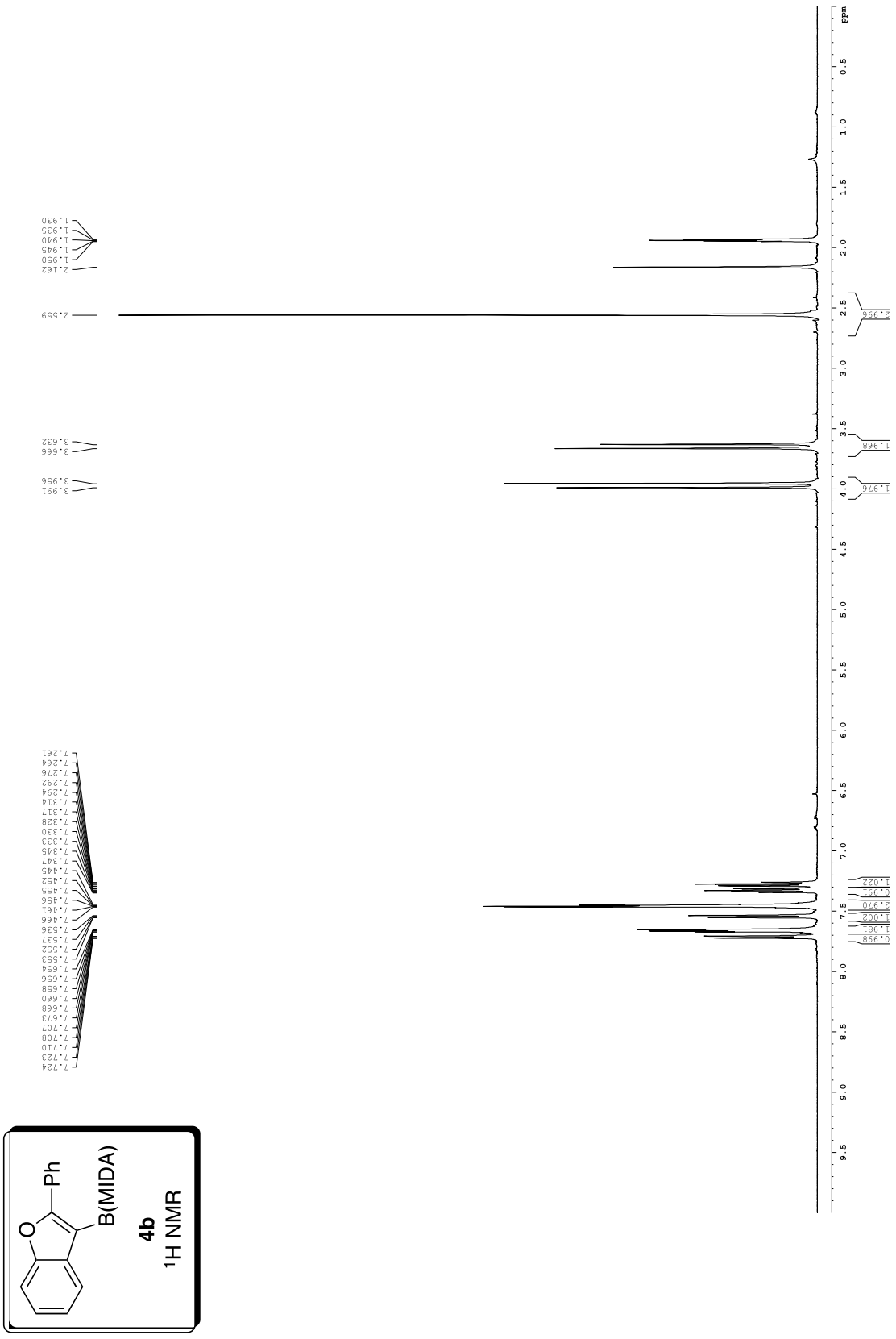


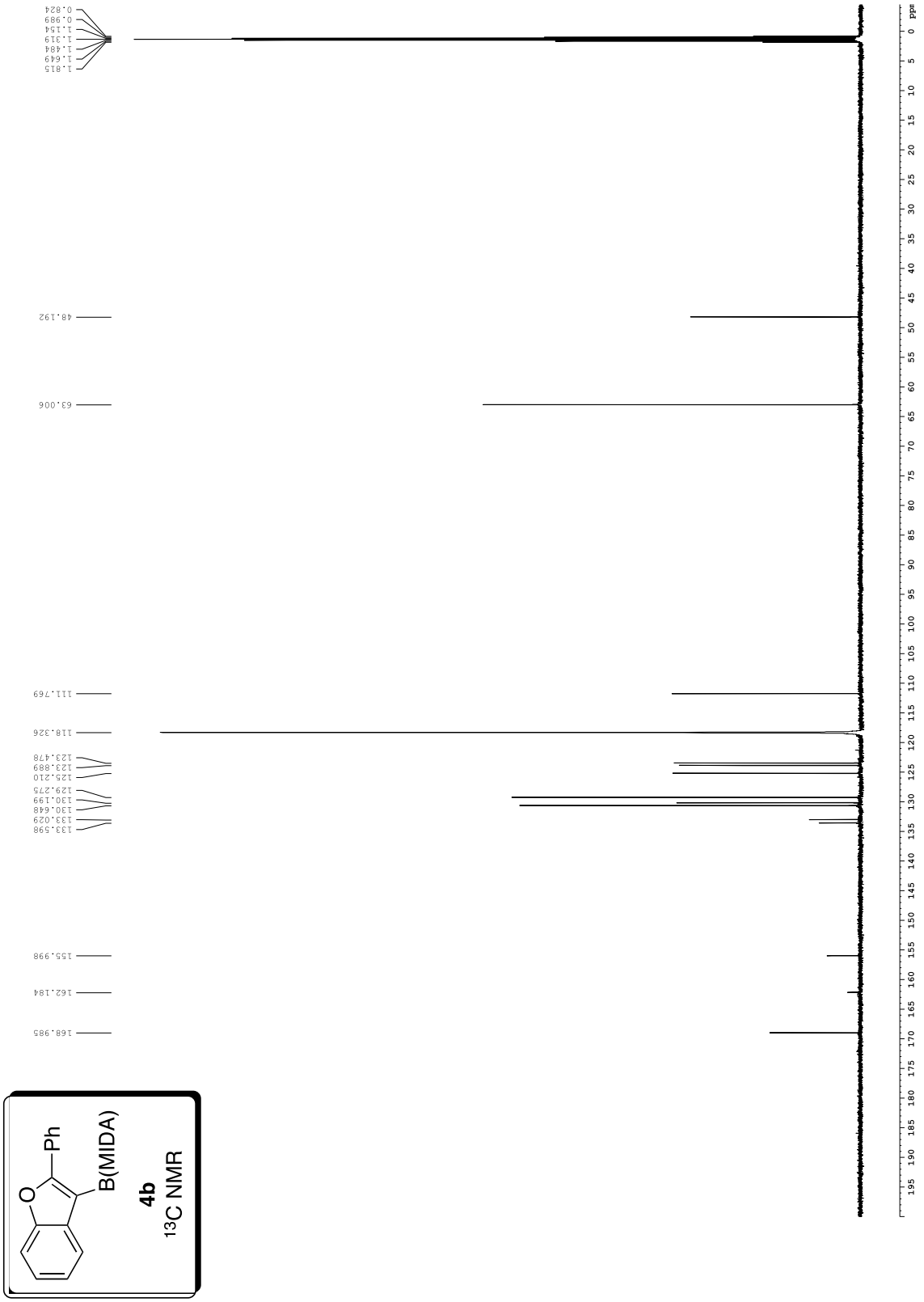

O
Ph
BF3K

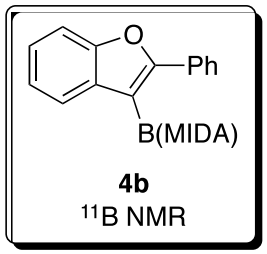
4a

^{19}F NMR


-73.463
-131.883
-148.236
-148.291
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
ppm
0.025
2.958
0.002

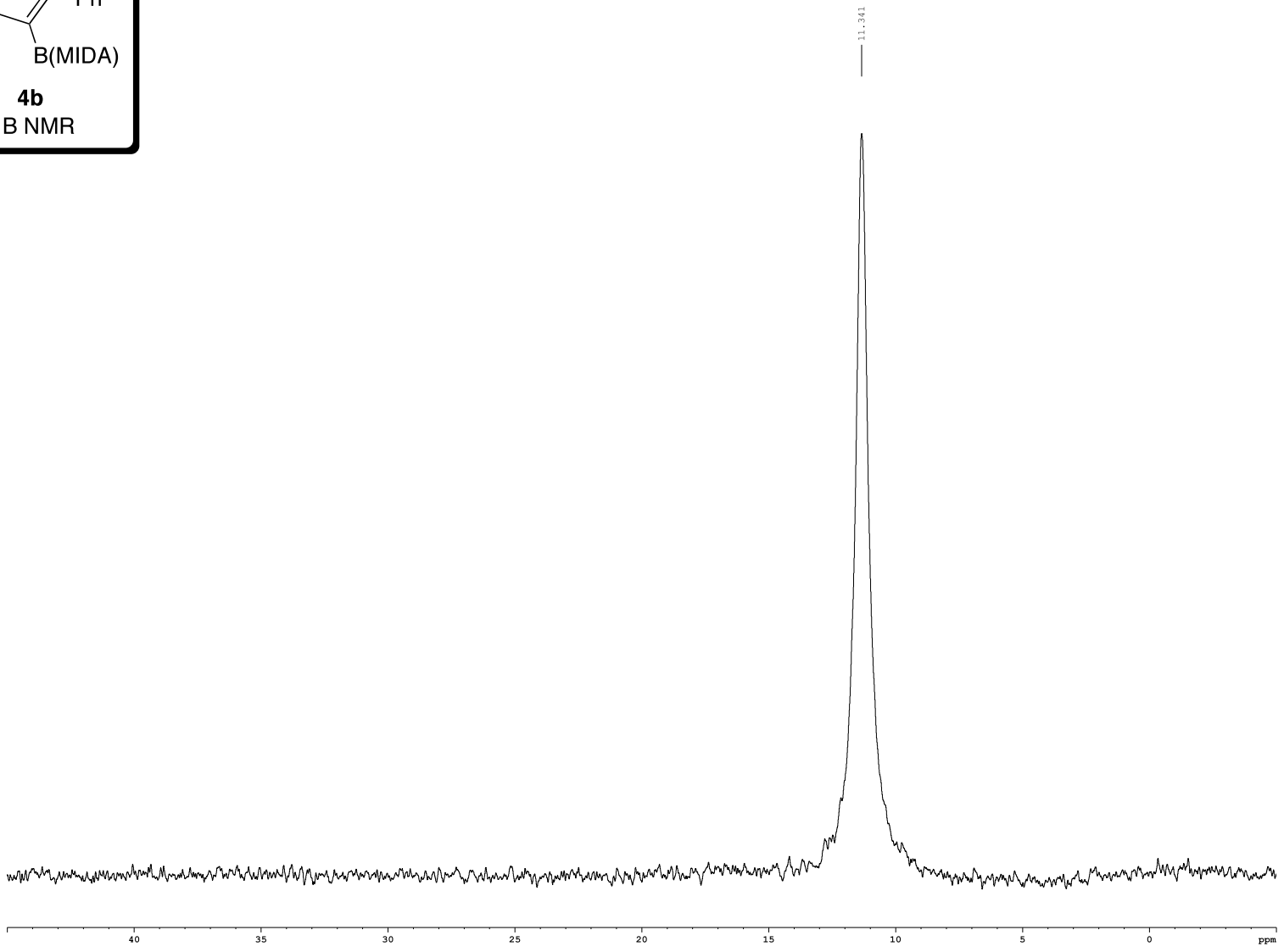

Ph
B(MIDA)
O
4b
^{1}H NMR

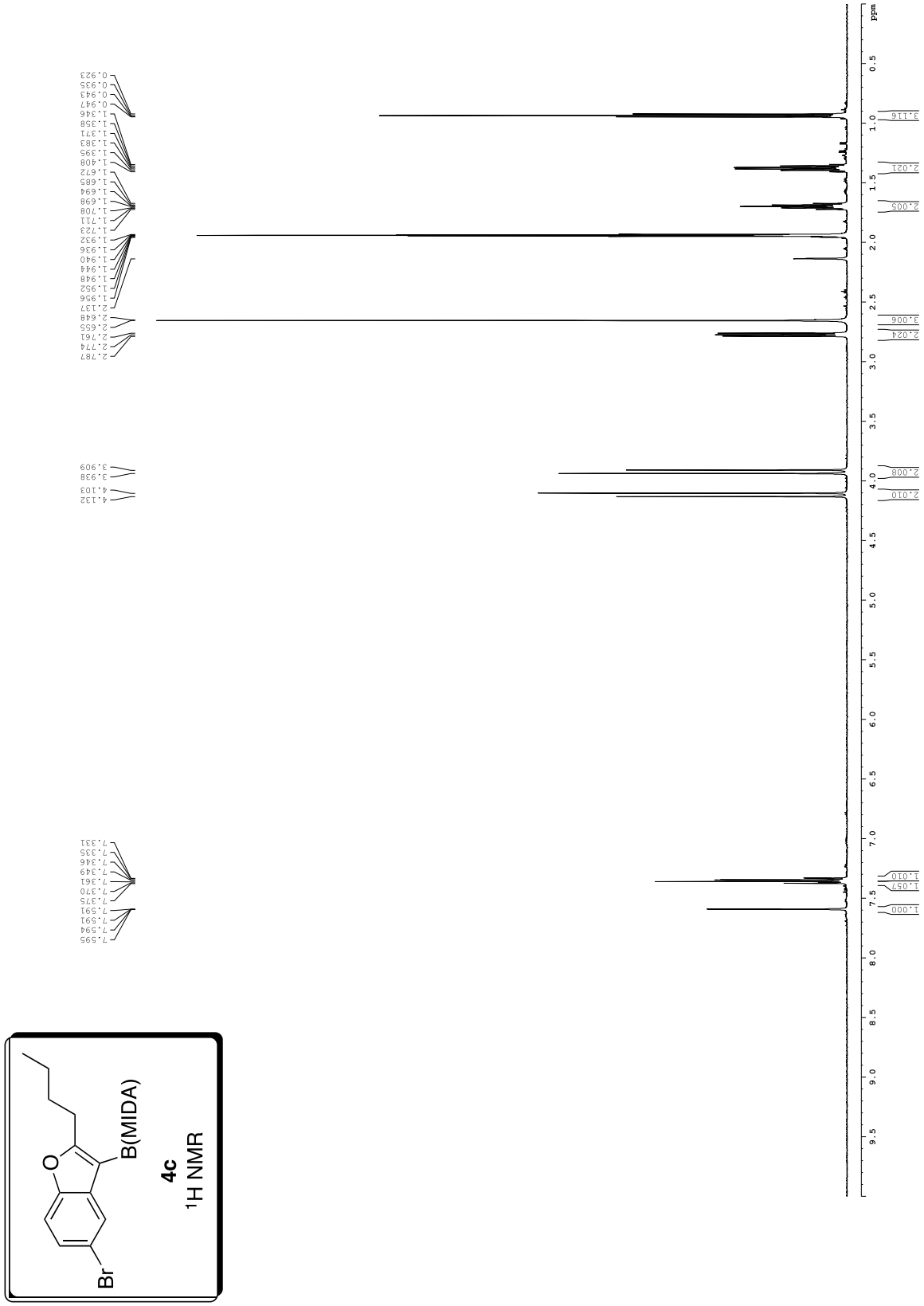

Ph
B(MIDA)
O
4b
13C NMR
0.824
0.989
1.154
1.319
1.484
1.649
1.815
48.192
63.006
111.769
118.326
123.478
123.889
125.210
129.275
130.199
130.648
133.029
133.598
155.998
162.184
168.985
ppm

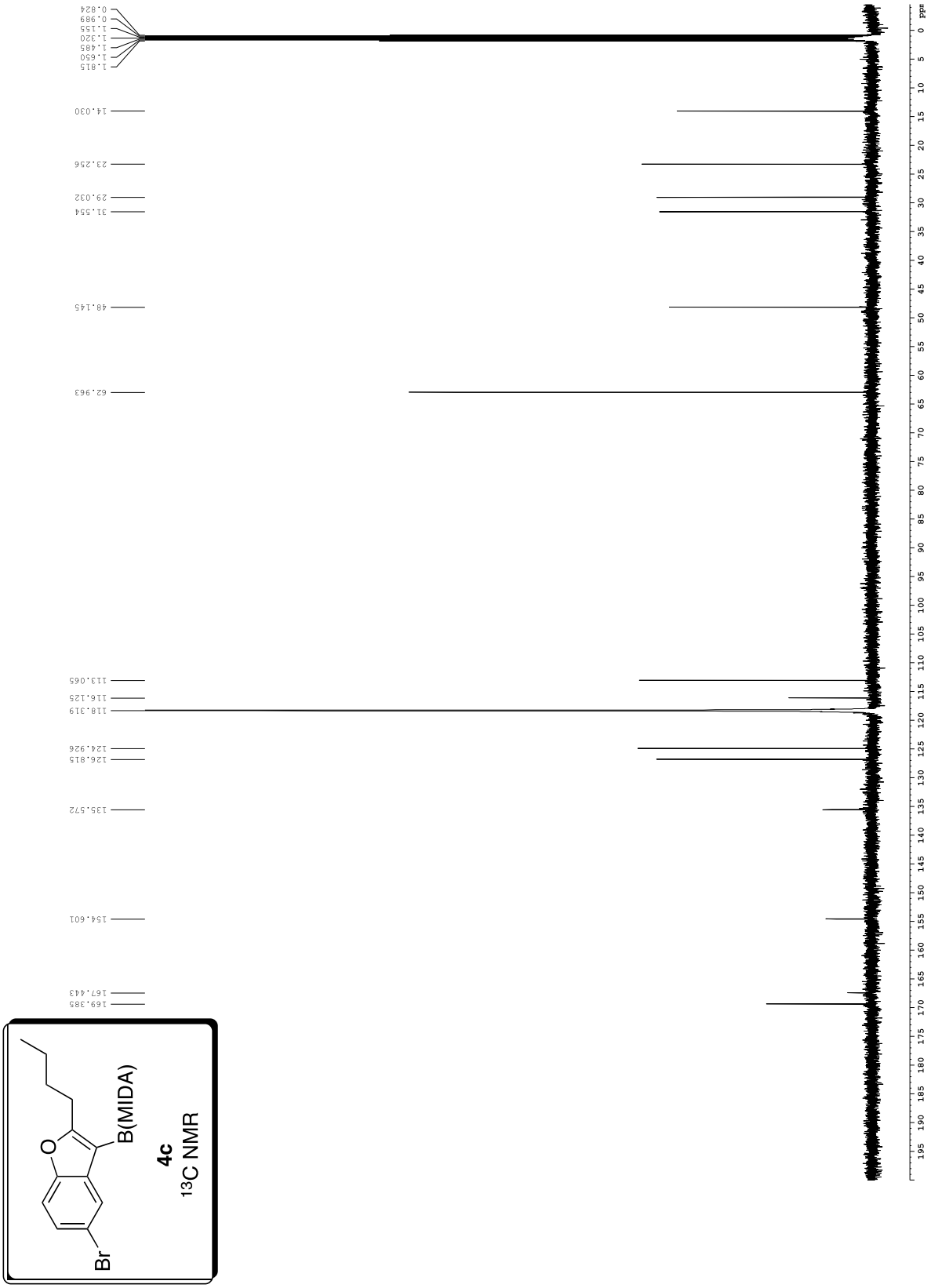


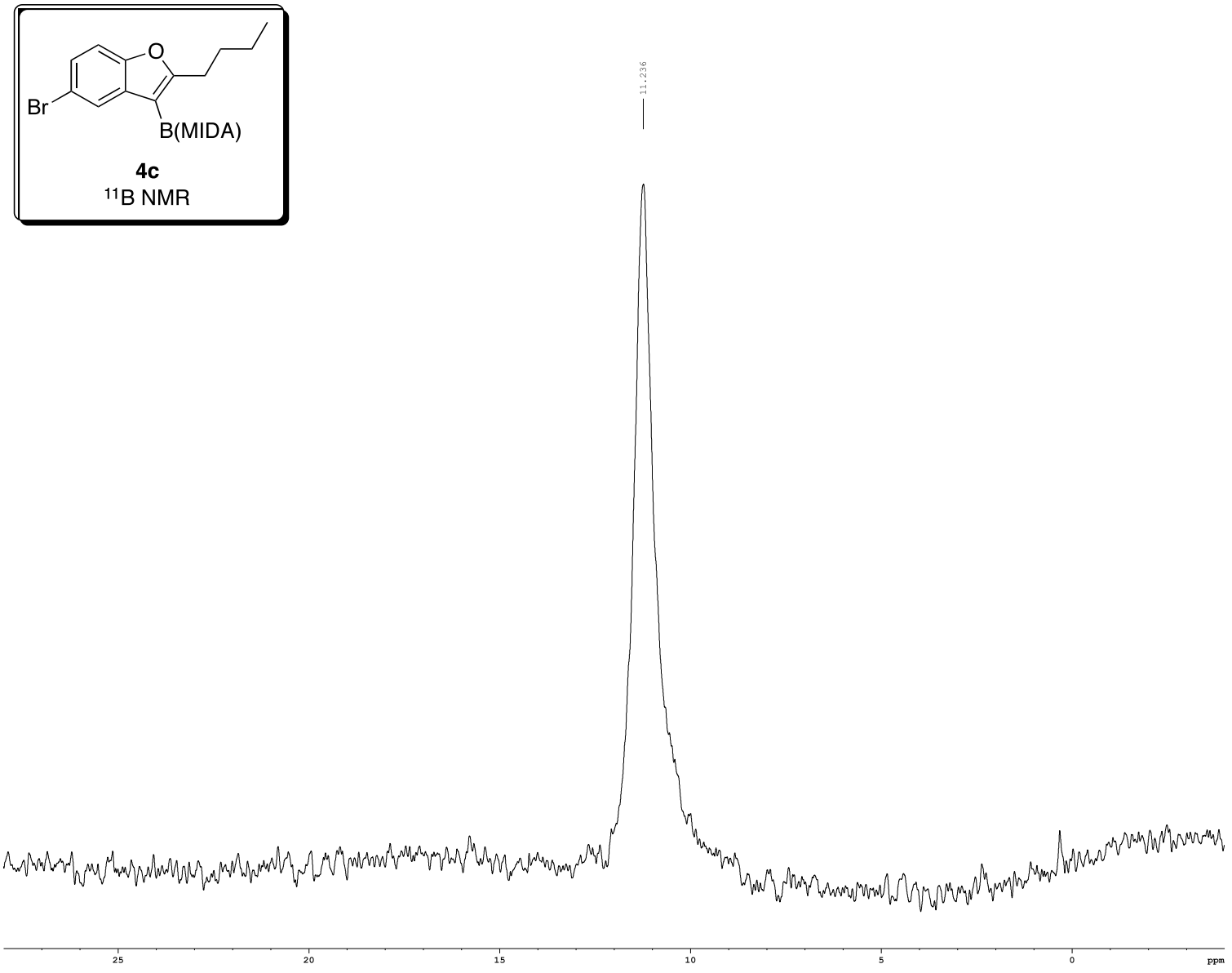
4b

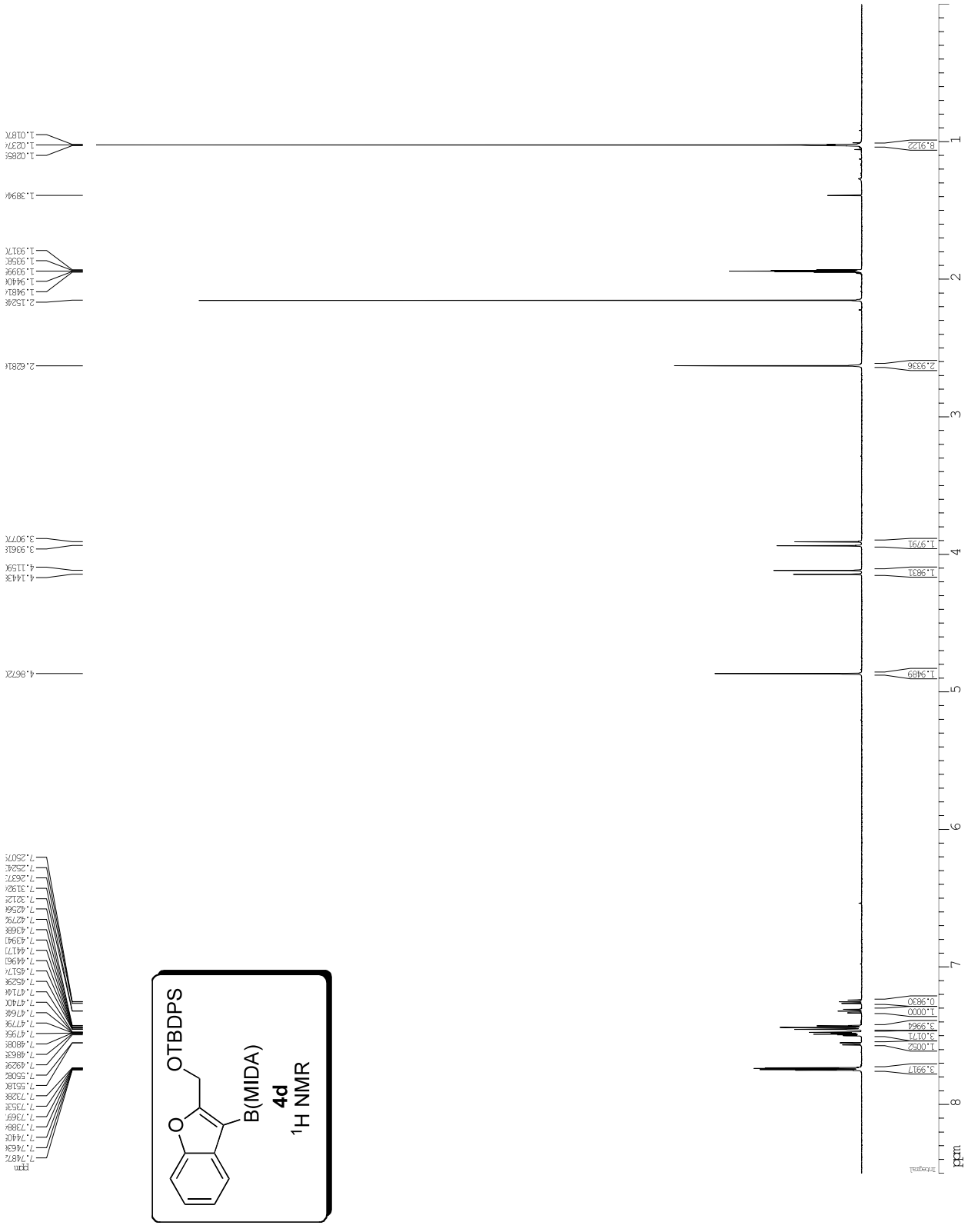
^{11}B NMR

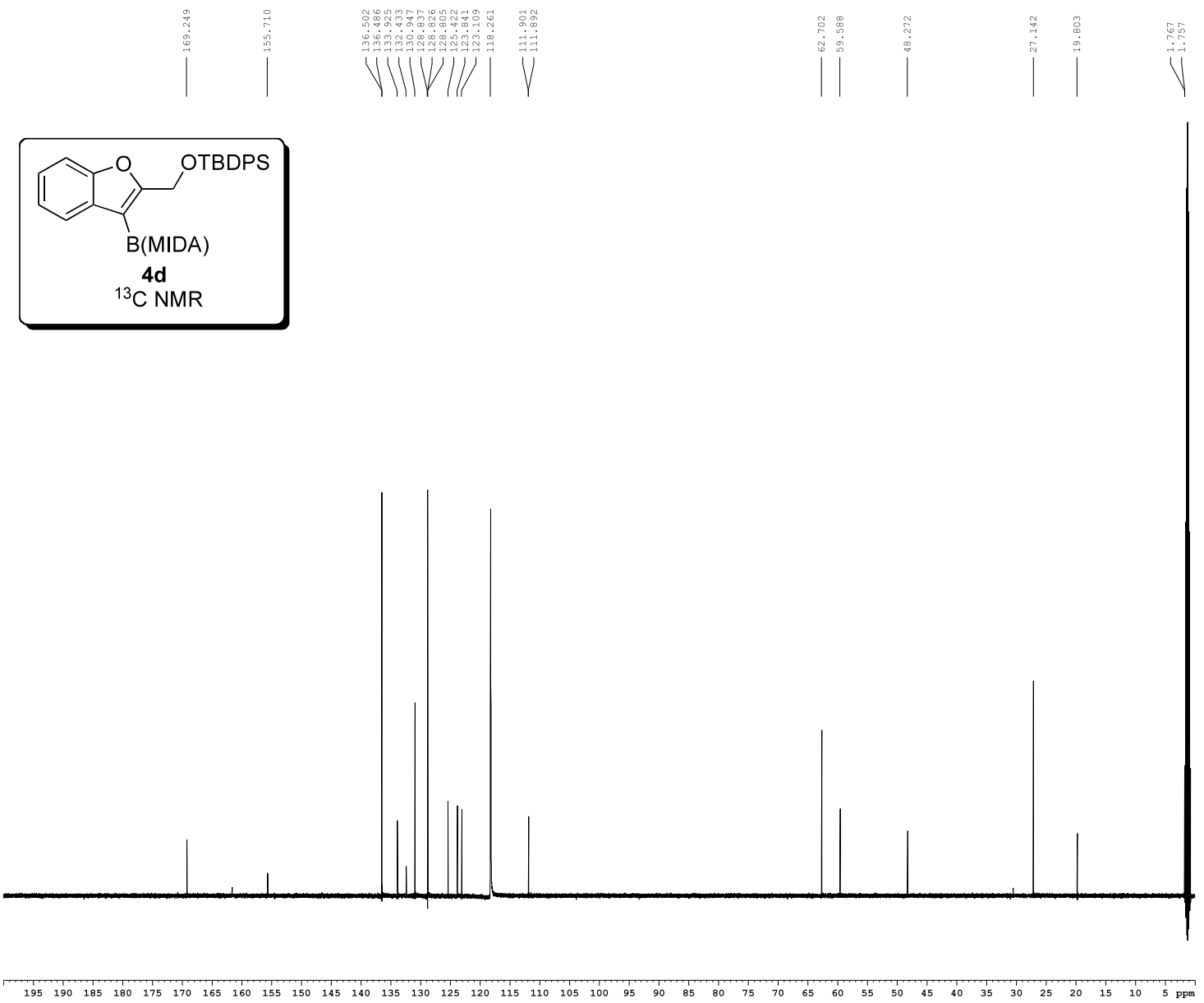


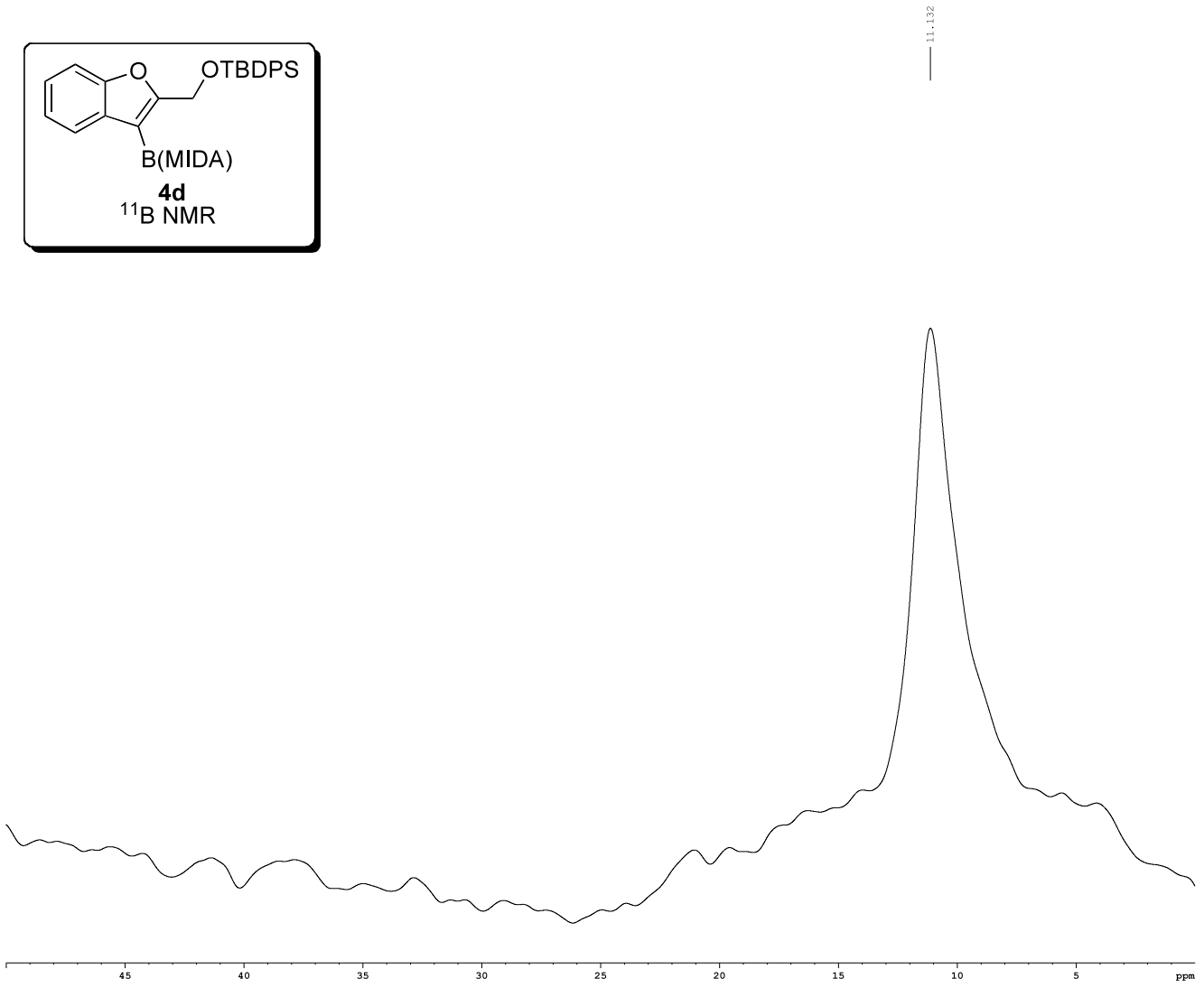

B(MIDA)
Br
O
4c
^{1}H NMR

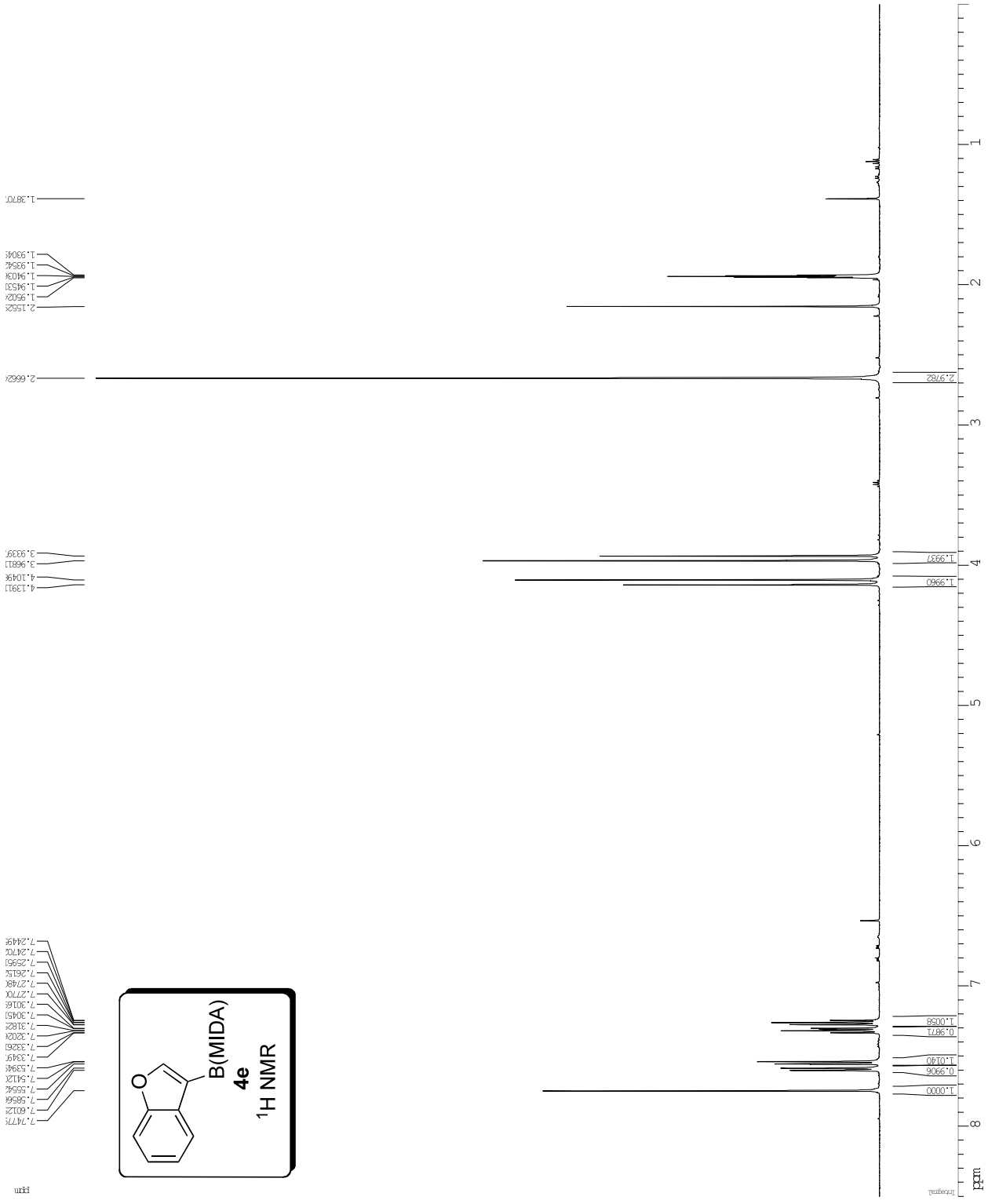

0.824
0.989
1.155
1.320
1.485
1.650
1.815
14.030
23.256
29.032
31.554
48.145
62.963
113.065
116.125
118.319
124.926
126.815
135.572
154.601
167.443
169.385
ppm
0
5
10
15
20
25
30
35
40
45
50
55
60
65
70
75
80
85
90
95
100
105
110
115
120
125
130
135
140
145
150
155
160
165
170
175
180
185
190
195
O
B(MIDA)
Br
4c
13C NMR


Br
O
B(MIDA)
4c
11B NMR
11.236
25
20
15
10
5
0
ppm


OTBDPS
O
B(MIDA)
4d
^{1}H NMR
ppm

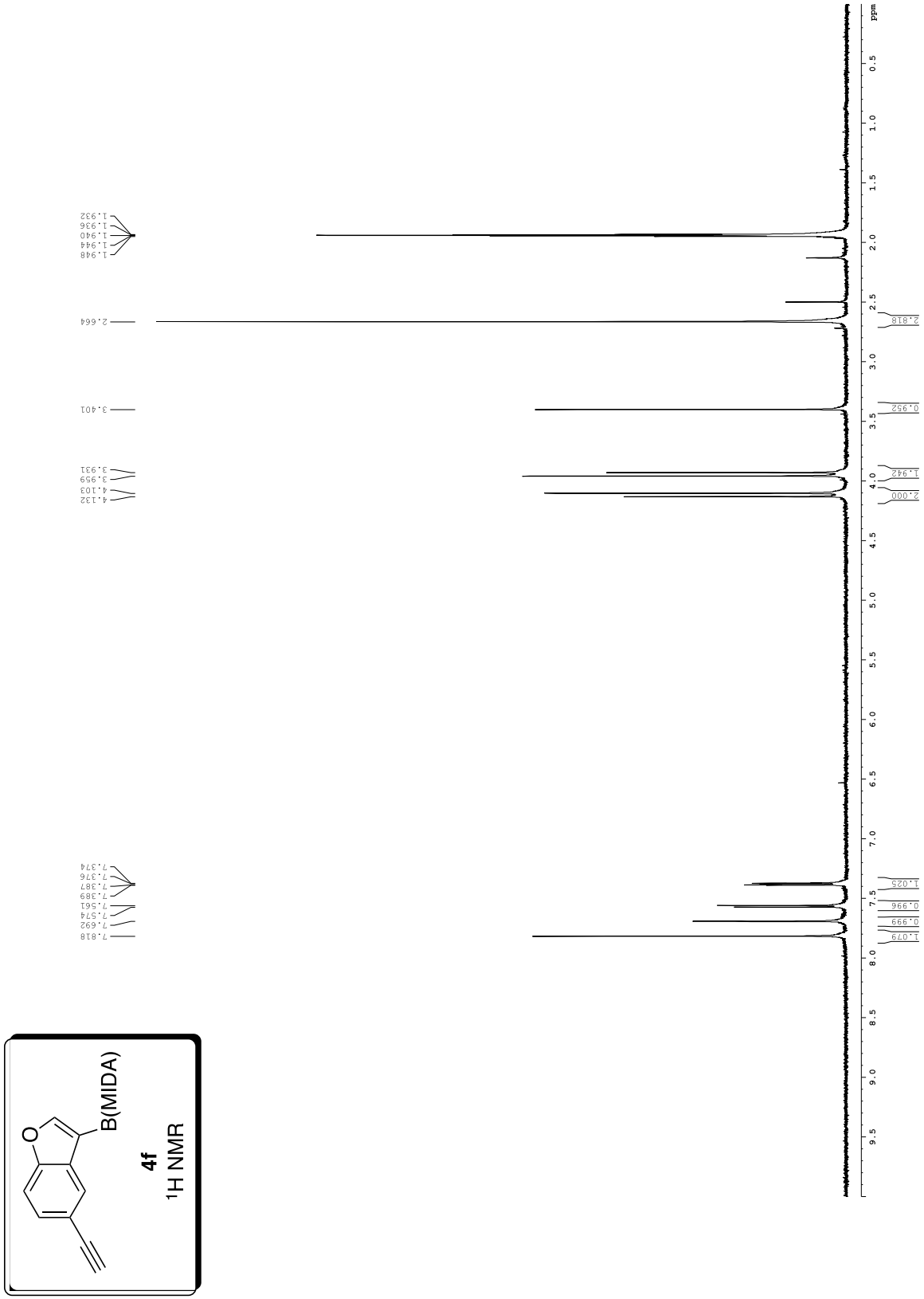

169.249
155.710
136.502
136.486
133.925
132.433
130.947
128.837
128.826
128.805
125.422
123.841
123.109
118.261
111.901
111.892
62.702
59.588
48.272
27.142
19.803
1.767
1.757
O
OTBDPS
B(MIDA)
4d
13C NMR
195 190 185 180 175 170 165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 ppm

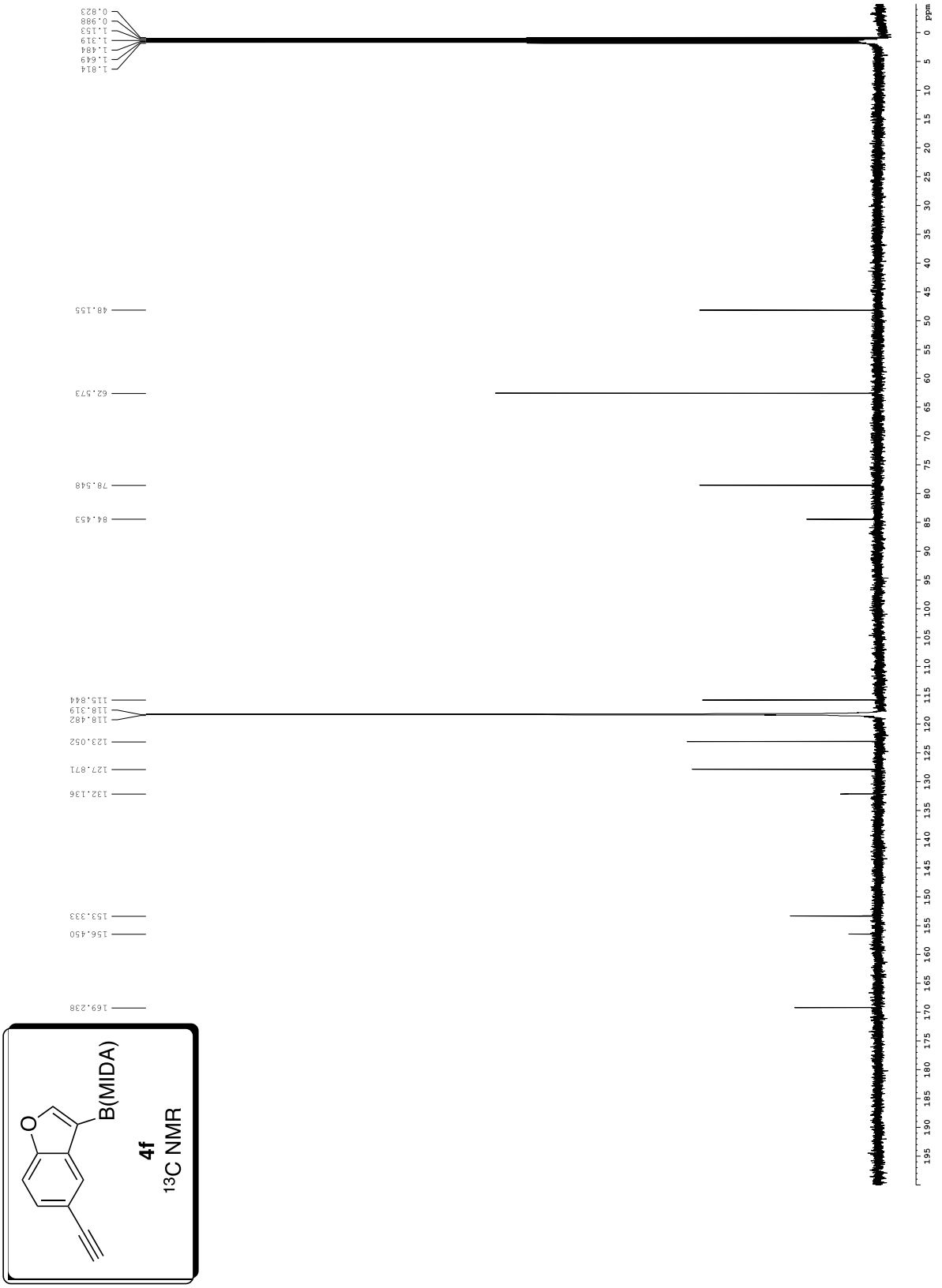

OTBDPS
O
B(MIDA)
4d
11B NMR
11.132
45
40
35
30
25
20
15
10
5
ppm

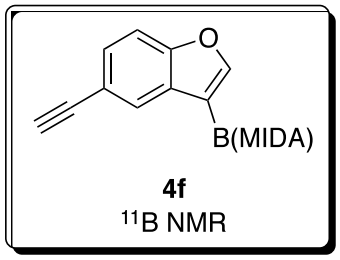

B(MIDA)
4e
1H NMR
O
ppm

0.80
0.97
0.98
1.13
1.15
1.30
1.31
1.46
1.48
1.63
1.64
1.79
48.12
48.13
62.53
112.17
112.19
118.31
122.85
122.87
123.87
123.89
125.16
125.17
131.02
151.68
156.97
169.32
ppm
20
40
60
80
100
120
140
160
180
ppm
O
B(MIDA)
4e
13C NMR

B(MIDA)
4e
11B NMR
11.156
ppm
5
10
15
20
25
30
35
40
45

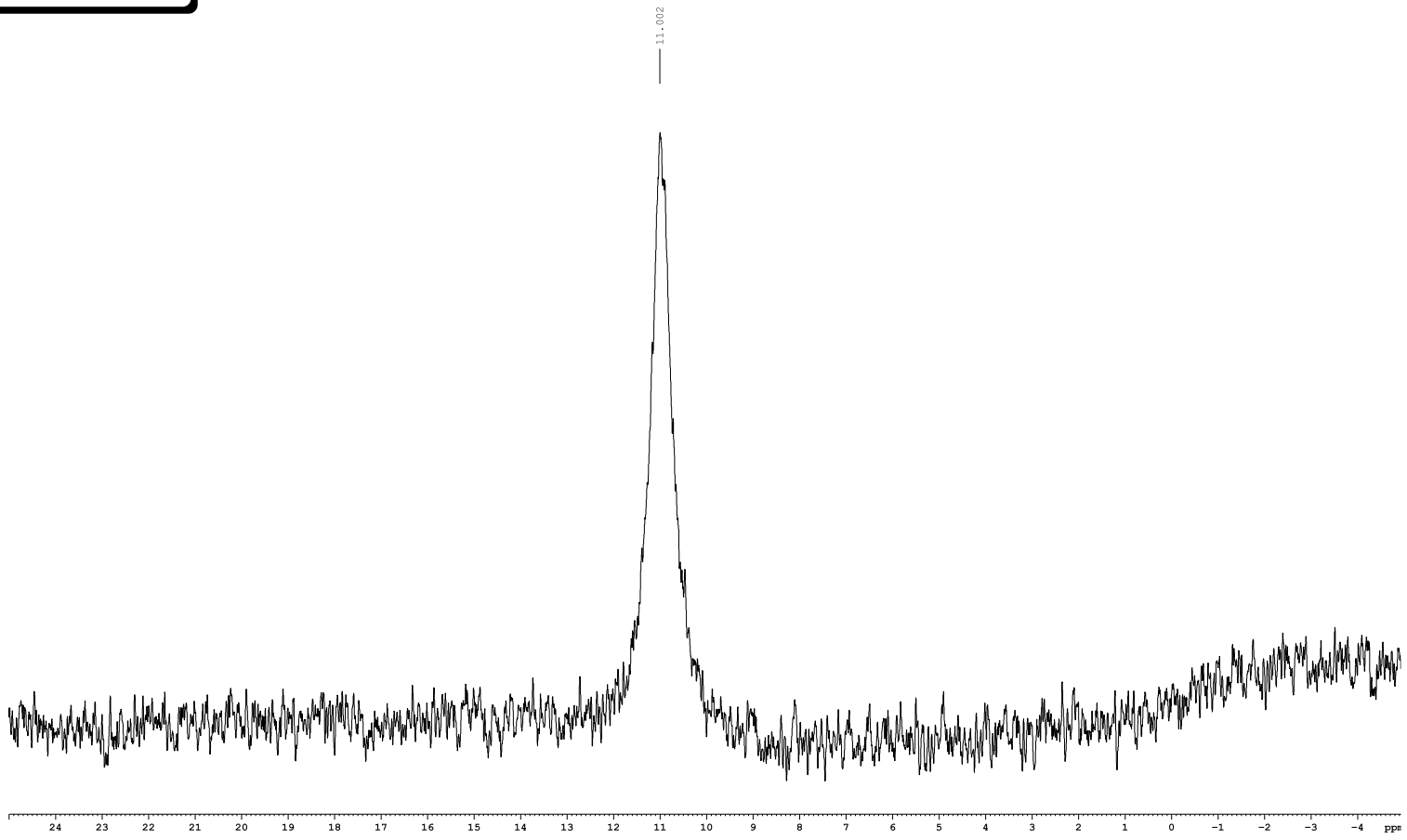

B(MIDA)
4f
1H NMR
7.818
7.692
7.574
7.561
7.389
7.387
7.376
7.374
4.132
4.103
3.959
3.931
3.401
2.664
1.948
1.944
1.940
1.936
1.932
1.079
0.999
0.996
1.025
2.000
1.942
0.952
2.818
ppm

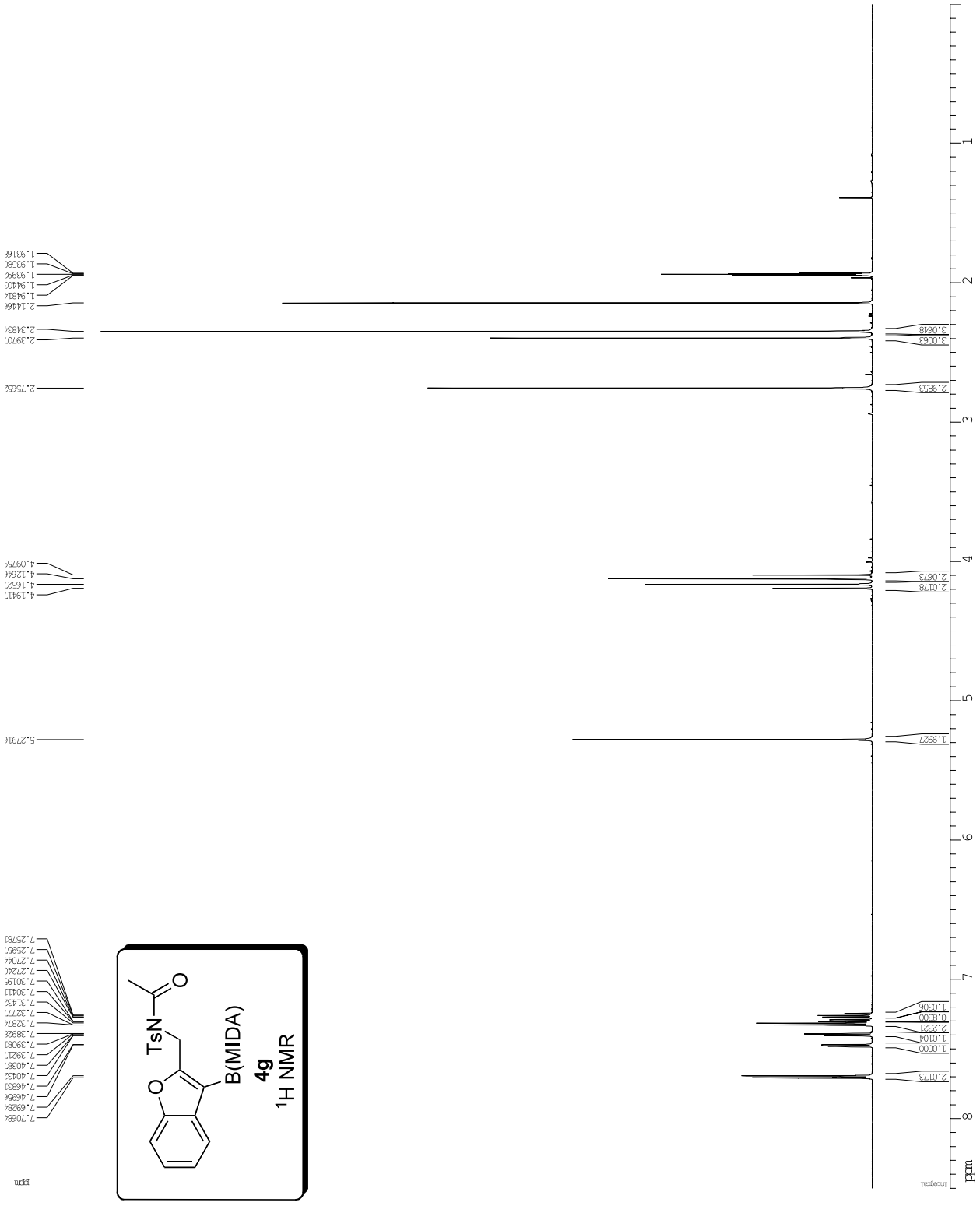

B(MIDA)
4f
13C NMR
169.238
156.450
153.333
132.136
127.871
123.052
118.482
118.319
115.844
84.453
78.548
62.573
48.155
1.814
1.649
1.484
1.319
1.153
0.988
0.823
ppm

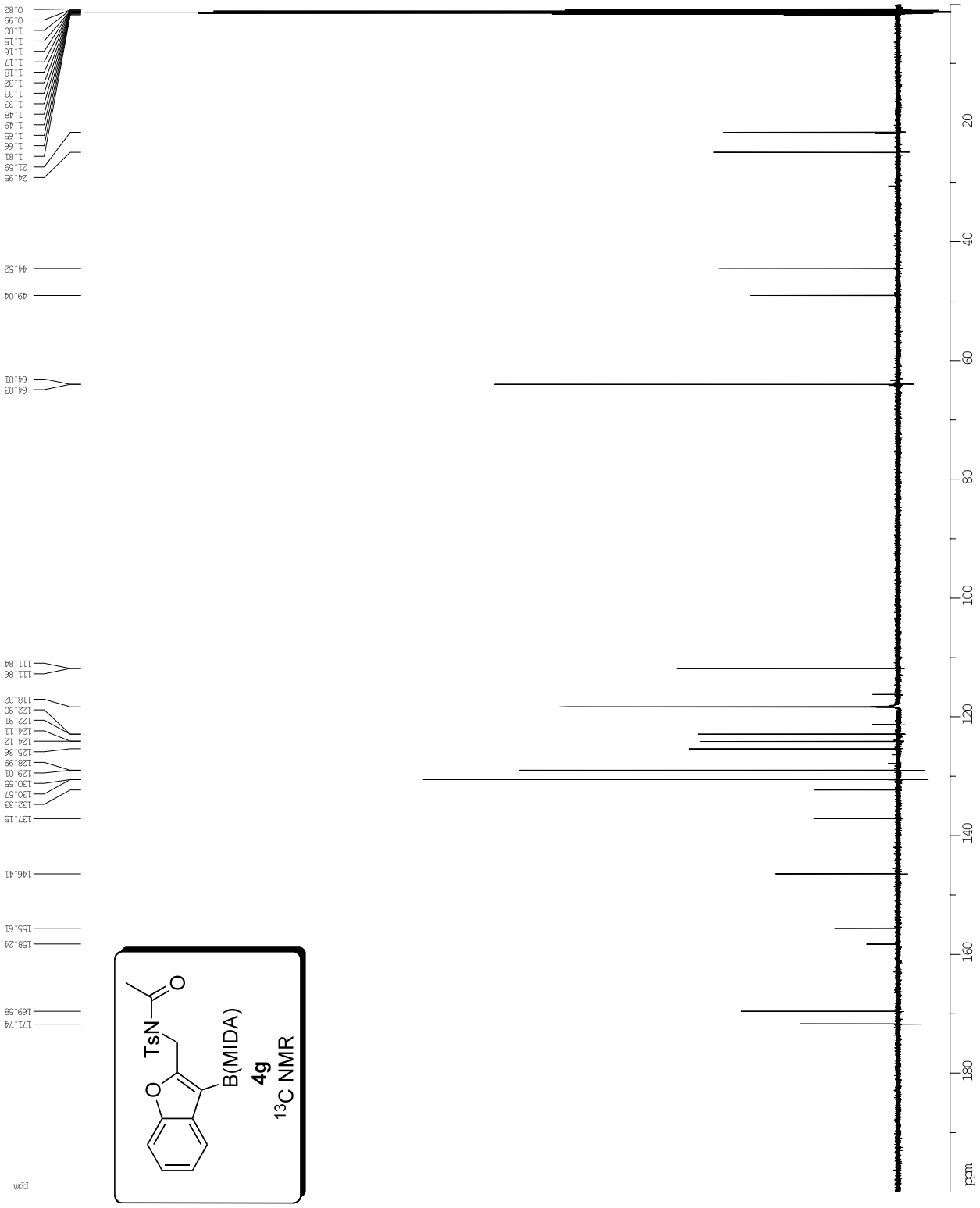

O
B(MIDA)

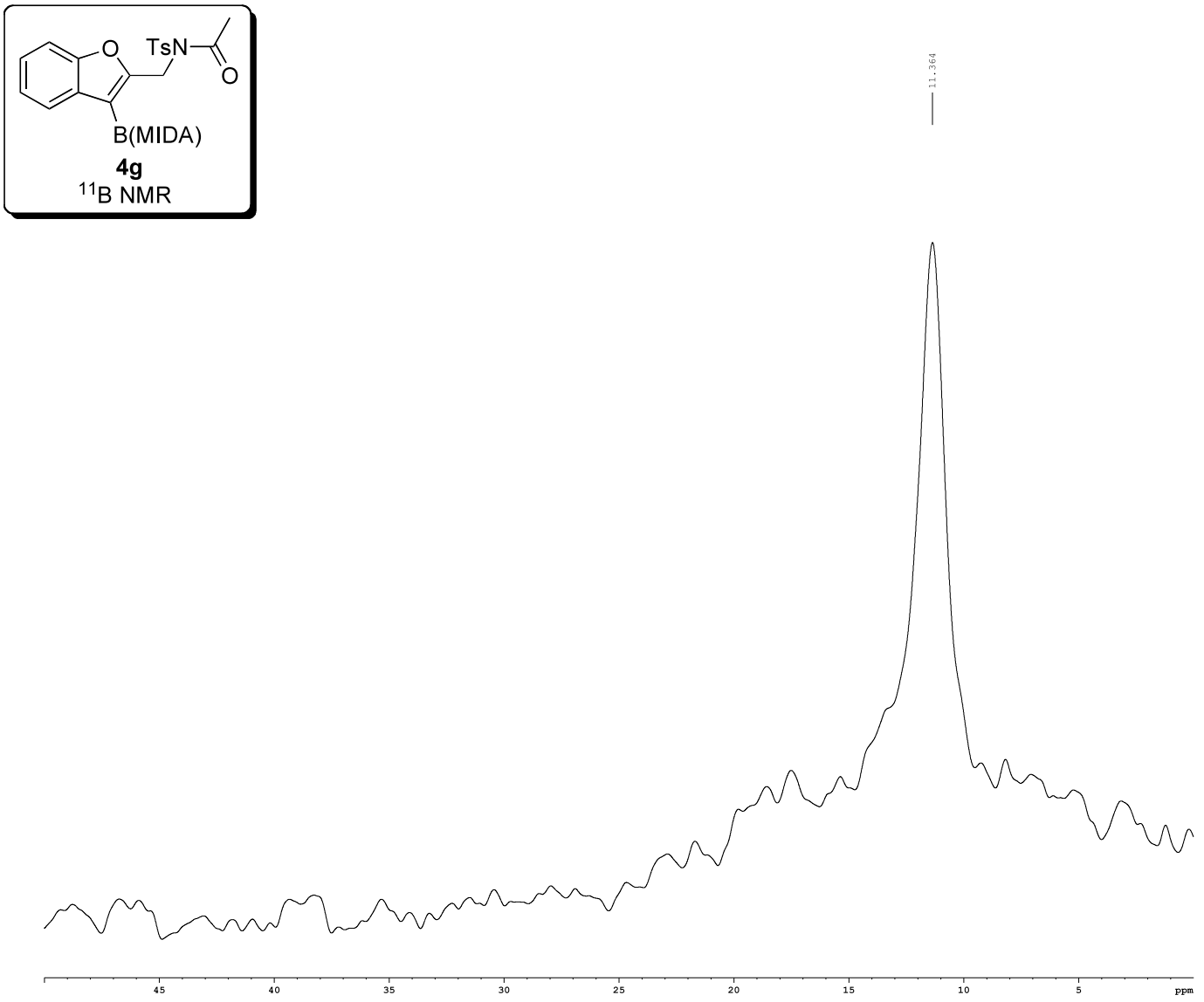
4f

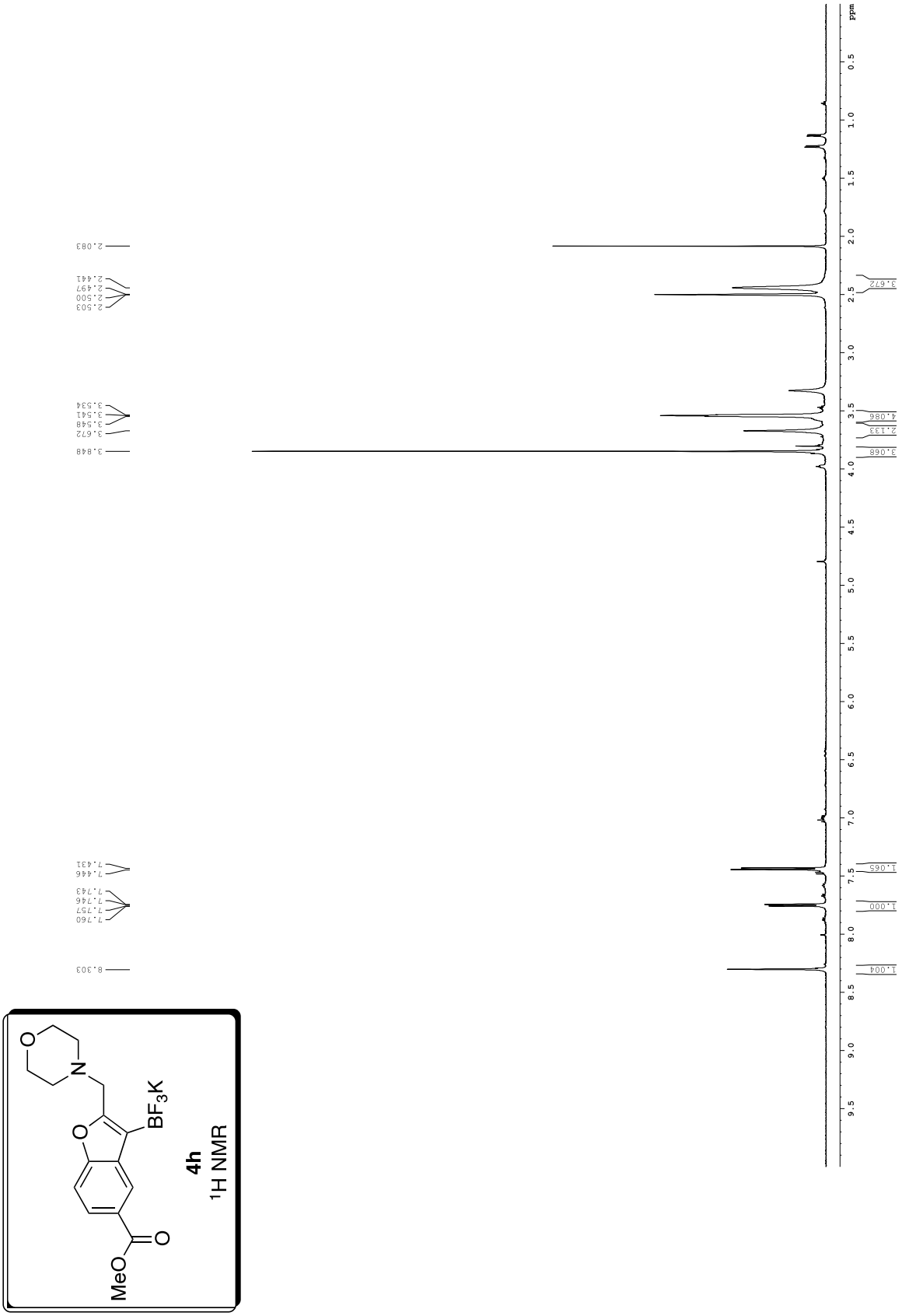
^{11}B NMR

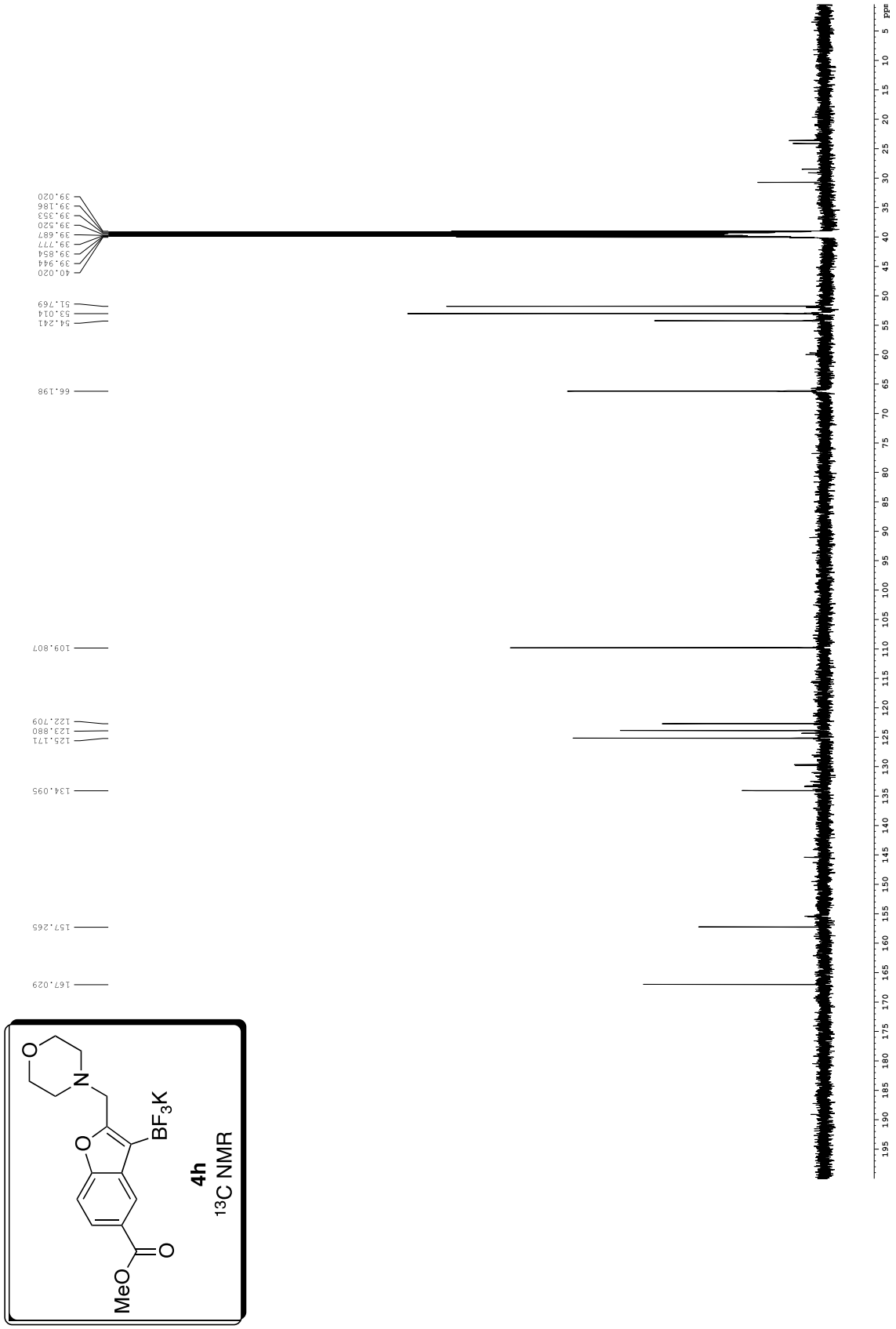

11.002
24 23 22 21 20 19 18 17 16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1 −2 −3 −4 ppm

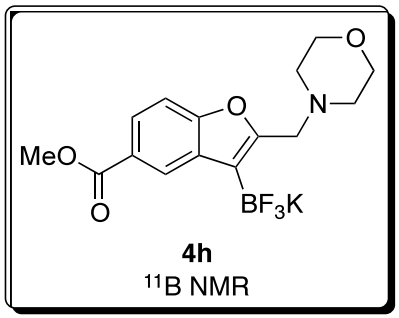

TsN
O
O
B(MIDA)
4g
^{1}H NMR
ppm


0.82
0.99
1.00
1.15
1.16
1.17
1.18
1.32
1.33
1.33
1.48
1.49
1.65
1.66
1.81
21.59
24.95
44.52
49.04
64.01
64.03
111.84
111.86
118.32
122.90
122.91
124.11
124.12
125.36
128.99
129.01
130.55
130.57
132.33
137.15
146.41
155.61
158.24
169.58
171.74
ppm
TsN
O
O
B(MIDA)
4g
13C NMR
20
40
60
80
100
120
140
160
180
ppm


O
TsN
O
B(MIDA)
4g
11B NMR
11.364
45
40
35
30
25
20
15
10
5
ppm


4h
^{1}H NMR
MeO
O
O
O
N
BF_3K
8.303
7.760
7.757
7.746
7.743
7.466
7.431
3.848
3.672
3.548
3.541
3.534
2.503
2.500
2.497
2.441
2.083
1.004
1.000
1.065
3.068
2.133
4.086
3.672
ppm

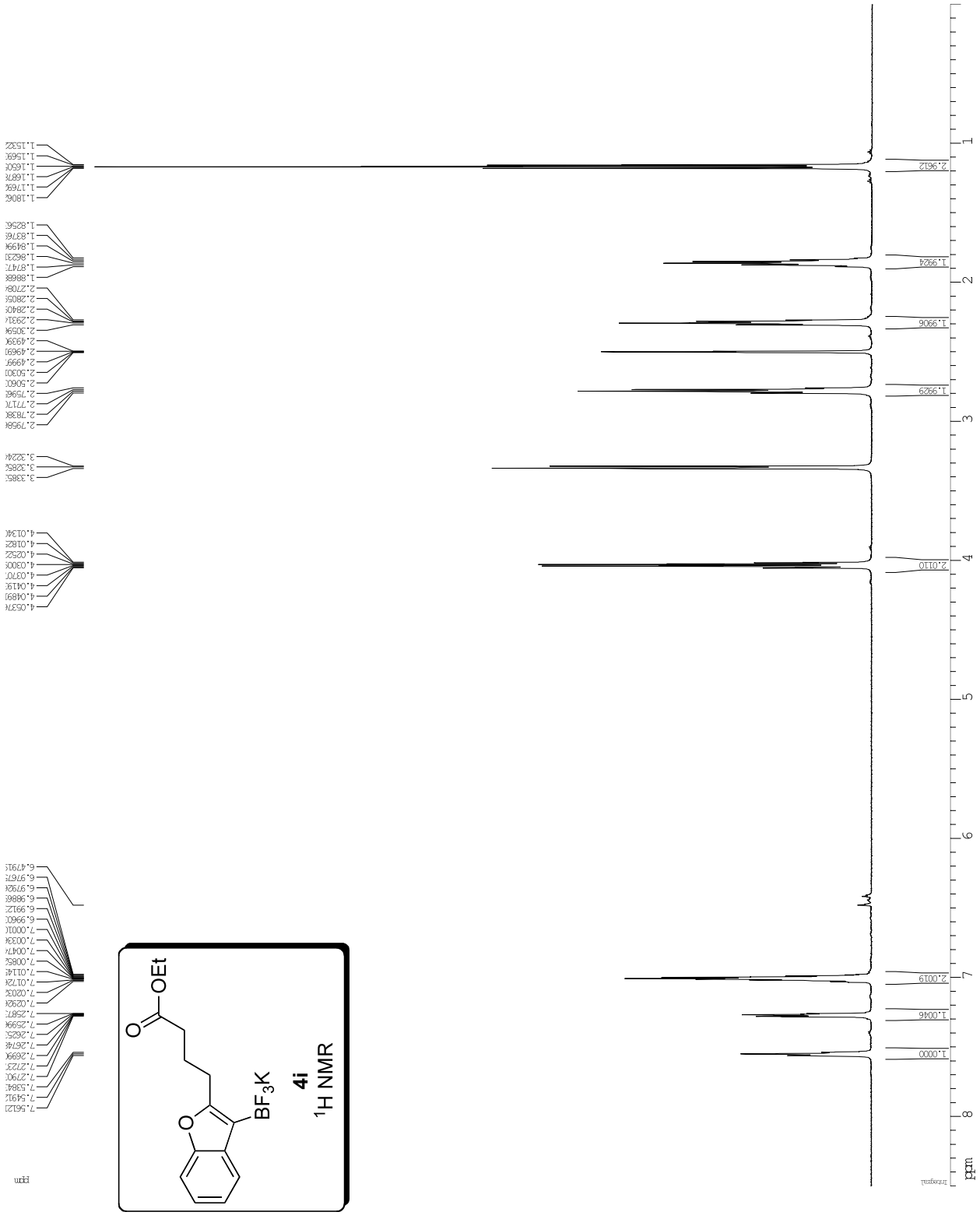

MeO
O
O
O
N
BF3K
4h
13C NMR
167.029
157.265
134.095
125.171
123.880
122.709
109.807
66.198
54.241
53.014
51.769
40.020
39.944
39.854
39.777
39.687
39.520
39.353
39.186
39.020
ppm

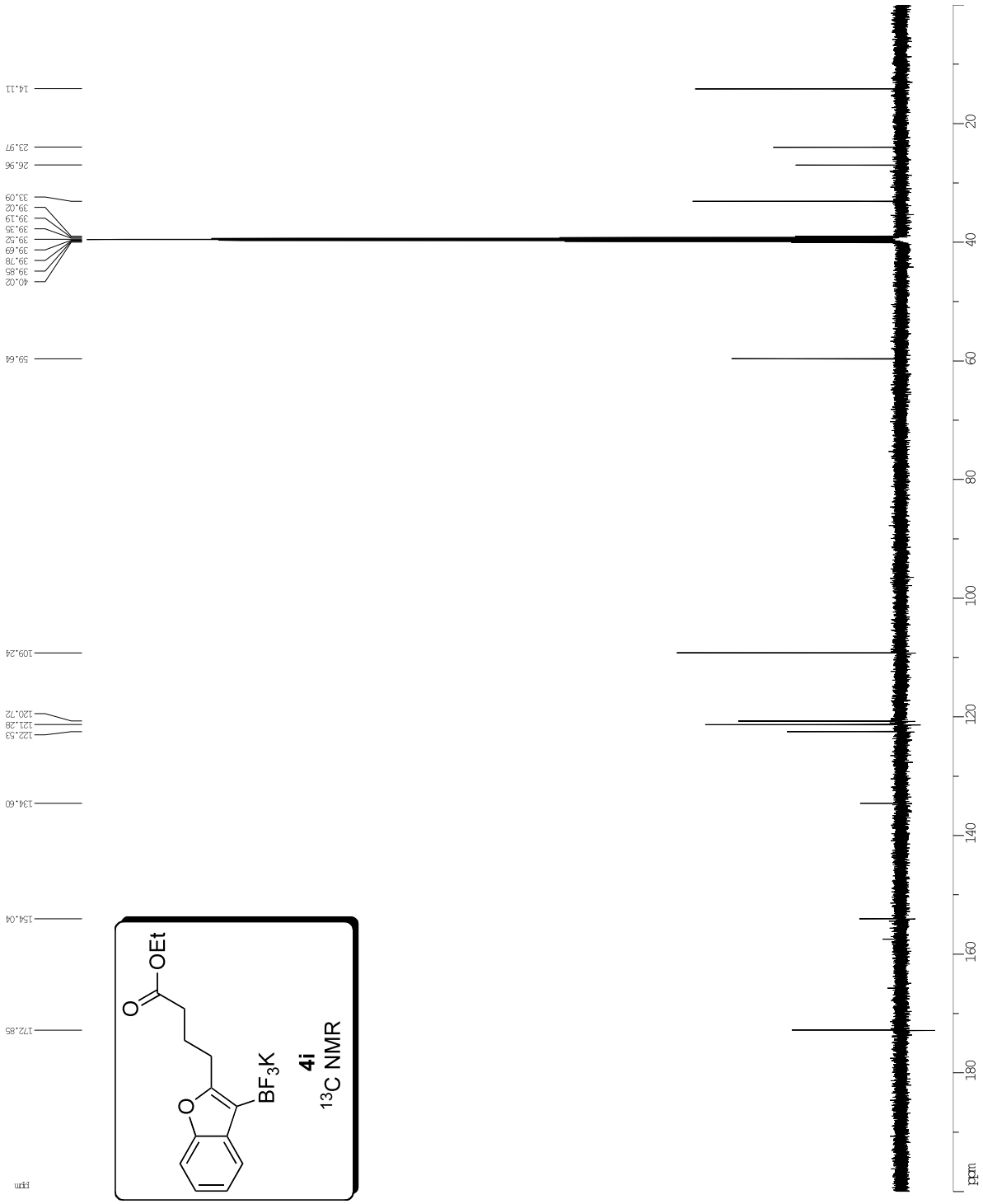


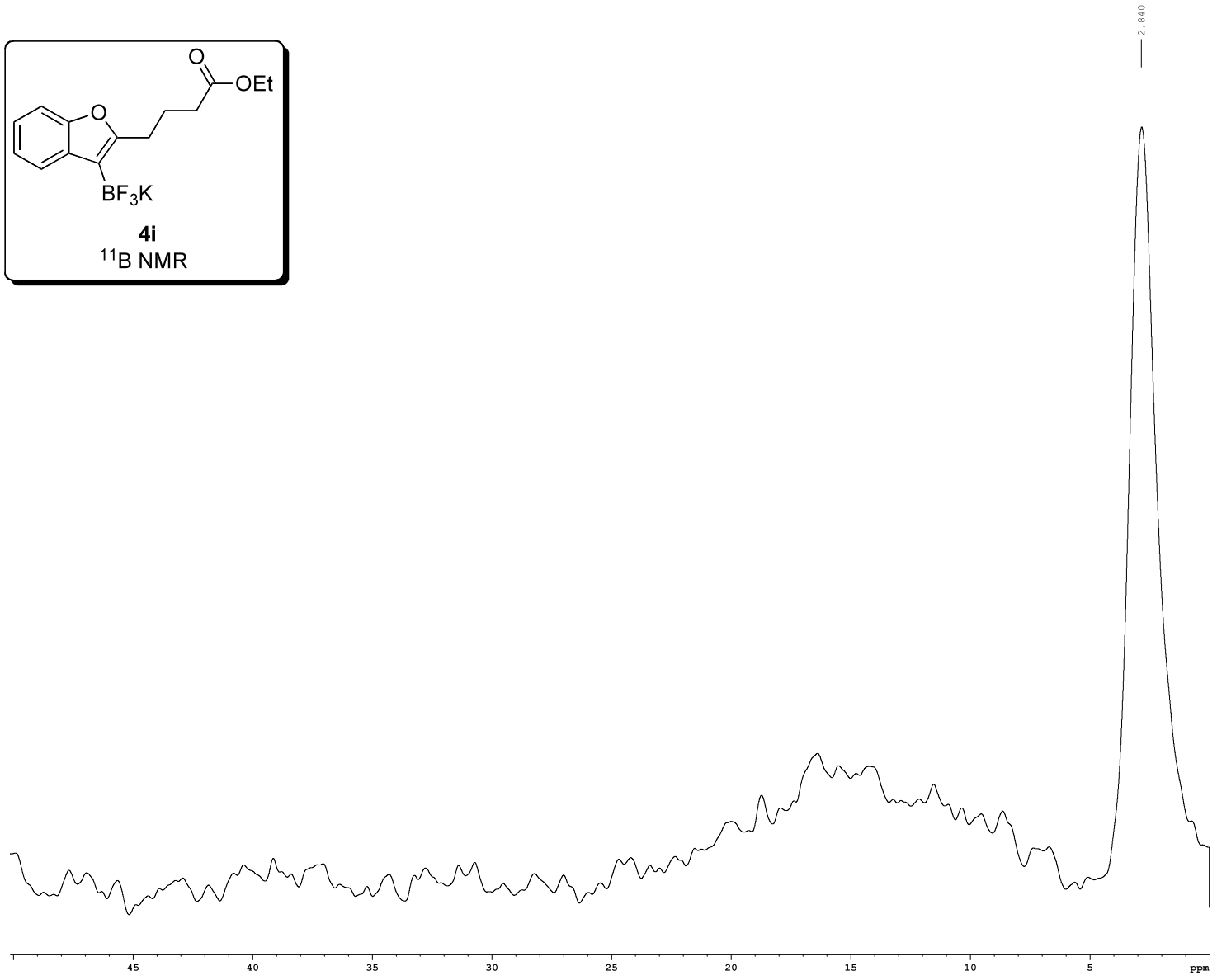
4h

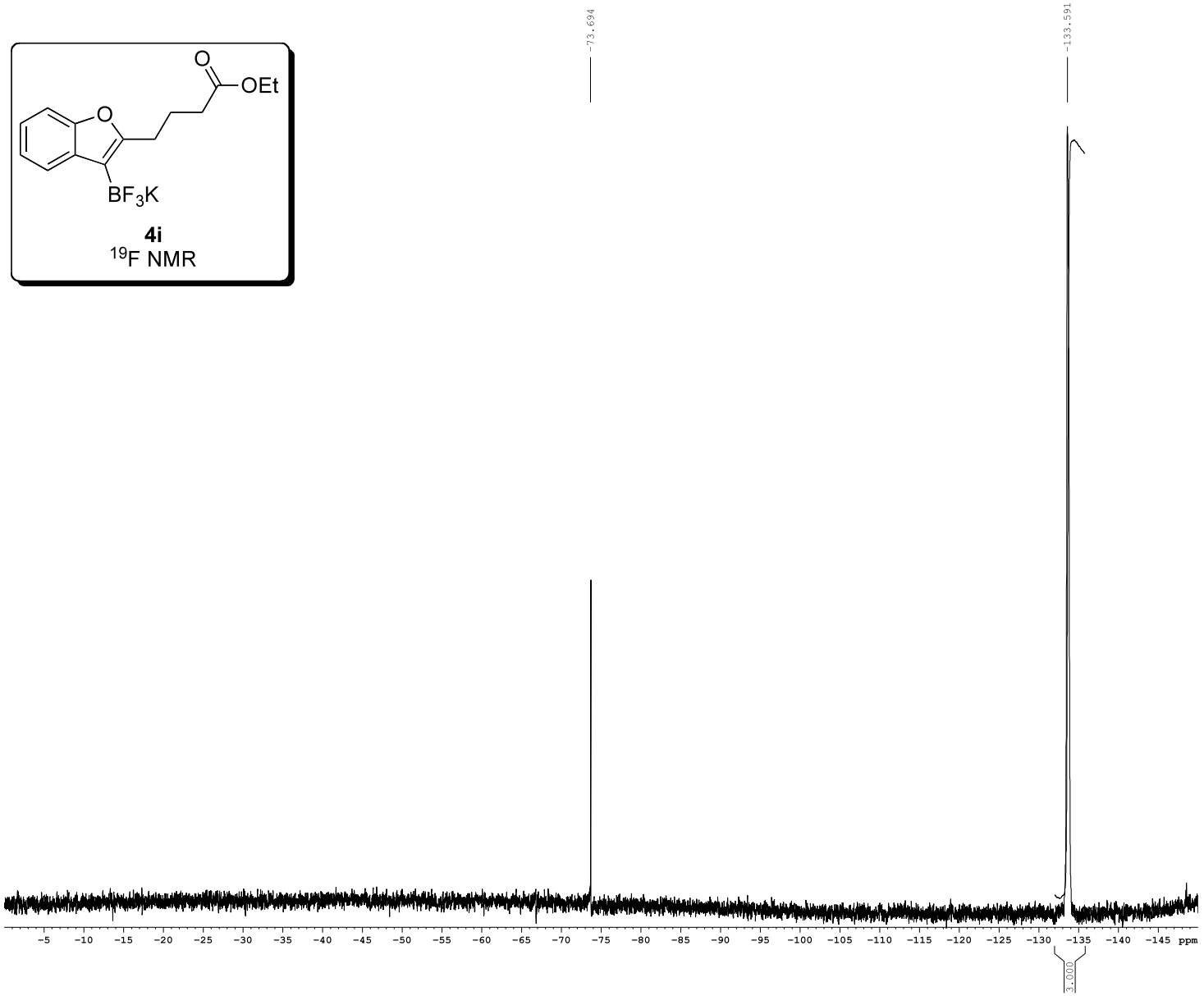
^{11}B NMR

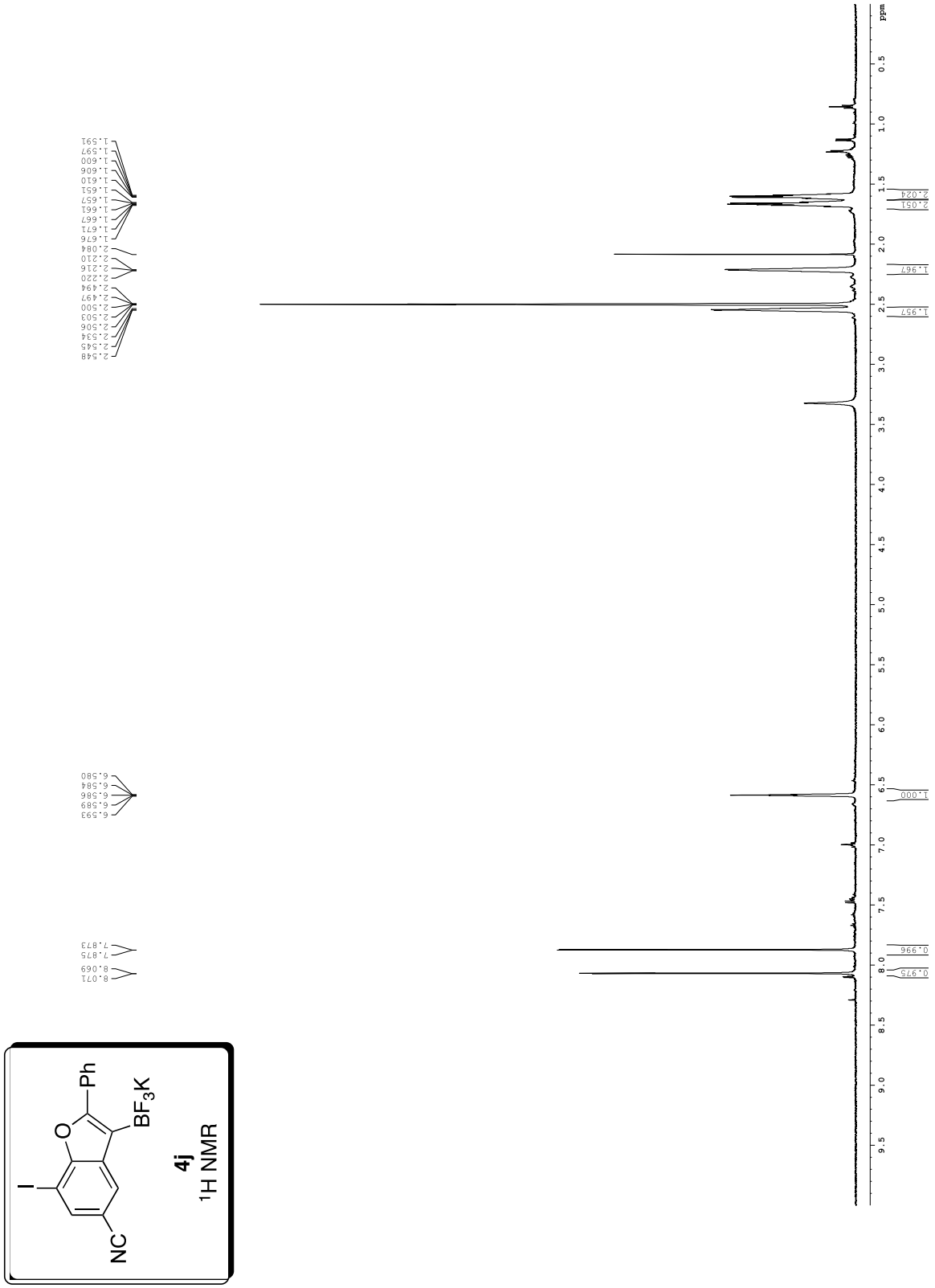
-133.117
-73.409
3.000
ppm
-10
-15
-20
-25
-30
-35
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125
-130
-135
O
N
O
BF3K
MeO
O
4h
19F NMR

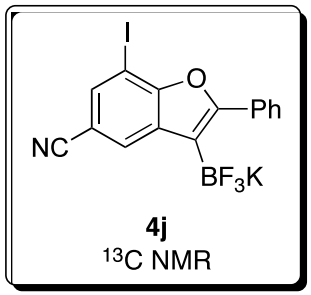

O
OEt
O
BF_3K
4i
^{1}H NMR
ppm


14.11
23.97
26.96
33.09
39.02
39.19
39.36
39.52
39.69
39.78
39.85
40.02
59.64
109.24
120.72
121.28
122.53
134.60
154.04
172.85
ppm
20
40
60
80
100
120
140
160
180
ppm
O
OEt
O
BF3K
4i
13C NMR

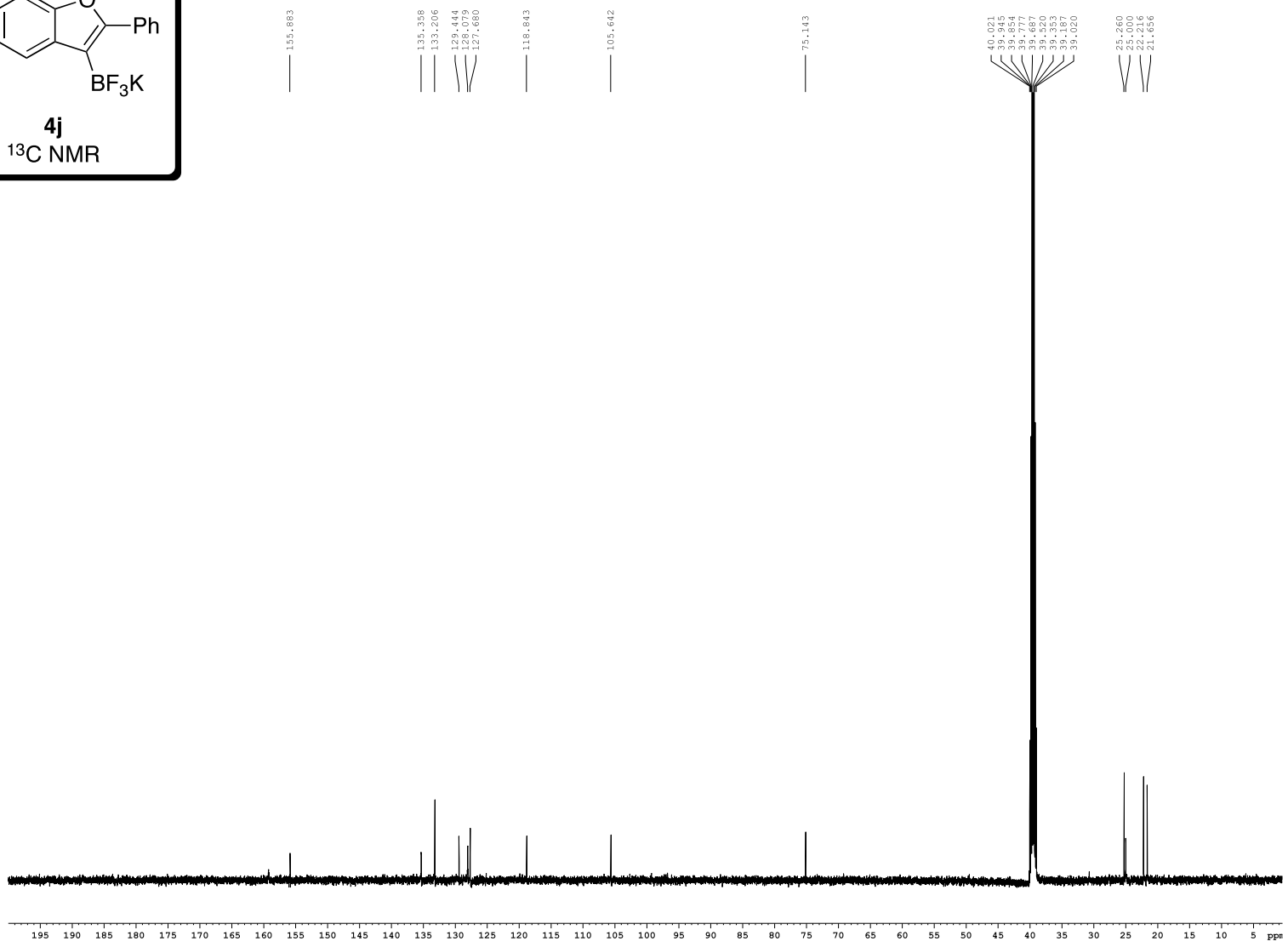

O
OEt
O
BF3K
4i
11B NMR
2.840
45
40
35
30
25
20
15
10
5
ppm

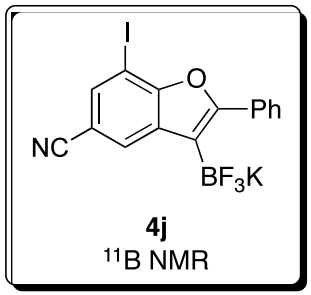

O
OEt
O
BF3K
4i
19F NMR
-73.694
-133.591
-5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 ppm
3.000


Ph
O
BF_3K
I
NC
4j
^{1}H NMR

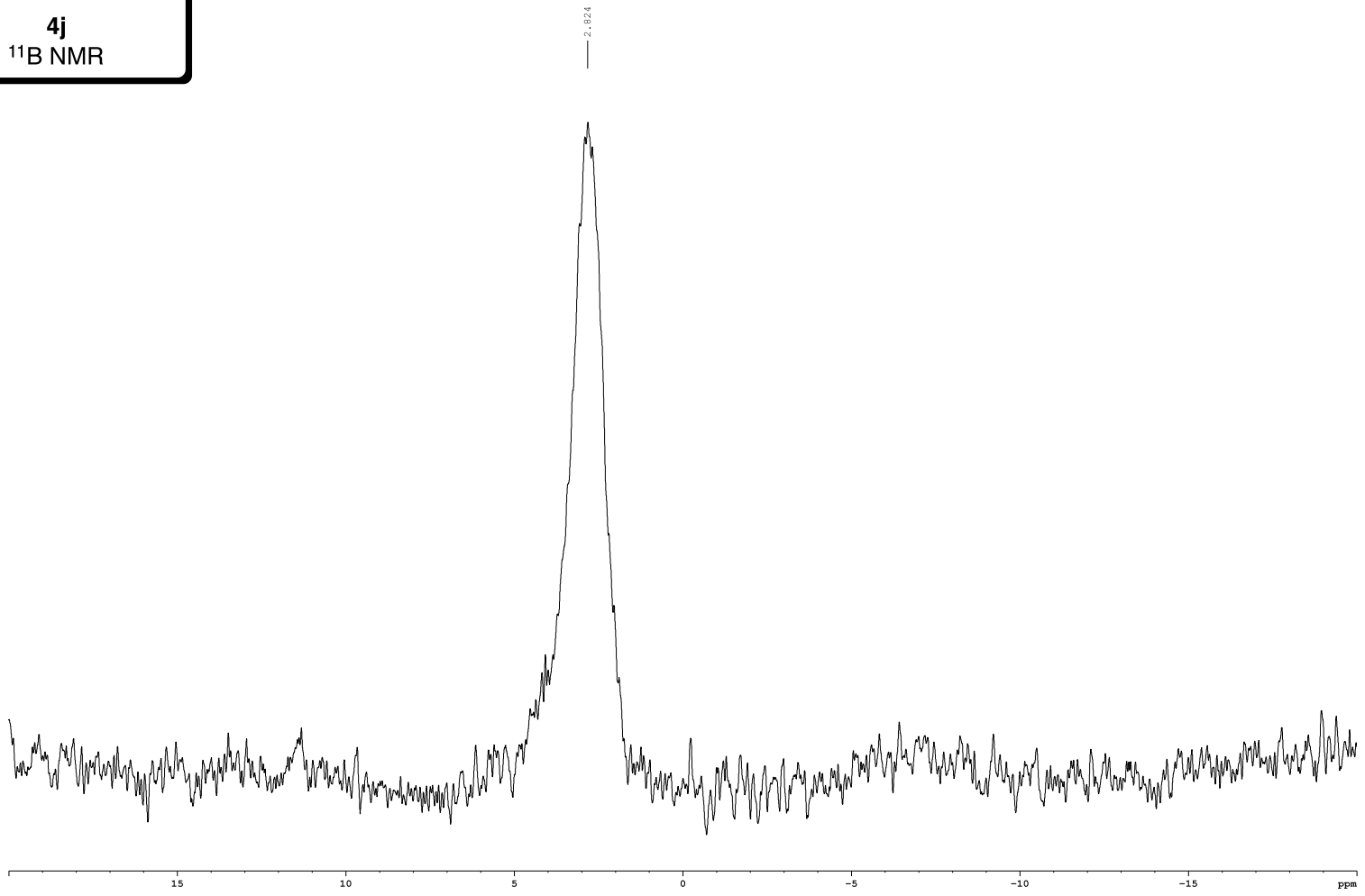

I
O
Ph
NC
BF_3K

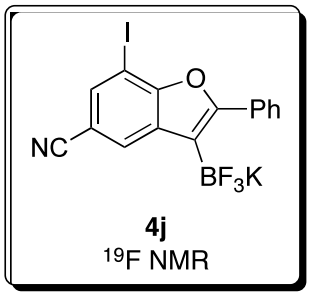
4j
^{13}C NMR


155.883
135.358
133.206
129.444
128.079
127.680
118.843
105.642
75.143
40.021
39.945
39.854
39.777
39.687
39.520
39.353
39.187
39.020
25.260
25.000
22.216
21.656
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

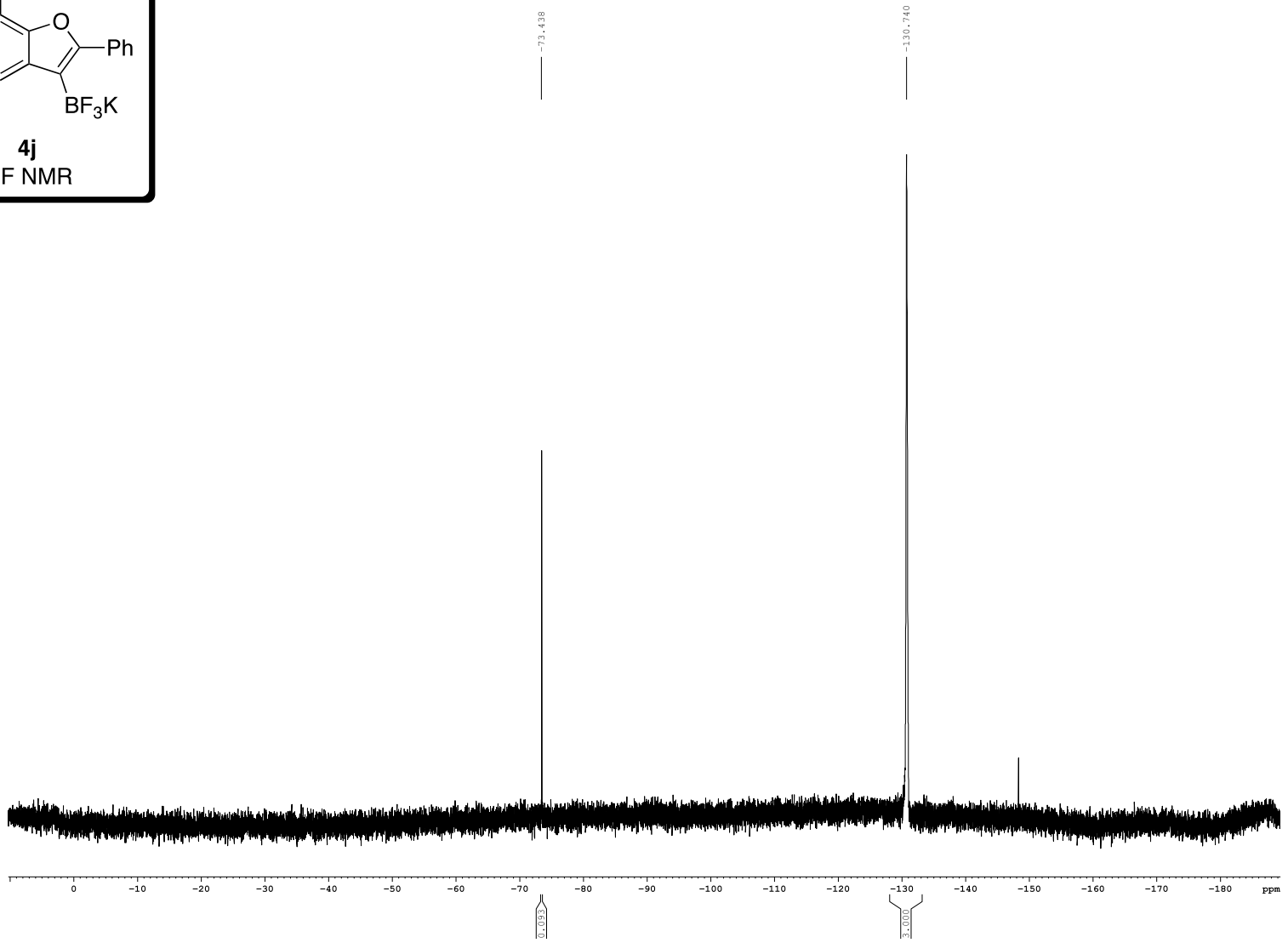


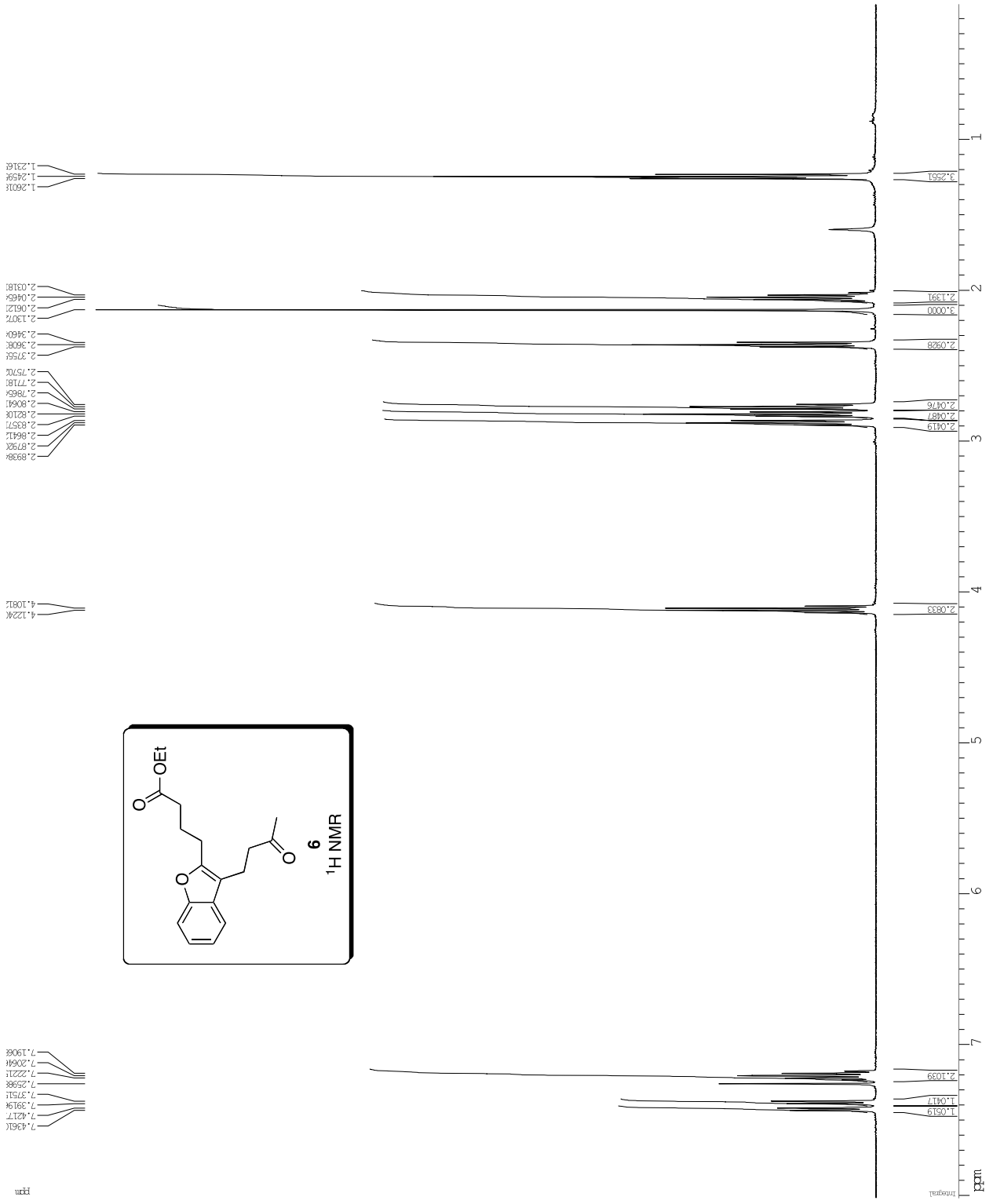
4j
^{11}B NMR

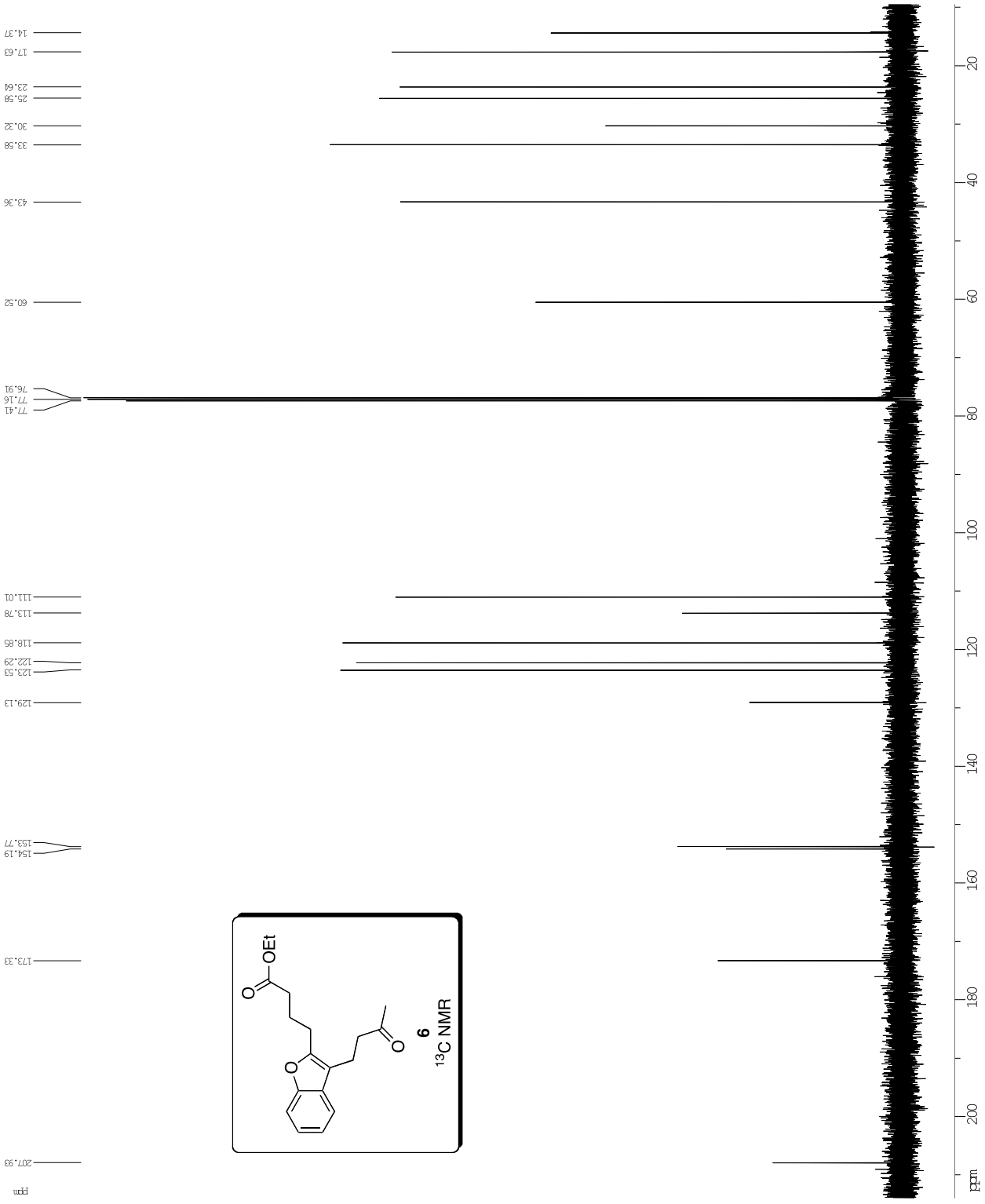


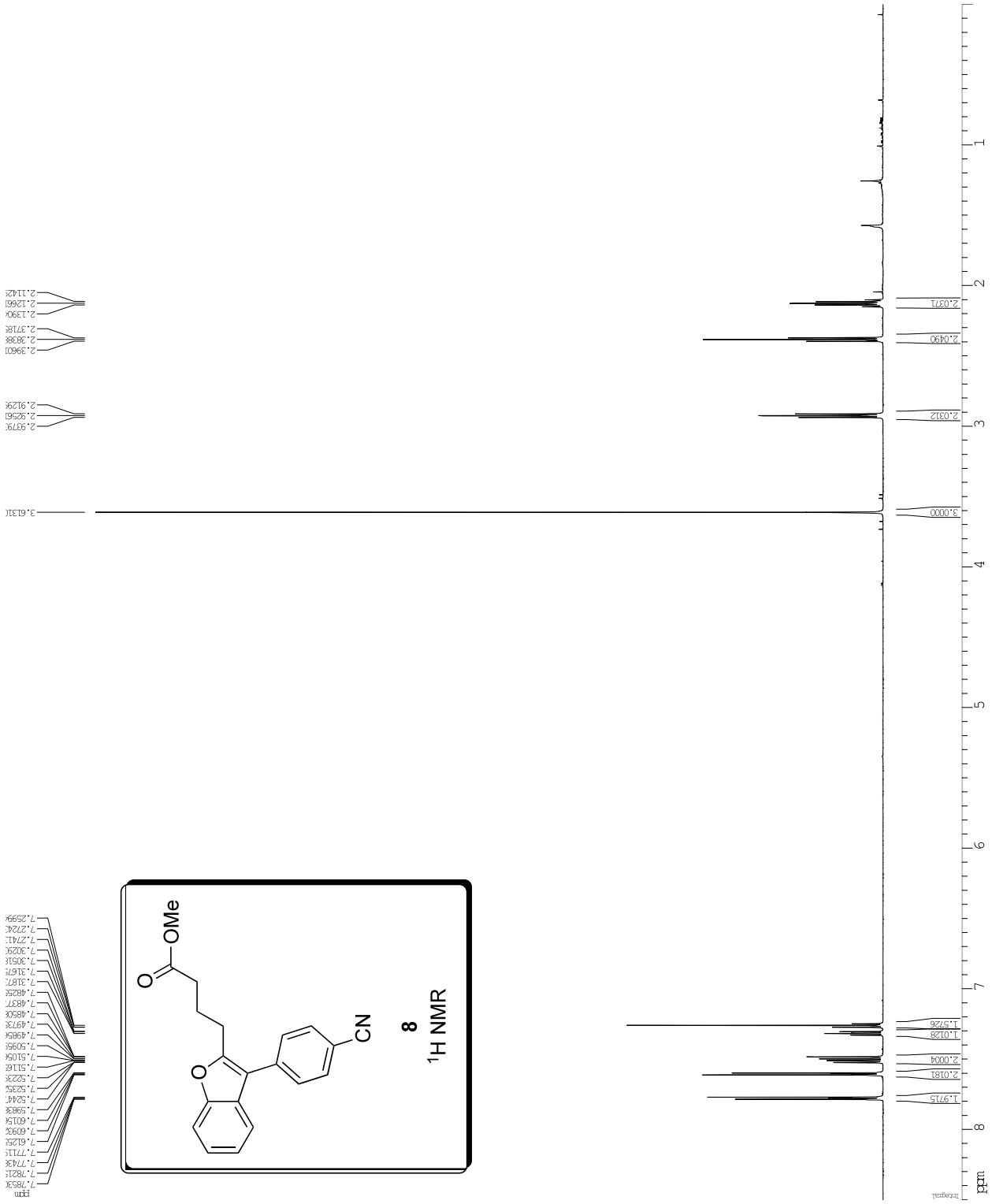

I
O
Ph
NC
BF_3K

4j
^{19}F NMR

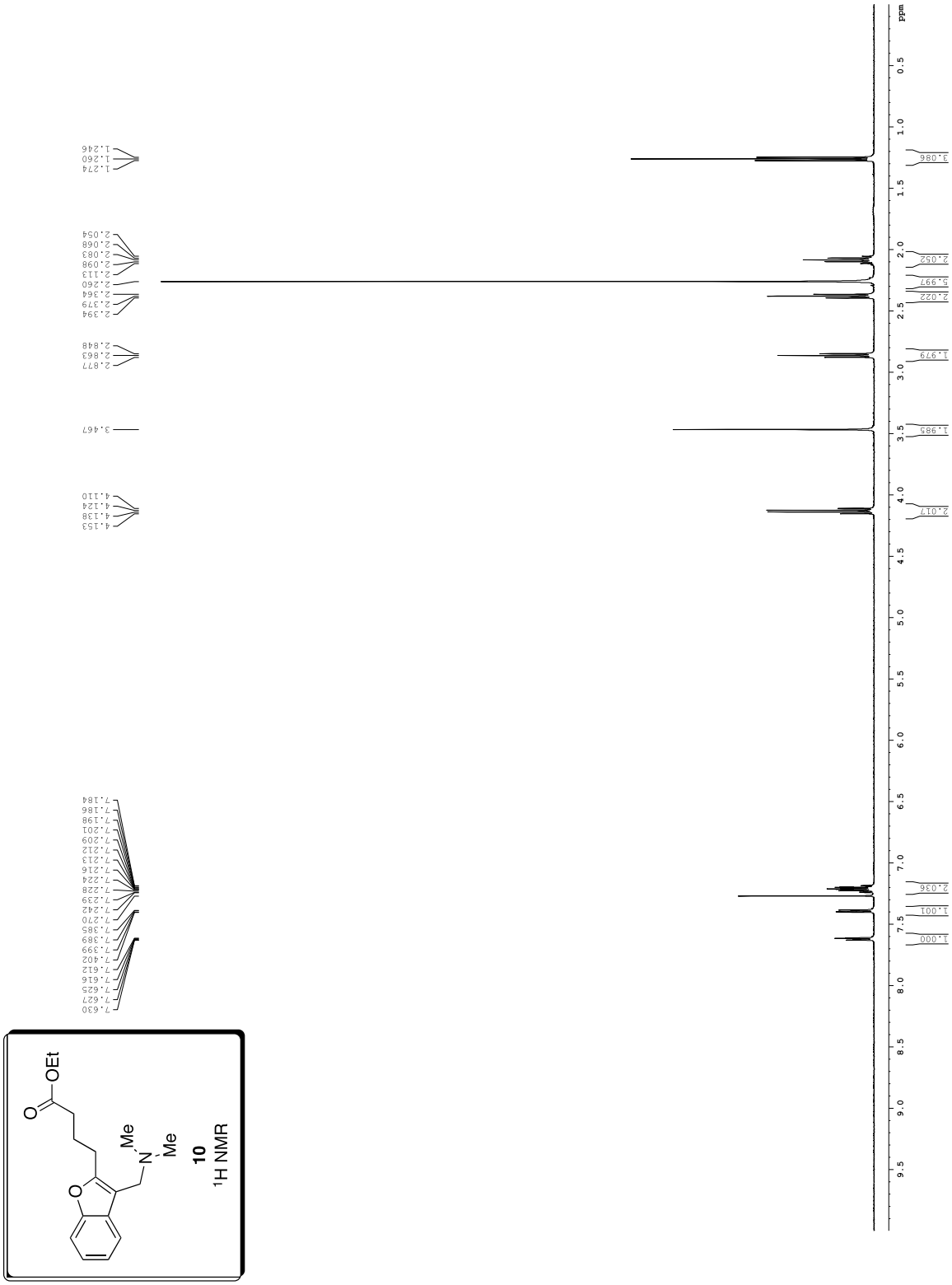

-73.438
-130.740
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
ppm
0.093
3.000

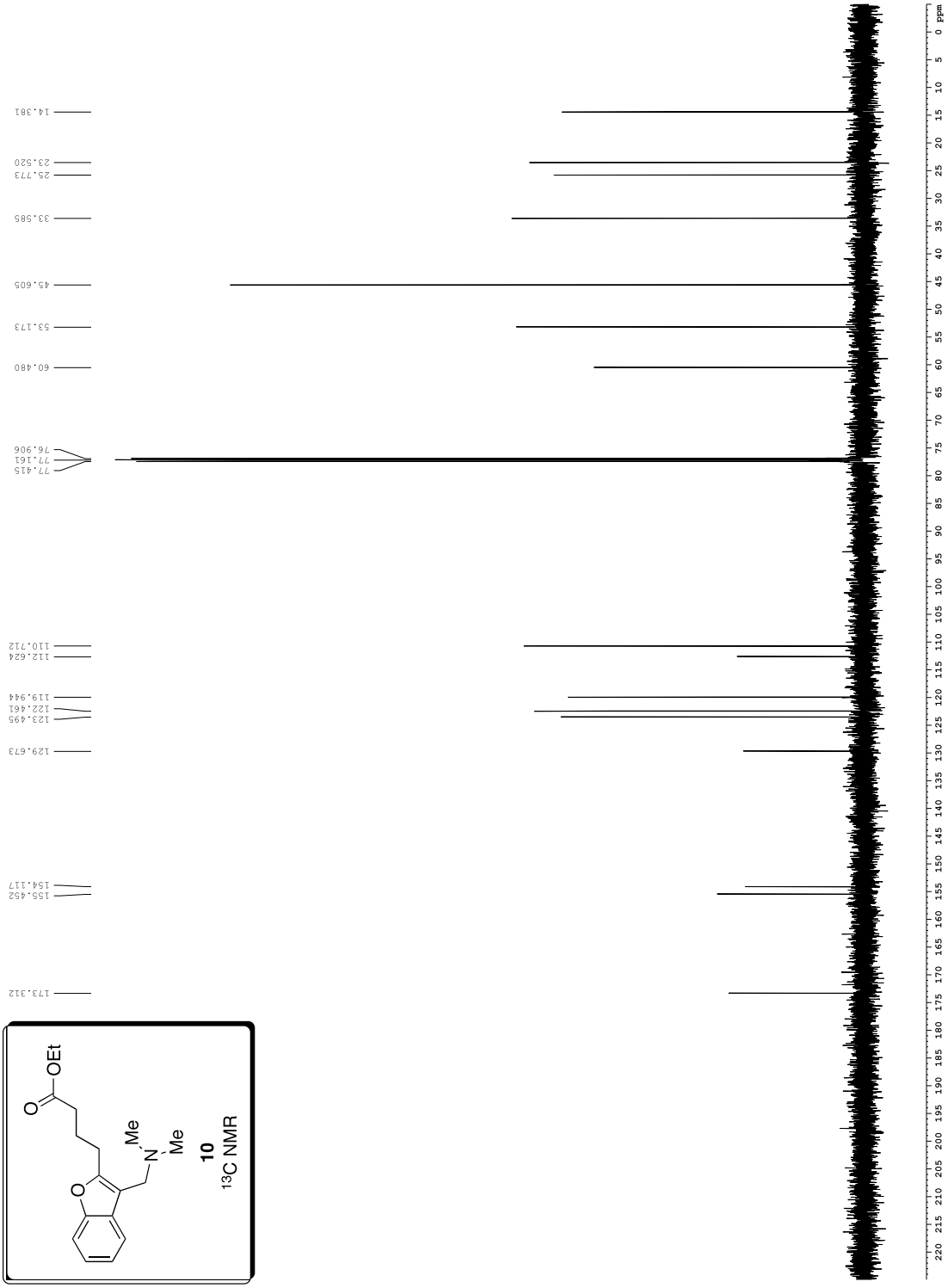

OEt
O
O
O
6
^{1}H NMR
ppm

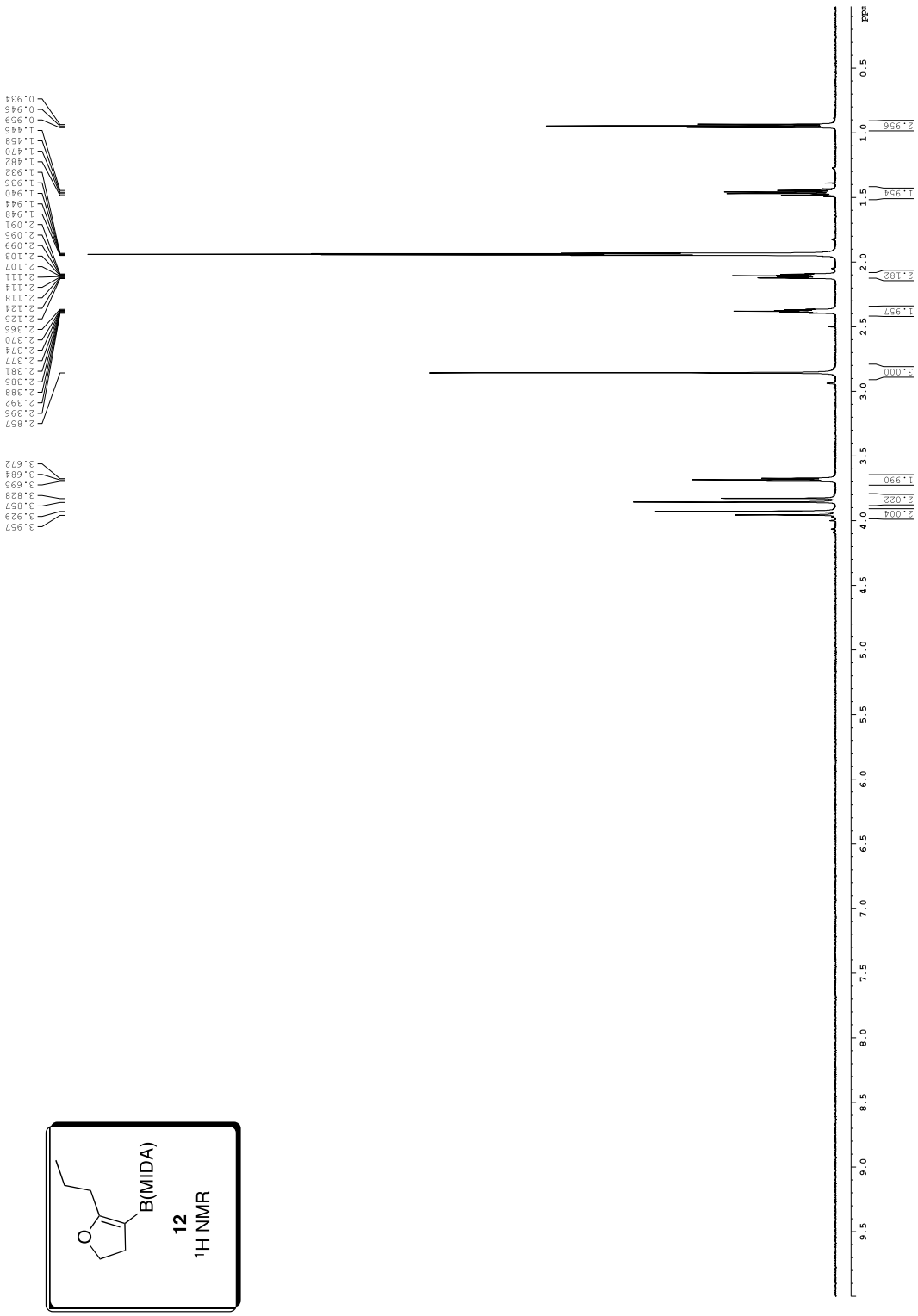

14.37
17.63
23.64
25.58
30.32
33.58
43.36
60.52
76.91
77.16
77.41
111.01
113.78
118.85
122.29
123.53
129.13
153.77
154.19
173.33
207.93
ppm
20
40
60
80
100
120
140
160
180
200
ppm
OEt
O
O
O
6
13C NMR

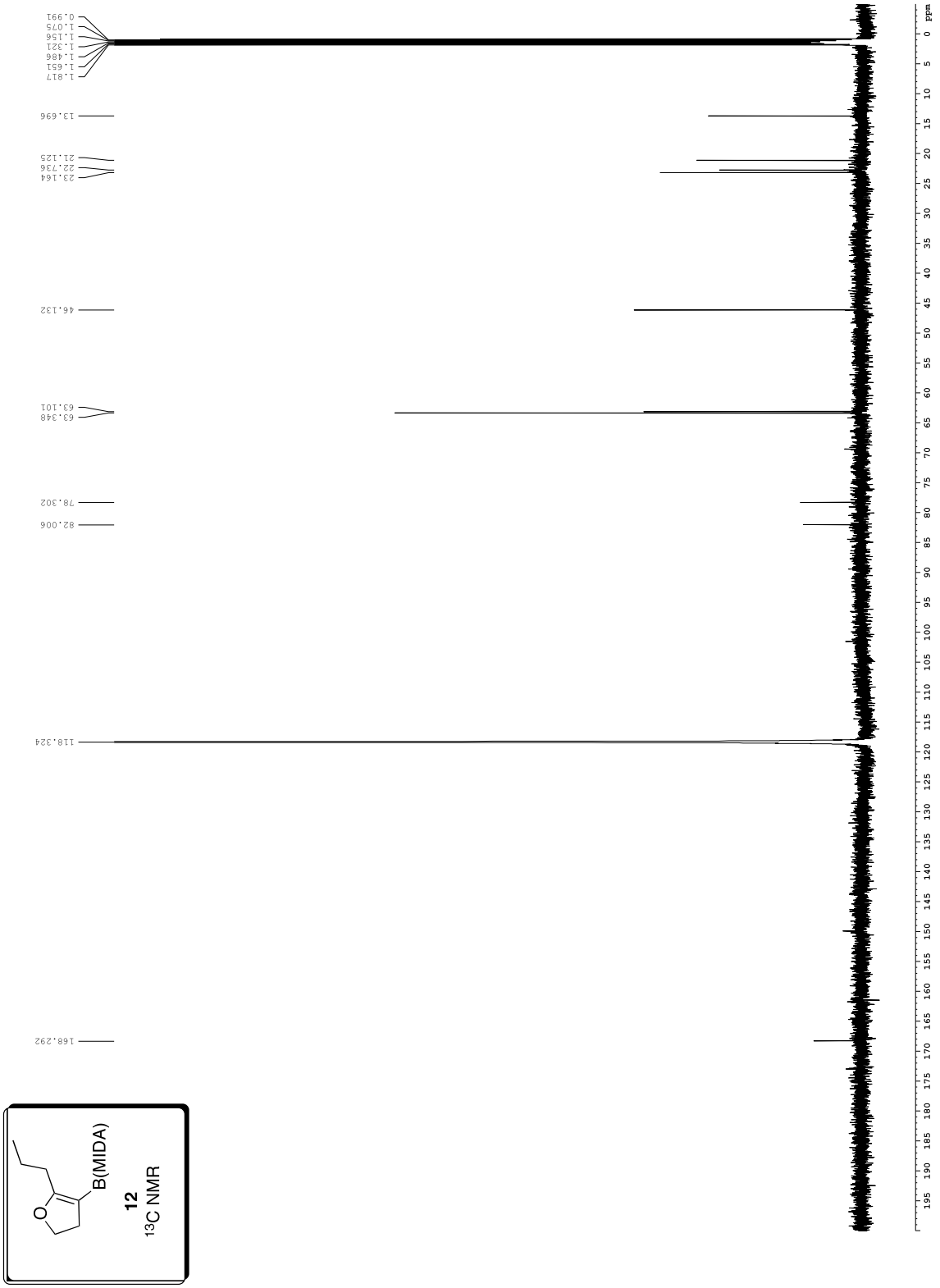

O
OMe
O
CN
8
1H NMR
ppm

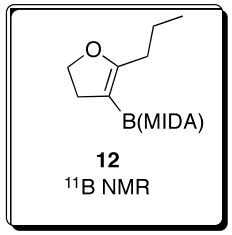
23.52
26.17
33.19
51.75
76.91
77.16
77.41
110.89
111.37
116.43
118.99
119.26
123.29
124.54
127.81
129.70
132.78
137.84
154.27
155.02
173.44
ppm
20
40
60
80
100
120
140
160
180
ppm
O
OMe
O
CN
8
13C NMR


O
OEt
Me
N
Me
O
10
1H NMR


14.381
23.520
25.773
33.585
45.605
53.173
60.480
76.906
77.161
77.415
110.712
112.624
119.944
122.461
123.495
129.673
154.117
155.452
173.312
O
OEt
Me
N
Me
10
13C NMR


B(MIDA)
12
1H NMR


0.991
1.075
1.156
1.321
1.486
1.651
1.817
13.696
21.125
22.736
23.164
46.132
63.101
63.348
78.302
82.006
118.324
168.292
ppm
B(MIDA)
12
13C NMR



12

^{11}B NMR