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

N-B dative bond-induced [3.3.0] bicyclic boronate-tethered *exo*-selective intramolecular Diels-Alder reaction

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Supporting Information

1. General considerations

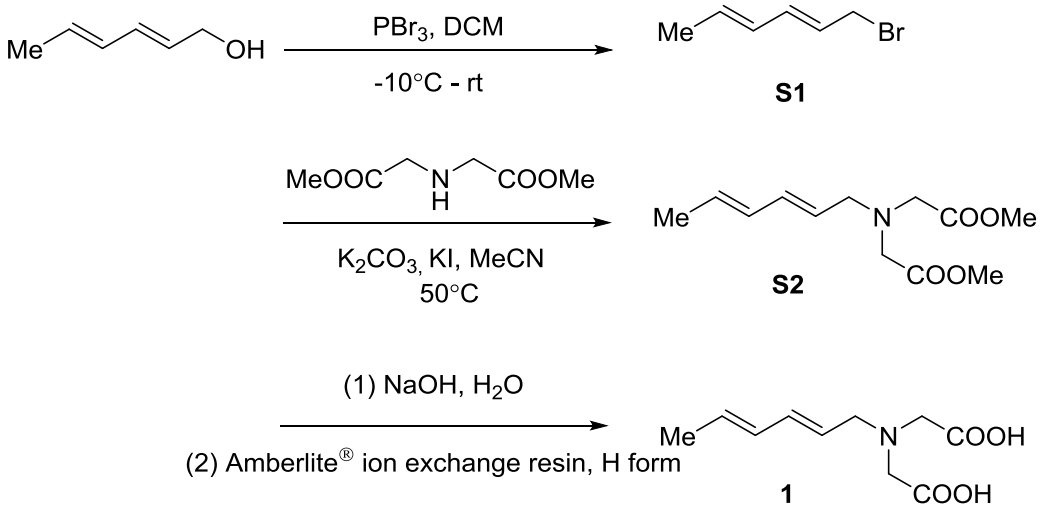
General. Unless otherwise noted, all reactions were carried out in a flame-dried flask under an atmosphere of nitrogen. Analytical thin-layer chromatography (TLC) was performed on glass plates coated with 0.25 mm 230–400 mesh silica gel containing a fluorescent indicator. Visualization was accomplished by exposure to a UV lamp, and/or treatment with a solution of Phosphomolybdic Acid (PMA) followed by brief heating with a heating gun. Most of the products in this article are compatible with standard silica gel chromatography. Column chromatography was performed on silica gel (200–300 mesh) using standard methods.

Structural analysis. NMR spectra were measured on a Bruker Avance-400 spectrometer and chemical shifts (δ) are reported in parts per million (ppm). ^{1}H NMR spectra were recorded at 400 MHz in NMR solvents ($CDCl_3$, DMSO-d_6, D_2O, Acetone-d_6) and referenced internally to corresponding solvent resonance, and ^{13}C NMR spectra were recorded at 100 MHz and referenced to corresponding solvent resonance. Coupling constants are reported in Hz with multiplicities denoted as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet) and br (broad). Infrared spectra were collected on a Thermo Fisher Nicolet 6700 FT-IR spectrometer using ATR (Attenuated Total Reflectance) method. Absorption maxima (ν max) are reported in wavenumbers (cm^{-1}). High resolution mass spectra (HRMS) were acquired with an ESI, APCI or EI source. Optical rotation date were collected on an Anton Paar MCP 200 polarimeter using anhydrous DCM. Single crystal X-ray diffraction analysis of **4a** and **7io** were carried out by Mr. Yousong Ding on a Bruker apex duo equipment at Center for Applied Chemistry Research, Frontier Institute of Science and Technology, Xi'an Jiaotong University. Melting points were determined on a Hannon MP300 apparatus and are not corrected

Materials. Commercial reagents were purchased from J&K, Energy, Sigma-Aldrich, Alfa Aesar, Acros Organics, TCI and used as received unless otherwise stated. Hexane, THF, Et_2O, toluene were purified by distillation over sodium and stored under N_2.

2. Preparation of the diene components and alkenyl boronic acids

2.1 Preparation of 2,2'-(((2E,4E)-hexa-2,4-dien-1-yl)azanediyl)diacetic acid



(2E,4E)-1-bromohexa-2,4-diene (S1):[1] In a 500 mL three-necked round bottom flask containing a stir bar, sorbitol (2.94 g, 30.0 mmol, 1.0 eq.) was dissolved in anhydrous DCM (150 mL) and the solution was cooled to -10 ^{o}C, a solution of phosphorus tribromide (2.71 g, 10.0 mmol, 0.33 eq.) in anhydrous DCM (50 mL) was added dropwise at -10 ℃ via a drop funnel under an atmosphere of N_2. Then the mixture was slowly warmed to 25 ℃ and stirred for 3 h. A saturated solution of $NaHCO_3$ in H_2O was added and the resulting mixture was extracted using DCM (3 × 50 mL). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered and concentrated under reduced pressure carefully (water bath <30 ℃, vacuum >300mbar). The crude product **S1** can be directly used for the next step without further purification.

Dimethyl 2,2'-(((2E,4E)-hexa-2,4-dien-1-yl)azanediyl)diacetate (S2): In a 250 mL three-necked round bottom flask containing a stir bar, KI (4.98 g, 30.0 mmol, 1.1 eq.), K_2CO_3 (7.46 g, 54.0 mmol, 2.0 eq.) was added in anhydrous MeCN (90 mL) under an atmosphere of N_2, a solution of **S1** in anhydrous MeCN (5 mL) was added dropwise via a syringe. Then the mixture was stirred at room temperature for 1 h. To this mixture was added a solution of dimethyl 2,2'-azanediyldiacetate (4.35 g, 27.0 mmol, 1.0 eq.) in anhydrous MeCN (27 mL) via addition funnel and the resulting the mixture was warmed to 50 ℃ and stirred for another 5 h. The organic solvent was removed under reduced pressure and the residue was dissolved in water, and extracted with ethyl acetate (3 x 20 mL). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure to give **S2** as yellow oil (5.50 g, 85% over 2 steps). The product was used for next step without further purification.

^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 6.18-5.94 (m, 2H), 5.70-5.61 (m, 1H), 5.61-5.48 (m, 1H), 3.68 (s, 6H), 3.52 (s, 4H), 3.34 (d, *J* = 7.2 Hz, 2H), 1.72 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 171.5, 134.1, 130.7, 129.5, 126.8, 56.5, 54.0, 51.4, 17.9.

HRMS (APCI): Calculated for $C_{12}H_{20}NO_4$ $[M+H]^+$: 22.13492, Found: 242.1381.

IR (ν, cm^{-1}): 3019, 2953, 1738, 1681, 1436, 1198, 1166.

2,2'-(((2E,4E)-hexa-2,4-dien-1-yl)azanediyl)diacetic acid (1): In a 250 mL round bottom flask containing a stir bar, a solution of **S2** (3.62 g, 15.0 mmol, 1.0 eq.), NaOH (1.80 g, 45.0 mmol, 3.0 eq.) in deoxygenated water (100 mL) was stirred at room temperature overnight. The mixture was concentrated under reduced pressure to about 90 mL and was charged on an Amberlite® cation exchange resin[2] (H form) column (Q = 2.8mmol/g, 16.0 g). After complete elution with deionized water, **1** was obtained by lyophilization *in vacuo* as yellow solid (m.p.: < 50 °C, 2.88 g, 90%).

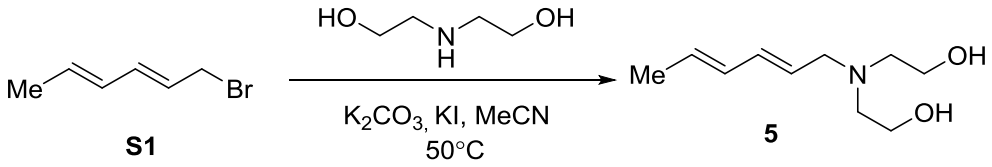
^{1}H NMR (400 MHz, D_2O): δ ppm 6.49-6.42 (m, 1H), 6.25-6.05 (m, 1H), 5.97-5.87 (m, 1H), 5.59-5.47 (m, 1H), 3.87-3.80 (m, 6H), 1.72 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, D_2O): δ ppm 170.6, 143.0, 136.4, 130.4, 116.9, 58.9, 56.0, 18.5.

HRMS (APCI): Calculated for $C_{10}H_{15}NO_4$ $[M-H]^-$: 212.0923, Found: 212.0929.

IR (*v*, cm^{-1}): 3006, 2956, 2921, 2850, 1732, 1455, 1298, 1122, 1076, 1039.

2.2 Preparation of 2,2'-(((2E,4E)-hexa-2,4-dien-1-yl)azanediyl)bis(ethan-1-ol)



2,2'-(((2E,4E)-hexa-2,4-dien-1-yl)azanediyl)bis(ethan-1-ol) (5): In a 250 mL three-necked round bottom flask containing a stir bar, KI (4.98 g, 30.0 mmol, 1.1 eq.), K_2CO_3 (7.46 g, 54.0 mmol, 2.0 eq.) was added in anhydrous MeCN (90 mL) under an atmosphere of N_2, a solution of **S1** in anhydrous MeCN (5 mL) was added dropwise via a syringe. Then the mixture was stirred at room temperature for 1 h. To this mixture was added a solution of 2,2'-azanediylbis(ethan-1-ol) (2.84 g, 27.0 mmol, 1.0 eq.) in anhydrous MeCN (27 mL) via addition funnel and the resulting the mixture was warmed to 50 ℃ and stirred for another 5 h. The organic solvent was removed under reduced pressure and the residue was dissolved in water, and extracted with ethyl acetate (3 x 20 mL). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure to give **5** as yellow oil (4.40 g, 88% over 2 steps). The product was used for next step without further purification.

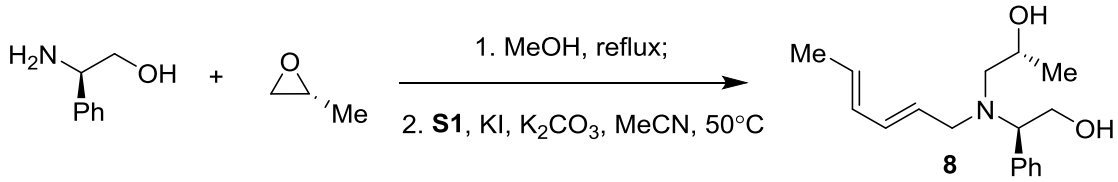
^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 6.17-5.97 (m, 2H), 5.73-5.60 (m, 1H), 5.60-5.48 (m, 1H), 3.61 (t, *J* = 5.2 Hz, 4H), 3.20 (d, *J* = 6.9 Hz, 2H), 2.65 (t, *J* = 5.3 Hz, 4H), 1.73 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 134.1, 131.0, 129.5, 126.7, 59.6, 56.6, 55.6, 18.2.

HRMS (APCI): Calculated for $C_{10}H_{20}NO_2$ $[M+H]^+$: 186.1494, Found: 186.1486.

IR (*v*, cm^{-1}): 3356, 3018, 2879, 1738, 1445, 1373, 1242, 1043.

2.3 Preparation of (R)-1-(((2E,4E)-hexa-2,4-dien-1-yl)((R)-2-hydroxy-1-phenylethyl)amino)propan-2-ol



(R)-1-(((2E,4E)-hexa-2,4-dien-1-yl)((R)-2-hydroxy-1-phenylethyl)amino)propan-2-ol (8): In a dried Schlenk flask (25 mL in volume) equipped with a stirring bar were placed with D-Phenylglycinol (0.69 g, 5.0 mmol, 1.0 eq.) and (S)-(-)-propylene oxide (0.29 g, 5.0 mmol, 1.0 eq.)[3], anhydrous methanol (5 mL) was added via syringe under a stream of N_2. The resulting mixture was allowed to stir at reflux overnight. After cooling to room temperature, solvent was

removed under reduced pressure and the residue was directly used without further purification to the next step.

In a 50 mL three-necked round bottom flask containing a stir bar, KI (0.91 g, 5.5 mmol, 1.1 eq.), K_2CO_3 (1.38 g, 10.0 mmol, 2.0 eq.) was added in anhydrous MeCN (15 mL) under an atmosphere of N_2, a solution of **S1** in anhydrous MeCN (1 mL) was added dropwise via a syringe. Then the mixture was stirred at room temperature for 1 h. To this mixture was added a solution of the above crude product in anhydrous MeCN (5 mL) via a syringe and the resulting the mixture was warmed to 50 ℃ and stirred for another 5 h. The organic solvent was removed under reduced pressure and the residue was dissolved in water, and extracted with ethyl acetate (3 x 5 mL). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated. The product **8** was purified by silica gel chromatography as a light yellow solid (m.p.: 101.9-103.5°C, 0.98 g, 71% over 2 steps).

^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.38-7.28 (m, 3H), 7.22-7.15 (m, 2H), 6.19-5.99 (m, 2H), 5.73-5.60 (m, 1H), 5.60-5.47 (m, 1H), 4.06-3.96 (m, 2H), 3.91-3.82 (m, 1H), 3.77-3.58 (m, 1H), 3.32 (dd, *J* = 14.3, 5.1 Hz, 1H), 2.97 (dd, *J* = 14.4, 8.4 Hz, 1H), 2.58 (dd, *J* = 13.3, 10.2 Hz, 1H), 2.20 (dd, *J* = 13.3, 2.4 Hz, 1H), 1.76 (d, *J* = 6.8 Hz, 3H), 1.13 (t, *J* = 4.7 Hz, 3H).

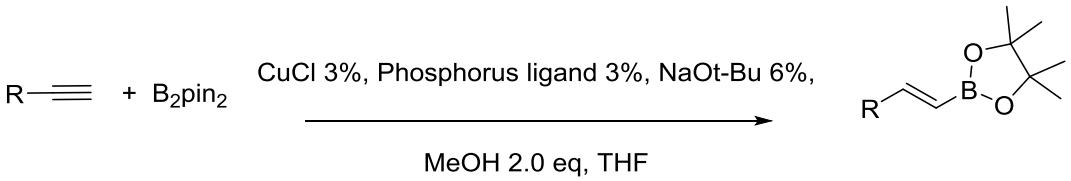
^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 136.9, 133.5, 131.1, 129.3, 128.9, 128.5, 127.9, 65.1, 64.2, 62.0, 56.8, 53.6, 20.5, 18.2.

HRMS (APCI): Calculated for $C_{17}H_{26}NO_2$ $[M+H]^+$: 276.1964, Found: 276.1949.

IR (*v*, cm^{-1}): 3331, 3019, 2972, 2894, 1451, 1379, 1261, 1094, 1075, 1027.

2.3 Preparation of Alkenyl boronates

A. General procedure A for synthesis of Alkenyl boronates:

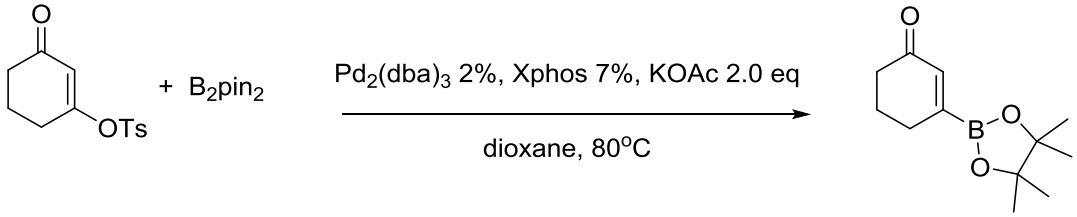


CuCl (30 mg, 0.3 mmol, 3 mol%), NaOt-Bu (60 mg, 0.3 mmol, 6 mol%) and DPEphos ligand (160 mg, 0.3 mmol, 3 mol%) were placed in an oven-dried Schlenk flask (100 mL in volume) and THF (10 mL) were added under nitrogen. The reaction mixture was stirred for 30 min at room temperature and then, bis(pinacolato)diboron (2.79 g, 11.0 mmol, 1.1 eq.) and THF (5 mL) were added. The reaction mixture was stirred for another 10 min and the alkyne (10.0 mmol) was added, followed by MeOH (0.81 mL, 20.0 mmol, 2.0 eq.). The reaction tube was washed with THF (3 mL), sealed, and stirred until no starting material was detected by TLC. The reaction mixture was filtered through a pad of Celite and concentrated. The product was purified by silica gel chromatography.

General procedure B for synthesis of Alkenyl boronates:[4]

CuCl (30.0 mg, 0.3 mmol, 3 mol%), NaOt-Bu (60.0 mg, 0.3 mmol, 6 mol%) and Xantphos ligand (173 mg, 0.3 mmol, 3%) were placed in an oven-dried Schlenk flask (100 mL in volume) and THF (10 mL) were added under nitrogen. The reaction mixture was stirred for 30 min at room temperature and then, bis(pinacolato)diboron (2.79 g, 11.0 mmol, 1.1 eq.) and THF (5 mL) were added. The reaction mixture was stirred for another 10 min and the alkyne compound (10.0 mmol) was added, followed by MeOH (0.81 mL, 20.0 mmol, 2.0 eq.). The reaction tube was washed with THF (3 mL), sealed, and stirred until no starting material was detected by TLC. The reaction mixture was filtered through a pad of Celite and concentrated. The product was purified by silica gel chromatography.

B. Special procedure for synthesis of Alkenyl boronates:

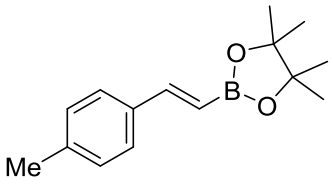


3-oxocyclohex-1-en-1-yl 4-methylbenzenesulfonate (426 mg, 1.6 mmol, 1.0 eq.) was placed in an oven-dried Schlenk flask and anhydrous dioxane (6 mL) were added under nitrogen, to this stirred solution was added $Pd_2(dba)_3$ (29.0 mg, 0.032 mmol, 2 mol%), KOAc (266 mg, 3.2 mmol, 6 mol%), XPhos ligand (53.0 mg, 0.112 mmol, 7 mol%), and bis(pinacolato)diboron (488 mg, 1.92 mmol, 1.2 eq.). The reaction mixture was stirred at 80 °C until no starting material was detected by TLC (~ 10 h). The reaction mixture was filtered through a pad of Celite and concentrated. The product was purified by silica gel chromatography (PE:EA = 2:1, R_f = 0.3).

C. Spectra data of the alkenyl boronates:

(2b') (E)-4,4,5,5-tetramethyl-2-(4-methylstyryl)-1,3,2-dioxaborolane

The general procedure A was followed using 1-ethynyl-4-methylbenzene (1.16 g, 10.0 mmol, 1.0 eq.) as starting material, **2b'** was obtained as a white solid (m.p.: 56.0-57.0 °C, 2.32 g, 95%).



Chemical Formula: $C_{15}H_{21}BO_2$
Exact Mass: 244.1635
Molecular Weight: 244.1410

^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.45-7.31 (m, 3H), 7.14 (d, *J* = 7.6 Hz, 2H), 6.11 (d, *J* = 18.4 Hz, 2H), 2.35 (s, 3H), 1.31 (s, 12H).

^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 149.5, 139.0, 134.8, 129.3, 127.0, 83.3, 24.8, 21.3.

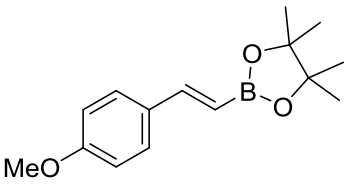
^{11}B NMR (128 MHz, $CDCl_3$): δ ppm 30.48.

HRMS (APCI): Calculated for $C_{15}H_{22}BO_2$ $[M+H]^+$: 245.1713, Found: 245.1702.

IR (*v*, cm^{-1}): 2977, 2927, 1625, 1510, 1412, 1350, 1323, 1140, 1110.

(2c') (E)-2-(4-methoxystyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

The general procedure A was followed using 1-ethynyl-4-methoxybenzene (1.32 g, 10.0 mmol, 1.0 eq.) as starting material, **2c'** was obtained as a yellow oil (2.34 g, 90%).



Chemical Formula: $C_{15}H_{21}BO_3$
Exact Mass: 260.1584
Molecular Weight: 260.1400

^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.43 (d, *J* = 8.0 Hz, 2H), 7.35 (d, *J* = 18.4 Hz, 1H), 6.86 (d, *J* = 8.0 Hz, 2H), 6.01 (d, *J* = 18.4 Hz, 1H), 3.81 (s, 3H), 1.31 (s, 12H).

^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 160.4, 149.2, 130.6, 128.6, 114.1, 83.4, 55.4, 25.0.

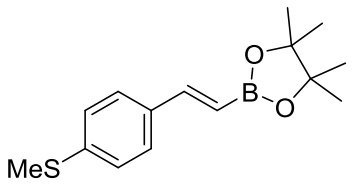
^{11}B NMR (128 MHz, $CDCl_3$): δ ppm 29.97.

HRMS (APCI): Calculated for $C_{15}H_{22}BO_3$ $[M+H]^+$:261.1662, Found: 261.1656.

IR (*v*, cm^{-1}): 2977, 2837, 1738, 1624, 1604, 1575, 1511, 1421, 1354, 1251, 1140, 1030.

(2d') (E)-4,4,5,5-tetramethyl-2-(4-(methylthio)styryl)-1,3,2-dioxaborolane

The general procedure A was followed using (4-ethynylphenyl)(methyl)sulfane (1.48 g, 10.0 mmol, 1.0 eq.) as starting material, **2d'** was obtained as a yellow solid (m.p.: 62.2-64.0 °C, 2.21 g, 80%).



Chemical Formula: $C_{15}H_{21}BO_2S$
Exact Mass: 276.1355
Molecular Weight: 276.2010

^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.40 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 18.4 Hz, 1H), 7.19 (d, *J* = 8.4 Hz, 2H), 6.11 (d, *J* = 18.4 Hz, 1H), 2.47 (s, 3H), 1.30 (s, 12H).

^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 148.9, 139.8, 134.3, 127.5, 126.2, 83.4, 24.9, 15.5.

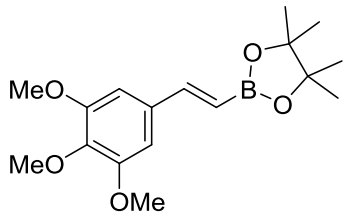
^{11}B NMR (128 MHz, $CDCl_3$): δ ppm 30.77.

HRMS (APCI): Calculated for $C_{15}H_{22}BO_2S$ $[M+H]^+$: 277.1434, Found: 277.1423.

IR(*v*, cm^{-1}): 2977, 2837, 1622, 1605, 1511, 1422, 1354, 1251, 1140, 1030.

(2e') (E)-4,4,5,5-tetramethyl-2-(3,4,5-trimethoxystyryl)-1,3,2-dioxaborolane

The general procedure A was followed using 5-ethynyl-1,2,3-trimethoxybenzene (1.92 g, 10.0 mmol, 1.0 eq.) as starting material, **2e'** was obtained as a white solid (m.p.: 126.3-127.1 °C, 2.82 g, 88%).



Chemical Formula: $C_{17}H_{25}BO_5$
Exact Mass: 320.1795
Molecular Weight: 320.1920

^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.31 (d, *J* = 18.4 Hz, 1H), 6.73 (s, 2H), 6.06 (d, *J* = 18.4 Hz, 1H), 3.86 (s, 9H), 1.31 (s, 12H).

^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 153.4, 149.5, 139.1, 133.3, 104.3, 83.5, 61.1, 56.2, 25.0.

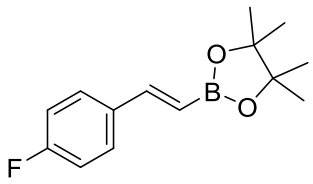
^{11}B NMR (128 MHz, $CDCl_3$): δ ppm 29.76.

HRMS (APCI): Calculated for $C_{17}H_{26}BO_5$ $[M+H]^+$: 321.1873, Found: 321.1861.

IR (*v*, cm^{-1}): 2942, 2837, 1718, 1580, 1418, 1315, 1244, 1120, 1001.

(2f') (E)-2-(4-fluorostyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

The general procedure A was followed using 1-ethynyl-4-fluorobenzene (1.20 g, 10.0 mmol, 1.0 eq.) as starting material, **2f'** was obtained as a colorless oil (2.21 g, 89%).



Chemical Formula: $C_{14}H_{18}BFO_2$
Exact Mass: 248.1384
Molecular Weight: 248.1044

^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.45 (t, *J* = 8.0 Hz, 2H), 7.34 (d, *J* = 18.4 Hz, 1H), 7.02 (t, *J* = 8.6 Hz, 2H), 6.07 (d, *J* = 18.4 Hz, 1H), 1.31 (s, 12H).

^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 164.5, 162.1, 148.3, 133.9, 128.9, 128.8, 115.8, 115.6, 83.6, 25.0.

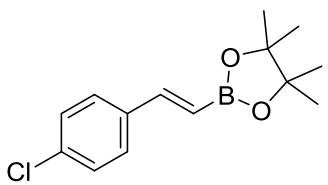
^{11}B NMR (128 MHz, $CDCl_3$): δ ppm 30.80.

^{19}F NMR (376 MHz, Acetone-d_6): δ ppm -112.39.

HRMS (APCI): Calculated for $C_{14}H_{18}BFO_2$ $[M+H]^+$: 249.1462, Found: 249.1457.

IR (*v*, cm^{-1}): 2979, 1623, 1600, 1507, 1349, 1324, 1222, 1208, 1142.

(2g') (E)-2-(4-chlorostyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane



Chemical Formula: $C_{14}H_{18}BClO_2$
Exact Mass: 264.1088
Molecular Weight: 264.5560

The general procedure A was followed using 1-chloro-4-ethynylbenzene (1.37 g, 10.0 mmol, 1.0 eq.) as starting material, **2g'** was obtained as a white solid (m.p.: 86.1-87.5 °C, 2.32 g, 88%).

^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.40 (d, *J* = 8.4 Hz, 2H), 7.36-7.29 (m, 3H), 6.13 (d, *J* = 18.4 Hz, 1H), 1.31 (s, 12H).

^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 148.1, 136.1, 134.7, 128.9, 128.4, 83.6, 24.9.

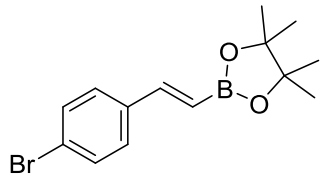
^{11}B NMR (128 MHz, $CDCl_3$): δ ppm 30.28.

HRMS (APCI): Calculated for $C_{14}H_{19}BClO_2$ $[M+H]^+$: 265.1167, Found: 265.1157.

IR (ν, cm^{-1}): 2976, 2931, 1623, 1599, 1507, 1489, 1352, 1270, 1210, 1142, 1087.

(2h') (E)-2-(4-bromostyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

The general procedure A was followed using 1-bromo-4-ethynylbenzene (1.81 g, 10.0 mmol, 1.0 eq.) as starting material, **2h'** was obtained as a slight white solid (m.p.: 95.2-96.5 °C, 2.89 g, 93%).



Chemical Formula: $C_{14}H_{18}BBrO_2$
Exact Mass: 308.0583
Molecular Weight: 309.0100

^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.46 (d, J = 8.0 Hz, 2H), 7.34 (d, J = 7.6 Hz, 2H), 7.32 (d, J = 16.8 Hz, 1H), 6.15 (d, J = 18.4 Hz, 1H), 1.31 (s, 12H).

^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 148.2, 136.6, 131.9, 128.7, 123.1, 83.6, 25.0.

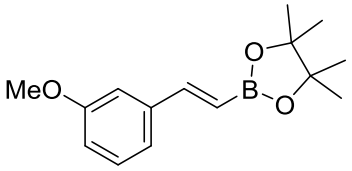
^{11}B NMR (128 MHz, $CDCl_3$): δ ppm 30.54.

HRMS (APCI): Calculated for $C_{14}H_{19}BBrO_2$ $[M+H]^+$: 309.0661, Found: 309.0653.

IR (ν, cm^{-1}): 2973, 1625, 1487, 1402, 1318, 1140, 1067, 1006.

(2i') (E)-2-(3-methoxystyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

The general procedure A was followed using 1-ethynyl-3-methoxybenzene (1.32 g, 10.0 mmol, 1.0 eq.) as starting material, **2i'** was obtained as a yellow oil (2.13 g, 82%).



Chemical Formula: $C_{15}H_{21}BO_3$
Exact Mass: 260.1584
Molecular Weight: 260.1400

^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.40 (d, J = 18.4 Hz, 1H), 7.33-7.27 (m, 1H), 7.11 (d, J = 7.6 Hz, 1H), 7.06 (s, 1H), 6.88 (d, J = 8 Hz, 1H), 6.19 (d, J = 18.4 Hz, 1H), 3.84 (s, 3H), 1.34 (s, 12H).

^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 159.9, 149.5, 139.1, 129.7, 112.0, 115.0, 112.1, 83.5, 55.3, 25.0.

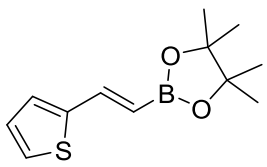
^{11}B NMR (128 MHz, $CDCl_3$): δ ppm 30.61.

HRMS (APCI): Calculated for $C_{15}H_{22}BO_3$ $[M+H]^+$: 261.1662, Found: 261.1651.

IR (ν, cm^{-1}): 2978, 2930, 1740, 1625, 1371, 1351, 1325, 1283, 1143, 1124, 1045.

(2j') (E)-4,4,5,5-tetramethyl-2-(2-(thiophen-2-yl)vinyl)-1,3,2-dioxaborolane

The general procedure A was followed using 2-ethynylthiophene (1.08 g, 10.0 mmol, 1.0 eq.) as starting material, **2j'** was obtained as a yellow oil (2.15 g, 91%).



Chemical Formula: $C_{12}H_{17}BO_2S$
Exact Mass: 236.1042
Molecular Weight: 236.1360

^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.47 (d, J = 18.4 Hz, 1H), 7.24 (d, J = 5.2 Hz, 1H), 7.08 (d, J = 3.6 Hz, 1H), 7.02-6.94 (m, J = 4.2 Hz, 1H), 5.91 (d, J = 18.0 Hz, 1H), 1.30 (s, 12H).

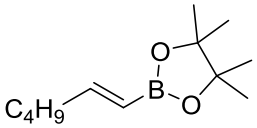
^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 144.1, 141.9, 127.9, 127.8, 126.4, 83.5, 24.9.

^{11}B NMR (128 MHz, $CDCl_3$): δ ppm 30.38.

HRMS (APCI): Calculated for $C_{12}H_{17}BO_2S$ $[M+H]^+$: 237.1121, Found: 237.1114.

IR (ν, cm^{-1}): 2977, 2929, 1616, 1371, 1324, 1282, 1236, 1206, 1143, 1124.

(2k') (E)-2-(hex-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane



Chemical Formula: $C_{12}H_{23}BO_2$
Exact Mass: 210.1791
Molecular Weight: 210.1240

The general procedure A was followed using hex-1-yne (0.82 g, 10.0 mmol, 1.0 eq.) as starting material, **2k'** was obtained as a colorless oil (1.47 g, 70%).

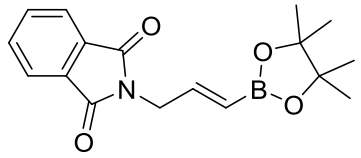
Spectra data was same to liturature.[5]

HRMS (APCI): Calculated for $C_{12}H_{24}BO_2$ $[M+H]^+$: 211.1869, Found: 211.1863.

IR (ν, cm^{-1}): 2957, 2927, 2856, 1639, 1613, 1398, 1363, 1313, 1247, 1147, 1002.

(2l') (E)-2-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)allyl)isoindoline-1,3-dione

The general procedure A was followed using 2-(prop-2-yn-1-yl)isoindoline-1,3-dione (1.85 g, 10.0 mmol, 1.0 eq.) as starting material, **2l'** was obtained as a light yellow oil (2.98 g, 95%).



Chemical Formula: $C_{17}H_{20}BNO_4$
Exact Mass: 313.1485
Molecular Weight: 313.1600

^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.89-7.81 (m, 2H), 7.75-7.70 (m, 2H), 6.58 (dt, J = 18.0 Hz, 4.5 Hz, 1H), 5.46 (dd, J = 18.0, 1.6 Hz, 1H), 4.37 (dd, J = 4.5, 1.7Hz, 2H), 1.21 (s, 12H).

^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 168.0, 145.4, 134.2, 132.2, 123.5, 83.5, 41.1, 24.9.

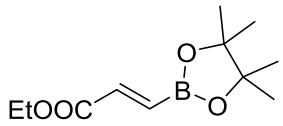
^{11}B NMR (128 MHz, $CDCl_3$): δ ppm 30.19.

HRMS (APCI): Calculated for $C_{17}H_{21}BNO_4$ $[M+H]^+$: 314.1564, Found: 314.1557.

IR (ν, cm^{-1}): 2977, 2837, 1738, 1707, 1643, 1624, 1423, 1362, 1138, 1043.

(2m') ethyl (E)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)acrylate

The general procedure B was followed using ethyl propiolate (0.98 g, 10.0 mmol, 1.0 eq.) as starting material, **2m'** was obtained as a colorless liquid (1.81 g, 80%).



Chemical Formula: $C_{11}H_{19}BO_4$
Exact Mass: 226.1376
Molecular Weight: 226.0790

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.75 (d, J = 18.2 Hz, 1H), 6.60 (d, J = 18.2 Hz, 1H), 4.17 (q, J = 7.2 Hz, 2H), 1.26 (s, 12H).

^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 166.1, 138.9, 84.1, 60.7, 24.9, 14.3.

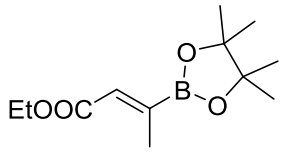
^{11}B NMR (128 MHz, $CDCl_3$): δ ppm 29.78.

HRMS (APCI): Calculated for $C_{11}H_{19}BO_4$ $[M+H]^+$: 227.1455, Found: 227.1446.

IR (ν, cm^{-1}): 2981, 1723, 1642, 1386, 1337, 1303, 1258, 1166, 1140, 1033.

(2n') ethyl (Z)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-2-enoate

The general procedure B was followed using ethyl but-2-ynoate (0.56 g, 5.0 mmol, 1.0 eq.) as starting material, **2n'** was obtained as a colorless liquid (1.02 g, 85%).



Chemical Formula: $C_{12}H_{21}BO_4$
Exact Mass: 240.1533
Molecular Weight: 240.1060

^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 6.42 (s, 1H), 4.14 (q, J = 7.1 Hz, 2H), 2.14 (s, 3H), 1.30-1.21 (m, 15H).

^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 166.3, 130.7, 84.2, 59.9, 24.9, 16.4, 14.4.

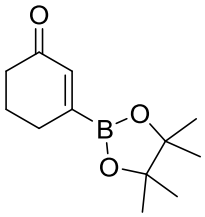
^{11}B NMR (128 MHz, $CDCl_3$): δ ppm 30.18.

HRMS (APCI): Calculated for $C_{12}H_{22}BO_4$ $[M+H]^+$: 241.1611, Found: 241.1604.

IR (ν, cm^{-1}): 2980, 1719, 1363, 1319, 1255, 1185, 1146, 1109, 1037.

(2o') 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohex-2-en-1-one

The special procedure C was followed using 3-oxocyclohex-1-en-1-yl 4-methylbenzenesulfonate (426 mg, 1.6 mmol, 1.0 eq.) as starting material, **2o'** was obtained as a yellow oil (278 mg, 78%).



Chemical Formula: $C_{12}H_{19}BO_3$
Exact Mass: 222.1427
Molecular Weight: 222.0910

^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 6.51 (s, 1H), 2.45-2.35 (m, 4H), 2.05-1.92 (m, 2H), 1.29 (s, 12H).

^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 200.0, 138.6, 84.5, 38.4, 27.1, 24.9, 23.3.

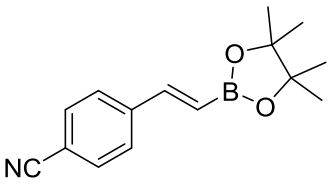
^{11}B NMR (128 MHz, $CDCl_3$): δ ppm 30.66.

HRMS (APCI): Calculated for $C_{12}H_{19}BO_3$ $[M+H]^+$: 223.1506, Found: 223.1500.

IR (*v*, cm^{-1}): 2979, 1671, 1381, 1372, 1320, 1282, 1269, 1143, 1022.

(2p') (E)-4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)benzonitrile

The general procedure A was followed using 4-ethynylbenzonitrile (1.27 g, 10.0 mmol, 1.0 eq.) as starting material, **2p'** was obtained as a white solid (m.p.: 111.8-112.9 °C, 1.81 g, 71%).



Chemical Formula: $C_{15}H_{18}BNO_2$
Exact Mass: 255.1431
Molecular Weight: 255.1240

^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.62 (d, *J* = 8.4 Hz, 2H), 7.54 (d, *J* = 8.4 Hz, 2H), 7.36 (d, *J* = 18.4 Hz, 1H), 6.27 (d, *J* = 18.4 Hz, 1H), 1.31 (s, 12H).

^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 147.3, 141.8, 132.6, 127.6, 119.0, 112.1, 83.9, 24.9.

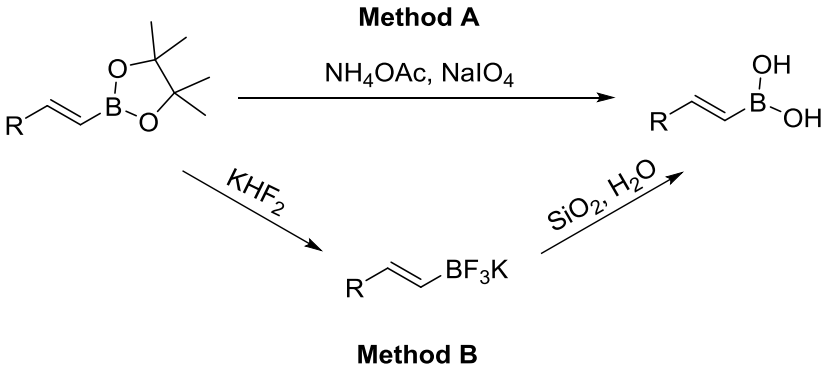
^{11}B NMR (128 MHz, $CDCl_3$): δ ppm 30.23.

HRMS (APCI): Calculated for $C_{15}H_{18}BNO_2$ $[M+H]^+$: 256.1509, Found: 256.1503.

IR (*v*, cm^{-1}): 2999, 2978, 2227, 1717, 1368, 1334, 1310, 1262, 1135, 1107.

2.4 Preparation of Alkenyl boronic acids

A. Two methods for synthesis of alkenyl boronic acids:



Method A:[6]

To a solution of the pinacol boronate (5.0 mmol, 1.0 eq.) in acetone (25 mL) and water (25 mL) was added ammonium acetate (1.93 g, 25.0 mmol, 5.0 eq.) and sodium periodate (5.35 mg, 25.0 mmol, 5.0 eq.). The mixture was stirred until no starting material was left based on TLC monitoring before removal of acetone under reduced pressure. Then ethyl acetate (20 mL) was added, the phases were separated and the aqueous phase extracted with ethyl acetate (2 x 20 mL). The combined organic phases were washed with brine (20 mL), dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The residue was directly used in the next dehydration without purification.

Method B:[7]

To a solution of the pinacol boronate (3.0 mmol, 1.0 eq.) in methanol (20 mL) and water (20 mL) was added potassium hydrogen fluoride (1.41 g, 18.0 mmol, 6.0 eq.). The mixture was stirred at room temperature for 3 h. Then it

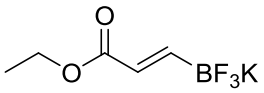
was concentrated in vacuum and the resulting solid was extracted with acetone (3 x 5 mL). The combined acetone extracts were filtered and concentrated in vacuum. The residue was dispersed with Et_2O (10 mL) and the resulting suspension was filtered to afford the potassium vinyltrifluoroborate as white solid.

To a 50 mL round-bottom flask containing a mixture of potassium vinyltrifluoroborate (3.0 mmol, 1.0 eq.) and silica gel (200-300 mesh, 180 mg, 3.0 mmol) under N_2 was added deoxygenated water (9 mL) in one portion. The reaction was stirred at room temperature until ^{11}B NMR indicated completion of the reaction (~10 h). The reaction mixture was filtered to remove silica gel, and the filter cake was thoroughly rinsed with ethyl acetate. The aqueous and organic layers were separated, and the aqueous layer was extracted with ethyl acetate(2 x 5 mL), the combined organic layers were washed with brine, dried over anhydrous $MgSO_4$, filtered, concentrated, and dried in vacuum to afford the desired products.

B. Spectra data of alkenyl BF_3K:

(2m") ethyl (E)-3-(trifluoro-l4-boranyl)acrylate, potassium salt

The general method B was followed using ethyl (E)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)acrylate **2m'** (0.68 g, 3.0 mmol, 1.0 eq.) as starting material, **2m"** was obtained as white solid (m.p.: 173.1-174.8 °C, 0.59 g, 95%).



Chemical Formula: $C_5H_7BF_3KO_2$
Exact Mass: 206.0128
Molecular Weight: 206.0125

^1H NMR (400 MHz, Acetone-d_6): δ ppm 7.02 (dq, J = 18.0, 4.0 Hz, 1H), 5.98 (d, J = 18.0 Hz, 1H), 4.06 (q, J = 7.1 Hz, 2H), 1.20 (t, J = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, Acetone-d_6): δ ppm 168.2, 126.0, 59.6, 25.2, 14.7.

^{11}B NMR (128 MHz, Acetone-d_6): δ ppm 2.44.

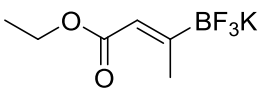
^{19}F NMR (376 MHz, Acetone-d_6): δ ppm -143.50.

HRMS (ESI): Calculated for $C_5H_7BF_3O_2$ $[M–K]^-$: 167.0491, Found: 167.0490.

IR (v, cm^{-1}): 2984, 1682, 1654, 1615, 1371, 1224, 1152, 1125.

(2n") ethyl (Z)-3-(trifluoro-l4-boranyl)but-2-enoate, potassium salt

The general method B was followed using ethyl (Z)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-2-enoate **2n'** (0.72 g, 3.0 mmol, 1.0 eq.) as starting material, **2n"** was obtained as white solid (m.p.: 216.1-216.6 °C, 0.61 g, 92%).



Chemical Formula: $C_6H_9BF_3KO_2$
Exact Mass: 220.0285
Molecular Weight: 220.0395

^1H NMR (400 MHz, Acetone-d_6): δ ppm 5.92 (s, 1H), 4.01 (q, J = 7.2 Hz, 2H), 2.08 (s, 3H), 1.18 (t, J = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, Acetone-d_6): δ ppm 168.0, 117.8, 100.9, 58.6, 17.3, 14.8.

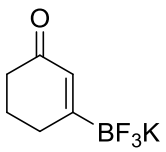
^{11}B NMR (128 MHz, Acetone-d_6): δ ppm 2.41.

^{19}F NMR (376 MHz, Acetone-d_6): δ ppm -148.80.

HRMS (ESI): Calculated for $C_6H_9BF_3O_2$ $[M-K]^-$: 181.0648, Found: 181.0648.

IR (v, cm^{-1}): 2930, 1705, 1695, 1654, 1215, 1188, 1152, 1127, 1007.

(2o") 3-(trifluoro-l4-boranyl)cyclohex-2-en-1-one, potassium salt



Chemical Formula: $C_6H_7BF_3KO$
Exact Mass: 202.0179
Molecular Weight: 202.0245

The general method B was followed using 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohex-2-en-1-one **2o'** (0.67 g, 3.0 mmol, 1.0 eq.) as starting material, **2o"** was obtained as white solid (m.p.: 173.7-174.4 °C, 0.55 g, 91%).

^1H NMR (400 MHz, Acetone-d_6): δ ppm 6.00 (s, 1H), 2.30 (t, J = 5.8 Hz, 2H), 2.15 (t, J = 6.8 Hz, 2H), 1.89-1.75 (m, 2H).

^{13}C NMR (100 MHz, Acetone-d_6): δ ppm 200.0, 128.9, 39.0, 28.5, 25.2, 24.6.

^{11}B NMR (128 MHz, Acetone-d_6): δ ppm 2.03.

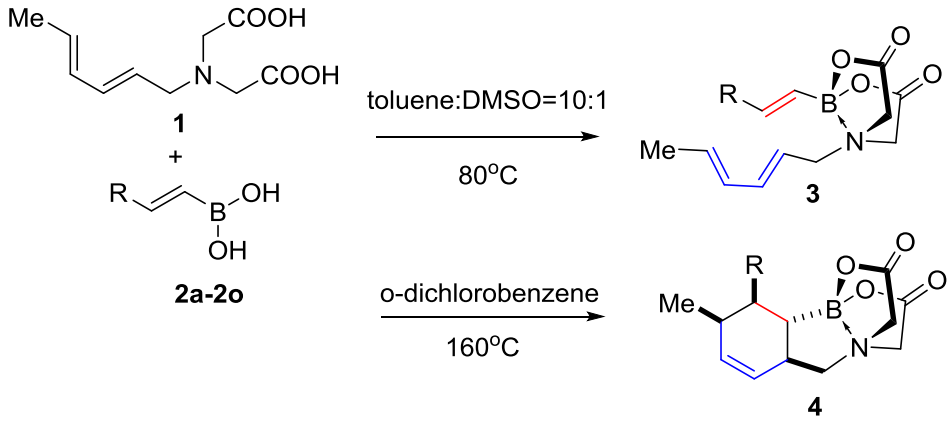
^{19}F NMR (376 MHz, Acetone-d_6): δ ppm -148.1.

HRMS (ESI): Calculated for $C_6H_7BF_3O$ [M-K]$^-$: 163.0542, Found: 163.0541.

IR (ν, cm^{-1}): 2958, 2926, 1655, 1603, 1151, 1127.

3. MIDA-type boronate tethered intramolecular Diels-Alder reactions

A. General procedure for synthesis of MIDA-type boronates and corresponding D-A products:



In a dried Schlenk flask (25 mL in volume) equipped with a stirring bar were placed with molecular sieves, alkenyl boronic acid (0.30 mmol, 1.0 eq.) and 2, 4-diene amino acids (0.33 mmol, 1.1 eq.). After evacuation and refill with dry N_2 for three times, toluene (3 mL) and DMSO (0.3 mL) were added with syringes under a stream of N_2. The resulting mixture was allowed to stir at 80 ℃ for 12 h. After cooling to room temperature, molecular sieves was filtered off and the filtrate was concentrated under high vacuum to removal the solvents. The resulting residue was used for the next step without further purification.

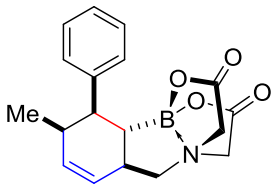
In a dried Schlenk flask (25 mL in volume) equipped with a stirring bar was added the above crude product. After evacuation and refill with dry N_2 for three times, o-dichlorobenzene (3 mL) were added with syringe under a stream of N_2. The resulting mixture was allowed to stir at 160 ℃ until no starting material detected by TLC. After cooling to room temperature, the mixture was directly purified by silica gel chromatography. (Apply PE to elute the o-dichlorobenzene, PE:EA = 1:2 to elute the product, R_f = 0.2)

B. Spectra data of the D-A products:

(4a)

8-methyl-9-phenyl-5a,8,9,9a-tetrahydro-5H-4λ^4,10λ^4-10,4-(epoxyethano)benzo[3,4][1,2]azaborolo[2,1-b][1,3,2]oxazaborole-2,12(3H)-dione

The general procedure was followed using (E)-styrylboronic acid (148 mg, 1.0 mmol, 1.0 eq.) and compound **1** (235 mg, 1.1 mmol, 1.1 eq.) as starting material. **4a** was obtained as a white solid (m.p.: >300 °C, 208 mg, 64%).



Chemical Formula: $C_{18}H_{20}BNO_4$
Exact Mass: 325.1485
Molecular Weight: 325.1710

^{1}H NMR (400 MHz, DMSO-d_6): δ ppm 7.30 (t, *J* = 7.5 Hz, 2H), 7.23 (d, *J* = 7.5 Hz, 2H), 7.17 (t, *J* = 7.2 Hz, 1H), 5.75 (dt, *J* = 9.8, 2.8 Hz, 1H), 5.67 (d, *J* = 9.9 Hz, 1H), 4.30-4.10 (m, 4H), 3.77 (dd, *J* = 11.2, 5.2 Hz, 1H), 3.08 (d, *J* = 12.8 Hz, 1H), 3.04 (t, *J* = 6.0 Hz, 1H), 2.49-2.32 (m, 2H), 1.12 (t, *J* = 11.8 Hz, 1H), 0.46 (d, *J* = 7.0 Hz, 3H).

^{13}C NMR (100 MHz, DMSO-d_6): δ ppm 170.7, 170.6, 144.4, 136.1, 127.9, 127.8, 125.5, 124.7, 67.9, 63.3, 62.4, 45.1, 41.7, 36.6, 16.2.

^{11}B NMR (128 MHz, DMSO-d_6): δ ppm 15.68.

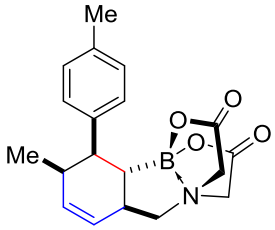
HRMS (APCI): Calculated for $C_{18}H_{19}BNO_4$ [M-H]$^-$: 324.1407, Found: 324.1406.

IR (*v*, cm^{-1}): 3014, 2956, 2854, 1748, 1299, 1250, 1176, 1120, 1059, 1035.

(4b)

8-methyl-9-(p-tolyl)-5a,8,9,9a-tetrahydro-5H-4λ^4,10λ^4-10,4-(epoxyethano)benzo[3,4][1,2]azaborolo[2,1-b][1,3,2]oxazaborole-2,12(3H)-dione

The general procedure was followed using (E)-(4-methylstyryl)boronic acid (48.6 mg, 0.30 mmol, 1.0 eq.) and compound **1** (70.3 mg, 0.33 mmol, 1.1 eq.) as starting material. **4b** was obtained as a white solid (m.p.: 282.1-283.5 °C, 68.2 mg, 67%).



Chemical Formula: $C_{19}H_{22}BNO_4$
Exact Mass: 339.1642
Molecular Weight: 339.1980

^{1}H NMR (400 MHz, Acetone-d_6): δ ppm 7.18 (d, *J* = 8.0 Hz, 2H), 7.09 (d, *J* = 8.0 Hz, 2H), 5.79 (dt, *J* = 9.8, 4.0 Hz, 1H), 5.72 (dt, *J* = 10.0, 1.5 Hz, 1H), 4.33-4.11 (m, 4H), 4.03 (dd, *J* = 11.2, 5.2 Hz, 1H), 3.26-3.10 (m, 2H), 2.64-2.52 (m, 1H), 2.51-2.41 (m, 1H), 2.29 (s, 3H), 1.25 (t, *J* = 12.0 Hz, 1H), 0.54 (d, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, Acetone-d_6): δ ppm 170.6,170.4, 142.3, 137.6, 135.4, 129.3, 129.0, 125.0, 70.0, 64.8, 64.0, 46.1, 43.2, 38.0, 21.1, 16.8.

^{11}B NMR (128 MHz, Acetone-d_6): δ ppm 15.76.

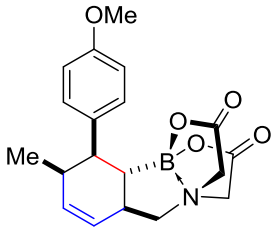
HRMS (APCI): Calculated for $C_{19}H_{21}BNO_4$ [M-H]$^-$: 338.1564, Found: 338.1563.

IR (*v*, cm^{-1}): 3016, 2969, 2853, 1748, 1515, 1293, 1066, 1032, 1003.

(4c)

9-(4-methoxyphenyl)-8-methyl-5a,8,9,9a-tetrahydro-5H-4λ^4,10λ^4-10,4-(epoxyethano)benzo[3,4][1,2]azaborolo[2,1-b][1,3,2]oxazaborole-2,12(3H)-dione

The general procedure was followed using (E)-(4-methoxystyryl)boronic acid (53.4 mg, 0.30 mmol, 1.0 eq.) and compound **1** (70.3 mg, 0.33 mmol, 1.1 eq.) as starting material. **4c** was obtained as a white solid (m.p.: 275.7-276.3 °C, 80.0 mg, 75%).



Chemical Formula: $C_{19}H_{22}BNO_5$
Exact Mass: 355.1591
Molecular Weight: 355.1970

^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.14 (d, *J* = 8.4 Hz, 2H), 6.84 (d, *J* = 8.4 Hz, 2H), 5.78 (dt, *J* = 10.0, 3.2 Hz, 1H), 5.57 (d, *J* = 9.8 Hz, 1H), 3.83 (dd, *J* =18.4, 10.8 Hz, 2H), 3.78 (s, 3H), 3.61 (d, *J* = 18.0 Hz, 1H), 3.52-3.38 (m, 2H), 3.10 (dd, *J* =11.6, 5.6 Hz, 1H), 2.54-2.36 (m, 2H), 2.33-2.30 (m, 1H), 1.06 (t, *J* = 11.6 Hz, 1H), 0.55 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, Acetone-d_6): δ ppm 170.6, 170.5, 158.7, 137.6, 137.3, 129.9, 125.0, 114.0, 70.0, 64.8, 65.0, 55.3, 45.6, 43.2, 38.1, 16.8.

^{11}B NMR (128 MHz, Acetone-d_6): δ ppm 15.64.

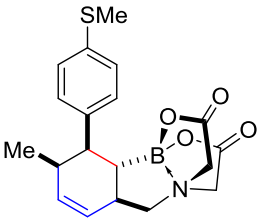
HRMS (APCI): Calculated for $C_{19}H_{21}BNO_5$ $[M-H]^-$: 354.1513, Found: 354.1513.

IR (ν, cm^{-1}): 3010, 2956, 2839, 1744, 1512, 1289, 1244, 1065, 1027.

(4d)

8-methyl-9-(4-(methylthio)phenyl)-5a,8,9,9a-tetrahydro-5H-4λ⁴,10λ⁴-10,4-(epoxyethano)benzo[3,4][1,2]azaborolo[2,1-b][1,3,2]oxazaborole-2,12(3H)-dione

The general procedure was followed using (E)-(4-(methylthio)styryl)boronic acid (58.2 mg, 0.30 mmol, 1.0 eq.) and compound **1** (70.3 mg, 0.33 mmol, 1.1 eq.) as starting material. **4d** was obtained as a yellow solid (m.p.: >300 °C, 95.1mg, 86%).



Chemical Formula: $C_{19}H_{22}BNO_4S$
Exact Mass: 371.1363
Molecular Weight: 371.2580

^{1}H NMR (400 MHz, Acetone-d_6): δ ppm 7.63 (d, J = 8.4 Hz, 2H), 7.51 (d, J = 8.0 Hz, 2H), 5.80 (dt, J = 10.0, 3.2 Hz, 1H), 5.74 (d, J = 10.0 Hz, 1H), 4.41-4.16 (m, 4H), 4.06 (dd, J =11.2, 5.2 Hz, 1H), 3.34-3.16 (m, 2H), 2.70 (d, J = 1.2 Hz, 3H), 2.68-2.49 (m, 2H), 1.33 (t, J = 12.0 Hz, 1H), 0.53 (d, J = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, Acetone-d_6): δ ppm 170.6, 170.4, 148.6, 144.9, 144.9, 137.2, 129.9, 125.2, 123.9, 69.9, 64.9, 64.0, 46.3, 44.2, 44.1, 43.0, 37.7, 37.7, 16.7.

^{11}B NMR (128 MHz, Acetone-d_6): δ ppm 15.96.

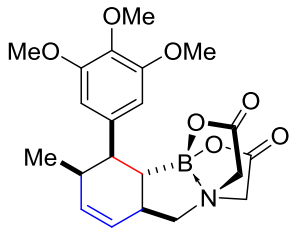
HRMS (APCI): Calculated for $C_{19}H_{22}{}^{10}BNO_5$ [M]: 370.1399, Found: 370.1399.

IR (ν, cm^{-1}): 3006, 2956, 2921, 2850, 1730, 1455, 1298, 1265, 1122, 1077, 1039, 1015.

(4e)

8-methyl-9-(3,4,5-trimethoxyphenyl)-5a,8,9,9a-tetrahydro-5H-4λ⁴,10λ⁴-10,4-(epoxyethano)benzo[3,4][1,2]azaborolo[2,1-b][1,3,2]oxazaborole-2,12(3H)-dione

The general procedure was followed using (E)-(3,4,5-trimethoxystyryl)boronic acid (71.4 mg, 0.30 mmol, 1.0 eq.) and compound **1** (70.3 mg, 0.33 mmol, 1.1 eq.) as starting material. **4e** was obtained as a white solid (m.p.: >300 °C, 105 mg, 84%).



Chemical Formula: $C_{21}H_{26}BNO_7$
Exact Mass: 415.1802
Molecular Weight: 415.2490

^{1}H NMR (400 MHz, Acetone-d_6): δ ppm 6.63 (s, 2H), 5.84-5.76 (m, 1H), 5.80 (dt, J = 10.0, 2.8 Hz, 1H), 5.71 (d, J = 10.0 Hz, 1H), 4.40-4.15 (m, 4H), 4.05 (dd, J =11.2, 5.2 Hz, 1H), 3.84 (s, 6H), 3.69 (s, 3H), 3.23 (dd, J = 13.6, 11.2Hz, 1H), 3.13 (dd, J = 11.8, 5.8 Hz, 1H), 2.65-2.45 (m, 2H), 1.23 (t, J = 12.0 Hz, 1H), 0.55 (d, J = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, Acetone-d_6): δ ppm 170.6, 170.3, 153.9, 141.0, 137.5, 125.0, 106.1, 70.2, 65.0, 64.1, 60.4, 56.2, 46.3, 43.6, 37.9, 30.6, 16.7.

^{11}B NMR (128 MHz, Acetone-d_6): δ ppm 15.84.

HRMS (APCI): Calculated for $C_{21}H_{26}BNO_7$ $[M-H]^-$: 414.1724, Found: 414.1729.

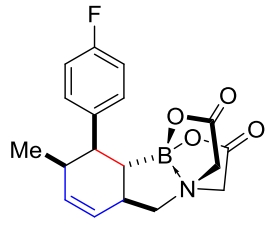
IR (ν, cm^{-1}): 3014, 2964, 2930, 1750, 1585, 1278, 1123, 1105, 1064, 1029.

(4f)

9-(4-fluorophenyl)-8-methyl-5a,8,9,9a-tetrahydro-5H-4λ⁴,10λ⁴-10,4-(epoxyethano)benzo[3,4][1,2]azaborolo[2,1-b][1,3,2]oxazaborole-2,12(3H)-dione

The general procedure was followed using (E)-(4-fluorostyryl)boronic acid (50.0 mg, 0.30 mmol, 1.0 eq.) and compound **1** (70.3 mg, 0.33 mmol, 1.1 eq.) as starting material. **4f** was obtained as a white solid (m.p.: 216.8-217.2 °C, 71.0 mg, 69%).

^{1}H NMR (400 MHz, Acetone-d_6): δ ppm 7.31 (dd, *J* = 8.0, 4.0 Hz, 2H), 7.05 (t, *J* = 8.0 Hz, 2H), 5.79 (dt, *J* = 8.0, 4.0 Hz, 1H), 5.73 (d, *J* = 10.0 Hz, 1H), 4.40-4.15 (m, 4H), 4.04 (dd, *J* =11.2, 5.3 Hz, 2H), 3.23 (d, *J* = 12.0 Hz, 1H), 3.18 (t, *J* = 6.0 Hz, 1H), 2.59 (t, *J* =11.3 Hz, 1H), 2.55-2.40 (m, 1H), 1.26 (t, *J* = 12.0 Hz, 1H), 0.54 (d, *J* = 7.2 Hz, 3H).



Chemical Formula: $C_{18}H_{19}BFNO_4$
Exact Mass: 343.1391
Molecular Weight: 343.1614

^{13}C NMR (100 MHz, Acetone-d_6): δ ppm 170.5, 170.4, 163.2, 160.8, 141.4, 141.4, 137.3, 130.7, 130.6, 125.1, 115.2, 115.0, 69.9, 64.8, 64.0, 45.6, 43.1, 37.9, 16.6.

^{11}B NMR (128 MHz, Acetone-d_6): δ ppm 15.65.

^{19}F NMR (376 MHz, Acetone-d_6): δ ppm -119.54.

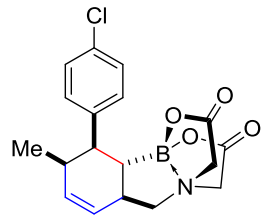
HRMS (APCI): Calculated for $C_{18}H_{18}BFNO4$ $[M-H]^-$: 342.1313, Found: 342.1314.

IR (*v*, cm^{-1}): 3015, 2959, 2927, 1750, 1510, 1295, 1222, 1031.

(4g)

9-(4-chlorophenyl)-8-methyl-5a,8,9,9a-tetrahydro-5H-4λ^4,10λ^4-10,4-(epoxyethano)benzo[3,4][1,2]azaborolo[2,1-b][1,3,2]oxazaborole-2,12(3H)-dione

The general procedure was followed using (E)-(4-chlorostyryl)boronic acid (54.7 mg, 0.30 mmol, 1.0 eq.) and compound **1** (70.3 mg, 0.33 mmol, 1.1 eq.) as starting material. **4g** was obtained as a white solid (m.p.: 237.8-239.0 °C, 76.5 mg, 71%).



Chemical Formula: $C_{18}H_{19}BClNO_4$
Exact Mass: 359.1096
Molecular Weight: 359.6130

^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.27 (d, J = 8.0 Hz, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 5.79 (dt, *J* = 9.6, 4.0 Hz, 1H), 5.59 (d, *J* = 9.8 Hz, 1H), 3.84 (dd, *J* = 18.0, 10.6 Hz, 2H), 3.63 (d, *J* = 18.0 Hz, 1H), 3.54-3.39 (m, 2H), 3.13 (dd, *J* = 11.8, 5.8 Hz, 1H), 2.65-2.48 (m, 1H), 2.47-2.40 (m, 1H), 2.39-2.27 (m, 1H), 0.54 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, Acetone-d_6): δ ppm 170.5, 170.4, 144.3, 137.2, 131.7, 130.8, 128.6, 125.1, 69.9, 64.8, 64.0, 45.8, 43.0, 37.7, 16.6.

^{11}B NMR (128 MHz, Acetone-d_6): δ ppm 15.70.

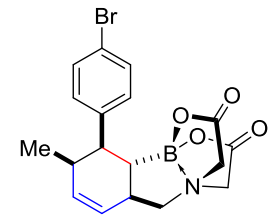
HRMS (APCI): Calculated for $C_{18}H_{18}BClNO_4$ $[M-H]^-$: 358.1017, Found: 358.1017.

IR (*v*, cm^{-1}): 3006, 2956, 2921, 2858, 1732, 1646, 1456, 1298, 1122, 1076, 1039, 1015.

(4h)

9-(4-bromophenyl)-8-methyl-5a,8,9,9a-tetrahydro-5H-4λ^4,10λ^4-10,4-(epoxyethano)benzo[3,4][1,2]azaborolo[2,1-b][1,3,2]oxazaborole-2,12(3H)-dione

The general procedure was followed using (E)-(4-bromostyryl)boronic acid (68.1 mg, 0.30 mmol, 1.0 eq.) and compound **1** (70.3 mg, 0.33 mmol, 1.1 eq.) as starting material. **4h** was obtained as a white solid (m.p.: 277.1-278.9 °C, 109 mg, 90%).



Chemical Formula: $C_{18}H_{19}BBrNO_4$
Exact Mass: 403.0591
Molecular Weight: 404.0670

^{1}H NMR (400 MHz, Acetone-d_6): δ ppm 7.47 (d, J = 8.4 Hz, 2H), 7.26 (d, *J* = 8.4 Hz, 2H), 5.79 (dt, *J* = 10.0, 2.8 Hz, 1H), 5.73 (d, *J* = 9.9 Hz, 1H), 4.35-4.12 (m, 4H), 4.05 (dd, *J* =11.2, 5.2 Hz, 1H), 3.22 (dd, *J* = 12.5, 10.3 Hz, 1H), 3.17 (dd, *J* = 10.9, 4.8 Hz, 1H), 2.60 (dd, *J* = 16.9, 8.2 Hz, 1H), 2.55-2.42 (m, 1H), 1.26 (t, *J* = 11.6 Hz, 1H), 0.54 (d, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, Acetone-d_6): δ ppm 170.5, 170.4, 144.8, 137.3, 131.6, 131.3, 125.1, 119.8, 69.9, 64.8, 64.0, 45.9, 43.1, 37.6, 16.7.

^{11}B NMR (128 MHz, Acetone-d_6): δ ppm 15.64.

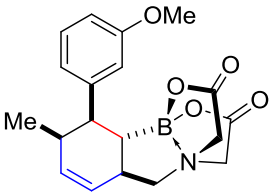
HRMS (ESI): Calculated for $C_{18}H_{18}BBrNO4$ $[M-H]^-$: 402.0512, Found: 402.0520.

IR (ν, cm^{-1}): 3021, 2974, 2917,1771, 1739, 1285, 1064, 1029, 1007.

(4i)

9-(3-methoxyphenyl)-8-methyl-5a,8,9,9a-tetrahydro-5H-4λ^4,10λ^4-10,4-(epoxyethano)benzo[3,4][1,2]azaborolo[2,1-b][1,3,2]oxazaborole-2,12(3H)-dione

The general procedure was followed using (E)-(3-methoxystyryl)boronic acid (54.0 mg, 0.30 mmol, 1.0 eq.) and compound **1** (70.3 mg, 0.33 mmol, 1.1 eq.) as starting material. **4i** was obtained as a white solid (m.p.: >300 °C, 73.7 mg, 69%).



Chemical Formula: $C_{19}H_{22}BNO_5$
Exact Mass: 355.1591
Molecular Weight: 355.1970

^{1}H NMR (400 MHz, Acetone-d_6): δ ppm 7.18 (t, J = 7.8 Hz, 1H), 6.94 (s, 1H), 6.87 (d, J = 7.6 Hz, 1H), 6.72 (dd, J = 8.0, 2.6 Hz, 1H), 5.79 (dt, J = 10.0, 2.8 Hz, 1H), 5.72 (d, J = 10.0 Hz, 1H), 4.35-4.15 (m, 4H), 4.04 (dd, J = 10.8, 5.2Hz, 1H), 3.80 (s, 3H), 3.28-3.12 (m, 2H), 2.65-2.54 (m, 1H), 2.54-2.46 (m, 1H), 1.26 (t, J = 11.6 Hz, 1H), 0.55 (d, J = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, Acetone-d_6): δ ppm 170.6, 170.4, 160.5, 147.0, 137.5, 129.5, 125.1, 121.3, 114.3, 112.2, 70.0, 64.9, 64.0, 55.2, 46.4, 43.1, 38.0, 16.7.

^{11}B NMR (128 MHz, Acetone-d_6): δ ppm 15.76.

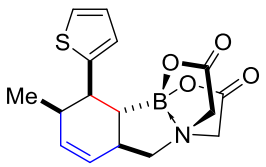
HRMS (APCI): Calculated for $C_{19}H_{21}BNO_5$ $[M-H]^-$: 354.1513, Found: 354.1522.

IR (ν, cm^{-1}): 3014, 2961, 2927, 2871, 1750, 1601, 1275, 1123, 1064, 1030.

(4j)

8-methyl-9-(thiophen-2-yl)-5a,8,9,9a-tetrahydro-5H-4λ^4,10λ^4-10,4-(epoxyethano)benzo[3,4][1,2]azaborolo[2,1-b][1,3,2]oxazaborole-2,12(3H)-dione

The general procedure was followed using (E)-(2-(thiophen-2-yl)vinyl)boronic acid (46.2 mg, 0.30 mmol, 1.0 eq.) and compound **1** (70.3 mg, 0.33 mmol, 1.1 eq.) as starting material. **4j** was obtained as a white solid (m.p.: 178.9-180.0 °C, 79.2 mg, 80%).



Chemical Formula: $C_{16}H_{18}BNO_4S$
Exact Mass: 331.1050
Molecular Weight: 331.1930

^{1}H NMR (400 MHz, DMSO-d_6): δ ppm 7.34 (d, J = 4.9 Hz, 1H), 6.99-6.93 (m, 2H), 5.75-5.69 (m, 1H), 5.65 (d, J = 9.9 Hz, 1H), 4.33-4.08 (m,4H), 3.75 (dd, J = 10.8, 5.2 Hz, 1H), 3.23 (dd, J = 11.6, 5.6 Hz, 1H), 3.11-2.99 (m, 1H), 2.48-2.32 (m, 2H), 1.08 (t, J = 12.0 Hz, 1H), 0.56 (d, J = 7.0 Hz, 3H).

^{13}C NMR (100 MHz, DMSO-d_6): δ ppm 170.7, 170.6, 147.9, 135.4, 126.5, 124.6, 123.8, 123.2, 67.7, 63.4, 62.5, 41.5, 40.5, 37.3, 16.2.

^{11}B NMR (128 MHz, Acetone-d_6): δ ppm 15.53.

HRMS (APCI): Calculated for $C_{16}H_{17}BNO_4S$ $[M-H]^-$: 330.0971, Found: 330.0974.

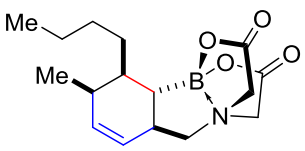
IR (ν, cm^{-1}): 3014, 2956, 2855, 1744, 1292, 1251, 1177, 1051, 1060, 1034.

(4k)

9-butyl-8-methyl-5a,8,9,9a-tetrahydro-5H-4λ^4,10λ^4-10,4-(epoxyethano)benzo[3,4][1,2]azaborolo[2,1-b][1,3,2]oxazaborole-2,12(3H)-dione

The general procedure was followed using (E)-(4-bromostyryl)boronic acid (68.1 mg, 0.30 mmol, 1.0 eq.) and compound **1** (70.3 mg, 0.33 mmol, 1.1 eq.) as starting material. **4k** was obtained as a white solid (m.p.: 227.6-229.0 °C, 78.8 mg, 86%).

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 5.77 (d, *J* = 10.0 Hz, 1H), 5.51 (d, *J* = 9.7 Hz, 1H), 3.96-3.81 (m, 4H), 3.69 (dd, *J* = 11.1, 5.2 Hz, 1H), 2.78-2.69 (m, 1H), 2.36 (s, 2H), 1.85-1.72 (m, 1H), 1.44-1.26 (m, 6H), 0.91 (t, *J* = 6.4 Hz, 3H), 0.86 (d, *J* = 7.0 Hz, 3H), 0.59 (t, *J* = 11.7 Hz, 1H).



Chemical Formula: $C_{16}H_{24}BNO_4$
Exact Mass: 305.1798
Molecular Weight: 305.1810

^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 169.2, 168.8, 139.0, 122.1, 71.4, 64.9, 64.0, 41.7, 37.9, 32.6, 31.5, 29.2, 23.1, 14.7, 14.3.

^{11}B NMR (128 MHz, Acetone-d_6): δ ppm 15.56.

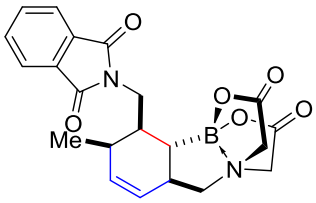
HRMS (APCI): Calculated for $C_{16}H_{23}BNO_4$ $[M-H]^-$: 304.1720, Found: 304.1719.

IR (*v*, cm^{-1}): 3012, 2956, 2925, 2857, 1747, 1467, 1297, 1230, 1026.

(4l)

9-((1,3-dioxoisoindolin-2-yl)methyl)-8-methyl-5a,8,9,9a-tetrahydro-5H-4λ^4,10λ^4-10,4-(epoxyethano)benzo[3,4][1,2]azaborolo[2,1-b][1,3,2]oxazaborole-2,12(3H)-dione

The general procedure was followed using (E)-(3-(1,3-dioxoisoindolin-2-yl)prop-1-en-1-yl)boronic acid (69.3mg, 0.30 mmol, 1.0 eq.) and compound **1** (70.3 mg, 0.33 mmol, 1.1 eq.) as starting material. **4l** was obtained as a light yellow solid (m.p.: >300 °C, 86.0 mg, 70%).



Chemical Formula: $C_{21}H_{21}BN_2O_6$
Exact Mass: 408.1493
Molecular Weight: 408.2170

^{1}H NMR (400 MHz, DMSO-d_6) δ ppm 7.89-7.77 (m, 4H), 5.63 (d, *J* = 9.2 Hz, 1H), 5.57 (d, *J* = 10.0 Hz, 1H), 4.26-4.02 (m, 4H), 3.71 (dd, *J* = 10.5, 4.8 Hz, 1H), 3.57 (d, *J* = 8.4 Hz, 2H), 2.96 (t, *J* = 12.0 Hz, 1H), 2.69-2.55 (m, 1H), 2.34-2.14 (m, 2H), 0.87 (d, *J* = 6.8 Hz, 3H), 0.57 (t, *J* = 11.8 Hz, 1H)..

^{13}C NMR (100 MHz, Acetone-d_6): δ ppm 170.6, 170.4, 168.3, 135.9, 134.2, 131.8, 124.3, 122.9, 68.4, 63.6, 62.8, 41.0, 40.3, 35.4, 31.5, 14.8.

^{11}B NMR (128 MHz, Acetone-d_6): δ ppm 15.89.

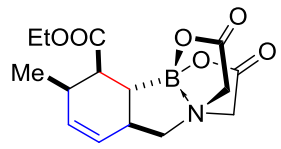
HRMS (APCI): Calculated for $C_{21}H_{22}BN_2O_6$ $[M+H]^+$: 409.1571, Found: 409.1583.

IR (*v*, cm^{-1}): 3013, 2918, 2850, 1770, 1750, 1703, 1405, 1290, 1044, 1026.

(4m)

ethyl-8-methyl-2,12-dioxo-2,3,5a,8,9,9a-hexahydro-5H-4λ^4,10λ^4-10,4-(epoxyethano)benzo[3,4][1,2]azaborolo[2,1-b][1,3,2]oxazaborole-9-carboxylate

The general procedure was followed using (E)-(3-ethoxy-3-oxoprop-1-en-1-yl)boronic acid (43.2mg, 0.30 mmol, 1.0 eq.) and compound **1** (70.3 mg, 0.33 mmol, 1.1 eq.) as starting material. **4m** was obtained as a white solid (m.p.: 188.9-190.9 °C, 60.0 mg, 62%).



Chemical Formula: $C_{15}H_{20}BNO_6$
Exact Mass: 321.1384
Molecular Weight: 321.1360

^{1}H NMR (400 MHz, Acetone-d_6) δ ppm 5.74-5.64 (m, 2H), 4.35-4.04 (m, 6H), 4.00 (dd, *J* = 11.2, 5.3 Hz, 1H), 3.12 (dd, *J* = 13.3, 11.4 Hz, 1H), 2.73 (dd, *J* = 11.4, 6.0 Hz, 1H), 2.70-2.62 (m, 1H), 2.41 (td, *J* = 13.1, 5.2 Hz, 1H), 1.25 (t, *J* = 7.2 Hz, 3H), 0.96 (t, *J* = 11.6 Hz, 1H), 0.88 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, Acetone-d_6): δ ppm 174.0, 170.6, 135.8, 125.7, 69.4, 64.8, 63.9, 60.3, 46.7, 41.6, 33.6, 17.1, 14.6.

^{11}B NMR (128 MHz, Acetone-d_6): δ ppm 15.83 .

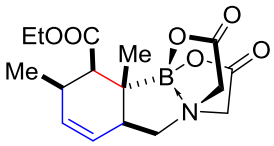
HRMS (APCI): Calculated for $C_{15}H_{19}BNO_6$ $[M-H]^-$: 320.1305, Found: 320.1305.

IR (*v*, cm^{-1}): 3005, 2956, 2921, 2851, 1728, 1456, 1298, 1264, 1122, 1077, 1039, 1015.

(4n)

ethyl-8,9a-dimethyl-2,12-dioxo-2,3,5a,8,9,9a-hexahydro-5H-4λ^4,10λ^4-10,4-(epoxyethano)benzo[3,4][1,2]azaborolo[2,1-b][1,3,2]oxazaborole-9-carboxylate

The general procedure was followed using (Z)-(4-ethoxy-4-oxobut-2-en-2-yl)boronic acid (47.3mg, 0.30 mmol, 1.0 eq.) and compound **1** (70.3 mg, 0.33 mmol, 1.1 eq.) as starting material. **4n** was obtained as a white solid (m.p.: >300 ^{o}C, 49.0 mg, 49%).



Chemical Formula: $C_{16}H_{22}BNO_6$
Exact Mass: 335.1540
Molecular Weight: 335.1630

^{1}H NMR (400 MHz, Acetone-d$_6$) δ ppm 5.75 (dt, *J* = 10.0, 3.2 Hz, 1H), 5.53 (d, *J* = 10.0 Hz, 1H), 4.39-4.08 (m, 6H), 3.91 (dd, *J* = 11.6, 5.8 Hz, 1H), 3.42-3.28 (m, 1H), 2.78-2.70 (m, 1H), 2.60-2.48 (m, 1H), 1.26 (t, *J* = 7.2 Hz, 3H), 1.05 (d, *J* = 7.4 Hz, 3H), 0.91 (s, 3H).

^{13}C NMR (100 MHz, Acetone-d$_6$): δ ppm 173.5, 170.9, 170.7, 135.9, 122.2, 67.7, 65.3, 65.1, 60.1, 50.5, 46.0, 32.6, 18.4, 14.6, 11.7.

^{11}B NMR (128 MHz, Acetone-d$_6$): δ ppm 16.38.

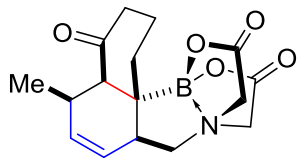
HRMS (APCI): Calculated for $C_{16}H_{21}BNO_6$ [M-H]$^-$: 334.1462, Found: 334.1464.

IR (*v*, cm^{-1}): 3013, 2967, 2876, 1773, 1750, 1290, 1104, 1030.

(4o)

5-methyl-2,3,4a,5,7a,8-hexahydro-9λ^4,13λ^4-13,9-(epoxyethano)naphtho[8a',1':3,4][1,2]azaborolo[2,1-b][1,3,2]oxazaborole-4,11,15(1H,10H)-trione

The general procedure was followed using (3-oxocyclohex-1-en-1-yl)boronic acid (42.0mg, 0.30 mmol, 1.0 eq.) and compound **1** (70.3 mg, 0.33 mmol, 1.1 eq.) as starting material. **4o** was obtained as a white solid (m.p.: 199.2-201.3 ^{o}C, 22.0 mg, 23%).



Chemical Formula: $C_{16}H_{20}BNO_5$
Exact Mass: 317.1435
Molecular Weight: 317.1480

^{1}H NMR (400 MHz, Acetone-d$_6$) δ ppm 5.83 (dt, *J* = 9.6, 2.7 Hz, 1H), 5.74 (dt, *J* = 9.6, 2.9 Hz, 1H), 4.43-4.24 (m, 4H), 4.09-4.01 (m, 1H), 3.51 (dd, *J* = 14.2, 12.0 Hz, 1H), 2.86 (d, *J* = 11.0 Hz, 2H), 2.58-2.38 (m, 2H), 2.34 (dt, *J* = 14.8, 5.4 Hz, 1H), 2.13-2.06 (m, 1H), 1.83-1.71 (m, 1H), 1.66-1.54 (m, 1H), 1.38-1.26 (m, 1H), 1.01 (d, J = 7.8 Hz, 3H)..

^{13}C NMR (100 MHz, Acetone-d$_6$): δ ppm 213.7, 170.5, 136.1, 125.3, 67.1, 65.3, 65.2, 54.0, 44.5, 41.3, 22.1, 21.3, 18.9.

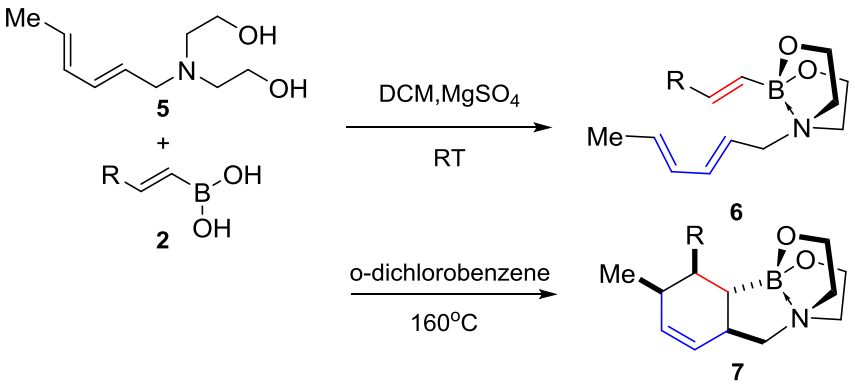
^{11}B NMR (128 MHz, Acetone-d$_6$): δ ppm 15.65 .

HRMS (APCI): Calculated for $C_{16}H_{19}BNO_5$ [M-H]$^-$: 316.1356, Found: 316.1358.

IR (*v*, cm^{-1}): 3004, 2955, 1735, 1691, 1292, 1243, 1183, 1115, 1036.

4. DABO-type boronate tethered intramolecular Diels-Alder reactions

A. General procedure for synthesis of DABO-type boronates and corresponding D-A products:



In a dried round bottom flask equipped with a stirring bar were placed with magnesium sulfate (301 mg, 2.5 mmol, 5.0 eq.) and alkenyl boronic acid (0.50 mmol, 1.0 eq.), After evacuation and refill with dry N_2 for three times, 2,4-diene amino alcohol (0.55 mmol, 1.1 eq.) in DCM (5 mL) were added with syringes. The resulting mixture was allowed to stir at room temperature overnight. After filtered the residue, the filtrate was concentrated under vacuum without further purification.

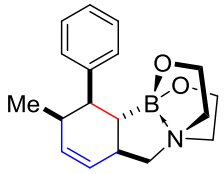
In a dried Schlenk flask (25 mL in volume) equipped with a stirring bar were placed with the solid from the last step. After evacuation and refill with dry N_2 for three times, o-dichlorobenzene (2.5 mL) were added with syringe under a stream of N_2. The resulting mixture was allowed to stir at 160 ℃ for 8 h. After cooling to room temperature, the mixture was directly purified by silica gel chromatography. (Apply PE to elute the o-dichlorobenzene, PE:EA = 1:2 to elute the product, R_f = 0.3)

B. Spectra data :

(7a)

8-methyl-9-phenyl-2,3,5a,8,9,9a-hexahydro-5H-4λ^4,10λ^4-10,4-(epoxyethano)benzo[3,4][1,2]azaborolo[2,1-b][1,3,2]oxazaborole

The general procedure was followed using (E)-styrylboronic acid (74.0 mg, 0.50 mmol, 1.0 eq.) and compound **5** (102 mg, 0.55 mmol, 1.1 eq.) as starting material. **7a** was obtained as a white solid (m.p.:138.8-140.6 °C, 89.0 mg, 60%).



Chemical Formula: $C_{18}H_{24}BNO_2$
Exact Mass: 297.1900
Molecular Weight: 297.2050

^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.35 (d, *J* = 7.6 Hz, 2H), 7.31-7.21 (m, 2H), 7.10 (t, *J* = 7.2 Hz, 1H), 5.76 (dt, *J* = 10.0, 2.8 Hz, 1H), 5.63 (d, *J* = 9.8 Hz, 1H), 4.11 (dd, *J* = 10.0, 6.4 Hz, 1H), 3.97-3.89 (m, 3H), 3.38-3.22 (m, 2H), 3.13 (dd, *J* = 11.6, 4.2 Hz, 1H), 3.03 (dd, *J* = 11.2, 3.6 Hz, 1H), 2.86-2.69 (m, 2H), 2.65-2.41 (m, 3H), 0.88 (t, *J* = 11.2 Hz, 1H), 0.53 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 145.1, 137.1, 128.4, 127.9, 125.6, 125.3, 63.2, 62.1, 61.9, 60.5, 58.7, 45.5, 42.6, 37.5, 31.1, 16.5.

^{11}B NMR (128 MHz, $CDCl_3$): δ ppm 17.35.

HRMS (APCI): Calculated for $C_{18}H_{25}BNO_2$ $[M+H]^+$: 298.1978, Found: 298.1974.

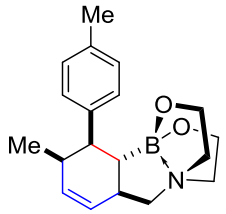
IR (*v*, cm^{-1}): 3012, 2919, 2848, 1705, 1448, 1407, 1295, 1266, 1225, 1120.

(7b)

8-methyl-9-(p-tolyl)-2,3,5a,8,9,9a-hexahydro-5H-4λ^4,10λ^4-10,4-(epoxyethano)benzo[3,4][1,2]azaborolo[2,1-b][1,3,2]oxazaborole

The general procedure was followed using (E)-(4-methylstyryl)boronic acid (48.6 mg, 0.50 mmol, 1.0 eq.) and compound **5** (102 mg, 0.55 mmol, 1.1 eq.) as starting material. **7b** was obtained as a white solid (m.p.: 139.9-140.6 °C,

100 mg, 64%).



Chemical Formula: $C_{19}H_{26}BNO_2$
Exact Mass: 311.2057
Molecular Weight: 311.2320

^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.22 (d, *J* = 7.8 Hz, 2H), 7.06 (d, *J* = 7.7 Hz, 2H), 5.75 (dt, *J* = 9.6, 3.2 Hz, 1H), 5.62 (d, *J* = 9.8 Hz, 1H), 4.09 (dd, *J* = 10.0, 6.4 Hz, 1H), 4.01-3.83 (m, 3H), 3.29 (dd, *J* = 10.8, 4.8 Hz, 1H), 3.21 (dd, *J* = 11.6, 5.8 Hz, 1H), 3.12 (dd, *J* = 11.8, 4.2 Hz, 1H), 3.03 (dd, *J* = 11.6, 3.2 Hz, 1H), 2.86-2.67 (m, 2H), 2.62-2.50 (m, 1H), 2.50-2.36 (m, 2H), 2.26 (s, 3H), 0.86 (t, *J* = 11.4 Hz, 1H), 0.55 (d, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 142.0, 137.2, 134.4, 128.6, 128.2, 125.6, 63.3, 62.2, 61.9, 60.5, 58.8, 45.2, 42.6, 37.5, 31.1, 21.2, 16.6.

^{11}B NMR (128 MHz, $CDCl_3$): δ ppm 17.31.

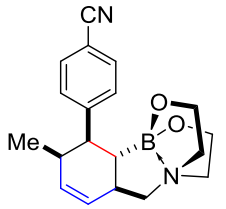
HRMS (APCI): Calculated for $C_{19}H_{27}BNO_2$ $[M+H]^+$: 312.2135, Found: 312.2130.

IR (*v*, cm^{-1}): 3006, 2921, 2850, 1515, 1457, 1263, 1124, 1081, 1052, 1017.

(7c)

4-(8-methyl-2,3,5a,8,9,9a-hexahydro-5H-4λ^4,10λ^4-10,4-(epoxyethano)benzo[3,4][1,2]azaborolo[2,1-b][1,3,2]oxazaborol-9-yl)benzonitrile

The general procedure was followed using (E)-(4-cyanostyryl)boronic acid (86.5 mg, 0.50 mmol, 1.0 eq.) and compound **5** (102 mg, 0.55 mmol, 1.1 eq.) as starting material. **7c** was obtained as a white solid (m.p.: 146.5-147.2 °C, 93.5 mg, 58%).



Chemical Formula: $C_{19}H_{23}BN_2O_2$
Exact Mass: 322.1853
Molecular Weight: 322.2150

^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.55 (d, *J* = 8.1 Hz, 2H), 7.46 (d, *J* = 8.2 Hz, 2H), 5.72 (dt, *J* = 9.6, 3.2 Hz, 1H), 5.64 (d, *J* = 10.0 Hz, 1H), 4.10 (dd, *J* = 10.2, 6.4 Hz, 1H), 4.00-3.82 (m, 3H), 3.35-3.25 (m, 2H), 3.16 (dd, *J* = 11.8, 4.3 Hz, 1H), 3.07 (dd, *J* = 10.8, 3.2 Hz, 1H), 2.86-2.72 (m, 2H), 2.60-2.42 (m, 3H), 0.85 (t, *J* = 11.2 Hz, 1H), 0.49 (d, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 151.2, 136.4, 131.9, 129.2, 125.7, 119.8, 109.0, 63.2, 62.0, 61.9, 60.5, 58.7, 45.8, 42.3, 37.0, 16.3.

^{11}B NMR (128 MHz, $CDCl_3$): δ ppm 16.52.

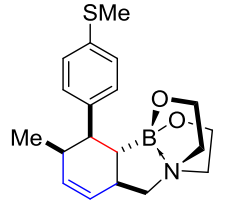
HRMS (APCI): Calculated for $C_{19}H_{24}BN_2O_2$ $[M+H]^+$: 323.1931, Found: 323.1928.

IR (*v*, cm^{-1}): 3009, 2962, 2922, 2852, 2218, 1603, 1464, 1270, 1077, 1047, 1014.

(7d)

8-methyl-9-(4-(methylthio)phenyl)-2,3,5a,8,9,9a-hexahydro-5H-4λ^4,10λ^4-10,4-(epoxyethano)benzo[3,4][1,2]azaborolo[2,1-b][1,3,2]oxazaborole

The general procedure was followed using (E)-(4-(methylthio)styryl)boronic acid (97.0 mg, 0.50 mmol, 1.0 eq.) and compound **5** (102 mg, 0.55 mmol, 1.1 eq.) as starting material. **7d** was obtained as a white-yellow solid (m.p.: 199.3-200.5 °C, 86.0 mg, 64%).



Chemical Formula: $C_{19}H_{26}BNO_2S$
Exact Mass: 343.1777
Molecular Weight: 343.2920

^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.66-7.45 (m, 4H), 5.78-5.72 (m, 1H), 5.64 (d, *J* = 9.8 Hz, 1H), 4.20-4.05 (m, 1H), 4.00-3.83 (m, 3H), 3.32 (dd, *J* = 10.6, 4.6 Hz, 2H), 3.16 (dd, *J* = 11.8, 4.2 Hz, 1H), 3.07 (dd, *J* = 10.4, 3.2 Hz, 1H), 2.87-2.72 (m, 2H), 2.68 (d, *J* = 4.2 Hz, 3H), 2.63-2.43 (m, 3H), 0.96-0.78 (m, 2H), 0.49 (d, *J* = 7.0 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 149.2, 141.9, 136.8, 129.5, 125.6, 123.6,

123.5, 63.3, 62.2, 61.9, 60.6, 58.8, 45.5, 43.9, 43.8, 42.4, 37.4, 29.8, 16.4.

^{11}B NMR (128 MHz, $CDCl_3$): δ ppm 17.35.

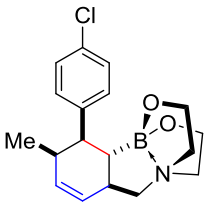
HRMS (EI): Calculated for $C_{19}H_{26}{}^{10}BNO_2S$ [M]: 342.1814, Found: 342.1814.

IR (ν, cm^{-1}): 3005, 2920, 2850, 1717, 1456, 1299, 1263, 1077, 1040, 1015.

(7e)

9-(4-chlorophenyl)-8-methyl-2,3,5a,8,9,9a-hexahydro-5H-4λ^4,10λ^4-10,4-(epoxyethano)benzo[3,4][1,2]azaborolo[2,1-b][1,3,2]oxazaborole

The general procedure was followed using (E)-(4-chlorostyryl)boronic acid (91.2 mg, 0.50 mmol, 1.0 eq.) and compound **5** (102 mg, 0.55 mmol, 1.1 eq.) as starting material. **7e** was obtained as a white solid (m.p.: 161.5-162.9 °C, 116 mg, 70%).



Chemical Formula: $C_{18}H_{23}BClNO_2$
Exact Mass: 331.1510
Molecular Weight: 331.6470

^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.29 (d, J = 8.2 Hz, 2H), 7.22 (d, J = 8.2 Hz, 2H), 5.74 (m, 1H), 5.63 (d, J = 9.8 Hz, 1H), 4.09 (dd, J = 10.0, 6.4 Hz, 1H), 4.00-3.82 (m, 3H), 3.30 (dd, J = 10.8, 4.6 Hz, 1H), 3.22 (dd, J = 12.0, 5.8 Hz, 1H), 3.13 (dd, J = 11.6, 4.0 Hz, 1H), 3.04 (dd, J = 10.8, 2.8 Hz, 1H), 2.86-2.66 (m, 2H), 2.60-2.37 (m, 3H), 0.83 (t, J = 11.4 Hz, 1H), 0.52 (d, J = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 143.7, 136.9, 130.9, 129.8, 128.0, 125.6, 63.3, 62.1, 61.9, 60.5, 58.8, 45.0, 42.5, 37.3, 31.1, 16.4.

^{11}B NMR (128 MHz, $CDCl_3$): δ ppm 17.35.

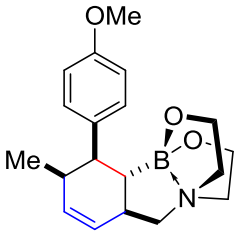
HRMS (APCI): Calculated for $C_{18}H_{24}BClNO_2$ $[M+H]^+$: 332.1589, Found: 332.1585.

IR (ν, cm^{-1}): 3009, 2924, 2851, 1490, 1456, 1263, 1228, 1079, 1053, 1013.

(7f)

9-(4-methoxyphenyl)-8-methyl-2,3,5a,8,9,9a-hexahydro-5H-4λ^4,10λ^4-10,4-(epoxyethano)benzo[3,4][1,2]azaborolo[2,1-b][1,3,2]oxazaborole

The general procedure was followed using (E)-(4-methoxystyryl)boronic acid (89.0 mg, 0.50 mmol, 1.0 eq.) and compound **5** (102 mg, 0.55 mmol, 1.1 eq.) as starting material. **7f** was obtained as a white-yellow solid (m.p.: 153.6-154.6 °C, 90.0 mg, 55%).



Chemical Formula: $C_{19}H_{26}BNO_3$
Exact Mass: 327.2006
Molecular Weight: 327.2310

^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.26 (d, J = 8.0 Hz, 2H), 6.82 (d, J = 8.0 Hz, 2H), 5.81-5.68 (m, 1H), 5.62 (d, J = 10.0 Hz, 1H), 4.17-4.03 (m,1H), 4.00-3.82 (m, 3H), 3.75 (s, 3H), 3.29 (dd, J = 10.6, 4.6 Hz, 1H), 3.21 (dd, J = 11.6, 5.6 Hz, 1H), 3.12 (dd, J = 12.0, 4.0 Hz, 1H), 3.03 (d, J = 10.8 Hz, 1H), 2.85-2.65 (m, 2H), 2.64-2.36 (m, 3H), 0.83 (t, J = 11.2 Hz, 1H), 0.53 (d, J = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 157.3, 137.4, 137.1, 129.1, 125.5, 113.3, 63.2, 62.1, 61.8, 60.4, 58.7, 55.2, 44.6, 42.6, 37.5, 31.0, 16.4.

^{11}B NMR (128 MHz, $CDCl_3$): δ ppm 17.53.

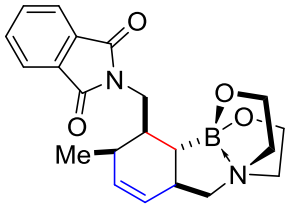
HRMS (APCI): Calculated for $C_{19}H_{27}BNO_3$ $[M+H]^+$: 328.2084, Found: 328.2083.

IR (ν, cm^{-1}): 3008, 2951, 2924, 2850, 1511, 1457, 1241, 1077, 1053, 1014.

(7g)

2-(-8-methyl-2,3,5a,8,9,9a-hexahydro-5H-4λ^4,10λ^4-10,4-(epoxyethano)benzo[3,4][1,2]azaborolo[2,1-b][1,3,2]oxazaborol-9-yl)methyl)isoindoline-1,3-dione

The general procedure was followed using (E)-(3-(1,3-dioxoisoindolin-2-yl)prop-1-en-1-yl)boronic acid (116 mg, 0.5 mmol, 1.0 eq.) and compound **5** (102 mg, 0.55 mmol, 1.1 eq.) as starting material. **7g** was obtained as a white-yellow solid (m.p.: 143.9-145.9 °C, 108 mg, 57%).



Chemical Formula: $C_{21}H_{25}BN_2O_4$
Exact Mass: 380.1907
Molecular Weight: 380.2510

^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.87-7.72 (m, 2H), 7.72-7.58 (m, 2H), 5.67-5.57 (m, 1H), 5.51 (d, *J* = 10.0 Hz, 1H), 4.01 (dd, *J* = 10.4, 6.0 Hz, 1H), 3.95-3.67 (m, 5H), 3.23 (dd, *J* = 10.5, 4.4 Hz, 1H), 3.15-2.94 (m, 2H), 2.88-2.64 (m, 3H), 2.50-2.37 (m, 1H), 2.33 (dd, *J* = 13.2, 10.8 Hz, 1H), 2.28-2.15 (m, 1H), 0.95 (d, *J* = 7.0 Hz, 3H), 0.39 (t, *J* = 11.2 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 169.0, 136.7, 133.5, 132.6, 125.3, 123.0, 63.1, 62.5, 62.0, 60.7, 58.9, 42.2, 41.2, 36.7, 32.5, 15.4.

^{11}B NMR (128 MHz, $CDCl_3$): δ ppm 17.60.

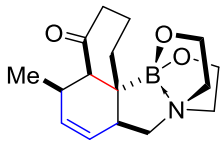
HRMS (APCI): Calculated for $C_{21}H_{26}BN_2O_4$ $[M+H]^+$: 381.1986, Found: 381.1976.

IR (*v*, cm^{-1}): 3005, 2954, 2849, 1770, 1735, 1700, 1396, 1301, 1245, 1184, 1074, 1040, 1016.

(7h)

5-methyl-2,3,4a,5,7a,8,10,11-octahydro-9λ^4,13λ^4-13,9-(epoxyethano)naphtho[8a',1':3,4][1,2]azaborolo[2,1-b][1,3,2]oxazaborol-4(1H)-one

The general procedure was followed using (3-oxocyclohex-1-en-1-yl)boronic acid (42.0 mg, 0.30 mmol, 1.0 eq.) and compound **1** (70.3 mg, 0.33 mmol, 1.1 eq.) as starting material. **7h** was obtained as a white solid (m.p.: 169.2-170.1 °C, 66.1 mg, 76%).



Chemical Formula: $C_{16}H_{24}BNO_3$
Exact Mass: 289.1849
Molecular Weight: 289.1820

^{1}H NMR (400 MHz, Acetone-d_6) δ ppm 5.69 (dt, *J* = 9.8, 3.2 Hz, 1H), 5.53 (dt, *J* = 10.0, 3.2 Hz, 1H), 4.10-3.89 (m, 2H), 3.88-3.74 (m, 2H), 3.39 (dd, *J* = 11.6, 5.5 Hz, 1H), 3.36-3.25 (m, 2H), 3.23-3.13 (m, 1H), 3.08-2.91 (m, 3H), 2.51-2.33 (m, 3H), 2.28-2.12 (m, 1H), 2.00-1.90 (m, 1H), 1.72-1.58 (m, 1H), 1.48-1.37 (m, 2H), 0.96 (d, *J* = 7.8 Hz, 3H).

^{13}C NMR (100 MHz, Acetone-d_6): δ ppm 215.5, 135.1, 126.3, 66.4, 64.3, 62.5, 61.0, 60.9, 54.5, 46.1, 41.7, 21.7, 21.0, 19.7.

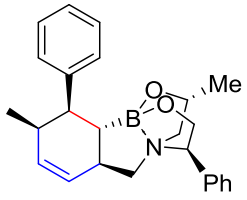
^{11}B NMR (128 MHz, Acetone-d_6): δ ppm 17.28 .

HRMS (APCI): Calculated for $C_{16}H_{24}BNO_3$ $[M+H]^+$: 290.1927, Found: 290.1921.

IR (*v*, cm^{-1}): 2919, 2851, 1683, 1417, 1073, 1015.

(7i$_O$)

(2R,5aR,8R,9S,9aS,13R)-2,8-dimethyl-9,13-diphenyl-2,3,5a,8,9,9a-hexahydro-5H--4λ^4,10λ^4-10,4-(epoxyethano)benzo[3,4][1,2]azaborolo[2,1-b][1,3,2]oxazaborole



Chemical Formula: $C_{25}H_{30}BNO_2$
Exact Mass: 387.2370
Molecular Weight: 387.3300

The general procedure was followed using (E)-styrylboronic acid (74.0 mg, 0.50 mmol, 1.0 eq.) and compound **8** (151.5 mg, 0.55 mmol, 1.1 eq.) as starting material. **7i$_O$** was obtained as a white solid (m.p.: 229.8-231.4 °C, 77.0 mg, 40%, $[\alpha]_D^{20}$ = -38.9° (c 0.50, CH_2Cl_2)), and **7i'$_O$** was obtained as a colorless oil (77.0 mg, 40%, $[\alpha]_D^{20}$ = -69.1° (c 0.50, CH_2Cl_2))

^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.50-7.37 (m, 5H), 7.37-7.31 (m, 2H), 7.32-7.26 (m, 2H), 7.11 (t, *J* = 8.0 Hz, 1H), 5.72 (dt, *J* = 10.0, 3.6 Hz, 1H), 5.52

(d, *J* = 9.8 Hz, 1H), 4.44-4.33 (m, 1H), 4.33-4.24 (m, 2H), 4.01 (t, *J* = 8.2 Hz, 1H), 3.45 (dd, *J* = 11.6, 3.6 Hz, 1H), 3.30 (dd, *J* = 11.6, 5.6 Hz, 1H), 2.59-2.43 (m, 2H), 2.40 (dd, *J* = 11.6, 4.8 Hz, 1H), 2.36-2.19 (m, 2H), 1.22 (d, *J* = 6.4 Hz, 3H), 0.86 (t, *J* = 11.2Hz, 1H), 0.50 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 145.5, 137.0, 133.2, 129.4, 129.1, 128.5, 128.4, 127.9, 125.8, 125.2, 69.2, 68.8, 66.4, 64.1, 56.6, 45.1, 42.1, 37.4, 19.0, 16.6.

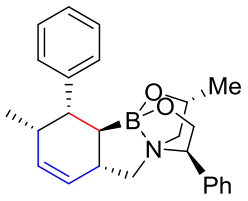
^{11}B NMR (128 MHz, $CDCl_3$): δ ppm 18.63.

HRMS (APCI): Calculated for $C_{25}H_{31}BNO_2$ $[M+H]^+$: 388.2448, Found: 388.2444.

IR (*v*, cm^{-1}): 3004, 2962, 2924, 2848, 1599, 1497, 1451, 1130, 1069, 1019.

(7i'$_O$)

(2R,5aS,8S,9R,9aR,13R)-2,8-dimethyl-9,13-diphenyl-2,3,5a,8,9,9a-hexahydro-5H--4λ^4,10λ^4-10,4-(epoxyethano)benzo[3,4][1,2]azaborolo[2,1-b][1,3,2]oxazaborole



Chemical Formula: $C_{25}H_{30}BNO_2$
Exact Mass: 387.2370
Molecular Weight: 387.3300

^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.46-7.35 (m, 5H), 7.35-7.25 (m, 4H), 7.11 (t, *J* = 7.2 Hz, 1H), 5.80 (dt, *J* = 9.6, 3.0 Hz, 1H), 5.71 (d, *J* = 10.0 Hz, 1H), 4.28 (t, *J* = 10.0 Hz, 1H), 4.23-4.15 (m, 1H), 4.15-4.03 (m, 2H), 3.68 (dd, *J* = 11.4, 5.2 Hz, 1H), 3.35 (dd, *J* = 11.6, 5.6 Hz, 1H), 2.86-2.73 (m, 1H), 2.60-2.39 (m, 2H), 2.33 (dd, *J* = 12.4, 3.6 Hz, 1H), 2.18 (t, *J* = 11.2 Hz, 1H), 1.30 (d, *J* = 6.0 Hz, 3H), 0.98 (t, *J* = 11.6 Hz, 1H), 0.55 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 145.1, 137.3, 133.2, 129.4, 129.2, 128.5, 128.4, 128.0, 125.6, 125.3, 69.4, 67.7, 65.6, 61.6, 59.4, 45.6, 42.2, 37.7, 19.5, 16.5.

^{11}B NMR (128 MHz, $CDCl_3$): δ ppm 17.99.

HRMS (APCI): Calculated for $C_{25}H_{31}BNO_2$ $[M+H]^+$: 388.2448, Found: 388.2444.

IR (*v*, cm^{-1}): 3004, 2986, 2870, 1699, 1653, 1450, 1260, 1152, 1055, 1029, 1010.

5. X-ray diffraction data of 4a. (CCDC 1058696)

The two enantiomers of **4a** co-crystalized as the following:

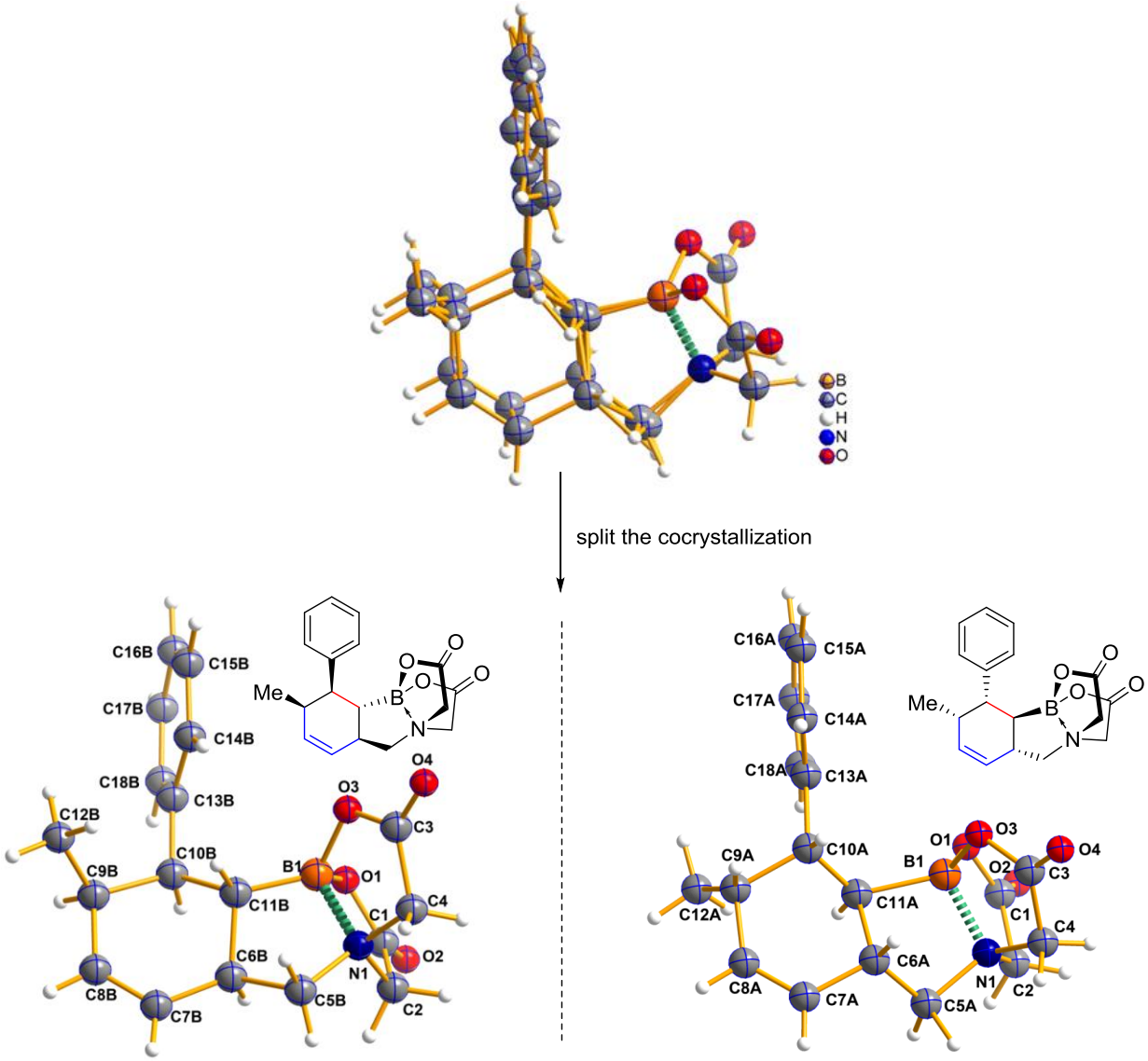


Table S1. Crystal data and structure refinement for **4a**.

Identification code	**4a**
Empirical formula	C18 H20 B N O4
Formula weight	325.16
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P21/c
Unit cell dimensions	a = 13.048(2) A alpha = 90 deg.
	b = 10.7891(19) A beta = 112.161(2) deg.

	c = 12.787(2) A gamma = 90 deg.
Volume	1667.1(5) A^3
Z, Calculated density	4, 1.296 Mg/m^3
Absorption coefficient	0.090 mm^-1
F(000)	688
Crystal size	0.097 x 0.452 x 0.698 mm
Theta range for data collection	1.69 to 24.92 deg.
Limiting indices	-15<=h<=15, -12<=k<=12, -12<=l<=15
Reflections collected / unique	9639 / 2885 [R(int) = 0.0469]
Completeness to theta = 24.92	99.3 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2885 / 381 / 359
Goodness-of-fit on F^2	1.098
Final R indices [I>2sigma(I)]	R1 = 0.0634, wR2 = 0.1492
R indices (all data)	R1 = 0.0740, wR2 = 0.1547
Largest diff. peak and hole	0.235 and -0.255 e.A^-3

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

	x	y	z	U(eq)
B(1)	3734(2)	467(3)	1992(2)	27(1)
C(1)	5380(2)	520(3)	3602(2)	33(1)
C(2)	5232(2)	1852(3)	3200(2)	35(1)
C(3)	4070(2)	930(3)	358(2)	34(1)
C(4)	4527(2)	2044(3)	1096(2)	39(1)
C(5A)	3385(19)	2800(20)	2140(30)	28(3)
C(5B)	3290(12)	2680(11)	2142(16)	37(3)
C(6A)	2289(6)	1970(6)	1531(7)	36(2)
C(6B)	2780(4)	1913(4)	2784(4)	33(1)
C(7A)	1258(6)	2481(7)	1628(8)	50(2)
C(7B)	1764(4)	2369(5)	2928(5)	48(1)
C(8A)	549(6)	1736(7)	1807(8)	50(2)
C(8B)	964(4)	1600(5)	2901(5)	48(1)
C(9A)	668(8)	366(8)	1985(10)	44(2)
C(9B)	950(5)	213(5)	2671(6)	38(1)
C(10A)	1623(5)	-148(7)	1669(6)	37(2)
C(10B)	2104(3)	-248(4)	2716(4)	31(1)
C(11A)	2502(18)	630(20)	2140(20)	25(2)
C(11B)	2640(12)	708(15)	2115(15)	30(2)
C(12A)	744(8)	33(10)	3143(10)	59(3)

C(12B)	-10(4)	-76(5)	1573(5)	49(1)
C(13B)	2056(9)	-1568(11)	2358(8)	38(2)
C(13A)	1920(11)	-1531(14)	1996(10)	33(2)
C(14B)	1796(5)	-1837(7)	1197(7)	42(2)
C(14A)	1499(8)	-2331(11)	1124(9)	48(2)
C(15A)	1700(9)	-3605(12)	1274(11)	54(2)
C(15B)	1690(5)	-3056(7)	801(7)	53(2)
C(16A)	2219(13)	-4042(14)	2369(13)	46(2)
C(16B)	1927(7)	-4026(7)	1593(10)	52(2)
C(17A)	2612(8)	-3213(10)	3286(9)	50(2)
C(17B)	2261(10)	-3800(11)	2720(10)	53(2)
C(18A)	2444(7)	-1946(10)	3054(9)	44(2)
C(18B)	2319(6)	-2572(8)	3100(7)	45(2)
N(1)	4257(2)	1889(2)	2118(2)	28(1)
O(1)	4601(1)	-209(2)	2902(2)	32(1)
O(2)	6107(2)	154(2)	4441(2)	49(1)
O(3)	3692(1)	77(2)	872(1)	33(1)
O(4)	4037(2)	831(2)	-592(2)	50(1)

Table S3. Bond lengths [A] and angles [deg] for **4a**.

B(1)-O(3)	1.473(3)
B(1)-O(1)	1.474(3)
B(1)-N(1)	1.662(3)
B(1)-C(11A)	1.70(2)
C(1)-O(2)	1.199(3)
C(1)-O(1)	1.330(3)
C(1)-C(2)	1.513(4)
C(2)-N(1)	1.486(3)
C(2)-H(2A)	0.9700
C(2)-H(2B)	0.9700
C(3)-O(4)	1.203(3)
C(3)-O(3)	1.330(3)
C(3)-C(4)	1.505(4)
C(4)-N(1)	1.487(3)
C(4)-H(4A)	0.9700
C(4)-H(4B)	0.9700
C(5A)-N(1)	1.512(16)
C(5A)-C(6A)	1.62(3)
C(5A)-H(5AA)	0.9700
C(5A)-H(5AB)	0.9700

C(5A)-H(5BA)	0.95(6)
C(5A)-H(5BB)	0.92(6)
C(5B)-C(6B)	1.487(15)
C(5B)-H(5BA)	0.92(5)
C(5B)-H(5BB)	1.05(5)
C(6A)-C(7A)	1.502(11)
C(6A)-C(11A)	1.62(3)
C(6A)-H(5BA)	1.20(5)
C(6A)-H(6A)	0.9800
C(6A)-H(11B)	1.33(6)
C(6B)-C(7B)	1.490(6)
C(6B)-C(11B)	1.529(18)
C(6B)-H(6B)	1.09(6)
C(7A)-C(8A)	1.309(11)
C(7A)-H(7A)	0.9300
C(7B)-C(8B)	1.323(7)
C(7B)-H(7B)	0.9300
C(8A)-C(9A)	1.494(11)
C(8A)-H(8A)	0.9300
C(8B)-C(9B)	1.524(7)
C(8B)-H(8B)	0.9300
C(9A)-C(12A)	1.491(13)
C(9A)-C(10A)	1.550(11)
C(9A)-H(9A)	0.9800
C(9B)-C(12B)	1.520(8)
C(9B)-C(10B)	1.567(7)
C(9B)-H(9B)	0.9800
C(10A)-C(11A)	1.36(2)
C(10A)-C(13A)	1.558(16)
C(10A)-H(10A)	0.9800
C(10A)-H(11B)	1.27(6)
C(10B)-C(13B)	1.490(12)
C(10B)-C(11B)	1.597(16)
C(10B)-H(10B)	0.9800
C(11A)-H(11A)	0.9800
C(11A)-H(11B)	0.97(6)
C(11B)-H(11B)	1.00(6)
C(12A)-H(12A)	0.9600
C(12A)-H(12B)	0.9600
C(12A)-H(12C)	0.9600
C(12B)-H(12D)	0.9600
C(12B)-H(12E)	0.9600
C(12B)-H(12F)	0.9600

C(13B)-C(18B)	1.394(12)
C(13B)-C(14B)	1.423(12)
C(13A)-C(18A)	1.342(14)
C(13A)-C(14A)	1.352(17)
C(14B)-C(15B)	1.398(9)
C(14B)-H(14B)	0.9300
C(14A)-C(15A)	1.399(15)
C(14A)-H(14A)	0.9300
C(15A)-C(16A)	1.387(18)
C(15A)-H(15A)	0.9300
C(15B)-C(16B)	1.406(11)
C(15B)-H(15B)	0.9300
C(16A)-C(17A)	1.408(16)
C(16A)-H(16A)	0.9300
C(16B)-C(17B)	1.362(15)
C(16B)-H(16B)	0.9300
C(17A)-C(18A)	1.399(12)
C(17A)-H(17A)	0.9300
C(17B)-C(18B)	1.403(13)
C(17B)-H(17B)	0.9300
C(18A)-H(18A)	0.9300
C(18B)-H(18B)	0.9300
O(3)-B(1)-O(1)	111.2(2)
O(3)-B(1)-N(1)	102.86(19)
O(1)-B(1)-N(1)	102.47(19)
O(3)-B(1)-C(11A)	116.6(10)
O(1)-B(1)-C(11A)	116.1(10)
N(1)-B(1)-C(11A)	105.4(9)
O(2)-C(1)-O(1)	123.6(3)
O(2)-C(1)-C(2)	124.9(2)
O(1)-C(1)-C(2)	111.5(2)
N(1)-C(2)-C(1)	107.2(2)
N(1)-C(2)-H(2A)	110.3
C(1)-C(2)-H(2A)	110.3
N(1)-C(2)-H(2B)	110.3
C(1)-C(2)-H(2B)	110.3
H(2A)-C(2)-H(2B)	108.5
O(4)-C(3)-O(3)	124.0(3)
O(4)-C(3)-C(4)	123.9(3)
O(3)-C(3)-C(4)	112.1(2)
N(1)-C(4)-C(3)	107.0(2)
N(1)-C(4)-H(4A)	110.3
C(3)-C(4)-H(4A)	110.3

N(1)-C(4)-H(4B)	110.3
C(3)-C(4)-H(4B)	110.3
H(4A)-C(4)-H(4B)	108.6
N(1)-C(5A)-C(6A)	99.5(14)
N(1)-C(5A)-H(5AA)	111.9
C(6A)-C(5A)-H(5AA)	111.9
N(1)-C(5A)-H(5AB)	111.9
C(6A)-C(5A)-H(5AB)	111.9
H(5AA)-C(5A)-H(5AB)	109.6
N(1)-C(5A)-H(5BA)	105(3)
C(6A)-C(5A)-H(5BA)	47(3)
H(5AA)-C(5A)-H(5BA)	66.4
H(5AB)-C(5A)-H(5BA)	140.5
N(1)-C(5A)-H(5BB)	111(4)
C(6A)-C(5A)-H(5BB)	148(4)
H(5AA)-C(5A)-H(5BB)	67.2
H(5AB)-C(5A)-H(5BB)	46.8
H(5BA)-C(5A)-H(5BB)	129(5)
C(6B)-C(5B)-H(5BA)	114(4)
C(6B)-C(5B)-H(5BB)	112(3)
H(5BA)-C(5B)-H(5BB)	117(4)
C(7A)-C(6A)-C(11A)	106.6(9)
C(7A)-C(6A)-C(5A)	114.4(8)
C(11A)-C(6A)-C(5A)	107.6(12)
C(7A)-C(6A)-H(5BA)	110(2)
C(11A)-C(6A)-H(5BA)	137(3)
C(5A)-C(6A)-H(5BA)	36(3)
C(7A)-C(6A)-H(6A)	109.4
C(11A)-C(6A)-H(6A)	109.4
C(5A)-C(6A)-H(6A)	109.4
H(5BA)-C(6A)-H(6A)	78.9
C(7A)-C(6A)-H(11B)	101(3)
C(11A)-C(6A)-H(11B)	37(3)
C(5A)-C(6A)-H(11B)	138(3)
H(5BA)-C(6A)-H(11B)	146(4)
H(6A)-C(6A)-H(11B)	77.4
C(5B)-C(6B)-C(7B)	119.3(5)
C(5B)-C(6B)-C(11B)	98.5(9)
C(7B)-C(6B)-C(11B)	115.2(6)
C(5B)-C(6B)-H(6B)	113(3)
C(7B)-C(6B)-H(6B)	107(3)
C(11B)-C(6B)-H(6B)	103(3)
C(8A)-C(7A)-C(6A)	120.2(7)

C(8A)-C(7A)-H(7A)	119.9
C(6A)-C(7A)-H(7A)	119.9
C(8B)-C(7B)-C(6B)	121.3(4)
C(8B)-C(7B)-H(7B)	119.3
C(6B)-C(7B)-H(7B)	119.3
C(7A)-C(8A)-C(9A)	126.4(8)
C(7A)-C(8A)-H(8A)	116.8
C(9A)-C(8A)-H(8A)	116.8
C(7B)-C(8B)-C(9B)	125.0(4)
C(7B)-C(8B)-H(8B)	117.5
C(9B)-C(8B)-H(8B)	117.5
C(12A)-C(9A)-C(8A)	110.7(9)
C(12A)-C(9A)-C(10A)	114.5(8)
C(8A)-C(9A)-C(10A)	111.3(7)
C(12A)-C(9A)-H(9A)	106.7
C(8A)-C(9A)-H(9A)	106.7
C(10A)-C(9A)-H(9A)	106.7
C(12B)-C(9B)-C(8B)	109.0(5)
C(12B)-C(9B)-C(10B)	114.5(4)
C(8B)-C(9B)-C(10B)	111.3(4)
C(12B)-C(9B)-H(9B)	107.2
C(8B)-C(9B)-H(9B)	107.2
C(10B)-C(9B)-H(9B)	107.2
C(11A)-C(10A)-C(9A)	106.9(12)
C(11A)-C(10A)-C(13A)	112.8(12)
C(9A)-C(10A)-C(13A)	114.6(7)
C(11A)-C(10A)-H(10A)	107.4
C(9A)-C(10A)-H(10A)	107.4
C(13A)-C(10A)-H(10A)	107.4
C(11A)-C(10A)-H(11B)	43(3)
C(9A)-C(10A)-H(11B)	106(3)
C(13A)-C(10A)-H(11B)	138(3)
H(10A)-C(10A)-H(11B)	66.5
C(13B)-C(10B)-C(9B)	111.3(5)
C(13B)-C(10B)-C(11B)	116.5(8)
C(9B)-C(10B)-C(11B)	111.5(7)
C(13B)-C(10B)-H(10B)	105.5
C(9B)-C(10B)-H(10B)	105.5
C(11B)-C(10B)-H(10B)	105.5
C(10A)-C(11A)-C(6A)	112.0(16)
C(10A)-C(11A)-B(1)	124.2(17)
C(6A)-C(11A)-B(1)	92.2(13)
C(10A)-C(11A)-H(11A)	108.9

C(6A)-C(11A)-H(11A)	108.9
B(1)-C(11A)-H(11A)	108.9
C(10A)-C(11A)-H(11B)	63(4)
C(6A)-C(11A)-H(11B)	55(4)
B(1)-C(11A)-H(11B)	99(4)
H(11A)-C(11A)-H(11B)	148.7
C(6B)-C(11B)-C(10B)	105.2(11)
C(6B)-C(11B)-H(11B)	111(4)
C(10B)-C(11B)-H(11B)	101(3)
C(9B)-C(12B)-H(12D)	109.5
C(9B)-C(12B)-H(12E)	109.5
H(12D)-C(12B)-H(12E)	109.5
C(9B)-C(12B)-H(12F)	109.5
H(12D)-C(12B)-H(12F)	109.5
H(12E)-C(12B)-H(12F)	109.5
C(18B)-C(13B)-C(14B)	116.9(9)
C(18B)-C(13B)-C(10B)	124.3(8)
C(14B)-C(13B)-C(10B)	118.8(8)
C(18A)-C(13A)-C(14A)	120.8(13)
C(18A)-C(13A)-C(10A)	124.8(12)
C(14A)-C(13A)-C(10A)	114.1(10)
C(15B)-C(14B)-C(13B)	121.5(8)
C(15B)-C(14B)-H(14B)	119.3
C(13B)-C(14B)-H(14B)	119.3
C(13A)-C(14A)-C(15A)	121.2(11)
C(13A)-C(14A)-H(14A)	119.4
C(15A)-C(14A)-H(14A)	119.4
C(16A)-C(15A)-C(14A)	117.8(12)
C(16A)-C(15A)-H(15A)	121.1
C(14A)-C(15A)-H(15A)	121.1
C(14B)-C(15B)-C(16B)	118.3(8)
C(14B)-C(15B)-H(15B)	120.8
C(16B)-C(15B)-H(15B)	120.8
C(15A)-C(16A)-C(17A)	120.7(13)
C(15A)-C(16A)-H(16A)	119.7
C(17A)-C(16A)-H(16A)	119.7
C(17B)-C(16B)-C(15B)	121.6(9)
C(17B)-C(16B)-H(16B)	119.2
C(15B)-C(16B)-H(16B)	119.2
C(18A)-C(17A)-C(16A)	117.7(11)
C(18A)-C(17A)-H(17A)	121.1
C(16A)-C(17A)-H(17A)	121.1
C(16B)-C(17B)-C(18B)	119.3(10)

C(16B)-C(17B)-H(17B)	120.4
C(18B)-C(17B)-H(17B)	120.4
C(13A)-C(18A)-C(17A)	121.3(12)
C(13A)-C(18A)-H(18A)	119.4
C(17A)-C(18A)-H(18A)	119.4
C(13B)-C(18B)-C(17B)	122.1(9)
C(13B)-C(18B)-H(18B)	119.0
C(17B)-C(18B)-H(18B)	119.0
C(2)-N(1)-C(4)	114.7(2)
C(2)-N(1)-C(5A)	112.6(12)
C(4)-N(1)-C(5A)	112.1(10)
C(2)-N(1)-B(1)	103.97(19)
C(4)-N(1)-B(1)	104.04(19)
C(5A)-N(1)-B(1)	108.5(10)
C(1)-O(1)-B(1)	113.7(2)
C(3)-O(3)-B(1)	113.4(2)

Symmetry transformations used to generate equivalent atoms.

Table S4. Anisotropic displacement parameters (A^2 x 10^3) for **4a**
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
B(1)	26(1)	23(1)	33(2)	-5(1)	12(1)	-3(1)
C(1)	29(1)	39(2)	32(1)	-4(1)	10(1)	1(1)
C(2)	29(1)	34(2)	39(2)	-5(1)	11(1)	-3(1)
C(3)	37(1)	35(2)	33(2)	2(1)	16(1)	3(1)
C(4)	47(2)	38(2)	40(2)	-2(1)	24(1)	-9(1)
C(5A)	24(4)	28(4)	38(4)	3(3)	16(3)	-10(3)
C(5B)	34(5)	20(4)	53(4)	-9(3)	13(4)	6(4)
C(6A)	30(3)	29(3)	49(3)	5(3)	15(3)	-6(2)
C(6B)	31(2)	27(2)	45(2)	-7(2)	19(2)	-1(2)
C(7A)	36(3)	33(3)	75(4)	8(3)	16(3)	-1(3)
C(7B)	43(2)	39(2)	70(3)	-16(2)	31(2)	5(2)
C(8A)	25(3)	39(4)	81(4)	14(3)	16(3)	5(3)
C(8B)	44(3)	42(3)	71(3)	-8(2)	36(2)	10(2)
C(9A)	29(4)	41(4)	60(4)	19(4)	17(4)	-3(3)
C(9B)	39(3)	40(3)	44(3)	4(3)	27(3)	5(2)
C(10A)	28(3)	36(3)	45(3)	11(3)	12(2)	-6(3)

C(10B)	29(2)	31(2)	34(2)	0(2)	13(2)	3(2)
C(11A)	16(4)	26(4)	40(3)	-5(4)	18(3)	6(3)
C(11B)	27(4)	26(3)	36(3)	3(2)	13(3)	-9(3)
C(12A)	45(5)	60(6)	84(7)	26(5)	40(5)	8(4)
C(12B)	30(3)	53(3)	63(3)	0(3)	17(2)	14(2)
C(13B)	32(3)	30(3)	56(4)	9(4)	23(3)	8(2)
C(13A)	29(3)	32(3)	50(4)	7(4)	27(3)	-11(3)
C(14B)	37(3)	28(3)	68(4)	-5(3)	27(3)	-3(2)
C(14A)	45(4)	42(4)	62(4)	3(4)	28(3)	-1(3)
C(15A)	49(4)	42(5)	77(5)	7(4)	30(4)	0(4)
C(15B)	43(3)	35(4)	89(4)	-6(3)	33(3)	-3(3)
C(16A)	44(4)	32(4)	76(6)	10(4)	39(4)	-1(3)
C(16B)	41(4)	26(3)	95(5)	6(4)	32(4)	2(3)
C(17A)	44(4)	35(5)	76(4)	17(4)	28(3)	7(3)
C(17B)	39(3)	30(5)	90(6)	14(4)	25(4)	4(3)
C(18A)	33(3)	35(4)	63(4)	10(4)	18(3)	0(3)
C(18B)	33(3)	31(4)	76(3)	23(4)	24(2)	8(3)
N(1)	28(1)	26(1)	31(1)	-2(1)	14(1)	-2(1)
O(1)	32(1)	29(1)	36(1)	1(1)	12(1)	2(1)
O(2)	42(1)	52(1)	41(1)	3(1)	3(1)	3(1)
O(3)	39(1)	29(1)	35(1)	-5(1)	17(1)	-2(1)
O(4)	73(2)	49(1)	34(1)	0(1)	25(1)	3(1)

Table S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for **4a**.

	x	y	z	U(eq)
H(2A)	5111	2382	3756	42
H(2B)	5888	2138	3087	42
H(4A)	5322	2094	1305	47
H(4B)	4195	2798	698	47
H(5AA)	3382	3547	1722	34
H(5AB)	3476	3017	2911	34
H(5BA)	2840(40)	2800(50)	1400(40)	44
H(5BB)	3700(40)	3460(50)	2600(40)	44
H(6A)	2169	1868	732	43
H(7A)	1122	3329	1561	60
H(7B)	1690	3211	3039	57
H(8A)	-92	2094	1826	60
H(8B)	366	1931	3032	58

H(9A)	-16	-8	1457	52
H(9B)	802	-210	3278	46
H(10A)	1389	-85	847	44
H(10B)	2589	-238	3517	38
H(11A)	2637	740	2940	30
H(12A)	1445	300	3685	88
H(12B)	678	-849	3195	88
H(12C)	158	434	3295	88
H(12D)	-676	289	1588	74
H(12E)	-103	-958	1486	74
H(12F)	141	259	950	74
H(14B)	1695	-1187	690	51
H(14A)	1069	-2029	412	57
H(15A)	1491	-4142	660	65
H(6B)	3370(50)	1650(50)	3620(50)	65
H(11B)	2030(50)	780(50)	1350(50)	65
H(15B)	1467	-3223	34	64
H(16A)	2309	-4890	2498	55
H(16B)	1854	-4842	1340	63
H(17A)	2970	-3499	4020	60
H(17B)	2450	-4453	3233	63
H(18A)	2702	-1380	3644	53
H(18B)	2539	-2423	3870	54

Table S6. Torsion angles [deg] for **4a**.

O(2)-C(1)-C(2)-N(1)	178.4(2)
O(1)-C(1)-C(2)-N(1)	-1.3(3)
O(4)-C(3)-C(4)-N(1)	171.3(3)
O(3)-C(3)-C(4)-N(1)	-7.8(3)
N(1)-C(5A)-C(6A)-C(7A)	167.4(9)
N(1)-C(5A)-C(6A)-C(11A)	49.2(17)
C(11A)-C(6A)-C(7A)-C(8A)	-21.1(15)
C(5A)-C(6A)-C(7A)-C(8A)	-139.8(13)
C(5B)-C(6B)-C(7B)-C(8B)	142.7(10)
C(11B)-C(6B)-C(7B)-C(8B)	25.8(10)
C(6A)-C(7A)-C(8A)-C(9A)	2.9(15)
C(6B)-C(7B)-C(8B)-C(9B)	-3.1(9)
C(7A)-C(8A)-C(9A)-C(12A)	115.6(11)
C(7A)-C(8A)-C(9A)-C(10A)	-12.8(15)
C(7B)-C(8B)-C(9B)-C(12B)	-115.4(6)

C(7B)-C(8B)-C(9B)-C(10B)	11.8(9)
C(12A)-C(9A)-C(10A)-C(11A)	-80.8(15)
C(8A)-C(9A)-C(10A)-C(11A)	45.5(16)
C(12A)-C(9A)-C(10A)-C(13A)	45.0(12)
C(8A)-C(9A)-C(10A)-C(13A)	171.4(8)
C(12B)-C(9B)-C(10B)-C(13B)	-49.1(8)
C(8B)-C(9B)-C(10B)-C(13B)	-173.3(6)
C(12B)-C(9B)-C(10B)-C(11B)	82.8(9)
C(8B)-C(9B)-C(10B)-C(11B)	-41.4(9)
C(9A)-C(10A)-C(11A)-C(6A)	-69.3(18)
C(13A)-C(10A)-C(11A)-C(6A)	163.9(12)
C(9A)-C(10A)-C(11A)-B(1)	-178.2(17)
C(13A)-C(10A)-C(11A)-B(1)	55(2)
C(7A)-C(6A)-C(11A)-C(10A)	57.6(19)
C(5A)-C(6A)-C(11A)-C(10A)	-179.3(16)
C(7A)-C(6A)-C(11A)-B(1)	-173.9(9)
C(5A)-C(6A)-C(11A)-B(1)	-50.8(15)
O(3)-B(1)-C(11A)-C(10A)	39(2)
O(1)-B(1)-C(11A)-C(10A)	-95(2)
N(1)-B(1)-C(11A)-C(10A)	152.6(19)
O(3)-B(1)-C(11A)-C(6A)	-79.4(12)
O(1)-B(1)-C(11A)-C(6A)	146.5(8)
N(1)-B(1)-C(11A)-C(6A)	33.9(13)
C(5B)-C(6B)-C(11B)-C(10B)	179.2(9)
C(7B)-C(6B)-C(11B)-C(10B)	-52.7(10)
C(13B)-C(10B)-C(11B)-C(6B)	-169.7(7)
C(9B)-C(10B)-C(11B)-C(6B)	61.0(10)
C(9B)-C(10B)-C(13B)-C(18B)	-94.0(10)
C(11B)-C(10B)-C(13B)-C(18B)	136.7(10)
C(9B)-C(10B)-C(13B)-C(14B)	90.3(9)
C(11B)-C(10B)-C(13B)-C(14B)	-39.0(12)
C(11A)-C(10A)-C(13A)-C(18A)	50(2)
C(9A)-C(10A)-C(13A)-C(18A)	-72.4(14)
C(11A)-C(10A)-C(13A)-C(14A)	-136.4(16)
C(9A)-C(10A)-C(13A)-C(14A)	100.9(12)
C(18B)-C(13B)-C(14B)-C(15B)	6.9(13)
C(10B)-C(13B)-C(14B)-C(15B)	-177.1(7)
C(18A)-C(13A)-C(14A)-C(15A)	-7.1(19)
C(10A)-C(13A)-C(14A)-C(15A)	179.3(10)
C(13A)-C(14A)-C(15A)-C(16A)	8.3(17)
C(13B)-C(14B)-C(15B)-C(16B)	-4.7(10)
C(14A)-C(15A)-C(16A)-C(17A)	-5.1(19)
C(14B)-C(15B)-C(16B)-C(17B)	-0.5(12)

C(15A)-C(16A)-C(17A)-C(18A)	0.9(18)
C(15B)-C(16B)-C(17B)-C(18B)	3.2(15)
C(14A)-C(13A)-C(18A)-C(17A)	2.5(18)
C(10A)-C(13A)-C(18A)-C(17A)	175.4(9)
C(16A)-C(17A)-C(18A)-C(13A)	0.5(15)
C(14B)-C(13B)-C(18B)-C(17B)	-4.1(14)
C(10B)-C(13B)-C(18B)-C(17B)	-179.9(9)
C(16B)-C(17B)-C(18B)-C(13B)	-0.8(15)
C(1)-C(2)-N(1)-C(4)	-106.0(2)
C(1)-C(2)-N(1)-C(5A)	124.2(9)
C(1)-C(2)-N(1)-B(1)	6.9(2)
C(3)-C(4)-N(1)-C(2)	120.3(2)
C(3)-C(4)-N(1)-C(5A)	-109.7(12)
C(3)-C(4)-N(1)-B(1)	7.4(3)
C(6A)-C(5A)-N(1)-C(2)	-136.8(10)
C(6A)-C(5A)-N(1)-C(4)	92.1(11)
C(6A)-C(5A)-N(1)-B(1)	-22.3(15)
O(3)-B(1)-N(1)-C(2)	-125.4(2)
O(1)-B(1)-N(1)-C(2)	-9.9(2)
C(11A)-B(1)-N(1)-C(2)	112.0(10)
O(3)-B(1)-N(1)-C(4)	-5.0(2)
O(1)-B(1)-N(1)-C(4)	110.5(2)
C(11A)-B(1)-N(1)-C(4)	-127.6(10)
O(3)-B(1)-N(1)-C(5A)	114.5(12)
O(1)-B(1)-N(1)-C(5A)	-130.0(12)
C(11A)-B(1)-N(1)-C(5A)	-8.1(16)
O(2)-C(1)-O(1)-B(1)	174.2(2)
C(2)-C(1)-O(1)-B(1)	-6.1(3)
O(3)-B(1)-O(1)-C(1)	119.2(2)
N(1)-B(1)-O(1)-C(1)	9.9(3)
C(11A)-B(1)-O(1)-C(1)	-104.3(10)
O(4)-C(3)-O(3)-B(1)	-174.7(3)
C(4)-C(3)-O(3)-B(1)	4.4(3)
O(1)-B(1)-O(3)-C(3)	-108.6(2)
N(1)-B(1)-O(3)-C(3)	0.5(3)
C(11A)-B(1)-O(3)-C(3)	115.2(10)

Symmetry transformations used to generate equivalent atoms.

6. X-ray diffraction data of 7i$_o$. (CCDC 1058694)

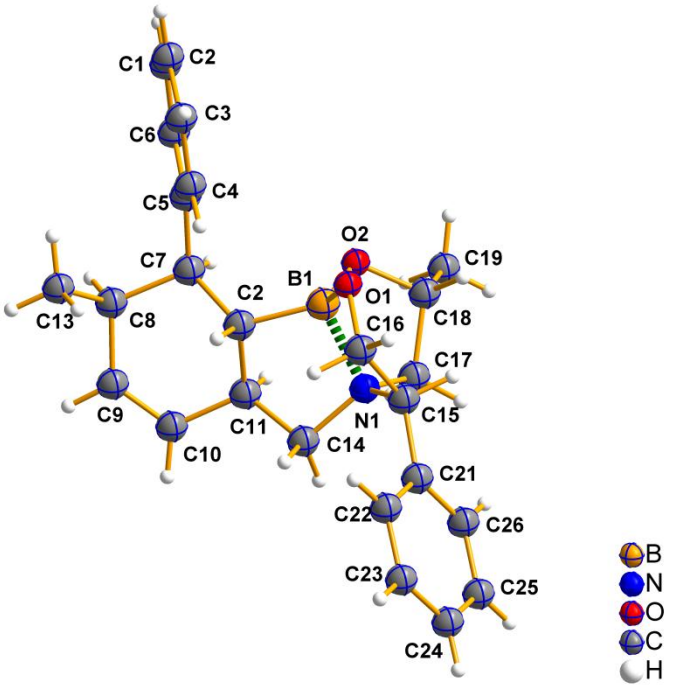


Table S8. Crystal data and structure refinement for **7i**.

Identification code	**7i**
Empirical formula	C25 H30 B N O2
Formula weight	387.31
Temperature	296(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P2(1)
Unit cell dimensions	a = 9.835(4) A alpha = 90 deg. b = 10.412(4) A beta = 97.195(6) deg. c = 10.568(4) A gamma = 90 deg.
Volume	1073.8(7) A^3
Z, Calculated density	2, 1.198 Mg/m^3
Absorption coefficient	0.074 mm^-1
F(000)	416
Crystal size	0.17 x 0.15 x 0.03 mm
Theta range for data collection	1.94 to 24.66 deg.
Limiting indices	-11<=h<=11, -11<=k<=12, -10<=l<=12
Reflections collected / unique	6277 / 3511 [R(int) = 0.0361]
Completeness to theta = 24.66	98.4 %
Max. and min. transmission	0.9975 and 0.9877
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3511 / 1 / 264

Goodness-of-fit on F^2	1.041
Final R indices [I>2sigma(I)]	R1 = 0.0537, wR2 = 0.0798
R indices (all data)	R1 = 0.0909, wR2 = 0.0903
Absolute structure parameter	-1.5(16)
Largest diff. peak and hole	0.187 and -0.190 e.A^-3

Table S9. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for **7i**.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
B(1)	5108(3)	5154(3)	6661(3)	26(1)
N(1)	4162(2)	6517(2)	6248(2)	24(1)
O(1)	4026(2)	4194(2)	6554(2)	30(1)
O(2)	6001(2)	5100(2)	5690(2)	28(1)
C(1)	8916(3)	1779(3)	8204(3)	44(1)
C(2)	7899(3)	974(3)	8516(3)	45(1)
C(3)	6669(3)	1490(3)	8735(3)	41(1)
C(4)	6462(3)	2796(3)	8676(3)	36(1)
C(5)	7481(3)	3642(3)	8410(3)	26(1)
C(6)	8716(3)	3098(3)	8161(3)	34(1)
C(7)	7318(3)	5079(3)	8447(3)	26(1)
C(8)	7894(3)	5638(3)	9766(3)	32(1)
C(9)	7413(3)	6993(3)	9962(3)	35(1)
C(10)	6491(3)	7621(3)	9175(3)	34(1)
C(11)	5900(3)	7022(3)	7941(3)	27(1)
C(12)	5860(3)	5554(2)	8028(3)	23(1)
C(13)	7586(3)	4808(3)	10891(3)	42(1)
C(14)	4464(3)	7406(3)	7360(3)	28(1)
C(15)	2718(3)	6028(3)	6009(3)	30(1)
C(16)	2798(3)	4799(3)	6792(3)	34(1)
C(17)	4741(3)	6967(3)	5081(3)	32(1)
C(18)	5420(3)	5774(3)	4582(3)	32(1)
C(19)	6544(3)	6130(3)	3796(3)	44(1)
C(21)	1614(3)	6997(3)	6192(3)	28(1)
C(22)	753(3)	6841(3)	7125(3)	40(1)
C(23)	-289(3)	7714(3)	7240(3)	44(1)
C(24)	-482(3)	8746(3)	6438(3)	42(1)
C(25)	372(3)	8923(3)	5522(3)	45(1)

C(26)	1404(3)	8051(3)	5404(3)	40(1)

Table S10. Bond lengths [A] and angles [deg] for **7i**

B(1)-O(2)	1.433(3)
B(1)-O(1)	1.454(4)
B(1)-C(12)	1.594(4)
B(1)-N(1)	1.723(4)
N(1)-C(14)	1.496(3)
N(1)-C(17)	1.497(3)
N(1)-C(15)	1.501(3)
O(1)-C(16)	1.413(3)
O(2)-C(18)	1.421(3)
C(1)-C(2)	1.376(4)
C(1)-C(6)	1.387(4)
C(2)-C(3)	1.370(4)
C(3)-C(4)	1.375(4)
C(4)-C(5)	1.390(4)
C(5)-C(6)	1.394(4)
C(5)-C(7)	1.505(4)
C(7)-C(12)	1.530(3)
C(7)-C(8)	1.551(4)
C(8)-C(9)	1.511(4)
C(8)-C(13)	1.531(4)
C(9)-C(10)	1.324(4)
C(10)-C(11)	1.496(4)
C(11)-C(14)	1.521(4)
C(11)-C(12)	1.532(4)
C(15)-C(21)	1.512(4)
C(15)-C(16)	1.521(4)
C(17)-C(18)	1.535(4)
C(18)-C(19)	1.509(4)
C(21)-C(26)	1.378(4)
C(21)-C(22)	1.388(4)
C(22)-C(23)	1.386(4)
C(23)-C(24)	1.367(4)
C(24)-C(25)	1.371(4)
C(25)-C(26)	1.379(4)
O(2)-B(1)-O(1)	115.2(3)
O(2)-B(1)-C(12)	113.8(2)
O(1)-B(1)-C(12)	120.1(2)

O(2)-B(1)-N(1)	102.2(2)
O(1)-B(1)-N(1)	100.4(2)
C(12)-B(1)-N(1)	100.9(2)
C(14)-N(1)-C(17)	113.3(2)
C(14)-N(1)-C(15)	115.6(2)
C(17)-N(1)-C(15)	114.7(2)
C(14)-N(1)-B(1)	105.2(2)
C(17)-N(1)-B(1)	102.55(19)
C(15)-N(1)-B(1)	103.4(2)
C(16)-O(1)-B(1)	108.2(2)
C(18)-O(2)-B(1)	110.6(2)
C(2)-C(1)-C(6)	120.4(3)
C(3)-C(2)-C(1)	119.0(3)
C(2)-C(3)-C(4)	120.6(3)
C(3)-C(4)-C(5)	122.0(3)
C(4)-C(5)-C(6)	116.6(3)
C(4)-C(5)-C(7)	122.9(3)
C(6)-C(5)-C(7)	120.5(3)
C(1)-C(6)-C(5)	121.4(3)
C(5)-C(7)-C(12)	114.4(2)
C(5)-C(7)-C(8)	111.6(2)
C(12)-C(7)-C(8)	111.3(2)
C(9)-C(8)-C(13)	108.9(2)
C(9)-C(8)-C(7)	112.8(2)
C(13)-C(8)-C(7)	113.6(2)
C(10)-C(9)-C(8)	125.3(3)
C(9)-C(10)-C(11)	120.2(3)
C(10)-C(11)-C(14)	118.8(2)
C(10)-C(11)-C(12)	111.9(2)
C(14)-C(11)-C(12)	104.9(2)
C(7)-C(12)-C(11)	108.1(2)
C(7)-C(12)-B(1)	119.3(2)
C(11)-C(12)-B(1)	102.7(2)
N(1)-C(14)-C(11)	103.7(2)
N(1)-C(15)-C(21)	115.6(2)
N(1)-C(15)-C(16)	102.2(2)
C(21)-C(15)-C(16)	118.7(2)
O(1)-C(16)-C(15)	105.4(2)
N(1)-C(17)-C(18)	104.9(2)
O(2)-C(18)-C(19)	109.2(2)
O(2)-C(18)-C(17)	105.3(2)
C(19)-C(18)-C(17)	111.7(2)
C(26)-C(21)-C(22)	117.6(3)

C(26)-C(21)-C(15)	120.7(3)
C(22)-C(21)-C(15)	121.7(3)
C(23)-C(22)-C(21)	120.6(3)
C(24)-C(23)-C(22)	120.5(3)
C(23)-C(24)-C(25)	119.6(3)
C(24)-C(25)-C(26)	119.9(3)
C(21)-C(26)-C(25)	121.8(3)

Symmetry transformations used to generate equivalent atoms.

Table S11. Anisotropic displacement parameters (A^2 x 10^3) for **7i**.
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
B(1)	33(2)	18(2)	28(2)	4(2)	8(2)	7(2)
N(1)	28(1)	22(1)	22(1)	-1(1)	8(1)	2(1)
O(1)	32(1)	19(1)	40(1)	-3(1)	5(1)	-1(1)
O(2)	38(1)	26(1)	23(1)	1(1)	10(1)	9(1)
C(1)	41(2)	39(2)	54(2)	-1(2)	8(2)	18(2)
C(2)	52(2)	28(2)	56(3)	5(2)	7(2)	11(2)
C(3)	47(2)	22(2)	57(2)	4(2)	14(2)	-3(2)
C(4)	38(2)	30(2)	40(2)	1(2)	11(2)	4(2)
C(5)	29(2)	29(2)	19(2)	-1(2)	2(1)	2(1)
C(6)	30(2)	36(2)	38(2)	1(2)	11(2)	6(2)
C(7)	27(2)	22(2)	31(2)	-1(2)	11(1)	-1(1)
C(8)	30(2)	40(2)	27(2)	-6(2)	7(1)	-1(2)
C(9)	32(2)	39(2)	35(2)	-12(2)	8(2)	-2(2)
C(10)	31(2)	29(2)	43(2)	-14(2)	13(2)	-3(2)
C(11)	28(2)	23(2)	32(2)	-5(2)	14(1)	1(1)
C(12)	24(2)	20(2)	29(2)	0(1)	13(1)	-1(1)
C(13)	49(2)	50(2)	29(2)	-1(2)	9(2)	2(2)
C(14)	34(2)	20(2)	32(2)	-4(2)	15(1)	1(1)
C(15)	30(2)	26(2)	32(2)	-7(2)	2(1)	0(1)
C(16)	32(2)	27(2)	42(2)	1(2)	6(2)	-1(1)
C(17)	37(2)	27(2)	34(2)	6(2)	12(1)	5(2)
C(18)	44(2)	32(2)	23(2)	0(2)	10(2)	6(2)
C(19)	63(2)	37(2)	37(2)	4(2)	27(2)	14(2)
C(21)	26(2)	27(2)	29(2)	-4(2)	1(1)	1(1)

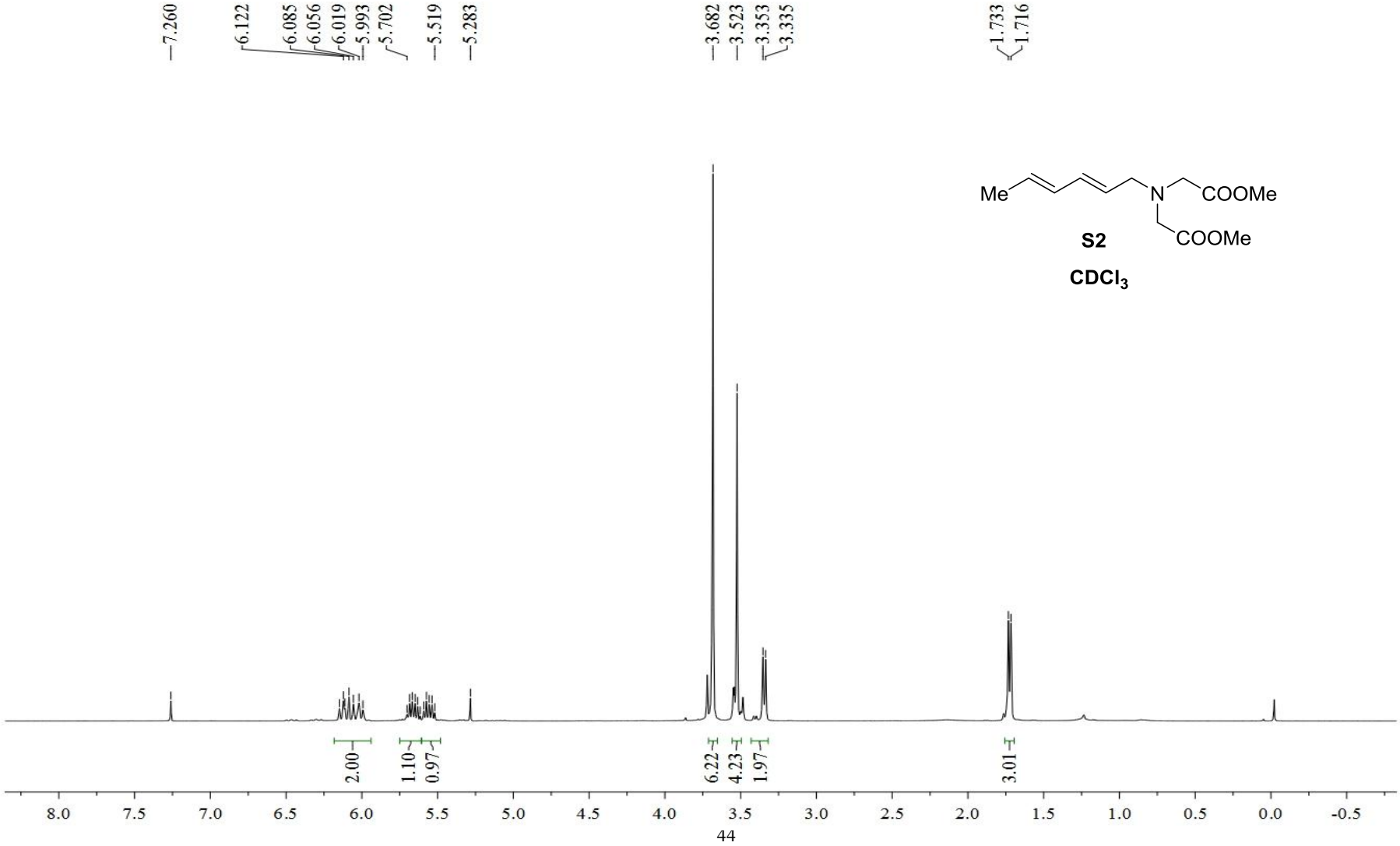
C(22)	39(2)	30(2)	53(2)	6(2)	15(2)	1(2)
C(23)	31(2)	44(2)	60(2)	0(2)	18(2)	5(2)
C(24)	28(2)	38(2)	58(2)	-5(2)	1(2)	10(2)
C(25)	39(2)	47(2)	45(2)	10(2)	-1(2)	15(2)
C(26)	36(2)	49(2)	37(2)	8(2)	7(2)	11(2)

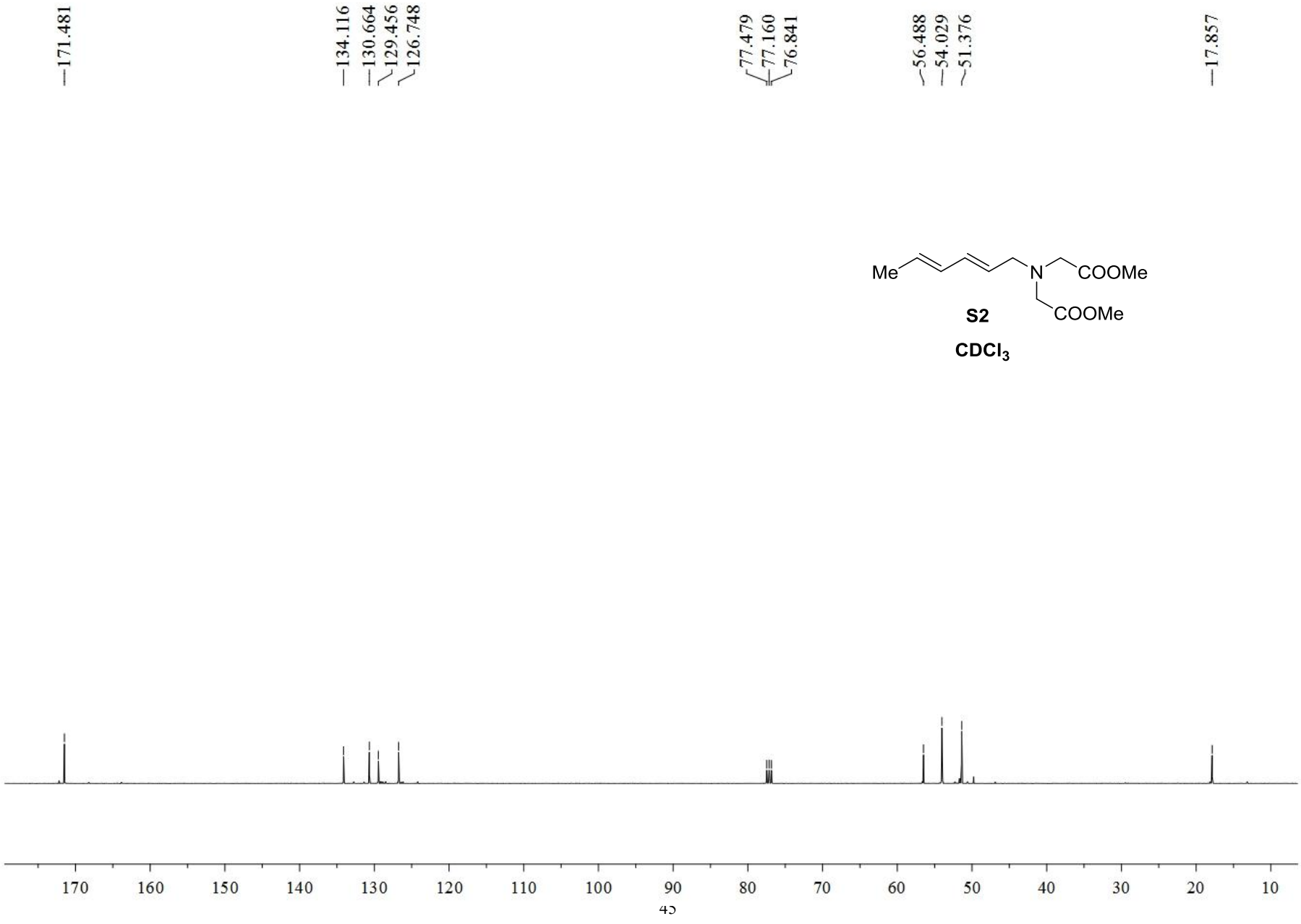
Table S12. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for **7i**.

	x	y	z	U(eq)
H(1)	9743	1437	8021	53
H(2)	8045	93	8577	54
H(3)	5967	952	8924	49
H(4)	5614	3122	8818	43
H(6)	9419	3629	7963	41
H(7)	7888	5429	7833	31
H(8)	8893	5672	9794	39
H(9)	7795	7420	10694	42
H(10)	6211	8437	9390	40
H(11)	6517	7236	7313	32
H(12)	5278	5311	8677	28
H(13A)	7969	5205	11676	63
H(13B)	7983	3972	10826	63
H(13C)	6612	4726	10878	63
H(14A)	3811	7289	7966	33
H(14B)	4440	8295	7084	33
H(15)	2566	5767	5111	35
H(16A)	2819	4992	7692	40
H(16B)	2015	4253	6528	40
H(17A)	5410	7643	5291	38
H(17B)	4021	7288	4449	38
H(18)	4732	5239	4080	39
H(19A)	7227	6629	4306	66
H(19B)	6164	6624	3070	66
H(19C)	6955	5363	3513	66
H(22)	875	6145	7678	48
H(23)	-861	7597	7867	53
H(24)	-1187	9325	6513	50
H(25)	256	9630	4981	53

H(26)	1973	8178	4776	48

7. Copy of NMR spectra

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N
COOMe
COOMe
S2
CDCl3
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150
140
130
120
110
100
90
80
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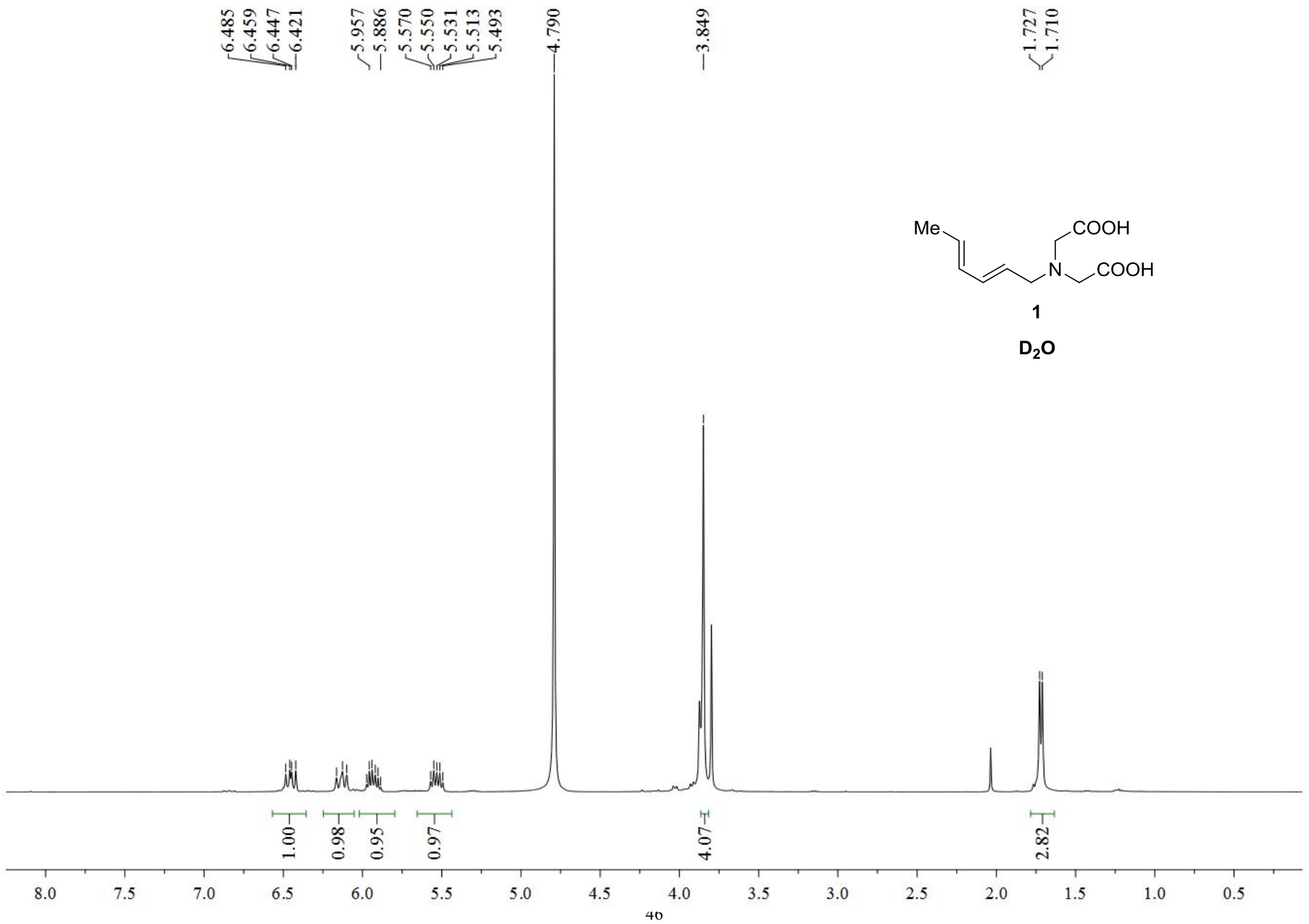
60
50
40
30
20
10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1.710
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N
COOH
1
D2O
1.00
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0.95
0.97
4.07
2.82
8.0
7.5
7.0
6.5
6.0
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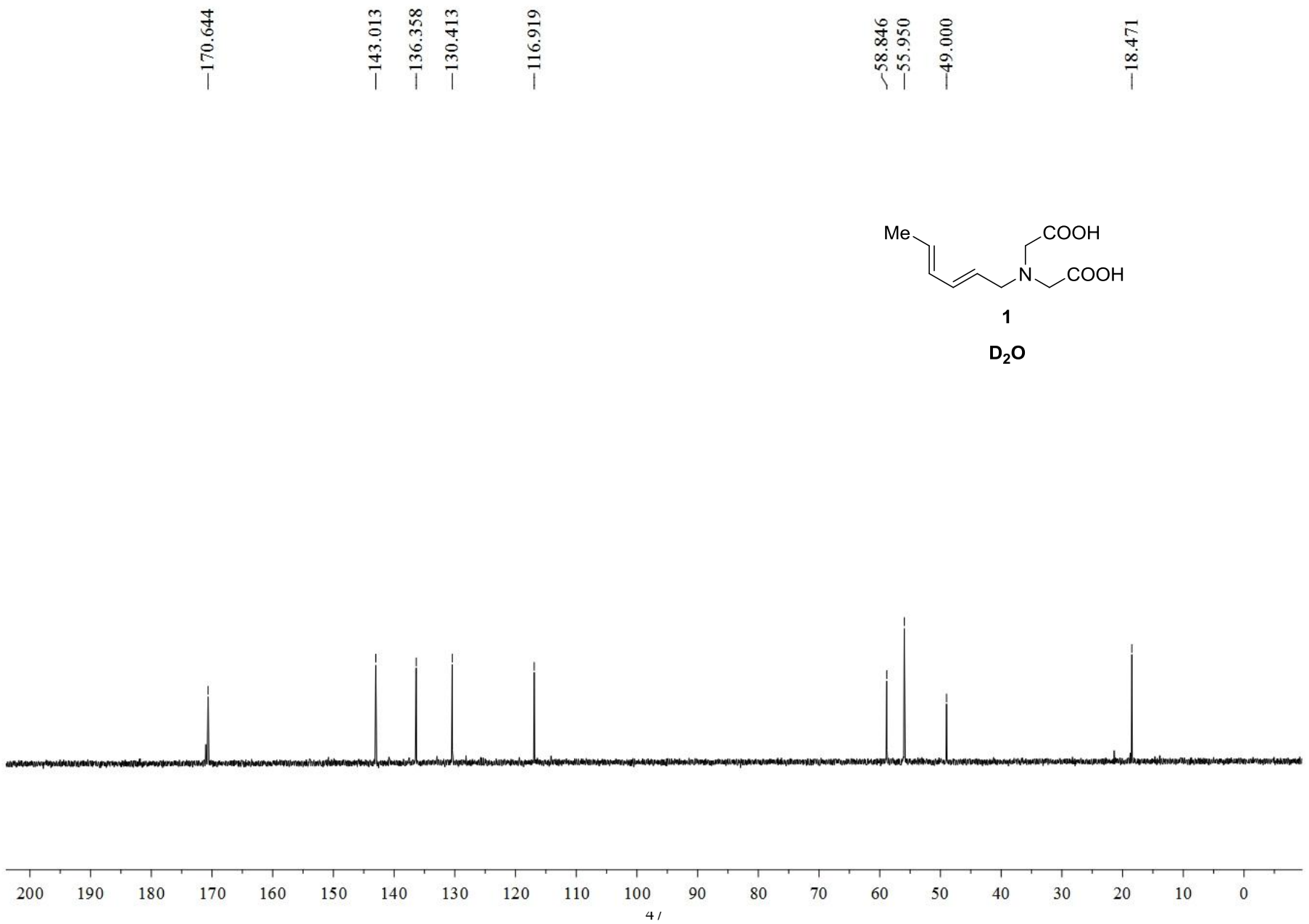
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D2O
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190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


7.260
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6.063
6.027
6.001
5.998
5.665
5.630
5.613
5.581
5.564
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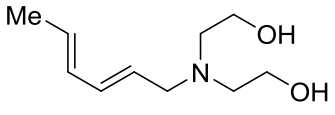
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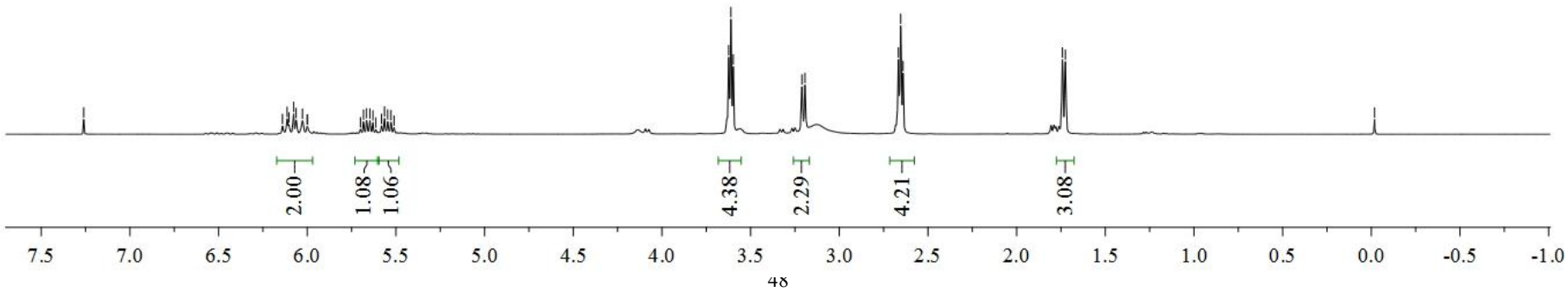
N
OH

5

$CDCl_3$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5.0
4.5
4.0
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3.0
2.5
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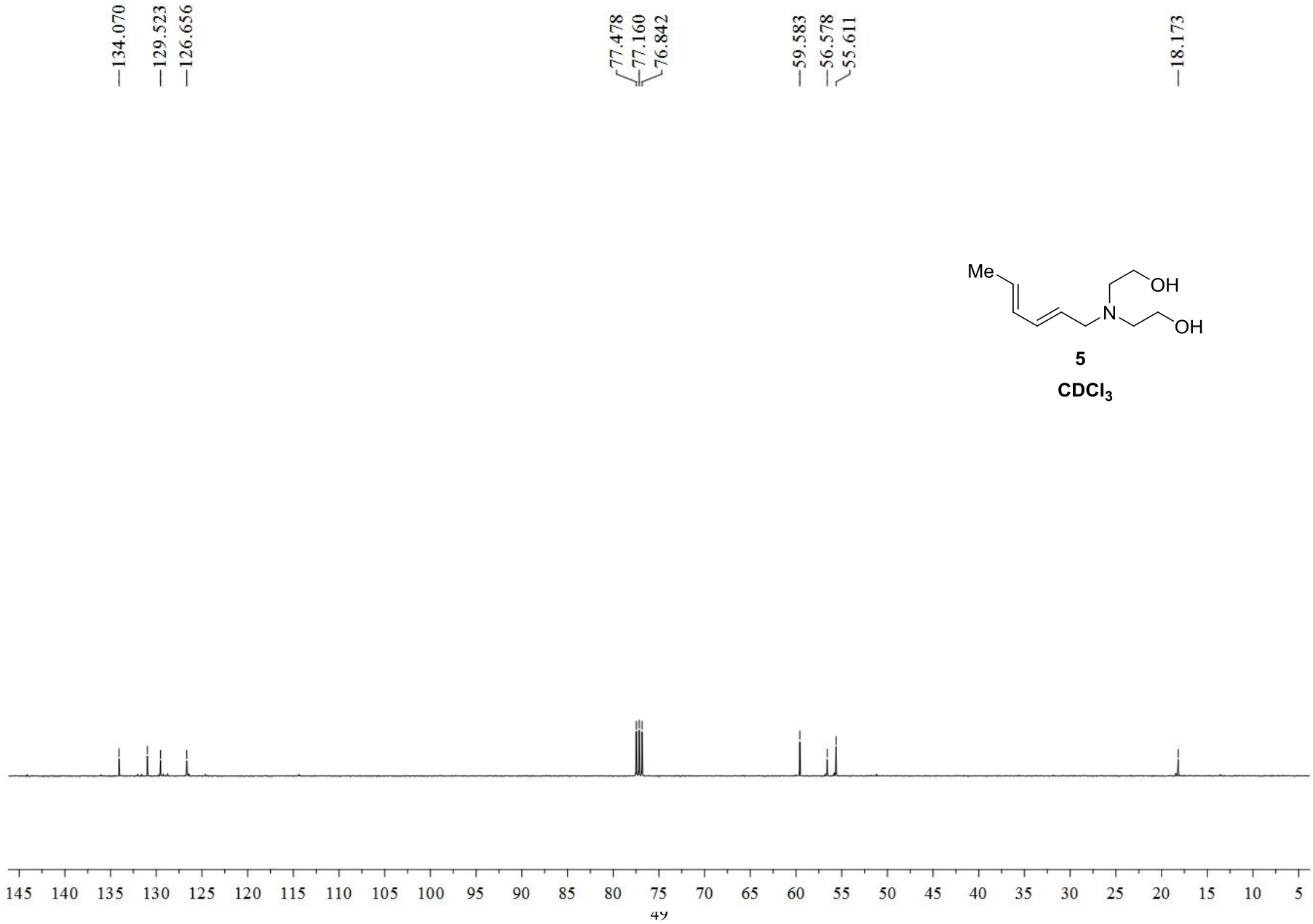
-1.0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N
OH
5
CDCl3
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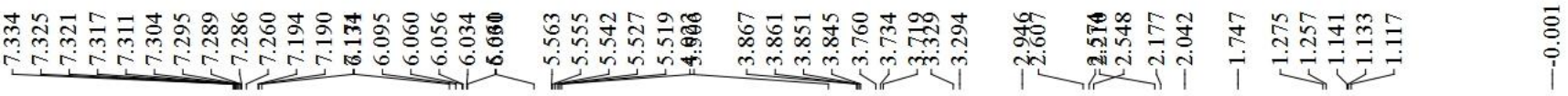
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6.060
6.056
6.034
5.563
5.555
5.542
5.527
5.519
3.867
3.861
3.851
3.845
3.760
3.734
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1.117
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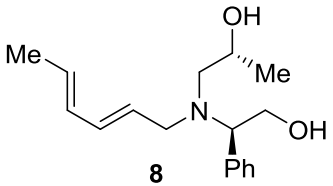
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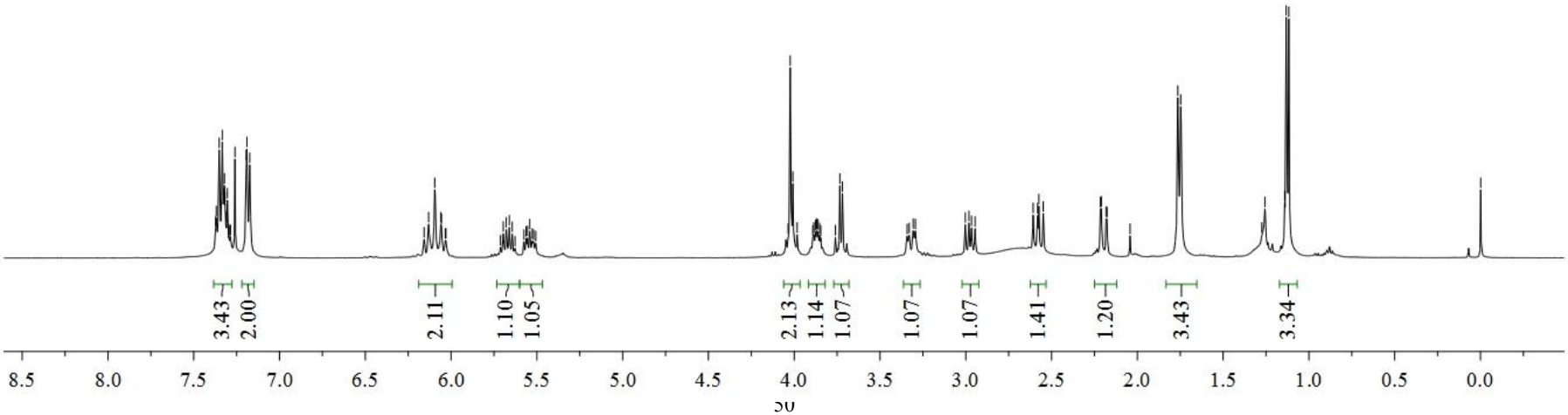
Me
Me
N
OH
Ph

8

$CDCl_3$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3.34
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8.0
7.5
7.0
6.5
6.0
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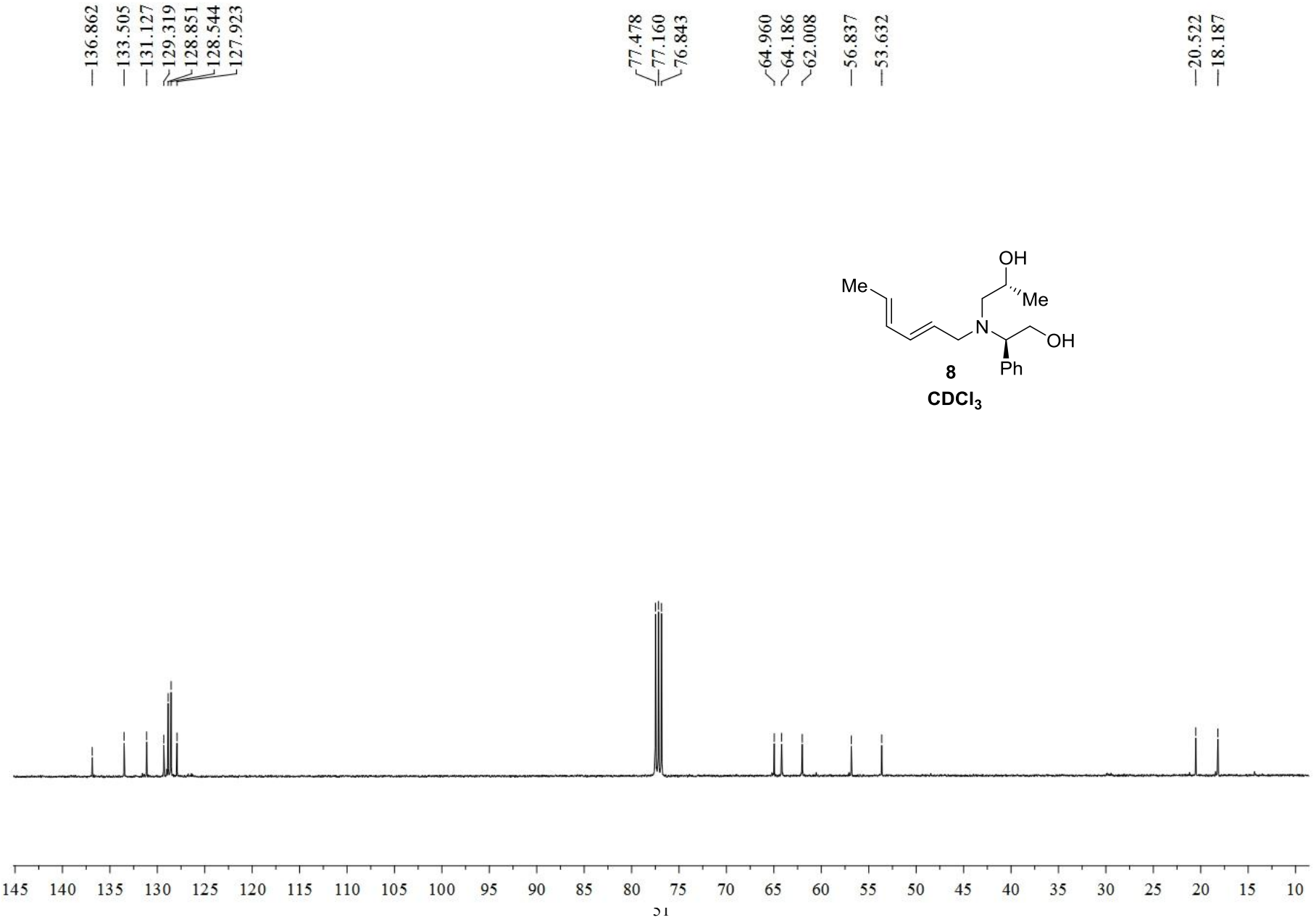
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56.837
53.632
20.522
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OH
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Me
N
OH
Ph
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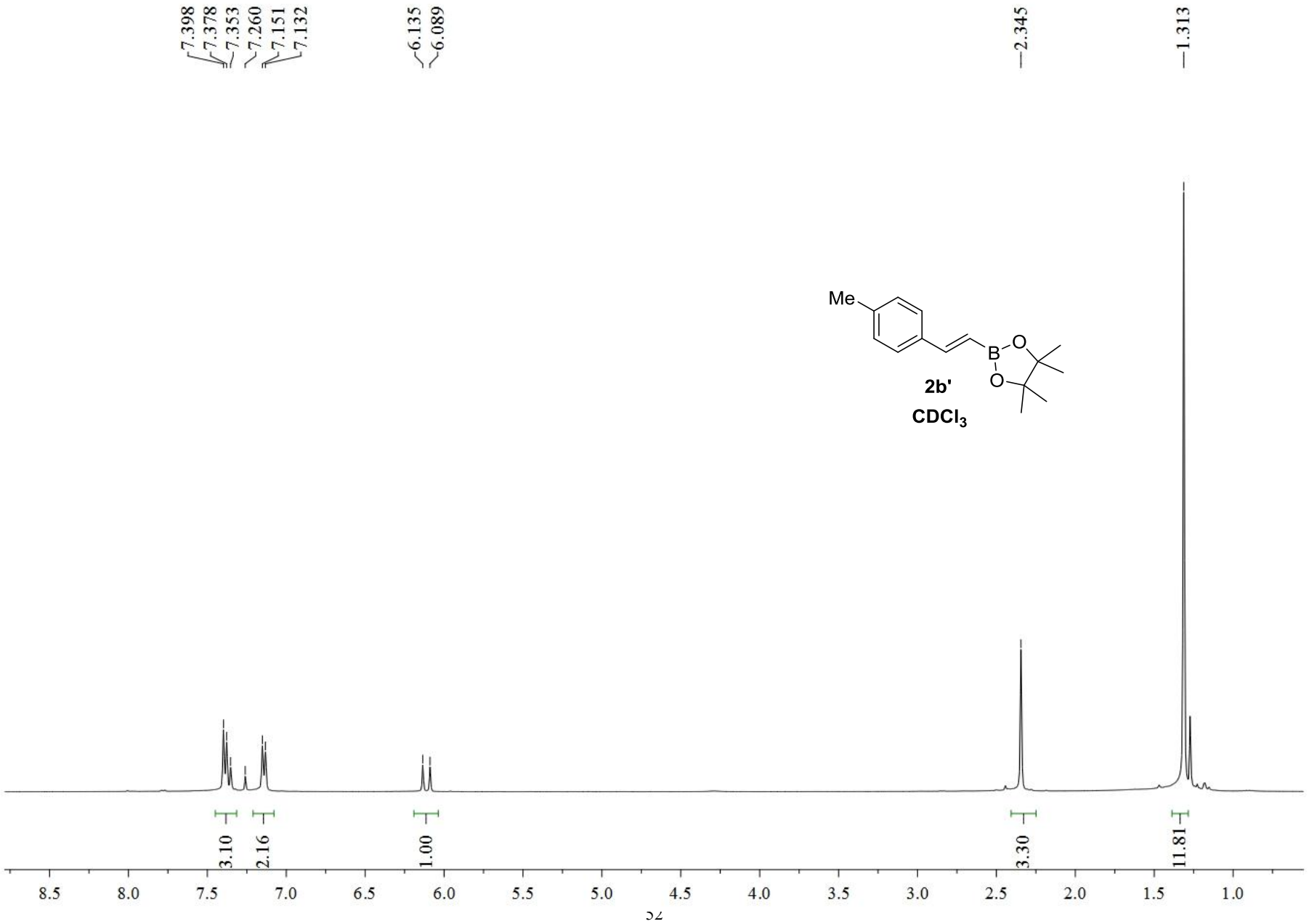
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O
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CDCl3
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2.16
1.00
3.30
11.81
8.5
8.0
7.5
7.0
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3.0
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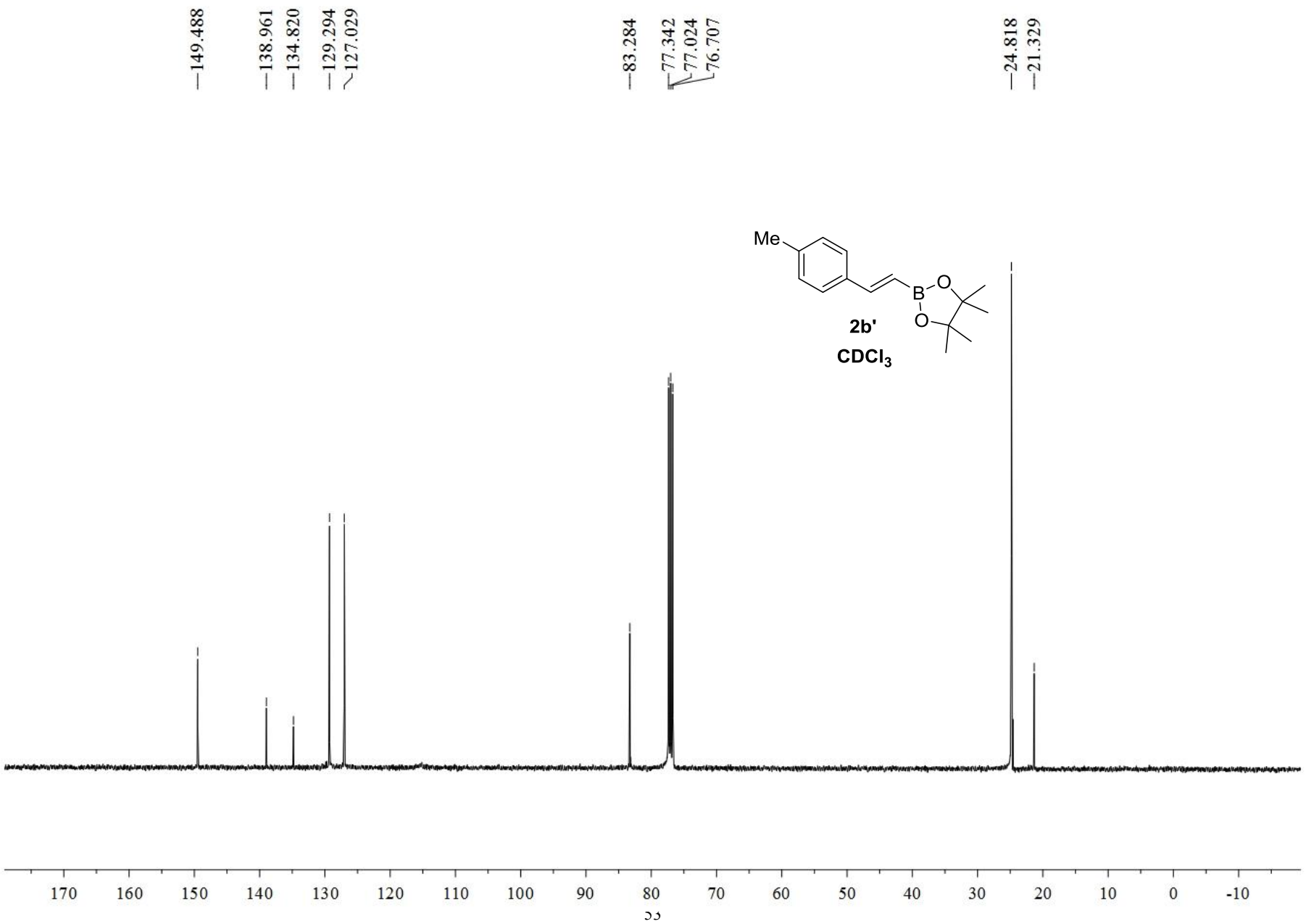
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O
2b'
CDCl3
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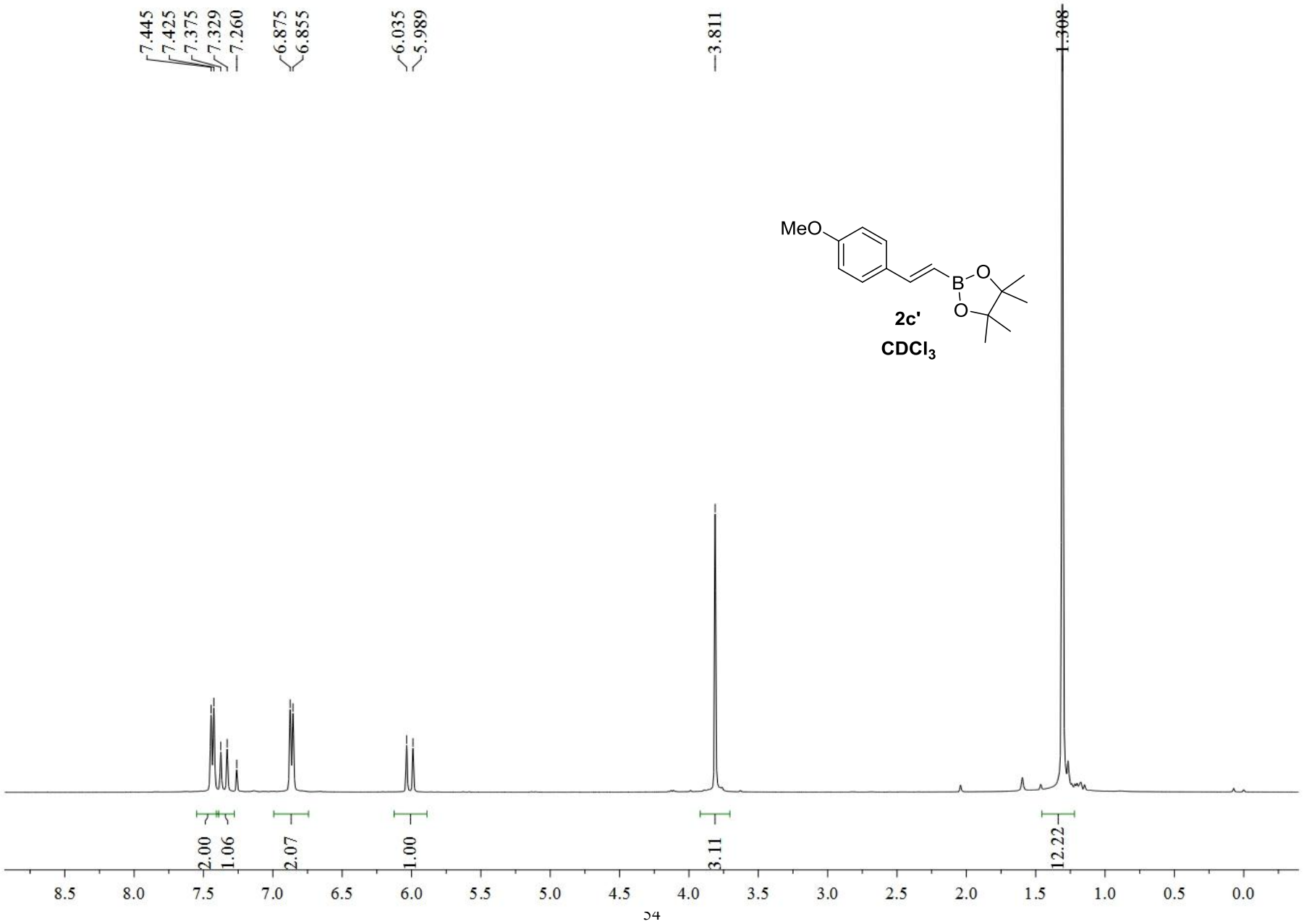
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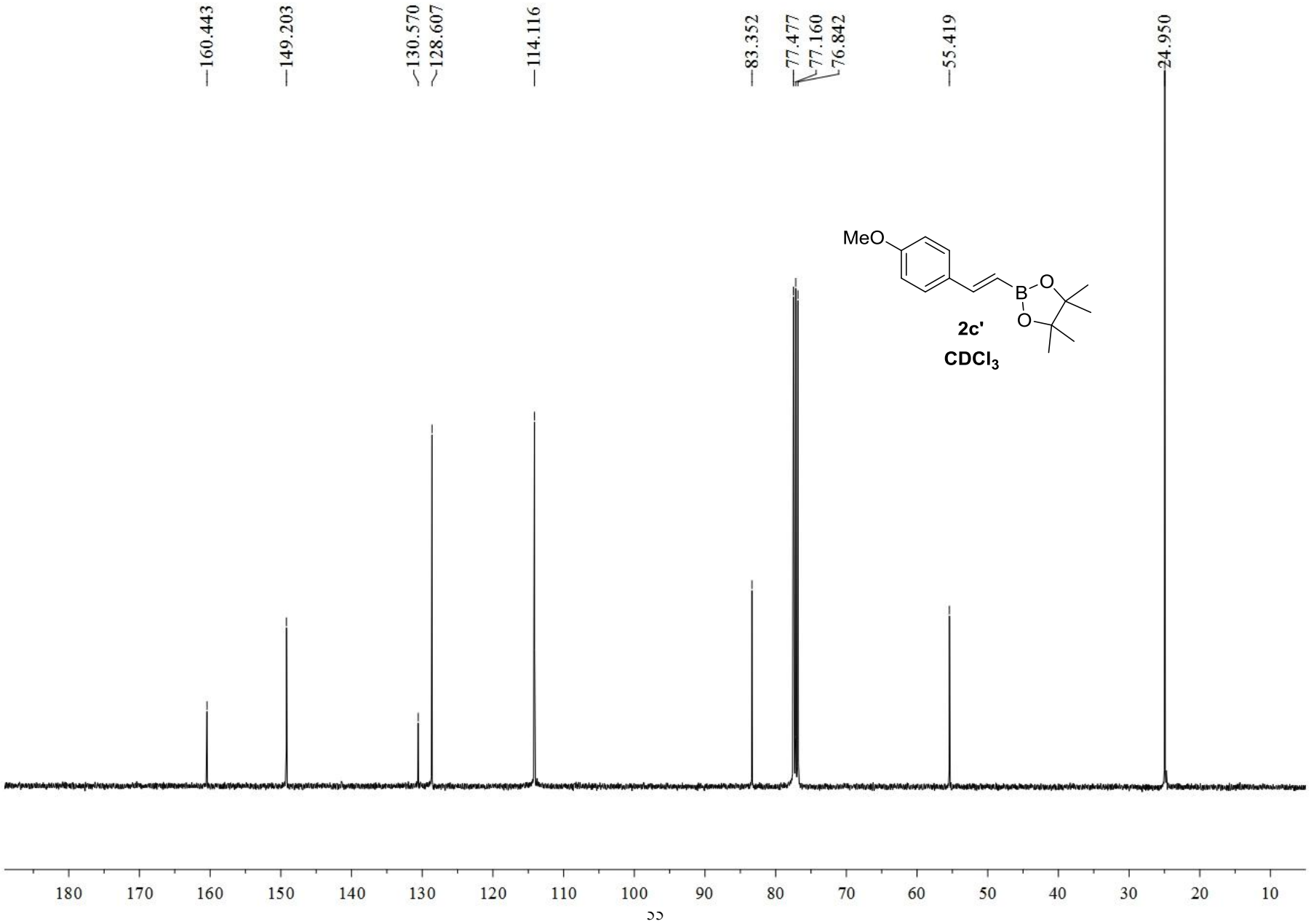
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O
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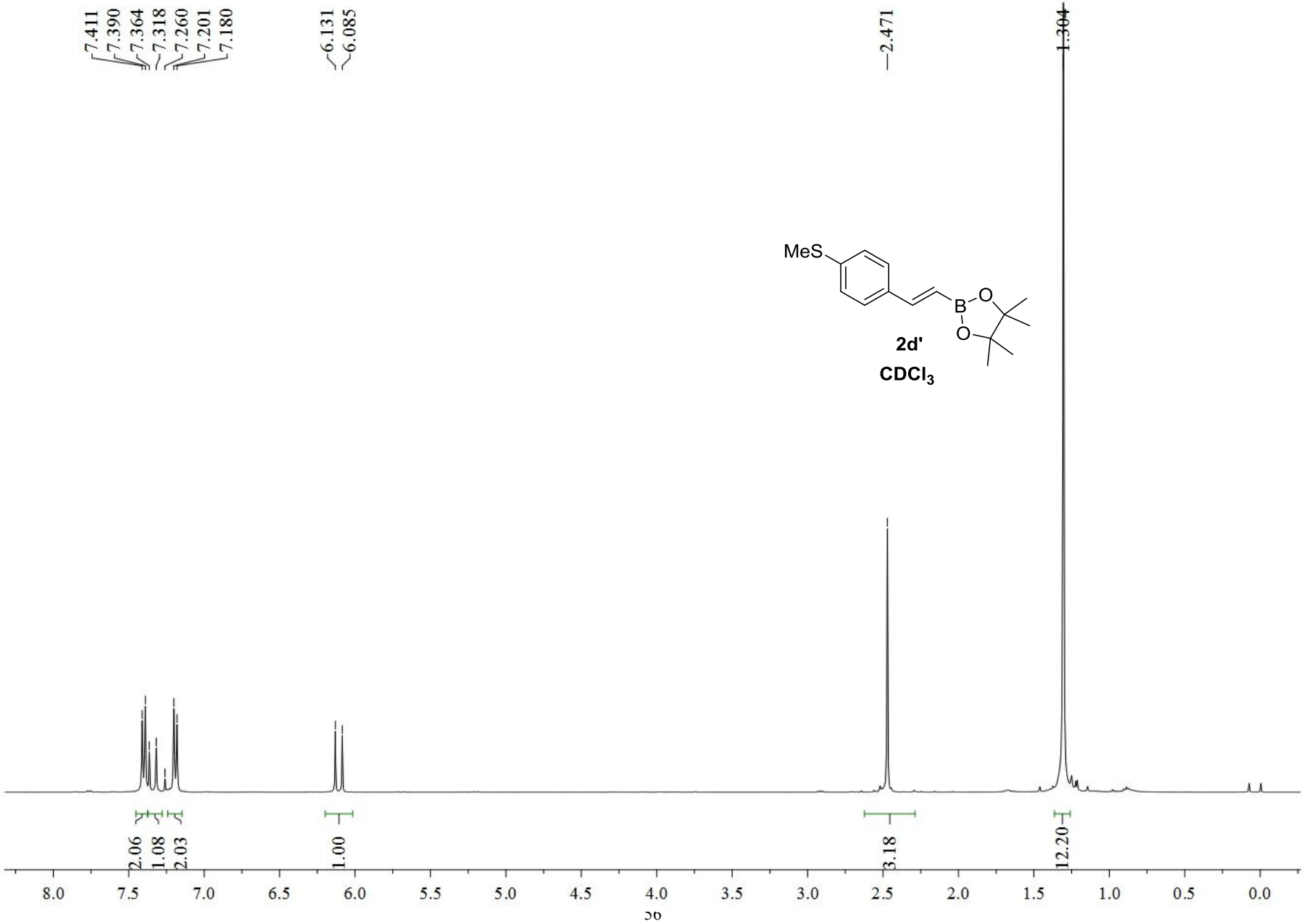
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2.03
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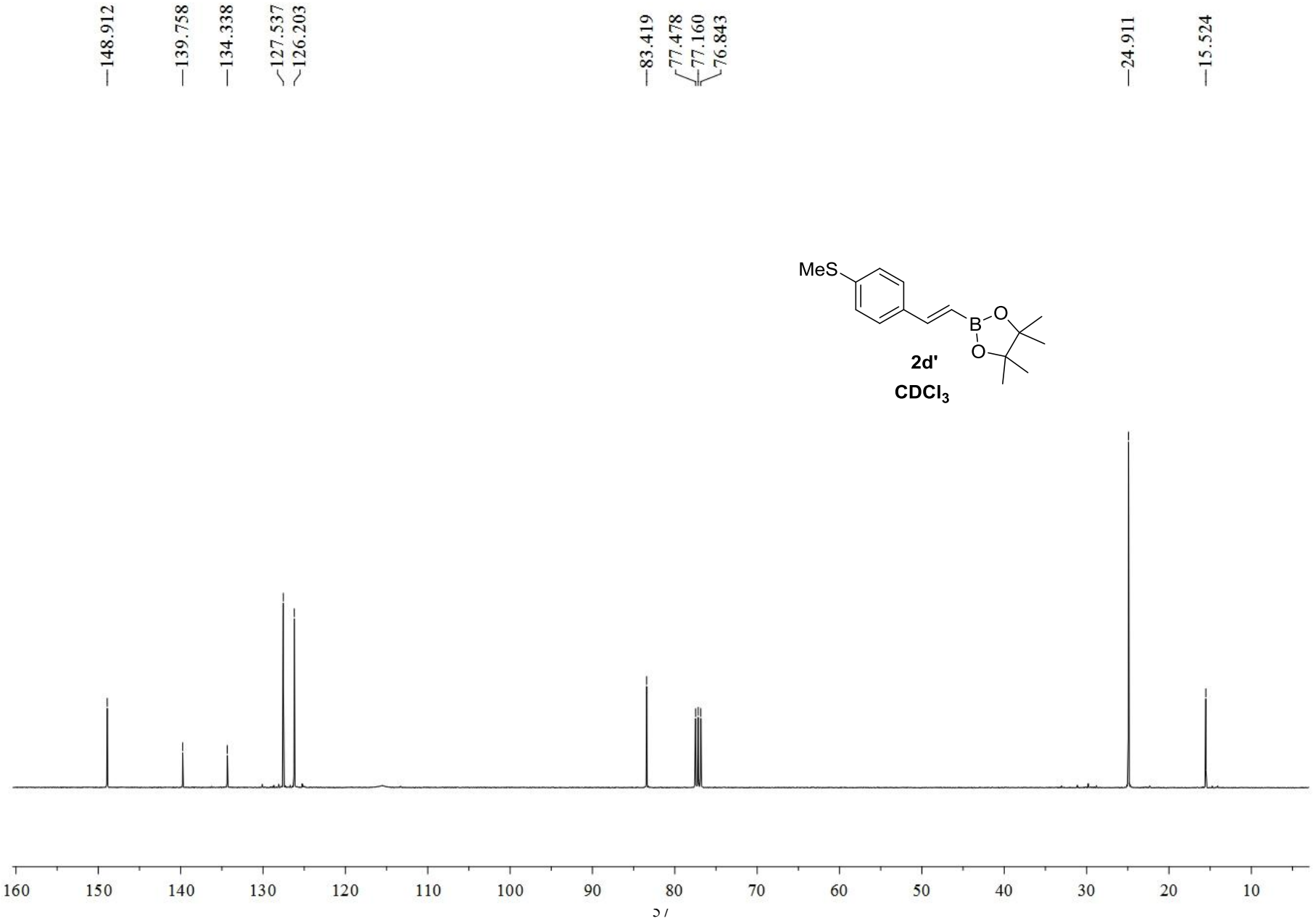
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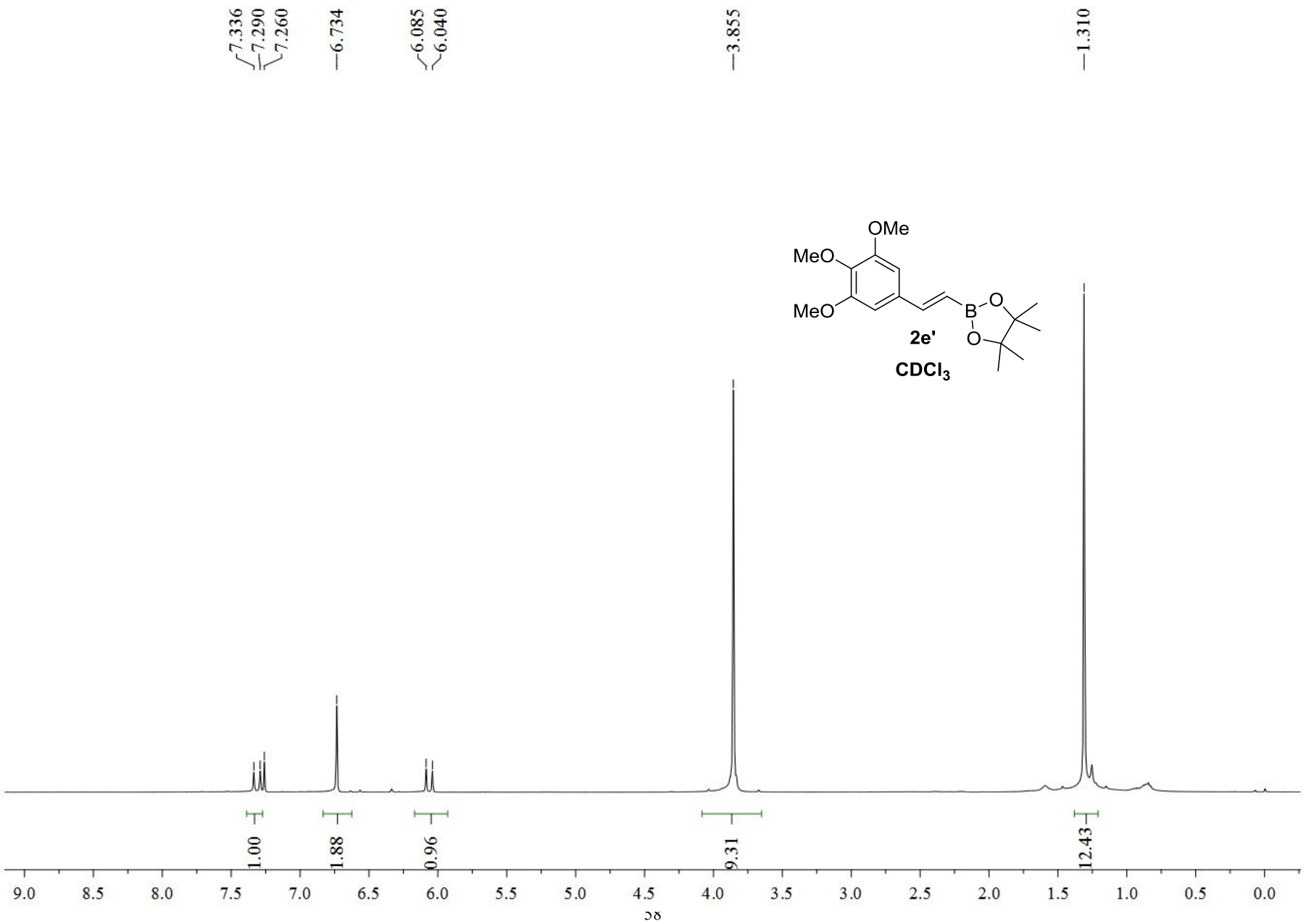
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MeO
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O
2e'
CDCl3
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6.0
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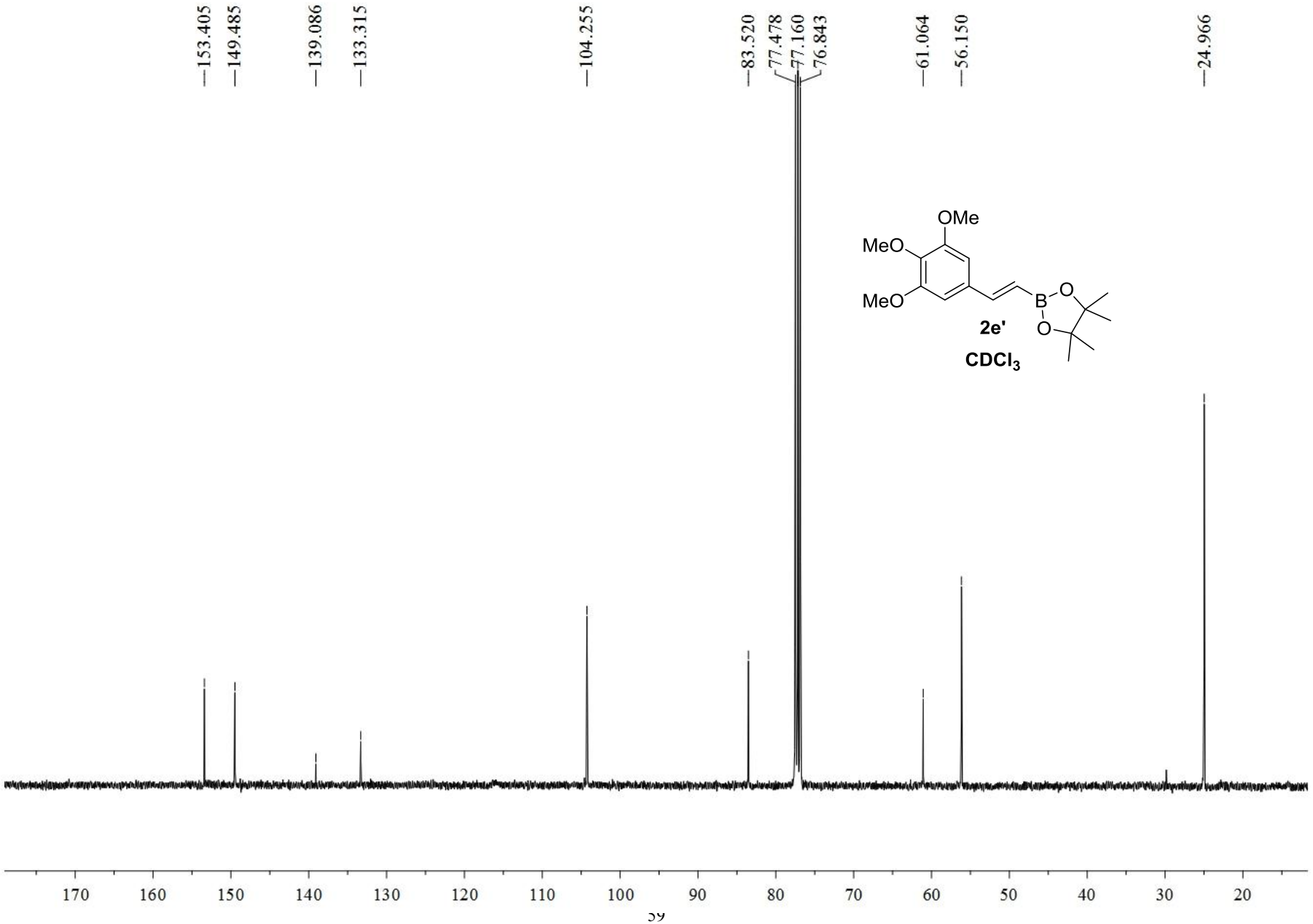
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MeO
MeO
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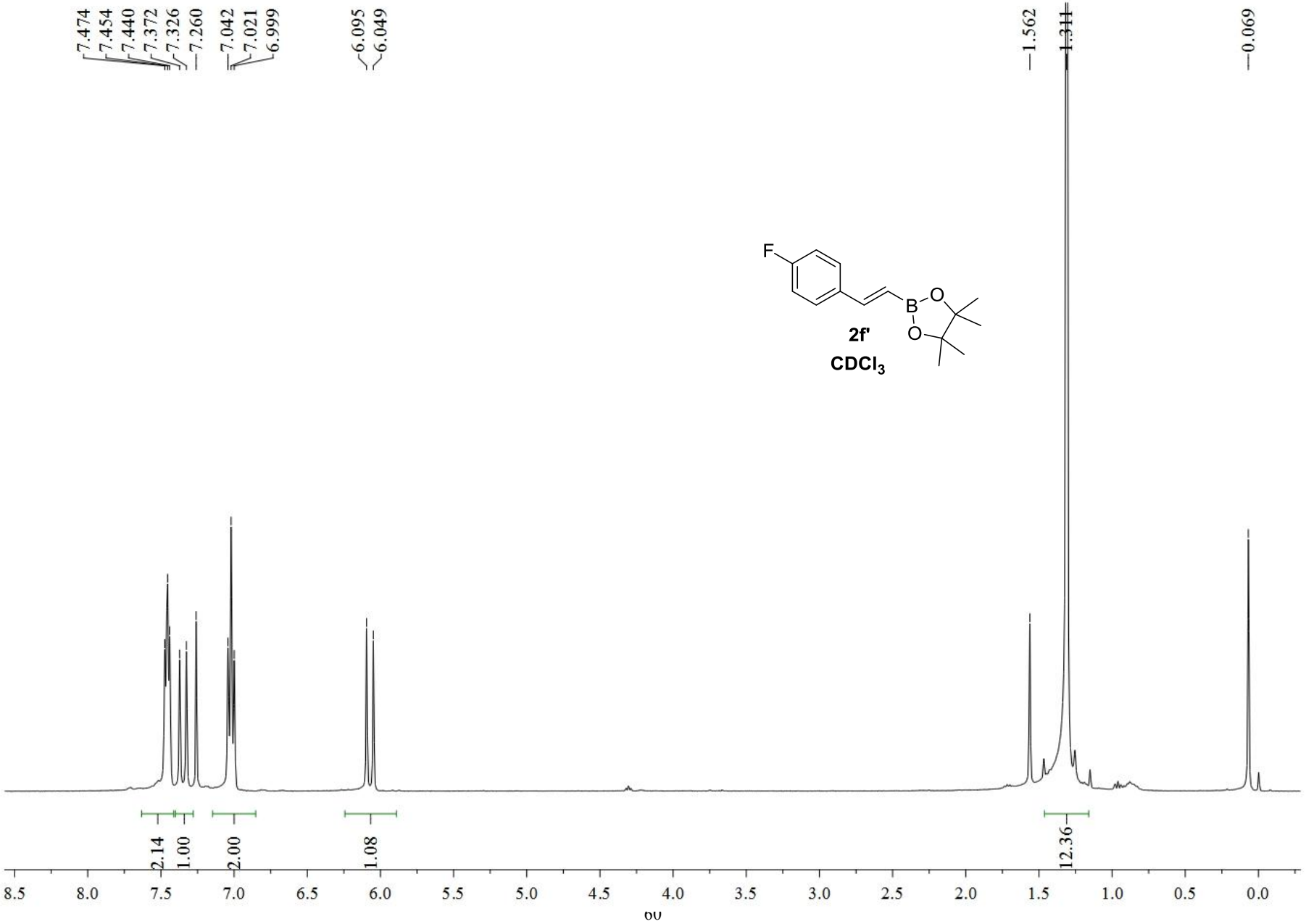
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B
O
O
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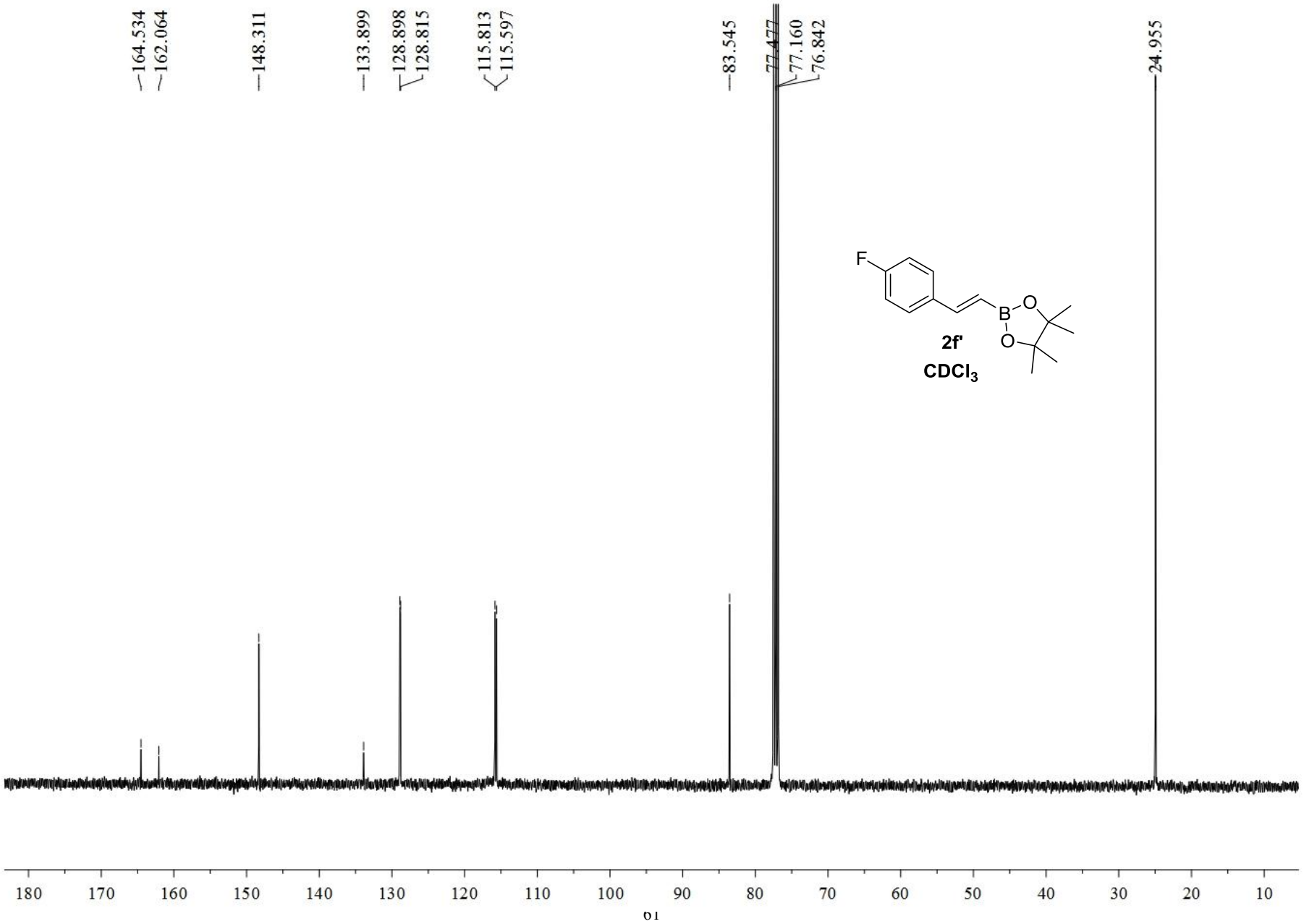
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F
B
O
O
2f'
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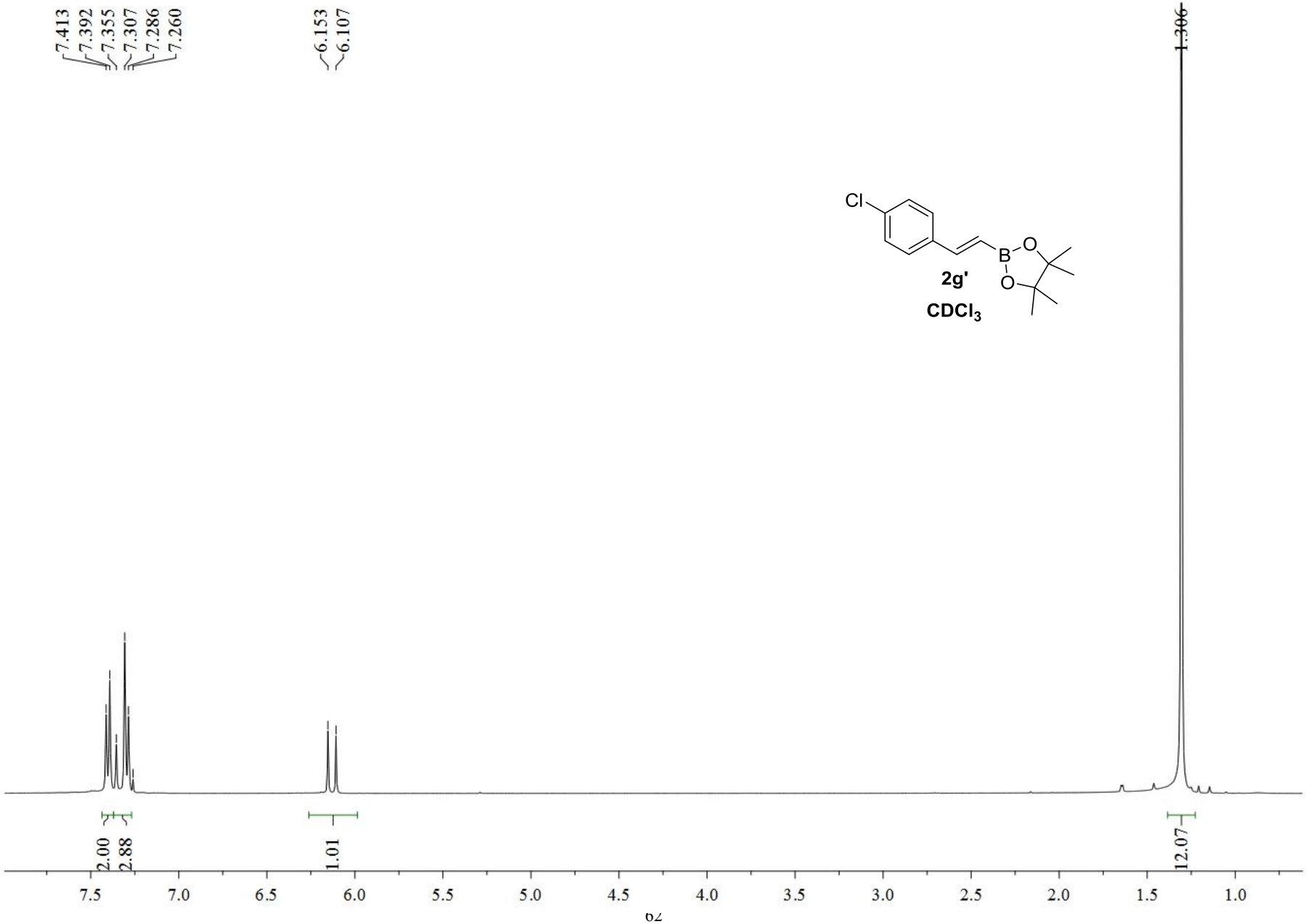
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B
O
O
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CDCl3
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2.88
1.01
12.07
7.5
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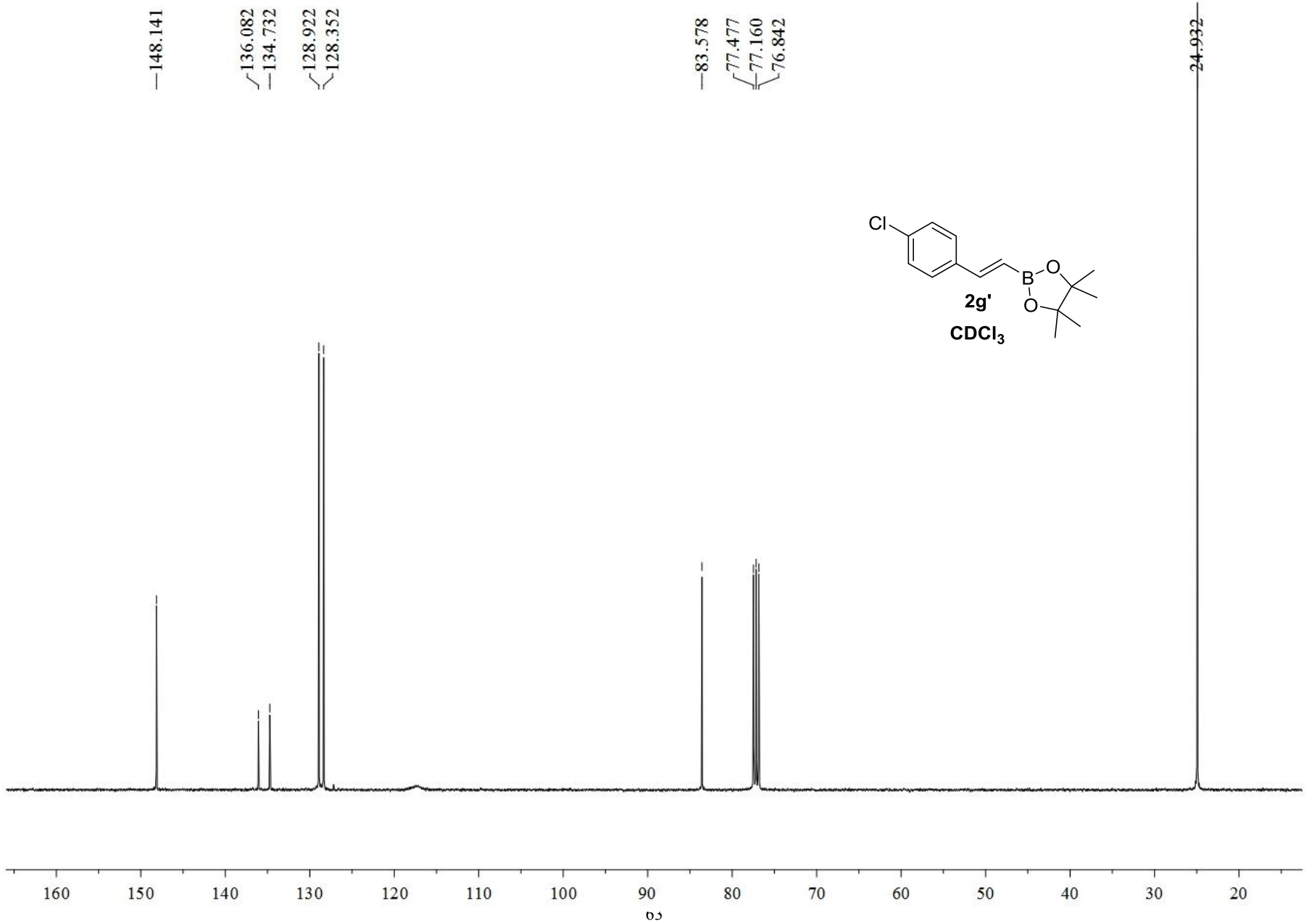
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24.932
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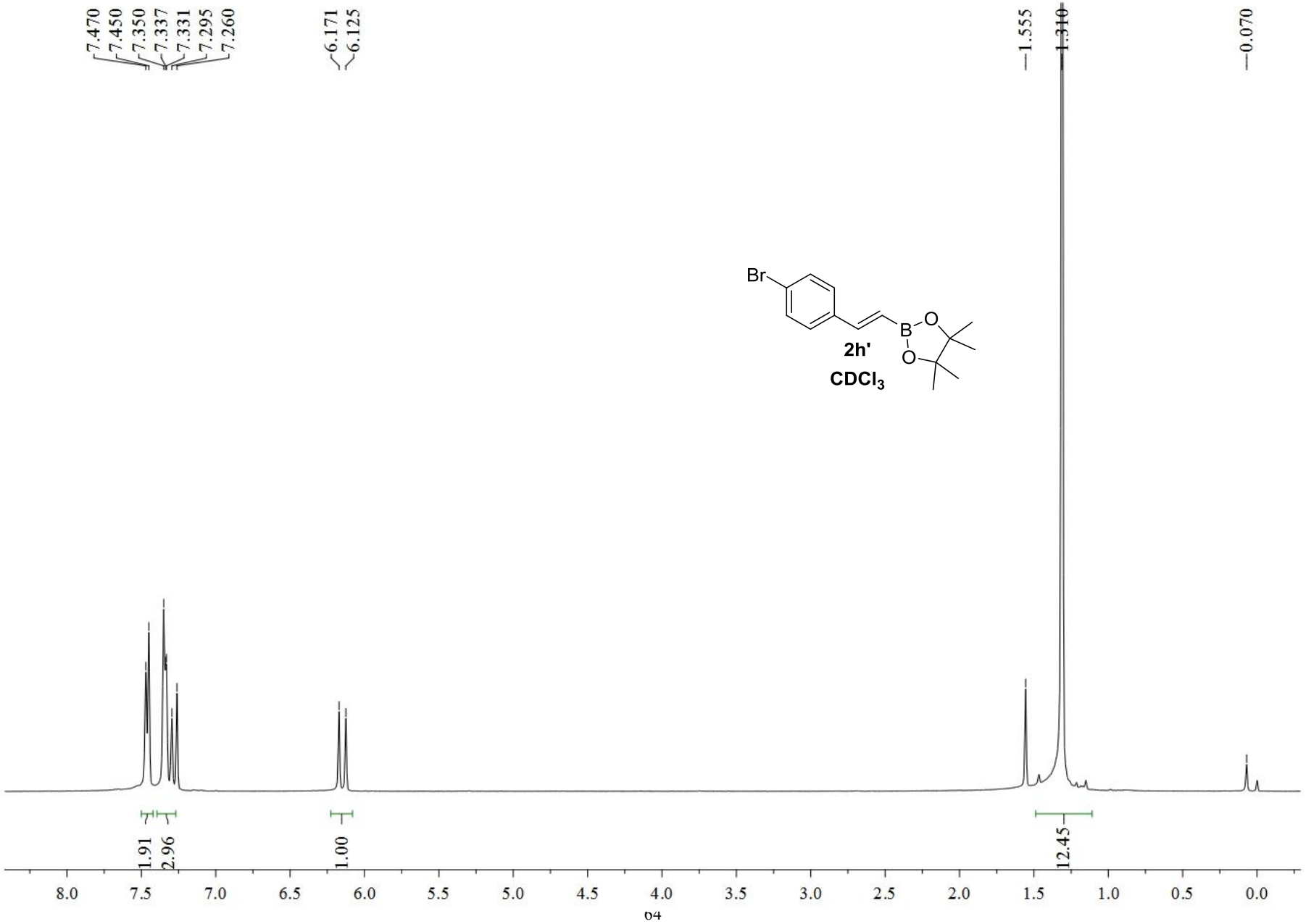
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B
O
O
2h'
CDCl3
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2.96
1.00
12.45
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7.5
7.0
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6.0
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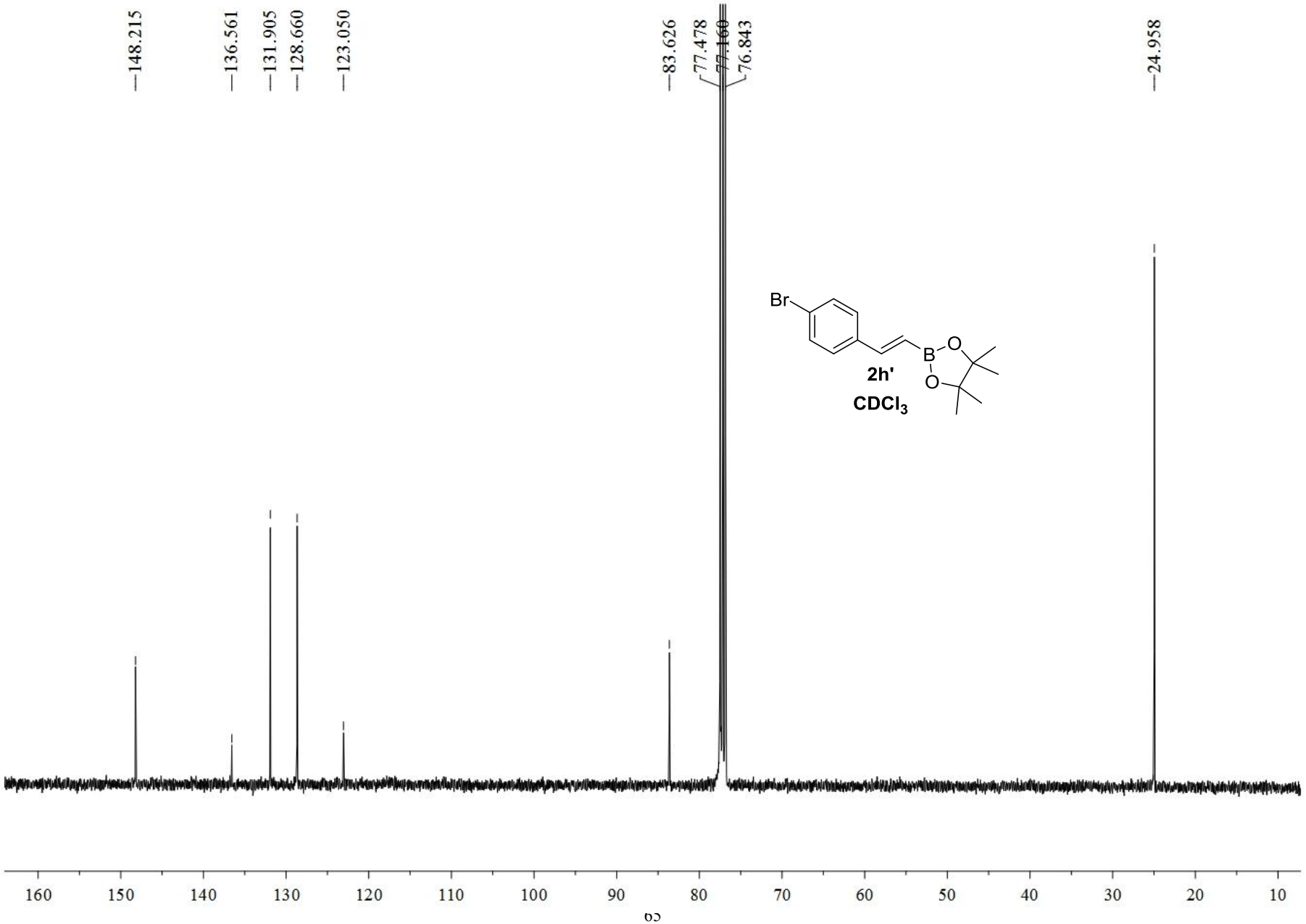
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77.160
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24.958
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20
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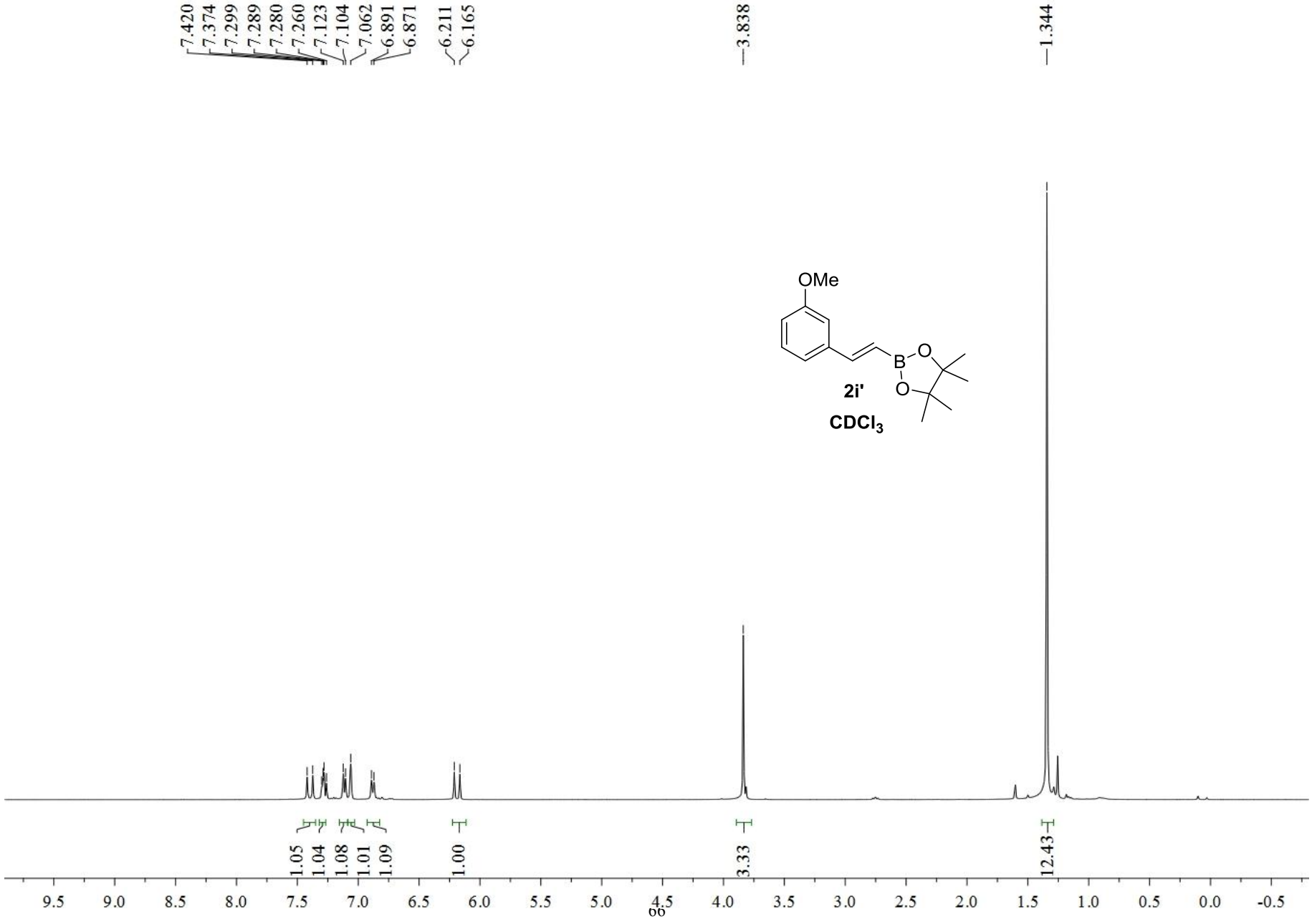
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3.838
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OMe
B
O
O
2i'
CDCl3
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1.04
1.08
1.01
1.09
1.00
3.33
12.43
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8.5
8.0
7.5
7.0
6.5
6.0
5.5
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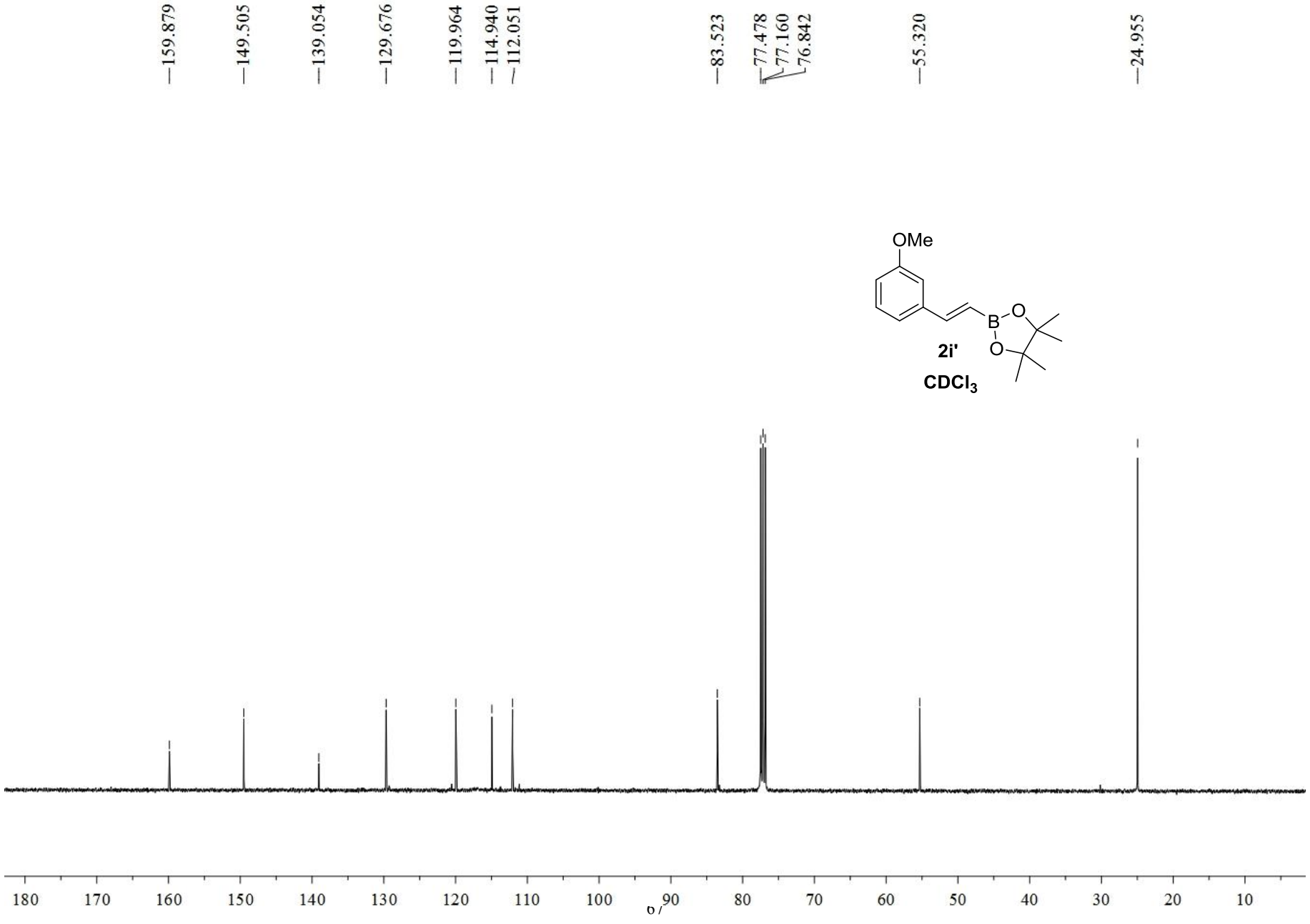
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55.320
24.955
OMe
B
O
O
2i'
CDCl3
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80
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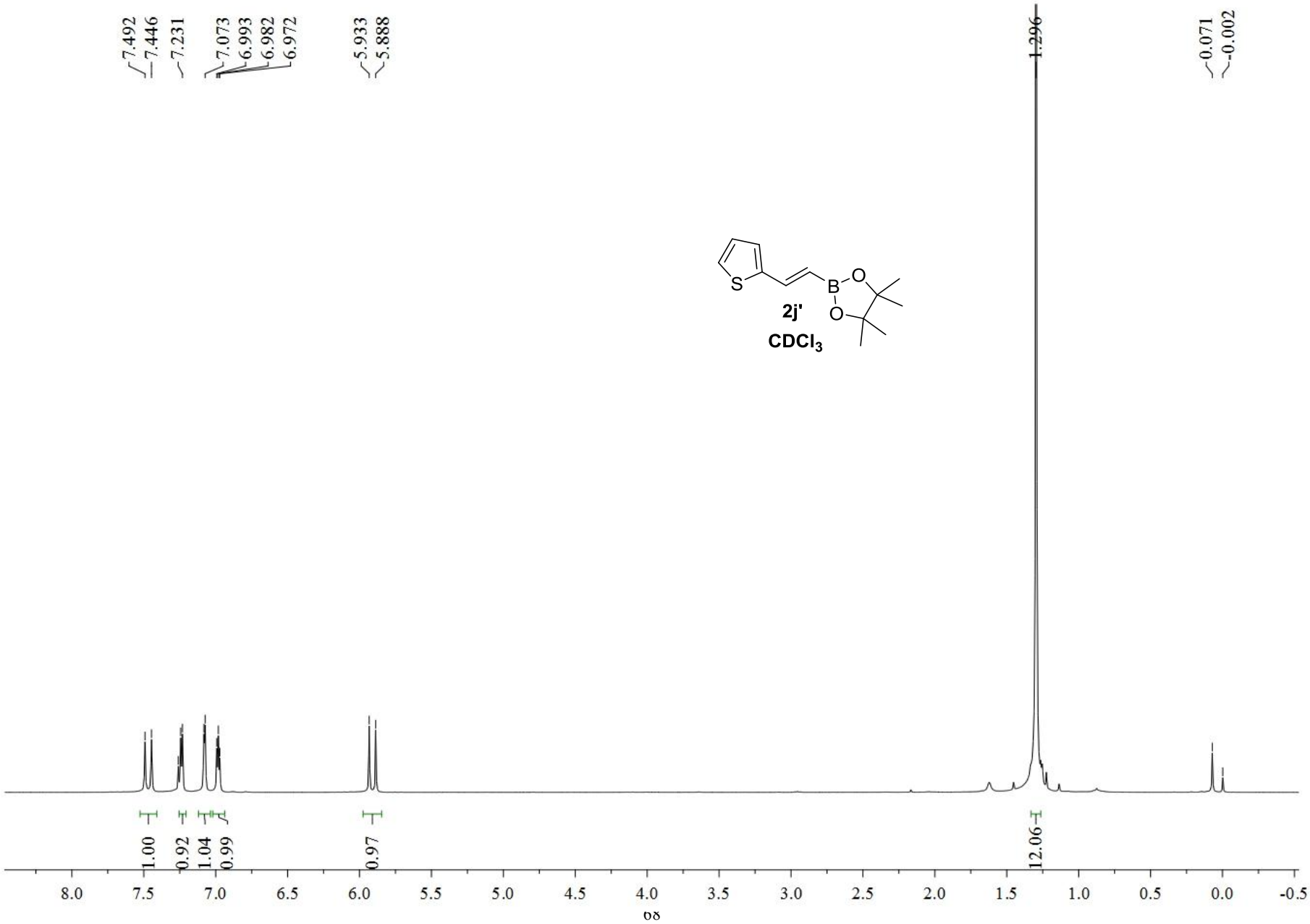
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S
B
O
O
2j'
CDCl3
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1.04
0.99
0.97
12.06
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6.0
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5.0
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1.0
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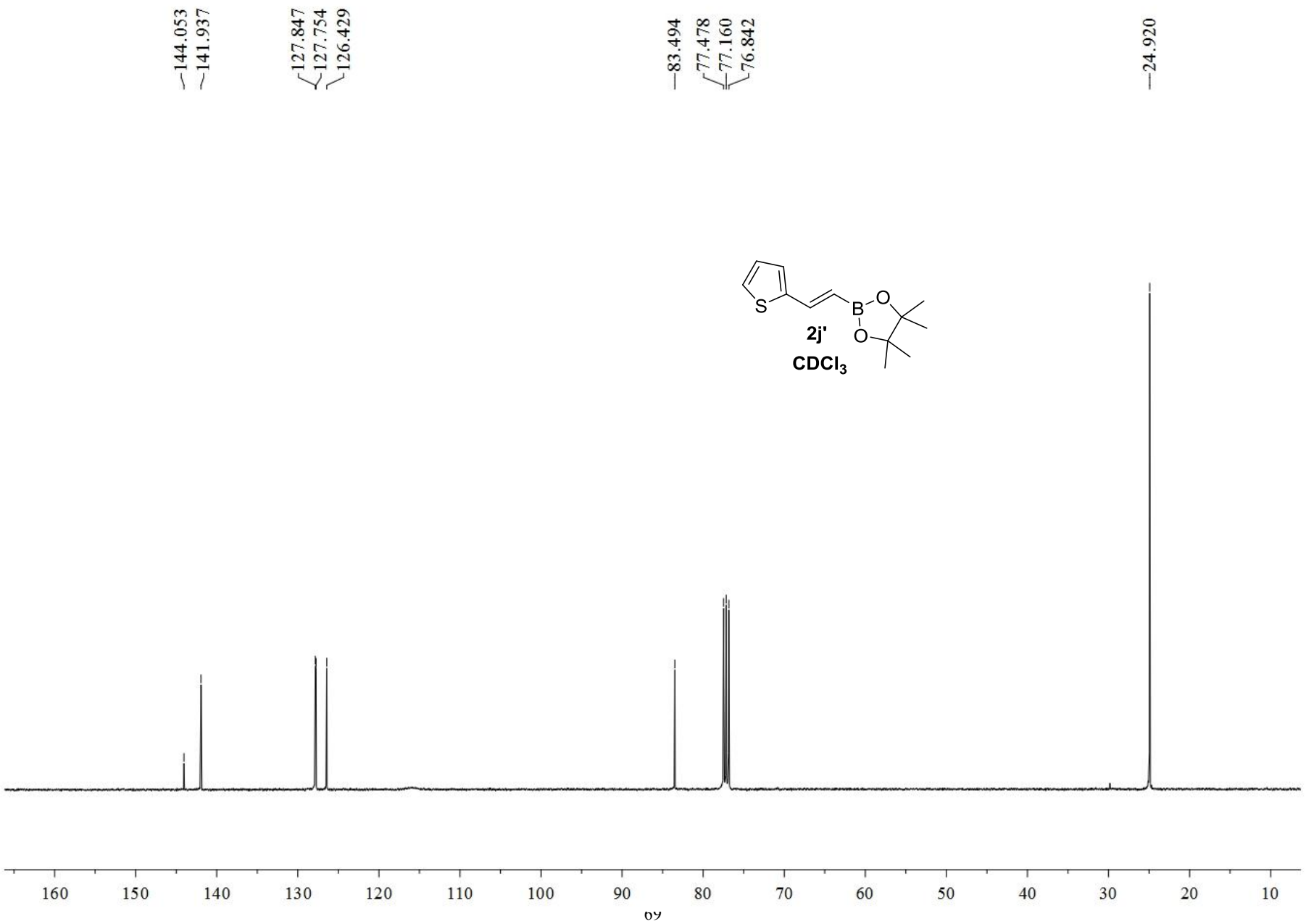
0.0
-0.5
δ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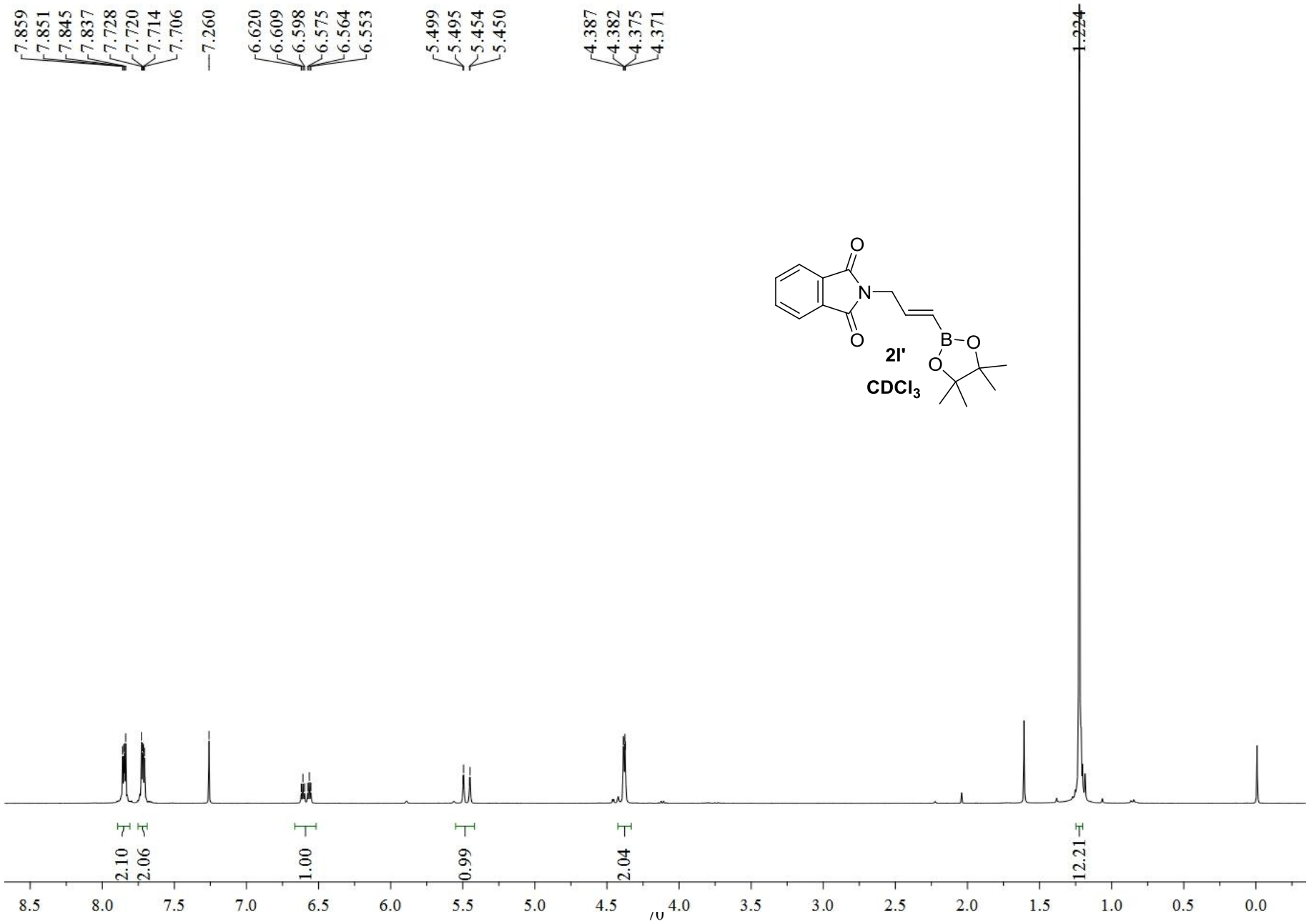
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6.609
6.598
6.575
6.564
6.553
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5.495
5.454
5.450
4.387
4.382
4.375
4.371
1.224
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CDCl3
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2.06
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2.04
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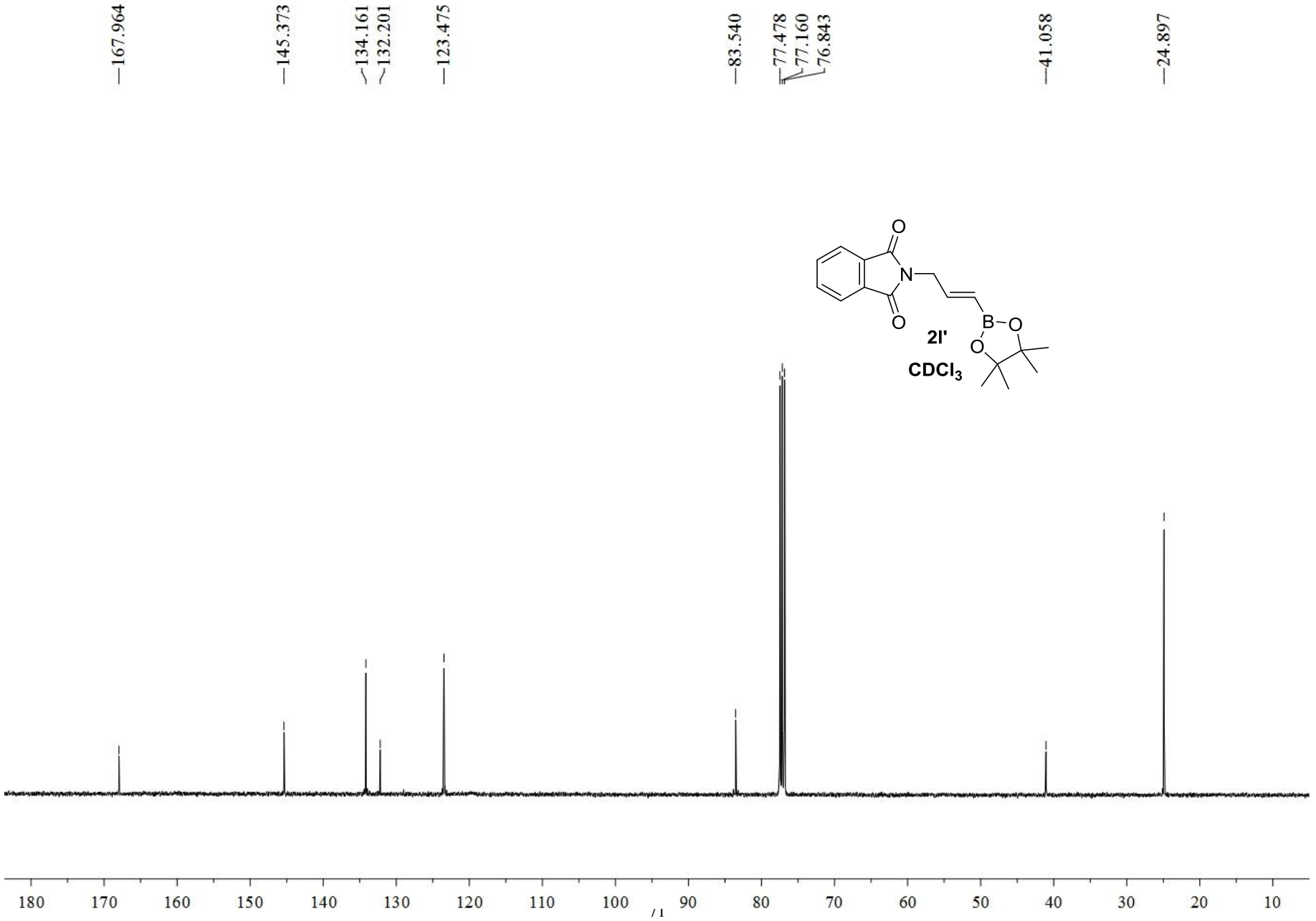
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O
2l'
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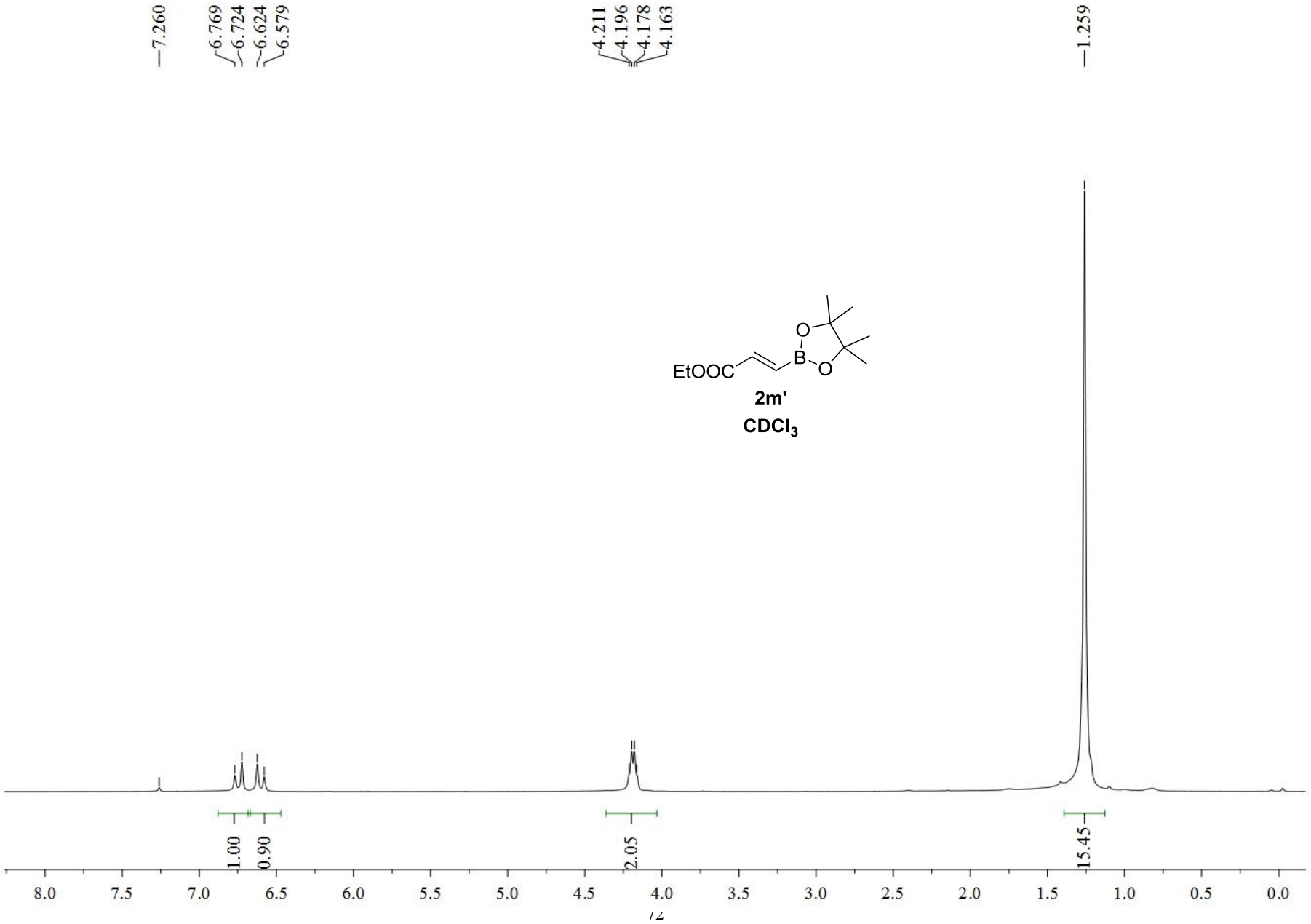
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B
O
2m'
CDCl3
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2.05
15.45
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7.5
7.0
6.5
6.0
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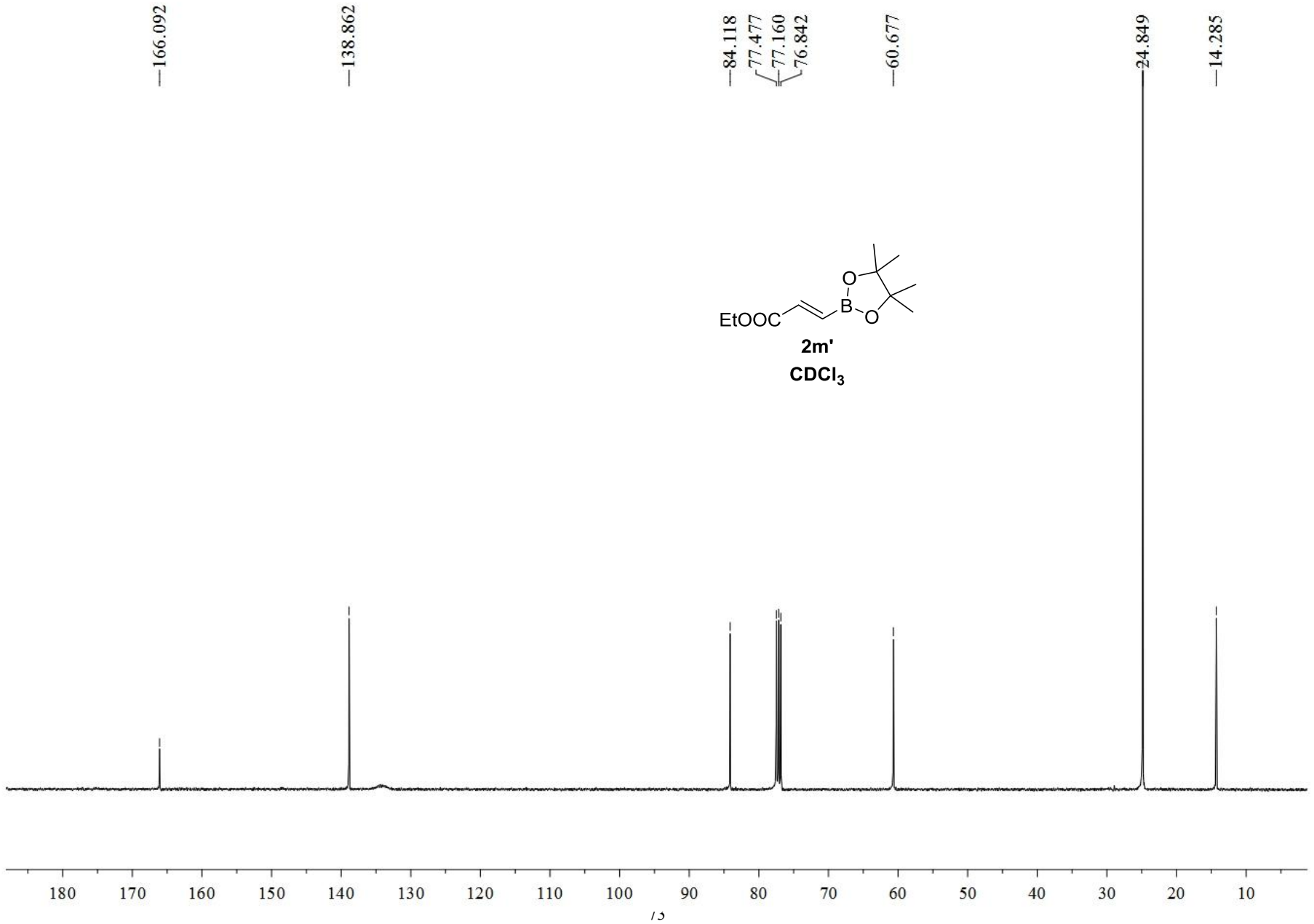
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B
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2m'
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20
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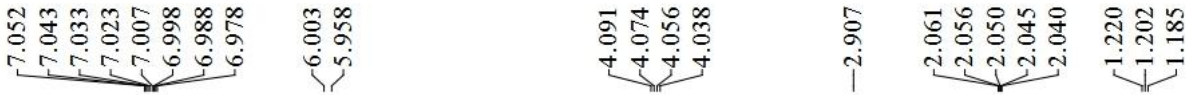
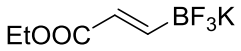
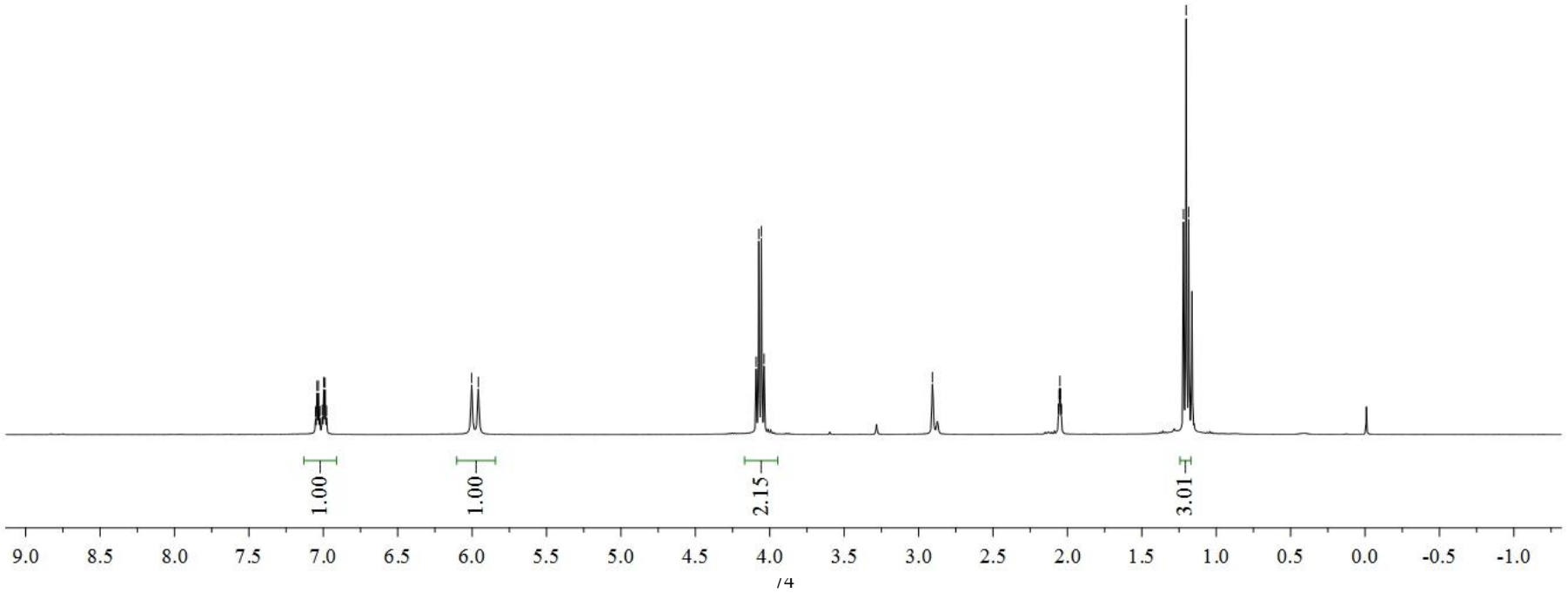
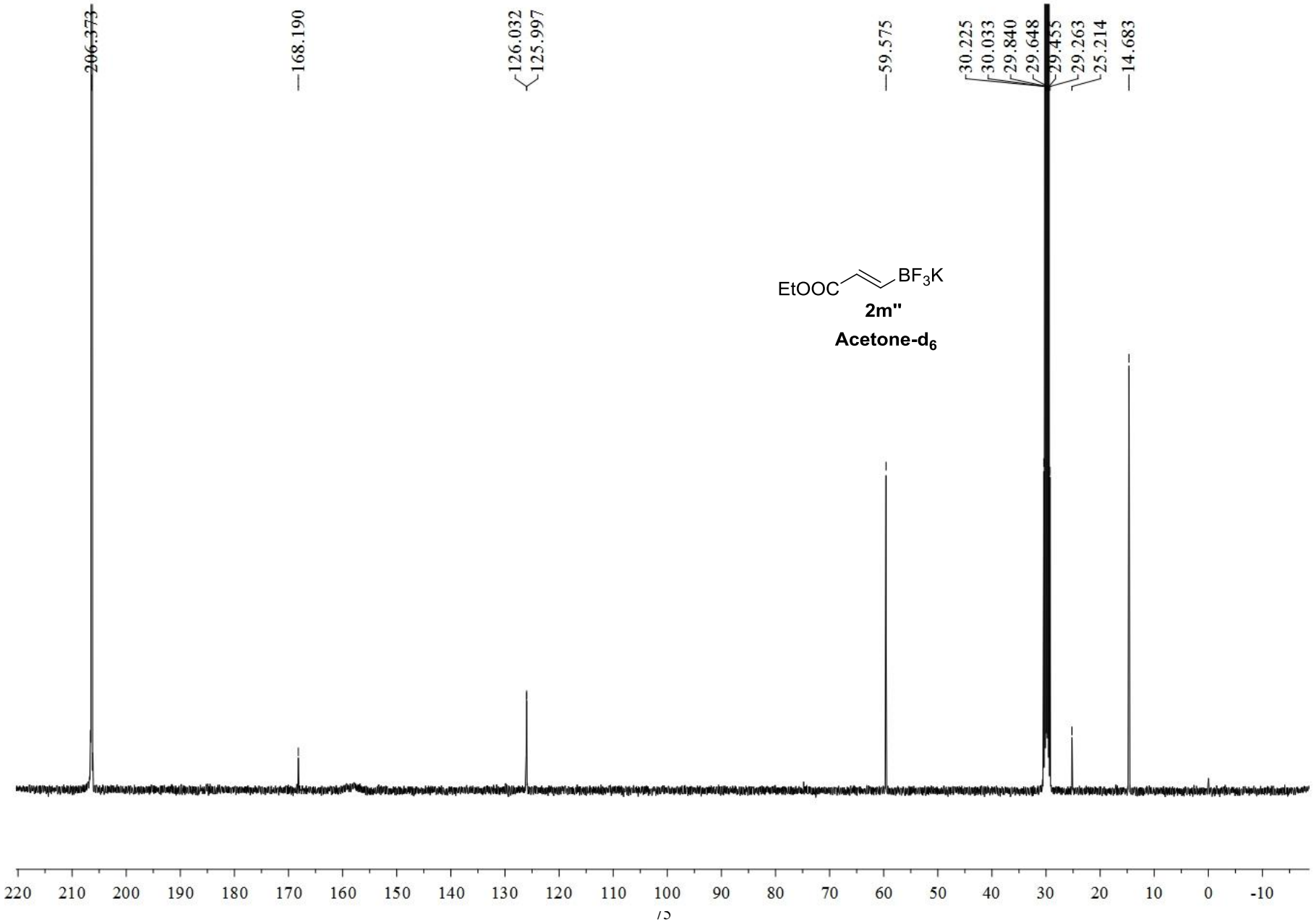




2m''

Acetone-d_6

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29.263
25.214
14.683
EtOOC
BF3K
2m''
Acetone-d6
220
210
200
190
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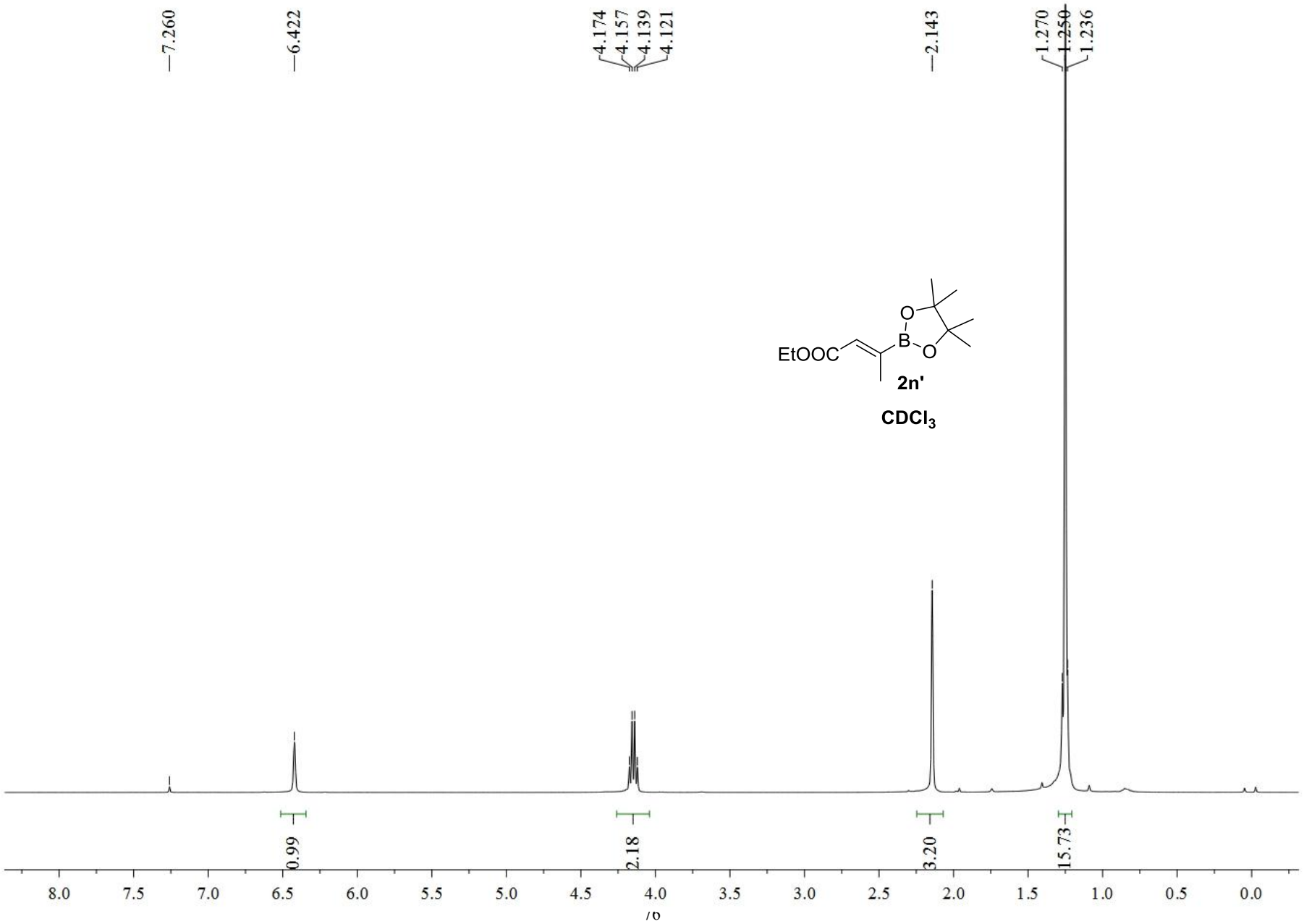
-10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B
O
2n'
CDCl3
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3.20
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7.0
6.5
6.0
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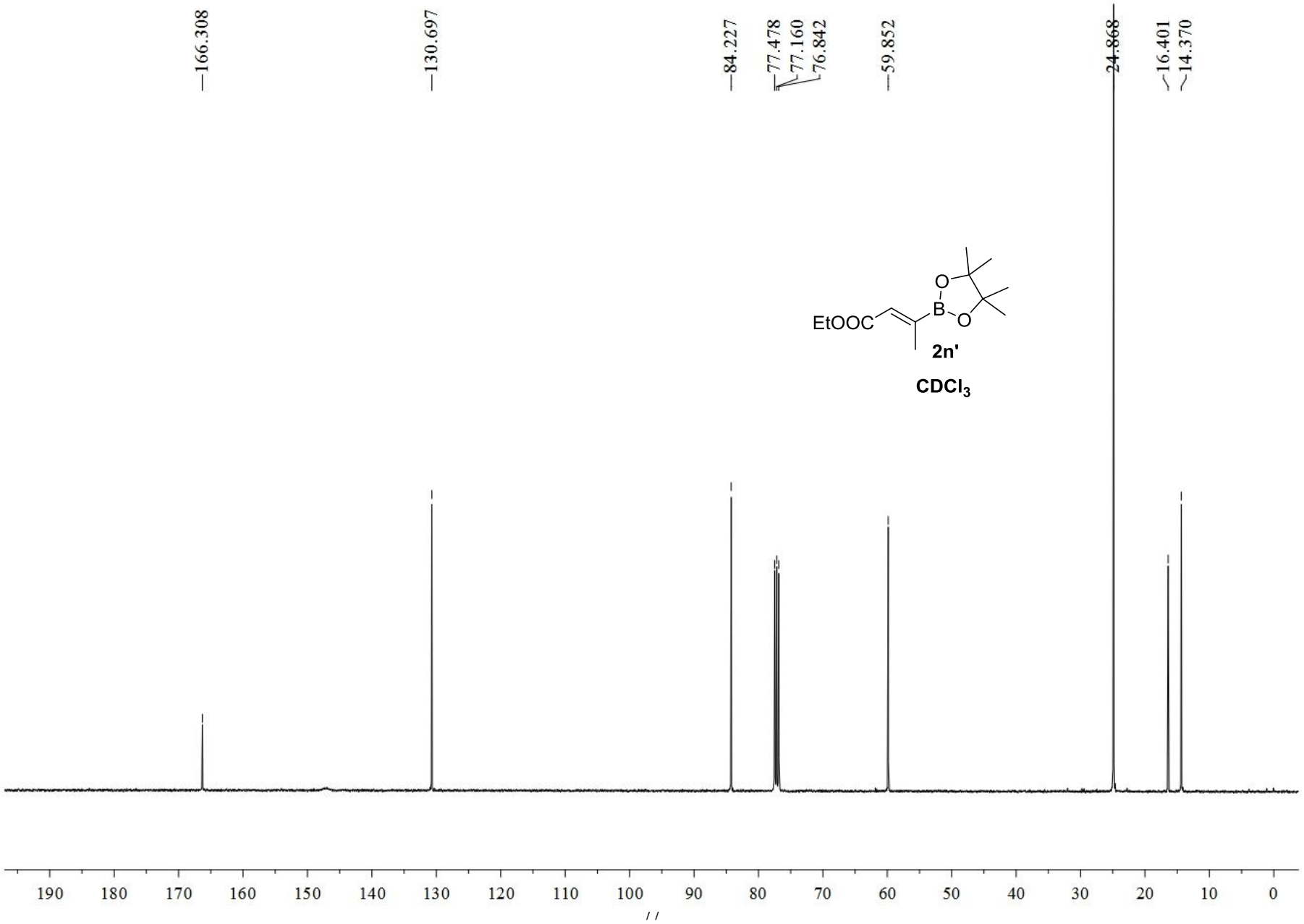
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14.370
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B
O
2n'
CDCl3
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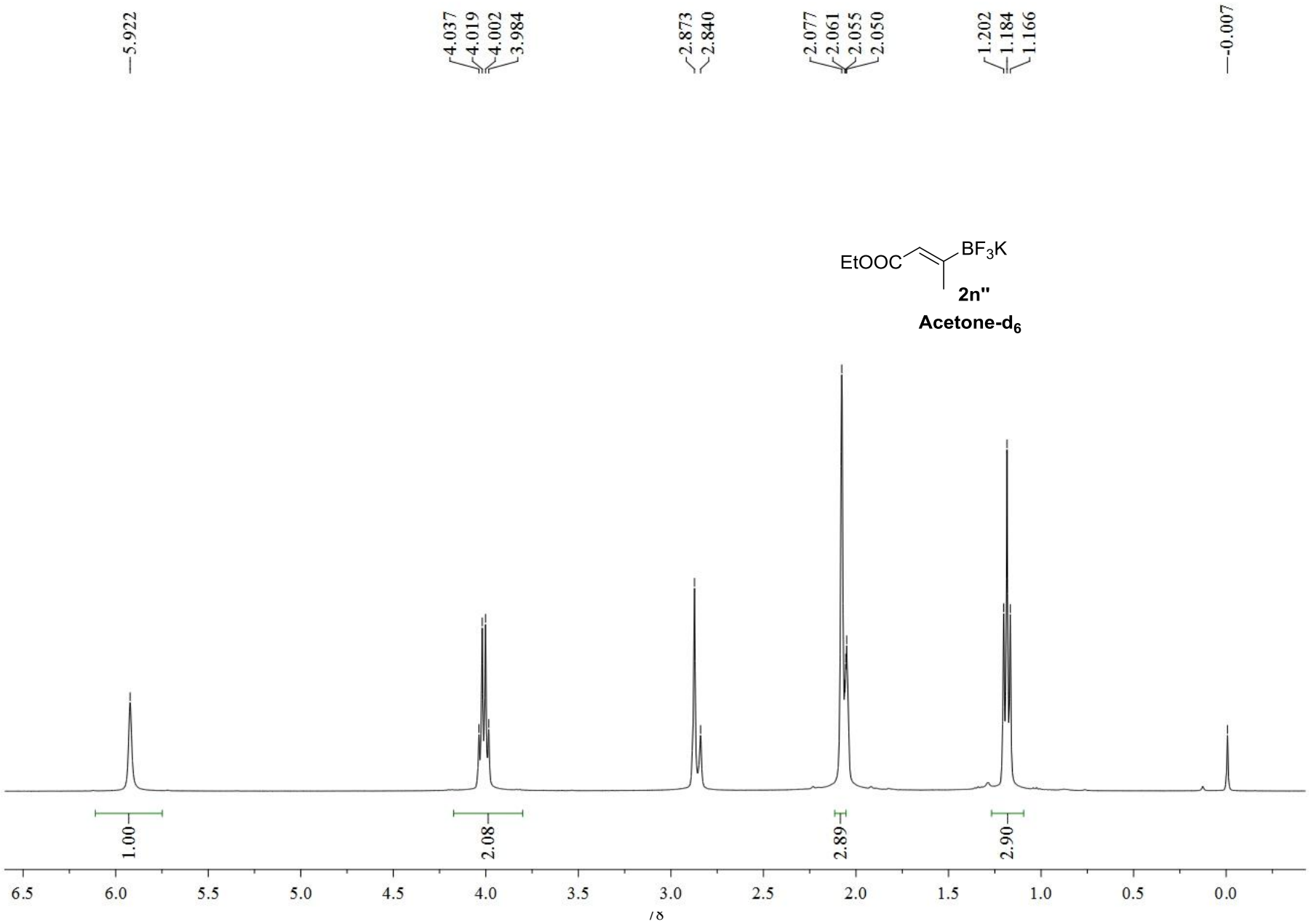
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2.055
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BF3K
2n''
Acetone-d6
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2.08
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6.5
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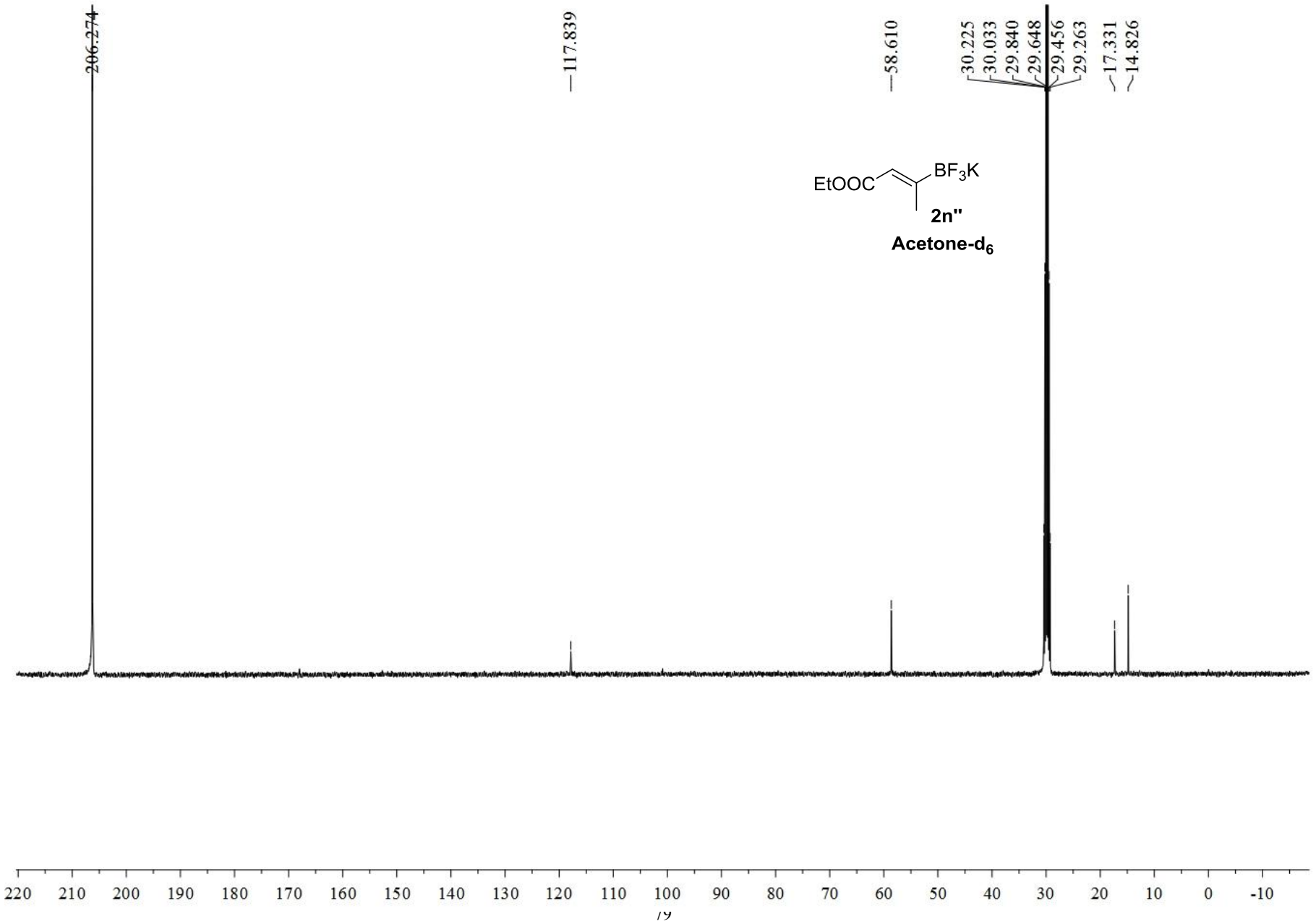
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17.331
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BF3K
2n''
Acetone-d6
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210
200
190
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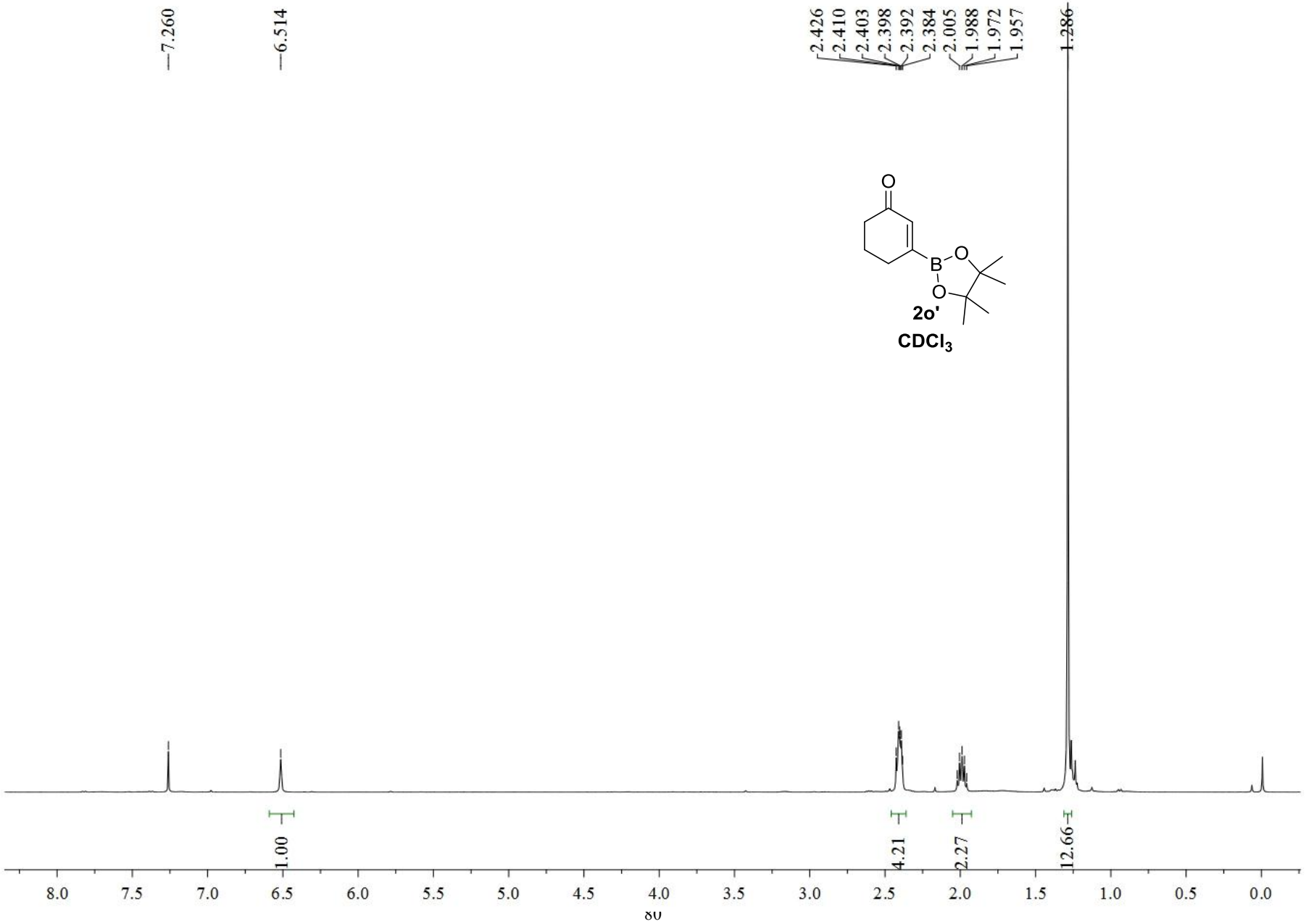
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O
B
O
O
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6.5
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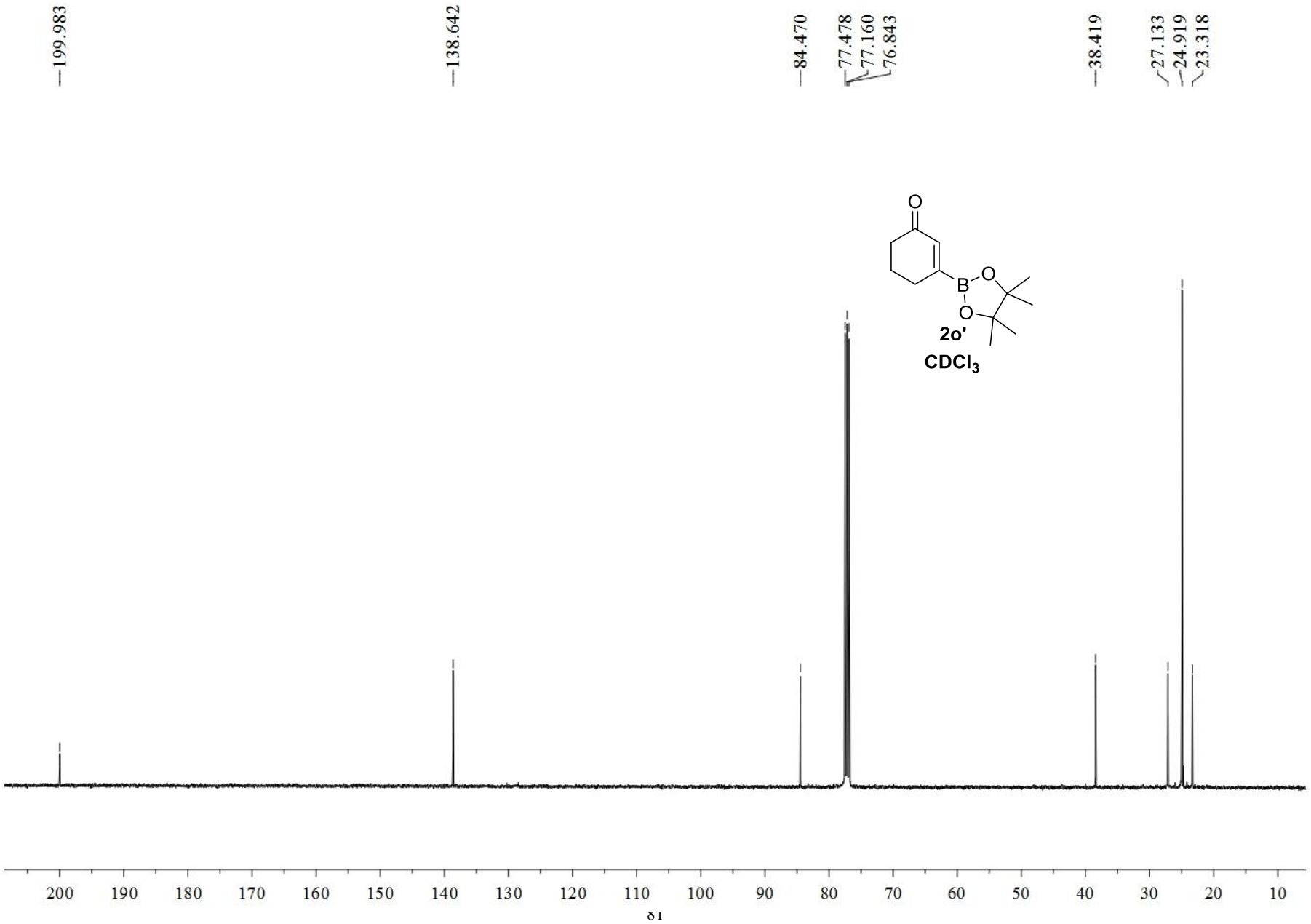
δ0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B
O
O
2o'
CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
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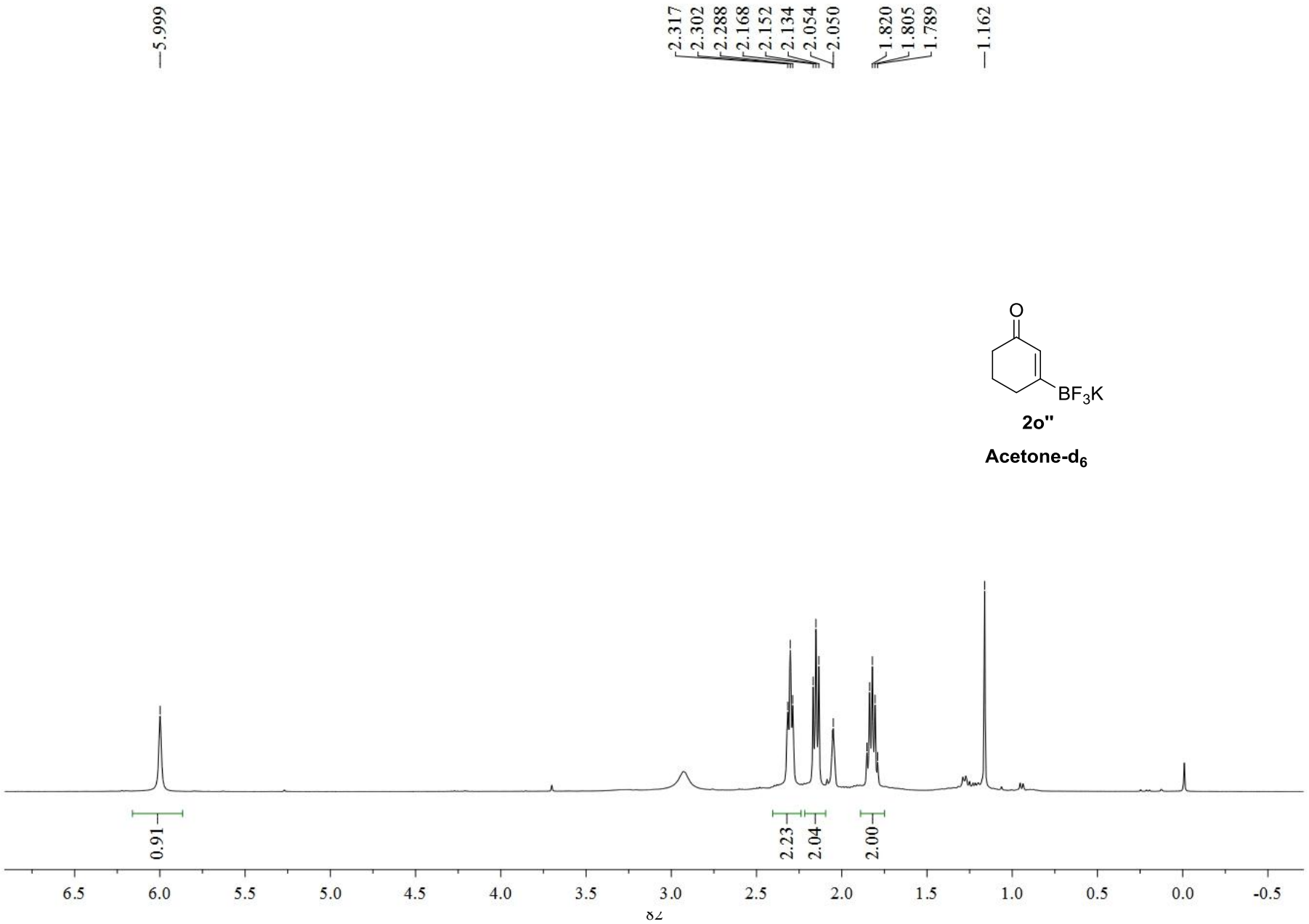
60
50
40
30
20
10
δ1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BF3K
2o''
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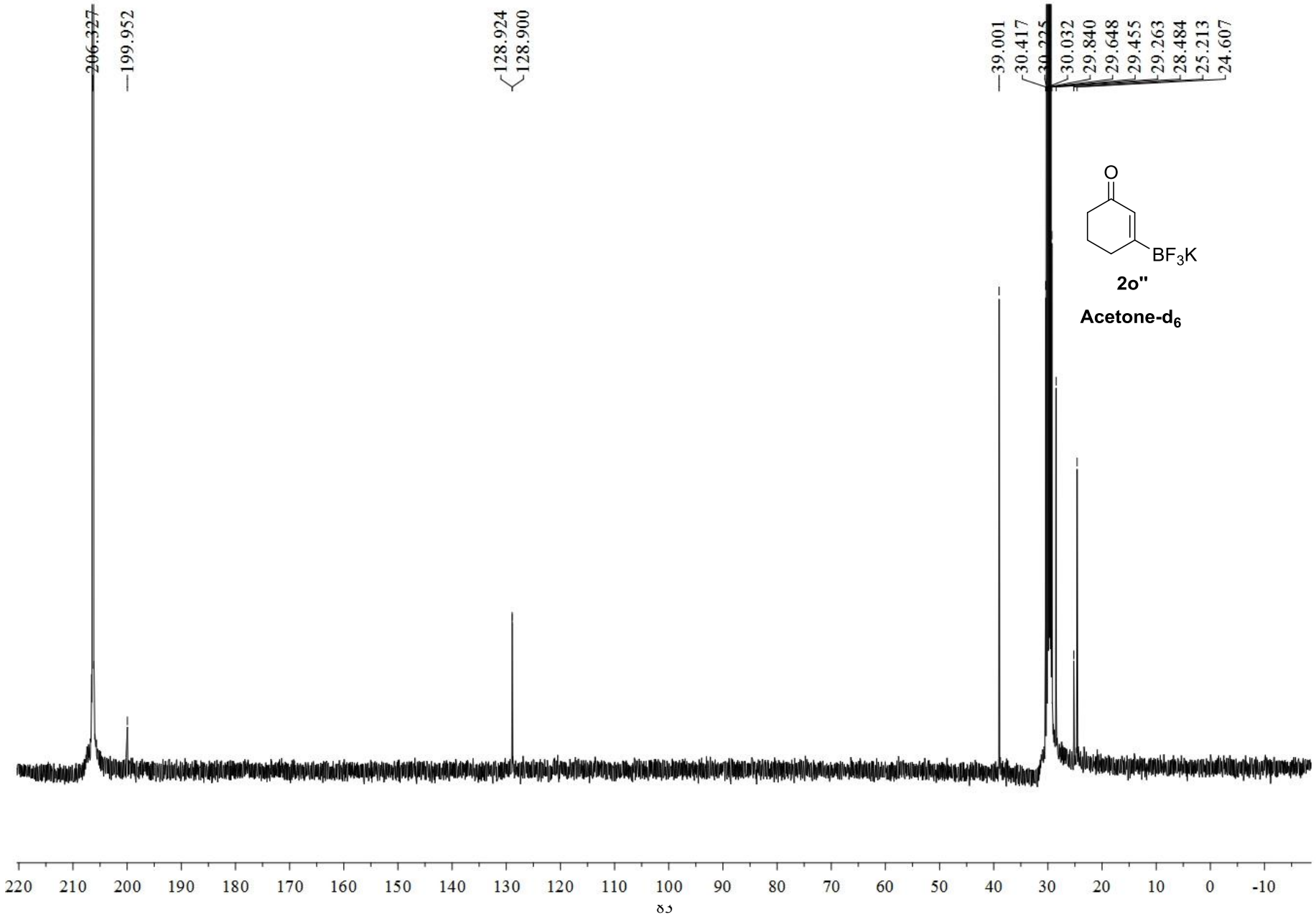
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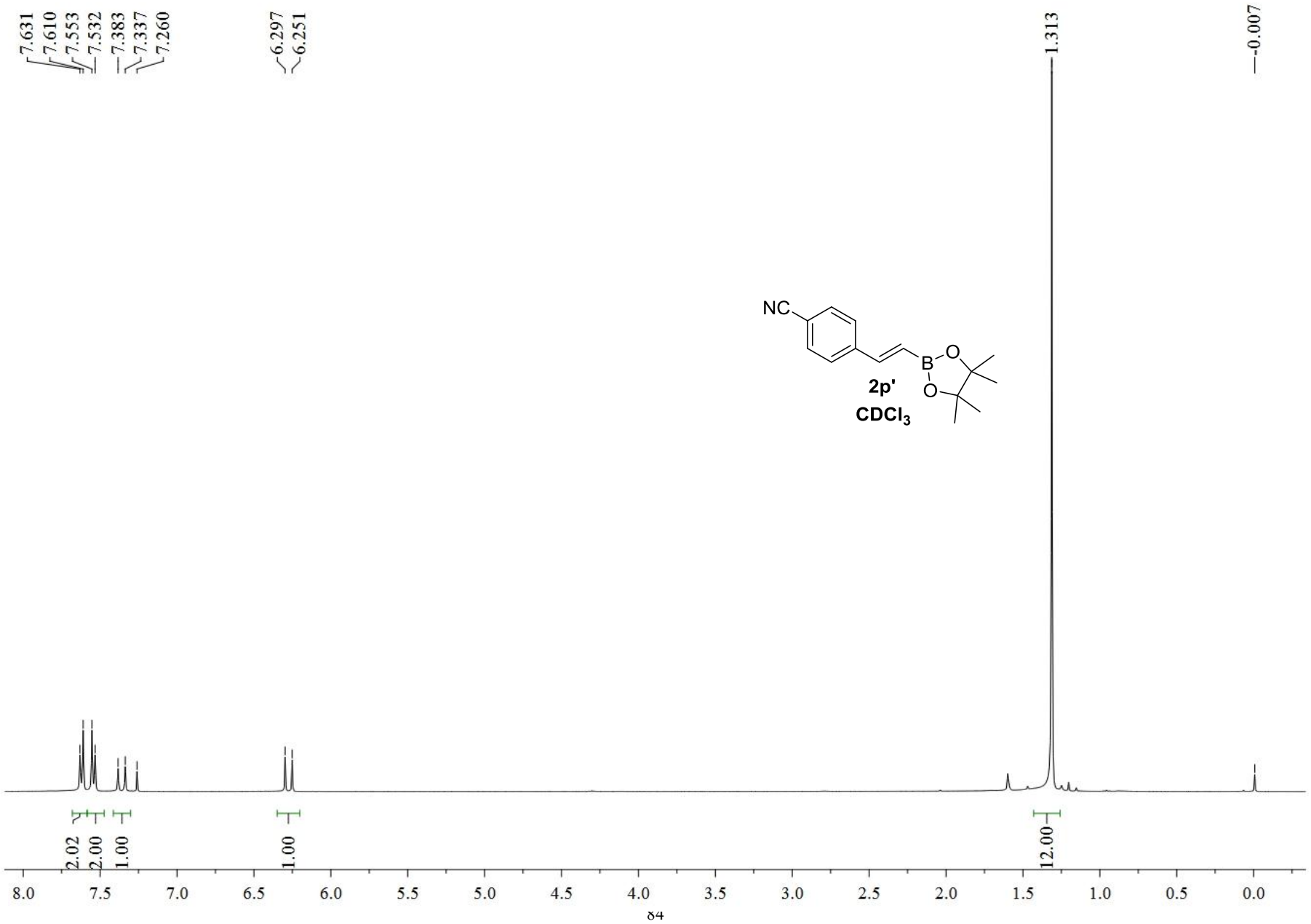
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O
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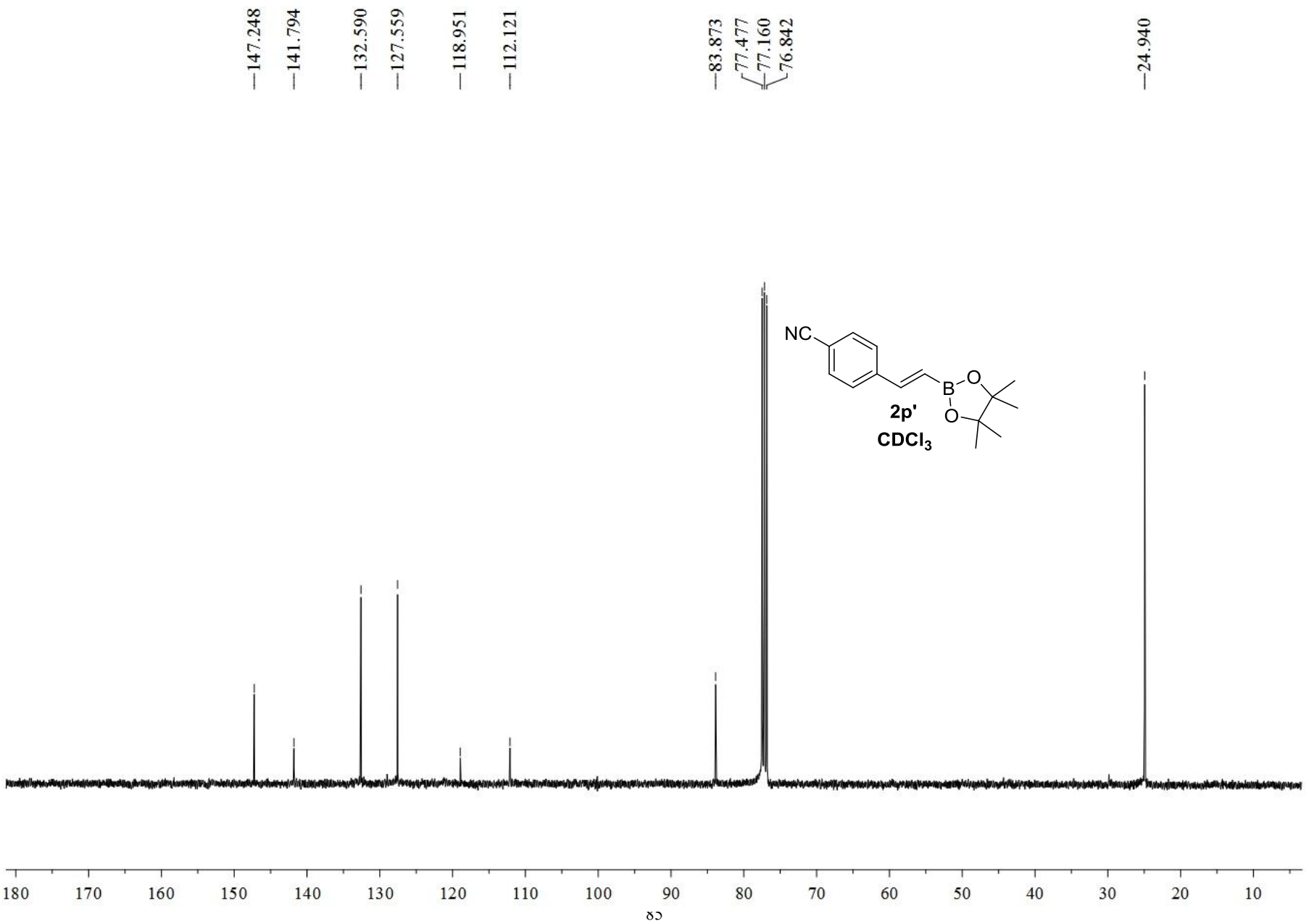
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2p'
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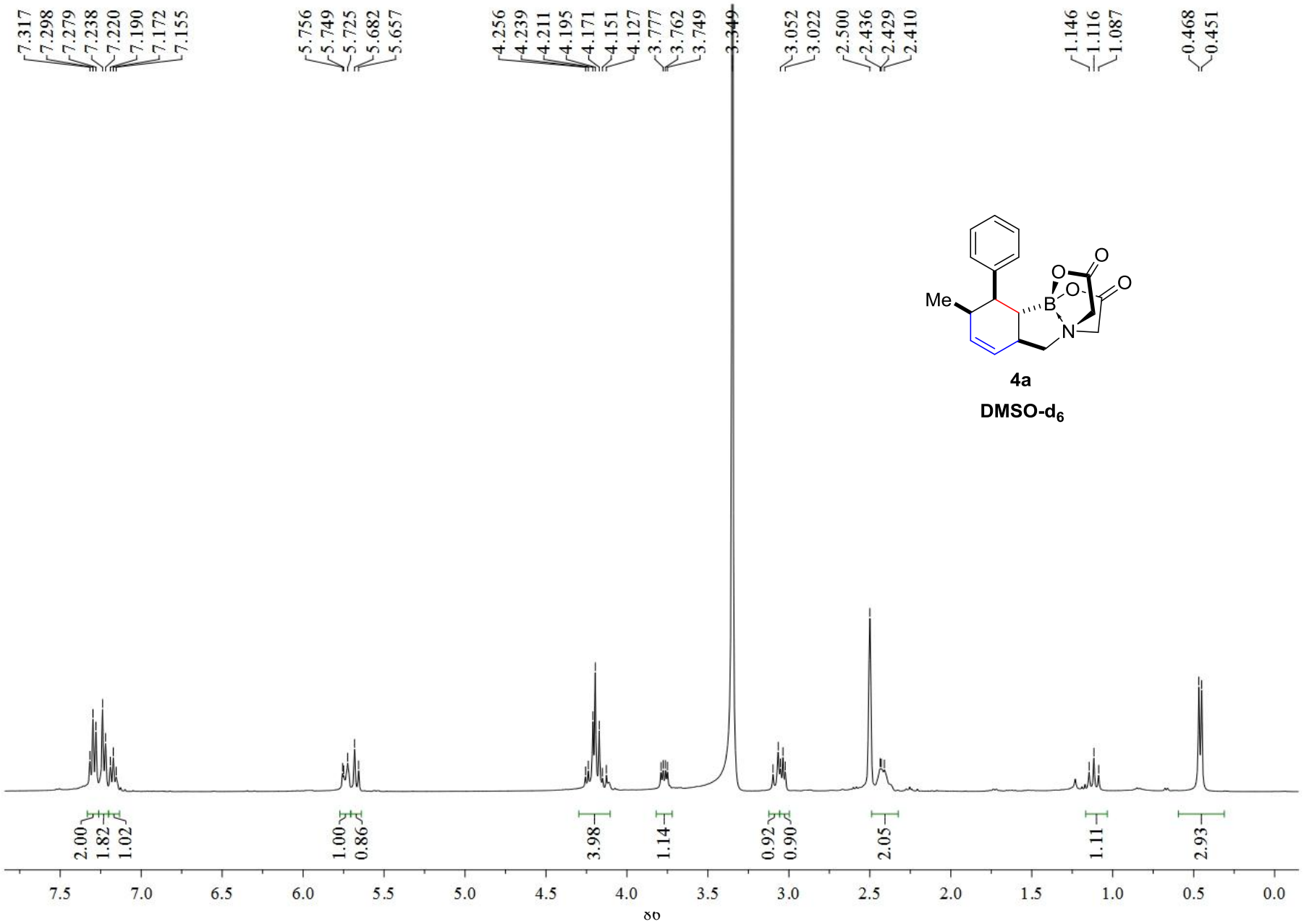
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3.052
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B
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O
O
O
N
4a
DMSO-d6
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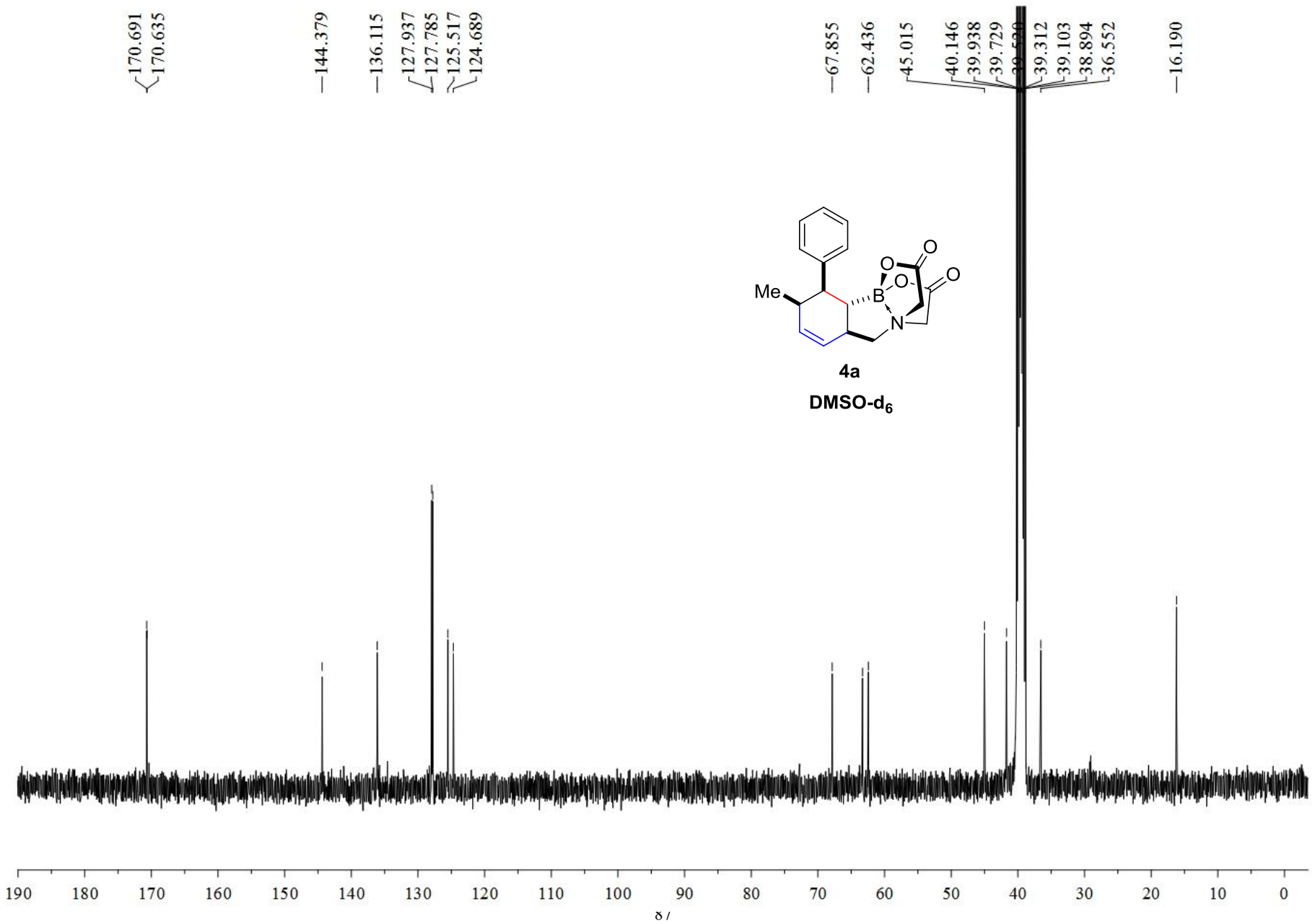
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B
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4a
DMSO-d6
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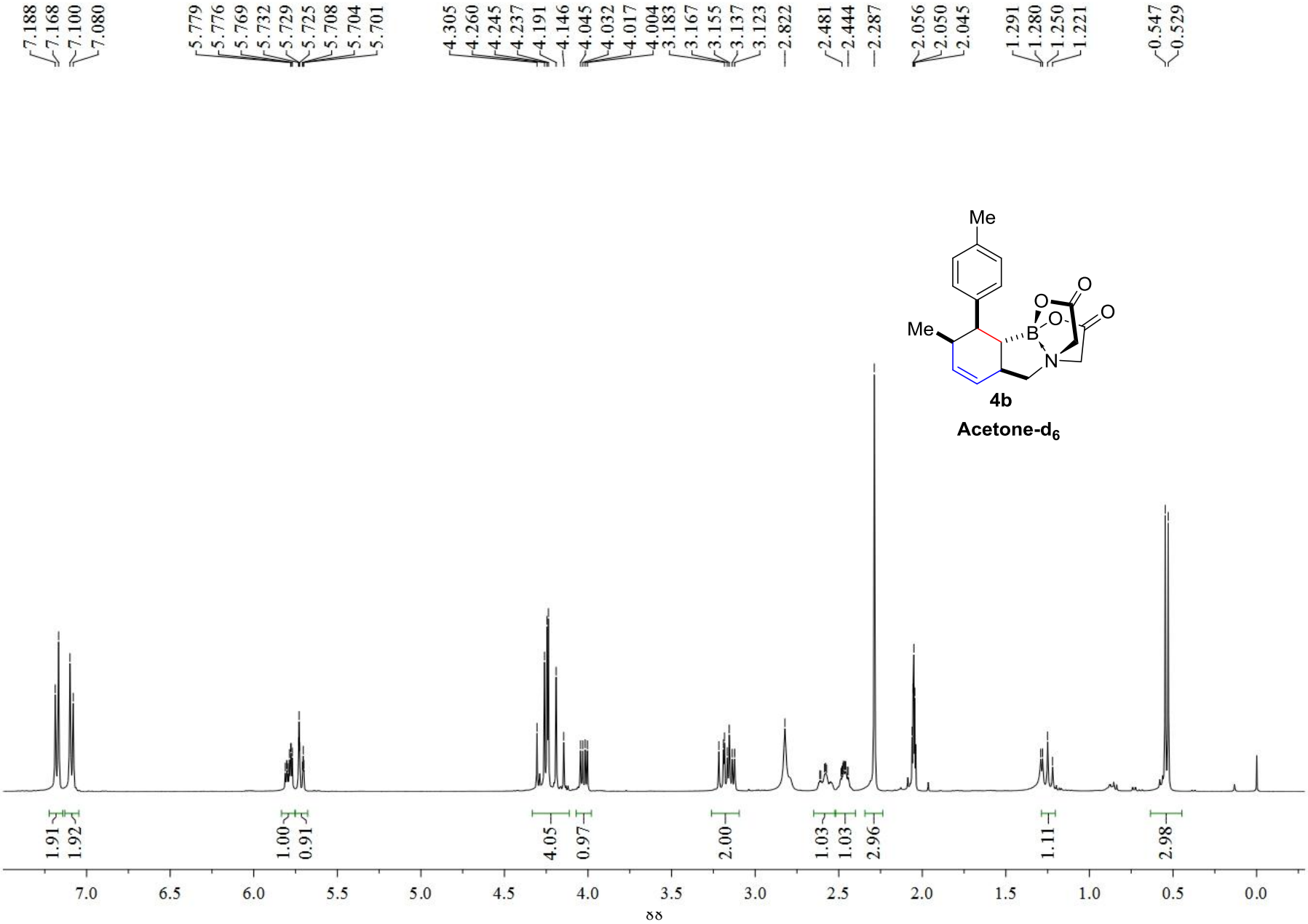
δ /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O
B
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Acetone-d6
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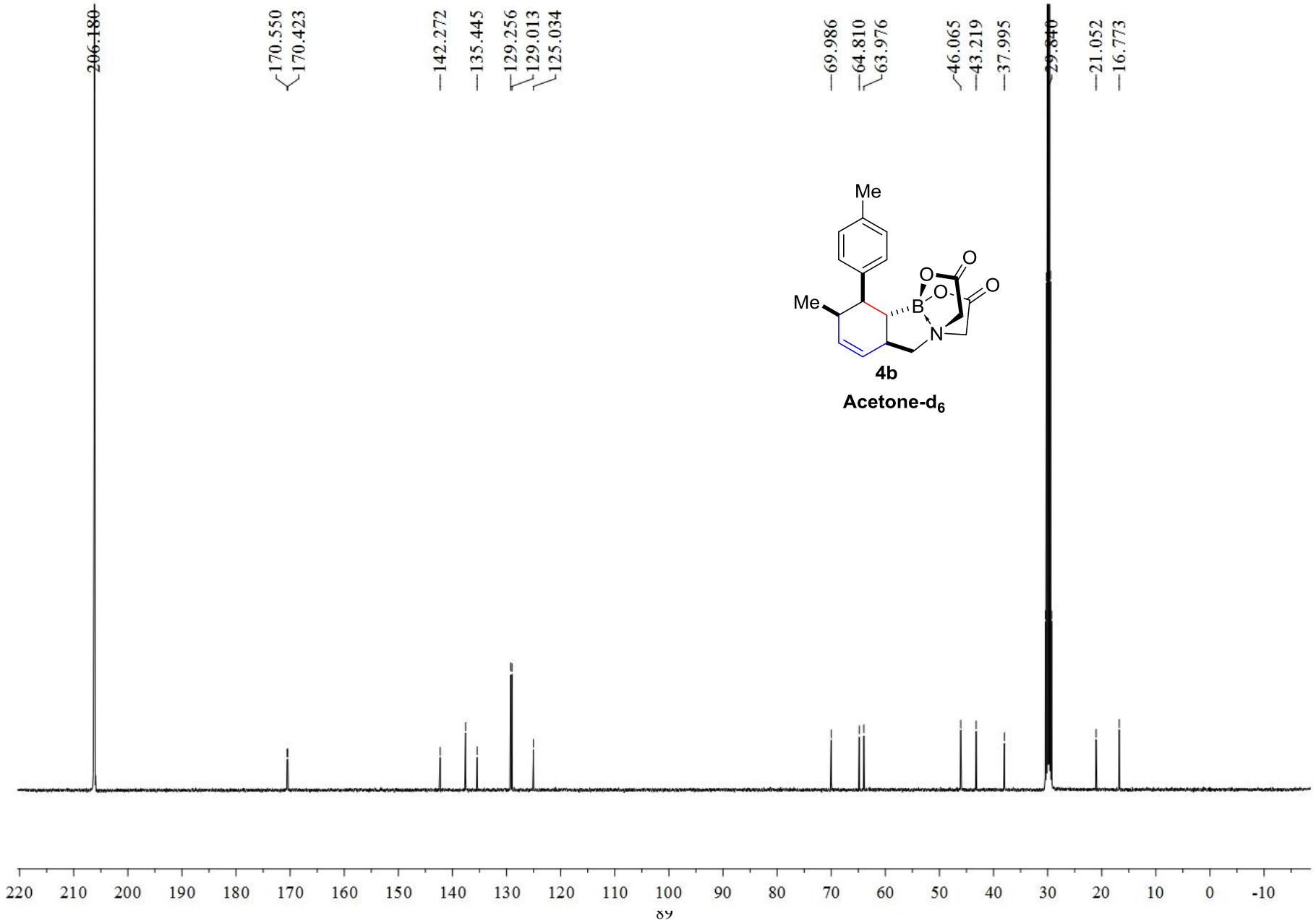
δδ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Me
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O
O
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B
N
4b
Acetone-d6
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200
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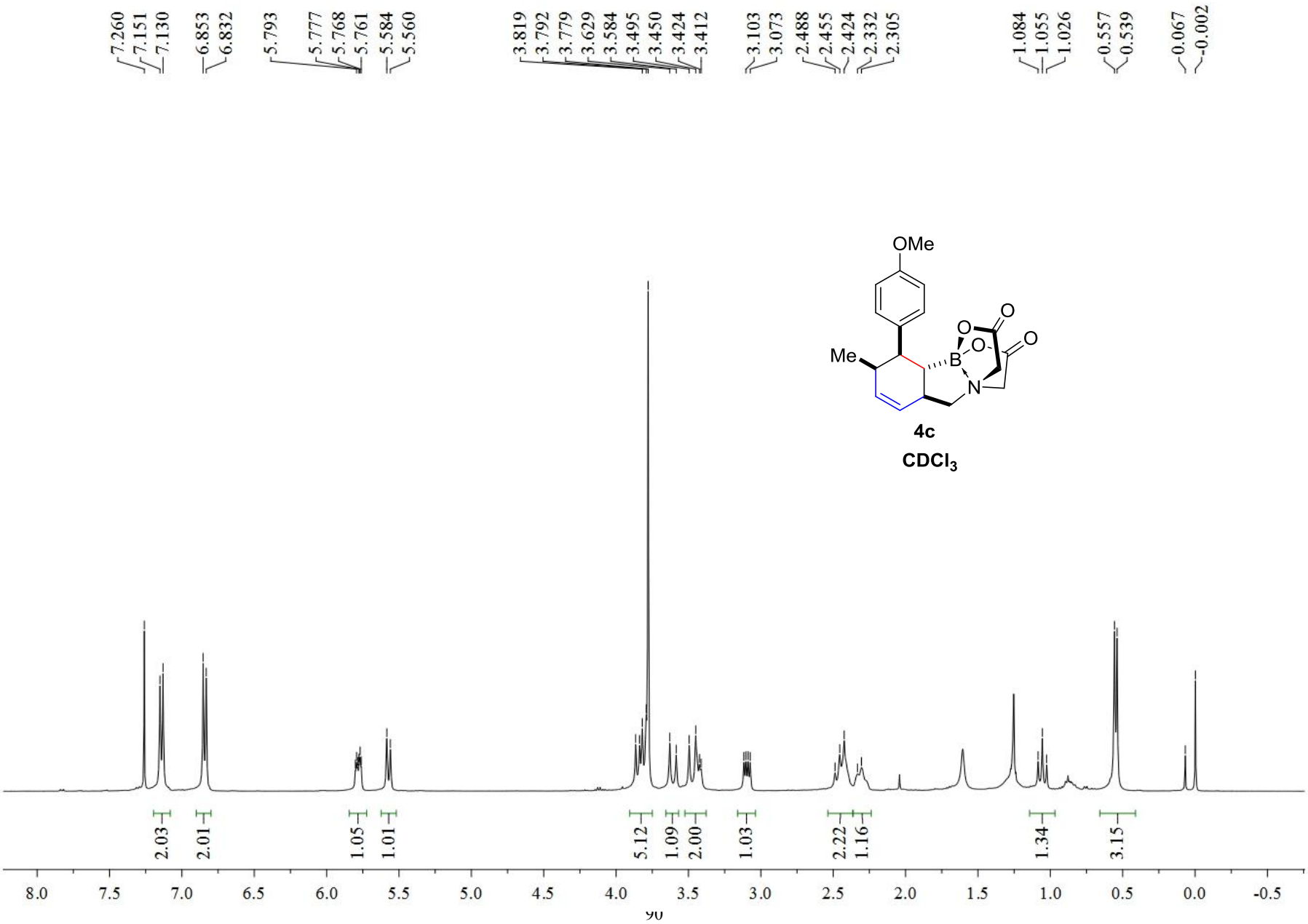
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B
O
N
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CDCl3
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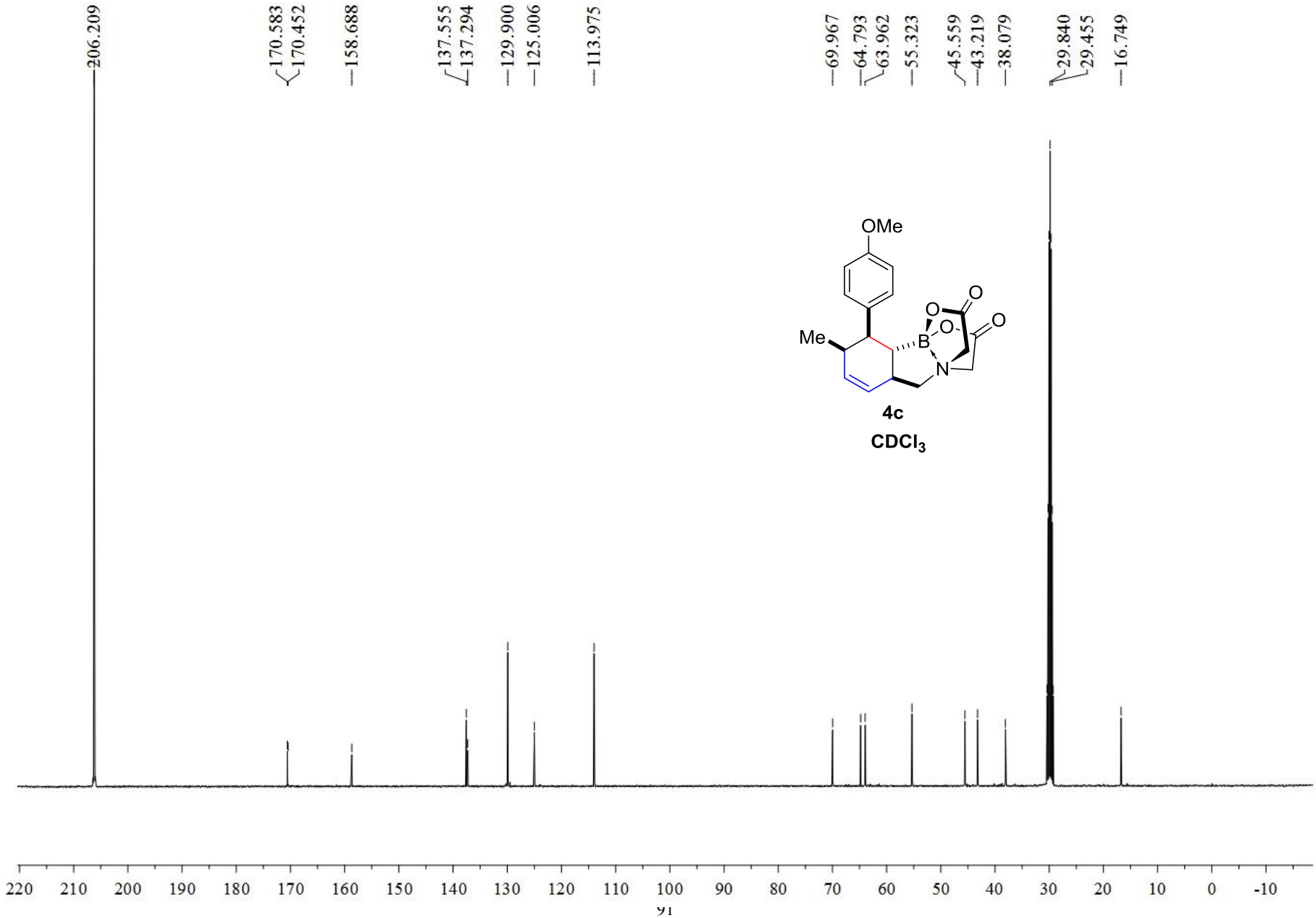
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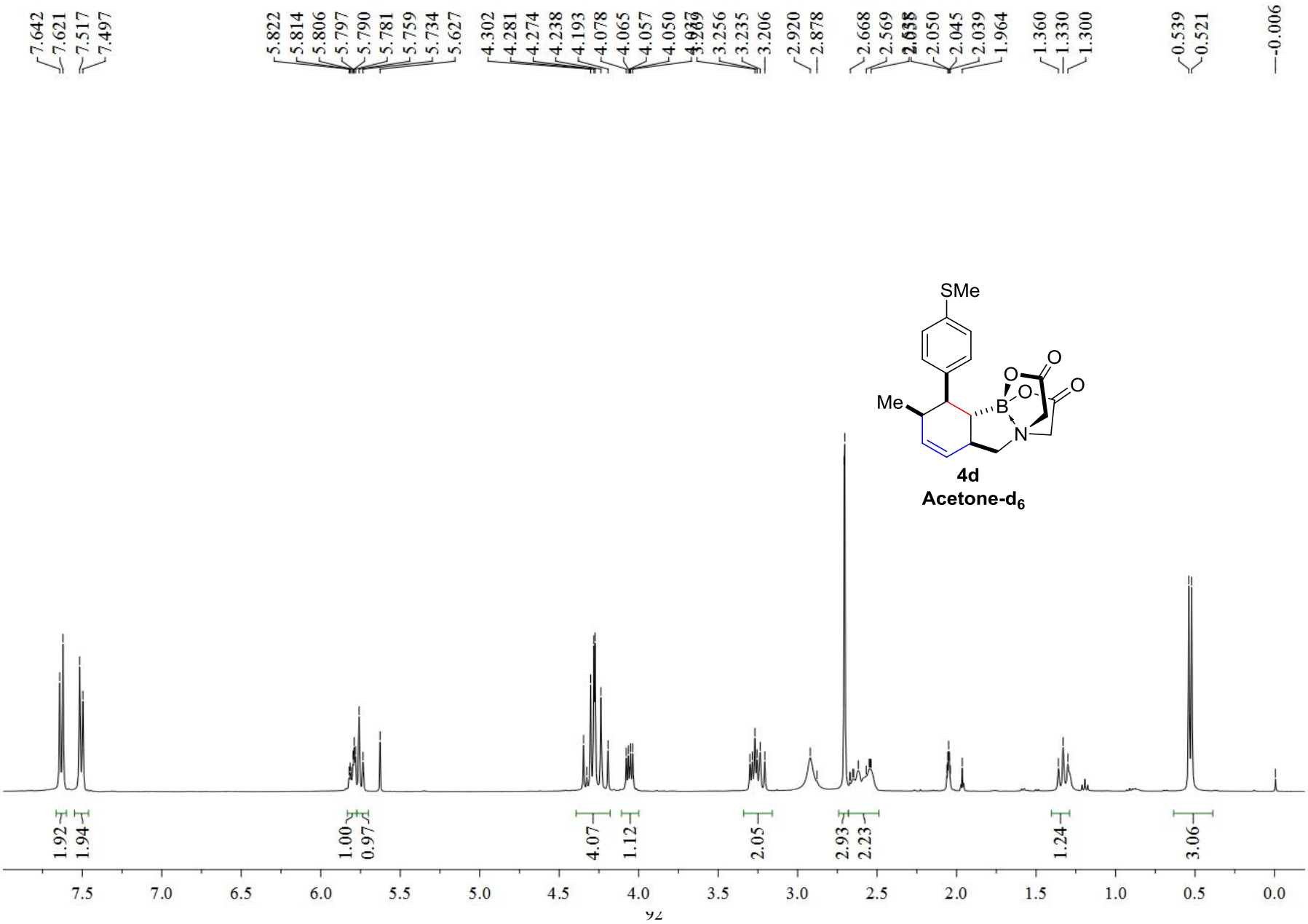
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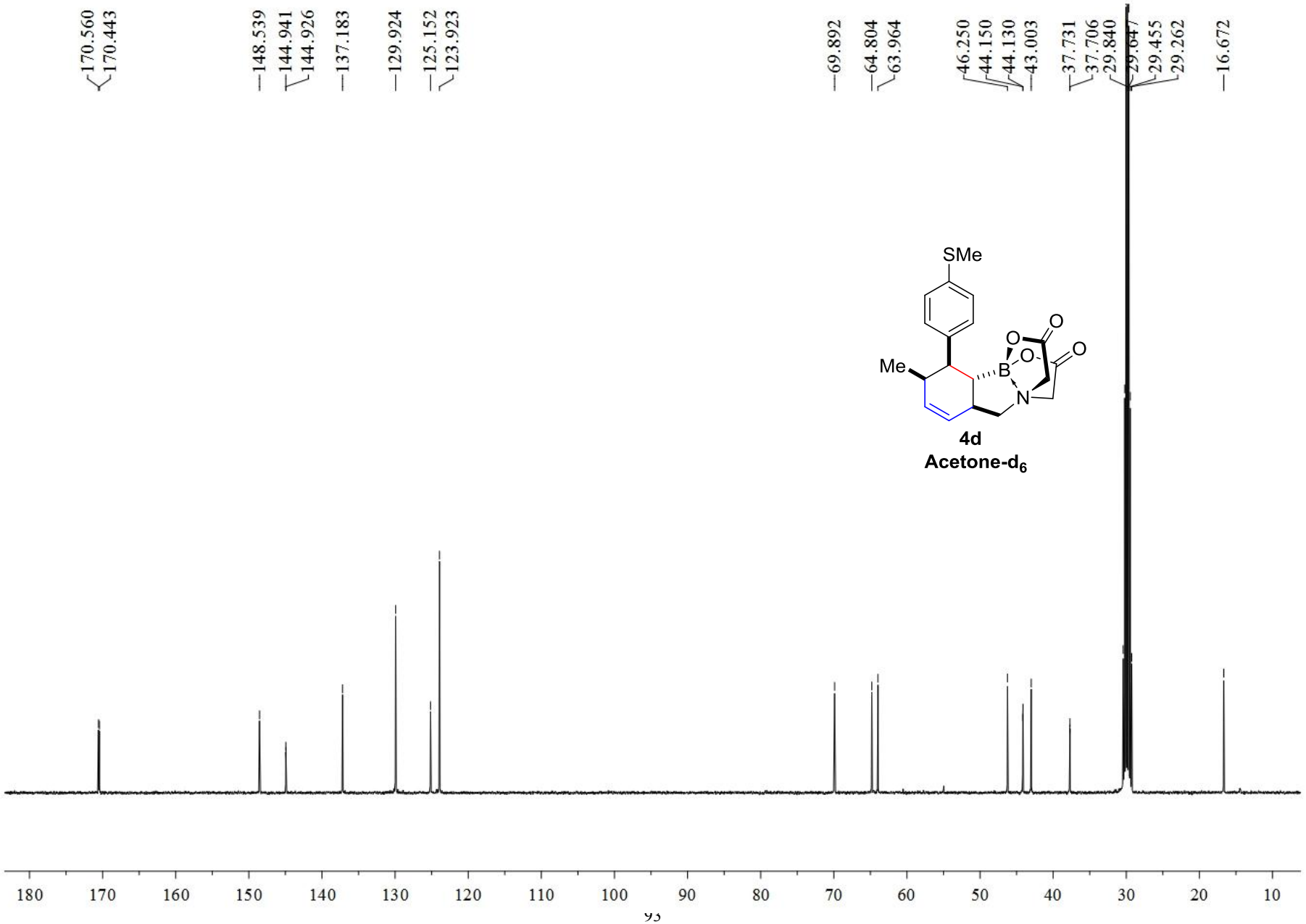
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4d
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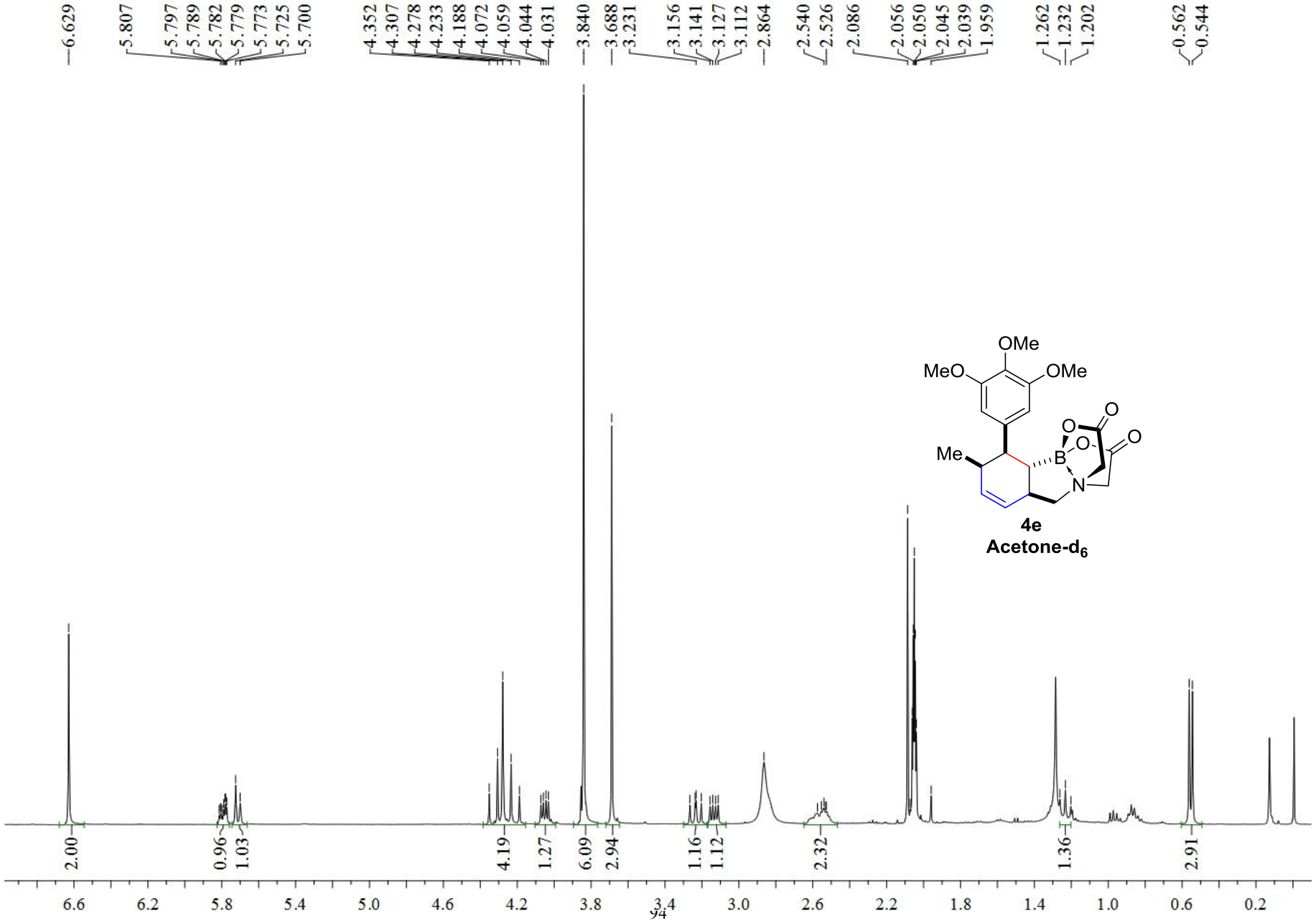
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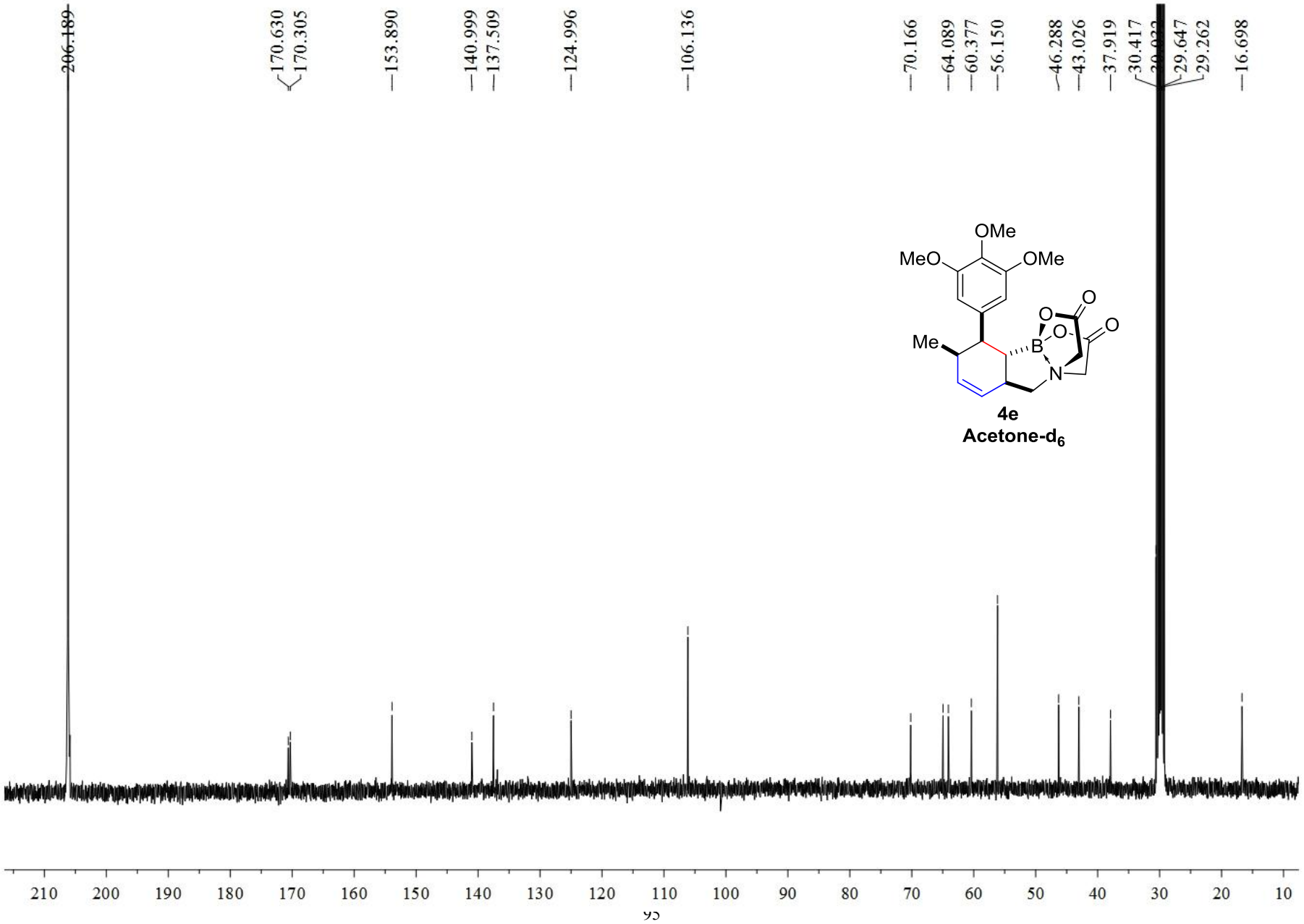
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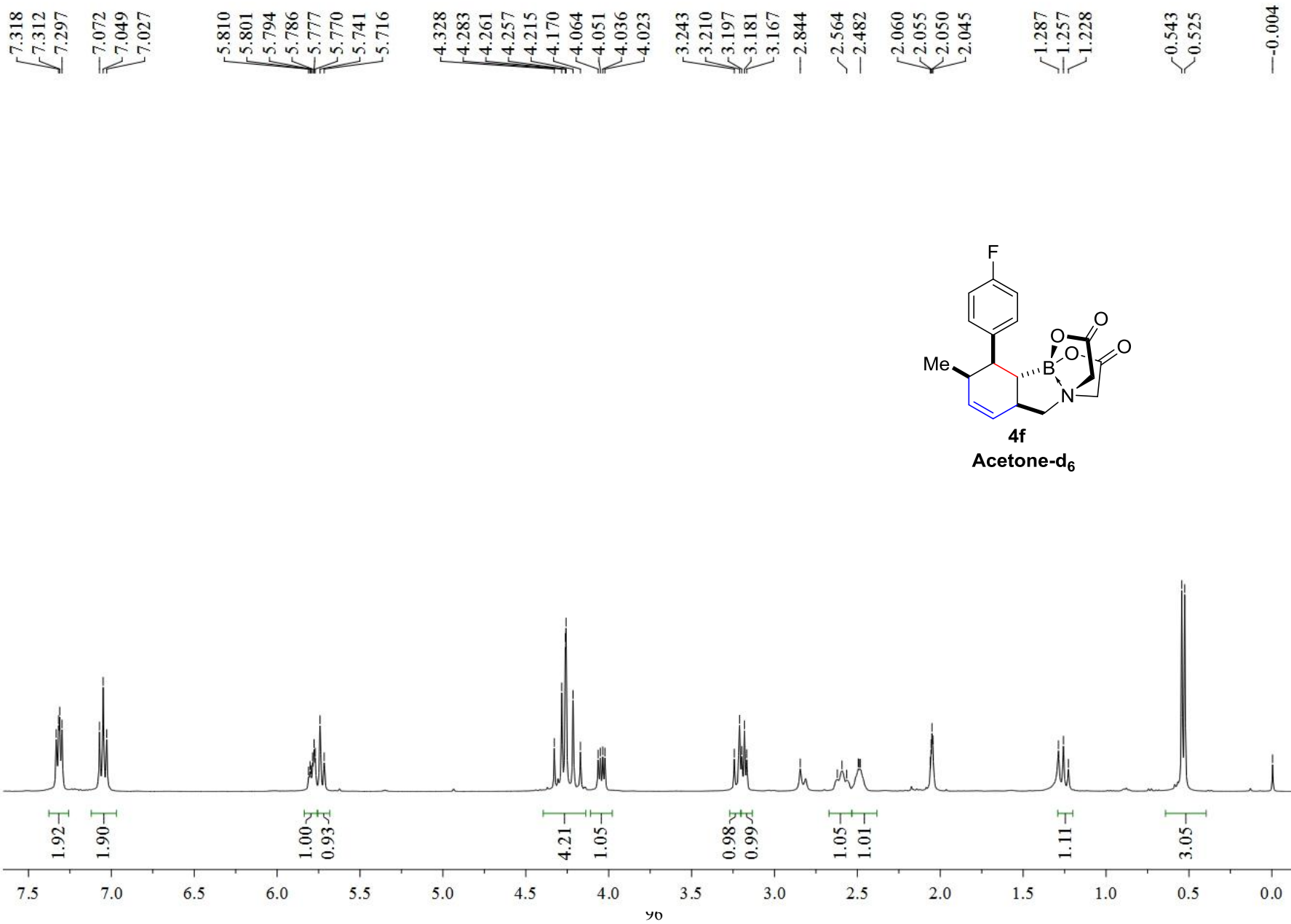
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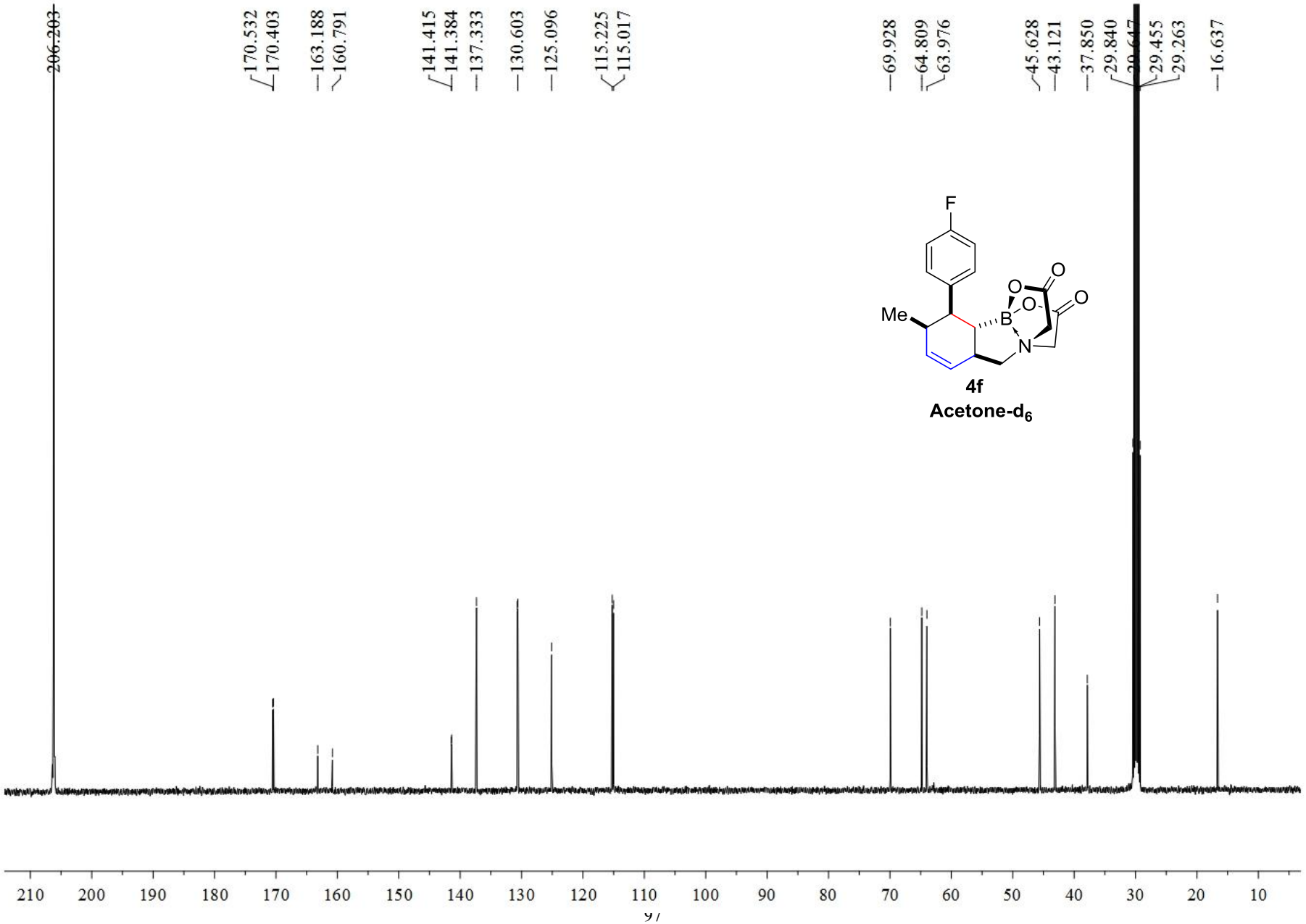
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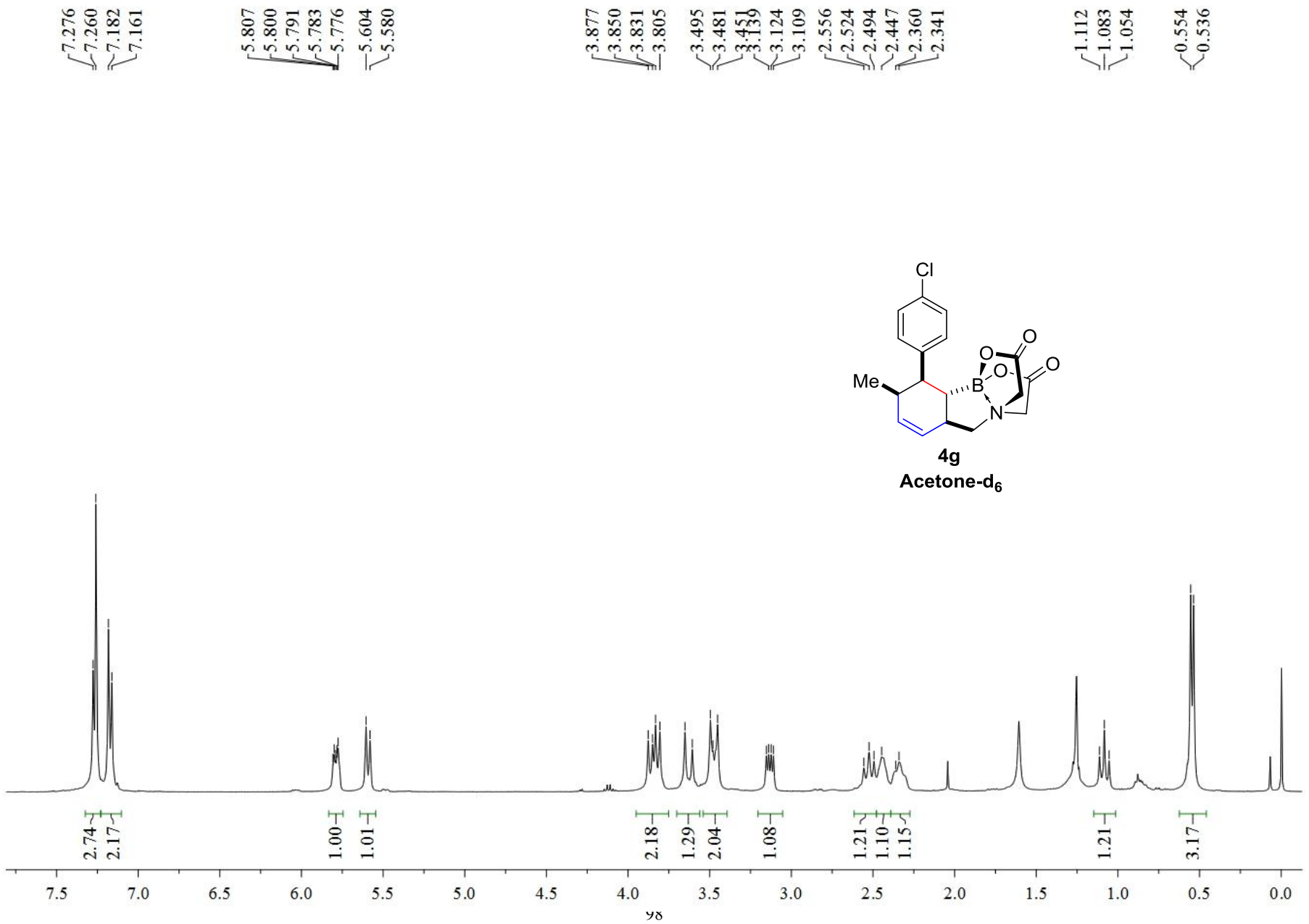
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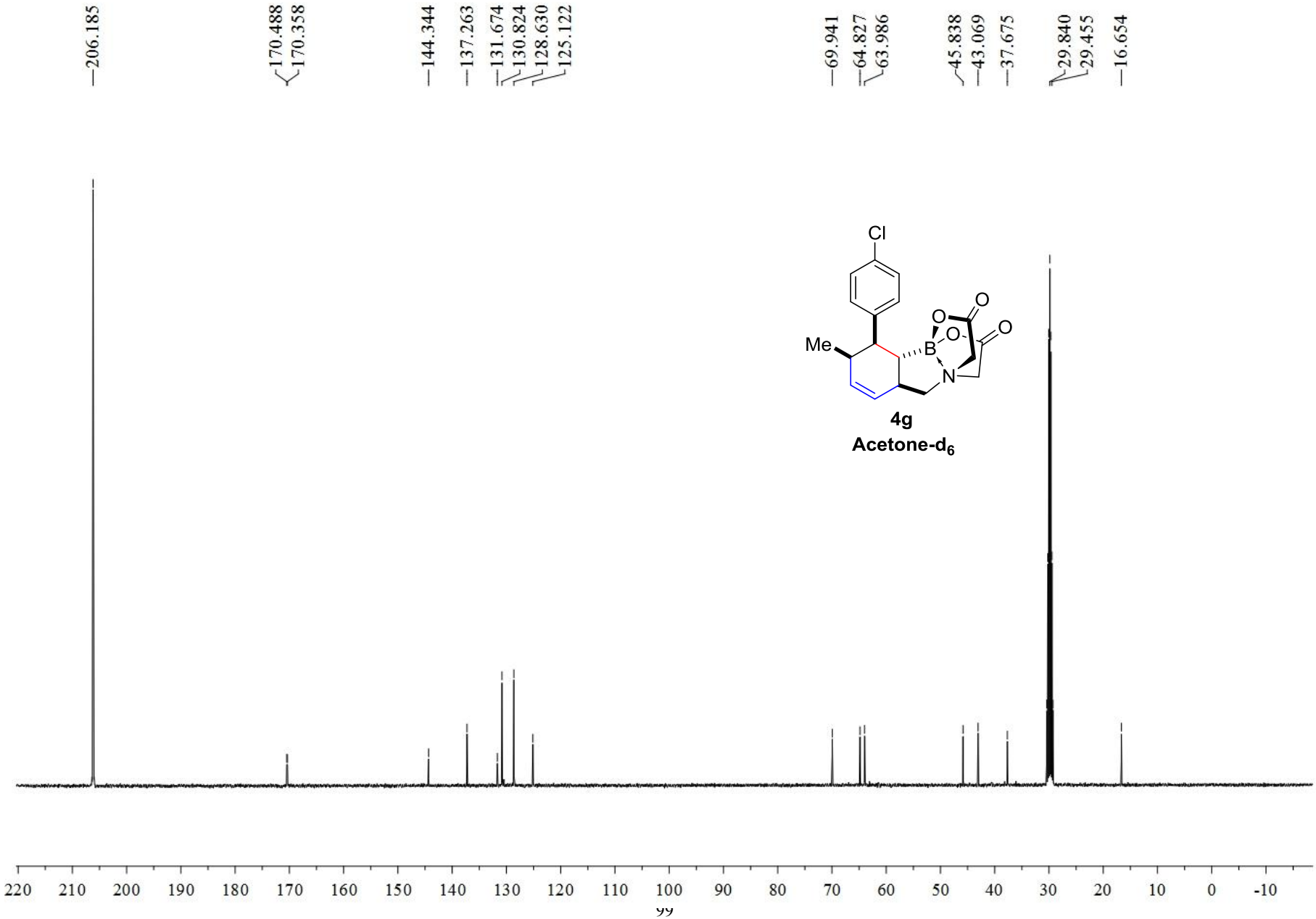
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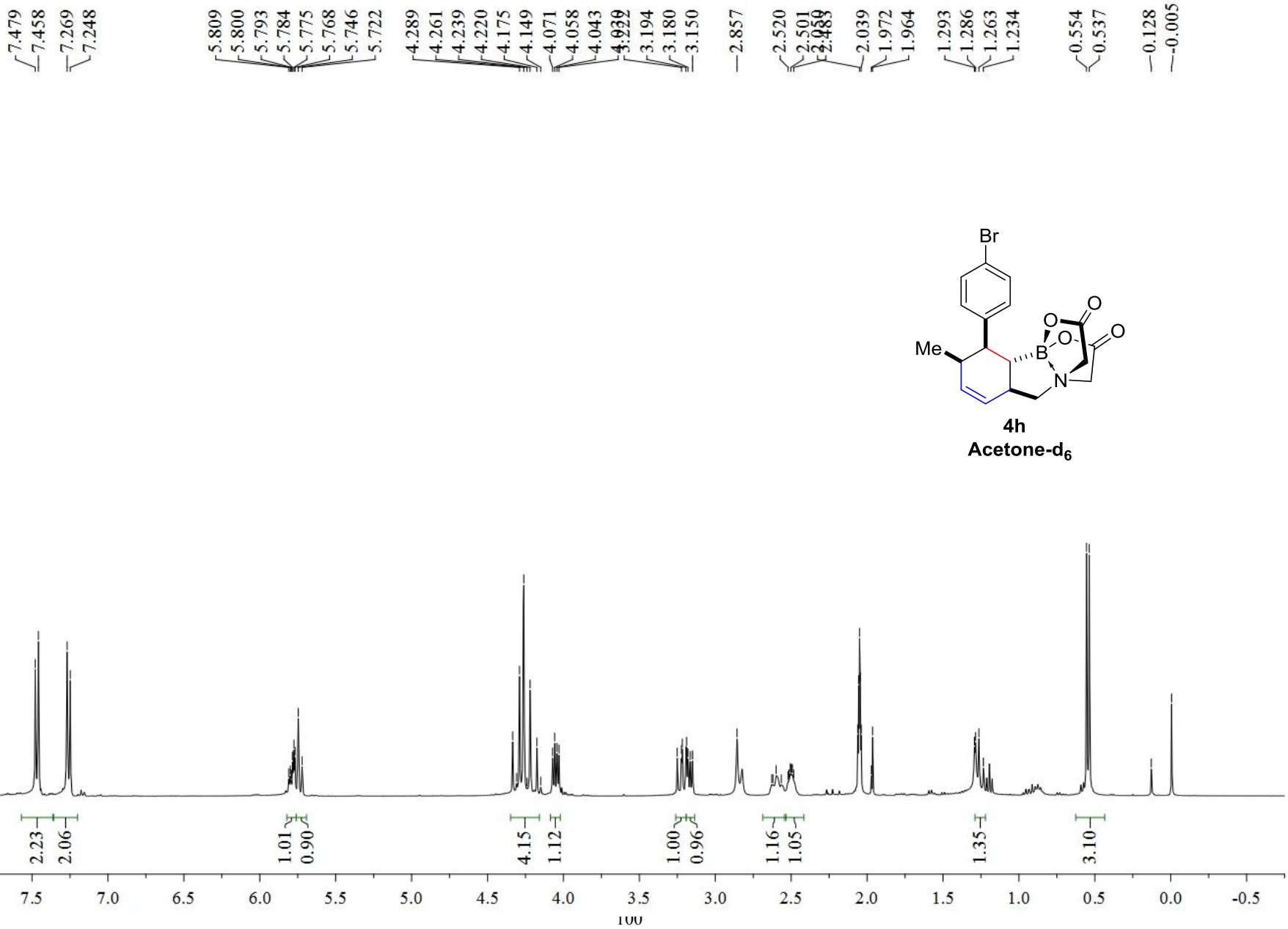
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4h
Acetone-d6
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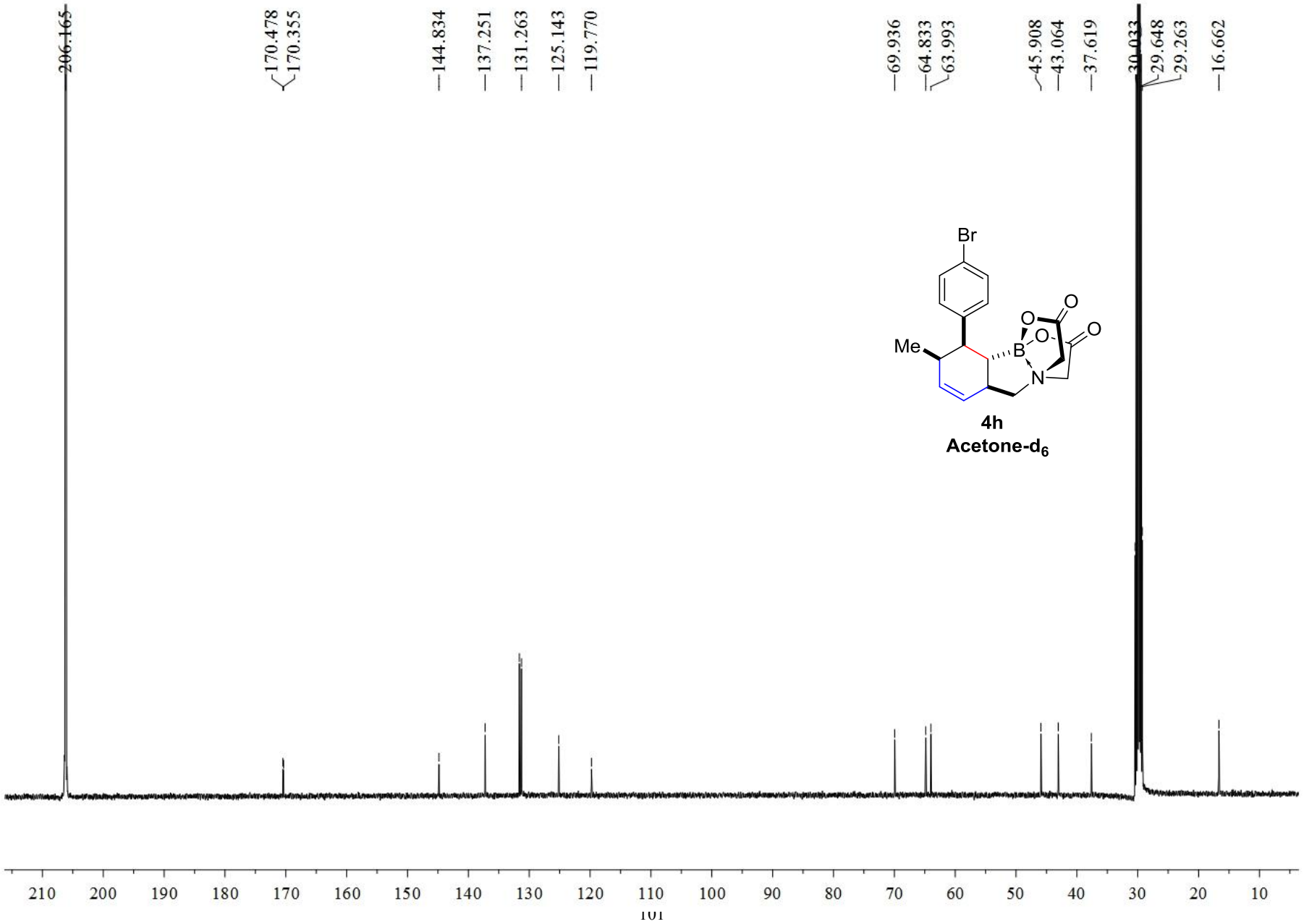
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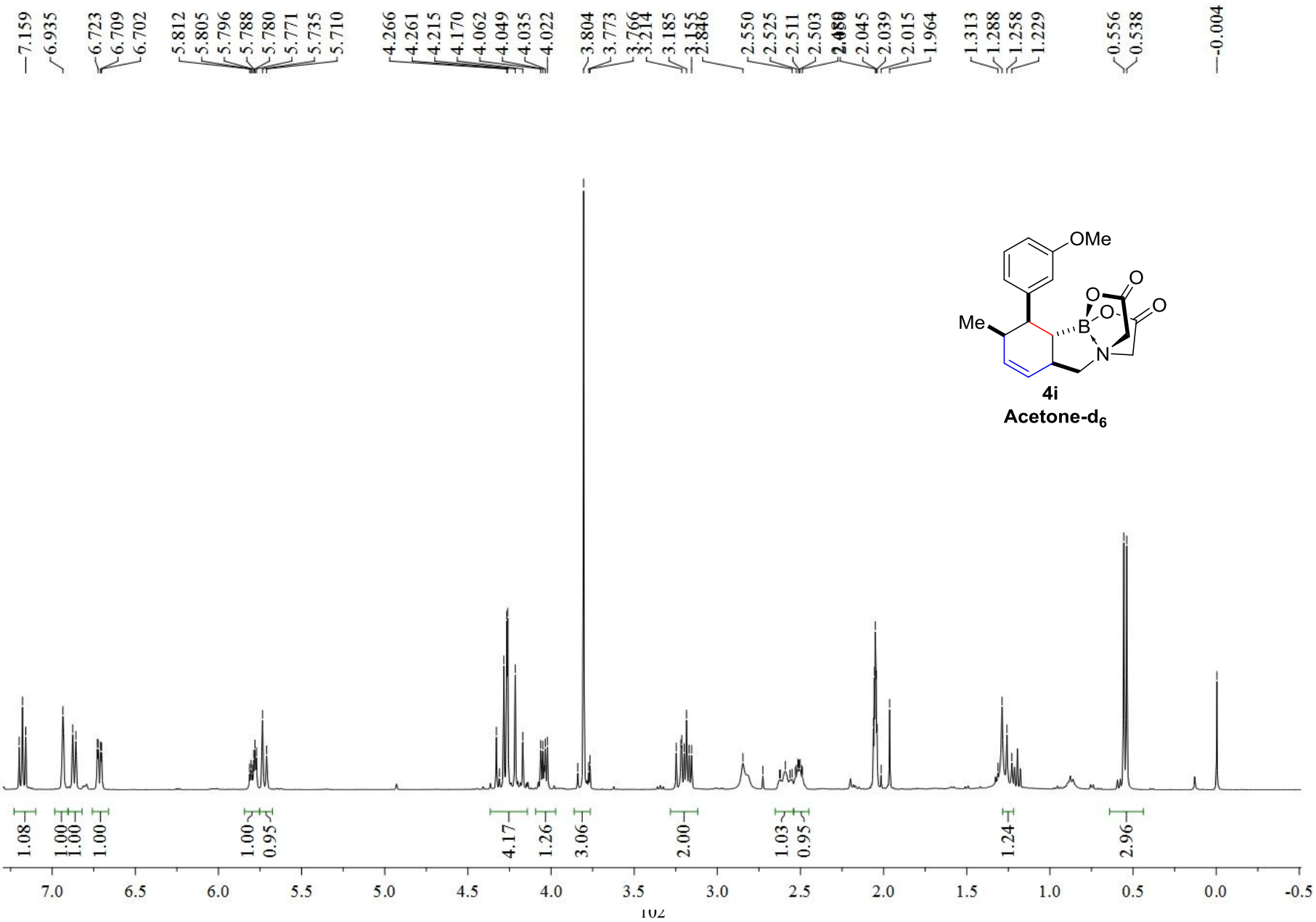
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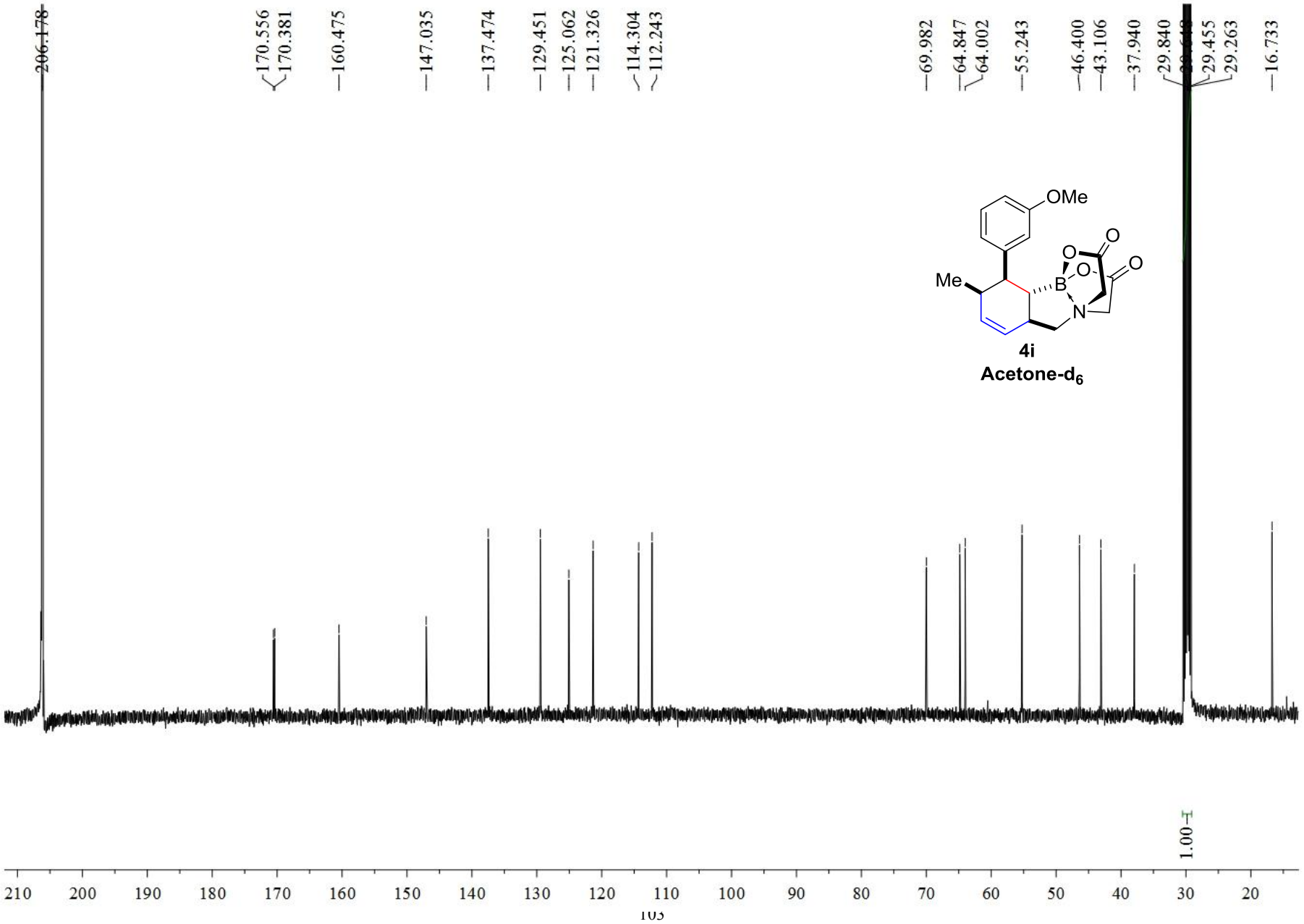
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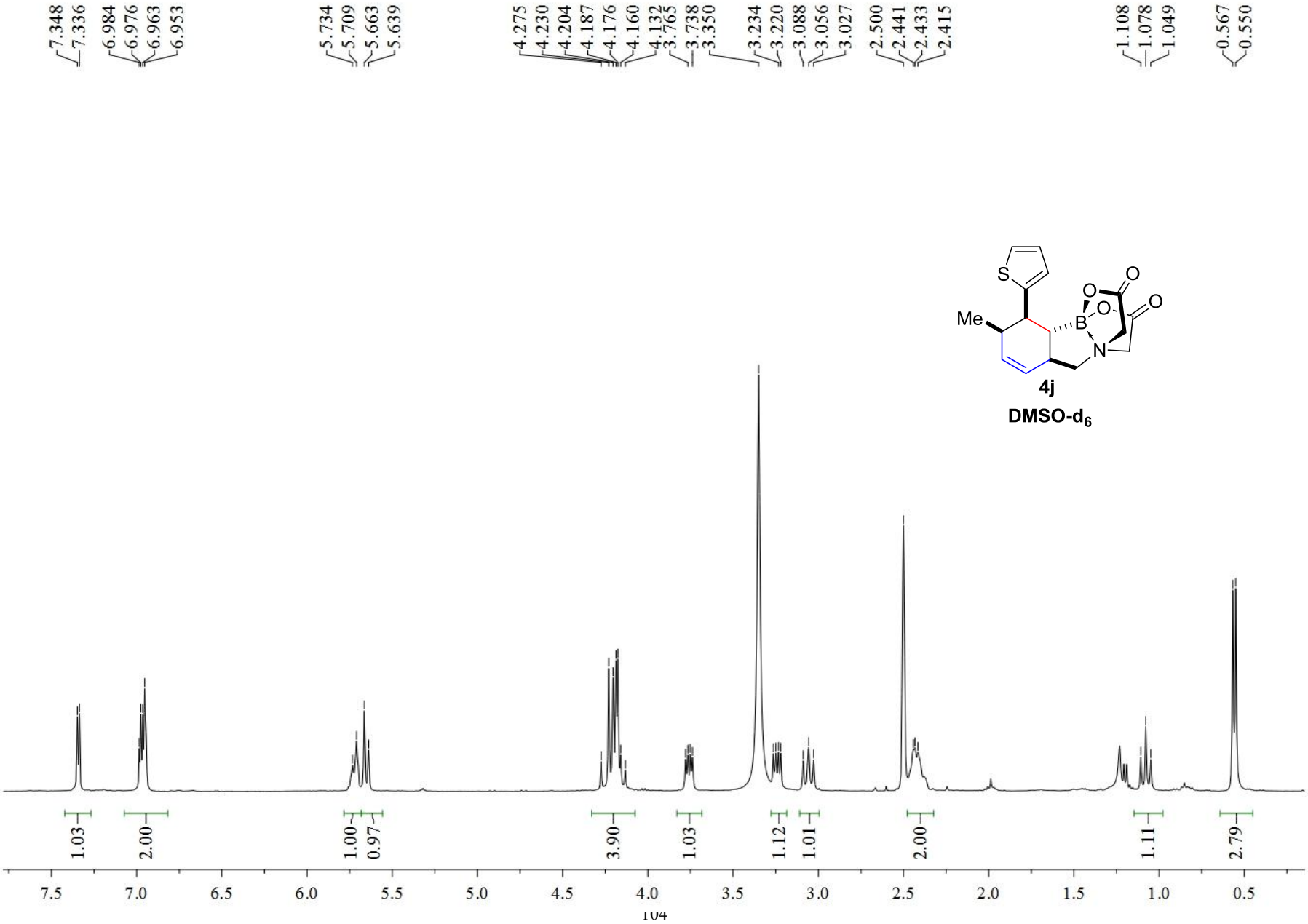
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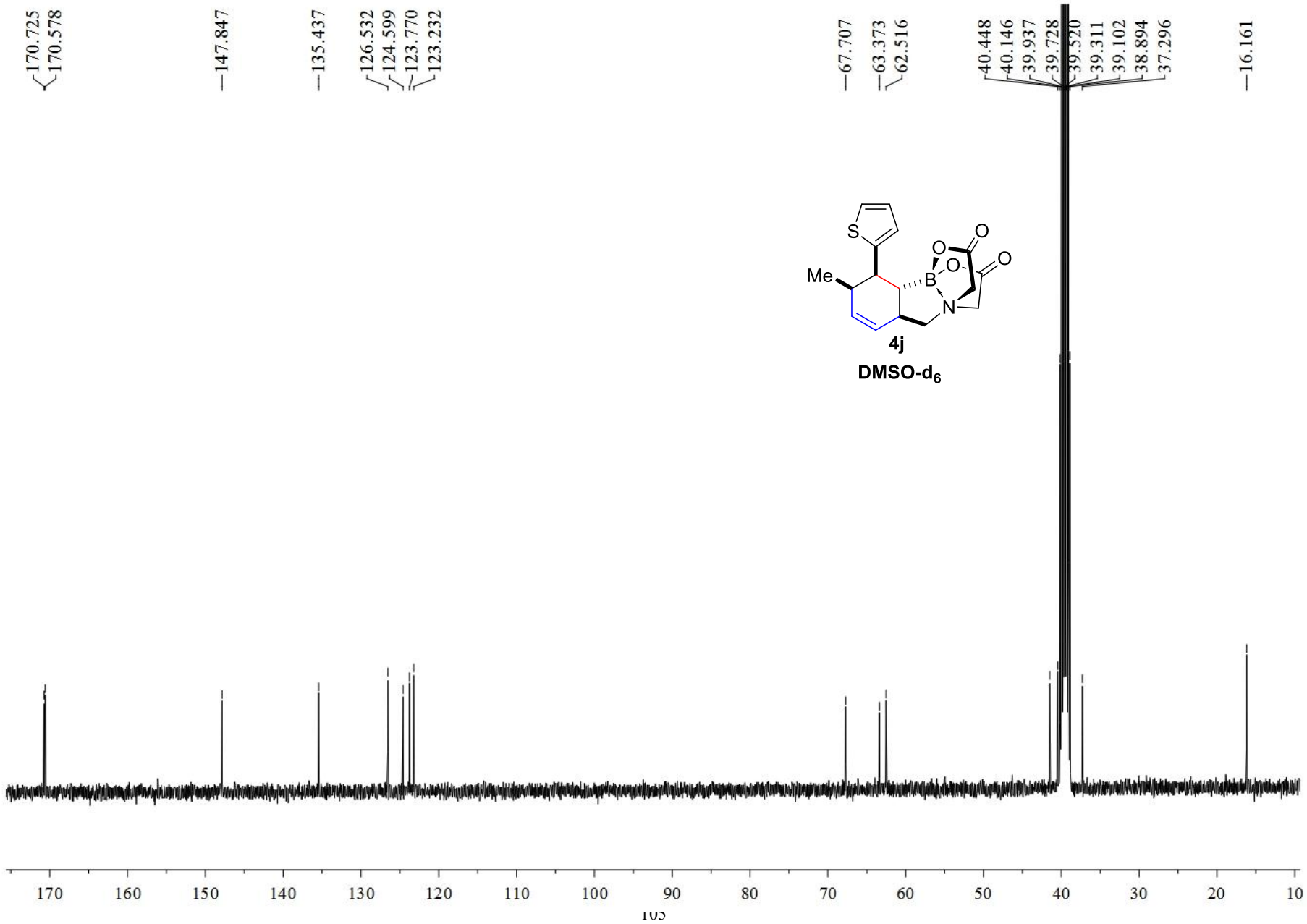
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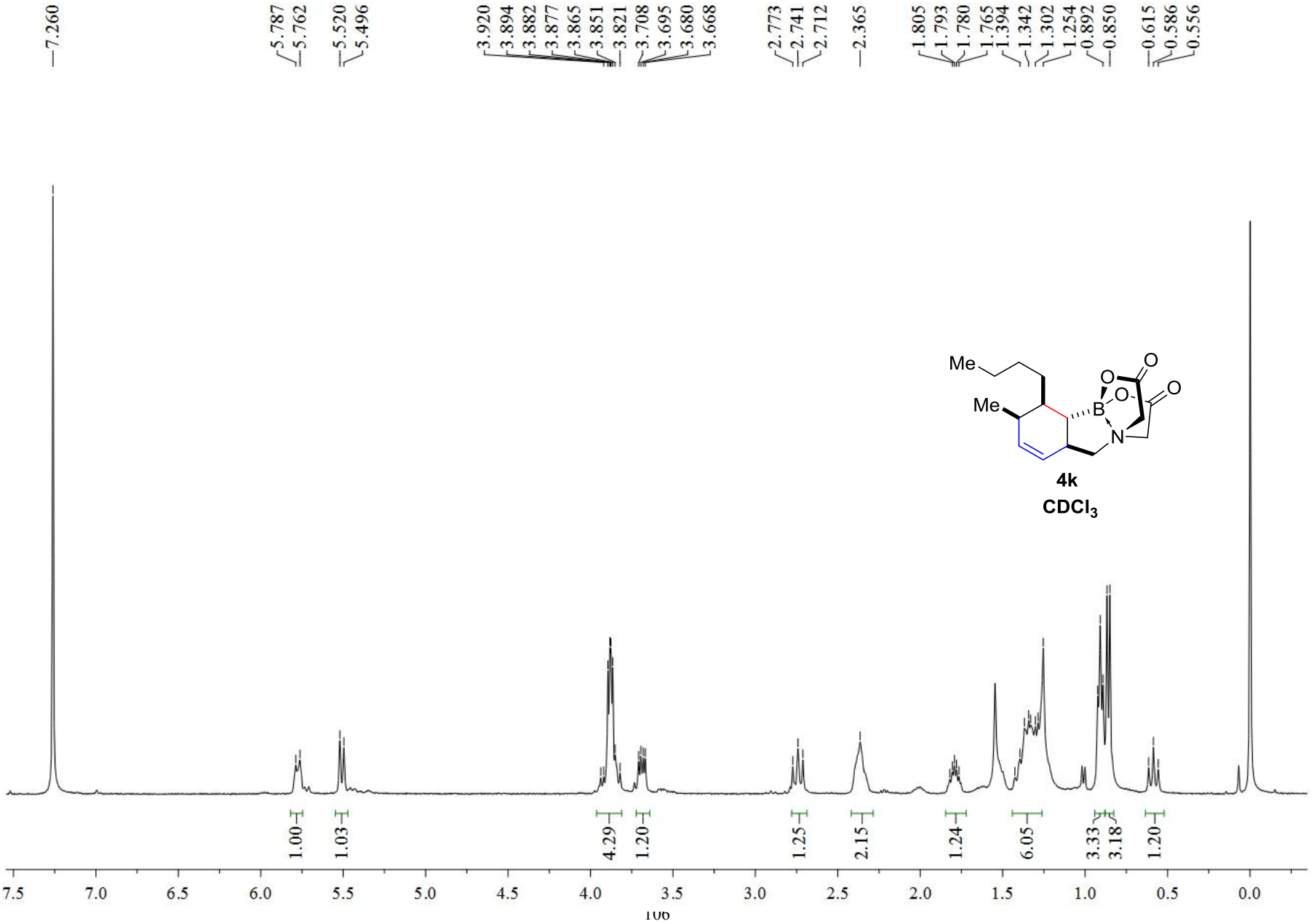
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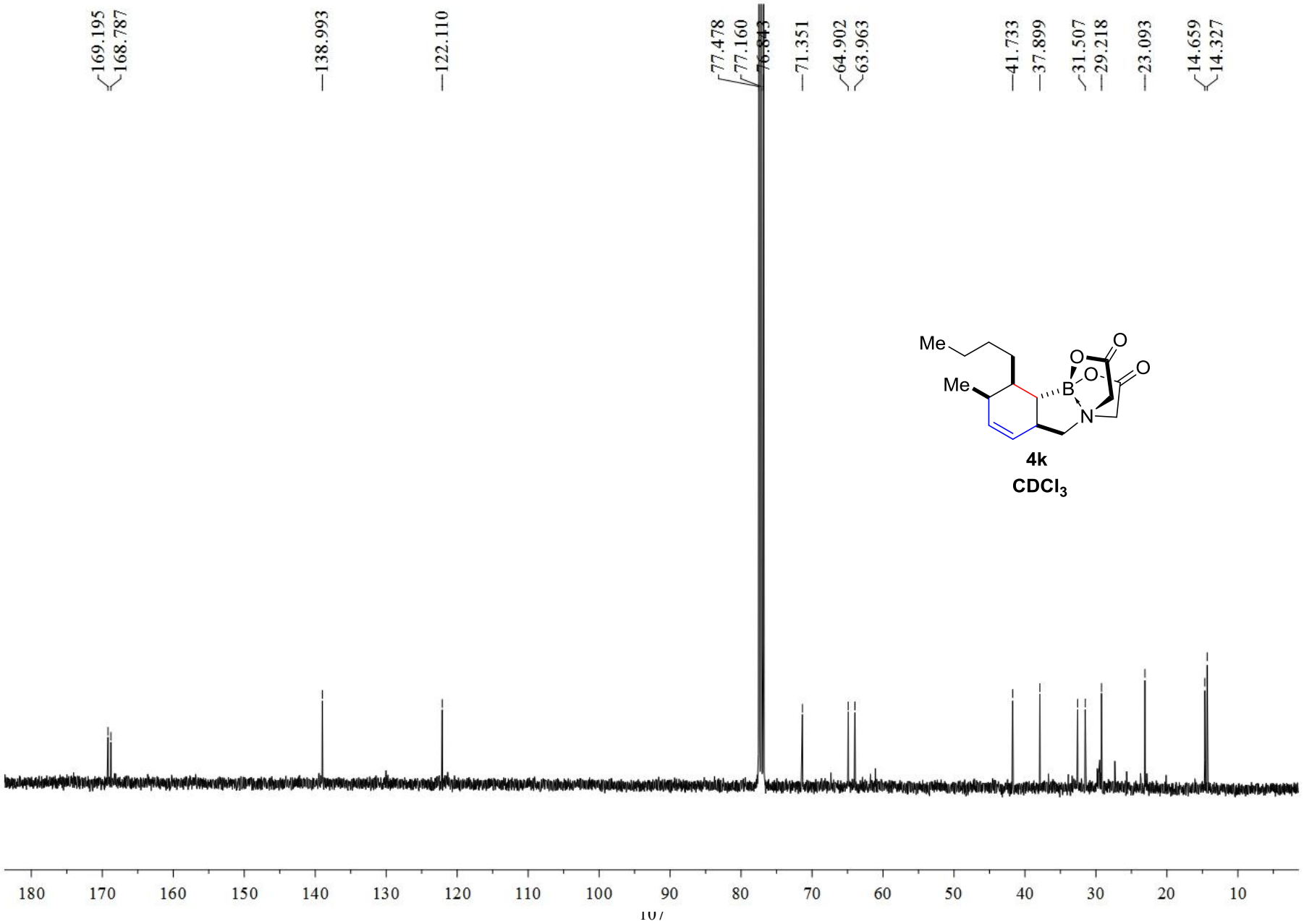
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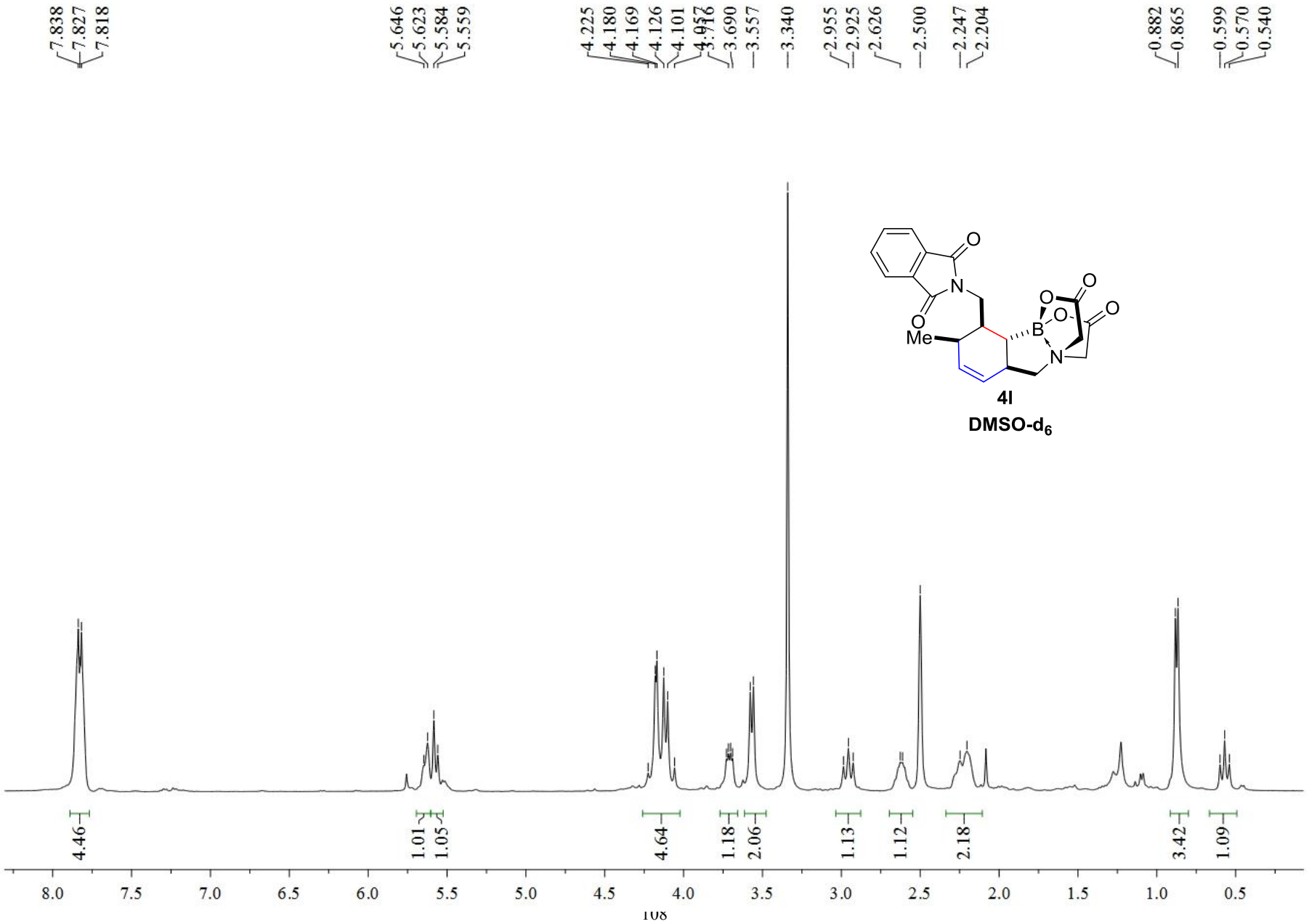
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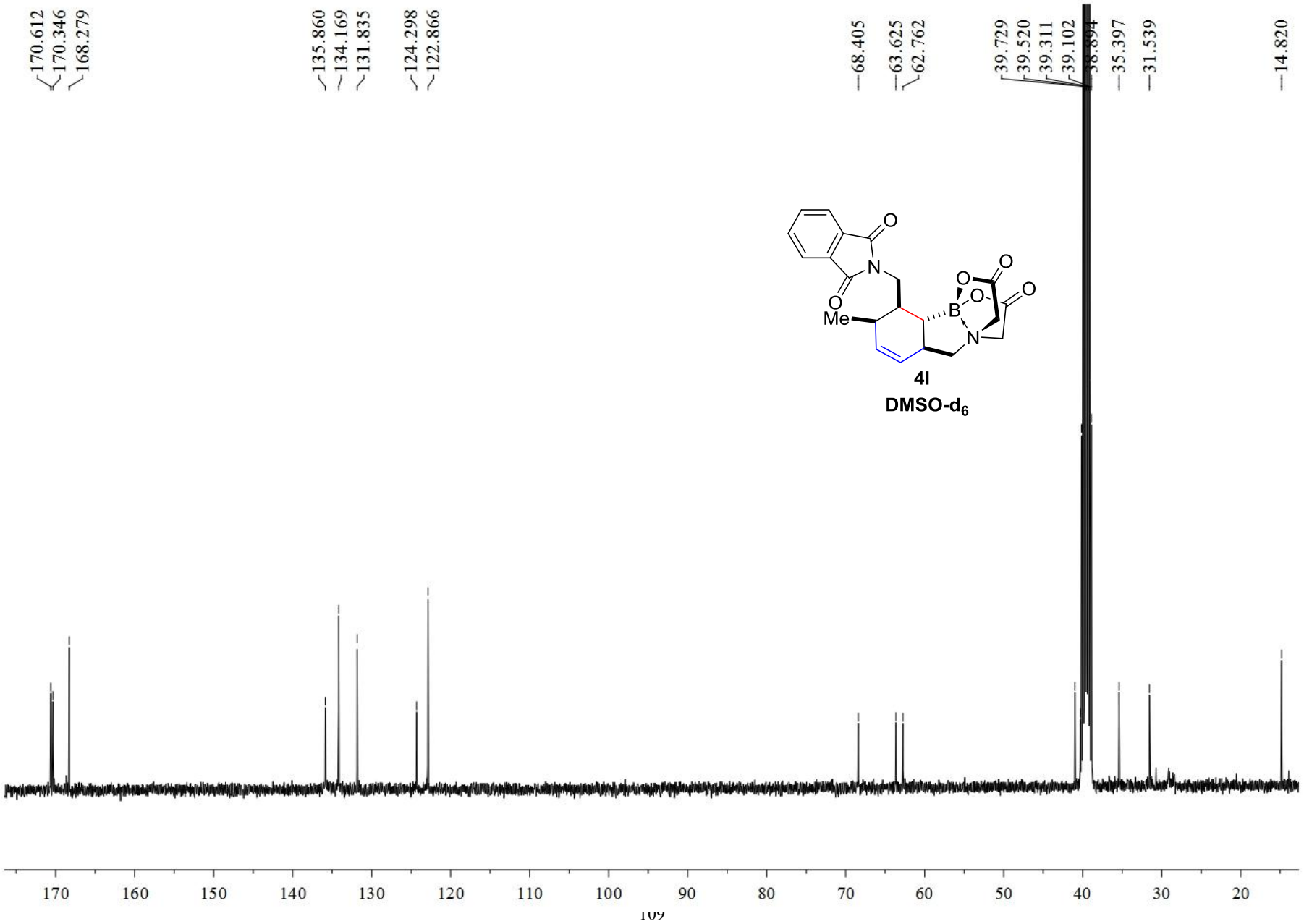
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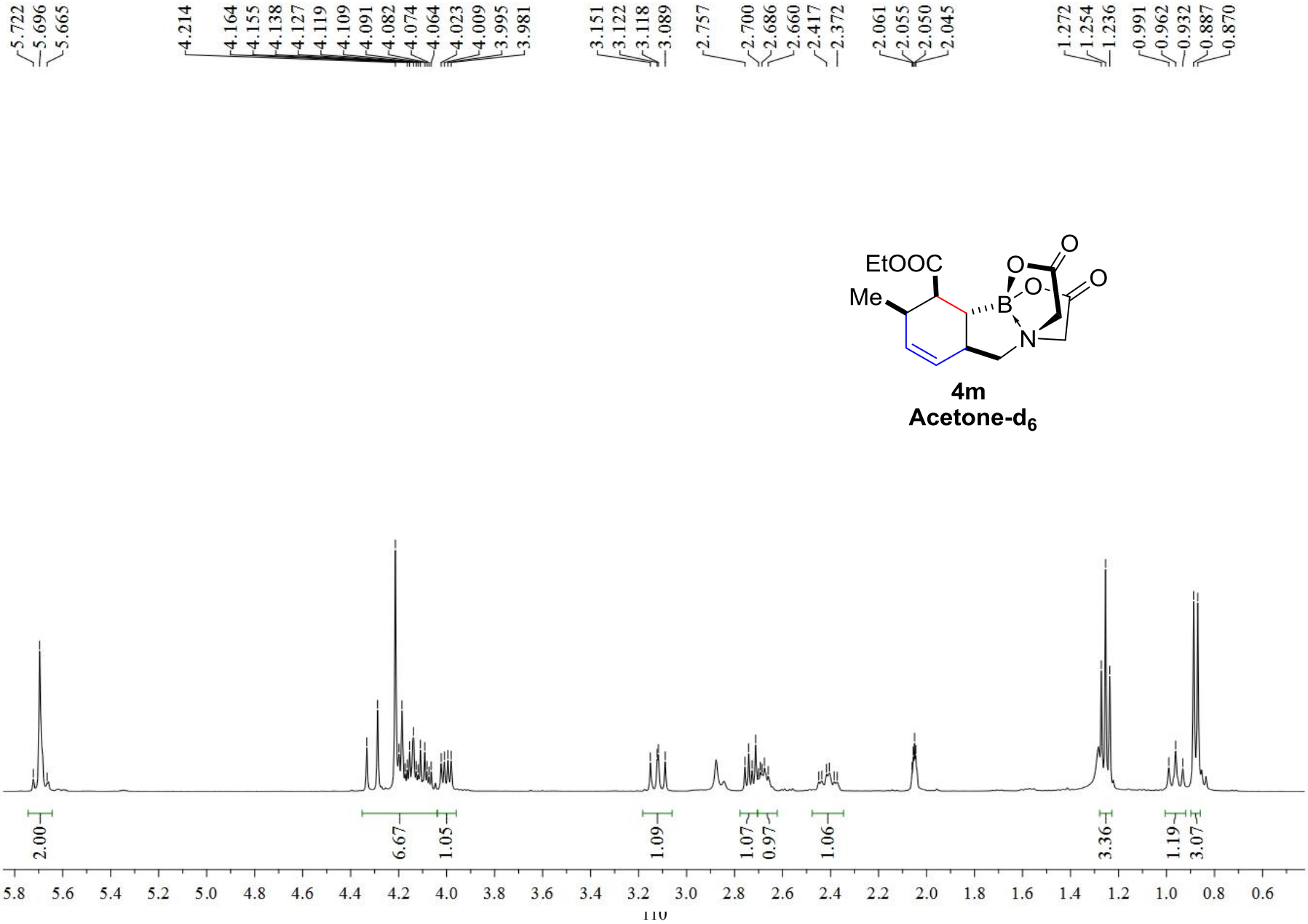
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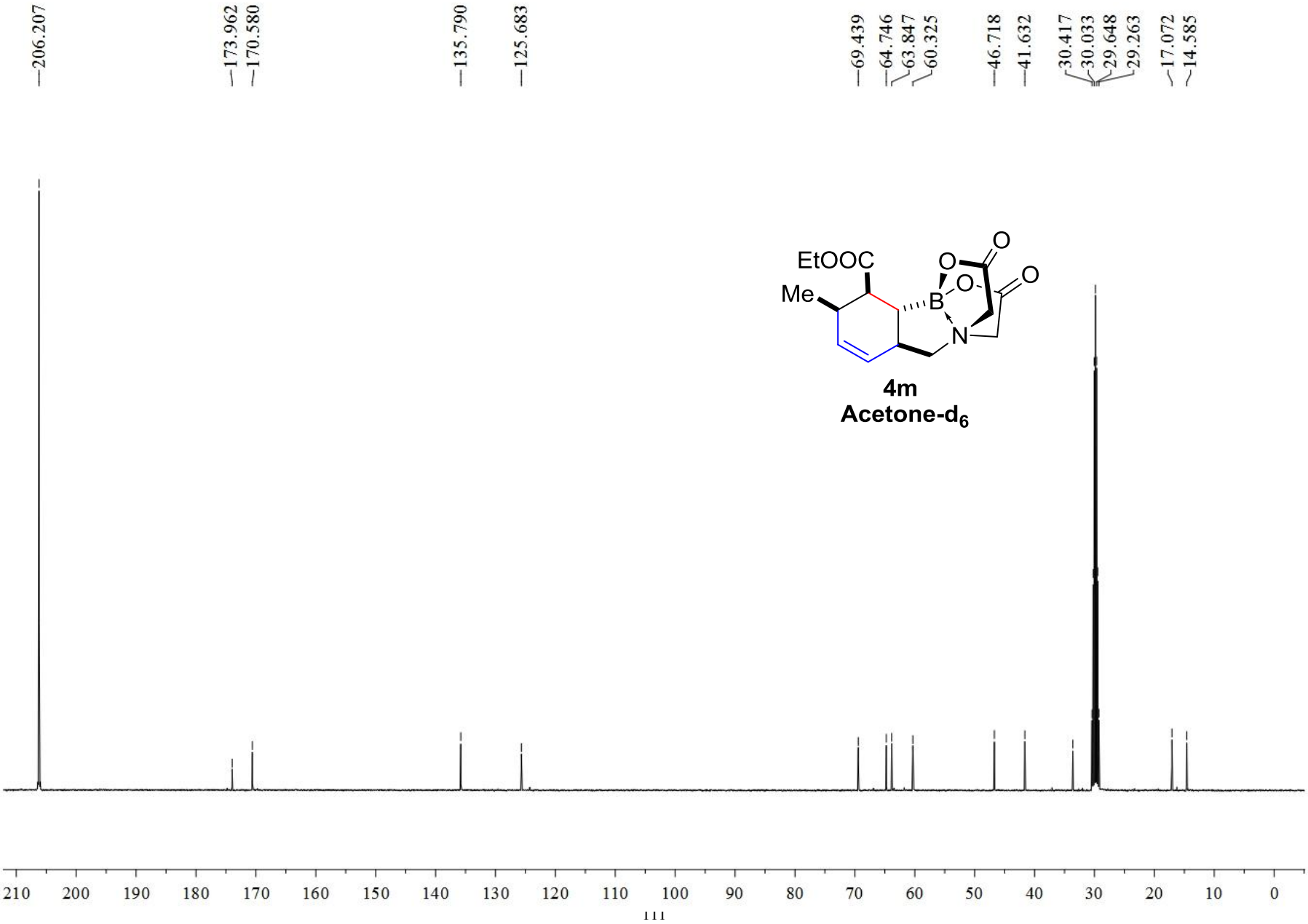
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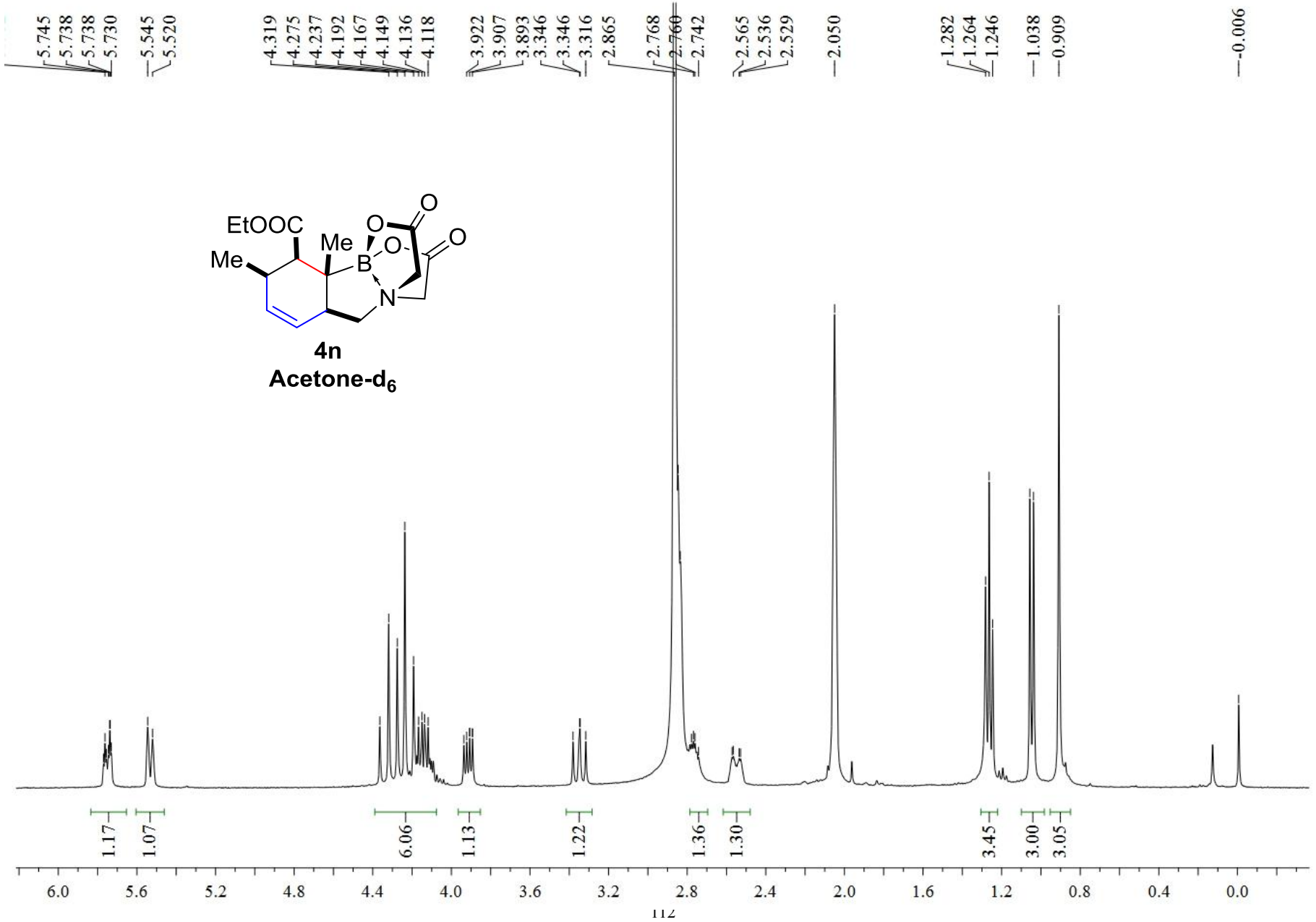
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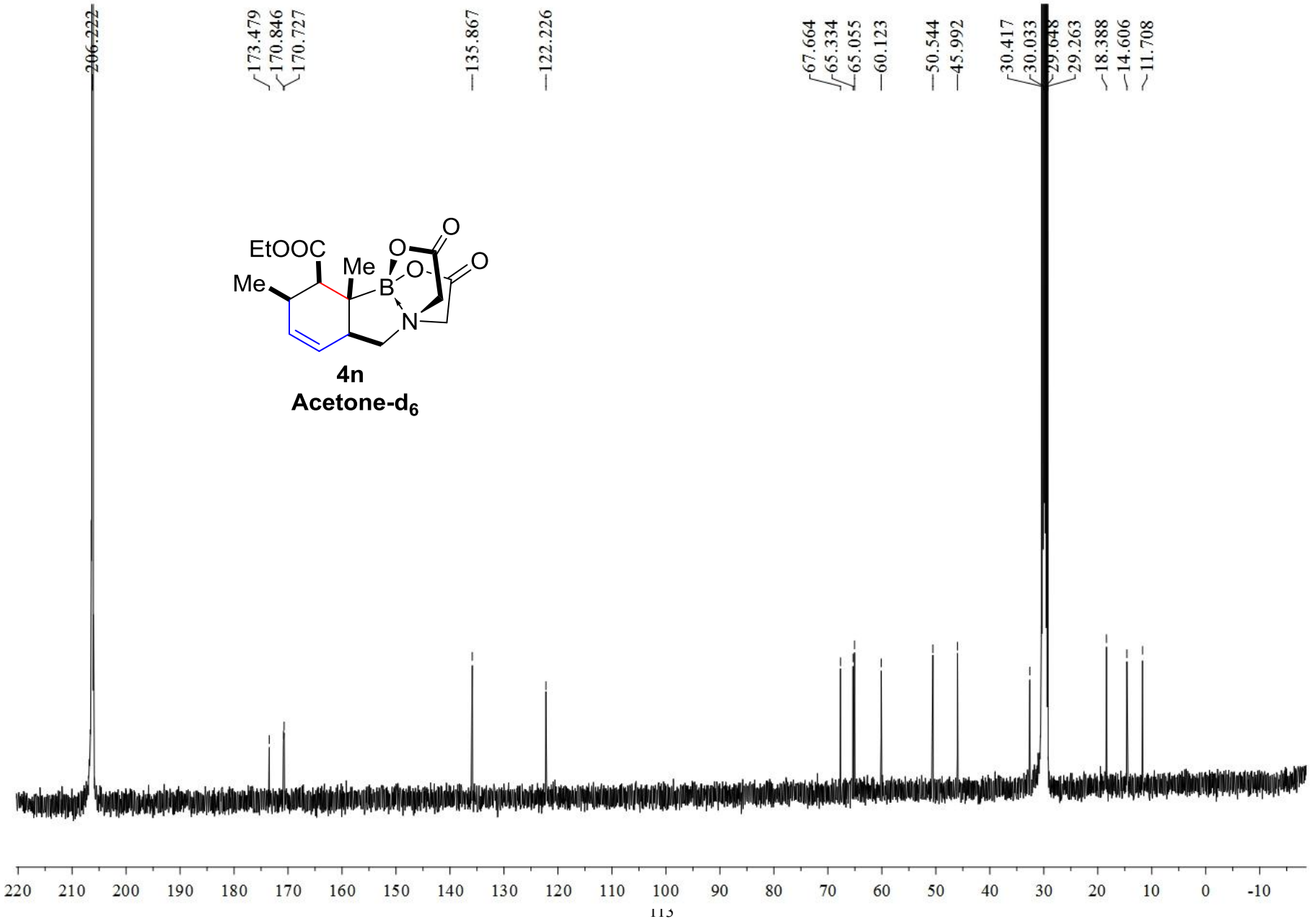
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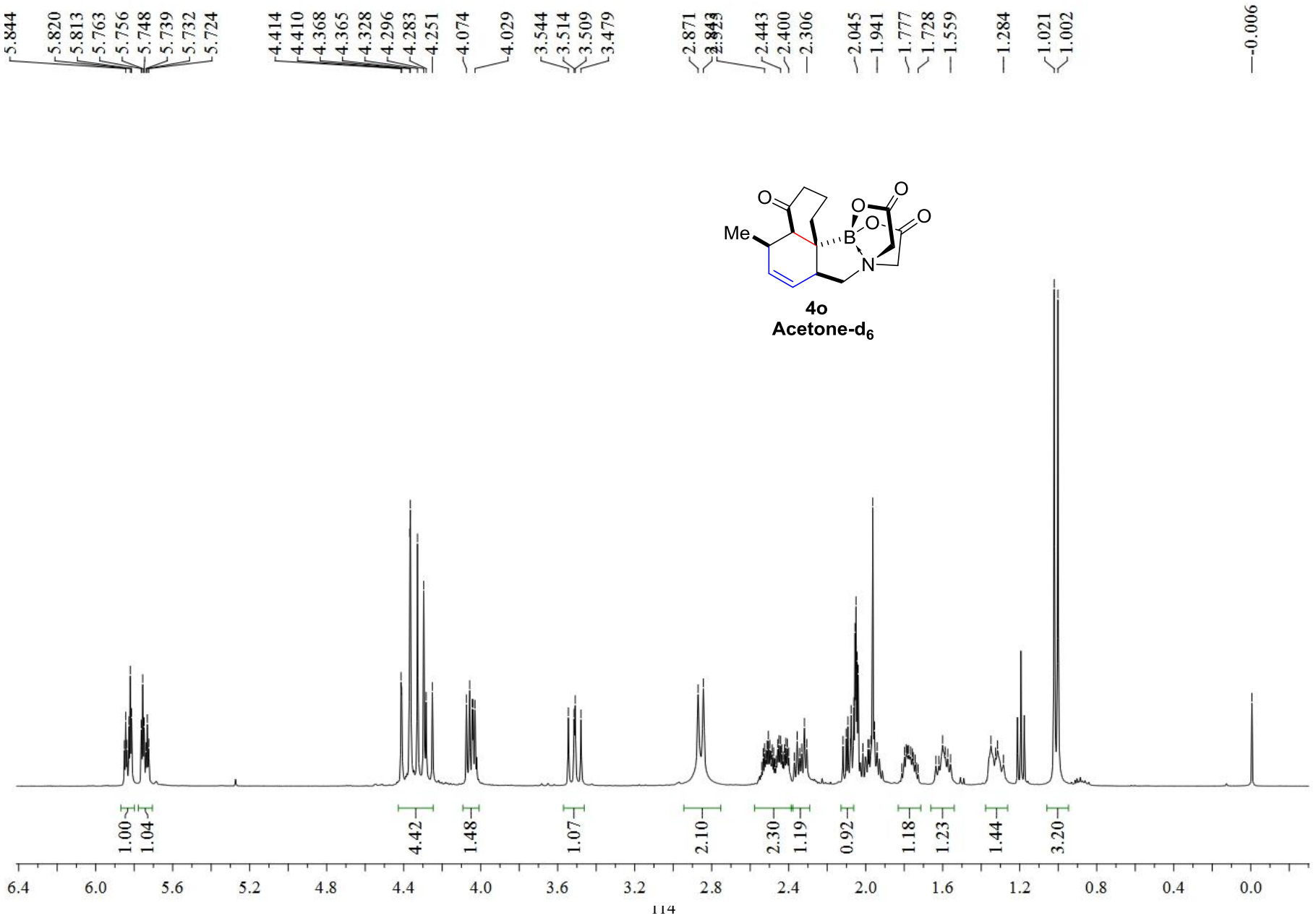
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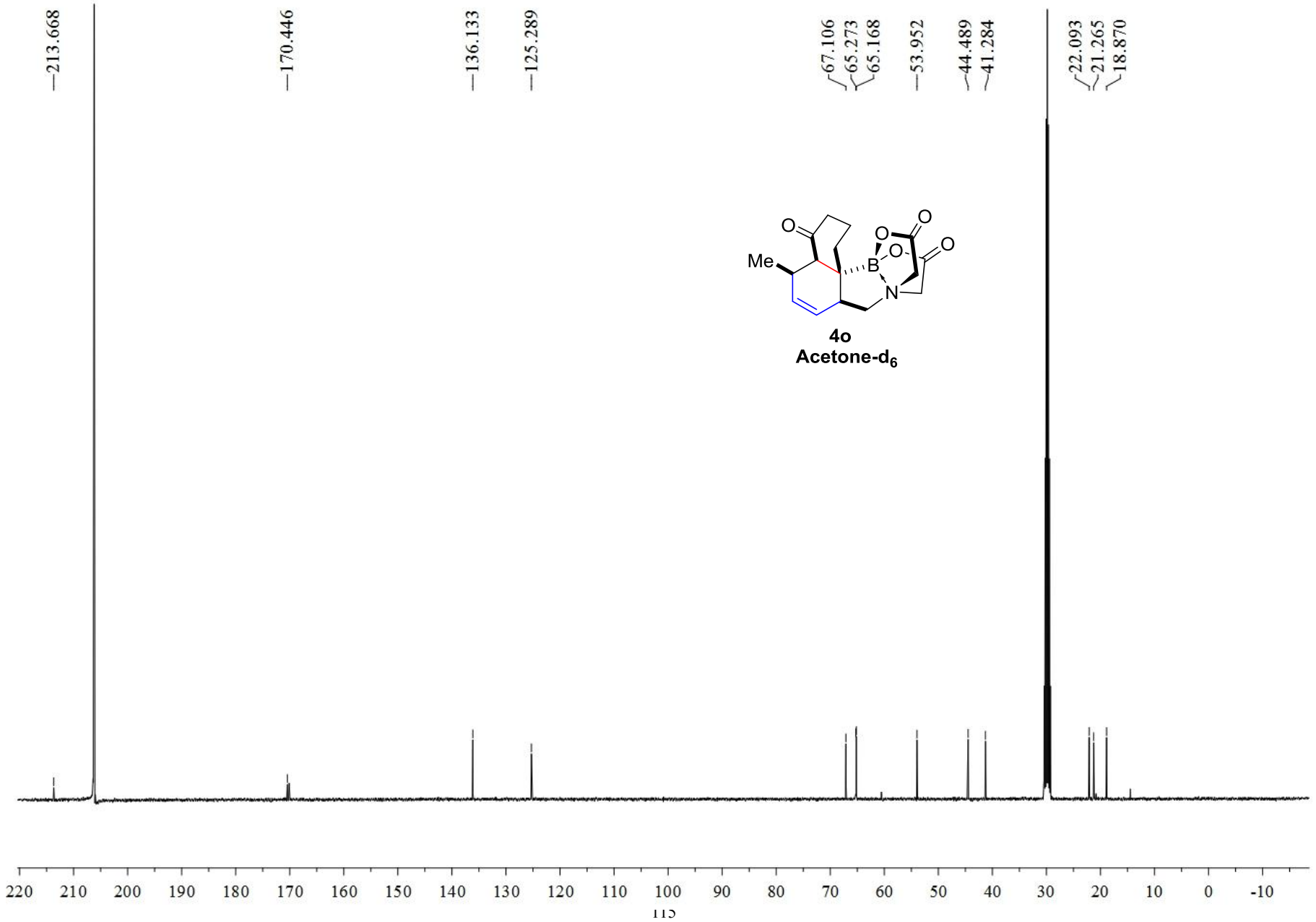
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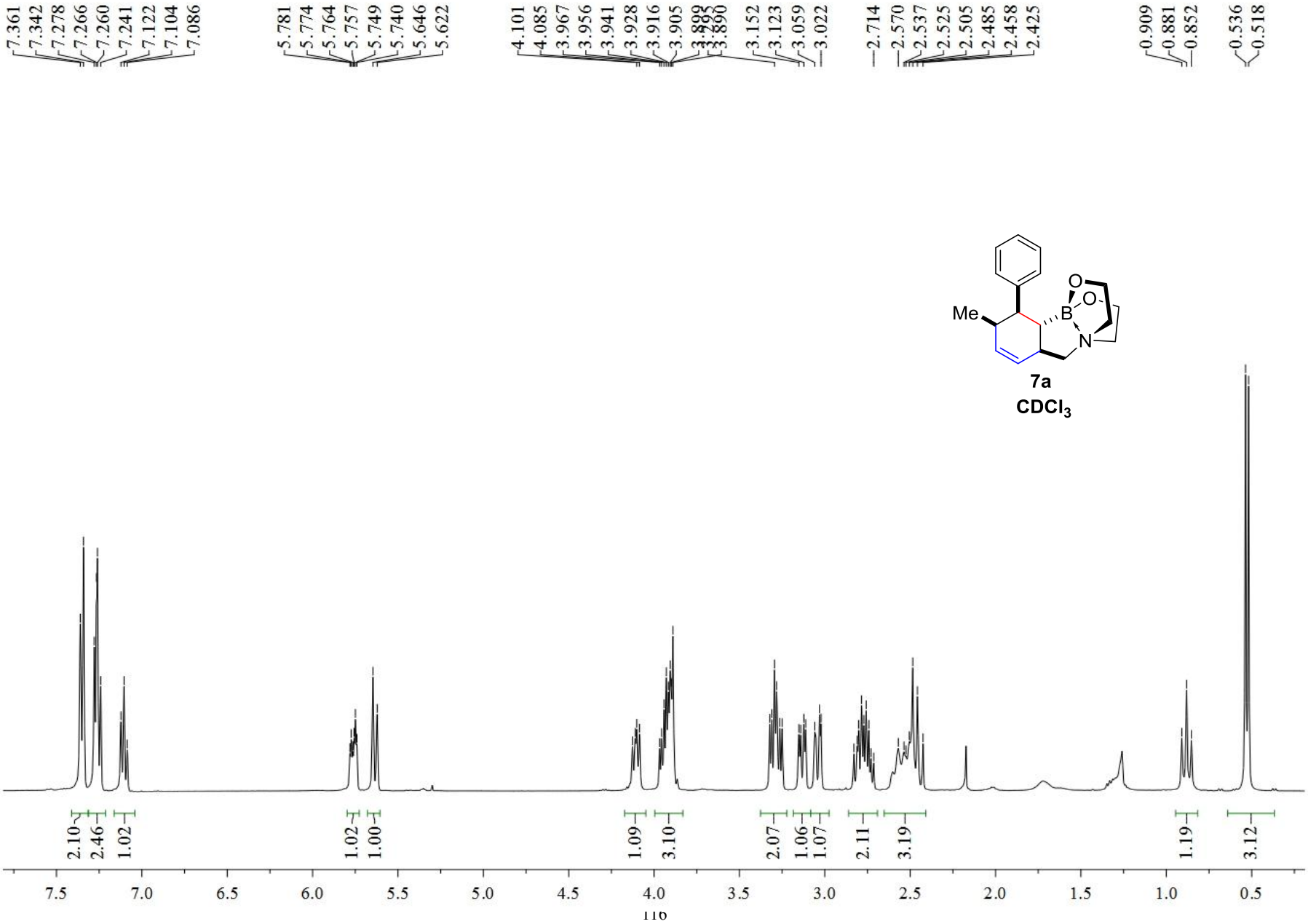
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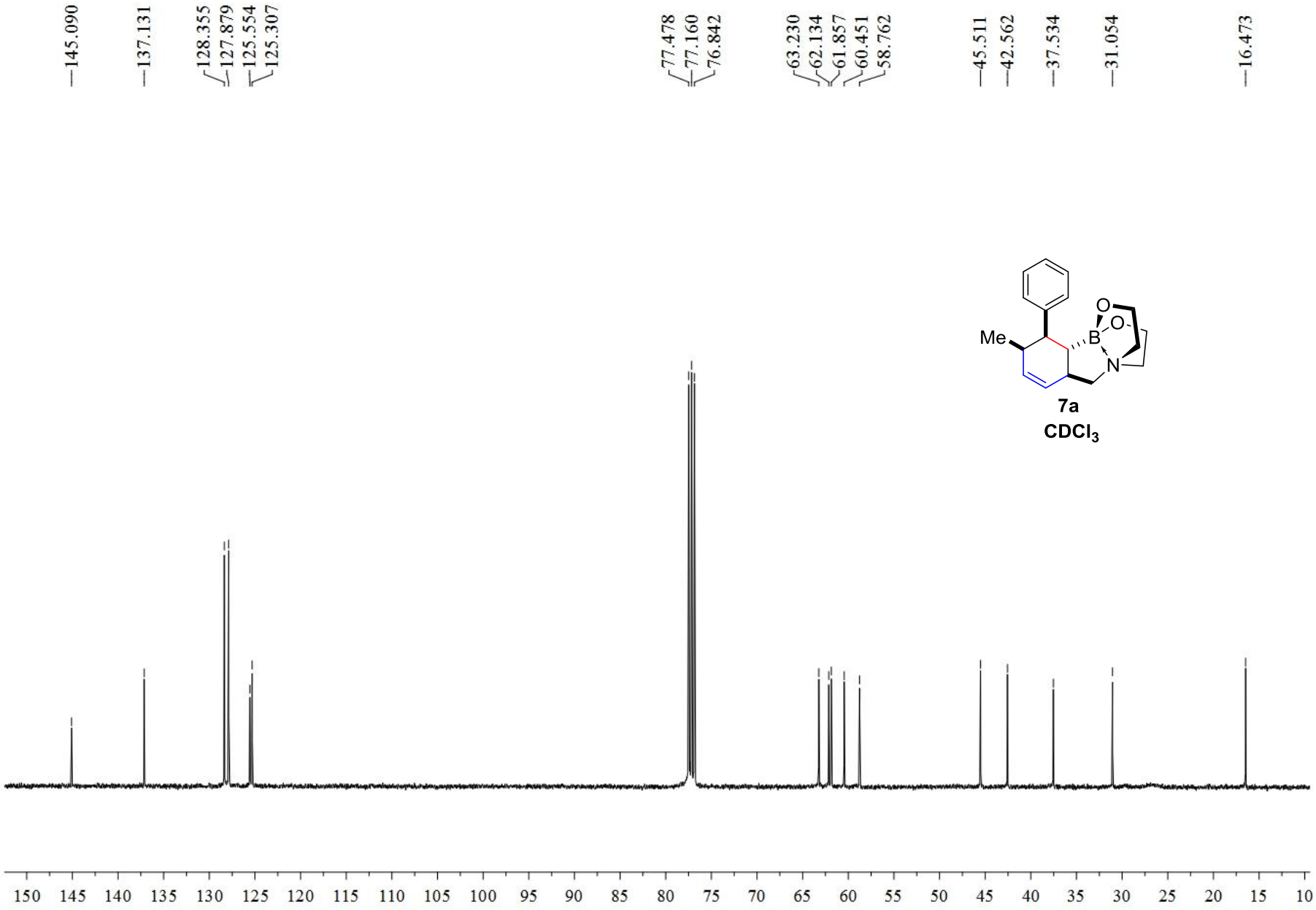
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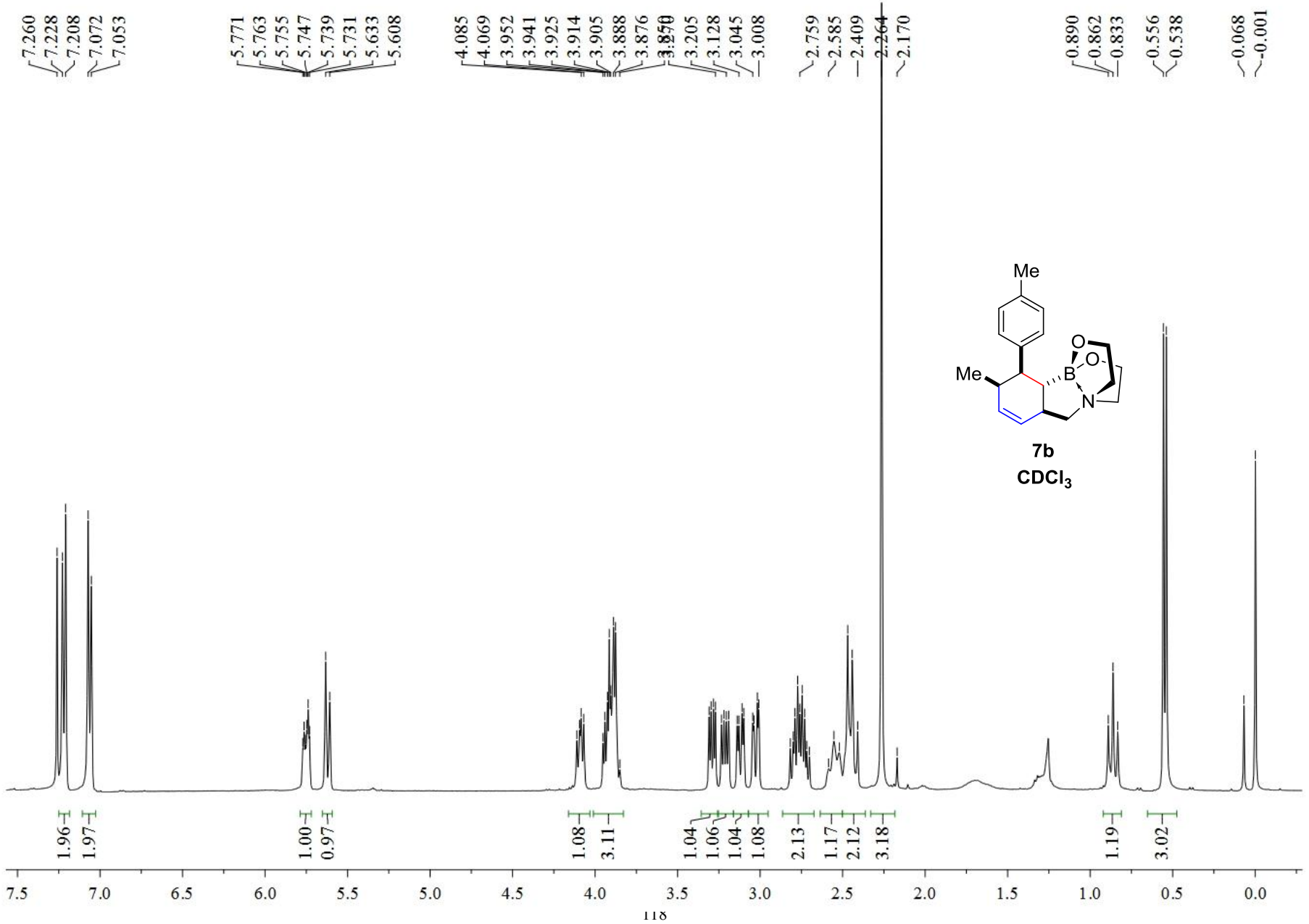
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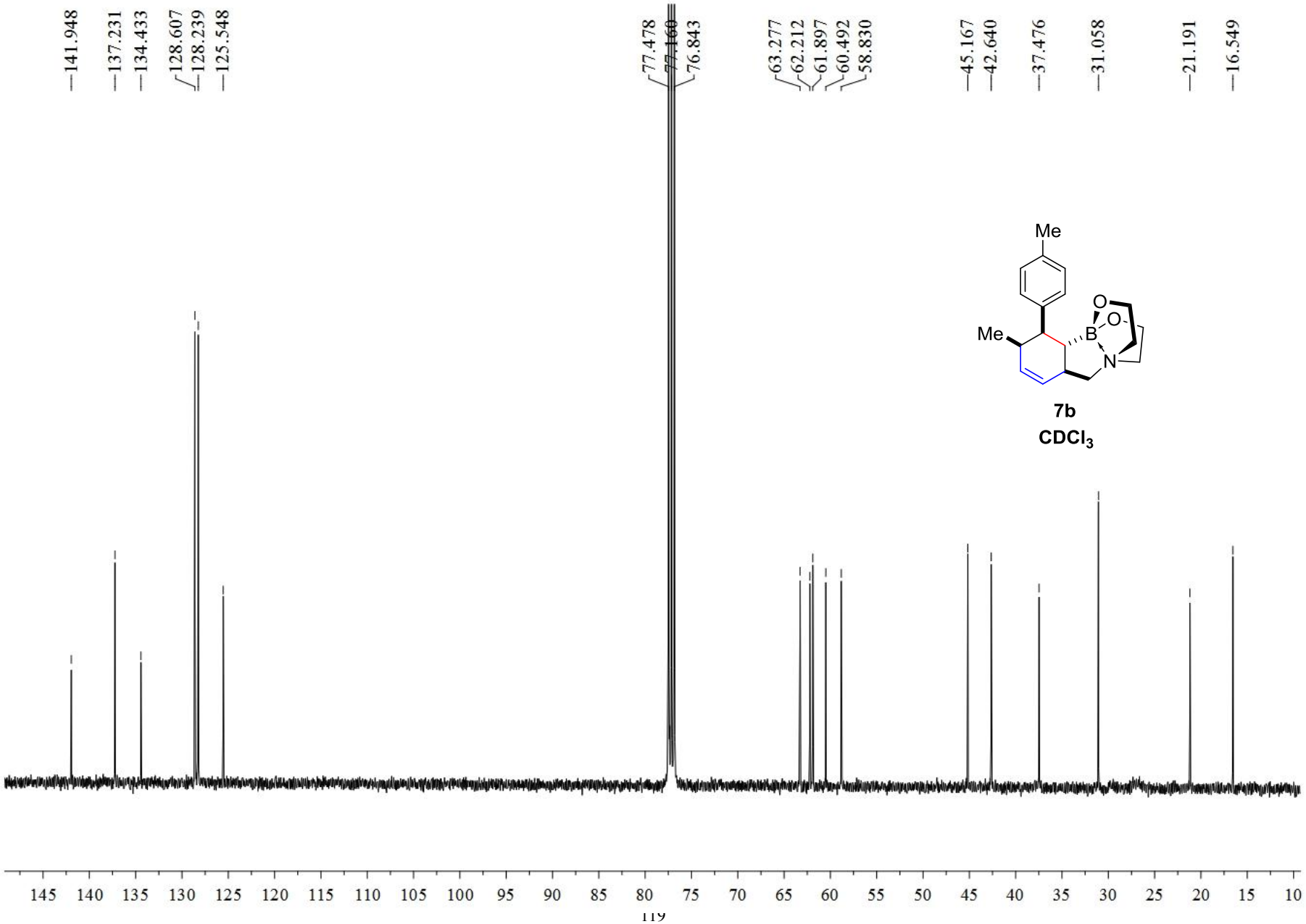
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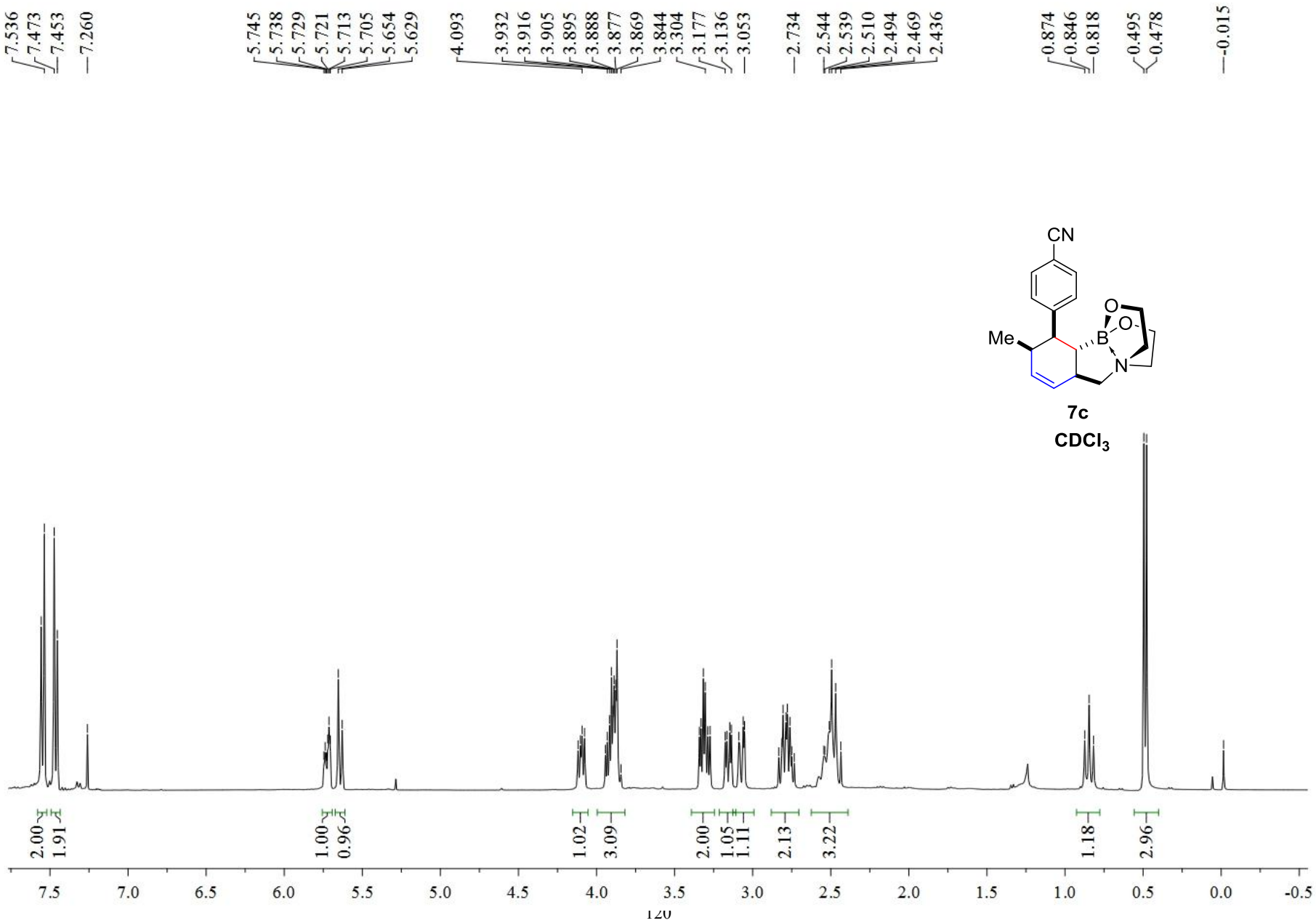
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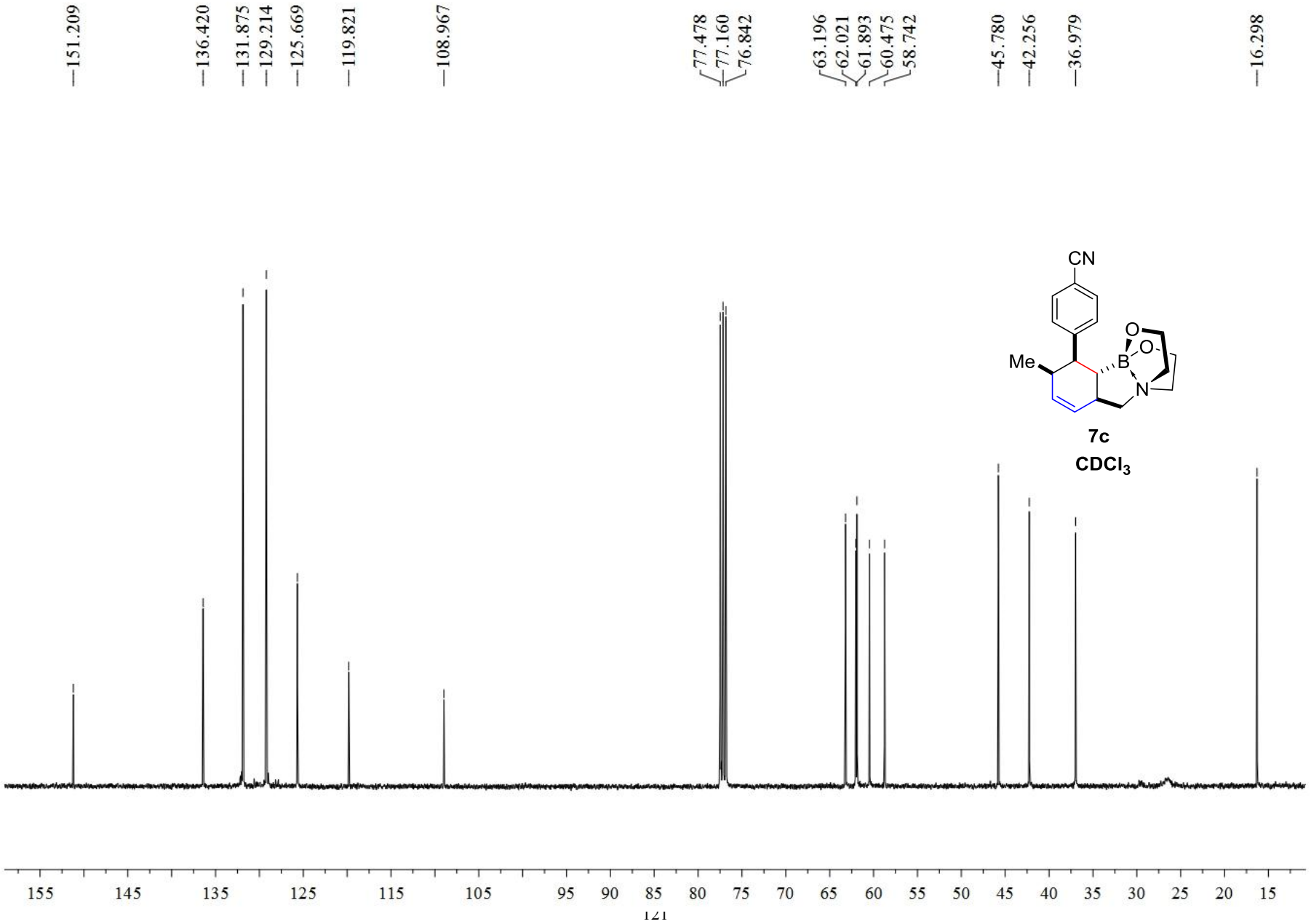
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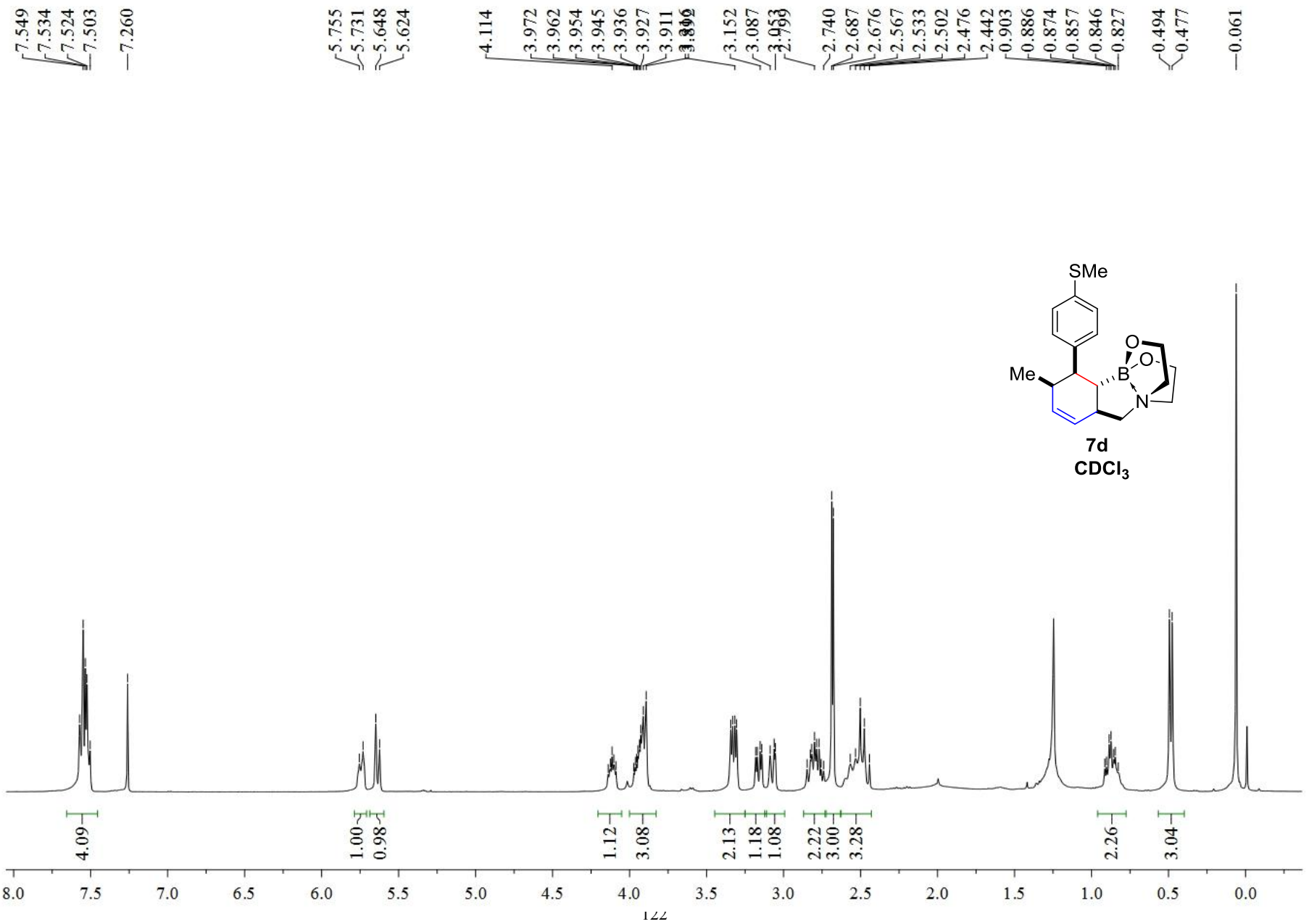
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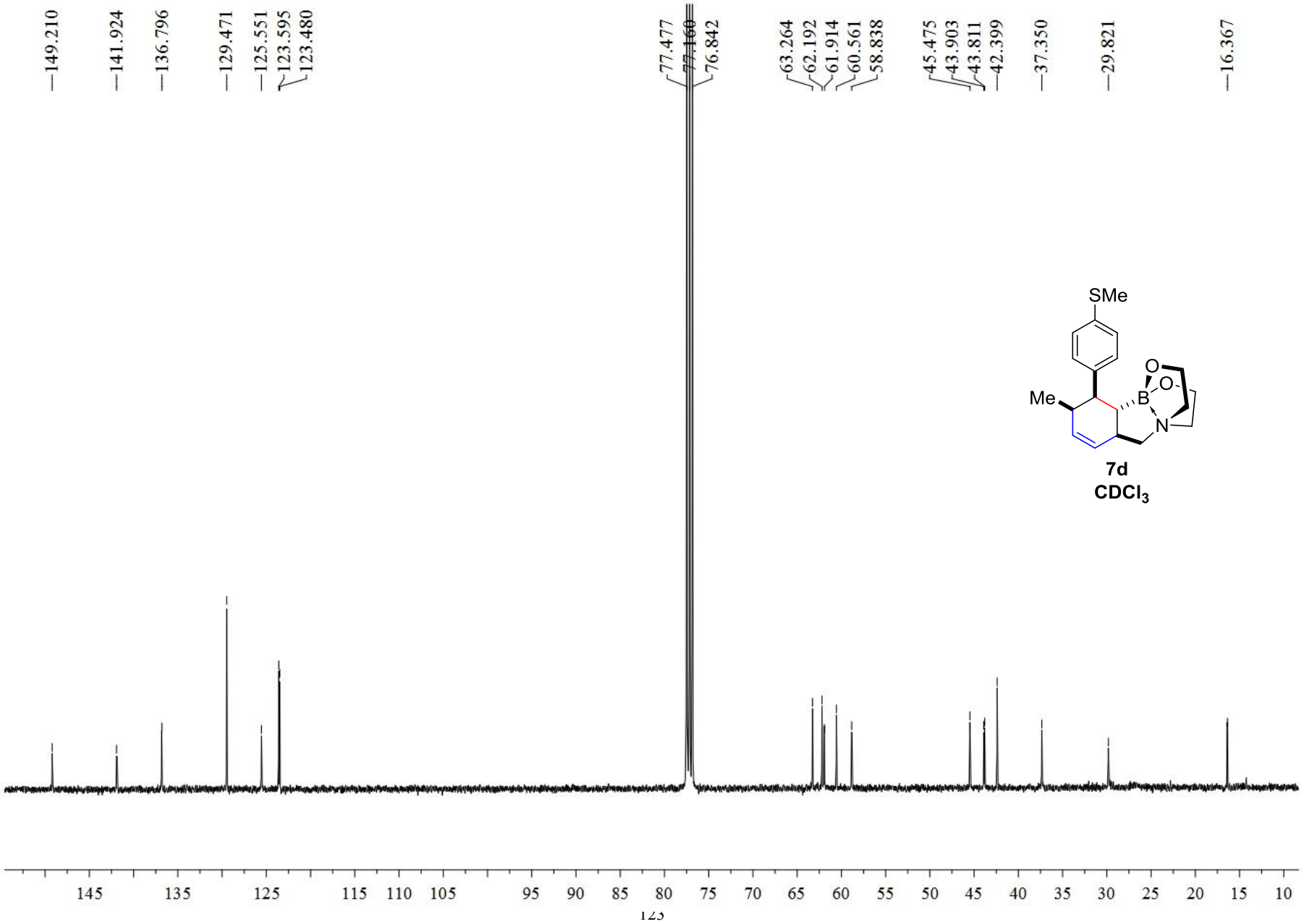
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43.811
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SMe
Me
O
O
B
N
7d
CDCl3
145
135
125
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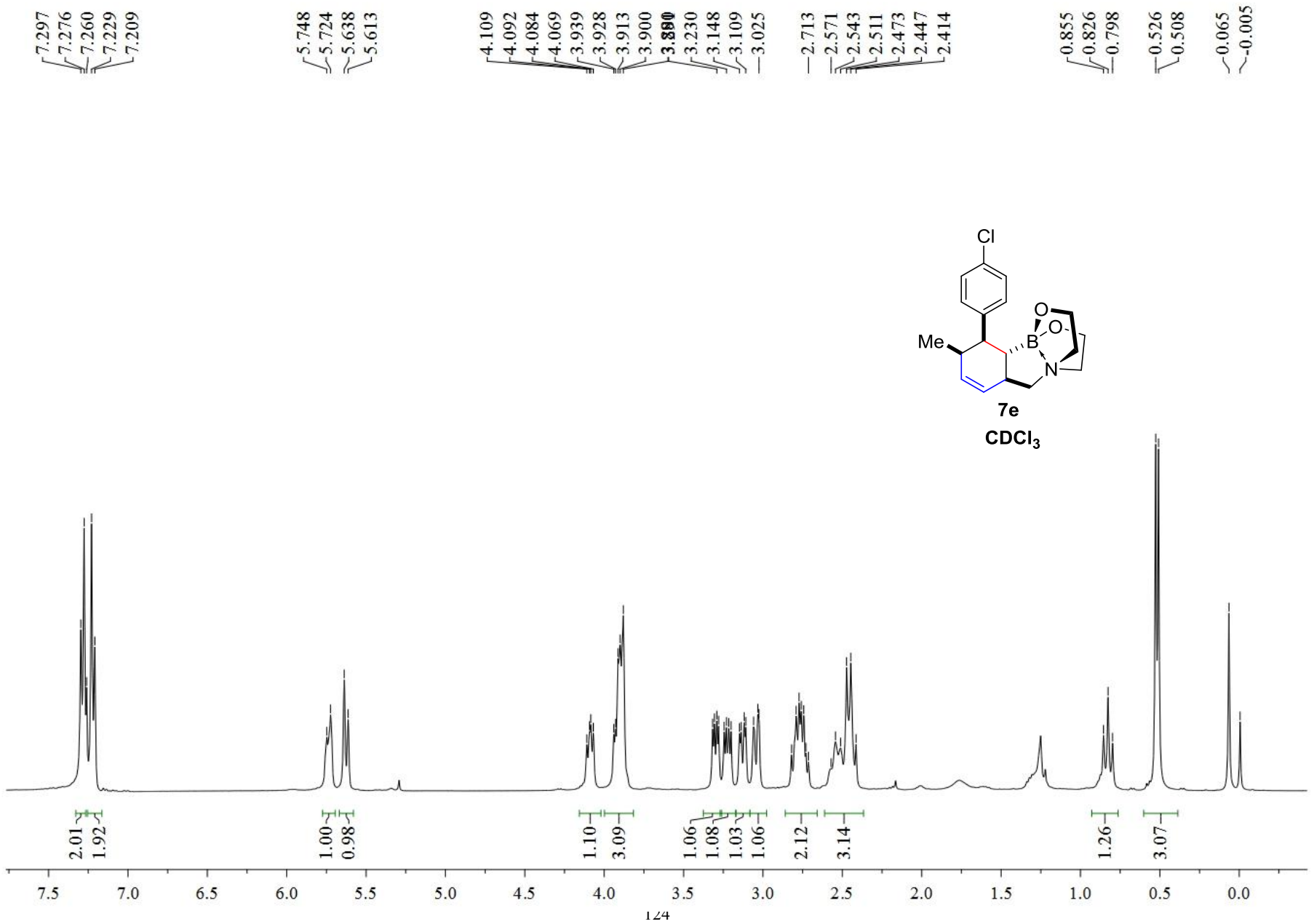
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3.939
3.928
3.913
3.900
3.230
3.148
3.109
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2.571
2.543
2.511
2.473
2.447
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-0.005
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O
B
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Me
7e
CDCl3
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3.09
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3.07
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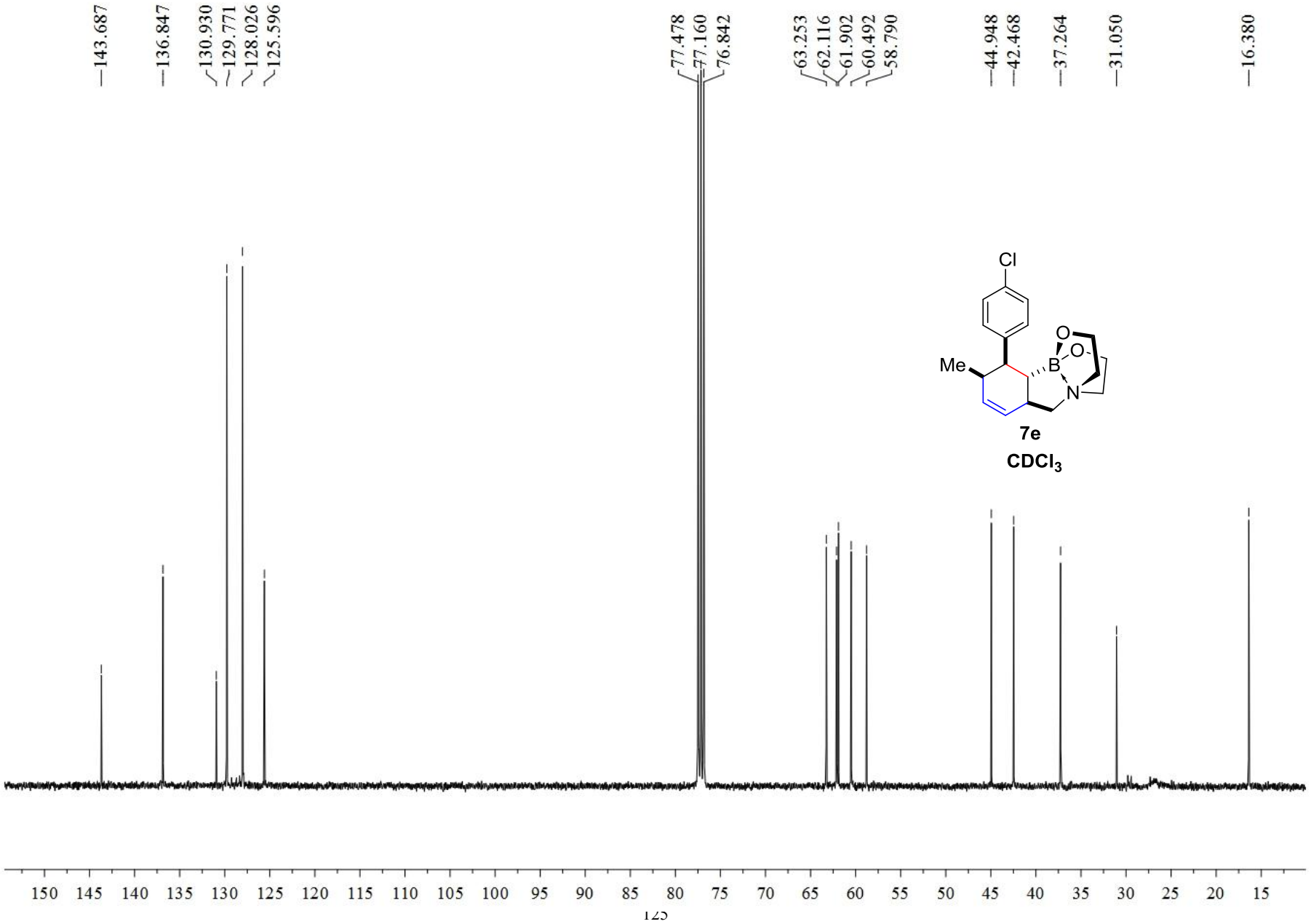
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44.948
42.468
37.264
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B
N
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7e
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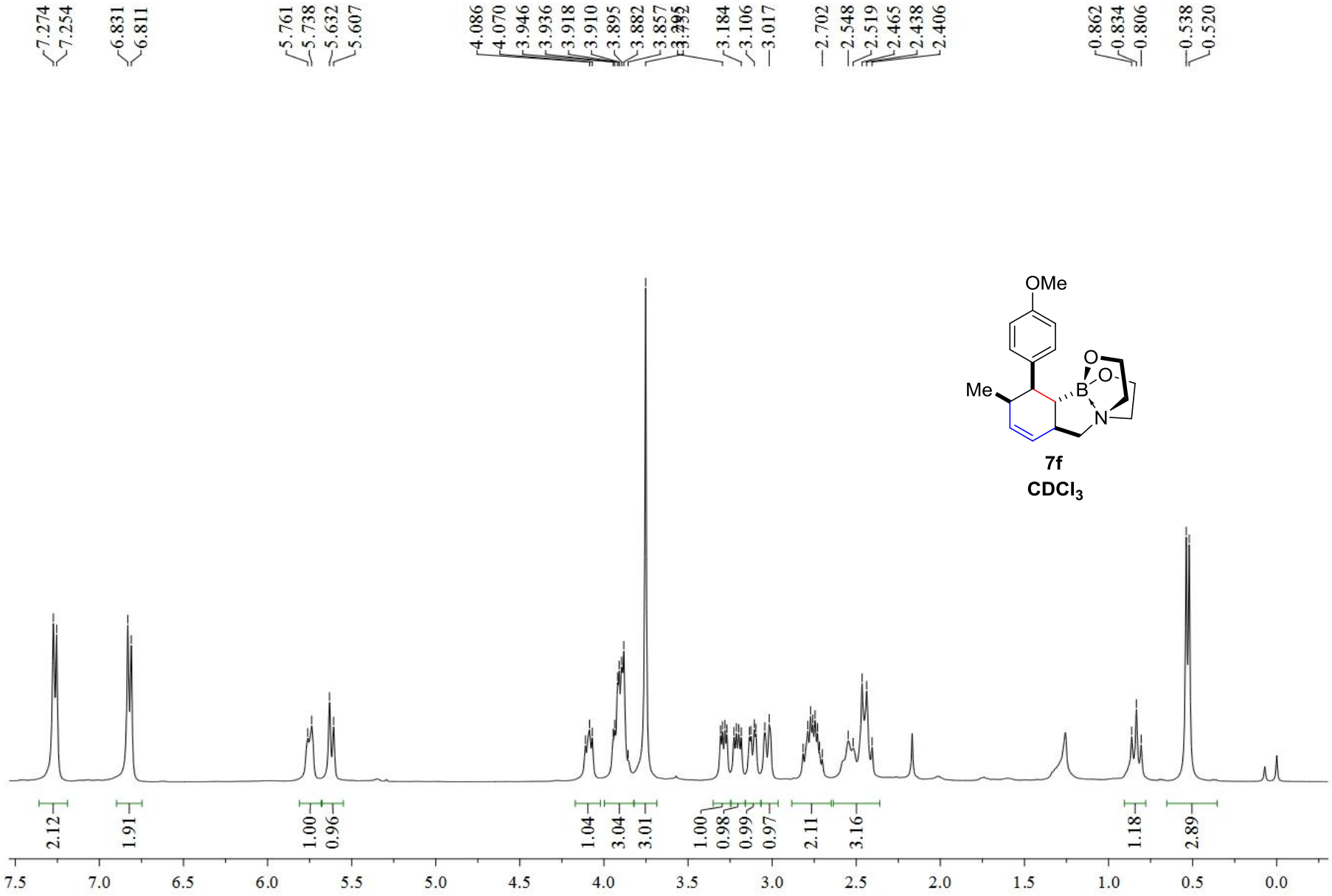
150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15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2.519
2.465
2.438
2.406
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0.520
OMe
Me
O
O
B
N
7f
CDCl3
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1.91
1.00
0.96
1.04
3.04
3.01
1.00
0.98
0.99
0.97
2.11
3.16
1.18
2.89
7.5
7.0
6.5
6.0
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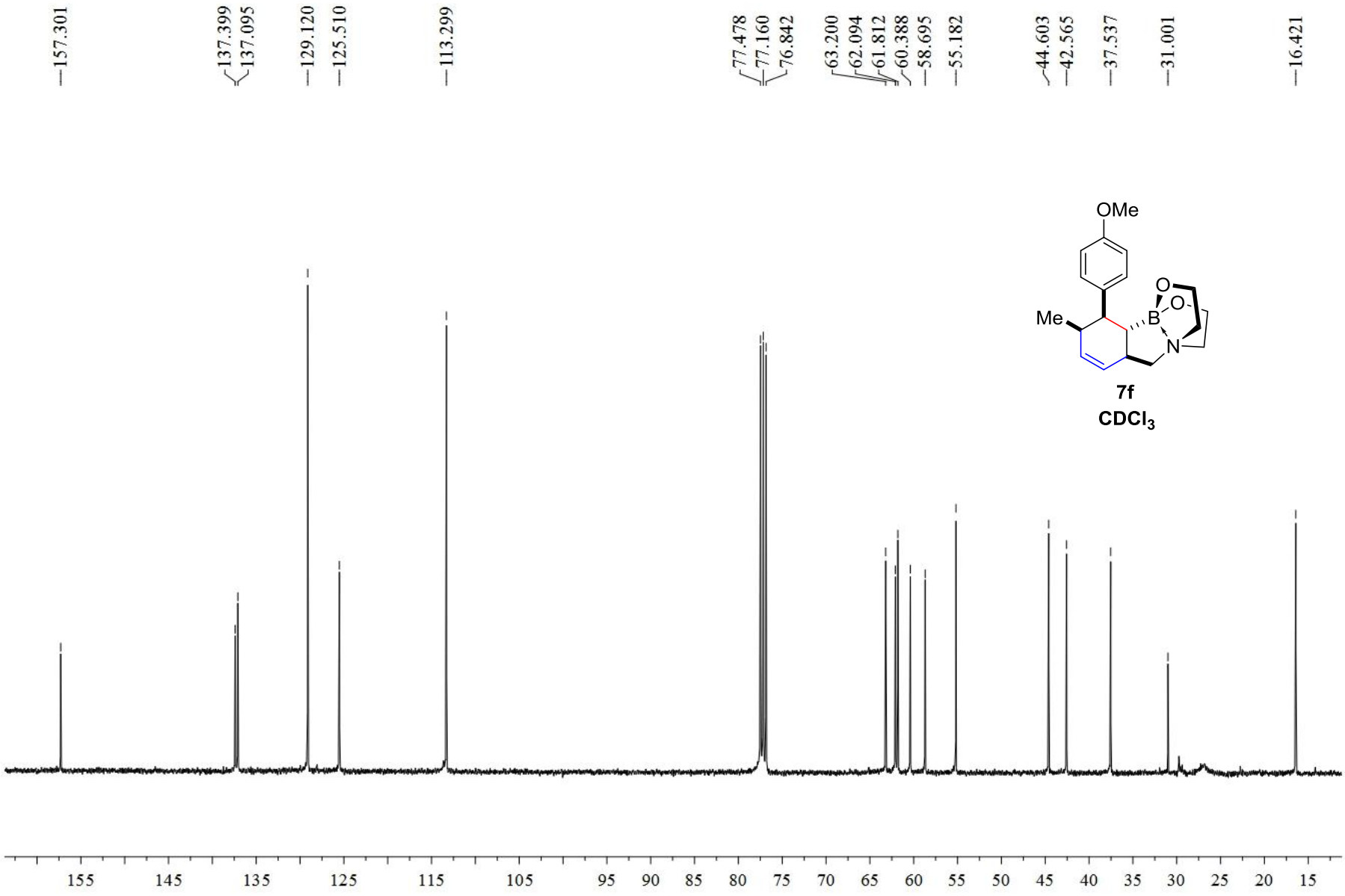
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60.388
58.695
55.182
44.603
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OMe
Me
O
O
B
N
7f
CDCl3
155
145
135
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115
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90
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50
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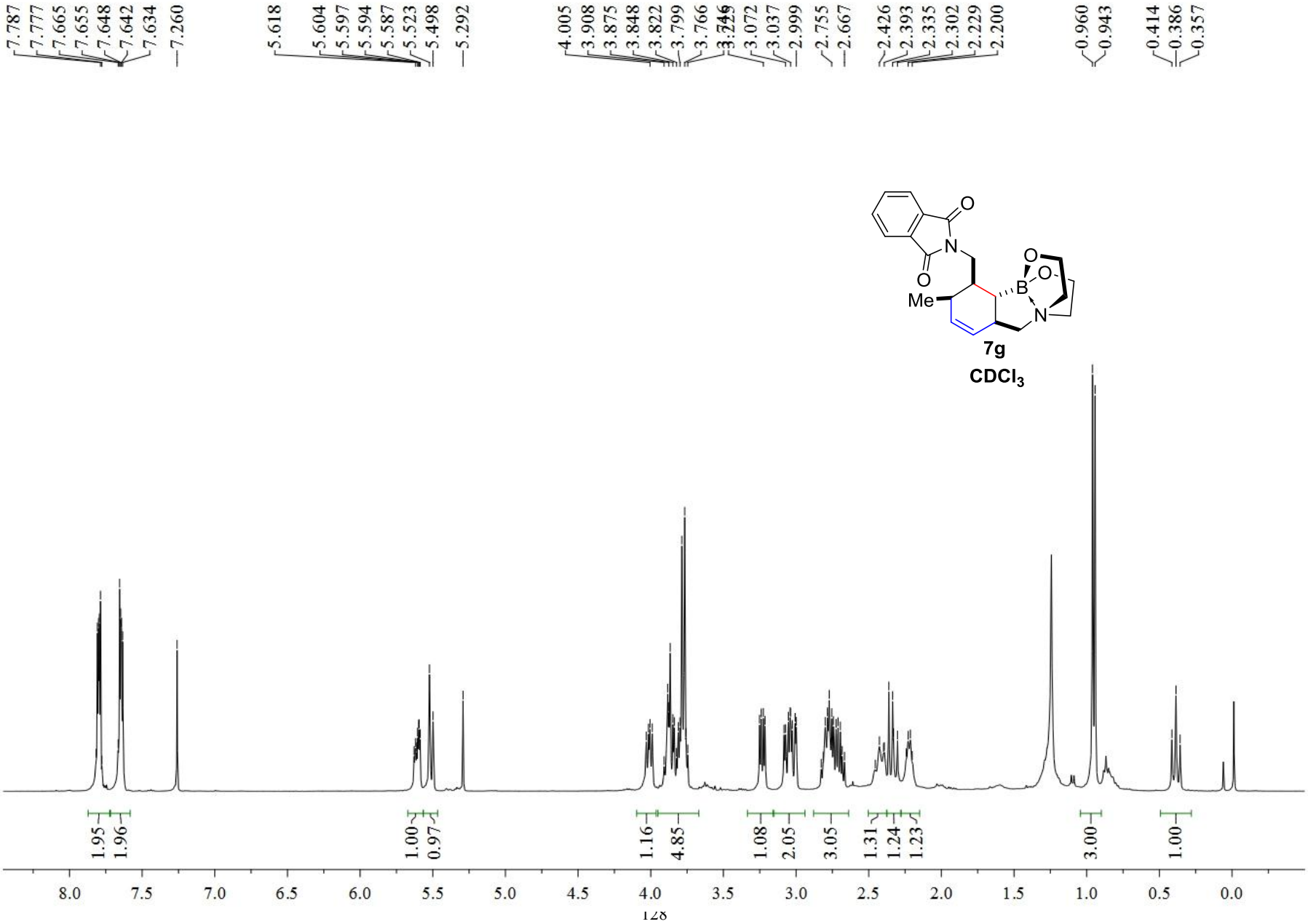
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5.587
5.523
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5.292
4.005
3.908
3.875
3.848
3.822
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3.766
3.072
3.037
2.999
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2.667
2.426
2.393
2.335
2.302
2.229
2.200
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0.943
0.414
0.386
0.357
O
N
O
Me
O
O
B
N
7g
CDCl3
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1.96
1.00
0.97
1.16
4.85
1.08
2.05
3.05
1.31
1.24
1.23
3.00
1.00
8.0
7.5
7.0
6.5
6.0
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4.0
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3.0
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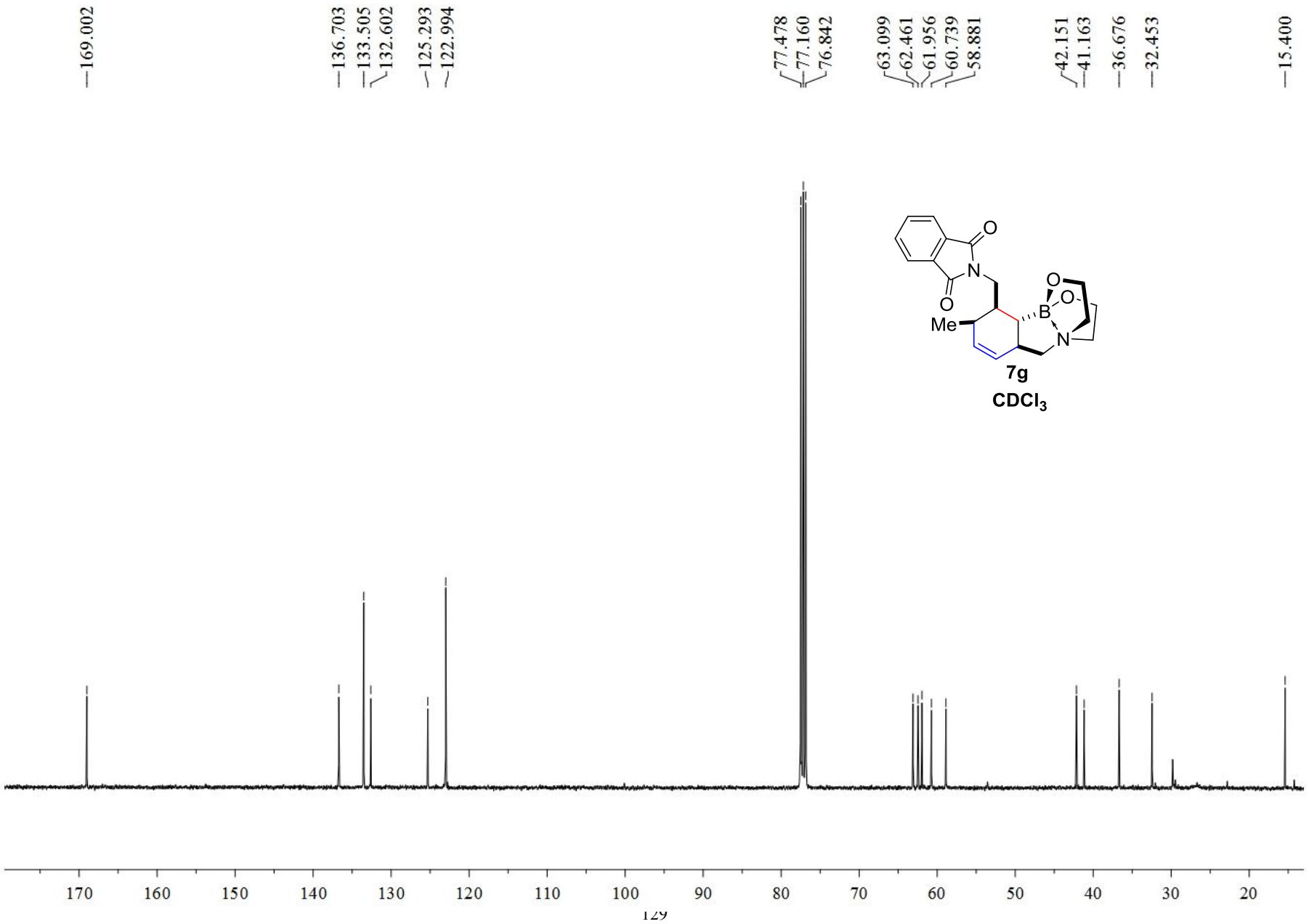
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77.160
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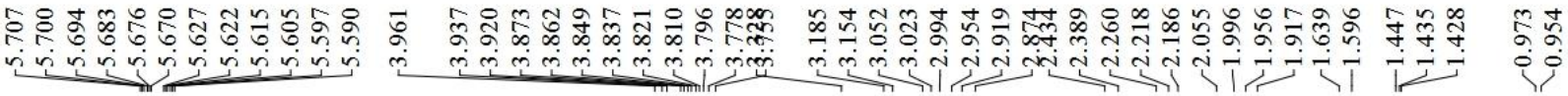
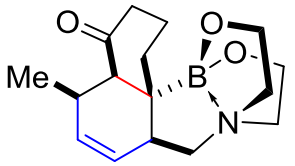
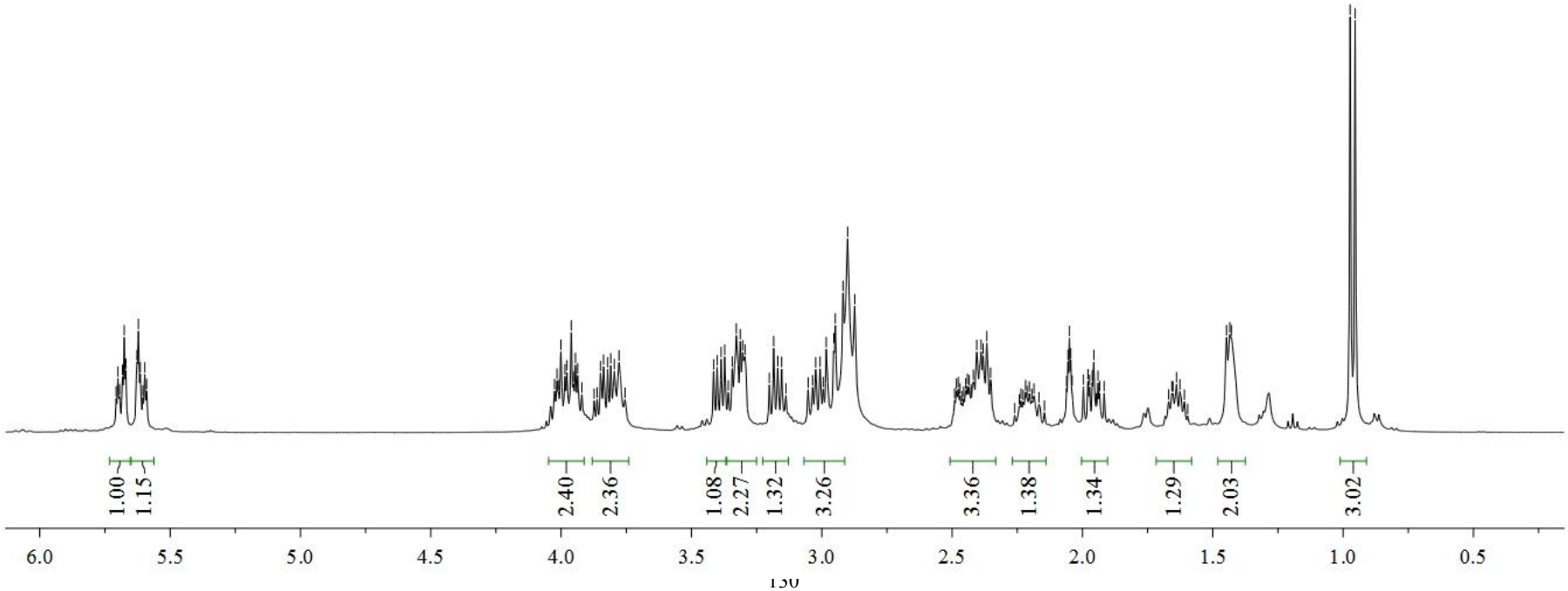
61.956
60.739
58.881
42.151
41.163
36.676
32.453
15.400
O
N
O
Me
B
O
O
N
7g
CDCl3
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20

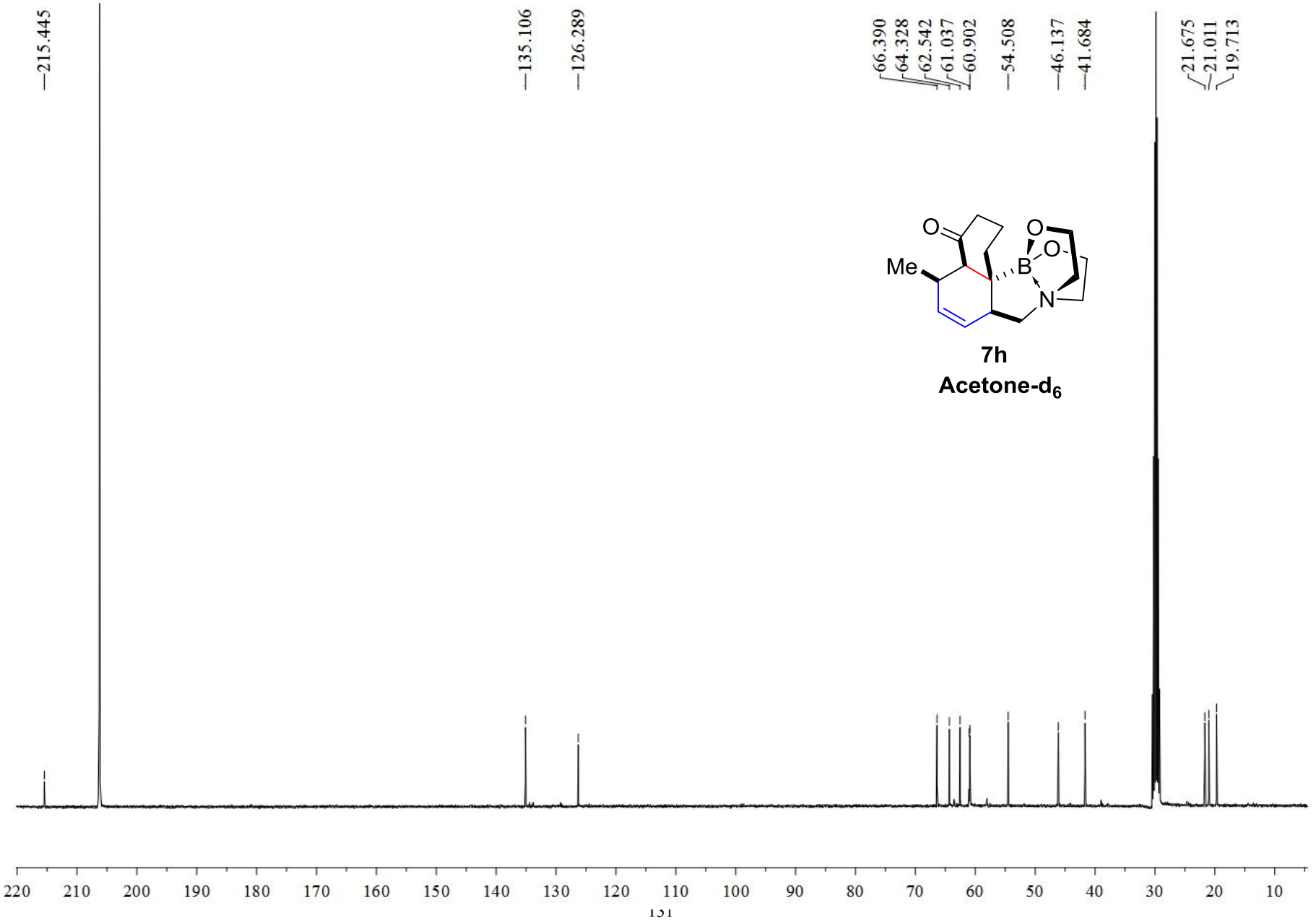




7h

Acetone-d_6

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21.011
19.713
O
O
O
B
Me
N
7h
Acetone-d6
220
210
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190
180
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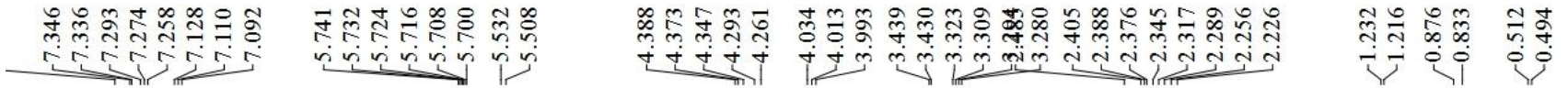
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10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7.092
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5.708
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5.508
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3.280
2.405
2.388
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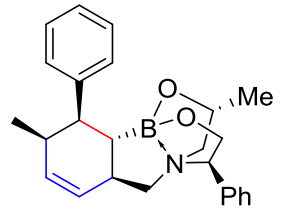
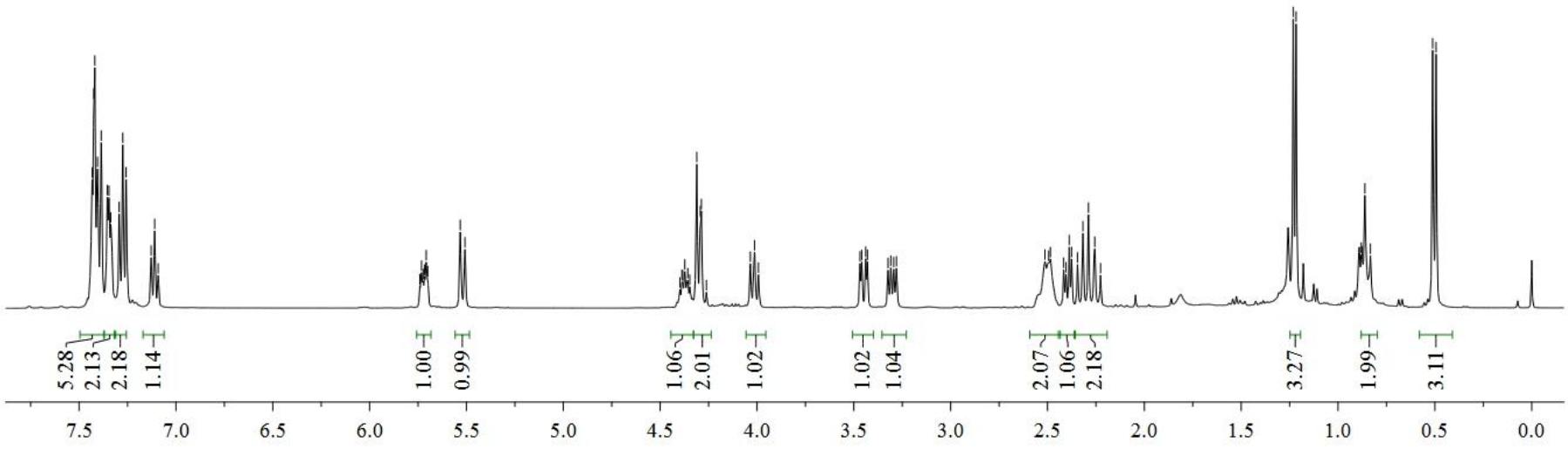

O
Me
B
O
N
Ph

$7i_o$

$CDCl_3$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1.02
1.04
2.07
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6.5
6.0
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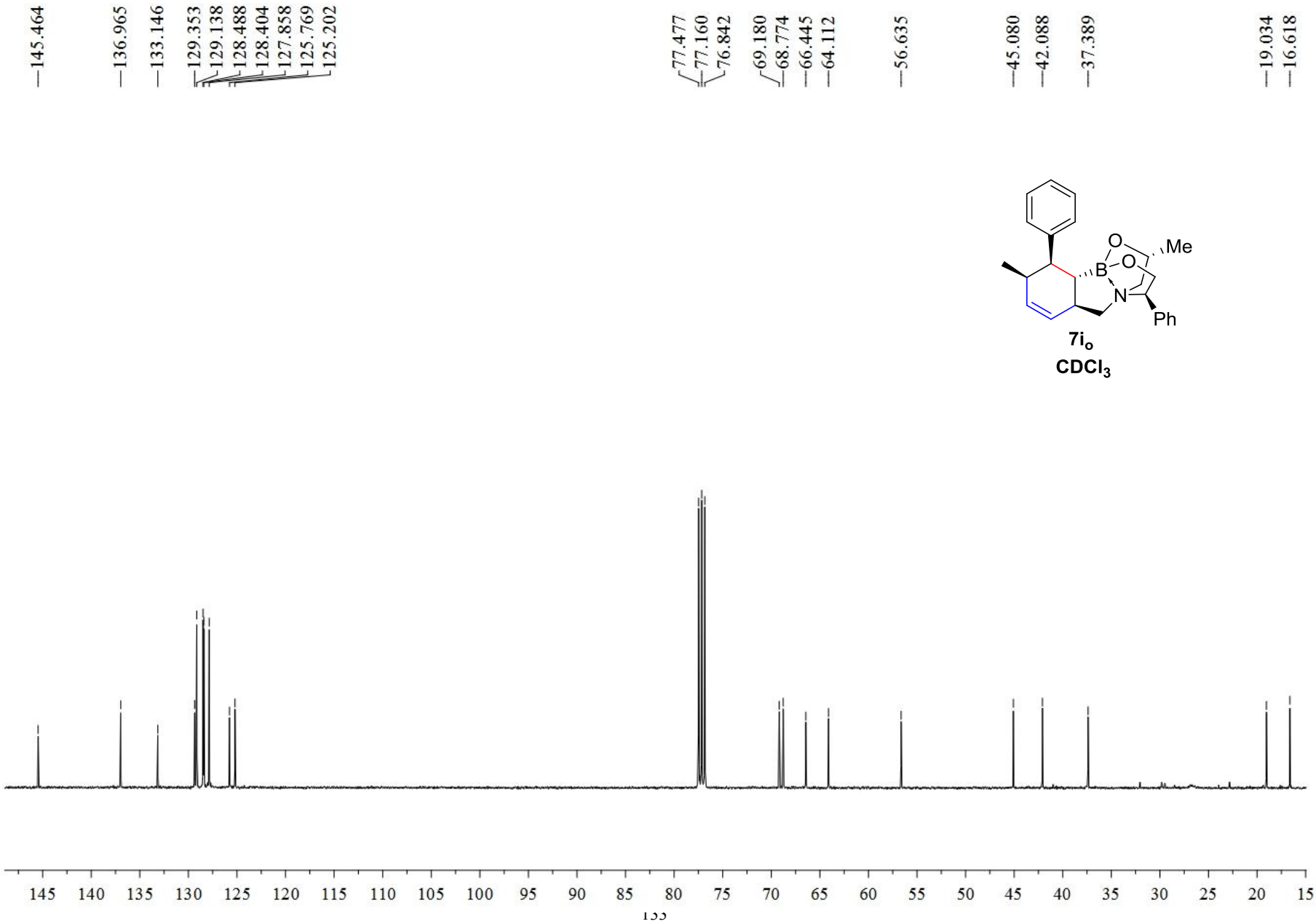
0.0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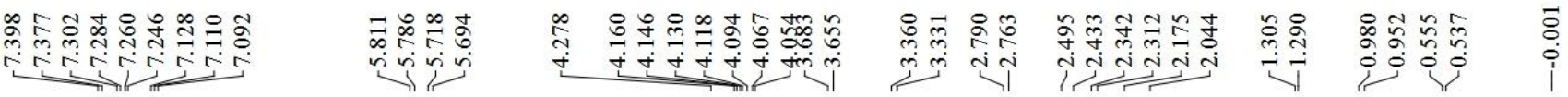
76.842
69.180
68.774
66.445
64.112
56.635
45.080
42.088
37.389
19.034
16.618
O
Me
B
O
N
Ph
7i$_o$
CDCl$_3$
145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15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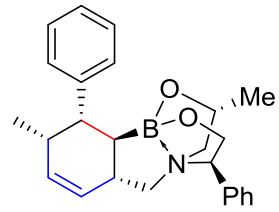
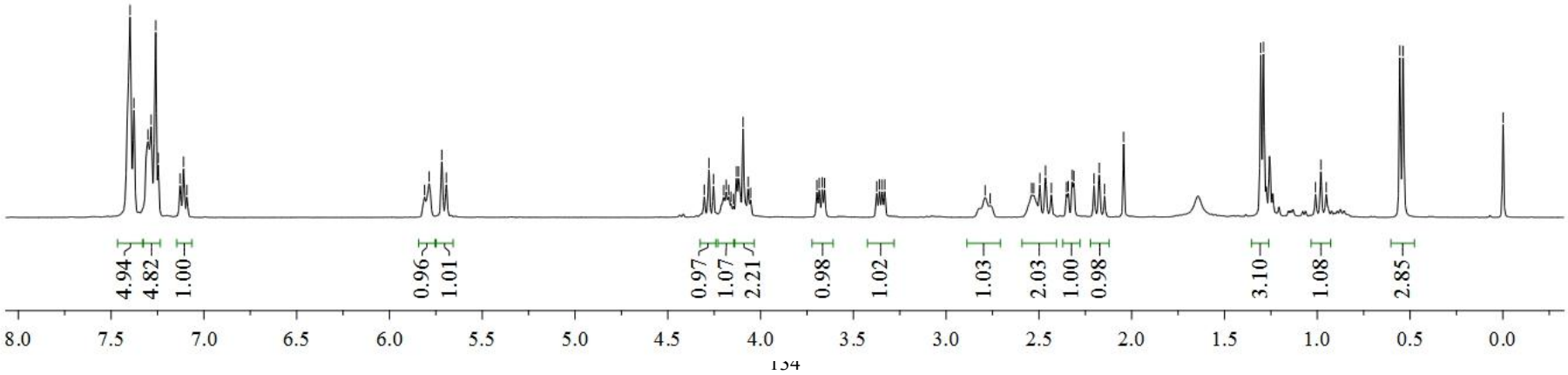

O
Me
B
O
N
Ph

7i'o

$CDCl_3$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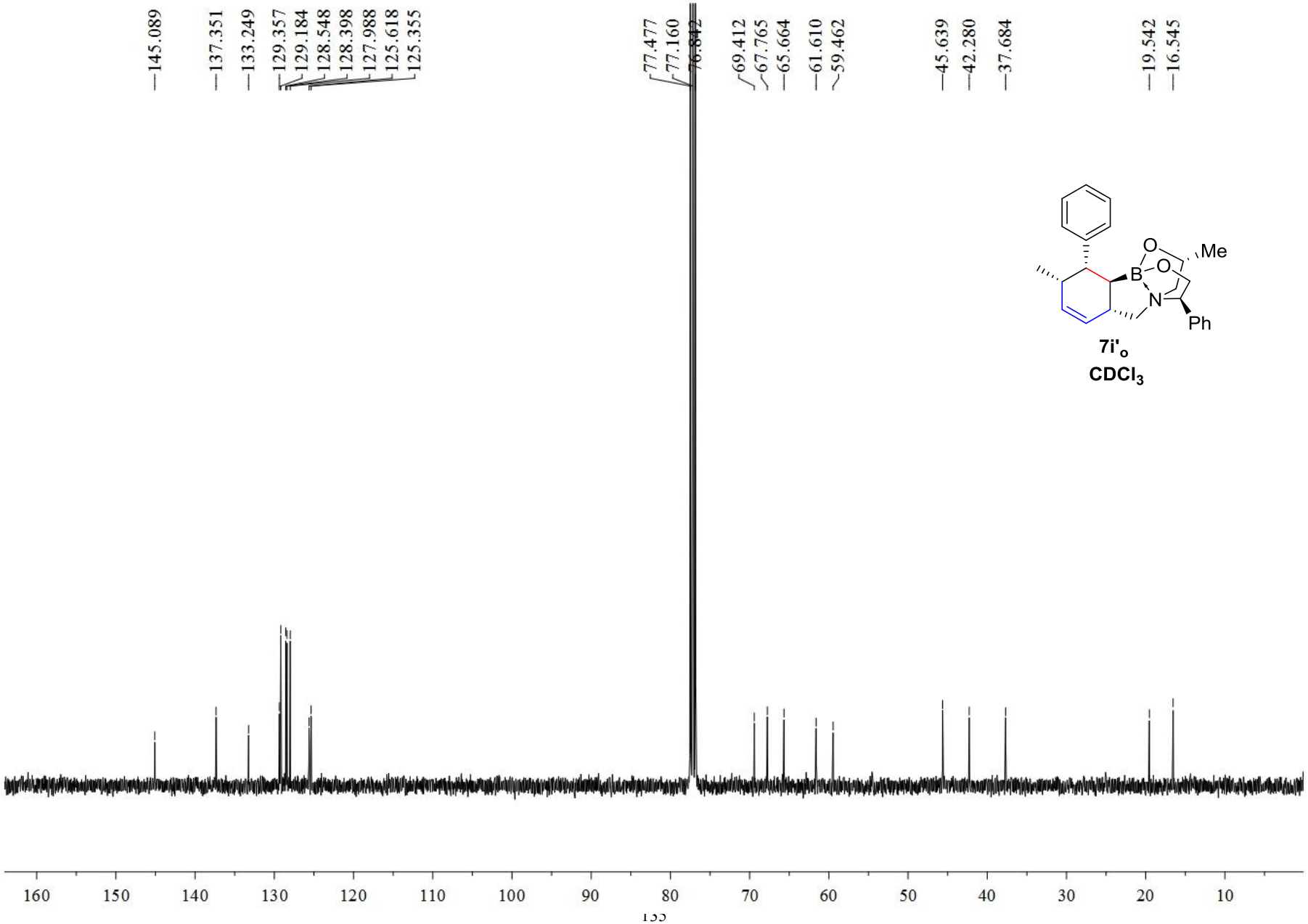
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65.664
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16.545
O
Me
B
O
N
Ph
7i'o
CDCl3
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150
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130
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60
50
40
30
20
10

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