Supporting Information

Electrochemical Stereoselective Borylation of Morita–Baylis–Hillman Adducts to Functionalized Allylic Boronates

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Table of contents:

Experimental:

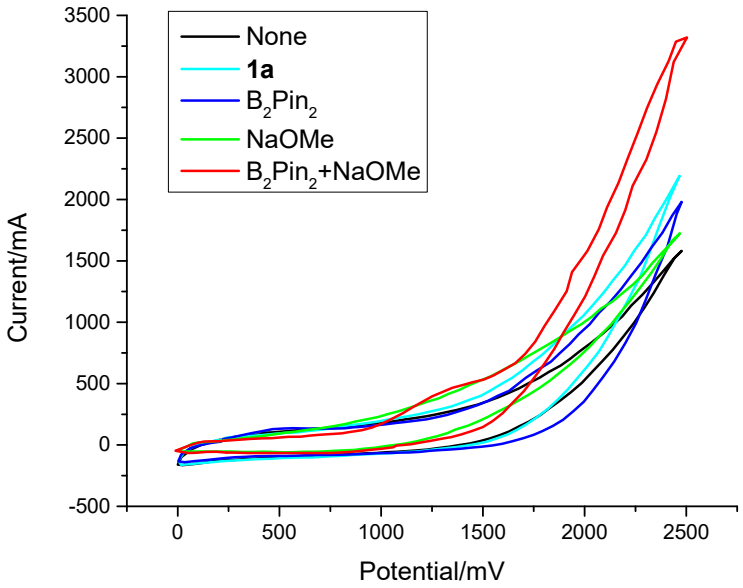
General Method:

IR spectra were recorded on a Bruker Tensor 37 (FTIR) spectrophotometer. ^{1}H NMR spectra were recorded on Bruker Avance 400 (400 MHz) and 600 (600 MHz) spectrometers at 295 K in $CDCl_3$; chemical shifts (δ ppm) and coupling constants (Hz) are reported in a standard fashion concerning either internal standard tetramethylsilane (TMS) (δ_H =0.00 ppm) or $CDCl_3$ (δ_H = 7.26 ppm). In the ^{1}H-NMR, the following abbreviations were used throughout: s = singlet, d = doublet, t = triplet, q = quartet, qui =quintet, sept = septet, dd = doublet of doublet, m = multiplet and br. s = broad singlet. $^{13}C\{^{1}H\}$ NMR spectra were recorded on Bruker Avance 400 (100 MHz) and 600 (150 MHz) spectrometers at room temperature in $CDCl_3$; chemical shifts (δ ppm) are reported relative to $CDCl_3$ [δ_C = 77.16 ppm (central line of the triplet)]. In the $^{13}C\{^{1}H\}$ NMR, the nature of carbons (C, CH, CH_2, and CH_3) was determined by recording the DEPT-135 spectra. The assignment of signals was confirmed by ^{1}H, $^{13}C\{^{1}H\}$ CPD, and DEPT spectra. High-resolution mass spectra (HR-MS) were recorded on an Agilent 6538 UHD Q-TOF electron spray ionization (ESI) mode and atmospheric pressure chemical ionization (APCI) modes. All small-scale reactions were carried out by using a Schlenk tube. Electrochemical reactions and cyclic voltammetry experiments were carried out using an IKA ElectraSyn 2.0. Reactions were monitored by TLC on silica gel using a combination of hexane and ethyl acetate as eluents. Solvents were distilled before use; petroleum ether in the boiling range of 60−80 °C was used. Aldehydes, DABCO, DCM, MeOH, acrylates, Acetic anhydride, DMAP, B_2Pin_2, and $LiClO_4$ were purchased from Sigma-Aldrich/TCI/local and used as received. Acme's silica gel (60–120 mesh) was used for column chromatography (approximately 20 g per gram of crude material).

General procedure for cyclic voltammetry (CV):

Cyclic voltammetry experiments were carried out in an IKA ElectraSyn 2.0. Cyclic voltammetry was performed in a three-electrode cell connected to a 5 mL vial at room temperature. The working electrode was a steady glassy carbon electrode, while the counter electrode was a platinum electrode. The reference was an Ag/AgCl electrode submerged in a saturated aqueous KCl solution. 8 mL of MeOH containing 0.1 M of $^{n}Bu_4NPF_6$ (310.0 mg) was poured into the electrochemical cell in cyclic voltammetry experiments. The scan rate was 200 mV/s, ranging from 0 V to 2.5 V. The CV measurements of **1a** (Light blue), B_2Pin_2 (blue), NaOMe (Green), and the

mixture of B_2Pin_2 and NaOMe (Red) in MeOH were carried out. To mimic the formation of intermediate **A**, which is unlikely during the CV measurement, NaOMe was added to the B_2Pin_2 species. The CV analysis of the mixture B_2Pin_2/NaOMe (Red) demonstrated an irreversible oxidation wave at +1.3 V *vs* Ag/AgCl, which is not observed in the CV analysis of B_2Pin_2 (Blue).



Scheme S1: Cyclic voltammetry

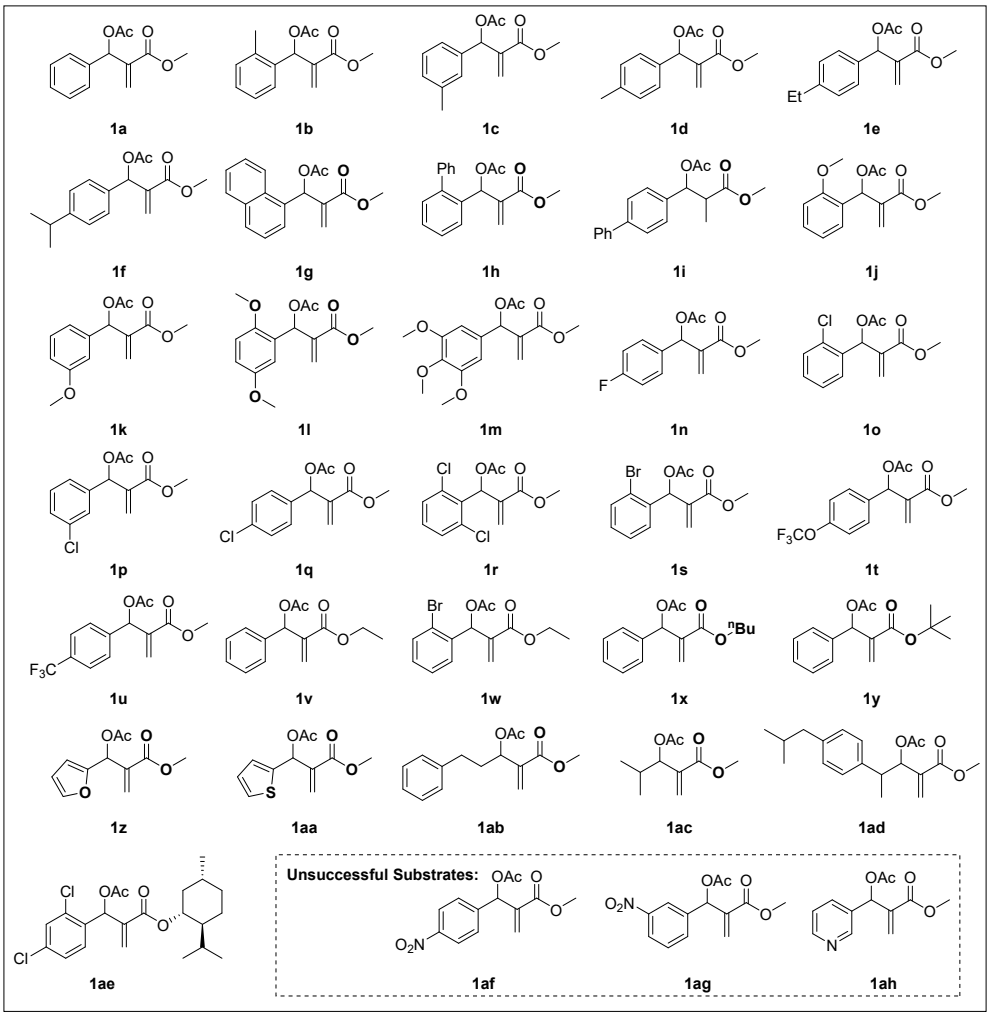
General procedure (GP-1) for the synthesis of Morita–Baylis-Hillman adducts (3a-3ag)1: [1–14]

To an oven-dried round-bottomed flask equipped with a magnetic stir bar, were added aldehyde **1** (144.22 mg to 380.6 mg, 2 mmol), DABCO (224.3 mg, 2 mmol), and acrylate (172.2 mg to 256.3 mg, 2 mmol). The reaction mixture was stirred at room temperature for 1-7 days. The completion of the reaction was monitored by using Thin Layer Chromatography (TLC). It was then quenched with saturated aqueous NH_4Cl solution and extracted with ethyl acetate (3×30 mL). The combined organic layers were dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure, and the residue was used for further reaction without purification.

General procedure (GP-1) for the synthesis of Morita–Baylis-Hillman acetates (1a-1ag):[1–14]

To an oven-dried round-bottomed flask equipped with a magnetic stir bar, were added Morita–Baylis-Hillman adduct (94.9 mg to 165.8 mg 0.6 mmol), DMAP (14.7 mg, 0.12 mmol), acetic anhydride (122.5 mg, 1.2 mmol), and DCM (2 mL). The reaction mixture was stirred at room temperature for 1 hour. The completion of the reaction was monitored by using Thin Layer Chromatography (TLC). It was then quenched with water and extracted with ethyl acetate (3×30 mL). The combined organic layers were dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure. The crude material was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (petroleum ether: ethyl acetate = 95:05 to 90:10) to obtain the pure product **1a-1ag** (78 to 90%), as colorless liquids (Table S1).

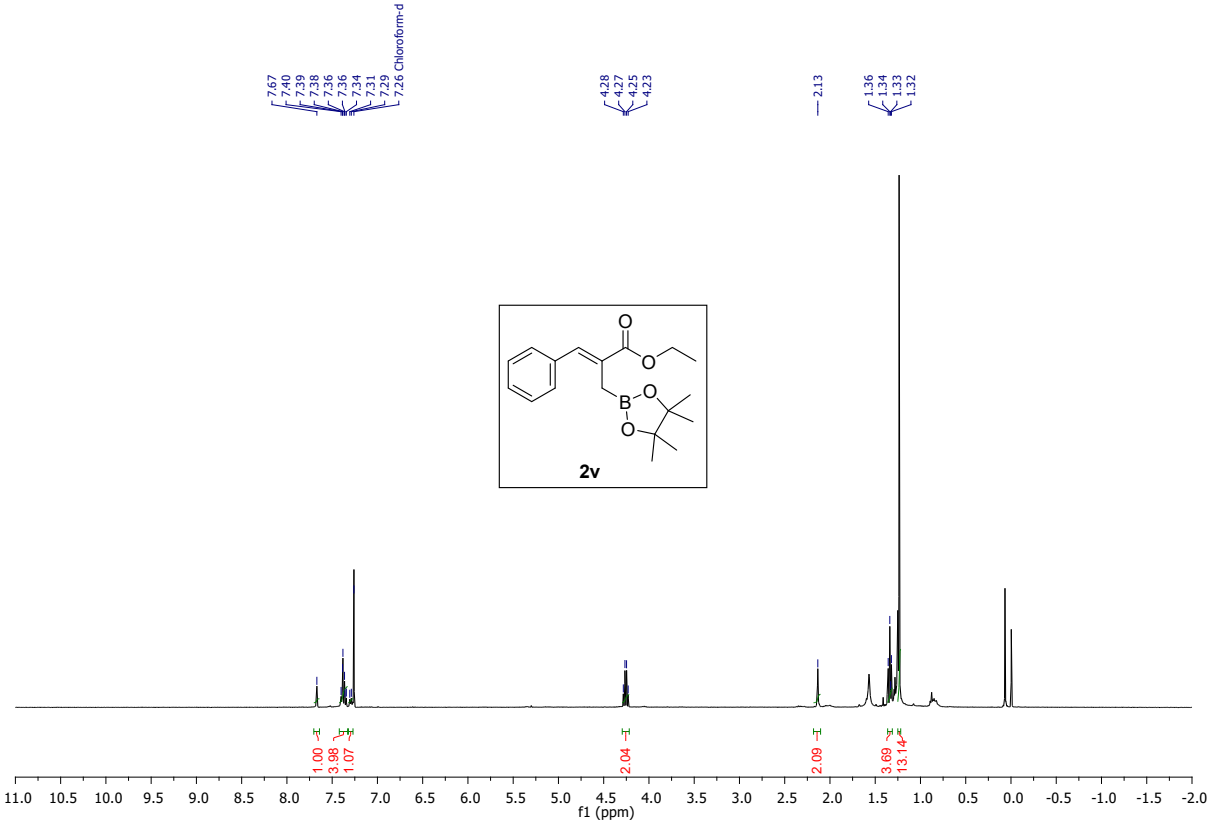
Table S1: The following Morita–Baylis-Hillman acetates are prepared by using the literature reports **1a-1ag.**[1–14]



General procedure (GP-3) for the electrochemical Borylation of Morita–Baylis–Hillman Acetates:

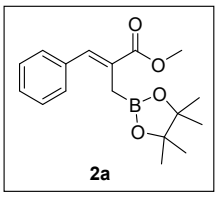
To an oven-dried ElectraSyn 2.0 undivided cell (5 mL) equipped with a magnetic stir bar, were added Morita–Baylis–Hillman acetates **1** (0.3 mmol), B_2Pin_2 **2** (0.45 mmol, 1.5 equiv), and lithium perchlorate (0.1 M) in a solvent MeOH (3 mL). The ElectraSyn vial cap equipped with two stainless steel electrodes as cathode and anode (5.2 cm × 0.8 cm × 0.2 cm) (1.2 cm × 0.8 cm × 0.2 cm area dipped in the reaction solution). The reaction mixture was stirred and electrolyzed at a constant current of 15 mA at room temperature for 4 h. After the reaction was complete, the residue was diluted with ethyl acetate (3 × 10 mL) and washed with water, dried over Na_2SO_4, concentrated under reduced pressure. Purification of the crude product by column chromatography on silica gel using petroleum ether/ethyl acetate (petroleum ether/ethyl acetate = 98:02 to 95:05) furnished the borylated products **2a-2ae** (68 to 90%), as colorless liquids.

Crude ^{1}H NMR Spectra of Compound 2v:



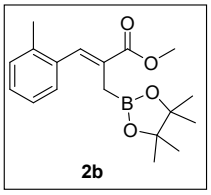
From the crude ^{1}H NMR of compound **2v**, it is observed that the alkene proton comes around 7.67 ppm. There is no peak within the region of 6.70 ppm. According to Chengjian Zhu's

work,[17] it was noticed that the alkene ^{1}H NMR of *Z*- isomer coming 6.70 ppm. So, it was confirmed that this isomer is *E*- isomer.



2a

Methyl (*E*)-3-phenyl-2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)acrylate (2a): **GP-3** was carried out with methyl 2-(acetoxy(phenyl)methyl)acrylate **1a** (70.3 mg, 0.3 mmol), B_2Pin_2 **2a** (114.3 mg, 0.45 mmol) and lithium perchlorate (32.0 mg, 0.1 M) in 3 mL of MeOH at room temperature for 4 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 98:02 to 95:05) furnished the product **2a** (79.8 mg, 88%), as colourless liquid. [TLC (petroleum ether/ethyl acetate 95:05), R_f(**1a**) = 0.50, R_f(**2a**) = 0.50, UV detection]. This compound is reported.[15]



2b

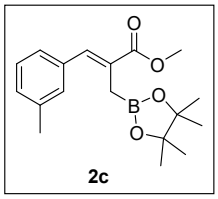
Methyl (*E*)-2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-3-(*o*-tolyl)acrylate (2b): **GP-3** was carried out with methyl 2-(acetoxy(*o*-tolyl)methyl)acrylate **1b** (74.4 mg, 0.3 mmol), B_2Pin_2 (114.3 mg, 0.45 mmol) and lithium perchlorate (32.0 mg, 0.1 M) in 3 mL of MeOH at room temperature for 4 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 98:02 to 95:05) furnished the product **2b** (79.9 mg, 84%), as colourless liquid. [TLC (petroleum ether/ethyl acetate 95:05), R_f(**1b**) = 0.50, R_f(**2b**) = 0.50, UV detection].

IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 3507, 2979, 2347, 1994, 1710, 1634, 1442, 1344, 1263, 1210, 1148, 1074, 846. 755 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (s, 1H), 7.27 – 7.25 (m, 1H), 7.21 – 7.15 (m, 3H), 3.80 (s, 3H), 2.28 (s, 3H), 1.96 (s, 2H), 1.22 (s, 12H) ppm.

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 169.1, 137.2, 137.0, 135.6, 130.8, 130.0, 128.8, 128.1, 125.6, 83.5 (2C), 52.1, 24.8 (4C), 20.1 ppm.

HRMS (ESI) m/z: $[(M + H)]^+$ calcd for $C_{18}H_{26}BO_4$ 317.1919; Found 317.1923.



2c

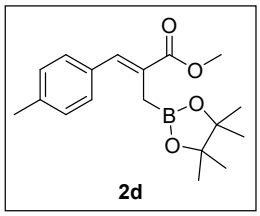
Methyl (*E*)-2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-3-(*m*-tolyl)acrylate (2c): **GP-3** was carried out with methyl 2-(acetoxy(*m*-tolyl)methyl)acrylate **1c** (74.4 mg, 0.3 mmol), B_2Pin_2 (114.3 mg, 0.45 mmol) and lithium perchlorate (32.0 mg, 0.1 M) in 3 mL of MeOH at room temperature for 4 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 98:02 to 95:05) furnished the product **2c** (82.5 mg, 87%), as colourless liquid. [TLC (petroleum ether/ethyl acetate 95:05), R_f(**1c**) = 0.50, R_f(**2c**) = 0.50, UV detection].

IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 3467, 2979, 2317, 2085, 1705, 1630, 1444, 1338, 1276, 1147, 1013, 845, 755, 694 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$) δ 7.57 (s, 1H), 7.22 – 7.09 (m, 3H), 7.03 (d, J = 7.4 Hz, 1H), 3.72 (s, 3H), 2.27 (s, 3H), 2.07 (s, 2H), 1.16 (s, 12H) ppm.

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 169.2, 137.9, 137.8, 136.2, 130.1, 129.9, 128.9, 128.3, 126.1, 83.5 (2C), 52.1, 24.8 (4C), 21.5 ppm.

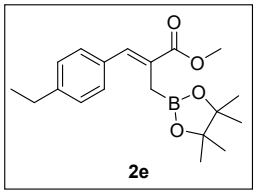
HRMS (ESI) m/z: $[(M + H)]^+$ calcd for $C_{18}H_{26}BO_4$ 317.1919; Found 317.1920.



2d

Methyl (*E*)-2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-3-(*p*-tolyl)acrylate (2d): **GP-3** was carried out with methyl 2-(acetoxy(*m*-tolyl)methyl)acrylate **1d** (74.4 mg, 0.3 mmol), B_2Pin_2 (114.3 mg, 0.45 mmol) and lithium perchlorate (32.0 mg, 0.1 M) in 3 mL of MeOH at room temperature for 4 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 98:02 to 95:05) furnished the product **2d** (75.9 mg, 80%), as

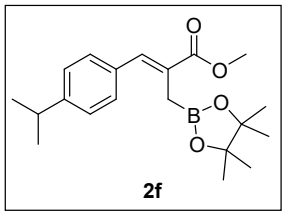
colourless liquid. [TLC (petroleum ether/ethyl acetate 95:05), R_f(**1d**) = 0.50, R_f(**2d**) = 0.50, UV detection]. This compound is reported.[16]



2e

Methyl (*E*)-3-(4-ethylphenyl)-2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)acrylate (2e):

GP-3 was carried out with methyl 2-(acetoxy(4-ethylphenyl)methyl)acrylate **1e** (78.7 mg, 0.3 mmol), B_2Pin_2 (114.3 mg, 0.45 mmol) and lithium perchlorate (32.0 mg, 0.1 M) in 3 mL of MeOH at room temperature for 4 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 98:02 to 95:05) furnished the product **2e** (83.2 mg, 84%), as colourless liquid. [TLC (petroleum ether/ethyl acetate 95:05), R_f(**1e**) = 0.50, R_f(**2e**) = 0.50, UV detection]. This compound is reported.[15]



2f

Methyl (*E*)-3-(4-isopropylphenyl)-2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)acrylate (2f):

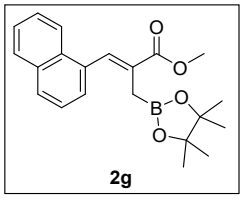
GP-3 was carried out with methyl 2-(acetoxy(4-isopropylphenyl)methyl)acrylate **1f** (82.9 mg, 0.3 mmol), B_2Pin_2 (114.3 mg, 0.45 mmol) and lithium perchlorate (32.0 mg, 0.1 M) in 3 mL of MeOH at room temperature for 4 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 98:02 to 95:05) furnished the product **2f** (82.6 mg, 80%), as colourless liquid. [TLC (petroleum ether/ethyl acetate 95:05), R_f(**1f**) = 0.50, R_f(**2f**) = 0.50, UV detection].

IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 3854, 3737, 2985, 2347, 2188, 1991, 1760, 1343, 1265, 1148, 844, 754, 698 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.65 (s, 1H), 7.33 (d, J = 8.2 Hz, 2H), 7.23 (d, J = 8.1 Hz, 2H), 3.79 (s, 3H), 2.94 – 2.87 (m, 1H), 2.16 (s, 2H), 1.25 (d, J = 6.9 Hz, 6H), 1.23 (s, 12H) ppm.

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 169.4, 149.1, 137.8, 133.8, 129.7 (2C), 129.4, 126.5 (2C), 83.5 (2C), 52.1, 34.2, 24.8 (4C), 23.9 (2C) ppm.

HRMS (ESI) m/z: $[(M + H)]^+$ calcd for $C_{20}H_{30}BO_4$ 345.2232; Found 345.2237.



2g

Methyl (*E*)-3-(naphthalen-1-yl)-2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)acrylate (2g):

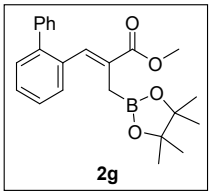
GP-3 was carried out with methyl 2-(acetoxy(naphthalen-1-yl)methyl)acrylate **1g** (85.3 mg, 0.3 mmol), B_2Pin_2 (114.3 mg, 0.45 mmol) and lithium perchlorate (32.0 mg, 0.1 M) in 3 mL of MeOH at room temperature for 4 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 98:02 to 95:05) furnished the product **2g** (82.4 mg, 78%), as colourless liquid. [TLC (petroleum ether/ethyl acetate 95:05), R_f(**1g**) = 0.50, R_f(**2g**) = 0.50, UV detection].

IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 2985, 2253, 1733, 1449, 1372, 1236, 1101, 1044, 914, 847, 731, 643 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.15 (s, 1H), 7.98 (dd, J = 6.2, 3.4 Hz, 1H), 7.87 – 7.84 (m, 1H), 7.83 – 7.80 (m, 1H), 7.50 (dd, J = 6.3, 3.3 Hz, 2H), 7.47 (d, J = 1.3 Hz, 1H), 7.46 (s, 1H), 3.86 (s, 3H), 1.99 (s, 2H), 1.21 (s, 12H) ppm.

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 168.9, 136.3, 133.7, 133.6, 132.4, 131.7, 128.5, 128.5, 126.7, 126.3, 126.2, 125.3, 125.2, 83.5 (2C), 52.2, 24.8 (4C) ppm.

HRMS (ESI) m/z: $[(M + Na)]^+$ calcd for $C_{21}H_{25}BNaO_4$ 375.1738; Found 375.1753.



Methyl (*E*)-3-([1,1'-biphenyl]-2-yl)-2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)acrylate (2h):

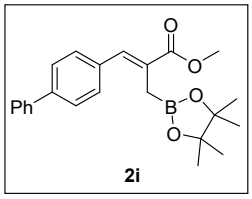
GP-3 was carried out with methyl 2-([1,1'-biphenyl]-2-yl(acetoxy)methyl)acrylate **1h** (93.1 mg, 0.3 mmol), B_2Pin_2 (114.3 mg, 0.45 mmol) and lithium perchlorate (32.0 mg, 0.1 M) in 3 mL of MeOH at room temperature for 4 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 98:02 to 95:05) furnished the product **2h** (84.0 mg, 74%), as colourless liquid. [TLC (petroleum ether/ethyl acetate 95:05), R_f(**1h**) = 0.50, R_f(**2h**) = 0.50, UV detection].

IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 3503, 2978, 2347, 2250, 2042, 1706, 1442, 1340, 1261, 1200, 1145, 1071, 967, 739 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$) δ 7.46 (s, 2H), 7.43 – 7.38 (m, 5H), 7.38 – 7.31 (m, 4H), 3.71 (s, 3H), 2.13 (s, 2H), 1.21 (s, 12H) ppm.

$^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 169.0, 141.9, 140.6, 138.6, 134.6, 130.3, 130.0, 129.8 (2C), 129.7, 128.3, 128.2 (2C), 127.4, 127.1, 83.5 (2C), 52.0, 24.8 (4C) ppm.

HRMS (ESI) m/z: $[(M + Na)]^+$ calcd for $C_{23}H_{27}BNaO_4$ 401.1895; Found 401.1882.



Methyl (*E*)-3-([1,1'-biphenyl]-4-yl)-2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)acrylate (2i):

GP-3 was carried out with methyl 3-([1,1'-biphenyl]-4-yl)-3-acetoxy-2-methylpropanoate **1i** (93.7 mg, 0.3 mmol), B_2Pin_2 (114.3 mg, 0.45 mmol) and lithium perchlorate (32.0 mg, 0.1 M) in 3 mL of MeOH at room temperature for 4 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 98:02 to 95:05) furnished the product **2i** (84.0 mg,

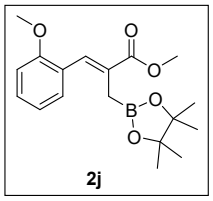
74%), as colourless liquid. [TLC (petroleum ether/ethyl acetate 95:05), R_f(**1i**) = 0.50, R_f(**2i**) = 0.50, UV detection].

IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 2984, 2256, 1734, 1448, 1372, 1234, 1098, 1043, 918,847, 786, 636 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$) δ 7.71 (s, 1H), 7.63 – 7.59 (m, 4H), 7.50 – 7.42 (m, 1H), 7.39 – 7.32 (m, 1H), 3.81 (s, 3H), 2.20 (s, 1H), 1.24 (s, 12H) ppm.

$^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 169.3, 140.9, 140.6, 137.3, 135.3, 130.3, 130.1 (2C), 128.9 (2C), 127.7, 127.2 (2C), 127.1 (2C), 83.7 (2C), 52.2, 24.8 (4C) ppm.

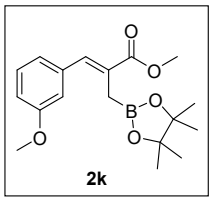
HRMS (ESI) m/z: $[(M + H)]^+$ calcd for $C_{23}H_{28}BO_4$ 379.2075; Found 379.2100.



2j

Methyl (*E*)-3-(2-methoxyphenyl)-2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)acrylate (2j):

GP-3 was carried out with methyl 2-(acetoxy(2-methoxyphenyl)methyl)acrylate **1j** (79.3 mg, 0.3 mmol), B_2Pin_2 (114.3 mg, 0.45 mmol) and lithium perchlorate (32.0 mg, 0.1 M) in 3 mL of MeOH at room temperature for 4 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 98:02 to 95:05) furnished the product **2j** (88.7 mg, 89%), as colourless liquid. [TLC (petroleum ether/ethyl acetate 95:05), R_f(**1j**) = 0.40, R_f(**2j**) = 0.40, UV detection]. This compound is reported.[15]

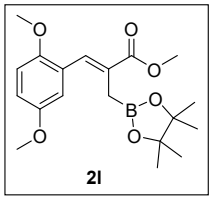


2k

Methyl (*E*)-3-(3-methoxyphenyl)-2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)acrylate (2k):

GP-3 was carried out with methyl 2-(acetoxy(3-methoxyphenyl)methyl)acrylate **1k** (79.3 mg, 0.3 mmol), B_2Pin_2 (114.3 mg, 0.45 mmol) and lithium perchlorate (32.0 mg, 0.1 M) in 3 mL of MeOH

at room temperature for 4 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 98:02 to 95:05) furnished the product **2k** (82.7 mg, 83%), as colourless liquid. [TLC (petroleum ether/ethyl acetate 95:05), R_f(**1k**) = 0.40, R_f(**2k**) = 0.40, UV detection]. This compound is reported.[16]



Methyl (*E*)-3-(2,5-dimethoxyphenyl)-2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)acrylate (2l):

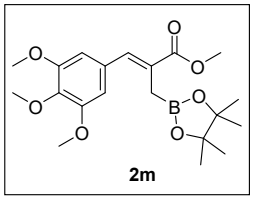
GP-3 was carried out with methyl 2-(acetoxy(2,5-dimethoxyphenyl)methyl)acrylate **1l** (89.4 mg, 0.3 mmol), B_2Pin_2 (114.3 mg, 0.45 mmol) and lithium perchlorate (32.0 mg, 0.1 M) in 3 mL of MeOH at room temperature for 4 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 98:02 to 95:05) furnished the product **2l** (89.1 mg, 82%), as colorless liquid. [TLC (petroleum ether/ethyl acetate 95:05), R_f(**1l**) = 0.40, R_f(**2l**) = 0.40, UV detection].

IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 3857, 3736, 3610, 2984, 2346, 2241, 2071, 1762, 1709, 1493, 1348, 1267, 1149, 1051, 969, 755 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$) δ 7.76 (s, 1H), 6.96 (d, J = 2.5 Hz, 1H), 6.83 – 6.81 (m, 2H), 3.79 (s, 3H), 3.79 (s, 3H), 3.76 (s, 3H), 2.08 (s, 2H), 1.23 (s, 12H) ppm.

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 169.1, 153.2, 152.0, 133.8, 130.5, 125.9, 115.6, 115.0, 111.71, 83.5 (2C), 56.2, 55.9, 52.1, 24.8 (4C) ppm.

HRMS (ESI) m/z: $[(M + H)]^+$ calcd for $C_{19}H_{28}BO_6$ 363.1973; Found 363.1988.



Methyl (*E*)-2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-3-(3,4,5-trimethoxyphenyl)acrylate (2m):

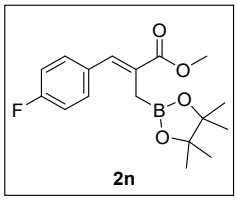
GP-3 was carried out with methyl 2-(acetoxy(3,4,5-trimethoxyphenyl)methyl)acrylate **1m** (97.3 mg, 0.3 mmol), B_2Pin_2 (114.3 mg, 0.45 mmol) and lithium perchlorate (32.0 mg, 0.1 M) in 3 mL of MeOH at room temperature for 4 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 98:02 to 95:05) furnished the product **2m** (84.7 mg, 72%), as colourless liquid. [TLC (petroleum ether/ethyl acetate 90:10), R_f(**1m**) = 0.50, R_f(**2m**) = 0.50, UV detection].

IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 3474, 2924, 2854, 2347, 1708, 1634, 1592, 1488, 1439, 1269, 1224, 1094, 1016, 831, 754, 691 cm^{-1}.

^1H NMR (600 MHz, $CDCl_3$) δ 7.60 (s, 1H), 6.67 (s, 2H), 3.86 (s, 9H), 3.80 (s, 3H), 2.17 (s, 2H), 1.22 (s, 12H) ppm.

$^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 169.2, 153.1, 138.1, 137.8, 131.8, 129.7, 106.8 (2C), 83.6, 61.0, 56.2 (2C), 52.2, 24.8 (4C) ppm.

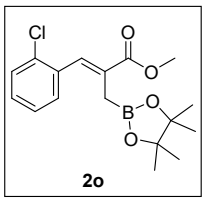
HRMS (ESI) m/z: $[(M + H)]^+$ calcd for $C_{20}H_{30}BO_7$ 393.2079; Found 393.2094.



Methyl (*E*)-3-(4-fluorophenyl)-2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)acrylate (2n):

GP-3 was carried out with methyl 2-(acetoxy(4-fluorophenyl)methyl)acrylate **1n** (75.7 mg, 0.3 mmol), B_2Pin_2 (114.3 mg, 0.45 mmol) and lithium perchlorate (32.0 mg, 0.1 M) in 3 mL of MeOH at room temperature for 4 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 98:02 to 95:05) furnished the product **2n** (75.9 mg, 79%), as

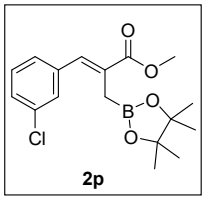
colourless liquid. [TLC (petroleum ether/ethyl acetate 95:05), R_f(**1n**) = 0.50, R_f(**2n**) = 0.50, UV detection]. This compound is reported.[15]



2o

Methyl (*E*)-3-(2-chlorophenyl)-2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)acrylate (2o):

GP-3 was carried out with methyl 2-(acetoxy(2-chlorophenyl)methyl)acrylate **1o** (80.6 mg, 0.3 mmol), B_2Pin_2 (114.3 mg, 0.45 mmol) and lithium perchlorate (32.0 mg, 0.1 M) in 3 mL of MeOH at room temperature for 4 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 98:02 to 95:05) furnished the product **2o** (88.9 mg, 88%), as colourless liquid. [TLC (petroleum ether/ethyl acetate 95:05), R_f(**1o**) = 0.50, R_f(**2o**) = 0.50, UV detection]. This compound is reported.[15]



2p

Methyl (*E*)-3-(3-chlorophenyl)-2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)acrylate (2p):

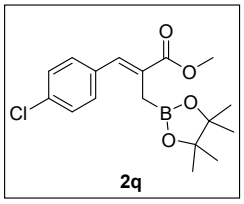
GP-3 was carried out with methyl 2-(acetoxy(3-chlorophenyl)methyl)acrylate **1p** (80.6 mg, 0.3 mmol), B_2Pin_2 (114.3 mg, 0.45 mmol) and lithium perchlorate (32.0 mg, 0.1 M) in 3 mL of MeOH at room temperature for 4 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 98:02 to 95:05) furnished the product **2p** (82.8 mg, 82%), as colourless liquid. [TLC (petroleum ether/ethyl acetate 95:05), R_f(**1p**) = 0.50, R_f(**2p**) = 0.50, UV detection].

IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 3507, 2980, 2341, 2040, 1711, 1637, 1438, 1338, 1261, 1204, 1145, 1066, 967, 846, 757, 680 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (s, 1H), 7.40 (s, 1H), 7.32 – 7.22 (m, 3H), 3.79 (s, 3H), 2.09 (s, 2H), 1.24 (s, 12H) ppm.

$^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) δ 168.8, 138.1, 136.1, 134.4, 131.7, 129.7, 129.3, 128.1, 127.6, 83.7 (2C), 52.2, 24.8 (4C) ppm.

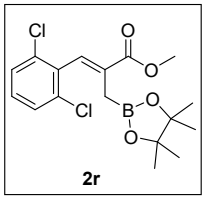
HRMS (ESI) m/z: $[(M + H)]^+$ calcd for $C_{17}H_{23}BClO_4$ 337.1372; Found 337.1394.



2q

Methyl (*E*)-3-(4-chlorophenyl)-2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)acrylate (2q):

GP-3 was carried out with methyl 2-(acetoxy(4-chlorophenyl)methyl)acrylate **1q** (80.6 mg, 0.3 mmol), B_2Pin_2 (114.3 mg, 0.45 mmol) and lithium perchlorate (32.0 mg, 0.1 M) in 3 mL of MeOH at room temperature for 4 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 98:02 to 95:05) furnished the product **2q** (78.8 mg, 78%), as colourless liquid. [TLC (petroleum ether/ethyl acetate 95:05), R_f(**1q**) = 0.50, R_f(**2q**) = 0.50, UV detection]. This compound is reported.[16]



2r

Methyl (*E*)-3-(2,6-dichlorophenyl)-2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)acrylate (2r):

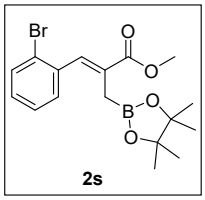
GP-3 was carried out with methyl 2-(acetoxy(2,6-dichlorophenyl)methyl)acrylate **1r** (90.9 mg, 0.3 mmol), B_2Pin_2 (114.3 mg, 0.45 mmol) and lithium perchlorate (32.0 mg, 0.1 M) in 3 mL of MeOH at room temperature for 4 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 98:02 to 95:05) furnished the product **2r** (83.3 mg, 75%), as colourless liquid. [TLC (petroleum ether/ethyl acetate 95:05), R_f(**1r**) = 0.50, R_f(**2r**) = 0.50, UV detection].

IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 3500, 2981, 2353, 1717, 1434, 1342, 1266, 1148, 969, 848, 757 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$) δ 7.41 (s, 1H), 7.32 (d, J = 8.1 Hz, 2H), 7.18 (t, J = 8.1 Hz, 1H), 3.82 (s, 3H), 1.76 (s, 2H), 1.20 (s, 12H) ppm.

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 167.9, 135.1, 134.6, 134.1, 132.2, 129.3, 128.1 (2C), 83.5 (2C), 52.2, 24.7 (4C) ppm.

HRMS (ESI) m/z: $[(M + H)]^+$ calcd for $C_{17}H_{22}BCl_2O_4$ 371.0983; Found 371.1000.



2s

Methyl (*E*)-3-(2-bromophenyl)-2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)acrylate (2s):

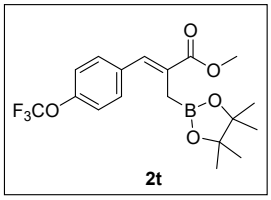
GP-3 was carried out with methyl 2-(acetoxy(2-bromophenyl)methyl)acrylate **1s** (93.9 mg, 0.3 mmol), B_2Pin_2 (114.3 mg, 0.45 mmol) and lithium perchlorate (32.0 mg, 0.1 M) in 3 mL of MeOH at room temperature for 4 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 98:02 to 95:05) furnished the product **2s** (89.2 mg, 78%), as colourless liquid. [TLC (petroleum ether/ethyl acetate 95:05), R_f(**1s**) = 0.50, R_f(**2s**) = 0.50, UV detection].

IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 3500, 2980, 2347, 1710, 1636, 1440, 1338, 1262, 1207, 1144, 1074, 754, 669 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$) δ 7.65 (s, 1H), 7.59 (dd, J = 8.0, 1.1 Hz, 1H), 7.38 (dd, J = 7.7, 1.6 Hz, 1H), 7.29 (td, J = 7.5, 1.1 Hz, 1H), 7.15 (td, J = 7.5, 1.6 Hz, 1H), 3.81 (s, 3H), 1.97 (s, 2H), 1.23 (s, 12H) ppm.

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 168.6, 136.9, 136.7, 132.8, 131.8, 130.6, 129.5, 127.1, 124.3, 83.6 (2C), 52.2, 24.8 (4C) ppm.

HRMS (ESI) m/z: $[(M + H)]^+$ calcd for $C_{17}H_{23}BBr^{79}O_4$ 381.0867; Found 381.0862.; $[(M + H)]^+$ calcd for $C_{17}H_{23}BBr^{81}O_4$ 383.0847; Found 383.0854.



Methyl (*E*)-2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-3-(4-(trifluoromethoxy)phenyl)acrylate (2t):

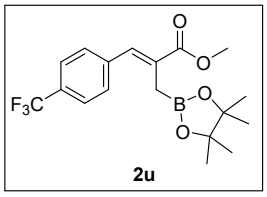
GP-3 was carried out with methyl 2-(acetoxy(4-(trifluoromethoxy)phenyl)methyl)acrylate **1t** (95.5 mg, 0.3 mmol), B_2Pin_2 (114.3 mg, 0.45 mmol) and lithium perchlorate (32.0 mg, 0.1 M) in 3 mL of MeOH at room temperature for 4 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 98:02 to 95:05) furnished the product **2t** (83.4 mg, 87%), as colourless liquid. [TLC (petroleum ether/ethyl acetate 95:05), R_f(**1t**) = 0.40, R_f(**2t**) = 0.40, UV detection].

IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 2981, 2347, 1713, 1620, 1438, 1320, 1263, 1122, 1064, 1016, 968, 893, 839, 747, 679 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$) δ 7.62 (s, 1H), 7.41 (d, J = 8.6 Hz, 2H), 7.21 (d, J = 8.1 Hz, 2H), 3.80 (s, 3H), 2.10 (s, 2H), 1.23 (s, 12H) ppm.

$^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 168.9, 148.8, 136.1, 135.0, 131.2, 130.9 (2C), 120.9 (2C), 120.6 ($J_{C\text{-}F}$ = 256.9 Hz), 83.7 (2C), 52.3, 24.8 (4C) ppm.

HRMS (ESI) m/z: $[(M + H)]^+$ calcd for $C_{18}H_{23}BF_3O_5$ 387.1585; Found 387.1599.



Methyl (*E*)-2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-3-(4-(trifluoromethyl)phenyl)acrylate (2u):

GP-3 was carried out with methyl 2-(acetoxy(4-(trifluoromethyl)phenyl)methyl)acrylate **1u** (90.7 mg, 0.3 mmol), B_2Pin_2 (114.3 mg, 0.45 mmol) and lithium perchlorate (32.0 mg, 0.1 M) in 3 mL of MeOH at room temperature for 4 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 98:02 to 95:05) furnished the product **2u** (75.5

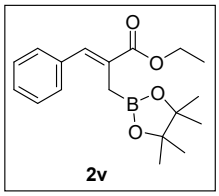
mg, 68%), as a colorless liquid. [TLC (petroleum ether/ethyl acetate 95:05), R_f(**1u**) = 0.50, R_f(**2u**) = 0.50, UV detection].

IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 3498, 2980, 2342, 2252, 1705, 1630, 1442, 1338, 1263, 1201, 1147, 1072, 1015, 969, 908, 842, 733 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, J = 9.2 Hz, 2H), 7.61 (s, 1H), 7.49 (d, J = 8.2 Hz, 2H), 3.81 (s, 3H), 2.09 (s, 1H), 1.24 (s, 12H) ppm.

$^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 168.7, 139.9, 135.9, 132.5, 129.9 ($J_{C\text{-}F}$ = 32.9 Hz), 129.6 (2C), 124.2 (2C) ($J_{C\text{-}F}$ = 3.8 Hz), 125.4 ($J_{C\text{-}F}$ = 272.2 Hz), 83.8 (2C), 52.3, 24.8 (4C) ppm.

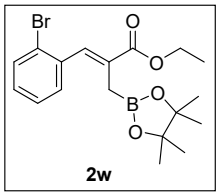
HRMS (ESI) m/z: $[(M + Na)]^+$ calcd for $C_{18}H_{22}BF_3NaO_4$ 393.1455; Found 393.1443.



2v

Ethyl (*E*)-3-phenyl-2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)acrylate (2v):

GP-3 was carried out with ethyl 2-(acetoxy(phenyl)methyl)acrylate **1v** (74.5 mg, 0.3 mmol), B_2Pin_2 (114.3 mg, 0.45 mmol) and lithium perchlorate (32.0 mg, 0.1 M) in 3 mL of MeOH at room temperature for 4 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 98:02 to 95:05) furnished the product **2v** (85.4 mg, 90%), as colourless liquid. [TLC (petroleum ether/ethyl acetate 95:05), R_f(**1v**) = 0.50, R_f(**2v**) = 0.50, UV detection]. This compound is reported.[20]



2w

Ethyl (*E*)-3-(2-bromophenyl)-2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)acrylate (2w):

GP-3 was carried out with methyl 2-(acetoxy(2-bromophenyl)methyl)acrylate **1w** (98.2 mg, 0.3 mmol), B_2Pin_2 (114.3 mg, 0.45 mmol) and lithium perchlorate (32.0 mg, 0.1 M) in 3 mL of MeOH at room temperature for 4 h. Purification of the crude material by silica gel column chromatography

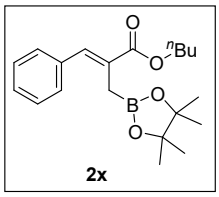
(petroleum ether/ethyl acetate: 98:02 to 95:05) furnished the product **2w** (93.6 mg, 79%), as colourless liquid. [TLC (petroleum ether/ethyl acetate 95:05), R_f(**1w**) = 0.50, R_f(**2w**) = 0.50, UV detection].

IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 3740, 3500, 2982, 2345, 2144, 1707, 1637, 1349, 1264, 1151, 1097, 1022, 967, 851, 755 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$) δ 7.65 (s, 1H), 7.59 (dd, J = 8.0, 1.1 Hz, 1H), 7.39 (dd, J = 7.7, 1.5 Hz, 1H), 7.29 (ddd, J = 7.5, 7.4, 0.8 Hz, 1H), 7.15 (ddd, J = 7.7, 7.6, 1.5 Hz, 1H), 4.27 (q, J = 7.1 Hz, 2H), 1.98 (s, 2H), 1.34 (t, J = 7.1 Hz, 3H), 1.24 (s, 12H) ppm.

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 168.2, 136.8, 136.6, 132.8, 132.1, 130.7, 129.5, 127.1, 124.3, 83.6 (2C), 61.1, 24.8 (4C), 14.4 ppm.

HRMS (ESI) m/z: $[(M + H)]^+$ calcd for $C_{18}H_{25}Br^{79}O_4$ 395.1024 Found 395.1028; $[(M + H)]^+$ calcd for $C_{18}H_{25}Br^{81}O_4$ 397.1003 Found 397.1014.



2x

Butyl (*E*)-3-phenyl-2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)acrylate (2x):

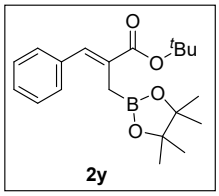
GP-3 was carried out with butyl 2-(acetoxy(phenyl)methyl)acrylate **1x** (83.0 mg, 0.3 mmol), B_2Pin_2 (114.3 mg, 0.45 mmol) and lithium perchlorate (32.0 mg, 0.1 M) in 3 mL of MeOH at room temperature for 4 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 98:02 to 95:05) furnished the product **2x** (98.1 mg, 95%), as colourless liquid. [TLC (petroleum ether/ethyl acetate 95:05), R_f(**1x**) = 0.50, R_f(**2x**) = 0.50, UV detection].

IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 3497, 2964, 2319, 2120, 1703, 1632, 1338, 1262, 1210, 1150, 1074, 1016, 848, 756, 699 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$) δ 7.66 (s, 1H), 7.41 – 7.33 (m, 4H), 7.23 – 7.18 (m, 1H), 4.20 (t, J = 6.7 Hz, 2H), 2.14 (s, 2H), 1.73 – 1.66 (m, 2H), 1.50 – 1.41 (m, 2H), 1.23 (s, 12H), 0.96 (t, J = 7.4 Hz, 3H) ppm.

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 168.9, 137.3, 136.4, 130.6, 129.5 (2C), 128.4 (2C), 128.1, 83.6 (2C), 64.9, 30.9, 24.8 (4C), 19.4, 13.9 ppm.

HRMS (ESI) m/z: $[(M + H)]^+$ calcd for $C_{20}H_{30}BO_4$ 345.2232; Found 345.2234.



2y

***tert*-Butyl (*E*)-3-phenyl-2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)acrylate (2y):**

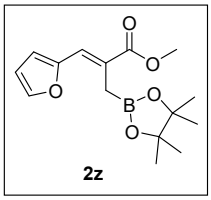
GP-3 was carried out with *tert*-butyl 2-(acetoxy(phenyl)methyl)acrylate **1y** (82.9 mg, 0.3 mmol), B_2Pin_2 (114.3 mg, 0.45 mmol) and lithium perchlorate (32.0 mg, 0.1 M) in 3 mL of MeOH at room temperature for 4 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 98:02 to 95:05) furnished the product **2y** (99.1 mg, 96%), as colourless liquid. [TLC (petroleum ether/ethyl acetate 95:05), R_f(**1y**) = 0.50, R_f(**2y**) = 0.50, UV detection].

IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 3737, 3393, 2978, 2927, 1699, 1631, 1455, 1370, 1327, 1263, 1156, 1013, 755, 697 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$) δ 7.58 (s, 1H), 7.40 – 7.32 (m, 4H), 7.30 – 7.24 (m, 1H), 2.08 (s, 2H), 1.53 (s, 9H), 1.24 (s, 12H) ppm.

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 167.9, 136.7, 136.5, 132.2, 129.4 (2C), 128.3 (2C), 127.9, 83.5 (2C), 80.6, 28.2 (4C), 24.9 (4C) ppm.

HRMS (ESI) m/z: $[(M + H)]^+$ calcd for $C_{20}H_{30}BO_4$ 345.2232; Found 345.2223.



2z

Methyl (*E*)-3-(furan-2-yl)-2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)acrylate (2z):

GP-3 was carried out with methyl 2-(acetoxy(furan-2-yl)methyl)acrylate **1z** (67.3 mg, 0.3 mmol), B_2Pin_2 (114.3 mg, 0.45 mmol) and lithium perchlorate (32.0 mg, 0.1 M) in 3 mL of MeOH at room temperature for 4 h. Purification of the crude material by silica gel column chromatography

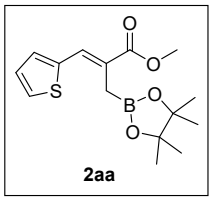
(petroleum ether/ethyl acetate: 98:02 to 95:05) furnished the product **2z** (68.4 mg, 87%), as colourless liquid. [TLC (petroleum ether/ethyl acetate 95:05), R_f(**1z**) = 0.50, R_f(**2z**) = 0.50, UV detection].

IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 3474, 2976, 2952, 2346, 1967, 1701, 1631, 1453, 1373, 1271, 1222, 1105, 1018, 761, 699 cm^{-1}.

^1H NMR (600 MHz, CDCl3) δ 7.48 (d, J = 1.7 Hz, 1H), 7.38 (s, 1H), 6.56 (d, J = 3.4 Hz, 1H), 6.45 (dd, J = 3.4, 1.7 Hz, 1H), 3.76 (s, 3H), 2.36 (s, 2H), 1.20 (s, 12H) ppm.

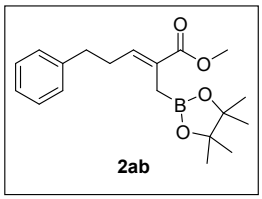
$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 169.2, 152.2, 143.7, 126.6, 124.5, 114.5, 111.9, 83.4 (2C), 52.1, 24.7 (4C) ppm.

HRMS (ESI) m/z: $[(M + H)]^+$ calcd for $C_{15}H_{22}BO_5$ 293.1555; Found 293.1576.



Methyl (*E*)-2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-3-(thiophen-2-yl)acrylate (2aa):

GP-3 was carried out with methyl 2-(acetoxy(thiophen-2-yl)methyl)acrylate **1aa** (72.1 mg, 0.3 mmol), B_2Pin_2 (114.3 mg, 0.45 mmol) and lithium perchlorate (32.0 mg, 0.1 M) in 3 mL of MeOH at room temperature for 4 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 98:02 to 95:05) furnished the product **2aa** (72.1 mg, 78%), as colourless liquid. [TLC (petroleum ether/ethyl acetate 95:05), R_f(**1aa**) = 0.50, R_f(**2aa**) = 0.50, UV detection]. This compound is reported.[15]



Methyl (*E*)-4-methyl-2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)pent-2-enoate (2ab):

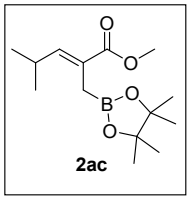
GP-3 was carried out with methyl 3-acetoxy-2-methylene-5-phenylpentanoate **1ab** (78.7 mg, 0.3 mmol), B_2Pin_2 (114.3 mg, 0.45 mmol) and lithium perchlorate (32.0 mg, 0.1 M) in 3 mL of MeOH at room temperature for 4 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 98:02 to 95:05) furnished the product **2ab** (73.3 mg, 74%), as colourless liquid. [TLC (petroleum ether/ethyl acetate 95:05), R_f(**1ab**) = 0.50, R_f(**2ab**) = 0.50, UV detection].

IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 3492, 2976, 2345, 2117, 1709, 1633, 1586, 1439, 1337, 1265, 1210, 1072, 968, 832, 763 cm^{-1}.

^1H NMR (600 MHz, $CDCl_3$) δ 7.29 (dd, J = 8.1, 7.1 Hz, 2H), 7.22 – 7.18 (m, 3H), 6.78 (t, J = 7.6 Hz, 1H), 3.71 (s, 3H), 2.77 – 2.73 (t, J = 7.6 Hz, 2H), 2.50 – 2.46 (m, 2H), 1.83 (s, 2H), 1.23 (s, 12H) ppm.

^{13}C {^1H} NMR (101 MHz, $CDCl_3$) δ 168.7, 141.6, 139.9, 129.8, 128.6 (2C), 128.5 (2C), 126.2, 83.5 (2C), 51.8, 34.9, 30.8, 24.8 (4C) ppm.

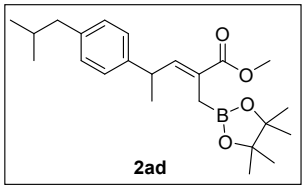
HRMS (ESI) m/z: $[(M + H)]^+$ calcd for $C_{19}H_{28}BO_4$ 331.2075; Found 331.2094.



2ac

Methyl (*E*)-5-phenyl-2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)pent-2-enoate (2ac):

GP-3 was carried out with methyl 3-acetoxy-4-methyl-2-methylenepentanoate **1ac** (60.1 mg, 0.3 mmol), B_2Pin_2 (114.3 mg, 0.45 mmol) and lithium perchlorate (32.0 mg, 0.1 M) in 3 mL of MeOH at room temperature for 4 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 98:02 to 95:05) furnished the product **2ac** (61.5 mg, 76%), as colourless liquid. [TLC (petroleum ether/ethyl acetate 95:05), R_f(**1ac**) = 0.50, R_f(**2ac**) = 0.50, UV detection]. This compound is reported.[15]



2ad

Methyl (*E*)-4-(4-isobutylphenyl)-2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)pent-2-enoate (2ad):

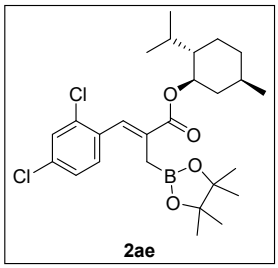
GP-3 was carried out with methyl 3-acetoxy-4-(4-isobutylphenyl)-2-methylenepentanoate **1ad** (95.5 mg, 0.3 mmol), B_2Pin_2 (114.3 mg, 0.45 mmol) and lithium perchlorate (32.0 mg, 0.1 M) in 3 mL of MeOH at room temperature for 4 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 98:02 to 95:05) furnished the product **2ad** (81.1 mg, 70%), as colourless liquid. [TLC (petroleum ether/ethyl acetate 95:05), R_f(**1ad**) = 0.50, R_f(**2ad**) = 0.50, UV detection].

IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 2981, 2355, 2103, 1731, 1447, 1370, 1242, 1160, 1100, 1044, 914, 846, 730, 647 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (d, J = 8.0 Hz, 2H), 7.06 (d, J = 8.1 Hz, 2H), 6.81 (d, J = 9.9 Hz, 1H), 3.74 – 3.71 (m, 1H), 3.70 (s, 3H), 2.42 (d, J = 7.2 Hz, 2H), 1.95 (s, 2H), 1.88 – 1.77 (m, 1H), 1.38 (d, J = 7.0 Hz, 3H), 1.22 (d, J = 2.0 Hz, 12H), 0.90 (s, 3H), 0.88 (s, 3H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$) δ 168.9, 145.1, 141.8, 139.8, 129.4 (2C), 127.7, 126.9 (2C), 83.5 (2C), 51.8, 45.2, 38.5, 30.4, 24.83 (2C), 24.81 (2C), 22.5 (2C), 21.1 ppm.

HRMS (ESI) m/z: $[(M + Na)]^+$ calcd for $C_{23}H_{35}BNaO_4$ 409.2521; Found 409.2543.



2ae

(1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl (*E*)-3-(2,4-dichlorophenyl)-2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)acrylate (2ae):

GP-3 was carried out with (1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl 2-(acetoxy(2,4-dichlorophenyl)methyl)acrylate **1ae** (128.2 mg, 0.3 mmol), B_2Pin_2 (114.3 mg, 0.45 mmol) and lithium perchlorate (32.0 mg, 0.1 M) in 3 mL of MeOH at room temperature for 4 h. Purification

of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 98:02 to 95:05) furnished the product **2ae** (118.6 mg, 80%), as colourless liquid. [TLC (petroleum ether/ethyl acetate 95:05), R_f(**1ae**) = 0.60, R_f(**2ae**) = 0.60, UV detection].

IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 2948, 2866, 2364, 1704, 2638, 1584, 1463, 1335, 1259, 1204, 1148, 1062, 969, 839, 760 cm^{-1}.

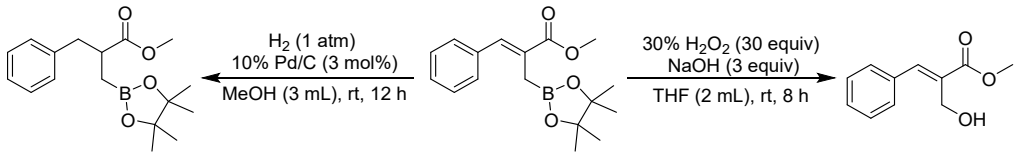
^1H NMR (600 MHz, $CDCl_3$) δ 7.59 (s, 1H), 7.42 (d, J = 2.1 Hz, 1H), 7.37 (d, J = 8.3 Hz, 1H), 7.23 (dd, J = 8.3, 2.1 Hz, 1H), 4.81 (td, J = 10.9, 4.4 Hz, 1H), 2.08 (dd, J = 8.1, 3.7 Hz, 1H), 1.97 (d, J = 4.8 Hz, 2H), 1.72 – 1.68 (m, 2H), 1.63 – 1.60 (m, 1H), 1.56 – 1.46 (m, 2H), 1.24 (s, 6H), 1.24 (s, 6H), 1.11 – 1.04 (m, 2H), 0.91 (dd, J = 6.8, 4.3 Hz, 6H), 0.88 (dd, J = 6.9, 4.4 Hz, 1H), 0.79 (d, J = 6.9 Hz, 3H) ppm.

$^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 167.6, 135.0, 134.3, 133.6, 133.5, 131.4, 129.5, 126.9, 83.7 (2C), 75.1, 47.3, 41.0, 34.5, 31.5, 26.5, 24.9 (4C), 23.7, 22.2, 20.9, 16.7 ppm.

HRMS (ESI) m/z: $[(M + Na)]^+$ calcd for $C_{26}H_{37}BCl_2NaO_4$ 517.2054; Found 517.2095.

Scale-up Reaction:

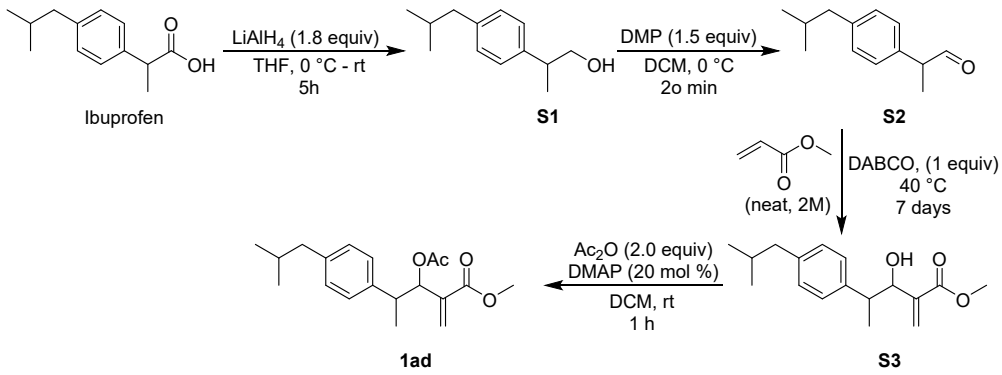
To an oven-dried ElectraSyn 2.0 undivided cell (10 mL) equipped with a magnetic stir bar, were added methyl 2-(acetoxy(phenyl)methyl)acrylate **1a** (2.4 mmol, 0.56 g), B_2Pin_2 (0.45 mmol, 1.5 equiv), and lithium perchlorate (0.1 M) in a solvent MeOH (10 mL). The ElectraSyn vial cap equipped with two stainless steel electrodes as cathode and anode (5.2 cm × 0.8 cm × 0.2 cm) (1.2 cm × 0.8 cm × 0.2 cm area dipped in the reaction solution). The reaction mixture was stirred and electrolyzed at a constant current of 25 mA at room temperature for 10 h. After the reaction was complete, the residue was diluted with ethyl acetate (3 × 20 mL) and washed with water, dried over Na_2SO_4, and concentrated under reduced pressure. Purification of the crude product by column chromatography on silica gel using petroleum ether/ethyl acetate (petroleum ether/ethyl acetate = 98:02 to 95:05) furnished the product methyl (*E*)-3-phenyl-2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)acrylate **2a** (0.54 g, 75%), as colorless liquid. [TLC (petroleum ether/ethyl acetate 95:05), R_f(**1a**) = 0.50, R_f(**2a**) = 0.50, UV detection].



4 (98%) **2a** **5** (92%)

To an oven-dried round-bottomed flask equipped with a magnetic stir bar, were added methyl (*E*)-3-phenyl-2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)acrylate (90.6 mg, 0.3 mmol), 10 wt% Pd/C (9 mg, 3 mol%) and MeOH (3 mL). The reaction mixture was stirred at room temperature for 12 hours. The completion of the reaction was monitored by using Thin Layer Chromatography (TLC). Then, saturated aqueous NH_4Cl (10 mL) was added and the aqueous layer was extracted with Et_2O (3×10 mL). The combined organic layers were dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure. The crude material was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (petroleum ether: ethyl acetate = 95:05 to 90:10) to obtain the pure product methyl 2-benzyl-3-hydroxypropanoate (89.4 mg, 98%) as a colorless liquid. [TLC (petroleum ether/ethyl acetate 85:15), R_f(**1a**) = 0.50, R_f(**4**) = 0.20, UV detection]. This compound is reported.[17]

To an oven-dried round-bottomed flask equipped with a magnetic stir bar, were added methyl (*E*)-3-phenyl-2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)acrylate (80 mg, 0.26 mmol), 30 % H_2O_2 (884.3 mg, 7.8 mmol), Sodium hydroxide (31.2 mg, 0.78 mmol), THF (2 mL). The reaction mixture was stirred at room temperature for 8 hours. The completion of the reaction was monitored by using Thin Layer Chromatography (TLC). It was then quenched with water and extracted with ethyl acetate (3×30 mL). The combined organic layers were dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure. The crude material was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (petroleum ether: ethyl acetate = 90:10 to 85:15) to obtain the pure product methyl (*E*)-2-(hydroxymethyl)-3-phenylacrylate (46 mg, 92%) as a colorless liquid. [TLC (petroleum ether/ethyl acetate 95:05), R_f(**1a**) = 0.50, R_f(**5**) = 0.50, UV detection]. This compound is reported.[18]



In an oven-dried Schlenk tube equipped with a magnetic stir bar, were added $LiAlH_4$ (15.6 mmol, 0.593 g) in anhydrous THF (11 mL) was cooled to 0 °C. Then the solution of 2-(4-isobutylphenyl)propanoic acid (8.69 mmol, 1.79 g) in anhydrous THF (4.5 mL) was added dropwise into the flask at 0 °C. Then the reaction mixture was allowed to stir at rt for 5 h. The reaction progress was monitored by TLC. After the complete consumption of starting material, the reaction mixture was cooled to 0 °C and slowly poured into a cold H_2O to quench the excess $LiAlH_4$. The resulting white precipitate was filtered through a shot pad of Celite and washed with ethyl acetate (50 ml) two times. The filtrate was collected and the volatiles were removed under reduced pressure to get 2-(4- isobutylphenyl)propan-1-ol (**S1**) as a white solid and the residue was directly taken to the next step without any further purification.

In an oven-dried Schlenk tube equipped with a magnetic stir bar, were added 2-(4-isobutylphenyl)propan-1-ol (7.8 mmol, 1.5 g) in DCM (50 mL) was cooled to 0 °C and added Dess-Martin periodinane (11.7 mmol, 4.96 g). Then the reaction mixture was stirred for 20 min at rt. The reaction progress was monitored by TLC. After the complete consumption of starting material, the reaction mixture was quenched with a mixture of saturated aqueous $NaHCO_3$ solution (40 mL) and saturated aqueous $Na_2S_2O_3$ (40 mL). Then the aqueous layer was extracted with DCM three times. The combined organic phases were dried over Na_2SO_4 and the solvent was evaporated under reduced pressure to get 2-(4- isobutylphenyl)propanal (**S2**) as a white solid and it was directly taken to the next step without any further purification.

To an oven-dried round-bottomed flask equipped with a magnetic stir bar, were added 2-(4-isobutylphenyl)propanal (380.6 mg, 2 mmol), DABCO (224.34 mg, 2 mmol), and methyl acrylate (10 mmol, 861 mg). The reaction mixture was stirred at 40 °C for 7 days. The completion of the reaction was monitored by using Thin Layer Chromatography (TLC). It was then quenched with saturated aqueous NH_4Cl solution and extracted with ethyl acetate (3×30 mL). The combined

organic layers were dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure to get methyl 3-hydroxy-4-(4-isobutylphenyl)-2-methylenepentanoate (**S3**) as a colorless liquid and the residue was used for the further reaction without purification.

To an oven-dried round-bottomed flask equipped with a magnetic stir bar, were added methyl 3-hydroxy-4-(4-isobutylphenyl)-2-methylenepentanoate (165.8 mg, 0.6 mmol), DMAP (14.7 mg, 0.12 mmol), acetic anhydride (122.5 mg, 1.2 mmol), and DCM (2 mL). The reaction mixture was stirred at room temperature for 1 hour. The completion of the reaction was monitored by using Thin Layer Chromatography (TLC). It was then quenched with water and extracted with ethyl acetate (3×30 mL). The combined organic layers were dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure. The crude material was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (petroleum ether: ethyl acetate = 95:05 to 90:10) to obtain the pure product methyl 3-acetoxy-4-(4-isobutylphenyl)-2-methylenepentanoate **1ae**, d.r (1:0.22) (171.9 mg, 90%) as a colorless liquid. [TLC (petroleum ether/ethyl acetate 95:05), R_f(**S3**) = 0.50, R_f(**1ae**) = 0.40, UV detection].

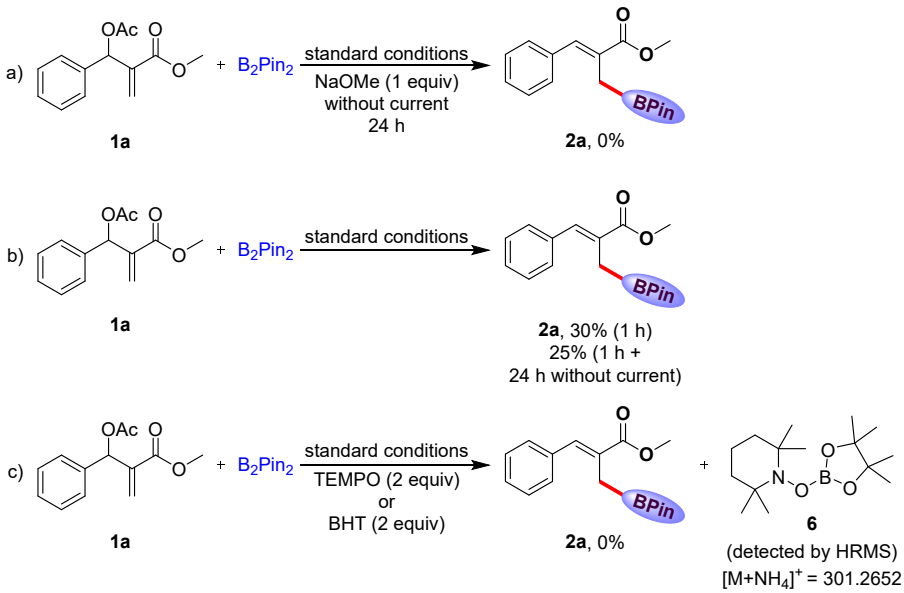
IR (MIR-ATR, 4000-600 cm^{-1}) ν_{max} = 3397, 2928, 2863, 2098, 1713, 1644, 1450, 1344, 1252, 1149, 1019, 969, 844 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, J = 8.1 Hz, 2H), 7.22 (d, J = 8.1 Hz, 2H), 6.43 (s, 1H), 5.93 (d, J = 6.1 Hz, 1H), 5.85 (s, 1H), 3.86 (s, 3H), 3.42 – 3.36 (m, 1H), 2.61 (d, J = 7.2 Hz, 2H), 2.23 (s, 2H), 2.07 – 1.95 (m, 1H), 1.47 (d, J = 7.1 Hz, 3H), 1.07 (d, J = 1.4 Hz, 3H), 1.06 (d, J = 1.4 Hz, 3H) ppm.

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 169.80, 165.70, 140.10, 139.56, 139.24, 128.99 (2C), 127.80 (2C), 126.36, 76.03, 51.87, 45.09, 42.39, 30.26, 22.44, 22.41, 21.01, 15.38 ppm.

HRMS (ESI) m/z: $[(M + Na)]^+$ calcd for $C_{19}H_{26}NaO_4$ 341.1723; Found 341.1742.

Control experiments



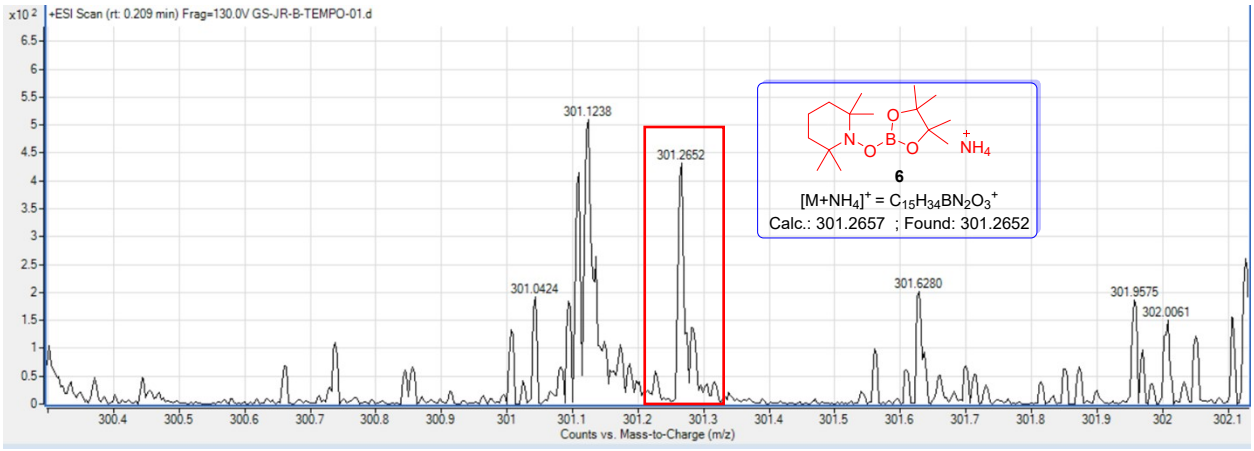
a) To an oven-dried ElectraSyn 2.0 undivided cell (5 ml) equipped with a magnetic stir bar, were added Morita–Baylis–Hillman Acetate **1a** (70.3 mg, 0.3 mmol), B_2Pin_2 (114.3 mg, 0.45 mmol), NaOMe (16.2 mg, 0.3 mmol) and lithium perchlorate (0.1 M) in a solvent MeOH (3 mL). The ElectraSyn vial cap is equipped with two stainless steel electrodes as cathode and anode (5.2 cm × 0.8 cm × 0.2 cm) (1.2 cm × 0.8 cm × 0.2 cm area dipped in the reaction solution. The reaction mixture was stirred at room temperature for 24 h. After the reaction was complete, the residue was diluted with ethyl acetate (10 mL) and washed with water, dried over Na_2SO_4, concentrated under reduced pressure.

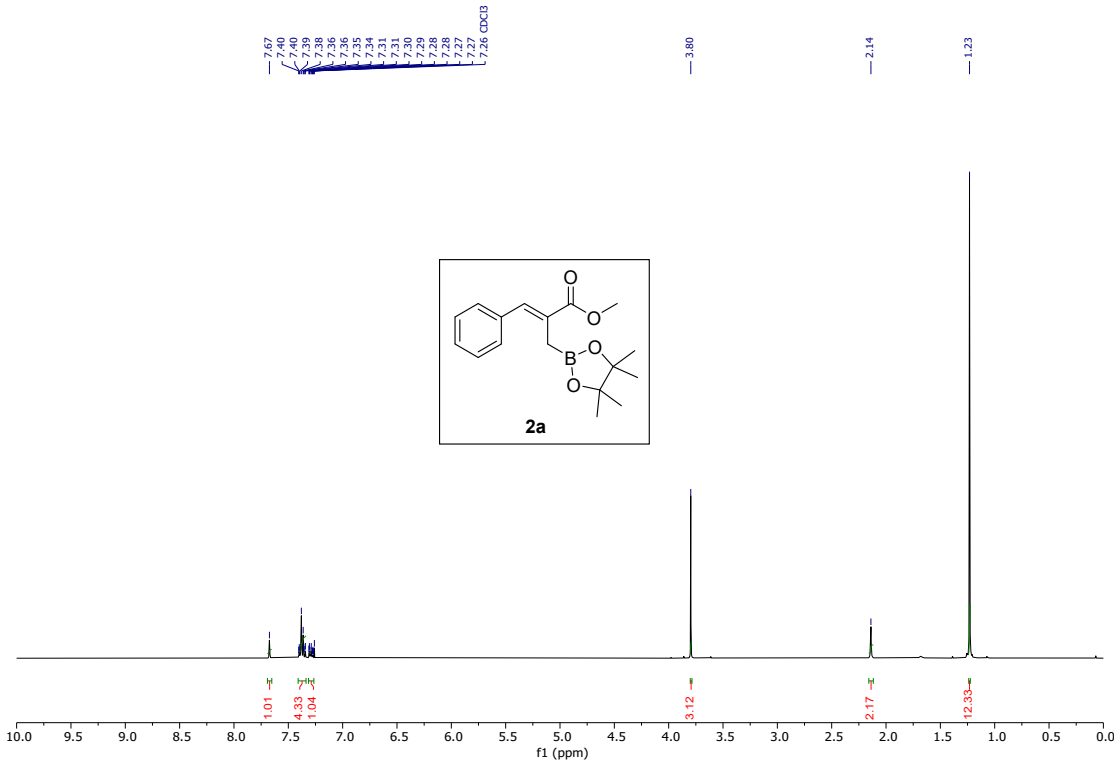
b) To an oven-dried ElectraSyn 2.0 undivided cell (5 ml) equipped with a magnetic stir bar, were added Morita–Baylis–Hillman acetate **1a** (70.3 mg, 0.3 mmol), B_2Pin_2 (114.3 mg, 0.45 mmol), and lithium perchlorate (32.0 mg, 0.1 M) in a solvent MeOH (3 mL). The ElectraSyn vial cap equipped with two stainless steel electrodes as cathode and anode (5.2 cm × 0.8 cm × 0.2 cm) (1.2 cm × 0.8 cm × 0.2 cm area dipped in the reaction solution). The reaction mixture was stirred and electrolyzed at a constant current of 15 mA at room temperature for 1 h. After that, the residue was diluted with ethyl acetate (3 × 10 mL) and washed with water, dried over Na_2SO_4, concentrated under reduced pressure. Purification of the crude product by column chromatography on silica gel using petroleum ether/ethyl

acetate (petroleum ether: ethyl acetate = 98:02 to 95:05) furnished the borylated products **2a** (27.2 mg, 30%), as colorless liquid.

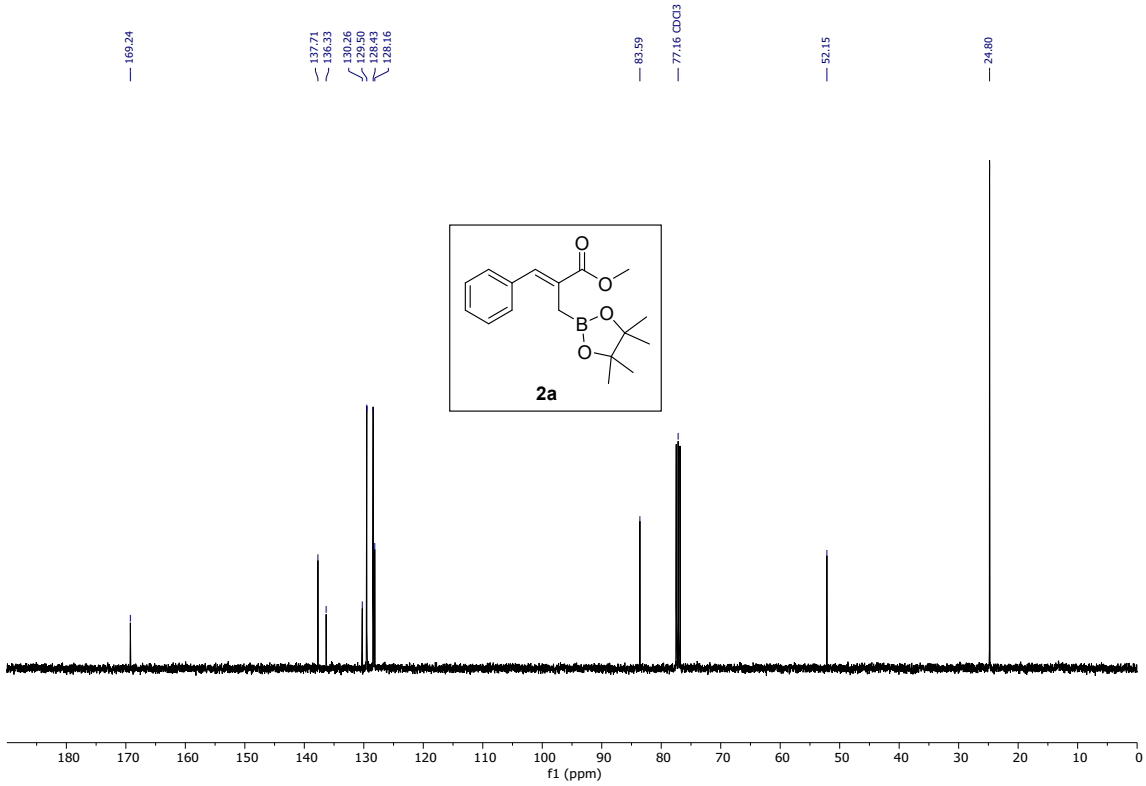
To an oven-dried ElectraSyn 2.0 undivided cell (5 ml) equipped with a magnetic stir bar, were added Morita–Baylis–Hillman acetate **1a** (70.3 mg, 0.3 mmol), B_2Pin_2 (114.3 mg, 0.45 mmol), and lithium perchlorate (32.0 mg, 0.1 M) in a solvent MeOH (3 mL). The ElectraSyn vial cap equipped with two stainless steel electrodes as cathode and anode (5.2 cm × 0.8 cm × 0.2 cm) (1.2 cm × 0.8 cm × 0.2 cm area dipped in the reaction solution). The reaction mixture was stirred and electrolyzed at a constant current of 15 mA at room temperature for 1 h. After that, the reaction further continued for 24 h without current. Then, the reaction mixture was diluted with ethyl acetate (3 × 10 mL) and washed with water, dried over Na_2SO_4, and concentrated under reduced pressure. Purification of the crude product by column chromatography on silica gel using petroleum ether/ethyl acetate (petroleum ether/ethyl acetate = 98:02 to 95:05) furnished the borylated products **2a** (22.6 mg, 25%), as colorless liquid.

c) To an oven-dried ElectraSyn 2.0 undivided cell (5 mL) equipped with a magnetic stir bar, were added Morita–Baylis–Hillman Acetate **1a** (70.3 mg, 0.3 mmol), B_2Pin_2 (114.3 mg, 0.45 mmol), TEMPO (93.7 mg, 0.6 mmol) or butylated hydroxytoluene (132.2 mg, 0.6 mmol) and lithium perchlorate (0.1 M) in a solvent MeOH (3 mL). The ElectraSyn vial cap is equipped with two stainless steel electrodes as cathode and anode (5.2 cm × 0.8 cm × 0.2 cm) (1.2 cm × 0.8 cm × 0.2 cm area dipped in the reaction solution. The reaction mixture was stirred and electrolyzed at a constant current of 15 mA at room temperature for 4 h. After the reaction was complete, the residue was diluted with ethyl acetate (10 mL) and washed with water, dried over Na_2SO_4, concentrated under reduced pressure. The crude mixture was subjected to mass spectrometric analysis to confirm the formation of 2,2,6,6-tetramethyl-1-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)piperidine **6**. HRMS-ESI (m/z): calcd for $C_{15}H_{34}BN_2O_3$ $[M + NH_4]^+$ 301.2657; found 301.2652.

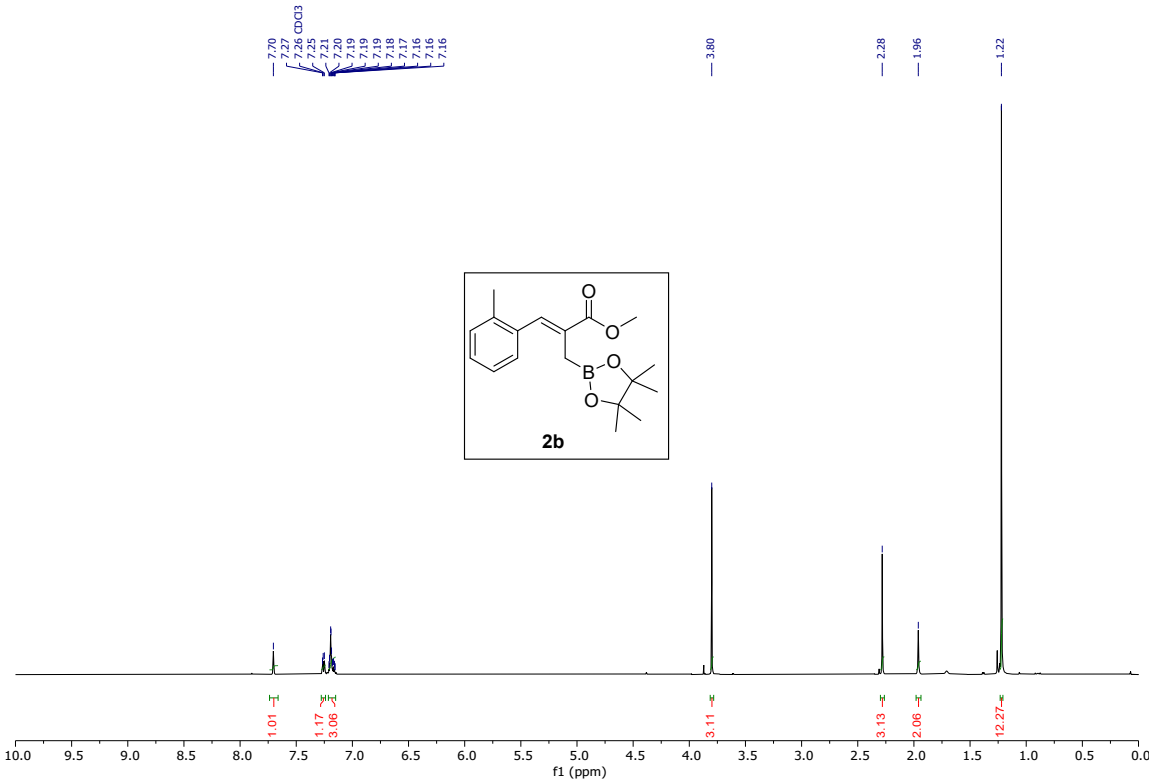

x10 2
+ESI Scan (rt: 0.209 min) Frag=130.0V GS-JR-B-TEMPO-01.d
301.1238
301.2652
301.0424
301.6280
301.9575
302.0061
Counts vs. Mass-to-Charge (m/z)
6
[M+NH4]+ = C15H34BN2O3+
Calc.: 301.2657 ; Found: 301.2652



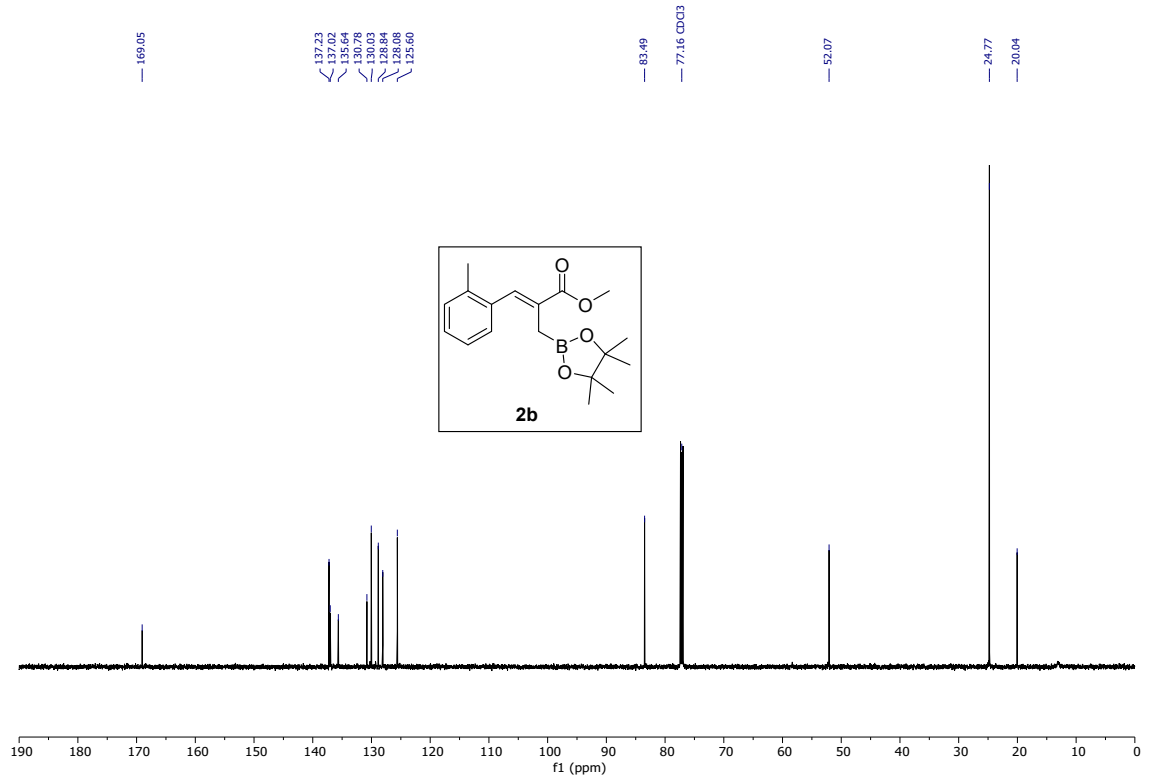
^{1}H NMR (400 MHz) spectrum of **2a** in $CDCl_3$



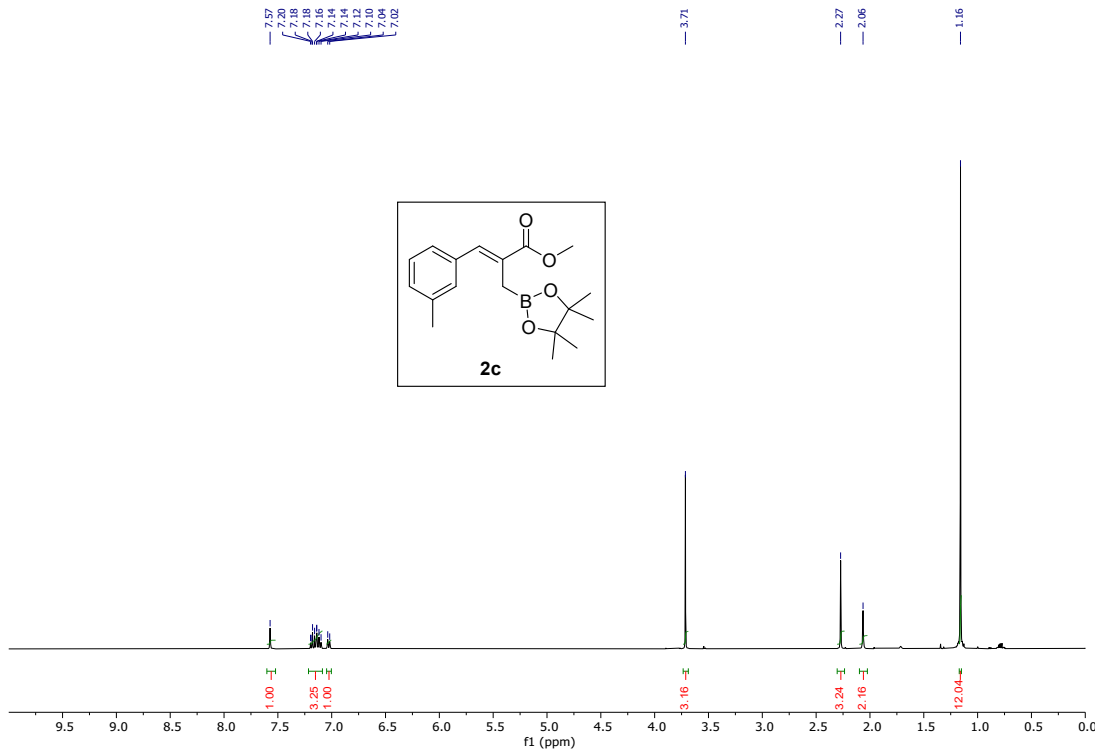
^{13}C{^{1}H} NMR (150 MHz) spectrum of **2a** in $CDCl_3$



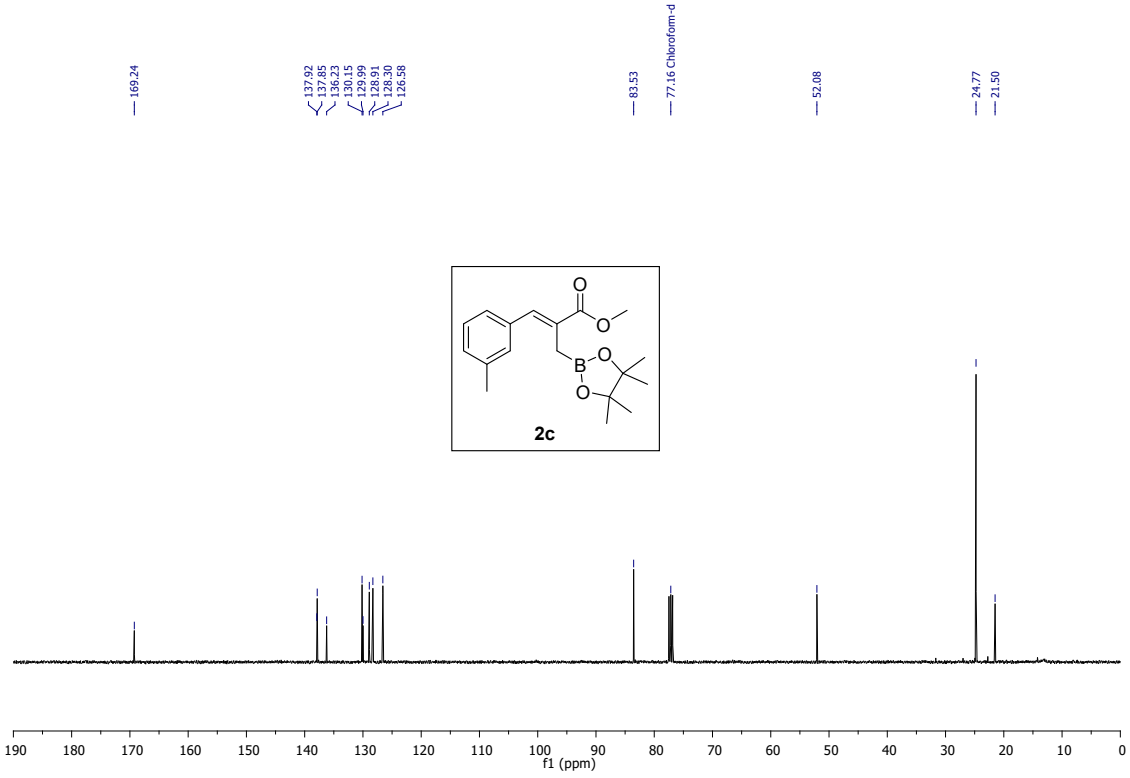
^{1}H NMR (400 MHz) spectrum of **2b** in $CDCl_3$



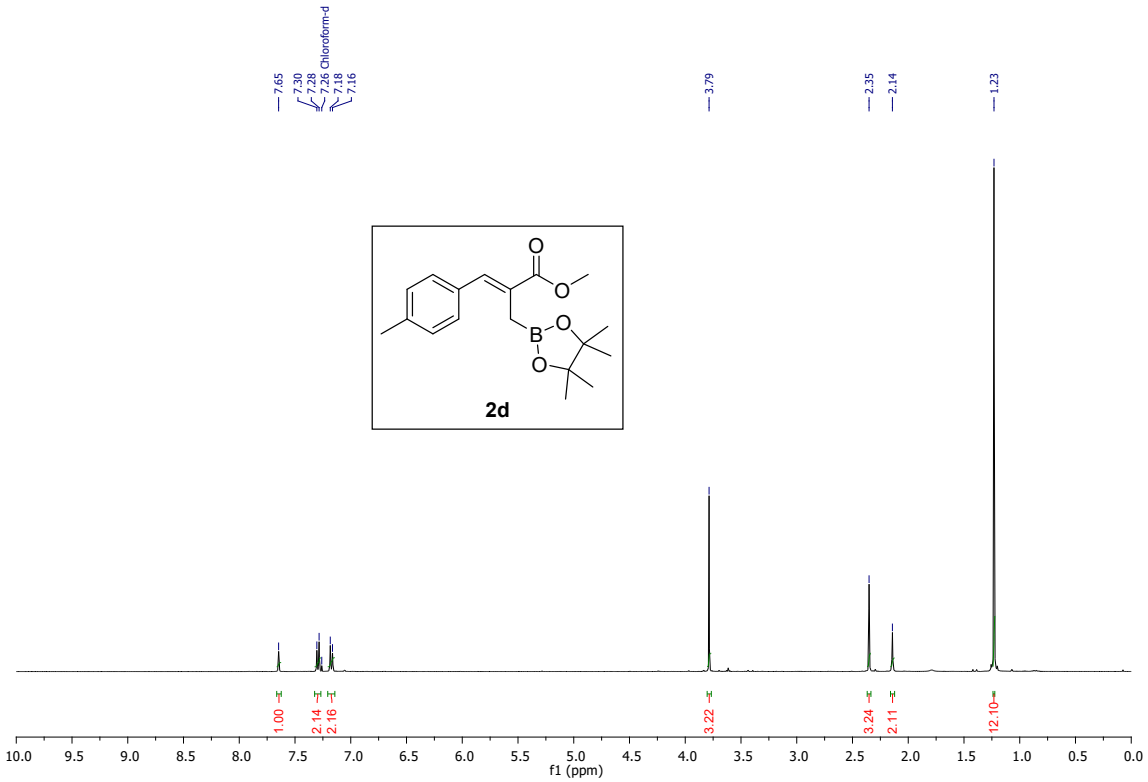
^{13}C{^{1}H} NMR (150 MHz) spectrum of **2b** in $CDCl_3$



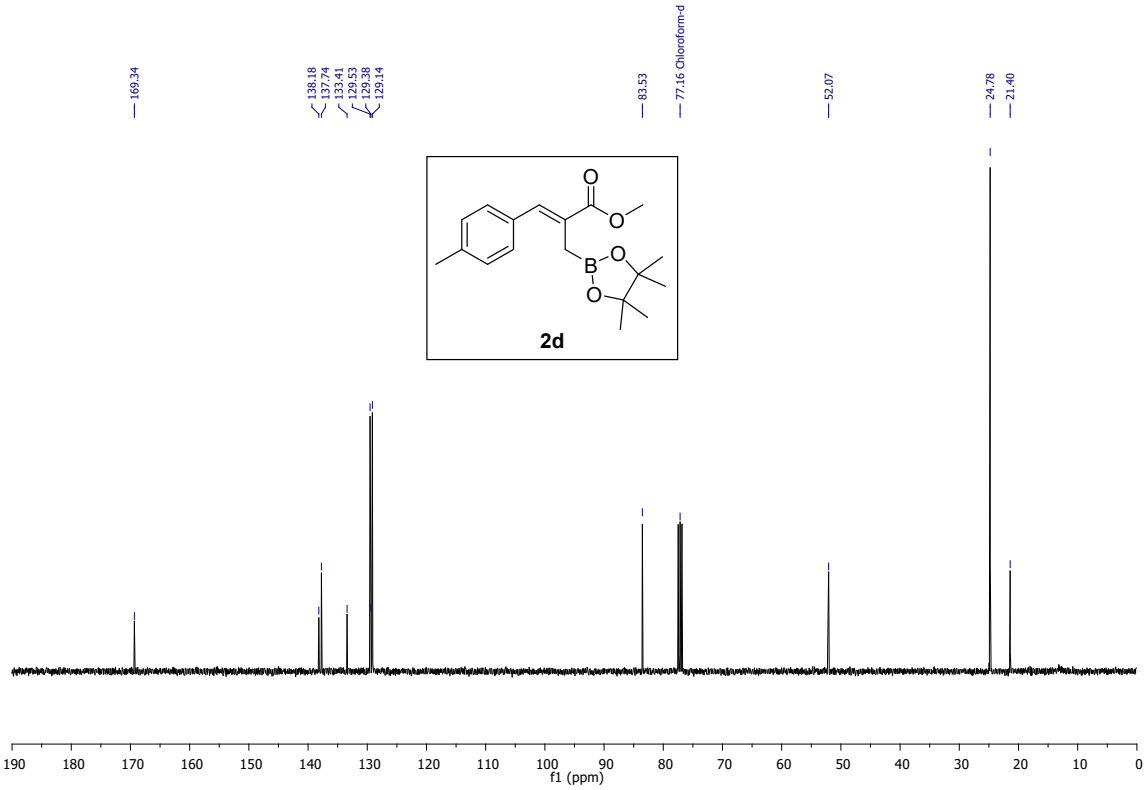
^{1}H NMR (400 MHz) spectrum of **2c** in $CDCl_3$



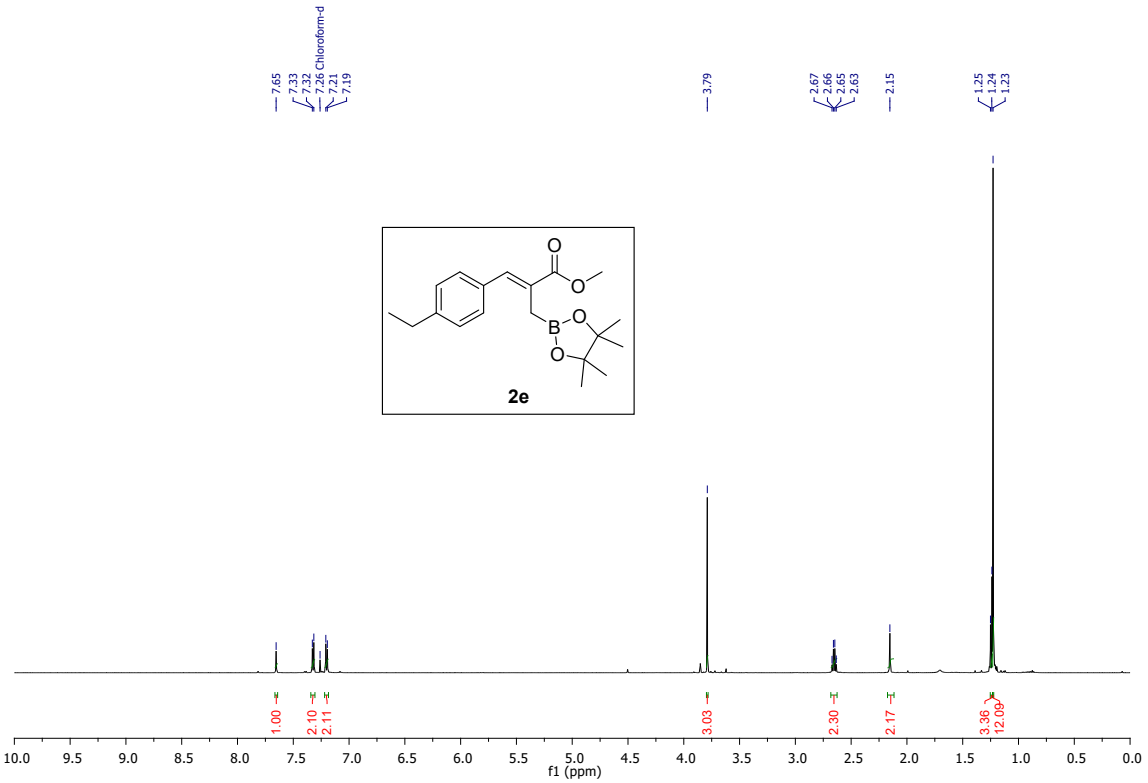
^{13}C{^{1}H} NMR (150 MHz) spectrum of **2c** in $CDCl_3$



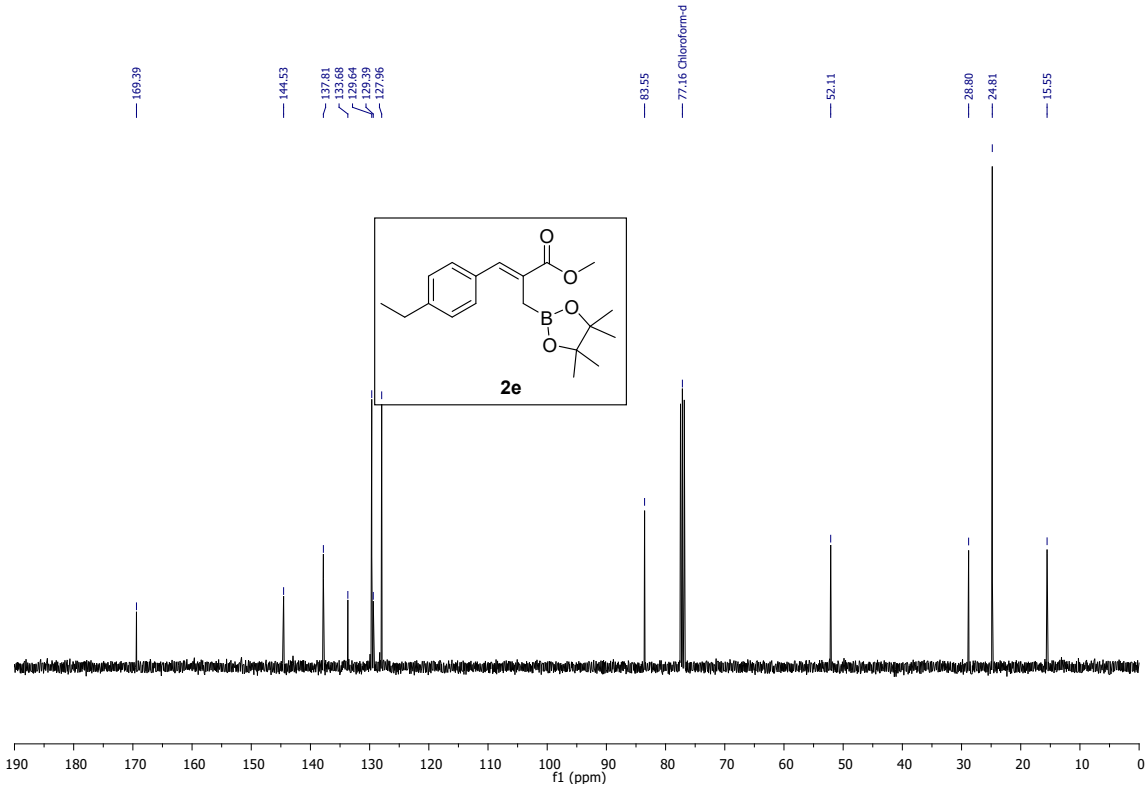
^{1}H NMR (400 MHz) spectrum of **2d** in $CDCl_3$



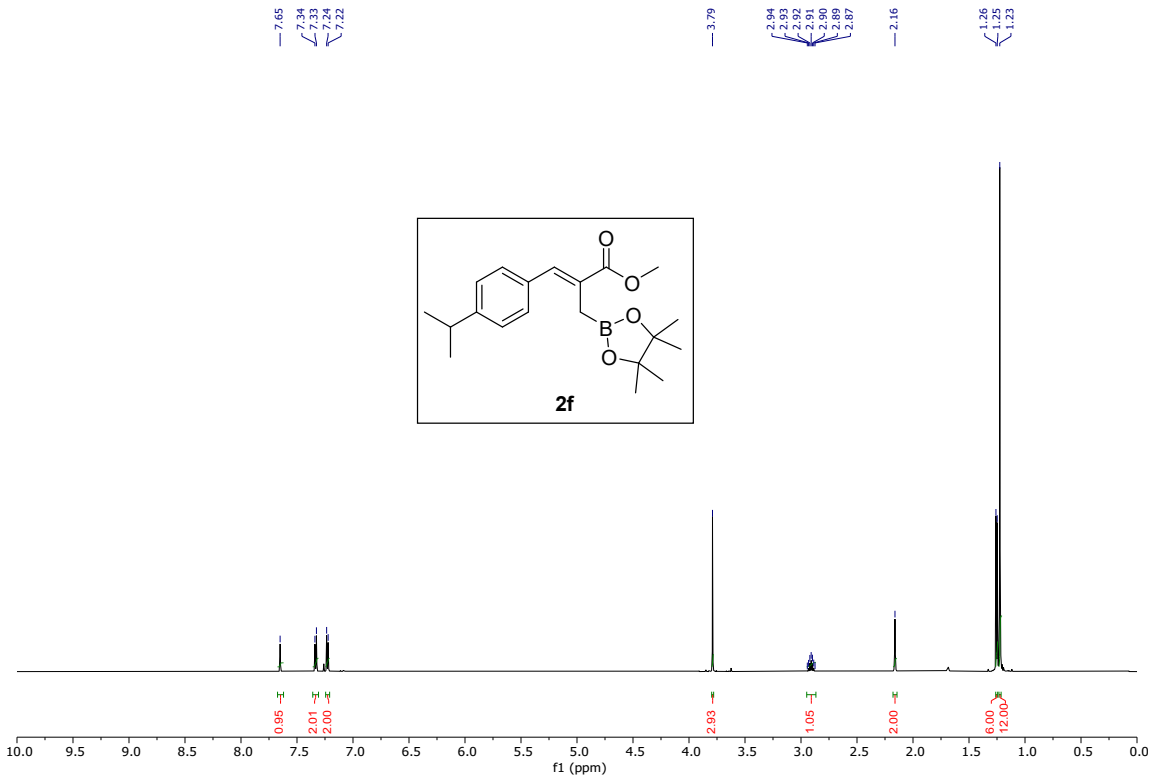
^{13}C{^{1}H} NMR (150 MHz) spectrum of **2d** in $CDCl_3$



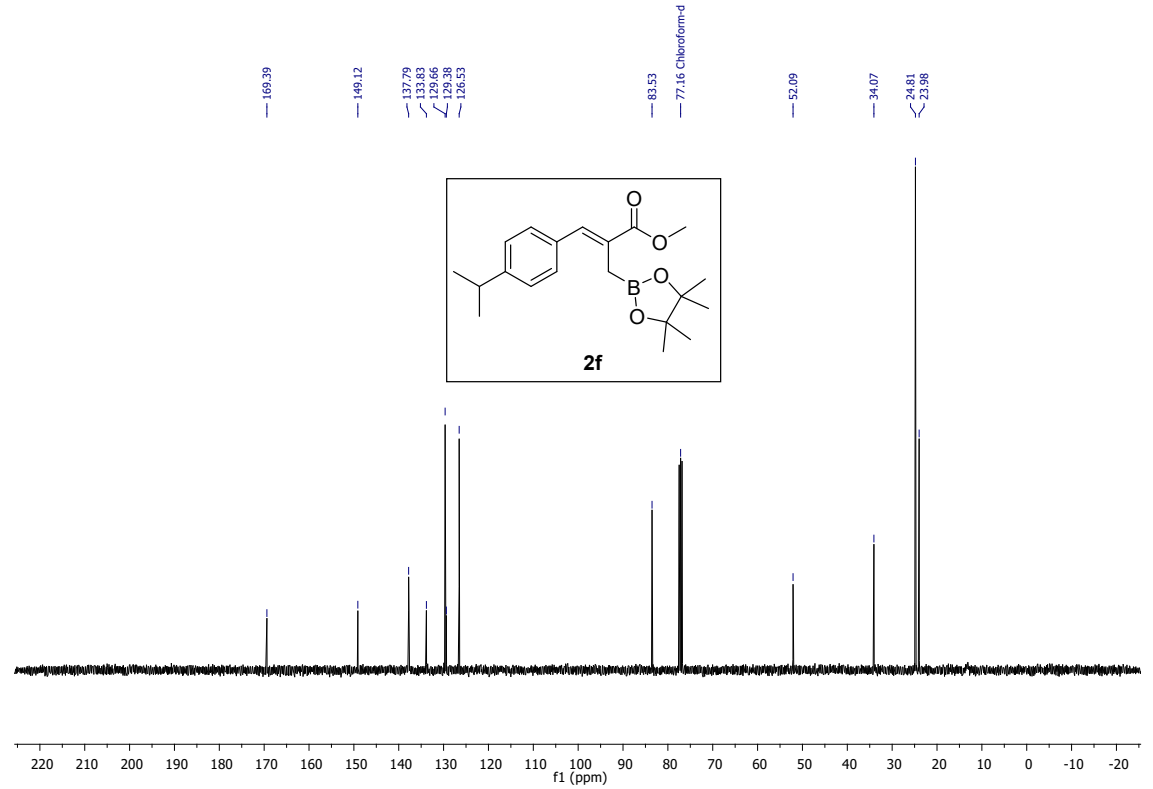
^{1}H NMR (400 MHz) spectrum of **2e** in $CDCl_3$



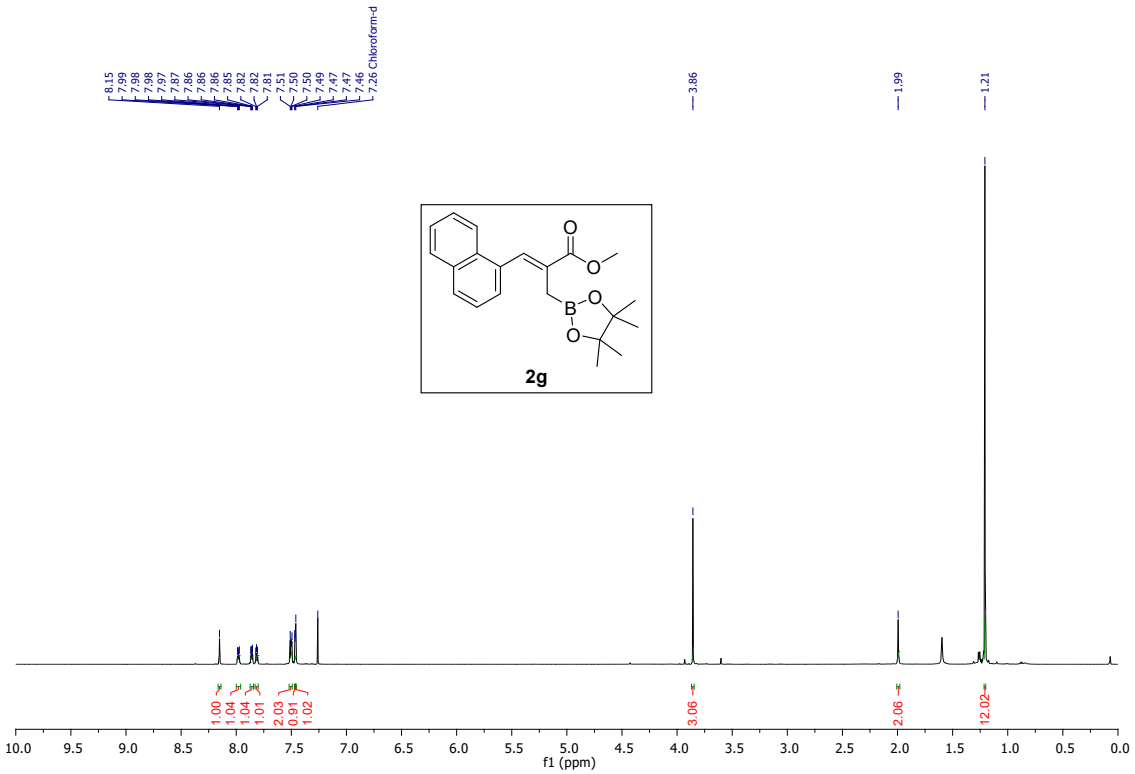
^{13}C{^{1}H} NMR (150 MHz) spectrum of **2e** in $CDCl_3$



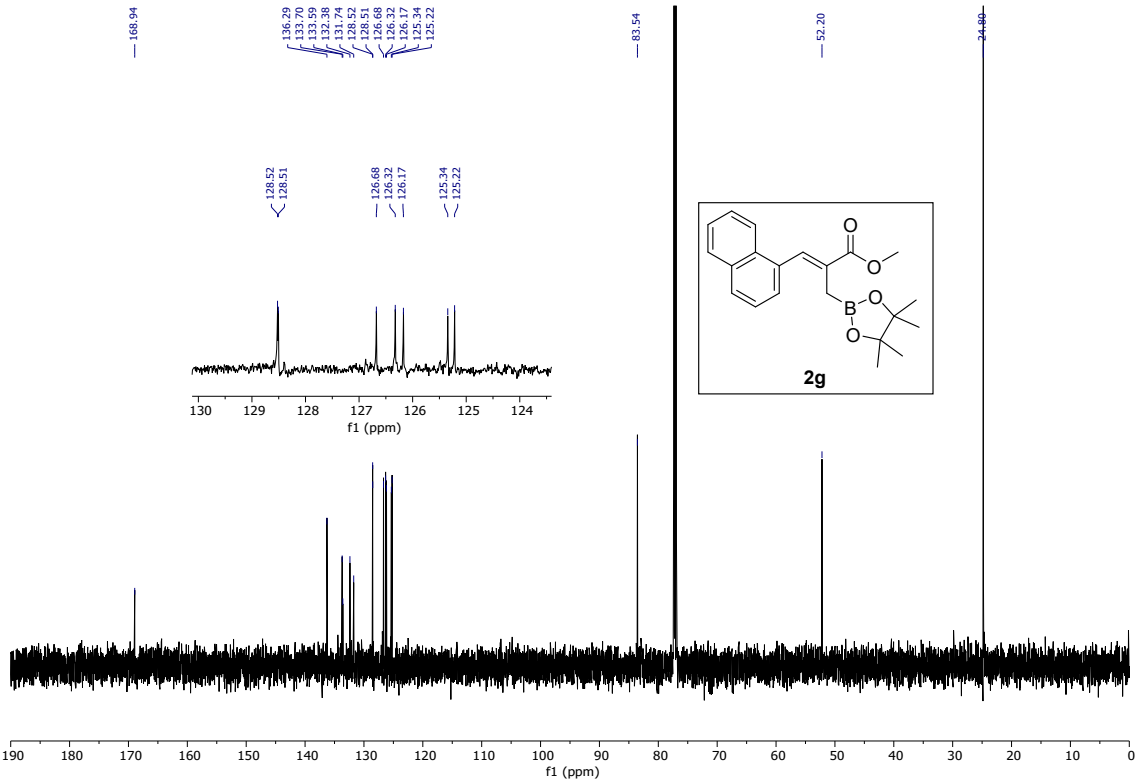
^{1}H NMR (400 MHz) spectrum of **2f** in $CDCl_3$



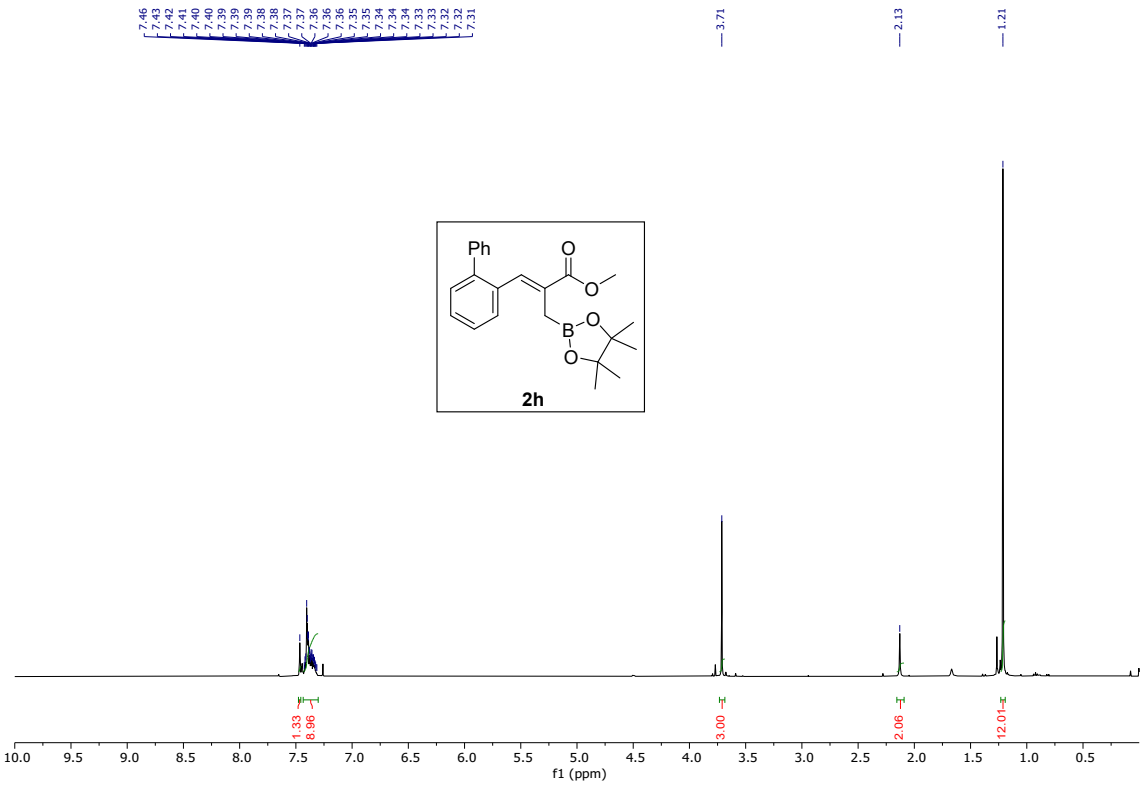
^{13}C{^{1}H} NMR (150 MHz) spectrum of **2f** in $CDCl_3$



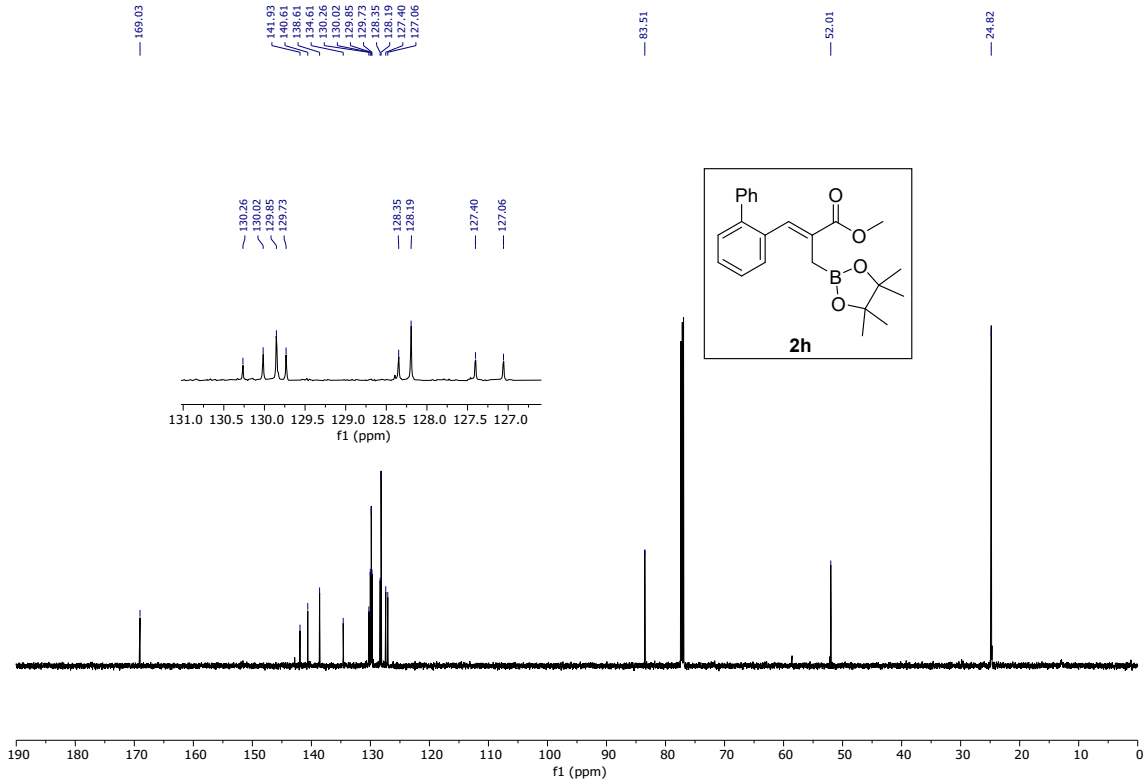
^{1}H NMR (400 MHz) spectrum of **2g** in $CDCl_3$



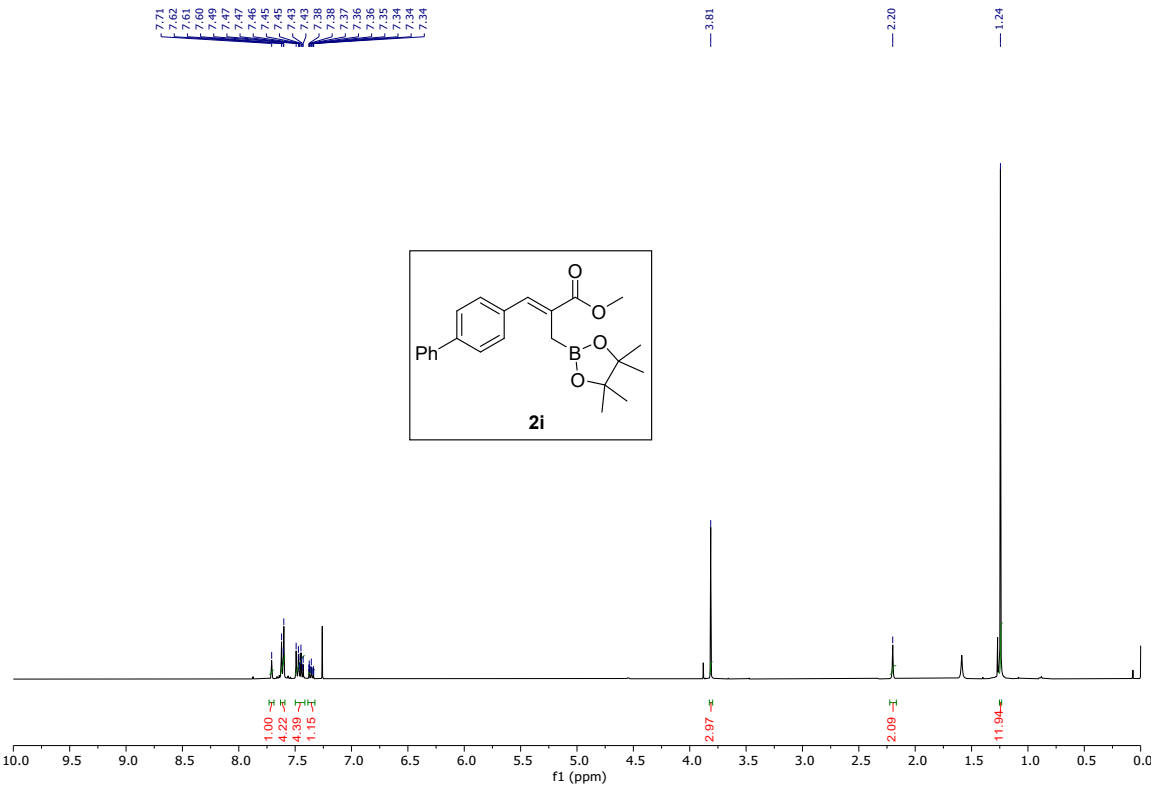
^{13}C{^{1}H} NMR (150 MHz) spectrum of **2g** in $CDCl_3$



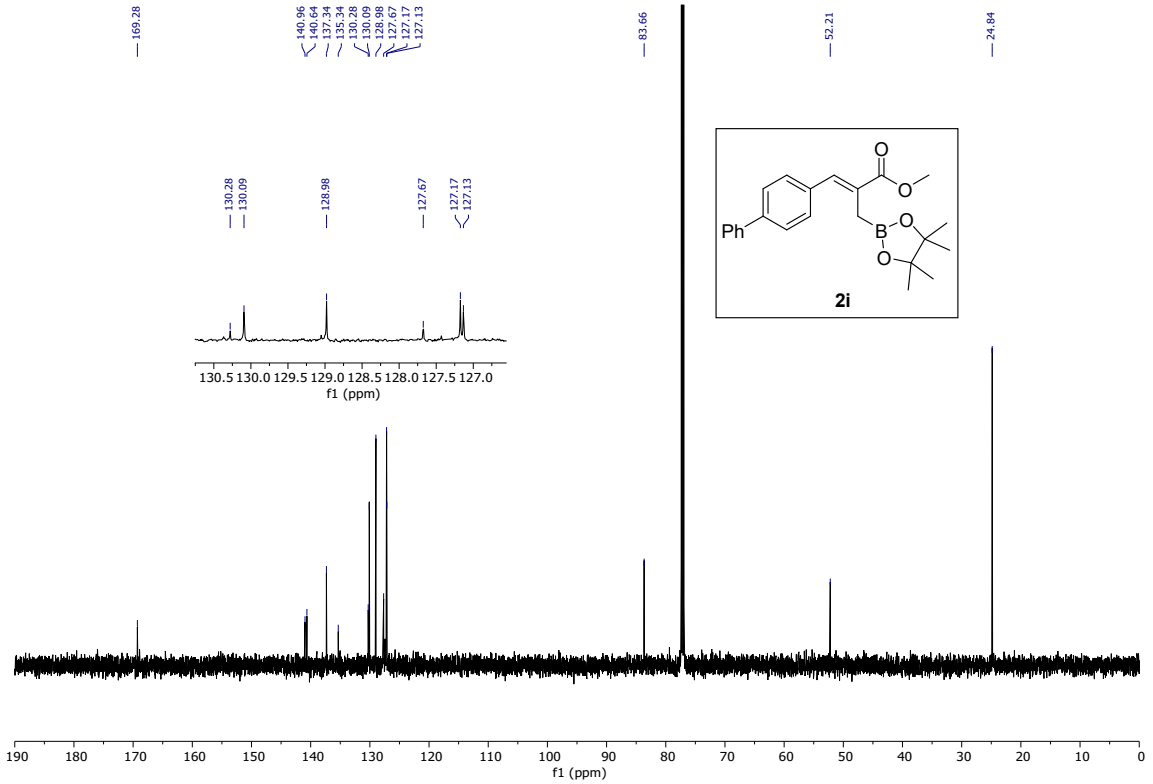
^{1}H NMR (400 MHz) spectrum of **2h** in $CDCl_3$



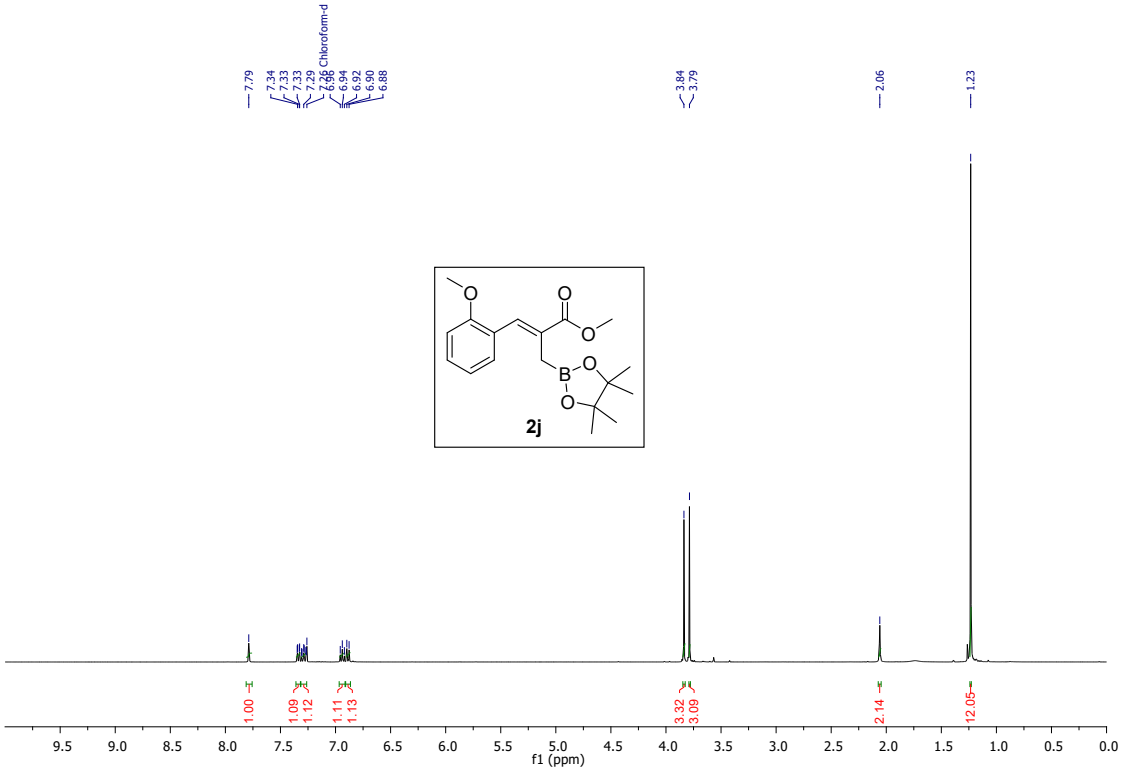
^{13}C{^{1}H} NMR (150 MHz) spectrum of **2h** in $CDCl_3$



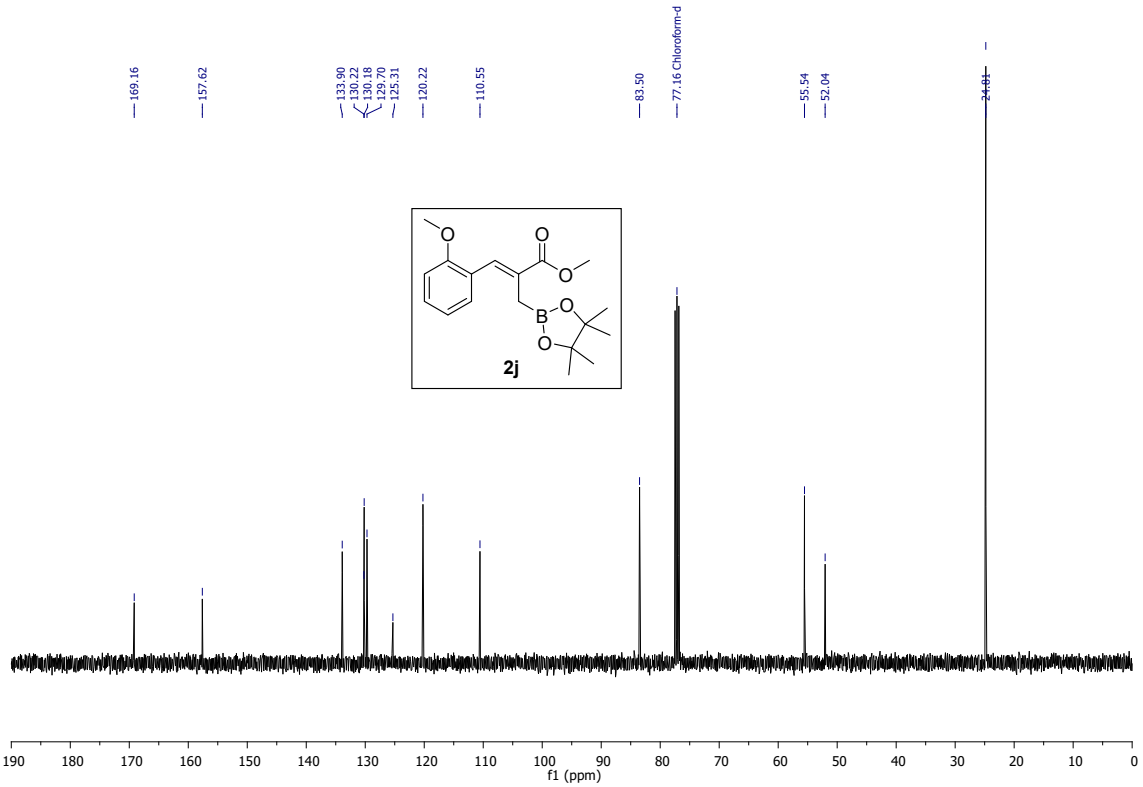
^{1}H NMR (400 MHz) spectrum of **2i** in $CDCl_3$



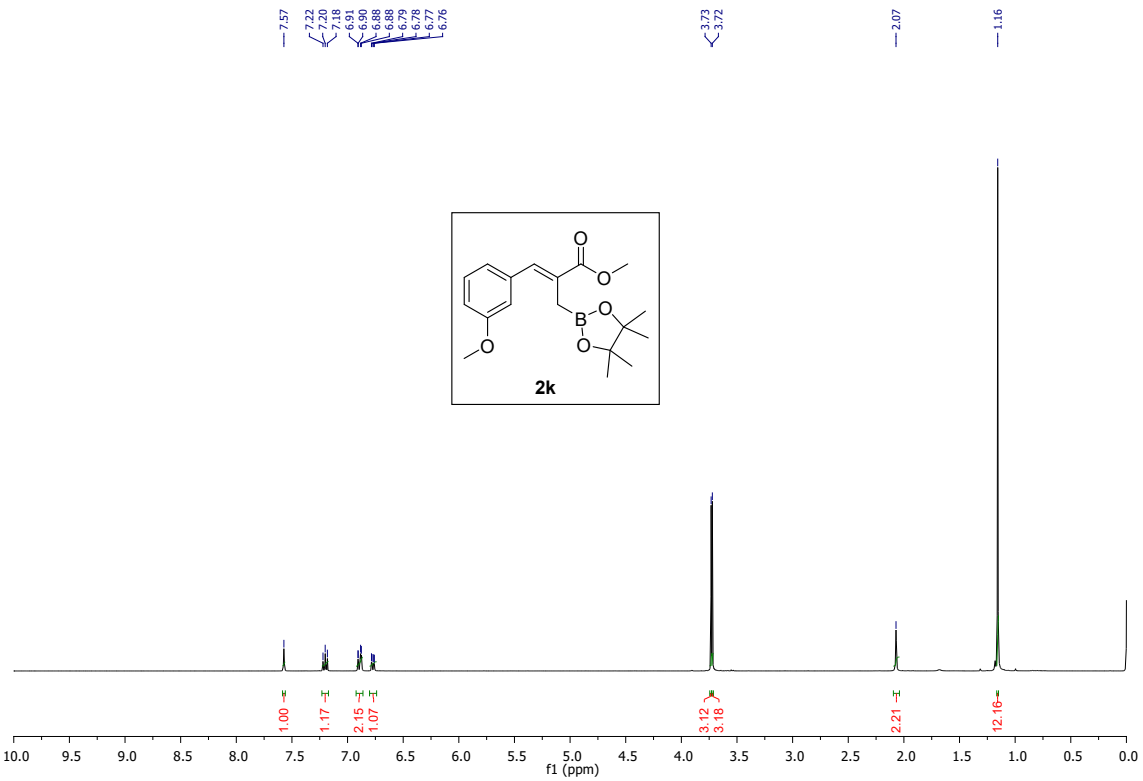
^{13}C{^{1}H} NMR (150 MHz) spectrum of **2i** in $CDCl_3$



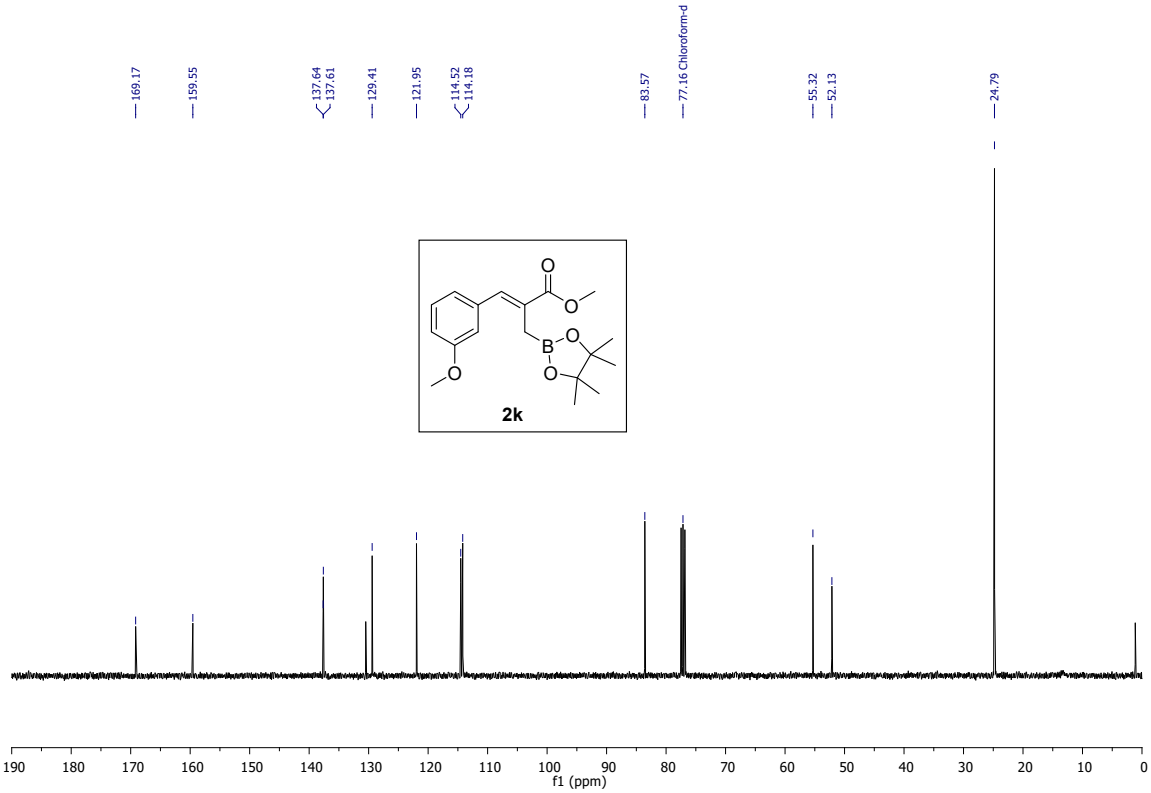
^{1}H NMR (400 MHz) spectrum of **2j** in $CDCl_3$



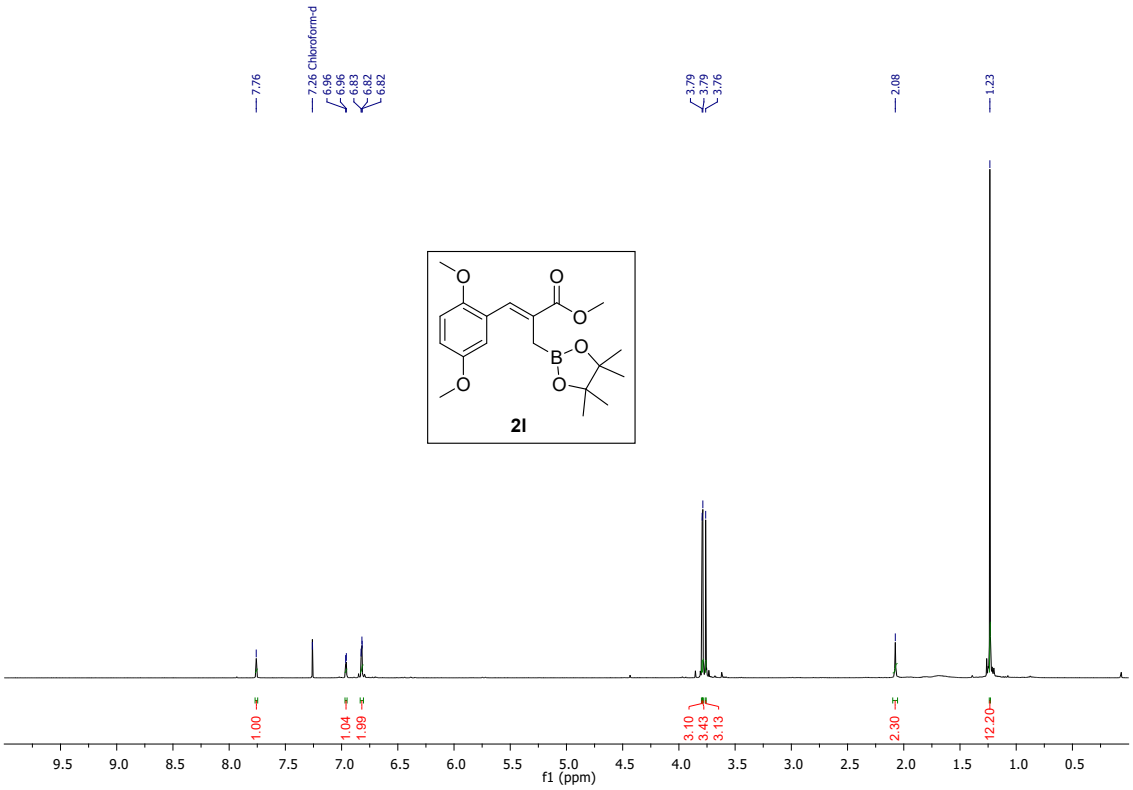
^{13}C{^{1}H} NMR (150 MHz) spectrum of **2j** in $CDCl_3$



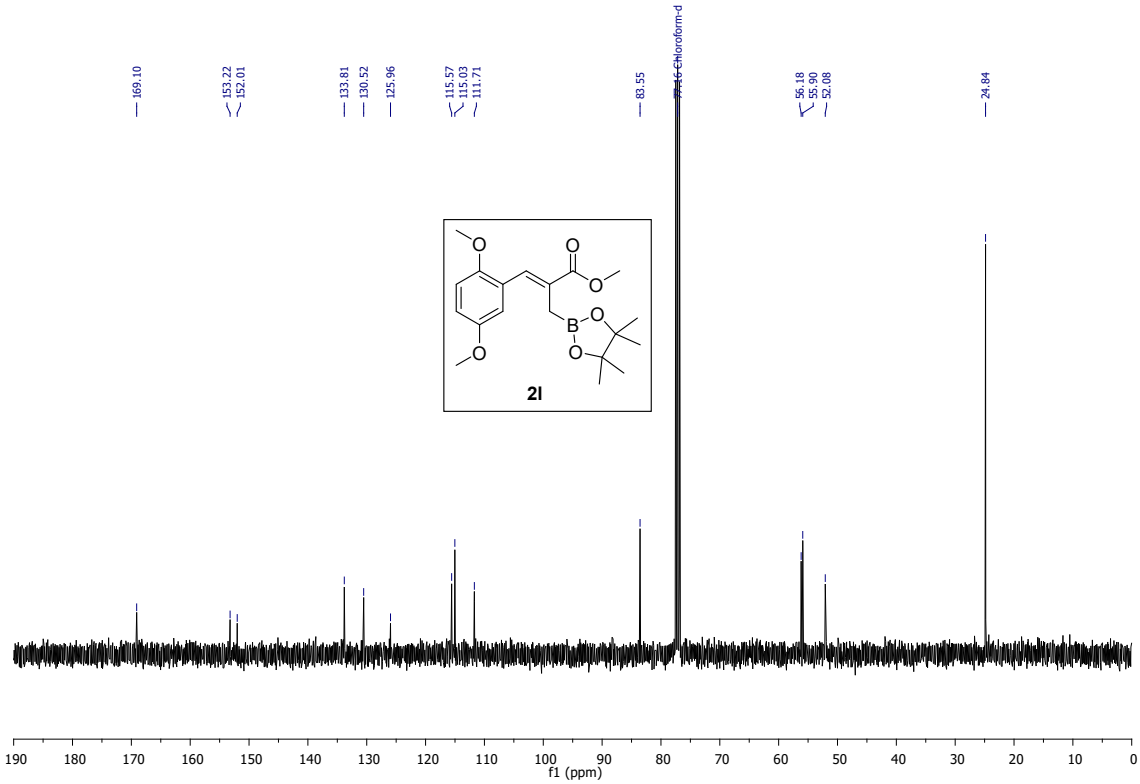
^{1}H NMR (400 MHz) spectrum of **2k** in $CDCl_3$



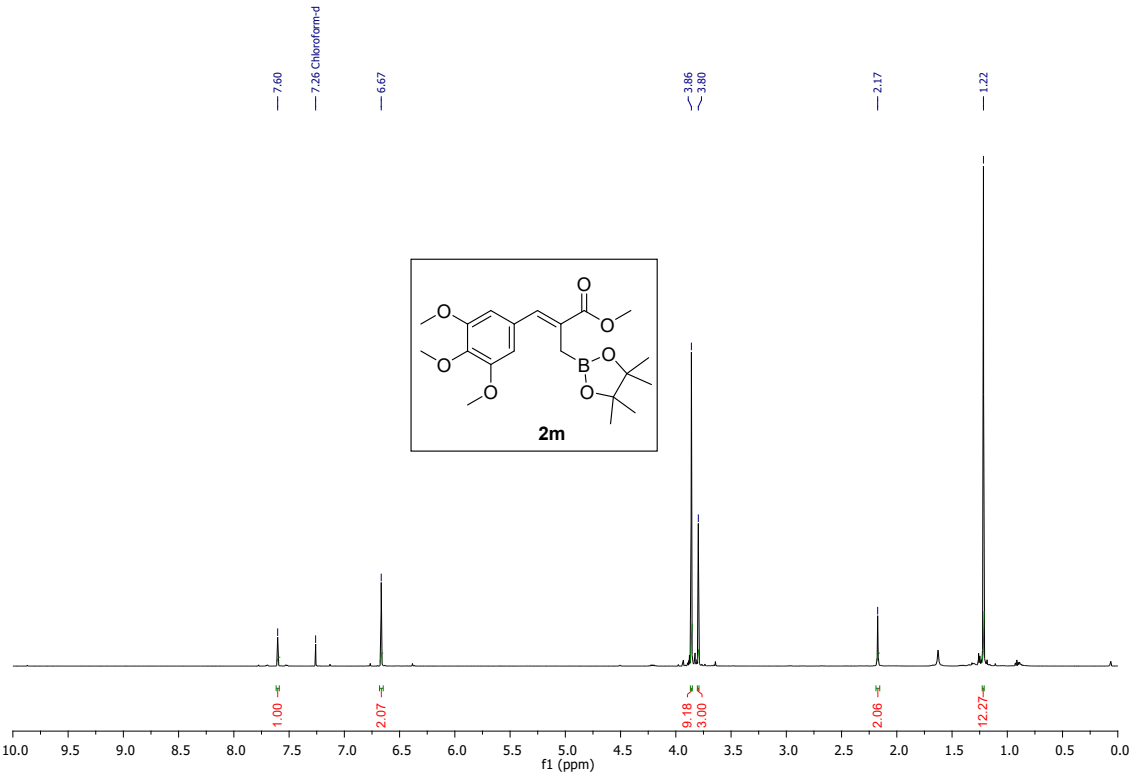
^{13}C{^{1}H} NMR (150 MHz) spectrum of **2k** in $CDCl_3$



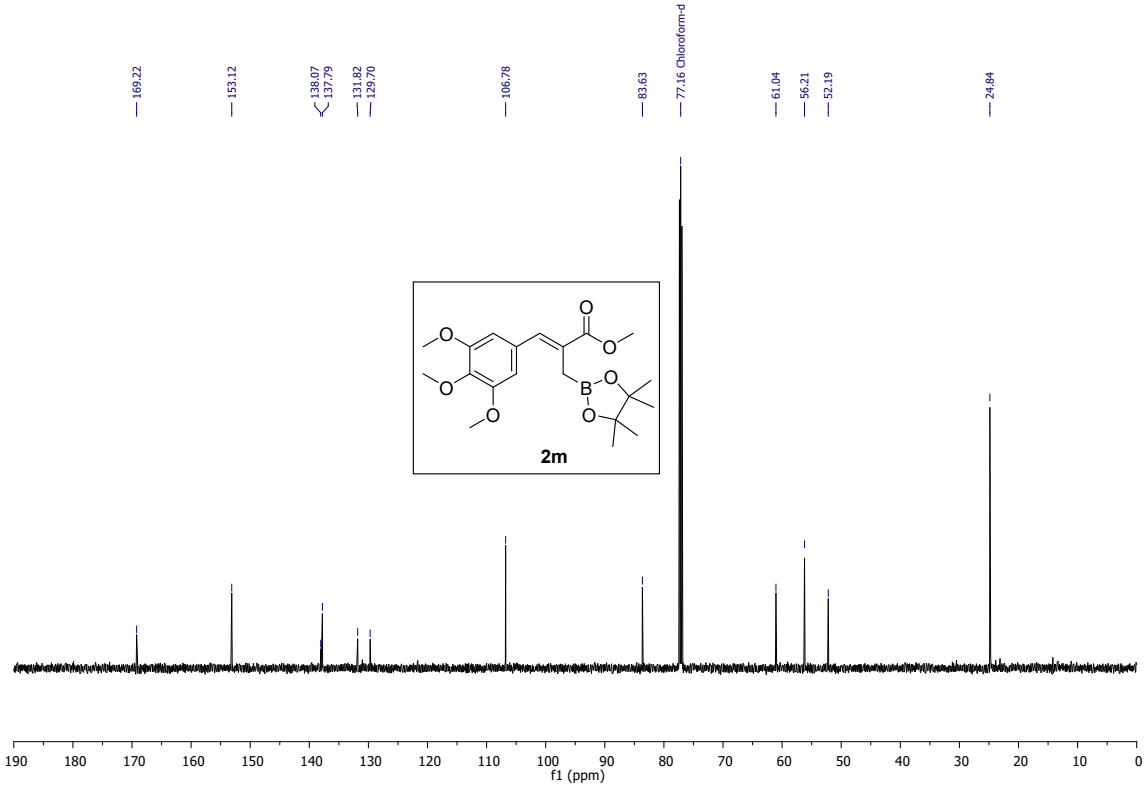
^{1}H NMR (400 MHz) spectrum of **2l** in $CDCl_3$



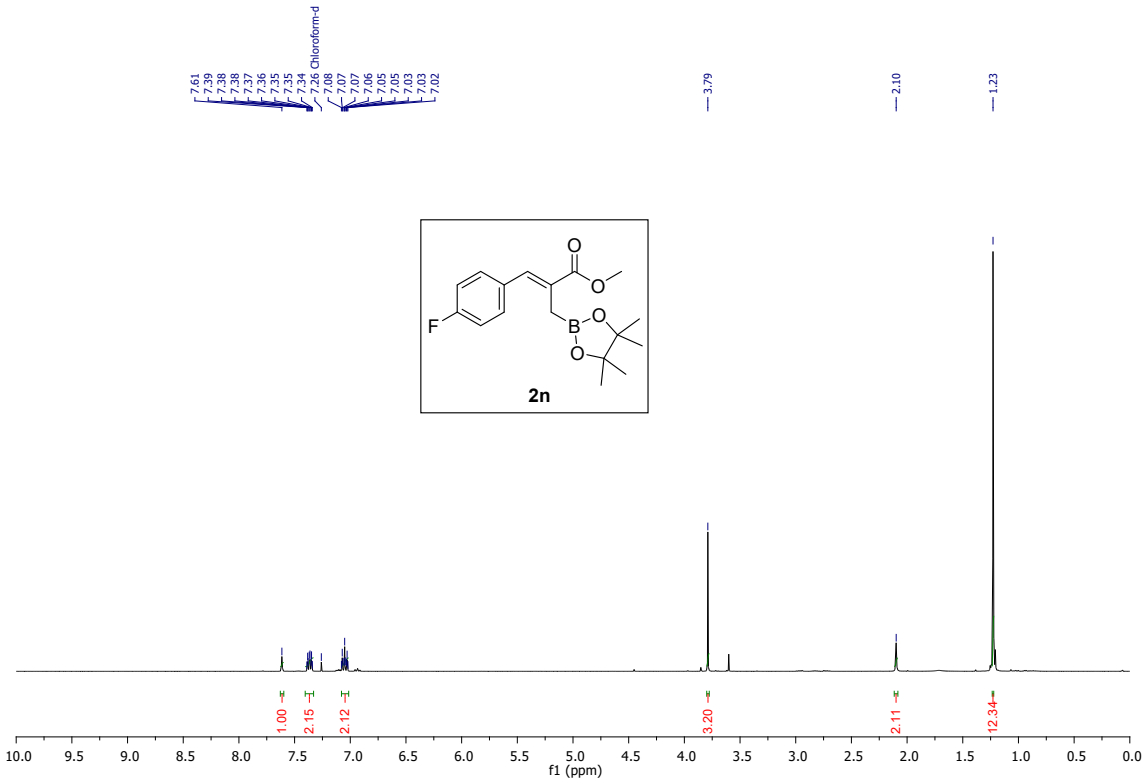
^{13}C{^{1}H} NMR (150 MHz) spectrum of **2l** in $CDCl_3$



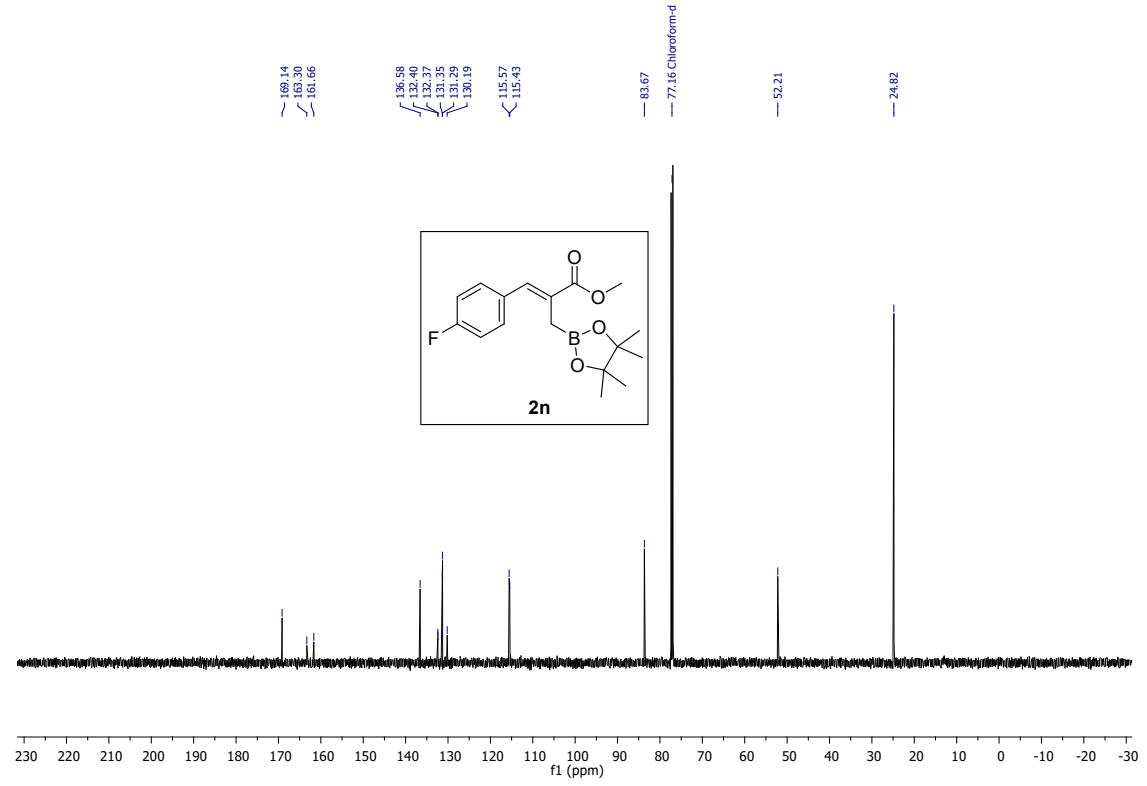
^{1}H NMR (400 MHz) spectrum of **2m** in $CDCl_3$



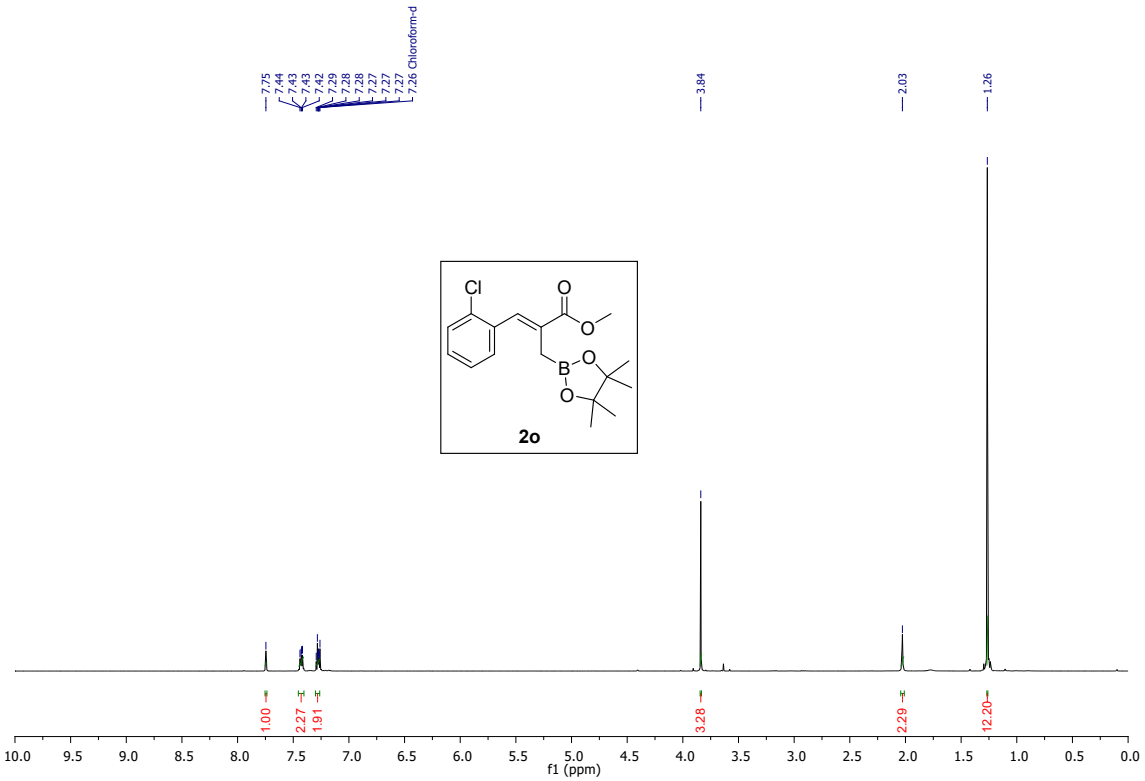
^{13}C{^{1}H} NMR (150 MHz) spectrum of **2m** in $CDCl_3$



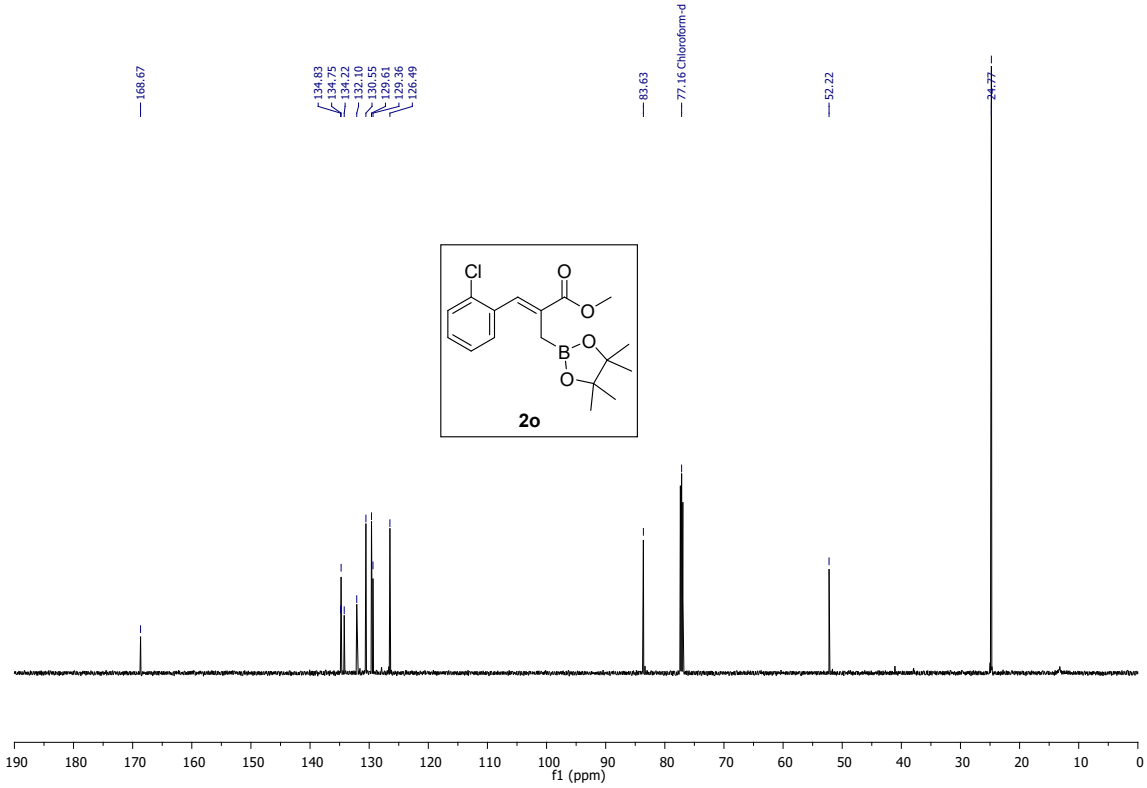
^{1}H NMR (400 MHz) spectrum of **2n** in $CDCl_3$



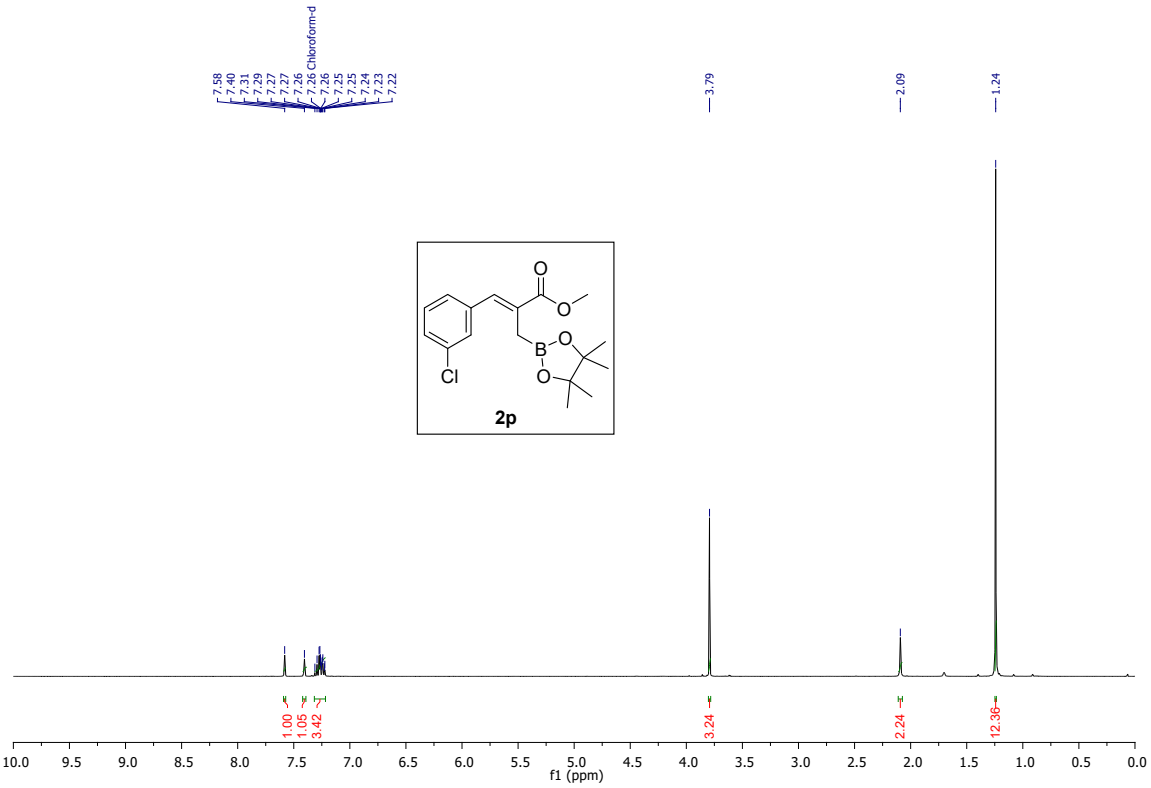
^{13}C{^{1}H} NMR (150 MHz) spectrum of **2n** in $CDCl_3$



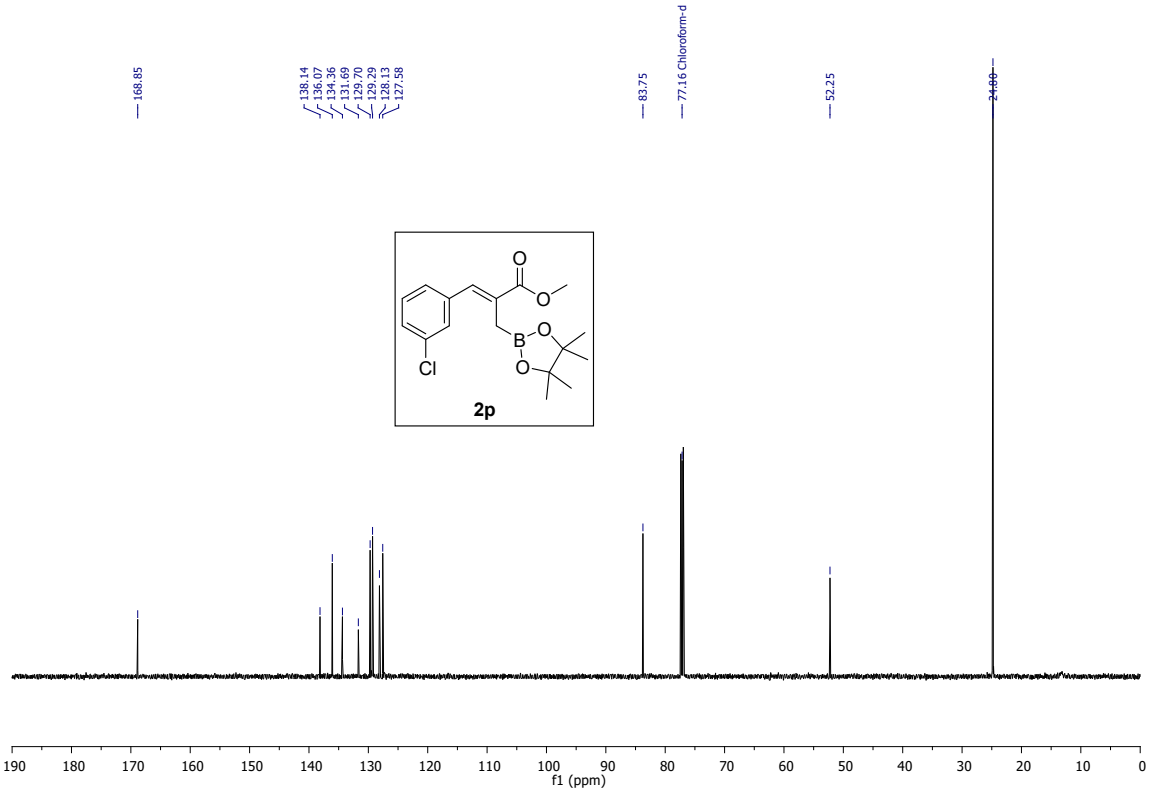
^{1}H NMR (400 MHz) spectrum of **2o** in $CDCl_3$



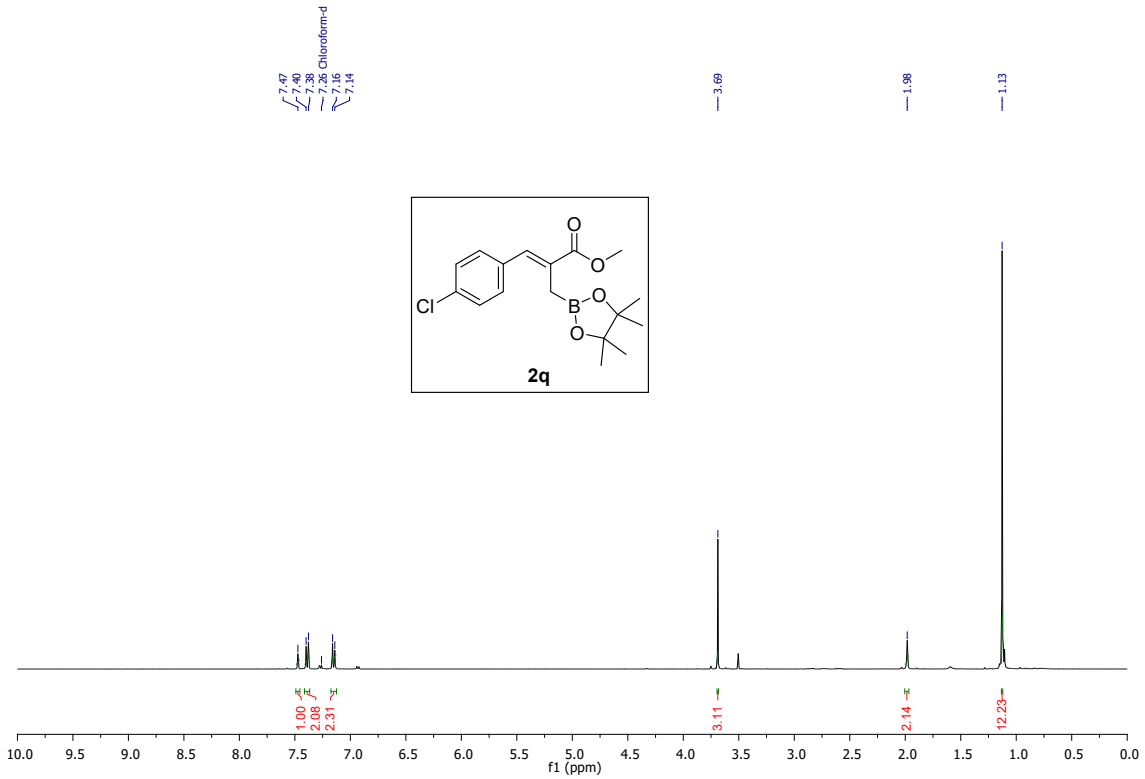
^{13}C{^{1}H} NMR (150 MHz) spectrum of **2o** in $CDCl_3$



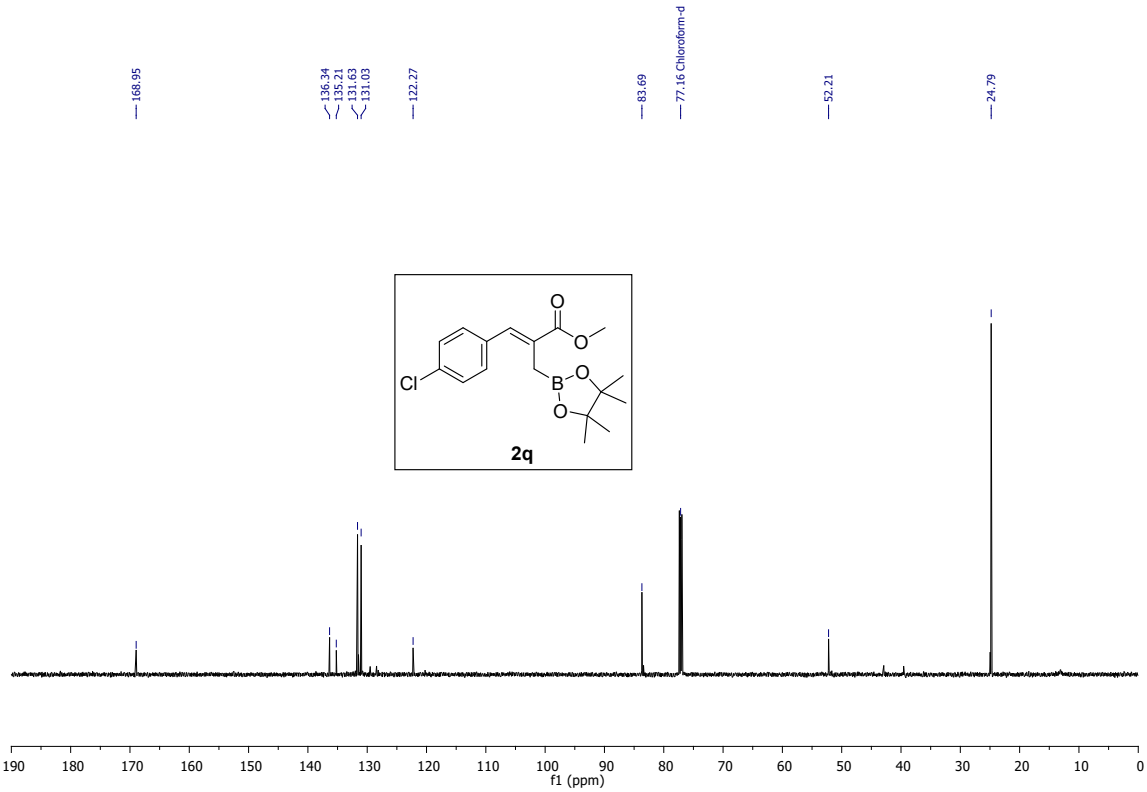
^{1}H NMR (400 MHz) spectrum of **2p** in $CDCl_3$



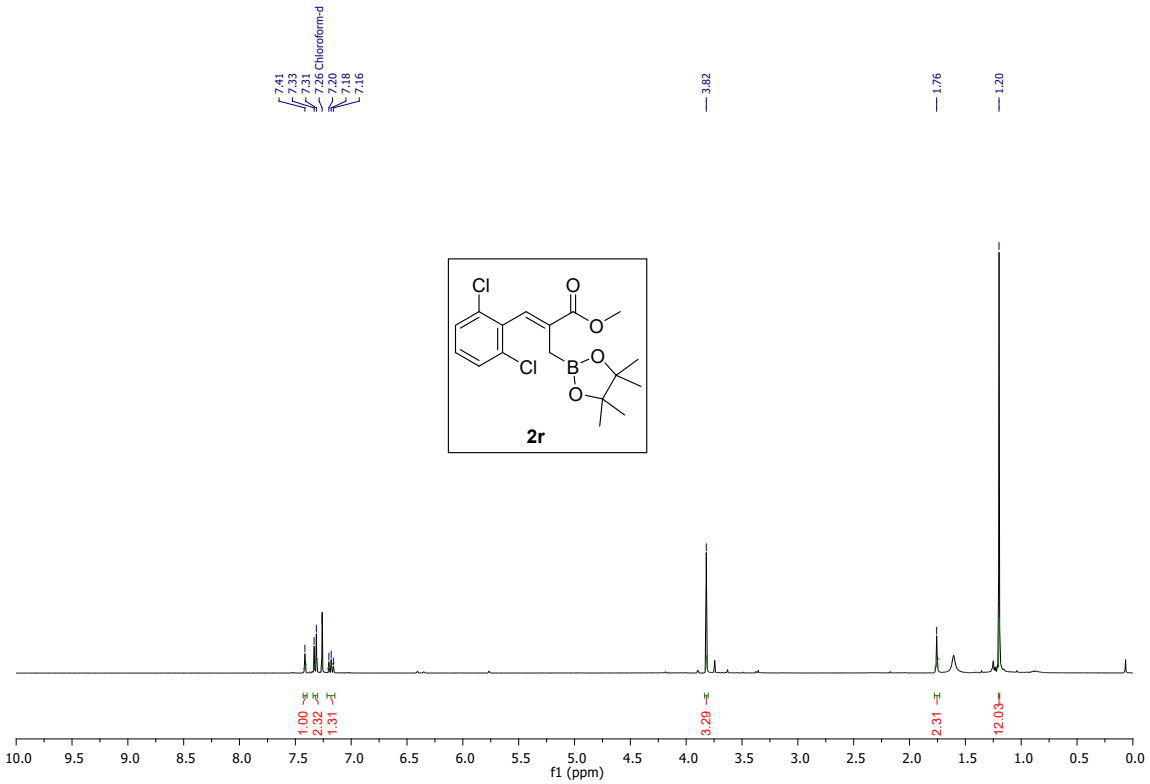
^{13}C{^{1}H} NMR (150 MHz) spectrum of **2p** in $CDCl_3$



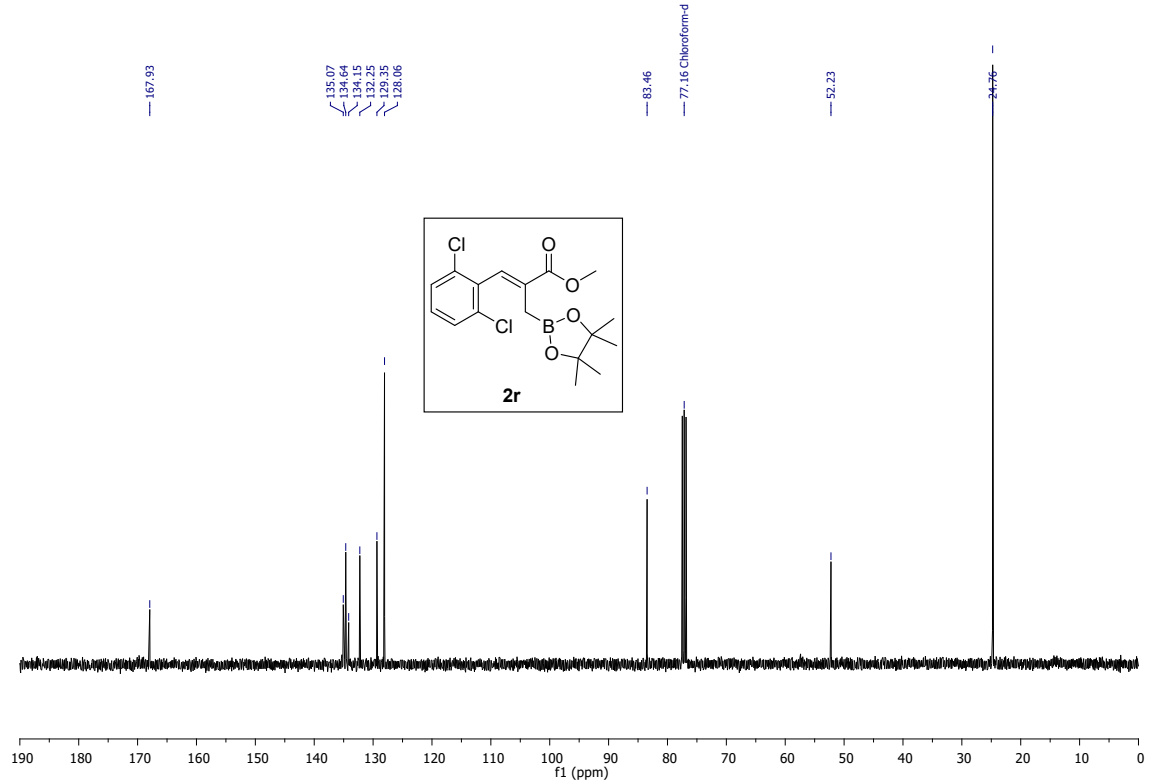
^{1}H NMR (400 MHz) spectrum of **2q** in $CDCl_3$



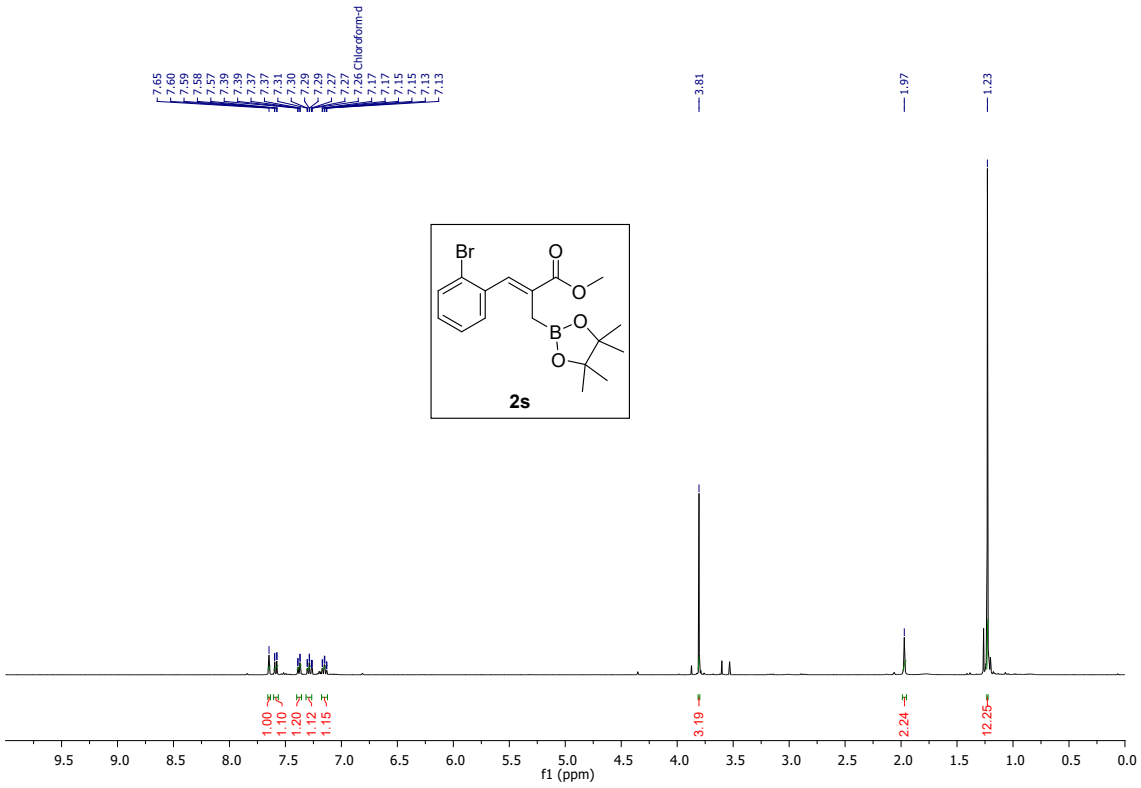
^{13}C{^{1}H} NMR (150 MHz) spectrum of **2q** in $CDCl_3$



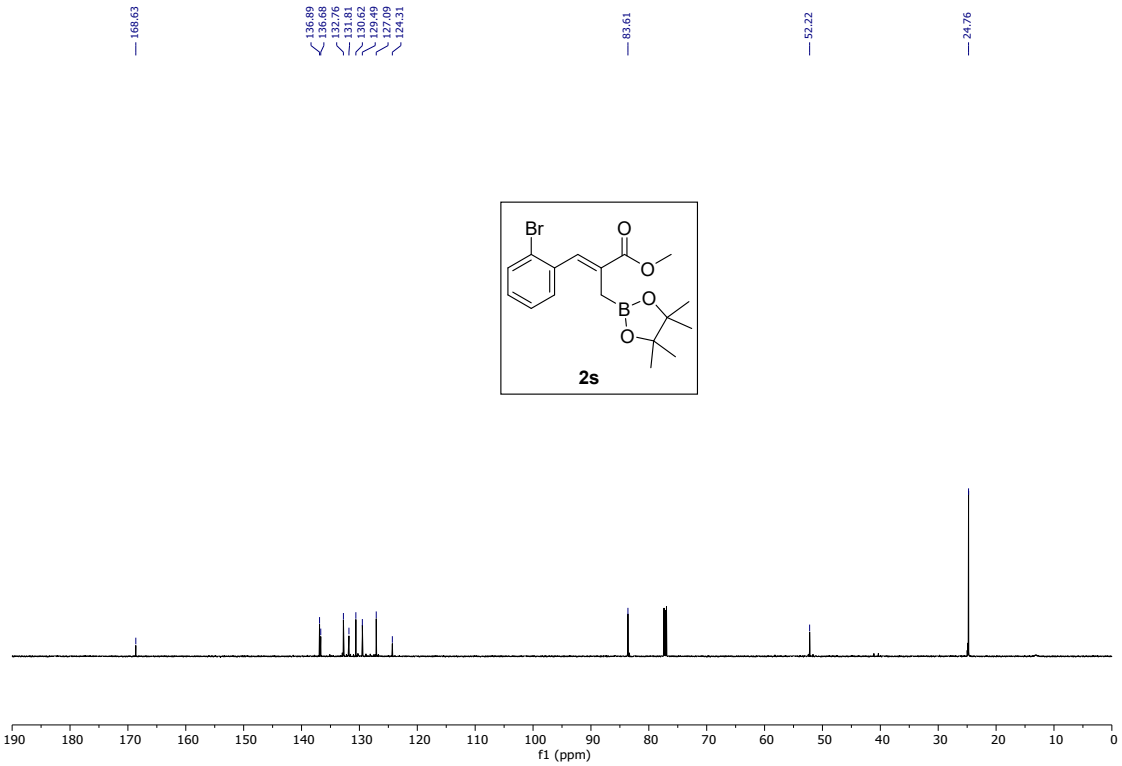
^{1}H NMR (400 MHz) spectrum of **2r** in $CDCl_3$



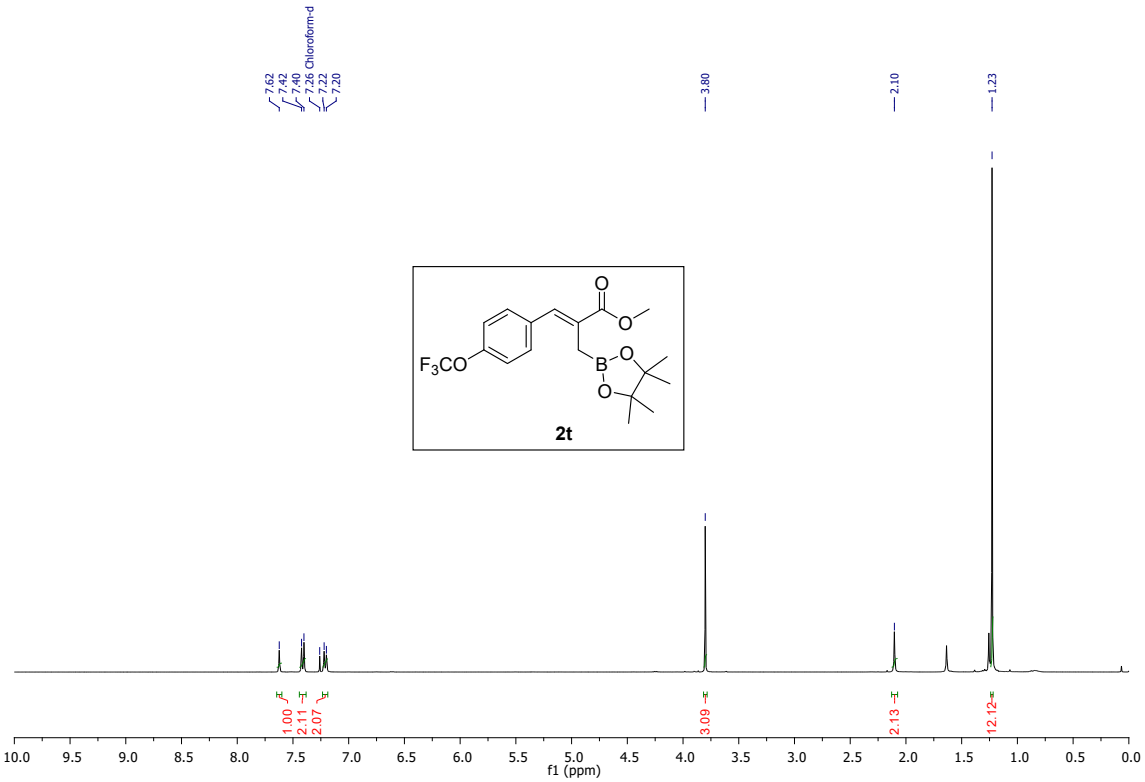
^{13}C{^{1}H} NMR (150 MHz) spectrum of **2r** in $CDCl_3$



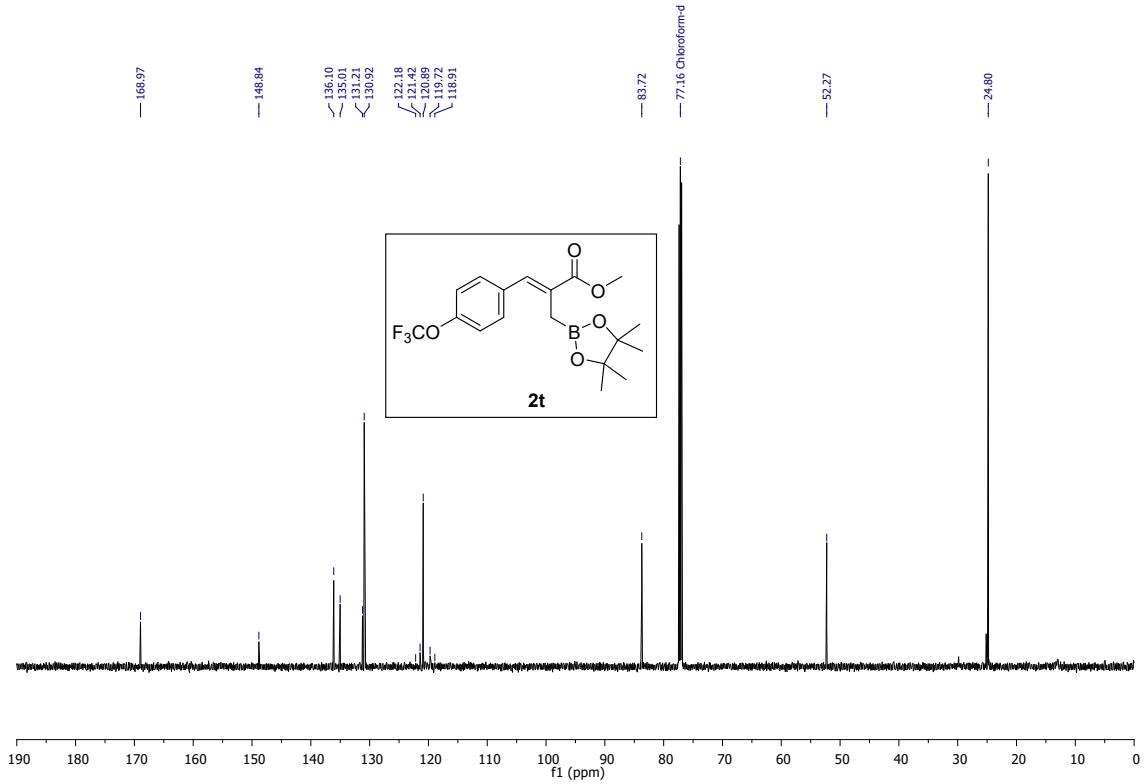
^{1}H NMR (400 MHz) spectrum of **2s** in $CDCl_3$



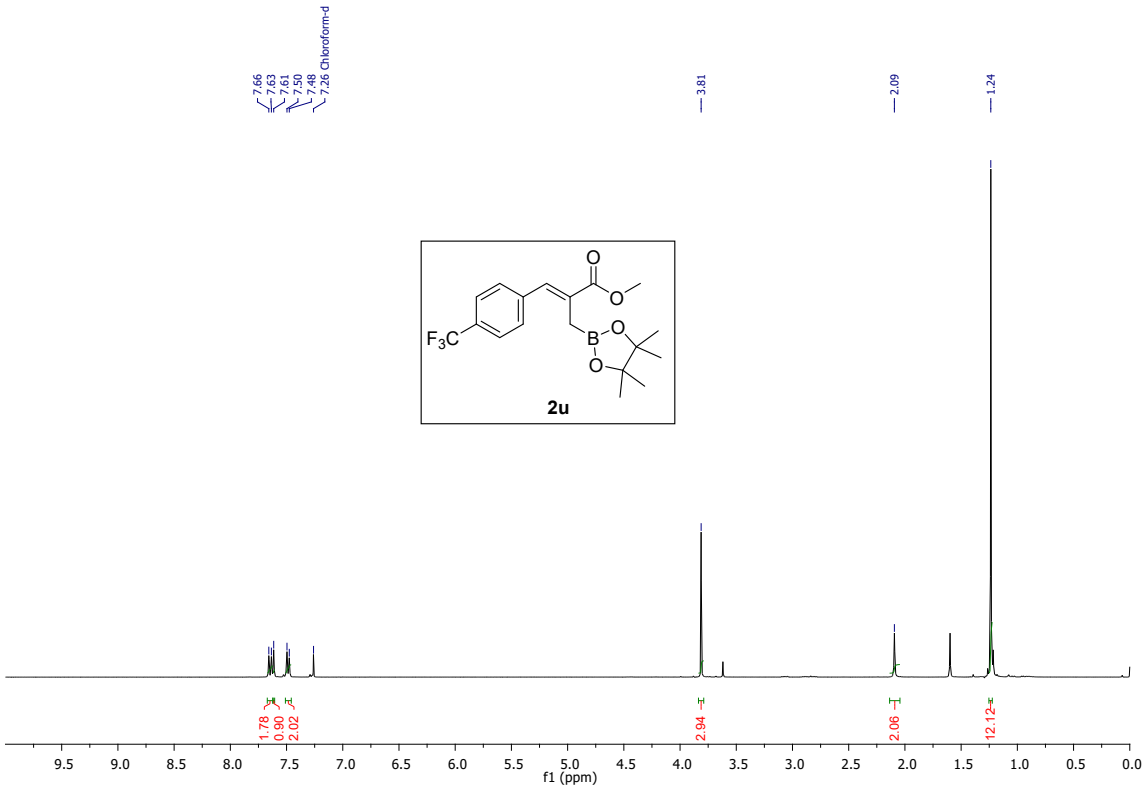
^{13}C{^{1}H} NMR (150 MHz) spectrum of **2s** in $CDCl_3$



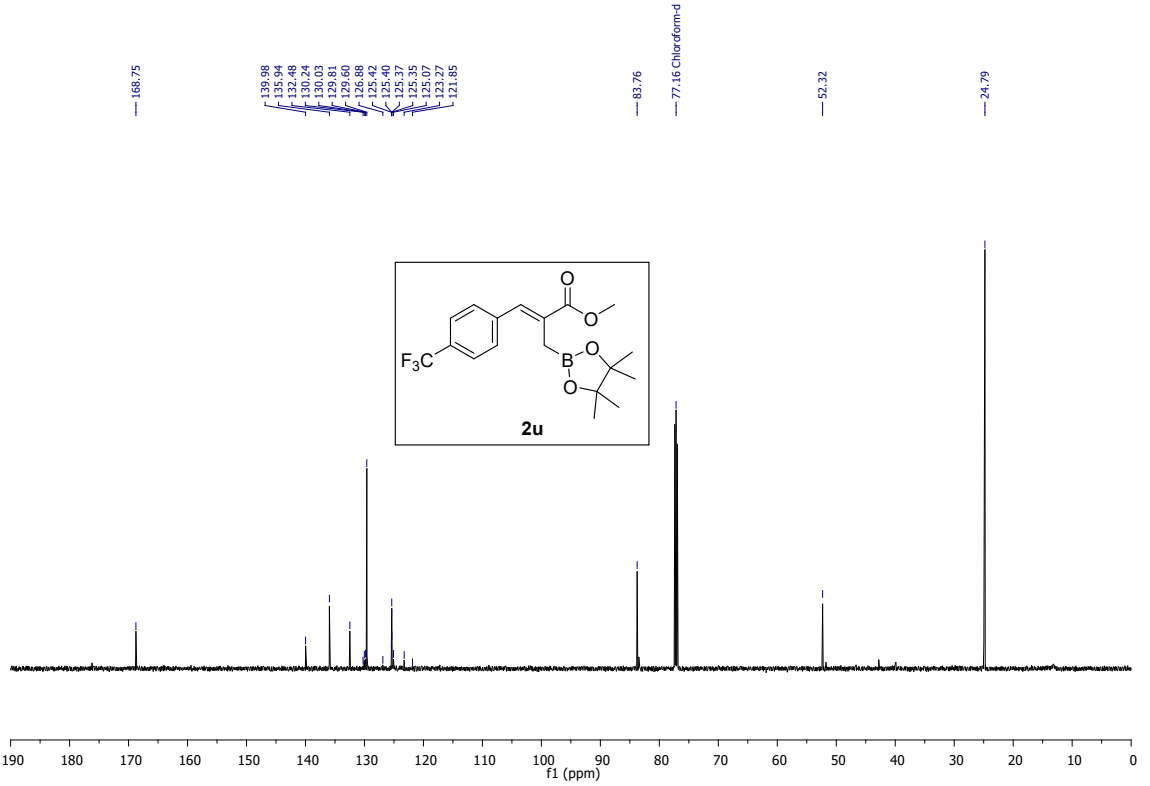
^{1}H NMR (400 MHz) spectrum of **2t** in $CDCl_3$



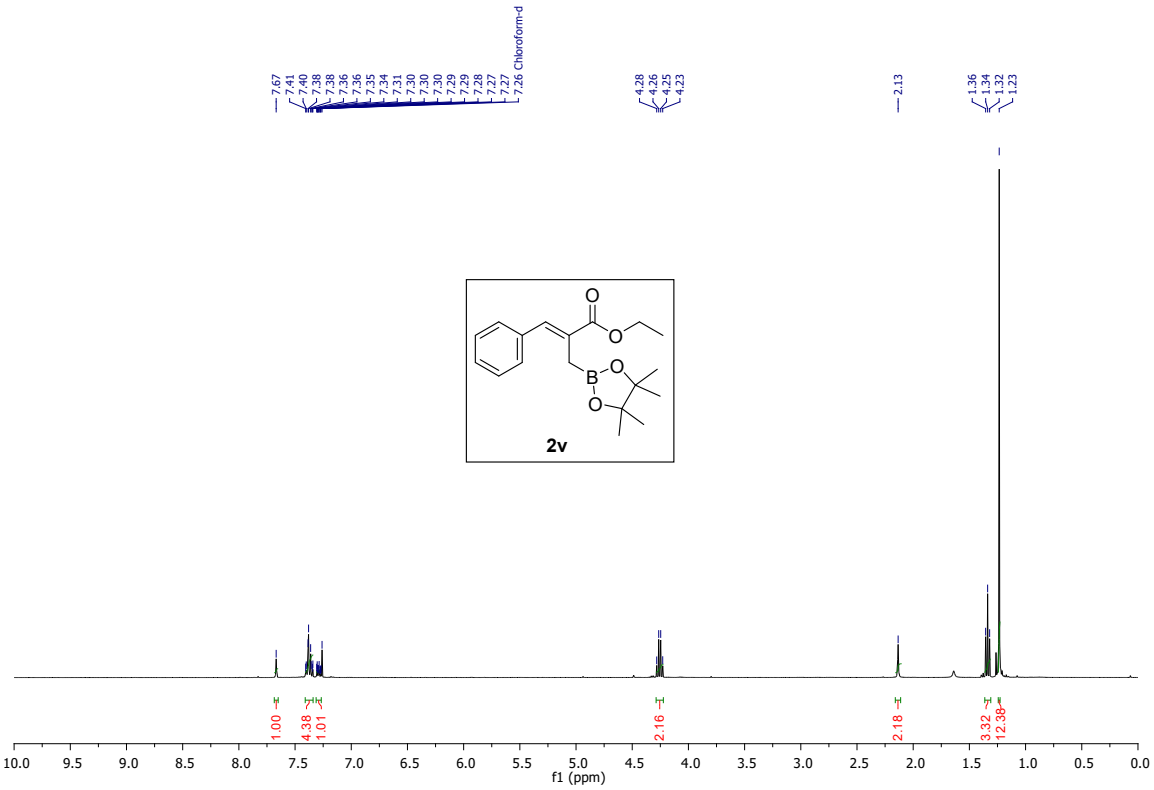
^{13}C{^{1}H} NMR (150 MHz) spectrum of **2t** in $CDCl_3$



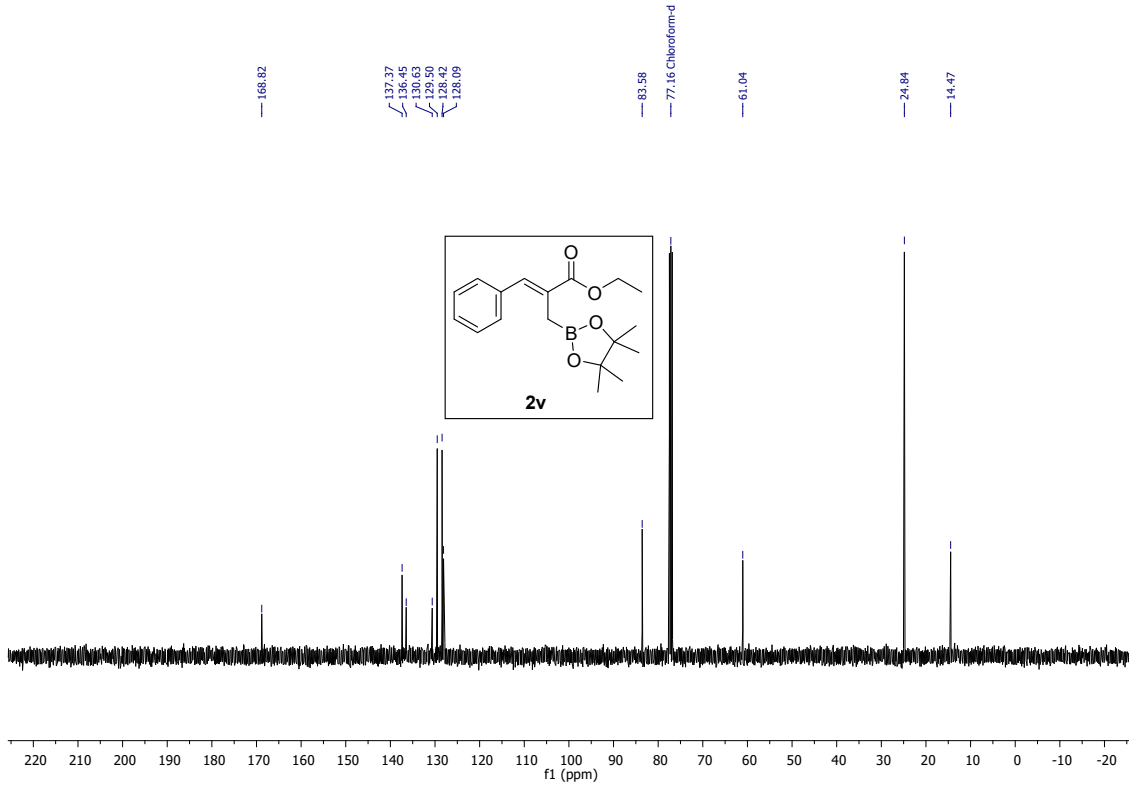
^{1}H NMR (400 MHz) spectrum of **2u** in $CDCl_3$



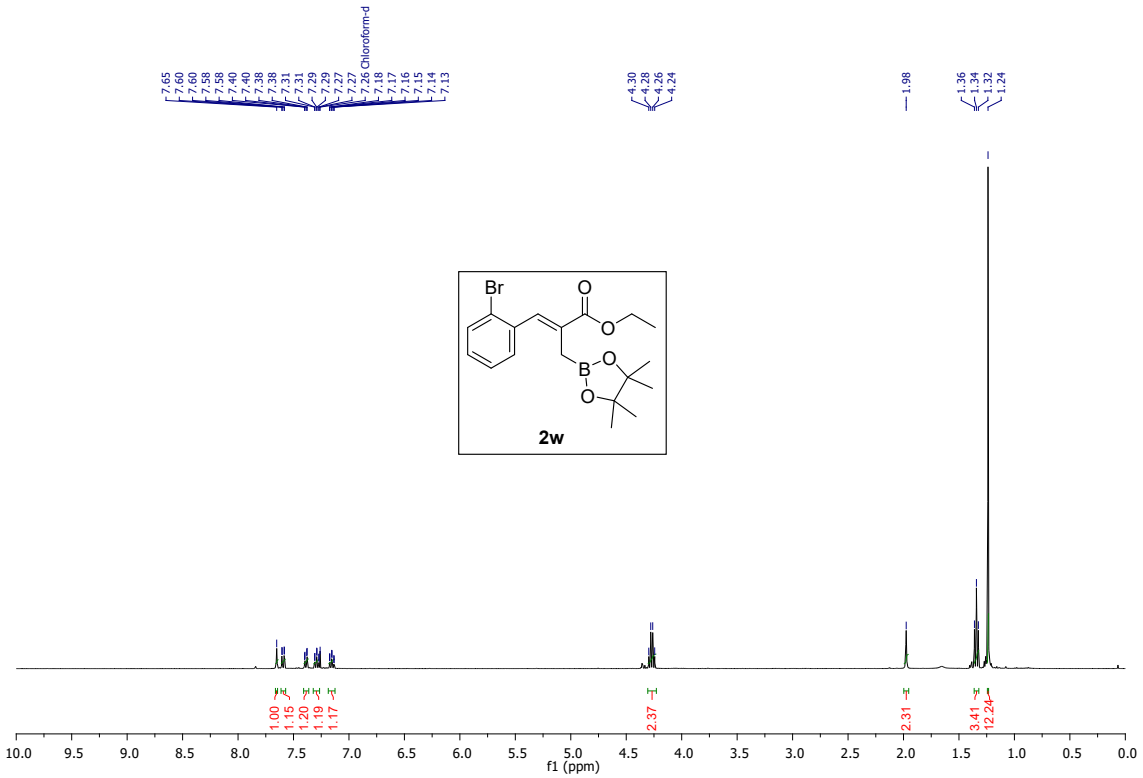
^{13}C{^{1}H} NMR (150 MHz) spectrum of **2u** in $CDCl_3$



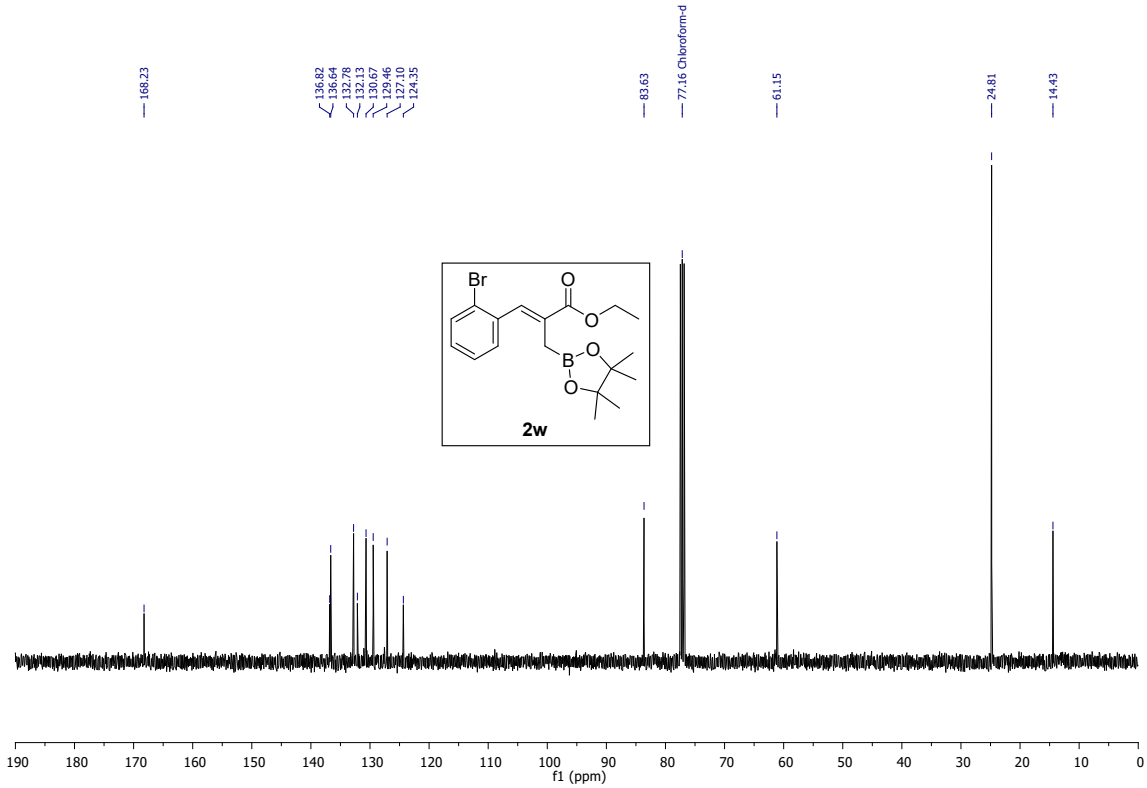
^{1}H NMR (400 MHz) spectrum of **2v** in $CDCl_3$



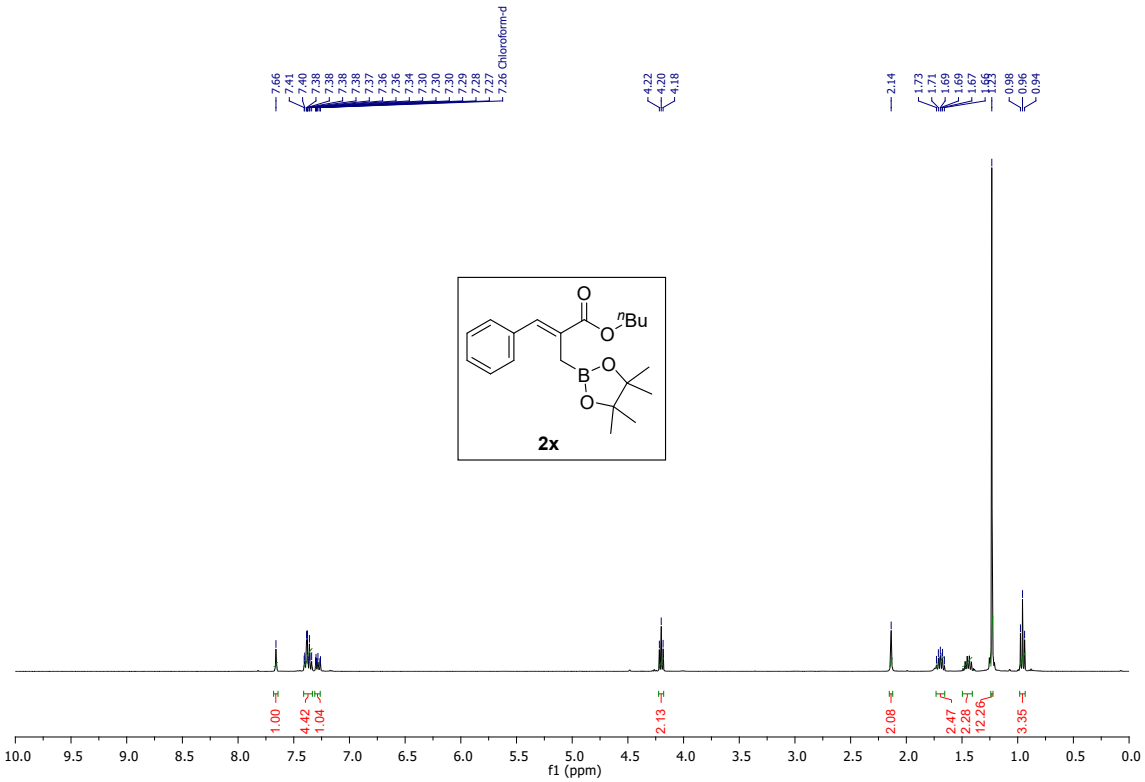
^{13}C{^{1}H} NMR (150 MHz) spectrum of **2v** in $CDCl_3$



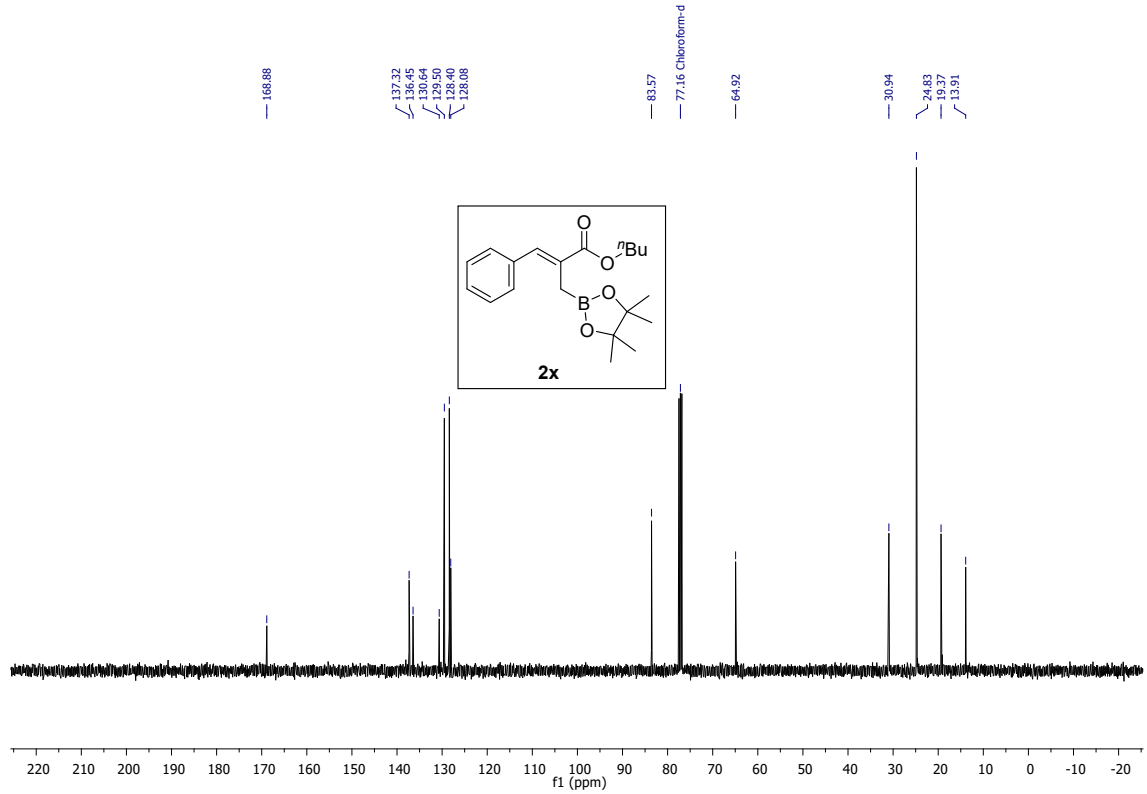
^{1}H NMR (400 MHz) spectrum of **2w** in $CDCl_3$



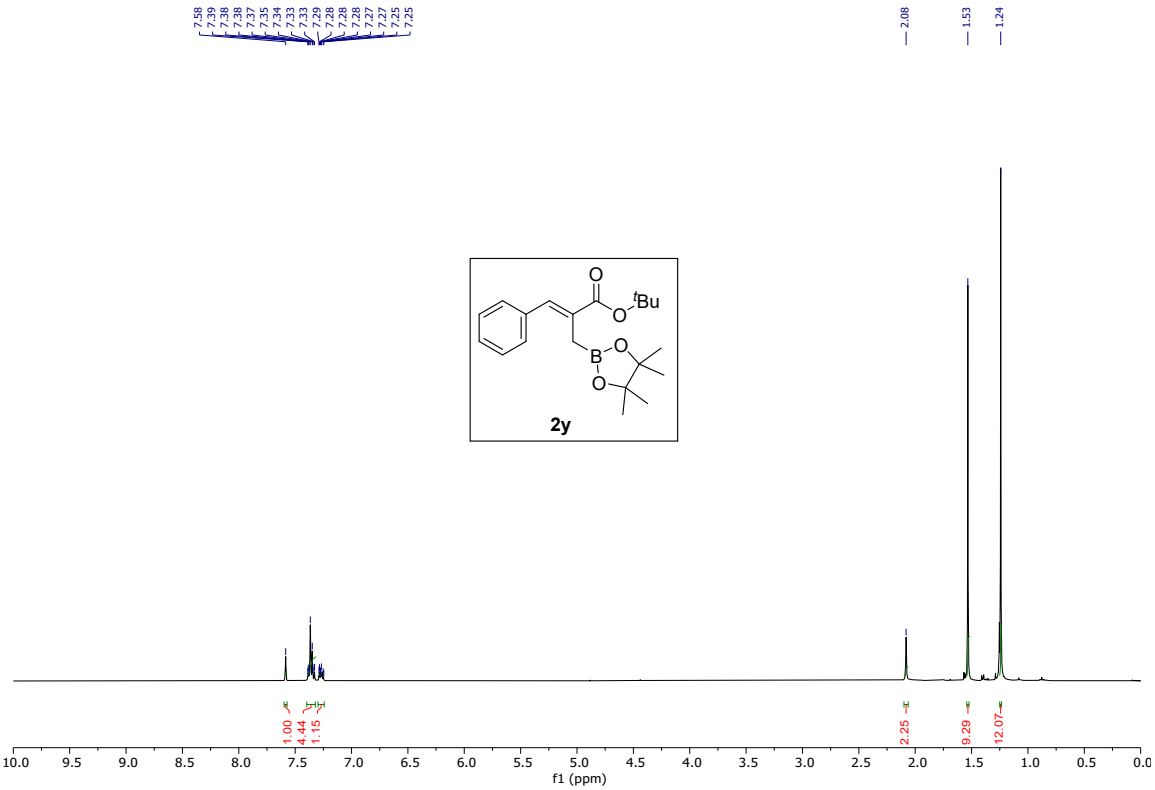
^{13}C{^{1}H} NMR (150 MHz) spectrum of **2w** in $CDCl_3$



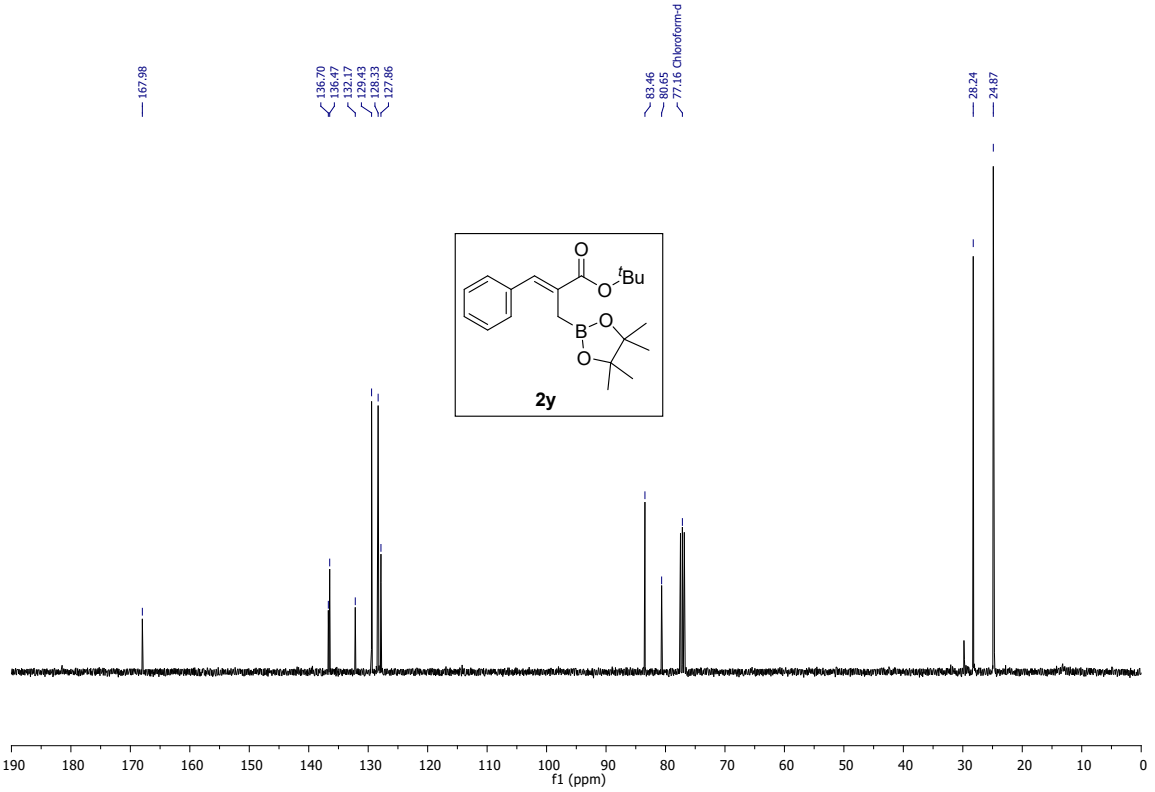
^{1}H NMR (400 MHz) spectrum of **2x** in $CDCl_3$



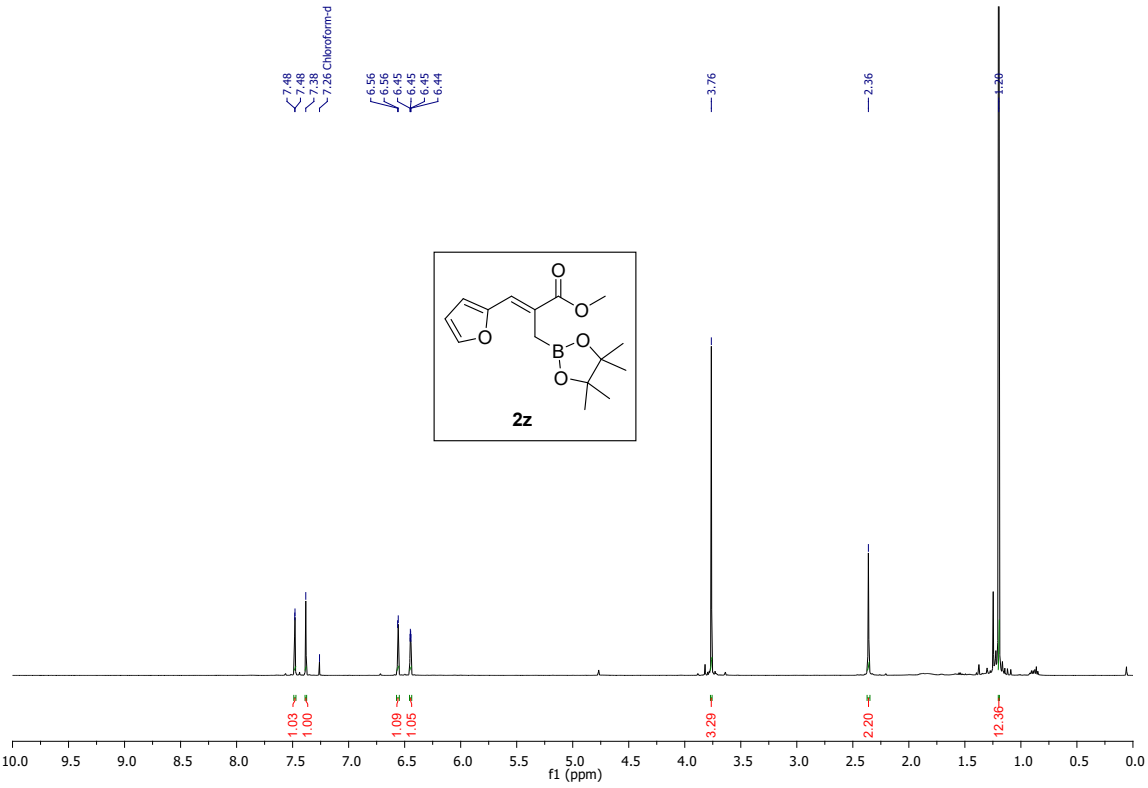
^{13}C{^{1}H} NMR (150 MHz) spectrum of **2x** in $CDCl_3$



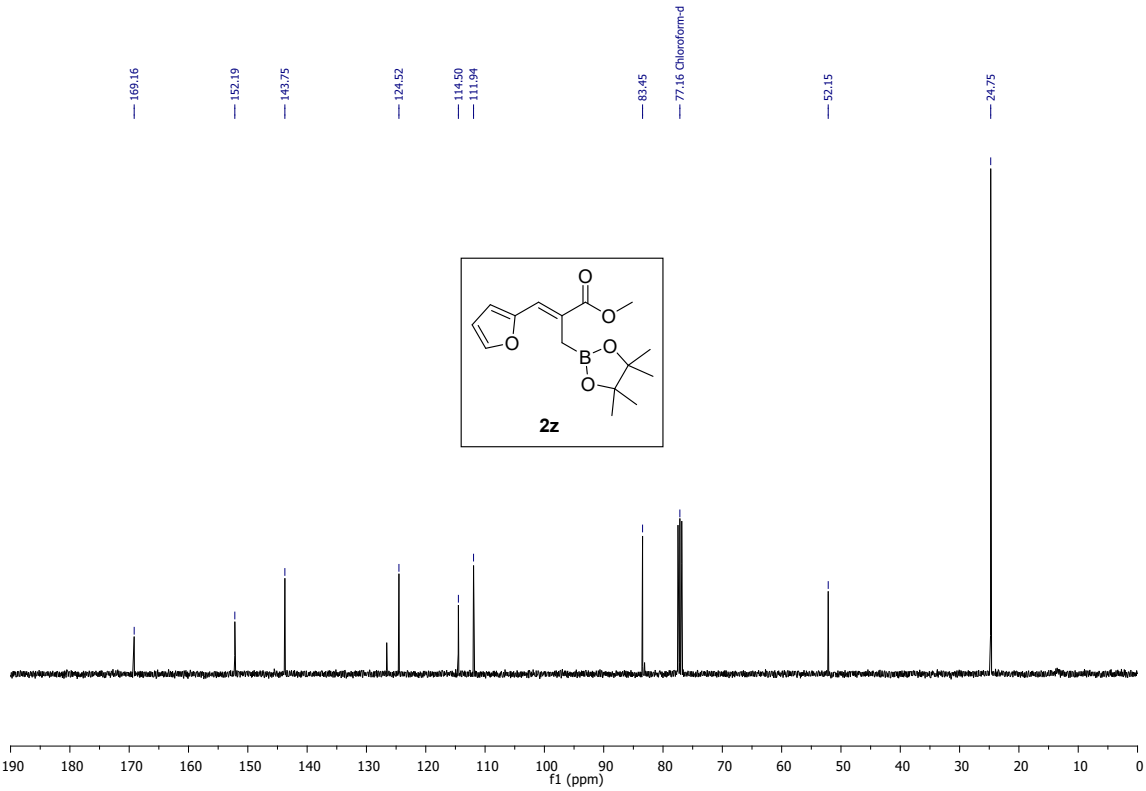
^{1}H NMR (400 MHz) spectrum of **2y** in $CDCl_3$



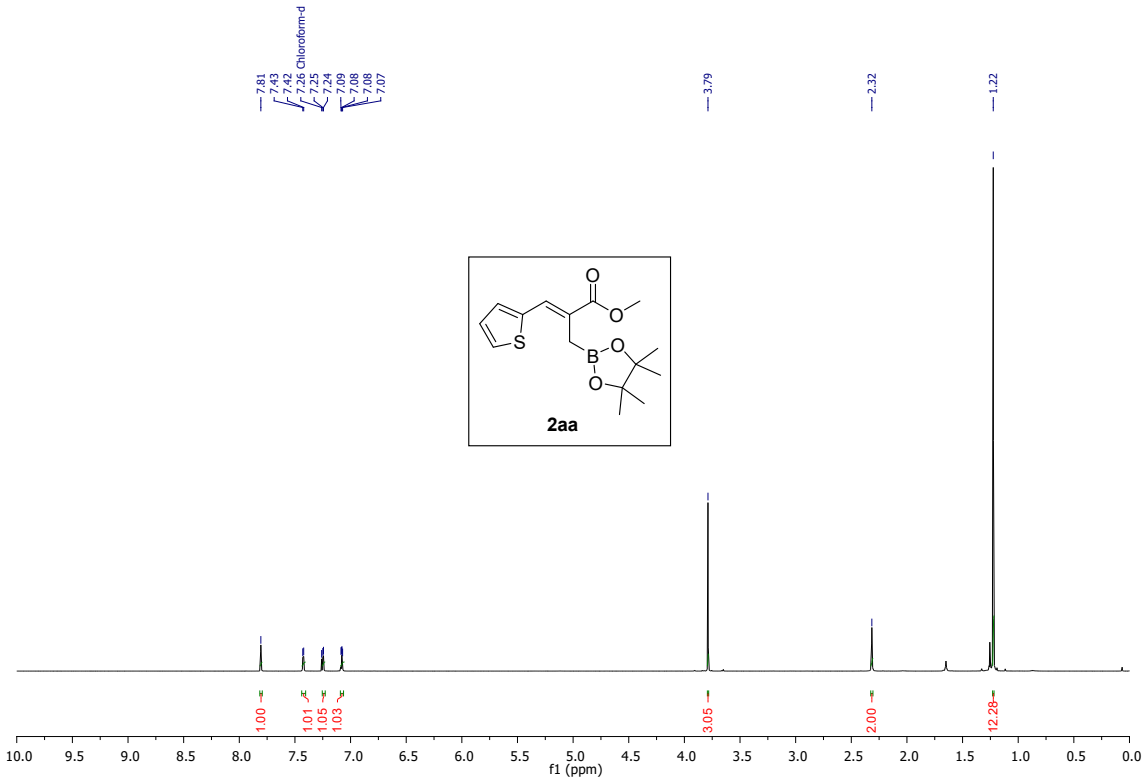
^{13}C{^{1}H} NMR (150 MHz) spectrum of **2y** in $CDCl_3$



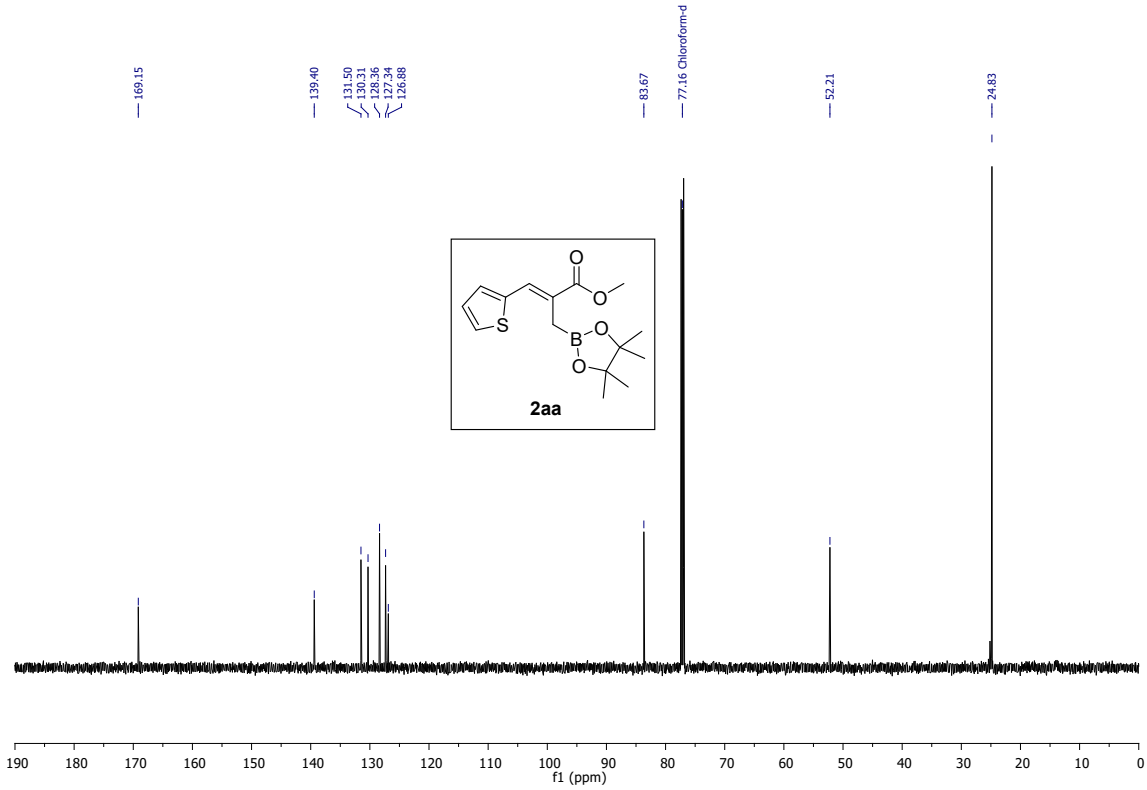
^{1}H NMR (400 MHz) spectrum of **2z** in $CDCl_3$



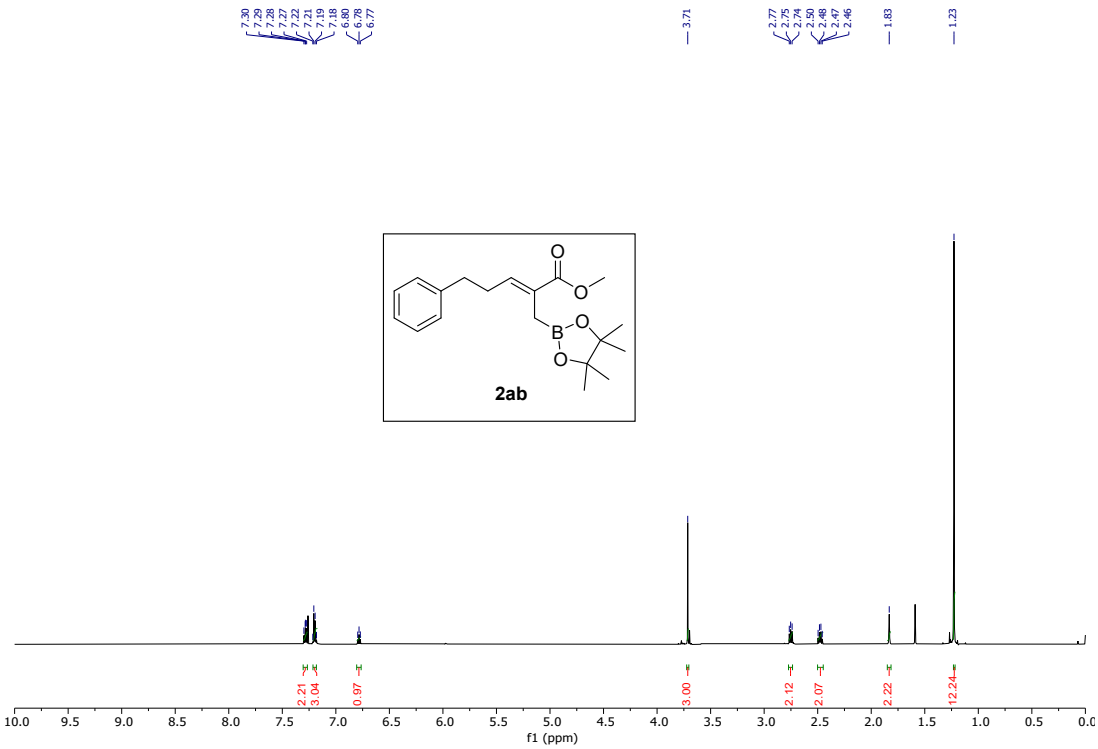
^{13}C{^{1}H} NMR (150 MHz) spectrum of **2z** in $CDCl_3$



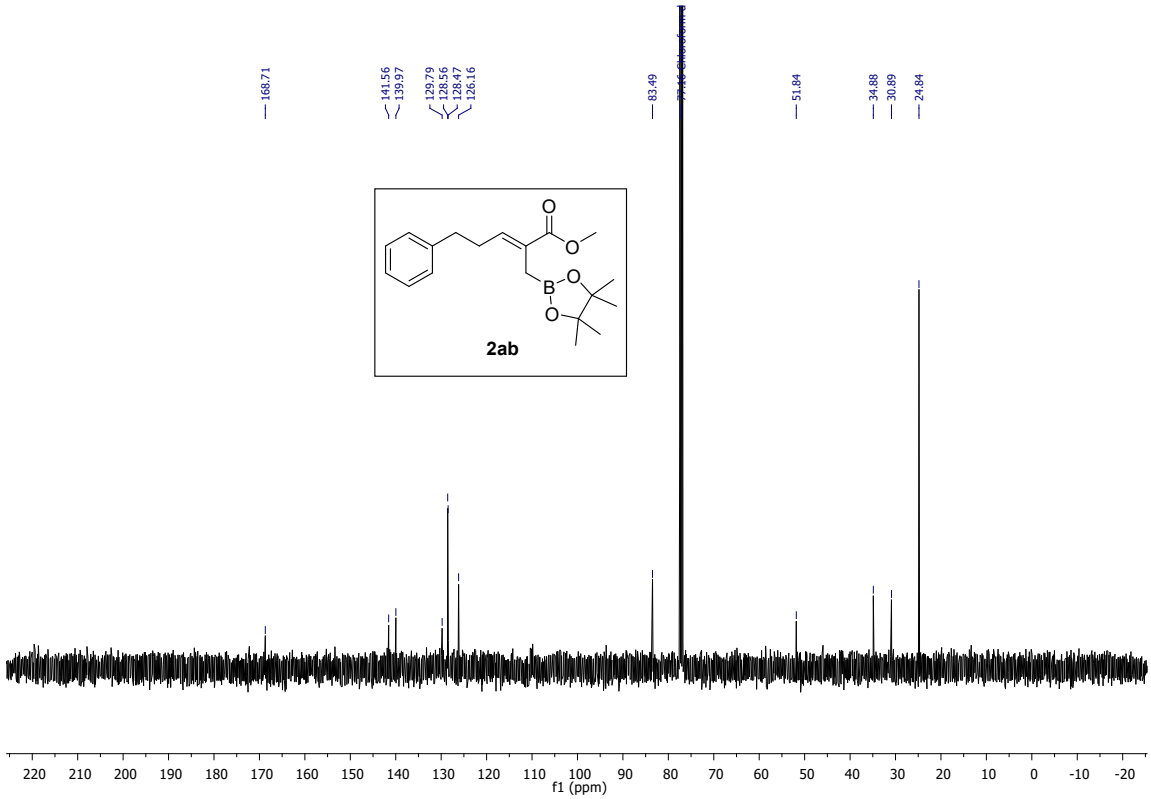
^{1}H NMR (400 MHz) spectrum of **2aa** in $CDCl_3$



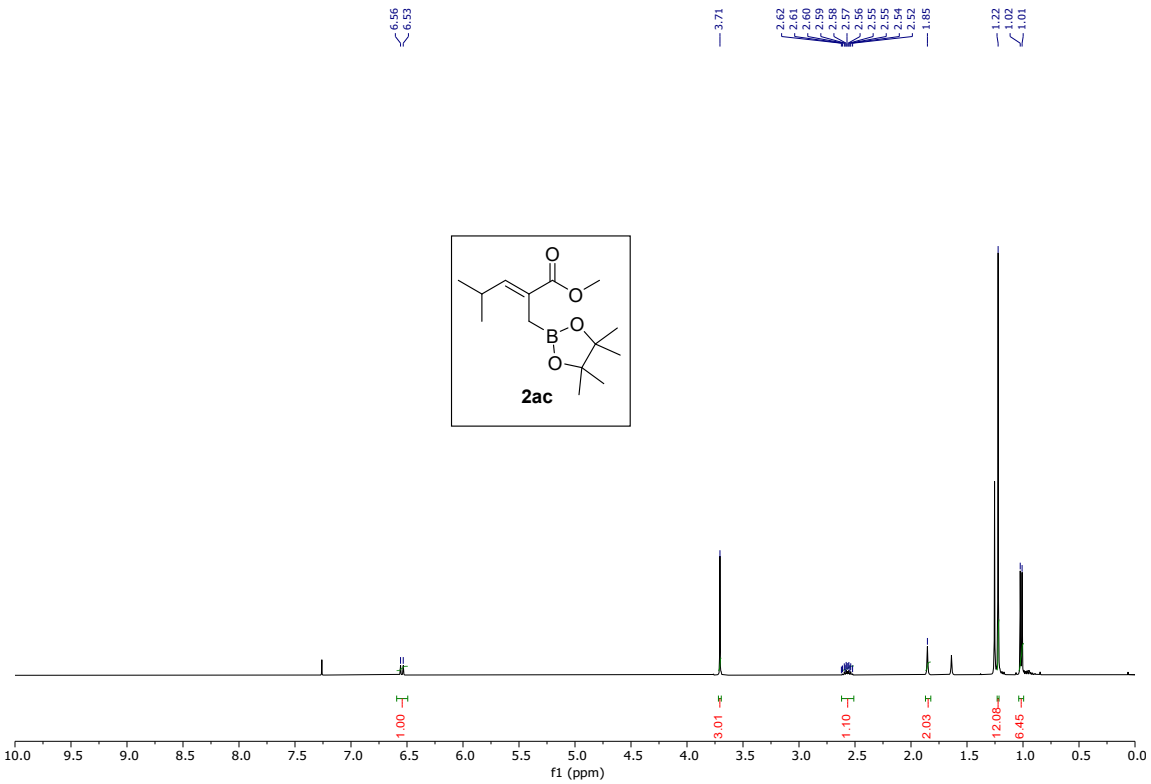
^{13}C{^{1}H} NMR (150 MHz) spectrum of **2aa** in $CDCl_3$



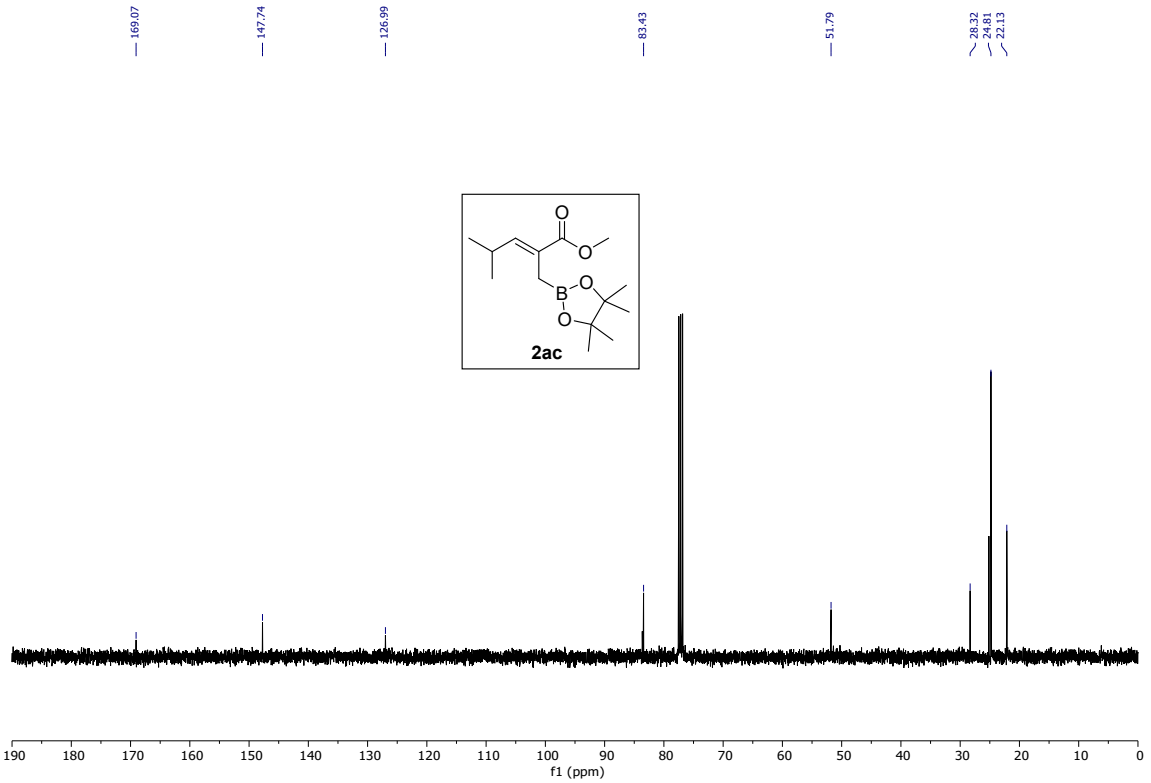
^{1}H NMR (400 MHz) spectrum of **2ab** in $CDCl_3$



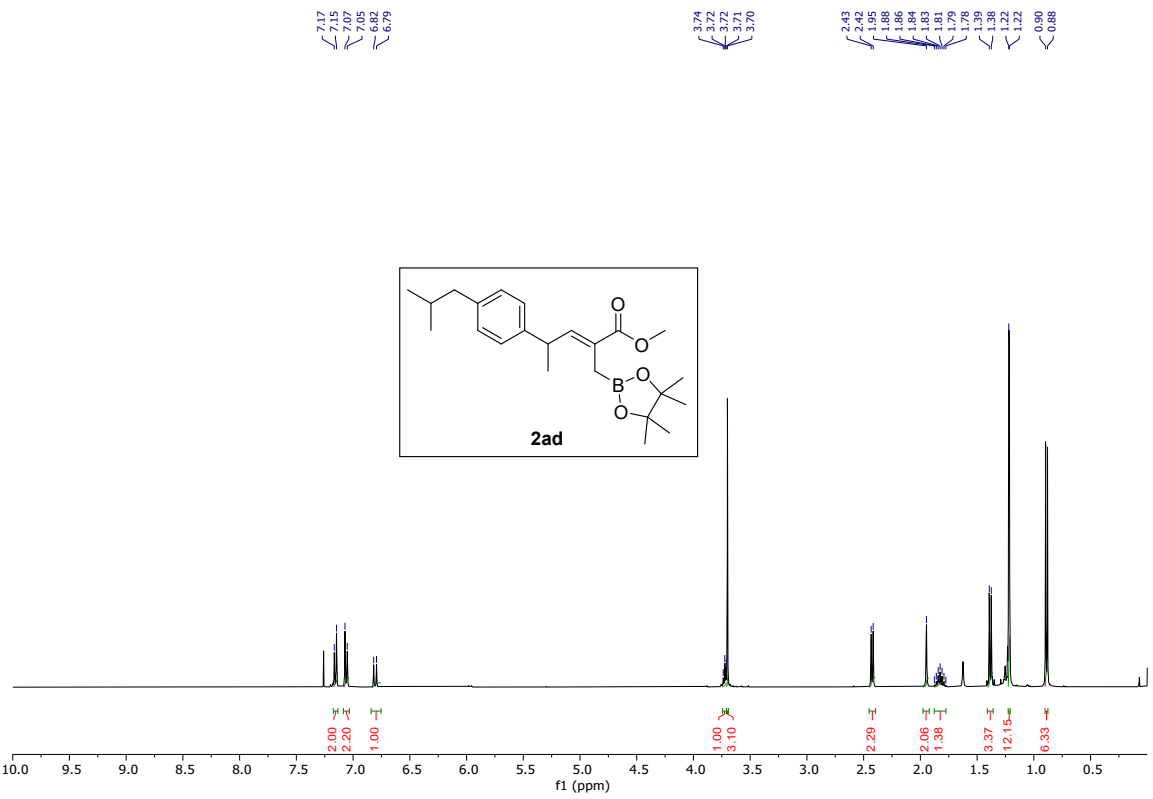
^{13}C{^{1}H} NMR (150 MHz) spectrum of **2ab** in $CDCl_3$



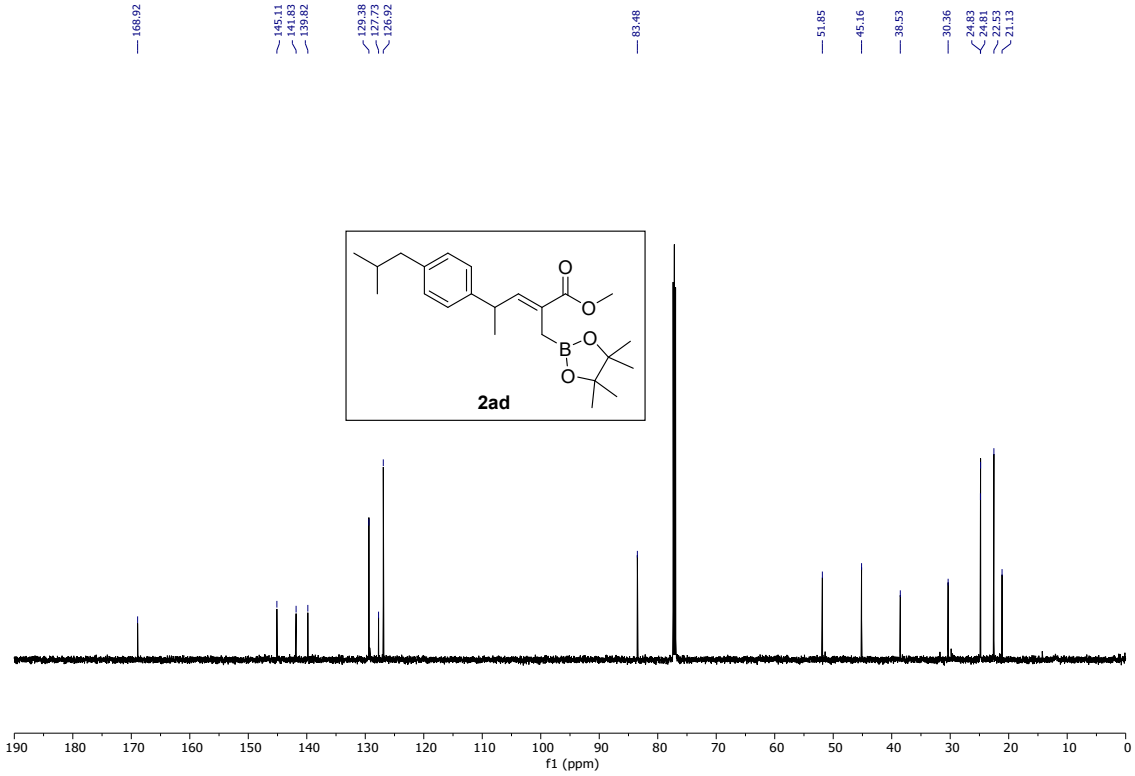
^{1}H NMR (400 MHz) spectrum of **2ac** in $CDCl_3$



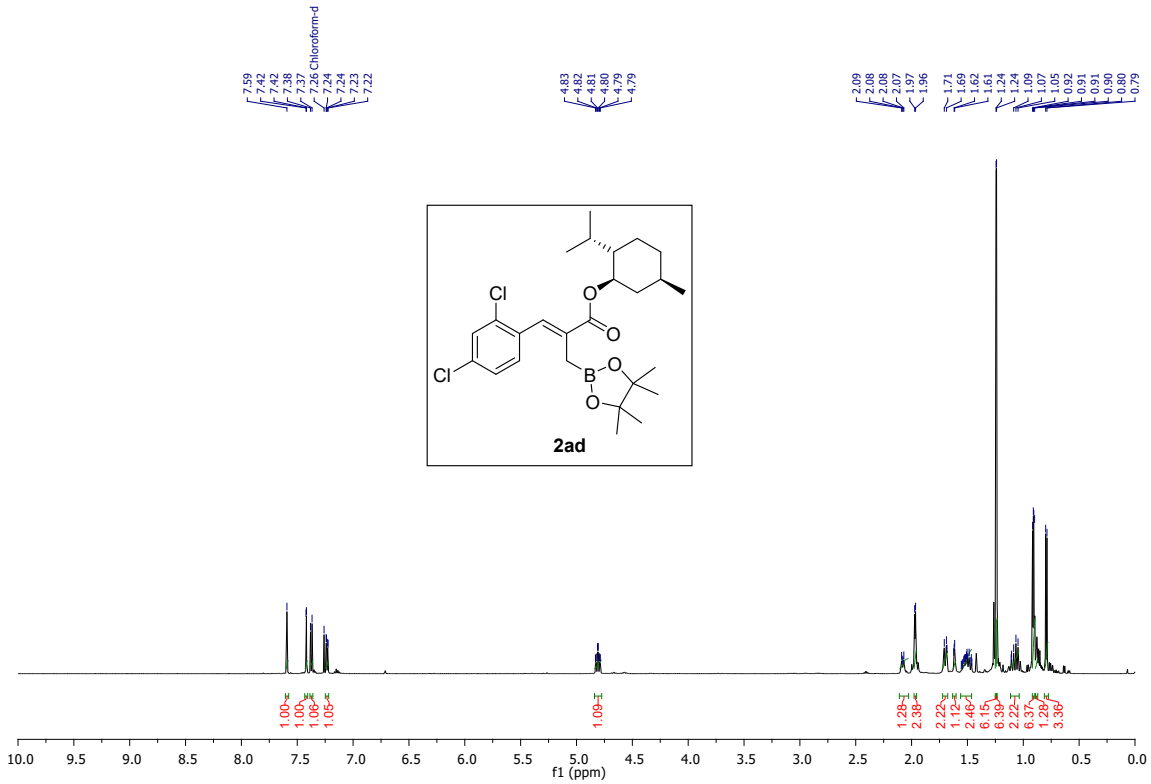
^{13}C{^{1}H} NMR (150 MHz) spectrum of **2ac** in $CDCl_3$



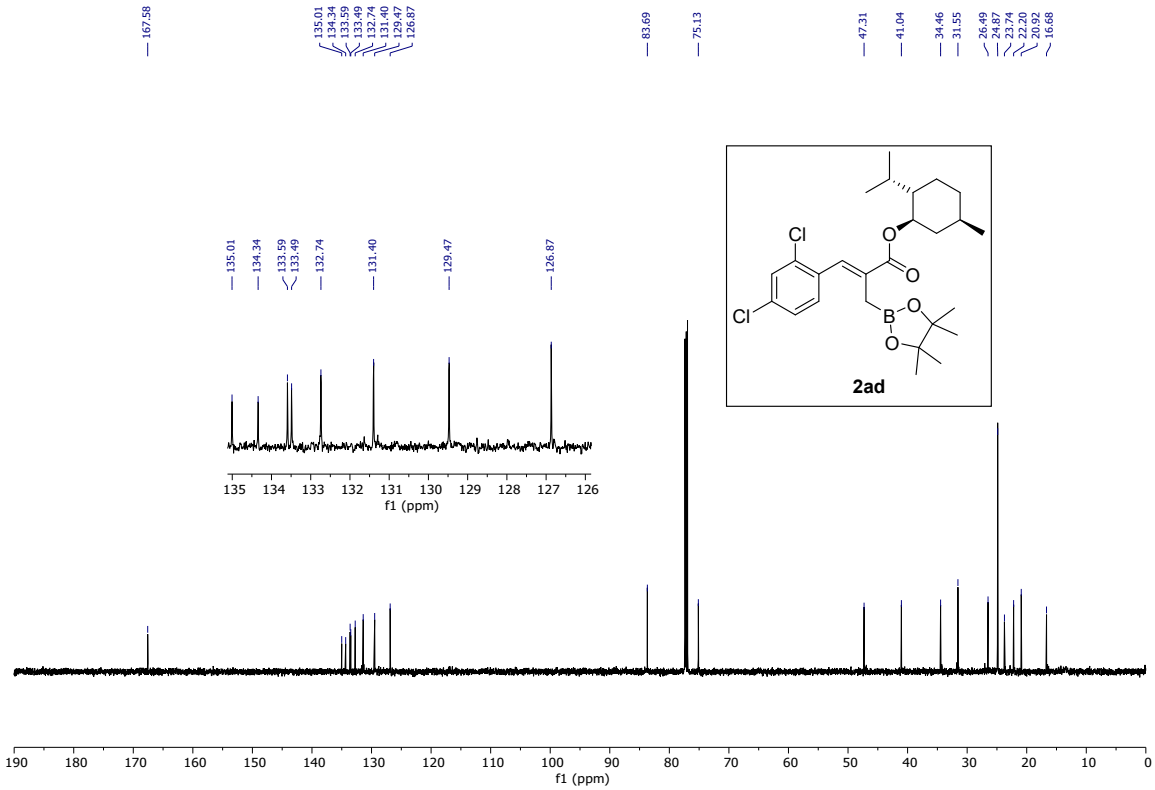
^{1}H NMR (400 MHz) spectrum of **2ad** in $CDCl_3$



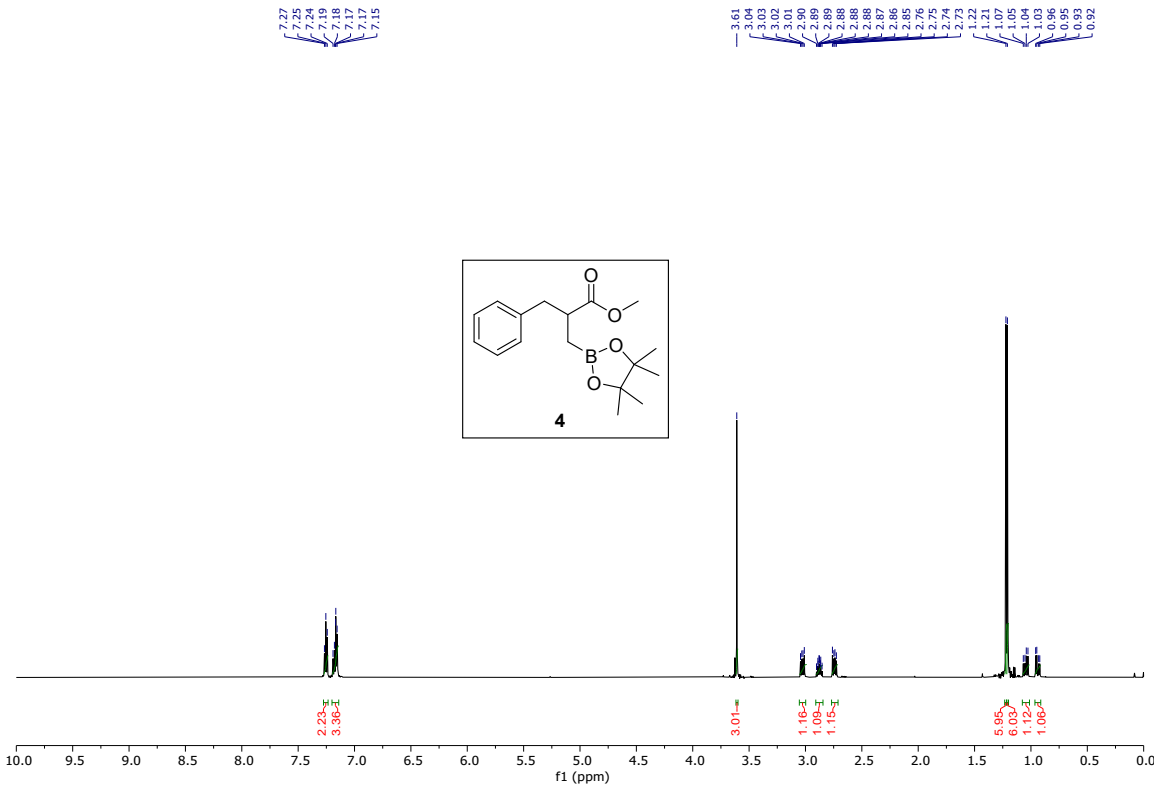
^{13}C{^{1}H} NMR (150 MHz) spectrum of **2ad** in $CDCl_3$



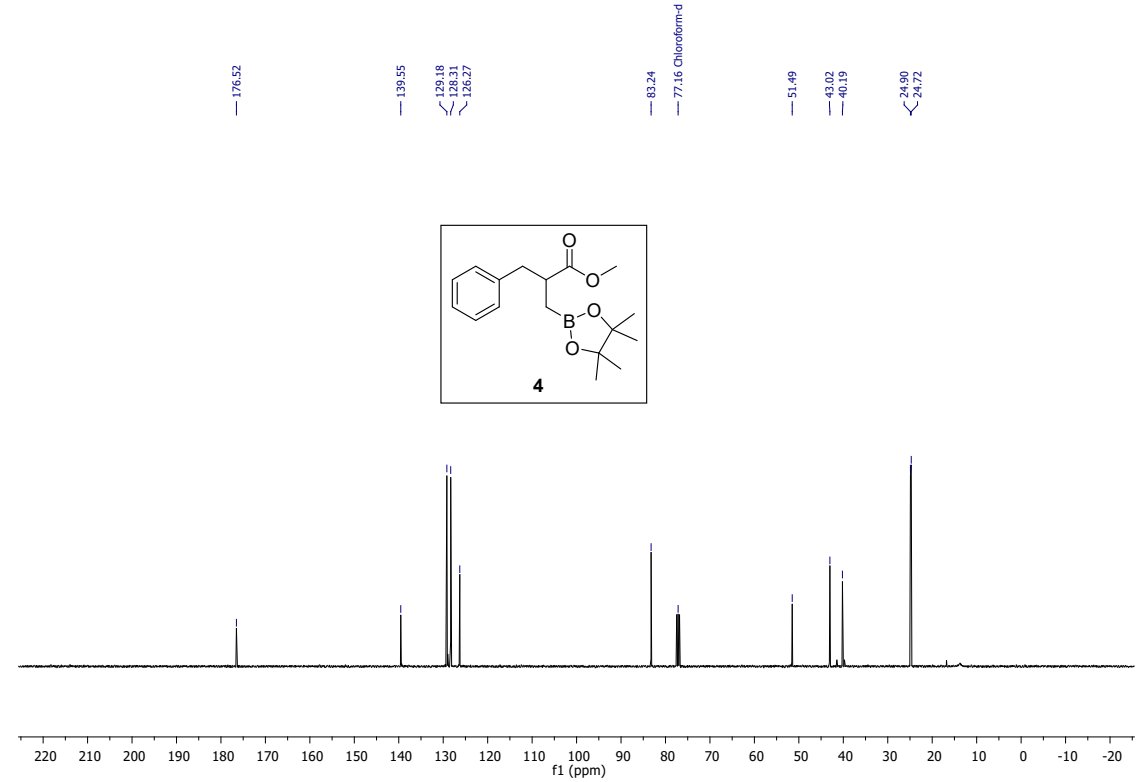
^{1}H NMR (400 MHz) spectrum of **2ad** in $CDCl_3$



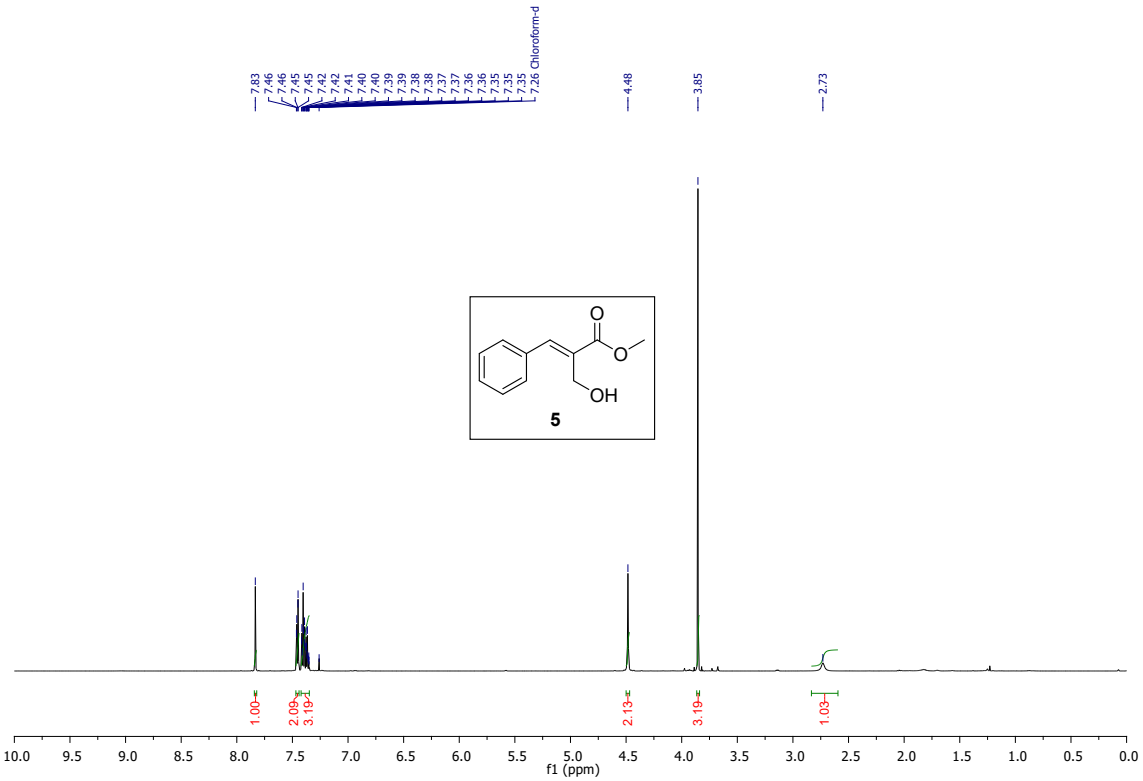
^{13}C{^{1}H} NMR (150 MHz) spectrum of **2ae** in $CDCl_3$



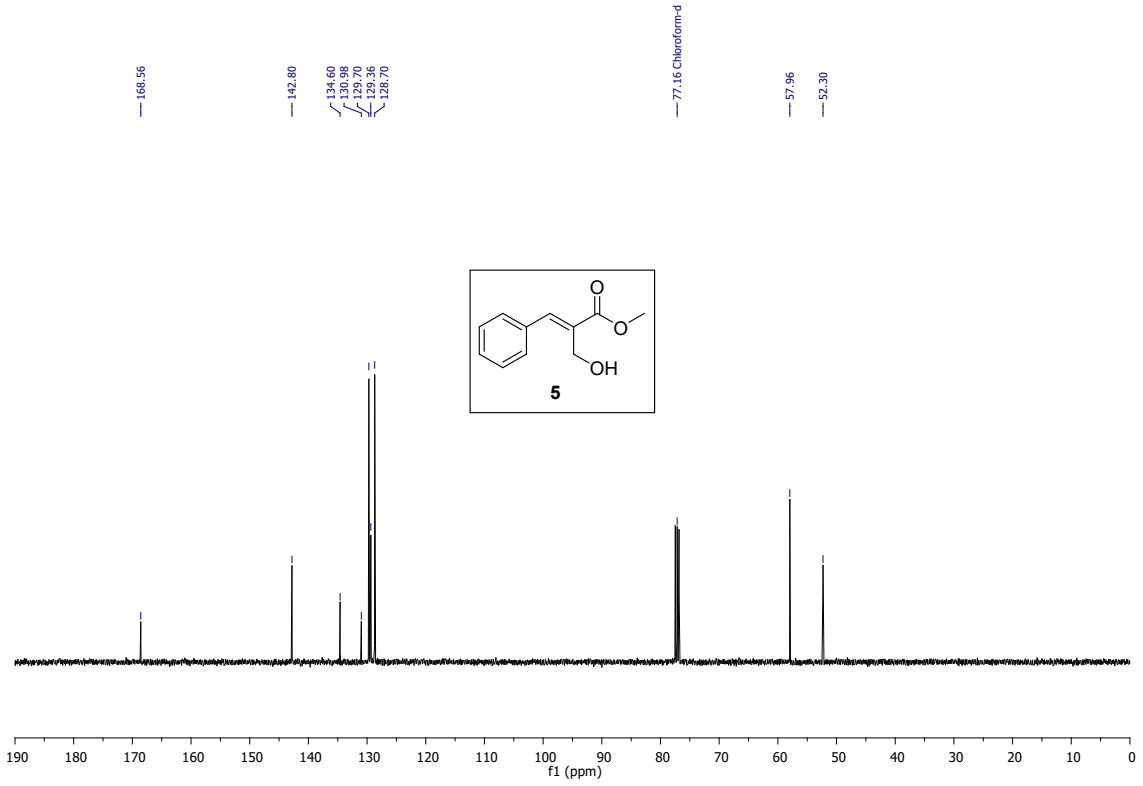
^{1}H NMR (400 MHz) spectrum of **4** in $CDCl_3$



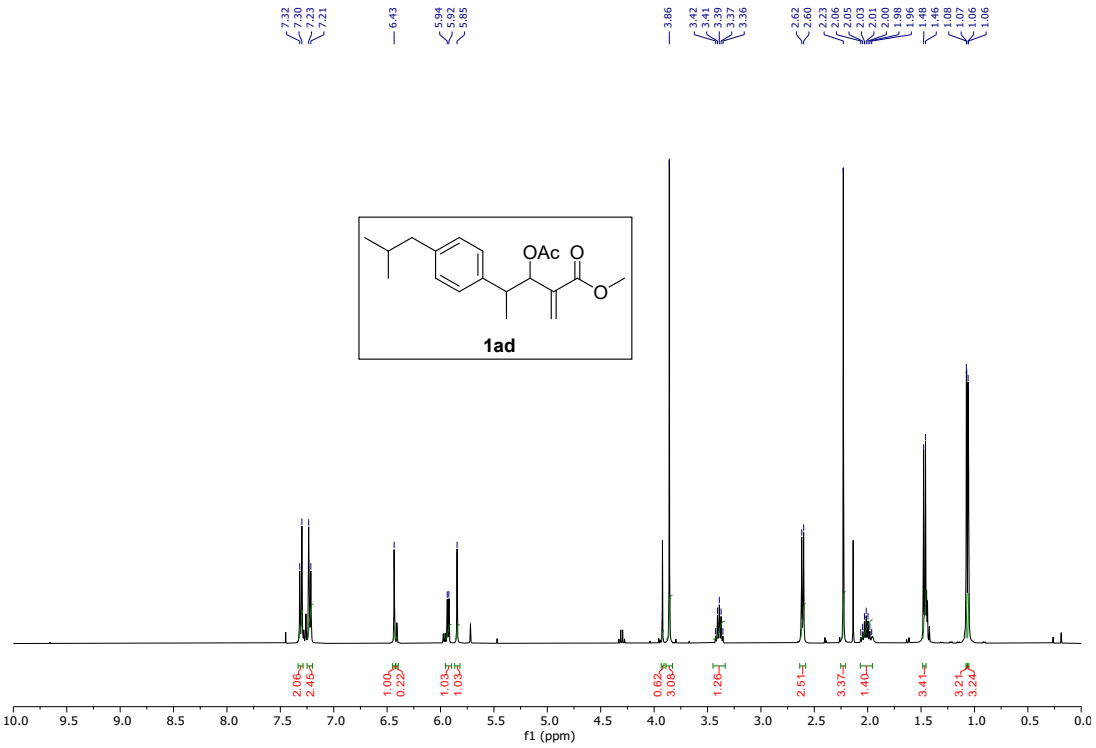
^{13}C{^{1}H} NMR (150 MHz) spectrum of **4** in $CDCl_3$



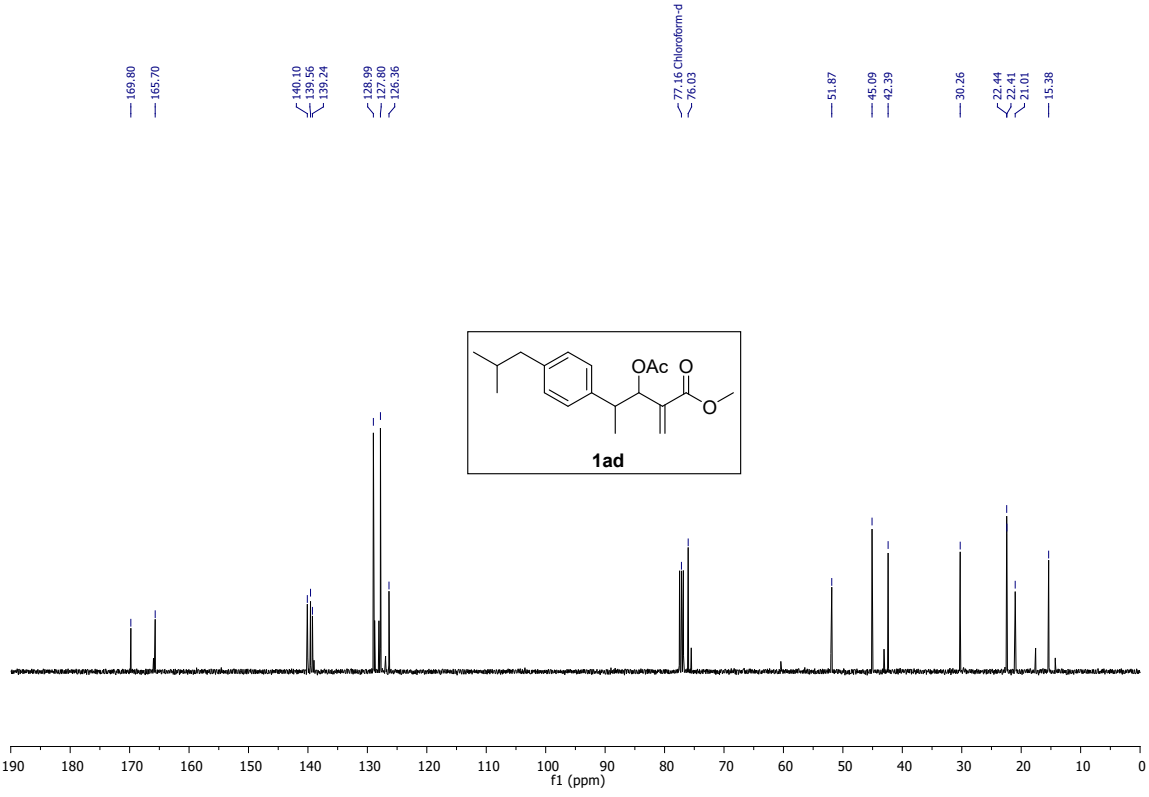
^{1}H NMR (400 MHz) spectrum of **5** in $CDCl_3$



^{13}C{^{1}H} NMR (150 MHz) spectrum of **5** in $CDCl_3$



^{1}H NMR (400 MHz) spectrum of **1ad** in $CDCl_3$



^{13}C{^{1}H} NMR (150 MHz) spectrum of **1ad** in $CDCl_3$

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