Regio- and stereoselective copper-catalyzed α,β-protoboration of allenoates: access to *Z*-β,γ-unsaturated β-boryl esters

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1. Materials and Methods

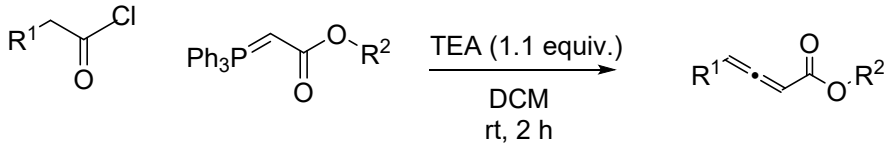
Reactions were performed using Schlenk technique under Argon or Nitrogen atmosphere. Chemicals were obtained from commercial sources unless otherwise noted. THF, $PhCH_3$, CH_2Cl_2 and CH_3CN were dried using the Innovative Technology Pure SolvMD solvent purification system. Column chromatography was performed using SiliaFlash P60 40-63 μm, 60 Å. TLC analyses were performed using Silicycle aluminum backed silica gel F-254 plates.

2. Instrumentation

NMR spectroscopic experiments were performed using an Agilent 400-MR 400 MHz, an Agilent U4-DD2 400 MHz, or a Bruker Avance II 500 MHz spectrometer. Chemical shifts are reported in δ ppm and ^1H and ^{13}C NMR are referenced to an internal standard ($CDCl_3$, CD_3OD, DMSO, TMS, or acetone-d_6). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, dt = doublet of triplets, td = triplet of doublets, tt = triplet of triplets, ddt = doublet of doublet of triplets, m = multiplet), coupling constants (Hz), and integration. ESI-HRMS were obtained on an Agilent 6220 accurate mass TOF LC/MS.

3. General Procedure for Preparing Allenoates

All allenoates were prepared in accordance with previous literature and references for the spectra of previously known allenoates are provided in Table S1.[1]



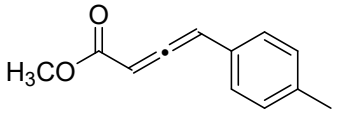
General Procedure 3.1 for Preparing Allenoates
A round bottom flask fixed with a stir bar was charged with methyl 2-(triphenyl-λ5-phosphaneylidene)acetate (3.88 mmol), TEA (4.27 mmol), and DCM (4 mL). A suspension of 2-phenylacetyl chloride (3.88 mmol) in DCM (2 mL) was added to the round bottom flask dropwise (1 drop every 5 seconds) at room temperature and the reaction was stirred overnight. The reaction mixture was concentrated *in vacuo* and the product purified via silica gel chromatography (5% ethyl acetate in hexanes) to afford the product as a yellow oil.

Table S1. References for Allenoate Substrates

Substrate	R^1	R^2	Reference
1a	H	CH_3	*Organic Syntheses*. 1984, 62, 202.
1h	4-Cl	CH_3	*Journal of Organic Chemistry*. 2009, 74, 3997.

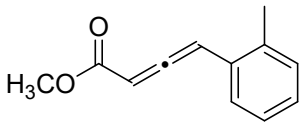
4. Characterization of Allenoates

methyl 4-(*p*-tolyl)buta-2,3-dienoate (1b)



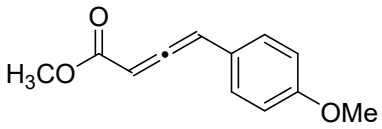
Prepared according to **Procedure 3.1**. Yellow oil (105 mg, 0.558 mmol, 27%). **^{1}H NMR** ($CDCl_3$, 400MHz) δ 7.20 (d, *J* = 8.0 Hz, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 6.60 (d, *J* = 8.0 Hz, 1H), 6.01 (d, *J* = 8.0 Hz, 1H), 3.76 (s, 3H), 2.35 (s, 3H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 214.9, 165.8, 138.3, 129.7, 128.1, 127.6, 98.7, 91.6, 52.3, 21.4. **HRMS** (ESI-TOF) m/z $[M+Na]^+$ Calcd for $C_{12}H_{12}NaO_2$, 211.0730; Found 211.0729.

methyl 4-(*o*-tolyl)buta-2,3-dienoate (1c)



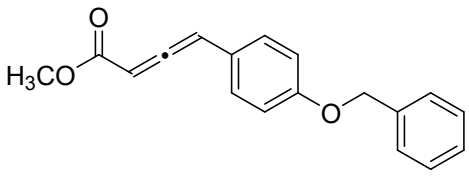
Prepared according to **Procedure 3.1**. Yellow oil. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.18 – 7.17 (m, 4H), 6.81 (d, *J* = 6.4 Hz, 1H), 5.99 (d, *J* = 6.4 Hz, 1H), 3.77 (s, 3H), 2.39 (s, 3H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 168.8, 140.4, 131.9, 129.3, 128.2, 125.4, 96.2, 90.7, 52.6, 26.6. **HRMS** (ESI-TOF) m/z $[M]^+$ Calc for $C_{12}H_{12}O_2$ 188.0837; Found 188.088.

methyl 4-(4-methoxyphenyl)buta-2,3-dienoate (1d)



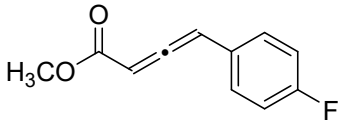
Prepared according to **Procedure 3.1**. Yellow oil (101 mg, 1.08 mmol, 45%). **^{1}H NMR** ($CDCl_3$, 400MHz) δ 7.23 (d, *J* = 8.0 Hz, 2H), 6.87 (d, *J* = 8.0 Hz, 2H), 6.59 (d, *J* = 8.0 Hz, 1H), 6.00 (d, *J* = 8.0 Hz, 1H), 3.81 (s, 3H), 3.76 (s, 3H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 214.7, 165.7, 159.6, 133.2, 128.7, 123.1, 114.4, 113.8, 98.2, 91.5, 55.3, 52.2. **HRMS** (ESI-TOF) m/z $[M+H]^+$ Calcd for $C_{12}H_{13}O_3$, 205.0859; Found 205.0866.

methyl 4-(4-(benzyloxy)phenyl)buta-2,3-dienoate (1e)



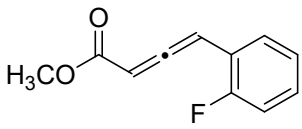
Prepared according to **Procedure 3.1**. Yellow oil (153 mg, 0.546 mmol, 24%). **^{1}H NMR** ($CDCl_3$, 400MHz) δ 7.43 – 7.36 (m, 5H), 7.23 (d, *J* = 8.0 Hz, 2H), 6.95 (d, *J* = 8.0 Hz, 2H), 6.59 (d, *J* = 8.0 Hz, 1H), 6.00 (d, *J* = 8.0 Hz, 1H), 5.07 (s, 2H), 3.76 (s, 3H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 214.7, 165.6, 158.8, 136.7, 133.2, 128.8, 128.6, 128.1, 127.4, 123.4, 115.4, 114.8, 98.2, 91.5, 70.06, 52.18. **HRMS** (ESI-TOF) m/z $[M+H]^+$ Calcd for $C_{18}H_{17}O_3$, 281.1172; Found 281.1172.

methyl 4-(4-fluorophenyl)buta-2,3-dienoate (1f)



Prepared according to **Procedure 3.1**. Yellow oil (101 mg, 1.08 mmol, 45%). **^{1}H NMR** ($CDCl_3$, 400MHz) δ 7.30 – 7.26 (m, 2H), 7.03 (t, *J* = 20.0 Hz, 2H), 6.60 (d, *J* = 8.0 Hz, 1H), 6.02 (d, *J* = 8.0 Hz, 1H), 3.77 (s, 3H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 214.7, 165.6, 162.7 (d, *J* = 248.0 Hz), 129.3 (d, *J* = 8.2 Hz), 127.1 (d, *J* = 3.4 Hz), 116.1 (d, *J* = 22.0 Hz), 98.0, 91.9, 52.4. **HRMS** (ESI-TOF) m/z $[M+Na]^+$ Calcd for $C_{11}H_9FNaNO_2$, 215.0479; Found 215.0482

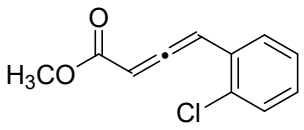
methyl 4-(2-fluorophenyl)buta-2,3-dienoate (1g)



Prepared according to **Procedure 3.1**. Yellow oil (263 mg, 1.37 mmol, 44%). **^{1}H NMR** ($CDCl_3$, 400MHz) δ 7.34 (t, J_{HF} = 16.0 Hz, 1H), 7.24

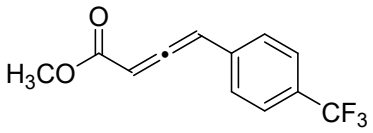
(q, *J* = 20.0 Hz, 1H), 7.13 – 7.04 (m, 2H), 6.83 (d, *J* = 8.0 Hz, 1H), 6.04 (d, *J* = 8.0 Hz, 1H), 3.77 (s, 3H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 215.2, 165.4, 159.8 (d, *J* = 251.3 Hz), 129.7 (d, *J* = 8.2 Hz), 128.9 (d, *J* = 3.0 Hz), 124.4 (d, *J* = 3.6 Hz), 118.9 (d, *J* = 12.2 Hz), 115.8 (d, *J* = 21.2 Hz), 91.5, 52.3. **HRMS** (ESI-TOF) m/z $[M+Na]^+$ Calcd for $C_{11}H_9FNaO_2$, 215.0479; Found 215.0482.

methyl 4-(2-chlorophenyl)buta-2,3-dienoate (1i)



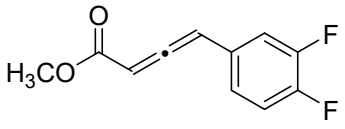
Prepared according to **Procedure 3.1**. Yellow oil (256 mg, 1.230 mmol, 39%). **^{1}H NMR** ($CDCl_3$, 400MHz) δ 7.34 (td, *J* = 4.0 Hz, 7.6 Hz, 1H), 7.28 – 7.22 (m, 1H), 7.12 (dd, *J* = 1.0 Hz, 8.0 Hz, 1H), 7.06 (m, 1H), 6.83 (d, *J* = 8.0 Hz, 1H), 6.04 (d, *J* = 8.0 Hz, 1H), 3.77 (s, 3H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 215.8, 165.8, 133.1, 130.4, 129.7, 129.7, 129.5, 127.5, 95.7, 92.3, 52.8. **HRMS** (ESI-TOF) m/z $[M+H]^+$ Calcd for $C_{11}H_{10}ClO_2$ 209.0364; Found 209.0359.

methyl 4-(4-(trifluoromethyl)phenyl)buta-2,3-dienoate (1j)



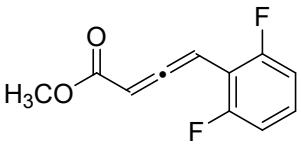
Prepared according to **Procedure 3.1**. Yellow oil (58 mg, 0.24 mmol, 11%). **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.59 (d, *J* = 8.2 Hz, 2H), 7.41 (d, *J* = 8.2 Hz, 2H), 6.66 (d, *J* = 6.4 Hz, 1H), 6.09 (d, *J* = 6.3 Hz, 1H), 3.78 (s, 3H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ *some peaks are not visible* 127.8, 125.9 (q, *J* = 3.8 Hz), 98.0, 92.3, 52.7. **HRMS** (ESI-TOF) m/z $[2M+H]^+$ Calcd for $C_{24}H_{19}F_6O_2$ 485.1188; Found 485.1126.

methyl 4-(3,4-difluorophenyl)buta-2,3-dienoate (1k)



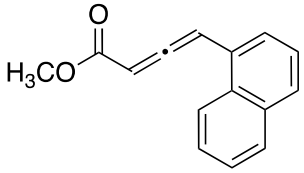
Prepared according to **Procedure 3.1**. Yellow oil (132 mg, 0.619 mmol, 39%). **^{1} HNMR** ($CDCl_3$, 400 MHz) δ 7.14 – 7.09 (m, 2H), 7.04 – 7.00 (m, 1H), 6.56 (d, *J* = 6.4 Hz, 1H), 6.05 (d, *J* = 7.5 Hz, 1H), 3.78 (s, 3H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 214.5, 165.2, 150.78 (dd, *J* = 248.2, 12.6 Hz), 150.31 (d, *J* = 237.4 Hz), 123.8 (dd, *J* = 6.4, 3.5 Hz), 117.9 (d, *J* = 17.6 Hz), 116.2 (d, *J* = 18.5 Hz), 97.5 (t, *J* = 1.9 Hz), 92.3, 52.5. **HRMS** (ESI-TOF) m/z $[M+H]^+$ Calcd for $C_{11}H_9F_2O_2$ 211.0564; Found 211.0562.

methyl 4-(2,6-difluorophenyl)buta-2,3-dienoate (1l)



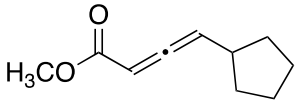
Prepared according to **Procedure 3.1**. Yellow oil (202 mg, 0.961 mmol, 37%). **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.21 (td, *J* = 4.0 Hz, 12.0 Hz, 1H), 6.89 (t, *J* = 16.0 Hz, 2H), 6.76 (dt, *J* = 2.8 Hz, 8.0 Hz, 1H), 5.97 (dd, *J* = 0.80 Hz, 8.0 Hz, 1H), 3.77 (s, 3H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 216.8, 165.5, 160.5 (dd, *J* = 7.0 Hz, 253.8 Hz), 129.2 (t, *J* = 10.4 Hz), 111.6 (d, *J* = 5.8 Hz), 111.4 (d, *J* = 5.8 Hz), 109.1 (t, *J* = 12.0 Hz), 89.9, 85.3 (t, *J* = 10.0 Hz), 52.3. **HRMS** (ESI-TOF) m/z $[M+H]^+$ Calcd for $C_{11}H_9F_2O_2$ 211.0564; Found 211.0563.

methyl 4-(naphthalen-2-yl)buta-2,3-dienoate (1m)



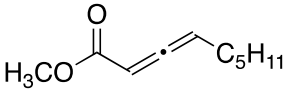
Prepared according to **Procedure 3.1**. Yellow oil (132 mg, 0.589 mmol, 48%). **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 8.39 (d, *J* = 8.3 Hz, 1H), 7.83 (t, *J* = 8.9 Hz, 2H), 7.68 (d, *J* = 7.0 Hz, 1H), 7.54 (dt, *J* = 25.3, 8.0 Hz, 3H), 7.44 – 7.38 (m, 1H), 3.83 (s, 3H), 3.68 (s, 2H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 215.8, 168.9, 133.7, 133.3, 130.5, 128.8, 128.3, 126.9, 126.5, 126.4, 125.3, 120.7, 86.0, 81.9, 52.9, 26.9. **HRMS** (ESI-TOF) m/z $[M+H]^+$ Calcd for $C_{15}H_{12}O_2$ 225.0910; Found 225.0909.

methyl 4-cyclopentylbuta-2,3-dienoate (1n)



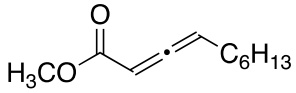
Prepared according to **Procedure 3.1**. Yellow oil (316 mg, 1.90 mmol, 58%). **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 5.68 – 5.64 (m, 1H), 5.60 (dd, *J* = 6.1, 2.9 Hz, 1H), 3.73 (s, 3H), 2.66 – 2.55 (m, 1H), 1.92 – 1.76 (m, 2H), 1.73 – 1.64 (m, 2H), 1.62 – 1.53 (m, 2H), 1.49 – 1.37 (m, 2H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 211.8, 166.9, 100.4, 88.7, 52.1, 38.3, 32.7, 32.7, 24.8, 24.8. **HRMS** (ESI-TOF) m/z $[M+H]^+$ Calcd for $C_{10}H_{15}O_2$ 167.1067; Found 167.1047.

methyl nona-2,3-dienoate (1o)



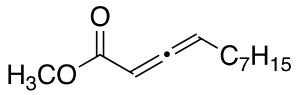
Prepared according to **Procedure 3.1**. Yellow oil (96 mg, 0.49 mmol, 39%). **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 5.65 – 5.54 (m, 1H), 3.74 (d, *J* = 0.9 Hz, 3H), 3.26 (t, *J* = 2.4 Hz, 1H), 2.24 – 2.06 (m, 2H), 1.55 – 1.40 (m, 2H), 1.40 – 1.25 (m, 4H), 0.96 – 0.82 (m, 3H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 212.5, 166.9, 95.6, 88.0, 52.1, 31.3, 28.5, 27.6, 22.5, 14.2. **HRMS** (ESI-TOF) m/z $[M+H]^+$ Calcd for $C_{10}H_{17}O_2$ 169.1229; Found 169.1225.

methyl deca-2,3-dienoate (1p)



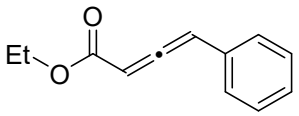
Prepared according to **Procedure 3.1**. Yellow oil (201 mg, 1.02 mmol, 67%). **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 5.65 – 5.56 (m, 1H), 3.73 (s, 3H), 3.26 (t, *J* = 2.5 Hz, 1H), 2.22 – 2.09 (m, 2H), 1.52 – 1.39 (m, 2H), 1.38 – 1.23 (m, 6H), 0.92 – 0.85 (m, 3H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 212.5, 166.9, 95.6, 88.0, 52.1, 31.7, 28.8, 27.6, 22.7, 18.9, 14.2. **HRMS** (ESI-TOF) m/z $[M+H]^+$ Calcd for $C_{11}H_{19}O_2$ 183.1385; Found 183.1383.

methyl undeca-2,3-dienoate (1q)



Prepared according to **Procedure 3.1**. Yellow oil (126 mg, 1.41 mmol, 43%). **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 5.63 – 5.55 (m, 1H), 3.73 (d, *J* = 1.1 Hz, 3H), 3.26 (td, *J* = 2.4, 1.0 Hz, 1H), 2.23 – 2.07 (m, 2H), 1.55 – 1.40 (m, 2H), 1.40 – 1.20 (m, 8H), 0.92 – 0.83 (m, 3H).**^{13}C NMR** ($CDCl_3$, 100 MHz) δ 212.5, 166.7, 95.6, 88.0, 52.1, 31.9, 29.0, 28.8, 27.6, 22.8, 18.9, 14.2. **HRMS** (ESI-TOF) m/z $[M+H]^+$ Calcd for $C_{12}H_{21}O_2$ 197.1542; Found 197.1533.

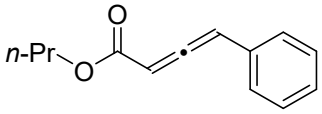
ethyl 4-phenylbuta-2,3-dienoate (3a)



Prepared according to **Procedure 3.1**. Yellow oil (120 mg, 0.638 mmol, 14%). **^{1}H NMR** ($CDCl_3$, 400MHz) δ 7.36 – 7.27 (m, 5H), 6.62 (d, *J* = 8.0 Hz, 1H), 6.01 (d, *J* = 8.0 Hz, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 1.29 (t, *J* = 16.0 Hz, 3H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 214.6, 165.1, 131.8,

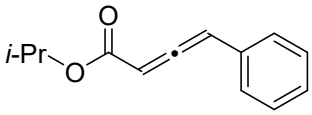
131.2, 128.8, 128.2, 128.1, 127.5, 98.7, 91.9, 61.1, 14.2. **HRMS** (ESI-TOF) m/z $[M+H]^+$ Calcd for $C_{12}H_{13}O_2$ 189.0910; Found 189.0906.

propyl 4-phenylbuta-2,3-dienoate (3b)



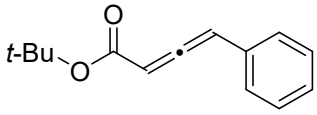
Prepared according to **Procedure 3.1**. Yellow oil. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.31 – 7.20 (m, 5H), 6.57 (d, *J* = 8.0 Hz, 1H), 5.97 (d, *J* = 8.0 Hz, 1H), 4.08 (m, 2H), 1.68 – 1.58 (m, 2H), 0.89 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 214.7, 165.2, 131.8, 131.3, 129.0, 128.2, 127.6, 98.7, 91.9, 66.7, 26.8, 22.0, 10.4. **HRMS** (ESI-TOF) m/z $[M+H]^+$ Calcd for $C_{13}H_{15}O_2$ 203.1067; Found 203.1069.

isopropyl 4-phenylbuta-2,3-dienoate (3c)



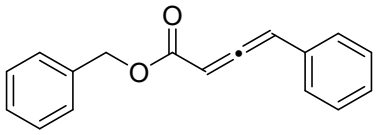
Prepared according to **Procedure 3.1**. Yellow oil (50 mg, 0.25 mmol, 10%). **^{1}H NMR** ($CDCl_3$, 400MHz) δ 7.34 – 7.26 (m, 5H), 6.59 (d, *J* = 8.0 Hz, 1H), 5.97 (d, *J* = 8.0 Hz, 1H), 5.12 – 5.03 (m, 1H), 1.27 – 1.22 (m, 6H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 214.5, 164.6, 131.7, 131.3, 128.8, 128.0, 127.5, 98.6, 92.3, 68.6, 21.8. **HRMS** (ESI-TOF) m/z $[M+NH_4]^+$ Calcd for $C_{13}H_{18}NO_2$ 220.1332; Found 220.1329.

***tert*-butyl 4-phenylbuta-2,3-dienoate (3d)**



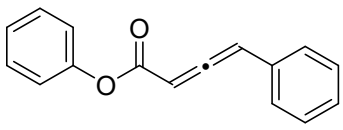
Prepared according to **Procedure 3.1**. Yellow oil (150 mg, 0.694 mmol, 18%). **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.33 – 7.26 (m, 5H), 6.56 (d, *J* = 8.0 Hz, 1H), 5.01 (d, *J* = 8.0 Hz, 1H), 1.47 (s, 9H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 214.1, 164.3, 131.7, 131.5, 128.8, 128.1, 128.0, 127.4, 98.4, 93.4, 81.3, 28.1. **HRMS** (ESI-TOF) m/z $[2M+K]^+$ Calcd for $C_{28}H_{32}KO_4$ 471.1932; Found 471.1930.

benzyl 4-phenylbuta-2,3-dienoate (3e)



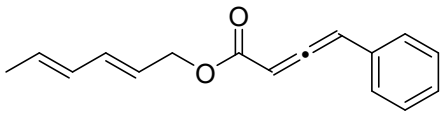
Prepared according to **Procedure 3.1**. Yellow oil (440 mg, 1.76 mmol, 45%). **^{1}H NMR** ($CDCl_3$, 400MHz) δ 7.39 – 7.27 (m, 10H), 6.65 (d, *J* = 8.0 Hz, 1H), 6.07 (d, *J* = 8.0 Hz, 1H), 5.22 (s, 2H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 215.0, 164.9, 135.9, 131.8, 131.0, 128.9, 128.6, 128.5, 128.3, 128.2, 128.1, 128.0, 127.5, 98.9, 91.7, 81.3, 66.7. **HRMS** (ESI-TOF) m/z $[M+H]^+$ Calcd for $C_{17}H_{15}O_2$, 251.1067; Found 251.1064.

phenyl 4-phenylbuta-2,3-dienoate (3f)



Prepared according to **Procedure 3.1**. Yellow oil (613 mg, 3.88 mmol, 67%). **^{1}H NMR** ($CDCl_3$, 400MHz) δ 7.30 – 7.26 (m, 5H), 7.22 – 7.17 (m, 2H), 7.15 - 7.11 (m, 1H), 7.05 (d, *J* = 8.0 Hz, 2H), 6.63 (d, *J* = 8.0 Hz, 1H), 6.11 (d, *J* = 8.0 Hz, 1H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 215.6, 165.6, 163.3, 150.6, 131.6, 130.5, 129.2, 128.7, 128.1, 127.4, 125.7, 121.3, 98.9, 91.3. **HRMS** (ESI-TOF) m/z $[M+H]^+$ Calcd for $C_{16}H_{13}O_2$, 237.0910; Found 237.0907.

(2*E*,4*E*)-hexa-2,4-dien-1-yl 4-phenylbuta-2,3-dienoate (3g)



Prepared according to **Procedure 3.1**. Yellow oil (128 mg, 0.533 mmol, 13%). **^{1}H NMR** ($CDCl_3$, 400MHz) δ 7.36 – 7.27 (m, 5H), 6.63 (d, *J* = 8.0 Hz, 1H), 6.25 (q, *J* = 8.0 Hz, 1H), 6.08 – 6.01 (m, 2H), 5.80 – 5.61 (m, 2H), 4.67 (d, *J* = 8.0 Hz, 2H), 1.76 (d, *J* = 8.0 Hz, 3H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 214.8, 164.8, 135.4, 134.9, 131.8, 131.3, 131.1, 130.4, 128.8, 128.1, 127.5, 123.5, 98.7, 91.8, 65.5, 18.1. **HRMS** (ESI-TOF) m/z $[2M+NH_4]^+$ Calcd for $C_{32}H_{36}NO_4$, 498.2639; Found 498.2589.

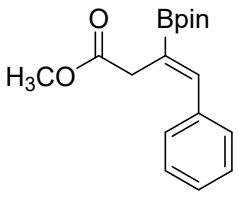
5. General Procedure for Preparing (*Z*)-acrylates

Procedure 5.1 Copper(I) chloride (7.62 mg, 0.0770 mmol) and B_2pin_2 (215 mg, 0.847 mmol) were added to a 2-dram vial and purged with N_2 *via* Schlenk technique. MeOH (0.40 mL) was added and the suspension stirred for 15 min at 60 ºC, producing a light yellow/brown mixture. A solution of the dienoate (0.770 mmol) in MeOH (0.30 mL) was added, then additional MeOH (0.10 mL) was used to transfer any residual reagent. The reaction was stirred at 60 ºC and monitored by TLC until the starting material was consumed (16-20 hours). The crude mixture was concentrated *in vacuo* and purified by silica gel chromatography (eluted with 0-10% gradient ethyl acetate in hexanes) to afford the product as a yellow oil.

Procedure 5.2 Copper(I) chloride (23.0 mg, 0.234 mmol) and B_2pin_2 (218 mg, 0.858 mmol) were added to a 2-dram vial and purged with N_2 *via* Schlenk technique. MeOH (0.40 mL) was added and the suspension stirred for 15 min at 60 ºC, producing a light yellow/brown mixture. Methyl 4-(naphthalen-2-yl)buta-2,3-dienoate (175 mg, 0.780 mmol) dissolved in MeOH (0.30 mL) was added, then additional MeOH (0.10 mL) was used to transfer any residual reagent. The reaction was stirred at 60 ºC and monitored by TLC until the starting material was consumed (72 hours). The crude mixture was concentrated *in vacuo* and purified by silica gel chromatography (eluted with 0-10% gradient ethyl acetate in hexanes) to afford the product as a yellow oil.

6. Characterization of *Z*-acrylates

methyl (*Z*)-4-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-enoate (2a)

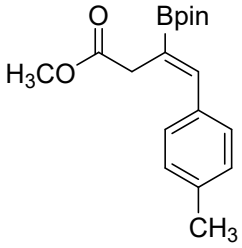


Prepared according to **Procedure 5.1**. Yellow oil (174 mg, 0.576 mmol, 76%, >1:99 E/Z). **^{1}H NMR** (CD_2Cl_2, 400MHz) δ 7.36 – 7.33 (m, 3H), 7.30 – 7.26 (m, 3H), 3.65 (s, 3H), 3.37 (d, *J* = 1.30 Hz, 2H), 1.28 (s, 12H). **^{13}C NMR** (CD_2Cl_2, 100 MHz) δ 173.2, 144.5, 137.5, 129.4, 128.9, 128.2, 84.3, 52.2, 35.4, 25.1. **^{11}B NMR** (CD_2Cl_2, 160 MHz) δ 32.2. **HRMS** (ESI-TOF) m/z $[M+H]^+$ Calcd for $C_{17}H_{24}BO_4$ 303.1765; Found 303.1763.

1.09 g-scale reaction: Copper(I) chloride (62.0 mg, 0.626 mmol) and B_2pin_2 (1.75 g, 6.88 mmol) were added to a 50 mL round bottom flask and purged with N_2 *via* Schlenk technique. MeOH (3.00 mL) was added and the suspension stirred for 30 min at 60 ºC, producing a light yellow/brown mixture. Methyl 4-phenylbuta-2,3-dienoate (1.09 g, 6.26 mmol) dissolved in MeOH (2.00 mL) was added, washing once more with MeOH (1.00 ml), and the reaction was stirred at 60 ºC and followed by TLC until the starting material was consumed (typically 16-20 hours). The contents were then concentrated by rotary evaporation and purified by silica gel

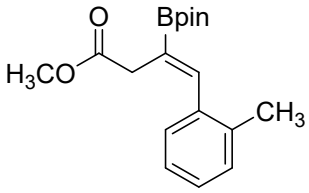
chromatography (eluted with 0-10% gradient ethyl acetate in hexanes) to afford the product as a yellow oil in a 66% yield.

methyl (*Z*)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4-(*p*-tolyl)but-3-enoate (2b)



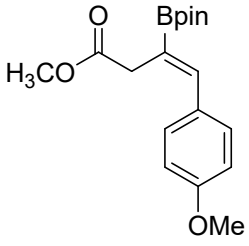
Prepared according to **Procedure 5.1**. Yellow oil (115 mg, 0.364 mmol, 69%, >1:99 E/Z). **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.36 (s, 1H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 3.67 (s, 3H), 3.42 (d, *J* = 1.20 Hz, 2H), 1.30 (s, 12H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 172.8, 142.2, 137.5, 134.0, 128.9, 128.9, 83.7, 51.7, 35.0, 24.7, 21.2. **^{11}B NMR** ($CDCl_3$, 160 MHz) δ 30.3. **HRMS** (ESI-TOF) m/z $[M+H]^+$ Calcd for $C_{18}H_{26}BO_4$, 317.1922; Found 317.1917.

methyl (*Z*)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4-(*o*-tolyl)but-3-enoate (2c)



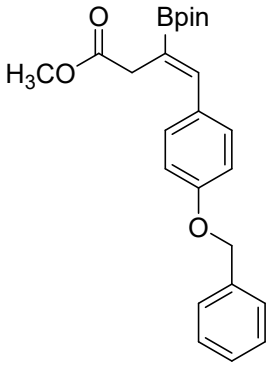
Prepared according to **Procedure 5.1**. Yellow oil (63 mg, 0.20 mmol, 29%, >1:99 E/Z). **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.40 (s, 1H), 7.19 – 7.08 (m, 4H), 3.65 (s, 3H), 3.24 (d, *J* = 1.20 Hz, 2H), 2.26 (s, 3H), 1.31 (s, 12H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 173.4, 144.3, 136.8, 136.8, 130.3, 129.1, 128.1, 125.9, 84.2, 52.1, 35.5, 25.2, 20.3. **^{11}B NMR** ($CDCl_3$, 160 MHz) δ 30.4. **HRMS** $[M+H]^+$ Calcd for $C_{18}H_{26}BO_4$ 317.1924; Found 317.1920.

methyl (*Z*)-4-(4-methoxyphenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-enoate (2d)



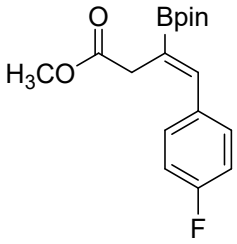
Prepared according to **Procedure 5.1**. Yellow oil (83 mg, 0.25 mmol, 73%, >1:99 E/Z). **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.32 (s, 1H), 7.29 – 7.23 (m, 2H), 7.03 (t, *J* = 8.0 Hz, 2H), 3.67 (s, 3H), 3.37 (d, *J* = 1.20 Hz, 2H), 1.29 (s, 12H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 172.5, 142.9, 135.3, 133.5, 130.2, 128.5, 127.9, 83.8, 51.8, 34.9, 24.7. **^{11}B NMR** ($CDCl_3$, 160 MHz) δ 30.4. **HRMS** (ESI-TOF) m/z $[M+H]^+$ Calcd for $C_{18}H_{26}BO_4$, 333.1871; Found 333.1876.

methyl (*Z*)-4-(4-(benzyloxy)phenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-enoate (2e)



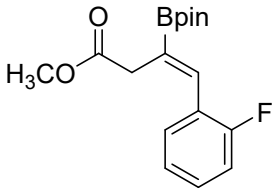
Prepared according to **Procedure 5.1**. Yellow oil (140 mg, 0.334 mmol, 79%, >1:99 E/Z). **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.45 – 7.37 (m, 4H), 7.35 – 7.31 (m, 2H), 7.28 – 7.25 (m, 2H), 6.95 (d, *J* = 8.0 Hz, 2H), 5.07 (s, 2H), 3.68 (s, 3H), 3.43 (d, *J* = 1.20 Hz, 2H), 1.30 (s, 12H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 173.4, 158.8, 144.3, 137.3, 130.9, 130.2, 129.1, 128.5, 127.9, 115.1, 84.12, 70.4, 52.2, 35.5, 25.2. **^{11}B NMR** ($CDCl_3$, 160 MHz) δ 30.4. **HRMS** (ESI-TOF) m/z $[M+H]^+$ Calcd for $C_{24}H_{30}BO_5$, 409.2185; Found 409.2191

methyl (*Z*)-4-(4-fluorophenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-enoate (2f)



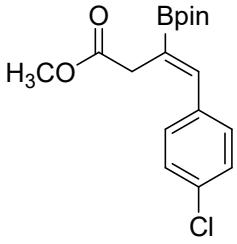
Prepared according to **Procedure 5.1**. Yellow oil (145mg, 0.453 mmol, 75%, >1:99 E/Z). **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.33 (s, 1H), 7.29 – 7.23 (m, 2H), 7.03 (t, *J* = 16.0 Hz, 2H), 3.67 (s, 3H), 3.37 (d, *J* = 1.20 Hz, 2H), 1.29 (s, 12H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 172.8, 162.3 (d, *J* = 247.6 Hz), 143.2, 133.1 (d, *J* = 3.0 Hz), 130.8 (d, *J* = 8.1 Hz), 115.4 (d, *J* = 21.4 Hz), 83.9, 51.9, 35.0, 24.9. **^{11}B NMR** ($CDCl_3$, 160 MHz) δ 30.4. **HRMS** (ESI-TOF) m/z $[M+H]^+$ Calcd for $C_{17}H_{23}O_4FB$ 321.1673; Found 321.1701.

methyl (*Z*)-4-(2-fluorophenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-enoate (2g)



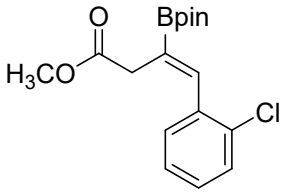
Prepared according to **Procedure 5.1**. Yellow oil (160 mg, 0.500 mmol, 81%, >1:99 E/Z). **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.32 (s, 1H), 7.23 (t, *J* = 16.0 Hz, 2H), 7.10 – 7.01 (m, 2H), 3.65 (s, 3H), 3.29 (s, 2H), 1.28 (s, 12H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 172.7, 160.1 (d, *J* = 248.1 Hz), 136.9 (d, *J* = 2.02 Hz), 130.6 (d, *J* = 3.4 Hz), 129.6 (d, *J* = 8.2 Hz), 124.7 (d, *J* = 15.0 Hz), 123.9 (d, *J* = 3.0 Hz), 115.7 (d, *J* = 22.1 Hz), 83.9, 51.9, 35.6, 24.8. **^{11}B NMR** ($CDCl_3$, 160 MHz) δ 30.2. **HRMS** (ESI-TOF) m/z $[M+H]^+$ Calcd for $C_{17}H_{23}O_4FB$, 321.1673; Found 321.1701.

methyl (*Z*)-4-(4-chlorophenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-enoate (2h)



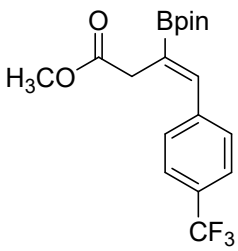
Prepared according to **Procedure 5.1**. Yellow oil (67 mg, 0.200 mmol, 70% >1:99 E/Z). **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.32 – 7.29 (m, 3H), 7.22 (d, *J* = 8.0 Hz, 2H), 3.68 (s, 3H), 3.36 (d, *J* = 1.20 Hz, 2H), 1.30 (s, 12H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 172.8, 163.5, 161.1, 143.2, 133.1, 130.8, 130.7, 115.5, 115.3, 83.9, 51.9, 35.0, 24.9. **^{11}B NMR** ($CDCl_3$, 160 MHz) δ 30.3. **HRMS** (ESI-TOF) m/z $[M+H]^+$ Calcd for $C_{17}H_{23}BClO_4$, 337.1376; Found 337.1381.

methyl (*Z*)-4-(2-chlorophenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-enoate (2i)



Prepared according to **Procedure 5.1**. Yellow oil (165 mg, 0.448 mmol, 66%, >1:99 E/Z). **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.41 – 7.36 (m, 2H), 7.24 – 7.18 (m, 3H), 3.67 (s, 3H), 3.26 (d, *J* = 1.40 Hz, 2H), 1.30 (s, 12H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 172.7, 141.4, 135.5, 133.7, 130.5, 129.6, 129.0, 126.5, 84.0, 51.9, 35.4, 24.9. **^{11}B NMR** ($CDCl_3$, 160 MHz) δ 30.3. **HRMS** (ESI-TOF) m/z $[M+H]^+$ Calcd for $C_{17}H_{23}BO_4Cl$, 337.1378; Found 337.1371.

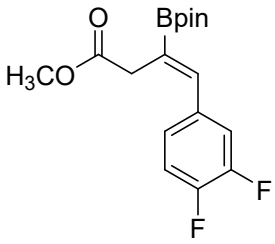
methyl (*Z*)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4-(4-(trifluoromethyl)phenyl)but-3-enoate (2j)



Prepared according to **Procedure 5.1**. Yellow oil (8.0 mg, 0.0216 mmol, 65%, >1:99 E/Z) **^{1}H NMR** ($CDCl_3$, 400MHz) δ 7.60 (d, *J* = 8.0 Hz, 2H), 7.38 (d, *J* = 8.0 Hz, 3H), 7.10 – 7.01 (m, 2H), 3.65 (s, 3H), 3.29(s, 2H), 1.28

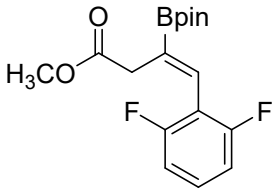
(s, 12H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ *some peaks are not visible* 172.4, 142.5, 129.0, 125.2 (q, J = 3.80 Hz), 84.0, 51.8, 34.9, 24.7. **^{11}B NMR** ($CDCl_3$, 160 MHz) δ 30.5. **HRMS** (ESI-TOF) m/z $[M+H]^+$ Calcd for $C_{18}H_{23}BF_3O_4$ 371.1641; Found 371.1673.

methyl (*Z*)-4-(3,4-difluorophenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-enoate (2k)



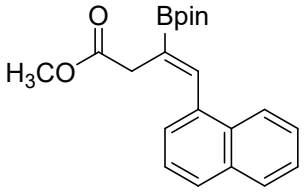
Prepared according to **Procedure 5.1**. Yellow oil (14 mg, 0.41 mmol, 81%, >1:99 E/Z). **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.16 – 7.09 (m, 3H), 7.02 – 7.00 (m, 1H), 3.69 (s, 3H), 3.36 (d, J = 1.20 Hz, 2H), 1.30 (s, 12H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ *some carbons are not visible* 172.6, 158.9, 158.7, 142.3, 139.4, 84.3, 52.3, 35.2, 25.1. **^{11}B NMR** ($CDCl_3$, 160 MHz) δ 30.4. **HRMS** (ESI-TOF) m/z $[M+Na]^+$ Calcd for $C_{17}H_{21}BF_2O_4Na$ 361.1399; Found 361.1360.

methyl (*Z*)-4-(2,6-difluorophenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-enoate (2l)



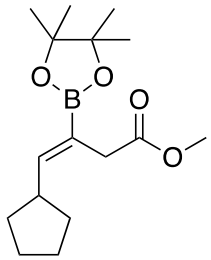
Prepared according to **Procedure 5.1**. Yellow oil (187 mg, 0.553 mmol, 59%, >1:99 E/Z). **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.25 – 7.19 (m, 1H), 7.04 (s, 1H), 6.88 (t, J = 16.0 Hz, 2H), 3.64 (s, 3H), 3.17 (d, J = 1.20 Hz, 2H), 1.30 (s, 12H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 172.3, 160.2 (dd, J = 249.3, 7.8 Hz), 129.9, 129.5 (t, J = 10.3 Hz), 114.1 (t, J = 20.2 Hz), 111.5 (d, J = 6.6 Hz), 111.3 (d, J = 6.6 Hz), 84.1, 51.8, 36.9, 24.9. **^{11}B NMR** ($CDCl_3$, 160 MHz) δ 30.0. **HRMS** (ESI-TOF) m/z $[M+H]^+$ Calcd for $C_{17}H_{22}BF_2O_4$ 339.1579; Found 339.1542.

methyl (*Z*)-4-(naphthalen-1-yl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-enoate (2m)



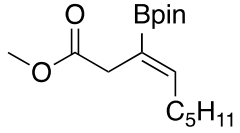
Prepared according to **Procedure 5.2**. Yellow oil (50 mg, 0.140 mmol, 18%, >1:99 *E/Z*). **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.98 – 7.95 (m, 1H), 7.86 – 7.84 (m, 2H), 7.79 (d, J = 8.3 Hz, 1H), 7.51 – 7.47 (m, 2H), 7.46 – 7.43 (m, 1H), 7.33 (dt, J = 7.1, 1.2 Hz, 1H), 3.64 (s, 3H), 3.28 (d, J = 1.2 Hz, 2H), 1.36 (s, 12H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 173.8, 134.8, 133.9, 131.9, 128.8, 128.4, 126.6, 126.4, 126.4, 125.7, 125.6, 84.3, 52.1, 35.8, 25.2. **^{11}B NMR** ($CDCl_3$, 160 MHz) δ 30.4. **HRMS** (ESI-TOF) m/z $[M+H]^+$ Calcd for $C_{21}H_{26}BO_4$ 353.1922; Found 353.1927.

methyl (*Z*)-4-cyclopentyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-enoate (2n)



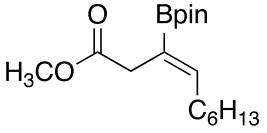
Prepared according to **Procedure 5.1**. Yellow oil (168 mg, 0.571 mmol, 66%, 2:98 *E/Z*). **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 6.35 (d, J = 9.3 Hz, 1H), 3.64 (s, 3H), 3.20 (s, 2H), 2.76 – 2.70 (m,1H) 1.83 – 1.73 (m, 3H), 1.70 – 1.64 (m, 2H), 1.59 – 1.52 (m, 3H), 1.25 (s, 12H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 173.2, 153.7, 83.5, 51.7, 39.6, 33.3, 25.7, 25.2, 24.8. **^{11}B NMR** ($CDCl_3$, 160 MHz) δ 30.3. **HRMS** (ESI-TOF) m/z $[M+H]^+$ Calcd for $C_{16}H_{28}BO_4$ 295.2081; Found 295.2062.

methyl (*Z*)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)non-3-enoate (2o)



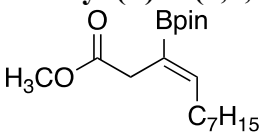
Prepared according to **Procedure 5.1**. Yellow oil (72 mg, 0.24 mmol, 43%, 3:97 *E/Z*). **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 6.45 (t, *J* = 7.1 Hz, 1H), 3.64 (s, 3H), 3.21 – 3.17 (m, 2H), 2.12 (q, *J* = 7.3 Hz, 2H), 1.42 – 1.37 (m, 2H), 1.31 – 1.27 (m, 4H), 1.25 (s, 12H), 0.90 – 0.86 (m, 3H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 167.2, 148.9, 83.5, 51.8, 33.9, 31.7, 29.0, 28.6, 24.9, 22.7, 14.2. **^{11}B NMR** ($CDCl_3$, 160 MHz) δ 27.7. **HRMS** (ESI-TOF) m/z $[M+H]^+$ Calcd for $C_{16}H_{30}BO_4$ 297.2237; Found 297.2239.

methyl (*Z*)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)dec-3-enoate (2p)



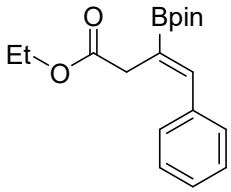
Prepared according to **Procedure 5.1**. Yellow oil (102 mg, 0.329 mmol, 60%, 6:94 *E/Z*). **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 6.44 (t, *J* = 7.2 Hz, 1H), 3.64 (s, 3H), 3.18 (d, *J* = 1.2 Hz, 2H), 2.12 (q, *J* = 7.3 Hz, 2H), 1.42 – 1.37 (m, 2H), 1.28 (d, *J* = 10.6 Hz, 6H), 1.25 (s, 12H), 0.89 – 0.85 (m, 3H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 173.0, 148.9, 83.5, 51.7, 33.9, 31.9, 29.3, 29.1, 28.9, 24.8, 22.7, 14.2. **^{11}B NMR** ($CDCl_3$, 160 MHz) δ 30.2. **HRMS** (ESI-TOF) m/z $[M+H]^+$ Calcd for $C_{17}H_{32}BO_4$ 311.2394; Found 311.2395.

methyl (*Z*)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)undec-3-enoate (2q)



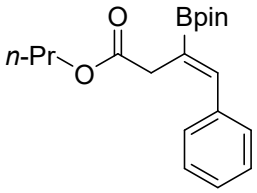
Prepared according to **Procedure 5.1**. Yellow oil (98 mg, 0.30 mmol, 49%, 4:96 *E/Z*). **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 6.43 (tt, *J* = 7.2, 1.3 Hz, 1H), 3.63 (s, 3H), 3.17 (d, *J* = 1.3 Hz, 2H), 2.11 (q, *J* = 7.3 Hz, 2H), 1.43 – 1.35 (m, 2H), 1.24 (s, 20H), 0.90 – 0.83 (m, 3H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 172.9, 148.9, 83.5, 51.7, 33.9, 31.9, 29.5, 29.3, 29.0, 28.9, 24.8, 22.8, 14.2. **^{11}B NMR** ($CDCl_3$, 160 MHz) δ 30.0. **HRMS** (ESI-TOF) m/z $[M+H]^+$ Calcd for $C_{18}H_{34}BO_4$ 325.2550; Found 325.2545.

ethyl (*Z*)-4-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-enoate (4a)



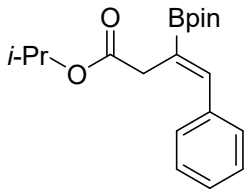
Prepared according to **Procedure 5.1**. Yellow oil (108 mg, 0.510 mmol, 65%, >1:99 *E/Z*). **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.40 (s, 1H), 7.34 – 7.24 (m, 5H), 4.15 (q, *J* = 7.2 Hz, 2H), 3.40 (d, *J* = 1.20 Hz, 2H), 1.31 (s, 12H), 1.26 (t, *J* = 12.0 Hz, 3H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 172.5, 144.2, 137.1, 129.0, 128.3, 127.7, 83.8, 60.6, 35.3, 24.8, 14.4. **^{11}B NMR** ($CDCl_3$, 160 MHz) δ 30.5. **HRMS** (ESI-TOF) m/z $[M+H]^+$ Calcd for $C_{18}H_{26}BO_4$ 317.1922; Found 317.1920.

propyl (*Z*)-4-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-enoate (4b)



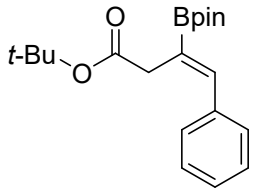
Prepared according to **Procedure 5.1**. Yellow oil (138 mg, 0.418 mmol, 65%, >1:99 *E/Z*). **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.36 (s, 1H), 7.32 – 7.20 (m, 5H), 4.02 (t, *J* = 6.7 Hz, 2H), 3.37 (d, *J* =1.40 Hz, 2H), 1.62 (h, *J* = 7.2 Hz, 2H), 1.27 (s, 12H), 0.91 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 172.6, 144.3, 137.0, 131.8, 129.0, 128.4, 127.7, 83.8, 66.2, 35.2, 24.8, 22.1, 10.5. **^{11}B NMR** ($CDCl_3$, 160 MHz) δ 30.5. **HRMS** (ESI-TOF) m/z $[M+H]^+$ Calcd for $C_{19}H_{28}BO_4$ 331.2081; Found 331.2095.

isopropyl (*Z*)-4-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-enoate (4c)



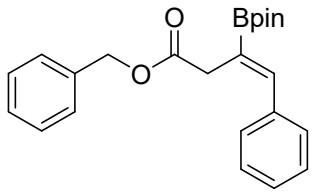
Prepared according to **Procedure 5.1**. Yellow oil (27 mg, 0.082 mmol, 61%, >1:99 *E/Z*). **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.37 (s, 1H), 7.34 – 7.22 (m, 5H), 5.06 – 4.96 (m, 1H), 3.34 (d, *J* = 1.20 Hz, 2H), 1.29 (s, 12H), 1.22 (d, *J* = 8.0 Hz, 6H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 172.5, 144.6, 137.5, 129.4, 128.7, 128.0, 84.2, 68.2, 35.9, 25.2, 22.3. **^{11}B NMR** ($CDCl_3$, 160 MHz) δ 30.5. **HRMS** (ESI-TOF) m/z $[M+H]^+$ Calcd for $C_{19}H_{28}BO_4$, 331.2079; Found 331.2077.

***tert*-butyl (*Z*)-4-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-enoate (4d)**



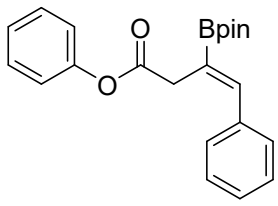
Prepared according to **Procedure 5.1**. Yellow oil (25 mg, 0.073 mmol, 60%, >1:99 *E/Z*). **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.36 – 7.28 (m, 6H), 3.31 (d, *J* = 1.20 Hz, 2H), 1.45 (s, 9H), 1.31 (s, 12H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 171.9, 143.8, 137.3, 129.1, 128.3, 127.6, 83.8, 80.4, 36.4, 28.2, 24.9. **^{11}B NMR** ($CDCl_3$, 160 MHz) δ 30.3. **HRMS** (ESI-TOF) m/z $[M+H]^+$ Calcd for $C_{20}H_{30}BO_4$ 345.2237; Found 345.2253.

benzyl (*Z*)-4-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-enoate (4e)



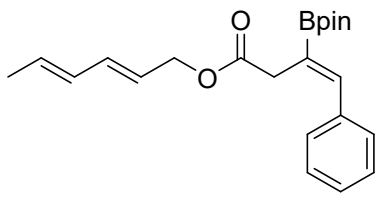
Prepared according to **Procedure 5.1**. Yellow oil (69 mg, 0.18 mmol, 59%, >1:99 *E/Z*). **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.40 (s, 1H), 7.37 – 7.24 (m, 10H), 5.13 (s, 2H), 3.46 (d, *J* = 1.20 Hz, 2H), 1.25 (s, 12H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 172.4, 144.6, 137.0, 136.3, 129.0, 128.6, 128.4, 128.2, 128.1, 127.8, 83.9, 66.4, 35.2, 24.8. **^{11}B NMR** ($CDCl_3$, 160 MHz) δ 30.5. **HRMS** (ESI-TOF) m/z $[M+H]^+$ Calcd for $C_{23}H_{28}BO_4$ 379.2079; Found 379.2090.

phenyl (*Z*)-4-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-enoate (4f)



Prepared according to **Procedure 5.1**. Yellow oil (189 mg, 0.519 mmol, 78%, >1:99 *E/Z*). **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.52 (s, 1H), 7.41 – 7.38 (m, 6H), 7.37 – 7.36 (m, 1H), 7.34 – 7.29 (m, 1H), 7.26 (ddt, *J* = 7.9, 6.9, 1.2 Hz, 1H), 7.14 – 7.10 (m, 1H), 3.68 (d, *J* = 1.20 Hz, 2H), 1.34 (s, 12H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 171.0, 151.1, 145.1, 137.0, 129.4, 129.0, 128.5, 127.9, 125.7, 121.6, 84.0, 35.3, 24.9. **^{11}B NMR** ($CDCl_3$, 160 MHz) δ 30.5. **HRMS** (ESI-TOF) m/z $[M+H]^+$ Calcd for $C_{22}H_{26}BO_4$ 365.1924; Found 365.1885.

(2*E*,4*E*)-hexa-2,4-dien-1-yl (*Z*)-4-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-enoate (4g)



Prepared according to **Procedure 5.1**. Yellow oil (165 mg, 0.448 mmol, 74%, >1:99 *E/Z*). **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.37 (s, 1H), 7.34 – 7.22 (m, 5H), 6.26 – 6.18 (m, 1H), 6.06 – 5.97 (m, 1H), 5.76 – 5.56 (m, 2H), 4.57 (d, *J* = 16.0 Hz, 2H), 3.39 (d, *J* = 1.30 Hz, 2H), 1.74 (d, *J* = 6.7 Hz, 3H), 1.28 (s, 12H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 172.3, 144.3, 137.1, 134.7, 131.1, 130.6,

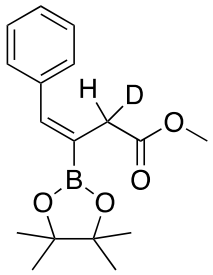
129.0, 128.4, 127.7, 124.1, 83.9, 65.2, 35.3, 24.9, 18.2. **^{11}B NMR** ($CDCl_3$, 160 MHz) δ 30.0. **HRMS** (ESI-TOF) m/z $[M+Na]^+$ Calcd for $C_{22}H_{29}BO_4Na$ 391.2061; Found 391.2057.

7. General Procedure for Deuterium Labeling Study

Procedure 7.1 Copper(I) chloride (3.53 mg, 0.0360 mmol) and B_2pin_2 (115 mg, 0.428 mmol) were added to a 2-dram vial and purged with N_2 *via* Schlenk technique. CD_3OD (0.200 mL) was added and the suspension stirred for 15 min at 60 ºC, producing a light yellow/brown mixture. Methyl 4-phenylbuta-2,3-dienoate (40.0 mg, 0.357 mmol) dissolved in CD_3OD (0.200 mL) was added, then CD_3OD (0.100 mL) was used to transfer any residual reagent. The reaction was stirred at 60 ºC and monitored by TLC until the starting material was consumed (16-20 hours). The crude mixture was concentrated *in vacuo* and purified by silica gel chromatography (eluted with 0-10% gradient ethyl acetate in hexanes) to afford the product as a yellow oil. Where applicable, the *E*-isomer is labeled as major when the *Z*-isomer is present, which is labeled as minor.

8. Characterization of Deuterium Labeled Boryl Acrylate

methyl (*E*)-4-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-2-enoate-4-*d* (7)



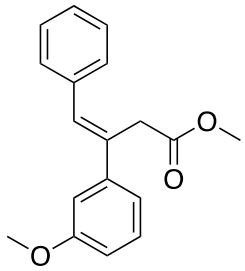
Prepared according to **Procedure 9.1**. Yellow oil (160.0 mg, 0.528 mmol, 64%, >1:99 E/Z). **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.12 (s, 1H), 7.36 – 7.24 (m, 5H) 3.68 (s, 3H), 3.40 (s, 1H), 1.31 (s, 12H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 172.3, 144.3, 136.9, 128.9, 128.3, 127.7, 83.8, 51.8, 24.8. **^{11}B NMR** ($CDCl_3$, 160 MHz) δ 30.5. **HRMS** (ESI-TOF) m/z $[M+H]^+$ Calcd for $C_{17}H_{23}DBO_4$ 304.1830; Found 304.1830.

9. General Procedure for Suzuki-Miyaura Cross-Coupling

Suzuki Cross-Coupling was performed in accordance with previous literature.[2]

10. Characterization of Cross-Coupled Product

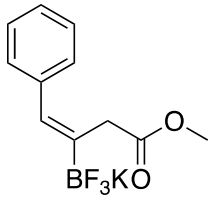
methyl (*E*)-3-(3-methoxyphenyl)-4-phenylbut-3-enoate (8)



Yellow oil (68 mg, 0.30 mmol, 81%). **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.39 (d, *J* = 4.9 Hz, 3H), 7.34 – 7.27 (m, 2H), 7.10 (ddd, *J* = 7.7, 1.8, 0.9 Hz, 1H), 7.06 (d, *J* = 1.9 Hz, 1H), 6.87 (ddd, *J* = 8.2, 2.5, 0.9 Hz, 2H), 3.85 (s, 3H), 3.72 (s, 2H), 3.67 (s, 3H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 172.1, 159.8, 143.2, 137.4, 134.4, 131.6, 129.6, 128.9, 128.6, 127.4, 118.8, 113.2, 112.2, 55.4, 52.2, 36.6. **HRMS** (ESI-TOF) m/z $[M+H]^+$ Calc for $C_{18}H_{19}O_3$ 283.1334; Found 283.1310.

11. Characterization of BF_3K salt

methyl (*Z*)-4-phenyl-3-(trifluoro-λ^4-boraneyl)but-3-enoate, potassium salt (9)



White solid (16 mg, 0.057 mmol, 78%). **^{1}H NMR** (CD_3CN, 400 MHz) δ 7.31 – 7.28 (m, 4H), 7.20 – 7.15 (m, 1H), 6.75 (s, 1H), 3.60 (s, 3H), 3.16 (d, *J* =

1.20 Hz, 2H). **^{13}C NMR** (CD_3CN, 100 MHz) δ 175.6, 132.1, 132.0, 132.0, 131.9, 129.4, 128.9, 126.6, 51.9, 36.4. **^{11}B NMR** (CD_3CN, 160 MHz) δ 2.80, 2.41. **^{19}F NMR** (CD_3CN, 376 MHz) δ 152.0, 152.1. **HRMS** (ESI-TOF) m/z $[M+NH_4]^+$ Calcd for $C_{11}H_{15}BF_3NO_2$ 261.1148; Found 261.1107.

12. General Procedure for Oxidation of Borylated Product (10)

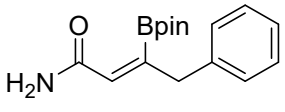
Oxidation of the borylated product was performed in accordance to previous literature.[3]
2a (89.0 mg, 0.290 mmol) was added to a 6 dram vial followed by the addition of THF/H_2O (1:1 solution (0.400 mL)). $NaBO_3$•H_2O (59.0 mg, 0.590 mmol) was added to the solution and was allowed to stir for 3 hours at room temperature. Product was isolated using column chromatography using a gradient from 0 – 10% ethyl acetate/hexanes to afford **10** in a 78% yield.
Reference spectra is also provided in previous literature.[4] Copies of spectra are provided.

13. General Procedure for Amidation of Boryl Acrylate (11)

Procedure 11.1 Compound **2a** (70.0 mg, 0.230 mmol) dissolved in THF (0.13 mL) was added to a 2 dram vial under nitrogen. Ammonia (7 N in MeOH, 0.099 mL, 0.69 mmol) was added to the mixture and allowed to stir overnight at room temperature. The contents were then concentrated by rotary evaporation and purified by silica gel chromatography (eluted with a gradient of 20-50% ethyl acetate in hexanes) to afford the product as a white solid.

14. Characterization of Amidation Product (11)

(*E*)-4-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-2-enamide (11)



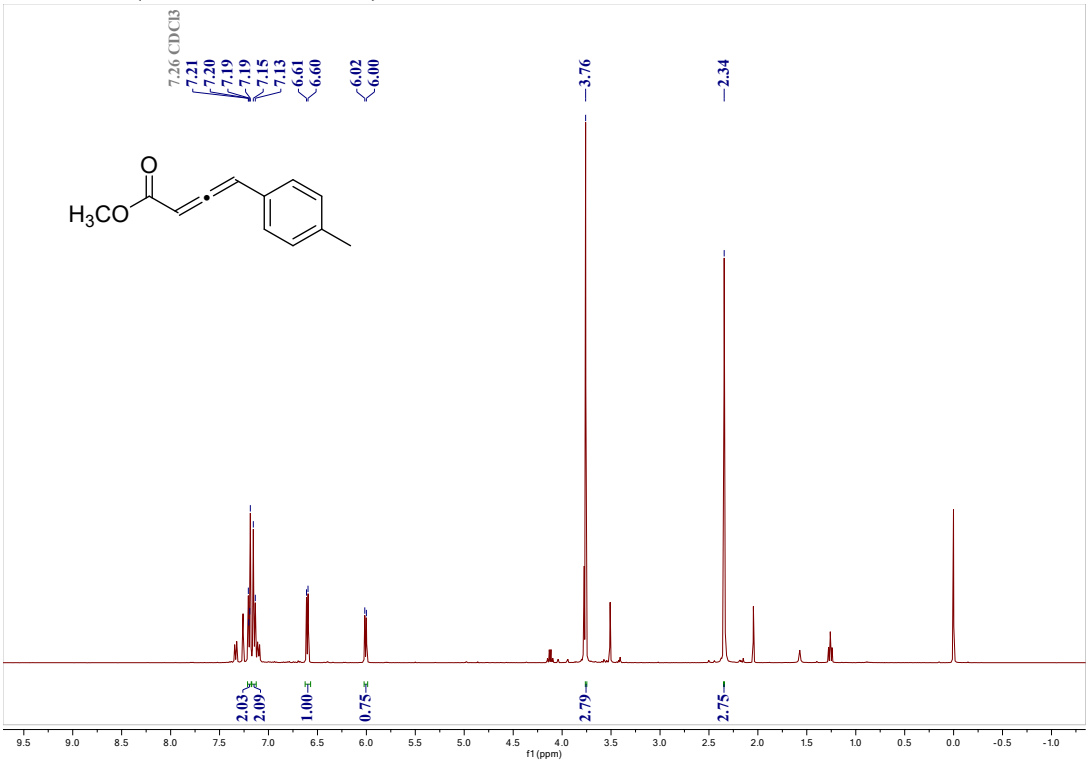
Prepared according to **Procedure 11.1**. White solid (52 mg, 0.18 mmol, 78% >99:1 *E*/*Z*). **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 8.92 (s, 1H), 7.28 – 7.24 (m, 2H), 7.19 (t, *J* = 7.20 Hz, 1H), 7.08 – 7.06 (m, 2H), 5.80 (s, 1H), 5.51 (s, 1H), 3.49 (s, 2H), 1.14 (s, 12H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 174.2, 146.5, 136.5, 129.5, 128.5, 128.2, 84.3, 37.4, 24.9. **^{11}B NMR** ($CDCl_3$, 160 MHz) δ 30.4. **HRMS** (ESI-TOF) m/z $[M+H]^+$ Calcd for $C_{16}H_{23}BNO_3$ 288.1771; Found 288.1770.

15. General Procedure for Silver Fluoride addition to re-form allenoate (1a)

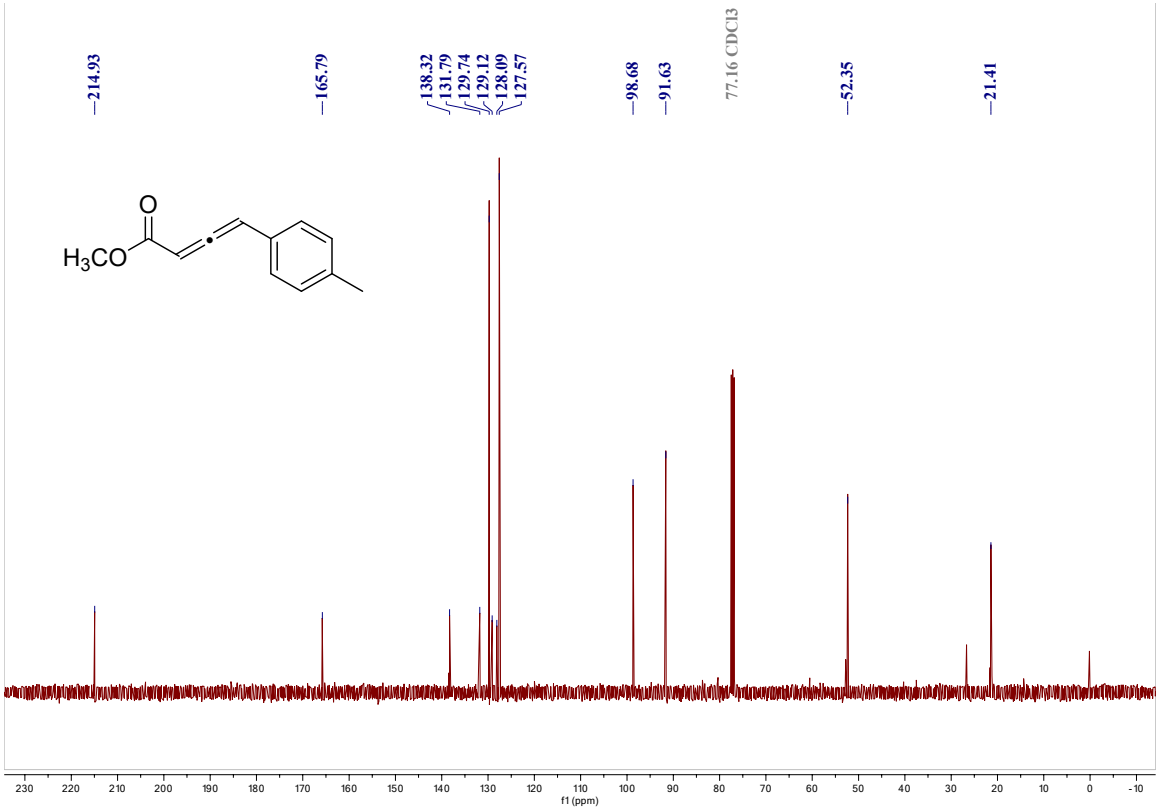
2a (133 mg, 0.440 mmol) was added to a 6 dram vial followed by the addition of methanol (1.00 mL), THF (1.00 mL), and water (0.100 mL). Silver fluoride (112 mg, 0.880 mmol) was then added to the reaction mixture and was allowed to stir open to air for 3 hours. The reaction was monitored using 10% EtOAc/hexanes TLC conditions and was purified via silica gel column chromatography through a gradient of 0– 10% ethyl acetate/hexanes to afford to phenyl allenoate in 68% yield.

16. NMR Characterizations of Allenoates

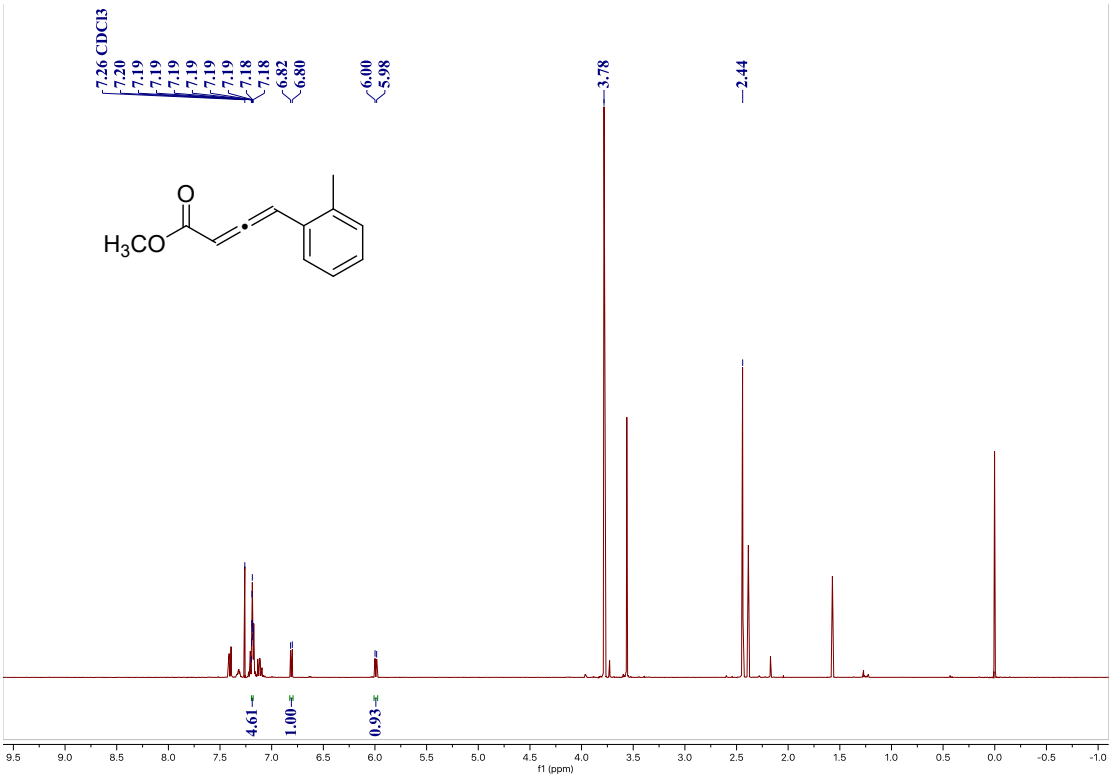
^{1}H NMR ($CDCl_3$, 400 MHz) of 1b



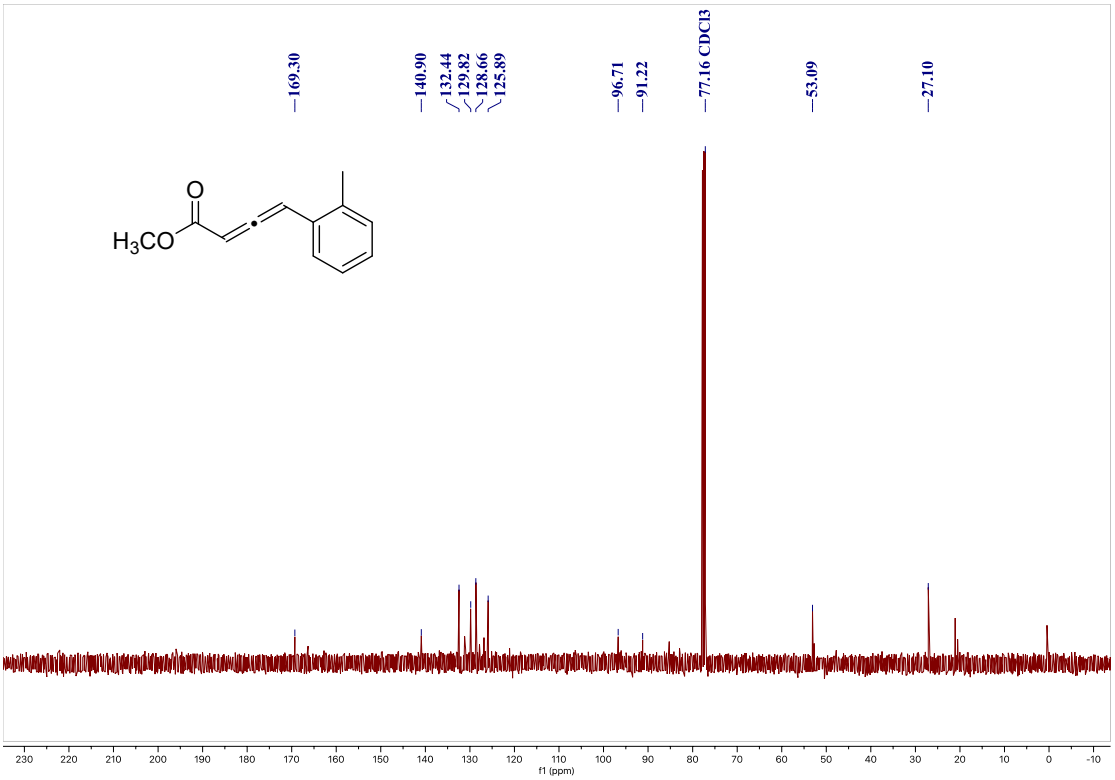
^{13}C NMR ($CDCl_3$, 100 MHz) of 1b



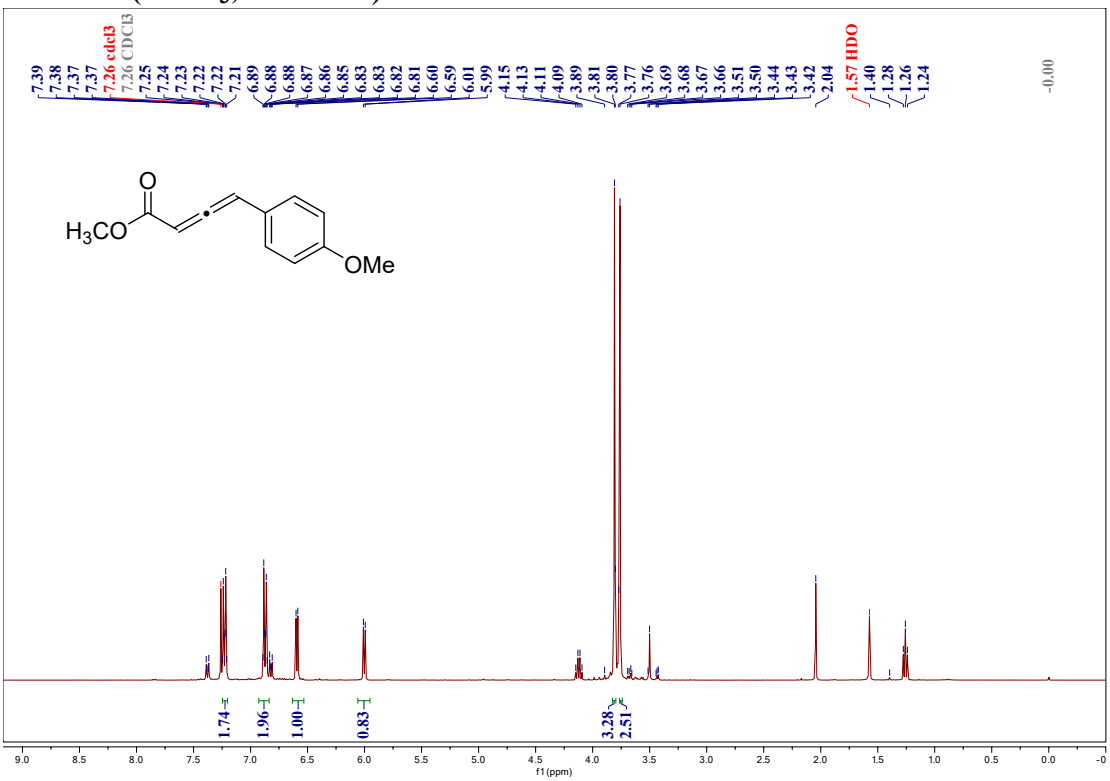
^{1}H NMR ($CDCl_3$, 400 MHz) of 1c



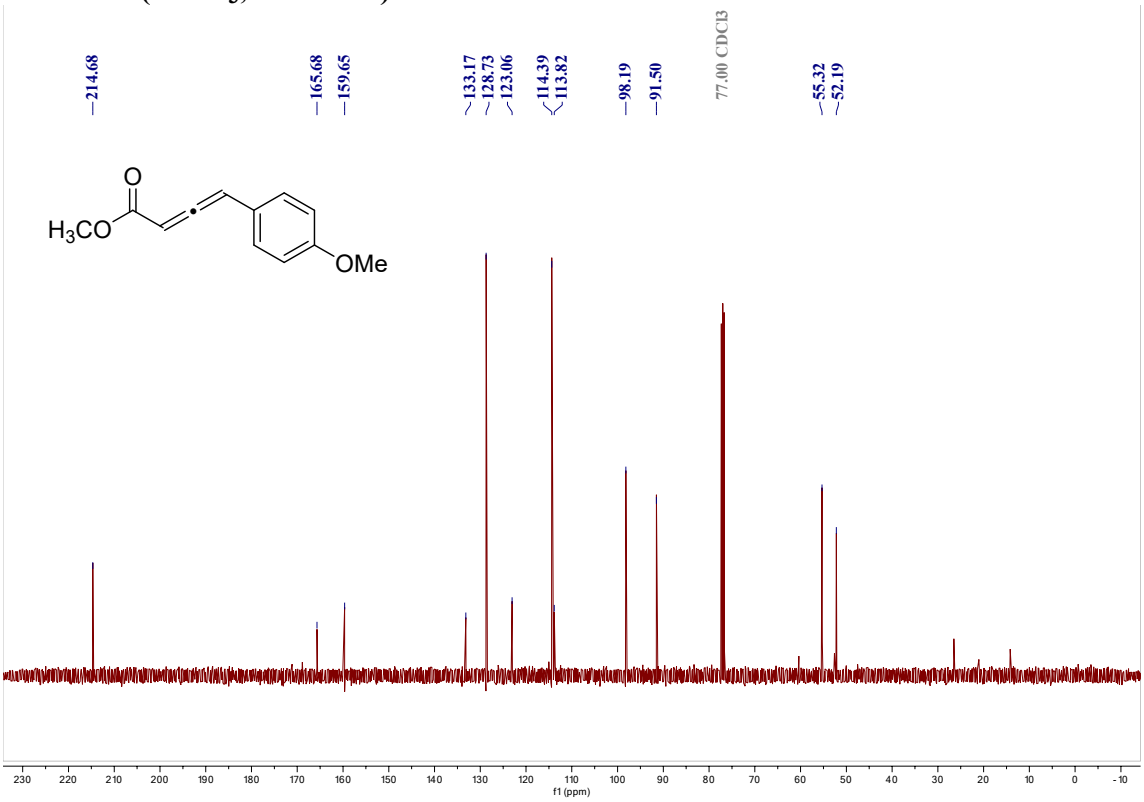
^{13}C NMR ($CDCl_3$, 100 MHz) of 1c



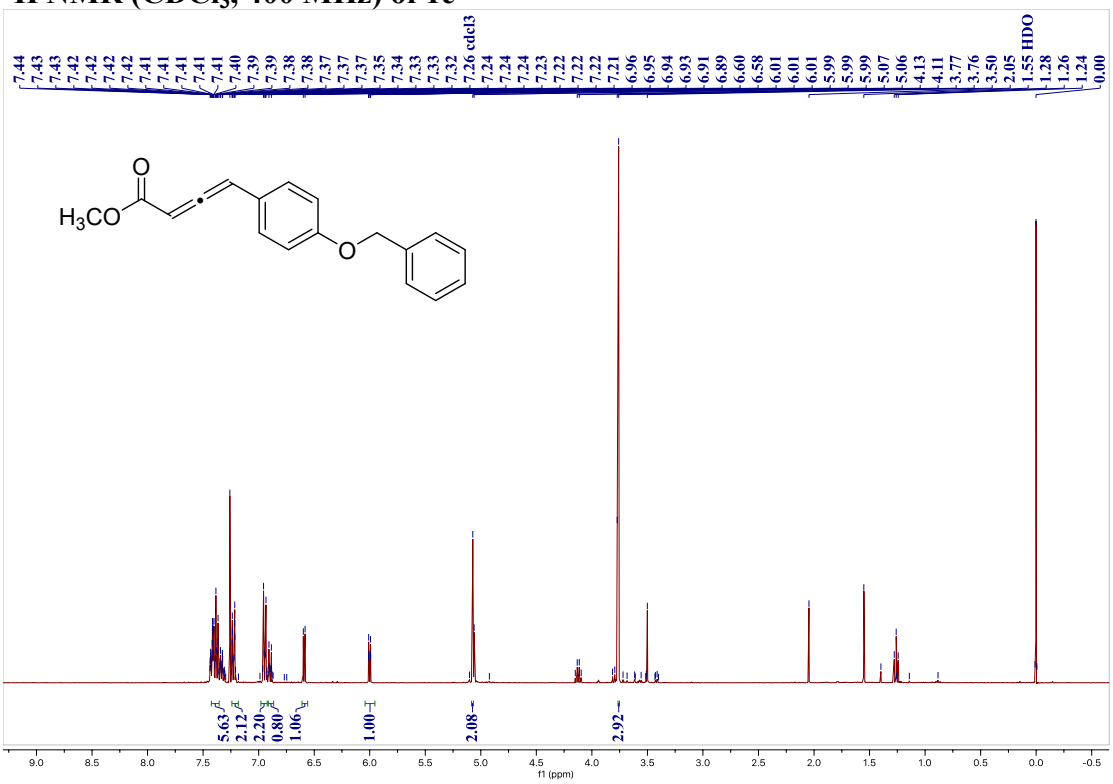
^{1}H NMR ($CDCl_3$, 400 MHz) of 1d



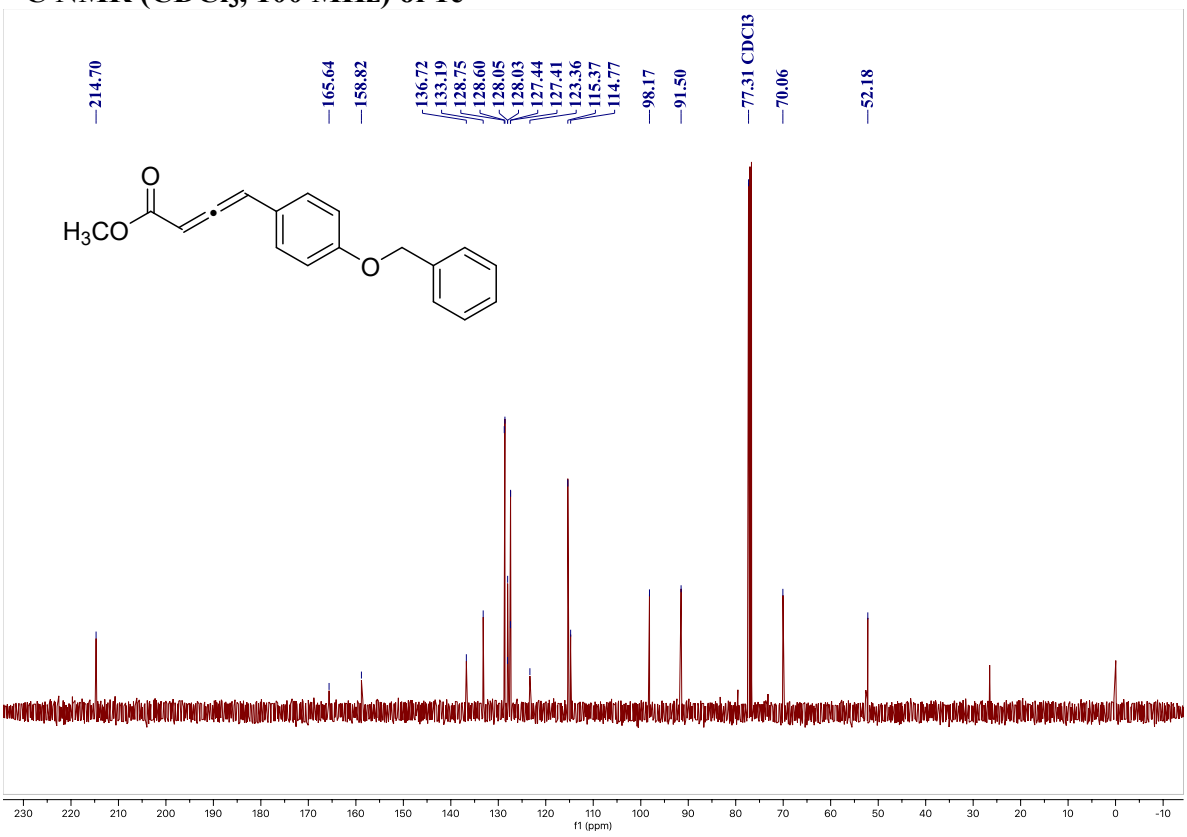
^{13}C NMR ($CDCl_3$, 100 MHz) of 1d



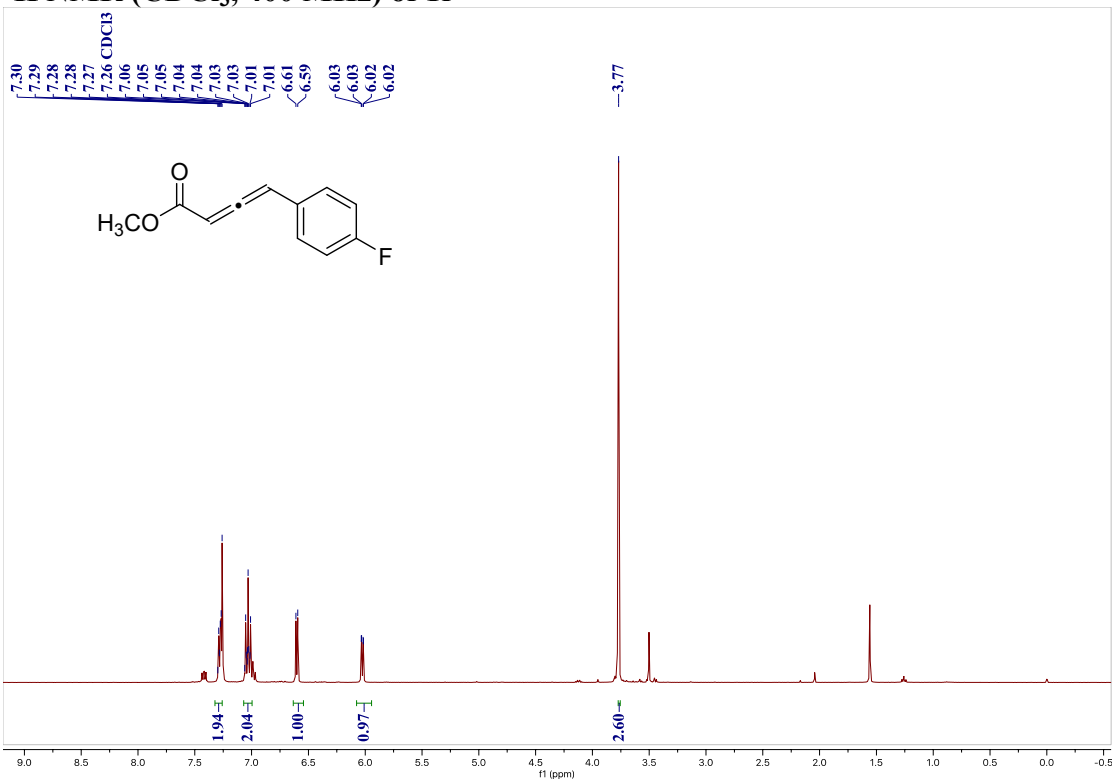
^{1}H NMR ($CDCl_3$, 400 MHz) of 1e



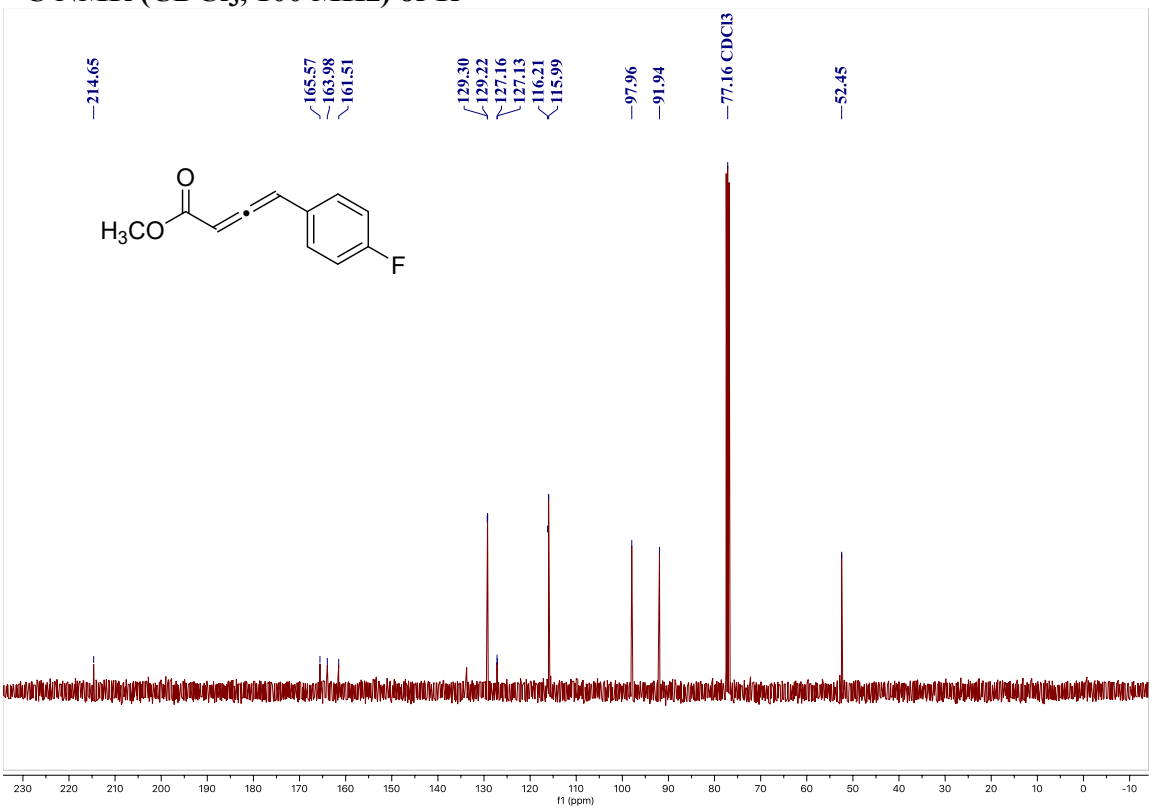
^{13}C NMR ($CDCl_3$, 100 MHz) of 1e



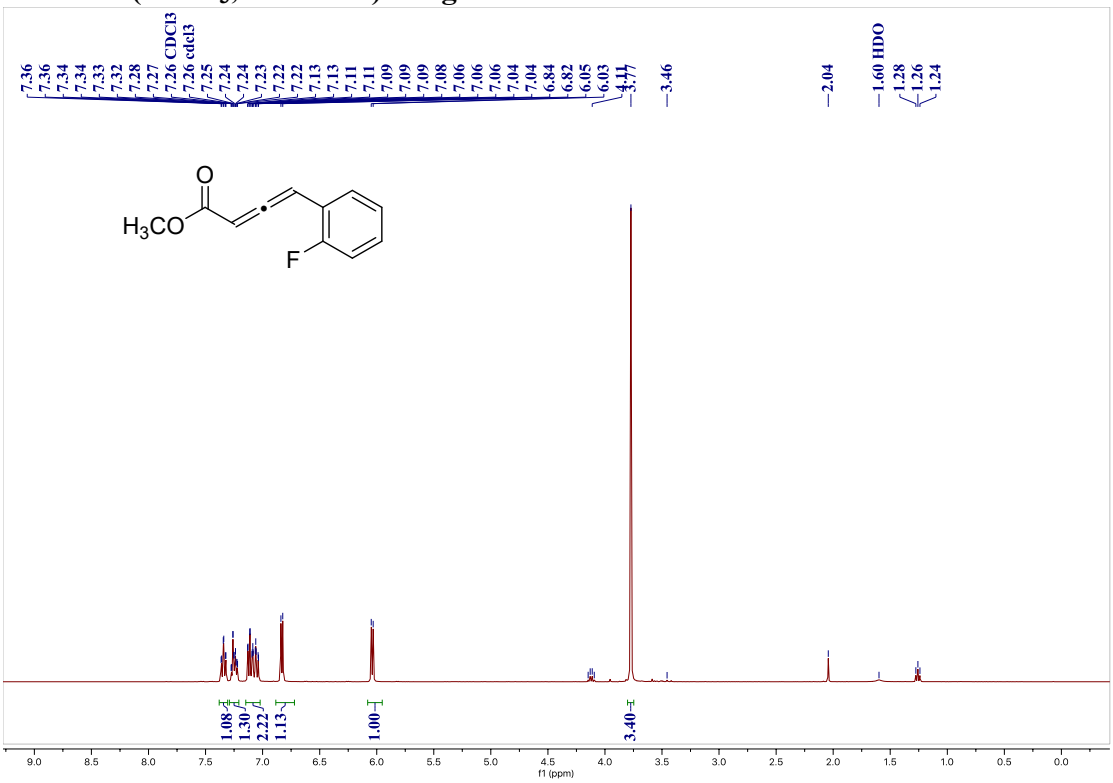
^{1}H NMR ($CDCl_3$, 400 MHz) of 1f



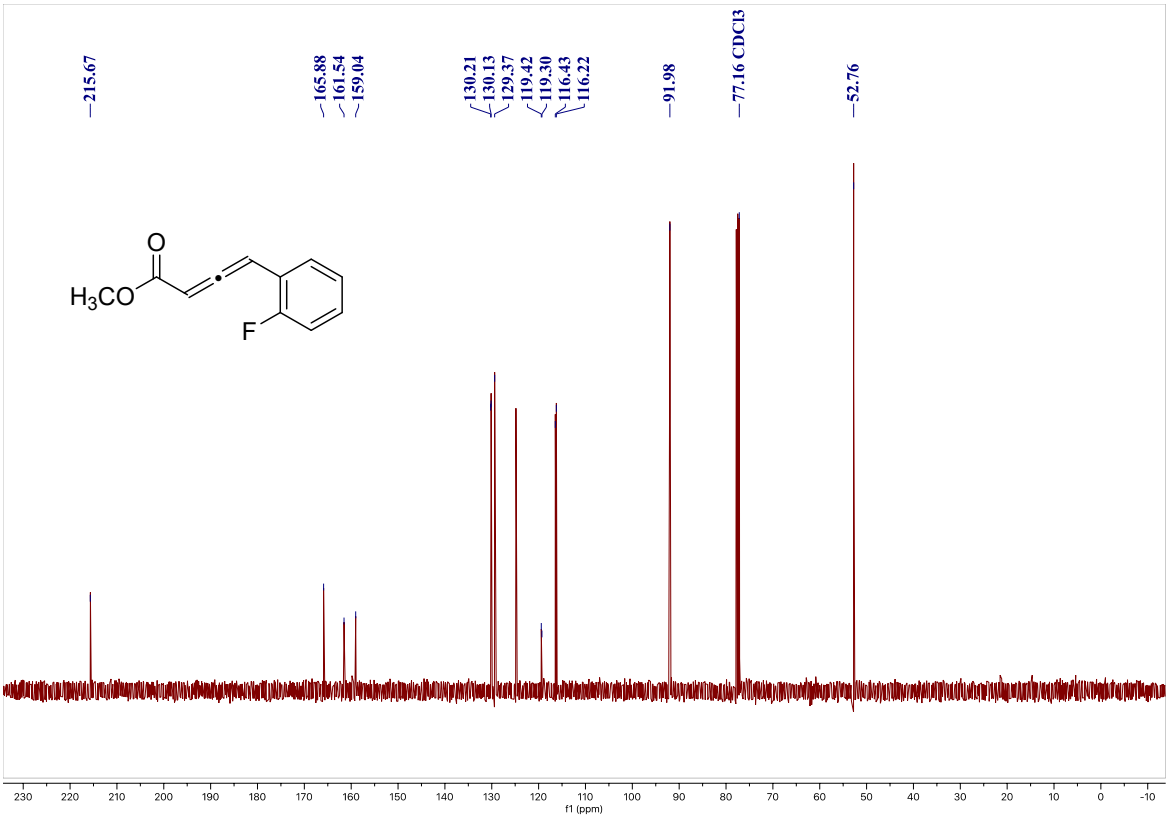
^{13}C NMR ($CDCl_3$, 100 MHz) of 1f



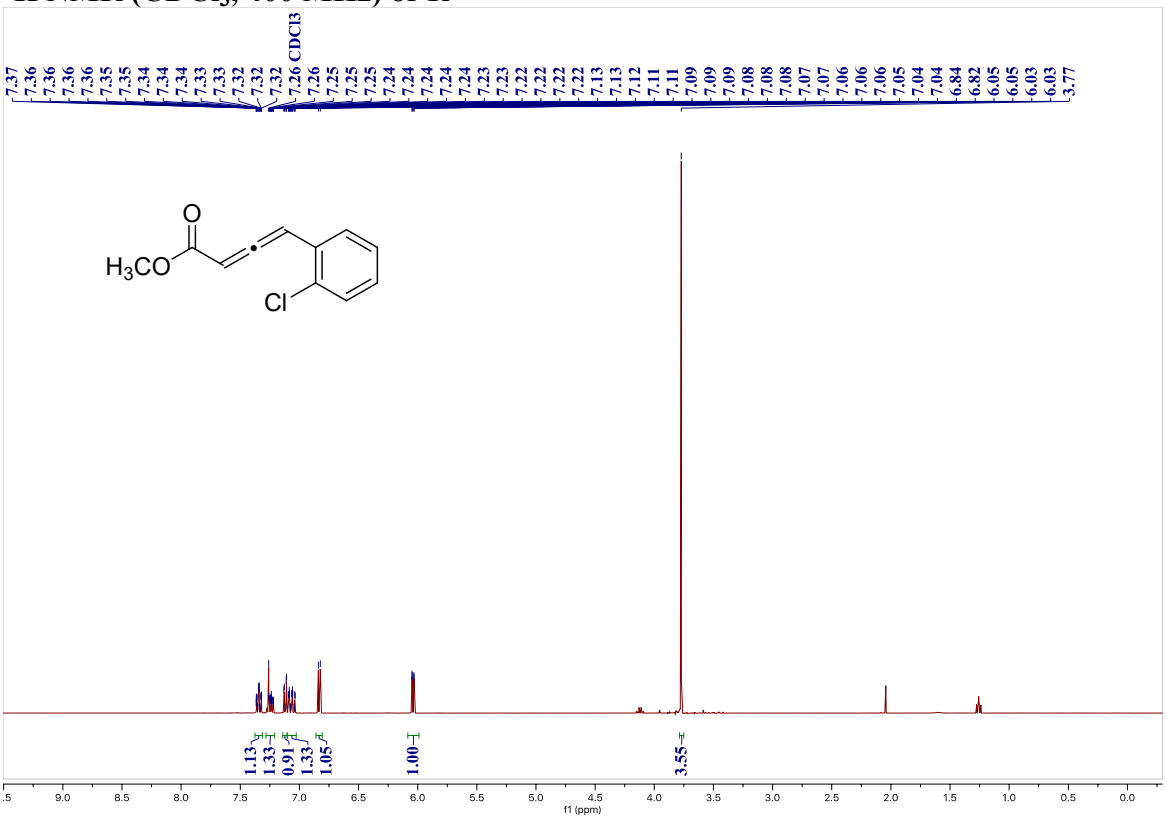
^{1}H NMR ($CDCl_3$, 400 MHz) of 1g



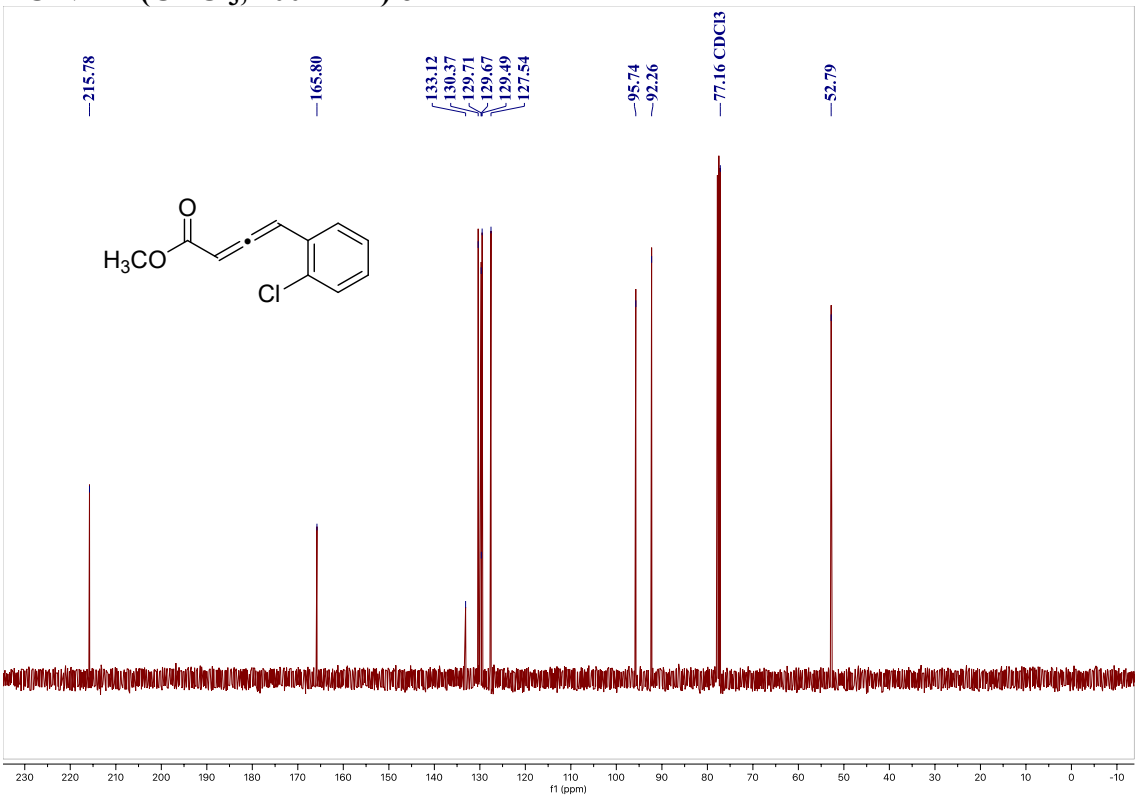
^{13}C NMR ($CDCl_3$, 100 MHz) of 1g



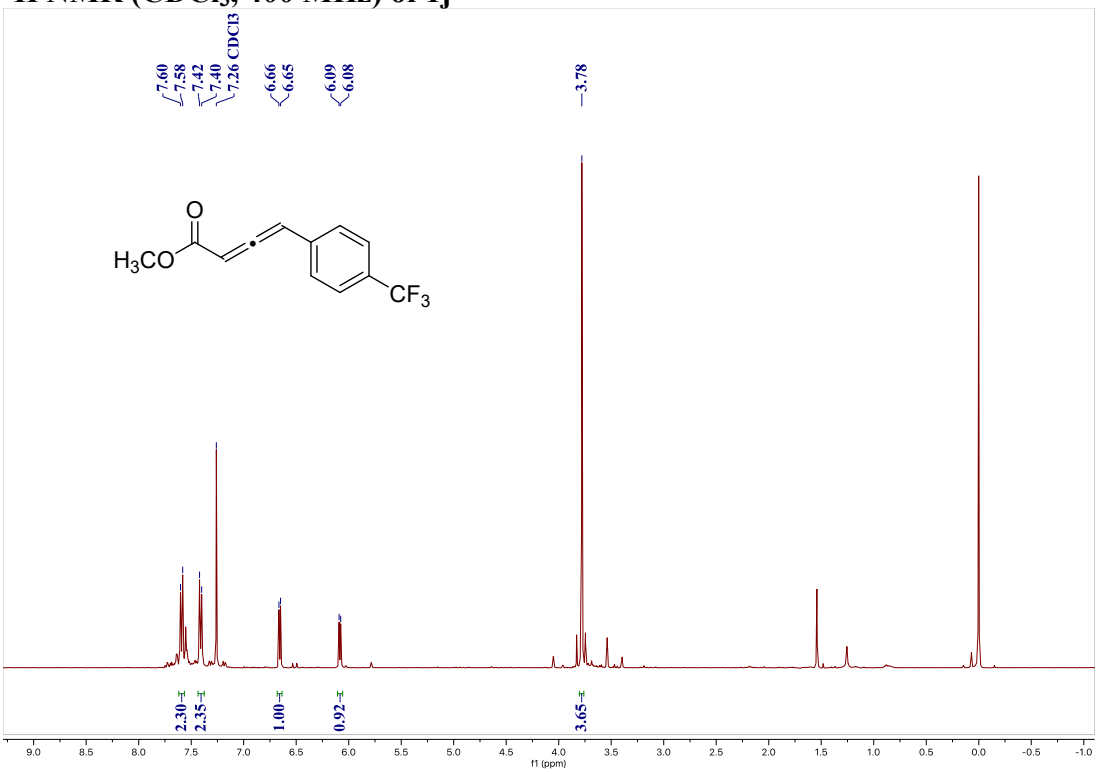
^{1}H NMR ($CDCl_3$, 400 MHz) of 1i



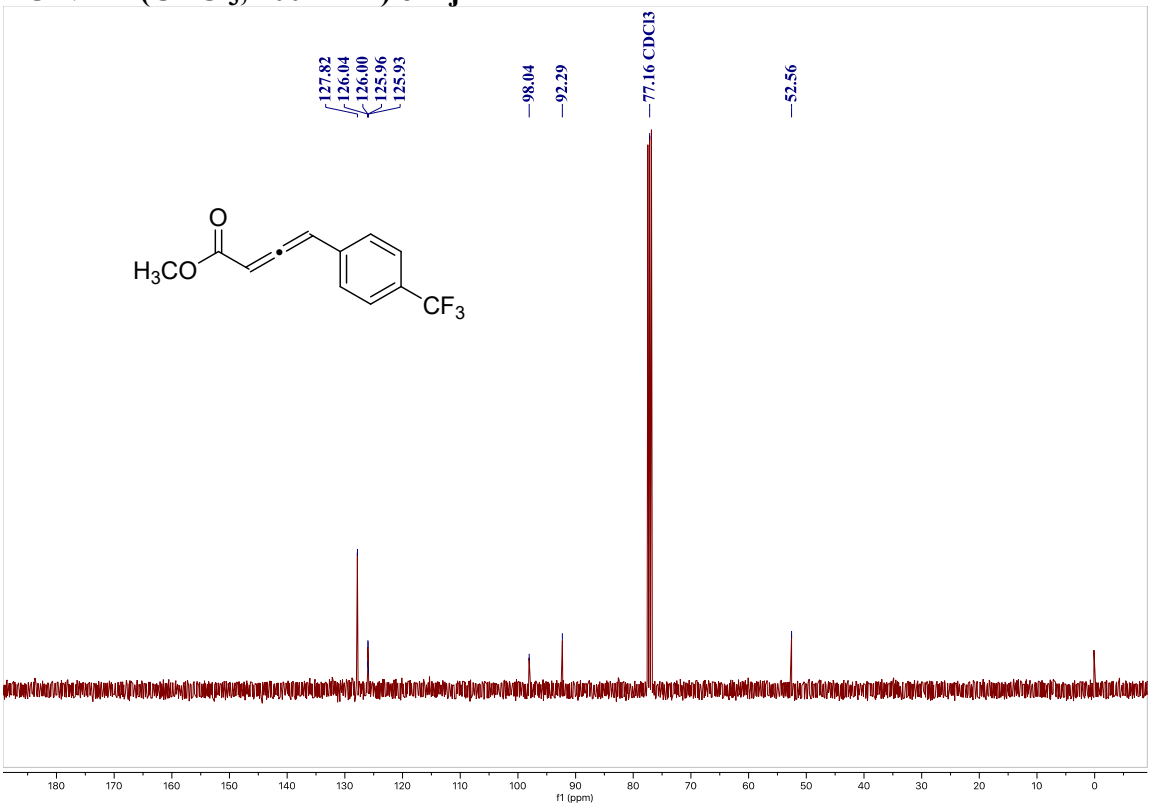
^{13}C NMR ($CDCl_3$, 100 MHz) of 1i



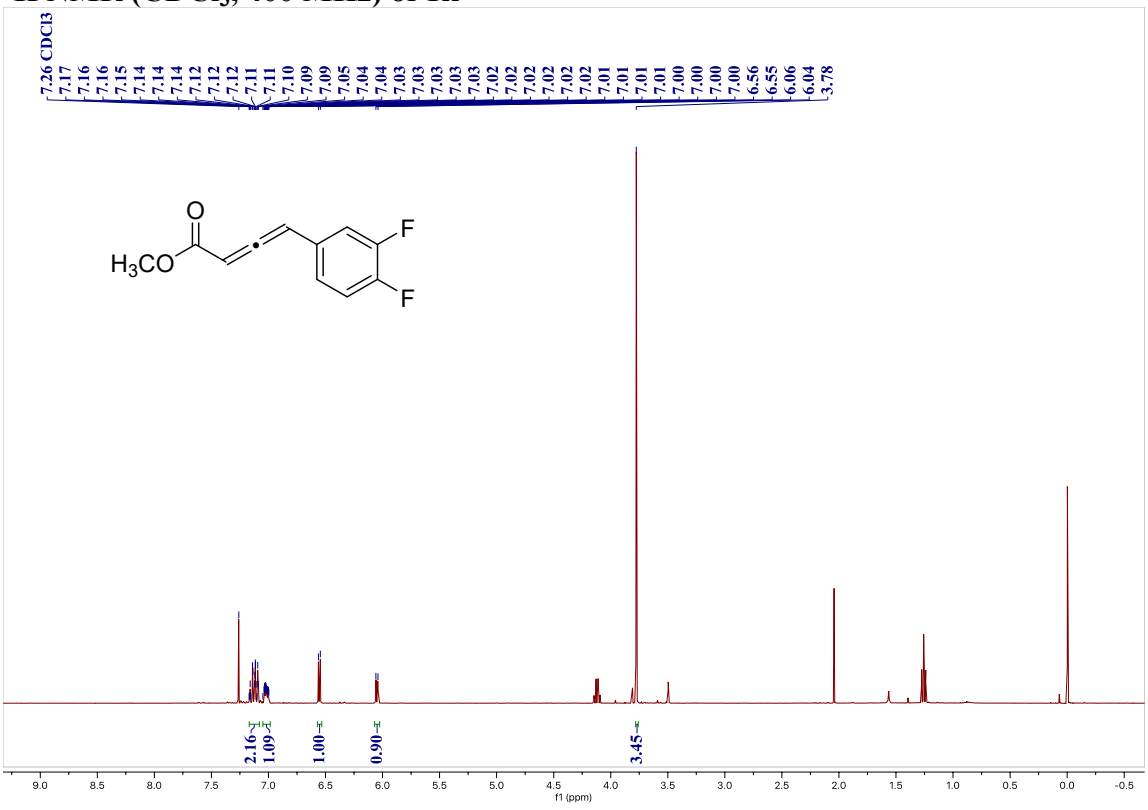
^{1}H NMR ($CDCl_3$, 400 MHz) of 1j



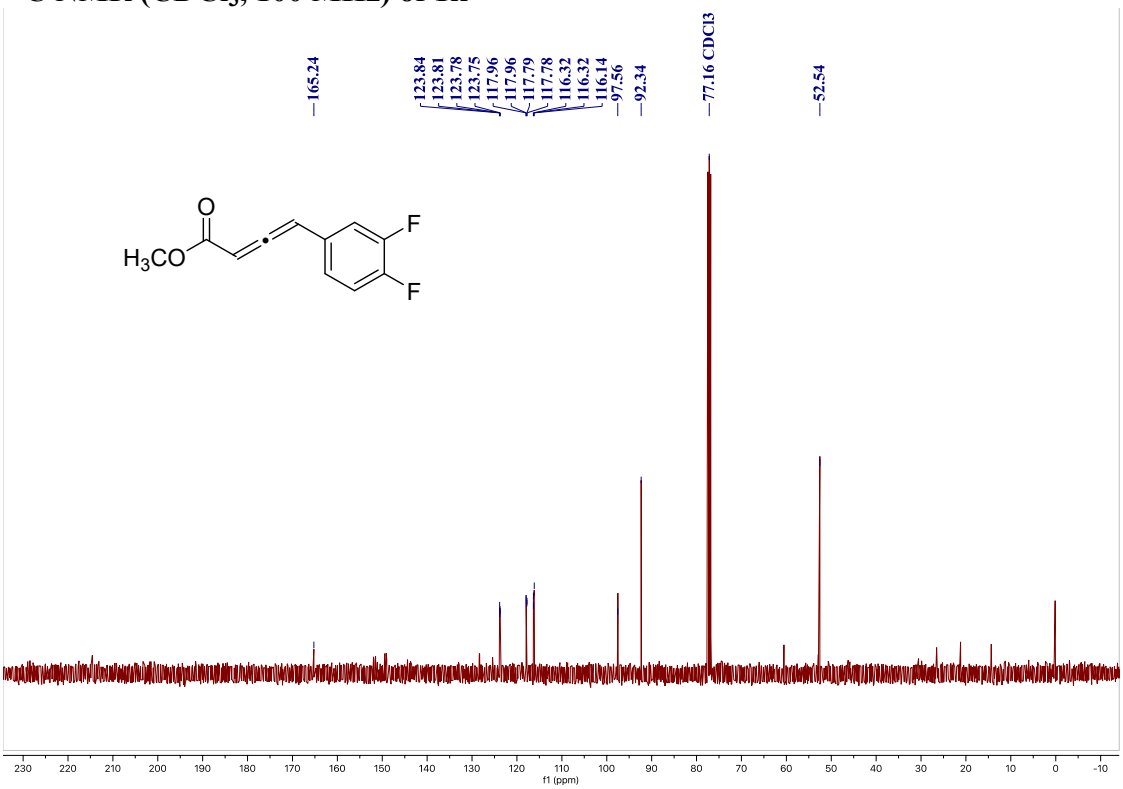
^{13}C NMR ($CDCl_3$, 400 MHz) of 1j



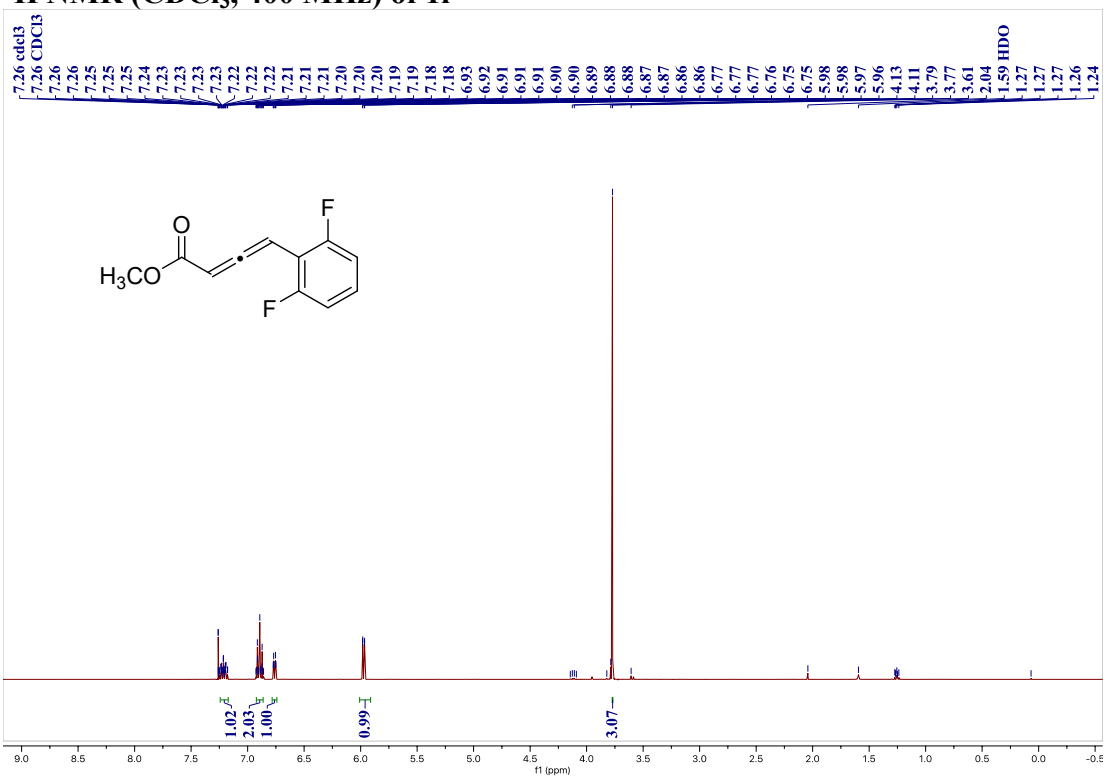
^{1}H NMR ($CDCl_3$, 400 MHz) of 1k



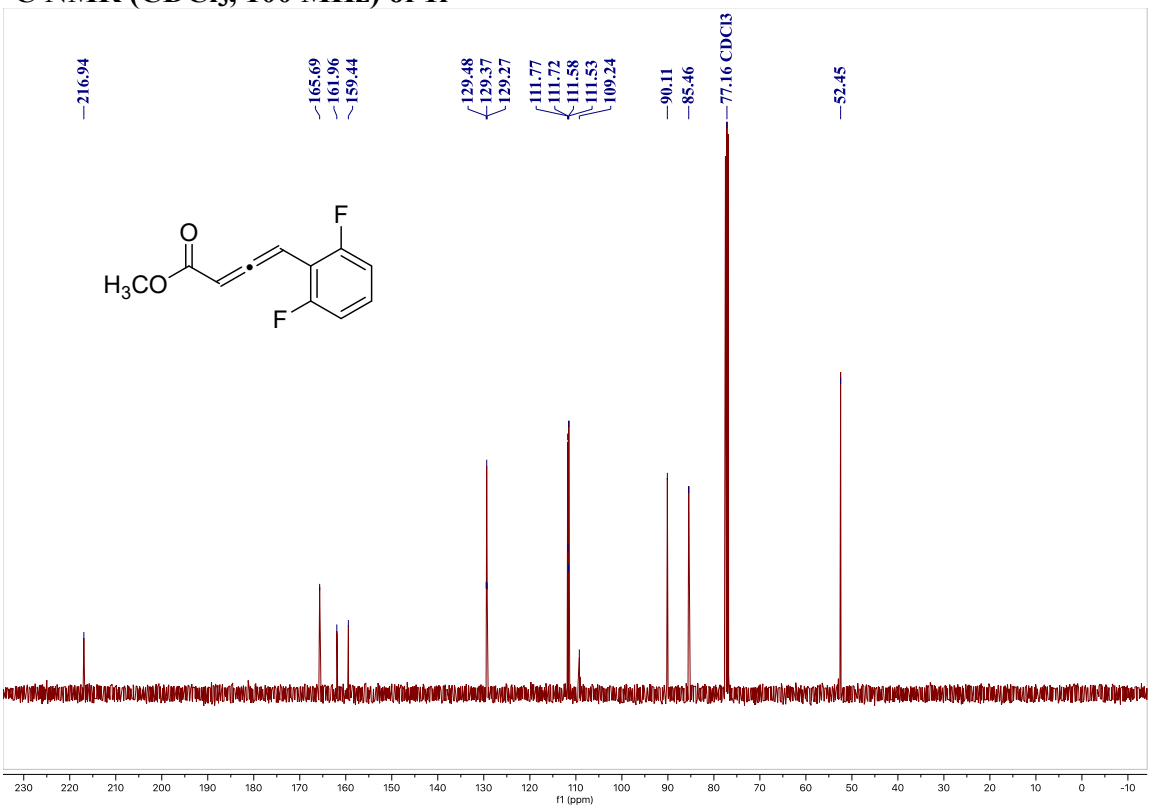
^{13}C NMR ($CDCl_3$, 100 MHz) of 1k



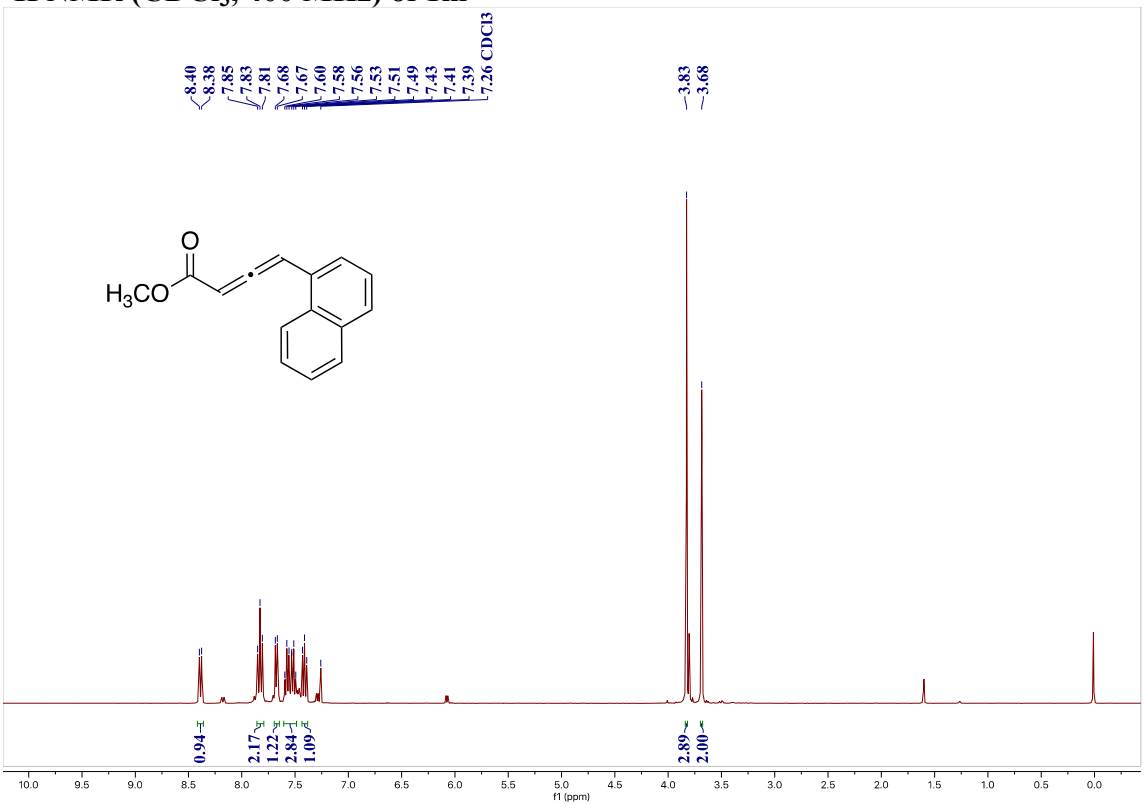
^{1}H NMR ($CDCl_3$, 400 MHz) of 1l



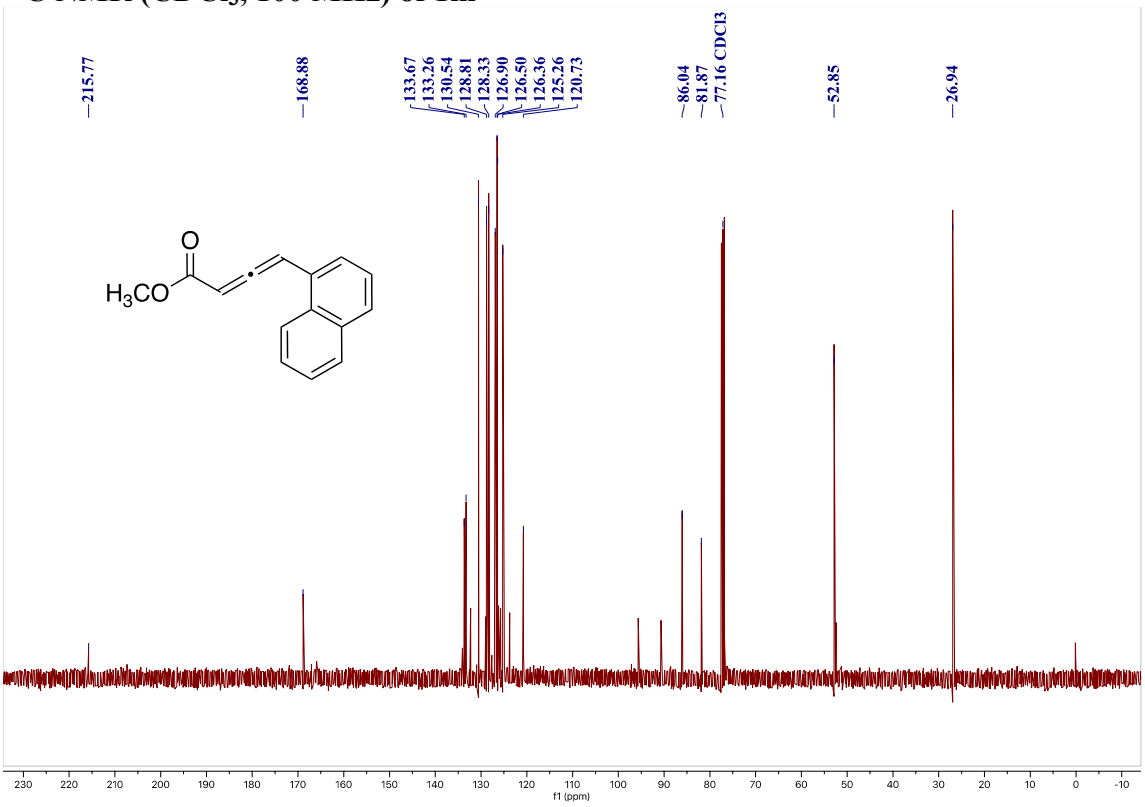
^{1}C NMR ($CDCl_3$, 100 MHz) of 1l



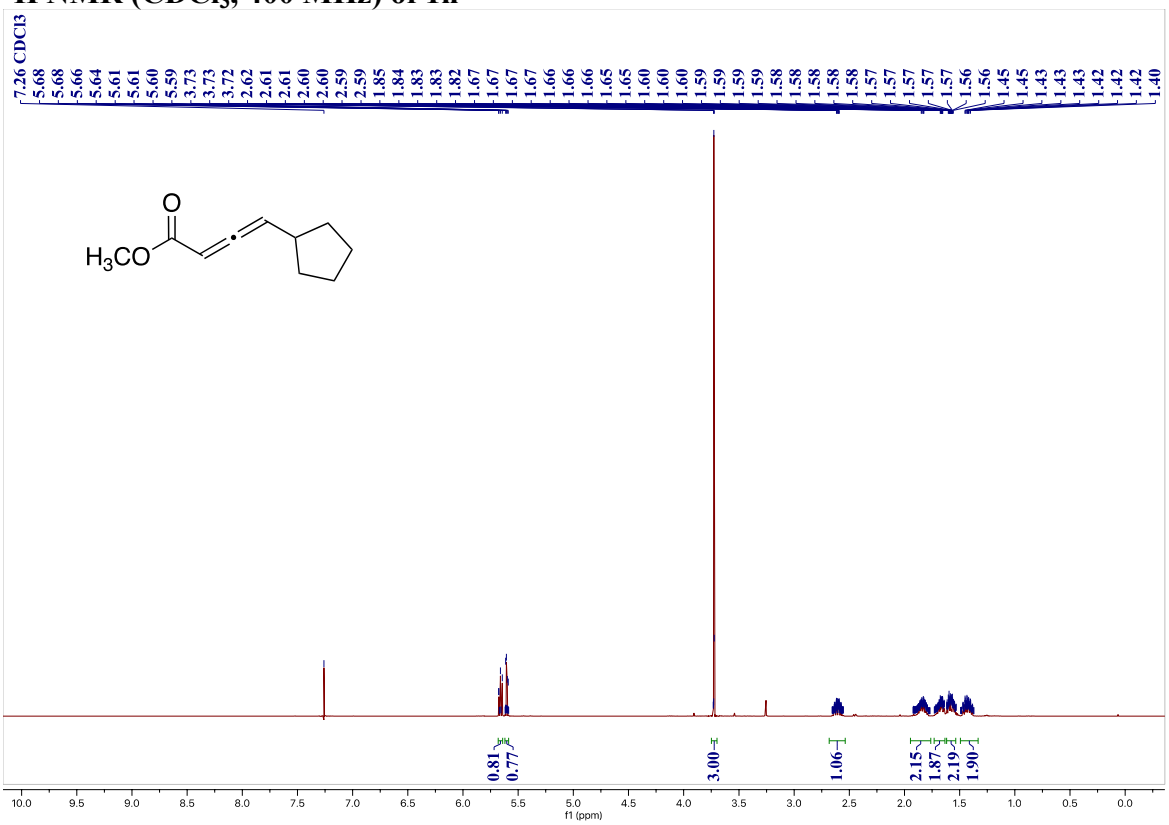
^{1}H NMR ($CDCl_3$, 400 MHz) of 1m



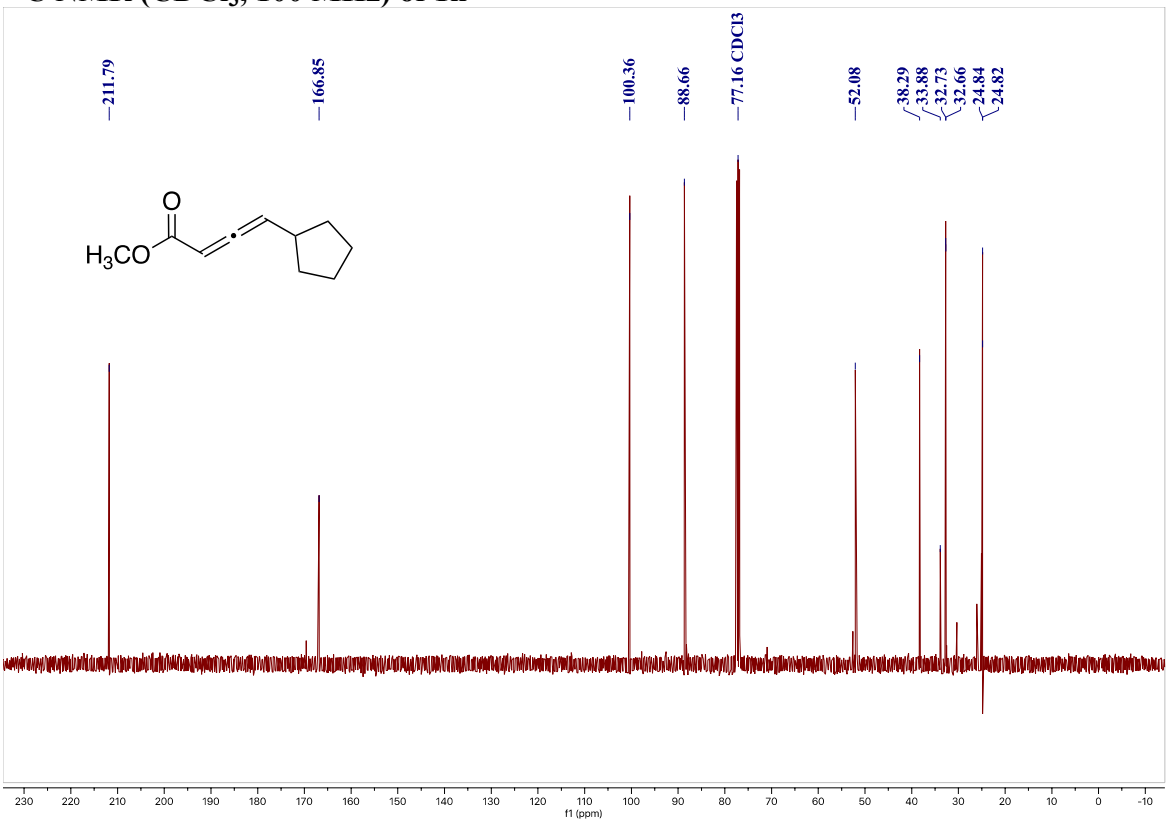
^{13}C NMR ($CDCl_3$, 100 MHz) of 1m



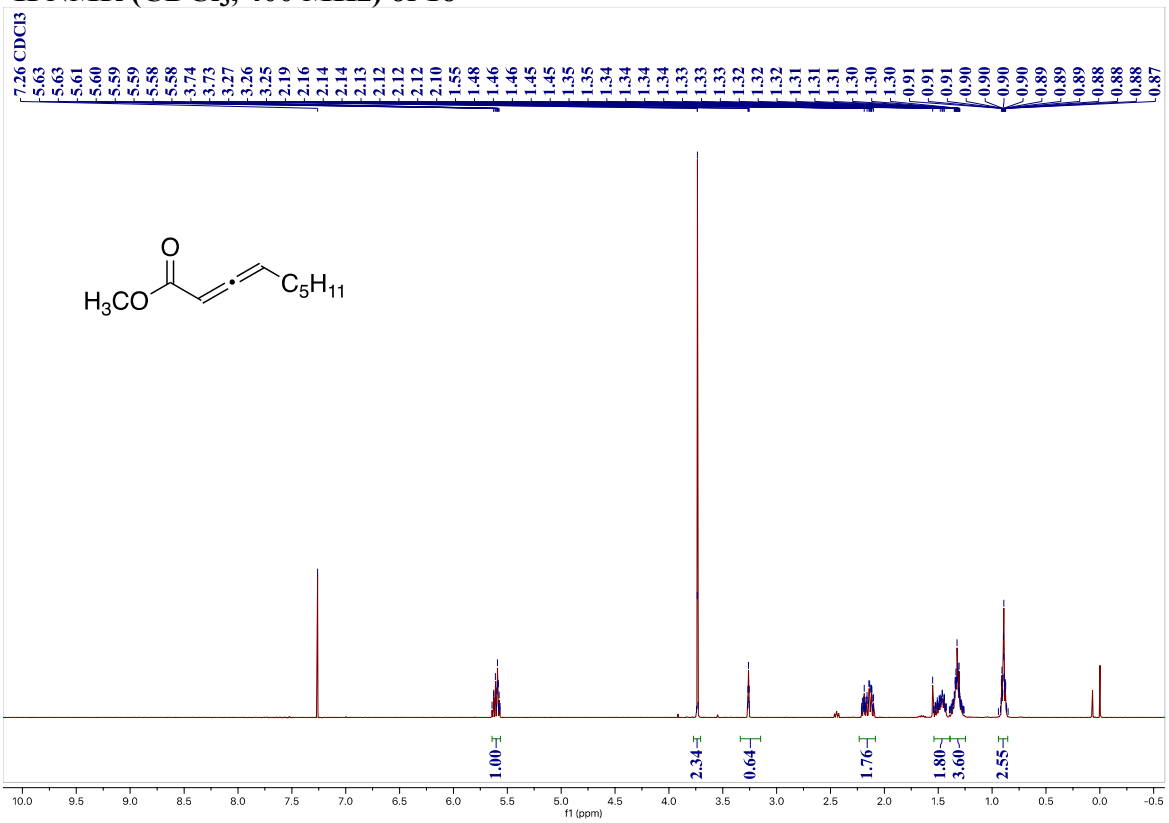
^{1}H NMR ($CDCl_3$, 400 MHz) of 1n



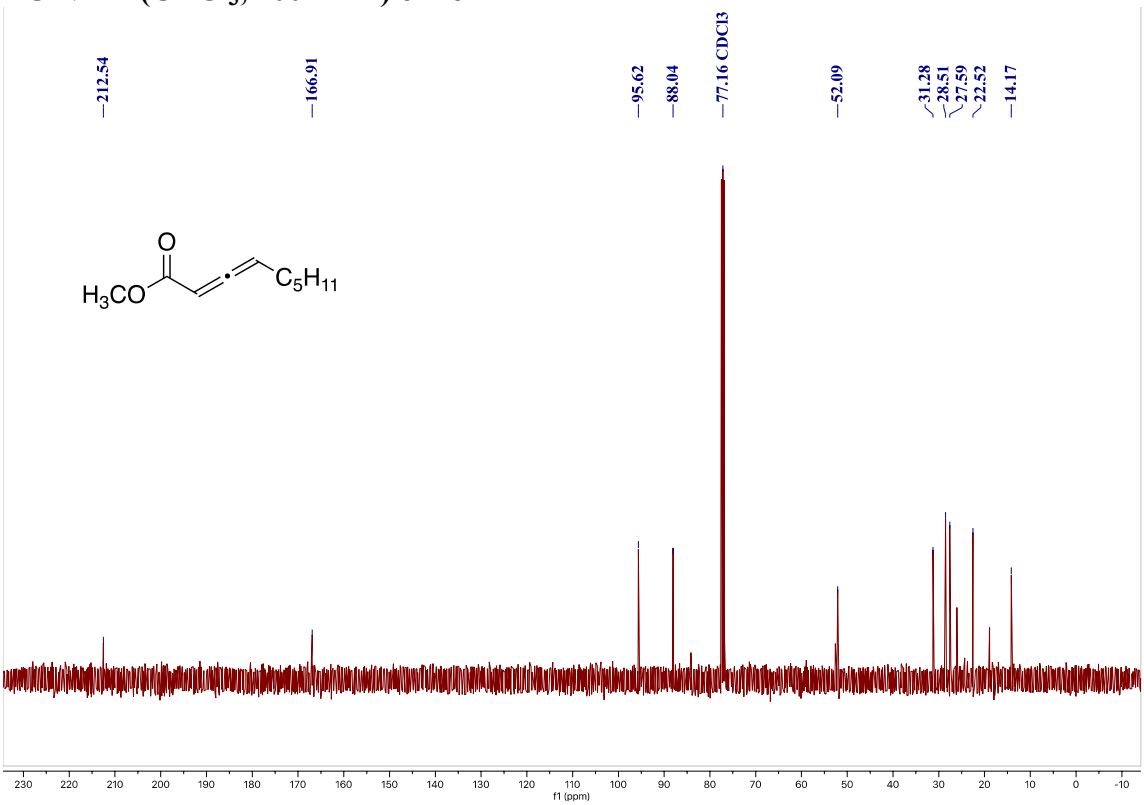
^{13}C NMR ($CDCl_3$, 100 MHz) of 1n



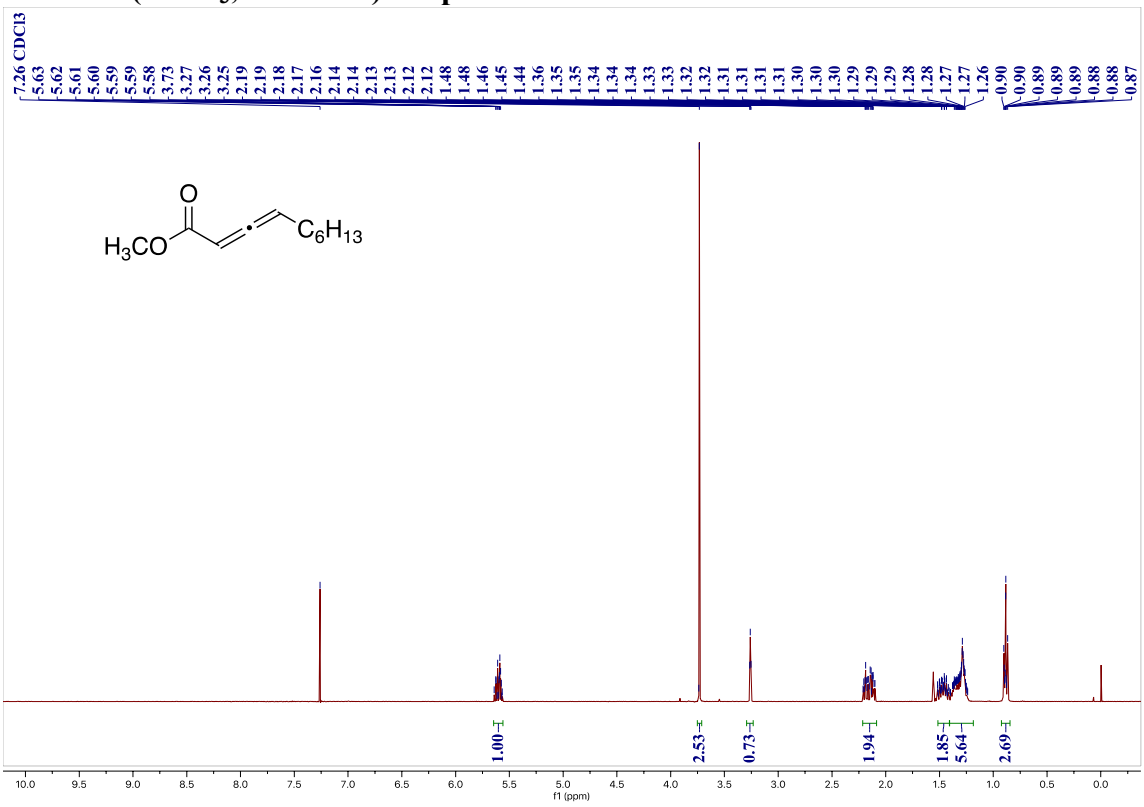
^{1}H NMR ($CDCl_3$, 400 MHz) of 1o



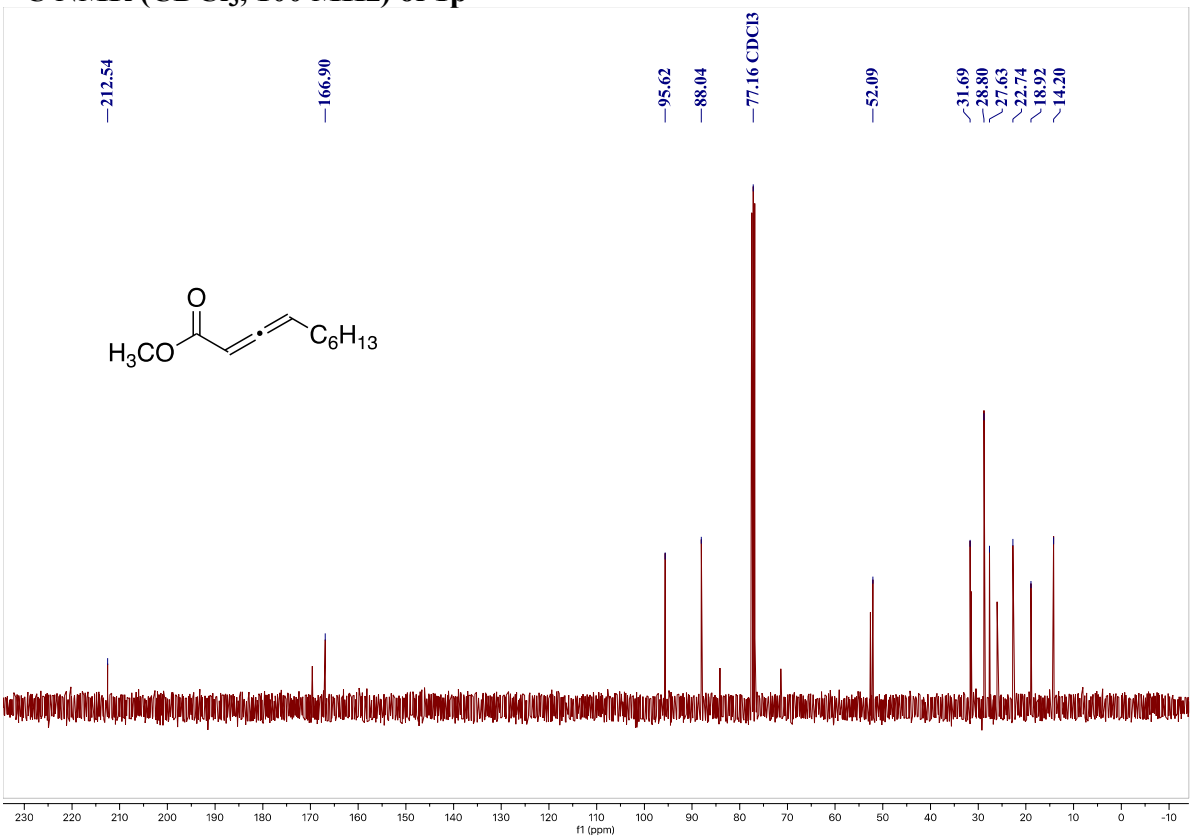
^{13}C NMR ($CDCl_3$, 100 MHz) of 1o



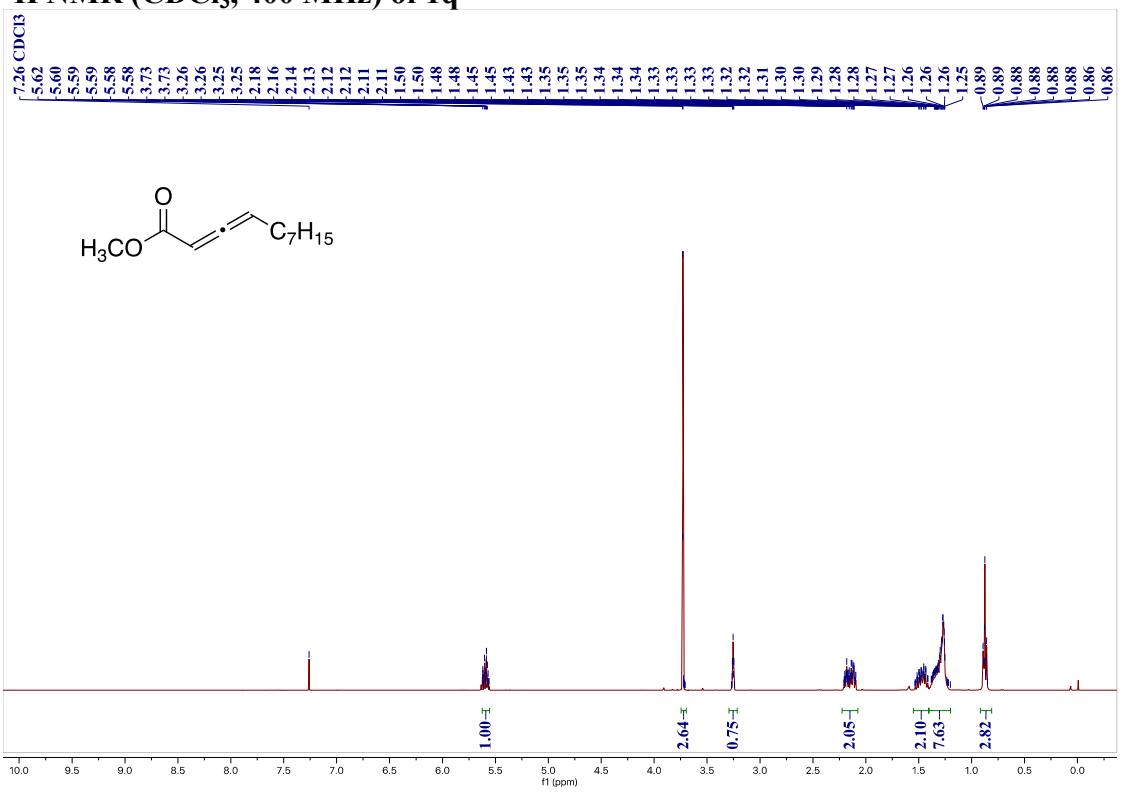
^{1}H NMR ($CDCl_3$, 400 MHz) of 1p



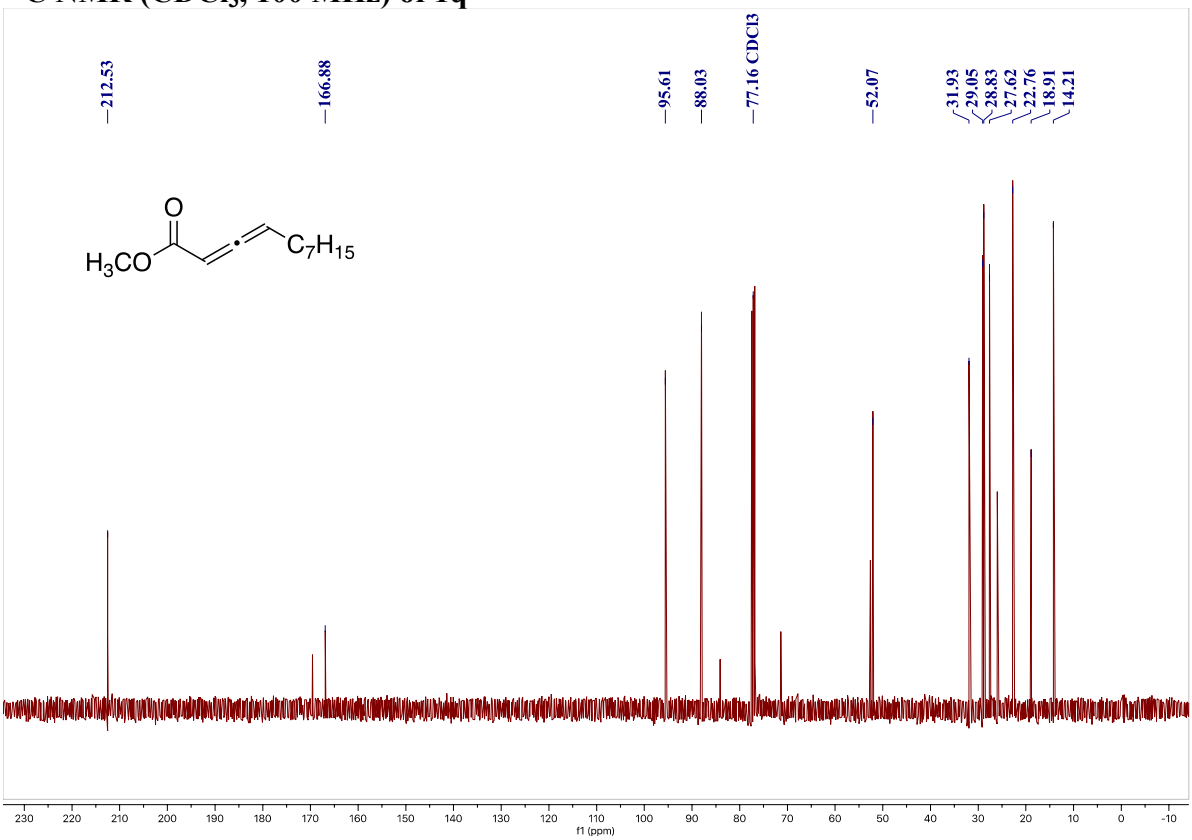
^{13}C NMR ($CDCl_3$, 100 MHz) of 1p



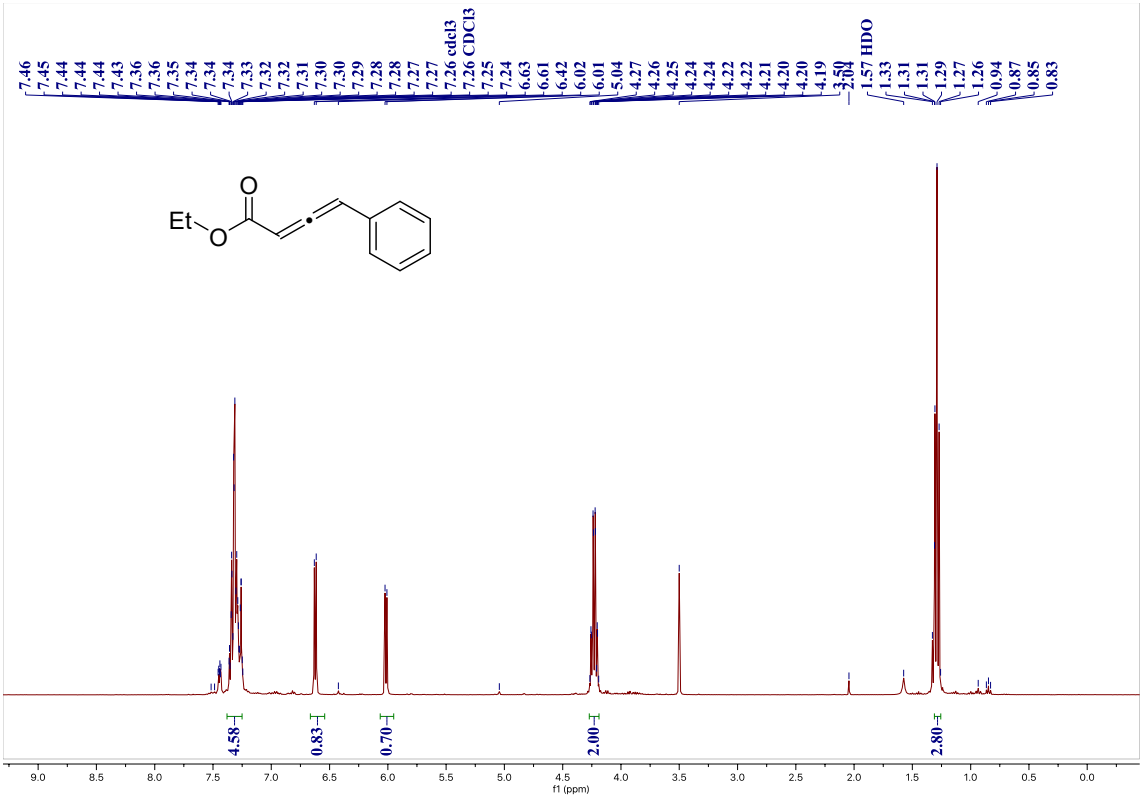
^{1}H NMR ($CDCl_3$, 400 MHz) of 1q



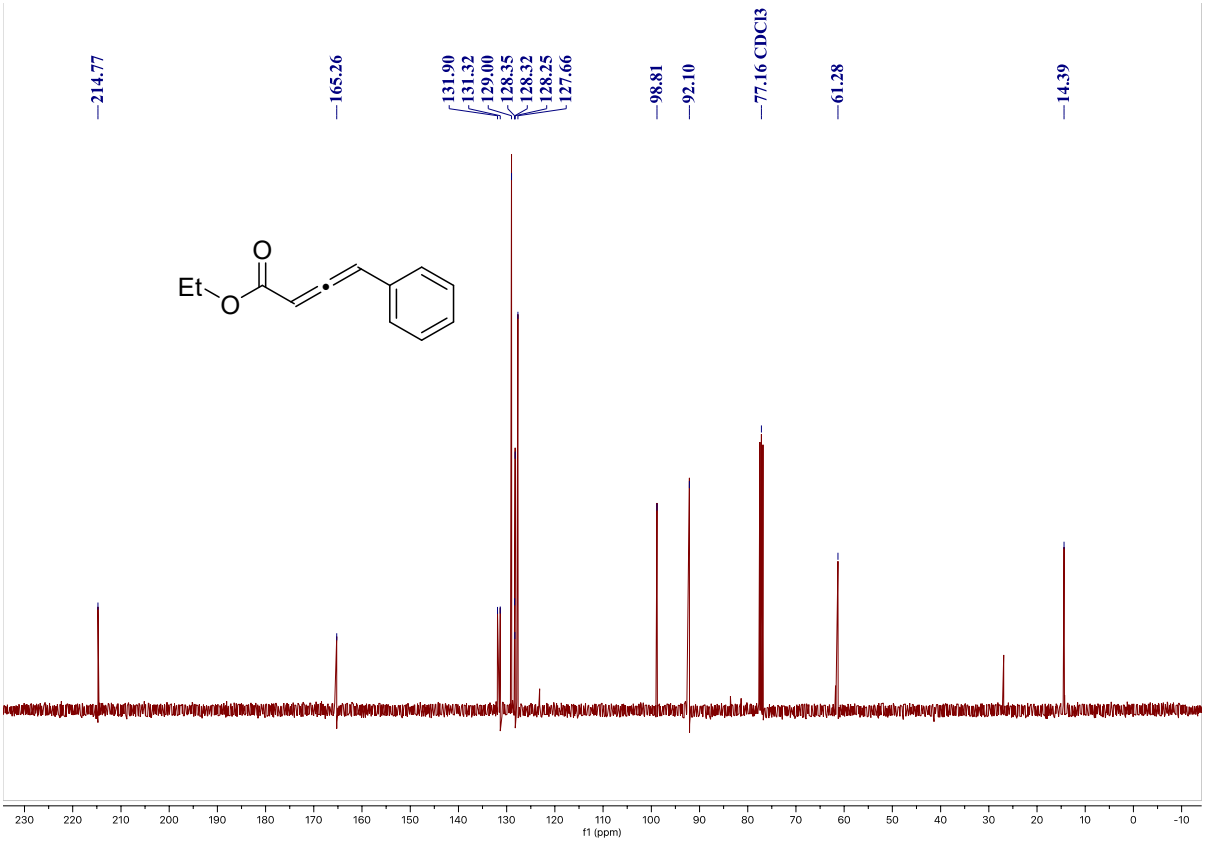
^{13}C NMR ($CDCl_3$, 100 MHz) of 1q



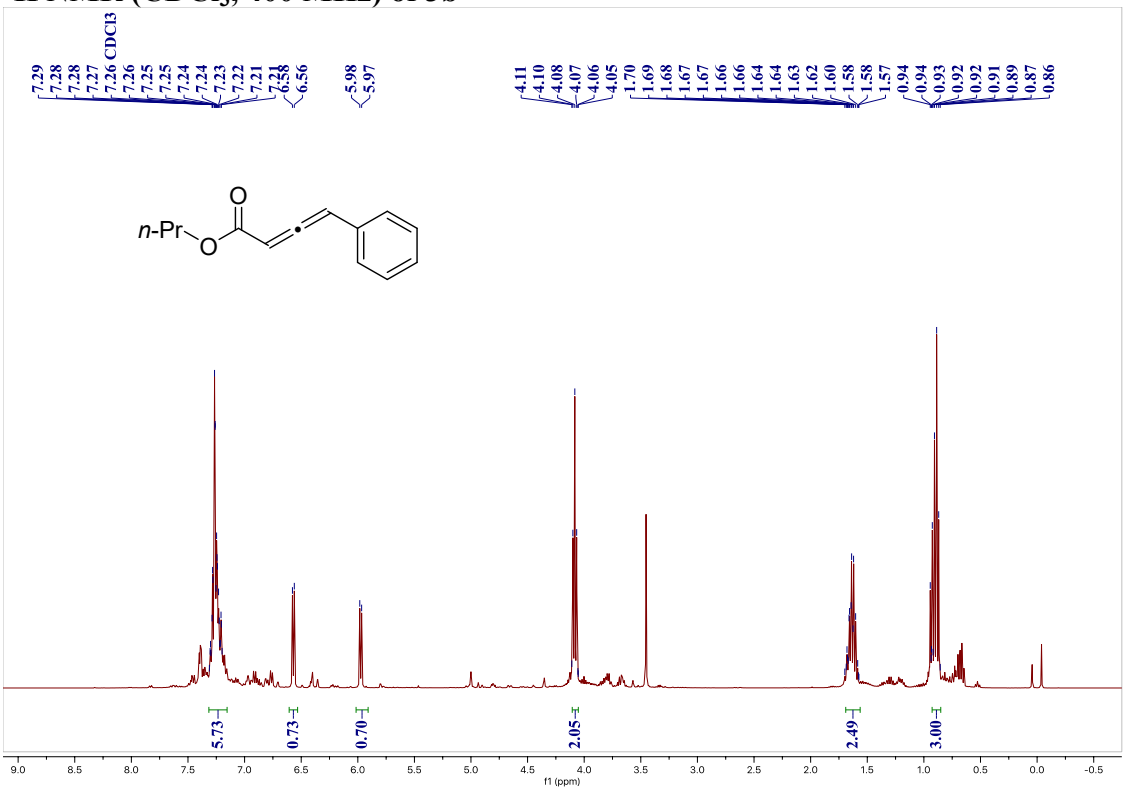
^{1}H NMR ($CDCl_3$, 400 MHz) of 3a



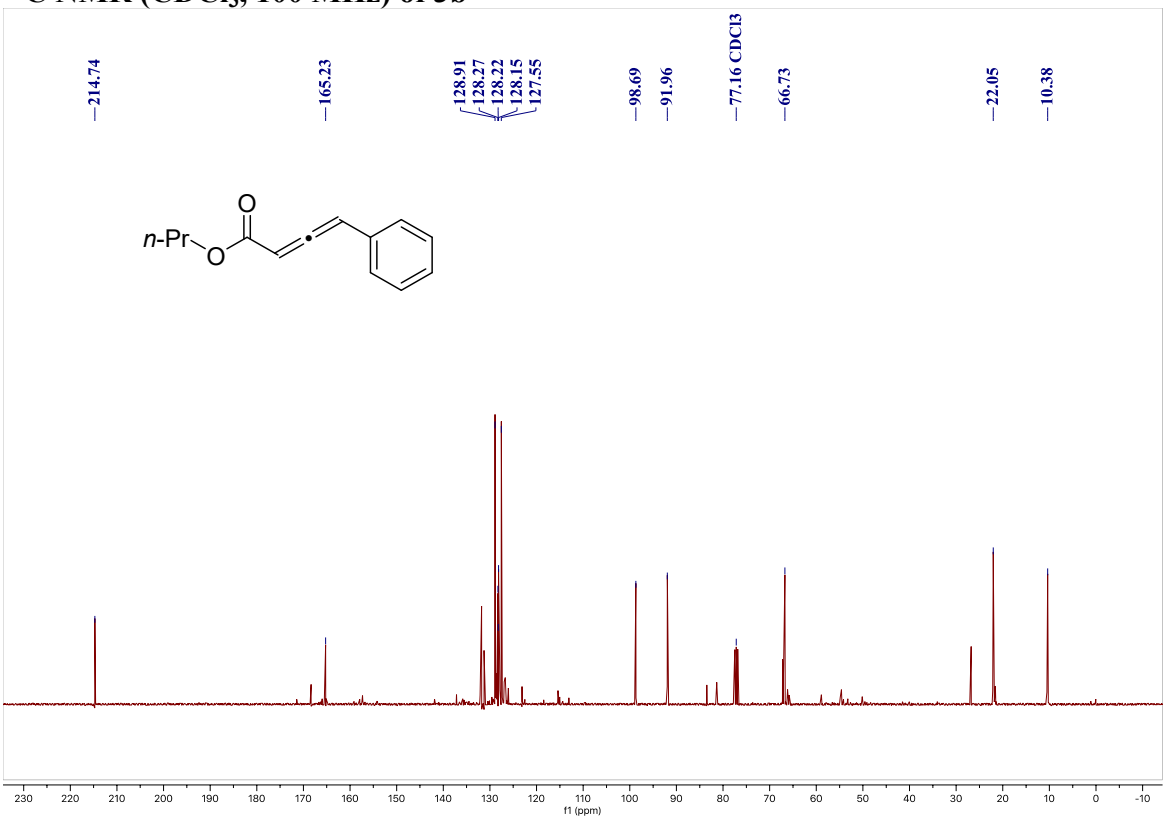
^{13}C NMR ($CDCl_3$, 100 MHz) of 3a



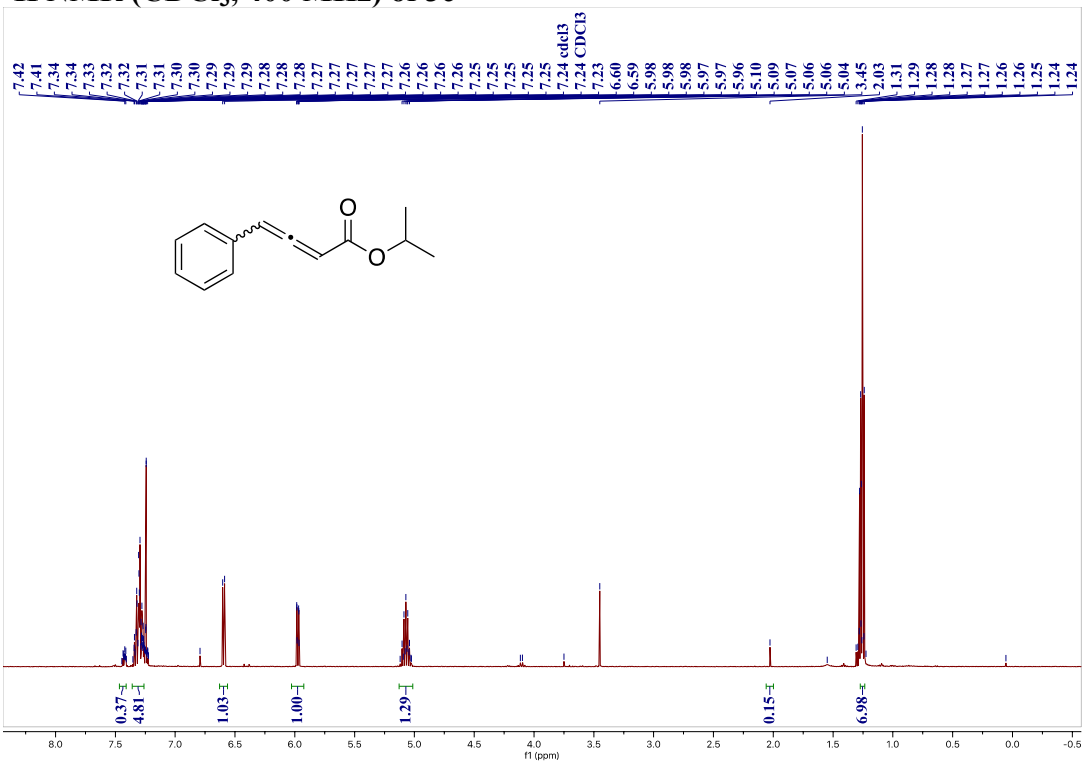
^{1}H NMR ($CDCl_3$, 400 MHz) of 3b



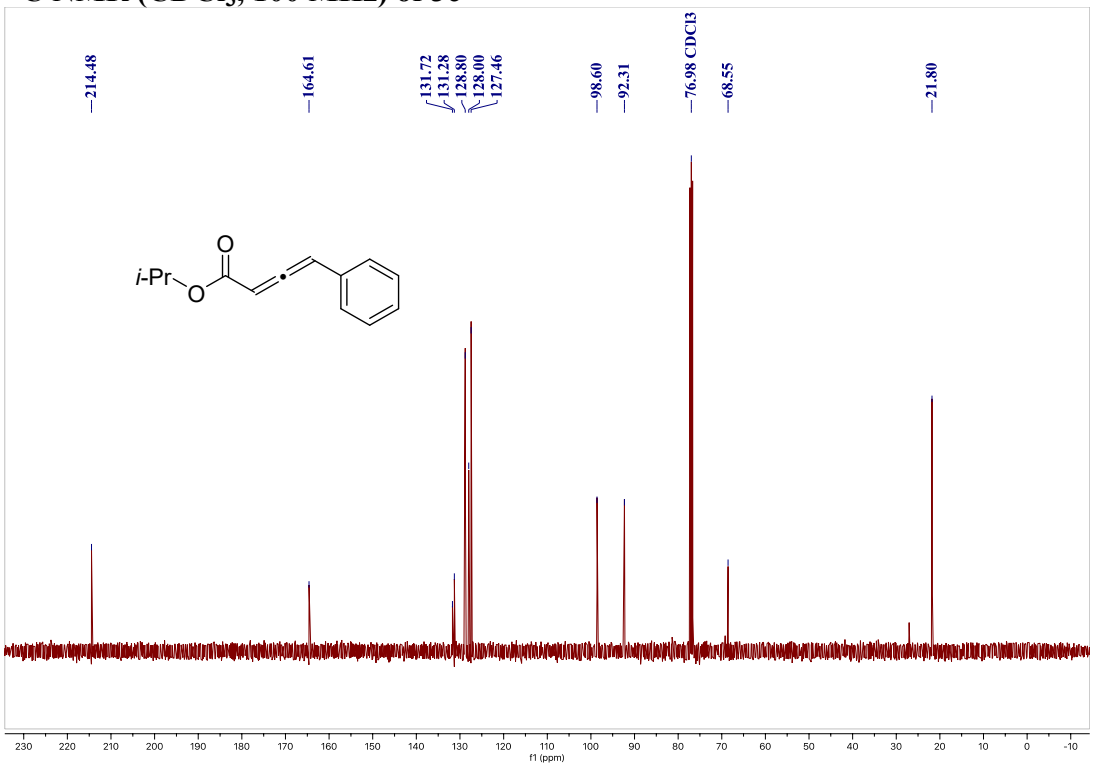
^{13}C NMR ($CDCl_3$, 100 MHz) of 3b



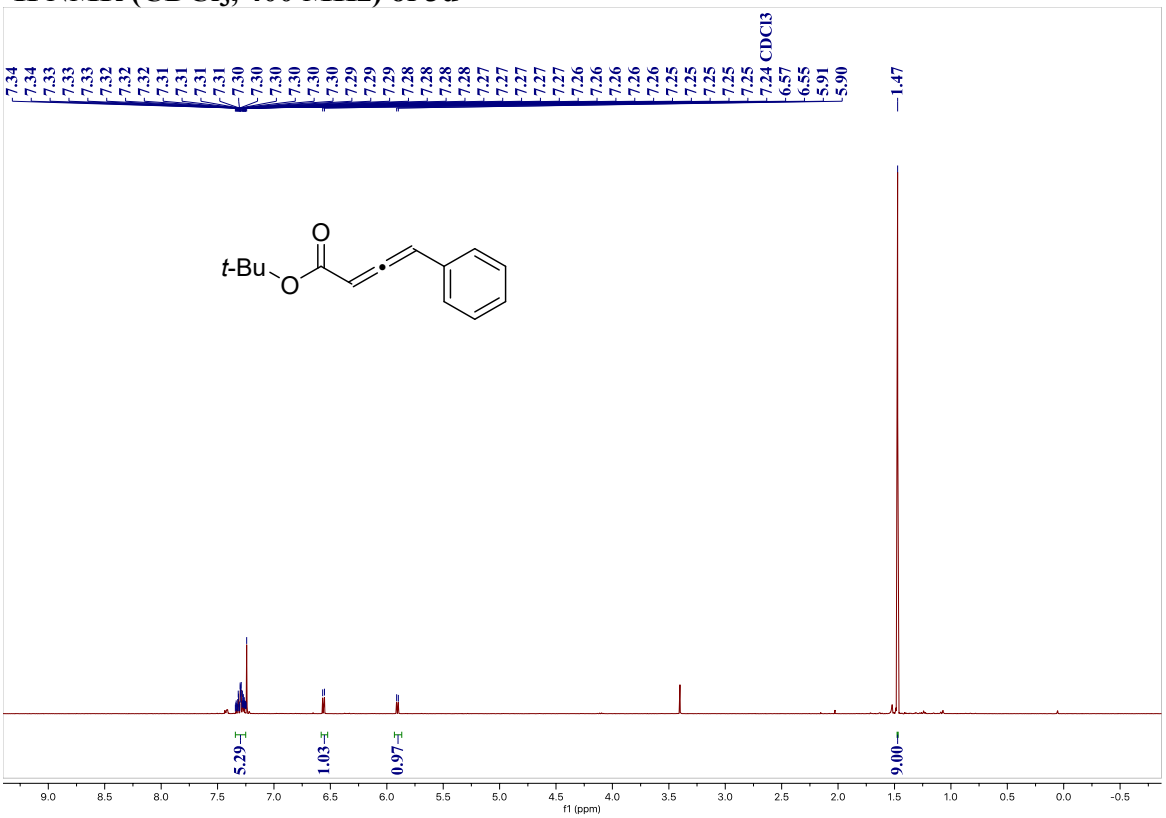
^{1}H NMR ($CDCl_3$, 400 MHz) of 3c



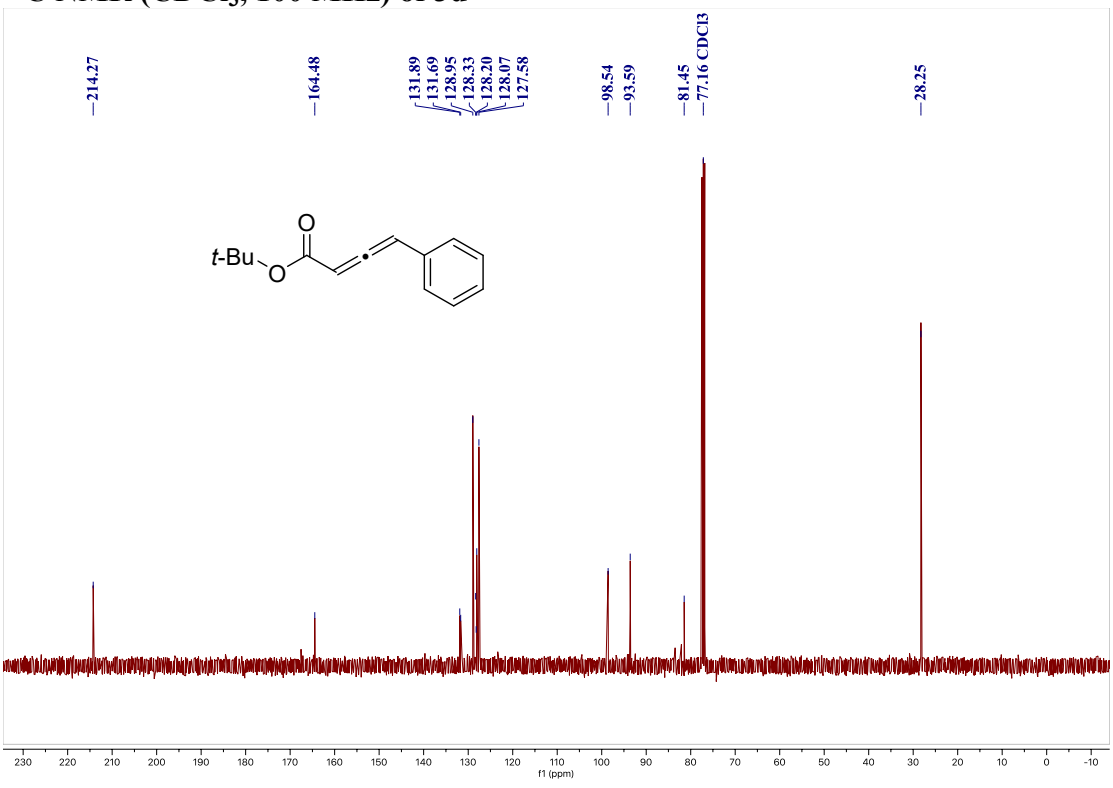
^{13}C NMR ($CDCl_3$, 100 MHz) of 3c



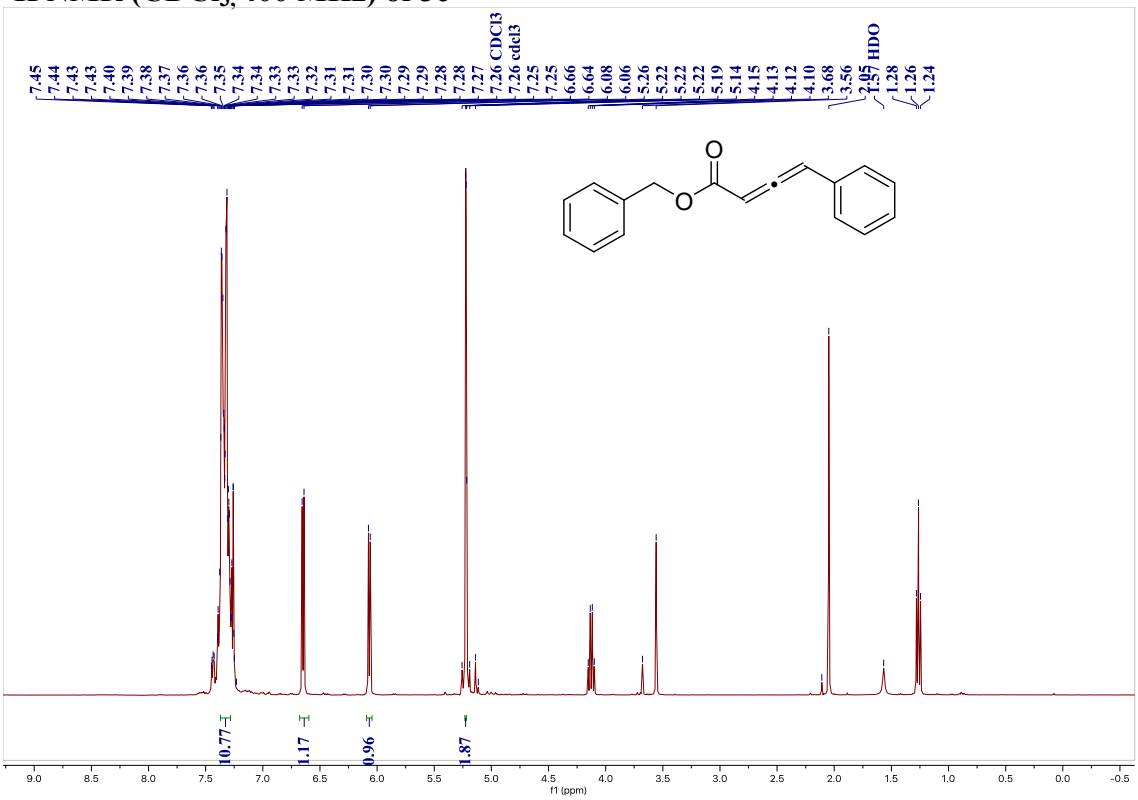
^{1}H NMR ($CDCl_3$, 400 MHz) of 3d



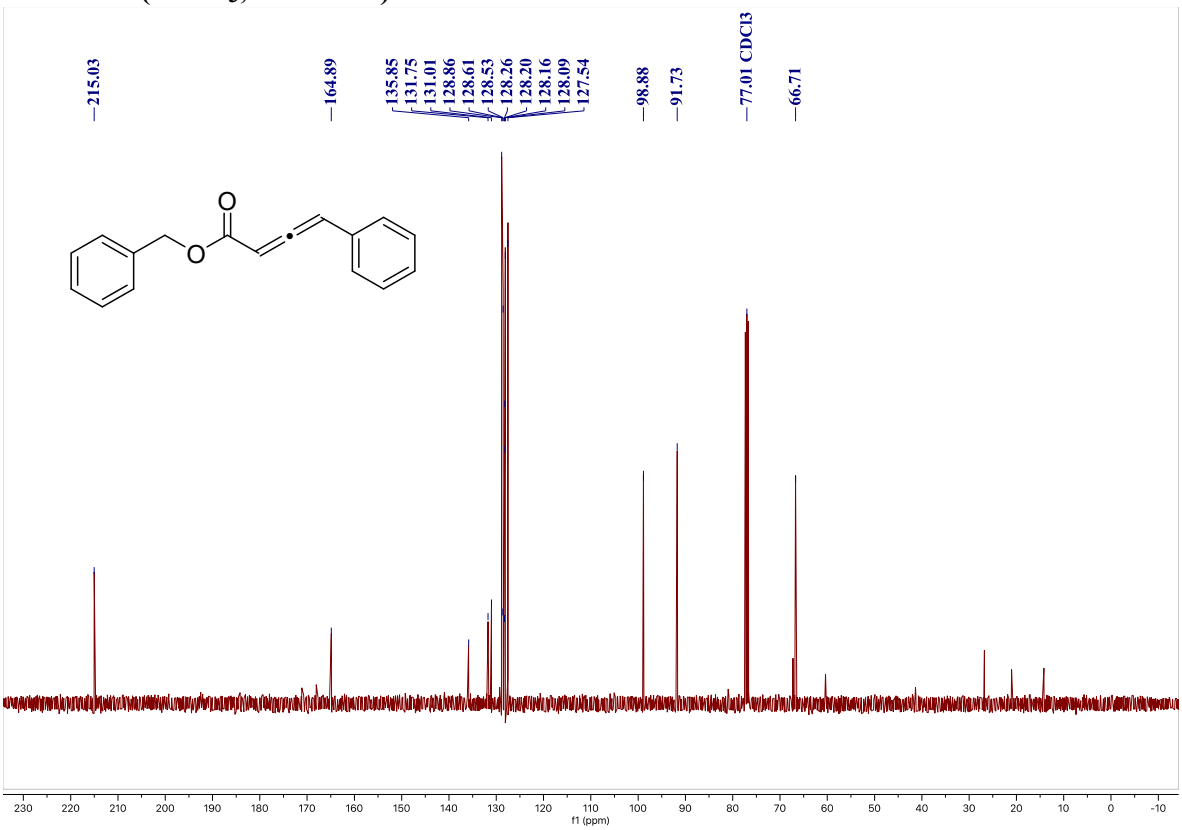
^{13}C NMR ($CDCl_3$, 100 MHz) of 3d



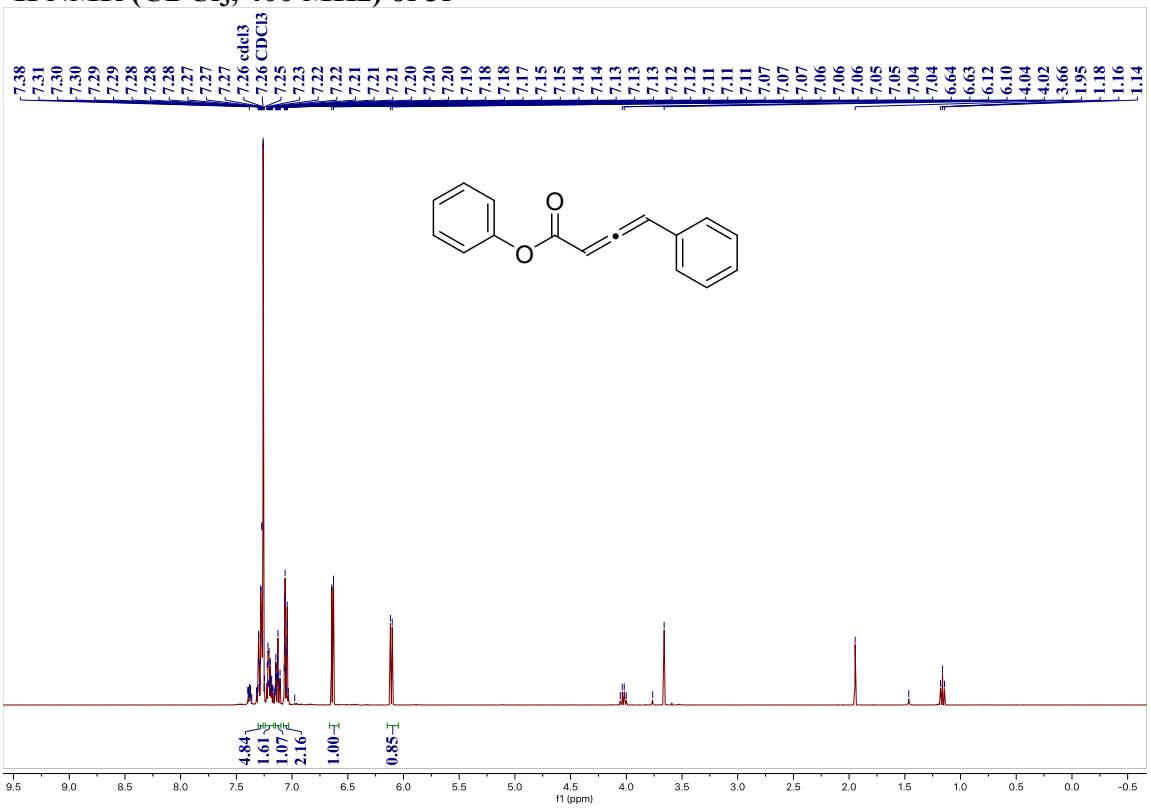
^{1}H NMR ($CDCl_3$, 400 MHz) of 3e



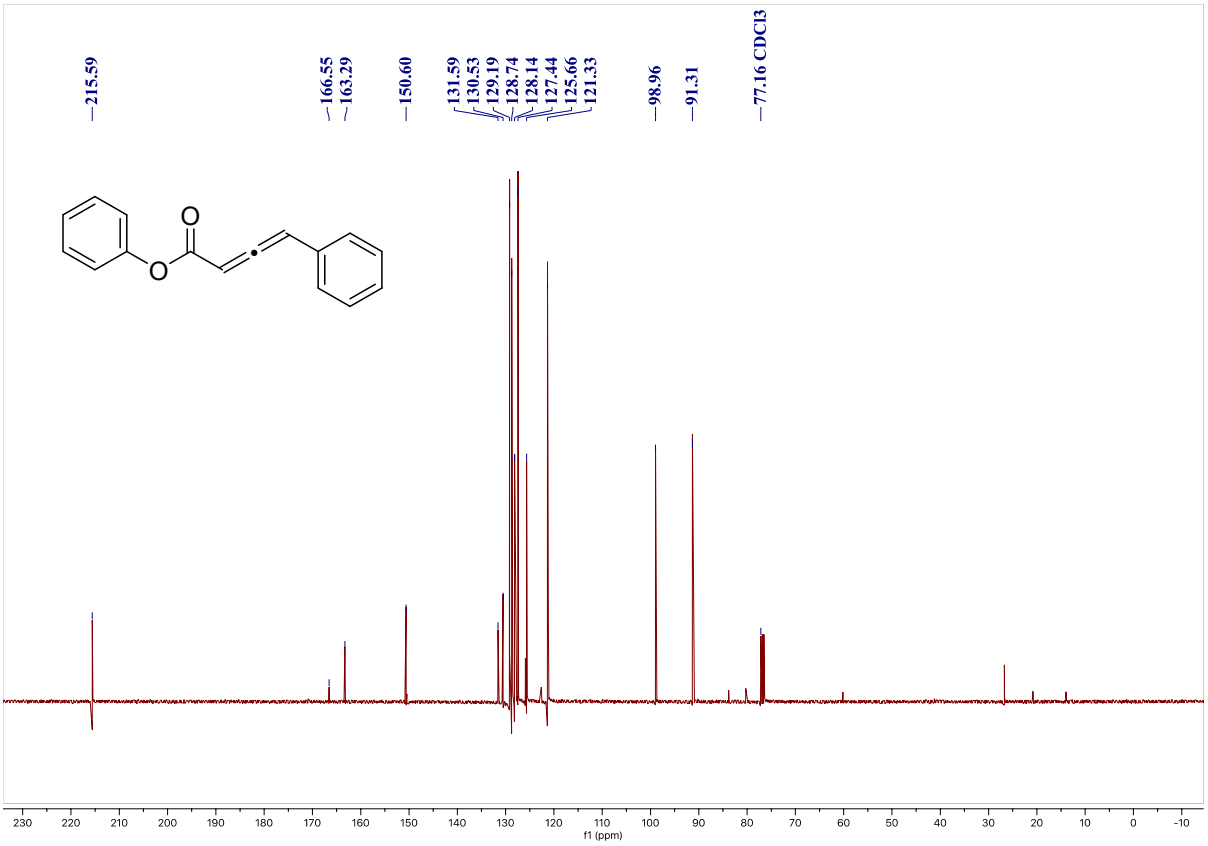
^{13}C NMR ($CDCl_3$, 100 MHz) of 3e



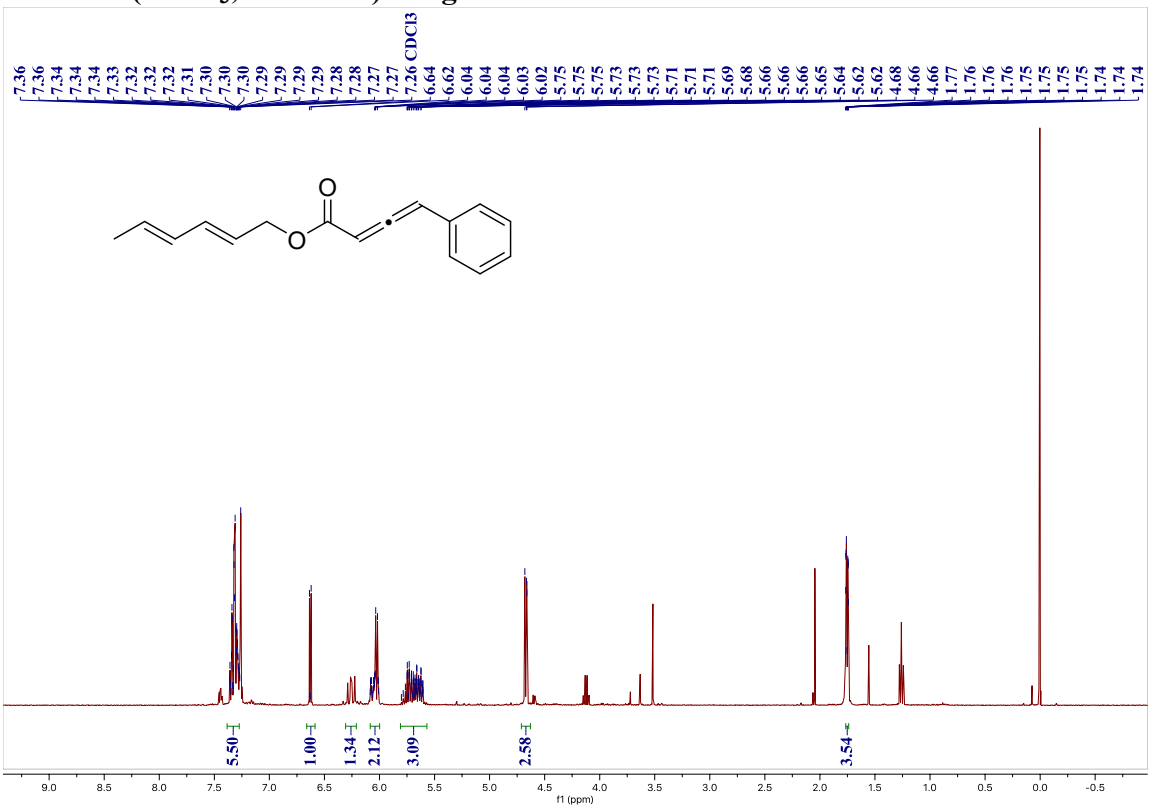
^{1}H NMR ($CDCl_3$, 400 MHz) of 3f



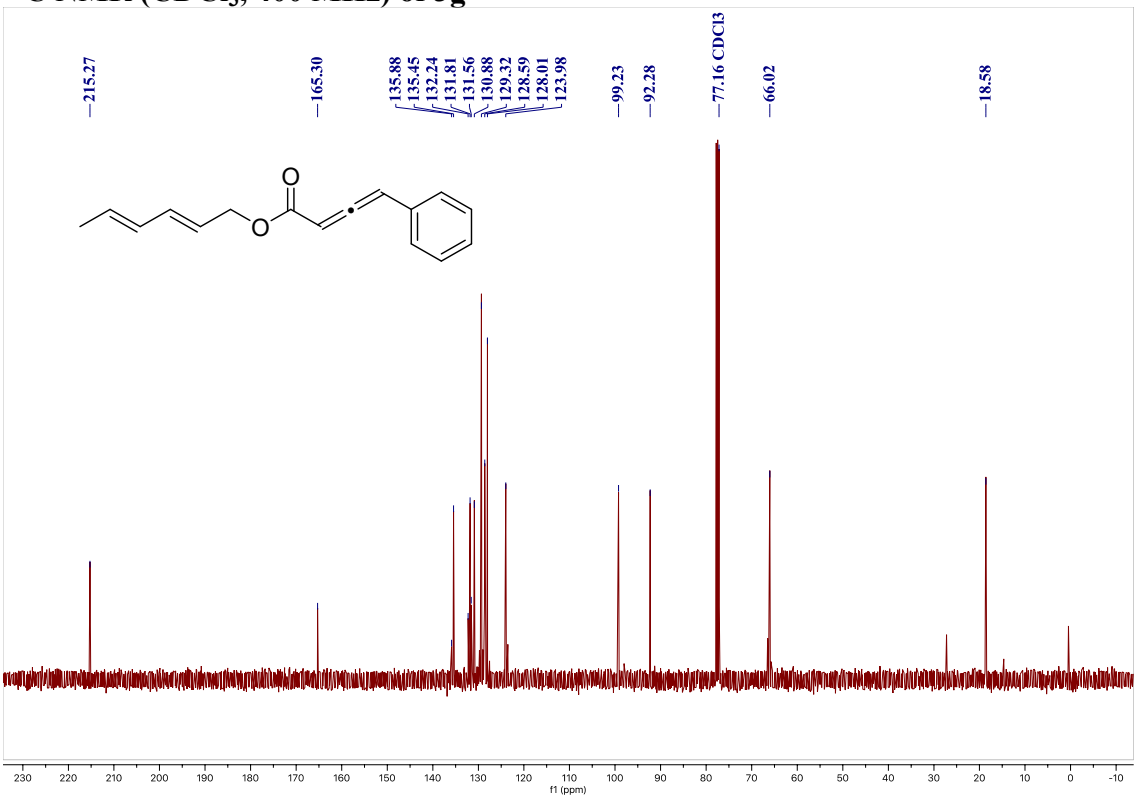
^{13}C NMR ($CDCl_3$, 100 MHz) of 3f



^{1}H NMR ($CDCl_3$, 400 MHz) of 3g

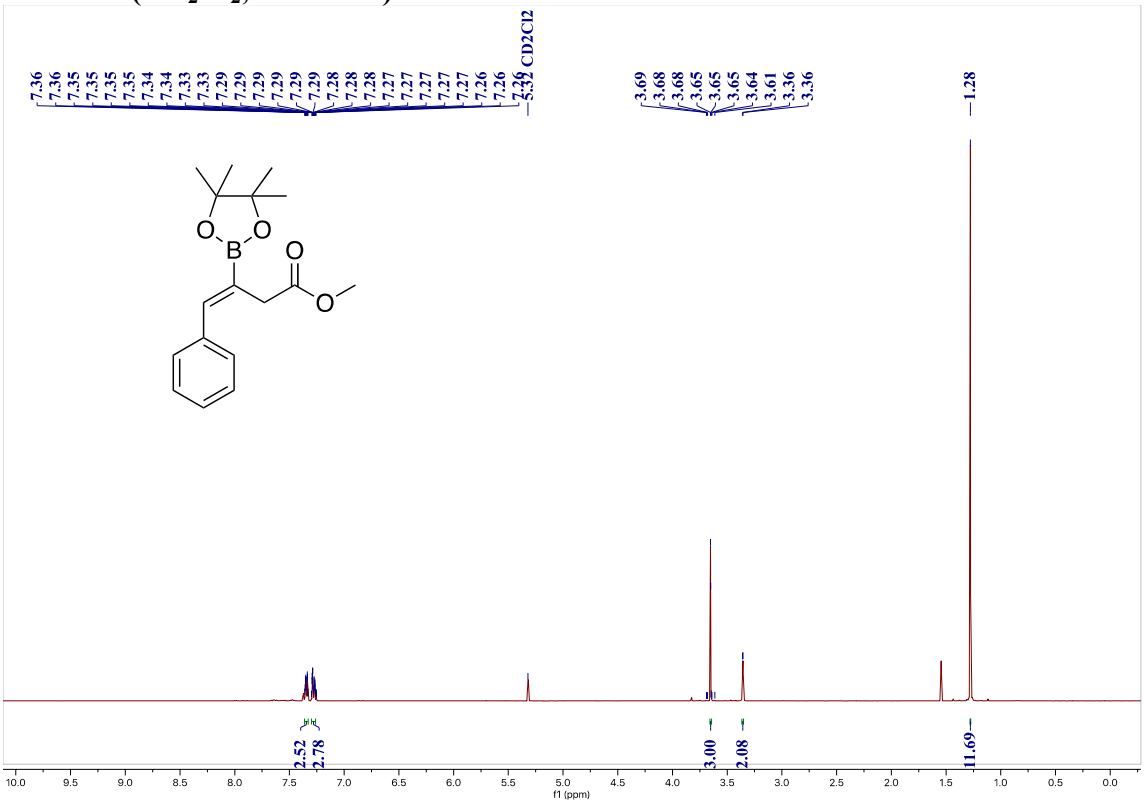


^{13}C NMR ($CDCl_3$, 400 MHz) of 3g

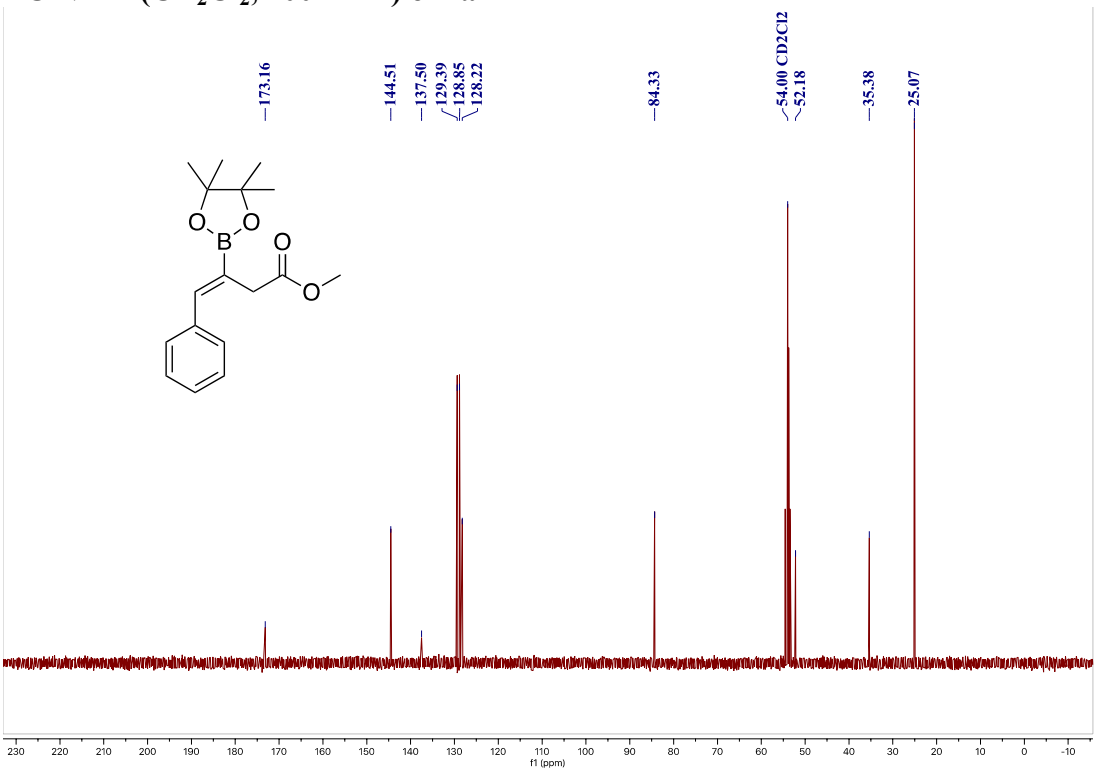


17. Characterization of *Z*-acrylates

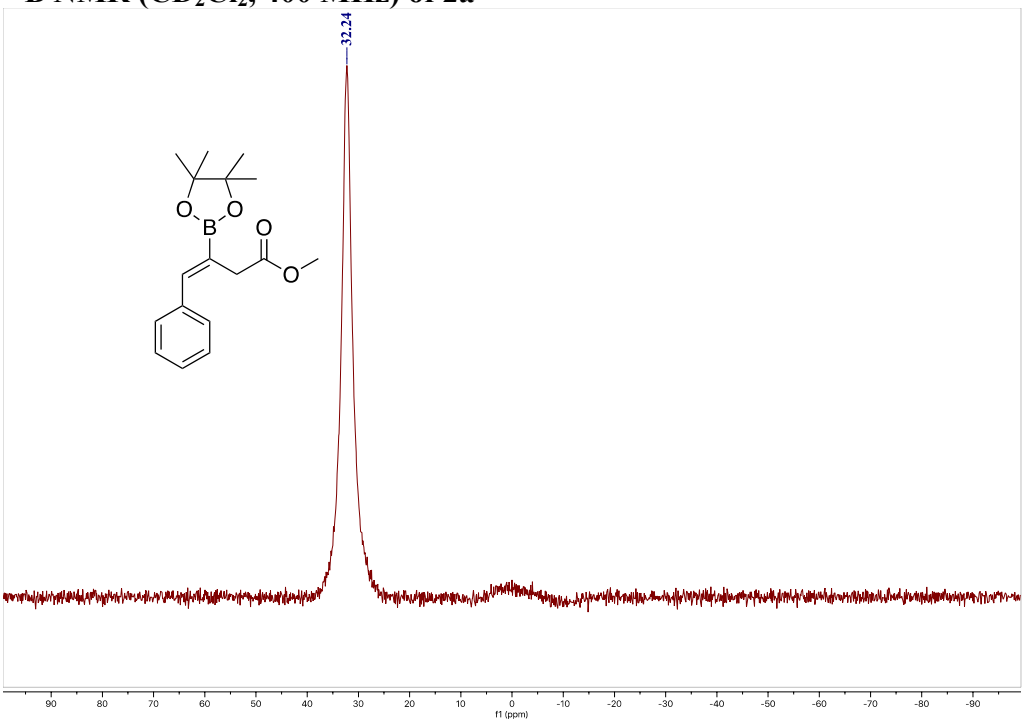
^{1}H NMR (CD_2Cl_2, 400 MHz) of 2a



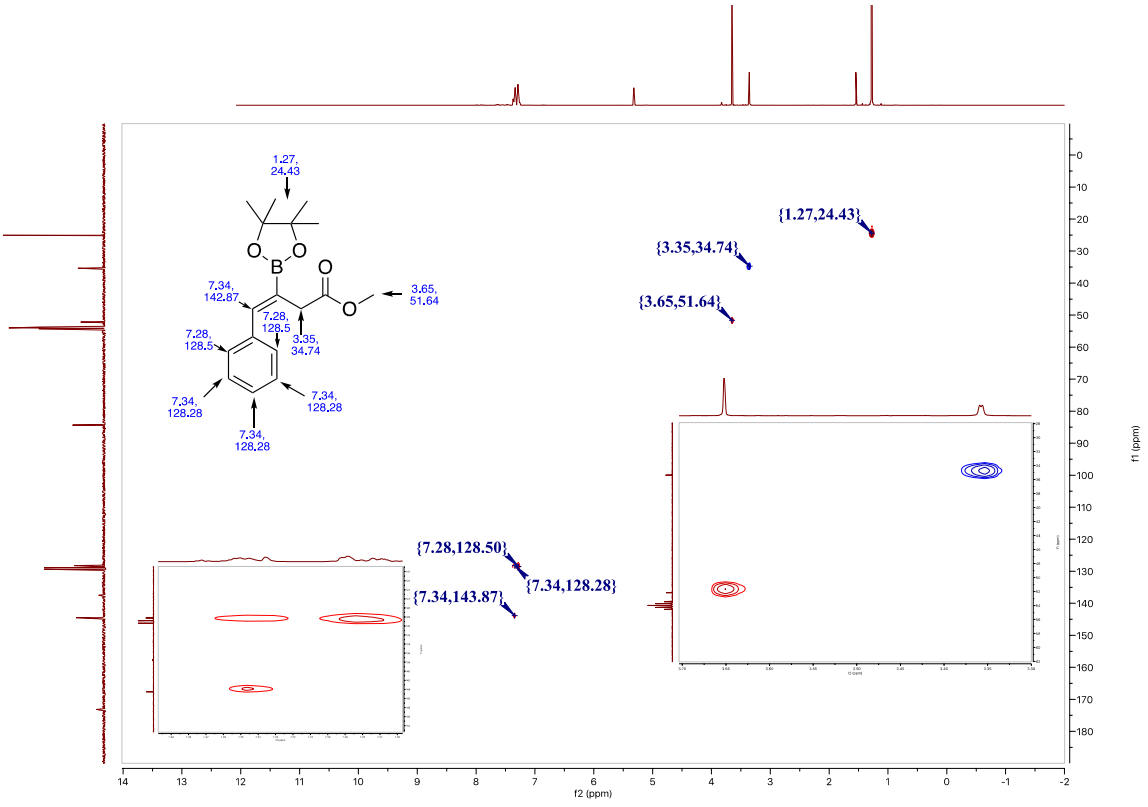
^{13}C NMR (CD_2Cl_2, 100 MHz) of 2a



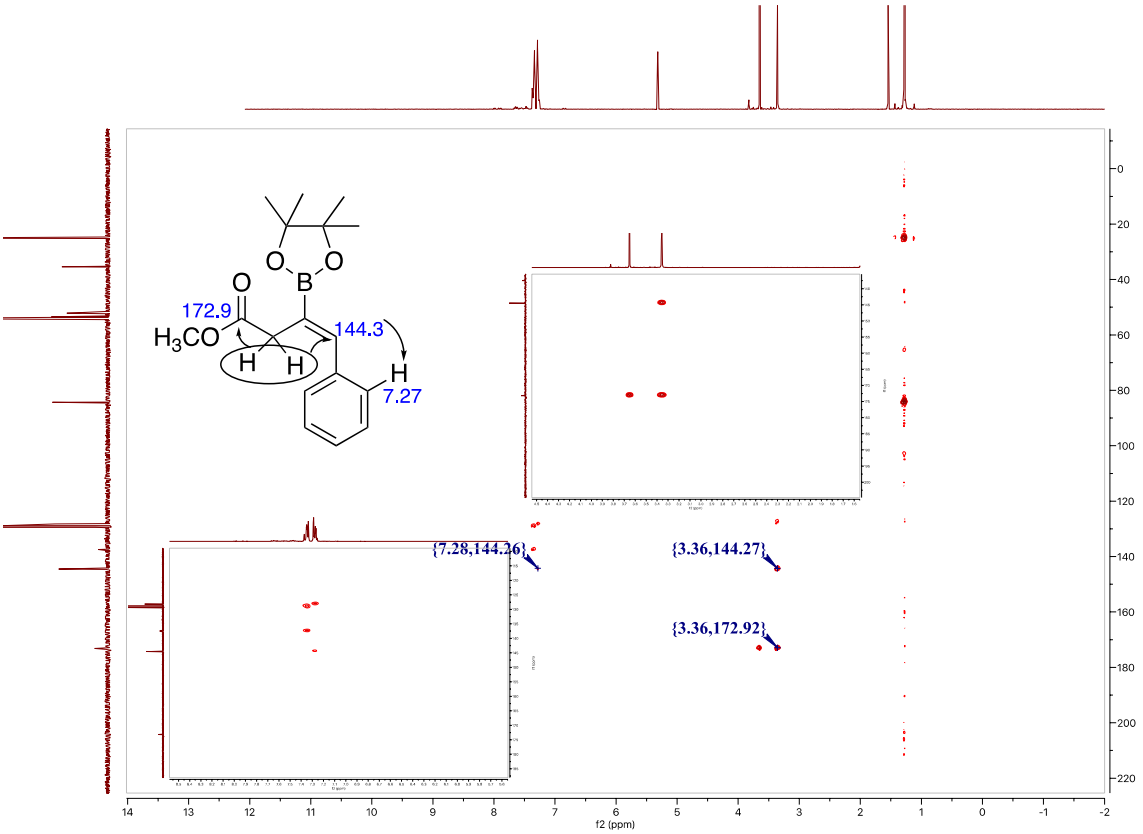
^{11}B NMR (CD_2Cl_2, 400 MHz) of 2a



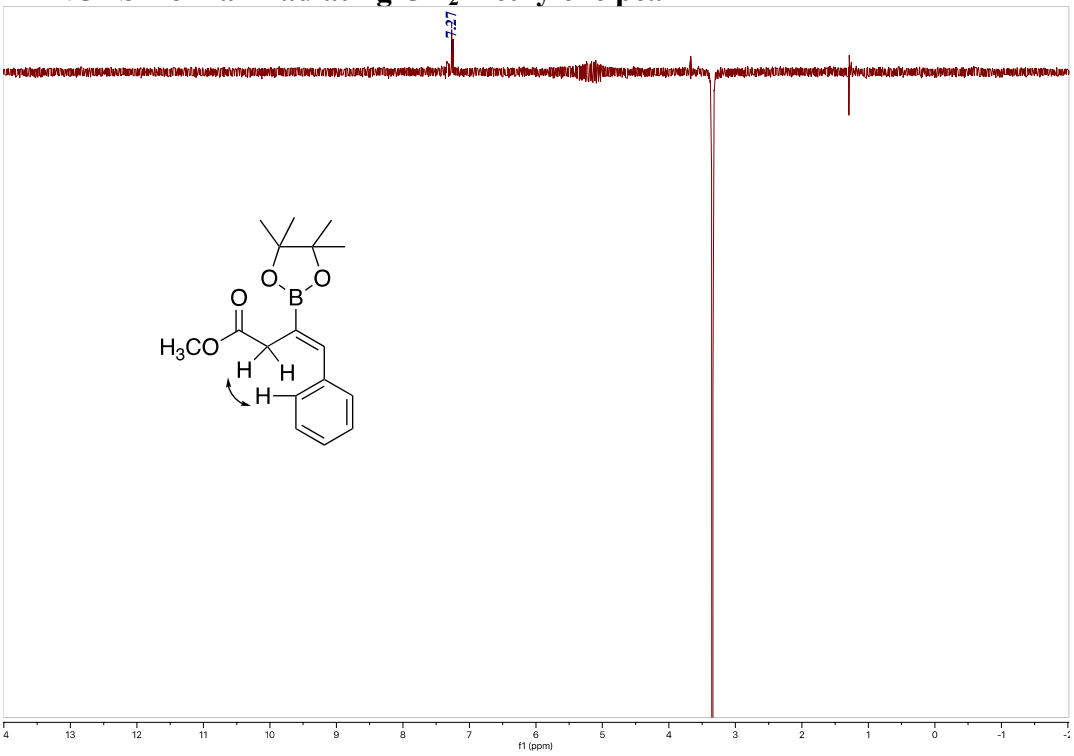
^{1}H–^{13}C HSQC of 2a



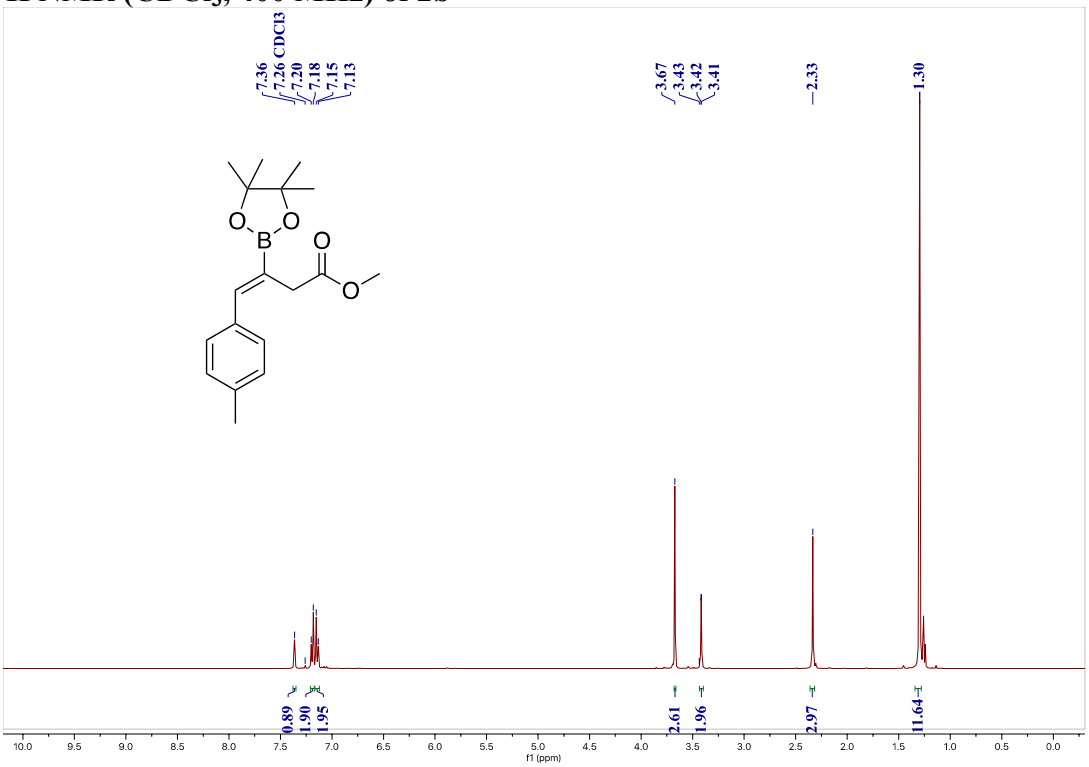
^{1}H-^{13}C HMBC of 2a



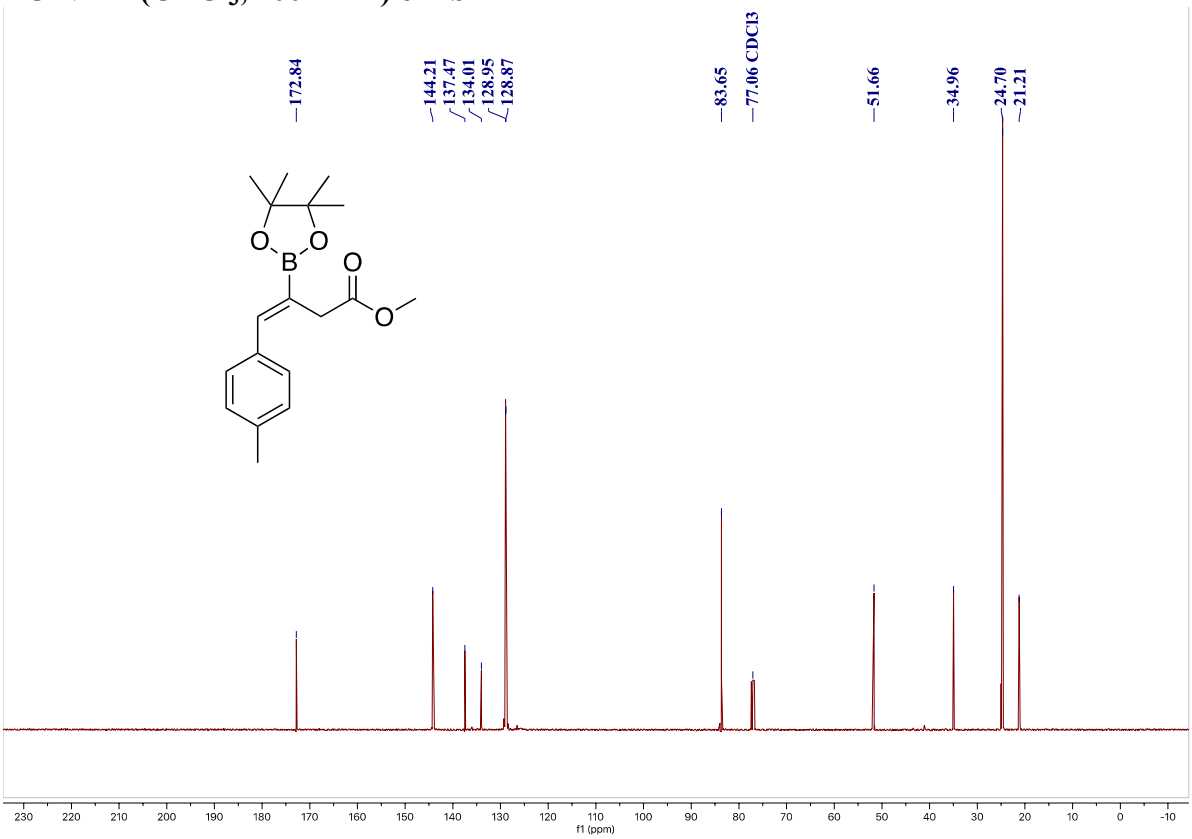
1D NOESY of 2a irradiating CH_2 methylene peak



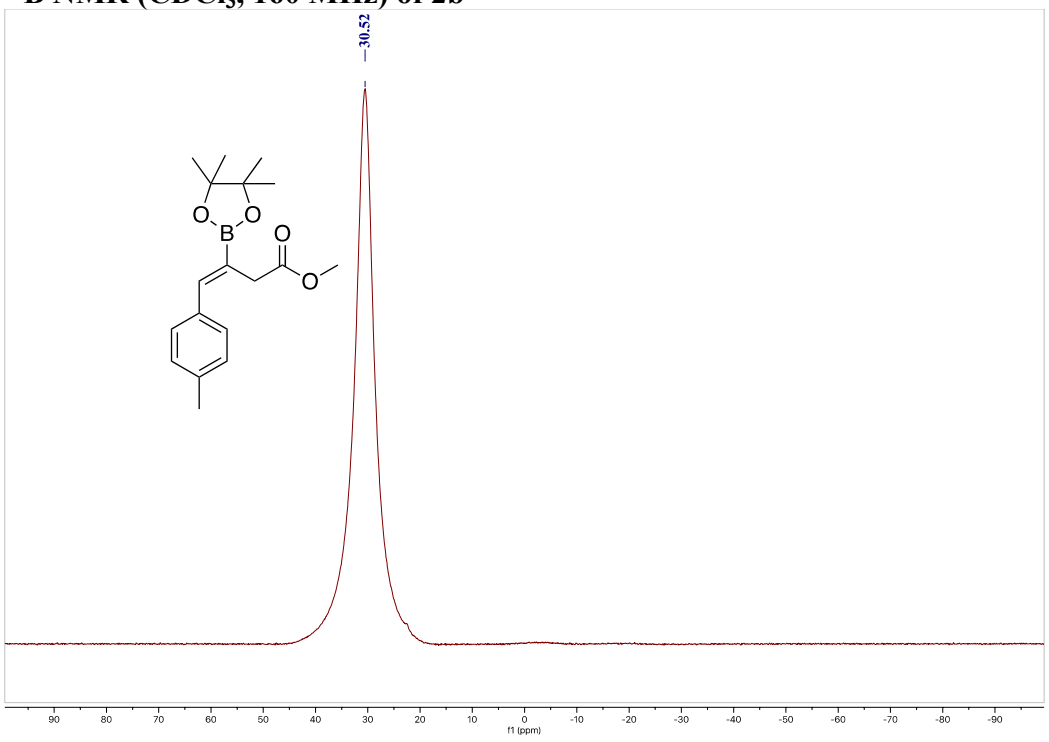
^{1}H NMR ($CDCl_3$, 400 MHz) of 2b



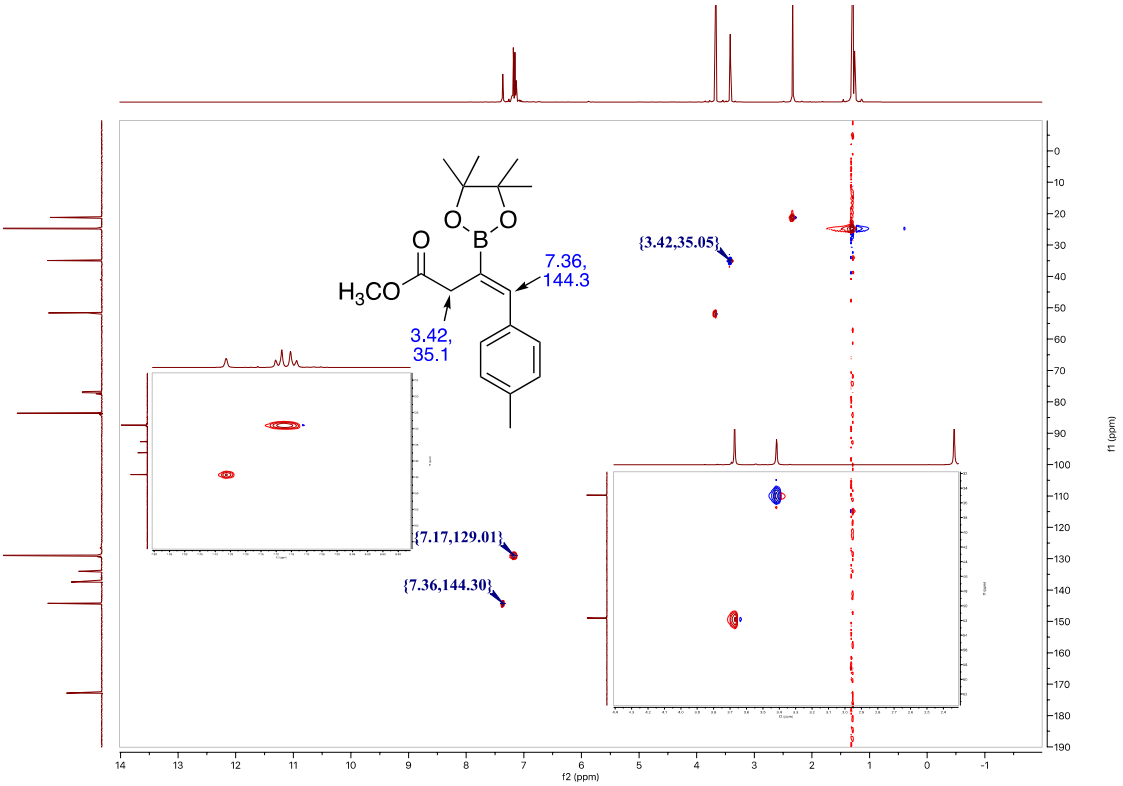
^{13}C NMR ($CDCl_3$, 100 MHz) of 2b



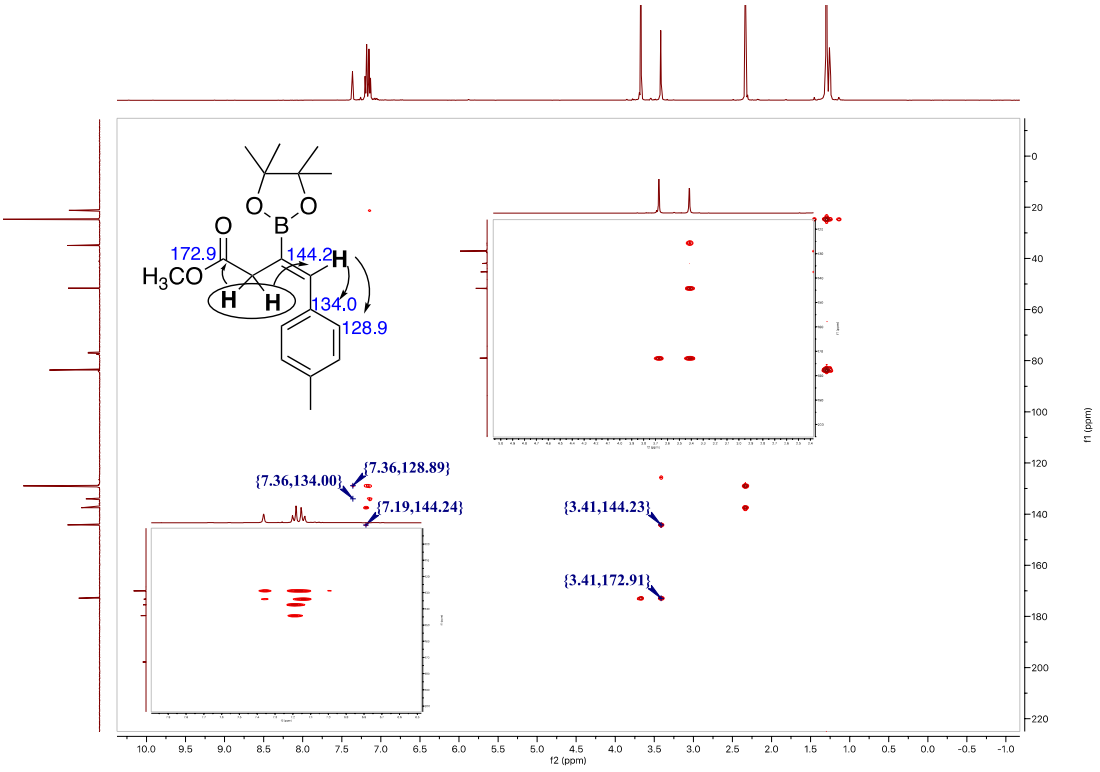
^{11}B NMR ($CDCl_3$, 160 MHz) of 2b



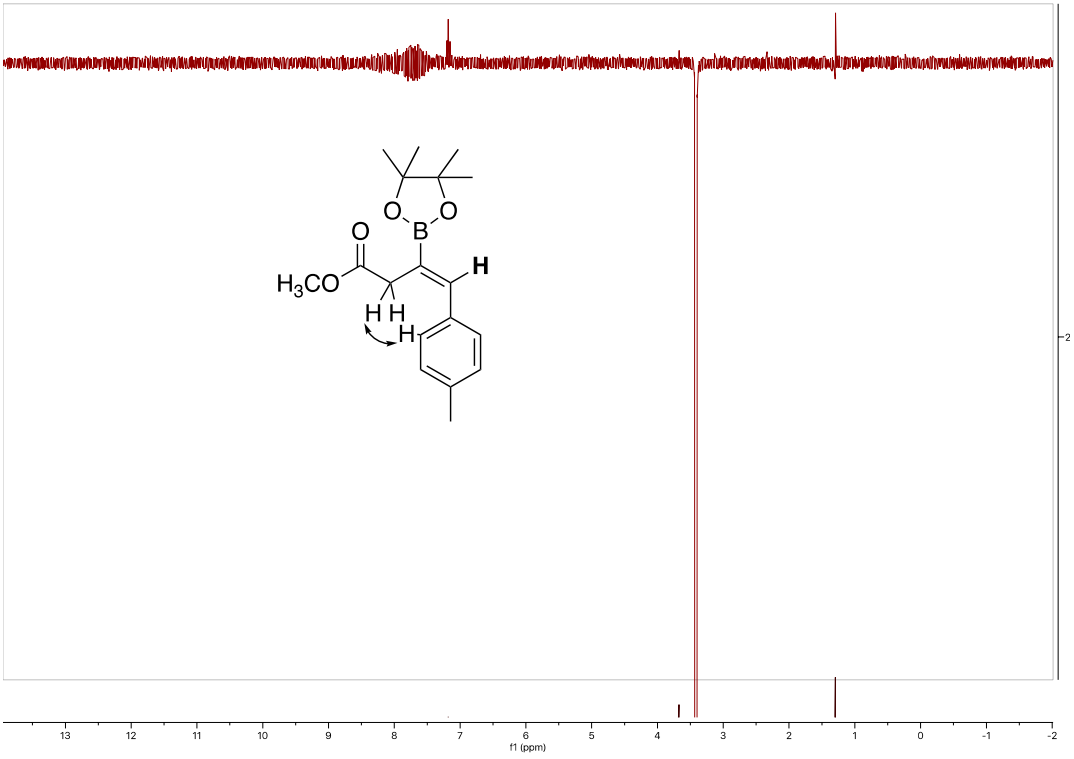
^{1}H-^{13}C HSQC of 2b



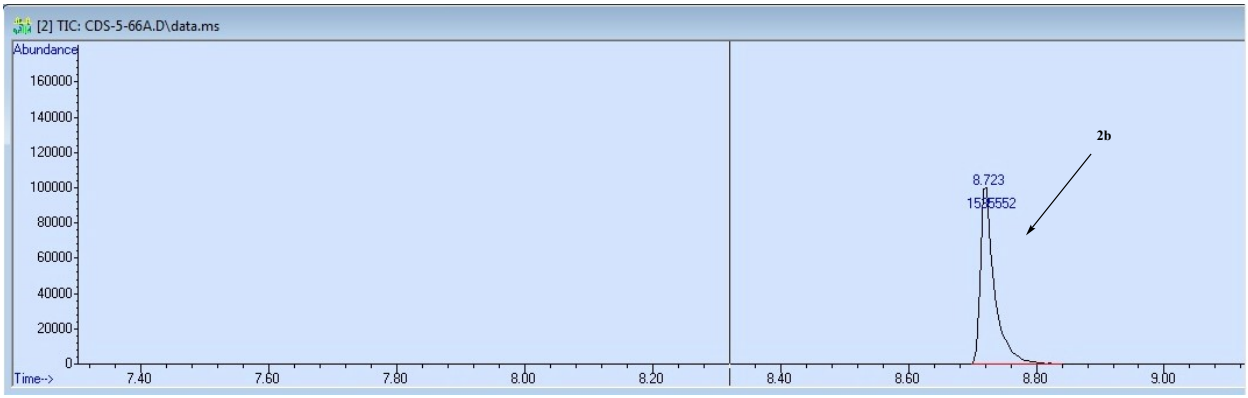
^{1}H-^{13}C HMBC of 2b



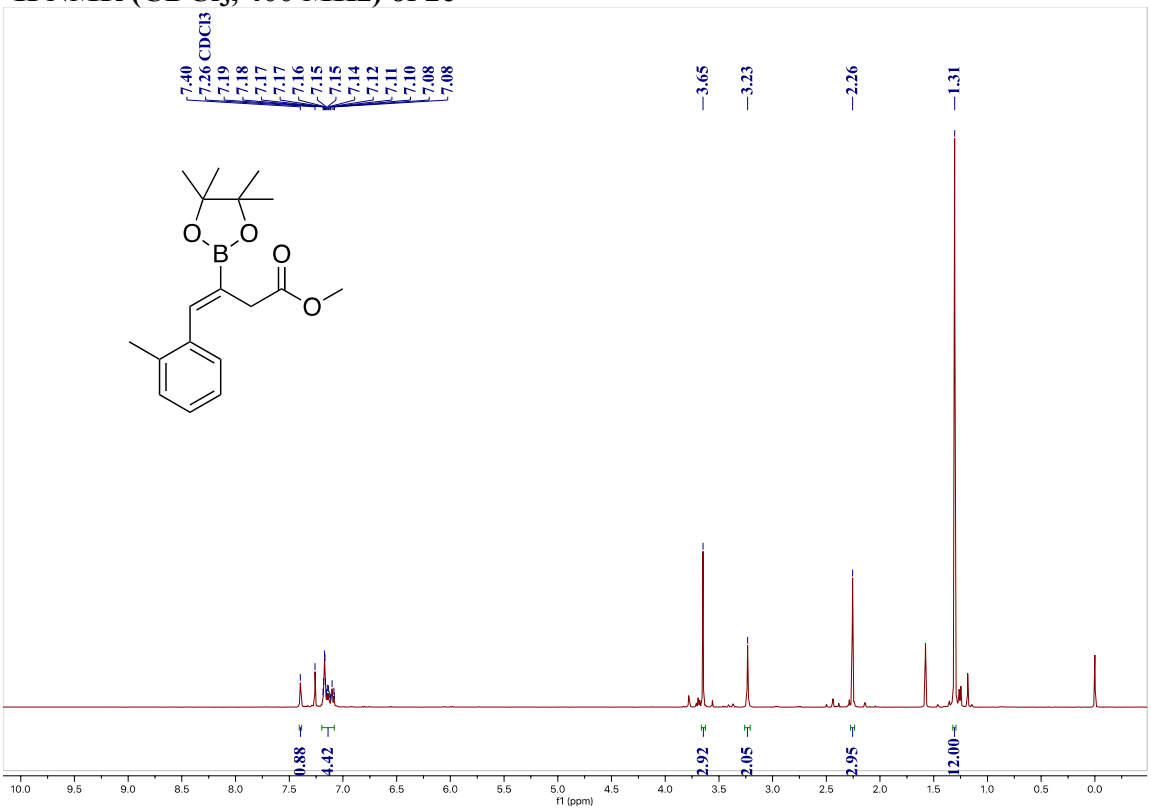
1D NOESY of 2b



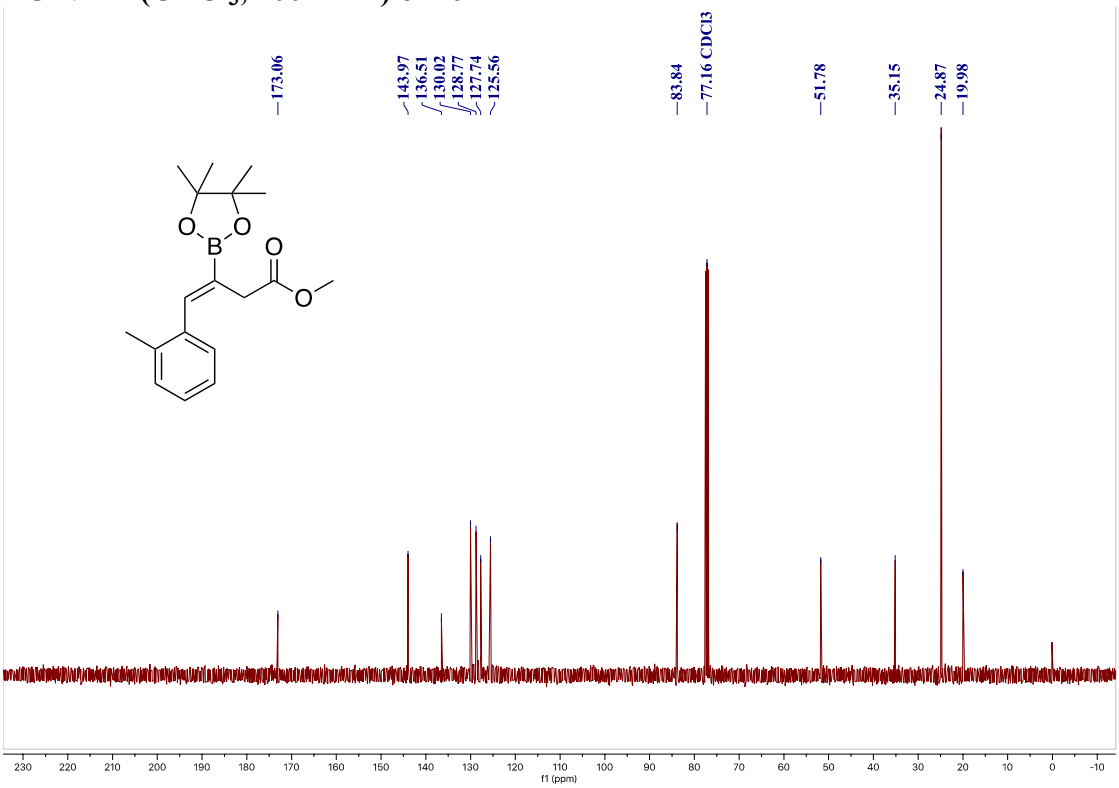
Crude GC of 2b



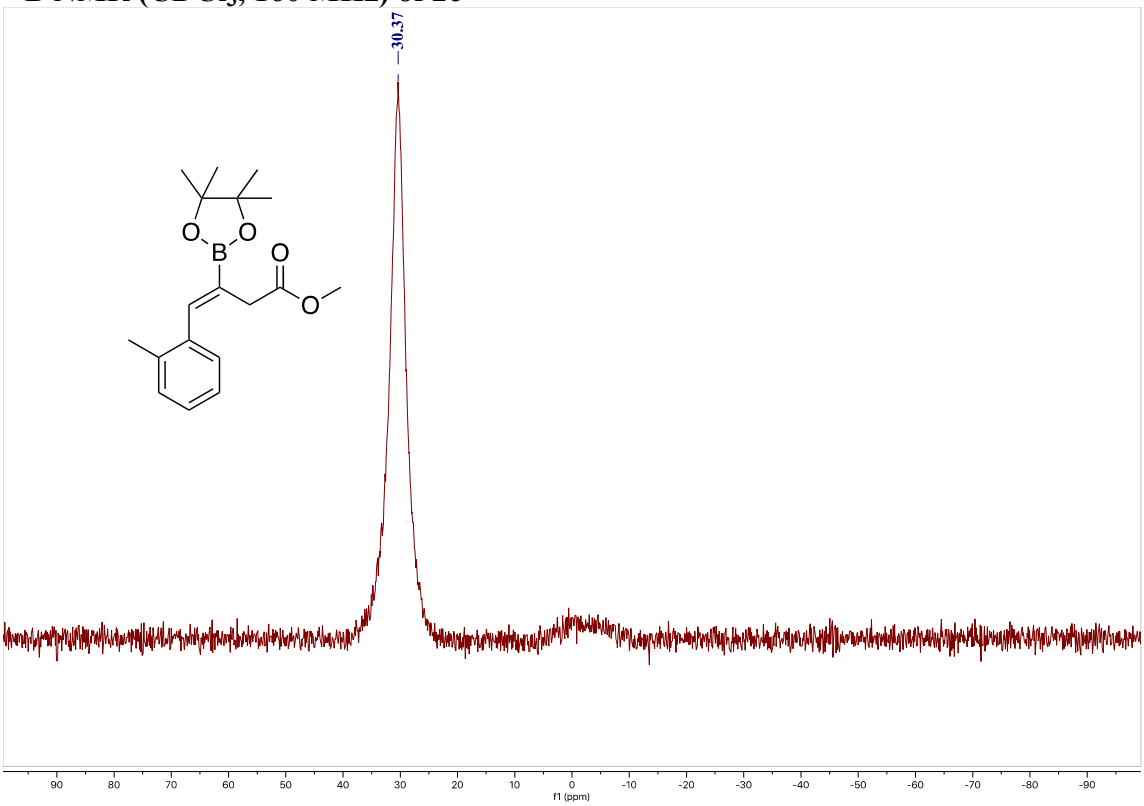
^{1}H NMR ($CDCl_3$, 400 MHz) of 2c



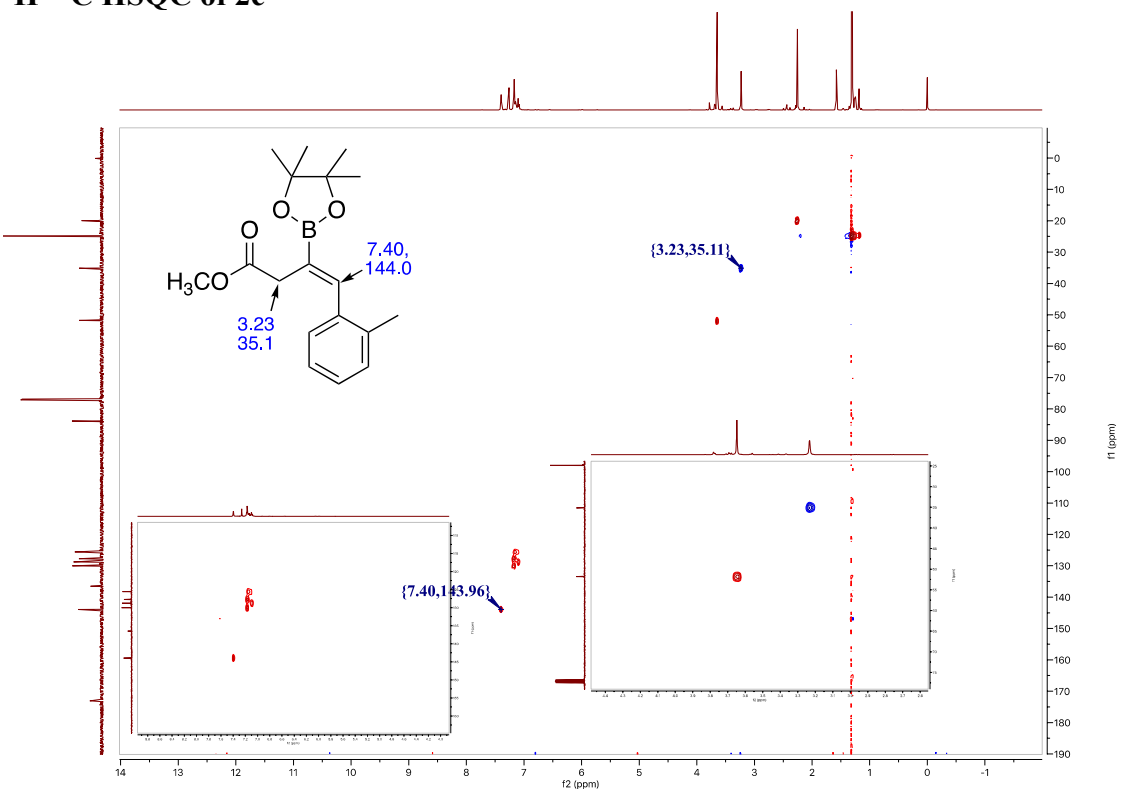
^{13}C NMR ($CDCl_3$, 100 MHz) of 2c



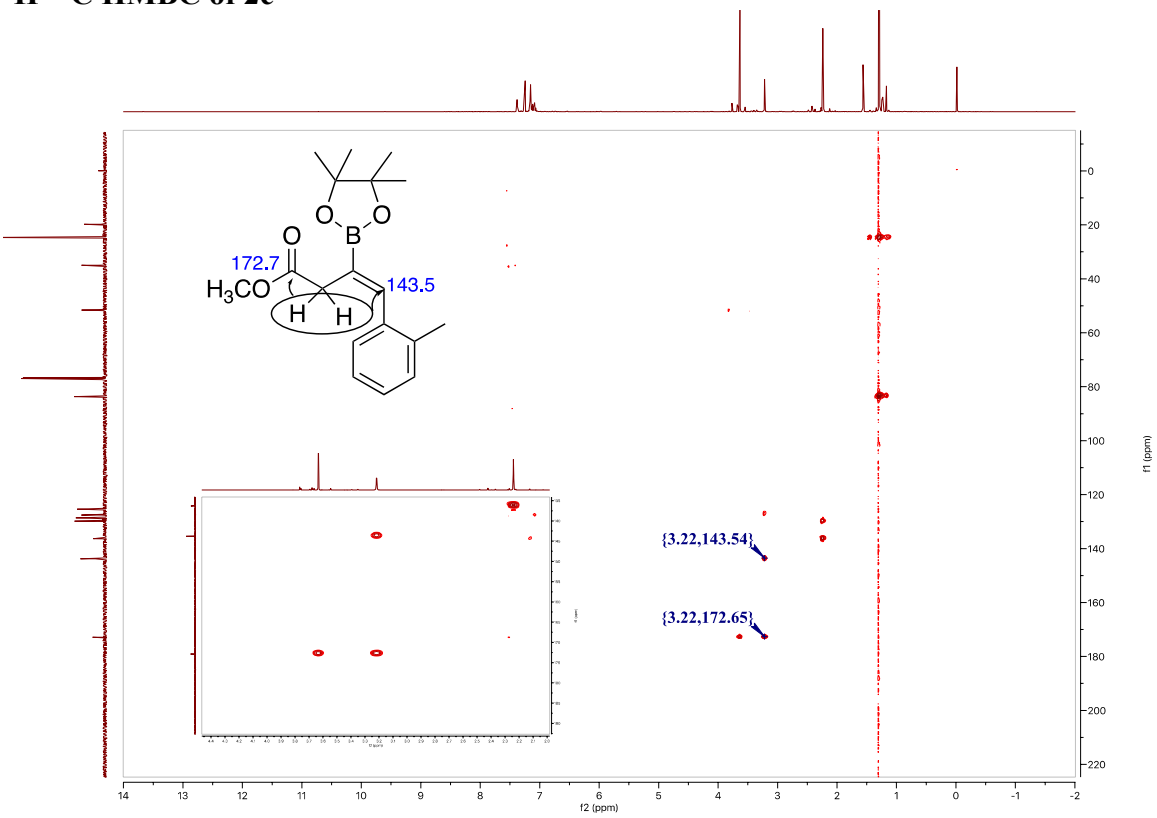
^{11}B NMR ($CDCl_3$, 160 MHz) of 2c



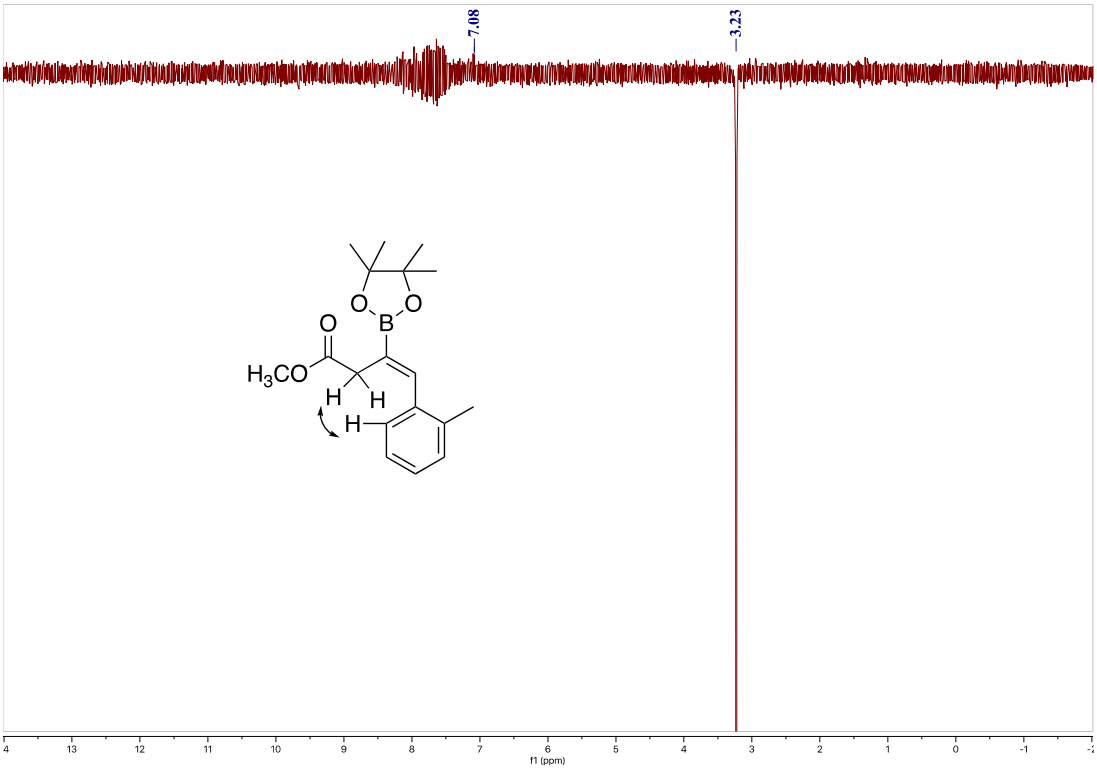
^{1}H-^{13}C HSQC of 2c



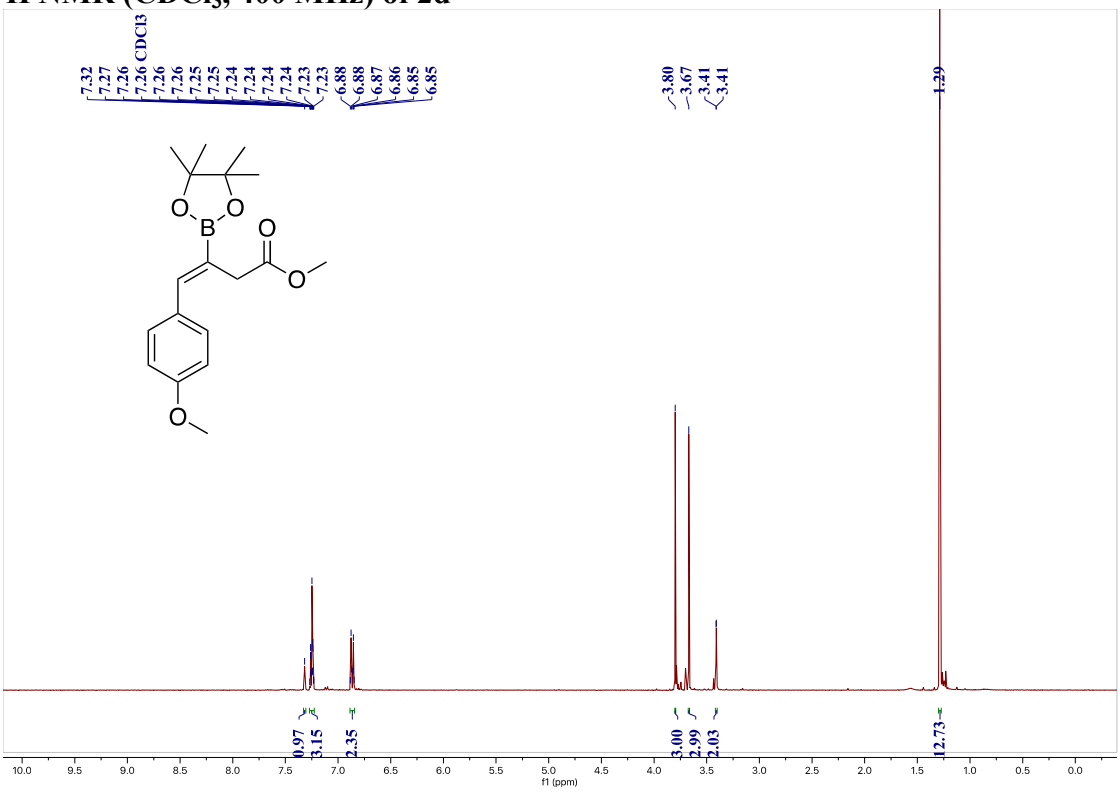
^{1}H-^{13}C HMBC of 2c



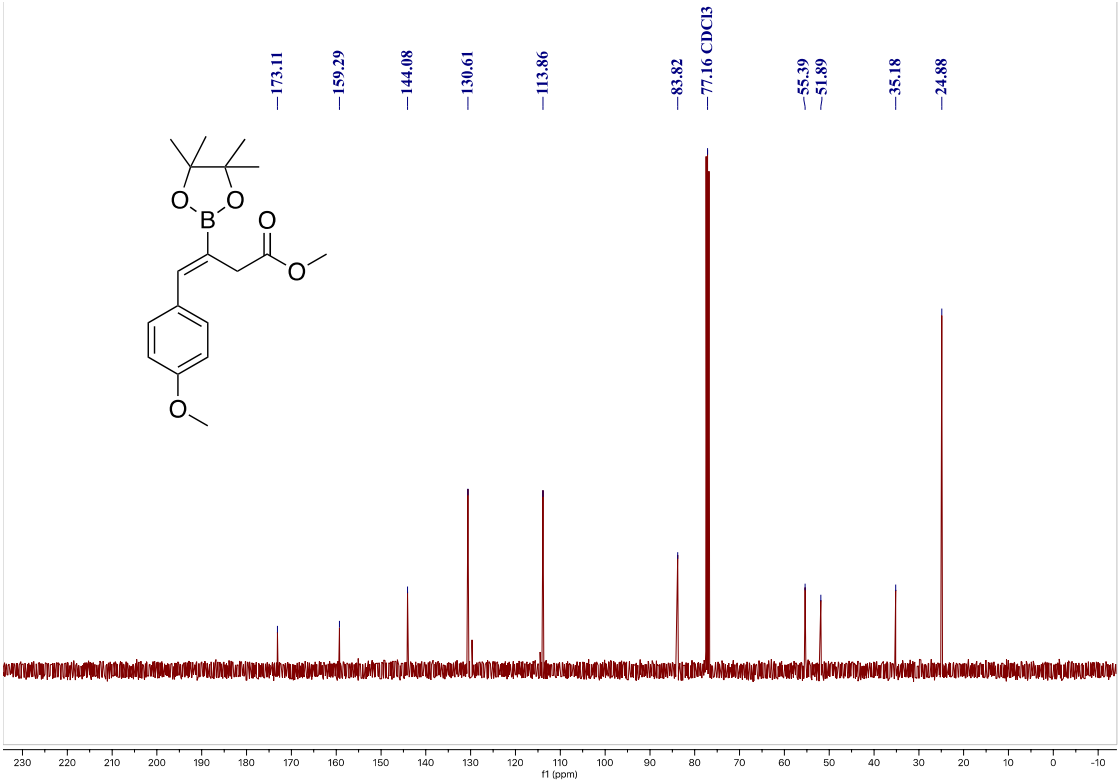
1D NOESY of 2c



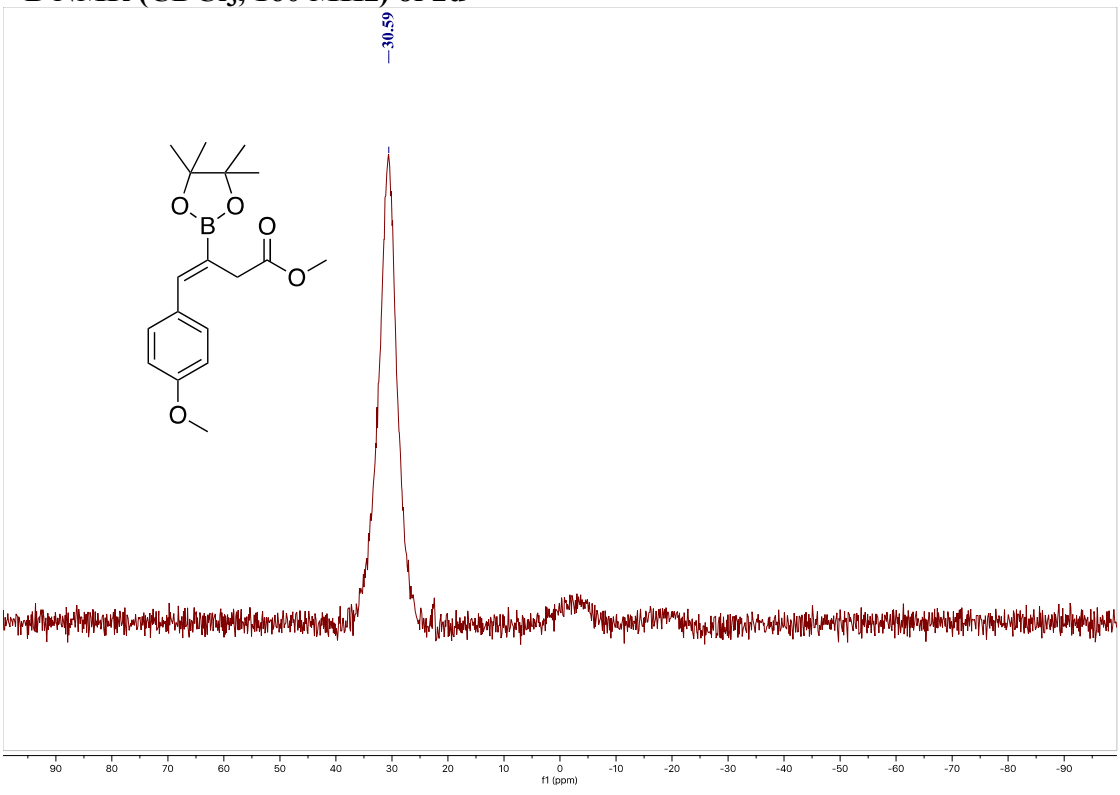
^{1}H NMR ($CDCl_3$, 400 MHz) of 2d



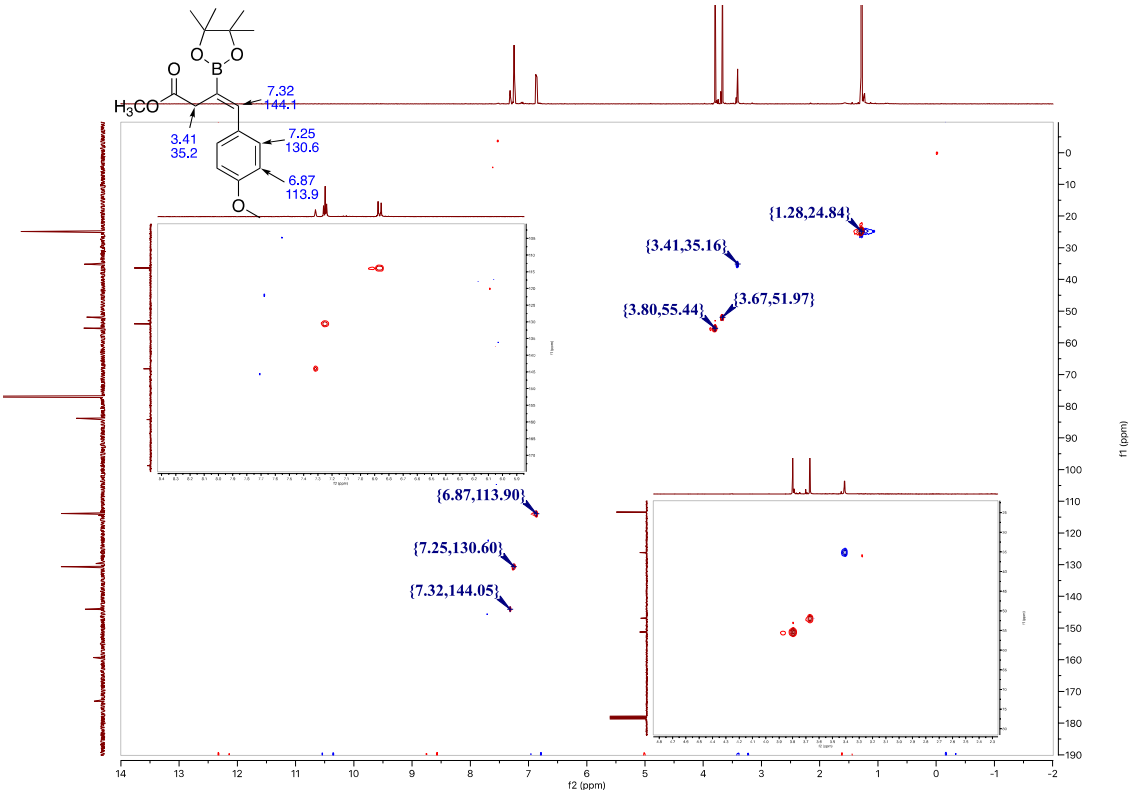
^{13}C NMR ($CDCl_3$, 400 MHz) of 2d



^{11}B NMR ($CDCl_3$, 160 MHz) of 2d



^{1}H-^{13}C HSQC of 2d



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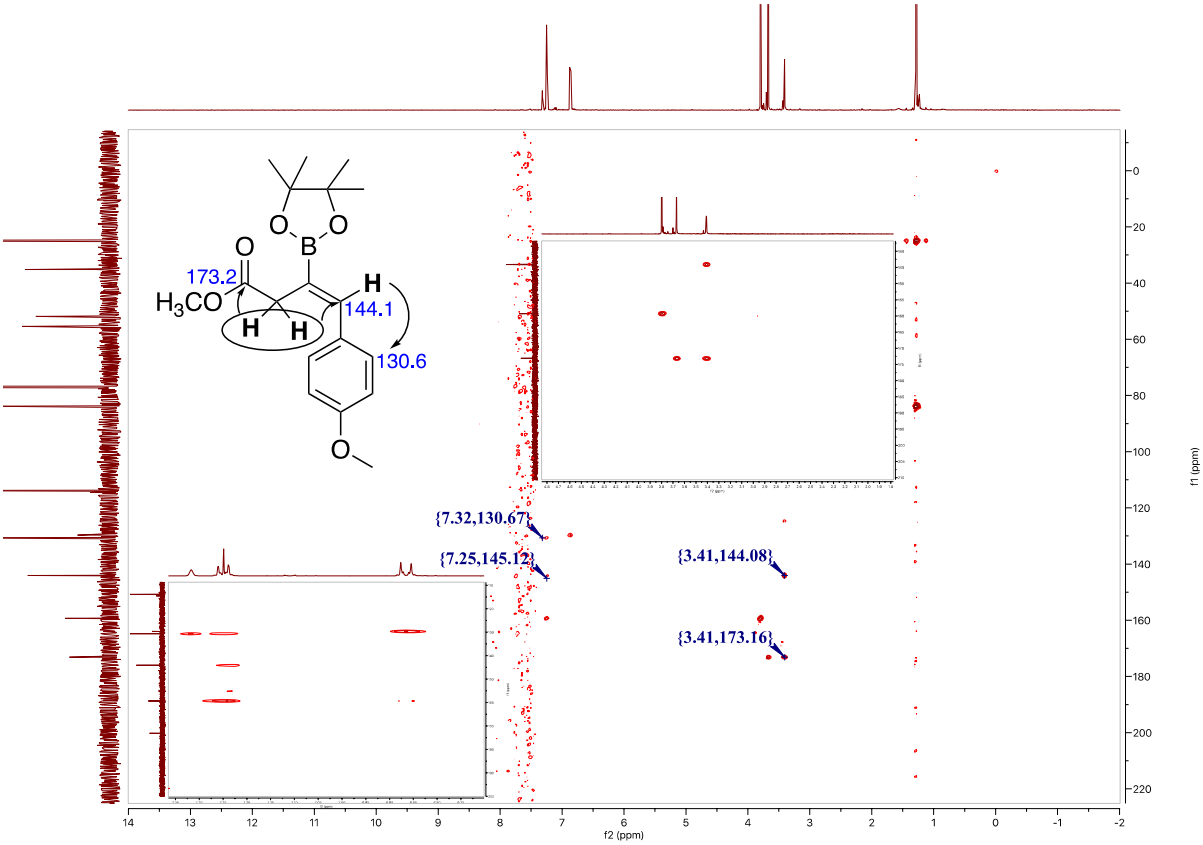
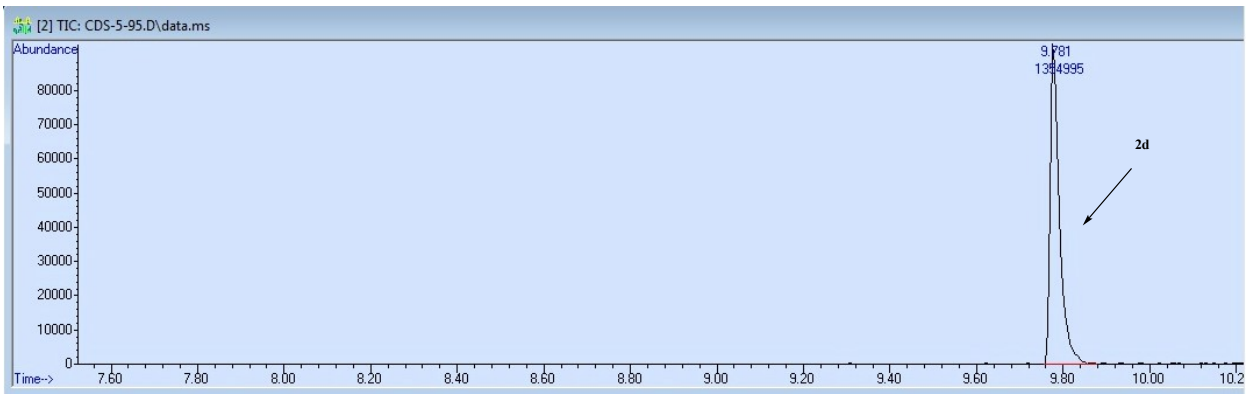
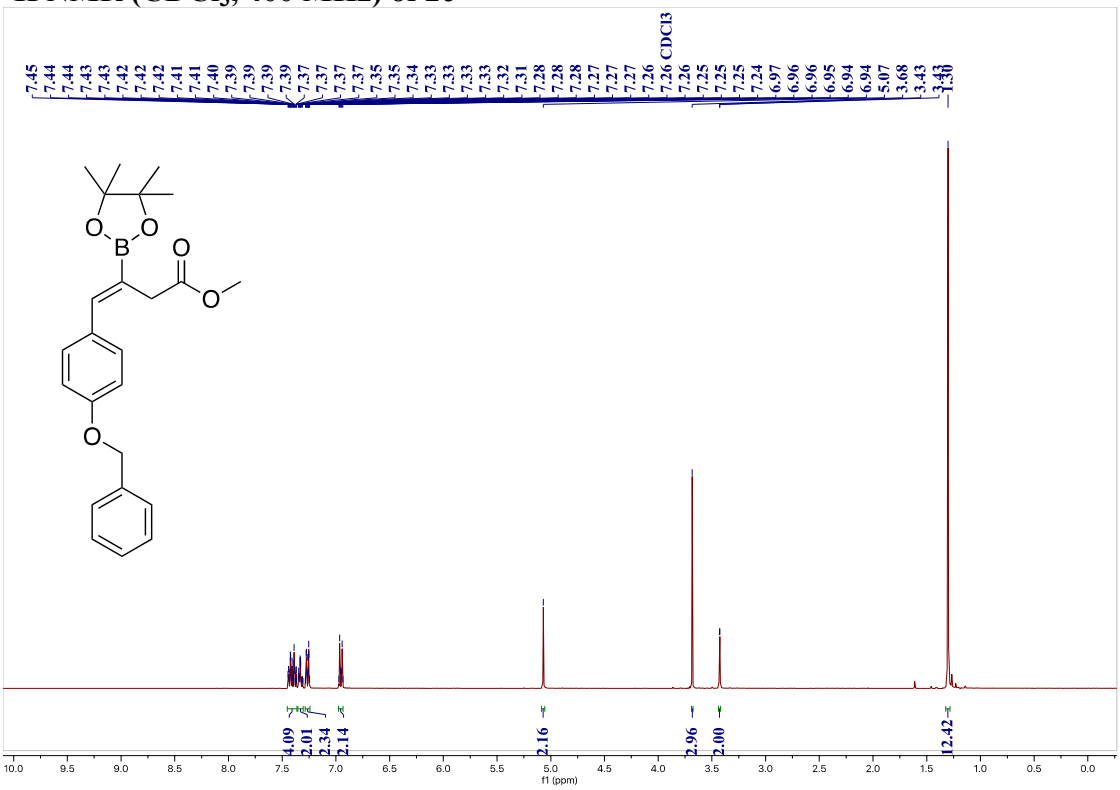


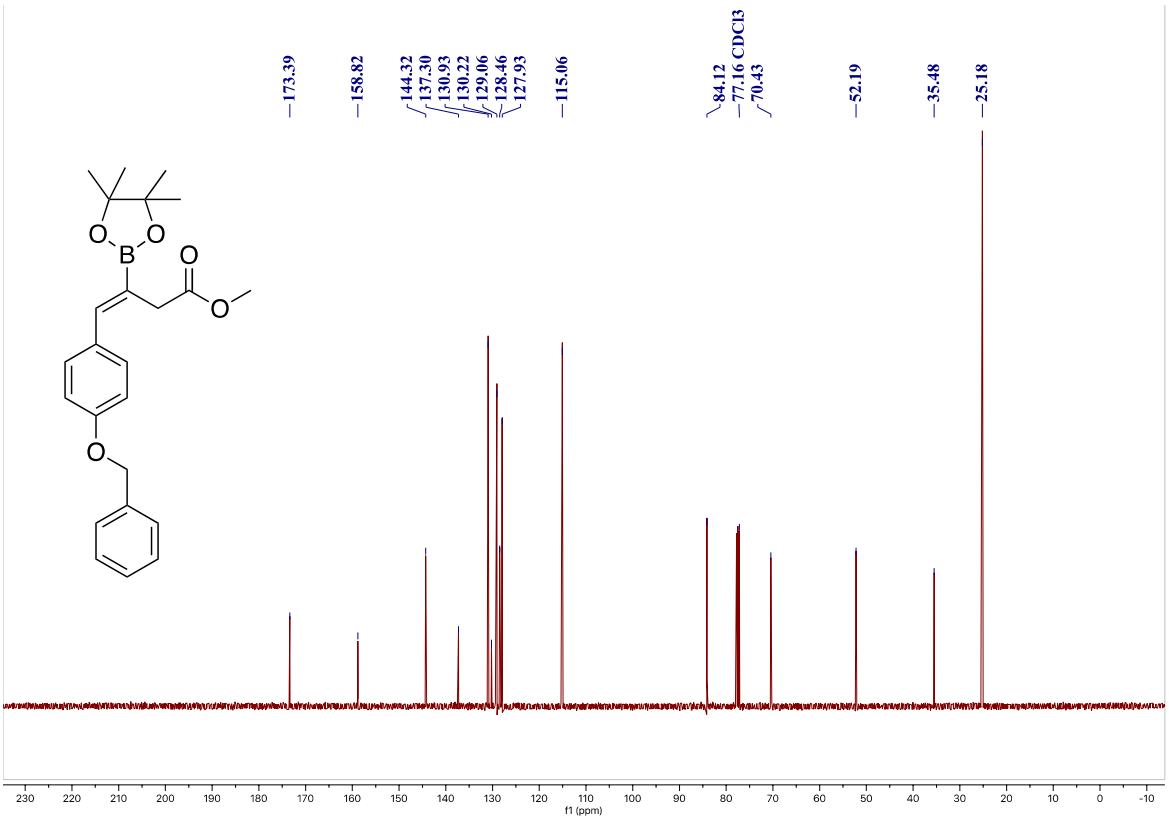
Crude GC of 2d



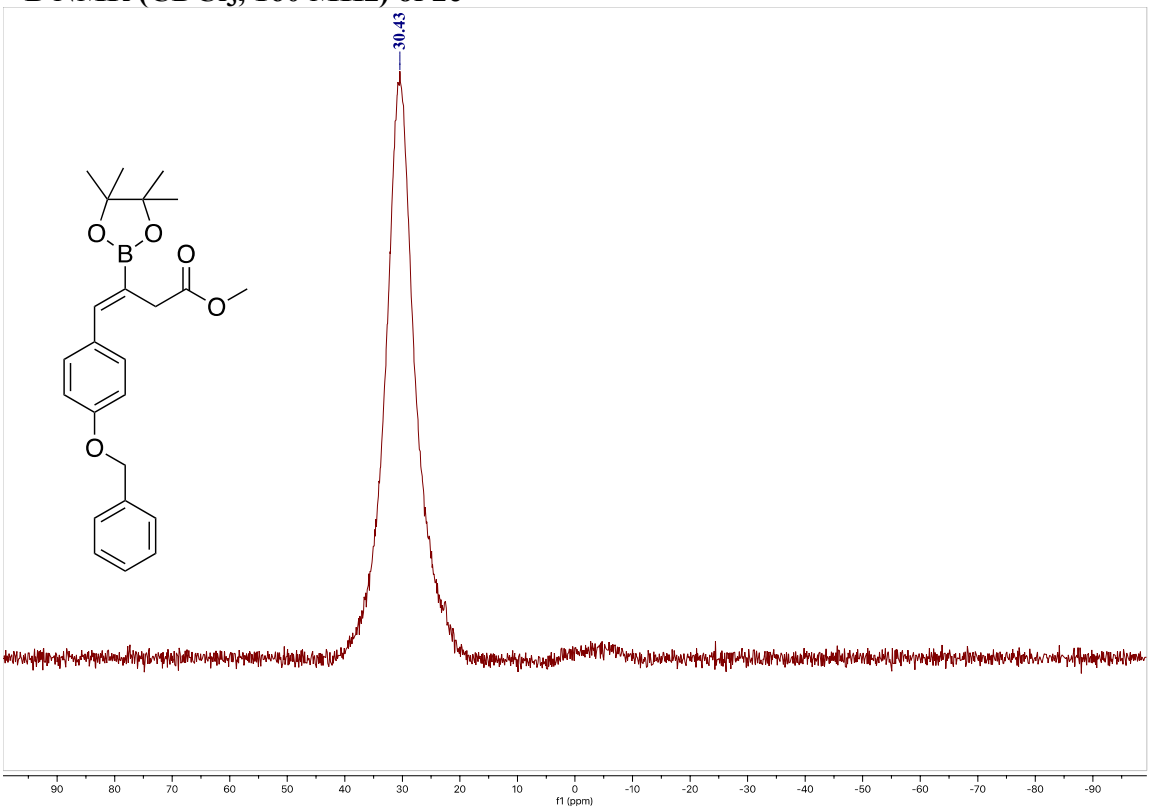
^{1}H NMR ($CDCl_3$, 400 MHz) of 2e



^{13}C NMR ($CDCl_3$, 100 MHz) of 2e



^{11}B NMR ($CDCl_3$, 160 MHz) of 2e



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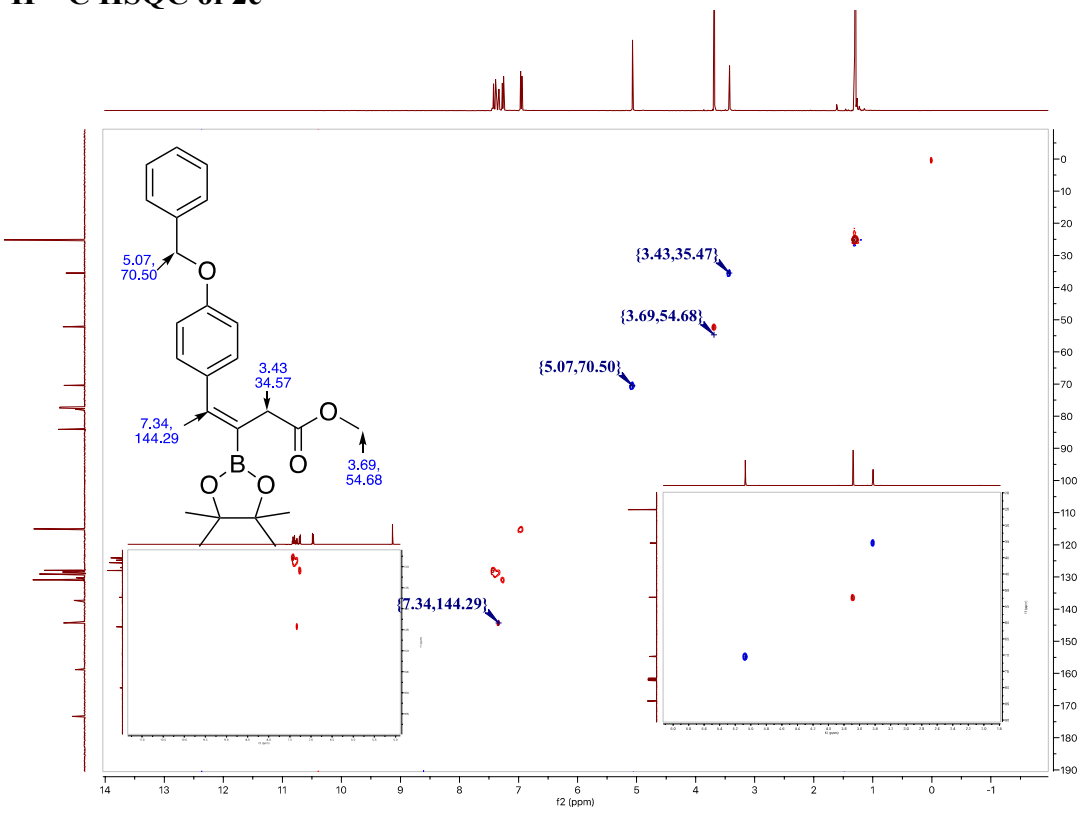

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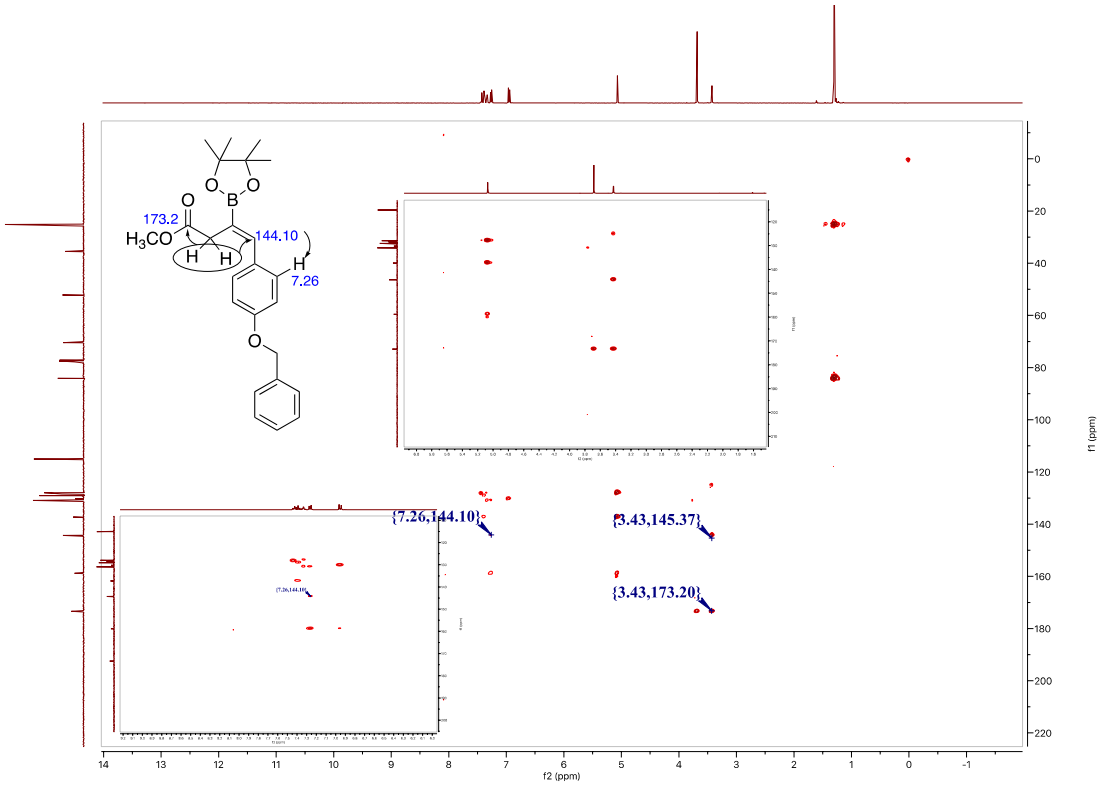
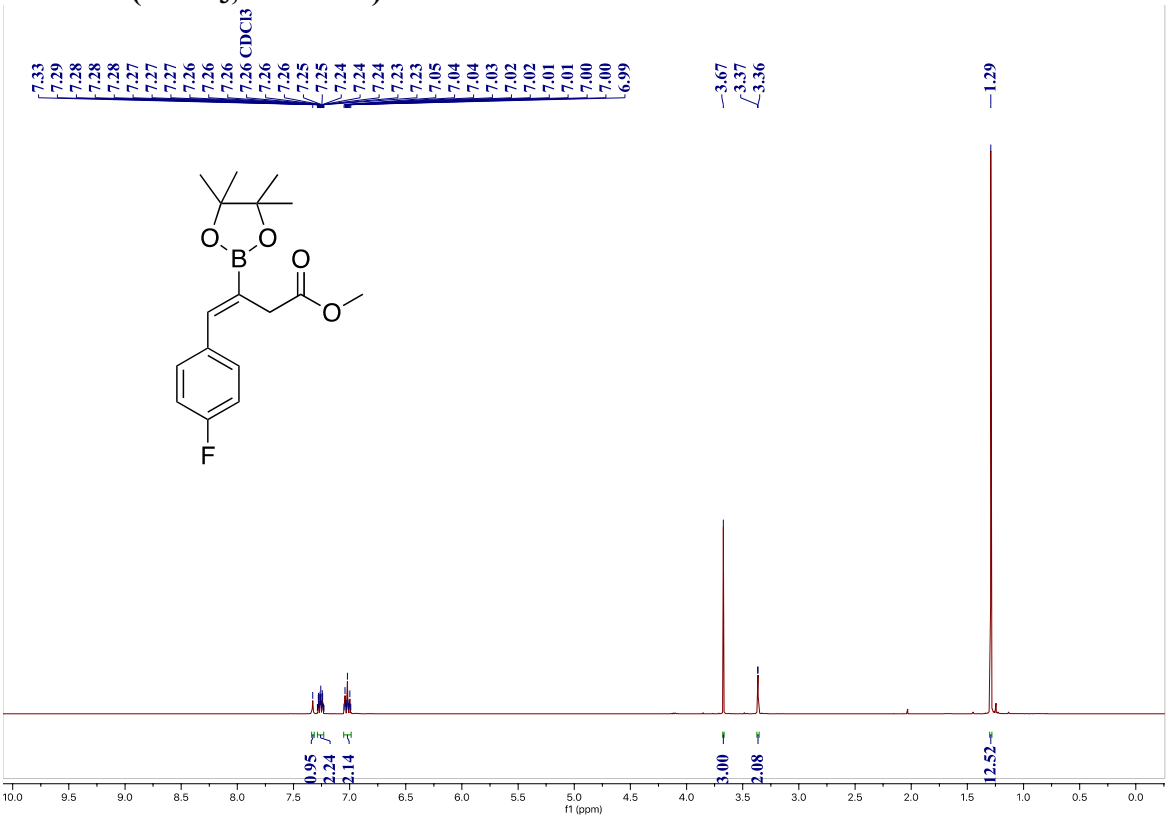
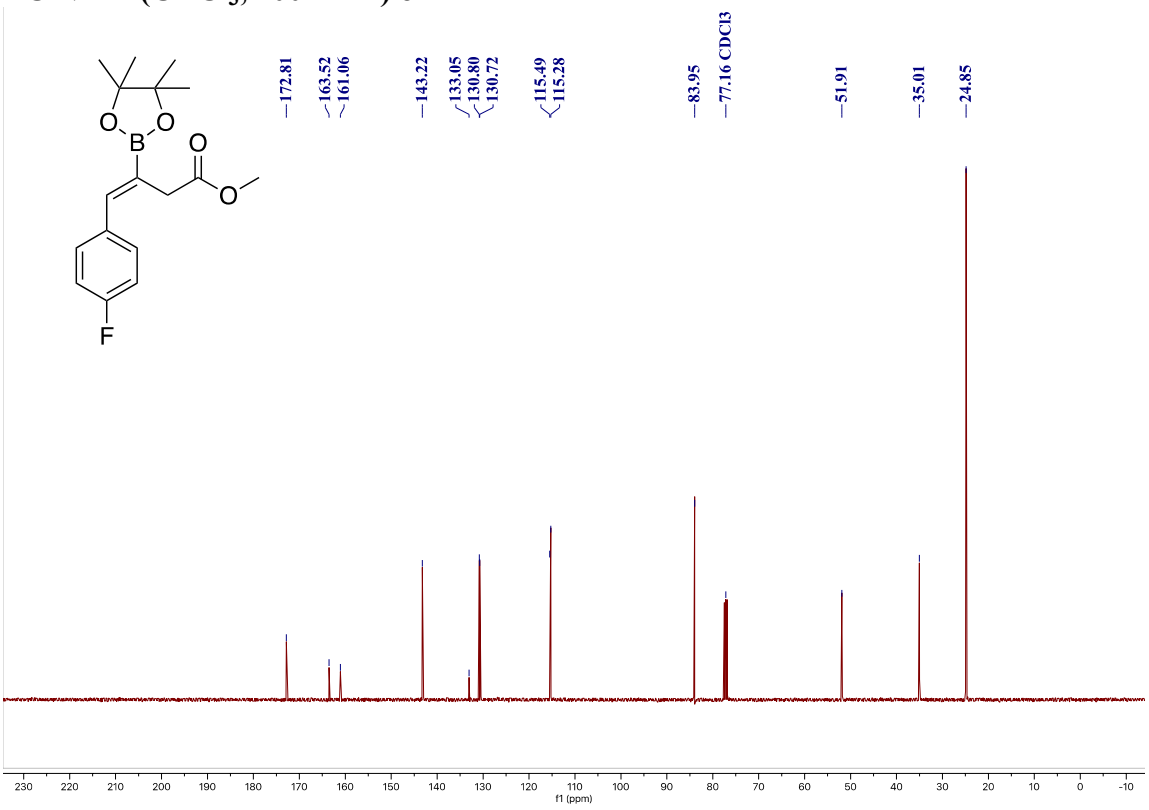


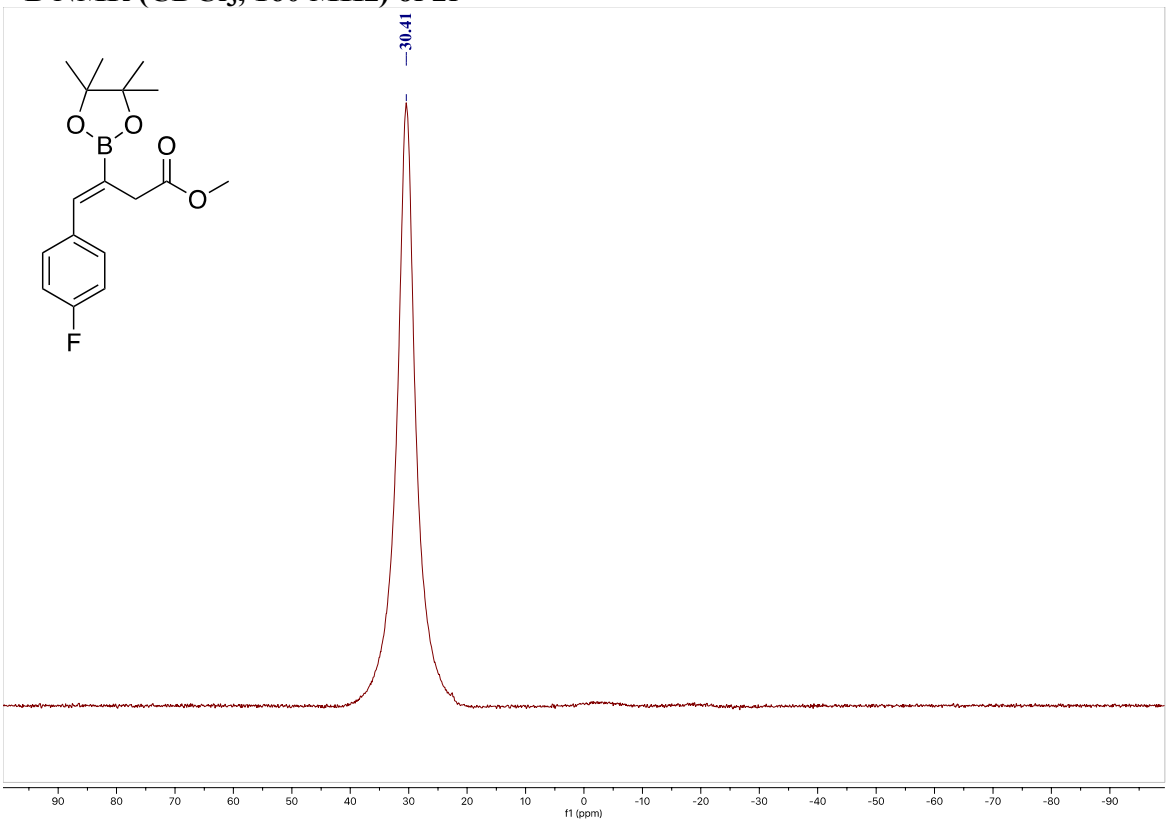
^{1}H NMR ($CDCl_3$, 400 MHz) of 2f



^{13}C NMR ($CDCl_3$, 100 MHz) of 2f



^{11}B NMR ($CDCl_3$, 160 MHz) of 2f



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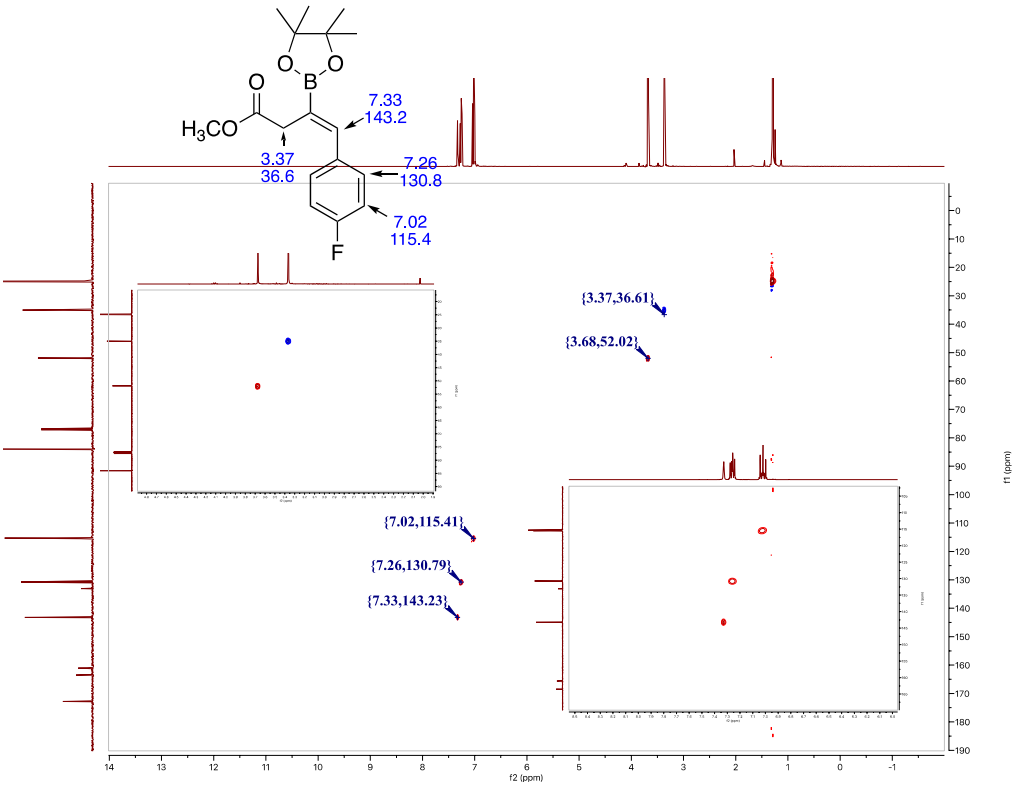

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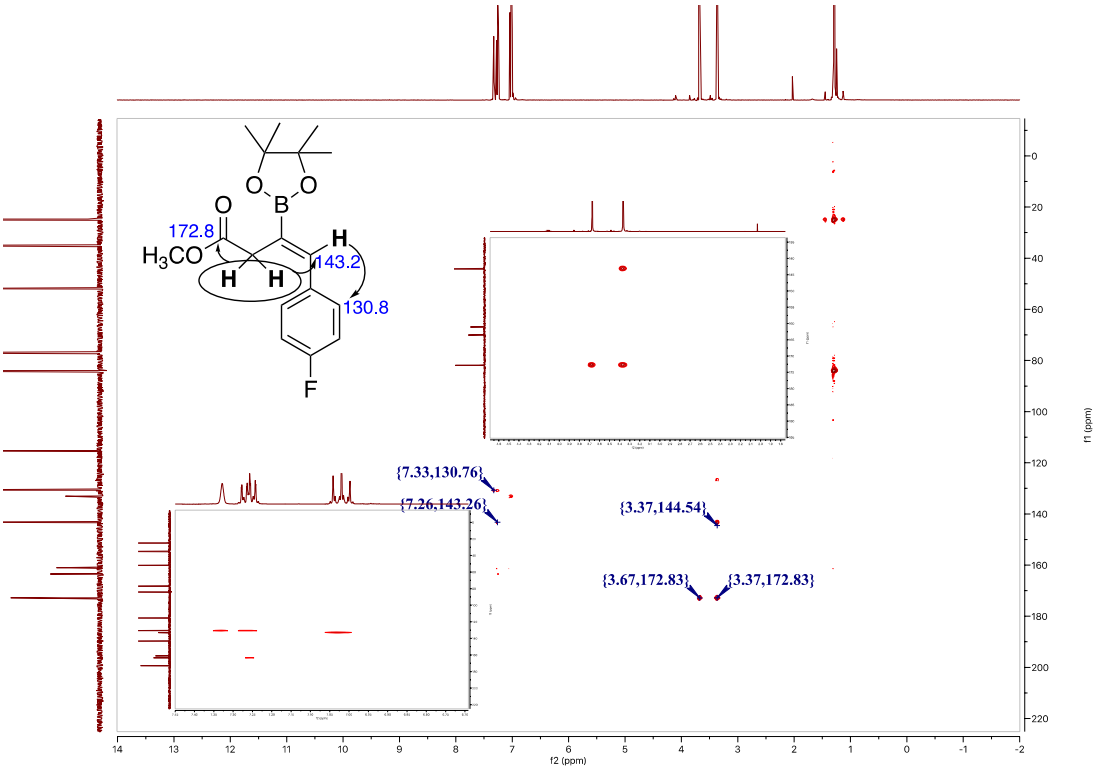
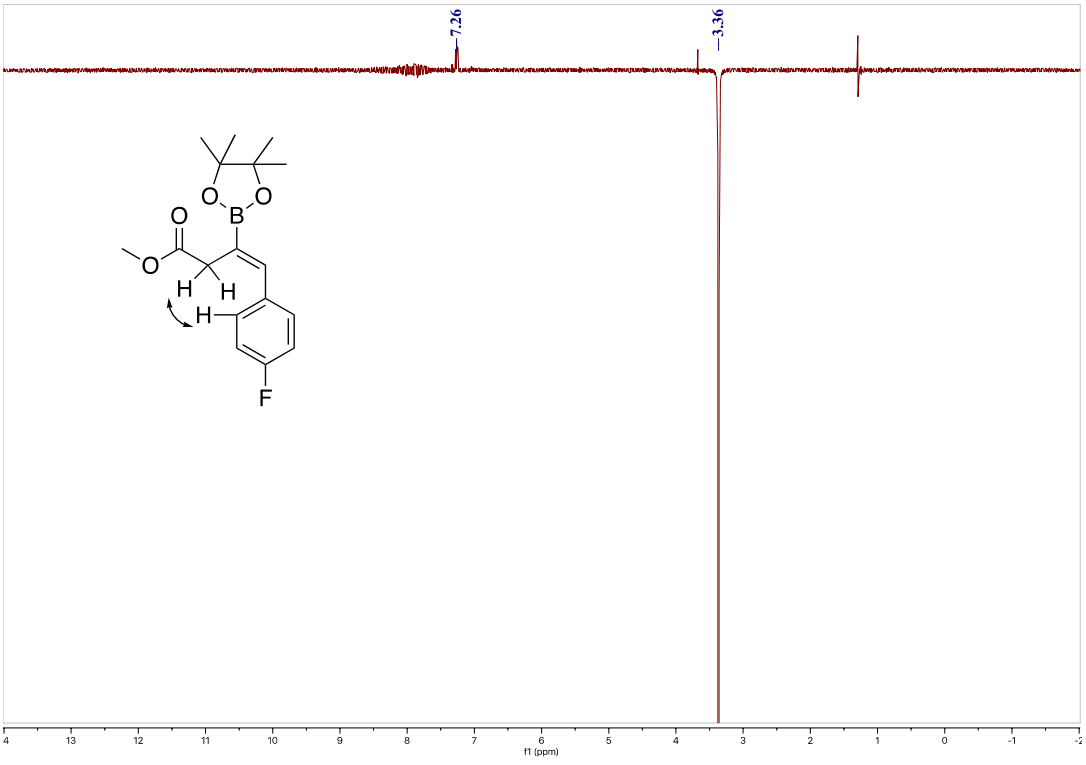
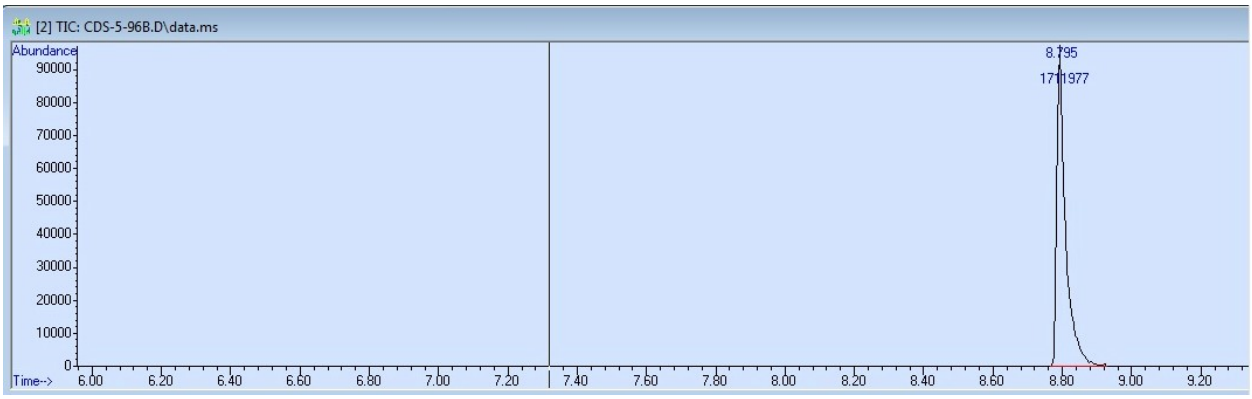


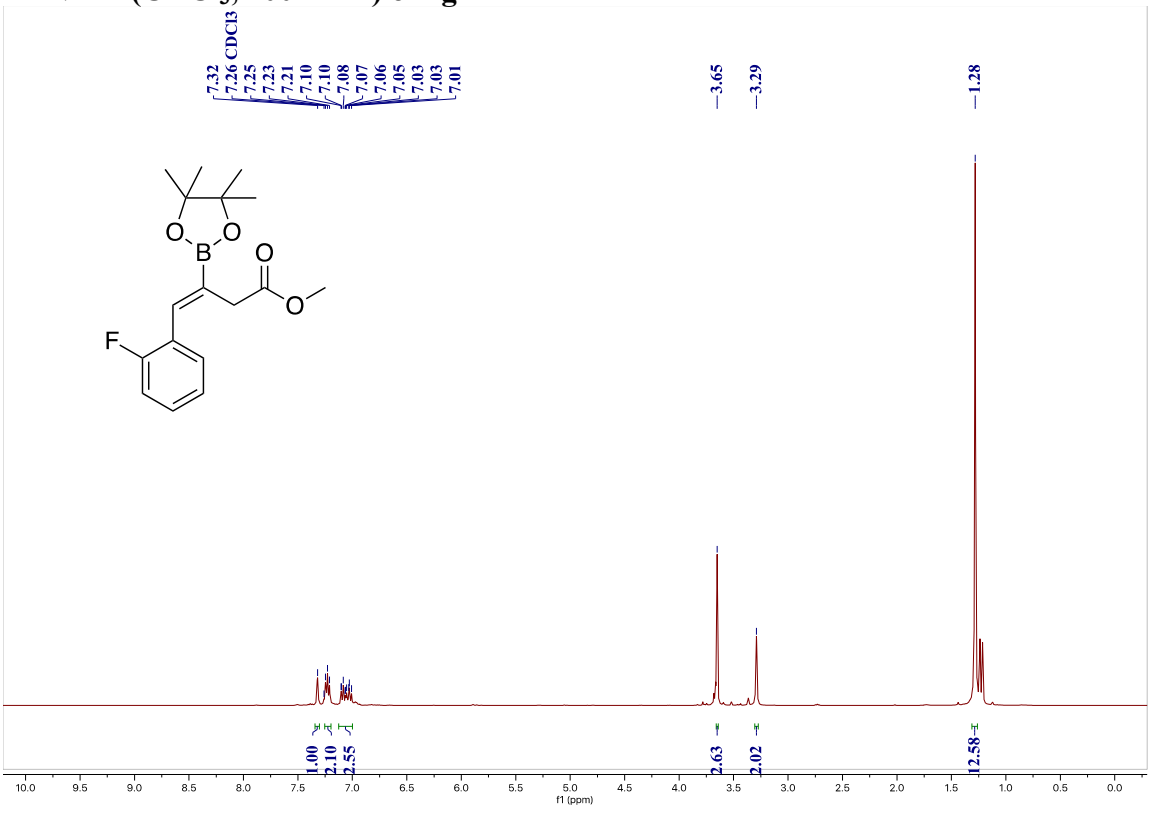
1D NOESY of 2f



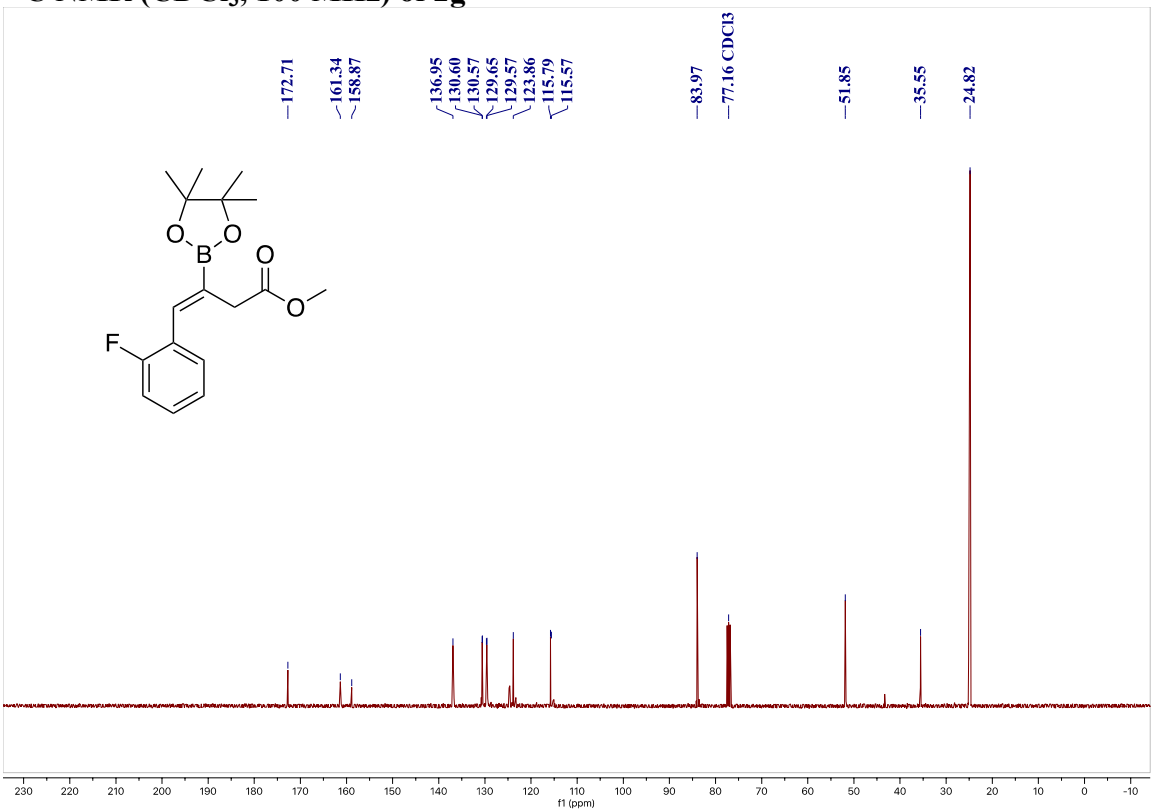
Crude GC of 2f



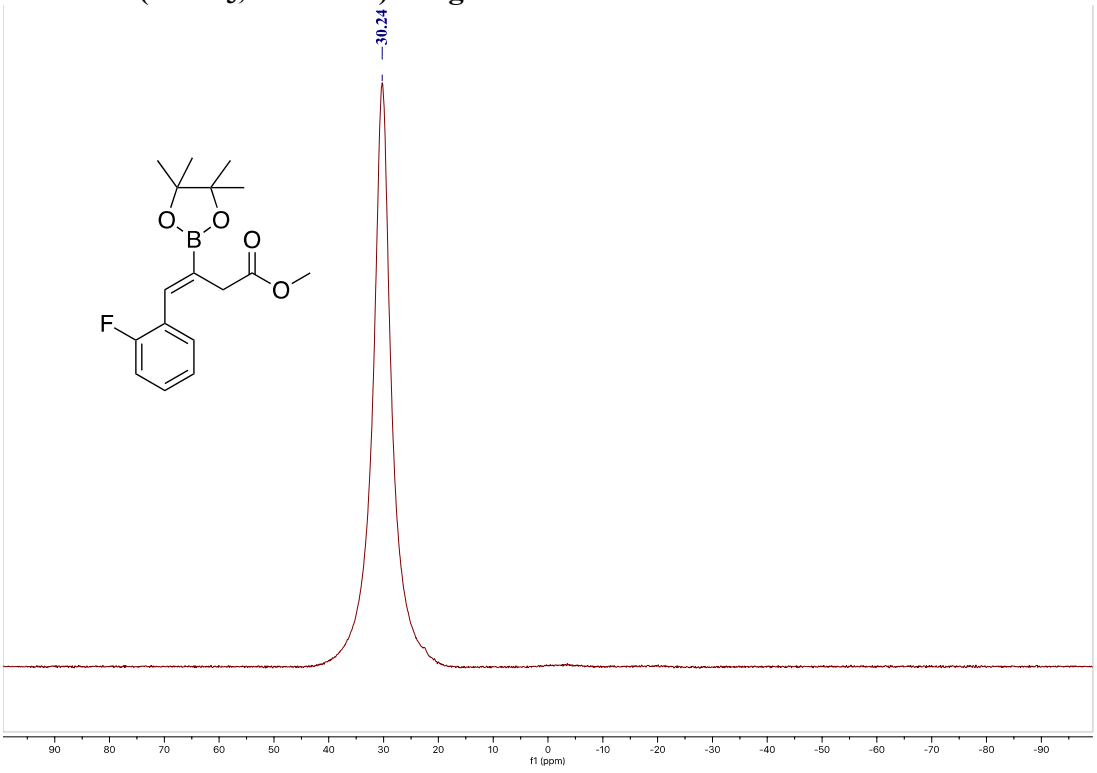
^{1}H NMR ($CDCl_3$, 400 MHz) of 2g



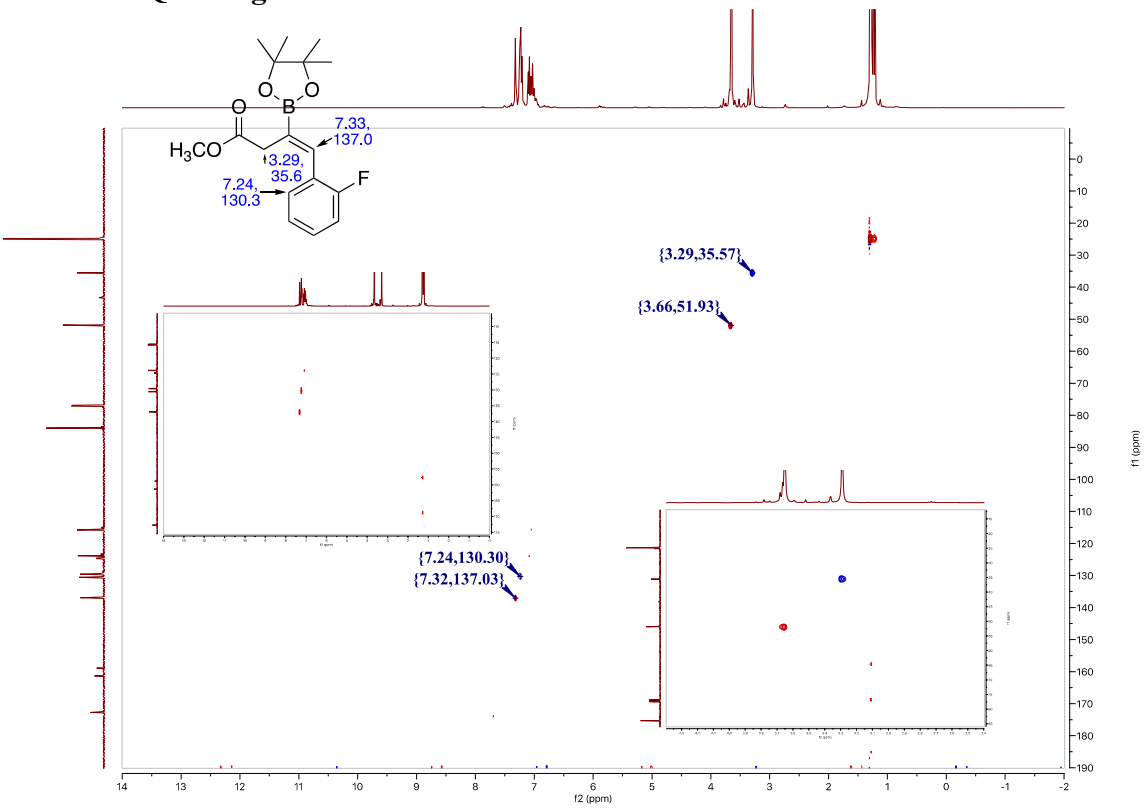
^{13}C NMR ($CDCl_3$, 100 MHz) of 2g



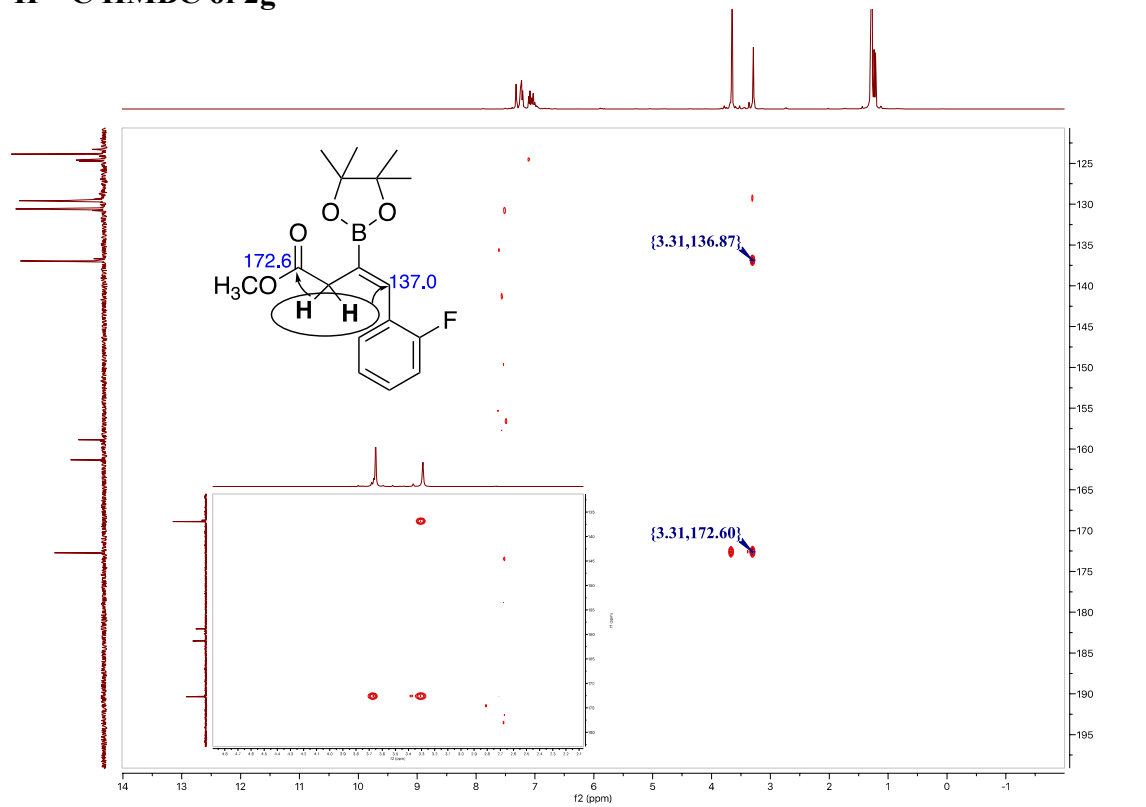
^{11}B NMR ($CDCl_3$, 160 MHz) of 2g



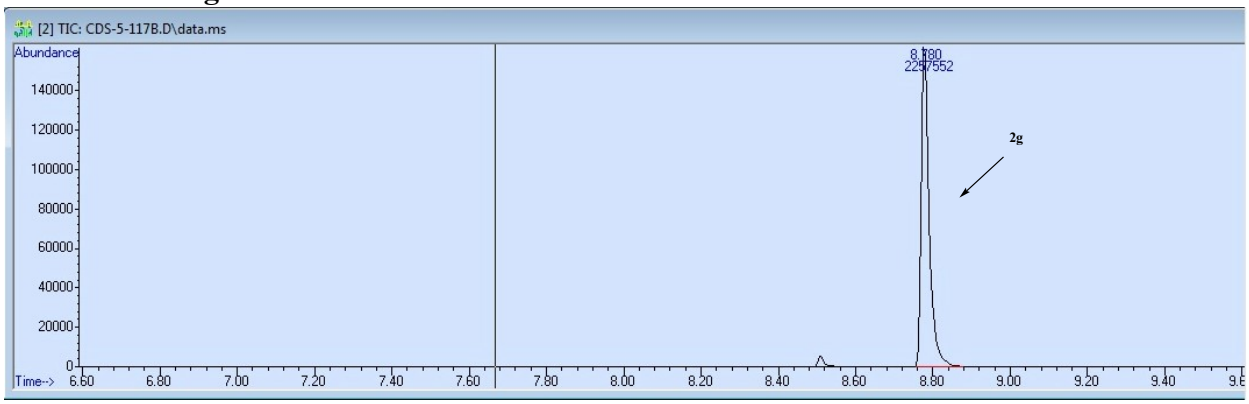
^{1}H-^{13}C HSQC of 2g



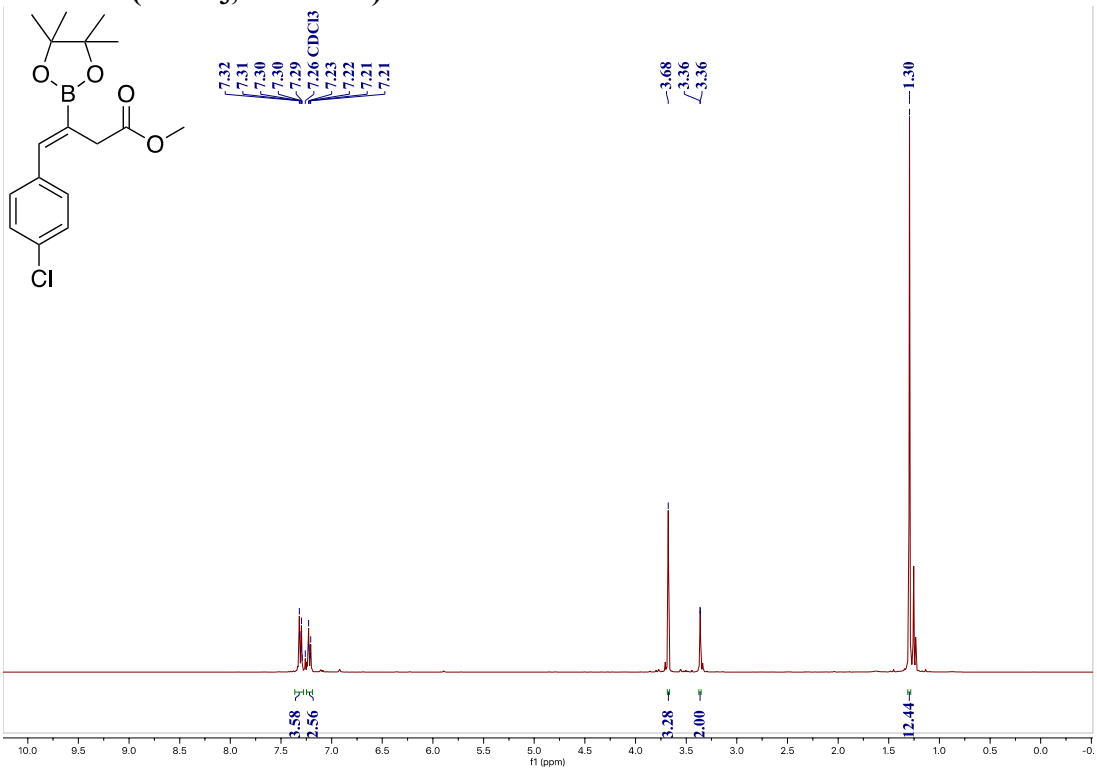
^{1}H-^{13}C HMBC of 2g



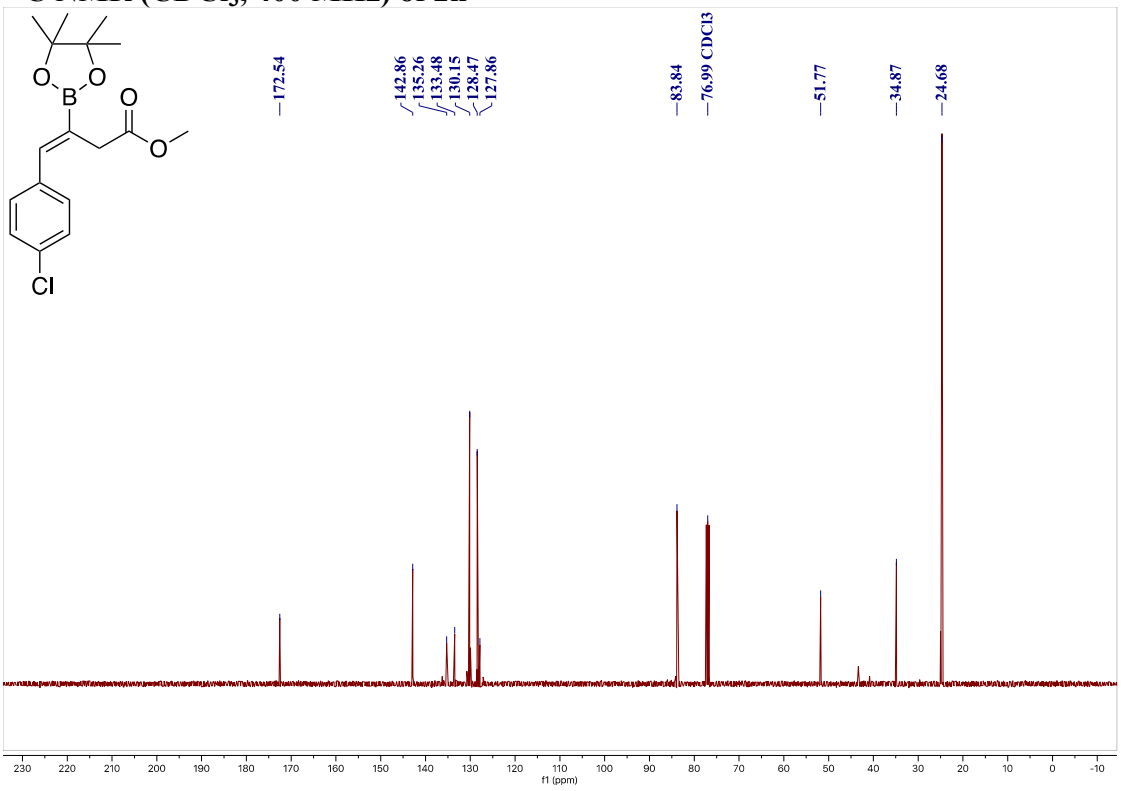
Crude GC of 2g



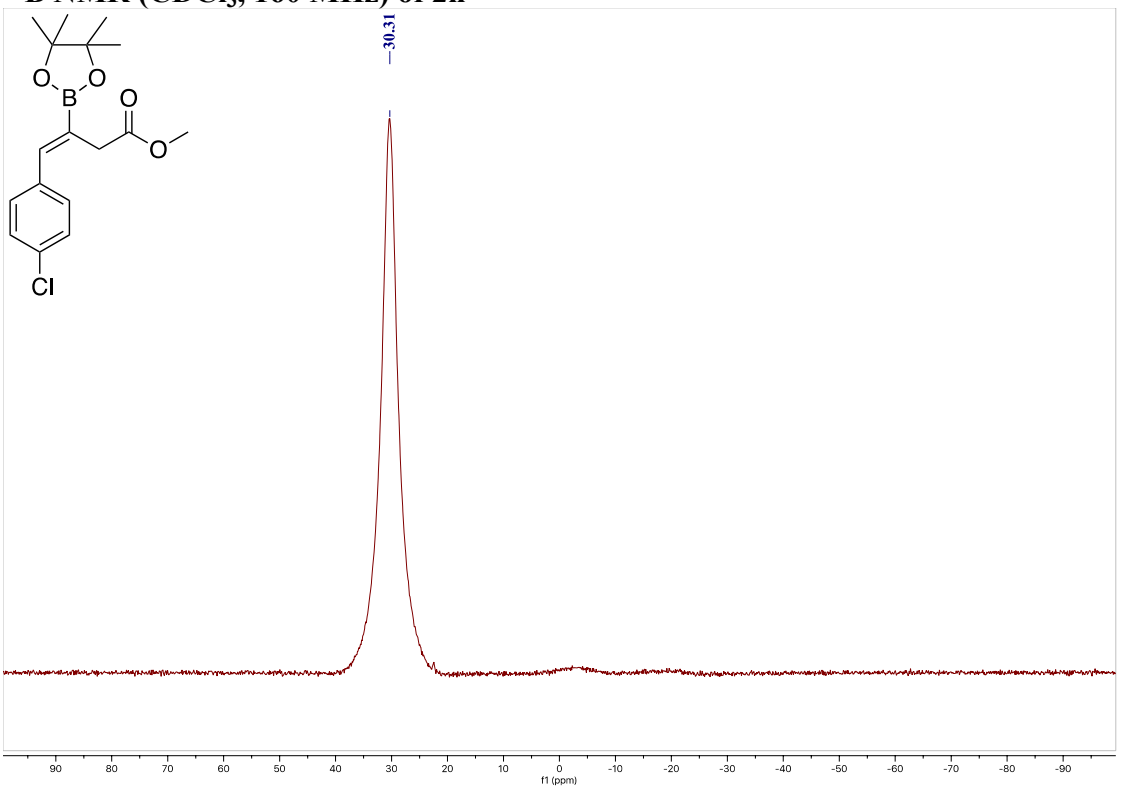
^{1}H NMR ($CDCl_3$, 400 MHz) of 2h



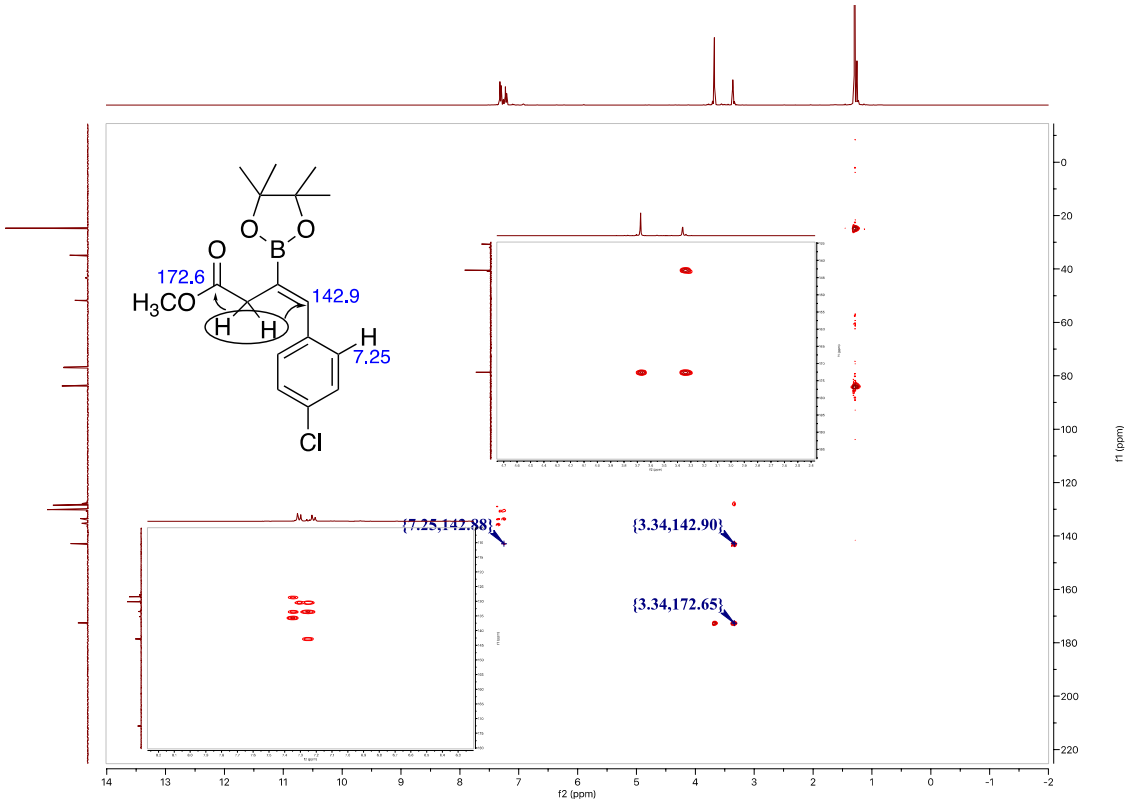
^{13}C NMR ($CDCl_3$, 400 MHz) of 2h



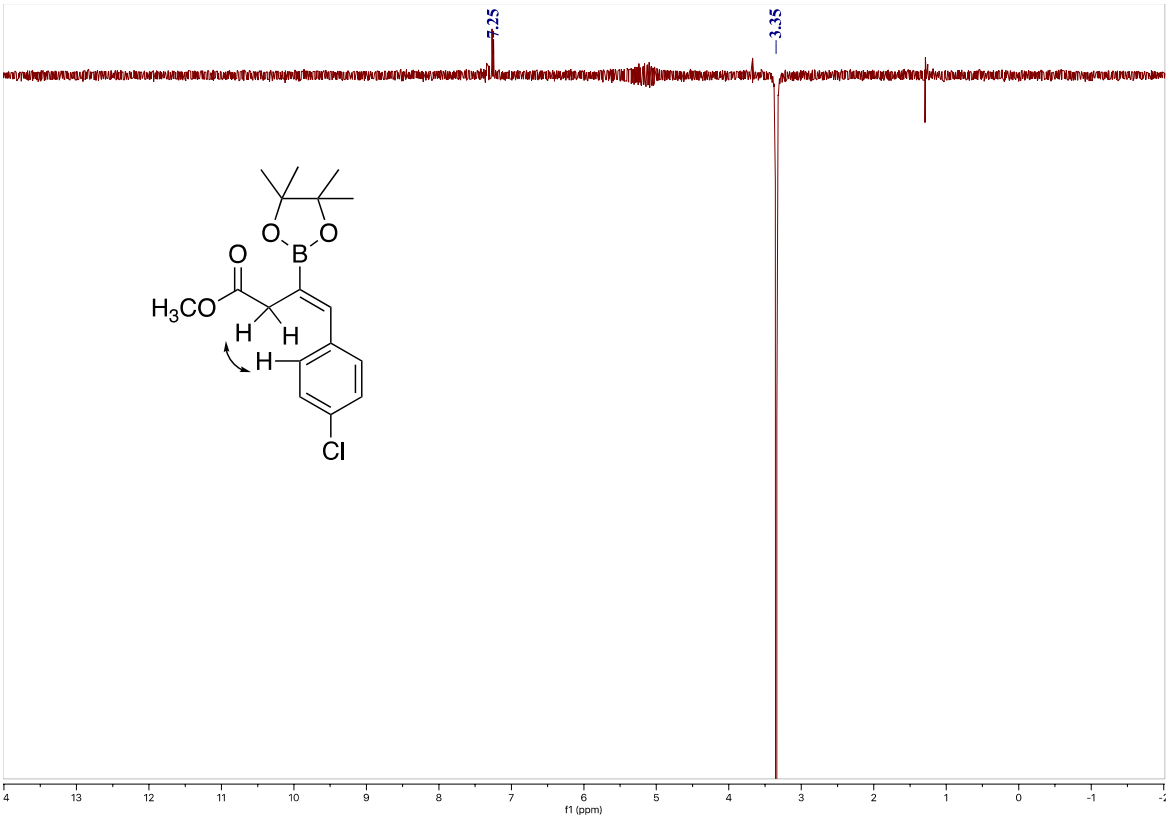
^{11}B NMR ($CDCl_3$, 160 MHz) of 2h



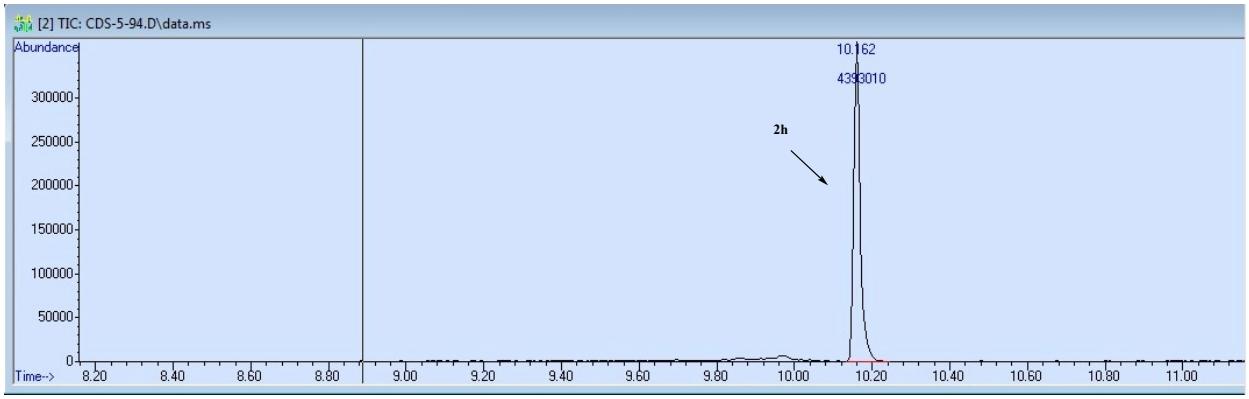
^{1}H-^{13}C HMBC of 2h



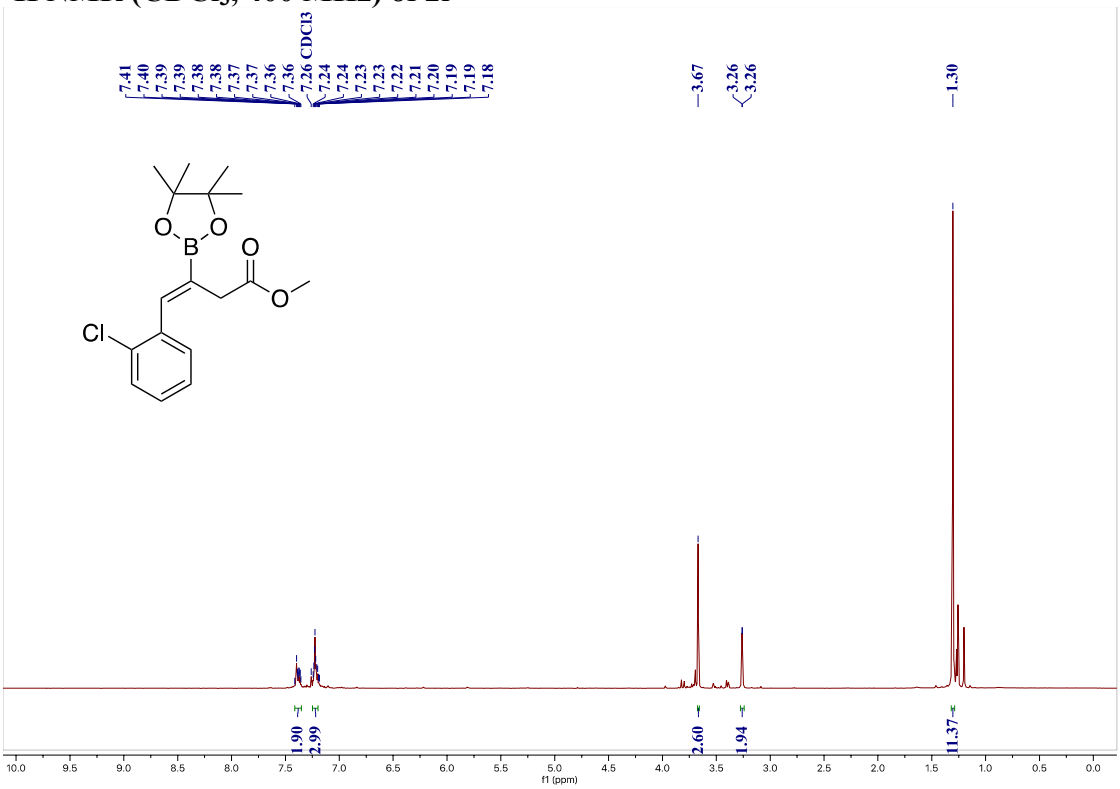
1D NOESY of 2h



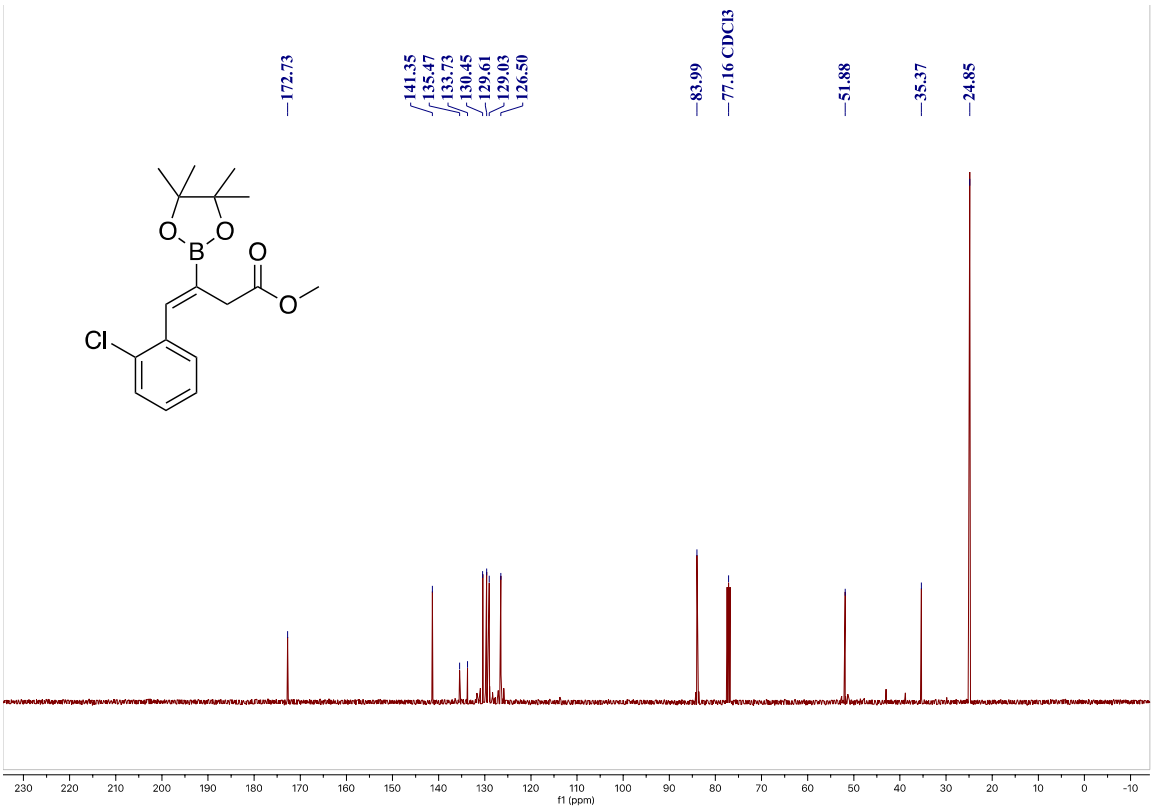
Crude GC of 2h



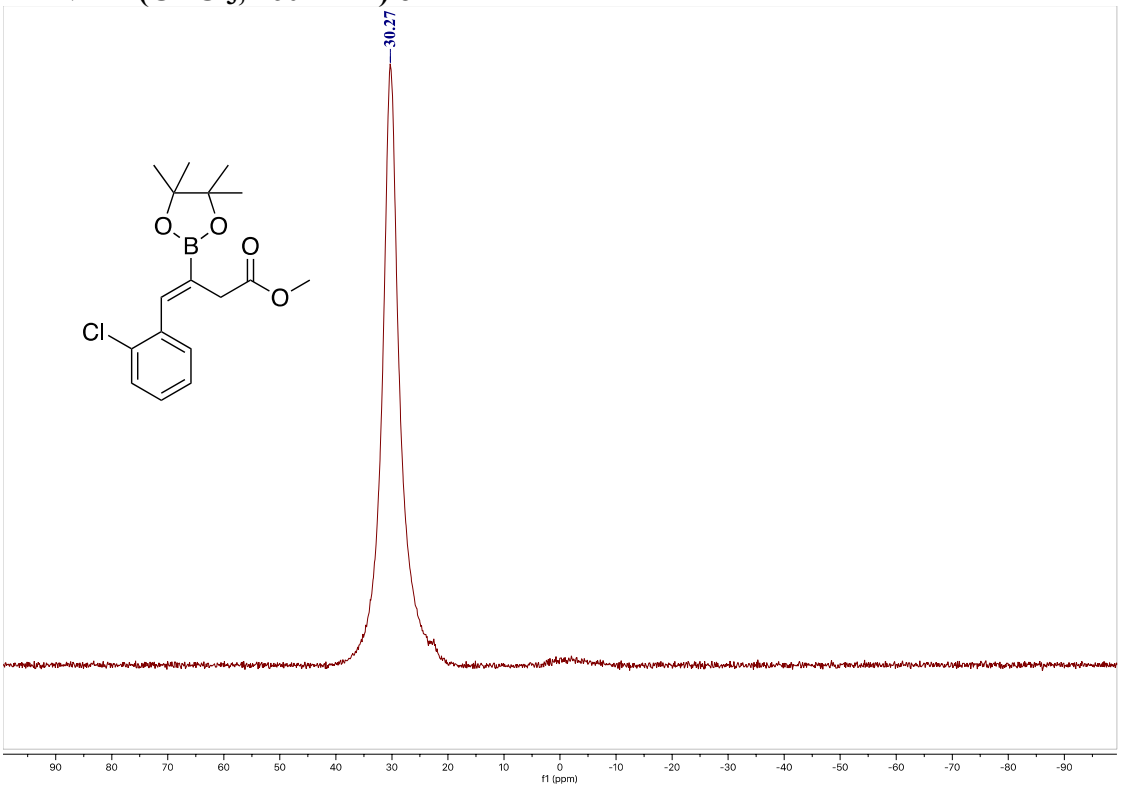
^{1}H NMR ($CDCl_3$, 400 MHz) of 2i



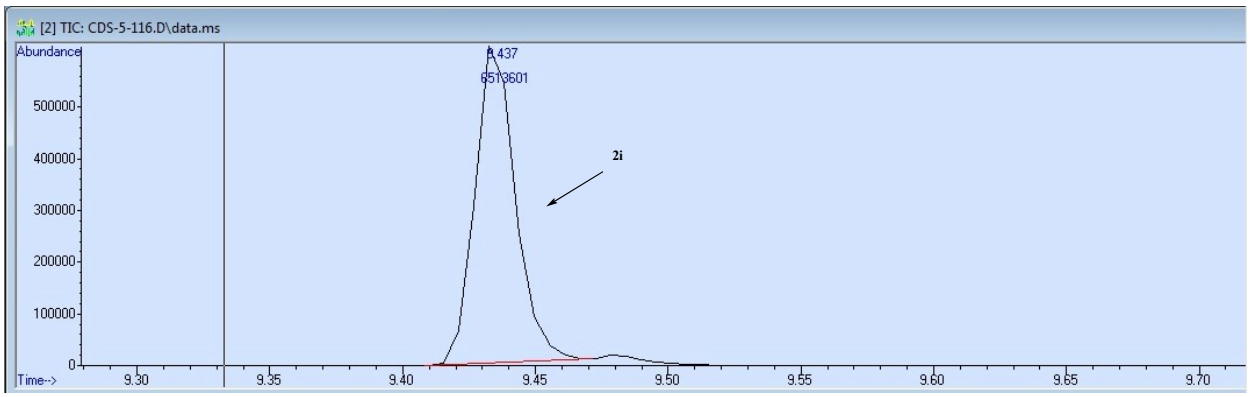
^{13}C NMR ($CDCl_3$, 100 MHz) of 2i



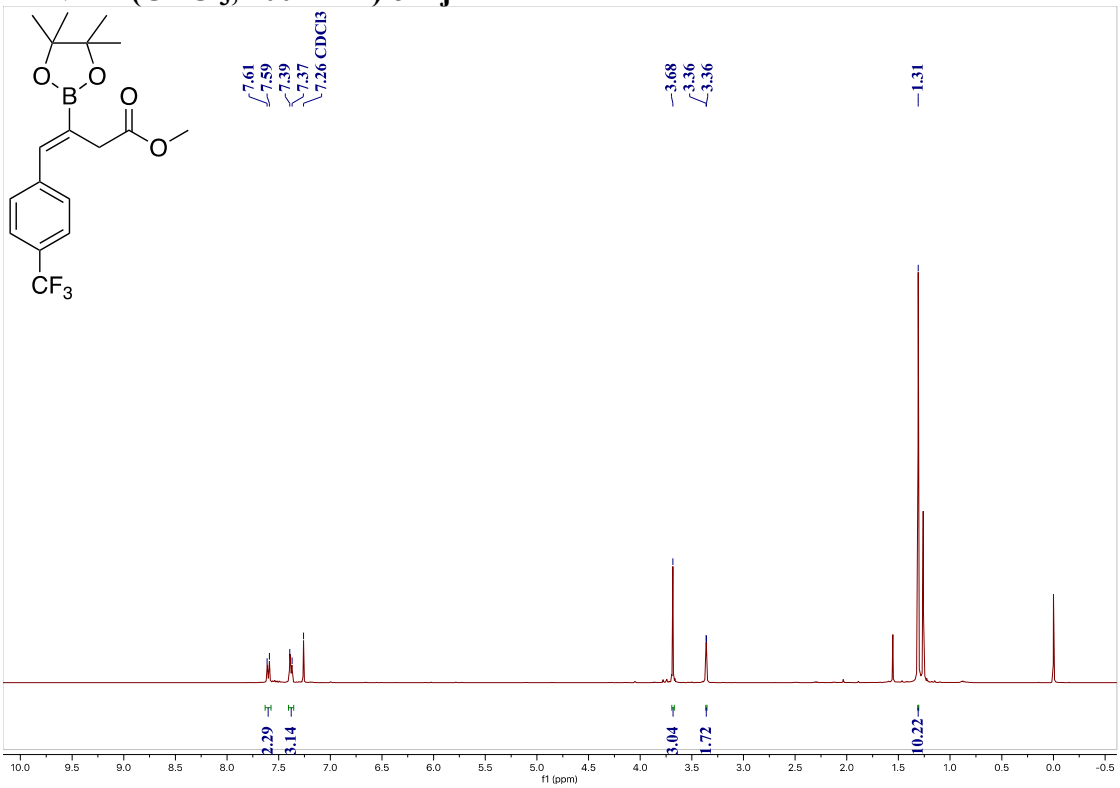
^{11}B NMR ($CDCl_3$, 160 MHz) of 2i



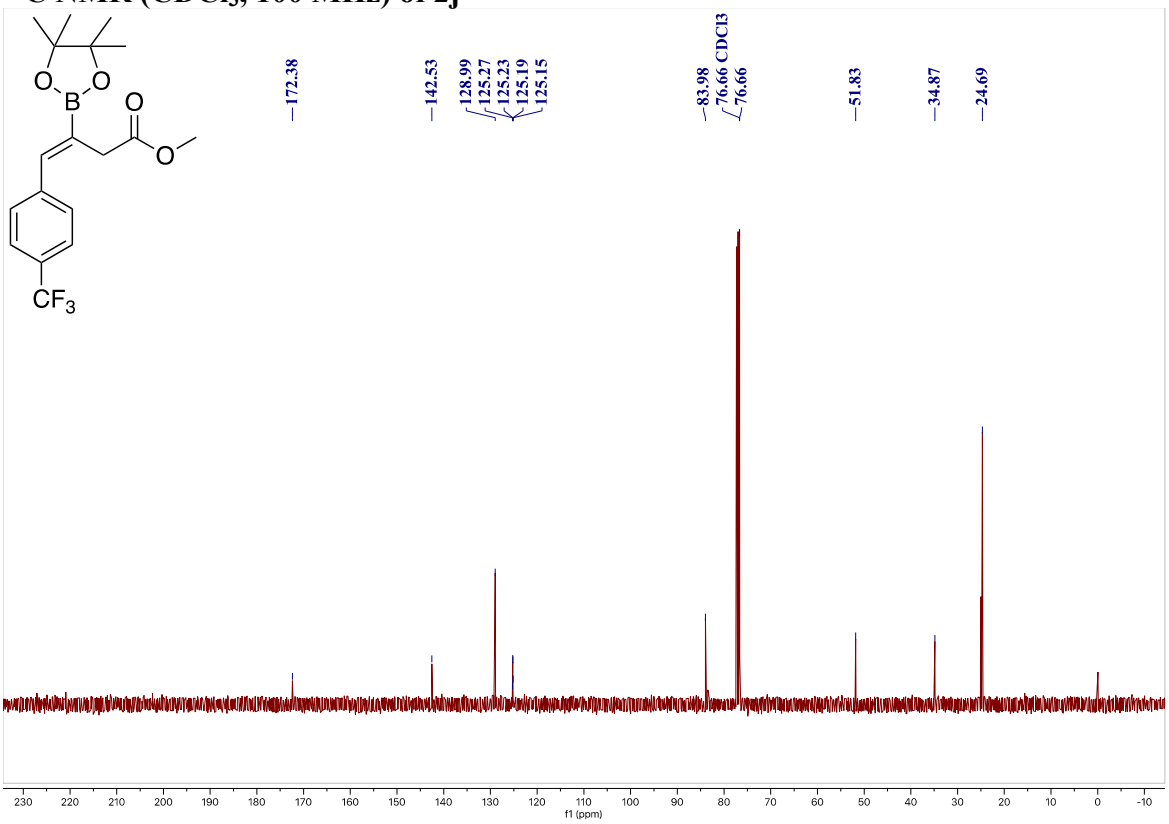
Crude GC of 2i



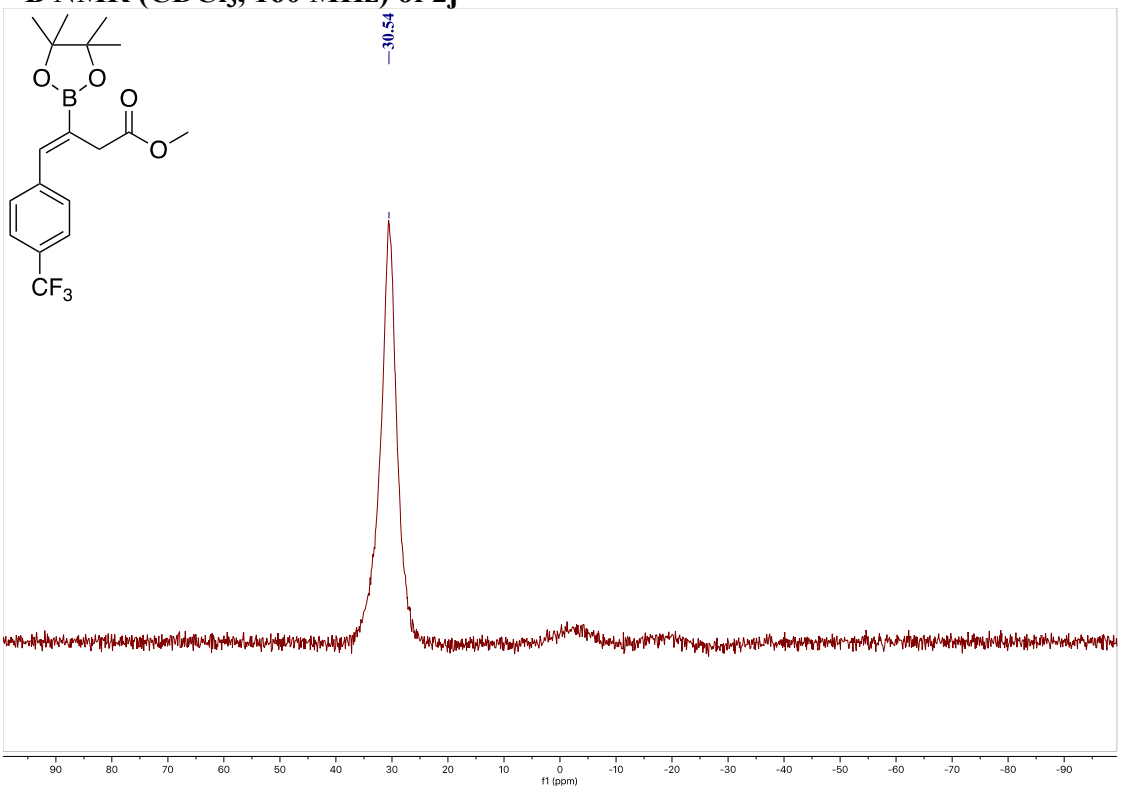
^{1}H NMR ($CDCl_3$, 400 MHz) of 2j



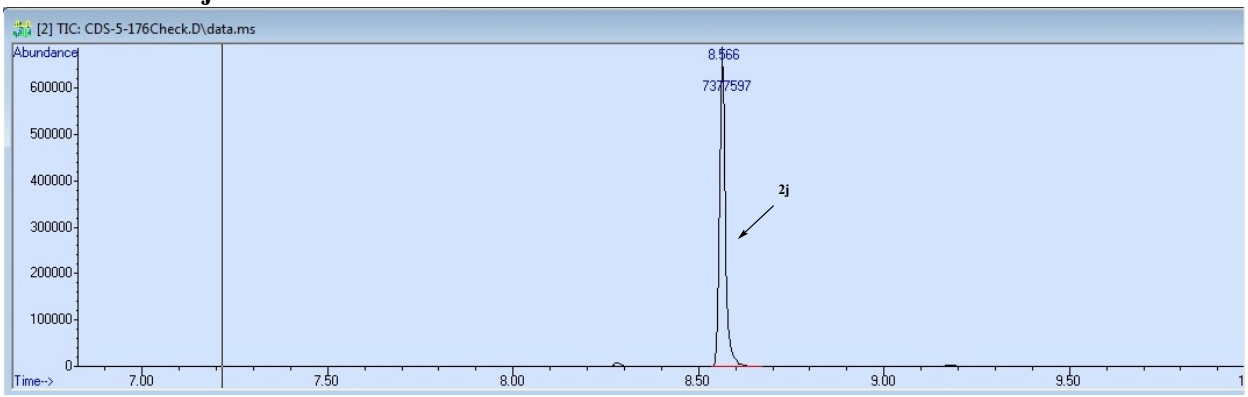
^{13}C NMR ($CDCl_3$, 100 MHz) of 2j



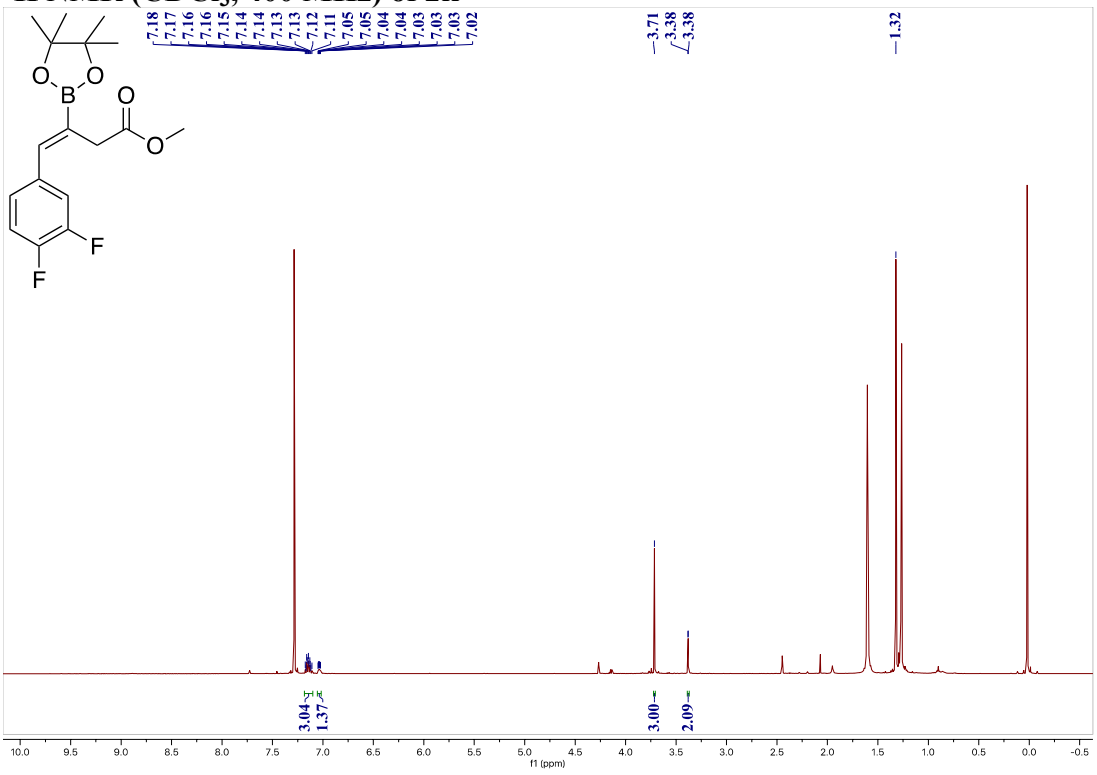
^{11}B NMR ($CDCl_3$, 160 MHz) of 2j



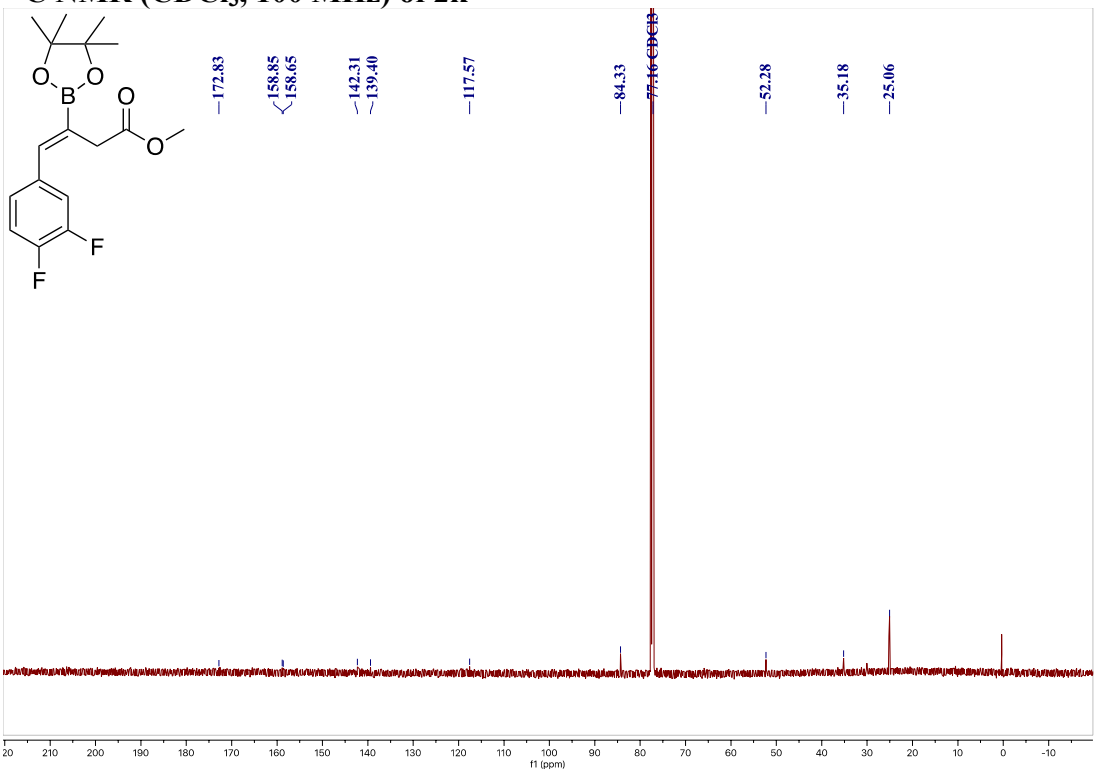
Crude GC of 2j



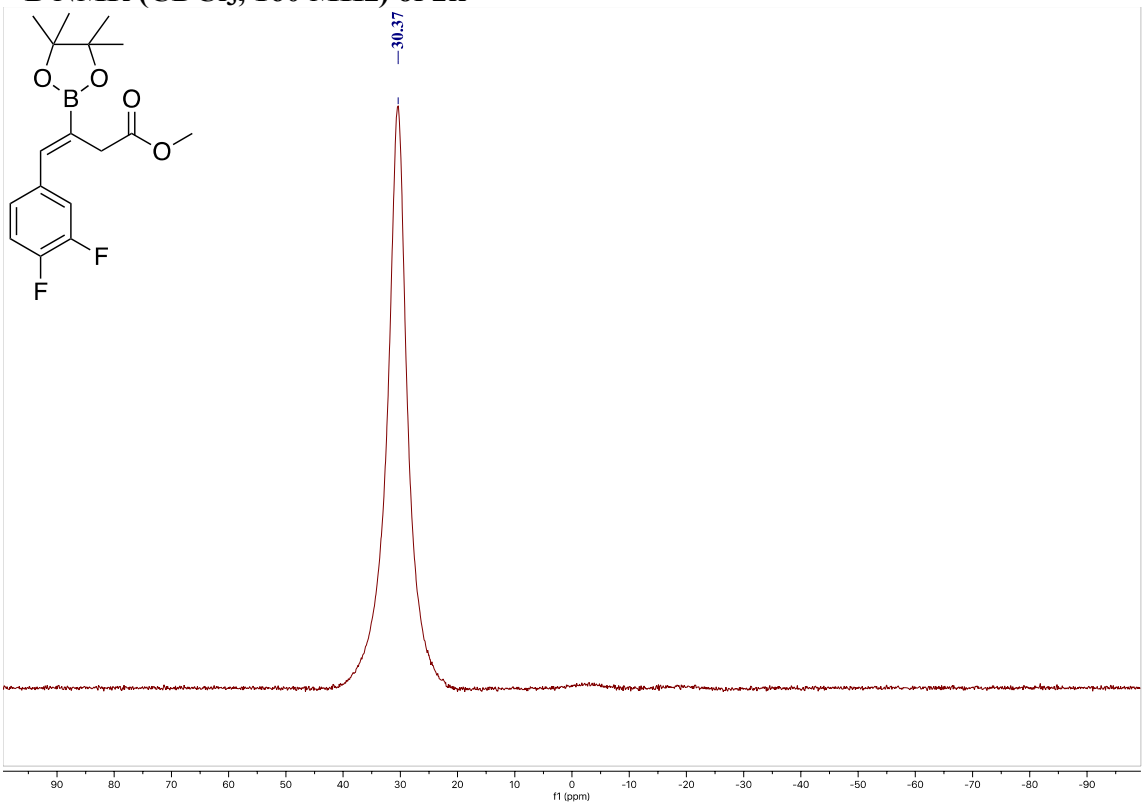
^{1}H NMR ($CDCl_3$, 400 MHz) of 2k



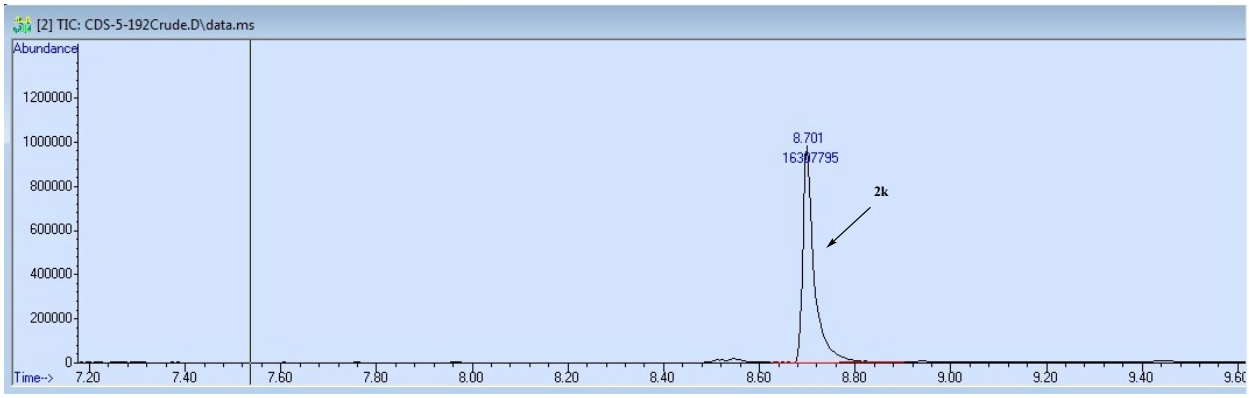
^{13}C NMR ($CDCl_3$, 100 MHz) of 2k



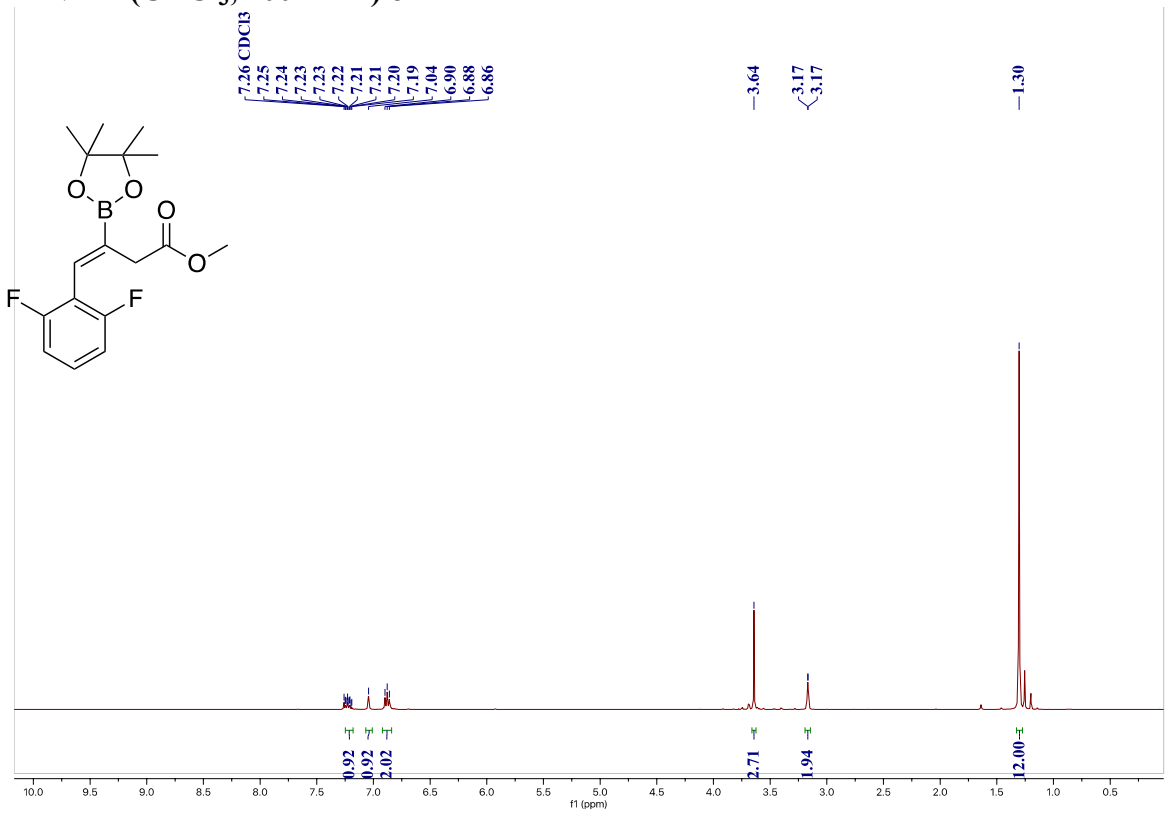
^{11}B NMR ($CDCl_3$, 160 MHz) of 2k



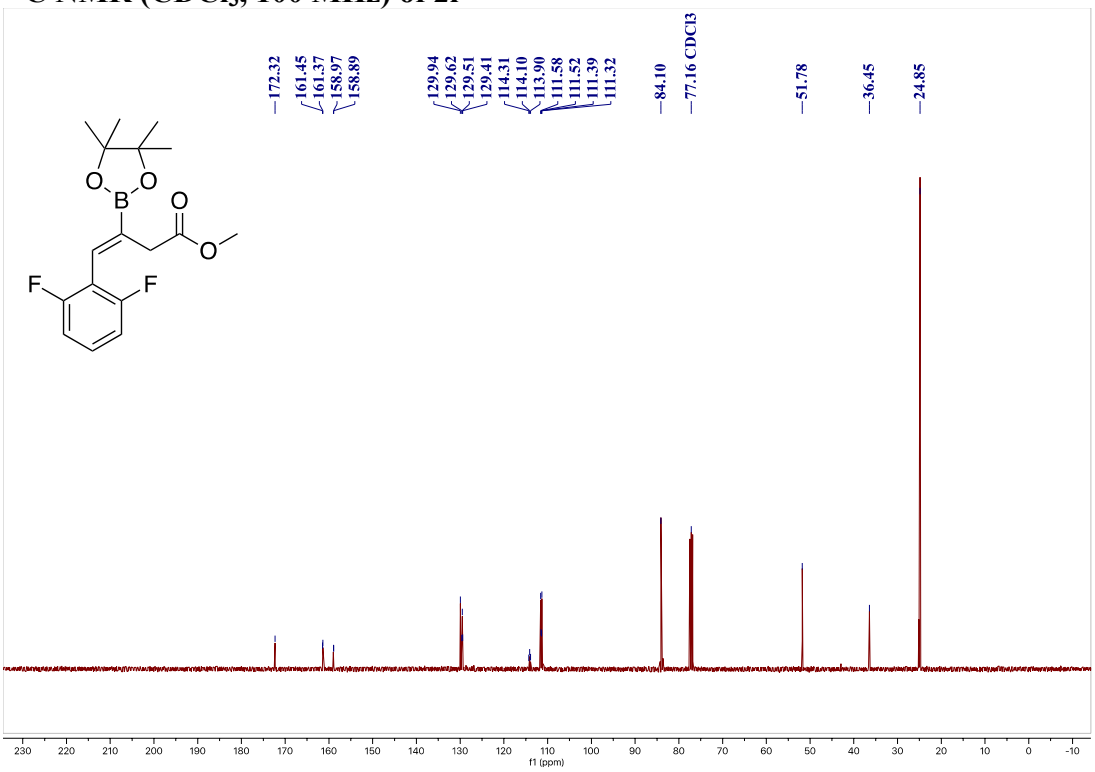
Crude GC of 2k



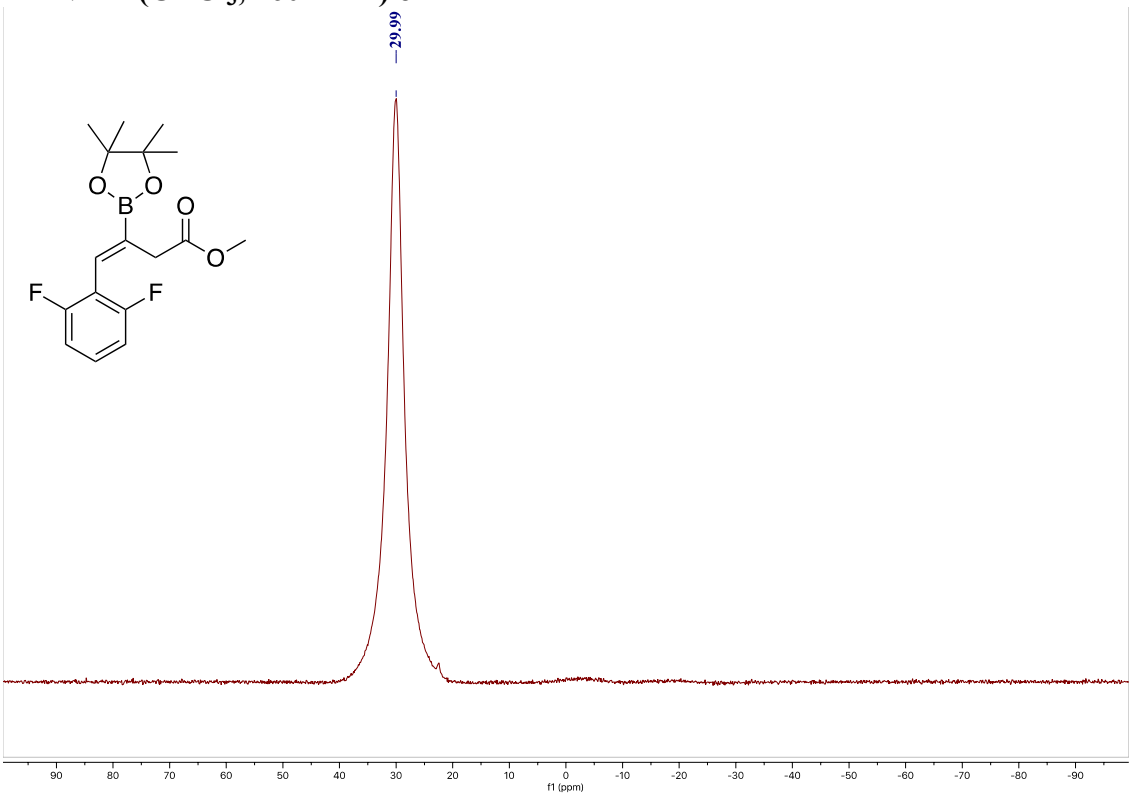
^{1}H NMR ($CDCl_3$, 400 MHz) of 2l



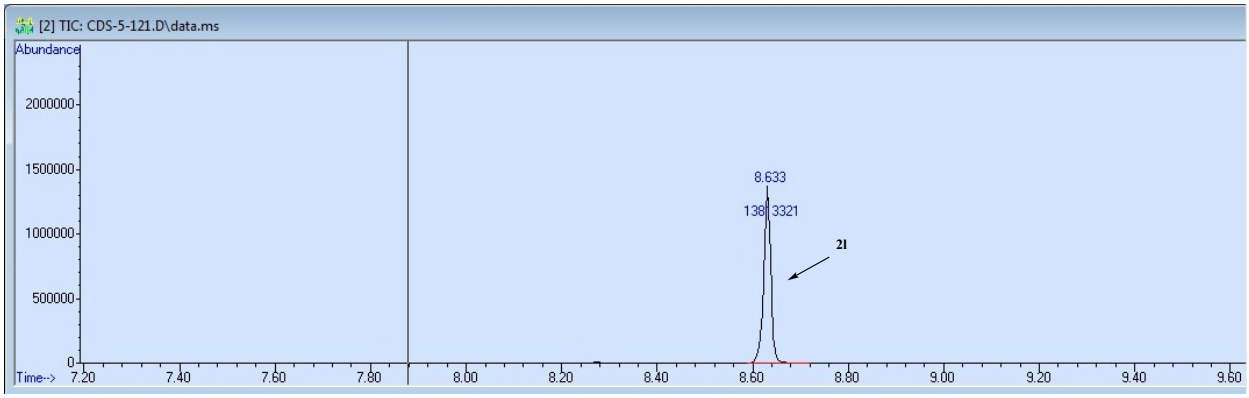
^{13}C NMR ($CDCl_3$, 100 MHz) of 2l



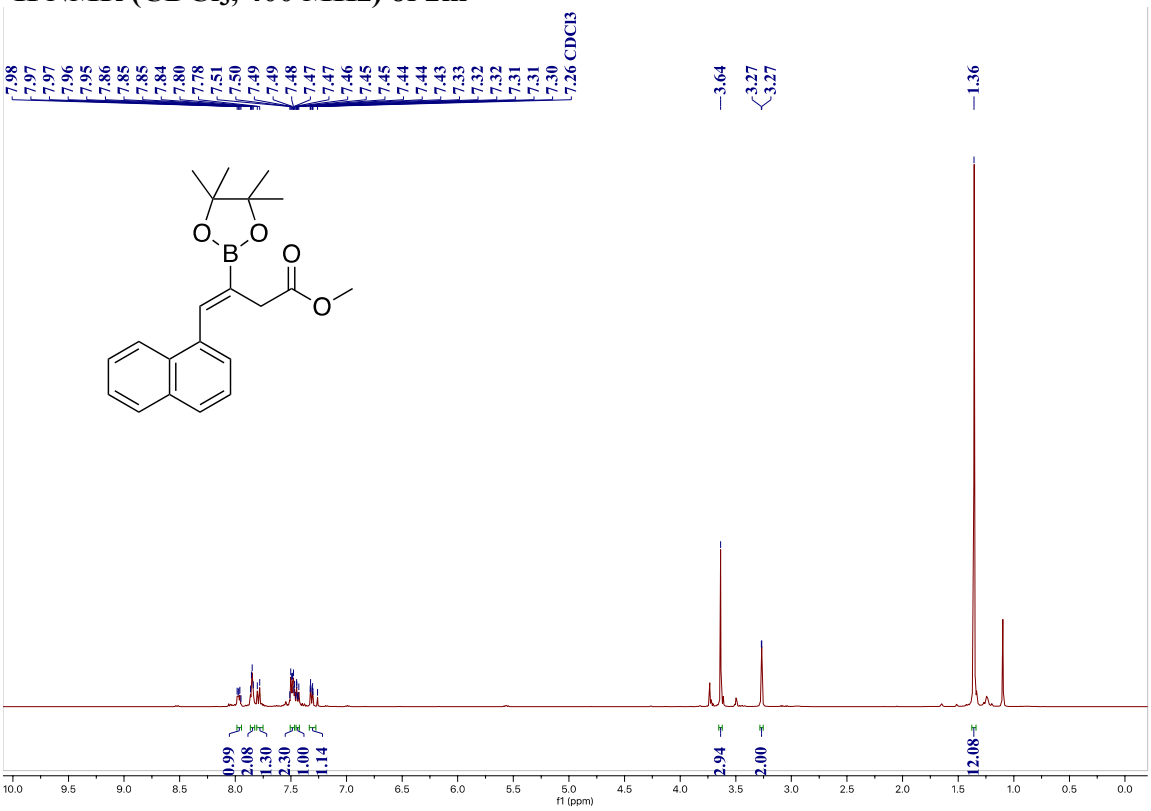
^{11}B NMR ($CDCl_3$, 160 MHz) of 2l



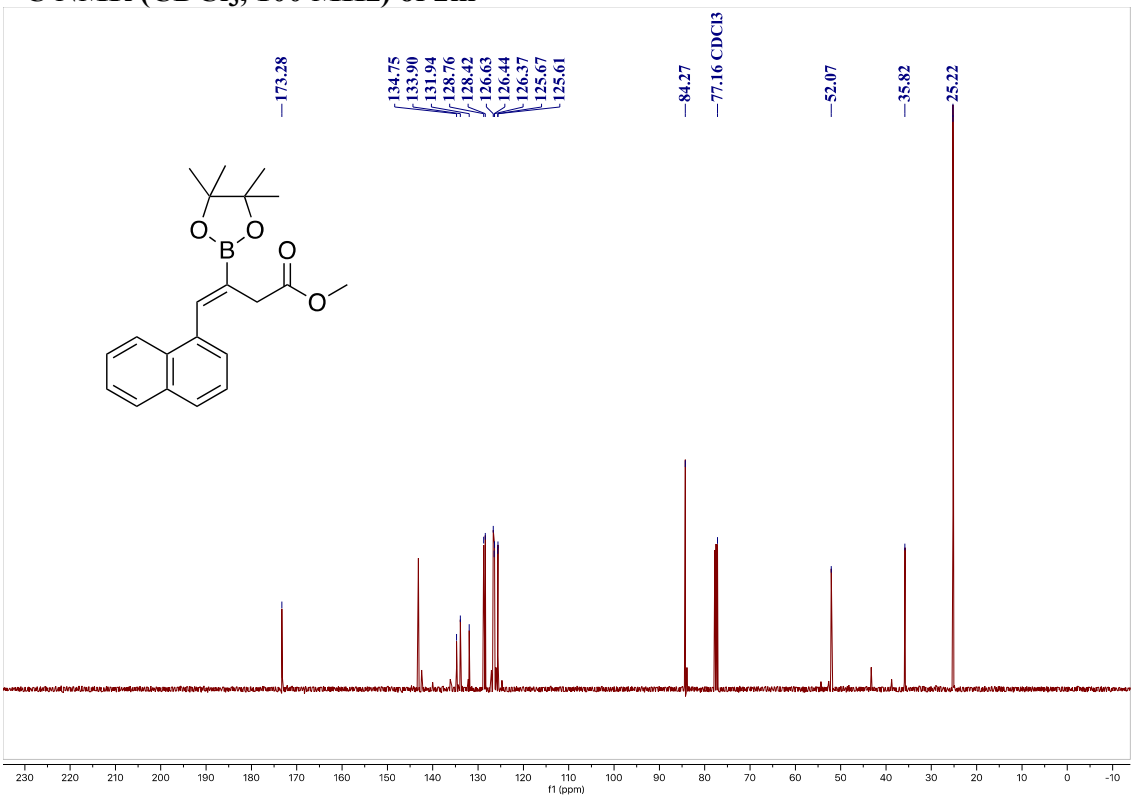
Crude GC of 2l



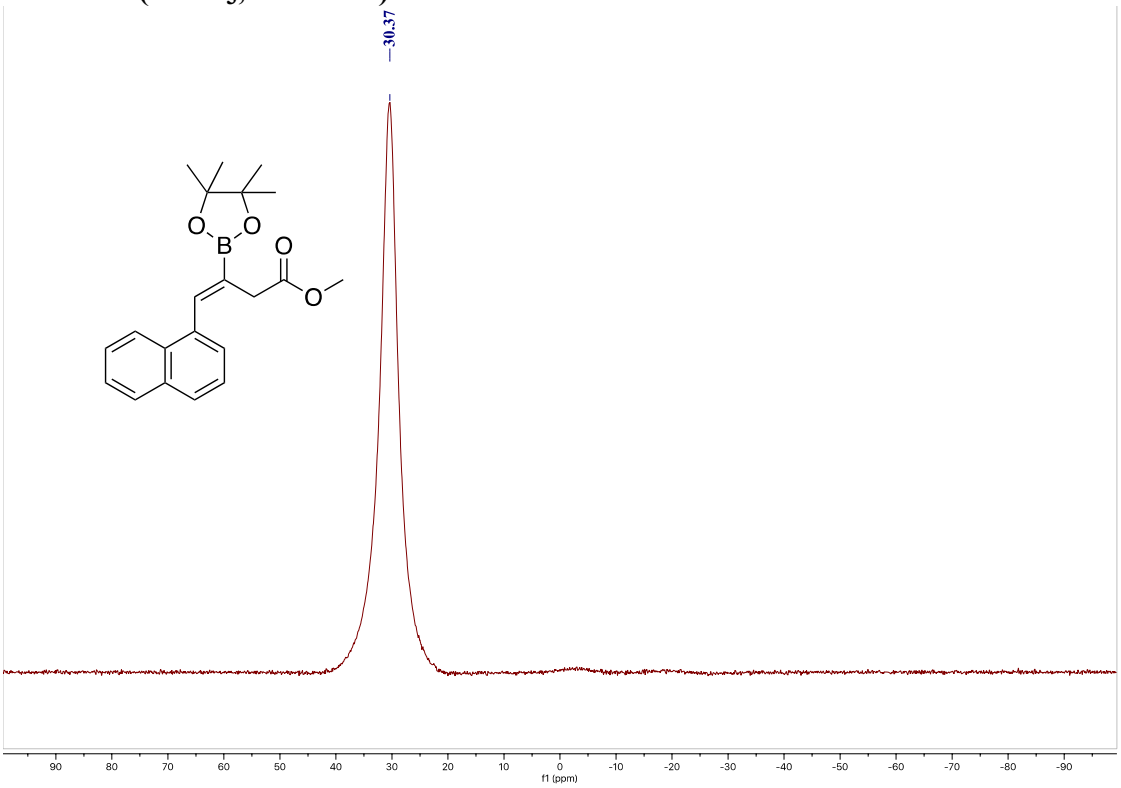
^{1}H NMR ($CDCl_3$, 400 MHz) of 2m



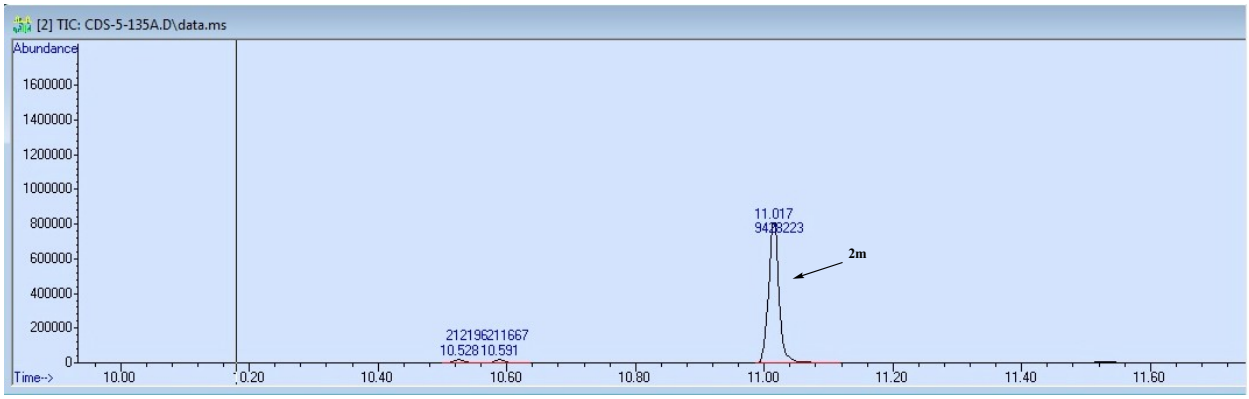
^{13}C NMR ($CDCl_3$, 100 MHz) of 2m



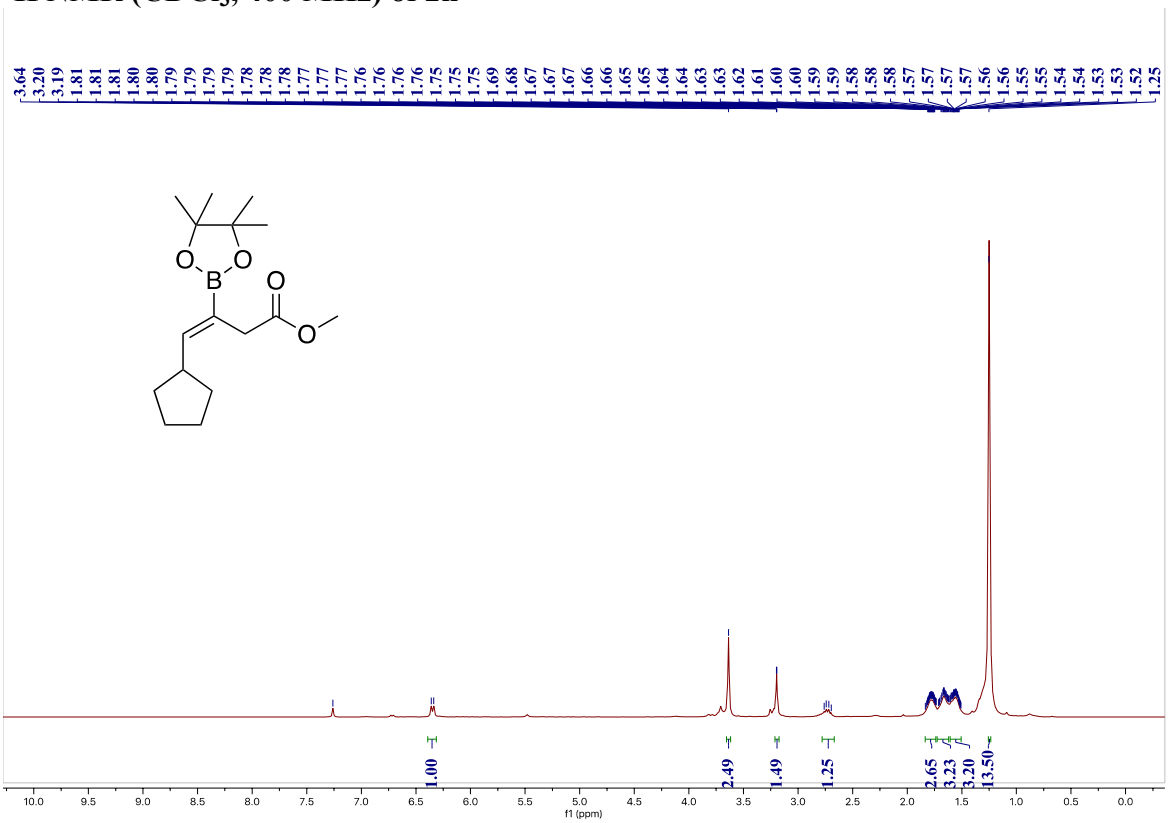
^{11}B NMR ($CDCl_3$, 160 MHz) of 2m



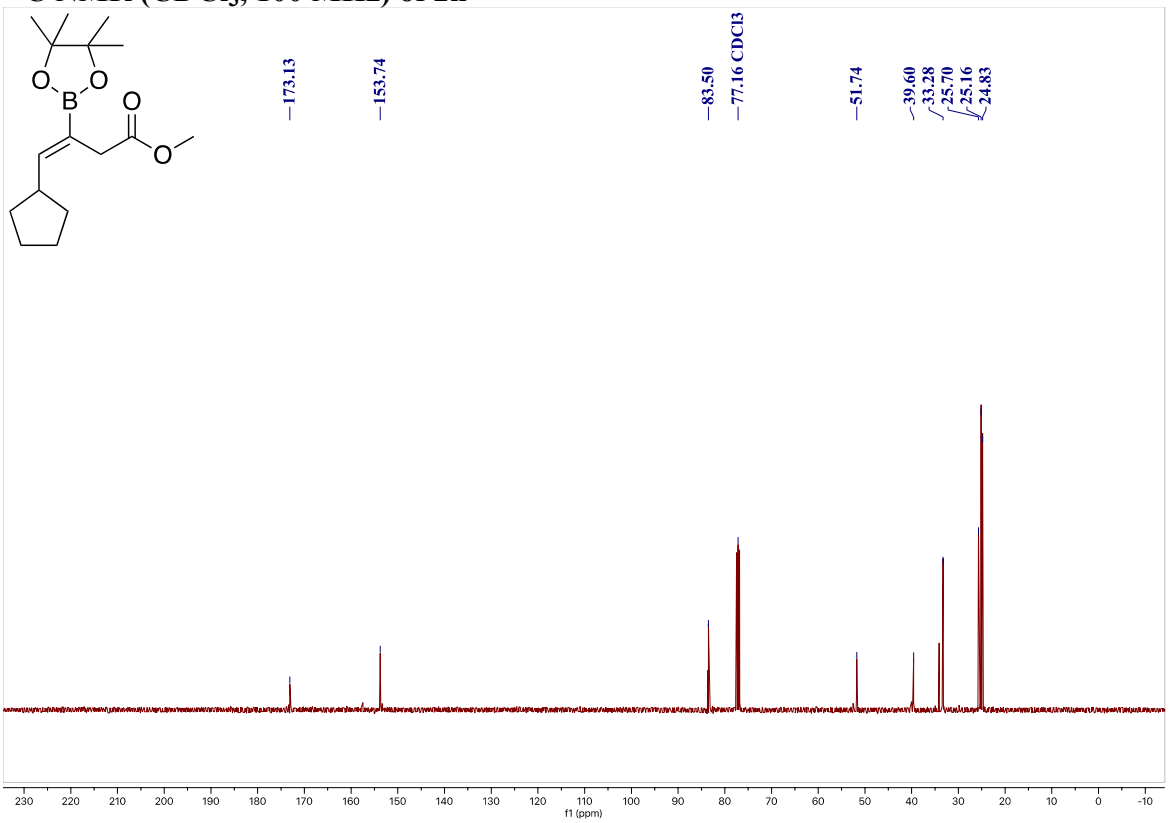
Crude GC of 2m



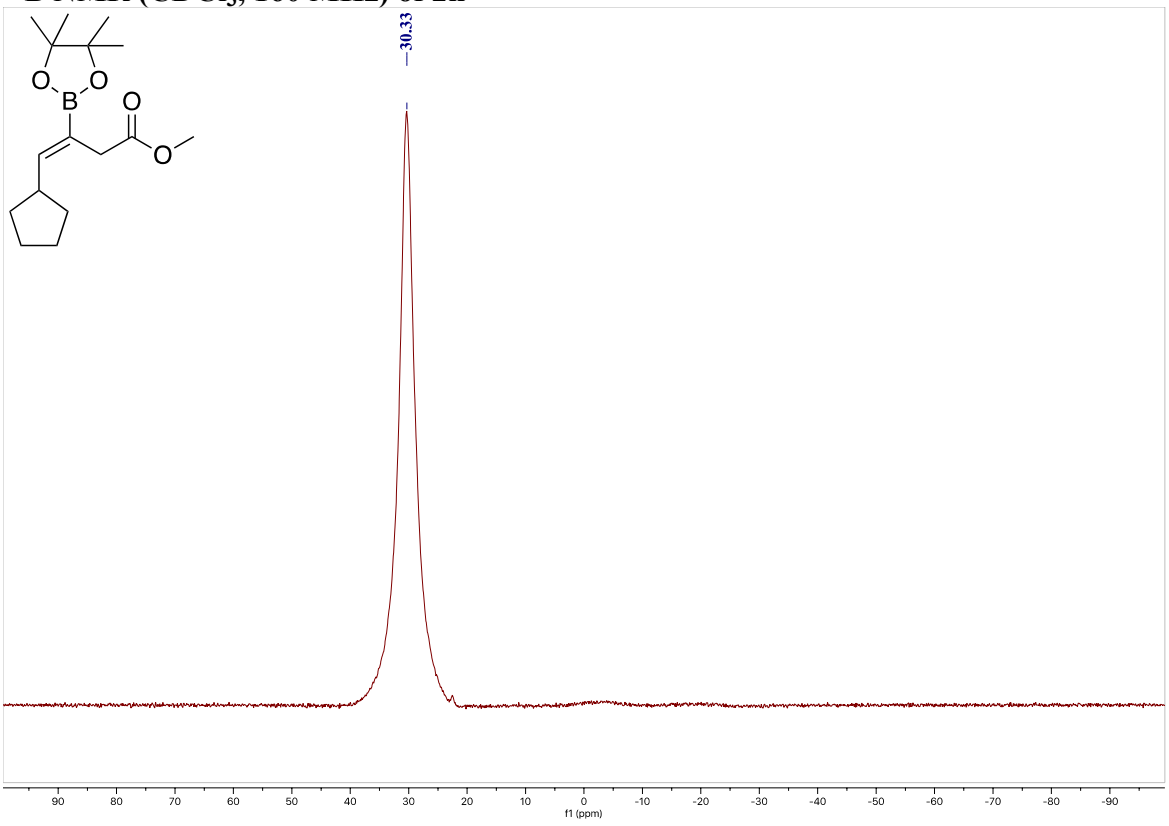
^{1}H NMR ($CDCl_3$, 400 MHz) of 2n



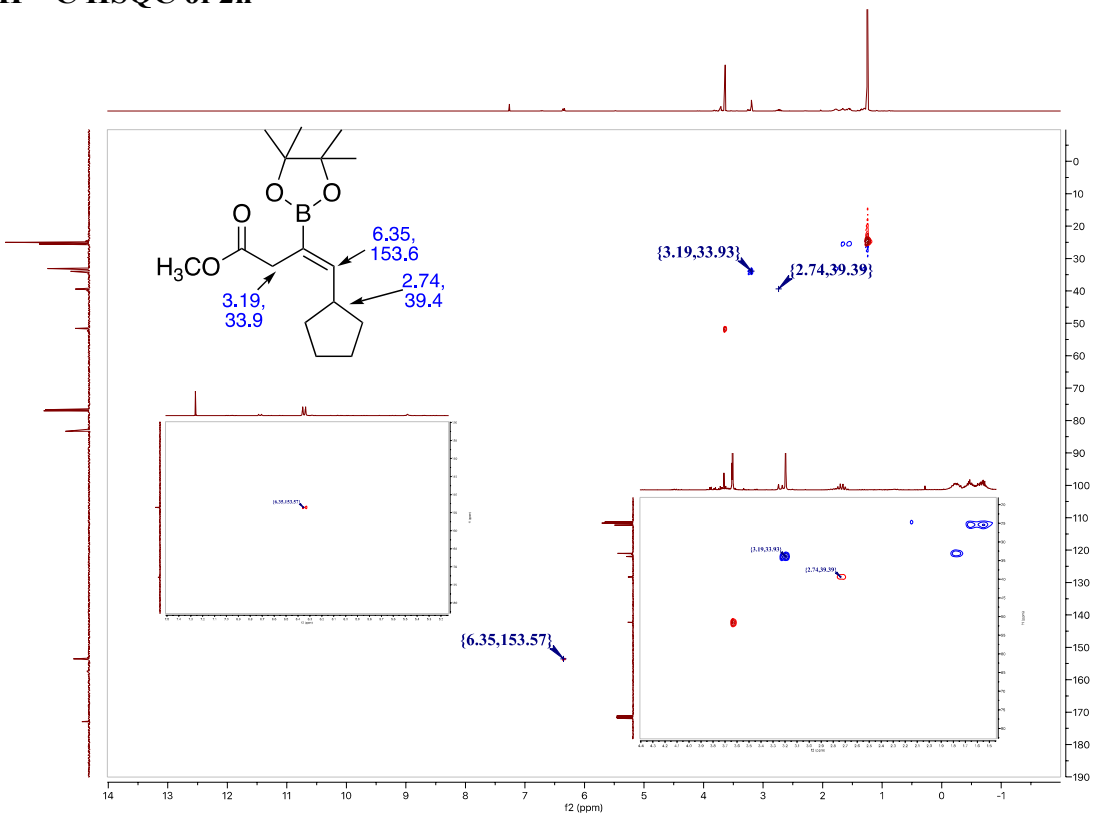
^{13}C NMR ($CDCl_3$, 100 MHz) of 2n



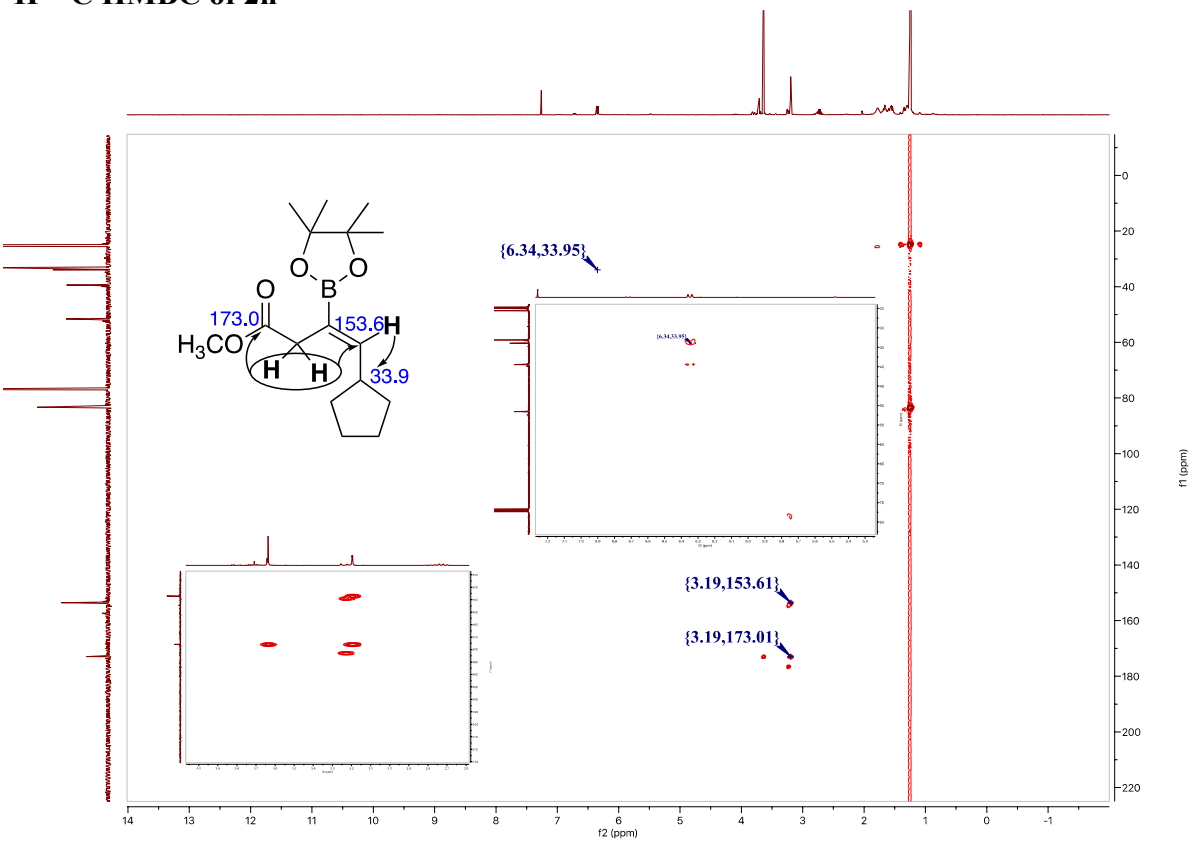
^{11}B NMR ($CDCl_3$, 160 MHz) of 2n



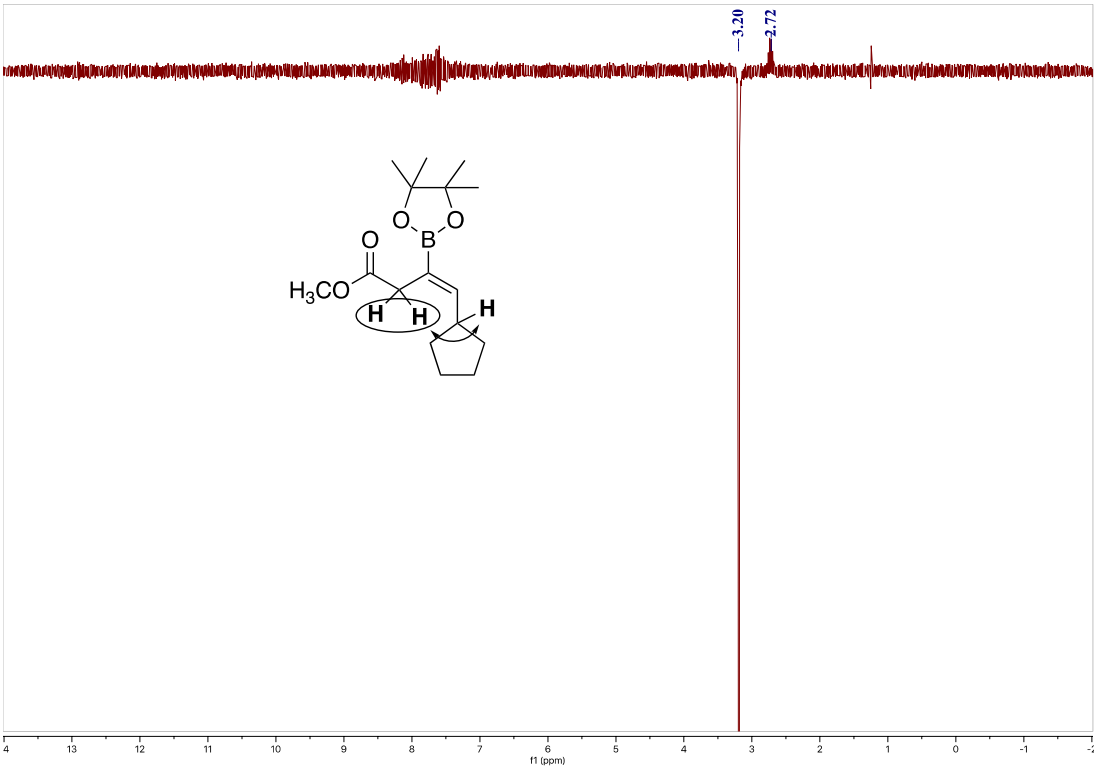
^{1}H-^{13}C HSQC of 2n



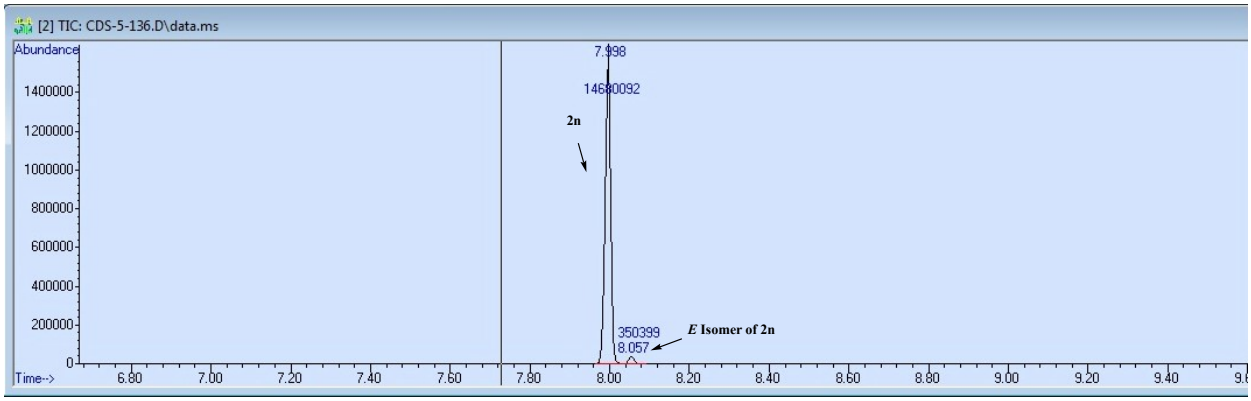
^{1}H-^{13}C HMBC of 2n



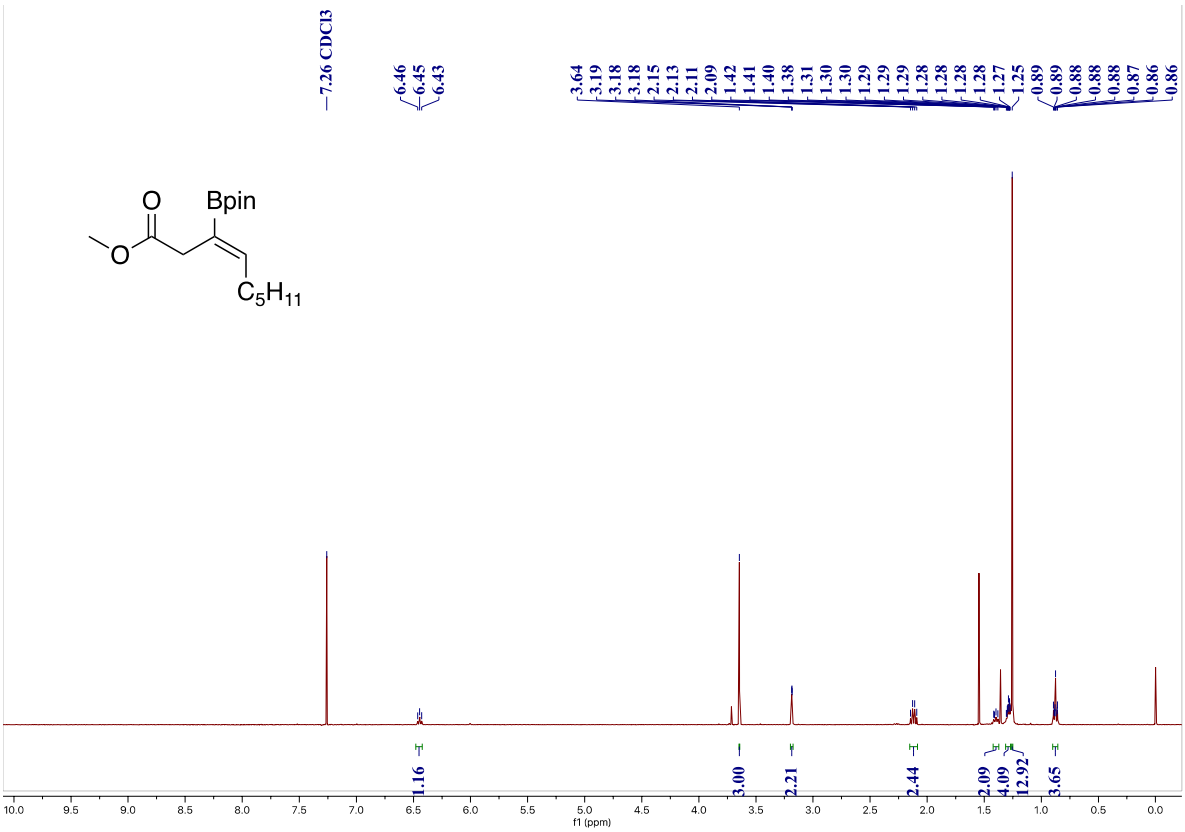
1D NOESY of 2n



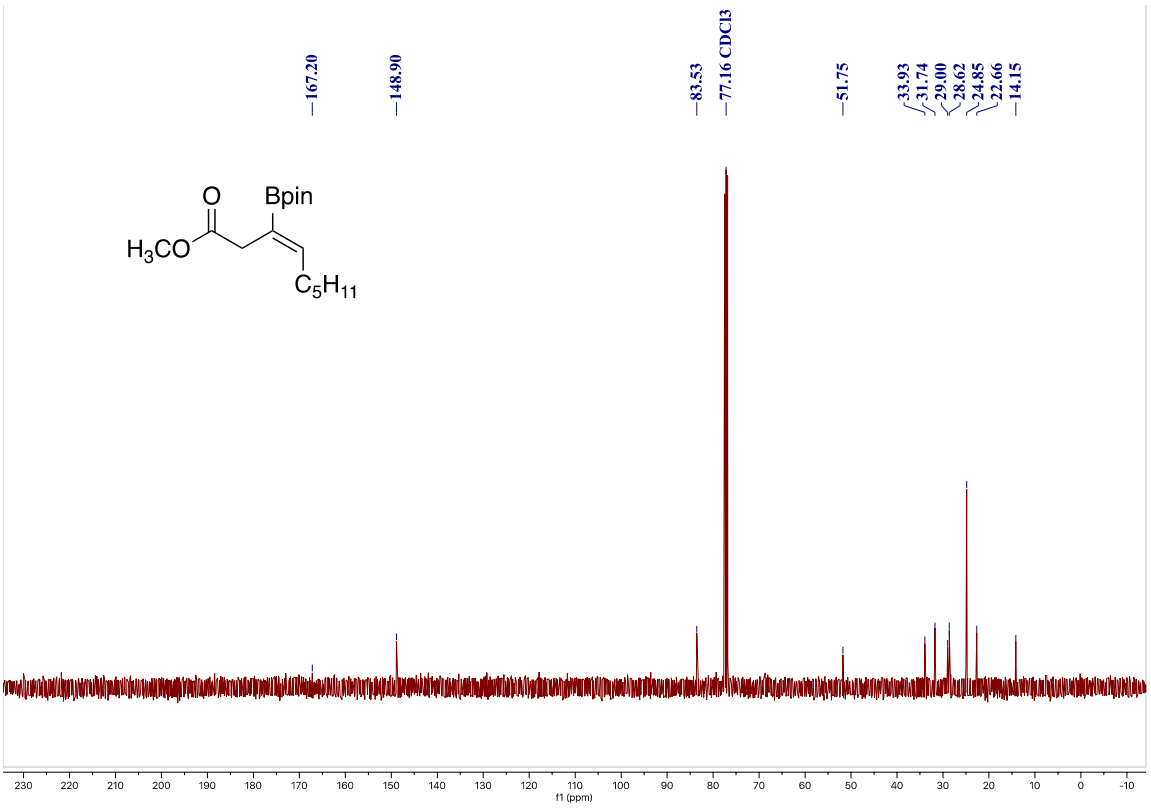
Crude GC of 2n



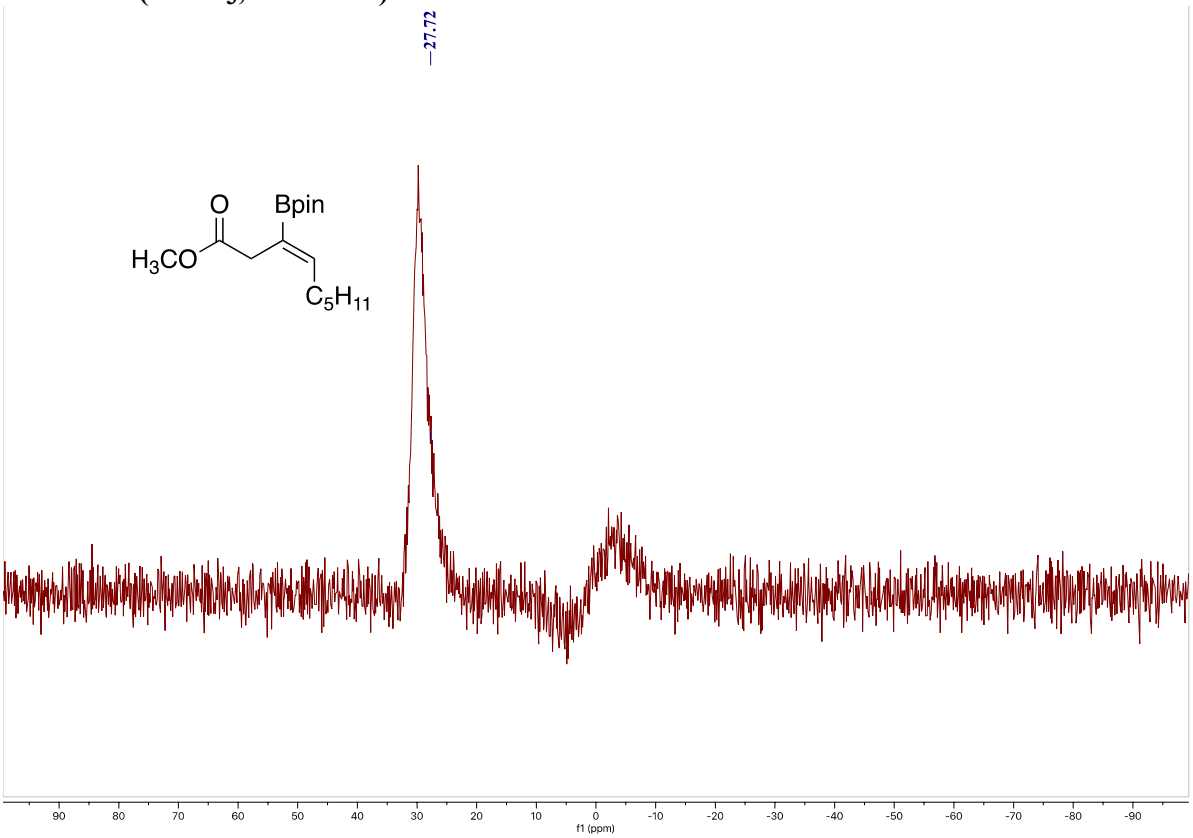
^{1}H NMR ($CDCl_3$, 400 MHz) of 2o



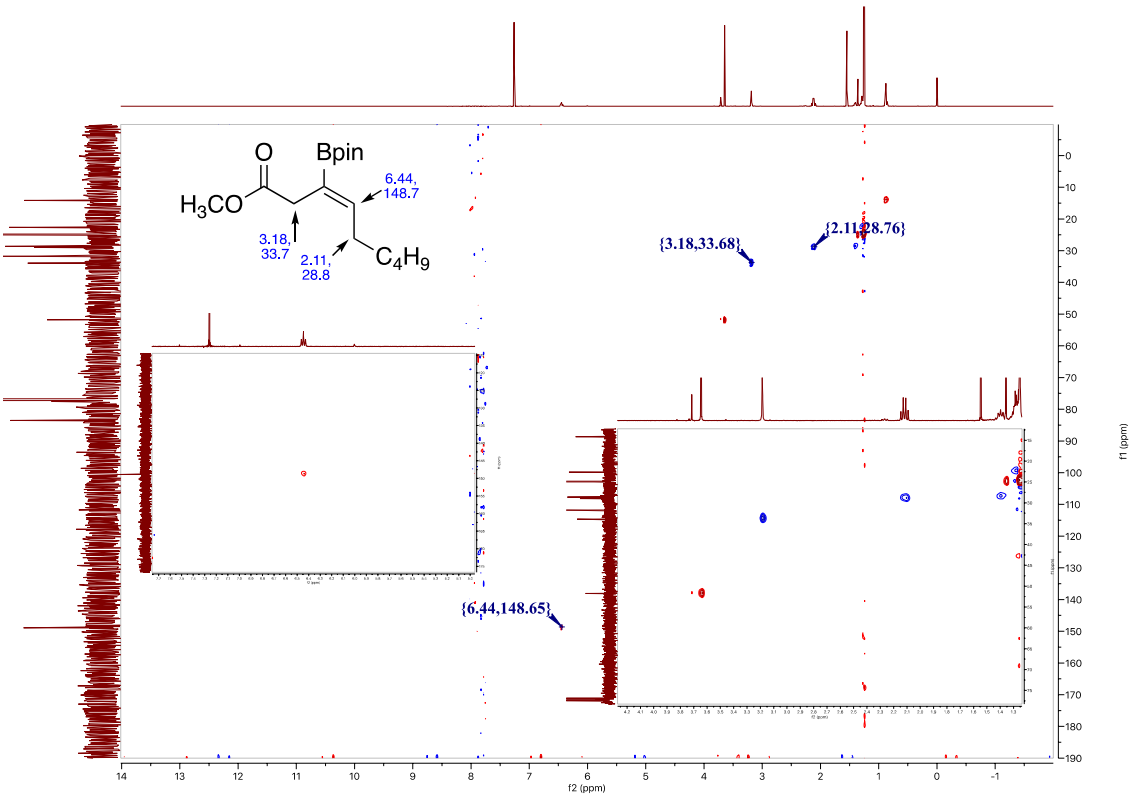
^{13}C NMR ($CDCl_3$, 100 MHz) of 2o



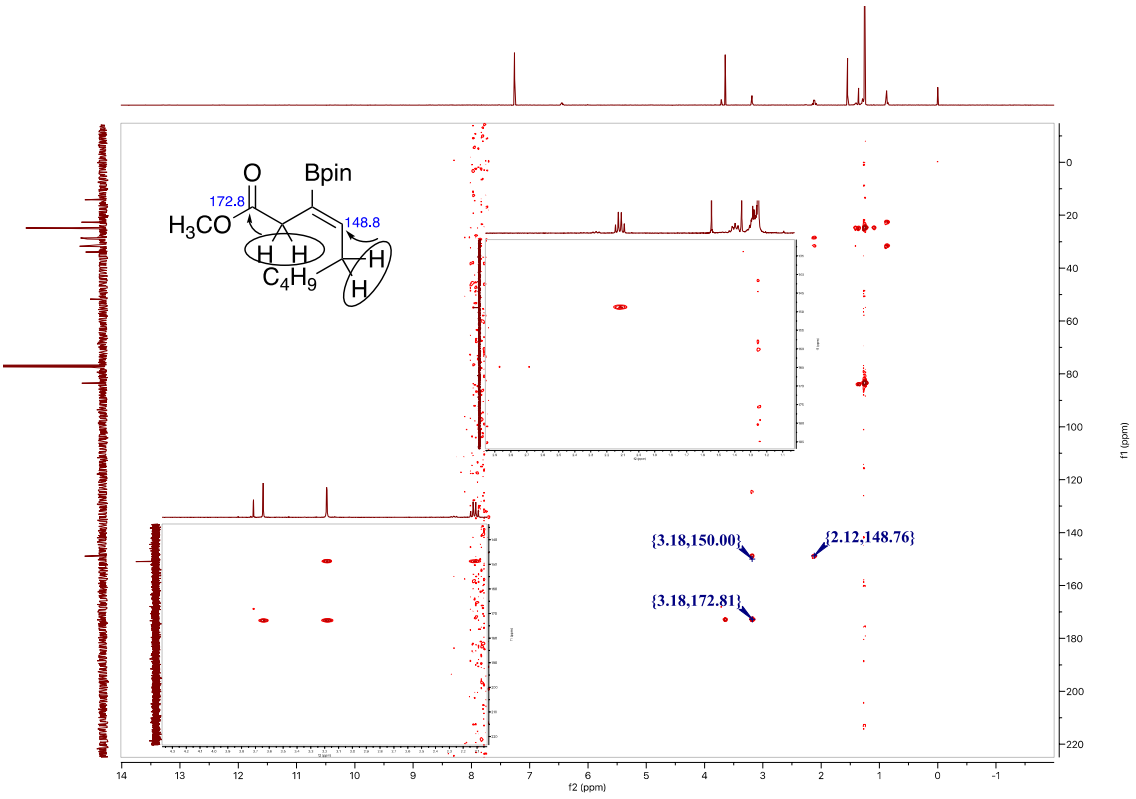
^{11}B NMR ($CDCl_3$, 160 MHz)



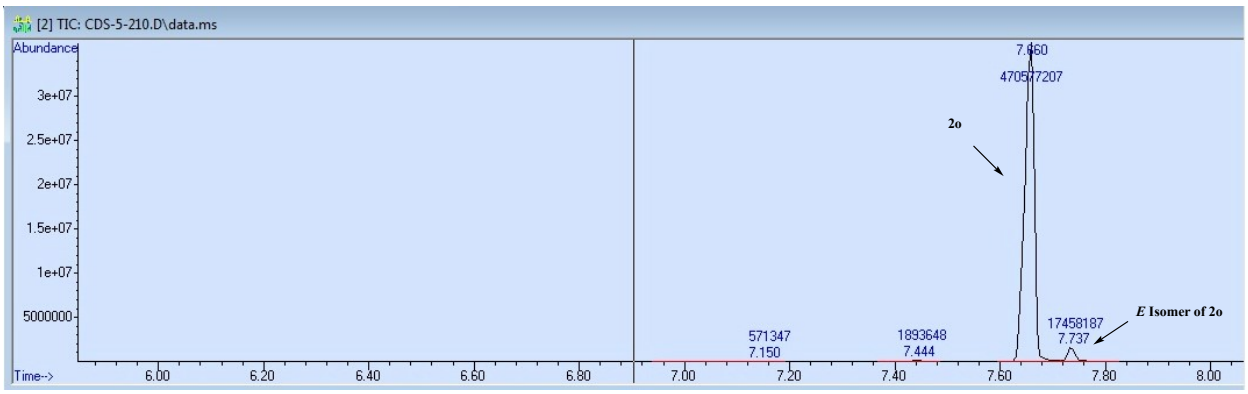
^{1}H-^{13}C HSQC of 2o



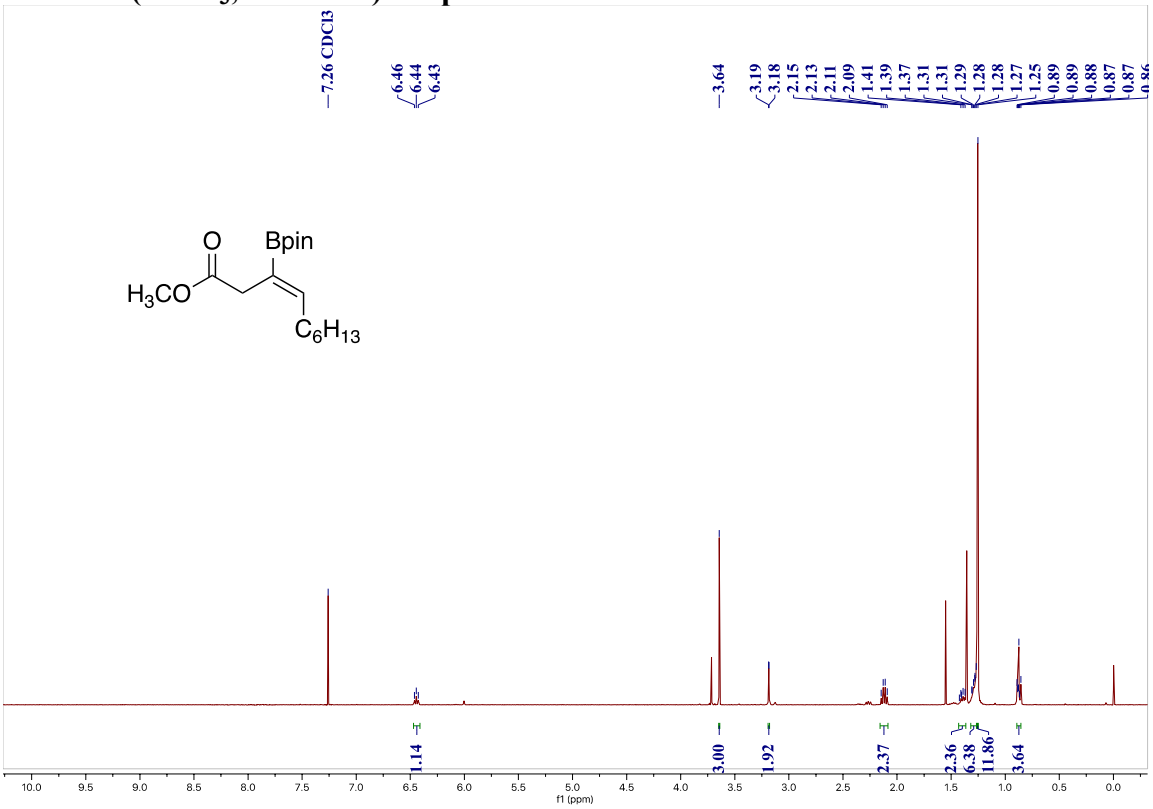
^{1}H-^{13}C HMBC of 2o



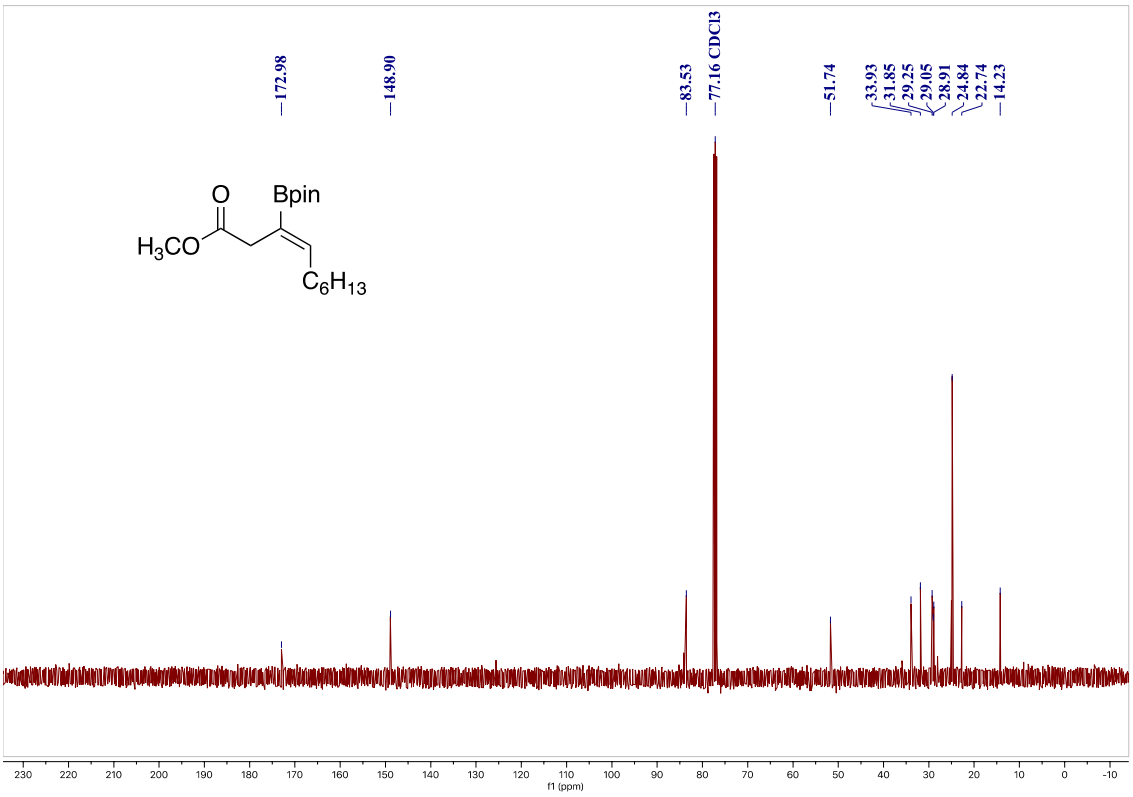
Crude GC of 2o



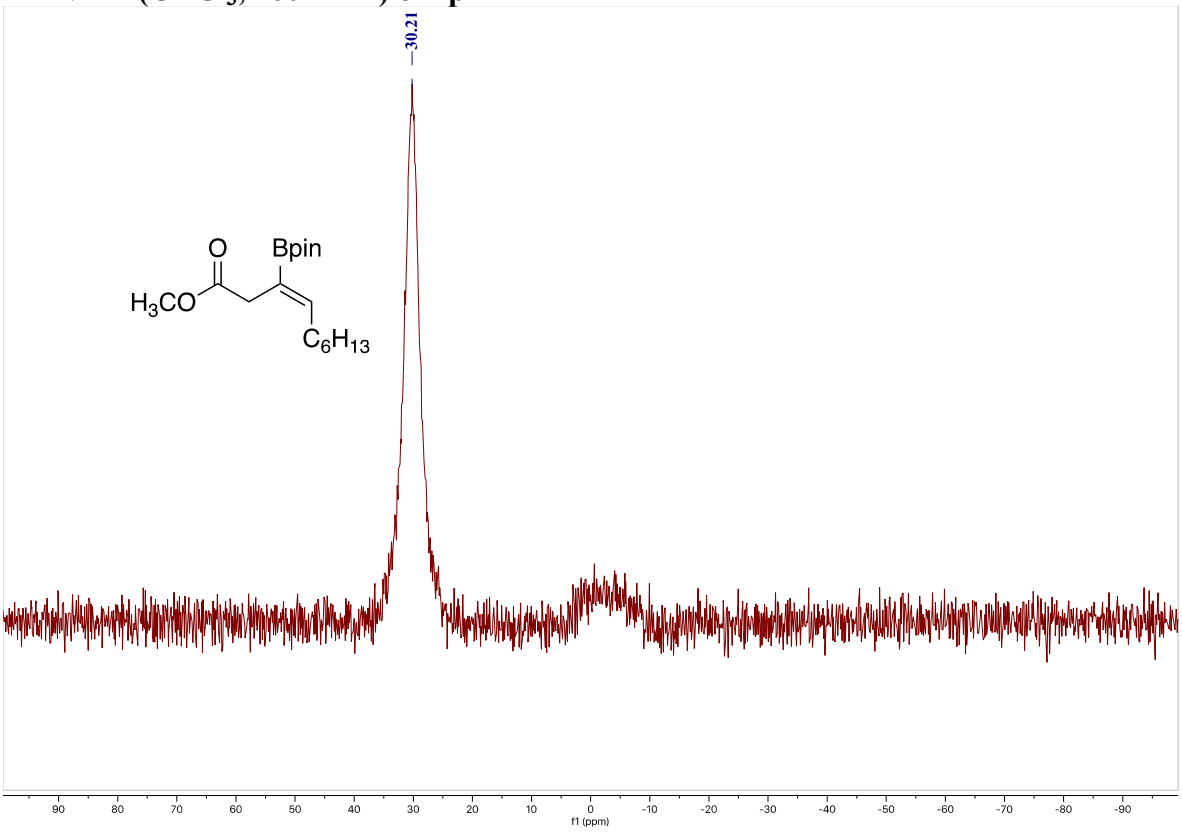
^{1}H NMR ($CDCl_3$, 400 MHz) of 2p



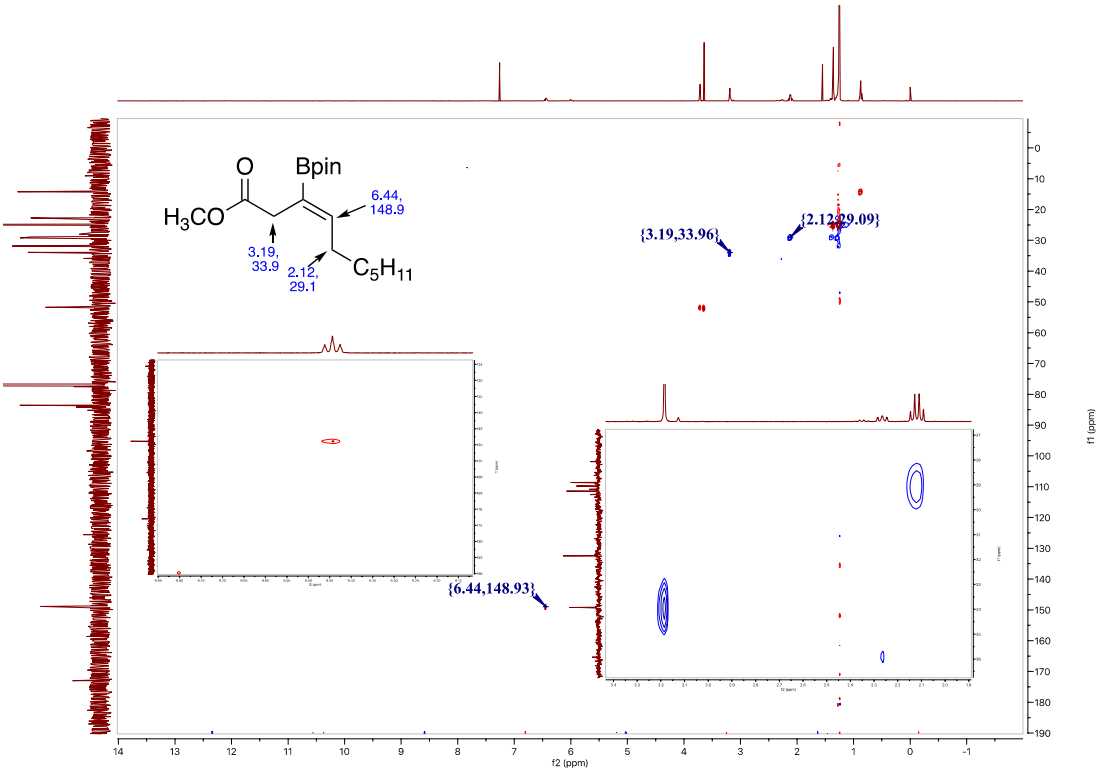
^{13}C NMR ($CDCl_3$, 100 MHz) of 2p



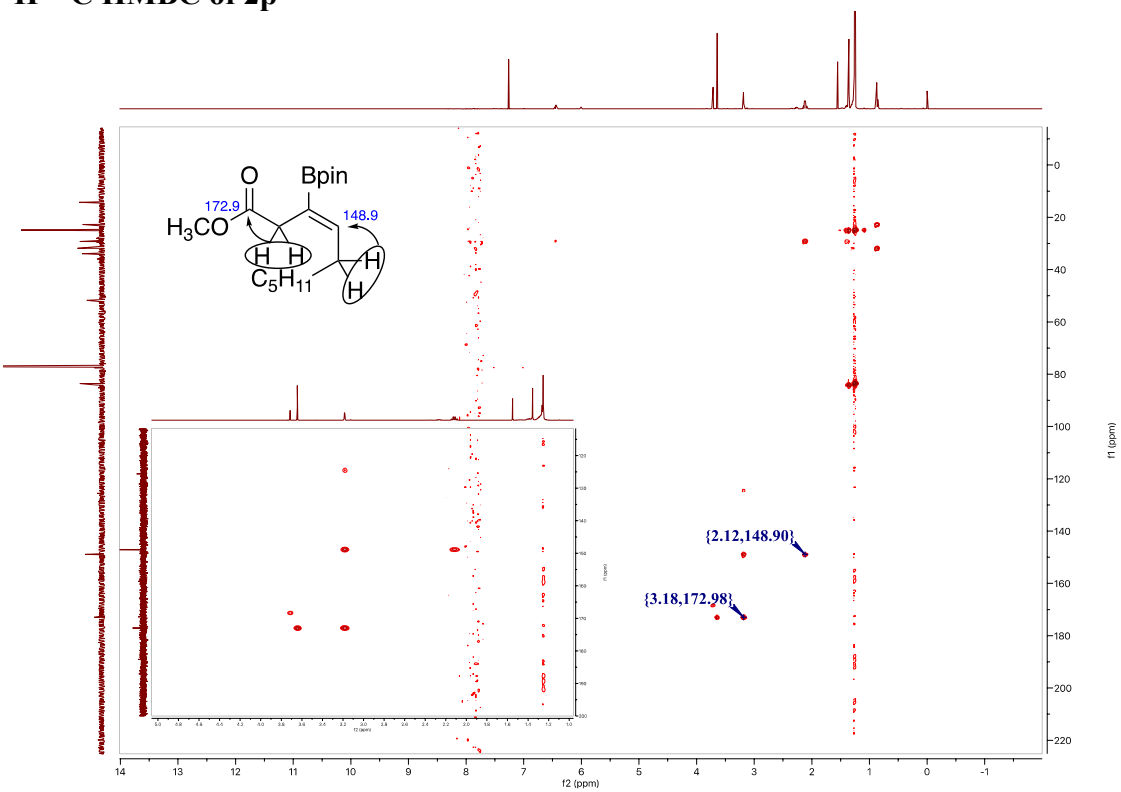
^{11}B NMR ($CDCl_3$, 160 MHz) of 2p



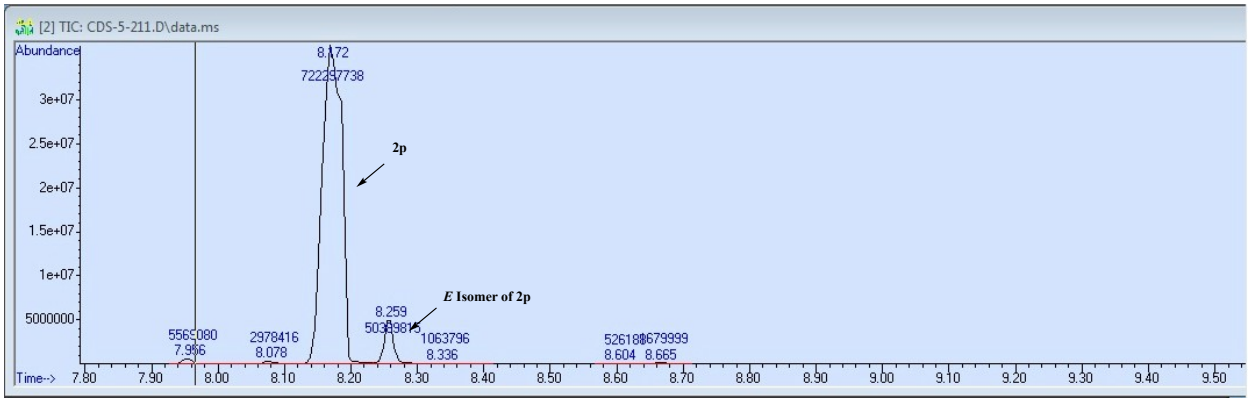
^{1}H-^{13}C HSQC of 2p



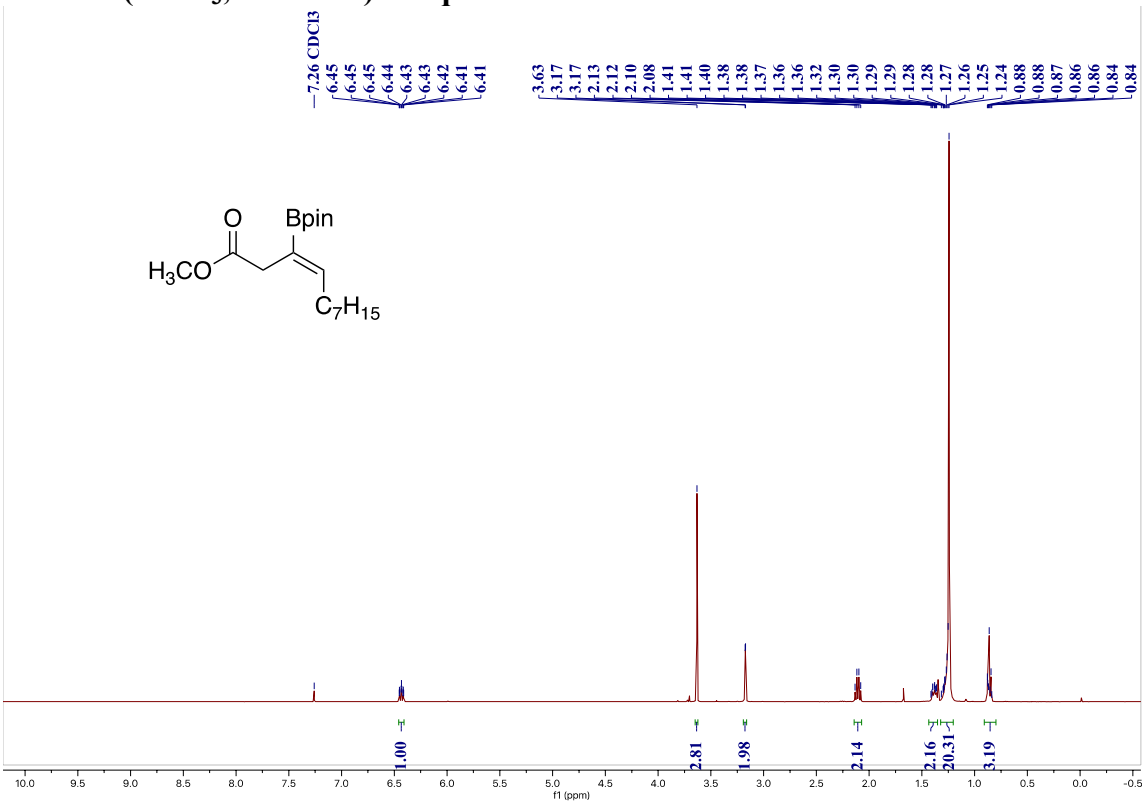
^{1}H-^{13}C HMBC of 2p



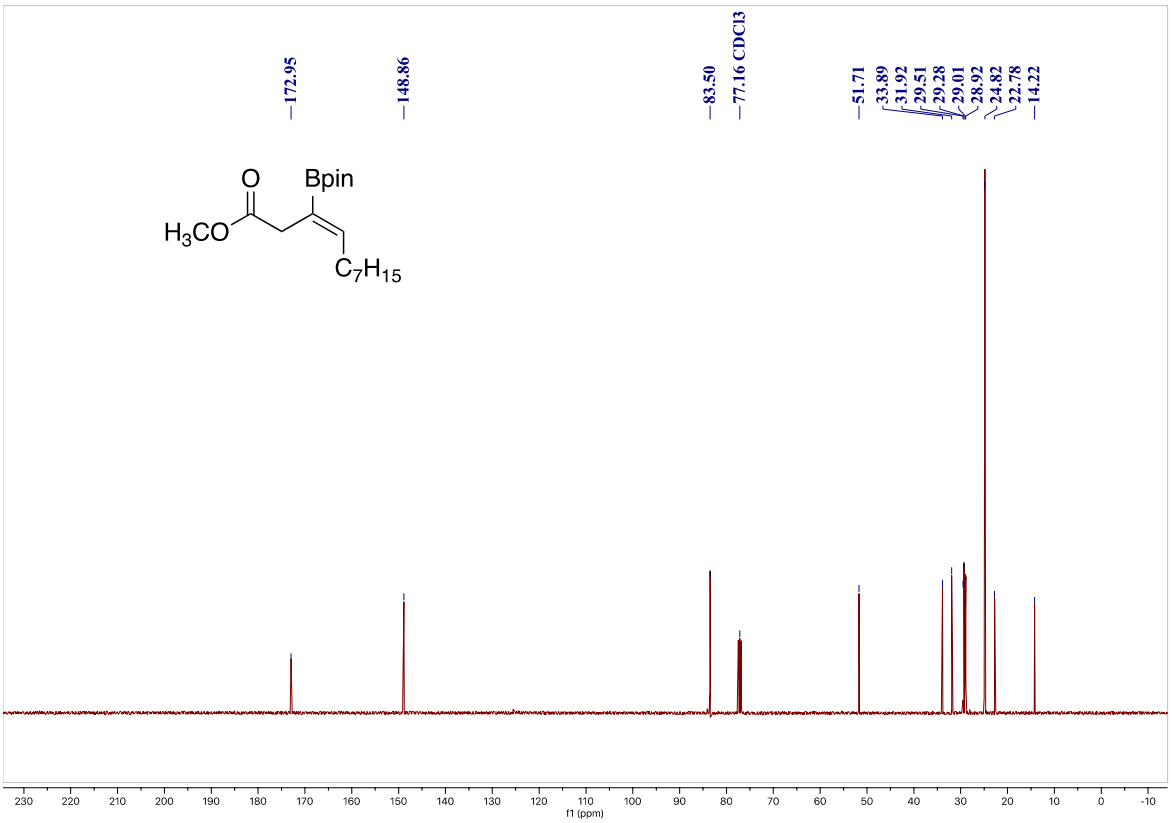
Crude GC of 2p



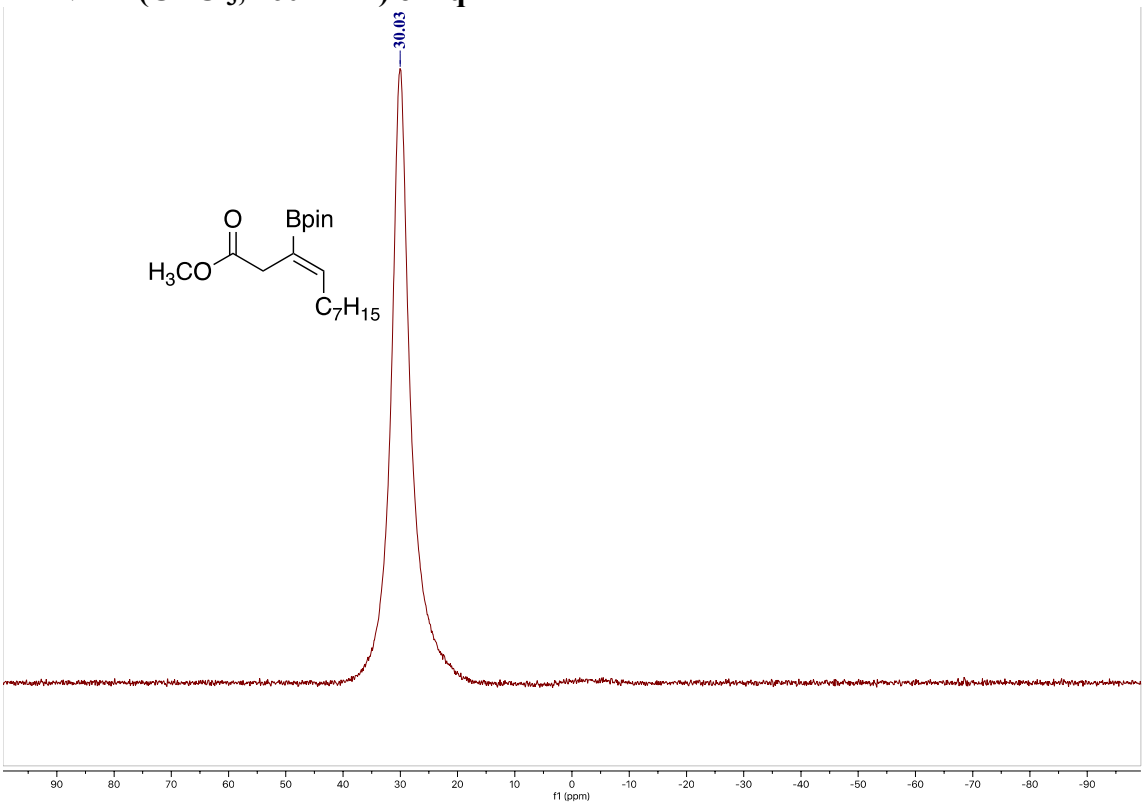
^{1}HNMR ($CDCl_3$, 400 MHz) of 2q



^{13}C NMR ($CDCl_3$, 100 MHz) of 2q



^{11}B NMR ($CDCl_3$, 160 MHz) of 2q



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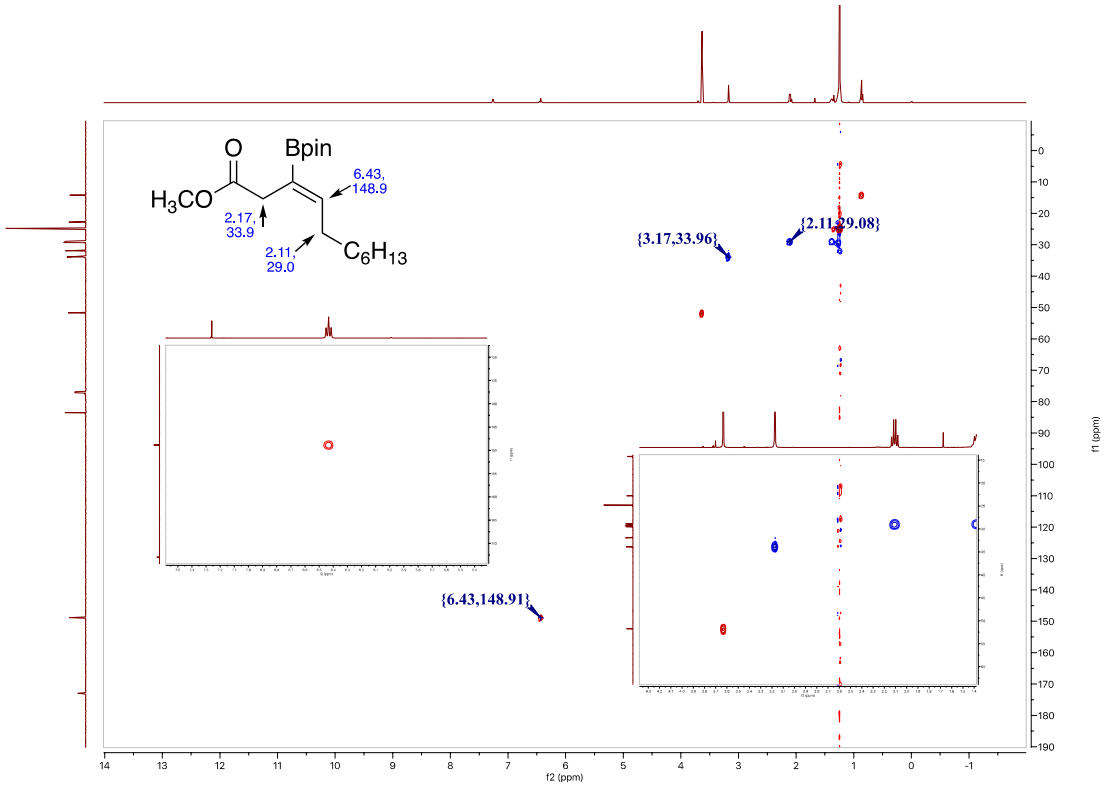

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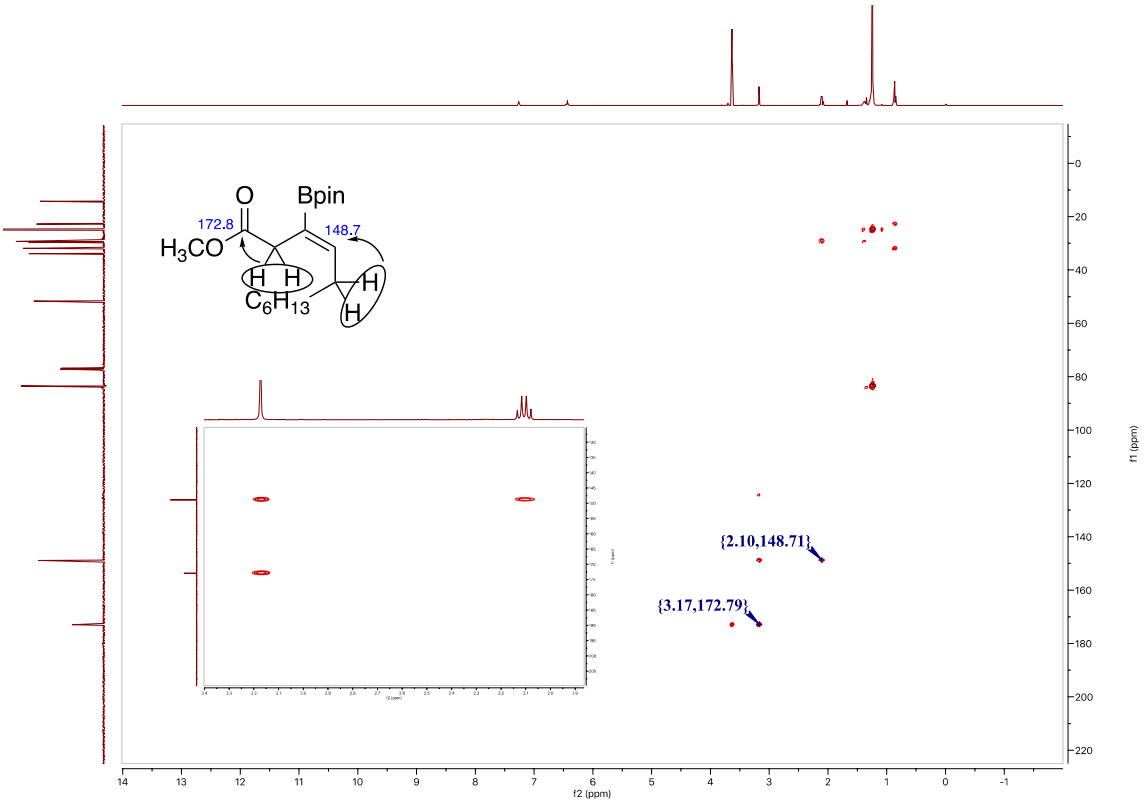
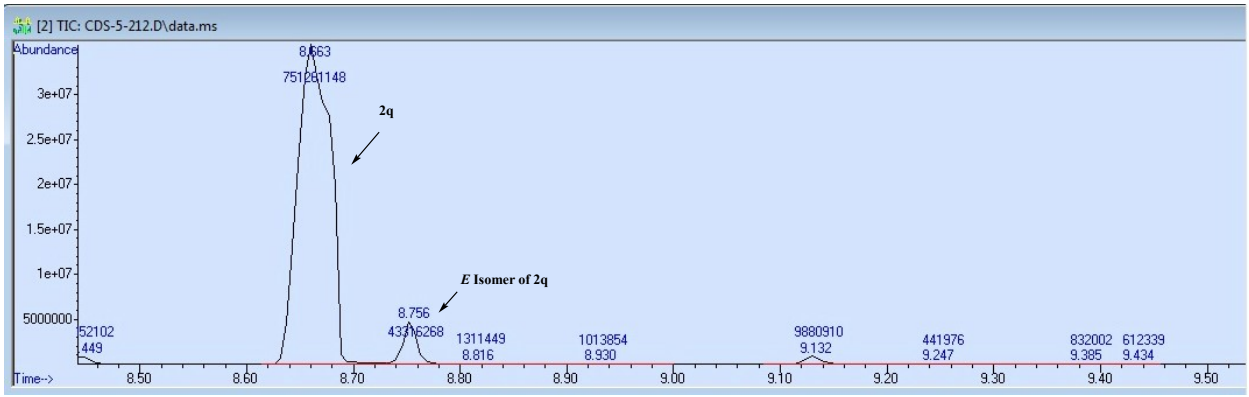
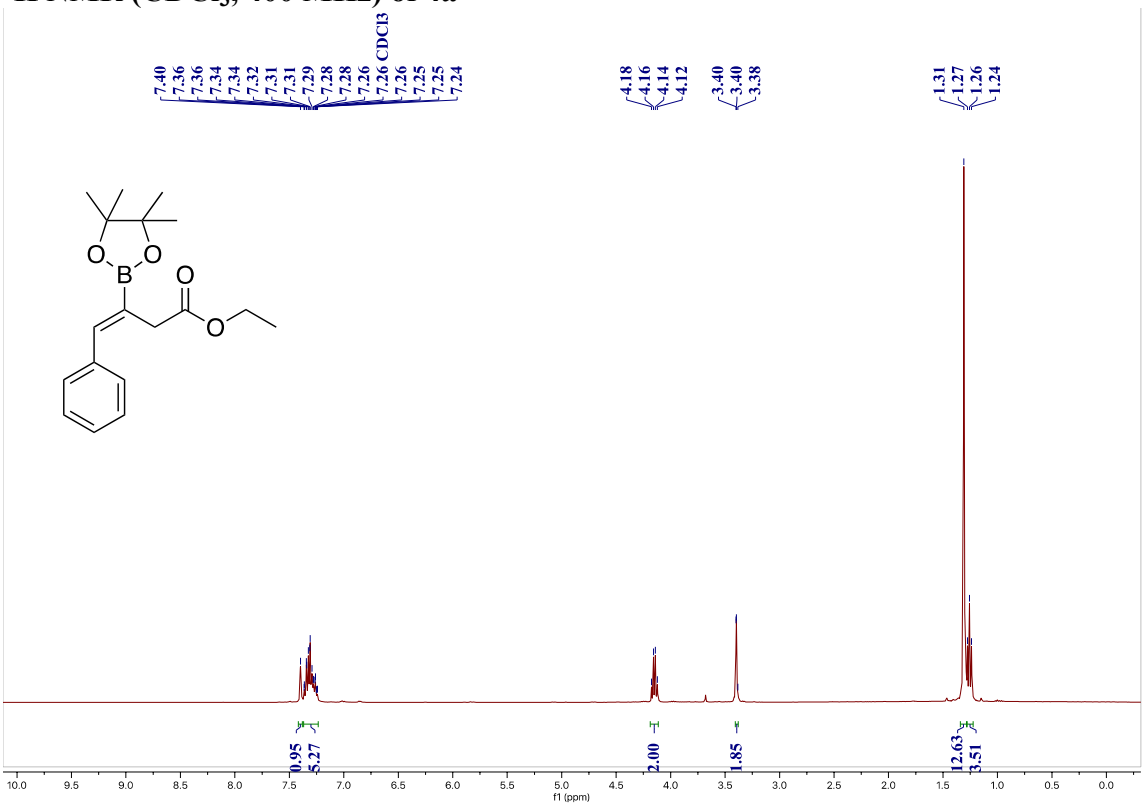


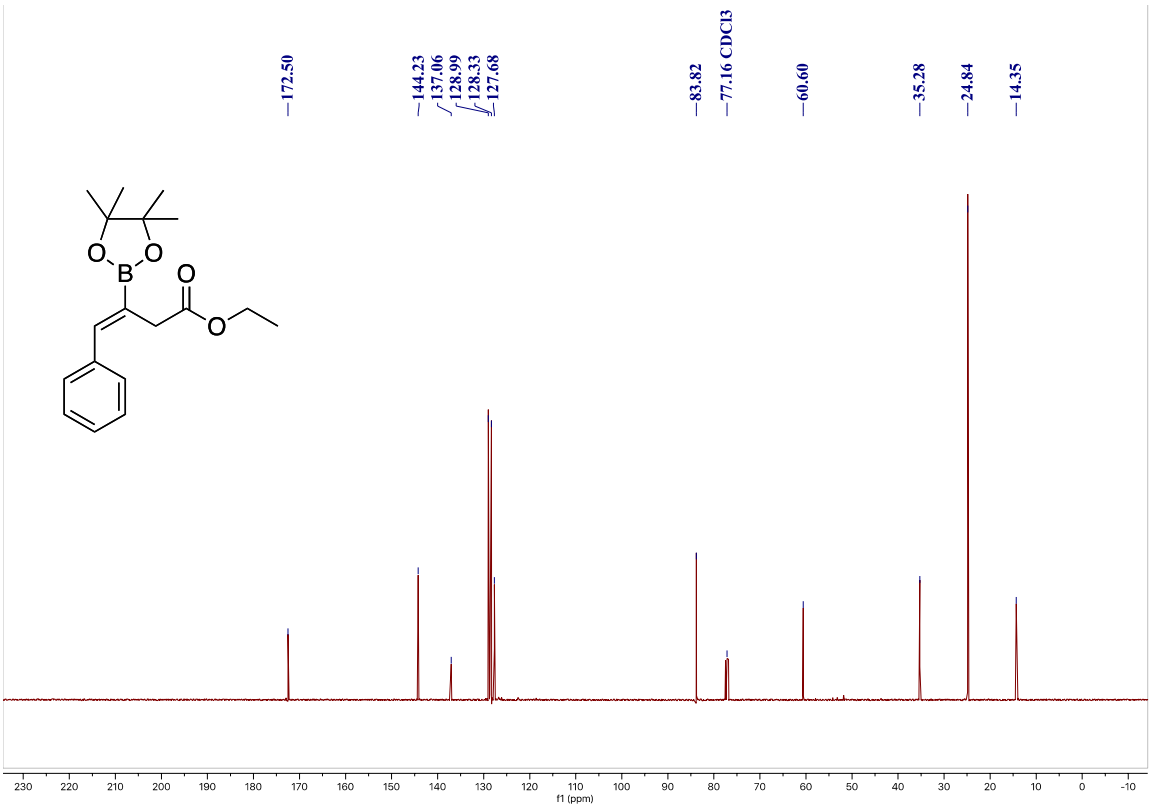
Crude GC of 2q



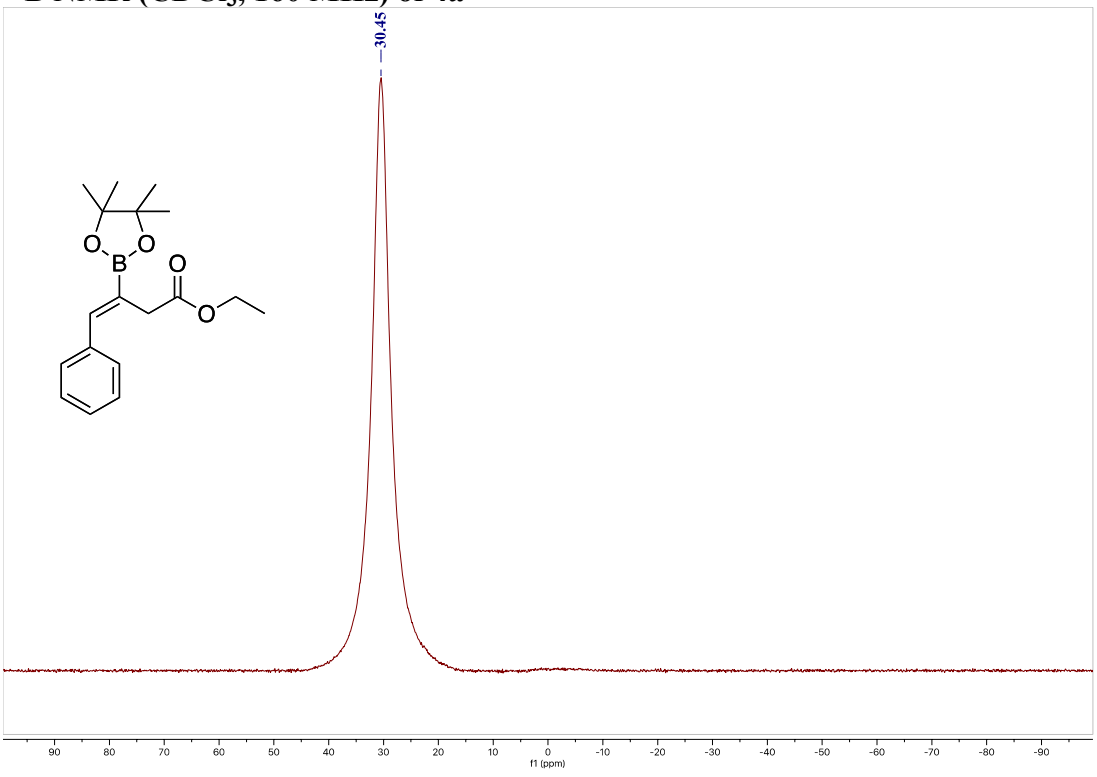
^{1}H NMR ($CDCl_3$, 400 MHz) of 4a



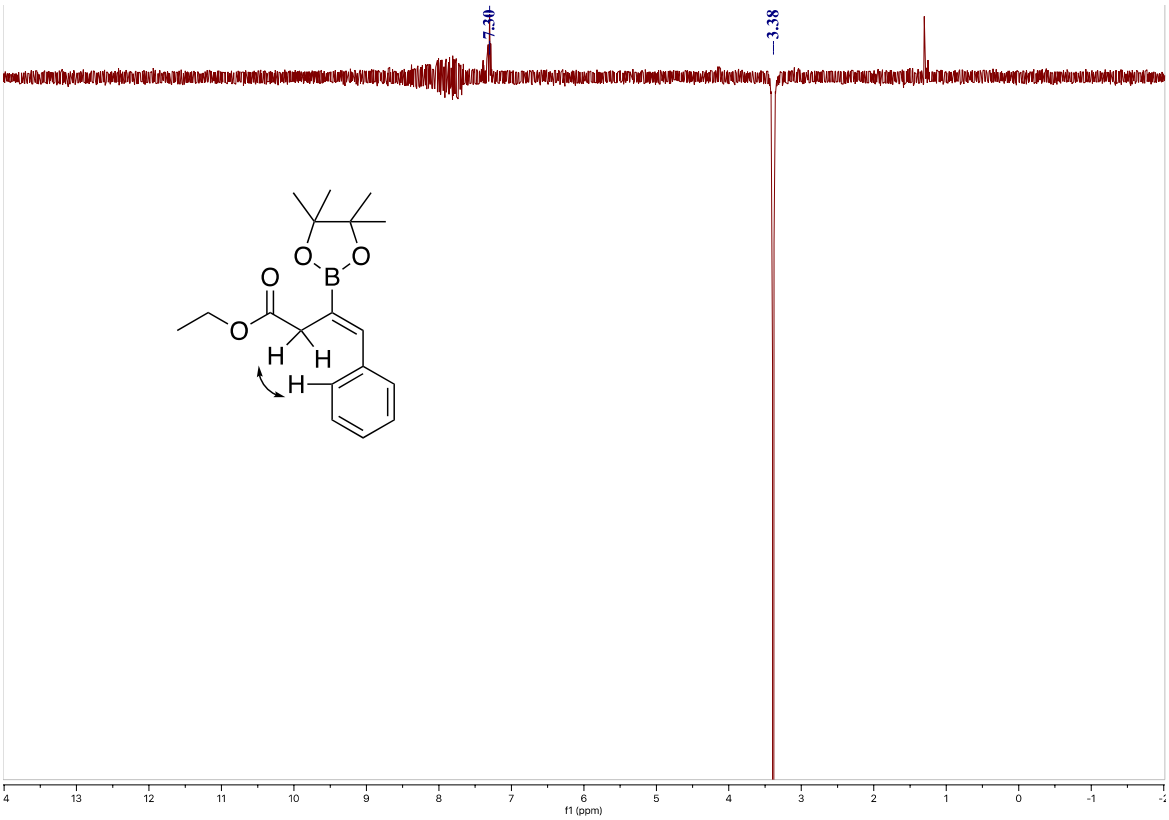
^{13}C NMR ($CDCl_3$, 100 MHz) of 4a



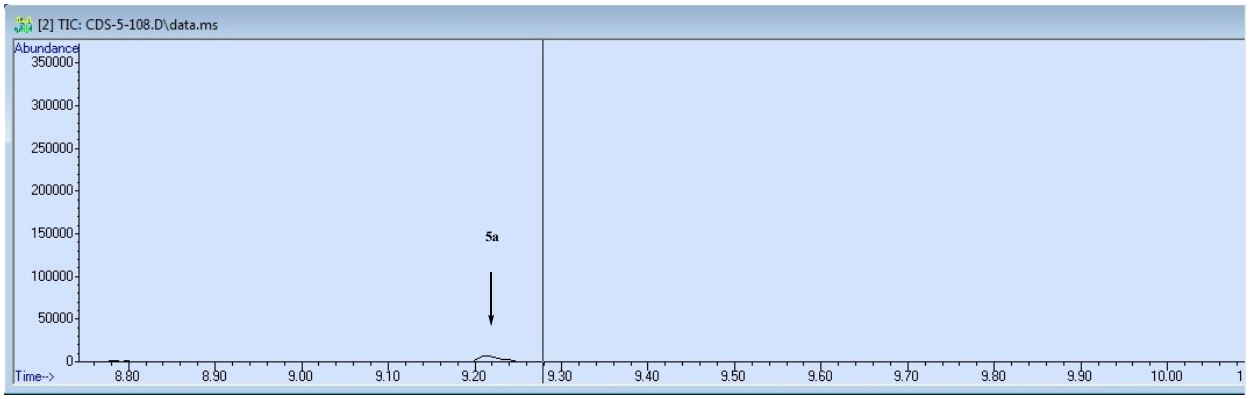
^{11}B NMR ($CDCl_3$, 160 MHz) of 4a



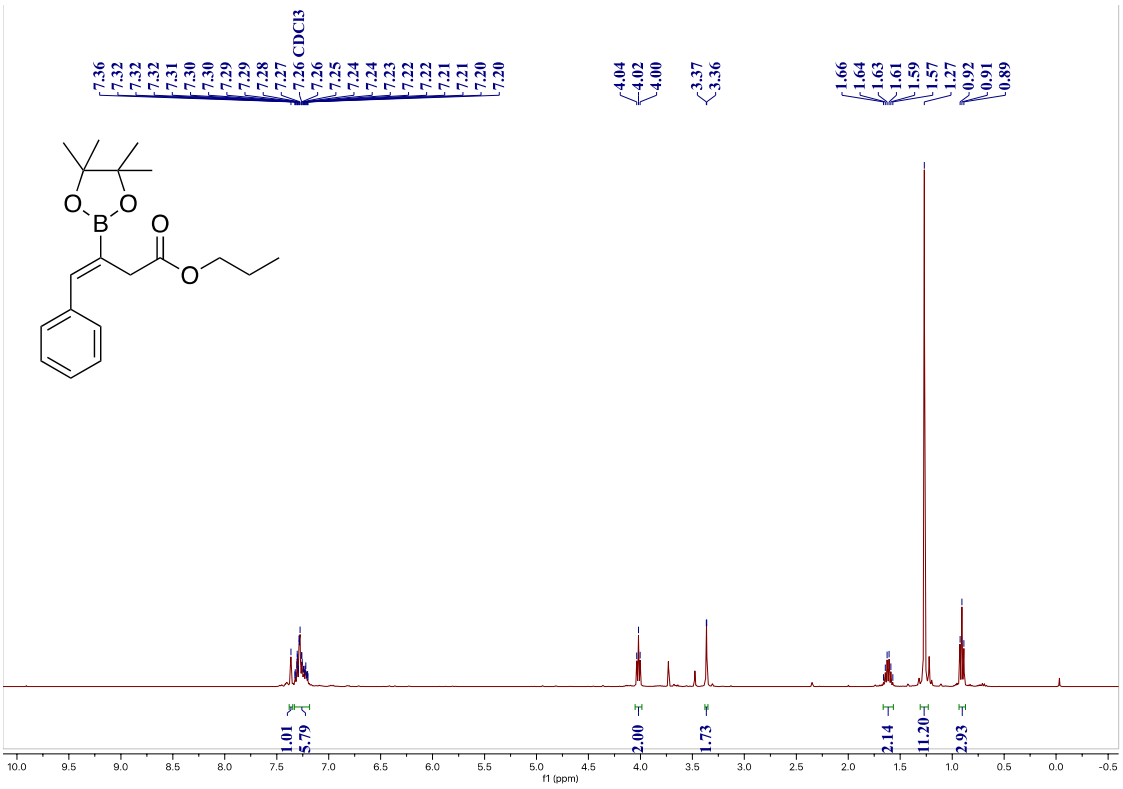
1D NOESY of 4a



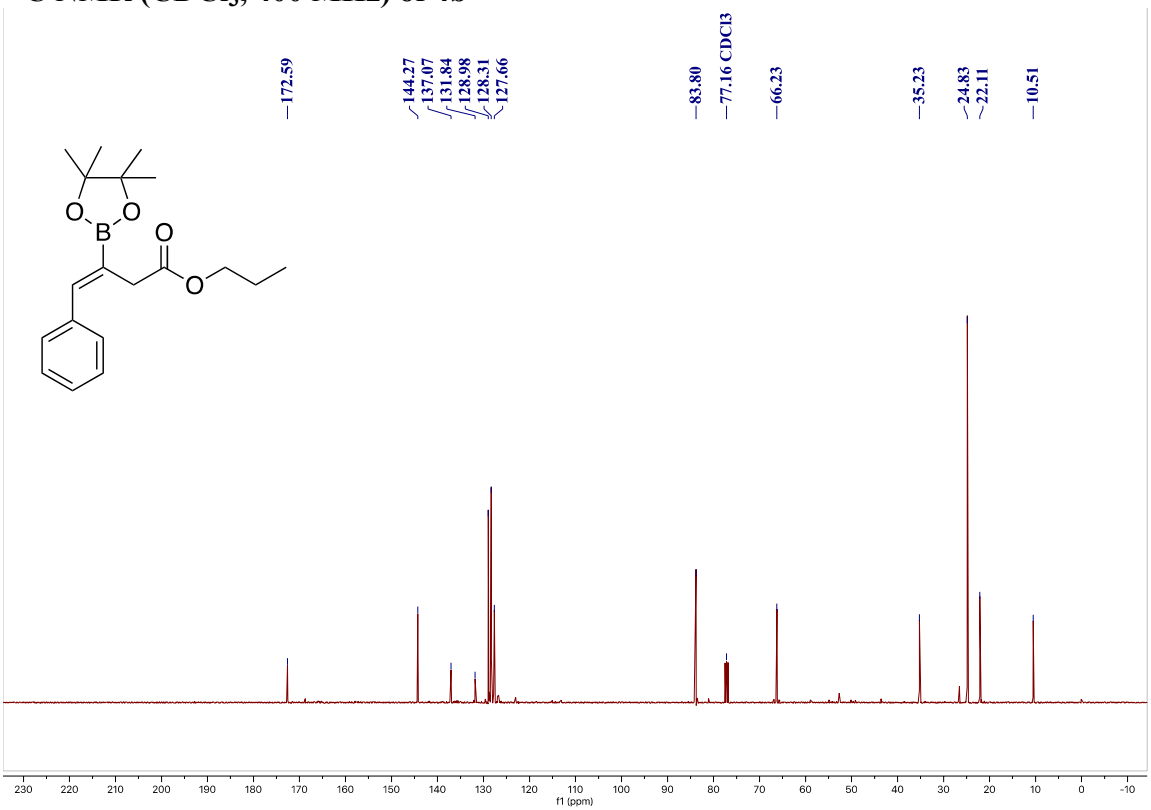
Crude GC of 4a



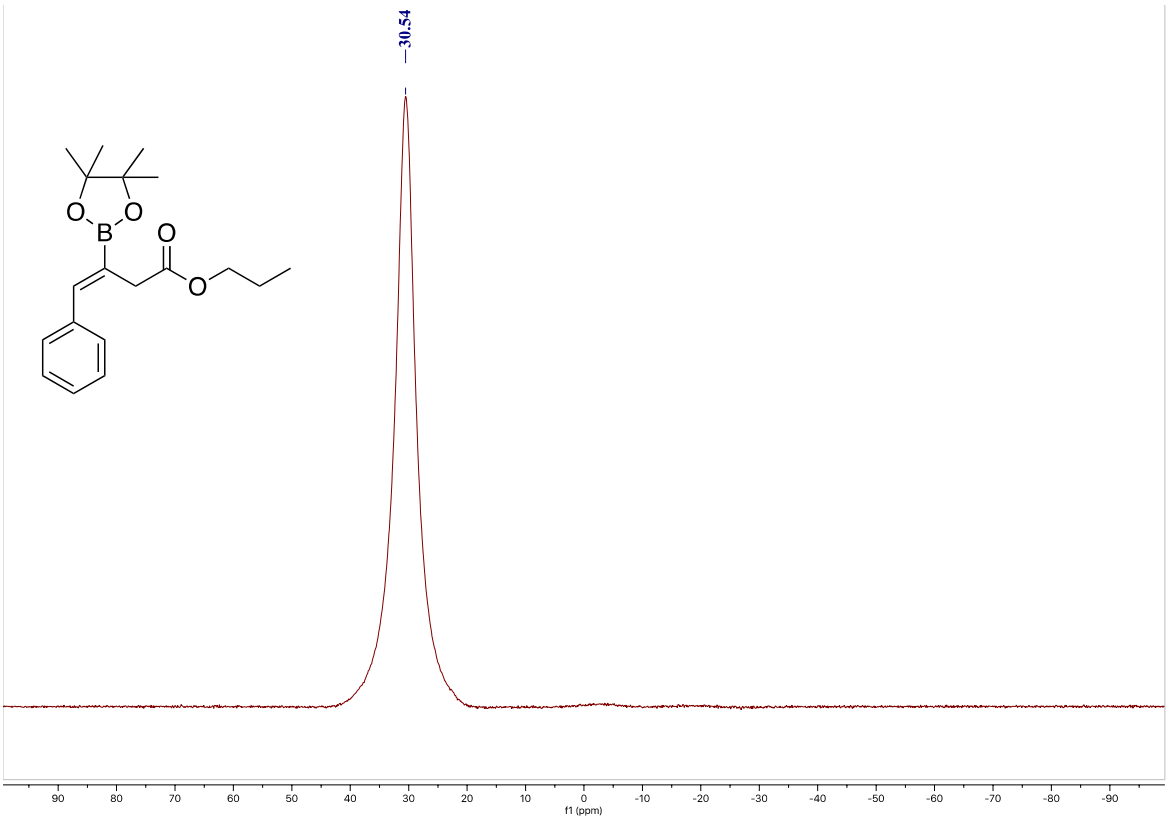
^{1}H NMR ($CDCl_3$, 400 MHz) of 4b



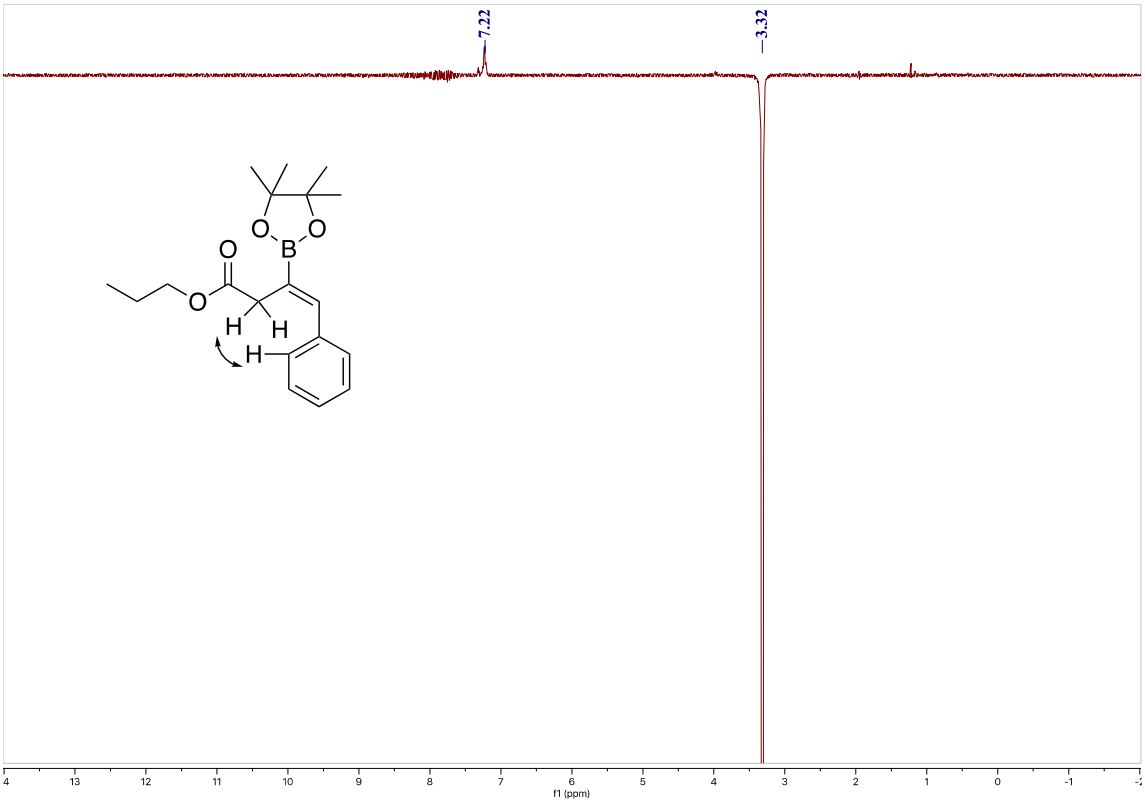
^{13}C NMR ($CDCl_3$, 400 MHz) of 4b



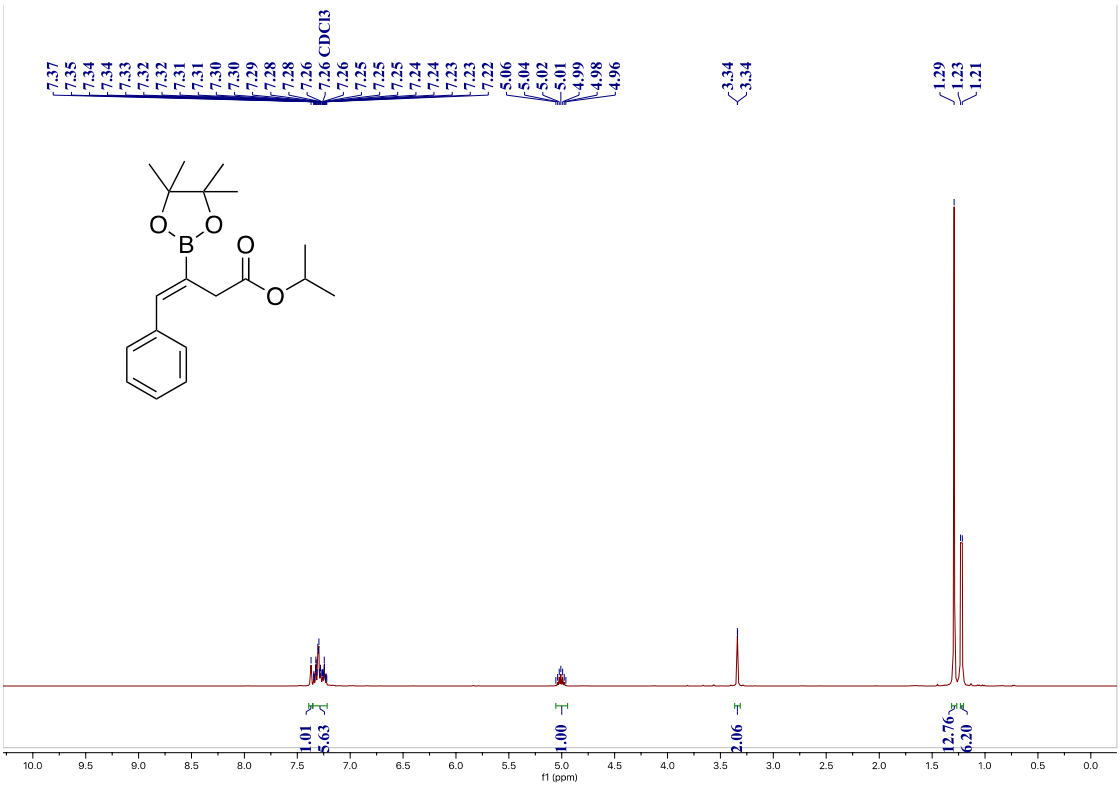
^{11}B NMR ($CDCl_3$, 160 MHz) of 4b



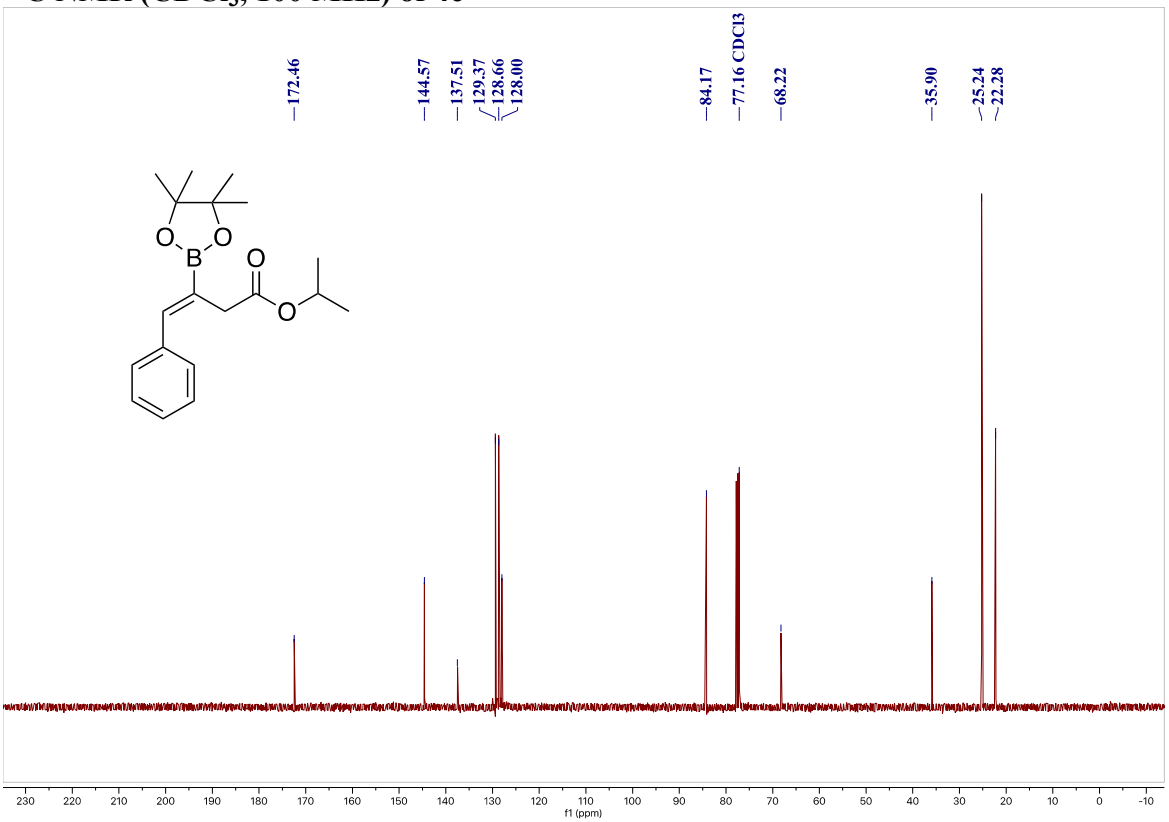
1D NOESY of 4b



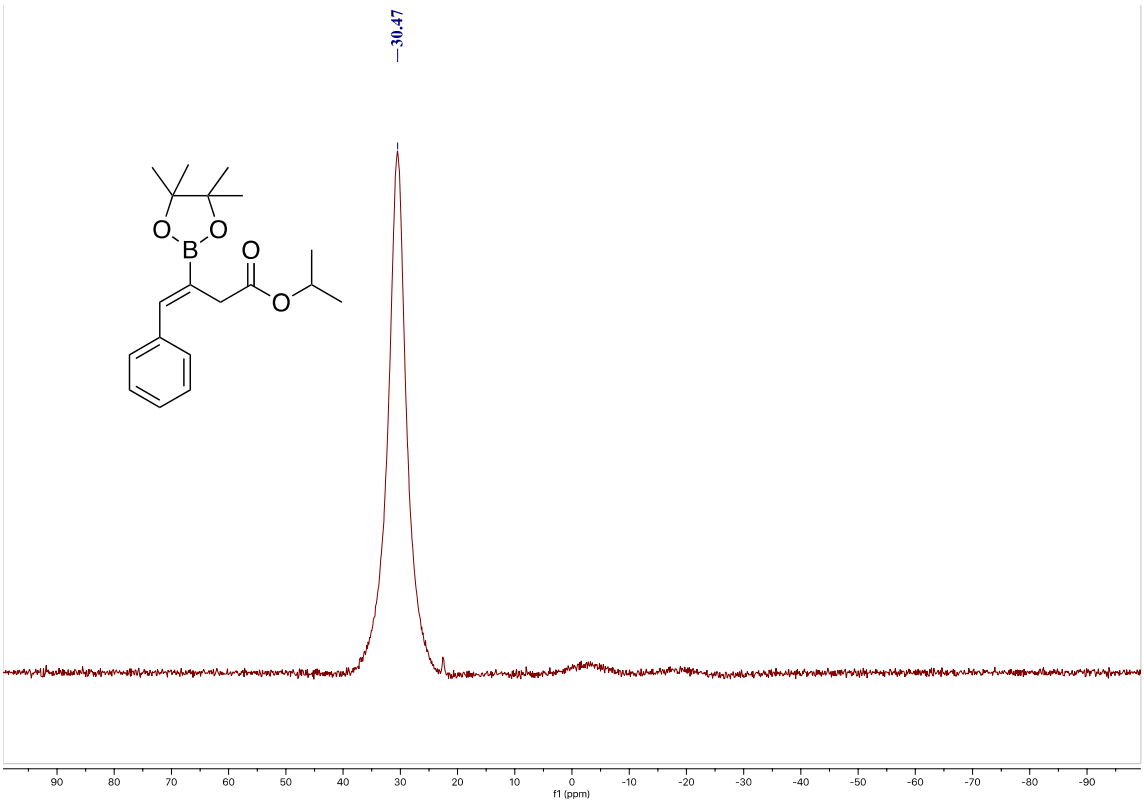
^{1}H NMR ($CDCl_3$, 400 MHz) of 4c



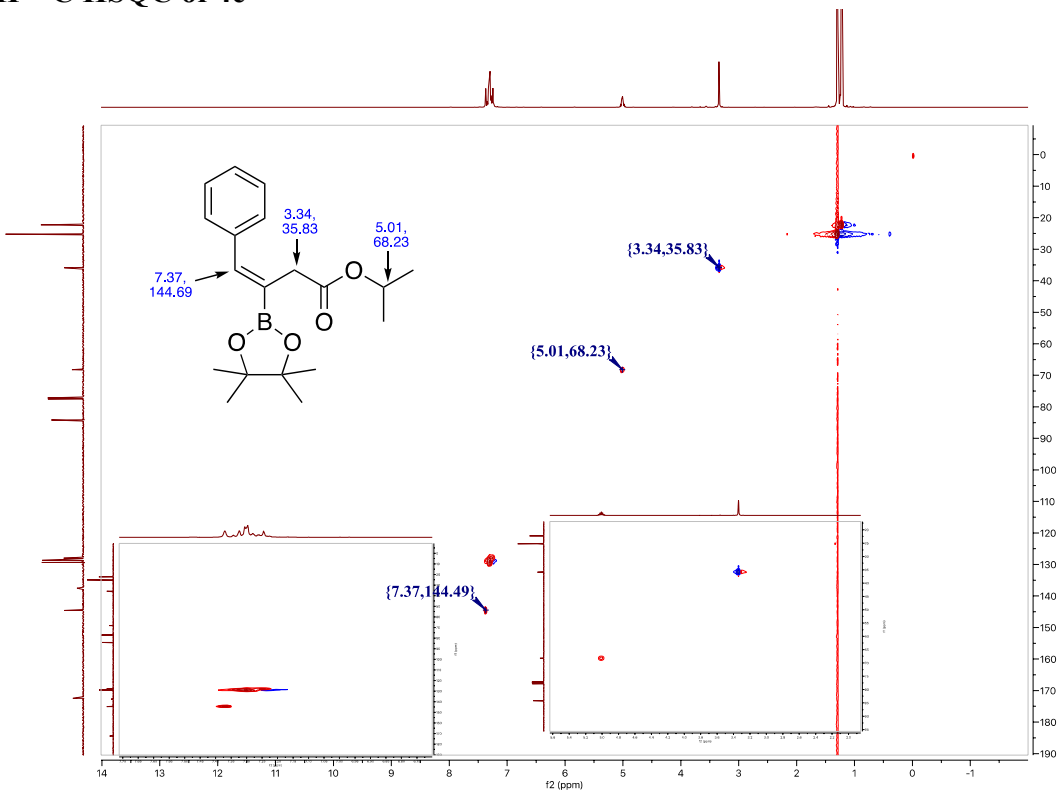
^{13}C NMR ($CDCl_3$, 100 MHz) of 4c



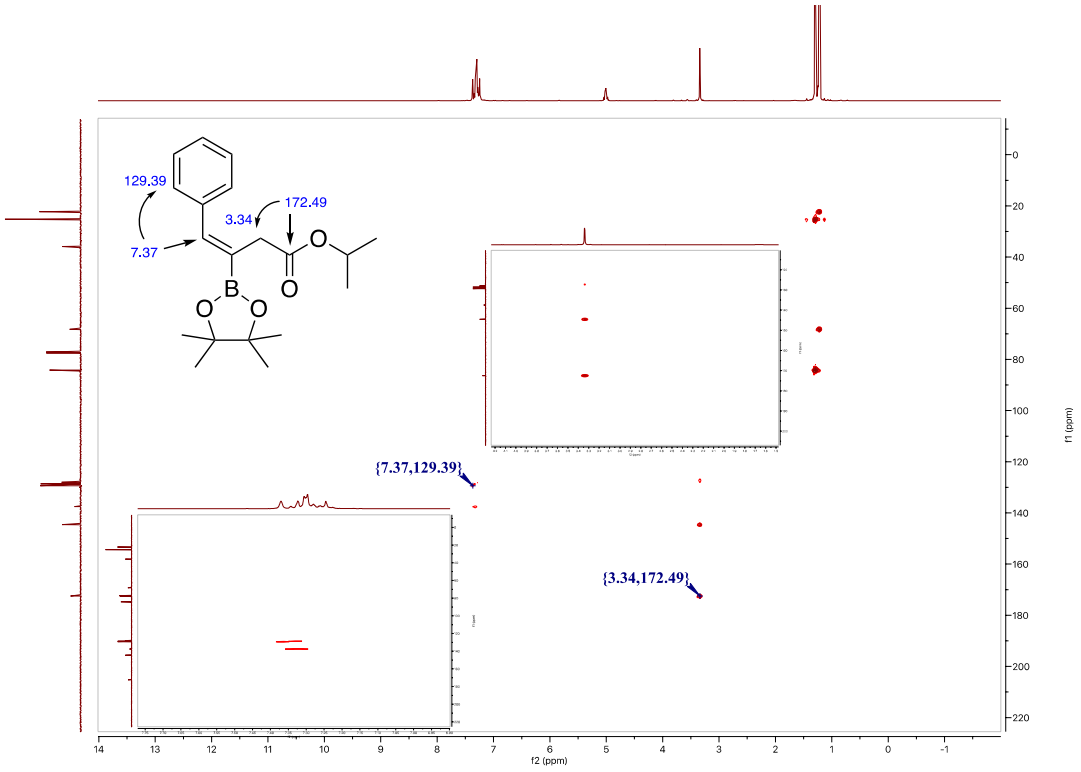
^{11}B NMR ($CDCl_3$, 160 MHz) of 4c



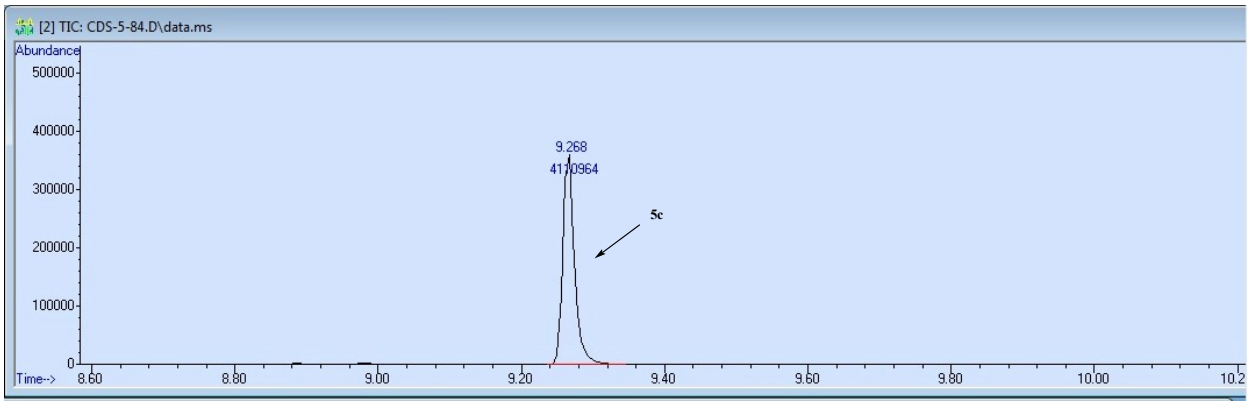
^{1}H-^{13}C HSQC of 4e



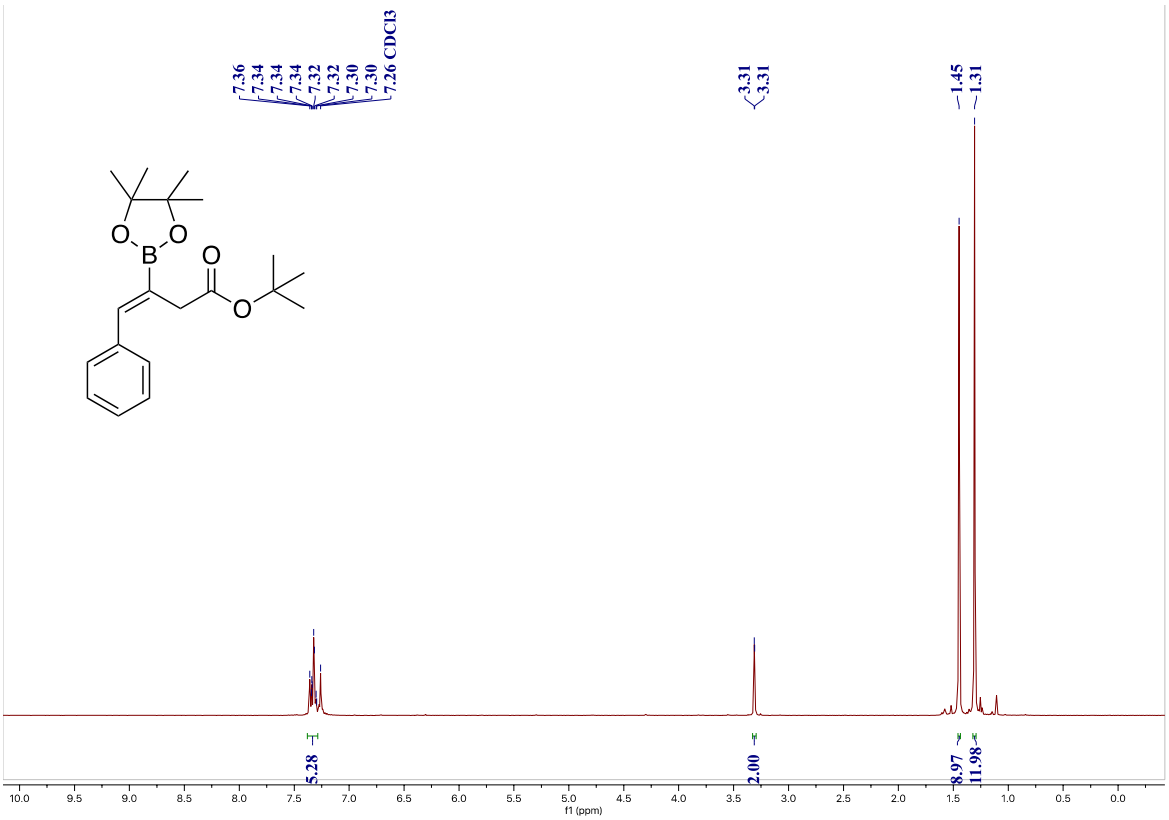
^{1}H-^{13}C HMBC of 4e



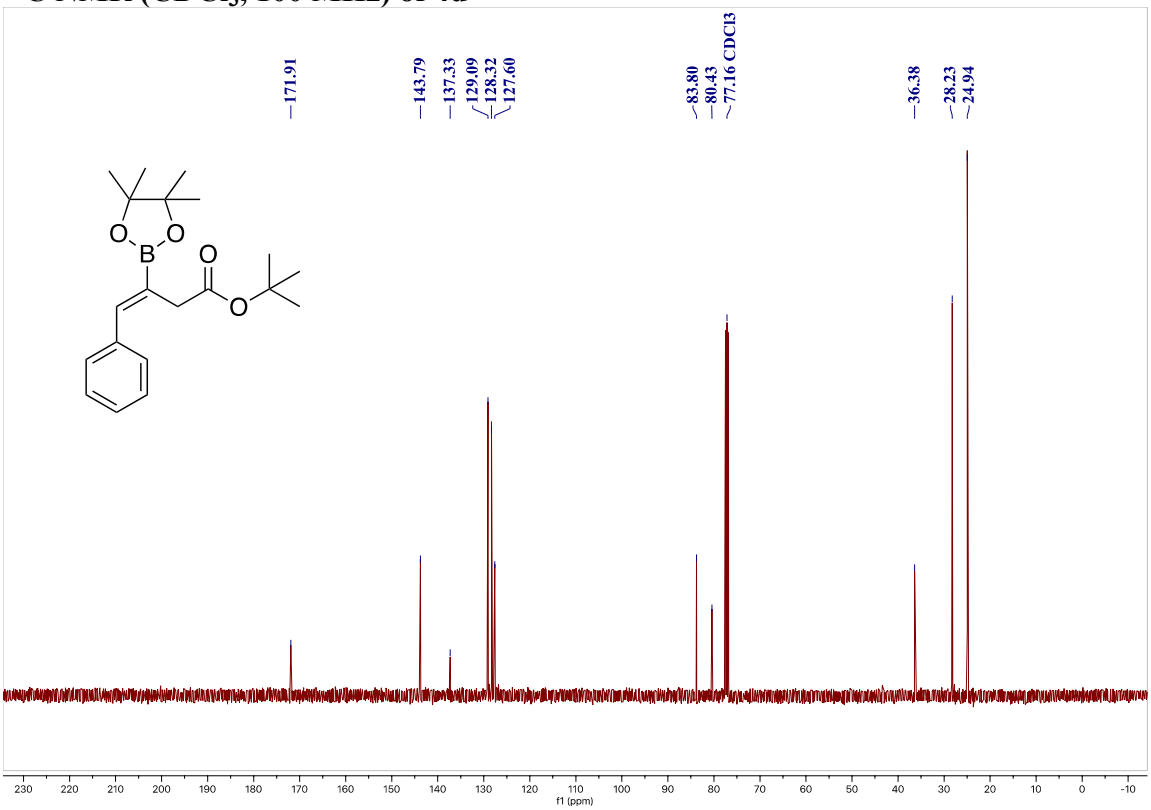
Crude GC of 4e



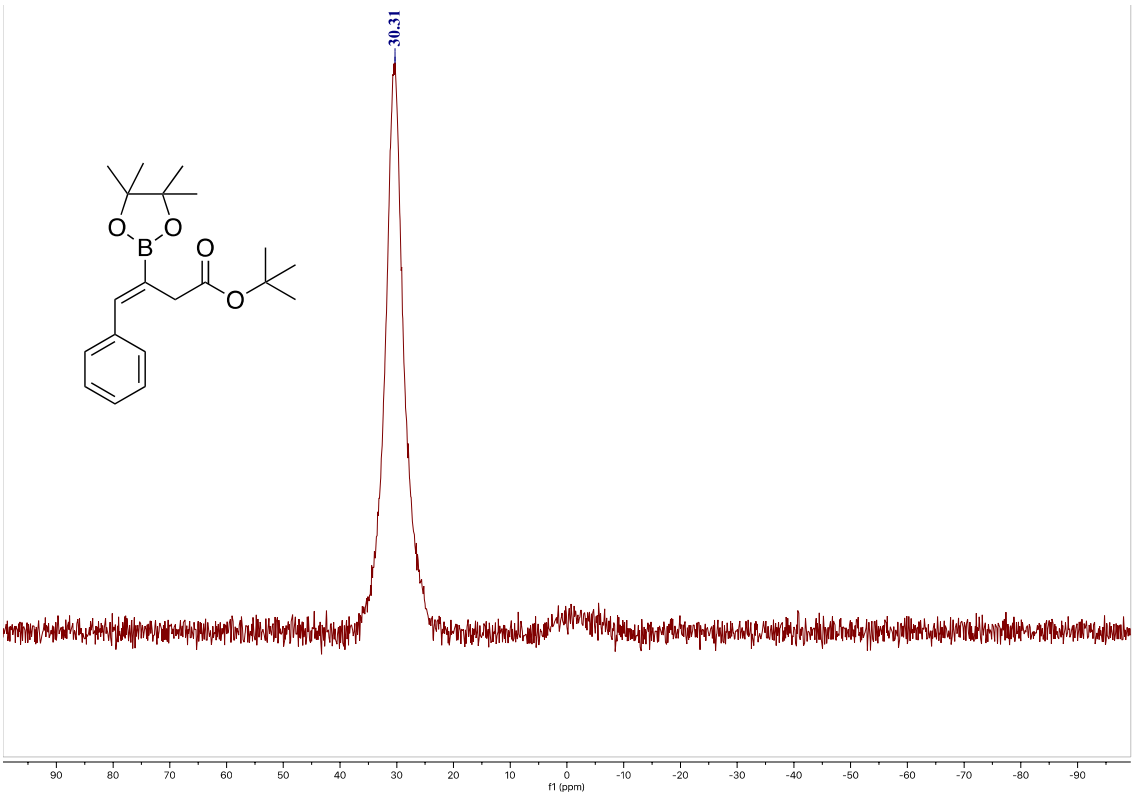
^{1}H NMR ($CDCl_3$, 400 MHz) of 4d



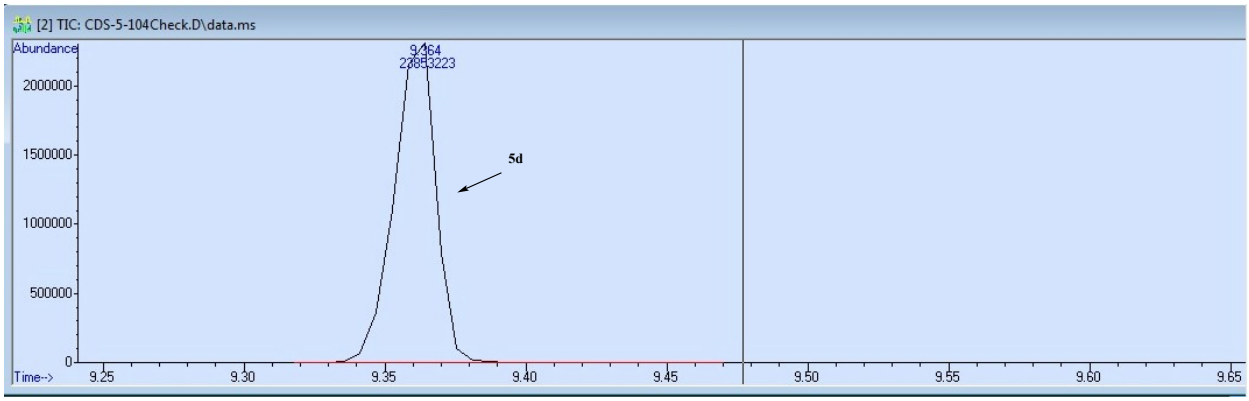
^{13}C NMR ($CDCl_3$, 100 MHz) of 4d



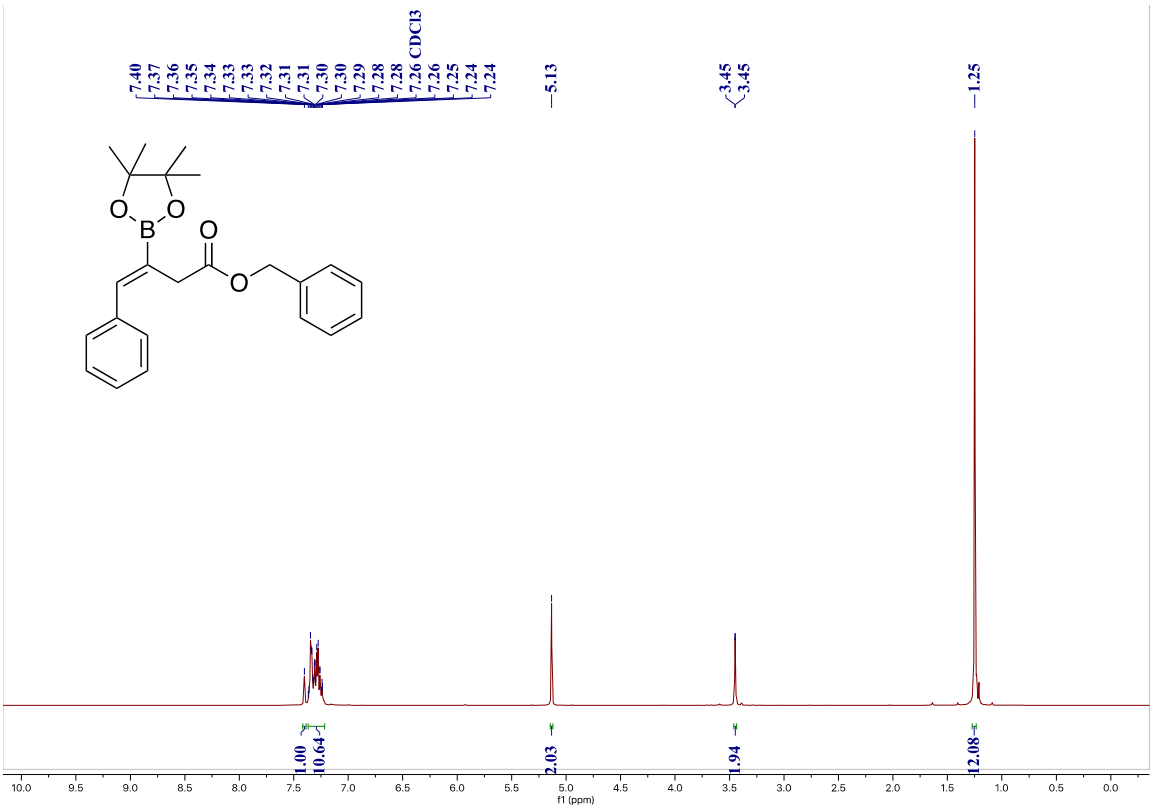
^{11}B NMR ($CDCl_3$, 160 MHz) of 4d



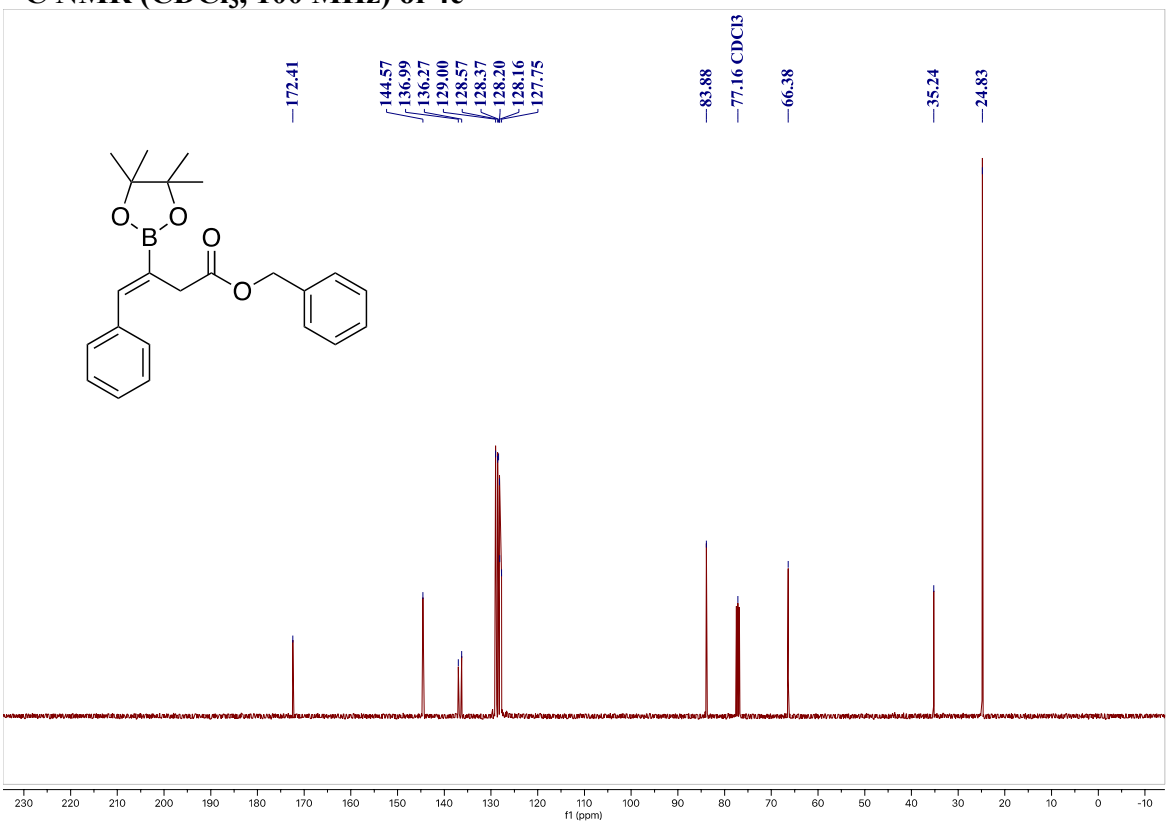
Crude GC of 4d



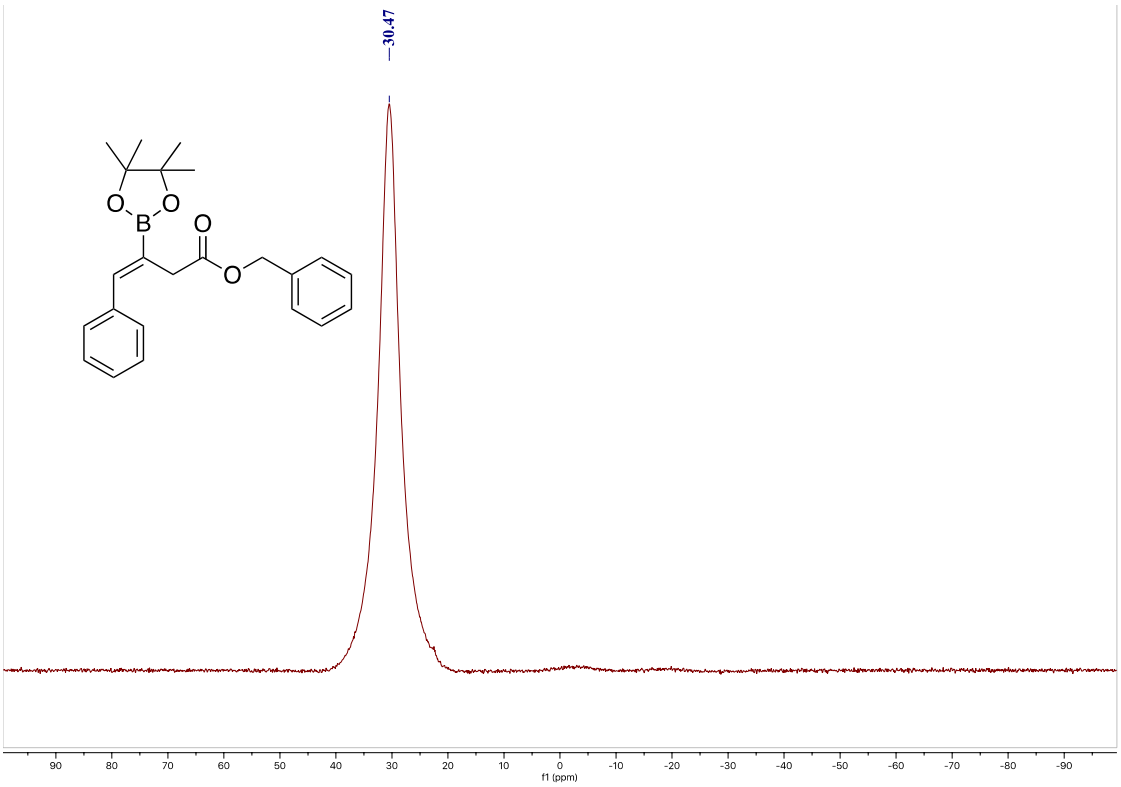
^{1}H NMR ($CDCl_3$, 400 MHz) of 4e



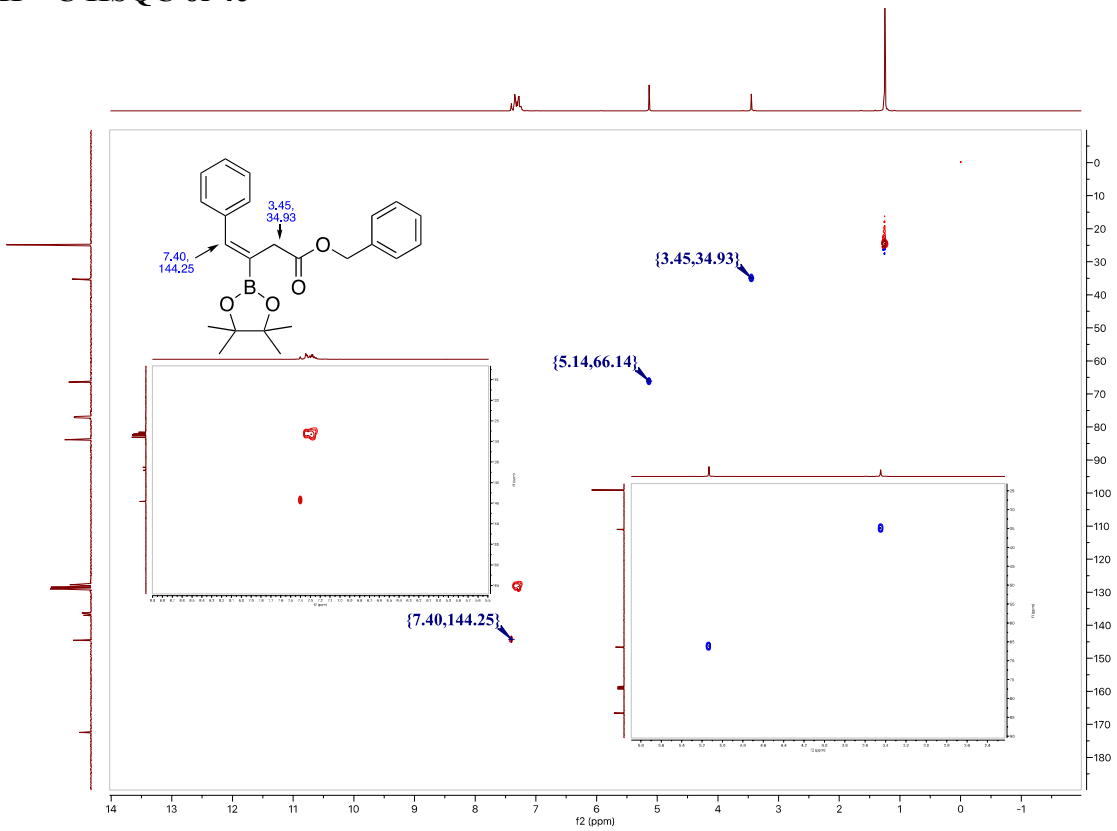
^{13}C NMR ($CDCl_3$, 100 MHz) of 4e



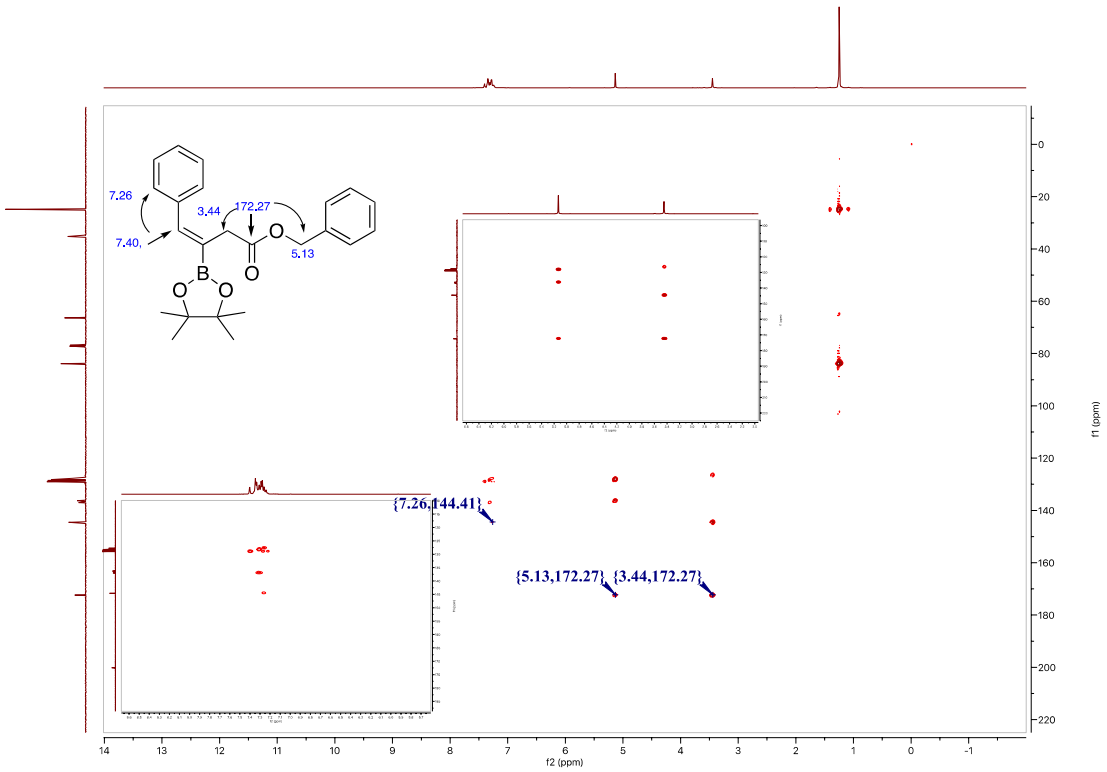
^{11}B NMR ($CDCl_3$, 160 MHz) of 4e



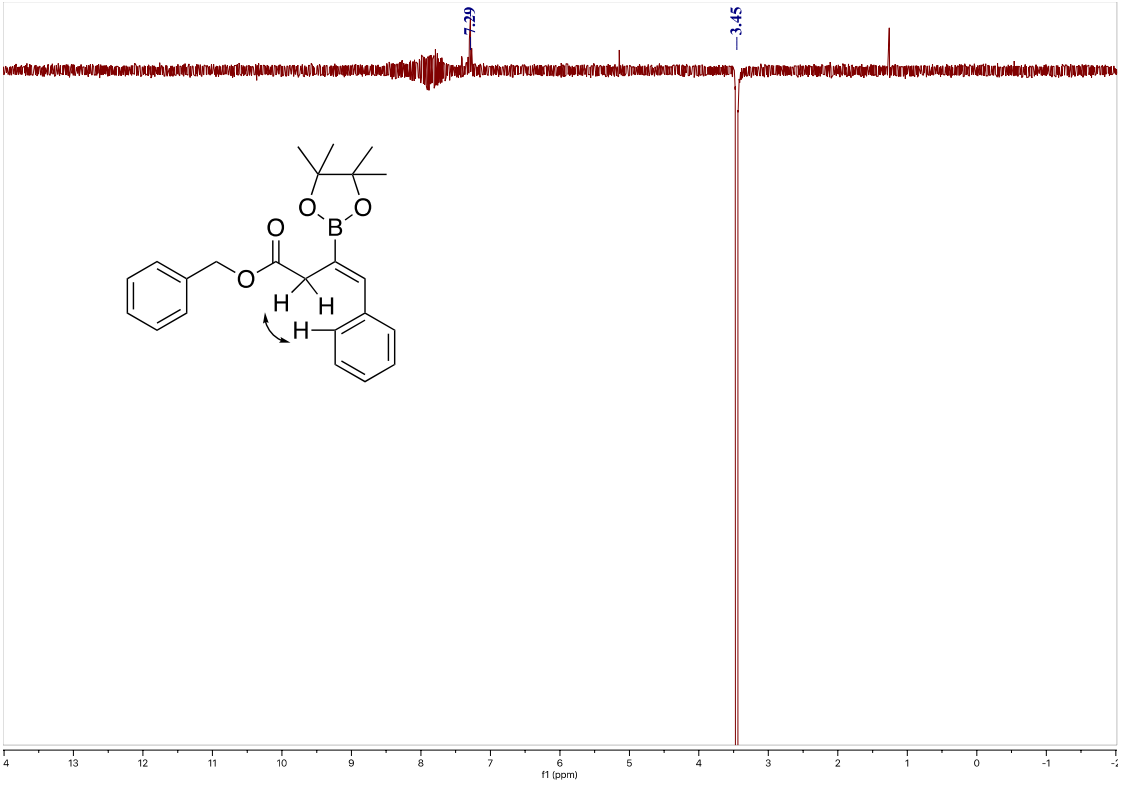
^{1}H-^{13}C HSQC of 4e



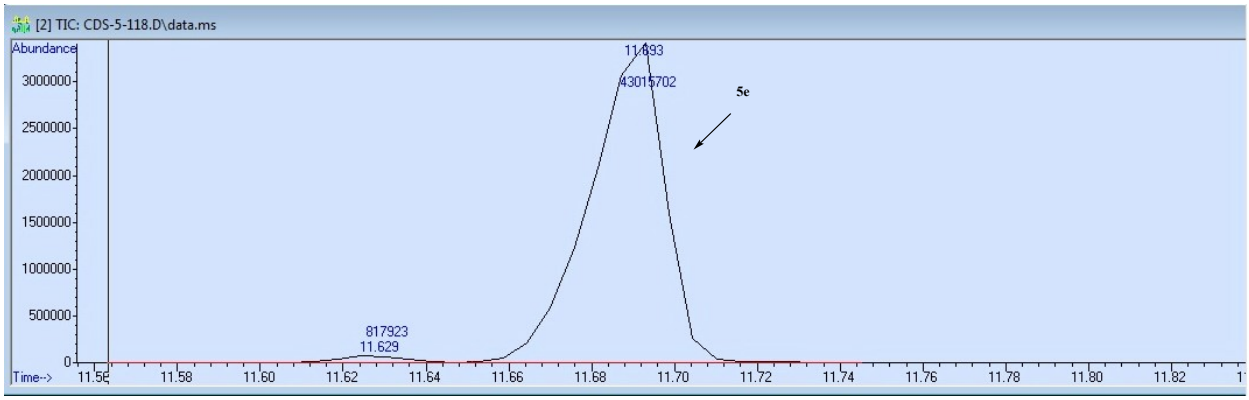
^{1}H-^{13}C HMBC of 4e



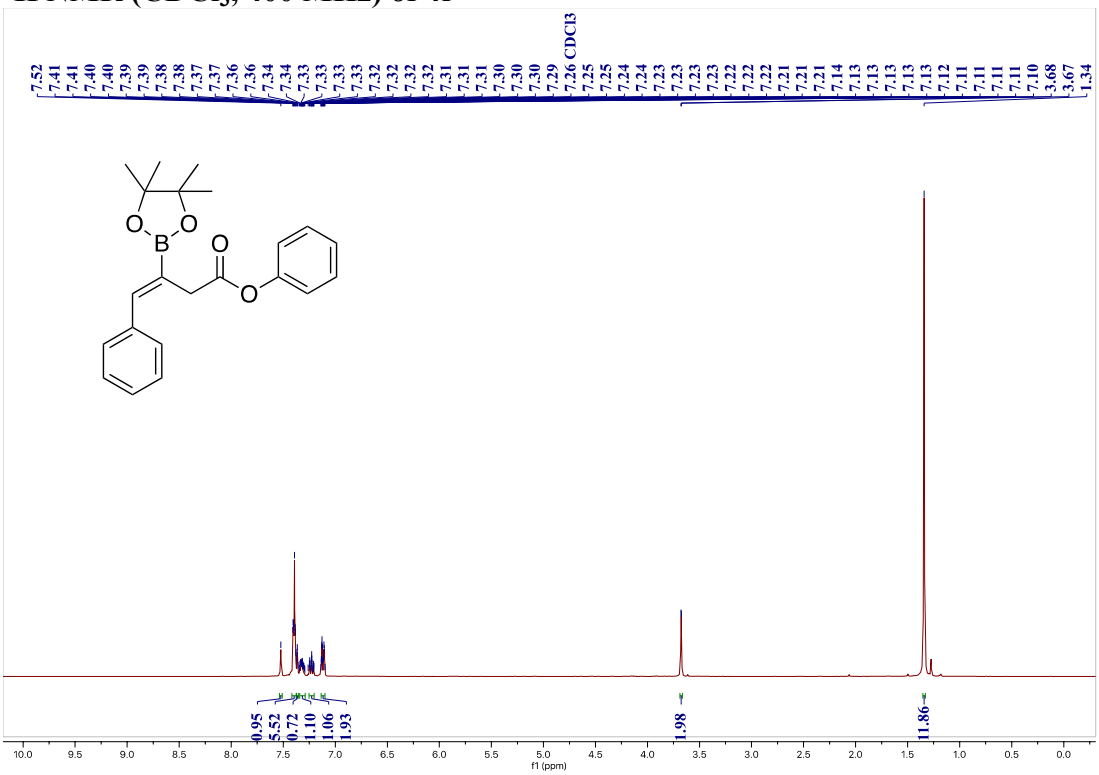
1D NOESY of 4e



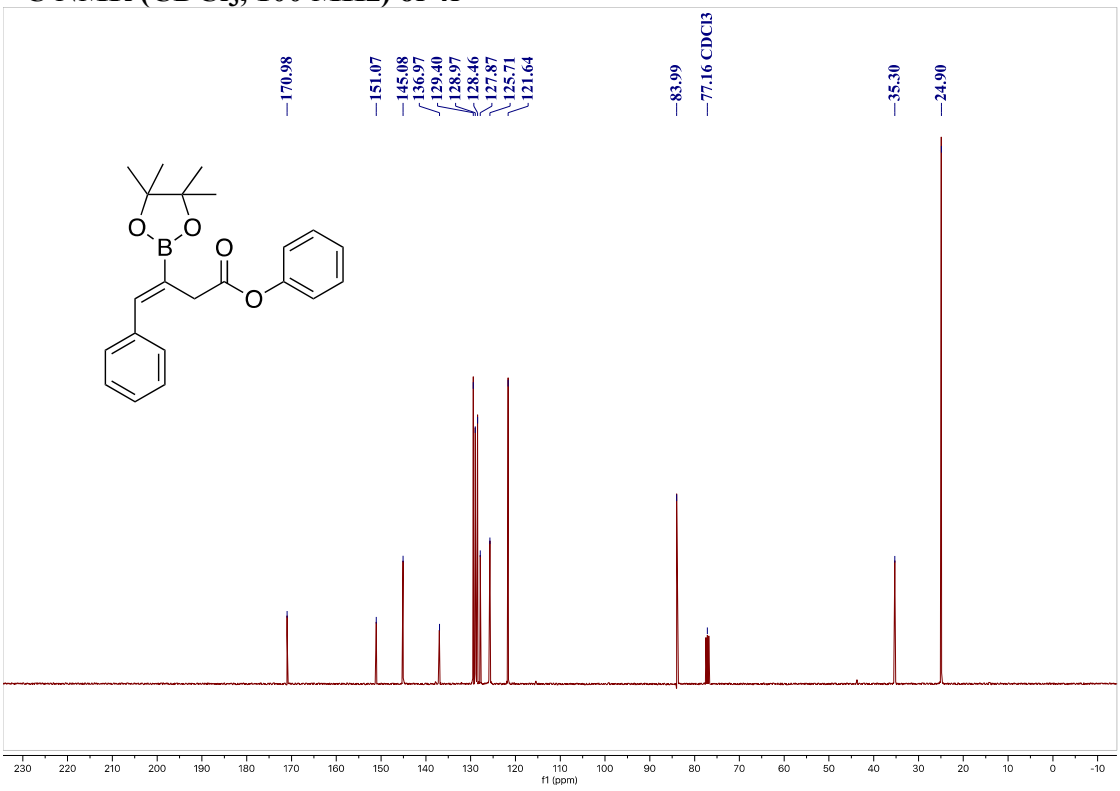
Crude GC of 4e



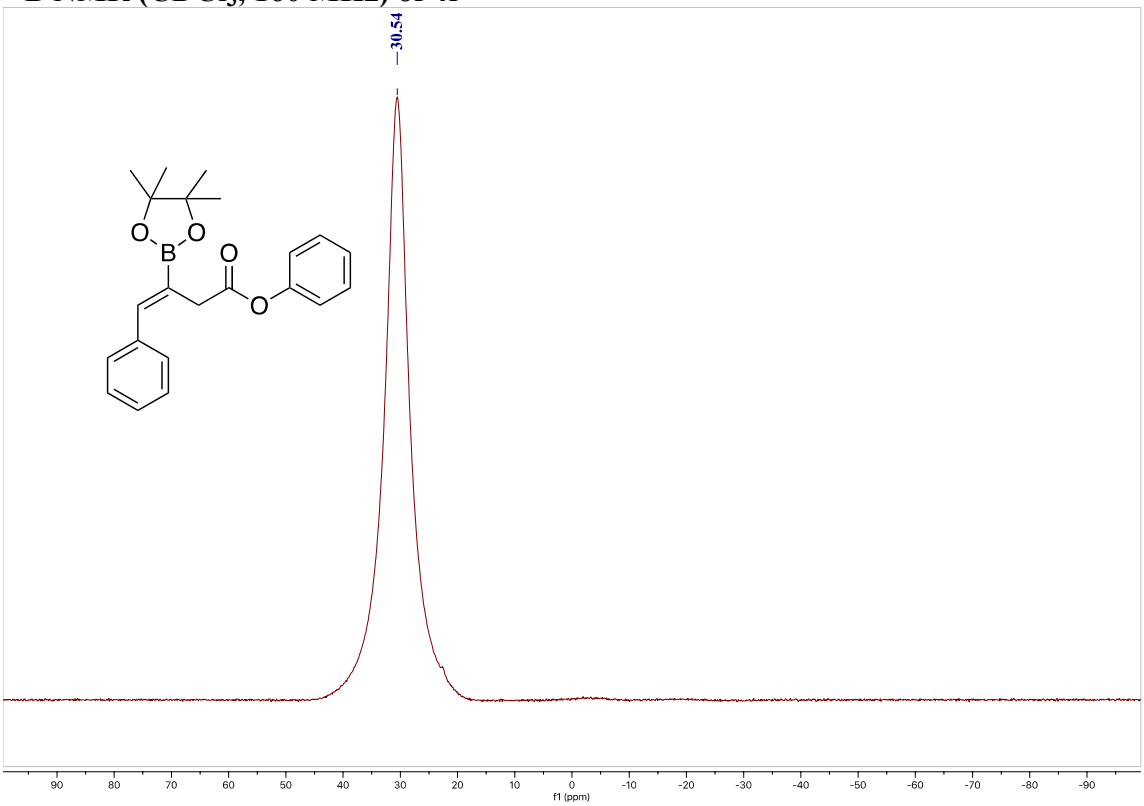
^{1}H NMR ($CDCl_3$, 400 MHz) of 4f



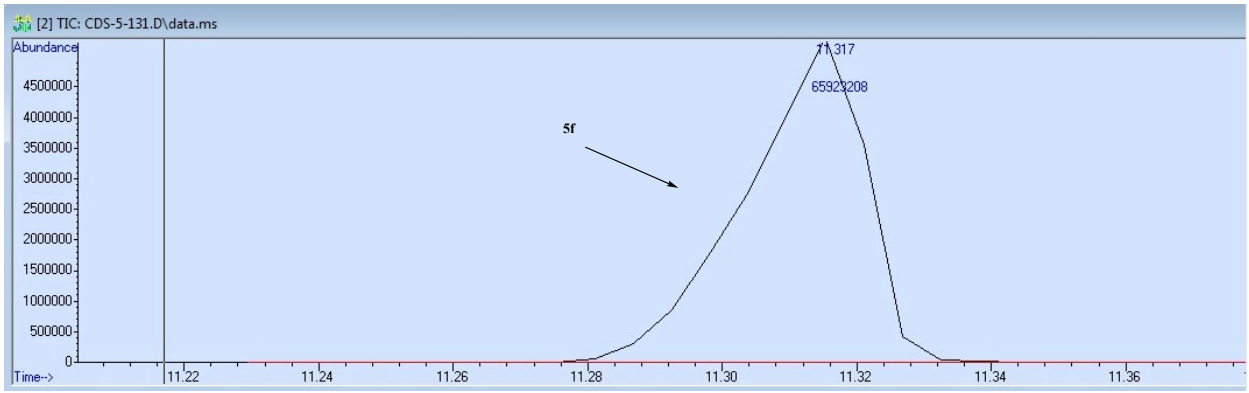
^{13}C NMR ($CDCl_3$, 100 MHz) of 4f



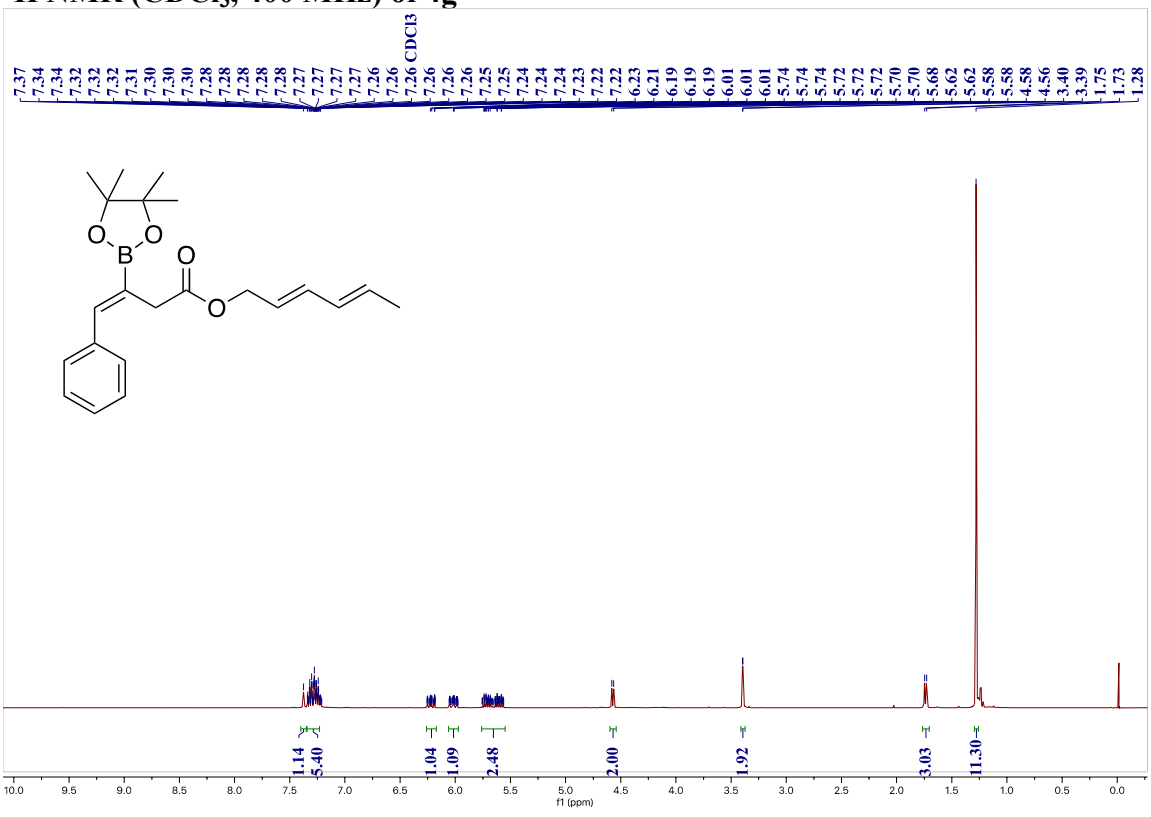
^{11}B NMR ($CDCl_3$, 160 MHz) of 4f



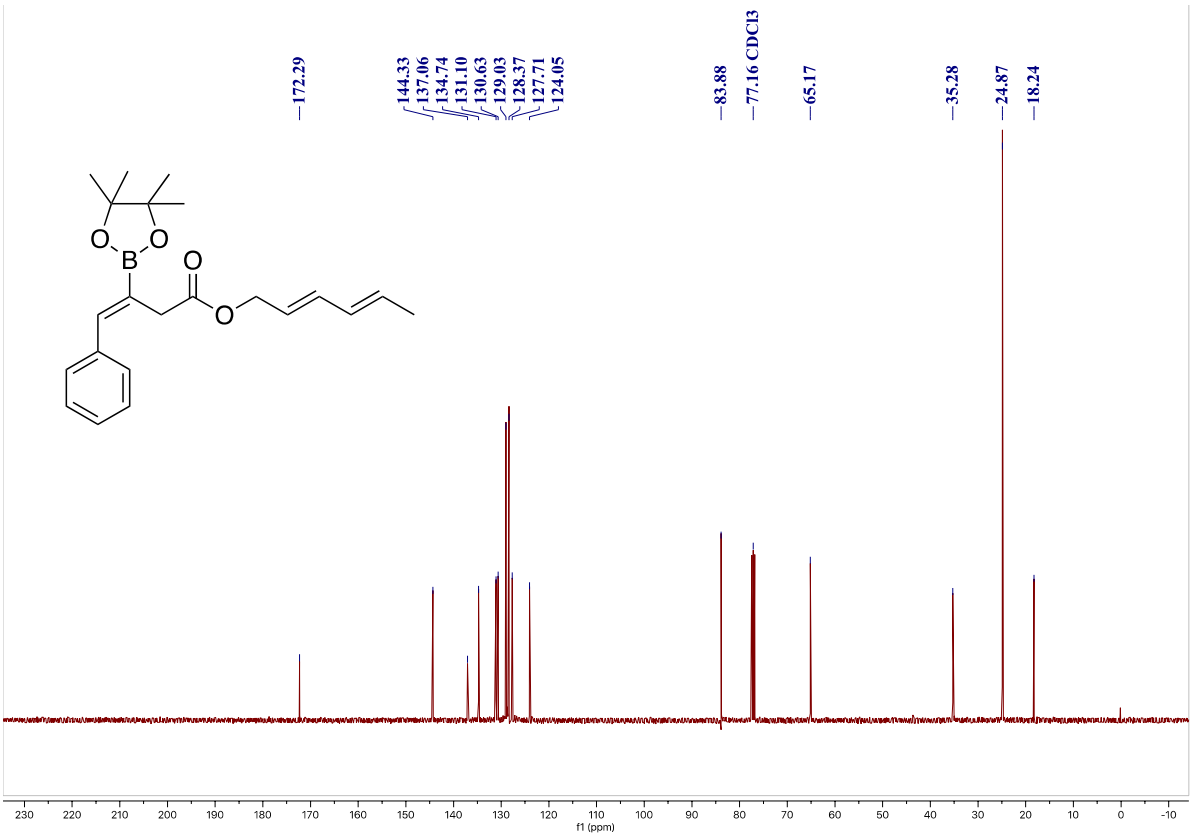
Crude GC of 4f



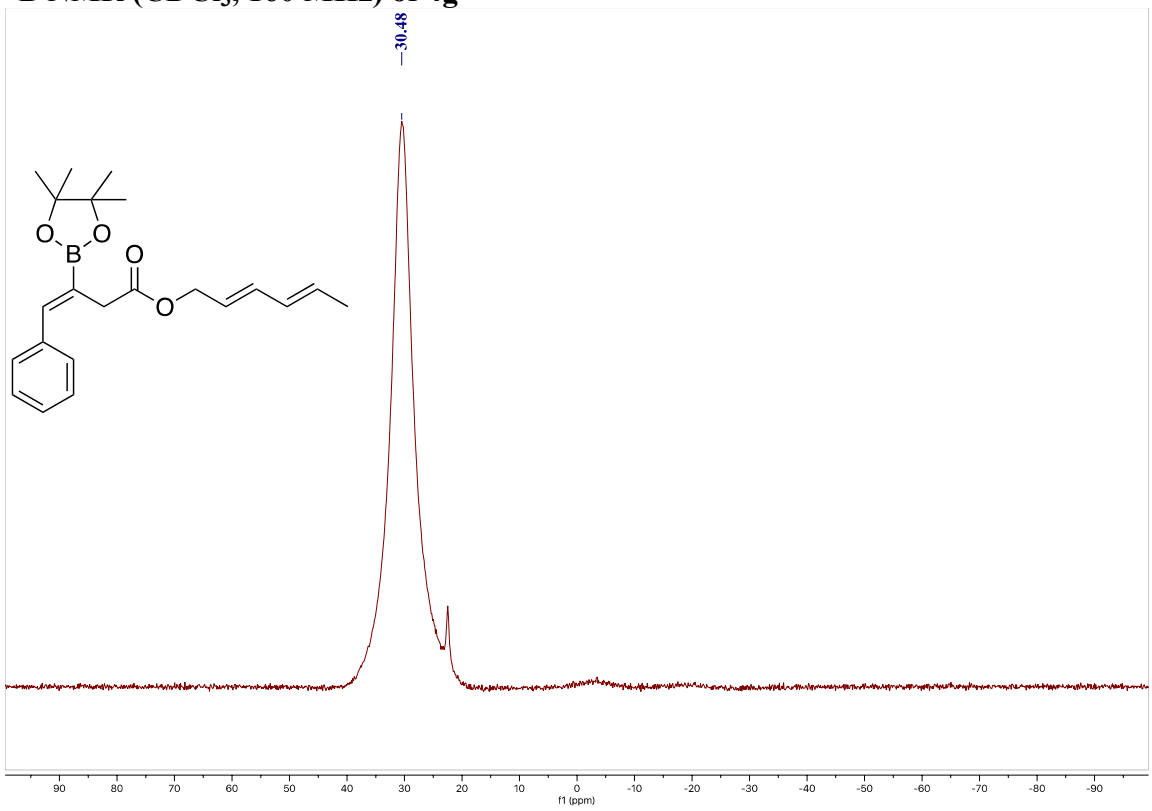
^{1}H NMR ($CDCl_3$, 400 MHz) of 4g



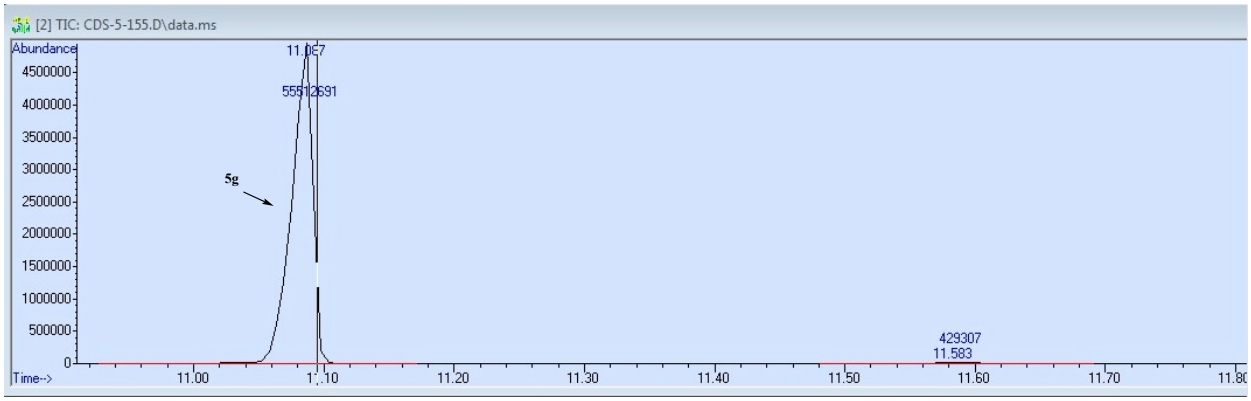
^{13}C NMR ($CDCl_3$, 100 MHz) of 4g



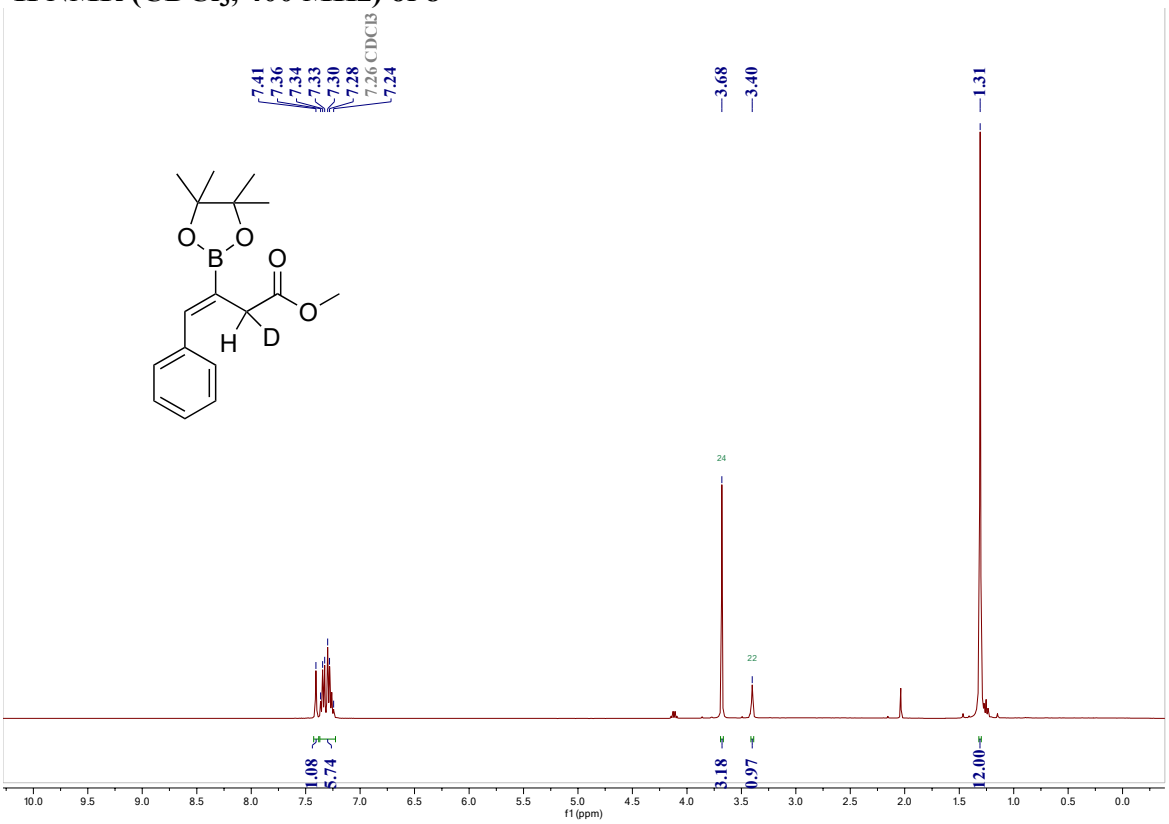
^{11}B NMR ($CDCl_3$, 160 MHz) of 4g



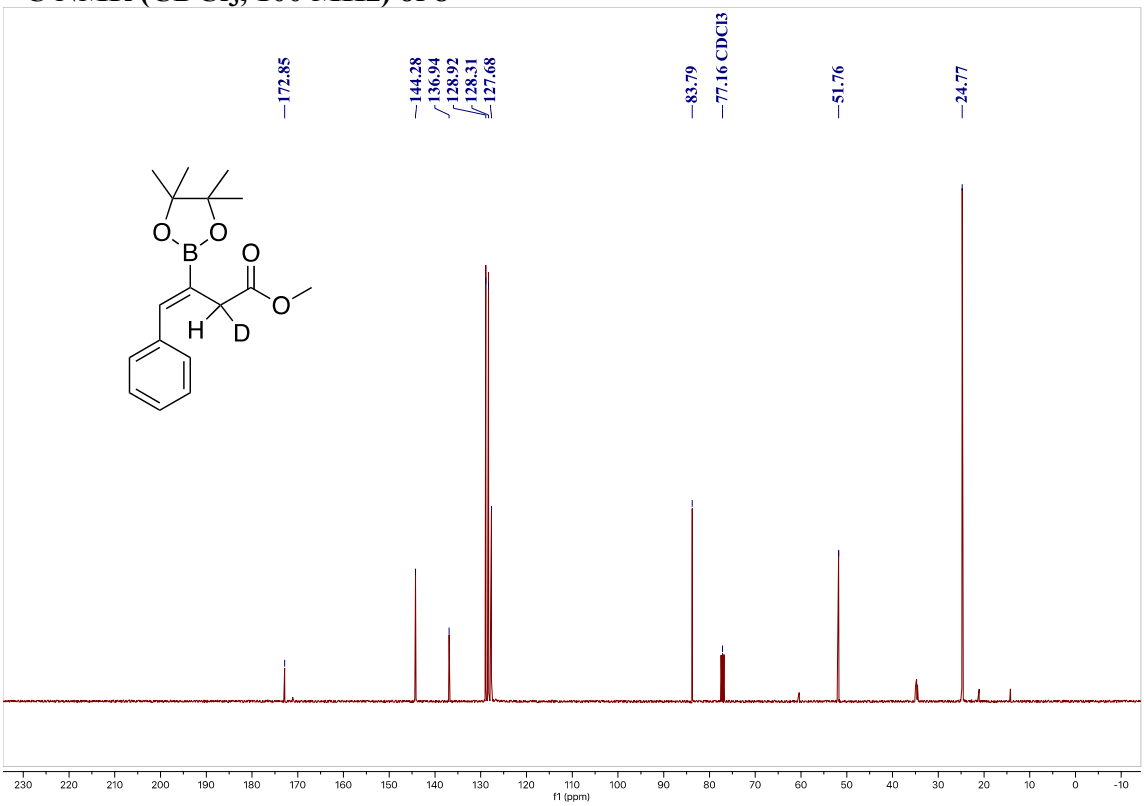
Crude GC of 4g



^{1}H NMR ($CDCl_3$, 400 MHz) of 8

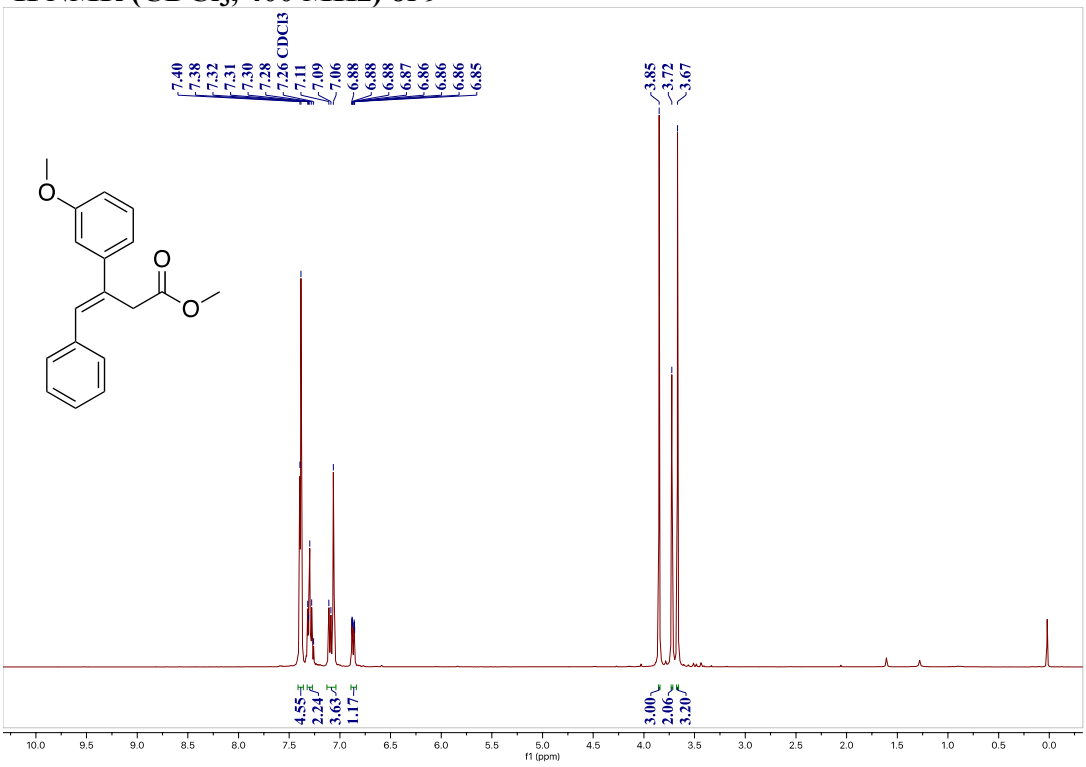


^{13}C NMR ($CDCl_3$, 100 MHz) of 8

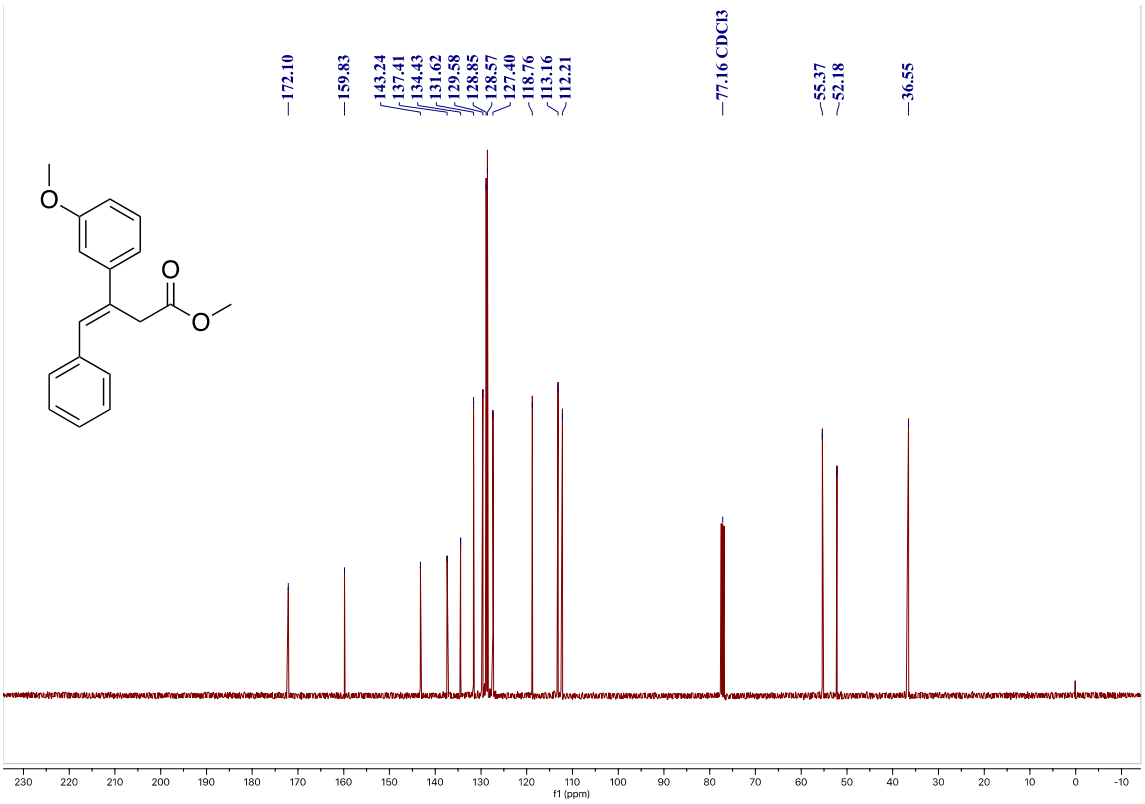


18. NMR Spectra of Cross-Coupled Product

^{1}H NMR ($CDCl_3$, 400 MHz) of 9

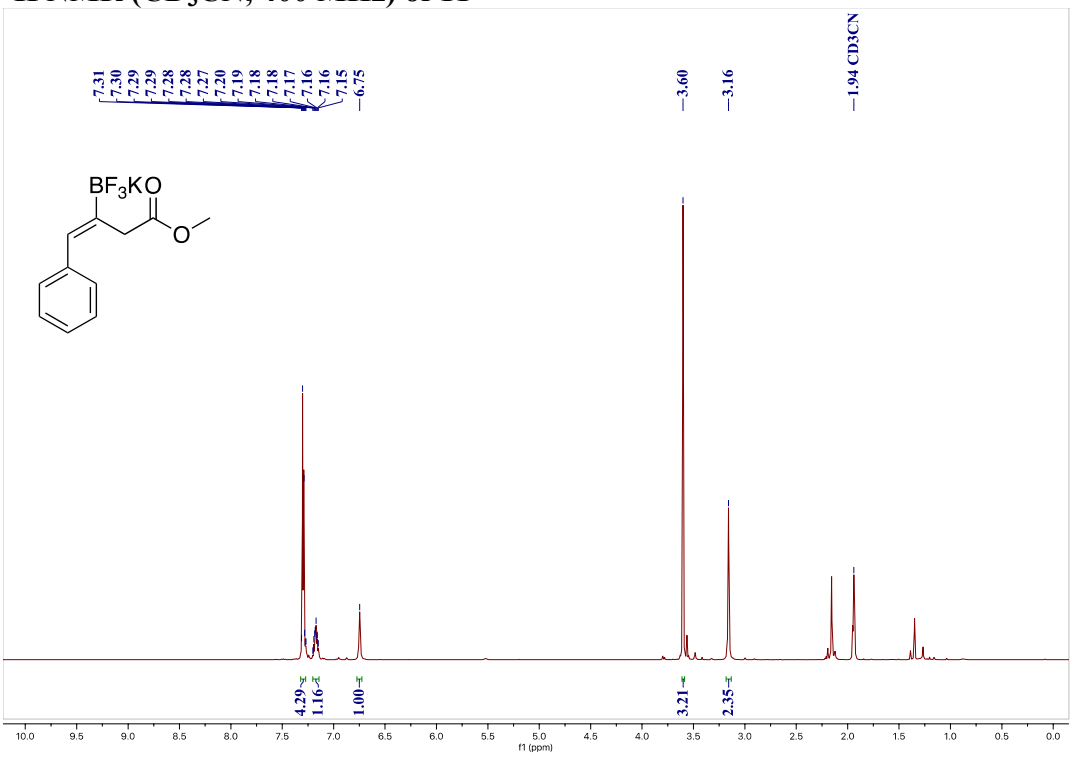


^{13}C NMR ($CDCl_3$, 100 MHz) of 9

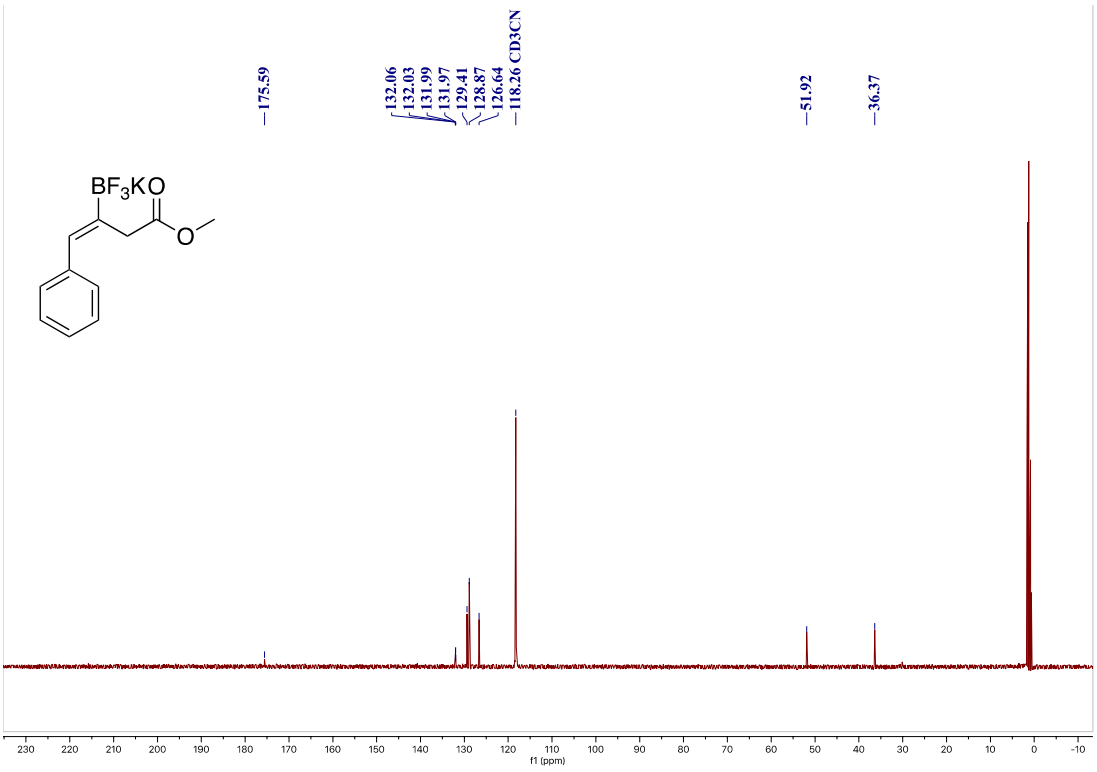


19. NMR Spectra of BF_3K Boryl Acrylate

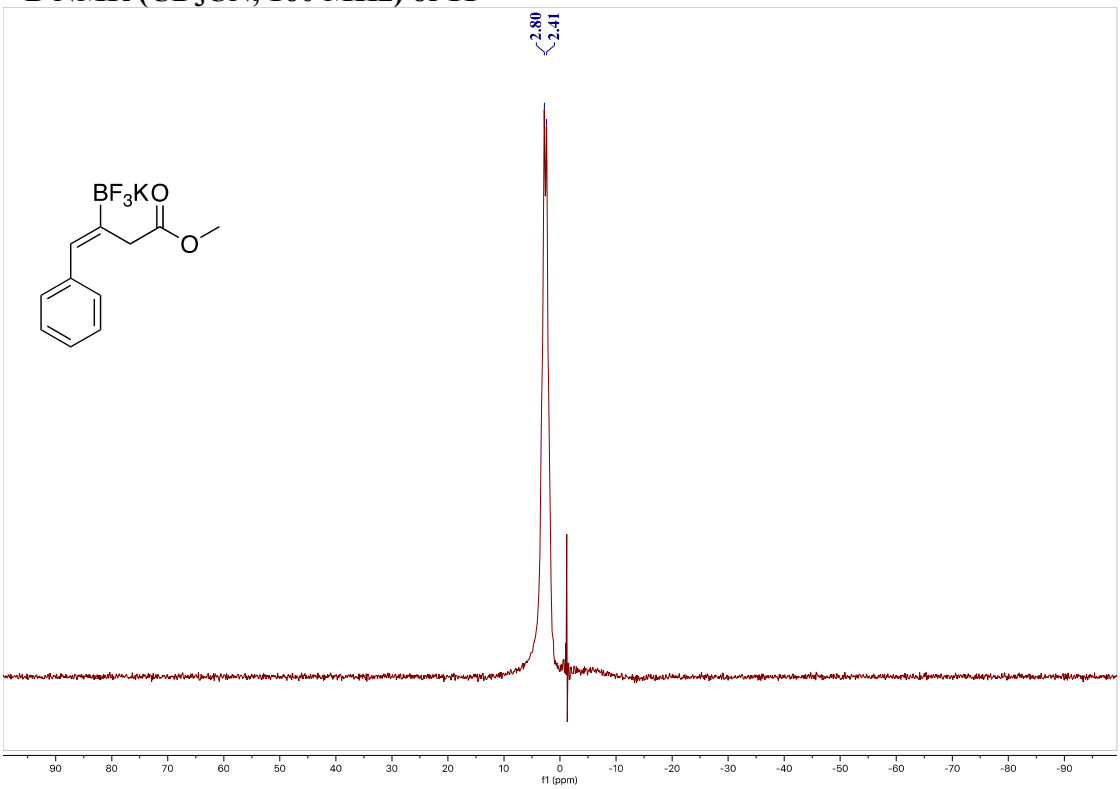
^1H NMR (CD_3CN, 400 MHz) of 11



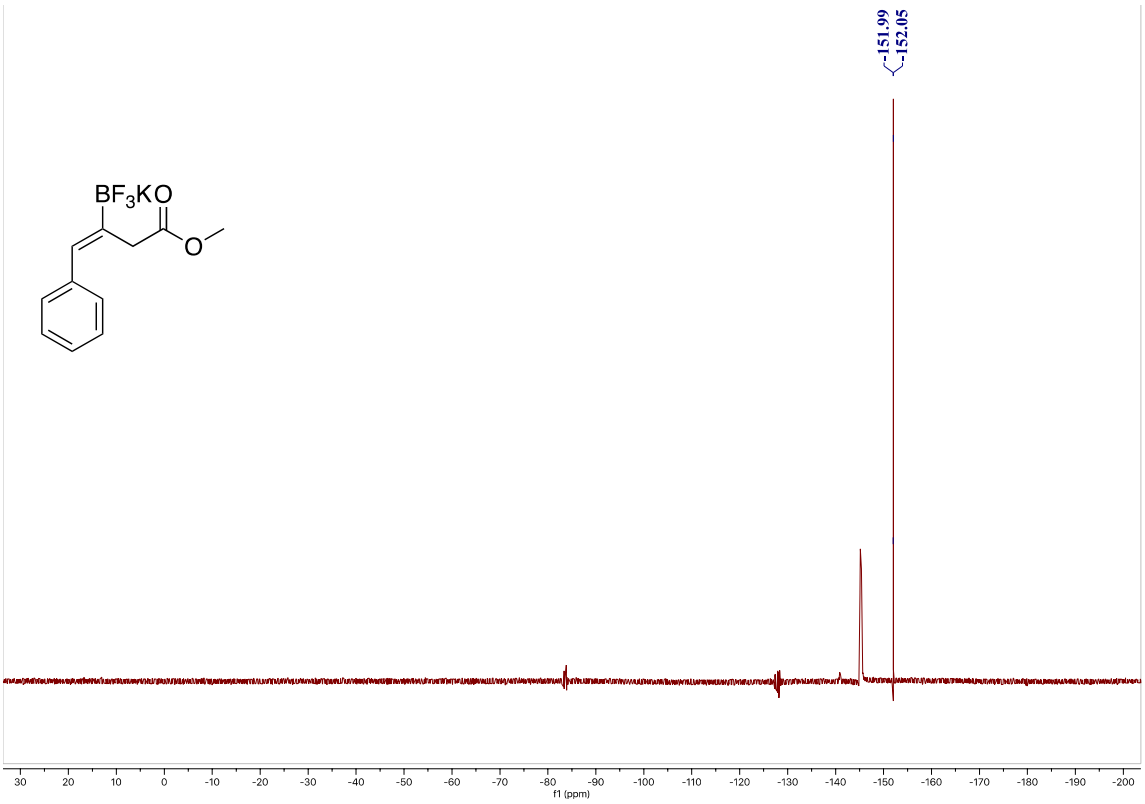
^{13}C NMR (CD_3CN, 100 MHz) of 11



^{11}B NMR (CD_3CN, 160 MHz) of 11

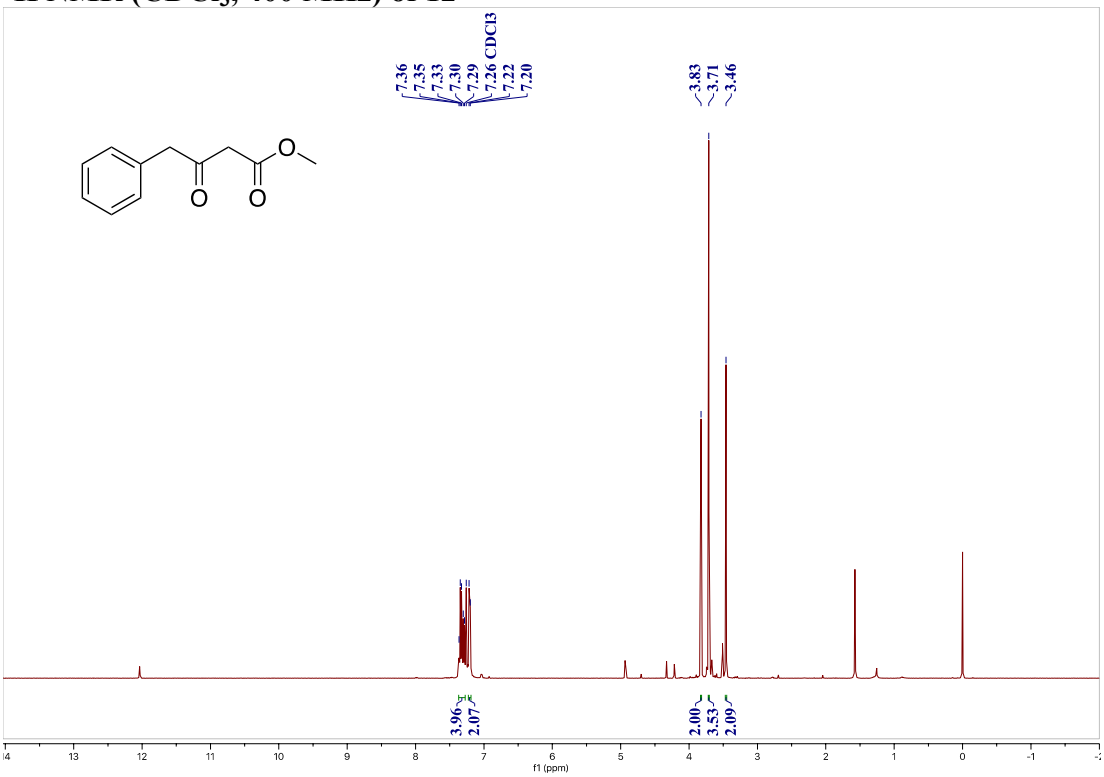


^{19}F NMR (CD_3CN, 376 MHz) of 11

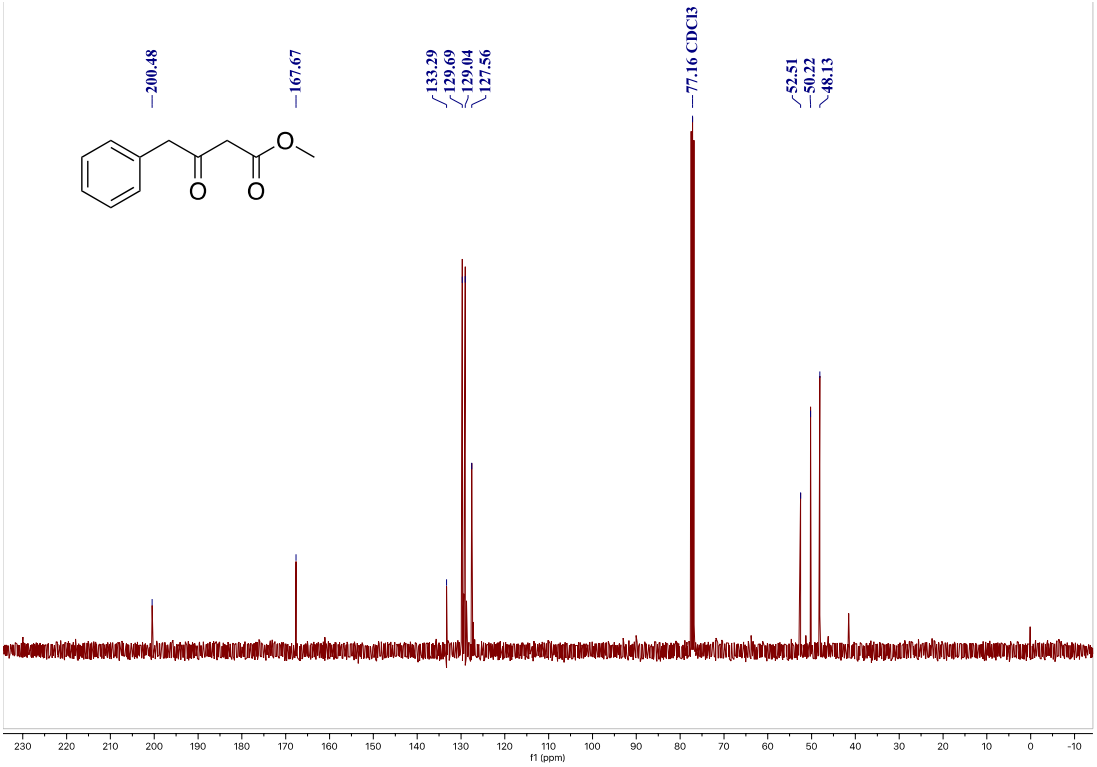


20. NMR Spectra of Diketo Ester

^{1}H NMR ($CDCl_3$, 400 MHz) of 12

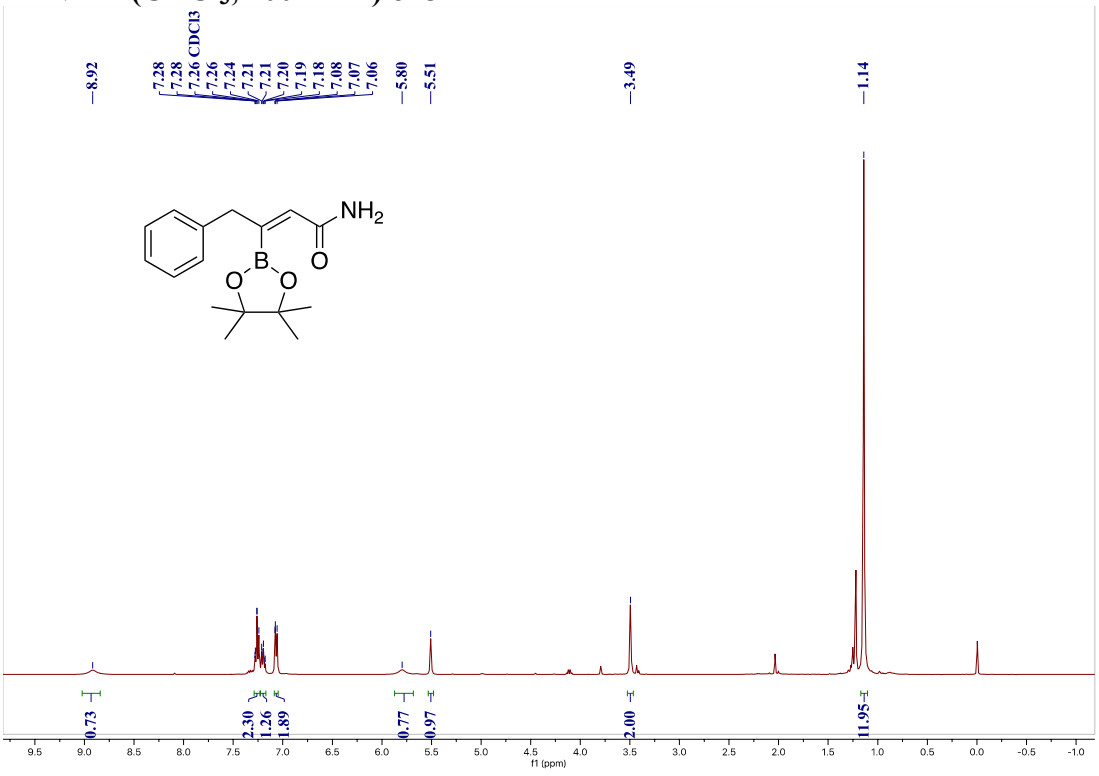


^{13}C NMR ($CDCl_3$, 100 MHz) of 12

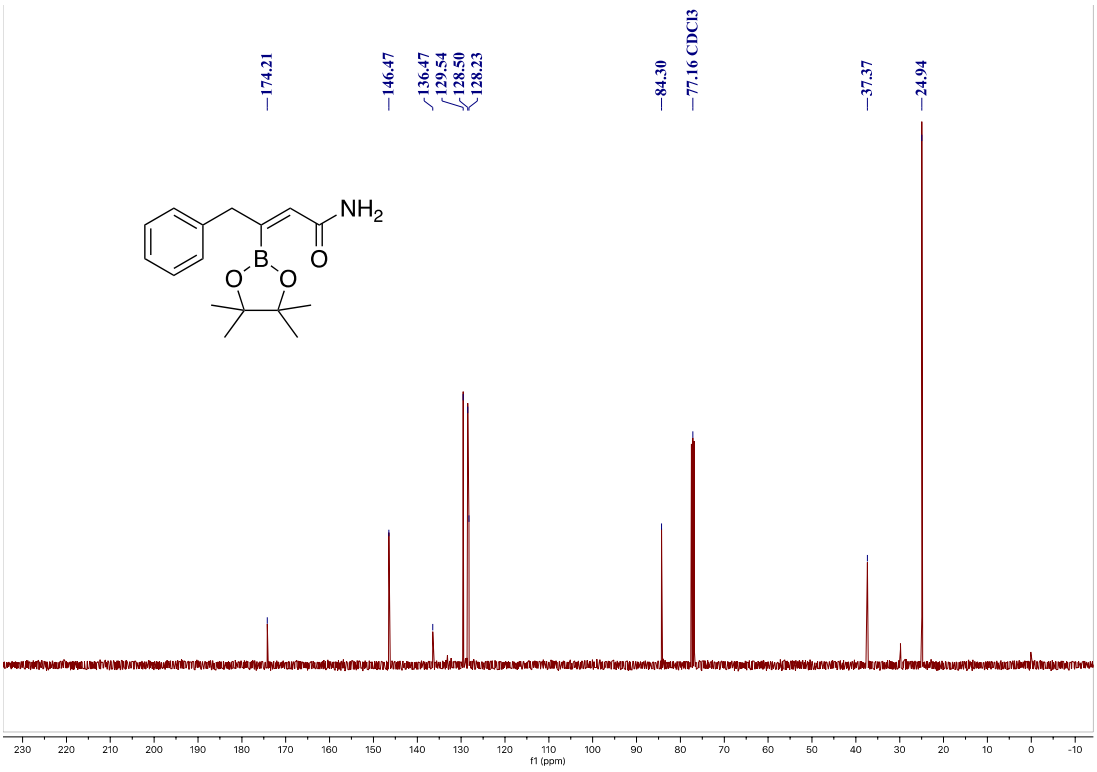


21. NMR Spectra of Amidation Product

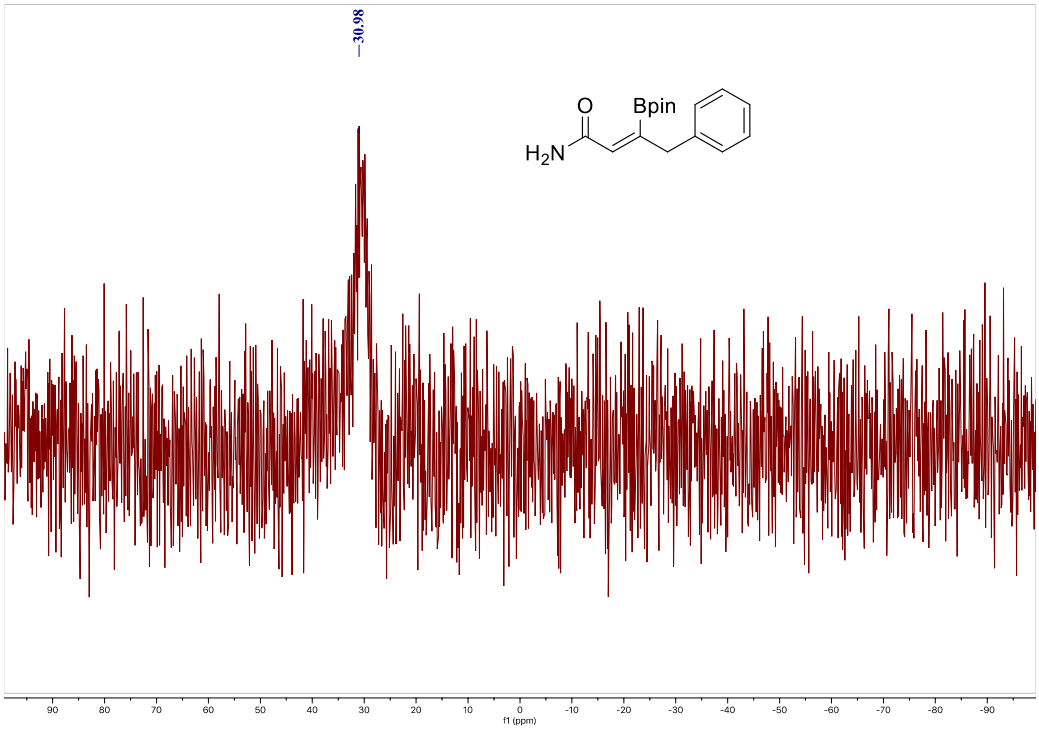
^{1}H NMR ($CDCl_3$, 400 MHz) of 3



^{13}C NMR ($CDCl_3$, 100 MHz) of 3

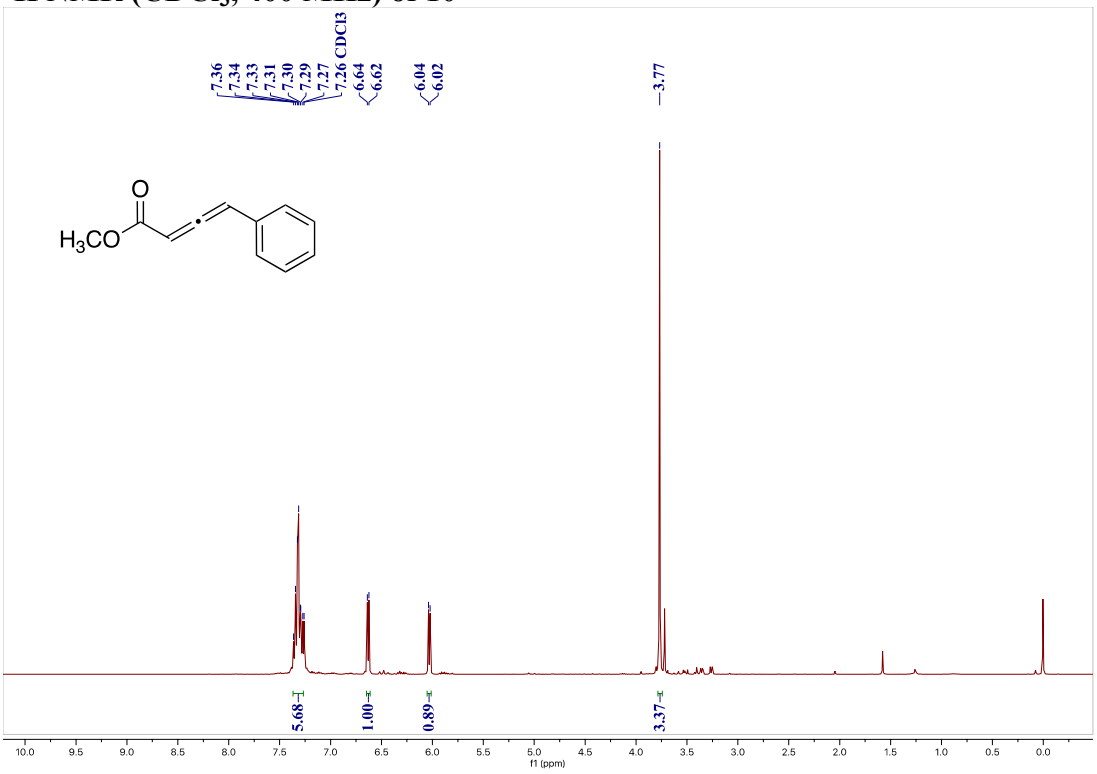


^{11}B NMR ($CDCl_3$, 160 MHz) of 3

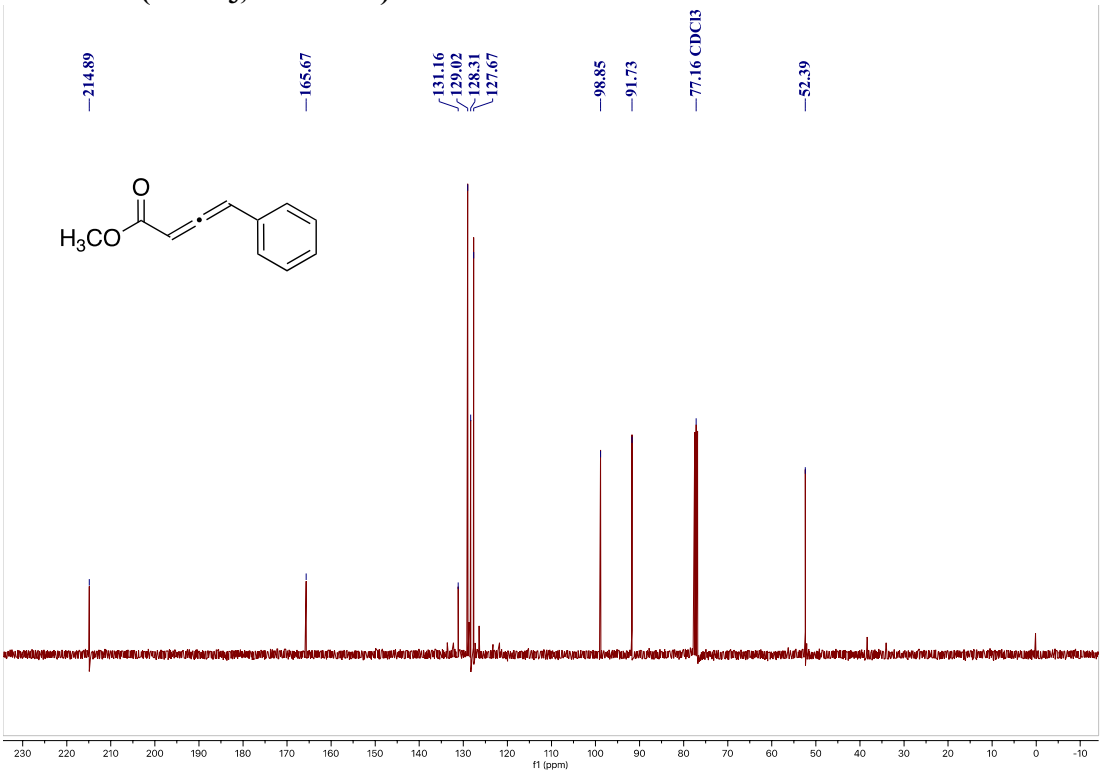


22. NMR Spectra of Silver Fluoride Allenoate Formation

^{1}H NMR ($CDCl_3$, 400 MHz) of 10

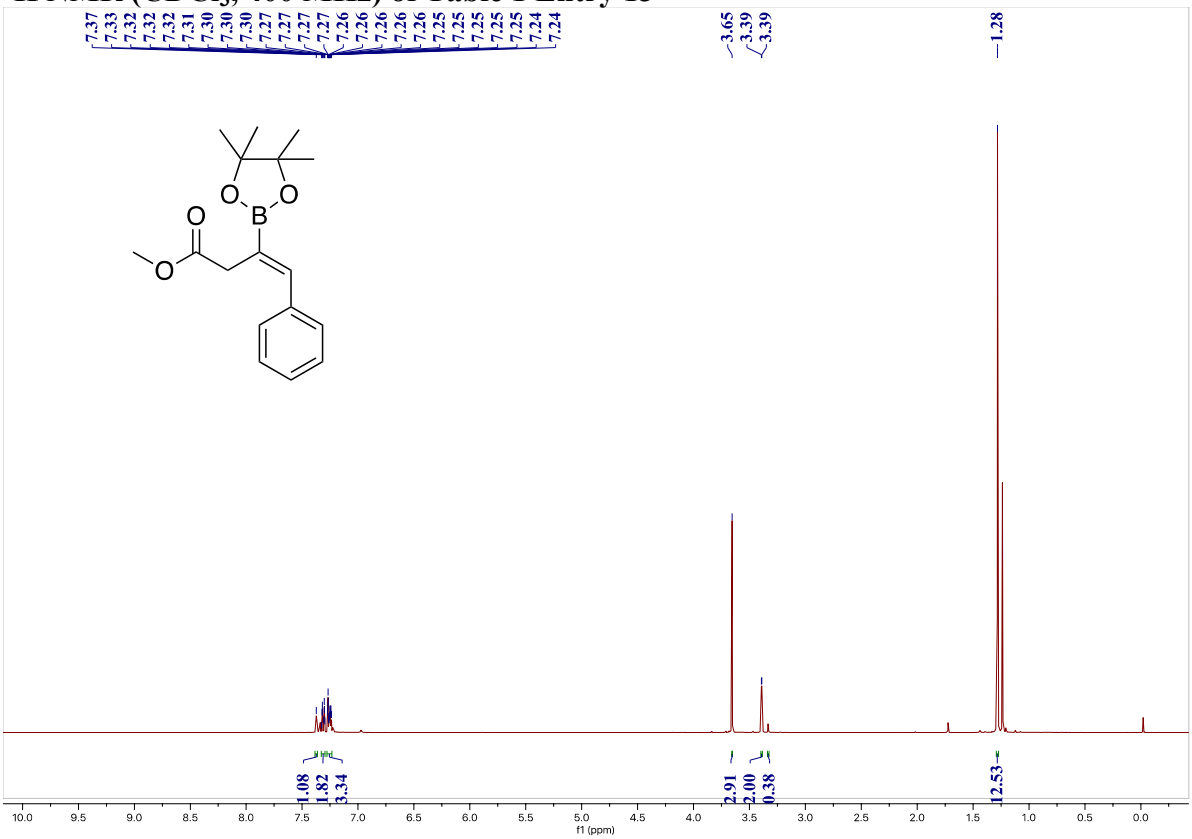


^{13}C NMR ($CDCl_3$, 100 MHz) of 10

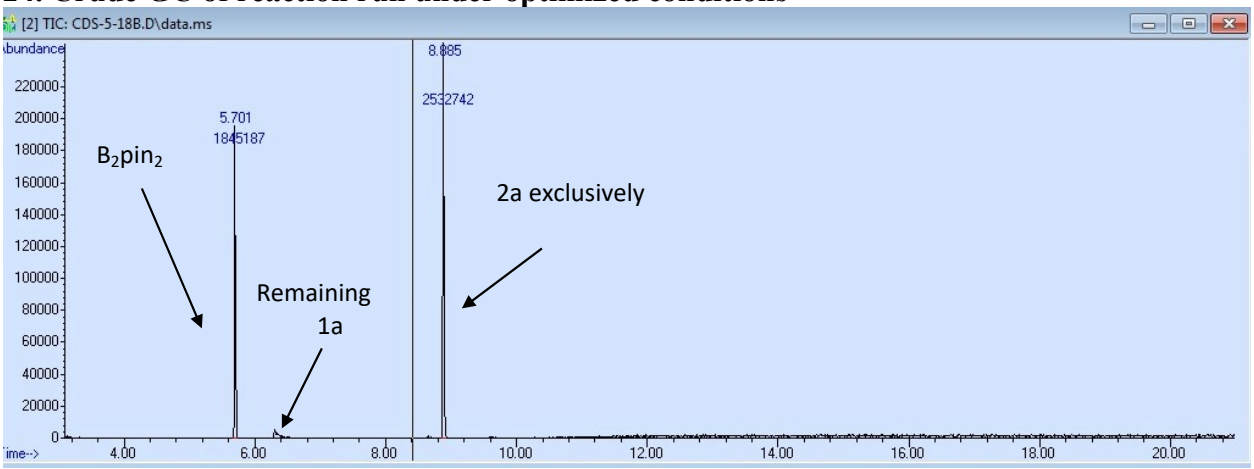


23. NMR Spectra for Optimization Table 1 in manuscript

^{1}H NMR ($CDCl_3$, 400 MHz) of Table 1 Entry 13



24. Crude GC of reaction run under optimized conditions



25. Procedure for Crystal Growth of 3

Compound **3** (40 mg, 0.140 mmol) was dissolved in chloroform (1.0 mL) and placed in a NMR tube. The solution in the tube was left overnight to allow slight degassing. After the solution was left overnight, crystals formed on the bottom and sides of the tube that were suitable for X-ray diffraction.

26. Crystal Structure Data

A colorless needle (0.05 x 0.06 x 0.41 mm^3) was centered on the goniometer of a Rigaku Oxford Diffraction Synergy-S diffractometer equipped with a HyPix6000HE detector and operating with CuKα radiation. The data collection routine, unit cell refinement, and data processing were carried out with the program CrysAlisPro.[1] The Laue symmetry and systematic absences were consistent with the monoclinic space groups *C*2/*c* and *Cc*. Only the noncentrosymmetric space group *Cc* , with Z'=1, gave a satisfactory solution. The structure was solved using SHELXT[2] and refined using SHELXL[3] via Olex2.[4] The final refinement model involved anisotropic displacement parameters for non-hydrogen atoms. A riding model was used for the C-H hydrogens. The -NH_2 hydrogens were located from the difference electron density map and the positions and isotropic thermal parameters were refined independently. Olex2[5] AND/OR Mercury[6] was used for molecular graphics generation.

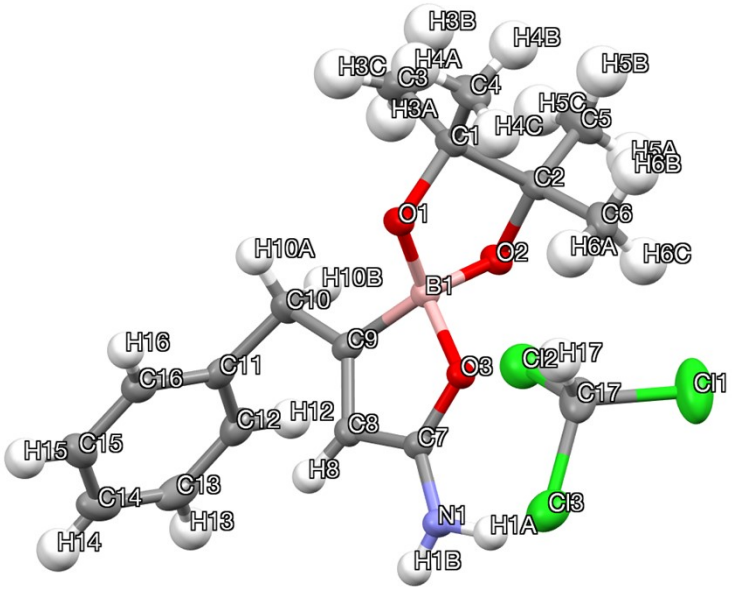


Figure S1: Crystal Structure of Primary Amide of **2a**

Table 1 Crystal data and structure refinement for cs2641.

Identification code	CDS-5-62
Empirical formula	$C_{17}H_{23}BCl_3NO_3$
Formula weight	406.52

(1) CrysAlisPro Software System, v1.171.40.68a, Rigaku Oxford Diffraction, **2020**, Rigaku Corporation, Oxford, UK.

(2) Sheldrick, G. M. "SHELXT – Integrated space-group and crystal structure determination." *Acta Cryst*. **2015**, *A71*, 3–8.

(3) Sheldrick, G. M. "Crystal structure refinement with SHELXL." *Acta Cryst.* **2015**, *C71*, 3-8.

(4) Dolomanov, O.V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *J. Appl. Cryst.* **2009**, ***42***, 339–341.

(5) Dolomanov, O.V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *J. Appl. Cryst.* **2009**, ***42***, 339–341.

(6) Macrae, C. F.; Sovago, I.; Cottrell, S. J.; Galek, P. T. A.; McCabe, P.; Pidcock, E.; Platings, M.; Shields, G. P.; Stevens, J. S.; Towler M.; Wood, P. A. *J. Appl. Cryst.* **2020**, *53*, 226-235. [DOI: 10.1107/S1600576719014092].

Temperature/K	99.99(13)
Crystal system	monoclinic
Space group	Cc
a/Å	8.8732(3)
b/Å	23.4482(5)
c/Å	10.7330(3)
α/°	90
β/°	109.856(3)
γ/°	90
Volume/Å^3	2100.35(11)
Z	4
ρ_{calc}g/cm^3	1.286
μ/mm^{-1}	4.074
F(000)	848.0
Crystal size/mm^3	0.41 × 0.06 × 0.05
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	7.54 to 156.14
Index ranges	$-11 \leq h \leq 11$, $-29 \leq k \leq 29$, $-13 \leq l \leq 12$
Reflections collected	16596
Independent reflections	3935 [R_{int} = 0.0834, R_{sigma} = 0.0587]
Data/restraints/parameters	3935/2/237
Goodness-of-fit on F^2	1.148
Final R indexes [I>=2σ (I)]	R_1 = 0.0535, wR_2 = 0.1462
Final R indexes [all data]	R_1 = 0.0557, wR_2 = 0.1481
Largest diff. peak/hole / e Å^{-3}	0.52/-0.33
Flack parameter	0.05(2)

Table 2 Bond Lengths for cs2641.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	C1	1.452(5)	C8	C9	1.334(6)
O1	B1	1.447(5)	C9	C10	1.504(6)
O2	C2	1.445(5)	C9	B1	1.628(6)
O2	B1	1.434(5)	C10	C11	1.499(6)
O3	C7	1.284(5)	C11	C12	1.391(6)
O3	B1	1.605(6)	C11	C16	1.407(6)
N1	C7	1.312(5)	C12	C13	1.391(7)
C1	C2	1.559(6)	C13	C14	1.379(9)
C1	C3	1.516(7)	C14	C15	1.397(7)
C1	C4	1.523(6)	C15	C16	1.384(6)
C2	C5	1.523(6)	Cl1	C17	1.761(5)
C2	C6	1.522(7)	Cl2	C17	1.778(6)
C7	C8	1.454(5)	Cl3	C17	1.762(6)

Table 3 Bond Angles for cs2641.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
B1	O1	C1	108.8(3)	C8	C9	B1	109.1(3)
B1	O2	C2	107.0(3)	C10	C9	B1	125.9(3)
C7	O3	B1	108.3(3)	C11	C10	C9	112.9(3)
O1	C1	C2	101.6(3)	C12	C11	C10	121.9(4)
O1	C1	C3	108.1(4)	C12	C11	C16	117.7(4)
O1	C1	C4	108.8(4)	C16	C11	C10	120.2(4)
C3	C1	C2	112.7(4)	C13	C12	C11	121.0(4)
C3	C1	C4	110.6(4)	C14	C13	C12	120.7(4)
C4	C1	C2	114.3(4)	C13	C14	C15	119.3(5)
O2	C2	C1	101.7(3)	C16	C15	C14	119.9(5)
O2	C2	C5	107.8(4)	C15	C16	C11	121.3(4)
O2	C2	C6	108.4(4)	O1	B1	O3	108.3(3)
C5	C2	C1	114.9(4)	O1	B1	C9	118.2(3)
C6	C2	C1	113.1(4)	O2	B1	O1	106.8(3)
C6	C2	C5	110.2(4)	O2	B1	O3	109.5(3)
O3	C7	N1	120.9(4)	O2	B1	C9	115.3(3)
O3	C7	C8	115.2(3)	O3	B1	C9	98.0(3)
N1	C7	C8	123.8(4)	Cl1	C17	Cl2	110.8(3)
C9	C8	C7	109.1(3)	Cl1	C17	Cl3	110.4(3)
C8	C9	C10	125.0(4)	Cl3	C17	Cl2	110.4(3)

Table 4 Hydrogen Bonds for cs2641.

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
N1	H1B	O1[1]	0.82(6)	1.94(6)	2.754(5)	172(6)
C17	H17	O2	1.00	2.05	3.009(6)	160.9

[1]+X,1-Y,-1/2+Z

Table 5 Torsion Angles for cs2641.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
O1	C1	C2	O2	35.6(4)	C8	C9	B1	O2	114.4(4)
O1	C1	C2	C5	151.7(4)	C8	C9	B1	O3	-1.6(4)
O1	C1	C2	C6	-80.5(4)	C9	C10	C11	C12	-90.0(5)
O3	C7	C8	C9	3.2(5)	C9	C10	C11	C16	85.8(5)
N1	C7	C8	C9	-176.5(4)	C10	C9	B1	O1	64.1(5)
C1	O1	B1	O2	2.6(4)	C10	C9	B1	O2	-64.0(5)
C1	O1	B1	O3	120.5(3)	C10	C9	B1	O3	179.9(4)
C1	O1	B1	C9	-129.4(4)	C10	C11	C12	C13	174.9(4)
C2	O2	B1	O1	21.8(4)	C10	C11	C16	C15	-175.6(4)
C2	O2	B1	O3	-95.3(4)	C11	C12	C13	C14	0.7(7)
C2	O2	B1	C9	155.3(4)	C12	C11	C16	C15	0.5(6)
C3	C1	C2	O2	-79.9(4)	C12	C13	C14	C15	0.3(7)
C3	C1	C2	C5	36.2(5)	C13	C14	C15	C16	-0.9(7)
C3	C1	C2	C6	164.0(4)	C14	C15	C16	C11	0.5(7)
C4	C1	C2	O2	152.7(4)	C16	C11	C12	C13	-1.1(6)
C4	C1	C2	C5	-91.3(5)	B1	O1	C1	C2	-23.6(4)
C4	C1	C2	C6	36.6(5)	B1	O1	C1	C3	95.3(4)
C7	O3	B1	O1	126.7(3)	B1	O1	C1	C4	-144.5(4)
C7	O3	B1	O2	-117.1(4)	B1	O2	C2	C1	-35.5(4)
C7	O3	B1	C9	3.4(4)	B1	O2	C2	C5	-156.7(4)
C7	C8	C9	C10	178.0(4)	B1	O2	C2	C6	84.0(4)
C7	C8	C9	B1	-0.5(4)	B1	O3	C7	N1	175.5(4)
C8	C9	C10	C11	4.2(6)	B1	O3	C7	C8	-4.2(4)
C8	C9	B1	O1	-117.5(4)	B1	C9	C10	C11	-177.6(4)

27. References

1) X. Zhu, C. Henry, J. Wang, T. Dudding and O. Kwon, *Org. Lett*., 2005, **7**, 1387-1390.
2) K. Nagao, H. Ohmiya, M. Sawamura, *J. Am. Chem. Soc.* 2014, **136**, 10605-10608.
3) Z. Niu, J. Chen, Z. Chen, M. Ma, C. Song, Y. Ma, *J. Org. Chem.*, **2015**, *80*, 602-608.
4) Knappmann, Inga; Schepmann, Dirk; Wünsch, Bernhard. *Bioorganic and Medicinal Chemistry*, **2016**, 24, 4045 - 4055.