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Synthesis and Characterization of Novel (E)-tert-butyl 7-(4-methoxyphenyl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hept-2-enoate and (E)-diethyl (6-(4-methoxyphenyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hex-1-en-1-yl)phosphonate; Application of Olefin Cross Metathesis

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ABSTRACT
Two novel compounds (E)-tert-butyl 7-(4-methoxyphenyl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hept-2-enoate and (E)-diethyl (6-(4-methoxyphenyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hex-1-en-1-yl)phosphonate were synthesized in excellent yields by olefin cross metathesis (CM). 3-(4-methoxyphenyl)propyl diisopropylcarbamate and allylboronic acid pinacol ester were reacted in the presence of s-BuLi/*N*,*N*,*N*,*N*-tetramethylethyllenediamine (TMEDA) to form sec. boronic ester which was further reacted with tert-butyl acrylate and diethyl vinylphosphonate respectively to get the desired products. Both novel compounds have applications as reactants for cyclopropanation and cyclopentataion for asymmetric synthesis.

Keywords: Allylic boronic ester, Lithiation Borylation, Olefin Cross Metathesis, Hoveyda-Grubbs Catalyst 2nd Generation, Asymmetric synthesis.

1. INTRODUCTION
The formation of carbon-carbon double bonds by olefin metathesis is the most powerful and broadly applicable synthetic tool of modern organic chemistry[1-3]. Olefin metathesis has become a mainstay in organic synthesis[4,5] that is becoming an increasingly important tool in the synthesis of small molecules, preparation of natural products, and construction of polymers. It is a metal-catalyzed transformation, which acts on carbon carbon double bonds and rearranges them via cleavage and reassembly[6,7]. According to this mechanism, first introduced by Chauvin, the coordination of an olefin to a metal carbene catalytic species leads to the reversible formation of a metallacyclobutane. This intermediate then proceeds by cycloreversion via either of the two possible paths: 1) non-productive—resulting in the re-formation of the starting materials or 2) product-forming—yielding an olefin that has exchanged a carbon with the catalyst's alkylidene. Since all of these processes are fully reversible only statistical mixtures of starting materials as well as all of possible rearrangement products are produced in the absence of thermodynamic driving forces[8]. This method is especially effective in the case of cross metathesis (CM) reactions involving terminal olefins[9]. In particular, cross metathesis (CM) reactions promoted by ruthenium-based catalysts have been widely utilized by synthetic organic as well as polymer chemists in the construction of higher olefins from simple alkene precursors[10]. *N*-Heterocyclic carbene (NHC) ligand-containing catalysts, such as the second-generation Grubbs catalyst[11] are widely used. Karl Voigtritter[12] studied iodide effect on olefin cross metathesis reactions. Many attempts had been made for cyclopropanation and cyclopentanation reactions using boron-ate complexes. A number of boronic esters were tried for cyclopropanation and cyclopentanation. Abbasi[13] synthesized different sulfonamides including heterocyclic moieties for the evaluation of their various biological activities.

In this study, we synthesized such boronic esters which have electron withdrawing groups by carrying out CM reactions used. These compounds might be used as starting materials for asymmetric synthesis if electron withdrawing groups could promote cyclopropanation and cyclopentanation. It was expected that the presence of electron withdrawing groups on boronic esters definitely promote 1, 3-migration to cyclopropanation and cyclopentanation. Allylic boronic ester **(3)** was first synthesized by the reaction of 3-(4-methoxyphenyl)propyl diisopropylcarbamate **(1)** with allylboronic acid pinacol ester **(2)**. Allylic boronic ester **(3)** was the reacted with tert-butyl acrylate **(4)** and diethyl vinylphosphonate **(6)** to synthesize novel compounds (E)-tert-butyl 7-(4-methoxyphenyl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hept-2-enoate **(5)** and (E)-diethyl (6-(4-methoxyphenyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hex-1-en-1-yl)phosphonate **(7)**.

2. EXPERIMENTAL SECTION

2.1 *Materials*
Sec. butyllithium solution (sBuLi) (1.6M), allylboronic acid pinacol ester, *N*,*N*,*N*,*N*-tetramethylethyllenediamine (TMEDA), diethyl vinylphosphonate and Hoveyda-Grubbs Catalyst 2nd Generation were purchased form Sigma Aldrich and tert-butyl acrylate was taken from Acros. All chemicals were used as such as received. TMEDA was distilled over CaH_2. Anhydrous diethyl ether (Et_2O) and dichloromethane (DCM) were obtained under nitrogen andstored in Young's flasks over 4A^o molecular sieves. Reaction was carried out in flame-dried glassware under nitrogen atmosphere.

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2.2 *Synthesis and Characterization of 2-(1-(4-methoxyphenyl)hex-5-en-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3)*

To a solution of 3-(4-methoxyphenyl)propyl diisopropylcarbamate (1.0g, 3.41mmol, 1.0eq) **(1)** and *N,N,N,N*-tetramethylethyllenediamine (TMEDA) (0.61mL, 4.09mmol, 1.2eq) **(2a)** in Et_2O (17mL) at -78°C was added Sec. BuLi (1.6M in 92:8 cyclohexane/hexane, 2.9mL, 3.75mmol, 1.1eq) dropwise. After stirring the reaction mixture for 5h at -78°C, allylboronic acid pinacol ester (0.77mL, 4.09mmol, 1.2eq) **(2)** was added dropwise. The reaction mixture was further stirred at -78°C for 1h and then allowed to warm to room temperature. A solution of $MgBr_2.OEt_2$ in Et_2O, made as follows, was added to the reaction mixture at this point: [1,2-dibromoethane (0.60mL, 6.88mmol, 1.0eq) was added to a suspension of magnesium (0.17g, 6.88mmol, 1.0eq) in Et_2O (8.6mL) at room temperature. The reaction flask was then placed into a water bath in order to control the moderate exotherm and was further stirred for 2h]. Both layers of the biphasic mixture thus obtained were transferred to the former mixture via syringe. The mixture was refluxed for 16h.

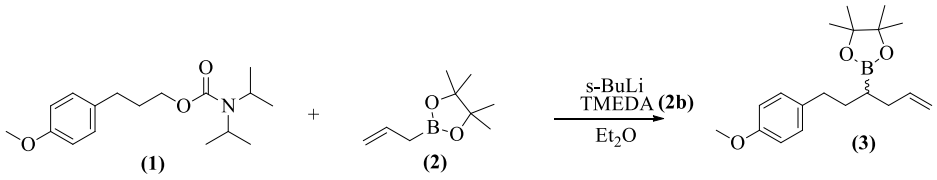


Figure 1: Synthesis of 2-(1-(4-methoxyphenyl)hex-5-en-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

The reaction mixture was allowed to cool down to room temperature and was carefully quenched with water. Et_2O was added, the layers were separated and the aqueous phase was extracted with Et_2O. The combined organic layers were washed with 1N HCl, 1N NaOH, water and brine, dried ($MgSO_4$), concentrated and purified by column chromatography (SiO_2) to obtain the pure 2-(1-(4-methoxyphenyl)hex-5-en-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **(3)** (0.81g, 75.3%) as colorless oil. The reaction is given in Figure 1.

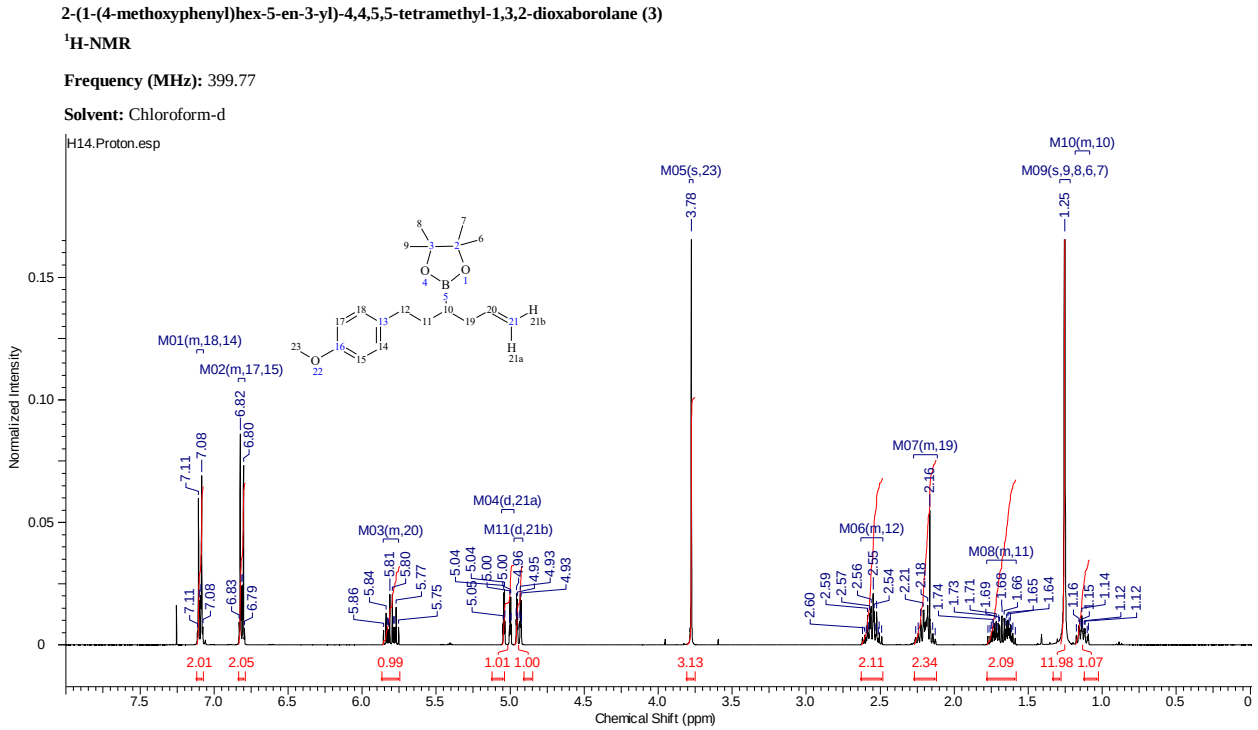
Complete characterization was done by taking ^{1}H NMR, ^{13}C NMR and IR. It was used as starting material for reaction (Figure 2, 3).

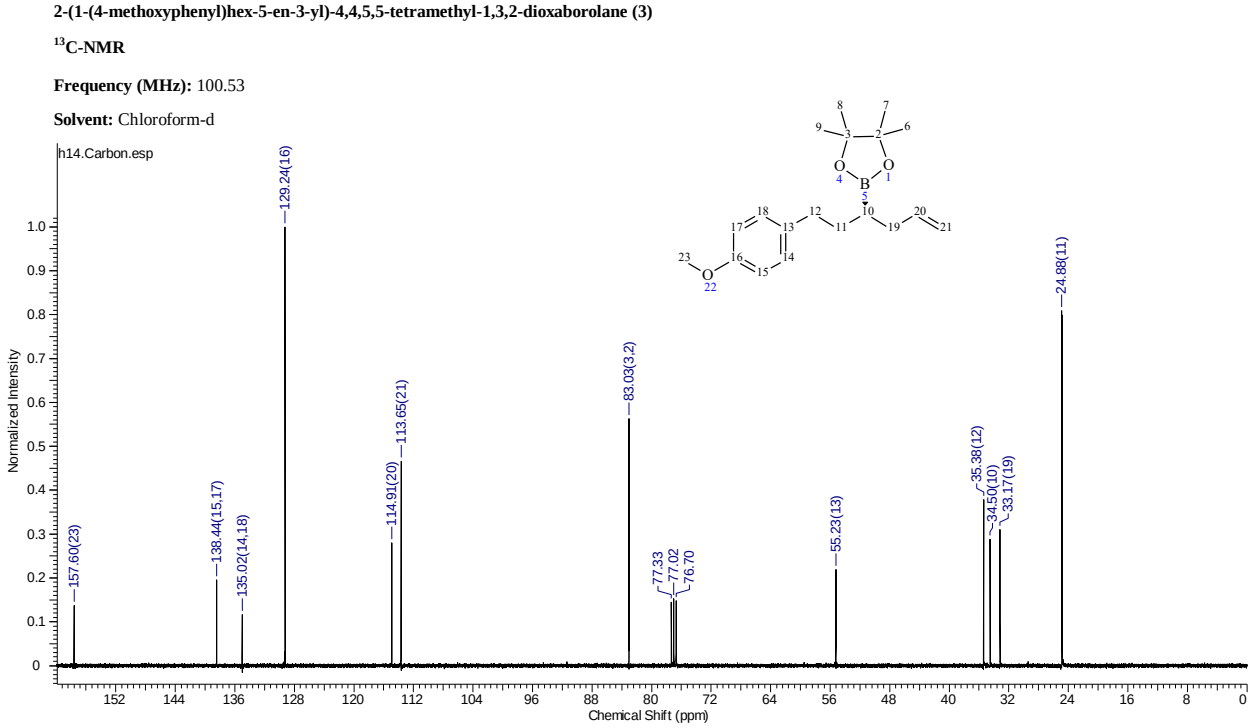
IR (film): ν (cm^{-1}) 3026 (sp^{2}C-H Stretch), 2977, 2924, 2852 (sp^3 C-H Stretch), 1511, 1456(sp^2 C=C Stretch), 1243, 1175, 1142 (sp^{3}C-O Stretch), 846, 822, 670 (sp^2 C-H oop bending).

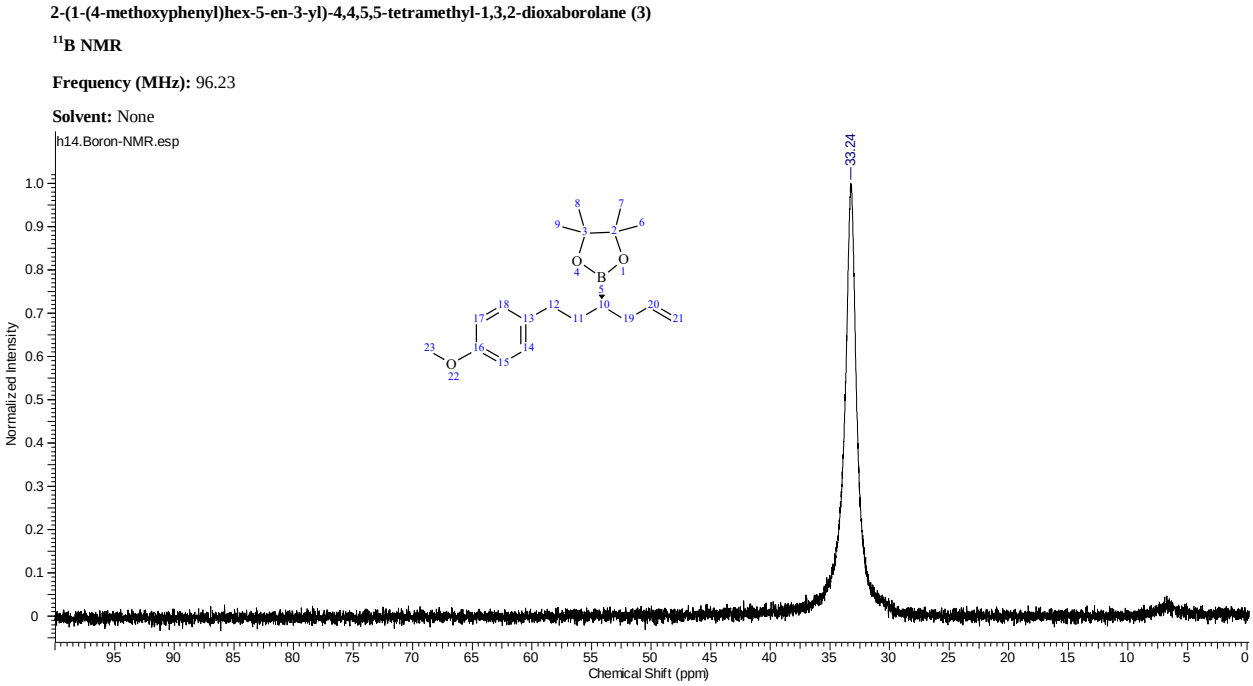
^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.09 (2H, d, *J*=8.80 Hz, 2 × Ar*H*) 6.81 (2H, d, *J*=8.80 Hz, 2 × Ar*H*) 5.86 – 5.75 (1H, m, C*H*=CH_2) 5.04 (1H, d, *J*=2.20 Hz, CH=CH*H*) 4.94 (1H, d, *J*=10.27 Hz, CH=C*H*H) 3.78 (3H, s, OCH_3) 2.63 - 2.48 (2H, m, ArCH_2CH_2CHBCH_2) 2.27 - 2.11 (2H, m, ArCH_2CH_2CHBCH_2) 1.78 - 1.58 (2H, m, ArCH_2CH_2CHBCH_2) 1.25 (12H, s, 4 × CH_3) 1.08 - 1.18 (1H, m, ArCH_2CH_2CHBCH_2)

^{13}C NMR (100 MHz, CDCl3) δ ppm 157.6 (1C, -OCH_3), 138.4 (2C, 2 × Ar*C*H), 135.0 (2C, 2 × Ar*C*H), 129.2 (1C, Ar*C*-O), 114.9 (1C, -CH_2*C*H=CH_2), 113.6 (1C, -CH=*C*H_2), 83.0 (2C, 2 × *C*$(CH_3)_2$), 55.2 (1C, Ar*C*CH_2), 35.3 (1C, -*C*H_2CH_2CHB), 34.5 (1C, -CH_2*C*HB), 33.1 (1C, -CHB*C*H_2CH), 24.9 (1C, -CH_2*C*H_2CHB), 24.8 (4C, 2 × $(CH_3)_2$C).

^{11}B NMR (96.23 MHz, None) δ ppm 33.24







2.3. *Synthesis and Characterization of (E)-tert-butyl 7-(4-methoxyphenyl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hept-2-enoate (5)*

To a solution of allyl boronic ester (0.75g, 2.37mmol, 1.0eq) **(3)** and tert. butyl acrylate (0.75mL, 4.74mmol, 2.0eq) **(4)** in CH_2Cl_2 (30mL) was added Grubbs-Hoveyda II (0.027g, 0.043mmol, 0.02eq) **(4a)**. The flask was fitted with a condenser and refluxed under nitrogen for 15h. Reaction was monitored by TLC. The reaction mixture was then reduced in volume to 0.5mL and purified directly on a silica gel column eluting with 9:1 Pet. Ether/ EtOAc to get the desired product (E)-tert-butyl 7-(4-methoxyphenyl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hept-2-enoate (0.78g, 78.82%) **(5)**[14].

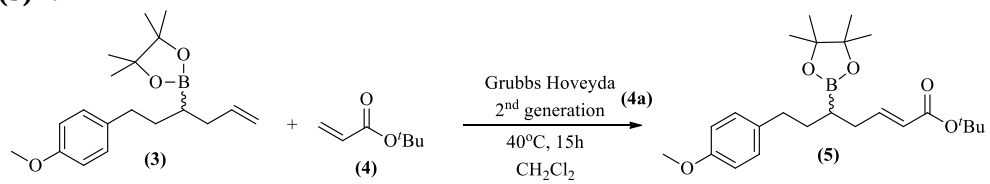


Figure 2: (*E*)-*tert*-butyl 7-(4-methoxyphenyl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hept-2-enoate

The product **(5)** was completely characterized by ^{1}H NMR, ^{13}C NMR and IR.

IR (film): ν (cm^{-1}) 2977, 2930 (sp^3 C-H Stretch), 1711 (sp^{2}C=O Stretch), 1651, 1612 (C-C=C Stretch), 1512, 1456(sp^2 C=C Stretch), 1244, 1214, 1139 (sp^{3}C-O Stretch), 849, 822, 682 (sp^2 C-H oop bending).

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.08 (2H, d, *J*=8.56 Hz, 2 × Ar*H*) 6.85 (1H, t, *J*=7.21 Hz, CH=C*H*COO) 6.81 (2H, d, *J*=8.56 Hz, 2 × Ar*H*) 5.73 (1H, dt, *J*=15.41, 1.47 Hz, , C*H*=CHCOO) 3.77 (3H, s, OCH_3) 2.62-2.47 (2H, m, ArCH_2CH$_2$CHBCH$_2$), 2.36-2.21 (2H, m, ArCH$_2$CH$_2$CHBCH_2) 1.78-1.57 (2H, m, ArCH$_2$CH_2CHBCH) 1.46 (9H, s, 3 × CCH_3) 1.24 (12H, s, 4 × CCH_3) 1.21-1.16 (1H, m, ArCH$_2$CH$_2$C*H*BCH$_2$)

^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 165.9 (1C, *C*OO) 157.6 (1C, Ar*C*) 147.5 (1C, *C*H=CHCOO) 134.6 (1C, Ar*C*) 129.2 (2C, 2 × Ar*C*H) 123.5 (1C, CH=*C*HCOO) 113.6 (2C, 2 × Ar*C*H) 83.2 (2C, 2 × *C*(CH$_3$)$_2$) 79.8 (1C, *C*(CH$_3$)$_3$) 55.2 (1C, OCH$_3$) 34.3 (1C, ArCH$_2$CH$_2$*C*HBCH$_2$) 33.5 (1C, Ar*C*H$_2$CH$_2$CHBCH$_2$) 33.1 (3C, C(*C*H$_3$)$_3$) 28.1 (4C, 2 × C(*C*H$_3$)$_2$) 24.82 (1C, ArCH$_2$CH$_2$CHBC*H*$_2$) 24.81 (1C, ArCH$_2$*C*H$_2$CHBCH$_2$).

^{11}B NMR (96.23 MHz, None) δ ppm 29.54

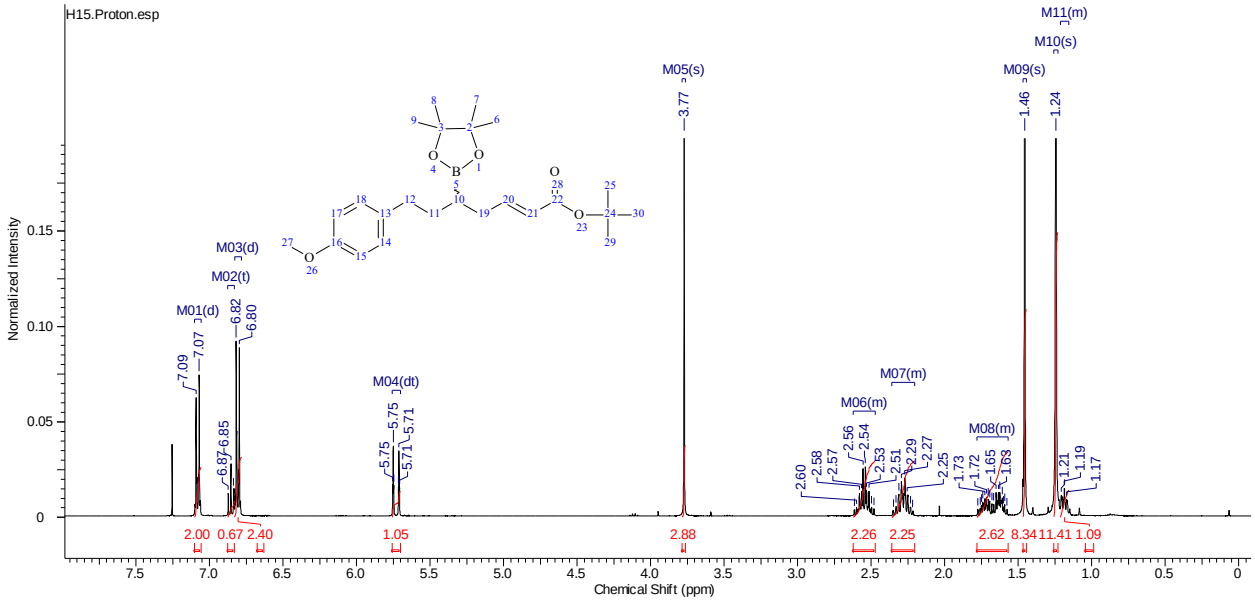
HRMS (ESI) calcd. for $C_{24}H_{37}BO_5$ $[M+H]^+$ 417.2811, found 417.2811.

(E)-tert-butyl 7-(4-methoxyphenyl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hept-2-enoate (5)

^{1}H-NMR

Frequency (MHz): 399.77

Solvent: Chloroform-d

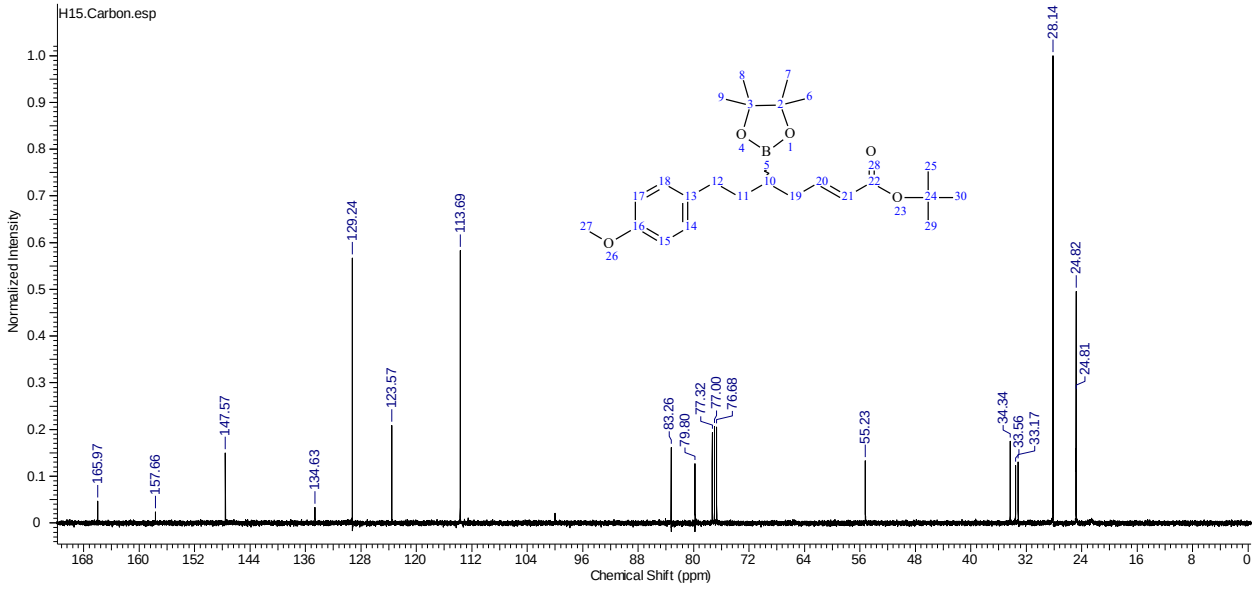


(E)-tert-butyl 7-(4-methoxyphenyl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hept-2-enoate (5)

^{13}C-NMR

Frequency (MHz): 100.53

Solvent: Chloroform-d

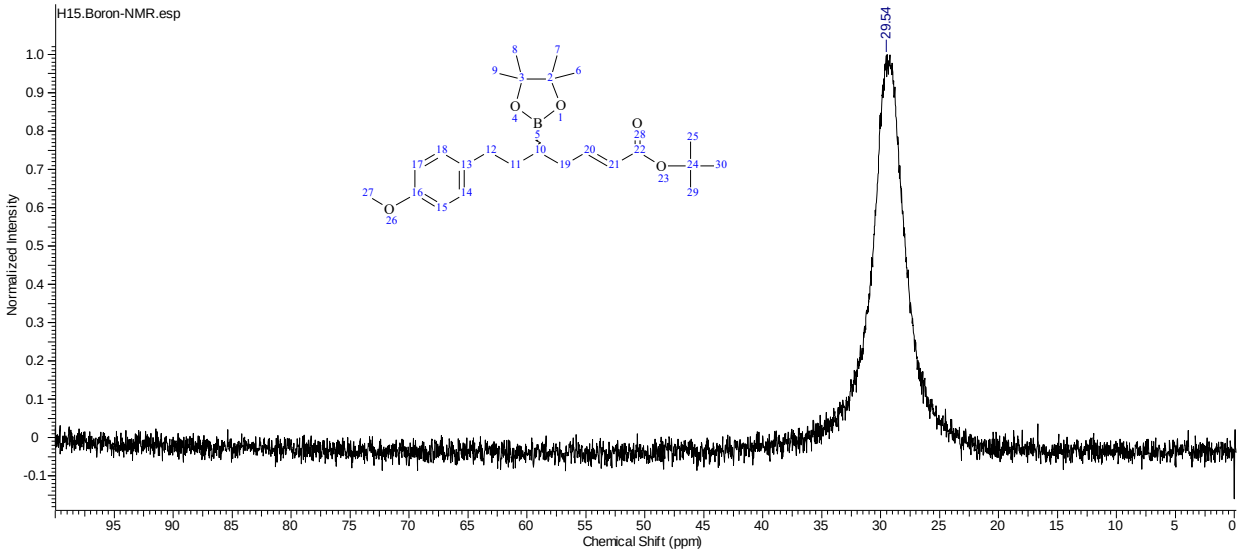


(E)-tert-butyl 7-(4-methoxyphenyl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hept-2-enoate (5)

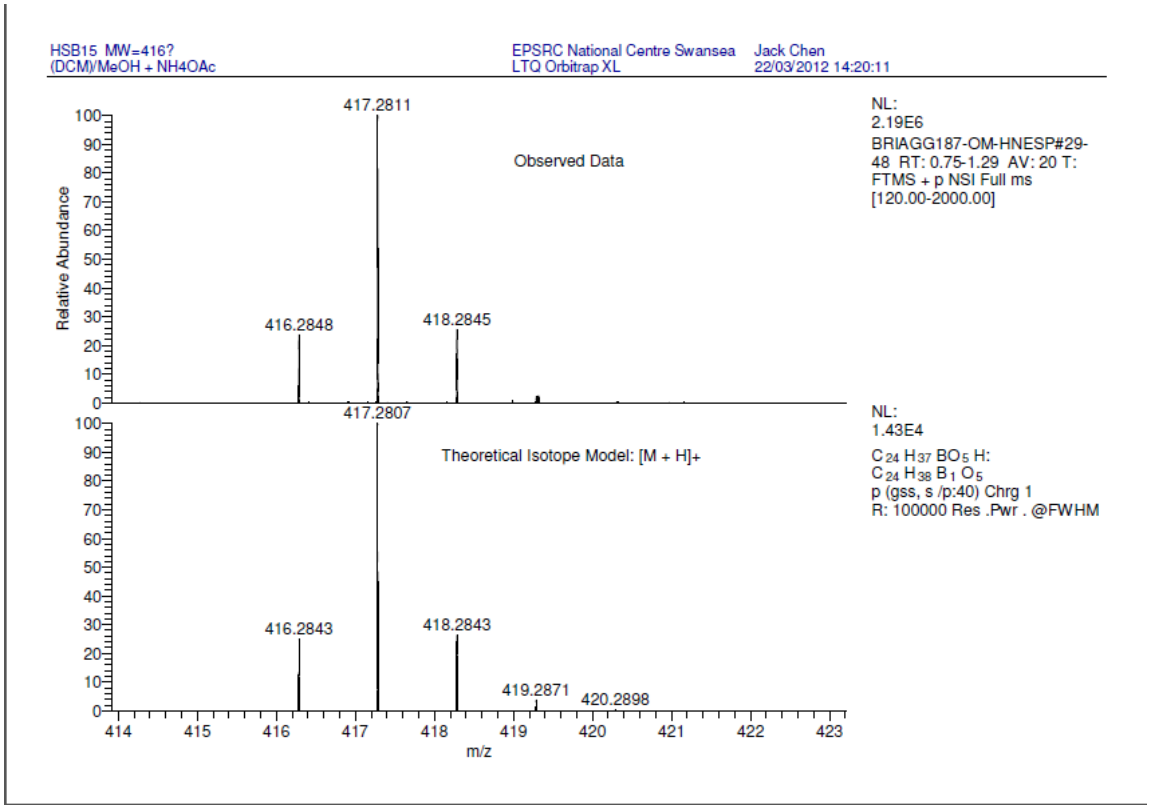
^{11}B-NMR

Frequency (MHz): 96.23

Solvent: None



(E)-tert-butyl 7-(4-methoxyphenyl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hept-2-enoate (5)



2.4 *Synthesis and Characterization of (E)-diethyl (6-(4-methoxyphenyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hex-1-en-1-yl)phosphonate (7)*

To a solution of allyl boronic ester (0.10g, 0.316mmol, 1.0eq) **(3)** and diethyl vinylphosphonate (0.12mL, 0.632mmol, 2.0eq) **(6)** in CH_2Cl_2 (20mL) was added Grubbs-Hoveyda II (0.0039g, 0.0063mmol, 0.02eq) **(4a)**. After fitting a condenser to the flask, reaction mixture was refluxed under nitrogen for 15h. Reaction completion was monitored by TLC. The reaction mixture was then reduced in volume to 0.5mL and purified directly on a silica gel column eluting with 9:1 Pet. Ether/ EtOAc to get pure (E)-diethyl (6-(4-methoxyphenyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hex-1-en-1-yl)phosphonate (0.11g, 79%) **(7)**[13].

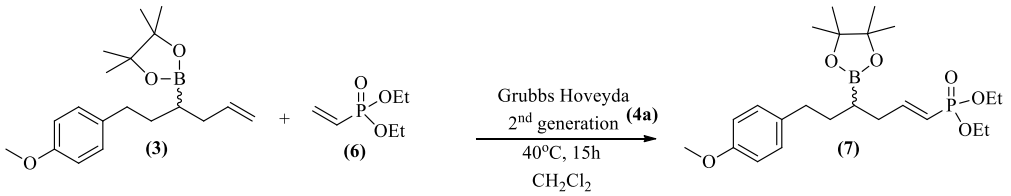


Figure 3: (*E*)-diethyl (6-(4-methoxyphenyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hex-1-en-1-yl)phosphonate

^{1}H NMR, ^{13}C NMR and IR were taken to characterize (E)-diethyl (6-(4-methoxyphenyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hex-1-en-1-yl)phosphonate **(7)**.

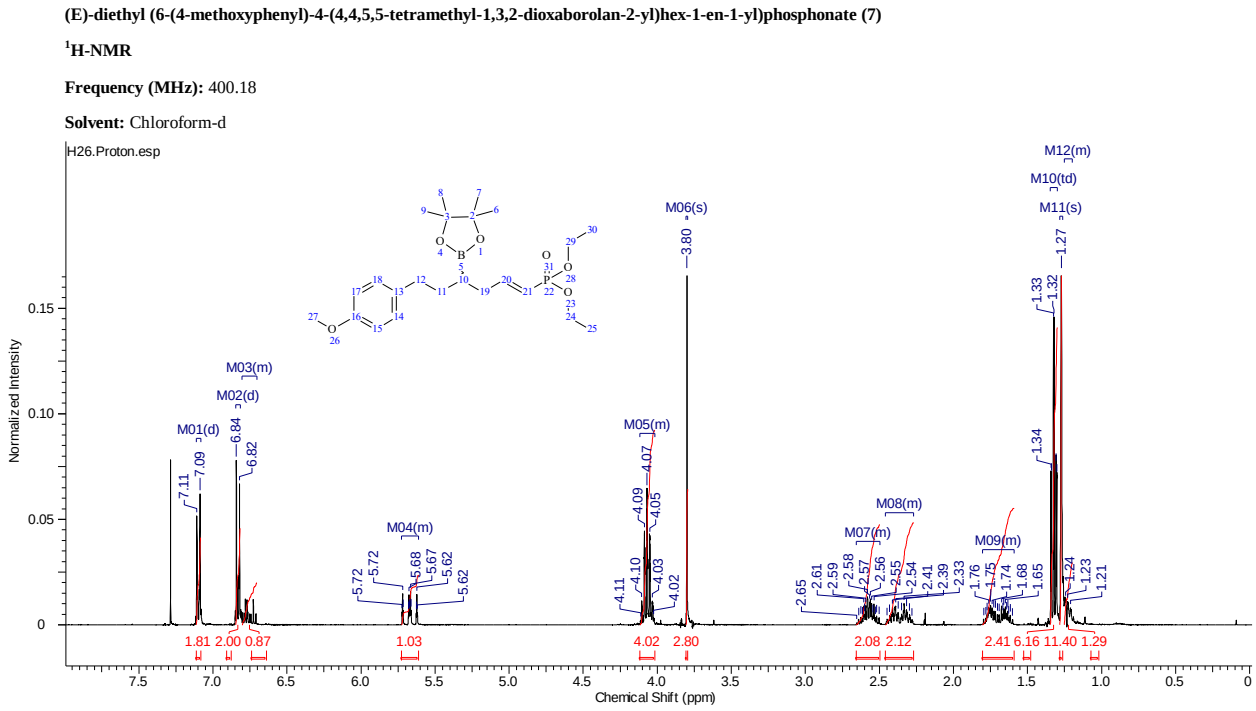
IR (film): ν (cm^{-1}) 2978, 2930 (sp^3 C-H Stretch), 1630, 1612 (C-C=C Stretch), 1512, 1443 (sp^2 C=C Stretch), 1242, 1166, 1142 (sp^{3}C-O Stretch), 960, 821, 731 (sp^2 C-H oop bending).

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.10 (2H, d, *J*=8.61 Hz, 2 × Ar*H*) 6.83 (2H, d, *J*=8.61 Hz, 2 × Ar*H*) 6.80-6.70 (1H, m, CH=C*H*PO) 5.73-5.61 (1H, m, C*H*=CHPO) 4.12-4.02 (4H, m, 2 × CH_2CH$_3$) 3.80 (3H, s, OCH_3) 2.66-2.50 (2H, m, ArCH_2CH$_2$CHBCH$_2$) 2.46-2.27 (2H, m, ArCH$_2$CH$_2$CHBCH_2) 1.80-1.59 (2H, m, ArCH$_2$CH_2CHBCH) 1.32 (6H, td, *J*=7.15, 1.65 Hz, 2 × CH$_2$CH_3) 1.27 (12H, s, 4 × CCH_3) 1.25-1.20 (1H, m, ArCH$_2$CH$_2$C*H*BCH$_2$).

^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 157.6 (1C, Ar*C*-O), 153.3 (*C*H=CHPO), 134.5 (1C, Ar*C*), 129.2 (2C, 2 × Ar*C*H), 118.1 (1C, CH=*C*HPO), 116.2 (2C, 2 × Ar*C*H), 113.7 (2C, 2 × *C*(CH$_3$)$_2$), 83.3 (2C, 2 × *C*H$_2$CH$_3$), 61.5, 61.4 (1P, d, CH*P*O), 55.2 (1C, OCH_3), 35.6 (1C, ArCH$_2$CH$_2$*C*HBCH$_2$), 34.2 (1C, Ar*C*H$_2$CH$_2$CHBCH$_2$), 33.0 (1C, ArCH$_2$CH$_2$CHB*C*H$_2$), 24.8 (4C, 2 × C(*C*H$_3$)$_2$), 16.38 (1C, ArCH$_2$*C*H$_2$CHBCH$_2$), 16.31 (2C, 2 × CH$_2$*C*H$_3$).

^{11}B NMR (96.23 MHz, None) δ ppm 29.73

HRMS (ESI) calcd. for $C_{23}H_{38}BO_6P$ $[M+H]^+$ 453.2574, found 453.2574.



2.5 *Equipments*

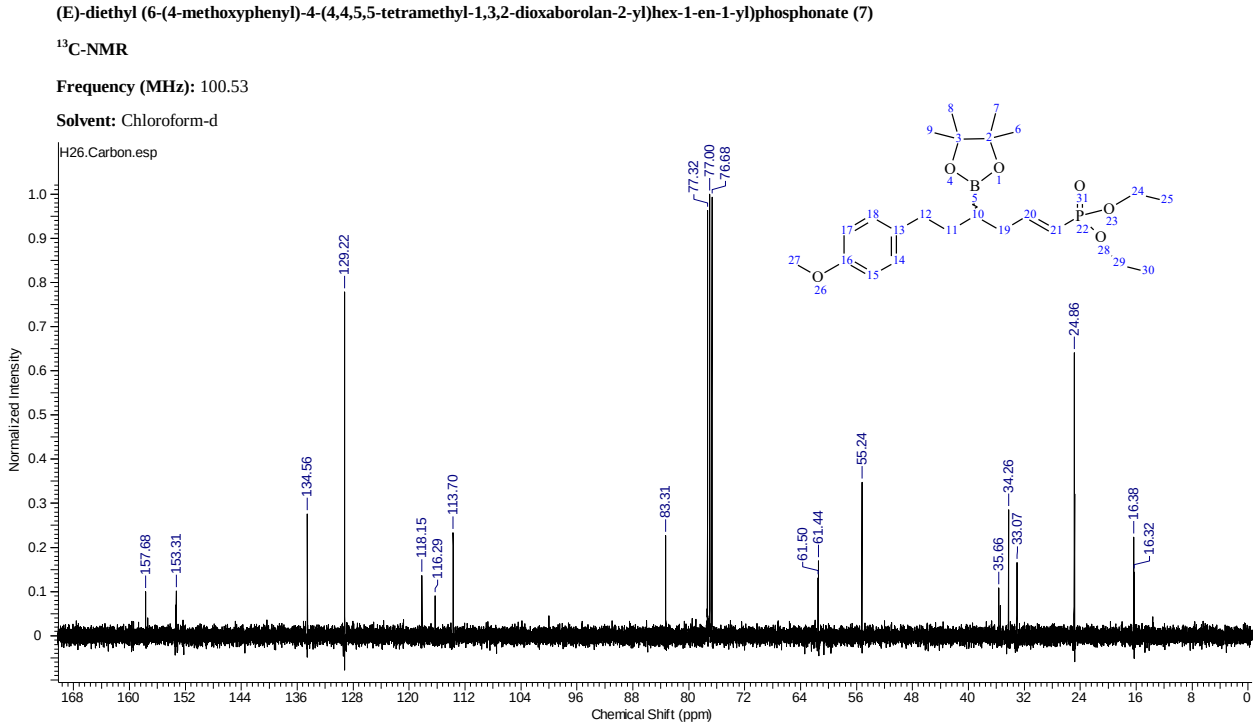
To take ^{1}H NMR and ^{13}C NMR measurements Varian NMR (400 MHz) spectrometer was used. Chemical shifts for protons were measured .Relative to tetramethylsilane (TMS) at δ= 0 ppm all chemical shift for protons were measured.

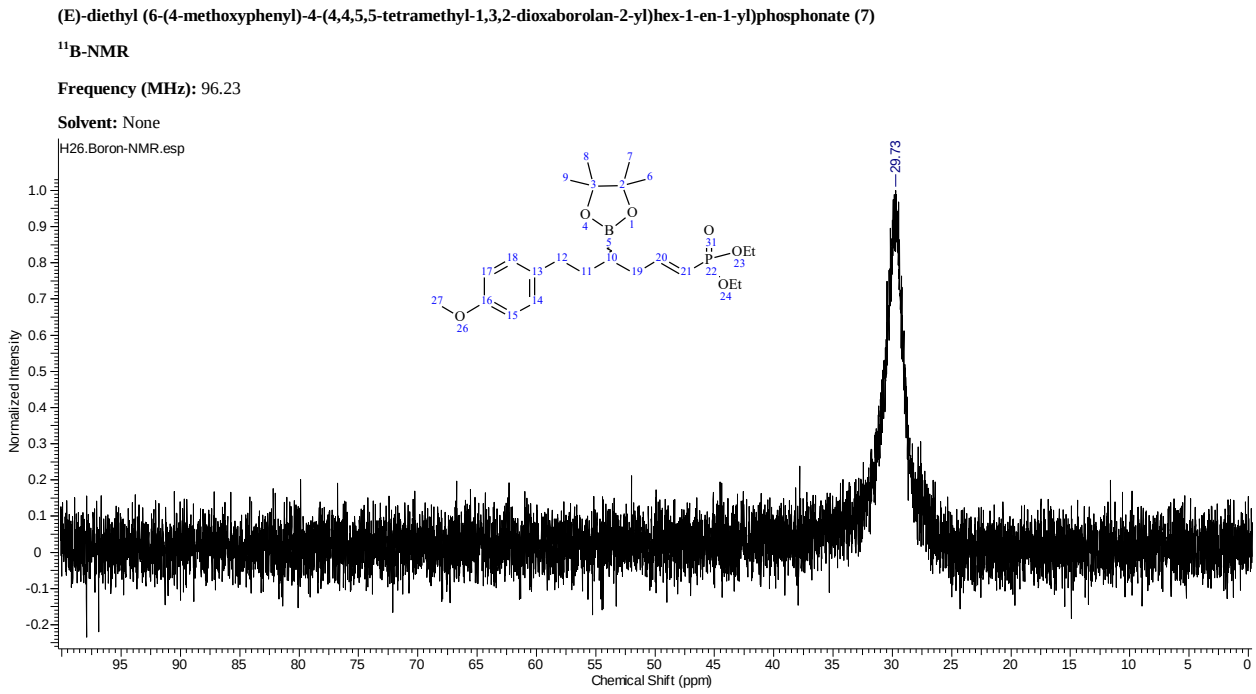
3. RESULTS AND DISCUSSION

First allylic boronic ester **(3)** was synthesized by Lithiation-borylation methodology mentioned in section 4.2 by reacting Carbamate **(1)** with allylboronic ester **(2)** as colorless oil in excellent yields (75.3%) (table 1, entry 1). Conditions for this reaction are given in figure 1.

Table-1: Data of Starting Materials

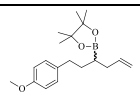
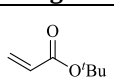
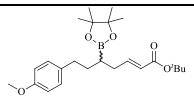
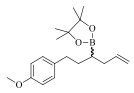
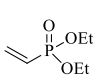
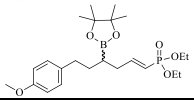
Entry	Starting Material	Color	Yield (%)
1	2-(1-(4-methoxyphenyl)hex-5-en-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane	Colorless oil	75.3

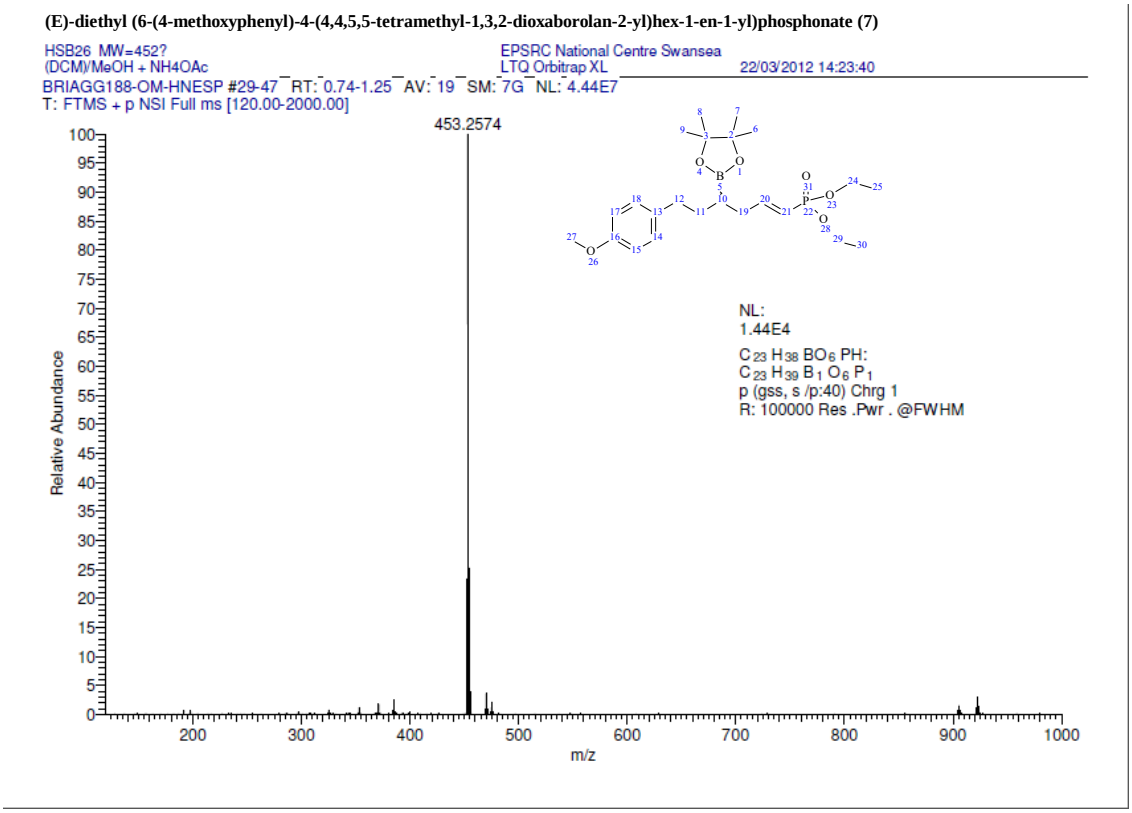




Allylic boronic ester **(3)** was used as starting material for the synthesis of novel compounds. (E)-tert-butyl 7-(4-methoxyphenyl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hept-2-enoate **(5)** and (E)-diethyl (6-(4-methoxyphenyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hex-1-en-1-yl)phosphonate **(7)** were synthesized by reacting boronic ester **(3)** with tert-butyl acrylate **(4)** and diethyl vinylphosphonate **(6)**. Chemical reactions with detailed conditions are mentioned in figure 2 and 3 respectively.

Table-2: Yields of Products

Entry	Boronic Ester	Reagents	Products	Yield (%)
1				78.82
2				79



For the product (E)-diethyl (6-(4-methoxyphenyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hex-1-en-1-yl)phosphonate **(7)**, yield was quite high (table 2, entry 2) while for (E)-tert-butyl 7-(4-methoxyphenyl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hept-2-enoate **(5)** yield was comparable (table 2, entry 1) and reasonably high. Both novel compounds **(5, 7)** were characterized by ^{1}H NMR, ^{13}C NMR, ^{11}B NMR and IR; detailed study of which is given in section 4.3 and 4.4.

4. CONCLUSIONS

In the recent study, two novel compounds (E)-tert-butyl 7-(4-methoxyphenyl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hept-2-enoate **(5)** and (E)-diethyl (6-(4-methoxyphenyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hex-1-en-1-yl)phosphonate **(7)** were synthesized in excellent yields by olefin cross metathesis. These compounds could have applications as starting materials for asymmetric synthesis. Presence of electron withdrawing groups in these compounds could promote cyclopropanation and cyclopentanation. For the product **(5)** yield was 78.82% (table 2, entry 1) while for the other product **(7)** yield was slightly great 79% (table 2, entry 2).

5. ACKNOWLEDGMENT

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6. REFERENCES

1. Chauvin, Y., *Angew Chem, Int Ed.* **(2006)**, 45, 3740-3747, http://dx.doi.org/10.1002/anie.200601234.
2. Schrock, R. R., *Angew Chem, Int Ed.* **(2006)**, 45, 3748-3759, http://dx.doi.org/10.1002/anie.200600085.
3. Grubbs, R. H., *Angew Chem, Int Ed.* **(2006)**, 45, 3760-3765, http://dx.doi.org/10.1002/anie.200600680.
4. Hoveyda, A. H., Zhugralin, A. R. *Nature* **(2007)**, 450, 243-251, http://dx.doi.org/10.1038/nature06351.
5. Furstner, A., *Angew. Chem., Int. Ed.* **(2000)**, 39, 3012-3043, http://dx.doi.org/10.1002/1521-3773(20000901)39:17<3012::AID-ANIE3012>3.0.CO;2-G.
6. Grubbs, R. H., *Tetrahedron* **(2004)**, 60, 7117-7140, http://dx.doi.org/10.1016/j.tet.2004.05.124.
7. Trnka, T. M., Grubbs, R. H. *Acc. Chem. Res.* **(2001)**, 34, 18-29, http://dx.doi.org/10.1021/ar000114f.
8. Herrison, J. L., Chauvin, Y. Makromol. *Chem.* **(1971)**, 141, 161-167, http://dx.doi.org/10.1002/macp.1971.021410112.
9. Connon, S. J., Blechert, S. *Angew. Chem. Int. Ed.* **(2003)**, 42, 1900-1923, http://dx.doi.org/10.1002/anie.200200556.
10. Schrodi, Y., Pederson RL *Aldrichimica Acta*. **(2007)**, 40, 45-52.

11. Scholl, M., Ding, S., Lee, C. W., Grubbs, R. H., *Org Lett.* **(1999)**, 6, 953, http://dx.doi.org/10.1021/ol990909q.
12. Voigtritter, K., Ghorai, S., Lipshutz, B. H., *J Org Chem.* **(2011)**, 76(11), 4697-4702, http://dx.doi.org/10.1021/jo200360s.
13. Abbasi, M. A., Aziz-ur-Rehman, Muhmood, T., Khan, K. M., Ashraf, M., Ejaz, S. A., Arshad, S., *J. Chem. Soc. Pak.* **(2013)**, 35(2), 404.
14. Lipshutz, B. H., Ghorai, S., Boskovic, Z. V., *Tetrahedron* **(2008)**, 64, 6949-6954, http://dx.doi.org/10.1016/j.tet.2008.04.027.