Organic Syntheses

Preparation of a *Z*-Iodoalkene through Stork-Zhao-Wittig Olefination, Stereo-retentive Lithium–iodine Exchange and *Z*-Boronic acid Pinacol Ester Synthesis

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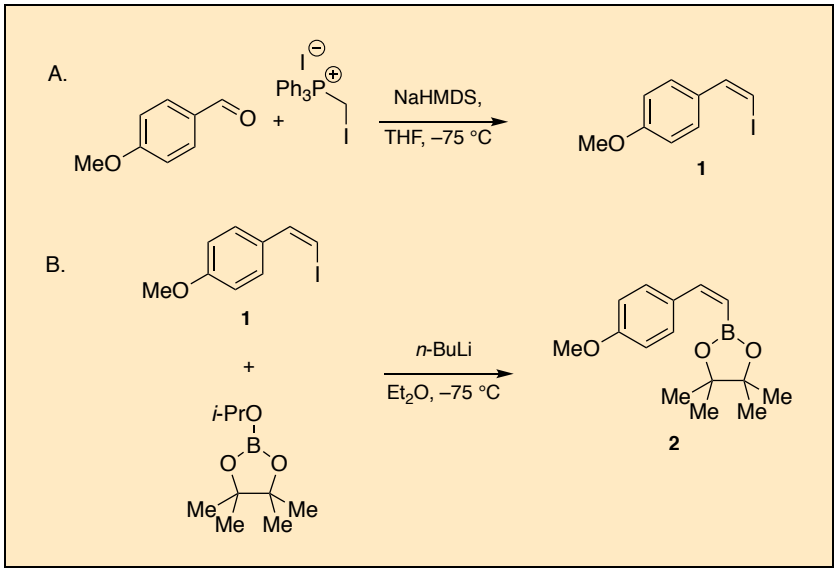
Checked by Alexander Preinfalk, Martin Berger, and Nuno Maulide



Procedure (Note 1)

A. *(Z)-1-(2-Iodovinyl)-4-methoxybenzene* (**1**). The reaction is performed with the lights turned off in the fume hood and the laboratory. A 1000 mL, three-necked (NS29, NS14, NS14) round-bottomed flask with a 40 mm egg-shaped, Teflon-coated magnetic stirrer is stored overnight in a 200 °C oven.

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The flask is removed from the oven, equipped with a NS29 glass stopper, a glass gas adaptor with an argon inlet (NS14) (Note 2), and a 100 mL pressure-equalizing addition funnel (NS14) dried overnight in the oven and topped with a NS14 glass stopper (**Figure 1**), and the argon inlet is connected to a Schlenk line. The setup is allowed to cool to ambient temperature while under reduced pressure (0.04 mmHg).

Figure 1. Setup for procedure A (Note 3)

Once at ambient temperature, the Schlenk line is switched to argon flow (Note 2) and the setup is maintained under a slight positive argon pressure. (Iodomethyl)triphenylphosphonium iodide (47 g, 88 mmol, 1.2 equiv) (Note 4) is added, then the NS14 and NS29 glass stoppers are replaced with rubber septa. Tetrahydrofuran (250 mL) (Note 5) is transferred into the flask by cannula, then stirring (500 rpm) is initiated, forming a cloudy off-white suspension. The rubber septum (NS29) is replaced with a glass thermometer adapter (NS29) equipped with a thermometer (range of –100 °C to 50 °C). (**Figure 2i**).

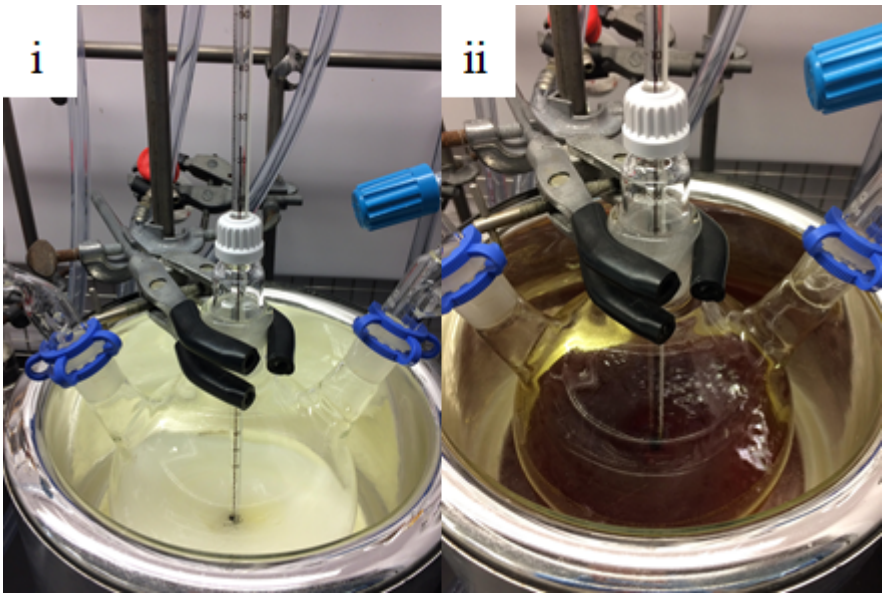

Figure 2. (i) Appearance of suspension after (iodomethyl)triphenyl-phosphonium iodide added and stirring initiated. (ii) Appearance of suspension after NaHMDS addition has been completed (Note 3)

The 100-mL addition funnel is charged with NaHMDS (2.0 M in THF, 45 mL, 88 mmol, 1.2 equiv) (Note 6) by two successive additions using a 25- mL gastight syringe. The solution of NaHMDS in THF is added to the white suspension through the dropping funnel in a dropwise manner over 10 min at 21 °C, which results in a clear red solution that transitions into a turbid dark red solution over 5 min (**Figure 2ii**). No discernable exotherm is observed over the course of the addition.

The walls of the addition funnel are rinsed three times with THF (3 x 5 mL), delivered by a 5-mL gastight syringe. The reaction flask is then placed in a Dewar vessel and cooled to –75 ºC (internal reaction temperature) using a dry ice-acetone mixture. This process takes around 15 minutes. To the rinsed 100-mL addition funnel is added a solution of *p*-methoxybenzaldehyde (10 g, 73 mmol) (Note 7) in THF (50 mL). The aldehyde solution is added dropwise to the reaction flask via the addition funnel over 1 h, with close monitoring to ensure the internal temperature does not rise above –75 ºC. The walls of the addition funnel are then rinsed with THF (2 x 5 mL), which are added dropwise over 5 min to the reaction flask. The addition funnel is removed and replaced by a NS14 rubber septum to allow for removal of aliquots. The clear deep red solution is stirred at – 75 ºC (internal temperature) until completion of the reaction (Note 8), which requires 1.5 h. Upon completion, the reaction is quenched with aqueous saturated solution of NH_4Cl (150 mL) added as a single portion using a 250-mL graduated cylinder. The dry ice-acetone bath is removed and the reaction mixture is allowed to warm to ambient temperature. The contents of the flask are diluted with *n*-pentane (150 mL) and are filtered by suction filtration through a celite pad (3 cm deep) on a 10-cm diameter sintered funnel (porosity 2, coarse) into a 1000 mL Erlenmeyer flask. The reaction flask is rinsed with diethyl ether (2 x 30 mL) and the celite pad is flushed with diethyl ether (150 mL). The resulting biphasic mixture is transferred into a 1-L separatory funnel. The organic layer is collected and the aqueous layer is extracted with diethyl ether (3 x 50 mL). The combined organic extracts are dried with $MgSO_4$ and filtered through a 10 cm diameter sintered funnel (porosity 2, coarse) into a 2-L single-necked, round-bottomed flask. The round-bottomed flask, covered with aluminum foil, is placed on a rotary evaporator and the solvent is removed at 250 to 35 mmHg at 30 °C resulting in the crude product as a viscous brown oil. The crude residue is subjected to flash column chromatography (Note 9) to give iodoalkene **1** (13.61 g, 72%, 99% purity; *Z:E* = 97:3) as a clear yellow oil (Notes 10 and 11).

B. *(Z)-2-(4-Methoxystyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane* (**2**). The reaction is performed with the lights turned off in the fume hood and the laboratory. A 250-mL, three-necked (NS29, NS14, NS14) round-bottomed flask with a 40-mm egg-shaped, Teflon-coated magnetic stirrer bar is stored overnight in a 200 °C oven. The flask is removed from the oven, equipped with a glass stopper (NS29), a glass gas adaptor with a argon inlet (NS14), and a 50-mL pressure-equalizing addition funnel (NS14) dried overnight in the oven topped with a glass stopper (NS14), and the argon adapter is

connected to a Schlenk line. The setup is allowed to cool to ambient temperature while under reduced pressure (0.15 mmHg). Once at ambient temperature, the reduced pressure is replaced by a slightly positive pressure of argon (Note 2), the NS29 and NS14 glass stoppers are replaced with rubber septa (**Figure 3**). To the reaction flask is added, successively by syringe, diethyl ether (80 mL) (Note 5), followed by (*Z*)-1-(2-iodovinyl)-4-methoxybenzene **1** (4.0 g, 15 mmol, 1 equiv) and finally 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (8.0 mL, 39 mmol, 2.6 equiv) (Note 12) and the NS29 rubber septum is replaced with a glass thermometer adapter equipped with a thermometer (range –100 °C to 50 °C). Stirring is initiated (500 rpm) and a clear pale-yellow solution is formed, which is cooled to –75 °C (internal temperature) using a dry ice-acetone bath over 10 min.

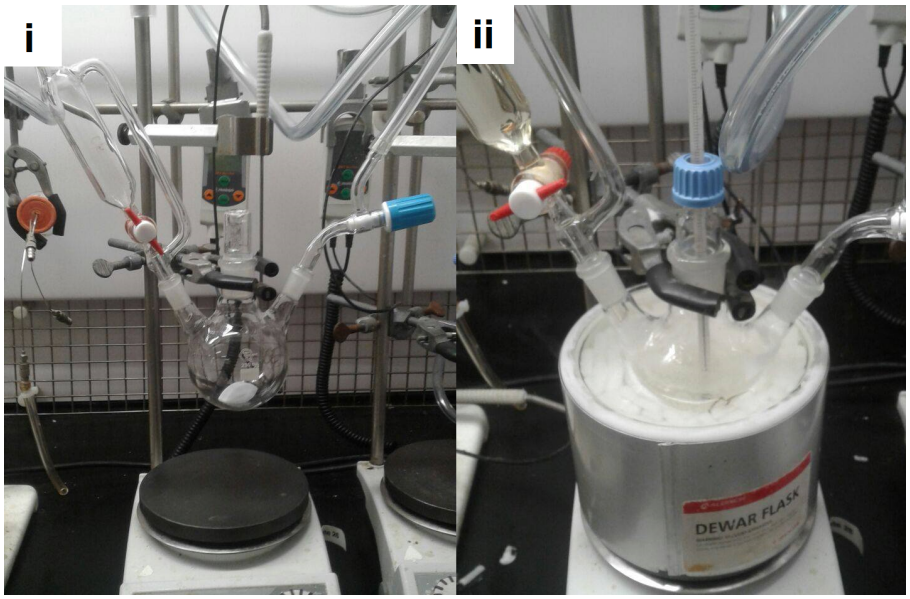

Figure 3. (i) Setup for procedure B. (ii) Dropwise addition of *n*-butyllithium at –75 °C (Note 3)

Once cooled, the dropping funnel is charged with *n*-butyllithium (1.51 M in hexanes, 23 mL, 35 mmol, 2.3 equiv) (Note 13) *via* a 30-mL gas tight syringe and is subsequently added dropwise at such a rate that maintains an internal reaction temperature below –75 °C. The addition is complete after 1.6 h, which results in formation of a clear pale-yellow solution. The walls of the

addition funnel are rinsed with diethyl ether (5 mL) delivered by syringe and the reaction mixture is stirred at –75 °C for a further 30 min. The reaction mixture is then removed from the dry-ice bath and is stirred for a further 2 h (Note 14). The reaction mixture is transferred to a 500-mL separatory funnel containing saturated aqueous NH_4Cl (120 mL) and deionized water (60 mL). The reaction flask is rinsed into the separatory funnel with diethyl ether (10 mL), deionized water (10 mL) and diethyl ether (10 mL). The organic layer is collected and the aqueous layer is extracted with EtOAc (3 x 60 mL). The organic layers are combined and washed with saturated aqueous NaCl solution (100 mL), dried with $MgSO_4$ (16 g, 5 min), and finally filtered through a 10-cm diameter sintered funnel (porosity 2, coarse) into a 500-mL, single-necked, round-bottomed flask at water aspirator pressure. The flask containing $MgSO_4$ is rinsed with EtOAc (3 x 20 mL) and filtered. The round-bottomed flask is placed on a rotary evaporator and the solvent is removed at 150 mmHg to 20 mmHg at 25 °C resulting in the crude product as a pale-yellow oil. The crude residue is subjected to column chromatography (Note 15) to give the desired alkenylboronic ester **2** (3.28 g, 82%, 99% purity) as a pale-yellow oil (Notes 16 and 17).

Notes

1. Prior to performing each reaction, a thorough hazard analysis and risk assessment should be carried out with regard to each chemical substance and experimental operation on the scale planned and in the context of the laboratory where the procedures will be carried out. Guidelines for carrying out risk assessments and for analyzing the hazards associated with chemicals can be found in references such as Chapter 4 of "Prudent Practices in the Laboratory" (The National Academies Press, Washington, D.C., 2011; the full text can be accessed free of charge at https://www.nap.edu/catalog/12654/prudent-practices-in-the-laboratory-handling-and-management-of-chemical. See also "Identifying and Evaluating Hazards in Research Laboratories" (American Chemical Society, 2015) which is available via the associated website "Hazard Assessment in Research Laboratories" at https://www.acs.org/content/acs/en/about/governance/committees/chemicalsafety/hazard-assessment.html. In the case of this procedure, the risk assessment should include (but not necessarily be limited to) an

evaluation of the potential hazards associated with tetrahydrofuran, *n*-pentane, diethyl ether, toluene, NH_4Cl (aq), (iodomethyl)-triphenylphosphonium iodide, sodium bis(trimethylsilyl) amide, *n*-butyllithium, isopropyl pinacolyl borate, *p*-methoxybenzaldehyde, silica gel, magnesium sulfate, as well as the proper procedures for working with dry ice and under an inert atmosphere.

2. Argon gas (Argon 5.0, Messer Austria GmbH, ≥99.999% purity) was used.
3. All photos have been provided by the submitters.
4. (Iodomethyl)triphenylphosphonium iodide was purchased from Manchester Organics (98%).
5. Anhydrous THF was used as purchased from Sigma-Aldrich (1 L, 250 ppm BHT as inhibitor). Anhydrous diethyl ether was used as purchased from Acros Organics (100 mL, AcroSeal over molecular sieves).
6. A solution of NaHMDS was purchased as a 2.0 M solution in THF from Alfa Aesar and titrated three times for an average of 2.0 M. The titration was performed as described by Duhamel and Plaquevent.[2]
7. 4-Methoxybenzaldehyde was purchased from Alfa Aesar, 98% GC. Before use in the reaction, a 0.1-mL sample was analyzed by ^{1}H NMR spectroscopy. No carboxylic acid autoxidation product was detected; hence this reagent was used as received.
8. The reaction is monitored every 30 mins by TLC and ^{1}H NMR spectroscopy. TLC is performed on aluminum-backed silica gel plates eluting in 5% diethyl ether in *n*-pentane, visualized first with UVA and then stained with *p*-anisaldehyde. The R_f of *Z*-iodo-olefin **1** is 0.6 and the compound stains purple (Figure 4). For analysis by ^{1}H NMR spectroscopy, 0.1 mL aliquots are withdrawn by needle and syringe, and are injected into a vial containing 1 mL of $CDCl_3$ and 1 mL aqueous saturated solution of $NaHCO_3$. The layers are mixed thoroughly then the $CDCl_3$ layer is collected and transferred into an NMR tube.

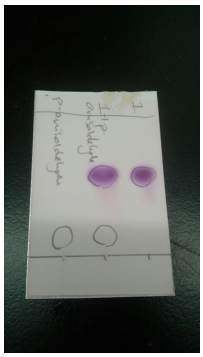

Figure 4. TLC plate showing *p*-methoxybenzaldehyde (left); co-spot (middle); and *Z*-iodoalkene 1 (right) (Note 3)

9. Column chromatography is performed using 240 g of Merck 60 (230-400 mesh) silica gel in a 70-mm diameter column.[3] An initial elution with 100% *n*-pentane (500 mL) does not contain product and is discarded. Fraction of 50 mL are collected after this point, eluting successively with 100% *n*-pentane(250 mL), followed by 1% diethyl ether in *n*-pentane (1250 mL), and finally 2% diethyl ether in *n*-pentane (1000 mL) for a total of 50 fractions. The desired product is obtained in fractions 2–48. Fractions containing the product are combined and the solvent is removed by rotary evaporation (250 mmHg at 30 °C for the bulk of the solvent, followed by 35 mmHg at 30 °C for the residual solvent).
10. The product (**1**) possesses the following properties: bp 102–108 °C (0.08 mmHg); ^{1}H NMR (700 MHz, $CDCl_3$) δ: 3.84 (s, 3H), 6.42 (d, J = 8.6 Hz, 1H), 6.92 (d, J = 8.6 Hz, 2H), 7.24 – 7.28 (m, 1H), 7.64 (d, J = 8.2 Hz, 2H); ^{13}C NMR (175 MHz, $CDCl_3$) δ: 55.4 (CH_3), 76.9 (CH), 113.7 (2 CH), 129.3 (C_q), 130.0 (2 CH), 137.9 (CH), 159.8 (C_q); GCQMS (EI^+) m/z calculated for C_9H_9IO $[M]^{\bullet+}$ 260.0, found 260.0. IR (thin film): ν_{max} = 3062, 1607, 1508, 1253, 1178, 1032 cm^{-1}. Purity was determined by quantitative ^{1}H NMR spectroscopy using dibromomethane as an internal standard to be 99% by weight (*Z*:*E* = 97:3).
11. A second run on an identical scale provided 13.55 g (72%) of the product.
12. 2-Isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane was purchased from Alfa Aesar (98%). This reagent was used as received. Using less than 2.5 equiv of this reagent reduces the yield of the desired product.
13. *n*-Butyllithium was purchased as a 1.6 M solution from Sigma-Aldrich and titrated three times in THF using diphenylacetic acid as the titrant for an average of 1.51 M.

14. TLC was performed on aluminum-backed silica gel plates eluting with 100% toluene, visualized first with UVA and then stained with *p*-anisaldehyde. The R_f of *Z*-alkenylboronic ester **2** is 0.2 and the compound stains purple (Figure 5). As shown below, traces of starting material remain by TLC and do not disappear completely even after prolonged reaction time.

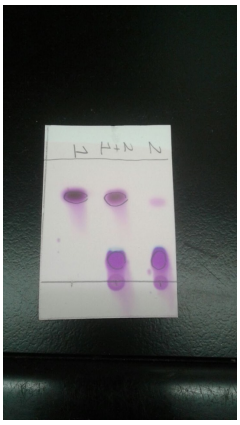

Figure 5. TLC plate showing *Z*-iodoalkene 1 (left); co-spot (middle); and the *Z*-alkenyl boronic ester 2 (right) (Note 3)

15. Column chromatography is performed using 145 g of Merck 60 (230-400 mesh) silica gel in a 55-mm diameter column.[3] An initial elution with 97:3 *n*-pentane:diethyl ether (950 mL) does not contain product and that eluent is discarded. The product elutes in the next 3.3 L of 85:15 *n*-pentane:diethyl ether. The solvent was removed by rotary evaporation (250-20 mmHg at 25 °C for the bulk of the solvent with the remainder at 0.15 mmHg at 23 °C for 1.5 h).
16. The product (**2**) possesses the following properties: bp 128–132 °C (0.8 mmHg); ^{1}H NMR (600 MHz, $CDCl_3$) δ: 1.30 (s, 12H), 3.82 (s, 3H), 5.46 (d, J = 14.9 Hz, 1H), 6.83 – 6.85 (m, 2H), 7.15 (d, J = 14.9 Hz, 1H), 7.50–7.59 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ: 24.9 (4 CH_3), 55.4 (CH_3), 83.5 (2 C_q), 113.4 (3 CH), 130.4 (2 CH), 131.4 (C_q), 148.2 (CH), 159.7 (C_q); HRMS (ESI$^+$) m/z calculated for $C_{15}H_{22}{}^{11}BO_3$ $[M + H]^+$: 261.1657, found 261.1655. IR (thin film): ν_{max} = 2979, 2936, 1605, 1511, 1317, 1249, 1142, 841 cm^{-1}. Purity was determined by quantitative ^{1}H NMR spectroscopic analysis using dibromomethane as an internal standard to be 99% by weight.
17. A second run on an identical scale provided 3.22 g (81%) of the product.

Working with Hazardous Chemicals

The procedures in *Organic Syntheses* are intended for use only by persons with proper training in experimental organic chemistry. All hazardous materials should be handled using the standard procedures for work with chemicals described in references such as "Prudent Practices in the Laboratory" (The National Academies Press, Washington, D.C., 2011; the full text can be accessed free of charge at http://www.nap.edu/catalog.php?record_id=12654). All chemical waste should be disposed of in accordance with local regulations. For general guidelines for the management of chemical waste, see Chapter 8 of Prudent Practices.

In some articles in *Organic Syntheses*, chemical-specific hazards are highlighted in red "Caution Notes" within a procedure. It is important to recognize that the absence of a caution note does not imply that no significant hazards are associated with the chemicals involved in that procedure. Prior to performing a reaction, a thorough risk assessment should be carried out that includes a review of the potential hazards associated with each chemical and experimental operation on the scale that is planned for the procedure. Guidelines for carrying out a risk assessment and for analyzing the hazards associated with chemicals can be found in Chapter 4 of Prudent Practices.

The procedures described in *Organic Syntheses* are provided as published and are conducted at one's own risk. *Organic Syntheses, Inc.*, its Editors, and its Board of Directors do not warrant or guarantee the safety of individuals using these procedures and hereby disclaim any liability for any injuries or damages claimed to have resulted from or related in any way to the procedures herein.

Discussion

Olefination reactions (i.e. those which unite two separate groups by generating a new C=C bond) are essential synthetic processes. The most well established olefination is Wittig reaction.[4] The Wittig reaction involves the union of an aldehyde or ketone with a (usually triphenyl) phosphorane. Phosphoranes have been classified as stabilized, non-stabilized and semi-stabilized, depending upon the nature of the substituents on the carbon of the P=C group. Stabilized phosphoranes can generally be stored and dispensed

as needed, whereas semi-stabilized and non-stabilized phosphoranes are usually generated *in situ* by deprotonation of the phosphonium salt. Wittig reactions can generate predominantly *E* or *Z*-isomers of alkene products, or mixtures, and proportions of *E* and *Z*-isomers are determined by both substrate structures (the type of phosphorane deployed is particularly important in this regard) and the reaction conditions.[5] Stabilized phosphoranes generally give predominantly *E*-alkenes whereas non-stabilized phosphoranes generally give predominantly *Z*-alkenes, particularly with solvents such as DMF.[6] The Schlosser modification favors the formation of *E*-alkenes from non-stabilized phosphoranes.[7]

The Stork-Zhao-Wittig olefination enables the synthesis of *Z*-iodoalkenes by reaction between an aldehyde and *in situ*–generated iodomethylene triphenylphosphorane.[8] *Z*-Iodoalkenes are useful building blocks for the synthesis of substituted alkenes, and are used widely in total synthesis. They are useful as electrophilic cross-coupling partners and, through metal–iodine exchange, for the generation of nucleophilic alkenylmetal species. Alternative methods for the synthesis of *Z*-iodoalkenes include di-imide reductions of iodoalkynes,[9] hydroindation-iodination of alkynes,[10] conjugate nucleophilic addition to alkynoic esters,[11] and iodinative destannylation,[12] desilylation[13] and deborylation.[14]

The original Stork-Zhao method reports that HMPA is necessary for high levels of *Z*-selectivity.[7] Many highly *Z*-selective Stork-Zhao-Wittig olefinations have been subsequently reported that proceed at low temperature in the absence of this carcinogenic additive. Here we show that *para*-methoxybenzaldehyde can be Stork-Zhao-Wittig olefinated in good yield with high *Z*-selectivity. The protocol described is a variation of a reported procedure by Cheung and Yudin.[15] When the reaction was run in DMF–a solvent reported to deliver high *Z*-selectivity[5] at temperatures between –60 °C and 0 °C, the 1,1-diiodoalkene was formed as a side product in 5-15% of the product mixture.[16] This compound has the same R_f as the desired *Z*-iodoalkene, which is difficult to separate from the desired product. We recommend that the reaction be performed in THF.

The conversion of *Z*-iodoalkene **1** into *Z*-alkenylboronic acid pinacol ester **2** is also described. The process involves lithium-iodine exchange with 2.3 mol equiv of *n*-BuLi, to generate the *Z*-lithioalkene intermediate, which is trapped *in situ* with 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane. Related lithium-halogen exchange reactions and boronic acid/ester formations to the one described here have been reported.[17] This compound has been previously prepared by *trans*-hydroboration of the *para*-

methoxyphenylacetylene[18] and by *Z*-selective olefin metathesis of *para*-methoxystyrene.[19]

Z-Alkenylboronic acid pinacol esters have been prepared in several ways, including Rh(I)-catalyzed *trans*-hydroboration of alkynes,[20] from alkynylboronic esters by hydrozirconation then hydrolysis,[21] by way of *Z*- selective olefin metathesis, and by alkyl radical addition to ethynylboronic acid pinacol ester.[22] *Z*-Alkenylboronic acids and their derivatives have been widely used as nucleophilic building blocks in Suzuki-Miyaura couplings.

Notes on Stability

The authors recommend storage of *Z*-iodoalkenes and *Z*-boronic acid pinacol esters at –20 °C in the dark, under which conditions these compounds show no change. A sample of *Z*-iodoalkene **1** in a colorless glass vial was left for 18 h at ambient temperature in a laboratory with fluorescent lighting and showed no sign of decomposition or *Z*/*E* isomerization. Under the same conditions, *Z*-boronic acid pinacol ester **2** underwent a change in isomer ratio from 98:2 to 94:6.

References

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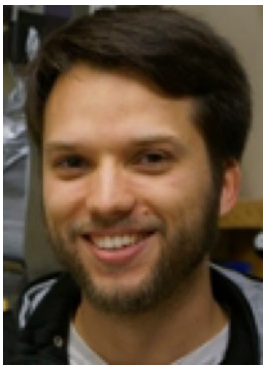
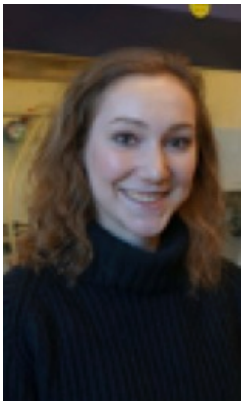
Appendix
Chemical Abstracts Nomenclature (Registry Number)

NaHMDS: Sodium bis(trimethylsilyl)amide; (1070-89-9)
(Iodomethyl)triphenylphosphonium iodide; (3020-28-8)
4-Methoxybenzaldehyde; (123-11-5)
2-Isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane; (61676-62-8)
n-Butyllithium; (109-72-8)



Mathieu André Morin is from New Brunswick, Canada. After obtaining his B.Sc. at the University of Ottawa, he proceeded to complete his Ph. D. studying gold Lewis acid chemistry and photochemistry under the supervision of Prof. Louis Barriault. Mathieu's interest lays in mechanistic studies and synthetic method development.



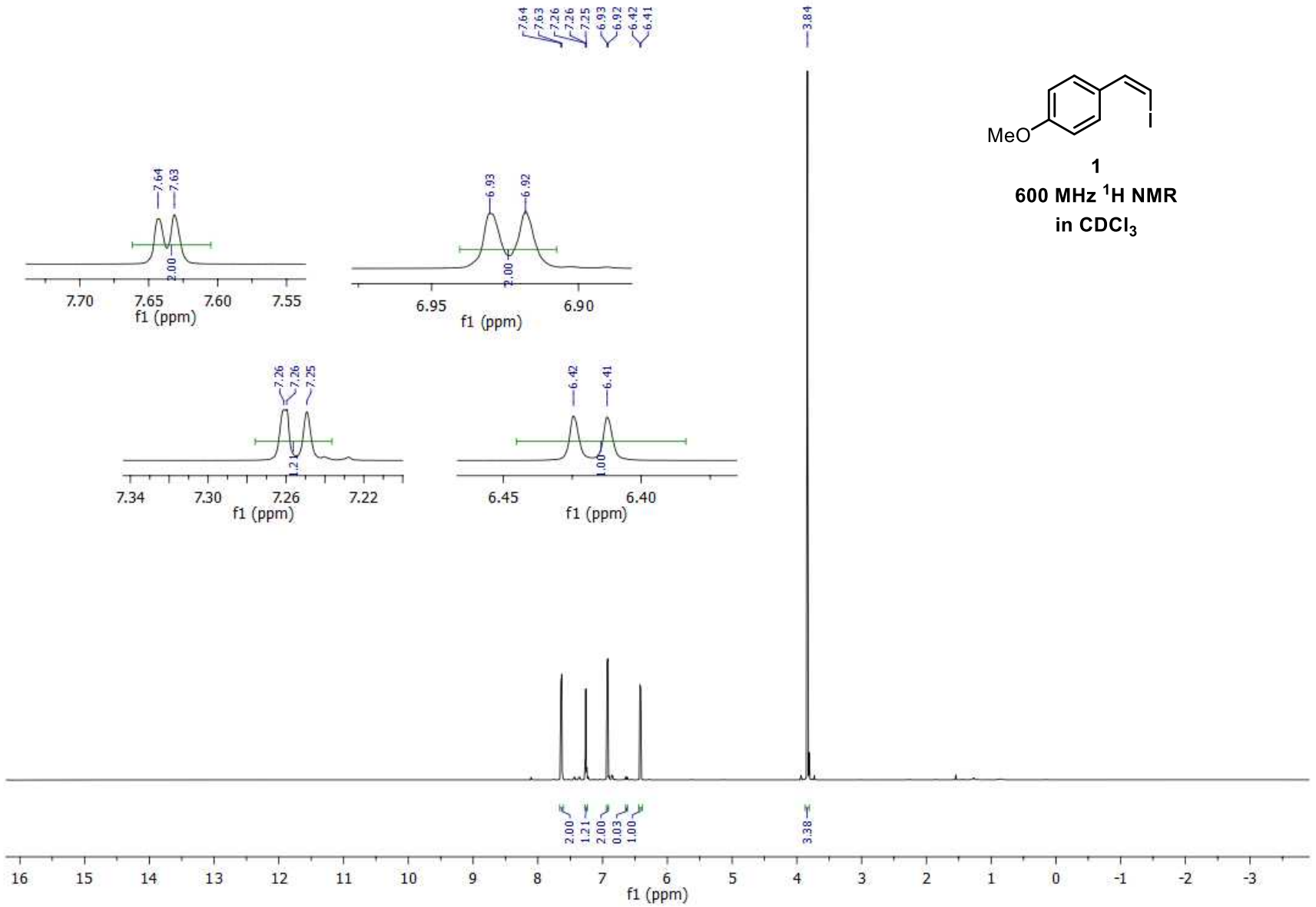
Samantha Rohe is from Nova Scotia, Canada. Upon completion of her BSc at the University of Ottawa, she moved to Australia to work with the Sherburn group as a visiting researcher. After learning the tricks to handling hydrocarbons and moving batch reactions into flow, she returned to the University of Ottawa to complete her MSc in photochemistry.

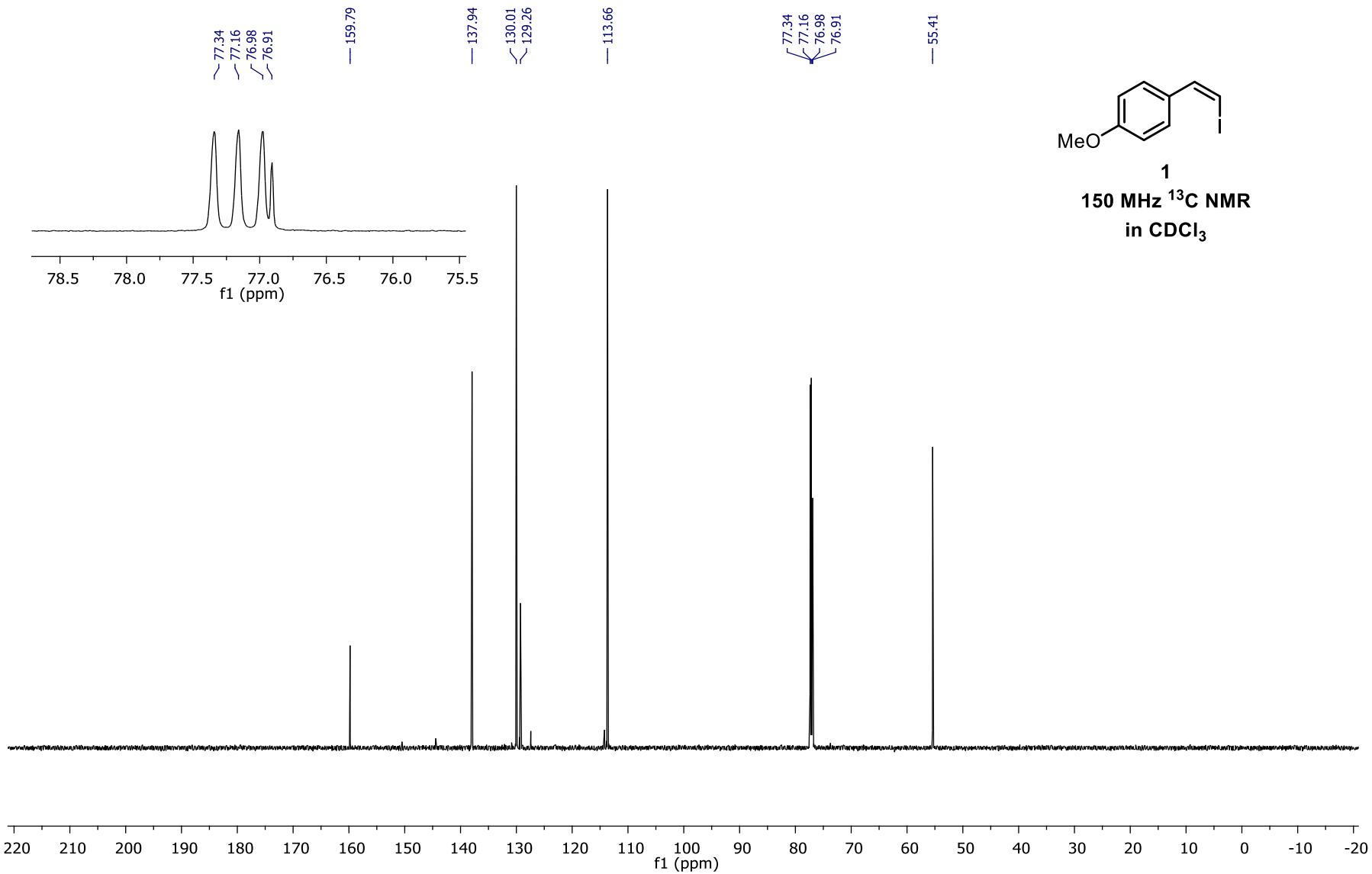
Cecile Elgindy is from Sydney, Australia and received her B.Sc. (Honours) at the University of Sydney. She moved to The Australian National University, Canberra where she is currently undertaking postgraduate studies under the supervision of Professor Michael Sherburn. The main focus of Cecile's research is the synthesis of novel acyclic π-bond rich hydrocarbons.

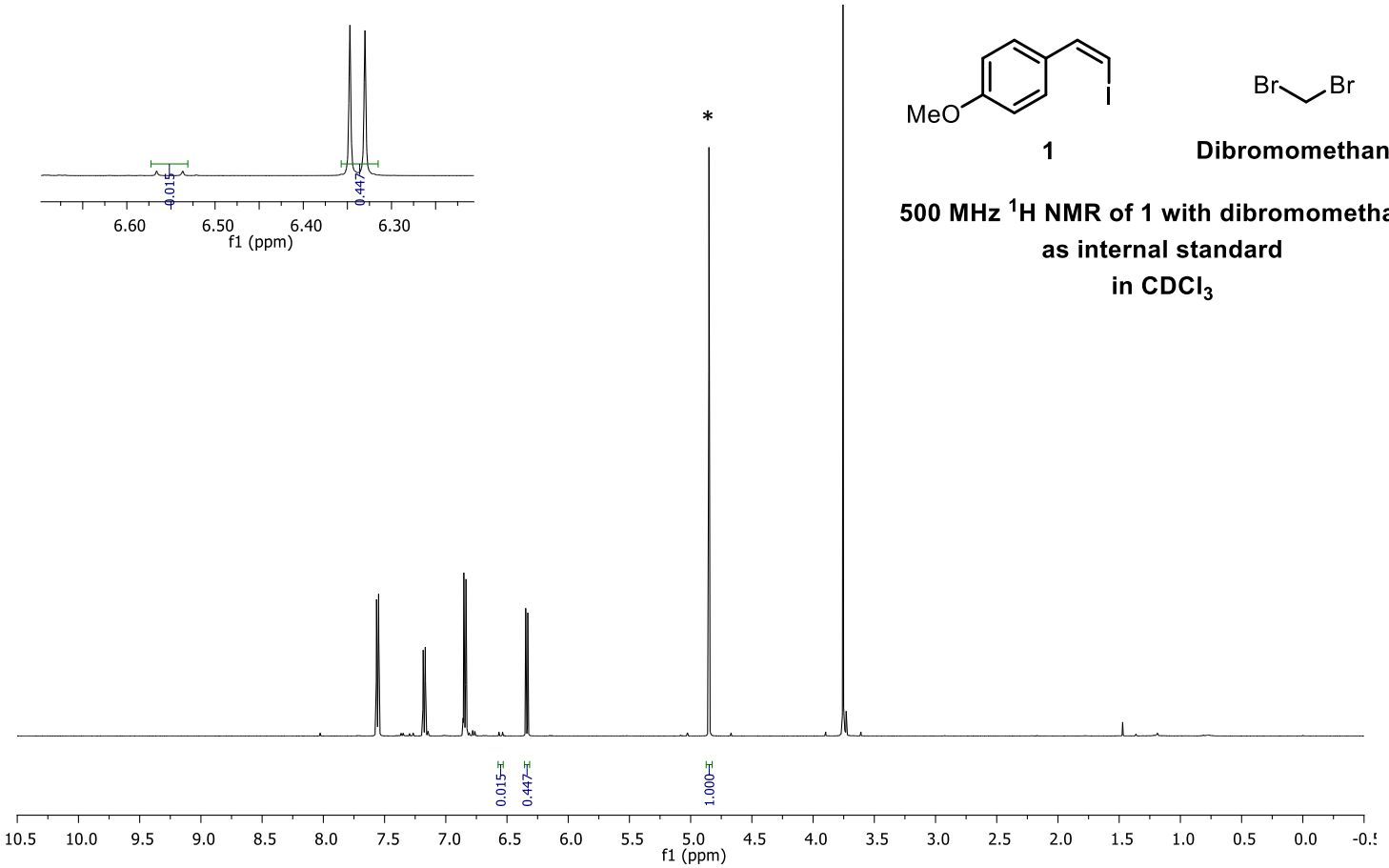
Michael Sherburn studied chemistry at the University of Nottingham, received his Ph.D. with John Murphy at Nottingham, and did post-doctoral research with Lew Mander in Canberra at the Australian National University (ANU). He held academic positions at Massey University in New Zealand and the University of Sydney before being appointed at the Research School of Chemistry, ANU in 2002. His awards include the Birch Medal of the Royal Australian Chemical Institute.

Alexander Preinfalk obtained his M.Sc. from the University of Vienna in 2016 working on palladium and gold catalysis. He is currently a Ph.D. student in the group of Prof. Nuno Maulide, where his doctoral research is aimed at carbocation chemistry, asymmetric palladium catalysis and total synthesis.

Martin Berger is from Gresten, Austria. After obtaining his M.Sc. at the University of Vienna, he joined the group of Professor Nuno Maulide to complete his PhD with focus on the synthesis of natural products and analogues utilizing C-H activation and the development of new synthetic methods.


7.64
7.63
7.26
7.26
7.25
6.93
6.92
6.42
6.41
3.84
MeO
1
600 MHz 1H NMR
in CDCl3
7.64
7.63
2.00
7.70
7.65
7.60
7.55
f1 (ppm)
6.93
6.92
2.00
6.95
6.90
f1 (ppm)
7.26
7.26
7.25
1.21
7.34
7.30
7.26
7.22
f1 (ppm)
6.42
6.41
1.00
6.45
6.40
f1 (ppm)
2.00
1.21
2.00
0.03
1.00
3.38
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)


77.34
77.16
76.98
76.91
159.79
137.94
130.01
129.26
113.66
77.34
77.16
76.98
76.91
55.41
MeO
1
150 MHz 13C NMR
in CDCl3
78.5
78.0
77.5
77.0
76.5
76.0
75.5
f1 (ppm)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)



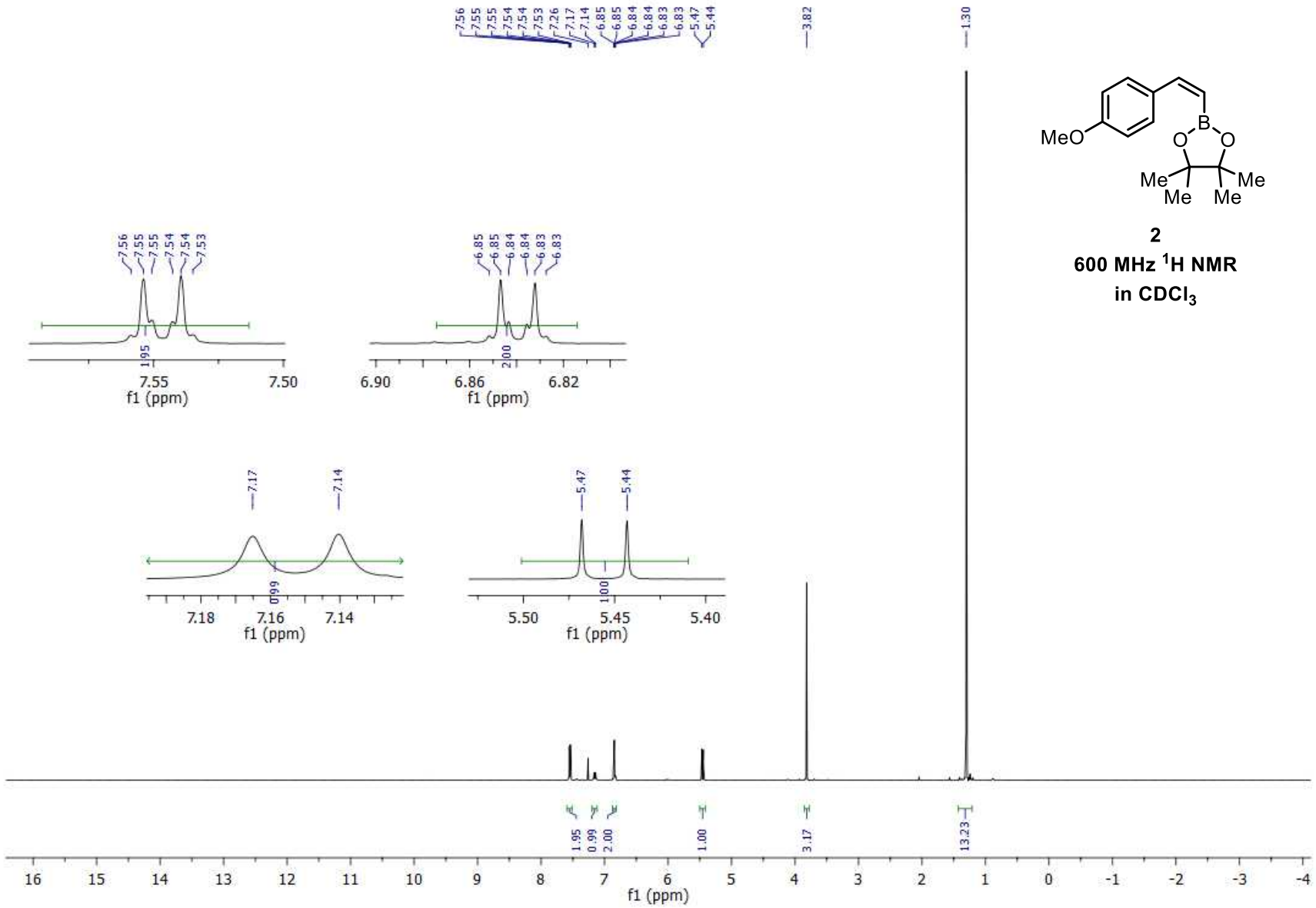
1

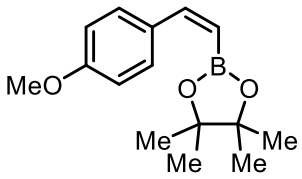
Dibromomethane *

500 MHz ^{1}H NMR of 1 with dibromomethane as internal standard in $CDCl_3$

$$\frac{Sample\ integral\ \times No.protons\ std.\ \times\ mass\ std\ \times MW\ sample}{Standard\ integral\ \times No.protons\ sample\ \times mass\ sample\ \times MW\ std} \times purity\ std = Purity\ sample$$

$$\frac{(0.447 + 0.015)\ \times\ 2\ \times 36.1\ \times 260.07}{1\ \times 1\ \times 50\ \times 173.83} \times 99 = 98.8\,\% \approx 99\,\%$$

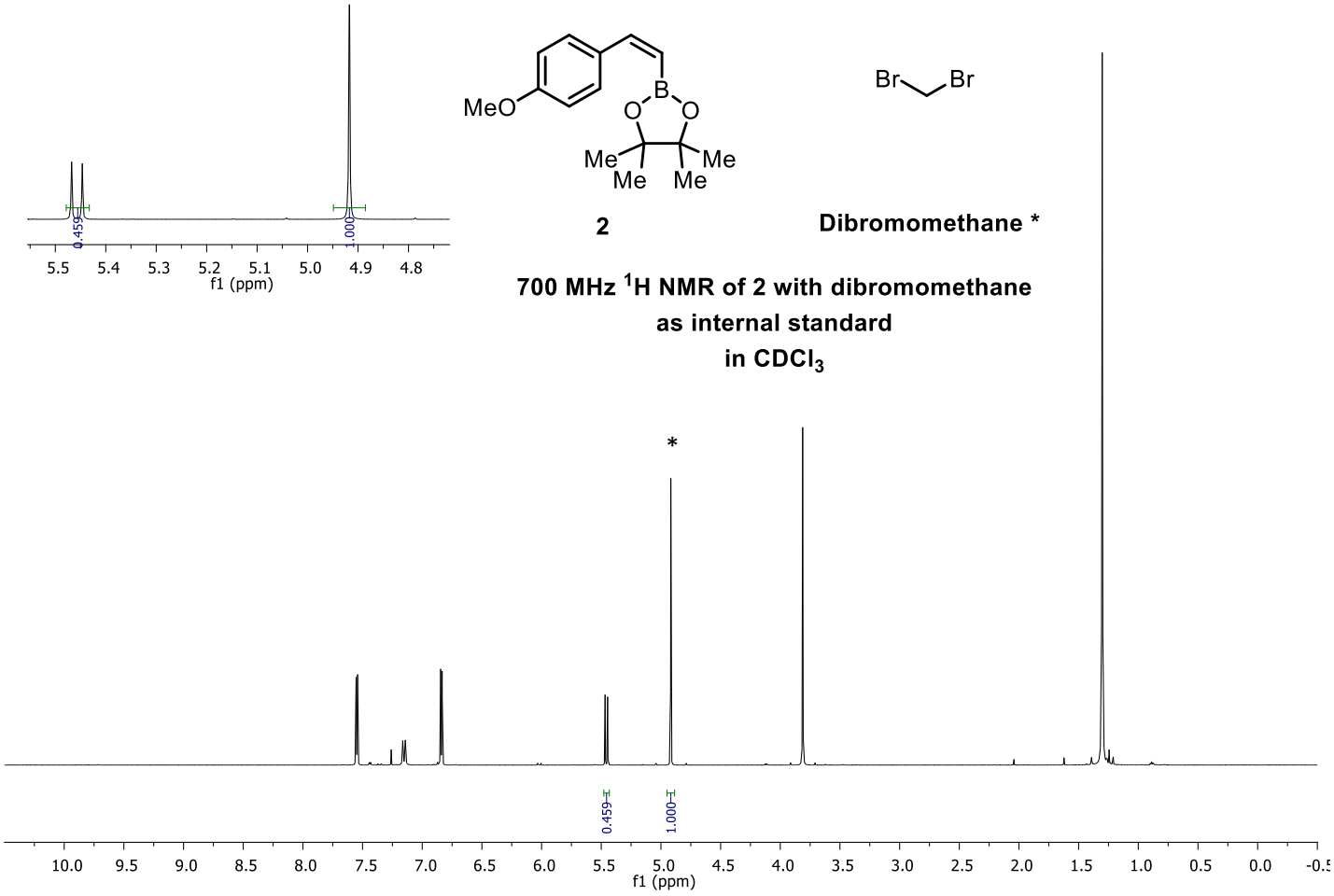

7.56
7.55
7.55
7.54
7.54
7.53
7.26
7.17
7.14
6.85
6.85
6.84
6.84
6.83
6.83
5.47
5.44
3.82
1.30
MeO
B
O
O
Me
Me
Me
Me
2
600 MHz 1H NMR
in CDCl3
1.95
7.55
7.50
f1 (ppm)
2.00
6.90
6.86
6.82
f1 (ppm)
0.99
7.18
7.16
7.14
f1 (ppm)
1.00
5.50
5.45
5.40
f1 (ppm)
1.95
0.99
2.00
1.00
3.17
13.23
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
-4
f1 (ppm)



2

150 MHz ^{13}C NMR

in $CDCl_3$



$$\frac{Sample\ integral\ \times No.protons\ std.\ \times\ mass\ std\ \times MW\ sample}{Standard\ integral\ \times No.protons\ sample\ \times mass\ sample\ \times MW\ std} \times purity\ std = Purity\ sample$$

$$\frac{0.459\ \times\ 2\ \times 48.2\ \times 260.14}{1\ \times 1\ \times 66.1\ \times 173.83} \times 99 = 99.2\ \%\ \approx 99\ \%$$