Catalytic cross-dimerisation giving reactive borylated polyenes toward Cross-Coupling

Masafumi Hirano,* Ayumi Kuramochi, Keita, Shimada, Nobuyuki Komine, Sayori Kiyota, and Stephen A. Westcott

Abstract: A series of borylated conjugated trienes and skipped dienes is prepared by Ru-catalysed cross-dimerisation using alkynyl-, dienyl-, and vinyl boronate. As an example, cross-dimerisation of 1-pentynyl boronic acid diisopropyl ester (**2a**) with methyl (*E*)-pentadienoate (**3a**) was catalysed by [Ru(η^6-naphthalene)(η^4-1,5-cyclooctadiene)] (**1**: 10 mol %) at room temperature for 24 h produced a borylated conjugated triene, methyl (2*E*,4*E*,6*E*)-(7-diisopropoxylboraneyl)-6-propylhepta-2,4,6-trienoate in 93% yield. These products are used for synthetic building blocks of polyene substructures by subsequent Pd-catalysed cross-coupling in a one-pot vessel without deprotection. For example, after treatment of **2a** with **3a** in the presence of **1** in benzene for 24 h at room temperature, the subsequent cross-coupling of the product with phenyl iodide catalyzed by [Pd(PPh_3)$_4$] (**9**: 8 mol %)/NaOMe (1.2 equiv) in the same vessel produced methyl 7-phenyl-6-propylhepta-2,4,6-trienoate (**10**) in 79% yield [(2*E*,4*E*,6*E*)-**10**/(2*E*,4*E*,6*Z*)-**10** = 5/1]. This procedure provides a straightforward and efficient access to polyene substructures with high step economy.

Abbreviations used in this paper: cod: cyclooctadiene, Cp: cyclopentadienyl, dan: 2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinin-2-yl, dba: dibenzylidene acetone, dmpu: *N,N'*-dimethylpropyleneurea, dppf: 1,1'-bis(diphenylphosphino)ferrocene, mida: *N*-methyliminodiacetato, pin: pinacolato, thf: tetrahydrofuran, TMS: trimethylsilyl.

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Experimental Procedures

1. General

All procedures described in this paper were carried out under a nitrogen or argon atmosphere by use of Schlenk and vacuum line techniques. Unless otherwise noted, all reactants or reagents were obtained from commercial suppliers and stored under a nitrogen atmosphere after three freeze-pump-thaw cycles. Solvents are dried and deoxygenized by Glass Contour Ultimate Solvent Purification System. [D_6]Benzene was dried over sodium wire and stored under vacuum, and was transferred into an NMR tube by distillation prior to use. [Ru(η^6-naphthalene)(η^4-1,5-cod)] (**1**),[S1] 1-pentynyl boronic acid diisopropyl ester (**2a**),[S2] phenylethynyl boronic acid diisopropyl ester (**2b**),[S2] phenylethynyl boronic acid dimethyl ester (**2c**),[S3] phenylethynyl boronic acid pinacol ester (**2d**),[S4] pentynyl boronic acid pinacol ester (**2e**),[S5] and butadienyl boronic acid pinacol ester (**3d**)[S6] were prepared according to literature methods. Vinyl boronic acid pinacol ester (**6a**) and vinyl boronic acid dibutyl ester (**6b**) were purchased from commercial suppliers.

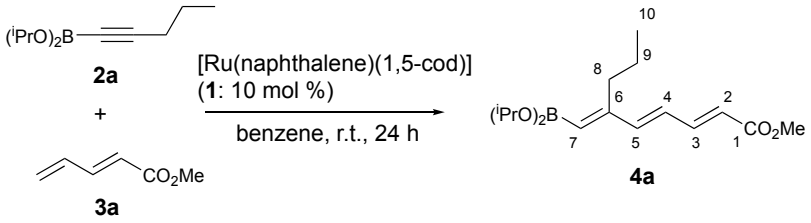
All work-up and purification procedures were carried out with reagent-grade solvents in air. Analytical thin-layer chromatography was performed using Merck silica gel 60 F254 precoated plates (0.25 mm). The developed chromatogram was analysed by UV lamp or phosphomolybdic acid/sulfuric acid solution. Flush column chromatography was performed with Merck silica gel 60. Preparative scale HPLC was performed with a Japan Analytica Industry LaboACE LC-5060 equipped with JAIGEL-1H and JAIGEL-2HR tandem columns using chloroform as the eluent.

^{1}H and ^{13}C NMR spectra were measured on a JEOL ECX-400P spectrometer (400 MHz for ^{1}H). The chemical shifts were reported from tetramethylsilane (0.00 ppm). Coupling constants for the second-order splitting were estimated by gNMR.[S7] GC and GC-MS were performed on Shimadzu GC-2014 (FID) and Shimadzu GCMS-2010 (EI) instruments, respectively, equipped with a TC-1 column (0.25 mm i.d. x 30 m). HRMS (APCI) analysis was performed on a Bruker Daltonics micrOTOF-QII instrument.

[S1] M. A. Bennett, H. Neumann, M. Thomas, X.-Q Wang, P. Pertici, P. Salvadori, G. Vitulli, *Organometallics*, 1991, **10**, 3251.
[S2] H. C. Brown, N. G. Bhat, M. Srebnik, *Tetrahedron Lett.*, 1988, **29,** 2631.
[S3] P. K. Elkin, V. V. Levin, A. D. Dilman, M. I. Struchkova, P. A. Belyakov, D. E. Arkhipov, A. A. Korlyukov, V. A. Tartakovsky, *Tetrahedron Lett.*, **2**011, **52**, 5259.
[S4] Y. Nishihara, JP2008-74711.
[S5] Y. Nishihara, Y. Okada, J. Jiao, M. Suetsugu, M. T. Lan, M. Kinoshita, M. Iwasaki, K. Takagi, *Angew. Chem. Int. Ed.,* 2011, **50**, 8660.
[S6] J. R. Coombs, L. Zhang, J. P. Morken, *Org. Lett.*, 2015, **17**, 1708.
[S7] P. H. M. Budzelar, gNMR: NMR simulation program, ver. 5.0.6.0; IvorySoft, 2006.

2. Cross-dimerisations of alkynyl boronates with conjugated dienes

2-1. Reaction of 1-pentynyl boronic acid diisopropyl ester (2a) with methyl penta-2,4-dienoate (3a).



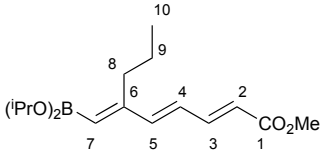
(a) To an NMR tube were added [D_6]benzene (600 μL), 1-pentynyl boronic acid diisopropyl ester (**2a**) (20.25 μL, 0.08840 mmol), methyl penta-2,4-dienoate (**3a**) (10.25 μL, 0.08812 mmol), and [Ru(η^6-naphthalene)(η^4-1,5-cod)] (**1**) (2.99 mg, 0.00886 mmol). The solution was allowed to react at room temperature and the progress of the reaction was monitored by ^{1}H NMR. After 24 h, formation of (2*E*,4*E*,6*E*)-**4a** was observed in 93% yield.

(b) A similar treatment using [D_2]dichloromethane (600 μL), **2a** (20.5 μL, 0.0894 mmol), **3a** (10.4 μL, 0.00873 mmol) and **1** (2.94 mg, 0.00873 mmol) at room temperature for 7 h gave (2*E*,4*E*,6*E*)-**4a** in 50% yield.

(c) **2a** (140.0 μL, 0.614 mmol), **3a** (93.0 μL, 0.796 mmol) and **1** (20.26 mg, 0.0601 mmol) were dissolved in benzene (1 mL) in a Schlenk tube (25 mL). Reaction at room temperature for 24 h gave a black liquid. This compound was used for cross-coupling reaction without isolation.

Because the product **4a** was decomposed during the purification process, this compound was characterised by NMR experiments in [D_6]benzene.

methyl (2*E*,4*E*,6*E*)-7-(diisopropoxyboraneyl)-6-propylhepta-2,4,6-trienoate [(2*E*,4*E*,6*E*)-4a]:



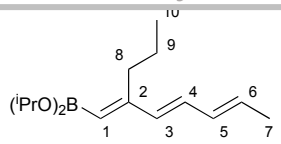
^{1}H NMR (400 MHz, [D_6]benzene, r.t.): δ 7.52 (dd, $^3J_{H,H}$=15.6, 11.0 Hz, 1H; 3-C*H*), 6.29 (dd, $^3J_{H,H}$=15.1, 11.0 Hz, 1H; 4-C*H*), 6.28 (d, $^3J_{H,H}$=15.1 Hz, 1H; 5-C*H*), 5.91 (d, $^3J_{H,H}$=15.6 Hz, 1H; 2-C*H*), 5.54 (s, 1H; 1-C*H*), 4.43 (sept, $^3J_{H,H}$=6.2 Hz, 2H; OC*H*Me$_2$), 3.45 (s, 3H; CO_2*Me*), 2.59 (t, $^3J_{H,H}$=7.7 Hz, 2H; 8-CH_2), 1.55 (sext, $^3J_{H,H}$=7.7 Hz, 2H; 9-CH_2), 1.13 (d, $^3J_{H,H}$=6.2 Hz, 12H; OCH*Me*$_2$), 0.98 (t, $^3J_{H,H}$=7.4 Hz, 3H; 10-*Me*); ^{13}C{^{1}H} NMR (100 MHz, [D_6]benzene, r.t.): δ 167.0 (s), 155.3 (s), 146.3 (s), 145.2 (s), 142.9 (s), 126.0 (s), 121.5 (s), 65.5 (s), 51.1 (s), 32.7 (s), 24.5 (s), 23.7 (s), 14.4 (s).

2-2. Reaction of 1-pentynyl boronic acid diisopropyl ester (2a) with 1,3-pentadiene (3b).

Because the product **4b** was decomposed during the purification process, this compound was characterised by NMR experiments in [D_6]benzene.

Yield: 36% (NMR).

(1*E*,3*E*,5*E*)-1-(diisopropoxyboraneyl)-2-propylhepta-1,3,5-triene [(1*E*,3*E*,5*E*)-4b]:



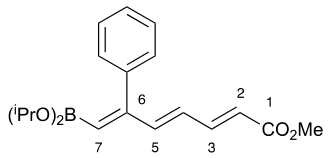
^{1}H NMR (400 MHz, [D$_6$]benzene, r.t.): δ 6.48 (ddd, $^3J_{H,H}$=15.4, 10.6 Hz, $^4J_{H,H}$=4.4 Hz, 1H; 4-C*H*), 6.28 (d, $^3J_{H,H}$=14.0 Hz, 1H; 3-C*H*), 5.99 (dd, $^3J_{H,H}$=15.2, 10.4 Hz, 1H; 5-C*H*), 5.60 (dqd, $^3J_{H,H}$=15.8, 6.0 Hz, $^4J_{H,H}$=4.4 Hz, 1H; 6-C*H*), 5.58 (s, 1H; 1-C*H*), 4.45 (sept, $^3J_{H,H}$=6.0 Hz, 2H; OC*H*Me$_2$), 2.80 (t, $^3J_{H,H}$=7.7 Hz, 2H; 8-C*H*$_2$), 1.55 (m, 2H; 9-C*H*$_2$), 1.17 (d, $^3J_{H,H}$=6.2 Hz, 12H; OCH*Me*$_2$), 1.15 (t, $^3J_{H,H}$=6.4 Hz, 3H; 10-*Me*), 0.94 (d, $^3J_{H,H}$=6.0 Hz, 3H; 7-*Me*).

2-3. Reaction of 2-phenylethynyl boronic acid diisopropyl ester (2b) with methyl 2,4-pentadienoate (3a).

Because the products **4c** and **5c** were decomposed during the purification process, this compound was characterised by NMR experiments in [D$_6$]benzene.

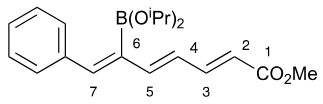
Yield: 52% (NMR). **4c**/**5c** = 37/63.

methyl (2*E*,4*E*,6*E*)-7-(diisopropoxyboraneyl)-6-phenylhepta-2,4,6-trienoate [(2*E*,4*E*,6*E*)-4c]:



^{1}H NMR (400 MHz, [D$_6$]benzene, r.t.): δ 7.50 (dd, $^3J_{H,H}$=15.5, 10.9 Hz, 3-C*H*), 7.18-7.28 (m, *Ph* overlapped with resonances of **5c**), 6.43-6.54 (obscured by overlapping with **5c**, 5-C*H*), 6.09 (dd, $^3J_{H,H}$=15.5, 11.5 Hz, 1H; 4-C*H*), 5.82 (s, 1H, obscured by overlapping with reactant, 7-C*H*), 5.59 (d, $^3J_{H,H}$=15.5 Hz, 1H; 2-C*H*), 4.37 (sept, $^3J_{H,H}$=5.8 Hz, 2H; C*H*Me$_2$), 3.36 (s, 3H; CO$_2$*Me*), 0.95 (d, $^3J_{H,H}$=6.3 Hz, 12H; CH*Me*$_2$).

methyl (2*E*,4*E*,6*E*)-6-(diisopropoxyboraneyl)-7-phenylhepta-2,4,6-trienoate [(2*E*,4*E*,6*E*)-5c]:



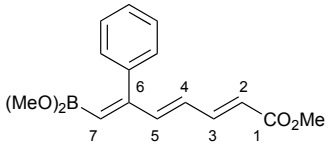
^{1}H NMR (400 MHz, [D$_6$]benzene, r.t.): δ 7.58 (dd, $^3J_{H,H}$=15.5, 10.9 Hz, 3-C*H* overlapped with resonances of **4c**), 7.18-7.28 (m, *Ph* overlapped with resonances of **4c**), 7.02 (t, $^3J_{H,H}$=6.9 Hz, 1H; *Ph*), 6.68 (s, 1H; 7-C*H*), 6.43-6.54 (m, 2H; obscured by overlapping with **4c** 4- and 5-C*H*), 5.96 (d, $^3J_{H,H}$=15.5 Hz, 1H; 2-C*H*), 4.37 (sept, $^3J_{H,H}$=5.8 Hz, 2H; C*H*Me$_2$), 3.45 (s, 3H; CO$_2$*Me*), 1.04 (d, $^3J_{H,H}$=5.7 Hz, 12H; CH*Me*$_2$).

2-4. Reaction of 2-phenylethynyl boronic acid dimethyl ester (2c) with methyl 2,4-pentadienoate (3a).

Because the products **4d** and **5d** were decomposed during the purification process, this compound was characterised by NMR experiments in [D$_6$]benzene.

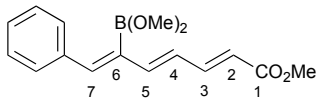
Yield: 68% (NMR). **4d**/**5d** = 19/81.

methyl (2*E*,4*E*,6*E*)-6-(dimethoxyboraneyl)-7-phenylhepta-2,4,6-trienoate [(2*E*,4*E*,6*E*)-4d]:



^{1}H NMR (400 MHz, [D$_6$]benzene, r.t.): δ 7.49 (dd, $^3J_{H,H}$=15.5, 11.0 Hz, 1H; 3-C*H*), 7.28-7.30 (m, obscured by overlapping with **5d** and reactant. *Ph*), 6.45 (d, $^3J_{H,H}$=15.5 Hz, 1H; 5-C*H*), 6.12 (dd, $^3J_{H,H}$=15.5, 11.0 Hz, 1H; 4-C*H*), 5.70 (s, 1H; 7-C*H*), 5.62 (d, $^3J_{H,H}$=15.5 Hz, 1H; 2-C*H*), 3.35 (s, 6H; O*Me*), 3.22 (s, 3H; CO_2*Me*).

methyl (2*E*,4*E*,6*E*)-6-(dimethoxyboraneyl)-7-phenylhepta-2,4,6-trienoate [(2*E*,4*E*,6*E*)-5d]:

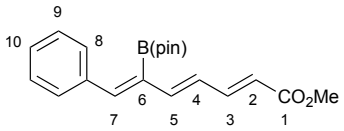


^{1}H NMR (400 MHz, [D$_6$]benzene, r.t.): δ 7.55 (dd, $^3J_{H,H}$=15.5, 10.9 Hz, 1H; 3-C*H*), 7.28-7.30 (m, obscured by overlapping with **4d** and reactant. *Ph*), 6.70 (s, 1H; 7-C*H*), 6.46 (d, $^3J_{H,H}$=15.5 Hz, 1H; 5-C*H*), 6.28 (dd, $^3J_{H,H}$=15.5, 10.9 Hz, 1H; 4-C*H*), 5.82 (d, $^3J_{H,H}$=15.5 Hz, 1H; 2-C*H*), 3.32 (s, 6H; O*Me*), 3.23 (s, 3H; CO_2*Me*).

2-5. Reaction of 2-phenylethynyl boronic acid pinacol ester (2d) with methyl 2,4-pentadienoate (3a).

Yield: 47%. pale yellow oil.

methyl (2*E*,4*E*,6*E*)- 6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-7-phenylhepta-2,4,6-trienoate [(2*E*,4*E,*6*E*)-5e]:

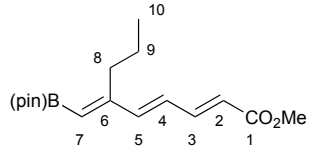


^{1}H NMR (400 MHz, [D$_6$]benzene, r.t.): δ 7.61 (dd, $^3J_{H,H}$=15.2, 10.9 Hz, 1H; 3-C*H*), 7.39-7.40 (m, 1H; 8-C*H*), 7.00-7.13 (m, 3H; 9- and 10-C*H*), 6.80 (s, 1H; 6-C*H*), 6.80 (dd, $^3J_{H,H}$=15.2, 10.9 Hz, 1H; 4-C*H*), 6.55 (d, $^3J_{H,H}$=15.5 Hz, 1H; 5-C*H*), 6.07 (d, $^3J_{H,H}$=14.9 Hz, 1H; 2-C*H*), 3.45 (s, 3H; CO_2*Me*), 1.02 (s, 12H; pinacolato-*Me*); ^{13}C{^{1}H} NMR (100 MHz, [D$_6$]benzene, r.t.): δ 167.1 (s), 147.3 (s), 147.1 (s), 145.7 (s) 138.7 (s), 129.1 (s), 128.9 (s), 120.5 (s), 83.9 (s, pinacolato-*C*Me$_2$), 51.0 (s), 24.9 (s, pinacolato-*Me*). HRMS (APCI): *m*/*z* calcd for $C_{20}H_{25}BO_4$+H$^+$: 341.1922 [*M*+H]$^+$; found: 341.1914.

2-6. Reaction of 1-pentynyl boronic acid pinacol ester (2e) with methyl 2,4-pentadienoate (3a).

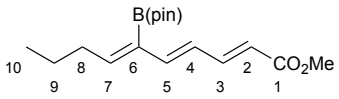
Yield: 42% (NMR). 24% (isolated). This compound was isolated as a regioisomeric micture: (2*E*,4*E*,6*E*)-**4f**/(2*E*,4*E*,6*E*)-**5f** = 42/58. yellow oil.

methyl (2*E*,4*E*,6*E*)-7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-6-propylhepta-2,4,6-trienoate [(2*E*,4*E*,6*E*)-4f]:



^{1}H NMR (400 MHz, [D_6]benzene, r.t.): δ 7.38 (dd, $^3J_{H,H}$=15.2, 9.76 Hz, 1H; 3-C*H*), 6.15-6.25 (m, 2H; 4- and 5-C*H*), 5.87 (d, $^3J_{H,H}$=15.5 Hz, 1H; 2-C*H*), 5.71 (s, 3H; 7-C*H*), 3.43 (s, 3H; CO_2*Me*), 2.71 (t, $^3J_{H,H}$=7.44 Hz, 2H; 8-CH_2), 1.51 (sext, $^3J_{H,H}$=7.44 Hz, 2H; 9-CH_2), 1.06 (s, 12H; pinacolato-*Me*), 1.01 (t, $^3J_{H,H}$=7.44 Hz, 3H; 10-*Me*); ^{13}C{^{1}H} NMR (100 MHz, [D_6]benzene, r.t.): δ 166.95 (s, 1-*C*O_2Me), 159.11 (s, 6-*C*Pr), 145.37 (s, 5- or 4-*C*H), 145.02 (s, 4- or 5-*C*H), 127-129 (3-*C*H obscured by overlapping with C_6D_6), 124 (br. coalesced with base line, 7-*C*H), 122.04 (s, 2-*C*H), 83.24 (s, pinacolato-*C*Me_2), 51.04 (s, CO_2*Me*), 32.19 (s, 8-*C*H_2), 24.81 (s, pinacolate-*Me*), 23.81 (s, 9-*C*H_2), 14.13 (s, 10-*Me*).

methyl (2*E*,4*E*,6*E*)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)deca-2,4,6-trienoate [(2*E*,4*E*,6*E*)-5f]:

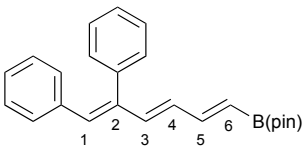


^{1}H NMR (400 MHz, [D_6]benzene, r.t.): δ 7.64 (dd, $^3J_{H,H}$=15.5, 11.4 Hz, 1H; 3-C*H*), 6.97 (dd, $^3J_{H,H}$=15.2, 11.4 Hz, 1H; 4-C*H*), 6.49 (d, $^3J_{H,H}$=15.4 Hz, 1H; 5-C*H*), 6.20 (t, $^3J_{H,H}$=7.44 Hz, 1H; 7-C*H*), 6.06 (d, $^3J_{H,H}$=14.7 Hz, 1H; 2-C*H*), 3.43 (s, 3H; CO_2*Me*), 2.46 (q, $^3J_{H,H}$=7.44 Hz, 2H; 8-CH_2), 1.36 (sext, $^3J_{H,H}$=7.44 Hz, 2H; 9-CH_2), 1.01 (s, 12H; pinacolato-*Me*), 0.88 (t, $^3J_{H,H}$=7.48 Hz, 3H; 10-*Me*); ^{13}C{^{1}H} NMR (100 MHz, [D_6]benzene, r.t.): δ 167.27 (s, 1-*C*O_2Me), 154.90 (s, 7-*C*H), 147.25 (s, 5-*C*H), 146.56 (s, 3-*C*H), 127-129 (4-*C*H obscured by overlapping with C_6D_6), 119.75 (s, 2-*C*H), 82.91 (s, pinacolato-*C*Me_2), 50.91 (s, CO_2*Me*), 34.06 (s, 8-*C*H_2), 24.74 (s, pinacolato-*Me*), 23.11 (s, 9-*C*H_2), 13.95 (s, 10-*Me*), 6-*C*B(pin) was not observed. HRMS (APCI): *m*/*z* calcd for $C_{17}H_{25}BO_4$+H^+: 307.2078 [*M*+H]$^+$; found: 307.2082.

2-7. Reaction of diphenylacetylene (2f) with (*E*)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butadiene (3d).

Yield: 93%. pale yellow oil.

(1*Z*,3*E*,5*E*)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2-dphenylhexa-1,3,5-triene [(1*Z*,3*E*,5*E*)-4g]:

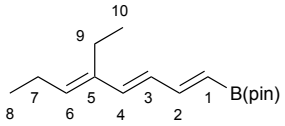


^{1}H NMR (400 MHz, [D_6]benzene, r.t.): δ 7.56 (dd, $^3J_{H,H}$=17.8, 10.9 Hz,1H; 5-C*H*), 7.04-7.10 (m, 5H; *Ph*), 6.8-6.9 (m, 5H; -*Ph*), 6.61 (d, $^3J_{H,H}$=14.9 Hz, 1H; 3-C*H*), 6.46 (s, 1H; 1-C*H*), 6.16 (dd, $^3J_{H,H}$=14.9, 10.9 Hz, 1H; 4-C*H*), 5.67 (d, $^3J_{H,H}$=17.8 Hz, 1H; 6-C*H*), 1.07 (s, 12H; pinacolato-*Me*); ^{13}C{^{1}H} NMR (100 MHz, [D_6]benzene, r.t.): δ 50.41 (s, 5-*C*H), 141.98 (s, 3*C*H), 141.85 (s), 138.45 (s), 137.08 (s), 133.89 (s), 133.67 (s, 4-*C*H), 129.91 (s), 129.70 (s), 129.17 (s), 128 (obscured by overlapping with C_6D_6), 127.40 (s), 122 (br, 6-*C*H), 82.02 (s, pinacolato-*C*Me_2), 77.61 (s), 24.86 (s, pinacolato-*Me*), 24.55 (s). MS(EI): *m*/*z* = 358 (M+). HRMS (APCI): *m*/*z* calcd for $C_{24}H_{27}BO_2$+H^+: 359.2181 [M+H]$^+$; found: 359.2183.

2-8. Reaction of 3-hexyne (2g) with (*E*)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butadiene (3d).

Yield: 89%. pale yellow oil.

(1*E*,3*E*,5*E*)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-ethylocta-1,3,5-triene [(1*E*,3*E*,5*E*)-4h]:

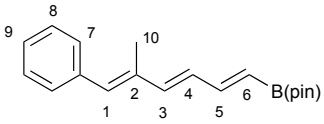


^{1}H NMR (400 MHz, [D_6]benzene, r.t.): δ 7.53 (dd, $^3J_{H,H}$=17.5, 9.7 Hz, 1H; 2-C*H*), 6.35 (dd, $^3J_{H,H}$=15.5, 9.8 Hz, 1H; 3-C*H*), 6.24 (d, $^3J_{H,H}$=15.5 Hz, 1H; 4-C*H*), 5.93 (d, $^3J_{H,H}$=17.8 Hz, 1H; 1-C*H*), 5.28 (t, $^3J_{H,H}$=7.4 Hz, 1H; 6-C*H*), 2.06 (q, $^3J_{H,H}$=7.4 Hz, 2H; 9-CH_2), 1.90 (quint, $^3J_{H,H}$=7.4 Hz, 2H; 7-CH_2), 1.11 (s, 12H; pinacolato-*Me*), 0.89 (t, $^3J_{H,H}$=7.4 Hz, 3H; 10-*Me*), 0.81 (t, $^3J_{H,H}$=7.4 Hz, 3H; 8-*Me*); ^{13}C{^{1}H} NMR (100 MHz, [D_6]benzene, r.t.): δ 151.49 (s, 2-*C*H), 140.64 (s, 4-*C*H), 137.01 (s, 6-*C*H), 126.01 (s), 127-128 (obscured by overlapping with C_6D_6, 3-*C*H), 120 (br. almost obscured, 1-*C*H), 82.99 (s, pinacolato-*C*Me$_2$), 24.92 (s, pinacolato-*Me*), 19.94 (s, 9-*C*H$_2$), 21.69 (s, 7-*C*H$_2$), 14.14 (s, 8-*Me*), 13.84 (s, 10-*Me*). HRMS (APCI): *m*/*z* calcd for $C_{16}H_{28}BO_2$+H$^+$: 263.2180 [*M*+H]$^+$; found: 263.2177.

2-9. Reaction of 1-phenyl-1-propyne (2h) with (*E*)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butadiene (3d).

Yield: 76%. pale yellow oil.

(1*E*,3*E*,5*E*)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-methyl-1-phenylhexa-1,3,5-triene [(1*E*,3*E*,5*E*)-4i]:

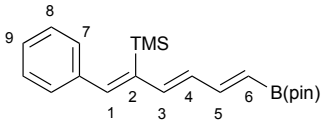


^{1}H NMR (400 MHz, [D_6]benzene, r.t.): δ 7.57 (dd, $^3J_{H,H}$=17.8, 9.8 Hz, 1H; 5-C*H*), 7.0-7.15 (partly obscured by overlapping with C_6D_5H, *Ph*), 6.42 (s, 1H; 1-C*H*), 6.36-6.42 (m, 2H; 3- and 4-C*H*), 6.00 (d, $^3J_{H,H}$=17.8 Hz, 1H; 6-C*H*), 1.12 (s, 12H; pinacolato-*Me*), 1.08 (s, 3H,; 10-*Me*); ^{13}C{^{1}H} NMR (100 MHz, [D_6]benzene, r.t.): δ 150.96 (s, 5-*C*H), 142.08 (s, 4-*C*H), 138.00 (s), 136.01 (s), 134.09 (s), 130.68 (s), 129.60 (s), 127.00 (s), 121 (br. 6-*C*H), 83.08 (s, pinacolato-*C*Me$_2$), 24.94 (s, pinacolato-*Me*), 13.78 (s, 10-*Me*), 6-*C*H was not observed by HMQC probably due to broadening. HRMS (APCI): *m*/*z*. calcd for $C_{19}H_{25}BO_2$+H$^+$: 297.2024 [*M*+H]$^+$; found: 297.2010.

2-10. Reaction of 1-trimethylsilyl-2-phenylacetylene (2i) with (*E*)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butadiene (3d).

Yield: 92 % (NMR), 59 % (isolated). pale yellow oil.

(1*Z*,3*E*,5*E*)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-phenyl-2-trimethylsilylhexa-1,3,5-triene [(1*Z*,3*E*,5*E*)-4j]:



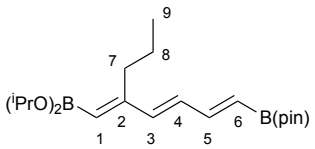
^{1}H NMR (400 MHz, [D$_6$]benzene, r.t.): δ 7.44 (dd, $^3J_{H,H}$=17.2, 10.3 Hz, 1H; 5-C*H*), 7.24 (d, $^3J_{H,H}$=6.9 Hz, 2H; 7-C*H*), 7.0-7.1 (m, overlapped, *Ph*), 6.91(s, 1H; 1-C*H*), 6.66 (dd, $^3J_{H,H}$=15.8, 10.3 Hz, 1H; 4-C*H*), 6.53 (d, $^3J_{H,H}$=16.0 Hz, 1H; 3-C*H*), 5.91 (d, $^3J_{H,H}$=17.8 Hz, 1H; 6-C*H*), 1.08 (s, 12H; pinacolato-*Me*), 0.20 (s, 9H; TMS); ^{13}C{^{1}H} NMR (100 MHz, [D$_6$]benzene, r.t.): δ=151.33 (s, 5-*C*H), 142.91 (s), 141.78 (s, 3-C*H*), 140.84 (s, 1-*C*H), 138.14 (s, *Ph*), 137.70 (s), 134.85 (s, 4-*C*H), 129.93 (s, 7-*C*H), 128 (overlapped with C$_6$D$_6$, *Ph*), 120.92 (br, 6-*C*H), 83.02 (s, pinacolato-*C*Me$_2$), 24.88 (s, pinacolato-*Me*), 0.45 (s, Si*Me*). HRMS (APCI): *m*/*z* calcd for $C_{21}H_{31}BO_2Si+H^+$: 355.2263 [*M*+H]$^+$; found: 355.2263.

2-11. Reaction of 1-pentynyl boronic acid diisopropyl ether (2a) with (*E*)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butadiene (3d).

Because the product **4k** was decomposed during the purification process, this compound was characterised by NMR experiments in [D$_6$]benzene.

Yield: 83% (NMR).

(1*E*,3*E*,5*E*)-1-(diisopropoxylboraneyl)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-propylhexa-1,3,5-triene [(1*E*,3*E*,5*E*)-4k]:

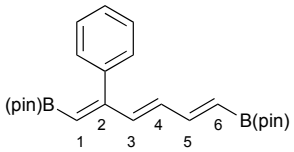


^{1}H NMR (400 MHz, [D$_6$]benzene, r.t.): δ 7.45 (dd, $^3J_{H,H}$=17.2, 10.3 Hz, 1H; 5-C*H*), 6.52 (dd, $^3J_{H,H}$=15.5, 10.9 Hz, 1H, 4-C*H*), 6.34 (d, $^3J_{H,H}$=15.4 Hz, 1H; 3-C*H*), 5.92 (d, $^3J_{H,H}$=17.8 Hz, 1H; 6-C*H*), 5.51 (s, 1H; 1-C*H*), 4.42 (sept, $^3J_{H,H}$=6.28 Hz, 2H; OC*H*Me$_2$), 2.60-2.64 (m, 2H; 7-C*H*$_2$), 1.56-1.61 (m, 2H; 8-C*H*$_2$), 1.16 (d, $^3J_{H,H}$=8.6 Hz, 12H; OCH*Me*$_2$), 1.10 (s, 12H; pinacolato-*Me*), 0.96 (t, $^3J_{H,H}$=7.6 Hz, 3H; 9-*Me*); ^{13}C{^{1}H} NMR (100 MHz, [D$_6$]benzene, r.t.): δ 156.18 (s), 150.92 (s), 142.42 (s), 131.45 (s), 126.01 (s), 122 (br, 6-*C*H), 83.05 (s, pinacolato-*C*Me$_2$), 65.56 (s, *C*HMe$_2$), 32.78 (s, 7-*C*H$_2$), 24.91 (s, pinacolato-*Me*), 24.86 (s, CH*Me*$_2$), 23.87 (s, 8-*C*H$_2$), 14.46 (s, 9-*Me*).

2-12. Reaction of 2-phenylethynyl boronic acid pinacol ester (2d) with (*E*)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butadiene (3d).

Yield: 58%. This compound was isolated as a regioisomeric mixture: **4l**/**5l** = 23/77. pale yellow oil.

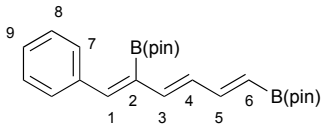
(1*Z*,3*E*,5*E*)-1,6-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-phenylhexa-1,3,5-triene [(1*Z*,3*E*,5*E*)-4l]:



^{1}H NMR (400 MHz, [D$_6$]benzene, r.t.): δ 7.77 (s, 1H; 1-C*H*), 7.53 (dd, $^3J_{H,H}$=17, 12 Hz, 1H; 5-C*H*), 7.27 (d, $^3J_{H,H}$=8.6 Hz, 2H, *o-Ph*), 7.21 (d, $^3J_{H,H}$=14.9 Hz, 1H, 3-C*H*), 7.1-6.9 (obscured by overlapping with **5l**), 6.09 (d, $^3J_{H,H}$=16.6 Hz, 1H; 6-C*H*), 1.06 (s, 12H; pinacolato-*Me*), 1.04 (s, 12H;

pinacolato-*Me*); $^{13}C\{^1H\}$ NMR (100 MHz, [D_6]benzene, r.t.): δ 152.20 (s, 5-*C*H), 145.95 (s, 1-*C*H), 137.90 (s), 136.82 (s), 135.88 (s, 3-*C*H), 128.49 (s, *Ph*), 128-127.5 (obscured by overlapping with C_6D_6), 121 (br, 6-*C*H), 83.54 (s, pinacolato-*C*Me_2), 82.91 (s, pinacolato-*C*Me_2), 24.61 (s, pinacolato-*Me*).

(1*E*,3*E*,5*E*)-2,6-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-phenylhexa-1,3,5-triene [(1*E*,3*E*,5*E*)-5l]:

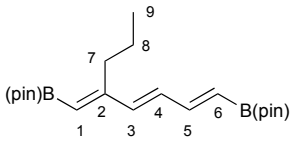


^1H NMR (400 MHz, [D_6]benzene, r.t.): δ 7.56 (dd, $^3J_{H,H}$=17.2, 10.3 Hz, 1H; 5-C*H*), 7.39 (d, $^3J_{H,H}$=6.9 Hz, 2H; 7-C*H*), 7.10 (t, $^3J_{H,H}$= 6.9 Hz, 2H; 8-C*H*), 7.03 (t, $^3J_{H,H}$=7.4 Hz, 1H; 9-C*H*), 6.96 (dd, $^3J_{H,H}$=15.4, 10.9 Hz, 1H; 4-C*H*), 6.86 (s, 1H; 1-C*H*), 6.59 (d, $^3J_{H,H}$=15.4 Hz, 1H; 3-C*H*), 6.04 (d, $^3J_{H,H}$=17.2 Hz, 1H; 6-C*H*), 1.10 (s, 12H; pinacolato-*Me*), 1.03 (s, 12H; pinacolato-*Me*); $^{13}C\{^1H\}$NMR (100 MHz, [D_6]benzene, r.t.): δ 151.24 (s, 5-*C*H), 144.78 (s, 1-*C*H), 143.07 (s, 3-*C*H), 133.91 (s, 4-*C*H), 128-130 (overlapped with C_6D_6, *Ph*), 121 (br, 6-*C*H), 83.83 (s, pinacolato-*C*Me_2), 83.02 (s, pinacolato-*C*Me_2), 24.91 (s, pinacolato-*Me*). HRMS (APCI): *m*/*z* calcd for $C_{24}H_{34}B_2O_4$+H^+: 409.2724 [*M*+H]$^+$; found: 409.2715.

2-13. Reaction of 1-pentynyl boronic acid pinacol ester (2e) with (*E*)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butadiene (3d).

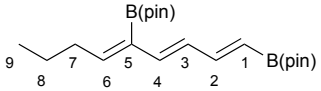
Yield: 34%. Isolated as a regioisomeric mixture: **4m**/**5m** = 25/75. pale yellow oil.

(1*E*,3*E*,5*E*)-1,6-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-propylhexa-1,3,5-triene [(1*E*,3*E*,5*E*)-4m]:



^1H NMR (400 MHz, [D_6]benzene, r.t.): δ 7.36 (dd, $^3J_{H,H}$=17.2, 11.5 Hz, 1H; 5-C*H*), 6.50 (dd, $^3J_{H,H}$=15.5, 10.3 Hz, 1H; 4-C*H*), 6.27 (d, $^3J_{H,H}$=15.5 Hz, 1H; 3-C*H*), 5.92 (d, $^3J_{H,H}$=17.2 Hz, 1H; 6-C*H*), 5.70 (s, 1H; 1-C*H*), 2.75 (t, $^3J_{H,H}$=7.4 Hz, 2H; 7-CH_2), 1.55 (sext, $^3J_{H,H}$=7.4 Hz, 2H; 8-CH_2), 1.09 (obscured by overlapping with **5m**, pinacolato-*Me*), 1.05 (s, 12H; pinacolato-*Me*), 0.97 (t, $^3J_{H,H}$=7.4 Hz, 3H; 9-*Me*); $^{13}C\{^1H\}$ NMR (100 MHz, [D_6]benzene, r.t.): δ 159.97 (s), 150.82 (s), 141.59 (s, 3-*C*H), 132.64 (s, 4-*C*H), 122 (br. 1-*C*H), 83.05 (pinacolato-*C*Me_2), 82.72 (s, pinacolato-*C*Me_2), 32.28 (s, 7-*C*H_2), 24.82 (s, pinacolato-*Me*), 23.91 (s, 8-*C*H_2), 14.14 (s, 9-*Me*), some resonances were obscured by overlapping with the resonances of **5m** and solvent.

(1*E*,3*E*,5*E*)-1,5-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)nona-1,3,5-triene [(1*E*,3*E*,5*E*)-5m]:



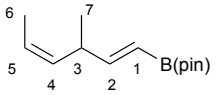
^1H NMR (400 MHz, [D_6]benzene, r.t.): δ 7.56 (ddd, $^3J_{H,H}$=17.2, 10.3 Hz, $^4J_{H,H}$=2.3 Hz, 1H; 2-C*H*), 7.07 (dd, $^3J_{H,H}$=15.5, 10.9 Hz, 1H; 3-C*H*), 6.55 (d, $^3J_{H,H}$=15.5 Hz, 1H; 4-C*H*), 6.13-6.20 (obscured by

overlapping with an impurity, 6-C*H*), 6.02 (dd, $^{3}J_{H,H}$=17.2 Hz, $^{4}J_{H,H}$=1.7 Hz, 1H; 1-C*H*), 2.44 (q, $^{3}J_{H,H}$=7.4 Hz, 2H; 7-CH_2), 1.36 (sext, $^{3}J_{H,H}$=6.9 Hz, 2H; 8-CH_2), 1.09 (s, 12H; pinacolato-*Me*), 1.01 (s, 12H; pinacolato-*Me*), 0.88 (t, $^{3}J_{H,H}$=7.4 Hz, 3H; 9-*Me*); ^{13}C{^{1}H} NMR (100 MHz, [D_6]benzene, r.t.): δ 151.9 (s, 2-C*H*), 151.8 (s, 6-*C*H), 142.84 (s, 4-*C*H), 132.23 (s, 3-*C*H), 120 (br. 1- and 5-*C*), 83.14 (s, pinacolato-*C*Me$_2$), 82.89 (s, pinacolato-*C*Me$_2$), 34.09 (s, 8-*C*H$_2$), 24.90 (s, pinacolato-*Me*), 24.61 (s, pinacolato-*Me*), 23.22 (s, 8-*C*H$_2$), 13.99 (s, 9-*Me*). HRMS (APCI): *m*/*z* calcd for $C_{21}H_{36}B_2O_4$+H$^+$: 375.2880 [*M*+H]$^+$; found: 365.2881.

2-14. Reaction of 1,3-pentadiene (3b) with vinyl boronic acid pinacol ester (6a).

Yield: 93%. pale yellow oil.

(1*E*,4*Z*)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-methylhexa-1,4-diene [(1*E*,4*Z*)-7a]:

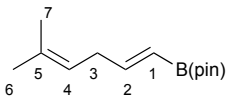


^{1}H NMR (400 MHz, [D_6]benzene, r.t.): δ 6.93 (dd, $^{3}J_{H,H}$=17.8, 5.7 Hz, 1H; 2-*CH*), 5.79 (dd, $^{3}J_{H,H}$=17.8 Hz, $^{4}J_{H,H}$=1.7 Hz, 1H; 1-*CH*), 5.36 (ddq, $^{3}J_{H,H}$=10, 9 Hz, $^{4}J_{H,H}$=1.7 Hz, 1H; 4-*CH*), 5.23 (dq, $^{3}J_{H,H}$=10, 7 Hz, 1H; 5-*CH*), 3.18 (br. sext, $^{3}J_{H,H}$=7 Hz, 1H; 3-*CH*), 1.42 (dd, $^{3}J_{H,H}$=6.8 Hz, $^{4}J_{H,H}$=1.7 Hz, 3H; 6-*Me*), 1.07 (s, 12H; pinacolato-*Me*), 0.99 (d, $^{3}J_{H,H}$=6.4 Hz, 3H; 7-*Me*); ^{13}C{^{1}H} NMR (100 MHz, [D_6]benzene, r.t.): δ 157. 87 (s), 133.80 (s), 126.02 (s), 123.83 (s), 82.90 (s, pinacolato-*C*Me$_2$), 37.34 (s), 24.91 (s), 20.12(s), 12.92 (s), HRMS (APCI): *m*/*z* calcd for $C_{13}H_{23}BO_2$+H$^+$: 223.1866 [*M*+H]$^+$; found: 223.1864.

2-15. Reaction of isoprene (3e) with vinyl boronic acid pinacol ester (6a).

Yield: 59%. pale yellow oil.

(*E*)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-methylhexa-1,4-diene [(*E*)-7b]:



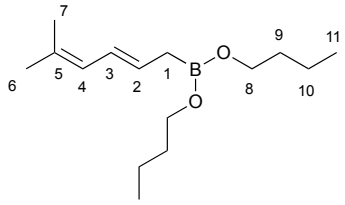
^{1}H NMR (400 MHz, [D_6]benzene, r.t.): δ 6.95 (dt, $^{3}J_{H,H}$=17.8, 6.3 Hz, 1H; 2-*CH*), 5.82 (dt, $^{3}J_{H,H}$=17.8 Hz, $^{4}J_{H,H}$=1.7 Hz, 1H; 1-*CH*), 5.16 (tq, $^{3}J_{H,H}$= 6.8 Hz, $^{4}J_{H,H}$=1.7 Hz, 1H; 4-*CH*), 2.77 (br.t, $^{3}J_{H,H}$=6.3 Hz, 2H; 3-*CH*$_2$), 1.56 (s, 3H; 7- or 6-*Me*), 1.40 (s, 3H; 6- or 7-*Me*), 1.08 (s, 12H; pinacolato-*Me*) ; ^{13}C{^{1}H} NMR (100 MHz, [D]chloroform, r.t.): δ 152.77 (s), 133.49 (s), 120.44 (s), 118.17 (br. s), 83.01(s, pinacolato-*C*Me$_2$), 34.28 (s), 25.69 (s), 24.77 (s), 17.66 (s). HRMS (APCI): *m*/*z* calcd for $C_{13}H_{23}BO_2$+H$^+$: 223.1866 [*M*+H]$^+$; found: 223.1865.

2-16. Reaction of isoprene (3e) with vinyl boronic acid dibutyl ester (6b).

Because the product **7c** was decomposed during the purification process, this compound was characterised by NMR experiments in [D_6]benzene.

Yield: 62% (NMR).

(*E*)-1-(dibutoxyboraneyl)-5-methylhexa-2,4-diene [(*E*)-7c]:

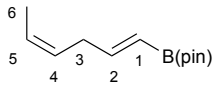


^{1}H NMR(400 MHz, [D$_6$]benzene, r.t.): δ 6.41 (dd, $^3J_{H,H}$=14.9 ,10.7 Hz, 1H; 3-C*H*), 5.97 (d, $^3J_{H,H}$=10.6 Hz, 1H; 4-C*H*), 5.91 (dt, $^3J_{H,H}$=15.0, 7.6 Hz, 1H; 2-C*H*), 3.79 (t, $^3J_{H,H}$=6.4 Hz, 4H; 8-CH_2), 1.82 (d, $^3J_{H,H}$=7.0 Hz, 2H; 1-CH_2),1.65 (s, 3H; 6- or 7-*Me*), 1.49 (m, 4H; 9-CH_2), 1.3 (sext, $^3J_{H,H}$=7.4 Hz, 4H; 10-CH_2), 0.84 (t, $^3J_{H,H}$=7.3 Hz, 6H; 11-*Me*).

2-17. Reaction of butadiene (3f) with vinyl boronic acid pinacol ester (6a).

Yield: 24%. pale yellow oil.

(1*E*,4*Z*)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexa-1,4-diene [(1*E*,4*Z*)-7d]:



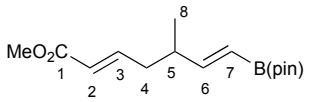
^{1}H NMR (400 MHz, [D$_6$]benzene, r.t.): δ 6.93 (dt, $^3J_{H,H}$=17.8, 5.7 Hz, 1H; 2-*CH*), 5.81 (d, $^3J_{H,H}$=17.8 Hz, 1H; 1-*CH*), 5.43 (m, 2H; 4-*CH* and 5-*CH*), 2.78 (t, $^3J_{H,H}$=5.8 Hz, 2H; 3-CH_2), 1.40 (d, $^3J_{H,H}$=4.6 Hz, 3H; 6-*Me*), 1.07 (s, 12H; pinacolato-*Me*); ^{13}C{^{1}H} NMR (100 MHz, [D$_6$]benzene, r.t.): δ 152.36 (s), 126.86 (s), 125.66 (s), 119.64 (br. s), 82.90 (s, pinacolato-*C*Me$_2$), 33.40 (s), 24.89 (s, pinacolato-*Me*), 12.67 (s). HRMS (APCI): *m*/*z* calcd for $C_{12}H_{21}BO_2$+H$^+$; 209.1710 [*M*+H]$^+$; found: 209.1709.

.

2-18. Reaction of methyl (2*E*,4*E*)-hepta-2,4-dienoate (3g) with vinyl boronic acid pinacol ester (6a).

Yield: 44%. pale yellow oil.

methyl (2*E*,6*E*)-5-methyl-7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hepta-2,6-dienoate [(2*E*,6*E*)-7e]:



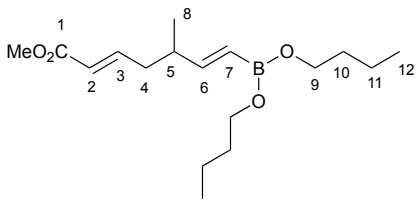
^{1}H NMR (400 MHz, [D]chloroform, r.t.): δ 6.89 (dt, $^3J_{H,H}$=15.5, 7.4 Hz, 1H; 3-*CH*), 6.73 (dd, $^3J_{H,H}$=17.8, 6.9 Hz, 1H; 6-*CH*), 5.75 (d, $^3J_{H,H}$=15.5 Hz, 1H; 2-*CH*), 5.64 (dd, $^3J_{H,H}$=17.8 Hz, $^4J_{H,H}$=1.7 Hz, 1H; 7-*CH*), 3.36 (s, 3H; CO_2*Me*), 2.02 (sept, $^3J_{H,H}$=6.9 Hz, 1H; 5-C*H*), 1.88 (dtd, $^3J_{H,H}$=15.5, 7.4 Hz, $^4J_{H,H}$=1.7 Hz, 1H; 4-CH_2), 1.70 (dtd, $^3J_{H,H}$=15.5, 7.4 Hz, $^4J_{H,H}$=1.7 Hz, 1H; 4-CH_2), 1.06 (s, 12H; pinacolato-*Me*), 0.73 (d, $^3J_{H,H}$=6.9 Hz, 3H; 8-*Me*); ^{13}C{^{1}H} NMR (100 MHz, [D]chloroform, r.t.): δ 157.76 (s), 147.60 (s), 122.41 (s), 118.26 (br.s), 82.26 (s, pinacolato-*C*Me$_2$), 77.33 (s), 51.53 (s), 38.67 (s), 38.42 (s), 24.88 (s, pinacolato-*Me*), 19.12 (s). HRMS (APCI): *m*/*z* calcd for $C_{15}H_{25}BO_4$+H$^+$: 281.1921 [*M*+H]$^+$; found: 281.1913.

2-19. Reaction of methyl (2*E*,4*E*)-hexa-2,4-dienoate (3g) with vinyl boronic acid dibutyl ester (6b).

Because the products **7f** was decomposed during the purification process, this compound was characterised by NMR experiments in [D_6]benzene.

Yield: 52% (NMR).

methyl (2*E*,6*E*)-7-(dibutoxyboraneyl)- 5-methylhepta-2,6-dienoate [(2*E*,6*E*)-7f]:

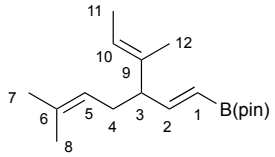


^{1}H NMR(400 MHz, [D_6]benzene, r.t.): δ 6.96 (dt, $^3J_{H,H}$=15.4, 7.5 Hz, 1H; 3-C*H*), 6.70 (dd, $^3J_{H,H}$=17.8, 7.4 Hz, 1H; 6-C*H*), 5.82 (d, $^3J_{H,H}$=15.5 Hz, 2H; 2-C*H* and 7-C*H*), 3.93 (t, $^3J_{H,H}$=6.3 Hz, 4H; 9-CH_2), 3.38 (s, 3H; CO_2*Me*), 1.94 (sept, $^3J_{H,H}$=6.9 Hz, 1H; 7-C*H*), 1.82 (m, 1H; 4-C*H*), 1.75 (m, 1H; 4-C*H*), 1.54 (m, 4H; 10-CH_2), 1.33 (m, 4H; 11-CH_2), 0.86 (t, $^3J_{H,H}$=7.4 Hz, 6H; 12-*Me*), 0.74 (d, $^3J_{H,H}$=6.9 Hz, 3H; 8-*Me*).

2-20. Reaction of (*E*)-3,7-dimethylocta-1,3,6-triene (*β*-ocimene) (3h) with vinyl boronic acid pinacol ester (6a).

Yield: 67%. pale yellow oil.

(*E*)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-{(E)-but-2-en-2-yl}-6-methylhepta-1,5-diene [(*E*)-7g]:



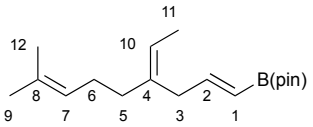
^{1}H NMR(400 MHz, [D]chloroform, r.t.): δ 7.00 (dd, $^3J_{H,H}$=18.4, 6.3 Hz, 1H; 2-*CH*), 5.83 (dd, $^3J_{H,H}$=17.8, 1.7 Hz, 1H; 1-*CH*), 5.14 (t, $^3J_{H,H}$=5.7 Hz, 1H; 5-*CH*), 3.43 (q, $^3J_{H,H}$=6.9 Hz, 1H; 3-*CH*), 2.27 (dt, $^3J_{H,H}$=14, 7.4 Hz, 1H; 4-CH_2), 2.19 (dt, $^3J_{H,H}$=14, 7.4 Hz, 1H; 4-CH_2), 1.66 (d, $^3J_{H,H}$=9.2 Hz, 3H; 11-*Me*), 1.58 (s, 6H; 8-*Me* and 12-*Me*), 1.49 (s, 3H; 7-*Me*), 1.07 (s, 12H; pinacolato-*Me*); ^{13}C {^{1}H} NMR (100 MHz, [D]chloroform, r.t.): δ 155.35 (s), 135.91 (s), 132.17 (s), 122.34 (s), 121.06 (s), 117.55 (br. s), 83.02 (s, pinacolato-*C*Me_2), 45.55 (s), 29.83 (s), 25.75 (s), 24.78 (s, pinacolato-*Me*), 19.13 (s), 17.90 (s), 12.98 (s). HRMS (APCI): *m*/*z* calcd for $C_{18}H_{31}BO_2$+H^+: 291.2493 [*M*+H]$^+$; found: 291.2494.

2-21. Reaction of 7-methyl-3-methyleneocta-1,6-diene (*β*-myrcene) (3i) with vinyl boronic acid pinacol ester (6a).

This product was isolated as a regioisomeric mixture of **7h** and **8h**.

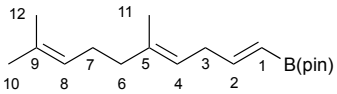
8h: Yield: 43%. **7h:** Yield: 15%. pale yellow oil.

(1*E*,4*Z*)-4-ethylidenyl-8-methyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)nona-1,7-diene [(1*E,*4*Z*)-7h]:



^{1}H NMR (400 MHz, [D]chloroform, r.t.): δ 6.52 (dt, $^{3}J_{H,H}$=17.8, 6.3 Hz, 1H; 2-C*H*), 5.42 (dt, $^{3}J_{H,H}$=18.3 Hz, $^{4}J_{H,H}$=1.7 Hz, 1H; 1-C*H*), 5.30 (t, $^{3}J_{H,H}$=6.3 Hz, 1H; 7-C*H*), 5.14 (br.q, $^{3}J_{H,H}$=6 Hz, 1H; 10-C*H*), 2.86 (d, $^{3}J_{H,H}$=6.3 Hz, 2H; 3-CH_2), 2.1-1.9 (m, 4H; 5- and 6-CH_2), 1.65 (s, 3H; 12- or 9-*Me*), 1.55 (s, 3H; 9- or 12-*Me*), 1.55 (d, $^{3}J_{H,H}$=5.9 Hz, 3H; 11-*Me*), 1.23 (s, 12H; pinacolato-*Me*); ^{13}C{^{1}H} NMR (100 MHz, [D]chloroform, r.t.): δ 151.4 (s), 136.6 (s), 131.4 (s), 124.3 (s), 120.3 (s), 83.0 (s, pinacolato-*C*Me$_2$), 37.2 (s), 36.6 (s), 31.6 (s), 25.7 (s, pinacolato-*Me*), 22.6 (s), 18.0 (s), 14.1 (s), 13.1 (s). HRMS (APCI): *m*/*z* calcd for $C_{18}H_{31}BO_2$+H$^+$: 291.2493 [*M*+H]$^+$; found: 291.2496.

(1*E*,4*E*)-5,9-dimethyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)deca-1,4,8-triene [(1*E*,4*E*)-8h]:



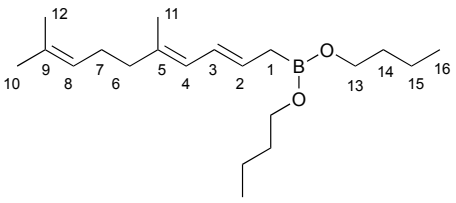
^{1}H NMR (400 MHz, [D]chloroform, r.t.): δ 6.59 (dt, $^{3}J_{H,H}$=18.4, 5.6 Hz, 1H; 2-C*H*); 5.41 (dd, $^{3}J_{H,H}$=17.6 Hz, $^{4}J_{H,H}$=1.6 Hz, 1H; 1-*CH*), 5.14 (t, $^{3}J_{H,H}$=7.2 Hz, 1H; 6-C*H* or 4-C*H*), 5.05 (t, $^{3}J_{H,H}$=5.2 Hz, 1H; 4-C*H* or 8-C*H*), 2.82 (t, $^{3}J_{H,H}$=6.8 Hz, 2H; 3-CH_2), 2.01 (m, 4H; 6-CH_2 and 7-CH_2), 1.65 (s, 3H; 10-, 12- or 9-*Me*), 1.56 (s, 6H; 9-, 10- or 12-*Me*), 1.23 (s, 12H; pinacolato-*Me*); ^{13}C{^{1}H} NMR (100 MHz, [D]chloroform, r.t.): δ 152.76 (s) 137.10 (s), 135.34 (s), 131.45 (s), 124.22 (s), 118.03 (br. s), 82.99 (s, pinacolato-*C*Me$_2$), 39.67 (s), 34.14 (s), 26.62 (s), 25.69 (s), 24.75 (s, pinacolato-*Me*), 17.68(s), 16.02 (s). HRMS (APCI): *m*/*z* calcd for $C_{18}H_{31}BO_2$+H$^+$: 291.2493 [*M*+H]$^+$; found: 291.2489.

2-22. Reaction of 7-methyl-3-methyleneocta-1,6-diene (*β*-myrcene) (3i) with vinyl boronic acid dibutyl ester (6b).

Because the product **8i** was decomposed during the purification process, this compound was characterised by NMR experiments in [D$_6$]benzene.

Yield: 33% (NMR).

(2*E*,4*E*)-1-(dibutoxyboraneyl)- 5,9-dimethyldeca-2,4,8-triene [(2*E*,4*E*)-8i]:



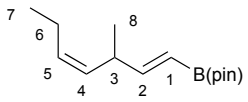
^{1}H NMR(400 MHz, [D$_6$]benzene, r.t.): δ 6.44 (dd, $^{3}J_{H,H}$=14.9, 10.9 Hz, 1H; 3-C*H*), 6.05 (d, $^{3}J_{H,H}$=10.9 Hz, 1H; 4-C*H*), 5.94 (dt, $^{3}J_{H,H}$=14.9, 7.4 Hz, 1H; 2-C*H*), 5.20 (t, $^{3}J_{H,H}$=8 Hz, 1H; 8-C*H*), 3.79 (t, $^{3}J_{H,H}$=6.3 Hz, 4H; 13-CH_2), 2.14 (t, $^{3}J_{H,H}$=6.3 Hz, 2H; 7- or 6-CH_2),2.08 (t, $^{3}J_{H,H}$=6.9 Hz, 2H; 6- or 7-*CH*$_2$),1.83 (d, $^{3}J_{H,H}$=7.5 Hz, 2H; 1-CH_2), 1.71 (s, 3H; 12-, 10- or 11-*Me*), 1.64 (s, 3H; 11-, 12- or 10-

Me), 1.52 (s, 3H; 10-, 11- or 12-*Me*), 1.47 (quint, $^{3}J_{H,H}$=6.3 Hz, 4H; 14-CH_2), 1.33 (m, 4H; 15-CH_2), 0.85 (t, $^{3}J_{H,H}$=7.4 Hz, 6H; 16-*Me*).

2-23. Reaction of (2*E*,4*E*)-hexa-2,4-diene (3j) with vinyl boronic acid pinacol ester (6a).

Yield: 36%. brown oil.

(1*E*,4*Z*)-3-methyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hepta-1,4-diene [(1*E*,4*Z*)-7j]:

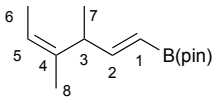


^{1}H NMR (400 MHz, [D]chloroform, r.t.): δ 6.94 (dd, $^{3}J_{H,H}$=18, 6.1 Hz, 1H; 2-C*H*), 5.80 (dd, $^{3}J_{H,H}$=18 Hz, $^{4}J_{H,H}$=1.6 Hz, 1H; 1-C*H*), 5.31 (dtd, $^{3}J_{H,H}$=10.7, 7.2 Hz, $^{4}J_{H,H}$=0.9 Hz, 1H; 5-C*H*), 5.19 (ddt, $^{3}J_{H,H}$=9.2, 7.7 Hz, $^{4}J_{H,H}$=1.4 Hz, 1H; 4-C*H*), 3.18 (sext, $^{3}J_{H,H}$=6.9 Hz, 1H; 3-C*H*), 1.89 (quint, $^{3}J_{H,H}$=7.4 Hz, 2H; 6-CH_2), 1.07 (s, 12H; pinacolato-*Me*), 0.99 (d, $^{3}J_{H,H}$= 6.9 Hz, 3H; 8-*Me*), 0.82 (t, $^{3}J_{H,H}$=7.6 Hz, 3H; 7-*Me*); ^{13}C{^{1}H} NMR (100 MHz, [D]chloroform, r.t.): δ 157.78 (s), 131.88 (s), 131.37 (s), 115.89 (br.s), 83.02 (s, pinacolato-*C*Me$_2$), 37.21 (s), 24.75 (s, pinacolato-*Me*), 20.72 (s), 20.16 (s), 14.38 (s). HRMS (APCI): *m*/*z* calcd for $C_{14}H_{25}BO_2$+H$^+$: 237.2023[*M*+H]$^+$; found: 237.2016.

2-24. Reaction of (2*E*,4*E*)-hexa-2,4-diene (3k) with vinyl boronic acid pinacol ester (6a).

Yield: 30%. brown oil.

(1*E*,4*Z*)-3,8-dimethyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexa-1,4-diene [(1*E*,4*Z*)-7k]:

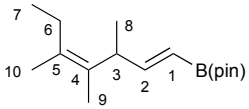


^{1}H NMR (400 MHz, [D$_6$]benzene, r.t.): δ 6.99 (dd, $^{3}J_{H,H}$=18.4, 5.6 Hz, 1H; 2-C*H*), 5.81 (dd, $^{3}J_{H,H}$=17.6 Hz, $^{4}J_{H,H}$=1.6 Hz, 1H; 1-C*H*), 5.19 (qd, $^{3}J_{H,H}$=6.8 Hz, $^{4}J_{H,H}$=1.2 Hz, 1H; 5-*CH*), 3.43 (quintd, $^{3}J_{H,H}$=7.2 Hz, $^{4}J_{H,H}$=2 Hz, 1H; 3-C*H*), 1.53 (q, $^{5}J_{H,H}$=1.7 Hz, 3H; 8-*Me*), 1.46 (dq, $^{3}J_{H,H}$=7.4 Hz, $^{5}J_{H,H}$=2 Hz, 3H; 6-*Me*), 1.07 (s, 12H; pinacolato-*Me*), 1.01 (d, $^{3}J_{H,H}$=7.2 Hz, 3H; 7-*Me*); ^{13}C{^{1}H} NMR (100 MHz, [D$_6$]benzene, r.t.): δ 157.10 (s), 137.53 (s), 120.09 (s), 82.90 (s, pinacolato-*C*Me$_2$), 39.47 (s), 24.92 (s, pinacolato-*Me*), 24.92(s), 19.19 (s), 16.93 (s), 12.92 (s). HRMS (APCI): *m*/*z* calcd for $C_{14}H_{25}BO_2$+H$^+$: 237.2023 [*M*+H]$^+$; found: 237.2022.

2-25. Reaction of (2*E*,4*E*)-3,4-dimethylhexa-2,4-diene (3l) with vinyl boronic acid pinacol ester (6a).

Yield: 29%. brown oil.

(1*E*,4*Z*)-3,4,5-trimethyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hepta-1,4-diene [(1*E*,4*Z*)-7l]:

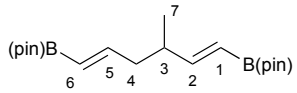


^{1}H NMR(400 MHz, [D]chloroform, r.t.): δ 6.57 (dd, $^3J_{H,H}$=18.4, 5.2 Hz, 1H; 2-C*H*), 5.36 (dd, $^3J_{H,H}$=17.6 Hz, $^4J_{H,H}$=1.6 Hz, 1H; 1-C*H*), 3.44 (quintd, $^3J_{H,H}$=7.6 Hz, $^4J_{H,H}$=2 Hz, 1H; 3-C*H*), 2.03 (dq, $^2J_{H,H}$=14.3 Hz, $^3J_{H,H}$=7.4 Hz, 1H; 6-CH_2), 1.99 (dq, $^2J_{H,H}$=14.3 Hz, $^3J_{H,H}$=7.4 Hz, 1H; 6-CH_2), 1.60 (s, 3H; 10- or 9-*Me*), 1.44 (s, 3H; 9- or 10-*Me*), 1.24 (s, 12H; pinacolato-*Me*), 1.05 (d, $^3J_{H,H}$=6.8 Hz, 3H; 8-*Me*), 0.92 (t, $^3J_{H,H}$=7.4 Hz, 3H; 7-*Me*); ^{13}C{^{1}H} NMR (100 MHz, [D]chloroform, r.t.): δ 158.05 (s), 131.05 (s), 128.88 (s), 116.47 (br. s), 83.09 (s, pinacolato *C*Me$_2$), 40.61 (s), 27.18 (s), 24.89 (s, pinacolato-*Me*), 18.56 (s), 17.27 (s), 13.58 (s), 13.46 (s). HRMS (APCI): *m*/*z* calcd for $C_{16}H_{30}BO_2$+H$^+$: 265.2336 [*M*+H]$^+$; found: 265.2324.

2-26. Reaction of (*E*)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)penta-1,3-diene (3m) with vinyl boronic acid pinacol ester (6a).

Yield: 58%. brown oil.

(1*E*,5*E*)-3-methyl-1,6-bis(4,4,5,5-tetramethyl-1,3,2-dioxaboloran-2-yl)hexa-1,5-diene [(1*E*,5*E*)-7m]:

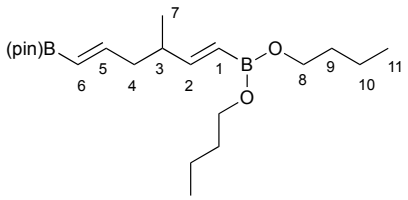


^{1}H NMR (400 MHz, [D]chloroform, r.t.): δ 6.58 (dd, $^3J_{H,H}$=17.8, 6.3 Hz, 1H; 2-C*H*), 6.57 (br.dt, $^3J_{H,H}$=17, 6 Hz, 1H; 5-C*H*), 5.42(d, $^3J_{H,H}$=17.8 Hz, 1H; 6- or 1-C*H*), 5.38 (d, $^3J_{H,H}$=17.8 Hz, 1H; 1- or 6-C*H*), 2.34-2.32 (m, 2H; 4-CH_2 and 3-C*H*), 2.06 (dtd, $^2J_{H,H}$=13.6 Hz, $^3J_{H,H}$=7.6, 6,Hz, 1H; 4-CH_2), 1.24 (s, 24H; pinacolato-*Me*), 0.98 (d, $^3J_{H,H}$=6 Hz, 3H; 3-*Me*); ^{13}C{^{1}H} NMR (100 MHz, [D]chloroform, r.t.): δ 158.90 (s). 152.34 (s), 120.60 (br. s), 116.41 (br. s), 83.01 (s, pinacolato-*C*Me$_2$), 42.47 (s), 38.32 (s), 24.75(s, pinacolato-*Me*), 18.77 (s, 7-*Me*). HRMS (APCI): *m*/*z* calcd for $C_{19}H_{34}B_2O_4$+H$^+$: 349.2722 [*M*+H]$^+$; found: 349.2715.

2-27. Reaction of (*E*)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)penta-1,3-diene (3m) with vinyl boronic acid dibutyl ester (6b).

Yield: 60% (NMR).

(1*E*,5*E*)-3-methyl-1-(dibutoxyboraneyl)-6-bis(4,4,5,5-tetramethyl-1,3,2-dioxaboloran-2-yl)hexa-1,5-diene [(1*E*,5*E*)-7n]:



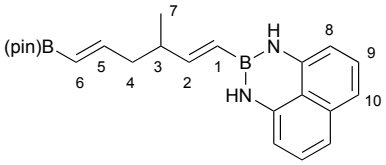
^{1}H NMR(400 MHz, [D$_6$]benzene, r.t.): δ 6.93 (ddd, $^3J_{H,H}$=18.0, 7.6, 6.4 Hz, 1H; 5-C*H*), 6.81 (dd, $^3J_{H,H}$=18.0, 7.2 Hz, 2-C*H*), 5.78 (dt, $^3J_{H,H}$=18.0 Hz, $^4J_{H,H}$=0.8 Hz, 1H; 6-C*H*), 5.60 (d, $^3J_{H,H}$=17.8 Hz, 1H; 1-C*H*), 3.89 (t, $^3J_{H,H}$=7.5 Hz, partly obscured by overlapping with a reactant, 8-CH_2), 2.26 (m,

1H; 4-CH_2), 2.2 (m, 1H; 3-C*H*), 2.04 (dt, $^3J_{H,H}$=15, 7Hz, 1H; 4-CH_2), 1.51 (m, obscured by overlapping with a reactant, 9-CH_2), 1.33 (m, obscured by overlapping with a reactant, 10-CH_2), 1.08 (s, 12H; pinacol-*Me*), 0.93 (d, $^3J_{H,H}$=6.8 Hz, 3H; 7-*Me*), 0.86 (t, $^3J_{H,H}$=6.8 Hz, 6H; 11-*Me*).

2-28. Reaction of (*E*)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)penta-1,3-diene (3m) with (2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinin-2-yl)ethene (6c).

Yield: 89%. Brown oil.

(1*E*,5*E*)-1-(2,3-dihydro-1H-naphtho[1,8-de][1,3,2]diazaborinin-2-yl)-3-methyl-6-(4,4,5,5,-tetramethyl-1,3,2-dioxaborolan-2-yl)hexa-1,5-diene [(1*E*,5*E*)-7o]:



^{1}H NMR (400 MHz, [D]chloroform, r.t.): δ 7.08 (t, $^3J_{H,H}$=8 Hz, 2H; 9-*CH*), 6.98 (d, $^3J_{H,H}$=8.4 Hz, 2H; 8-*CH*), 6.58 (dt, $^3J_{H,H}$=17.6, 6.8 Hz, 1H; 5-*CH*), 6.30 (d, $^3J_{H,H}$=7 Hz, 2H; 8-*CH*), 6.29 (dd, $^3J_{H,H}$=17.6, 6.4 Hz, 1H; 2-*CH*), 5.70 (s, 2H; N*H*), 5.52 (d, $^3J_{H,H}$=18.4 Hz, 1H; 1-*CH*), 5.47 (d, $^3J_{H,H}$=18.4 Hz, 1H; 6-*CH*), 2.39 (sept, $^3J_{H,H}$=7.6 Hz, 1H; 3-*CH*), 2.23 (dtd, $^2J_{H,H}$=16.4 Hz, $^3J_{H,H}$=7.2 Hz, $^4J_{H,H}$=1.2 Hz, 1H; 4-CH_2), 2.16 (dtd, $^2J_{H,H}$=16.4 Hz, $^3J_{H,H}$=6.9 Hz, $^4J_{H,H}$=1.1 Hz, 1H; 4-CH_2), 1.26 (s, 12H; pinacolato-*Me*), 1.04 (d, $^3J_{H,H}$=6.8 Hz, 3H; 7-*Me*); ^{13}C{^{1}H} NMR (100 MHz, [D]chloroform, r.t.): δ 152.50 (s), 152.29 (s), 141.35 (s), 136.41 (s), 127.66 (s), 121.88 (br.s), 120.80 (br.s), 117.44 (s), 115.98 (s), 105.67 (s), 83.23 (s, pinacolato-*C*Me$_2$), 42.90 (s), 38.51 (s), 24.89 (s, pinacolato-*Me*), 19.50 (s, 7-*Me*). HRMS (APCI): *m*/*z* calcd for $C_{23}H_{30}B_2N_2O_2$+H^+: 389.2574 [*M*+H]$^+$; found: 389.2566.

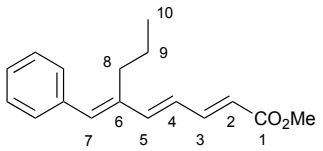
3. One pot cross-dimerization and cross-coupling

3-1. One pot reaction of 1-pentynyl boronic acid diisopropyl ester (2a), methyl (*E*)-penta-2,4-dienoate (3a) with phenyl iodide.

1-Pentynyl boronic acid diisopropyl ester (**2a**) (22.5 μL, 0.0982 mmol) and methyl (*E*)-penta-2,4-dienoate (**3a**) (11.5 μL, 0.0987 mmol) were placed in benzene-d_6 (500 μL) in the presence of [Ru(η^6-naphthalene)(η^4-1,5-cod)] (**1**) (3.35 mg, 0.00993 mmol) at room temperature for 24 h. Then, phenyl iodide (11.0 μL, 0.0987 mmol), NaOMe (120 μL in methanol, 0.120 mmol), and [Pd(PPh_3)$_4$] (**9**) (9.28 mg, 0.00803 mmol) were added in this order and warmed at 50 ˚C for 15 min. The product was purified by the recycle HPLC and was obtained as a stereoisomeric mixture of **10**.

Yield: 79%. (2*E*,4*E*,6*E*)-**10**/(2*E*,4*E*,6*Z*)-**10** = 5/1.

methyl (2*E*,4*E*,6*E*)-7-phenyl-6-propylhepta-2,4,6-trienoate [(2*E*,4*E*,6*E*)-10]:



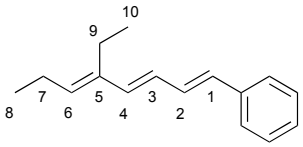
^{1}H NMR (400 MHz, [D]chloroform, r.t.): δ 7.38 (dd, $^3J_{H,H}$=15.5, 10.9 Hz, 1H; 3-C*H*), 7.35-7.26 (m, 5H; *Ph*), 6.64 (d, $^3J_{H,H}$=15 Hz, 1H; 5-C*H*), 6.62 (s, 1H; 7-C*H*), 6.40 (dd, $^3J_{H,H}$=15.4, 10.9 Hz, 1H; 4-

C*H*), 5.91 (d, $^{3}J_{H,H}$=15.5 Hz, 1H; 2-C*H*), 3.74 (s, 3H; CO_2*Me*), 2.43 (m, 2H; 8-CH_2), 1.56 (sext, $^{3}J_{H,H}$=7.4 Hz, 9-CH_2 partly overlapped with an impurity), 0.99 (t, $^{3}J_{H,H}$=7.4 Hz, 3H; 10-*Me*); ^{13}C{^{1}H} NMR (100 MHz, [D]chloroform, r.t.): δ 167.68 (s, 1-*C*O_2Me), 145.67 (s), 145.42 (s), 140.18 (s), 137.03 (s), 135.64 (s), 128.91 (s), 128.40 (s), 127.33 (s), 125.45 (s), 119.81 (s), 51.53 (s, CO_2*Me*), 29.38 (s, 8-*C*H_2), 22.44 (s, 9-*C*H_2), 14.36 (s, 10-*Me*). HRMS (APCI): *m*/*z* calcd for $C_{17}H_{20}O_2$+H^+: 257.1536 [*M*+H]$^+$; found: 257.1528.

3-2. One pot reaction of 3-hexyne (2g), (*E*)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butadiene (3d) with phenyl iodide.

This reaction was performed as shown in the formation for **10**.
Yield: 62%. yellow oil

(1*E*,3*E*,5*E*)-5-ethyl-1-phenylocta-1,3,5-triene [(1*E*,3*E*,5*E*)-11]:



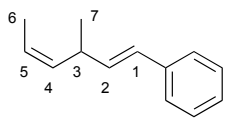
^{1}H NMR (400 MHz, [D_6]benzene, r.t.): δ 7.30 (d, $^{3}J_{H,H}$=7.5 Hz, 2H; *o*-*Ph*), 7.2-7.1 (overlapped with solvent, *Ph*), 7.05 (t, 1H, *p*-*Ph*), 6.85 (dd, $^{3}J_{H,H}$=15.5, 10.3 Hz, 1H; 2-C*H*), 6.44 (d, $^{3}J_{H,H}$=15.5 Hz, 1H; 1-C*H*), 6.39 (dd, $^{3}J_{H,H}$=15.5, 10.3 Hz, 1H; 3-C*H*), 6.27 (d, $^{3}J_{H,H}$=15.5 Hz, 1H; 4-C*H*), 5.45 (t, $^{3}J_{H,H}$=7.44 Hz, 1H; 6-C*H*), 2.24 (q, $^{3}J_{H,H}$=7.44 Hz, 2H; 9-CH_2), 2.03 (quint, $^{3}J_{H,H}$=7.44 Hz, 2H; 7-CH_2), 1.05 (t, $^{3}J_{H,H}$=7.48 Hz, 3H; 10-*Me*), 0.91 (t, $^{3}J_{H,H}$=7.44 Hz, 3H; 8-*Me*).

lit.[8] ^{1}H NMR (400 MHz, [D_6]benzene, r.t.): δ 7.30 (d, $^{3}J_{H,H}$=7.48 Hz, 2H), 7.16−7.12 (2H, overlapped with resonances for C_6D_5H), 7.04 (t, $^{3}J_{H,H}$=7.44 Hz, 1H), 6.84 (dd, $^{3}J_{H,H}$=15.5, 10.3 Hz, 1H), 6.44 (d, $^{3}J_{H,H}$=15.5 Hz, 1H), 6.39 (dd, $^{3}J_{H,H}$=15.5, 10.3 Hz, 1H,), 6.27 (d, $^{3}J_{H,H}$=15.5 Hz, 1H), 5.44 (t, $^{3}J_{H,H}$=7.4 Hz, 1H), 2.24 (q, $^{3}J_{H,H}$=7.5 Hz, 2H), 2.03 (quint, $^{33}J_{H,H}$=7.4 Hz, 2H), 1.05 (t, $^{3}J_{H,H}$=7.4 Hz, 3H), 0.92 (t, $^{3}J_{H,H}$=7.4 Hz, 3H).

3-3. One pot reaction of (*E*)-1,3-pentadiene (3b), vinyl boronic acid pinacol ester (6a).with phenyl iodide.

This reaction was performed as shown in the formation for **10**.
Yield: 81%. yellow oil,

(1*E*,4*Z*)-3-methyl-1-phenylhexa-1,4-diene [(1*E*,4*Z*)-12]:



[S8] S. Kiyota, S. In, R. Saito, N. Komine, M. Hirano, *Organometallics* **2016**, *35*, 4033-4043.

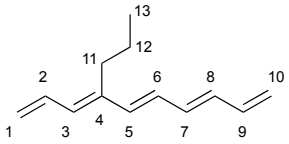
^{1}H NMR (400 MHz, [D]chloroform, r.t.): δ 7.35 (d, $^3J_{H,H}$=7.4 Hz, 2H; *o-Ph*), 7.29 (t, $^3J_{H,H}$=6.9 Hz, 2H; *m-Ph*), 7.18 (t, $^3J_{H,H}$=6.9 Hz, 1H; *p-Ph*), 6.36 (d, $^3J_{H,H}$=16 Hz, 1H; 1-C*H*), 6.17 (dd, $^3J_{H,H}$=16.0, 6.3 Hz, 1H; 2-C*H*), 5.50 (dq, $^3J_{H,H}$=10.9, 6.9 Hz, 1H; 5-C*H*), 5.33 (ddq, $^3J_{H,H}$=10.9, 9.2 Hz, $^4J_{H,H}$=1.7 Hz, 1H; 4-C*H*), 3.36 (sext, $^3J_{H,H}$=7.4 Hz, 1H; 3-C*H*), 1.68 (dd, $^3J_{H,H}$=6.9 Hz, $^4J_{H,H}$=1.7 Hz, 3H; 6-*Me*), 1.16 (d, $^3J_{H,H}$=6.3 Hz, 3H; 7-*Me*). HRMS (APCI): *m*/*z* calcd for $C_{13}H_{16}$+H$^+$: 173.1325 [*M*+H]$^+$; found: 173.1320.

3-4. One pot reaction of 1-pentynyl boronic acid diisopropyl ester (2a), (*E*)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butadiene (3d) with vinyl bromide

1-Pentynyl boronic acid diisopropyl ester (**2a**) (22.5 μL, 0.0982 mmol) and (*E*)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butadiene (**3d**) (22.0 μL, 0.110 mmol), and [Ru(η^6-naphthalene)(η^4-1,5-cod)] (**1**) (3.34 mg, 0.00990 mmol) in [D_6]benzene were warmed at 50 ˚C for 3 h. Then, vinyl bromide (15.0 μL, 0.212 mmol), NaOEt (240 μL in EtOH, 0.240 mmol), and [Pd(PPh_3)$_4$] (**9**) (18.46 mg, 0.01597 mmol) were added and warmed at 50 ˚C for 5 h. After addition of 1,4-dioxane (5.0 μL, 0.058 mmol)as an internal standard, the product yield was estimated. The products were purified by the recycle HPLC. The product was obtained as a mixture of (3*E*,5*E*,7*E*)-**13** and (3*E*,5*E*)-**14**.

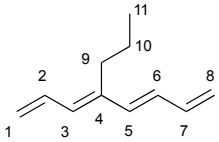
Yields: (3*E*,5*E*,7*E*)-**13**: 46%, (3*E*,5*E*)-**14**: 20%. yellow oil.

(3*E*,5*E*,7*E*)-4-propyldeca-1,3,5,7,9-pentaene [(3*E*,5*E*,7*E*)-13]:



^{1}H NMR (400 MHz, [D]chloroform, r.t.): δ 6.60 (ddd, $^3J_{H,H}$=17.8, 11.5, 10.3 Hz, 1H; 2-C*H*), 6.38 (ddddd, $^3J_{H,H}$=16.0, 11.8, 10.3 Hz, $^4J_{H,H}$=–1.0, –0.5 Hz, 1H; 8-C*H*), 6.32 (dd, $^3J_{H,H}$=17.8, 10.3 Hz, 1H; 9-C*H*), 6.30 (ddd, $^3J_{H,H}$=16.0, 10.5 Hz, $^4J_{H,H}$=–1.0 Hz, 1H; 7-C*H*), 6.28 (ddd, $^3J_{H,H}$=17.5, 10.5 Hz, $^4J_{H,H}$=–1.0 Hz, 1H; 6-C*H*), 6.19 (dd, $^3J_{H,H}$=17.5 Hz, $^4J_{H,H}$=–1.0 Hz, 1H; 5-C*H*), 6.08 (ddt, $^3J_{H,H}$=10.5, $^4J_{H,H}$=–2.5, $^4J_{H,H}$=–1.0 Hz, 1H; 3-C*H*), 5.23 (ddd, $^3J_{H,H}$=17.8, $^2J_{H,H}$=–3.0, $^4J_{H,H}$=–0.5 Hz, 1H; 10-CH_2), 5.19 (dt, $^3J_{H,H}$=17.8, $^2J_{H,H}$=2.5 Hz,$^4J_{H,H}$=2.5 Hz, 1H; 1-CH_2), 5.12 (ddd, $^3J_{H,H}$=10.3 Hz, $^2J_{H,H}$=–3.0 Hz, $^4J_{H,H}$=–0.5 Hz, 1H; 10-CH_2), 5.09 (ddd, $^3J_{H,H}$=10.3 Hz, $^2J_{H,H}$=–1.0 Hz, $^4J_{H,H}$=–0.9 Hz, 1H; 1-CH_2), 2.33 (t, $^3J_{H,H}$=7.4 Hz, 2H; 11-CH_2), 1.46 (sext, $^3J_{H,H}$=7.4 Hz, 2H; 12-CH_2), 0.92 (t, $^3J_{H,H}$=7.4 Hz, 3H; 13-*Me*); ^{13}C{^{1}H} NMR (100 MHz, [D]chloroform, r.t.): δ 140.63 (s, 4-*C*Pr), 137.13 (s, 7- or 6-*C*H), 137.02 (s, 5-*C*H), 134.04 (s, 8-*C*H), 133.97 (s, 9-*C*H), 133.05 (s, 2-*C*H), 132.32 (s, 3-*C*H), 128.21 (s, 6- or 7-*C*H), 117.92 (s, 10-CH_2), 117.00 (s, 1-CH_2), 28.89 (s, 11-CH_2), 22.70 (s, 12-CH_2), 14.22 (s, 13-*Me*). HRMS (APCI): *m*/*z* calcd for $C_{13}H_{18}$+H$^+$: 175.1481 [*M*+H]$^+$; found: 175.1474.

(3*E*,5*E*)-4-propylocta-1,3,5,7-tetraene [(3*E*,5*E*)-14]:



^{1}H NMR (400 MHz, [D]chloroform, r.t.): δ 6.82 (dt, $^3J_{H,H}$=16.7, 11 Hz, 1H; 2-C*H*), 6.4-6.2 (obscured by overlapping with **13**, 5-, 6- and 7-C*H*), 5.97 (d, $^3J_{H,H}$=11 Hz, 1H; 3-C*H*), 5.2-5.1 (obscured by overlapping with **13**, 1- and 8-CH_2), 2.21 (t, $^3J_{H,H}$=7.5 Hz, 2H; 9-CH_2), 1.48 (sext, $^3J_{H,H}$= 7 Hz, partly

obscured by overlapping with **13**, 10-CH_2), 0.91 (t, $^3J_{H,H}$=7 Hz, partly obscured by overlapping with **13**, 11-*Me*); ^{13}C{^{1}H} NMR (100 MHz, [D]chloroform, r.t.): δ 138.6 (s). 133.7 (s), 132.1 (s), 130.1 (s), 129.4 (s), 129.2 (s), 117.3 (s, 8- or 1-*C*H_2), 117.1 (s, 1- or 8-*C*H_2), 28.8 (s, 9-*C*H_2), 22.3 (s, 10-*C*H_2), 14.1 (s, 11-*Me*). MS (EI): *m*/*z* = 148 (M^+).

3-5. One pot reaction of (1*E*,3*E*)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)penta-1,3-diene (3g), vinylboronic acid dibutyl ester (6b), phenyl iodide with 4-tolyl iodide

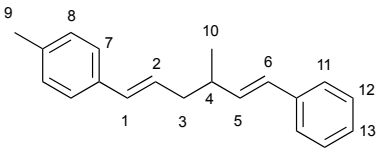
Vinyl boronic acid dibutyl ester (**6b**) (122 μL, 0.455 mmol) and (1*E*,3*E*)-1-(4,4,5,5,-tetramethyl-1,3,2-dioxaborolan-2-yl)penta-1,3-diene (**3g**) (100 μL, 0.464 mmol) were dissolved in thf (4 mL) and [Ru(η^6-naphthalene)(η^4-1,5-cod)] (**1**) (15.0 mg, 0.0444 mmol) was add. The mixture was warmed at 40 ˚C for 2 h. Then, phenyl iodide (50.9 μL, 0.464 mmol), Cs_2CO_3 (309.7 mg, 0.9505 mmol) and [Pd(PPh_3)$_4$] (**9**) [28.49 mg, 0.02465 mmol] were added into the solution and the mixture was warmed at 40 ˚C for 48 h. Then, 4-tolyl iodide (205.62 mg, 0.9430 mmol), Cs_2CO_3 (312.9 mg, 0.9576 mg), and [Pd(PPh_3)$_4$] (**9**) [27.4 mg, 0.02372 mg] were added into the solution and the mixture was warmed at 65 ˚C for 16 h. After a short column chromatography (SiO_2), the product was purified by the recycling HPLC. (1*E*,5*E*)-**15** was obtained in 29% yield (35.4 mg, 0.135 mmol).

(1*E*,5*E*)-**15**: Yield: 29%. pale yellow oil.

Compound **6b** (50 μL, 0.225 mmol) and **3g** (55 μL, 0.227 mmol) were dissolved in thf (4 mL) and **1** (2.8 mg, 0.0083 mmol) was added into the solution. The solution was warmed at 30 ˚C for 3 h. Then, phenyl iodide (22.0 μL, 0.201 mmol), Cs_2CO_3 (174.0 mg, 0.5340 mmol), and **9** (19.1 mg, 0.0165 mmol) were added into the solution. The solution was warmed at 40 ˚C for 8 h. After a short column chromatography by silica gel, the product was purified by the recycling HPLC to give (1*E*,5*E*)-**16** in 24% yield (14.1 mg, 0.0473 mmol).

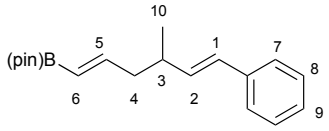
(1*E*,5*E*)-**16**: Yield: 24%. pale red oil.

(1*E*,5*E*)-4-methyl-6-phenyl-1-(4-tolyl)hexa-1,5-diene [(1*E*,5*E*)-15]:



^{1}H NMR(400 MHz, [D]chloroform, r.t.):δ 7.36 (d, $^3J_{H,H}$=7.6 Hz, 2H; 11-C*H*), 7.30 (t, $^3J_{H,H}$=7.2 Hz, 2H, 12-C*H*), 7.24 (partly overlapped with C_6D_5H, 7-C*H*), 7.20 (t, $^3J_{H,H}$=6.4 Hz, 1H; 13-C*H*), 7.10 (d, $^3J_{H,H}$=7.6 Hz, 2H; 8-C*H*), 6.39 (d, $^3J_{H,H}$=16.1 Hz, 2H; 1- and 6-C*H*), 6.18 (dd, $^3J_{H,H}$=15.2, 7.5 Hz, 1H; 5-C*H*), 6.17 (dt, $^3J_{H,H}$=15.5, 7.4 Hz, 1H; 2-C*H*), 2.48 (sept, $^3J_{H,H}$=6.9 Hz, 1H; 4-C*H*), 2.33 (s, 3H; 9-*Me*), 2.34 (dt, $^2J_{H,H}$=13.7 Hz, $^3J_{H,H}$=7.4 Hz, 1H; 3-CH_2), 2.25 (dt, $^2J_{H,H}$=13.7 Hz, $^3J_{H,H}$=7.4 Hz, 1H; 3-CH_2), 1.14 (d, $^3J_{H,H}$= 6.8 Hz, 3H;10-*Me*); ^{13}C {^{1}H} NMR (100 MHz, [D]chloroform, r.t.): δ 137.74 (s), 136.61 (s), 136.03 (s), 134.91 (s), 131.109 (s), 129.15 (s), 128.46 (s), 128.21 (s), 127.76 (s), 126.86 (s), 126.01 (s), 125.87 (s), 40.58(s), 37.40 (s), 21.13 (s),19.97 (s). HRMS (APCI): *m*/*z* calcd for $C_{20}H_{23}$+H^+: 263.1794 [*M*+H]$^+$; found: 263.1782.

(1*E*,5*E*)-3-methyl-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-phenyl-hexa-1,5-diene [(1*E*,5*E*)-16]:



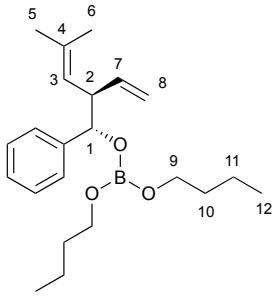
^{1}H NMR (400 MHz, [D]chloroform, r.t.): δ 7.31 (d, $^3J_{H,H}$=7.5 Hz, 2H; 7-C*H*), 7.27 (t, $^3J_{H,H}$=7.6 Hz, 2H; 8-C*H*), 7.17 (t, $^3J_{H,H}$=7.2 Hz, 1H; 9-C*H*), 6.59 (dt, $^3J_{H,H}$=17.6 ,6.8 Hz, 1H; 5-C*H*), 6.34 (d, $^3J_{H,H}$=16 Hz, 1H; 1-C*H*), 6.13 (dd, $^3J_{H,H}$=15.2, 7.6 Hz, 1H; 2-C*H*), 5.47 (d, $^3J_{H,H}$=17.6 Hz, 1H; 6-C*H*), 2.44 (sept, $^3J_{H,H}$= 6.8 Hz, 1H; 3-*CH*), 2.30 (dt, $^3J_{H,H}$=13.7 Hz, $^3J_{H,H}$=6.9 Hz, 1H; 4-CH_2), 2.18 (dt, $^2J_{H,H}$=13.7 Hz, $^3J_{H,H}$=7.5 Hz, 1H; 4-CH_2), 1.24 (s, 12H; pinacolato-*Me*), 1.07 (d, $^3J_{H,H}$=6.8 Hz, 3H;10-*Me*); ^{13}C{^{1}H} NMR (100 MHz, [D]chloroform, r.t.): δ 152.40 (s), 137.73 (s), 135.92 (s), 128.43 (s), 128.11 (s), 126.83 (s), 126.00 (s), 120.57 (br. s), 82.30 (s, pinacolato-*C*Me$_2$), 43.46 (s), 36.29 (s), 24.74 (s, pinacolato-*Me*), 20.03 ppm (s). HRMS (APCI): *m*/*z* calcd for $C_{19}H_{287}BO_2$+H$^+$: 299.2180 [*M*+H]$^+$; found: 299.2169.

4. Allylboration

4-1. Reaction of 7be with benzaldehyde.

Treatment of vinyl boronic acid dibutyl ester (**6b**) (10.0 μL, 0.0455 mmol) with isoprene (**3e**) (4.5 μL, 0.046 mmol) in the presence of [Ru(η^6-naphthalene)(η^4-1,5-cod)] (**1**) (1.6 mg, 0.0047 mmol) in [D$_6$]benzene (500 μL) at 50 ˚C for 1 h produced **7c** in 62 % yield. Then, benzaldehyde (4.6 μL, 0.045 mmol) was added into the solution and the solution was warmed at 30 ˚C for 3 h to give **17** in 77% yield (NMR) based on **7c**.

Dibutyl {*rac*-(1*S*,2*R*)-4-methyl-1-phenyl-2-vinylpent-3-en-1-yl}boronate (17):



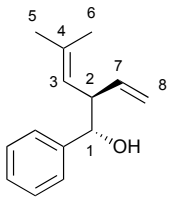
^{1}H NMR (400 MHz, [D$_6$]benzene, r.t.): δ 7.19-6.95 (m, obscured by C_6D_6 and reactant), 6.05 (ddd, $^3J_{H,H}$=18.0, 10.4, 7.6 Hz, 1H; 7-C*H*), 5.34 (d, $^3J_{H,H}$=6.8 Hz, 1H; 1-C*H*), 5.19 (dm, $^3J_{H,H}$=9Hz, 1H; 3-C*H*), 5.11 (dm, $^3J_{H,H}$=18.0 Hz, 1H; 8-CH_2), 5.10 (dm, $^3J_{H,H}$=10.4 Hz, 1H; 8-CH_2), 3.9 (obscured by overlapping with a reactant, 9-CH_2), 3.47 (q, $^3J_{H,H}$=9.2 Hz, 1H; 2-C*H*), 1.5 (obscured by overlapping with a reactant, 10-CH_2 and 6- or 5-*Me*), 1.3 (obscured by overlapping with a reactant, 11-CH_2 and 5- or 6-*Me*), 0.86 (obscured by overlapping with a reactant, 12-*Me*).

4-2. Hydrolysis of 17.

Treatment of **17**, derived from the reaction of **6b** (200 μL, 0.91 mmol) with isoprene (95 μL, 0.95 mmol), **1** (10.5 mg, 0.0311 mmol) and benzaldehyde (92 μL, 0.90 mmol), with H_2O_2 (35% in H_2O) and NaOH (3 M) at room temperature for 1 h followed by purification by recycling HPLC produced *rac-anti*-**18** (66.4 mg, 0.328 mmol), which was reported by a literature.[S9]

anti-**18**: Yield 36%. pale yellow oil.

***rac*-(1*S*,2*R*)-4-methyl-1-phenyl-2-vinylpent-3-en-1-ol (18).**



^{1}H NMR (400 MHz, [D]chloroform, r.t.): δ 7.28-7.24 (m, overlapped with $CHCl_3$, *Ph*), 5.74 (d, $^{3}J_{H,H}$=19.5 Hz, 1H; 8-C*H*), 5.73 (ddd, $^{3}J_{H,H}$=19.5, 10.3, 7.4 Hz, 1H; 7-C*H*), 5.09 (d, $^{3}J_{H,H}$=5.7 Hz, 1H; 3-C*H*), 4.97 (dd, $^{3}J_{H,H}$=9.2 Hz, $^{4}J_{H,H}$=1.2 Hz, 1H; 8-CH_2), 4.44 (dd, $^{3}J_{H,H}$=7.4 Hz, $^{4}J_{H,H}$=2.3 Hz, 1H; 1-C*H*), 3.19 (q, $^{3}J_{H,H}$=8.0 Hz, 1H; 2-C*H*), 1.58 (s, 3H; 6- or 5-*Me*), 1.29 (s, 3H; 5- or 6-*Me*); ^{13}C{^{1}H} NMR (100 MHz, [D]chloroform, r.t.): δ 142.15 (s), 137.98 (s), 134.41 (s), 127.82 (s), 127.24 (s), 126.71 (s), 122.07 (s), 116.90 (s), 51.56 (s), 25.78 (s), 17.85 (s). HRMS (APCI): *m*/*z* calcd for $C_{14}H_{18}O+H^{+}$: 203.1436 $[M+H]^{+}$; found: 203.1425.

[S9] P. Bertus, L. Frouin, C. Laroche, J. Szymoniak, *Tetrahedron*, 2004, **60**, 1375.

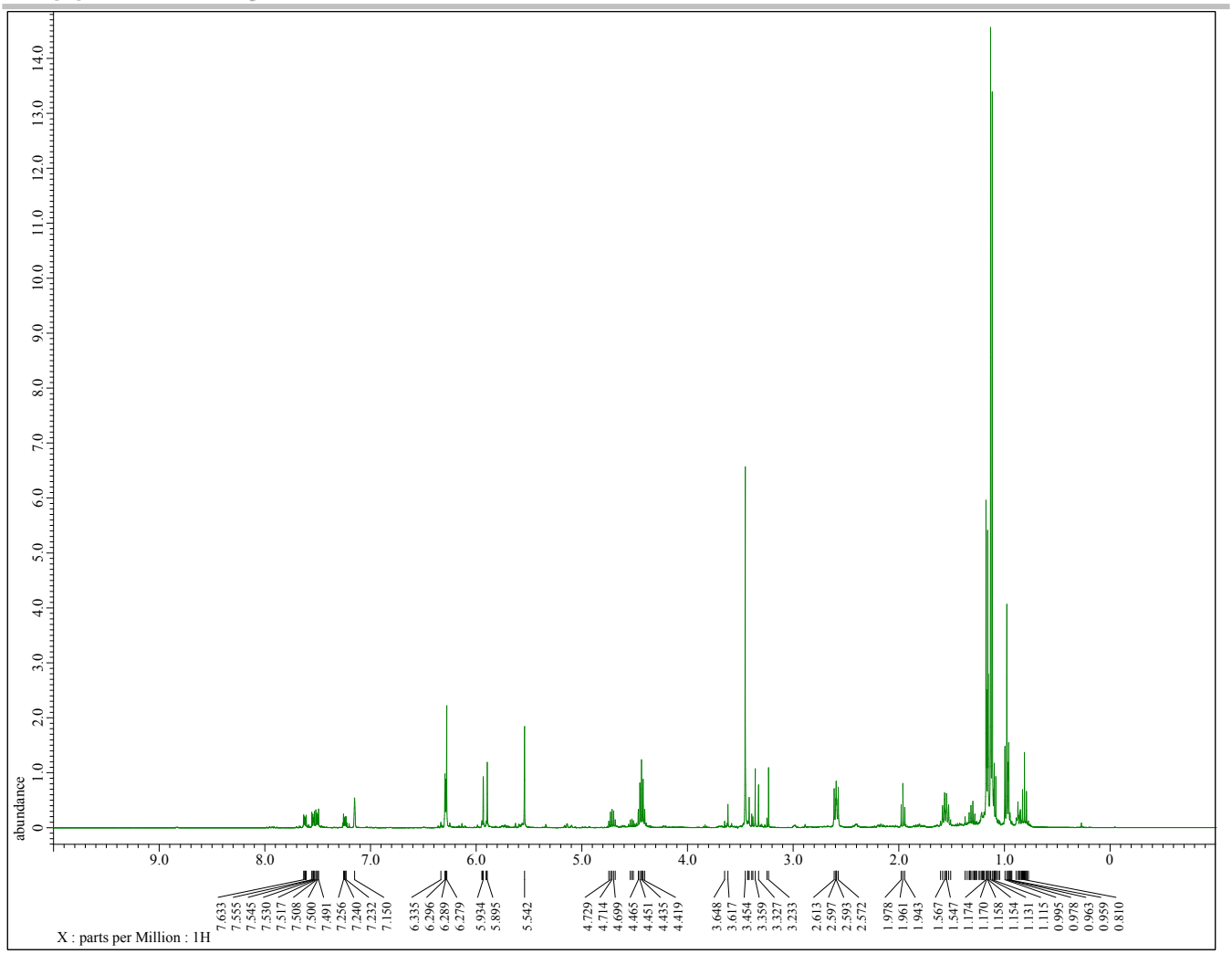
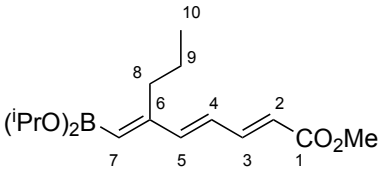


Figure S1. ^{1}H NMR spectrum of methyl (2*E*,4*E*,6*E*)-7-(diisopropoxyboraneyl)-6-propylhepta-2,4,6-trienoate [(2*E*,4*E*,6*E*)-**4a**] (an *in situ* reaction in an NMR tube) (400 MHz, [D_6]benzene).



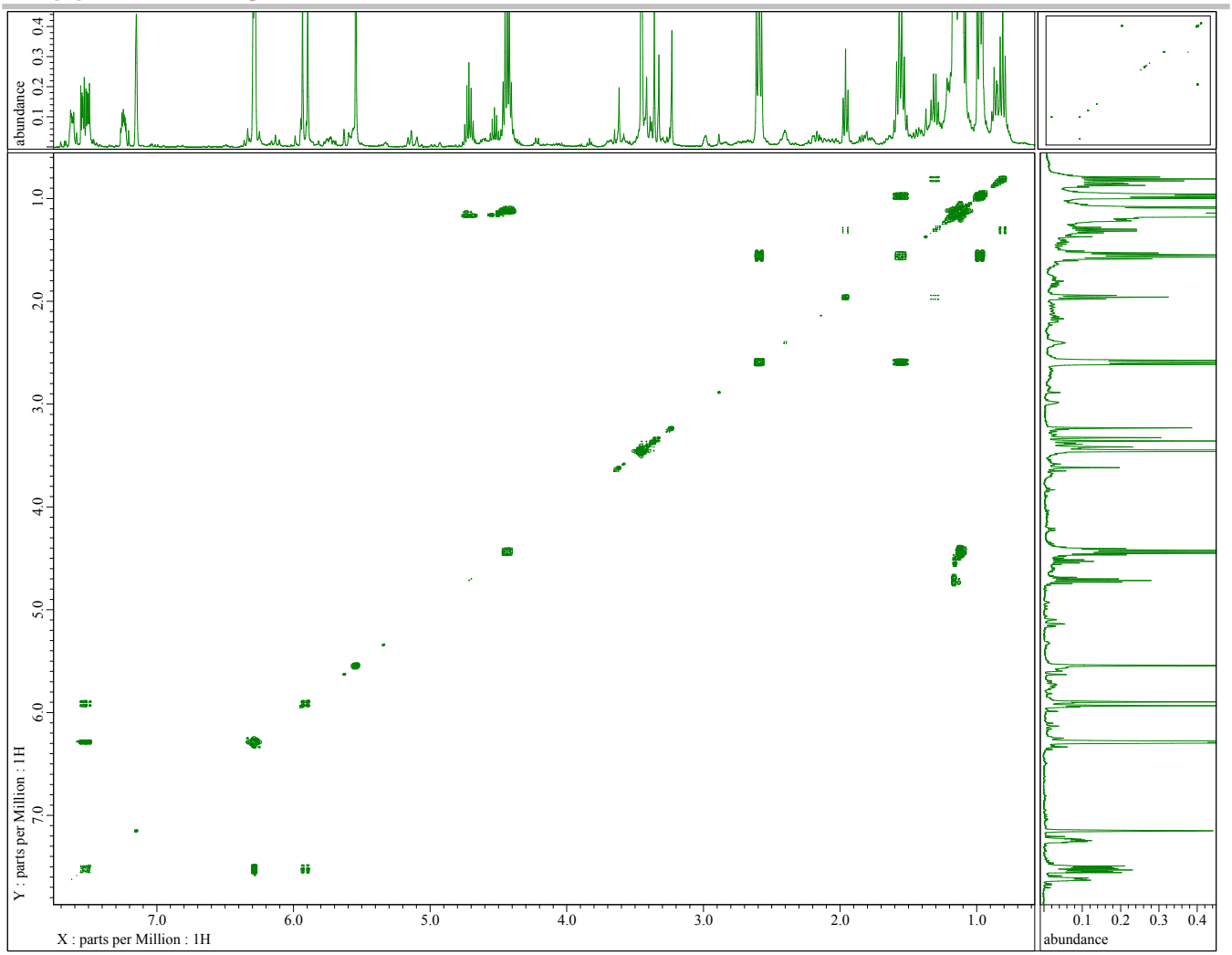
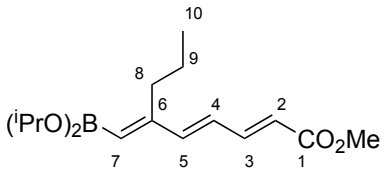


Figure S2. ^{1}H-^{1}H COSY of methyl (2*E*,4*E*,6*E*)-7-(diisopropoxyboraneyl)-6-propylhepta-2,4,6-trienoate [(2*E*,4*E*,6*E*)-**4a**] (an *in situ* reaction in an NMR tube) (400 MHz, [D_6]benzene).



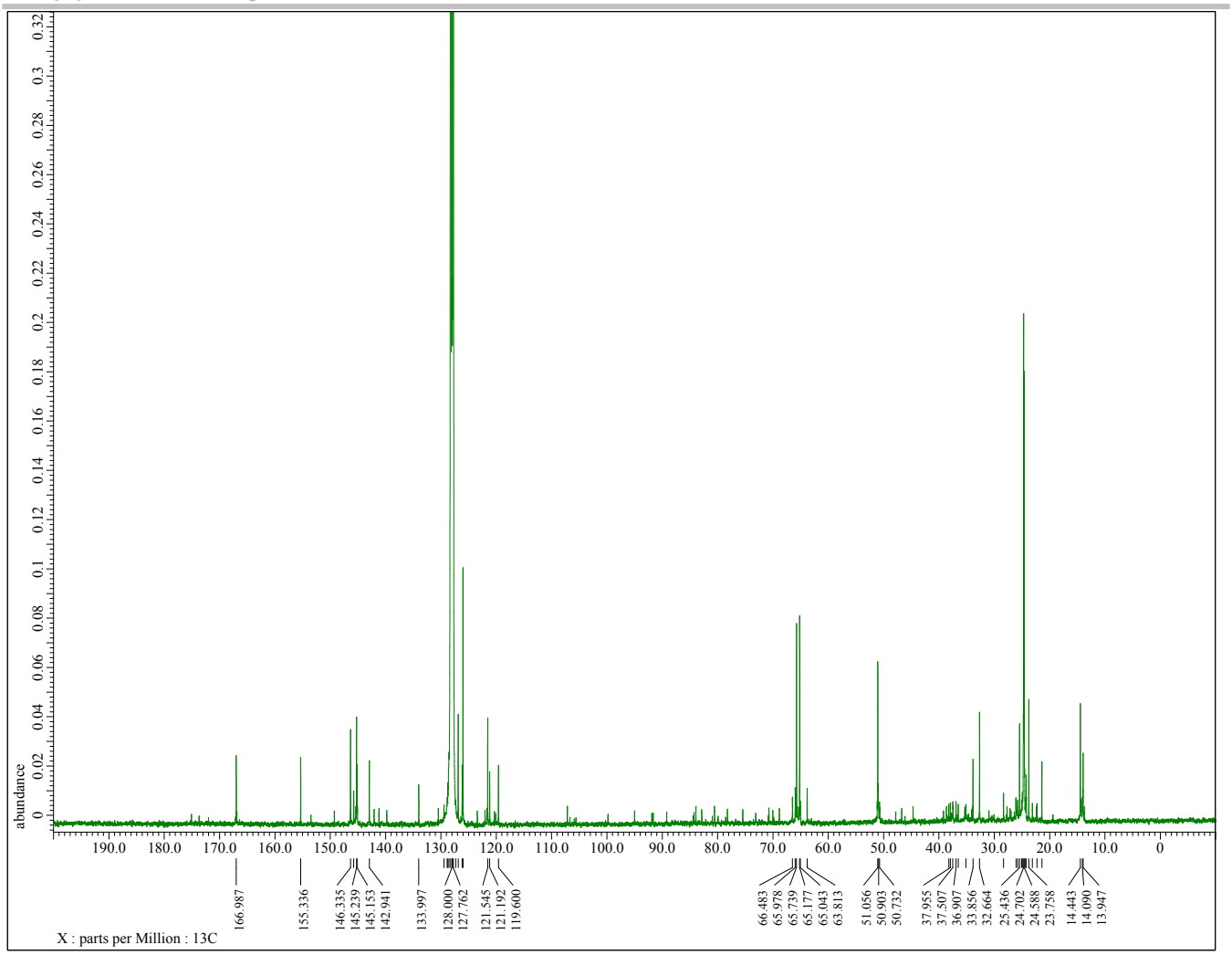
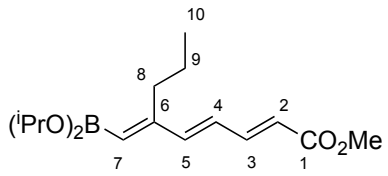


Figure S3. $^{13}C\{^{1}H\}$ NMR spectrum of methyl (2*E*,4*E*,6*E*)-7-(diisopropoxyboraneyl)-6-propylhepta-2,4,6-trienoate [(2*E*,4*E*,6*E*)-**4a**] (an *in situ* reaction in an NMR tube) (100 MHz, [D_6]benzene).



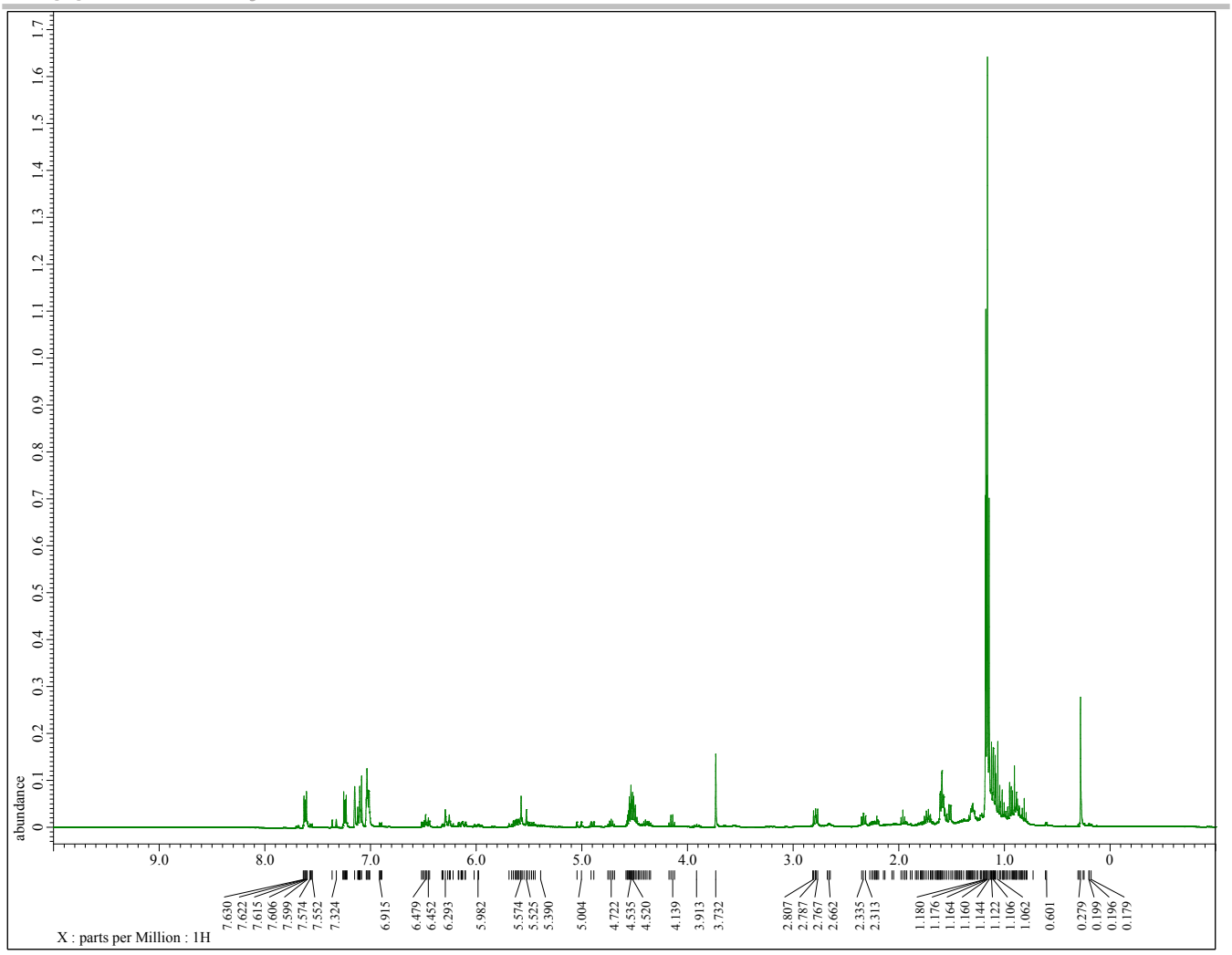
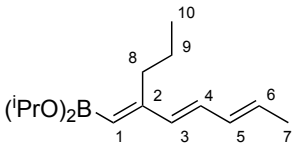


Figure S4. ^{1}H NMR spectrum of methyl (1*E*,3*E*,5*E*)-1-(diisopropoxyboraneyl)-2-propylhepta-1,3,5-trienoate [(1*E*,3*E*,5*E*)-**4b**] (an i*n situ* reaction in an NMR tube) (400 MHz, [D_6]benzene).



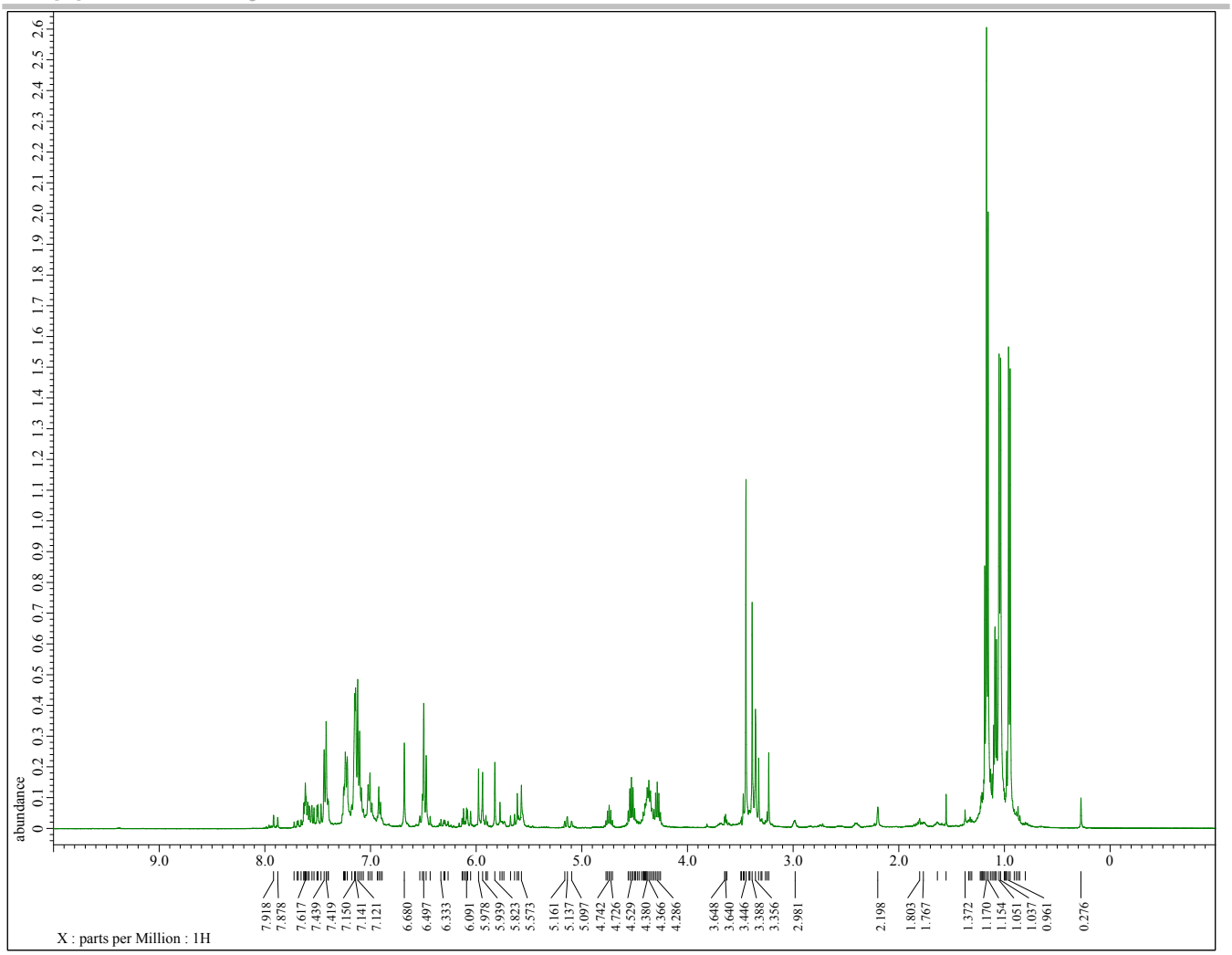
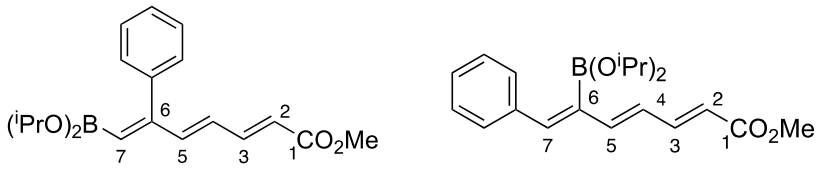


Figure S5. ^{1}H NMR spectrum of methyl (2*E*,4*E*,6*E*)-6-(diisopropoxyboraneyl)-7-phenylhepta-2,4,6-trienoate [(2*E*,4*E*,6*E*)-**4c**] and methyl (2*E*,4*E*,6*E*)-6-(diisopropoxyboraneyl)-7-phenylhepta-2,4,6-trienoate [(2*E*,4*E*,6*E*)-**5c**] (an *in situ* reaction in an NMR tube) (400 MHz, [D_6]benzene).



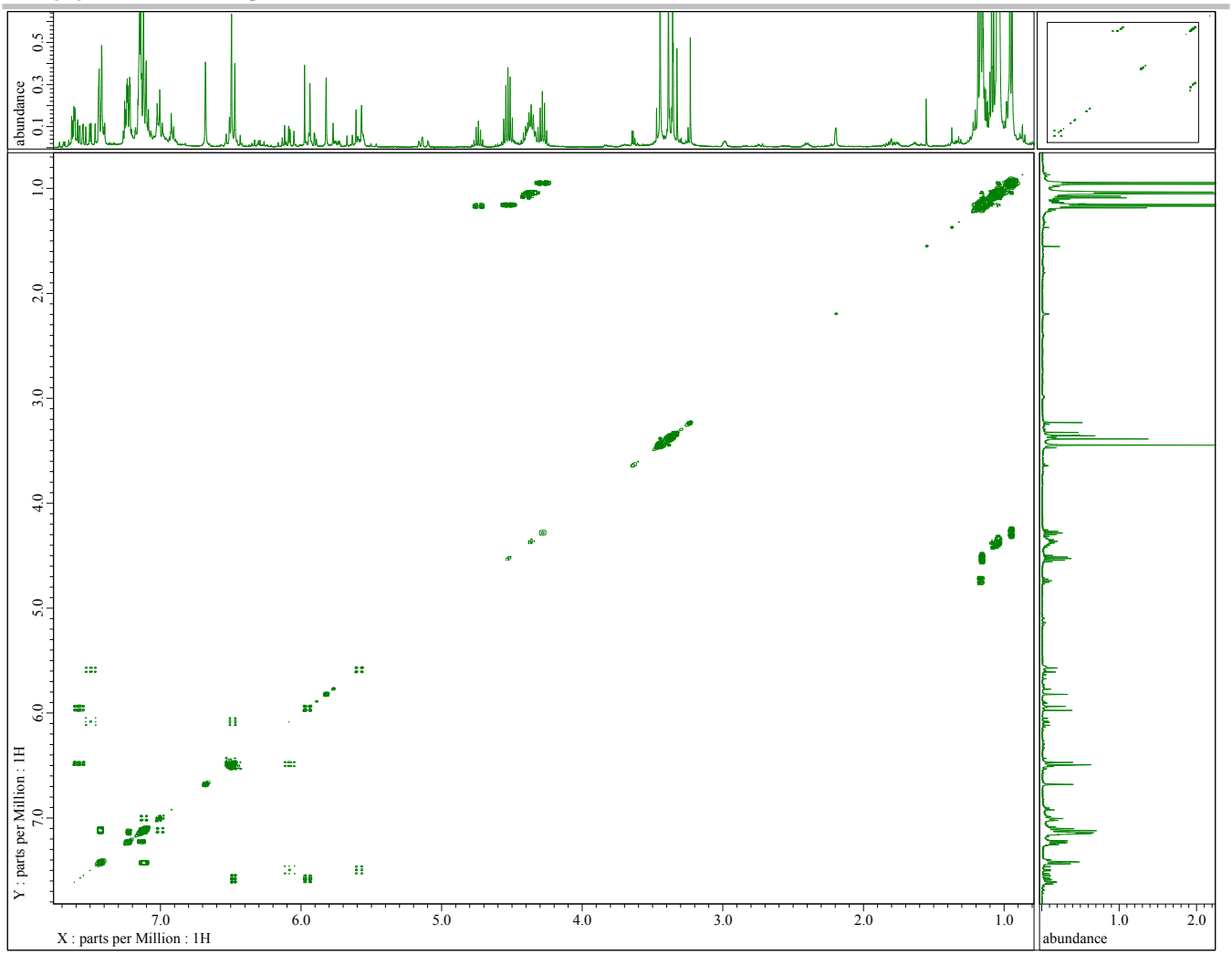
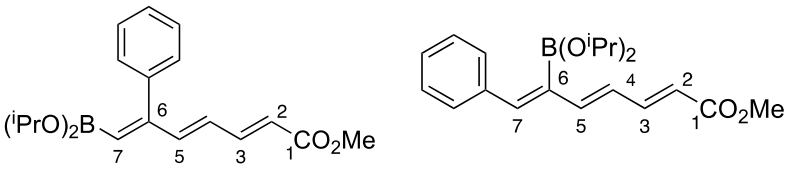


Figure S6. ^{1}H-^{1}H COSY of methyl (2*E*,4*E*,6*E*)-6-(diisopropoxyboraneyl)-7-phenylhepta-2,4,6-trienoate [(2*E*,4*E*,6*E*)-**4c**] and methyl (2*E*,4*E*,6*E*)-6-(diisopropoxyboraneyl)-7-phenylhepta-2,4,6-trienoate [(2*E*,4*E*,6*E*)-**5c**] (an *in situ* reaction in an NMR tube) (400 MHz, [D_6]benzene).



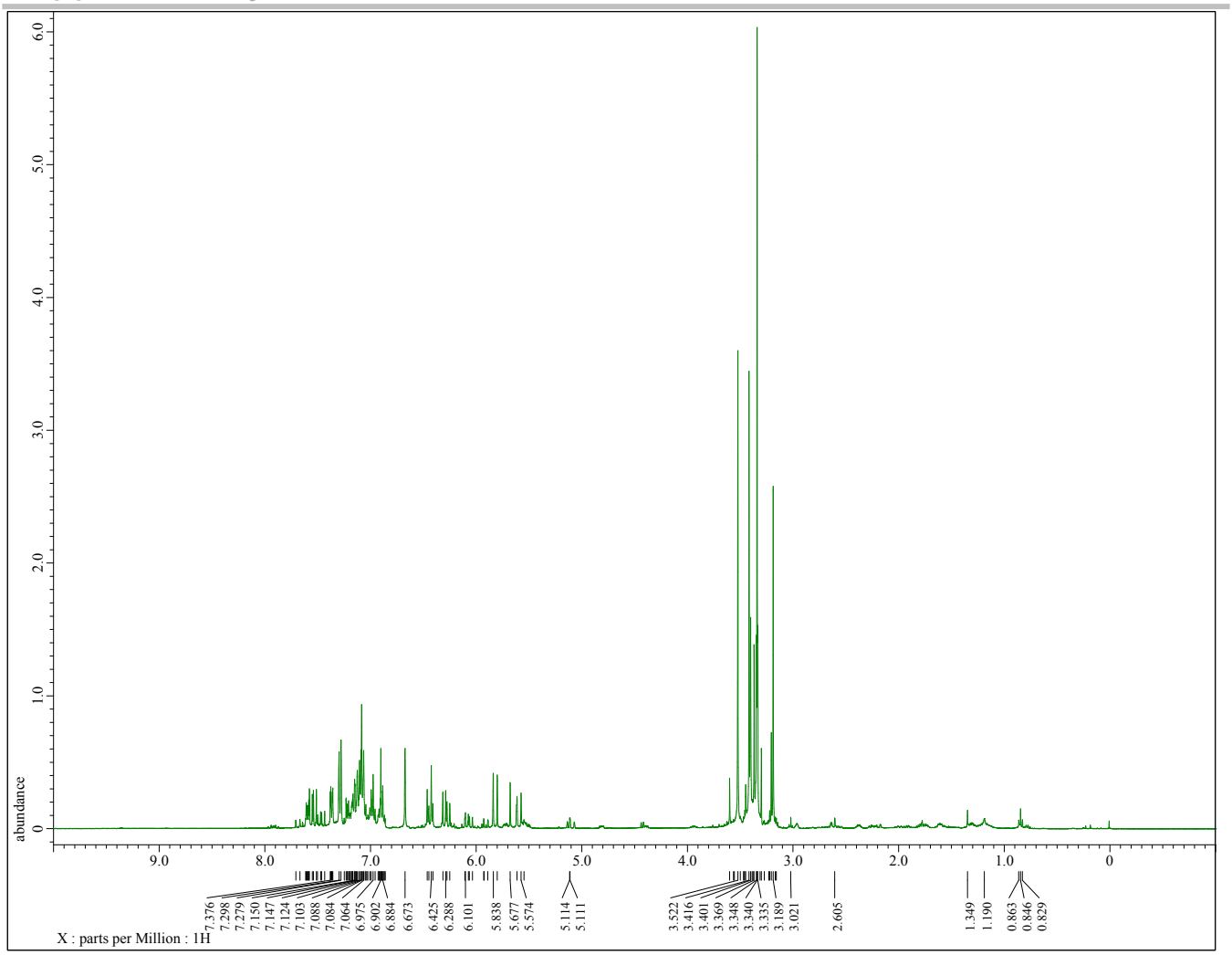
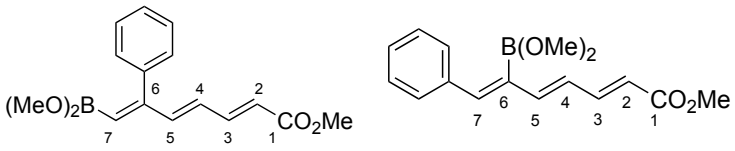


Figure S7. ^{1}H NMR spectrum of a mixture of methyl (2*E*,4*E*,6*E*)-7-(dimethoxyboraneyl)-6-phenylhepta-2,4,6-trienoate [(2*E*,4*E*,6*E*)-**4d**] and (2*E*,4*E*,6*E*)-6-(dimethoxyboraneyl)-7-phenylhepta-2,4,6-trienoate [(2*E*,4*E*,6*E*)-**5d**] (an *in situ* reaction in an NMR tube) (400 MHz, [D_6]benzene).



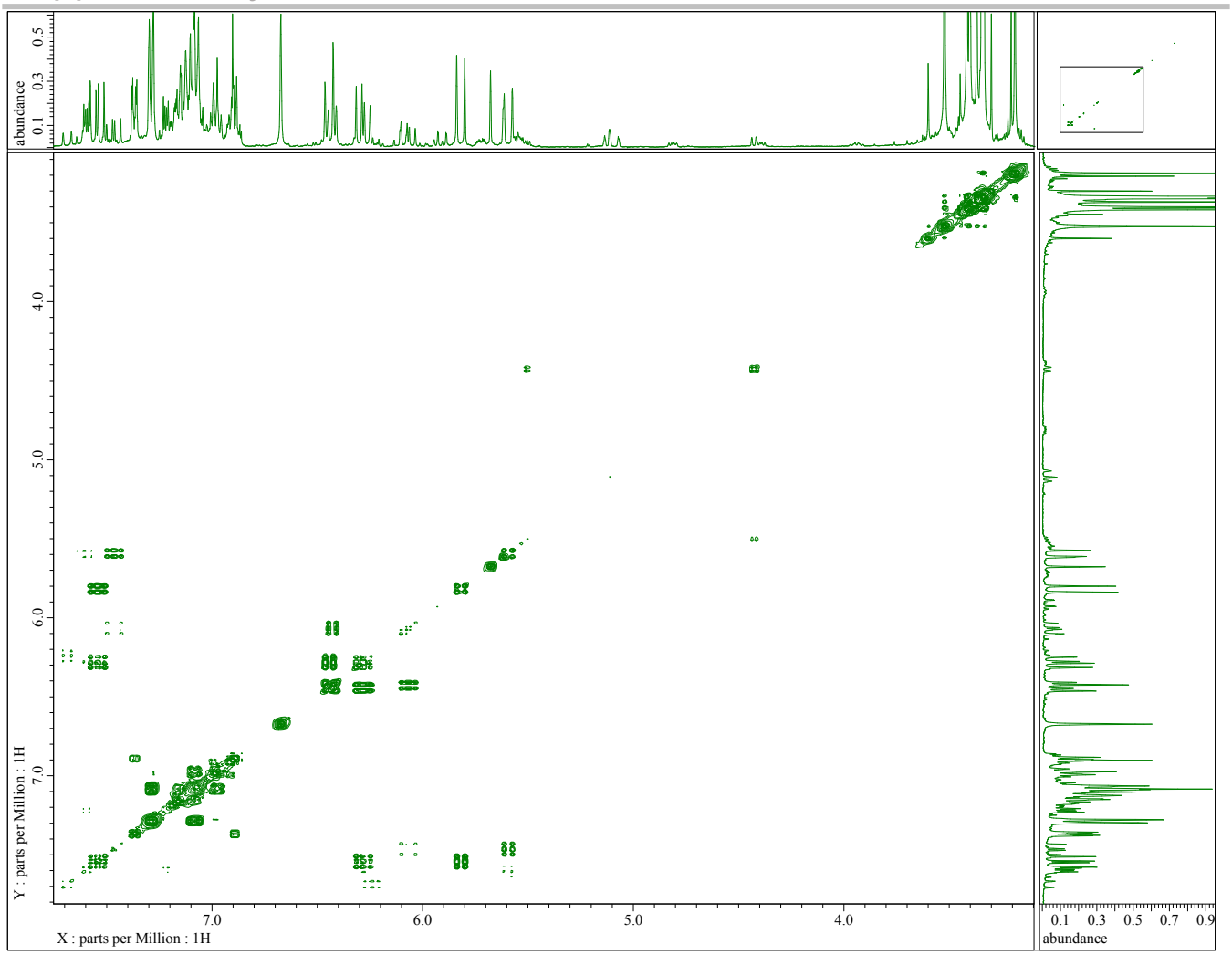
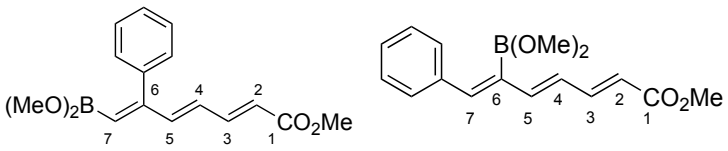


Figure S8. ^{1}H-^{1}H COSY of of a mixture of methyl (2*E*,4*E*,6*E*)-7-(dimethoxyboraneyl)-6-phenylhepta-2,4,6-trienoate [(2*E*,4*E*,6*E*)-**4d**] and (2*E*,4*E*,6*E*)-6-(dimethoxyboraneyl)-7-phenylhepta-2,4,6-trienoate [(2*E*,4*E*,6*E*)-**5d**] (an *in situ* reaction in an NMR tube) (400 MHz, [D_6]benzene).



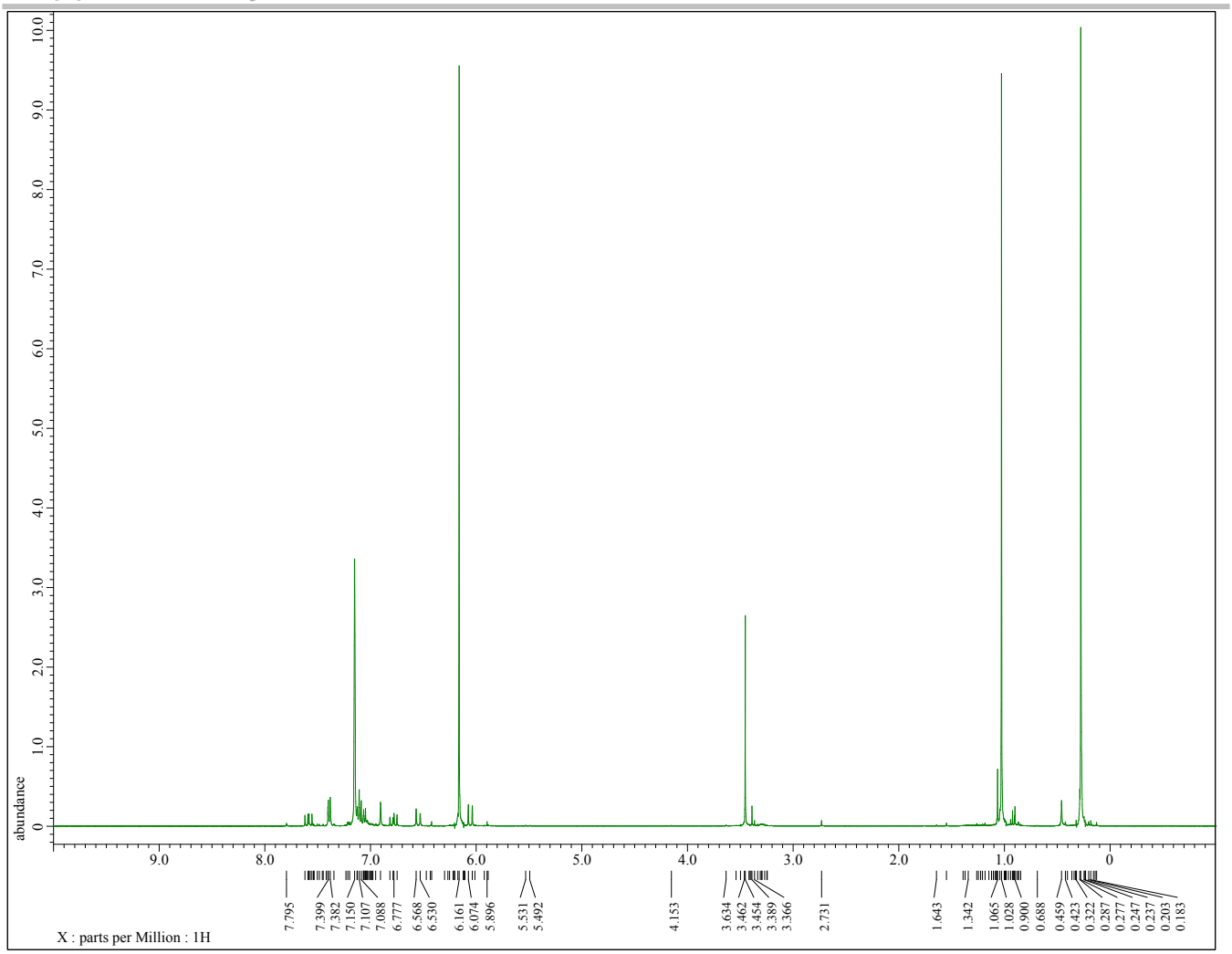
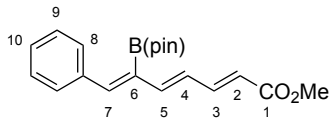


Figure S9. ^{1}H NMR spectrum of methyl (2*E*,4*E*,6*E*)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-7-phenylhepta-2,4,6-trienoate [(2*E*,4*E*,6*E*)-**5e**] (400 MHz, [D_6]benzene).



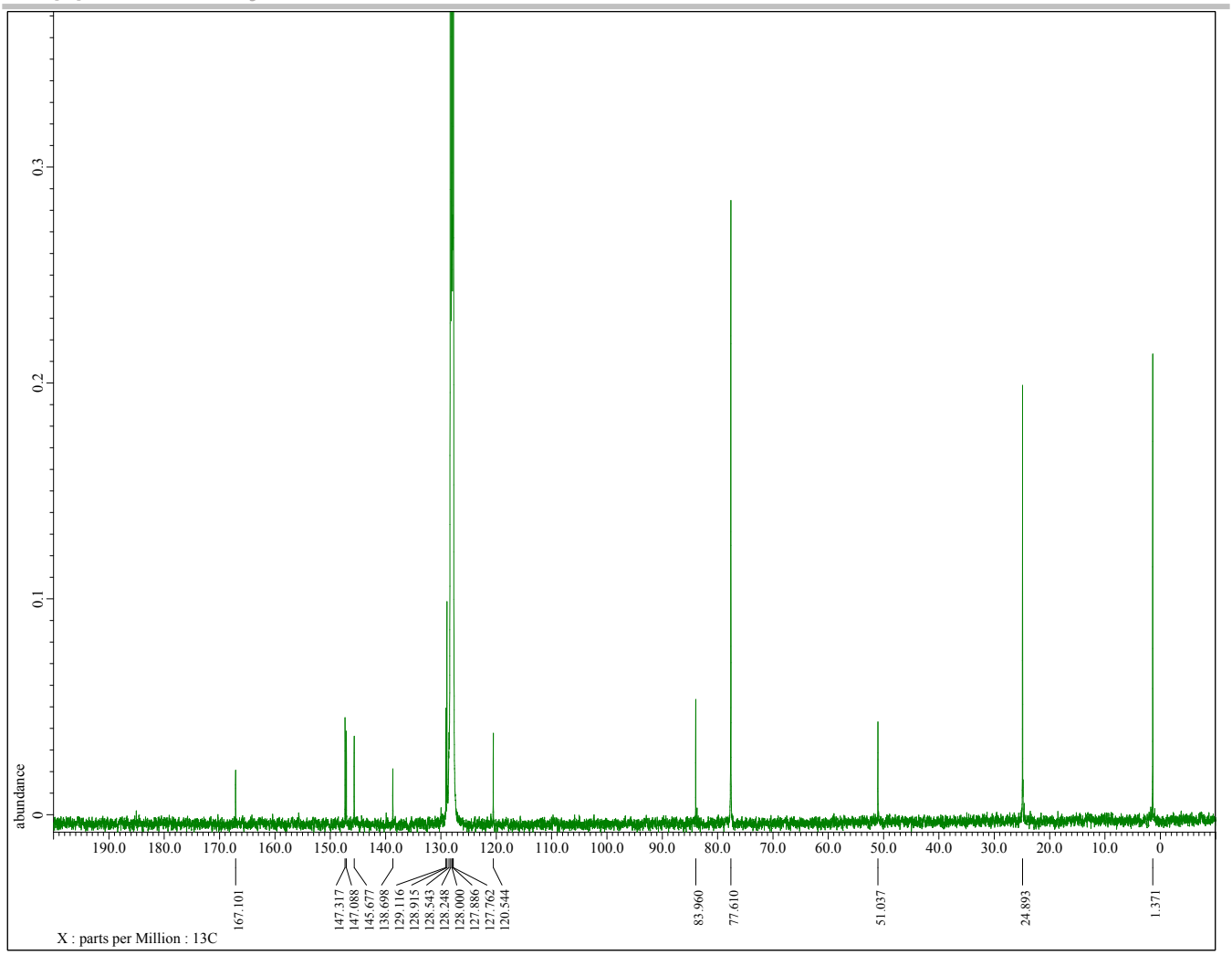
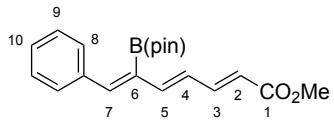


Figure S10. $^{13}C\{^{1}H\}$ NMR spectrum of methyl (2*E*,4*E*,6*E*)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-7-phenylhepta-2,4,6-trienoate [(2*E*,4*E*,6*E*)-**5e**] (100 MHz, [D_6]benzene).



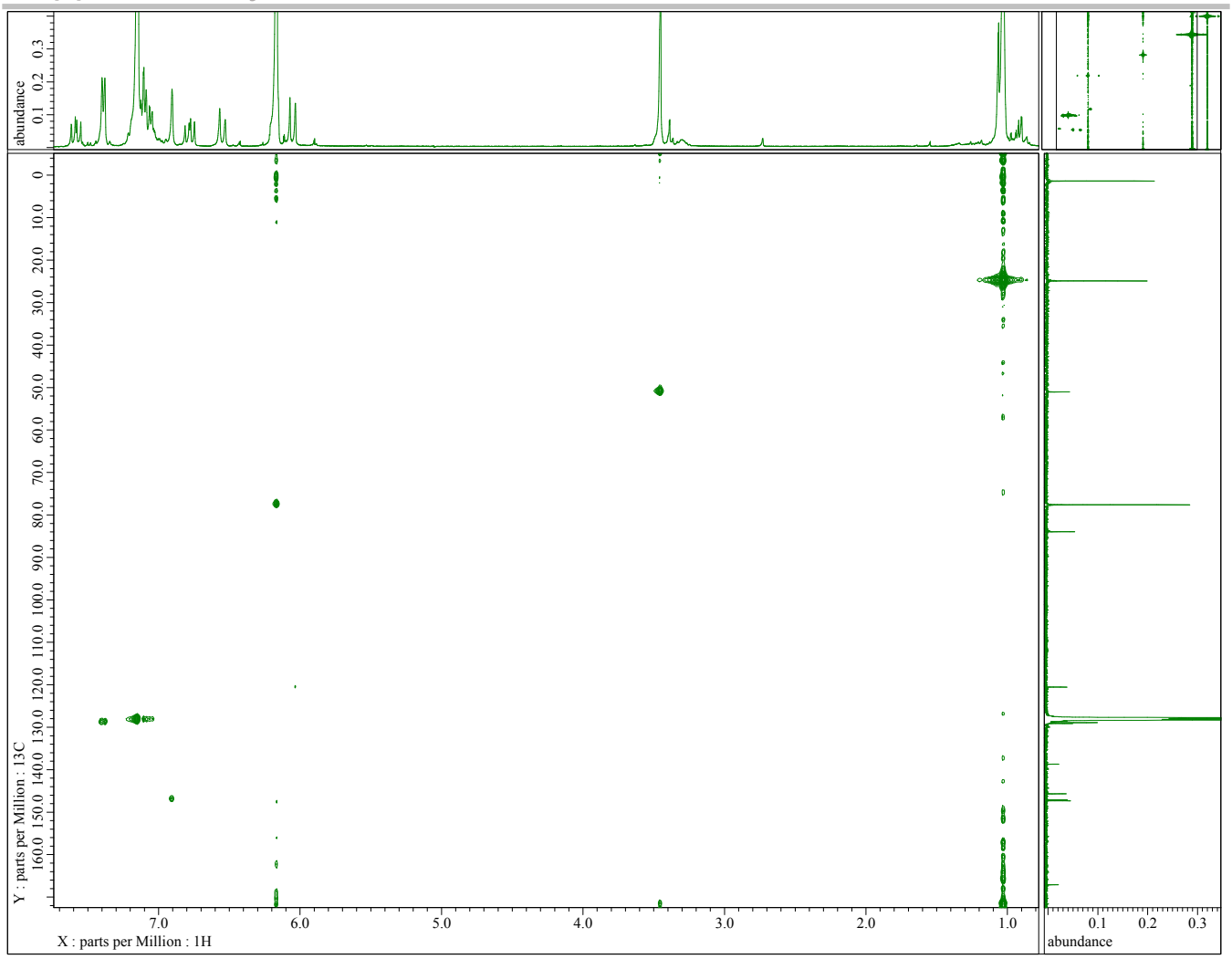
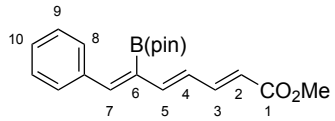
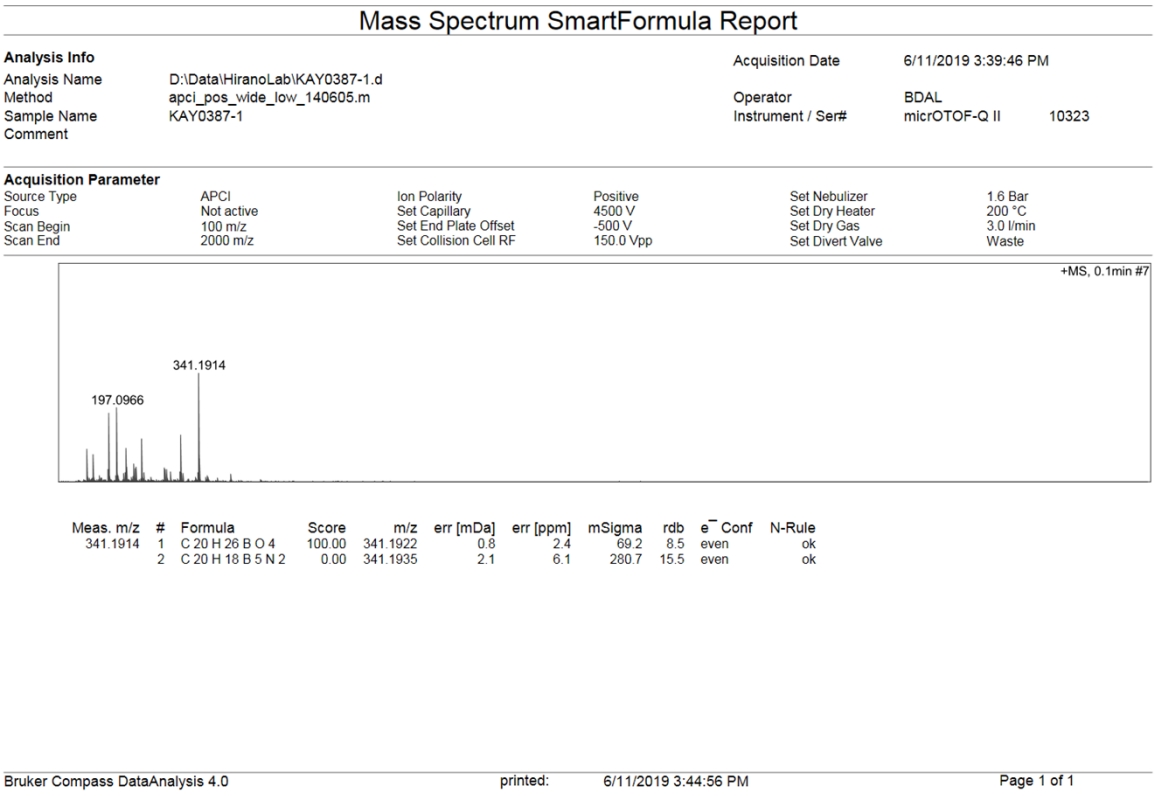


Figure S11. ^{1}H-^{13}C HMQC spectrum of methyl (2*E*,4*E*,6*E*)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-7-phenylhepta-2,4,6-trienoate [(2*E*,4*E*,6*E*)-**5e**] (400 MHz for ^{1}H, 100 MHz for ^{13}C, [D_6]benzene).





Mass Spectrum SmartFormula Report

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Comment			

Acquisition Parameter

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Scan End	2000 m/z	Set Collision Cell RF	150.0 Vpp	Set Divert Valve	Waste

Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e¯ Conf	N-Rule
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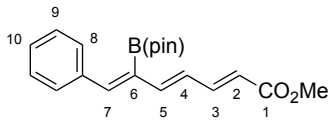
	2	C 20 H 18 B 5 N 2	0.00	341.1935	2.1	6.1	280.7	15.5	even	ok

Bruker Compass DataAnalysis 4.0 printed: 6/11/2019 3:44:56 PM Page 1 of 1

Figure S12. HRMS (APCI) spectrum of methyl (2*E*,4*E*,6*E*)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-7-phenylhepta-2,4,6-trienoate [(2*E*,4*E*,6*E*)-**5e**].



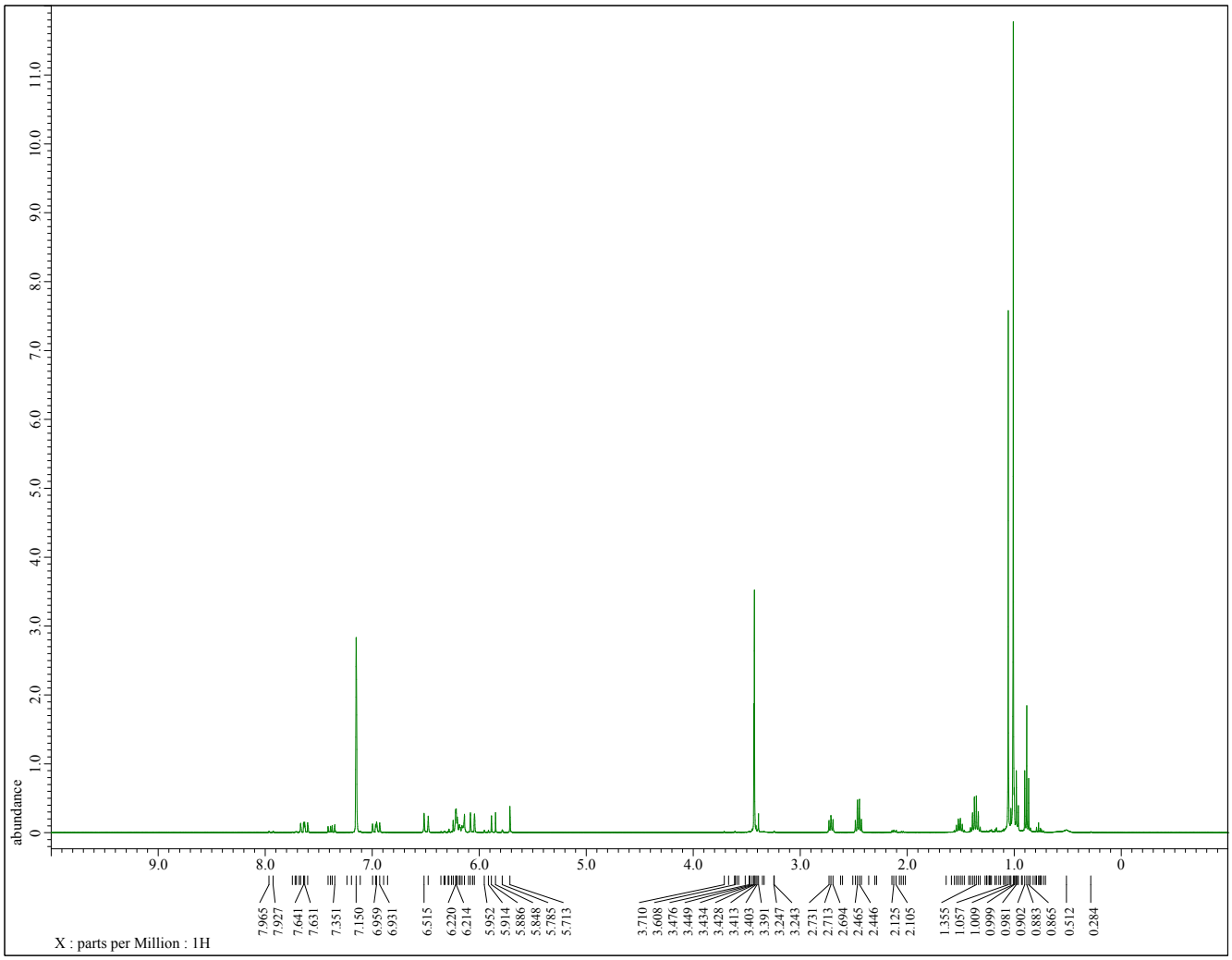
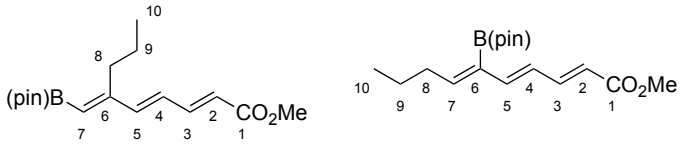


Figure S13. ^{1}H NMR spectrum of methyl (2*E*,4*E*,6*E*)-7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-6-propylhepta-2,4,6-trienoate [(2*E*,4*E*,6*E*)-**4f**] and methyl (2*E*,4*E*,6*E*)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)deca-2,4,6-trienoate [(2*E*,4*E*,6*E*)-**5f** (400 MHz, [D_6]benzene).



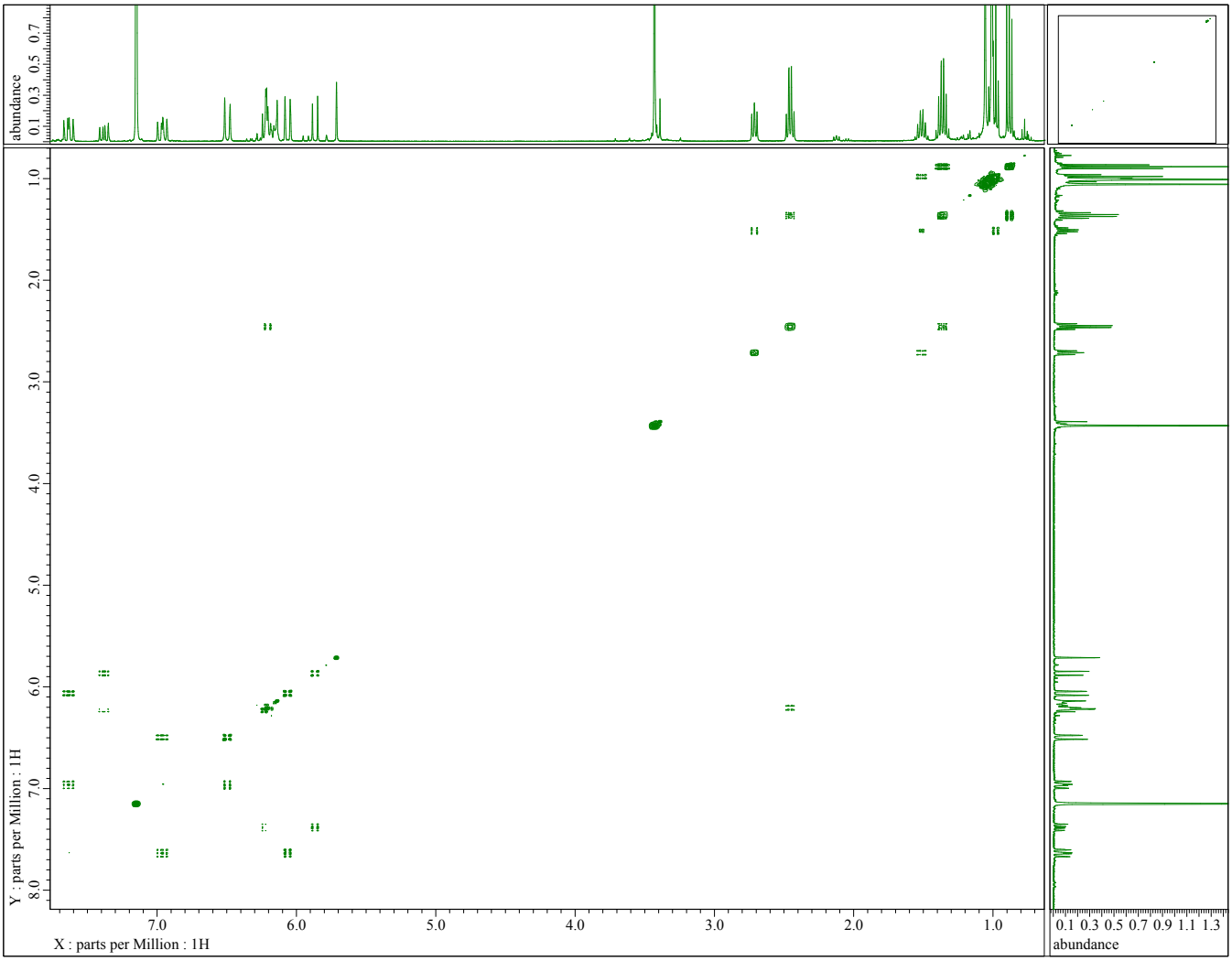
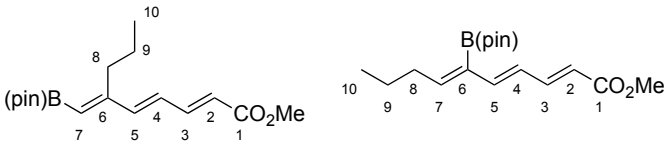


Figure S14. ^{1}H-^{1}H COSY of methyl (2*E*,4*E*,6*E*)-7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-6-propylhepta-2,4,6-trienoate [(2*E*,4*E*,6*E*)-**4f**] and methyl (2*E*,4*E*,6*E*)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)deca-2,4,6-trienoate [(2*E*,4*E*,6*E*)-**5f**] (400 MHz, [D_6]benzene).



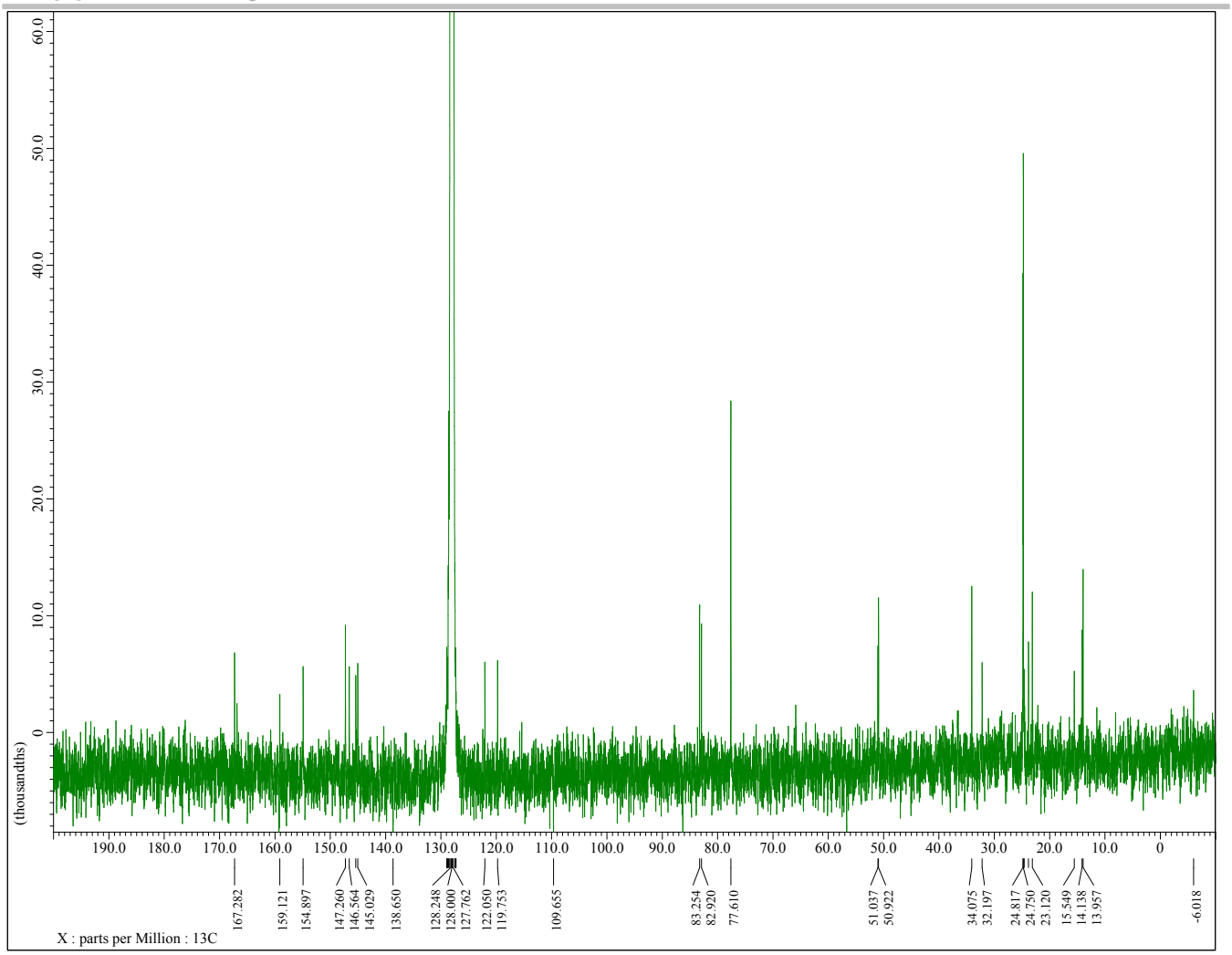
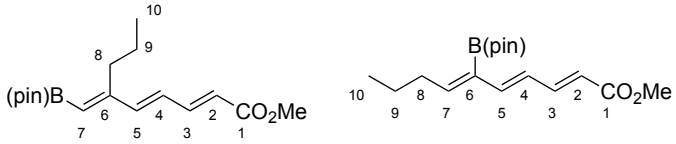


Figure S15. $^{13}C\{^{1}H\}$ NMR of methyl (2*E*,4*E*,6*E*)-7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-6-propylhepta-2,4,6-trienoate [(2*E*,4*E*,6*E*)-**4f**] and methyl (2*E*,4*E*,6*E*)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)deca-2,4,6-trienoate [(2*E*,4*E*,6*E*)-**5f**].



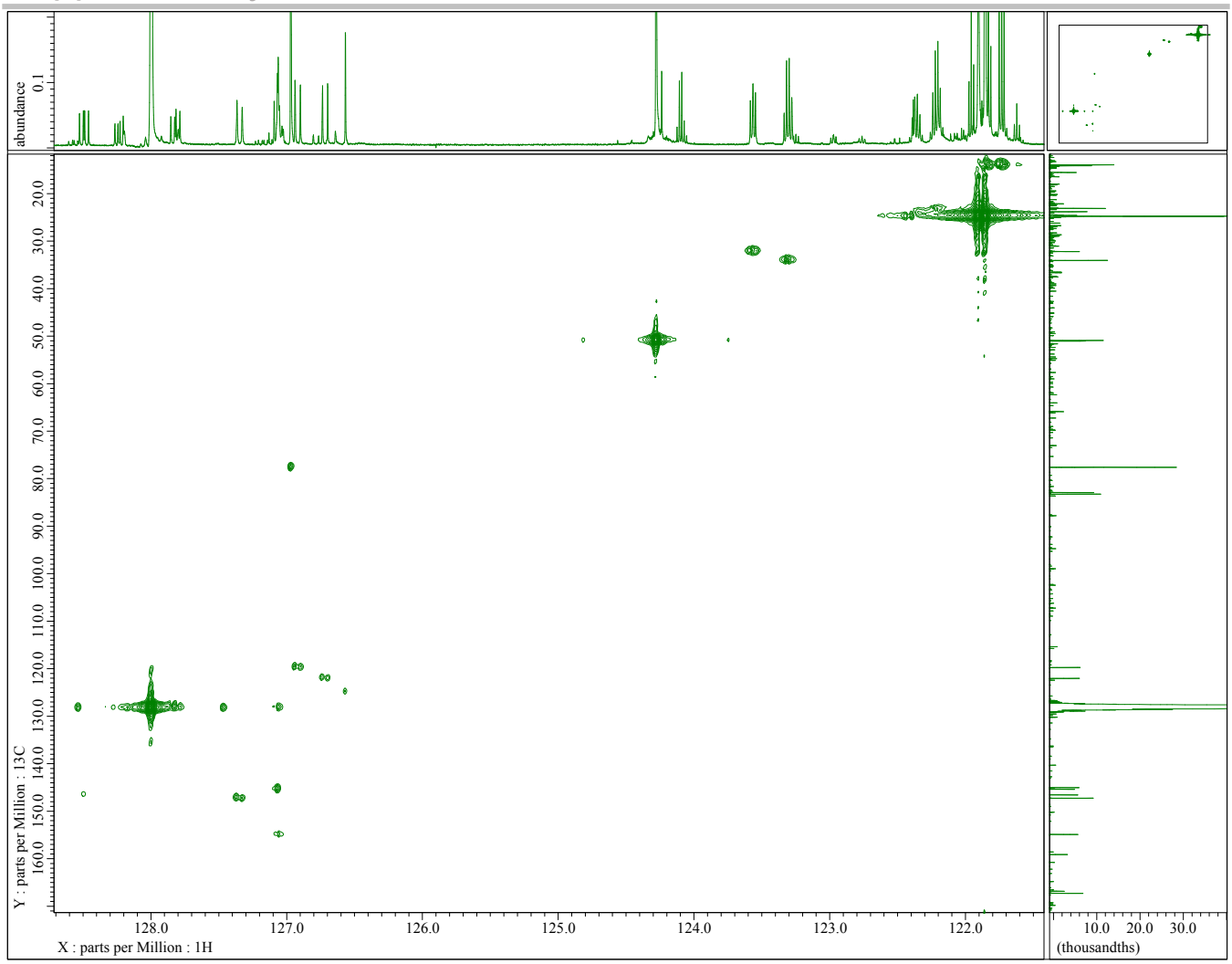
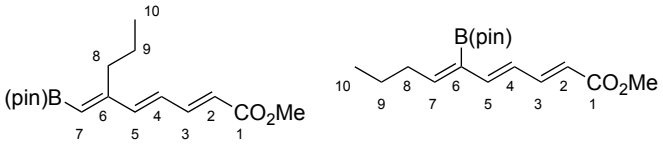
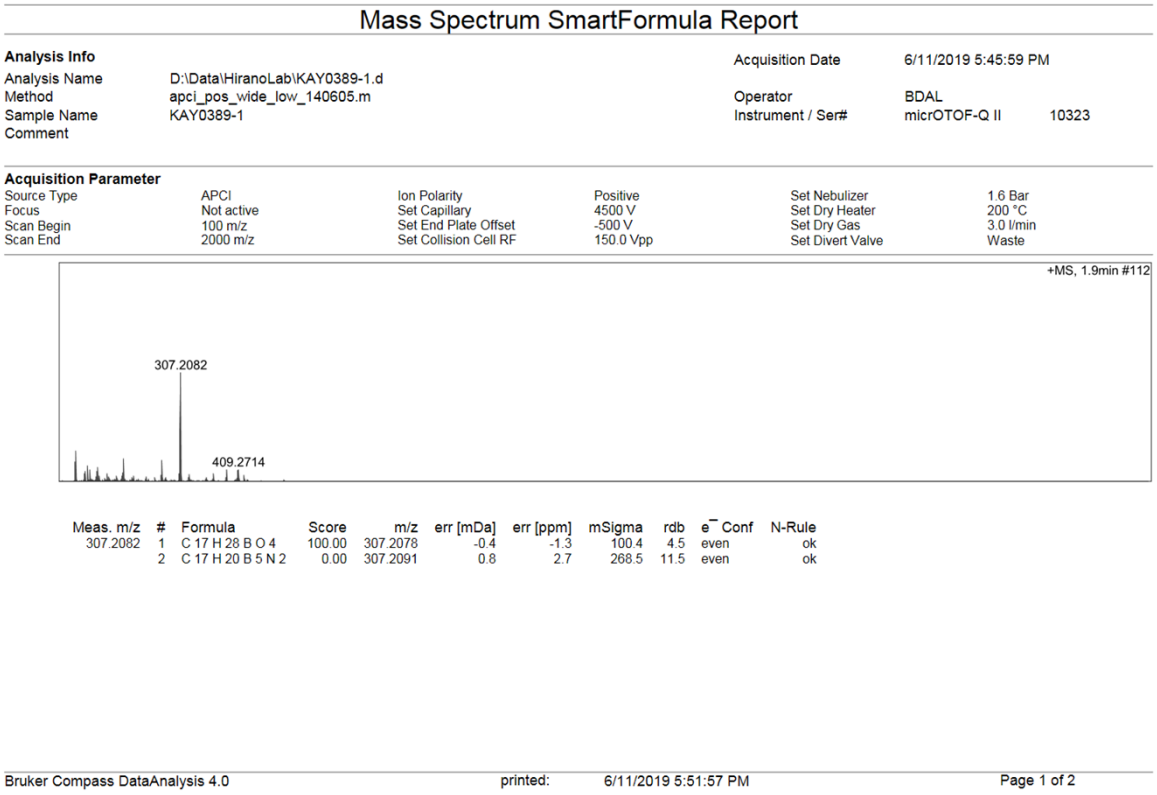


Figure S16. ^{1}H-^{13}C HMQC spectrum of methyl (2*E*,4*E*,6*E*)-7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-6-propylhepta-2,4,6-trienoate [(2*E*,4*E*,6*E*)-**4f**] and methyl (2*E*,4*E*,6*E*)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)deca-2,4,6-trienoate [(2*E*,4*E*,6*E*)-**5f**] (400 MHz for ^{1}H, 100 MHz for ^{13}C, [D_6]benzene).





Mass Spectrum SmartFormula Report

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Sample Name	KAY0389-1	Instrument / Ser#	micrOTOF-Q II 10323
Comment			

Acquisition Parameter

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Focus	Not active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	100 m/z	Set End Plate Offset	-500 V	Set Dry Gas	3.0 l/min
Scan End	2000 m/z	Set Collision Cell RF	150.0 Vpp	Set Divert Valve	Waste

Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e¯ Conf	N-Rule
307.2082	1	C 17 H 28 B O 4	100.00	307.2078	-0.4	-1.3	100.4	4.5	even	ok
	2	C 17 H 20 B 5 N 2	0.00	307.2091	0.8	2.7	268.5	11.5	even	ok

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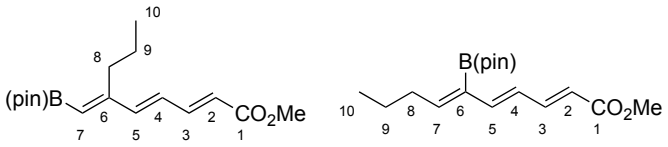
Figure S17. HRMS (APCI) spectrum of methyl (2*E*,4*E*,6*E*)-7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-6-propylhepta-2,4,6-trienoate [(2*E*,4*E*,6*E*)-**4f**] and methyl (2*E*,4*E*,6*E*)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)deca-2,4,6-trienoate [(2*E*,4*E*,6*E*)-**5f**].



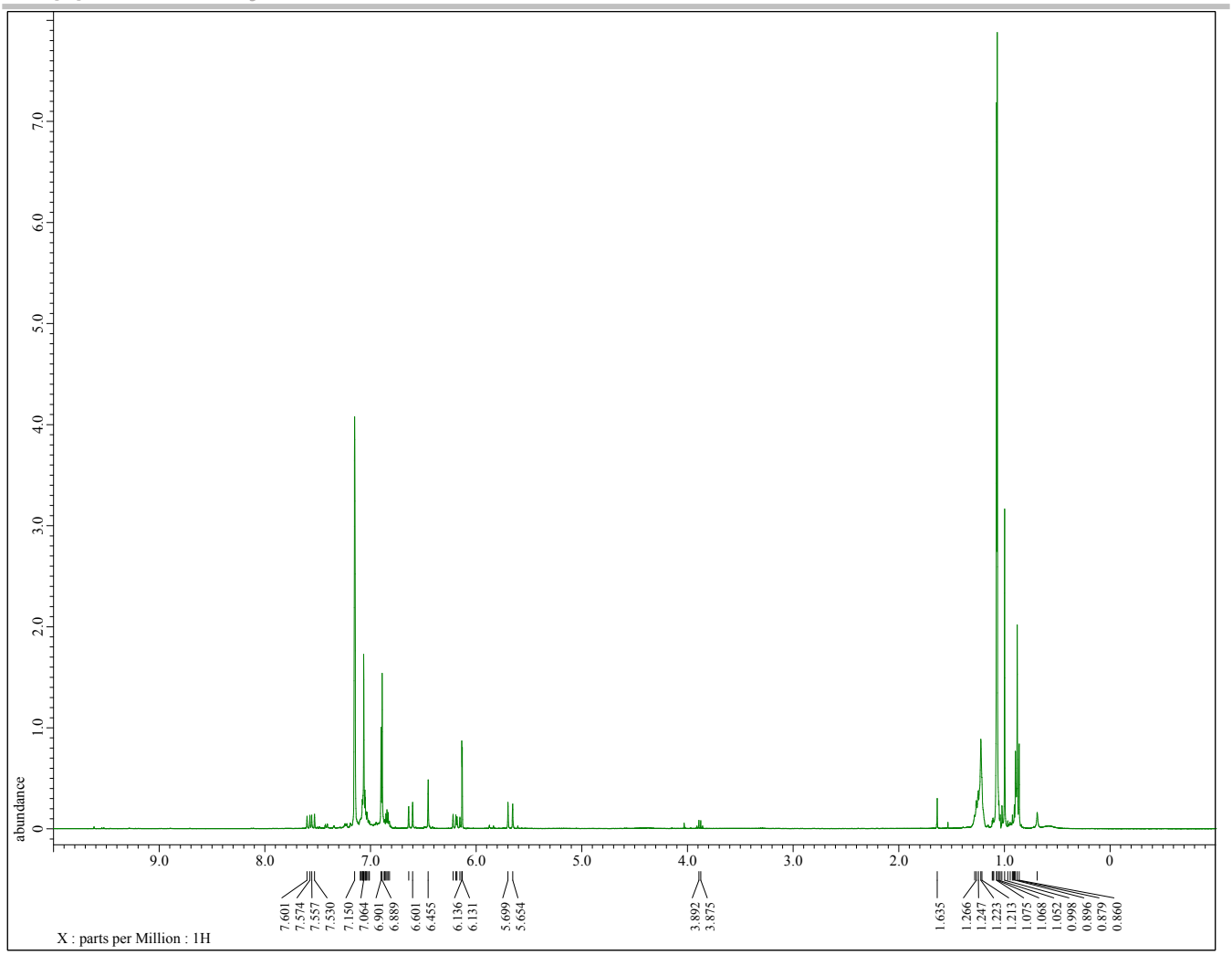
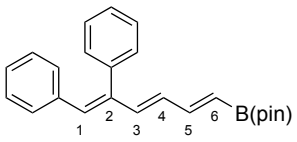


Figure S18. ^{1}H NMR spectrum of (1*Z*,3*E*,5*E*)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2-dphenylhexa-1,3,5-triene [(1*Z*,3*E*,5*E*)-**4g**] (400 MHz, [D_6]benzene).



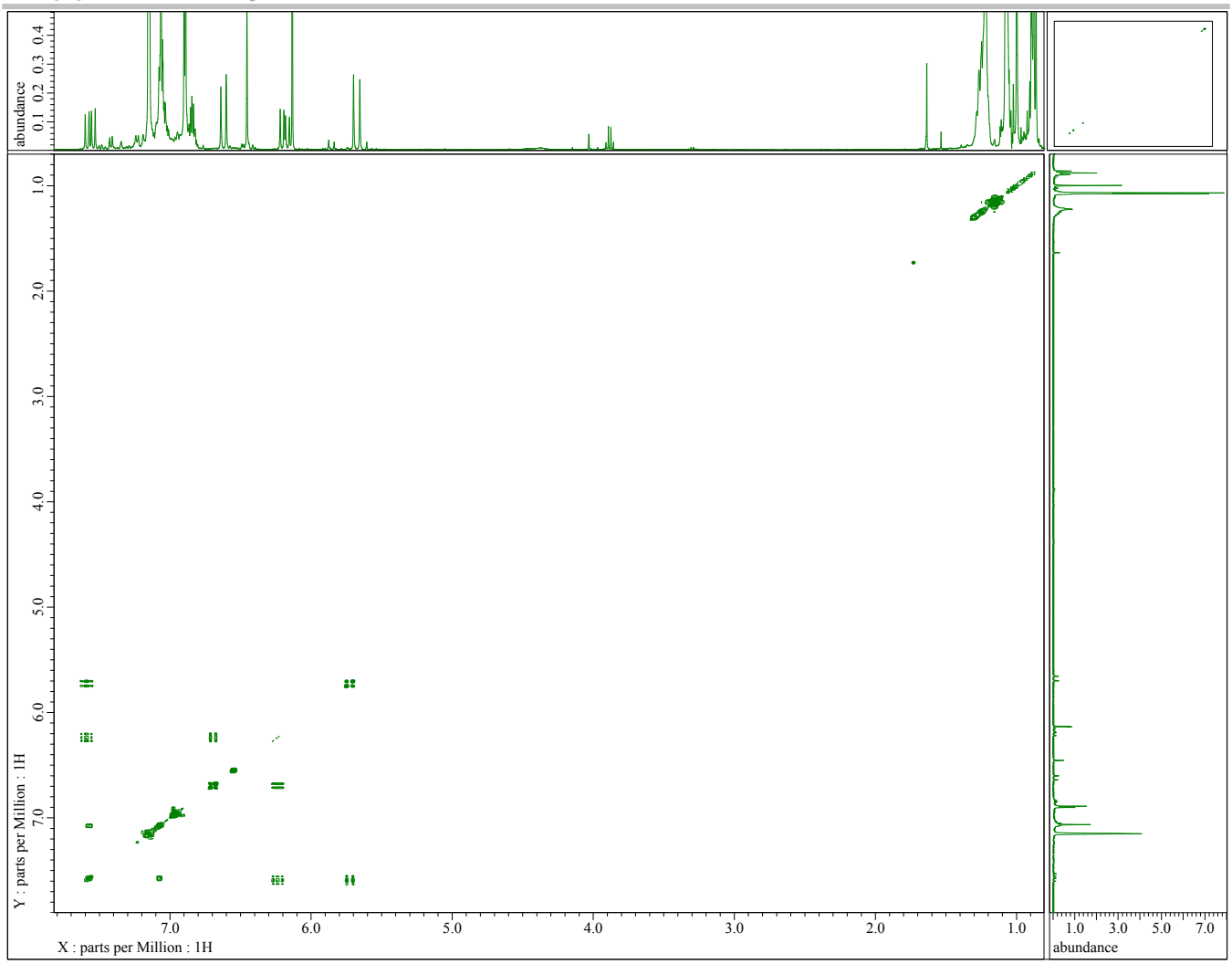
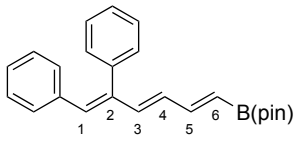


Figure S19. ^{1}H-^{1}H COSY of (1*Z*,3*E*,5*E*)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2-dphenylhexa-1,3,5-triene [(1*Z*,3*E*,5*E*)-**4g**] (400 MHz, [D_6]benzene).



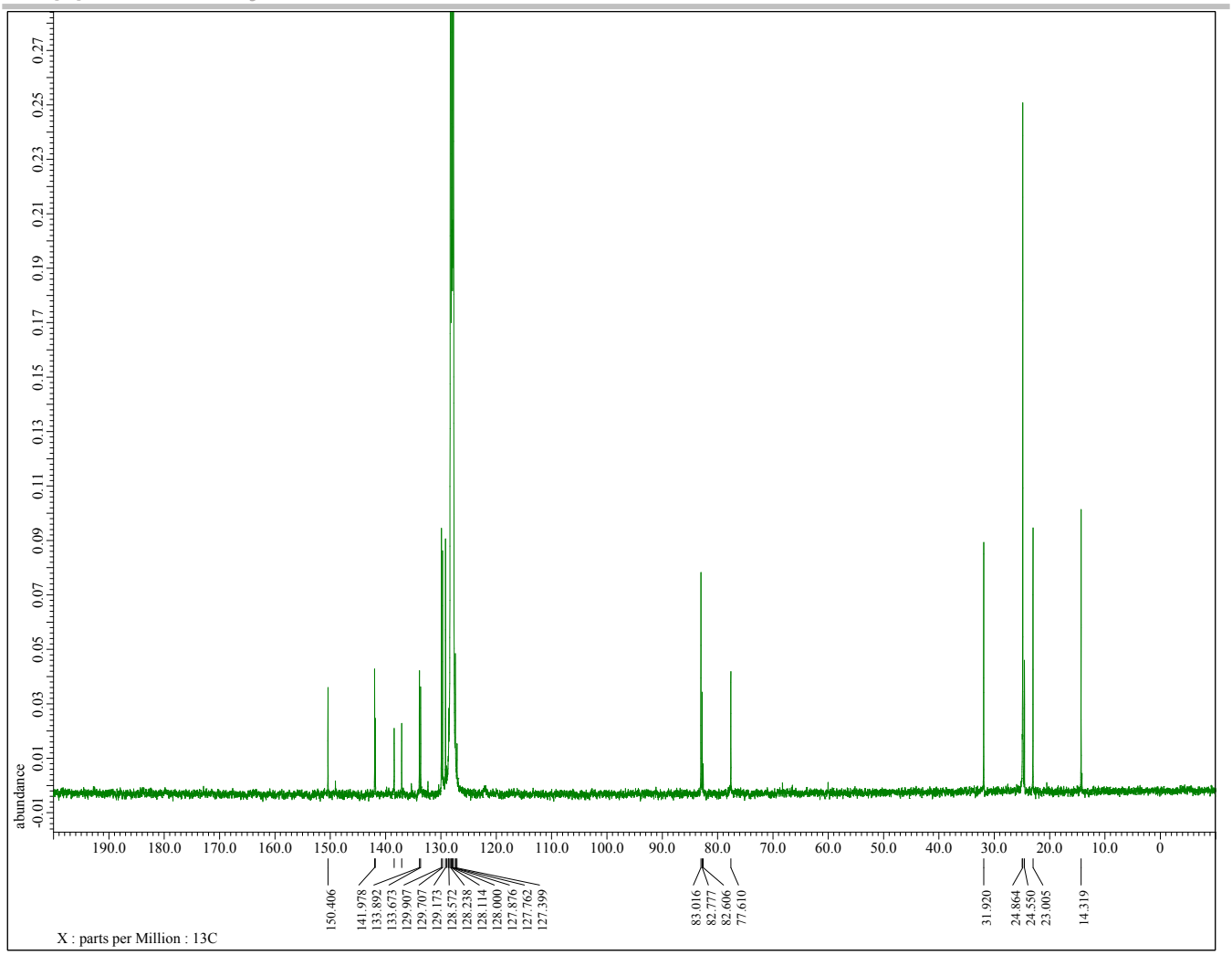
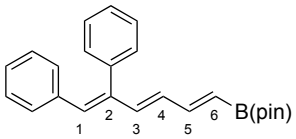


Figure S20. $^{13}C\{^{1}H\}$ NMR spectrum of (1*Z*,3*E*,5*E*)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2-dphenylhexa-1,3,5-triene [(1*Z*,3*E*,5*E*)-**4g**] (100 MHz, [D_6]benzene).



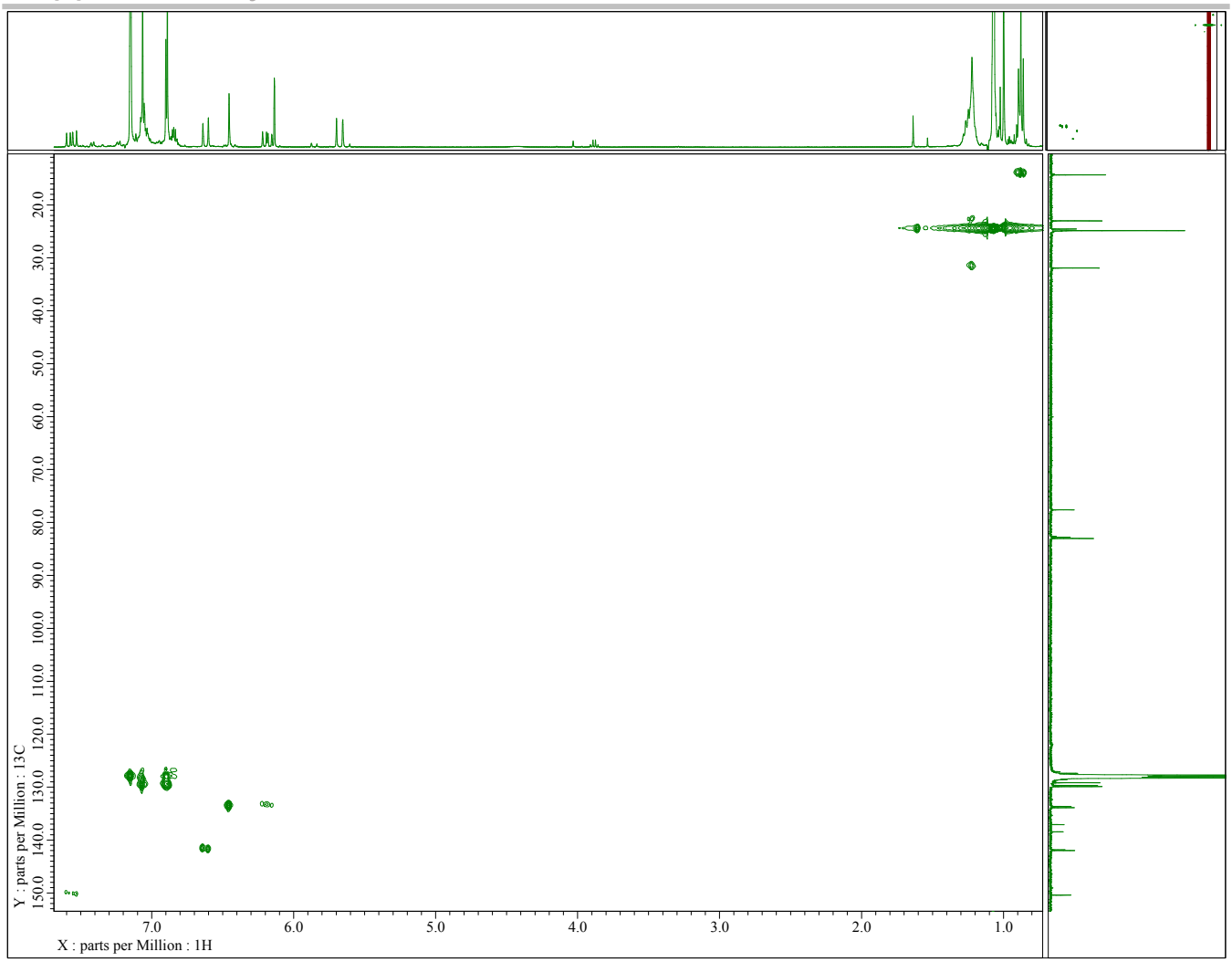
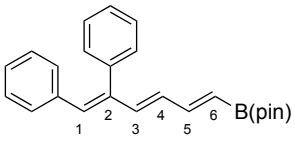
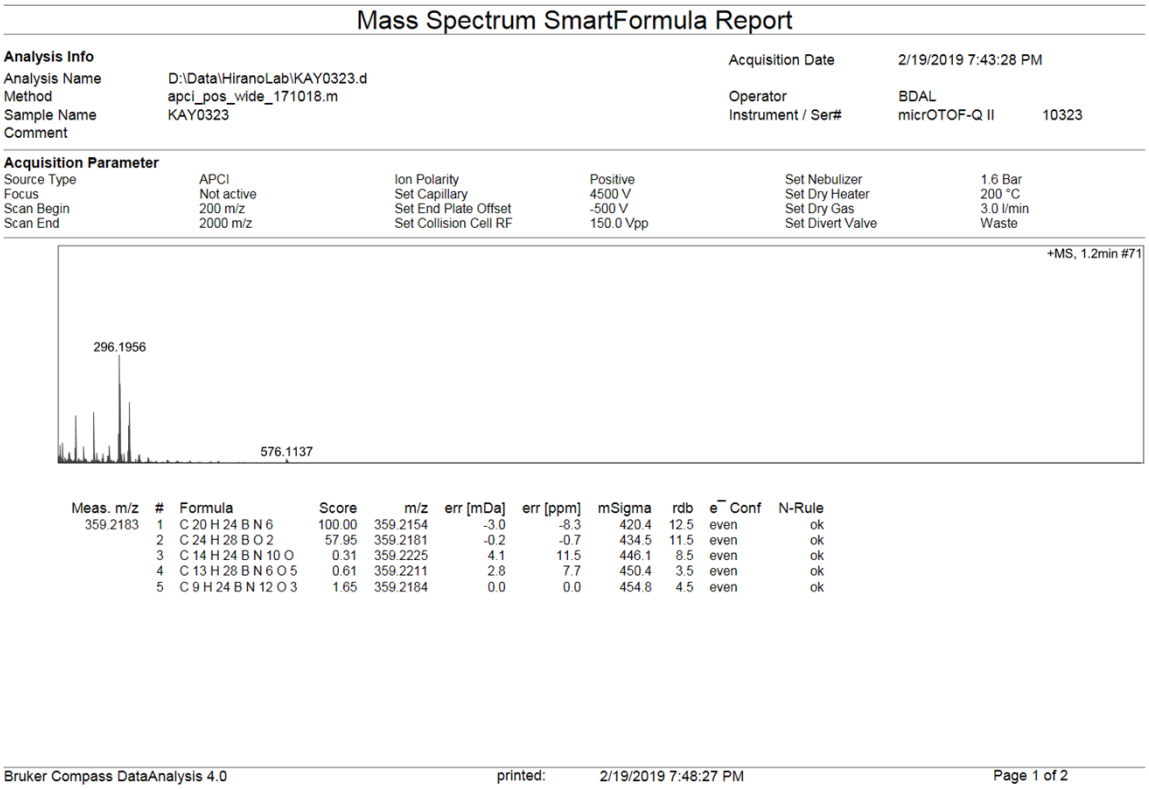


Figure S21. ^{1}H-^{13}C HMQC of (1*Z*,3*E*,5*E*)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2-dphenylhexa-1,3,5-triene [(1*Z*,3*E*,5*E*)-**4g**] (400 MHz for ^{1}H, 100 MHz for ^{13}C, [D_6]benzene).





Mass Spectrum SmartFormula Report

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Comment			

Acquisition Parameter

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Scan Begin	200 m/z	Set End Plate Offset	-500 V	Set Dry Gas	3.0 l/min
Scan End	2000 m/z	Set Collision Cell RF	150.0 Vpp	Set Divert Valve	Waste

Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
359.2183	1	C 20 H 24 B N 6	100.00	359.2154	-3.0	-8.3	420.4	12.5	even	ok
	2	C 24 H 28 B O 2	57.95	359.2181	-0.2	-0.7	434.5	11.5	even	ok
	3	C 14 H 24 B N 10 O	0.31	359.2225	4.1	11.5	446.1	8.5	even	ok
	4	C 13 H 28 B N 6 O 5	0.61	359.2211	2.8	7.7	450.4	3.5	even	ok
	5	C 9 H 24 B N 12 O 3	1.65	359.2184	0.0	0.0	454.8	4.5	even	ok

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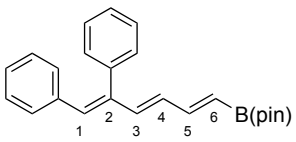
Figure S22. HRMS (APCI) spectrum of (1*Z*,3*E*,5*E*)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2-dphenylhexa-1,3,5-triene [(1*Z*,3*E*,5*E*)-**4g**].



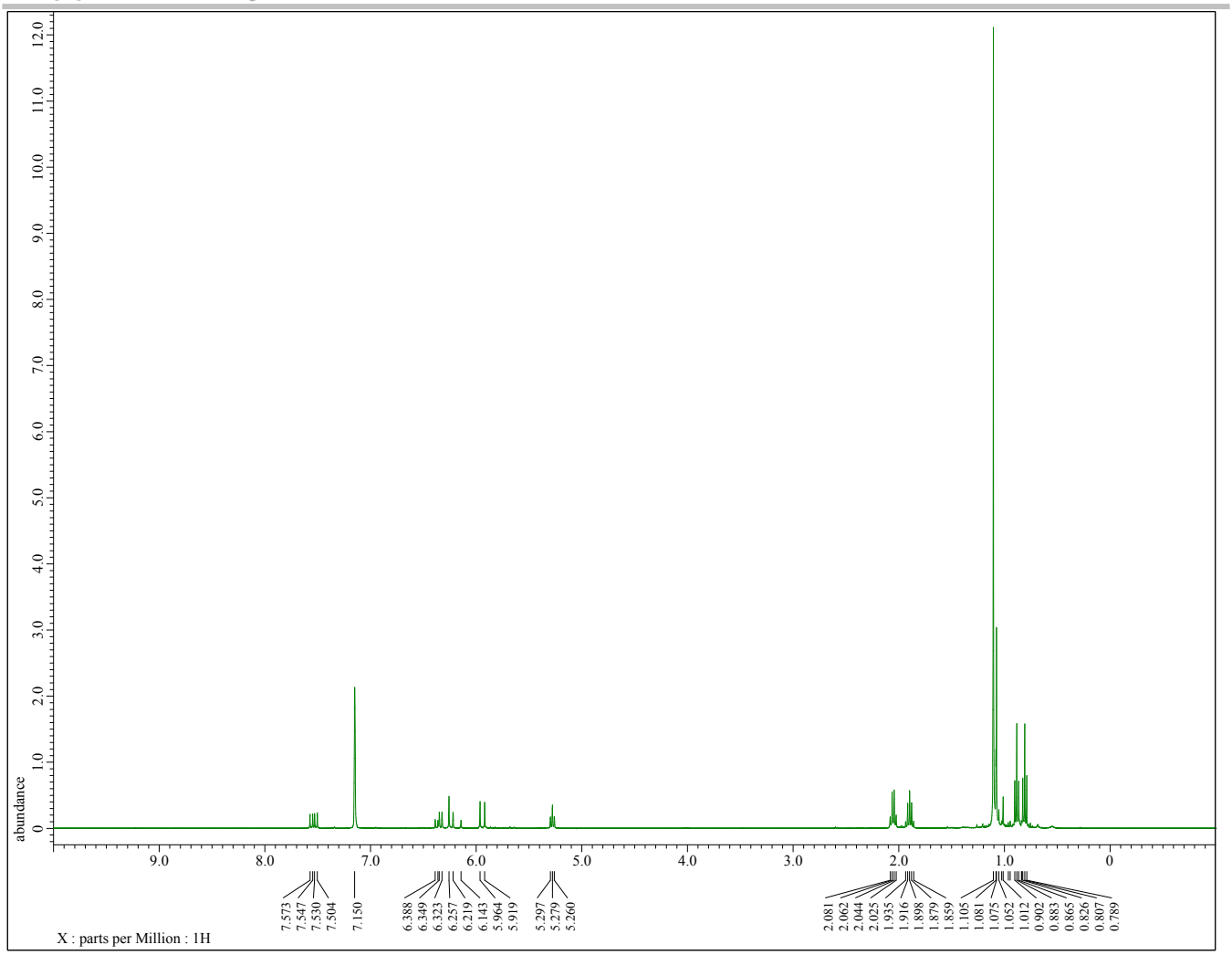
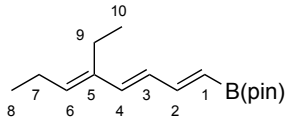


Figure S23. ^{1}H NMR spectrum of (1*E*,3*E*,5*E*)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-ethylocta-1,3,5-triene [(1*E*,3*E*,5*E*)-**4h**] (400 MHz, [D_6]benzene).



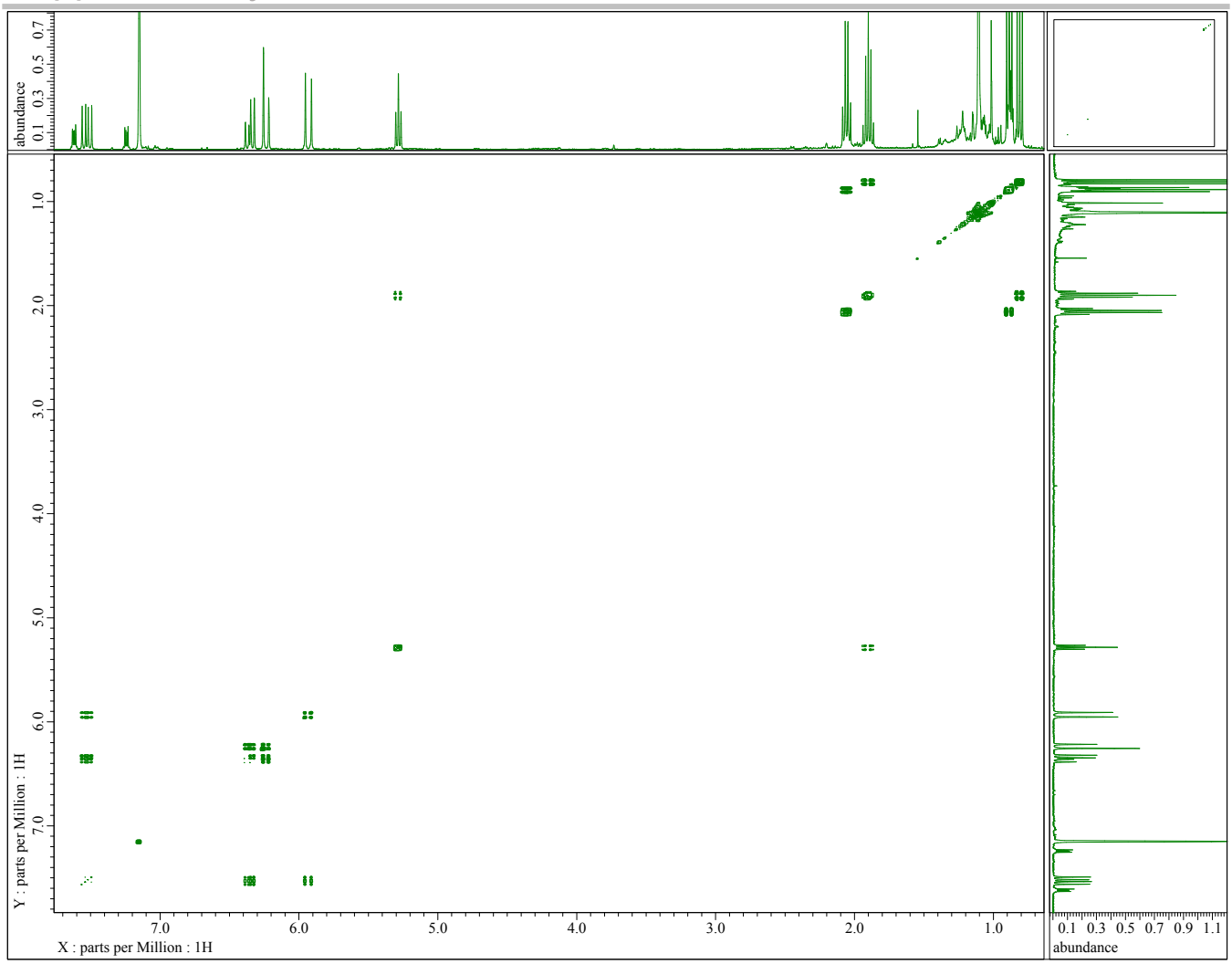
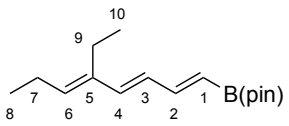


Figure S24. ^{1}H-^{1}H COSY of (1*E*,3*E*,5*E*)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-ethylocta-1,3,5-triene [(1*E*,3*E*,5*E*)-**4h**] (400 MHz, [D_6]benzene).



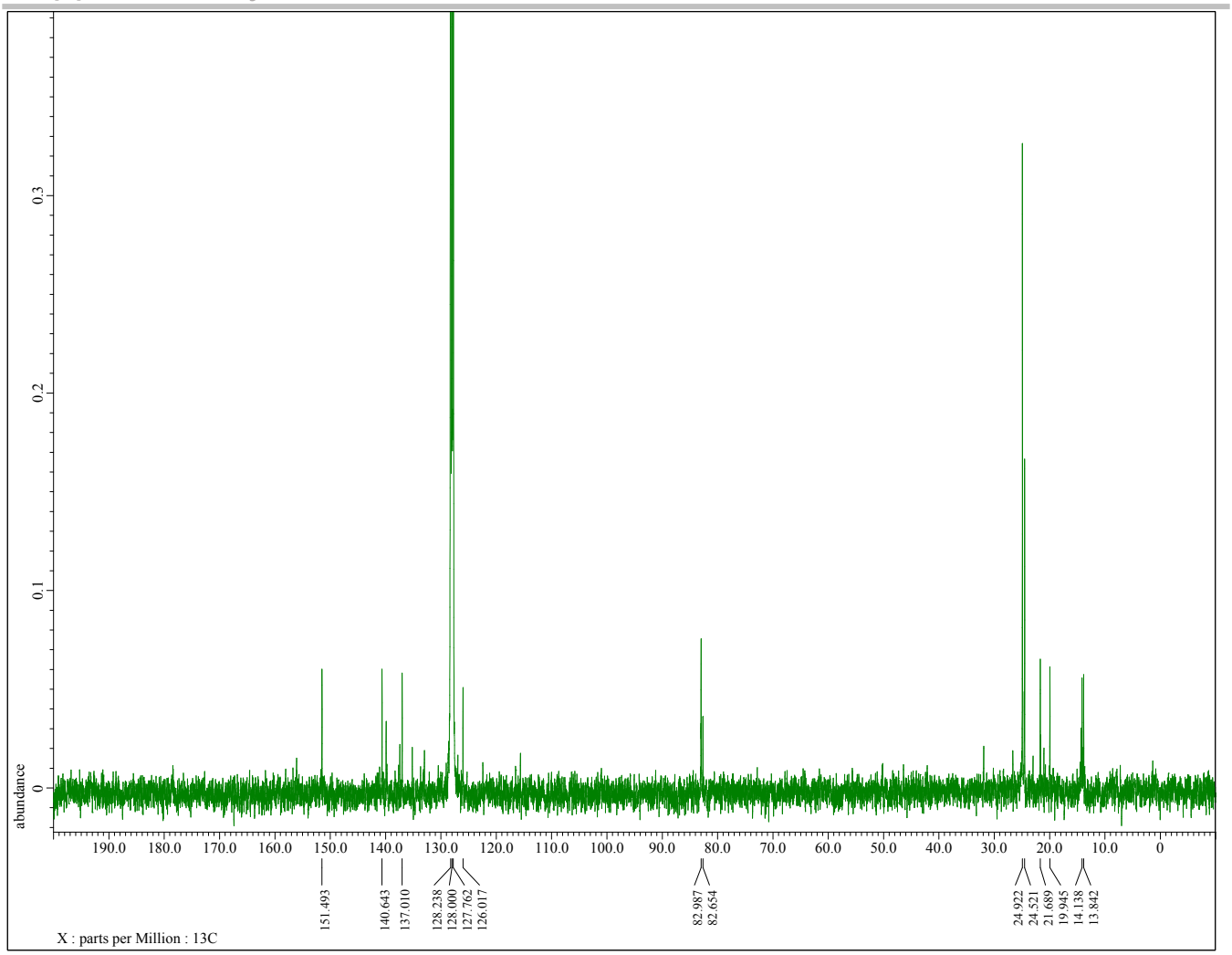
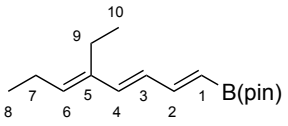


Figure S25. $^{13}C\{^{1}H\}$ NMR spectrum of (1*E*,3*E*,5*E*)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-ethylocta-1,3,5-triene [(1*E*,3*E*,5*E*)-**4h**] (100 MHz, [D_6]benzene).



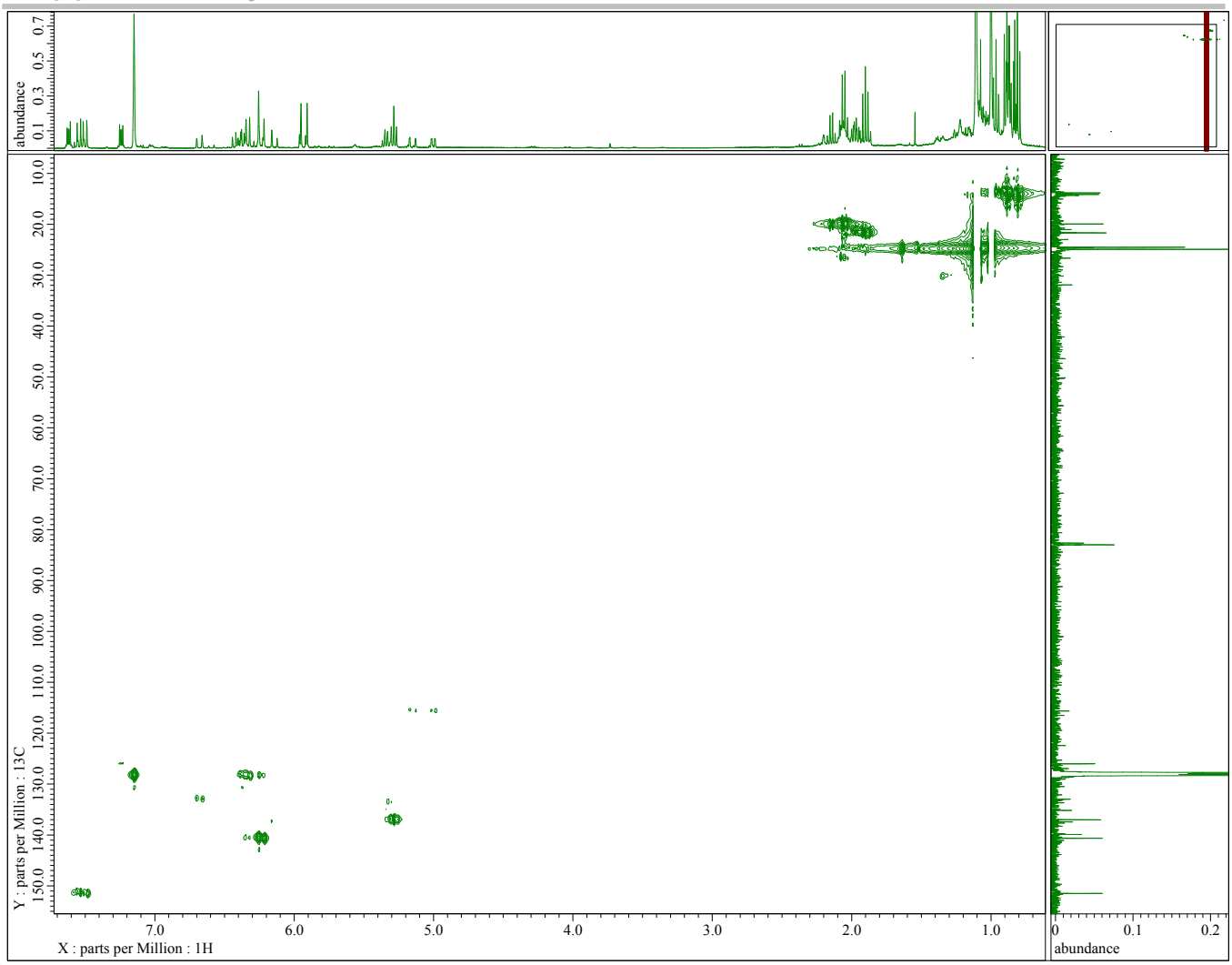
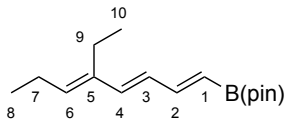
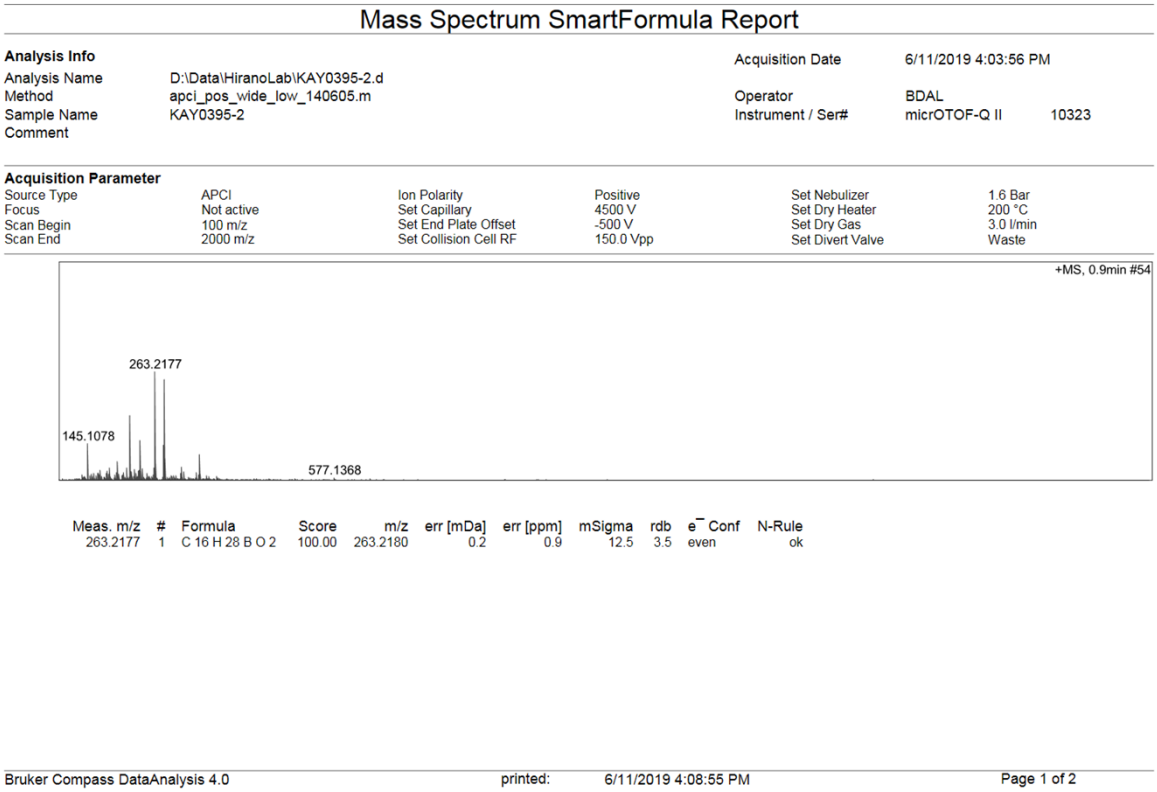


Figure S26. ^{1}H-^{13}C HMQC of (1*E*,3*E*,5*E*)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-ethylocta-1,3,5-triene [(1*E*,3*E*,5*E*)-**4h**] (400 MHz for ^{1}H, 100 MHz for ^{13}C, [D_6]benzene).





Mass Spectrum SmartFormula Report

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Comment			

Acquisition Parameter

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Scan Begin	100 m/z	Set End Plate Offset	-500 V	Set Dry Gas	3.0 l/min
Scan End	2000 m/z	Set Collision Cell RF	150.0 Vpp	Set Divert Valve	Waste

Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e¯ Conf	N-Rule
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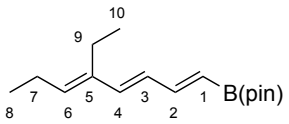
Bruker Compass DataAnalysis 4.0 printed: 6/11/2019 4:08:55 PM Page 1 of 2

Figure S27. HRMS (APCI) spectrum of (1*E*,3*E*,5*E*)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-ethylocta-1,3,5-triene [(1*E*,3*E*,5*E*)-**4h**].



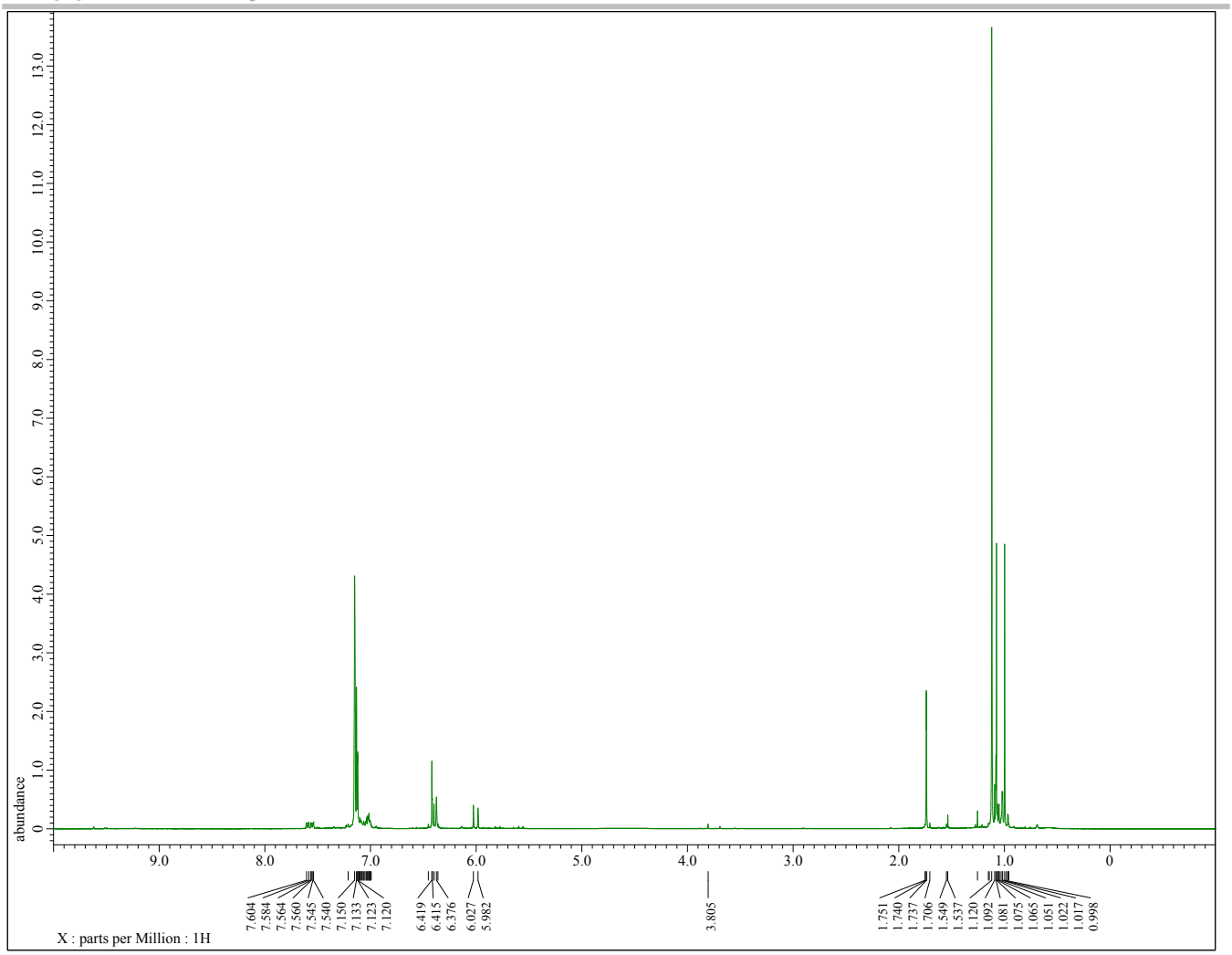
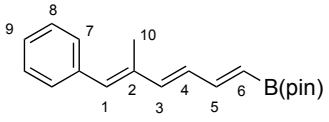


Figure S28. ^{1}H NMR spectrum of (1*E*,3*E*,5*E*)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-methyl-1-phenylhexa-1,3,5-triene [(1*E*,3*E*,5*E*)-**4i**] (400 MHz, [D_6]benzene).



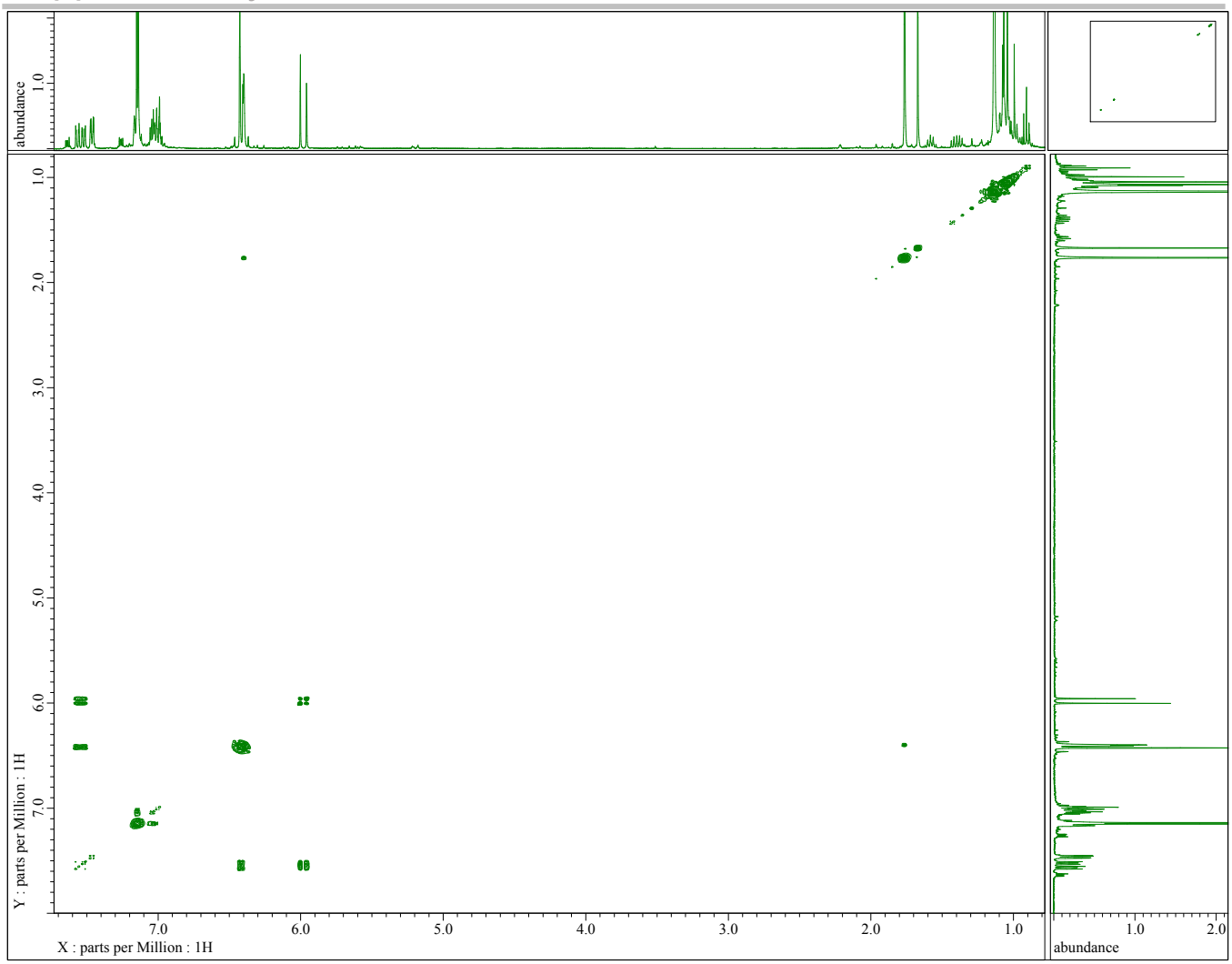
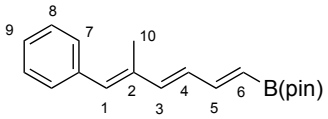


Figure S29. ^{1}H-^{1}H COSY of (1*E*,3*E*,5*E*)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-methyl-1-phenylhexa-1,3,5-triene [(1*E*,3*E*,5*E*)-**4i**] (400 MHz, [D_6]benzene).



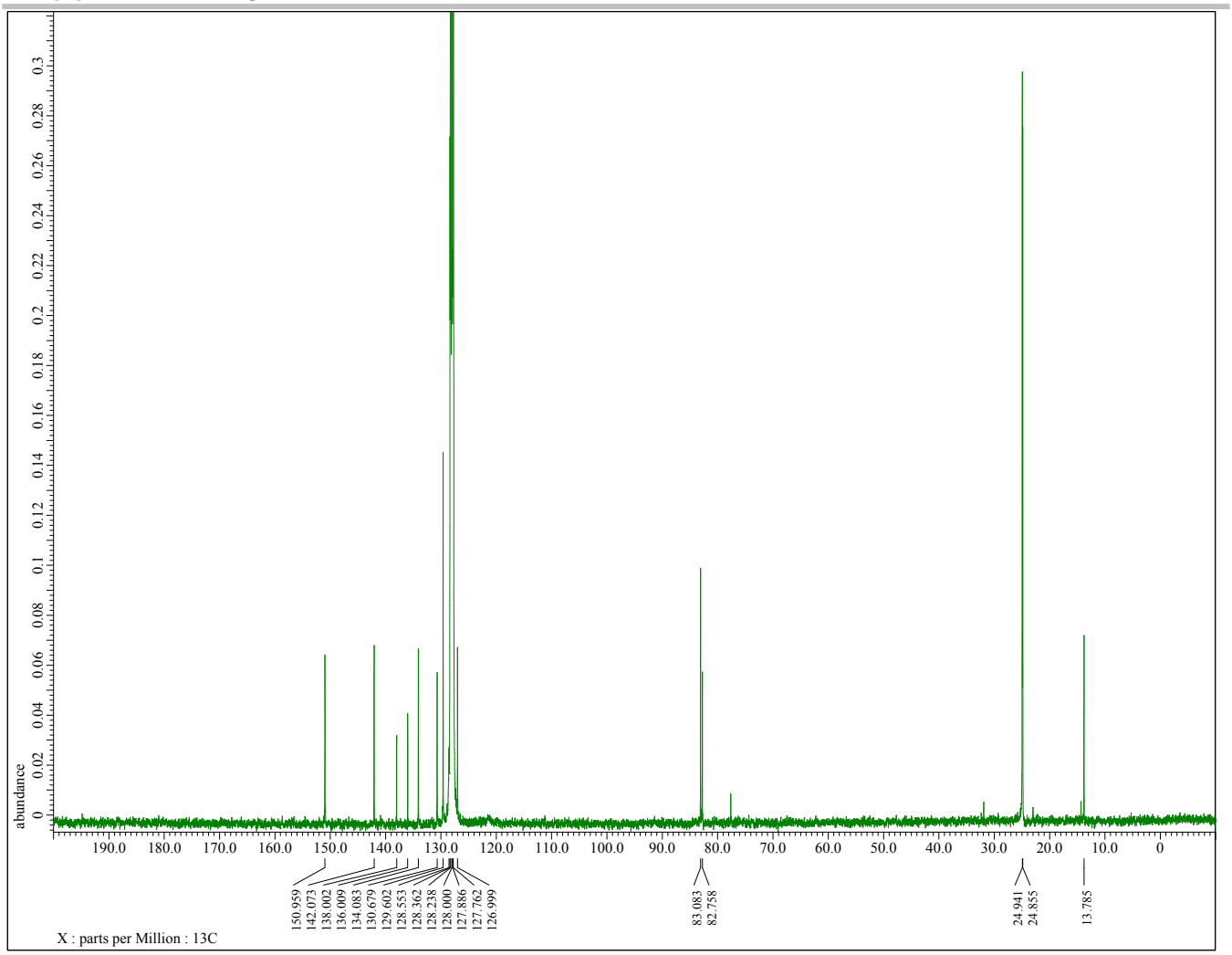
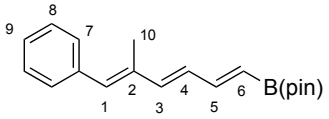


Figure S30. $^{13}C\{^{1}H\}$ NMR spectrum of (1*E*,3*E*,5*E*)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-methyl-1-phenylhexa-1,3,5-triene [(1*E*,3*E*,5*E*)-**4i** (100 MHz, [D_6]benzene)].



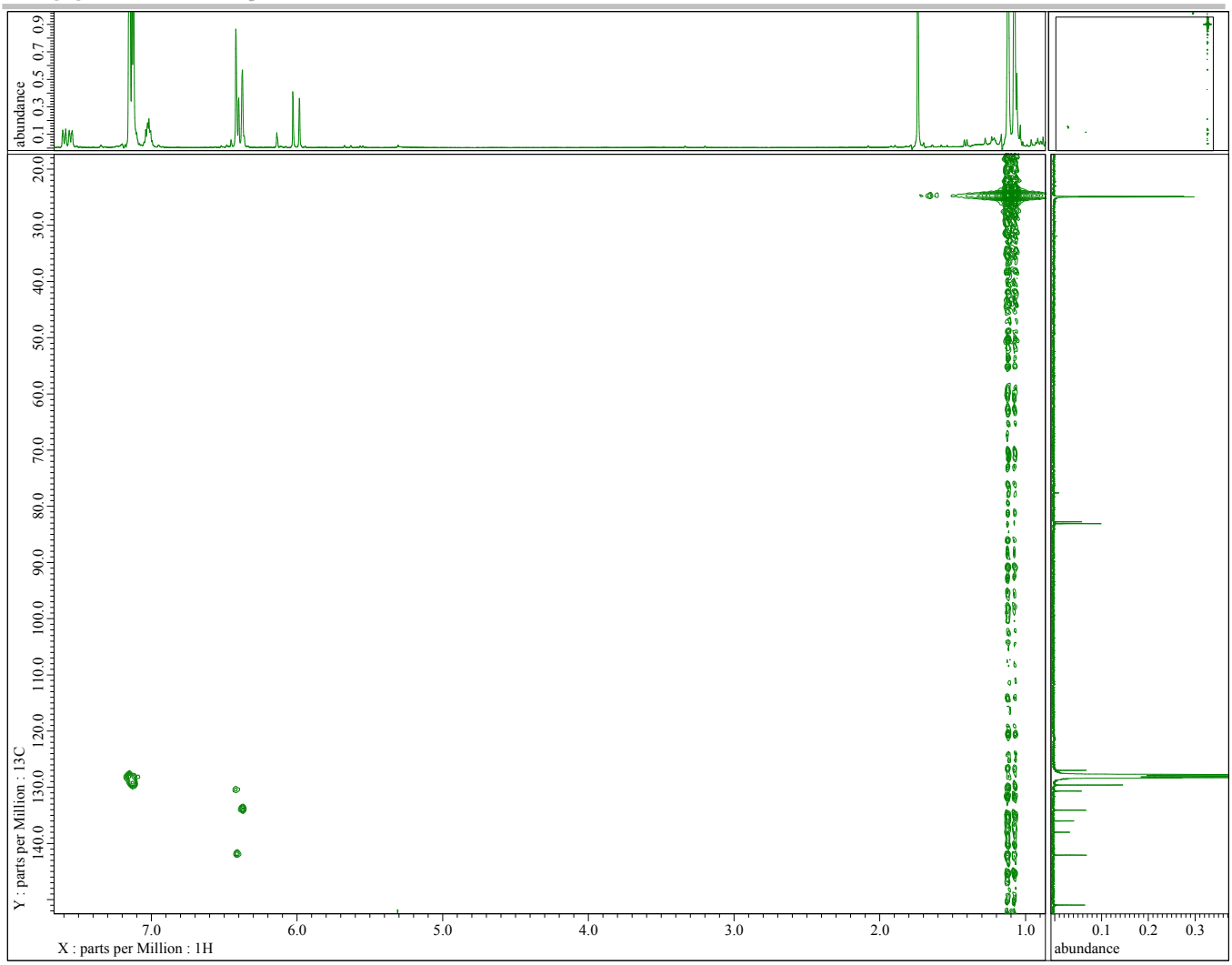
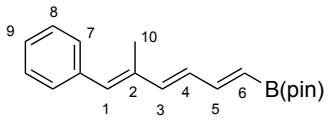
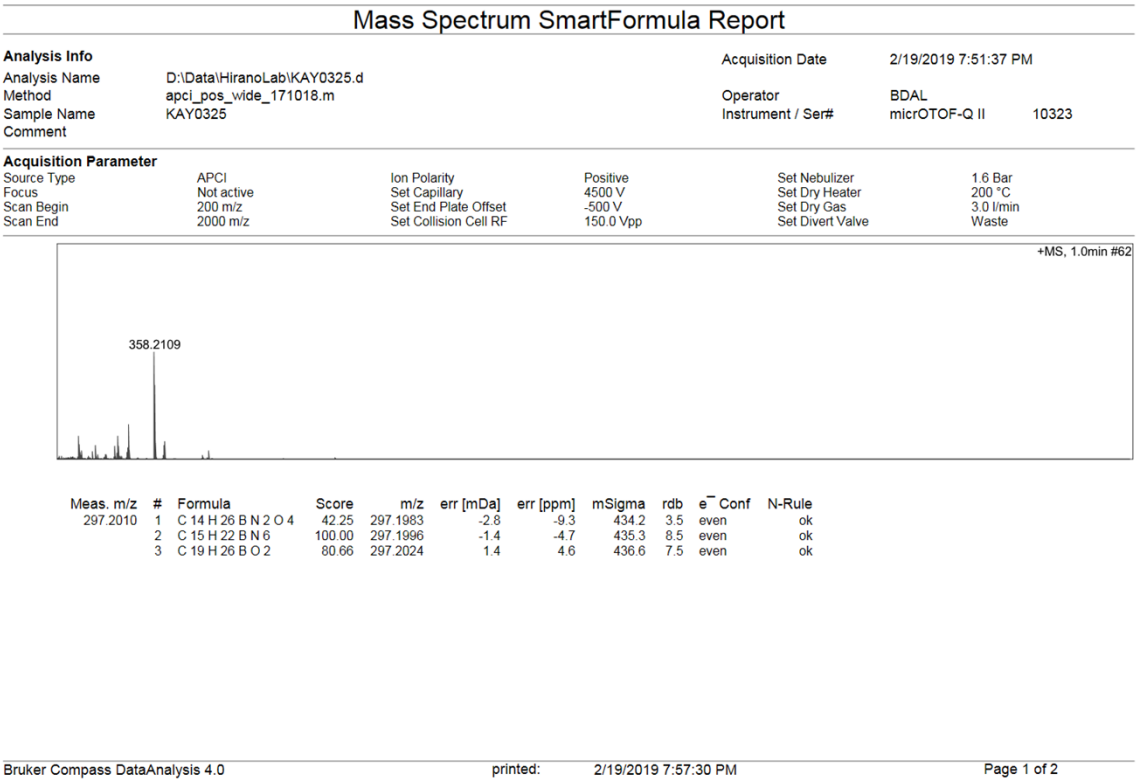


Figure S31. ^{1}H-^{13}C HMQC of (1*E*,3*E*,5*E*)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-methyl-1-phenylhexa-1,3,5-triene [(1*E*,3*E*,5*E*)-**4i**] (400 MHz for ^{1}H, 100 MHz for ^{13}C, [D_6]benzene).





Mass Spectrum SmartFormula Report

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Sample Name	KAY0325	Instrument / Ser#	micrOTOF-Q II 10323
Comment			

Acquisition Parameter

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Focus	Not active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	200 m/z	Set End Plate Offset	-500 V	Set Dry Gas	3.0 l/min
Scan End	2000 m/z	Set Collision Cell RF	150.0 Vpp	Set Divert Valve	Waste

Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e¯ Conf	N-Rule
297.2010	1	C 14 H 26 B N 2 O 4	42.25	297.1983	-2.8	-9.3	434.2	3.5	even	ok
	2	C 15 H 22 B N 6	100.00	297.1996	-1.4	-4.7	435.3	8.5	even	ok
	3	C 19 H 26 B O 2	80.66	297.2024	1.4	4.6	436.6	7.5	even	ok

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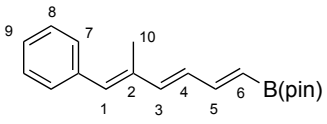
Figure S32. HRMS (APCI) spectrum of (1*E*,3*E*,5*E*)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-methyl-1-phenylhexa-1,3,5-triene [(1*E*,3*E*,5*E*)-**4i**].



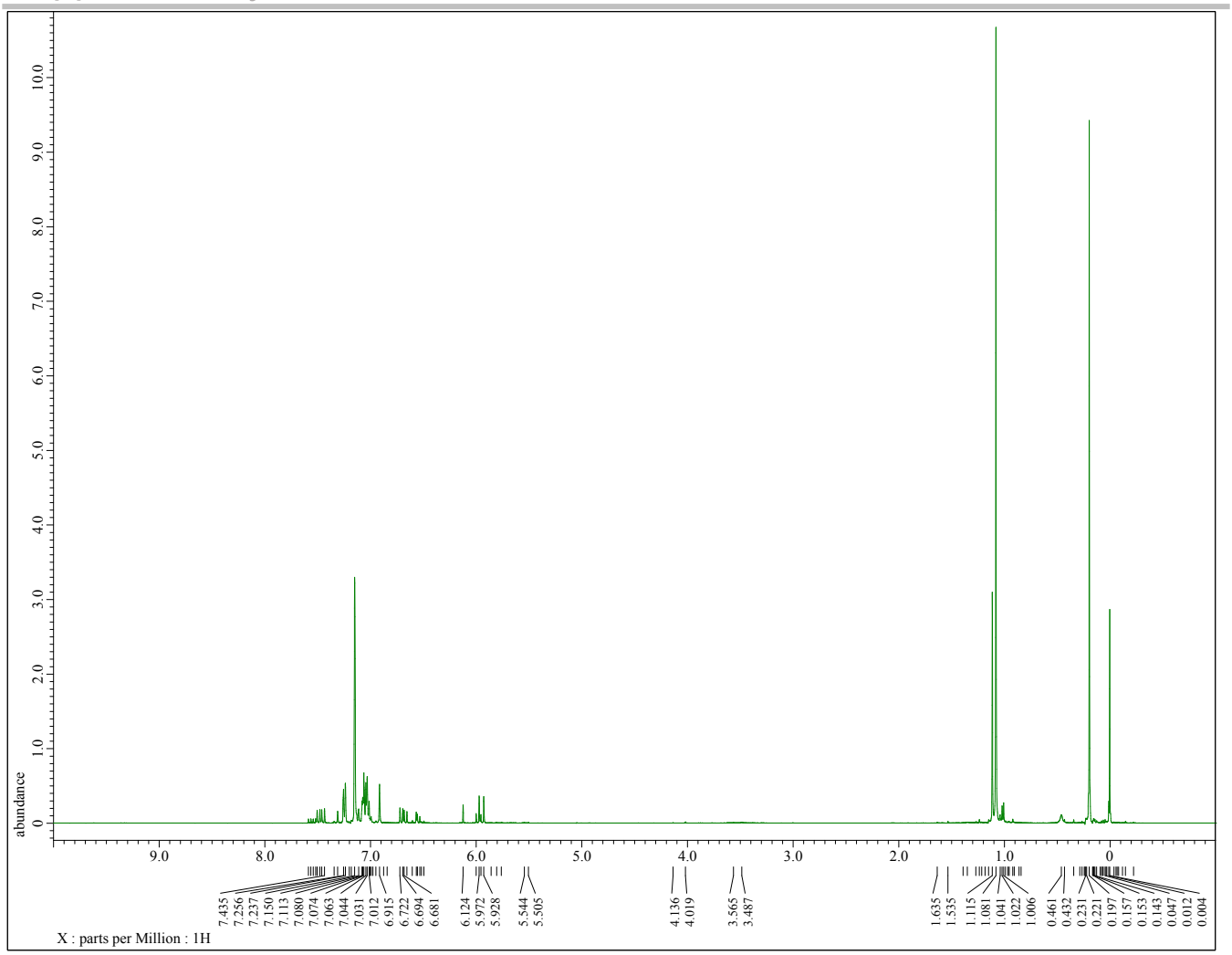
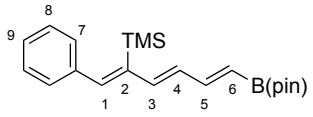


Figure S33. ^{1}H NMR spectrum of (1*Z*,3*E*,5*E*)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-phenyl-2-trimethylsilylhexa-1,3,5-triene [(1*Z*,3*E*,5*E*)-**4j**] (400 MHz, [D_6]benzene).



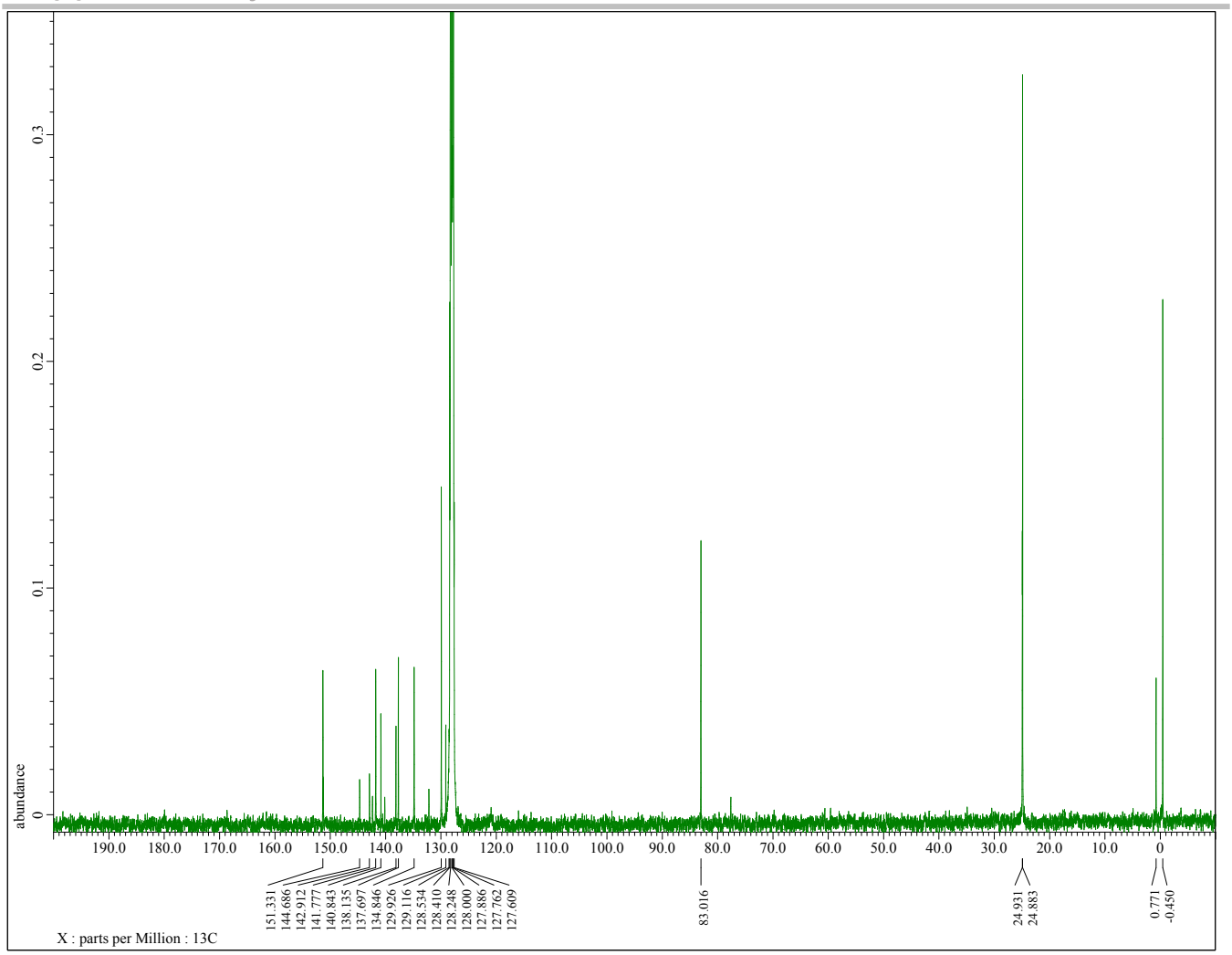
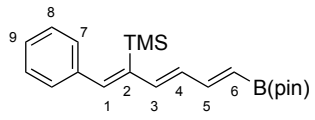


Figure S34. $^{13}C\{^{1}H\}$ NMR spectrum of (1*Z*,3*E*,5*E*)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-phenyl-2-trimethylsilylhexa-1,3,5-triene [(1*Z*,3*E*,5*E*)-**4j**] (100 MHz, [D_6]benzene).



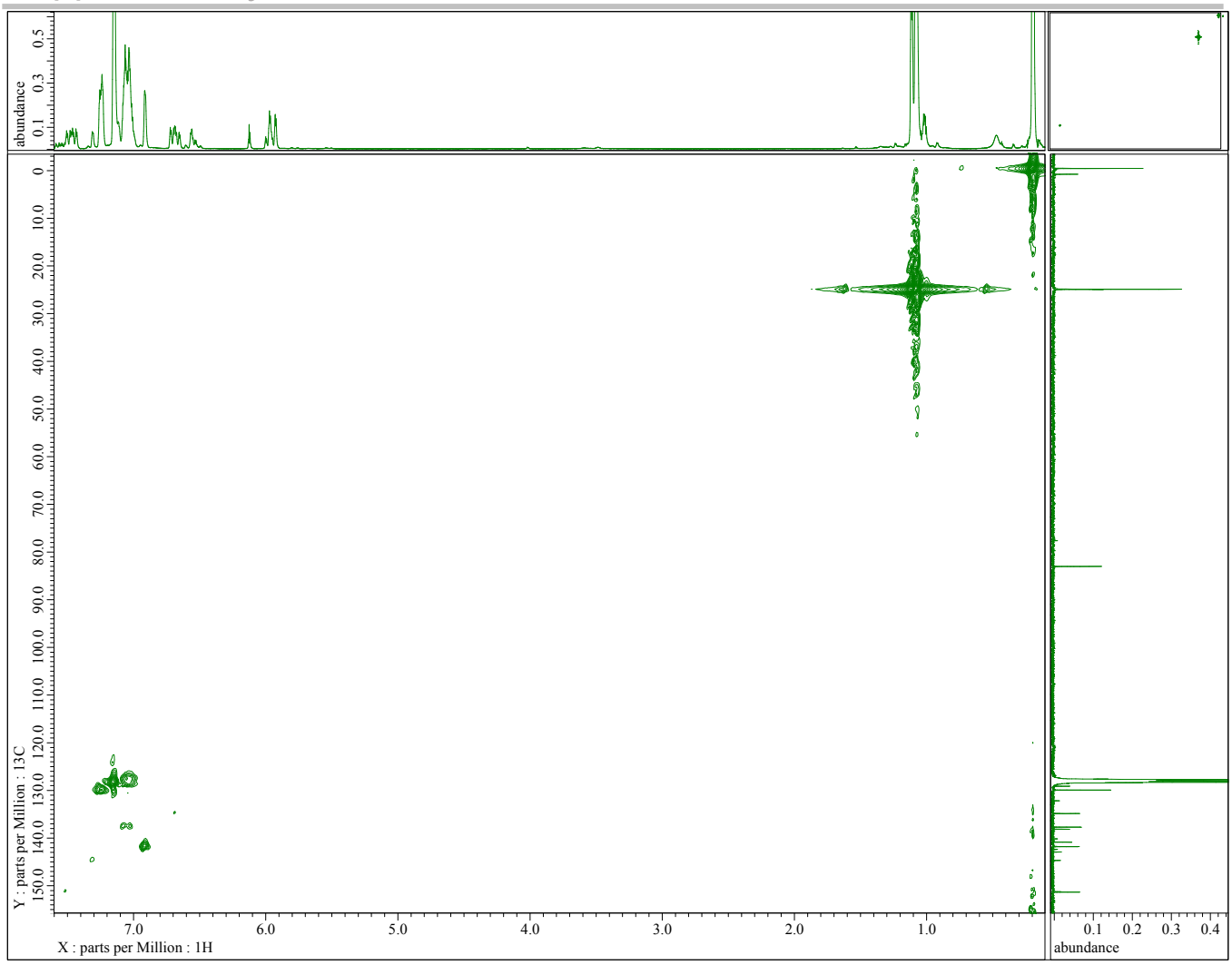
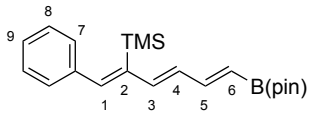
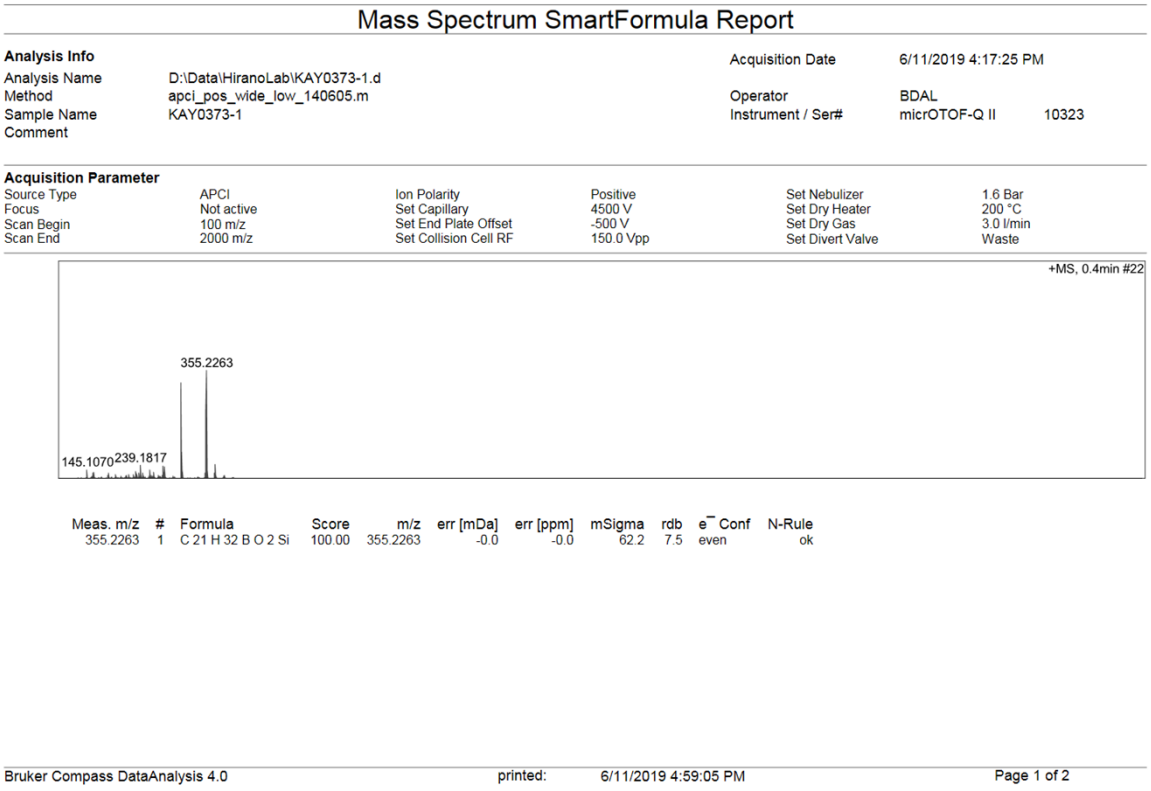


Figure S35. ^{1}H-^{13}C HMQC of (1*Z*,3*E*,5*E*)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-phenyl-2-trimethylsilylhexa-1,3,5-triene [(1*Z*,3*E*,5*E*)-**4j**] (400 MHz for ^{1}H, 100 MHz for ^{13}C, [D_6]benzene).





Mass Spectrum SmartFormula Report

Analysis Info

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Sample Name	KAY0373-1	Instrument / Ser#	micrOTOF-Q II 10323
Comment			

Acquisition Parameter

Source Type	APCI	Ion Polarity	Positive	Set Nebulizer	1.6 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	100 m/z	Set End Plate Offset	-500 V	Set Dry Gas	3.0 l/min
Scan End	2000 m/z	Set Collision Cell RF	150.0 Vpp	Set Divert Valve	Waste

Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
355.2263	1	C 21 H 32 B O 2 Si	100.00	355.2263	-0.0	-0.0	62.2	7.5	even	ok

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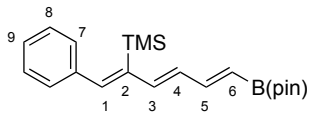
Figure S36. HRMS (APCI) spectrum of (1*Z*,3*E*,5*E*)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-phenyl-2-trimethylsilylhexa-1,3,5-triene [(1*Z*,3*E*,5*E*)-**4j**].



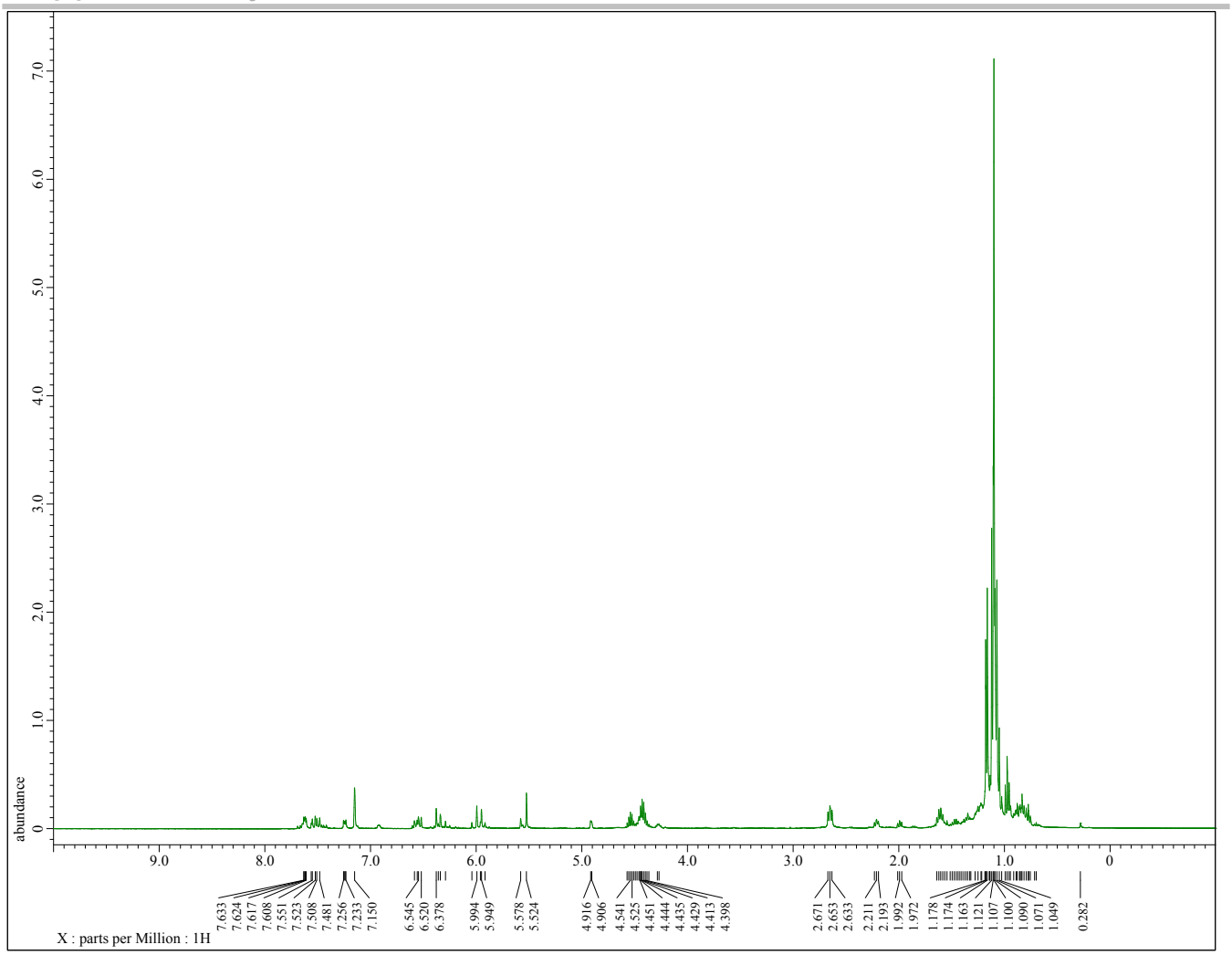
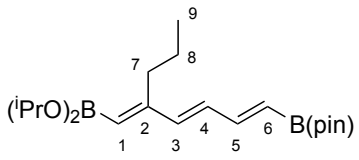


Figure S37. ^{1}H NMR spectrum of (1*E*,3*E*,5*E*)-1-(diisopropoxylboraneyl)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-propylhexa-1,3,5-triene [(1*E*,3*E*,5*E*)-**4k**] (an *in situ* reaction in an NMR tube) (400 MHz, [D_6]benzene).



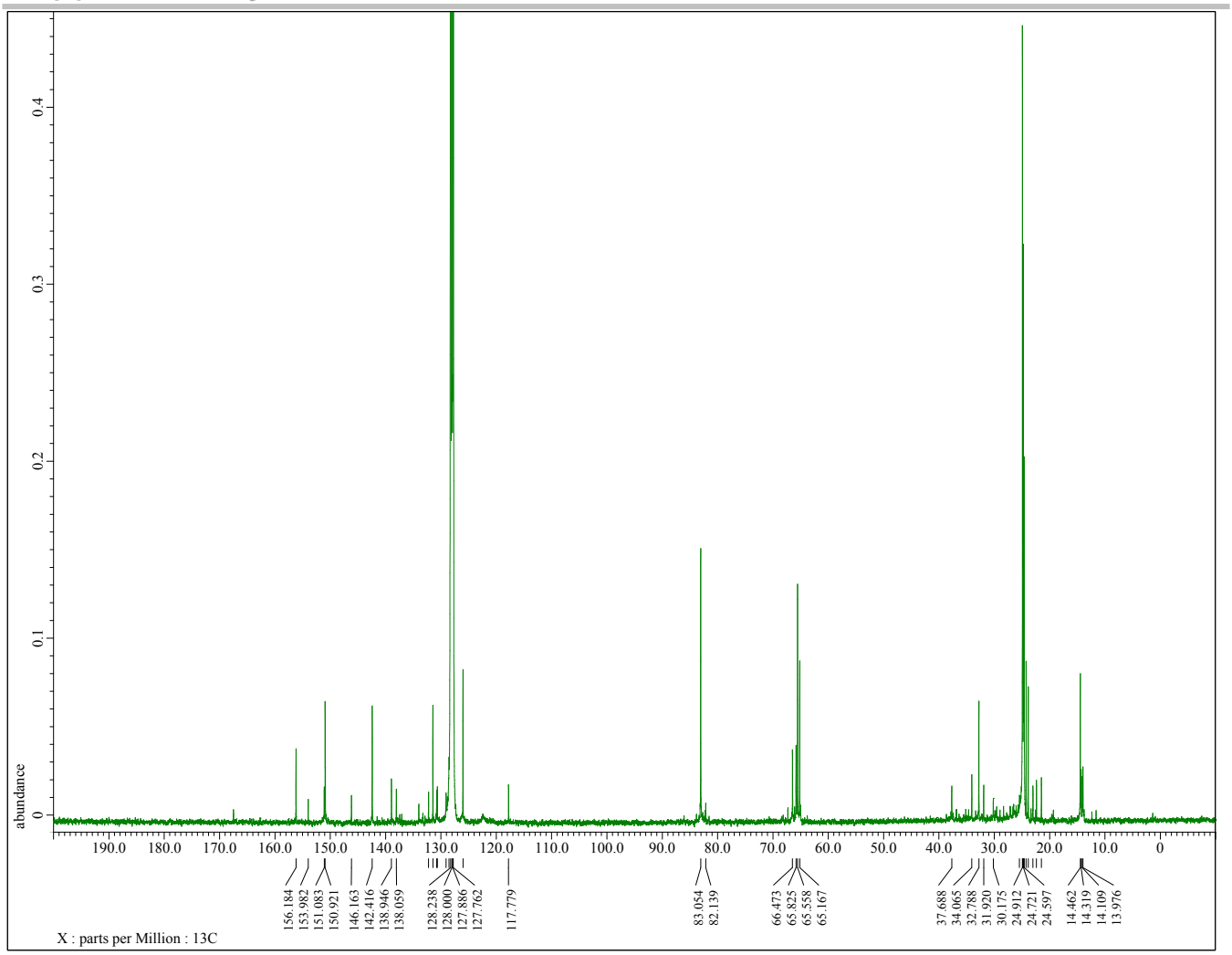
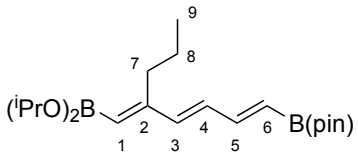


Figure S38. $^{13}C\{^{1}H\}$ NMR spectrum of (1*E*,3*E*,5*E*)-1-(diisopropoxylboraneyl)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-propylhexa-1,3,5-triene [(1*E*,3*E*,5*E*)-**4k**] (an *in situ* reaction in an NMR tube) (100 MHz, [D_6]benzene).



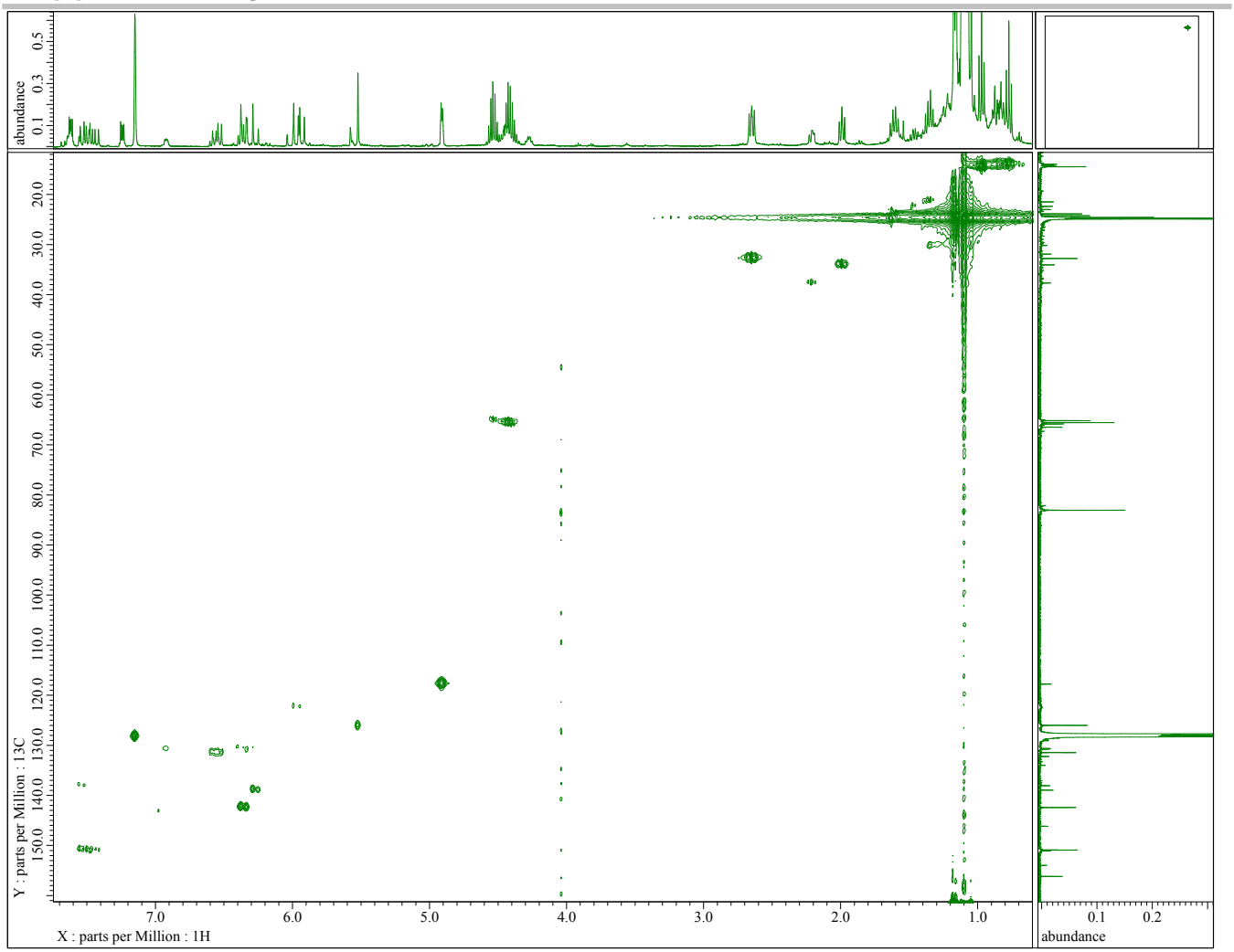
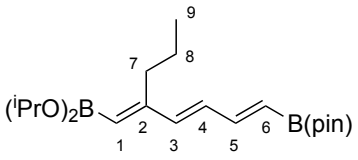


Figure S39. ^{1}H-^{13}C HMQC of (1*E*,3*E*,5*E*)-1-(diisopropoxylboraneyl)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-propylhexa-1,3,5-triene [(1*E*,3*E*,5*E*)-**4k**] (an *in situ* reaction in an NMR tube) (400 MHz for ^{1}H, 100 MHz for ^{13}C, [D_6]benzene).



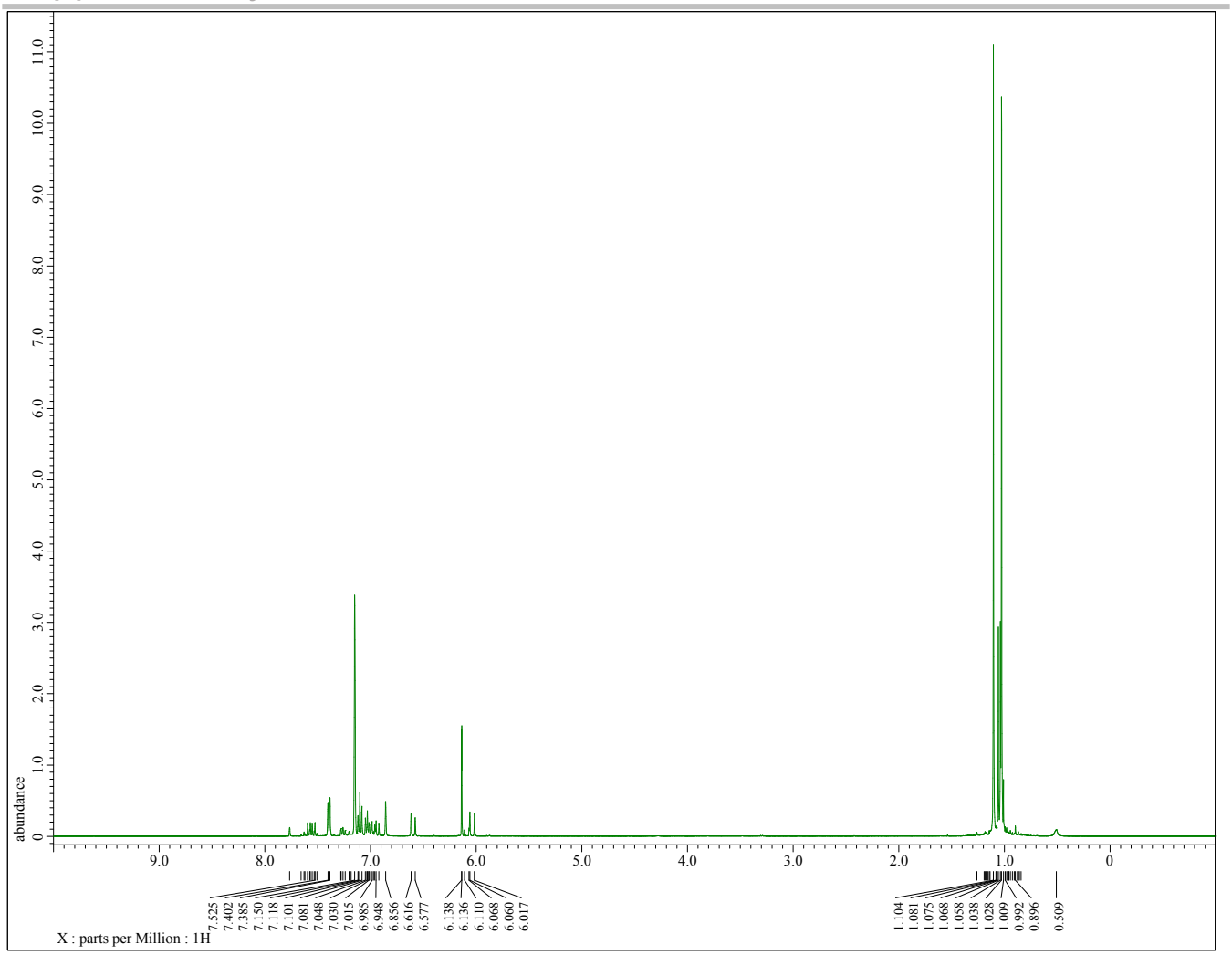
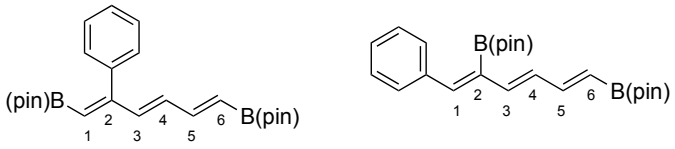


Figure S40. ^{1}H NMR spectrum of (1*Z*,3*E*,5*E*)-1,6-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-phenylhexa-1,3,5-triene and [(1*Z*,3*E*,5*E*)-**4l**] (1*E*,3*E*,5*E*)-2,6-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-phenylhexa-1,3,5-triene [(1*E*,3*E*,5*E*)-**5l**] (400 MHz, [D_6]benzene).



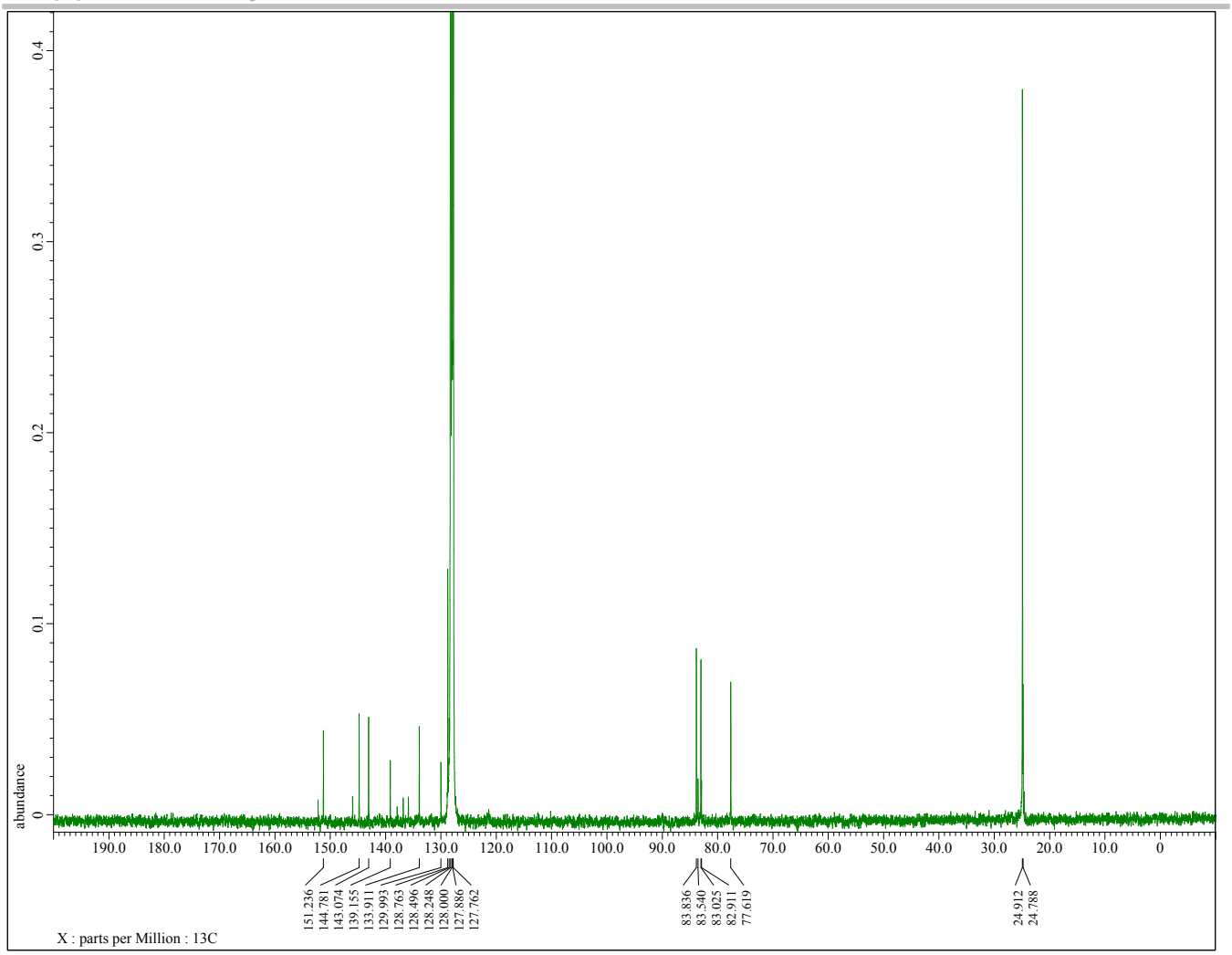
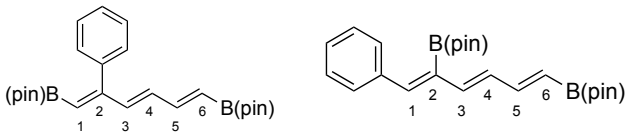


Figure S41. $^{13}C\{^{1}H\}$ NMR spectrum of(1*Z*,3*E*,5*E*)-1,6-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-phenylhexa-1,3,5-triene [(1*Z*,3*E*,5*E*)-**4l** and (1*E*,3*E*,5*E*)-2,6-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-phenylhexa-1,3,5-triene [(1*E*,3*E*,5*E*)-**5l**] (100 MHz, [D_6]benzene).



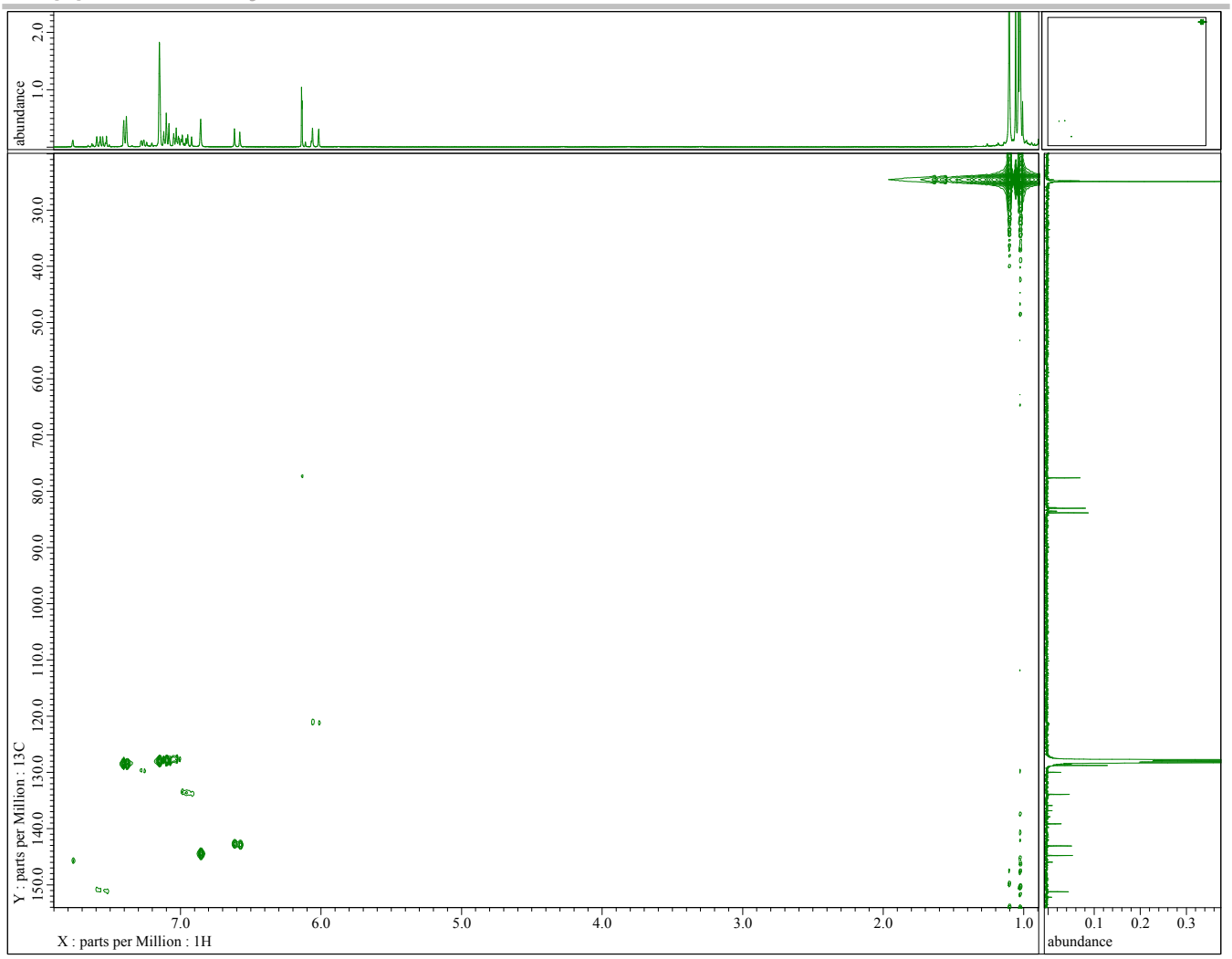
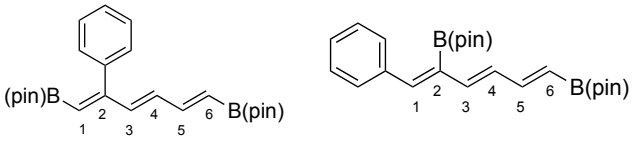
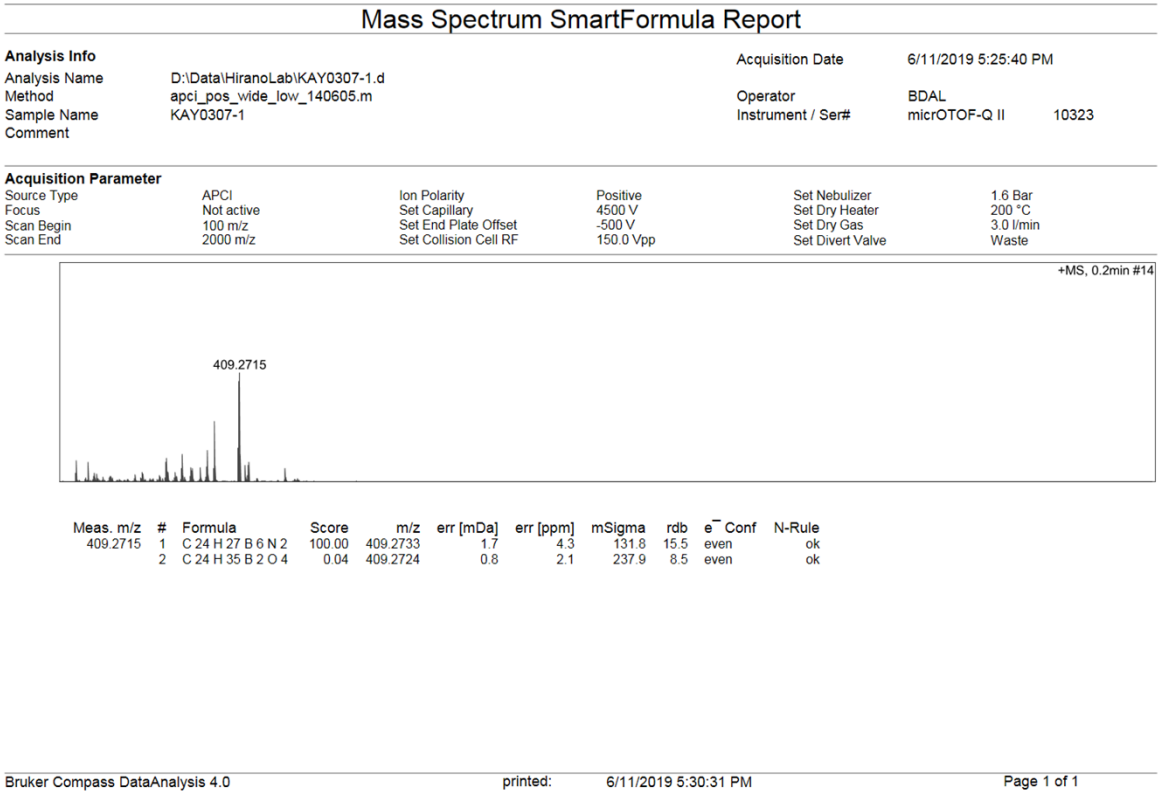


Figure S42. ^{1}H-^{13}C HMQC of (1*Z*,3*E*,5*E*)-1,6-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-phenylhexa-1,3,5-triene [(1*Z*,3*E*,5*E*)-**4l**] and (1*E*,3*E*,5*E*)-2,6-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-phenylhexa-1,3,5-triene [(1*E*,3*E*,5*E*)-**5l**] (400 MHz for ^{1}H, 100 MHz for ^{13}C, [D_6]benzene).





Mass Spectrum SmartFormula Report

Analysis Info

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Comment			

Acquisition Parameter

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Scan Begin	100 m/z	Set End Plate Offset	-500 V	Set Dry Gas	3.0 l/min
Scan End	2000 m/z	Set Collision Cell RF	150.0 Vpp	Set Divert Valve	Waste

Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
409.2715	1	C 24 H 27 B 6 N 2	100.00	409.2733	1.7	4.3	131.8	15.5	even	ok
	2	C 24 H 35 B 2 O 4	0.04	409.2724	0.8	2.1	237.9	8.5	even	ok

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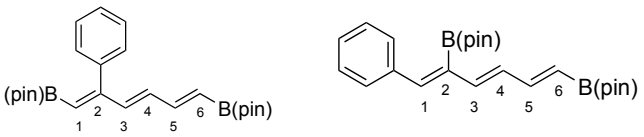
Figure S43. HRMS (APCI) spectrum of (1*Z*,3*E*,5*E*)-1,6-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-phenylhexa-1,3,5-triene [(1*Z*,3*E*,5*E*)-**4l**] and (1*E*,3*E*,5*E*)-2,6-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-phenylhexa-1,3,5-triene [(1*E*,3*E*,5*E*)-**5l**].



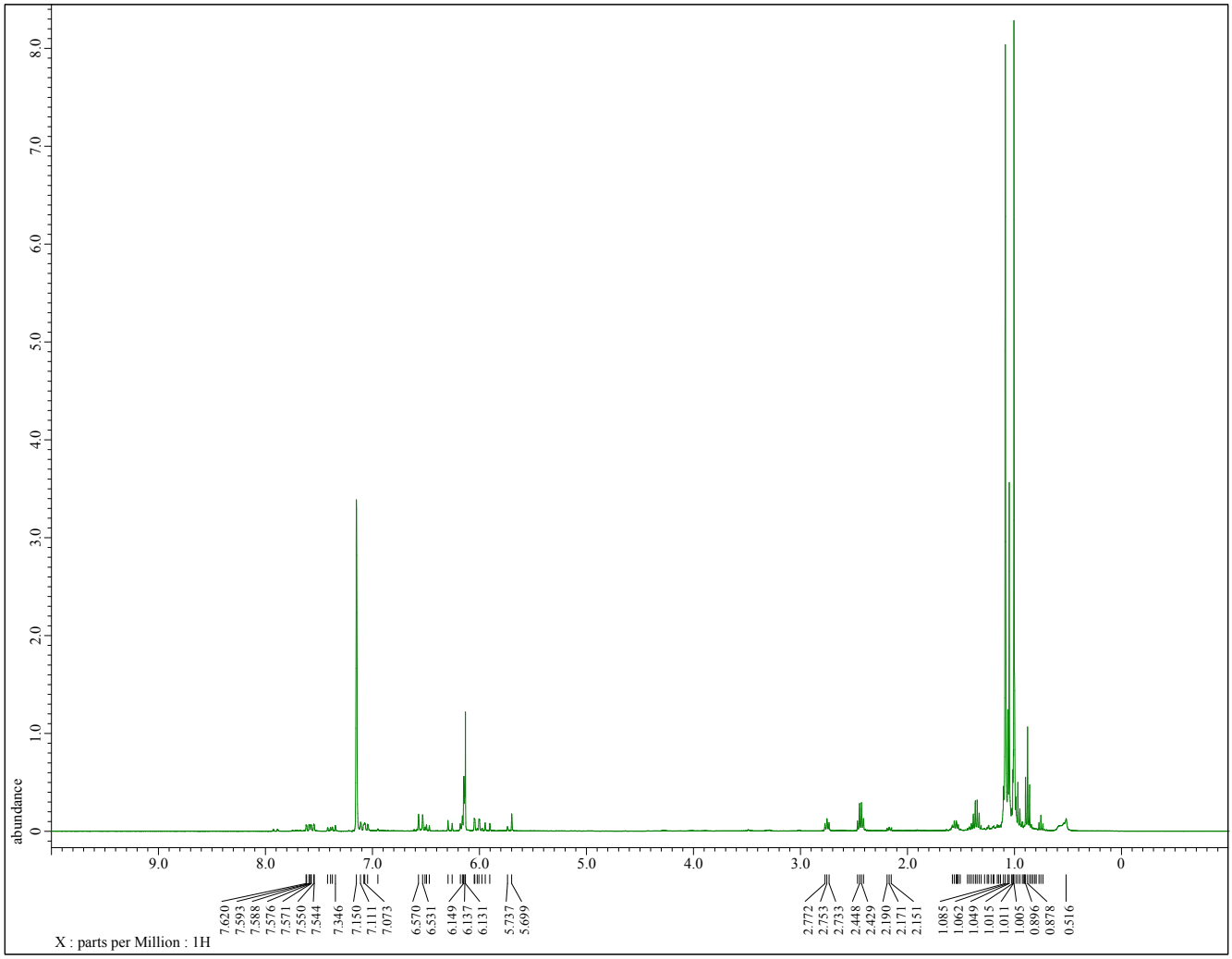
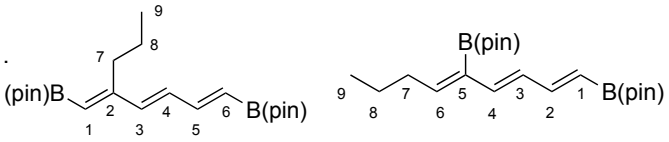


Figure S44. ^{1}H NMR spectrum of (1*E*,3*E*,5*E*)-1,6-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-propylhexa-1,3,5-triene [(1*E*,3*E*,5*E*)-**4m**] and (1*E*,3*E*,5*E*)-1,5-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)nona-1,3,5-triene [(1*E*,3*E*,5*E*)-**5m**] (400 MHz, [D_6]benzene).



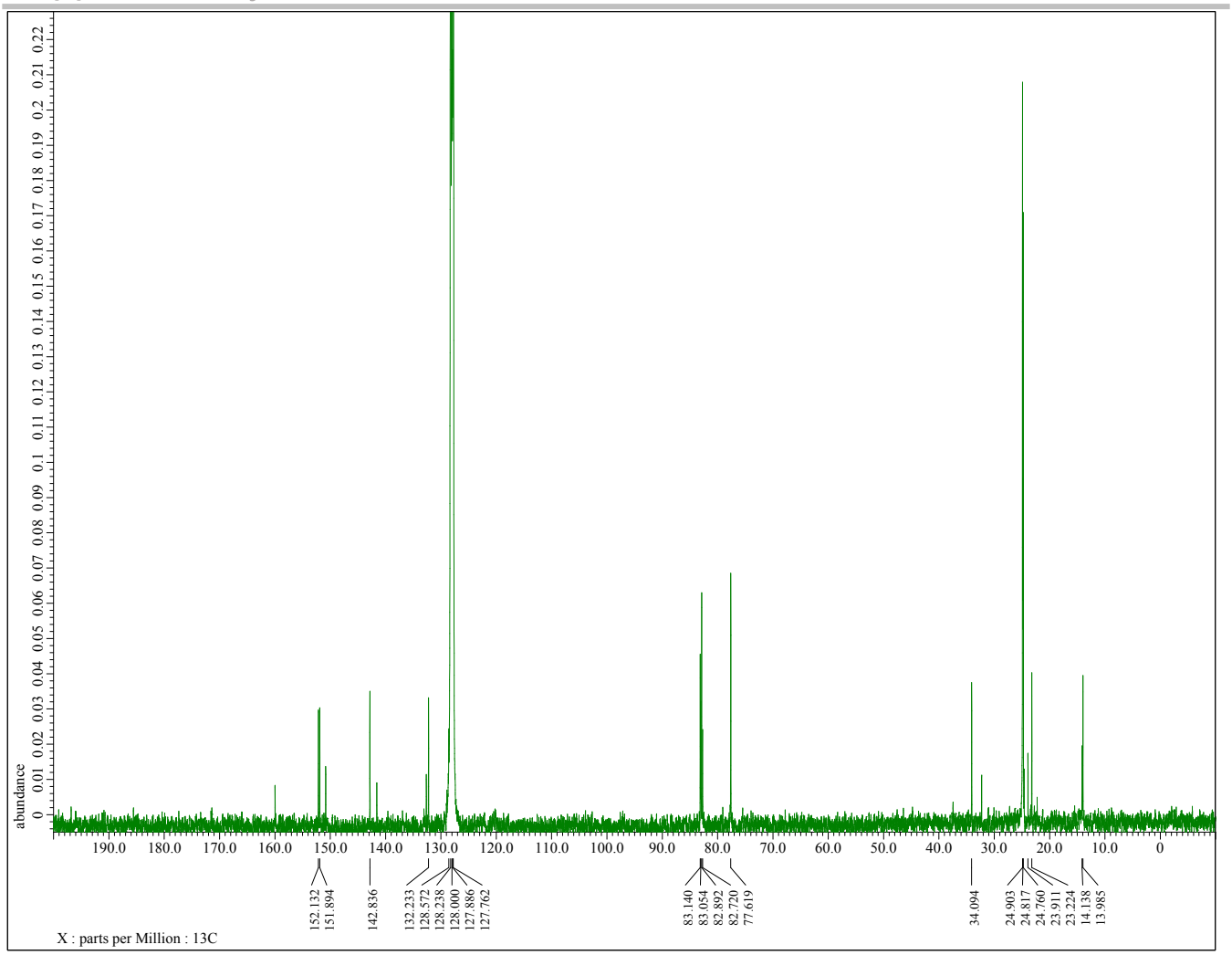
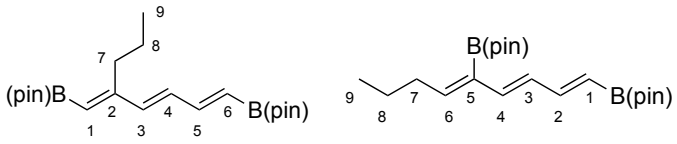


Figure S46. $^{13}C\{^{1}H\}$ NMR spectrum of (1*E*,3*E*,5*E*)-1,6-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-propylhexa-1,3,5-triene [(1*E*,3*E*,5*E*)-**4m**] and (1*E*,3*E*,5*E*)-1,5-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)nona-1,3,5-triene [(1*E*,3*E*,5*E*)-**5m**] (100 MHz, [D_6]benzene).



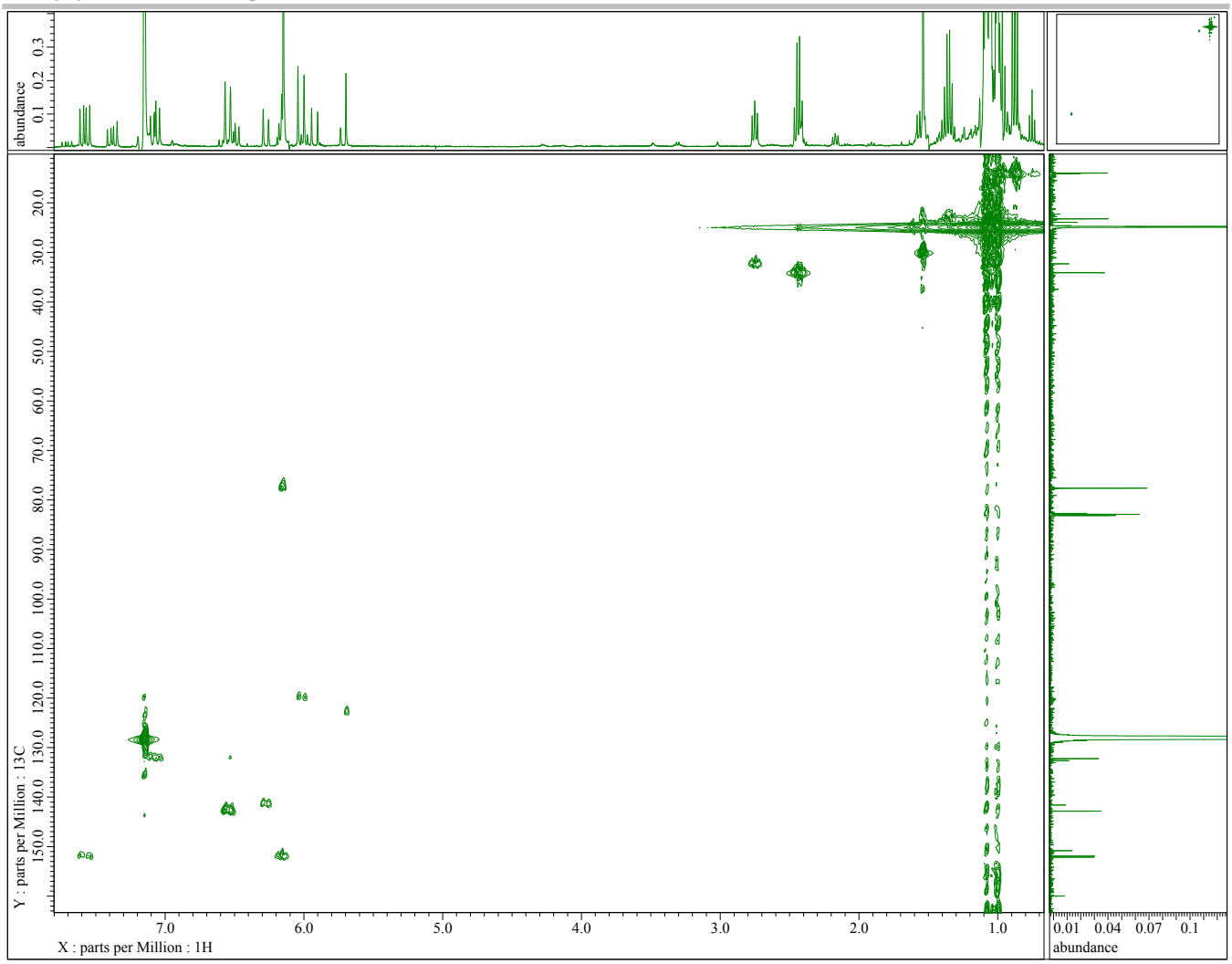
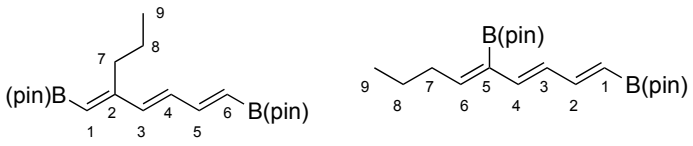
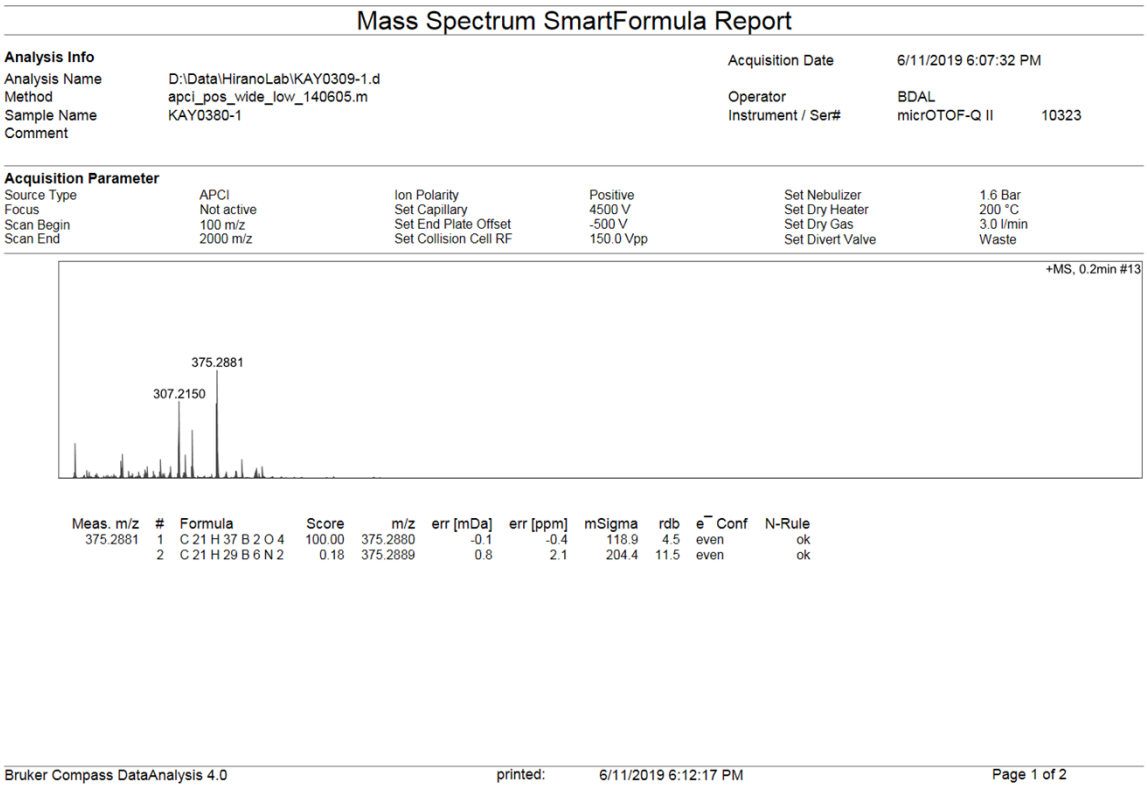


Figure S47. ^{1}H-^{13}C HMQC of (1*E*,3*E*,5*E*)-1,6-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-propylhexa-1,3,5-triene [(1*E*,3*E*,5*E*)-**4m**] and (1*E*,3*E*,5*E*)-1,5-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)nona-1,3,5-triene [(1*E*,3*E*,5*E*)-**5m**] (400 MHz for ^{1}H, 100 MHz for ^{13}C, [D_6]benzene).





Mass Spectrum SmartFormula Report

Analysis Info

Analysis Name	D:\Data\HiranoLab\KAY0309-1.d	Acquisition Date	6/11/2019 6:07:32 PM
Method	apci_pos_wide_low_140605.m	Operator	BDAL
Sample Name	KAY0380-1	Instrument / Ser#	micrOTOF-Q II 10323
Comment			

Acquisition Parameter

Source Type	APCI	Ion Polarity	Positive	Set Nebulizer	1.6 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	100 m/z	Set End Plate Offset	-500 V	Set Dry Gas	3.0 l/min
Scan End	2000 m/z	Set Collision Cell RF	150.0 Vpp	Set Divert Valve	Waste

Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
375.2881	1	C 21 H 37 B 2 O 4	100.00	375.2880	-0.1	-0.4	118.9	4.5	even	ok
	2	C 21 H 29 B 6 N 2	0.18	375.2889	0.8	2.1	204.4	11.5	even	ok

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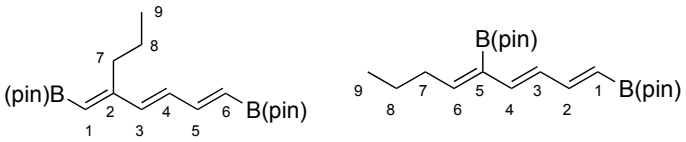
Figure S48. HRMS (APCI) spectrum of (1*E*,3*E*,5*E*)-1,6-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-propylhexa-1,3,5-triene [(1*E*,3*E*,5*E*)-**4m**] and (1*E*,3*E*,5*E*)-1,5-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)nona-1,3,5-triene [(1*E*,3*E*,5*E*)-**5m**].



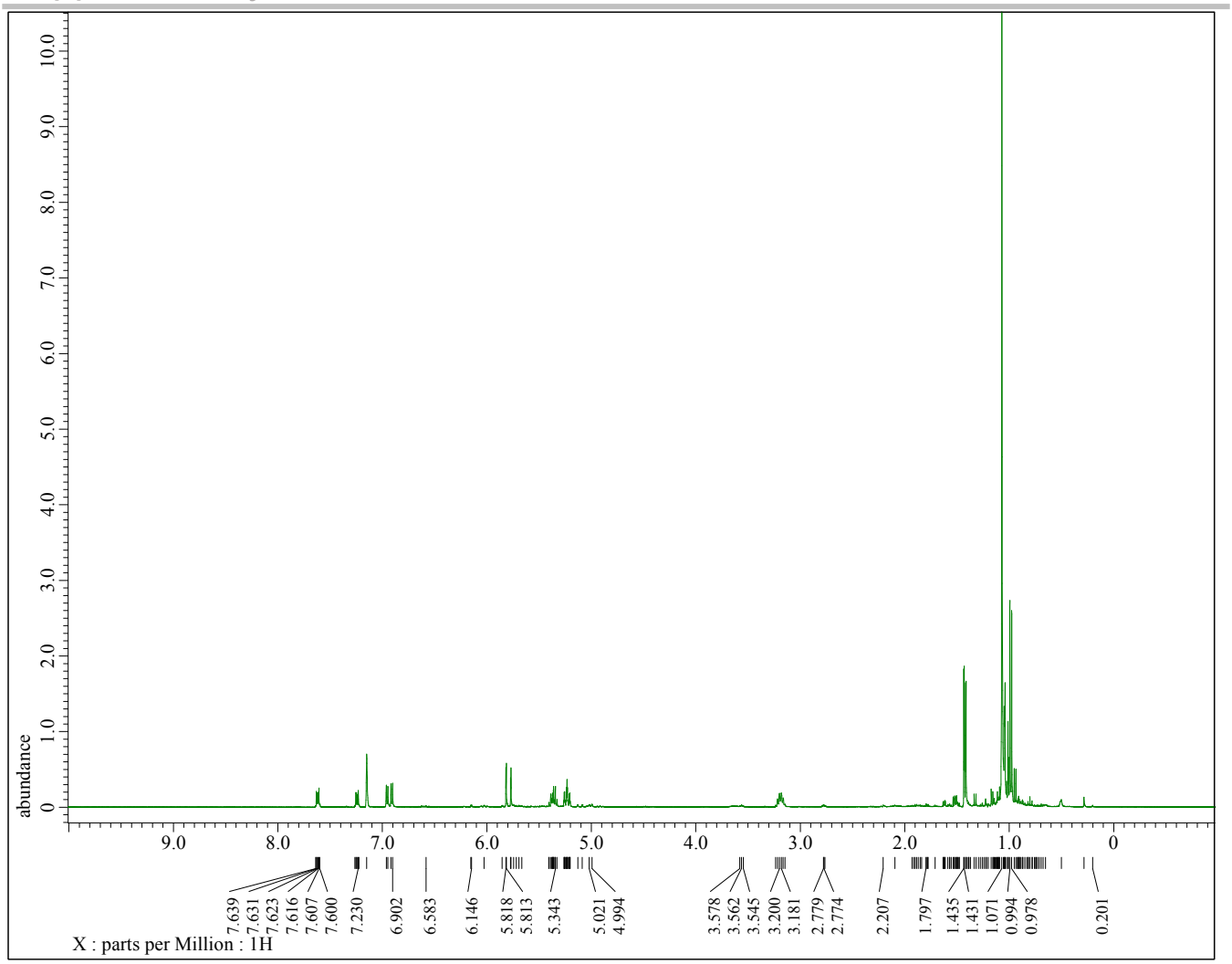
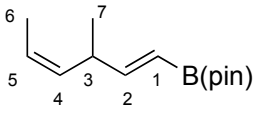


Figure S49. ^{1}H NMR spectrum of (1*E*,4*Z*)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-methylhexa-1,4-diene [(1*E*,4*Z*)-**7a**] (400 MHz, [D_6]benzene).



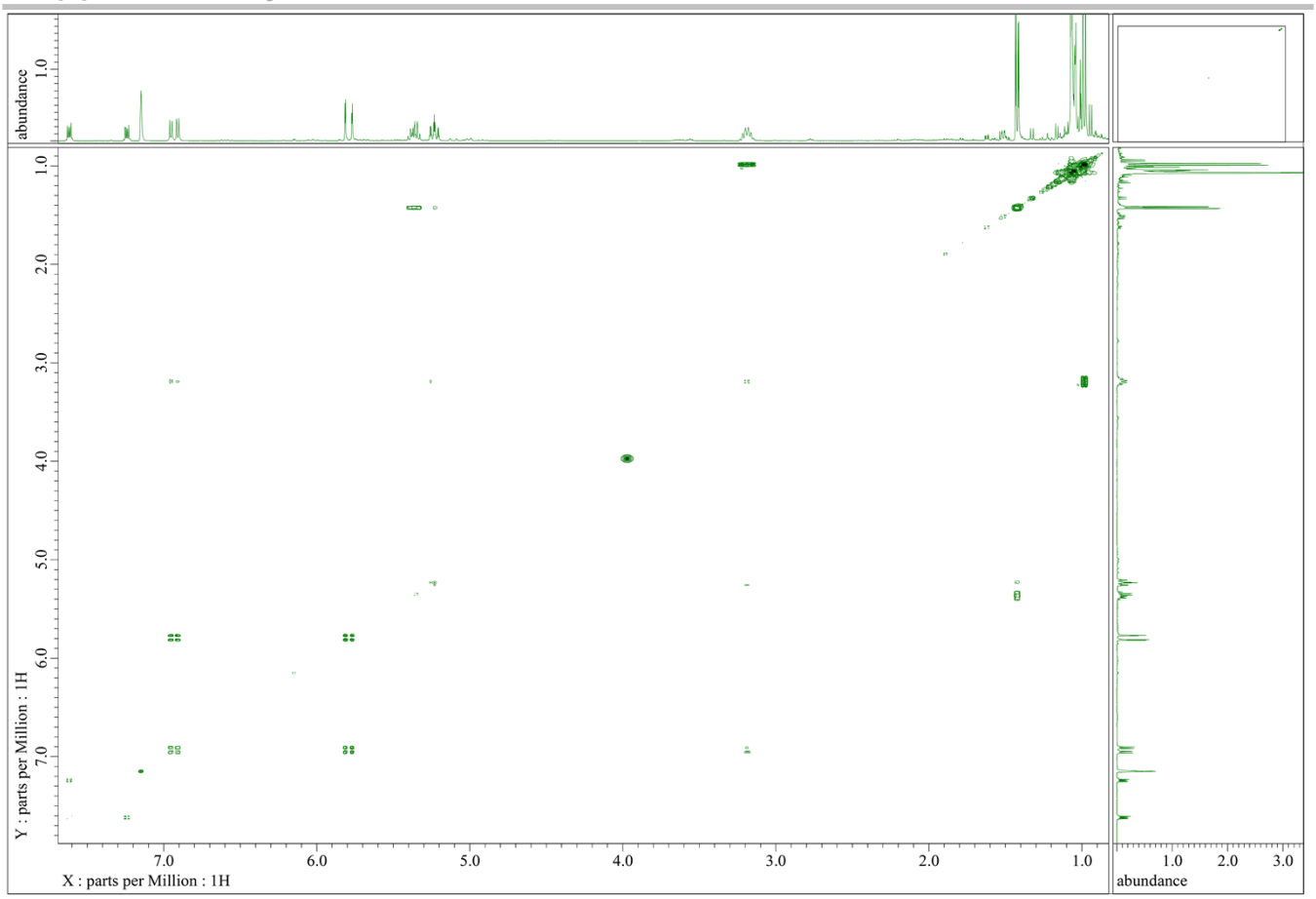
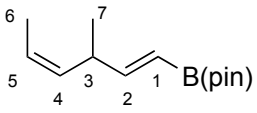


Figure S50. ^{1}H-^{1}H COSY of (1*E*,4*Z*)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-methylhexa-1,4-diene [(1*E*,4*Z*)-**7a**] (400 MHz, [D_6]benzene).



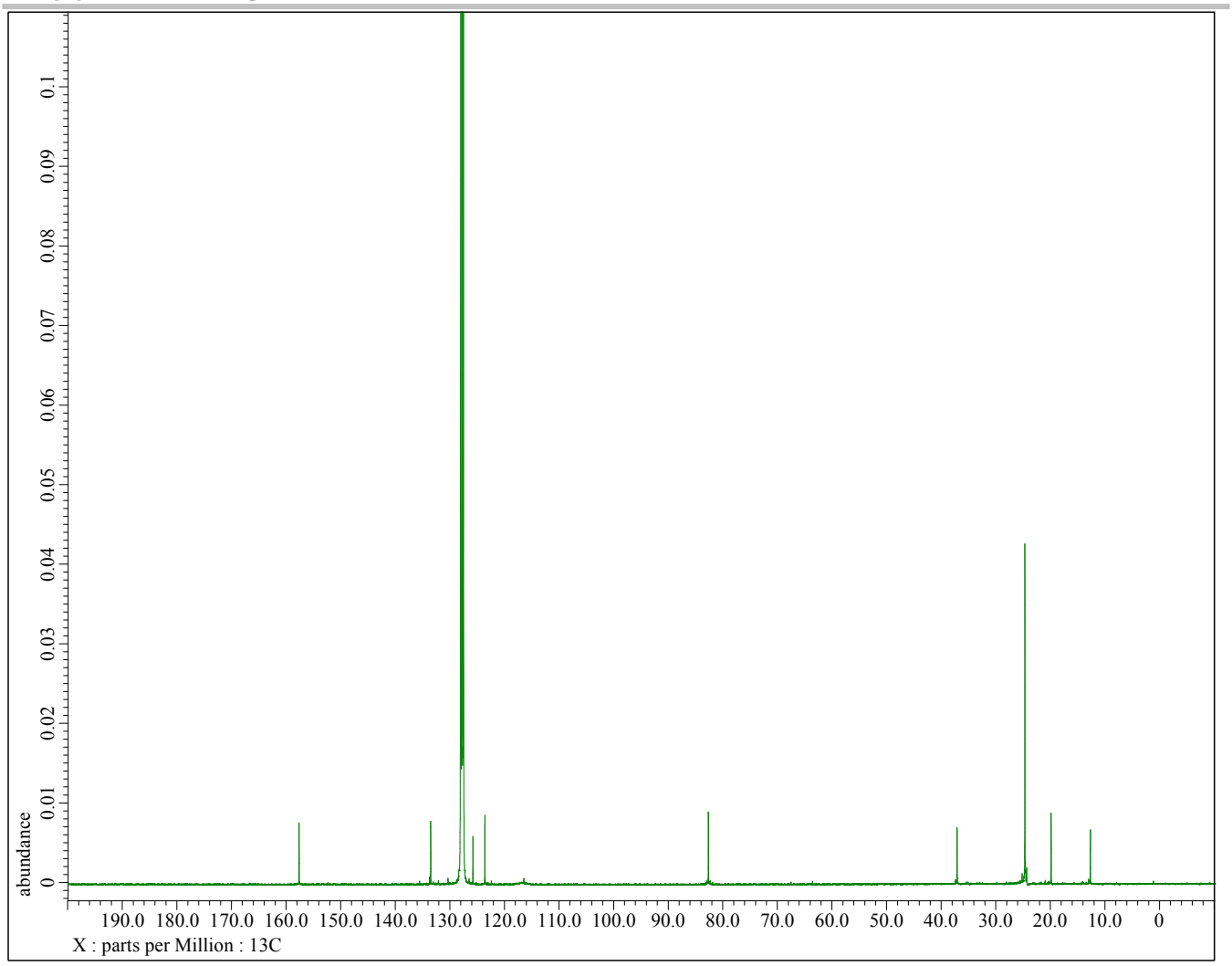
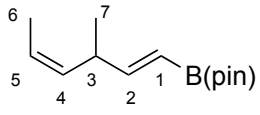


Figure S51. $^{13}C\{^{1}H\}$NMR spectrum of (1*E*,4*Z*)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-methylhexa-1,4-diene [(1*E*,4*Z*)-**7a**] (100 MHz, $[D_6]$benzene).



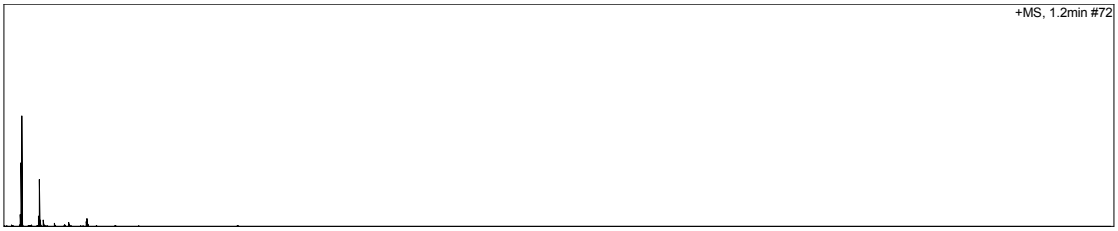
Mass Spectrum SmartFormula Report

Analysis Info

Analysis Name	D:\Data\HiranoLab\SMD0475.d	Acquisition Date	2/19/2019 6:42:37 PM
Method	apci_pos_wide_171018.m	Operator	BDAL
Sample Name	SMD0475	Instrument / Ser#	micrOTOF-Q II 10323
Comment			

Acquisition Parameter

Source Type	APCI	Ion Polarity	Positive	Set Nebulizer	1.6 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	200 m/z	Set End Plate Offset	-500 V	Set Dry Gas	3.0 l/min
Scan End	2000 m/z	Set Collision Cell RF	150.0 Vpp	Set Divert Valve	Waste



Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e¯ Conf	N-Rule
223.1864	1	C 9 H 20 B N 6	22.89	223.1839	-2.5	-11.4	168.4	3.5	even	ok
	2	C 13 H 24 B O 2	100.00	223.1866	0.2	1.0	168.7	2.5	even	ok

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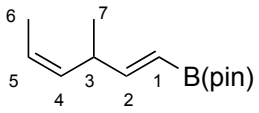
Figure S52. HRMS (APCI) spectrum of (1*E*,4*Z*)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-methylhexa-1,4-diene [(1*E*,4*Z*)-**7a**].



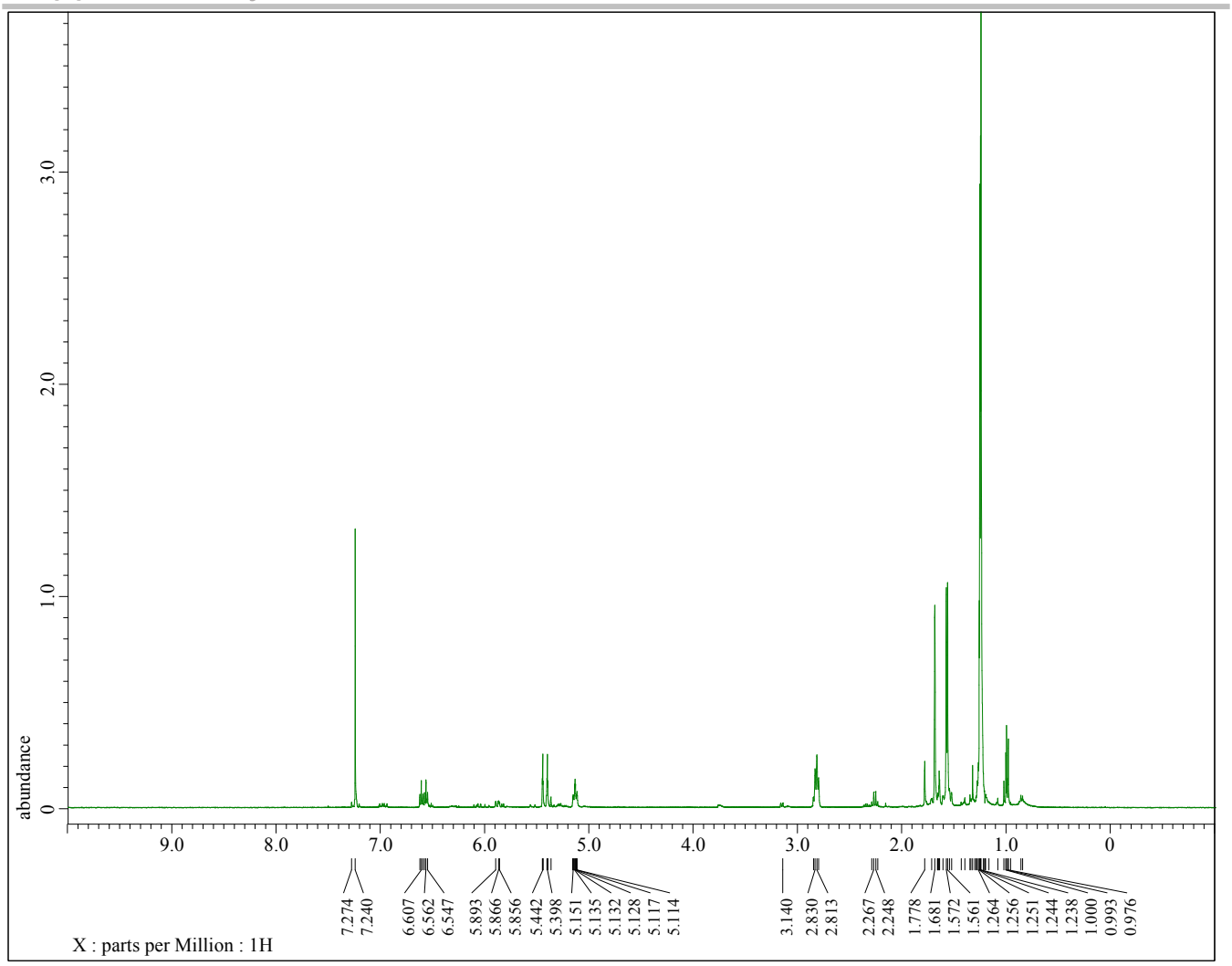
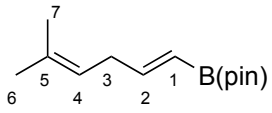


Figure S53 ^{1}H NMR spectrum of (*E*)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-methylhexa-1,4-diene [(*E*)-**7b**] (400 MHz, [D_6]benzene).



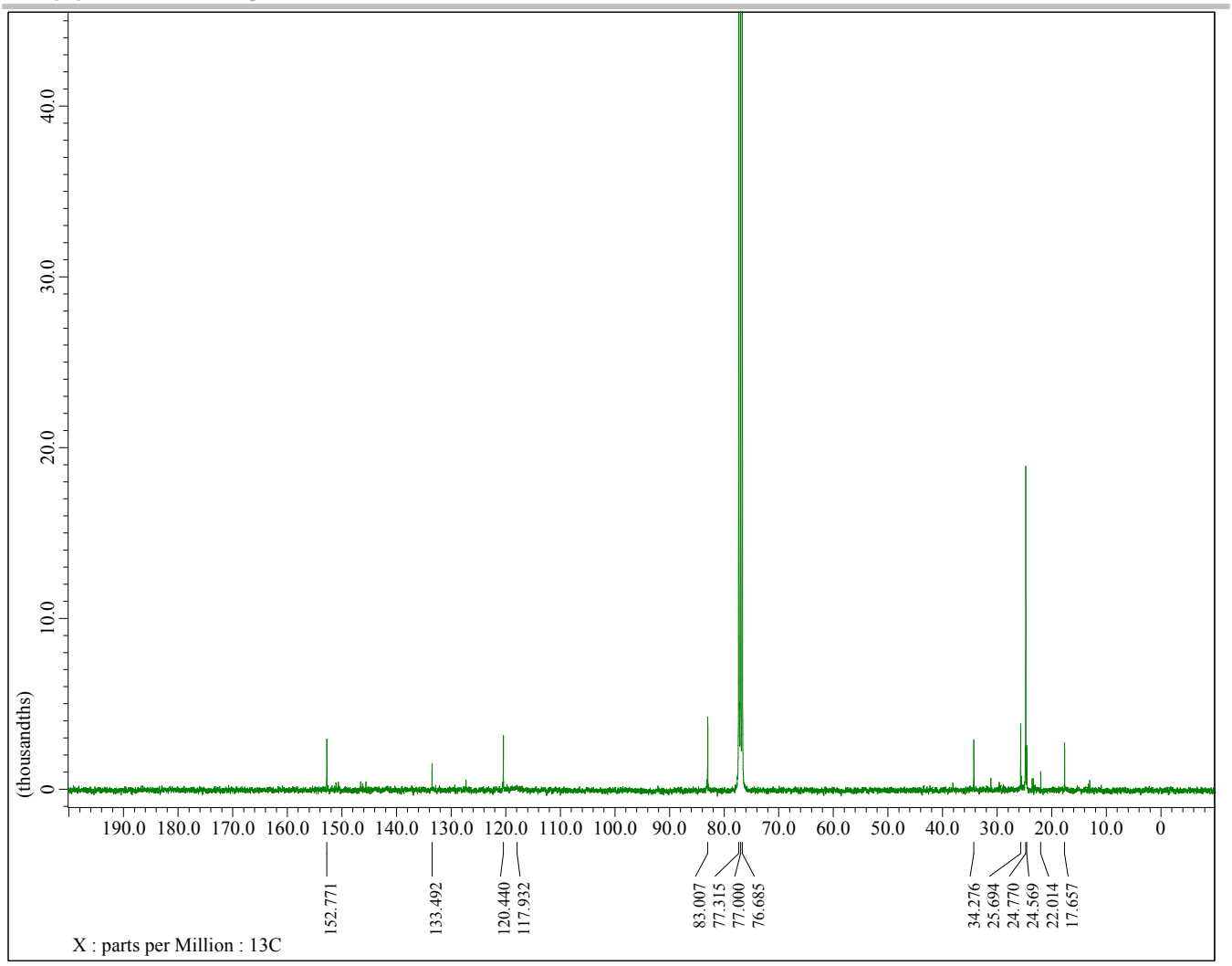
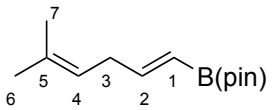


Figure S54. $^{13}C\{^{1}H\}$ NMR spectrum of (*E*)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-methylhexa-1,4-diene [(*E*)-**7b**] (100 MHz, [D]chloroform).



Mass Spectrum SmartFormula Report

Analysis Info

Analysis Name	D:\Data\HiranoLab\SMD0477.d	Acquisition Date	2/19/2019 6:51:20 PM
Method	apci_pos_wide_171018.m	Operator	BDAL
Sample Name	SMD0477	Instrument / Ser#	micrOTOF-Q II 10323
Comment			

Acquisition Parameter

Source Type	APCI	Ion Polarity	Positive	Set Nebulizer	1.6 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	200 m/z	Set End Plate Offset	-500 V	Set Dry Gas	3.0 l/min
Scan End	2000 m/z	Set Collision Cell RF	150.0 Vpp	Set Divert Valve	Waste

Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e¯ Conf	N-Rule
223.1865	1	C 13 H 24 B O 2	100.00	223.1866	0.1	0.7	283.5	2.5	even	ok
	2	C 9 H 20 B N 6	20.38	223.1839	-2.6	-11.7	283.6	3.5	even	ok

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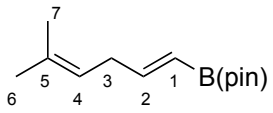
Figure S55. HRMS (APCI) spectrum of (*E*)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-methylhexa-1,4-diene [(*E*)-**7b**].



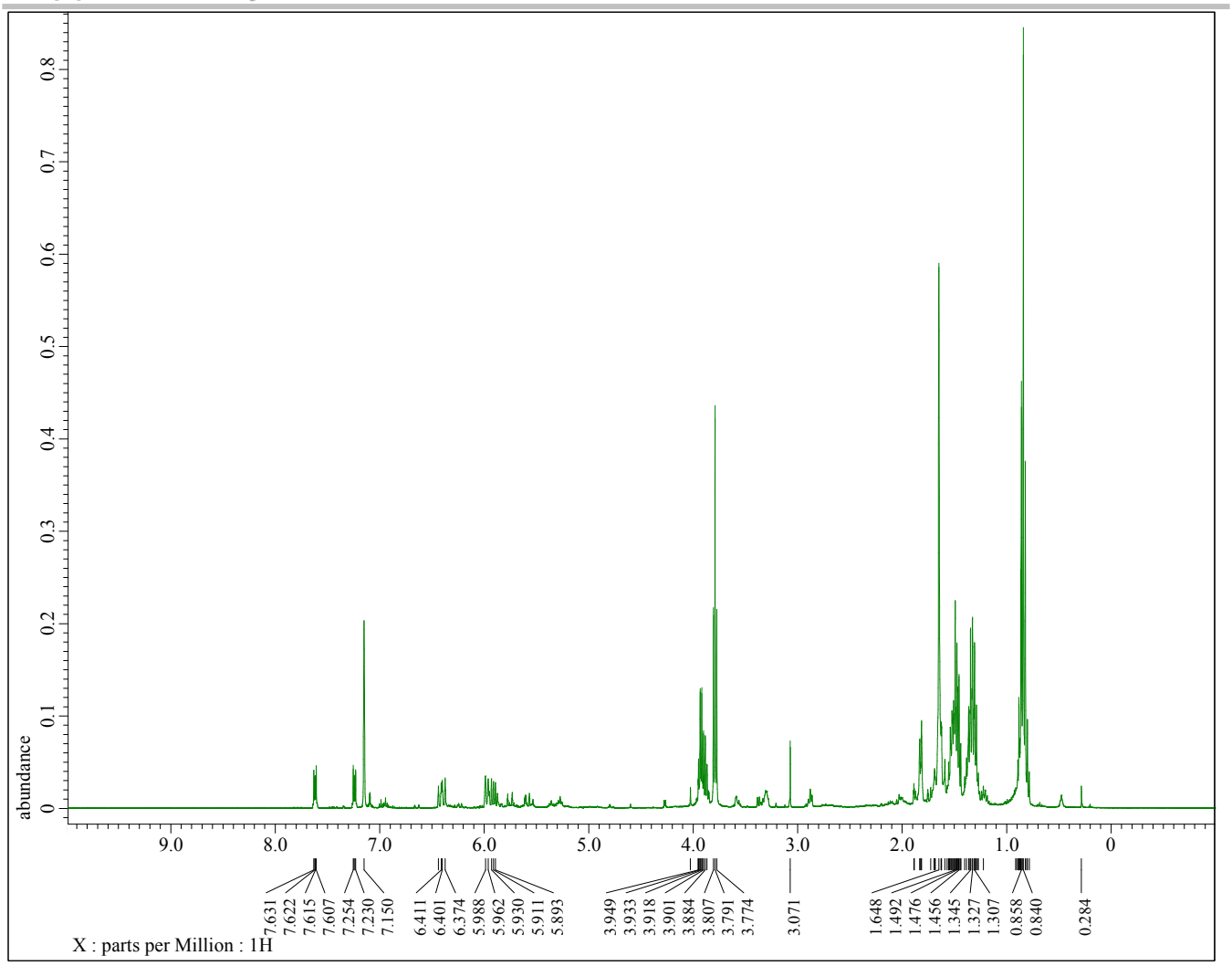
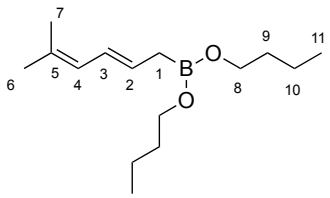


Figure S56. ^{1}H NMR spectrum of (*E*)-1-(dibutoxyboraneyl)-5-methylhexa-2,4-diene (an *in situ* reaction in an NMR tube) [(*E*)-**7c**] (an *in situ* reaction in an NMR tube) (400 MHz, [D_6]benzene).



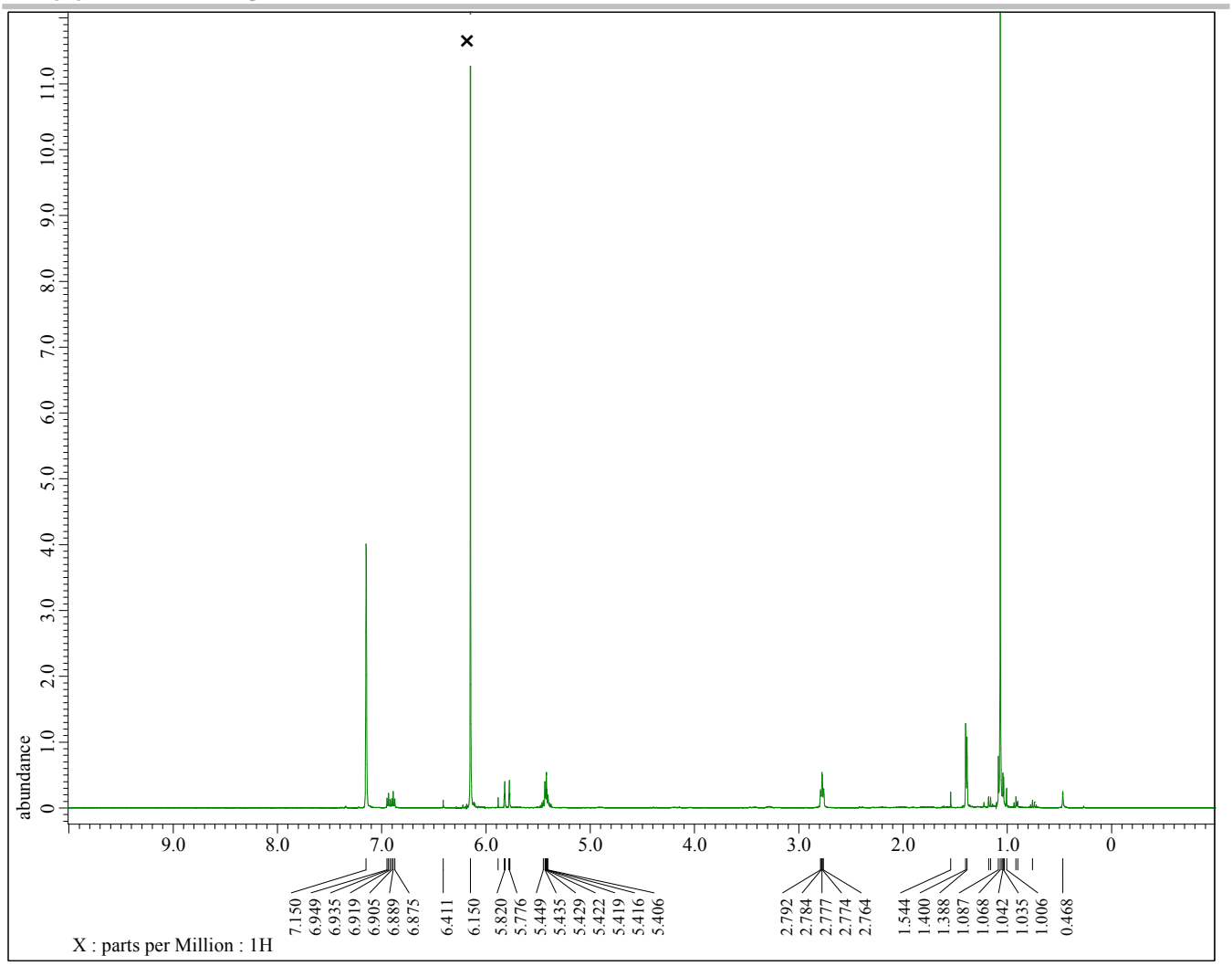
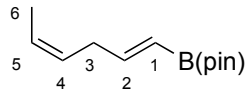


Figure S57. ^{1}H NMR spectrum of (1*E*,4*Z*)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexa-1,4-diene [(1*E*,4*Z*)-**7d**] (400 MHz, [D_6]benzene). X indicates incorporated chloroform.



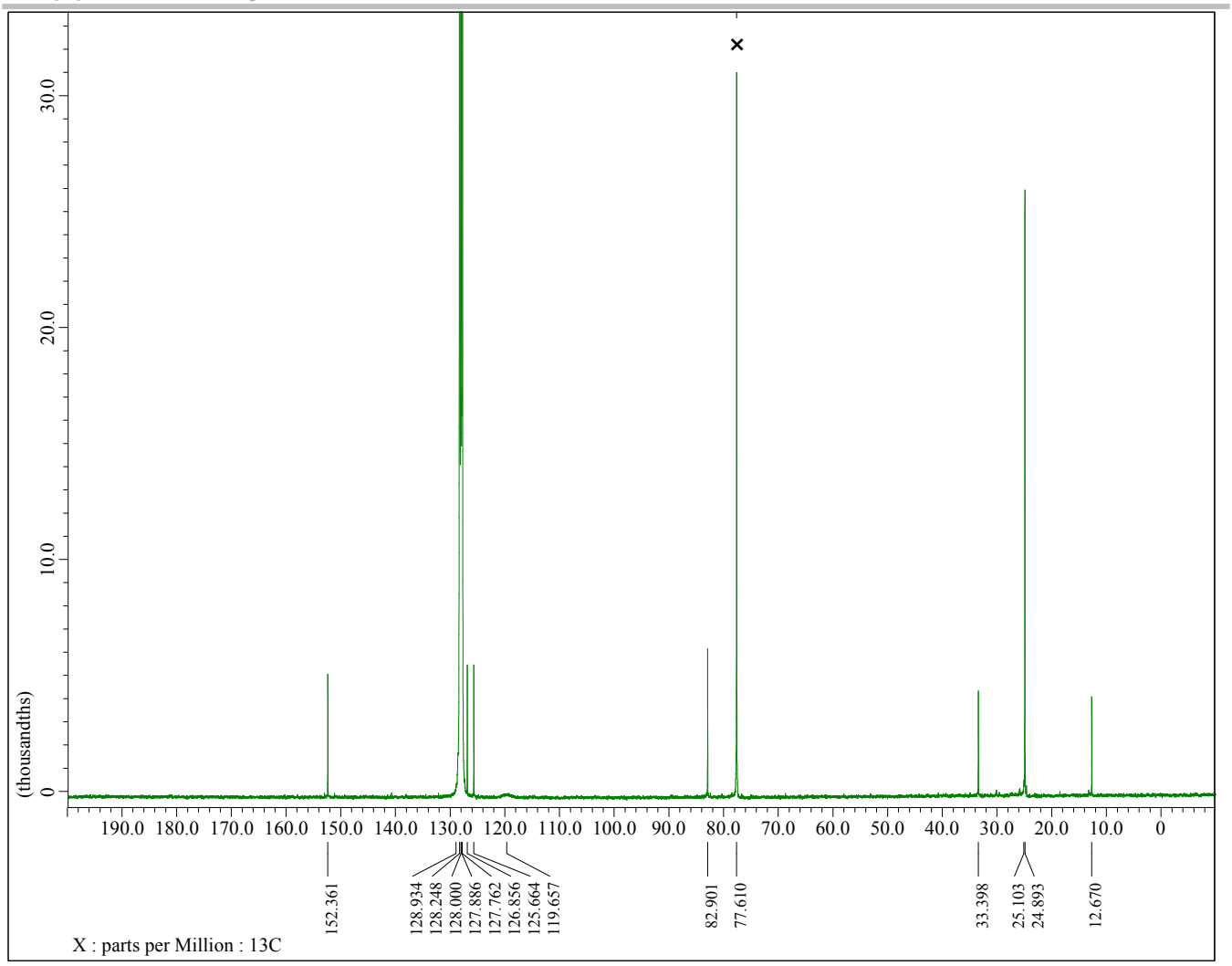
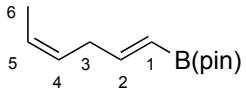


Figure S58. $^{13}C\{^{1}H\}$ NMR spectrum of (1*E*,4*Z*)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexa-1,4-diene [(1*E*,4*Z*)-**7d**] (100 MHz, [D_6]benzene). X indicates an incorporated chloroform.



Mass Spectrum SmartFormula Report

Analysis Info

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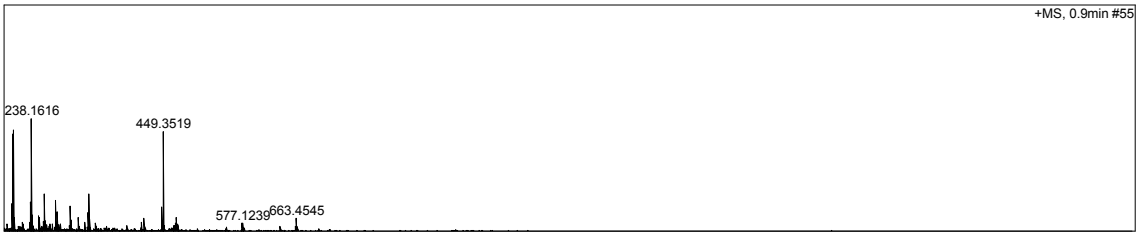
Method	apci_pos_wide_171018.m	Operator	BDAL
Sample Name	SMD0485	Instrument / Ser#	micrOTOF-Q II 10323
Comment			

Acquisition Parameter

Source Type	APCI	Ion Polarity	Positive	Set Nebulizer	1.6 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	200 m/z	Set End Plate Offset	-500 V	Set Dry Gas	3.0 l/min
Scan End	2000 m/z	Set Collision Cell RF	150.0 Vpp	Set Divert Valve	Waste



Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e¯ Conf	N-Rule
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	2	C 8 H 18 B N 6	0.00	209.1682	-2.7	-13.1	416.2	3.5	even	ok

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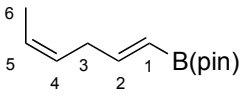
Figure S59. HRMS (APCI) spectrum of (1*E*,4*Z*)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexa-1,4-diene [(1*E*,4*Z*)-**7d**].



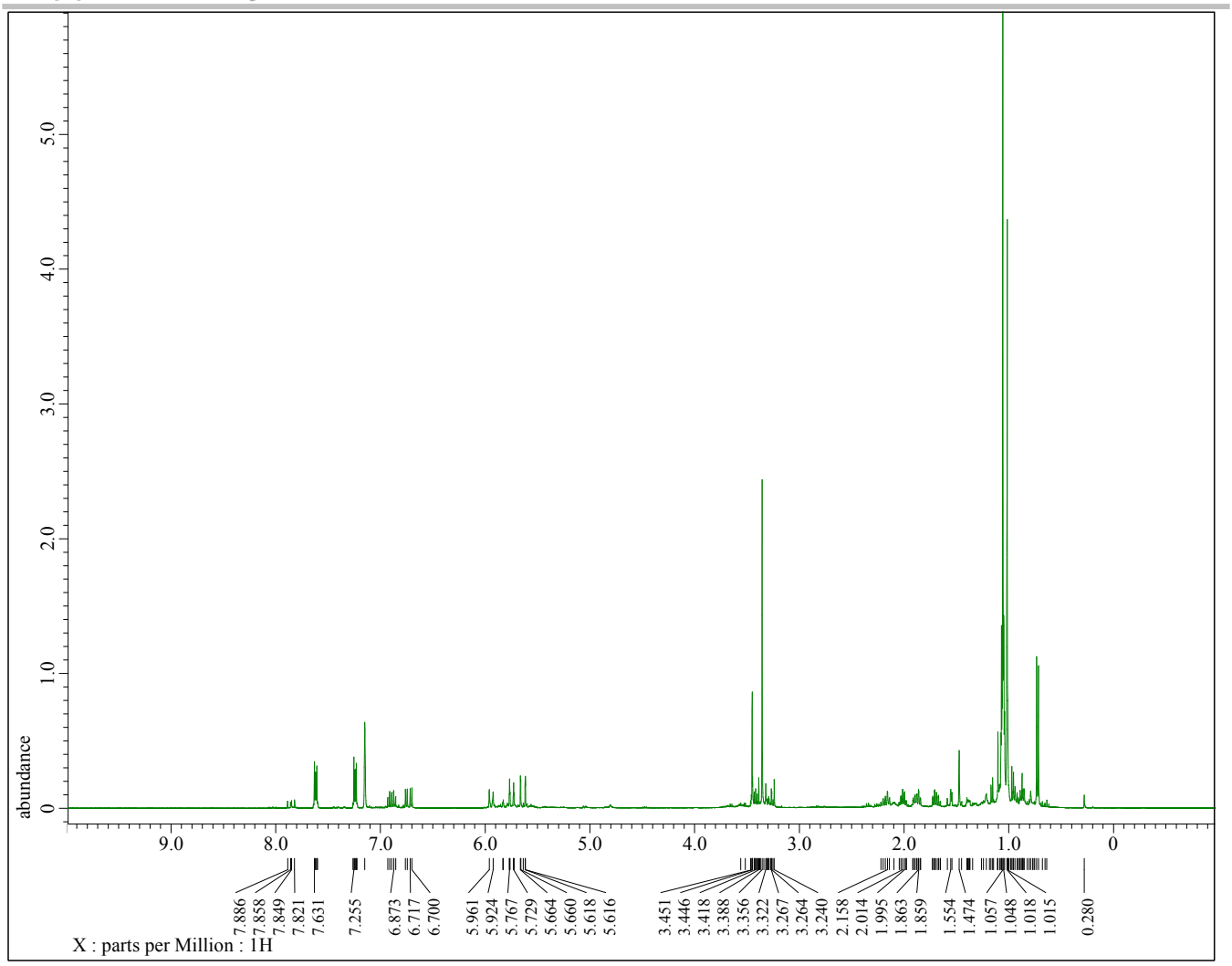
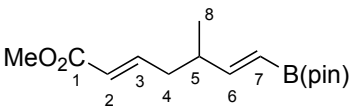


Figure S60. ^{1}H NMR spectrum of methyl (2*E*,6*E*)-5-methyl-7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hepta-2,6-dienoate [(2*E*,6*E*)-**7e**] (400 MHz, [D]chloroform).



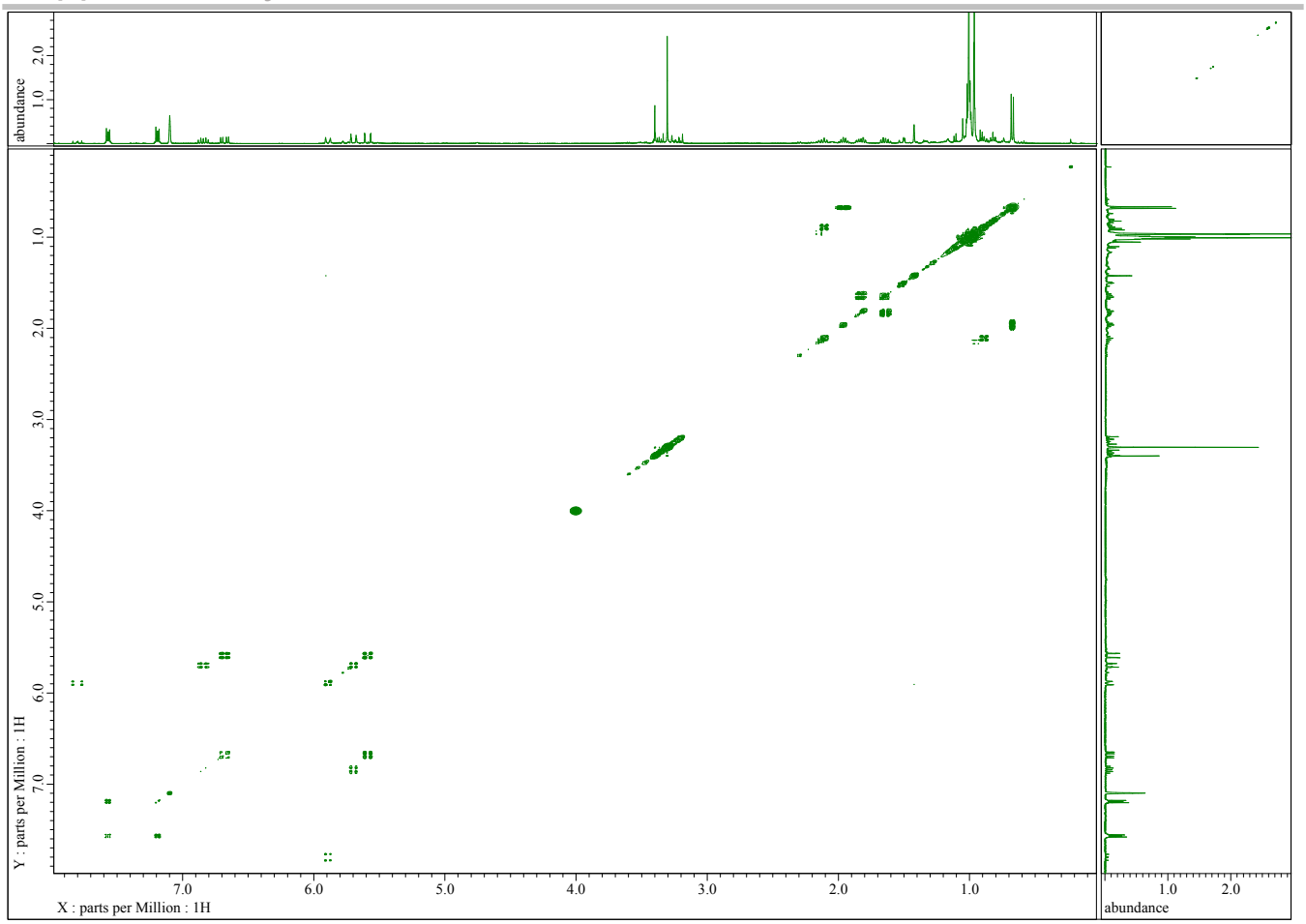
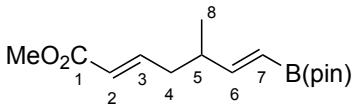


Figure S61 ^{1}H-^{1}H COSY of methyl (2*E*,6*E*)-5-methyl-7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hepta-2,6-dienoate [(2*E*,6*E*)-**7e**] (400 MHz, [D]chloroform).



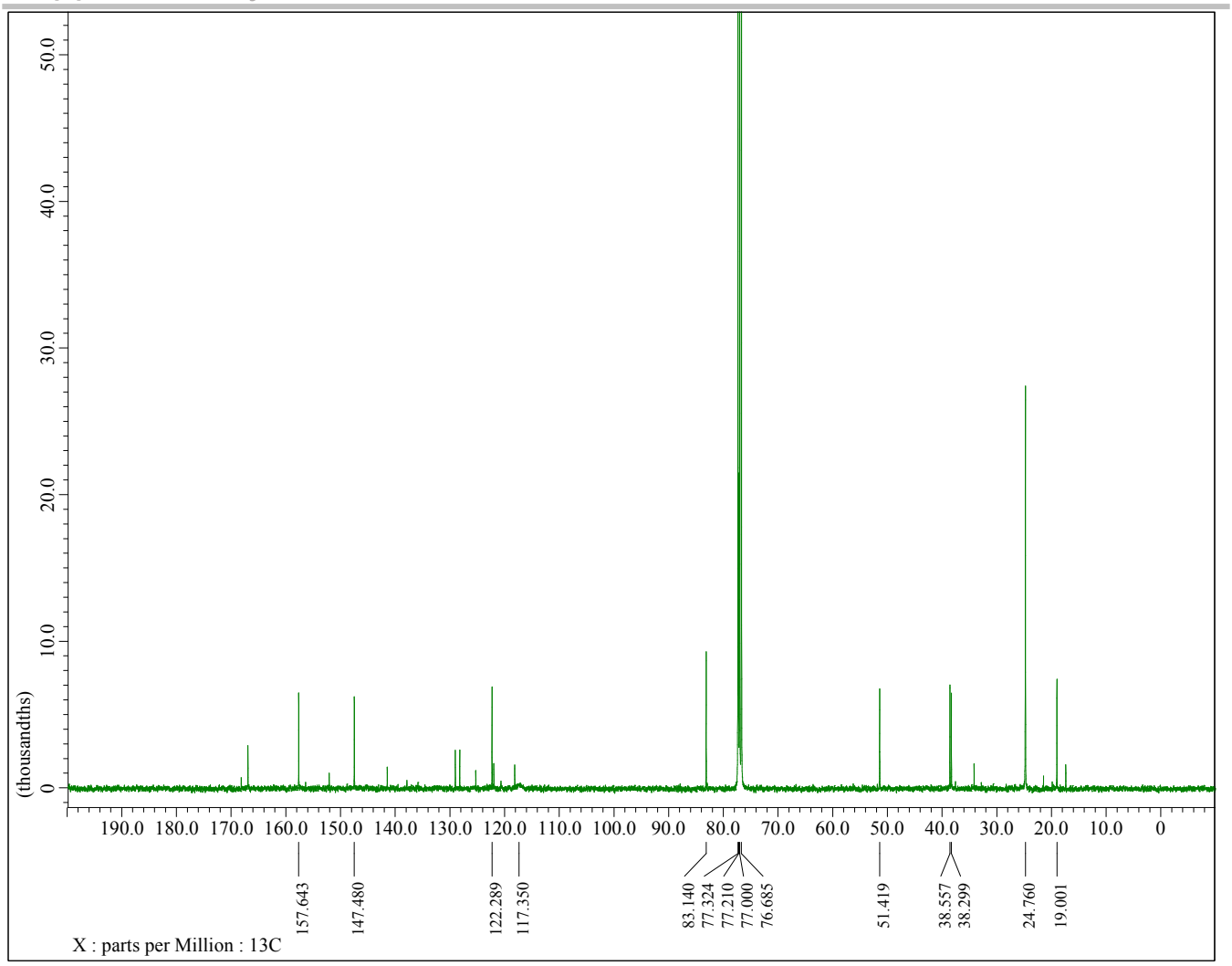
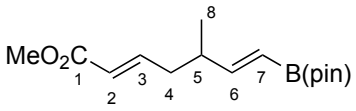


Figure S62. $^{13}C\{^{1}H\}$ NMR spectrum of methyl (2*E*,6*E*)-5-methyl-7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hepta-2,6-dienoate [(2*E*,6*E*)-**7e**] (100 MHz, [D]chloroform).



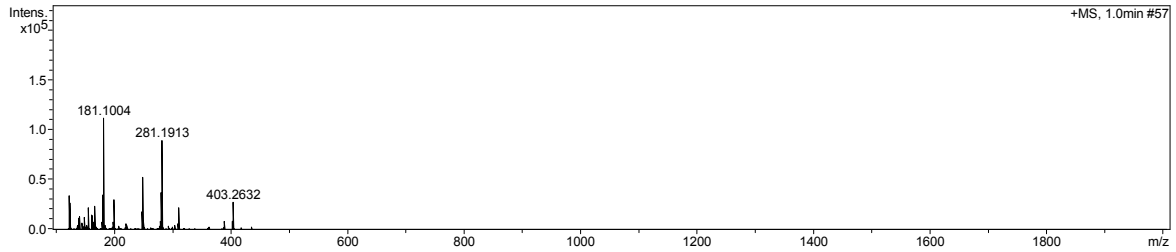
Mass Spectrum SmartFormula Report

Analysis Info

Analysis Name	D:\Data\HiranoLab\SMD0605-1.d	Acquisition Date	7/18/2019 11:13:54 AM
Method	apci_pos_wide_low_140605.m	Operator	BDAL
Sample Name	SMD0605-1	Instrument / Ser#	micrOTOF-Q II 10323
Comment			

Acquisition Parameter

Source Type	APCI	Ion Polarity	Positive	Set Nebulizer	1.6 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	100 m/z	Set End Plate Offset	-500 V	Set Dry Gas	3.0 l/min
Scan End	2000 m/z	Set Collision Cell RF	150.0 Vpp	Set Divert Valve	Waste



Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e¯ Conf	N-Rule
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	2	C 15 H 2 B 7	0.00	259.0806	1.5	6.0	540.6	18.5	even	ok
281.1913	1	C 15 H 26 B O 4	100.00	281.1921	0.9	3.1	89.5	3.5	even	ok
	2	C 15 H 18 B 5 N 2	0.00	281.1934	2.1	7.5	270.3	10.5	even	ok

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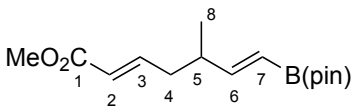
Figure S63. HRMS (APCI) spectrum of methyl (2*E*,6*E*)-5-methyl-7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hepta-2,6-dienoate [(2*E*,6*E*)-**7e**].



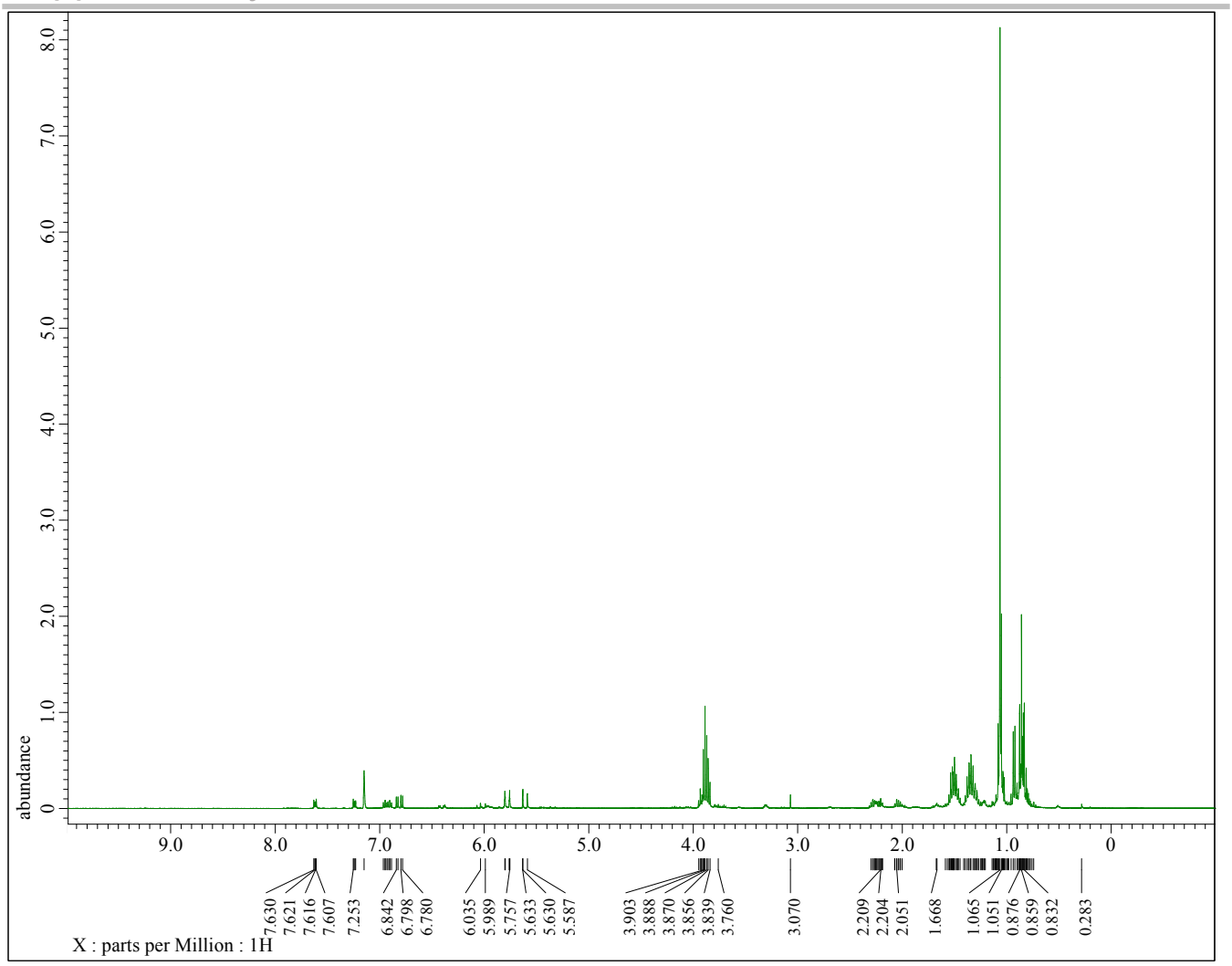
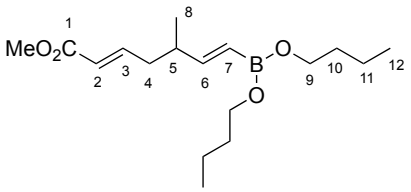


Figure S64. ^{1}H NMR spectrum of methyl (2*E*,6*E*)- 7-(dibutoxyboraneyl)-5-methylhepta-2,6-dienoate [(2*E*,6*E*)-**7f**] (an *in situ* reaction in an NMR tube) (400 MHz, [D_6]benzene).



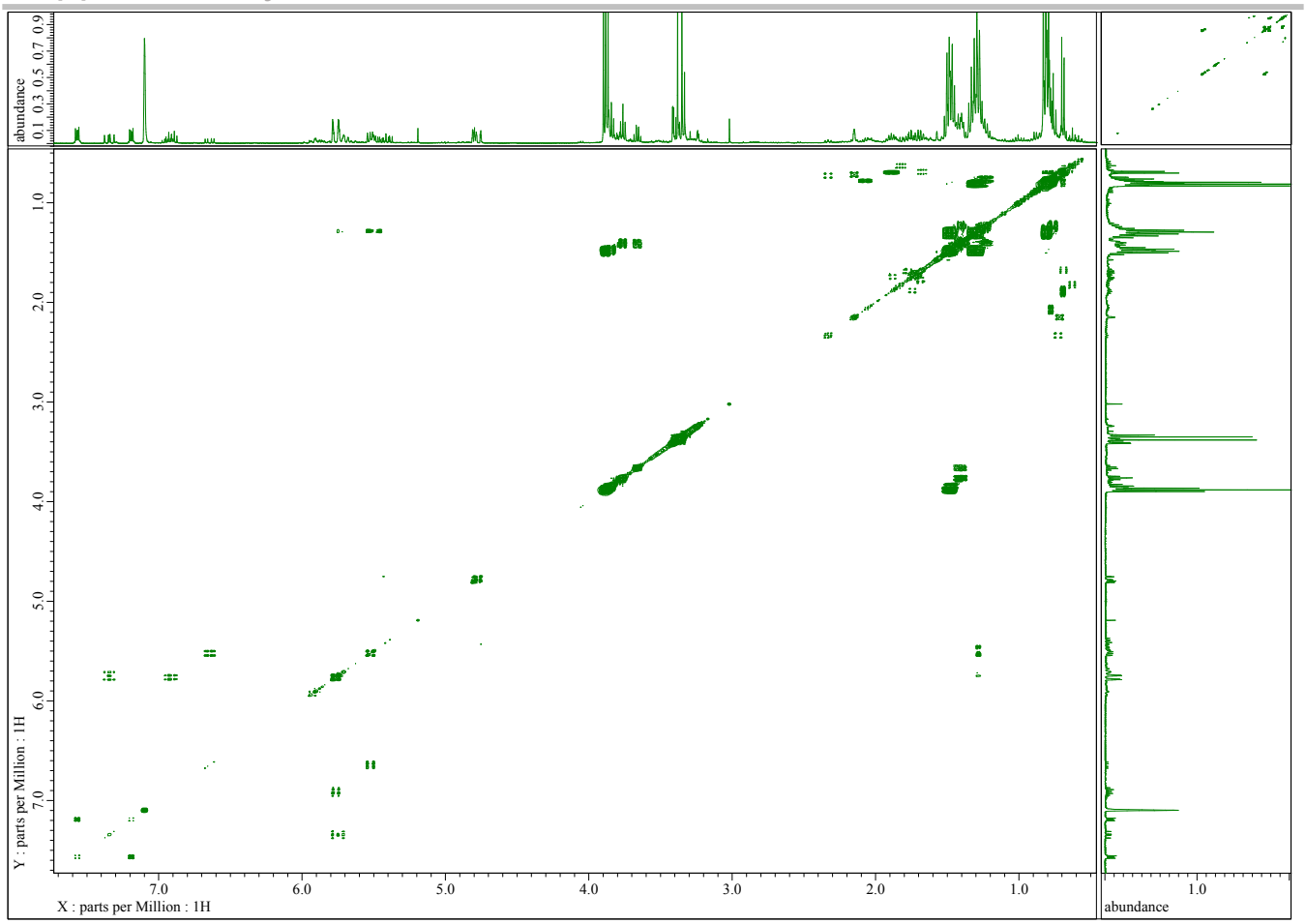
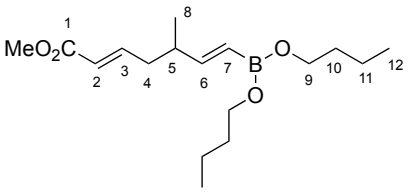


Figure S65. ^{1}H-^{1}H COSY of methyl (2*E*,6*E*)- 7-(dibutoxyboraneyl)-5-methylhepta-2,6-dienoate [(2*E*,6*E*)-**7f**] (an *in situ* reaction in an NMR tube) (400 MHz, [D_6]benzene).



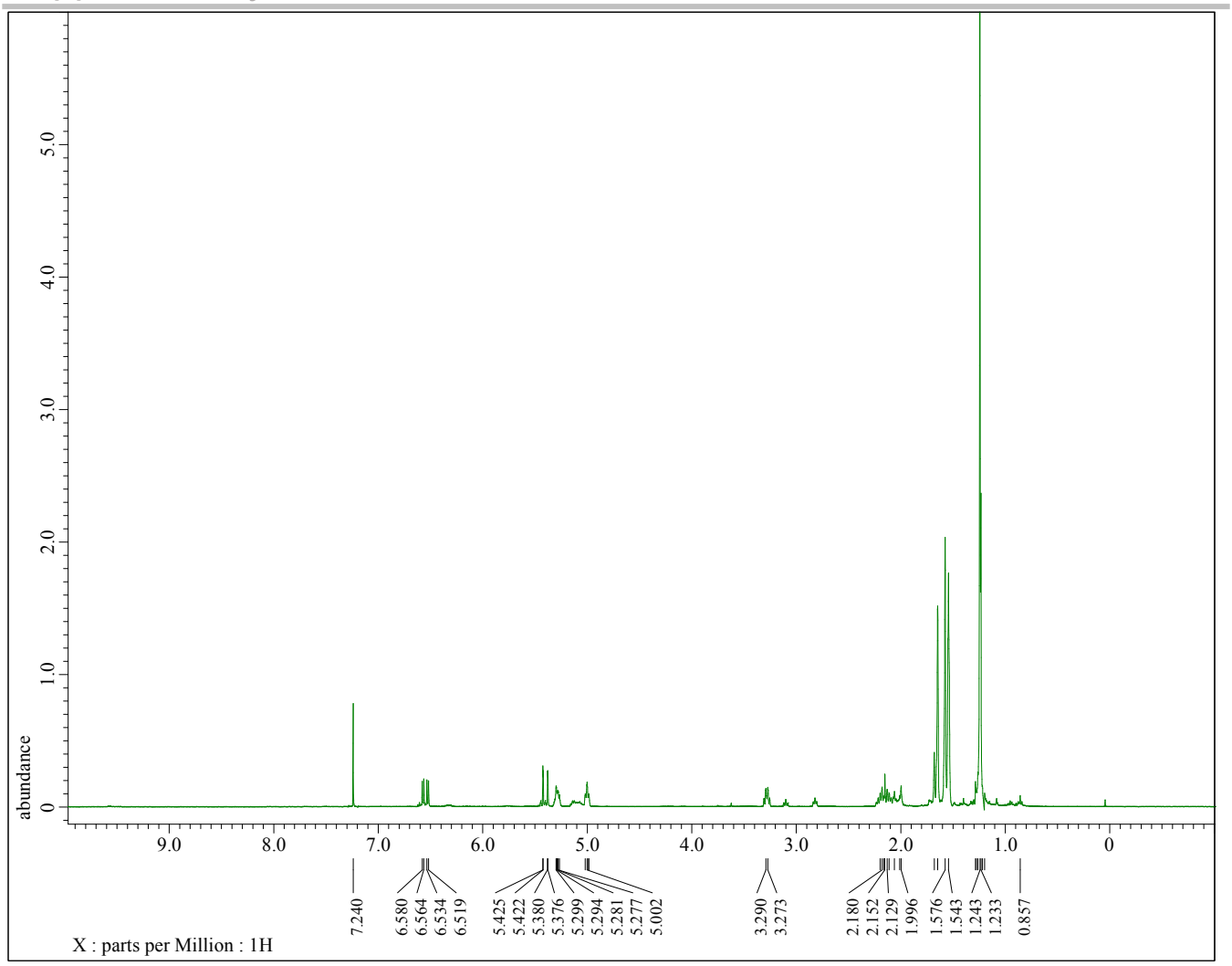
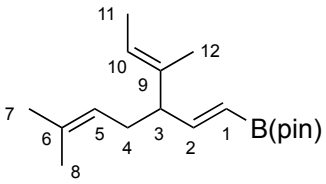


Figure S66. ^{1}H NMR spectrum of (*E*)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-{(*E*)-but-2-en-2-yl}-6-methylhepta-1,5-diene [(*E*)-**7g**] (400 MHz, [D]chloroform).



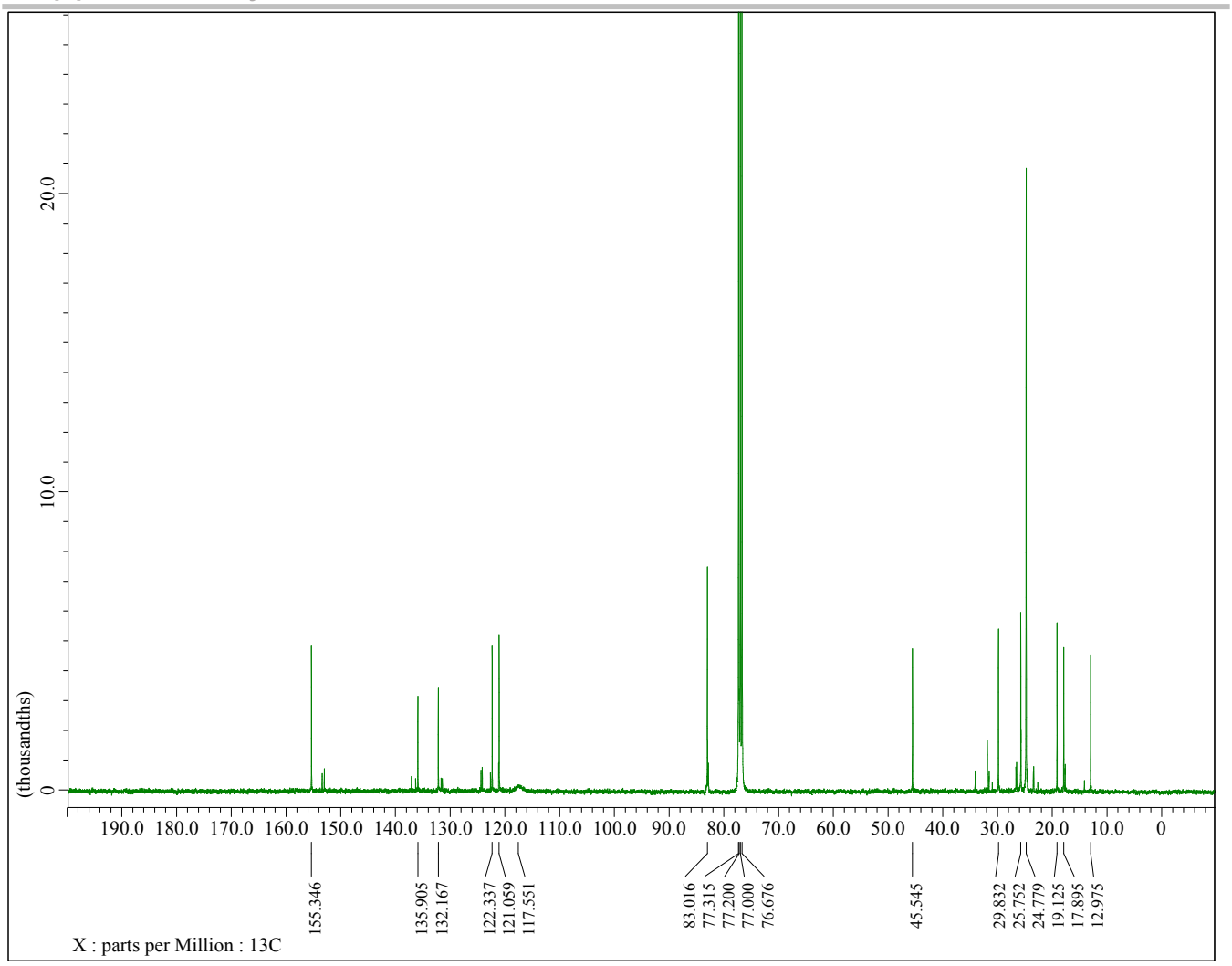
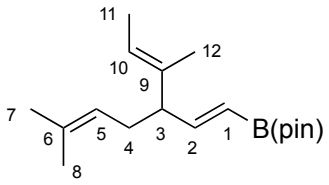


Figure S67. $^{13}C\{^{1}H\}$ NMR spectrum of (*E*)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-{(*E*)-but-2-en-2-yl}-6-methylhepta-1,5-diene [(*E*)-**7g**] (100 MHz, [D]chloroform).



Mass Spectrum SmartFormula Report

Analysis Info

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Method	apci_pos_wide_low_140605.m	Operator	BDAL
Sample Name	SMD0541-1	Instrument / Ser#	micrOTOF-Q II 10323
Comment			

Acquisition Parameter

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Focus	Not active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	100 m/z	Set End Plate Offset	-500 V	Set Dry Gas	3.0 l/min
Scan End	2000 m/z	Set Collision Cell RF	150.0 Vpp	Set Divert Valve	Waste

Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e¯ Conf	N-Rule
291.2494	1	C 18 H 32 B O 2	100.00	291.2493	-0.1	-0.3	216.1	3.5	even	ok

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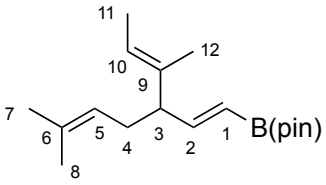
Figure S68. HRMS (APCI) spectrum of (*E*)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-{(*E*)-but-2-en-2-yl}-6-methylhepta-1,5-diene [(*E*)-**7g**].



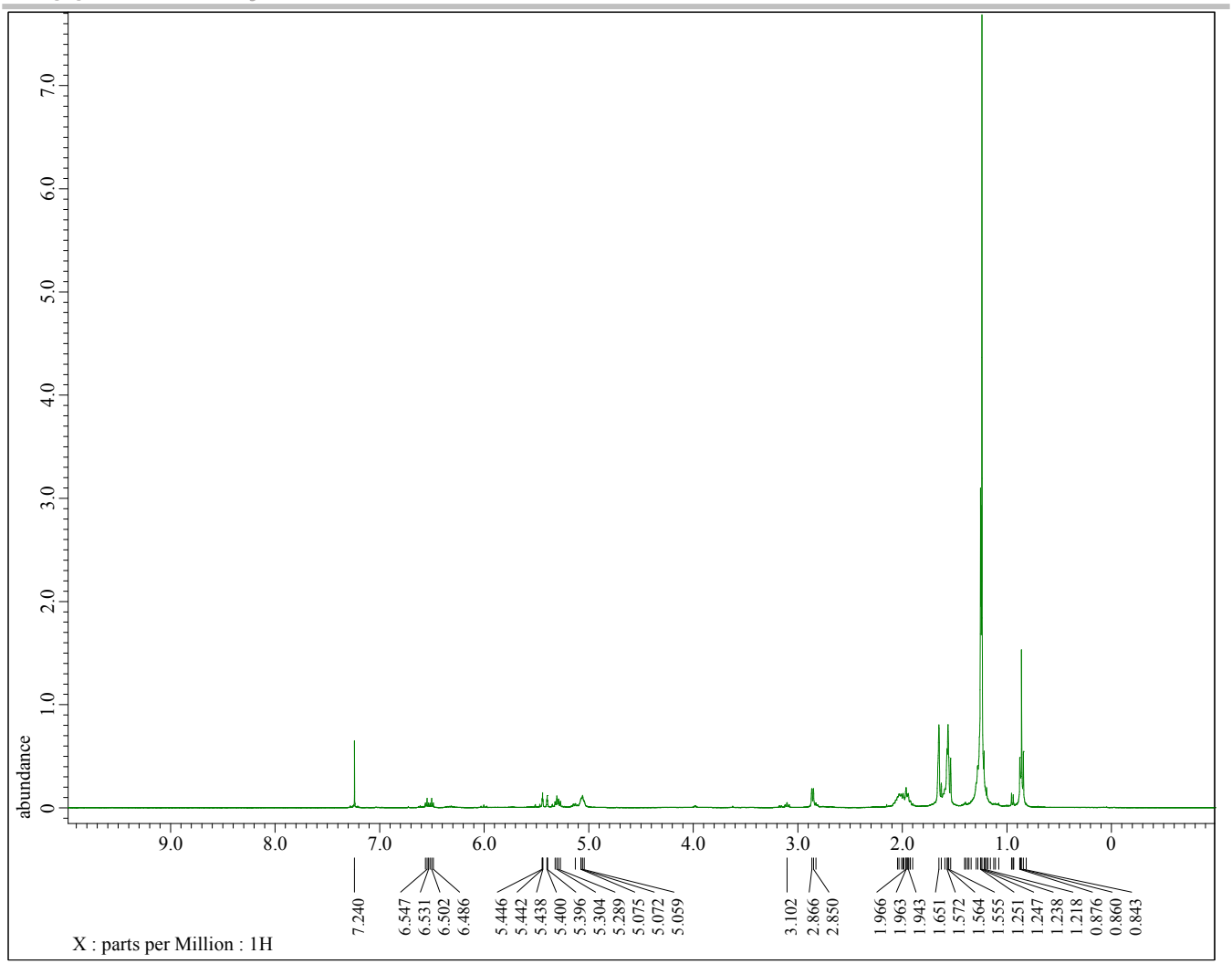
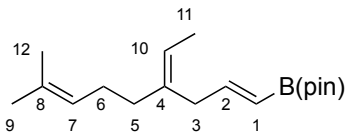


Figure S69. ^{1}H NMR spectrum of (1*E*,4*Z*)-4-ethylidenyl-8-methyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)nona-1,7-diene [(1*E*,4*Z*)-**7h**] (400 MHz, [D]chloroform).



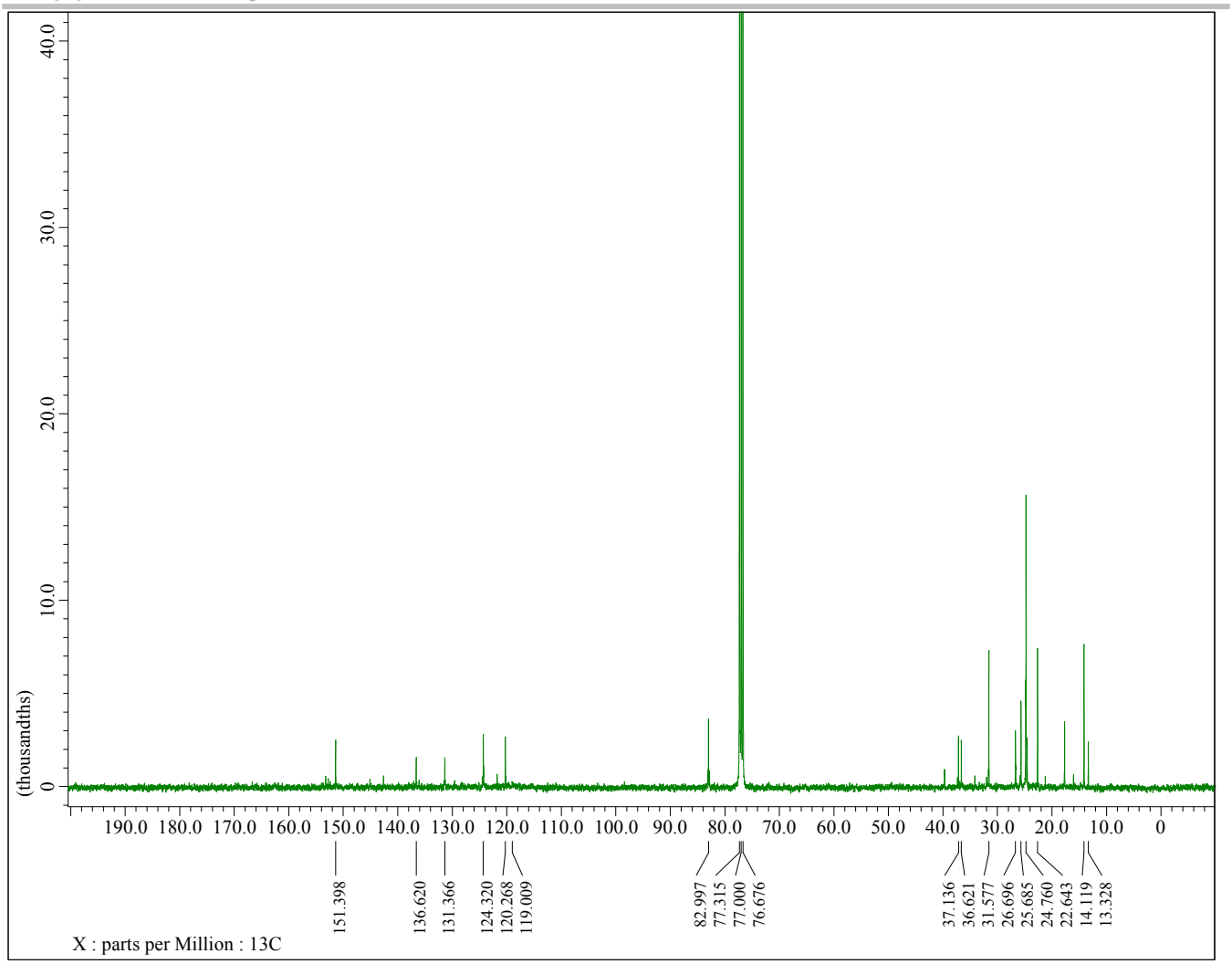
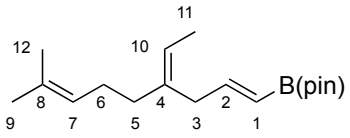


Figure S70. $^{13}C\{^{1}H\}$ NMR spectrum of (1*E*,4*Z*)-4-ethylidenyl-8-methyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)nona-1,7-diene [(1*E*,4*Z*)-**7h**] (100 MHz, [D]chloroform).



Mass Spectrum SmartFormula Report

Analysis Info

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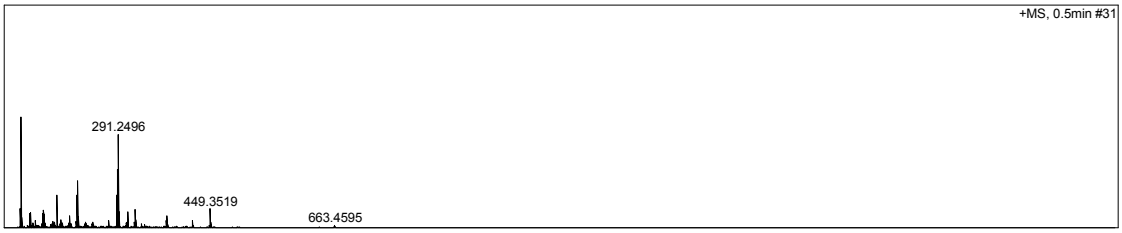
Method	apci_pos_wide_low_140605.m	Operator	BDAL
Sample Name	SMD0533-2	Instrument / Ser#	micrOTOF-Q II 10323
Comment			

Acquisition Parameter

Source Type	APCI	Ion Polarity	Positive	Set Nebulizer	1.6 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	100 m/z	Set End Plate Offset	-500 V	Set Dry Gas	3.0 l/min
Scan End	2000 m/z	Set Collision Cell RF	150.0 Vpp	Set Divert Valve	Waste



Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e¯ Conf	N-Rule
291.2496	1	C 18 H 32 B O 2	100.00	291.2493	-0.2	-0.8	193.1	3.5	even	ok

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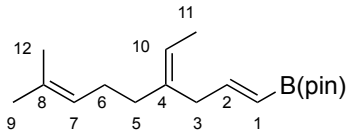
Figure S71. HRMS (APCI) spectrum of (1*E*,4*Z*)-4-ethylidenyl-8-methyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)nona-1,7-diene [(1*E*,4*Z*)-**7h**].



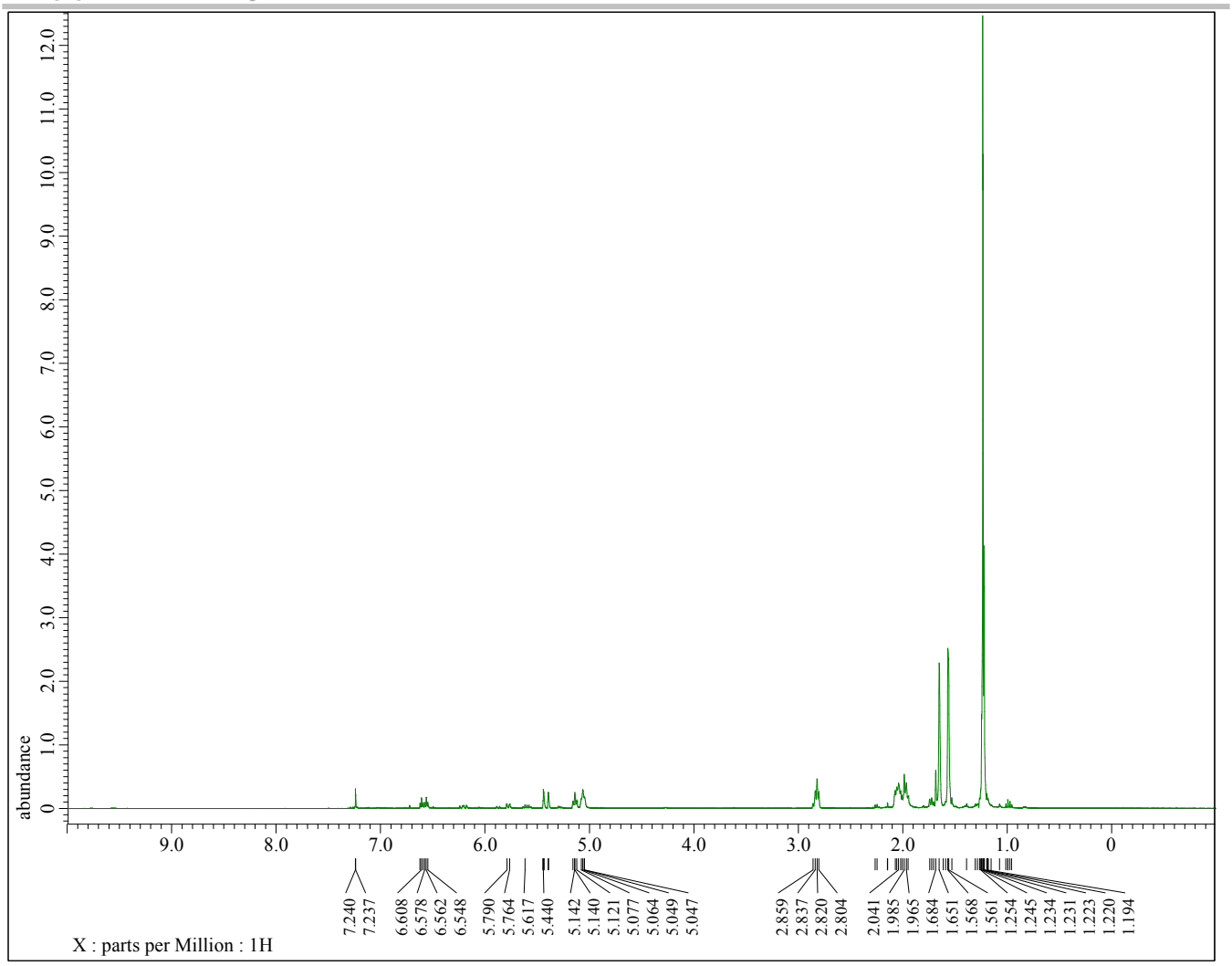
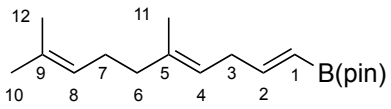


Figure S72. ^{1}H NMR spectrum of (1*E*,4*E*)-5,9-dimethyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)deca-1,4,8-triene [(1*E*,4*E*)-**8h**] (400 MHz, [D]chloroform).



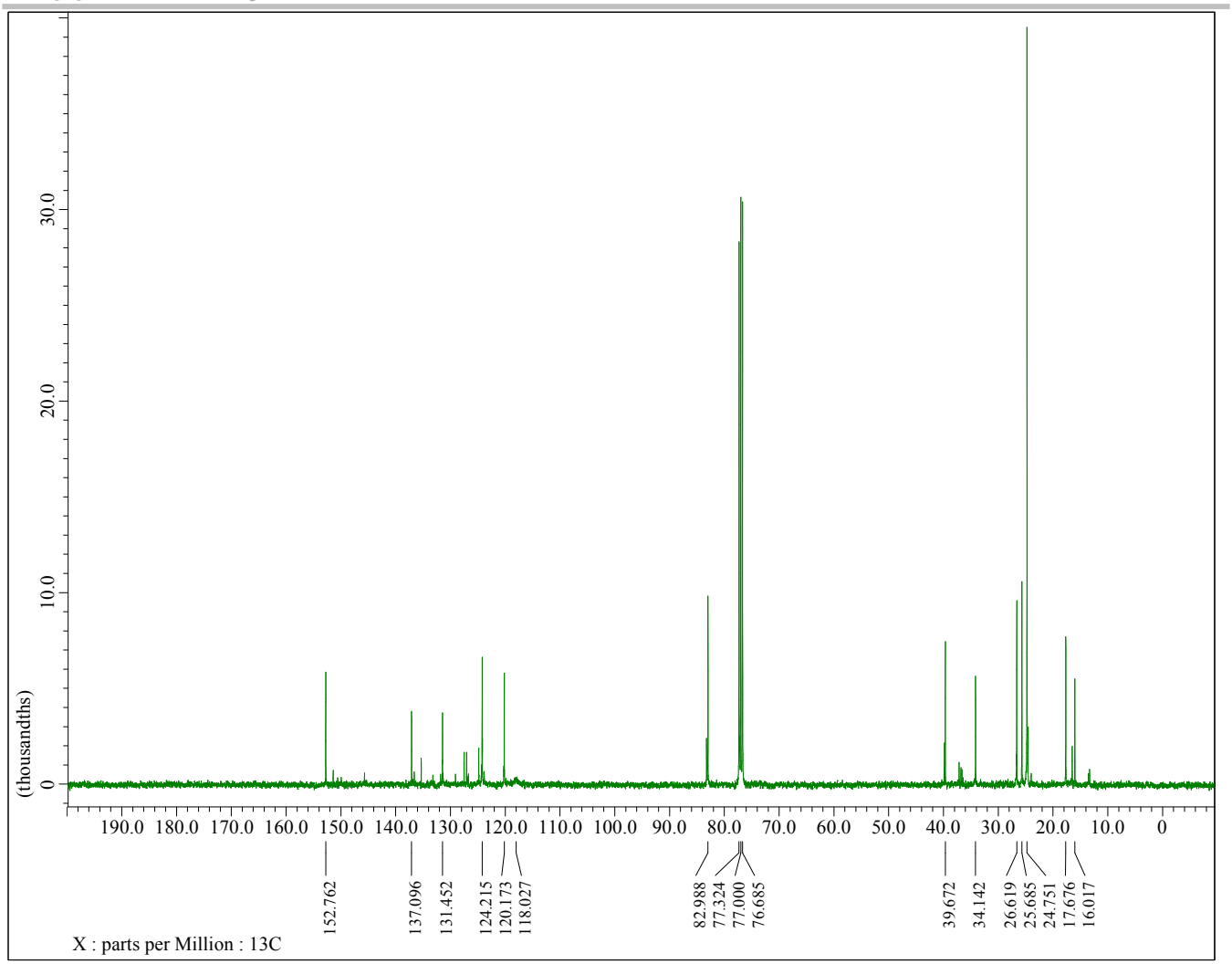
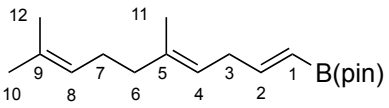


Figure S73. $^{13}C\{^{1}H\}$ NMR spectrum of (1*E*,4*E*)-5,9-dimethyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)deca-1,4,8-triene [(1*E*,4*E*)-**8h**] (100 MHz, [D]chloroform).



Mass Spectrum SmartFormula Report

Analysis Info

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Sample Name	SMD0623-1	Instrument / Ser#	micrOTOF-Q II 10323
Comment			

Acquisition Parameter

Source Type	APCI	Ion Polarity	Positive	Set Nebulizer	1.6 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	200 °C
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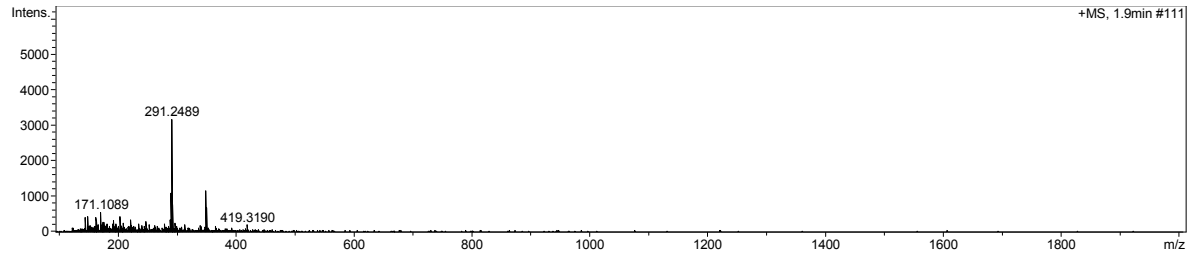
Scan End	2000 m/z	Set Collision Cell RF	150.0 Vpp	Set Divert Valve	Waste



Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e¯ Conf	N-Rule
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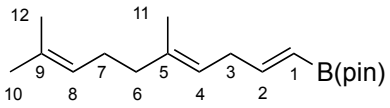
Figure S74. HRMS (APCI) spectrum of (1*E*,4*E*)-5,9-dimethyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)deca-1,4,8-triene [(1*E*,4*E*)-**8h**].



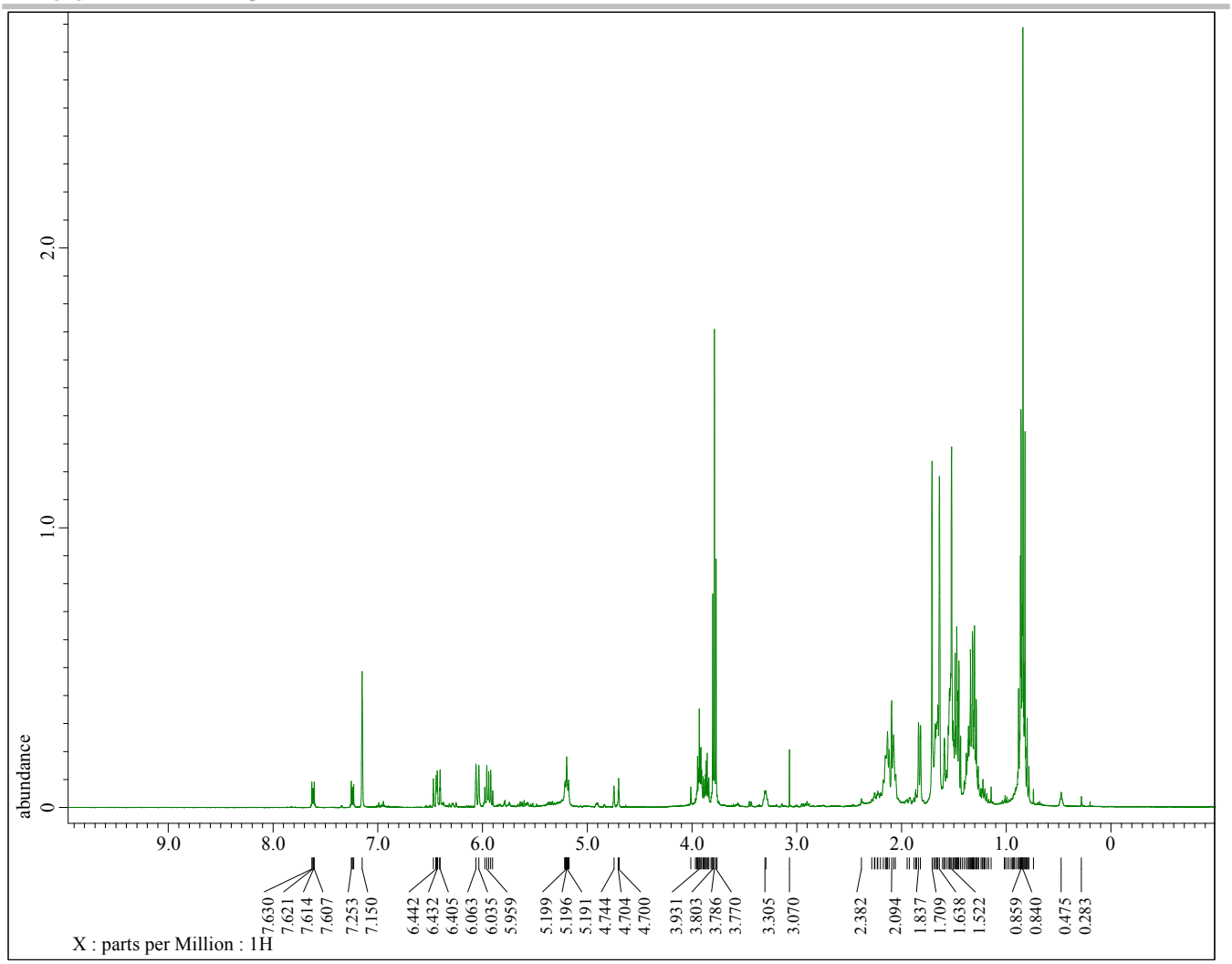
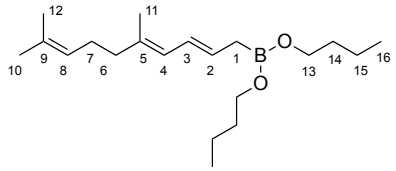


Figure S75. ^{1}H NMR spectrum of (1*E*,4*E*)- 1-(dibotoxyboraneyl)-5,9-dimethyldeca-1,4,8-triene [(1*E*,4*E*)-**8i**] (an *in situ* reaction in an NMR tube) (400 MHz, [D]chloroform).



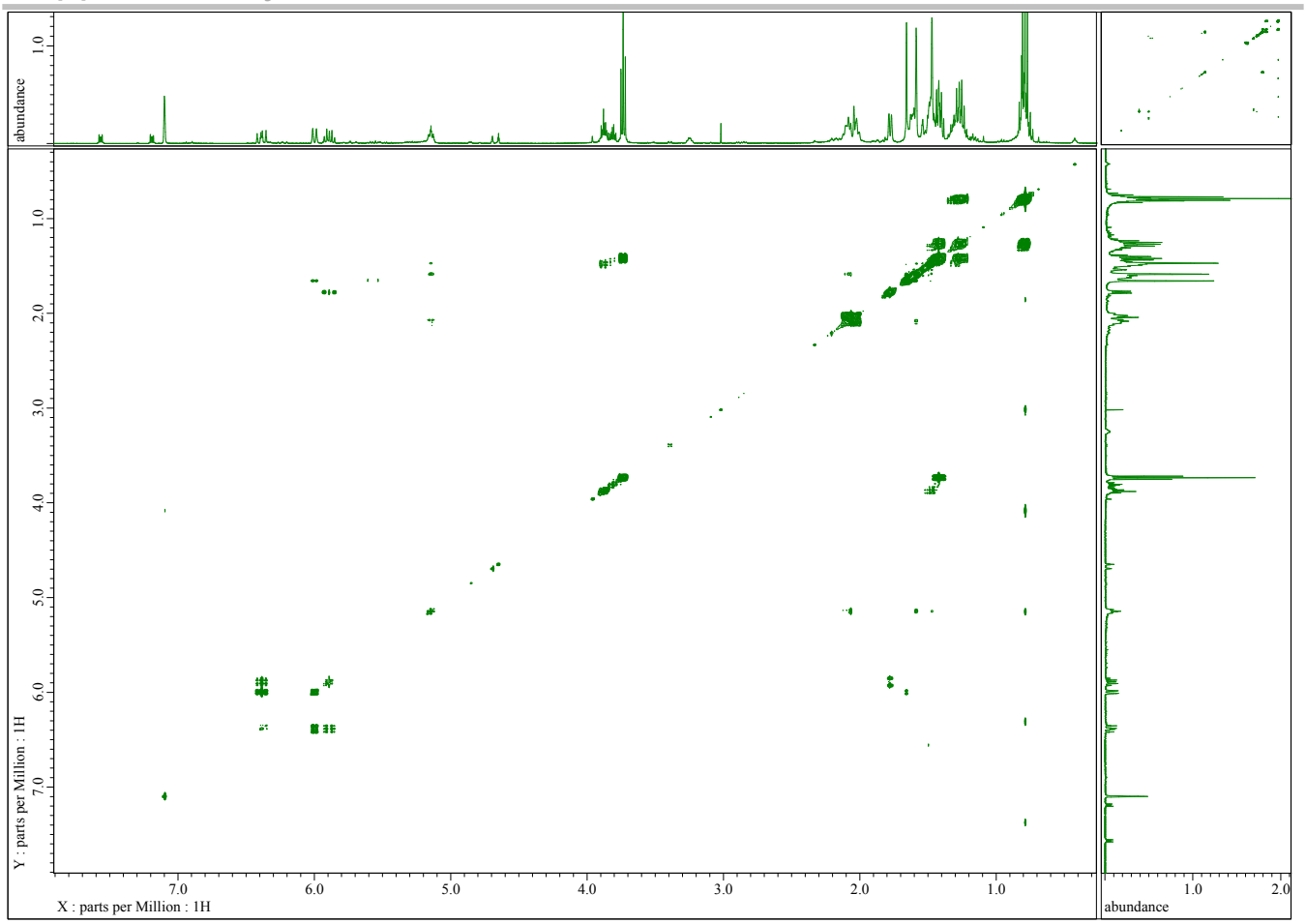
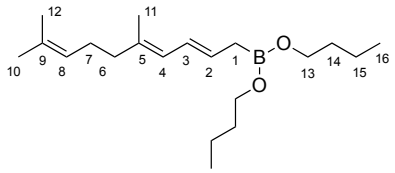


Figure S76. ^{1}H-^{1}H COSY of (1*E*,4*E*)- 1-(dibotoxyboraneyl)-5,9-dimethyldeca-1,4,8-triene [(1*E*,4*E*)-**8i**] (an *in situ* reaction in an NMR tube) (400 MHz, [D]chloroform).



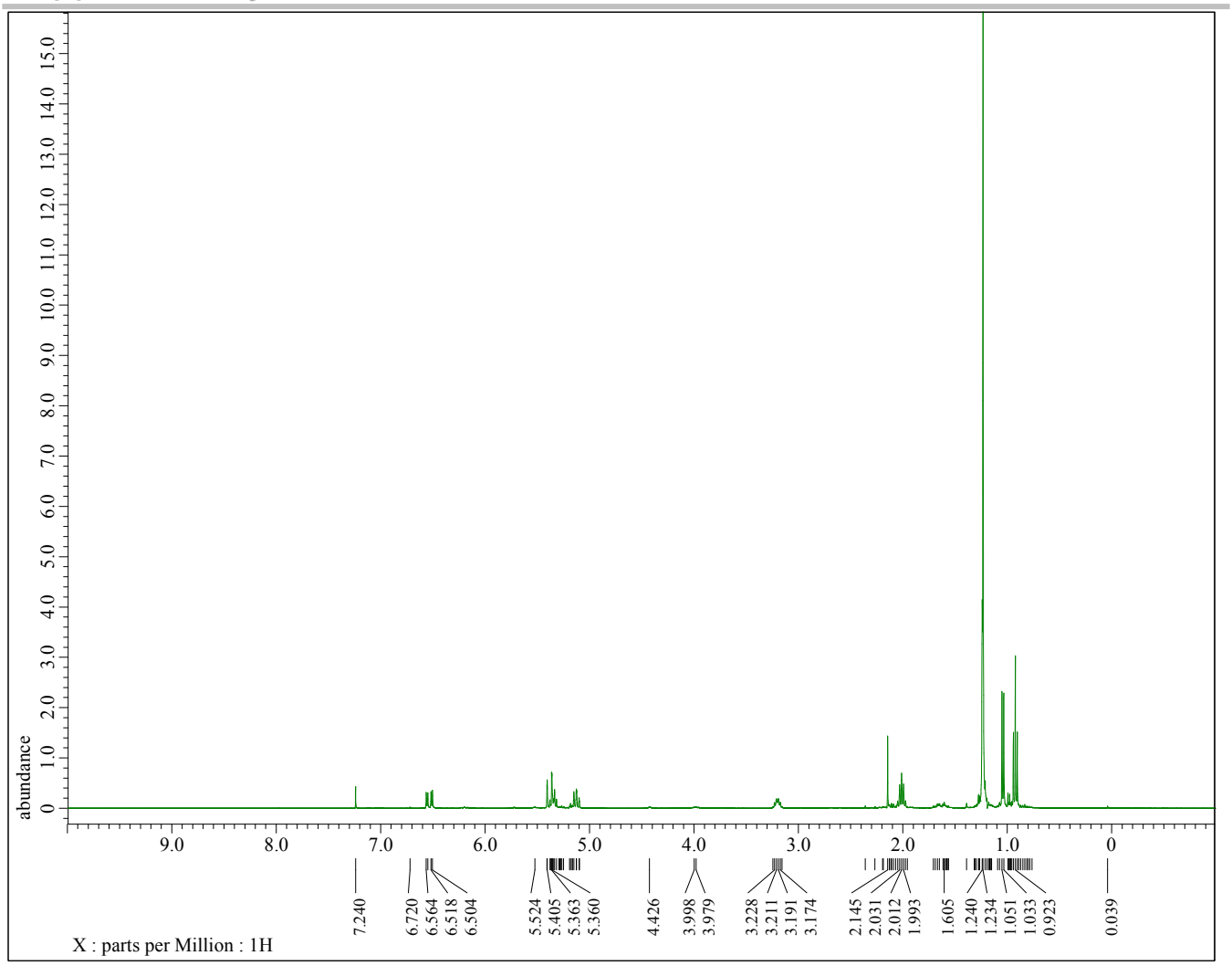
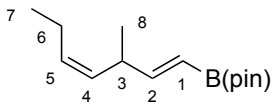


Figure S77. ^{1}H NMR spectrum of (1*E*,4*Z*)-3-methyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hepta-1,4-diene [(1*E*,4*Z*)-**7j**] (400 MHz, [D]chloroform).



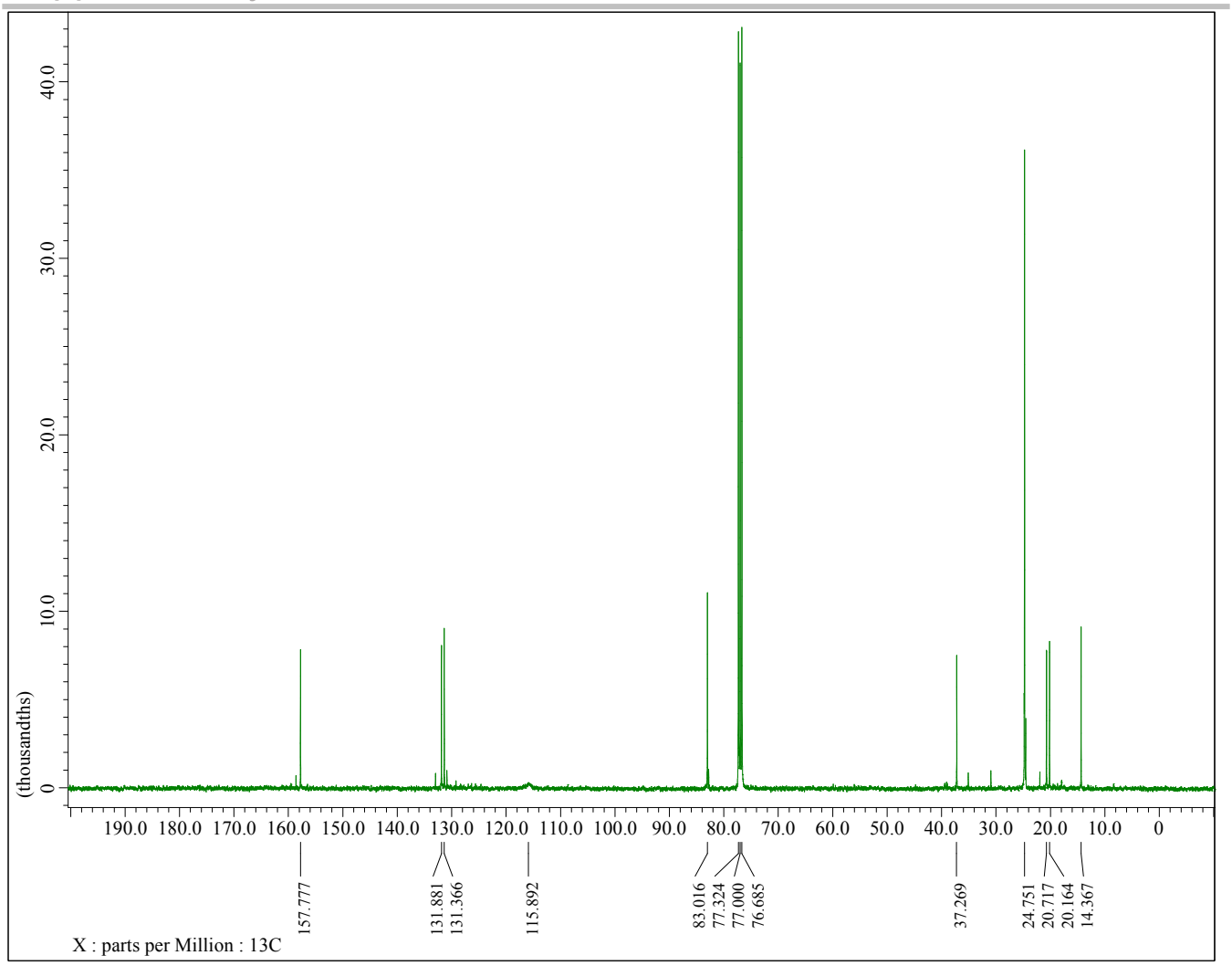
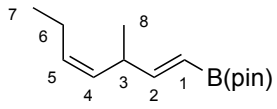


Figure S78. $^{13}C\{^{1}H\}$ NMR spectrum of (1*E*,4*Z*)-3-methyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hepta-1,4-diene [(1*E*,4*Z*)-**7j**] (100 MHz, [D]chloroform).



Mass Spectrum SmartFormula Report

Analysis Info

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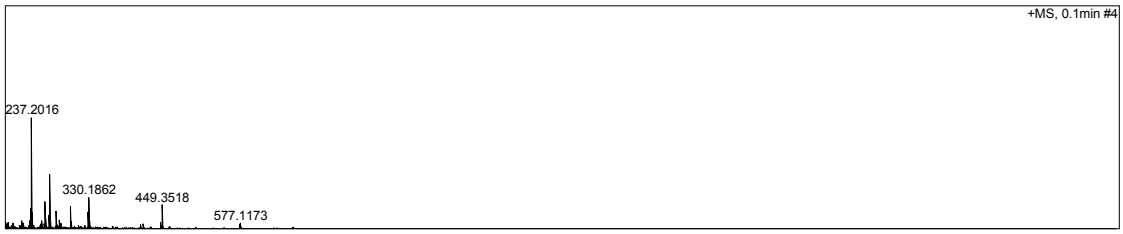
Sample Name	SMD0479	Instrument / Ser#	micrOTOF-Q II 10323
Comment			

Acquisition Parameter

Source Type	APCI	Ion Polarity	Positive	Set Nebulizer	1.6 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	200 m/z	Set End Plate Offset	-500 V	Set Dry Gas	3.0 l/min
Scan End	2000 m/z	Set Collision Cell RF	150.0 Vpp	Set Divert Valve	Waste



Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e¯ Conf	N-Rule
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	2	C 14 H 26 B O 2	100.00	237.2023	0.7	2.7	170.3	2.5	even	ok

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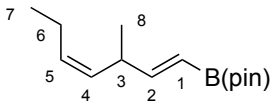
Figure S79. HRMS (APCI) spectrum of (1*E*,4*Z*)-3-methyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hepta-1,4-diene [(1*E*,4*Z*)-**7j**].



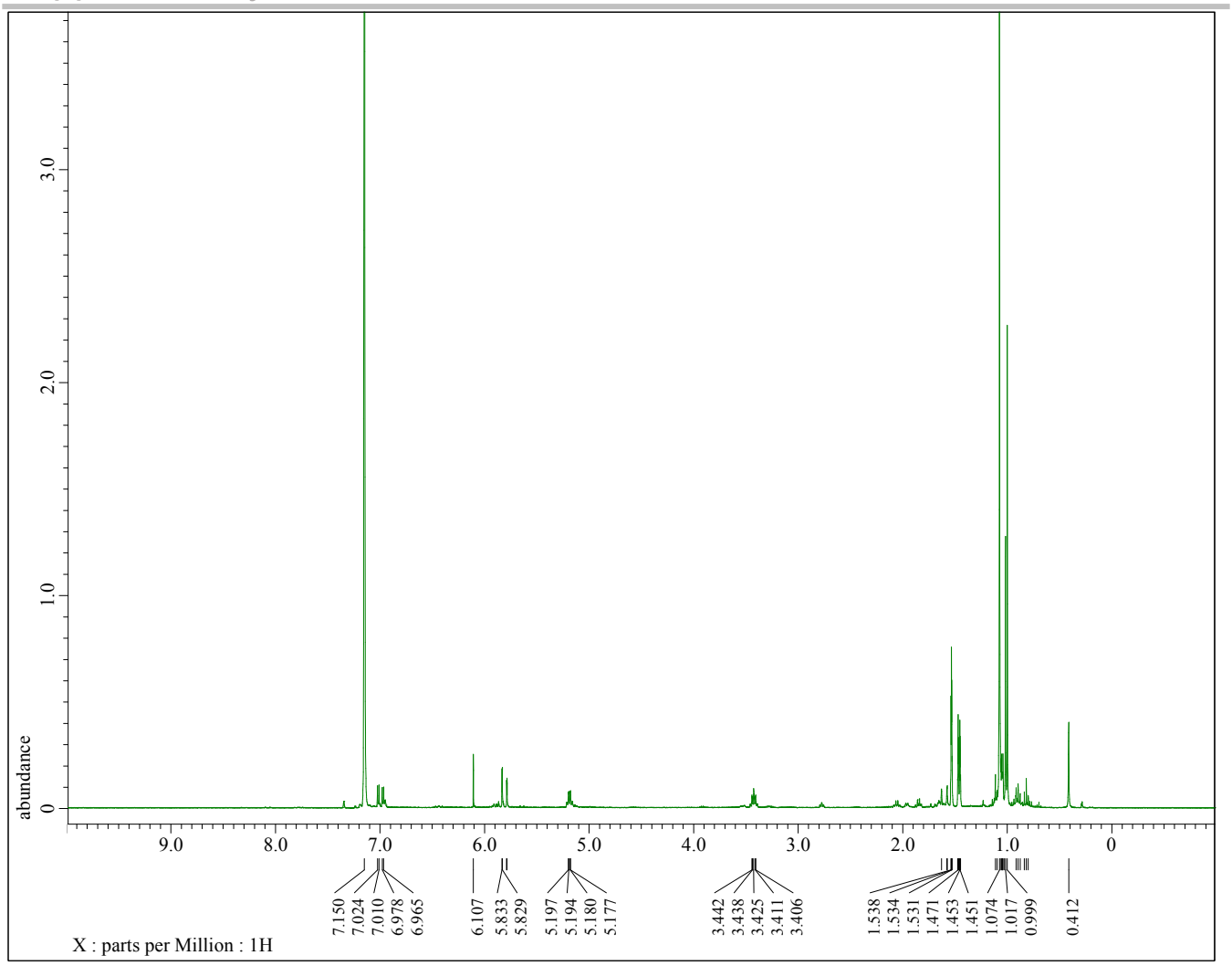
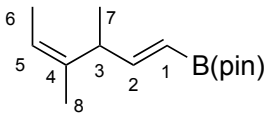


Figure S80. ^{1}H NMR spectrum of (1*E*,4*Z*)-3,8-dimethyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexa-1,4-diene [(1*E*,4*Z*)-**7k**] (400 MHz, [D_6]benzene).



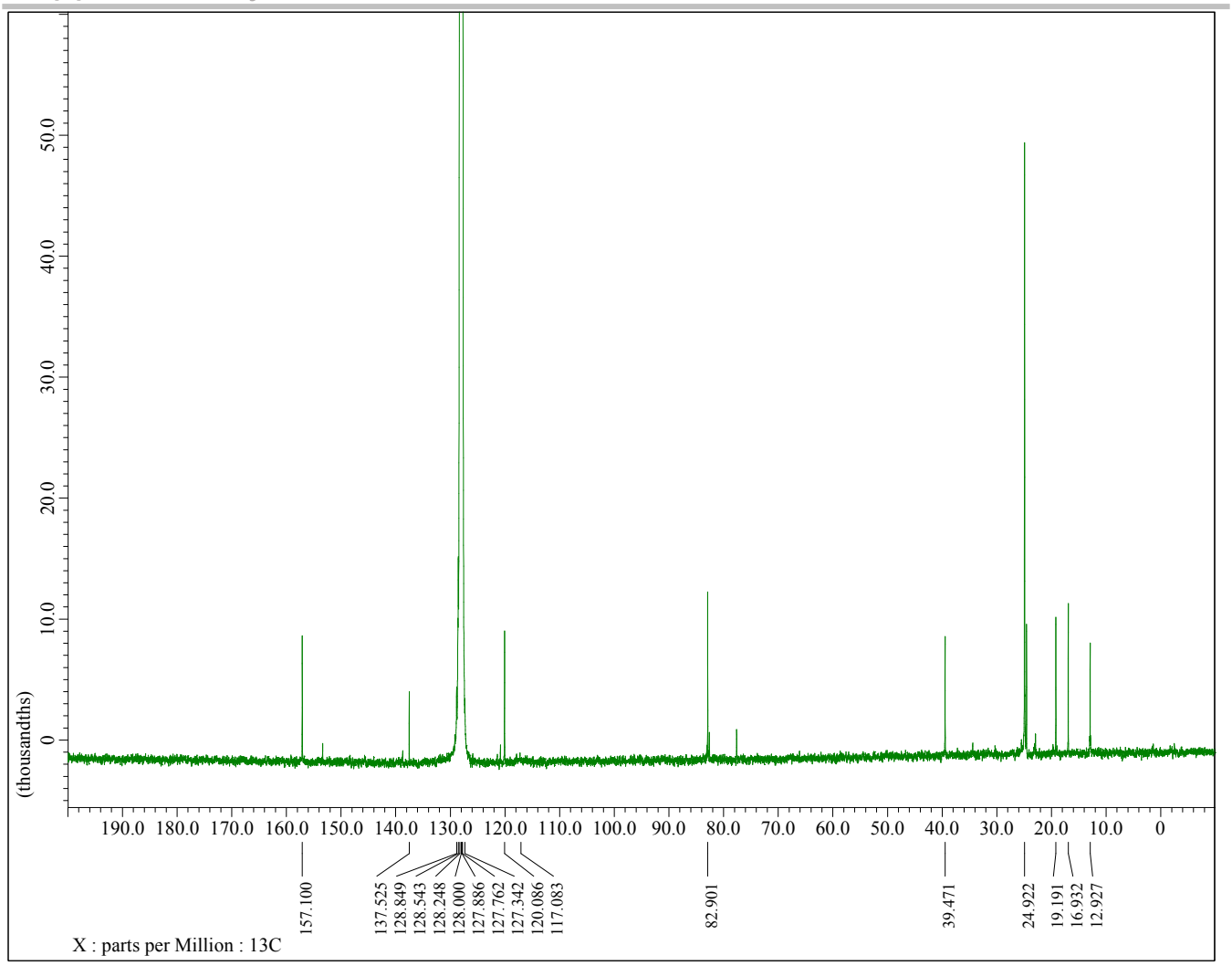
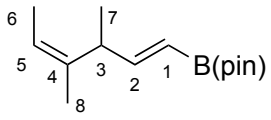


Figure S81. $^{13}C\{^{1}H\}$ NMR spectrum of (1*E*,4*Z*)-3,8-dimethyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexa-1,4-diene [(1*E*,4*Z*)-**7k**] (100 MHz, $[D_6]$benzene).



Mass Spectrum SmartFormula Report

Analysis Info

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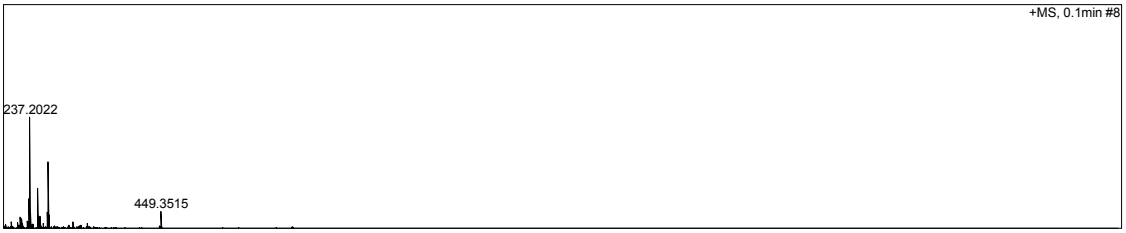
Sample Name	SMD0487	Instrument / Ser#	micrOTOF-Q II 10323
Comment			

Acquisition Parameter

Source Type	APCI	Ion Polarity	Positive	Set Nebulizer	1.6 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	200 m/z	Set End Plate Offset	-500 V	Set Dry Gas	3.0 l/min
Scan End	2000 m/z	Set Collision Cell RF	150.0 Vpp	Set Divert Valve	Waste



Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e¯ Conf	N-Rule
237.2022	1	C 10 H 22 B N 6	20.20	237.1995	-2.6	-11.1	191.9	3.5	even	ok
	2	C 14 H 26 B O 2	100.00	237.2023	0.1	0.5	192.1	2.5	even	ok

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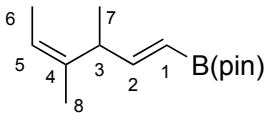
Figure S82. HRMS (APCI) spectrum of (1*E*,4*Z*)-3,8-dimethyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexa-1,4-diene [(1*E*,4*Z*)-**7k**].



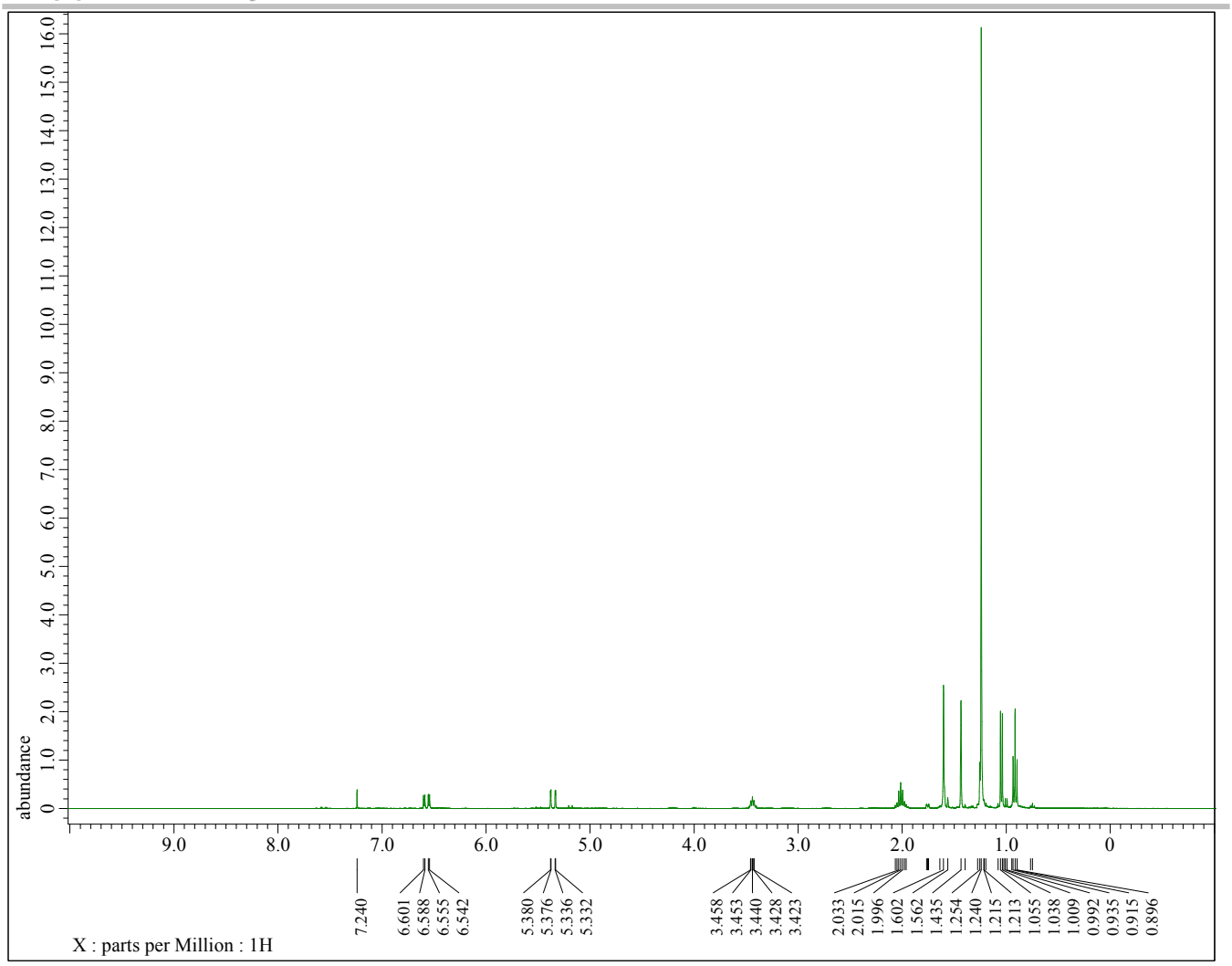
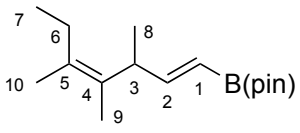


Figure S83. ^{1}H NMR spectrum of (1*E*,4*Z*)-3,4,5-trimethyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hepta-1,4-diene [(1*E*,4*Z*)-**7l**] (400 MHz, [D]chloroform).



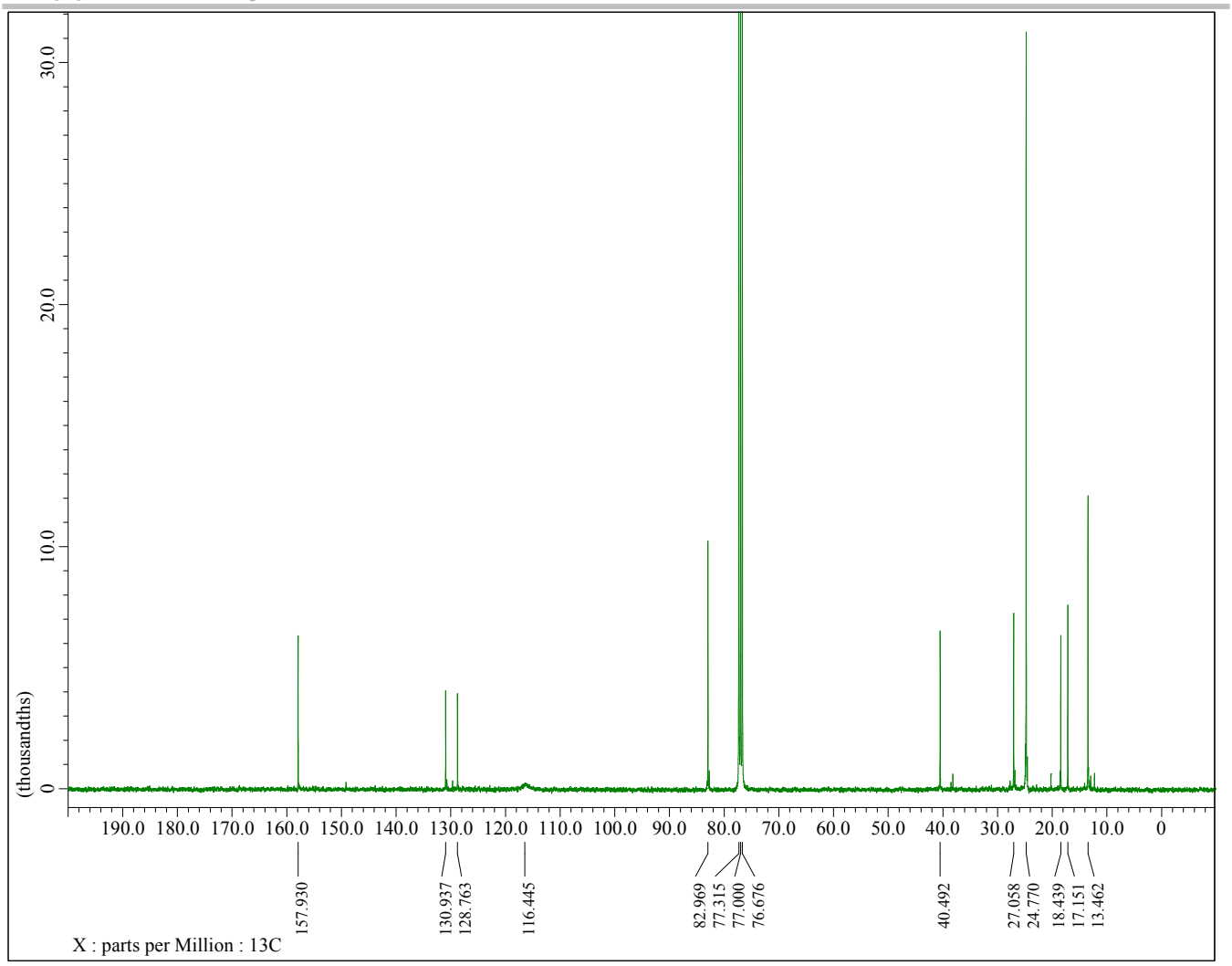
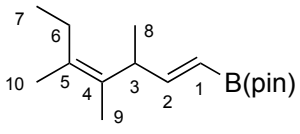


Figure S84. $^{13}C\{^{1}H\}$ NMR spectrum of (1*E*,4*Z*)-3,4,5-trimethyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hepta-1,4-diene [(1*E*,4*Z*)-**7l**] (100 MHz, [D]chloroform).



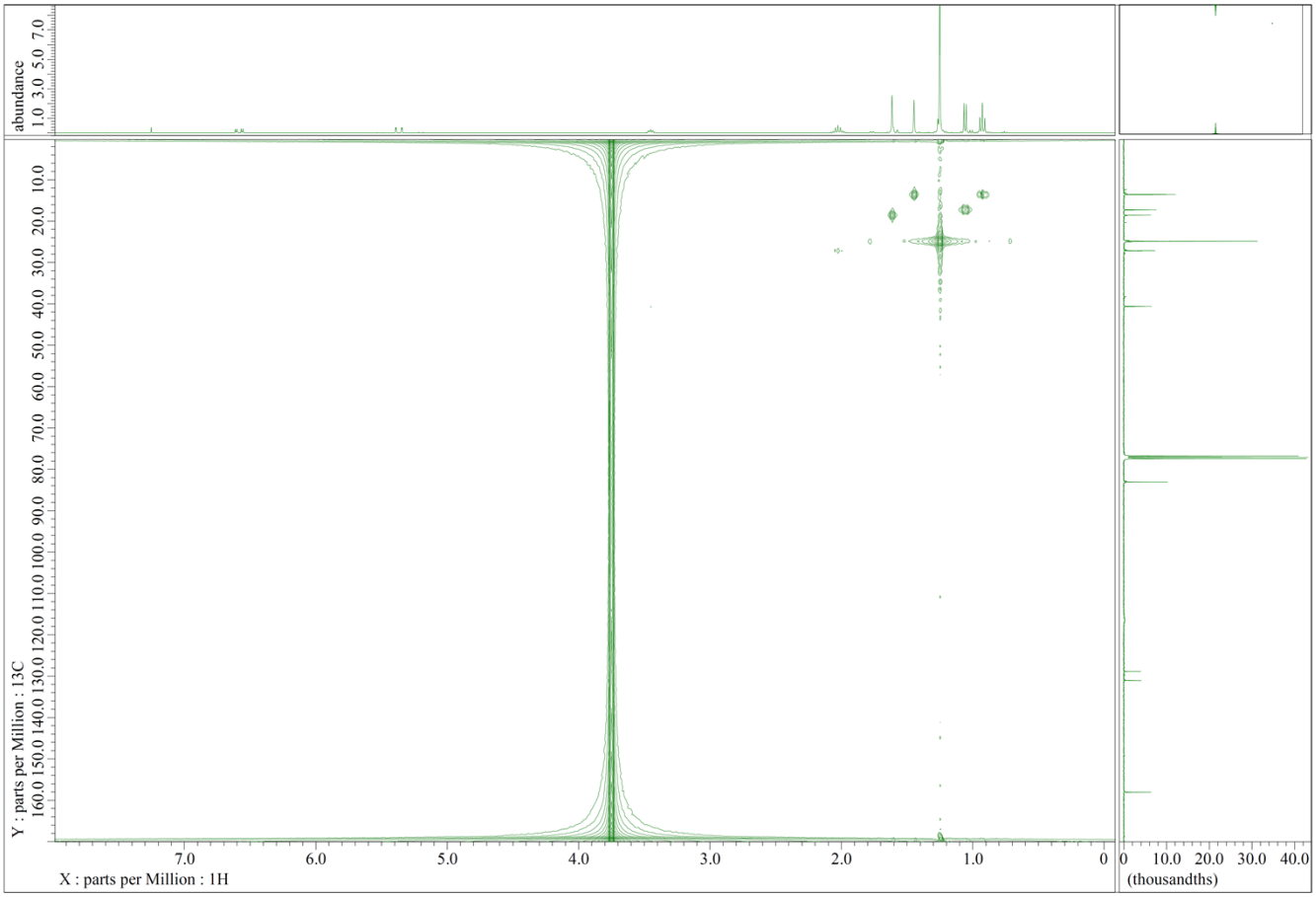
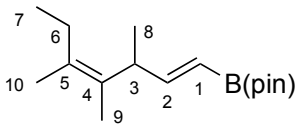


Figure S85. ^{1}H-^{13}C HMQC of (1*E*,4*Z*)-3,4,5-trimethyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hepta-1,4-diene [(1*E*,4*Z*)-**7l**] (400 MHz for ^{1}H, 100 MHz for ^{13}C, [D]chloroform).



Mass Spectrum SmartFormula Report

Analysis Info

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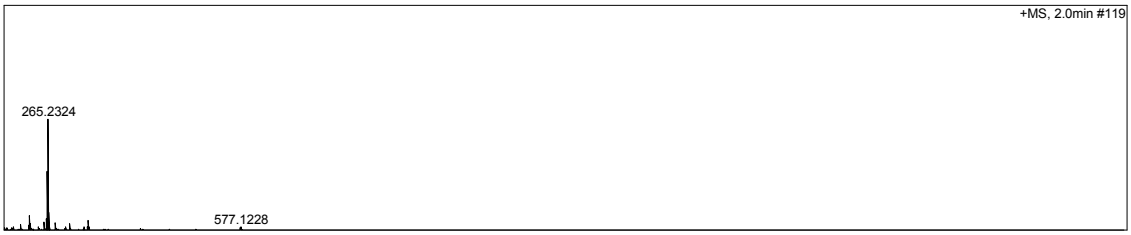
Method	apci_pos_wide_171018.m	Operator	BDAL
Sample Name	SMD0481	Instrument / Ser#	micrOTOF-Q II 10323
Comment			

Acquisition Parameter

Source Type	APCI	Ion Polarity	Positive	Set Nebulizer	1.6 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	200 m/z	Set End Plate Offset	-500 V	Set Dry Gas	3.0 l/min
Scan End	2000 m/z	Set Collision Cell RF	150.0 Vpp	Set Divert Valve	Waste



Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e¯ Conf	N-Rule
265.2324	1	C 12 H 26 B N 6	83.54	265.2309	-1.5	-5.8	144.8	3.5	even	ok
	2	C 16 H 30 B O 2	100.00	265.2336	1.2	4.6	145.2	2.5	even	ok

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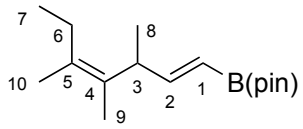
Figure S86. HRMS (APCI) spectrum of (1*E*,4*Z*)-3,4,5-trimethyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hepta-1,4-diene [(1*E*,4*Z*)-**7l**].



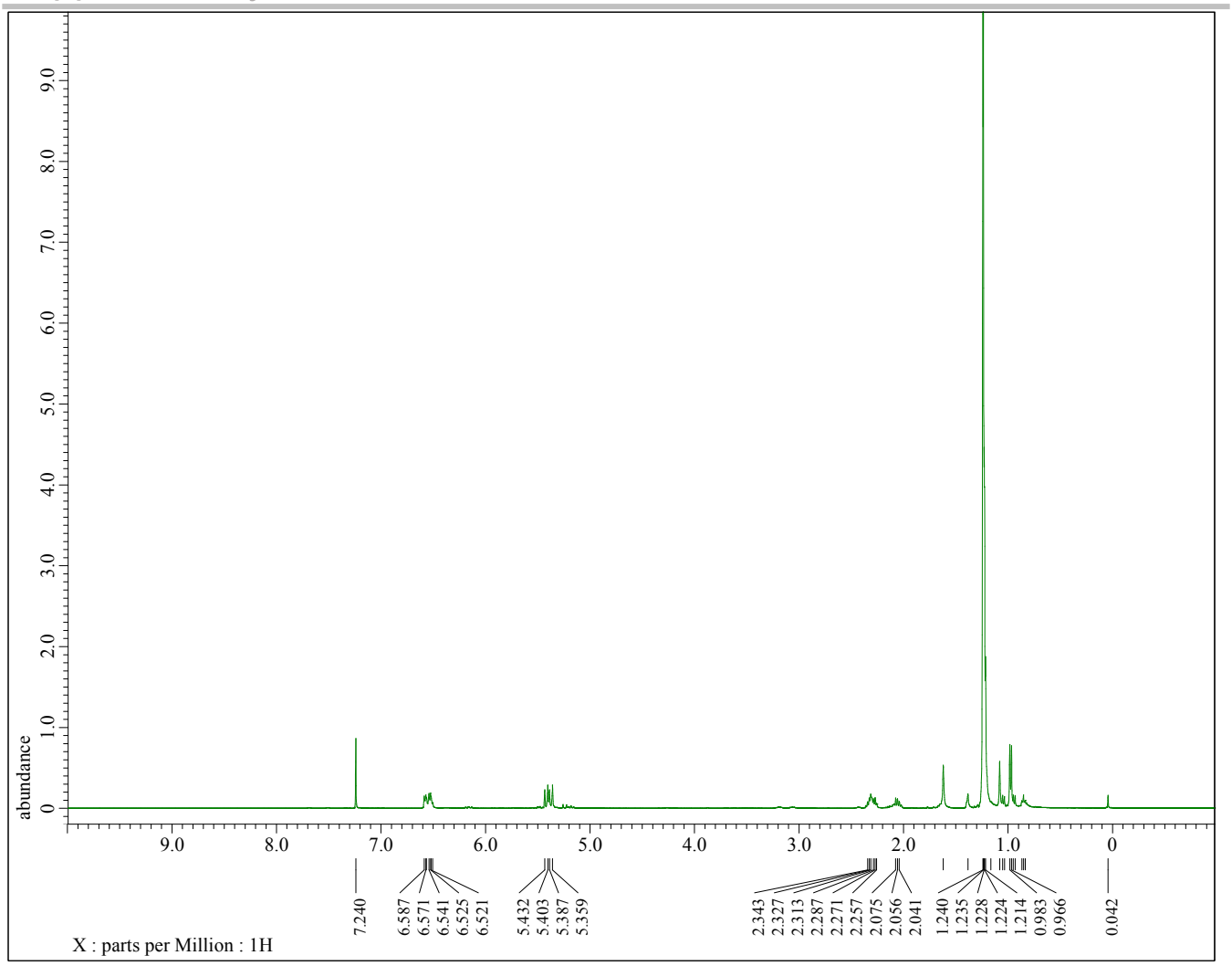
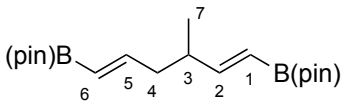


Figure S87. ^{1}H NMR spectrum of (1*E*,5*E*)-3-methyl-1,6-bis(4,4,5,5-tetramethyl-1,3,2-dioxaboloran-2-yl)hexa-1,5-diene [(1*E*,5*E*)-**7m**] (400 MHz, [D]chloroform).



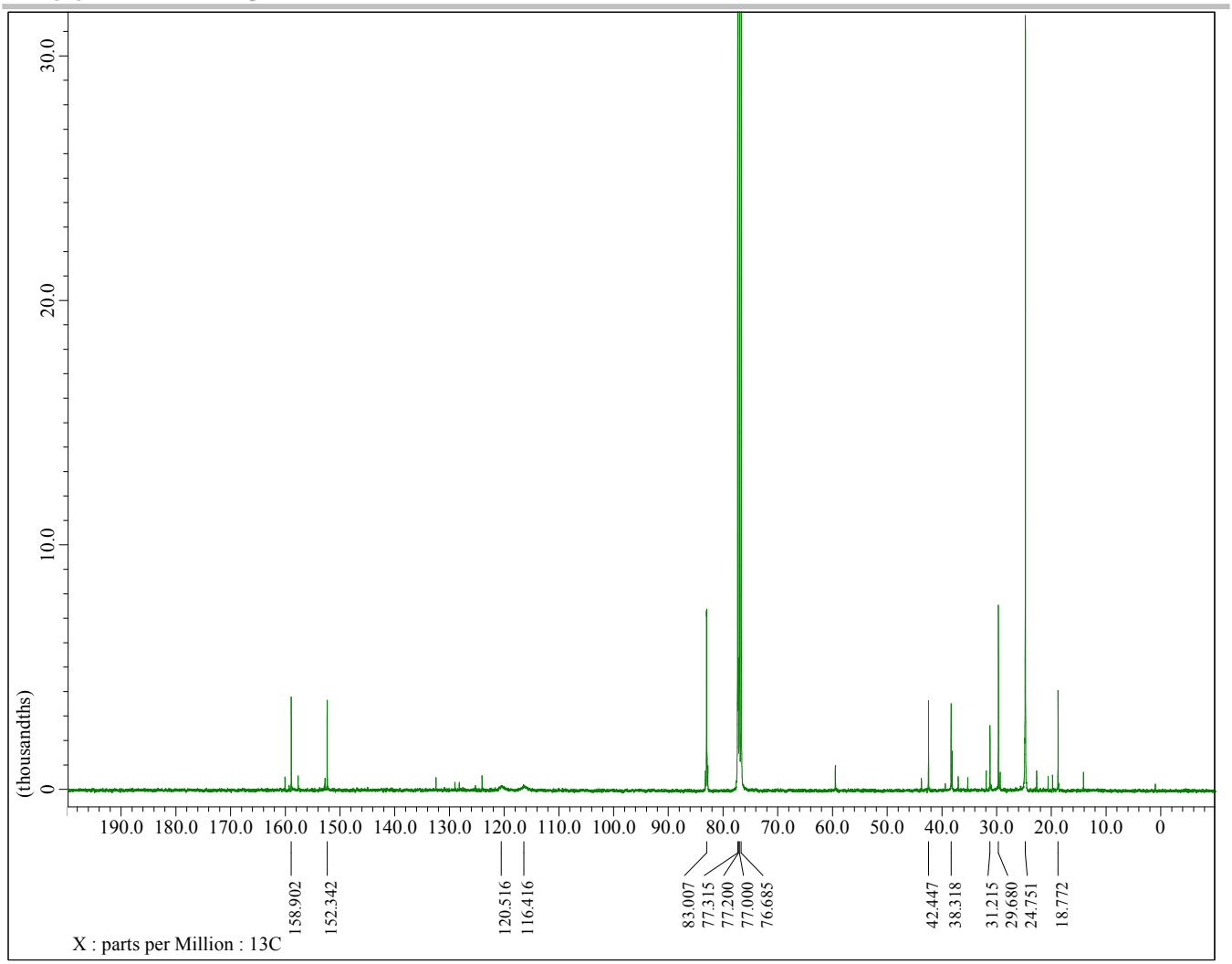
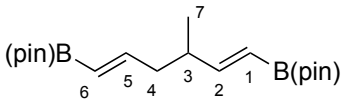


Figure S88. $^{13}C\{^{1}H\}$ NMR spectrum of (1*E*,5*E*)-3-methyl-1,6-bis(4,4,5,5-tetramethyl-1,3,2-dioxaboloran-2-yl)hexa-1,5-diene [(1*E*,5*E*)-**7m**] (100 MHz, [D]chloroform).



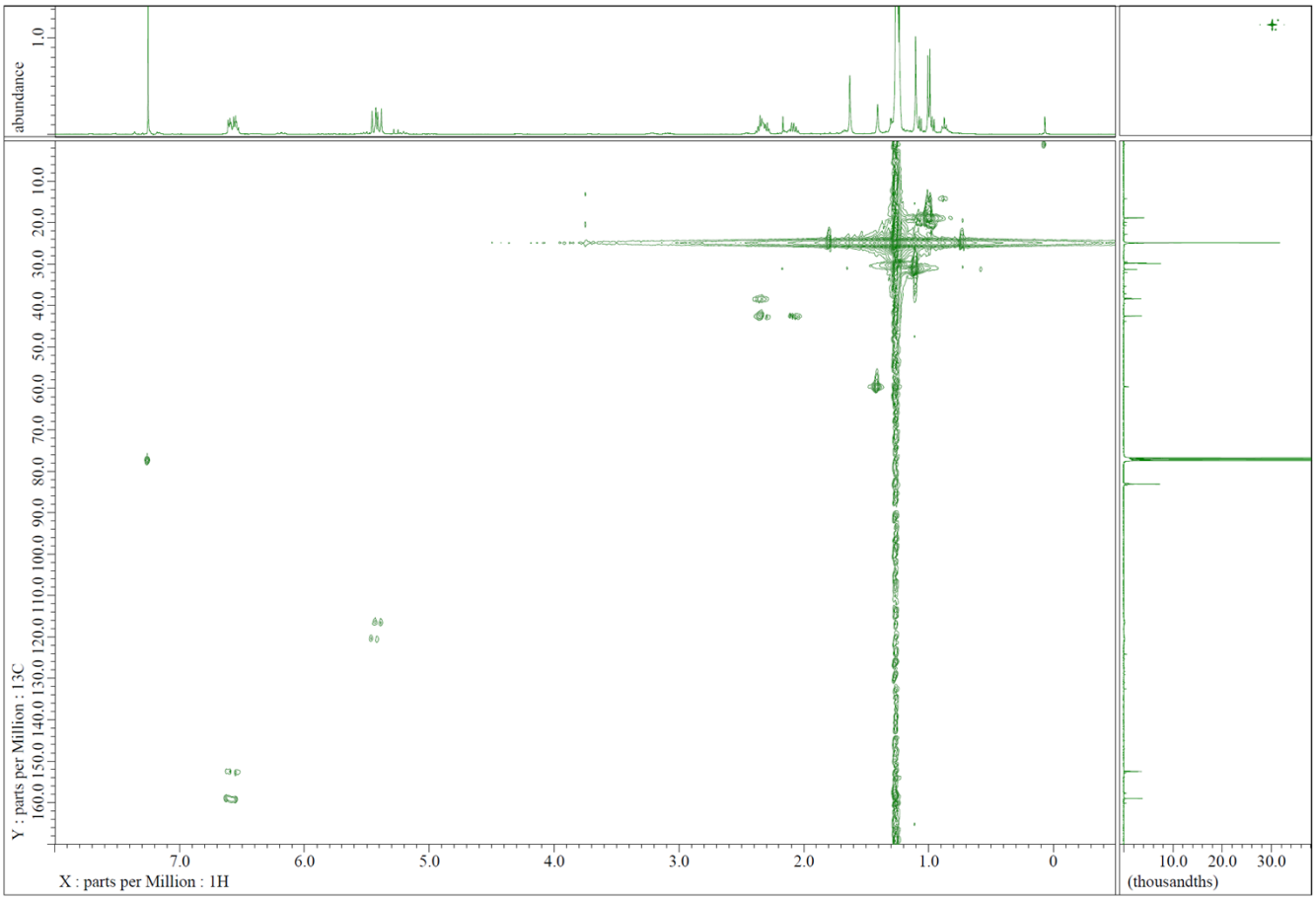
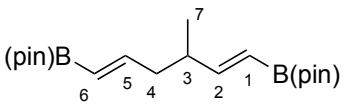


Figure S89. ^{1}H-^{13}C HMQC of (1*E*,5*E*)-3-methyl-1,6-bis(4,4,5,5-tetramethyl-1,3,2-dioxaboloran-2-yl)hexa-1,5-diene [(1*E*,5*E*)-**7m**] (400 MHz for ^{1}H, 100 MHz for ^{13}C, [D]chloroform).



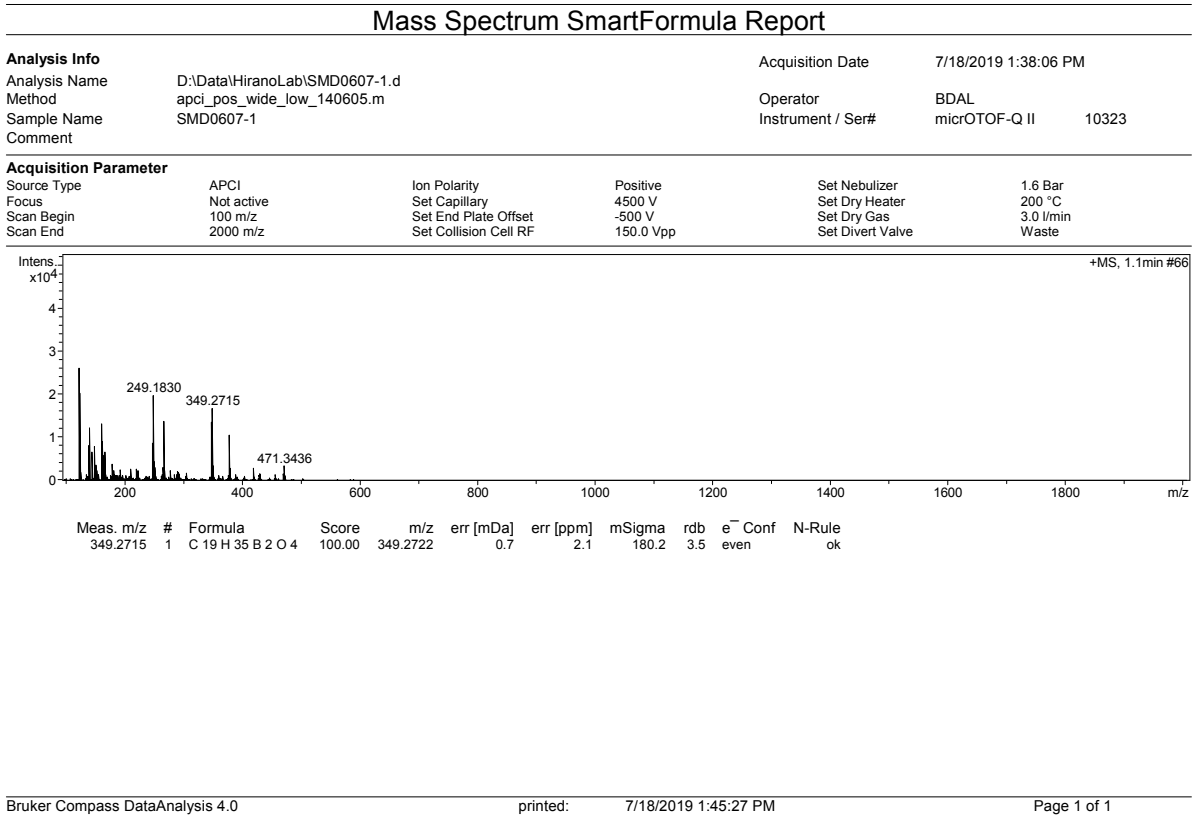
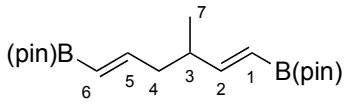


Figure S90. HRMS (APCI) of (1*E*,5*E*)-3-methyl-1,6-bis(4,4,5,5-tetramethyl-1,3,2-dioxaboloran-2-yl)hexa-1,5-diene [(1*E*,5*E*)-**7m**].



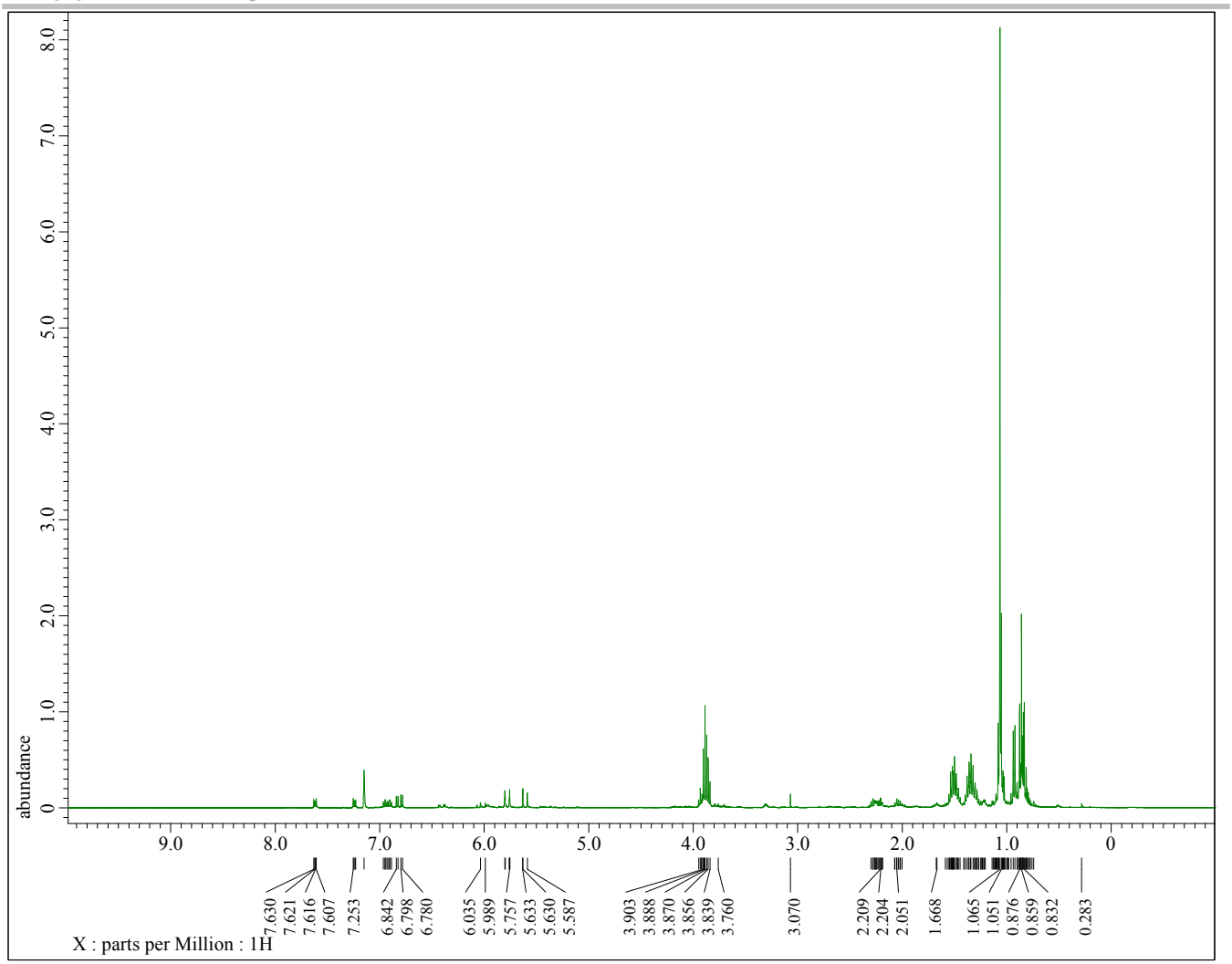
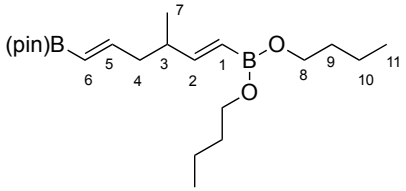


Figure S91. ^{1}H NMR spectrum of (1*E*,5*E*)-3-methyl-1-(butoxyboraneyl)-6-bis(4,4,5,5-tetramethyl-1,3,2-dioxaboloran-2-yl)hexa-1,5-diene [(1*E*,5*E*)-**7n**] (an *in situ* reaction in an NMR tube) (400 MHz, [D_6]benzene).



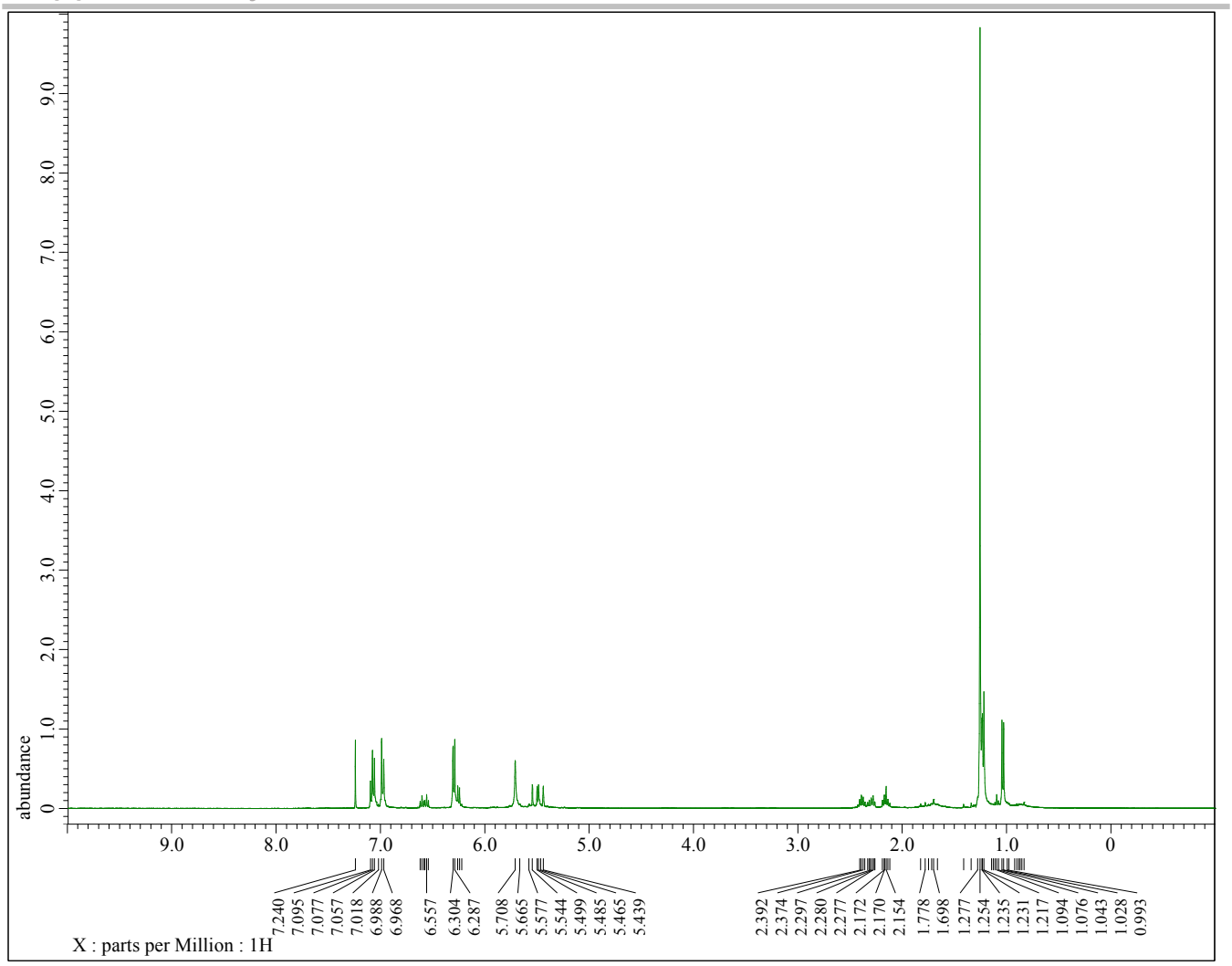
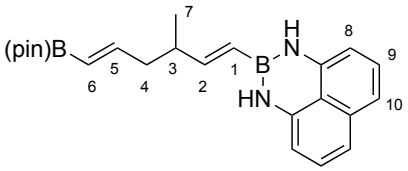


Figure S92. ^{1}H NMR spectrum of (1*E*,5*E*)-1-(2,3-dihydro-1H-naphtho[1,8-de][1,3,2]diazaborinin-2-yl)-3-methyl-6-(4,4,5,5,-tetramethyl-1,3,2-dioxaborolan-2-yl)hexa-1,5-diene [(1*E*,5*E*)-**7o**] (400 MHz, [D]chloroform).



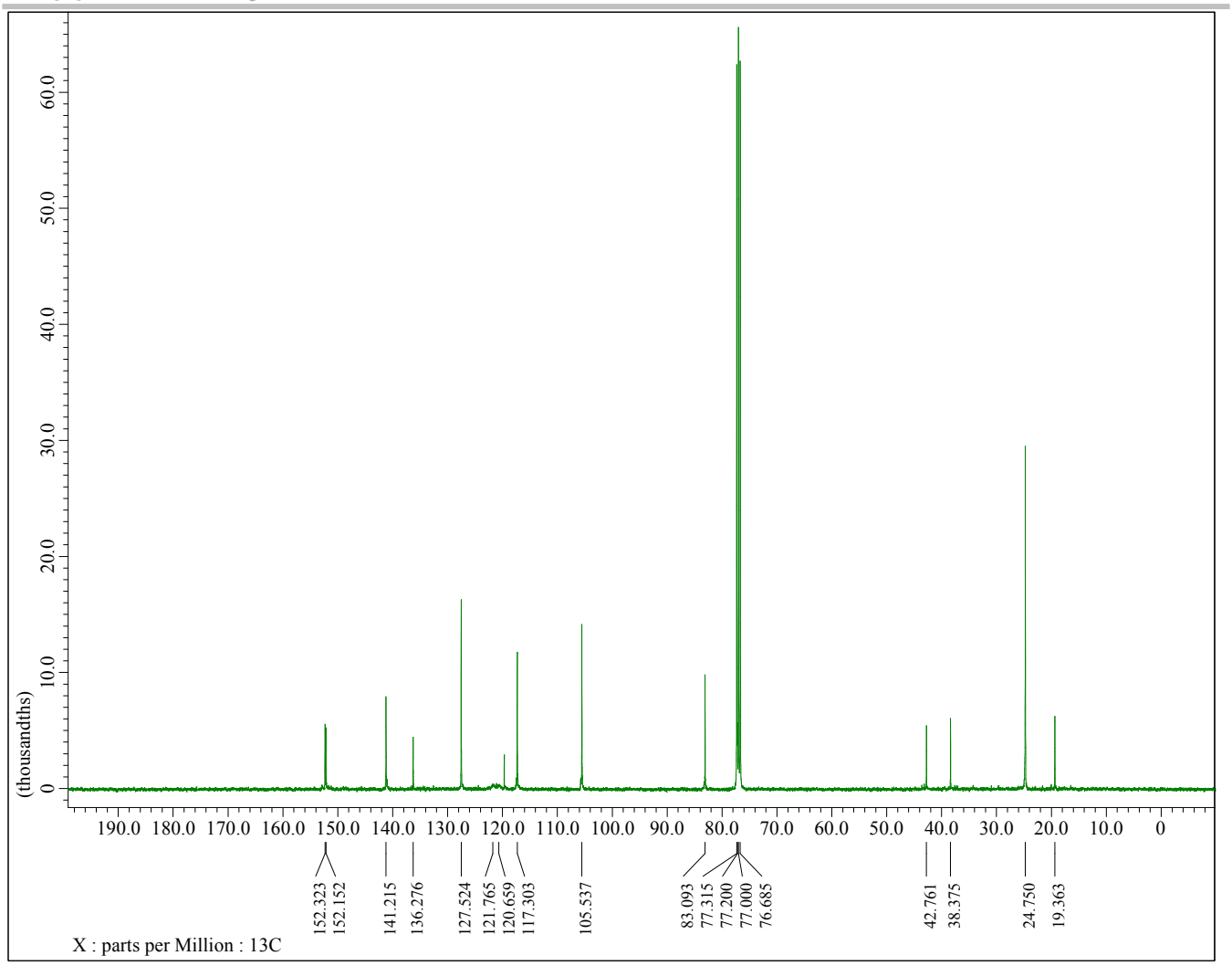
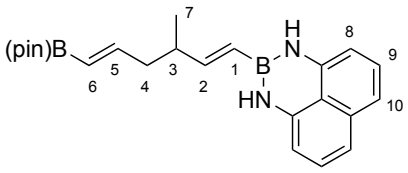


Figure S93. $^{13}C\{^{1}H\}$ NMR spectrum of (1*E*,5*E*)-1-(2,3-dihydro-1H-naphtho[1,8-de][1,3,2]diazaborinin-2-yl)-3-methyl-6-(4,4,5,5,-tetramethyl-1,3,2-dioxaborolan-2-yl)hexa-1,5-diene [(1*E*,5*E*)-**7o**] (100 MHz, [D]chloroform).



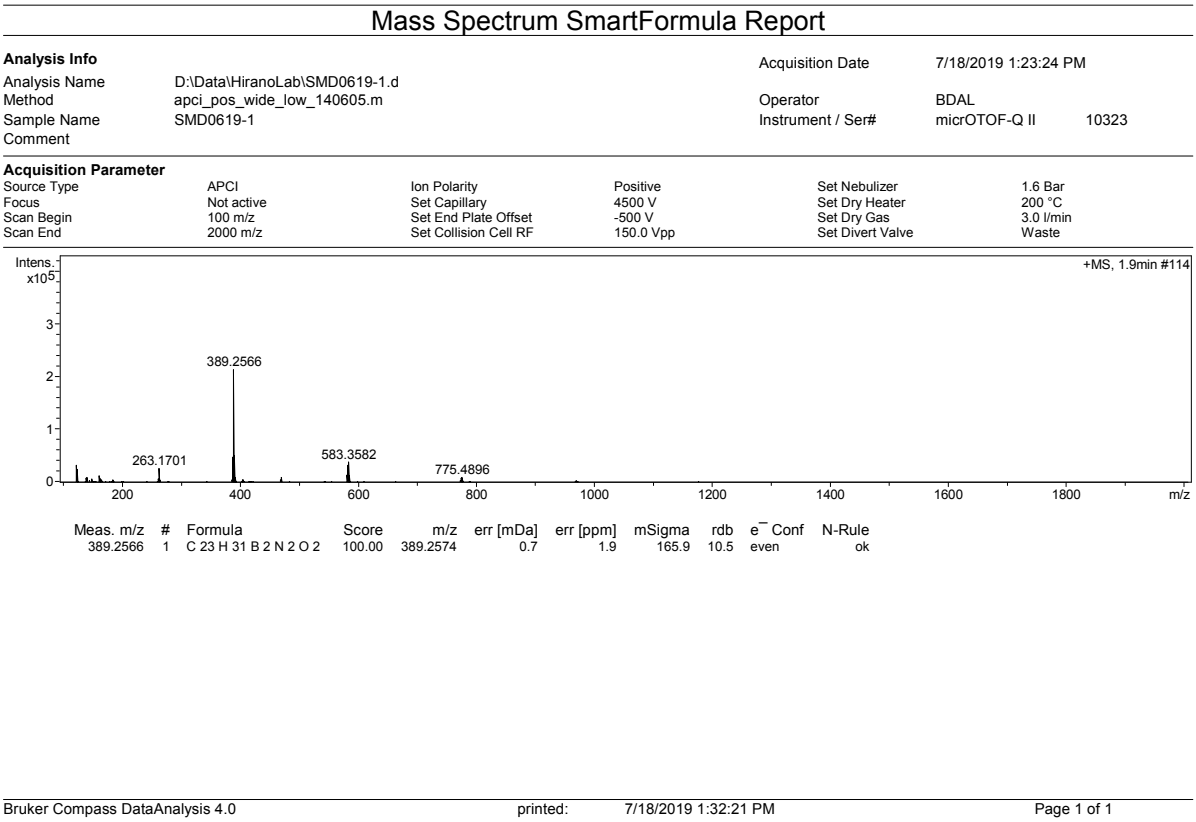
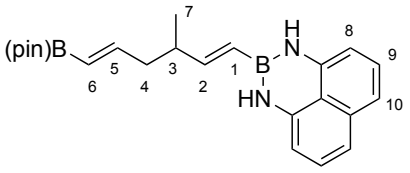


Figure S94. HRMS (APCI) spectrum of (1*E*,5*E*)-1-(2,3-dihydro-1H-naphtho[1,8-de][1,3,2]diazaborinin-2-yl)-3-methyl-6-(4,4,5,5,-tetramethyl-1,3,2-dioxaborolan-2-yl)hexa-1,5-diene [(1*E*,5*E*)-**7o**].



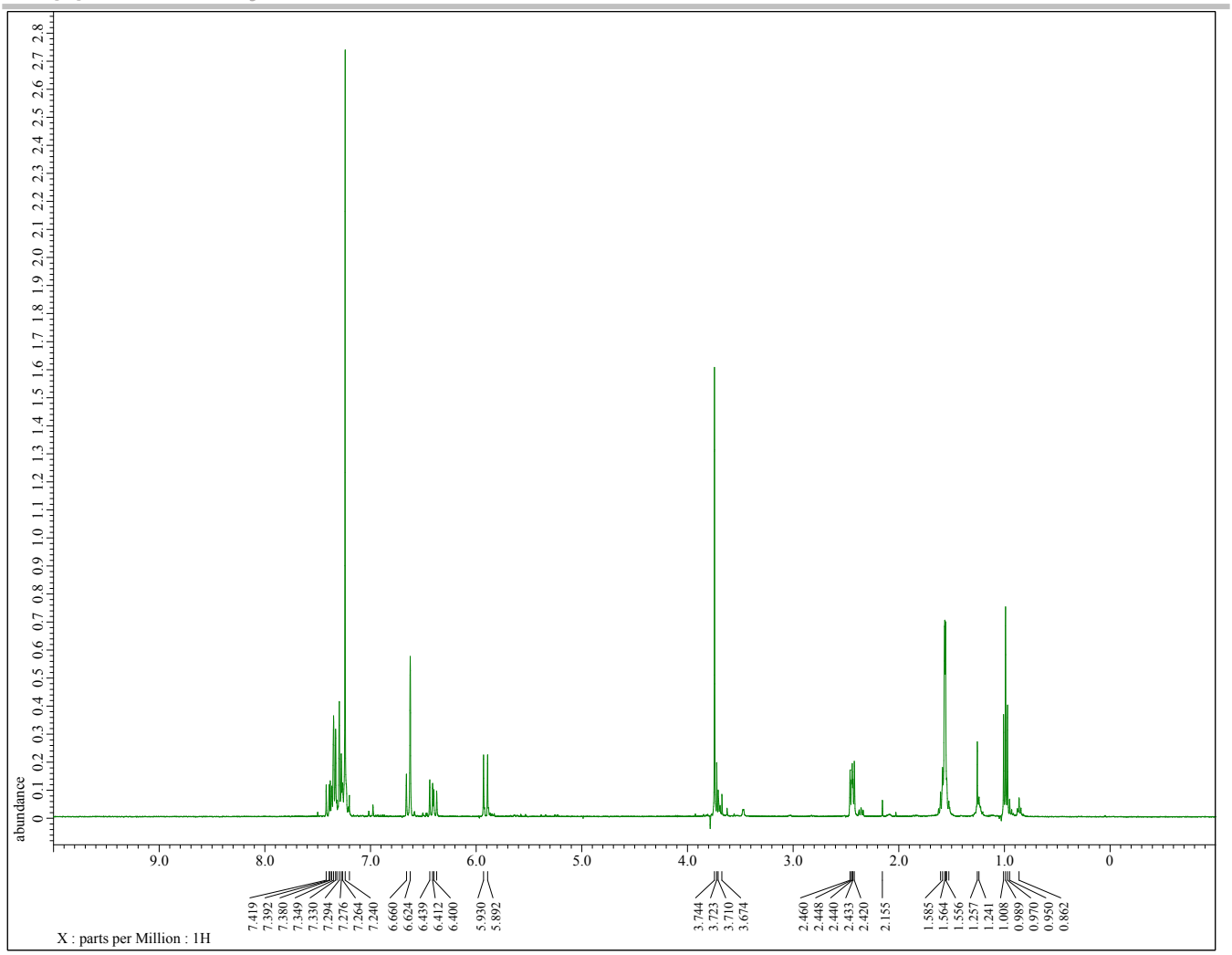
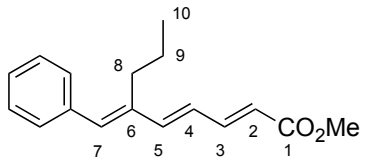


Figure S95. ^{1}H NMR spectrum of methyl (2*E*,4*E*,6*E*)-7-phenyl-6-propylhepta-2,4,6-trienoate [(2*E*,4*E*,6*E*)-**10**] (400 MHz, [D]chloroform).



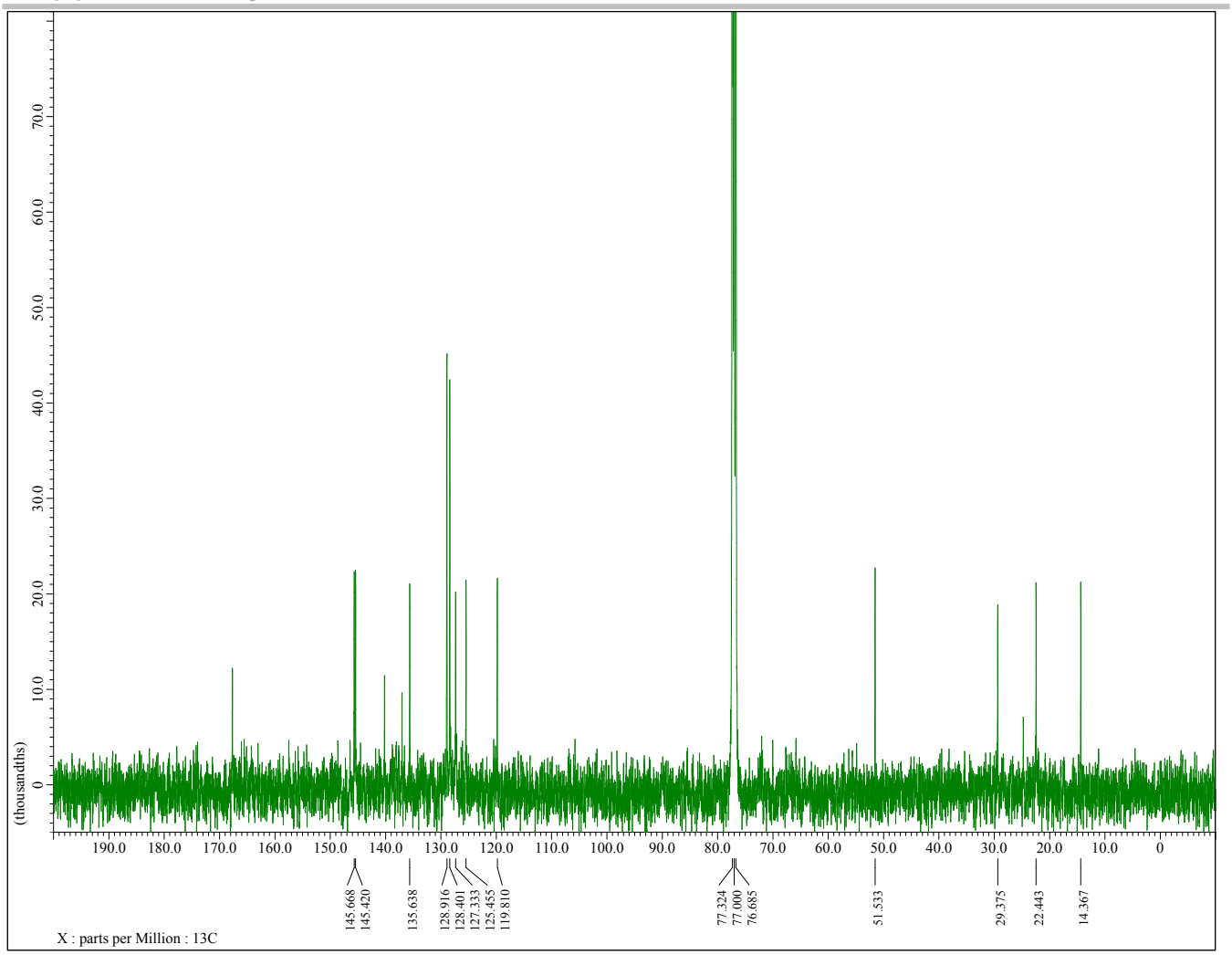
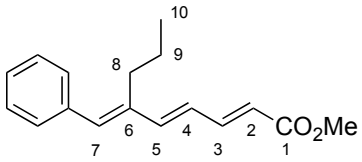


Figure S96. $^{13}C\{^{1}H\}$ NMR spectrum of methyl (2*E*,4*E*,6*E*)-7-phenyl-6-propylhepta-2,4,6-trienoate [(2*E*,4*E*,6*E*)-**10**] (100 MHz, [D]chloroform).



Mass Spectrum SmartFormula Report

Analysis Info

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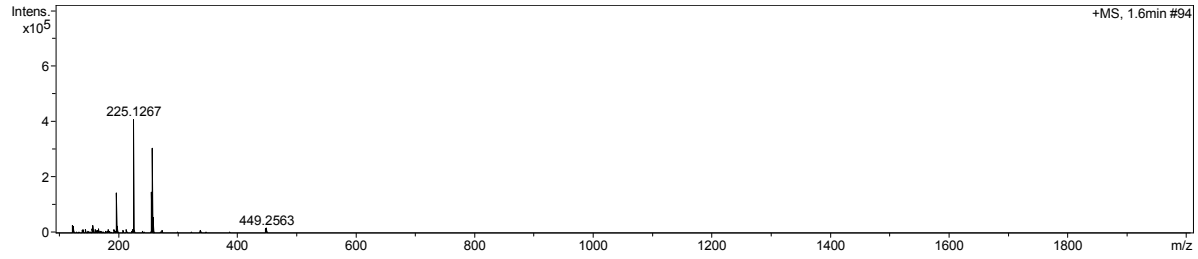
Sample Name	KAY0369-1	Instrument / Ser#	micrOTOF-Q II 10323
Comment			

Acquisition Parameter

Source Type	APCI	Ion Polarity	Positive	Set Nebulizer	1.6 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	100 m/z	Set End Plate Offset	-500 V	Set Dry Gas	3.0 l/min
Scan End	2000 m/z	Set Collision Cell RF	150.0 Vpp	Set Divert Valve	Waste



Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
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	2	C 13 H 17 N 6	42.46	257.1509	-1.9	-7.3	12.5	8.5	even	ok
	3	C 12 H 21 N 2 O 4	9.94	257.1496	-3.2	-12.5	26.0	3.5	even	ok
261.1490	1	C 16 H 21 O 3		261.1485	-0.5	-1.8	n.a.	6.5	even	ok
	2	C 12 H 17 N 6 O		261.1458	-3.2	-12.1	n.a.	7.5	even	ok

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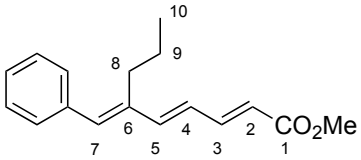
Figure S97. HRMS (APCI) spectrum of methyl (2*E*,4*E*,6*E*)-7-phenyl-6-propylhepta-2,4,6-trienoate [(2*E*,4*E*,6*E*)-**10**].



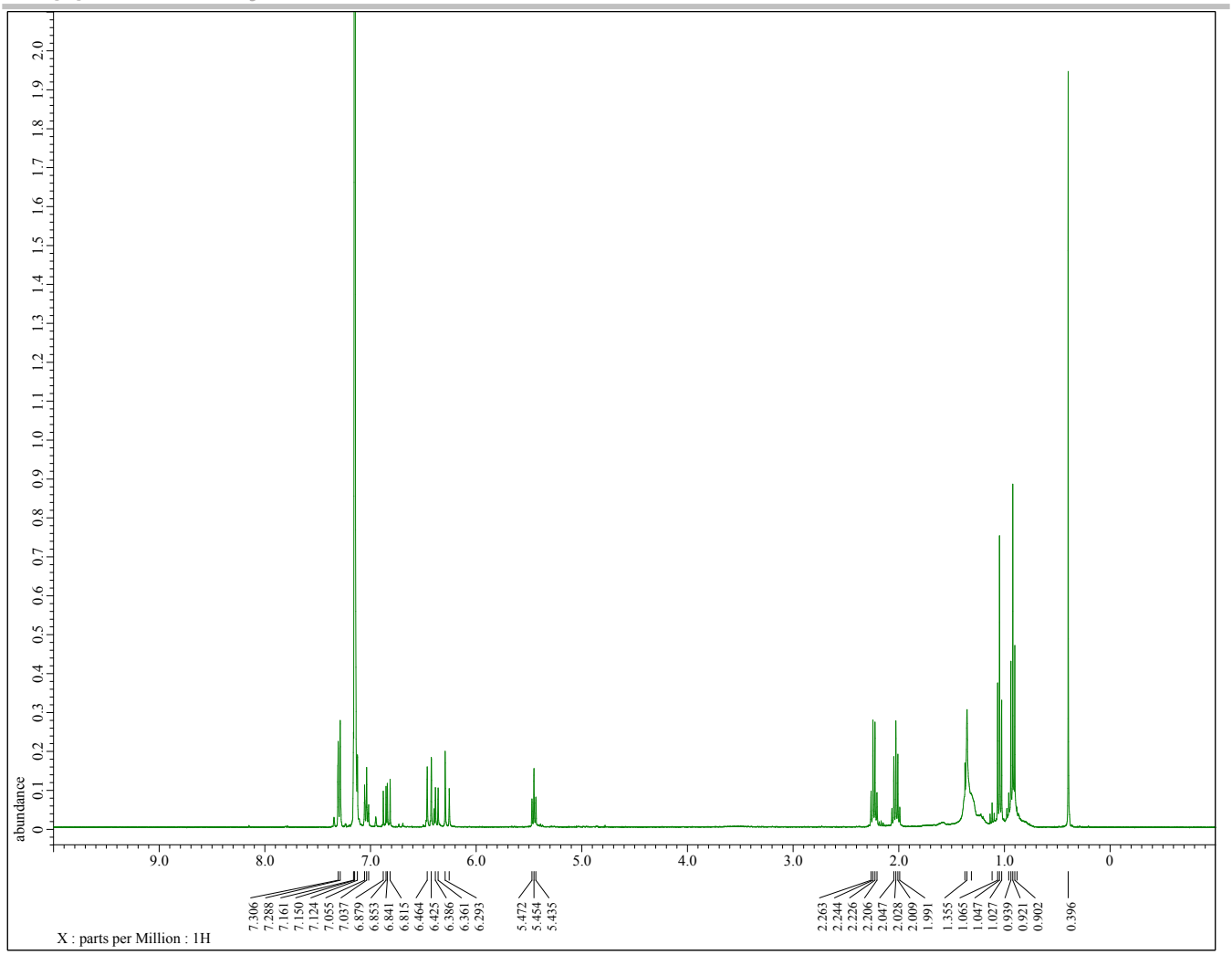
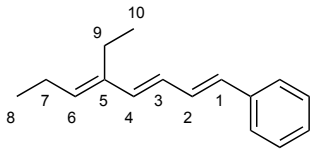


Figure S98. ^{1}H NMR spectrum of (1*E*,3*E*,5*E*)-5-ethyl-1-phenylocta-1,3,5-triene [(1*E*,3*E*,5*E*)-**11**] (400 MHz, [D]chloroform).



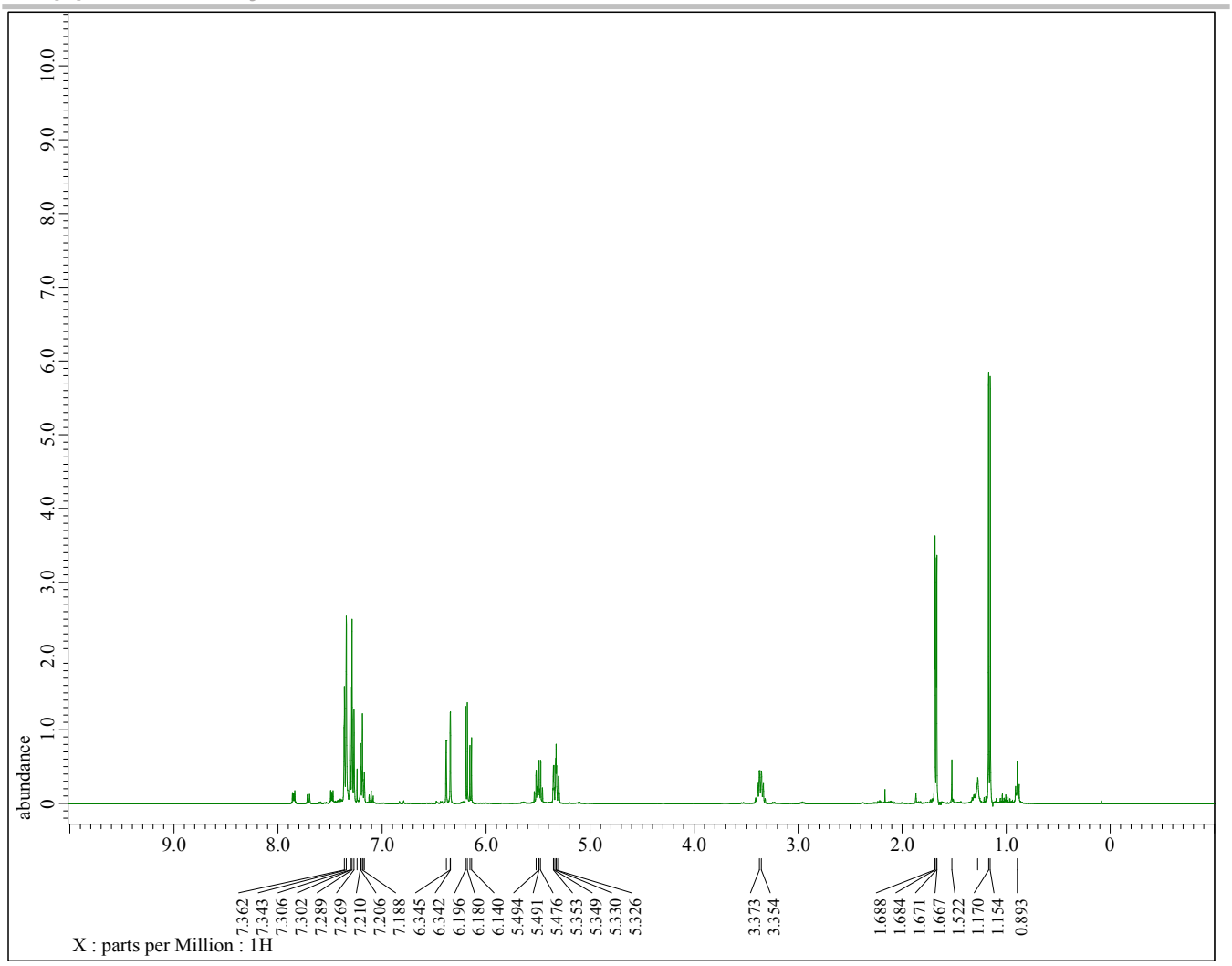
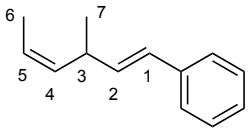


Figure S99. ^{1}H NMR spectrum of (1*E*,4*Z*)-3-methyl-1-phenylhexa-1,4-diene [(1*E*,4*Z*)-**12**] (400 MHz, [D]chloroform).



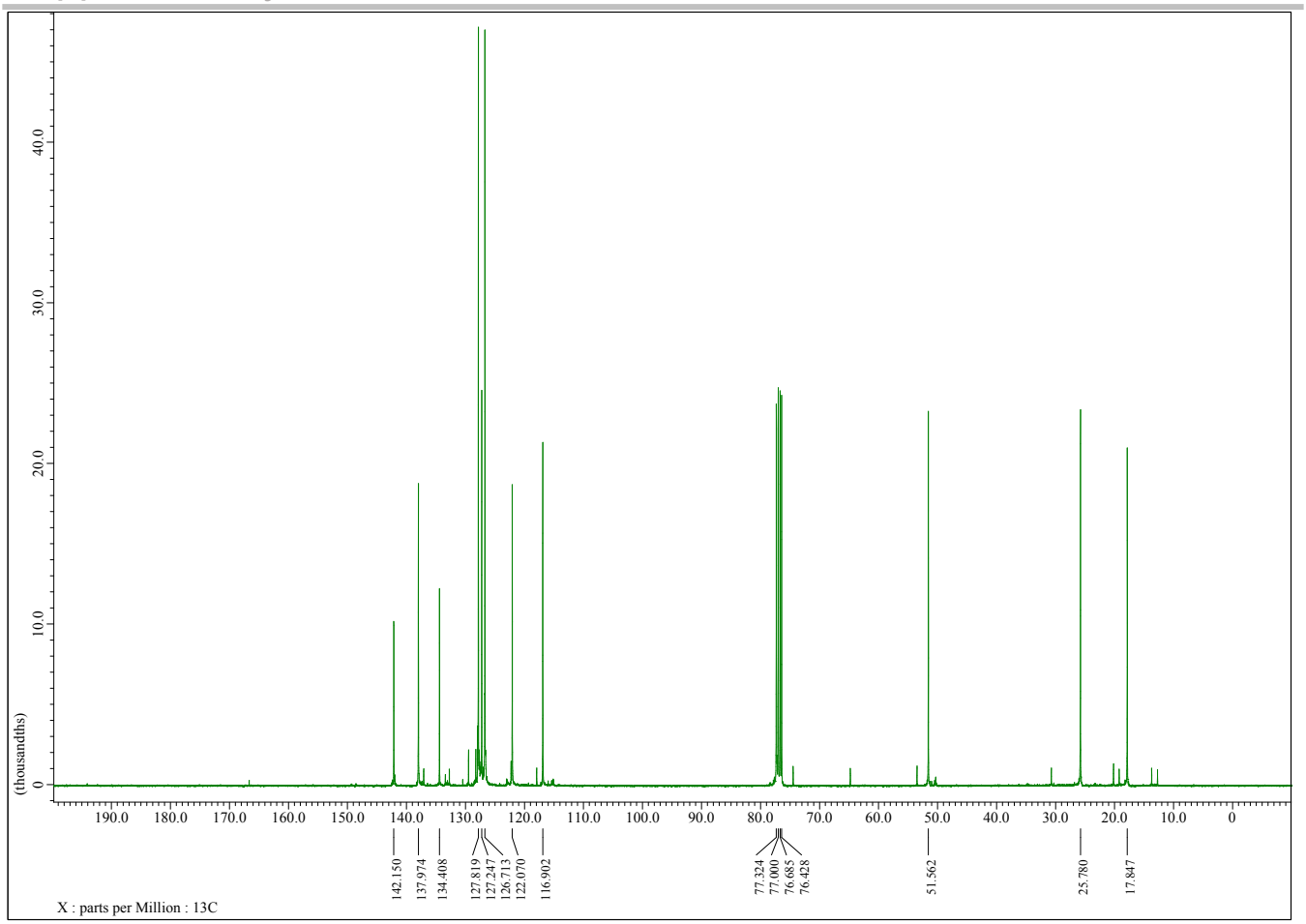
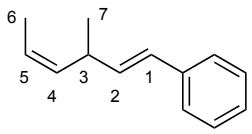


Figure S100. $^{13}C\{^{1}H\}$ NMR spectrum of (1*E*,4*Z*)-3-methyl-1-phenylhexa-1,4-diene [(1*E*,4*Z*)-**12**] (100 MHz, [D]chloroform).



Mass Spectrum SmartFormula Report

Analysis Info

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Sample Name	SMD0629-2	Instrument / Ser#	micrOTOF-Q II 10323
Comment			

Acquisition Parameter

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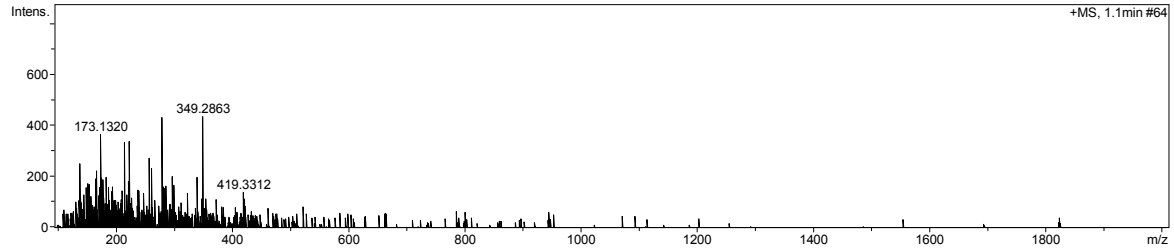
Scan End	2000 m/z	Set Collision Cell RF	150.0 Vpp	Set Divert Valve	Waste



Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e¯ Conf	N-Rule
173.1320	1	C 13 H 17	100.00	173.1325	0.5	2.8	223.2	5.5	even	ok
	2	C 8 H 17 N 2 O 2	0.68	173.1285	-3.5	-20.4	250.2	1.5	even	ok

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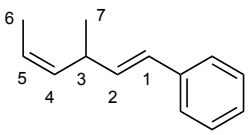
Figure S101. HRMS (APCI) spectrum of (1*E*,4*Z*)-3-methyl-1-phenylhexa-1,4-diene [(1*E*,4*Z*)-**12**].



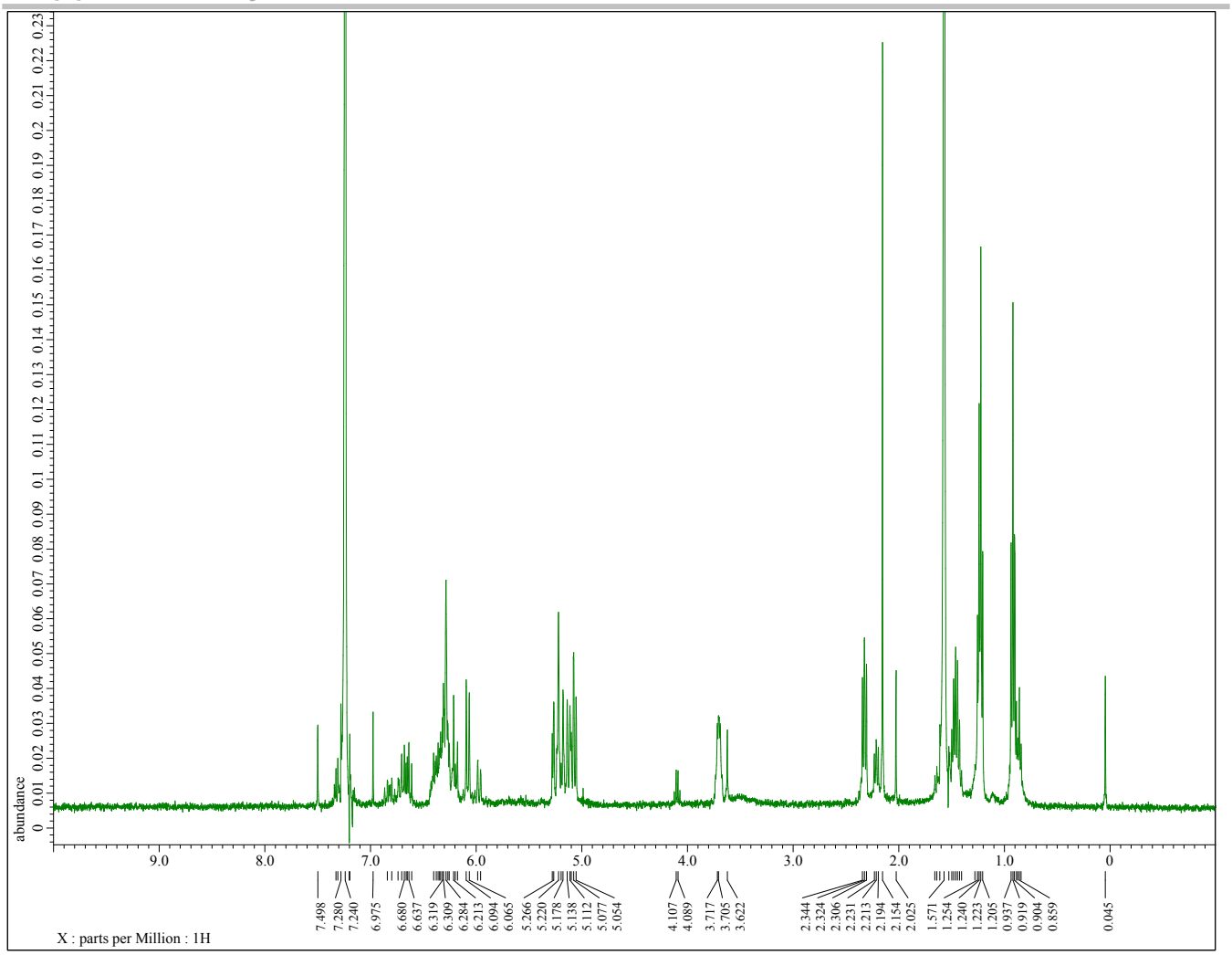
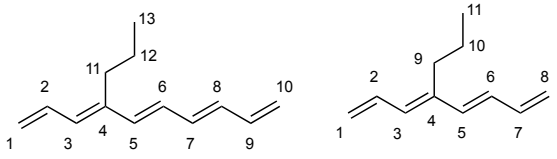


Figure S102. ^{1}H NMR spectrum of (3*E*,5*E*,7*E*)-4-propyldeca-1,3,5,7,9-pentaene [(3*E*,5*E*,7*E*)-**13**] and (3*E*,5*E*)-4-propylocta-1,3,5,7-tetraene [(3*E*,5*E*)-**14**] (400 MHz, [D]chloroform).



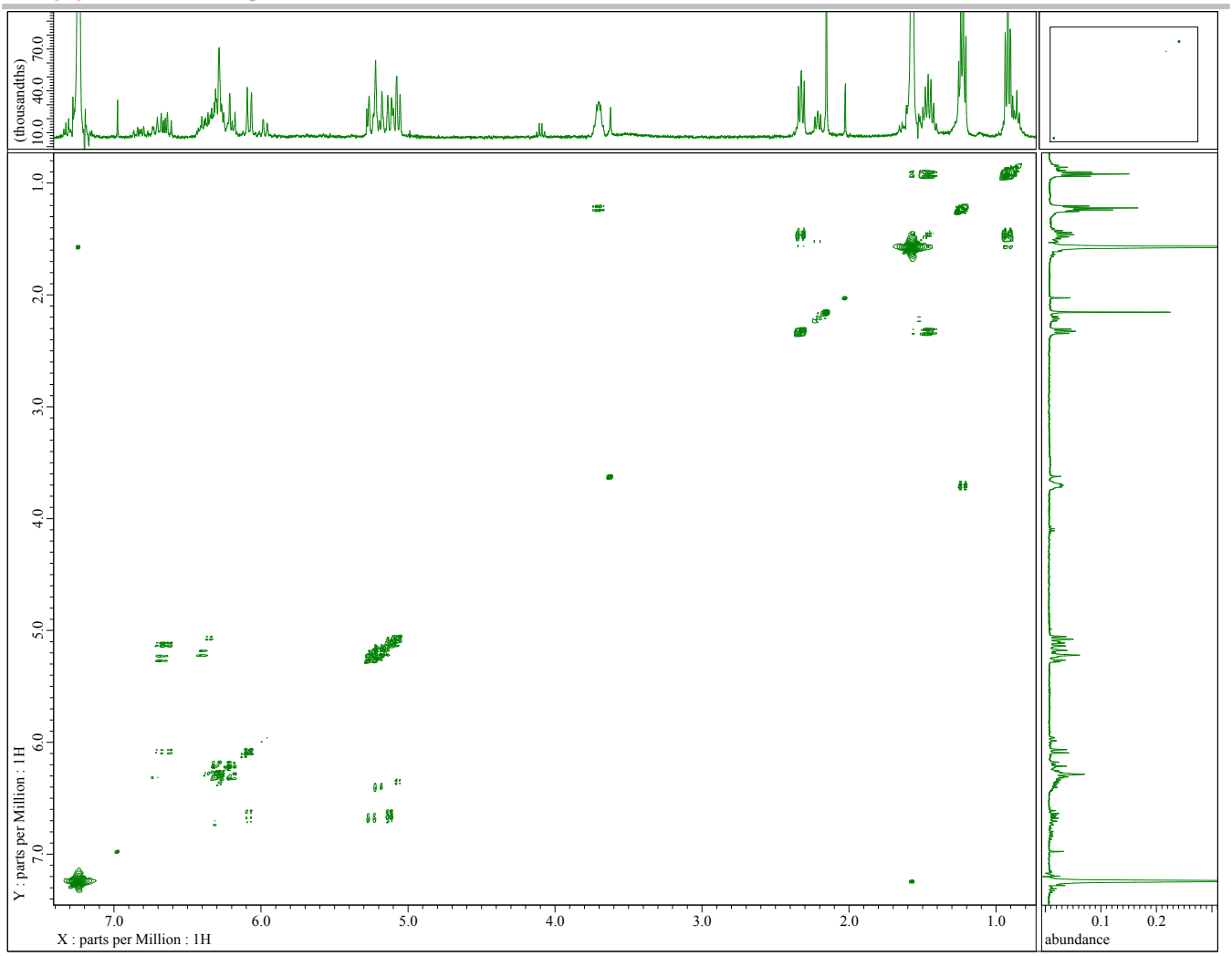
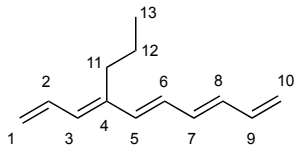
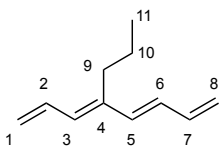


Figure S103. ^{1}H-^{1}H COSY of (3*E*,5*E*,7*E*)-4-propyldeca-1,3,5,7,9-pentaene [(3*E*,5*E*,7*E*)-**13**] and (3*E*,5*E*)-4-propylocta-1,3,5,7-tetraene [(3*E*,5*E*)-**14**] (400 MHz, [D]chloroform).





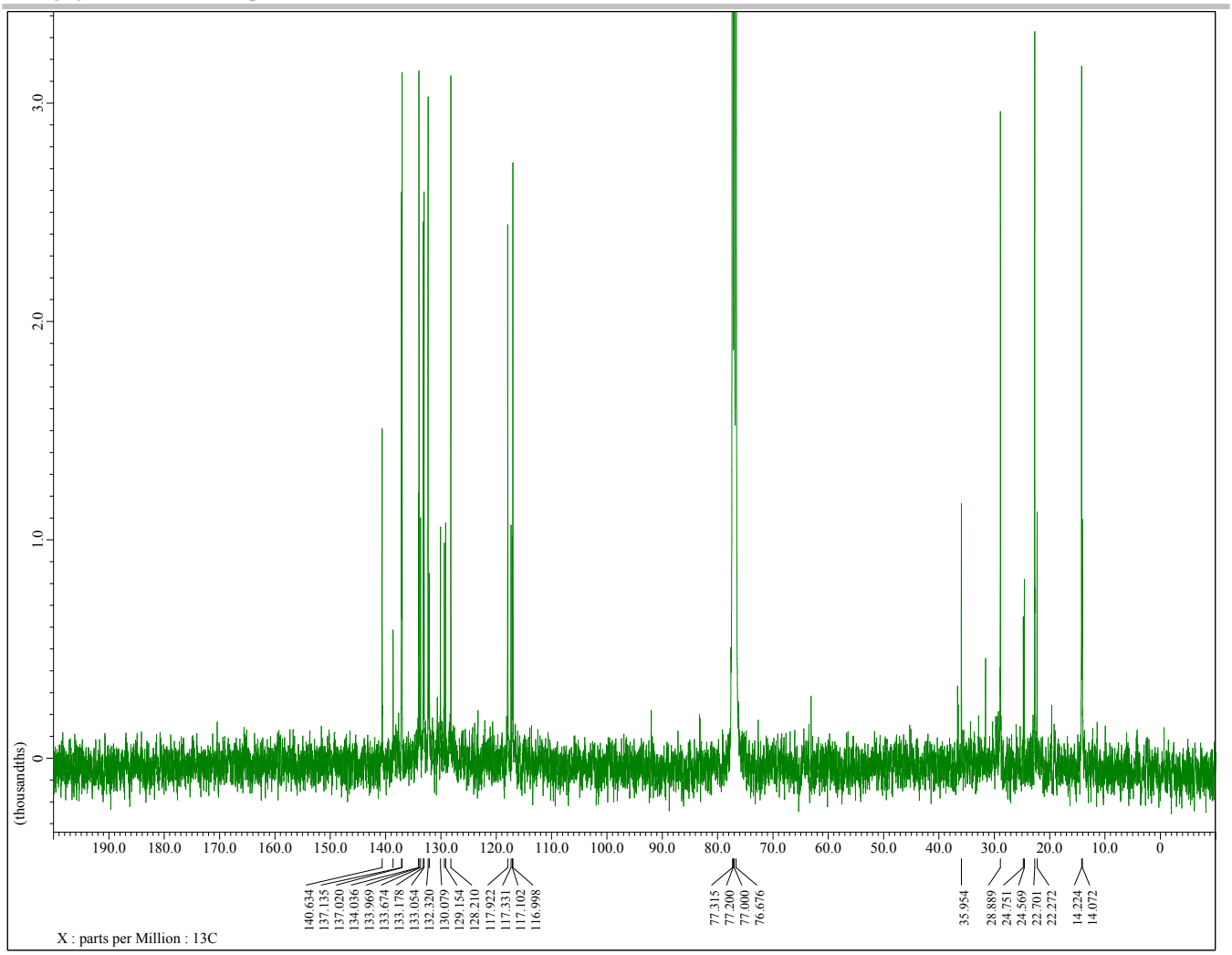
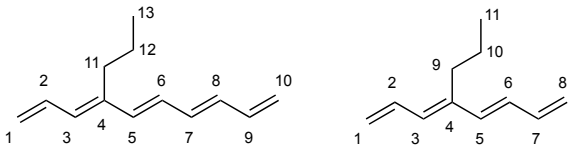


Figure S104. $^{13}C\{^{1}H\}$ spectrum of (3*E*,5*E*,7*E*)-4-propyldeca-1,3,5,7,9-pentaene [(3*E*,5*E*,7*E*)-**13**] and (3*E*,5*E*)-4-propylocta-1,3,5,7-tetraene [(3*E*,5*E*)-**14**] (100 MHz, [D]chloroform).



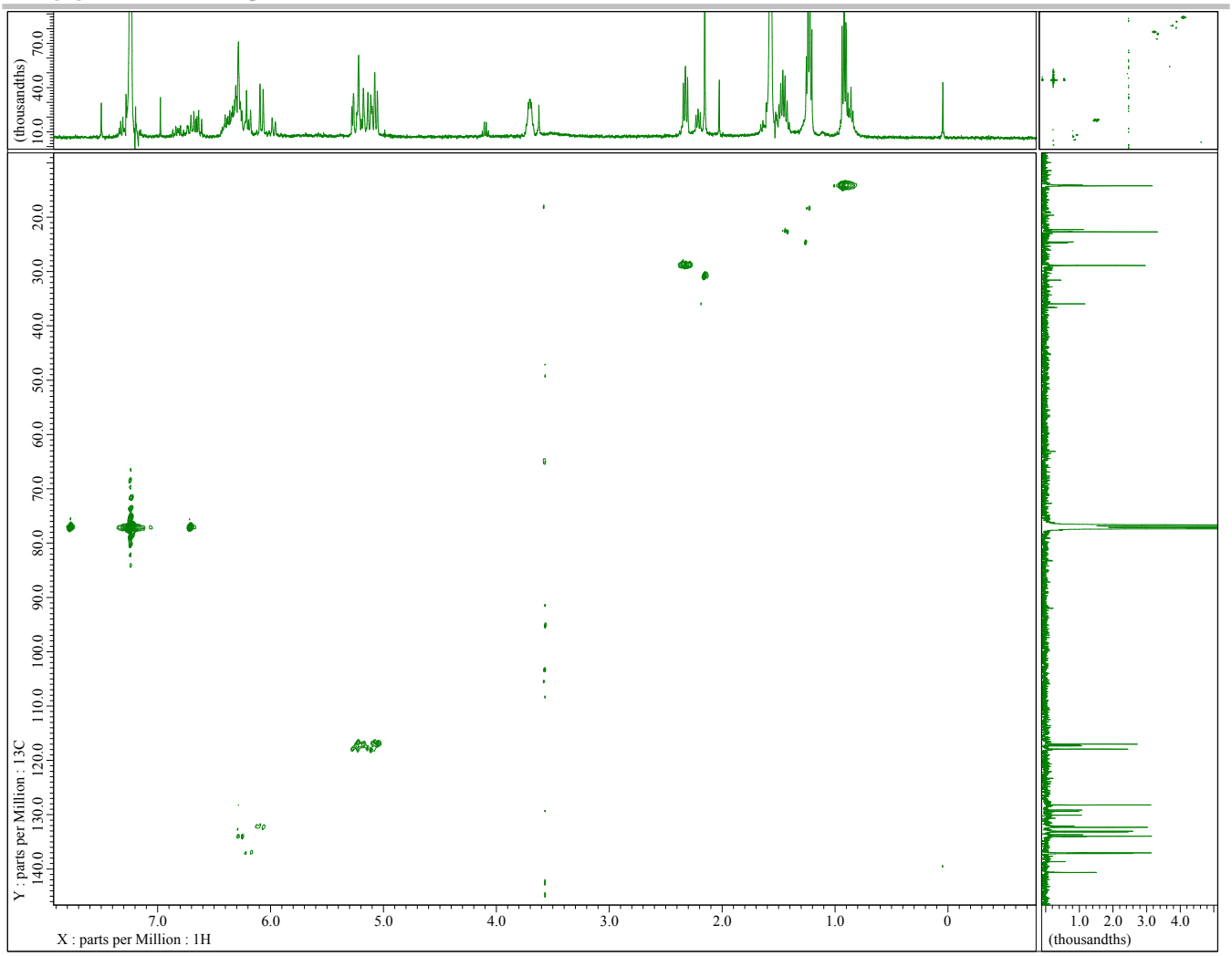
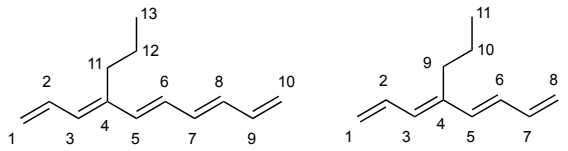


Figure S105. ^{1}H-^{13}C HMQC of (3*E*,5*E*,7*E*)-4-propyldeca-1,3,5,7,9-pentaene [(3*E*,5*E*,7*E*)-**13**] and (3*E*,5*E*)-4-propylocta-1,3,5,7-tetraene [(3*E*,5*E*)-**14**] (400 MHz for ^{1}H, 100 MHz for ^{13}C, [D]chloroform).



Mass Spectrum SmartFormula Report

Analysis Info

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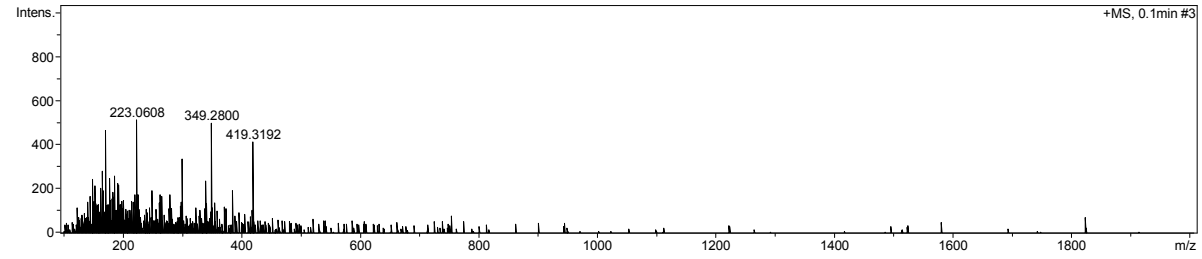
Method	apci_pos_wide_low_140605.m	Operator	BDAL
Sample Name	KAY0463-2	Instrument / Ser#	micrOTOF-Q II 10323
Comment			

Acquisition Parameter

Source Type	APCI	Ion Polarity	Positive	Set Nebulizer	1.6 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	100 m/z	Set End Plate Offset	-500 V	Set Dry Gas	3.0 l/min
Scan End	2000 m/z	Set Collision Cell RF	150.0 Vpp	Set Divert Valve	Waste



Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
175.1474	1	C 8 H 19 N 2 O 2	34.38	175.1441	-3.3	-19.1	54.3	0.5	even	ok
	2	C 13 H 19	100.00	175.1481	0.7	3.9	81.3	4.5	even	ok

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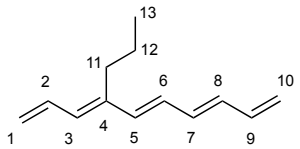
Figure S106. HRMS (APCI) spectrum of (3*E*,5*E*,7*E*)-4-propyldeca-1,3,5,7,9-pentaene [(3*E*,5*E*,7*E*)-**13**] and (3*E*,5*E*)-4-propylocta-1,3,5,7-tetraene [(3*E*,5*E*)-**14**].



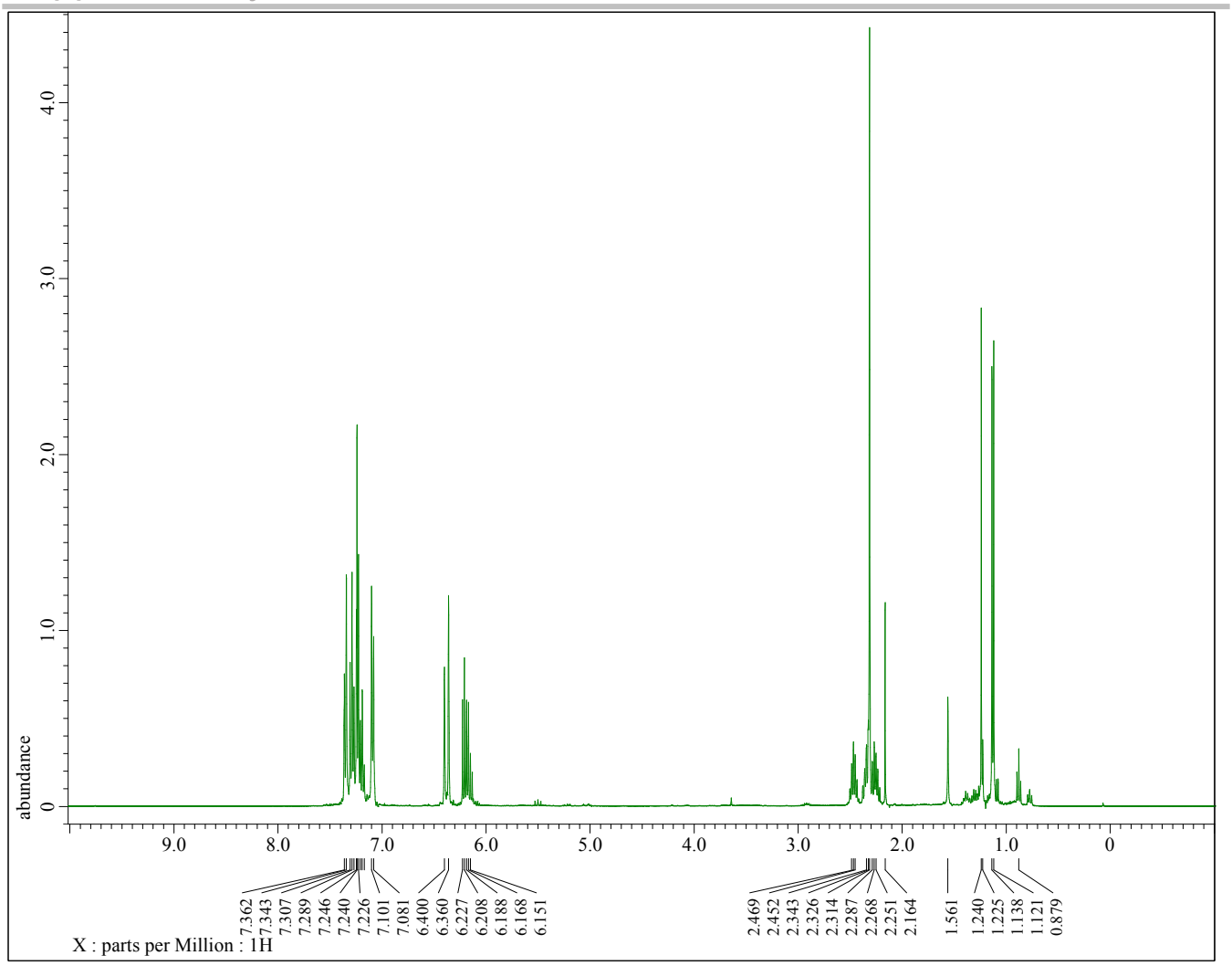
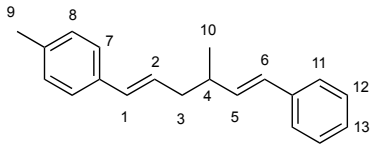


Figure S107. ^{1}H NMR spectrum of (1*E*,5*E*)-4-methyl-6-phenyl-1-(4-tolyl)hexa-1,5-diene [(1*E*,5*E*)-**15**] (400 MHz, [D]chloroform).



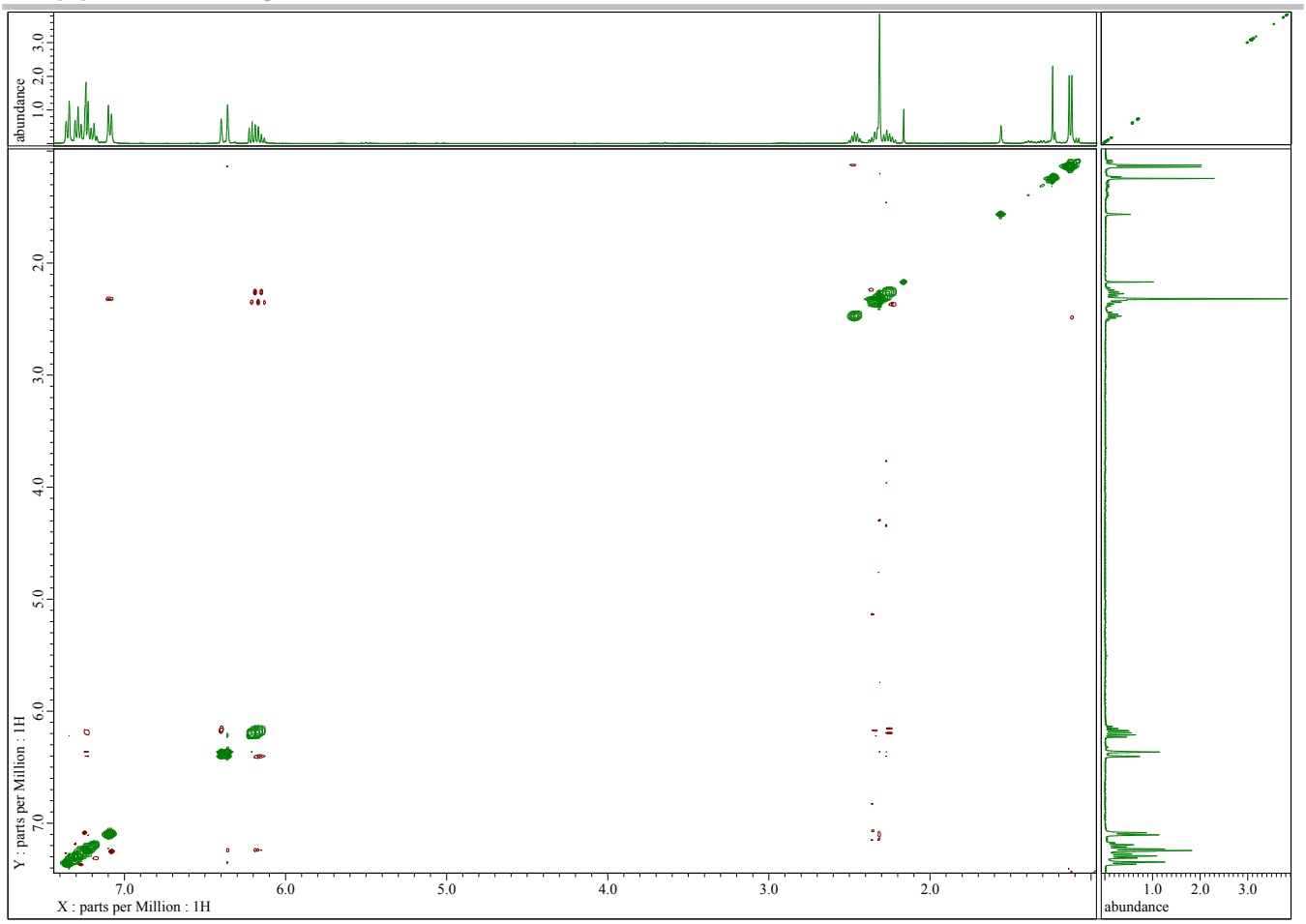
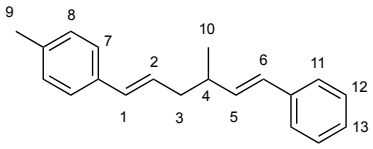


Figure S108. *p*NOESY of (1*E*,5*E*)-4-methyl-6-phenyl-1-(4-tolyl)hexa-1,5-diene [(1*E*,5*E*)-**15**] (400 MHz, [D]chloroform).



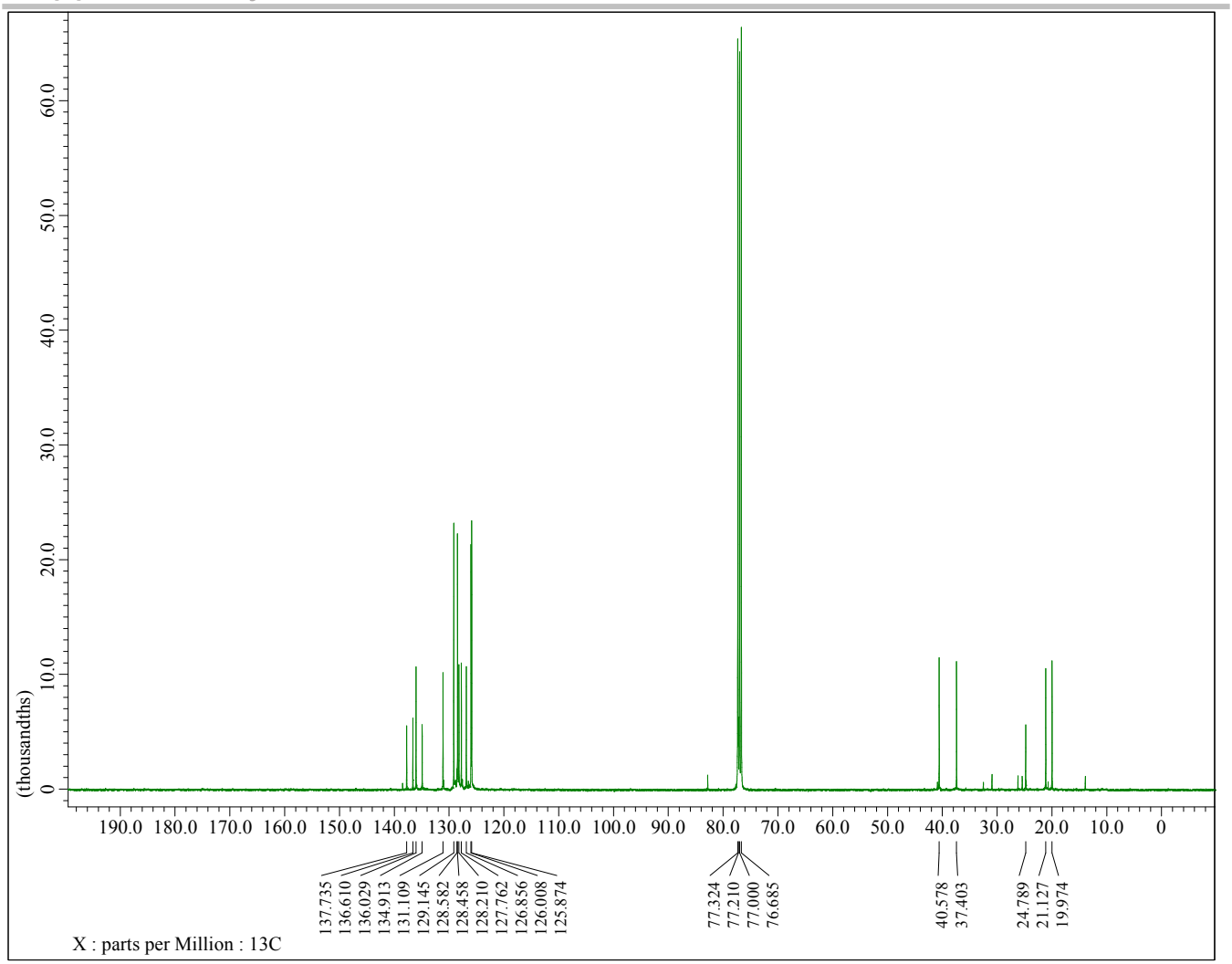
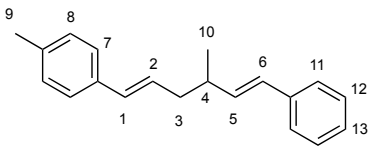


Figure S109. $^{13}C\{^{1}H\}$ NMR spectrum of (1*E*,5*E*)-4-methyl-6-phenyl-1-(4-tolyl)hexa-1,5-diene [(1*E*,5*E*)-**15**] (100 MHz, [D]chloroform).



Mass Spectrum SmartFormula Report

Analysis Info

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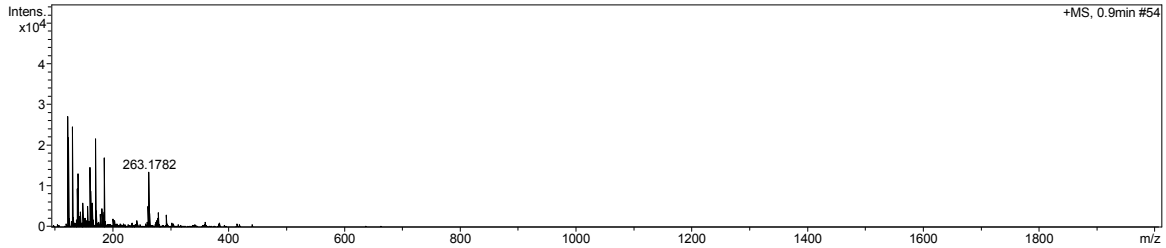
Sample Name	SMD0583-major	Instrument / Ser#	micrOTOF-Q II 10323
Comment			

Acquisition Parameter

Source Type	APCI	Ion Polarity	Positive	Set Nebulizer	1.6 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	100 m/z	Set End Plate Offset	-500 V	Set Dry Gas	3.0 l/min
Scan End	2000 m/z	Set Collision Cell RF	150.0 Vpp	Set Divert Valve	Waste



Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
263.1782	1	C 20 H 23	100.00	263.1794	1.2	4.7	23.8	9.5	even	ok
	2	C 15 H 23 N 2 O 2	15.14	263.1754	-2.8	-10.6	50.5	5.5	even	ok

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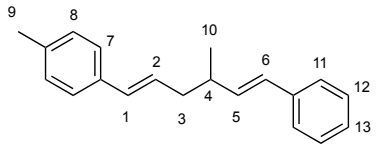
Figure S110. HRMS (APCI) spectrum of (1*E*,5*E*)-4-methyl-6-phenyl-1-(4-tolyl)hexa-1,5-diene [(1*E*,5*E*)-**15**].



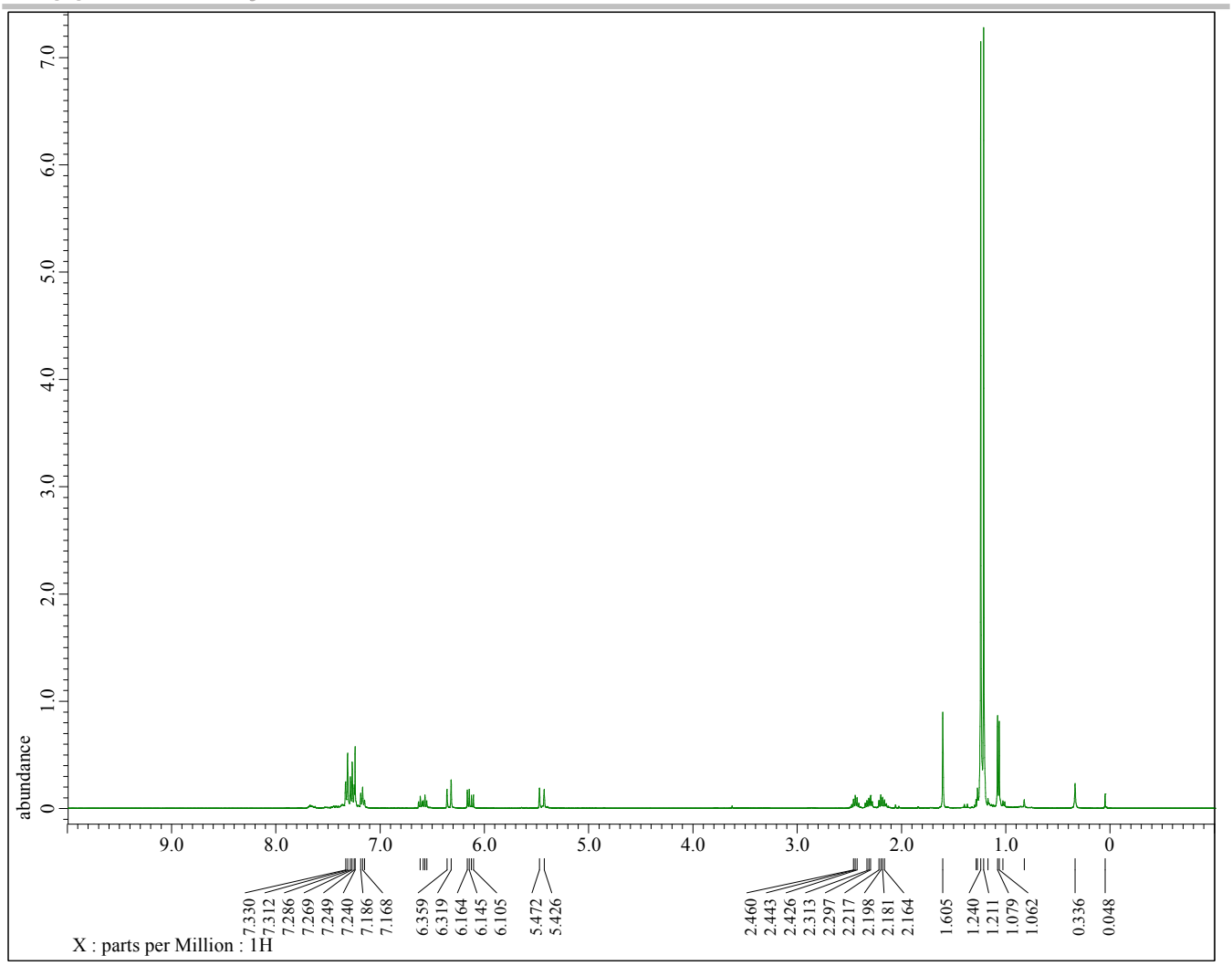
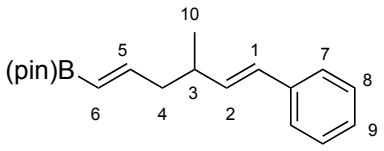


Figure S111. ^{1}H NMR spectrum of (1*E*,5*E*)-3-methyl-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-phenyl-hexa-1,5-diene [(1*E*,5*E*)-**16**] (400 MHz, [D]chloroform).



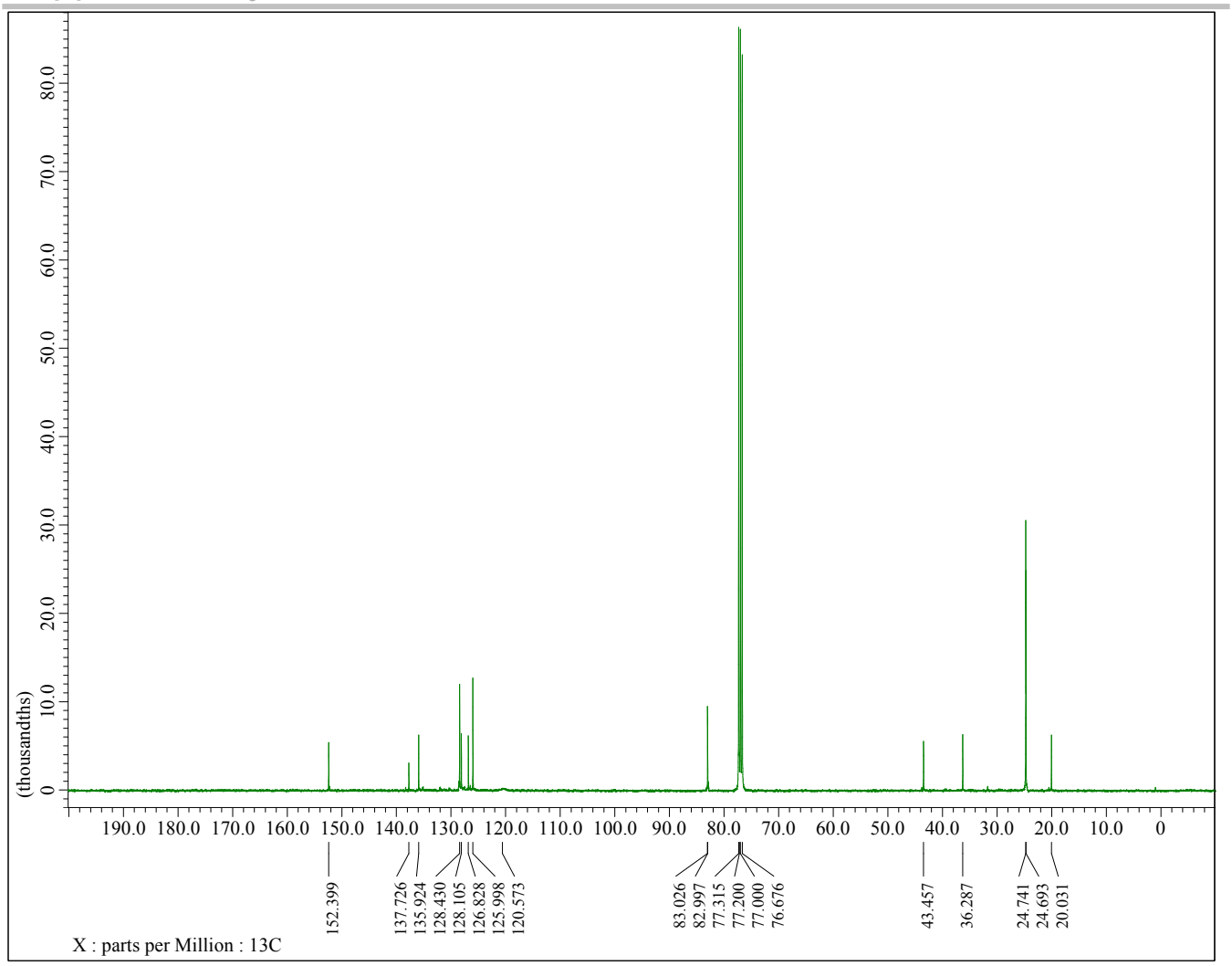
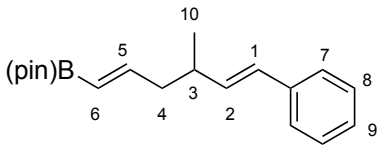


Figure S112. $^{13}C\{^{1}H\}$ NMR spectrum of (1*E*,5*E*)-3-methyl-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-phenyl-hexa-1,5-diene [(1*E*,5*E*)-**16**] (100 MHz, [D]chloroform).



Mass Spectrum SmartFormula Report

Analysis Info

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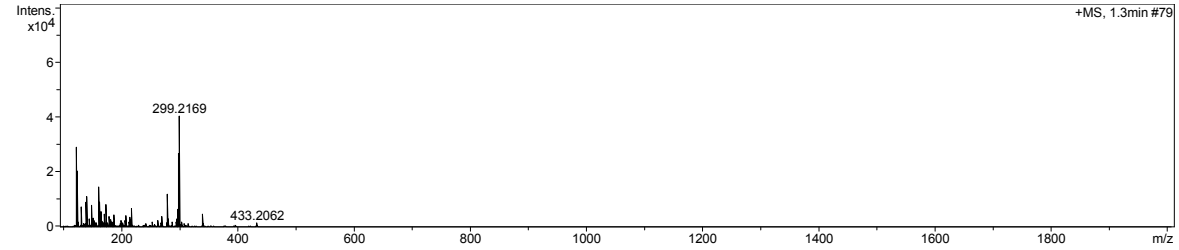
Method	apci_pos_wide_low_140605.m	Operator	BDAL
Sample Name	SMD0579-1	Instrument / Ser#	micrOTOF-Q II 10323
Comment			

Acquisition Parameter

Source Type	APCI	Ion Polarity	Positive	Set Nebulizer	1.6 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	100 m/z	Set End Plate Offset	-500 V	Set Dry Gas	3.0 l/min
Scan End	2000 m/z	Set Collision Cell RF	150.0 Vpp	Set Divert Valve	Waste



Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
299.2169	1	C 19 H 28 B O 2	100.00	299.2180	1.1	3.8	212.8	6.5	even	ok

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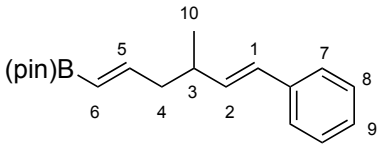
Figure S113. HRMS (APCI) spectrum of (1*E*,5*E*)-3-methyl-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-phenyl-hexa-1,5-diene [(1*E*,5*E*)-**16**].



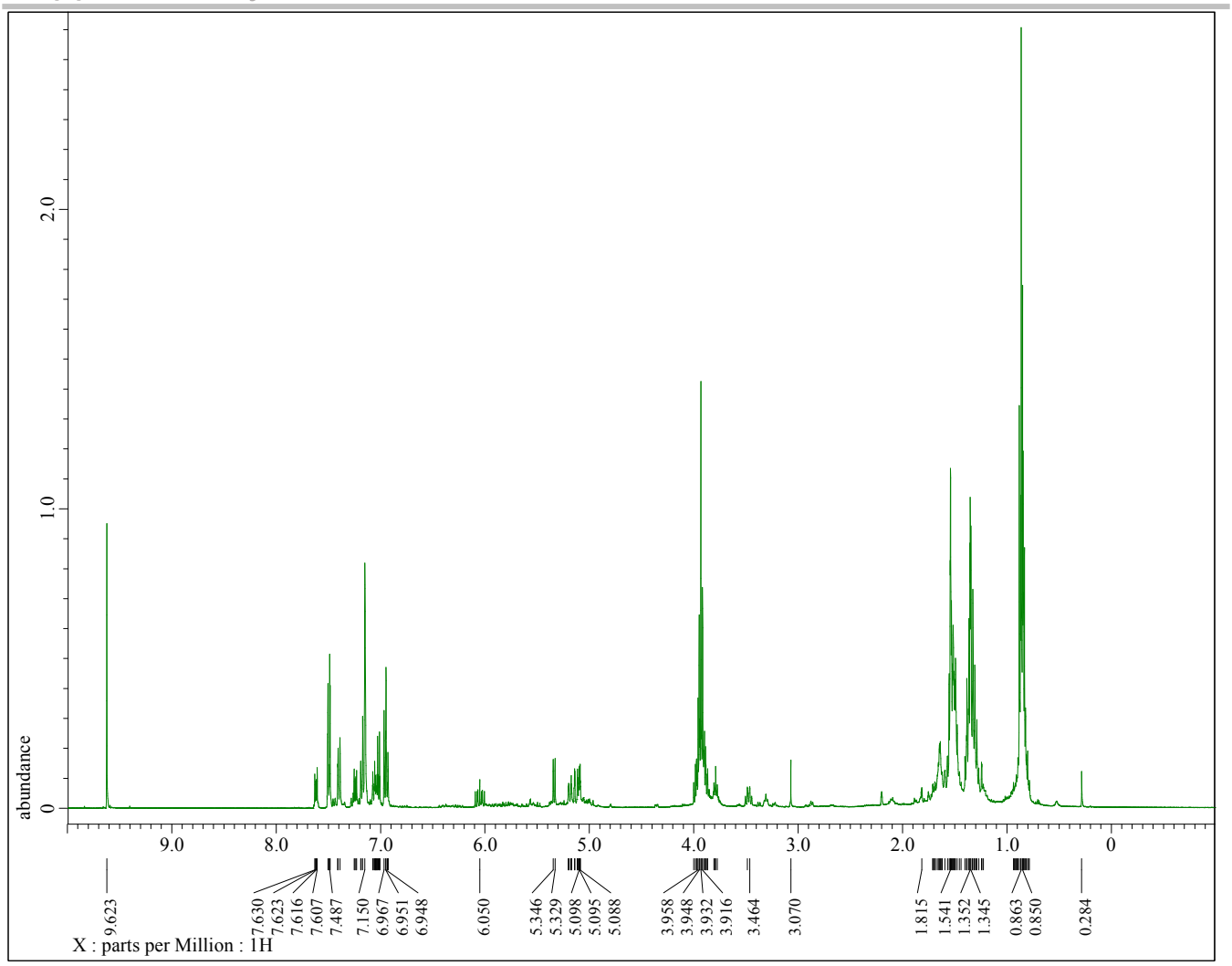
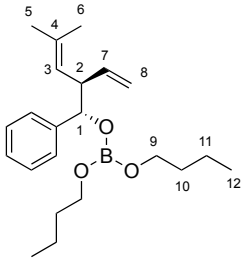


Figure S114. ^{1}H NMR spectrum of {*rac*-(1*S*,2*R*)-4-methyl-1-phenyl-2-binylpent-3-en-1-yl}boronate [*anti*-**17**] (an *in situ* reaction in an NMR tube) (400 MHz, [D_6]benzene).



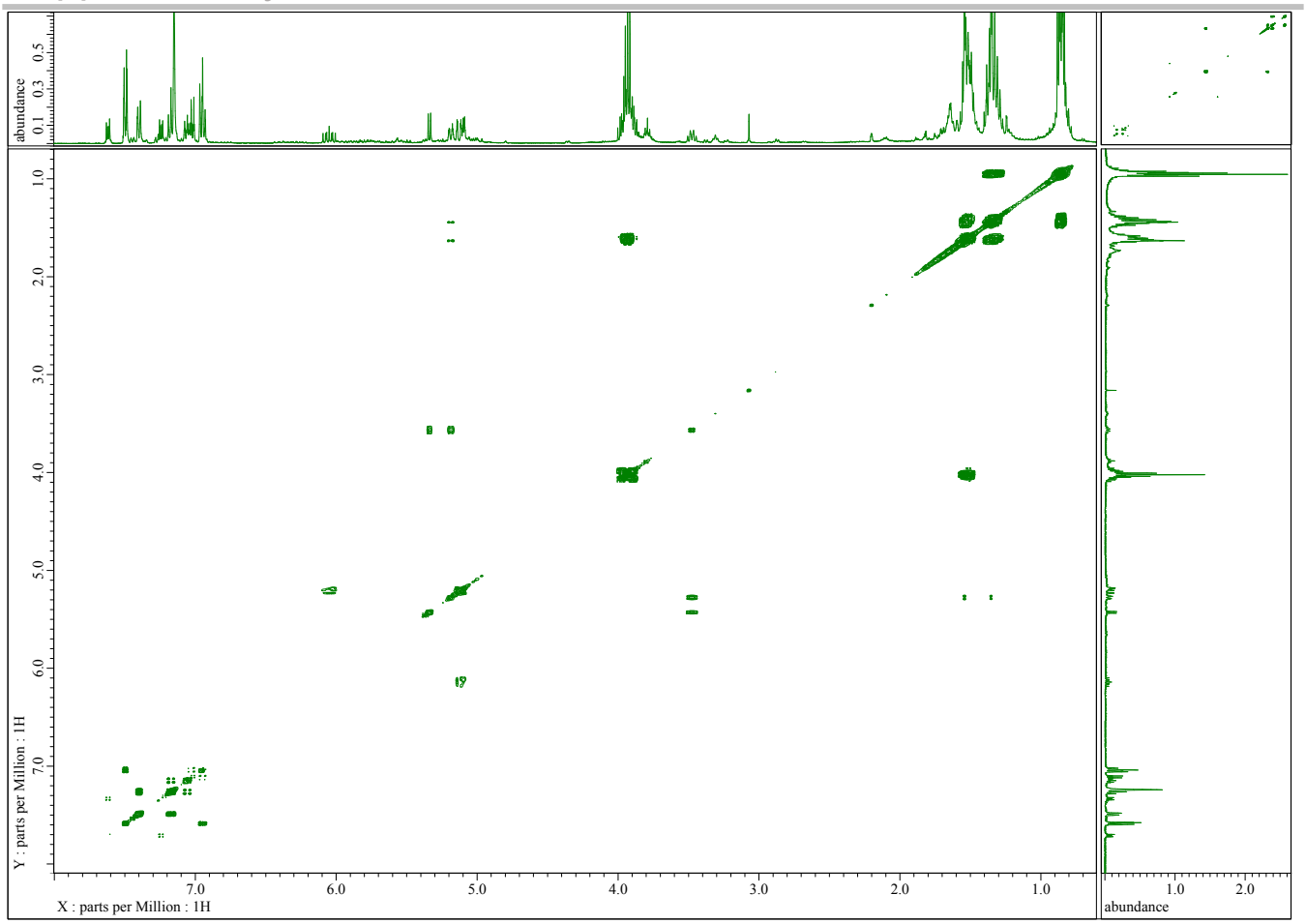
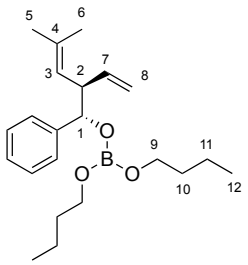


Figure S115. ^{1}H-^{1}H COSY of {*rac*-(1*S*,2*R*)-4-methyl-1-phenyl-2-binylpent-3-en-1-yl}boronate [*anti*-**17**] (an *in situ* reaction in an NMR tube) (400 MHz, [D_6]benzene).



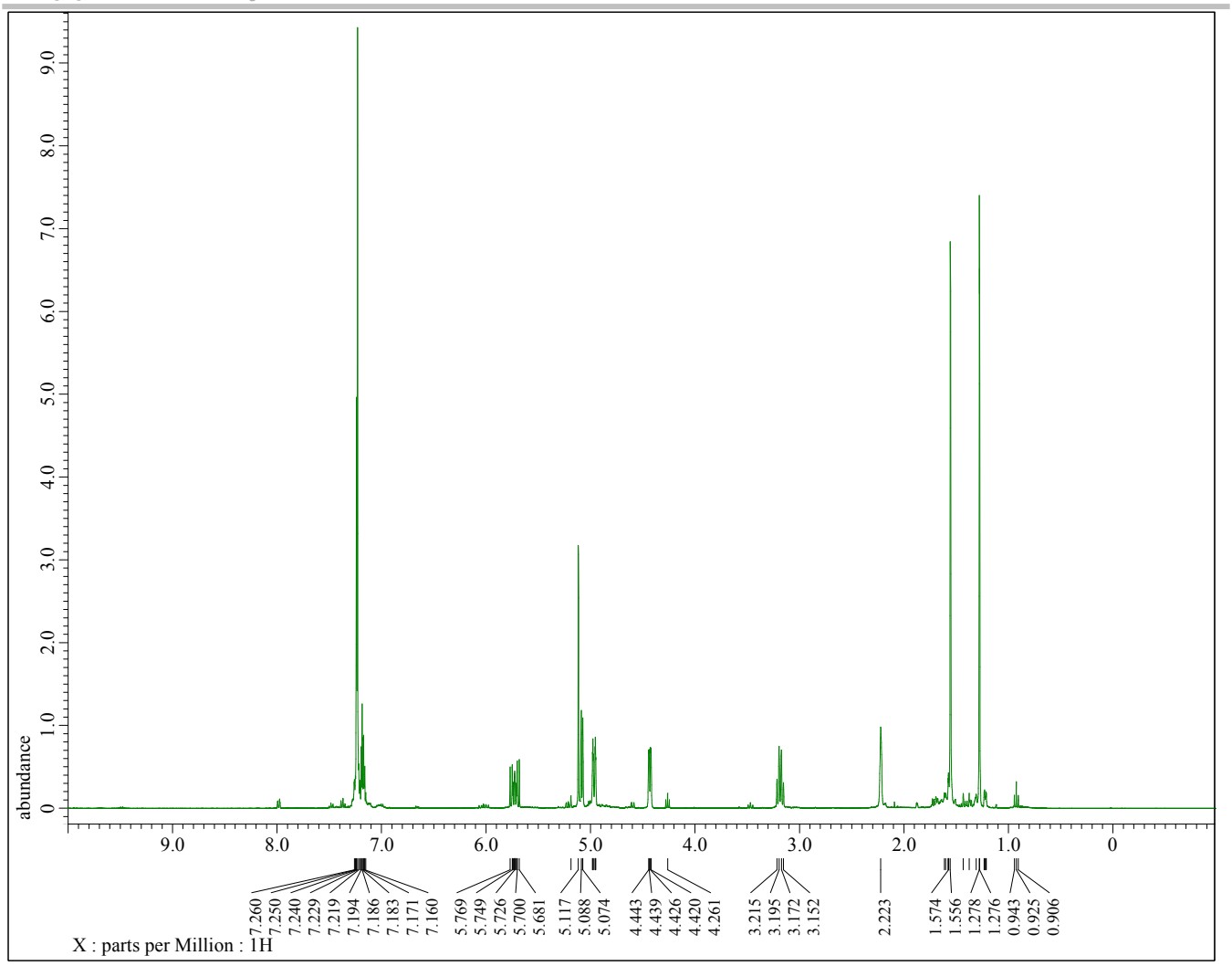
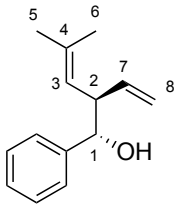


Figure S116. ^{1}H NMR spectrum of *rac*-(1*S*,2*R*)-4-methyl-1-phenyl-2-vinylpent-3-en-1-ol [*anti*-**18**] (In situ reaction in an NMR tube) (400 MHz, [D]chloroform).



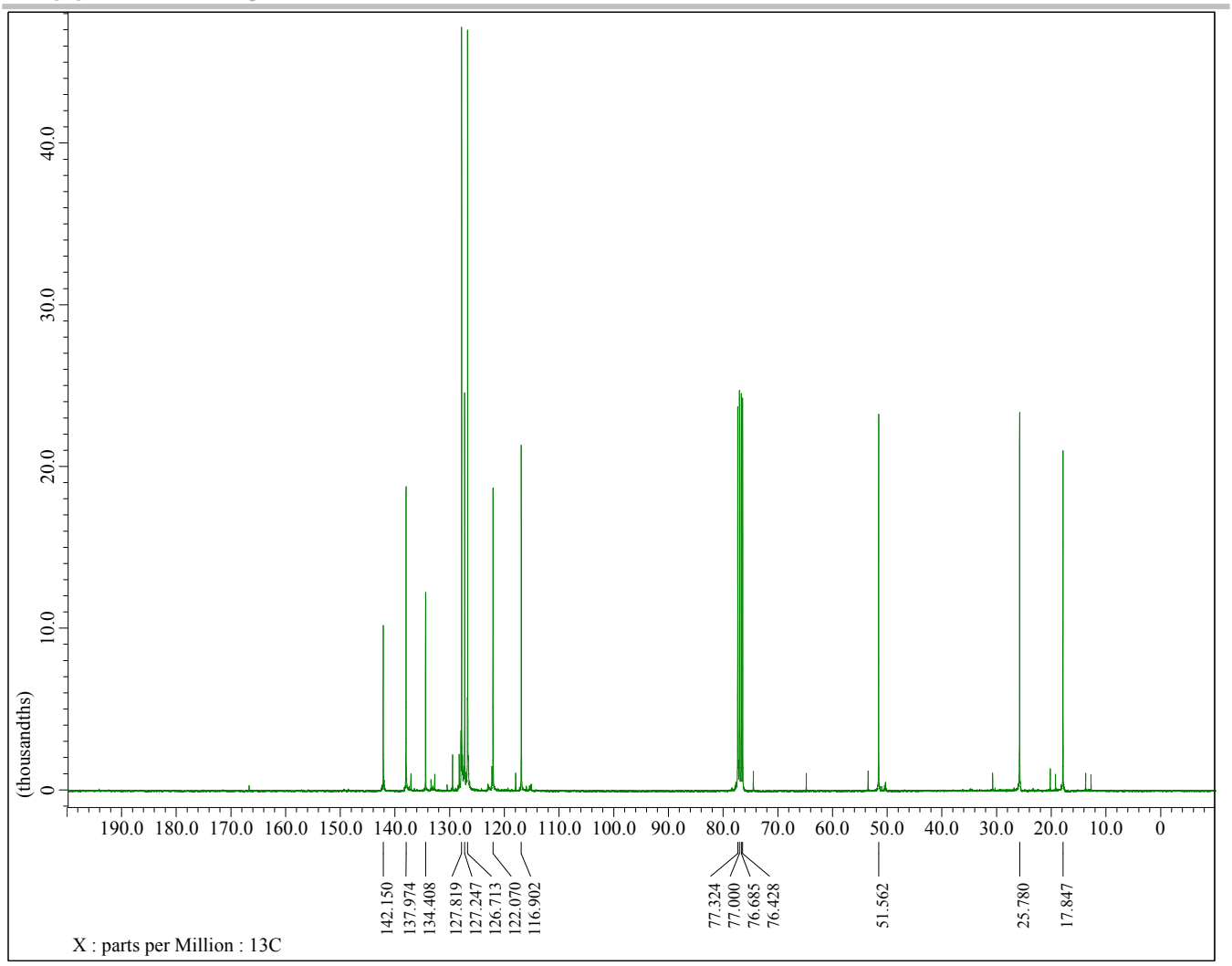


Figure S117. $^{13}C\{^{1}H\}$ NMR spectrum of *rac*-(1*S*,2*R*)-4-methyl-1-phenyl-2-vinylpent-3-en-1-ol [*anti*-**18**] (In situ reaction in an NMR tube) (100 MHz, [D]chloroform).