

Iterative reactions of transient boronic acids enable sequential C-C bond formation

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General experimental section. ^1H -NMR spectra were recorded on a Bruker Avance DPX-400 DRX-500 Cryo or DRX-600 spectrometer with the residual solvent peak as the internal reference ($\text{CDCl}_3 = 7.26 \text{ ppm}$). ^1H resonances are reported to the nearest 0.01 ppm. ^{13}C -NMR spectra were recorded on the same spectrometers with the central resonance of the solvent peak as the internal reference ($\text{CDCl}_3 = 77.16 \text{ ppm}$). All ^{13}C resonances are reported to the nearest 0.1 ppm. The multiplicity of ^1H signals are indicated as: s = singlet, d = doublet, t = triplet, m = multiplet, br. = broad, or combinations of thereof. Coupling constants (J) are quoted in Hz and reported to the nearest 0.1 Hz. Where appropriate, averages of the signals from peaks displaying multiplicity were used to calculate the value of the coupling constant. Infrared spectra were recorded neat on a PerkinElmer Spectrum One FT-IR spectrometer using Universal ATR sampling accessories. High resolution mass spectrometry (HRMS) was performed using a Waters Micromass LCT Premier[™] spectrometer using time of flight with positive ESI, or conducted by Mr Paul Skelton on a Bruker BioApex 47e FTICR spectrometer using (positive) ESI or EI at 70 eV within a tolerance of 5 ppm of the theoretically calculated value. Alternatively, samples were analysed at the Mass Spectrometry Centre at Swansea. LC-MS analysis was performed on an Agilent HP 1100 series chromatography (Mercury Luna 3u C18 (2) column) attached to a Waters ZQ2000 mass spectrometer with ESI ionization source in ESI mode. Elution was carried out at a flow rate of 0.6 mL min^{-1} using a reverse phase gradient of acetonitrile and water containing 0.1% formic acid. Retention time (R_t) is given in min to the nearest 0.1 min and the m/z value is reported to the nearest mass unit (m.u.).

All the flow reactions were performed using a Vapourtec R2+R4 platform¹. In-line IR spectroscopy was performed using the Mettler Toledo FlowIR[®] device². The solutions of diazo compounds were dispensed using a Masterflex peristaltic pump.³

Unless stated otherwise, reagents were obtained from commercial sources and used without purification. Activated MnO_2 was purchased from Sigma Aldrich.⁴ The removal of solvent under reduced pressure was carried out on a standard rotary evaporator. Unless otherwise stated, yields of compounds were calculated based on the titrated diazo compounds and refer to isolated compounds estimated to be $\geq 95\%$ pure as determined by ^1H NMR.

General procedure for the preparation of aryl and allylhydrazones

Aryl and allylic hydrazones were synthesized following a procedure reported in the literature. These compounds were used without further purification.⁵

General procedure for the preparation of diazo compounds in flow

Diazo compounds **2a-t** were prepared under flow conditions, following the procedure previously reported.⁶ The solution containing the diazo compound was collected into a double jacketed cryogenic reservoir, kept at -20°C , in the presence of molecular sieves $4 \text{ \AA}$. The concentration of the diazo solution was exactly determined via comparison with an internal standard (i.e. trimethoxy benzene): 1 ml of solution containing the diazo compound was quenched dropwise with a solution containing a slight excess of glacial acetic acid. After

stirring for 15 min the solvent was removed *in vacuo* and the residue dissolved in a solution of trimethoxy benzene (0.10 M) in CDCl₃.

General procedure (P1) for the preparation of pinacol esters 5a1-5a9 and 5b-r

Boronic acid (4.5 mL, 1.5 equiv, 0.45 mmol, 0.1 M) and DIPEA (3.0 equiv) were dissolved in dry CH₂Cl₂ and stored over molecular sieves (4 Å) under inert atmosphere. This solution was then transferred to a round-bottom flask equipped with a stirring bar under inert atmosphere. Afterwards, the solution of the corresponding diazo compound **2** (0.3 mmol) was added using a peristaltic pump (addition time reported in **Table S1**). The reaction mixture was stirred for the time indicated (reaction time) in **Table S1**, followed by addition of pinacol (2.5 M in CH₂Cl₂, 0.6 mL, 5.0 equiv, 1.5 mmol). After stirring for 16 h the reaction mixture was concentrated and passed through a plug of silica gel to remove the excess pinacol and DIPEA. The crude material was purified *via* flash chromatography using a Biotage SP4 system at high flow rate (10-15 min run time).

Table S1. Addition and reaction times for different diazo species.

Entry	Compound	Addition time	Reaction time ^a
2a	1-(diazomethyl)-3-methoxybenzene	120 min	15 min
2b	1-(diazomethyl)-4-methoxybenzene	30 min	15 min
2c	4-(diazomethyl)-N,N-dimethylaniline	45 min	15 min
2d	1-(diazomethyl)-3-nitrobenzene	6h	72 h
2e	3-(diazomethyl)pyridine	120 min	60 min
2f	5-(diazomethyl)-1,3-diiodo-2-methoxybenzene	90 min	30 min
2g	3-(diazomethyl)benzonitrile	120 min	15 min
2h	1-bromo-3-(diazomethyl)benzene	150 min	30 min
2i	1-(diazomethyl)-2-methylbenzene	120 min	15 min
2j	1-(diazomethyl)-4-(trifluoromethyl)benzene	120 min	15 min
2k	2-(diazomethyl)-1,3,5-trimethoxybenzene	60 min	15 min
2l	methyl 4-(diazomethyl)benzoate	180 min	60 min
2m	2-(diazomethyl)furan	30 min	15 min
2n	3-(diazomethyl)thiophene	60 min	15 min
2o	(3-diazoprop-1-en-1-yl)benzene	30 min	60 min
2p	1-diazo-3,7-dimethylocta-2,6-diene	30 min	15 min
2q	(3-diazoprop-1-en-1-yl)furan	10 min	30 min
2r	1-(1-diazoethyl)-4-fluorobenzene	120 min	360 min
2s	1-diazo-7-methoxy-1,2,3,4-tetrahydronaphthalene	120 min	360 min
2t	1-(diazomethyl)-4-bromobenzene	120 min	360 min

^a Reaction time refers to the additional time of stirring after addition of the entire solution of the diazo compound.

General procedure (P2) for the preparation of benzyl and allylic boronic pinacol esters 6a-g

Boronic acid (1.0 equiv, 0.2 mmol, 0.1 M) and DIPEA (2.0 equiv) were dissolved in dry CH₂Cl₂ (2 mL) and stored over molecular sieves (4 Å) under inert atmosphere. This solution was then transferred into a round-bottom flask equipped with a stirring bar under inert atmosphere. Afterwards, the solution of the diazo compound **2** (0.2 mmol) was added using a peristaltic pump (addition time reported in **Table S1**). The reaction mixture was stirred for the time indicated (reaction time) in **Table S1** followed by a second portion of the solution of diazo compound **2** (0.2 mmol) under analogous conditions. The reaction mixture was stirred for further 30 min and then quenched by adding a solution of pinacol (2.5 M in CH₂Cl₂, 0.4 mL, 5 equiv, 1.0 mmol) and 0.5 g of sodium sulfate. After stirring for 16 h the reaction mixture was passed through a plug of silica gel to remove the excess pinacol and DIPEA and then concentrated. The crude material was purified *via* flash chromatography using a Biotage SP4 system at high flow rate (10-15 min run time).

General procedure (P3) for the preparation of protodeboronated compounds 6h-o

Boronic acid (1.2 equiv, 0.24 mmol, 0.1 M) and DIPEA (2.4 equiv) were dissolved in dry CH₂Cl₂ (2.4 mL) and stored over molecular sieves (4 Å) under inert atmosphere. This solution was then transferred into a round-bottom flask equipped with a stirring bar under inert atmosphere. Afterwards, the solution of the diazo compound **2** (0.2 mmol) was added using a peristaltic pump (time of addition reported in **Table S1**). Then a solution of the second diazo compound **2e/2l** (0.3 mmol) was added to the reaction mixture using a peristaltic pump (**Table S1**). The reaction mixture was stirred for 48h, passed through a plug of silica gel to remove DIPEA and concentrated. The crude material was then purified *via* flash chromatography using a Biotage SP4 system.

General procedure (P4) for the preparation of triple addition products 8a-c

Boronic acid (1.2 equiv, 0.24 mmol, 0.1 M) and DIPEA (2.4 equiv) were dissolved in dry CH₂Cl₂ (2.4 mL) and stored over molecular sieves (4 Å) under inert atmosphere. This solution was then transferred into a round-bottom flask equipped with a stirring bar under inert atmosphere. Afterwards, the solution of the diazo compound **2** (0.2 mmol) was added using a peristaltic pump (addition time reported in **Table S1**). The reaction mixture was stirred for 30 min before a second portion of diazo compound (0.22 mmol, 1.1 equiv) was added using a peristaltic pump (addition time reported in **Table S1**). The mixture was stirred for 30 min and then a third portion of a diazo compound **2e/2l** (0.4 mmol, 2.0 equiv) was added using a peristaltic pump (addition time reported in **Table S1**). After 48h the reaction mixture was passed through a plug of silica gel to remove DIPEA and then concentrated *in vacuo*. The crude material was then purified *via* flash chromatography using a Biotage SP4 system.

General procedure (P5) for the preparation of compounds 11a-o

Method A:

A solution of the allylic diazo compound **2** (0.20 mmol) was added to a solution of boronic acid (0.30 mmol, 1.50 equiv.), aldehyde (0.24 mmol, 1.20 equiv.) and DIPEA (0.10 mL) in dry CH_2Cl_2 (2 mL), under inert atmosphere at room temperature, using a peristaltic pump. The reaction mixture was stirred for 16 h and then quenched by addition of MeOH (2 mL). The solvent was removed under reduced pressure and the crude product was purified by column chromatography using a Biotage SP4 system.

Alternative flow protocol

A solution of the allylic diazo compound **2** (0.20 mmol) was combined with a solution of boronic acid (0.30 mmol, 1.50 equiv.), aldehyde (0.24 mmol, 1.20 equiv.) and DIPEA (0.10 mL) in dry CH_2Cl_2 /THF (5:1, v/v, 2 mL),* under inert atmosphere and reacted in a 10 mL CPF reactor at 40 °C (residence time 33 min) and collected in a flask. The reaction mixture was then quenched by addition of MeOH (2 mL). The solvent was removed under reduced pressure and the crude product was purified by column chromatography using a Biotage SP4 system.

*loaded in a 2 mL reaction loop

Method B:

A solution of the allylic diazo compound **2** (0.70 mmol)** was added to a solution of boronic acid (0.30 mmol), aldehyde (0.20 mmol) and DIPEA (0.10 mL) in dry CH_2Cl_2 (2 mL), under inert atmosphere at room temperature, using a peristaltic pump. The reaction mixture was stirred for 16 h and then quenched by addition of MeOH (2 mL) and SiO_2 . The solvent was removed under reduced pressure and the crude product was purified by column chromatography using a Biotage SP4 system. The yield was calculated based on the amount of aldehyde.

Alternative flow protocol

A solution of the allylic diazo compound **2** (0.70 mmol)** was combined with a solution of boronic acid (0.30 mmol), aldehyde (0.20 mmol) and DIPEA (0.10 mL) in dry CH_2Cl_2 /THF (5:1, v/v, 2 mL),*** under inert atmosphere, and reacted in a 10 mL CPF reactor at 40 °C (residence time 33 min) and collected in a flask. The reaction mixture was then quenched by addition of MeOH (2 mL) and SiO_2 . The solvent was removed under reduced pressure and the crude product was purified by column chromatography using a Biotage SP4 system. The yield was calculated based on the amount of aldehyde.

**the amount of diazo could not be exactly detected and we used an excess based on 0.70 mmol of the starting material hydrazone

***loaded in a 2 mL reaction loop

General procedure (P6) for the 4-component reaction for compounds 13a-b

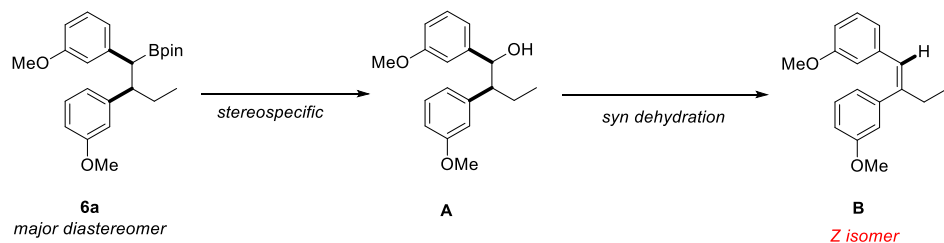
A solution of the first diazo compound (0.20 mmol, 1.0 equiv.) was added to a solution of boronic acid (0.24 mmol, 1.2 equiv.) and DIPEA (0.10 mL) in dry CH₂Cl₂ (2 mL) using a peristaltic pump (**Table S1**). After complete discoloring of the reaction mixture, a solution of the aldehyde (0.36 mmol) in CH₂Cl₂ (2 mL) was added. This was followed by addition of the solution of the allylic diazo compound (0.20 mmol) over 15 min, using a peristaltic pump. The reaction mixture was stirred for 16 h and then quenched by addition of MeOH (2 mL) and SiO₂. The solvent was removed under reduced pressure and the crude product was purified by column chromatography using a Biotage SP4 system. The yield was based on the first diazo compound.

General procedure (P7) for the 4-component reaction for compound 13c

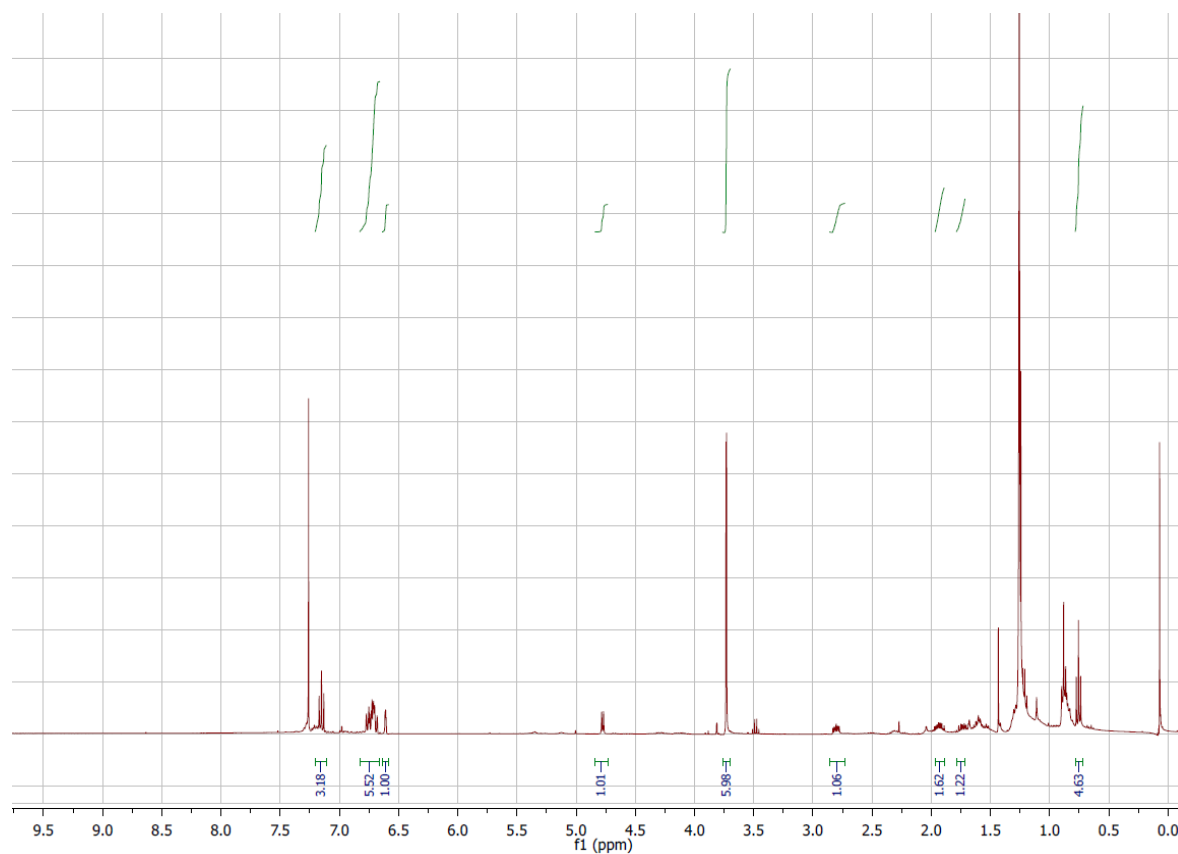
A solution of diazo compound (0.20 mmol, 1.0 equiv.) was added to a solution of boronic acid (0.24 mmol, 1.2 equiv.) and DIPEA (0.10 mL) in CH₂Cl₂ (2 mL), using a peristaltic pump (**Table S1**). After complete discoloring of the reaction mixture, another portion of solution of the allylic diazo compound (0.20 mmol) was added over 15 min (using a peristaltic pump). After 30 min, a solution of the aldehyde (0.36 mmol) in CH₂Cl₂ (2 mL) was slowly added. The reaction mixture was stirred for 16 h and then quenched by addition of MeOH (2 mL) and SiO₂. The solvent was removed under reduced pressure and the crude product was purified by column chromatography using a Biotage SP4 system.

Oxidation and dehydration of 6a (major diastereomer)

Oxidation of **6a** was performed using H_2O_2 and NaOH (3 M) under inert atmosphere as previously reported in the literature.⁷

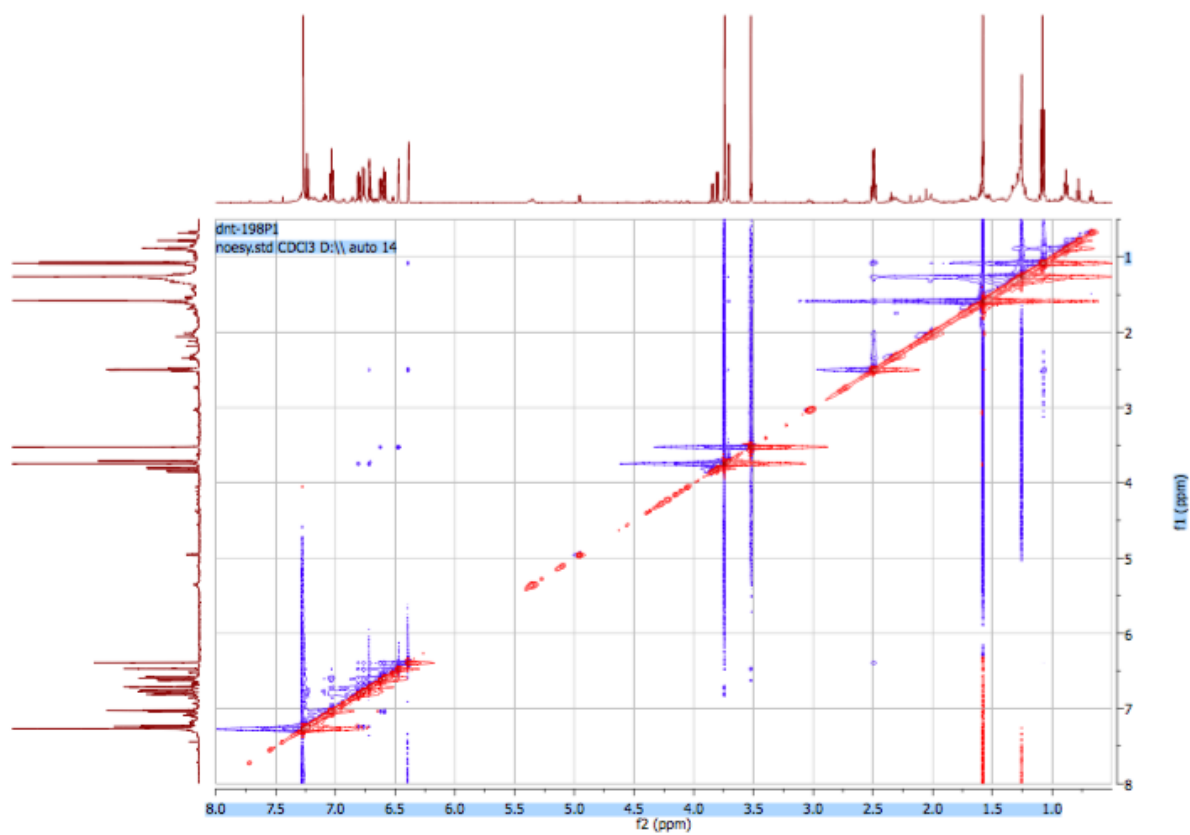


Alcohol A (crude) ^1H -NMR



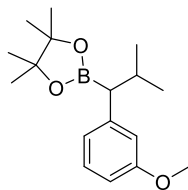
The alcohol was then treated (under inert conditions) with Burgess reagent (1.5 eq.) in toluene (80°C for 30 min). The reaction mixture was passed through a plug of silica gel to obtain the corresponding alkene.

Alkene **B** NOE



COMPOUNDS CHARACTERIZATION

2-(1-(3-Methoxyphenyl)-2-methylpropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5a1)



The product was obtained following **P1**, after purification by chromatography using a Biotage SP4 (hexane/ethyl acetate, 100:1–40:1, v/v, 48 ml column volume), as a colorless oil (73 mg, 87% yield). $R_f = 0.57$ (hexane/ethyl acetate, 10:1 v/v). This example was run on a 3.5 mmol scale to afford 1.091 g of product (81% yield).

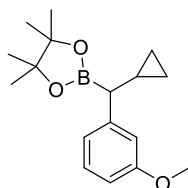
^1H NMR (400 MHz, CDCl_3) δ 7.15 (t, $J = 7.8$ Hz, 1H), 6.84 – 6.75 (m, 2H), 6.68 (dd, $J = 8.2$, 1.9 Hz, 1H), 3.78 (s, 3H), 2.16 – 2.03 (m, 1H), 1.94 (d, $J = 10.4$ Hz, 1H), 1.20 (s, 6H), 1.18 (s, 6H), 1.02 (d, $J = 6.5$ Hz, 3H), 0.74 (d, $J = 6.5$ Hz, 3H) ppm.

^{13}C NMR (151 MHz, CDCl_3) δ 159.5, 144.1, 129.0, 121.8, 114.7, 110.8, 83.3, 55.1, 31.1, 24.8, 24.7, 23.2, 22.1 ppm.

FT-IR (neat, ν_{max}) 2975, 1598, 1581, 1486, 1465, 1380, 1353, 1318, 1258, 1214, 1139, 1139, 1113, 1047, 971, 865, 848, 777, 714, 694, 672 cm^{-1} .

HRMS ($\text{C}_{17}\text{H}_{28}\text{O}_3$ $^{11}\text{B} = [\text{M}+\text{H}]^+$): calcd. 291.2126; found 291.2115.

2-(Cyclopropyl(3-methoxyphenyl)methyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5a2)



The product was obtained following **P1**, after purification by chromatography using a Biotage SP4 (hexane/ethyl acetate, 100:1–40:1, v/v, 48 ml column volume), as a yellowish oil (49 mg, 56% yield). $R_f = 0.61$ (hexane/ethyl acetate, 10:1 v/v).

^1H NMR (600 MHz, CDCl_3) δ 7.19 (t, $J = 7.9$ Hz, 1H), 6.88 (d, $J = 7.3$ Hz, 2H), 6.71 (dd, $J = 7.4$, 1.7 Hz, 1H), 3.80 (s, 3H), 1.70 (d, $J = 9.7$ Hz, 1H), 1.23 (s, 6H), 1.23 (s, 6H), 1.18 – 1.10 (m, 1H), 0.61 – 0.53 (m, $J = 9.3$, 7.3, 5.0 Hz, 1H), 0.51 – 0.45 (m, 1H), 0.24 (td, $J = 9.5$, 4.9 Hz, 1H), 0.10 (td, $J = 9.6$, 5.0 Hz, 1H) ppm.

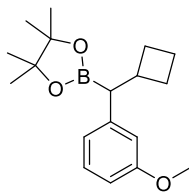
^{13}C NMR (151 MHz, CDCl_3) δ 159.6, 144.9, 129.2, 120.9, 114.1, 110.7, 83.5, 55.2, 24.8, 24.8, 13.1, 5.2, 4.8 ppm.

^{11}B NMR (128 MHz, CDCl_3) δ 22.27.

FT-IR (neat, ν_{max}) 2927, 1670, 1598, 1584, 1487, 1453, 1429, 1381, 1323, 1230, 1205, 1147, 1036, 1108, 968, 897, 851, 786, 741, 698, 671 cm^{-1} .

LC-MS: retention time 5.22 min, m/z $[\text{M}+\text{H}] = 289.24$.

2-(Cyclobutyl(3-methoxyphenyl)methyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5a3)



The product was obtained following **P1**, after purification by chromatography using a Biotage SP4 (hexane/ethyl acetate, 100:1–30:1, v/v, 48 ml column volume) as a slightly yellowish oil (0.26 mmol scale, 51 mg, 65% yield). R_f = 0.54 (hexane/ethyl acetate, 10:1 v/v).

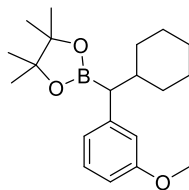
^1H NMR (600 MHz, CDCl_3) δ 7.15 (t, J = 7.9 Hz, 1H), 6.78 (d, J = 7.6 Hz, 1H), 6.76 – 6.74 (m, 1H), 6.68 (ddd, J = 8.2, 2.6, 0.8 Hz, 1H), 3.78 (s, 3H), 2.75 (m, 1H), 2.32 (d, J = 11.1 Hz, 1H), 2.21 – 2.10 (m, 1H), 1.91 (ddq, J = 14.9, 7.5, 3.8 Hz, 1H), 1.86 – 1.76 (m, 2H), 1.76 – 1.68 (m, 1H), 1.62 – 1.55 (m, 1H), 1.21 (s, 6H), 1.19 (s, 6H) ppm.

^{13}C NMR (151 MHz, CDCl_3) δ 159.6, 143.6, 129.1, 121.1, 114.2, 110.7, 83.3, 55.2, 38.5, 29.0, 28.7, 24.8, 24.7, 18.3 ppm.

FT-IR (neat, ν_{max}) 2976, 2935, 2863, 1682, 1599, 1583, 1487, 1452, 1435, 1371, 1355, 1320, 1259, 1140, 1044, 982, 969, 851, 776, 746, 713, 700, 671 cm^{-1} .

HRMS ($\text{C}_{20}\text{H}_{28}\text{O}_3$ ^{11}B = $[\text{M}+\text{H}]^+$): calcd. 303.2121; found 303.2126.

2-(Cyclohexyl(3-methoxyphenyl)methyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5a4)



The product was obtained following **P1**, after purification by chromatography using a Biotage SP4 (hexane/ethyl acetate, 100:1–40:1, v/v, 48 ml column volume), as a colorless oil (73 mg, 74% yield). R_f = 0.64 (hexane/ethyl acetate, 10:1 v/v).

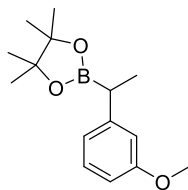
^1H NMR (600 MHz, CDCl_3) δ 7.14 (t, J = 7.8 Hz, 1H), 6.78 (dd, J = 9.6, 4.9 Hz, 2H), 6.68 (dd, J = 8.1, 2.0 Hz, 1H), 3.78 (s, 3H), 2.02 (d, J = 10.5 Hz, 1H), 1.87 – 1.74 (m, 2H), 1.74 – 1.66 (m, 1H), 1.60 (dd, J = 11.1, 8.0 Hz, 2H), 1.48 (d, J = 13.0 Hz, 1H), 1.37 – 1.28 (m, 1H), 1.20 (s, 6H), 1.18 (s, 6H), 1.11 (dt, J = 15.6, 7.8 Hz, 2H), 1.03 (ddd, J = 23.8, 12.5, 3.5 Hz, 1H), 0.72 (qd, J = 12.6, 3.4 Hz, 1H) ppm.

^{13}C NMR (151 MHz, CDCl_3) δ 159.5, 143.6, 129.0, 121.9, 114.7, 110.8, 83.3, 55.2, 40.5, 33.9, 32.6, 26.7, 26.7, 26.5, 24.9, 24.7 ppm.

FT-IR (neat, ν_{max}) 2976, 2921, 2850, 1598, 1581, 1486, 1448, 1379, 1370, 1353, 1317, 1254, 1214, 1140, 1047, 972, 864, 849, 778, 715, 693, 672 cm^{-1} .

HRMS ($\text{C}_{20}\text{H}_{32}\text{O}_3$ ^{11}B = $[\text{M}+\text{H}]^+$): calcd. 331.2437; found 331.2439.

2-(1-(3-Methoxyphenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5a5)



The product was obtained following **P1**, after purification by chromatography using a Biotage SP4 (hexane/ethyl acetate, 100:1–20:1, v/v, 48 ml column volume), as a colorless oil (16.5 mg, 21 % yield). R_f = 0.51 (hexane/ethyl acetate, 10:1 v/v).

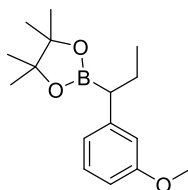
^1H NMR (600 MHz, CDCl_3) δ 7.18 (t, J = 7.9 Hz, 1H), 6.83 – 6.77 (m, 2H), 6.69 (ddd, J = 8.2, 2.5, 0.7 Hz, 1H), 3.79 (s, 3H), 2.41 (q, J = 7.5 Hz, 1H), 1.32 (d, J = 7.5 Hz, 3H) 1.22 (s, 6H), 1.20 (s, 6H) ppm.

^{13}C NMR (151 MHz, CDCl_3) δ 159.6, 146.6, 129.2, 120.3, 113.5, 110.52, 83.3, 55.1, 24.6, 24.6, 17.0 ppm.

^{11}B NMR (128 MHz, CDCl_3) δ 22.24 ppm.

FT-IR (neat, ν_{max}) 2975, 2927, 1599, 1484, 1454, 1436, 1372, 1349, 1321, 1258, 1141, 1142, 1045, 982, 859, 780, 699, 672 cm^{-1} .

2-(1-(3-Methoxyphenyl)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5a6)



The product was obtained following **P1**, after purification by chromatography using a Biotage SP4 (hexane/ethyl acetate, 100:1–40:1, v/v, 48 ml column volume) as a colorless oil (34.0 mg, 41% yield). R_f = 0.55 (hexane/ethyl acetate, 10:1 v/v).

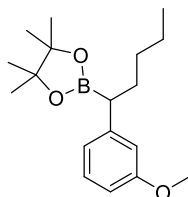
^1H NMR (600 MHz, CDCl_3) δ 7.16 (t, J = 7.9 Hz, 1H), 6.80 (d, J = 7.6 Hz, 1H), 6.79 – 6.76 (m, 1H), 6.70 – 6.66 (m, 1H), 3.78 (s, 3H), 2.20 (t, J = 7.9 Hz, 1H), 1.92 – 1.82 (m, 1H), 1.71 – 1.63 (m, 1H), 1.21 (s, 6H), 1.20 (s, 6H), 0.91 (t, J = 7.3 Hz, 3H) ppm.

^{13}C NMR (151 MHz, CDCl_3) δ 159.7, 145.2, 129.2, 121.1, 114.1, 110.7, 83.4, 55.2, 25.9, 24.8, 24.8, 14.1 ppm.

FT-IR (neat, ν_{max}) 2973, 2935, 1703, 1600, 1586, 1486, 1454, 1432, 1372, 1322, 1260, 1192, 1147, 1041, 981, 964, 851, 780, 738, 699, 671 cm^{-1} .

HRMS ($\text{C}_{16}\text{H}_{25}\text{O}_3$ ^{11}BNa = $[\text{M}+\text{Na}]^+$): calcd. 299.1789; found 299.1776.

2-(1-(3-Methoxyphenyl)pentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5a7)



The product was obtained following **P1**, after purification by chromatography using a Biotage SP4 (hexane/ethyl acetate, 100:1–40:1, v/v 48 ml column volume), as a colorless oil. R_f = 0.55 (hexane/ethyl acetate, 10:1 v/v). 63.0 mg (69%).

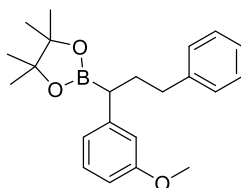
^1H NMR (600 MHz, CDCl_3) δ 7.16 (t, J = 7.9 Hz, 1H), 6.81 (d, J = 7.6 Hz, 1H), 6.78 (d, J = 2.0 Hz, 1H), 6.68 (dd, J = 8.1, 2.2 Hz, 1H), 3.79 (s, 3H), 2.27 (t, J = 7.9 Hz, 1H), 1.83 (td, J = 15.3, 7.9 Hz, 1H), 1.64 (td, J = 15.2, 7.7 Hz, 1H), 1.37 – 1.22 (m, 4H), 1.21 (s, 6H), 1.20 (s, 6H), 0.86 (t, J = 7.2 Hz, 3H) ppm.

^{13}C NMR (151 MHz, CDCl_3) δ 159.7, 145.3, 129.2, 121.0, 114.1, 110.7, 83.4, 55.2, 32.4, 31.7, 24.8, 24.8, 22.8, 14.2 ppm.

FT-IR (neat, ν_{max}) 2977, 2956, 2926, 2352, 1599, 1582, 1487, 1466, 1437, 1358, 1321, 1257, 1214, 1141, 1111, 1049, 968, 862, 779, 728, 706, 691 cm^{-1} .

HRMS ($\text{C}_{18}\text{H}_{30}\text{O}_3$ ^{11}B = $[\text{M}+\text{H}]^+$): calcd. 305.2283; found 305.2272.

2-(1-(3-Methoxyphenyl)-3-phenylpropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5a8)



The product was obtained following **P1**, after purification by chromatography using a Biotage SP4 (hexane/ethyl acetate/THF = 100:1:1–30:1:1, v/v, 48 ml column volume), as a yellowish oil (65 mg, 62% yield). R_f = 0.53 (hexane/ethyl acetate, 10:1 v/v).

^1H NMR (600 MHz, CDCl_3) δ 7.27 (dd, J = 10.0, 5.2 Hz, 2H), 7.21 – 7.14 (m, 4H), 6.83 (d, J = 7.6 Hz, 1H), 6.81 – 6.79 (m, 1H), 6.71 (dd, J = 8.2, 2.1 Hz, 1H), 3.80 (s, 3H), 2.58 (t, J = 7.9 Hz, 2H), 2.35 (t, J = 7.9 Hz, 1H), 2.21 – 2.10 (m, 1H), 2.05 – 1.93 (m, 1H), 1.23 (s, 6H), 1.21 (s, 6H).

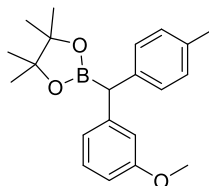
^{13}C NMR (151 MHz, CDCl_3) δ 159.7, 144.7, 142.7, 129.3, 128.6, 128.4, 125.8, 121.1, 114.1, 110.9, 83.5, 55.2, 35.5, 34.5, 24.8, 24.8 ppm.

^{11}B NMR (128 MHz, CDCl_3) δ 22.23 ppm.

FT-IR (neat, ν_{max}) 3026, 2978, 2933, 2365, 1705, 1598, 1582, 1487, 1454, 1359, 1320, 1259, 1214, 1140, 1108, 1045, 1106, 967, 850, 778, 750, 699, 671 cm^{-1} .

LC-MS : retention time 5.94 min, m/z $[\text{M}+\text{H}] = 353.17$.

2-((3-Methoxyphenyl)(p-tolyl)methyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5a9)



The product was obtained following **P1**, after purification by chromatography using a Biotage SP4 (hexane/ethyl acetate = 100:1–20:1, v/v, 48 ml column volume), as a colorless oil (40 mg, 39% yield). R_f = 0.52 (hexane/ethyl acetate, 10:1 v/v).

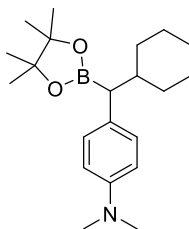
^1H NMR (400 MHz, CDCl_3) δ 7.20 – 7.12 (m, 3H), 7.07 (d, J = 7.9 Hz, 2H), 6.83 (m, 2H), 6.70 (ddd, J = 8.2, 2.5, 0.8 Hz, 1H), 3.79 (s, 1H), 3.75 (s, 3H), 2.29 (s, 3H), 1.23 (s, 12H) ppm.

^{13}C NMR (100 MHz, CDCl_3) δ 159.7, 144.2, 138.9, 135.2, 129.4, 129.3, 129.1, 121.7, 115.0, 111.1, 83.8, 55.2, 24.8, 24.6, 21.1 ppm.

^{11}B NMR (128 MHz, CDCl_3) δ 22.27 ppm.

FT-IR (neat, ν_{max}) 2927, 2856, 1705, 1598, 1582, 1511, 1487, 1453, 1372, 1329, 1258, 1215, 1138, 1106, 1089, 1050, 969, 851, 819, 785, 747, 724, 696, 671 cm^{-1} .

4-(Cyclohexyl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-N,N-dimethylaniline (5b)



The product was obtained following **P1**, after purification by chromatography using a Biotage SP4 (gradient hexane/ethyl acetate, 100:1–40:1, v/v, 48 ml column volume), as a yellowish solid (73 mg, 69% yield). R_f = 0.36 (hexane/ethyl acetate, 10:1 v/v).

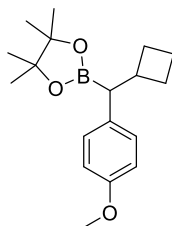
^1H NMR (600 MHz, CDCl_3) δ 7.07 (d, J = 8.7 Hz, 2H), 6.67 (d, J = 8.5 Hz, 2H), 2.90 (s, 6H), 1.94 (d, J = 10.3 Hz, 1H), 1.82 (d, J = 12.6 Hz, 1H), 1.74 – 1.66 (m, 2H), 1.64 – 1.56 (m, 2H), 1.54 – 1.46 (m, 1H), 1.37 – 1.25 (m, 1H), 1.20 (s, 6H), 1.18 (s, 6H), 1.14 – 1.08 (m, J = 9.3, 3.1 Hz, 2H), 1.02 (ddd, J = 24.0, 12.5, 3.6 Hz, 1H), 0.71 (ddd, J = 24.0, 12.5, 3.4 Hz, 1H) ppm.

^{13}C NMR (151 MHz, CDCl_3) δ 148.5, 129.9, 113.0, 83.1, 41.1, 40.6, 33.9, 32.6, 26.8, 26.7, 26.5, 24.9, 24.7 ppm.

FT-IR (neat, ν_{max}) 2969, 2917, 2851, 2806, 1741, 1612, 1518, 1445, 1378, 1347, 1316, 1275, 1217, 1166, 1144, 1066, 973, 949, 885, 850, 811, 794, 738, 725, 683, 656 cm^{-1} .

HRMS ($\text{C}_{21}\text{H}_{35}\text{O}_2\text{N}_1^{11}\text{B}$ = $[\text{M}+\text{H}]^+$): calcd. 344.2755; found 344.2750.

2-(Cyclobutyl(4-methoxyphenyl)methyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5c)



The product was obtained following **P1**, after purification by chromatography using a Biotage SP4 (gradient hexane/ethyl acetate, 80:1–30:1, v/v, 48 ml column volume), as a colorless oil (0.35 mmol scale, 88 mg, 84 % yield). R_f = 0.55 (hexane/ethyl acetate, 10:1 v/v).

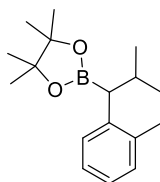
^1H NMR (600 MHz, CDCl_3) δ 7.09 (d, J = 8.6 Hz, 2H), 6.79 (d, J = 8.7 Hz, 2H), 3.76 (s, 3H), 2.70 (m, 1H), 2.27 (d, J = 11.0 Hz, 1H), 2.13 (dtt, J = 14.7, 7.3, 3.8 Hz, 1H), 1.89 (dtt, J = 11.4, 7.6, 3.9 Hz, 1H), 1.85 – 1.74 (m, 2H), 1.74 – 1.65 (m, 1H), 1.56 (dt, J = 12.9, 8.7 Hz, 1H), 1.21 (s, 6H), 1.18 (s, 6H) ppm.

^{13}C NMR (151 MHz, CDCl_3) δ 157.3, 133.8, 129.3, 113.6, 83.1, 55.1, 38.6, 28.7, 28.5, 24.9, 24.7, 24.6, 18.1 ppm.

FT-IR (neat, ν_{max}) 2977, 2933, 1671, 1612, 1512, 1472, 1436, 1371, 1322, 1246, 1168, 1147, 1034, 1008, 982, 968, 905, 850, 832, 789, 696, 669 cm^{-1} .

HRMS ($\text{C}_{18}\text{H}_{28}\text{O}_3$ ^{11}B = $[\text{M}+\text{H}]^+$): calcd. 303.2126; found 303.2116.

2-(2-Methyl-1-(o-tolyl)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5d)



The product was obtained following **P1**, after purification by chromatography using a Biotage SP4 (hexane/ethyl acetate, 100:1–25:1, v/v, 48 ml column volume) as a yellowish solid (0.42 mmol scale, 96 mg, 84% yield). R_f = 0.54 (hexane/ethyl acetate, 10:1 v/v).

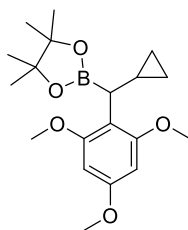
^1H NMR (600 MHz, CDCl_3) δ 7.28 – 7.26 (m, 1H), 7.11 (t, J = 6.7 Hz, 2H), 7.01 (td, J = 7.5, 1.2 Hz, 1H), 2.32 (s, 3H), 2.27 (d, J = 10.5 Hz, 1H), 2.23 – 2.11 (m, 1H), 1.18 (s, J = 17.1 Hz, 6H), 1.15 (s, 6H), 1.06 (t, J = 7.4 Hz, 3H), 0.73 (d, J = 6.5 Hz, 3H) ppm.

^{13}C NMR (151 MHz, CDCl_3) δ 140.9, 136.6, 130.1, 128.4, 125.8, 124.9, 83.2, 31.1, 24.8, 24.7, 23.3, 22.0, 20.7 ppm.

FT-IR (neat, ν_{max}) 2974, 2950, 2868, 1602, 1485, 1465, 1380, 1371, 1351, 1314, 1275, 1252, 1216, 1165, 1143, 1121, 1088, 1033, 969, 893, 863, 850, 775, 761, 727, 686, 669 cm^{-1} .

HRMS ($\text{C}_{17}\text{H}_{28}\text{O}_2$ $^{11}\text{B}_1$ $[\text{M}^++\text{H}]$): calcd. 275.2177; found 275.2171.

2-(Cyclopropyl(2,4,6-trimethoxyphenyl)methyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5e)



The product was obtained following **P1**, after purification by chromatography using a Biotage SP4 (hexane/ethyl acetate = 60:1–10:1, v/v, 48 ml column volume), as a colorless solid (0.2 mmol scale, 64 mg, 90% yield). R_f = 0.49 (hexane/ethyl acetate = 10:1).

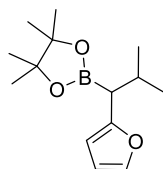
^1H NMR (600 MHz, CDCl_3) δ 6.12 (s, 2H), 3.79 (s, 3H), 3.76 (s, 6H), 1.94 (d, J = 9.7 Hz, 1H), 1.27 (s, 6H), 1.22 (s, 6H), 1.15 – 1.08 (m, 1H), 0.57 – 0.50 (m, 1H), 0.22 – 0.14 (m, 1H), 0.15 – 0.06 (m, 2H) ppm.

^{13}C NMR (151 MHz, CDCl_3) δ 158.9, 158.3, 112.8, 90.6, 82.8, 55.4, 55.3, 25.1, 24.6, 12.8, 5.6, 4.2 ppm.

FT-IR (neat, ν_{max}) 2994, 2968, 2841, 1591, 1497, 1466, 1418, 1387, 1369, 1347, 1329, 1301, 1274, 1229, 1206, 1174, 1145, 1104, 1063, 1042, 1014, 974, 951, 885, 852, 814, 801, 716, 670, 658 cm^{-1} .

HRMS ($\text{C}_{19}\text{H}_{30}\text{O}_5$ ^{11}B = $[\text{M}+\text{H}]^+$): calcd. 349.2181; found 349.2174.

2-(1-(Furan-2-yl)-2-methylpropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5f)



The product was obtained following **P1**, after purification by chromatography using a Biotage SP4 (hexane/ethyl acetate = 100:1–20:1, v/v, 48 ml column volume) as a yellowish oil (0.2 mmol scale, 31 mg, 69% yield). R_f = 0.67 (hexane/ethyl acetate, 10:1 v/v).

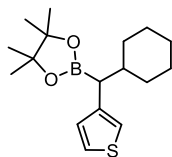
^1H NMR (600 MHz, CDCl_3) δ 7.29 (dd, J = 1.8, 0.8 Hz, 1H), 6.26 (dd, J = 3.0, 1.9 Hz, 1H), 6.04 (d, J = 3.1 Hz, 1H), 2.25 (d, J = 8.3 Hz, 1H), 2.15 – 2.07 (m, 1H), 1.25 (s, 6H), 1.24 (s, 6H), 0.96 (d, J = 6.7 Hz, 3H), 0.85 (d, J = 6.7 Hz, 3H) ppm.

^{13}C NMR (151 MHz, CDCl_3) δ 156.0, 140.8, 110.2, 106.0, 83.6, 30.0, 24.8, 24.8, 22.5, 22.2 ppm.

^{11}B NMR (128 MHz, CDCl_3) δ 22.13 ppm.

FT-IR (neat, ν_{max}) 2977, 1436, 1372, 1326, 1272, 1219, 1145, 1072, 1009, 981, 925, 884, 851, 808, 733, 697, 670 cm^{-1} .

2-(Cyclohexyl(thiophen-3-yl)methyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5g)



The product was obtained following **P1**, after purification by chromatography using a Biotage SP4 (hexane/ethyl acetate = 100:1–30:1, v/v, 48 ml column volume), as a yellow oil (0.2 mmol scale, 37mg, 61% yield). R_f = 0.61 (hexane/ethyl acetate, 10:1 v/v).

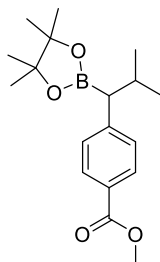
^1H NMR (600 MHz, CDCl_3) δ 7.09 – 7.05 (m, 1H), 6.90 (dd, J = 5.1, 3.4 Hz, 1H), 6.79 (dd, J = 3.4, 0.6 Hz, 1H), 2.40 (d, J = 9.6 Hz, 1H), 1.83 – 1.76 (m, 1H), 1.76 – 1.53 (m, 4H), 1.37 – 1.25 (m, 3H), 1.23 (s, 6H), 1.22 (s, 6H), 1.18 – 1.10 (m, 1H), 1.08 – 0.78 (m, 2H) ppm.

^{13}C NMR (151 MHz, CDCl_3) δ 144.5, 126.5, 124.7, 122.6, 83.5, 41.6, 33.3, 32.4, 28.0, 27.1, 26.8, 26.5, 24.8, 24.7 ppm.

FT-IR (neat, ν_{max}) 2978, 2921, 2851, 1663, 1448, 1380, 1371, 1322, 1273, 1241, 1213, 1166, 1142, 1101, 1006, 971, 883, 850, 689 cm^{-1} .

HRMS ($\text{C}_{17}\text{H}_{28}\text{O}_2$ $^{11}\text{B}^{32}\text{S}$ = $[\text{M}+\text{H}]^+$): calcd. 307.1898; found 307.1892.

Methyl-4-(2-methyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)benzoate (5h)



The product was obtained following **P1**, after purification by chromatography using a Biotage SP4 (hexane/ethyl acetate = 100:1–40:1, v/v, 48 ml column volume), as a colorless solid (0.35 mmol scale, 58 mg, 52% yield). R_f = 0.64 (hexane/ethyl acetate, 10:1 v/v).

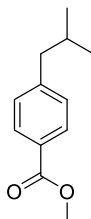
^1H NMR (600 MHz, CDCl_3) δ 7.93 (d, J = 8.4 Hz, 2H), 7.28 (d, J = 8.3 Hz, 2H), 3.89 (s, 3H), 2.22 – 2.13 (m, 1H), 2.06 (d, J = 10.5 Hz, 1H), 1.19 (s, J = 11.2 Hz, 6H), 1.17 (s, 6H), 1.05 (t, J = 7.7 Hz, 3H), 0.73 (d, J = 6.5 Hz, 3H) ppm.

^{13}C NMR (151 MHz, CDCl_3) δ 167.5, 148.5, 129.6, 129.1, 127.3, 83.5, 52.0, 31.0, 24.7, 24.7, 23.2, 22.1 ppm.

FT-IR (neat, ν_{max}) 2977, 2952, 2868, 1719, 1605, 1435, 1416, 1381, 1356, 1313, 1326, 1278, 1213, 1193, 1174, 1139, 1109, 1016, 972, 896, 865, 852, 819, 718, 690 cm^{-1} .

HRMS ($\text{C}_{18}\text{H}_{28}\text{O}_4$ ^{11}B = $[\text{M}+\text{H}]^+$): calcd. 319.2075; found 319.2075.

The protodeboronated side product methyl 4-isobutylbenzoate (**5h'**) was isolated in 25% yield.



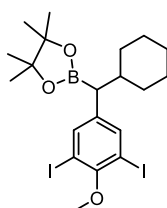
Compound **5h'** was isolated as colorless solid (17 mg, 25% yield). R_f = 0.82 (hexane/ethyl acetate, 10:1 v/v).

$^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.94 (d, J = 8.2 Hz, 2H), 7.21 (d, J = 8.3 Hz, 2H), 3.90 (s, 3H), 2.53 (d, J = 7.2 Hz, 2H), 1.89 (m, 1H), 0.91 (d, J = 6.6 Hz, 6H) ppm.

$^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 167.4, 147.4, 129.6, 129.3, 127.8, 52.1, 45.6, 30.3, 22.5 ppm.

FT-IR (neat, ν_{max}) 2955, 2870, 1720, 1610, 1574, 1425, 1416, 1385, 1309, 1273, 1178, 1106, 1078, 1021, 969, 861, 839, 799, 754, 704 cm^{-1} .

2-(Cyclohexyl(3,5-diiodo-4-methoxyphenyl)methyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**5i**)



The product was obtained following **P1**, after purification by chromatography using a Biotage SP4 (hexane/dichloromethane/ethyl acetate, 100:3:0.5–30:3:0.5, v/v, 48 ml column volume), as a colorless solid (0.24 mmol scale, 131 mg, 94 %). R_f = 0.58 (hexane/ethyl acetate = 10:1 v/v).

$^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.59 (s, 2H), 3.82 (s, 3H), 1.88 (d, J = 10.3 Hz, 1H), 1.77 (d, J = 12.5 Hz, 1H), 1.73 – 1.58 (m, 4H), 1.44 (d, J = 12.7 Hz, 1H), 1.34 – 1.22 (m, 1H), 1.20 (s, 12H), 1.15 – 1.04 (m, 2H), 0.97 (ddd, J = 24.2, 12.5, 3.5 Hz, 1H), 0.75 – 0.65 (m, 1H) ppm.;

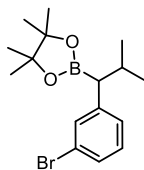
$^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 156.3, 142.1, 140.3, 90.2, 83.6, 60.8, 40.7, 33.6, 32.5, 26.5, 26.3, 25.0, 24.5 ppm.

FT-IR (neat, ν_{max}) 2976, 2918, 2850, 1740, 1574, 1530, 1460, 1443, 1414, 1380, 1366, 1348, 1321, 1245, 1214, 1128, 1099, 1056, 998, 969, 887, 866, 845, 777, 742, 699, 670 cm^{-1} .

HRMS ($\text{C}_{20}\text{H}_{30}\text{O}_3^{11}\text{B}_1^{127}\text{I}_2 = [\text{M}+\text{H}]^+$): calcd. 583.0372; found 583.0359.

The structure was unambiguously confirmed by single X-ray crystallography and deposited at Cambridge University (Crystallographic Data Centre) with the unique reference CCDC1407697; space group P-1, unit cell parameters: a = 8.9972(2) Å, b = 11.7352(3) Å, c = 12.5645(3) Å.

2-(1-(3-Bromophenyl)-2-methylpropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5j)



The product was obtained following **P1**, after purification by chromatography using a Biotage SP4 (hexane/THF, 100:1–15:1, v/v, 48 ml column volume), as a yellowish solid (0.2 mmol scale, 68 mg, 88%). R_f = 0.57 (hexane/ethyl acetate = 10:1).

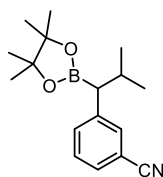
^1H NMR (600 MHz, CDCl_3) δ 7.36 (t, J = 1.7 Hz, 1H), 7.29 – 7.23 (m, 1H), 7.13 (dt, J = 7.7, 1.4 Hz, 1H), 7.10 (t, J = 7.6 Hz, 1H), 2.13 – 2.04 (m, 1H), 1.93 (d, J = 10.3 Hz, 1H), 1.20 (s, 6H), 1.18 (s, 6H), 1.01 (d, J = 6.6 Hz, 3H), 0.73 (d, J = 6.6 Hz, 3H) ppm.

^{13}C NMR (151 MHz, CDCl_3) δ 144.9, 132.0, 129.6, 128.3, 127.7, 122.2, 83.4, 31.0, 24.7, 24.5, 23.0, 21.9 ppm.

FT-IR (neat, ν_{max}) 2957, 2868, 1591, 1563, 1471, 1425, 1379, 1354, 1323, 1272, 1213, 1166, 1073, 997, 971, 878, 849, 780, 662 cm^{-1} .

HRMS ($\text{C}_{16}\text{H}_{25}\text{O}_2^{11}\text{B}^{79}\text{Br}$ = $[\text{M}+\text{H}]^+$): calcd. 339.1125; found 339.1121.

3-(2-Methyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)benzonitrile (5k)



The product was obtained following **P1**, after purification by chromatography using a Biotage SP4 (hexane/ethyl acetate, 100:1–30:1, v/v, 48 ml column volume), as a colorless oil (74 mg, 86% yield). R_f = 0.55 (hexane/ethyl acetate, 10:1 v/v).

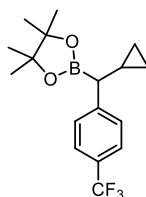
^1H NMR (600 MHz, CDCl_3) δ 7.51 (t, J = 1.5 Hz, 1H), 7.43 (dd, J = 7.8, 1.3 Hz, 2H), 7.33 (t, J = 7.7 Hz, 1H), 2.16 – 2.05 (m, 1H), 2.02 (d, J = 10.2 Hz, 1H), 1.19 (s, 6H), 1.18 (s, 6H), 1.02 (d, J = 6.5 Hz, 3H), 0.71 (d, J = 6.5 Hz, 3H) ppm.

^{13}C NMR (151 MHz, CDCl_3) δ 144.1, 133.9, 132.7, 129.2, 129.0, 119.5, 112.2, 83.7, 31.2, 24.8, 24.7, 23.0, 22.0 ppm.

FT-IR (neat, ν_{max}) 2956, 2867, 2228, 1579, 1480, 1465, 1380, 1355, 1315, 1275, 1251, 1216, 1165, 1138, 1084, 1007, 970, 906, 878, 849, 803, 754, 710, 686, 674 cm^{-1} .

HRMS ($\text{C}_{17}\text{H}_{25}\text{O}_2\text{N}_1^{11}\text{B}$ = $[\text{M}+\text{H}]^+$): calcd. 286.1973; found 286.1967.

2-(Cyclopropyl(4-(trifluoromethyl)phenyl)methyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5l)



The product was obtained following **P1**, after purification by chromatography using a Biotage SP4 (hexane/ethyl acetate, 50:1–20:1, v/v, 48 ml column volume), as a colorless oil (0.2 mmol scale, 31 mg, 49% yield). R_f = 0.51 (hexane/ethyl acetate, 10:1 v/v).

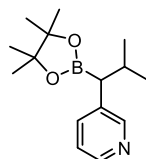
^1H NMR (600 MHz, CDCl_3) δ 7.55 (s, 1H), 7.47 (d, J = 7.5 Hz, 1H), 7.39 (dt, J = 15.3, 7.7 Hz, 2H), 1.79 (d, J = 9.7 Hz, 1H), 1.24 – 1.22 (m, 12H), 1.18 – 1.09 (m, 1H), 0.65 – 0.56 (m, 1H), 0.55 – 0.45 (m, 1H), 0.29 (td, J = 9.5, 4.8 Hz, 1H), 0.09 (td, J = 9.6, 4.9 Hz, 1H) ppm.

^{13}C NMR (151 MHz, CDCl_3) δ 144.3, 131.7, 130.5 (q, J = 31.8 Hz), 128.7, 125.5, δ 125.0 (q, J = 3.8 Hz), 124.6 (q, J = 272.2 Hz), 83.7, 83.0, 24.8, 24.7, 24.7, 13.0, 5.2, 5.0, 3.9 ppm.

FT-IR (neat, ν_{max}) 2980, 1447, 1372, 1274, 1160, 1141, 1121, 1074, 1017, 972, 894, 867, 849, 820, 799, 752, 702, 673 cm^{-1} .

HRMS ($\text{C}_{17}\text{H}_{23}\text{O}_2^{11}\text{BF} = [\text{M}+\text{H}]^+$): calcd. 327.1738; found 327.1743.

3-(2-Methyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)pyridine (5m)



The product was obtained following **P1**, after purification by chromatography using a Biotage SP4 (hexane/ethyl acetate, 50:1–10:1, 48 ml column volume), as a yellowish solid (0.35 mmol scale, 62 mg, 64% yield). R_f = 0.43 (hexane/ethyl acetate, 10:1 v/v).

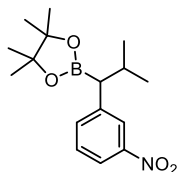
^1H NMR (600 MHz, CDCl_3) δ 8.50 – 8.32 (m, 2H), 7.61 – 7.53 (m, 1H), 7.20 (dd, J = 7.7, 4.9 Hz, 1H), 2.16 – 2.06 (m, 1H), 2.00 (d, J = 9.9 Hz, 1H), 1.19 (d, J = 4.0 Hz, 6H), 1.19 (s, 6H), 1.02 (d, J = 6.6 Hz, 3H), 0.74 (d, J = 6.6 Hz, 3H) ppm.

^{13}C NMR (151 MHz, CDCl_3) δ 150.3, 146.4, 138.2, 137.0, 123.4, 83.7, 31.1, 25.0, 24.8, 24.7, 23.0, 22.0 ppm.

FT-IR (neat, ν_{max}) 2924, 2853, 2331, 1723, 1454, 1378, 1278, 1149, 1014, 977, 899, 860, 845, 760, 699 cm^{-1} .

HRMS ($\text{C}_{15}\text{H}_{25}\text{O}_2^{11}\text{B} = [\text{M}+\text{H}]^+$): calcd. 262.1973; found 262.1975.

2-(2-Methyl-1-(3-nitrophenyl)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5n)



The product was obtained following **P1**, after purification by chromatography using a Biotage SP4 (hexane/ethyl acetate, 50:1–10:1, v/v, 48 ml column volume), as a yellowish solid (0.24 mmol scale, 61 mg, 83% yield). R_f = 0.45 (hexane/ethyl acetate, 10:1 v/v).

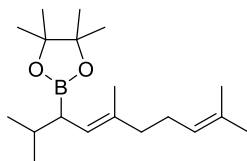
^1H NMR (600 MHz, CDCl_3) δ 8.09 (t, J = 1.9 Hz, 1H), 8.00 (ddd, J = 8.2, 2.2, 0.9 Hz, 1H), 7.53 (t, J = 8.0 Hz, 1H), 7.40 (t, J = 7.9 Hz, 1H), 2.19 – 2.06 (m, 2H), 1.20 (s, 6H), 1.19 (s, 6H), 1.04 (d, J = 6.3 Hz, 3H), 0.73 (d, J = 6.3 Hz, 3H) ppm.

^{13}C NMR (151 MHz, CDCl_3) δ 148.3, 144.8, 135.6, 129.0, 124.0, 120.7, 83.8, 31.3, 24.8, 24.6, 23.04, 22.0 ppm.

FT-IR (neat, ν_{max}) 3068, 2955, 2922, 2867, 1746, 1523, 1464, 1380, 1339, 1326, 1276, 1252, 1215, 1166, 1139, 1077, 1009, 972, 907, 881, 849, 926, 812, 798, 750, 717, 691, 660 cm^{-1} .

HRMS ($\text{C}_{16}\text{H}_{25}\text{O}_4$ ^{11}B = $[\text{M}+\text{H}]^+$): calcd. 306.1871; found 306.1860.

(E)-4,4,5,5-tetramethyl-2-(2,5,9-trimethyldeca-4,8-dien-3-yl)-1,3,2-dioxaborolane (5o)



The product was obtained following **P1**, after purification by chromatography using a Biotage SP4 (hexane/ethyl acetate, 100:1–50:1, v/v, 48 ml column volume) as a colorless oil (0.5 mmol scale, 137 mg, 92% yield). R_f = 0.82 (hexane/ethyl acetate = 10:1).

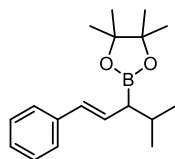
^1H NMR (600 MHz, CDCl_3) δ 5.12 – 5.05 (m, 1H), 5.03 (d, J = 9.8 Hz, 1H), 2.11 – 1.93 (m, 4H), 1.75 (tt, J = 15.4, 6.5 Hz, 1H), 1.69 (t, J = 9.5 Hz, 1H), 1.64 (s, 3H), 1.57 (s, 6H), 1.21 (s, 6H), 1.20 (s, 6H), 0.91 (d, J = 6.6 Hz, 3H), 0.84 (d, J = 6.6 Hz, 3H) ppm.

^{13}C NMR (151 MHz, CDCl_3) δ 134.6, 131.1, 124.9, 124.7, 82.9, 40.2, 30.3, 26.7, 25.8, 24.8, 24.6, 22.9, 22.1, 18.1, 17.8, 16.5 ppm.

FT-IR (neat, ν_{max}) 2977, 1444, 1371, 1317, 1272, 1216, 1143, 1009, 971 893, 851, 756, 673 cm^{-1} .

HRMS ($\text{C}_{19}\text{H}_{34}\text{O}_2$ ^{11}B = $[\text{M}+\text{H}]^+$): calcd. 305.2646; found 305.2638.

2-(4-Methyl-1-phenylpent-1-en-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5p)



The product was obtained following **P1**, after purification by chromatography using a Biotage SP4 (hexane/ethyl acetate, 100:1–20:1, v/v, 48 ml column volume), as a yellowish oil (0.35 mmol scale, 82 mg, 82% yield). R_f = 0.65 (hexane/ethyl acetate, 10:1 v/v).

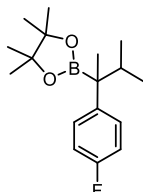
^1H NMR (600 MHz, CDCl_3) δ 7.34 (d, J = 7.2 Hz, 2H), 7.28 (t, J = 7.8 Hz, 2H), 7.17 (t, J = 7.3 Hz, 1H), 6.35 (d, J = 15.8 Hz, 1H), 6.19 (dd, J = 15.8, 9.9 Hz, 1H), 1.97 – 1.88 (m, 1H), 1.74 (t, J = 9.3 Hz, 1H), 1.24 (s, J = 2.3 Hz, 6H), 1.24 (s, 6H), 0.98 (d, J = 6.7 Hz, 3H), 0.93 (d, J = 6.7 Hz, 3H) ppm.

^{13}C NMR (151 MHz, CDCl_3) δ 138.4, 131.2, 130.1, 128.5, 126.6, 126.1, 83.3, 30.1, 24.9, 24.8, 22.8, 22.3 ppm.

^{11}B NMR (128 MHz, CDCl_3) δ 22.22 ppm.

FT-IR (neat, ν_{max}) 2959, 1436, 1372, 1324, 1271, 1218, 1146, 1071, 1010, 967, 905, 851, 748, 693, 670 cm^{-1} .

2-(2-(4-Fluorophenyl)-3-methylbutan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5q)



The product was obtained following **P1**, after purification by chromatography using a Biotage SP4 (hexane/chloroform/ethyl acetate, 100:2:1–15:2:1, v/v/v, 48 ml column volume), as a white solid (0.28 mmol scale, 76 mg, 92% yield). R_f = 0.71 (hexane/ethyl acetate, 10:1 v/v).

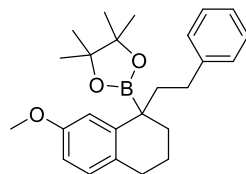
^1H NMR (600 MHz, CDCl_3) δ 7.34 – 7.28 (m, 2H), 6.98 – 6.92 (m, 2H), 2.32 (hept, J = 6.8 Hz, 1H), 1.23 (s, 3H), 1.19 (s, 6H), 1.16 (s, 6H), 0.97 (d, J = 6.8 Hz, 3H), 0.57 (d, J = 6.9 Hz, 3H) ppm.

^{13}C NMR (151 MHz, CDCl_3) δ 160.8 (d, J = 242.8 Hz), 141.9 (d, J = 3.1 Hz), 128.8 (d, J = 7.5 Hz), 114.5 (d, J = 20.6 Hz) 83.4, 34.5, 24.9, 24.7, 24.6, 20.4, 16.6, 14.2 ppm.

FT-IR (neat, ν_{max}) 2975, 2873, 1602, 1508, 1469, 1389, 1372, 1344, 1312, 1301, 1272 1232, 1164, 1140, 1121, 1088, 1064, 1015, 966, 881, 841, 832, 795, 743, 714, 671 cm^{-1} .

HRMS ($\text{C}_{17}\text{H}_{25}\text{O}_2$ ^{11}BF = $[\text{M}+\text{H}]^+$): calcd. 291.1926; found 291.1925.

2-(7-Methoxy-1-phenethyl-1,2,3,4-tetrahydronaphthalen-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5r)



The product was obtained following **P1**, after purification by chromatography using a Biotage SP4 (hexane/THF, 50:2–15:1, v/v, 48 ml column volume) as a colorless oil (0.24 mmol scale, 73 mg, 78% yield). R_f = 0.51 (hexane/ethyl acetate, 10:1 v/v).

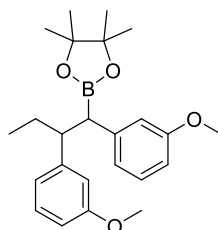
^1H NMR (600 MHz, CDCl_3) δ 7.28 – 7.25 (m, 2H), 7.21 – 7.14 (m, 3H), 6.96 (dd, J = 11.2, 5.5 Hz, 2H), 6.64 (dd, J = 8.3, 2.7 Hz, 1H), 3.78 (s, 3H), 2.71 (t, J = 6.3 Hz, 2H), 2.57 (m, 2H), 2.17 – 2.05 (m, 2H), 2.00 – 1.94 (m, 1H), 1.91 – 1.79 (m, 2H), 1.76 (ddd, J = 12.4, 9.1, 2.9 Hz, 1H), 1.24 (s, 6H), 1.23 (s, 6H) ppm.

^{13}C NMR (151 MHz, CDCl_3) δ 157.5, 143.6, 142.6, 130.1, 129.5, 128.5, 128.4, 128.1, 125.6, 113.7, 111.3, 83.4, 55.4, 42.1, 32.7, 29.9, 29.8, 24.9, 24.8, 20.5 ppm.

FT-IR (neat, ν_{max}) 2977, 2933, 2859, 1606, 1574, 1497, 1453, 1371, 1331, 1310, 1260, 1237, 1216, 1140, 1112, 1043, 967, 909, 856, 807, 762, 699, 679 cm^{-1} .

HRMS ($\text{C}_{25}\text{H}_{34}\text{O}_3$ ^{11}B = $[\text{M}+\text{H}]^+$): calcd. 393.2596; found 393.2596.

2-(1,2-bis(3-methoxyphenyl)butyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (6a)



The product (0.35 mmol scale) was obtained following **P2**, after purification by chromatography using a Biotage SP4 (hexane/ CHCl_3 /ethyl acetate/THF, 100:2:1:1–20:2:1:1, v/v, 48 ml column volume) as a colorless solid (137 mg, 69% yield). R_f = 0.39/0.42 (hexane/ethyl acetate, 10:1 v/v).

Major Diastereomer

^1H NMR (400 MHz, CDCl_3) δ 7.01 (t, J = 7.8 Hz, 1H), 6.96 (t, J = 7.9 Hz, 1H), 6.67 – 6.48 (m, 6H), 3.68 (s, 3H), 3.66 (s, 3H), 3.00 (td, J = 11.0, 3.6 Hz, 1H), 2.60 (d, J = 11.4 Hz, 1H), 1.82 (ddq, J = 14.7, 7.3, 3.6 Hz, 1H), 1.72 – 1.58 (m, J = 14.5, 10.8, 7.3 Hz, 1H), 1.23 (s, 6H), 1.20 (s, 6H), 0.75 (t, J = 7.3 Hz, 3H) ppm.

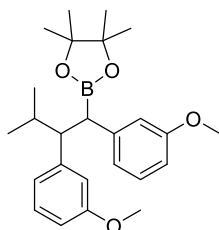
^{13}C NMR (101 MHz, CDCl_3) δ 159.1, 159.1, 145.8, 142.5, 128.7, 128.6, 121.8, 120.9, 114.5, 114.1, 111.1, 110.9, 83.6, 55.2, 50.4, 29.8, 24.9, 24.8, 12.5 ppm.

^{11}B NMR (128 MHz, CDCl_3) δ 33.27 ppm.

FT-IR (neat, ν_{max}) 2959, 2926, 1598, 1583, 1488, 1464, 1435, 1360, 1317, 1258, 1138, 1108, 1042, 968, 857, 780, 755, 715, 702, 689, 669 cm^{-1} .

HRMS ($C_{24}H_{34}O_4^{10}B = [M+H]^+$): calcd. 396.2581; found 396.2586.

2-(1,2-Bis(3-methoxyphenyl)-3-methylbutyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (6b)



The product (0.35 mmol scale) was obtained following **P2**, after purification by chromatography using a Biotage SP4 (hexane/ $CHCl_3$ /ethyl acetate/THF, 100:2:1:1–20:2:1:1, v/v, 48 ml column volume) as a colorless solid (139 mg, 58% yield). R_f = 0.43/0.45 (hexane/ethyl acetate, 10:1 v/v).

Major Diastereomer

1H NMR (600 MHz, $CDCl_3$) δ 6.99 (t, J = 7.9 Hz, 1H), 6.94 (t, J = 7.9 Hz, 1H), 6.68 (d, J = 7.7 Hz, 1H), 6.65 – 6.59 (m, 2H), 6.57 – 6.53 (m, 2H), 6.47 (ddd, J = 8.1, 2.5, 0.7 Hz, 1H), 3.68 (s, 3H), 3.66 (s, 3H), 3.20 (dd, J = 12.1, 5.0 Hz, 1H), 2.91 (d, J = 12.1 Hz, 1H), 2.08 – 1.99 (m, 1H), 1.18 (s, 6H), 1.17 (s, 6H), 0.91 (d, J = 6.8 Hz, 3H), 0.84 (d, J = 6.9 Hz, 3H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$) δ 159.1, 158.7, 143.0, 142.7, 128.6, 128.0, 122.6, 122.0, 115.8, 14.6, 111.0, 110.7, 83.5, 55.1, 55.1, 53.2, 33.2, 24.7, 24.6, 22.6, 18.2 ppm.

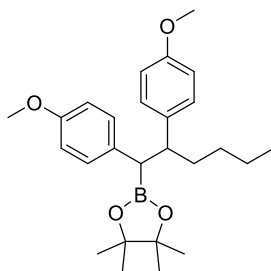
^{11}B NMR (128 MHz, $CDCl_3$) δ 33.27 ppm.

FT-IR (neat, ν_{max}) 2969, 2920, 1598, 1582, 1489, 1464, 1434, 1371, 1330, 1287, 1258, 1212, 1120, 1140.0, 108, 105, 104, 96, 945, 898, 858, 845, 781, 766, 746, 717, 704, 689, 667 cm^{-1} .

HRMS ($C_{25}H_{35}O_3^{10}BNa = [M+Na]^+$): calcd. 432.2557; found 432.2558.

LC-MS : retention time 7.47 min, m/z $[M+H] = 411.21$.

2-(1,2-bis(4-methoxyphenyl)hexyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (6c)



The product (0.2 mmol scale) was obtained following **P2**, after purification by chromatography using a Biotage SP4 (hexane/ $CHCl_3$ /ethyl acetate 100:2:1:1–10:2:1, v/v, 48 ml column volume) as colorless solid (46 mg, 73% yield). R_f = 0.34 (hexane/ethyl acetate = 10:1, v/v).

Diastereoisomer 1

1H NMR (600 MHz, $CDCl_3$) 6.90 (d, J = 8.6 Hz, 2H), 6.87 (d, J = 8.6 Hz, 2H), 6.64 (d, J = 8.6 Hz, 2H), 6.60 (d, J = 8.7 Hz, 2H), 3.70 (s, 3H), 3.68 (s, 3H), 3.00 (td, J = 11.1, 3.4 Hz, 1H), 2.51 (d, J

= 11.5 Hz, 1H), 1.77 – 1.68 (m, 1H), 1.66 – 1.56 (m, 1H), 1.34 – 1.24 (m, 2H), 1.23 (s, 6H), 1.19 (s, 6H), 1.15 – 1.04 (m, 2H), 0.82 (t, $J = 7.4$ Hz, 3H) ppm.

^{13}C NMR (151 MHz, CDCl_3) δ 157.4, 157.0, 136.7, 133.2, 130.1, 129.0, 113.3, 113.2, 83.43, 77.6, 55.1, 55.1, 47.8, 36.9, 29.9, 24.8, 24.7, 22.8, 14.1 ppm.

Diastereoisomer 2

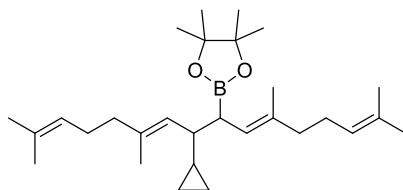
^1H NMR (600 MHz, CDCl_3) δ 7.23 (t, $J = 8.5$ Hz, 2H), 7.19 (d, $J = 8.6$ Hz, 2H), 6.85 – 6.81 (m, 4H), 3.80 (s, 3H), 3.78 (s, 3H), 2.90 (td, $J = 11.4, 3.1$ Hz, 1H), 2.49 (d, $J = 11.5$ Hz, 1H), 1.66 – 1.56 (m, 1H), 1.49 (m, 1H), 1.34 – 1.24 (m, 2H), 1.16 – 0.97 (m, 2H), 0.89 (s, 6H), 0.87 (s, 6H), 0.68 (t, $J = 7.3$ Hz, 3H) ppm.

^{13}C NMR (151 MHz, CDCl_3) δ 158.0, 157.6, 137.9, 133.7, 130.1, 129.4, 113.8, 113.5, 83.04, 55.4, 55.3, 47.6, 35.0, 29.5, 24.6, 24.3, 22.7, 14.1 ppm.

FT-IR (neat, ν_{max}) 2928, 1610, 1582, 1463, 1357 1320, 1301, 1243, 1177, 1140, 1105, 1036, 967, 900, 852, 828, 758, 710, 667 cm^{-1} .

HRMS ($\text{C}_{26}\text{H}_{37}\text{O}_4$ $^{11}\text{BNa} = [\text{M}+\text{Na}]^+$): calcd. 447.2677; found 447.2663.

2-(-9-cyclopropyl-2,6,11,15-tetramethylhexadeca-2,6,10,14-tetraen-8-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (6d)



The product (0.2 mmol scale) was obtained following **P2**, after purification by chromatography using a Biotage SP4 (hexane:ethyl acetate 100:1–25:1, v/v, 48 ml column volume), as colorless oil (94 mg, 90 % yield). The product contains a mixture of non-separable isomers.

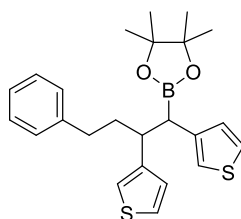
^1H -NMR (400 MHz, CDCl_3) δ 5.27 – 4.78 (4H), 2.24 – 1.87 (8H), 1.60 (13H), 1.26 – 1.09 (10H), 0.89 – 0.21 (6H).

^{13}C NMR (151 MHz, CDCl_3) δ 134.91, 134.44, 134.34, 134.23, 133.91, 131.33, 131.19, 131.11, 131.06, 128.21, 126.73, 124.79, 124.74, 124.70, 124.60, 124.58, 124.53, 124.25, 83.05, 82.92, 82.83, 43.69, 42.11, 40.20, 40.12, 40.08, 40.00, 27.14, 27.02, 26.98, 26.73, 25.84, 24.87, 24.80, 24.75, 24.72, 24.70, 17.83, 17.80, 17.78, 16.83, 16.59, 16.54, 16.49, 16.45, 15.43, 12.71, 4.93, 4.35, 3.94, 3.92, 3.38, 2.88, 0.77.

^{11}B NMR (128 MHz, CDCl_3) δ 22.13 ppm.

FT-IR (neat, ν_{max}) 2977, 2919, 1448, 1372, 1318, 1271, 1216, 1143, 1106, 1011, 967, 851, 674 cm^{-1} .

4,4,5,5-tetramethyl-2-(4-phenyl-1,2-di(thiophen-3-yl)butyl)-1,3,2-dioxaborolane (6e)



The product was obtained following **P2**, after purification by chromatography using a Biotage SP4 (hexane:ethyl acetate 100:1–20:1, v/v, 48 ml column volume) as yellowish solid (52 mg, 62 % yield). R_f = 0.52 (hexane/ethyl acetate = 10:1, v/v).

Major Diastereomer

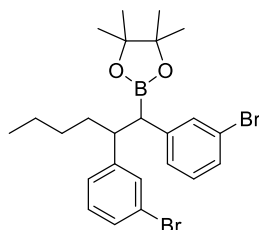
^1H NMR (400 MHz, CDCl_3) δ 7.31 – 7.11 (m, 5H), 7.09 (d, J = 5.0 Hz, 1H), 6.98 (d, J = 5.1 Hz, 1H), 6.81 (dd, J = 5.0, 3.5 Hz, 1H), 6.78 (dd, J = 5.1, 3.5 Hz, 1H), 6.64 (dd, J = 8.6, 3.0 Hz, 2H), 3.39 (td, J = 10.5, 3.1 Hz, 1H), 2.88 (d, J = 10.5 Hz, 1H), 2.66 – 2.46 (m, 2H), 2.17 (dddd, J = 13.5, 10.3, 6.7, 3.3 Hz, 1H), 2.11 – 1.95 (m, 1H), 1.26 (s, 6H), 1.23 (s, 6H) ppm.

^{13}C NMR (100 MHz, CDCl_3) δ 148.2, 143.2, 142.3, 128.5, 128.4, 126.5, 126.3, 125.8, 125.4, 125.1, 123.3, 123.0, 84.1, 5.50, 4.40, 3.11, 249, 24.8 ppm.

FT-IR (neat, ν_{max}) 2921, 2854, 1603, 496, 1454, 1371, 1349, 1327, 1271, 1214, 1140, 1077, 1038, 966, 890, 849, 825, 748, 692 cm^{-1} .

HRMS ($\text{C}_{24}\text{H}_{30}\text{O}_2$ $^{11}\text{BS}_2$ = $[\text{M}+\text{H}]^+$): calcd. 425.1775; found 425.1763.

2-(1,2-bis(3-bromophenyl)hexyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane(6f)



The product was obtained following **P2**, after purification by chromatography using a Biotage SP4 (hexane: ethyl acetate 100:1–20:1, v/v, 48 ml column volume) as colorless oil (94 mg, 70 % yield). R_f = 0.48 (hexane/ethyl acetate = 10:1, v/v).

Major Diastereomer

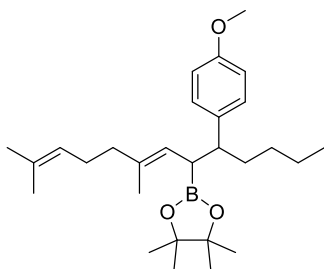
^1H NMR (600 MHz, CDCl_3) δ 7.20 – 7.14 (m, 2H), 7.14 – 7.09 (m, 2H), 6.97 (t, J = 7.8 Hz, 1H), 6.93 (t, J = 7.7 Hz, 1H), 6.88 (d, J = 7.7 Hz, 1H), 6.85 (d, J = 7.7 Hz, 1H), 3.03 (td, J = 11.1, 3.5 Hz, 1H), 2.52 (d, J = 11.2 Hz, 1H), 1.81 – 1.70 (m, 1H), 1.68 – 1.57 (m, 1H), 1.35 – 1.25 (m, 1H), 1.23 (m, 6H), 1.20 (s, 6H), 1.17 – 1.03 (m, 3H), 0.83 (t, J = 7.4 Hz, 3H) ppm.

^{13}C NMR (151 MHz, CDCl_3) δ 146.6, 143.1, 132.2, 131.1, 129.5, 129.0, 128.5, 128.0, 126.9, 122.6, 122.2, 122.1, 83.9, 48.4, 36.3, 29.8, 24.8, 24.7, 24.6, 22.7, 14.0 ppm.

FT-IR (neat, $\tilde{\nu}$ cm^{-1}) 2977, 2927, 2858, 1592, 1473, 1426, 1380, 1356, 1320, 1270, 1213, 1167, 1139, 1109, 1072, 996, 966, 877, 849, 784, 756, 719, 697, 669 cm^{-1} .

HRMS ($\text{C}_{24}\text{H}_{32}\text{O}_2$ $^{11}\text{BBr}_2$ = $[\text{M}+\text{H}]^+$): calcd. 521.0857; found 521.0852.

2-(5-(4-Methoxyphenyl)-8,12-dimethyltrideca-7,11-dien-6-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (6g)



The product was obtained following **P2**, after purification by chromatography using a Biotage SP4 (hexane: ethyl acetate 100:1–30:1, v/v, 48 ml column volume) as colorless (65 mg 51% yield). R_f = 0.56 (hexane/ethyl acetate = 10:1, v/v).

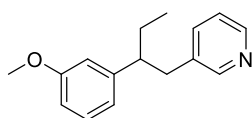
^1H NMR (400 MHz, CDCl_3) δ 6.96 (d, J = 8.6 Hz, 1H), 6.75 (d, J = 8.6 Hz, 1H), 4.88 (d, J = 8.3 Hz, 1H), 4.77 (d, J = 9.7 Hz, 1H), 3.76 (s, J = 4.3 Hz, 1H), 2.75 (dd, J = 11.1, 5.5 Hz, 1H), 2.50 (t, J = 10.4 Hz, 1H), 1.60 – 1.55 (m, J = 6.5, 5.7 Hz, 4H), 1.50 (s, 3H), 0.85 (d, J = 6.7 Hz, 1H), 0.73 (d, J = 6.8 Hz, 1H).

^{13}C NMR (100 MHz, CDCl_3) δ 157.60, 134.77, 134.03, 130.98, 130.42, 124.71, 124.57, 112.80, 112.67, 83.03, 83.03, 82.94, 82.94, 77.48, 77.36, 77.36, 76.84, 76.84, 55.20, 55.20, 53.46, 52.54, 52.54, 52.54, 45.01, 39.97, 39.97, 38.57, 33.24, 33.24, 33.12, 26.90, 26.90, 25.89, 25.82, 25.82, 25.72, 25.72, 25.11, 25.11, 24.78, 24.78, 24.66, 24.66, 24.60, 24.60, 22.34, 18.70, 17.76, 17.76, 17.73, 17.73, 17.30, 16.73, 16.58, 16.58.

^{11}B NMR (128 MHz, CDCl_3) δ 22.34 ppm.

FT-IR (neat, ν_{max}) 2926, 1611, 1511, 1444, 1371, 1313, 1246, 1178, 1141, 1103, 1038, 967, 896, 829, 757, 673 cm^{-1} .

3-(2-(3-Methoxyphenyl)butyl)pyridine (6h)



The product (0.35 mmol scale) was obtained following **P3**, after purification by chromatography using a Biotage SP4 (hexane/ ethyl acetate 10:1–10:3, v/v, 48 ml column volume), as a yellowish oil (41% yield). R_f = 0.10 (hexane/ethyl acetate = 10:1 v/v).

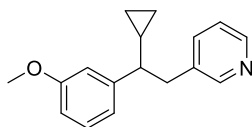
^1H NMR (600 MHz, CDCl_3) δ 8.40 (d, J = 4.0 Hz, 1H), 8.31 (s, 1H), 7.33 (d, J = 7.8 Hz, 1H), 7.23 – 7.11 (m, 2H), 6.73 (dd, J = 8.1, 2.4 Hz, 1H), 6.67 (d, J = 7.6 Hz, 1H), 6.62 (d, J = 1.7 Hz, 1H), 3.78 (s, 3H), 2.95 (dd, J = 13.7, 6.4 Hz, 1H), 2.86 (dd, J = 13.7, 8.5 Hz, 1H), 2.76 – 2.61 (m, 1H), 1.82 – 1.71 (m, 1H), 1.71 – 1.56 (m, 1H), 0.82 (t, J = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, CDCl_3) δ 149.52, 146.41, 145.43, 137.28, 136.44, 129.31, 123.22, 120.21, 113.81, 111.26, 55.12, 49.65, 40.35, 28.57, 12.10.

FT-IR (neat, ν_{max}) 2959, 2926, 2855, 1599, 1584, 1487, 1454, 1423, 1258, 1154, 1045, 908, 779, 730.

HRMS ($\text{C}_{16}\text{H}_{20}\text{NO} = [\text{M}+\text{H}]^+$): calcd. 242.1545; found 242.1541.

3-(2-Cyclopropyl-2-(3-methoxyphenyl)ethyl)pyridine (6i)



The product (0.35 mmol scale) was obtained following **P3**, after purification by chromatography using a Biotage SP4 (hexane/ ethyl acetate 10:1–10:3, v/v, 48 ml column volume), as a yellowish oil (40% yield). R_f = 0.10 (hexane/ethyl acetate = 10:1 v/v).

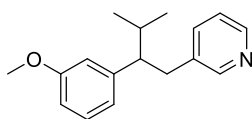
^1H NMR (400 MHz, CDCl_3) δ 8.40 (dd, J = 4.8, 1.5 Hz, 3H), 8.32 (d, J = 1.8 Hz, 3H), 7.33 – 7.24 (m, 4H), 7.20 (t, J = 7.9 Hz, 3H), 7.17 – 7.06 (m, 3H), 6.82 – 6.73 (m, 4H), 6.72 – 6.65 (m, 4H), 3.78 (s, 9H), 3.09 (dd, J = 13.6, 6.4 Hz, 3H), 3.01 (dd, J = 13.6, 8.0 Hz, 3H), 2.04 (dd, J = 16.2, 7.8 Hz, 3H), 1.06 (ddq, J = 9.7, 8.1, 5.0 Hz, 3H), 0.66 – 0.51 (m, 3H), 0.51 – 0.36 (m, 3H), 0.25 – 0.01 (m, 6H).

^{13}C NMR (100 MHz, CDCl_3) δ 159.49, 150.60, 147.29, 145.91, 136.58, 135.66, 129.22, 122.84, 120.10, 113.77, 111.24, 55.12, 52.87, 40.49, 16.58, 5.92, 3.91.

FT-IR (neat, ν_{max}) 3000, 2922, 1600, 1583, 1423, 1261, 1153, 1044, 1026, 871, 781, 714, 698.

HRMS ($\text{C}_{17}\text{H}_{20}\text{NO}$ = $[\text{M}+\text{H}]^+$): calcd. 254.1545; found 254.1533.

3-(2-(3-Methoxyphenyl)-3-methylbutyl)pyridine (6j)



The product (0.35 mmol scale) was obtained following **P3**, after purification by chromatography using a Biotage SP4 (hexane/ ethyl acetate 10:1–10:3, v/v, 48 ml column volume), as a yellowish oil (48% yield). R_f = 0.10 (hexane/ethyl acetate = 10:1 v/v).

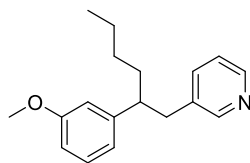
^1H NMR (600 MHz, CDCl_3) δ 8.33 (dd, J = 4.8, 1.4 Hz, 1H), 8.24 (d, J = 1.8 Hz, 1H), 7.22 (dd, J = 6.1, 1.8 Hz, 1H), 7.13 (t, J = 7.9 Hz, 1H), 7.06 (dd, J = 7.8, 4.8 Hz, 1H), 6.72 – 6.67 (m, 1H), 6.62 (d, J = 7.6 Hz, 1H), 6.59 – 6.51 (m, 1H), 3.74 (s, 3H), 3.14 (dd, J = 13.8, 4.7 Hz, 1H), 2.79 (dd, J = 13.7, 10.5 Hz, 1H), 2.52 (ddd, J = 10.5, 7.7, 4.8 Hz, 1H), 1.94 (dd, J = 14.0, 6.8 Hz, 1H), 1.07 (d, J = 6.7 Hz, 3H), 0.81 (d, J = 6.7 Hz, 3H).

^{13}C NMR (151 MHz, CDCl_3) δ 159.3, 150.0, 146.7, 144.2, 136.5, 128.9, 122.9, 121.1, 114.7, 111.0, 55.1, 55.0, 36.8, 32.7, 21.2, 20.4.

FT-IR (neat, ν_{max}) 2971, 2920, 1599, 1470, 1394, 1260, 1052, 723.

HRMS ($\text{C}_{17}\text{H}_{22}\text{NO}$ = $[\text{M}+\text{H}]^+$): calcd. 256.1701; found 256.1692.

3-(2-(3-Methoxyphenyl)hexyl)pyridine (6k)



The product (0.35 mmol scale) was obtained following **P3**, after purification by chromatography using a Biotage SP4 (hexane/ ethyl acetate 10:1–10:3, v/v, 48 ml column volume), as a yellowish oil (32% yield). R_f = 0.10 (hexane/ethyl acetate = 10:1 v/v).

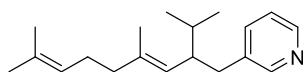
^1H NMR (600 MHz, CDCl_3) δ 8.41 (s, 1H), 8.31 (s, 1H), 7.35 (d, J = 7.8 Hz, 1H), 7.24 – 7.14 (m, 2H), 6.73 (dd, J = 8.0, 2.3 Hz, 1H), 6.66 (d, J = 7.6 Hz, 1H), 6.65 – 6.54 (m, 1H), 3.77 (s, 3H), 2.95 (dd, J = 13.6, 6.2 Hz, 1H), 2.85 (dd, J = 13.6, 8.6 Hz, 1H), 2.76 (td, J = 8.5, 4.3 Hz, 1H), 1.76 – 1.64 (m, 2H), 1.27 – 1.12 (m, 5H), 0.84 (t, J = 7.3 Hz, 3H).

^{13}C NMR (151 MHz, CDCl_3) δ 159.5, 148.6, 145.8, 145.5, 137.9, 136.7, 129.4, 123.5, 120.2, 113.7, 111.2, 54.8, 47.5, 40.5, 35.3, 29.6, 22.5, 13.7.

FT-IR (neat, ν_{max}) 2961, 2924, 1600, 1486, 1454, 1258, 1156, 1045, 777.

HRMS ($\text{C}_{18}\text{H}_{24}\text{NO} = [\text{M}+\text{H}]^+$): calcd. 270.1858; found 270.1850.

3-(2-Isopropyl-4,8-dimethylnona-3,7-dien-1-yl)pyridine (6l)



The product (0.35 mmol scale) was obtained following **P3**, after purification by chromatography using a Biotage SP4 (hexane/ ethyl acetate 50:1–10:1 v/v, 48 ml column volume), as a colorless solid (79 mg, 66% yield). R_f = 0.29 (hexane/ethyl acetate = 10:1 v/v).

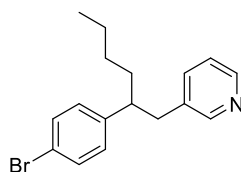
^1H NMR (400 MHz, CDCl_3) δ 8.37 (s, 2H), 7.39 (t, J = 10.3 Hz, 1H), 7.13 (dd, J = 7.5, 4.8 Hz, 1H), 5.06 – 4.99 (m, 1H), 4.90 (d, J = 9.9 Hz, 1H), 2.77 (dd, J = 12.9, 4.0 Hz, 1H), 2.37 (dd, J = 12.8, 9.9 Hz, 1H), 2.29 (m, 1H), 2.02 – 1.86 (m, 4H), 1.66 (s, 3H), 1.65 – 1.60 (m, 1H), 1.56 (d, J = 8.9 Hz, 3H), 1.22 (d, J = 1.1 Hz, 3H), 0.91 (dd, J = 16.1, 6.8 Hz, 6H).

^{13}C NMR (151 MHz, CDCl_3) δ 150.52, 146.87, 136.95, 136.58, 136.55, 131.27, 125.45, 124.36, 122.82, 46.09, 39.95, 36.79, 32.28, 26.57, 25.75, 20.90, 18.73, 17.71, 16.18.

FT-IR (neat, ν_{max}) 2956, 2932, 1575, 1333, 1423, 1384, 1107, 1027, 792, 714.

HRMS ($\text{C}_{19}\text{H}_{30}\text{N} = [\text{M}+\text{H}]^+$): calcd. 272.2373; found 272.2369.

3-(2-(4-Bromophenyl)hexyl)pyridine (6m)



The product (0.35 mmol scale) was obtained following **P3**, after purification by chromatography using a Biotage SP4 (hexane/ ethyl acetate 50:1–10:1, v/v, 48 ml column volume), as a colorless oil (35% yield). R_f = 0.10 (hexane/ethyl acetate = 10:1 v/v).

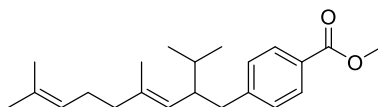
^1H NMR (600 MHz, CDCl_3) δ 8.40 (dd, J = 4.7, 1.4 Hz, 1H), 8.27 (d, J = 1.8 Hz, 1H), 7.40 – 7.35 (m, 2H), 7.23 (dt, J = 7.7, 1.8 Hz, 1H), 7.12 (dd, J = 7.7, 4.8 Hz, 1H), 6.96 – 6.92 (m, 2H), 2.97 – 2.89 (m, 1H), 2.76 (ddd, J = 14.2, 13.4, 7.1 Hz, 2H), 1.75 – 1.67 (m, 1H), 1.67 – 1.59 (m, 1H), 1.30 – 1.25 (m, 4H), 1.19 – 1.08 (m, 3H), 0.83 (t, J = 7.3 Hz, 3H).

^{13}C NMR (151 MHz, CDCl_3) δ 150.3, 147.3, 143.1, 136.4, 135.5, 131.4, 129.4, 123.0, 119.9, 47.4, 40.6, 35.4, 29.7, 29.6, 22.6, 13.9.

FT-IR (neat, ν_{max}) 2955, 2925, 1575, 1486, 1422, 1072, 1009, 822, 713.

HRMS ($\text{C}_{17}\text{H}_{21}\text{NBr}$ = $[\text{M}+\text{H}]^+$): calcd. 318.0857; found 318.0859.

Methyl-4-(2-isopropyl-4,8-dimethylnona-3,7-dien-1-yl)benzoate (6n)



The product (0.3 mmol) was obtained following **P3**, after purification by chromatography using a Biotage SP4 (hexane: ethyl acetate 100:1–40:1, v/v, 48 ml column volume), as colorless oil (43 mg, 45% yield). R_f = 0.72 (hexane/ethyl acetate = 10:1, v/v).

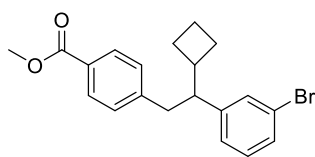
^1H NMR (600 MHz, CDCl_3) δ 7.89 (d, J = 8.1 Hz, 2H), 7.18 (d, J = 8.1 Hz, 2H), 5.05 – 4.99 (m, 1H), 4.92 (d, J = 9.9 Hz, 1H), 3.89 (s, 3H), 2.83 (dd, J = 13.0, 4.6 Hz, 1H), 2.43 (dd, J = 13.0, 9.7 Hz, 1H), 2.34 (dq, J = 14.8, 5.0 Hz, 1H), 2.20 – 2.06 (m, 1H), 2.02 – 1.87 (m, 4H), 1.66 (s, 3H), 1.58 (s, 3H), 1.23 (d, J = 0.8 Hz, 3H), 0.92 (d, J = 6.7 Hz, 3H), 0.89 (d, J = 6.8 Hz, 3H) ppm.

^{13}C NMR (151 MHz, CDCl_3) δ 167.5, 147.7, 136.3, 131.3, 129.4, 129.3, 129.2, 127.5, 126.0, 124.6, 52.0, 46.3, 40.1, 40.0, 32.4, 26.8, 25.8, 21.0, 18.8, 17.8, 16.3 ppm.

FT-IR (neat, ν_{max}) 2955, 2922, 1722, 1610, 1435, 1415, 1383, 1274, 1178, 1106, 1021, 971, 853, 764, 105 cm^{-1} .

HRMS ($\text{C}_{22}\text{H}_{32}\text{O}_2\text{Na}$ = $[\text{M}+\text{Na}]^+$): calcd. 351.2295; found 351.2288.

Methyl-4-(2-(3-bromophenyl)-2-cyclobutylethyl)benzoate (6o)



The product (0.3 mmol) was obtained following **P3**, after purification by chromatography using a Biotage SP4 (hexane: ethyl acetate 100:1–30:1, v/v, 48 ml column volume) as colorless solid (57 mg 51% yield). R_f = 0.61 (hexane/ethyl acetate = 10:1, v/v).

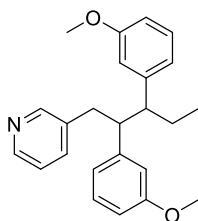
^1H NMR (600 MHz, CDCl_3) δ 7.85 – 7.81 (m, 2H), 7.28 – 7.24 (m, 1H), 7.16 (t, J = 1.7 Hz, 1H), 7.04 (t, J = 7.8 Hz, 1H), 6.98 (d, J = 8.3 Hz, 2H), 6.86 (d, J = 7.7 Hz, 1H), 3.87 (s, 3H), 2.97 (dd, J = 12.4, 3.6 Hz, 1H), 2.77 – 2.66 (m, 2H), 2.64 – 2.52 (m, 1H), 2.17 – 2.09 (m, 1H), 1.87 – 1.69 (m, 4H), 1.56 – 1.48 (m, 1H) ppm.

^{13}C NMR (151 MHz, CDCl_3) δ 167.2, 145.8, 145.2, 130.9, 129.8, 129.5, 129.44, 129.2, 128.0, 127.0, 122.4, 54.9, 52.1, 41.0, 40.5, 28.3, 27.0, 17.7 ppm.

FT-IR (neat, ν_{max}) 2931, 1718, 1610, 1592, 1567, 1374, 1434, 1416, 1311, 1275, 1178, 1103, 1072, 1020, 996, 969, 878, 858, 838, 803, 754, 696, 667 cm^{-1} .

HRMS ($\text{C}_{20}\text{H}_{22}\text{O}_2\text{Br}$ = $[\text{M}+\text{H}]^+$) calcd. 373.0803; found 373.0805.

3-(2,3-Bis(3-methoxyphenyl)pentyl)pyridine (8a)



The product (0.3 mmol) was obtained following **P4**, after preparative TLC (hexane: ethyl acetate 100:1–30:1, v/v, 48 ml column volume) as colorless oil (37% yield).

Diastereomer 1

^1H NMR (600 MHz, CDCl_3) δ 8.25 (dd, J = 4.2, 2.2 Hz, 1H), 7.96 (s, 1H), 7.31 (t, J = 7.8 Hz, 1H), 7.18 – 7.13 (m, 1H), 6.97 – 6.93 (m, 2H), 6.90 (d, J = 7.6 Hz, 1H), 6.85 – 6.80 (m, 2H), 6.70 (dt, J = 9.5, 4.7 Hz, 1H), 6.65 (d, J = 9.0 Hz, 1H), 6.58 (s, 1H), 3.86 (d, J = 8.2 Hz, 3H), 3.74 (s, 3H), 3.18 – 3.11 (m, 1H), 2.91 – 2.84 (m, 1H), 2.75 – 2.68 (m, 1H), 2.53 (dd, J = 13.7, 11.2 Hz, 1H), 1.67 (ddq, J = 14.4, 10.4, 7.3 Hz, 1H), 1.33 (ddq, J = 14.3, 11.1, 7.2 Hz, 1H), 0.58 (t, J = 7.3 Hz, 3H) ppm.

^{13}C NMR (151 MHz, CDCl_3) δ 160.0, 159.2, 150.3, 147.1, 145.8, 143.8, 136.5, 136.3, 129.7, 129.4, 123.1, 122.8, 121.1, 115.2, 114.6, 111.5, 111.4, 55.4, 55.3, 55.2, 54.9, 38.7, 27.5, 12.4 ppm.

Diastereomer 2

^1H NMR (600 MHz, CDCl_3) δ 8.32 (dd, J = 4.8, 1.5 Hz, 1H), 8.28 (d, J = 2.0 Hz, 1H), 7.25 – 7.21 (m, 1H), 7.09 (dd, J = 10.4, 5.3 Hz, 1H), 7.04 (dd, J = 7.8, 4.8 Hz, 1H), 7.00 (t, J = 7.9 Hz, 1H), 6.69 – 6.66 (m, 1H), 6.61 – 6.59 (m, 1H), 6.56 (d, J = 7.6 Hz, 1H), 6.45 (d, J = 7.6 Hz, 1H), 6.43

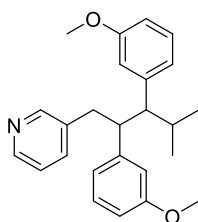
– 6.41 (m, 1H), 6.36 – 6.34 (m, 1H), 3.69 (s, 3H), 3.64 (s, 3H), 3.14 (ddd, $J = 14.7, 10.5, 5.1$ Hz, 2H), 2.88 – 2.78 (m, $J = 10.9, 8.3, 4.0$ Hz, 1H), 2.72 – 2.66 (m, 1H), 1.94 (dq, $J = 14.6, 7.3, 4.5$ Hz, 1H), 1.48 – 1.41 (m, 1H), 0.79 (t, $J = 7.3$ Hz, 3H) ppm.

^{13}C NMR (151 MHz, CDCl_3) δ 160.0, 159.2, 150.6, 147.3, 144.6, 143.0, 136.3, 136.2, 128.7, 128.6, 122.0, 121.9, 120.9, 115.0, 114.7, 111.7, 111.6, 54.9, 54.1, 52.9, 52.8, 36.8, 26.3, 12.5 ppm.

FT-IR (neat, ν_{max}) 2928, 1599, 1584, 1387, 1453, 1326, 1320, 1288, 1258, 1044, 873, 779, 751, 714, 702 cm^{-1} .

HRMS ($\text{C}_{25}\text{H}_{28}\text{O}_2\text{N} = [\text{M}+\text{H}]^+$): calcd. 362.2115; found 362.2109.

3-(2,3-bis(3-Methoxyphenyl)-4-methylpentyl)pyridine (8b)



The product (0.3 mmol) was obtained following **P4**, after preparative TLC (hexane: ethyl acetate 100:1–30:1, v/v, 48 ml column volume) as colorless oil (30 % yield).

Major Diastereomer

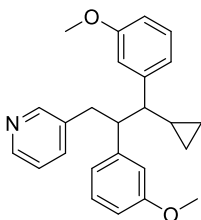
^1H NMR (600 MHz, CDCl_3) δ 8.43 – 8.23 (m, 2H), 7.25 (m, 1H), 7.08 (dd, $J = 7.6, 4.9$ Hz, 1H), 7.05 (t, $J = 7.9$ Hz, 1H), 6.99 – 6.96 (t, $J = 7.9$ Hz, 1H), 6.66 (dd, $J = 7.9, 2.4$ Hz, 1H), 6.59 (dd, $J = 7.9, 2.3$ Hz, 1H), 6.45 (dd, $J = 10.9, 7.7$ Hz, 2H), 6.35 – 6.29 (m, 2H), 3.65 (s, 3H), 3.63 (s, 3H), 3.46 (dt, $J = 9.3, 6.3$ Hz, 1H), 3.11 (dd, $J = 13.9, 5.8$ Hz, 1H), 2.77 (dd, $J = 13.8, 9.3$ Hz, 1H), 2.67 (t, $J = 7.3$ Hz, 1H), 2.22 – 2.13 (m, 1H), 1.05 (d, $J = 6.6$ Hz, 3H), 0.79 (d, $J = 6.7$ Hz, 3H) ppm.

^{13}C NMR (151 MHz, CDCl_3) δ 158.8, 158.5, 150.4, 147.2, 142.8, 141.4, 136.5, 136.1, 128.3, 127.9, 123.2, 123.0, 122.0, 116.1, 115.2, 111.6, 111.4, 57.0, 55.0, 54.9, 48.0, 37.7, 28.7, 22.2, 19.4 ppm.

FT-IR (neat, ν_{max}) 2926, 1599, 1583, 1488, 1453, 1436, 1367, 1257, 1159, 1044, 874, 784, 757, 714, 701 cm^{-1} .

HRMS ($\text{C}_{25}\text{H}_{30}\text{O}_2\text{N} = [\text{M}+\text{H}]^+$): calcd. 376.2271; found 376.2266.

3-(-3-cyclopropyl-2,3-bis(3-methoxyphenyl)propyl)pyridine (8c)



The product (0.3 mmol) was obtained following **P4**, after preparative TLC (hexane: ethyl acetate 100:1–30:1, v/v, 48 ml column volume) as colorless oil (28% yield).

Major Diastereomer

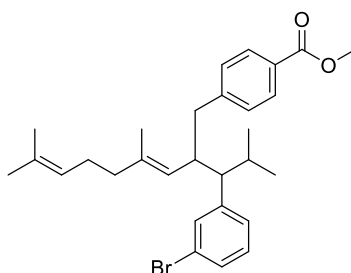
¹H NMR (600 MHz, CDCl₃) δ 8.27 (dd, J = 4.8, 1.6 Hz, 1H), 8.10 (d, J = 2.0 Hz, 1H), 7.30 – 7.26 (m, 1H), 7.13 (t, J = 7.9 Hz, 1H), 7.11 – 7.07 (m, 1H), 6.98 (dd, J = 7.9, 4.9 Hz, 1H), 6.84 – 6.78 (m, 2H), 6.76 – 6.74 (m, 1H), 6.72 – 6.68 (m, 2H), 6.62 – 6.59 (m, 1H), 3.82 (s, 3H), 3.73 (s, 3H), 3.14 (ddd, J = 11.1, 9.6, 3.8 Hz, 1H), 2.83 (dd, J = 13.9, 3.7 Hz, 1H), 2.72 (dd, J = 13.9, 11.2 Hz, 1H), 2.17 (t, J = 9.4 Hz, 1H), 0.90 – 0.82 (m, 1H), 0.26 – 0.17 (m, 2H), -0.10 (dq, J = 9.8, 5.0 Hz, 1H), -0.18 – -0.24 (m, 1H) ppm.

¹³C NMR (151 MHz, CDCl₃) δ 222.0, 159.6, 159.4, 150.3, 147.1, 146.1, 143.9, 136.293, 129.5, 129.1, 123.0, 121.5, 120.8, 115.2, 114.5, 111.5, 111.4, 56.7, 55.3, 55.3, 54.8, 37.7, 16.0, 7.2, 2.9 ppm.

FT-IR (neat, $\nu_{\max}$) 2924, 1736, 1599, 1584, 1488, 1454, 1436, 1319, 1259, 1150, 1044, 873, 822, 784, 753, 714, 700, 666 cm⁻¹.

HRMS (C₂₅H₂₈O₂N = [M+H]⁺): calcd. 374.2115; found 374.2107.

Methyl 4-(-2-(-1-(3-bromophenyl)-2-methylpropyl)-4,8-dimethylnona-3,7-dien-1-yl)benzoate (8d)



3.6 ml (1.2 equiv., 0.36 mmol) of isopropylboronic acid solution (0.10 M boronic acid and 2 equiv. DIPEA in dry CH₂Cl₂) were transferred into a round-bottom flask and 1-(diazomethyl)-3-bromobenzene (0.3 mmol) was added at a flow rate of 30 μ L min⁻¹. After 30 min stirring the reaction mixture was colorless and 1.40 equiv of 1-diazo-3,7-dimethylocta-2,6-diene solution were added at a flow rate of 20 μ L min⁻¹. After stirring for 15 min the reaction mixture was colorless again and 2.00 equiv of methyl 4-(diazomethyl)benzoate solution were added at a flow rate of 20 μ L min⁻¹. The reaction mixture was stirred for 72 h (over this period the reaction mixture became cloudy). The reaction mixture was then added with 2 ml MeOH and passed through a plug of silica gel. The crude material was purified via column chromatography (solid deposition, hexane:CHCl₃: diethyl ether 100:2:1–40:2:1, v/v). The

product was obtained as colorless oil. 31.2 mg (20% yield). $R_f = 0,78$ (hexane/ethyl acetate = 10:1, v/v).

Major Isomer

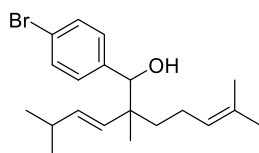
^1H NMR (600 MHz, CDCl_3) δ 7.91 (d, $J = 8.2$ Hz, 2H), 7.38 – 7.34 (m, 1H), 7.27 (s, 1H), 7.15 (dd, $J = 7.9, 6.0$ Hz, 3H), 7.07 – 7.03 (m, 1H), 5.03 – 4.94 (m, 1H), 4.81 (d, $J = 9.9$ Hz, 1H), 3.91 (s, 3H), 3.03 (tt, $J = 10.0, 4.9$ Hz, 1H), 2.74 (dd, $J = 13.2, 4.6$ Hz, 1H), 2.33 (dd, $J = 9.2, 5.2$ Hz, 1H), 2.14 (dd, $J = 13.1, 9.9$ Hz, 2H), 1.94 – 1.84 (m, 4H), 1.58 (d, $J = 12.5$ Hz, 6H), 1.19 (d, $J = 1.1$ Hz, 3H), 0.98 (d, $J = 6.5$ Hz, 3H), 0.72 (d, $J = 6.7$ Hz, 4H).

^{13}C NMR (151 MHz, CDCl_3) δ 167.44, 146.84, 144.10, 136.91, 133.12, 131.57, 129.57, 129.34, 129.24, 129.20, 129.17, 128.87, 127.70, 124.49, 124.29, 121.93, 77.37, 77.16, 77.16, 76.95, 57.95, 52.09, 41.48, 41.00, 40.10, 29.45, 26.61, 26.58, 25.85, 21.88, 21.06, 17.83, 16.44.

FT-IR (neat, ν_{max}) 2923, 1721, 1610, 1565, 1435, 1376, 1276, 1178, 1104, 1073, 1021, 997, 970, 852, 783, 763, 706, 687 cm^{-1} .

HRMS ($\text{C}_{29}\text{H}_{38}\text{O}_2\text{Br} = [\text{M}+\text{H}]^+$): calcd. 497.2050; found 497.2046.

(E)-1-(4-bromophenyl)-2,6-dimethyl-2-(3-methylbut-1-en-1-yl)hept-5-en-1-ol (11a)



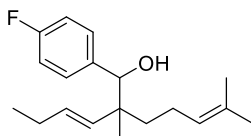
The product was obtained following **P5(A)** after purification by chromatography using a Biotage SP4 (0–20% hexane – ethyl acetate, v/v, 42 mL column volume) as a colorless liquid. $R_f = 0.68$ (hexane/ethyl acetate = 4:1, v/v). 64.4 mg (83% yield).

^1H NMR (400 MHz, CDCl_3) δ 7.48 – 7.36 (m, 2H), 7.22 – 7.11 (m, 2H), 5.45 (dd, $J = 15.9, 6.6$ Hz, 1H), 5.34 (dd, $J = 16.0, 0.6$ Hz, 1H), 5.09 – 5.01 (m, 1H), 4.32 (s, 1H), 2.44 – 2.29 (m, 1H), 2.10 (s, $J = 11.6$ Hz, 1H), 1.83 (dd, $J = 16.1, 7.8$ Hz, 2H), 1.70 – 1.64 (m, 3H), 1.55 (s, 3H), 1.41 – 1.30 (m, 1H), 1.29 – 1.17 (m, 1H), 1.03 (s, 3H), 1.01 (s, 3H), 0.85 (s, 3H) ppm.

^{13}C NMR (151 MHz, CDCl_3) δ 134.0, 139.5, 132.0, 131.4, 130.6, 129.9, 124.8, 121.3, 79.8, 77.2, 45.0, 38.1, 31.7, 25.9, 23.0, 22.9, 17.7, 16.7 ppm.

FT-IR (neat, ν_{max}) 3437, 2960, 2926, 2864, 1592, 1487, 1463, 1377, 1182, 1072, 1043, 1010, 983, 825, 778, 718, 684.

(E)-2-(but-1-en-1-yl)-1-(4-fluorophenyl)-2,6-dimethylhept-5-en-1-ol (11b)



The product was obtained following **P5(A)** after purification by chromatography using a Biotage SP4 (0–20% hexane – ethyl acetate, v/v, 42 mL column volume) as a colorless liquid. $R_f = 0.68$ (hexane/ethyl acetate = 4:1, v/v). 48.1 mg (87% yield).

^1H NMR (600 MHz, CDCl_3) δ 7.30 – 7.25 (m, 2H), 7.03 – 6.99 (m, 2H), 5.56 (dt, $J = 15.8, 6.3$ Hz, 1H), 5.40 (d, $J = 15.8$ Hz, 1H), 5.08 – 5.03 (m, 1H), 4.36 (s, 1H), 2.18 (s, 1H), 2.17 – 2.11 (m,

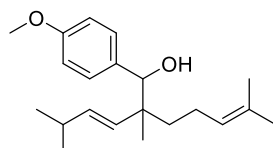
2H), 1.89 – 1.81 (m, 2H), 1.67 (s, 3H), 1.56 (s, 3H), 1.40 – 1.33 (m, 1H), 1.22 – 1.16 (m, 1H), 1.04 (dd, $J = 8.7, 6.2$ Hz, 3H), 0.88 (s, 3H) ppm.

^{13}C NMR (151 MHz, CDCl_3) δ 162.1 (d, $J = 245.0$ Hz), 136.0 (d, $J = 3.1$ Hz), 134.2, 134.1, 131.3, 129.6 (d, $J = 7.9$ Hz), 124.7, 114.2 (d, $J = 21.3$ Hz), 79.6, 45.1, 38.0, 26.0, 25.8, 22.8, 17.6, 16.4, 14.1 ppm.

^{19}F NMR (376 MHz, CDCl_3) δ -115.59 (s, 1F) ppm.

FT-IR (neat, ν_{max}) 2964, 2926, 2854, 1604, 1509, 1455, 1376, 1222, 1157, 1045, 1014, 982, 840, 778 cm^{-1} .

(E)-1-(4-methoxyphenyl)-2,6-dimethyl-2-(3-methylbut-1-en-1-yl)hept-5-en-1-ol (11c)



The product was obtained following **P5(A)** after purification by chromatography using a Biotage SP4 (0–20% hexane – ethyl acetate, v/v, 42 mL column volume) as a colorless oil. $R_f = 0.68$ (hexane/ethyl acetate = 3:1, v/v). 56.2 mg (93%).

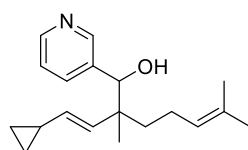
^1H NMR (600 MHz, CDCl_3) δ 7.23 (d, $J = 8.8$, 2H), 6.85 (d, $J = 8.8$ Hz, 2H), 5.46 (dd, $J = 15.9, 6.6$ Hz, 1H), 5.38 (d, $J = 15.9$ Hz, 1H), 5.09 – 5.05 (m, 1H), 4.33 (s, 1H), 3.82 (s, 3H), 2.42 – 2.35 (m, 1H), 2.11 (s, 1H), 1.87 – 1.80 (m, 2H), 1.67 (s, 3H), 1.57 (s, 3H), 1.40 – 1.34 (m, 1H), 1.27 – 1.19 (m, 1H), 1.04 (d, $J = 1.7$ Hz, 3H), 1.03 (d, $J = 1.7$ Hz, 3H), 0.88 (s, 3H) ppm.

^{13}C NMR (151 MHz, CDCl_3) δ 158.8, 139.3, 132.6, 132.3, 131.1, 129.2, 124.9, 112.8, 79.9, 55.2, 45.0, 38.0, 31.6, 25.8, 22.9, 22.9, 22.8, 17.6, 16.7 ppm.

FT-IR (neat, ν_{max}) 2960, 2927, 2864, 1611, 1511, 1462, 1376, 1302, 1245, 1173, 1036, 982, 833, 783, 768 cm^{-1} .

HRMS ($\text{C}_{21}\text{H}_{31}\text{O}_2 = [\text{M}+\text{H}]^+$): calcd. 315.2324; found 315.2322.

(E)-2-(2-cyclopropylvinyl)-2,6-dimethyl-1-(pyridin-3-yl)hept-5-en-1-ol (11d)



The product was obtained following **P5(A)** after purification by chromatography using a Biotage SP4 (0–50% hexane – ethyl acetate, v/v, 42 mL column volume) as a slightly yellow oil. $R_f = 0.08$ (hexane/ethyl acetate = 4:1 v/v). 55.3 mg (97%).

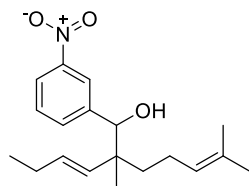
^1H NMR (600 MHz, CDCl_3) δ 8.47 – 8.42 (m, 1H), 7.65 (dt, $J = 7.8, 1.8$ Hz, 1H), 7.23 (dd, $J = 7.8, 4.8$ Hz, 1H), 5.47 (d, $J = 15.8$ Hz, 1H), 5.08 – 5.02 (m, 1H), 4.96 (dd, $J = 15.8, 8.7$ Hz, 1H), 4.38 (s, 1H), 2.93 (s, 1H), 1.89 – 1.81 (m, 2H), 1.65 (s, 3H), 1.55 (s, 3H), 1.49 – 1.36 (m, 2H), 1.23 – 1.16 (m, 1H), 0.83 (s, 3H), 0.73 – 0.71 (m, 2H), 0.40 – 0.32 (m, 2H) ppm.

^{13}C NMR (151 MHz, CDCl_3) δ 149.4, 148.5, 136.5, 136.3, 135.7, 131.9, 131.4, 124.6, 122.6, 78.2, 45.0, 37.9, 25.7, 22.8, 17.6, 16.8, 14.1, 6.9, 6.8 ppm.

FT-IR (neat, ν_{max}) 2965, 2916, 2849, 1453, 1426, 1376, 1057, 1041, 1024, 972, 955, 908, 808, 731, 714 cm^{-1} .

HRMS ($\text{C}_{19}\text{H}_{28}\text{NO} = [\text{M}+\text{H}]^+$): calcd. 286.2171; found 286.2167.

(E)-2-(but-1-en-1-yl)-2,6-dimethyl-1-(3-nitrophenyl)hept-5-en-1-ol (11e)



The product was obtained following **P5(A)** after purification by chromatography using a Biotage SP4 (0–25% hexane – ethyl acetate, v/v, 42 mL column volume) as a colorless oil. R_f = 0.55 (hexane/ethyl acetate = 4:1, v/v). 57.1 mg (90%).

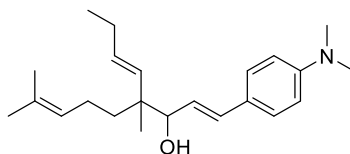
^1H NMR (600 MHz, CDCl_3) δ 8.18 (t, J = 1.8 Hz, 1H), 8.15 – 8.11 (m, 1H), 7.63 (d, J = 7.8 Hz, 1H), 7.48 (t, J = 7.8 Hz, 1H), 5.56 (dt, J = 15.8, 6.3 Hz, 1H), 5.41 (d, J = 15.8 Hz, 1H), 5.07 – 5.02 (m, 1H), 4.47 (s, 1H), 2.36 (s, 1H), 2.17 – 2.11 (m, 2H), 1.90 – 1.83 (m, 2H), 1.67 (s, 3H), 1.56 (s, 3H), 1.46 – 1.38 (m, 1H), 1.24 – 1.16 (m, 1H), 1.03 (dd, J = 8.9, 6.1 Hz, 3H), 0.88 (s, 3H) ppm.

^{13}C NMR (151 MHz, CDCl_3) δ 147.6, 142.6, 134.9, 134.3, 133.3, 131.6, 128.3, 124.4, 123.0, 122.4, 79.4, 45.1, 37.9, 26.0, 25.7, 22.8, 17.6, 16.7, 14.0 ppm.

FT-IR (neat, ν_{max}) 2966, 2926, 2873, 1529, 1456, 1376, 1349, 1095, 1048, 982, 902, 807, 735, 693 cm^{-1} .

HRMS ($\text{C}_{19}\text{H}_{28}\text{NO}_3$ = $[\text{M}+\text{H}]^+$): calcd. 318.2054; found 318.2064.

(E)-1-(4-(dimethylamino)phenyl)-4,8-dimethyl-4-((E)-3-methylbut-1-en-1-yl)nona-1,7-dien-3-ol (11f)



The product was obtained following **P5(A)** after purification by chromatography using a Biotage SP4 (0–25% hexane – ethyl acetate, v/v, 42 mL column volume) as a colorless oil. R_f = 0.75 (hexane/ethyl acetate = 4:1, v/v). 62.5 mg (88%).

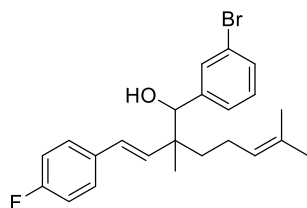
^1H NMR (600 MHz, CDCl_3) δ 7.31 (d, J = 8.8 Hz, 2H), 6.71 (d, J = 8.8 Hz, 2H), 6.51 (d, J = 15.8 Hz, 1H), 6.02 (dd, J = 15.8, 7.8 Hz, 1H), 5.50 (dd, J = 15.9, 6.8 Hz, 1H), 5.39 (d, J = 15.9 Hz, 1H), 5.14 – 5.09 (m, 1H), 3.91 (dd, J = 7.8, 2.3 Hz, 1H), 2.98 (s, 3H), 2.44 – 2.35 (m, 1H), 1.96 – 1.84 (m, 2H), 1.83 (d, J = 2.3 Hz, 1H), 1.69 (s, 3H), 1.60 (s, 3H), 1.46 – 1.32 (m, 2H), 1.05 (dd, J = 6.8, 3.4 Hz, 6H), 1.02 (s, 3H) ppm.

^{13}C NMR (151 MHz, CDCl_3) δ 150.1, 139.1, 132.6, 132.4, 131.1, 125.4, 125.0, 123.8, 112.4, 79.4, 44.5, 40.6, 38.1, 31.6, 25.8, 23.0, 23.0, 22.8, 17.6, 17.3 ppm.

FT-IR (neat, ν_{max}) 2957, 2926, 2868, 1610, 1520, 1446, 1353, 1229, 1186, 1165, 965, 948, 807 cm^{-1} .

HRMS ($\text{C}_{24}\text{H}_{38}\text{NO}$ = $[\text{M}+\text{H}]^+$): calcd. 356.2953; found 356.2961.

(E)-1-(3-bromophenyl)-2-(4-fluorostyryl)-2,6-dimethylhept-5-en-1-ol (11g)



The product was obtained following **P5(A)** after purification by chromatography using a Biotage SP4 (0–20% hexane – ethyl acetate, v/v, 42 mL column volume) as a colorless oil. R_f = 0.58 (hexane/ethyl acetate = 4:1, v/v). 81.5 mg (98%).

^1H NMR (600 MHz, CDCl_3) δ 7.49 (s, 1H), 7.42 (d, J = 7.8 Hz, 1H), 7.39 – 7.34 (m, 2H), 7.24 (d, J = 7.8 Hz, 1H), 7.19 (t, J = 7.8 Hz, 1H), 7.04 (t, J = 8.7 Hz, 2H), 6.34 (d, J = 16.4 Hz, 1H), 6.14 (d, J = 16.4 Hz, 1H), 5.13 – 5.07 (m, 1H), 4.49 (s, 1H), 2.08 (d, J = 1.9 Hz, 1H), 2.01 – 1.86 (m, 2H), 1.68 (s, 3H), 1.63 – 1.55 (m, 1H), 1.57 (s, 3H), 1.46 – 1.38 (m, 1H), 1.05 (s, 3H) ppm.

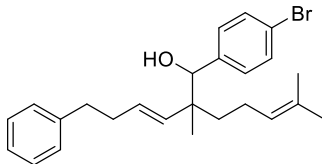
^{13}C NMR (151 MHz, CDCl_3) δ 162.2 (d, J = 246.5 Hz), 143.0, 134.8, 134.8, 133.4 (d, J = 3.3 Hz), 131.6, 131.1, 130.6, 129.7, 127.7 (d, J = 7.9 Hz), 126.7, 124.5, 121.8, 115.5 (d, J = 21.5 Hz), 80.2, 45.5, 37.9, 25.7, 22.9, 17.7, 17.6 ppm.

^{19}F NMR (376 MHz, CDCl_3) δ -114.89 (s, 1F) ppm.

FT-IR (neat, ν_{max}) 2968, 2926, 1602, 1508, 1377, 1229, 1157, 1046, 978, 819, 765, 784, 699 cm^{-1} .

HRMS ($\text{C}_{23}\text{H}_{26}\text{O}^{79}\text{BrF}^{23}\text{Na} = [\text{M}+\text{Na}]^+$): calcd. 439.1043; found 439.1035.

1-(4-Bromophenyl)-2,6-dimethyl-2-(4-phenylbut-1-en-1-yl)hept-5-en-1-ol (11h)



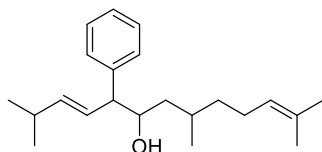
The product was obtained following **P5(A)**, under flow conditions) after purification by chromatography using a Biotage SP4 (0–20% hexane – ethyl acetate, v/v, 42 mL column volume) as a colorless oil. R_f = 0.60 (hexane/ethyl acetate = 4:1, v/v). 1.15 g (2.7 mmol, 90%).

^1H NMR (600 MHz, CDCl_3) δ 7.39 (d, J = 8.4 Hz, 2H), 7.30 (t, J = 7.5 Hz, 2H), 7.19 (dd, J = 13.4, 7.2 Hz, 3H), 7.07 (t, J = 8.5 Hz, 2H), 5.49 (dt, J = 15.7, 6.8 Hz, 1H), 5.31 (d, J = 15.8 Hz, 1H), 5.01 (t, J = 7.1 Hz, 1H), 4.24 (d, J = 2.2 Hz, 1H), 2.74 (dd, J = 12.5, 7.3 Hz, 2H), 2.47 – 2.43 (m, 2H), 1.86 (d, J = 2.5 Hz, 1H), 1.82 – 1.73 (m, 2H), 1.66 (s, 3H), 1.54 (s, J = 2.8 Hz, 3H), 1.35 – 1.28 (m, 1H), 1.19 – 1.13 (m, 1H), 0.83 (s, 3H) ppm.

^{13}C NMR (151 MHz, CDCl_3) δ 141.7, 139.5, 136.2, 131.6, 131.4, 130.6, 129.9, 128.6, 128.6, 126.1, 124.8, 121.3, 79.7, 45.3, 37.9, 36.0, 34.9, 25.8, 22.9, 17.8, 16.9 ppm.

FT-IR (neat, ν_{max}) 3502, 3026, 2966, 2922, 2854, 1738, 1592, 1487, 1454, 1404, 1376, 1243, 1184, 1195, 1010, 982, 907, 832, 780, 745, 698 cm^{-1} .

(E)-2,8,12-trimethyl-5-phenyltrideca-3,11-dien-6-ol (11i)



The product was obtained following **P5(A)** after purification by chromatography using a Biotage SP4 (0–10% hexane – ethyl acetate, v/v, 42 mL column volume) as a colorless oil. R_f = 0.59 (hexane/ethyl acetate = 9:1, v/v). 16.9 mg (27%).

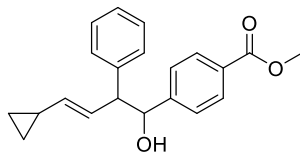
^1H NMR (600 MHz, CDCl_3) δ 7.33 (t, J = 7.6 Hz, 2H), 7.26 – 7.18 (m, 3H), 5.71 – 5.60 (m, 2H), 5.12 – 5.05 (m, 1H), 3.87 – 3.81 (m, 1H), 3.19 – 3.10 (m, 1H), 2.39 – 2.30 (m, 1H), 2.03 – 1.86 (m, 2H), 1.84 – 1.80 (m, 1H), 1.73 – 1.64 (m, 1H), 1.69 (d, J = 6.5 Hz, 3H), 1.59 (s, 3H), 1.44 – 1.10 (m, 3H), 1.06 – 0.99 (m, 1H), 1.03 (d, J = 6.6 Hz, 3H), 1.00 (dd, J = 6.8, 1.2 Hz, 3H), 0.91 – 0.83 (m, 3H) ppm.

^{13}C NMR (151 MHz, CDCl_3) δ 142.5, 142.4, 141.8, 141.8, 131.0, 131.0, 128.6, 127.9, 127.9, 126.7, 126.4, 126.3, 124.9, 124.9, 72.1, 71.6, 57.1, 56.5, 38.0, 36.1, 31.2, 31.2, 29.3, 29.0, 22.6, 22.5, 20.4, 18.8, 17.6, 17.6 ppm.

FT-IR (neat, ν_{max}) 2958, 2925, 2868, 1494, 1452, 1377, 1030, 974, 758, 735, 699 cm^{-1} .

HRMS ($\text{C}_{22}\text{H}_{35}\text{O}$ = $[\text{M}+\text{H}]^+$): calcd. 315.2682; found 315.2673.

Methyl (E)-4-(4-cyclopropyl-1-hydroxy-2-phenylbut-3-en-1-yl)benzoate (11j)



The product was obtained following **P5(A)** after purification by chromatography using a Biotage SP4 (0–20% hexane – ethyl acetate, v/v, 42 mL column volume) as a slightly yellow oil. R_f = 0.30 (hexane/ethyl acetate = 4:1, v/v). 31.0 mg (48%).

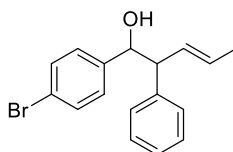
^1H NMR (600 MHz, CDCl_3) δ 7.86 (d, J = 8.3 Hz, 2H), 7.25 – 7.12 (m, 5H), 7.03 – 6.98 (m, 2H), 5.91 (dd, J = 15.2, 9.4 Hz, 1H), 5.21 (dd, J = 15.2, 8.8 Hz, 1H), 4.79 (d, J = 8.3 Hz, 1H), 3.89 (s, 3H), 3.39 (dd, J = 8.8, 8.3 Hz, 1H), 2.64 (s, 1H), 1.51 – 1.40 (m, 1H), 0.80 – 0.66 (m, 2H), 0.44 – 0.29 (m, 2H) ppm.

^{13}C NMR (151 MHz, CDCl_3) δ 167.1, 147.1, 140.5, 139.7, 129.1, 128.9, 128.5, 128.1, 126.8, 126.7, 126.1, 77.1, 58.8, 52.1, 13.9, 6.9, 6.9 ppm.

FT-IR (neat, ν_{max}) 1719, 1611, 1436, 1310, 1278, 1191, 1106, 1018, 962, 773, 700 cm^{-1} .

HRMS ($\text{C}_{21}\text{H}_{23}\text{O}_3$ = $[\text{M}+\text{H}]^+$): calcd. 323.1647; found 323.1646.

(E)-1-(4-bromophenyl)-2-phenylpent-3-en-1-ol (11k)



The product was obtained following **P5(A)** after purification by chromatography using a Biotage SP4 (0–20% hexane – ethyl acetate, v/v, 42 mL column volume) as a slightly yellow oil. $R_f = 0.47$ (hexane/ethyl acetate = 4:1, v/v). 26.1 mg (41%).

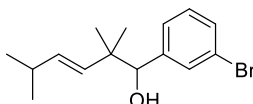
^1H NMR (600 MHz, CDCl_3) δ 7.37 – 7.29 (m, 2H), 7.26 – 7.13 (m, 3H), 7.10 – 6.96 (m, 4H), 5.96 – 5.62 (m, 2H), 4.72 (dd, $J = 8.7, 2.1$ Hz, 1H), 3.39 (t, $J = 8.7$ Hz, 1H), 2.42 (d, $J = 2.1$ Hz, 1H), 1.76 (dd, $J = 6.4, 1.5$ Hz, 2H) ppm.

^{13}C NMR (151 MHz, CDCl_3) δ 140.9, 140.7, 130.9, 130.3, 130.2, 128.5, 128.4, 128.2, 126.7, 121.1, 76.8, 58.7, 18.2 ppm.

FT-IR (neat, ν_{max}) 1593, 1487, 1451, 1380, 1071, 1046, 1010, 970, 821, 755, 699 cm^{-1} .

HRMS ($\text{C}_{17}\text{H}_{17}\text{O}^{79}\text{Br}^{23}\text{Na}$ [$\text{M}^+ + \text{Na}$]): calcd. 339.0355; found 339.0349.

(E)-1-(3-bromophenyl)-2,2,5-trimethylhex-3-en-1-ol (11l)



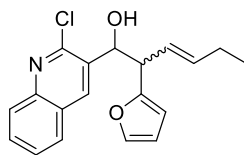
The product was obtained following **P5(B)** after purification by chromatography using a Biotage SP4 (0–10% hexane – ethyl acetate, v/v, 42 mL column volume) as a colorless oil. $R_f = 0.73$ (hexane/ethyl acetate = 4:1, v/v). 38.2 mg (64%).

^1H NMR (600 MHz, CDCl_3) δ 7.45 (d, $J = 1.7$ Hz, 1H), 7.40 (dt, $J = 7.7, 1.7$ Hz, 1H), 7.22 – 7.16 (m, 2H), 5.46 – 5.36 (m, 2H), 4.35 (d, $J = 2.8$ Hz, 1H), 2.33 (dhept, $J = 6.8, 5.3$ Hz, 1H), 2.07 (d, $J = 2.8$ Hz, 1H), 1.02 (d, $J = 6.8$ Hz, 3H), 1.01 (d, $J = 6.8$ Hz, 3H), 1.01 (s, 3H), 0.94 (s, 3H) ppm.

^{13}C NMR (151 MHz, CDCl_3) δ 143.3, 137.8, 132.9, 130.8, 130.3, 128.9, 126.5, 121.6, 80.2, 41.2, 31.3, 24.8, 22.6, 22.6, 21.8 ppm.

FT-IR (neat, ν_{max}) 2959, 2868, 1595, 1569, 1465, 1427, 1383, 1363, 1184, 1071, 1039, 981, 765, 699 cm^{-1} .

HRMS ($\text{C}_{15}\text{H}_{21}\text{O}^{79}\text{Br}^{23}\text{Na} = [\text{M} + \text{Na}]^+$): calcd. 319.0668; found 319.0662.

1-(2-Chloroquinolin-3-yl)-2-(furan-2-yl)hex-3-en-1-ol (11m)

The product was obtained following **P5(B)** after purification by chromatography using a Biotage SP4 (0–20% hexane – ethyl acetate, v/v, 42 mL column volume) as a yellow oil. R_f = 0.29 (hexane/ethyl acetate = 4:1, v/v). 39.3 mg (61%). The product was isolated as a mixture of isomers (E/Z = 3.7:1).

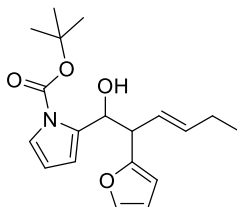
Major isomer

^1H NMR (600 MHz, CDCl_3) δ 8.28 (s, 1H), 8.01 (d, J = 8.4 Hz, 1H), 7.84 (d, J = 8.4 Hz, 1H), 7.73 (ddd, J = 8.4, 6.9, 1.4 Hz, 1H), 7.57 (ddd, J = 8.4, 6.9, 1.4 Hz, 1H), 7.42 (dd, J = 1.9, 0.8 Hz, 1H), 6.35 (dd, J = 3.2, 1.9 Hz, 1H), 6.16 (d, J = 3.2 Hz, 1H), 5.72 – 5.66 (m, 1H), 5.63 – 5.59 (m, 1H), 5.33 (dt, J = 15.2, 6.4 Hz, 1H), 3.95 (dd, J = 9.1, 3.7 Hz, 1H), 2.61 (d, J = 3.1 Hz, 1H), 1.95 (ddq, J = 7.5, 6.4, 1.3 Hz, 2H), 0.80 (t, J = 7.5 Hz, 3H) ppm.

^{13}C NMR (151 MHz, CDCl_3) δ 154.6, 148.7, 146.9, 141.9, 138.5, 137.5, 133.4, 130.2, 128.1, 127.7, 127.0, 127.0, 122.4, 110.4, 106.9, 72.0, 48.3, 25.5, 13.5 ppm.

FT-IR (neat, ν_{max}) 2963, 2932, 1619, 1590, 1566, 1491, 1379, 1327, 1170, 1139, 1069, 1037, 1012, 972, 951, 779, 753, 735 cm^{-1} .

HRMS ($\text{C}_{19}\text{H}_{19}\text{NO}_2\text{Cl} = [\text{M}+\text{H}]^+$) calcd. 328.1104; found 328.1091.

***tert*-Butyl (*E*)-2-(2-(furan-2-yl)-1-hydroxyhex-3-en-1-yl)-1H-pyrrole-1-carboxylate (11n)**

The product was obtained following **P5(B)** after purification by chromatography using a Biotage SP4 (0–25% hexane – ethyl acetate, v/v, 42 mL column volume) as a colorless liquid. R_f = 0.56 (hexane/ethyl acetate = 4:1, v/v). 24.2 mg (36%). The product was isolated as a mixture of isomers (E/Z = 7.4:1).

Major isomer

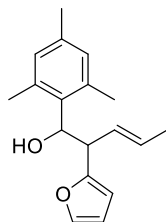
^1H NMR (600 MHz, CDCl_3) δ 7.26 (dd, J = 1.9, 0.8 Hz, 1H), 7.12 (dd, J = 3.4, 1.8 Hz, 1H), 6.22 (dd, J = 3.1, 1.9 Hz, 1H), 6.09 (dd, J = 3.4, 1.8 Hz, 1H), 6.00 (t, J = 3.4 Hz, 1H), 5.98 (d, J = 3.1 Hz, 1H), 5.78 (ddt, J = 15.4, 8.1, 1.5 Hz, 1H), 5.59 (ddt, J = 15.4, 6.3, 0.8 Hz, 1H), 5.21 (t, J = 7.4 Hz, 1H), 3.98 – 3.91 (m, 2H), 2.11 – 2.06 (m, 2H), 1.60 (s, 9H), 0.99 (t, J = 7.5 Hz, 3H) ppm.

^{13}C NMR (151 MHz, CDCl_3) δ 155.7, 150.3, 140.9, 135.9, 135.7, 126.0, 121.9, 113.4, 110.2, 110.0, 105.8, 84.5, 69.6, 47.6, 28.0, 25.6, 13.6 ppm.

FT-IR (neat, ν_{max}) 1737, 1409, 1371, 1334, 1228, 1164, 1123, 1050, 1010, 847, 725 cm^{-1} .

HRMS ($\text{C}_{19}\text{H}_{25}\text{O}_4\text{NNa} = [\text{M}+\text{Na}]^+$) calcd. 354.1676; found 354.1660.

(E)-2-(Furan-2-yl)-1-mesitylpent-3-en-1-ol (11o)



The product was obtained following **P5(B)** after purification by chromatography using a Biotage SP4 (0–5% hexane – ethyl acetate, v/v, 42 mL column volume) as a colorless liquid. R_f = 0.70 (hexane/ethyl acetate = 4:1, v/v). 19.0 mg (35%).

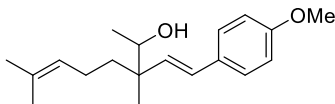
^1H NMR (600 MHz, CDCl_3) δ 7.23 (dd, J = 1.8, 0.7 Hz, 1H), 6.74 (s, 2H), 6.16 (dd, J = 3.1, 1.8 Hz, 1H), 5.94 – 5.88 (m, 1H), 5.80 (dd, J = 15.4, 6.4 Hz, 1H), 5.74 (d, J = 3.1 Hz, 1H), 5.21 (d, J = 9.3 Hz, 1H), 4.02 (t, J = 9.3 Hz, 1H), 2.29 (s, 6H), 2.22 (s, 3H), 2.14 (d, J = 1.7 Hz, 1H), 1.82 (dd, J = 6.4, 1.5 Hz, 3H) ppm.

^{13}C NMR (151 MHz, CDCl_3) δ 154.4, 140.9, 136.7, 136.5, 133.9, 130.3, 129.9, 128.7, 110.2, 105.9, 72.4, 48.6, 20.8, 20.6, 18.2 ppm.

FT-IR (neat, ν_{max}) 2916, 2342, 1611, 1504, 1448, 1376, 1199, 1146, 1010, 969, 926, 851, 783, 730 cm^{-1} .

HRMS ($\text{C}_{18}\text{H}_{22}\text{O}_2\text{Na}$ = $[\text{M}+\text{Na}]^+$): calcd. 293.1512; found 293.1512.

(E)-3-(4-methoxystyryl)-3,7-dimethyloct-6-en-2-ol (11p)

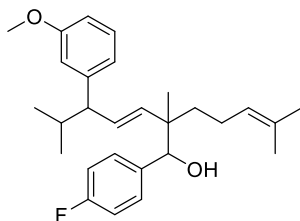


The product was obtained following **P5(A)** after purification by chromatography using a Biotage SP4 (0–5% hexane – ethyl acetate, v/v, 42 mL column volume) as a colorless liquid. 62% yield.

^1H NMR (600 MHz, CDCl_3) δ 7.36 – 7.30 (m, 2H), 6.90 – 6.85 (m, 2H), 6.36 (dd, J = 20.2, 16.4 Hz, 1H), 6.03 (dd, J = 16.4, 12.1 Hz, 1H), 5.26 – 5.11 (m, 1H), 3.83 (s, 3H), 3.72 – 3.50 (m, 1H), 2.00 – 1.88 (m, 2H), 1.69 (s, 3H), 1.59 (d, J = 5.0 Hz, 5H), 1.55 – 1.42 (m, 2H), 1.19 – 1.12 (m, 4H), 1.09 (s, 2H).

^{13}C NMR (151 MHz, CDCl_3) δ 158.97, 158.90, 133.60, 132.93, 131.39, 131.34, 130.18, 129.67, 129.03, 127.24, 127.19, 124.88, 124.80, 113.97, 113.95, 74.28, 73.49, 55.32, 44.75, 44.33, 38.15, 37.69, 25.69, 22.98, 22.88, 18.41, 18.27, 17.65, 17.64, 17.04, 16.92.

1-(4-fluorophenyl)-5-(3-methoxyphenyl)-2,6-dimethyl-2-(4-methylpent-3-en-1-yl)hept-3-en-1-ol (13a)



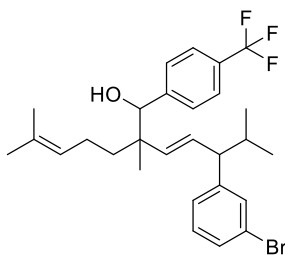
The product was obtained following **P6** after purification using a Biotage SP4 (hexane/ethyl acetate, 50:1–10:1, v/v, 48 ml column volume) as a colorless oil (59 mg 70% yield). R_f = 0.31 (hexane/ethyl acetate = 10:1, v/v).

^1H NMR (600 MHz, CDCl_3) δ 7.22 – 7.15 (m, J = 9.3, 8.6, 4.9 Hz, 3H), 6.94 (t, J = 8.7 Hz, 2H), 6.75 (d, J = 7.6 Hz, 1H), 6.71 (m, 2H), 5.64 (dd, J = 15.8, 8.9 Hz, 1H), 5.42 (d, J = 15.7 Hz, 1H), 5.01 – 4.95 (m, 1H), 4.36 (d, J = 2.3 Hz, 1H), 3.79 (s, 3H), 2.92 (t, J = 8.9 Hz, 1H), 2.01 – 1.92 (m, 2H), 1.78 – 1.70 (m, 2H), 1.62 (s, 3H), 1.42 (s, 3H), 1.39 – 1.29 (m, 1H), 1.27 – 1.17 (m, 1H), 0.97 – 0.93 (d, J = 6.6 Hz, 3H), 0.88 (s, 3H), 0.79 (d, J = 6.6 Hz, 3H) ppm.

^{13}C NMR (151 MHz, CDCl_3) δ 162.26 (d, J = 245.1 Hz), 159.77, 146.67, 136.40 (d, J = 3.0 Hz), 135.74, 134.89, 131.43, 129.63 (d, J = 7.9 Hz), 129.50, 129.46, 124.77, 120.35, 114.40 (d, J = 21.2 Hz), 113.98, 110.90, 79.98, 77.16, 57.85, 55.24, 45.35, 40.11, 37.83, 32.95, 25.79, 22.91, 21.38, 21.24, 17.74, 17.58 ppm.

FT-IR (neat, ν_{max}) 3573, 2959, 1603, 1509, 1487, 1454, 1382, 1261, 1223, 1157, 1047, 982, 828, 776, 700 cm^{-1} .

(*E*)-5-(3-Bromophenyl)-2,6-dimethyl-2-(4-methylpent-3-en-1-yl)-1-(4-(trifluoromethyl)phenyl)hept-3-en-1-ol (13b)



The product was obtained following **P6** after purification using a Biotage SP4 (0-20% hexane – ethyl acetate, v/v, 42 mL column volume) as a colorless oil, 44.5 mg (43% yield). R_f = 0.64 (hexane/ethyl acetate = 4:1, v/v).

^1H NMR (600 MHz, CDCl_3) δ 7.59 – 7.29 (m, 5H), 7.26 – 7.04 (m, 3H), 5.64 – 5.43 (m, 2H), 5.13 – 4.97 (m, 1H), 4.48 – 4.38 (m, 1H), 2.92 (dt, J = 9.2, 6.7 Hz, 1H), 2.08 – 1.85 (m, 1H), 1.81 – 1.55 (m, 7H), 1.46 – 1.24 (m, 4H), 1.00 – 0.86 (m, 6H), 0.82 – 0.76 (m, 3H) ppm.

^{13}C NMR (151 MHz, CDCl_3) δ 147.2, 144.6, 135.9, 135.7, 134.5, 134.3, 131.6, 131.5, 130.8, 130.6, 130.1, 130.0, 129.2, 129.1, 128.3, 128.3, 126.3, 126.1, 124.4, 124.4, 122.5, 80.4, 79.9,

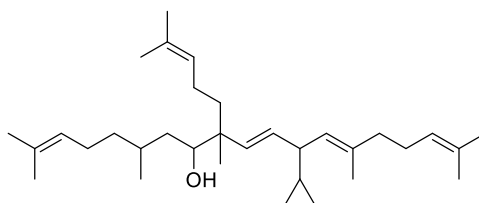
57.9, 57.5, 45.2, 45.0, 38.0, 37.5, 32.9, 32.8, 25.7, 25.6, 23.1, 22.7, 21.1, 21.0, 17.8, 17.5 ppm.

¹⁹F NMR (376 MHz, CDCl₃) δ -62.43 (s, 3F) ppm.

FT-IR (neat, ν_{max}) 2963, 2931, 1567, 1467, 1377, 1325, 1164, 1126, 1068, 1017, 983, 782, 696 cm⁻¹.

HRMS (C₂₈H₃₄O⁷⁹BrF₃²³Na = [M+Na]⁺): calcd. 545.1637; found 545.1630.

(10*E*,13*E*)-12-Isopropyl-2,6,9,14,18-pentamethyl-9-(4-methylpent-3-en-1-yl)nonadeca-2,10,13,17-tetraen-8-ol (13c)



The product was obtained following **P7** after purification using a Biotage SP4 (0-2% hexane – ethyl acetate, v/v, 42 mL column volume) as a colorless oil, 75.8 mg (73% yield). R_f = 0.90 (hexane/ethyl acetate = 4:1, v/v). The product was isolated as a mixture of non-separable isomers.

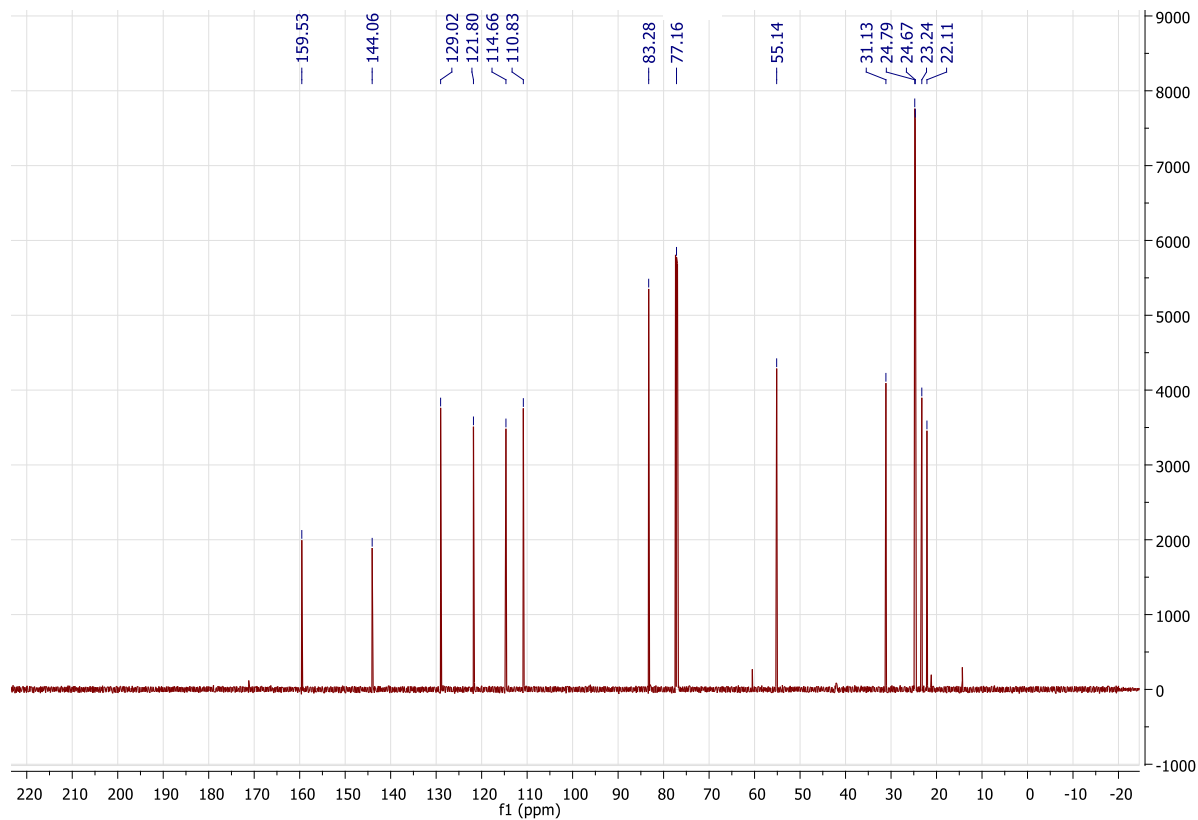
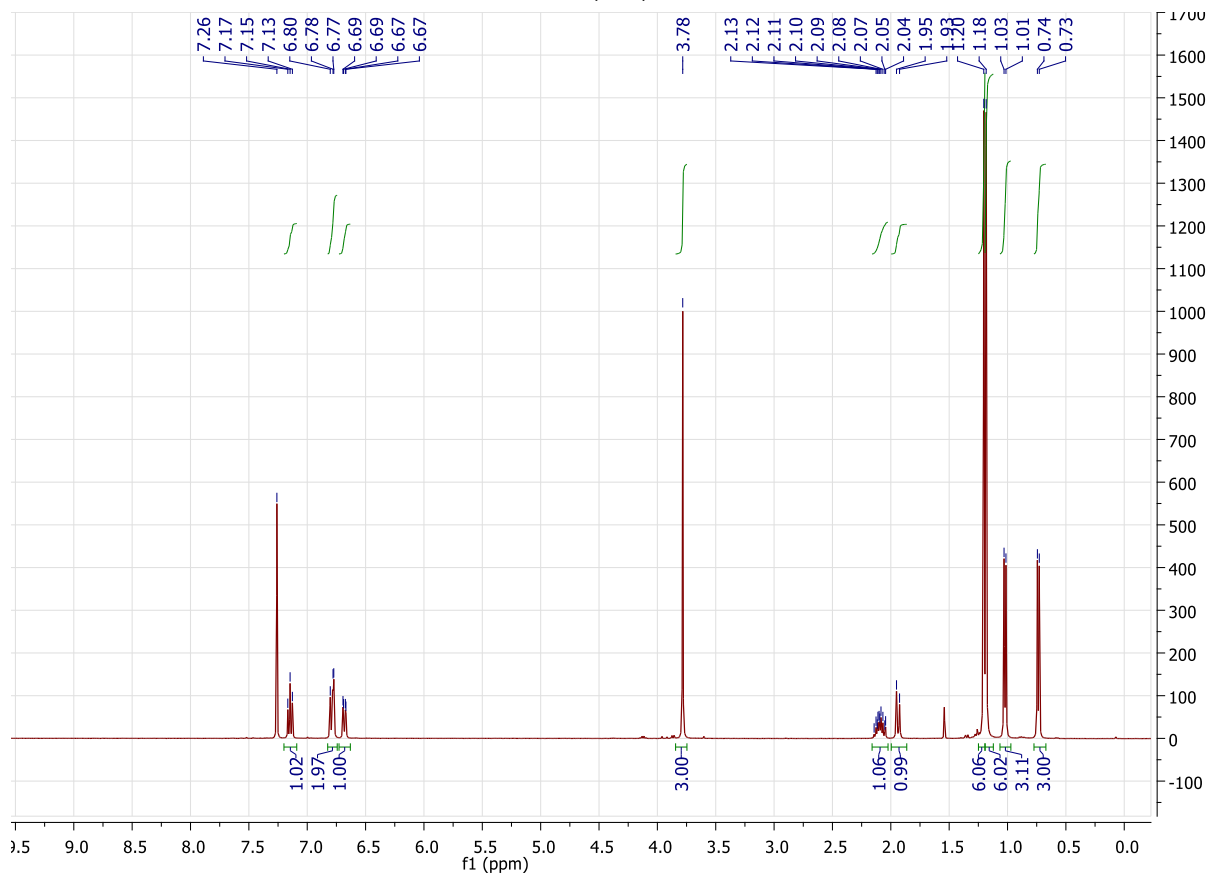
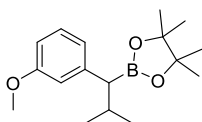
¹H NMR (600 MHz, CDCl₃) δ 5.50 – 5.20 (m, 2H), 5.18 – 4.97 (m, 4H), 3.42 – 3.00 (m, 1H), 2.54 – 0.63 (m, 45H), 0.49 – 0.00 (m, 4H) ppm.

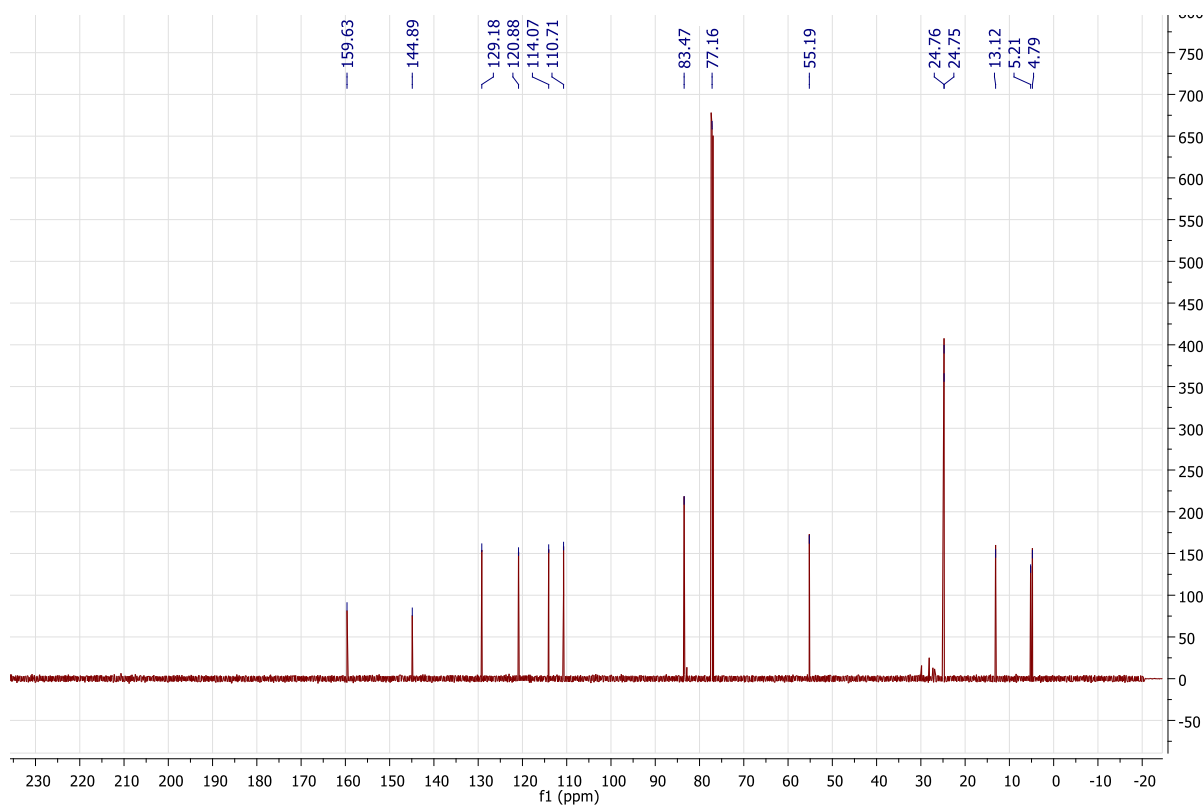
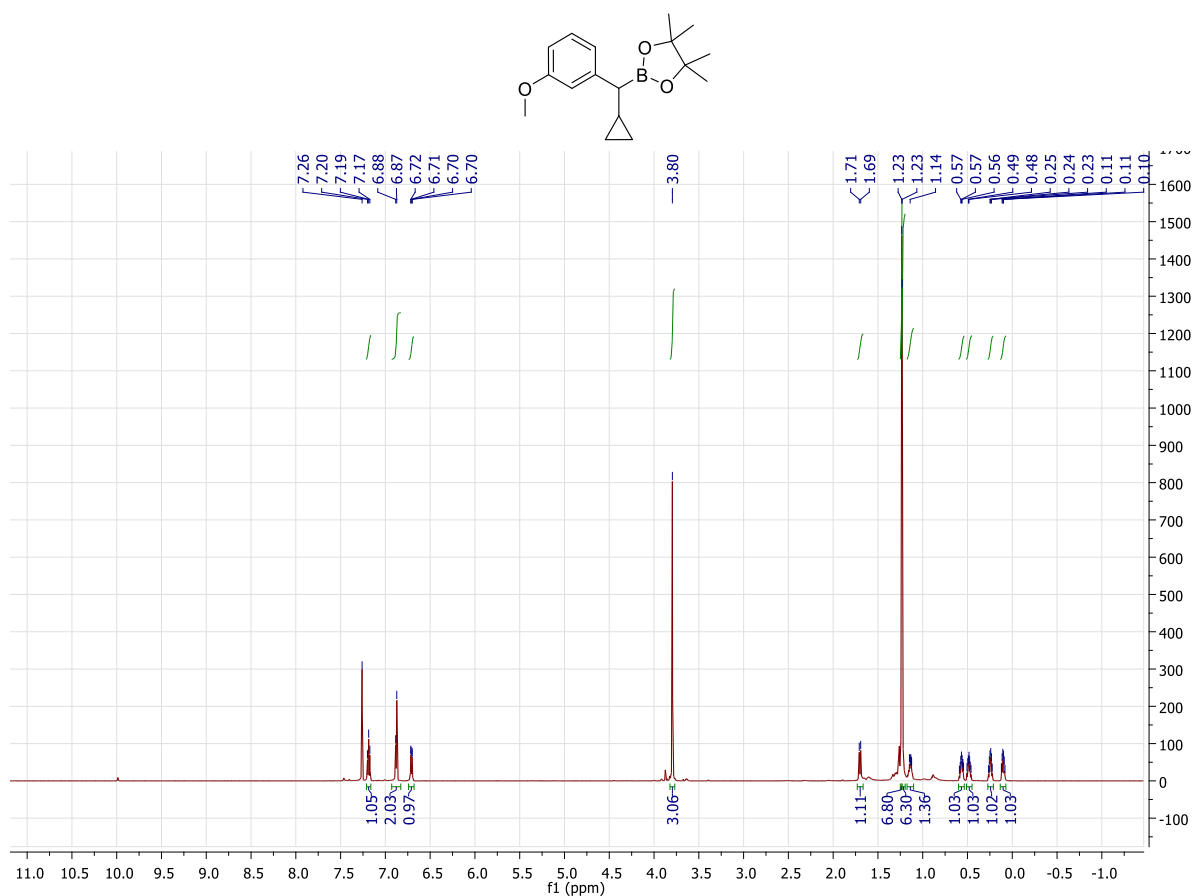
¹³C NMR (151 MHz, CDCl₃) δ 135.2, 135.1, 135.0, 134.8, 134.7, 134.7, 134.5, 134.4, 134.4, 134.3, 134.2, 134.1, 134.1, 134.0, 131.3, 131.3, 131.2, 131.2, 131.2, 131.1, 131.1, 131.0, 130.9, 130.9, 130.9, 130.9, 125.6, 125.6, 125.5, 125.4, 125.0, 125.0, 124.9, 124.9, 124.4, 124.4, 124.3, 124.2, 75.2, 75.0, 74.7, 74.6, 74.5, 47.5, 47.5, 47.5, 45.3, 45.2, 45.0, 45.0, 44.4, 44.3, 44.3, 44.3, 44.2, 44.2, 44.2, 40.0, 39.9, 39.7, 39.7, 38.5, 38.5, 38.4, 38.4, 38.0, 38.0, 37.9, 37.8, 37.8, 37.7, 37.8, 35.9, 35.8, 30.0, 30.0, 29.9, 29.9, 29.4, 29.3, 26.8, 26.7, 26.7, 26.6, 26.6, 26.6, 26.5, 25.7, 25.6, 25.6, 25.4, 22.9, 22.9, 22.8, 22.8, 20.9, 20.8, 18.8, 18.7, 17.7, 17.6, 17.6, 17.5, 17.5, 17.4, 16.9, 16.8, 16.8, 16.6, 16.6, 16.5, 16.5, 16.3, 4.6, 3.2, 3.1, 2.9, 2.9, 2.6 ppm.

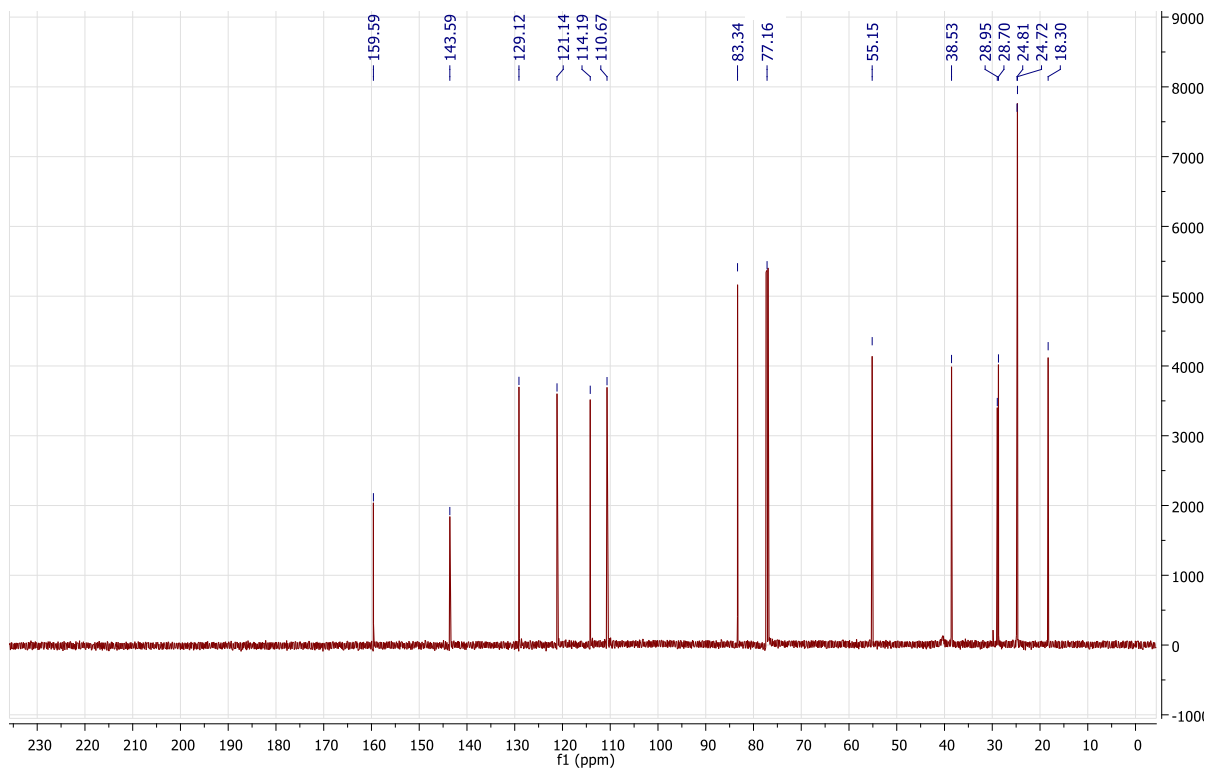
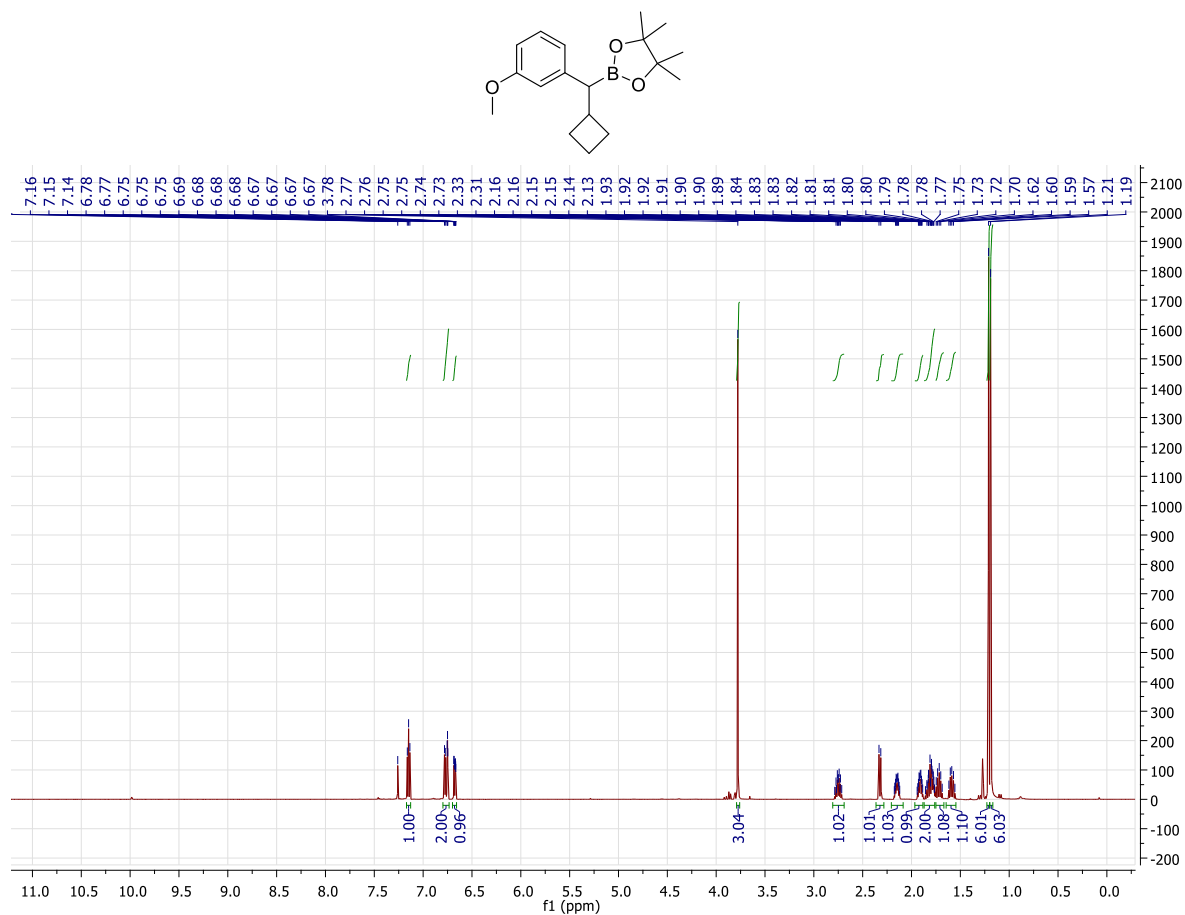
FT-IR (neat, ν_{max}) 2966, 2916, 1450, 1376, 1105, 1058, 1015, 981, 818, 744 cm⁻¹.

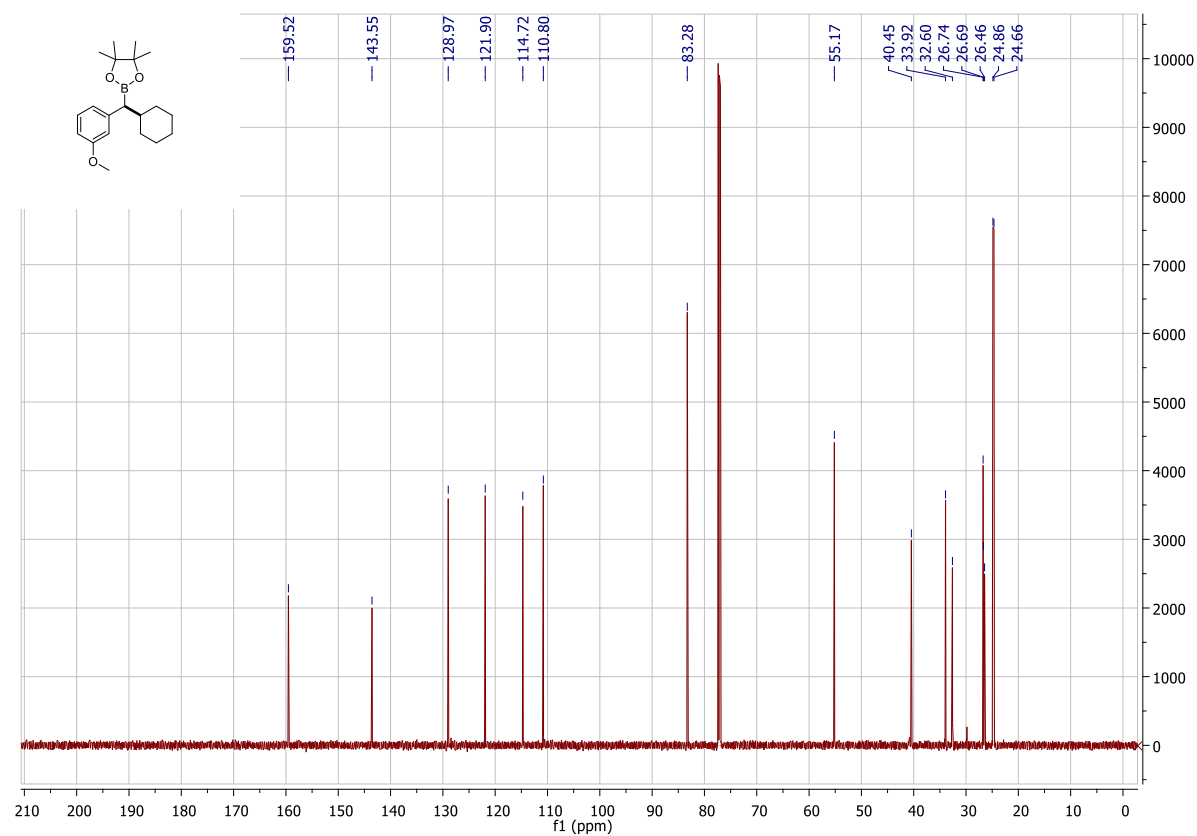
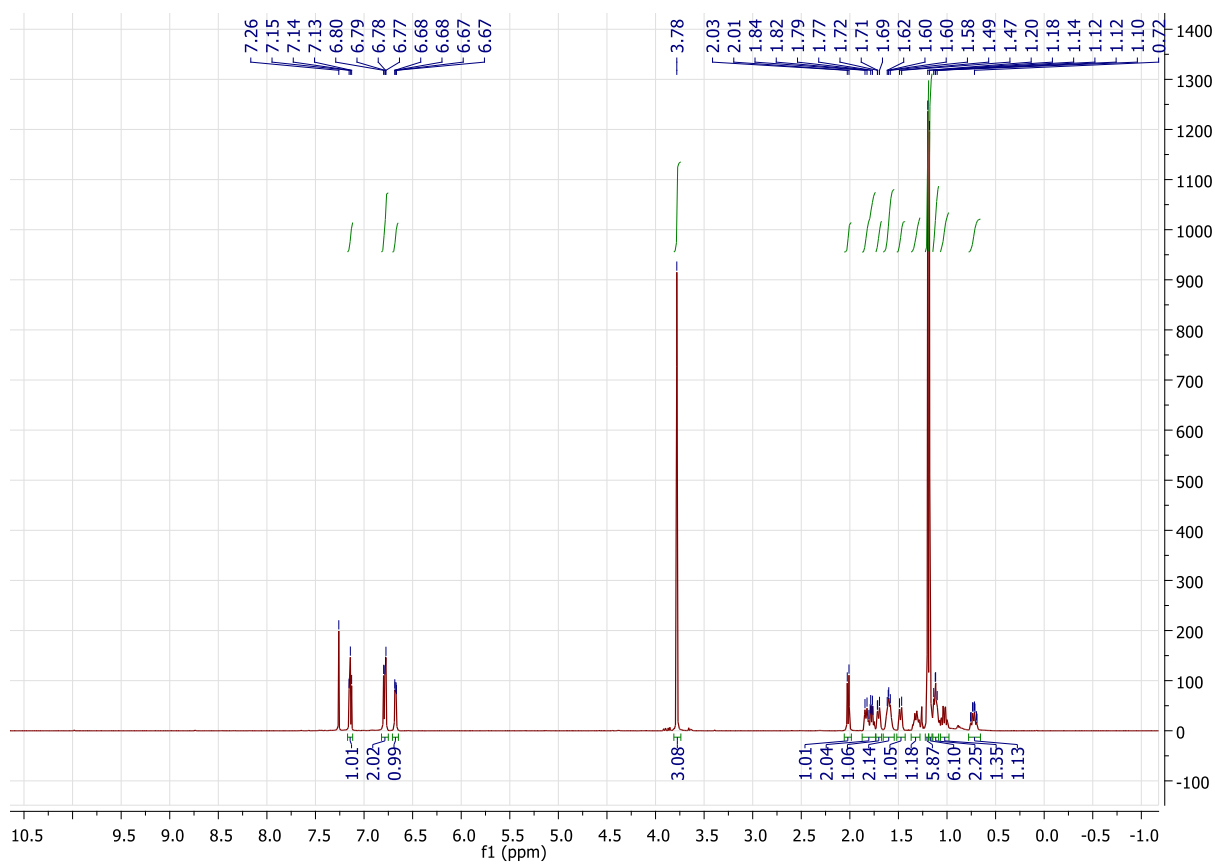
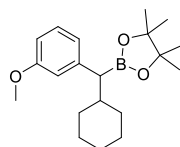
HRMS (C₃₃H₅₆O²³Na = [M+Na]⁺): calcd. 491.4223; found 491.4216.

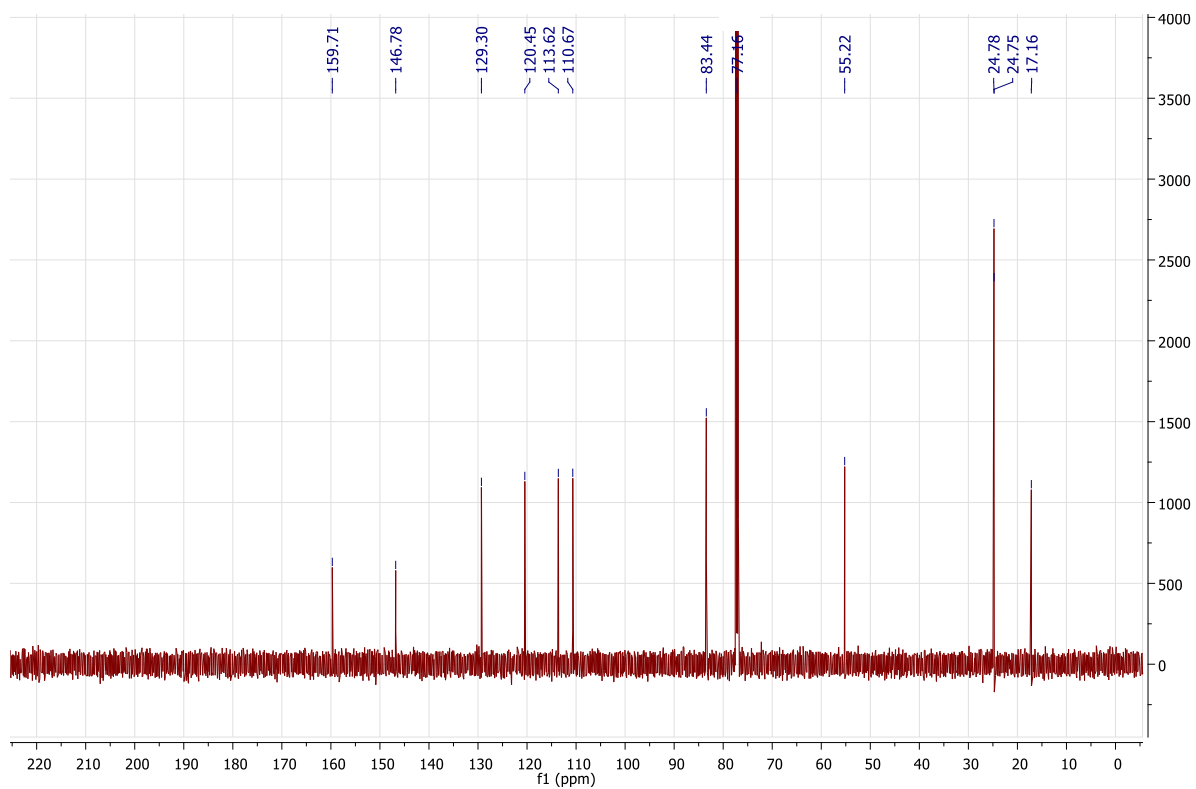
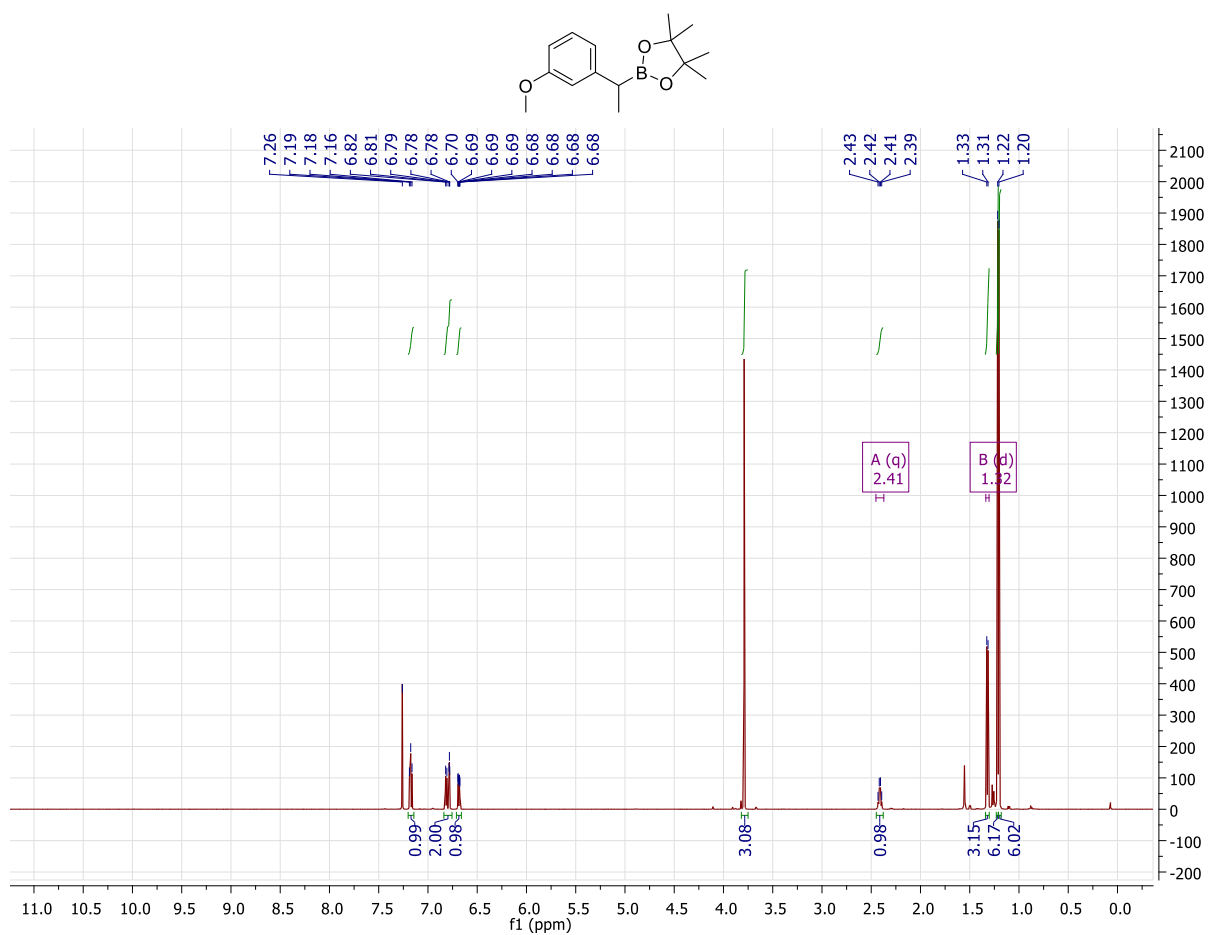
^1H -NMR and ^{13}C -NMR spectra

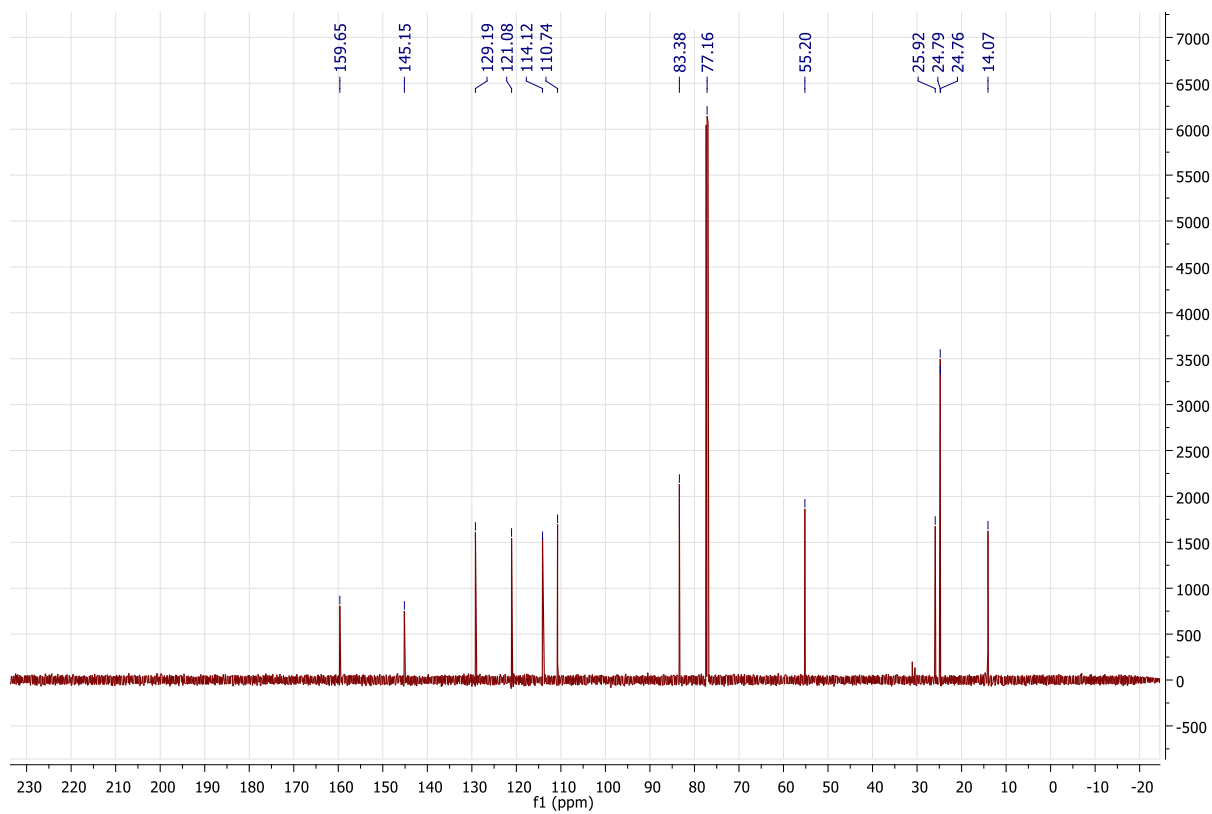
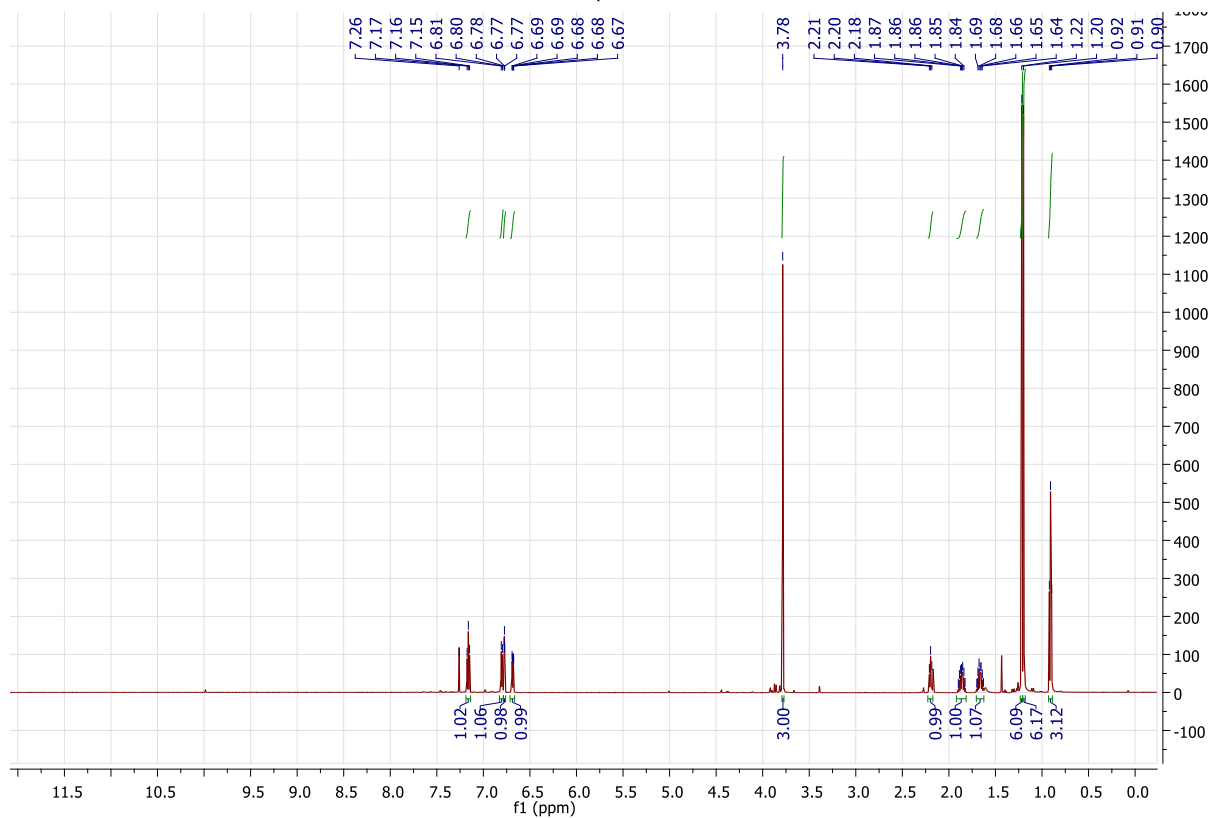
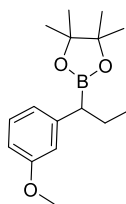


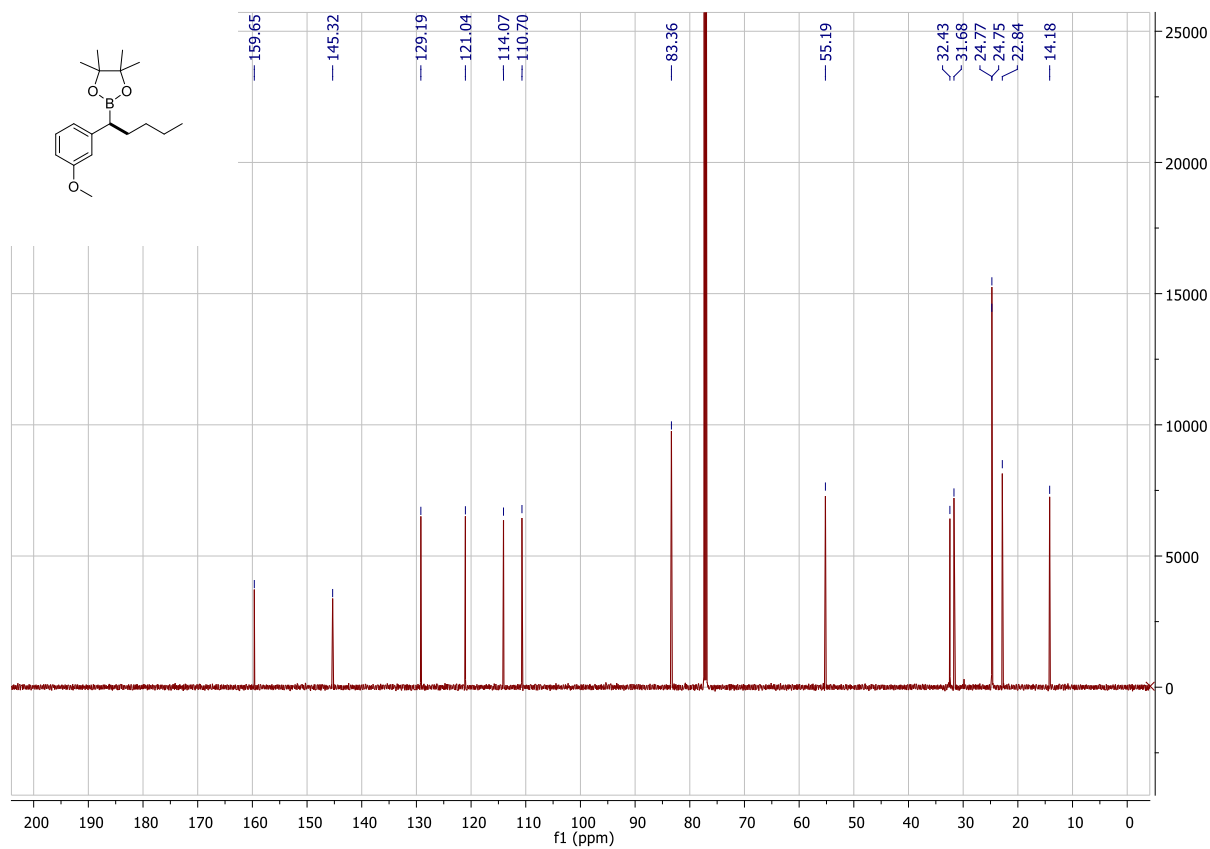
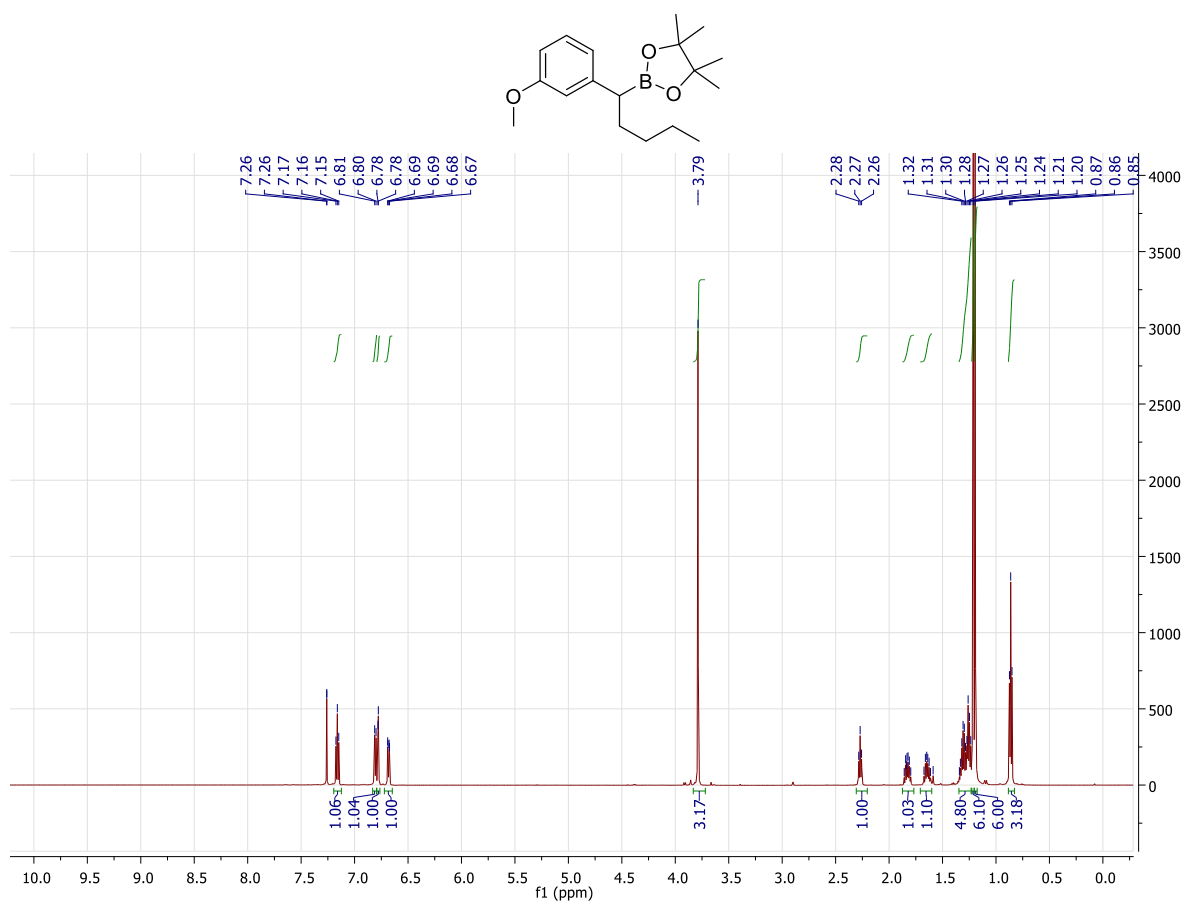


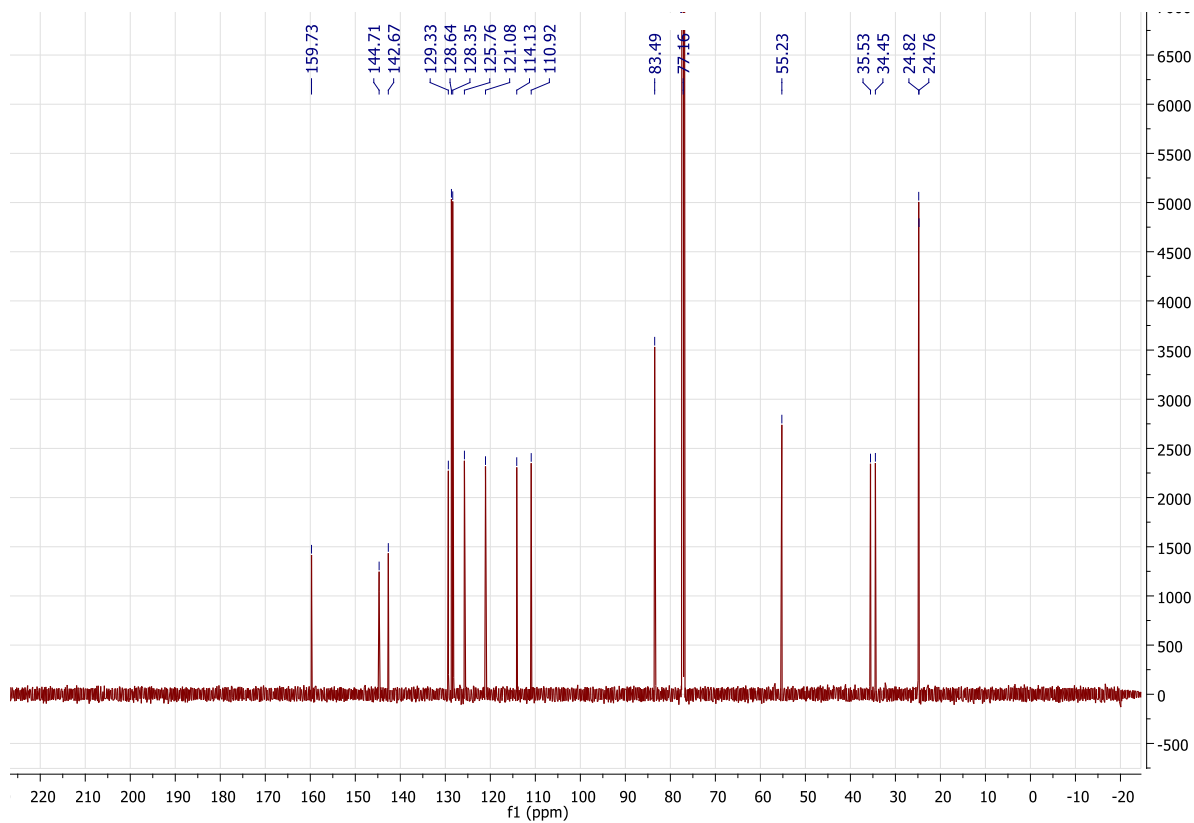
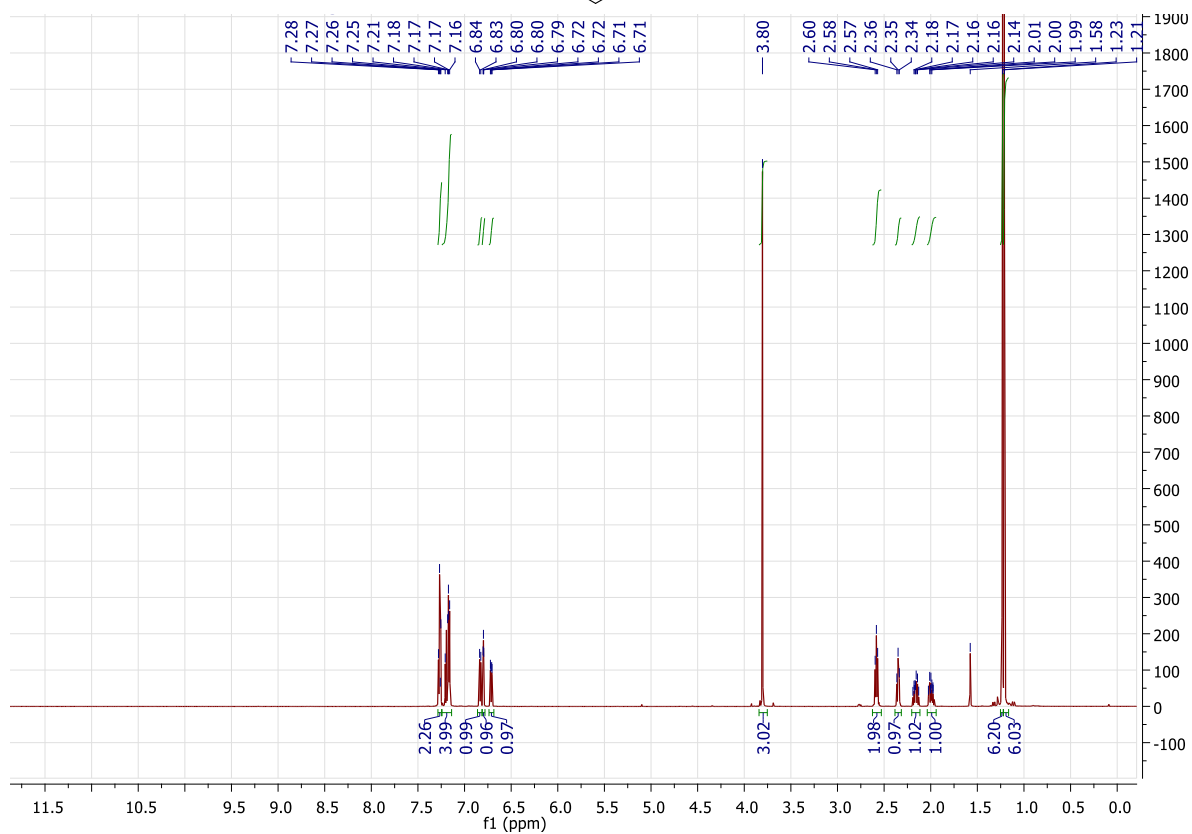
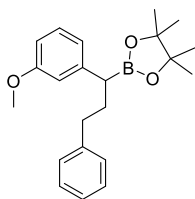


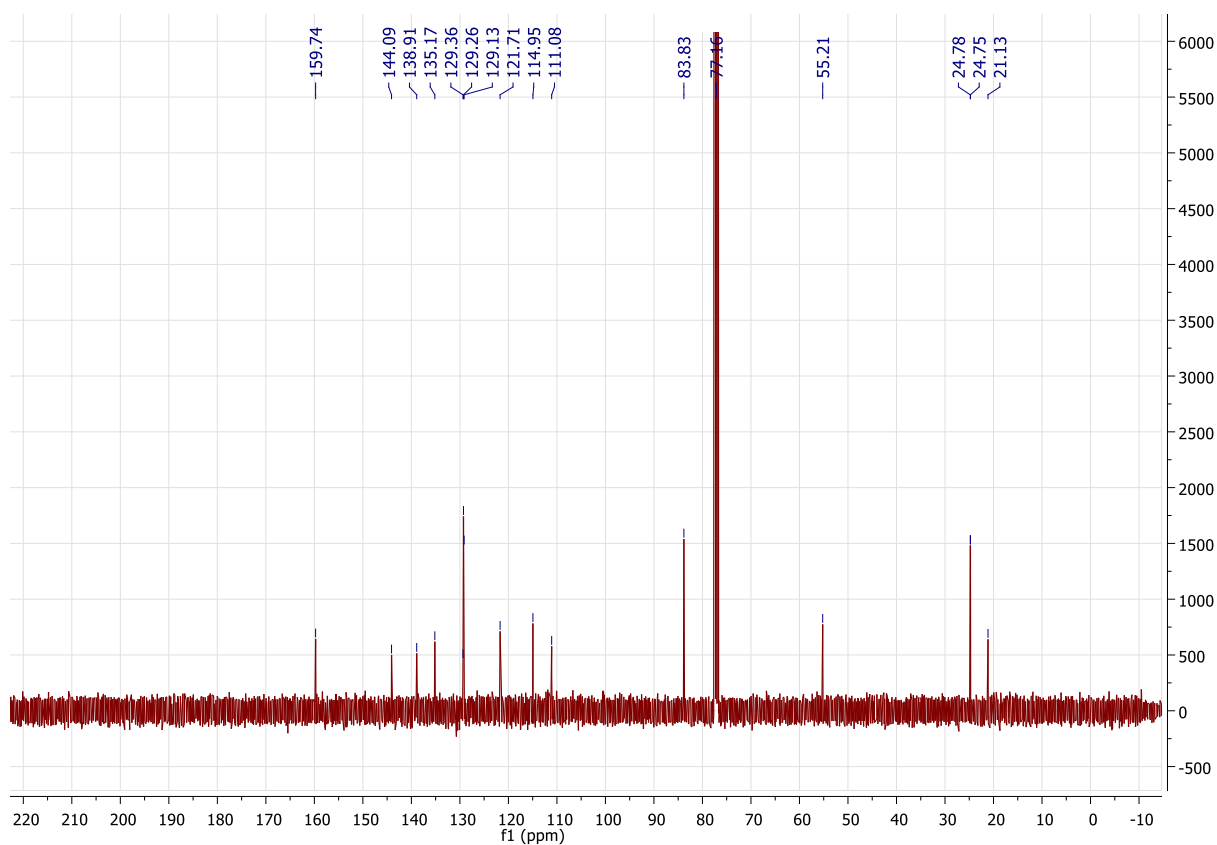
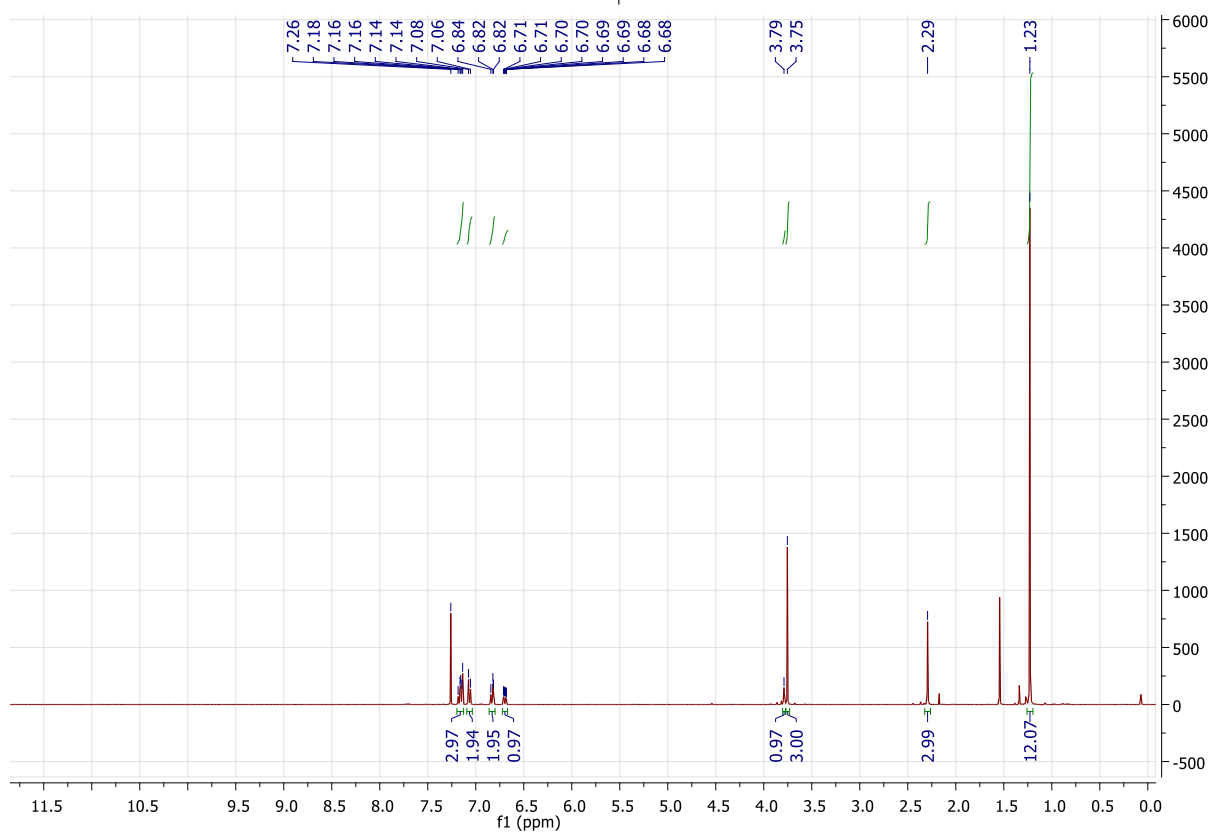
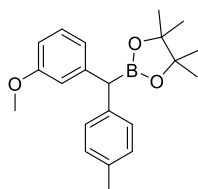


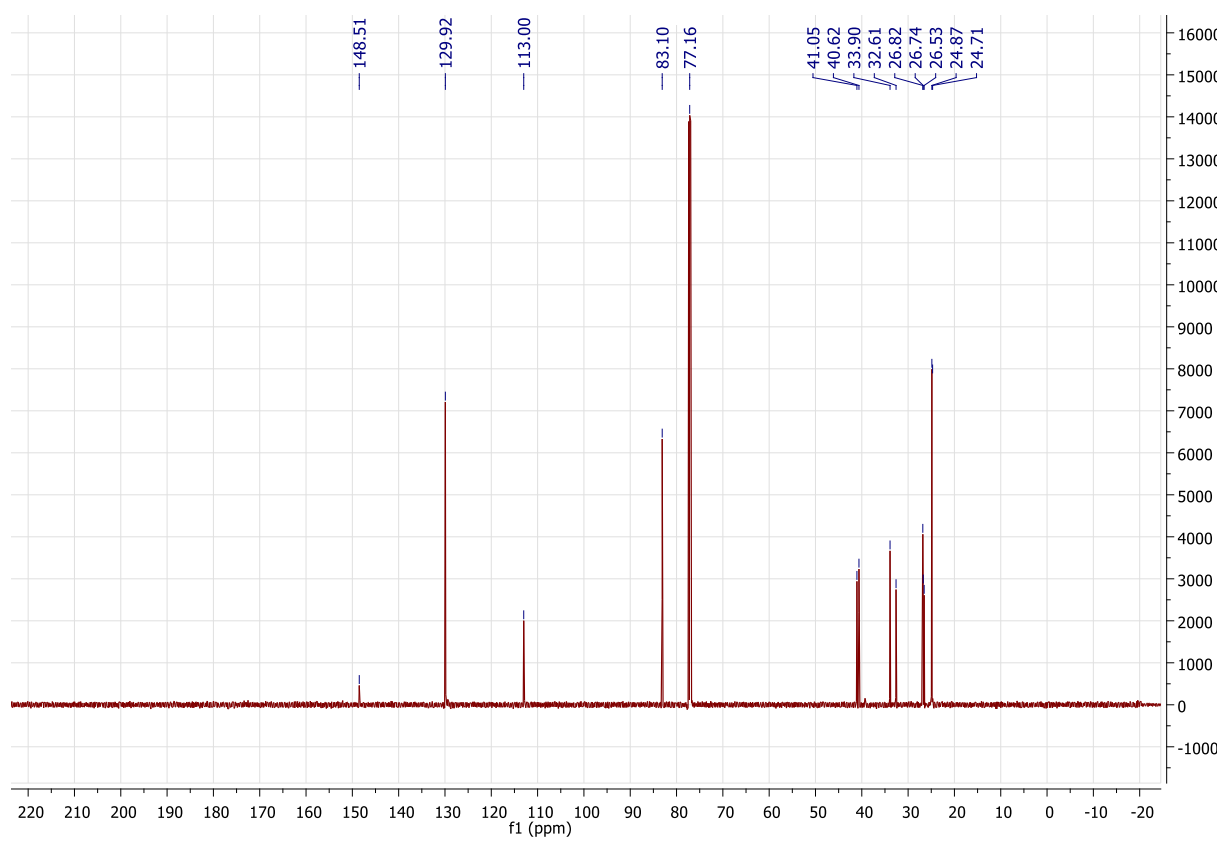
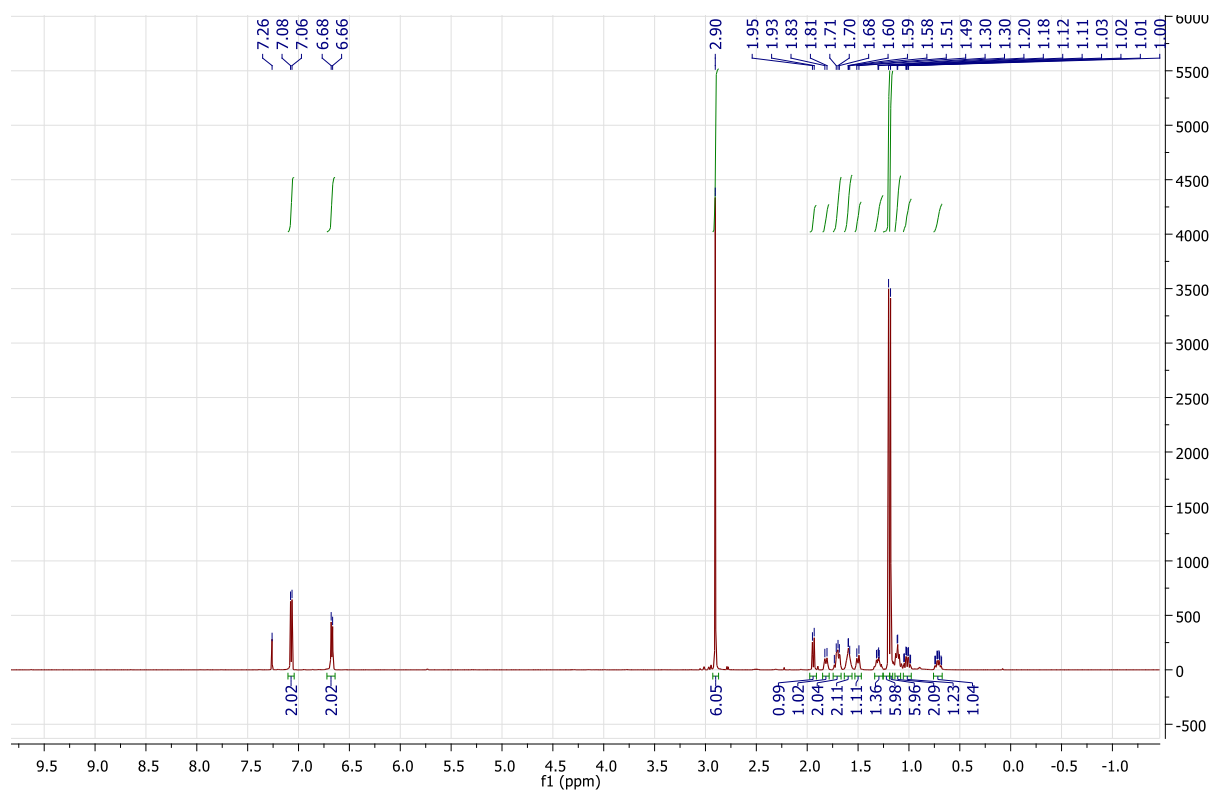
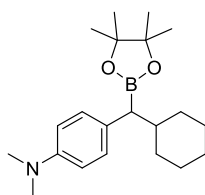


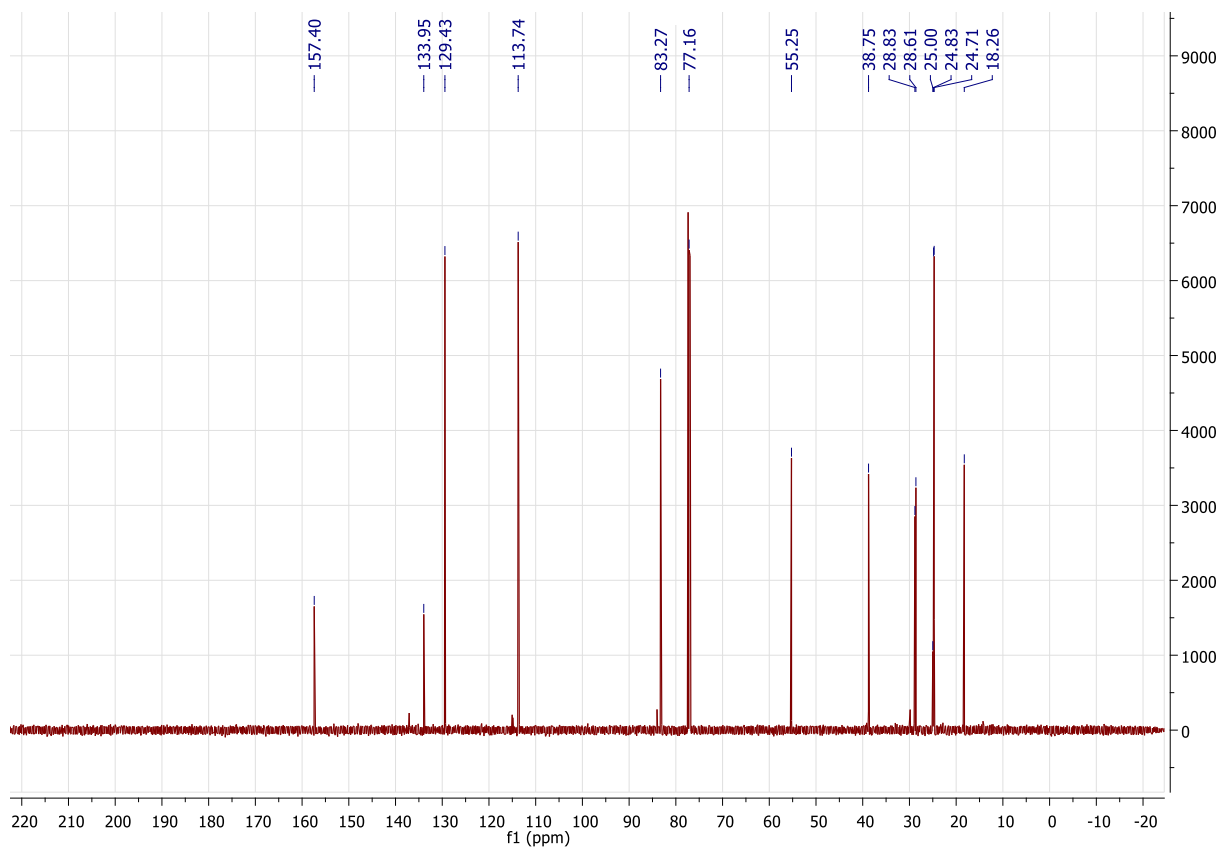
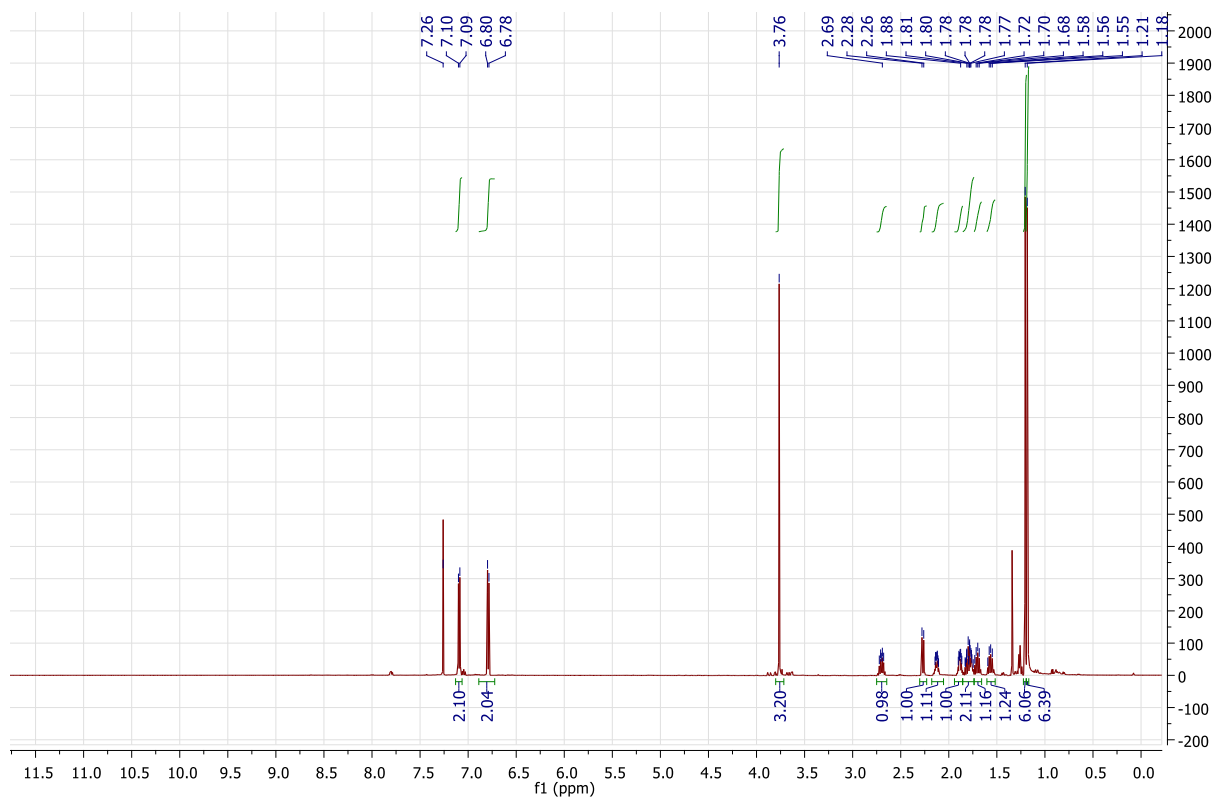
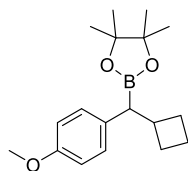


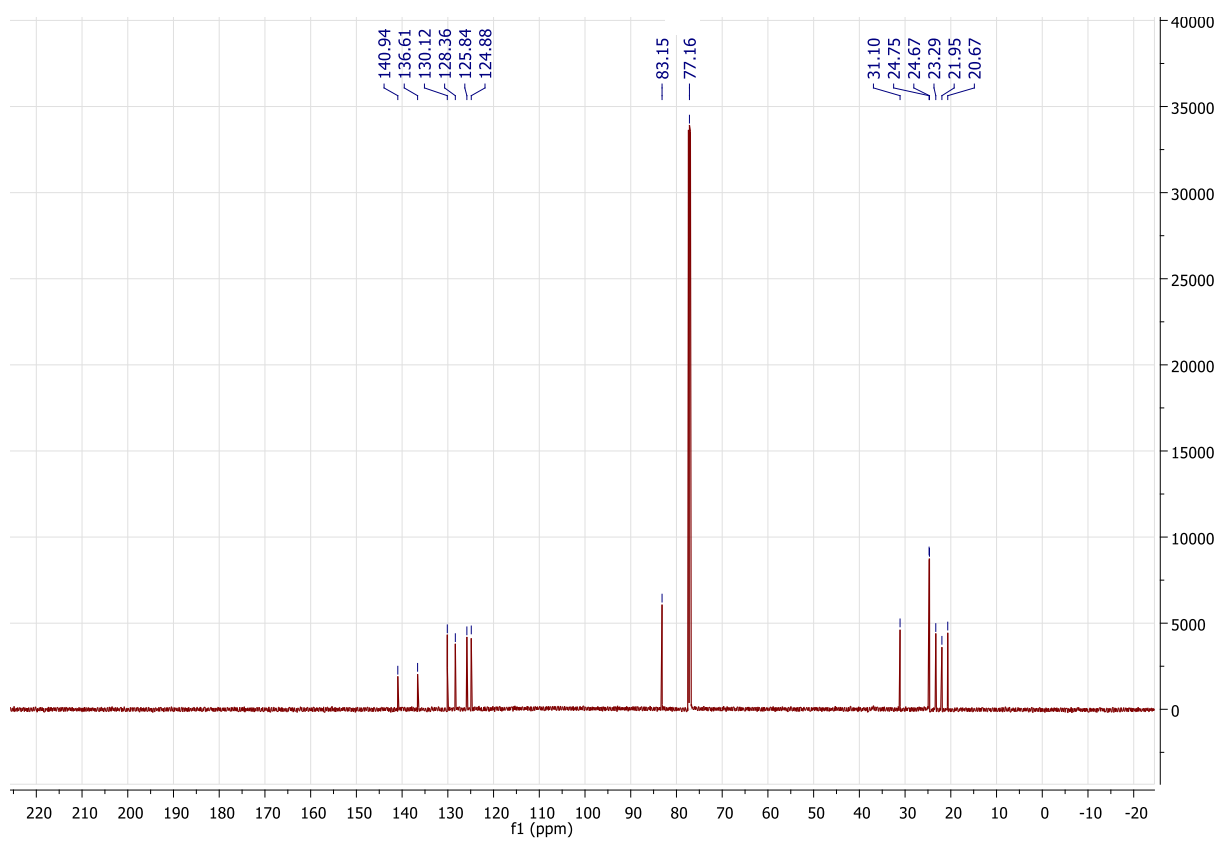
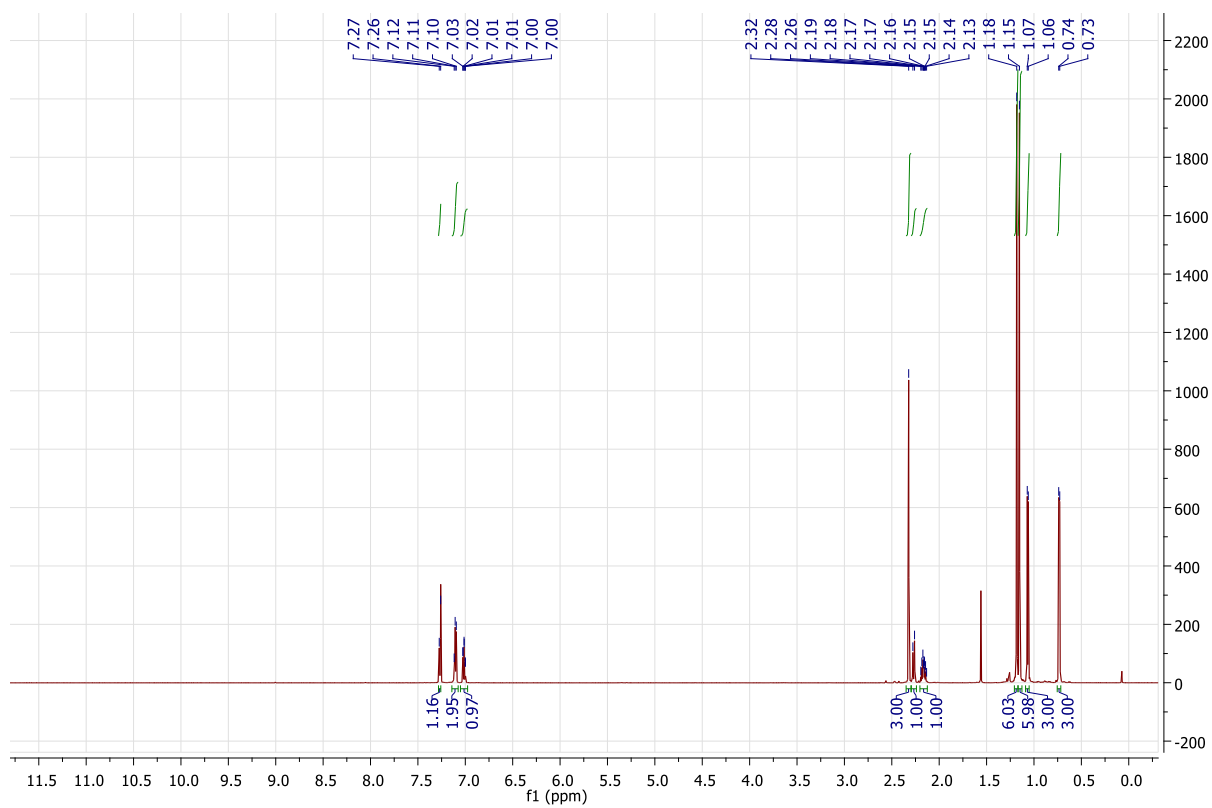
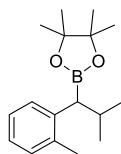


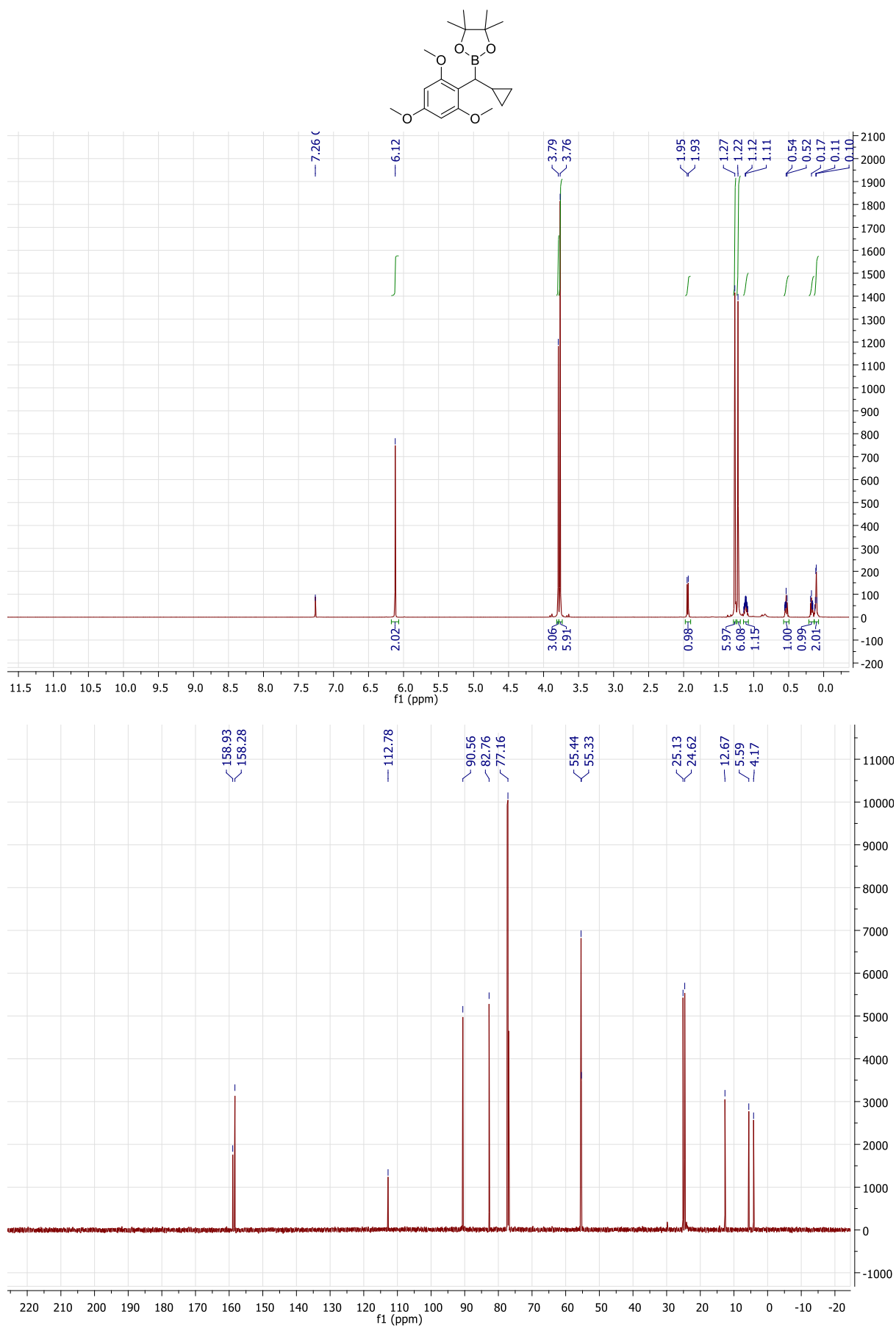


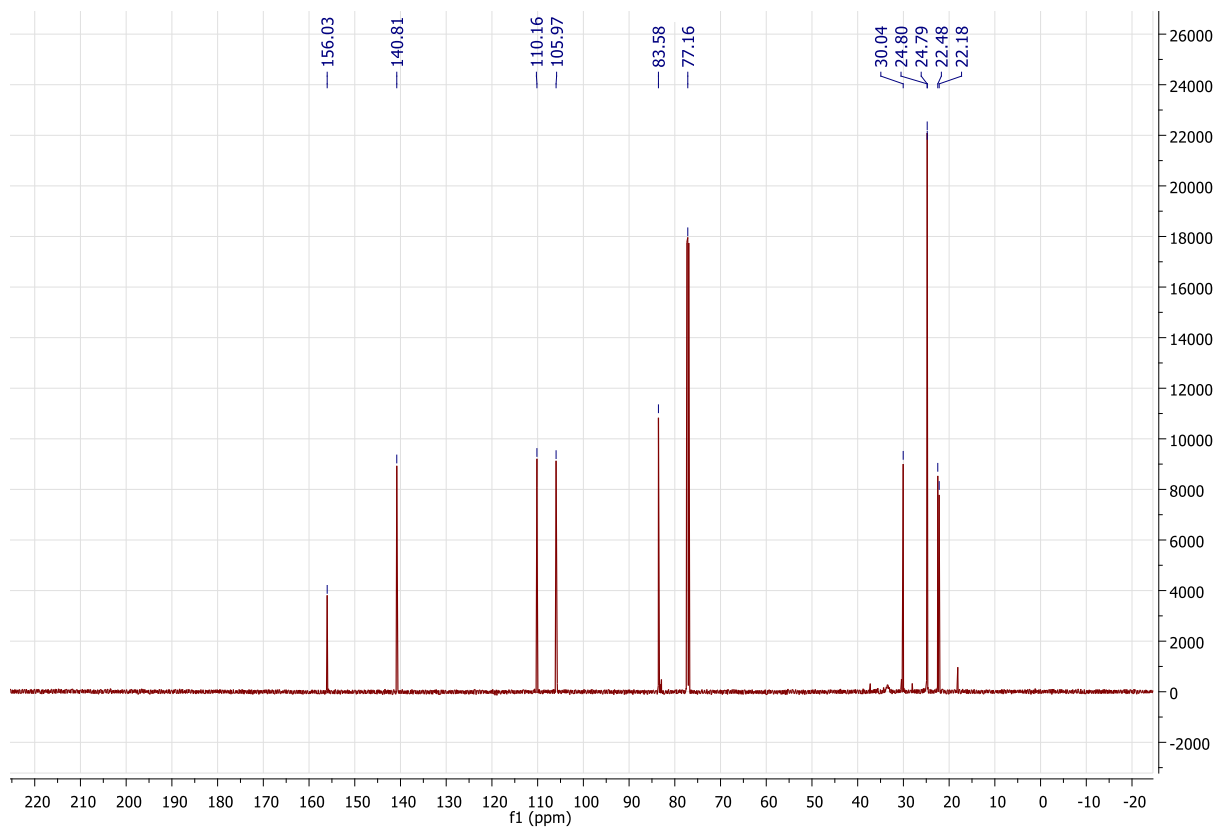
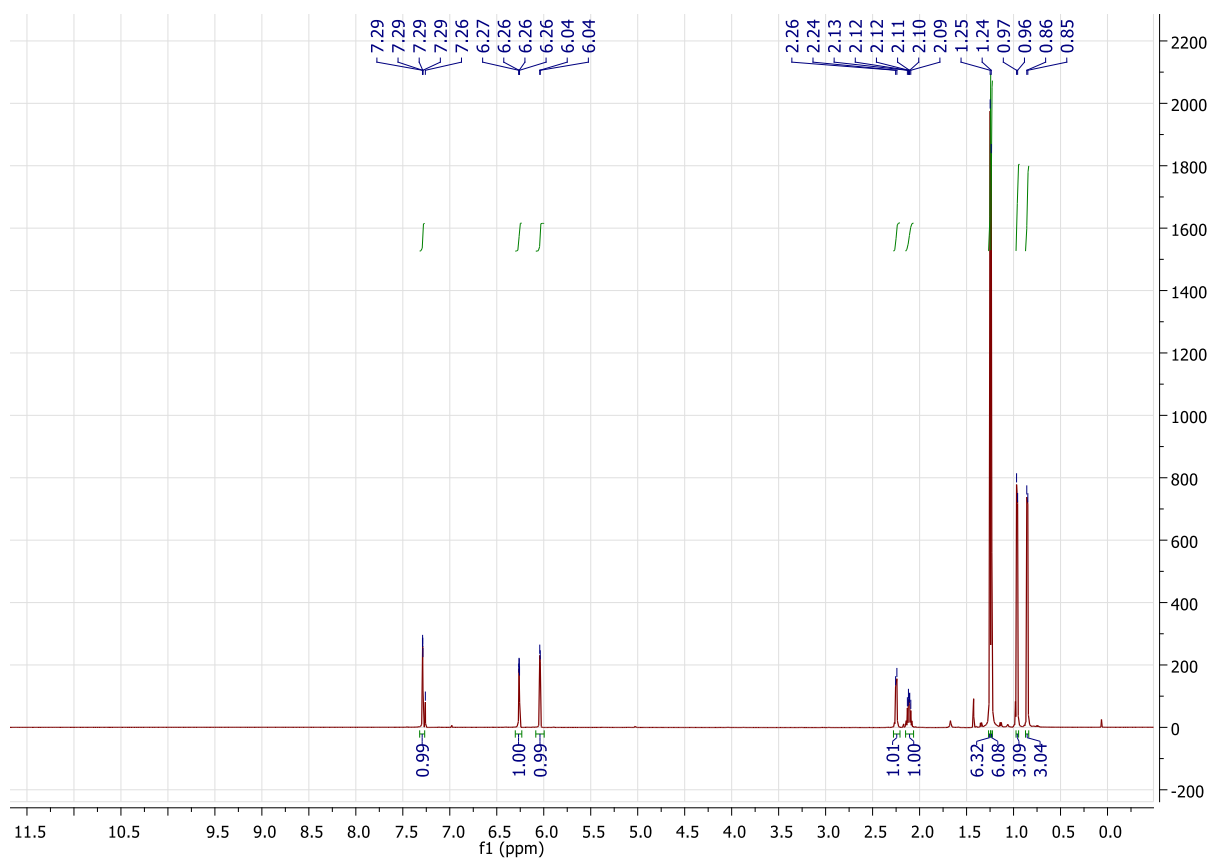
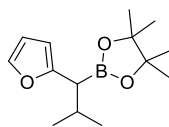


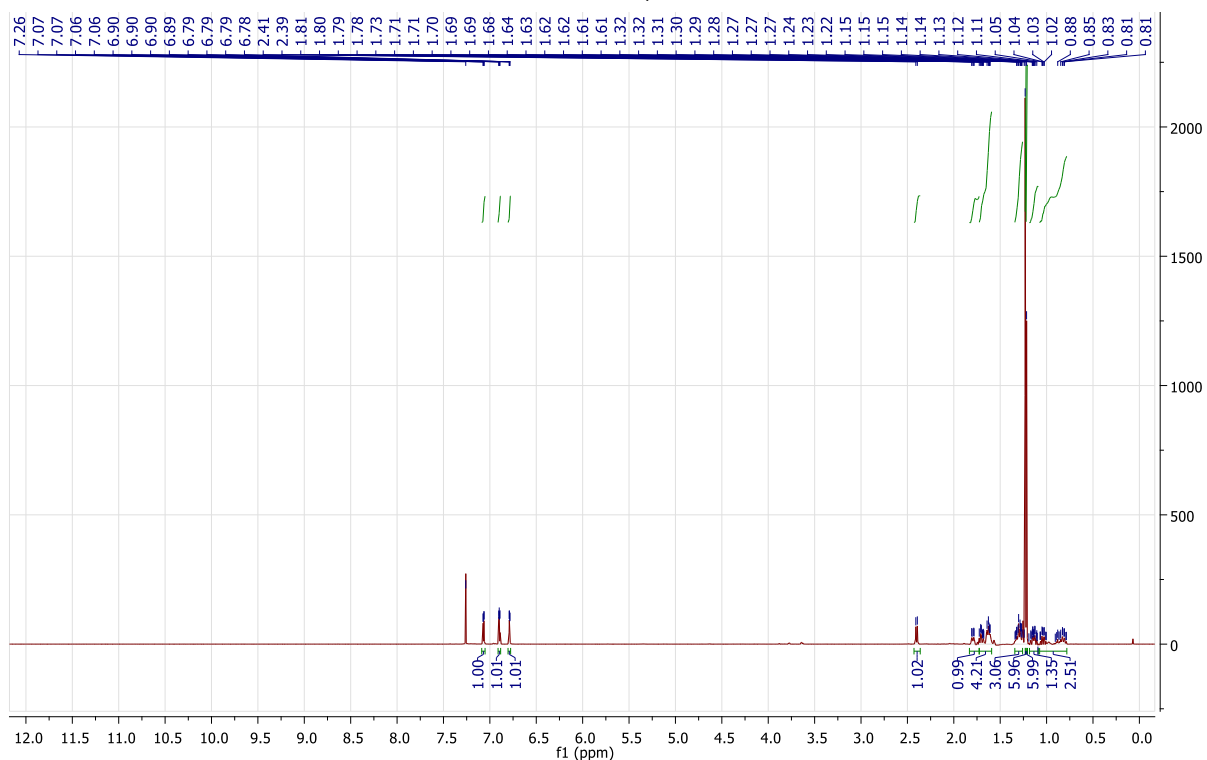


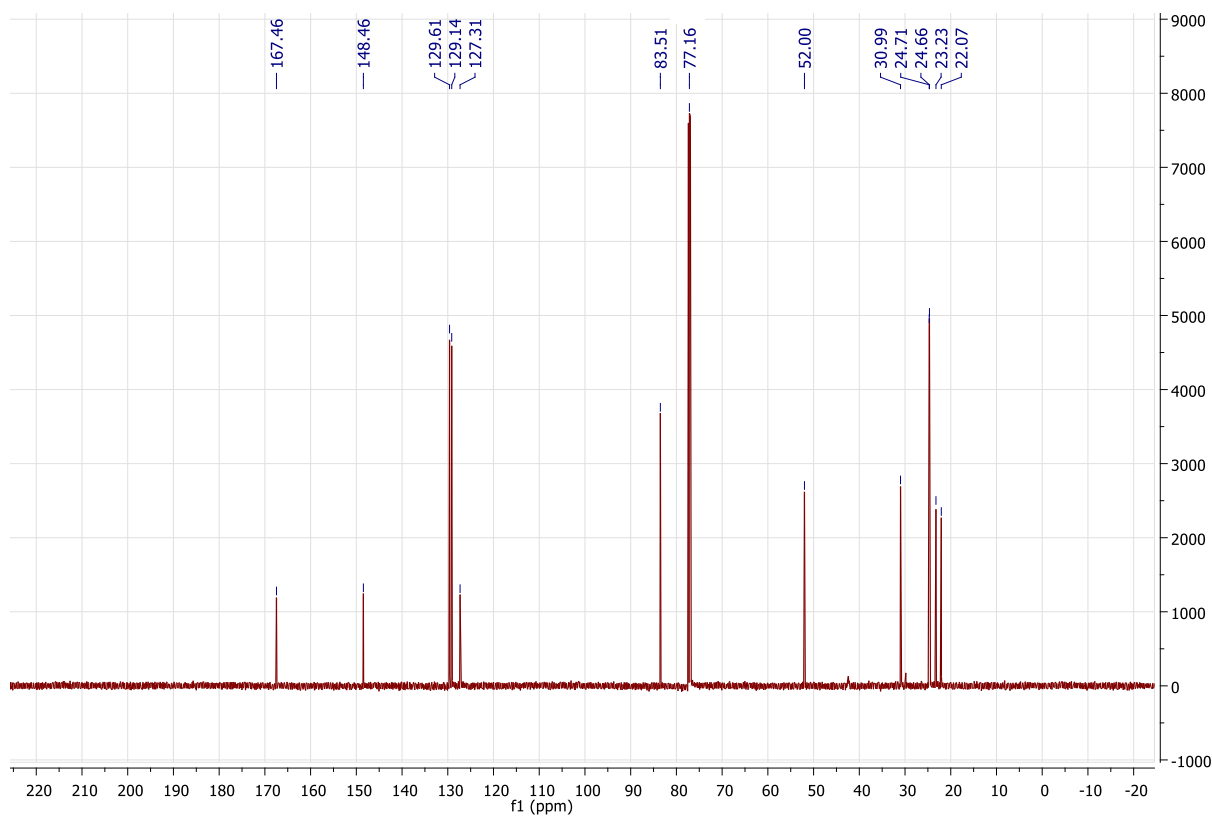
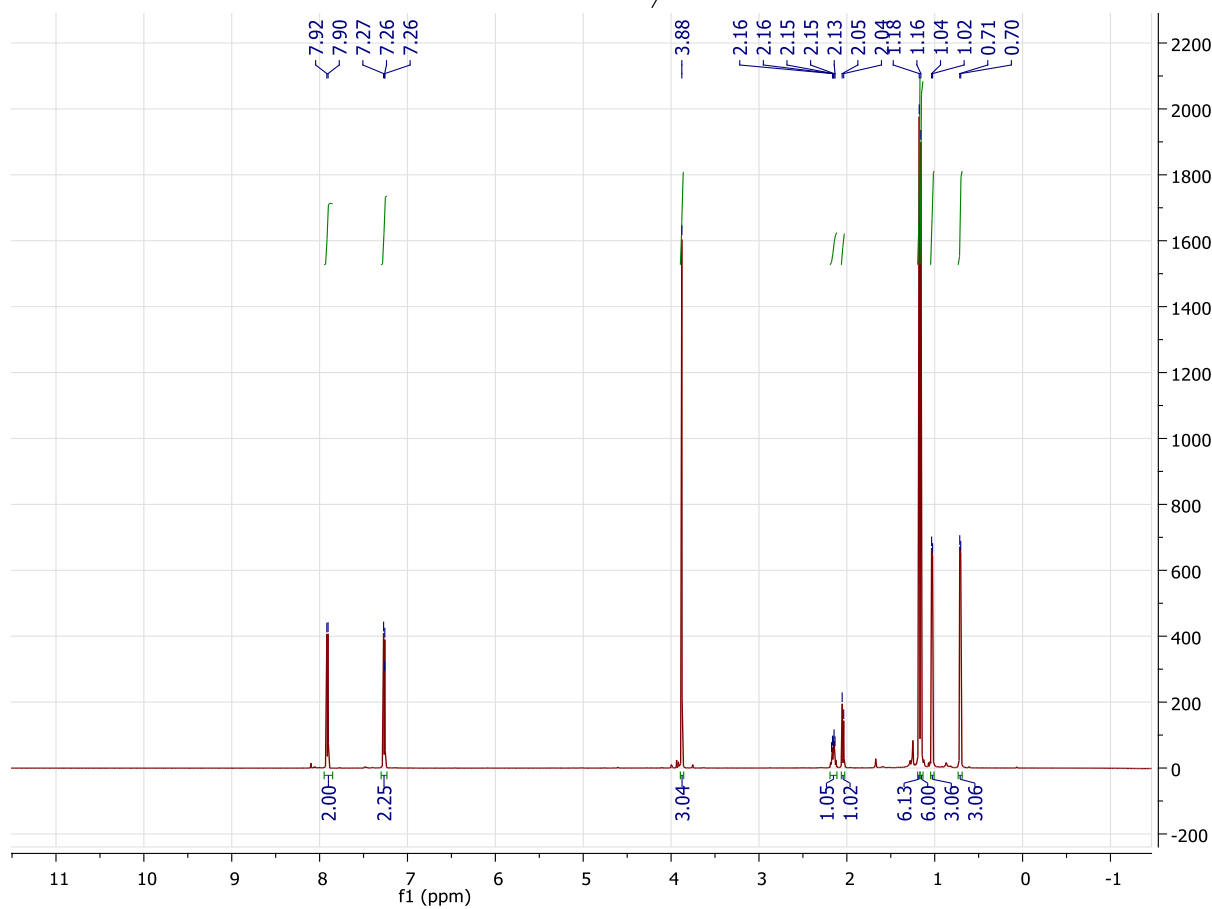
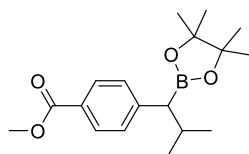


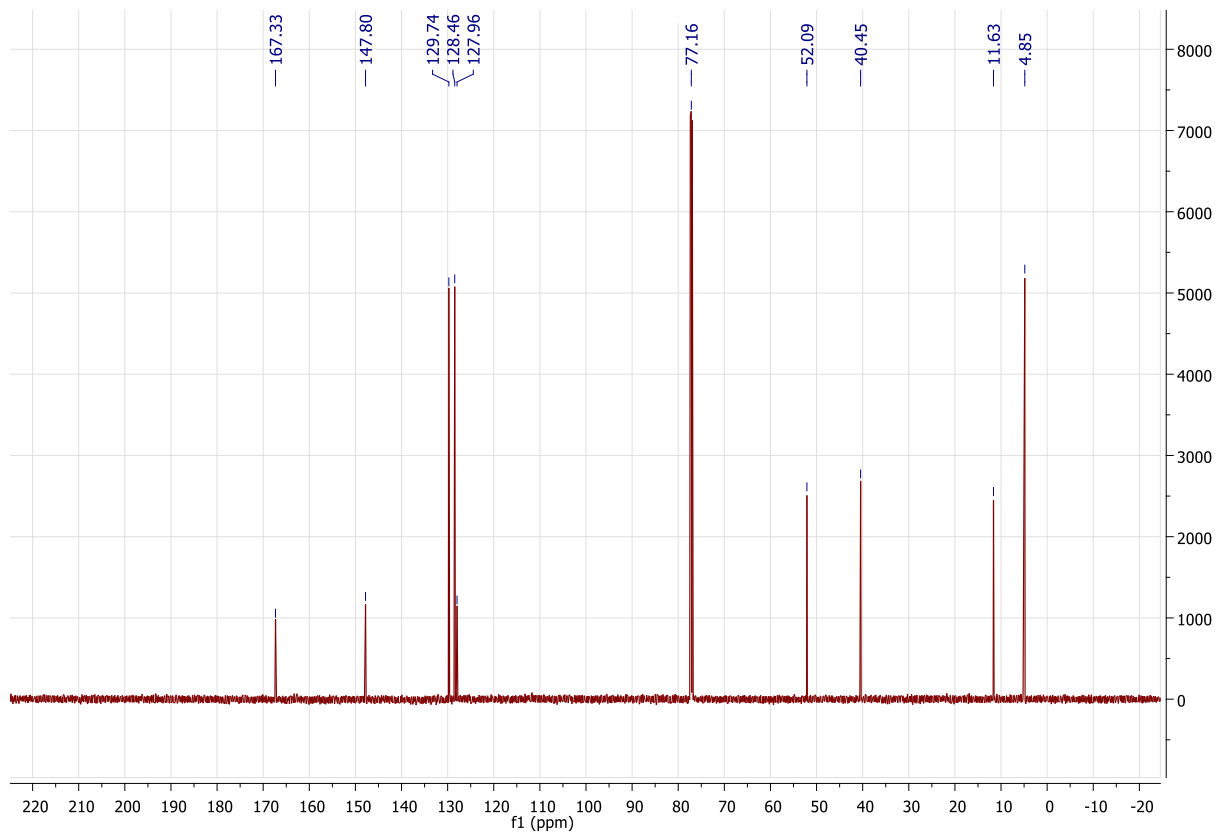
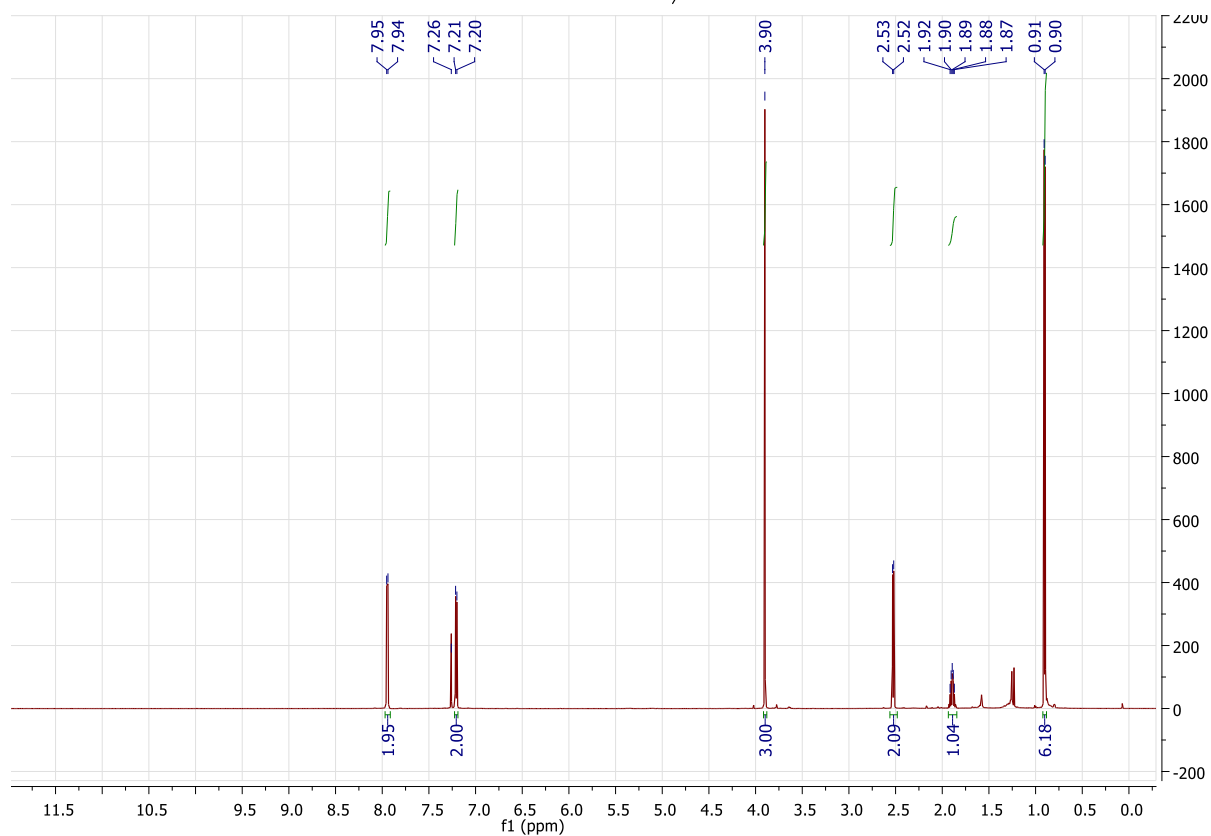
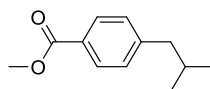


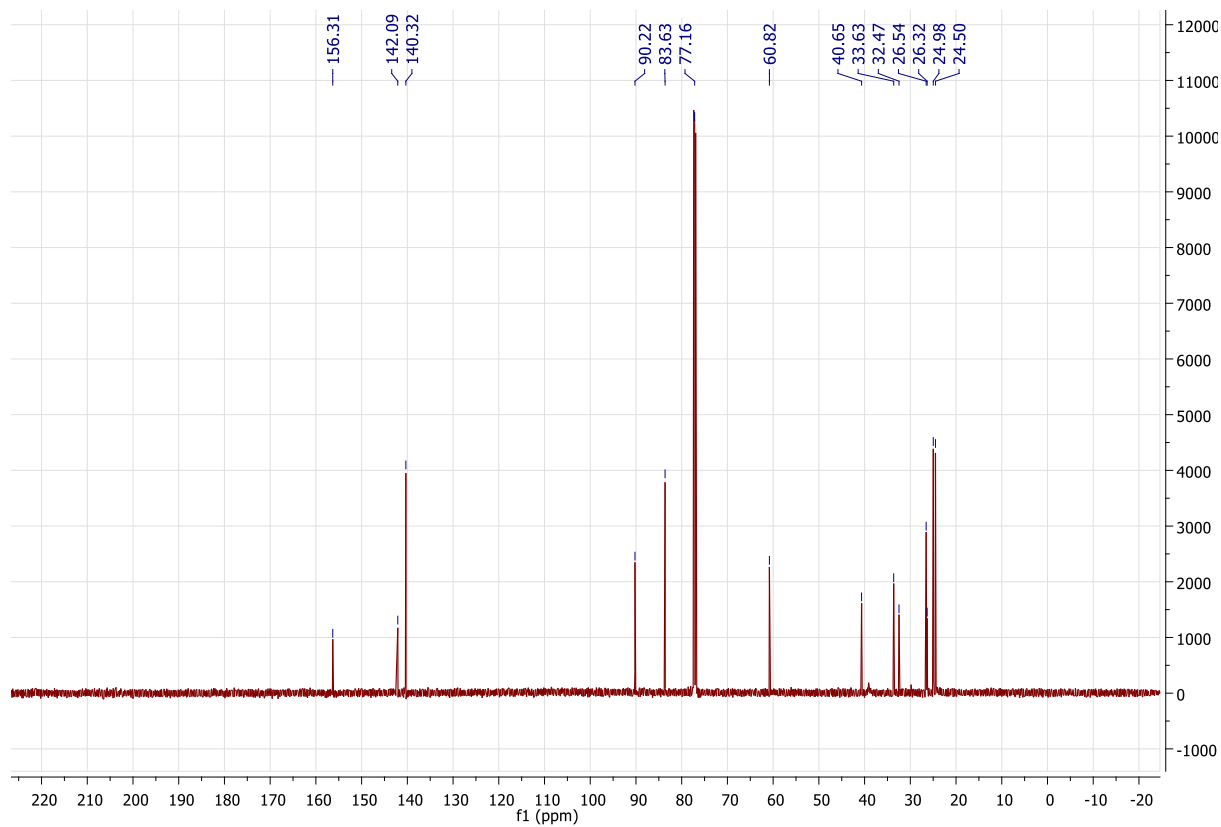
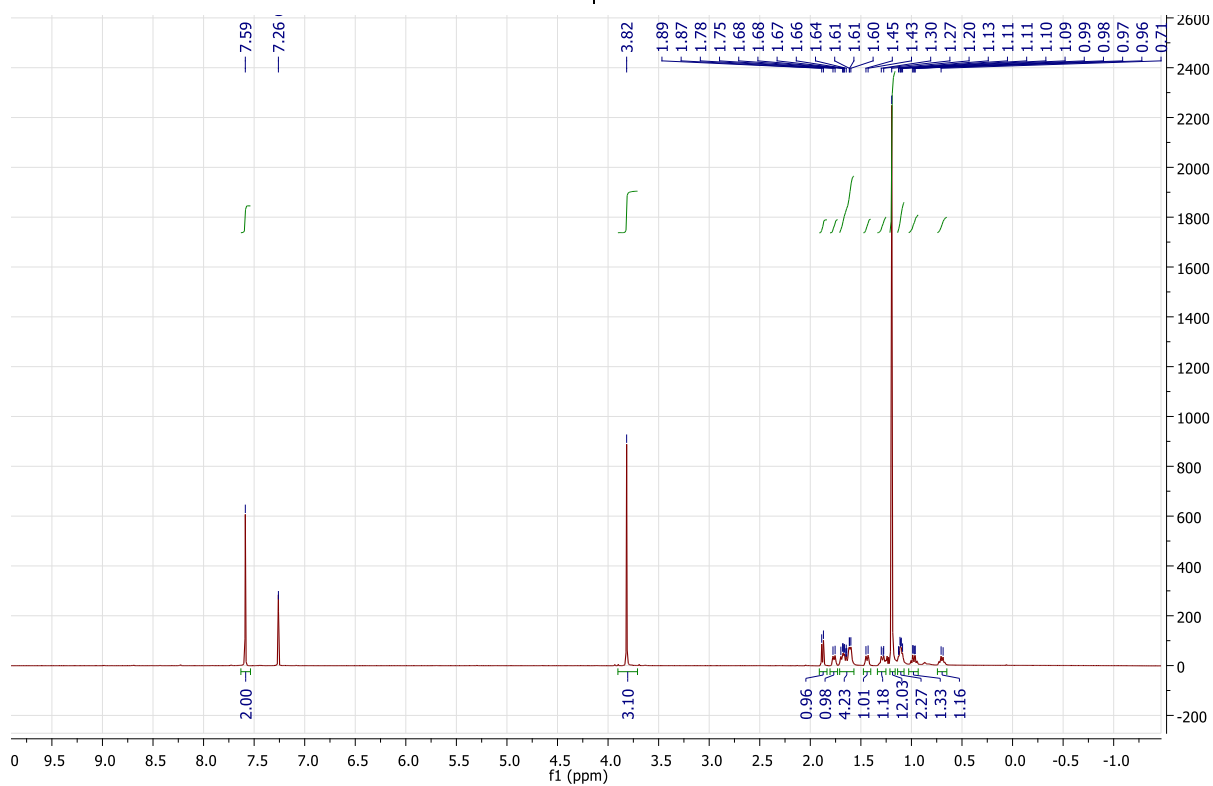
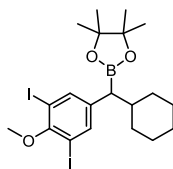


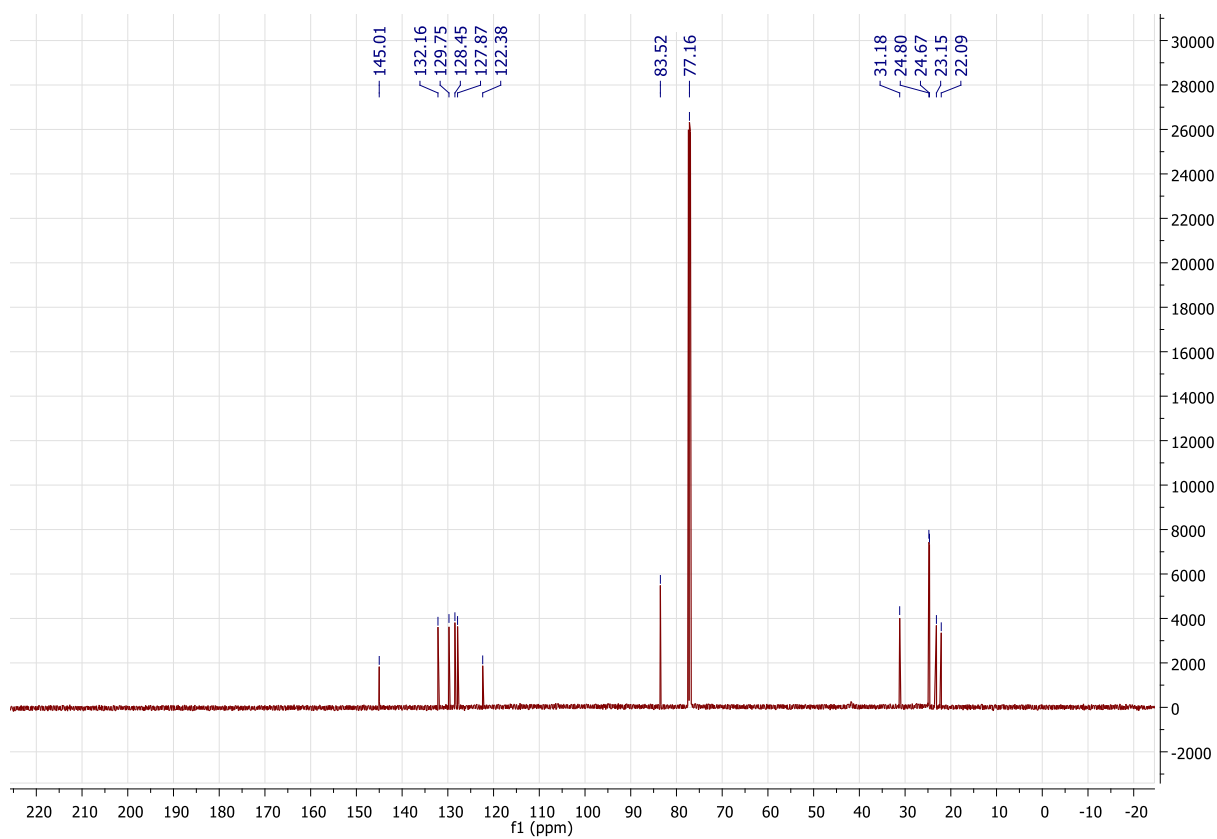
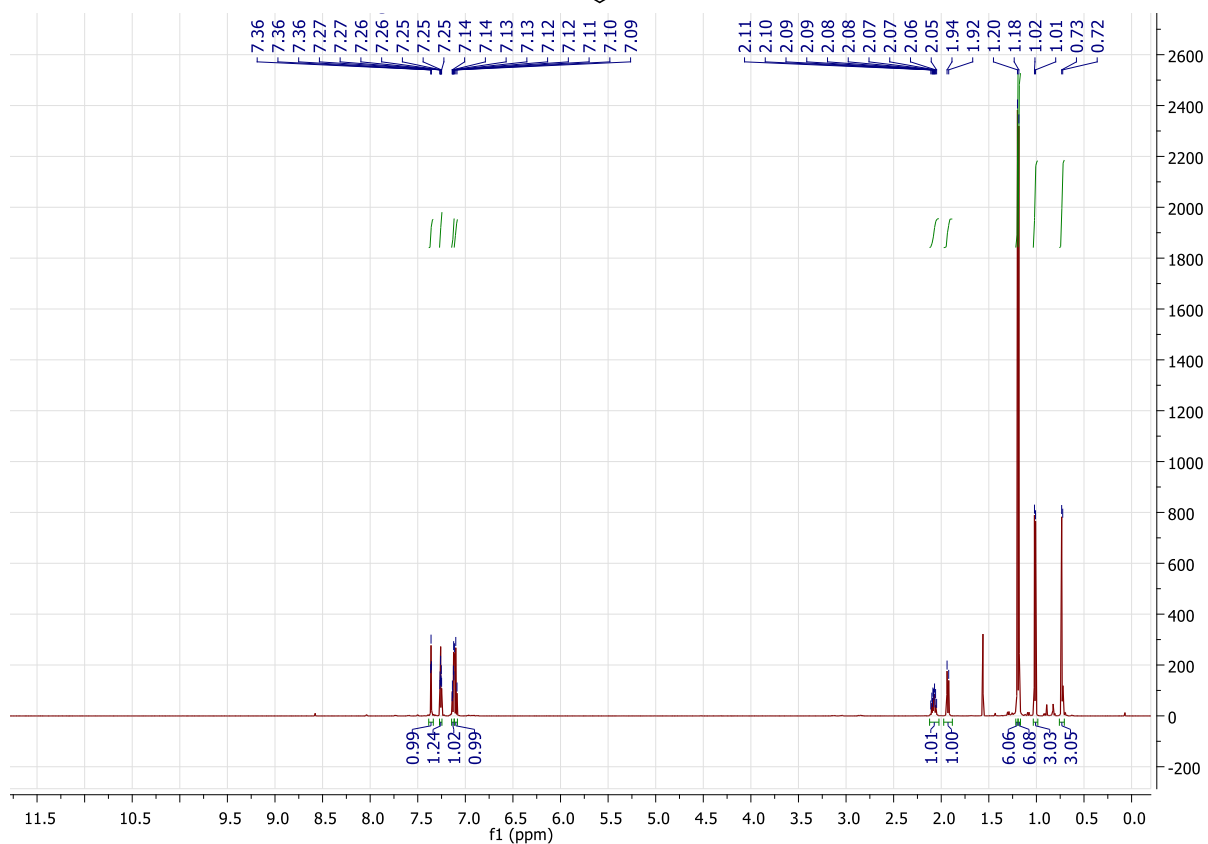
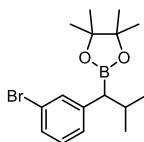


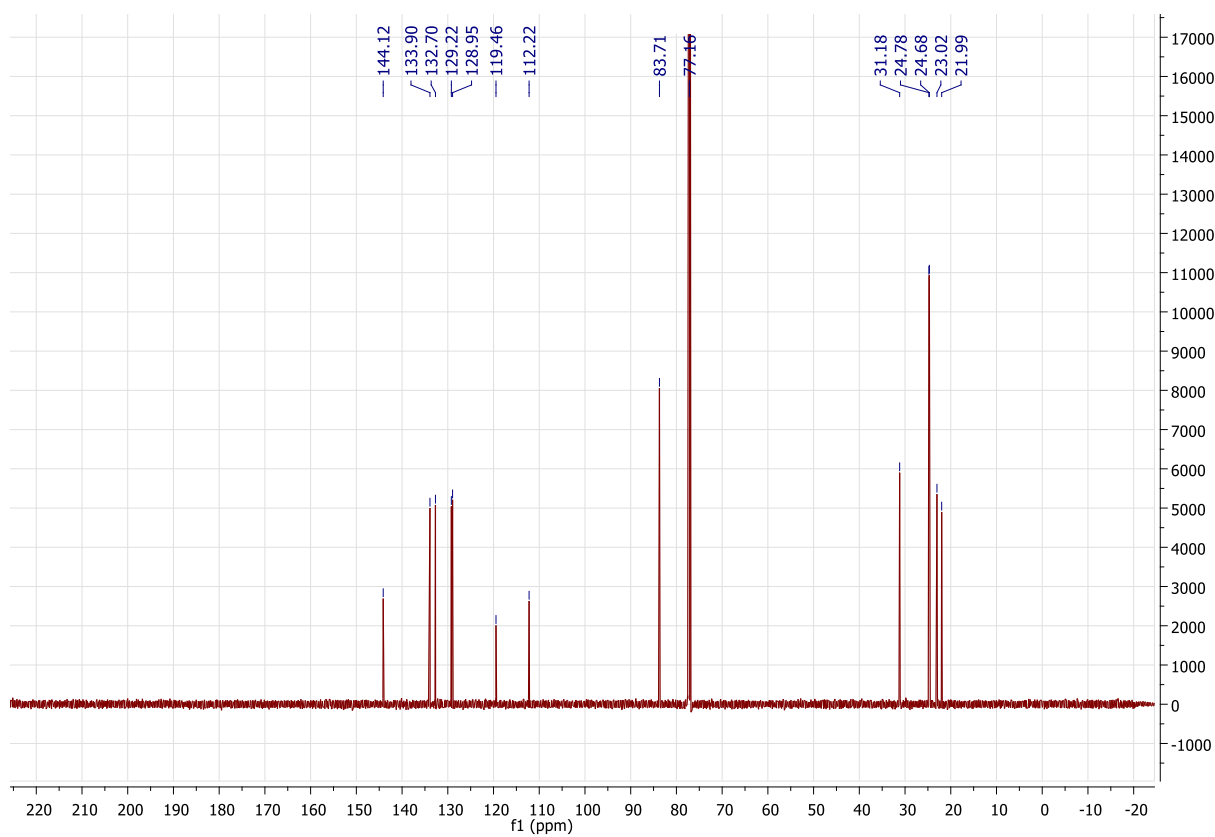
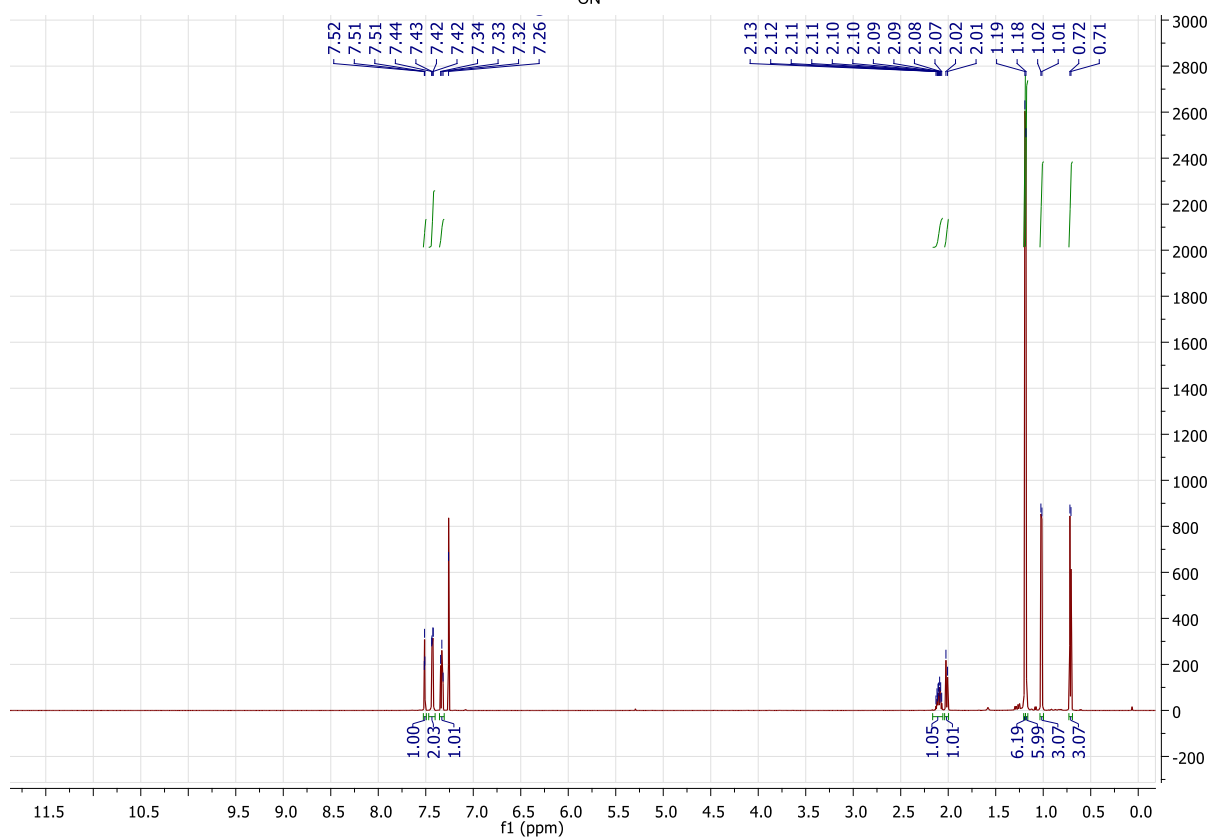
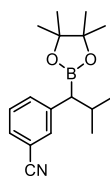


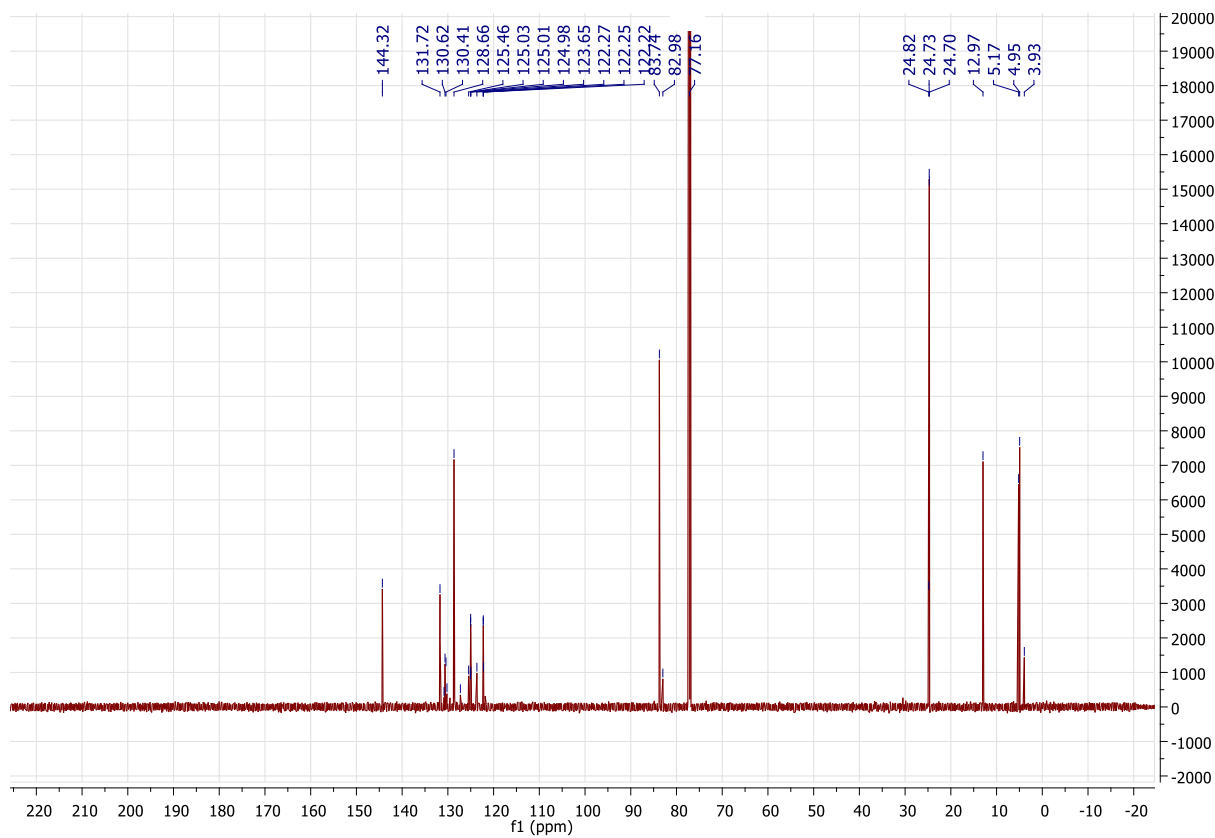
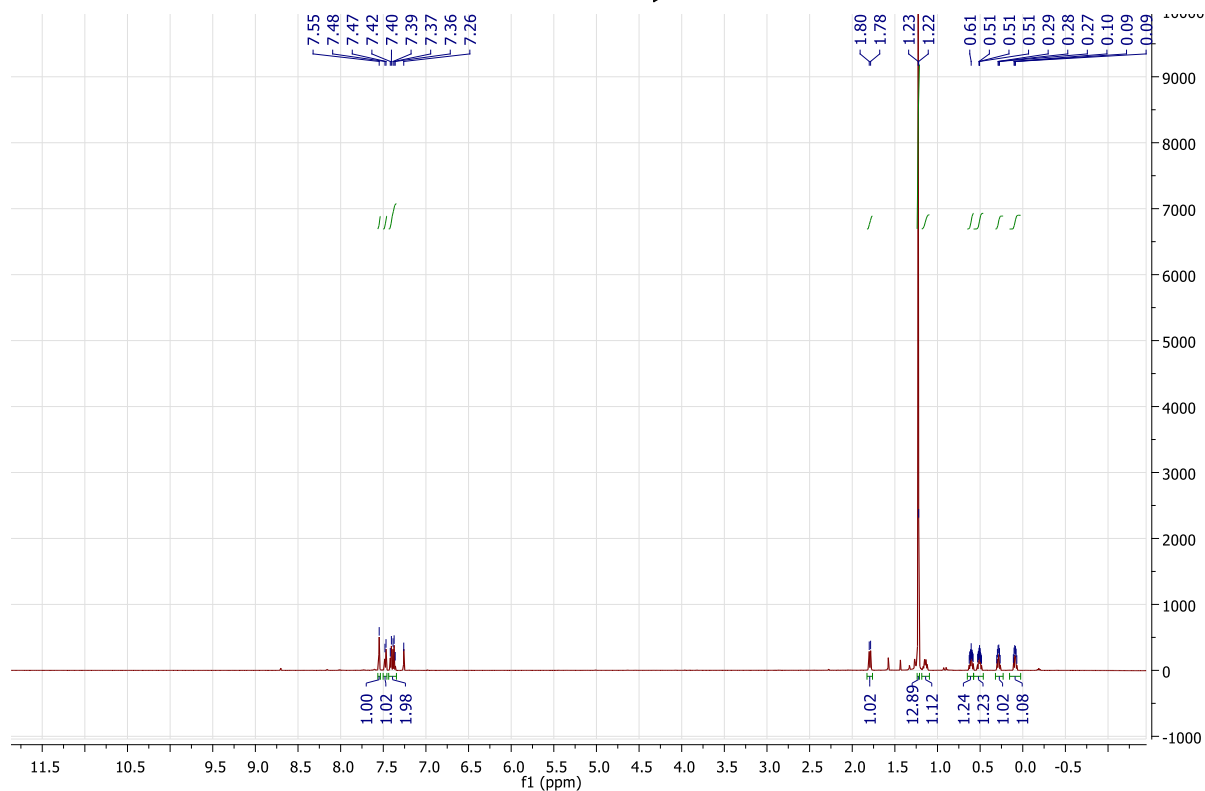
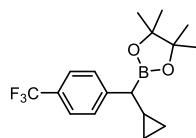


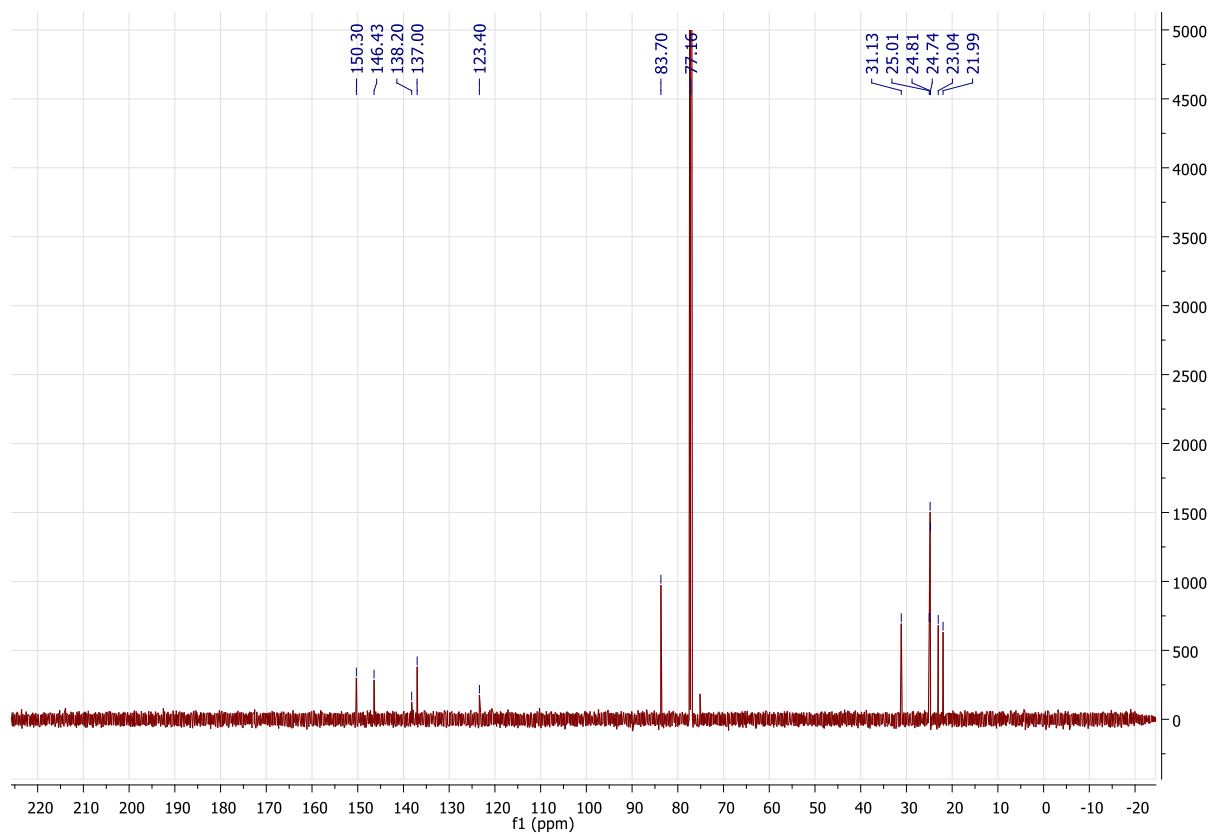
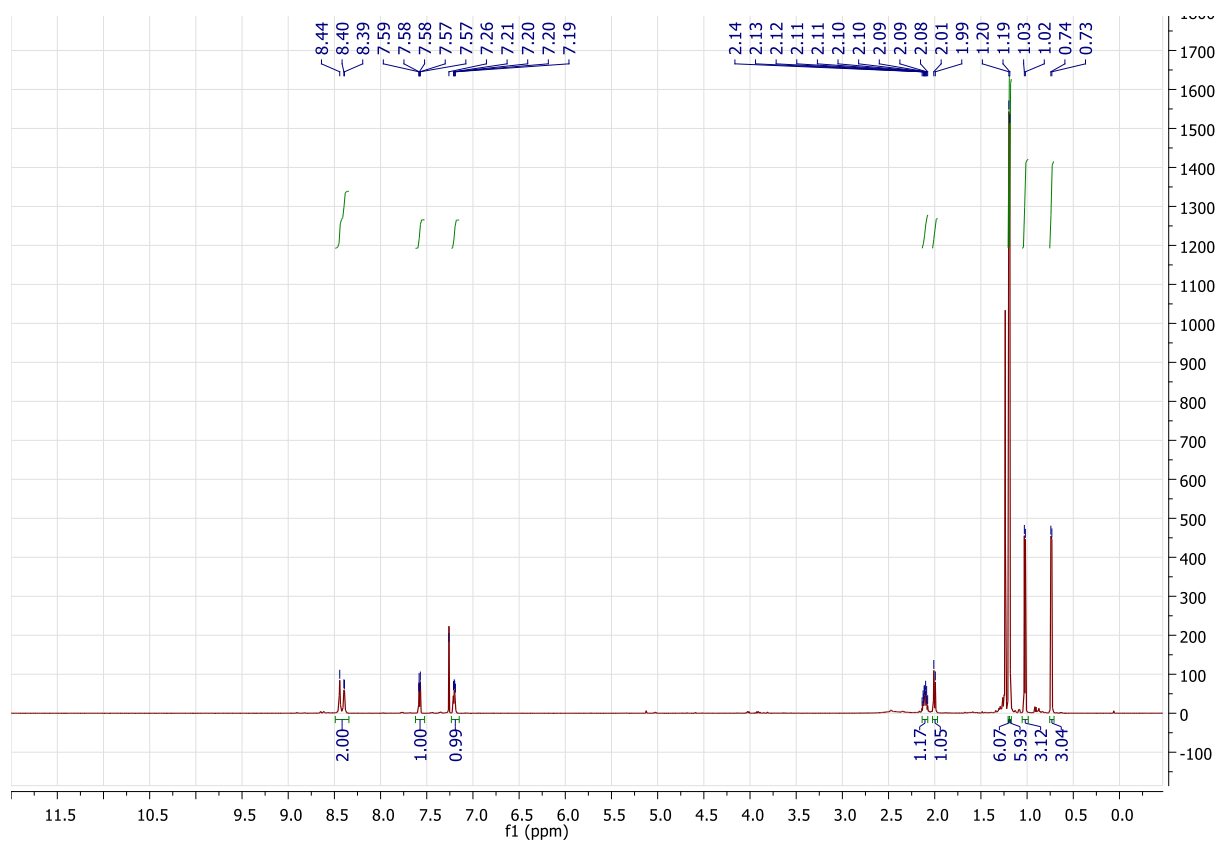
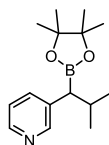


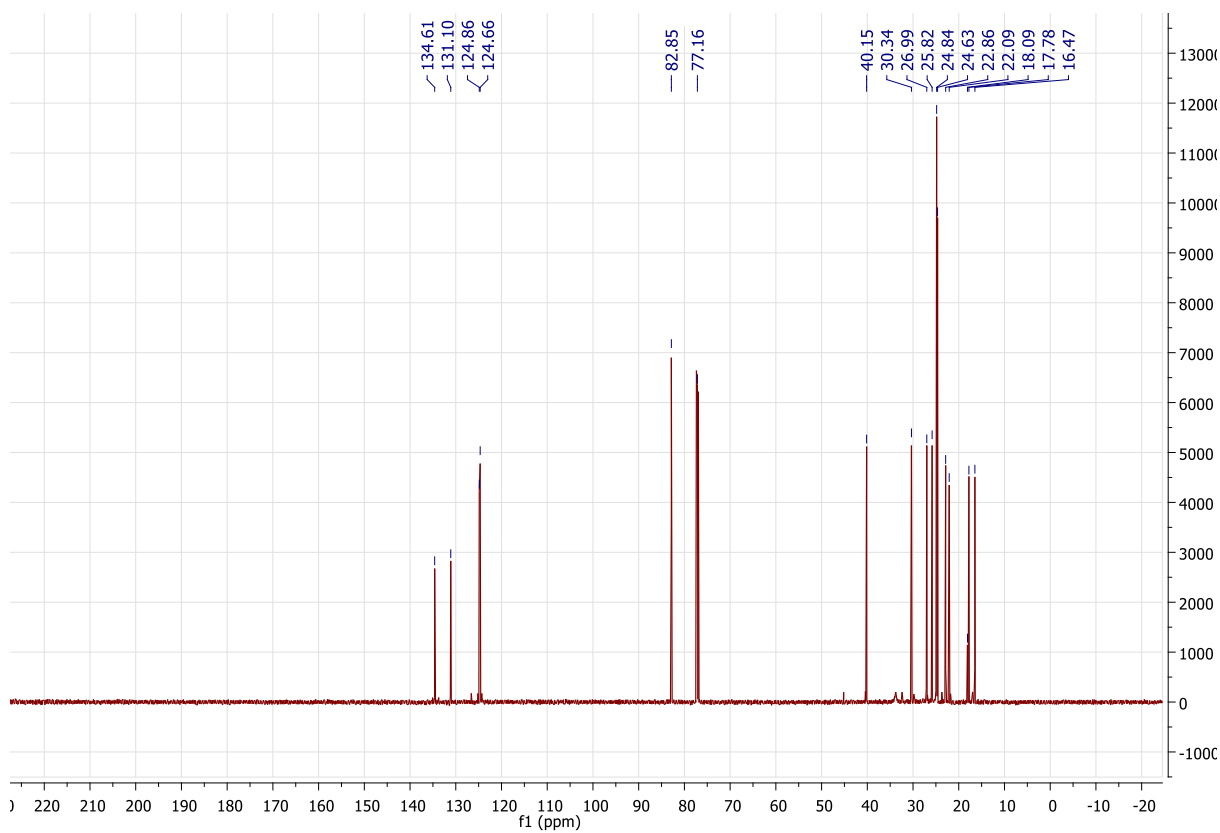
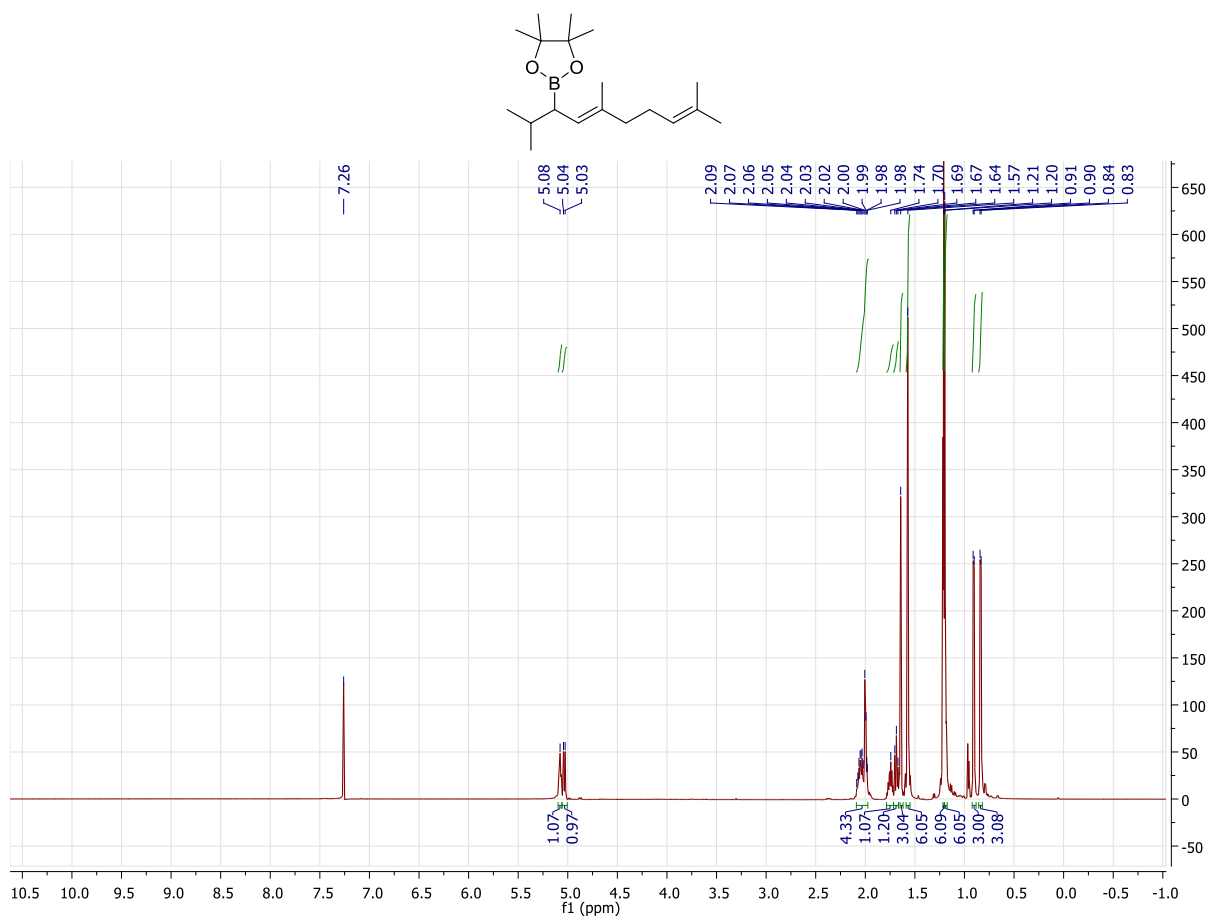


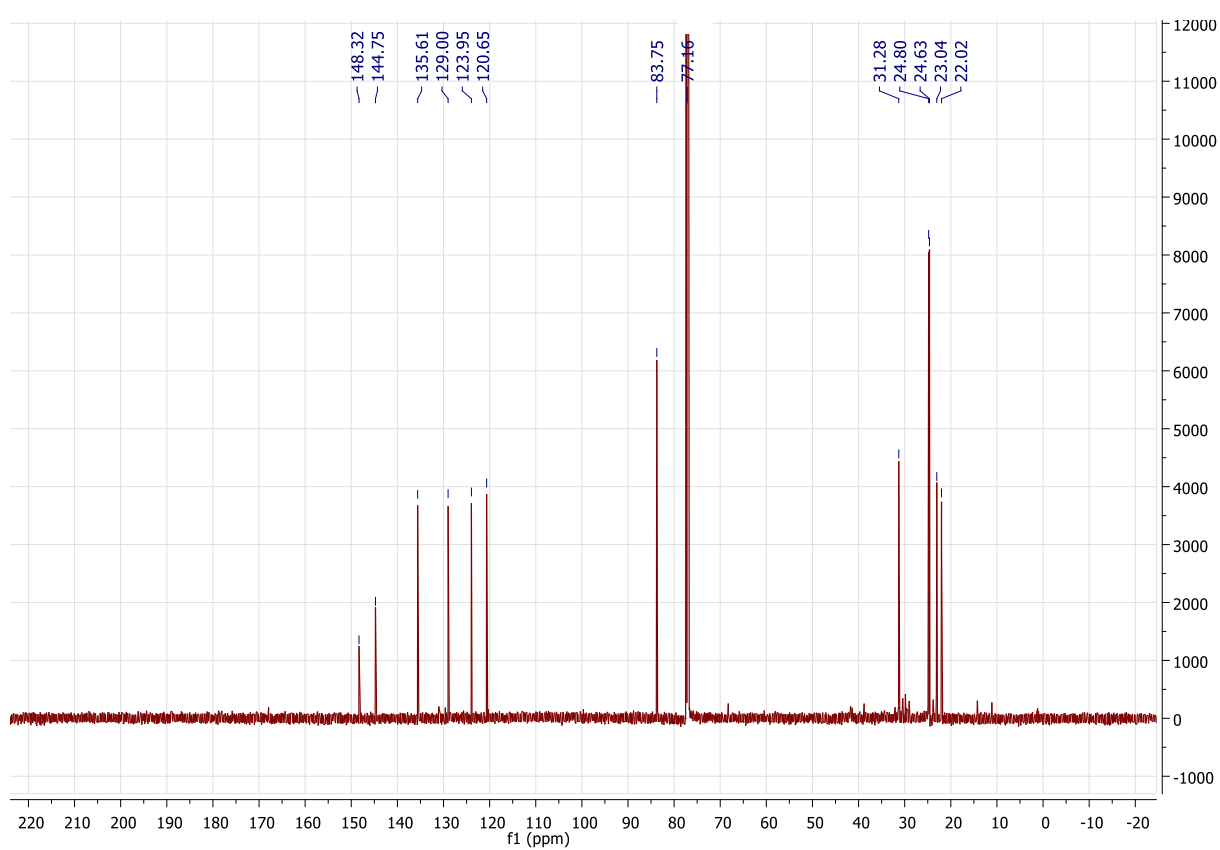
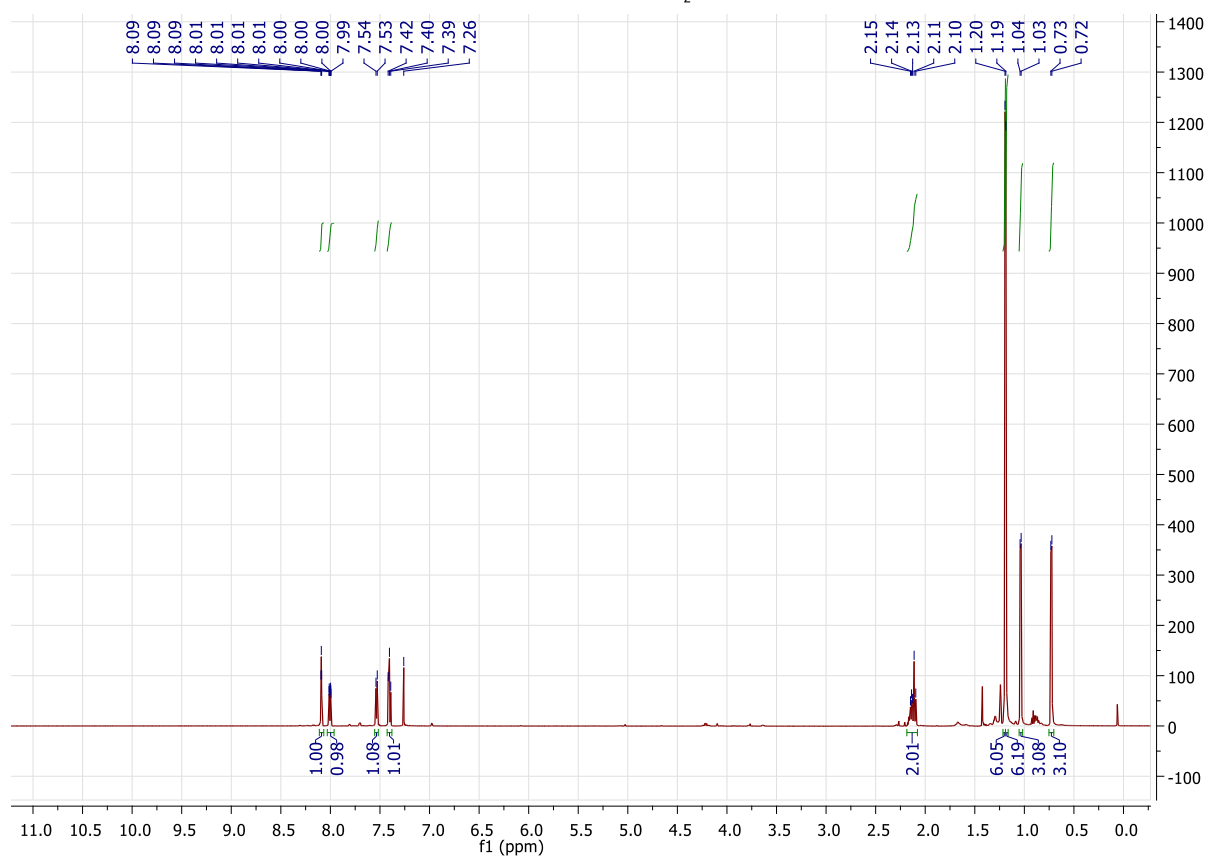
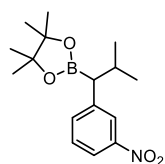


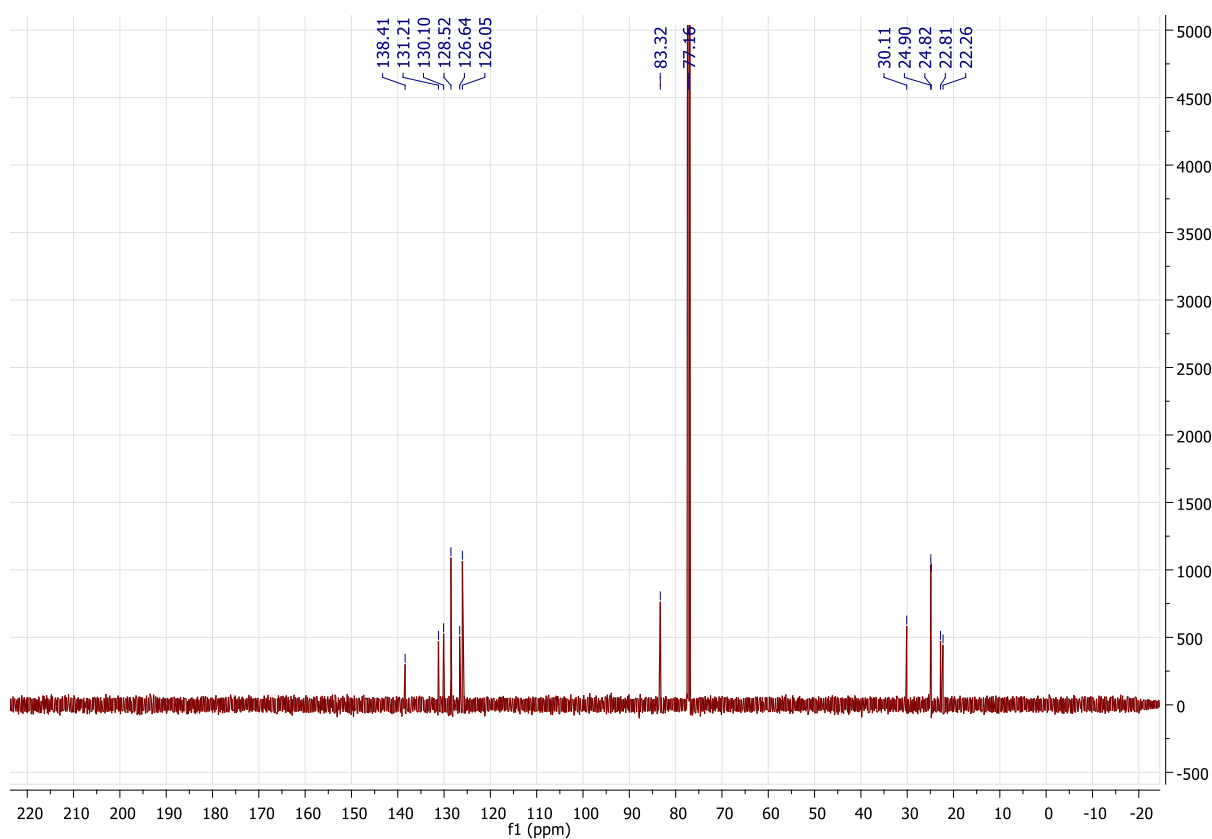
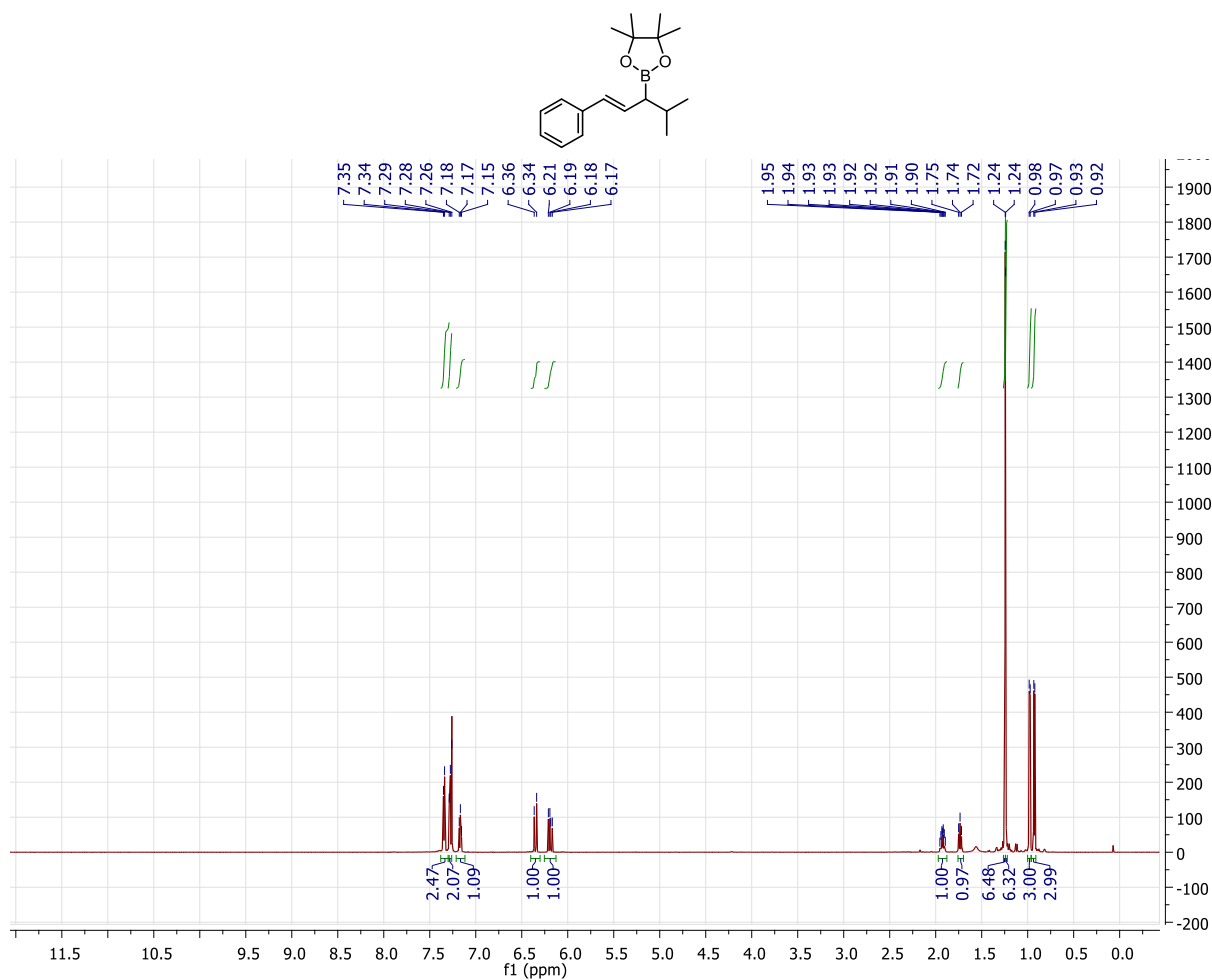


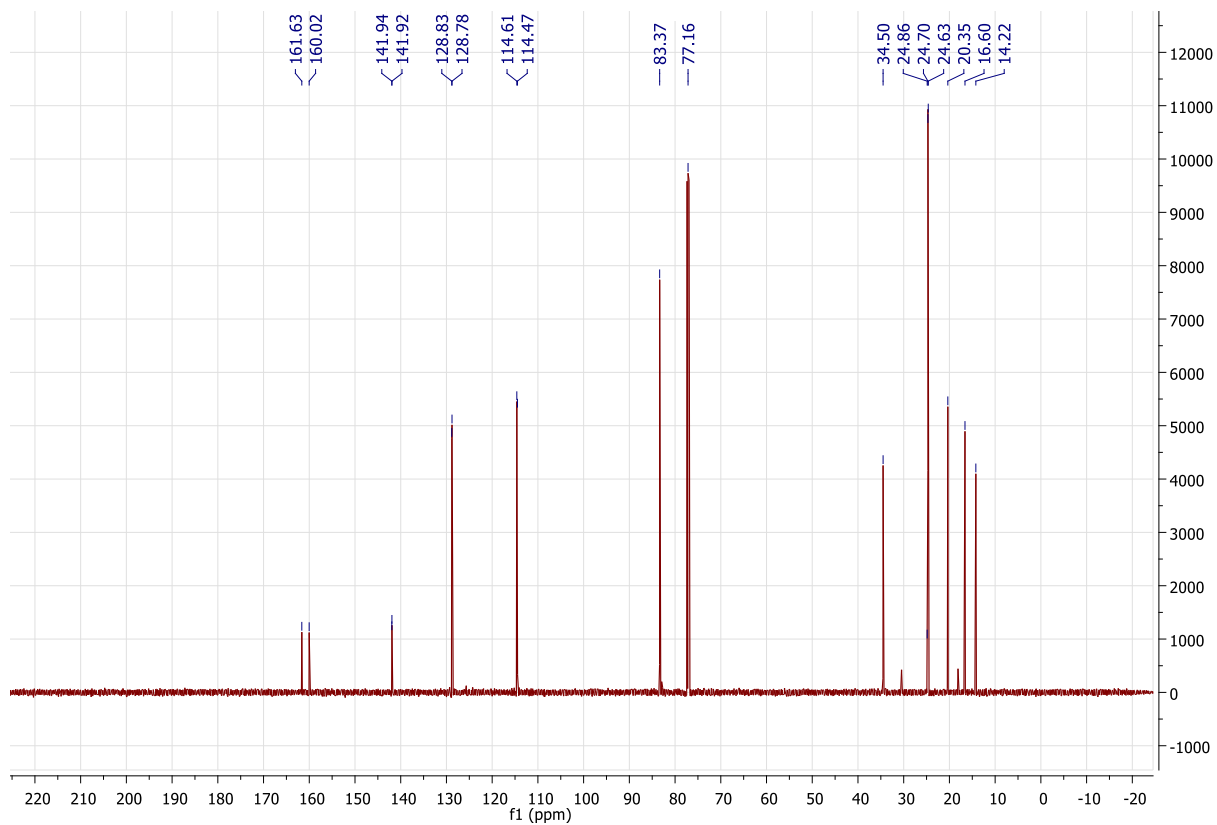
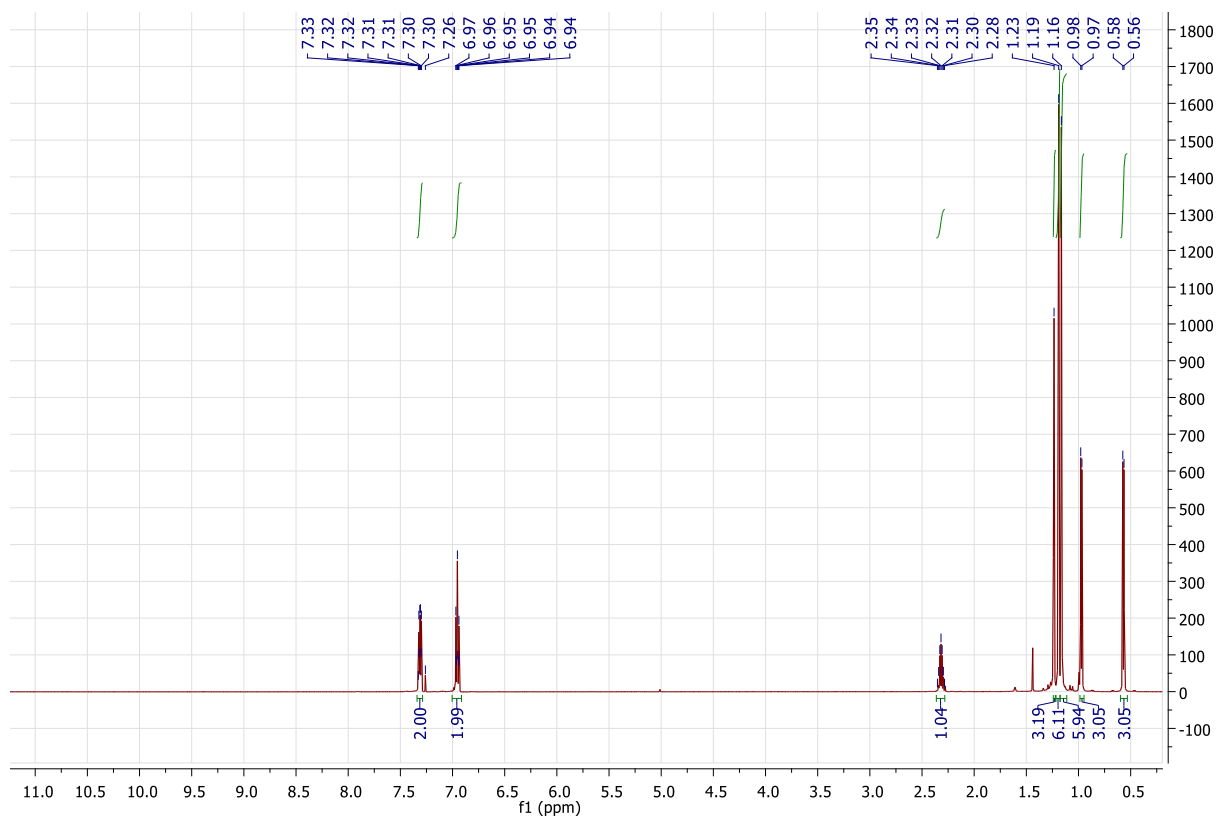
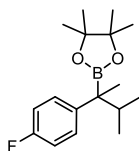


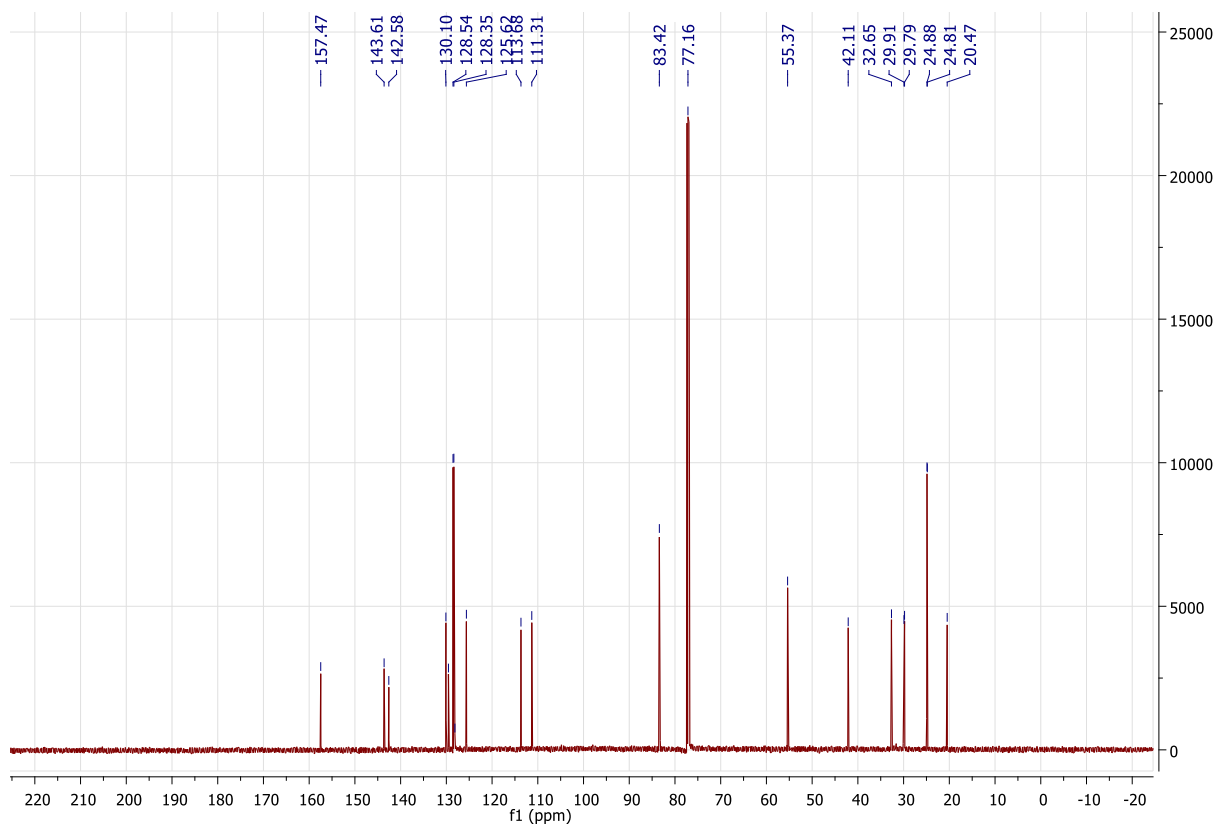
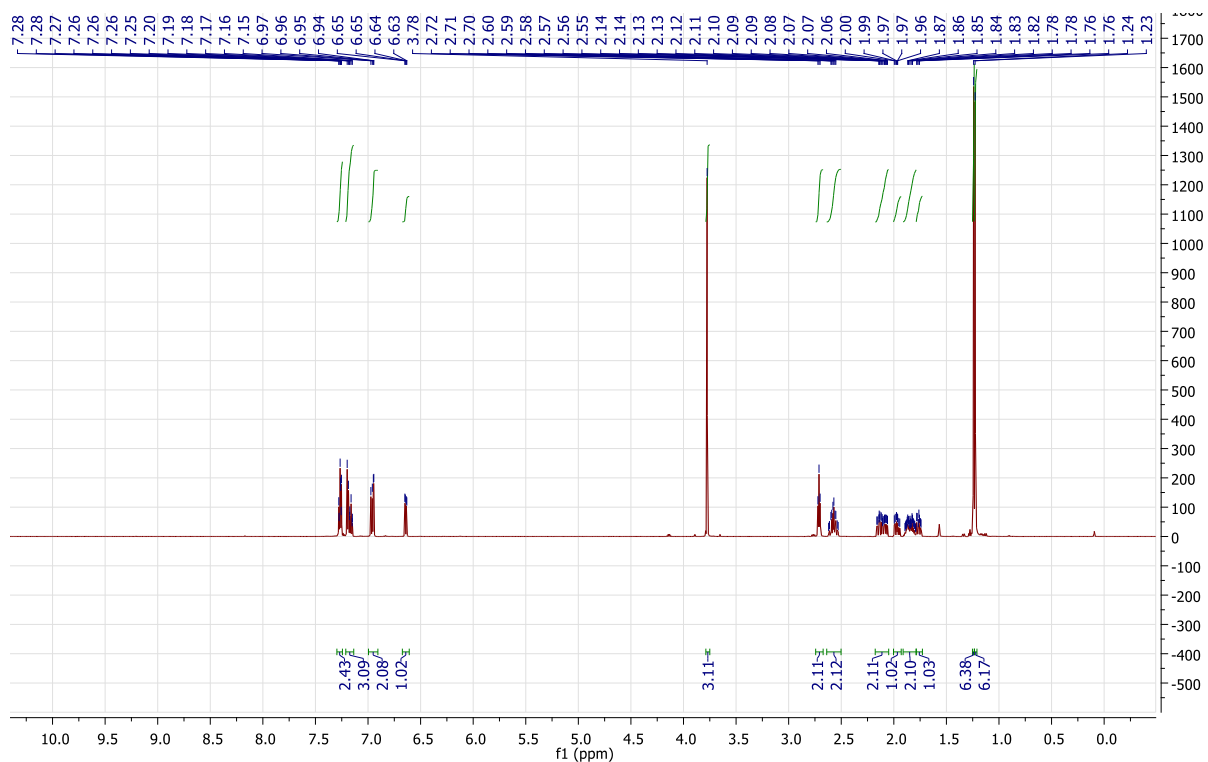
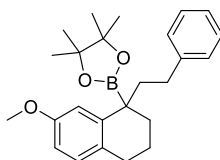


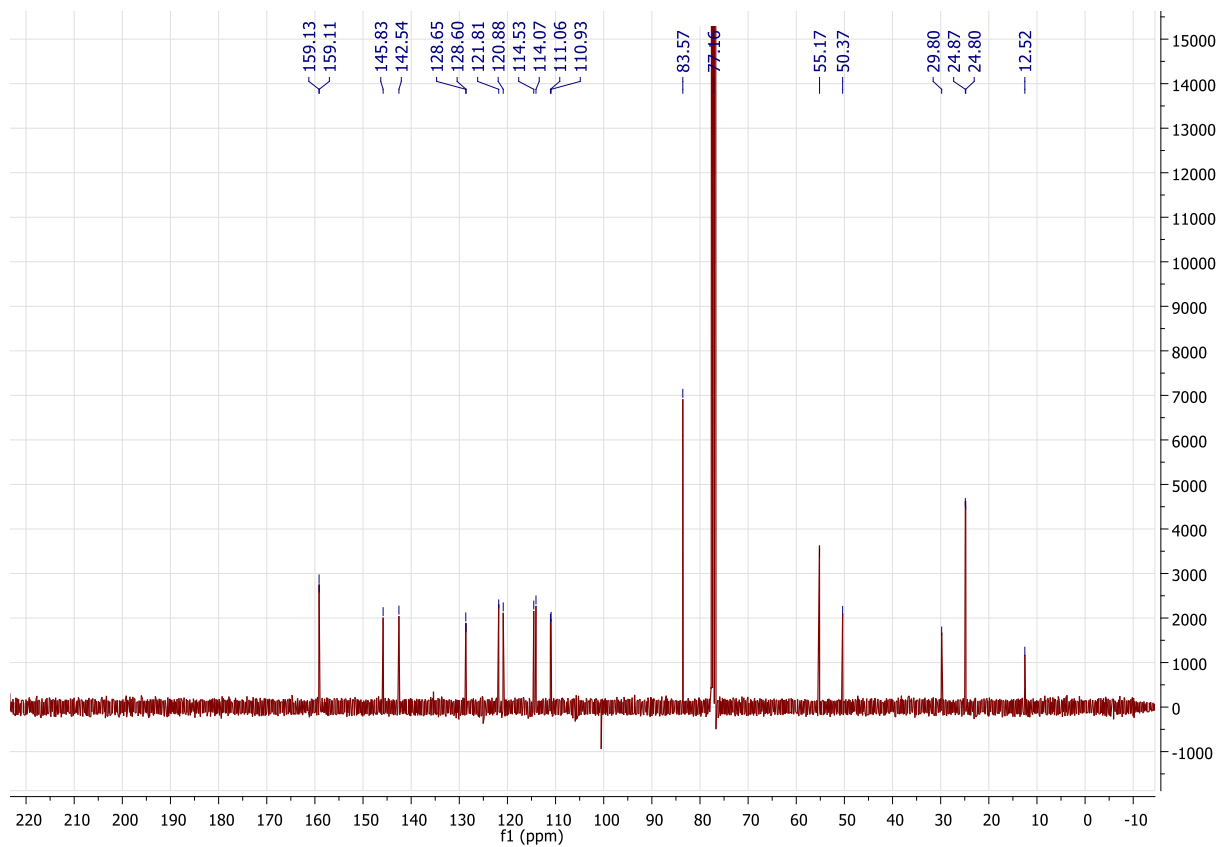
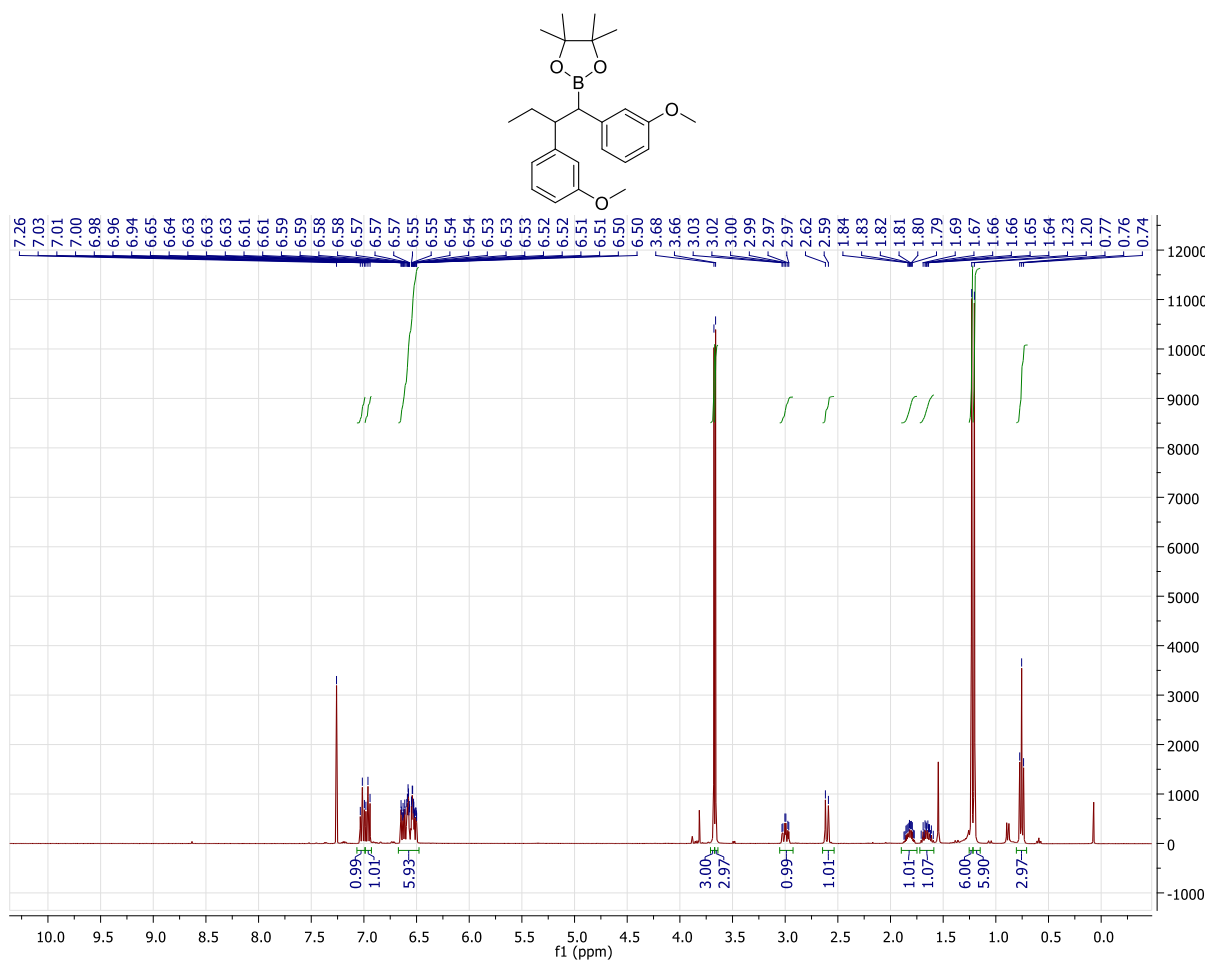


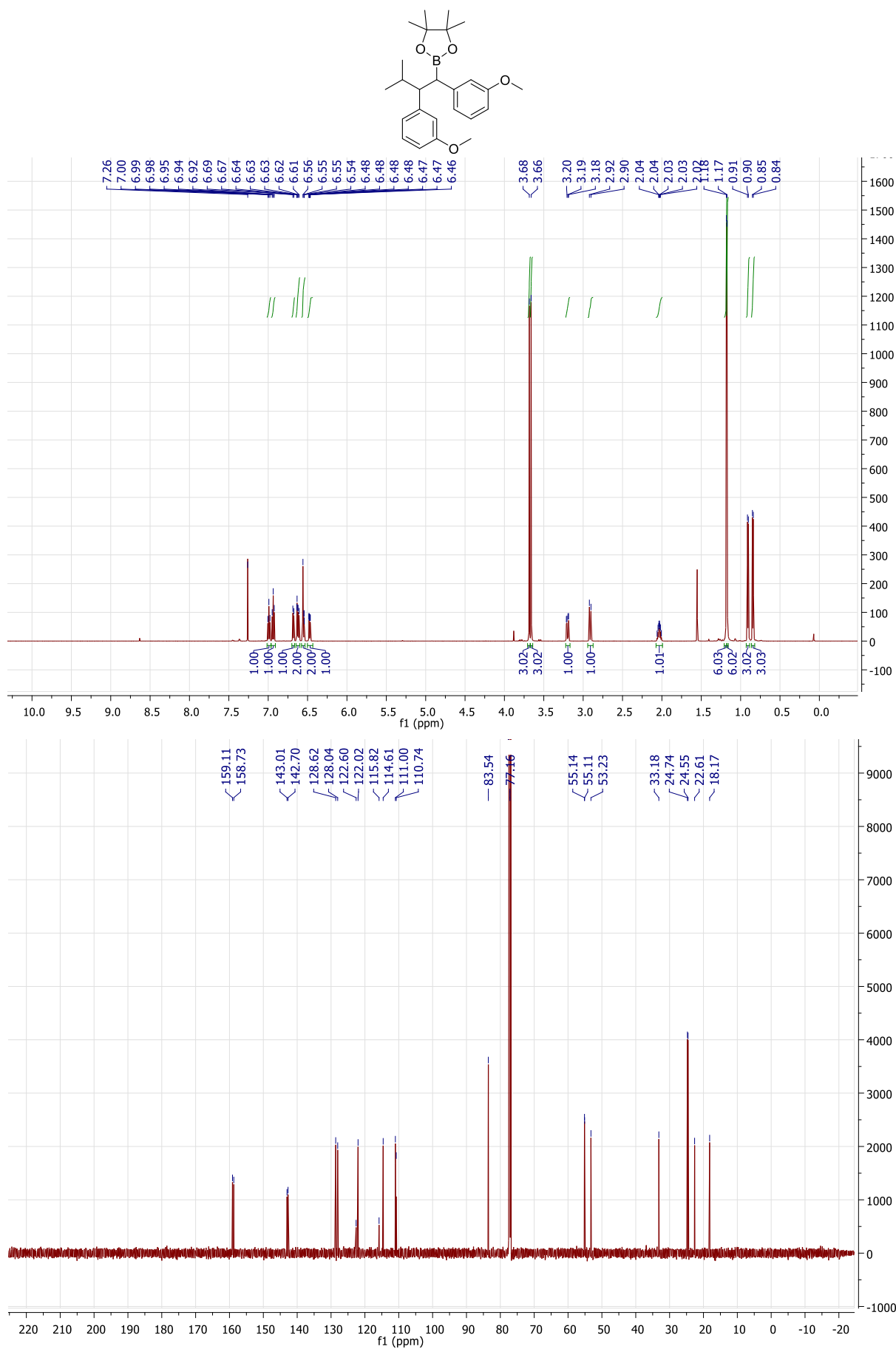


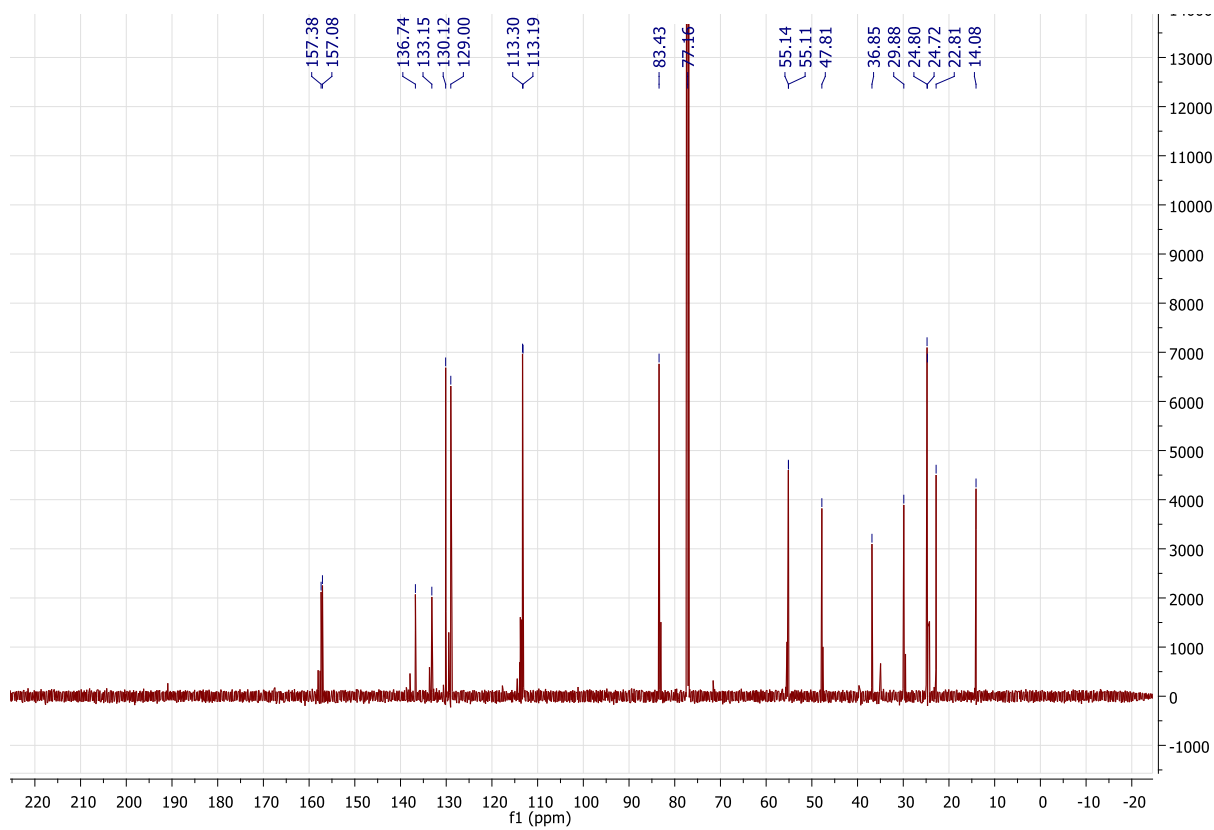
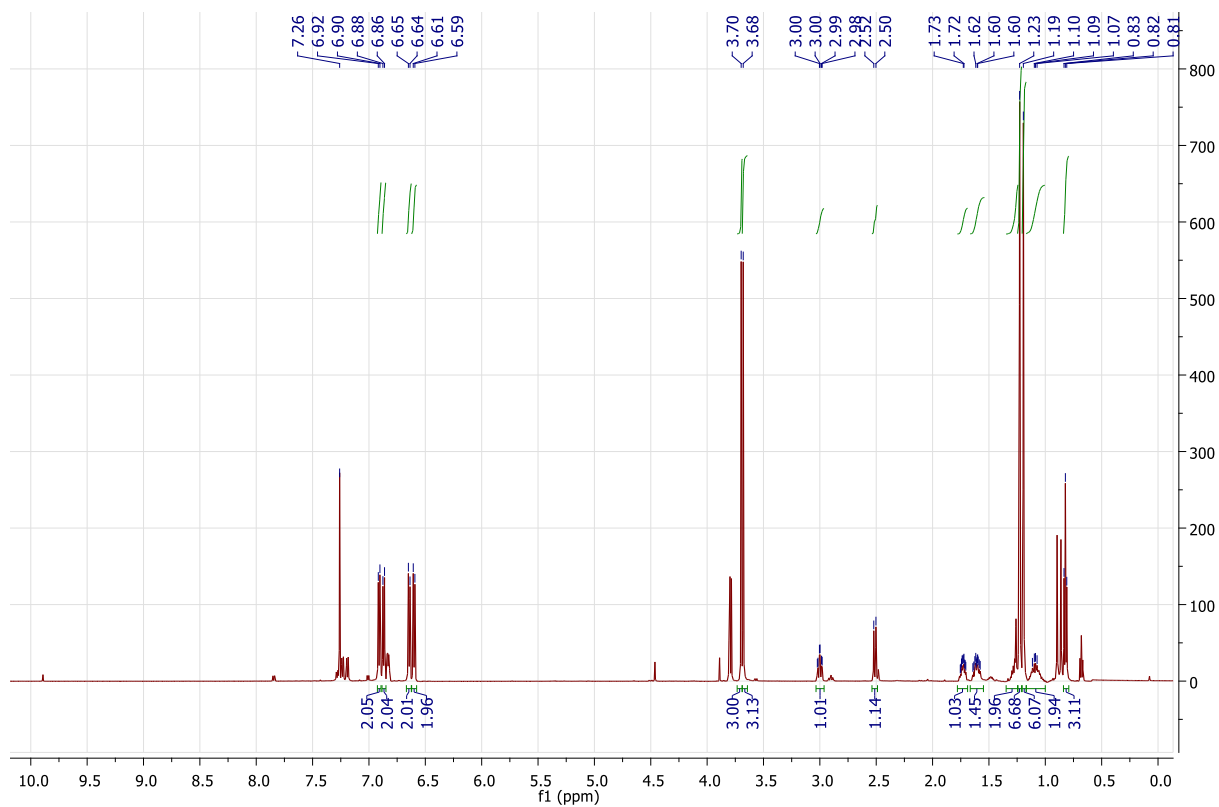
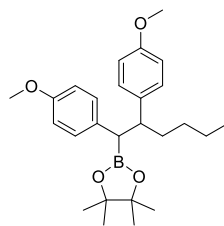


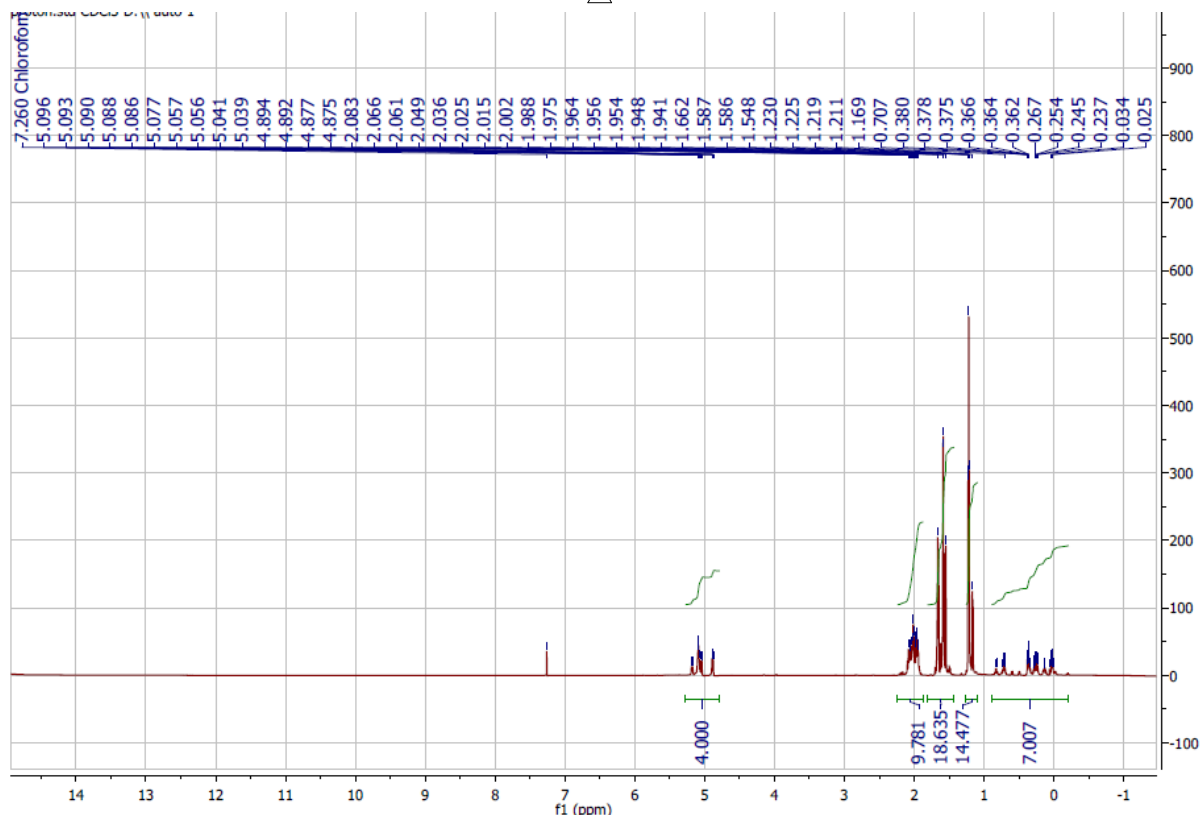


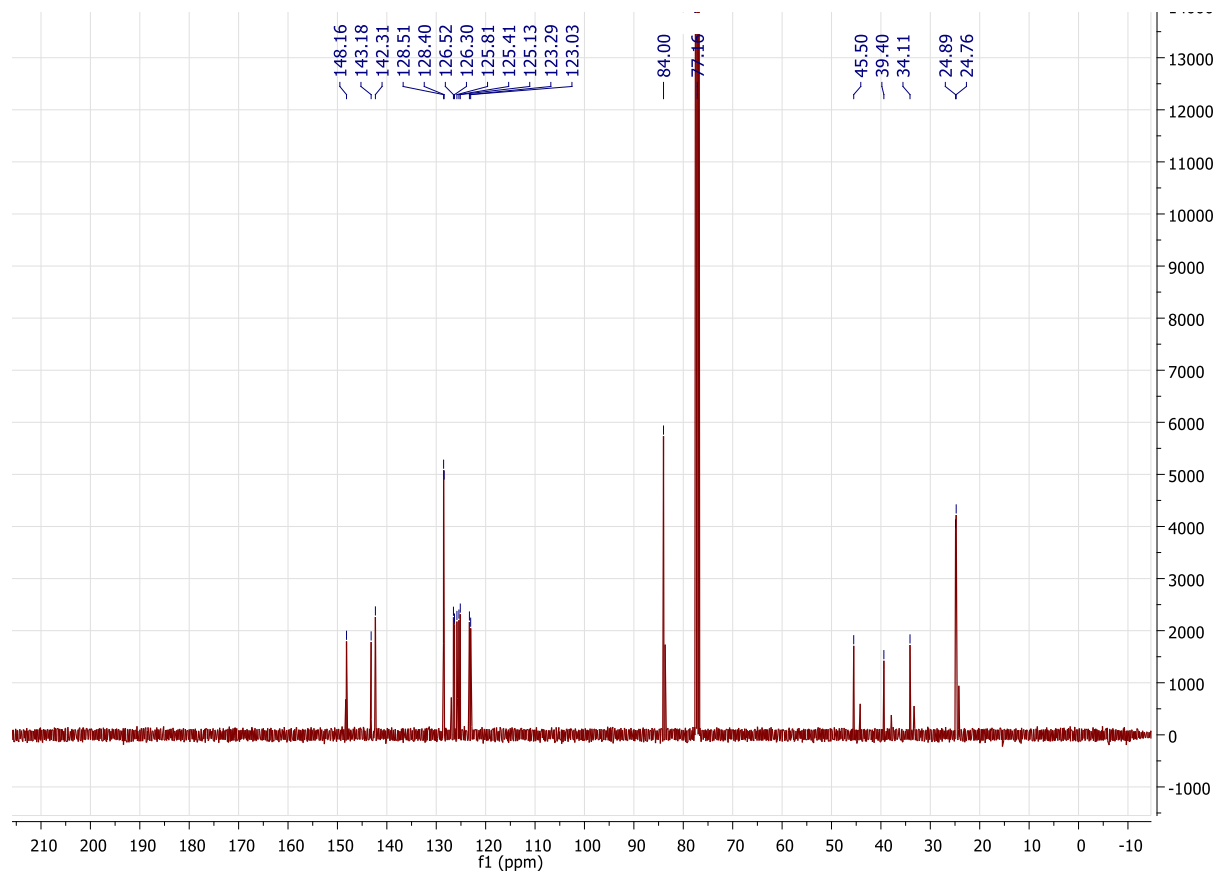
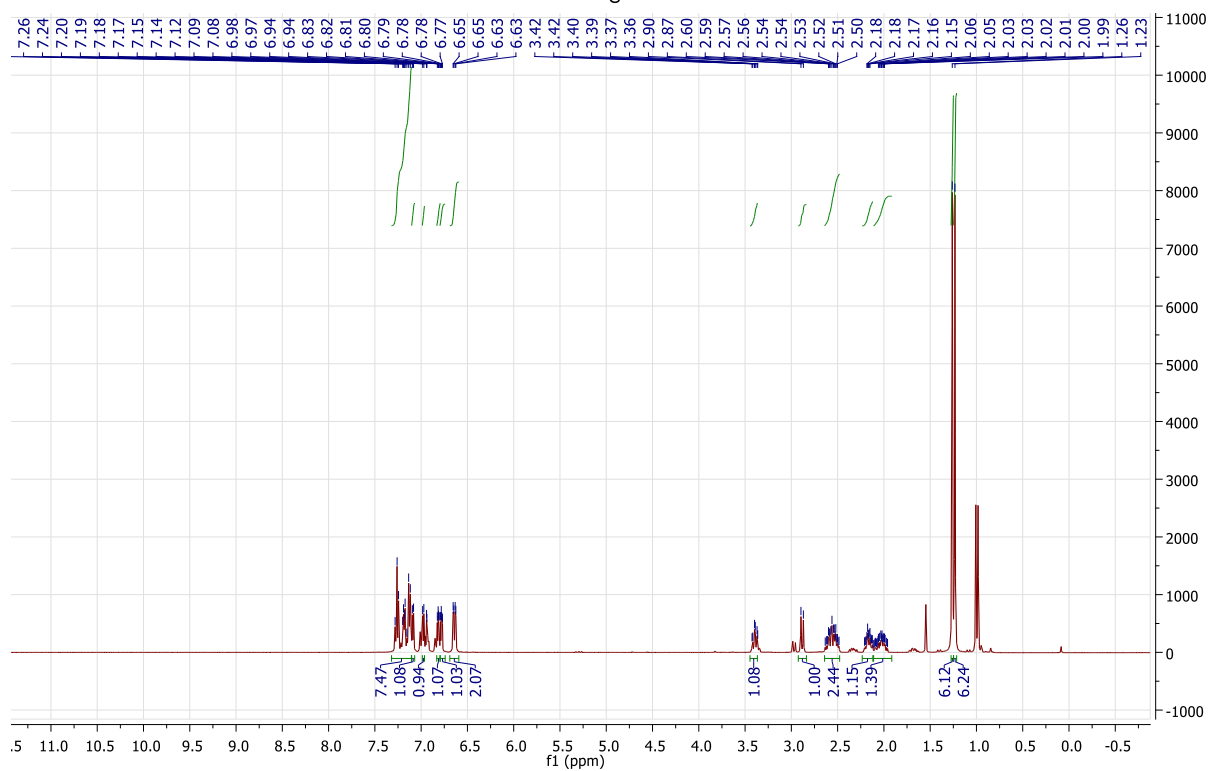
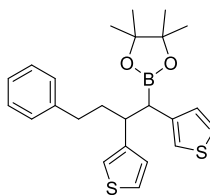


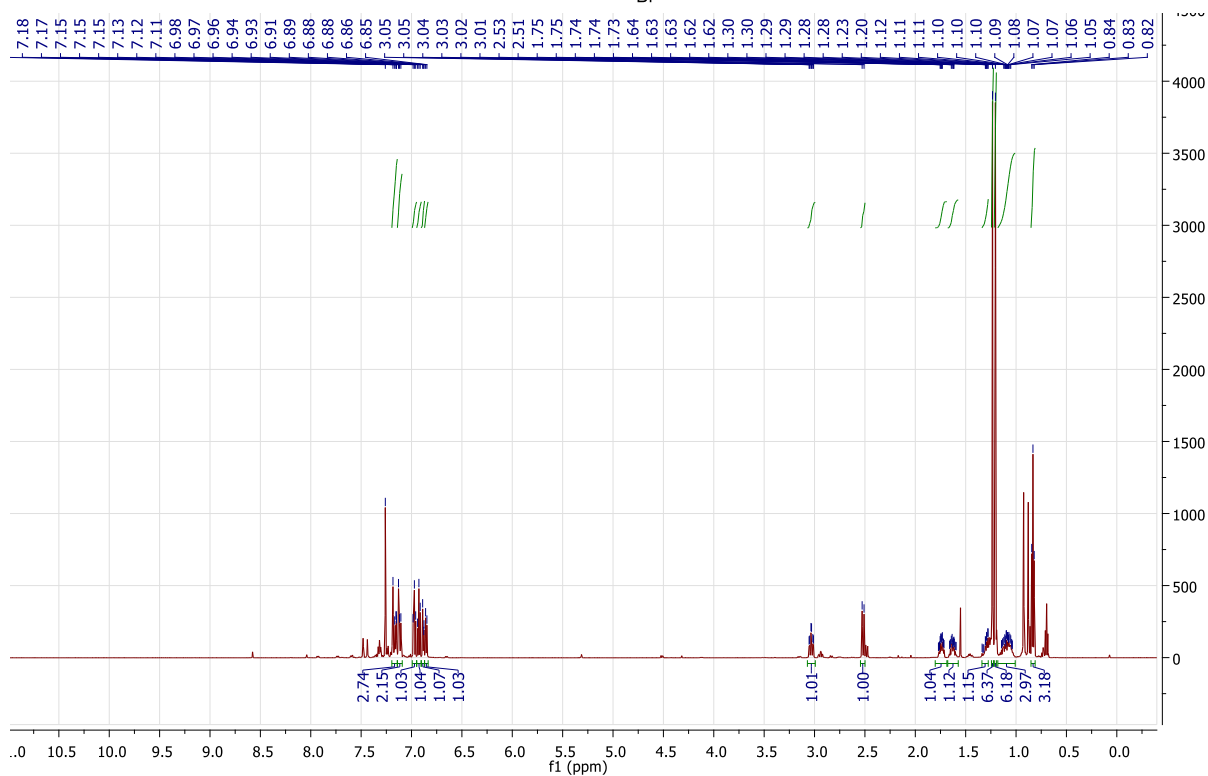


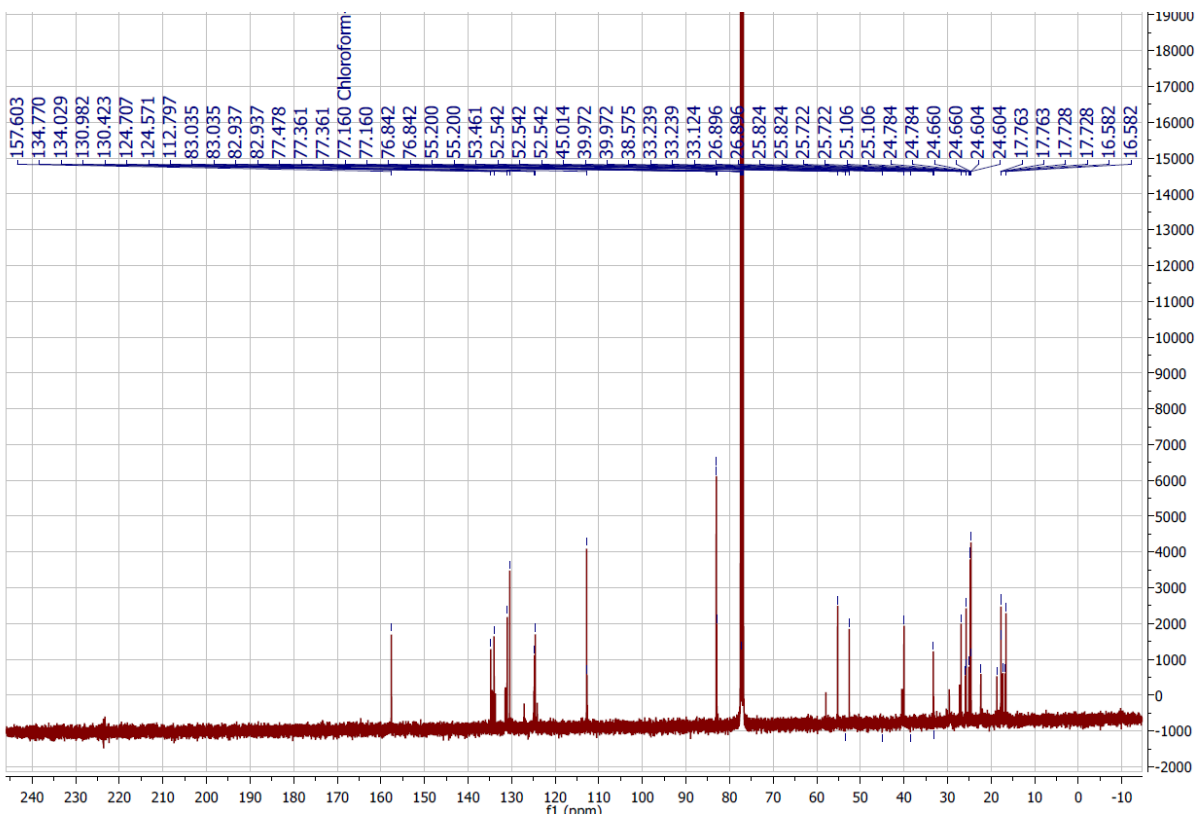
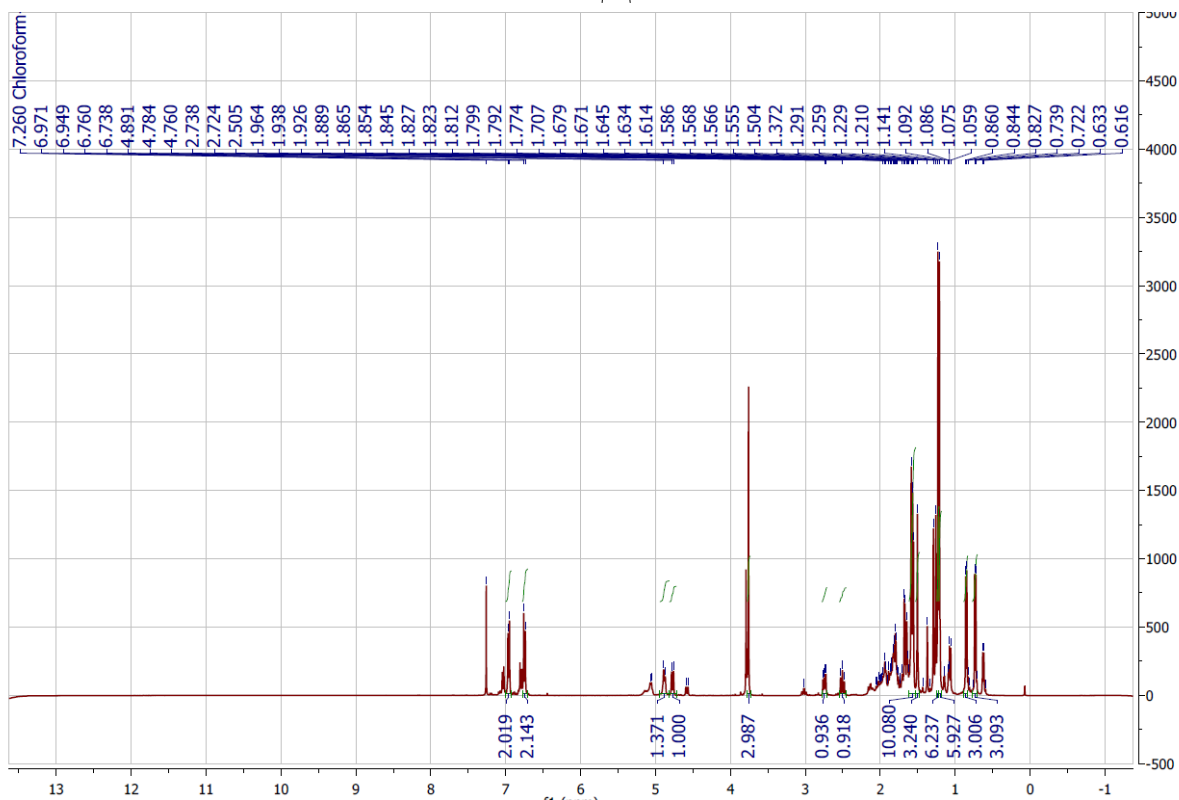
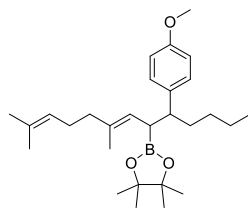


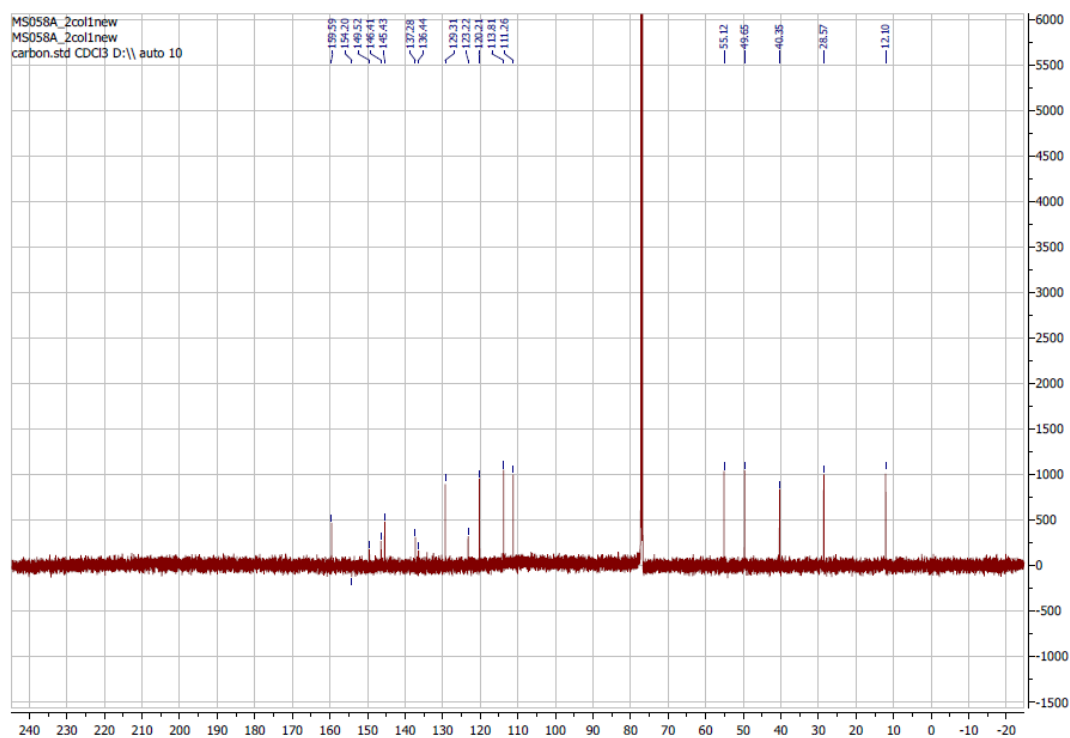
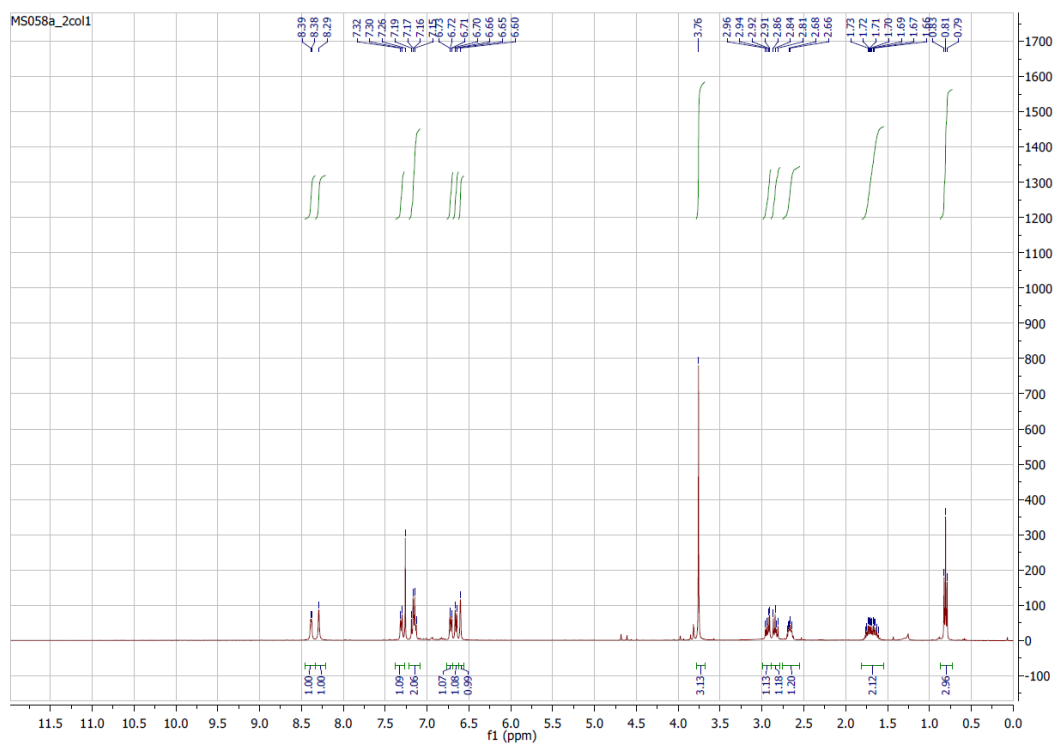
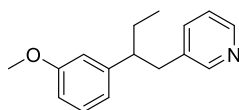


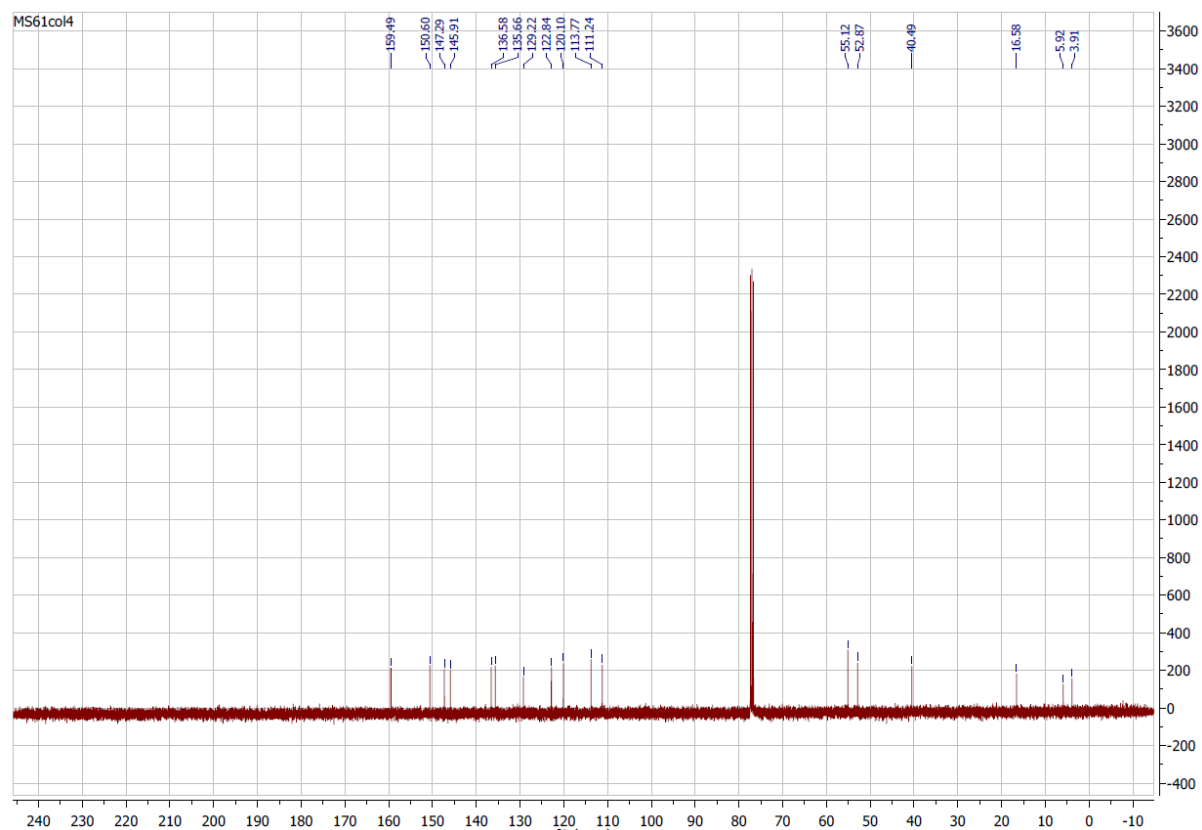


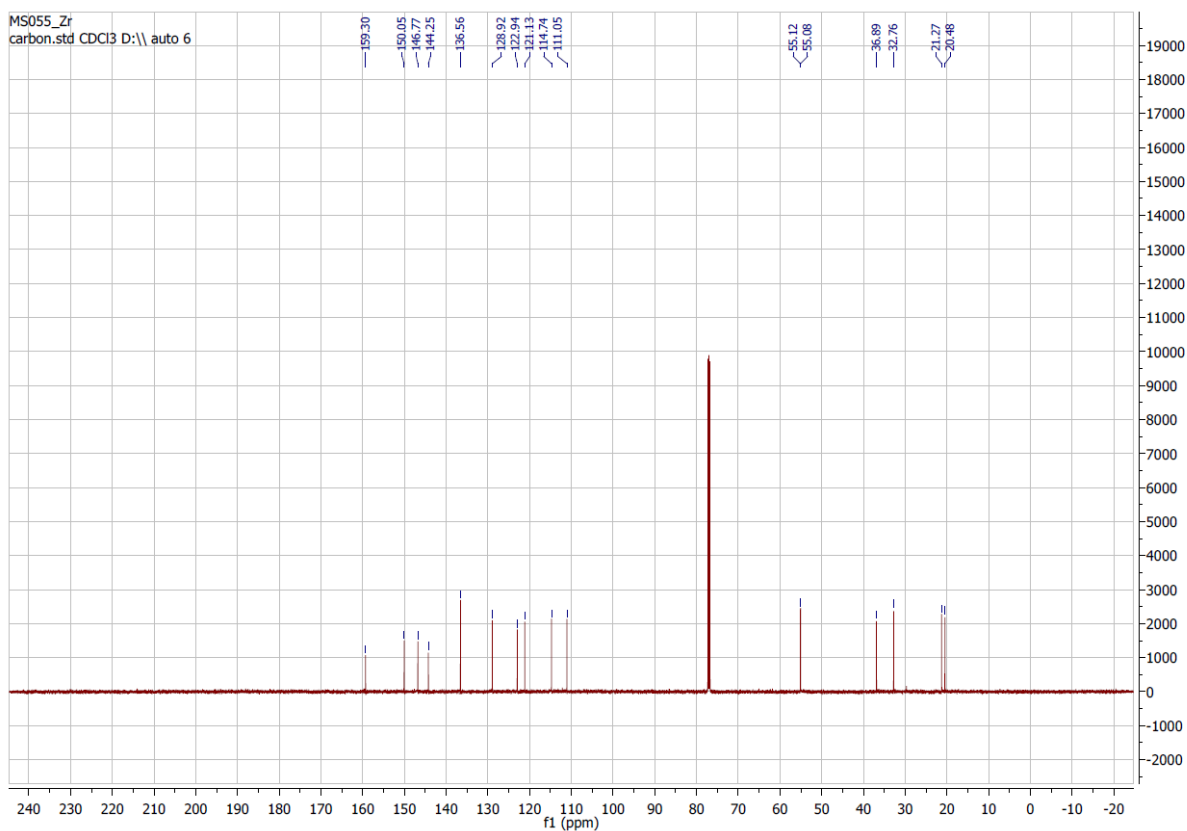
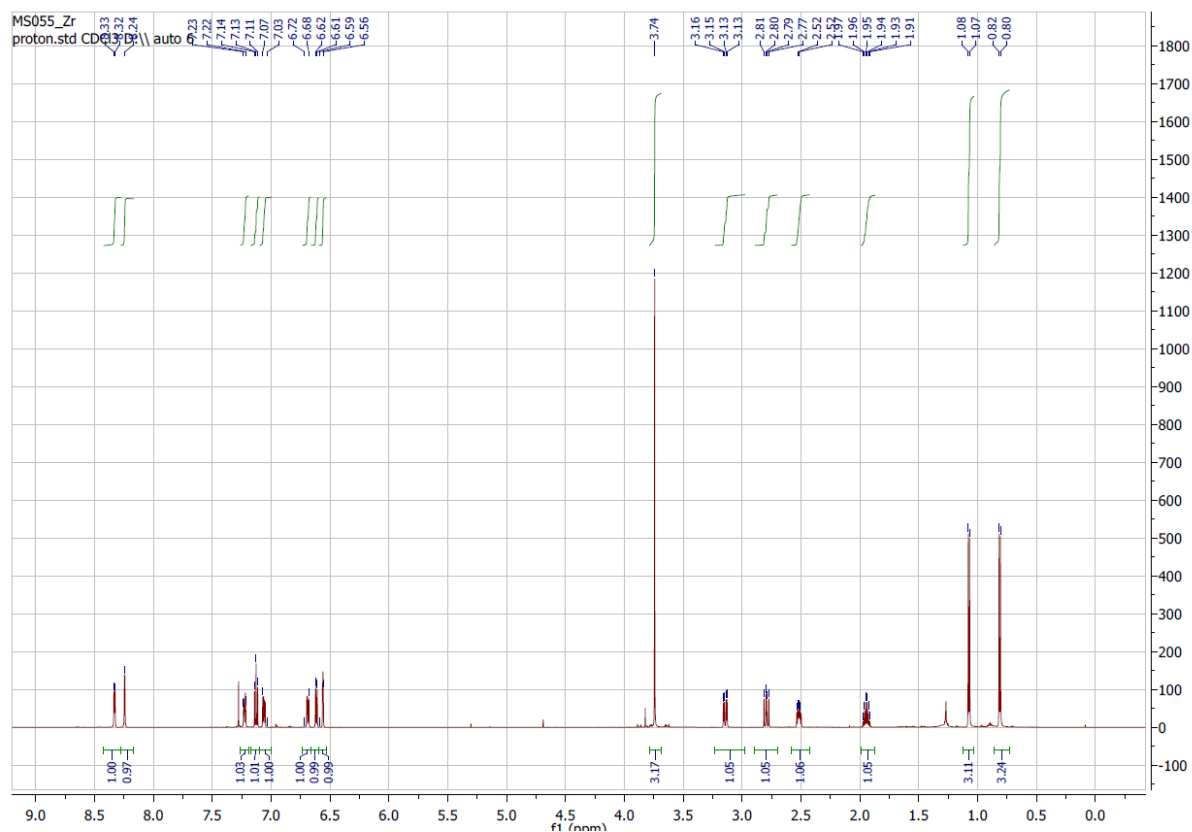
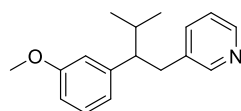


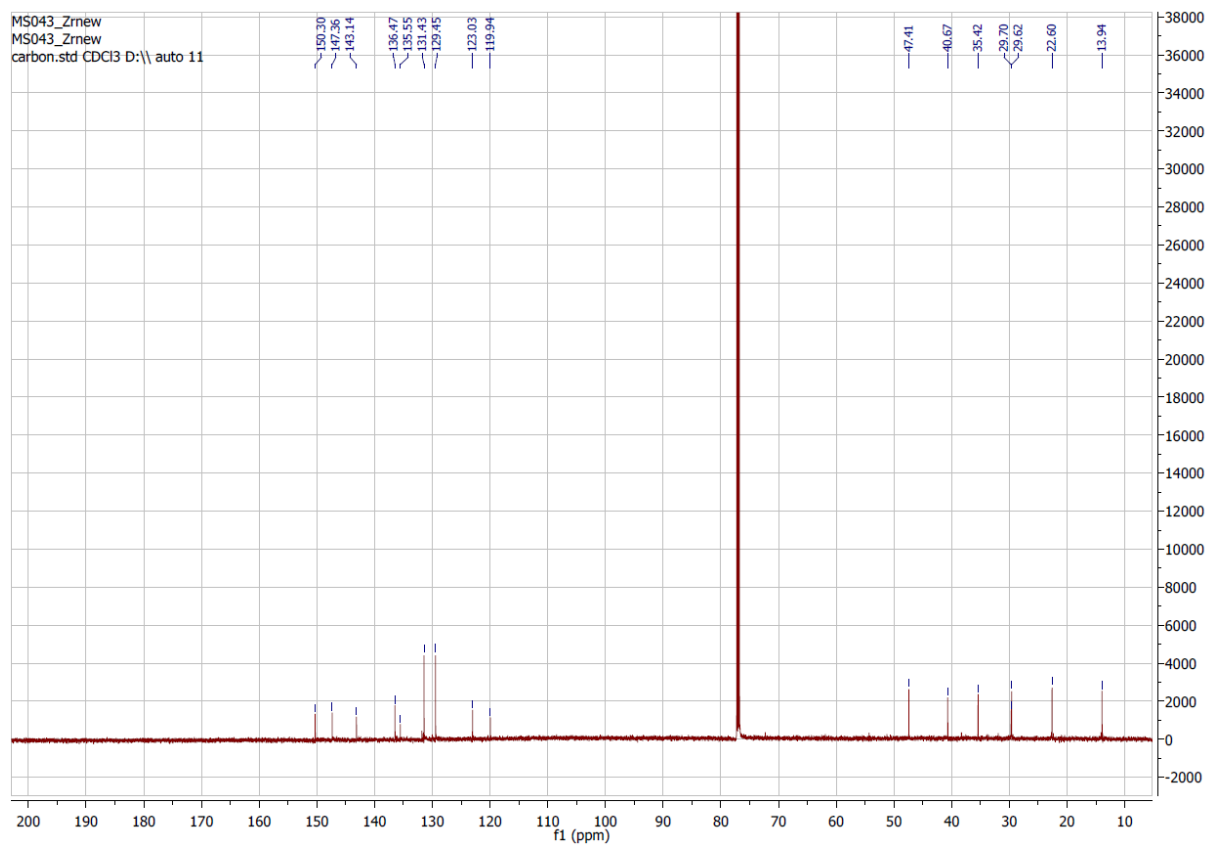
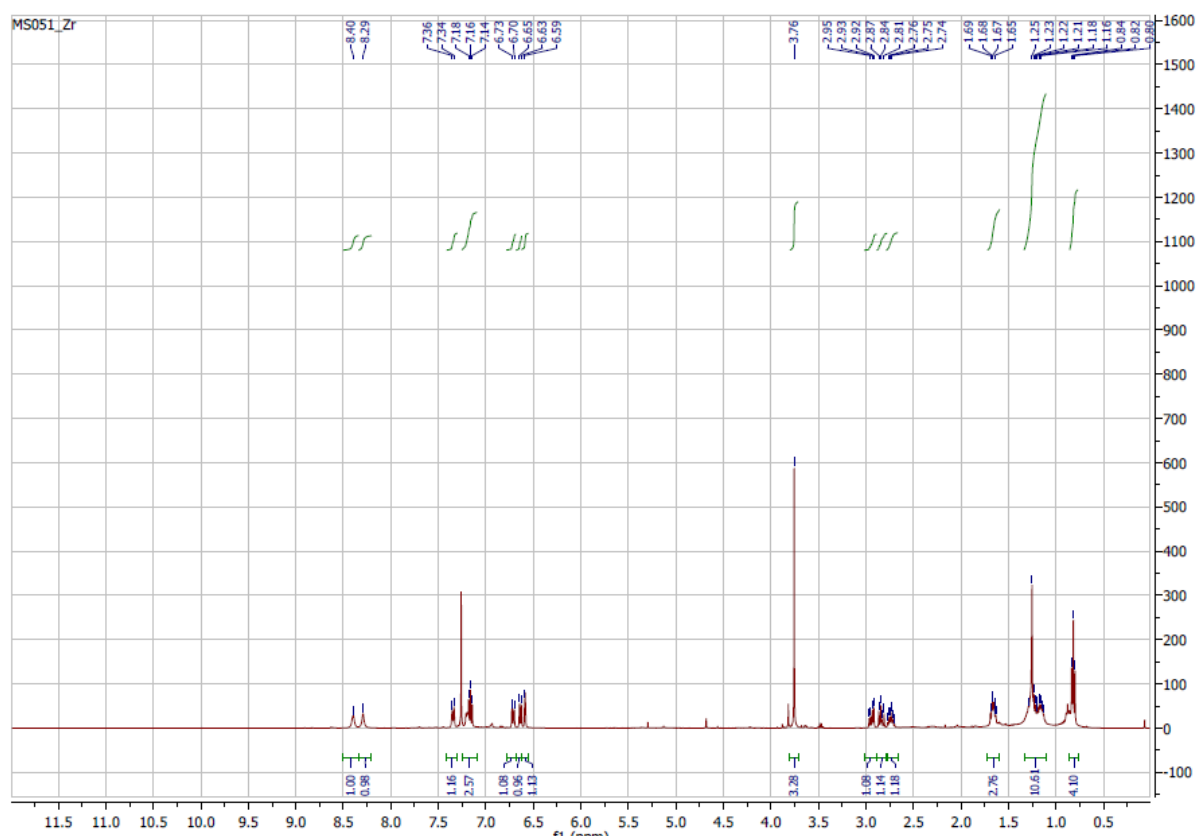
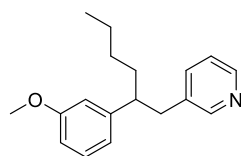


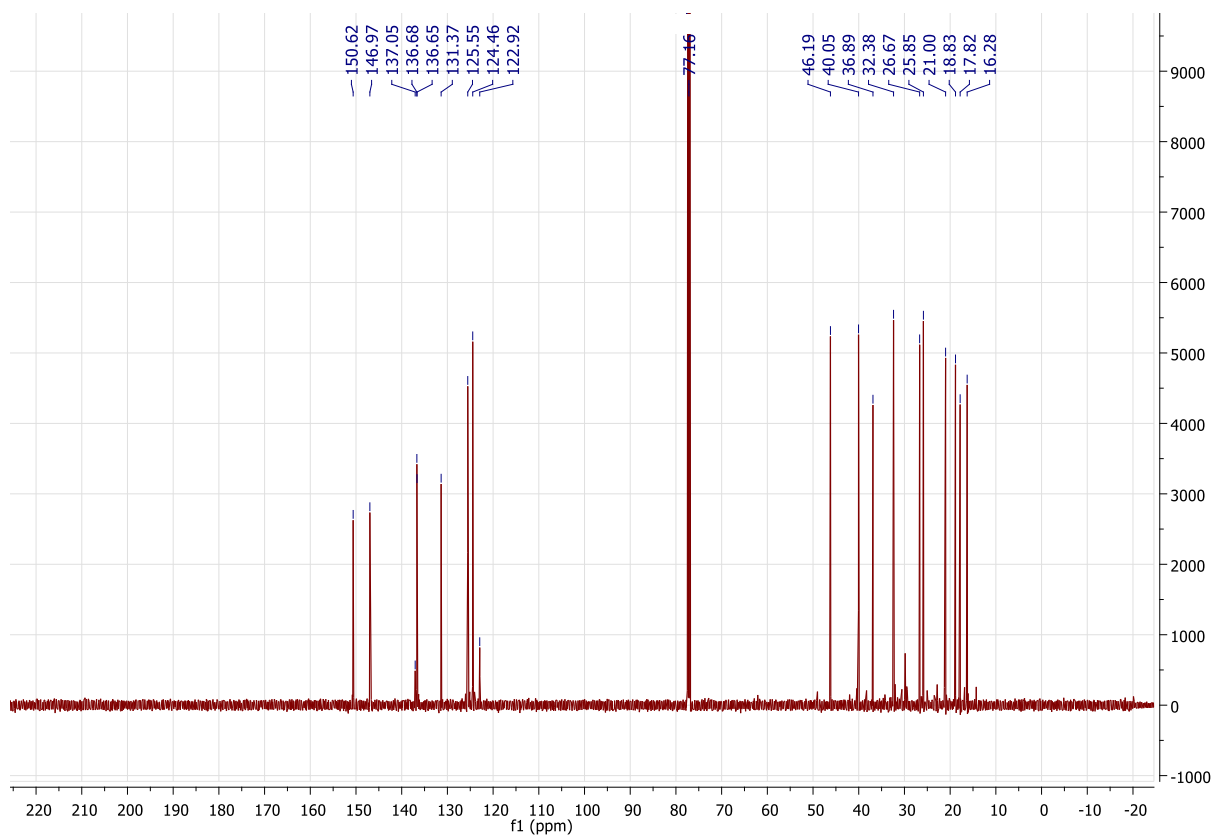
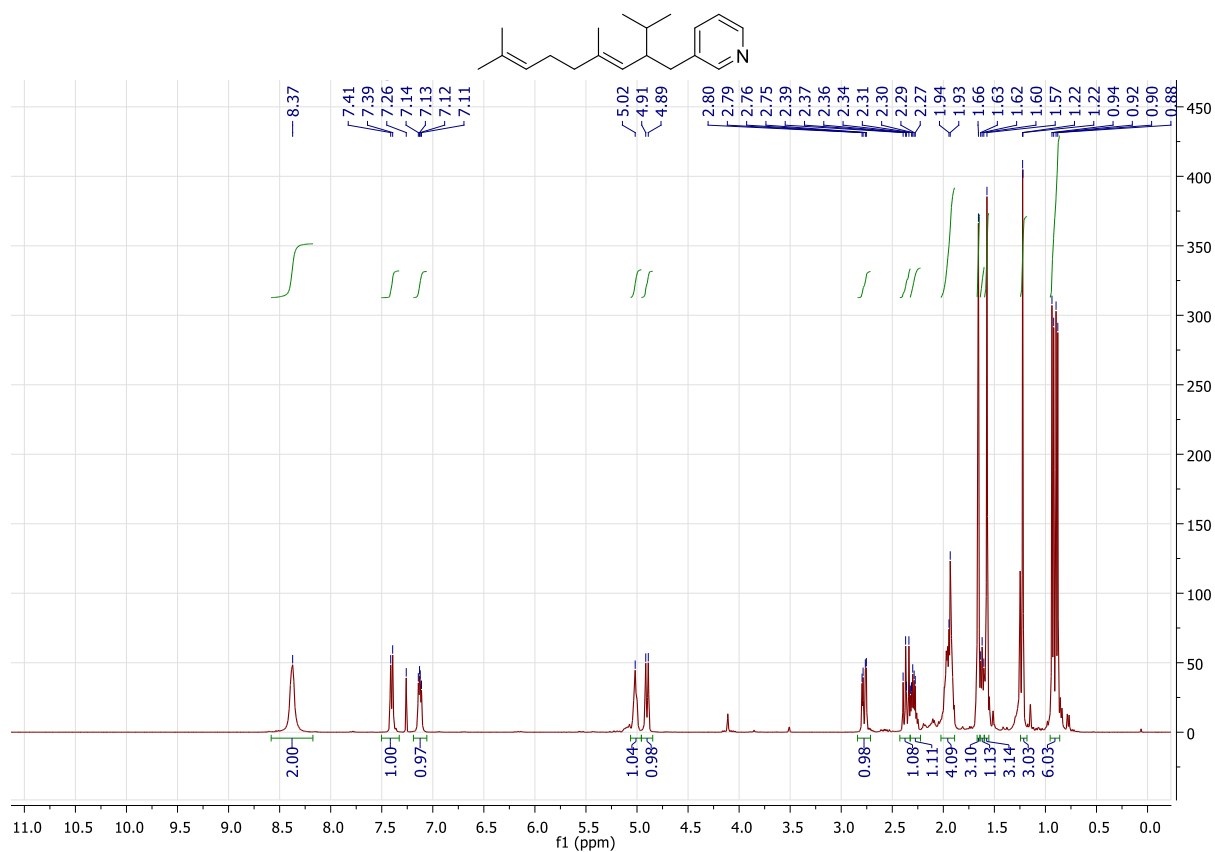


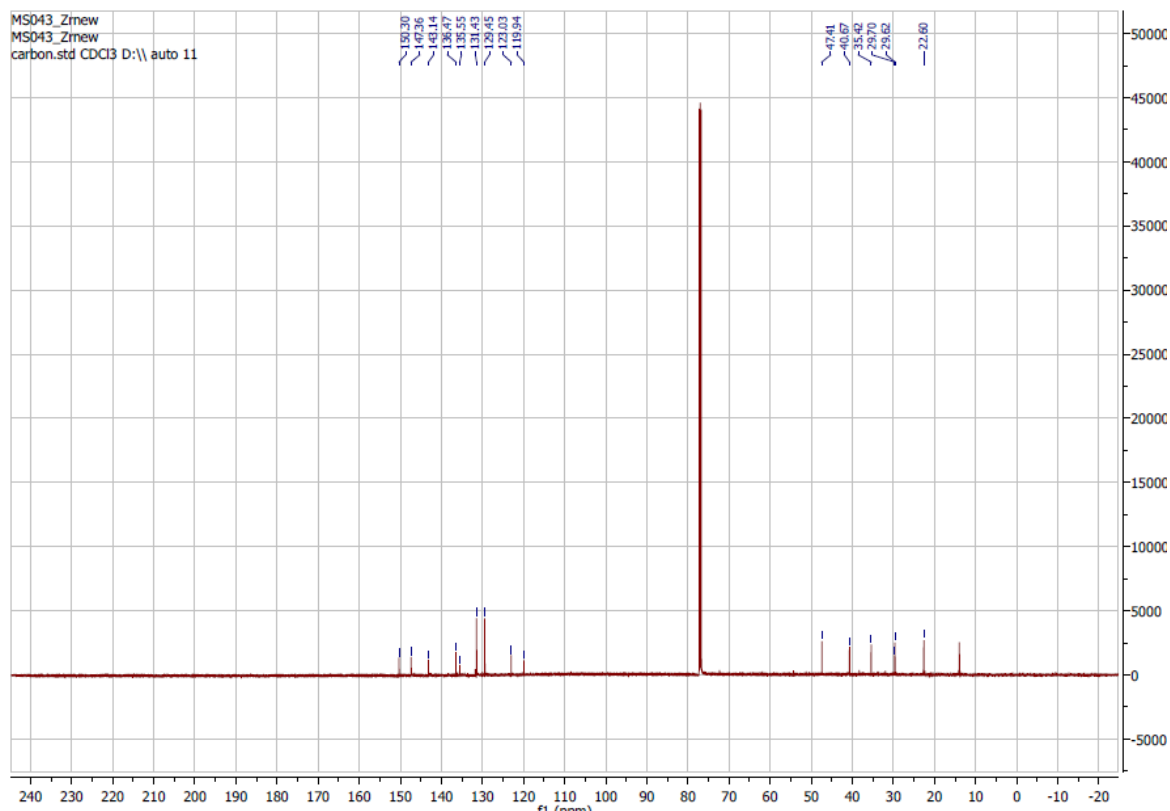
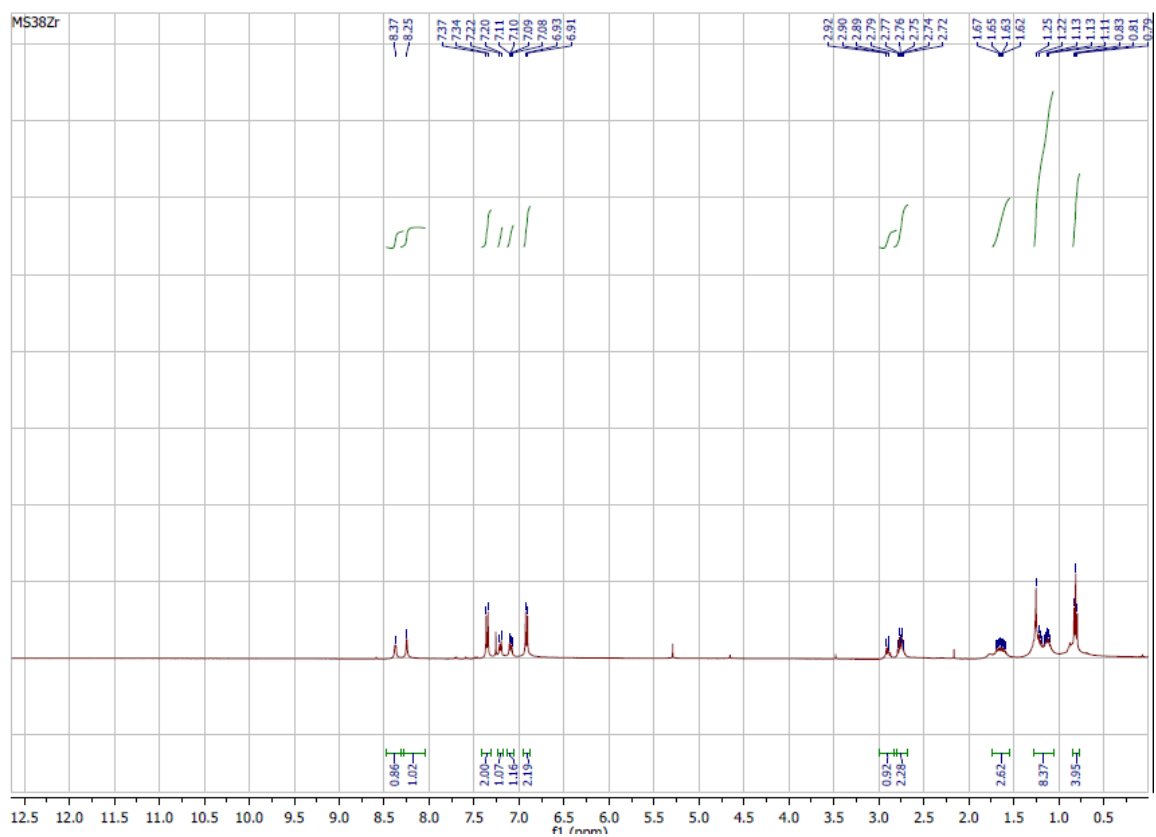
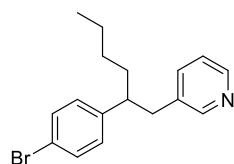


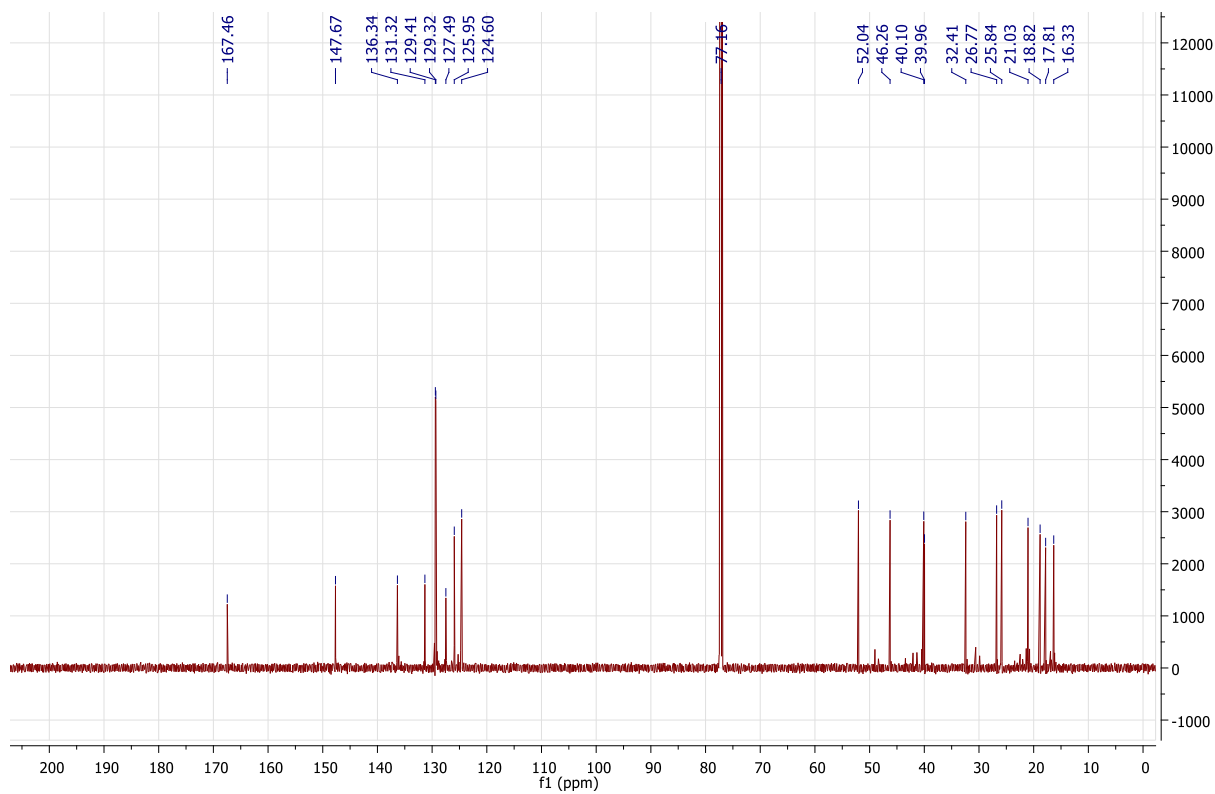
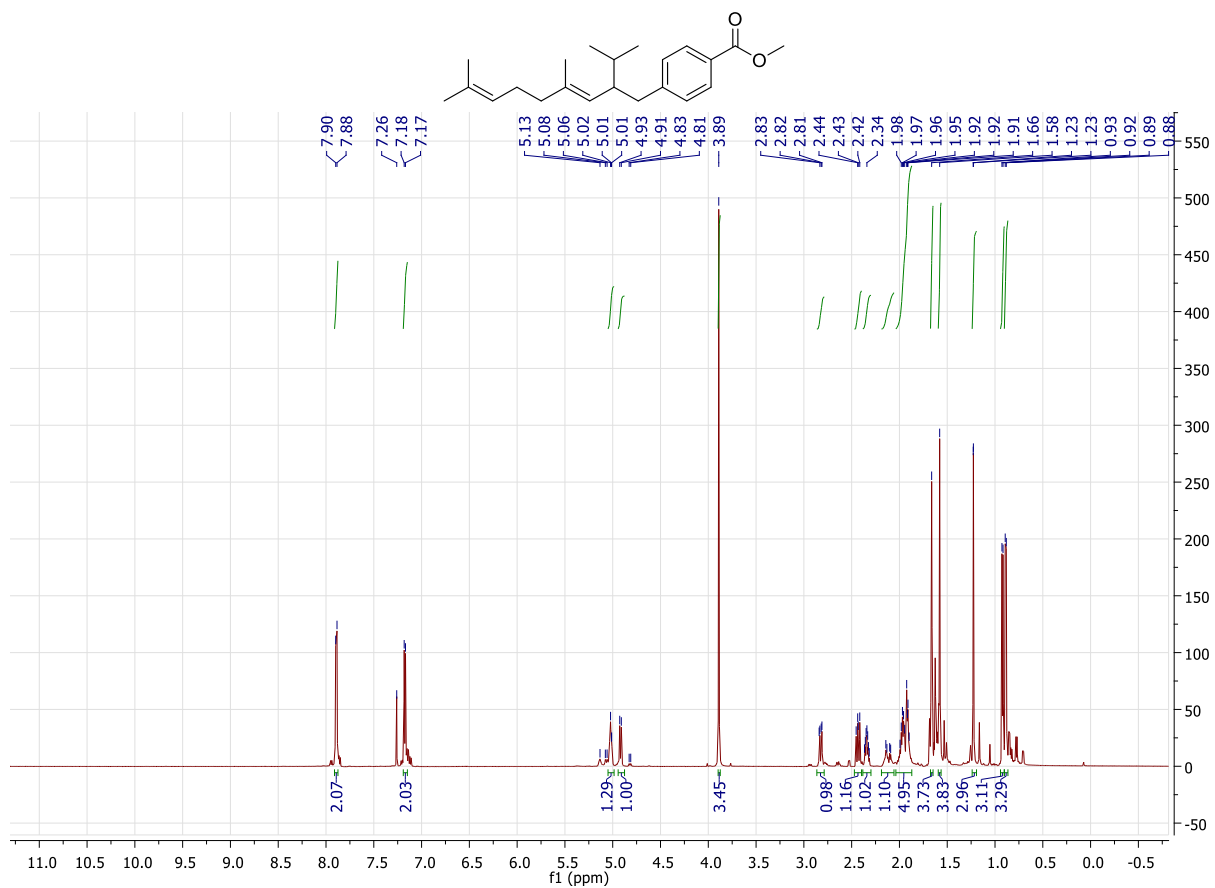


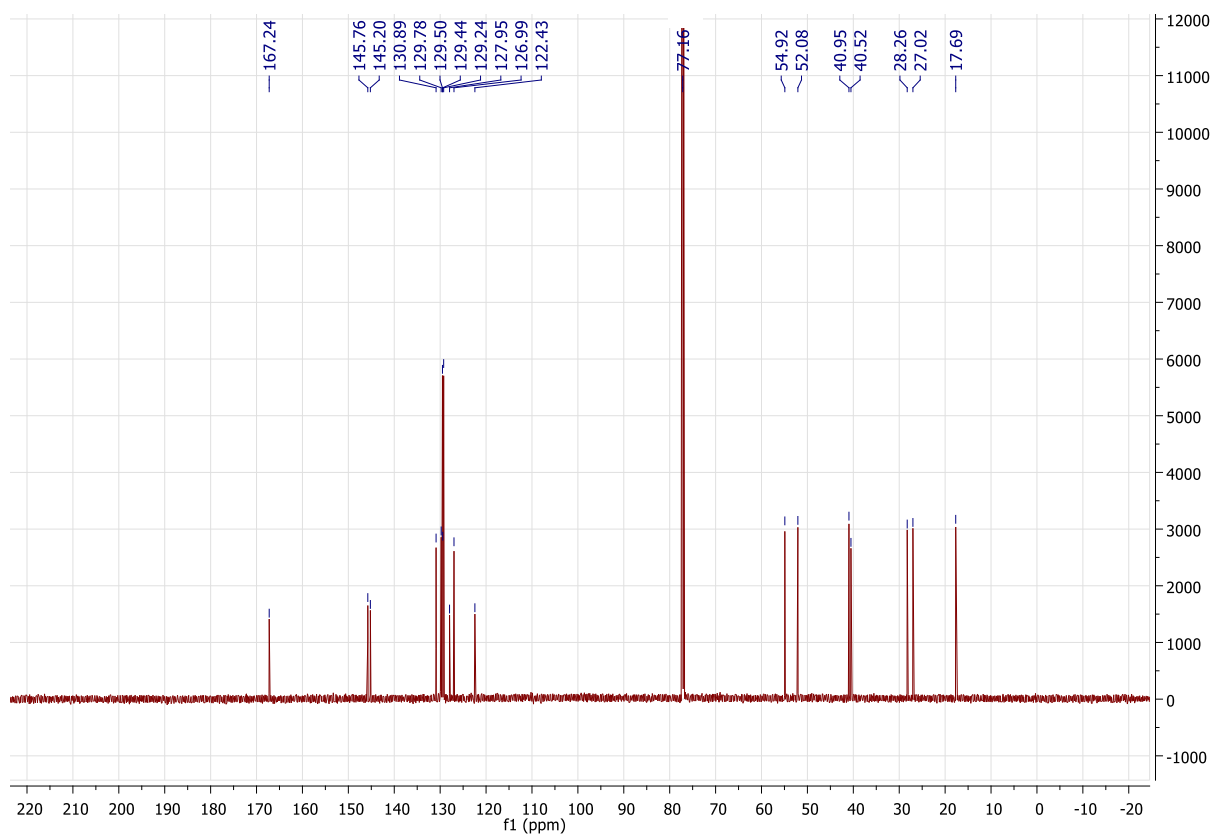
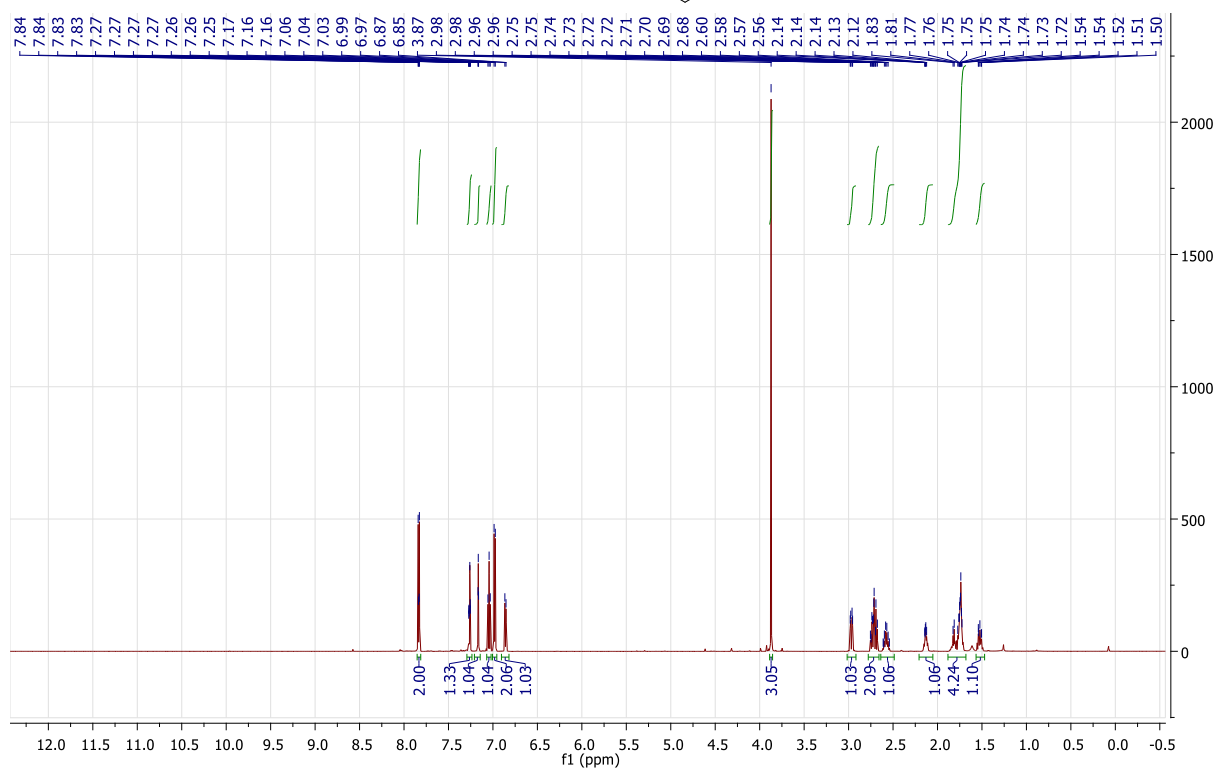
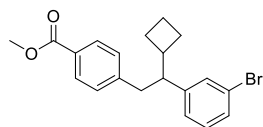


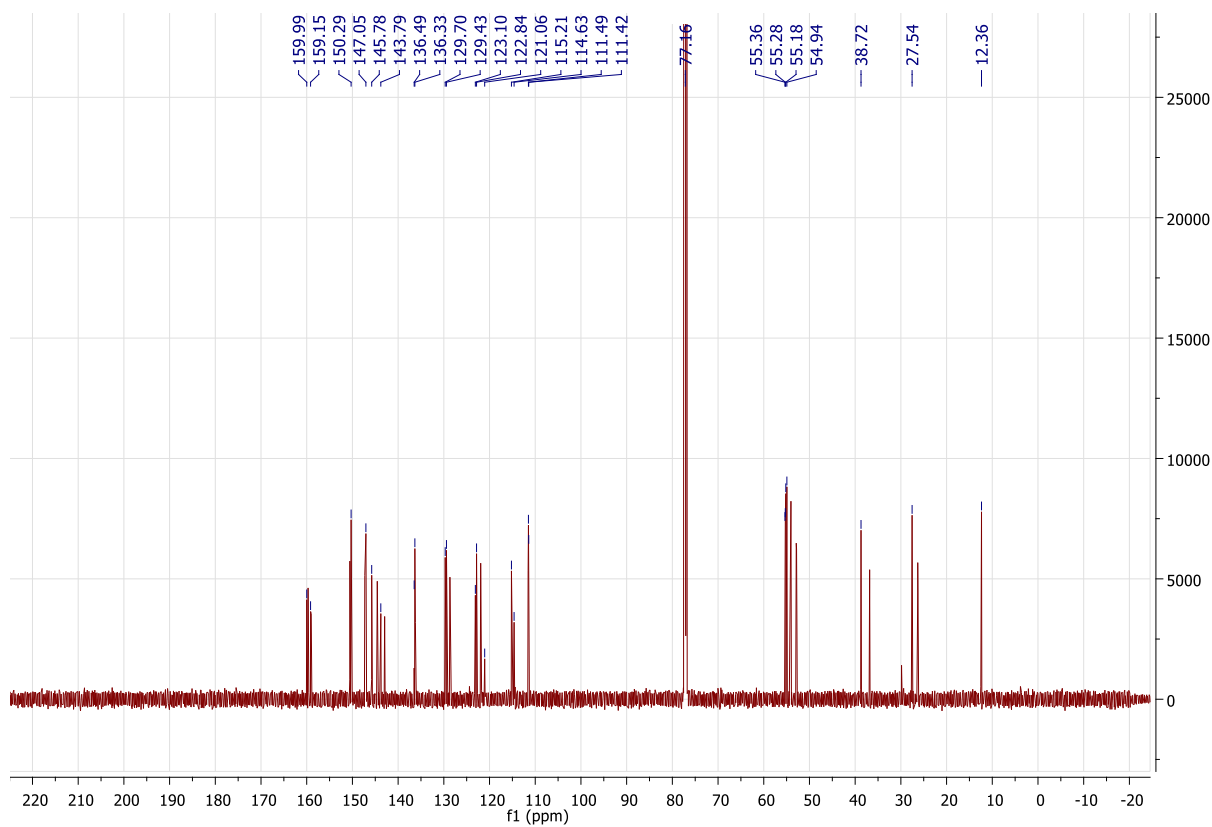
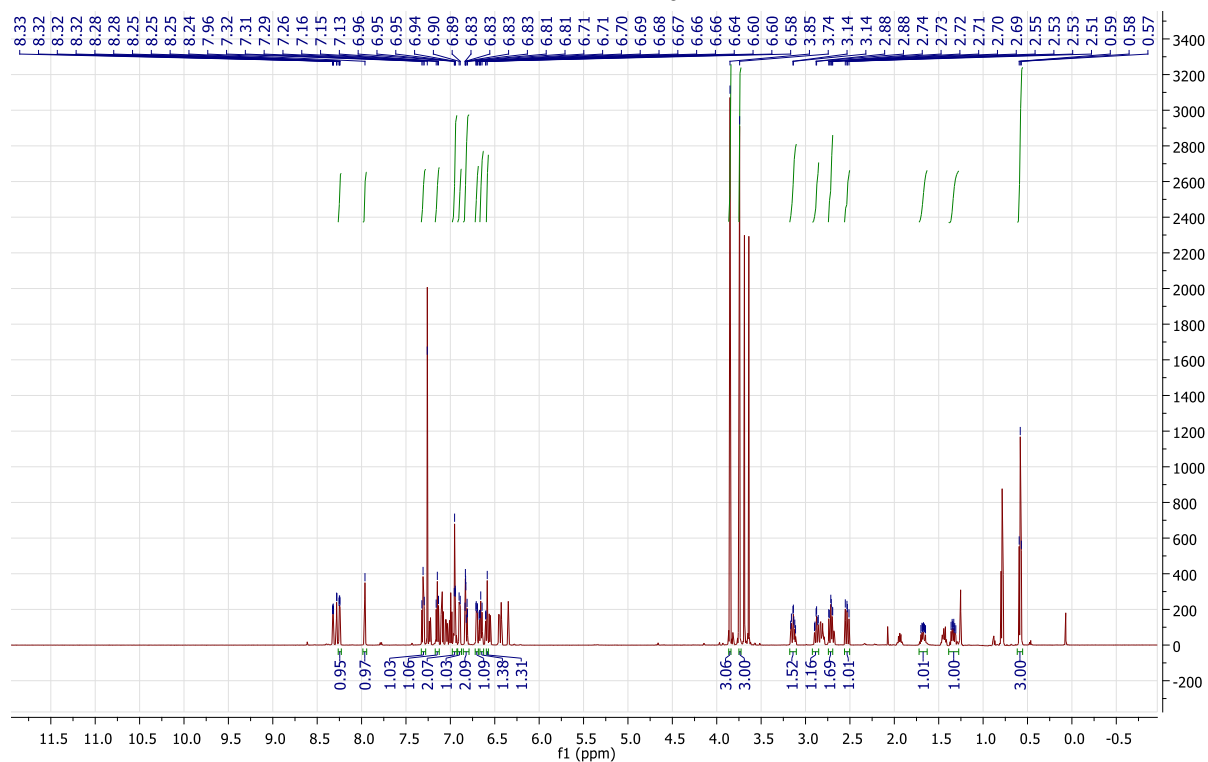
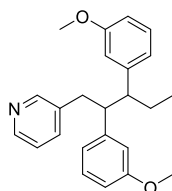


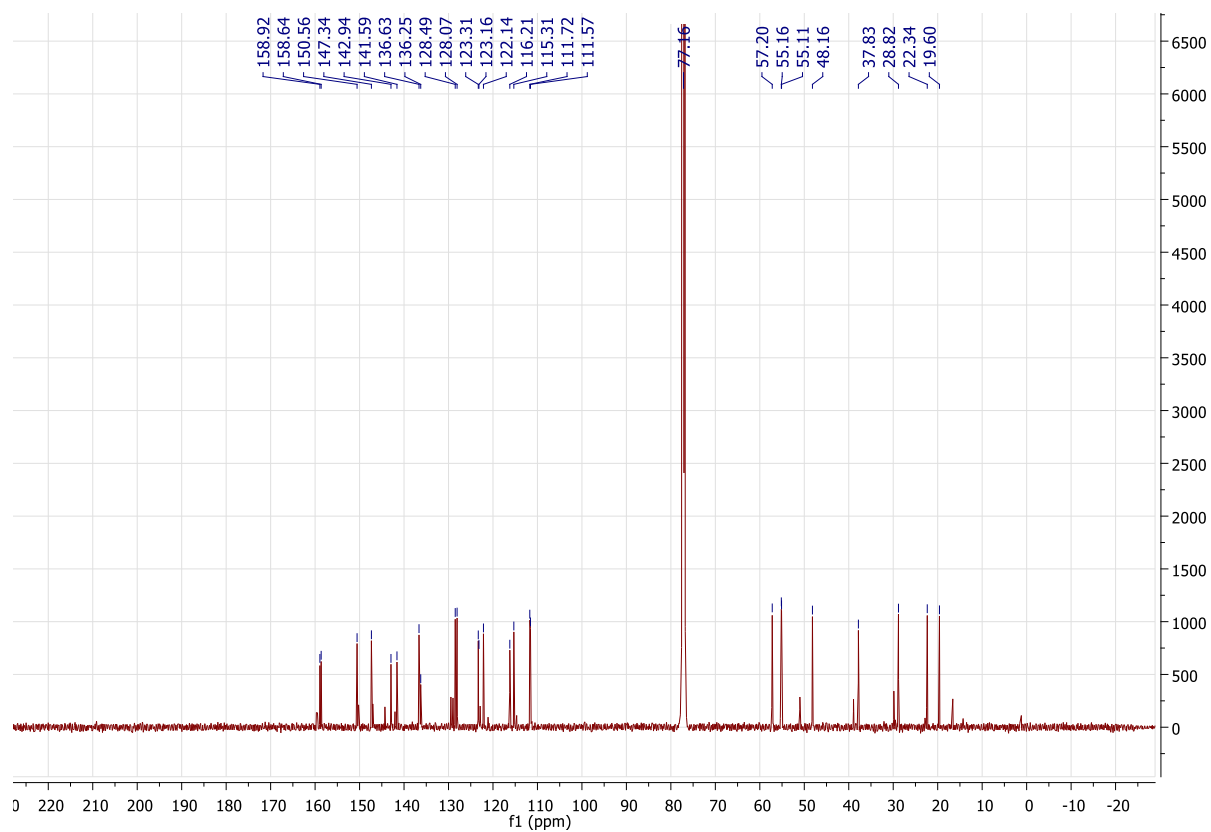
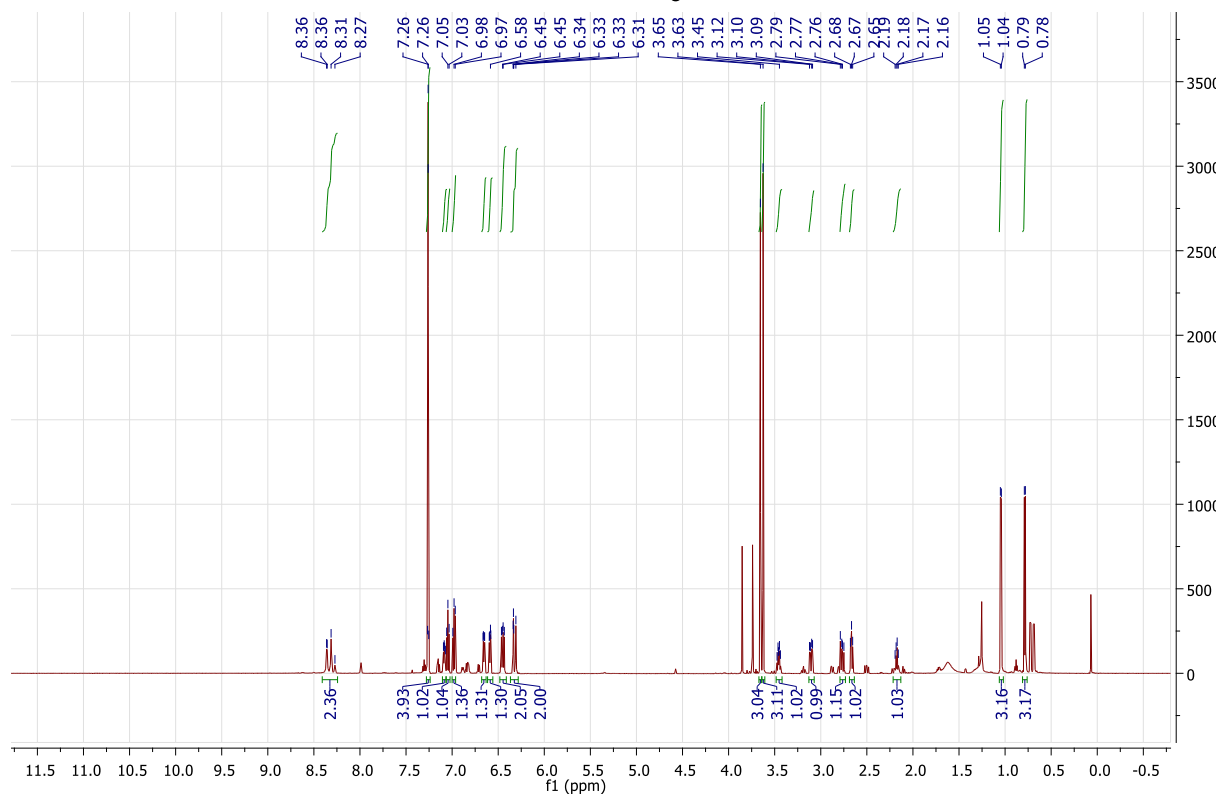
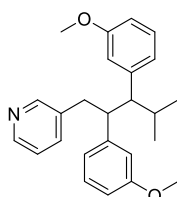


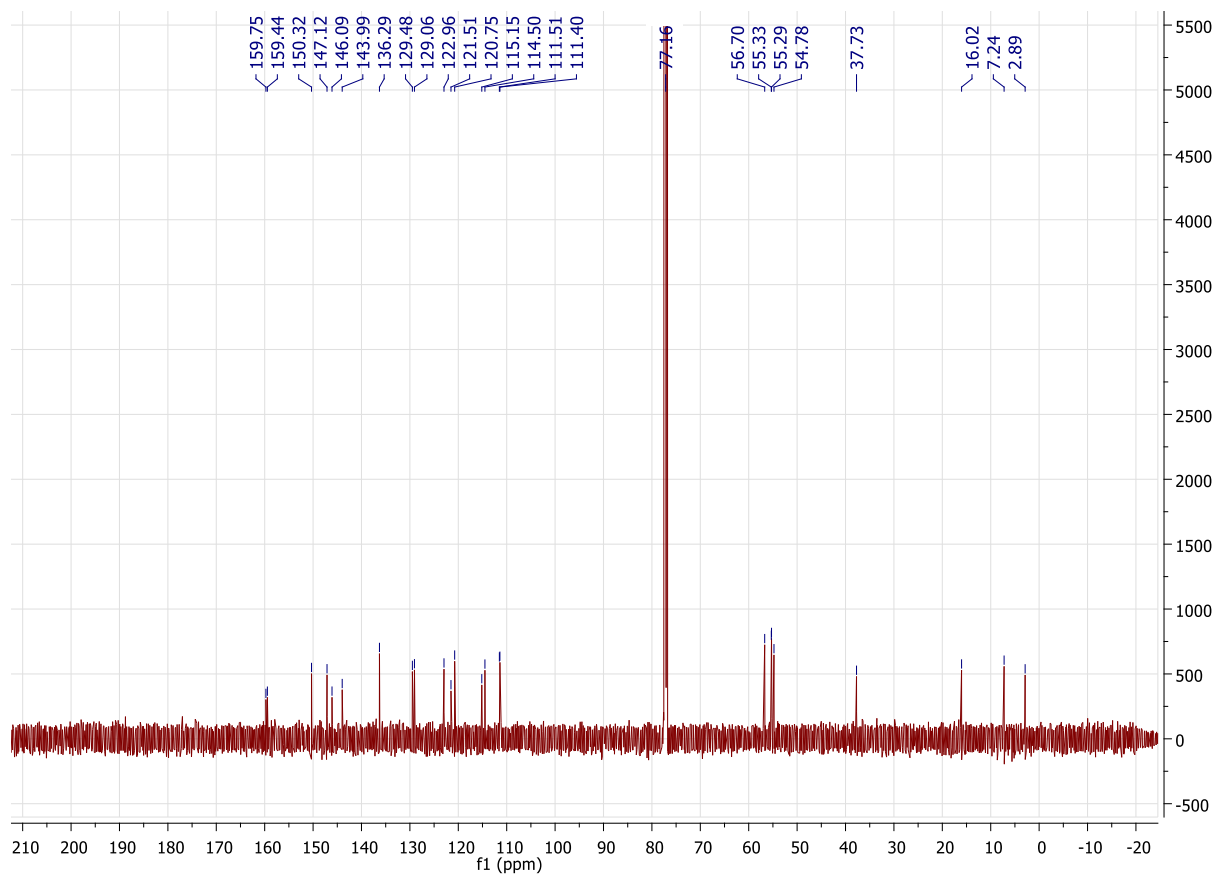
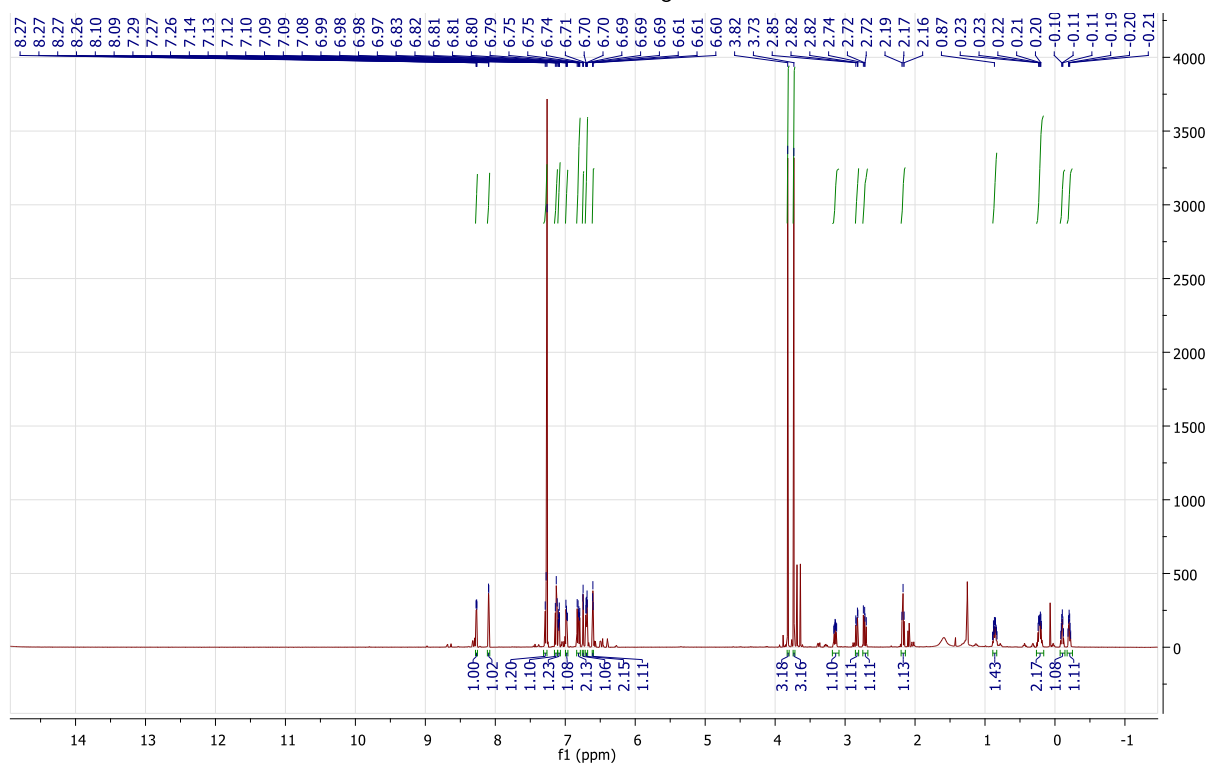
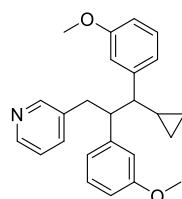


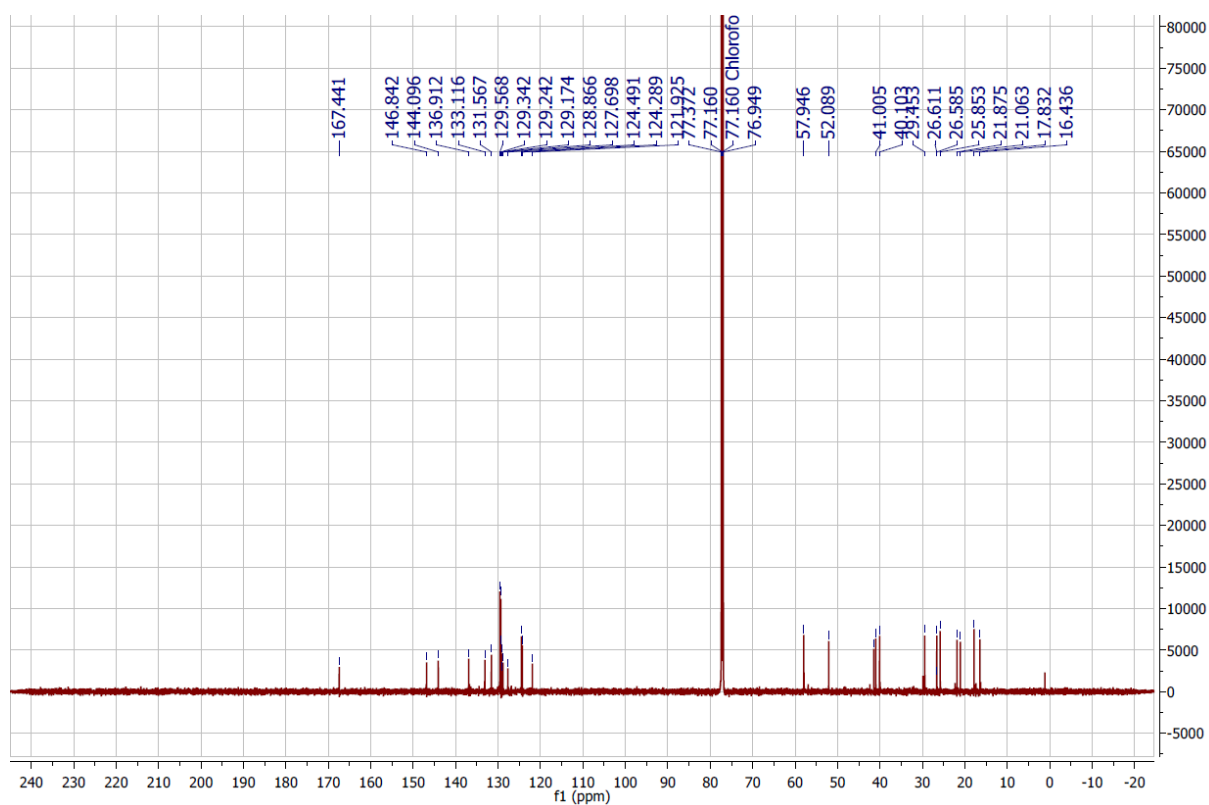
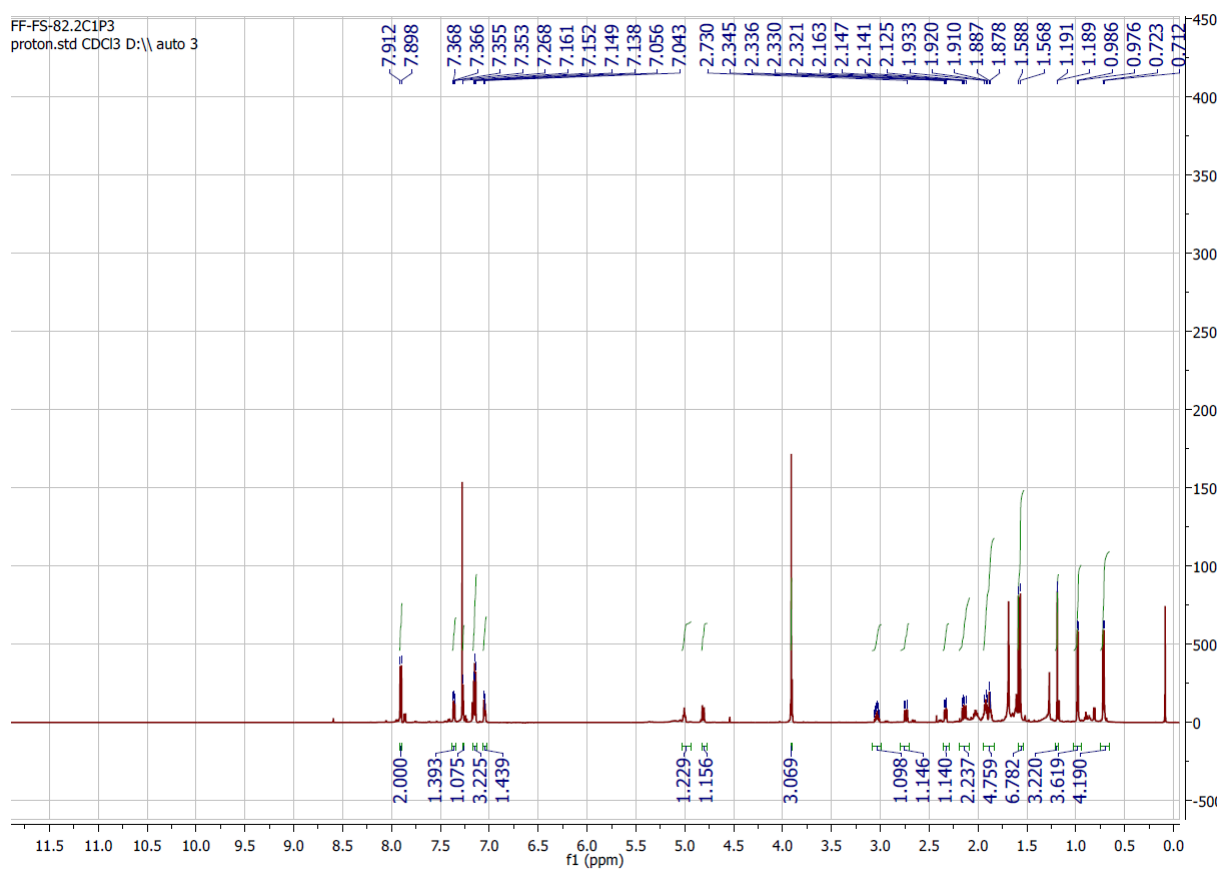
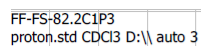


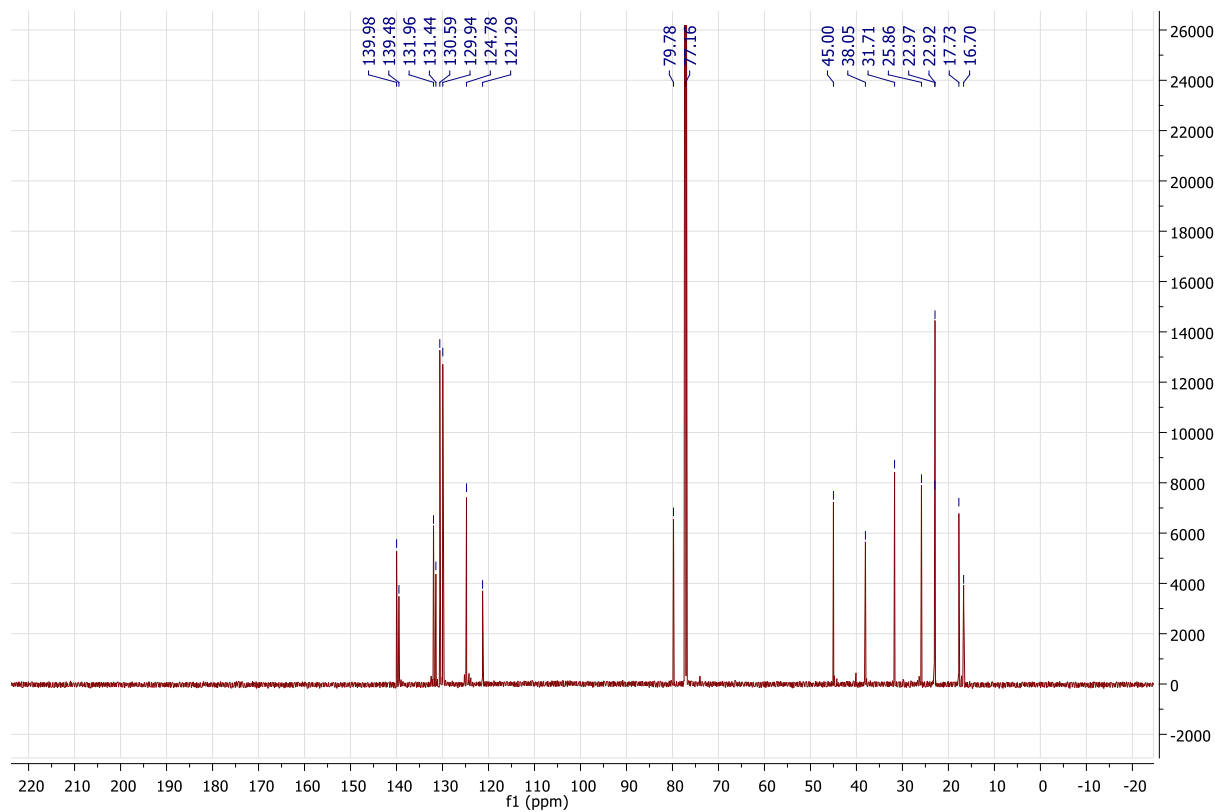
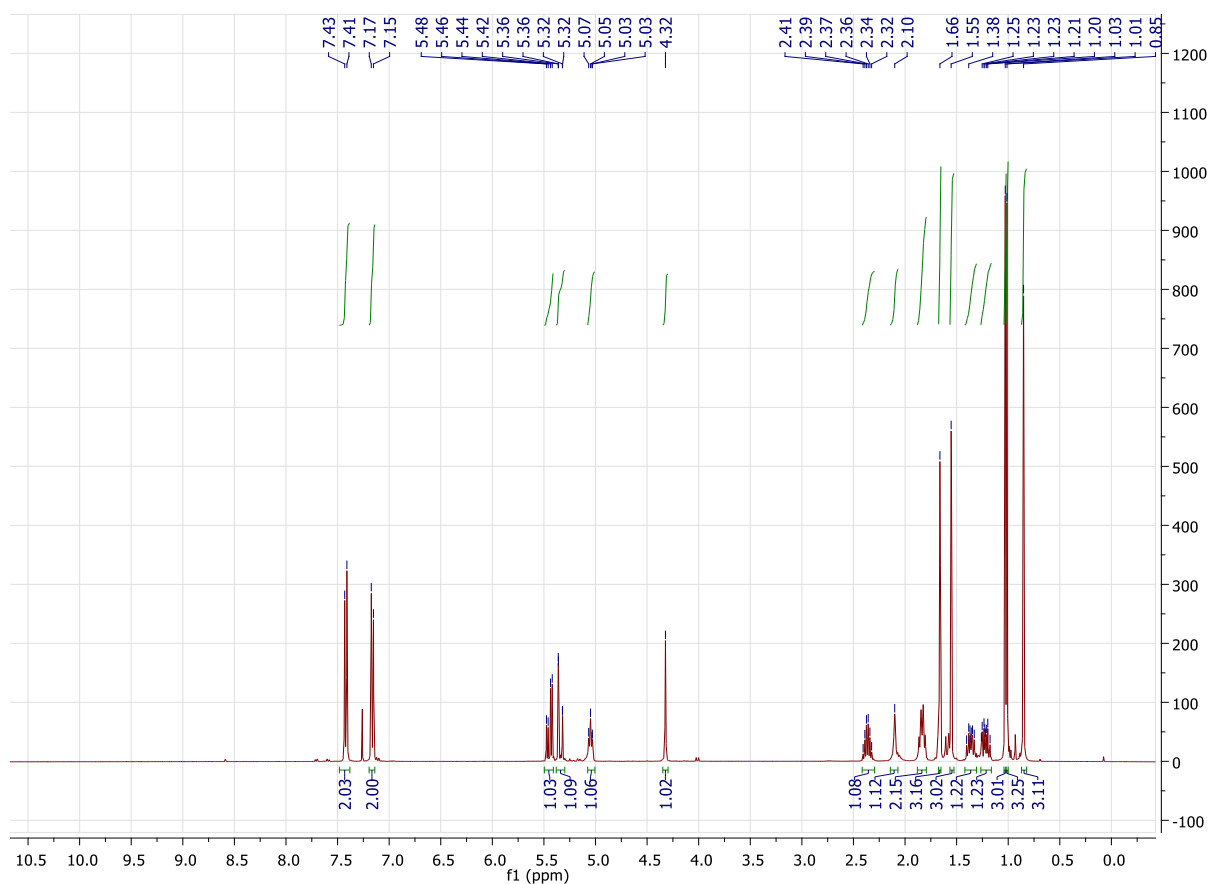
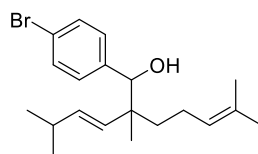


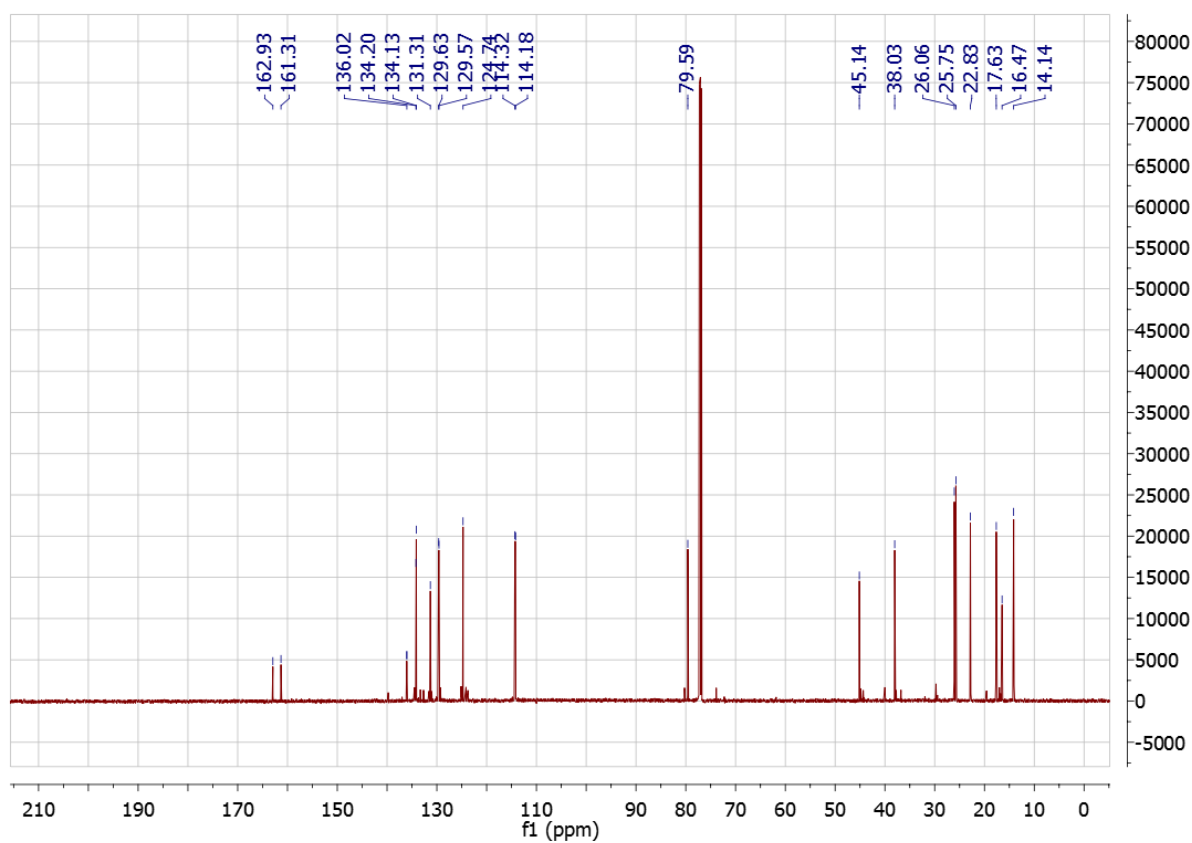
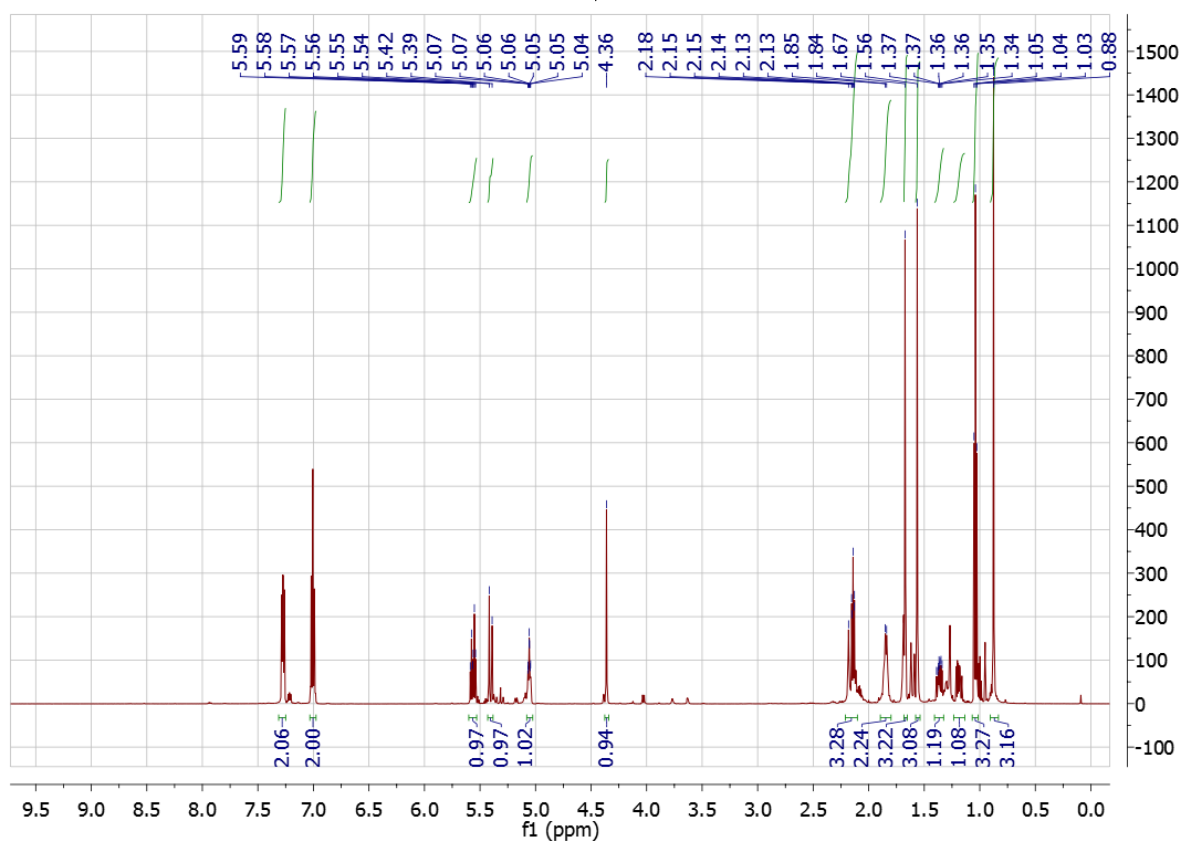
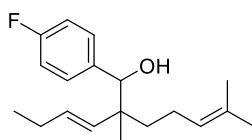


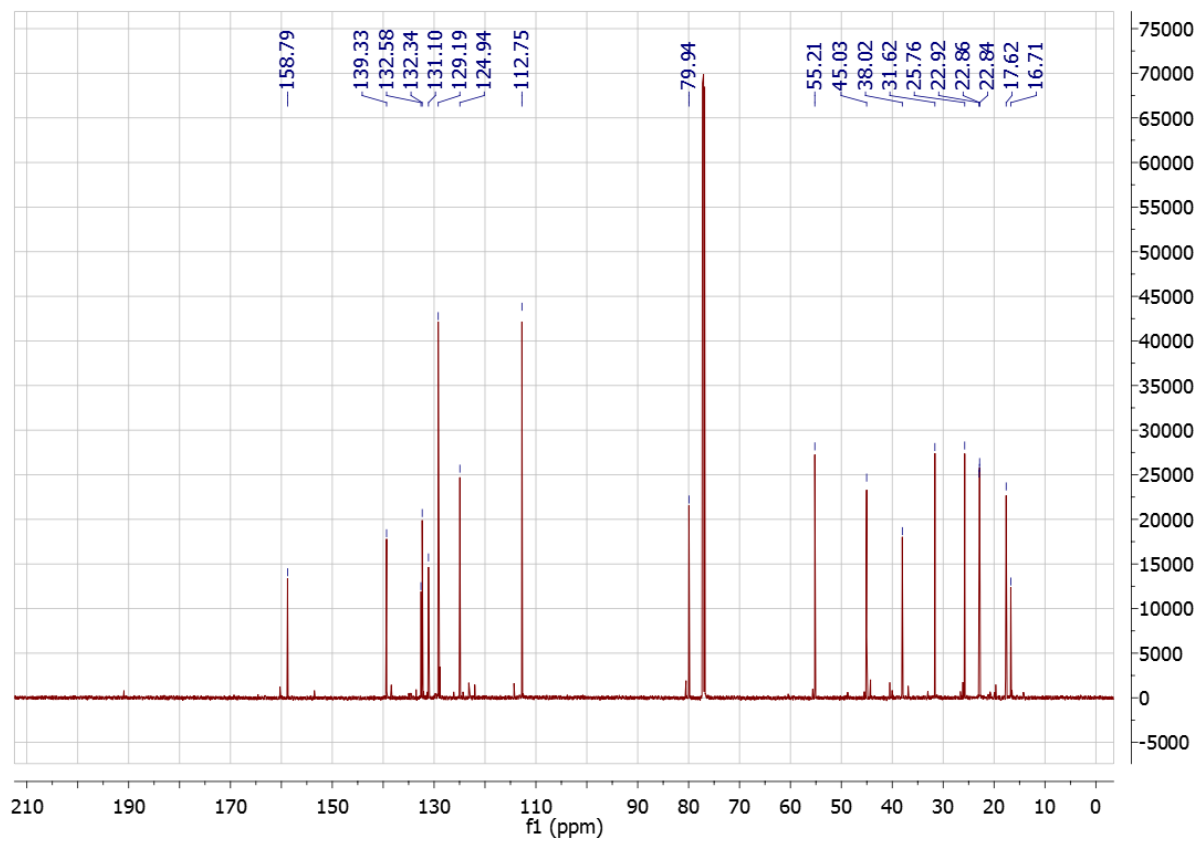
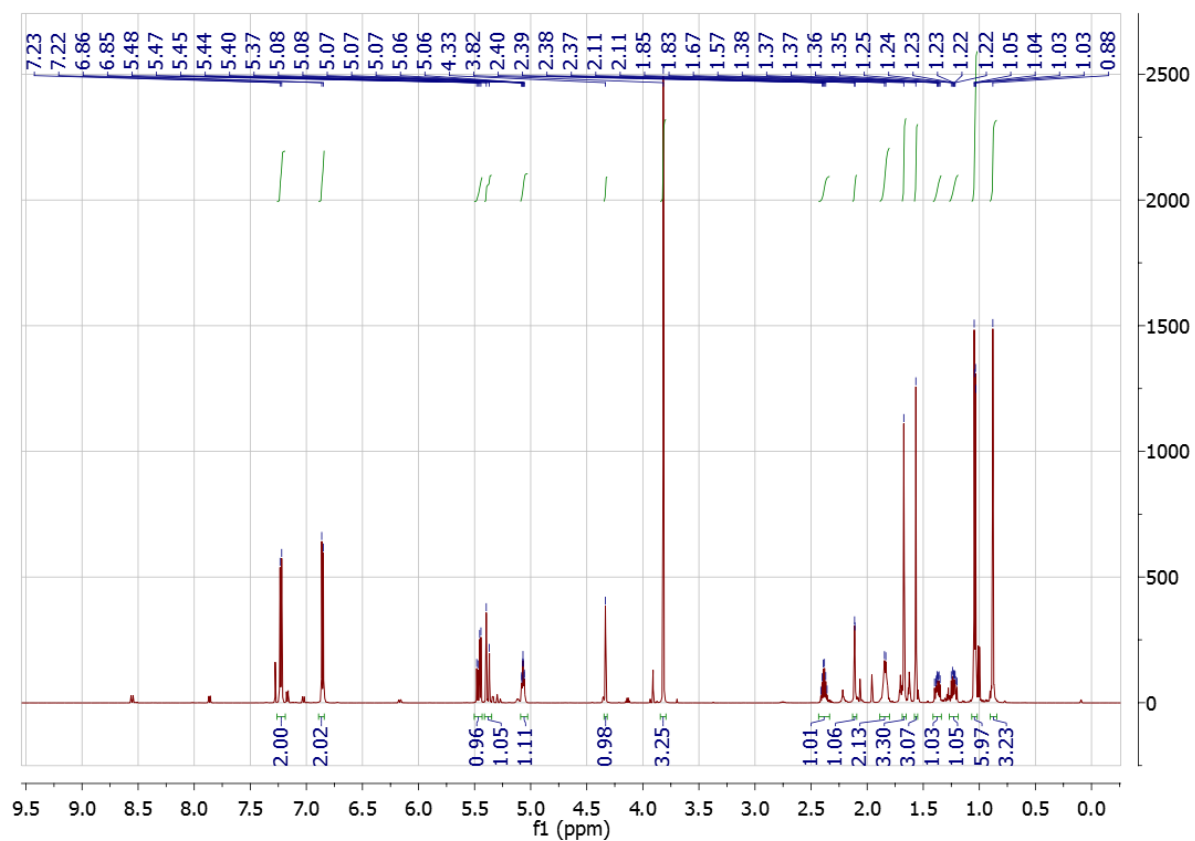
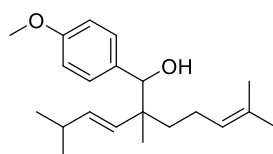


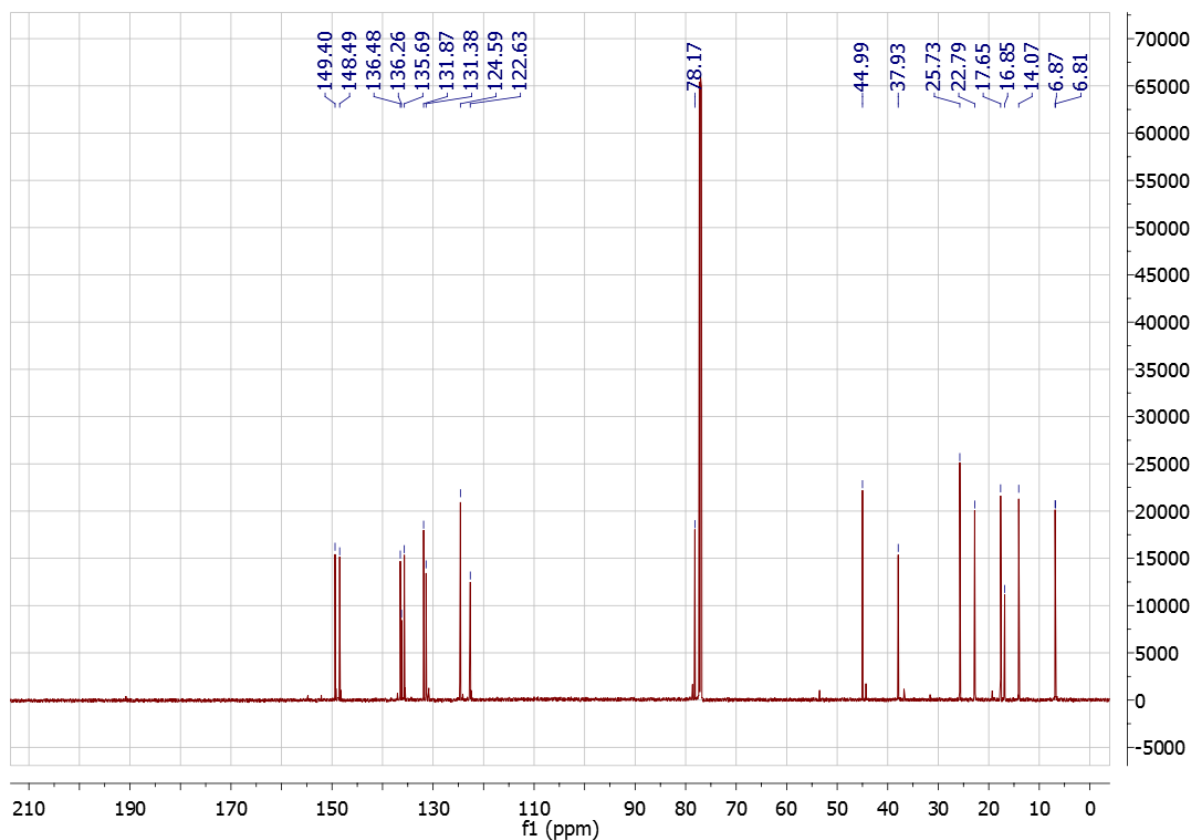
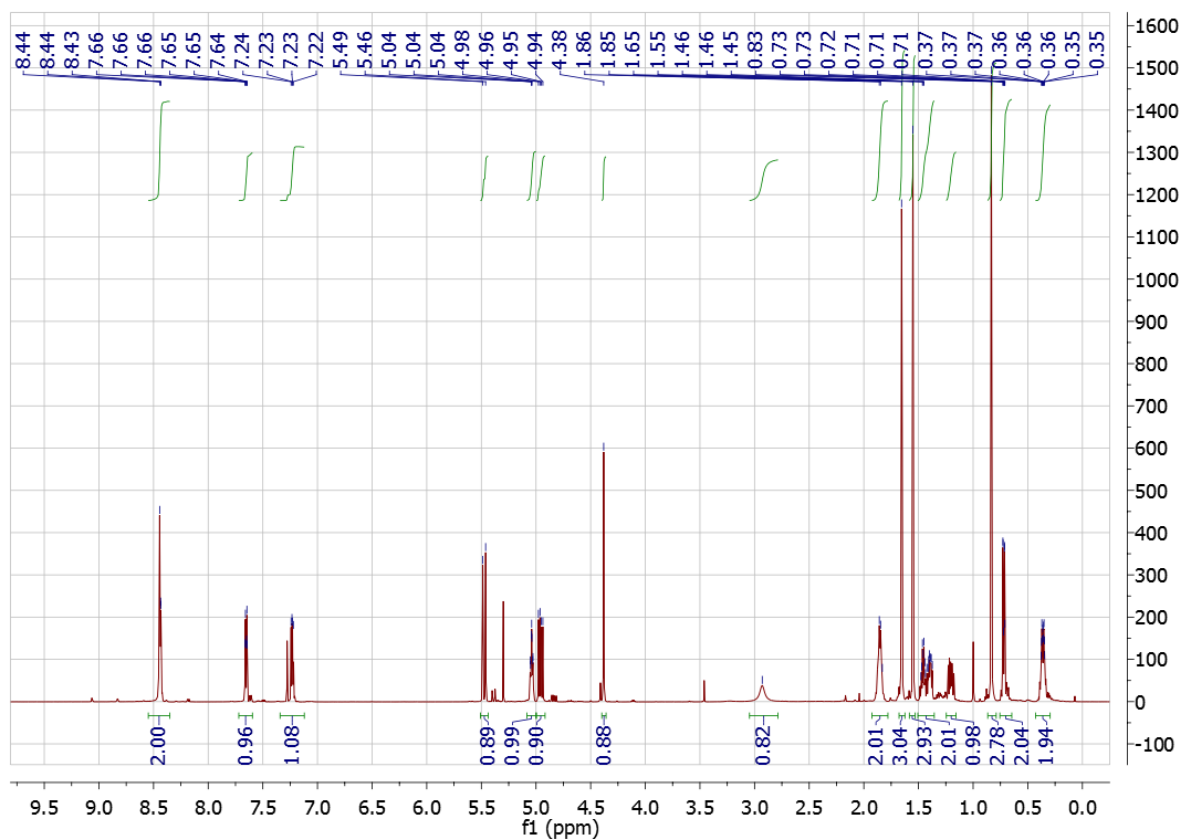
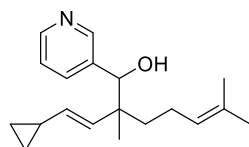


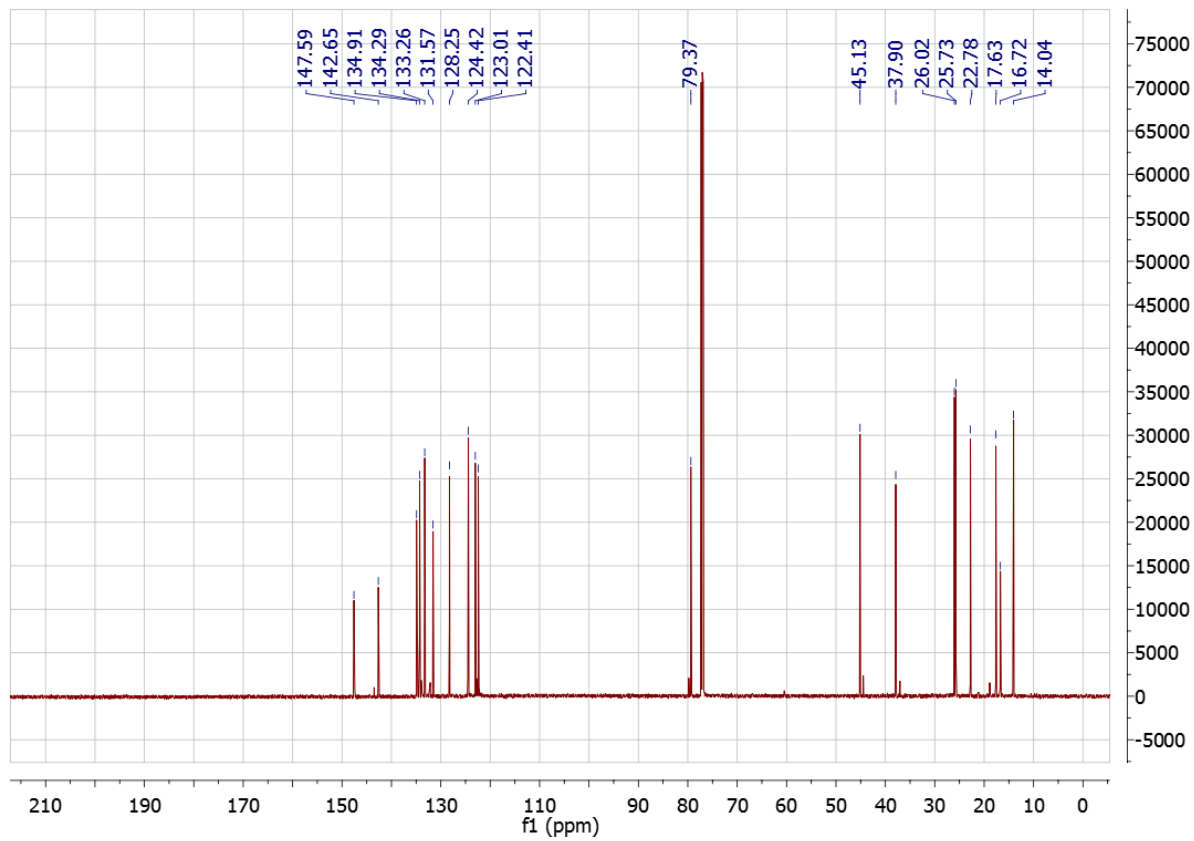
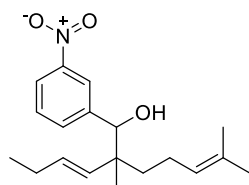


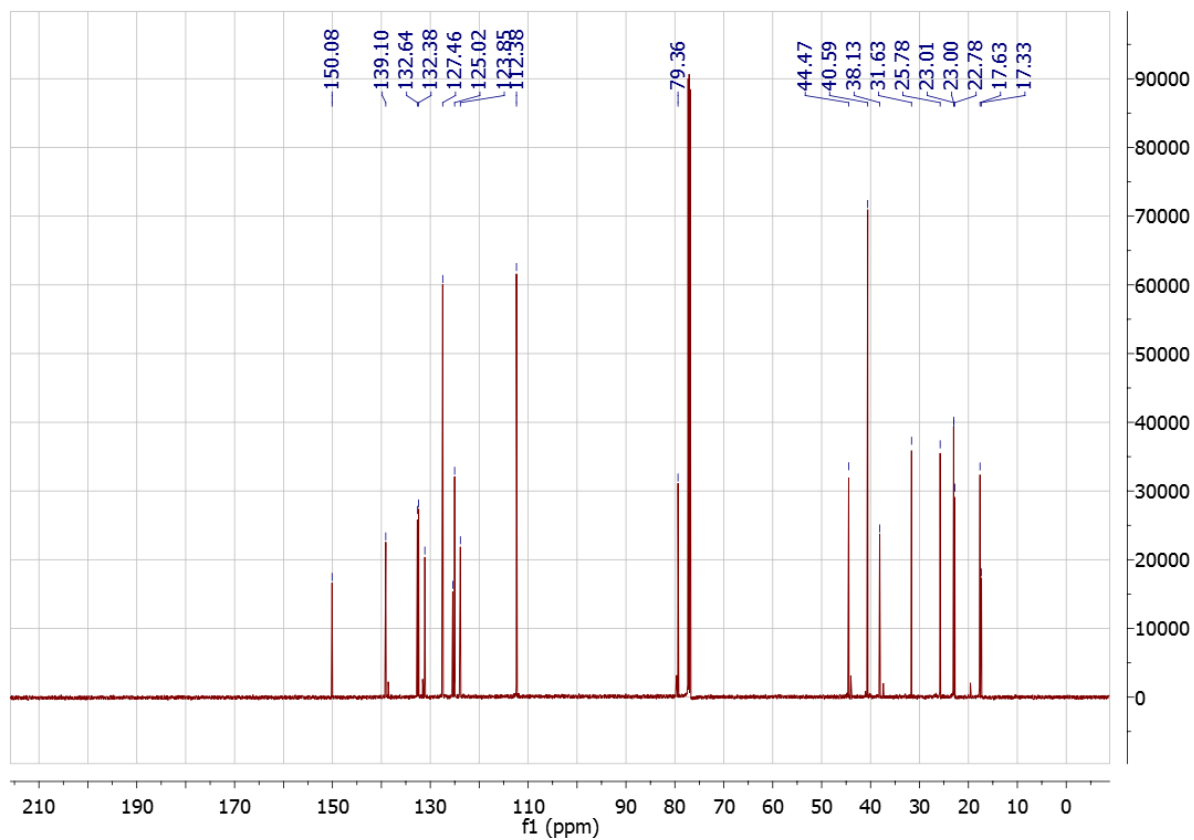
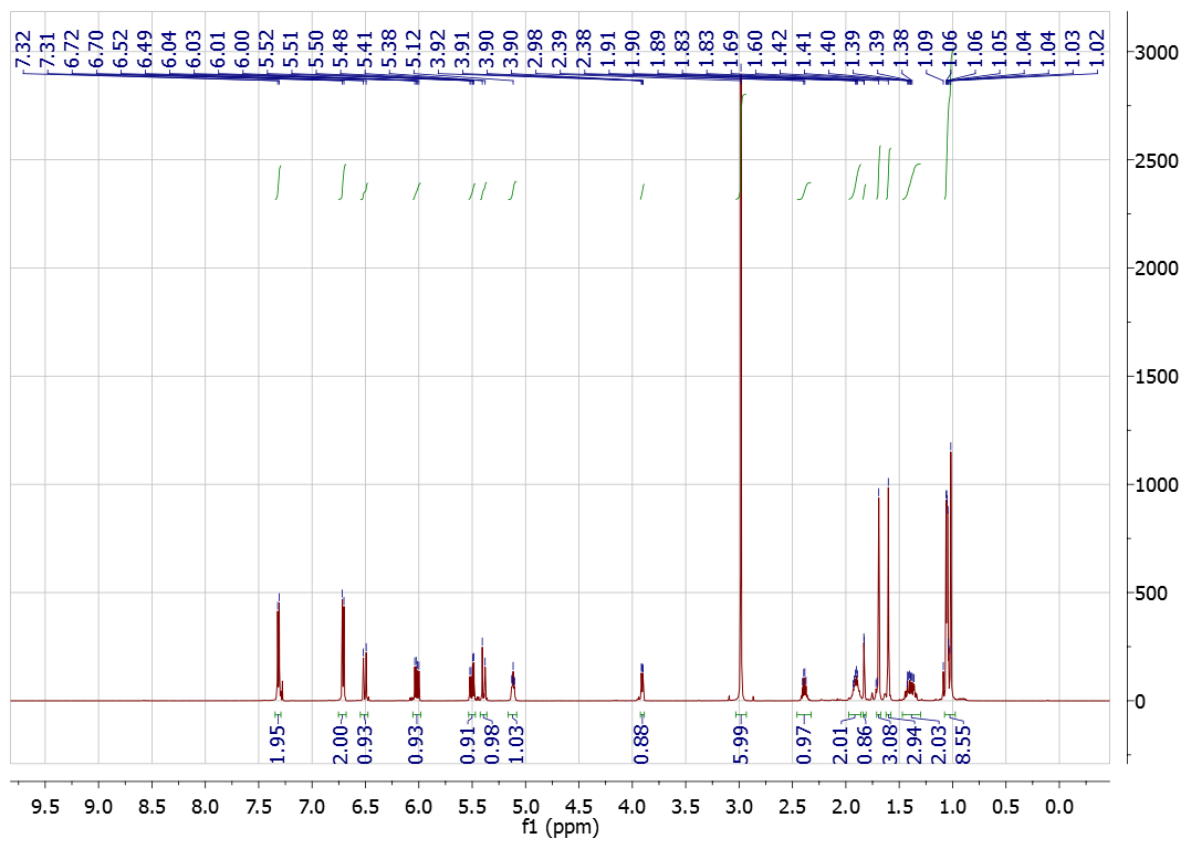
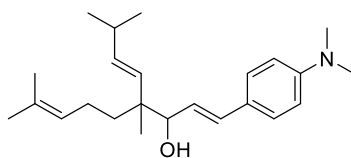


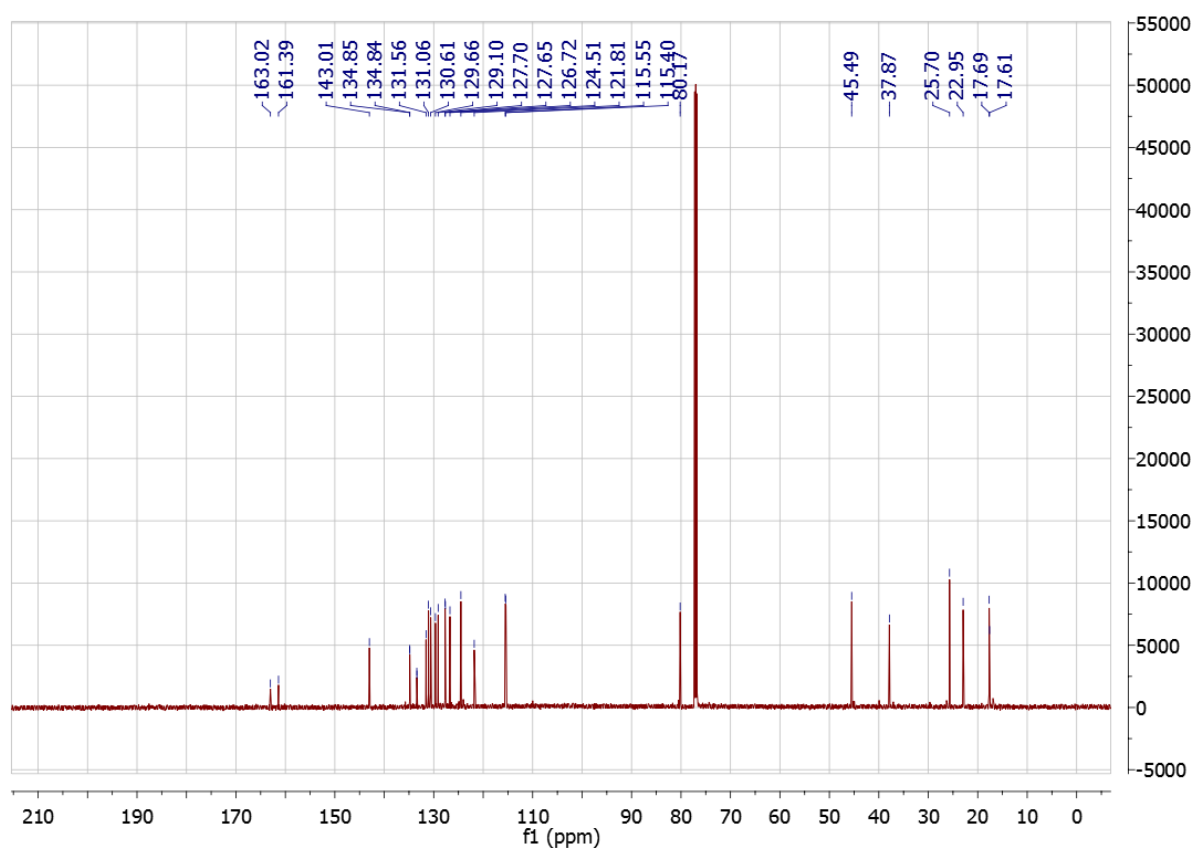
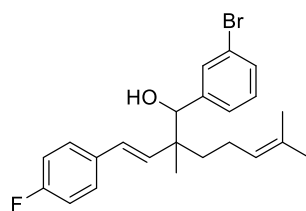


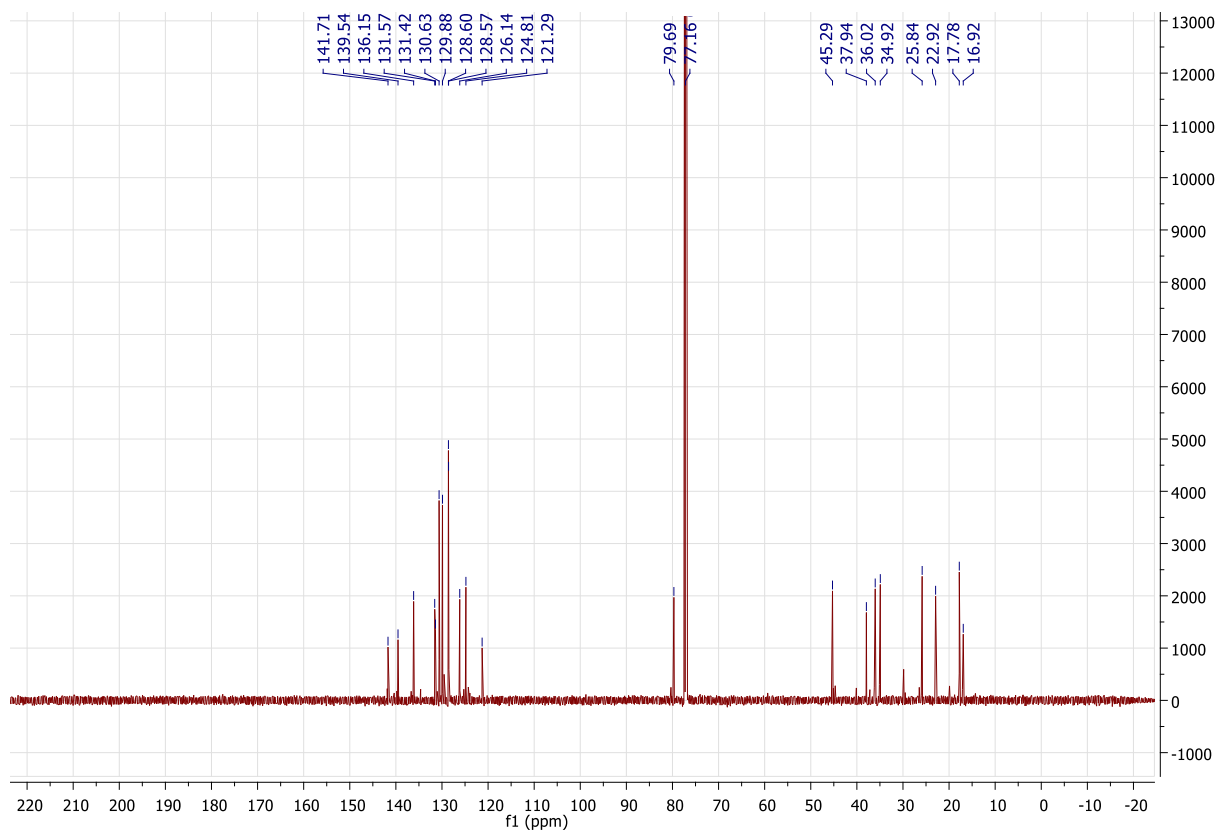
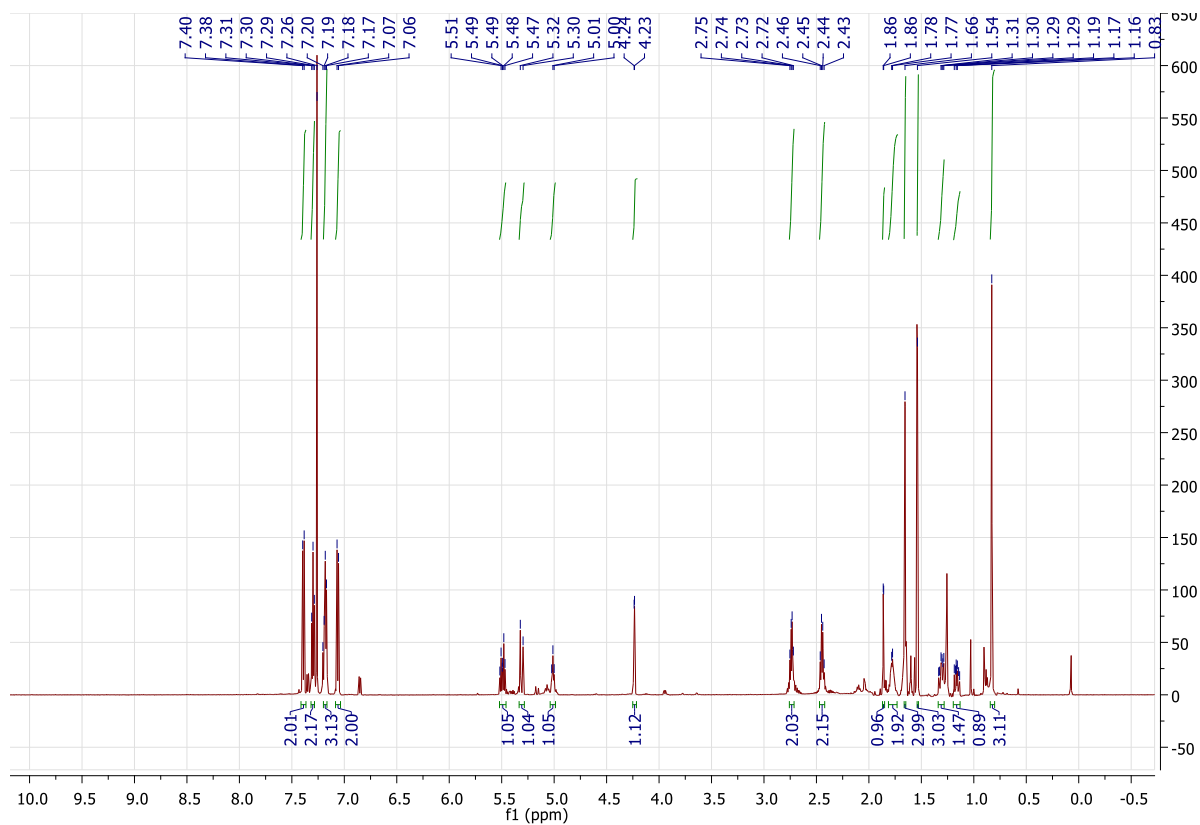
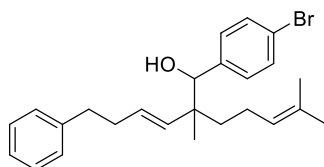


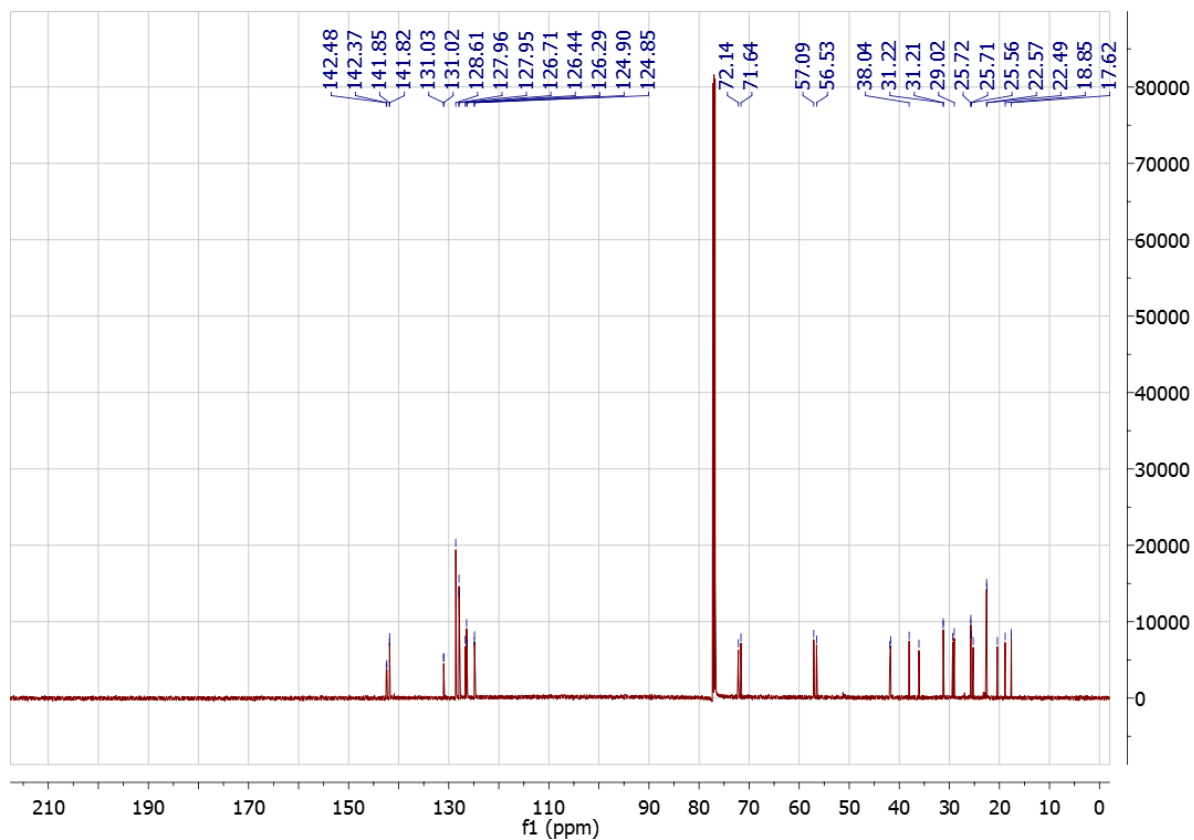


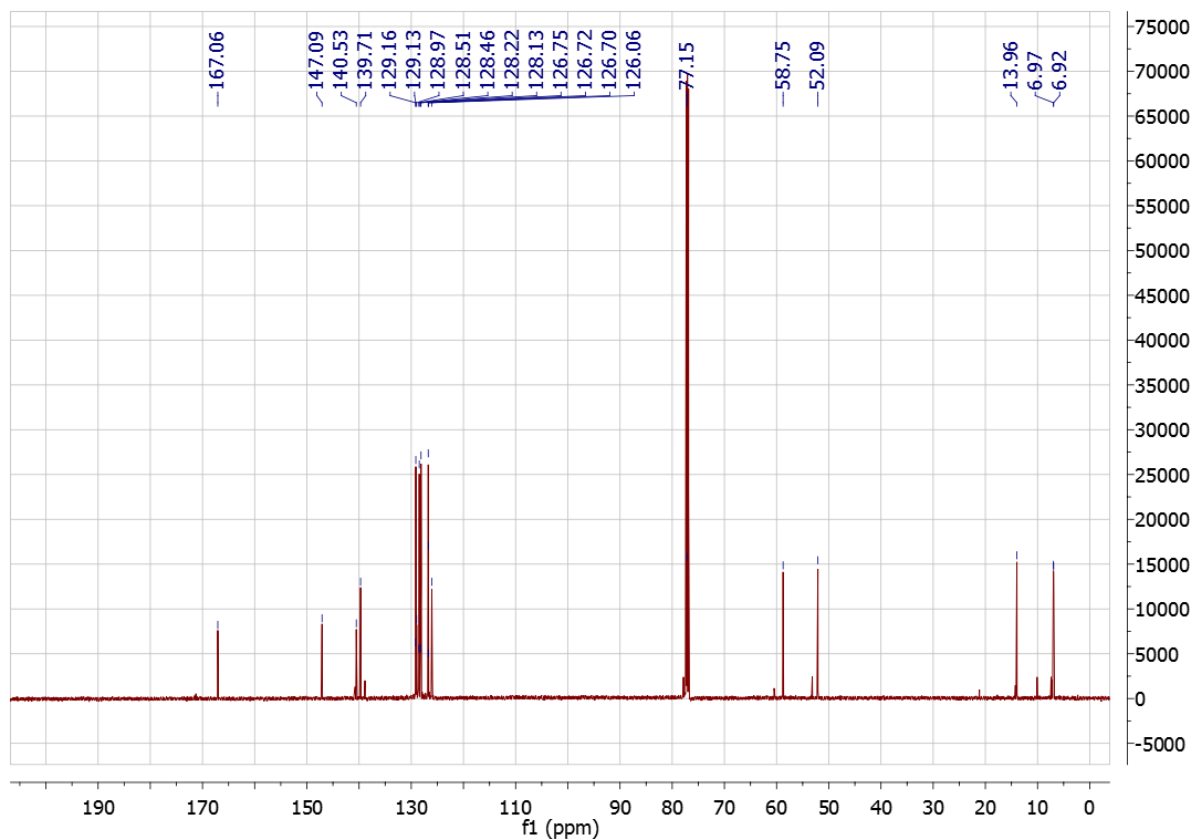
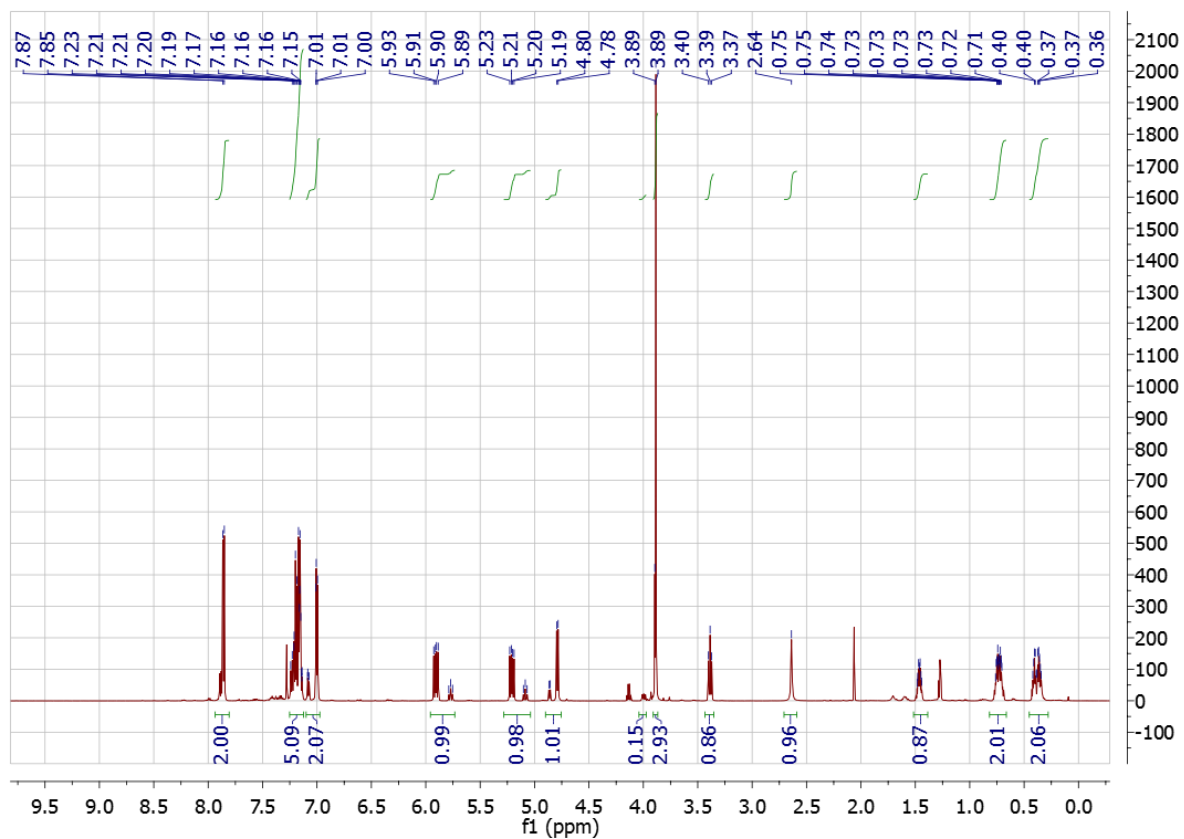
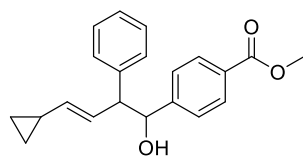


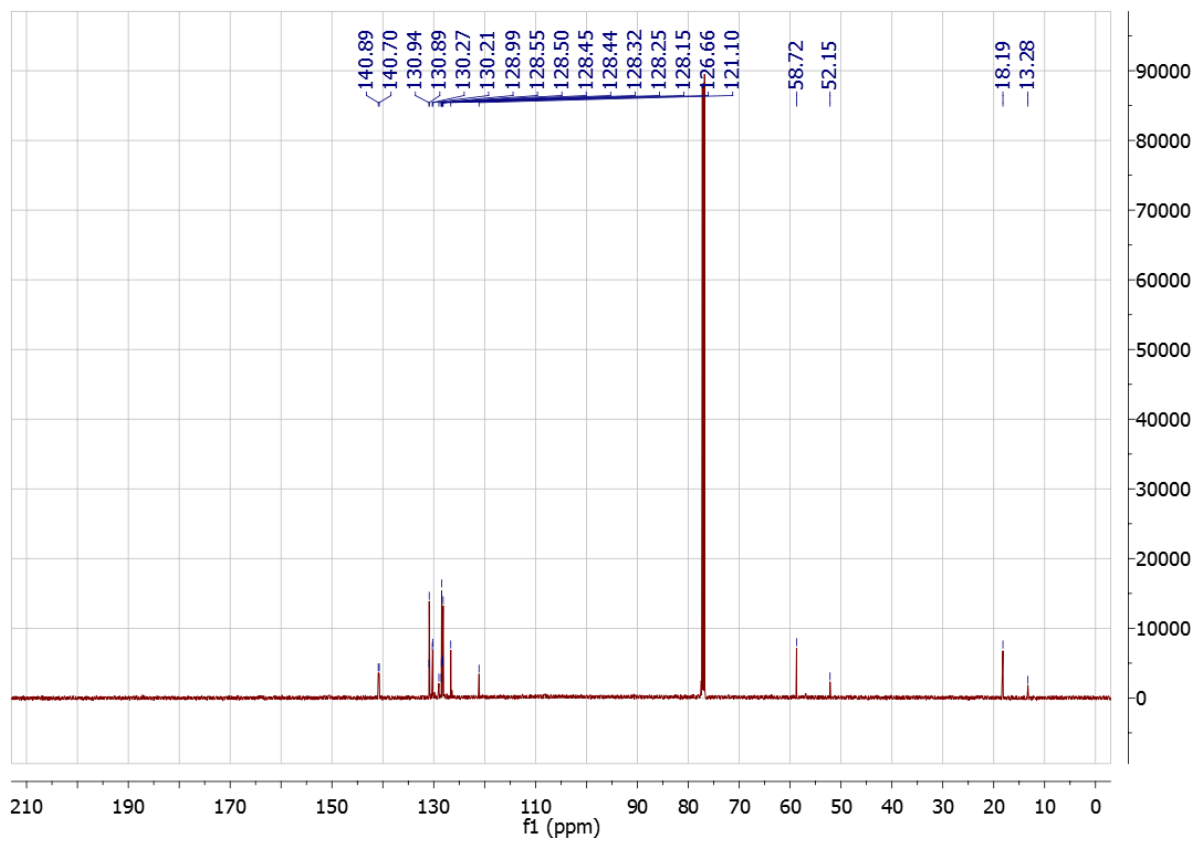
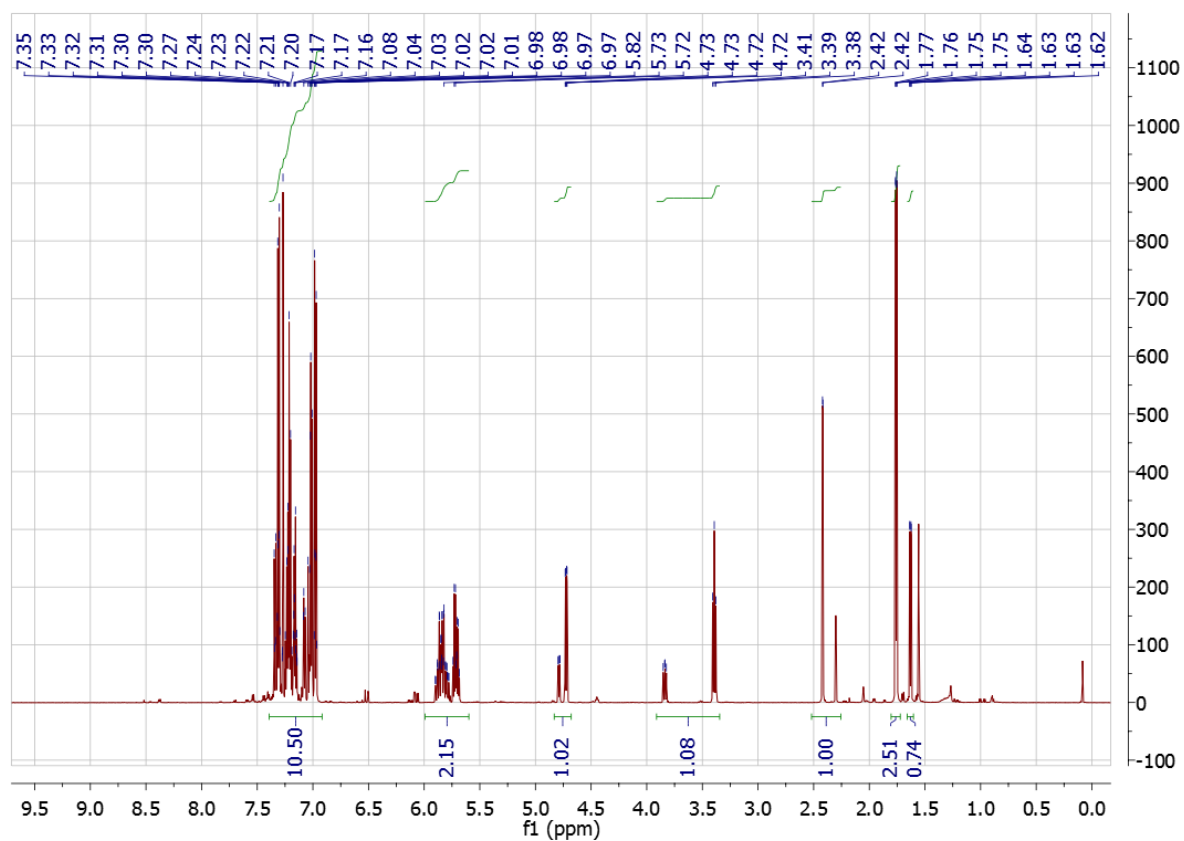
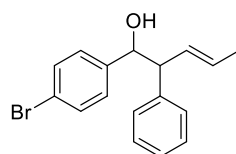


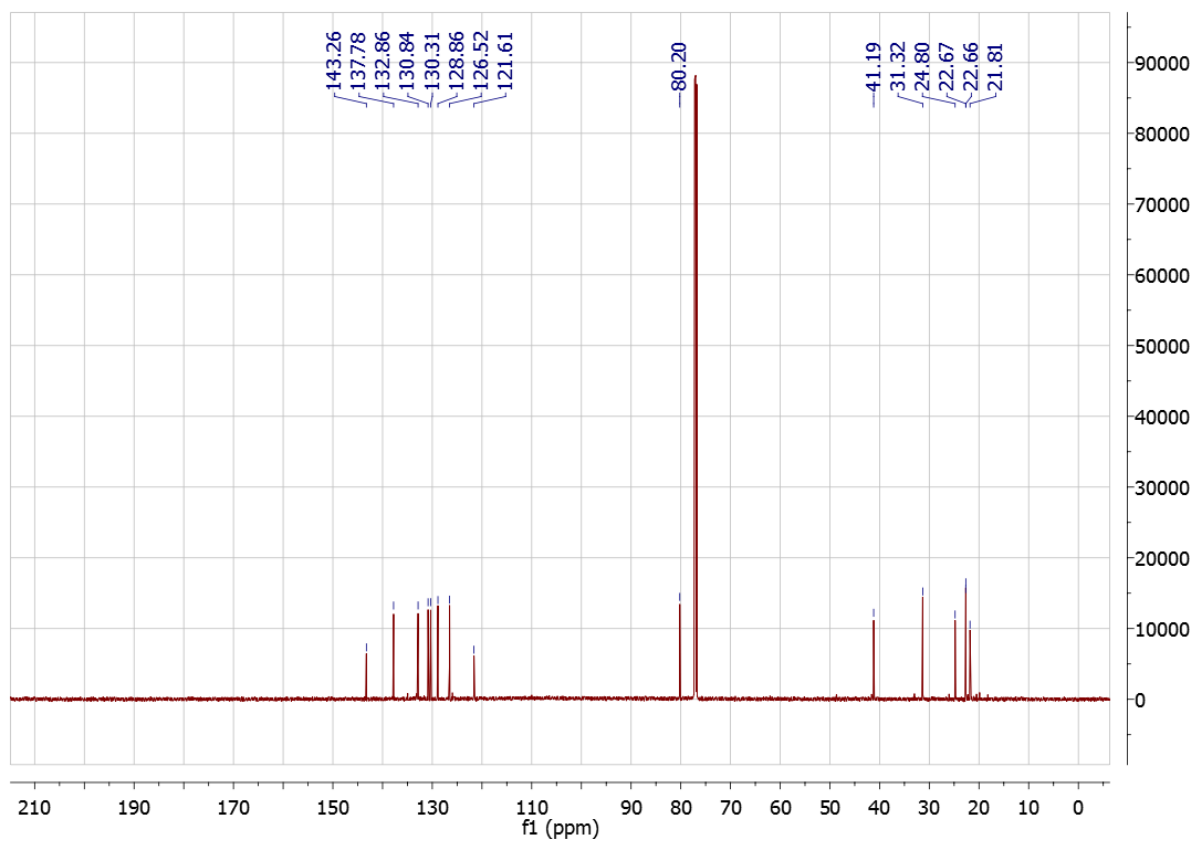
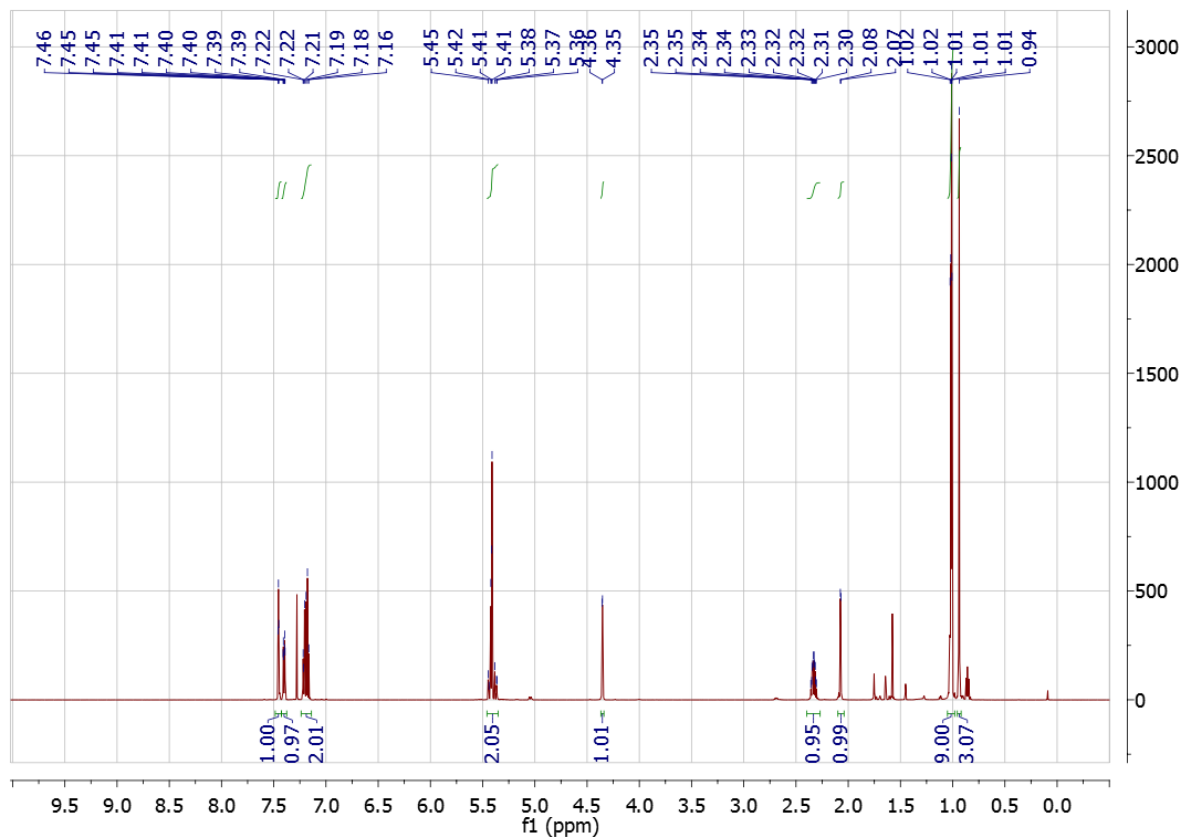
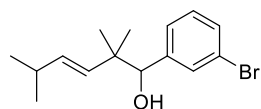


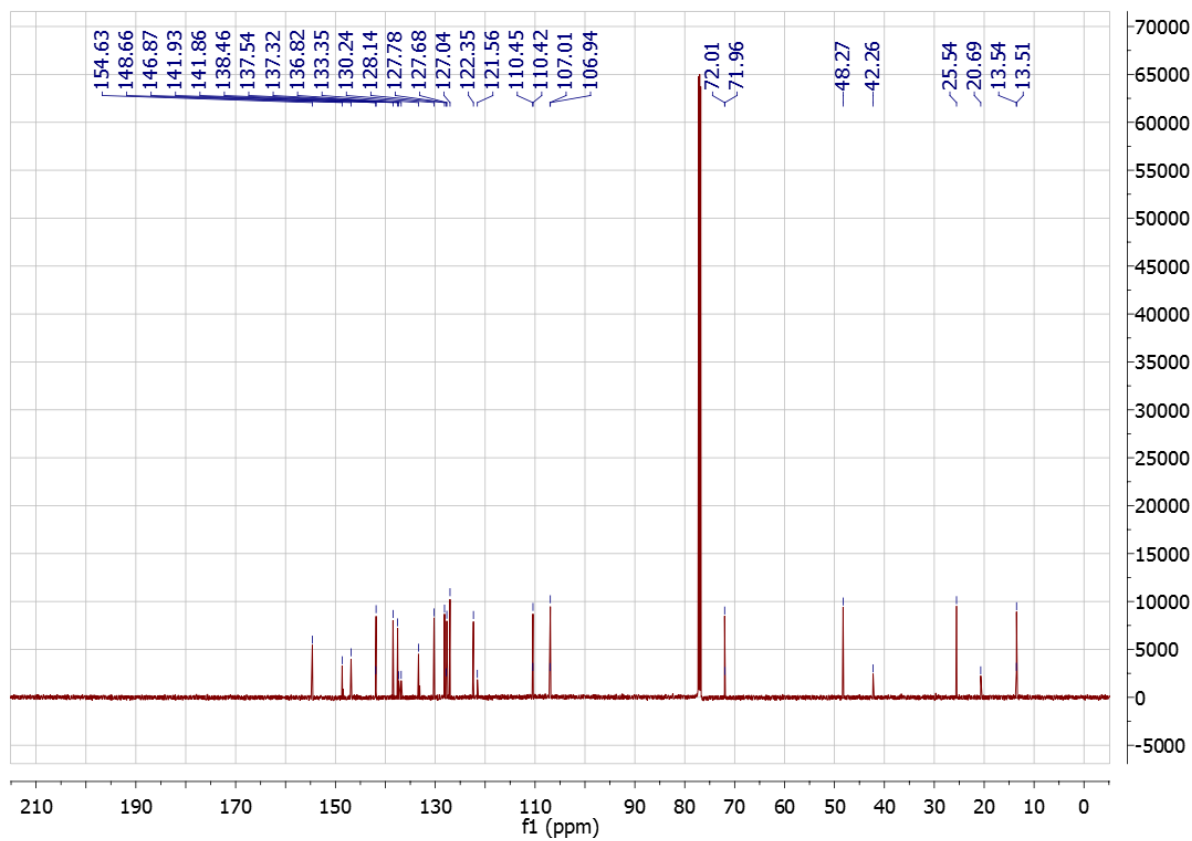
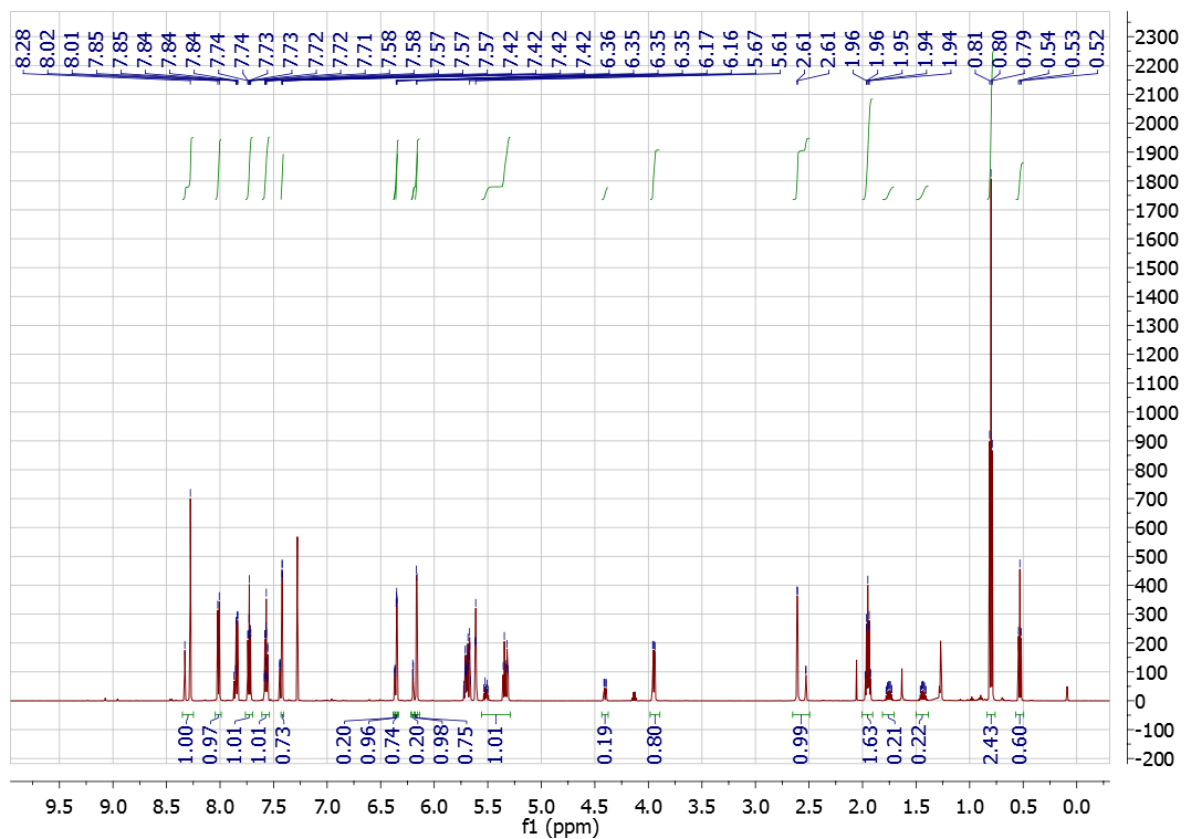
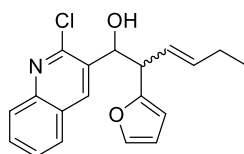


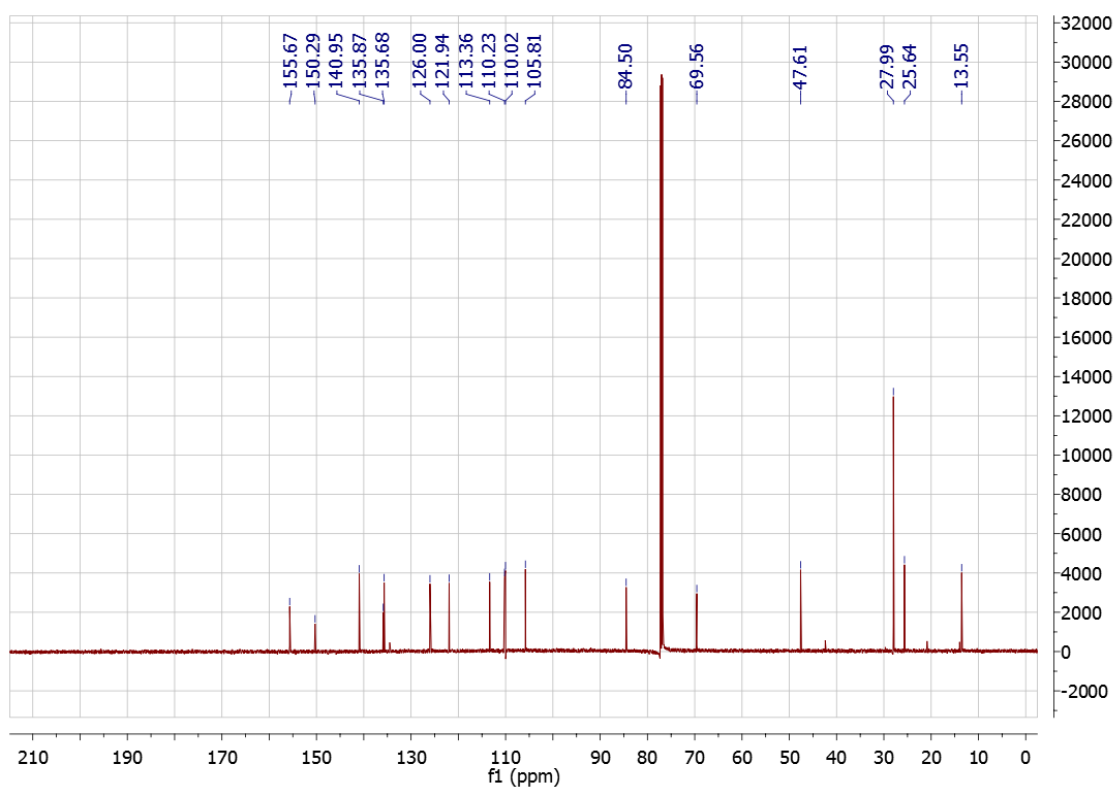
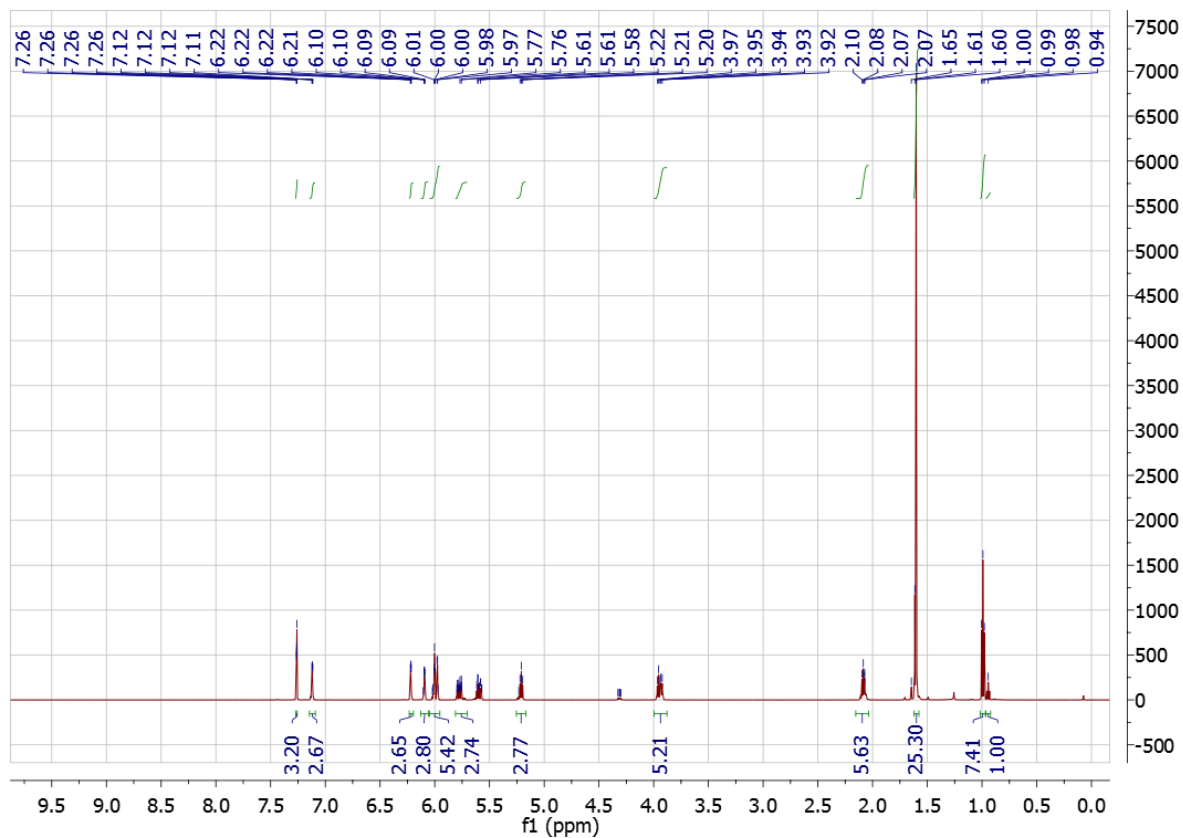
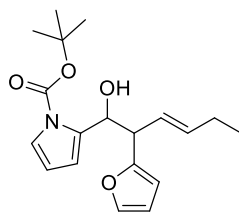


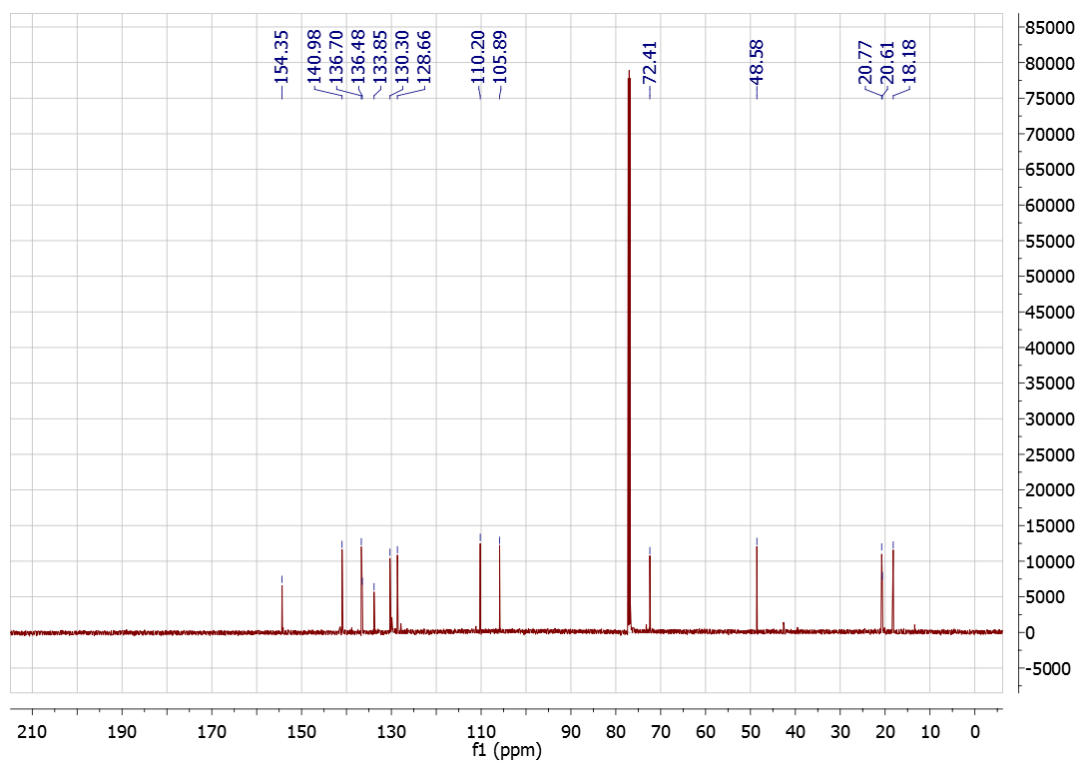
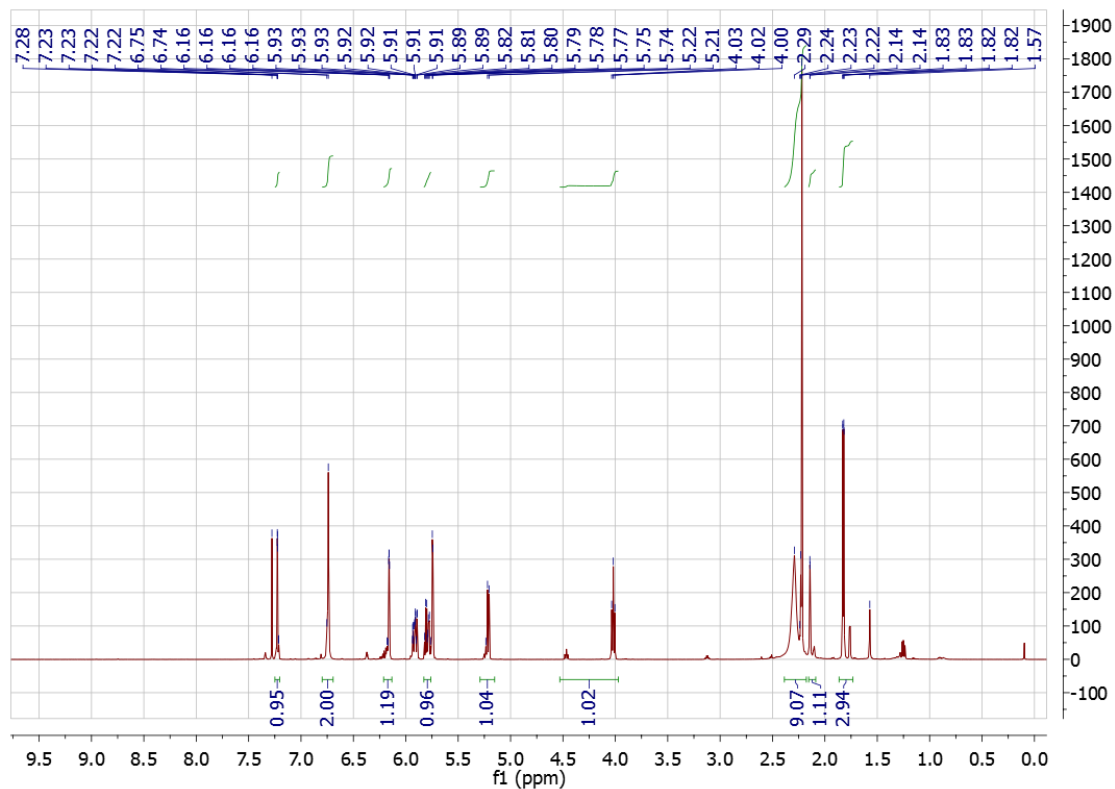


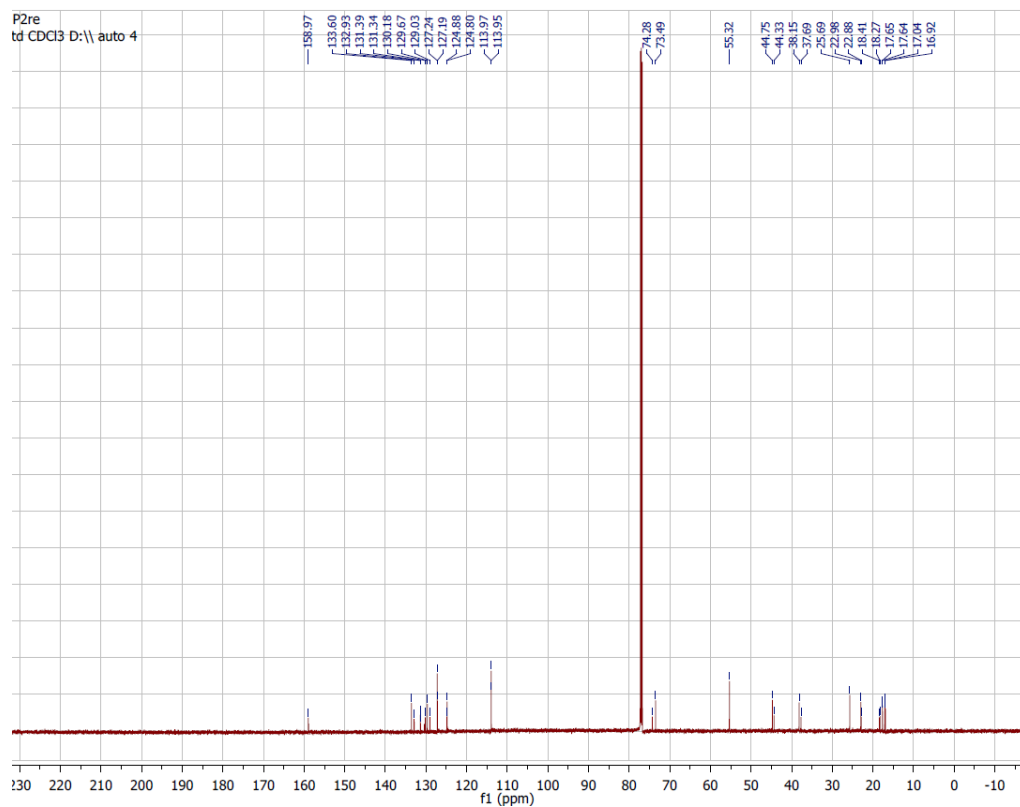
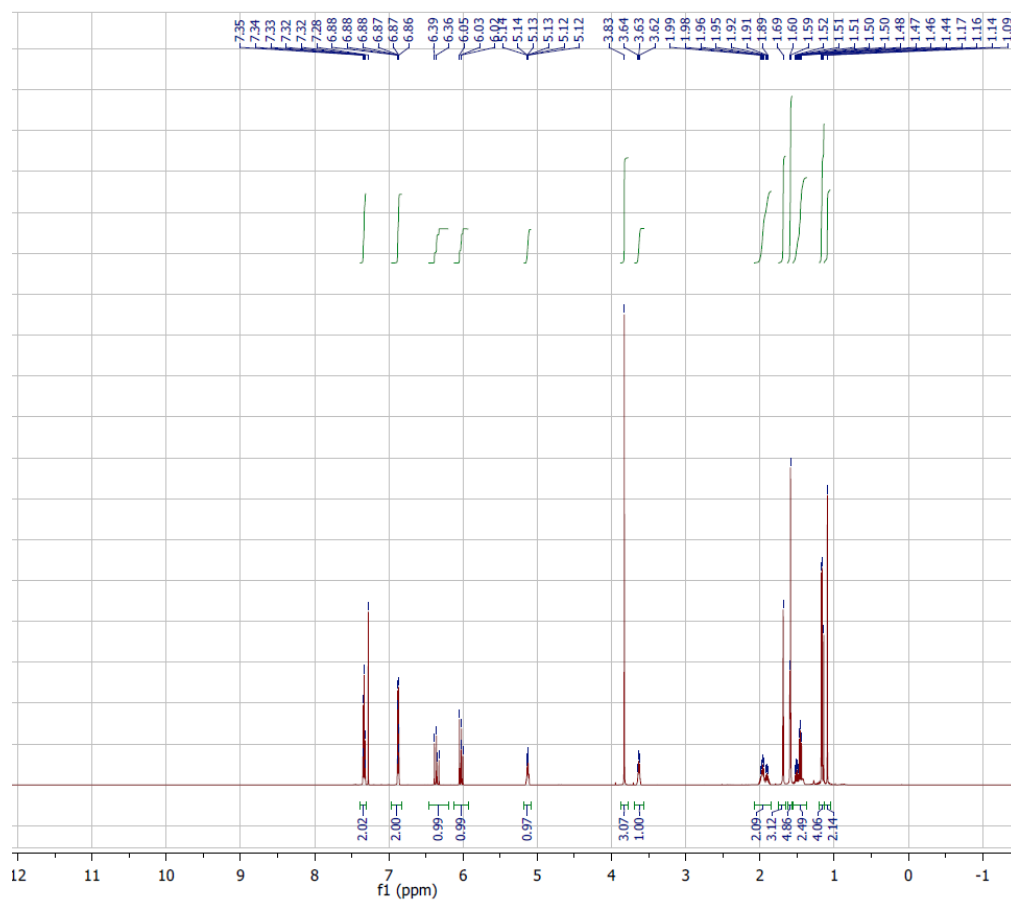
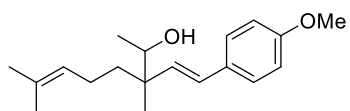


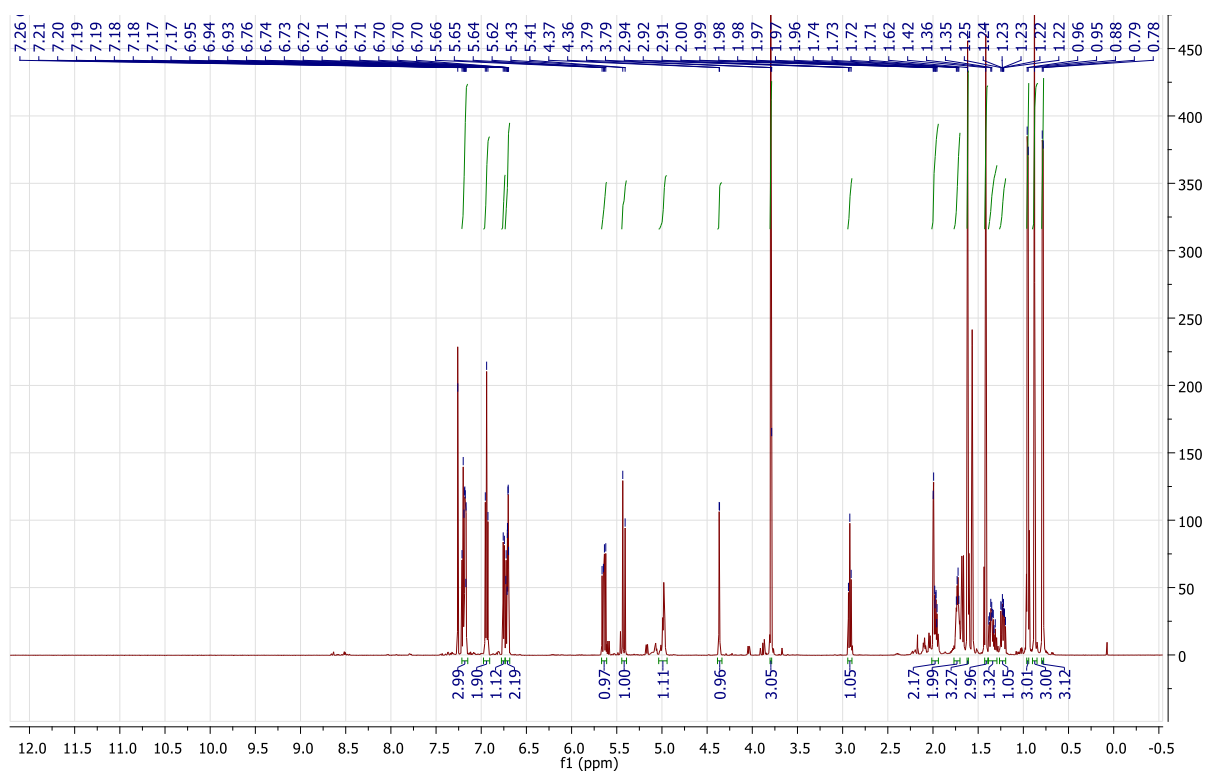


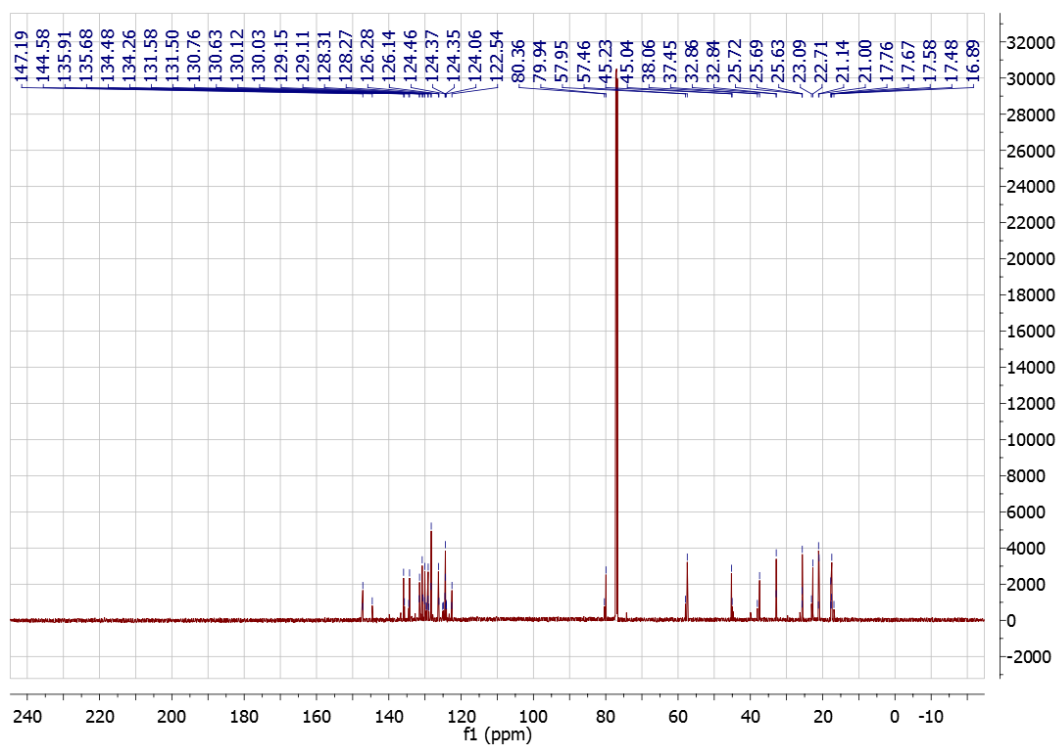
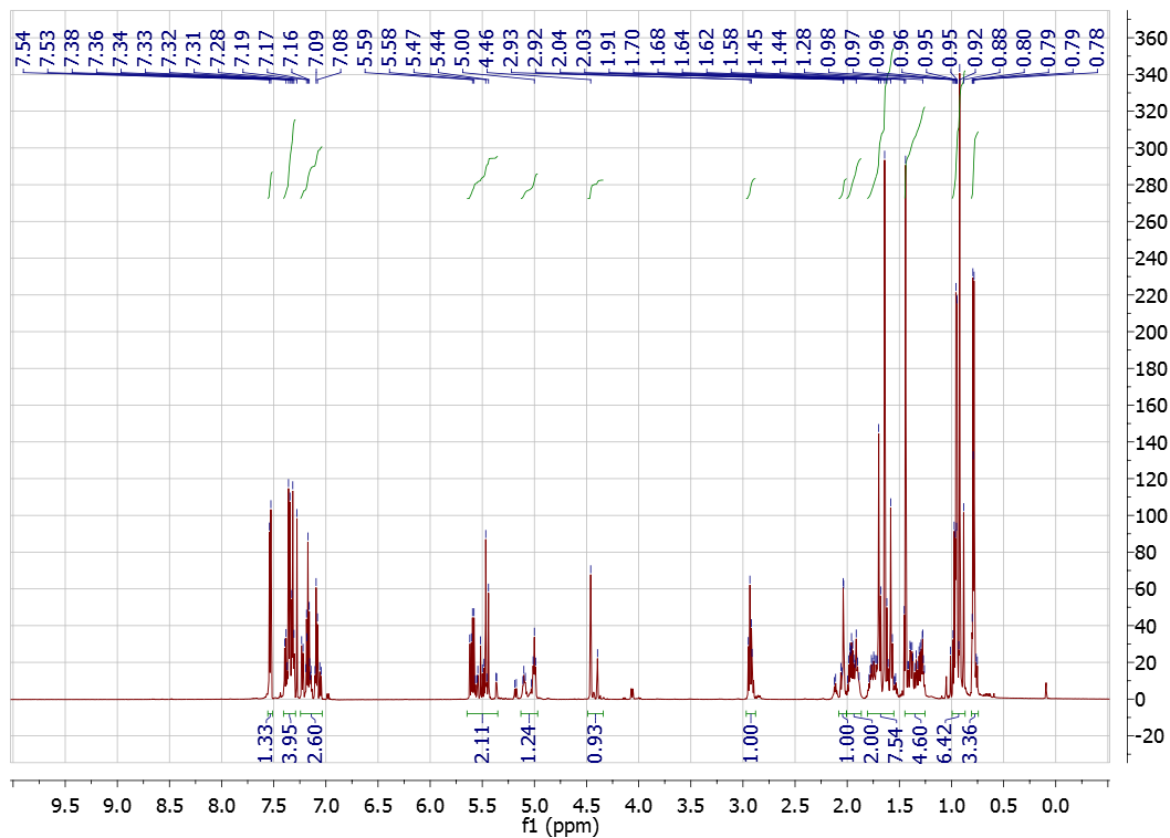
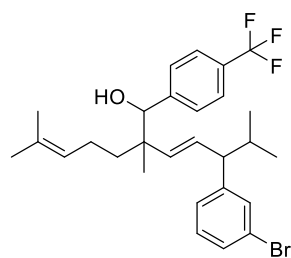


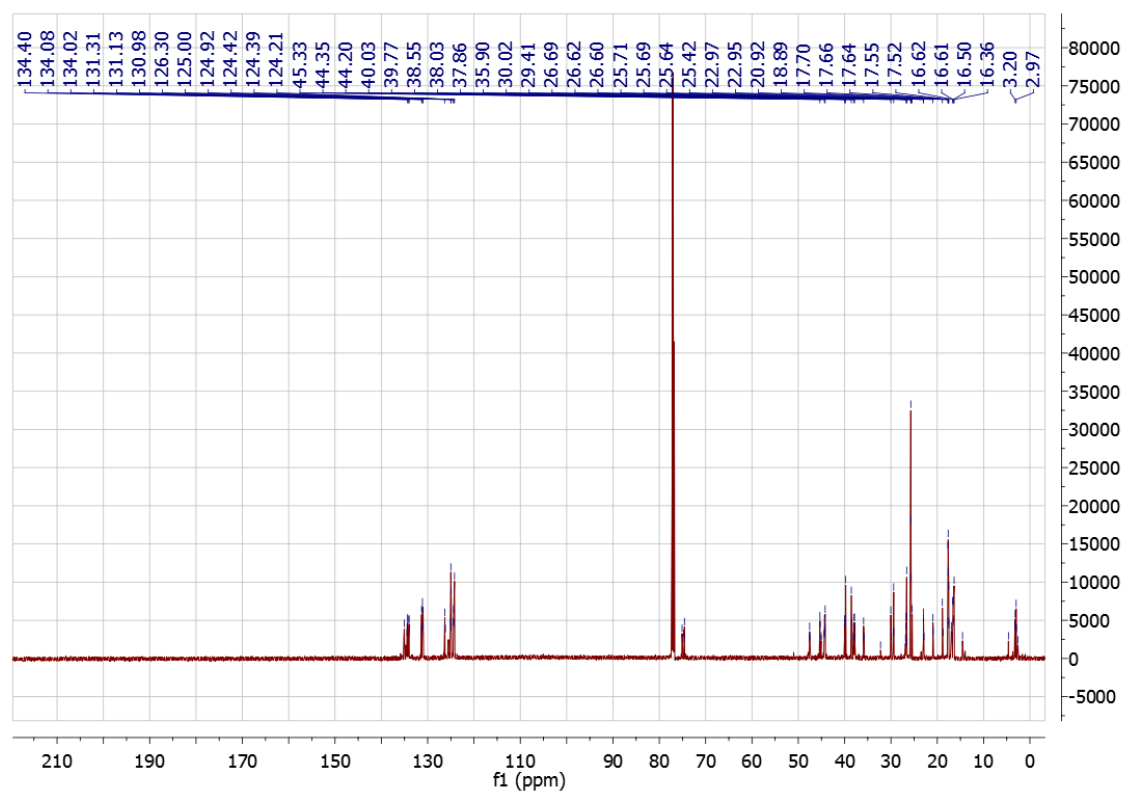












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1. For information about the Vapourtec R2+R4 platform, see:
<http://www.vapourtec.co.uk/>
2. For information about the Mettler Toledo FlowIR[®], see:
http://uk.mt.com/gb/en/home/products/L1_AutochemProducts/ReactIR/flow-ir-chemis.html
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