Electronic Supplementary Information for

Synthesis of substituted benzylboronates by light promoted homologation of boronic acids with *N*-sulfonylhydrazones

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Abstract: The synthesis of benzylboronates by photochemical homologation of boronic acids with *N*-sulfonylhydrazones under basic conditions is described. The reaction involves the photolysis of the *N*-tosylhydrazone salt to give a diazoalkane followed by the geminal carboborylation of the diazoalkane. Under the mild reaction conditions, the protodeboronation of the unstable benzylboronic acid is circumvented and the pinacolboronates can be isolated after reaction of the benzylboronic acid with pinacol. The metholodogy has been applied to the reactions of alkylboronic acids with *N*-tosylhydrazones of aromatic aldehydes and ketones, and to the reactions of arylboronic acids with *N*-tosylhydrazones of aliphatic ketones. Moreover, the employment of the DBU/DIPEA bases combination allows for homogeneous reactions which have been adapted to photochemical continuous flow conditions. Additionally, the synthetic versatility of boronates enables their further transformation via Csp^3-C or Csp^3-X bond forming reactions converting this methodology into a novel method for the geminal difunctionalization of carbonyls via *N*-tosylhydrazones.

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1. Experimental Procedures

1.1 General Considerations

Photochemical reactions in batch were performed in 5 mL glass vials sealed with a septum, under argon atmosphere. The specific reaction time corresponds to the total reaction time. A Kessil® PR160 Rig equipped with different lamps (PR160-370 nm, PR160-390 nm, PR160-427 nm) a cooling fan and a magnetic stirrer was used as the photochemistry setup. A PR time controller was additionally used to select the irradiation time. 5 mL glass vials purchased in VWR® were used to run the photochemical reactions. The vials were sealed with the septum after adding the chemicals and solvent and placed at a distance of 5 cm away from the lamp prior to irradiation at the proper intensity of the Kessil lamp (section 1.3, figure S2). Relevant photophysical properties of the Kessil® PR160L lamps are available at https://kessil.com/products/science_PR160L.php. The description of the setup of the continuous flow setup is described in section 1.4.

All the solvents were dried using the corresponding procedures described in D. Perrin, Purification of Laboratory Chemicals, Pergamon Press Ltd. 1980, 2nd Ed.

NMR spectra were recorded in $CDCl_3$ 600, 300 MHz for ^{1}H and 150 or 75 MHz for ^{13}C with the residual solvent signals as standard. ^{11}B NMR were recorded at 129 MHz and processed employing Whitaker base line correction as implemented in MestReNova 14.0. The data in the ^{1}H NMR spectra is being reported as s = singlet, bs= broad singlet, d = doublet, dd = double doblet, t = triplet, dt = double triplet, ddt = double double triplet, tt = triple triplet, q = quartet, p = pentuplet, qd = quartet of doublets and so on, m = multiplet or unresolved, chemical shifts in ppm and coupling constant(s) in Hz. The assignment of the ^{13}C NMR spectra have been carried out by means of DEPT-135 experiments. ^{13}C signals corresponding to carbon atoms adjacent to boron are generally not observed due to quadrupolar relaxation. HRMS were measured in ESI or APCI mode, with a TOF mass analyser (Bruker model Impact II). *N*-

sulfonylhydrazones were prepared from the corresponding carbonyl compounds through previously described standard methodologies.[1]

1.2 Synthesis and characterization data for *N*-sulfonylhydrazones.

The *N*-sulfonylhydrazones **H** employed in this work (figure S1) were prepared from the corresponding carbonyl compounds following the standard procedure described below unless otherwise indicated. See appropriate references for previously reported *N*-tosylhydrazones: (**H1**, **H4**)[1]; (**H2**, **H3**)[2], (**H5**, **H8**)[3] (**H6**)[4] (**H7**)[5] (**H9**)[6] (**H10**)[7] (**H15**)[8] (**H16**)[9] (**H17**, **H18**, **H21**, **H22**, **H24**, **H26**, **H27**, **H31**, **H36**, **H39**, **H40**)[10] **H19**[11] (**H20**, **H34**)[12] **H23**[13] **H25**[14] (**H28**, **H32**, **H33**)[15] **H29**[16] **H30**[17] **H37.**[18]

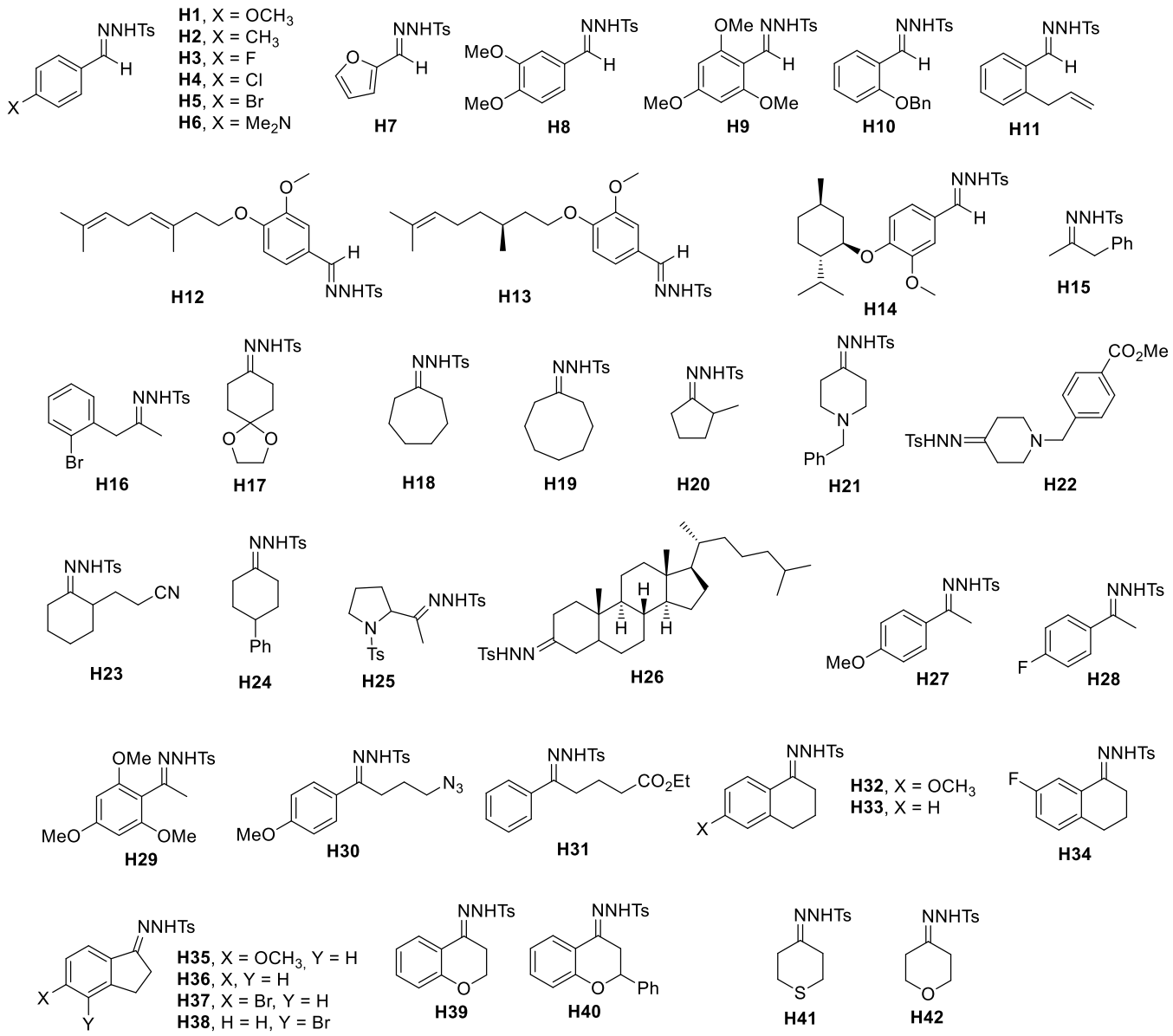


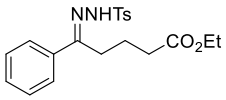
Figure S1: *N*-sulfonylhydrazones employed in the paper.

1.2.1 General procedure for the synthesis of *N*-sulfonylhydrazones

To a stirred solution of the aldehyde or ketone (2 mmol) in 2 mL of MeOH was added the *N*-sulfonylhydrazide (1.1 equiv). The mixture is stirred overnight at room temperature. The white solid formed is dried under vacuum. The *N*-sulfonylhydrazones can be used without further purification, otherwise can be purified by crystallization or flash chromatography.

1.2.2 Characterization data for previously undescribed *N*-sulfonylhydrazones

Ethyl 5-phenyl-5-(2-tosylhydrazineylidene)pentanoate H31



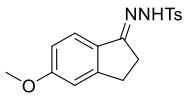
^{1}H NMR (300 MHz, $CDCl_3$) δ = 9.28 (s, 1H), 8.12 – 7.75 (m, 2H), 7.69 – 7.61 (m, 2H), 7.39 – 7.27 (m, 5H), 4.27 (q, *J*=7.2, 2H), 2.70 – 2.56 (m, 2H), 2.40 (s, 3H), 2.34 – 2.22 (m, 2H), 1.75 – 1.55 (m, 2H), 1.31 (t, *J*=7.1, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 174.5 (C), 153.9 (C), 143.8 (C), 136.3 (C), 136.1 (C), 129.6 (CH), 128.5 (CH), 128.0 (CH), 126.3 (CH), 61.4 (CH_2), 32.4 (CH_2), 26.0 (CH_2), 21.7 (CH_3), 21.1 (CH_2), 14.3 (CH_3).

m.p. = 103.9-105.3 ºC.

HRMS [ESI(+)]: *m/z* calcd. for $C_{20}H_{25}N_2SO_4$+H: 389.1530 [M+H]:, found: 389.1529.

***N'*-(5-methoxy-2,3-dihydro-1$_H$-inden-1-ylidene)-4-methylbenzenesulfonohydrazide H35**

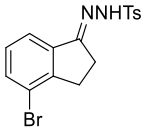


^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.03 – 7.85 (m, 2H), 7.61 (d, *J* = 8.5 Hz, 1H), 7.52 (s, 1H), 7.31 (d, *J* = 8.2 Hz, 2H), 6.80 (dd, *J* = 8.5, 2.4 Hz, 1H), 6.75 (d, *J* = 2.3 Hz, 1H), 3.80 (s, 3H), 3.10 – 2.92 (m, 2H), 2.74 – 2.59 (m, 2H), 2.40 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 162.6 (C), 150.8 (C), 144.1 (C), 135.6 (C), 129,8 (C), 129.6 (CH), 128.2 (CH), 123.5 (CH), 114.7 (CH), 109.4 (CH), 55.6 (CH_3), 28.6 (CH_2), 27.2 (CH_2), 21.7 (CH_3).

HRMS [ESI(+)]: *m/z* calcd. for $C_{17}H_{19}N_2SO_4$+H: 331.1111 [M+H], found: 389.1105.

***N'*-(4-fluoro-2,3-dihydro-1*H*-inden-1-ylidene)-4-methylbenzenesulfonohydrazide H38**



^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.90 (d, *J*=8.1, 2H), 7.66 (d, *J*=7.7, 1H), 7.50 (d, *J*=7.8, 1H), 7.32 (d, *J*=8.5, 2H), 7.15 (t, *J*=7.7, 1H), 3.12 – 2.99 (m, 2H), 2.71 – 2.60 (m, 2H), 2.41 (s, 3H).

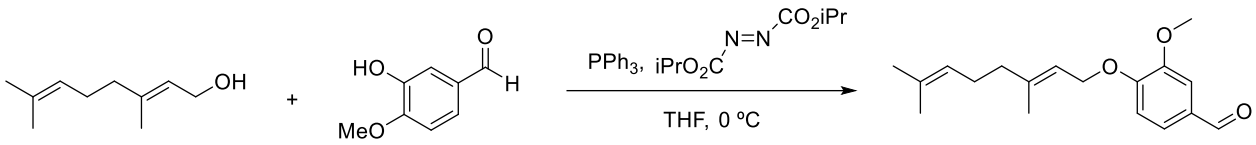
^{13}C NMR (75 MHz, $CDCl_3$) δ 161.35 (C), 148.23 (C), 144.39 (C), 139.15 (C), 135.38 (CH), 133.68 (CH), 129.78 (2 CH), 129.02 (CH), 128.18 (C), 121.08 (2 CH), 120.77 (C), 30.01 (CH_2), 26.30 (CH_2), 21.76 (CH_3).

m.p. = 199.7-201.0 dec.

HRMS [ESI(+)]: *m/z* calcd. for $C_{16}H_{15}N_2SO_4$+Na: 400.9930 [M+Na], found: 400.9916.

Synthesis of tosylhydrazone H43.

Synthesis of (*E*)-4-((3,7-dimethylocta-2,6-dien-1-yl)oxy)-3-methoxybenzaldehyde)



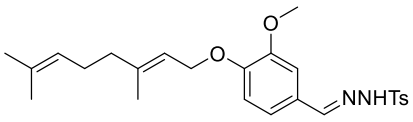
Geraniol (1.73 mL, 10 mmol, 1.0 equiv) was added to a solution of vanilin (2.42 g, 11 mmol, 1.1 equiv) and triphenylphosphine (2.88 g, 11 mmol, 1.1 equiv) in anhydrous THF (30 mL) under a N_2 atmosphere at 0ºC. The resulting suspension/solution was treated with diisopropylazodicarboxylate (2.15 mL, 11 mmol, 1.1 equiv) and the reaction mixture was continued stirring at room temperature up to completion of the reaction. The solvent was evaporated and the residue dissolved in ether, the triphenylphosphane oxide precipitated and was filtered off and then the filtrate evaporated under reduced pressure. The product was purified by column chromatography on silica gel (10:1 Hex/EtOAc, R_f= 0.25) to afford the pure product **I-A** (2.00 g, 70% yield).

^{1}H NMR (300 MHz, $CDCl_3$) δ 9.86 (s, 1H), 7.48 – 7.40 (m, 2H), 6.98 (d, *J* = 8.0 Hz, 1H), 5.71 – 5.33 (m, 1H), 5.09 (tq, *J* = 5.4, 1.5 Hz, 1H), 4.74 (d, *J* = 6.5 Hz, 2H), 3.95 (s, 3H), 2.19 – 2.05 (m, 4H), 1.77 (s, 1H), 1.68 (s, 2H), 1.61 (s, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 190.9 (CH), 153.8 (C), 149.8 (C), 141.7 (C), 131.9 (C), 129.9 (C), 126.7 (CH), 123.6 (CH), 118.7 (CH), 111.6 (CH), 109.0 (CH), 66.0 (CH_2), 56.0 (CH_3), 39.5 (CH_2), 26.1 (CH_2), 25.6 (CH_3), 17.7 (CH_3), 16.7 (CH_3).

HRMS [ESI(+)]: *m/z* calcd. for $C_{18}H_{24}O_3$+Na: 311.1618 [M+Na], found: 311.1628.

***N'*-((*Z*)-4-(((*E*)-3,7-dimethylocta-2,6-dien-1-yl)oxy)-3-methoxybenzylidene)-4-methylbenzenesulfonohydrazide H43**



The condensation of the aldehyde with *N*-sulfonylhydrazide was carried out following the standard procedure

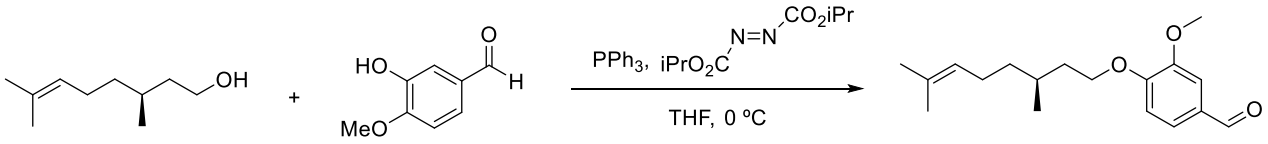
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.26 (s, 1H), 7.89 (d, *J* = 8.3 Hz, 2H), 7.75 (s, 1H), 7.30 (dd, *J* = 8.5, 2.4 Hz, 2H), 7.00 (dd, *J* = 8.3, 1.9 Hz, 1H), 6.81 (d, *J* = 8.3 Hz, 1H), 5.49 (tt, *J* = 5.2, 2.6 Hz, 1H), 5.16 – 5.00 (m, 1H), 4.63 (d, *J* = 6.5 Hz, 2H), 3.87 (s, 3H), 2.41 (s, 3H), 2.08 (h, *J* = 6.3, 5.8 Hz, 5H), 1.73 (s, 2H), 1.67 (s, 2H), 1.60 (s, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 150.5 (CH), 149.5 (C), 148.5 (C), 144.2 (C), 141.1 (C), 135.3 (C), 131.8 (C), 129.6 (CH), 127.9 (CH), 126.0 (CH), 123.7 (CH), 122.1 (CH), 119.2 (CH), 112.1 (C), 108.4 (CH), 65.8 (CH_2), 55.9 (CH_3), 39.5 (CH_2), 26.2 (CH_3), 25.6 (CH_2), 21.6 (CH_3), 17.7 (CH_3), 16.7 (CH_3).

HRMS [ESI(+)]: *m/z* calcd. for $C_{25}H_{33}N_2SO_4$: 457.2156 [M+H], found: 457.2153.

Synthesis of tosylhydrazone H44.

Synthesis of (*S*)-4-((3,7-dimethyloct-6-en-1-yl)oxy)-3-methoxybenzaldehyde



S-(-)-Citronellol (1.83 mL, 10 mmol, 1.0 equiv) was added to a solution of vanilin (2.42 g, 11 mmol, 1.1 equiv) and triphenylphosphine reagent (2.88 g, 11 mmol, 1.1 equiv) in anhydrous THF (30 mL) under a N2 atmosphere at 0ºC. The resulting suspension/solution was treated with diisopropylazodicarboxylate (2.15 mL, 11 mmol, 1.1 equiv) and the reaction mixture was continued stirring at room temperature up to completion of the reaction. The solvent was evaporated and the residue dissolved in ether, the triphenylphosphane oxide precipitated and was filtered off and then the filtrate evaporated under reduced pressure. The product was purified by column chromatography on silica gel (10:1 Hex/EtOAc, R_f= 0.35) to afford the pure product **I-B** (2.50 g, 72% yield).

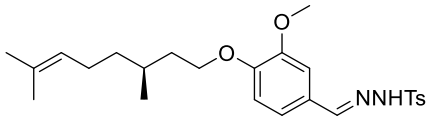
^{1}H NMR (300 MHz, $CDCl_3$) δ 9.86 (s, 1H), 7.52 – 7.36 (m, 2H), 6.99 (d, *J* = 8.1 Hz, 1H), 5.34 – 5.00 (m, 1H), 4.15 (dq, *J* = 9.2, 3.3 Hz, 2H), 3.94 (s, 3H), 2.20 – 1.86 (m, 3H), 1.79 – 1.66 (m, 5H), 1.62 (s, 2H), 1.42 (dddd, *J* = 14.1, 9.2, 6.6, 5.1 Hz, 1H), 1.33 – 1.18 (m, 1H), 0.99 (d, *J* = 6.2 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 190.9 (CH), 154.1 (C), 149.8 (C), 131.4 (C), 129.8 (C), 126.8 (CH), 124.5 (CH), 111.3 (CH), 109.1 (CH), 67.5 (CH_2), 56.0 (CH_3), 37.0 (CH), 35.6 (CH_2), 29.5 (CH_2), 25.7 (CH_3), 25.4 (CH_2), 19.5 (CH_3), 17.6 (CH_3).

HRMS [ESI(+)]: *m/z* calcd. for $C_{18}H_{26}O_3$+Na: 313.1774 [M+Na], found: 313.1774.

(*S*)-*N*'-(4-((3,7-dimethyloct-6-en-1-yl)oxy)-3-methoxybenzylidene)-4-methylbenzenesulfonohydrazide H44

The condensation of the aldehyde with *N*-sulfonylhydrazide was carried out following the standard procedure.



^{1}H NMR (300 MHz, $CDCl_3$) δ 8.37 (s, 1H), 7.89 (d, *J* = 8.3 Hz, 2H), 7.75 (s, 1H), 7.42 – 7.27 (m, 2H), 7.00 (dd, *J* = 8.3, 1.9 Hz, 1H), 6.81 (d, *J* = 8.3 Hz, 1H), 5.11 (ddt, *J* = 8.5, 7.1, 1.5 Hz, 1H), 4.13 – 3.98 (m, 2H), 3.86 (s, 3H), 2.40 (s, 3H), 2.11 – 1.82 (m, 3H), 1.69 (d, *J* = 1.4 Hz, 4H), 1.61 (d, *J* = 1.3 Hz, 3H), 1.39 (dddd, *J* = 14.1, 9.3, 6.5, 5.0 Hz, 1H), 1.23 (tdd, *J* = 16.0, 8.2, 5.7 Hz, 1H), 0.96 (d, *J* = 6.2 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 150.8 (CH), 149.5 (C), 148.6 (C), 144.1 (C), 135.3 (C), 131.3 (C), 129.6 (CH), 127.9 (CH), 126.0 (CH), 124.5 (CH), 122.2 (CH), 111.7 (CH), 108.7 (CH), 67.3 (CH_2), 56.0 (CH_2), 37.1 (CH), 35.8 (CH_2), 29.5 (CH_2), 25.7 (CH_2), 25.4 (CH_3), 21.6 (CH_3), 19.5 (CH_3), 17.6 (CH_3).

HRMS [ESI(+)]: calcd. for $(C_{25}H_{34}N_2SO_2+Na)^+$: 481.2131, found: 481.2140.

1.3 General procedures for the photochemical carboborylation reactions under batch conditions

See figure S2 for the reaction setup.

1.3.1 Procedure A: reactions with Cs_2CO_3.

A 5 mL glass vial provided with a stirring bar was charged with the corresponding *N*-sulfonylhydrazone (0.2 mmol) the boronic acid (2-3 equiv) and Cs_2CO_3 (0.6 mmol, 211 mg). The vial was sealed with a septum and evacuated under vacuum and filled with argon. Then a solution of DIPEA (0.4 mmol) in dry and degassed CH_2Cl_2 (2 mL) was added to the vial through the septum with the aid of a needle. The vial was placed in the Kessil® PR160 Rig in front of the Kessil® PR160L lamp (370 or 390 nm) at a distance of 5 cm. The cooling fan and the light were turned on keeping vigorous stirring at room temperature. After the time indicated (1-6 h) the light and the cooling fan were turned off, the septum was removed and 5 equiv of pinacol were added. The vial was sealed again and the reaction was stirred for 12 h at rt. Then, the vial was opened and the reaction was quenched with 5 mL of water and 5 mL of CH_2Cl_2. The layers were separated and the aqueous phase was extracted with CH_2Cl_2 (2x5 mL). The combined organic layers were washed with brine (2x5 mL), dried over Na_2CO_3, and concentrated under reduced pressure. The residue was dried under vacuum. The resulting reaction crude was purified by column chromatography.

1.3.2 Procedure B: reactions with DBU.

A 5 mL glass vial provided with a stirring bar was charged with the corresponding *N*-sulfonylhydrazone (0.2 mmol) and the boronic acid (2-3 equiv). The vial was sealed with a septum, evacuated under vacuum and filled with argon. Then a solution of DIPEA (0.4 mmol) and DBU (0.4 mmol) in dry and degassed CH_2Cl_2 (2 mL) was added to the vial through the septum with the aid of a needle. The vial was placed in the Kessil® PR160 Rig in front of the Kessil® PR160L lamp (370 or 390 nm) at a distance of 5 cm. The cooling fan and the light were turned on keeping vigorous stirring at room temperature. After the time indicated (1-6 h) the light and the cooling fan were turned off, the septum was removed and 5 equiv of pinacol were added. The vial was sealed again and the reaction was stirred for 12 h at rt. Then, the vial was opened and the reaction was quenched with 5 mL of water and 5 mL of CH_2Cl_2. The layers were

separated and the aqueous phase was extracted with CH_2Cl_2 (2x5 mL). The combined organic layers were washed with brine (3x5 mL), dried over Na_2CO_3, and concentrated under reduced pressure. The residue was dried under vacuum. The resulting reaction crude was purified by column chromatography.

1.3.3 Procedure C: reactions with DBU.

A 5 mL glass vial provided with a stirring bar was charged with the corresponding *N*-sulfonylhydrazone (0.4 mmol) and the boronic acid (0.2 mmol). The vial was sealed with a septum, evacuated under vacuum and filled with argon. Then a solution of DIPEA (0.6 mmol) and DBU (0.6 mmol) in dry and degassed CH_2Cl_2 (2 mL) was added to the vial through the septum with the aid of a needle. The vial was placed in the Kessil® PR160 Rig in front of the Kessil® PR160L lamp (370 or 390 nm) at a distance of 5 cm. The cooling fan and the light were turned on keeping vigorous stirring at room temperature. After the time indicated (1-6 h) the light and the cooling fan were turned off, the septum was removed and 5 equiv of pinacol were added. The vial was sealed again and the reaction was stirred for 12 h at rt. Then, the vial was opened and the reaction was quenched with 5 mL of water and 5 mL of CH_2Cl_2. The layers were separated and the aqueous phase was extracted with CH_2Cl_2 (2x5 mL). The combined organic layers were washed with brine (3x5 mL), dried over Na_2CO_3, and concentrated under reduced pressure. The residue was dried under vacuum. The resulting reaction crude was purified by column chromatography.

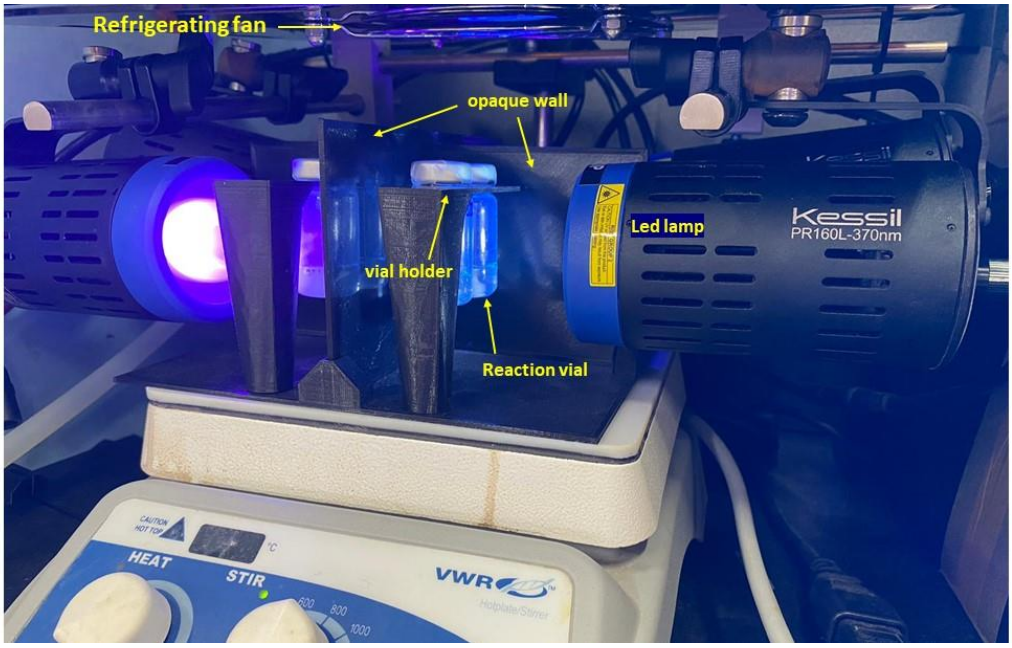


Figure S2: Setup for the photochemical reactions

1.4 Photochemical carboborylation reactions under continuous flow conditions

1.4.1 The Photochemical flow reactor.

The flow reactor was built employing PTFE tubing of 1 mm of internal diameter that was rolled around a transparent colorless polystyrene sheet (10cm x 10cm). A photoreactor of 9 mL of volume was used employing 11.45 m of the PTFE tube. Depending on the reactions, the final end of the tubing of the photoreactor may be connected to a 2 m long loop of the same PTFE tubing. The end of the loop or the photoreactor is connected through a flangless fitting to a 100 psi back pressure regulator (BPR). The exit part of the BPR is connected to the collector flask. The collector flask is capped with a septum provided with a balloon to allow the release of the overpressure. The initial end of the PTFE tubing of the flow reactor is connected through a flangless fitting to a three ways adaptor provided with a knob. One line is connected to a gas tight syringe that contains the solution, which is pumped into the flow reactor employing a high pressure syringe pump. The other line is connected to another syringe that contains solvent (CH_2Cl_2), placed on

another high pressure syringe pump which will be used to push the reaction solution through the reactor all the way to the collector flask once all the reaction solution has been introduced in the reactor. For procedure E, another syringe containing a pinacol solution is mounted in another syringe pump and connected directly to the collector flask. The flow reactor is illuminated by one or two Kessil® PR160L lamps (370 or 390 nm) at a distance of 3-7 cm from the photoreactor. The lamps are mounted on a PR160 Rig with Fan Kit by Kessil to avoid the overheating of the reaction due to the radiation (see figures S3 and S4).

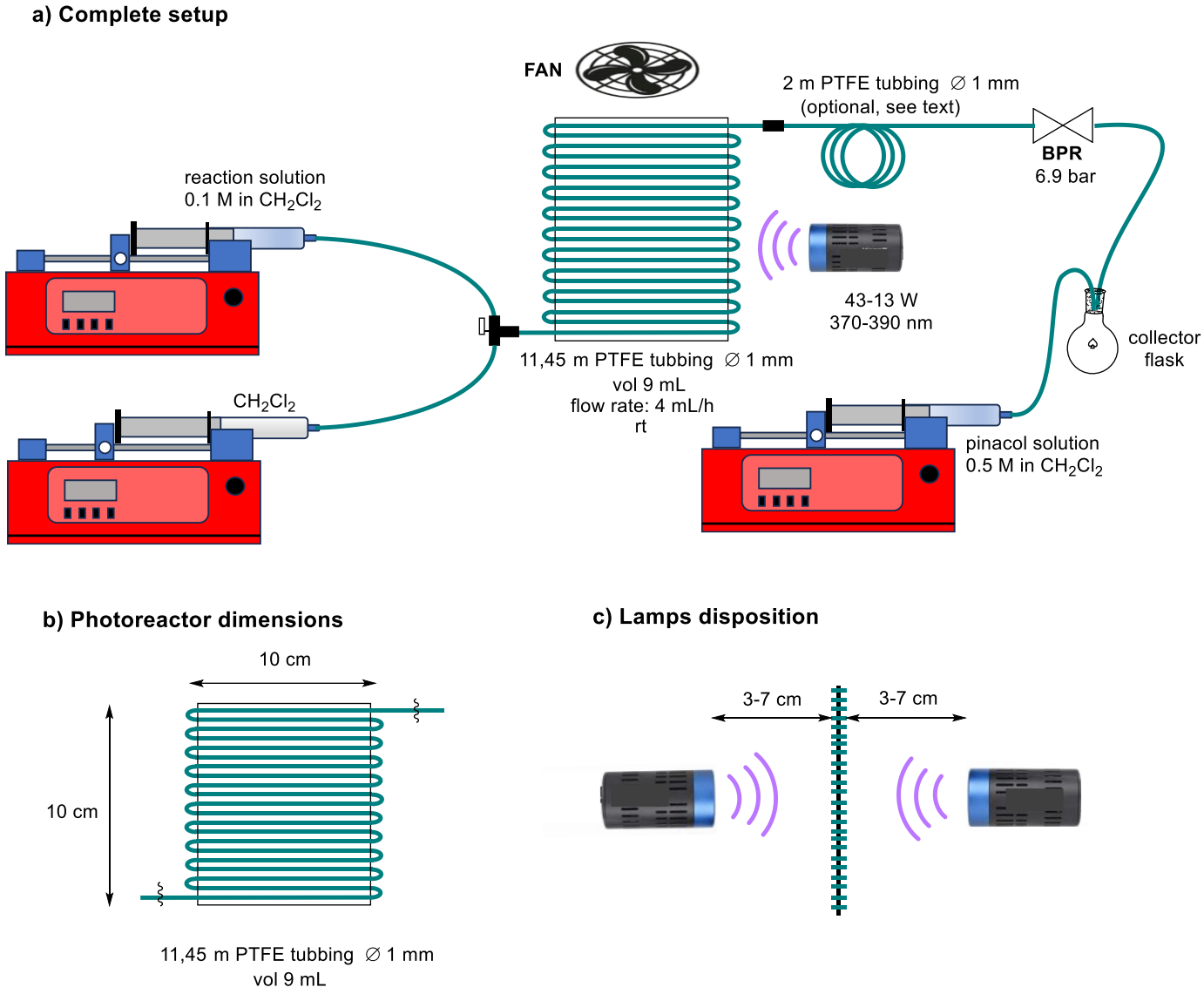


Figure S3: Scheme of the set up for the continuos flow reactions.

Materials:

PTFE tubing: Ø 0.1 mm X Ø 0.16 mm from BOLA (ref. S 1810-12)

Three way adaptor: Miniature 3-Way Stopcock from BOLA (ref. F731-02)

Back pressure regulator: P-763 BPR Cartridge from IDEX health and science

High pressure syringe pumps: NE-8000 from New Era pump systems Inc.

Gas tight syringes: Hamilton 1010 TLL (ref. 81610)

LED lamps: Kessil PR160L 370 nm and PR160L 390 nm.

Fan kit: Kessil PR160 Rig with Fan Kit

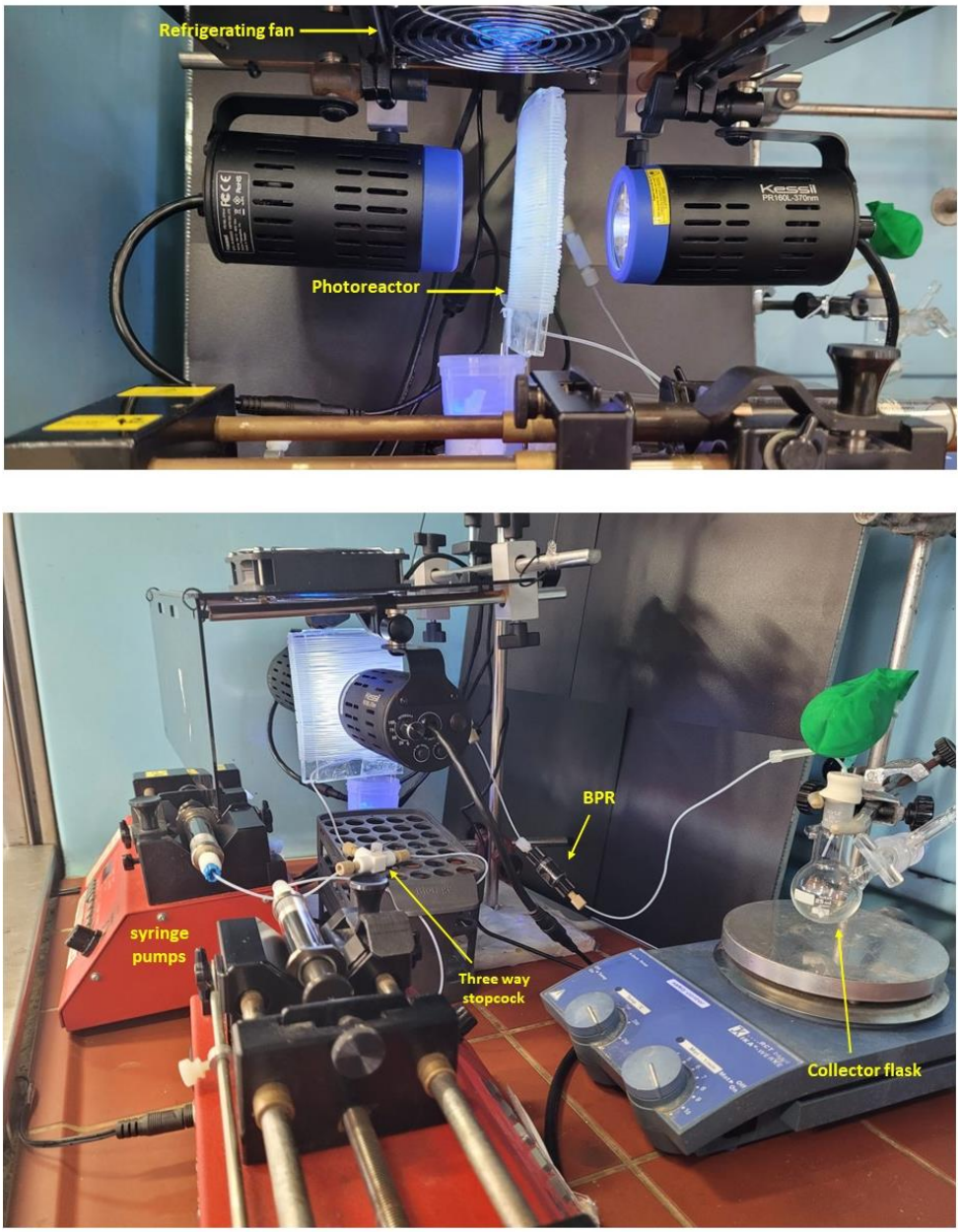


Figure S4: Photographs of the setup used in the photochemical continuous flow reactions.

1.4.2 Experimental Procedure D: Synthesis of pinacol boronic ester by reactions with aromatic *N*-tosylhydrazones:

A solution containing the *N*-tosylhydrazone (0,2 mmol, 1 equiv), the boronic acid (3 equiv), the DBU (1.5 equiv) and the DIPEA (1.5 equiv) dissolved in 2 mL of dry CH_2Cl_2 (0.1 M concentration of the *N*-tosylhydrazone) under Ar atmosphere is placed in a gas tight syringe, placed in a high pressure syringe pump and connected to one of inlet the lines of the three way adaptor. The other inlet line of is connected to a syringe containing CH_2Cl_2. The flow reactor is filled with solvent by pumping CH_2Cl_2 at a rate of 4 mL/min. Then, the three way knob is switched to allow the reaction solution to enter into the reactor. The lamps are turned on and the solution is pumped at a rate of 4 mL/h. (the number of lamps, the wavelength, the distance between the lamps and the photoreactor, and the intensity of the light are indicated for every specific example). Once all the reaction solution has been introduced into the flow reactor (35-40 min), the knob is switched and CH_2Cl_2 is pumped into the reactor to push the reaction solution through the flow reactor and the loop into the collector flask at the 4 mL/h rate. The solvent exiting the reactor is discarded for the initial 2h. After the proper time (2h since the beginning of the reaction for the 9 mL flow reactor) the exit solution starts to be collected in the collector flask. The reaction solution is

being collected for 2 h to make sure that all the material has exited the flow reactor. Then, 5 equiv of pinacol are added to the flask. The solution is stirred at rt for 14h. Then the reaction is quenched with water (5 mL), the layers are separated and the aqueous phase is extracted twice with CH_2Cl_2 (5 mL). The combined organic layers are washed with brine (3x5 mL), dried over Na_2SO_4 and concentrated under reduced pressure. The reaction crude is purified by column chromatography on SiO_2 or deactivated SiO_2, depending on the specific substrate.

1.4.3 Experimental Procedure E: Synthesis of pinacol boronic ester by reactions of aliphatic *N*-tosylhydrazones with arylboronic acids.

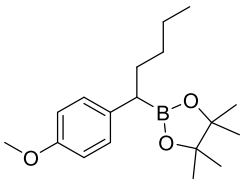
The method is similar to procedure D with the following differences. Two Kessil PRL160 370 nm lamps at 75 % power are employed. The photoreactor exit is directly connected to the BPR (no extra loop) and then to the collector flask. The stoichiometry of the reaction: *N*-tosylhydrazone (0,2 mmol, 1 equiv), the boronic acid (2 equiv), the DBU (1.5 equiv) and the DIPEA (1.5 equiv) dissolved in 2 mL of dry CH_2Cl_2 (0.1 M concentration of the *N*-tosylhydrazone). Once the reaction solution starts to be collected in the collector flask (1h 45 min after the start), 2 mL of a 0.5 M solution of pinacol in CH_2Cl_2 are simultaneously added to the collector flask at a rate of 4 mL/h. The reaction solution is being collected for 1 h 30 min to make sure that all the material has exited the flow reactor. The resulting solution is stirred at rt for 14h. Then the reaction is quenched with water (5 mL), the layers are separated and the aqueous phase is extracted twice with CH_2Cl_2 (5 mL). The combined organic layers are washed with brine (3x5 mL), dried over Na_2SO_4 and concentrated under reduced pressure. The reaction crude is purified by column chromatography on deactivated SiO_2 or neutral alumina, depending on the specific substrate.

1.4.4 Experimental Procedure F: Synthesis of pinacol boronic ester by reactions of aliphatic *N*-tosylhydrazones with arylboronic acids.

The method is similar to procedure E but with different stoichiometry of the reaction: *N*-tosylhydrazone (0,2 mmol, 2 equiv), boronic acid (0.1 mmol, 1 equiv), DBU (3 equiv), DIPEA (3 equiv) dissolved in 2 mL of dry CH_2Cl_2 (0.1 M concentration of the *N*-tosylhydrazone

1.5. Experimental and characterization data for boronic esters 4, 5, and 7.

2-(1-(4-methoxyphenyl)pentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 4a



Using procedure A (390 nm lamp) 60.8 mg of *N*-tosylhydrazone **H1** and 61 mg of butylboronic acid afforded 57 mg of **4a** (95 % yield) as a colourless oil after column chromatography on SiO_2. Rf = 0.2 (Hex/EtOAc 40:1).

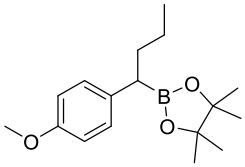
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.12 (d, *J* = 8.6 Hz, 2H), 6.80 (d, *J* = 8.6 Hz, 2H), 3.77 (s, 3H), 2.23 (t, *J* = 7.9 Hz, 1H), 1.81 (dd, *J* = 13.5, 7.6 Hz, 1H), 1.70 – 1.50 (m, 1H), 1.35-1.20 (m,4H), 1.21 (s. 6H), 1.19 (s, 6H,.86 (t, *J* = 7.0 Hz, 3H)

^{13}C NMR (75 MHz, $CDCl_3$) δ 157.4 (C), 135.6 (C), 129.3 (CH), 113.8 (CH), 83.3 (C), 55.3 (CH_3), 32.7 (CH_2), 31.6 (CH_2), 24.8 (CH_3), 24.7 (CH_3), 22.8 (CH_2), 14.8 (CH_3).

^{11}B NMR (129 MHz, $CDCl_3$) δ 33.58.

HRMS [ESI(+)]: *m/z* calcd. for $C_{12}H_{17}O_2$: 193.1223 [M+O-Bpin], found: 193.1224.

2-(1-(4-methoxyphenyl)butyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 4b

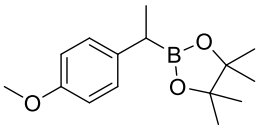


Using procedure A (390 nm lamp) 60.8 mg of *N*-tosylhydrazone **H1** and 53 mg of propylboronic acid afforded 54 mg of **4b** (92 % yield) as a colourless oil after column chromatography on SiO_2. Rf = 0.31 (Hex/EtOAc 10:1). Spectroscopic data in matches that previously reported in the literature.[19]

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.17 – 7.07 (m, 2H), 6.84 – 6.76 (m, 2H), 3.77 (s, 3H), 2.25 (t, *J* = 7.9 Hz, 1H), 1.78 (dq, *J* = 13.1, 7.8 Hz, 1H), 1.66 – 1.50 (m, 1H), 1.35 – 1.22 (m, 2H), 1.21 (s, 6H), 1.19 (s, 6H), 0.88 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 157.3 (C), 135.5 (C), 129.3 (CH), 113.8 (CH), 83.3 (C), 55.3 (CH_3), 35.2 (CH_2), 24.8 (CH_3), 24.7 (CH_3), 22.4 (CH_2), 14.2 (CH_3).

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

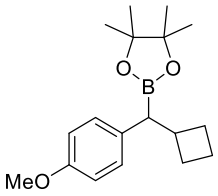


Using procedure A (390 nm lamp) 60.8 mg of *N*-tosylhydrazone **H1** and 36 mg of methylboronic acid afforded 26 mg of **4c** (50 % yield) as a colourless oil after column chromatography on SiO_2. Rf = 0.31 (Hex/EtOAc 8:1). Spectroscopic data in matches that previously reported in the literature.[20]

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.20 – 7.07 (m, 2H), 6.88 – 6.76 (m, 2H), 3.78 (s, 3H), 2.38 (q, *J* = 7.5 Hz, 1H), 1.30 (d, *J* = 7.5 Hz, 3H), 1.21 (s, 6H), 1.20 (s, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 157.3 (C), 137.1 (C), 128.7 (CH), 113.9 (CH), 83.4 (C), 55.3 (CH_3), 24.6 (CH_3), 24.7 (CH_3), 17.5 (CH_3).

2-(cyclobutyl(4-methoxyphenyl)methyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 4d

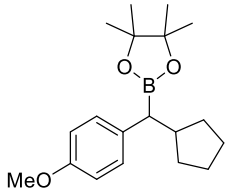


Using procedure A (390 nm lamp) 60.8 mg of *N*-tosylhydrazone **H1** and 60 mg of cyclobutylboronic acid afforded 36 mg of **4d** (60 % yield) as a colourless oil after column chromatography on SiO_2. Rf = 0.2 (Hex/EtOAc 40:1). Spectroscopic data in matches that previously reported in the literature.[21]

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.19 – 7.01 (m, 2H), 6.88 – 6.69 (m, 2H), 3.77 (s, 3H), 2.84 – 2.59 (m, 1H), 2.27 (d, *J* = 11.0 Hz, 1H), 2.13 (dt, *J* = 7.9, 3.9 Hz, 1H), 1.95 – 1.50 (m, 5H), 1.21 (s, 6H), 1.18 (s, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 157.4 (C), 133.9 (C), 129.4 (CH), 113.7 (CH), 83.3 (C), 55.2 (CH_3), 38.7 (CH), 28.8 (CH_2), 28.6 (CH_2), 24.8 CH_3), 24.7 (CH_3), 18.3 (CH_2).

2-(cyclopentyl(4-methoxyphenyl)methyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 4e



Using procedure A (390 nm lamp) 60.8 mg of *N*-tosylhydrazone **H1** and 68.5 mg of cyclopentylboronic acid afforded 54 mg of **4e** (85 % yield) as a colourless oil after column chromatography on SiO_2.

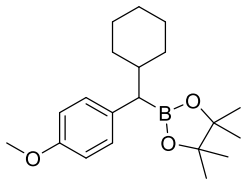
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.20 – 7.07 (m, 2H), 6.86 – 6.71 (m, 2H), 3.77 (s, 3H), 2.38 – 2.13 (m, 1H), 2.02 (d, *J* = 11.0 Hz, 1H), 1.90 (dtd, *J* = 11.6, 7.2, 4.0 Hz, 1H), 1.72 – 1.33 (m, 5H), 1.20 (s, 6H), 1.18 (s, 6H), 1.0 - 0.9 (m, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 157.3 (C), 135.1 (C), 129.6 (CH), 113.6 (CH), 83.2 (CH_3), 55.2 (CH_3), 43.3 (CH), 38.0 (CB), 32.7 (CH_2), 32.5 (CH_2), 25.3 (CH_2), 24.9 (CH_2), 24.7 (CH_3).

^{11}B NMR (129 MHz, $CDCl_3$) δ 34.29.

HRMS [ESI(+)]: *m/z* calcd. for $C_{19}H_{30}BO_3$: 317.2283 [M+H], found: 317.2276.

2-(cyclohexyl(4-methoxyphenyl)methyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 4f

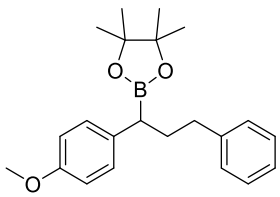


Using procedure A (390 nm lamp) 60,8 mg of *N*-tosylhydrazone **H1** and 77 mg of cyclohexylboronic acid afforded 45 mg of **4f** (68 % yield) as a white solid after column chromatography on SiO_2. Rf = 0.30 (Hex/EtOAc 40:1). Spectroscopic data in agreement with literature.[22]

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.09 (s, 2H), 6.79 (d, *J* = 8.6 Hz, 2H), 3.77 (s, 3H), 1.88 – 1.77 (m, 1H), 1.77 – 1.54 (m, 4H), 1.54 – 1.43 (m, 1H), 1.42 – 1.21 (m, 2H), 1.19 (s, 6H), 1.17 (s, 6H), 1.15 – 0.56 (m, 4H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 157.4 (C), 133.8 (C), 130.1 (CH), 113.6 (CH), 83.2 (C), 55.2 (CH_3), 40.6 (CH), 39.6 (CHB), 33.9 (CH_2), 32.5 (CH_2), 26.76 (CH_2), 26.70 (CH_2), 26.4 (CH_2), 24.8 (CH_3), 24.7 (CH_3).

2-(1-(4-methoxyphenyl)-3-phenylpropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 4g

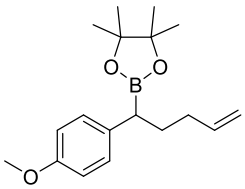


Using procedure A (390 nm lamp) 60,8 mg of *N*-tosylhydrazone **H1** and 90 mg of phenethylboronic acid afforded 46 mg of **4g** (65 % yield) as a white solid after column chromatography on SiO_2. Rf = 0.30 (Hex/EtOAc 40:1). Spectroscopic data in agreement with literature.[22]

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.27 (t, *J* = 7.4 Hz, 2H), 7.21 – 7.11 (m, 5H), 6.84 (d, *J* = 8.6 Hz, 2H), 3.80 (s, 3H), 2.57 (t, *J* = 7.9 Hz, 2H), 2.32 (t, *J* = 7.9 Hz, 1H), 2.22 – 2.06 (m, 1H), 1.95 (dq, *J* = 15.7, 8.1 Hz, 1H), 1.23 (s, 6H), 1.21 (s, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 157.5 (C), 142.7 (C), 135.0 (C), 129.4 (CH), 128.6 (CH), 128.3 (CH), 125.7 (CH), 113.9 (CH), 83.4 (C), 55.3 (CH_3), 35.5 (CH_2), 34.7 (CH_2), 24.8 (CH_3), 24.7 (CH_3).

2-(1-(4-methoxyphenyl)pent-4-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 4h



Using procedure A (390 nm lamp) 60,8 mg of *N*-tosylhydrazone **H1** and 61 mg of 3-butenylboronic acid afforded afforded 38 mg of **4h** (63 % yield) as a colourless oil after column chromatography on SiO_2. Rf = 0.28 (Hex/EtOAc 10:1).

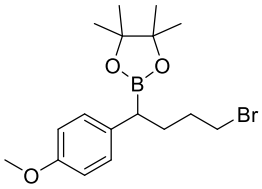
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.12 (d, *J* = 8.1, 2H), 6.81 (d, *J* = 8.1, 2H), 5.80 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H), 5.04 – 4.88 (m, 2H), 3.77 (s, 3H), 2.27 (t, *J* = 7.8 Hz, 1H), 2.08 – 1.95 (m, 2H), 1.95 – 1.83 (m, 1H), 1.77 – 1.62 (m, 1H), 1.20 (d, *J* = 5.8 Hz, 12H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 157.4 (C), 138.9 (CH), 135.1 (C), 129.4 (CH), 114.7 (CH2), 113.8 (CH), 83.4 (C), 55.3 (CH3), 33.4 (CH2), 32.1 (CH2), 24.8 (CH3), 24.7 (CH3).

^{11}B NMR (129 MHz, $CDCl_3$) δ 33.39.

HRMS [APCI(+)]: *m/z* calcd. for $C_{18}H_{28}BO_3$: 303.2126 [M+H], found: 303.2126.

2-(4-bromo-1-(4-methoxyphenyl)butyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 4i



Using procedure A (390 nm lamp) 60,8 mg of *N*-tosylhydrazone **H1** and 5 mg of 3-bromopropylboronic acid afforded 52.2 mg of **4i** (71 % yield) as yellow oil after column chromatography on SiO_2. Rf = 0.14 (Hex/EtOAc 40:1).

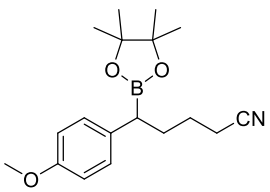
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.17 – 7.05 (m, 2H), 6.87 – 6.71 (m, 2H), 3.77 (s, 3H), 3.36 (t, *J* = 6.5 Hz, 2H), 2.24 (t, *J* = 7.5 Hz, 1H), 2.01 – 1.66 (m, 4H), 1.20 (s, 6H), 1.19 (s, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 157.6 (C), 134.5 (C), 129.3 (CH), 114.0 (CH), 83.5 (C), 55.3 (CH_3), 33.9 (CH_2), 32.5 (CH_2), 31.4 (CH_2), 24.8 (CH_3), 24.7 (CH_3).

^{11}B NMR (129 MHz, $CDCl_3$) δ 30.70.

HRMS [APCI(+)]: *m/z* calcd. for $C_{11}H_{14}BrO_2$: 257.0172 [M+O-Bpin], found: 257.0172.

5-(4-methoxyphenyl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentanenitrile 4j



Using procedure A (390 nm lamp) 60,8 mg of *N*-tosylhydrazone **H1** and 67 mg of (3-cyanopropyl)boronic acid afforded 40 mg of **4j** (63 % yield) as a colourless oil after column chromatography on SiO_2. Rf = 0.15 (Hex/EtOAc 8:1).

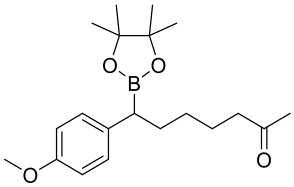
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.15 – 7.04 (m, 2H), 6.88 – 6.75 (m, 2H), 3.77 (s, 3H), 2.33 – 2.17 (m, 3H), 1.99 – 1.84 (m, 1H), 1.80 – 1.67 (m, 1H), 1.67 – 1.54 (m, 2H), 1.21 (s, 6H), 1.18 (s, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 157.7 (C), 134.1 (C), 129.3 (CH), 119.9 (CN), 114.1 (CH), 83.6 (C), 55.3 (CH_3), 31.8 (CH_2), 24.9 (CH_2), 24.8 (CH_3), 24.7 (CH_3), 17.3 (CH_2).

^{11}B NMR (129 MHz, $CDCl_3$) δ 33.31.

HRMS [ESI(+)]: *m/z* calcd. for $C_{12}H_{14}NO$, 188.1070 [M-Bpin], found: 188.1070.

7-(4-methoxyphenyl)-7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)heptan-2-one 4k



Using procedure A (390 nm lamp) 60,8 mg of *N*-tosylhydrazone **H1** and 85 mg of (5-oxohexyl)boronic acid afforded 33 mg of **4k** (48 % yield) as a colourless oil after column chromatography on SiO_2. Rf = 0.15 (Hex/EtOAc 8:1).

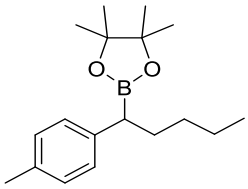
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.13 – 7.05 (m, 2H), 6.83 – 6.76 (m, 2H), 3.77 (s, 3H), 2.37 (t, *J* = 7.5 Hz, 2H), 2.21 (t, *J* = 7.9 Hz, 1H), 2.09 (s, 3H), 1.90 – 1.70 (m, 1H), 1.70 – 1.44 (m, 3H), 1.25 (q, *J* = 7.7 Hz, 2H), 1.20 (s, 6H), 1.17 (s, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 209.5 (C), 157.4 (C), 135.2 (C), 129.3 (CH), 113.8 (CH), 83.4 (C), 55.3 (CH_3), 43.8 (CH_2), 32.6 (CH_2), 29.9 (CH_2), 28.8 (CH_3), 24.8 (CH_3), 24.7 (CH_3), 24.0 (CH_2).

^{11}B NMR (129 MHz, $CDCl_3$) δ 34.25.

HRMS [APCI(+)]: *m/z* calcd. for $C_{14}H_{19}O_2$: 219.1380 [M-Bpin], found: 219.1381.

2-(1-(4-tolyl)pentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 4l



Batch reaction: Using procedure A (390 nm lamp) 57,6 mg of *N*-tosylhydrazone **H2** and 61 mg of butylboronic acid afforded 35.1 mg of **4l** (61 % yield) as a colourless oil after column chromatography on SiO_2. Rf = 0.47 (Hex/EtOAc 10:1).

Continuous flow reaction: Using procedure D with one 390 nm lamp (13 W, 25 %, 10 cm) 57,6 mg of *N*-tosylhydrazone **H2** and 61 mg of butylboronic acid afforded 33 mg of **4l** (35 % yield) as a colourless oil after column chromatography on SiO_2. Rf = 0.47 (Hex/EtOAc 10:1).

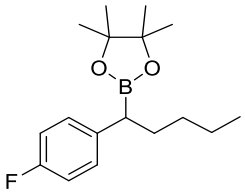
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.11 (d, *J* = 8.2 Hz, 2H), 7.06 (d, *J* = 8.2 Hz, 2H), 2.31 (s, 3H), 2.27 – 2.17 (m, 1H), 1.90 – 1.73 (m, 1H), 1.71 – 1.55 (m, 1H), 1.29 – 1.18 (m, 16H), 0.86 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 140.5 (C), 134.5 (C), 129.1 (CH), 128.4 (CH), 83.3 (C), 32.6 (CH_2), 31.7 (CH_2), 24.8 (CH_3), 24.7 (CH_3), 22.8 (CH_2), 21.1 (CH_3), 14.2 (CH_3).

^{11}B NMR (129 MHz, $CDCl_3$) δ 33.53.

HRMS [APCI(+)]: *m/z* calcd. for $C_{18}H_{30}BO_2$: 289.2333 [M+H], found: 289.2336.

2-(1-(4-fluorophenyl)pentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 4m



Using procedure A (390 nm lamp) 58.2 mg of *N*-tosylhydrazone **H3** and 61 mg of butylboronic acid afforded 34 mg of **4m** (58 % yield) as a yellow oil after column chromatography on SiO_2. Rf = 0.33 (Hex/EtOAc/CH_2Cl_2 20:1:1).

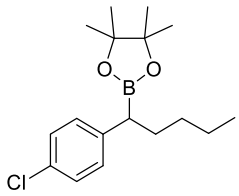
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.21 – 7.09 (m, 2H), 6.93 (t, *J* = 8.8 Hz, 2H), 2.26 (t, *J* = 7.9 Hz, 1H), 1.90 – 1.70 (m, 1H), 1.68 – 1.52 (m, 1H), 1.40 – 1.10 (m, 17H), 0.85 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 162.6 (C), 159.4 (C), 139.2 (C), 129.7 (CH), 129.6 (CH), 115.2 (CH), 114.9 (CH), 83.4 (C), 32.6 (CH_2), 31.6 (CH_2), 24.8 (CH_3), 24.7 (CH_3), 22.8 (CH_2), 14.2 (CH_3).

^{11}B NMR (129 MHz, $CDCl_3$) δ 33.26.

HRMS [APCI(+)]: *m/z* calcd. for $C_{11}H_{14}FO$: 181.1023 [M+O-Bpin], found: 181.1022.

2-(1-(4-chlorophenyl)pentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 4n



Using procedure A (390 nm lamp) 61.6 mg of *N*-tosylhydrazone **H4** and 61 mg of butylboronic acid afforded 42 mg of **4n** (80 % yield) as a yellow oil after column chromatography on SiO_2. Rf = 0.18 (Hex/EtOAc 80:1).

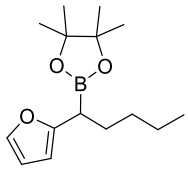
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.21 (d, *J* = 8.5 Hz, 2H), 7.13 (d, *J* = 8.5 Hz, 2H), 2.26 (t, *J* = 7.9 Hz, 1H), 1.90 – 1.72 (m, 1H), 1.68 – 1.53 (m, 1H), 1.37 – 1.07 (m, 16H), 0.85 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 142.1 (C), 130.8 (C), 129.8 (CH), 128.4 (CH), 83.5 (C), 32.3 (CH_2), 31.5 (CH_2), 24.8 (CH_3), 24.7 (CH_3), 22.8 (CH_2), 14.2 (CH_3).

^{11}B NMR (129 MHz, $CDCl_3$) δ 33.40.

HRMS [APCI(+)]: *m/z* calcd. for $C_{11}H_{14}ClO$: 197.0728 [M+O-Bpin], found: 197.0725.

2-(1-(furan-2-yl)pentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 4o



Using procedure A (390 nm lamp) 52.8 mg of *N*-tosylhydrazone **H7** and 61 mg of butylboronic acid afforded 38 mg of **4o** (71 % yield) as a yellow oil after column chromatography on SiO_2. Rf = 0.41 (Hex/EtOAc 10:1).

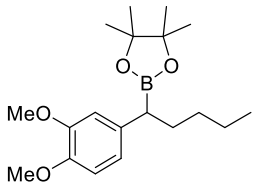
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.28 (d, *J* = 1.9 Hz, 1H), 6.26 (dd, *J* = 3.1, 1.9 Hz, 1H), 6.00 (d, *J* = 3.1 Hz, 1H), 2.44 (t, *J* = 7.6 Hz, 1H), 1.80 – 1.67 (m, 2H), 1.36 – 1.21 (m, 16H), 0.87 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 157.0 (C), 140.6 (CH), 110.1 (CH), 104.5 (CH), 83.5 (C), 31.4 (CH_2), 29.9 (CH_2), 24.7 (CH_3), 24.6 (CH_3), 22.7 (CH_2), 14.0 (CH_3).

^{11}B NMR (129 MHz, $CDCl_3$) δ 33.09.

HRMS [APCI(+)]: *m/z* calcd. for $C_9H_{13}O_2$: 153.0910 [M+O-Bpin], found: 153.0906.

2-(1-(3,4-dimethoxyphenyl)pentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 4p



Using procedure A (390 nm lamp) 67 mg of *N*-tosylhydrazone **H8** and 61 mg of butylboronic acid afforded 43 mg of **4p** (64 % yield) as a colourless oil after column chromatography on SiO_2. Rf = 0.24 (Hex/EtOAc 5:1).

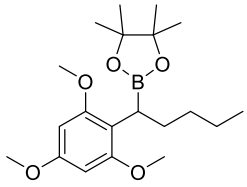
^{1}H NMR (300 MHz, $CDCl_3$) δ 6.80 – 6.67 (m, 3H), 3.85 (s, 3H), 3.83 (s, 3H), 2.21 (t, *J* = 8.0 Hz, 1H), 1.88 – 1.69 (m, 1H), 1.69 – 1.52 (m, 1H), 1.30 – 1.15 (m, 16H), 0.85 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 148.6 (C), 146.6 (C), 136.1 (C), 120.2 (CH), 111.6 (CH), 111.2 (CH), 83.3 (C), 55.8 (CH_3), 55.8 (CH_3), 32.7 (CH_2), 31.6 (CH_2), 24.7 (CH_3), 24.7 (CH_3), 22.8 (CH_2), 14.2 (CH_3).

^{11}B NMR (129 MHz, $CDCl_3$) δ 34.33.

HRMS [ESI(+)]: *m/z* calcd. for $C_{19}H_{32}BO_4$: 335.2388 [M+H], found: 365.2450.

4,4,5,5-tetramethyl-2-(1-(2,4,6-trimethoxyphenyl)pentyl)-1,3,2-dioxaborolane 4q



Using procedure A (390 nm lamp) 52.8 mg of *N*-tosylhydrazone **H9** and 61 mg of butylboronic acid afforded 34 mg of **4q** (48 % yield) as a yellow oil after column chromatography on SiO_2. Rf = 0.39 (Hex/EtOAc 3:1).

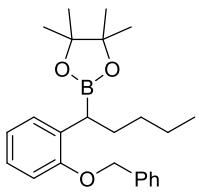
^{1}H NMR (300 MHz, $CDCl_3$) δ 6.11 (s, 2H), 3.79 (s, 3H), 3.76 (s, 6H), 2.57 (dd, *J* = 9.7, 5.2 Hz, 1H), 1.81 – 1.64 (m, 1H), 1.54 – 1.38 (m, 1H), 1.23 (d, *J* = 12.0 Hz, 16H), 0.81 (t, *J* = 6.9 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 158.8 (C), 158.6 (C), 113.4 (C), 90.7 (CH), 82.7 (C), 55.5 (CH_3), 55.3 (CH_3), 31.4 (CH_2), 30.3 (CH_2), 25.1 (CH_3), 24.8 (CH_3), 23.0 (CH_2), 14.4 (CH_3).

^{11}B NMR (129 MHz, $CDCl_3$) δ 34.09.

HRMS [APCI(+)]: *m/z* calcd. for $C_{20}H_{34}BO_5$: 365.2494 [M+H], found: 365.2499.

2-(1-(2-(benzyloxy)phenyl)pentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 4r



Using procedure A (390 nm lamp) 72 mg of *N*-tosylhydrazone **H10** and 61 mg of butylboronic acid afforded 35 mg of **4r** (46 % yield) as a colourless oil after column chromatography on SiO_2. Rf = 0.22 (Hex/EtOAc 20:1).

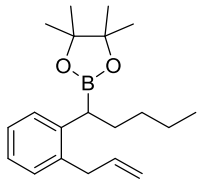
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.52 – 7.46 (m, 2H), 7.42 – 7.34 (m, 2H), 7.34 – 7.27 (m, 1H), 7.22 (dd, *J* = 7.4, 1.8 Hz, 1H), 7.11 (td, *J* = 7.7, 1.8 Hz, 1H), 6.90 (td, *J* = 7.5, 1.2 Hz, 1H), 6.85 (dd, *J* = 8.1, 1.2 Hz, 1H), 5.13 (d, *J* = 12.5 Hz, 1H), 5.08 (d, *J* = 12.5 Hz, 1H), 2.60 (dd, *J* = 8.6, 6.7 Hz, 1H), 1.94 – 1.67 (m, 2H), 1.40 – 1.21 (m, 5H), 1.15 (s, 12H), 0.87 (t, *J* = 6.9 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 156.2 (C), 137.7 (C), 132.7 (C), 129.9 (CH), 128.5 (CH), 127.6 (CH), 127.1 (CH), 126.2 (CH), 120.9 (CH), 111.6 (CH), 83.1 (C), 69.8 (CH_2), 31.8 (CH_2), 30.6 (CH_2), 24.9 (CH_3), 24.7(CH_3), 23.0 (CH_2), 14.3 (CH_3).

^{11}B NMR (129 MHz, $CDCl_3$) δ 34.02.

HRMS [APCI(+)]: *m/z* calcd. for $C_{24}H_{34}BO_3$: 381.2601 [M+H], found: 381.2598.

2-(1-(2-allylphenyl)pentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 4s



Using procedure A (390 nm lamp) 63 mg of *N*-tosylhydrazone **H11** and 61 mg of butylboronic acid afforded 31 mg of **4s** (25 % yield) as a colourless oil after column chromatography on SiO_2. Rf = 0.15 (Hex/EtOAc 20:1).

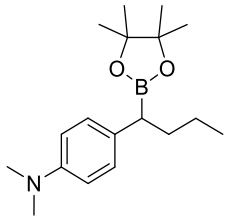
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31 – 7.24 (m, 1H), 7.20 – 7.04 (m, 3H), 5.99 (ddt, *J* = 16.6, 10.1, 6.3 Hz, 1H), 5.09 – 4.93 (m, 2H), 3.54 – 3.34 (m, 2H), 2.52 (t, *J* = 7.8 Hz, 1H), 1.94 – 1.77 (m, 1H), 1.66 – 1.54 (m, 1H), 1.36 – 1.23 (m, 5H), 1.19 (d, *J* = 6.4 Hz, 12H), 0.86 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 142.0 (C), 137.7 (CH), 129.6 (CH), 128.3 (CH), 126.4 (CH), 125.2 (CH), 115.6 (CH_2), 83.3 (C), 37.7 (CH_2), 32.5 (CH_2), 31.9 (CH_2), 24.8 (CH_3), 24.7 (CH_3), 23.0 (CH_2), 14.2 (CH_3).

^{11}B NMR (129 MHz, $CDCl_3$) δ 34.25.

HRMS [APCI(+)]: *m/z* calcd. for $C_{20}H_{32}BO_2$: 315.2490 [M+H], found: 315.2489.

***N,N*-dimethyl-4-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl)aniline 4t**



Using procedure A (390 nm lamp) 63 mg of *N*-tosylhydrazone **H6** and 53 mg of propylboronic acid afforded 58 mg of **4t** (95 % yield) as a yellow oil.

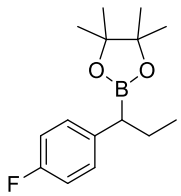
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.09 (d, *J* = 8.7 Hz, 2H), 6.69 (d, *J* = 8.7 Hz, 2H), 2.90 (s, 6H), 2.22 (t, *J* = 7.9 Hz, 1H), 1.87 – 1.68 (m, 1H), 1.62 – 1.50 (m, 1H), 1.36 – 1.14 (m, 16H), 0.88 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 148.5 (C), 131.8 (C), 129.0 (CH), 113.3 (CH), 83.1 (C), 41.1 (CH_3), 35.3 (CH_2), 24.7 (CH_3), 22.5 (CH_2), 14.3 (CH_3).

^{11}B NMR (129 MHz, $CDCl_3$) δ 33.63.

HRMS [ESI(+)]: *m/z* calcd. for $C_{12}H_{20}NO_2$: 194.1539 [M+H_2O-Bpin], found: 194.1543.

2-(1-(4-fluorophenyl)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 4u



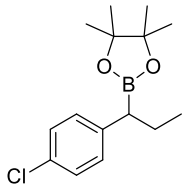
Using procedure A (390 nm lamp) 58.5 mg of *N*-tosylhydrazone **H3** and 44 mg of ethylboronic acid afforded 34 mg of **4u** (69 % yield) as a colourless oil after column chromatography on SiO_2. Rf = 0.22 (Hex/EtOAc 20:1). Spectroscopic data in matches that previously reported in the literature.[23]

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.21 – 7.09 (m, 1H), 6.99 – 6.87 (m, 1H), 1.94 – 1.76 (m, 1H), 1.64 (dq, *J* = 14.8, 7.3 Hz, 1H), 1.21 (s, 3H), 1.20 (s, 3H), 0.89 (t, *J* = 7.3 Hz, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 161.04 (CF, d, *J* = 242.5 Hz), 139.0 (C), 129.7 (CH. d, J_{CF}= 7.6 Hz), 115.05 (CH, d, J_{CF} = 20.8 Hz), 83.4 (C), 26.1 (CH_2), 24.8 (CH_3), 24.7 (CH_3), 13.9 (CH_3).

^{19}F NMR (282 MHz, $CDCl_3$) δ -118.90.

2-(1-(4-chlorophenyl)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 4v



Using procedure A (390 nm lamp) 61.6 mg of *N*-tosylhydrazone **H4** and 44 mg of ethylboronic acid afforded 37 mg of **4v** (66 % yield) as a yellow oil after column chromatography on SiO_2. Rf = 0.45 (Hex/EtOAc 25:1).

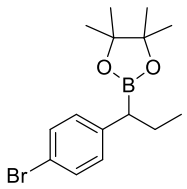
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.24 – 7.17 (m, 2H), 7.17 – 7.09 (m, 2H), 2.19 (t, *J* = 7.9 Hz, 1H), 1.96 – 1.76 (m, 1H), 1.73 – 1.53 (m, 1H), 1.20 (s, 3H), 1.19 (s, 3H), 0.89 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 142.0 (C), 130.9 (C), 129.8 (CH), 128.4 (CH), 83.5 (C), 25.8 (CH_2),, 24.77 2(CH_3),, 24.70 (2CH_3), 13.9 (CH_3).

^{11}B NMR (129 MHz, $CDCl_3$) δ 34.41.

HRMS [ESI(+)]: *m/z* calcd. for $C_{15}H_{22}BClO_2Na$: 303.1294 [M+Na], found: 303.1292.

2-(1-(4-bromophenyl)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 4w



Using procedure A (390 nm lamp) 70,4 mg of *N*-tosylhydrazone **H5** and 44 mg of ethylboronic acid afforded 41 mg of **4w** (64 % yield) as a yellow oil after column chromatography on SiO_2. Rf = 0.40 (Hex/EtOAc 25:1). Spectroscopic data in agreement with literature.[24]

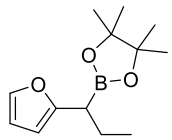
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41 – 7.29 (m, 2H), 7.12 – 7.00 (m, 2H), 2.17 (t, *J* = 7.9 Hz, 1H), 1.96 – 1.75 (m, 1H), 1.63 (dt, *J* = 13.3, 7.4 Hz, 1H), 1.20 (s, 6H), 1.19 (s, 6H), 0.88 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 142.5 (C), 131.4 (CH), 130.3 (CH), 119.0 (C), 83.5 (C), 25.8 (CH_2), 24.77 (2CH_3), 24.71 (2CH_3), 13.9 (CH_3).

^{11}B NMR (129 MHz, $CDCl_3$) δ 33.41.

HRMS [ESI(+)]: *m/z* calcd. for $C_{15}H_{23}BBrO_2$: 325.0969 [M+H], found: 325.0961.

2-(1-(furan-2-yl)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 4x



Using procedure A (390 nm lamp) 52.8 mg of *N*-tosylhydrazone **H7** and 44 mg of ethylboronic acid afforded 36 mg of (75 % yield) as a yellow oil after column chromatography on SiO_2. Rf = 0.41 (Hex/EtOAc 10:1).

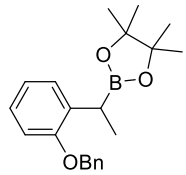
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.28 (d, *J* = 2.0 Hz, 1H), 6.26 (dd, *J* = 3.1, 2.0 Hz, 1H), 6.02 (d, *J* = 3.1 Hz, 1H), 2.39 (t, *J* = 7.4 Hz, 1H), 1.77 (m, 2H), 1.25 (s, 12H), 0.93 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 157.0 (C), 140.8 (CH), 110.2 (CH), 104.8 (CH), 83.7 (C), 24.83 (CH_3), 24.77 (CH_3) , 23.5 (CH_2), 13.7 (CH_3).

^{11}B NMR (129 MHz, $CDCl_3$) δ 33.11.

HRMS [APCI(+)]: m/z calcd. for $C_7H_9O_2$: 125.0597 [M+O-Bpin], found: 125.0593.

2-(1-(2-(benzyloxy)phenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 4y



Using procedure A (390 nm lamp) 76 mg of *N*-tosylhydrazone **H10** and 36 mg of methylboronic acid afforded 31 mg of **4y** (45 % yield) as a colourless oil after column chromatography on SiO_2. Rf = 0.31 (Hex/EtOAc 10:1).

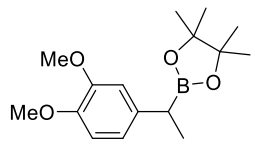
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50 (d, *J* = 7.1 Hz, 2H), 7.43 – 7.35 (m, 2H), 7.35 – 7.27 (m, 1H), 7.23 (dd, *J* = 7.4, 1.8 Hz, 1H), 7.13 (td, *J* = 7.8, 1.8 Hz, 1H), 6.94 (td, *J* = 7.4, 1.2 Hz, 1H), 6.86 (dd, *J* = 8.1, 1.2 Hz, 1H), 5.12 (s, 2H), 2.65 (q, *J* = 7.5 Hz, 1H), 1.38 (d, *J* = 7.5 Hz, 3H), 1.13 (s, 12H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 156.0 (C), 137.6 (C), 134.2 (C), 128.6 (CH), 128.5 (CH), 127.6 (CH), 127.0 (CH), 126.3 (CH), 121.1 (CH), 111.2 (CH), 83.2 (C), 69.7 (CH_2), 24.8 (CH_3), 24.7 (CH_3), 15.3 (CH_3).

^{11}B NMR (129 MHz, $CDCl_3$) δ 33.75.

HRMS [APCI(+)]: *m/z* calcd. for $C_{15}H_{15}O_2$: 227.1067 [M+O-Bpin], found: 227.1065.

2-(1-(3,4-dimethoxyphenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 4z

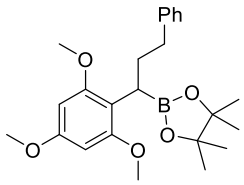


Using procedure A (390 nm lamp) 67 mg of *N*-tosylhydrazone **H8** and 36 mg of methylboronic acid afforded 20 mg of **4z** (45 % yield) as a colourless oil after column chromatography on SiO_2. Rf = 0.15 (Hex/EtOAc 10:1). Spectroscopic data in matches that previously reported in the literature.[25]

^{1}H NMR (300 MHz, $CDCl_3$) δ 6.76 (m, 3H), 3.86 (s, 3H), 3.84 (s, 3H), 2.36 (q, *J* = 7.5 Hz, 1H), 1.30 (d, *J* = 7.5 Hz, 3H), 1.21 (s, 6H), 1.20 (s, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 148.8 (C), 146.7 (C), 137.6 (C), 119.5 (CH), 111.4 (2CH), 83.4 (C), 55.9 (CH_3), 55.8 (CH_3), 24.74 (CH_3), 24.68 (CH_3), 17.4 (CH_3).

4,4,5,5-tetramethyl-2-(3-phenyl-1-(2,4,6-trimethoxyphenyl)propyl)-1,3,2-dioxaborolane 4aa

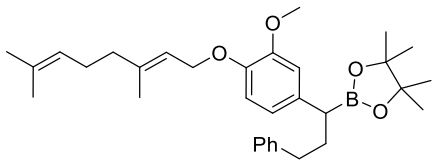


Using procedure A (390 nm lamp) 72 mg of *N*-tosylhydrazone **H9** and 90 mg of phenethylboronic acid afforded 40 mg of **4aa** (48 % yield) as a colourless oil after column chromatography on SiO_2. Rf = 0.35 (Hex/EtOAc 10:1). Spectroscopic data in matches that previously reported in the literature.[26]

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.28 – 7.10 (m, 5H), 6.16 (s, 2H), 3.83 (s, 3H), 3.79 (s, 6H), 2.84 – 2.39 (m, 3H), 2.12 (ddt, *J* = 13.2, 11.1, 5.7 Hz, 1H), 1.81 (dddd, *J* = 13.2, 10.7, 9.3, 5.7 Hz, 1H), 1.28 (s, 6H), 1.26 (s, *6*H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 159.0 (C), 158.6 (C), 143.9 (C), 128.7 (CH), 128.0 (CH), 125.2 (CH), 112.9 (C), 90.8 (CH), 82.8 (C), 55.5 (CH_3), 55.4 (CH_3), 35.4 (CH_2), 32.55, 25.1 (CH_3), 24.9 (CH_3).

(*E*)-2-(1-(4-((3,7-dimethylocta-2,6-dien-1-yl)oxy)-3-methoxyphenyl)-3-phenylpropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 4ab



Using procedure A (390 nm lamp) 92 mg of *N*-tosylhydrazone **H44** and 84 mg of phenethylboronic acid afforded 63 mg of **4ab** (60 % yield) as a colourless oil after column chromatography on SiO_2. Rf = 0.25 (Hex/EtOAc 10:1).

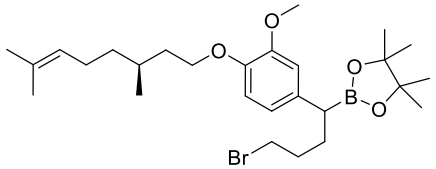
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38 – 7.11 (m, 6H), 6.88 – 6.70 (m, 3H), 5.56 (tq, *J* = 6.5, 1.4 Hz, 1H), 5.25 – 5.00 (m, 1H), 4.61 (d, *J* = 6.5 Hz, 2H), 3.88 (s, 3H), 2.60 (t, *J* = 7.9 Hz, 2H), 2.32 (t, *J* = 7.9 Hz, 1H), 2.25 – 1.92 (m, 6H), 1.73 (s, 3H), 1.70 (s, 3H), 1.62 (s, 3H), 1.24 (s, 3H), 1.22 (s, 12H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 149.1 (C), 145.9 (C), 142.5 (C), 140.1 (C), 135.4 (C), 131.7 (C), 128.5 (CH), 128.2 (CH), 125.6 (CH), 123.9 (CH), 120.1 (CH), 120.1 (CH), 113.3 (CH), 111.8 (CH), 83.3 (C), 65.9 (CH_2), 55.7 (CH_3), 39.5 (CH_2), 35.4 (CH_2), 34.5 (CH_2), 26.3 (CH_2), 25.7 (CH), 24.8 (CH_3), 24.6 (CH_3), 24.6 (CH_3), 17.7 (CH_3), 16.6 (CH_3).

^{11}B NMR (129 MHz, $CDCl_3$) 34.24.

HRMS [ESI(+)]: *m/z* calcd. for $C_{32}H_{46}BO_4$: 505.3484 [M+H], found: 505.3484.

2-(4-bromo-1-(4-(((*S*)-3,7-dimethyloct-6-en-1-yl)oxy)-3-methoxyphenyl)butyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 4ac



Using procedure A (390 nm lamp) 92 mg of *N*-tosylhydrazone **H44** and 100 mg of 3-bromopropylboronic acid afforded 63 mg of **4ac** (60 % yield, *d.r.* = 3.7:1) as a colourless oil after column chromatography on SiO_2. Rf = 0.28 (Hex/EtOAc 10:1).

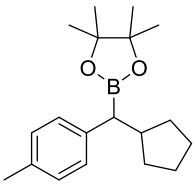
^{1}H NMR (300 MHz, $CDCl_3$) δ 6.88 – 6.61 (m, 3H), 5.28 – 4.98 (m, 1H), 4.02 (dq, *J* = 6.9, 4.1 Hz, 2H), 3.86 (s, 3H), 3.39 (t, *J* = 6.5 Hz, 2H), 2.24 (t, *J* = 7.5 Hz, 1H), 2.09 – 1.76 (m, 6H), 1.70 (s, 3H), 1.62 (s, 3H), 1.23 (s, 6H), 1.21 (s, 6H), 0.98 (s, *diast. minor*), 0.96 (s, *diast. minor*).

^{13}C NMR (75 MHz, $CDCl_3$) δ 149.1 (C), 146.4 (C), 134.9 (C), 131.2 (C), 124.7 (CH), 120.2 (CH), 113.0 (CH), 111.9 (CH), 83.4 (C), 83.2 (C), 67.3 (CH_2), 55.8 (CH_3), 37.1 (CH_2), 36.2 (CH_2), 36.1 (CH_2), 33.8 (CH_2), 32.3 (CH_2), 31.1 (CH_2), 29.6 (CH), 27.5 (CH_3), 25.7 (CH_3), 25.4 (CH_2), 24.8 (CH_3), 24.6 (CH_3), 24.6 (CH_3), 19.6 (CH_3), 17.6 (CH_3).

^{11}B NMR (129 MHz, $CDCl_3$) 33.77.

HRMS [ESI(+)]: *m/z* calcd. for $C_{27}H_{34}BBrO_4$+Na: 545.2409 [M+Na], found: 545.2408.

2-(cyclopentyl(*p*-tolyl)methyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 4ad



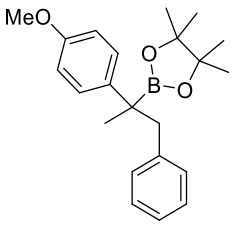
Continuous flow reaction: Using procedure D (390 nm lamp, 50 %, 7 cm) 57,6 mg of *N*-tosylhydrazone **H2** and 68 mg of butylboronic acid afforded 37 mg of **4l** (50 % yield) as a colorless oil after column chromatography on SiO_2 (Hex/EtOAc, 10:1). Rf = 0.63 (Hex/EtOAc 5:1).

^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.14 – 7.01 (m, 4H), 2.30 (s, 3H), 2.05 (d, *J*=11.1, 1H), 1.70 – 1.34 (m, 1H), 1.69 – 1.34 (m, 6H), 1.20 (d, *J*=6.3, 13H), 1.05 – 0.93 (m, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 139.9 (C), 134.5 (C), 129.0 (2 CH), 128.7 (2 CH), 83.3 (2 C), 43.2 (CH), 38.6 (CH_2), 32.8 (CH_2), 32.5 (CH_2), 25.3 (CH_2), 24.9 (4 CH_3), 24.7 (CH), 21.1 (CH_3).

^{11}B NMR (129 MHz, $CDCl_3$) δ 33.27.

2-(2-(4-methoxyphenyl)-1-phenylpropan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 5a



Using procedure B (370 nm lamp) 60,5 mg of *N*-tosylhydrazone **H15** and 60 mg of 4-methoxyphenylboronic acid afforded 46 mg of **5a** (65 % yield) as a colourless oil after column chromatography on SiO_2. Rf = 0.65 (Hex/CH_2Cl_2 1:4).

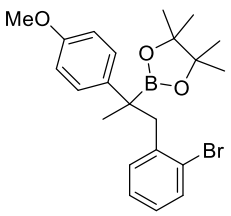
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25 – 7.20 (m, 2H), 7.15 (m, 3H), 7.04 – 6.95 (m, 2H), 6.87 – 6.80 (m, 2H), 3.80 (s, 3H), 3.17 (d, *J* = 13.0 Hz, 1H), 2.90 (d, *J* = 13.0 Hz, 1H), 1.25 (s, 3H), 1.22 (s, 6H), 1.18 (s, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 157.0 (C), 139.8 (C), 138.6 (C), 130.6 (CH), 128.2 (CH), 127.6 (CH), 125.8 (CH), 113.5 (CH), 83.6 (C), 55.3 (CH_3), 45.9 (CH_2), 24.9 (CH_3), 24.6 (CH_3), 20.8 (CH_3).

^{11}B NMR (129 MHz, $CDCl_3$) δ 30.85.

HRMS [ESI(+)]: *m/z* calcd. for $C_{16}H_{17}O_2$: 241.1223 [M+O-Bpin], found: 241.1226.

2-(1-(2-bromophenyl)-2-(4-methoxyphenyl)propan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 5b



Using procedure B (370 nm lamp) 76 mg of *N*-tosylhydrazone **H16** and 60 mg of 4-methoxyphenylboronic acid afforded 62 mg (72 % yield) as a colourless oil after column chromatography on SiO_2. Rf = 0.70 (Hex/CH_2Cl_2 1:4)..

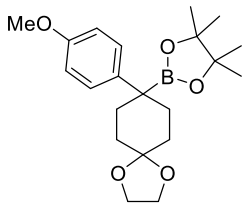
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.49 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.25 – 7.17 (m, 2H), 7.07 – 6.94 (m, 2H), 6.91 (dd, *J* = 7.3, 2.2 Hz, 1H), 6.87 – 6.79 (m, 2H), 3.80 (s, 3H), 3.44 (d, *J* = 13.9 Hz, 1H), 3.14 (d, *J* = 13.8 Hz, 1H), 1.30 (s, 4H), 1.22 (s, 6H), 1.21 (s, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 157.5 (C), 139.6 (C), 138.2 (C), 132.7 (CH), 131.5 (CH), 128.3 (CH), 127.4 (CH, 126.6 (CH), 113.5 (CH), 83.7 (C), 55.3 (CH_3), 43.6 (CH_2), 24.8 ($2CH_3$), 24.6 ($2CH_3$), 20.0 (CH_3).

^{11}B NMR (129 MHz, $CDCl_3$) δ 31.3.

HRMS [APCI(+)]: *m/z* calcd. for $C_{16}H_{16}BrO_2$ 319.0328 [M+O-Bpin], found: 319.0326.

2-(8-(4-methoxyphenyl)-1,4-dioxaspiro[4.5]decan-8-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 5c



Batch reaction: Using procedure B (370 nm lamp) 65 mg of *N*-tosylhydrazone **H17** and 61 mg of 4-methoxyphenylboronic acid afforded 42 mg (56 % yield) of **5c** as a colourless oil after column chromatography on SiO_2. Rf = 0.20 (Hex/EtOAc 20:1).

Continuous flow reaction: Using procedure F with two 370 nm lamps (32 W, 75 %, 3 cm) 65 mg of *N*-tosylhydrazone **H17** and 15 mg of 4-methoxyphenylboronic acid (1 equiv) afforded 21 mg (56 % yield) of **5c** as a colourless oil after column chromatography on SiO_2. Rf = 0.20 (Hex/EtOAc 20:1).

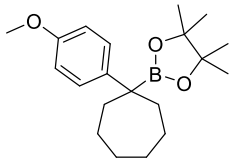
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34 – 7.20 (m, 2H), 6.91 – 6.75 (m, 2H), 4.07 – 3.88 (m, 4H), 3.79 (s, 3H), 2.30 (m, 2H), 1.91 – 1.63 (m, 6H), 1.18 (s, 12H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 157.3 (C), 138.0 (C), 127.4 (CH), 113.6 (CH), 108.9 (C), 83.6 (C), 64.3 (CH_2), 55.3 (CH_3), 34.1 (CH_2), 32.0 (CH_2), 24.7 (CH_3).

^{11}B NMR (129 MHz, $CDCl_3$) δ 34.84.

HRMS [APCI(+)]: *m/z* calcd. for $C_{21}H_{32}BO_5$: 375.2337 [M+H], found: 375.2329.

2-(1-(4-methoxyphenyl)cycloheptyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 5d



Batch reaction: Using procedure B (370 nm lamp) 56 mg of *N*-tosylhydrazone **H18** and 61 mg of 4-methoxyphenylboronic acid afforded 47 mg of **5d** (71 % yield) as a colourless oil after column chromatography on SiO_2. Rf = 0.75 (Hex/CH_2Cl_2 1:4).

Continuous flow reaction: Using procedure F with two 370 nm lamps (32 W, 75 %, 3 cm) 56 mg of *N*-tosylhydrazone **H18** (2 equiv) and 15 mg of 4-methoxyphenylboronic acid (1 equiv) afforded 14 mg of **5d** (42 % yield) as a colourless oil after column chromatography on SiO_2. Rf = 0.75 (Hex/CH_2Cl_2 1:4).

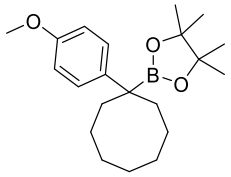
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32 – 7.21 (m, 2H), 6.89 – 6.77 (m, 2H), 3.80 (s, 3H), 2.20 (dd, *J* = 14.3, 7.8 Hz, 2H), 1.86 (m, 2H), 1.60 (m, 8H), 1.20 (s, 12H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 156.9 (C), 140.4 (C), 127.8 (CH), 113.5 (CH), 83.3 (C), 55.3 (CH_3), 36.7 (CH_2), 29.6 (CH_2), 24.7 (CH_3), 24.7 (CH_3).

^{11}B NMR (129 MHz, $CDCl_3$) δ 35.03.

HRMS [ESI(+)]: *m/z* calcd. for ($C_{14}H_{21}O_2$): 221.1536 [M+H_2O-Bpin], found: 221.1537.

2-(1-(4-methoxyphenyl)cyclooctyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 5e



Batch reaction: Using procedure B (370 nm lamp) 59 mg of *N*-tosylhydrazone **H19** and 61 mg of 4-methoxyphenylboronic acid afforded 66 mg of **5e** (95 % yield) as a colourless oil after column chromatography on SiO_2. Rf = 0.75 (Hex/CH_2Cl_2 1:4).

Continuous flow reaction: Using procedure E with two 370 nm lamps (32 W, 75 %, 7 cm) 59 mg of *N*-tosylhydrazone **H19** (2 equiv), 15 mg of 4-methoxyphenylboronic acid (1 equiv) 41 mg of DIPEA (3 equiv) and 49 mg of DBU (3 equiv) afforded 15 mg of **5e** (44 % yield) as a colourless oil after column chromatography on SiO_2. Rf = 0.75 (Hex/CH_2Cl_2 1:4).

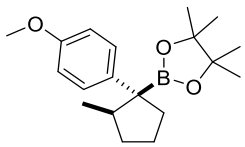
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32 – 7.19 (m, 2H), 6.89 – 6.79 (m, 2H), 3.80 (s, 3H), 2.24 – 2.08 (m, 2H), 2.01 (dd, *J* = 14.8, 7.9 Hz, 2H), 1.70-1.42 (m, 10H), 1.19 (s, 12H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 157.0 (C), 139.0 (C), 128.2 (CH), 113.5 (CH), 83.3 (2C), 55.2 (CH_3), 30.5 (CH_2), 29.0 (CH_2), 25.2 (CH_2), 24.6 (CH_3), 24.0 (CH_2).

^{11}B NMR (129 MHz, $CDCl_3$) δ 33.56

HRMS [ESI(+)]: *m/z* calcd. for $C_{21}H_{34}BO_3$: $(M+H)^+$: 345.2596 [M+H], found: 345.2590.

1-(4-methoxyphenyl)-2-methylcyclopentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 5f



Using procedure B (370 nm lamp) 53,3 mg of *N*-tosylhydrazone **H20** and 61 mg of 4-methoxyphenylboronic acid afforded 40 mg of **5f** (63 % yield) as a colourless oil after column chromatography on SiO_2 Rf = 0.75 (Hex/CH_2Cl_2 1:4).

Mixture of diastereoisomers 6,6: 1. Spectroscopic data of the major isomer

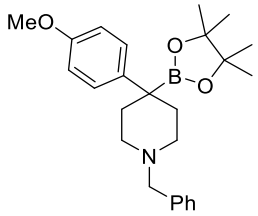
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25 – 7.18 (m, 2H), 6.86 – 6.78 (m, 2H), 3.78 (s, 3H), 2.36 – 2.12 (m, 2H), 1.93 – 1.49 (m, 4H), 1.45 – 1.31 (m, 1H), 1.21 (s, 6H), 1.19 (s, 6H), 1.14 (d, *J* = 6.7, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 157.1 (C), 138.8 (C), 127.9 (CH), 113.5 (CH), 83.2 (CH_2), 55.3 (CH_3), 42.7 (CH), 35.5 (CH_2), 33.3 (CH_2), 24.8 (CH_3), 24.7 (CH_3), 22.2 (CH_2), 18.5 (CH_3).

^{11}B NMR (129 MHz, $CDCl_3$) δ 34.16.

HRMS [ESI(+)]: *m/z* calcd. for $C_{19}H_{30}BO_3$: 317.2283 [M+H], found: 317.2268.

1-benzyl-4-(4-methoxyphenyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)piperidine 5g



Batch reaction: Using procedure B (370 nm lamp) 71 mg of *N*-tosylhydrazone **H21** and 60,8 mg of 4-methoxyphenylboronic acid afforded 59 mg of **5g** (72 % yield) as a colourless oil after column chromatography on SiO_2. Rf = 0.40 (Hex/EtOAc 1:1).

Continuous flow reaction: Using procedure E with two 370 nm lamps (32 W, 75 %, 7 cm) 71 mg of *N*-tosylhydrazone **H21** and 60,8 mg of 4-methoxyphenylboronic acid afforded 48 mg of **5g** (58 % yield) as a colourless oil after column chromatography on SiO_2. Rf = 0.40 (Hex/EtOAc 1:1).

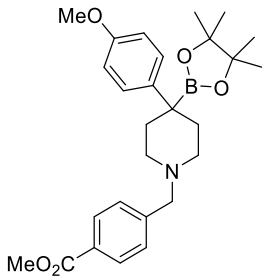
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38 – 7.31 (m, 4H), 7.28 – 7.20 (m, 3H), 6.89 – 6.80 (m, 2H), 3.80 (s, 3H), 3.56 (s, 2H), 3.04 – 2.86 (m, 2H), 2.38 – 2.24 (m, 2H), 2.23 – 2.09 (m, 2H), 1.72 (td, *J* = 12.5, 3.5 Hz, 2H), 1.14 (s, 12H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 157.3 (C), 138.4 (C), 138.2 (C), 129.5 (CH), 128.2 (CH), 127.2 CH), 127.0 (CH), 113.63 (c), 83.4 (s), 63.6 (CH_2), 55.3 (CH_3), 53.3 (CH_3), 34.1 (CH_2), 24.6 (CH_3).

^{11}B NMR (129 MHz, $CDCl_3$) δ 33.55.

HRMS [APCI(+)]: *m/z* calcd. for $C_{25}H_{35}BNO_3$: 408.2705 [M+H], found: 408.2708.

methyl 4-((4-(4-methoxyphenyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)piperidin-1-yl)methyl)benzoate 5h



Using procedure B (370 nm lamp) 83 mg of *N*-tosylhydrazone **H22** and 60,8 mg of 4-methoxyphenylboronic acid afforded 33 mg of **5h** (35 % yield) as a colourless oil after column chromatography on SiO_2. Rf = 0.45 (Hex/EtOAc 1:1).

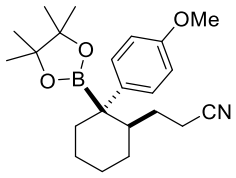
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.09 – 7.87 (m, 2H), 7.40 (d, *J* = 8.1 Hz, 2H), 7.25 – 7.18 (m, 2H), 6.88 – 6.74 (m, 2H), 3.90 (s, 3H), 3.77 (s, 3H), 3.56 (s, 2H), 2.90 (d, *J* = 11.4 Hz, 2H), 2.28 (d, *J* = 12.6 Hz, 2H), 2.21 – 2.07 (m, 2H), 1.70 (td, *J* = 12.6, 3.5 Hz, 2H), 1.12 (s, 12H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 167.2 (C), 157.3 (C), 144.0 (C), 138.2 (C), 129.6 (CH), 129.2 (CH), 128.9 (C), 127.1 (CH), 113.7 (CH), 83.5 (C), 63.2 (CH_2), 55.3 (CH_3), 53.5 (CH_2), 52. (CH_2), 34.0 (CH_2), 24.6 (CH_3).

^{11}B NMR (129 MHz, $CDCl_3$) δ 30.89.

HRMS [ESI(+)]: *m/z* calcd. for $C_{27}H_{37}BNO_5$: : 466.2759 [M+H], found: 466.2761.

3-(2-(4-methoxyphenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohexyl)propanenitrile 5i



Using procedure B (370 nm lamp) 64 mg of *N*-tosylhydrazone **H23** and 61 mg of 4-methoxyphenylboronic acid afforded 61 mg (82 % yield) as a colourless oil after column chromatography on SiO_2. Rf = 0.40 (Hex/EtOAc 5:1).

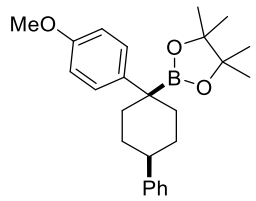
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.26 – 7.19 (m, 2H), 6.90 – 6.82 (m, 2H), 3.81 (s, 3H), 2.24 (ddd, *J* = 16.9, 8.4, 5.5 Hz, 1H), 2.13 (dt, *J* = 16.7, 8.2 Hz, 1H), 2.09 – 2.02 (m, 1H), 1.88 – 1.77 (m, 3H), 1.73 (m, 2H), 1.66 – 1.57 (m, 2H), 1.49 (m, 1H), 1.32 (m, 14H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 157.5 (C), 138.5 (C), 128.5 (CH), 120.5 (C), 113.8 (CH), 83.4 (C), 55.3 (CH_3), 45.2 (CH), 38.3 (CH_2), 29.3 (CH_2), 27.8 (CH_2), 26.2 (CH_2), 25.35 (CH_3), 25.25 (CH_3), 25.1 (CH_2), 15.9 (CH_2).

^{11}B NMR (129 MHz, $CDCl_3$) δ 34.55.

HRMS [ESI(+)]: calcd. for $(C_{22}H_{33}BNO_3)^+$ $(M+H)^+$: 370.2548, found: 370.2540.

1-(4-Methoxyphenyl)-4-phenylcyclohexyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 5j



Using procedure B (370 nm lamp) 137 mg of *N*-tosylhydrazone **H24** and 30 mg of 4-methoxyphenylboronic acid afforded 48 mg of **5j** (61 % yield) after column chromatography on SiO_2. Rf = 0.70 (Hex/CH_2Cl_2 1:4).

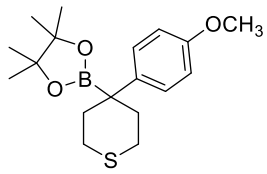
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37 – 7.27 (m, 4H), 7.22 (m, 3H), 6.92 – 6.80 (m, 2H), 3.80 (s, 3H), 2.59 – 2.40 (m, 3H), 2.10 – 1.94 (m, 2H), 1.78 – 1.61 (m, 2H), 1.51 (td, *J* = 12.8, 3.0 Hz, 2H), 1.21 (s, 12H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 157.3 (C), 147.9 (C), 139.3 (C), 128.5 (CH), 127.2 (CH), 126.9 (CH), 126.0 (CH), 113.7 (CH), 83.5 (C), 55.3 (CH_3), 44.2 (CH), 35.4, (CH_2), 33.8 (CH_2), 24.7 (CH_3).

^{11}B NMR (129 MHz, $CDCl_3$) δ 34.18.

HRMS [ESI(+)]: *m/z* calcd. for $C_{25}H_{34}BO_3$: 393.2596 [M+H], found: 393.2599.

2-(4-(4-methoxyphenyl)tetrahydro-2H-thiopyran-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 5k



Batch reaction: Using procedure B (370 nm lamp) 57 mg of *N*-tosylhydrazone **H41** and 53 mg of 4-methoxyphenylboronic acid afforded 10 mg of **5k** (27 % yield) after column chromatography on SiO_2.

Continuous flow reaction: Using procedure F with two 370 nm lamps (32 W, 75 %, 3 cm) 57 mg of *N*-tosylhydrazone **H41** and 15 mg of 4-methoxyphenylboronic acid (1 equiv) afforded 27 mg of **5k** (81 % yield) as a colourless oil after column chromatography on neutral alumina (Hex/EtOAc, 8:1). Rf = 0.68 (SiO_2, Hex/EtOAc 3:1).

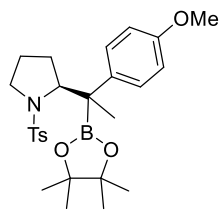
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25 – 7.18 (m, 2H), 6.87 – 6.80 (m, 2H), 3.78 (s, 3H), 2.93 – 2.78 (m, 2H), 2.73 – 2.61 (m, 2H), 2.61 – 2.49 (m, 2H), 1.79 (td, *J* = 12.6, 3.0 Hz, 2H), 1.19 (s, 12H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 157.5 (C), 138.4 (C), 127.2 (2 CH), 113.9 (2 CH), 83.7 (C), 55.3 (CH_3), 36.1 (2 CH_2), 27.8 (2 CH_2), 24.8 (4 CH_3).

^{11}B NMR (129 MHz, $CDCl_3$) δ 33.54.

HRMS [ESI(+)]: *m/z* calcd. for $C_{18}H_{28}BO_3S$: 335.1847 [M+H], found: 335.1847.

(2*S*)-2-(1-(4-methoxyphenyl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)-1-tosylpyrrolidine 5l



Using procedure B (370 nm lamp) 87 mg of *N*-tosylhydrazone **H25** and 53 mg of 4-methoxyphenylboronic acid afforded 62 mg of **5l** (63 % yield) as a colourless oil after column chromatography on SiO_2. Rf = 0.30 (Hex/EtOAc 3:1).

Spectroscopic data for the major isomer-

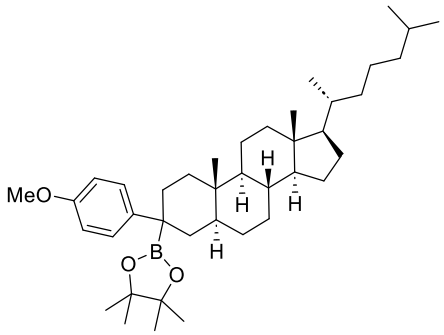
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.67 – 7.59 (m, 2H), 7.41 – 7.35 (m, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 6.87 – 6.82 (m, 2H), 4.41 – 4.24 (m, 1H), 4.13 (q, *J* = 7.1 Hz, 1H), 3.80 (s, 3H), 3.52 (ddd, *J* = 11.1, 7.7, 2.4 Hz, 1H), 3.20 (ddd, *J* = 11.6, 7.3, 5.7 Hz, 1H), 3.00 (ddd, *J* = 12.1, 10.4, 6.3 Hz, 1H), 2.41 (s, 3H), 1.88 – 1.61 (m, 2H), 1.42 (s, 3H), 1.27 (s, 6H), 1.24 (s, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 157.6 (C), 142.8 (C), 136.6 (C), 135.5 (C), 129.6 (CH), 129.4 (CH), 127.5 (CH), 113.0 (CH), 83.6 (CH_3), 67.5 (CH), 55.1 (CH_3), 50.5 (CH_2), 29.8 (CH_2), 24.99 (CH_3), 24.95 (CH_3), 24.5 (CH_2), 21.6 (CH_3), 19.2 (CH_3).

^{11}B NMR (129 MHz, $CDCl_3$) δ 34.47.

HRMS [APCI(+)]: *m/z* calcd. for $C_{26}H_{37}BNO_5S$: 486.2480 [M+H] , found: 486.2485.

Pinacol boronic ester from cholestanone *N*-tosylhydrazone 5m



Using procedure C (370 nm lamp) 221 mg of *N*-tosylhydrazone **H26** and 30,3 mg of 4-methoxyphenylboronic acid afforded 42 mg of **5m** (38 % yield) as a 2: 1 mixture of diastereoisimers after column chromatography on deactivated SiO_2. Rf = 0.80 (Hex/CH_2Cl_2 1:5).

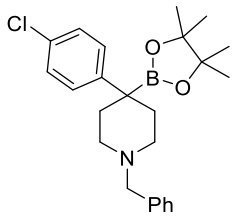
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.28 (m, 2H), 6.85 (m, 2H), 3.82 (s, 3H, major isomer), 3.80 (s, 3H, minor isomer), 2.30 – 2.12 (m, 1H), 2.02 – 0.56 (m, 56H).

^{13}C NMR (75 MHz, $CDCl_3$) (major isomer) δ 156.6, 136.0, 128.5, 113.6, 83.0, 56.6, 56.3, 55.1, 54.4, 42.7, 40.8, 40.1, 39.6, 36.4, 36.3, 35.9, 35.5, 34.0, 34.0, 32.0, 29.0, 28.4, 28.2, 24.7, 24.5, 24.5, 24.3, 24.0, 23.0, 22.7, 20.8, 18.8, 12.5, 12.2.

^{11}B NMR (129 MHz, $CDCl_3$) δ 35.09.

HRMS [ESI(+)]: *m/z* calcd. for ($C_{40}H_{66}BO_3$): 605.5100 [M+H], found: 605.5063.

1-benzyl-4-(4-chlorophenyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)piperidine 5n



Using procedure C 142 mg of *N*-tosylhydrazone **H21** and 31 mg of 4-chlorophenylboronic acid afforded 21 mg of **5n** (65 % yield) as a white solid after column chromatography on deactivated SiO_2. Rf = 0.50 (Hex/EtOAc 1:1).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31 (m, 4H), 7.28-7.20 (m, 5H), 3.53 (s, 2H), 2.93 (d, *J* = 11.4 Hz, 2H), 2.29 (dd, *J* = 12.9, 2.5 Hz, 2H), 2.13 (td, *J* = 11.9, 2.3 Hz, 2H), 1.67 (dd, *J* = 12.3, 3.5 Hz, 2H), 1.12 (s, 12H).

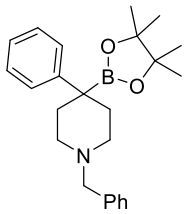
^{13}C NMR (75 MHz, $CDCl_3$) δ 144.9 (C), 138. (C), 131.0 (C), 129.5 (CH), 128.3 (CH), 128.2 (CH), 127.7 (CH), 127.1 (CH), 83.7 (C), 63.5 (CH_2), 53.2 (CH_2), 33.9 (CH_2), 24.6 (CH_3).

^{11}B NMR (129 MHz, $CDCl_3$) δ 32.58.

HRMS [ESI(+)]: *m/z* calcd. for $C_{24}H_{33}BClNO_2$: 412.2209 [M+H], found: 412.2218.

m.p. = 108 – 110 ºC

1-benzyl-4-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)piperidine 5o



Using procedure C (370 nm lamp) 142 mg of *N*-tosylhydrazone **H21** and 24 mg of phenylboronic acid afforded 38 mg of **5o** (50 % yield) as a colourless oil after column chromatography on deactivated SiO_2. Rf = 0.50 (Hex/EtOAc 1:1).

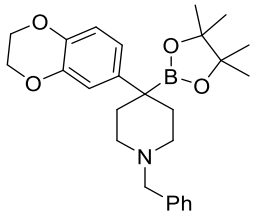
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44 – 7.20 (m, 9H), 3.57 (s, 2H), 3.09 – 2.90 (m, 2H), 2.35 (dq, *J* = 12.7, 3.0 Hz, 2H), 2.19 (td, *J* = 11.8, 2.3 Hz, 2H), 1.78 (td, *J* = 12.5, 3.6 Hz, 2H), 1.15 (s, 12H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 146.3 (C), 138.2 (C), 129.5 (CH), 128.3 (CH), 128.2 (CH), 127.0 (CH), 126.2 (CH), 125.3 (CH), 83.5 (C), 63.6 (CH_2), 53.3 (CH_2), 34.0 (CH_2), 24.6 (CH_3).

^{11}B NMR (129 MHz, $CDCl_3$) δ 34.68.

HRMS [ESI(+)]: *m/z* calcd. for $C_{24}H_{33}BNO_2$: 378.2599 [M+H], found: 378.2611.

1-benzyl-4-(2,3-dihydrobenzo[b][1,4]dioxin-6-yl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)piperidine 5p



Using procedure C (370 nm lamp) 137 mg of *N*-tosylhydrazone **H21** and 72 mg of (2,3-dihydrobenzo[b][1,4]dioxin-6-yl)boronic acid afforded 56 mg of **5p** (65 % yield) as a colourless oil after column chromatography on SiO_2. Rf = 0.20 (Hex/EtOAc 1:1).

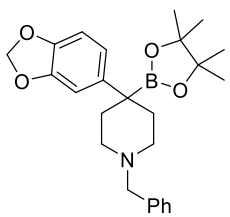
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41 – 7.18 (m, 5H), 6.87 – 6.75 (m, 3H), 4.23 (s, 4H), 3.53 (s, 2H), 2.92 (d, *J* = 11.4 Hz, 2H), 2.22 (d, *J* = 12.7 Hz, 2H), 2.12 (t, *J* = 11.7 Hz, 2H), 1.77 – 1.61 (m, 2H), 1.12 (s, 12H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 143.2 (C), 141.2 (C), 139.8 (C), 138.0 (C), 129.6 (CH), 128.2 (CH), 127.0 (CH), 119.4 (CH), 116.8 (CH), 115.1 (CH), 83.5 (C), 75.1, 64.5 (CH_2), 64.4 (CH_2), 63.5 (CH_2), 53.2 (CH_2), 34.1 (CH_2), 25.0 (CH_3), 24.6 (CH_3).

^{11}B NMR (129 MHz, $CDCl_3$) δ 31.22.

HRMS [APCI(+)]: *m/z* calcd. for $C_{26}H_{35}BNO_4$: 436.2654 [M+H], found: 436.2660.

4-(benzo[d][1,3]dioxol-5-yl)-1-benzyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)piperidine 5q



Using procedure C (370 nm lamp) 142 mg of *N*-tosylhydrazone **H21** and 33 mg of benzo[d][1,3]dioxol-5-ylboronic acid afforded 44 mg of **5q** (52 % yield) as a colourless oil after column chromatography on deactivated SiO_2. Rf = 0.40 (Hex/EtOAc 1:4).

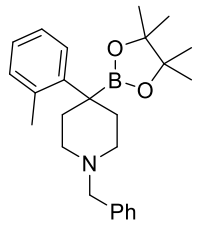
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39 – 7.20 (m, 5H), 6.87 (d, *J* = 1.6 Hz, 1H), 6.82 – 6.71 (m, 2H), 5.92 (s, 2H), 3.55 (s, 2H), 3.06 – 2.82 (m, 2H), 2.32 – 2.22 (m, 2H), 2.14 (td, *J* = 11.9, 2.3 Hz, 2H), 1.82 – 1.61 (m, 2H), 1.15 (s, 12H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 147.6 (C), 145.1 (C), 140.5 (C), 138.0 (C), 129.6 (CH), 128.2 (CH), 127.1 (CH), 119.1 (CH), 108.1 (CH), 107.1 (CH), 100.1 (CH_2), 83.6 (CH_3), 63.5 (CH_2), 53.2 (CH_2), 34.2 (CH_2), 24.6 (CH_3).

^{11}B NMR (129 MHz, $CDCl_3$) δ 33.63.

HRMS [APCI(+)]: *m/z* calcd. for $C_{25}H_{33}BNO_4$: 422.2497 [M+H], found: 422.2506.

1-benzyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4-(o-tolyl)piperidine 5r



Using procedure C (370 nm lamp) 142 mg of *N*-tosylhydrazone **H21** and 27 mg of 3-methoxyphenylboronic acid afforded 43 mg of **5r** (55 % yield) as a colourless oil after column chromatography on deactivated SiO_2. Rf = 0.43 (Hex/EtOAc 1:1).

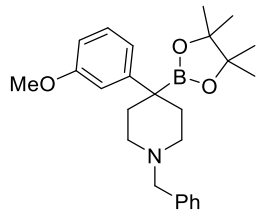
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25 (dd, *J* = 6.2, 2.4 Hz, 3H), 6.93 – 6.81 (m, 2H), 4.62 (dd, *J* = 7.5, 5.9 Hz, 1H), 3.80 (s, 3H), 2.41 (t, *J* = 7.4 Hz, 2H), 2.11 (s, 3H), 1.91 - 1.13 (m, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 144.7 (C), 138.1 (C), 136.3 (C), 131.7 (CH), 129.6 (CH), 128.2 (CH), 127.0 (CH), 126.2 (CH), 126.1 (CH), 125.4 (CH), 83.5 (C), 63.5 (CH_2), 51.9 (CH_2), 33.6 (CH_2), 25.0 (CH_3), 21.6.

^{11}B NMR (129 MHz, $CDCl_3$) δ 31.44.

HRMS [APCI(+)]: *m/z* calcd. for $C_{25}H_{35}BNO_2$: 392.2755 [M+H], found: 392.2761.

1-benzyl-4-(3-methoxyphenyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)piperidine 5s



Using procedure C (370 nm lamp) 142 mg of *N*-tosylhydrazone **H21** and 30,3 mg of 3-methoxyphenylboronic acid afforded 42 mg of **5s** (51 % yield) as a white solid after column chromatography on deactivated SiO_2. Rf = 0.40 (Hex/EtOAc 1:5).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35 – 7.15 (m, 6H), 6.95 – 6.86 (m, 2H), 6.69 (ddd, *J* = 8.2, 2.6, 0.9 Hz, 1H), 3.78 (s, 3H), 3.54 (s, 2H), 2.94 (d, *J* = 11.1 Hz, 2H), 2.34 – 2.24 (m, 2H), 2.15 (td, *J* = 11.8, 2.2 Hz, 2H), 1.75 (td, *J* = 12.4, 3.6 Hz, 2H), 1.13 (s, 12H).

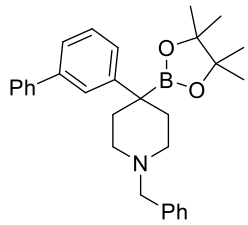
^{13}C NMR (75 MHz, $CDCl_3$) δ 159.6 (C), 148.1 (C), 138.1 (C)), 129.5 (CH), 129.1 (CH), 128.2 (CH), 127.0 (CH), 118.8 (CH), 112.2 (CH), 110.6 (CH), 83.5 (C), 63.6 (CH_2), 55. (CH_3), 53.3 (CH_2), 34.1 (CH_2), 24.6 (CH_2).

^{11}B NMR (129 MHz, $CDCl_3$) δ 36.64.

HRMS [ESI(+)]: *m/z* calcd. for $C_{25}H_{35}BNO_3$: 408.2705 [M+H], found: 408.2722.

m.p. = 76 – 78 ºC

4-([1,1'-biphenyl]-3-yl)-1-benzyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)piperidine 5t



Using procedure C (370 nm lamp) 142 mg of *N*-tosylhydrazone **H21** and 37 mg of 3-biphenylboronic acid afforded 40 mg of **5t** (44 % yield) as a colourless oil after column chromatography on deactivated SiO_2. Rf = 0.4 (Hex/EtOAc 1:1)

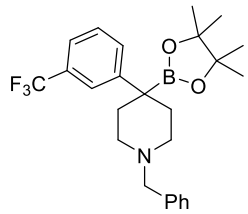
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.69 – 7.50 (m, 3H), 7.49 – 7.19 (m, 12H), 3.58 (s, 2H), 2.99 (d, *J* = 10.9 Hz, 2H), 2.39 (d, *J* = 12.6 Hz, 2H), 2.21 (td, *J* = 11.8, 2.2 Hz, 2H), 1.83 (td, *J* = 12.4, 3.6 Hz, 2H), 1.15 (s, 12H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 146.8 (C), 141.8 (C), 141.0 (C), 137.9 (C), 129.6 (CH), 128.8 (CH), 128.7 (CH), 128.2 (CH), 127.3 (CH), 127.1 (CH), 127.1 (CH), 125.3 (CH), 125.2 (CH), 124.3 (CH), 83.6 (C), 63.5 (CH_2), 53.2 (CH_2), 34.0 (CH_2), 24.7 (CH_3).

^{11}B NMR (129 MHz, $CDCl_3$) δ 34.01.

HRMS [ESI(+)]: *m/z* calcd. for $C_{30}H_{37}BNO_2$: 454.2912 [M+H], found: 454.2925.

1-benzyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4-(3-(trifluoromethyl)phenyl)piperidine 5u



Using procedure C (370 nm lamp) 142 mg of *N*-tosylhydrazone **H21** and 38 mg of 3-trifluoromethylphenylboronic acid afforded 41 mg of **5u** (45 % yield) as a white solid after column chromatography on deactivated SiO_2. Rf = 0.20 (Hex/EtOAc 1:5).

^{1}H NMR (300 MHz, $(CD_3)_2CO$) δ 7.71 – 7.40 (m, 4H), 7.38 – 7.16 (m, 5H), 3.50 (s, 2H), 2.43 – 2.27 (m, 2H), 2.19 (td, *J* = 11.8, 2.2 Hz, 2H), 1.68 (td, *J* = 12.3, 3.7 Hz, 2H), 1.15 (s, 12H).

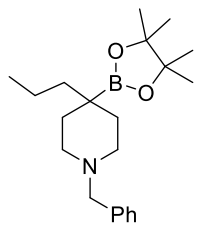
^{13}C NMR (75 MHz, $(CD_3)_2CO$) δ 149.6 (C), 139.7 (C), 130.8 (C), 130.0 (CH), 129.8 (CH), 129.0 (CH), 127.7 (CH), 123.8 (CH), 123.7 (CH), 123.0 (CH), 122.9 (CH), 84.6 (C), 63.8 (CH2), 53.8 (CH_2), 35.0 (CH_2), 24.9 (CH_3).

^{11}B NMR (129 MHz, $CDCl_3$) δ 34.71.

HRMS [ESI(+)]: *m/z* calcd. for $C_{25}H_{32}BF_3NO_2$: 446.2473 [M+H], found: 446.2487.

m.p. = 96 ºC

1-benzyl-4-propyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)piperidine 5v



Batch reaction: Using procedure B (370 nm lamp) 71 mg of *N*-tosylhydrazone **H21** and 53 mg of propylboronic acid afforded 40 mg of **5v** (58 % yield) as a colourless oil after column chromatography on deactivated SiO_2. Rf = 0.20 (EtOAc/Hex. 2:1).

Continuous flow reaction: Using procedure F with two 370 nm lamps (32 W, 75 %, 3 cm) 71 mg of *N*-tosylhydrazone **H21** (2 equiv) and 10 mg of propylboronic acid afforded 20 mg of **5v** (58 % yield) as a colourless oil after column chromatography on deactivated SiO_2. Rf = 0.20 (EtOAc/Hex. 1:2).

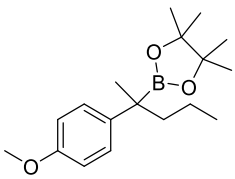
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38 – 7.13 (m, 5H), 3.48 (s, 2H), 2.86 – 2.69 (m, 2H), 1.97 (td, *J* = 11.8, 2.4 Hz, 2H), 1.90 – 1.79 (m, 2H), 1.30 – 1.20 (m, 4H), 1.21 (s, 12H), 0.93 – 0.79 (m, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 138.2 (C), 129.6 (C), 128.1 (CH), 126.9 (CH), 83.2 (C), 63.8 (CH_2), 53.0 (CH_2), 43.1 (CH_2), 34.7 (CH_2), 25.0 (CH_3), 19.0 (CH_2), 15.2 (CH_3).

^{11}B NMR (129 MHz, $CDCl_3$) δ 34.03.

HRMS [APCI(+)]: *m/z* calcd. for $C_{21}H_{35}BNO_2$: 344.2755 [M+H], found: 344.2762.

2-(2-(4-methoxyphenyl)pentan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 7a



Using procedure A (390 nm lamp) 63,7 mg of *N*-tosylhydrazone **H27** and 53 mg of propylboronic acid afforded 48 mg of **7a** (80 % yield) as a colourless oil after column chromatography in deactivated SiO_2. Rf = 0.22 (Hex/EtOAc 20:1).

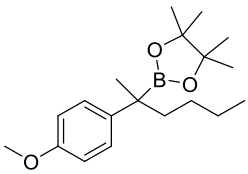
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31 – 7.18 (m, 2H), 6.88 – 6.77 (m, 2H), 3.78 (s, 3H), 1.83 – 1.68 (m, 1H), 1.61 (ddd, *J* = 13.2, 10.0, 6.5 Hz, 1H), 1.31 (s, 3H), 1.24 - 1.14 (m, 2H + 2s, 12H), 0.88 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 157.1 (C), 139.6 (C), 127.8 (CH), 113. (CH), 83.3 (C), 55.3 (CH_3), 42.1 (CH_2), 24.7 (CH_3), 21.9 (CH_3), 19.0 (CH_2), 15.1 (CH_3).

^{11}B NMR (129 MHz, $CDCl_3$) δ 34.20.

HRMS [APCI(+)]: *m/z* calcd. for $C_{18}H_{29}BO_3$+Na: 327.2102 [M+Na], found: 327.2102.

2-(2-(4-methoxyphenyl)hexan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 7b



Using procedure A (390 nm lamp) 63,7 mg of *N*-tosylhydrazone **H27** and 61 mg of butylboronic acid afforded 46 mg of **7b** (63 % yield) as a colourless oil after column chromatography in SiO_2. Rf = 0.20 (Hex/EtOAc 40:1).

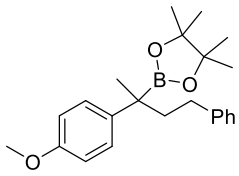
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.26 – 7.20 (m, 2H), 6.88 – 6.78 (m, 2H), 3.78 (s, 3H), 1.77 (ddd, *J* = 13.0, 9.5, 6.5 Hz, 1H), 1.69 – 1.56 (m, 1H), 1.30 (s, 3H), 1.28 – 1.15 (m, 4H), 1.20 (s, 6H), 1.19 (s, 6H), 0.86 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 157.1 (C), 139.7, 127.8 (CH), 113.5 (CH), 83.3 (C), 55.2 (CH_3), 39.3 (CH_2), 28.0 (CH_2), 24.7 (4CH_3), 23.7 (CH_2), 21.9 (CH_3), 14.3 (CH_3).

^{11}B NMR (129 MHz, $CDCl_3$) δ 34.03.

HRMS [ESI(+)]: *m/z* calcd. for $C_{19}H_{31}BO_3Na$: 341.2258 [M+Na], found: 341.2258

2-(2-(4-methoxyphenyl)-4-phenylbutan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 7c



Using procedure A (390 nm lamp) 63,7 mg of *N*-tosylhydrazone **H27** and 89 mg of phenethylboronic acid afforded 41 mg of **7c** (64 % yield) as a colourless oil after column chromatography in SiO_2. Rf = 0.25 (Hex/EtOAc 40:1).

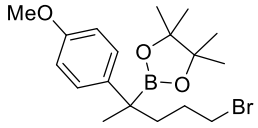
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35 – 7.23 (m, 5H), 7.19 (d, *J* = 7.0 Hz, 3H), 6.92 – 6.85 (m, 2H), 3.82 (s, 3H), 2.50 (m 2H), 2.09 (ddd, *J* = 11.1, 9.7, 5.1 Hz, 1H), 2.00 (ddd, *J* = 13.2, 10.3, 5.1 Hz, 1H), 1.47 (s, 3H), 1.26 (s, 6H), 1.25 (s, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 157.3 (C), 143.6 (C), 138.9 (C), 128.5 (CH), 128.4 (CH) 127.9 (CH), 125.6 (CH), 113.6 (CH), 83.5 (C), 55.3 (CH_3), 42.1 (CH_2), 32.3 (CH_2), 24.77 (CH_3), 24.7 (CH_3), 21.8 (CH_3).

^{11}B NMR (129 MHz, $CDCl_3$) δ 34.18.

HRMS [ESI(+)]: *m/z* calcd. for $C_{23}H_{32}BO_3$: 367.2489 [M+H], found: 367.2446.

2-(5-bromo-2-(4-methoxyphenyl)pentan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 7d



Using procedure A (390 nm lamp) 63,7 mg of *N*-tosylhydrazone **H27** and 100 mg of 3-bromopropylboronic acid afforded 48 mg of **7d** (63 % yield) as a colourless oil after column chromatography in SiO_2. Rf = 0.15 (Hex/EtOAc 40:1).

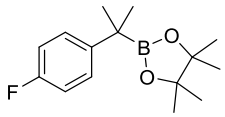
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.27 – 7.19 (m, 2H), 6.89 – 6.80 (m, 2H), 3.80 (s, 3H), 3.36 (t, *J* = 6.5 Hz, 2H), 1.90 – 1.66 (m, 4H), 1.34 (s, 3H), 1.23 (s,6H), 1.21 (s,6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 157.3 (C), 138.5 (C), 127.8 (CH), 113.7 (CH), 83.5 (C), 55.30 (CH_3), 38.4 (CH_2), 34.7 (CH_2), 29.3 (CH_2), 24.7 ($4CH_3$), 21.6 (CH_3).

^{11}B NMR (129 MHz, $CDCl_3$) δ 33.85.

HRMS [ESI(+)]: *m/z* calcd. for $C_{18}H_{29}BBrO_3$: 385.1368 [M+H], found: 385.1369.

2-(2-(4-fluorophenyl)propan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 7e



Using procedure A (390 nm lamp) 61 mg of *N*-tosylhydrazone **H28** and 35 mg of methylboronic acid afforded 25 mg of **7e** (47 % yield) as a colourless oil after column chromatography on neutral alumina. Rf = 0.41 (Hex/EtOAc 40:1) in alumina.

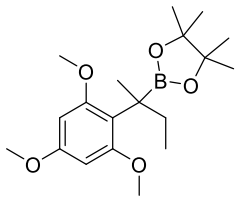
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.28 (m, 2H), 7.03 – 6.92 (m, 1H), 1.34 (s, 6H), 1.22 (s, 12H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 161.5 (d, *J* = 292 Hz, CF), 144.2 (C), 127.7 (d, *J* = 8.2 Hz CH), 114.7 (d, *J* = 20.3 Hz CH), 83.4 (2C), 25.7 ($2CH_3$), 24.5 ($4CH_3$).

^{11}B NMR (129 MHz, $CDCl_3$) δ 34.29.

HRMS [ESI(+)]: *m/z* calcd. for $C_{15}H_{23}BFO_2$: 265.1770 [M+H], found: 265.1772.

4,4,5,5-tetramethyl-2-(2-(2,4,6-trimethoxyphenyl)butan-2-yl)-1,3,2-dioxaborolane 7f



Using procedure A (390 nm lamp) 75.6 mg of *N*-tosylhydrazone **H29** and 44 mg of ethyllboronic acid afforded 42 mg of **7f** (55 % yield) as a colourless oil after column chromatography in SiO_2. Rf = 0.15 (Hex/EtOAc 8:1).

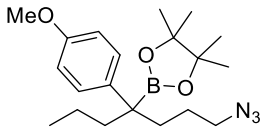
^{1}H NMR (300 MHz, $CDCl_3$) δ 6.11 (s, 2H), 3.79 (s, 3H), 3.75 (s, 6H), 2.49 (dd, *J* = 9.0, 5.8 Hz, 1H), 1.88 – 1.68 (m, 1H), 1.45 (ddq, *J* = 13.1, 8.9, 7.4 Hz, 1H), 1.25 (s, 6H), 1.21 (s, 6H), 0.80 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 158.8 (C), 158.6 (C), 113.0 (C), 90.7 (CH), 82.7 (C), 55.5 (CH_3), 55.4 (CH_3), 25.1 (CH_3), 24.8 (CH_3), 23.8 (CH_2), 13.7 (CH_3).

^{11}B NMR (129 MHz, $CDCl_3$) δ 33.77.

HRMS [APCI(+)]: *m/z* calcd. for $C_{18}H_{30}BO_5$: $(M+H)^+$: 337.2181 [M+H], found: 337.2184.

2-(1-azido-4-(4-methoxyphenyl)heptan-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 7g



Using procedure A (370 nm lamp) 77,5 mg of *N*-tosylhydrazone **H30** and 53 mg of propylboronic acid afforded 41 mg of **7g** (53 % yield) as a colourless oil after column chromatography on neutral alumina. Rf = 0.33 (Hex/EtOAc 40:1) in alumina.

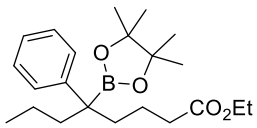
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25 – 7.15 (m, 2H), 6.88 – 6.75 (m, 2H), 3.78 (s, 3H), 3.18 (t, *J* = 6.9 Hz, 2H), 1.90 – 1.68 (m, 4H), 1.46 – 1.32 (m, 2H), 1.21 (s, 12H + m, 2H), 0.89 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 157.2 (C), 137.3 (C), 128.3 CH), 113.6 (CH), 83.5 (C), 55.2 (CH_3), 52.3 (CH_2), 37.5 (CH_2), 32.5 (CH_2), 24.8 (CH_3), 24.8 (CH_3), 24.61 (CH_2), 18.7 (CH_2), 15.1 (CH_3).

^{11}B NMR (129 MHz, $CDCl_3$) δ 34.60.

HRMS [APCI(+)]: *m/z* calcd. for $C_{20}H_{32}BN_3O_3$+Na: 396.2429 [M+Na], found: 396.2440.

Ethyl 5-phenyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)octanoate 7h



Using procedure A (370 nm lamp) 77 mg of *N*-tosylhydrazone **H31** and 53 mg of propylboronic acid afforded 51 mg (68 % yield) as a colourless oil after column chromatography on deactivated SiO_2. Rf = 0.20 (EtOAc/Hex. 2:1) 0.20 (Hex/EtOAc 8:1).

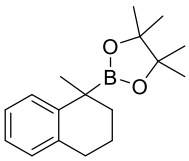
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38 – 7.22 (m, 4H), 7.20 – 7.08 (m, 1H), 4.11 (q, *J* = 7.1 Hz, 2H), 2.27 (t, *J* = 7.5 Hz, 2H), 1.90 – 1.74 (m, 4H), 1.58 – 1.33 (m, 2H), 1.31 – 1.08 (m, 17H), 0.91 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 173.9 (C), 145.7 (C), 128.1 (CH), 127.5 (CH), 125.2 (CH), 83.4 (C), 60.3 (CH_2), 36.9 (CH_2), 35.2 (CH_2), 34.4 (CH_2), 24.8 (CH_3), 24.7 (CH_3), 20.5 (CH_2), 18.5 (CH_2), 15.1 (CH_3), 14.3 (CH_2).

^{11}B NMR (129 MHz, $CDCl_3$) δ 33.35.

HRMS [APCI(+)]: *m/z* calcd. for $C_{22}H_{36}BO_4$: 375.2701 [M+H], found: 375.2706.

4,4,5,5-tetramethyl-2-(1-methyl-1,2,3,4-tetrahydronaphthalen-1-yl)-1,3,2-dioxaborolane 7i



Using procedure A (390 nm lamp) 62 mg of *N*-tosylhydrazone **H33** and 35 mg of methylboronic acid afforded 35 mg of **7i** (62 % yield) as a colourless oil after column chromatography on deactivated SiO_2. Rf = 0.35 (Hex/EtOAc 20:1).

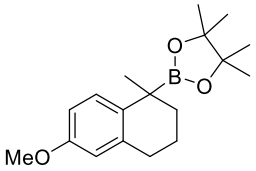
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.24 – 7.18 (m, 1H), 7.10 (dt, *J* = 7.9, 4.4 Hz, 1H), 7.06 – 7.01 (m, 2H), 2.76 (t, *J* = 6.4 Hz, 2H), 2.04 (ddd, *J* = 12.9, 7.4, 4.3 Hz, 1H), 1.88 – 1.73 (m, 2H), 1.53 (ddd, *J* = 12.9, 7.3, 4.2 Hz, 1H), 1.34 (s, 3H), 1.22 (s, 6H), 1.20 (s, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 143.4(C), 136.5 (C), 129.3 (CH), 128.8 (CH), 125.5 (CH), 124.8 (CH), 83.3 (C), 33.9 (CH_2), 30.5 (CH_2), 26.7 (CH_2), 24.7 (CH_3), 24.7 (CH_3), 19.9 (CH_2).

^{11}B NMR (129 MHz, $CDCl_3$) δ 34.80.

HRMS [APCI(+)]: *m/z* calcd. for $C_{17}H_{26}BO_2$: 273.2020 [M+H], found: 273.2025.

2-(6-methoxy-1-methyl-1,2,3,4-tetrahydronaphthalen-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 7j



Using procedure A (390 nm lamp) 69 mg of *N*-tosylhydrazone **H32** and 35 mg of methylboronic acid afforded 42 mg of **7j** (70 % yield) as a colourless oil after column chromatography on deactivated SiO_2. Rf = 0.35 (Hex/EtOAc 20:1).

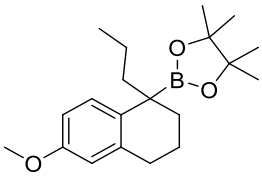
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.14 (d, *J* = 8.6 Hz, 1H), 6.70 (dd, *J* = 8.6, 2.8 Hz, 1H), 6.58 (d, *J* = 2.8 Hz, 1H), 3.77 (s, 3H), 2.74 (t, *J* = 6.4 Hz, 2H), 2.11 – 1.96 (m, 1H), 1.80 (m, 2H), 1.51 (ddd, *J* = 13.0, 7.4, 4.0 Hz, 1H), 1.31 (s, 3H), 1.22 (s, 6H), 1.21 (s, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 156.7 (C), 137.7 (C), 135.5 (C), 129.7 (CH), 113.7 (CH), 112.0 (CH), 83.3 (C), 55.2 (CH_3), 34.0 (CH_2), 30.8 (CH_2), 26.8 (CH_2), 24.68 ($2CH_3$), 24.66 ($2CH_3$), 19.9 (CH_2).

^{11}B NMR (129 MHz, CDCl3) δ 34.52.

HRMS [ESI(+)]: *m/z* calcd. for $C_{18}H_{28}BO_3$: 303.2126 [M+H], found: 303.2132.

2-(6-methoxy-1-propyl-1,2,3,4-tetrahydronaphthalen-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 7k



Continuous flow reaction: Using procedure D with one 370 nm lamp (10.8 W, 25 %, 7 cm) 68 mg of *N*-tosylhydrazone **H32** and 52 mg of propylboronic acid afforded 41 mg of **7k** (62 % yield) as a colourless oil after column chromatography on neutral alumina (Hex/EtOAc, 20:1). Rf = 0.45 (SiO_2, Hex/EtOAc 10:1).

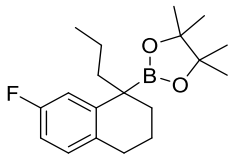
^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.26 (d, *J* = 8.6 Hz, 1H), 6.68 (dd, *J* = 8.7, 2.8 Hz, 1H), 6.57 (d, *J* = 2.8 Hz, 1H), 3.76 (s, 3H), 2.71 (t, *J* = 6.3 Hz, 2H), 2.04 – 1.92 (m, 1H), 1.84-1.71 (m, 3H), 1.68 –1.48 (m, 2H), 1.36 – 1.22 (m, 3H), 1.20 (s, 6H), 1.19 (s, 6H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 156.6 (C), 138.3(C), 134.1 (c), 129.9 (CH), 113.6 (CH), 111.7 (CH), 83.2 (2C), 55.1 (CH_3), 42.5 (CH_2), 31.0 (CH_2), 30.2 (CH_2), 24.7 (4 CH_3), 20.2 (CH_2), 19.3 (CH_2), 15.1 (CH_3) ppm).

^{11}B NMR (129 MHz, CDCl3) δ 33.71.

HRMS [ESI(+)]: *m/z* calcd. for $C_{20}H_{31}BO_3$: 331.2439 [M+H], found: 331.2441.

2-(7-fluoro-1-propyl-1,2,3,4-tetrahydronaphthalen-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 7l



Using procedure A (390 nm lamp) 66 mg of *N*-tosylhydrazone **H34** and 52 mg of propylboronic acid afforded 28 mg of **7l** (44 % yield) as a colourless oil after column chromatography on deactivated SiO_2. Rf = 0.31 (Hex/EtOAc 40:1).

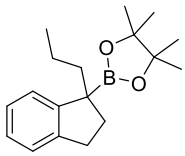
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.07 (dd, *J* = 11.3, 2.8 Hz, 1H), 6.99 – 6.90 (m, 1H), 6.72 (td, *J* = 8.4, 2.7 Hz, 1H), 2.67 (t, *J* = 6.3 Hz, 2H), 1.99 (ddd, *J* = 12.9, 7.2, 3.2 Hz, 1H), 1.78 (m, 3H), 1.66 – 1.52 (m, 2H), 1.33 – 1.23 (m, 2H), 1.20 (s, 6H), 1.19 (s, 6H), 0.89 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 161.0 (C, d, *J* = 241.0 Hz), 144.2 (C), 132.7 (C), 130.3 (CH, d, *J* = 7.9 Hz), 115.1 (CH, d, *J* = 20.9 Hz), 111.65 (CH, d, *J* = 21.2 Hz), 83.4 (C), 42.2 (CH_2), 29.9 (CH_2), 29.8 (CH_2), 24,7 (CH_3), 20,5 (CH_2), 18,1 (CH_2), 15.1 (CH_3).

^{11}B NMR (129 MHz, $CDCl_3$) δ 34.42.

HRMS [ESI(+)]: *m/z* calcd. for $C_{19}H_{29}BFO_2$: 319.2239 [M+H], found: 319.2248.

4,4,5,5-tetramethyl-2-(1-propyl-2,3-dihydro-1H-inden-1-yl)-1,3,2-dioxaborolane 7m



Using procedure B (390 nm lamp) 60 mg of *N*-tosylhydrazone **H36** and 52 mg of propylboronic acid afforded 36 mg of **7m** (62 % yield) as a white solid after column chromatography on deactivated SiO_2. Rf = 0.47 (Hex/EtOAc 10:1).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25 (dd, *J* = 7.3, 1.6 Hz, 1H), 7.21 – 7.03 (m, 3H), 2.92 (t, *J* = 7.4 Hz, 2H), 2.38 (dt, *J* = 12.3, 6.9 Hz, 1H), 2.01 – 1.70 (m, 2H), 1.51 – 1.25 (m, 3H), 1.18 (s, 6H), 1.17 (s, 6H), 0.92 (t, *J* = 7.1 Hz, 3H).

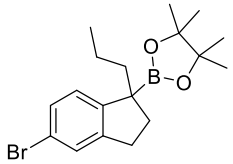
^{13}C NMR (75 MHz, $CDCl_3$) δ 149.3 (C), 143.8 (C), 126.0 (CH), 125.7 (CH), 124.3 (CH), 83.3 (C), 40.8 (CH_2), 34.1 (CH_2), 31.7 (CH_2), 24.7 (CH_3), 20.5 (CH_2), 15.02 (CH_3).

^{11}B NMR (129 MHz, $CDCl_3$) δ 34.05.

HRMS [ESI(+)]: *m/z* calcd. for $C_{18}H_{28}BO_2$: 287.2177 [M+H], found: 287.2178.

m.p. = 37 – 39 ºC

2-(5-bromo-1-propyl-2,3-dihydro-1H-inden-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 7n



Batch reaction: Using procedure B (390 nm lamp) 75 mg of *N*-tosylhydrazone **H37** and 52 mg of propylboronic acid afforded 58 mg of **7n** (80% yield) as a white solid after column chromatography on deactivated SiO_2. Rf = 0.47 (Hex/EtOAc 20:1).

Continuous flow reaction: Using procedure D with one 390 nm lamp (13 W, 25%, 7 cm) 75 mg of *N*-tosylhydrazone **H37** and 52 mg of propylboronic acid afforded 46 mg (63 % yield).

^{1}H NMR (300 MHz, $CDCl_3$)) δ 7.30 (d, *J* = 1.3 Hz, 1H), 7.26 – 7.20 (m, 1H), 7.09 (d, *J* = 8.1 Hz, 1H), 2.96 – 2.81 (m, 2H), 2.37 (dt, *J* = 12.3, 6.9 Hz, 1H), 1.95 – 1.70 (m, 2H), 1.47 – 1.21 (m, 4H), 1.17 (s, 6H), 1.16 (s, *6*H), 0.90 (t, *J* = 7.1 Hz, 3H).

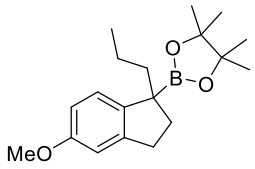
^{13}C NMR (75 MHz, $CDCl_3$) δ 148.4(C), 146.3 (C), 129.0 (CH), 127.4 (CH), 125.8 (CH), 119.3 (C), 83.5 (C), 40.6 (CH_2), 34.3 (CH_2), 31.6 (CH_2), 24.7 (CH_3), 20.3 (CH2), 15.0 (CH_3).

^{11}B NMR (129 MHz, $CDCl_3$) δ 34.25.

HRMS [ESI(+)]: *m/z* calcd. for $C_{18}H_{27}BBrO_2$: 365.1282 [M+H], found: 365.1282.

m.p. = 87 – 89 ºC

2-(5-Methoxy-1-propyl-2,3-dihydro-1H-inden-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 7o



Batch reaction: Using procedure B (390 nm lamp) 66 mg of *N*-tosylhydrazone **H35** and 52 mg of propylboronic acid afforded 47 mg of **7o** (73% yield) as a colourless oil after column chromatography on deactivated SiO_2. Rf = 0.23 (Hex/EtOAc 20:1).

Continuous flow reaction: Using procedure D with one 390 nm lamp (13 W, 25%, 7 cm) 66 mg of *N*-tosylhydrazone **H35** and 52 mg of propylboronic acid afforded 41 mg (63 % yield).

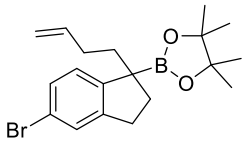
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.12 (d, *J* = 8.3 Hz, 1H), 6.74 (d, *J* = 2.5 Hz, 1H), 6.68 (dd, *J* = 8.3, 2.6 Hz, 1H), 3.77 (s, 3H), 2.88 (t, *J* = 7.5 Hz, 2H), 2.36 (dt, *J* = 12.3, 7.1 Hz, 1H), 1.93 – 1.66 (m, 2H), 1.43 – 1.23 (m, 5H), 1.17 (s, 6H), 1.16 (s, 6H), 0.90 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 158.3 (C), 145.3 (C), 141.4 (C), 124.7 (CH), 111.8 (CH), 109.8 (CH), 83.2 (C), 55.4 (CH_3), 41.0 (CH_2), 34.5 (CH_2), 31.9 (CH_2), 24.7 (CH_3), 20.5 (CH_2), 15.0 (CH_3).

^{11}B NMR (129 MHz, $CDCl_3$) δ 34.13.

HRMS [ESI(+)]: m/z calcd. for $C_{13}H_{17}O_2$: 205.1223 [M+O-Bpin], found: 205.1220.

2-(5-bromo-1-(but-3-en-1-yl)-2,3-dihydro-1H-inden-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 7p



Batch reaction: Using procedure B (390 nm lamp) 75 mg of *N*-tosylhydrazone **H37** and 52 mg of propylboronic acid afforded 48 mg of **7p** (64 % yield) as a white solid after column chromatography on deactivated SiO_2. Rf = 0.57 (Hex/EtOAc 10:1).

Continuous flow reaction: Using procedure D with one 390 nm lamp (26 W, 50 %, 7 cm) 75 mg of *N*-tosylhydrazone **H37** and 59 mg of 3-butenylboronic acid afforded 40 mg of **7p** (54% yield after column chromatography on deactivated SiO_2. Rf = 0.57 (Hex/EtOAc 10:1).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30 (t, *J* = 1.5 Hz, 1H), 7.27 – 7.20 (m, 1H), 7.09 (d, *J* = 8.1 Hz, 1H), 5.83 (ddt, *J* = 16.5, 10.1, 6.3 Hz, 1H), 5.00 (dq, *J* = 16.5, 1.1 Hz, 1H), 4.92 (ddt, *J* = 10.1, 2.2, 1.1 Hz, 1H), 2.90 (t, *J* = 7.5 Hz, 2H), 2.39 (dt, *J* = 12.3, 6.7 Hz, 1H), 2.12 – 1.89 (m, 3H), 1.80 (dt, *J* = 12.4, 8.1 Hz, 1H), 1.58 – 1.45 (m, 1H), 1.17 (s, 6H), 1.16 (s, 6H).

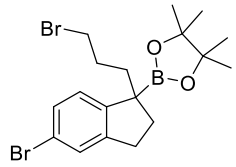
^{13}C NMR (75 MHz, $CDCl_3$) δ 148.0 (C), 146.3 (C), 139.2 (CH), 129.1 (CH), 127.5 (CH), 125.7 (CH), 119.5 (C), 114.5 (CH_2), 83.5 (C), 37.3 (CH_2), 34.1 (CH_2), 31.6 (CH_2), 31.4 (CH_2), 24.7 (CH_3), 24.7 (CH_3).

^{11}B NMR (129 MHz, $CDCl_3$) δ 34.27.

HRMS [ESI(+)]: *m/z* calcd. for $C_{29}H_{26}BBrO_2Na$: 399.1101 [M+Na], found: 399.1106.

m.p. = 78 – 80.0 ºC

2-(5-bromo-1-(3-bromopropyl)-2,3-dihydro-1*H*-inden-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 7q



Batch reaction: Using procedure B (390 nm lamp) 76 mg of *N*-tosylhydrazone **H37** and 100 mg of 3-bromopropylboronic acid afforded 30 mg of **7q** (34 % yield) as a yellow oil after column chromatography on deactivated SiO_2 (Hex/EtOAc, 20:1). Rf = 0.54 (SiO_2, Hex/EtOAc 10:1).

Continuous flow reaction: Using procedure D with one 390 nm lamp (26 W, 50 %, 7 cm) 76 mg of *N*-tosylhydrazone **H37** and 100 mg of 3-bromopropylboronic acid afforded 34 mg of **7q** (39% yield after column chromatography on deactivated SiO_2 (Hex/EtOAc, 20:1). Rf = 0.54 (SiO_2, Hex/EtOAc 10:1).

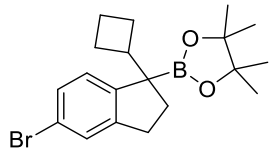
^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.30 (d, *J*=1.7, 1H), 7.23 (d, *J*=2.0, 1H), 7.07 (d, *J*=8.1, 1H), 3.43 – 3.31 (m, 2H), 2.91 (t, *J*=7.4, 2H), 2.44 – 2.30 (m, 1H), 2.02 – 1.71 (m, 4H), 1.64 – 1.54 (m, 1H), 1.17 (d, *J*=4.5, 12H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 147.6 (C), 146.3 (C), 129.2 (CH), 127.6 (CH), 125.6 (CH), 119.7 (C), 83.7 (2 C), 36.5 (CH_2), 34.2 (CH_2), 34.1 (CH_2), 31.6 (CH_2), 30.4 (CH_2), 24.7 (4 CH_3).

^{11}B NMR (129 MHz, $CDCl_3$) δ 33.87.

HRMS [ESI(+)]: *m/z* calcd. for $C_{18}H_{25}BBr_2O_2Na$: 465.0207 [M+Na], found: 464.0261.

2-(5-bromo-1-cyclobutyl-2,3-dihydro-1H-inden-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 7r



Batch reaction: Using procedure B (390 nm lamp) 75 mg of *N*-tosylhydrazone **H37** and 53 mg of cyclobutylboronic acid afforded 35 mg of **7r** (47% yield) as a colourless oil after column chromatography on neutral alumina (Hex/EtOAc, 20:1).

Continuous flow reaction: Using procedure D with one 390 nm lamp (26 W, 50 %, 7 cm) 75 mg of *N*-tosylhydrazone **H37** and 53 mg of cyclobutylboronic acid afforded 31 mg of **7r** (42% yield) as a colourless oil after column chromatography on neutral alumina (Hex/EtOAc, 20:1). Rf = 0. (SiO_2, Hex/EtOAc, 5:1).

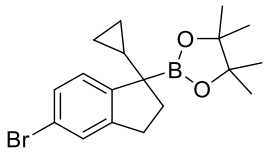
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.29 (d, *J* = 1.1 Hz, 1H), 7.22 (dd, *J* = 8.1, 1.1 Hz, 1H), 7.12 (d, *J* = 8.1 Hz, 1H), 2.96 – 2.80 (m, 2H), 2.80 – 2.67 (m, 1H), 2.27 (ddd, *J* = 12.6, 8.6, 7.3 Hz, 1H), 1.97 (ddd, *J* = 12.6, 8.4, 6.0 Hz, 1H), 1.89 – 1.69 (m, 5H), 1.67 – 1.60 (m, 1H), 1.19 (s, 12H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 146.79 (C), 146.73 (C), 128.9 (CH), 127.4 (CH), 126.3 (CH), 119. (C)1, 83.4 (C), 42.5 (CH), 31.6 (CH_2), 31.3 (CH_2), 25.4 (CH_2), 24.85 (CH_3), 24.80 (CH_3), 24.77 (CH_3), 18.2 (CH_2).

^{11}B NMR (129 MHz, $CDCl_3$) δ 33.76.

HRMS [ESI(+)]: *m/z* calcd. for $C_{19}H_{26}BBrO_2$: 399.1101 [M+Na], found: 399.1090.

2-(5-Bromo-1-cyclopropyl-2,3-dihydro-1*H*-inden-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 7s



Batch reaction: Using procedure B (390 nm lamp) 75 mg of *N*-tosylhydrazone **H37** and 51 mg of cyclopropylboronic acid afforded 23 mg of **7s** (32% yield) as a colourless oil after column chromatography on neutral alumina (Hex/EtOAc, 20:1).

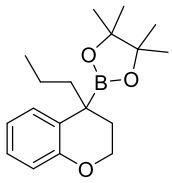
Continuous flow reaction: Using procedure D with one 390 nm lamp (26 W, 50%, 7 cm) 75 mg of *N*-tosylhydrazone **H37** and 51 mg of cyclopropylboronic acid afforded 43 mg of **7s** (60% yield) as a colourless oil after column chromatography on neutral alumina (Hex/EtOAc, 20:1). Rf = 0.59 (SiO_2, Hex/EtOAc 20:1).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30 (dd, *J* = 1.9, 1.0 Hz, 1H), 7.25 – 7.16 (m, 2H), 2.93 (dt, *J* = 15.4, 7.6 Hz, 1H), 2.79 (ddd, *J* = 15.5, 8.5, 5.9 Hz, 1H), 2.31 (ddd, *J* = 12.4, 8.5, 6.9 Hz, 1H), 1.86 (ddd, *J* = 12.4, 8.3, 5.9 Hz, 1H), 1.19 (s, 12H), 1.00 (tt, *J* = 8.4, 5.4 Hz, 1H), 0.93 – 0.77 (m, 1H), 0.44 – 0.26 (m, 2H), 0.25 – 0.12 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 147.2 (C), 146,7 (C), 128.9 (CH), 127.3 (CH), 126.6 (CH), 119.7 (C), 83.5 (C), 34.4 (CH_2), 31.6 (CH_2), 24.8 (CH_3), 24.7 (CH_3), 17.7 (CH), 1.6 (CH_2), 1.2 (CH_2).

^{11}B NMR (129 MHz, $CDCl_3$) δ 33.95.

4,4,5,5-tetramethyl-2-(4-propylchroman-4-yl)-1,3,2-dioxaborolane 7t



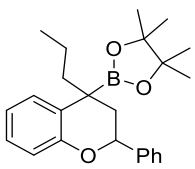
Continuous flow reaction: Using procedure D with two 370 nm lamps (32 W, 75 %, 7 cm) 63 mg of *N*-tosylhydrazone **H39** and 52 mg of propylboronic acid afforded 33 mg (53 % yield) of **7t** as a colourless oil after column chromatography on deactivated SiO_2. Rf = 0.42 (Hex/EtOAc 10:1).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.02 (ddd, *J* = 8.3, 7.2, 1.7 Hz, 1H), 6.83 (ddd, *J* = 7.8, 7.2, 1.4 Hz, 1H), 6.76 (dd, *J* = 8.3, 1.4 Hz, 1H), 4.31 – 4.04 (m, 2H), 2.16 (dt, *J* = 13.9, 3.9 Hz, 1H), 1.94 (ddd, *J* = 13.2, 11.1, 5.4 Hz, 1H), 1.85 – 1.71 (m, 1H), 1.60 – 1.45 (m, 2H), 1.42 – 1.22 (m, 3H), 1.19 (s, 12H), 0.91 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 154.7 (C), 129.4 (CH), 127.7 (C), 126.4 (CH), 120.1 (CH), 116.9 (CH), 83.6 (C), 64.3 (CH_2), 41.9 (CH_2), 29.5 (CH_2), 24.8 (CH_3), 19.3 (CH_2), 15,0 (CH_3).

^{11}B NMR (129 MHz, $CDCl_3$) δ 33.73.

4,4,5,5-tetramethyl-2-(2-phenyl-4-propylchroman-4-yl)-1,3,2-dioxaborolane 7u



Continuous flow reaction: Using procedure D with two 370 nm lamps (32 W, 75%, 7 cm) 78 mg of *N*-tosylhydrazone H**40** and 52 mg of propylboronic acid afforded 30 mg (40% yield) of **7u** as a colourless oil as (5:1 mixture of diastereoisomers after column chromatography on deactivated SiO_2). Rf = 0.5 (Hex/EtOAc 20:1).

Data for the major isomer:

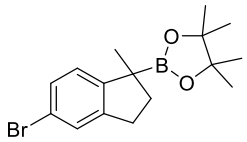
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.55 – 7.28 (m, 6H), 7.05 (dd, *J* = 7.6, 1.7 Hz, 1H), 6.96 – 6.82 (m, 2H), 5.21 (dd, *J* = 11.3, 1.7 Hz, 1H), 2.35 (dd, *J* = 13.4, 1.8 Hz, 1H), 2.27 – 1.98 (m, 1H), 1.74 (dd, *J* = 13.4, 11.3 Hz, 1H), 1.65 – 1.45 (m, 2H), 1.30-1.20 (m, 1H), 1.23 (s, 6H), 1.21 (s, 6H), 0.91 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 155.3 (C), 142.7 (C), 128.7 (CH), 128.5 (CH), 127.7 (CH), 127.4 (C), 126.3 (CH), 126.3 (CH), 126.1 (CH), 120.5 (CH), 117.1 (CH), 83.7 (C), 77.1 (CH), 41.67 (CH_2), 39.1 (CH_2), 24.8 ($2CH_3$), 24.7 ($2CH_3$), 19.6 (CH_2), 15.0 (CH_3).

^{11}B NMR (129 MHz, $CDCl_3$) δ 34.52.

HRMS [ESI(+)]: *m/z* calcd. for $C_{24}H_{32}BO_3$: 379.2439 [M+H], found: 379.2445.

2-(5-bromo-1-methyl-2,3-dihydro-1H-inden-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 7v



Continuous flow reaction: Using procedure D with one 390 nm lamp (13 W, 25%, 7 cm) 75 mg of *N*-tosylhydrazone **H37** and 35 mg of methylboronic acid afforded 36 mg of **7v** (52 % yield) as a colourless oil after column chromatography on neutral alumina (Hex/EtOAc, 20:1). Rf = 0.67 (SiO_2, Hex/EtOAc 10:1).

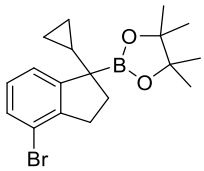
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30 (d, *J* = 1.7 Hz, 1H), 7.28 – 7.20 (m, 1H), 7.05 (d, *J* = 8.0 Hz, 1H), 2.89 (t, *J* = 8.0 Hz, 2H), 2.39 (dt, *J* = 12.3, 6.7 Hz, 1H), 1.71 (dt, *J* = 12.3, 8.2 Hz, 1H), 1.27 (s, 3H), 1.19 (s, 6H), 1.18 (s, 6H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 149.8 (C), 146.1 (C), 129.2 (CH), 127.5 (CH), 125.2 (CH), 119.3 (C), 83.5 (C), 37.3 (CH_2), 31.4 (CH_2), 24.7 ($2CH_3$), 24.6 ($2CH_3$), 23.7 (CH_3).

^{11}B NMR (129 MHz, $CDCl_3$) δ 33.87.

HRMS [ESI(+)]: *m/z* calcd. for $C_{10}H_{11}BrONa$: $(M\text{-}Bpin+NaHO)^+$: 248.988 [M+NaOH-Bpin], found: 248.9885.

2-(4-bromo-1-cyclopropyl-2,3-dihydro-1H-inden-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 7w



Continuous flow reaction: Using procedure D with one 390 nm lamp (26 W, 50%, 7 cm) 75 mg of *N*-tosylhydrazone **H38** and 51 mg of cyclopropylboronic acid afforded 43 mg of **7w** (63 % yield) as a colourless oil after column chromatography on neutral alumina. Rf = 0.52 (Hex/EtOAc 10:1).

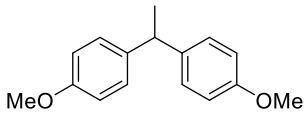
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35 – 7.23 (m, 2H), 7.03 (ddt, *J* = 8.1, 7.4, 0.8 Hz, 1H), 3.12 – 2.80 (m, 2H), 2.35 (ddd, *J* = 12.7, 8.7, 6.9 Hz, 1H), 1.88 (ddd, *J* = 12.6, 8.5, 5.8 Hz, 1H), 1.22 (s, 12H), 1.05 (ddd, *J* = 8.3, 5.4, 2.9 Hz, 1H), 0.44 – 0.31 (m, 2H), 0.31 – 0.16 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 150.3 (C), 144.5 (C), 129.1 (CH), 127.8 (CH), 124.0 (CH), 119.7 (C), 83.6 (C), 33.2 (CH_2), 32.9 (CH_2), 24.8 (CH_3), 24.7 (CH_3), 18.1 (CH), 1.7 (CH_2), 1.3 (CH_2).

^{11}B NMR (129 MHz, $CDCl_3$) δ 33.11.

HRMS [ESI(+)]: *m/z* calcd. for $C_{12}H_{13}BrONa$: 275.0042 [M+NaOH-Bpin], found: 275.0042.

4,4'-(ethane-1,1-diyl)bis(methoxybenzene) 8a

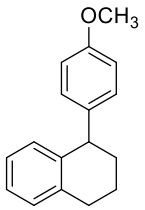


Using procedure A (390 nm lamp) 63 mg of *N*-tosylhydrazone **H27** and 91 mg of 4-methoxyphenylboronic acid afforded 41 mg of **8a** (86 % yield) as a yellow oil after column chromatography on SiO_2 (Hex/EtOAc, 20:1). Rf = 0.32 (SiO_2, Hex/EtOAc 10:1). Spectroscopic data in agreement with literature.[27]

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.23 – 7.09 (m, 4H), 6.94 – 6.76 (m, 4H), 4.09 (q, *J* = 7.2 Hz, 1H), 3.81 (s, 6H), 1.62 (d, *J* = 6.3 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 157.7 (C), 139,0 (C), 128.4 (CH), 113.7 (CH), 55.3 (CH_3), 43.1 (CH), 22.3 (CH_3).

1-(4-methoxyphenyl)-1,2,3,4-tetrahydronaphthalene 8b

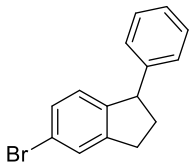


Using procedure A (390 nm lamp) 60 mg of *N*-tosylhydrazone **H32** and 91 mg of 4-methoxyphenylboronic acid afforded 33 mg of **8b** (69 % yield) as a yellow oil after column chromatography on SiO_2 (Hex/EtOAc, 20:1). Spectroscopic data in agreement with literature.[28]

^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.21 – 7.12 (m, 2H), 7.12 – 7.01 (m, 3H), 6.88 (m, 3H), 4.10 (t, *J* = 6.7 Hz, 1H), 3.83 (s, 3H), 3.03 – 2.80 (m, 2H), 2.26 – 2.10 (m, 1H), 2.01 – 1.70 (m, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 157.9 (C), 139.9 (C), 139.8 (C), 137.7 (C), 130.3 (CH), 129.8 (CH), 129.1 (CH), 126.0 (CH), 125.7 (CH), 113.7 (CH), 55.4 (CH_3), 44.9 (CH), 33.5 (CH_2), 29.9 (CH_2), 21.1 (CH_2).

5-bromo-1-phenyl-2,3-dihydro-1*H*-indene 8c

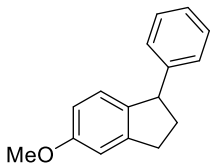


Using procedure B (390 nm lamp) 75 mg of *N*-tosylhydrazone **H37** and 73 mg of phenylboronic acid afforded 37 mg of **8c** (68 % yield) as a yellow oil after column chromatography on SiO_2 (Hex). Rf = 0.33 (SiO_2, Hex 10:1). Spectroscopic data in agreement with literature.[29]

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43 (d, *J* = 1.8 Hz, 1H), 7.36 – 7.28 (m, 2H), 7.28 – 7.21 (m, 2H), 7.20 – 7.12 (m, 2H), 6.82 (dd, *J* = 8.1, 1.1 Hz, 1H), 4.28 (t, *J* = 8.3 Hz, 1H), 3.17 – 2.82 (m, 2H), 2.59 (dtd, *J* = 12.7, 7.8, 3.9 Hz, 1H), 2.08 (dq, *J* = 12.7, 8.8 Hz, 1H).

13C NMR (75 MHz, CDCl3) δ 146.9 (C), 146.1 (C), 144.9 (C), 129.6 (CH), 128.7 (CH), 128.2 (CH), 127.7 (CH), 126.7 (CH), 126.6 (CH), 120.5 (C), 51.3 (CH), 36.8 (CH_2), 31.8 (CH_2).

5-bromo-1-phenyl-2,3-dihydro-1*H*-indene 8d



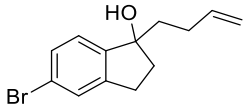
Using procedure B (390 nm lamp) 66 mg of *N*-tosylhydrazone **H35** and 73 mg of phenylboronic acid afforded 22 mg of **8d** (50 % yield) as a yellow oil after column chromatography on SiO_2 (Hex/EtOAc, 40:1). Rf = 0.27 (SiO_2, Hex/EtOAc 40:1). Spectroscopic data in agreement with literature.[29]

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43 (d, *J* = 1.8 Hz, 1H), 7.36 – 7.28 (m, 2H), 7.28 – 7.21 (m, 2H), 7.20 – 7.12 (m, 2H), 6.82 (dd, *J* = 8.1, 1.1 Hz, 1H), 4.28 (t, *J* = 8.3 Hz, 1H), 3.17 – 2.82 (m, 2H), 2.59 (dtd, *J* = 12.7, 7.8, 3.9 Hz, 1H), 2.08 (dq, *J* = 12.7, 8.8 Hz, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 159.0 (C), 146.1 (C), 145.9 (C), 139.2 (C), 128.6 (CH), 128.1 (CH), 126.4 (CH), 125.6 (CH), 112.4 (CH), 109.8 (CH), 55.6 (CH_3), 50.1 (CH), 37.1 (CH_2), 32.1 (CH_2).

1.6 Additional synthetic transformations

Continuous flow synthesis of 5-bromo-1-(but-3-en-1-yl)-2,3-dihydro-1H-inden-1-ol 9. Following procedure D, the solution collected is treated with a 5% H_2O_2 and water and stirred overnight. The solution is diluted with 5 mL of water and extracted with CH_2Cl_2 (3x10 mL): The combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated. The alcohol was purified by column chromatography in SiO_2 to yield 39 mg of **9** (73 %) as a colourless oil. Rf = 0.33 (Hex/EtOAc 5:1).

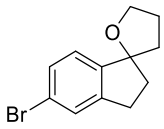


^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39 – 7.30 (m, 2H), 7.20 – 7.11 (m, 1H), 5.84 (ddt, *J* = 16.8, 10.1, 6.4 Hz, 1H), 5.03 (dq, *J* = 17.1, 1.7 Hz, 1H), 4.96 (dq, *J* = 10.1, 1.4 Hz, 1H), 2.97 (ddd, *J* = 16.4, 8.6, 4.8 Hz, 1H), 2.88 – 2.72 (m, 1H), 2.29 (ddd, *J* = 13.0, 8.1, 4.8 Hz, 1H), 2.23 – 2.02 (m, 2H), 1.95 (m, 2H), 1.79 (ddd, *J* = 13.5, 11.2, 5.1 Hz, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 146.5 (C), 145.4 (C), 138.6 (CH), 129.9 (CH), 128.3 (CH), 124.5 (CH), 122.2 (C), 114.8 (CH), 83.3 (C), 40.2 (CH_2), 39.4 (CH_2), 29.4 (CH_2), 28.7 (CH_2).

HRMS [ESI(+)]: *m/z* calcd. for $C_{13}H_{15}BNaO$: 289.0198 [M+Na], found: 289.0192.

Continuous flow synthesis of 5'-bromo-2',3',4,5-tetrahydro-3H-spiro[furan-2,1'-indene] 10. Following procedure D, the solution collected is treated with a 5% H_2O_2 and 1 M NaOH and stirred overnight. The solution is diluted with 5 mL of water and extracted with CH_2Cl_2 (3x10 mL): The combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated. The spiroindene **9** was purified by column chromatography in neutral alumina to yield 18 mg of **10** (36 %) as a colourless oil. Rf = 0.41 (Hex/EtOAc 5:1).

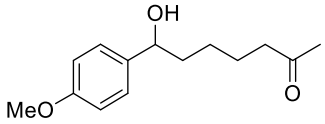


^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39 – 7.29 (m, 2H), 7.18 – 7.10 (m, 1H), 4.07 – 3.90 (m, 2H), 2.98 (ddd, *J* = 16.1, 8.3, 5.0 Hz, 1H), 2.86 – 2.70 (m, 1H), 2.28 – 1.92 (m, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 145.8 (C), 145.5 (C), 129.8 (CH), 127.9 (CH), 124.3 (CH), 121.8 (C), 91.38 (C), 68.1 (CH_2), 39.7 (CH_2), 37.2 (CH_2), 29.5 (CH_2), 26.5 (CH_2).

HRMS [ESI(+)]: *m/z* calcd. for $C_{12}H_{14}BrO$: 253.0223 [M+H], found: 253.0219.

Synthesis of 7-hydroxy-7-(4-methoxyphenyl)heptan-2-one 11. Following procedure A, once the carboborylation reaction is finished, the mixture is treated with H_2O_2 in H_2O and stirred overnight. The solution is diluted with 5 mL of water and extracted with CH_2Cl_2 (3x10 mL): The combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated. The hydroxyketone **10** was purified by column chromatography in SiO_2 to yield 23 mg of **11** (52 %) as a colourless oil. Rf = 0.20 (Hex/EtOAc 10:1).

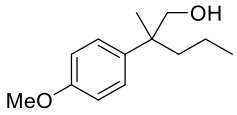


^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25 (m, 2H), 6.93 – 6.81 (m, 2H), 4.62 (dd, *J* = 7.5, 5.9 Hz, 1H), 3.80 (s, 3H), 2.41 (t, *J* = 7.4 Hz, 2H), 2.11 (s, 3H), 1.91 – 1.49 (m, 7H), 1.45 – 1.13 (m, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 209.3 (C), 159. (C), 137.0 (C), 127.2 (CH), 114.0 (CH), 74.1 (CH), 55.4 (CH_3), 43.7 (CH_2), 38.8 (CH_2), 30.0 (CH_3), 25.5 (CH_2), 23.7 (CH_2).

HRMS [ESI(+)]: *m/z* calcd. for $C_{14}H_{20}O_3Na$: 259.1305 [M+Na], found: 259.1303.

Matteson homologation: Synthesis of 2-(4-methoxyphenyl)-2-methylpentan-1-ol 12



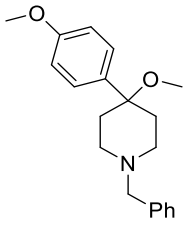
Experimental procedure: To a stirred solution of the tertiary boronate **7a** (0.10 mmol, 31 mg) and dibromomethane (0.5 mmol, 35 microL) in anhydrous THF (1 mL, 0.1 M) at –78 °C, was added *n*-BuLi (2.5 M in hexanes, 0.44 mmol, 176 microL) dropwise. The resulting mixture was stirred for 10 min at –78 °C, warmed to room temperature and stirred for 6 h. The reaction mixture was then cooled to 0 °C and a solution of 2 N NaOH / 30% H_2O_2 (2:1 v/v, 1.0 mL) was added dropwise. This mixture was stirred for overnight at room temperature and diluted with EtOAc (15 mL). The layers were separated and the aqueous layer was extracted with EtOAc (2 × 10 mL). The combined organic layers were washed with water (5 mL) and brine (5 mL), dried (Na_2SO_4), filtered and concentrated in vacuo. The crude residue was purified by flash column chromatography in SiO_2 to yield 19 mg of the alcohol **12** as a colourless oil (89 % yield). Rf = 0.35 (Hex/EtOAc 5:1).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39 – 7.17 (m, 2H), 6.98 – 6.84 (m, 2H), 3.82 (s, 3H), 3.70 (d, *J* = 10.8 Hz, 1H), 3.52 (d, *J* = 10.8 Hz, 1H), 1.78 – 1.58 (m, 1H), 1.49 (ddd, *J* = 13.4, 12.0, 4.7 Hz, 1H), 1.35 (s, 3H), 1.32 – 1.13 (m, 2H), 1.12 – 0.94 (m, 1H), 0.87 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 157.9 (C), 136.9 (C), 127.9 (CH), 113.9 (CH), 72.8 (CH_2), 55.3 (CH_3), 43,0 (C), 41.2 (CH_2), 21.7 (CH_3), 17.2 (CH_2), 14.9 (CH_3).

HRMS [ESI(+)]: *m/z* calcd. for $C_{13}H_{20}O_2Na$: 231.1356 [M+Na], found: 231.1356.

Methoxylation reaction: Synthesis of 1-benzyl-4-methoxy-4-(4-methoxyphenyl)piperidine 13



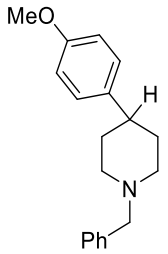
Experimental procedure: A flask containing the corresponding boronic ester **5g** (80 mg, 0.20 mmol, 1 equiv), aniline (98 mg, 0.8 mmol, 2 equiv), $Cu(OAc)_2$ (72 mg, 0.80 mmol), and Cs_2CO_3 (33 mg, 0.1 mmol) was purged with argon. Methanol (0.5 mL) and pyridine (0.15 mL) were added, and the mixture was stirred at 65°C until the reaction was complete (as determined by TLC). The mixture was cooled to room temperature, NH_4OH (10 mL) was added, and the mixture was extracted with Et_2O (3×10 mL), dried ($MgSO_4$), filtered, and concentrated in vacuo. The crude material was purified by column chromatography in SiO_2 affording the compound **13** (40 mg, 65% yield) as a yellow oil. Rf = 0.20 (Hex/EtOAc 1:1).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 – 7.21 (m, 7H), 6.93 – 6.84 (m, 2H), 3.81 (s, 3H), 3.55 (s, 2H), 2.94 (s, 3H), 2.78 – 2.66 (m, 2H), 2.42 (td, *J* = 10.4, 5.0 Hz, 2H), 2.08 – 1.93 (m, 4H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 158.7 (C), 138.8 (C), 136.9 (C), 129.4 (CH), 128.3 (CH), 127.4 (CH), 127.1 (CH), 113.7 (CH), 75.3 (C), 63.5 (CH_2), 55.3 (CH_3), 49.51 (CH_2), 49.47 (CH_3), 34.9 (CH_2).

HRMS [ESI(+)]: *m/z* calcd. for $C_{20}H_{26}NO_2$: 312.1958 [M+H], found: 312.1959.

Protodeboronation reaction of 5g: Synthesis of 1-benzyl-4-(4-methoxyphenyl)piperidine 14



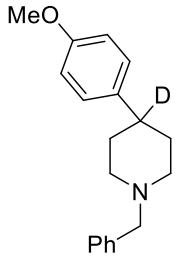
Experimental procedure: A 5 mL flash was charged with the tertiary boronic ester **5g** (30 mg, 0.075 mmol) and KO^{t}Bu (17 mg, 0.15 mmol) in 1.5 mL of dioxane and 1 mL H_2O. The mixture was heated at 120 ºC for 12 h. The flask was cooled down to room temperature and the mixture was extracted 3 times with Et2O (3 x 15 mL) and the combined organic phase was washed with brine (1 x 15 mL). The solvents were eliminated under reduced pressure and the crude of the reaction was purified by flash column chromatography in SiO_2 affording the compound **14** (13 mg, 62% yield) as a yellow oil. Rf = 0.25 (Hex/EtOAc 2:1).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39 – 7.23 (m, 5H), 7.16 (d, *J* = 8.6 Hz, 2H), 6.85 (d, *J* = 8.6 Hz, 2H), 3.79 (s, 3H), 3.56 (s, 2H), 3.07 – 2.97 (m, 2H), 2.45 (ddd, *J* = 16.0, 10.6, 6.7 Hz, 1H), 2.08 (td, *J* = 10.9, 5.2 Hz, 2H), 1.86 – 1.70 (m, 4H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 158.0 (C), 138.9 (C), 138.6 (C), 129.4 (CH), 128.3 (CH), 127.9 (CH), 127.1 (CH), 113.9 (CH), 63.7 (CH_2), 55.4 (CH_3), 54.5 (CH_2), 41.9 (CH), 33.9 (CH_2).

HRMS [ESI(+)]: *m/z* calcd. for $C_{19}H_{24}NO$: 282.1852 [M+H], found: 282.1864.

Deuterodeboronation reaction of 5g: Synthesis of 1-benzyl-4-(4-methoxyphenyl)piperidine-4-d 14D



Experimental procedure: A 5 mL flash was charged with the tertiary boronic ester **5g** (30 mg, 0.075 mmol) and KO^{t}Bu (17 mg, 0.15 mmol) in 0.5 mL of dioxane and 1 mL D_2O. The mixture was heated at 120 ºC for 12 h. The flask was cooled down to room temperature and the mixture was extracted 3 times with Et2O (3 x 15 mL) and the combined organic phase was washed with brine (1 x 15 mL). The solvents were eliminated under reduced pressure and the crude of the reaction was purified by flash column chromatography in SiO_2 affording the compound **14D** (13 mg, 62% yield) as a yellow oil. Rf = 0.25 (Hex/EtOAc 2:1).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39 – 7.23 (m, 5H), 7.16 (d, *J* = 8.6 Hz, 2H), 6.85 (d, *J* = 8.6 Hz, 2H), 3.79 (s, 3H), 3.56 (s, 2H), 3.07 – 2.97 (m, 2H), 2.08 (td, *J* = 10.9, 5.2 Hz, 2H), 1.86 – 1.70 (m, 4H).

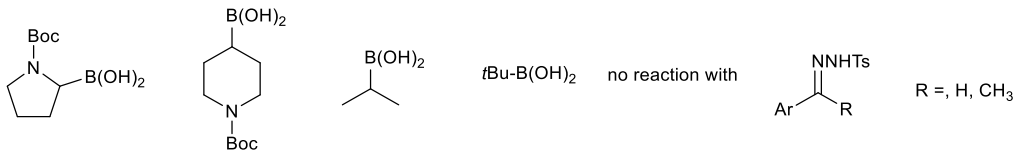
^{13}C NMR (75 MHz, $CDCl_3$) δ 158.0 (C), 138.9 (C), 138.6 (C), 129.4 (CH), 128.3 (CH), 127.9 (CH), 127.1 (CH), 113.9 (CH), 63.7 (CH_2), 55.4 (CH_3), 54.5 (CH_2), 33.9 (CH_2). The signal of the C atom adjacent to D is not observed due to bad relaxation.

HRMS [ESI(+)]: *m/z* calcd. for $C_{19}H_{23}DNO$: 283.1915 [M+H], found: 283.1917.

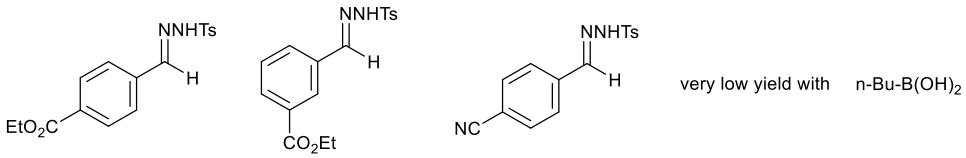
1.7 Failed substrates

The synthesis of benzylboronates features wide scope. Nevertheless, some boronic acids as well as *N*-tosylhydrazones failed to provide the desired coupling products under the photochemical conditions at room temperature. Below are indicated some of the systems that failed in our hands under the current reaction conditions:

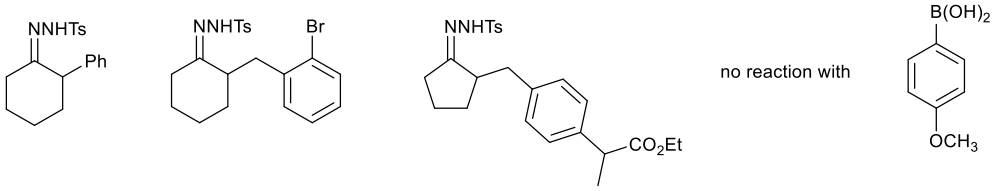
Alkyl boronic acids: the reactions with *N*-tosylhydrazones from aryl aldehydes and ketones proceeded smoothly with cyclic secondary boronic acids, but failed with heterocyclic as well as more hindered secondary anbdboronic acids:



Aryl aldehyde derived N-tosylhydrazones:



Hindered dialkyl N-tosylhydrazones: the reactions proceeded well with α-alkyl substituted *N*-tosylhydrazones (**5f**, **5i**) but failed with bulkier substituents.



2. Mechanistic considerations

As discussed in the main text, formation of a diazoalkane by photoexcitation of a hydrazonate salt upon irradiation with 370-390 nm led light followed by fragmentation is the triggering event for the carboborylation reaction. In their seminal paper, König et al. postulated that the batochromic shift observed upon addition of Cs_2CO_3 to a solution of a *N*-tosylhydrazone indicates that the hydrazonate salt can undergo photoexcitation with violet light promoting the subsequent fragmentiation and formation of the diazoalkane. We have observed the same bathochromic shift for the case of the *N*-tosylhydrazone **H1** derived from an aromatic aldehyde indicating that these hydrazonates can also undergo excitation upon iradiation with 390 nm light (figure S4). The UV-vis absorption spectra were measured in MeCN (for a better solubility of the *N*-tosylhydrazone salts).

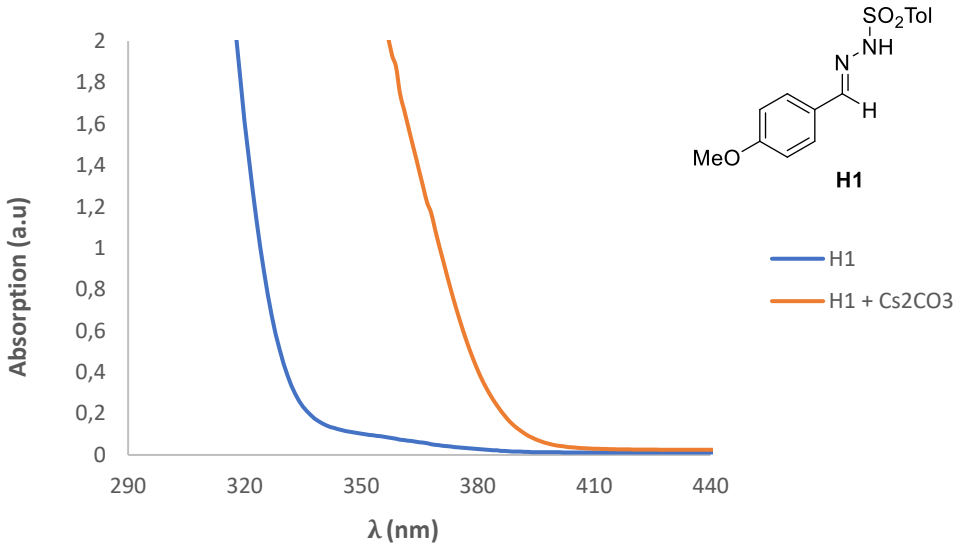


Figure S4. UV-vis spectrum of *N*-tosylhydrazone **H1** (0.1 M, blue line) and **H1** + Cs_2CO_3 (0.1M, orange line) in MeCN.

In our work we show that it is also possible to promote the fragmentation of the *N*-tosylhydrazones upon treatment with DBU instead of Cs_2CO_3. To prove the ability of the DBU-H·*N*-tosylhydrazonate complex to undergo photoexcitation upon irradiation with 370 – 390 nm led light the UV-Vis spectra were also recorded employing *N*-tosylhydrazone **H21** as a model substrate. Again, a substantial bathochromic shift is observed upon addition of DBU to a solution of the *N*-tosylhydrazone supporting this proposal. Of note, no change is observed in the UV-vis absorption spectra upon addition of DIPEA or a boronic acid to the solution, clearly showing the role of the DBU in the bathochromic shift observed (figure S5).

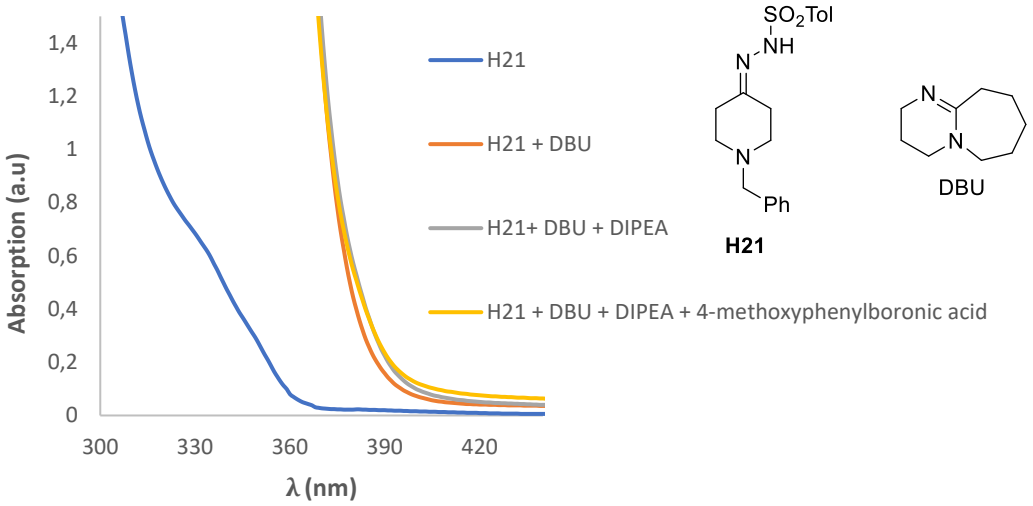
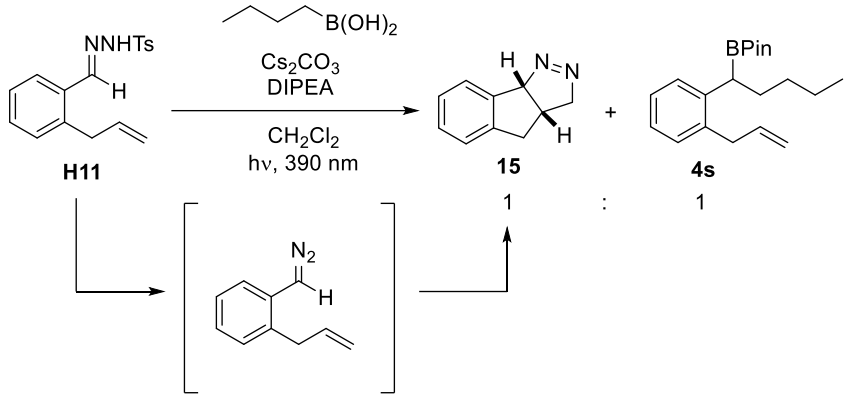


Figure S5. UV-vis spectrum of *N*-tosylhydrazone **H21** (0.1 M, blue line), **H21** + DBU (0.1M, orange line), **H21** + DBU + DIPEA (0.1M, grey line), **H21** + DBU + DIPEA + 4-methoxyphenylboronic acid (0.1M, yellow line) in MeCN.

The formation of a diazoalkane under the photochemical conditions is further supported by the analysis of the reaction of *N*-tosylhydrazone **H11** and butylboronic acid. In this reaction a 1:1 mixture of the boronate **4s** and the fused pyrazoline **15** derived from the intramolecular 1,3-dipolar cycloaddition was obtained. The ^{1}H NMR spectrum of the reaction crude, highlighting the signals corresponding to each compound is included below (figure S6).



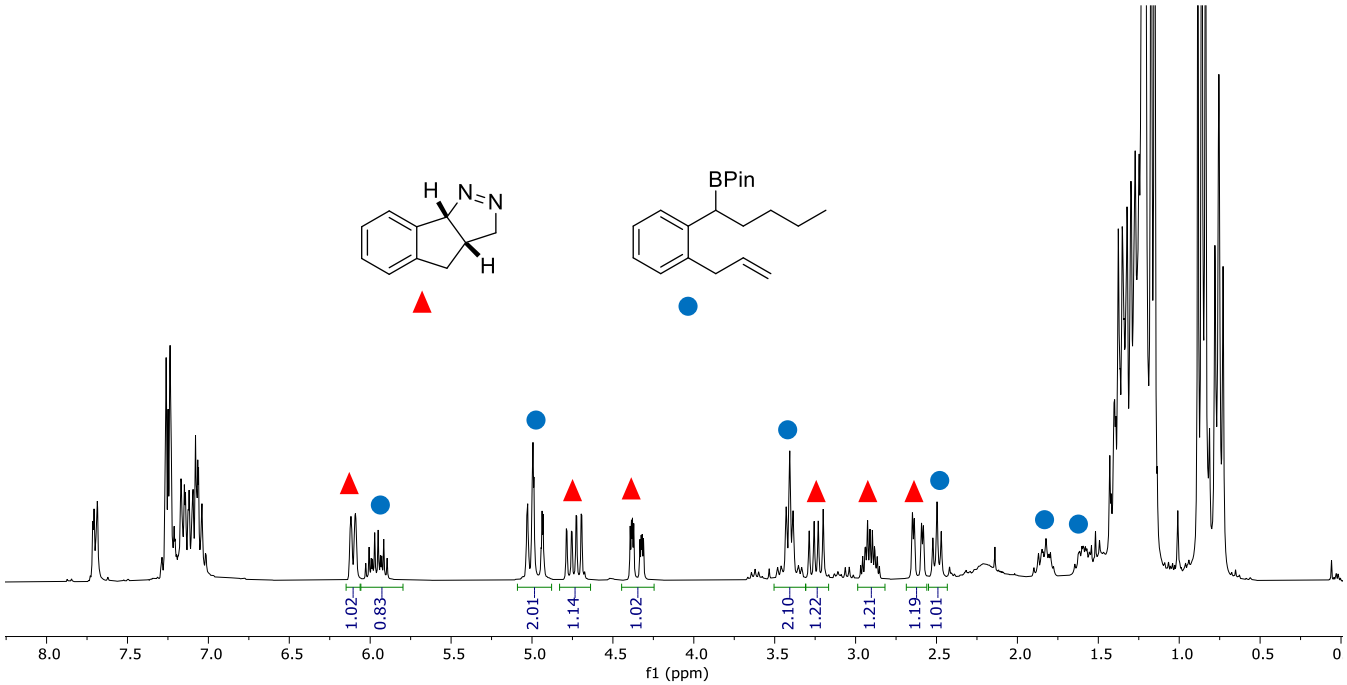


Figure S6. ^{1}H NMR spectrum of the crude of the reaction between *N*-tosylhydrazone **H11** and *n*-butylboronic acid. The signals corresponding to **4s** and the pyrazoline respectively can be clearly distinguished.

3. References

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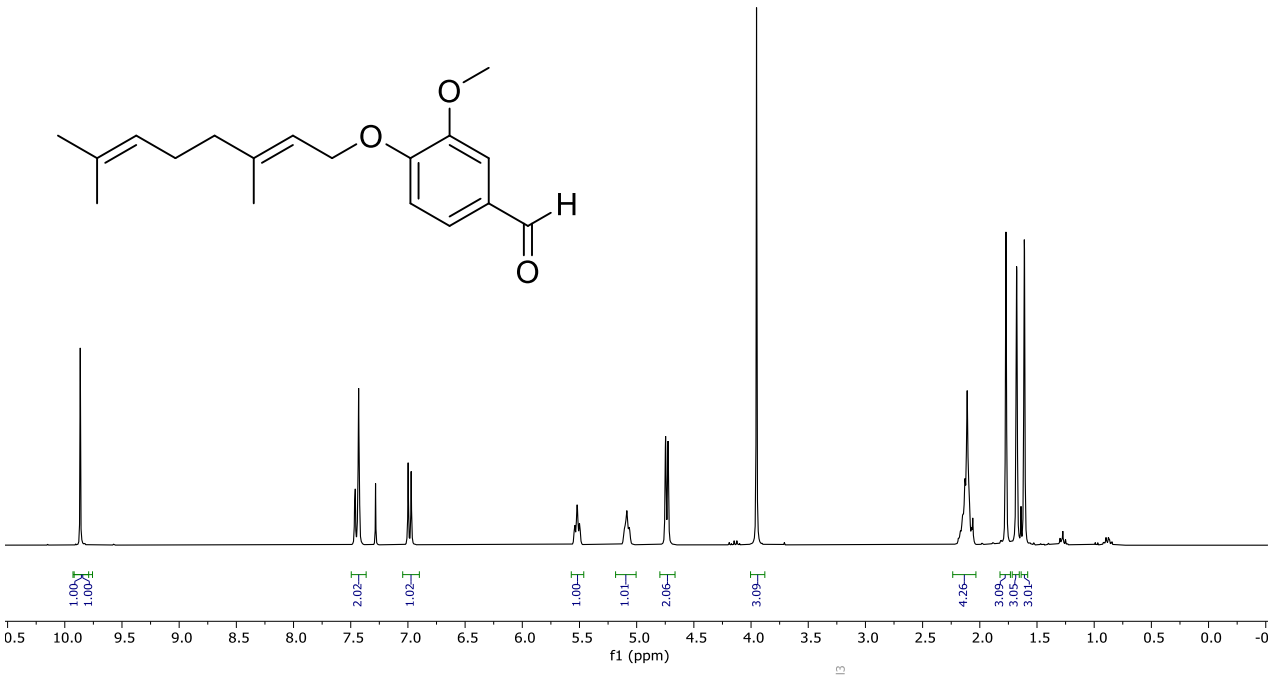
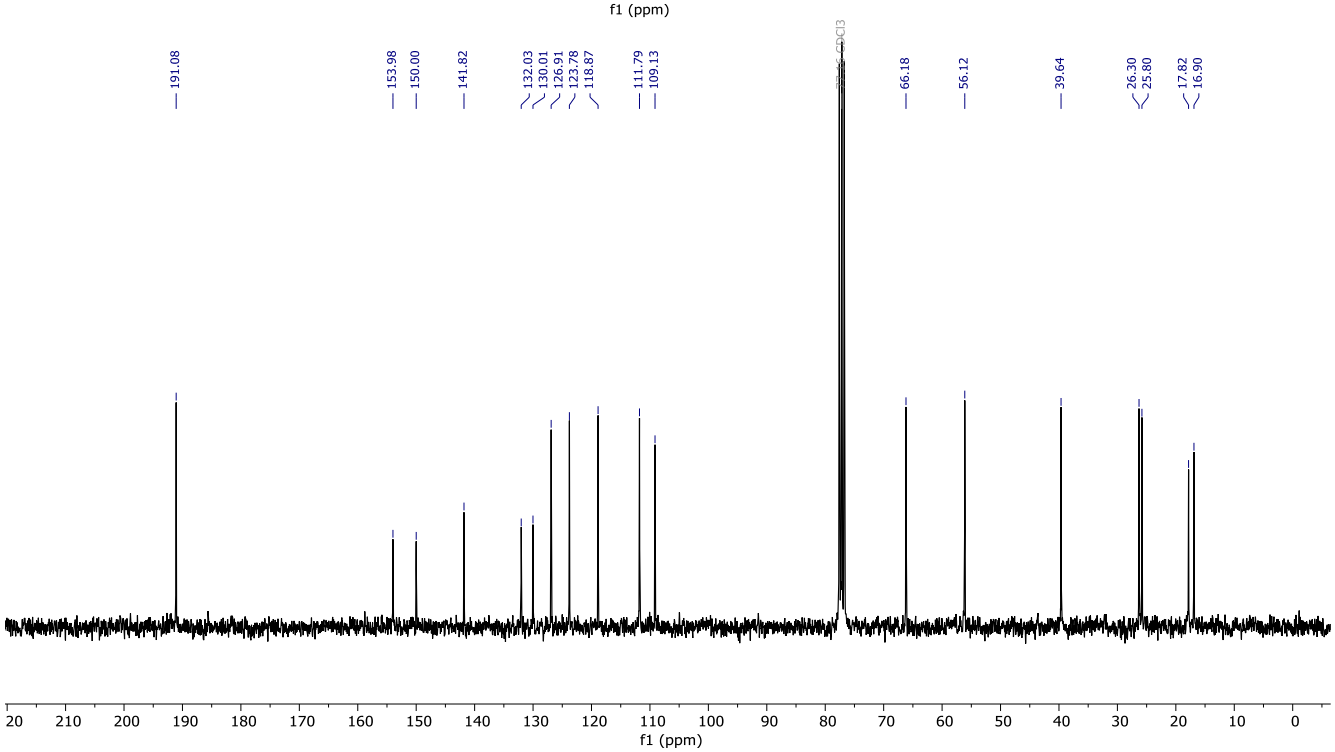
4. Author Contributions

C.V. and M.P. designed the idea and supervised the work. Á.V.-M., L.L. and M.P. performed the experiments on the batch reactions and continuous flow. All the authors discussed on the work and contributed to the preparation of the manuscript and the supporting information. C.V. and M.P. wrote the manuscript.

5. Copies of NMR spectra

(*E*)-4-((3,7-dimethylocta-2,6-dien-1-yl)oxy)-3-methoxybenzaldehyde





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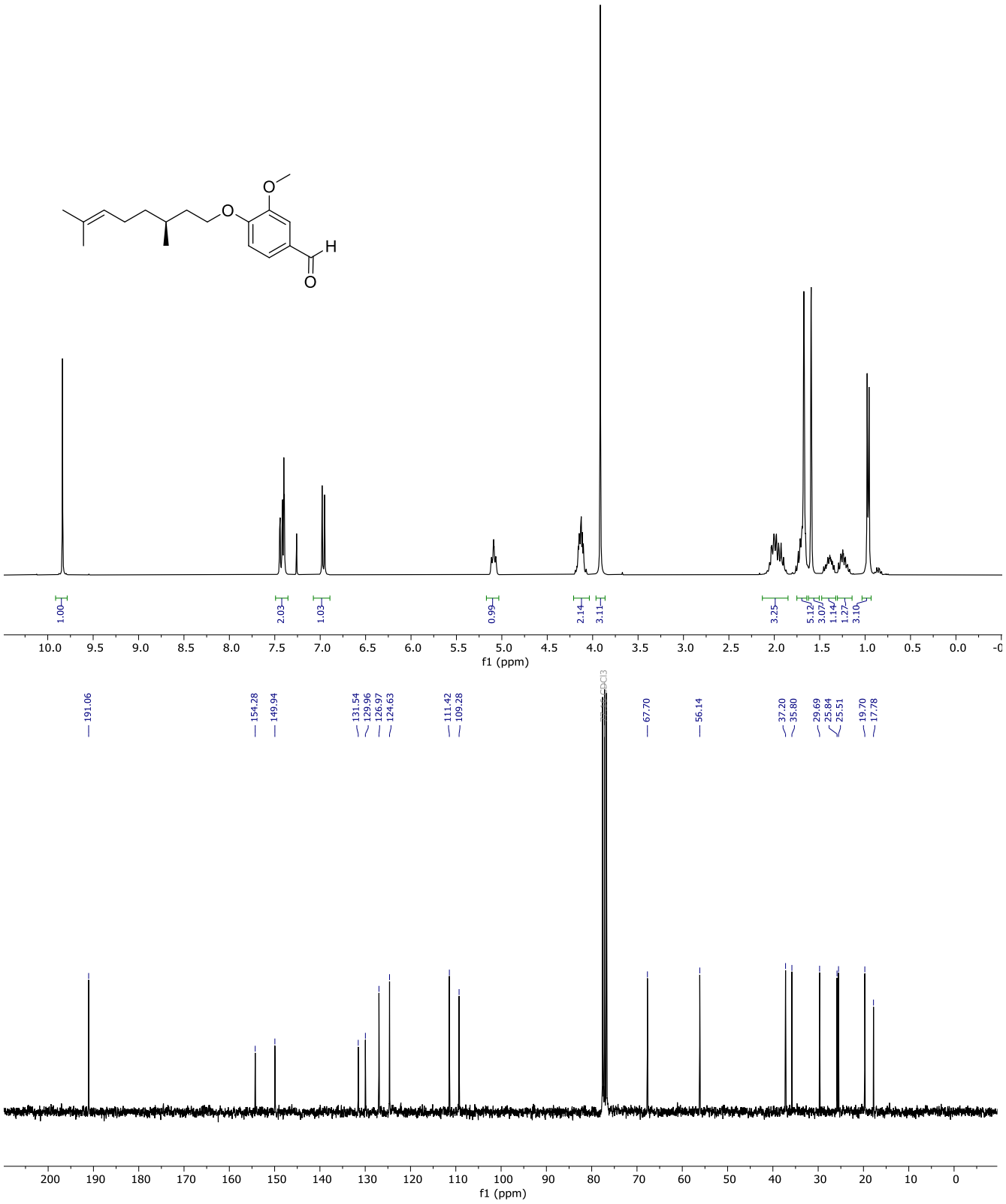
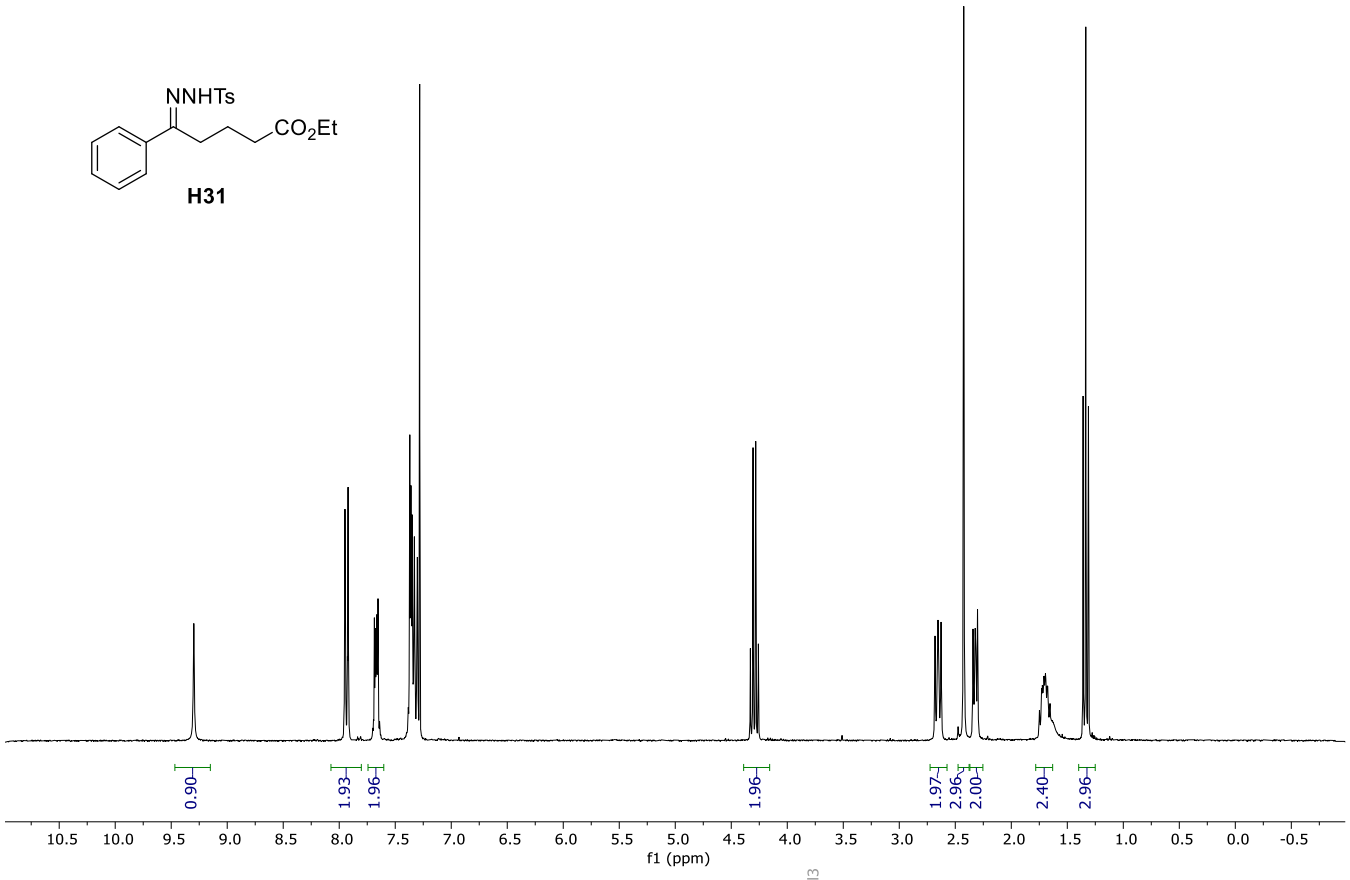
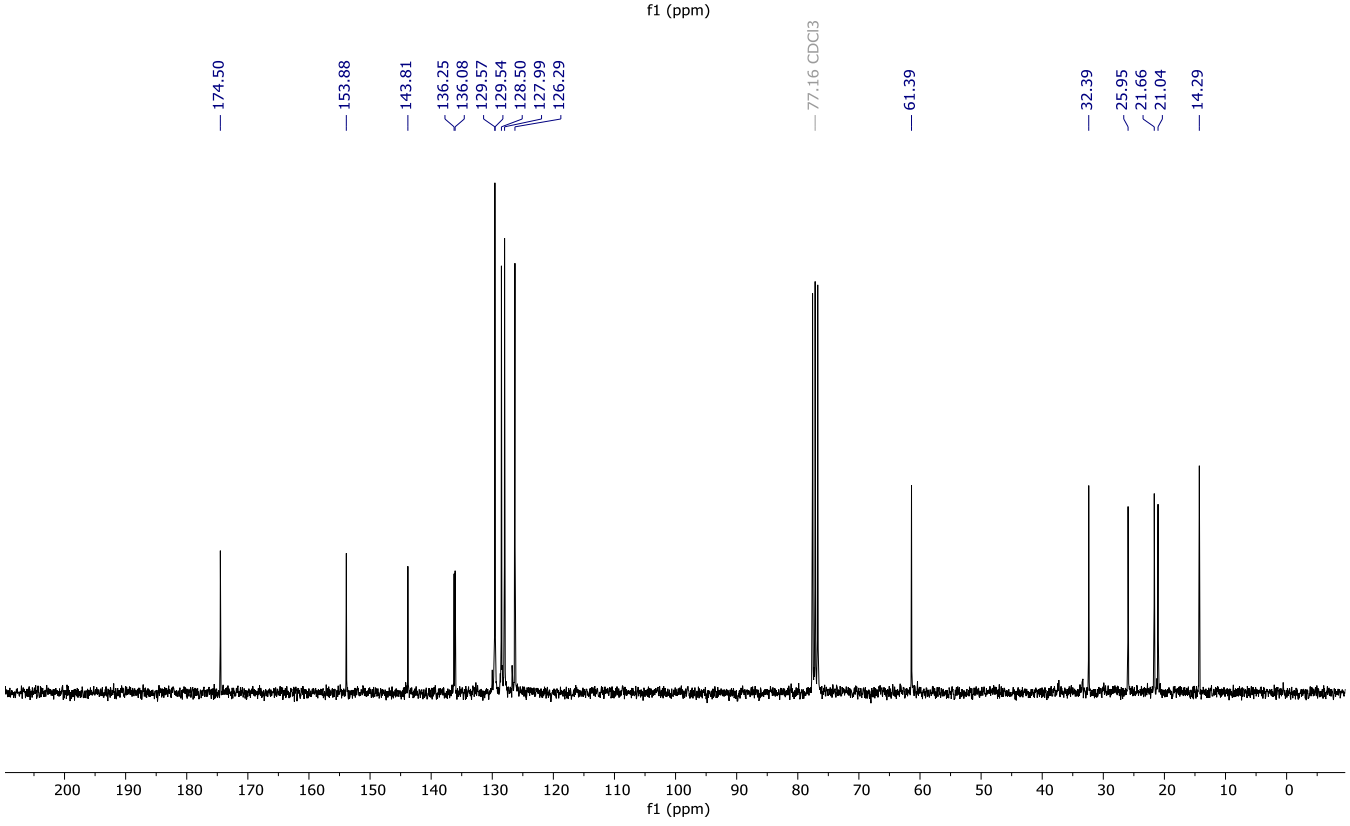


Ethyl 5-phenyl-5-(2-tosylhydrazineylidene)pentanoate H31





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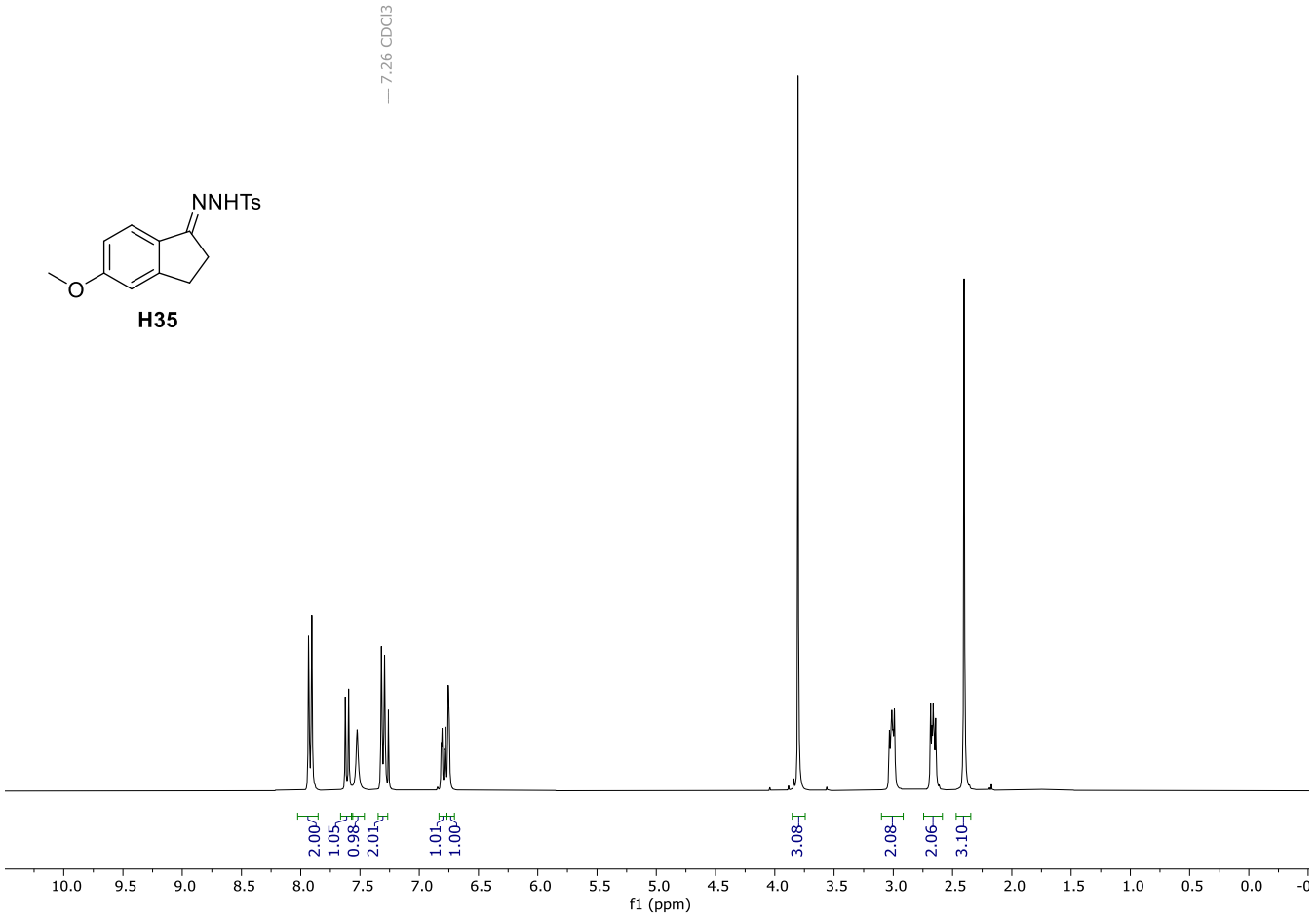

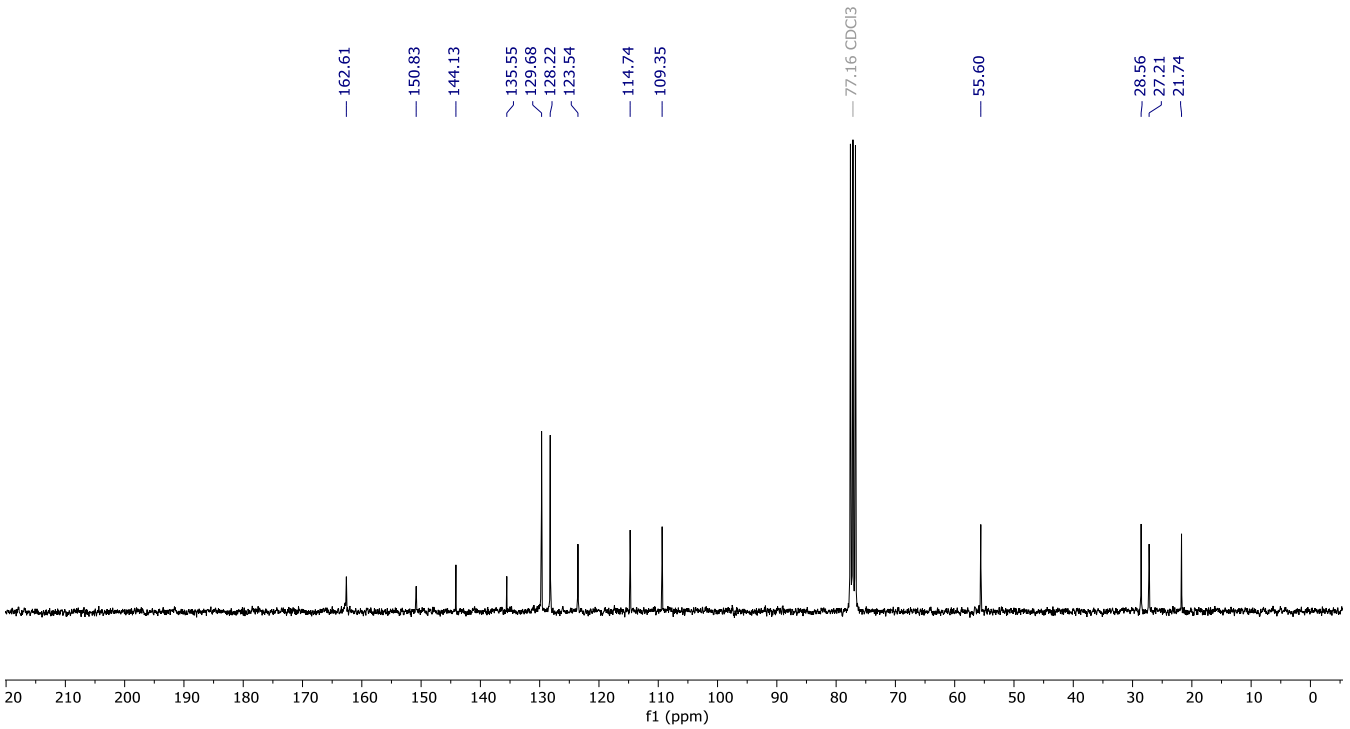

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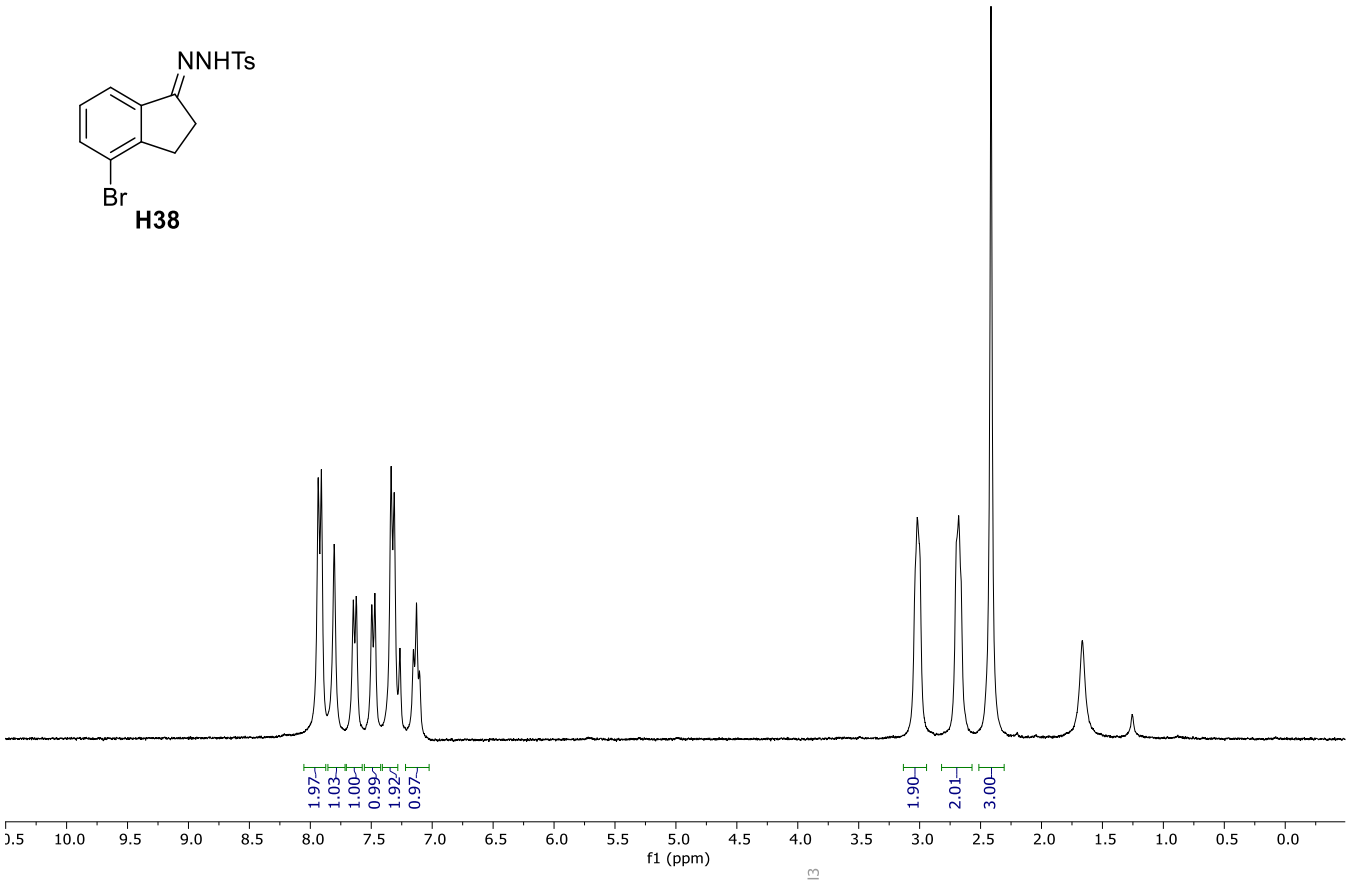

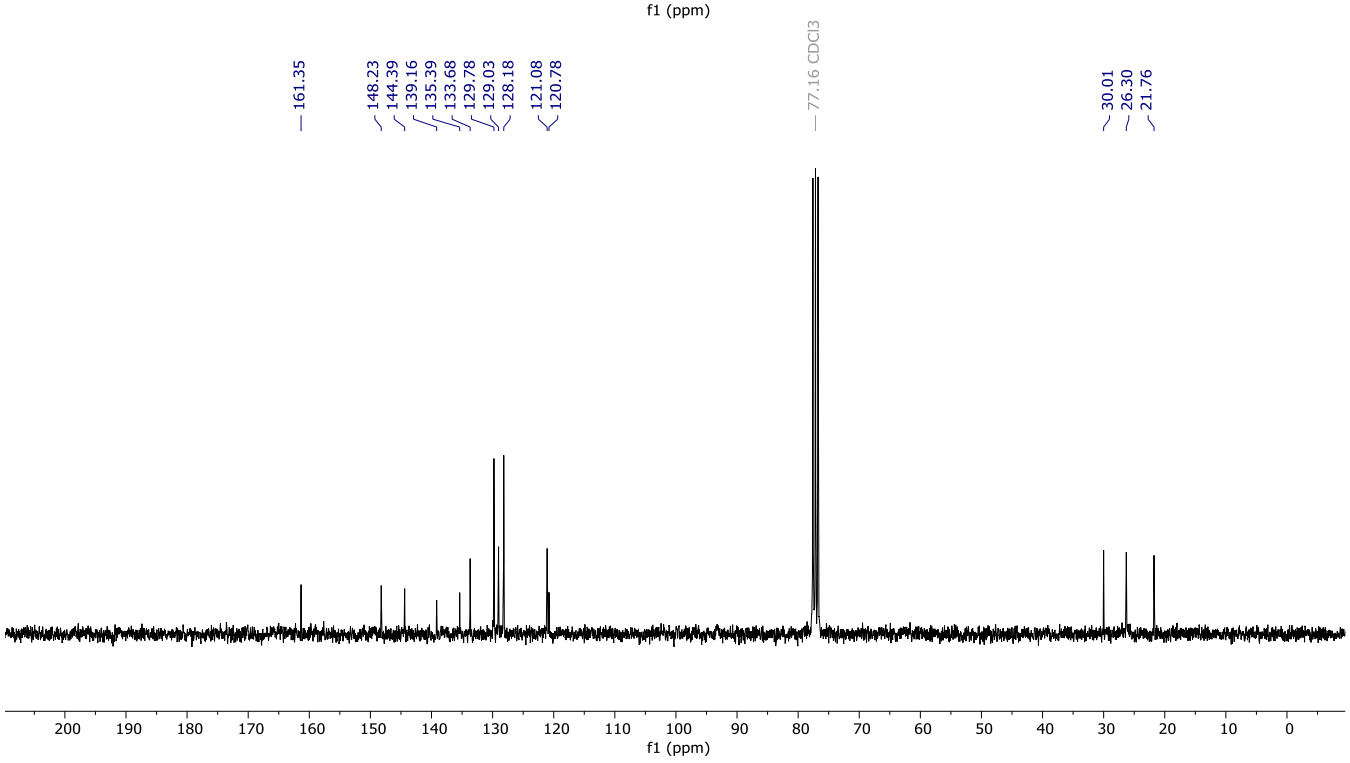

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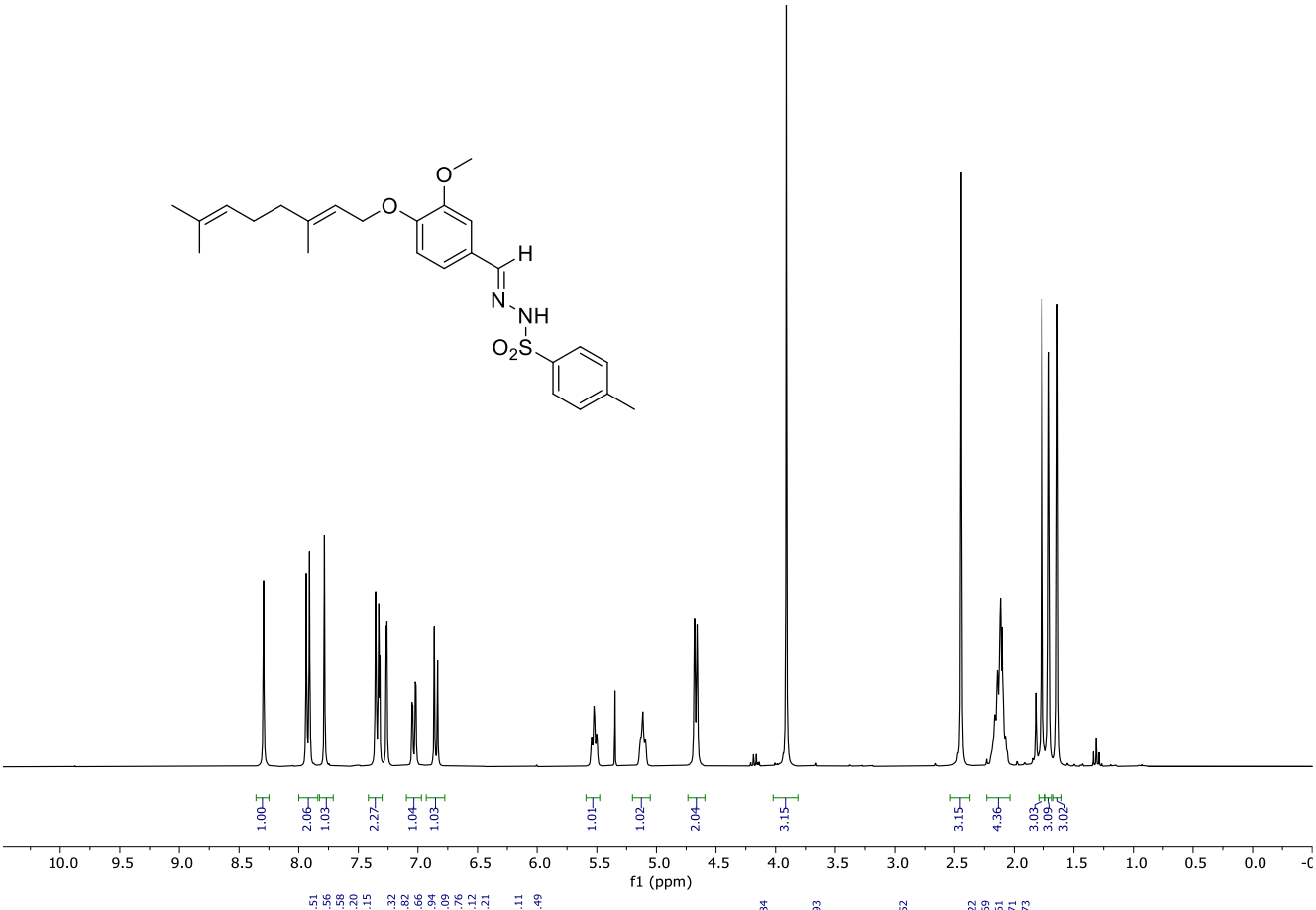

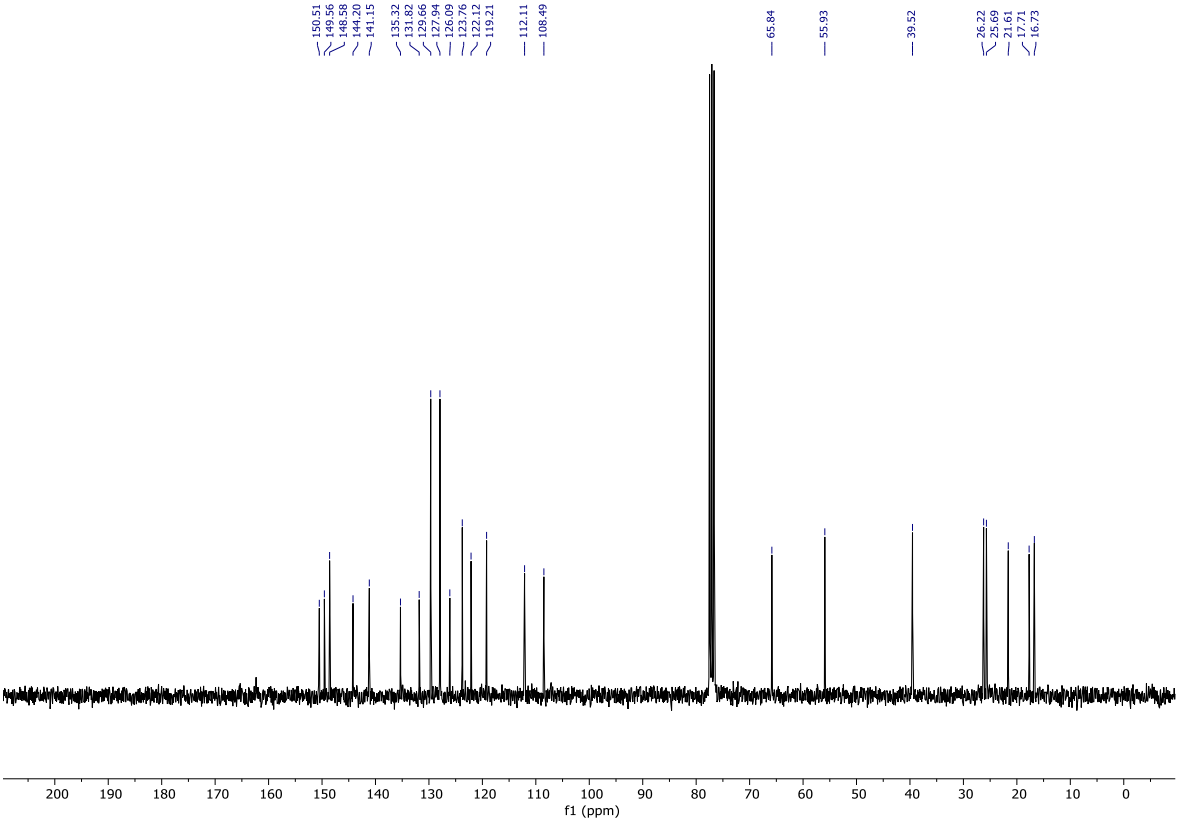

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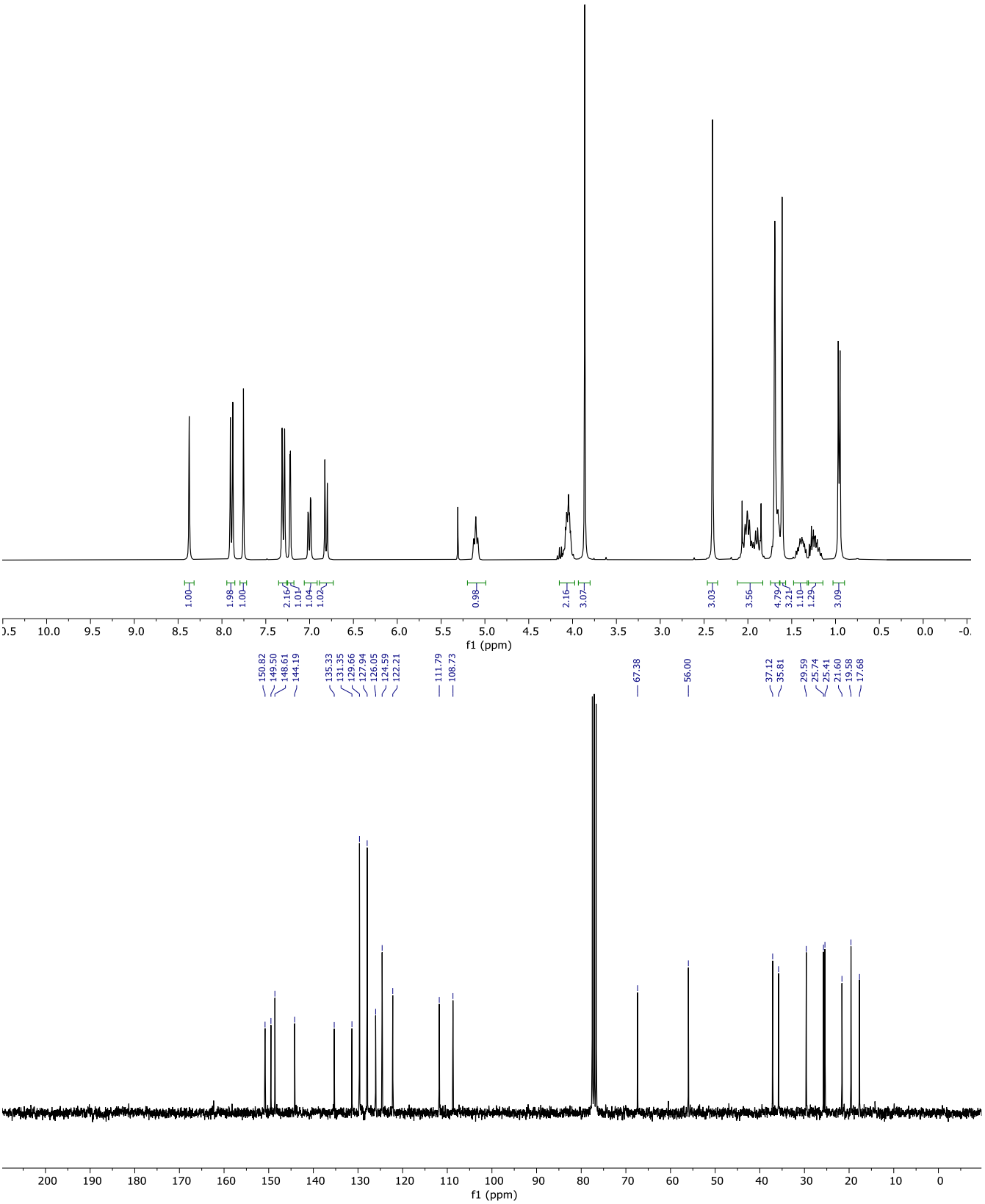
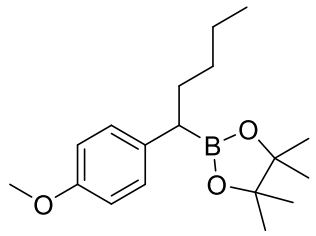


2-(1-(4-methoxyphenyl)pentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 4a



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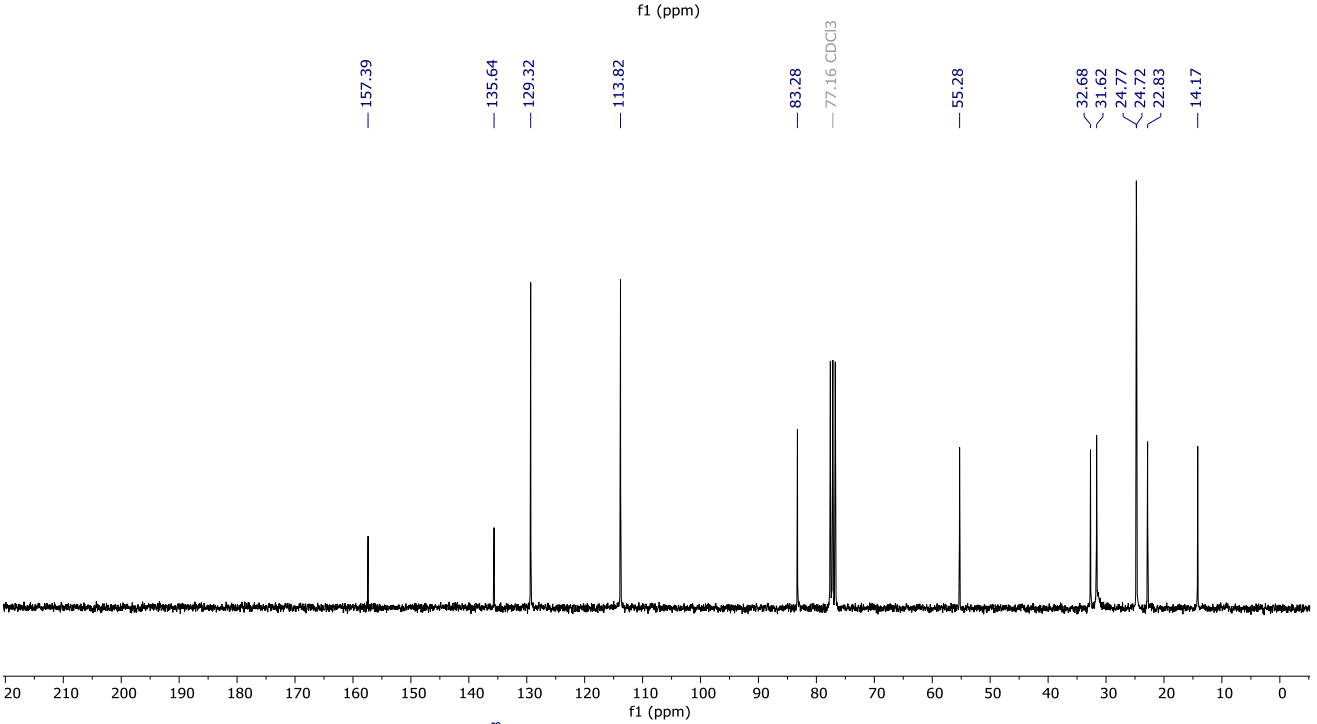

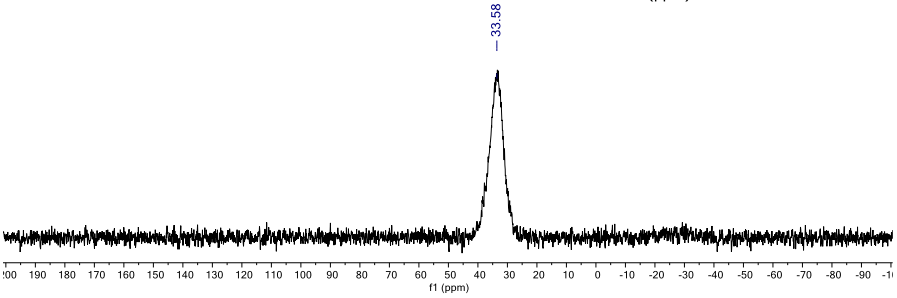

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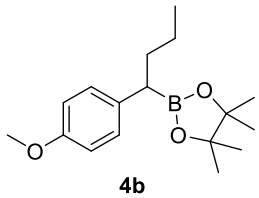

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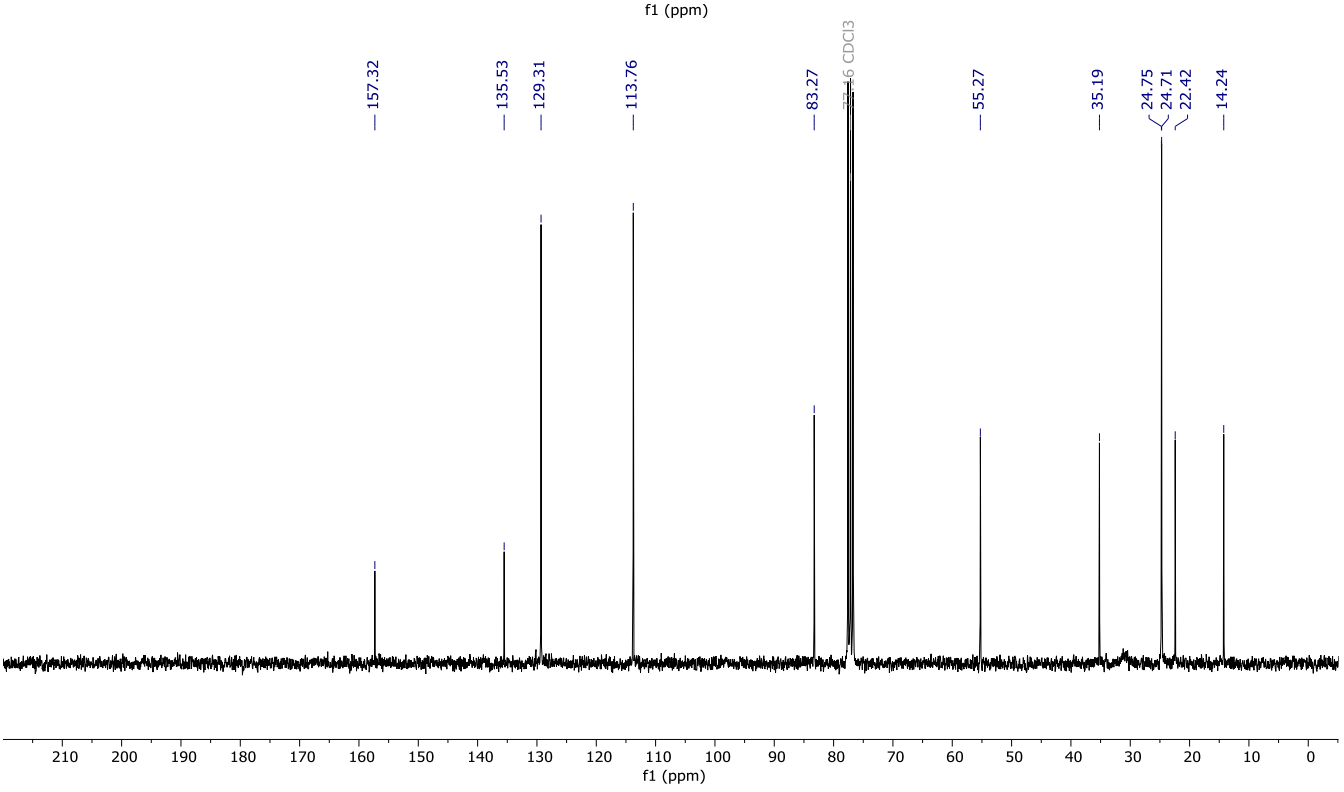

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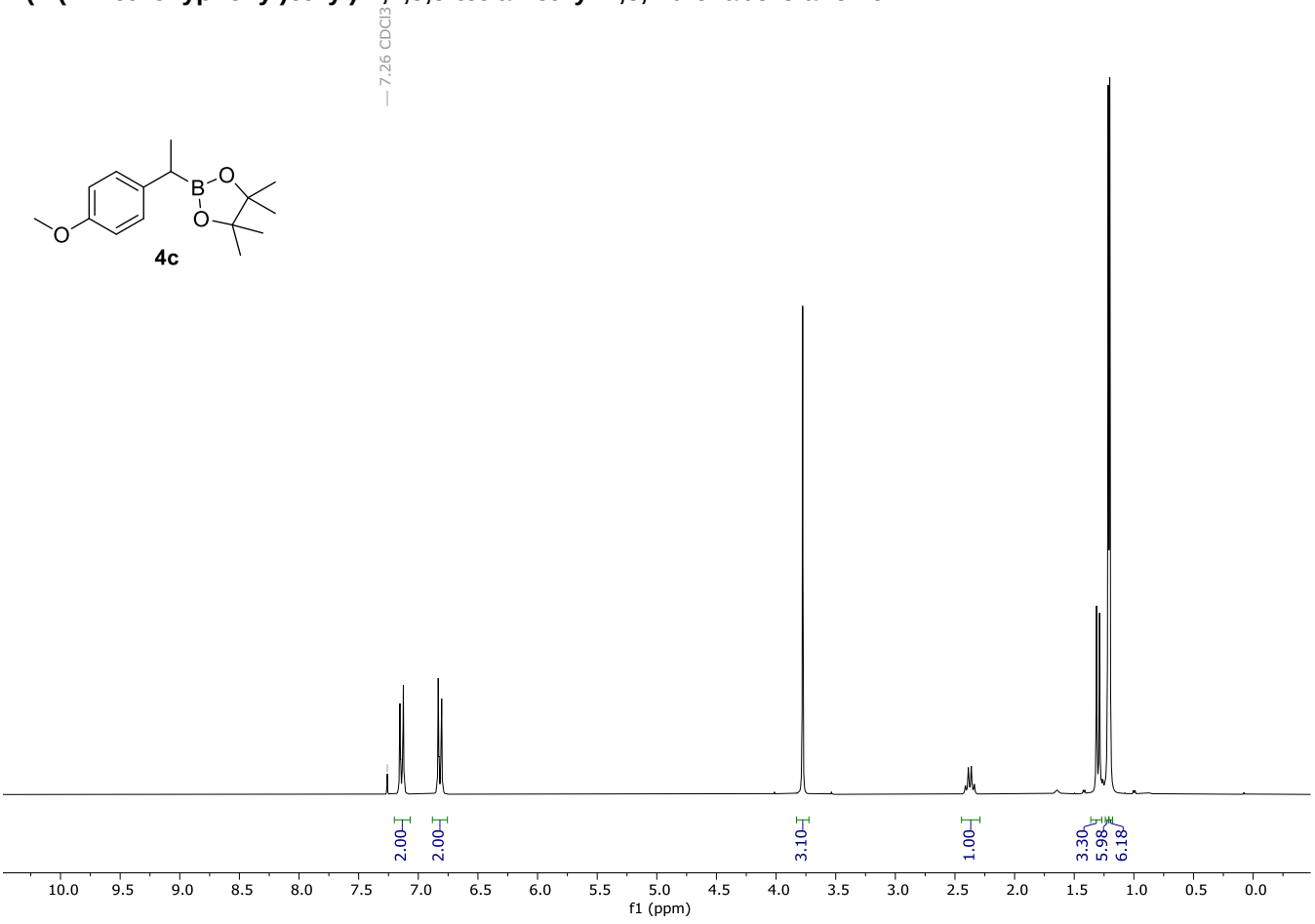

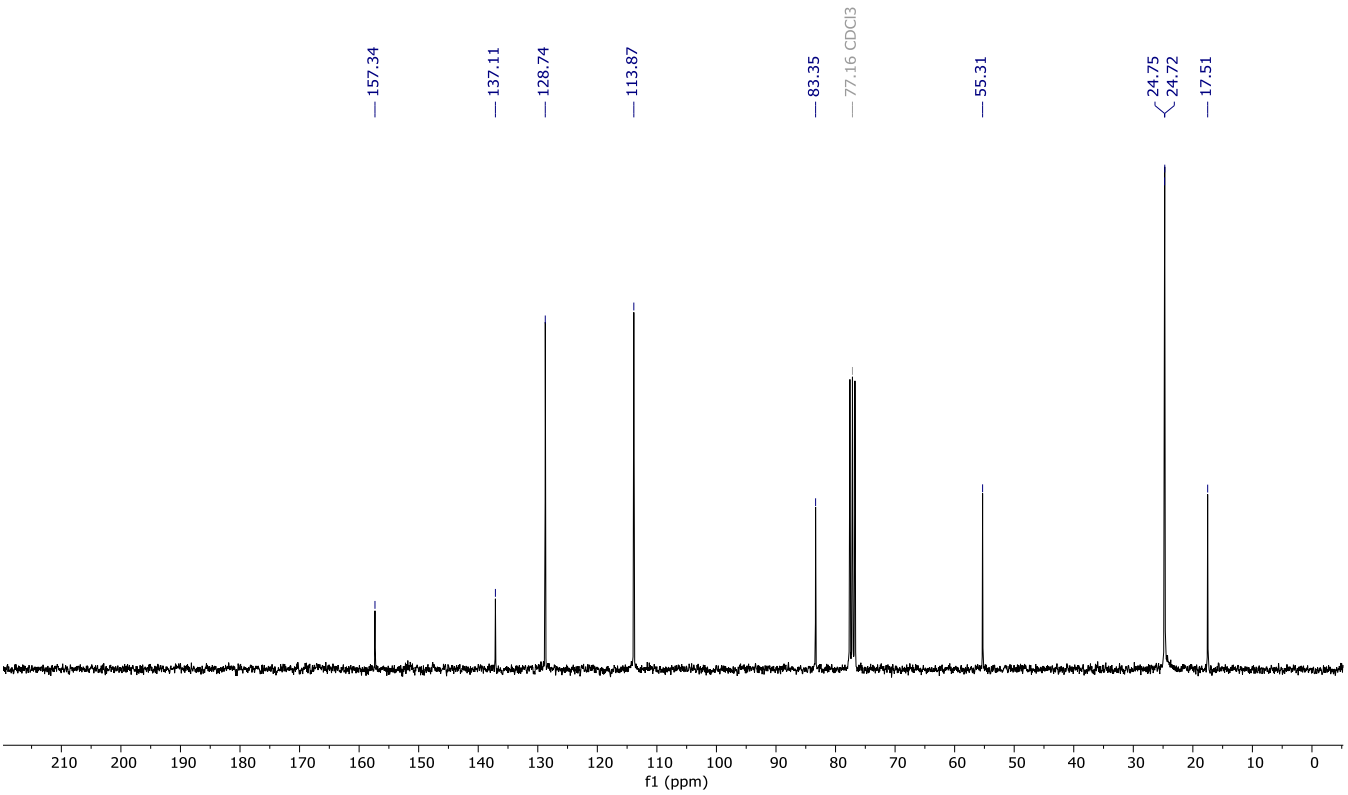

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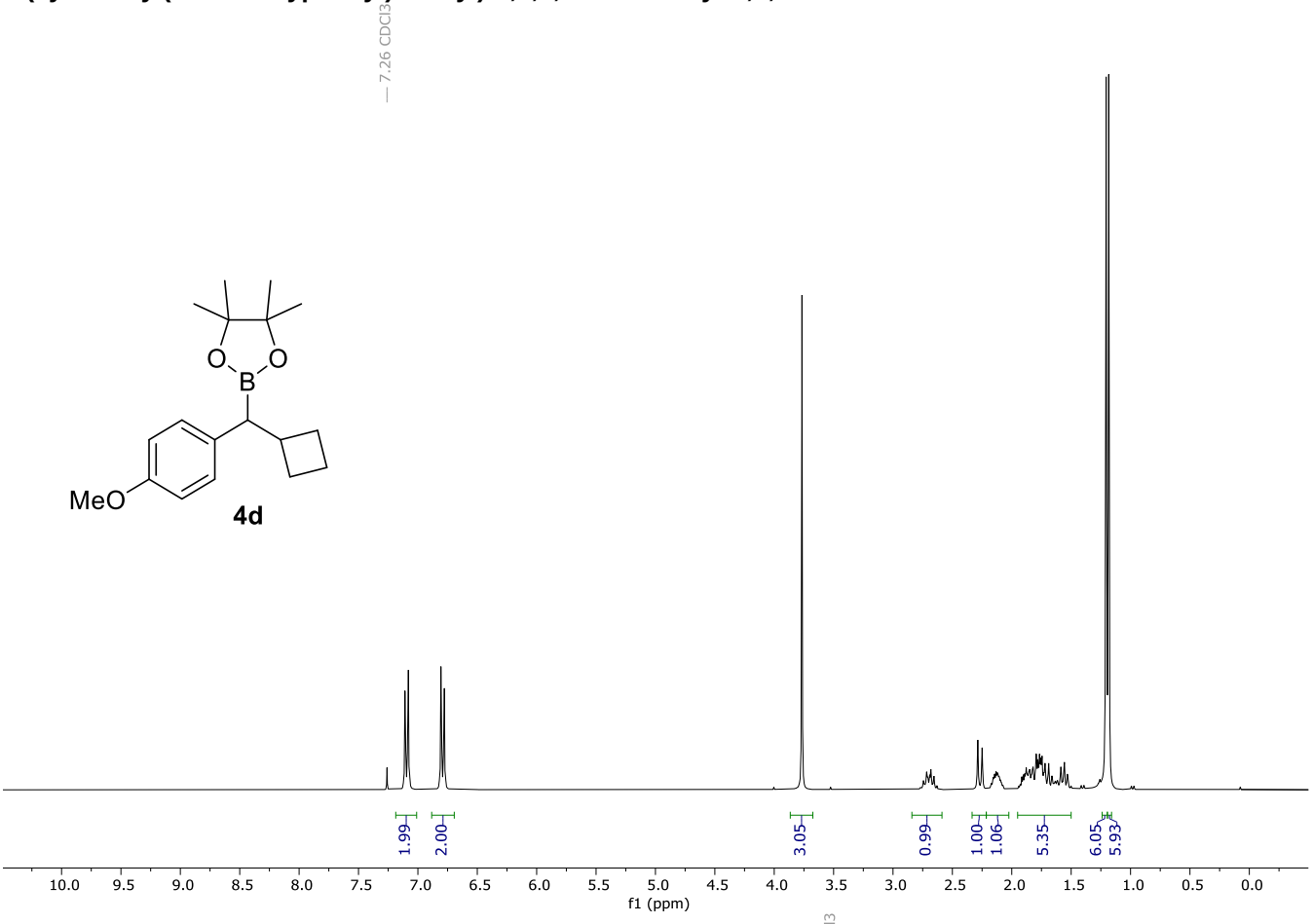

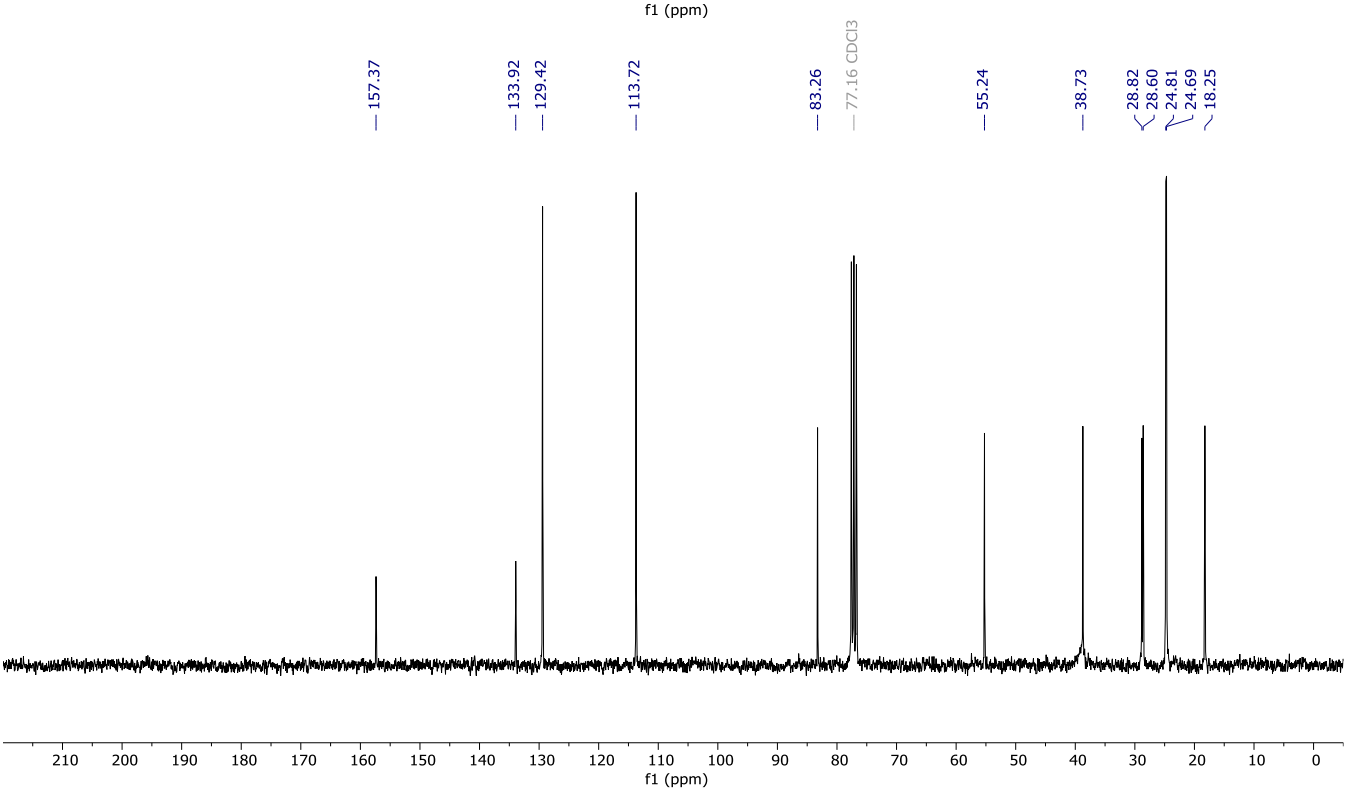

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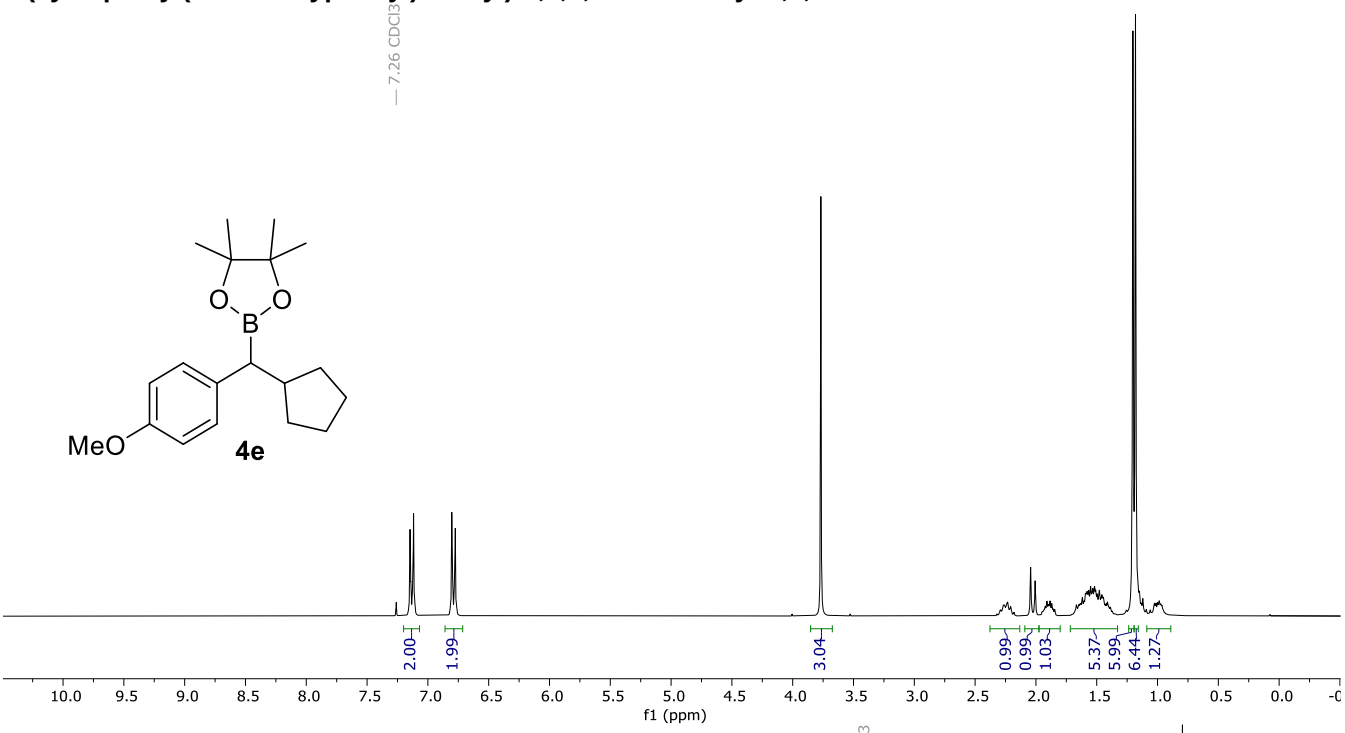

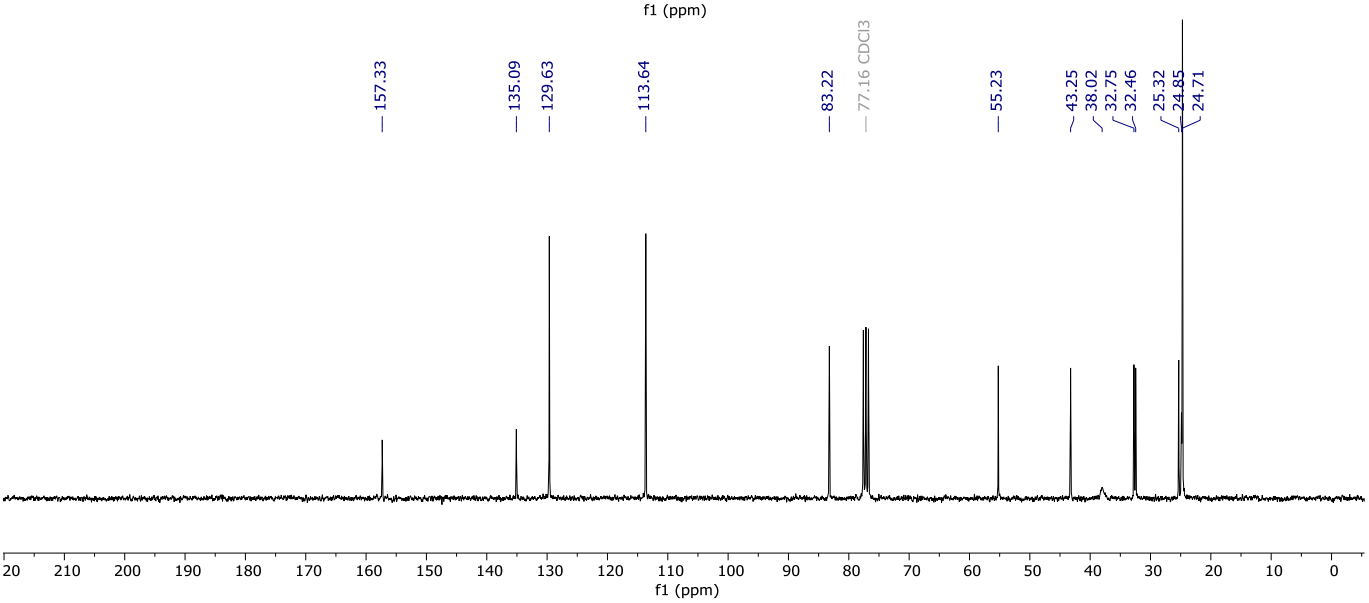

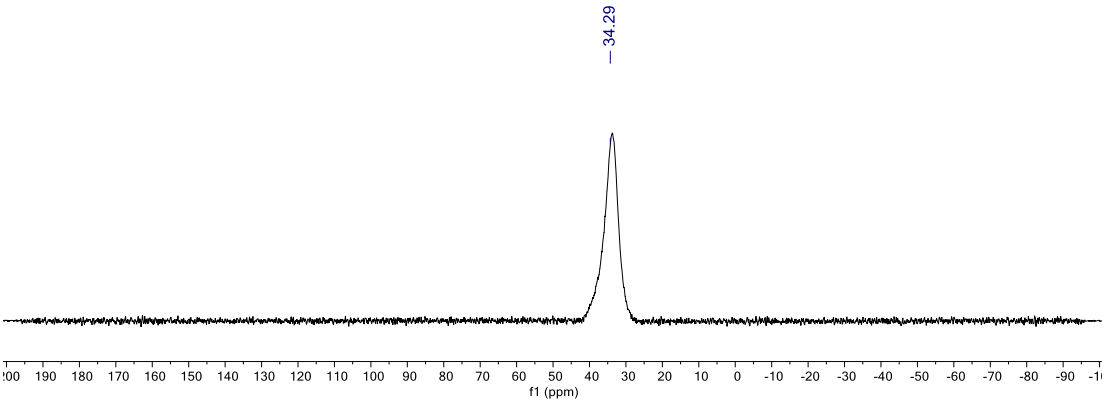

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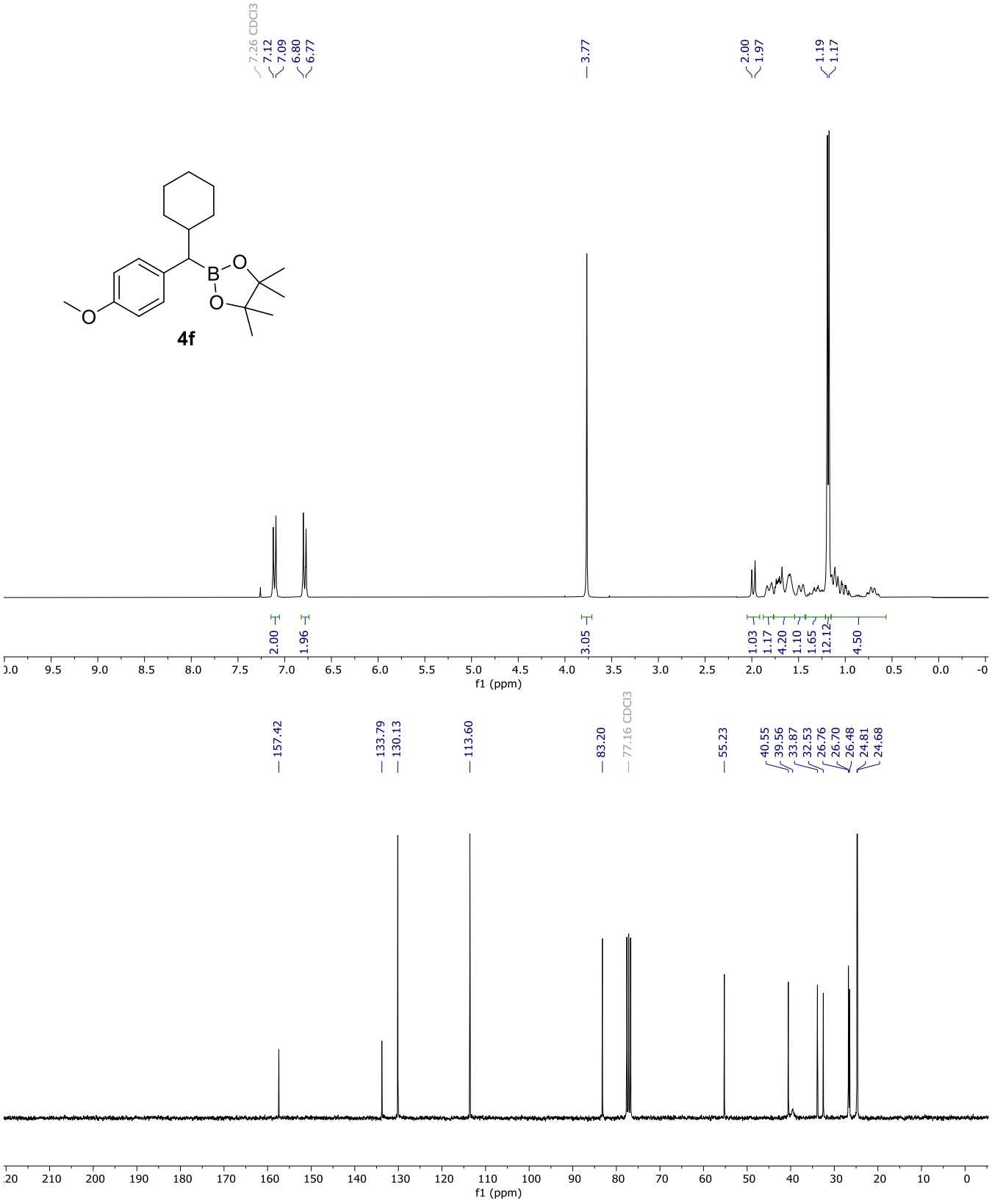

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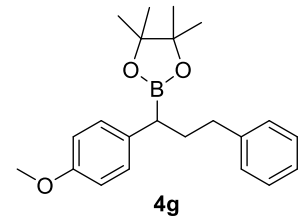

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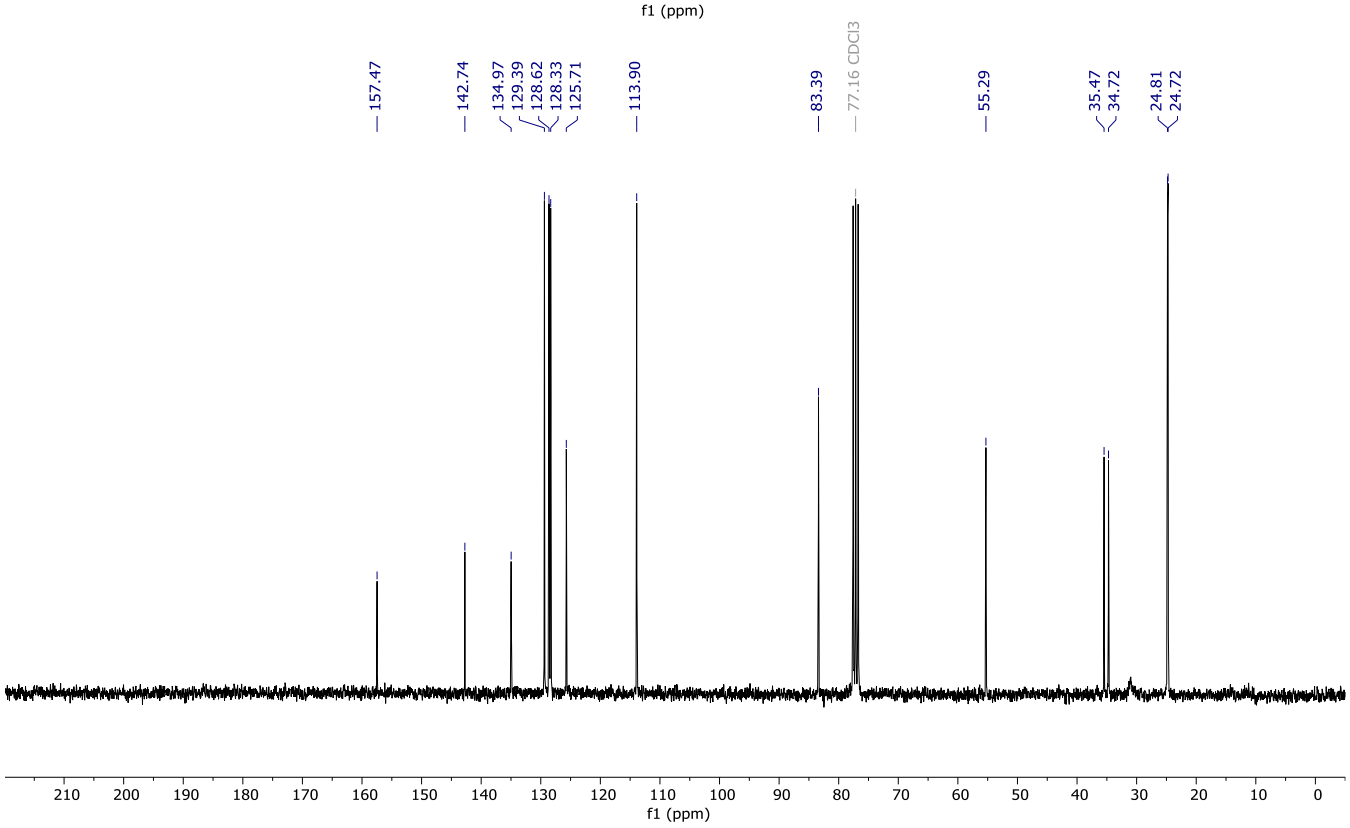

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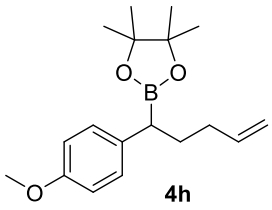

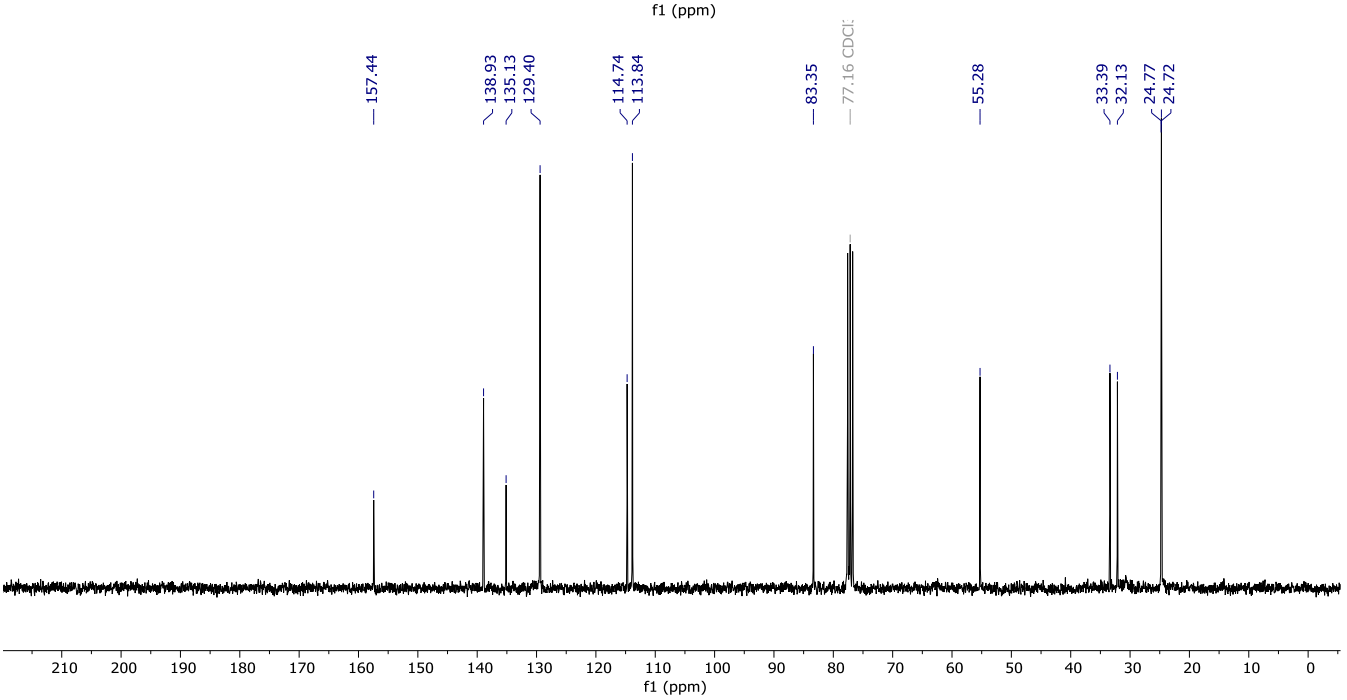

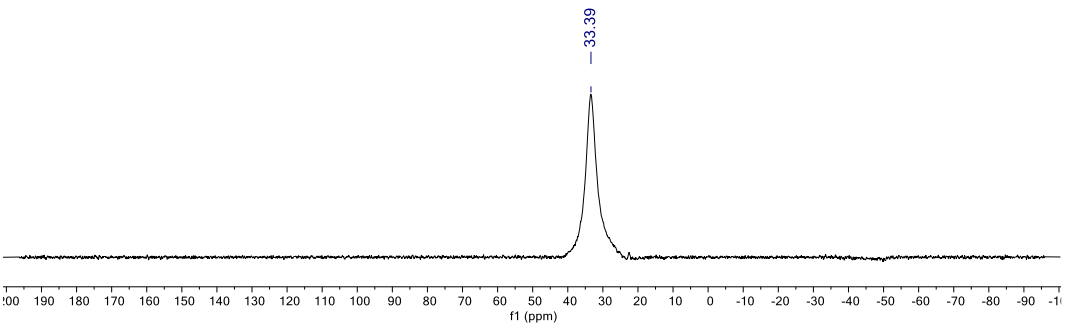

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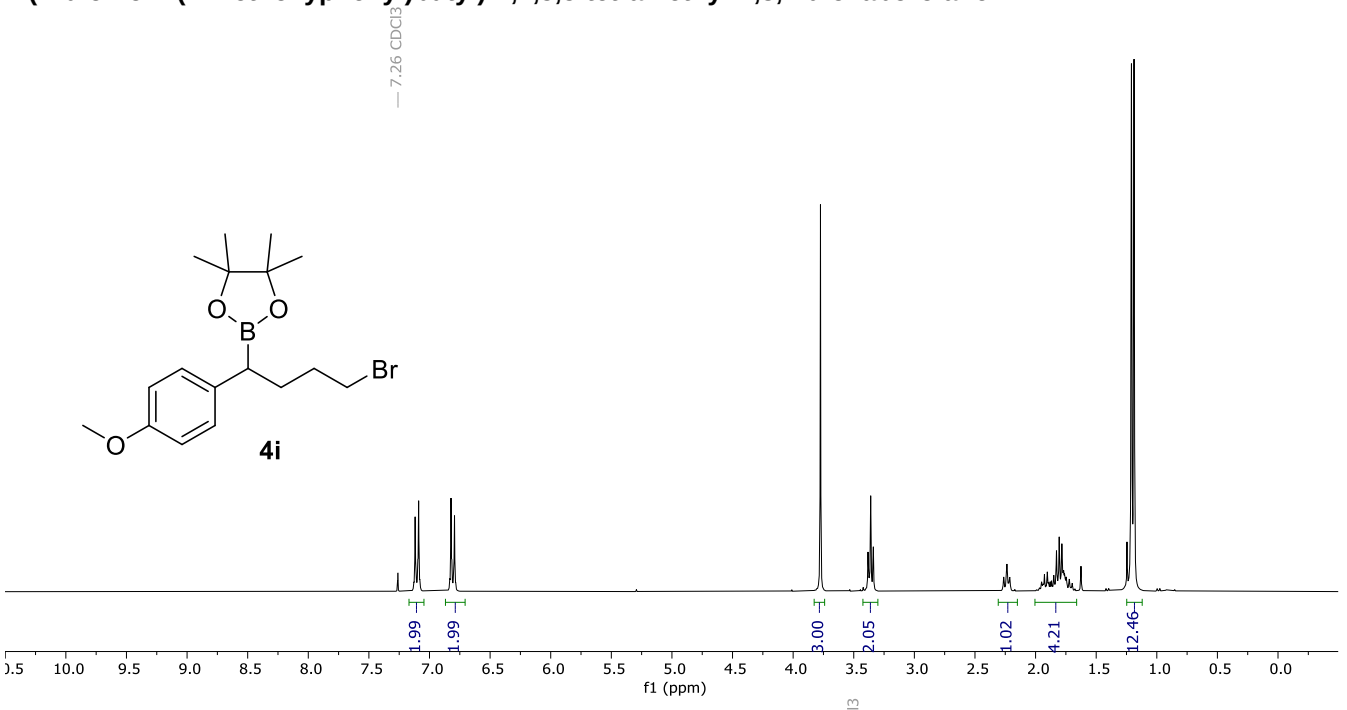

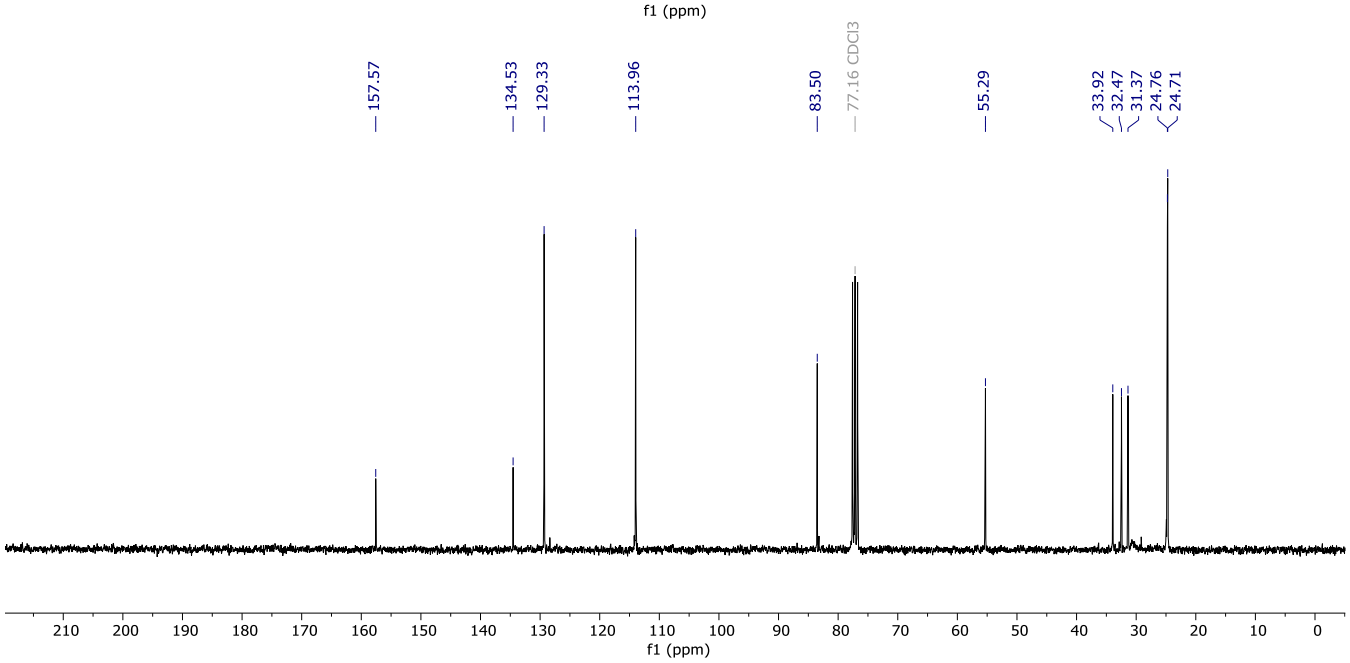

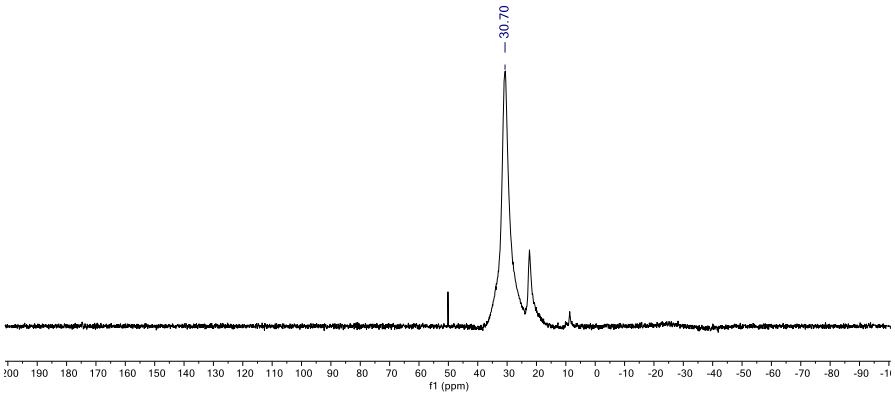

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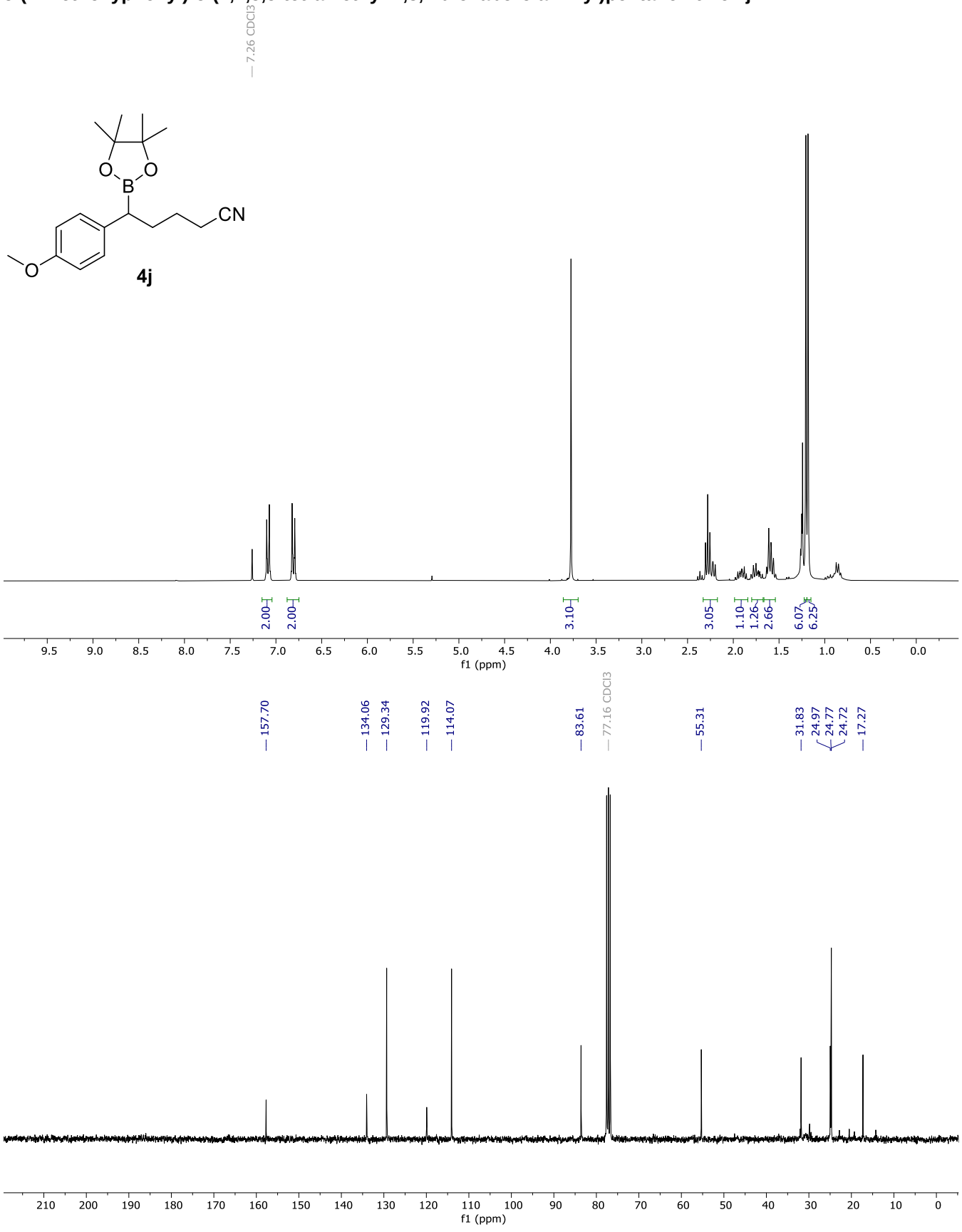

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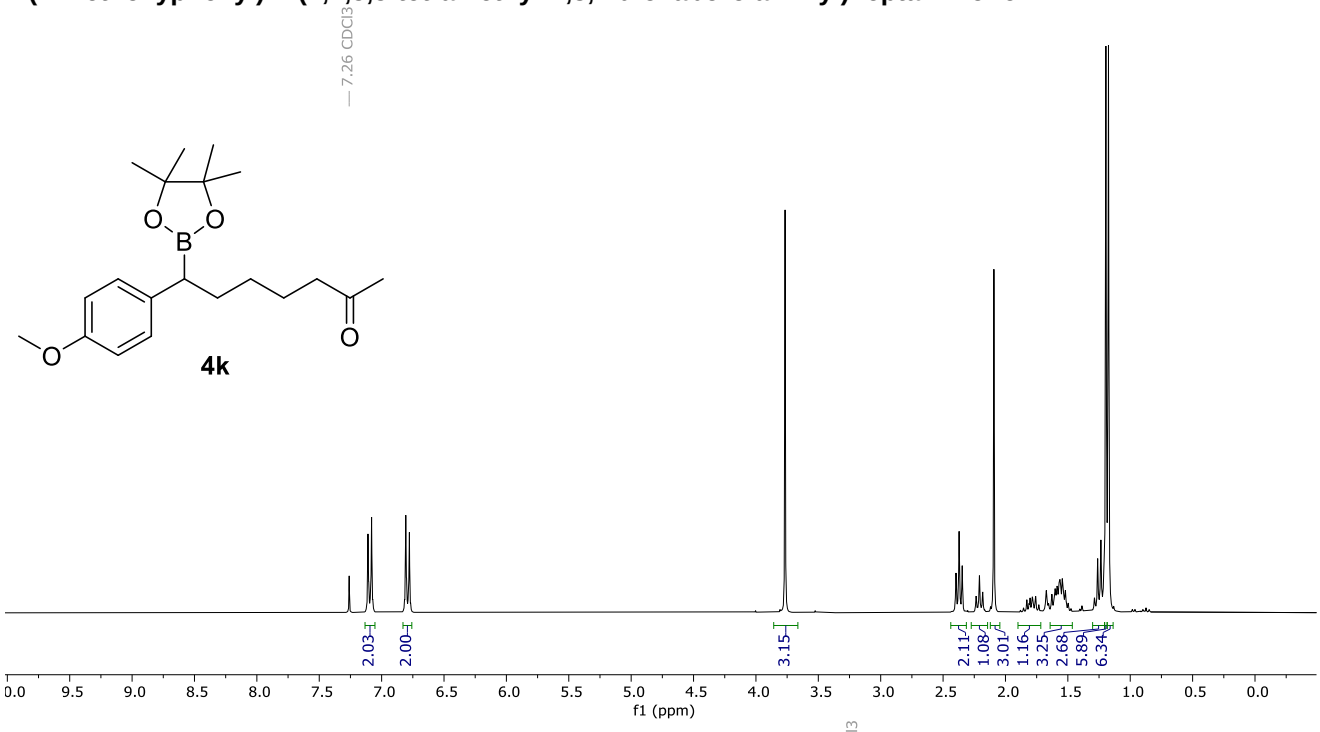

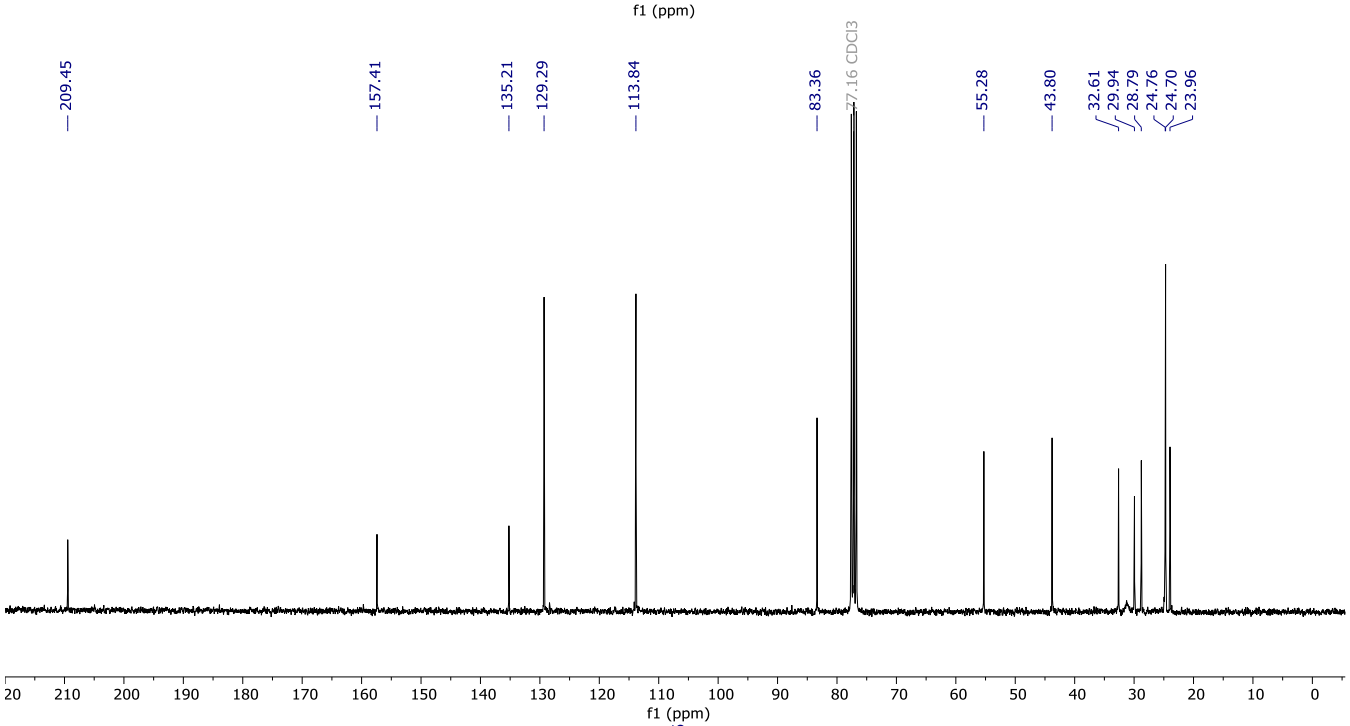

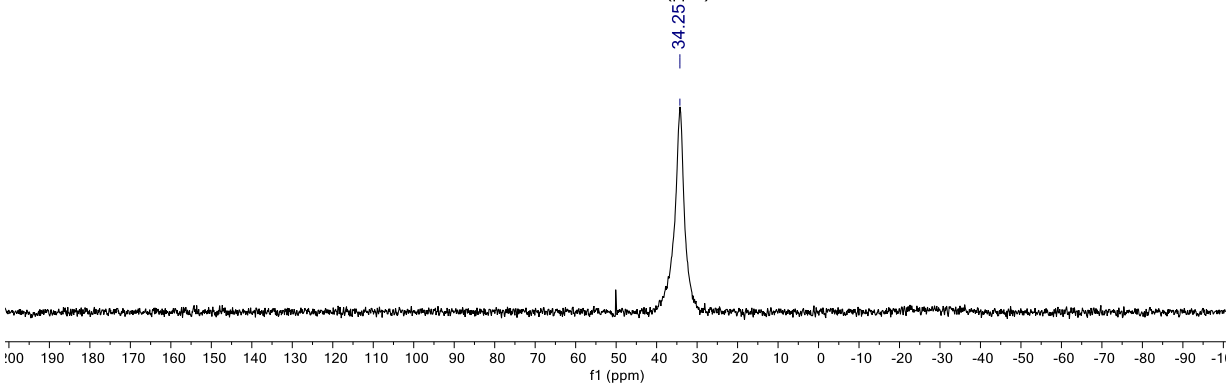

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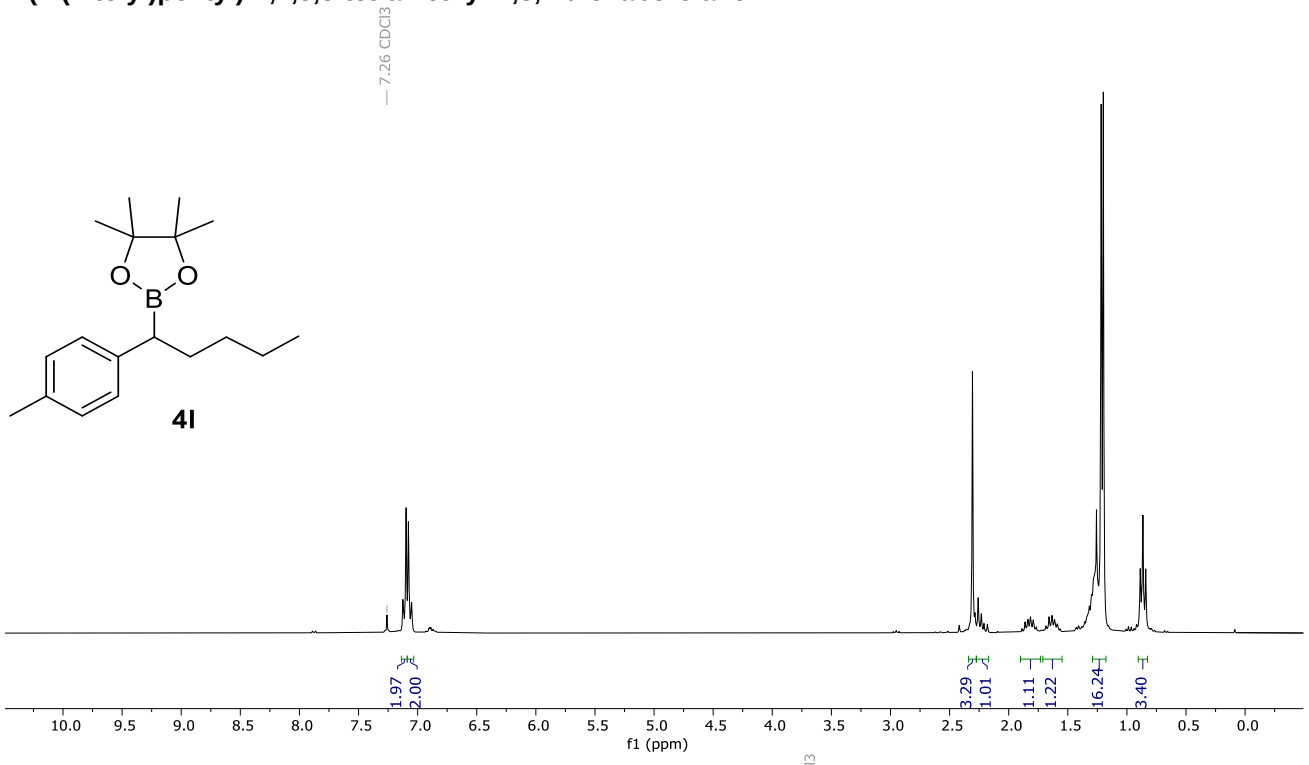
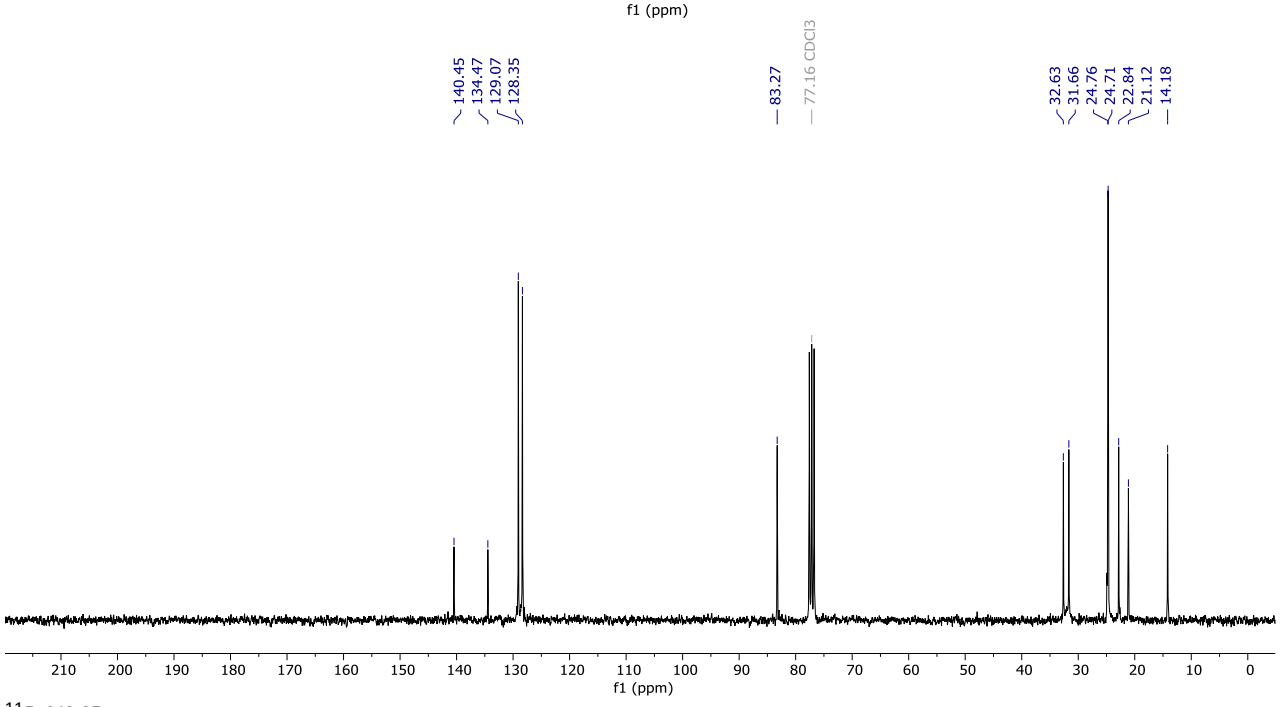
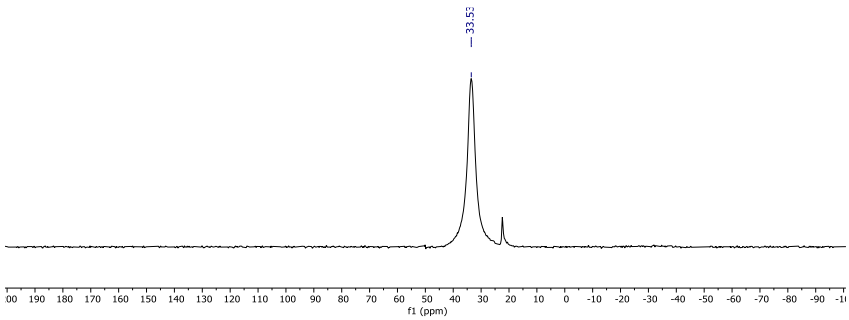




^{11}B NMR



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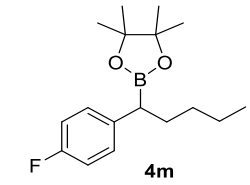

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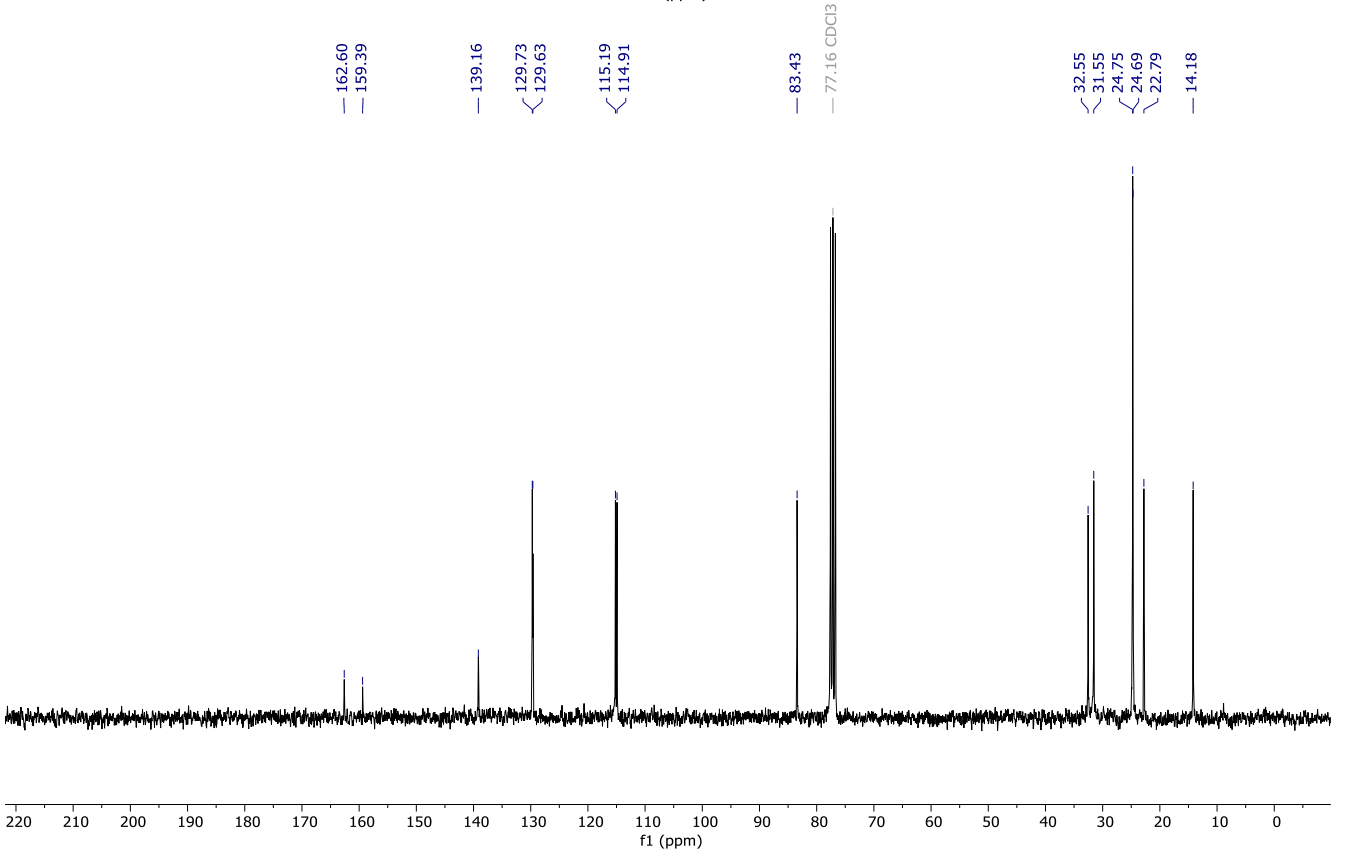
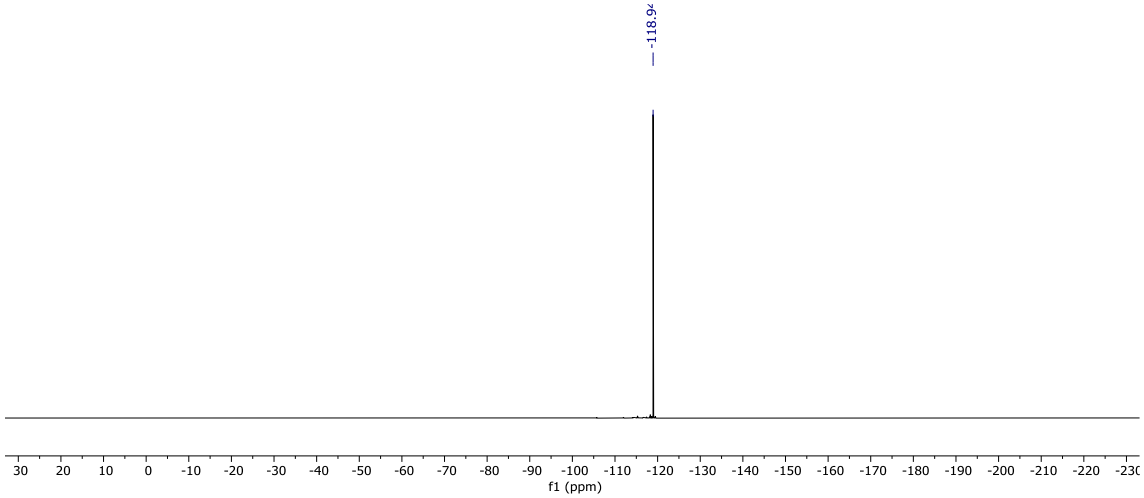
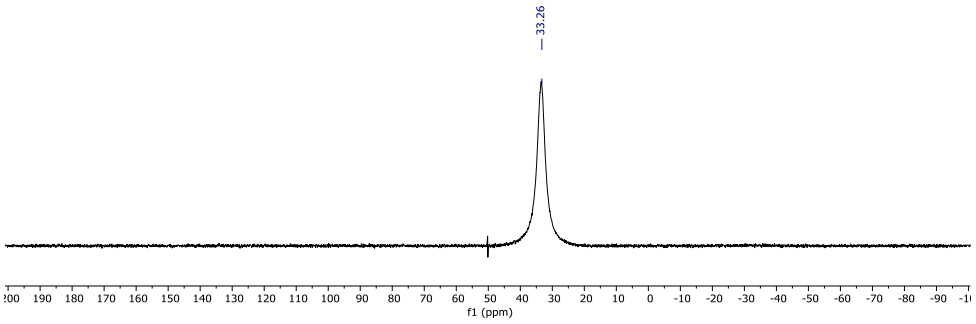



-118.94
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220
f1 (ppm)

11B NMR


33.26
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f1 (ppm)

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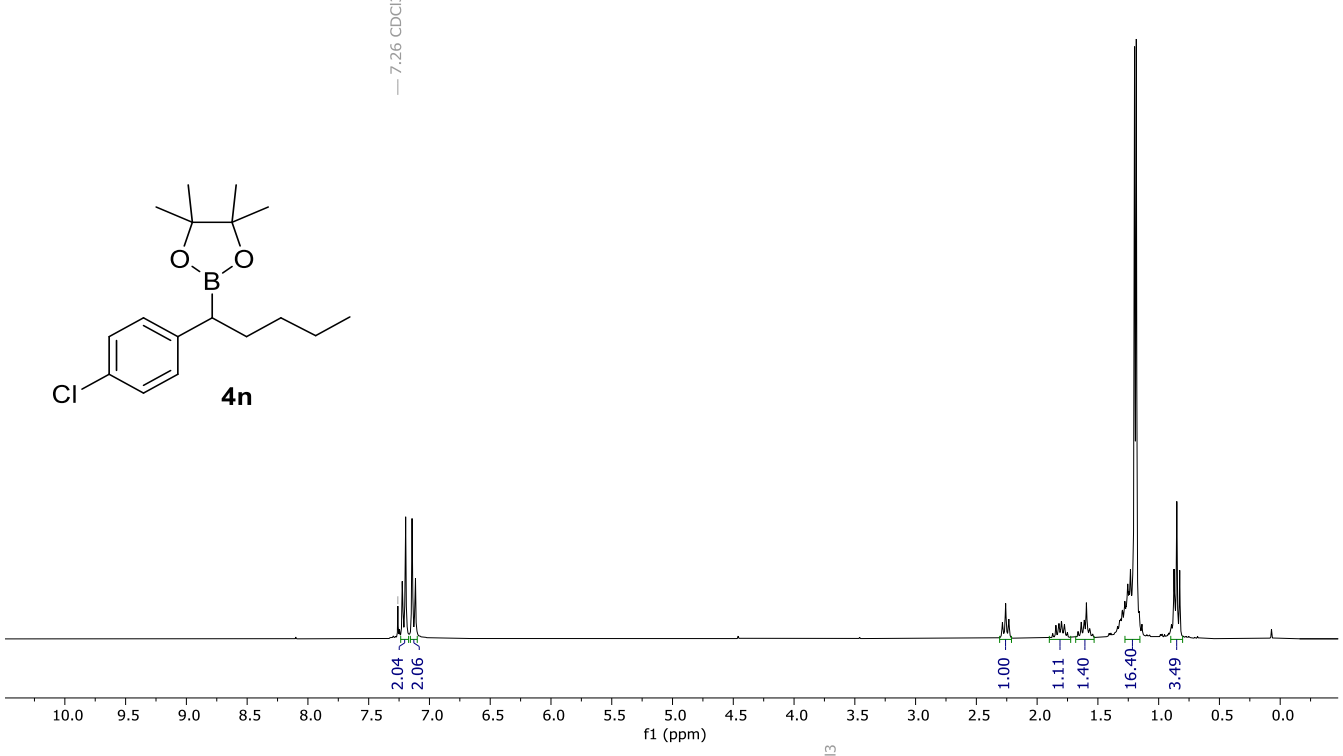
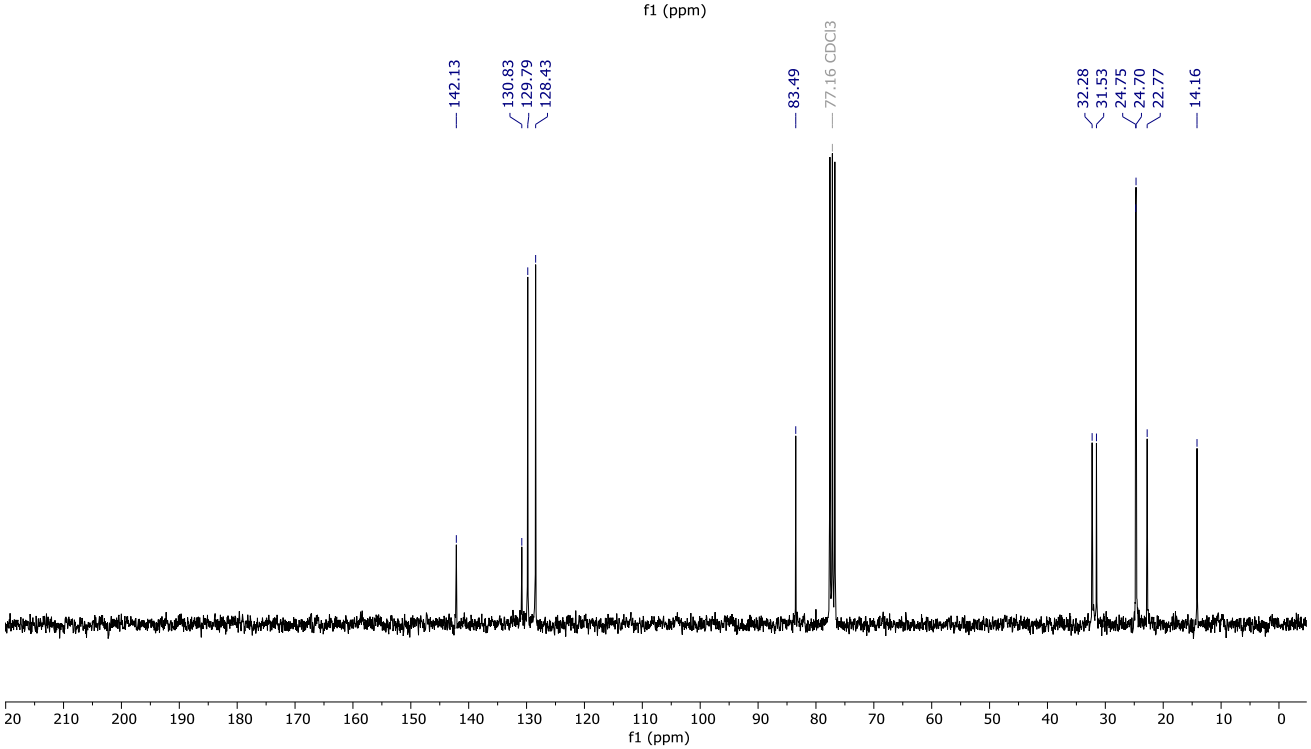
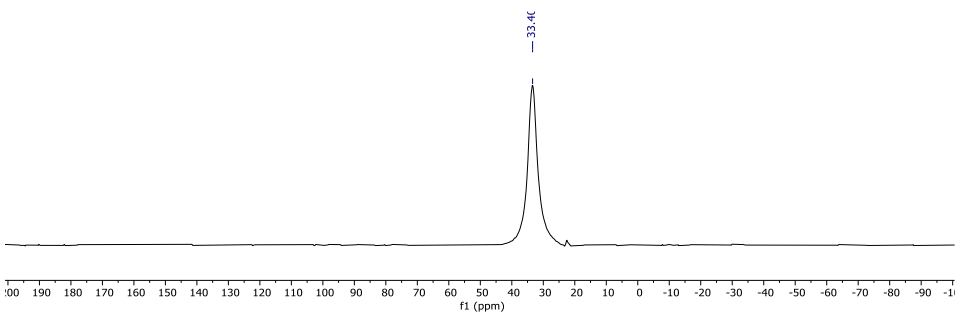
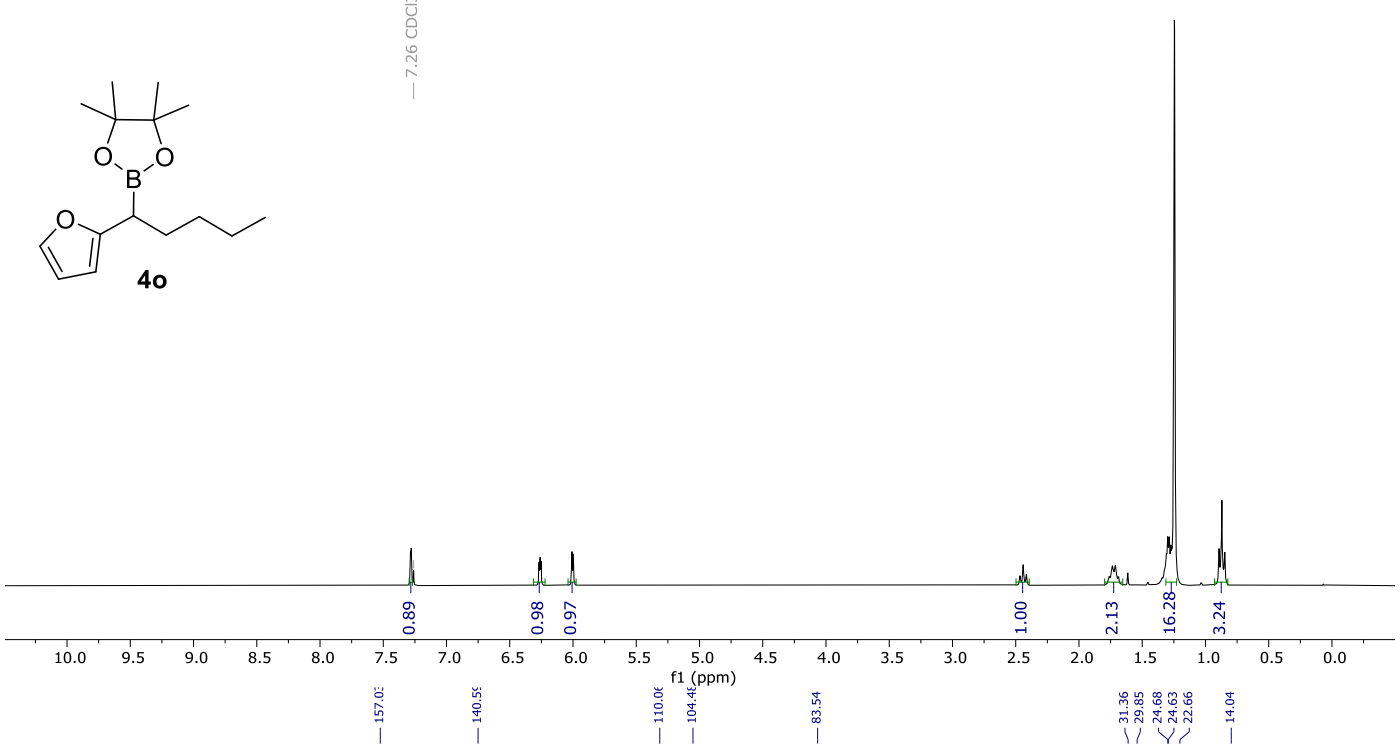
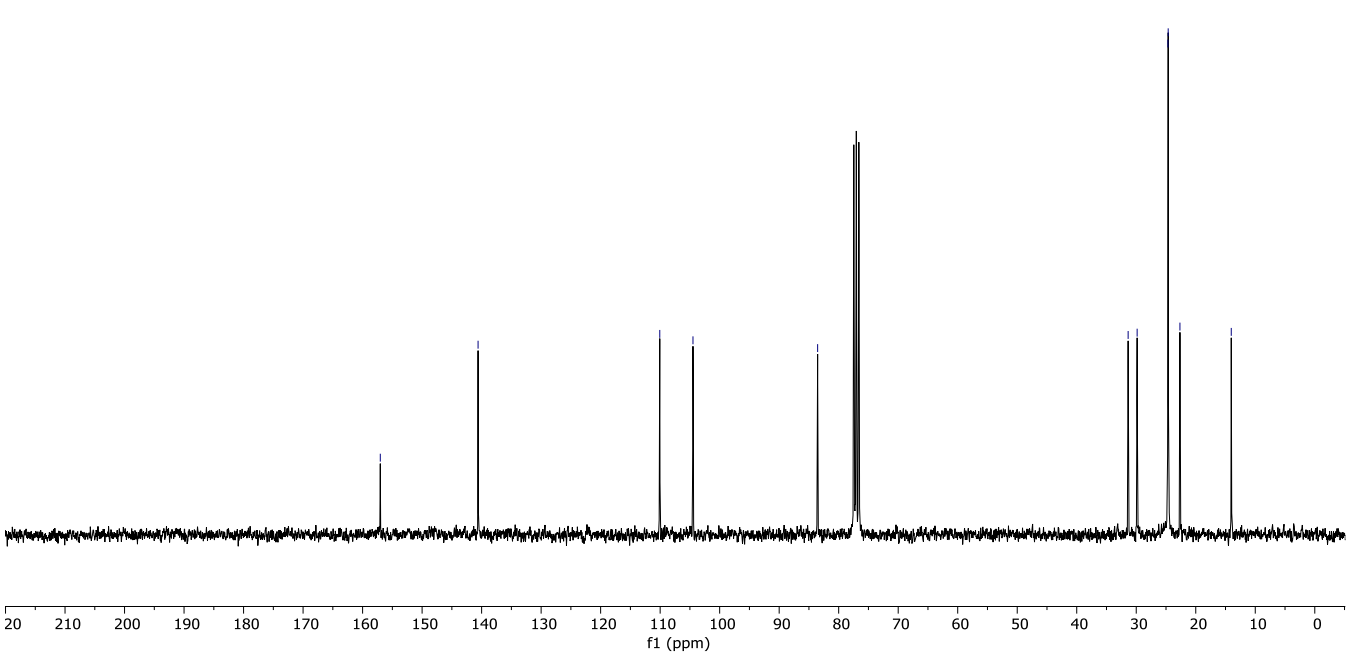




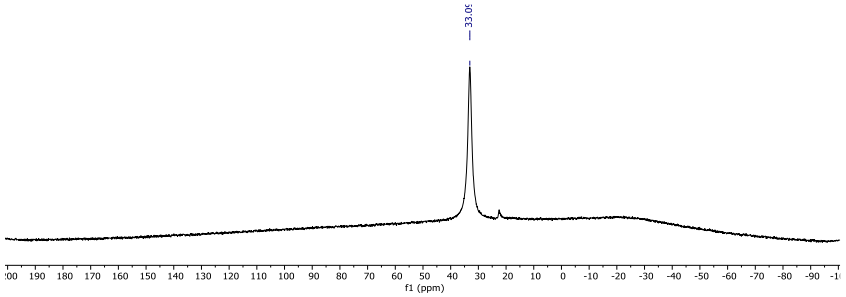


2-(1-(furan-2-yl)pentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 4o

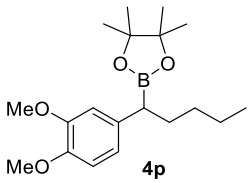


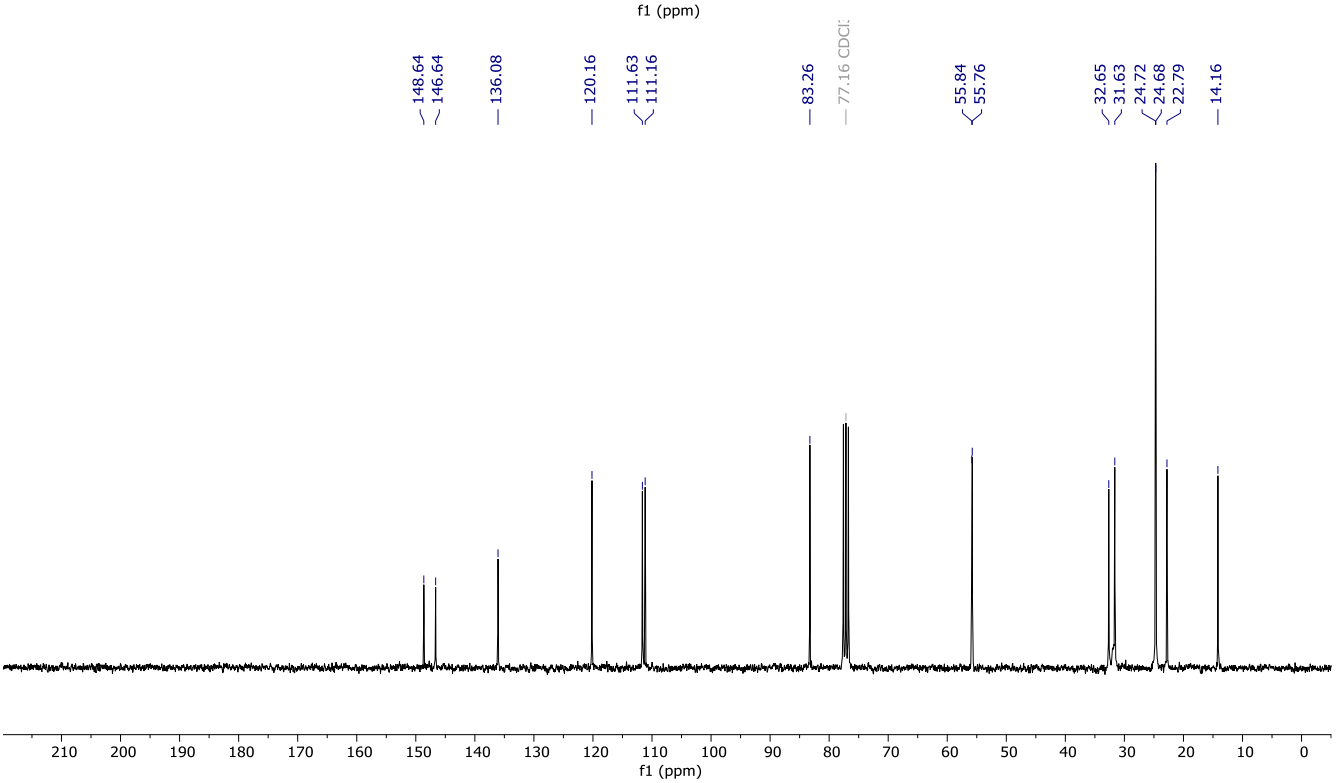


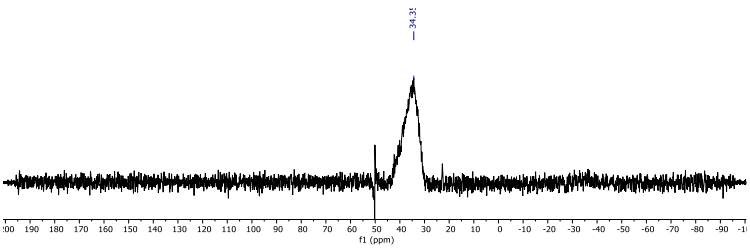
^{11}B NMR



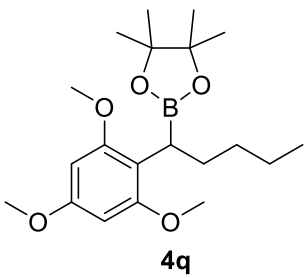
2-(1-(3,4-dimethoxyphenyl)pentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 4p



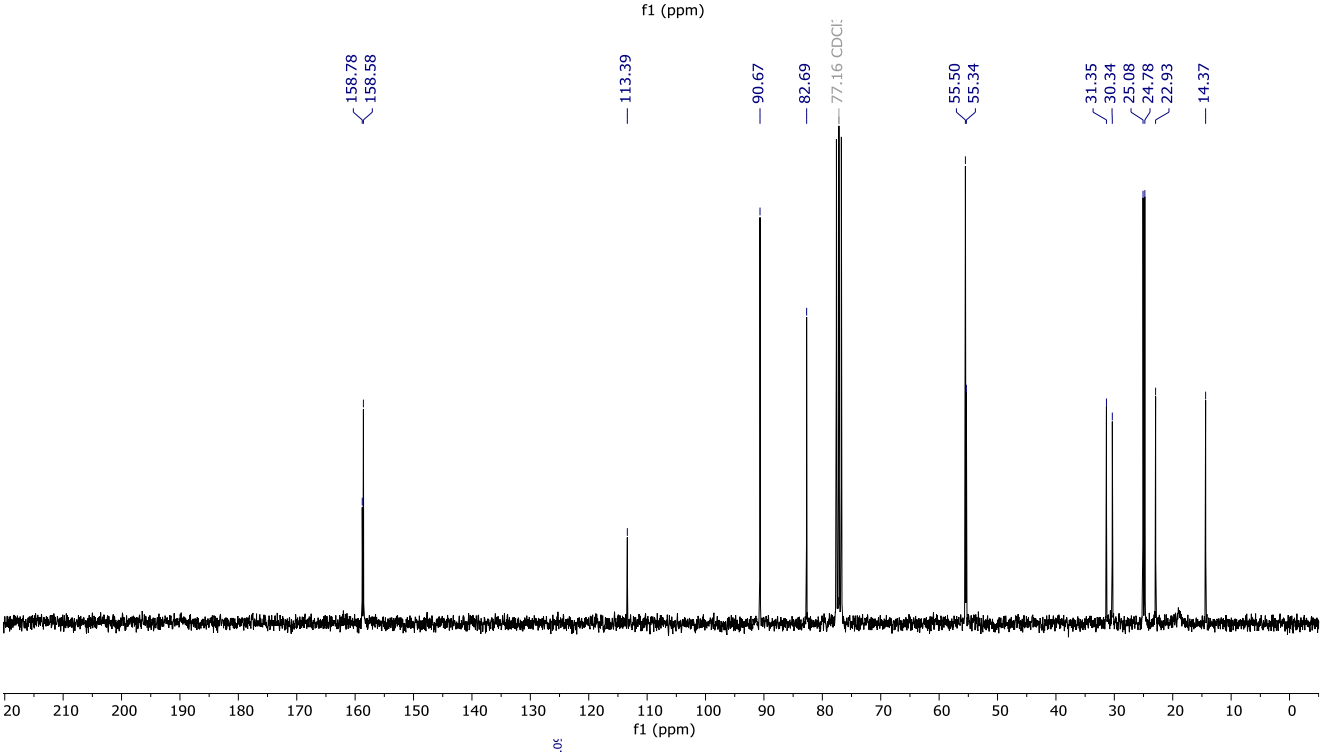


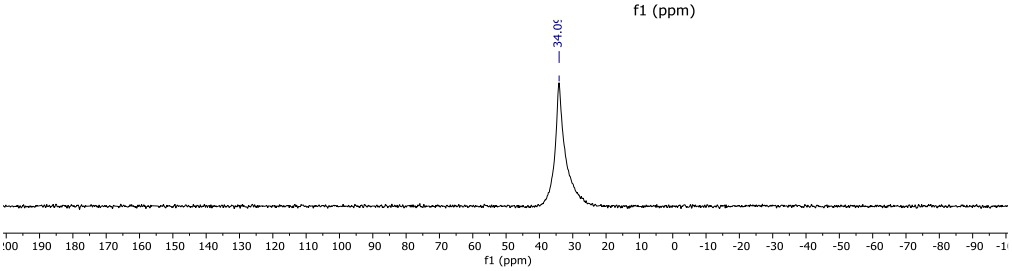


4,4,5,5-tetramethyl-2-(1-(2,4,6-trimethoxyphenyl)pentyl)-1,3,2-dioxaborolane 4q

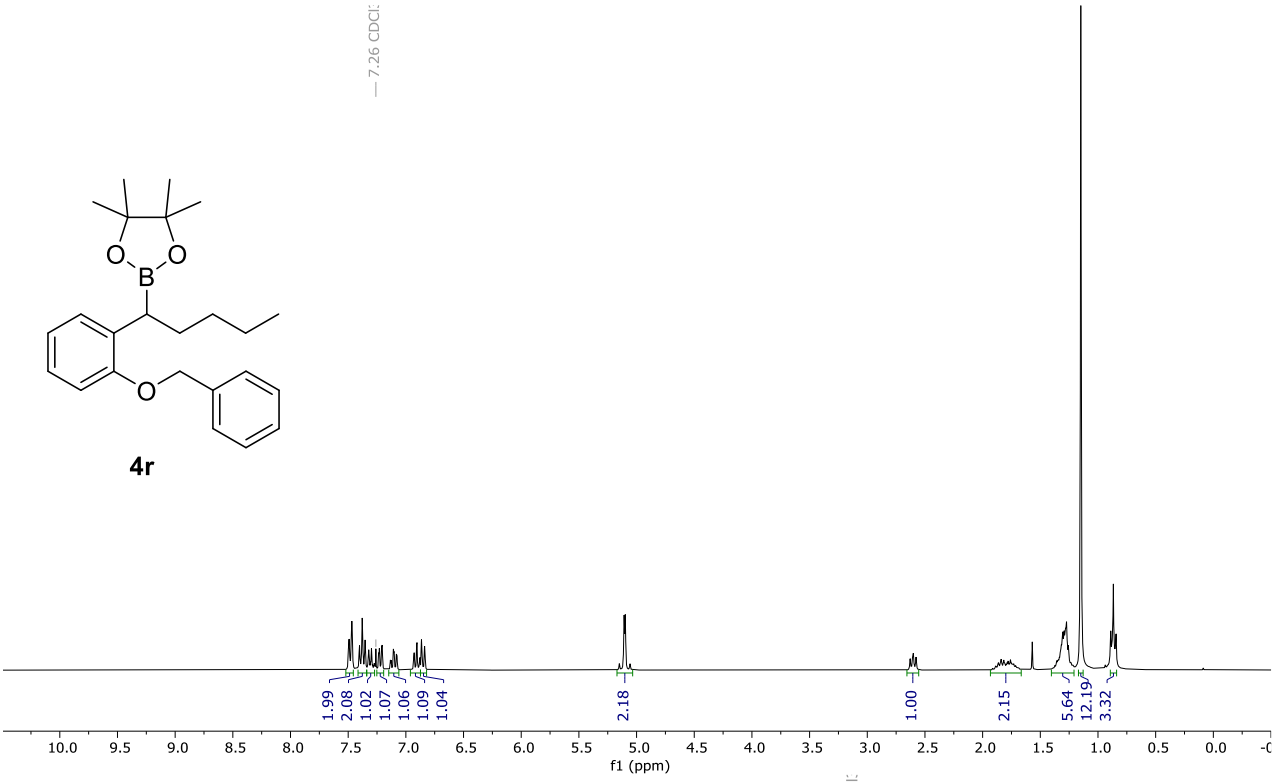


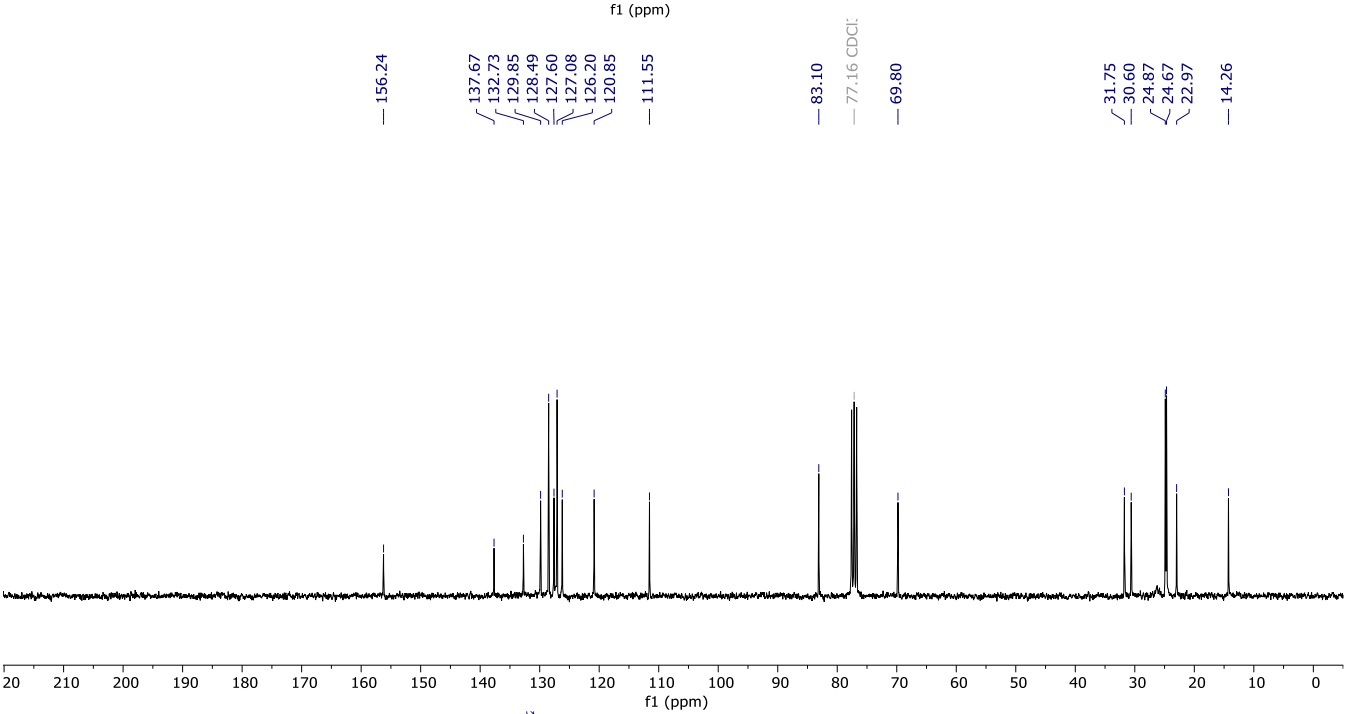
4q

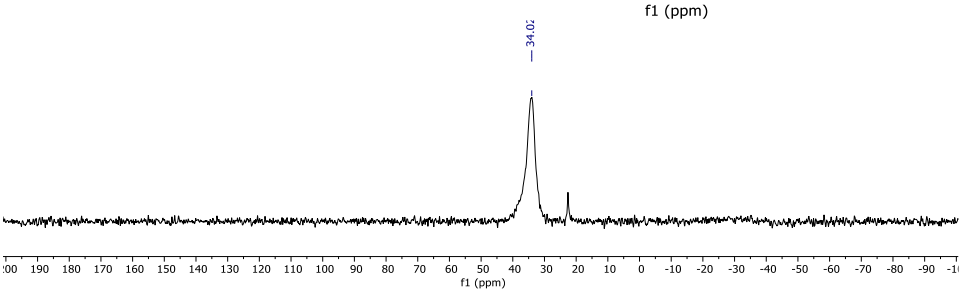




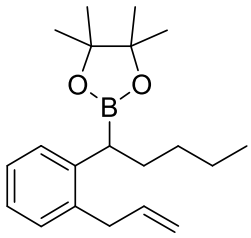
2-(1-(2-(benzyloxy)phenyl)pentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 4r







2-(1-(2-allylphenyl)pentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 4s



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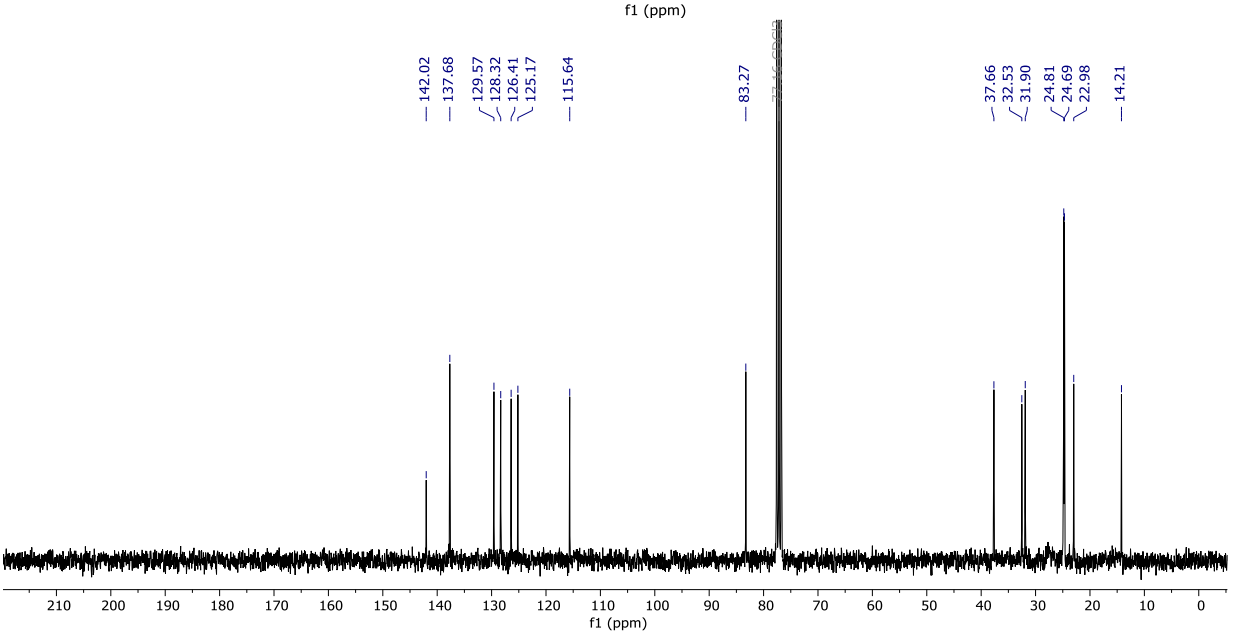
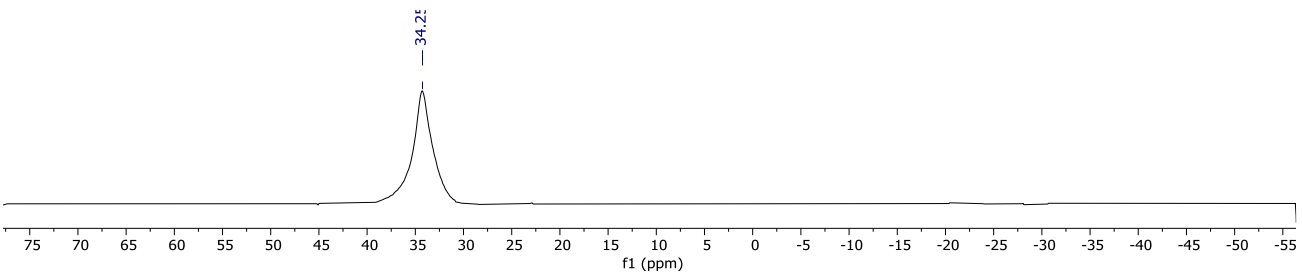
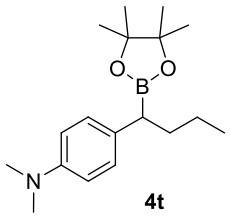
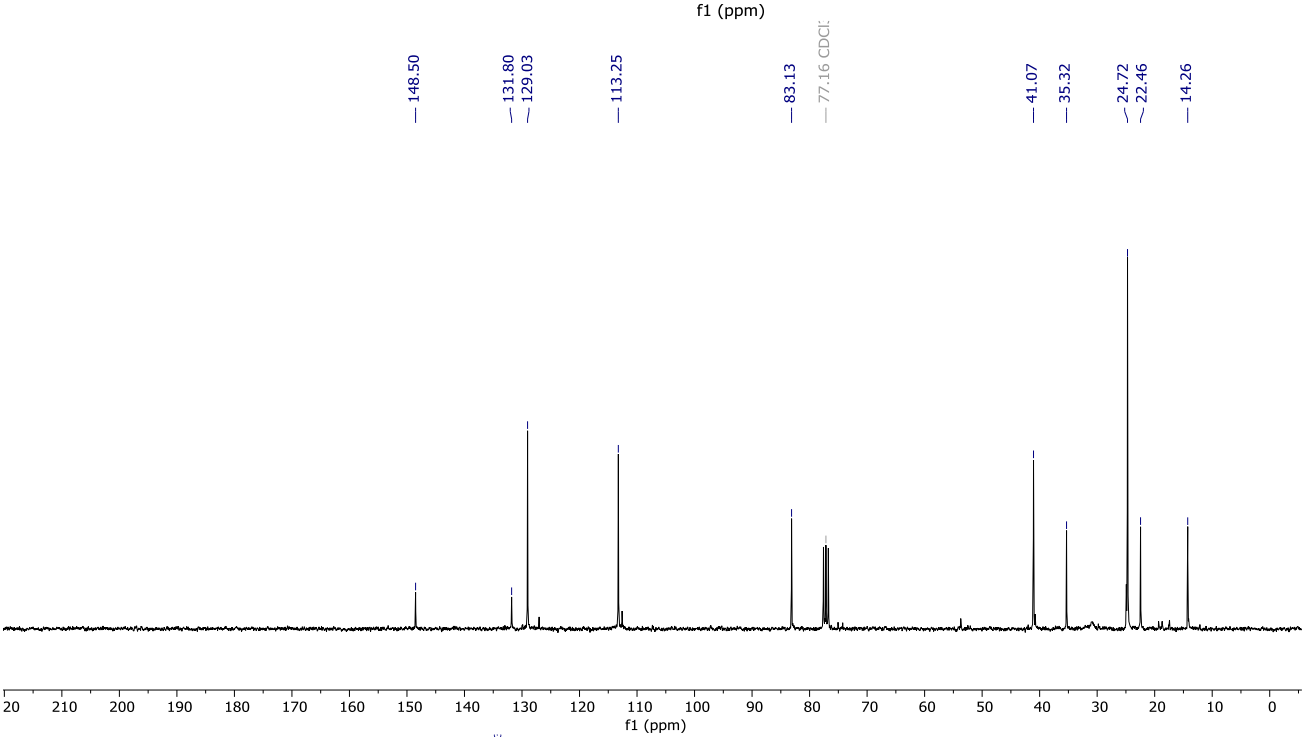


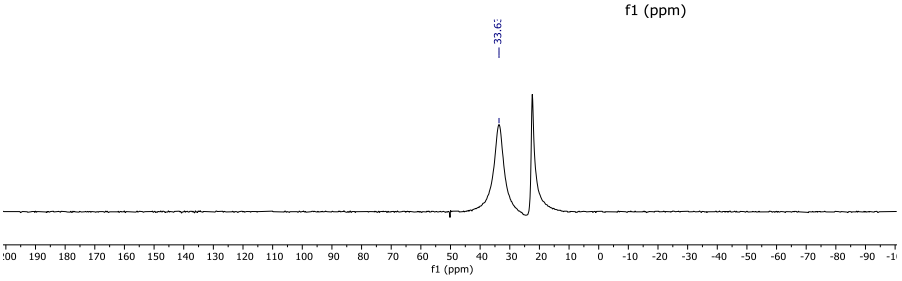


_N,N_-dimethyl-4-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl)aniline 4t

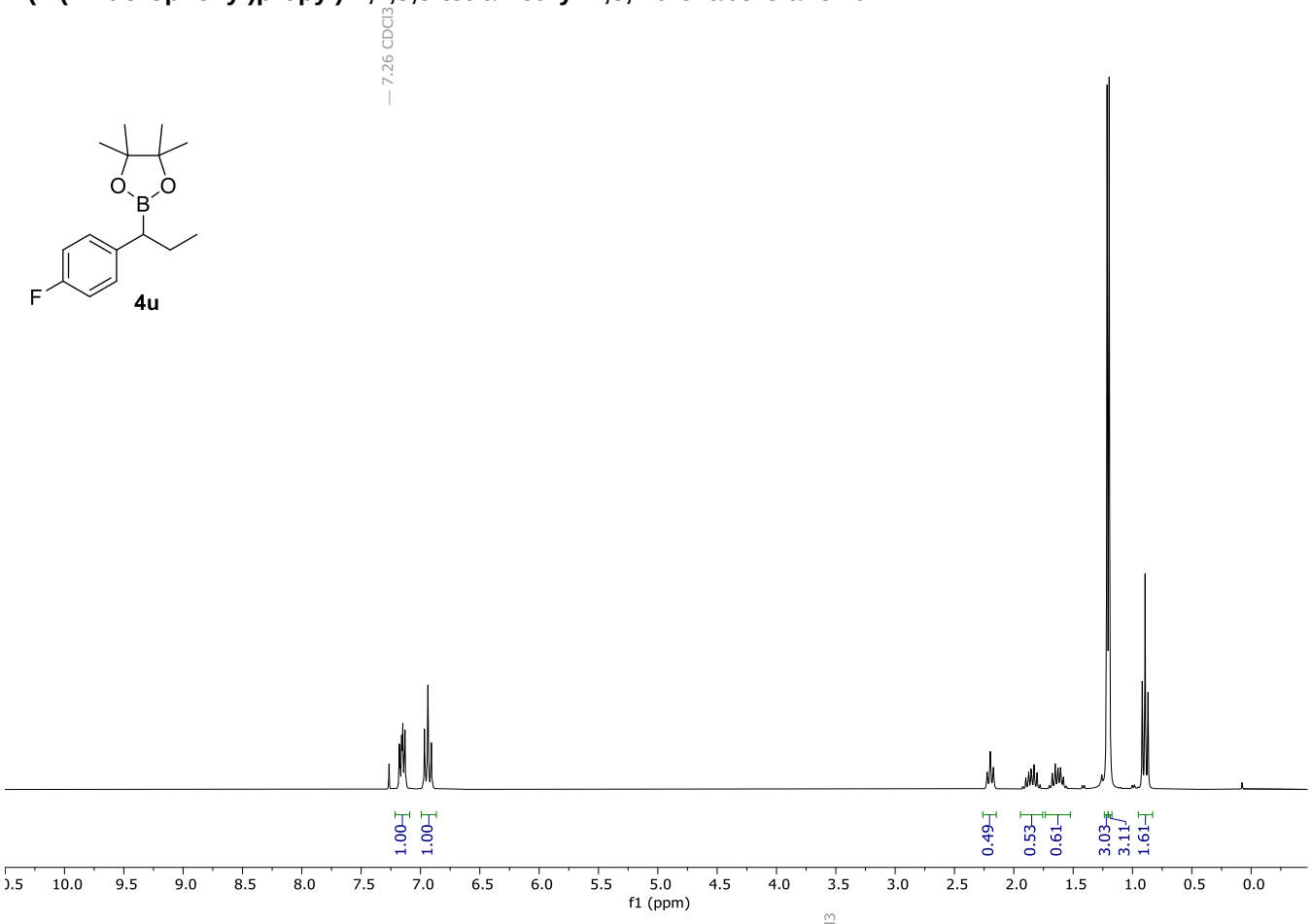


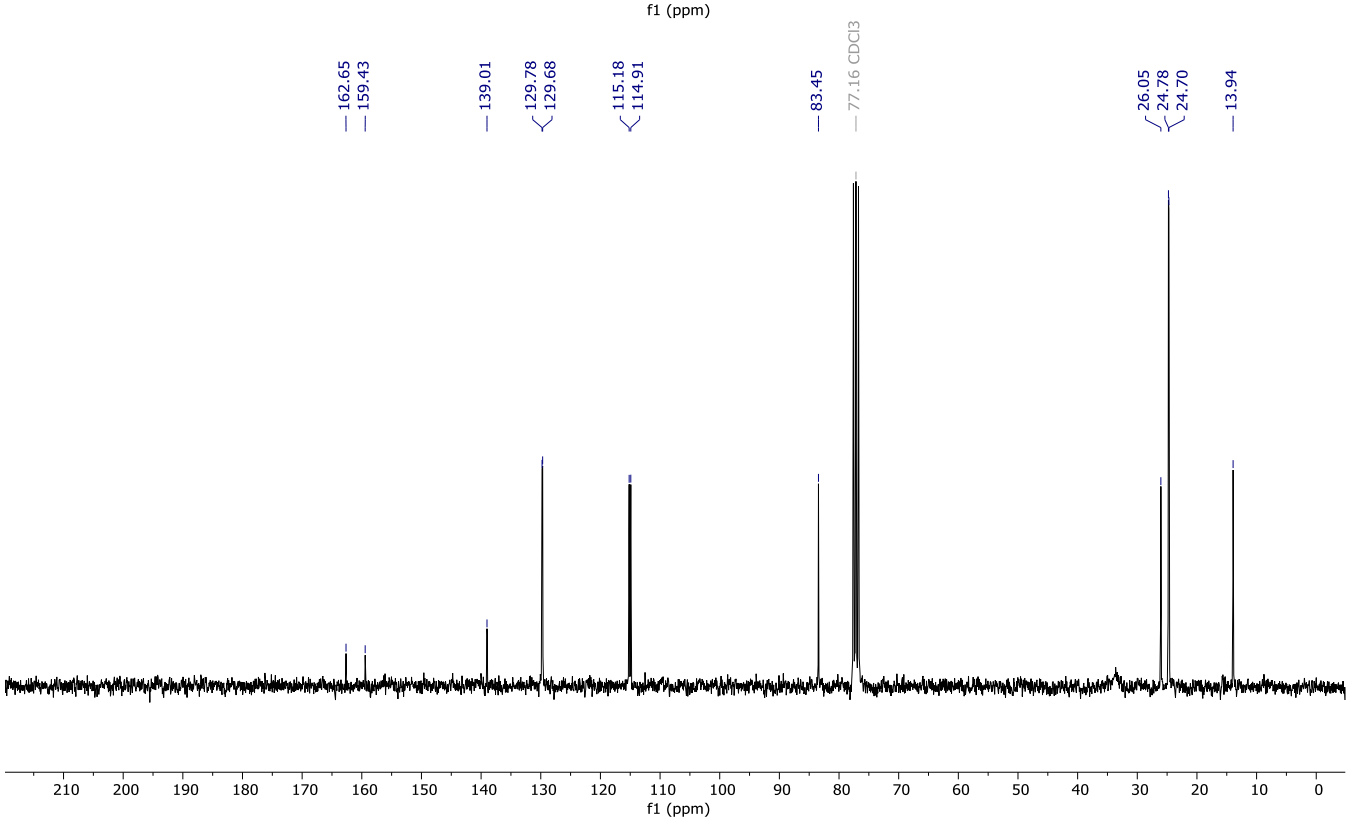
4t

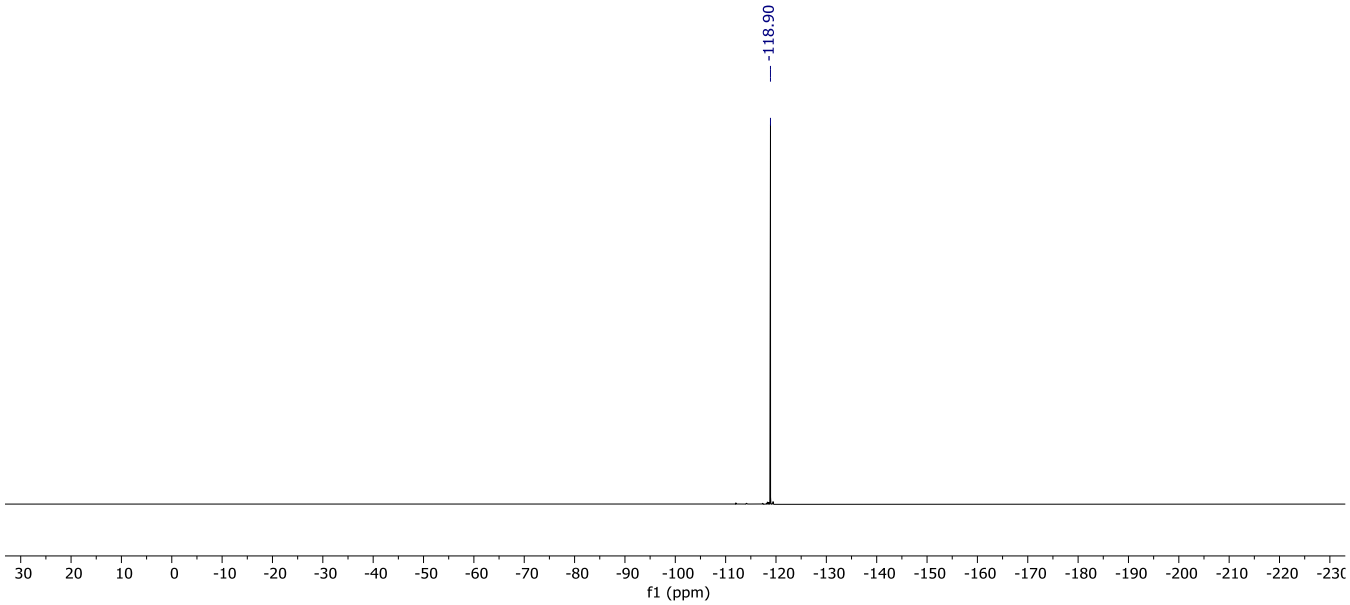




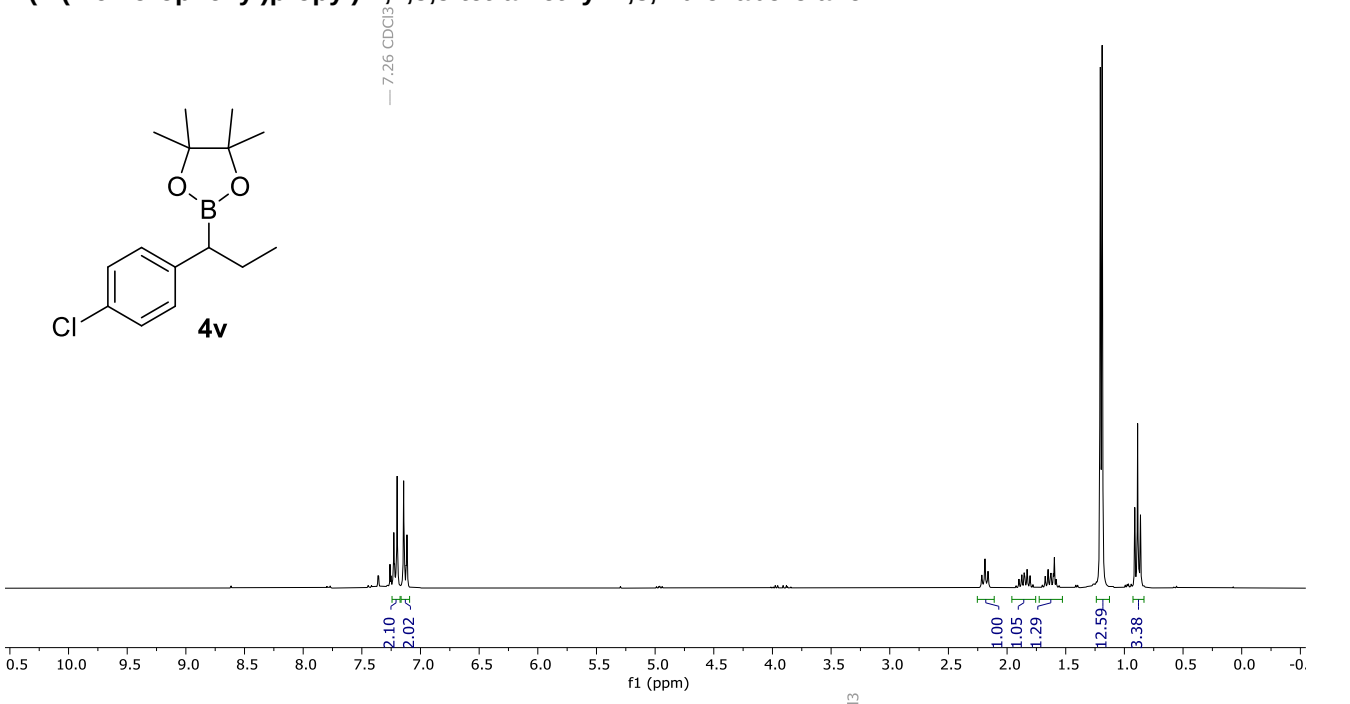
2-(1-(4-fluorophenyl)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 4u

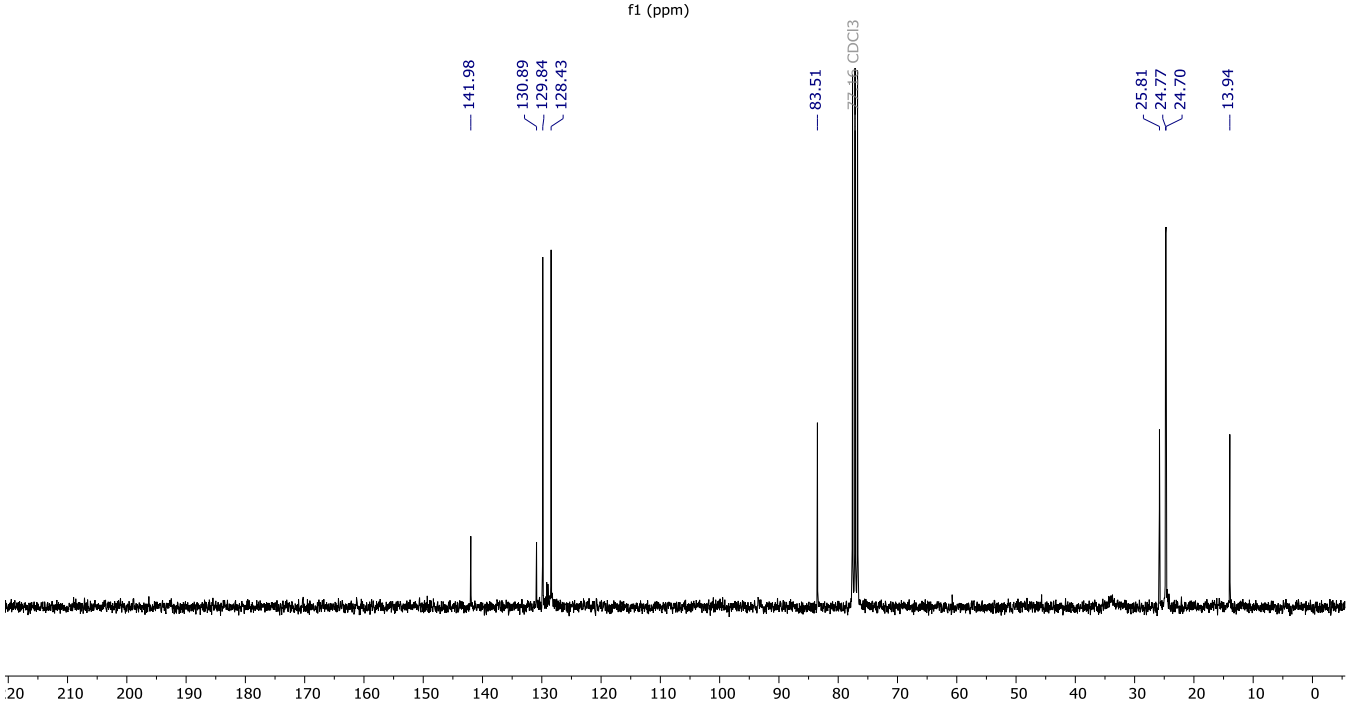


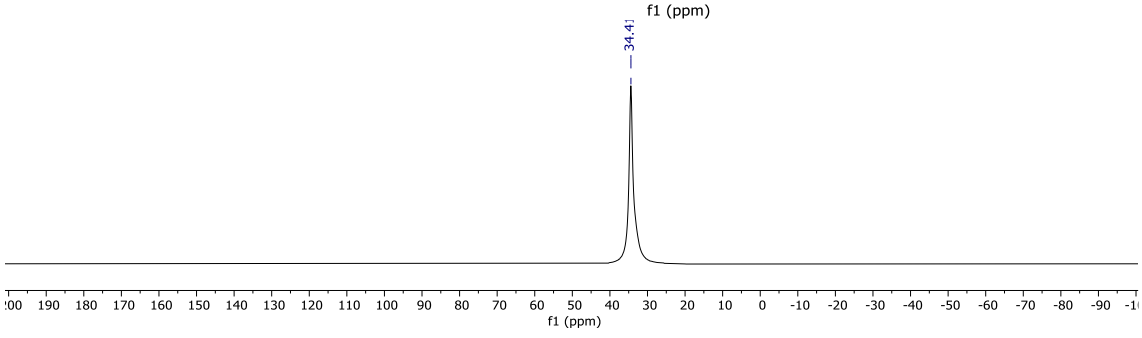



-118.90
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230
f1 (ppm)

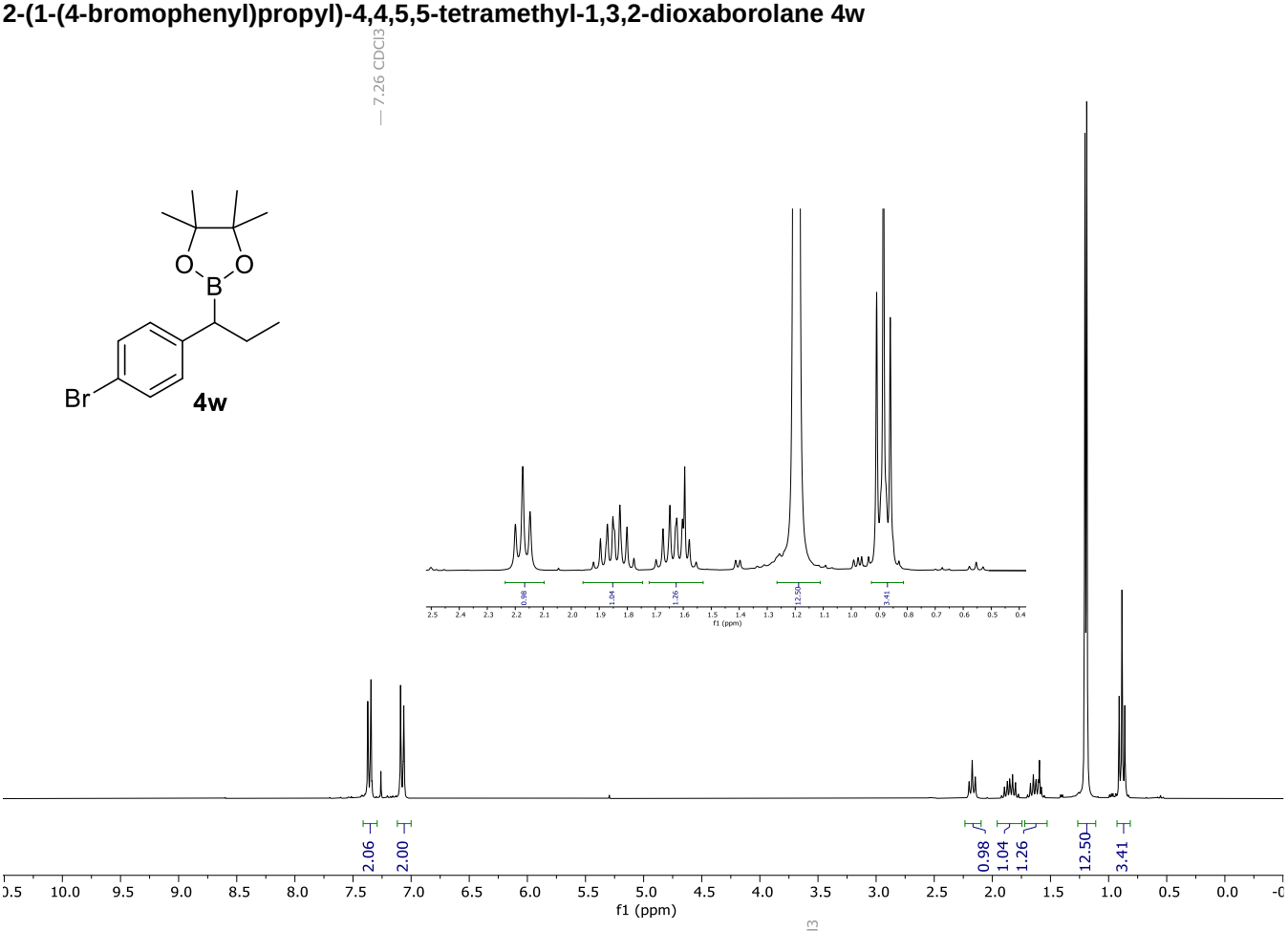
2-(1-(4-chlorophenyl)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 4v

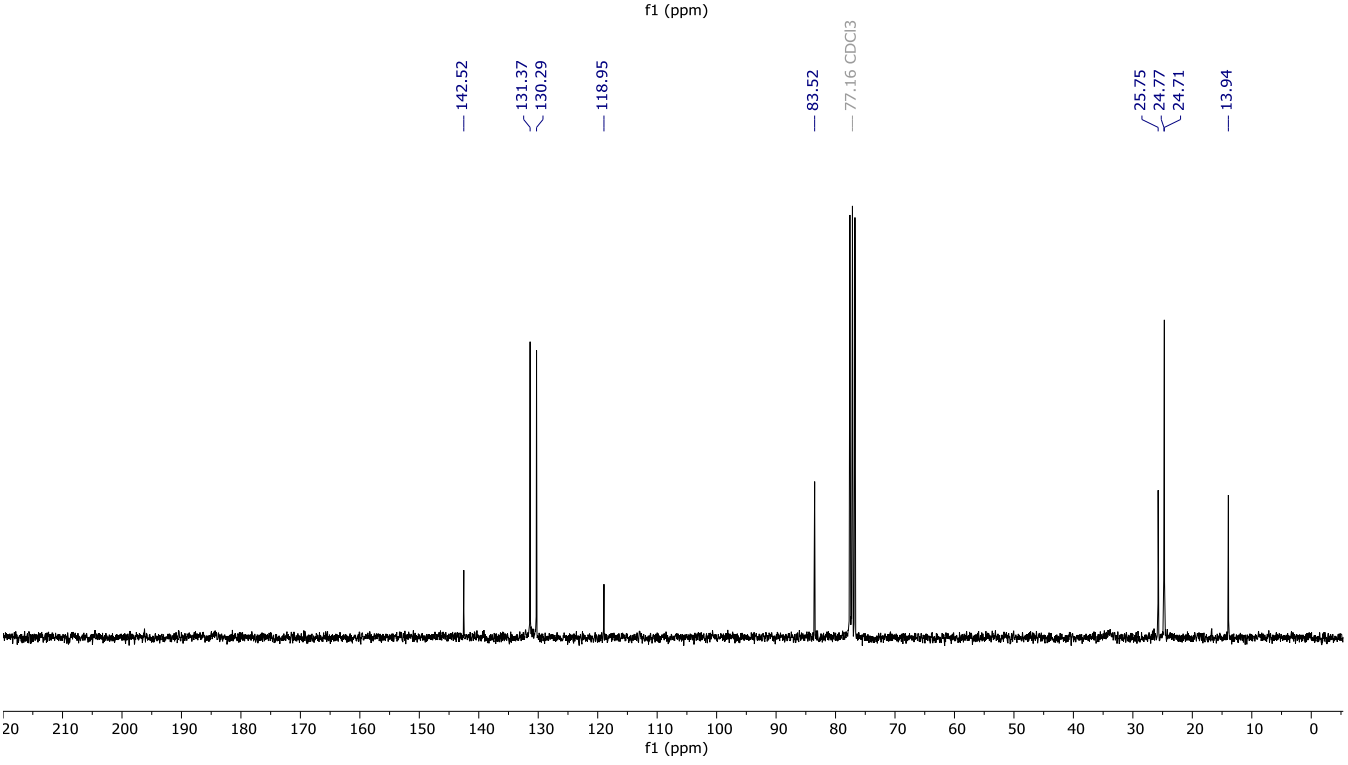




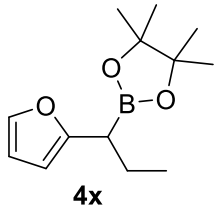


2-(1-(4-bromophenyl)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 4w

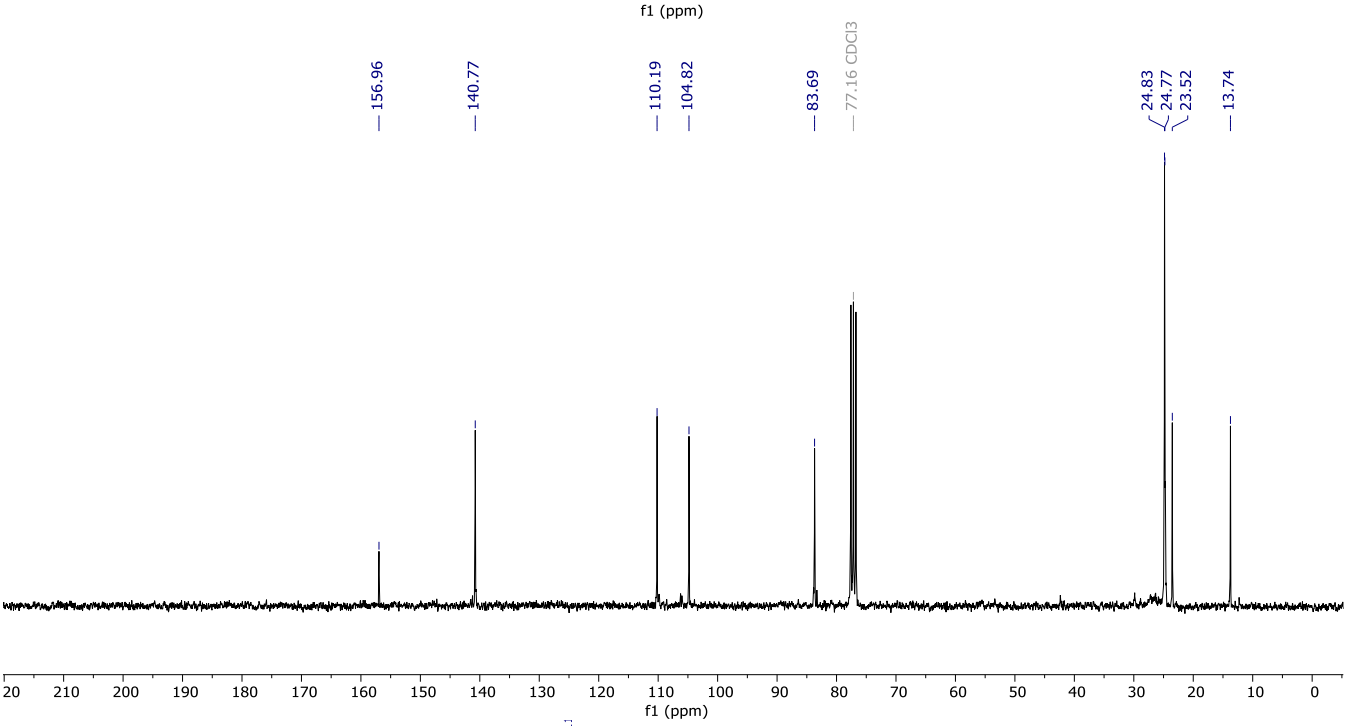


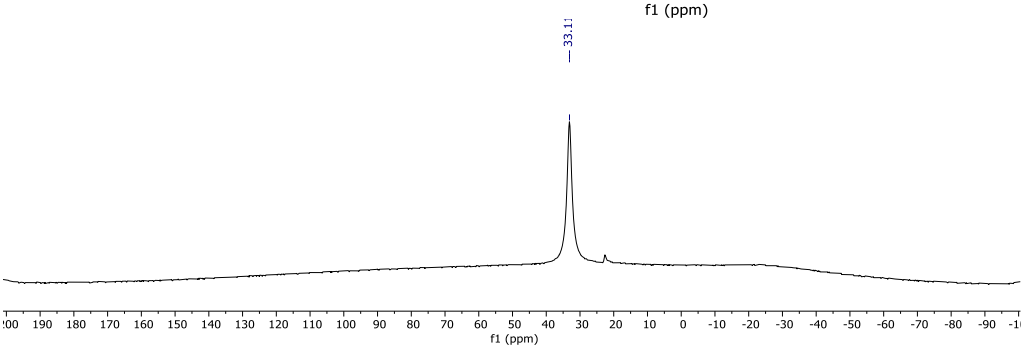


2-(1-(furan-2-yl)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 4x

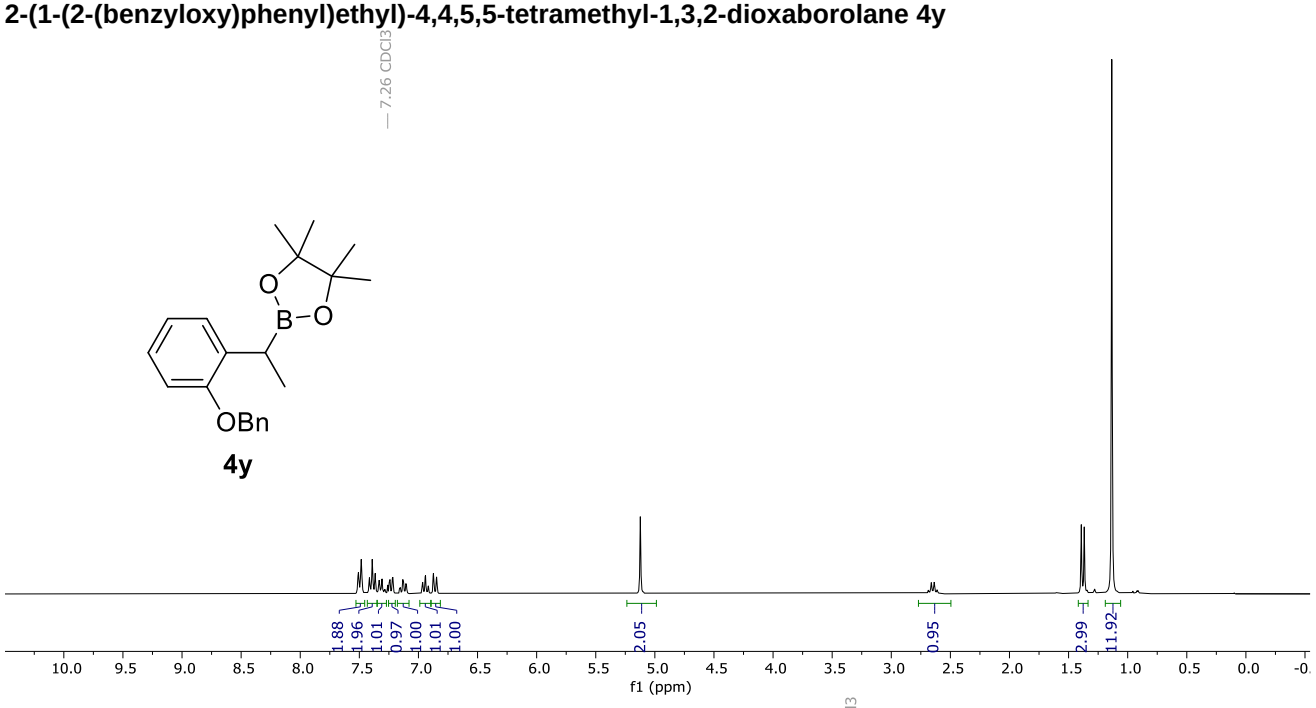


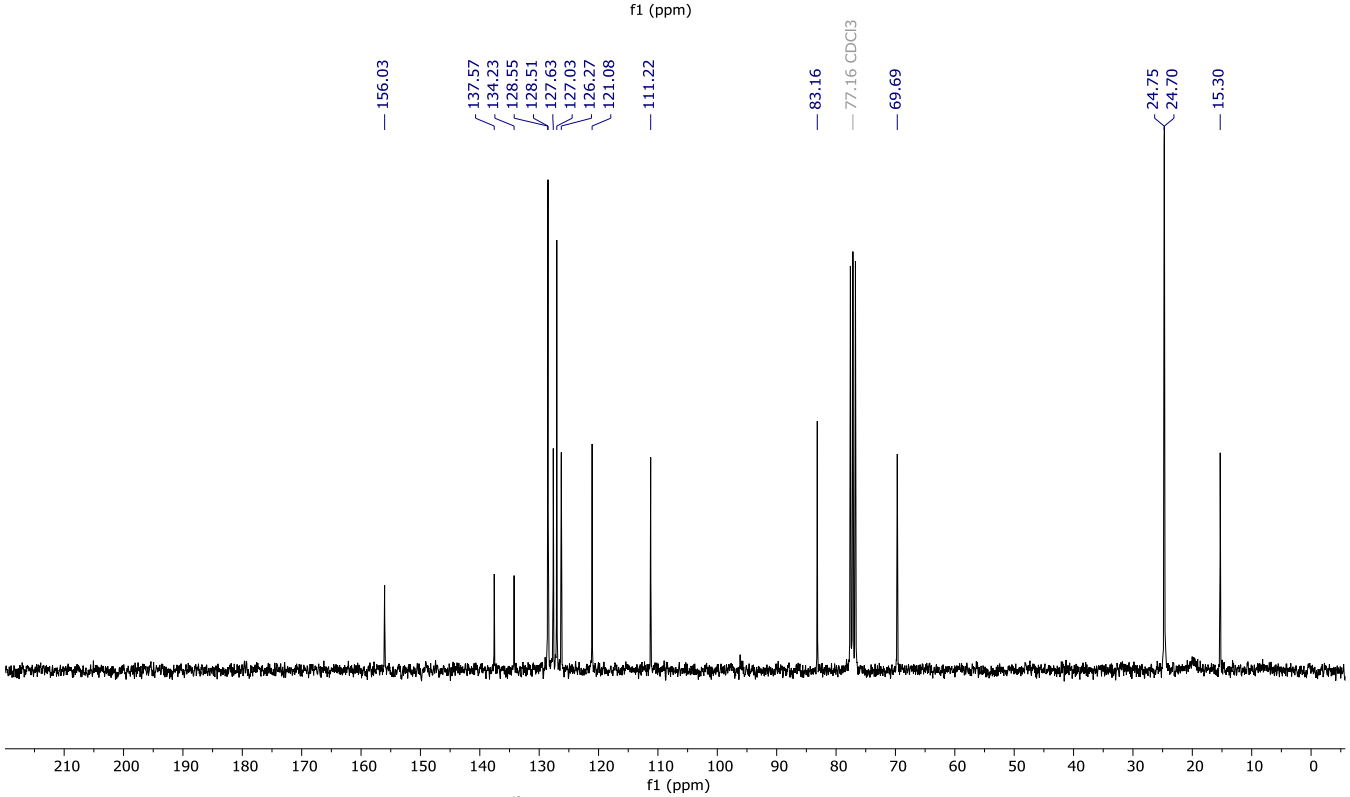
4x

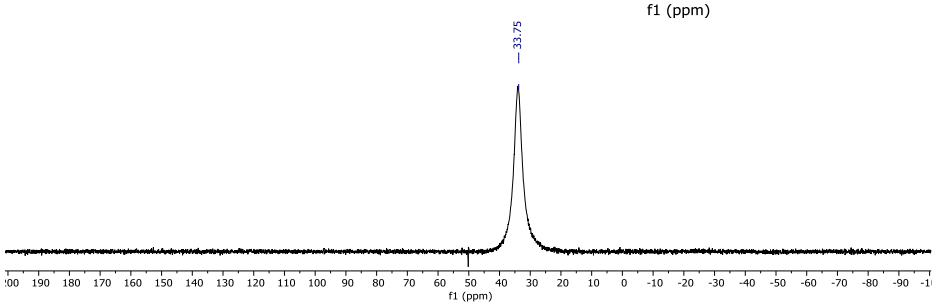




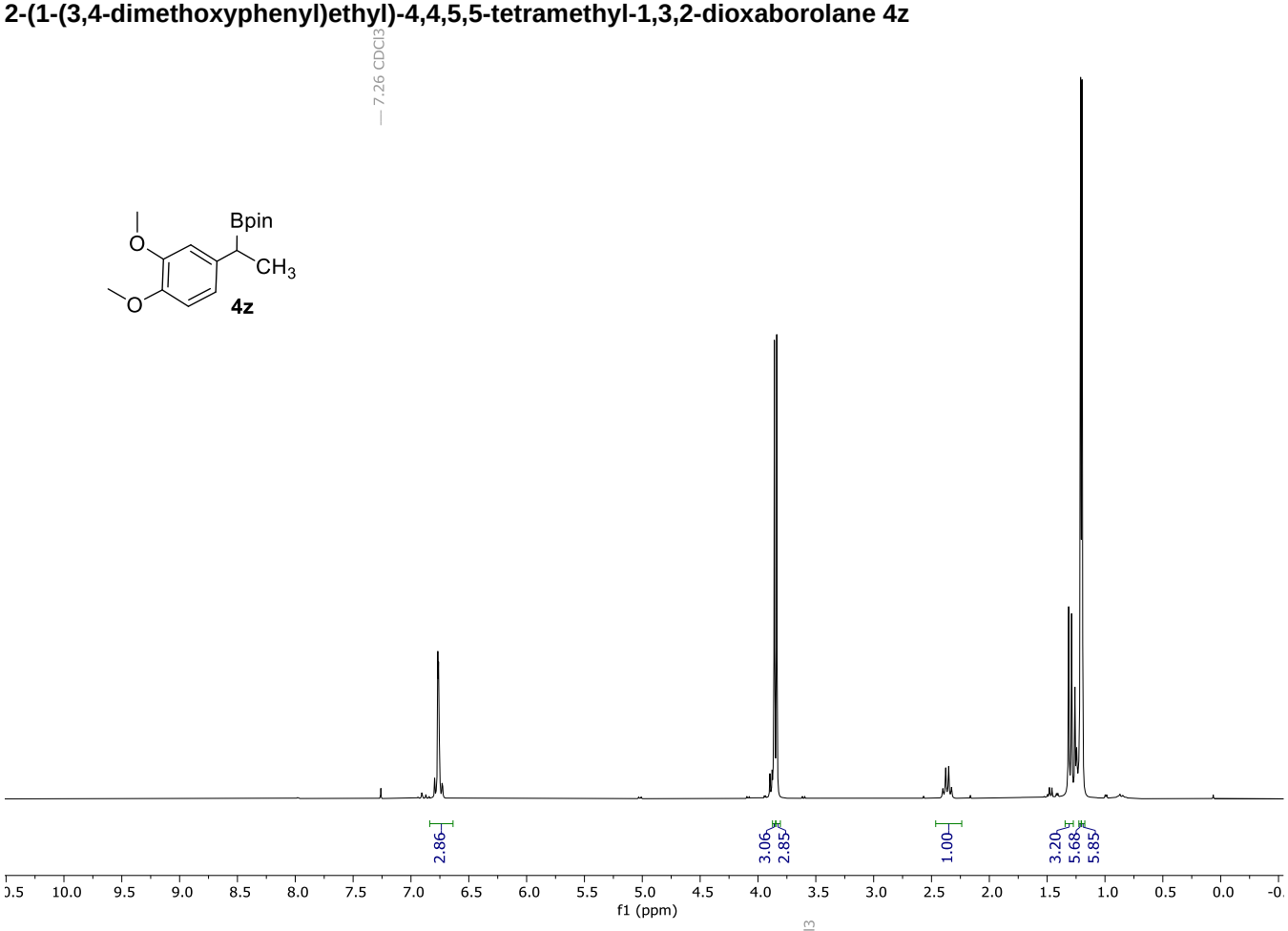
2-(1-(2-(benzyloxy)phenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 4y

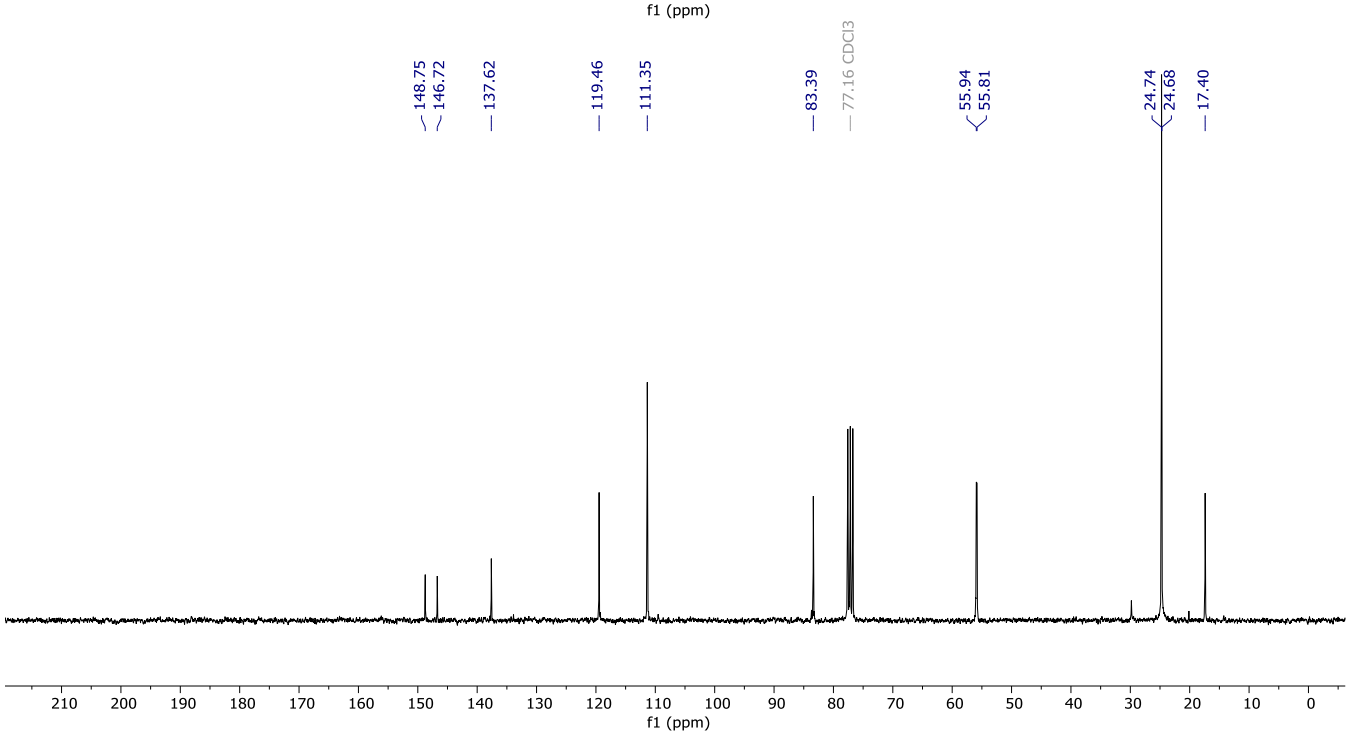




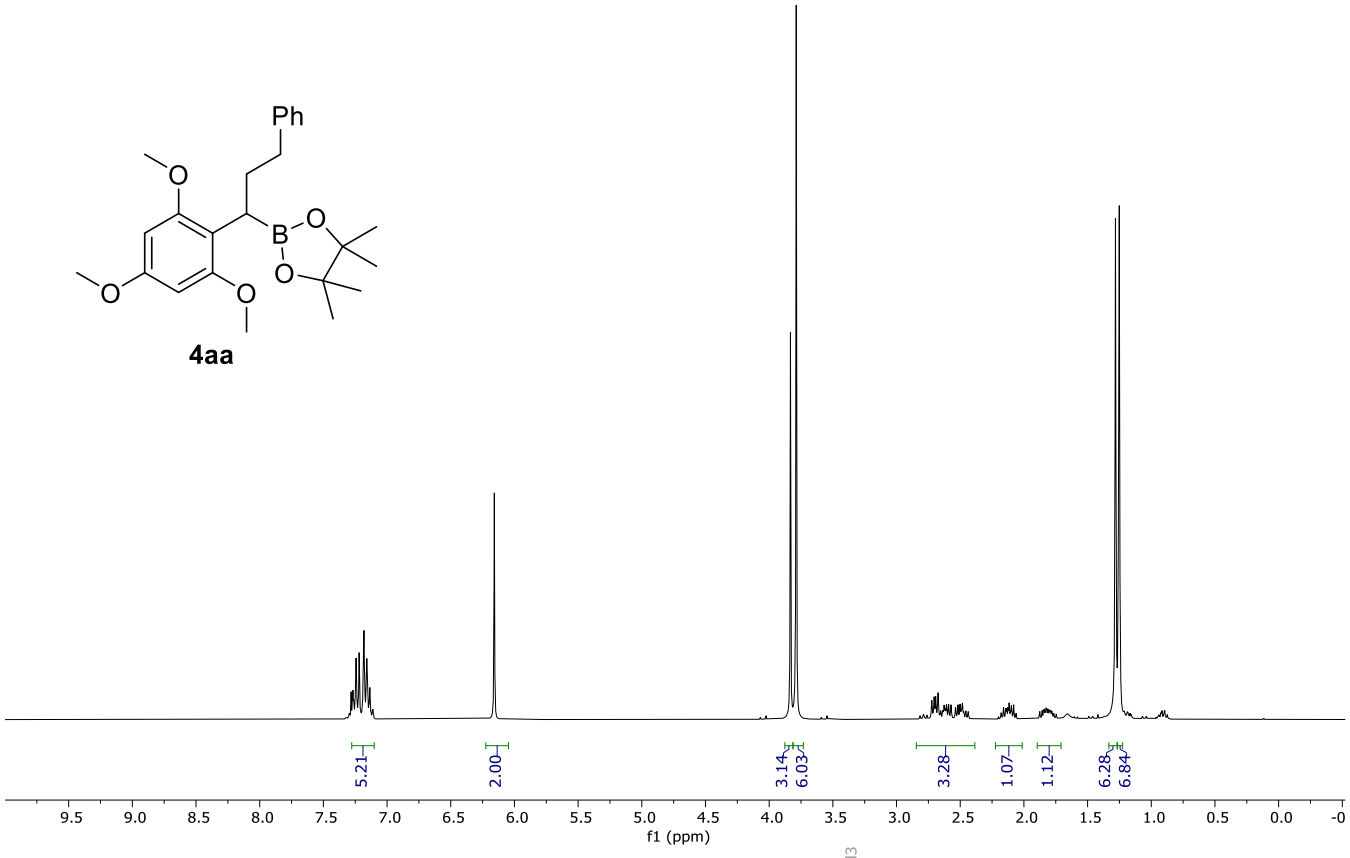


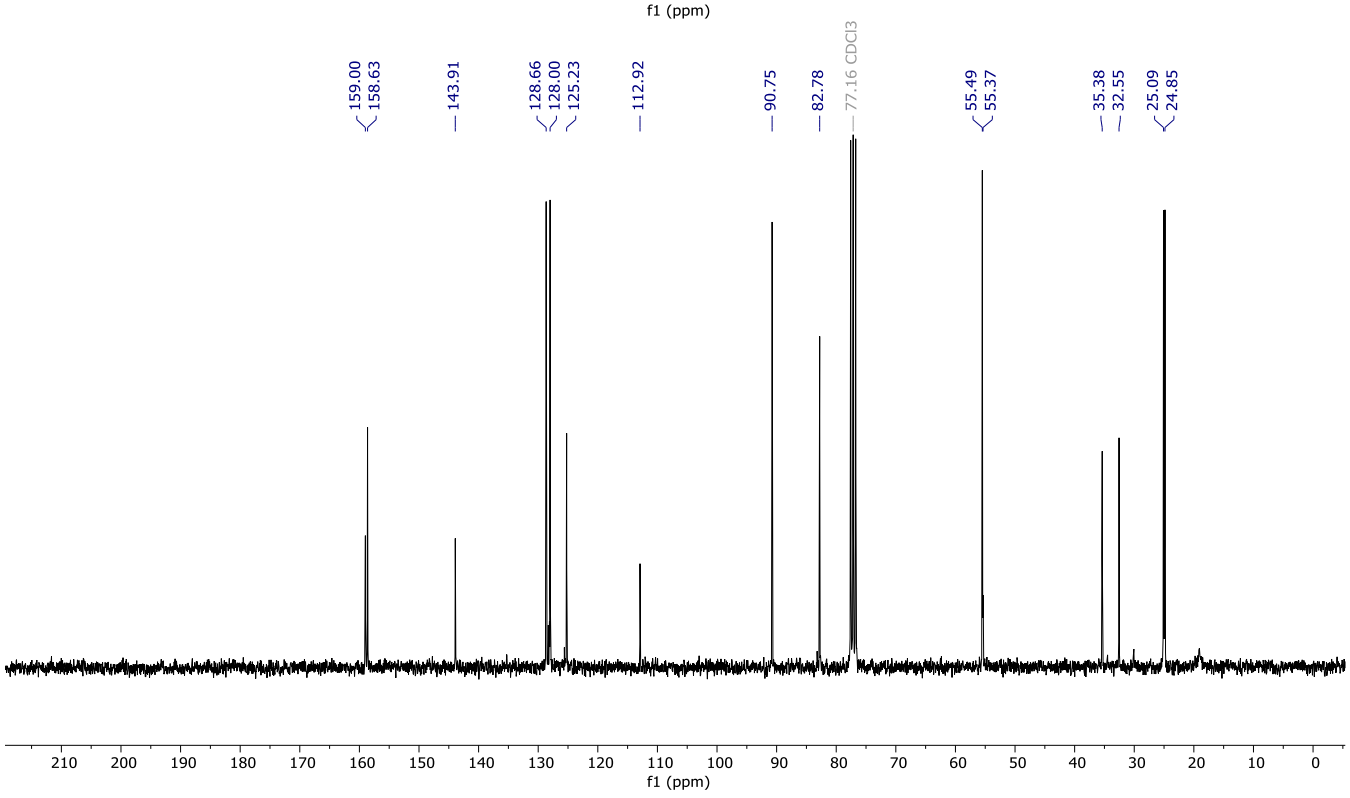
2-(1-(3,4-dimethoxyphenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 4z



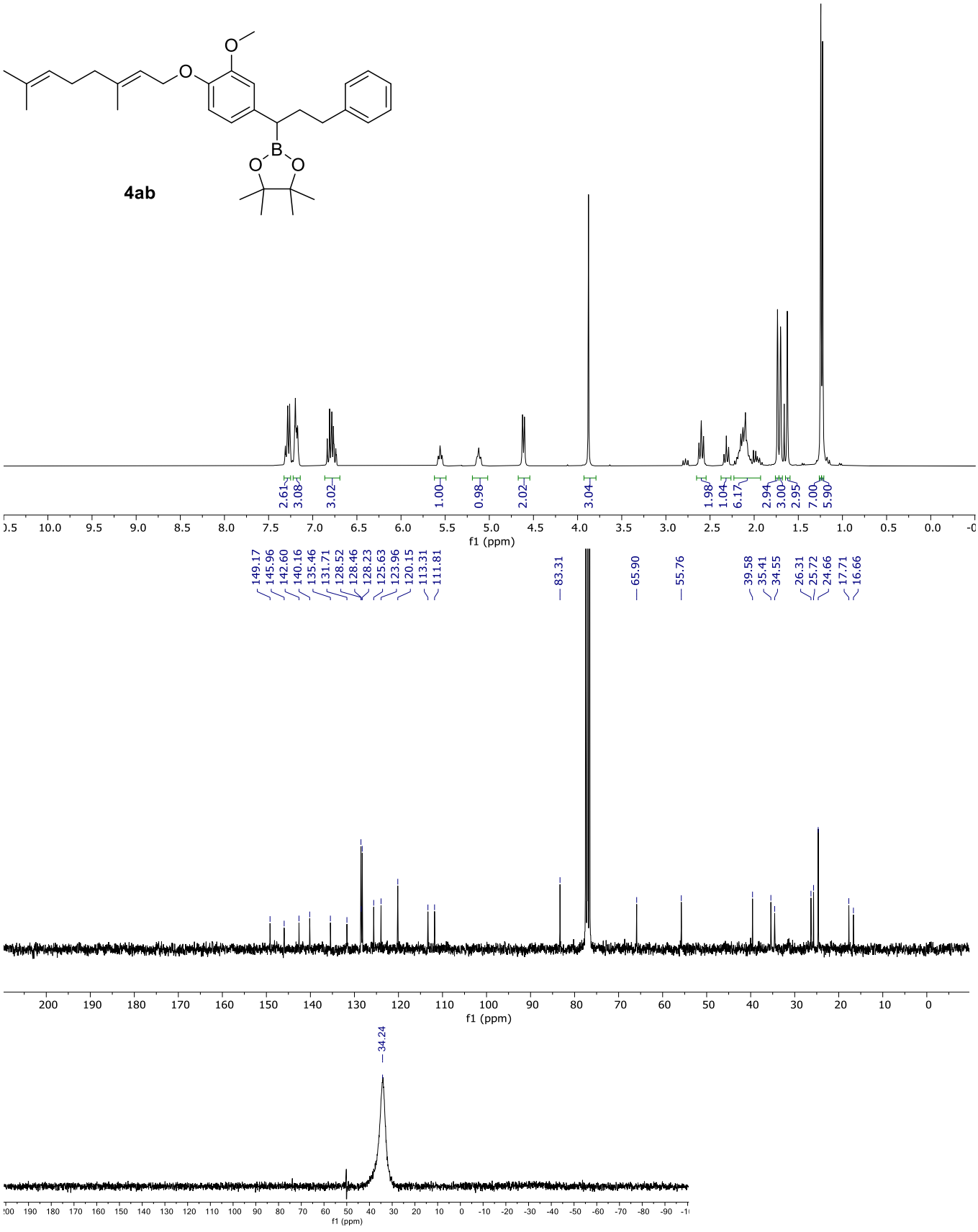


4,4,5,5-tetramethyl-2-(3-phenyl-1-(2,4,6-trimethoxyphenyl)propyl)-1,3,2-dioxaborolane 4aa

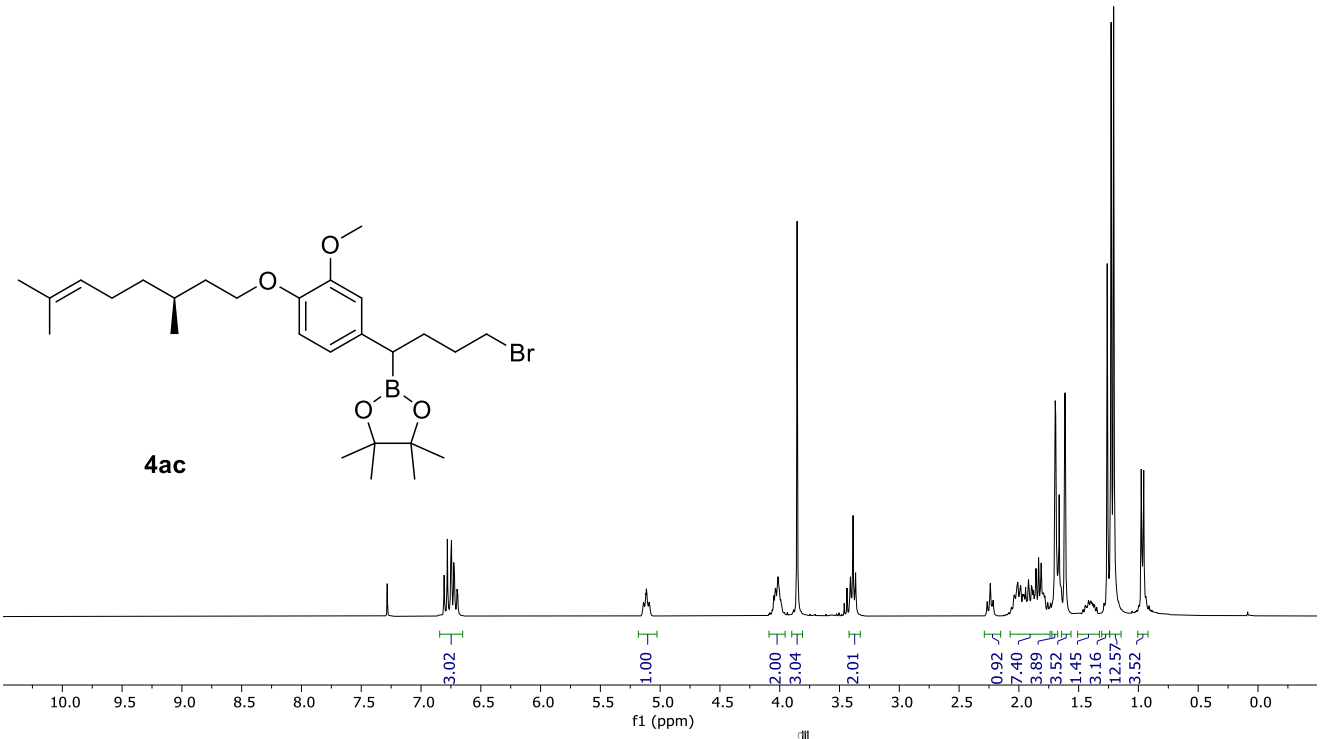


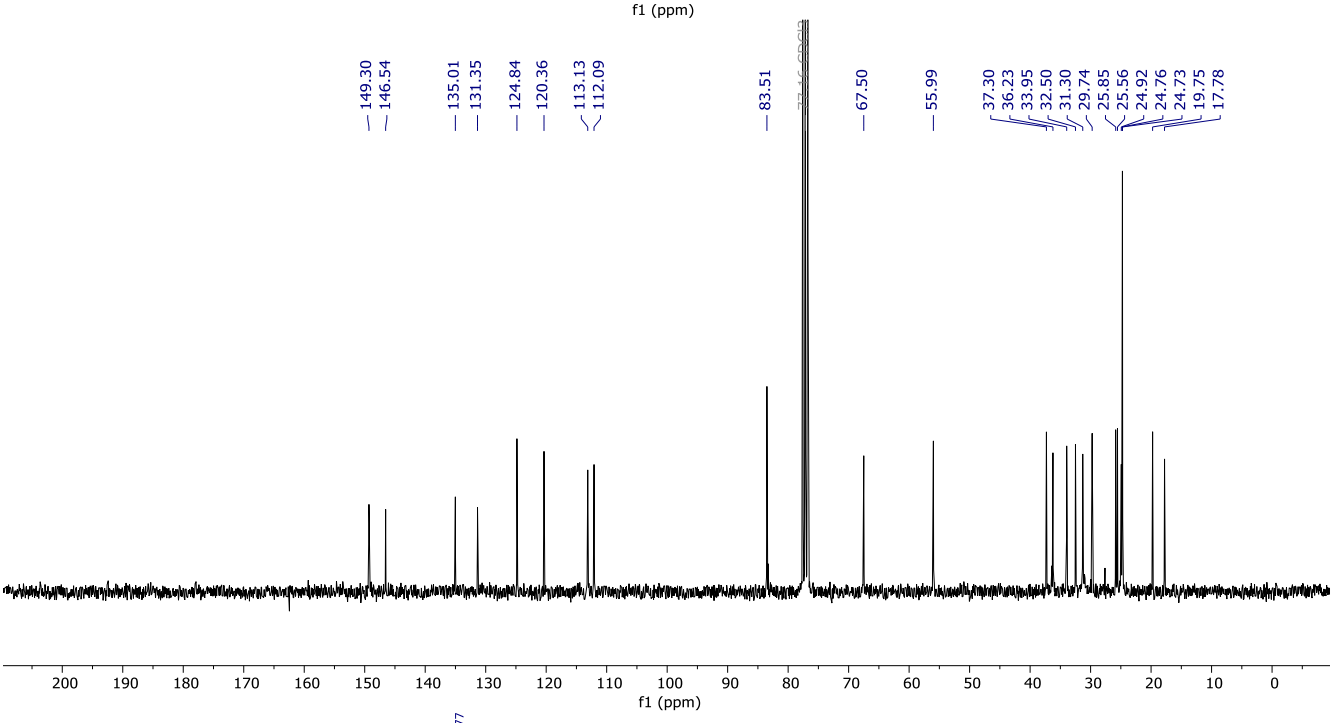


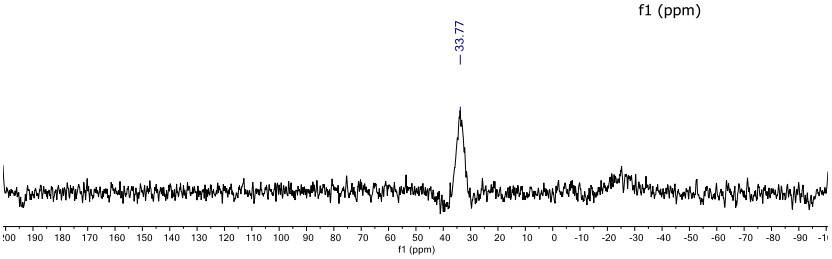
(*E*)-2-(1-(4-((3,7-dimethylocta-2,6-dien-1-yl)oxy)-3-methoxyphenyl)-3-phenylpropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 4ab



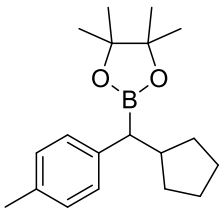
2-(4-bromo-1-(4-(((S)-3,7-dimethyloct-6-en-1-yl)oxy)-3-methoxyphenyl)butyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 4ac



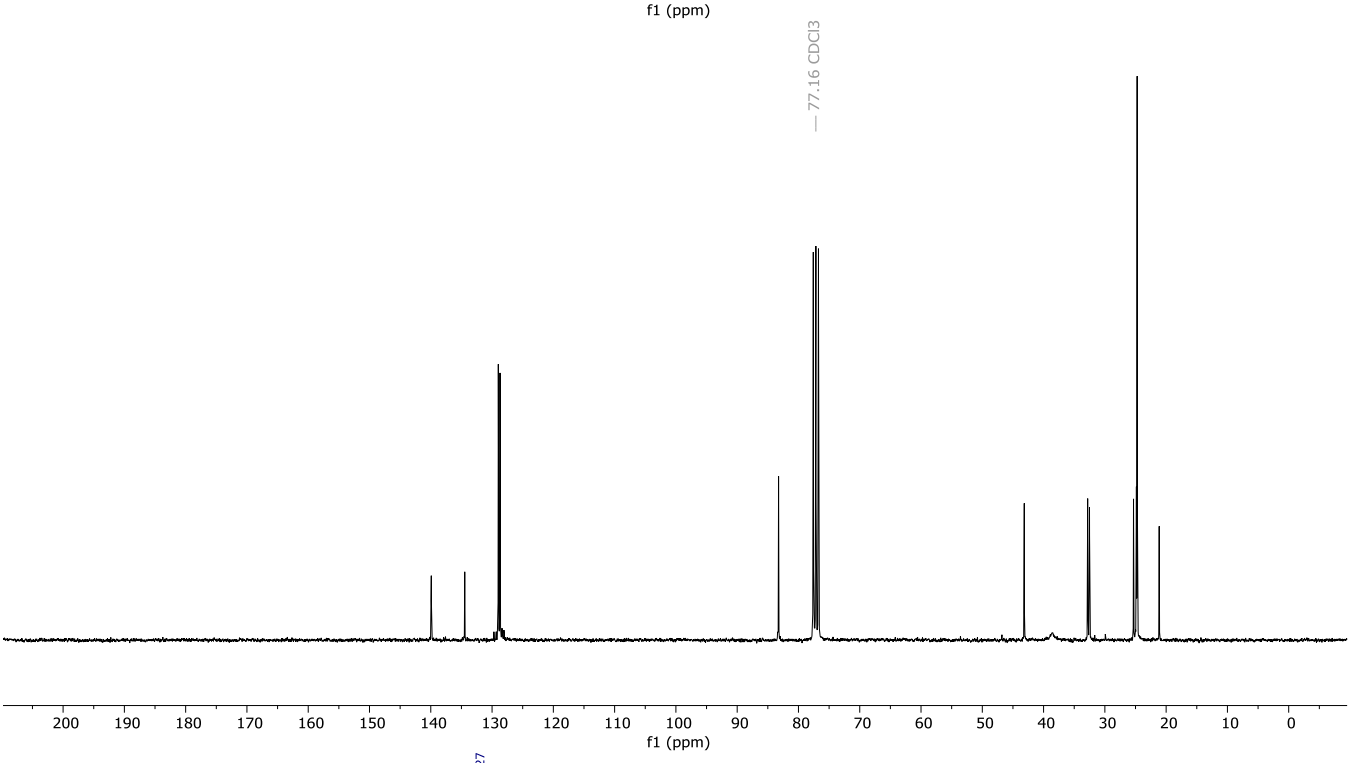


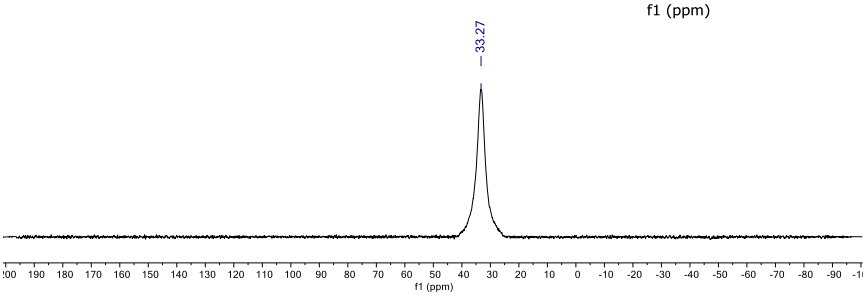


2-(cyclopentyl(*p*-tolyl)methyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 4ad

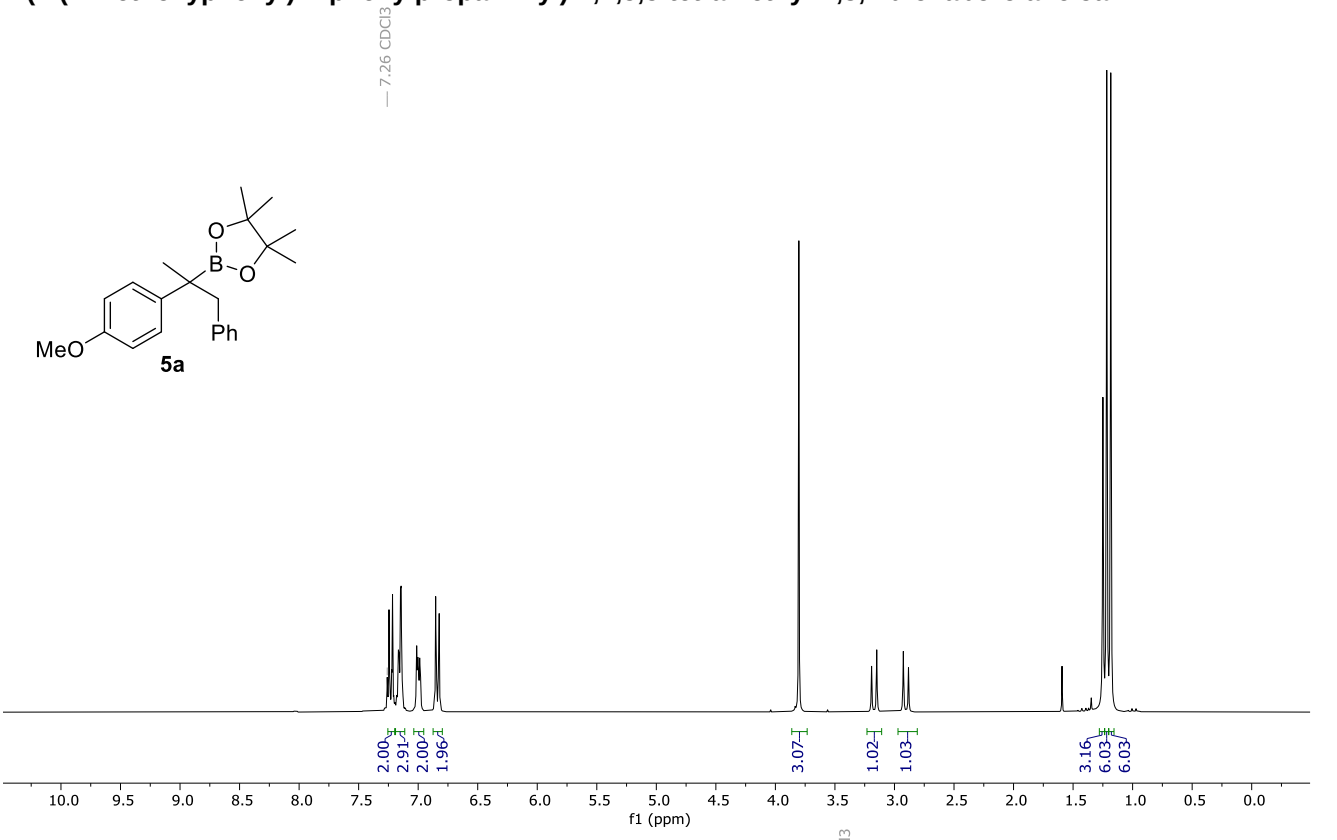


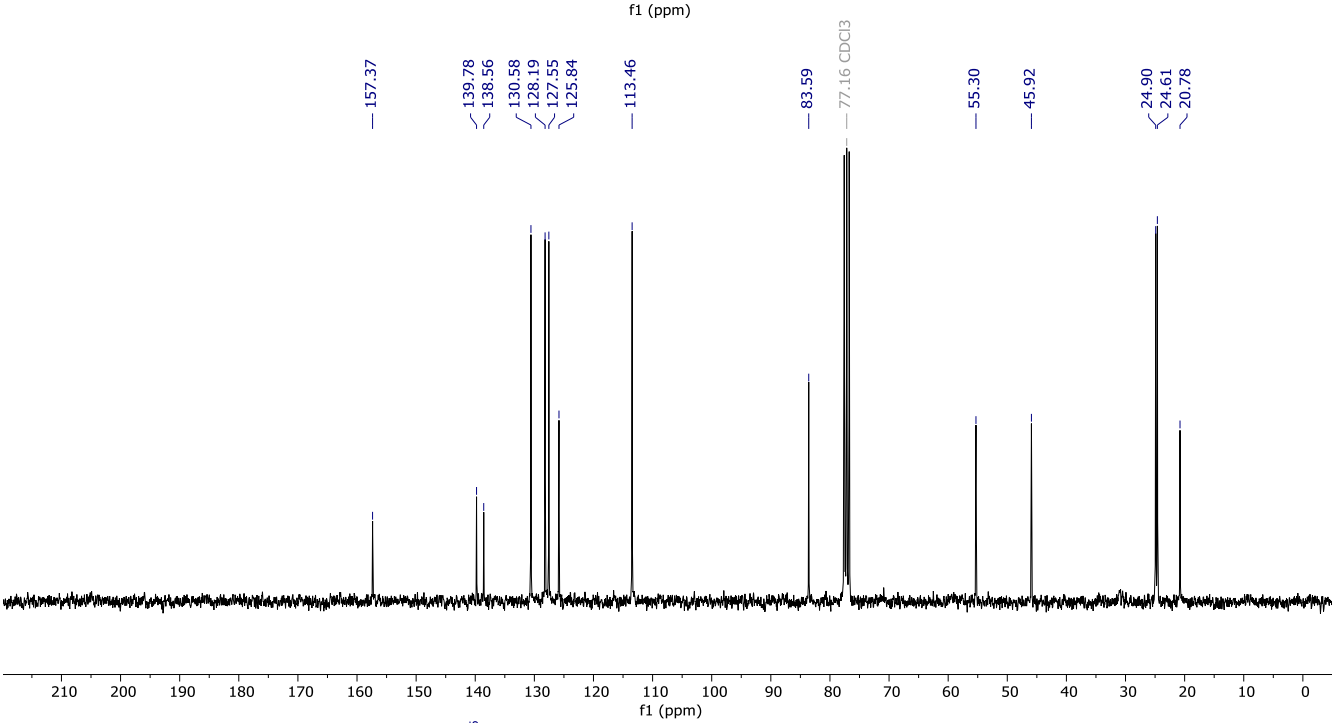
4ad

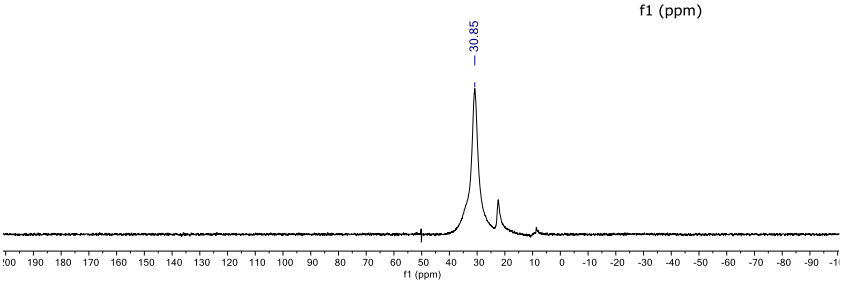




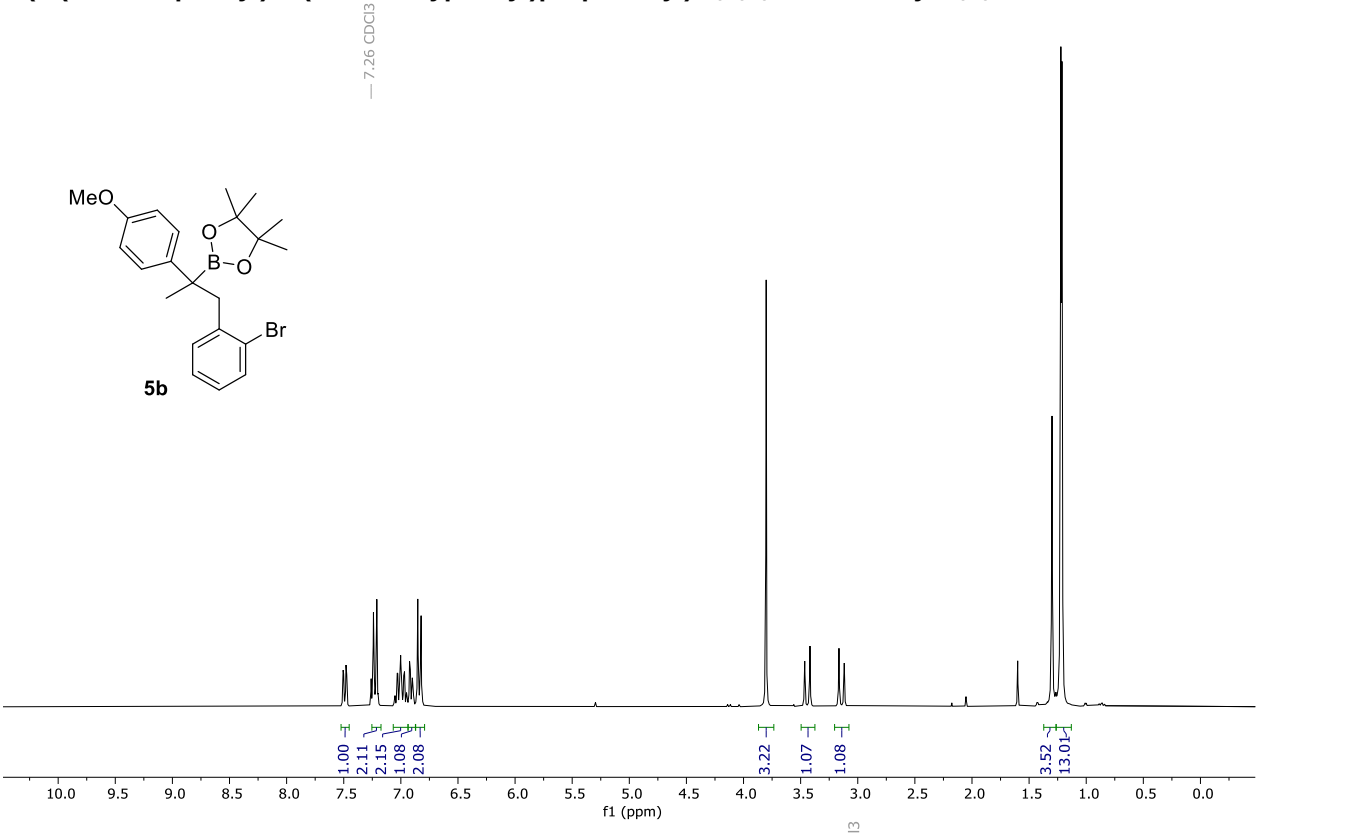
2-(2-(4-methoxyphenyl)-1-phenylpropan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 5a

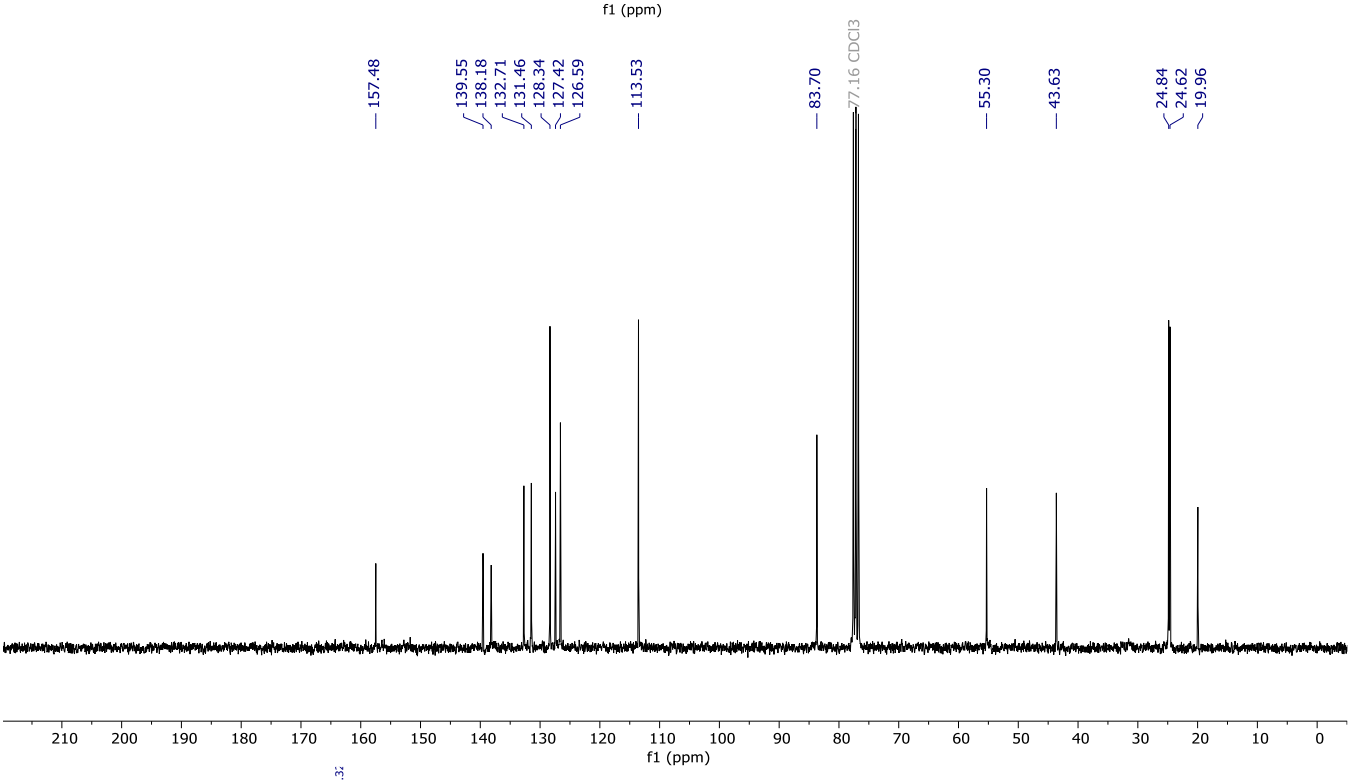


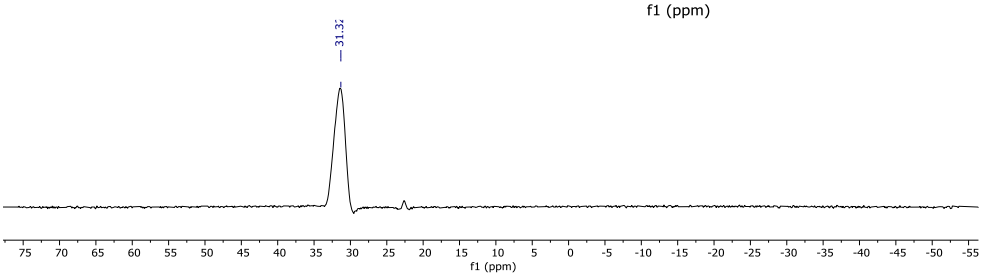




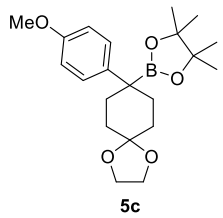
2-(1-(2-bromophenyl)-2-(4-methoxyphenyl)propan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 5b



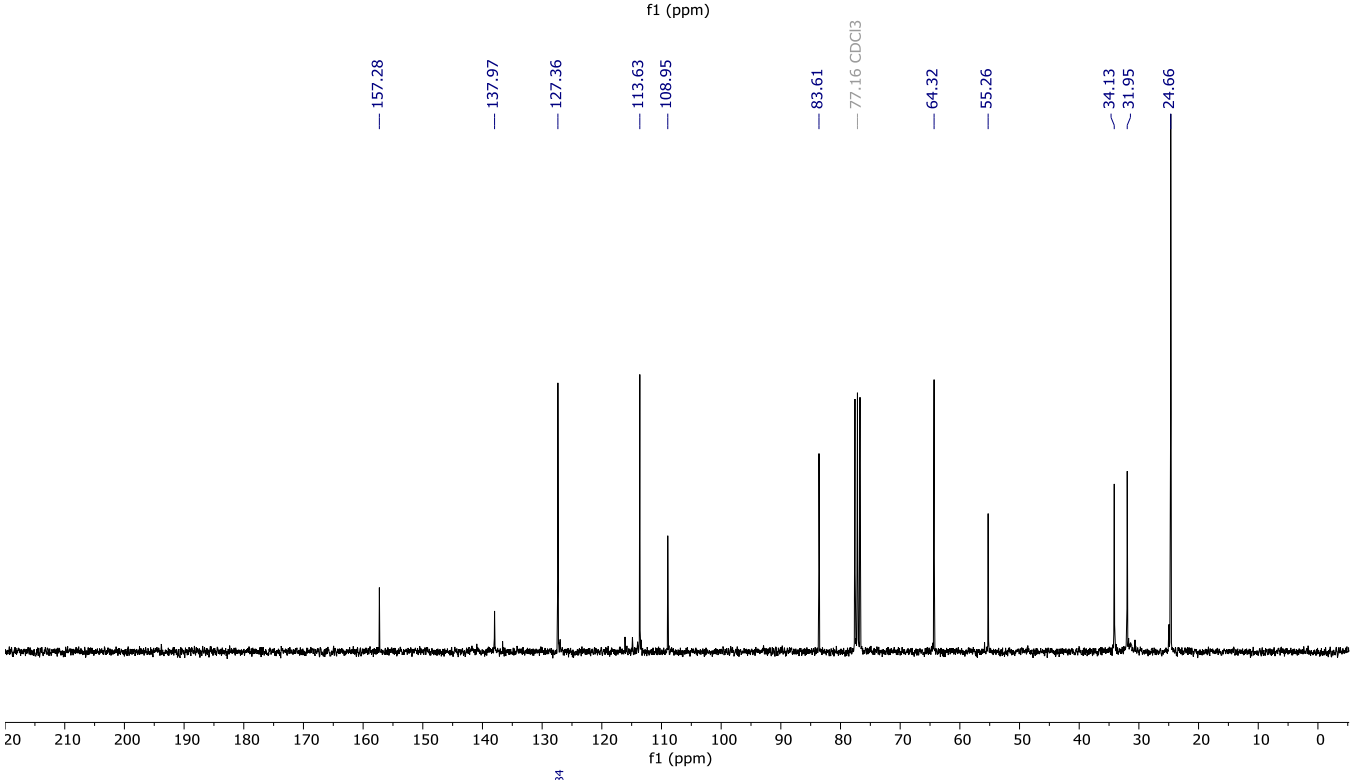


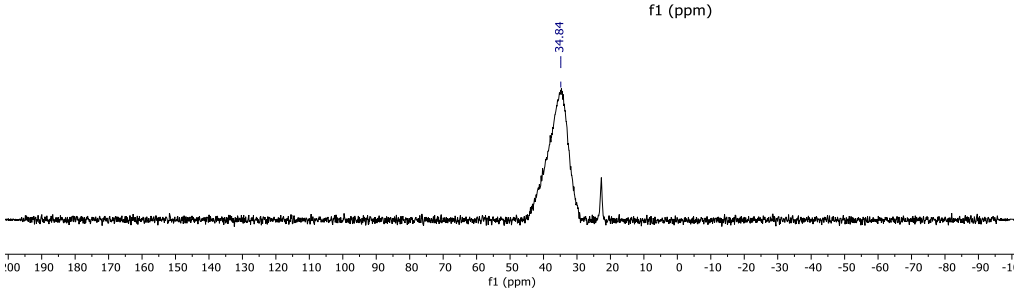


2-(8-(4-methoxyphenyl)-1,4-dioxaspiro[4.5]decan-8-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 5c

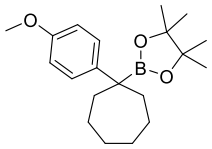


5c

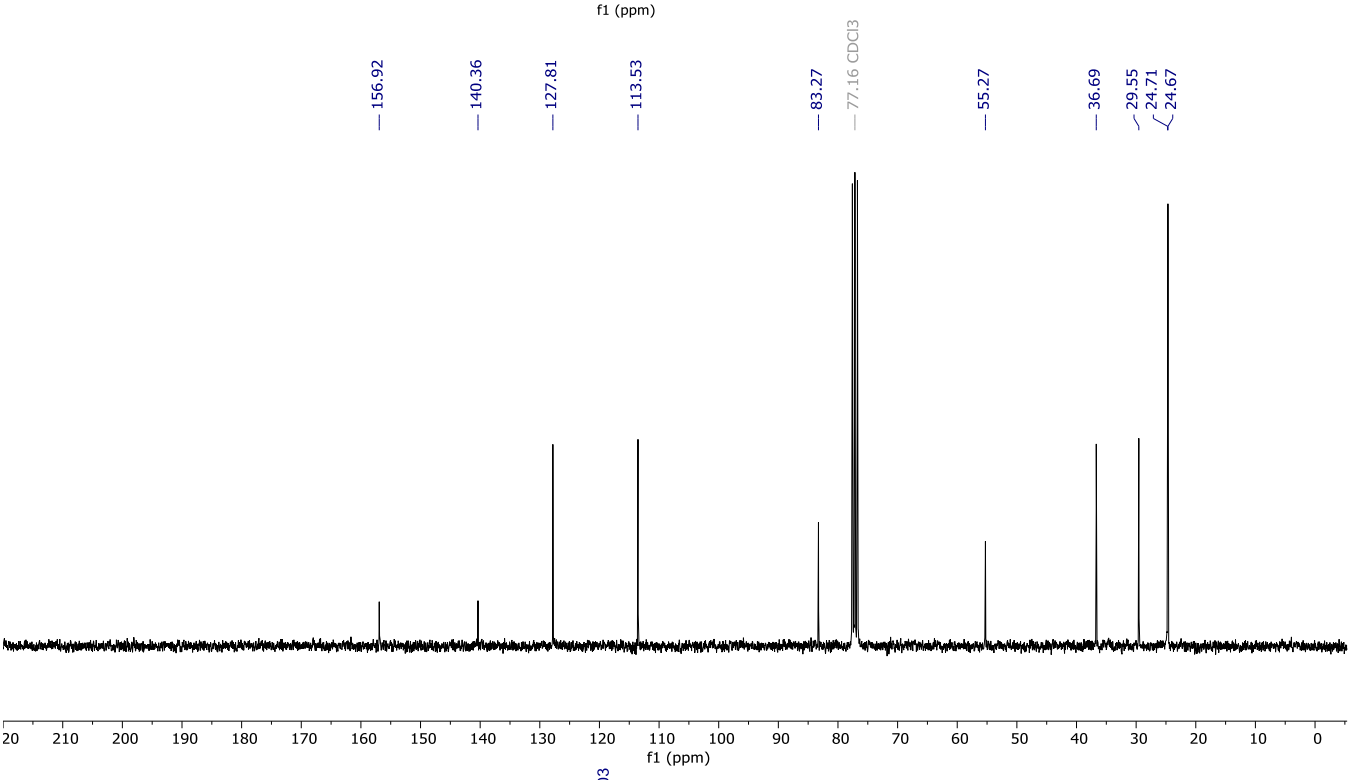


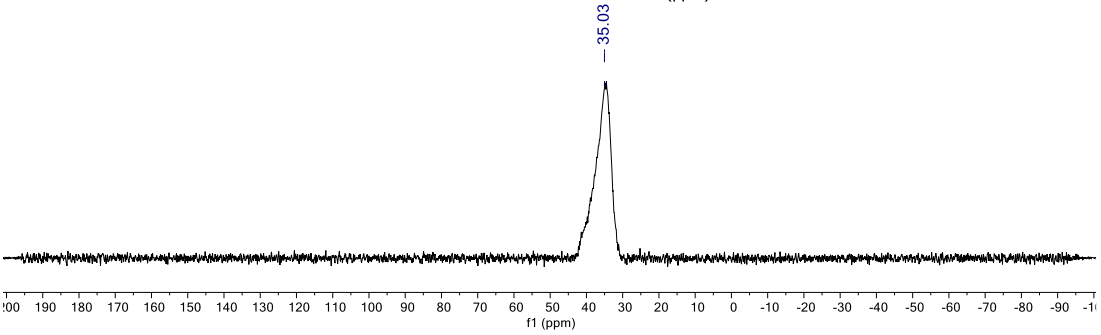


2-(1-(4-methoxyphenyl)cycloheptyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 5d

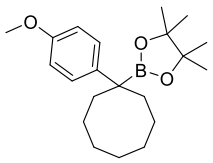


5d





2-(1-(4-methoxyphenyl)cyclooctyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 5e



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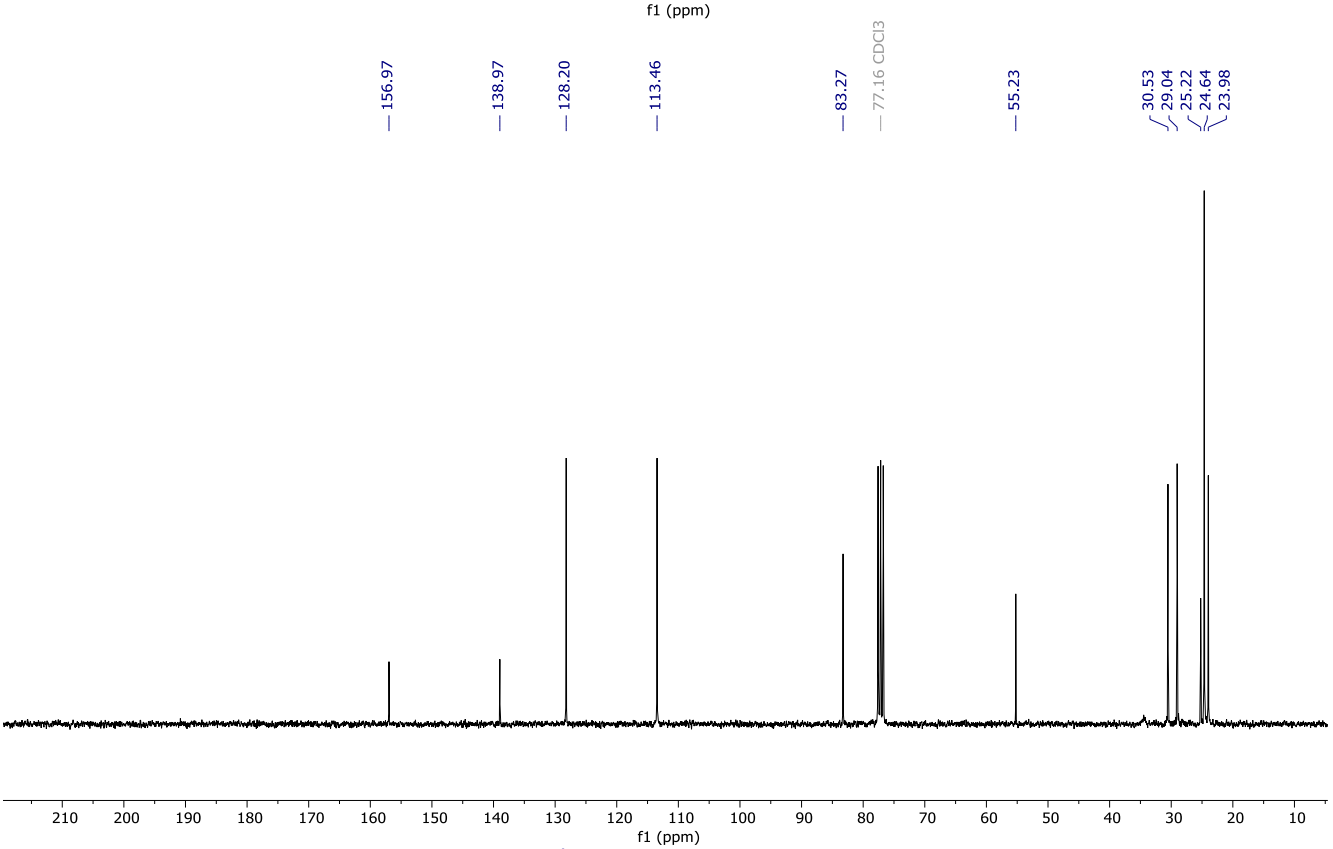
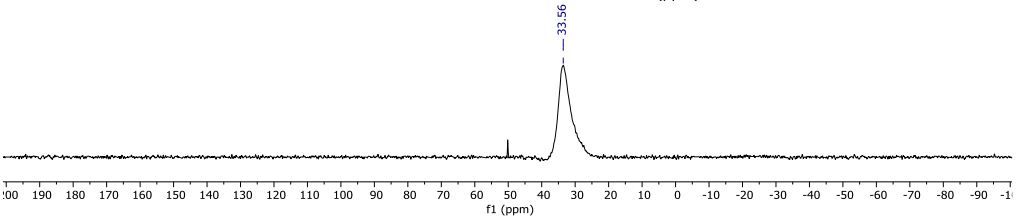
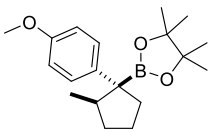


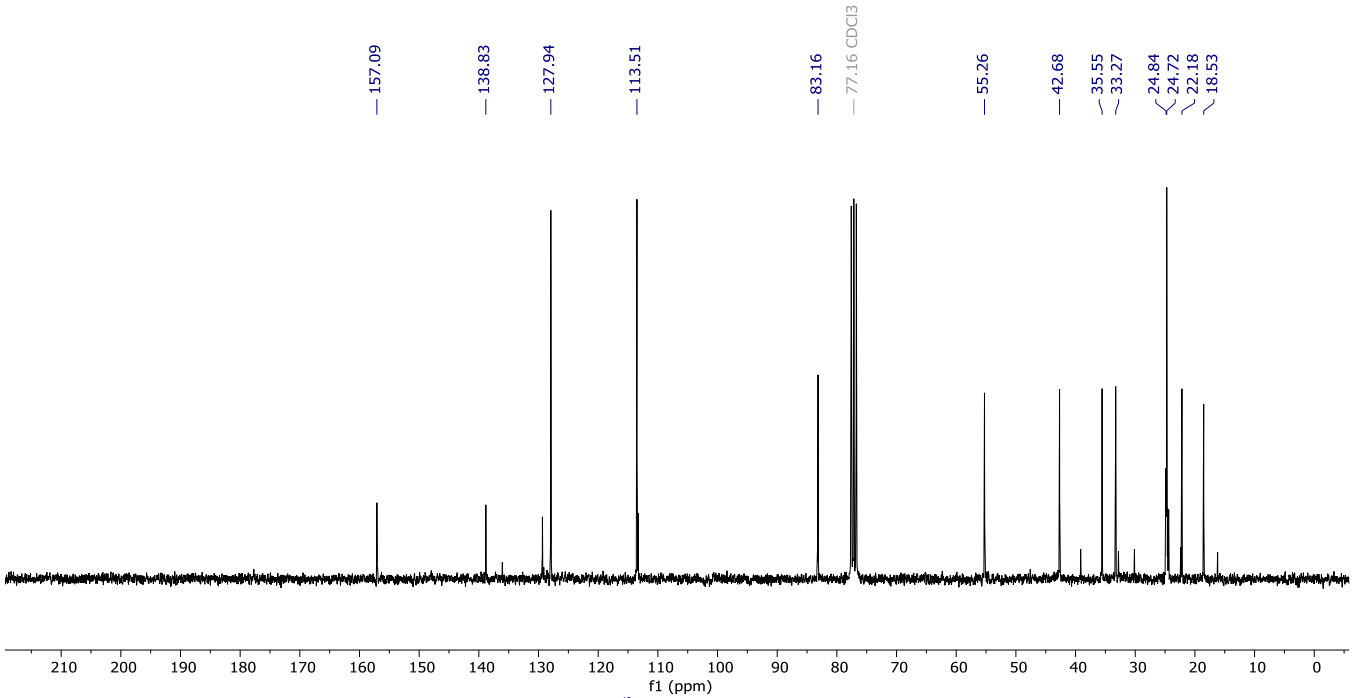


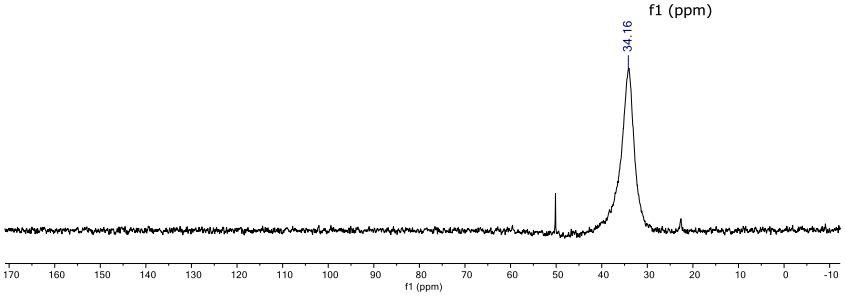
1-(4-methoxyphenyl)-2-methylcyclopentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 5f



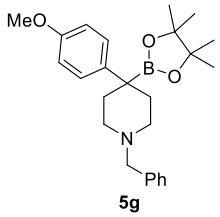
6.6: 1 mixture of diastereoisomers

5f





1-benzyl-4-(4-methoxyphenyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)piperidine 5g



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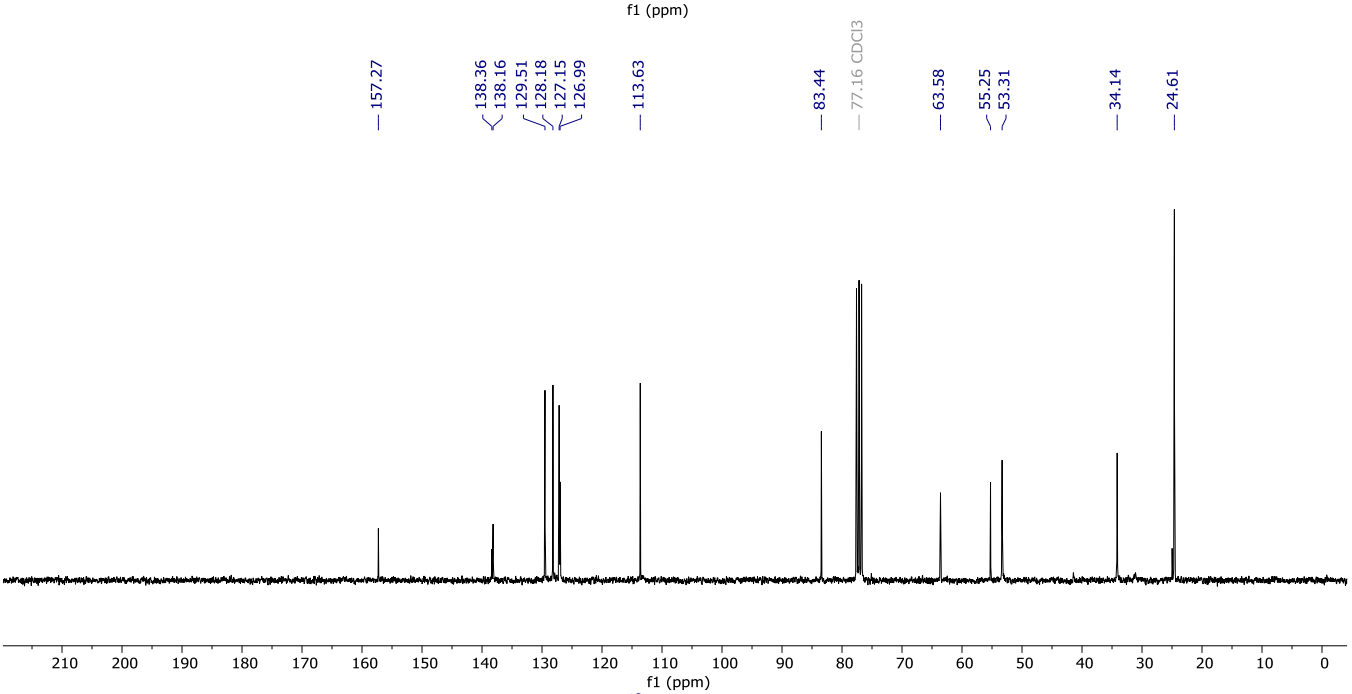
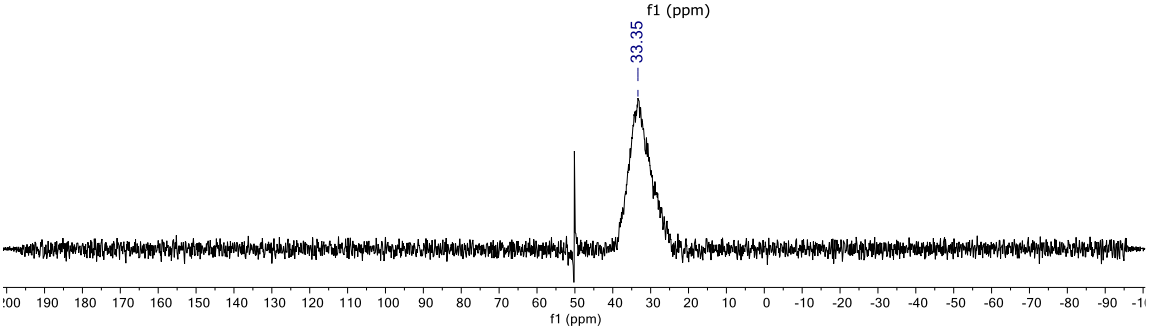
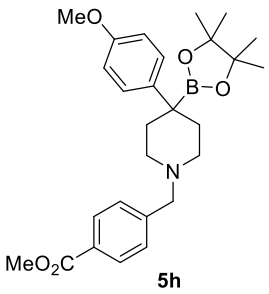




Methyl 4-((4-(4-methoxyphenyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)piperidin-1-yl)methyl)benzoate 5h



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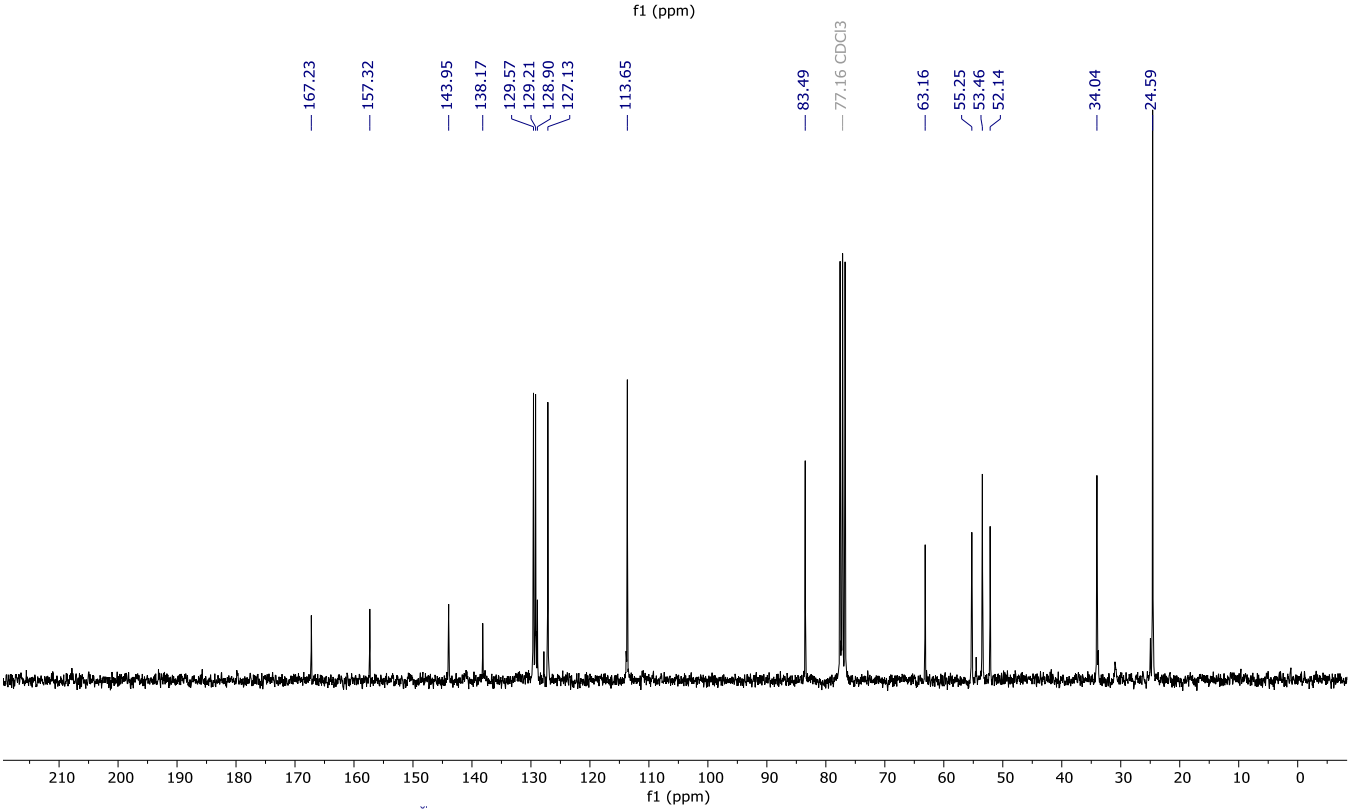
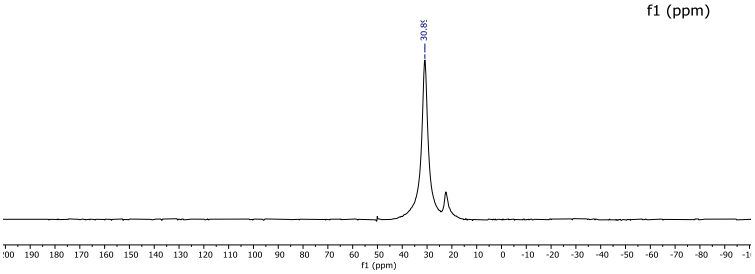
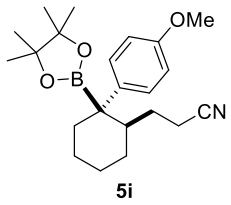
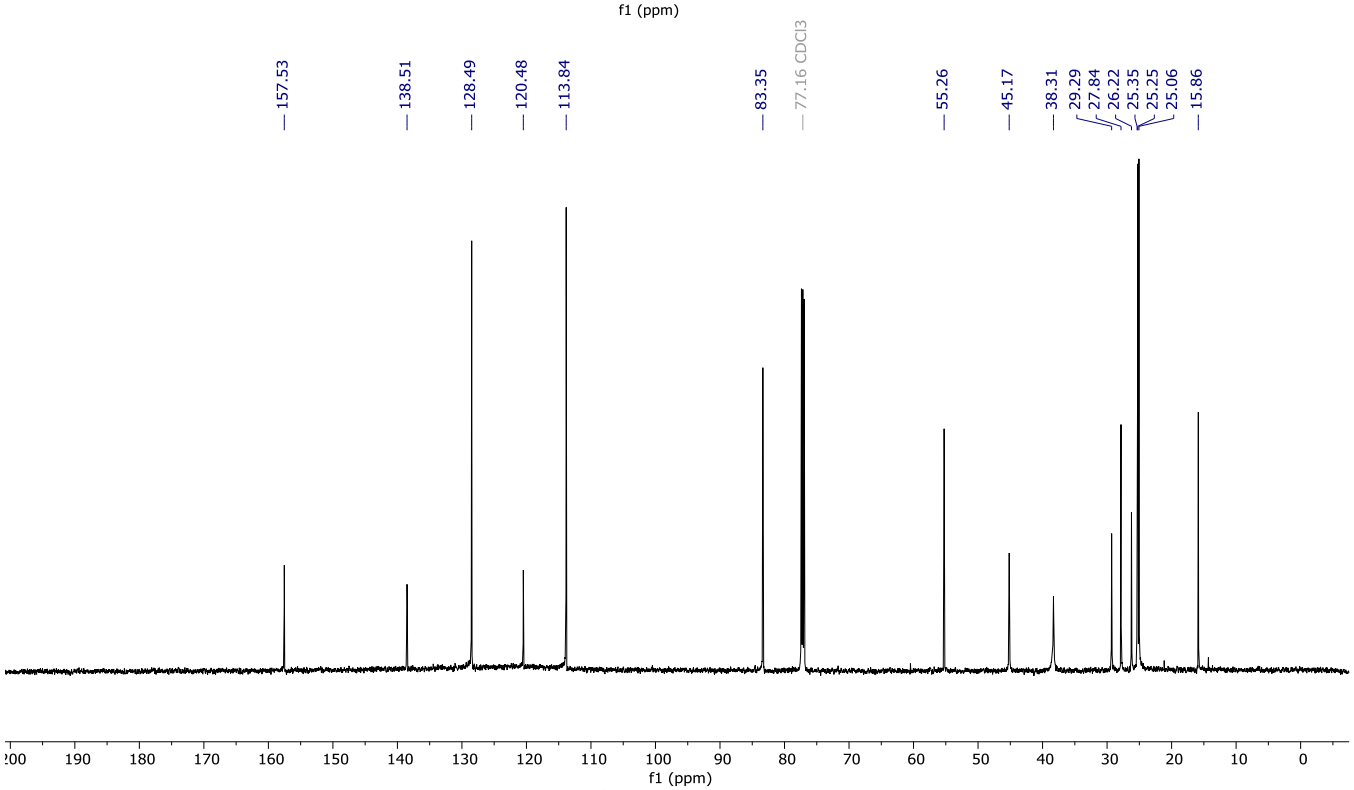


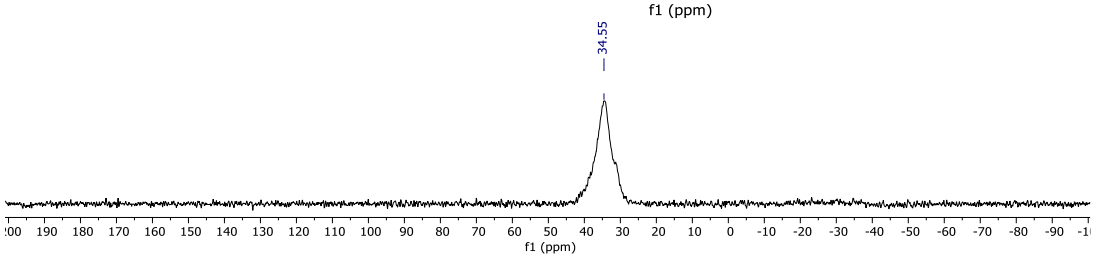


3-(2-(4-methoxyphenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohexyl)propanenitrile 5i

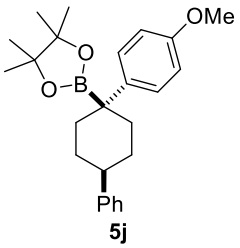


5i

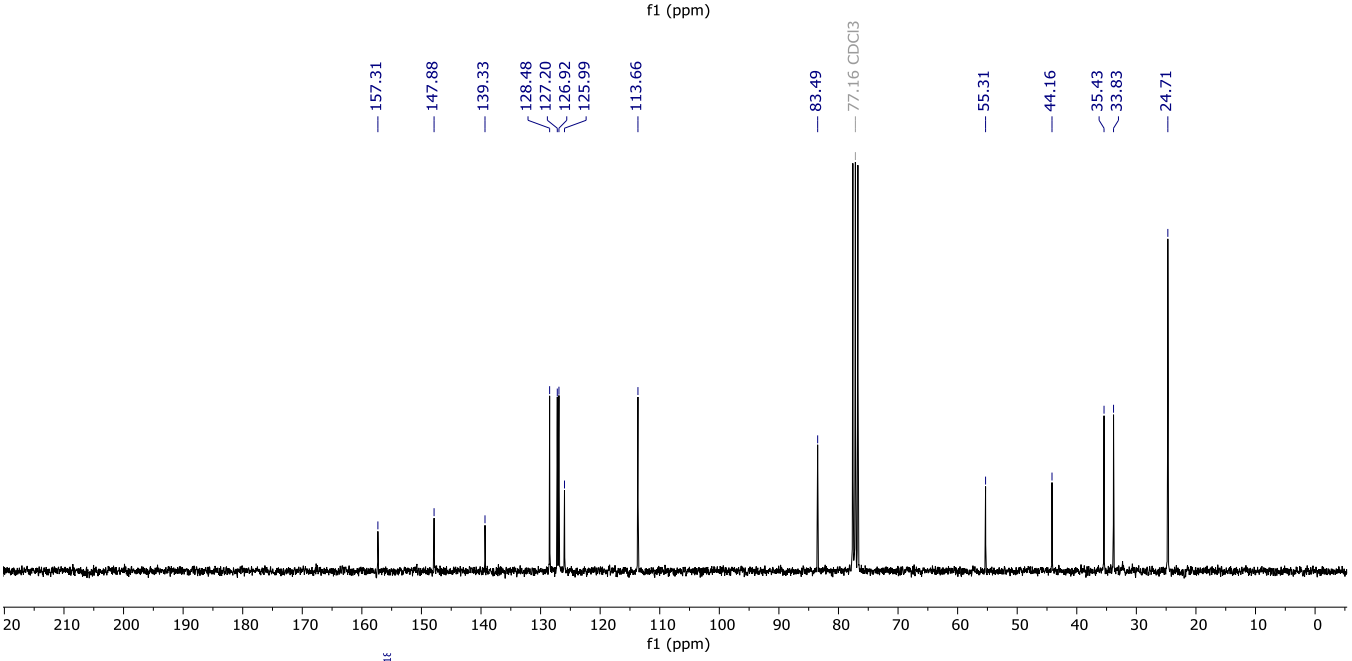


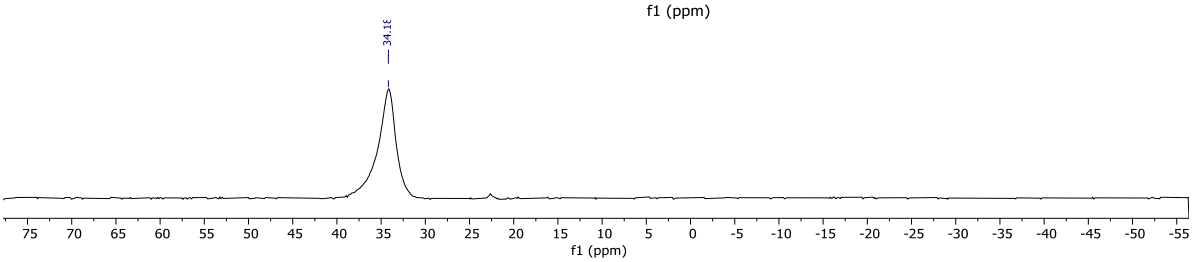


1-(4-Methoxyphenyl)-4-phenylcyclohexyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 5j

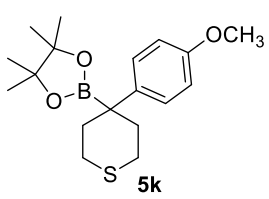


5j





2-(4-(4-methoxyphenyl)tetrahydro-2H-thiopyran-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 5k



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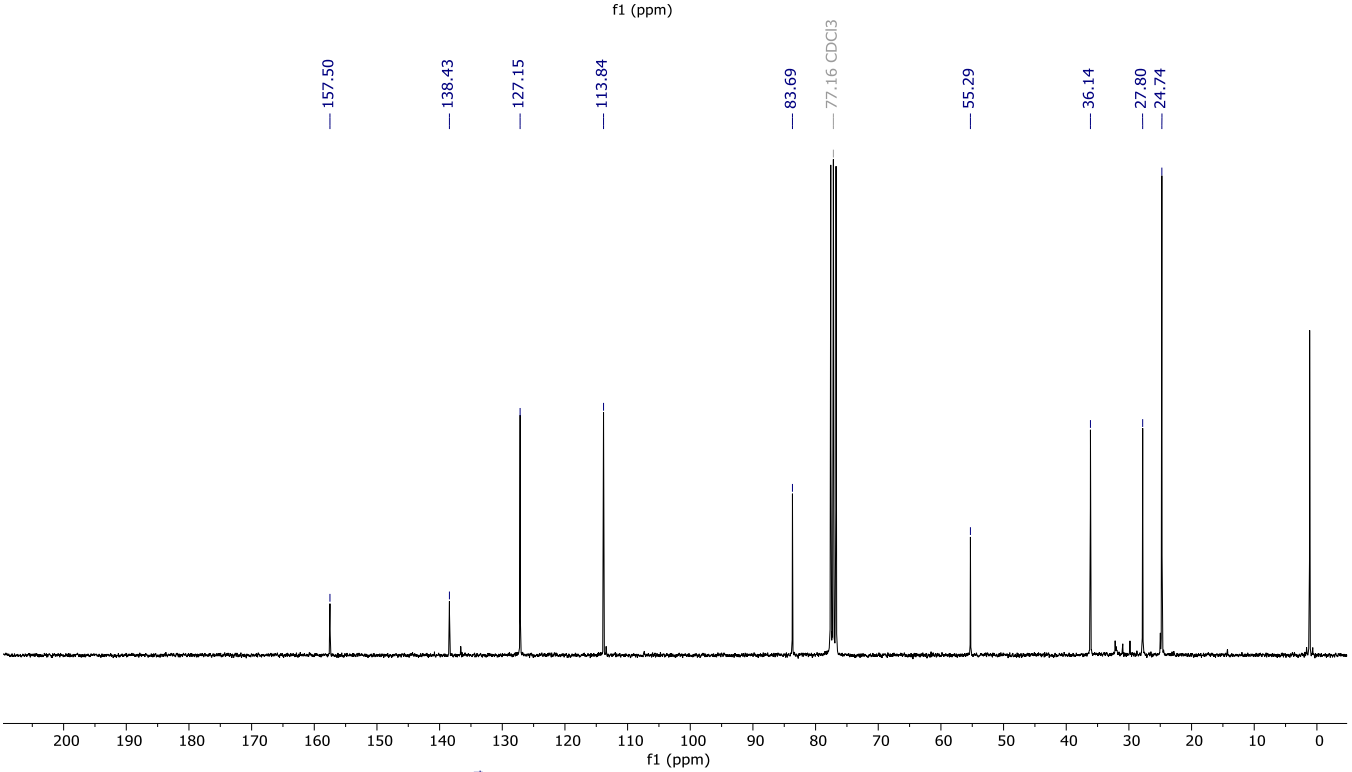
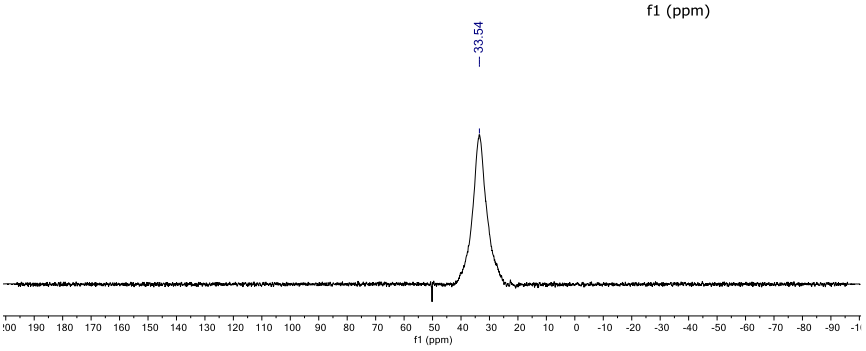
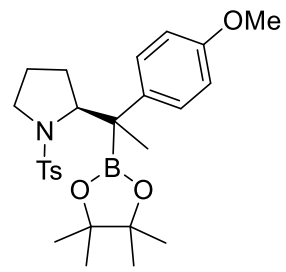


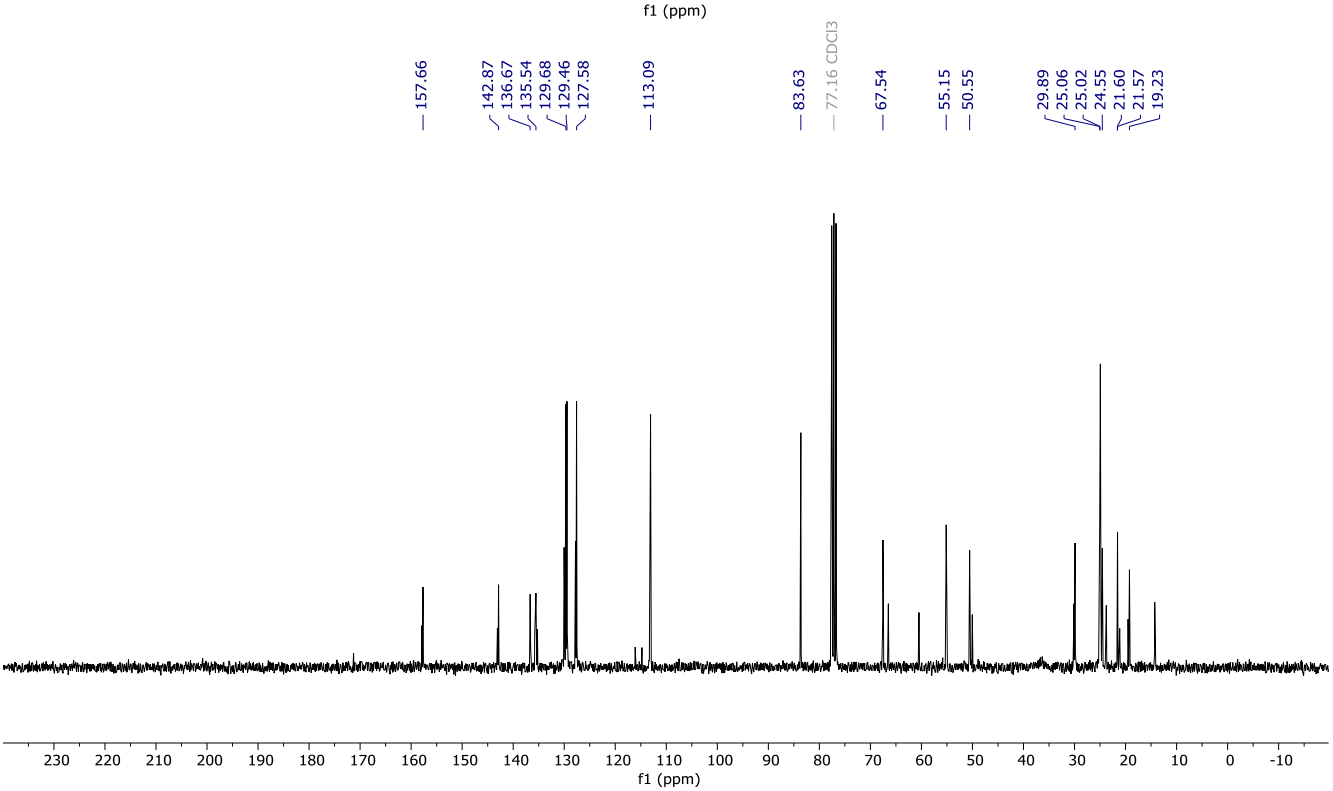


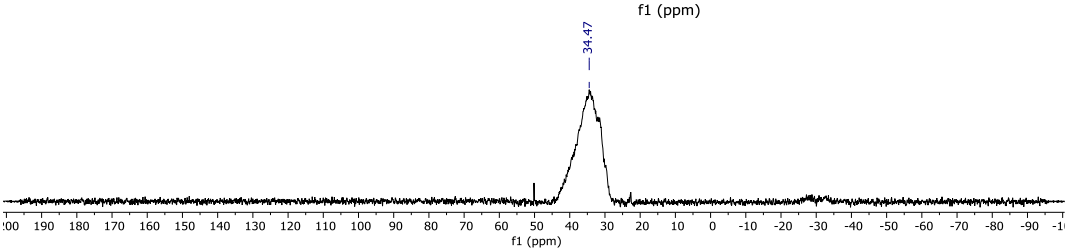
(2S)-2-(1-(4-methoxyphenyl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)-1-tosylpyrrolidine 5l



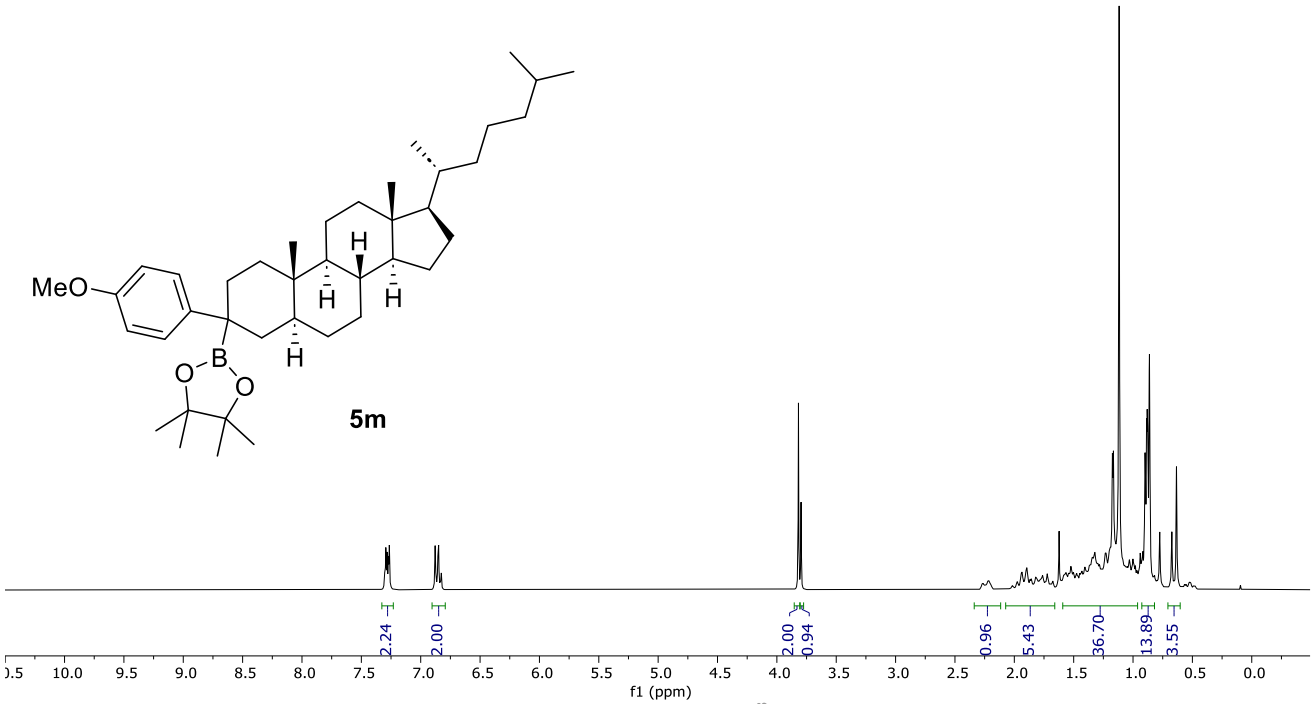
2: 1 mixture of isomers

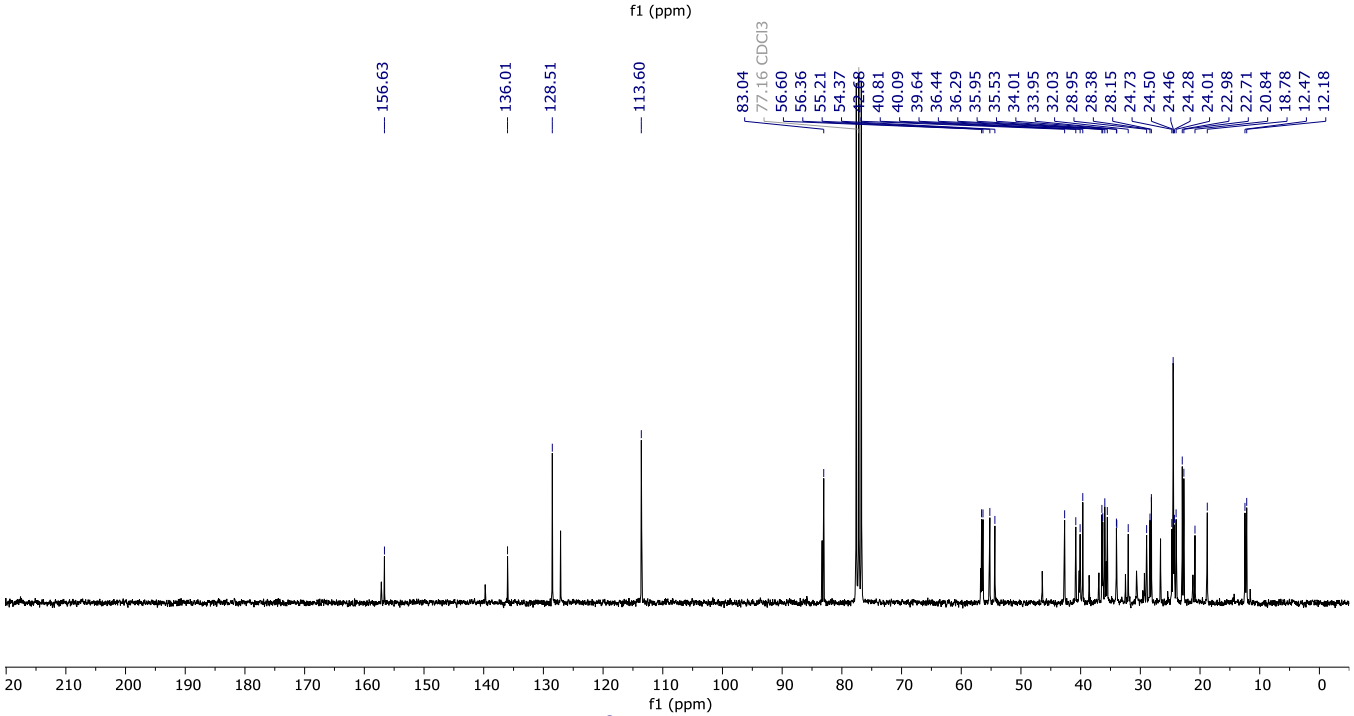
5l

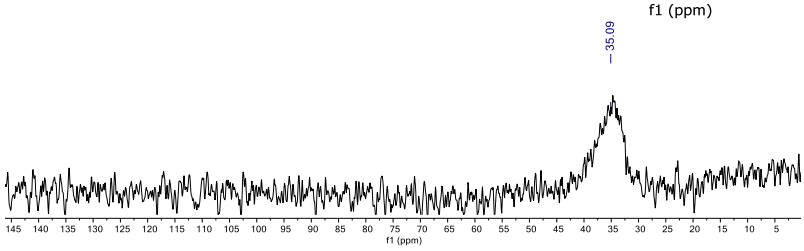




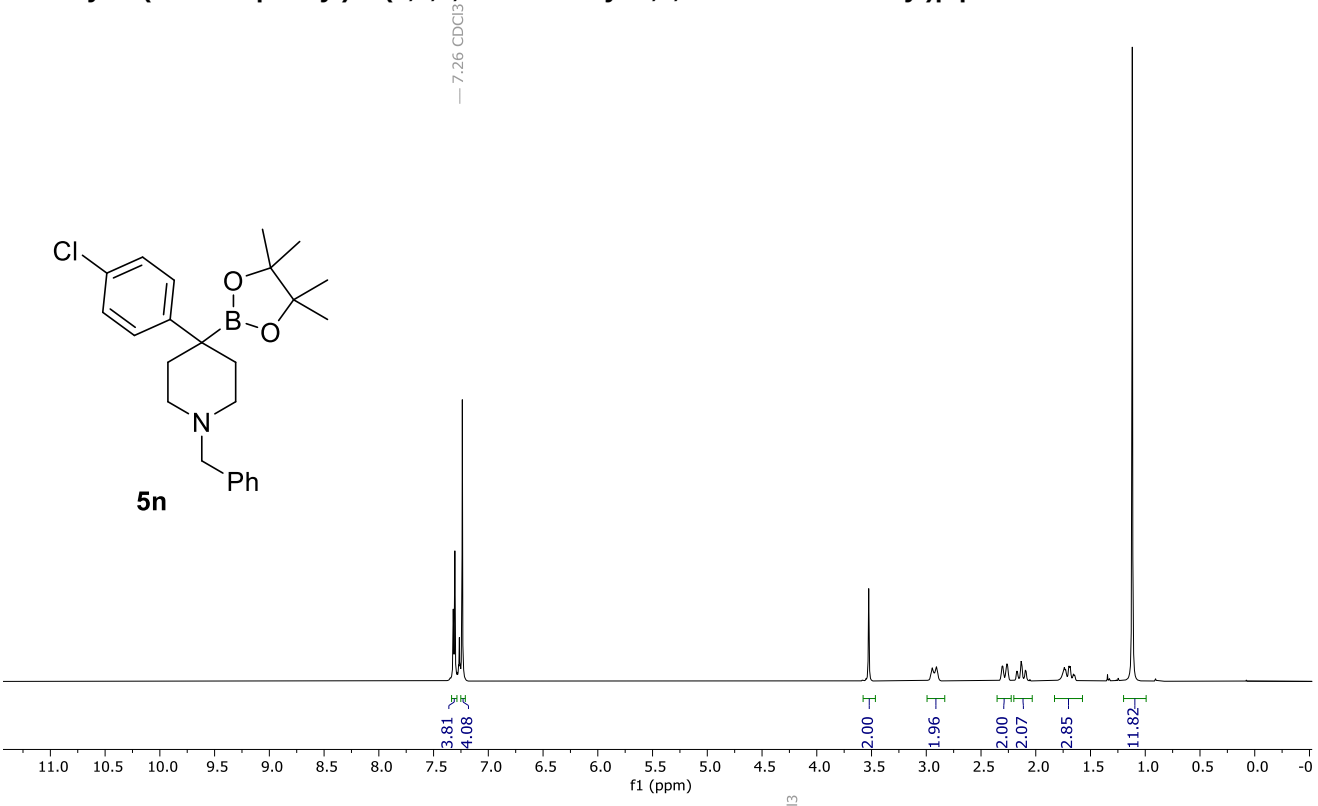
Pinacol boronic ester from Cholestanone *N*-tosylhydrazone 5m
2:1 mixture of isomers

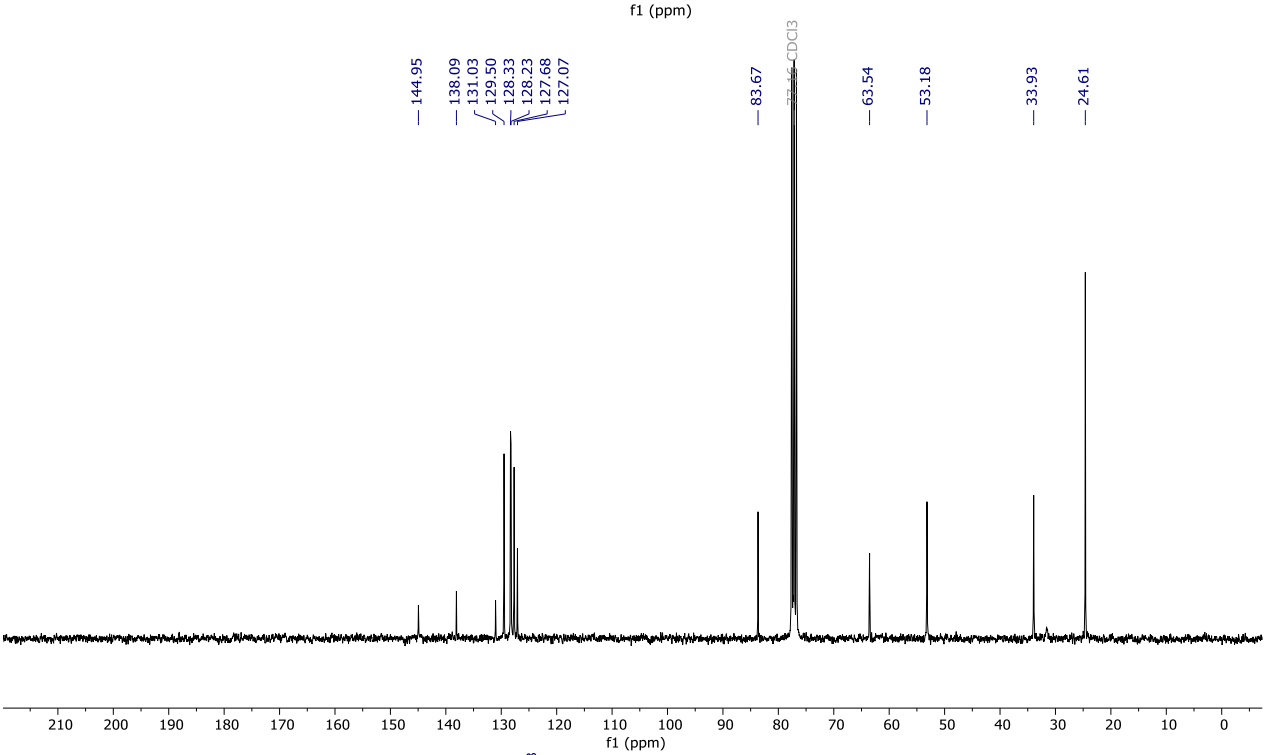


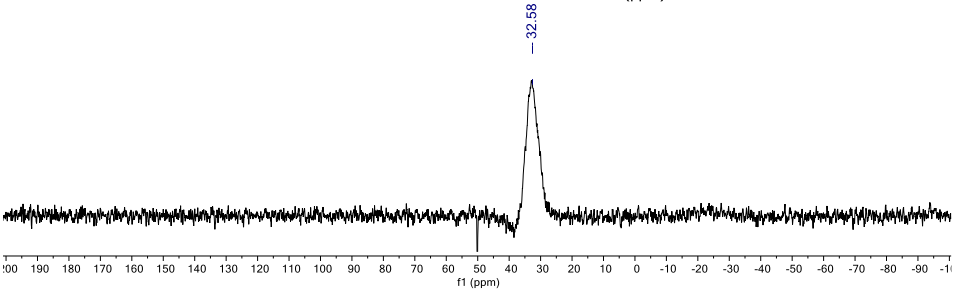




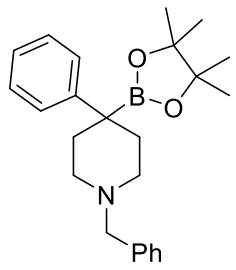
1-benzyl-4-(4-chlorophenyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)piperidine 5n



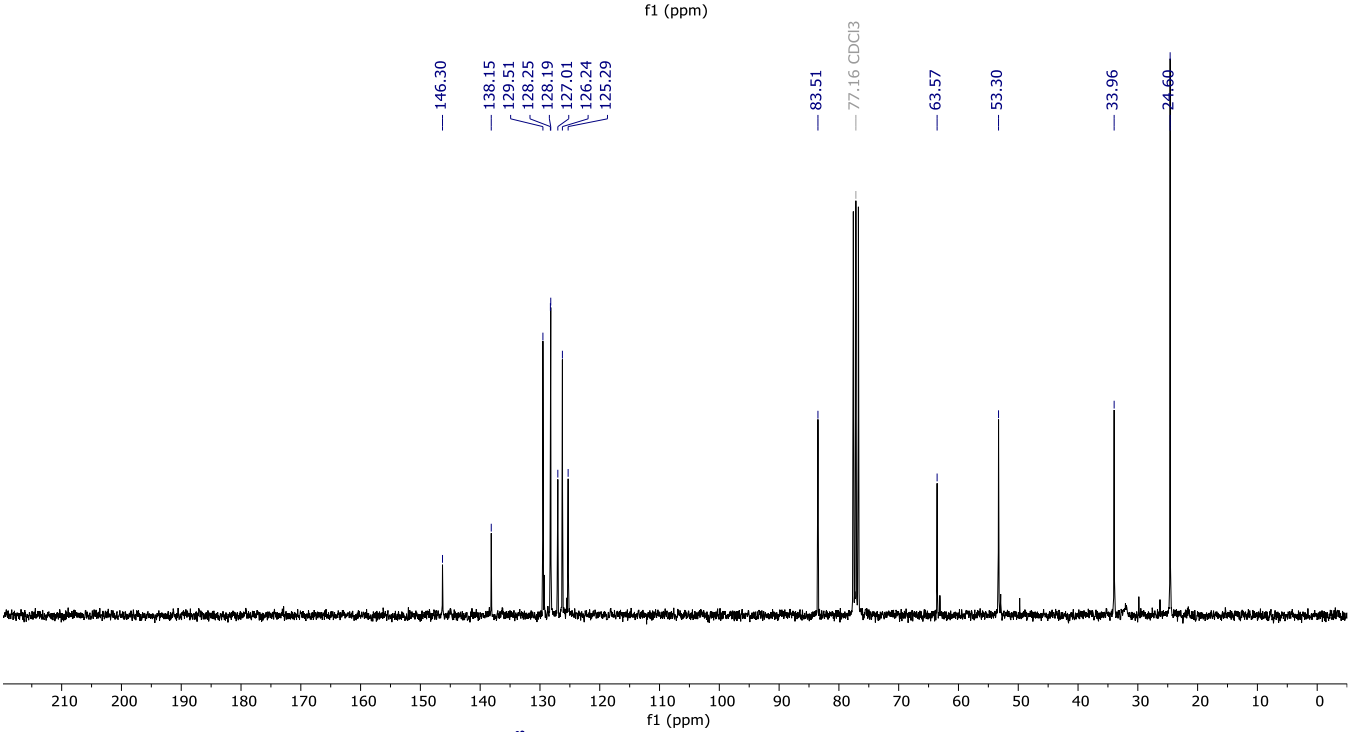


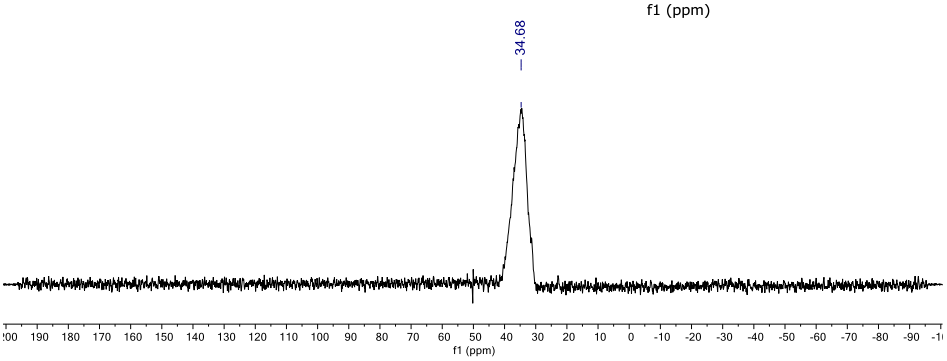


1-benzyl-4-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)piperidine 5o

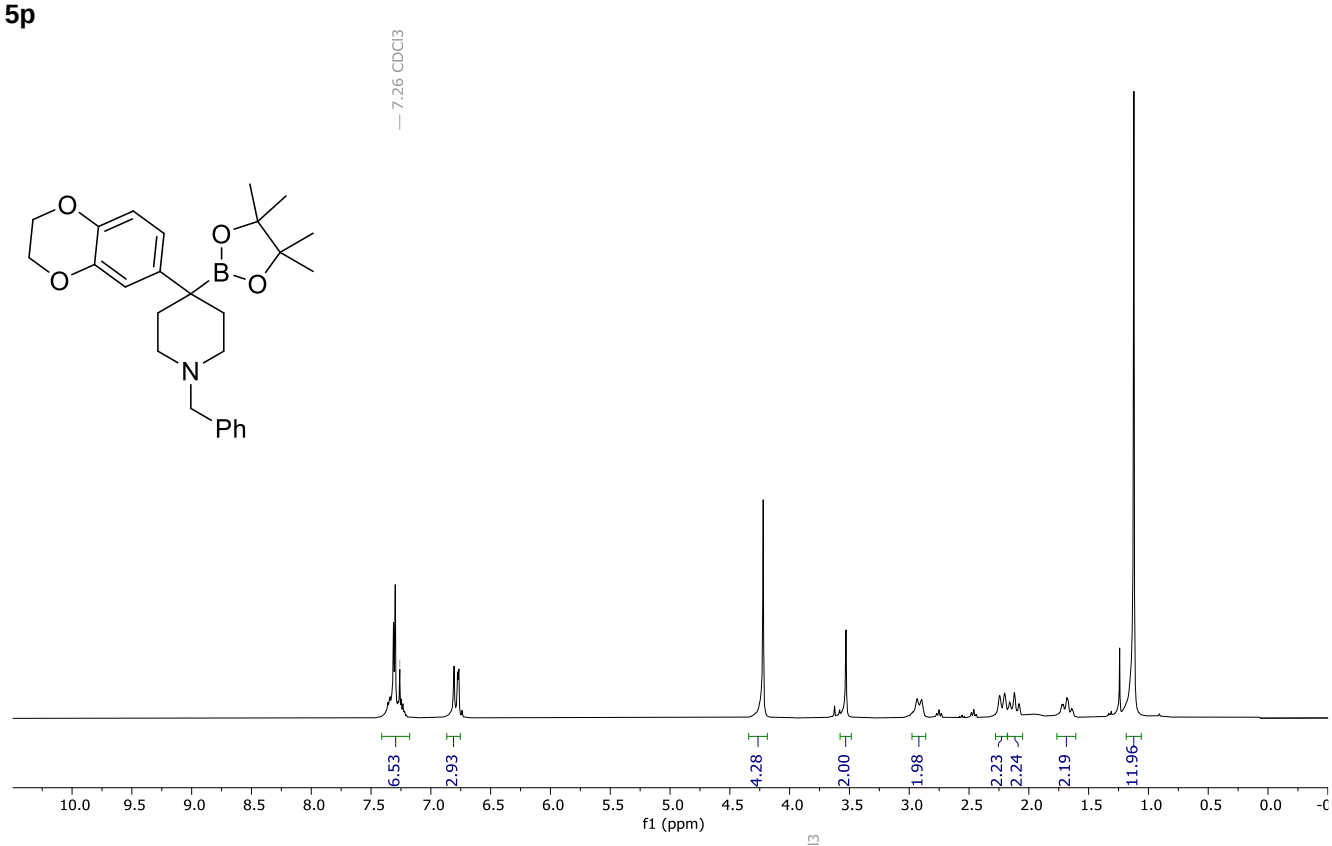


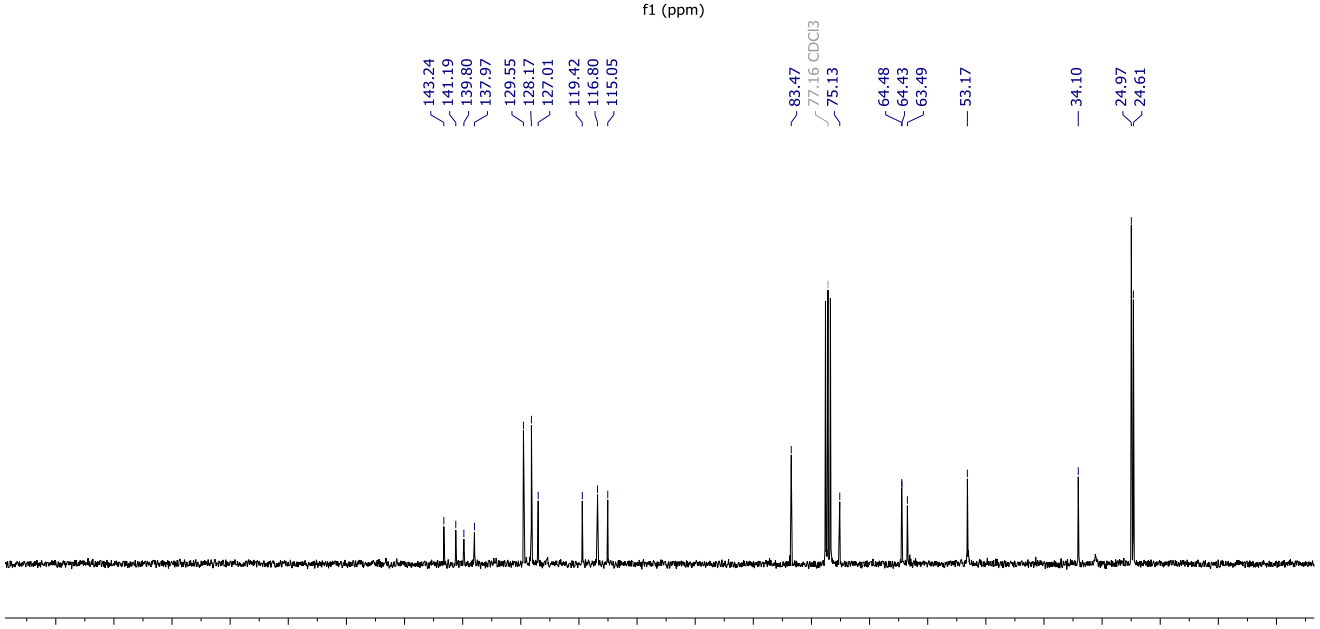
5o

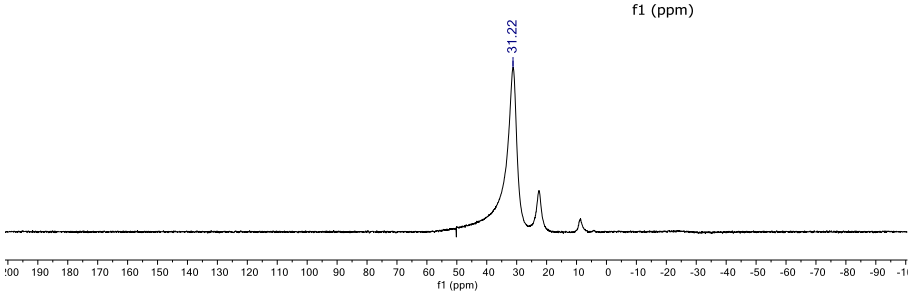




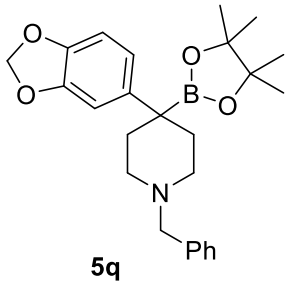
1-benzyl-4-(2,3-dihydrobenzo[b][1,4]dioxin-6-yl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)piperidine 5p



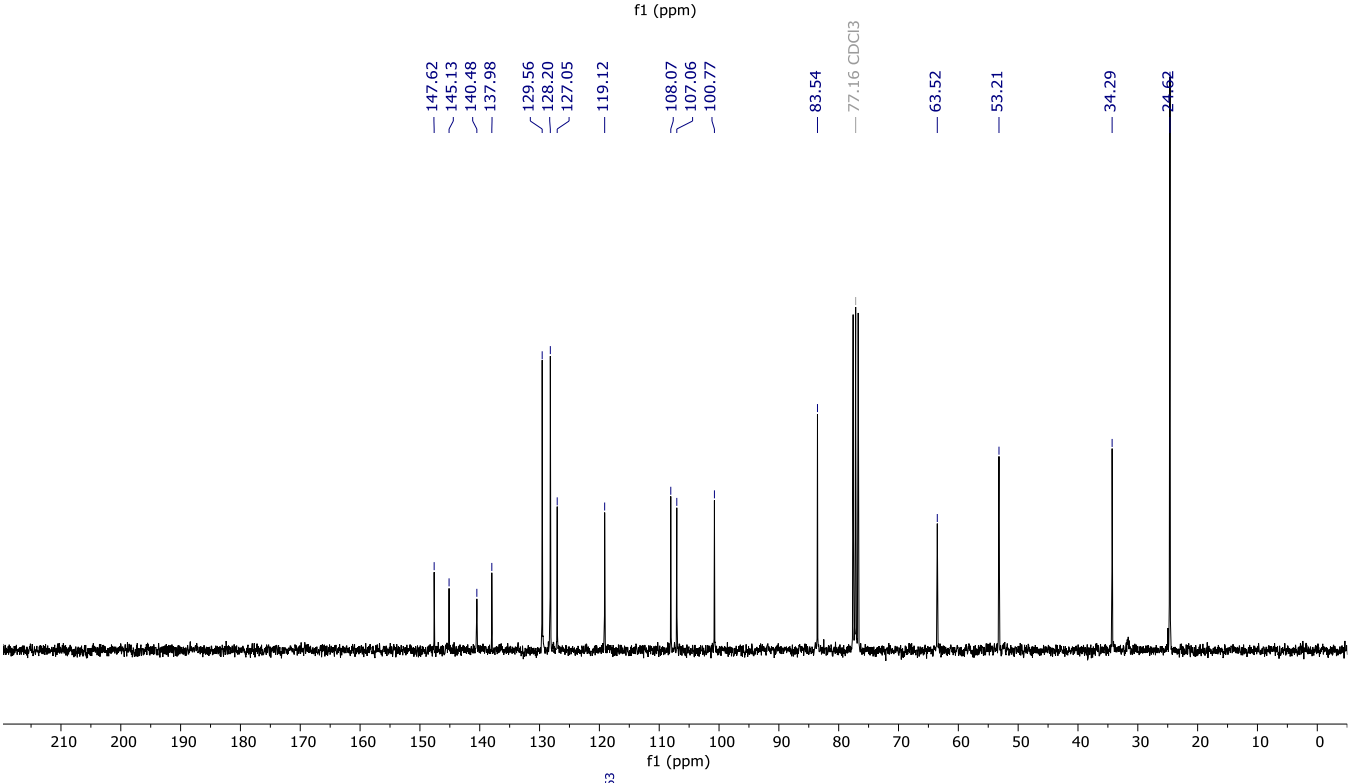


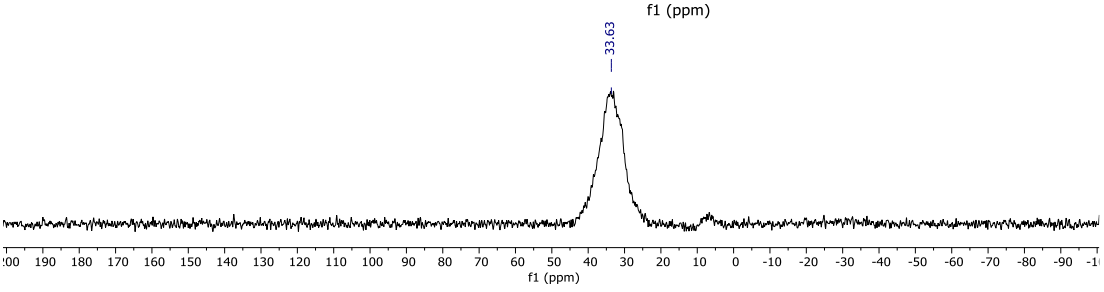


4-(benzo[d][1,3]dioxol-5-yl)-1-benzyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)piperidine 5q

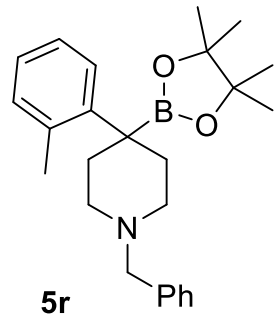


5q

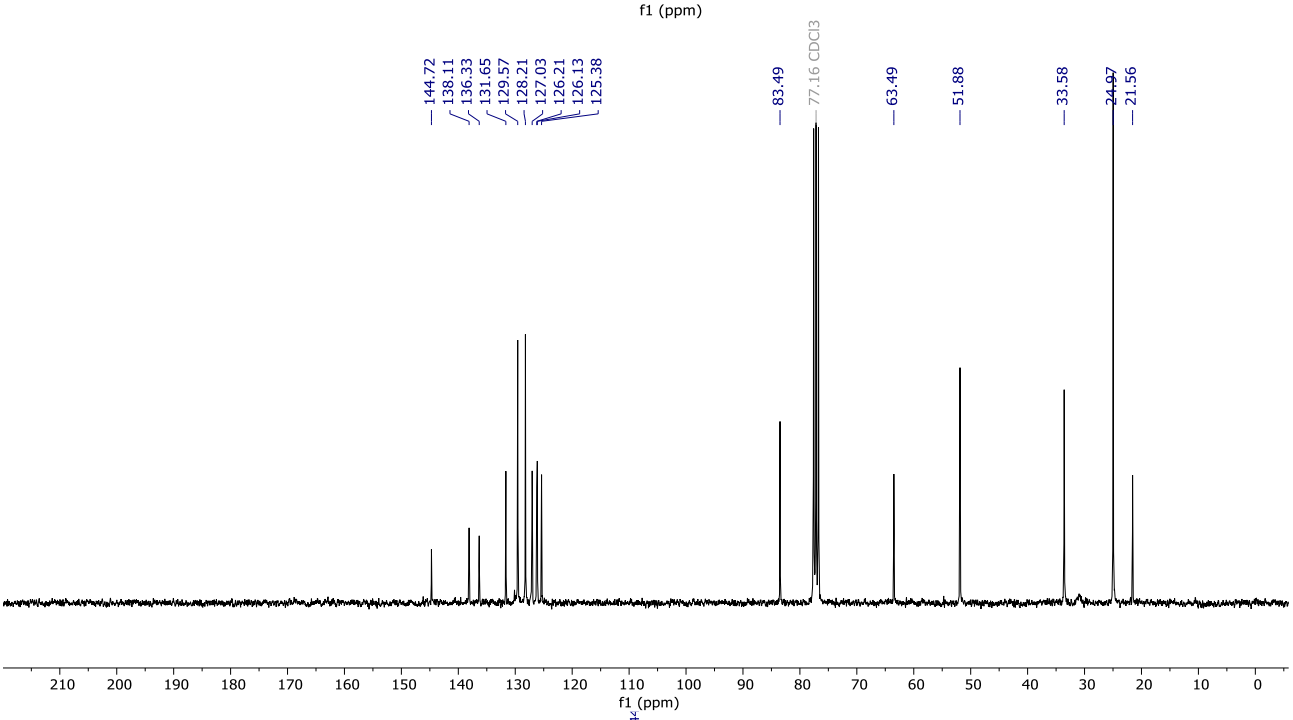


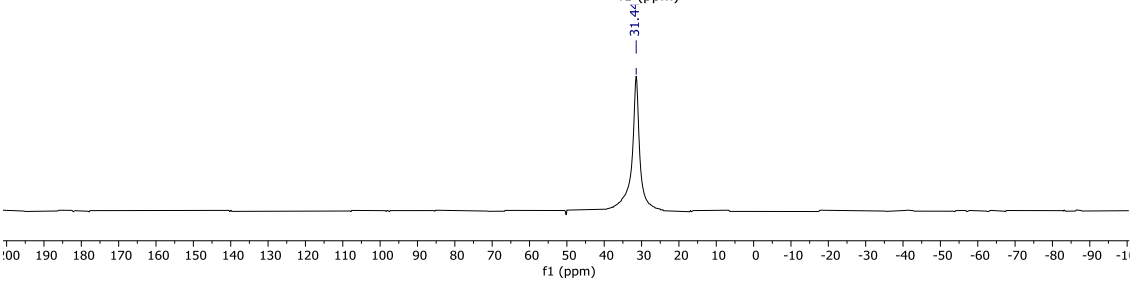


1-benzyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4-(o-tolyl)piperidine 5r

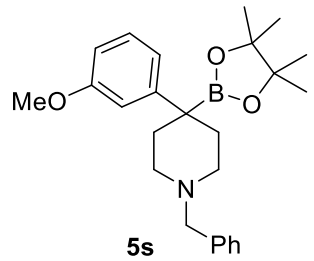


5r

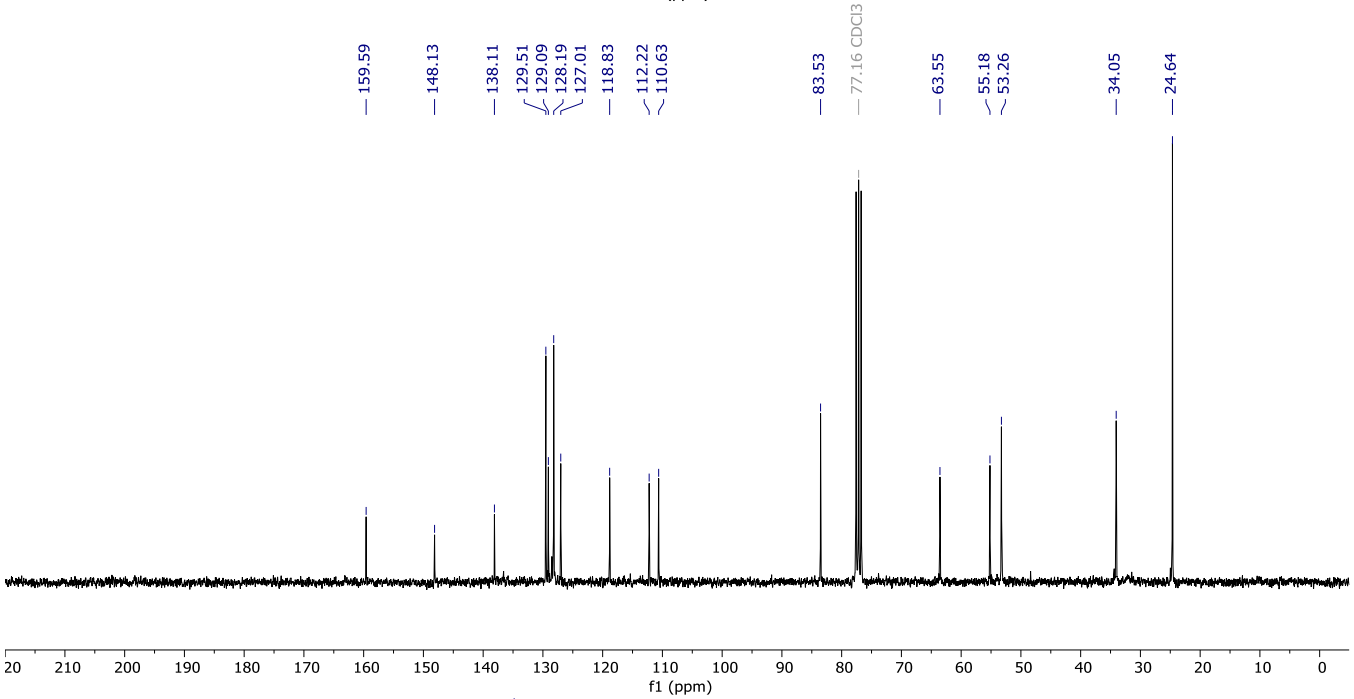


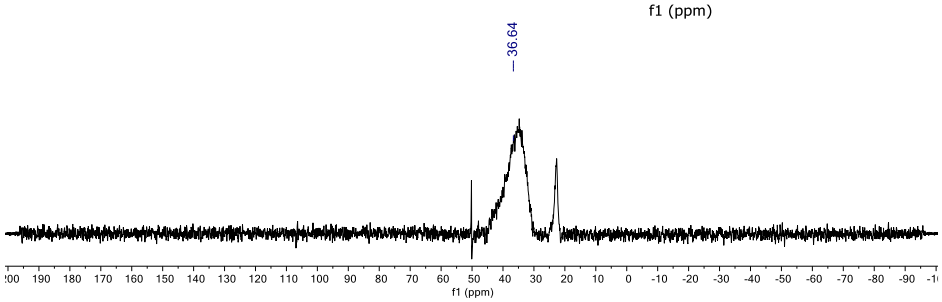


1-benzyl-4-(3-methoxyphenyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)piperidine 5s

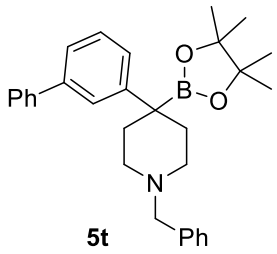


5s





4-([1,1'-biphenyl]-3-yl)-1-benzyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)piperidine 5t



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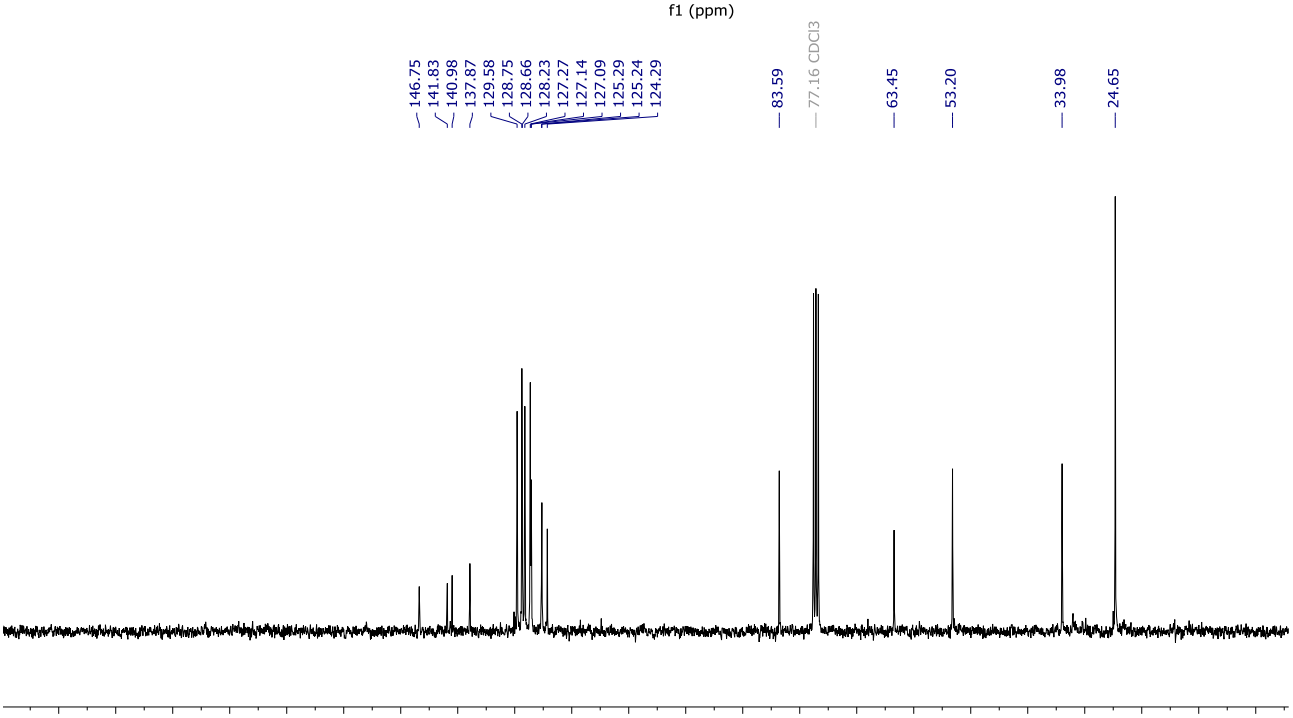
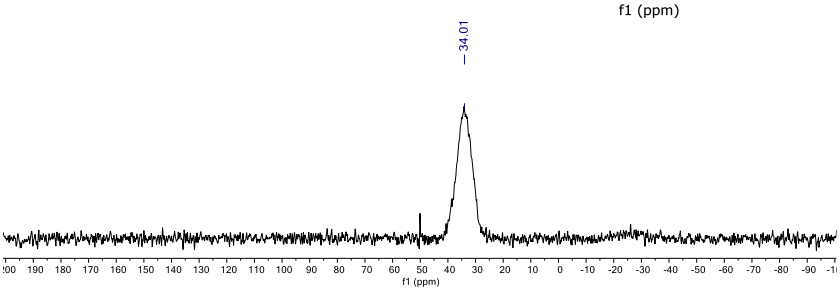
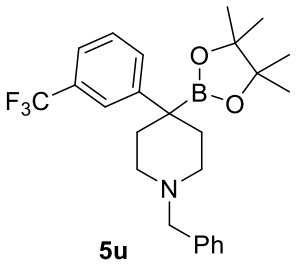
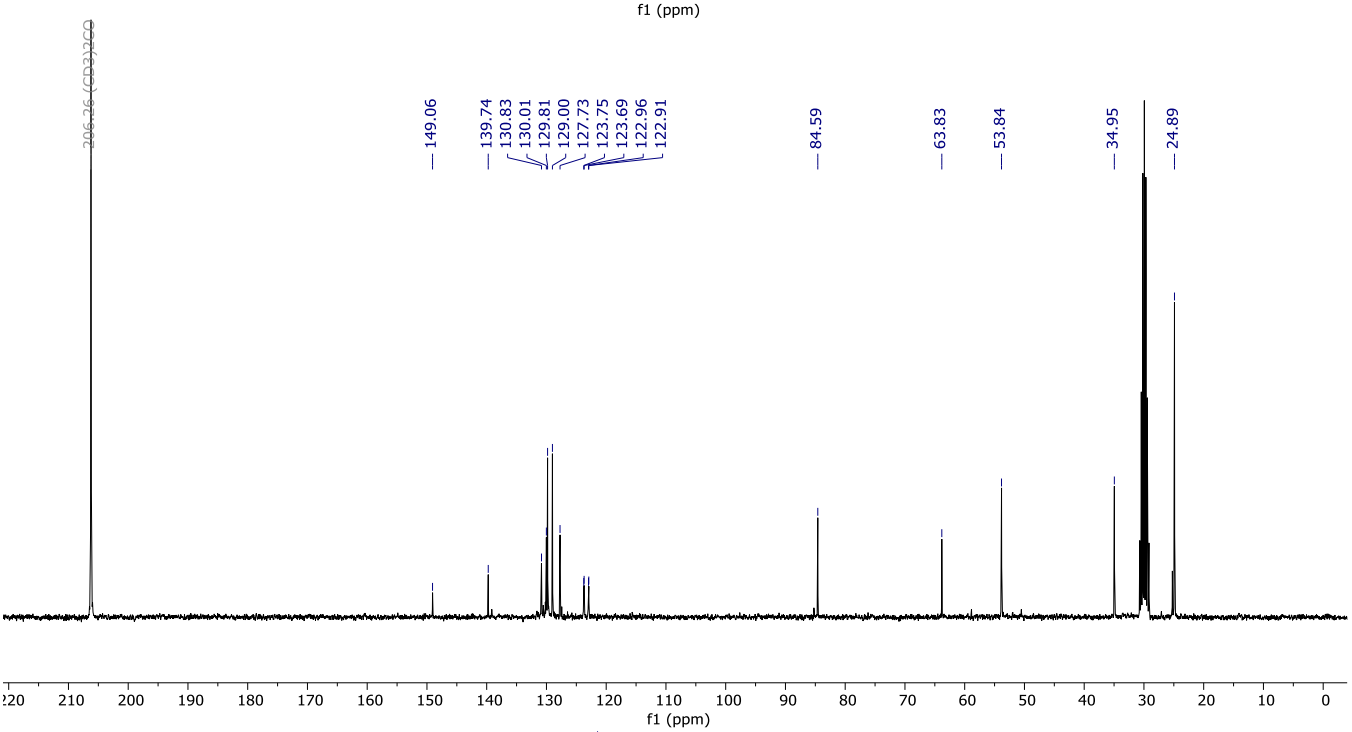


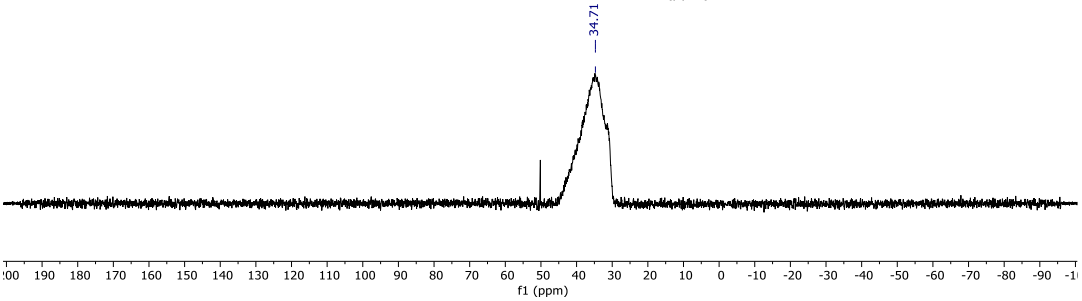


1-benzyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4-(3-(trifluoromethyl)phenyl)piperidine 5u

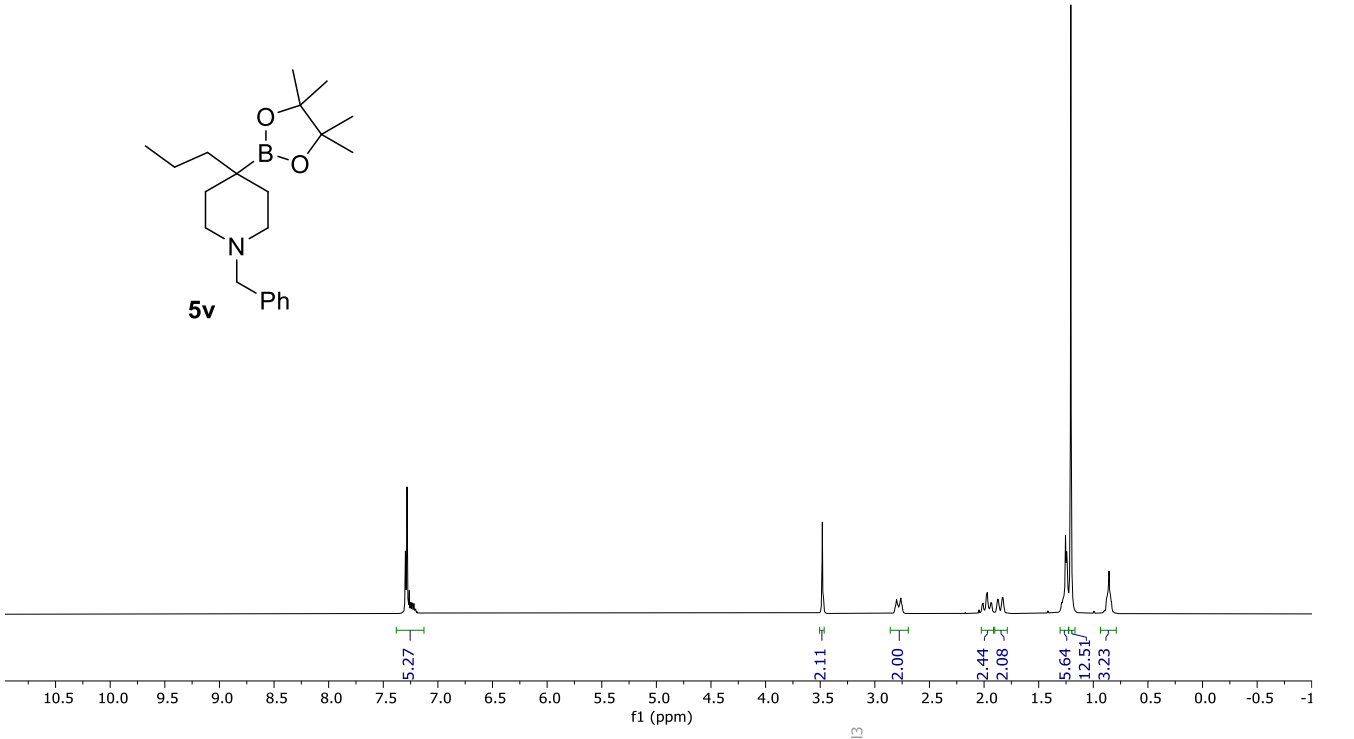


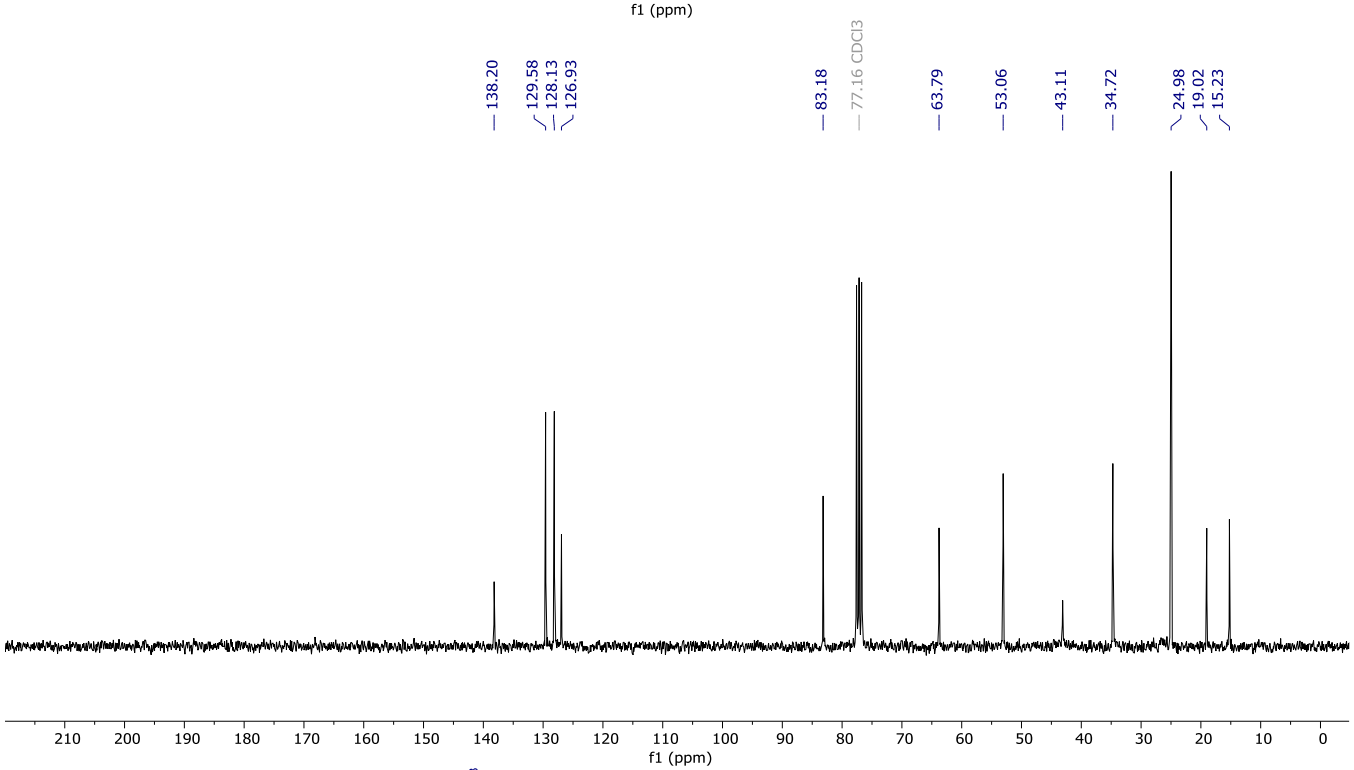
5u

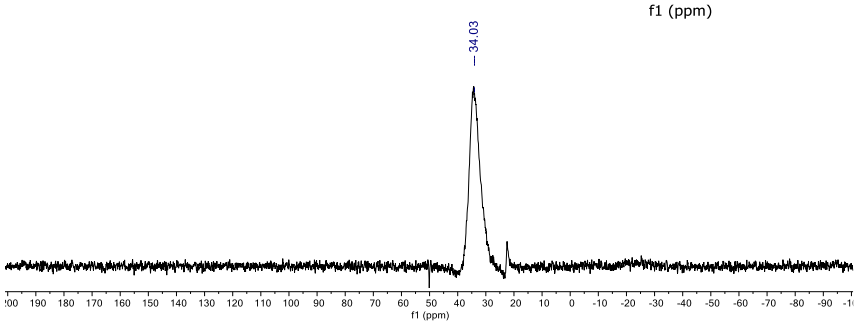




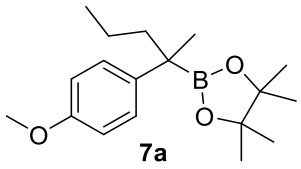
1-benzyl-4-propyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)piperidine 5v

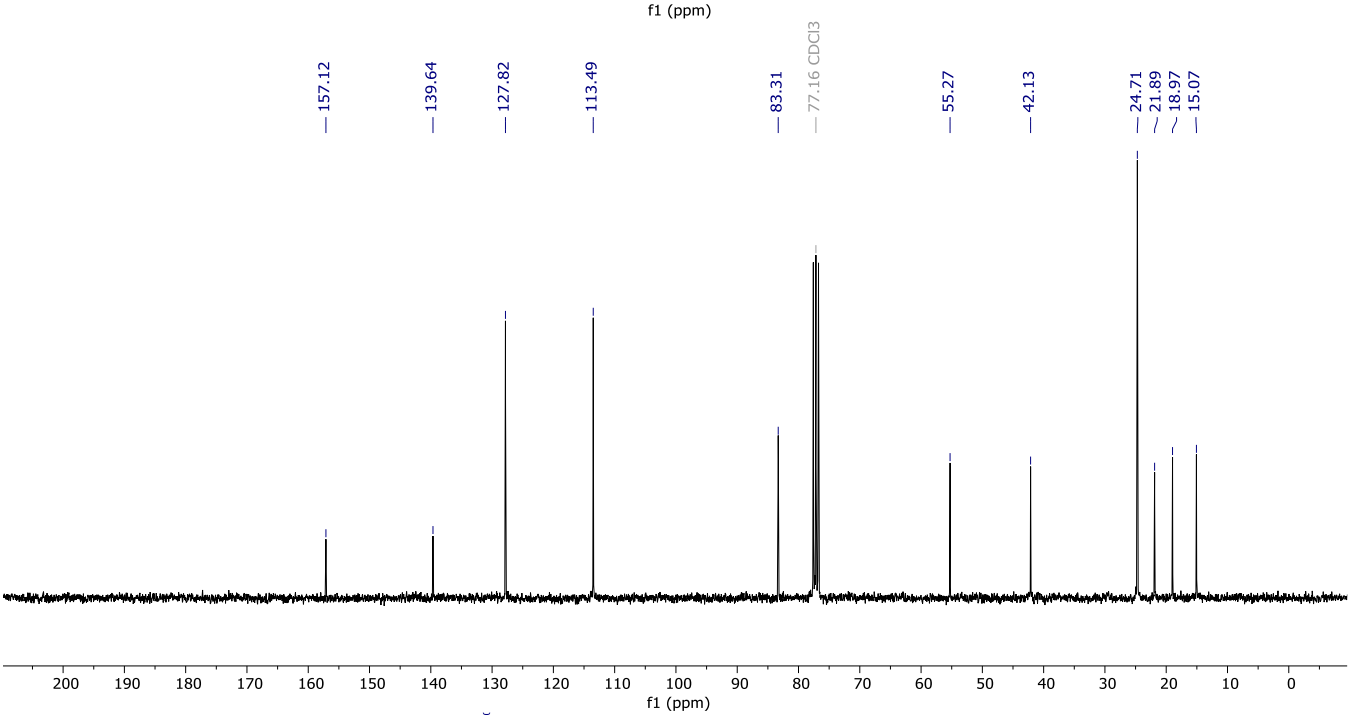


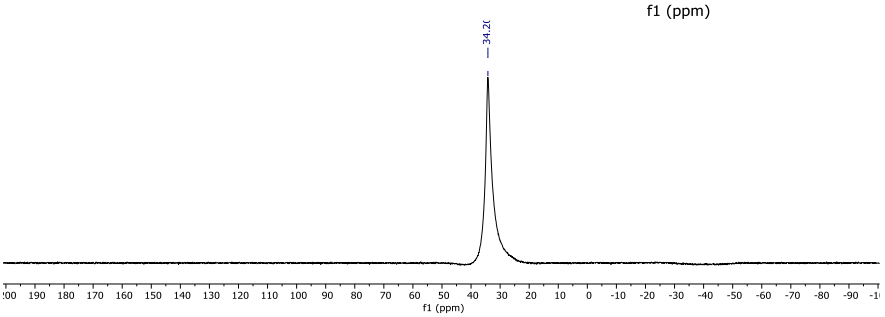




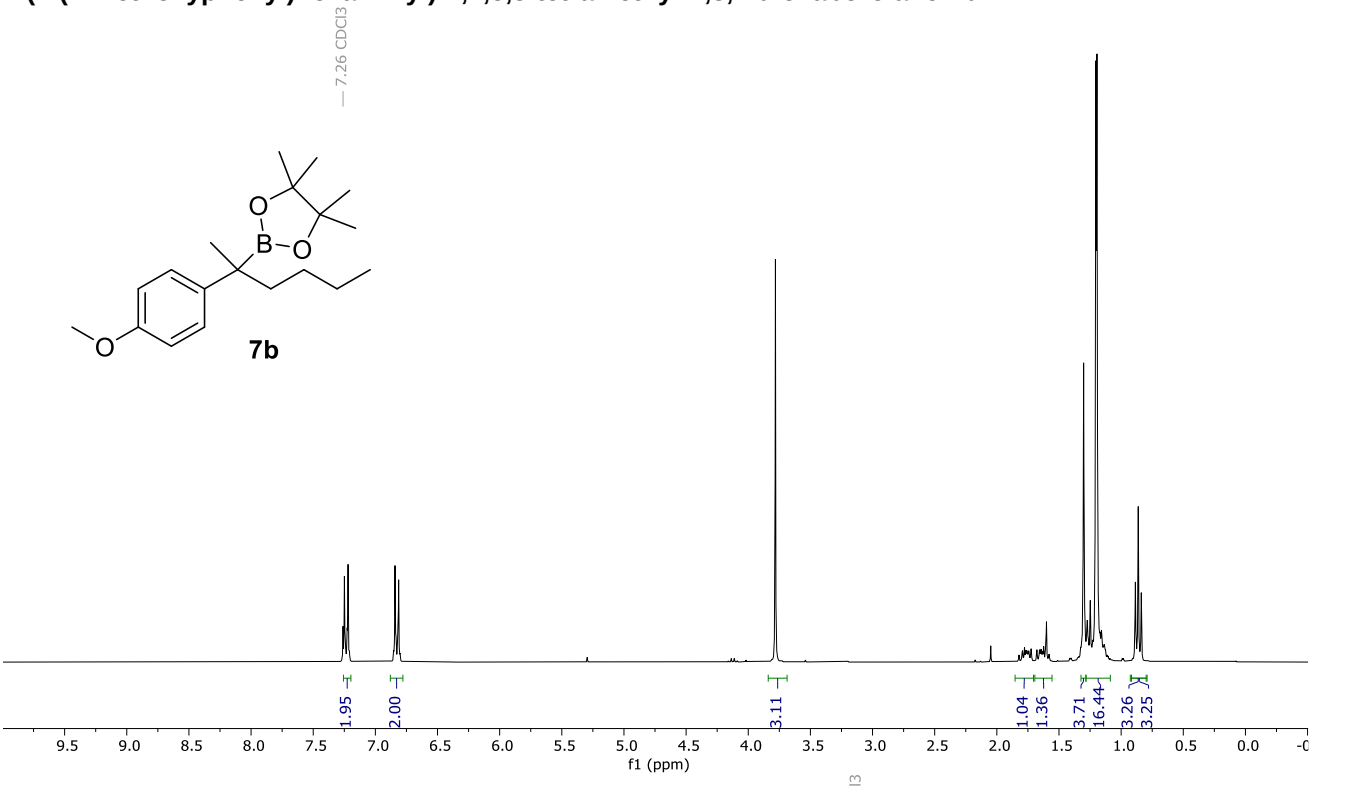
2-(2-(4-methoxyphenyl)pentan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 7a

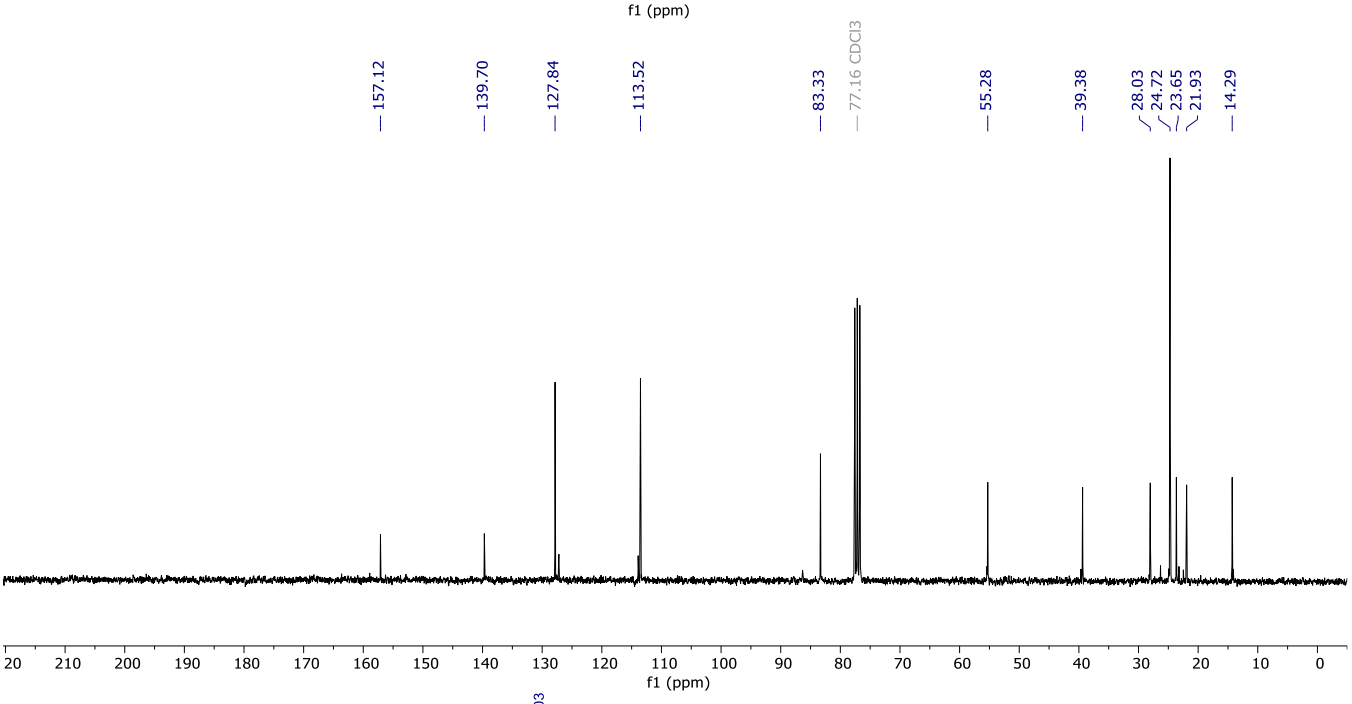


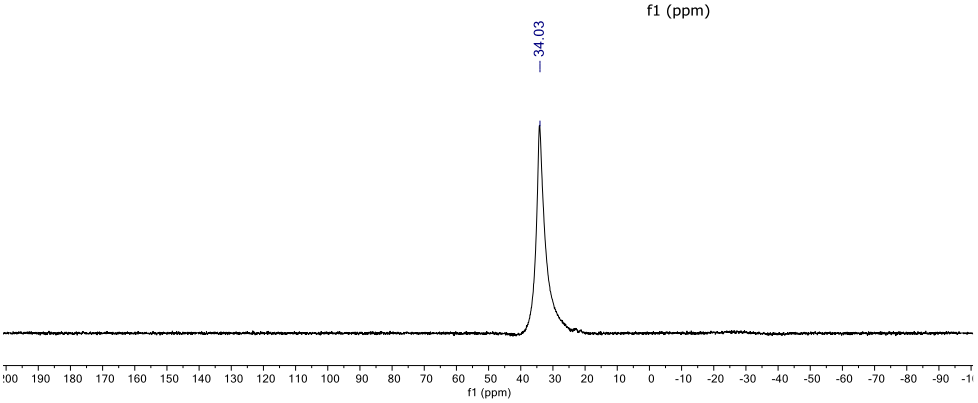




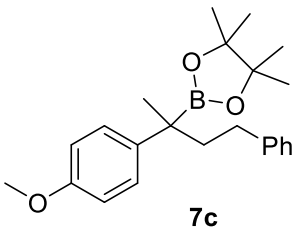
2-(2-(4-methoxyphenyl)hexan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 7b







2-(2-(4-methoxyphenyl)-4-phenylbutan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 7c



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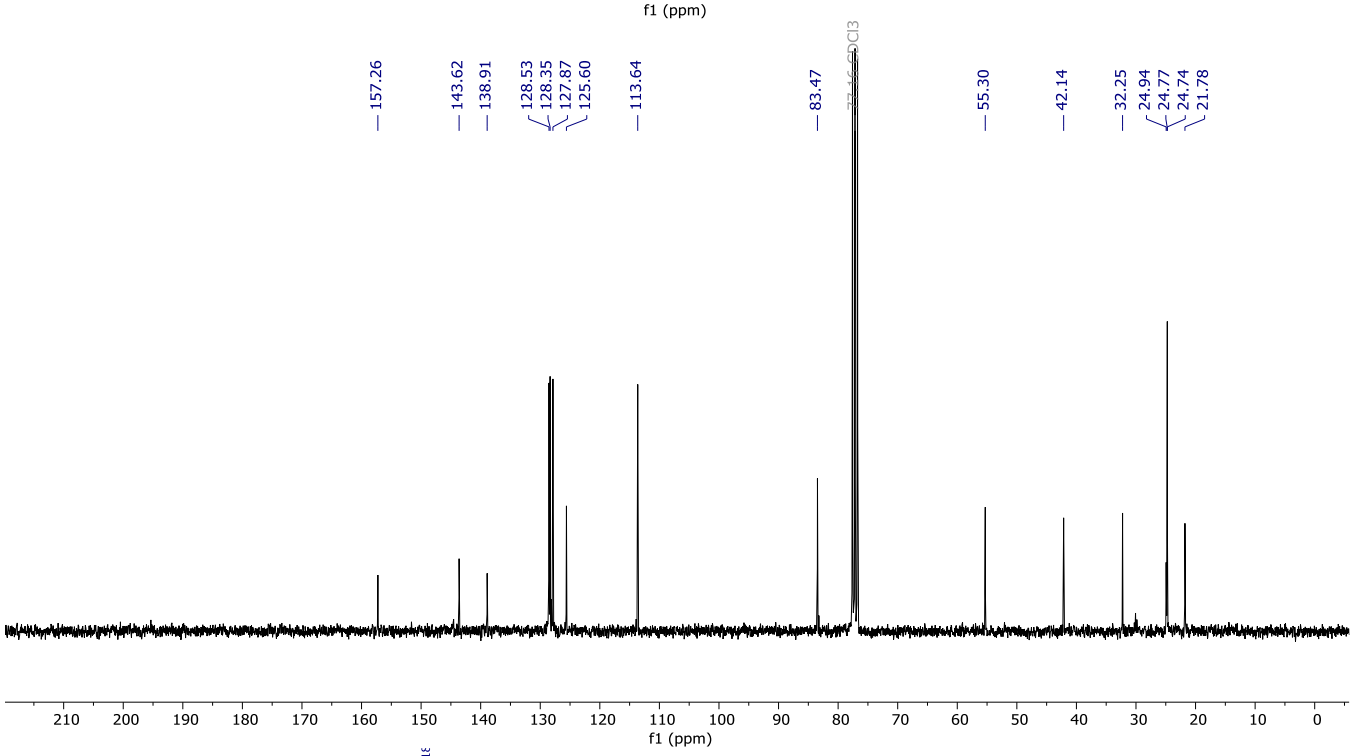
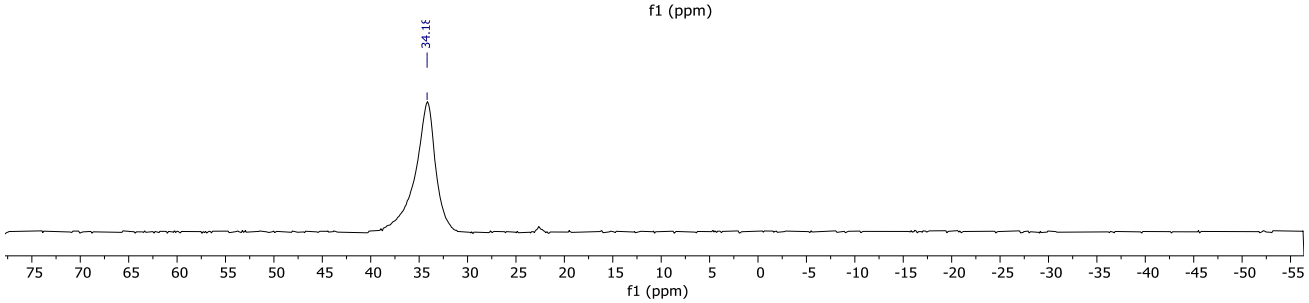
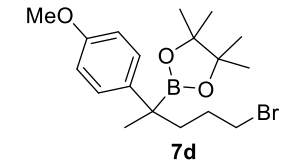




2-(5-bromo-2-(4-methoxyphenyl)pentan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 7d



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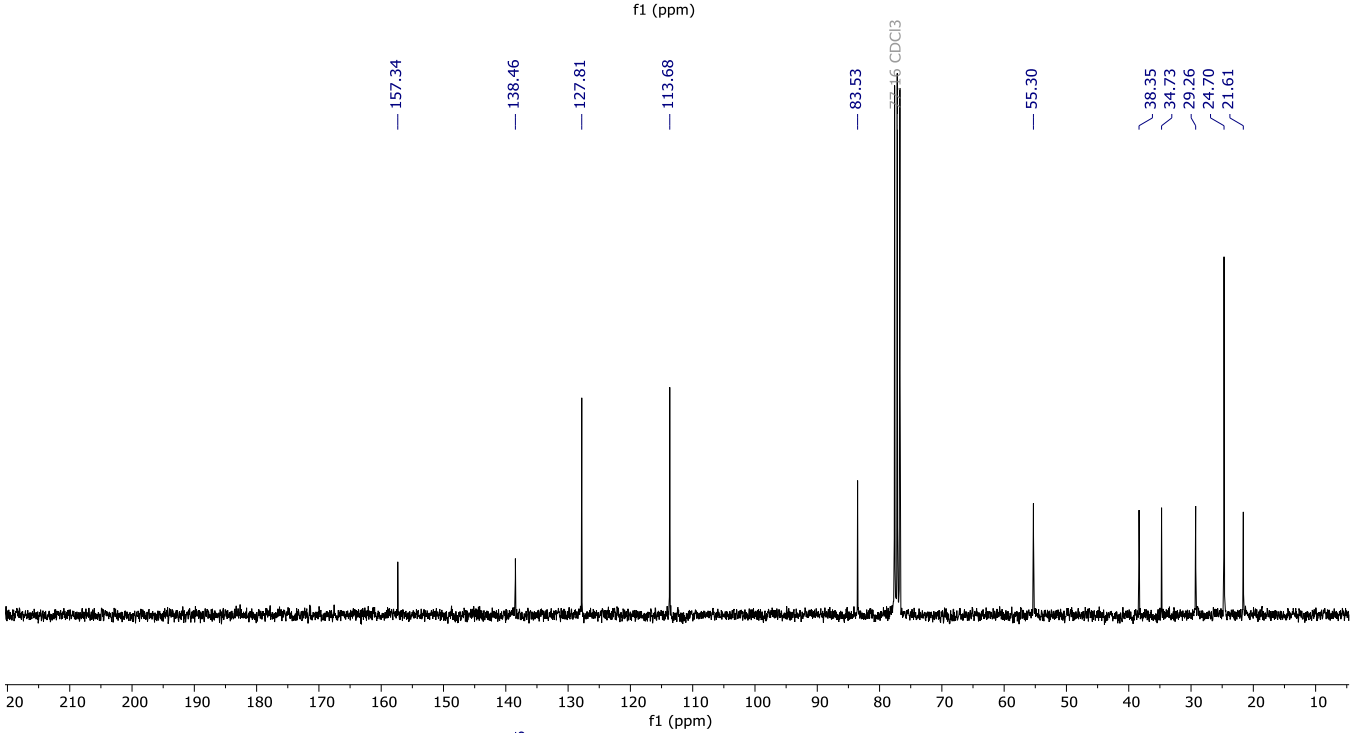
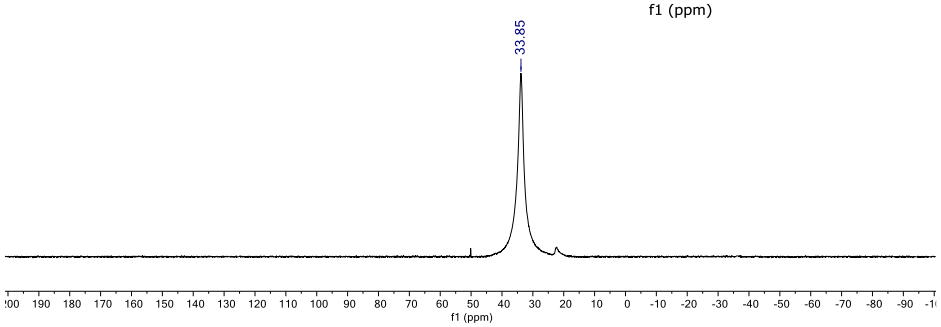
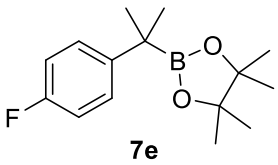




2-(2-(4-fluorophenyl)propan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 7e



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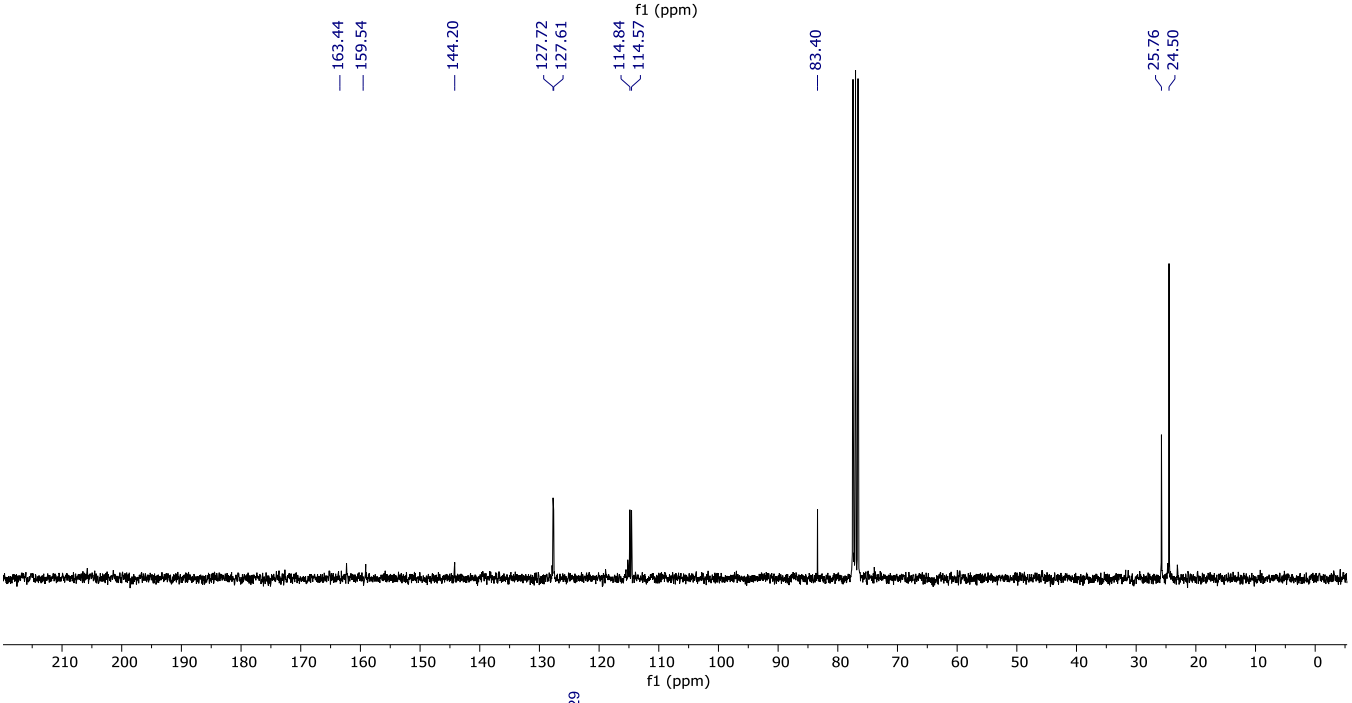
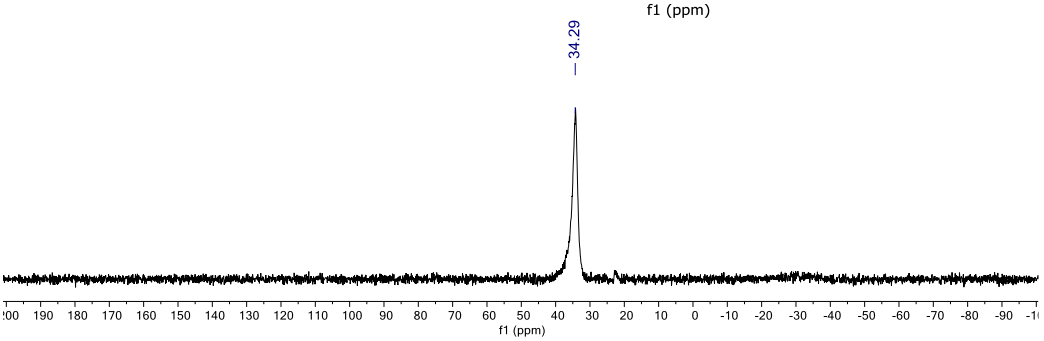
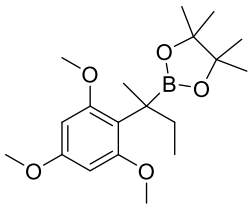




4,4,5,5-tetramethyl-2-(2-(2,4,6-trimethoxyphenyl)butan-2-yl)-1,3,2-dioxaborolane 7f



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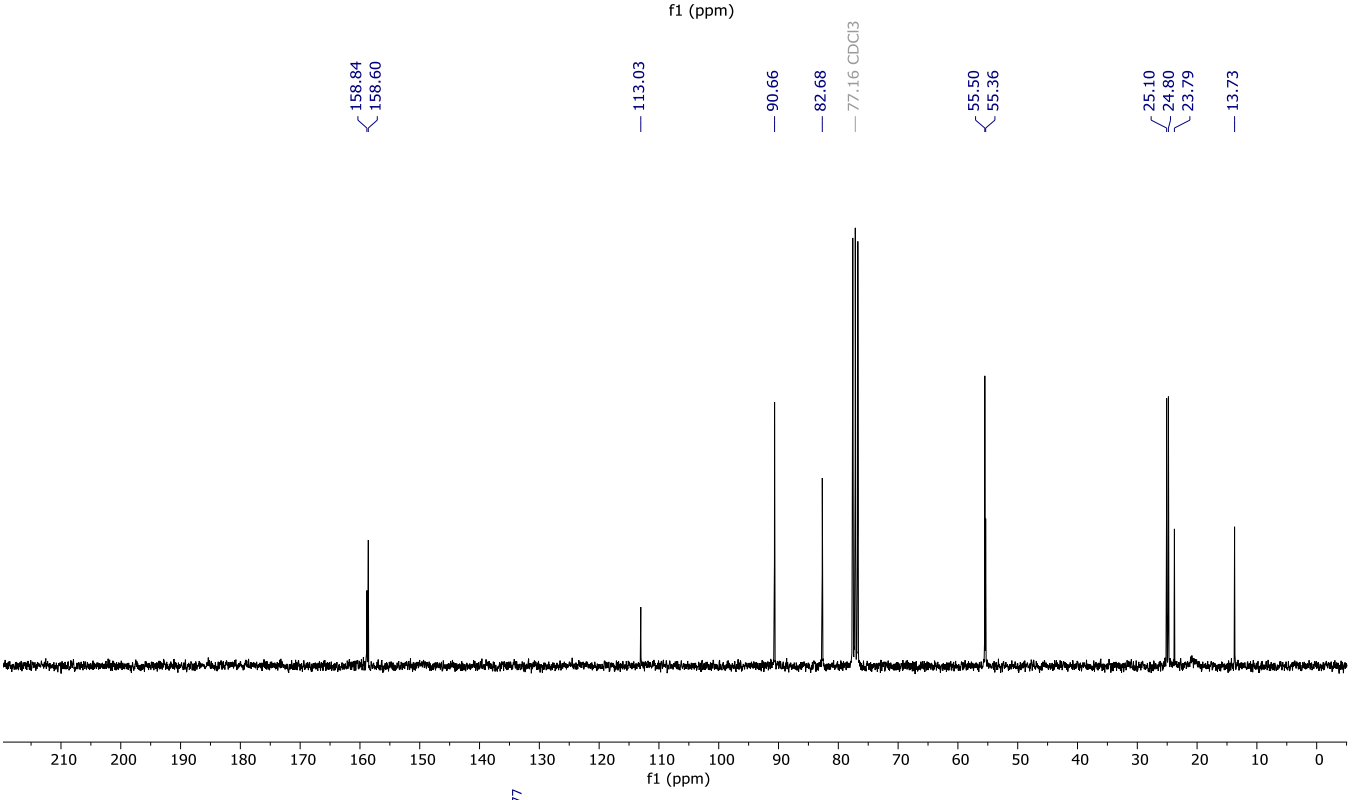
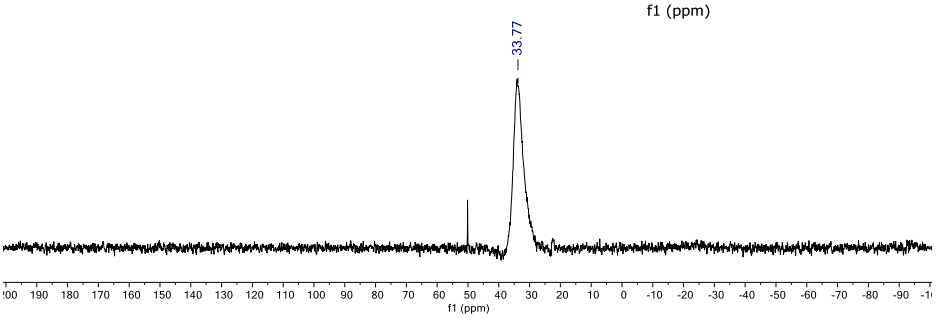
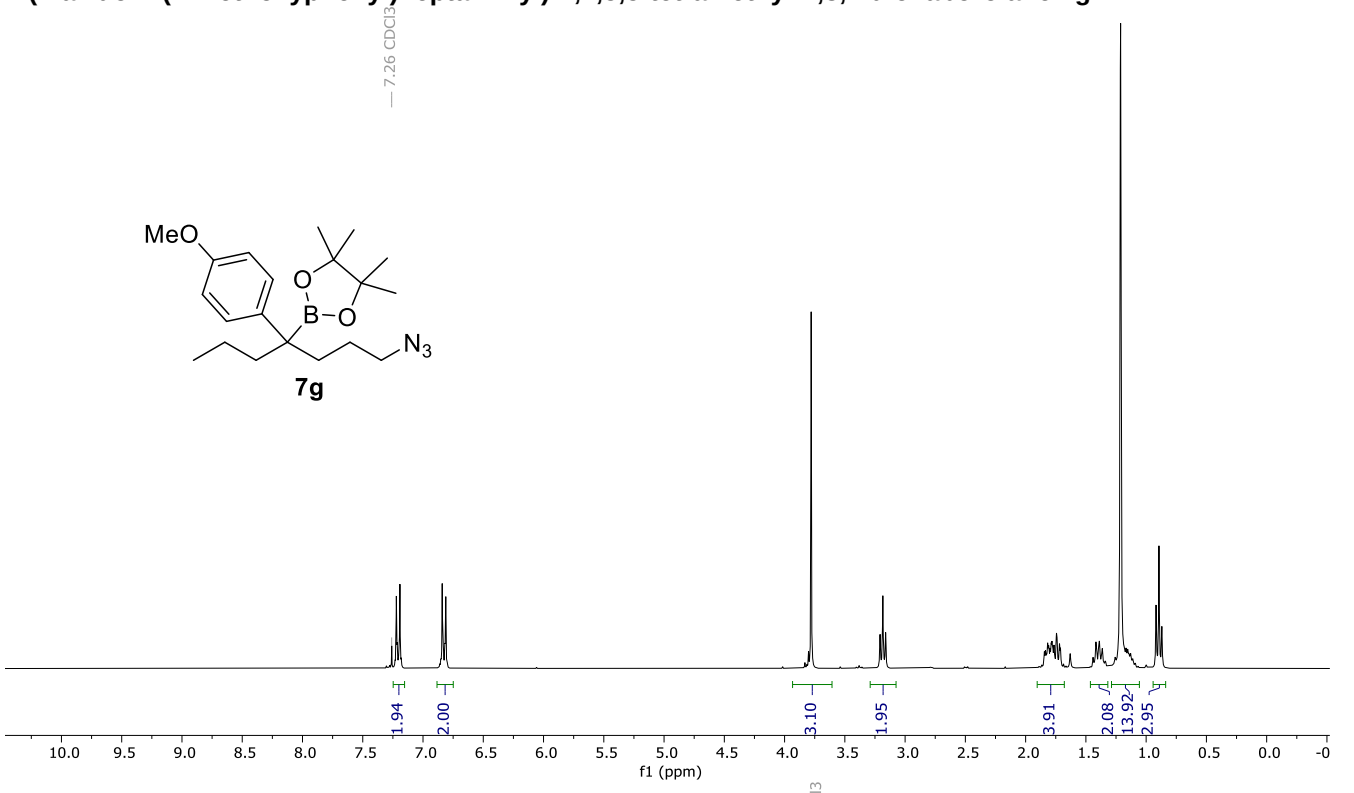
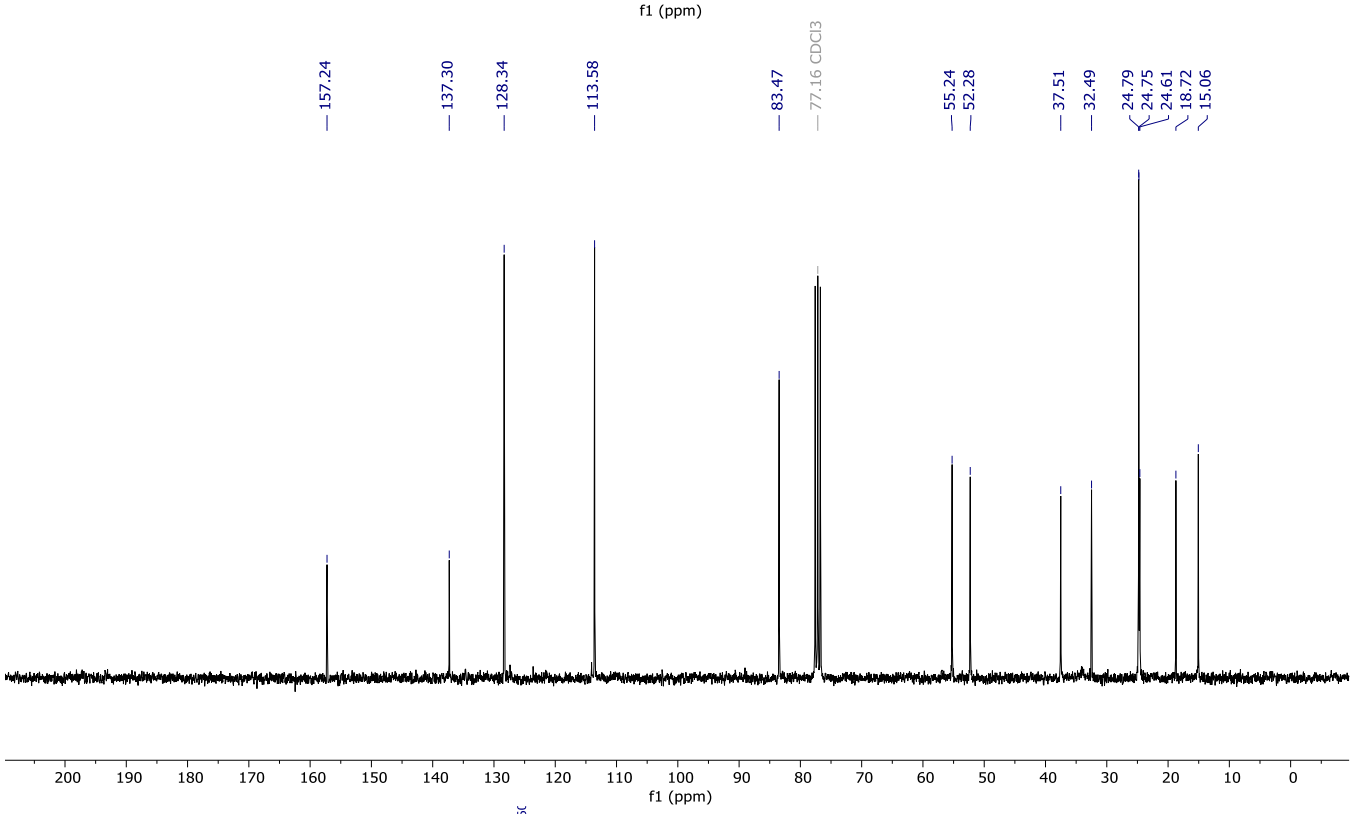
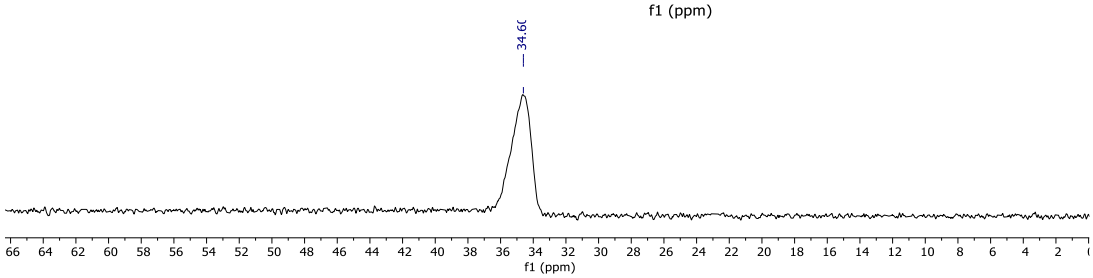




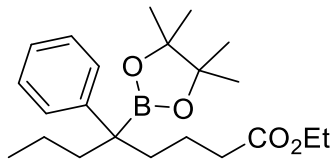
2-(1-azido-4-(4-methoxyphenyl)heptan-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 7g







Ethyl 5-phenyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)octanoate 7h



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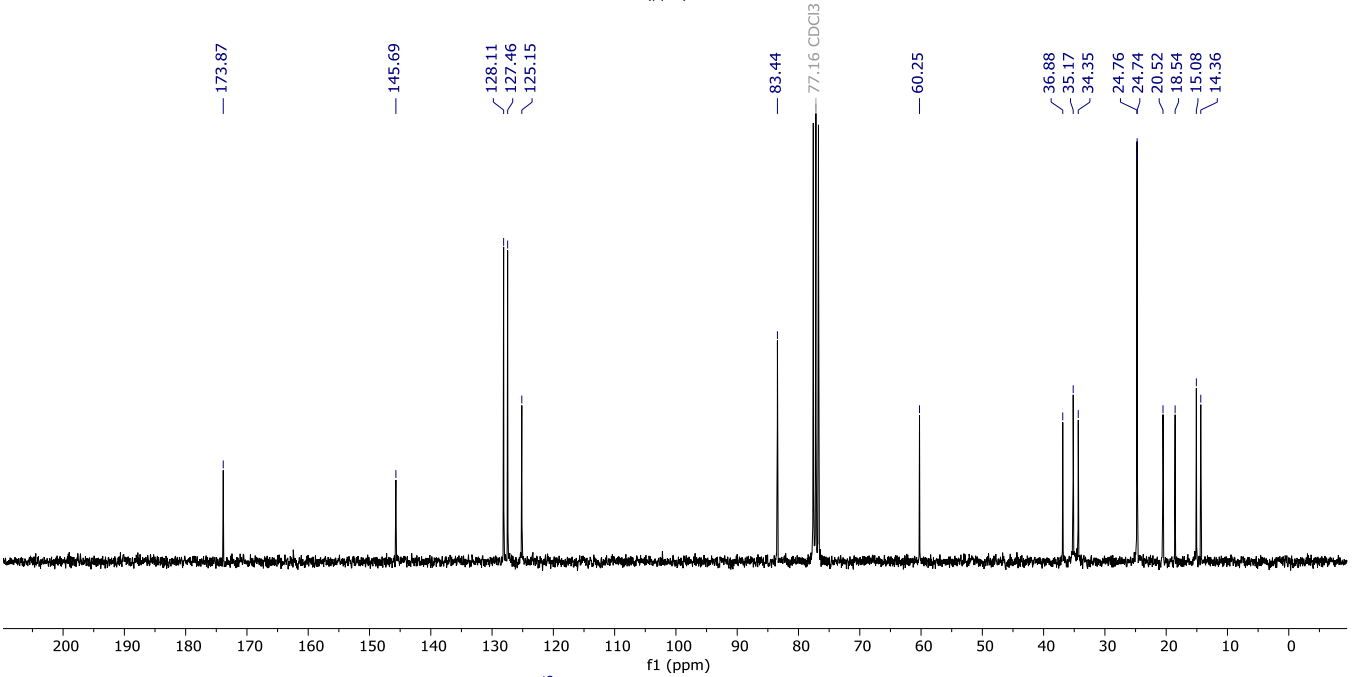
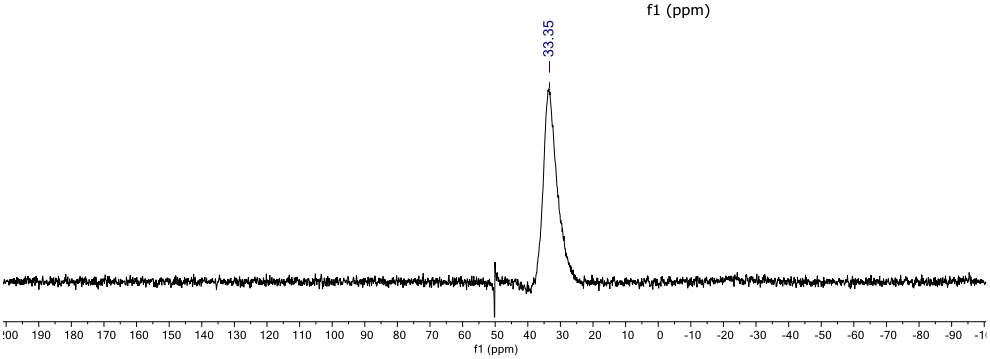
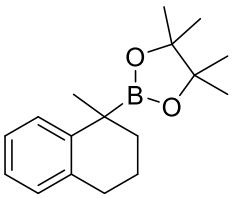




4,4,5,5-tetramethyl-2-(1-methyl-1,2,3,4-tetrahydronaphthalen-1-yl)-1,3,2-dioxaborolane 7i



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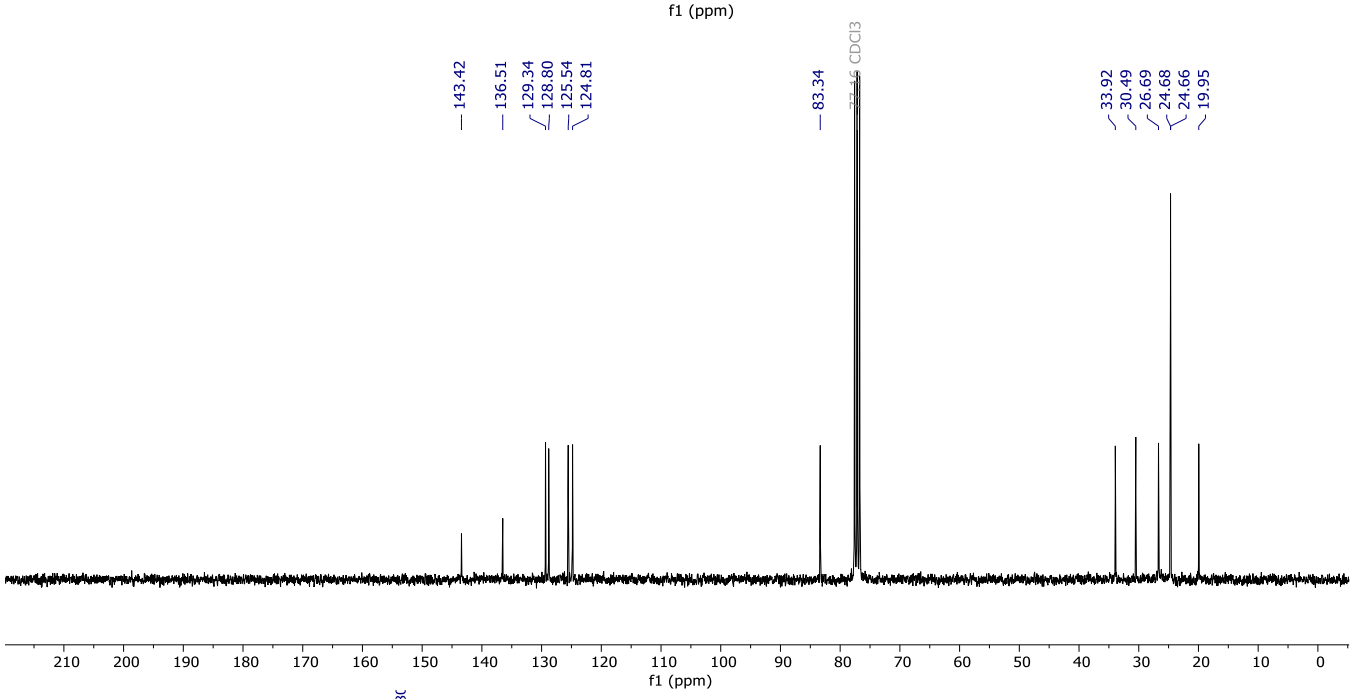
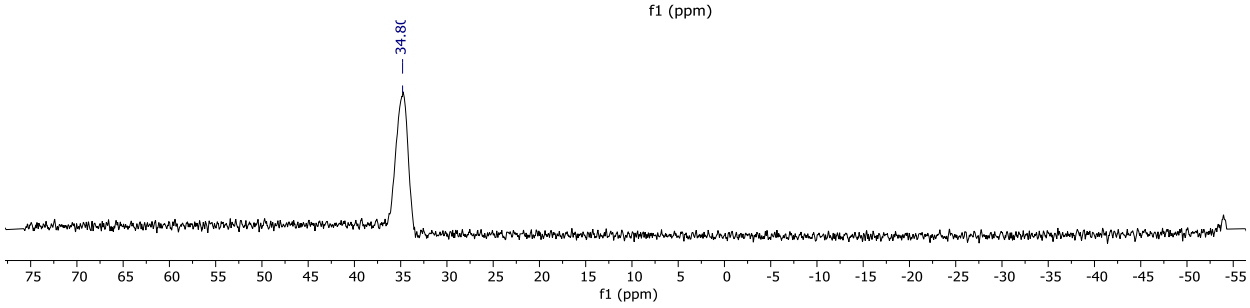
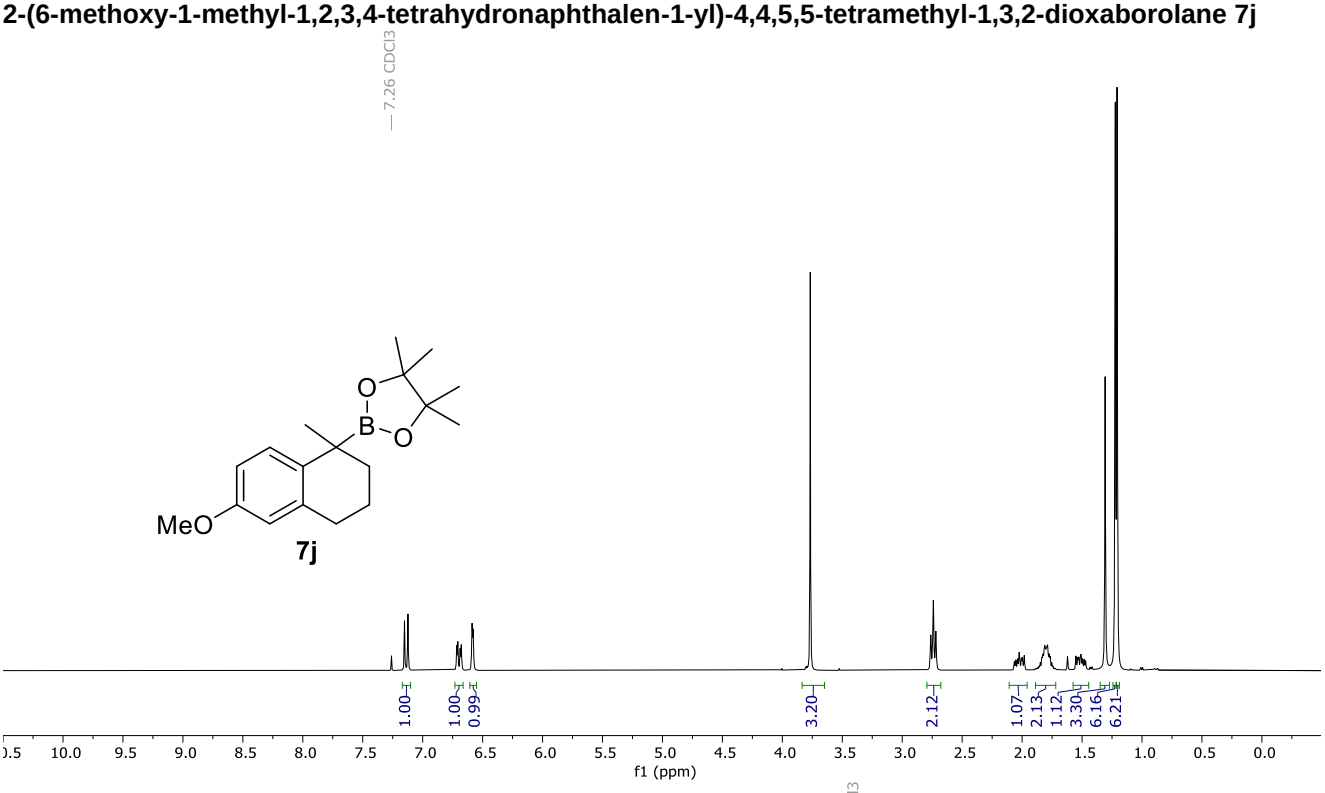
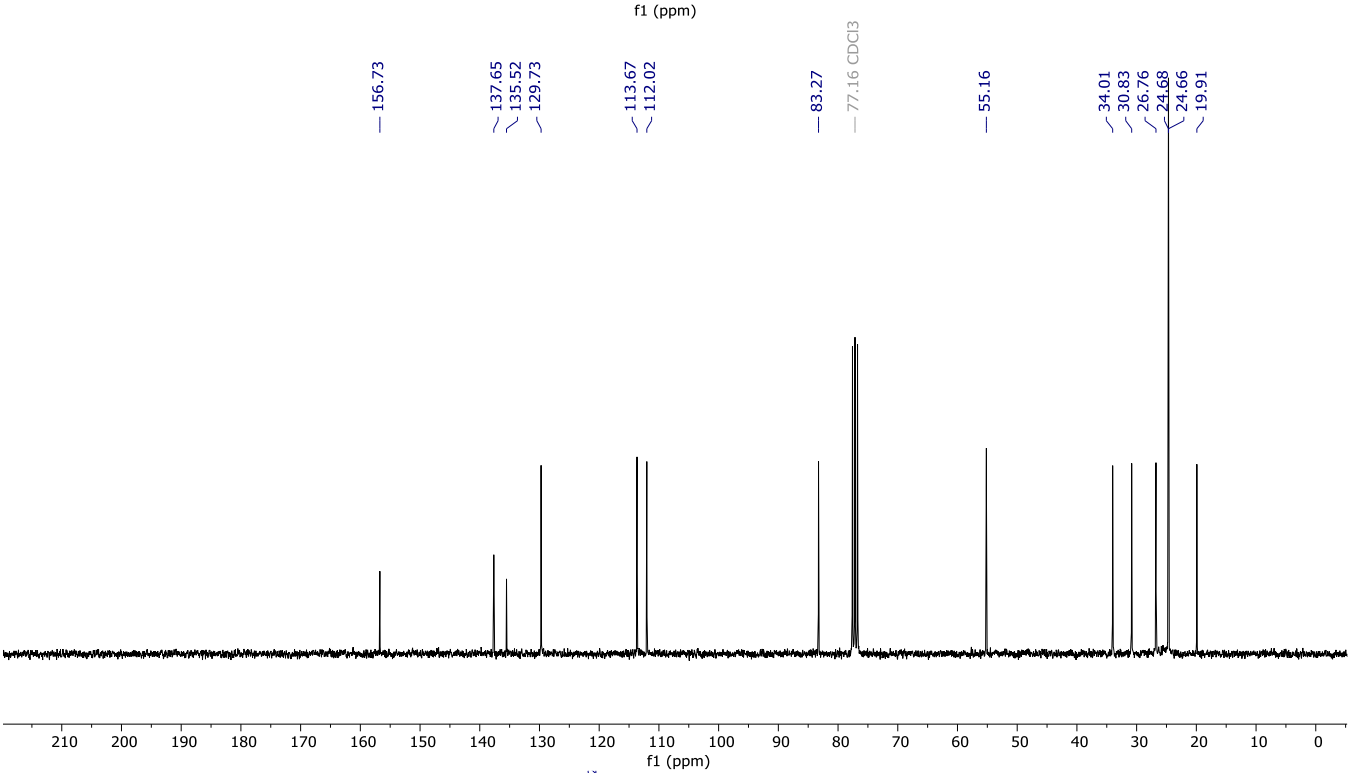
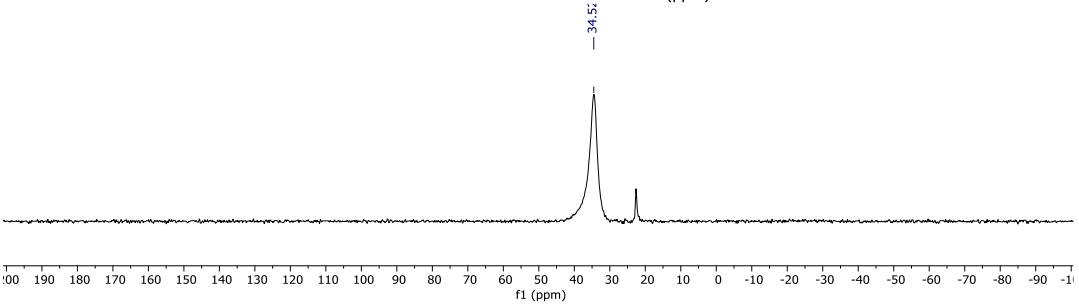




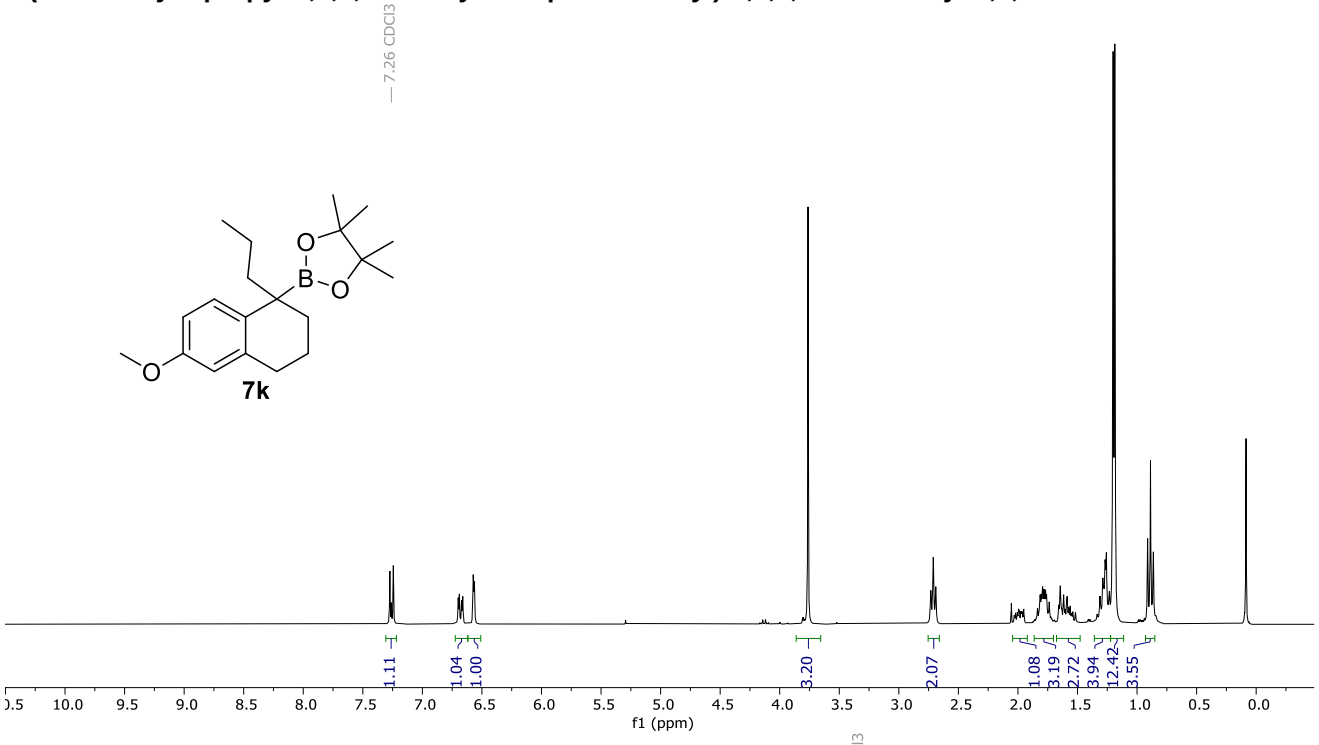
2-(6-methoxy-1-methyl-1,2,3,4-tetrahydronaphthalen-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 7j

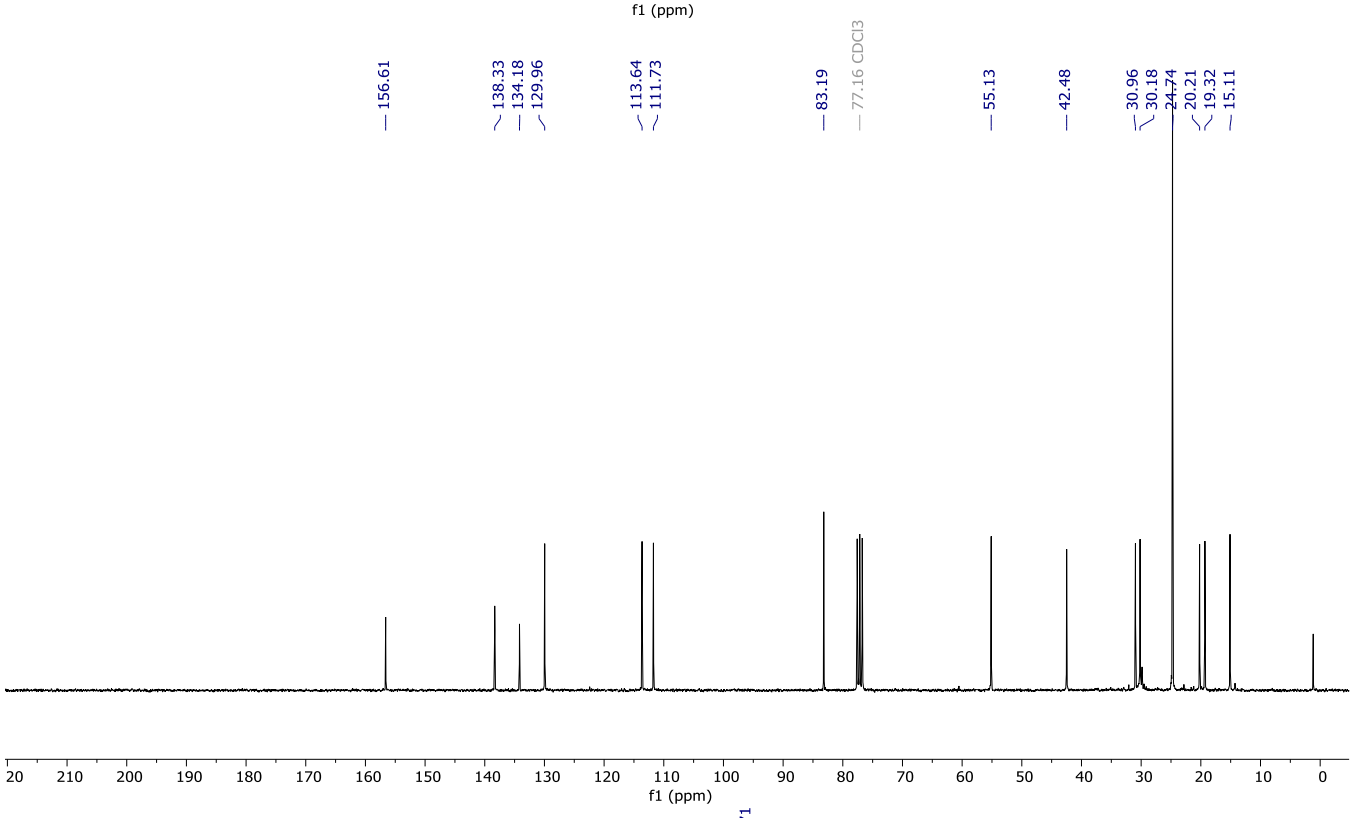


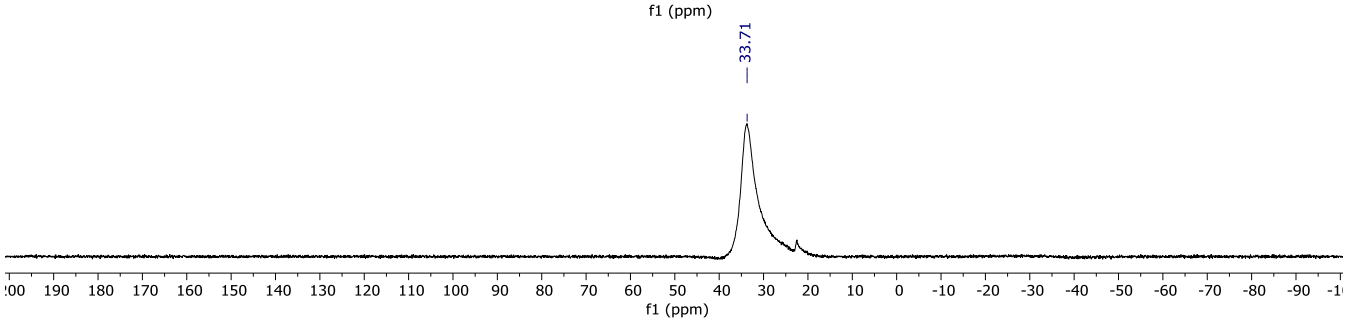




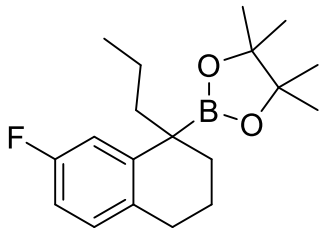
2-(6-methoxy-1-propyl-1,2,3,4-tetrahydronaphthalen-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 7k







2-(7-fluoro-1-propyl-1,2,3,4-tetrahydronaphthalen-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 7



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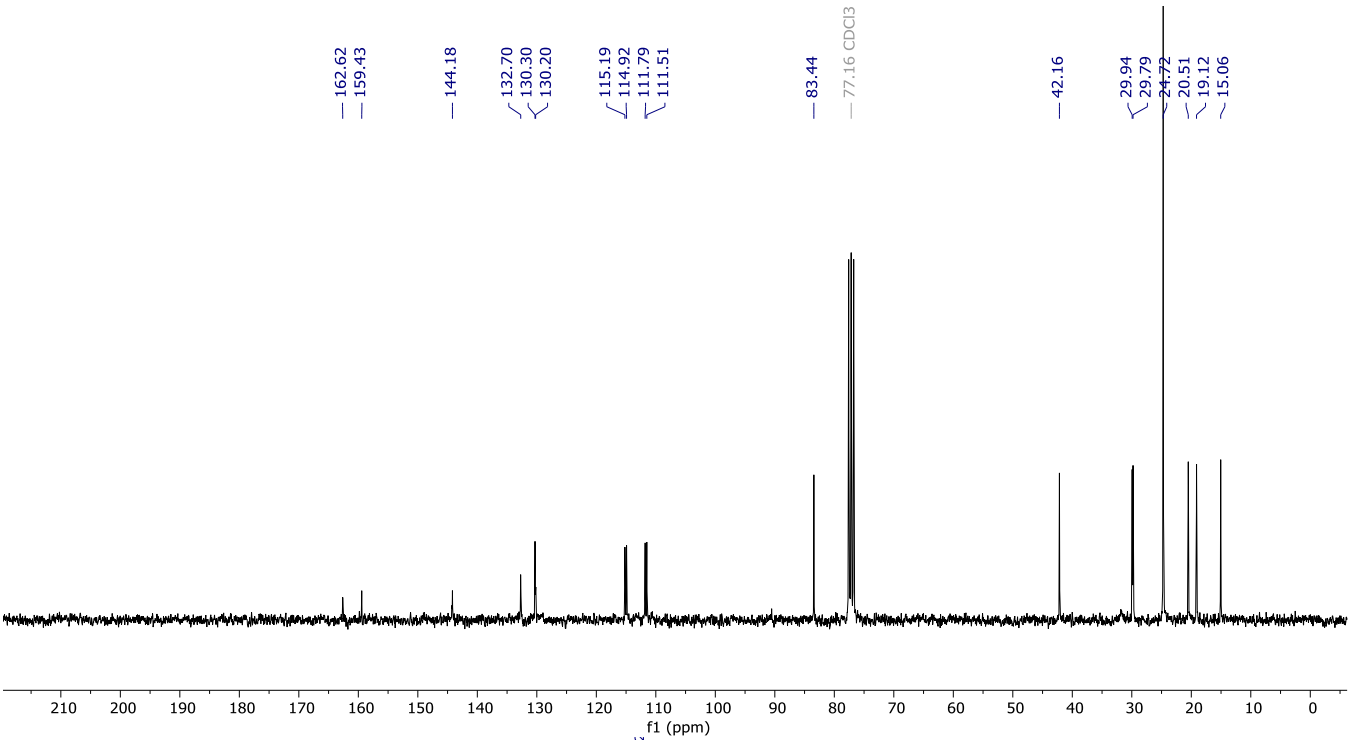
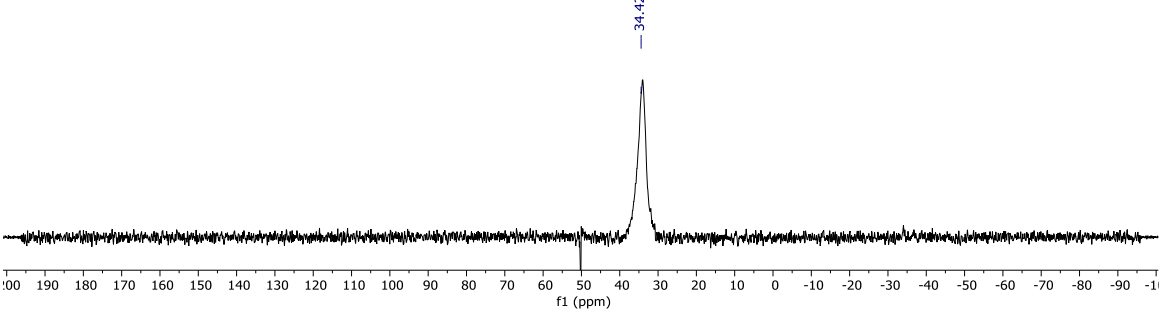
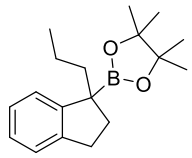




4,4,5,5-tetramethyl-2-(1-propyl-2,3-dihydro-1H-inden-1-yl)-1,3,2-dioxaborolane 7m



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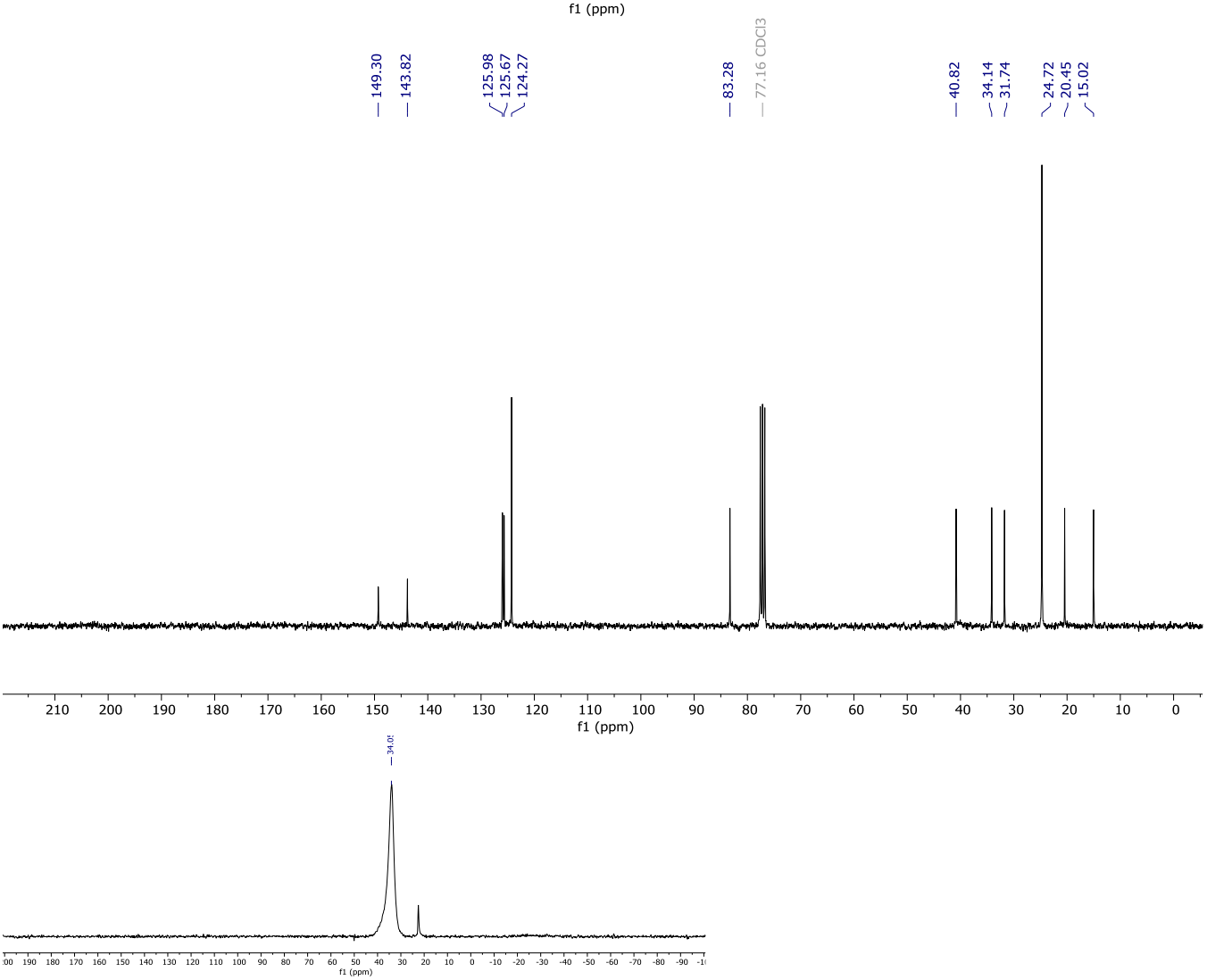
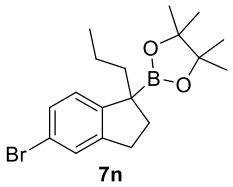


2-(5-bromo-1-propyl-2,3-dihydro-1H-inden-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 7n



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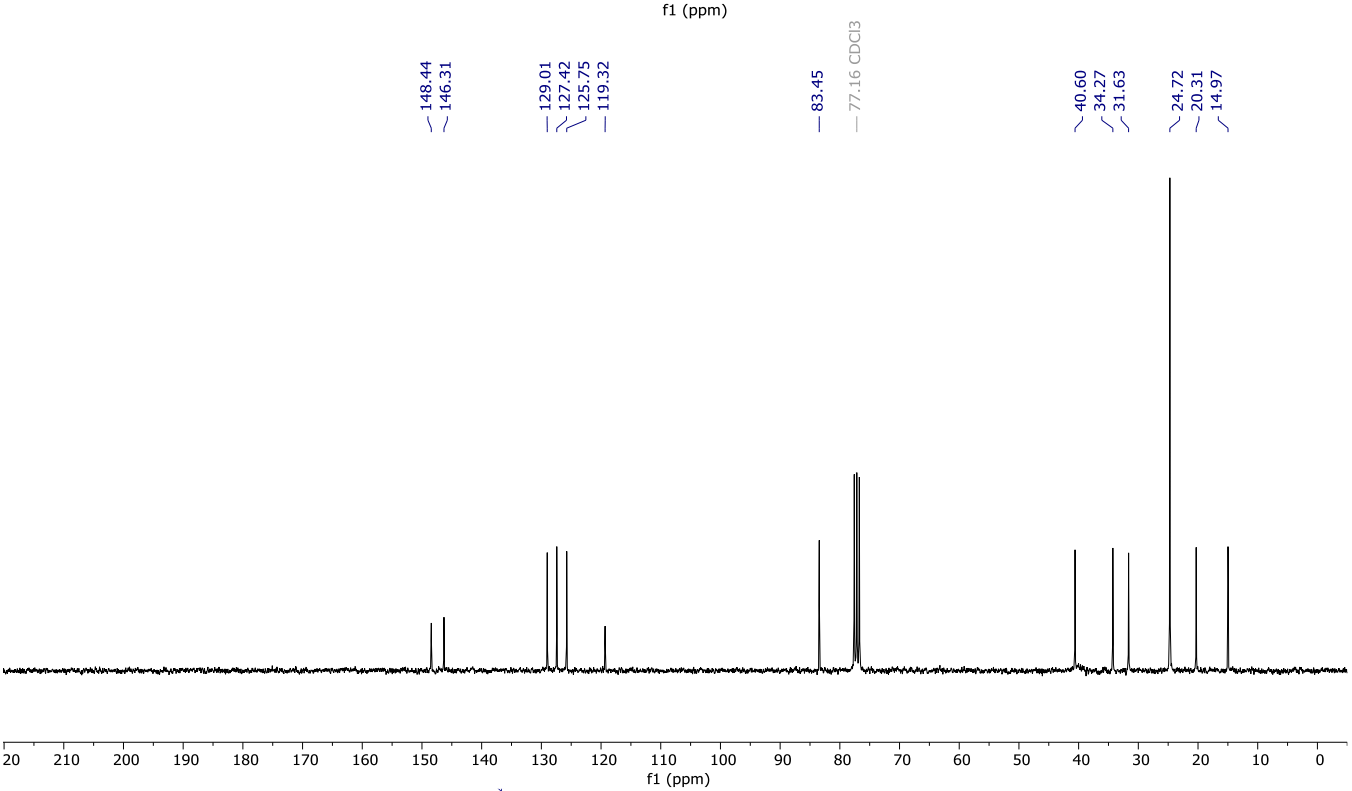
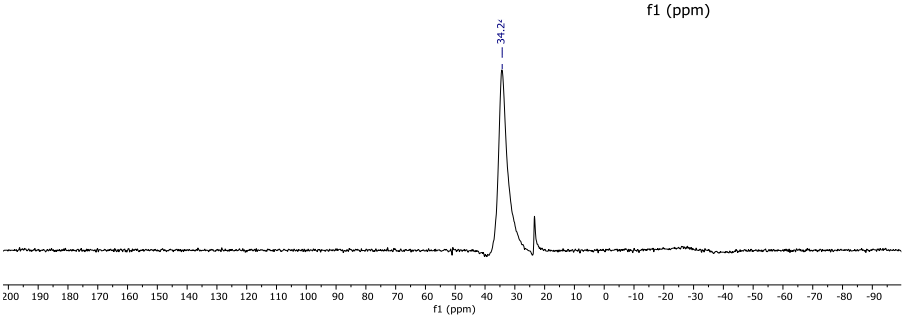
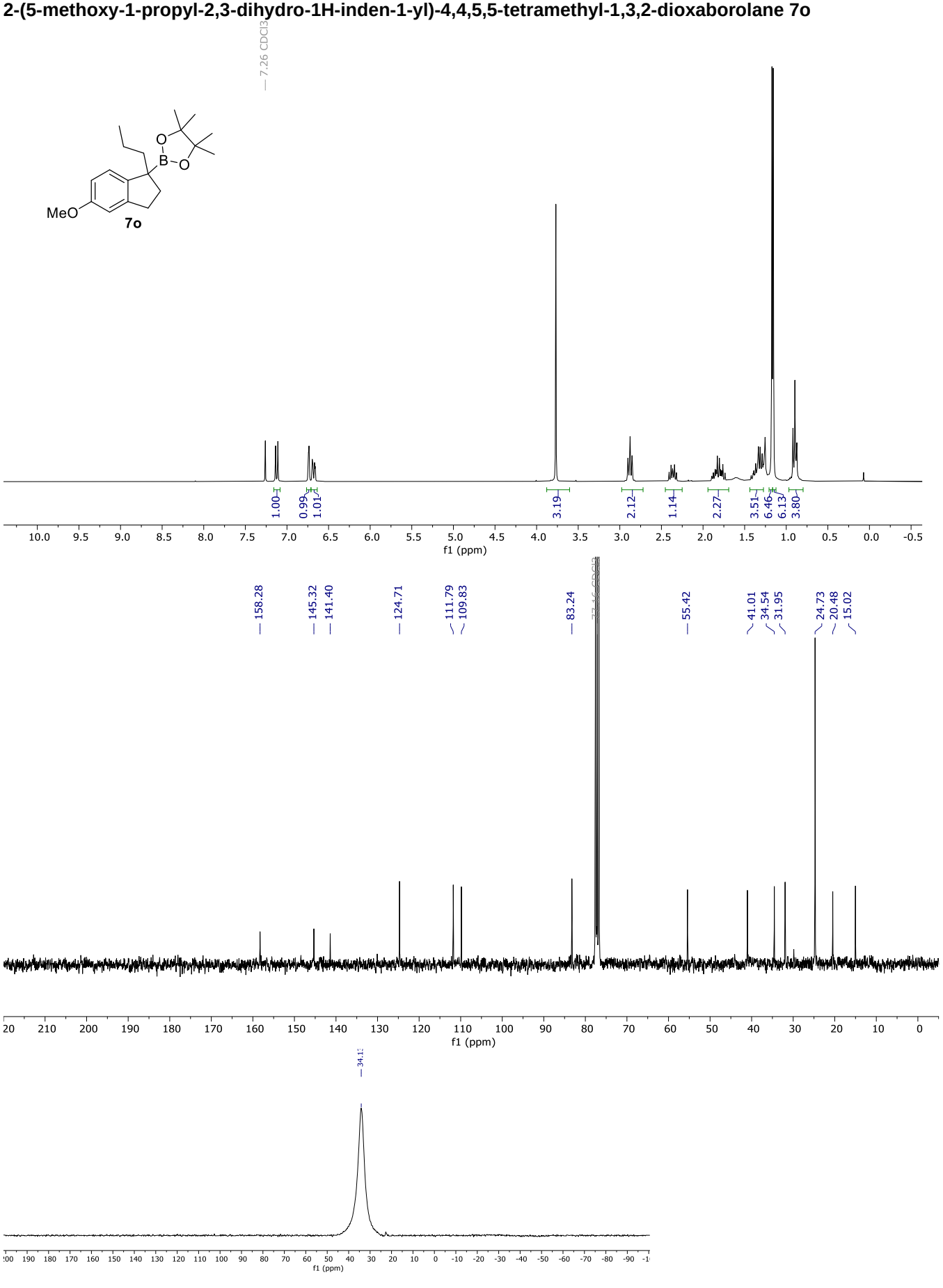
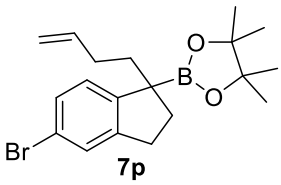




2-(5-methoxy-1-propyl-2,3-dihydro-1H-inden-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 7o



2-(5-bromo-1-(but-3-en-1-yl)-2,3-dihydro-1H-inden-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 7p



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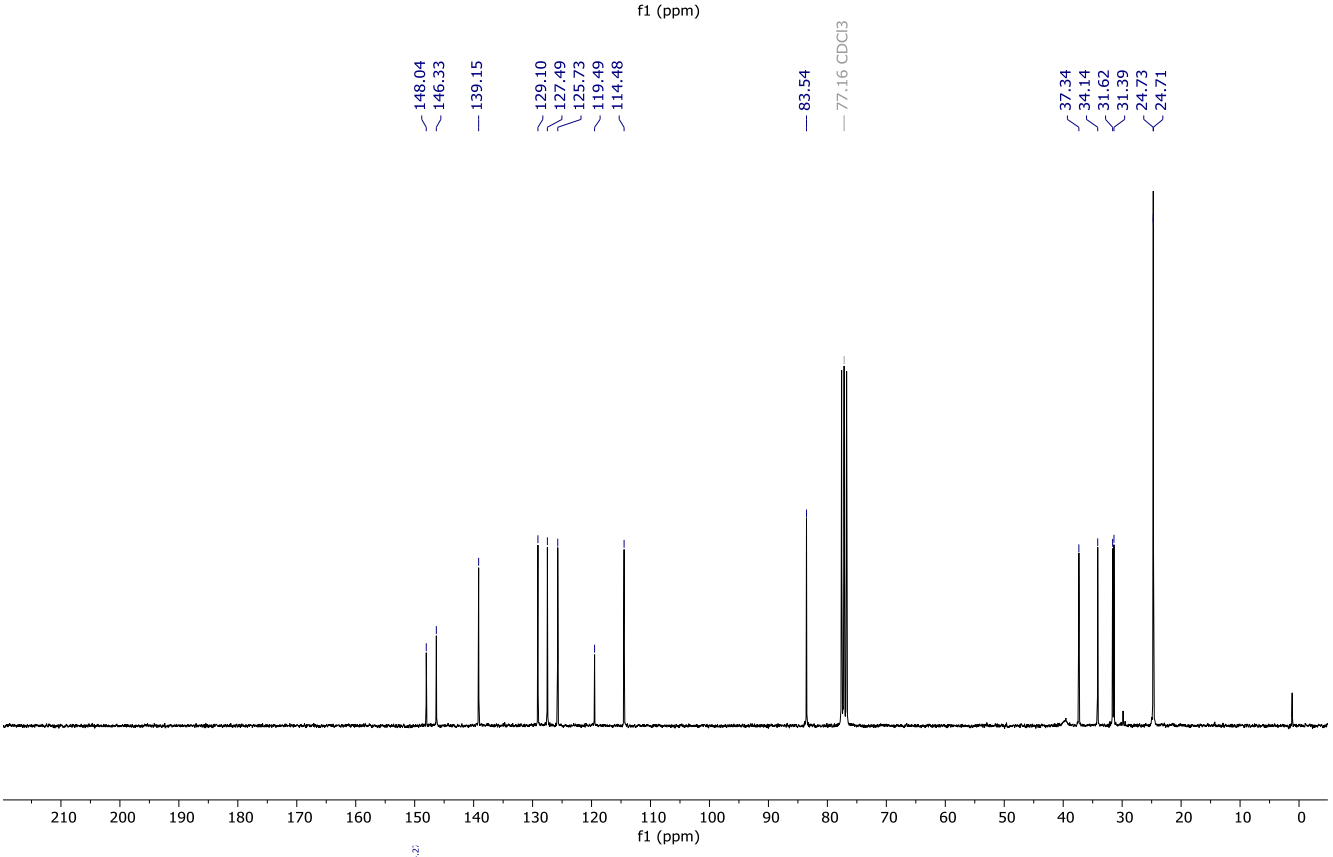
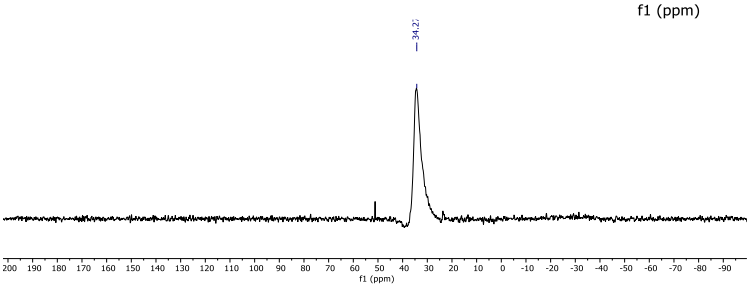
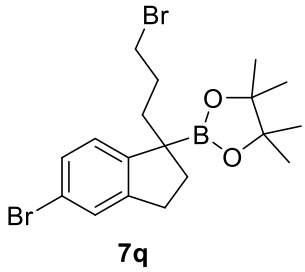




2-(5-bromo-1-(3-bromopropyl)-2,3-dihydro-1H-inden-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 7q



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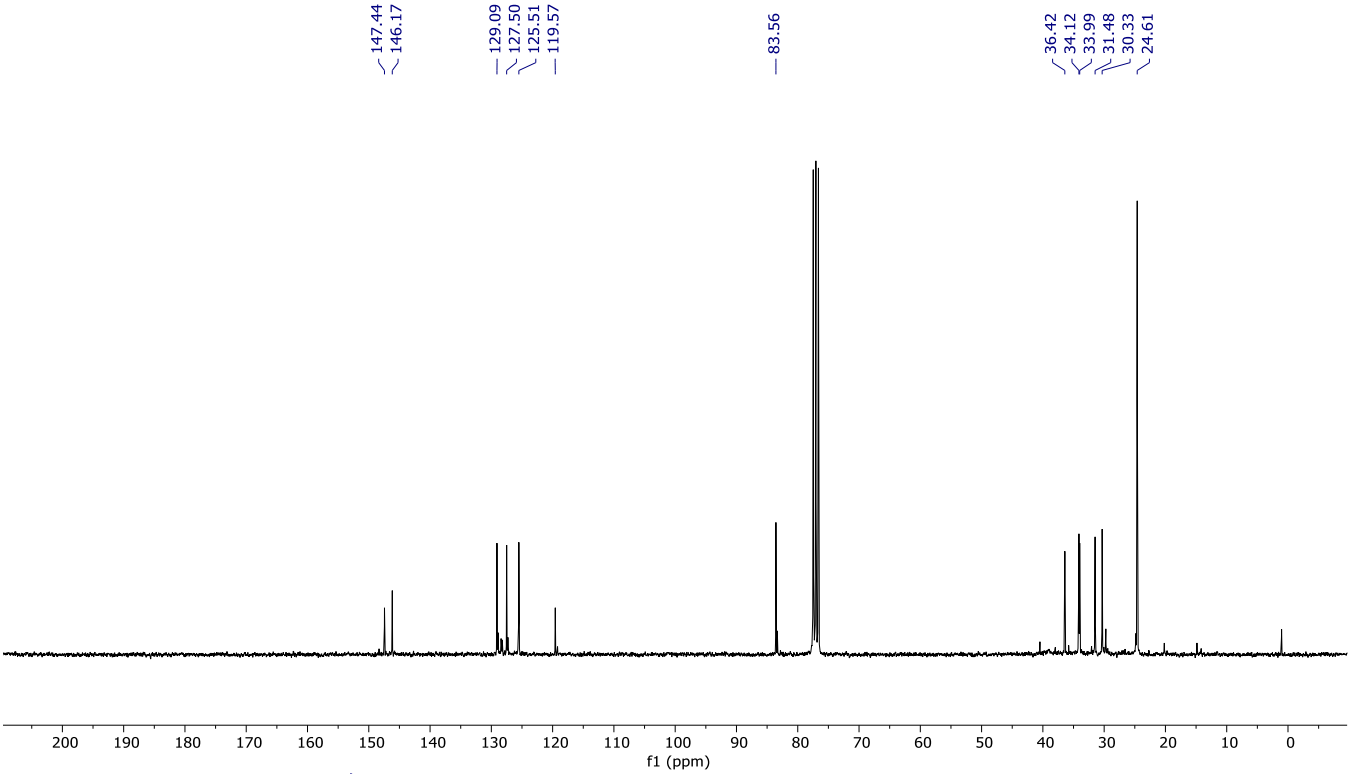
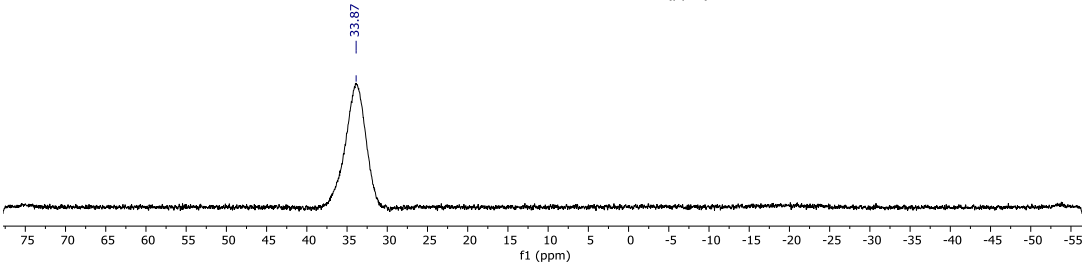
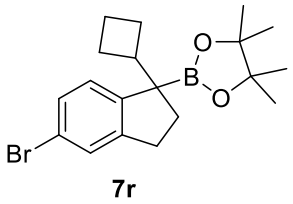




2-(5-bromo-1-cyclobutyl-2,3-dihydro-1H-inden-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 7r



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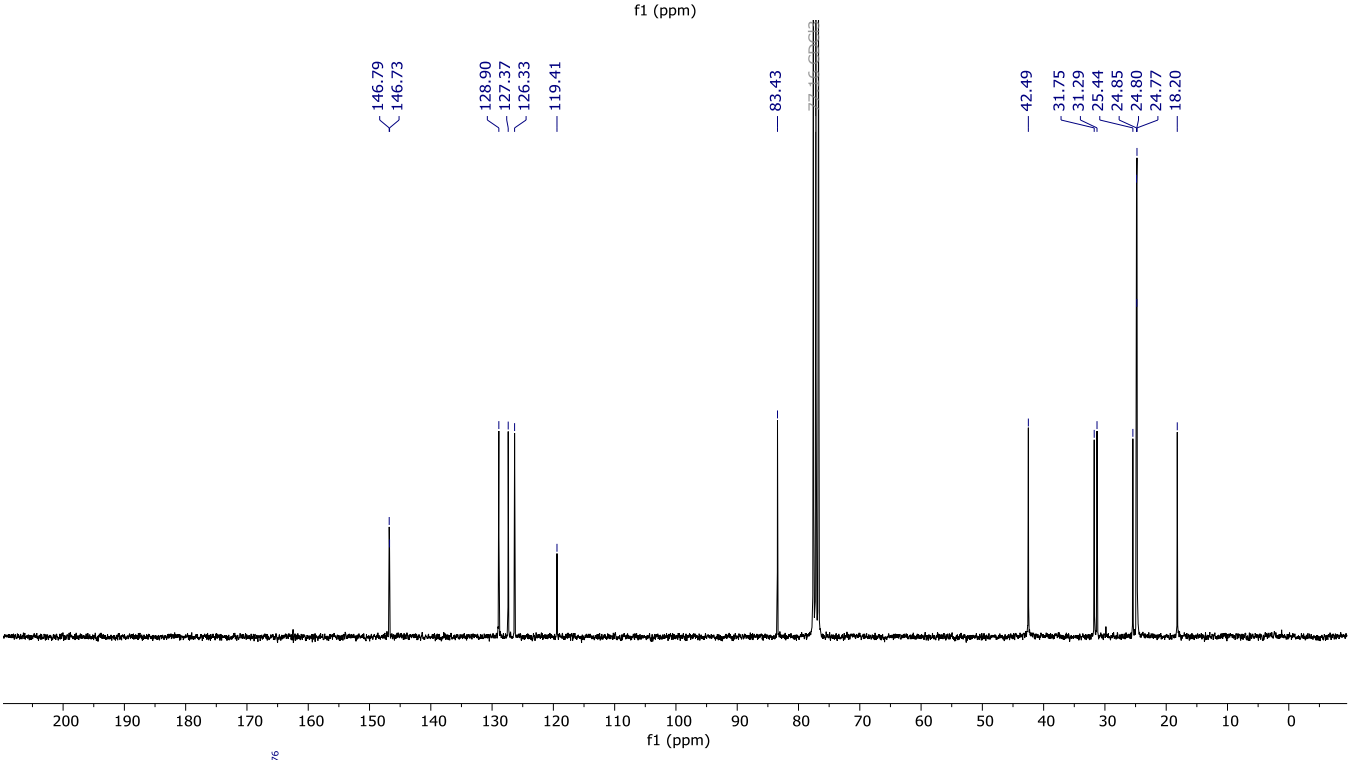
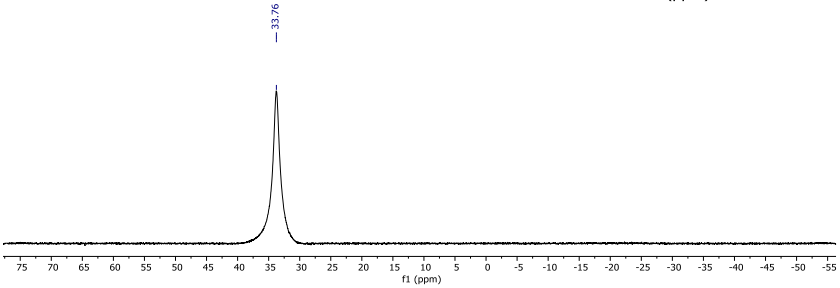
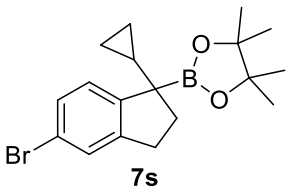




2-(5-Bromo-1-cyclopropyl-2,3-dihydro-1*H*-inden-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 7s



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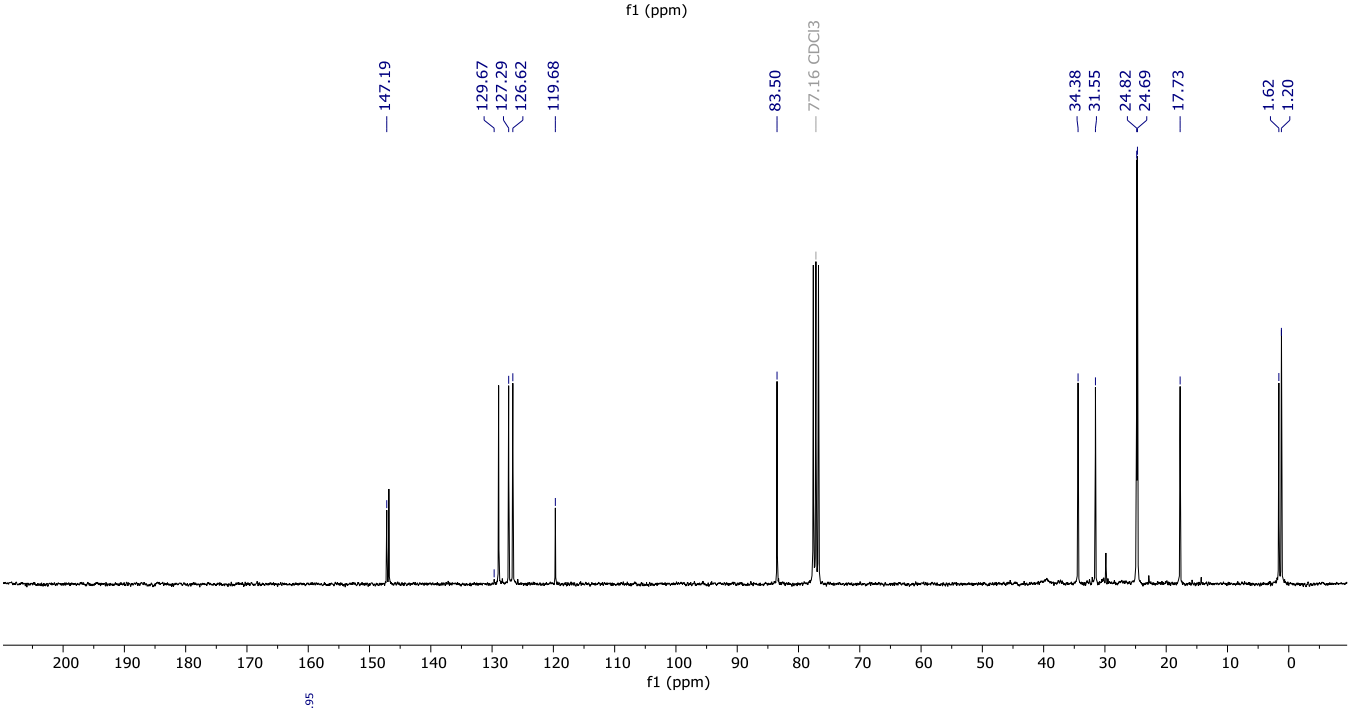
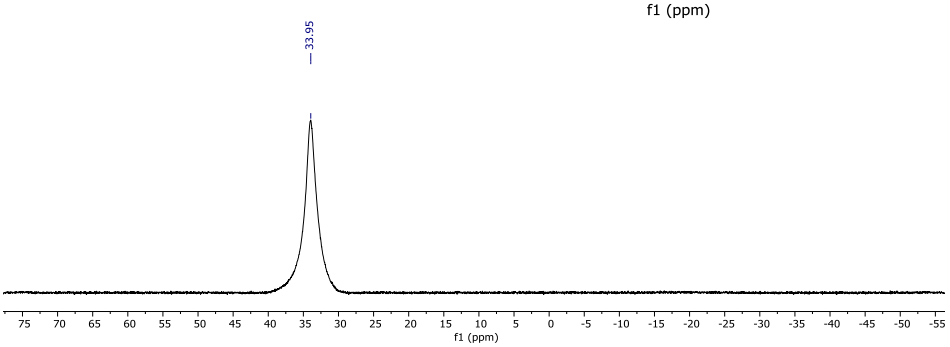
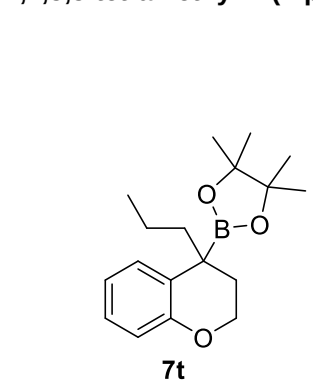




4,4,5,5-tetramethyl-2-(4-propylchroman-4-yl)-1,3,2-dioxaborolane 7t



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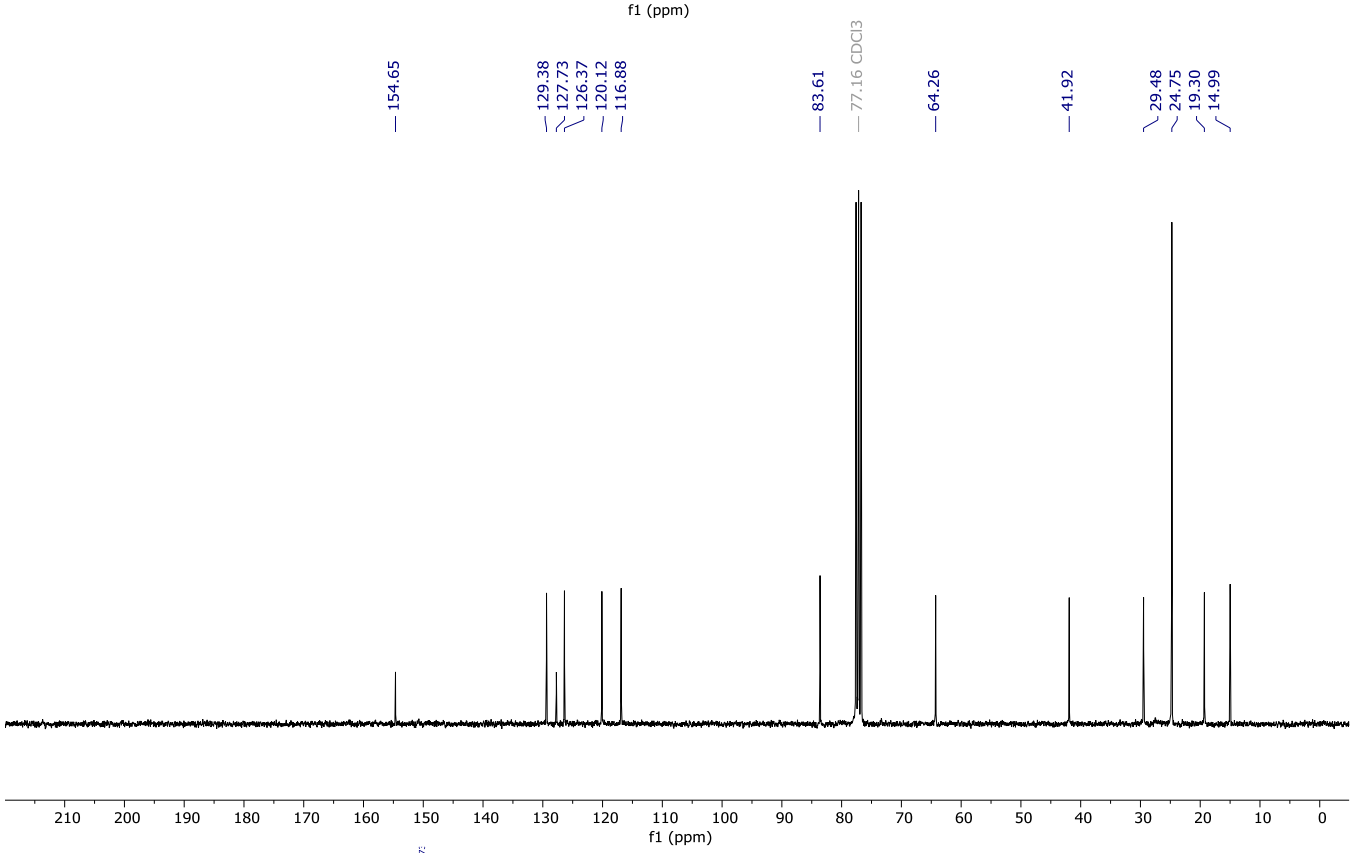
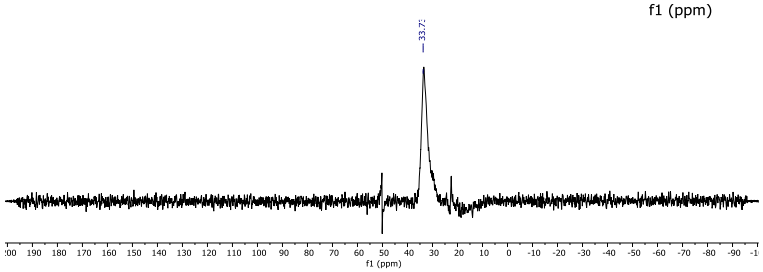
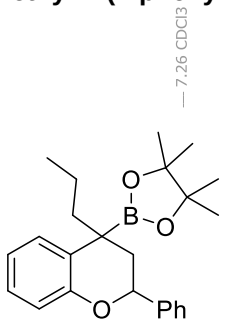


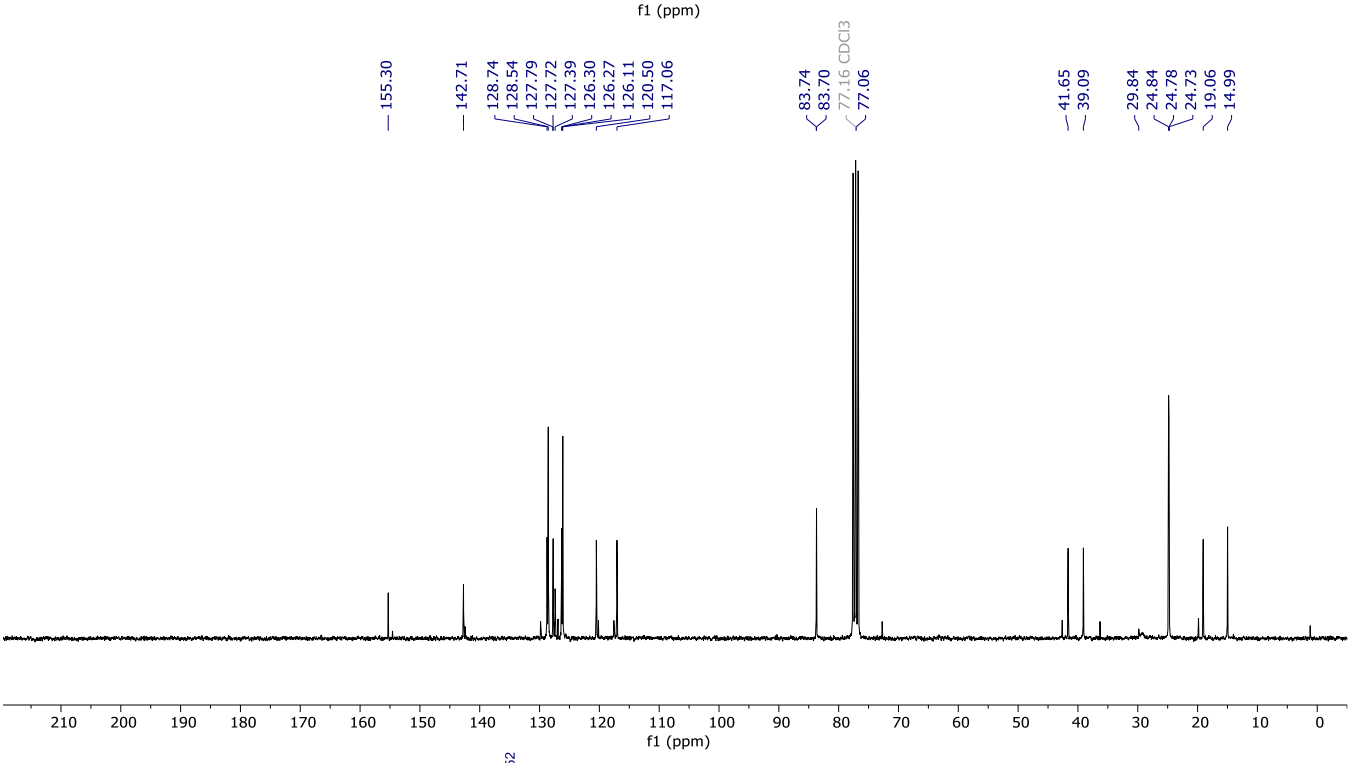


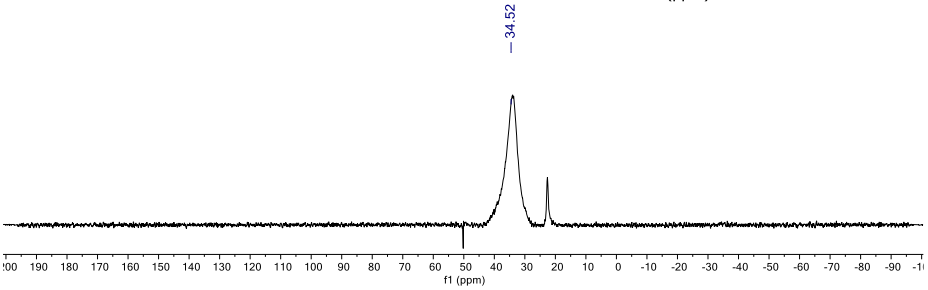
4,4,5,5-tetramethyl-2-(2-phenyl-4-propylchroman-4-yl)-1,3,2-dioxaborolane 7u



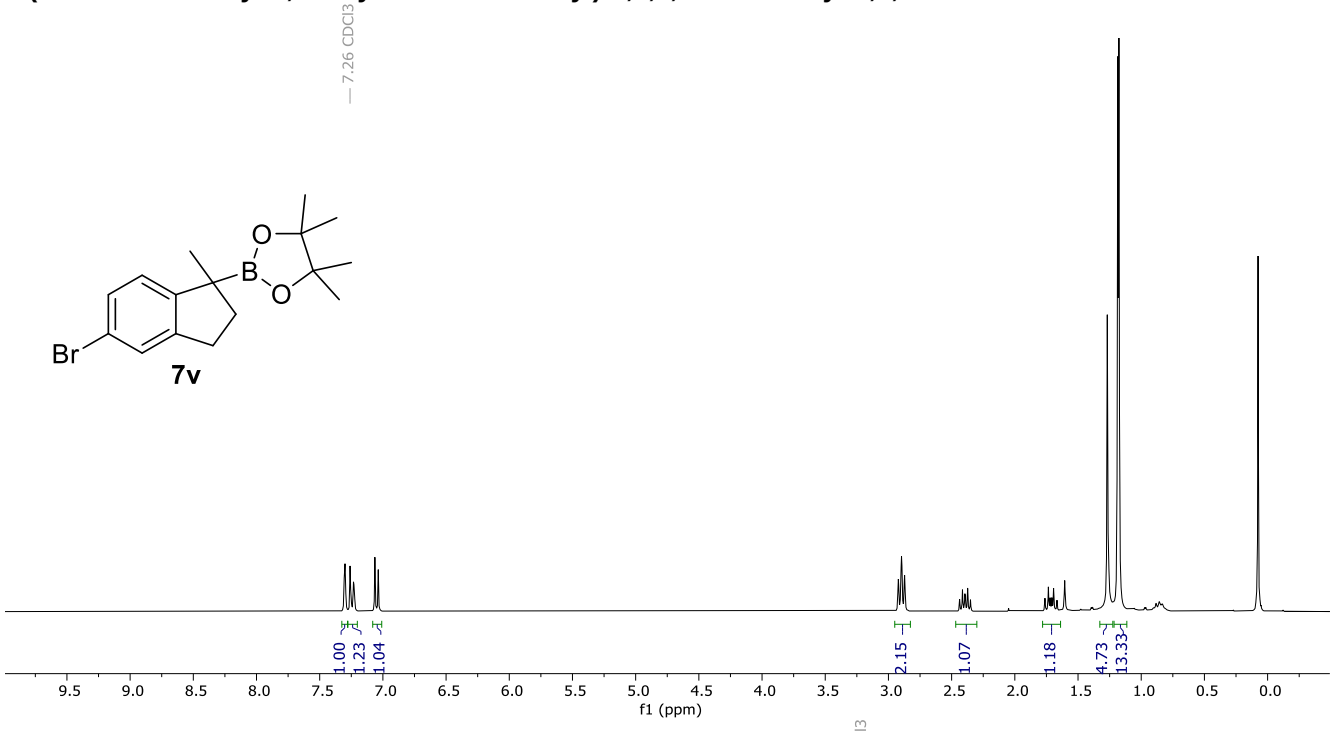
7u

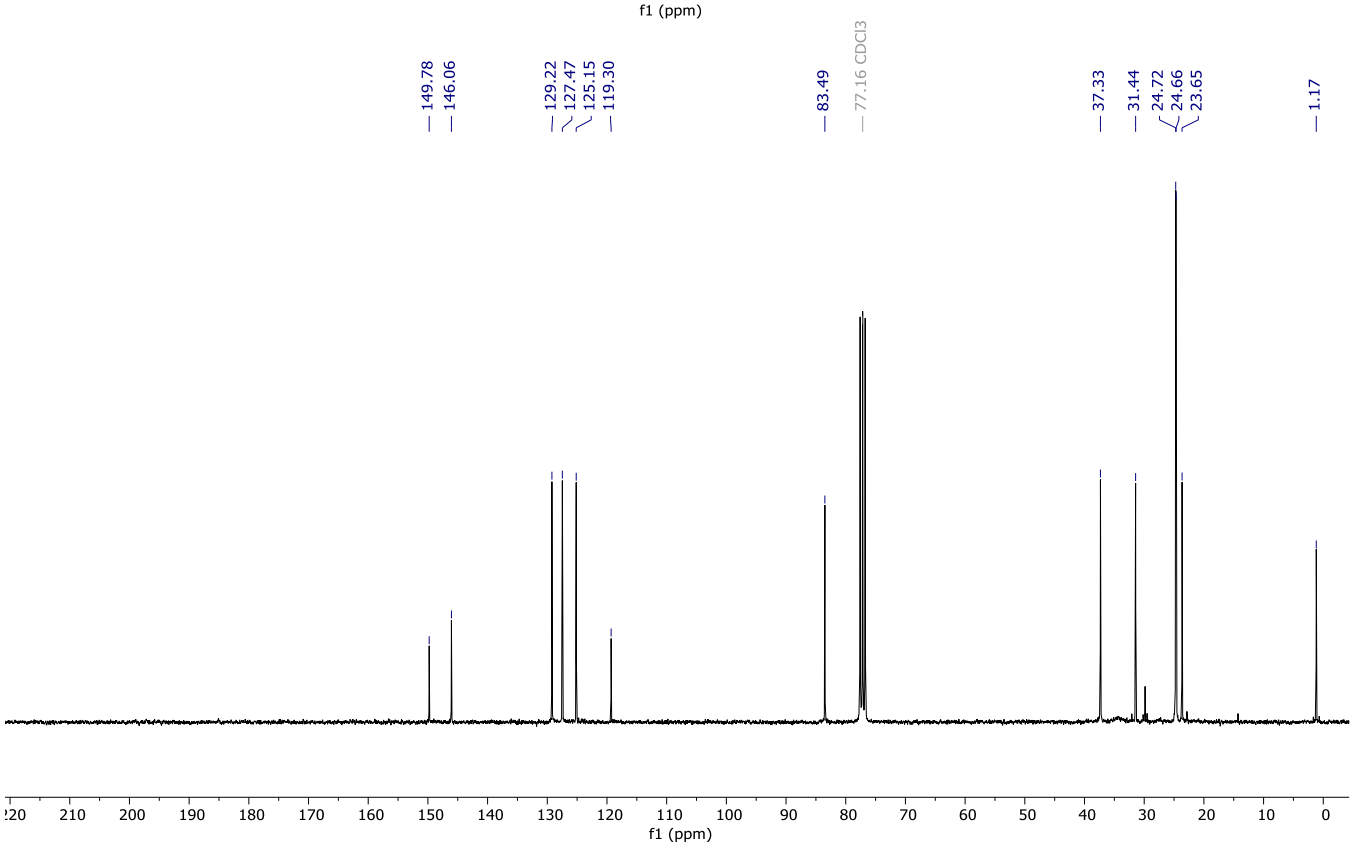
5: 1 mixture of diasereoisomers

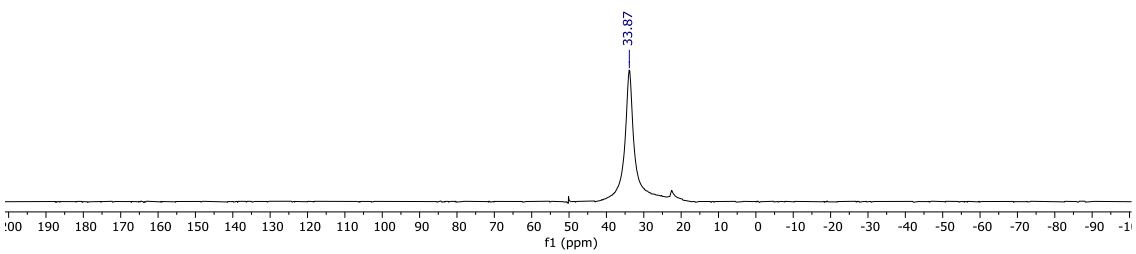




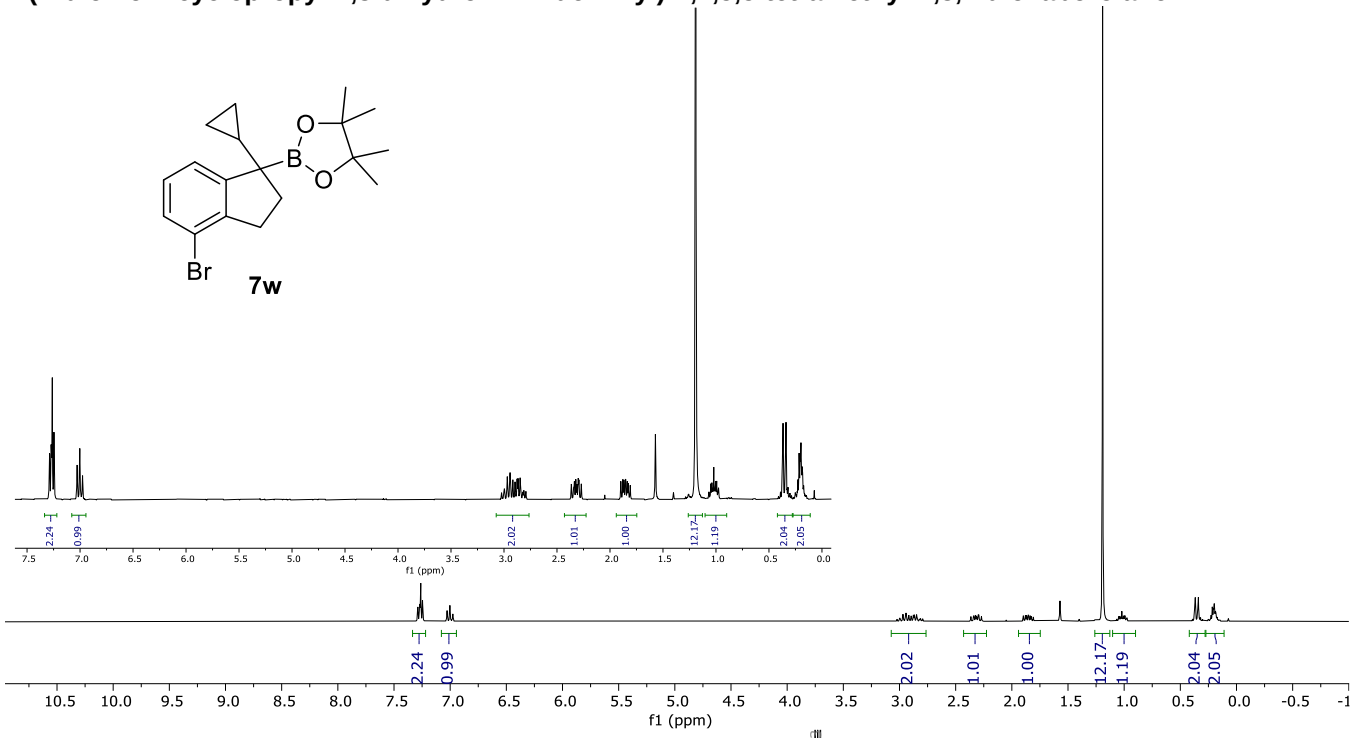
2-(5-bromo-1-methyl-2,3-dihydro-1H-inden-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 7v

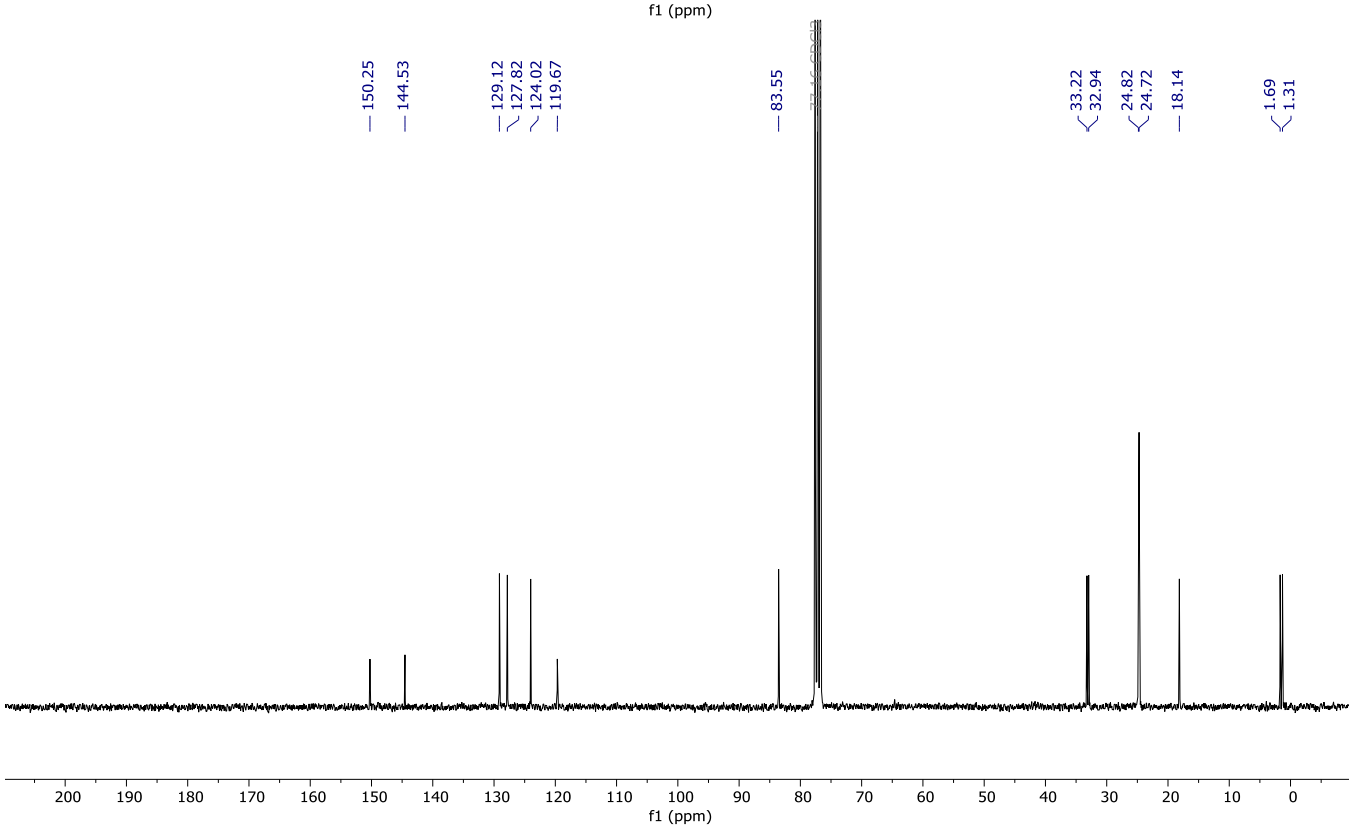


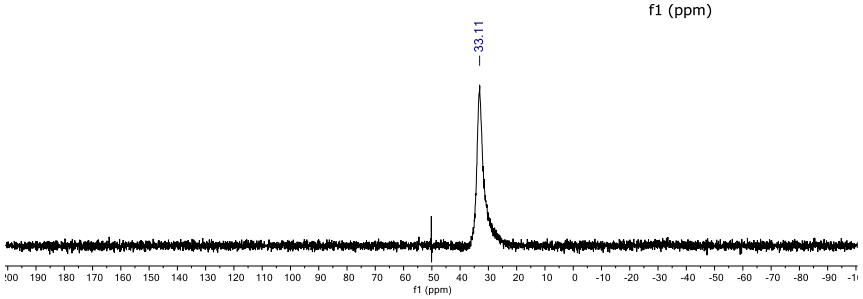




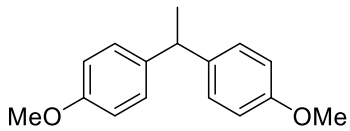
2-(4-bromo-1-cyclopropyl-2,3-dihydro-1H-inden-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 7w







4,4'-(ethane-1,1-diyl)bis(methoxybenzene) 8a



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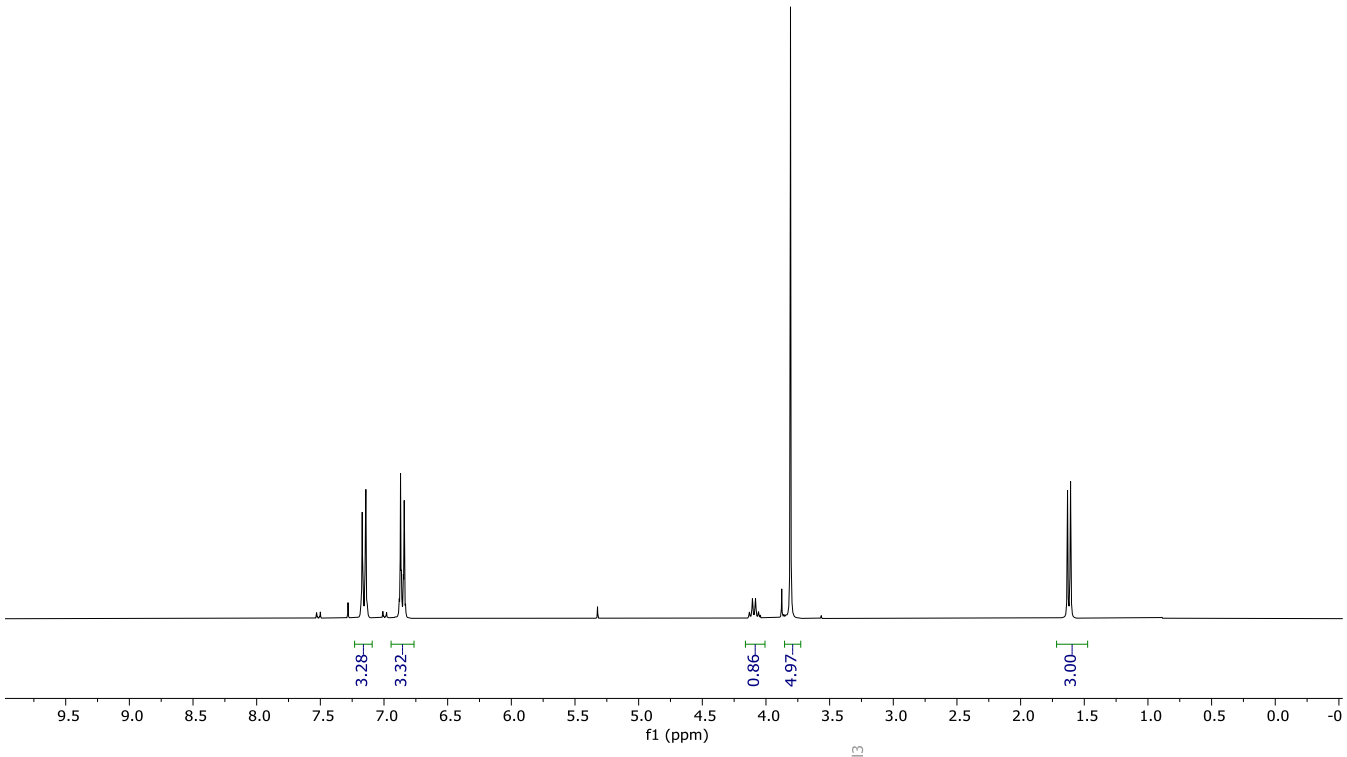
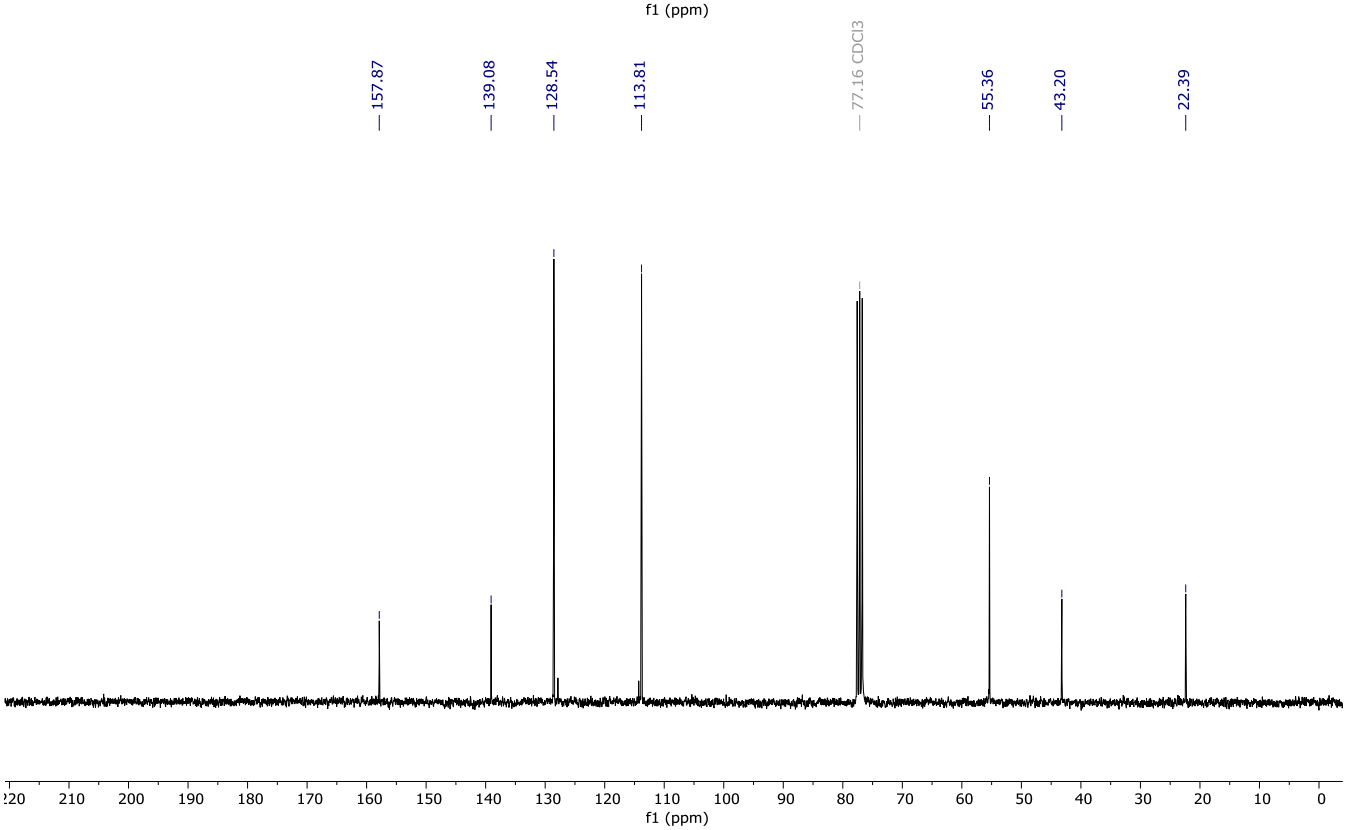
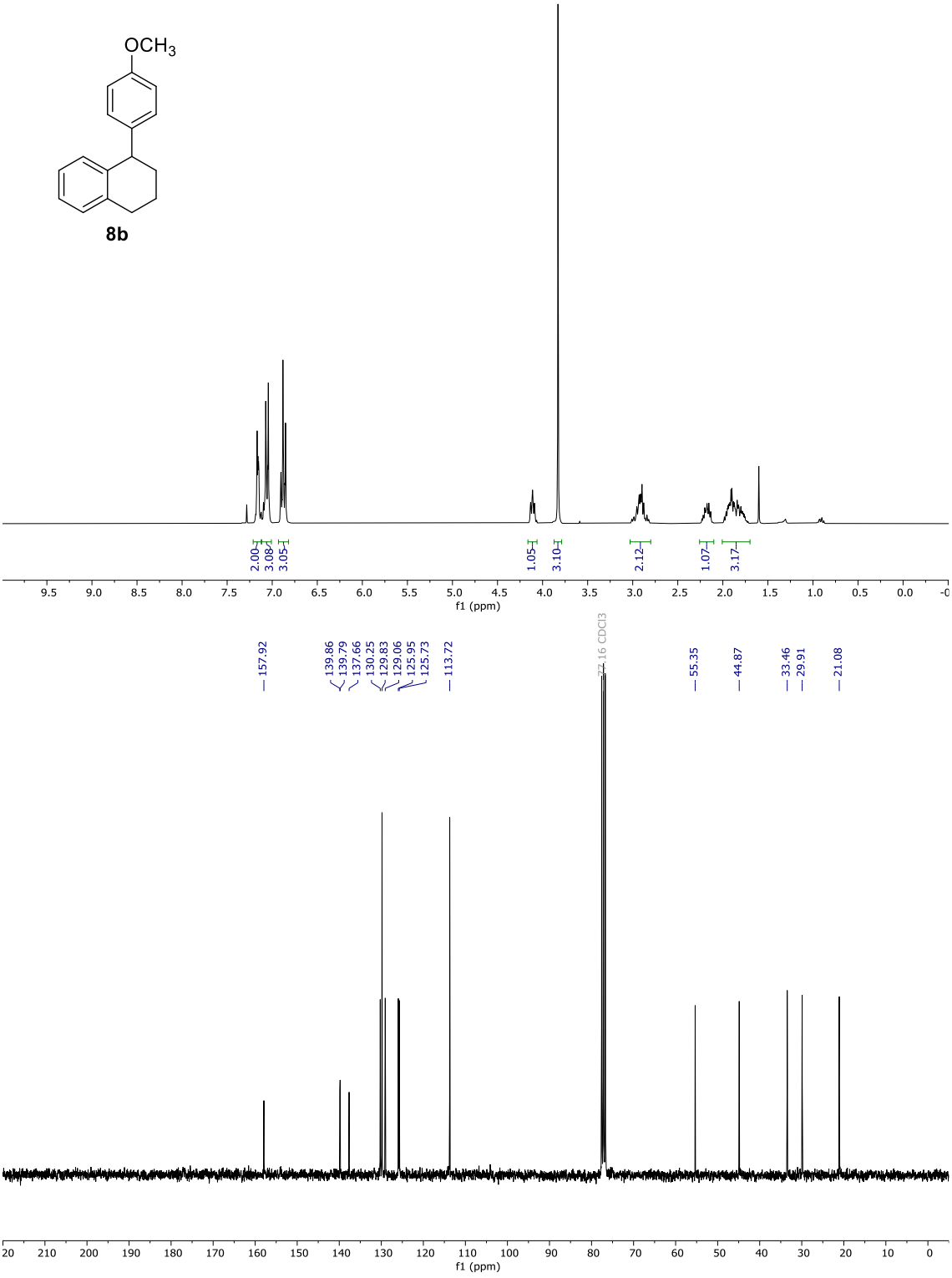
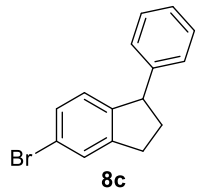




1-(4-methoxyphenyl)-1,2,3,4-tetrahydronaphthalene 8b



5-bromo-1-phenyl-2,3-dihydro-1*H*-indene 8c



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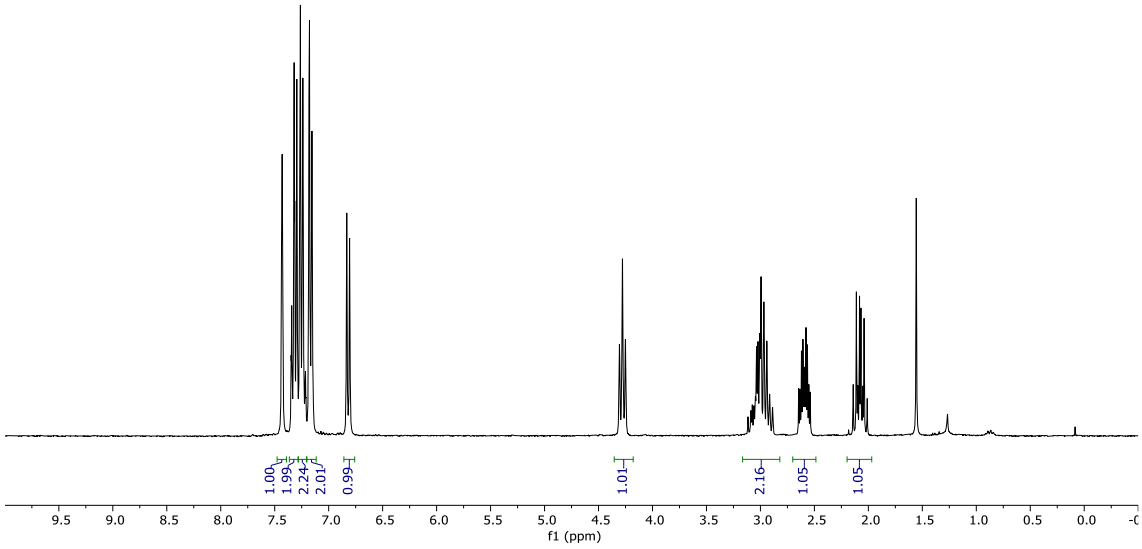
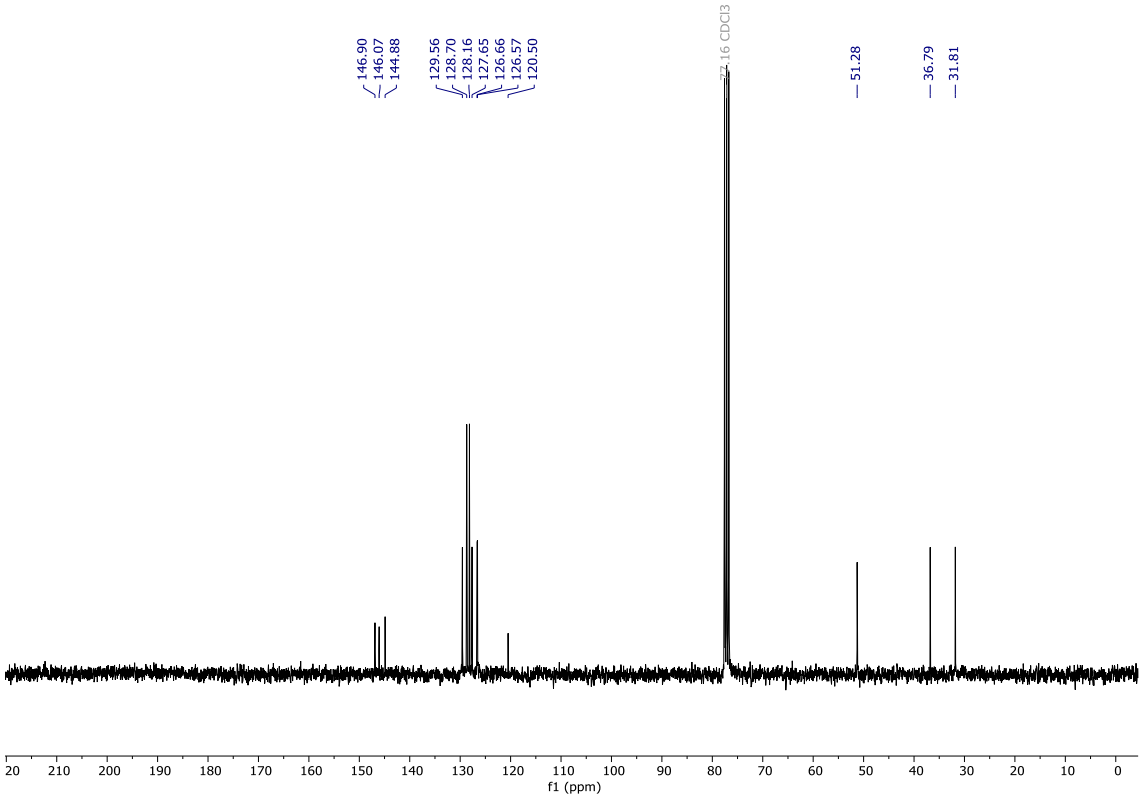
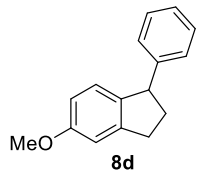




5-methoxy-1-phenyl-2,3-dihydro-1*H*-indene 8d



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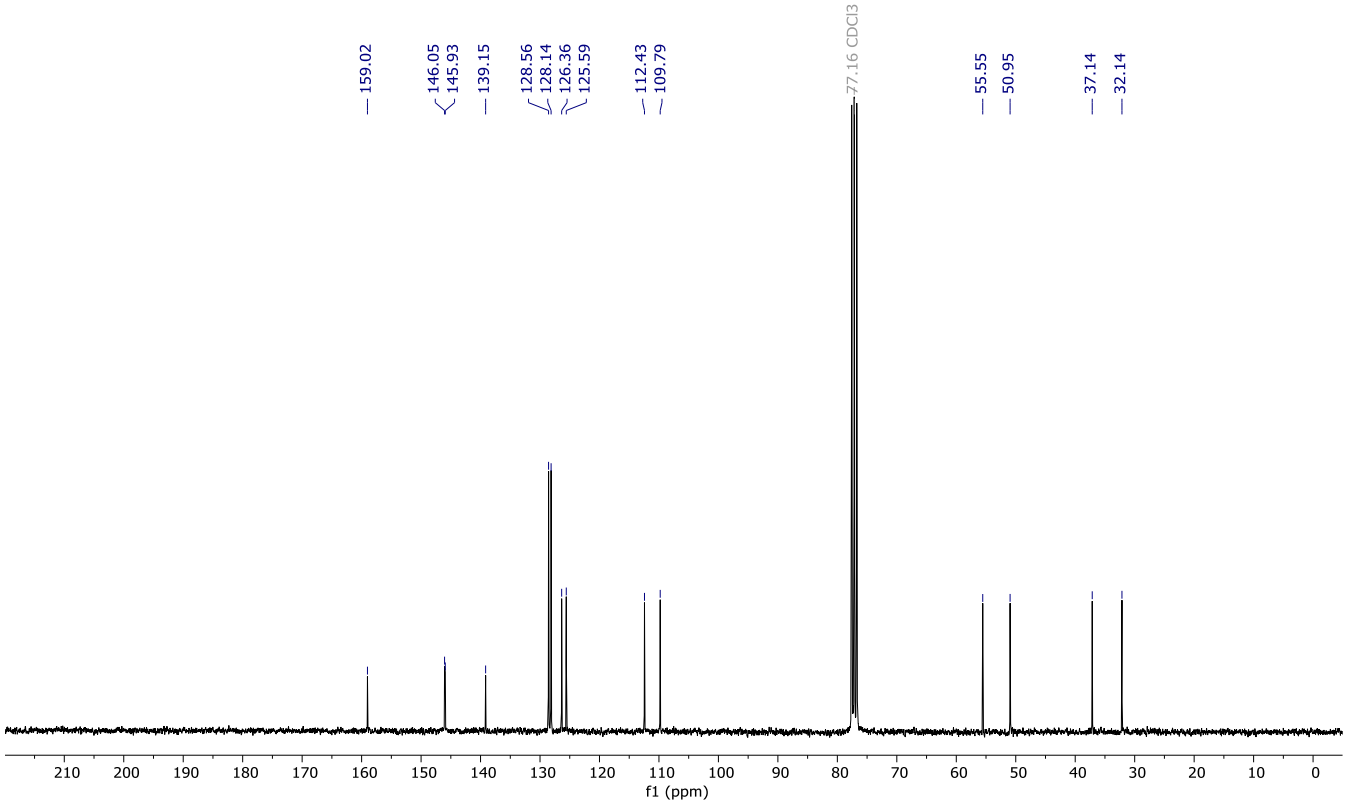
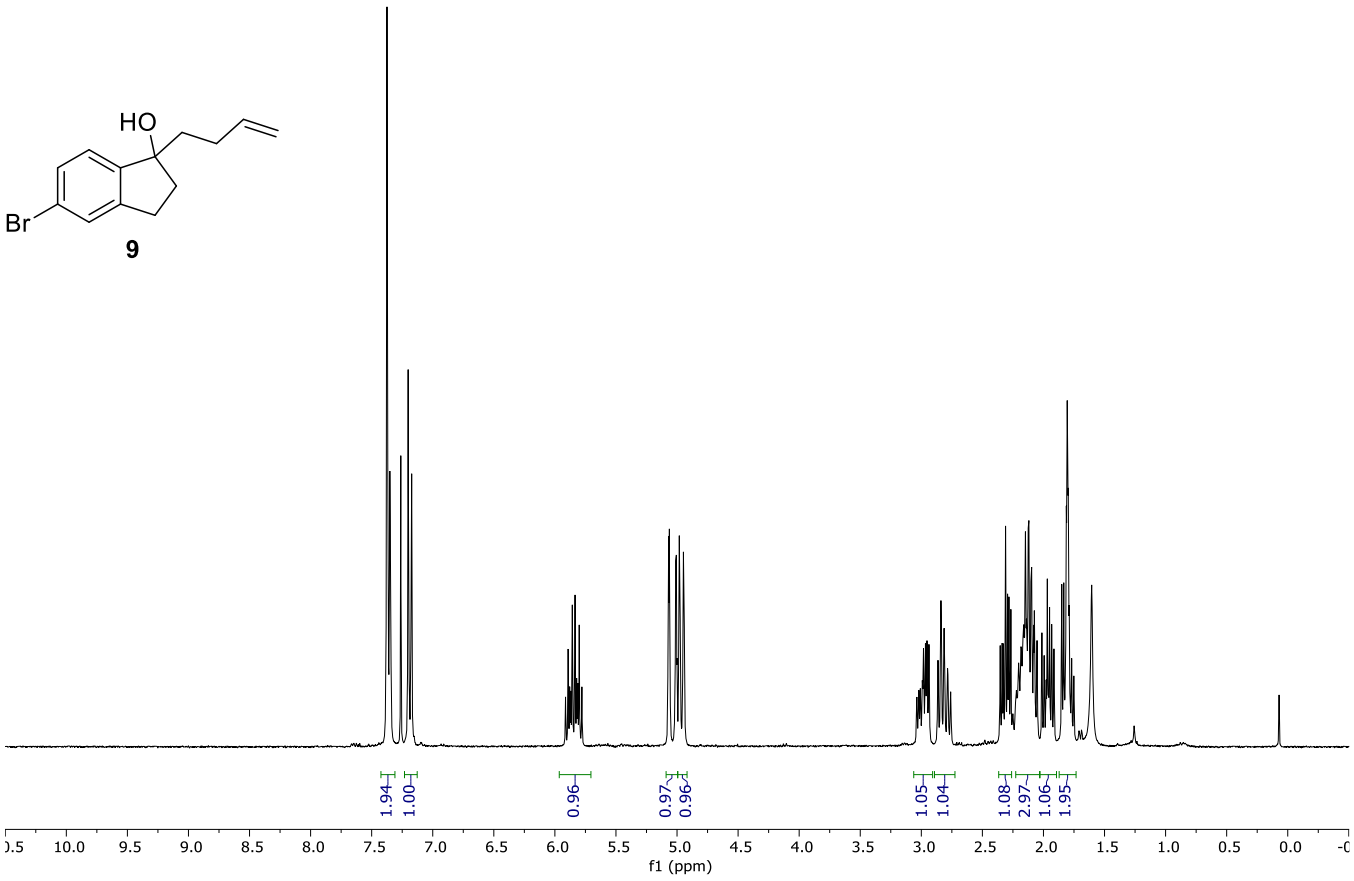
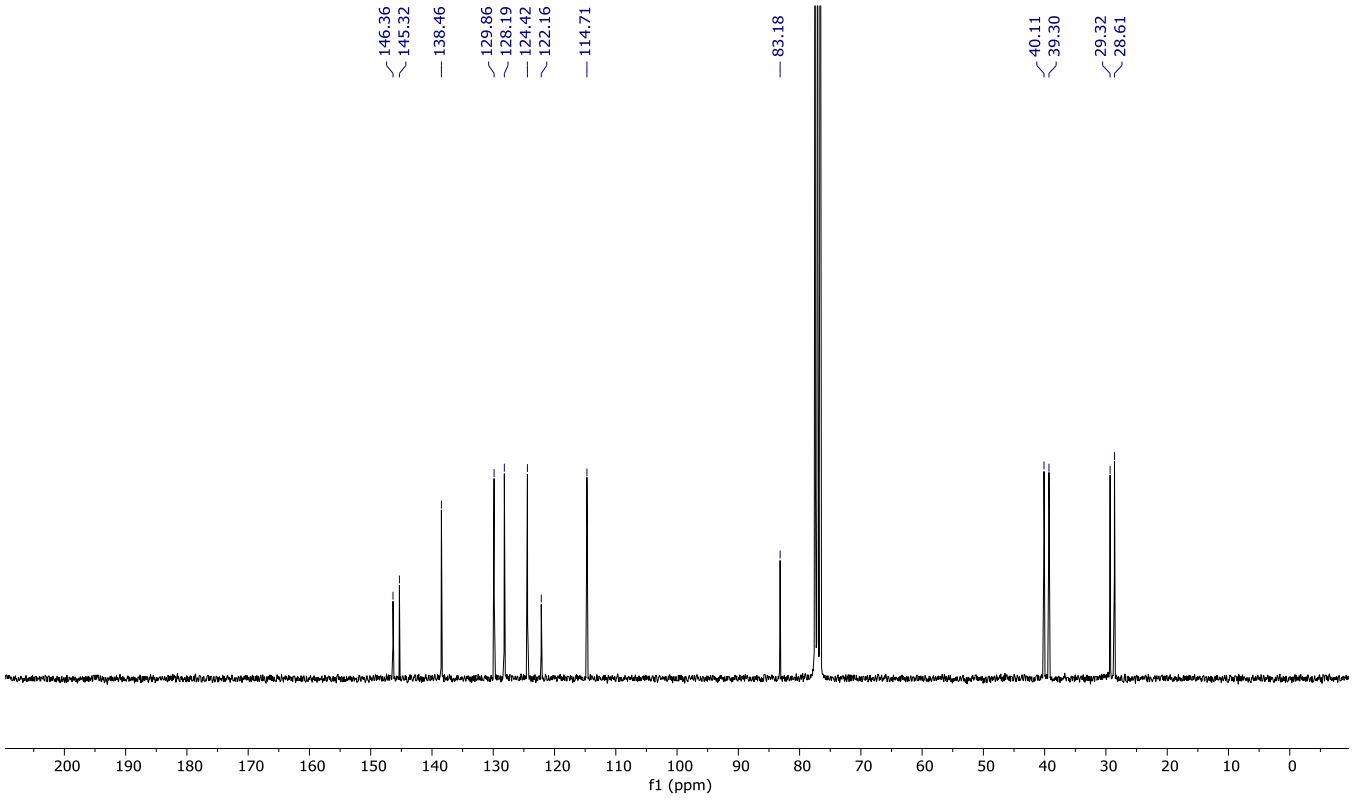
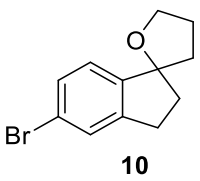


5-bromo-1-(but-3-en-1-yl)-2,3-dihydro-1H-inden-1-ol 9.





5’-bromo-2',3',4,5-tetrahydro-3H-spiro[furan-2,1'-indene] 10



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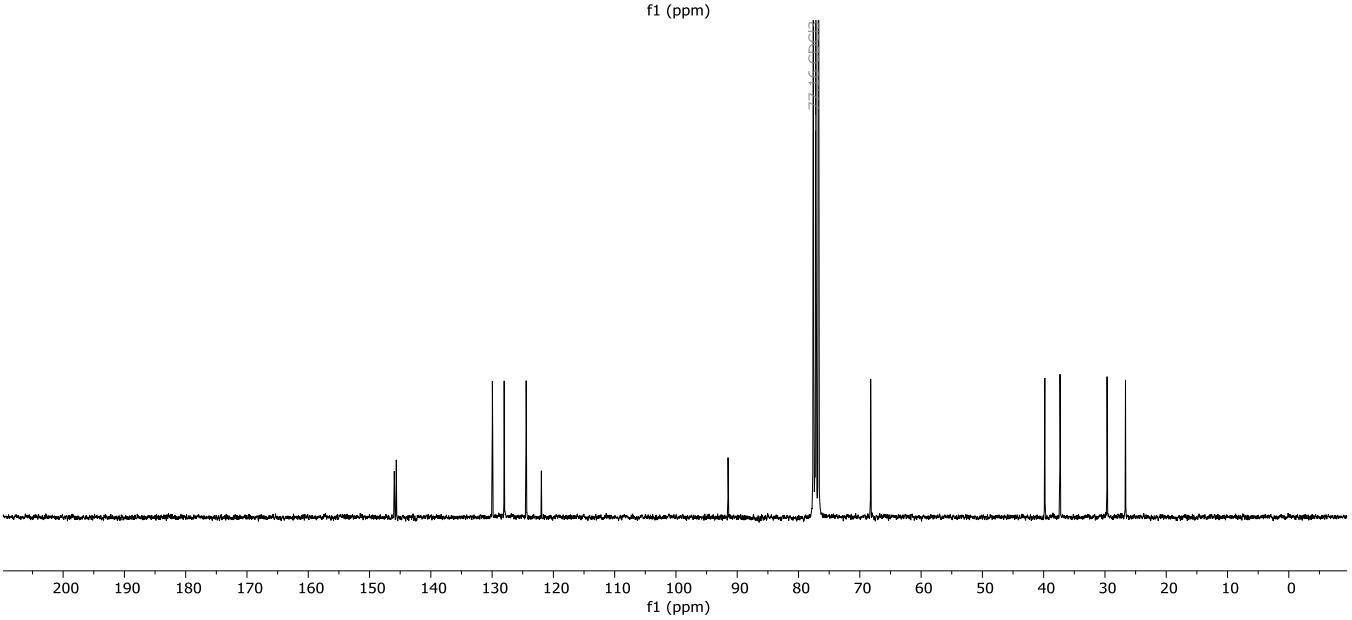
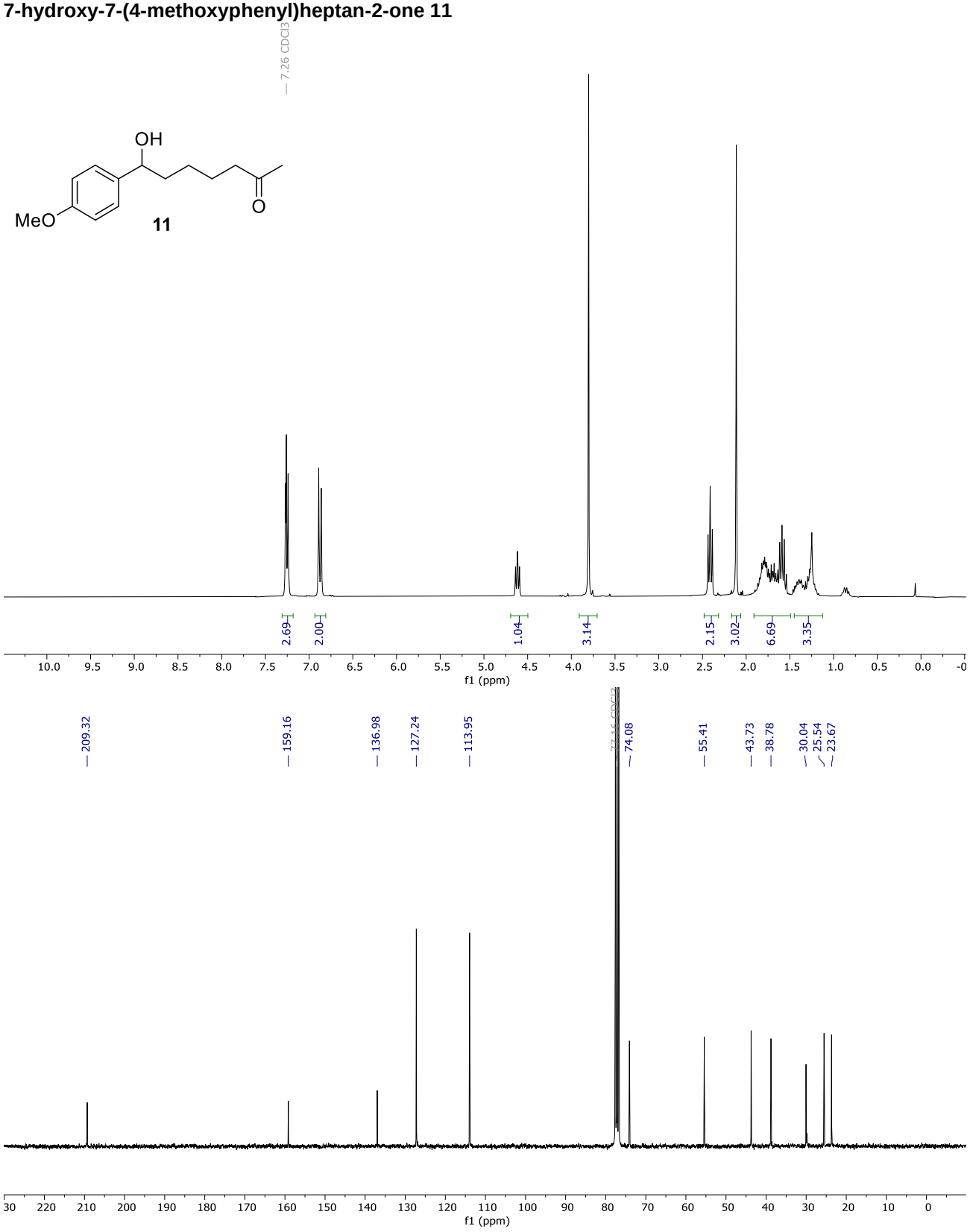
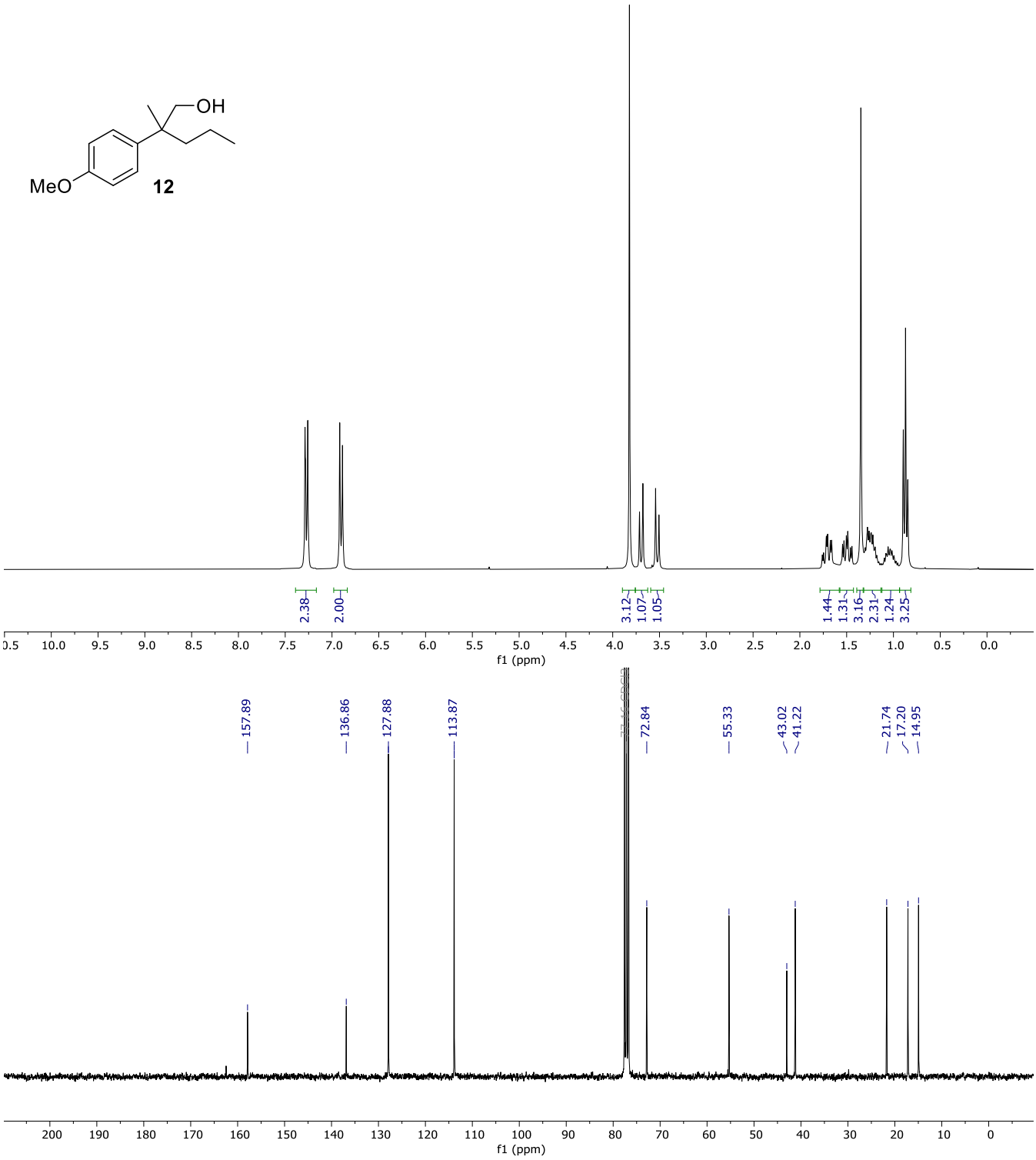


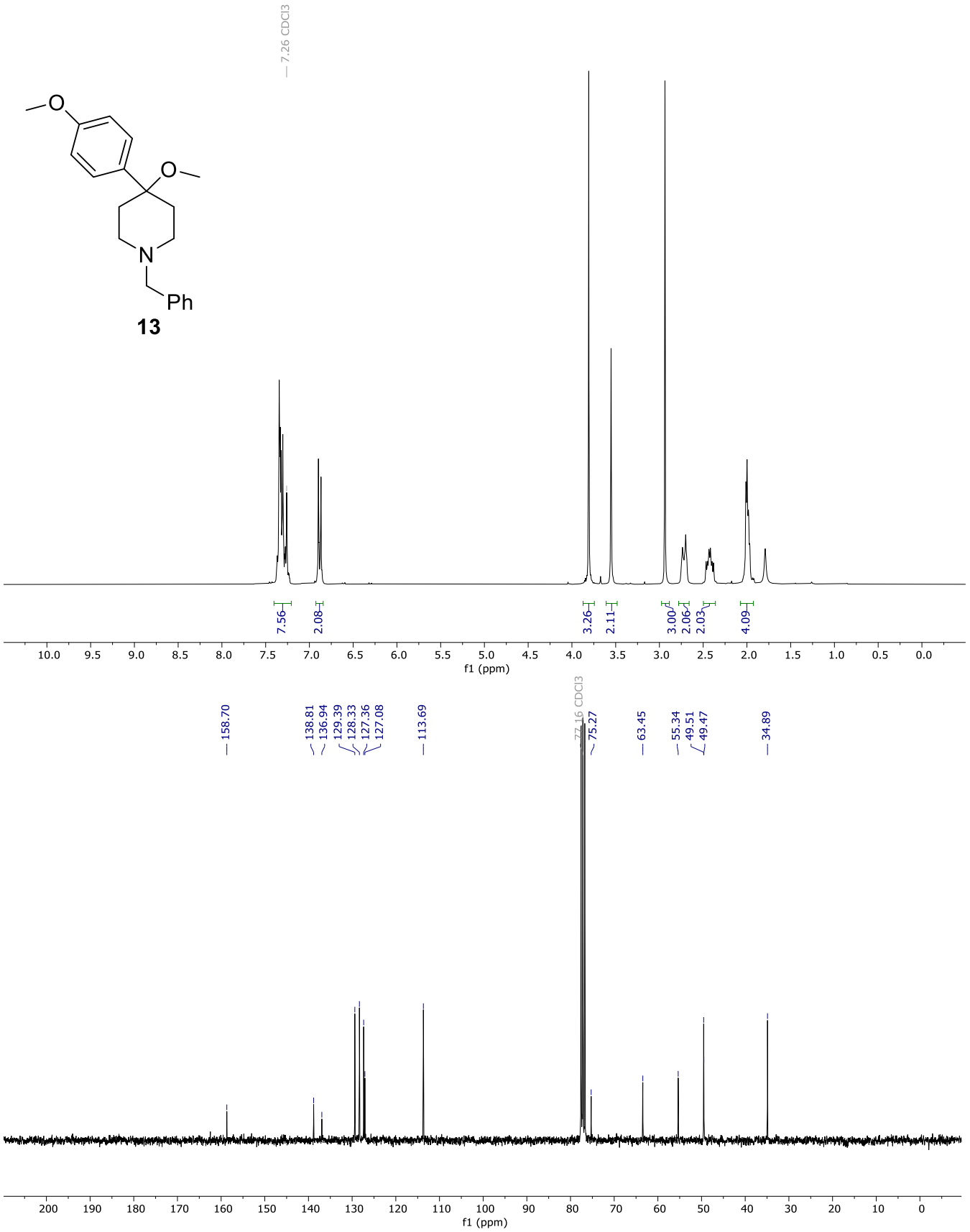
7-hydroxy-7-(4-methoxyphenyl)heptan-2-one 11



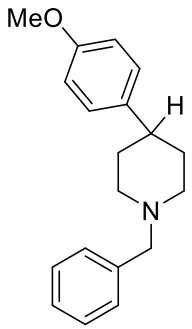
2-(4-methoxyphenyl)-2-methylpentan-1-ol 12



1-benzyl-4-methoxy-4-(4-methoxyphenyl)piperidine 13



1-benzyl-4-(4-methoxyphenyl)piperidine 14



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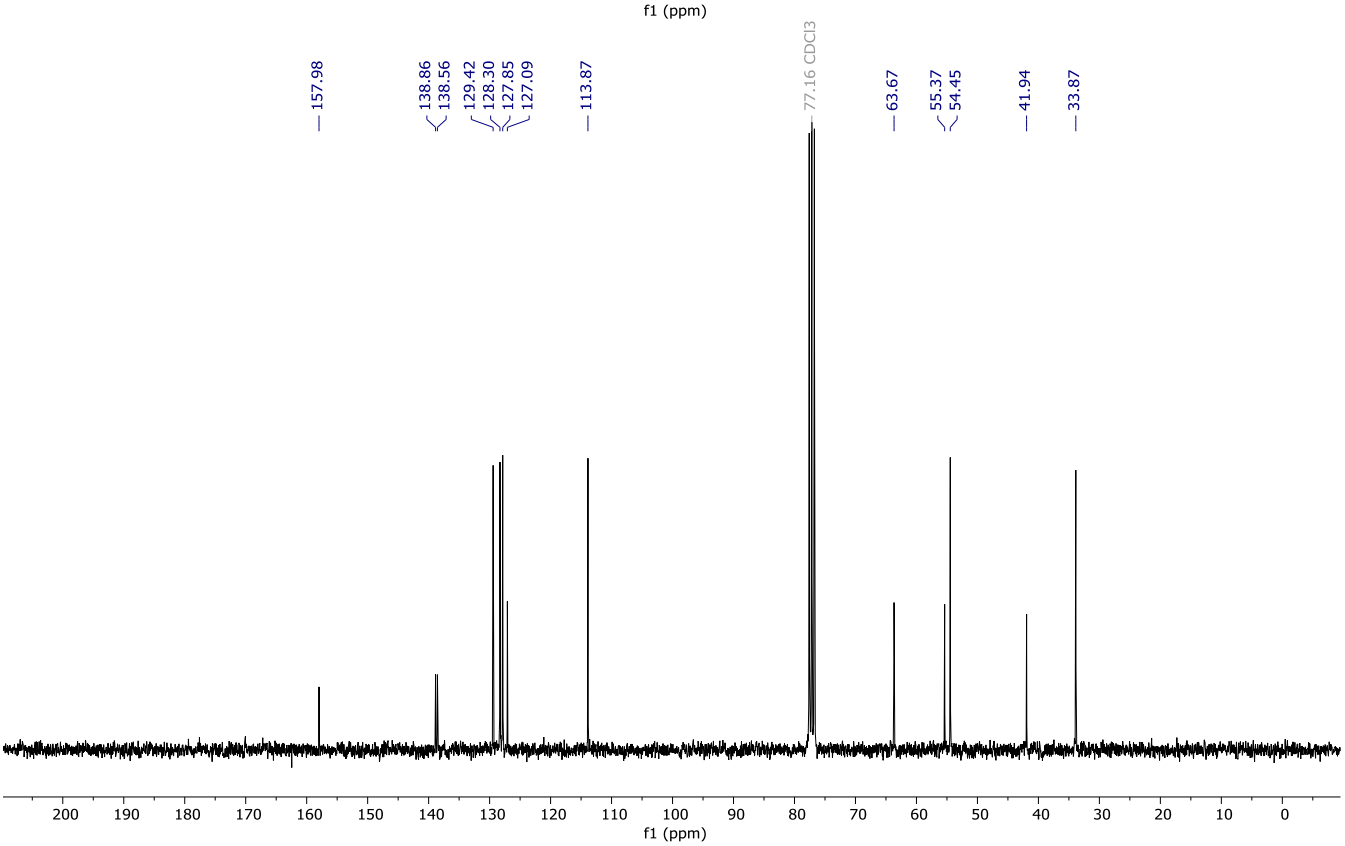
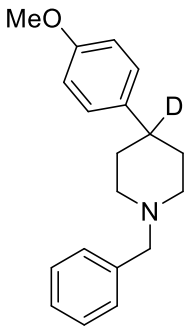


1-benzyl-4-(4-methoxyphenyl)piperidine-4-d 14D



14D