Supporting Information for:

Highly Diastereo- and Enantioselective Copper-Catalyzed Methylboration of 1,2-Dihydroquinolines and 2*H*-Chromenes

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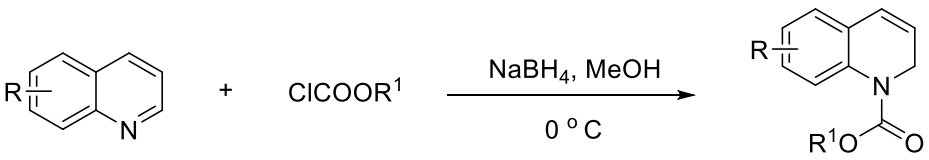
1. General Information

All the reactions were carried out under a nitrogen atmosphere unless otherwise apecified, the air or moisture sensitive reactions and manipulations were performed by using standard Schlenk techniques and in a nitrogen-filled glovebox. DME, THF and toluene were distilled from sodium benzophenone ketyl. DCE was distilled from calcium hydride. Anhydrous MeOH was distilled from magnesium. ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker AV (400 MHz) spectrometers and JEOL JNM-ECX600P and JNM-ECS600 (600 MHz) spectrometers ($CDC1_3$ was the solvent used for the NMR analysis, with TMS as the internal standard. Chemical shifts were reported upfield to TMS (0.00 ppm) for ^{1}H NMR. Data is represented as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, dd = double of doublets, t = triplet, q = quartet, m = multiplet) and coupling constants (*J*) in Hertz (Hz). Optical rotation was determined using Autopol III Automatic polarimeter (Rudolph research Analyical). HPLC analysis was conducted on Agilent 1260 series instrument. SFC analysis was conducted on Agilent 1260 series instrument. HRMS were recorded on a Waters LCT Premier XE mass spectrometer with APCI or ESI.

2. Preparation of Substrates

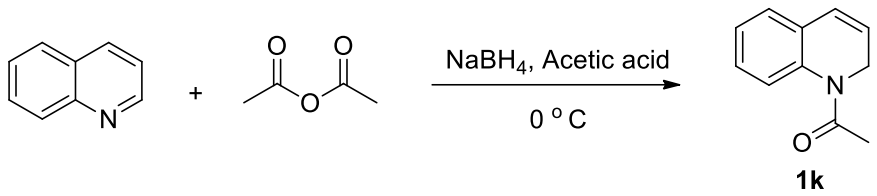
Preparation of Substrates 1



1a - 1j

To a solution of quinoline or substituted quinoline (20.0 mmol) in MeOH (30.0 mL) was added dropwise $ClCO_2R$ (24.0 mmol) at 0 ℃ under a nitrogen atmosphere, then $NaBH_4$ (20.0 mmol) was added portionwise at 0 ℃ over 1 h. The reaction mixture was then allowed to warm to room

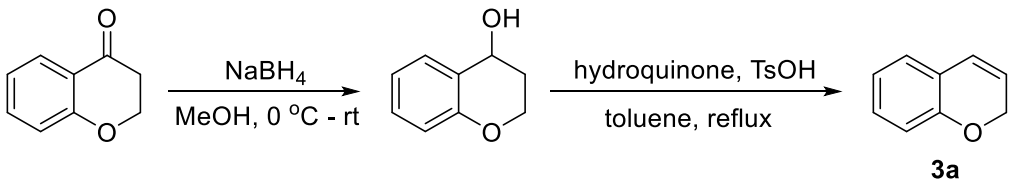
temperature. After 2-3 h, the solution was carefully quenched with H_2O and extracted with EtOAc. The organic layers were dried over $MgSO_4$, filtered and evaporated. The residue was purified by silica gel column chromatography using petroleum ether/EtOAc as an eluent (PE/EA/ = 4/1 to 30/1) to give the corresponding 1,2-dihydroquinoline (**1a - 1j**) as light yellow oil, which was immediately used and stored at -30 ℃ under a nitrogen atmosphere in order to prevent decomposition. [1]



To a mixture of quinoline (10.0 mmol), acetic anhydride (12.0 mL) and acetic acid (40.0 mL) was gradually added $NaBH_4$ (40.0 mmol) at 0 ºC over 1.5 h. After the addition was complete, the reaction mixture was then allowed to warm to room temperature. After 1 h, the reaction mixture was concentrated under vacuum, diluted with H_2O, neutralized with sodium carbonate and extracted with DCM. The organic layers were dried over $MgSO_4$, filtered and evaporated. The residue was purified by silica gel column chromatography using petroleum ether/EtOAc as an eluent (PE/EA/ = 5/1) to give the corresponding 1,2-dihydroquinoline **1f** as a light yellow oil. [2]

Preparation of Substrates 3

a. Procedure for the preparation of 3a.

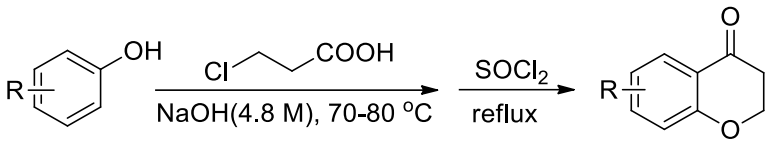


Chroman-4-one (5.0 mmol) was suspended in methanol (50.0 mL) and treated with an excess of $NaBH_4$ (7.5 mmol) at 0 ºC. The resulting mixture was stirred for 30 minutes at room temperature, then concentrated in vacuum. The residue was partitioned between CH_2Cl_2 and H_2O. The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2. The organic layers was then

combined, washed with H_2O, dried over anhydrous Na_2SO_4, filtered and concentrated to yield the desired compound.[3]

p-Toluenesulfonic acid (3.0 mg) and hydroquinone (5.0 mg) were added to a solution of chroman-4-ol (5.00 mmol) in toluene (20.0 mL). The reaction mixture was heated under reflux using a Dean–Stark trap (2 h), washed with water, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by silica gel chromatography (petroleum ether).[4]

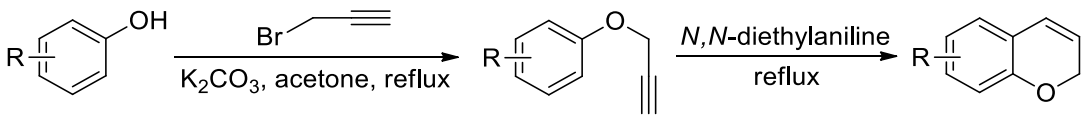
b. Procedure for the preparation of 3b, 3g, 3h, 3i and 3j.



Equimolar quantities of chloropropionic acid (0.05 mol) and appropriate Phenol (0.05 mol) were placed in a conical flask, to which aqueous solution of NaOH (0.12 mol in 25 mL water) was slowly added with constant stirring and then heating to 75 – 80 °C, reacting for 12 h. After the reaction, with sufficient cooling and acidified by adding con. HCl, extracted with ethyl acetate, followed by saturated brine. It was dried over anhydrous Na_2SO_4 and then solvent was removed. The crude product was purified by silica gel chromatography.[5]

3-Phenoxypropanoic acids were placed in a conical flask, to which sulfoxide chloride was quickly added with constant stirring. The reaction mixture was heated under reflux for 2 h, then concentrated in vacuo and CH_2Cl_2 was added to the mixture. The aluminum chloride anhydrous was added at 0 °C and the reaction stirred for 1 h at 0 °C, then the reaction mixture was allowed to warm to rt. The reaction was quenched with H_2O slowly at 0 °C, extracted with CH_2Cl_2, followed by saturated brine. It was dried over anhydrous Na_2SO_4 and then solvent was removed. The crude product was purified by silica gel chromatography (petroleum ether: EtOAc = 7:1); Then according to procedure for the preparation of **3**.

c. Procedure for the preparation of other substrates.

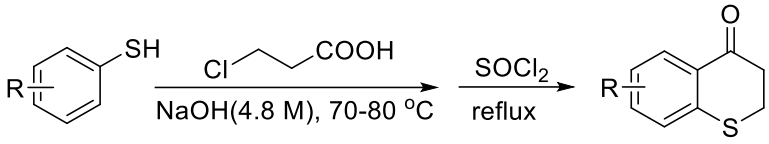


To a solution of phenols (50.0 mmol) in acetone (200 mL) was added K_2CO_3 (200.0 mmol) and 3-bromoprop-1-yne (60.0 mmol). The resulting mixture was stirred at reflux temperature during

overnight and the reaction stopped by filtration and evaporation under vacuum. The crude product was extracted with CH_2Cl_2, followed by saturated brine. It was dried over anhydrous Na_2SO_4 and then solvent was removed. The crude product was purified by silica gel chromatography.[6]

A mixture of (prop-2-yn-1-yloxy) benzene (10.0 mmol) and N, N-diethylaniline (1.6 mL) was refluxed for 8-12 h. After cooling to room temperature, the reaction mixture was diluted with ethyl acetate. The resulting mixture was washed with hydrochloric acid (2M), water and brine, and then dried over anhydrous Na_2SO_4. The solvent was evaporated and the crude product was purified by silica gel chromatography.[6]

d. Procedure for the preparation of 3k.

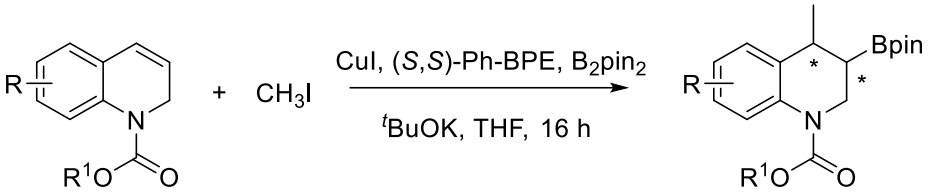


Equimolar quantities of chloropropionic acid (0.05 mol) and appropriate Phenthiol (0.05 mol) were placed in a conical flask, to which aqueous solution of NaOH (0.12 mol in 25 mL water) was slowly added with constant stirring and then heating to 75 – 80 °C, reacting for 12 h. After the reaction, with sufficient cooling and acidified by adding con. HCl, extracted with ethyl acetate, followed by saturated brine. It was dried over anhydrous Na_2SO_4 and then solvent was removed. The crude product was purified by silica gel chromatography.

3-(Phenylthio)propanoic acids were placed in a conical flask, to which sulfoxide chloride was quickly added with constant stirring. The reaction mixture was heated under reflux for 2 h, then concentrated in vacuo and CH_2Cl_2 was added to the mixture. The aluminum chloride anhydrous was added at 0 °C and the reaction stirred for 1 h at 0 °C, then the reaction mixture was allowed to warm to rt. The reaction was quenched with H_2O slowly at 0 °C, extracted with CH_2Cl_2, followed by saturated brine. It was dried over anhydrous Na_2SO_4 and then solvent was removed. The crude product was purified by silica gel chromatography (petroleum ether: EtOAc = 7:1); Then according to procedure for the preparation of **3**.

3. Copper-Catalyzed Enantioselective Methylboration of Substrates

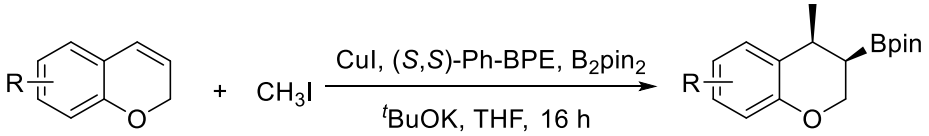
a. Copper-Catalyzed Enantioselective Methylboration of Substrates 1



1a **2a**

In a nitrogen-filled glovebox, CuI (3.8 mg, 0.02 mmol, 10 mol%), (*S*,*S*)-Ph-BPE (12.2mg, 0.024 mmol, 12 mol%) and THF (1 mL), then the mixture was stirred 30 minutes at room temperature. To the mixture was added B_2pin_2 (76.2 mg, 0.3 mmol, 1.5 equiv) and **1** (0.20 mmol, 1 equiv), CH_3I (85.2 mg, 0.6 mmol, 3 equiv) and ^{t}BuOK (33.7 mg, 0.3 mmol, 1.5 equiv) successively. After that, 0.5 mL of THF was added along the vial's wall to keep all reacts into the reaction solution. The vial was sealed was a rubber stopper, removed from the glovebox and stirred at room temperature for 16 hours. Upon completion of the reaction, the reaction mixture was passed through a short silica gel column eluting with Et_2O. The solvent was removed under vacuo, and the residue was purified by column chromatography on silica gel using petroleum ether/EtOAc as an eluent (PE/EA/ = 10/1 to 20/1) to give the corresponding borylation products **2**. The ee values of **2** were determined by HPLC or SFC analysis on a chiral stationary phase, the dr were determined by NMR analysis.

b. Copper-Catalyzed Enantioselective Methylboration of substrates 3



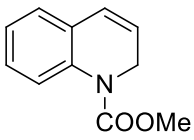
3 **4**

In a nitrogen-filled glovebox, CuI (3.8 mg, 0.02 mmol, 10 mol%), (*S*,*S*)-Ph-BPE (12.2mg, 0.024 mmol, 12 mol%) and THF (1 mL), then the mixture was stirred 30 minutes at room

temperature. To the mixture was added B_2pin_2 (76.2 mg, 0.3 mmol, 1.5equiv) and **3** (0.20 mmol, 1 equiv), CH_3I (85.2 mg, 0.6 mmol, 3 equiv) and ^tBuOK (33.7 mg, 0.3 mmol, 1.5 equiv) successively. After that, 0.5 mL of THF was added along the vial's wall to keep all reacts into the reaction solution. The vial was sealed was a rubber stopper, removed from the glovebox and stirred at room temperature for 16 hours. Upon completion of the reaction, the reaction mixture was passed through a short silica gel column eluting with Et_2O. The solvent was removed under vacuo, and the residue was purified by column chromatography on silica gel using petroleum ether/EtOAc as an eluent (PE/EA/ = 20/1 to 100/1) to give the corresponding borylation products **4**. The ee values of **4** were determined by HPLC or SFC analysis on a chiral stationary phase, the dr were determined by NMR analysis.

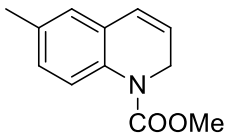
4. The Characterization Data for Substrates

Methyl quinoline-1(2*H*)-carboxylate (1a)



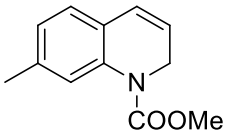
1.03 g, yield: 27%; ^1H NMR ($CDCl_3$, 600 MHz) δ: 7.57 (d, J = 7.2 Hz, 1H), 7.26-7.18 (m, 1H), 7.09-7.05 (m, 2H), 6.49 (d, J = 9.6 Hz, 1H), 6.02-5.98 (m, 1H), 4.41 (dd, J = 4.2 Hz, 1.8 Hz, 2H), 3.79 (s, 3H). ^{13}C NMR ($CDCl_3$, 150 MHz) δ: 154.8, 136.4, 128.1, 127.5, 126.5, 126.4, 125.6, 124.5, 123.7, 53.1, 43.6.

Methyl 6-methylquinoline-1(*2H*)-carboxylate (1b)



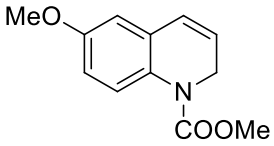
1.09 g, yield: 26%; ^1H NMR ($CDCl_3$, 600 MHz) δ: 7.44 (s, 1 H), 7.00 (dd, J = 8.2, 1.6 Hz, 1 H), 6.87 (s, 1 H), 6.43 (d, J = 9.5 Hz, 1 H), 5.97 (dt, J = 8.7, 3.8 Hz, 1 H), 4.38 (dd, J = 4.1, 1.7 Hz, 2 H), 3.77 (s, 3 H), 2.29 (s, 3 H). ^{13}C NMR ($CDCl_3$, 150 MHz) δ: 154.9, 134.1, 133.9, 128.1, 126.9, 126.5, 123.5, 53.1, 43.6, 20.9.

Methyl 7-methylquinoline-1(*2H*)-carboxylate (1c)



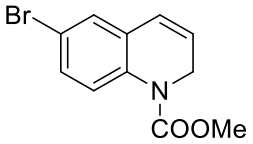
1.1g, yield: 27%; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.32 (s, 1 H), 6.85 (d, J = 7.7 Hz, 1 H), .79 (d, J = 7.8 Hz, 1 H), 6.36 (d, J = 9.5 Hz, 1 H), 5.83 (dt, J = 9.0, 4.1 Hz, 1 H), 4.28 (d, J = 3.7 Hz, 2 H), 3.69 (s, 3 H), 2.25 (s, 3 H). ^{13}C NMR ($CDCl_3$, 150 MHz) δ: 154.9, 137.5, 136.3, 126.4, 126.2, 125.5, 125.3, 124.2, 53.1, 43.6, 21.7.

Methyl 6-methoxyquinoline-1(2*H*)-carboxylate (1d)



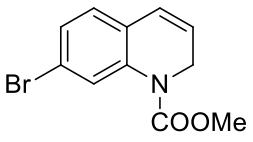
0.92g, yield: 21%; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.46 (s, 1H), 6.75 (dd, J = 11.8 Hz, 2.9 Hz, 1H), 6.60 (d, J = 2.9 Hz, 1H), 6.44 (d, J = 9.6 Hz, 1H), 6.04-5.99 (m, 1H), 4.37 (dd, J = 4.1 Hz, 1.7 Hz, 2H), 3.77 (d, J = 5.2 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 156.9, 155.4, 130.0, 129.7, 127.0, 125.3, 113.3, 111.7, 56.0, 53.5, 44.0.

Methyl 6-bromoquinoline-1(2*H*)-carboxylate (1e)



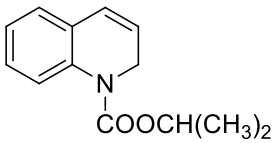
0.54 g, yield: 10%; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.46 (d, J = 8.0 Hz, 1H), 7.27 (dd, J = 8.7 Hz, 2.3 Hz, 1H), 7.16 (d, J = 2.3 Hz, 1H), 6.38 (d, J = 9.6 Hz, 1H), 6.03-5.98 (m, 1H), 4.38 (dd, J = 4.2 Hz, 1.8 Hz, 2H), 3.78 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 155.0, 135.8, 130.6, 130.3, 129.4, 127.4, 125.9, 125.7, 117.7, 53.7, 44.0.

Methyl 7-bromoquinoline-1(2*H*)-carboxylate (1f)



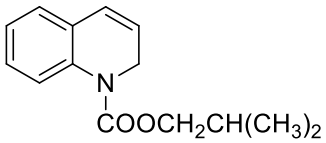
0.97 g, yield: 18%; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.78 (s, 1H), 7.16 (dd, J = 8.1 Hz, 2.0 Hz, 1H), 6.88 (d, J = 8.1 Hz, 1H), 6.41 (d, J = 9.6 Hz, 1H), 6.00-5.95 (m, 1H), 4.37 (dd, J = 4.2 Hz, 1.8 Hz, 2H), 3.79 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 154.9, 137.9, 128.0, 127.9, 127.2, 126.9, 126.2, 121.2, 53.8, 44.1.

Isopropyl quinoline-1(2*H*)-carboxylate (1g)



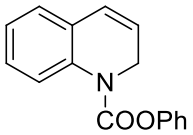
0.61 g, yield: 14%; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.60 (d, J = 8.1 Hz, 1H), 7.26-7.15 (m, 1H), 7.04 (d, J = 4.1 Hz, 2H), 6.47 (dd, J = 9.4, 1.4 Hz, 1H), 6.01-5.96 (m, 1H), 5.08-5.02 (m, 1H), 4.42-4.39 (m, 2H), 1.31 (d, J = 6.3 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 154.4, 137.1, 128.5, 127.8, 127.0, 126.8, 126.1, 124.7, 124.1, 70.3, 43.8, 22.6.

Isobutyl quinoline-1(2*H*)-carboxylate (1h)



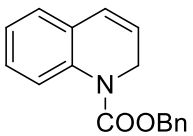
0.51 g, yield: 11%; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.59 (d, J = 8.0 Hz, 1H), 7.21-7.17 (m, 1H), 7.08-7.04 (m, 2H), 6.48 (dt, J = 9.5 Hz, 1.4 Hz, 1H), 6.02-5.98 (m, 1H), 4.42 (dd, J = 4.2 Hz, 1.8 Hz, 2H), 3.98 (d, J = 6.6 Hz, 2H), 2.03-1.93 (m, 1H), 0.95 (d, J = 6.7 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 154.9, 137.0, 128.5, 127.8, 127.0, 126.8, 126.1, 124.8, 124.2, 72.8, 43.9, 28.4, 19.7.

Phenyl quinoline-1(2*H*)-carboxylate (1i)



2.3 g, yield: 46%; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.72 (s, 1H), 7.42-7.38 (m, 2H), 7.26-7.12 (m, 6H), 6.58 (dd, J = 9.6 Hz, 1.3 Hz, 1H), 6.11-6.06 (m, 1H), 4.56 (s, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 153.2, 151.6, 136.5, 129.9, 128.8, 128.1, 127.1, 127.0, 126.2, 125.5, 124.3, 122.2, 44.4.

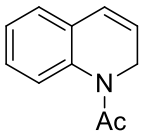
Benzyl quinoline-1(2*H*)-carboxylate (1j)



1.65 g, yield: 31%; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.68 (d, J = 6.6 Hz, 1H), 7.45-7.34 (m, 5H), 7.26-7.21 (m, 1H), 7.13-7.08 (m, 2H), 6.52 (d, J = 9.6 Hz, 1H), 6.03-5.99 (m, 1H), 5.29 (s, 2H), 4.47 (dd, J = 4.2 Hz, 1.8 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 154.7, 136.9, 136.8, 129.2, 128.8, 128.7, 128.6, 128.0, 127.0, 126.9, 126.0, 125.1, 124.3, 68.3,

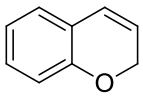
44.2.

1-(Quinolin-1(2*H*)-yl)ethanone (1k)



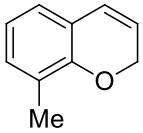
1.02 g, yield: 59%; ^{1}H NMR ($CDCl_3$, 600 MHz) δ: 7.28-7.11 (m, 4H), 6.53 (d, J = 9.5 Hz, 1H), 6.10-6.09 (m, 1H), 4.47 (s, 2H), 2.21 (s, 3H). ^{13}C NMR ($CDCl_3$, 150 MHz) δ: 170.1, 137.1, 129.4, 128.3, 127.2, 126.5, 126.2, 125.7, 123.9, 41.4, 22.5.

2*H*-chromene (3a)



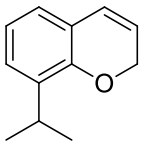
0.5 g, 75% yield; ^{1}H NMR (600 MHz, $CDCl_3$) δ: 6.67 (t, J = 6.2 Hz, 1H), 6.56 (d, J = 6.0 Hz, 1H), 6.50 – 6.47 (m, 1H), 6.41 (d, J = 6.3 Hz, 1H), 6.13 (dd, J = 7.8, 0.9 Hz, 1H), 5.63 – 5.59 (m, 1H), 4.85 (dt, J = 2.6, 1.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 143.3, 123.4, 121.3, 119.7, 118.0, 117.6, 117.1, 112.6, 72.5.

8-methyl-2*H*-chromene (3b)



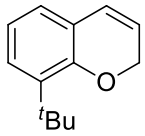
0.62 g, 85% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.87 (d, J = 7.2 Hz, 1H), 6.75 – 6.60 (m, 2H), 6.31 (dt, J = 9.8, 1.7 Hz, 1H), 5.66 (dt, J = 9.8, 3.5 Hz, 1H), 4.74 (dd, J = 3.5, 1.8 Hz, 2H), 2.07 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 152.0, 130.7, 125.0, 124.9, 124.3, 121.9, 121.6, 120.6, 65.4.

8-isopropyl-2*H*-chromene (3c)



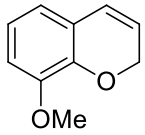
1.24 g, 71% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.03 (dd, J = 7.1, 2.1 Hz, 1H), 6.83 – 6.75 (m, 2H), 6.39 (dt, J = 9.8, 1.7 Hz, 1H), 5.73 (dt, J = 9.7, 3.6 Hz, 1H), 4.75 (dd, J = 3.6, 1.7 Hz, 2H), 3.27 – 3.12 (m, 1H), 1.19 (s, 1H), 1.18 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 151.1, 135.8, 126.1, 125.3, 124.2, 122.3, 121.8, 121.0, 65.3, 26.7, 22.6.

8-(*tert*-butyl)-2*H*-chromene (3d)



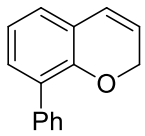
1.47 g, 78% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.14 – 6.90 (m, 1H), 6.90 – 6.67 (m, 2H), 6.37 (d, J = 9.7 Hz, 1H), 5.75 (dt, J = 9.4, 3.5 Hz, 1H), 4.84 – 4.29 (m, 2H), 1.30 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 150.4, 132.0, 126.0, 125.2, 124.4, 122.5, 121.4, 119.0, 64.3, 34.4, 29.7.

8-methoxy-2*H*-chromene (3e)



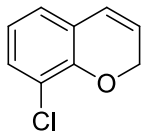
1.12 g, 69% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.88 – 6.68 (m, 2H), 6.59 (dd, J = 7.1, 1.4 Hz, 1H), 6.39 (d, J = 9.8 Hz, 1H), 5.76 (dt, J = 9.7, 3.5 Hz, 1H), 4.86 (dd, J = 3.4, 1.8 Hz, 2H), 3.84 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ: 147.6, 142.7, 124.5, 123.0, 122.0, 120.8, 118.9, 112.0, 65.7, 55.9.

8-phenyl-2*H*-chromene (3f)



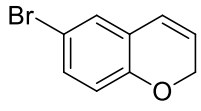
1.58g, 76% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.57 – 7.51 (m, 2H), 7.46 – 7.38 (m, 2H), 7.36 – 7.30 (m, 1H), 7.18 (dd, J = 7.1, 2.2 Hz, 1H), 7.01 – 6.90 (m, 2H), 6.49 (dt, J = 9.8, 1.8 Hz, 1H), 5.82 (dt, J = 9.8,3.6 Hz, 1H), 4.80 (dd, J = 3.6, 1.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 150.8, 137.9, 130.5, 129.3, 128.0, 127.0, 126.0, 124.9, 122.9, 122.1, 121.2, 65.4.

8-chloro-2*H*-chromene (3g)



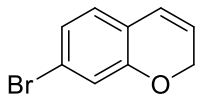
0.58 g, 70% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.13 (dd, J = 7.9, 1.7 Hz, 1H), 6.82 (dd, J = 7.5, 1.7 Hz, 1H), 6.78 – 6.73 (m, 1H), 6.37 (dt, J = 9.9, 1.9 Hz, 1H), 5.77 (dt, J = 9.9, 3.5 Hz, 1H), 4.92 (dd, J = 3.5, 1.9 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 149.8, 129.8, 125.1, 124.1, 123.7, 122.6, 121.6, 120.8, 66.4.

6-bromo-2*H*-chromene (3h)



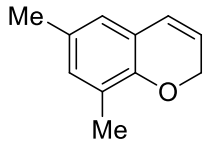
0.92 g, 87% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.16 (dd, J = 8.5, 2.4 Hz, 1H), 7.05 (d, J = 2.4 Hz, 1H), 6.63 (d, J = 8.5 Hz, 1H), 6.33 (dt, J = 9.9, 1.9 Hz, 1H), 5.79 (dt, J = 9.9, 3.5 Hz, 1H), 4.81 (dd, J = 3.5, 1.9 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 153.0, 131.9, 129.1, 124.2, 123.6, 123.4, 117.5, 113.3, 65.7.

7-bromo-*2H*-chromene (3i)



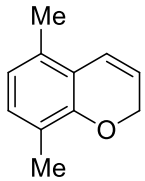
^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.17 (dd, J = 8.5, 2.4 Hz, 1H), 7.06 (d, J = 2.4 Hz, 1H), 6.65 (d, J = 8.5 Hz, 1H), 6.34 – 6.34 (m, 1H), 5.80 – 5.78 (m, 1H), 4.82 (dd, J = 3.5, 1.9 Hz, 2H). ^{13}C NMR ($CDCl_3$, 151 MHz) δ 153.1, 131.6, 129.0, 124.1, 123.6, 123.2, 117.5, 113.2, 65.6.

6, 8-dimethyl-2*H*-chromene (3j)



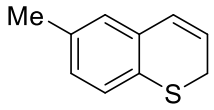
0.48 g, 59% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.69 (s, 1H), 6.53 (s, 1H), 6.28 (d, J = 9.8 Hz, 1H), 5.65 (dt, J = 9.5, 3.5 Hz, 1H), 4.69 (s, 2H), 2.12 (s, 3H), 2.05 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 150.4, 131.4, 129.9, 125.1, 124.8, 124.7, 121.9, 121.8, 65.5, 20.5, 15.5.

5, 8-dimethyl-2*H*-chromene (3k)



1.21 g, 76% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.90 (d, J = 7.6 Hz, 1H), 6.68 – 6.62 (m, 2H), 5.84 (dt, J = 9.9, 3.7 Hz, 1H), 4.78 (dd, J = 3.7, 1.7 Hz, 2H), 2.29 (s, 3H), 2.18 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 152.4, 131.6, 130.1, 122.8, 122.4, 122.3, 121.4, 120.7, 64.8, 18.3, 15.5.

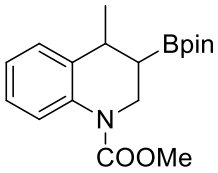
6-methyl-2H-thiochromene (3l)



0.52 g, 71% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.10 (d, J = 7.9 Hz, 1H), 6.91 (ddd, J = 7.8, 1.8, 0.5 Hz, 1H), 6.87 (s, 1H), 6.44 (dt, J = 10.1, 1.6 Hz, 1H), 5.94 (dt, J = 10.1, 5.1 Hz, 1H), 3.42 (dd, J = 5.1, 1.6 Hz, 2H), 2.28 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 135.37, 132.15, 129.40, 128.93, 128.78, 128.13, 127.05, 121.98, 25.32, 20.99.

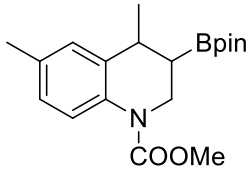
5. The Characterization Data for products

Methyl 4-methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3,4-dihydroquinoline-1(*2H*)-carboxylate (2a)



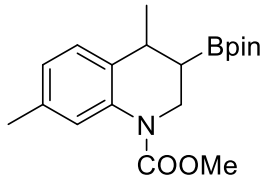
49.7 mg, 75% yield; ^{1}H NMR ($CDCl_3$, 600 MHz) δ: 7.74 (d, J = 8.2Hz, 1 H), 7.17-7.10 (m, 1 H), 7.07 (dd, J = 7.6, 1.7Hz, 1 H), 6.96 (td, J = 7.4, 1.2Hz, 1 H), 4.00 (ddd, J = 12.9, 5.7, 0.91Hz, 1 H), 3.79 (s, 3 H), 3.72-3.62 (m, 1 H), 3.06 (qd, J = 7.1, 3.9Hz, 1 H), 1.57 (ddd, J = 12.2, 5.7, 4.0 Hz, 1 H), 1.23 (d, J = 1.4 Hz, 12 H), 1.20 (d, J = 7.1 Hz, 3 H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 155.6, 136.8, 136.3, 127.2, 126.2, 123.6, 123.2, 83.6, 52.8, 43.3, 33.6, 25.1, 24.9, 24.8, 18.7. TOF-HRMS Calcd. for $C_{18}H_{26}BNO_4$ [M+H$^+$]: 332.2031, found 332.2028. 99.9% ee, dr > 99:1. $[\alpha]_D^{30}$ = 2.8 (c= 1.0, CH_2Cl_2). Enantiomeric excess of the corresponding hydroxyl compound obtained by oxidation with $NaBO_3$ in THF/H_2O (1:1); HPLC condition: Lux 5u Amylose-1 (250 × 4.60 mm), ipa : hex = 10:90, 1.0 mL/min, 254 nm; t_A = 19.5 min (minor), t_B = 20.6 min (major).

Methyl 4,6-dimethyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3,4-dihydroquinoline-1(*2H*)-carboxylate (2b)



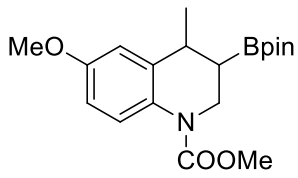
47.0 mg, 68% yield; ^{1}H NMR ($CDCl_3$, 600 MHz) δ: 7.61 (d, J = 8.5 Hz, 1 H), 6.94 (dd, J = 8.4, 1.8 Hz, 1 H), 6.88 (d, J = 1.9 Hz, 1 H), 3.99 (ddd, J = 12.9, 5.6, 0.8 Hz, 1 H), 3.78 (s, 3 H), 3.63 (d, J = 12.7 Hz, 1 H), 3.02 (qd, J = 7.1, 4.0 Hz, 1 H), 2.26 (s, 3 H), 1.59-1.52 (2 H, m), 1.23 (s, 12 H), 1.18 (d, J = 7.2 Hz, 3 H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 155.6, 136.1, 134.3, 132.6, 127.8, 126.8, 123.5, 83.6, 54.8, 52.8, 43.1, 33.5, 25.1, 25.0, 24.8, 20.8, 18.9. TOF-HRMS Calcd. for $C_{19}H_{28}BNO_4$ [M+H$^+$]: 346.2188, found 346.2190. 99.9% ee, dr > 99:1. $[\alpha]_D^{30}$ = 4.0 (c= 1.0, CH_2Cl_2). Enantiomeric excess of the corresponding hydroxyl compound obtained by oxidation with $NaBO_3$ in THF/H_2O (1:1); HPLC condition: Lux 5u Amylose-1 (250 × 4.60 mm), ipa : hex = 10:90, 1.0 mL/min, 254 nm; t_A = 10.1 min (major), t_B = 11.4 min (minor).

Methyl 4,7-dimethyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3,4-dihydroquinoline-1(*2H*)-carboxylate (2c)



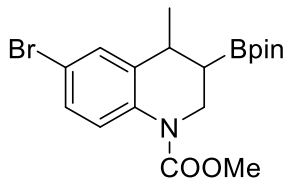
51.1 mg, 74% yield; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.60 (s, 1 H), 6.96 (d, J = 7.7 Hz, 1 H), 6.81-6.74 (m, 1 H), 4.00 (ddd, J = 13.0, 5.6, 0.8 Hz, 1 H), 3.79 (s, 3 H), 3.64 (t, J = 12.7 Hz, 1 H), 3.04 (qd, J = 7.1, 4.1 Hz, 1 H), 2.29 (s, 3 H), 1.56 (dd, J = 11.9, 5.4 Hz, 1 H), 1.23 (d, J = 2.21 Hz, 12 H), 1.17 (d, J = 7.1 Hz, 3 H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 155.6, 136.7, 135.7, 133.3, 127.2, 124.0, 123.9, 83.6, 52.8, 43.1, 33.1, 25.0, 24.8, 21.5, 19.0. TOF-HRMS Calcd. for $C_{19}H_{28}BNO_4$ [M+H$^+$]: 346.2188, found 346.2190. 99% ee, dr > 99:1. $[\alpha]_D^{30}$ = 3.6 (c= 1.0, CH_2Cl_2). Enantiomeric excess of the corresponding hydroxyl compound obtained by oxidation with $NaBO_3$ in THF/H_2O (1:1); SFC condition: Lux 5u Cellulose-1 (250 × 4.60 mm), MeOH : CO_2 = 10:90, 3.0 mL/min, 254 nm; t_A = 3.4 min (minor), t_B = 3.7 min (major).

Methyl 6-methoxy-4-methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3,4-dihydroquinoline-1(*2H*)-carboxylate (2d)



56.4 mg, 78% yield; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.63 (d, J = 7.7 Hz, 1 H), 6.70 (1 H, dd, J = 9.0, 3.0 Hz), 6.63 (1 H, d, J = 3.0 Hz), 3.96 (1 H, ddd, J = 12.9, 5.8, 0.7 Hz), 3.76 (6 H, d, J = 7.6 Hz), 3.70-3.62 (1 H, m), 3.02 (1 H, qd, J = 7.1, 4.0 Hz), 1.56 (ddd, J = 12.1, 5.8, 4.0 Hz, 1 H), 1.23 (s, 12 H), 1.19 (d, J = 7.1 Hz, 3 H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 155.6, 130.1, 124.7, 112.4, 111.4, 83.6, 55.5, 52.8, 43.2, 33.9, 25.0, 24.8, 18.6. TOF-HRMS Calcd. for $C_{19}H_{28}BNO_5$ [M+H$^+$]: 362.2137, found 362.2140. 99.9% ee, dr > 99:1. $[\alpha]_D^{30}$ = 4.3 (c= 1.0, CH_2Cl_2). Enantiomeric excess of the corresponding hydroxyl compound obtained by oxidation with $NaBO_3$ in THF/H_2O (1:1); SFC condition: Lux 5u Cellulose-1 (250 × 4.60 mm), MeOH : CO_2 = 10:90, 3.0 mL/min, 254 nm; t_A = 6.7 min (minor), t_B = 8.3 min (major).

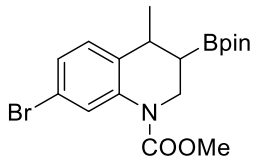
Methyl 6-bromo-4-methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3,4-dihydroquinoline-1(*2H*)-carboxylate (2e)



57.4 mg, 70% yield; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.68 (d, J = 8.7 Hz, 1 H), 7.25-7.21 (m, 1 H), 7.19 (d, J = 2.3 Hz, 1 H), 3.97 (ddd, J = 13.0, 5.7, 0.8 Hz, 1 H), 3.79 (s, 3 H), 3.69-3.61 (m, 1 H), 3.00 (1 H, td, J = 7.1, 4.1 Hz), 1.54 (dq, J = 9.6, 3.9, 2.8 Hz, 1 H), 1.22 (s, 12 H), 1.18 (s, 3 H). ^{13}C NMR ($CDCl_3$, 150 MHz) δ: 155.4, 138.3, 136.0, 129.8, 129.1, 125.1, 115.9, 100.0, 83.7, 52.9, 43.4, 33.5, 24.9, 24.8, 18.5. TOF-HRMS Calcd. for $C_{18}H_{25}BBrNO_4$ [M+H$^+$]: 410.1136, found 410.1139. 88% ee, dr > 99:1. $[\alpha]_D^{30}$ = 9.8 (c= 1.0, CH_2Cl_2). Enantiomeric excess of the corresponding hydroxyl compound obtained by oxidation with $NaBO_3$ in THF/H_2O (1:1); HPLC condition: Lux 5u

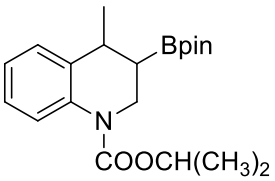
Amylose-1 (250 × 4.60 mm), ipa : hex = 10:90, 1.0 mL/min, 254 nm; t_A = 11.1 min (major), t_B = 13.9 min (minor).

Methyl 7-bromo-4-methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3,4-dihydroquinoline-1(*2H*)-carboxylate (2f)



57.4 mg, 70% yield; ^{1}H NMR ($CDCl_3$, 600 MHz) δ: 8.02 (s, 1 H), 7.08 (dd, J = 8.1, 2.0 Hz, 1 H), 6.93 (d, J = 8.1 Hz, 1 H), 3.98 (dd, J = 13.0, 5.6 Hz, 1 H), 3.81 (s, 3 H), 3.64 (t, J = 12.6 Hz, 1 H), 3.02 (m, 1 H), 1.56-1.50 (m, 1 H), 1.23 (d, J = 2.6 Hz, 12 H), 1.17 (d, J = 7.1 Hz, 3 H). ^{13}C NMR ($CDCl_3$, 150 MHz) δ: 155.3, 138.1, 134.8, 128.5, 126.1, 125.9, 119.4, 83.7, 53.0, 43.2, 33.2, 24.9, 24.8, 18.6. TOF-HRMS Calcd. for $C_{18}H_{25}BBrNO_4$ [M+H$^+$]: 410.1136, found 410.1138. 96% ee, dr > 99:1. $[\alpha]_D^{30}$ = -10.6 (c= 1.0, CH_2Cl_2). Enantiomeric excess of the corresponding hydroxyl compound obtained by oxidation with $NaBO_3$ in THF/H_2O (1:1); HPLC condition: Lux 5u Amylose-1 (250 × 4.60 mm), ipa : hex = 10:90, 1.0 mL/min, 254 nm; t_A = 4.9 min (minor), t_B = 5.6 min (major).

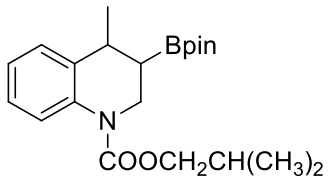
Isopropyl 4-methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3,4-dihydroquinoline-1(*2H*)-carboxylate (2g)



51.0 mg, 71% yield; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.73 (d, J = 8.2 Hz, 1 H), 7.16-7.03 (m, 2 H), 6.95 (td, J = 7.4, 1.2 Hz, 1 H), 5.04 (hept, J = 6.2 Hz, 1 H), 4.00 (ddd, J = 12.9, 5.7, 0.9 Hz, 1 H), 3.63 (dd, J = 12.8, 12.3 Hz, 1 H), 3.05 (qd, J = 7.1, 4.0 Hz, 1 H), 1.56 (qd, J = 5.9, 4.0 Hz, 1 H), 1.30 (dd, J = 6.2, 3.1 Hz, 6 H), 1.23-1.22 (12 H, m), 1.20 (d, J = 7.1 Hz, 3 H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 154.8, 137.1, 136.3, 127.1, 126.0, 123.8, 122.9, 83.6, 69.3, 43.1, 33.6, 25.0, 24.8, 22.2, 18.7. TOF-HRMS Calcd. for $C_{20}H_{30}BNO_4$ [M+H$^+$]: 360.2344, found 360.2341. 98% ee, dr > 99:1. $[\alpha]_D^{30}$ = 3.9 (c= 1.0,

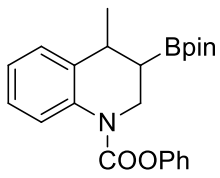
CH_2Cl_2). Enantiomeric excess of the corresponding hydroxyl compound obtained by oxidation with $NaBO_3$ in THF/H_2O (1:1); SFC condition: Lux 5u Cellulose-1 (250 × 4.60 mm), MeOH : CO_2 = 10:90, 3.0 mL/min, 254 nm; t_A = 2.8 min (minor), t_B = 3.0 min (major).

Isobutyl 4-methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3,4-dihydroquinoline-1(*2H*)-carboxylate (2h)



56.7 mg, 76% yield; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.73 (d, J = 8.3 Hz, 1 H), 7.17-7.03 (2 H, m), 6.96 (td, J 7.4, 1.2 Hz, 1 H), 4.04 (ddd, J = 12.9, 5.6, 0.9 Hz, 1 H), 4.00-3.95 (2 H, m), 3.66 (dd, J = 12.9, 12.1 Hz, 1 H), 3.06 (qd, J = 7.1, 4.1 Hz, 1 H), 2.00 (hept, J = 6.7 Hz, 1 H), 1.58 (ddd, J = 12.0, 5.5, 4.1 Hz, 1 H), 1.22 (s, 12 H), 1.20 (s, 3 H), 0.96 (d, J = 6.7 Hz, 6 H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 155.3, 137.0, 136.2, 127.2, 126.0, 123.9, 123.1, 100.0, 83.6, 43.2, 33.5, 28.1, 25.0, 24.8, 19.3, 18.9. TOF-HRMS Calcd. for $C_{21}H_{32}BNO_4$ [M+H$^+$]: 374.1498, found 374.2501. 98% ee, dr > 99:1. $[\alpha]_D^{30}$ = -3.0 (c= 1.0, CH_2Cl_2). Enantiomeric excess of the corresponding hydroxyl compound obtained by oxidation with $NaBO_3$ in THF/H_2O (1:1); SFC condition: Lux 5u Cellulose-1 (250 × 4.60 mm), MeOH : CO_2 = 10:90, 3.0 mL/min, 254 nm; t_A = 3.0 min (minor), t_B = 3.3 min (major).

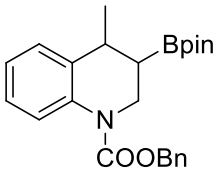
Phenyl 4-methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3,4-dihydroquinoline-1(*2H*)-carboxylate (2i)



56.6 mg, 72% yield; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.87 (d, J = 8.1 Hz, 1 H), 7.40-7.35 (m, 2 H), 7.24-7.16 (m, 4 H), 7.16-7.10 (m, 2 H), 7.01 (td, J = 7.4, 1.2 Hz, 1 H), 4.19 (dd, J = 13.0, 5.5 Hz, 1 H), 3.93-3.80 (m, 1 H), 3.14 (qd, J = 7.2, 4.1 Hz, 1 H), 1.68 (ddd, J = 12.1, 5.7, 4.0 Hz, 1 H), 1.28 (d, J = 7.1 Hz, 3 H), 1.24 (s, 12 H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 153.5, 151.4, 136.5, 129.4, 127.3, 126.4, 125.5, 123.7, 121.9, 100.0,

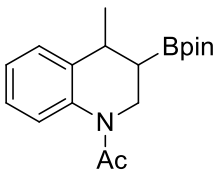
83.7, 83.6, 43.9, 33.6, 25.1, 25.0, 24.8, 18.8. TOF-HRMS Calcd. for $C_{23}H_{28}BNO_4$ [M+H$^+$]: 394.2188, found 394.2190. 99.9% ee, dr > 99:1. $[\alpha]_D^{30}$ = 10.4 (c= 1.0, CH_2Cl_2). Enantiomeric excess of the corresponding hydroxyl compound obtained by oxidation with $NaBO_3$ in THF/H_2O (1:1); SFC condition: Lux 5u Cellulose-1 (250 × 4.60 mm), MeOH : CO_2 = 10:90, 3.0 mL/min, 254 nm; t_A = 9.4 min (major), t_B = 10.2 min (minor).

Benzyl 4-methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3,4-dihydroquinoline-1(*2H*)-carboxylate (2j)



57.0 mg, 70% yield; ^{1}H NMR ($CDCl_3$, 600 MHz) δ: 7.75 (d, *J* = 5.5 Hz, 1 H), 7.42-7.39 (m, 2 H), 7.35 (td, *J* = 6.6, 6.1, 1.5 Hz, 2 H), 7.32-7.29 (m, 1 H), 7.12 (ddd, *J* = 8.5, 7.5, 1.6 Hz, 1 H), 7.08 (dd, *J* = 7.6, 1.5 Hz, 1 H), 6.97 (td, *J* = 7.4, 1.1 Hz, 1 H), 5.30-5.20 (m, 2 H), 4.10-4.03 (m, 1 H), 3.75-3.67 (m, 1 H), 3.07 (qd, *J* = 7.1, 4.1 Hz, 1 H), 1.61-1.56 (m, 1 H), 1.22 (d, *J* = 2.2 Hz, 12 H,), 1.20 (s, 3 H). ^{13}C NMR ($CDCl_3$, 150 MHz) δ: 155.0, 136.8, 136.8, 136.6, 128.6, 128.0, 127.9, 127.2, 126.2, 83.6, 67.3, 43.5, 33.5, 29.8, 25.0, 24.8, 18.8. TOF-HRMS Calcd. for $C_{24}H_{30}BNO_4$ [M+H$^+$]: 408.2345, found 408.2342. 99.9% ee, dr > 99:1. $[\alpha]_D^{30}$ = 4.6 (c= 1.0, CH_2Cl_2). Enantiomeric excess of the corresponding hydroxyl compound obtained by oxidation with $NaBO_3$ in THF/H_2O (1:1); SFC condition: Lux 5u Cellulose-1 (250 × 4.60 mm), MeOH : CO_2 = 10:90, 3.0 mL/min, 254 nm; t_A = 11.3 min (minor), t_B = 13.9 min (major).

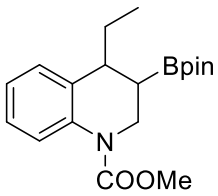
1-(4-methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3,4-dihydroquinolin-1(2H)-yl)ethanone (2k)



29.4 mg, 78% yield; ^{1}H NMR ($CDCl_3$, 600 MHz) δ: 7.27-7.22 (1 H, m), 7.17-7.12 (m, 2 H), 7.07-7.05 (m, 1 H), 3.89-3.84 (m, 2 H), 3.04 (qd, *J* = 7.2, 4.0

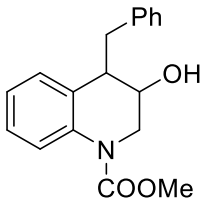
Hz, 1 H), 2.24 (s, 3 H), 1.57 (s, 3 H), 1.21 (s, 1 H), 1.19 (d, *J* = 3.6 Hz, 12H).^{13}C NMR ($CDCl_3$, 150 MHz) *δ*: 170.6, 126.7, 126.1, 124.9, 124.7, 83.6, 34.1, 29.4, 24.9, 24.8, 23.7. TOF-HRMS Calcd. for $C_{18}H_{26}BNO_4$ [M+H$^+$]: 316.2082, found 316.2080. 99% ee, dr > 99:1. $[\alpha]_D^{30}$ = 10.3 (c= 1.0, CH_2Cl_2). Enantiomeric excess of the corresponding hydroxyl compound obtained by oxidation with $NaBO_3$ in THF/H_2O (1:1); SFC condition: Lux 5u Cellulose-1 (250 × 4.60 mm), MeOH : CO_2 = 10:90, 3.0 mL/min, 254 nm; t_A = 5.08 min (minor), t_B = 5.37 min (major).

methyl 4-ethyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3,4-dihydroquinoline-1(*2H*)-carboxylate (2l)



Colorless oil, 21.8 mg, 54%. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.72 (d, *J* = 8.1 Hz, 1H), 7.19 – 7.14 (m, 1H), 7.03 – 7.00 (m, 1H), 6.96 (t, *J* = 7.4 Hz, 1H), 3.84 – 3.76 (m, 5H), 2.77 – 2.72 (m, 1H), 1.58 – 1.47 (m, 3H), 1.25 (s, 12H), 0.91 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR ($CDCl_3$, 101 MHz) δ 155.7, 136.5, 135.7, 127.8, 126.2, 123.9, 122.6, 83.5, 52.6, 44.1, 41.6, 24.8, 24.6, 23.9, 12.8. TOF-HRMS Calcd. for $C_{19}H_{29}BNO_4$ [M+H$^+$]: 346.2188, found 346.2190. 80% ee, dr > 99:1. $[\alpha]_D^{30}$ = 31.5 (c= 1.0, CH_2Cl_2). Enantiomeric excess of the corresponding hydroxyl compound obtained by oxidation with $NaBO_3$ in THF/H_2O (1:1); HPLC condition: Lux 5u Cellulose-1 (250 × 4.60 mm), ipa : hex = 5:95, 1.0 mL/min, 254 nm; t_A = 21.5 min (major), t_B = 23.4 min (minor).

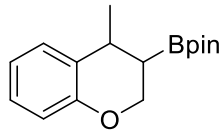
methyl 4-benzyl-3-hydroxy-3,4-dihydroquinoline-1(*2H*)-carboxylate (2m)



Colorless oil. ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.67 (d, *J* = 8.2 Hz, 1H), 7.31 – 7.30 (m, 2H), 7.25 – 7.24 (m, 4H), 7.21 (d, *J* = 7.6 Hz, 1H), 7.10 (td, *J* = 7.5, 1.2 Hz, 1H), 4.08 (s, 1H), 3.79 – 3.74 (m, 4H), 3.23 – 3.19 (m, 1H), 3.07 – 3.02 (m, 2H), 1.54 – 1.47 (m, 1H). ^{13}C NMR ($CDCl_3$, 101 MHz) δ 155.6, 139.5, 137.2, 130.1, 129.2, 128.5, 127.3, 126.9, 126.3, 124.4, 123.9, 66.4, 53.1, 51.4, 44.0, 34.2. TOF-HRMS Calcd. for

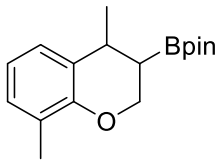
$C_{18}H_{20}NO_3$ [M+H$^+$]: 298.1438, found 298.1439. 89% ee, dr > 99:1. $[\alpha]_D^{30}$ = -41.1 (c= 1.0, CH_2Cl_2). HPLC condition: Lux 5u Amylose-2 (250 × 4.60 mm), CO_2 : MeOH = 94:6, 3.0 mL/min, 210 nm; t_A = 9.7 min (minor), t_B = 10.2 min (major).

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



60 mg, 73 % yield; ^{1}H NMR ($CDCl_3$, 600 MHz) δ: 7.07 – 7.03 (m, 2H), 6.81 (td, J = 7.5, 0.8 Hz, 1H), 6.77 (d, J = 8.2 Hz, 1H), 4.34 – 4.30 (ddd, J =11.8, 3.7, 0.9 Hz, 1H), 4.18 – 4.13 (m, 1H), 3.10 – 3.05 (m, 1H), 1.78 (dt, J = 12.5, 4.2 Hz, 1H), 1.27 (dd, J = 6.9 Hz, 3H), 1.26(s, 12H). ^{13}C NMR ($CDCl_3$, 150 MHz) δ: 152.97, 128.38, 127.97, 126.28, 118.90, 115.92, 82.69, 62.40, 29.02, 24.18, 23.89, 21.00. TOF-HRMS Calcd. for $C_{16}H_{24}BO_3$ [M+H$^+$]: 275.1816, found 275.1810. 99% ee, dr > 99:1; $[\alpha]_D^{25}$ = - 49.9 (c = 1, CH_2Cl_2); Enantiomeric excess of the corresponding hydroxyl compound obtained by oxidation with $NaBO_3$ in THF/H_2O (1:1); SFC condition: Lux 5u Cellulose-4 (250 × 4.60 mm), MeOH : CO_2 = 10:90, 3.0 mL/min, 230 nm; t_A = 2.9 min (major), t_B = 3.3 min (minor).

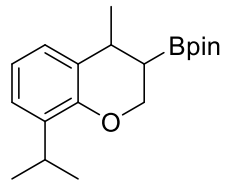
2-(4,8-dimethylchroman-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4b)



54 mg, 62 % yield; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 6.91 (dd, J = 11.5, 7.5 Hz, 2H), 6.71 (t, J = 7.4 Hz, 1H), 4.37 (ddd, J = 11.4, 3.7, 1.2 Hz, 1H), 4.15 (dd, J = 12.4, 11.6 Hz, 1H), 3.11 – 3.02 (m, 1 H), 2.16 (s, 3H), 1.76 (dt, J = 12.5, 4.1Hz, 1H), 1.26 (d, J =7.1Hz, 3H), 1.26(s, 12H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 151.95, 128.23, 128.17, 126.93, 125.64, 118.96, 83.40, 63.29, 30.01, 25.09, 24.77, 22.05, 16.24. TOF-HRMS Calcd. for $C_{17}H_{26}BO_3$ [M+H$^+$]: 289.1973, found 289.1972. 99.9% ee, dr > 99:1; $[\alpha]_D^{25}$ = - 42.4 (c = 1, CH_2Cl_2); Enantiomeric excess of the corresponding hydroxyl compound obtained by oxidation with $NaBO_3$ in THF/H_2O (1:1); SFC condition: Lux 5u Cellulose-4 (250 × 4.60 mm), MeOH : CO_2 =

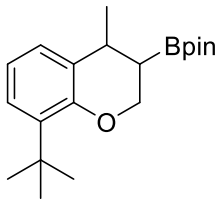
10:90, 3.0 mL/min, 230 nm; t_A = 3.1 min (major), t_B = 3.4 min (minor).

2-(8-isopropyl-4-methylchroman-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4c)



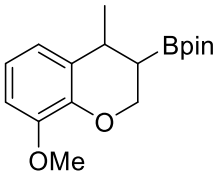
48 mg, 64 % yield; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.01 (dd, J = 7.5, 1.7 Hz, 1H), 6.90 (dd, J = 7.7, 1.5 Hz, 1H), 6.79 (t, J = 7.5 Hz, 1H), 4.38 (ddd, J = 11.4, 3.7, 1.3 Hz, 1H), 4.14 (dd, J = 12.4, 11.4 Hz, 1H), 3.25 (dt, J = 13.8, 6.9 Hz, 1H), 3.12 – 3.04 (m, 1H), 1.77 (dt, J = 12.4, 4.0 Hz 1H), 1.28 (d, J = 7.1 Hz, 3H), 1.26 (s, 12H), 1.19 (dd, J = 8.1, 6.9 Hz, 6H).^{13}C NMR ($CDCl_3$, 100 MHz) δ: 151.56, 136.49, 128.43, 126.98, 123.72, 119.40, 83.64, 77.53, 77.21, 76.89, 63.41, 30.37, 26.85, 25.20, 24.93, 22.86, 22.21. TOF-HRMS Calcd. for $C_{19}H_{29}BO_3$ [M+H$^+$]: 316.2106, found 316.2100. 99.9% ee, dr > 99:1; $[\alpha]_D^{25}$ = -29 (c = 0.3, CH_2Cl_2); Enantiomeric excess of the corresponding hydroxyl compound obtained by oxidation with $NaBO_3$ in THF/H_2O (1:1); SFC condition: Lux 5u Cellulose-1 (250 × 4.60 mm), MeOH: CO_2 =10:90, 3 mL/min, 230 nm; t_A = 2.6 min (major), t_B = 2.8 min (minor).

2-(8-(tert-butyl)-4-methylchroman-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4d)



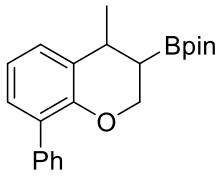
48 mg, 72 % yield; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.09 (dd, J = 7.7, 1.7 Hz, 1H), 6.94 (ddd, J = 7.5, 1.7, 0.5 Hz, 1H), 6.76 (t, J = 7.6 Hz, 1H), 4.41 (ddd, J = 11.3, 3.7, 1.4 Hz, 1H), 4.14 (dd, J = 12.4, 11.3 Hz, 1H), 3.10 (m, 1H), 1.81 – 1.74 (m, 1H), 1.36 (s, 9H), 1.30 (d, J = 6.9 Hz, 3H), 1.27 (s, 12 H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 153.33, 137.78, 129.02, 127.67, 124.29, 118.91, 83.33, 62.62, 34.96, 30.43, 29.78, 25.08, 24.83, 22.24. TOF-HRMS Calcd. for $C_{20}H_{32}BO_3$ [M+H$^+$]: 331.2443, found 331.2444. 99.9% ee, dr > 99:1; $[\alpha]_D^{25}$ = -52.5 (c = 0.5, CH_2Cl_2); Enantiomeric excess of the corresponding hydroxyl compound obtained by oxidation with $NaBO_3$ in THF/H_2O (1:1); HPLC condition: Lux 5u Amylose-1 (250 × 4.60 mm), ipa : hex =3: 97, 1 mL/min, 254 nm; t_A = 7.8 min (minor), t_B = 8.2 min (major).

2-(8-methoxy-4-methylchroman-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4e)



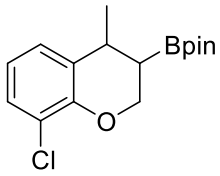
59 mg, 65 % yield; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 6.76 (dd, J = 8.2, 7.3 Hz, 1H), 6.70 – 6.65 (m, , 2H), 4.45 (ddd, J = 11.5, 3.8, 1.3 Hz, 1H), 4.19 (dd, J = 12.7, 11.5 Hz, 1H), 3.85 (s, 3H), 3.11 – 3.03 (m, 1H), 1.79 (dt, J = 12.7, 4.1 Hz, 1H), 1.26 (d, J = 7.1Hz, 3H), 1.26(s, 12H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 148.36, 143.51, 129.53, 121.39, 119.11, 108.75, 83.62, 63.65, 55.86, 29.78, 25.06, 24.83, 21.87. TOF-HRMS Calcd. for $C_{17}H_{26}BO_4$ [M+H$^+$]: 305.1922, found 305.1926. 99% ee, dr > 99:1; $[\alpha]_D^{25}$ = -25.0 (c = 0.5, CH_2Cl_2); Enantiomeric excess of the corresponding hydroxyl compound obtained by oxidation with $NaBO_3$ in THF/H_2O (1:1); SFC condition: Lux 5u Cellulose-1 (250 × 4.60 mm), MeOH: CO_2 =10:90, 3 mL/min, 210 nm; t_A = 5.3 min (minor), t_B = 5.9 min (major).

4,4,5,5-tetramethyl-2-(4-methyl-8-phenylchroman-3-yl)-1,3,2-dioxaborolane (4f)



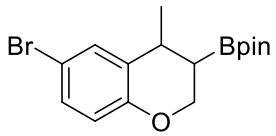
85 mg, 81 % yield; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.52 (dt, J = 8.1, 1.7 Hz, 2H), 7.40 – 7.35 (m, 2H), 7.29 (dt, J = 4.4, 1.7 Hz, 1H), 7.11 (dd, J = 7.5, 1.7 Hz, 1H), 7.05 (dd, J = 7.7, 1.9 Hz, 1H), 6.88 (t, J = 7.5 Hz, 1H), 4.34 (ddd, J = 11.5, 3.7, 1.3 Hz, 1H), 4.14 (dd, J = 12.3, 11.6 Hz, 1H), 3.19 – 3.10 (m, 1H), 1.84 – 1.77 (m, 1H), 1.32 (d, J = 7.1 Hz, 3H), 1.26 (s, 12H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 148.36, 129.52, 121.39, 119.11, 108.75, 83.62, 77.29, 63.65, 55.86, 29.78, 25.06, 24.83, 21.87. TOF-HRMS Calcd. for $C_{22}H_{28}BO_3$ [M+H$^+$]: 351.2130, found 351.2129. 99% ee, dr > 99:1; $[\alpha]_D^{25}$ = -48.6 (c = 1, CH_2Cl_2); Enantiomeric excess of the corresponding hydroxyl compound obtained by oxidation with $NaBO_3$ in THF/H_2O (1:1); SFC condition: Lux 5u Cellulose-1 (250 × 4.60 mm), MeOH: CO_2 =10:90, 3 mL/min, 230 nm; t_A = 5.9 min (minor), t_B = 7.4 min (major).

2-(8-chloro-4-methylchroman-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4g)



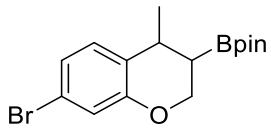
55 mg, 59% yield; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.14 (dd, J = 7.9, 1.4 Hz, 1H), 6.96 – 6.92 (m, 1H), 6.73 (t, J = 7.8 Hz, 1H), 4.48 (dd, J = 11.5, 3.8 Hz, 1H), 4.2 (t, J = 12.1 Hz ,1H), 3.13 – 3.05 (m, 1H), 1.77 (dt, J = 12.5, 4.1 Hz, 1H), 1.26 (d, J = 7.1 Hz, 3H), 1.26 (s, 12H).^{13}C NMR ($CDCl_3$, 100 MHz)δ: 149.88, 130.57, 127.83, 127.71, 121.38, 119.84, 83.73, 64.22, 30.15, 25.06, 24.78, 21.73. TOF-HRMS Calcd. for $C_{16}H_{23}BClO_3$ [M+H$^+$]: 309.1426, found 309.1420. 90% ee, dr > 99:1; $[\alpha]_D^{25}$ = -36.6 (c = 1, CH_2Cl_2); Enantiomeric excess of the corresponding hydroxyl compound obtained by oxidation with $NaBO_3$ in THF/H_2O (1:1); SFC condition: Lux 5u Cellulose-4 (250 × 4.60 mm), MeOH: CO_2 =10:90, 3 mL/min, 230 nm; t_A = 4.1 min (major), t_B = 5.5 min (minor).

2-(6-bromo-4-methylchroman-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4h)



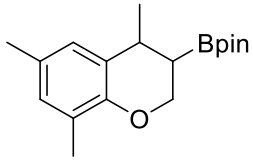
59 mg, 56% yield; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.13 (dd, J = 5.1, 1.5 Hz, 2H), 6.66 – 6.63 (m, 1H), 4.31 (ddd, J = 7.7, 2.4, 0.7 Hz, 1H), 4.15 – 4.09 (m, 1H), 3.06 – 3.00 (m, 1H), 1.73 (dt, J = 8.2, 2.8 Hz, 1H), 1.25 (d, J = 5.1 Hz, 3H), 1.25 (s, 12H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 153.33, 131.75, 130.94, 130.07, 118.69, 111.70, 83.72, 63.54, 29.94, 25.03, 24.79, 21.66. TOF-HRMS Calcd. for $C_{16}H_{23}BBrO_3$ [M+H$^+$]: 353.0921, found 353.0918. 84% ee, dr > 99:1; $[\alpha]_D^{25}$ = -8.2 (c = 1, CH_2Cl_2); Enantiomeric excess of the corresponding hydroxyl compound obtained by oxidation with $NaBO_3$ in THF/H_2O (1:1); SFC condition: Lux 5u Cellulose-1 (250 × 4.60 mm), MeOH: CO_2 =10:90, 3 mL/min, 230 nm; t_A = 4.0 min (major), t_B = 4.4 min (minor).

2-(7-bromo-4-methylchroman-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4i)



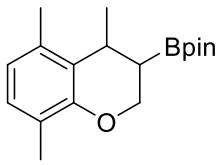
White soild, 43.1 mg, 61%. ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.15 – 7.13 (m, 2H), 6.67 – 6.65 (m, 1H), 4.32 (ddd, *J* = 11.4, 3.7, 1.3 Hz, 1H), 4.13 (dd, *J* = 12.5, 11.5 Hz, 1H), 3.07 – 3.02 (m, 1H), 1.74 (dt, *J* = 12.5, 4.2 Hz, 1H), 1.26 (d, *J* = 6.7 Hz, 15H). ^{13}C NMR ($CDCl_3$, 151 MHz) δ 153.2, 131.7, 130.8, 130.0, 118.6, 111.6, 83.6, 63.4, 29.8, 24.9, 24.7, 21.6. TOF-HRMS Calcd. for $C_{16}H_{23}BBrO_3$ [M+H$^+$]: 354.0918, found 354.0919. 99.9% ee, dr > 99:1. $[\alpha]_D^{30}$ = -31.8 (c = 1.0, CH_2Cl_2). Enantiomeric excess of the corresponding hydroxyl compound obtained by oxidation with $NaBO_3$ in THF/H_2O (1:1).

4,4,5,5-tetramethyl-2-(4,6,8-trimethylchroman-3-yl)-1,3,2-dioxaborolane (4j)



61 mg, 68 % yield; ^{1}H NMR ($CDCl_3$, 400 MHz) *δ*: 6.77 – 6.67 (dd, *J* = 24.0, 1.6 Hz, 2H), 4.35 (ddd, *J* = 11.4, 3.7, 1.3 Hz, 1H), 4.12 (dd, *J* = 12.5, 11.4 Hz, 1H), 3.07 – 2.98 (m, 1H), 2.17 (d, *J* = 31.0 Hz, 3H), 1.78 – 1.71 (m, 1H), 1.26 (d, *J* = 5.7 Hz, 3H), 1.26 (s, 12H). ^{13}C NMR ($CDCl_3$, 100 MHz) *δ*: 150.10, 129.20, 128.04, 127.90, 127.22, 125.60, 83.51, 63.23, 29.99, 25.08, 24.76, 22.07, 20.52, 16.10. TOF-HRMS Calcd. for $C_{18}H_{28}BO_3$ [M+H$^+$]: 303.2129, found 303.2132. 99.9% ee, dr > 99:1; $[\alpha]_D^{25}$ = -64.6 (c = 1, CH_2Cl_2); Enantiomeric excess of the corresponding hydroxyl compound obtained by oxidation with $NaBO_3$ in THF/H_2O (1:1); SFC condition: Lux 5u Cellulose-4 (250 × 4.60 mm), MeOH: CO_2 =10:90, 3 mL/min, 230 nm; t_A = 3.2 min (major), t_B = 3.5 min (minor).

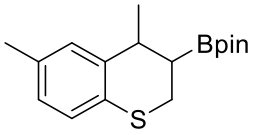
4,4,5,5-tetramethyl-2-(4,5,8-trimethylchroman-3-yl)-1,3,2-dioxaborolane (4k)



82 mg, 68% yield; ^{1}H NMR ($CDCl_3$, 600 MHz) *δ*: 6.86 (d, *J* = 7.5 Hz, 1H), 6.59 (d, *J* = 7.5 Hz, 1 H), 4.40 (ddd, *J* = 11.4, 3.9, 1.4 Hz, 1H), 4.23 (dd, *J* = 13.1, 11.5 Hz, 1H), 3.19 – 3.13 (m, 1H), 2.27 (s, 3H), 2.14 (s, 3H), 1.70 (dt, *J* = 13.1, 4.1 Hz, 1H), 1.29 (s, 12H), 1.21 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR ($CDCl_3$, 150 MHz) *δ*: 151.94,

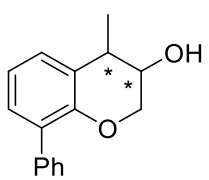
133.83, 127.90, 126.47, 123.51, 120.93, 83.57, 77.32, 77.11, 76.90, 62.59, 27.26, 25.10, 24.78, 19.27, 18.38, 16.26. TOF-HRMS Calcd. for $C_{18}H_{28}BO_3$ [M+H$^+$]: 303.2129, found 303.2131. 99% ee, dr > 99:1; $[\alpha]_D^{25}$ = -51.3 (c = 1, CH_2Cl_2); Enantiomeric excess of the corresponding hydroxyl compound obtained by oxidation with $NaBO_3$ in THF/H_2O (1:1); SFC condition: Lux 5u Amylose-1 (250 × 4.60 mm), MeOH: CO_2 =10:90, 3 mL/min, 230 nm; t_A = 3.0 min (major), t_B = 3.2 min (minor).

2-(4,6-dimethylthiochroman-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4l)



50 mg, 55% yield; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 6.98 – 6.93 (dd, J = 8.4, 0.6 Hz, 1H), 6.85 (d, J = 6.9 Hz, 2H), 3.26 – 3.18 (td, J = 13.5, 1.0 Hz, 1H), 3.14 (qd, J = 7.1, 3.0 Hz, 1H), 3.00 (dd, J = 12.6, 3.7 Hz, 1H), 2.23 (s, 3H), 1.62 – 1.55 (m, 1H), 1.25 (d, J = 1.1 Hz, 12H), 1.16 (dd, J = 7.1, 1.0 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 139.35, 133.10, 130.12, 128.32, 127.34, 126.32, 83.70, 77.41, 77.09, 76.77, 33.99, 25.00, 24.77, 23.66, 20.89, 19.81. TOF-HRMS Calcd. for $C_{17}H_{26}BO_2S$ [M+H$^+$]: 305.1744, found 305.1741. 99.9% ee, dr > 99:1; $[\alpha]_D^{25}$ = -25.9 (c = 1, CH_2Cl_2); Enantiomeric excess of the corresponding hydroxyl compound obtained by oxidation with $NaBO_3$ in THF/H_2O (1:1); SFC condition: Lux 5u Amylose-2 (250 × 4.60 mm), MeOH: CO_2 =10:90, 3 mL/min, 254 nm; t_A = 2.9 min (major), t_B = 3.1 min (minor).

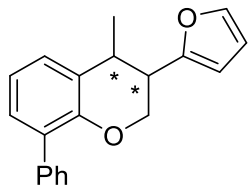
4-methyl-8-phenylchroman-3-ol (5)



48 mg, 92 % yield; ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.54 – 7.49 (m, 2H), 7.42 – 7.36 (m, 2H), 7.35 – 7.29 (m, 1H), 7.19 (dd, J = 15.5, 8.2 Hz, 2H), 6.99 (t, J = 7.6 Hz, 1H), 4.21 (dd, J = 11.1, 4.8 Hz, 1H), 4.14 – 4.05 (m, 2H), 3.18 (q, J = 9.4, 8.1 Hz, 1H), 1.78 (s, 1H), 1.44 (d, J = 7.1 Hz, 3H).^{13}C NMR (150 MHz, $CDCl_3$) δ:150.30,

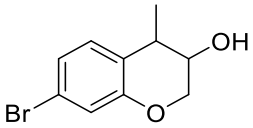
138.49, 129.96, 129.67, 129.31, 128.18, 128.06, 127.06, 125.59, 121.58, 69.03, 66.98, 35.45, 16.11.TOF-HRMS Calcd. for $C_{16}H_{16}O_2$ [M+H$^+$]: 263.1042, found 263.1041. 99.5% ee, dr > 99:1; $[\alpha]_D^{25}$ = -20.1 (c = 1, CH_2Cl_2); SFC condition:Lux 5u Cellulose-1 (250 × 4.60 mm), MeOH:CO_2 =10:90, 3 mL/min, 230 nm; t_A = 4.0 min (major), t_B = 4.4 min (minor).

3-(furan-2-yl)-4-methyl-8-phenylchromane (6)



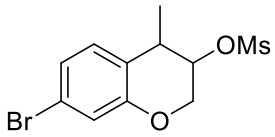
22 mg, 62 % yield; ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.54 (d, J = 7.1 Hz, 2H), 7.43 – 7.34 (m, 3H), 7.34 – 7.29 (m, 1H), 7.16 (dd, J = 22.7, 7.5 Hz, 2H), 6.96 (m, 1H), 6.33 (d, J = 3.3 Hz, 1H), 6.03 (d, J = 3.4 Hz, 1H), 4.42 (dd, J = 9.9, 3.8 Hz, 1H), 4.30 (m, 1H), 3.52 (dt, J = 10.2, 4.5 Hz, 1H), 3.37 (m, 1H), 1.13 (d, J = 6.9 Hz, 3H).^{13}C NMR (150 MHz, $CDCl_3$) δ: 153.62, 150.60, 141.44, 138.68, 130.06, 129.66, 129.12, 128.91, 128.03, 127.49, 126.96, 120.41, 110.16, 105.80, 63.79, 36.62, 33.58, 19.10.TOF-HRMS Calcd. for $C_{20}H_{18}O_2$ [M+H$^+$]: 291.1384, found 291.1382. 99.5% ee, dr > 99:1; $[\alpha]_D^{25}$ = -14.2 (c = 0.5, CH_2Cl_2); SFC condition:Lux 5u Cellulose-1 (250 × 4.60 mm), MeOH:CO_2 =5:95, 3 mL/min, 230 nm; t_A = 6.2 min (minor), t_B = 7.7 min (major).

7-bromo-4-methylchroman-3-ol (7)



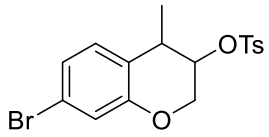
White soild, 41.3 mg, 85%. ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.26 – 7.25 (m, 1H), 7.18 (d, J = 8.7 Hz, 1H), 6.69 (d, J = 8.7 Hz, 1H), 4.20 – 4.17 (m, 1H), 4.06 (d, J = 11.3 Hz, 1H), 4.01 (s, 1H), 3.06 – 3.02 (m, 1H), 1.97 – 1.93 (m, 1H), 1.36 (d, J = 7.0 Hz, 3H). ^{13}C NMR ($CDCl_3$, 151 MHz,) δ 152.4, 131.2, 130.5, 127.1, 118.2, 113.2, 69.0, 66.4, 34.3, 15.5. TOF-HRMS Calcd. for $C_{10}H_{12}BrO_2$ [M+H$^+$]: 243.0015, found 243.0018. 99.9% ee, dr > 99:1. $[\alpha]_D^{30}$ = 36.2 (c = 1.0, CH_2Cl_2). HPLC condition: Lux 5u Amylose-1 (250 × 4.60 mm), ipa : hex = 10:90, 1.0 mL/min, 254 nm; t_A = 8.2 min (minor), t_B = 11.3 min (major).

7-bromo-4-methylchroman-3-yl methanesulfonate (8)



White soild, 57.3 mg, 89%. ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.27 (dd, *J* = 2.4, 1.1 Hz, 1H), 7.24 (ddd, *J* = 8.6, 2.5, 0.8 Hz, 1H), 6.73 (d, *J* = 8.7 Hz, 1H), 5.08 (td, *J* = 4.5, 1.8 Hz, 1H), 4.47 (dd, *J* = 12.1, 4.6 Hz, 1H), 4.19 (dt, *J* = 12.1, 1.5 Hz, 1H), 3.30 – 3.26 (m, 1H), 3.07 (s, 3H), 1.44 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR ($CDCl_3$, 101 MHz) δ 152.1, 131.0, 130.6, 125.5, 118.3, 113.4, 74.8, 66.2, 38.8, 33.1, 15.9. TOF-HRMS Calcd. for $C_{11}H_{14}BrO_4S$ [M+H$^+$]: 320.9791, found 320.9795. 99% ee, dr > 99:1. $[\alpha]_D^{30}$ = 1.34 (c = 1.0, CH_2Cl_2). HPLC condition: Lux 5u Amylose-1 (250 × 4.60 mm), ipa : hex = 7:93, 1.0 mL/min, 210 nm; t_A = 20.2 min (minor), t_B = 25.0 min (major).

7-bromo-4-methylchroman-3-yl 4-methylbenzenesulfonate (9)



White soild, 60.2 mg, 75%. ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.82 – 7.80 (m, 2H), 7.35 (dt, *J* = 7.6, 0.8 Hz, 2H), 7.20 – 7.18 (m, 2H), 6.67 – 6.66 (m, 1H), 4.88 (ddd, *J* = 5.7, 4.6, 2.4 Hz, 1H), 4.23 (dd, *J* = 11.7, 5.7 Hz, 1H), 4.06 (ddd, *J* = 11.7, 2.3, 1.2 Hz, 1H), 3.14 (dddd, *J* = 7.5, 6.5, 5.5, 4.1 Hz, 1H), 2.46 (s, 3H), 1.27 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR ($CDCl_3$, 151 MHz) δ 152.1, 145.2, 133.6, 130.9, 130.8, 130.0, 127.8, 125.8, 118.3, 113.2, 75.3, 65.3, 33.2, 21.7, 16.0. TOF-HRMS Calcd. for $C_{17}H_{18}BrO_4S$ [M+H$^+$]: 397.0104, found 397.0105. 97% ee, dr > 99:1. $[\alpha]_D^{30}$ = 39.3 (c = 1.0, CH_2Cl_2). HPLC condition: Lux 5u Amylose-1 (250 × 4.60 mm), ipa : hex = 10:90, 1.0 mL/min, 210 nm; t_A = 13.5 min (minor), t_B = 16.8 min (major).

6. X-ray Crystallography

Single-crystal X-ray diffraction measurements were carried out on a Rigaku Saturn CCD diffractometer at 100(2) K using graphite monochromated Cu Kα radiation (λ =

1.54184 Å). An empirical absorption correction was applied using the SADABS program.[7] All structures were solved by direct methods and refined by full-matrix least squares on F^2 using the SHELXL program package.[8] All the hydrogen atoms were geometrically fixed using the riding model. The crystal data and experimental data for **1b, 2a and 2p** are summarized in **Table S1**.

Crystal parameters

Table S1. Crystal Data and Experimental Parameters for Compounds 2i and 4j

Compound	**2i**	**4j**
Formula	$C_{23}H_{28}BNO_4$	$C_{18}H_{27}NBO_3$
Fw	393.27	302.2
crystal system	orthorhombic	orthorhombic
space group	$P2_12_12_1$	$P2_12_12_1$
a (Å)	9.566(2)	7.331(2)
b (Å)	12.058(3)	13.344(3)
c (Å)	18.415(4)	17.277(4)
α (deg)	90	90
β (deg)	90	90
γ (deg)	90	90
V (Å^3)	2124.16(8)	1690.05(7)
Z	4	4
D_{calc} (g/cm^3)	1.230	1.188
μ(Mo/Kα)$_{calc}$ (cm^{-1})	0.662	0.613
size (mm)	0.20 × 0.20 × 0.20	0.25 × 0.21 × 0.15
F(000)	840	656
2θ range (deg)	8.77 to 151.55	8.37 to 144.15
no. of reflns, collected	13039	6016
no of obsd reflns	4240	3222
no of variables	297	206
abscorr (T_{max}, T_{min})	1.00, 0.76	1.00, 0.94
R	0.044	0.038
R_w	0.11	0.098

R_{all}	0.045	0.039
Absolute structure parameter	-0.02(7)	-0.04(9)
Gof	1.053	1.06
CCDC	2174322	2174323

7. References

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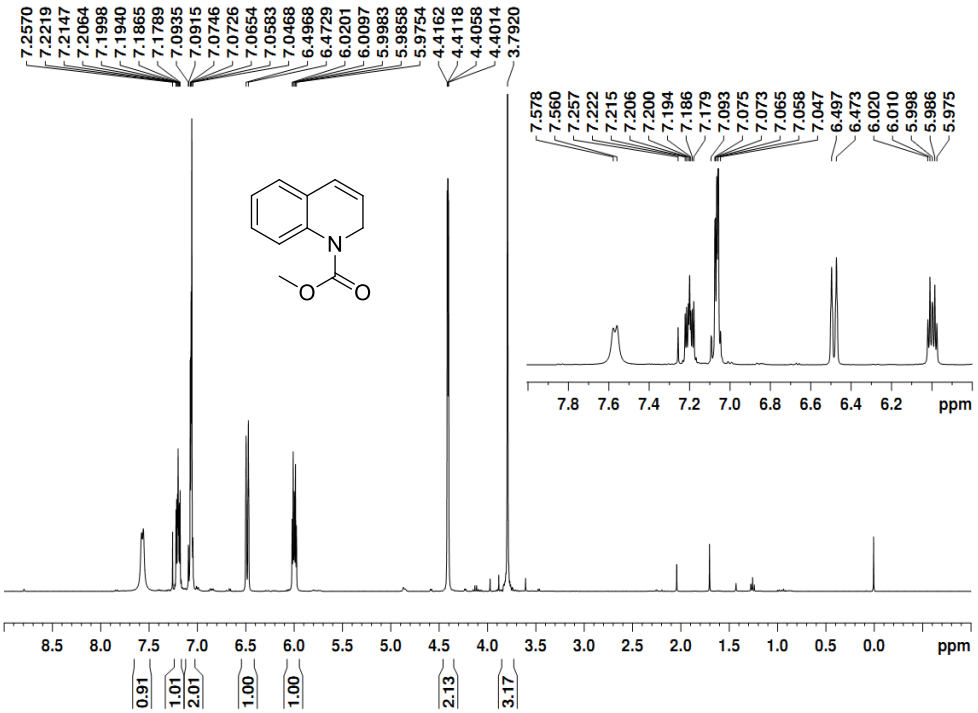
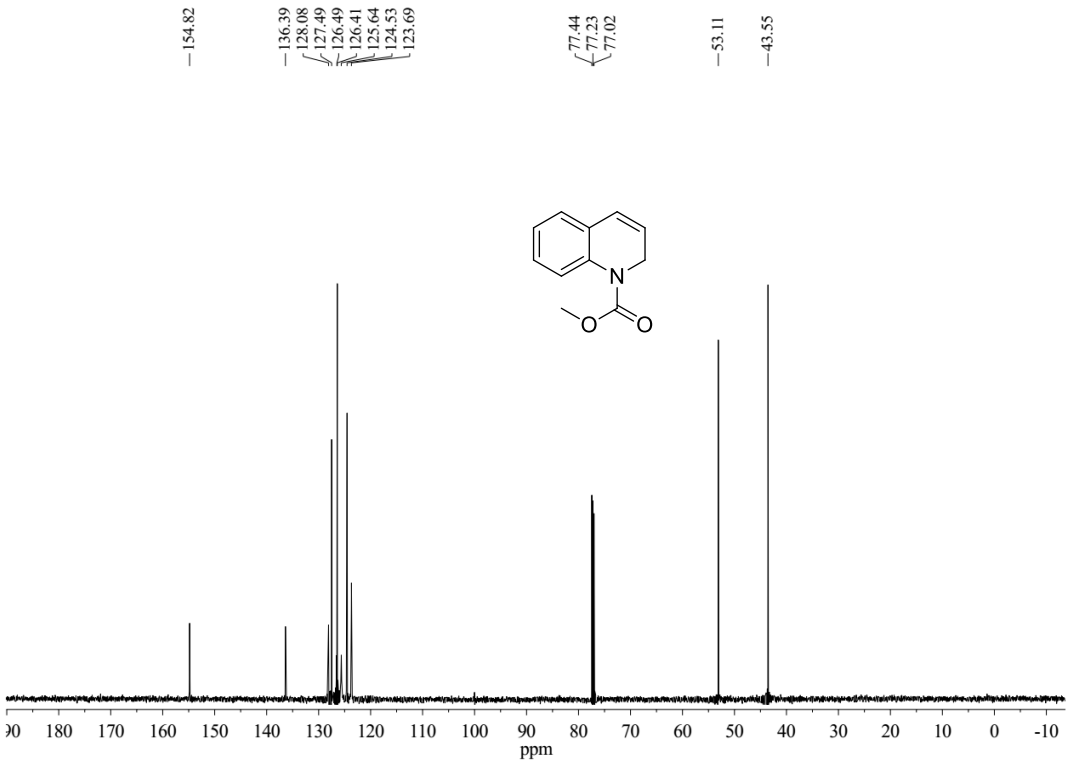
[7] G. M. Sheldrick, SADABS, Program for Empirical Absorption Correction of Area Detector Data, University of Göttingen, Göttingen, Germany, 1996.

[8] G. M. Sheldrick, *Acta Cryst.*, 2008, **A64**, 112.

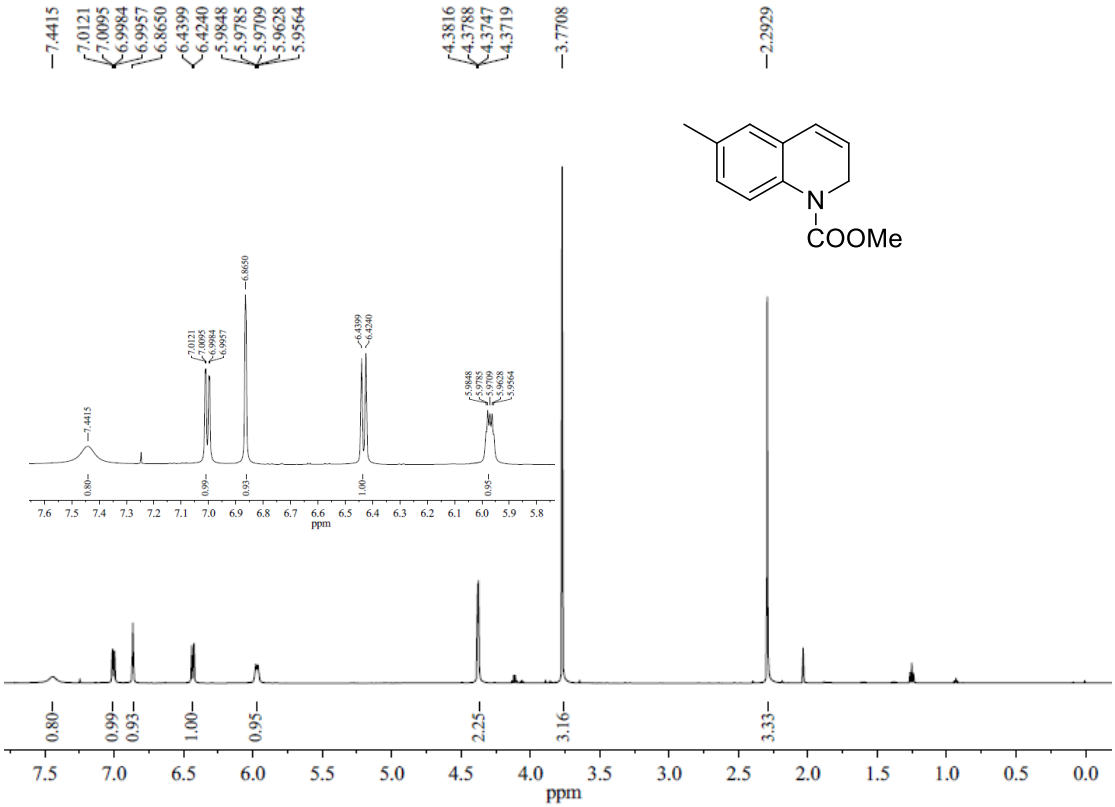
8. NMR spectra of all compounds.

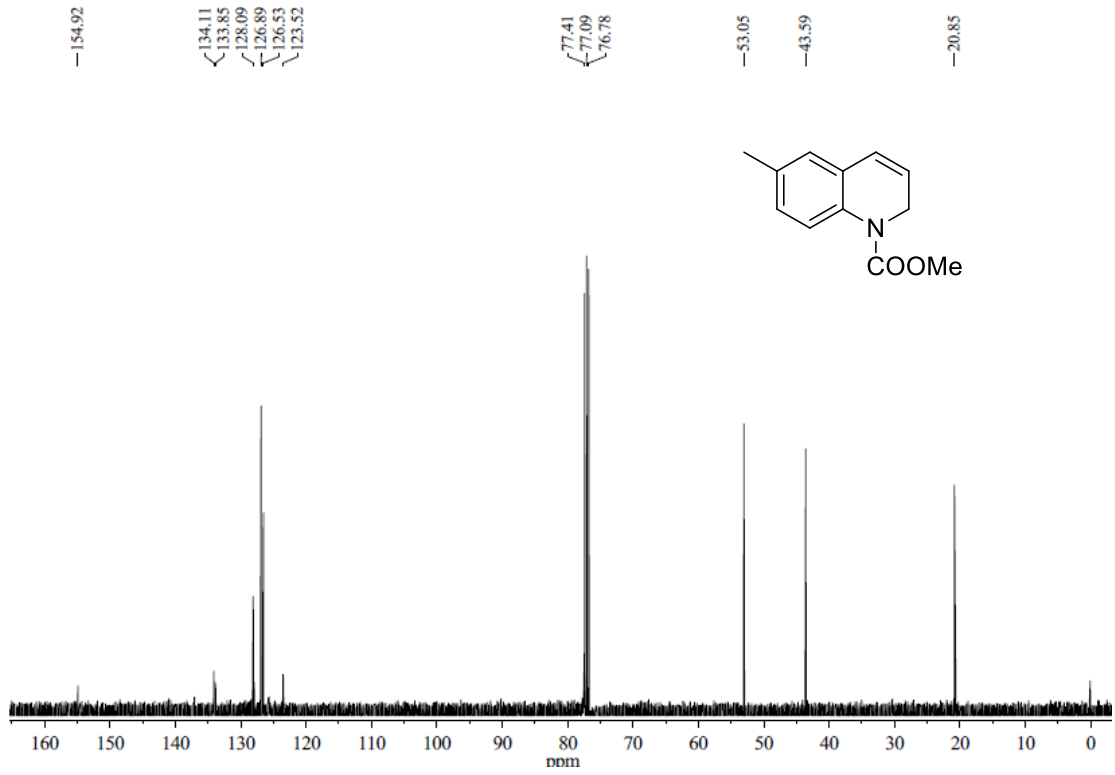
Methyl quinoline-1(2*H*)-carboxylate (1a)



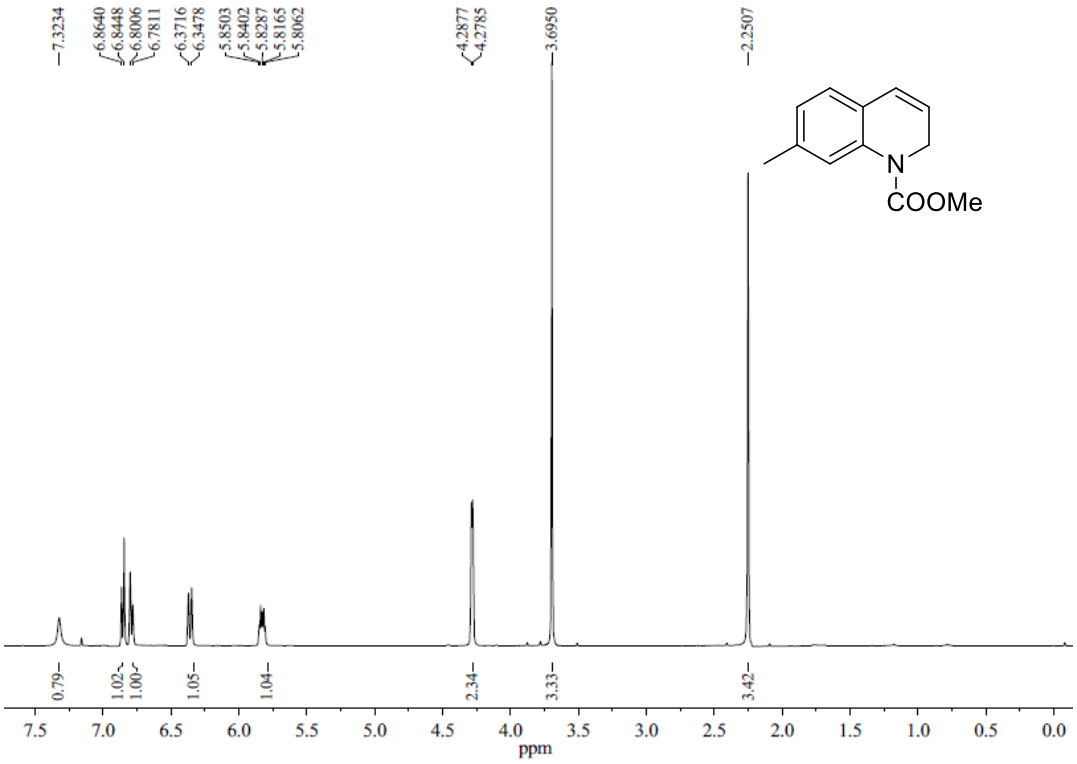


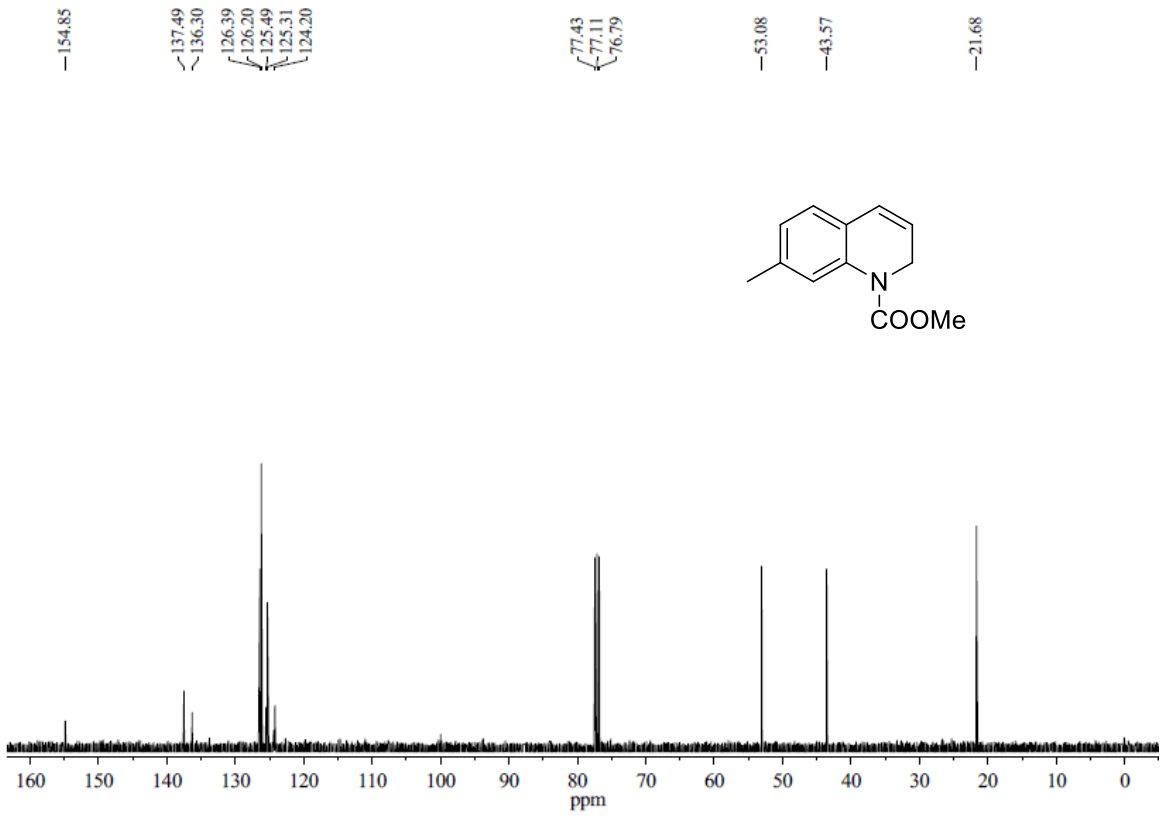
Methyl 6-methylquinoline-1(*2H*)-carboxylate (1b)



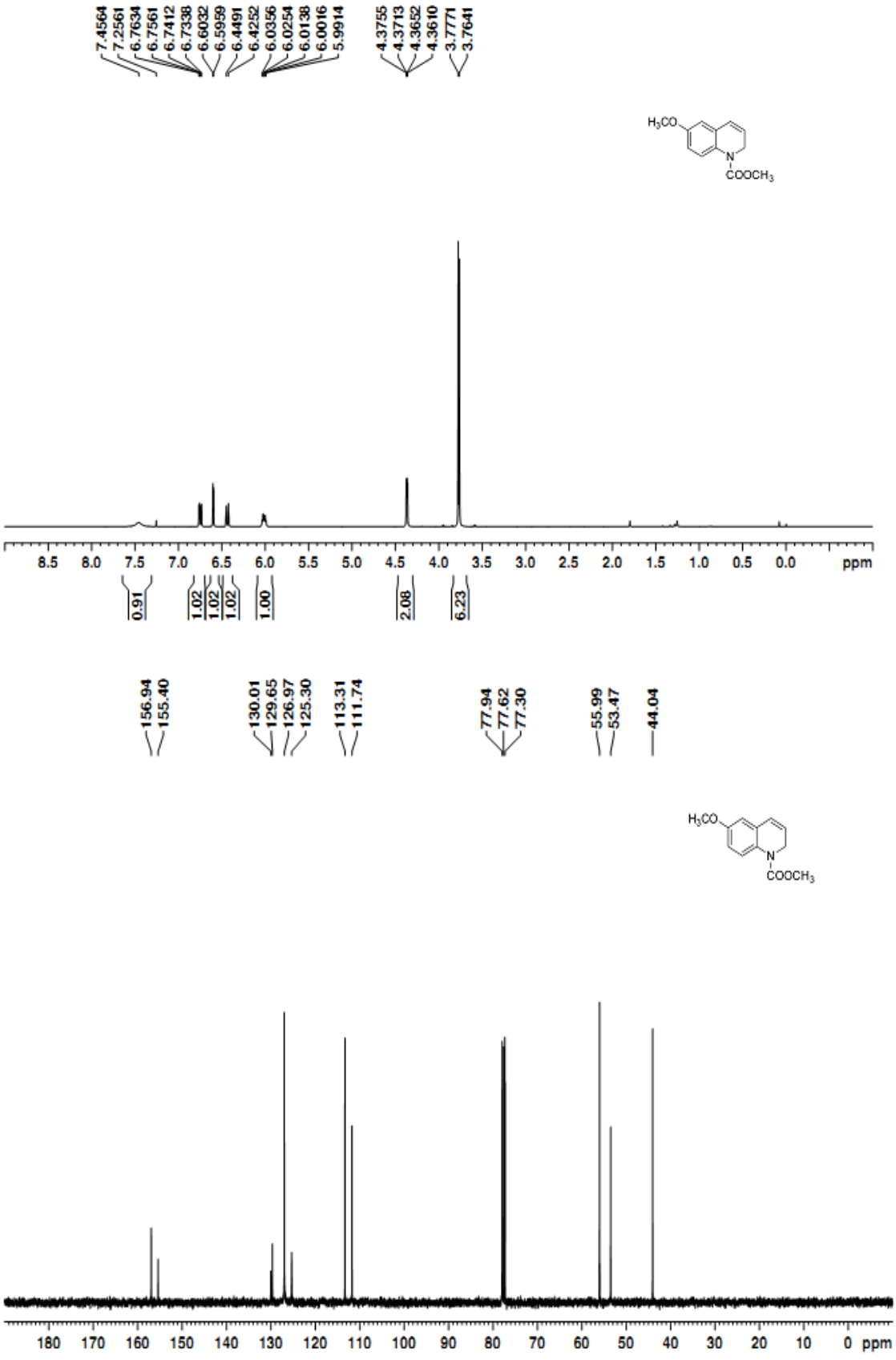


Methyl 7-methylquinoline-1(*2H*)-carboxylate (1c)

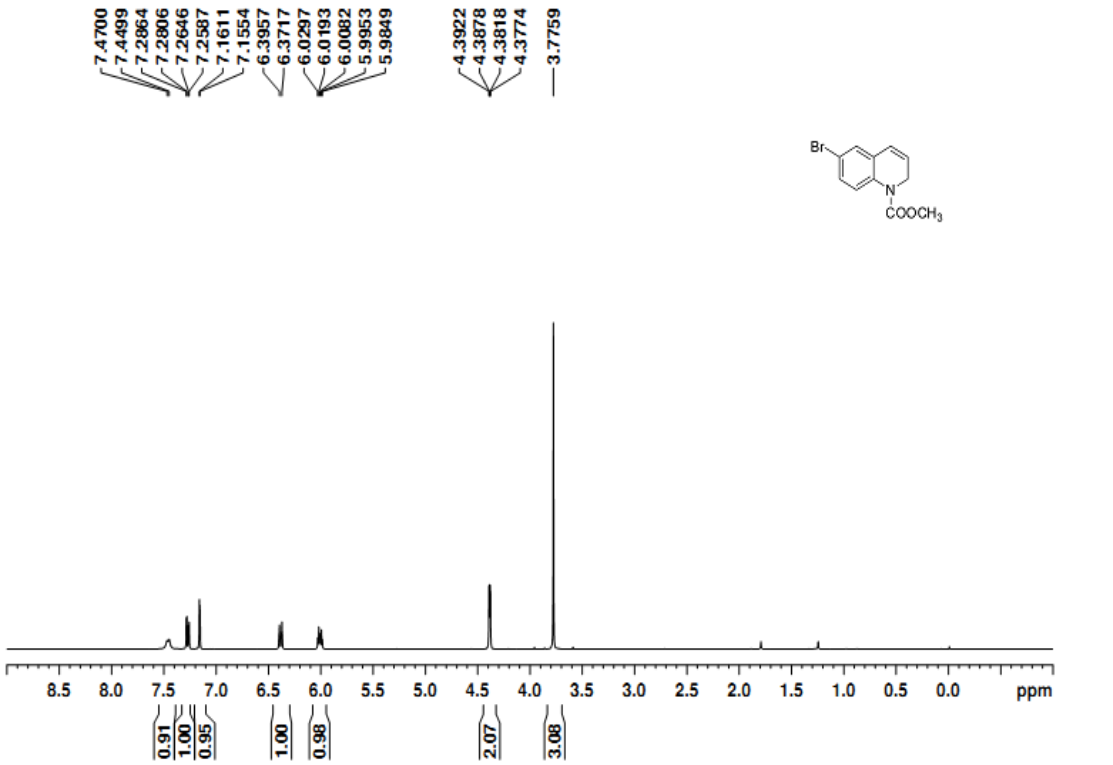


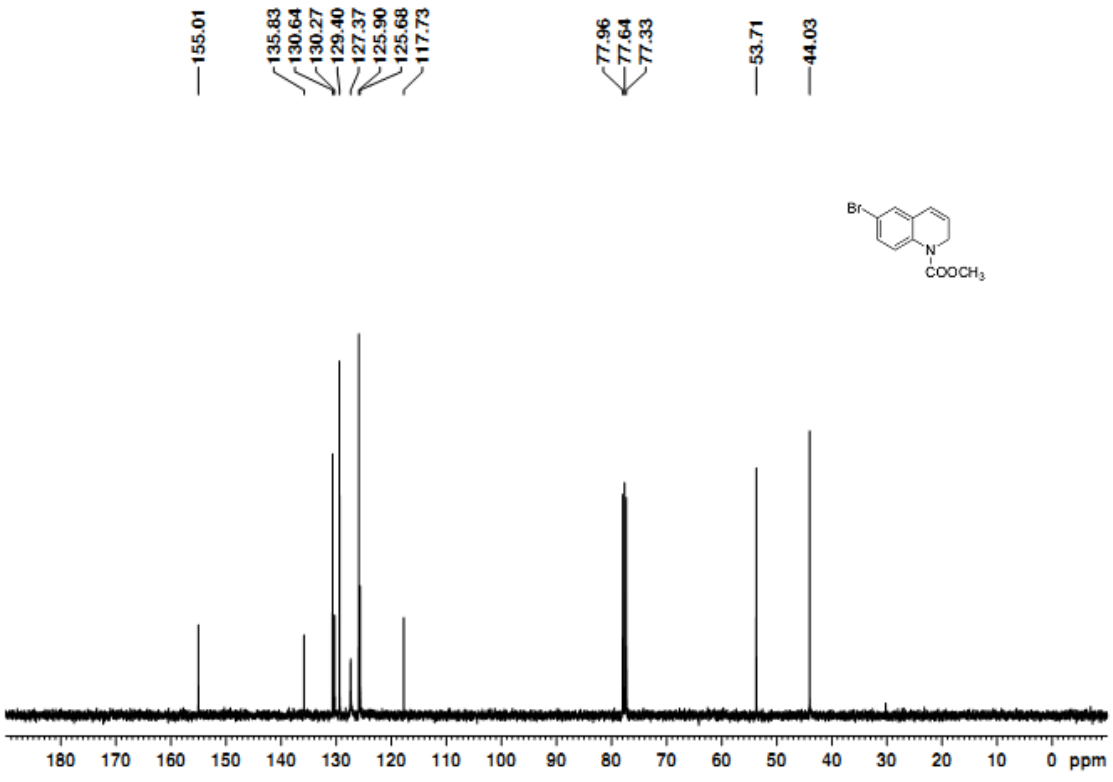


Methyl 6-methoxyquinoline-1(2*H*)-carboxylate (1d)

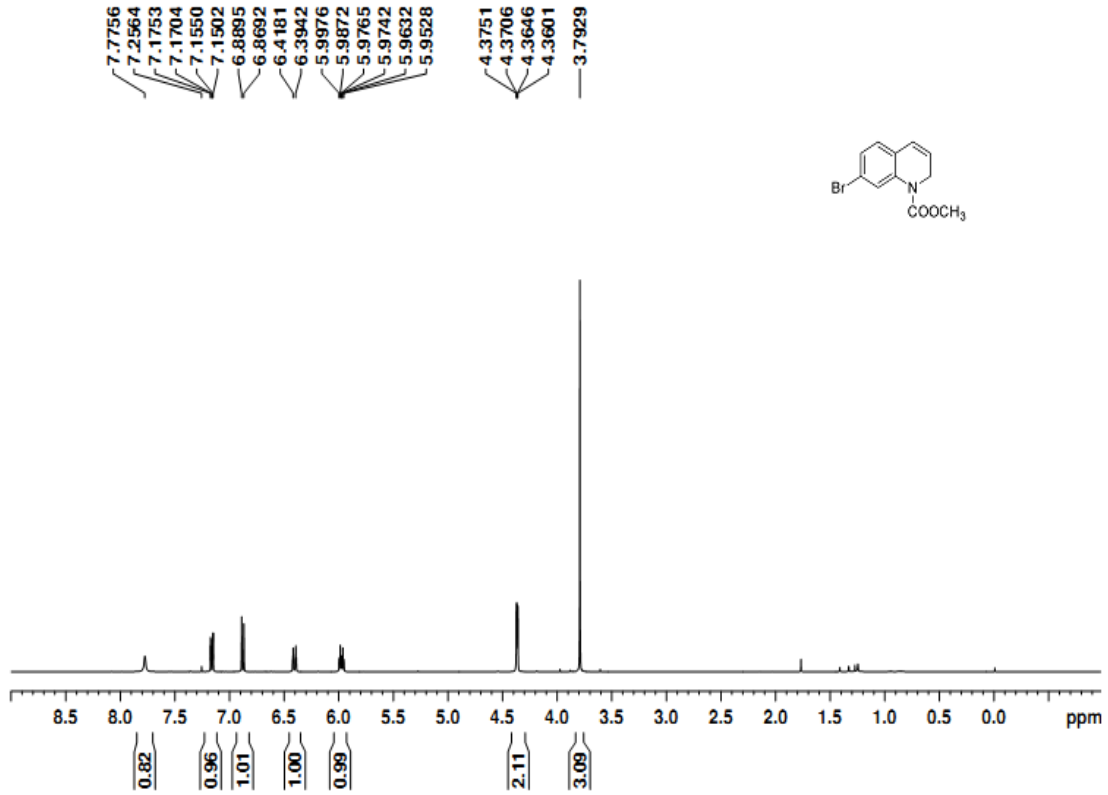


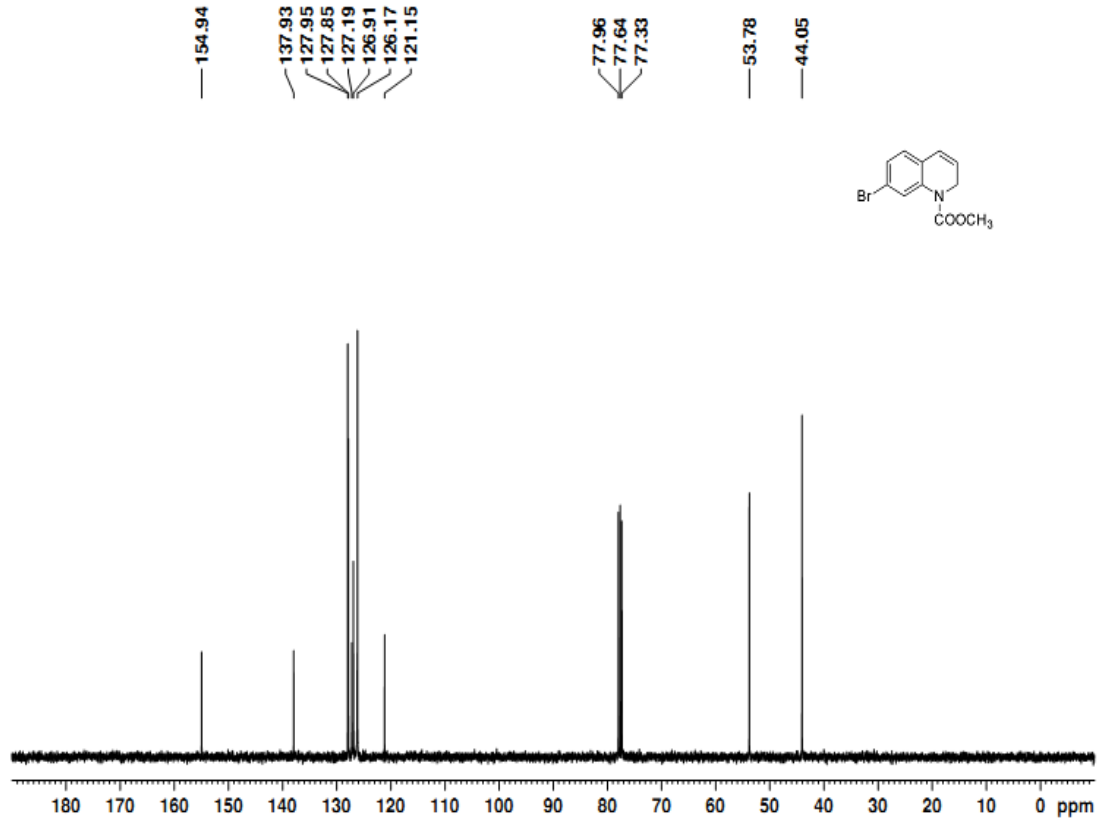
Methyl 6-bromoquinoline-1(2*H*)-carboxylate (1e)



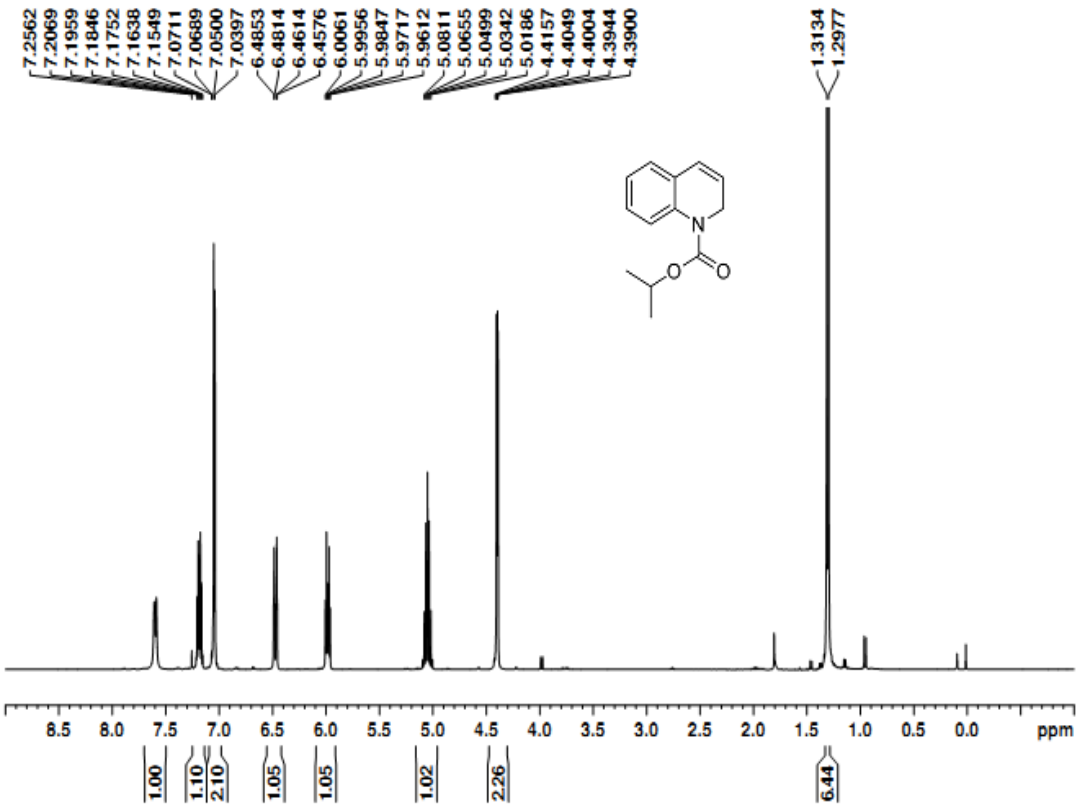


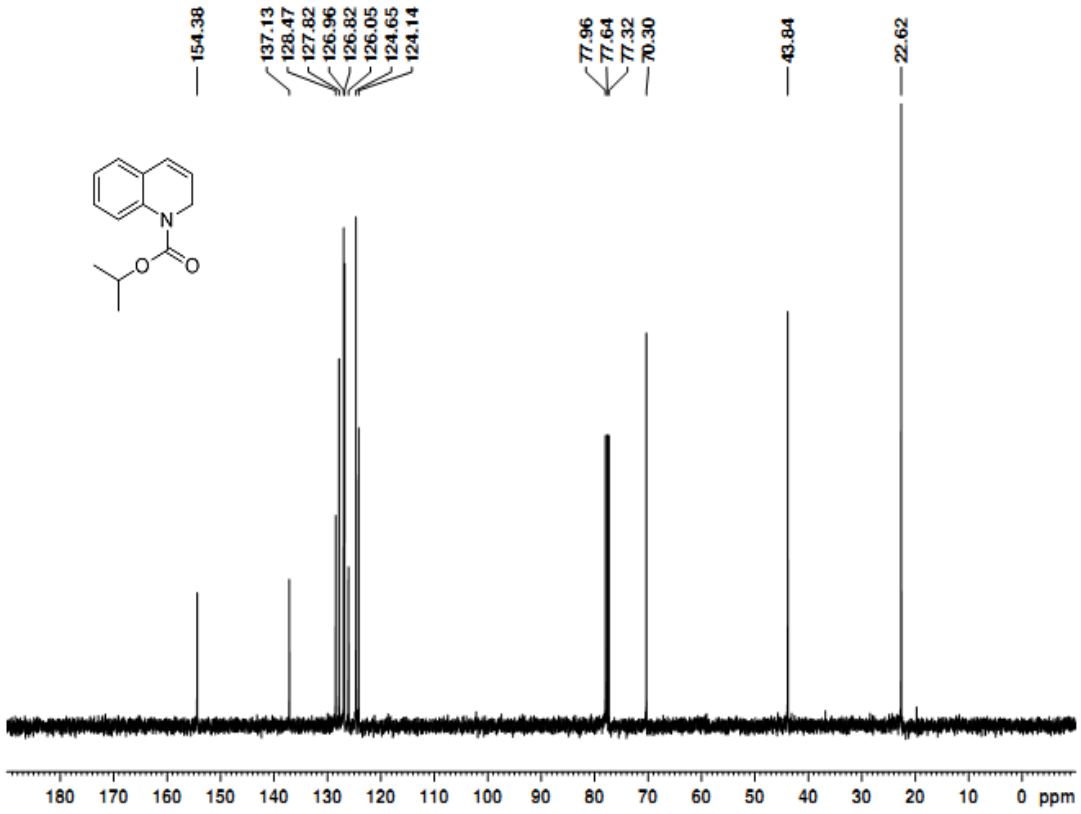
Methyl 7-bromoquinoline-1(2*H*)-carboxylate (1f)



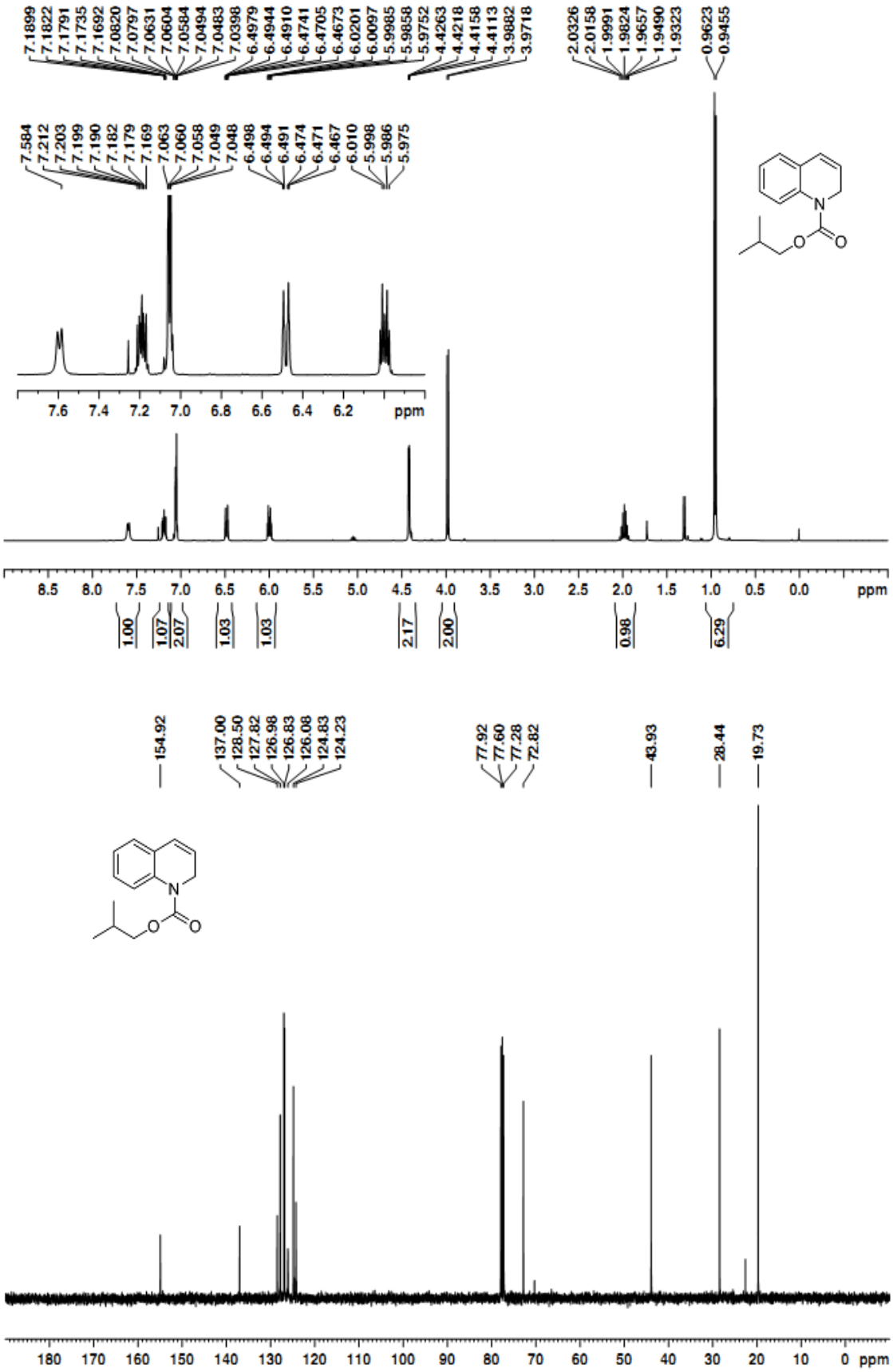


Isopropyl quinoline-1(2*H*)-carboxylate (1g)

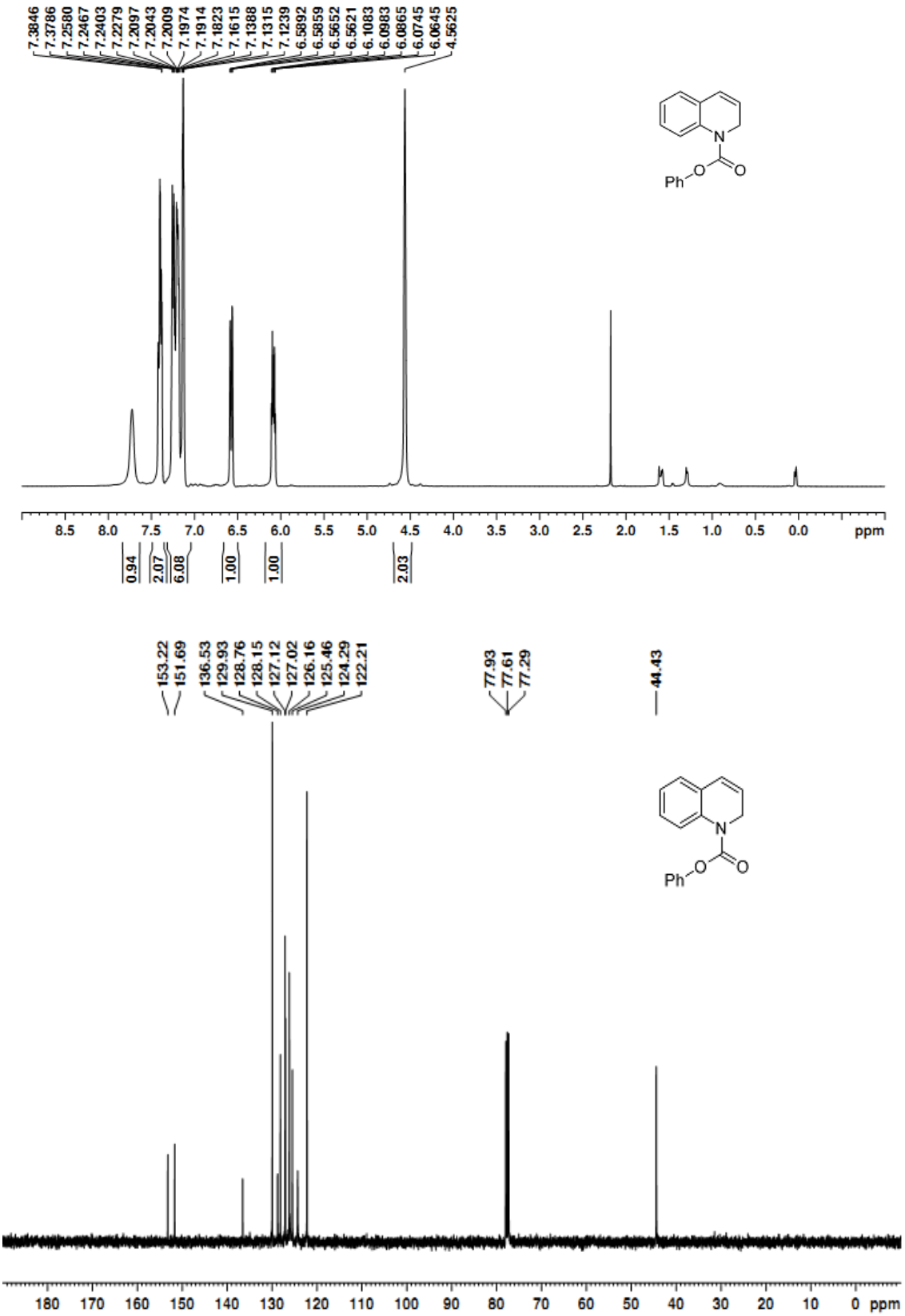




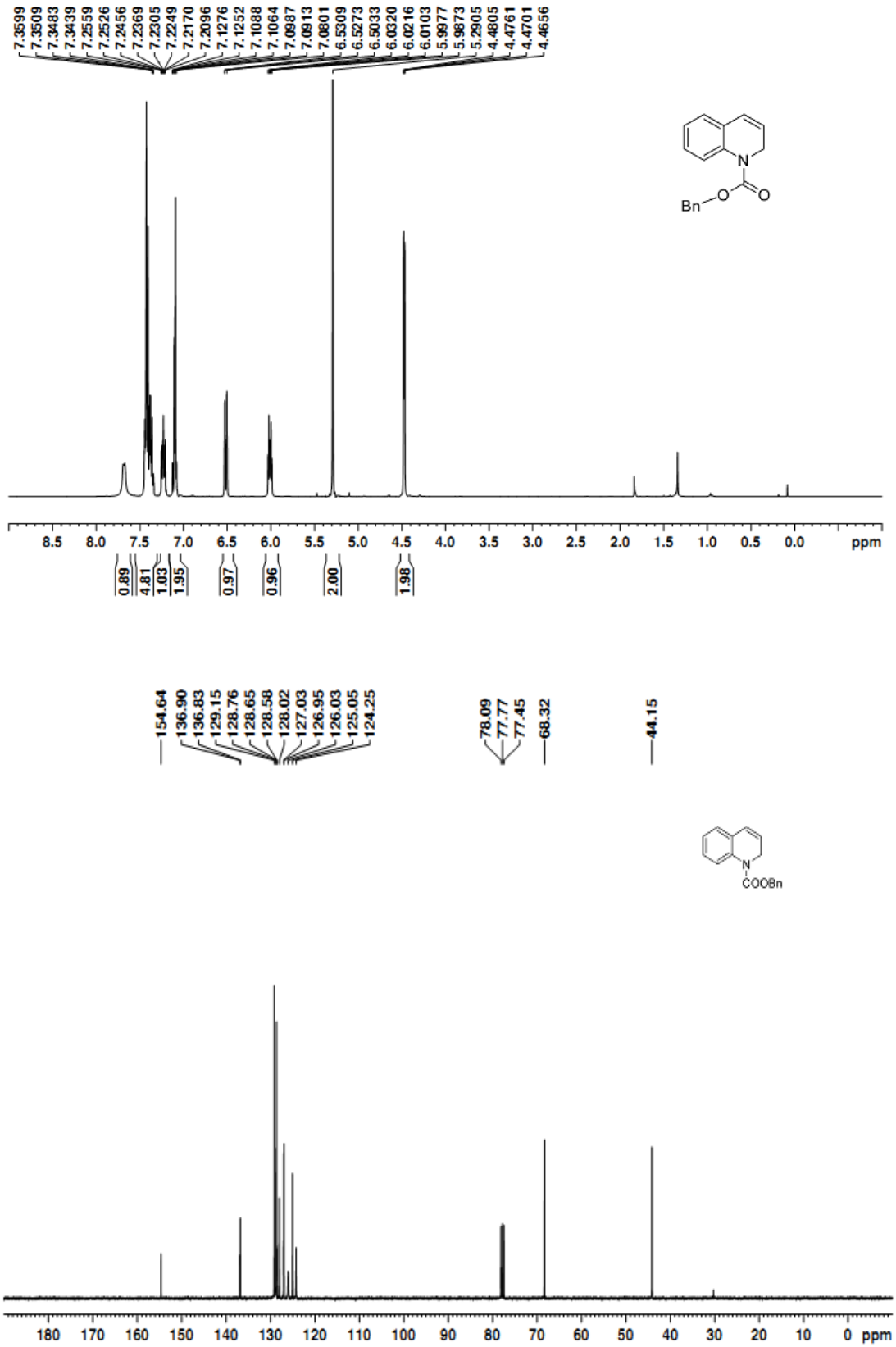
isobutyl quinoline-1(2*H*)-carboxylate (1h)



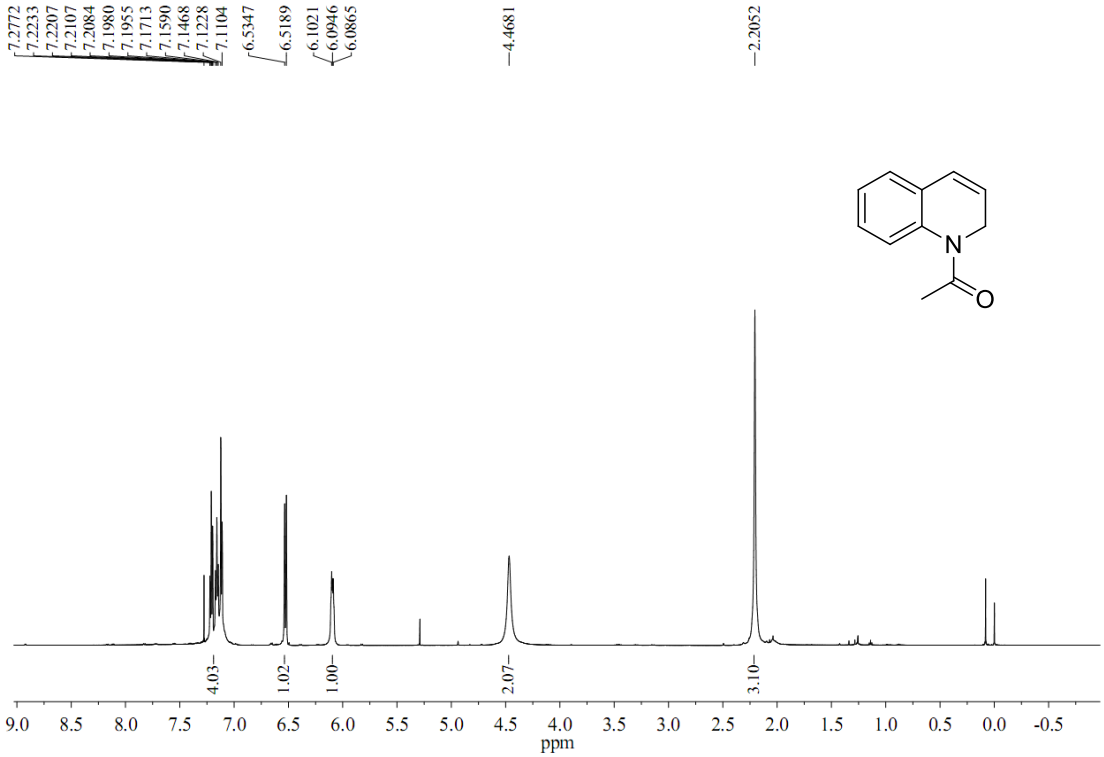
phenyl quinoline-1(2*H*)-carboxylate (1i)

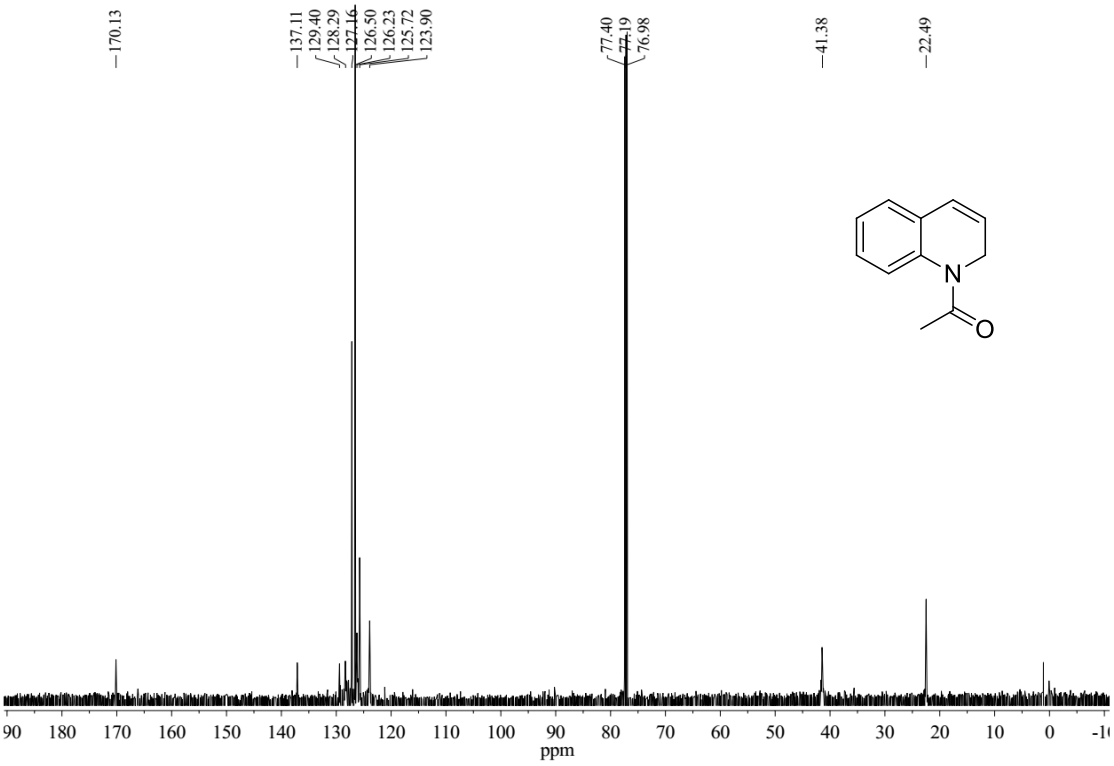


benzyl quinoline-1(2*H*)-carboxylate (1j)

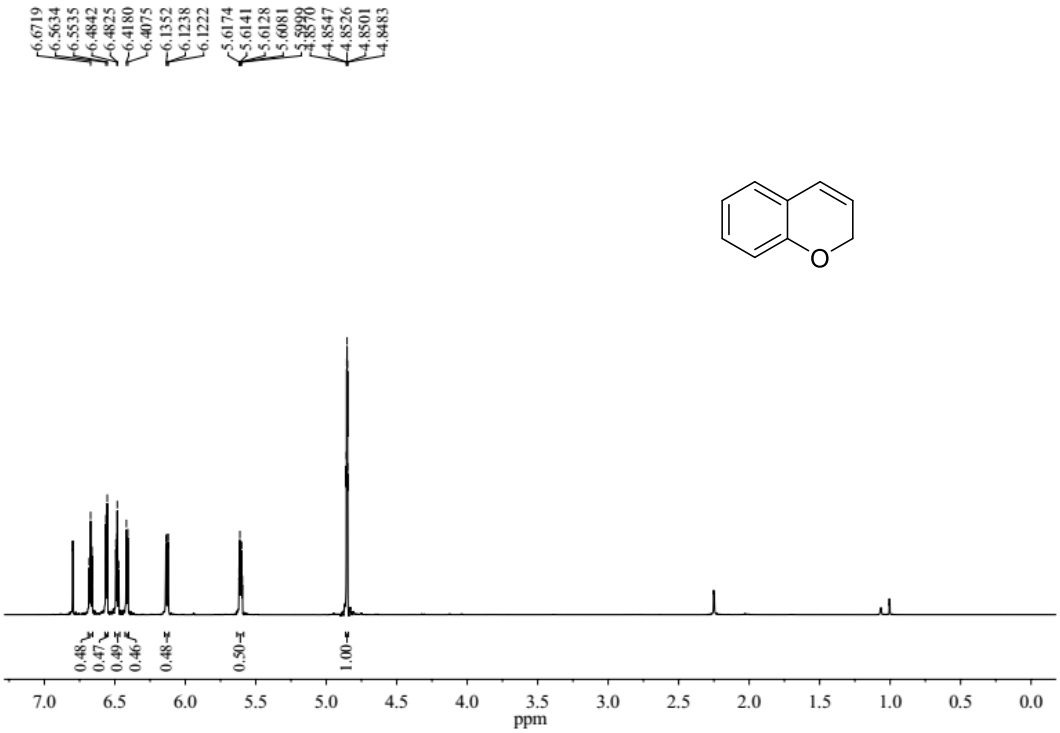


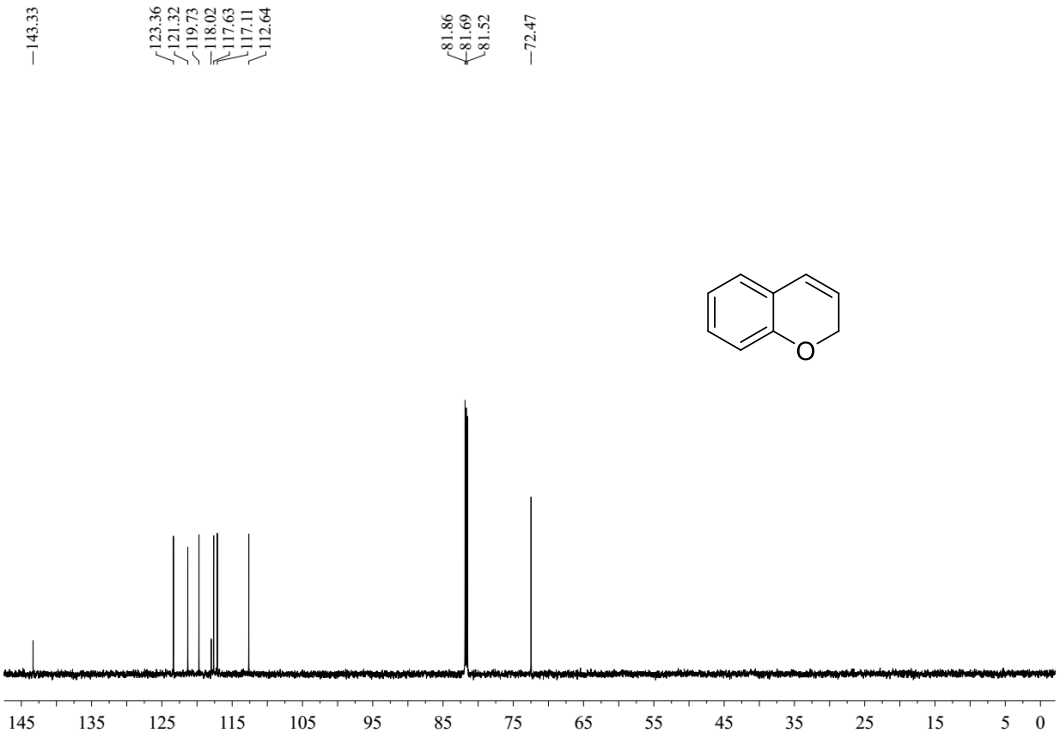
1-(quinolin-1(2*H*)-yl)ethanone (1k)



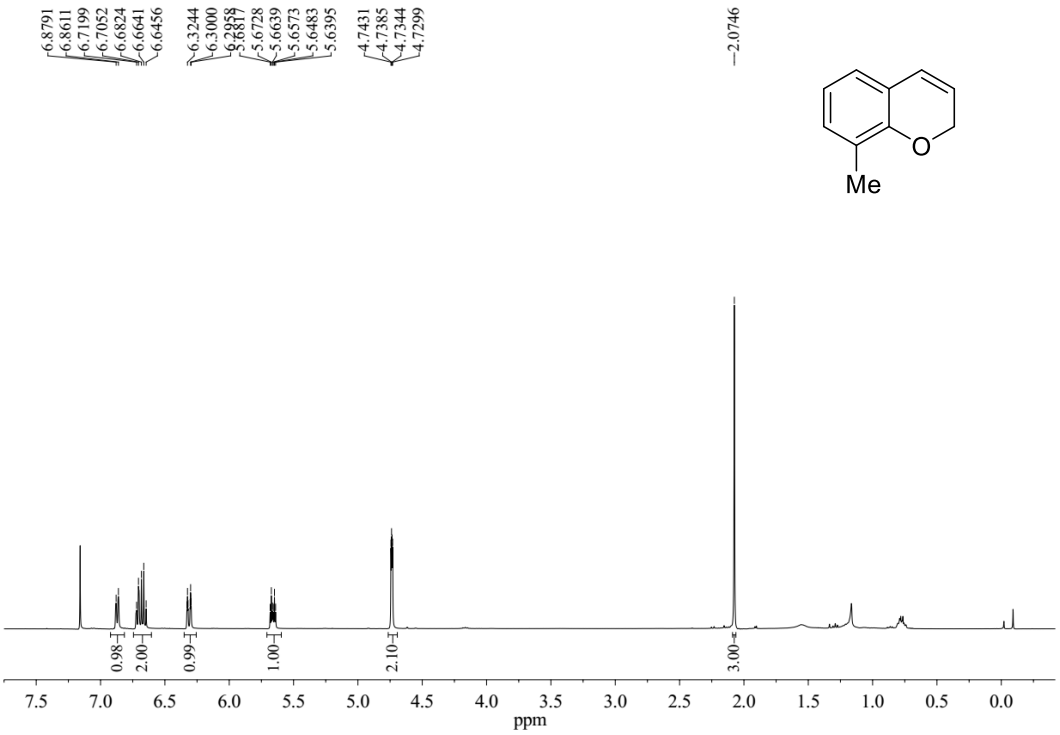


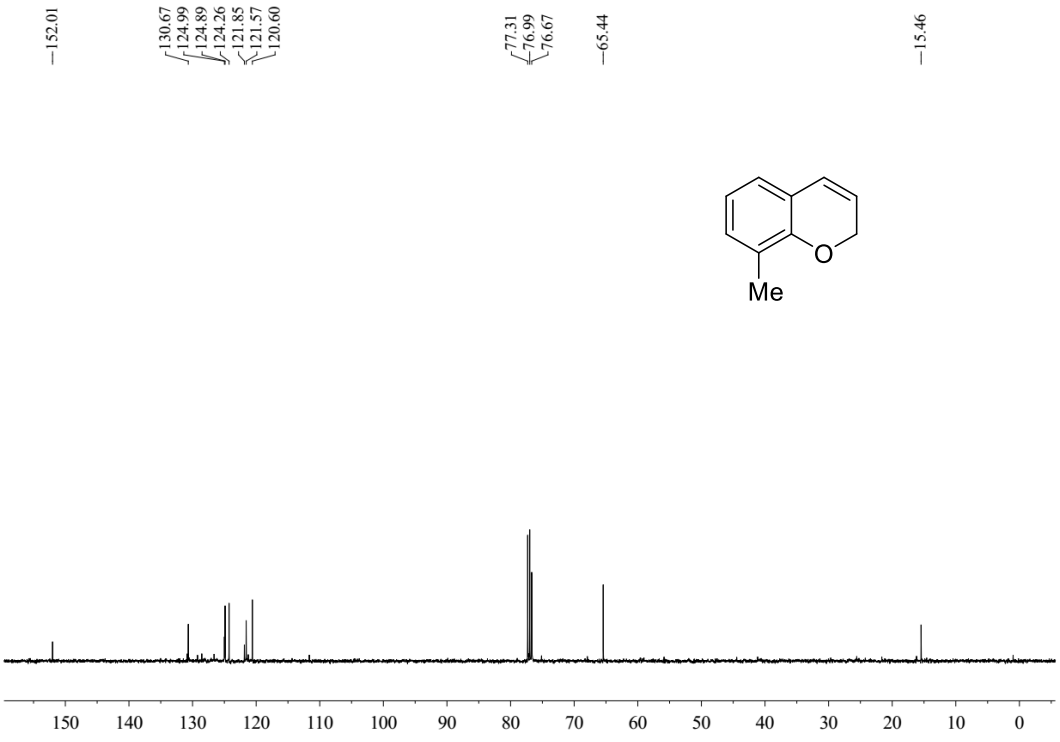
2H-chromene (3a)



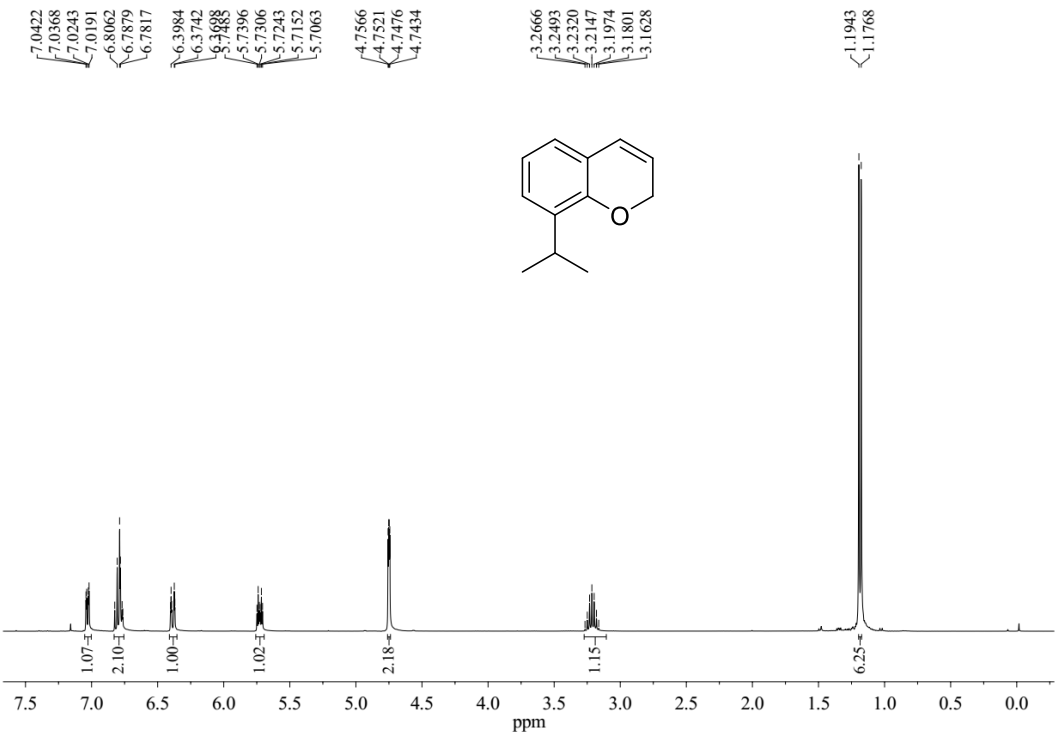


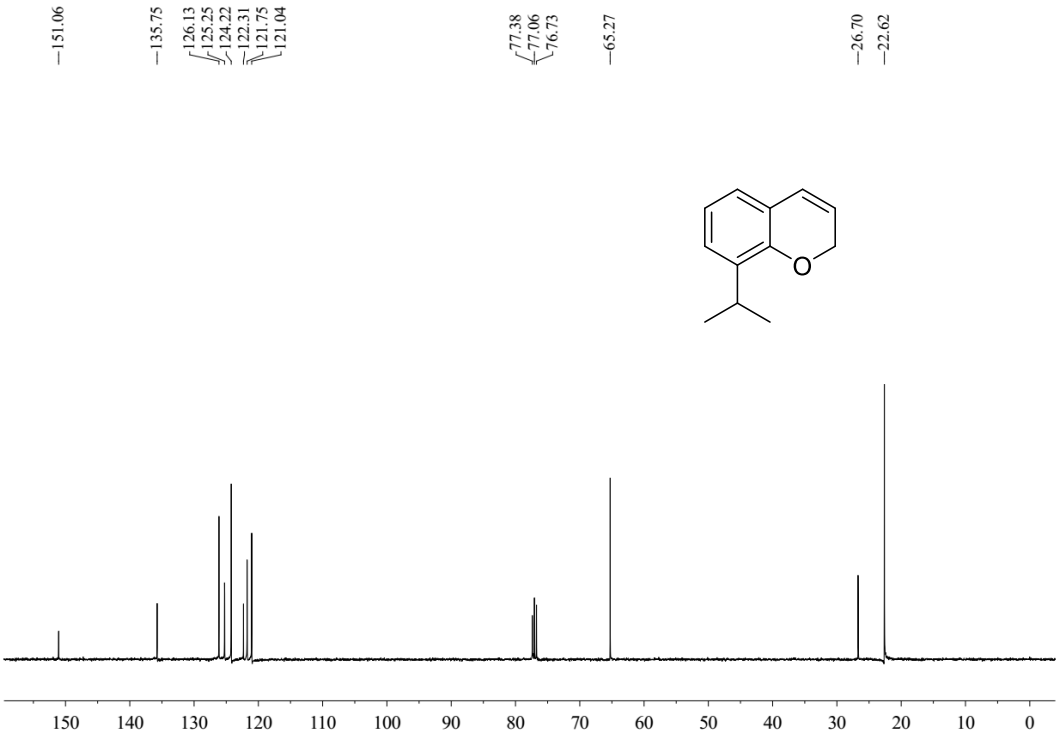
8-methyl-2H-chromene (3b)



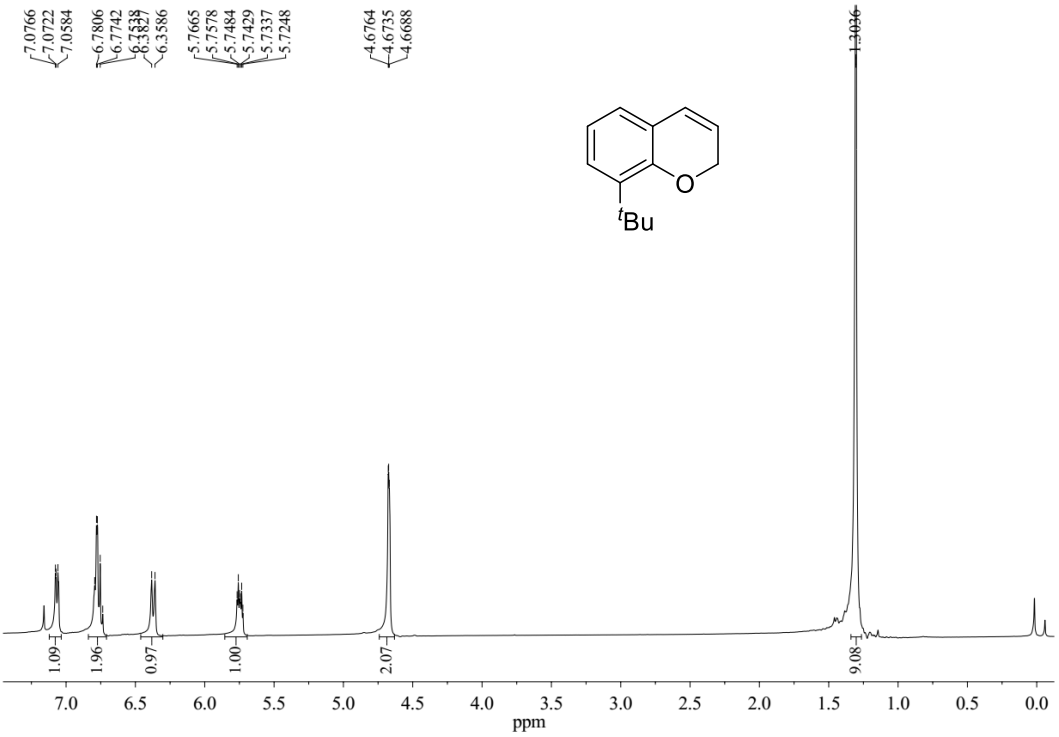


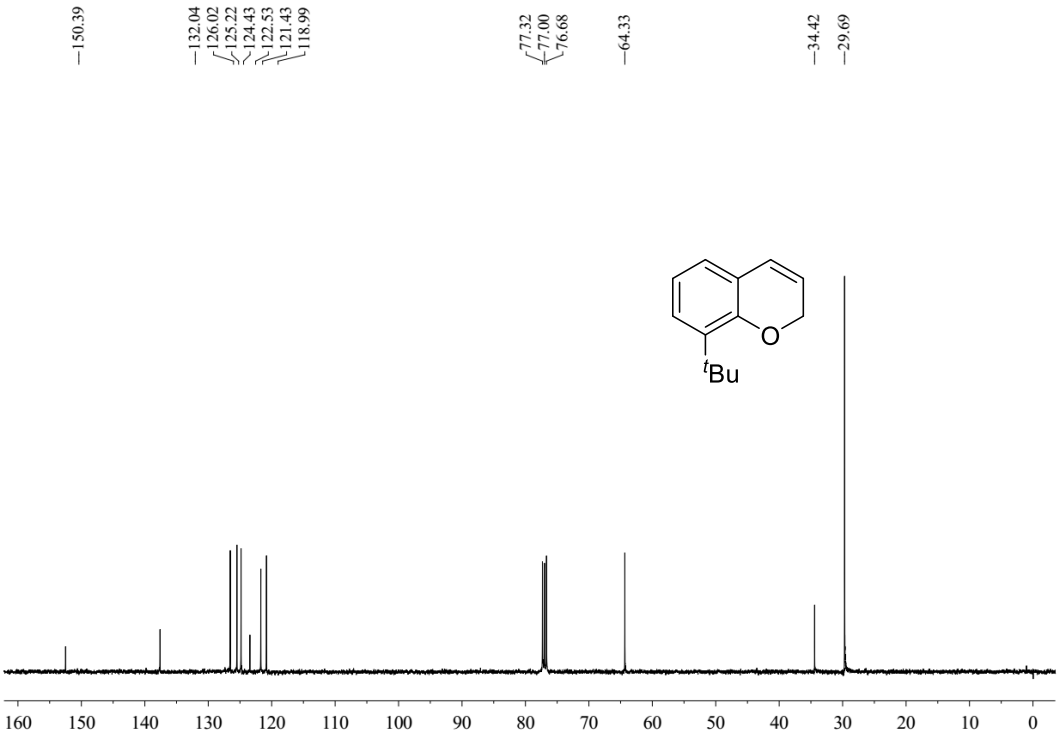
8-isopropyl-2H-chromene (3c)



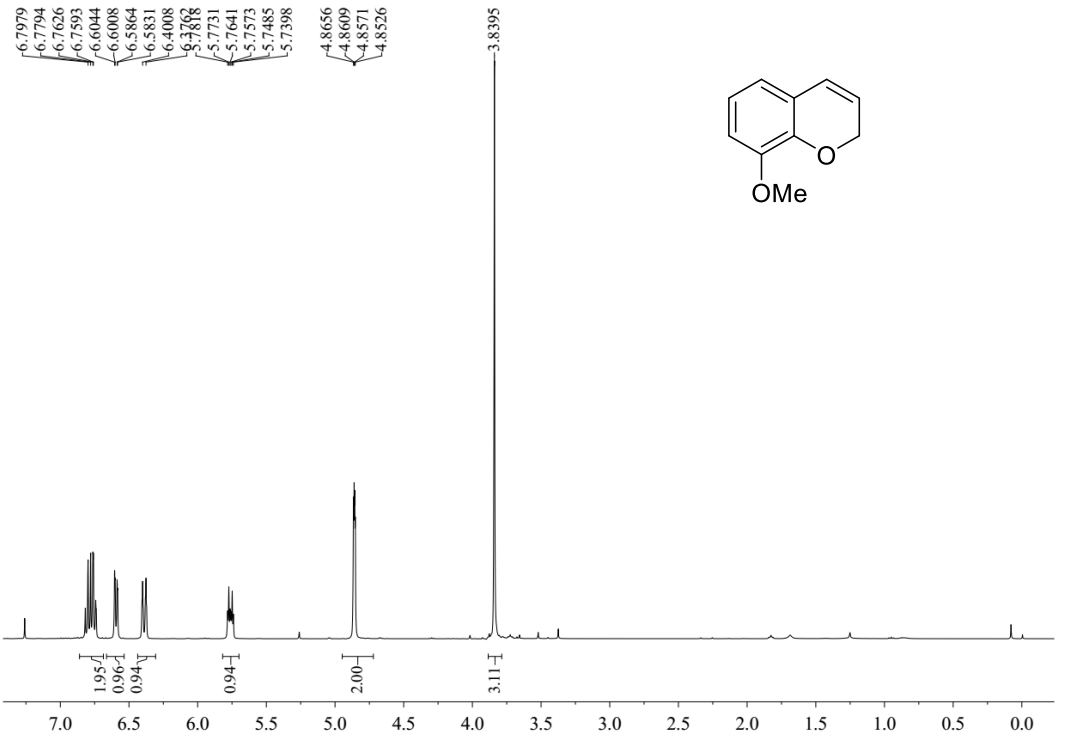


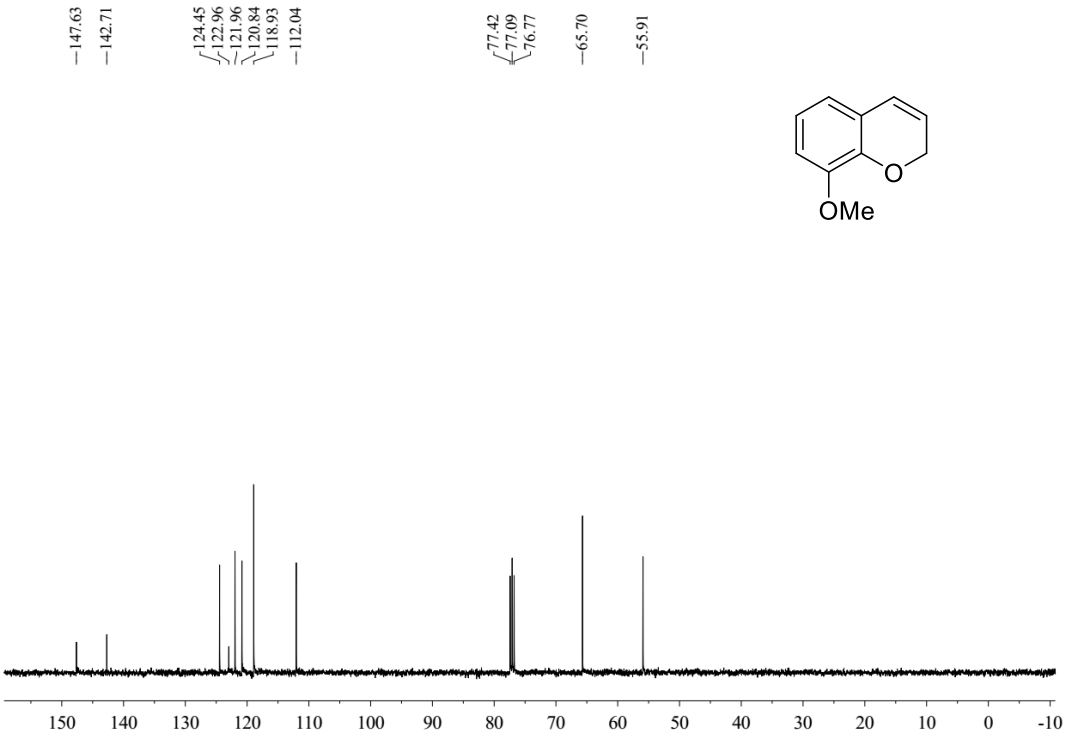
8-(tert-butyl)-2H-chromene (3d)



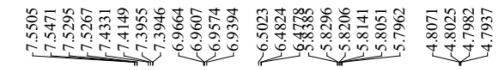


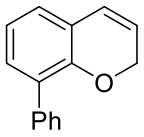
8-methoxy-2H-chromene (3e)

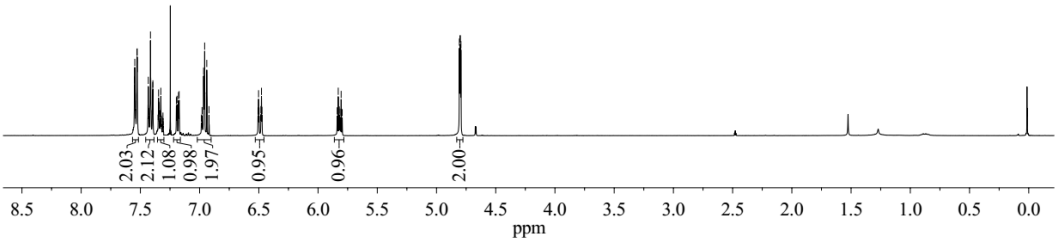


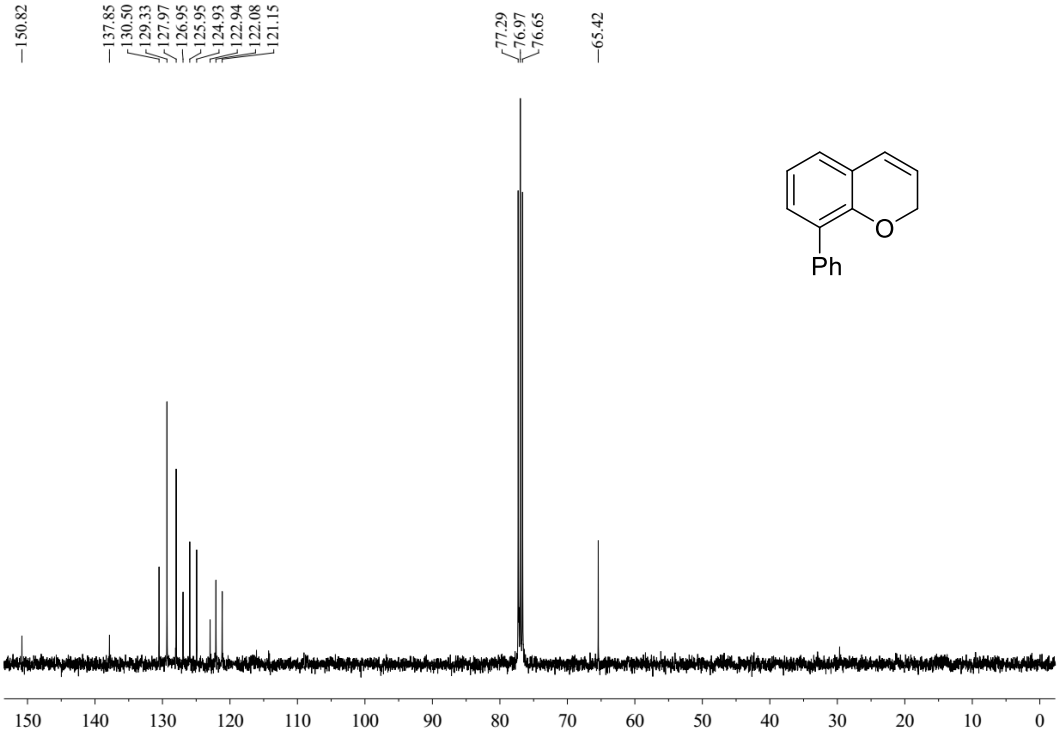


8-phenyl-2H-chromene (3f)

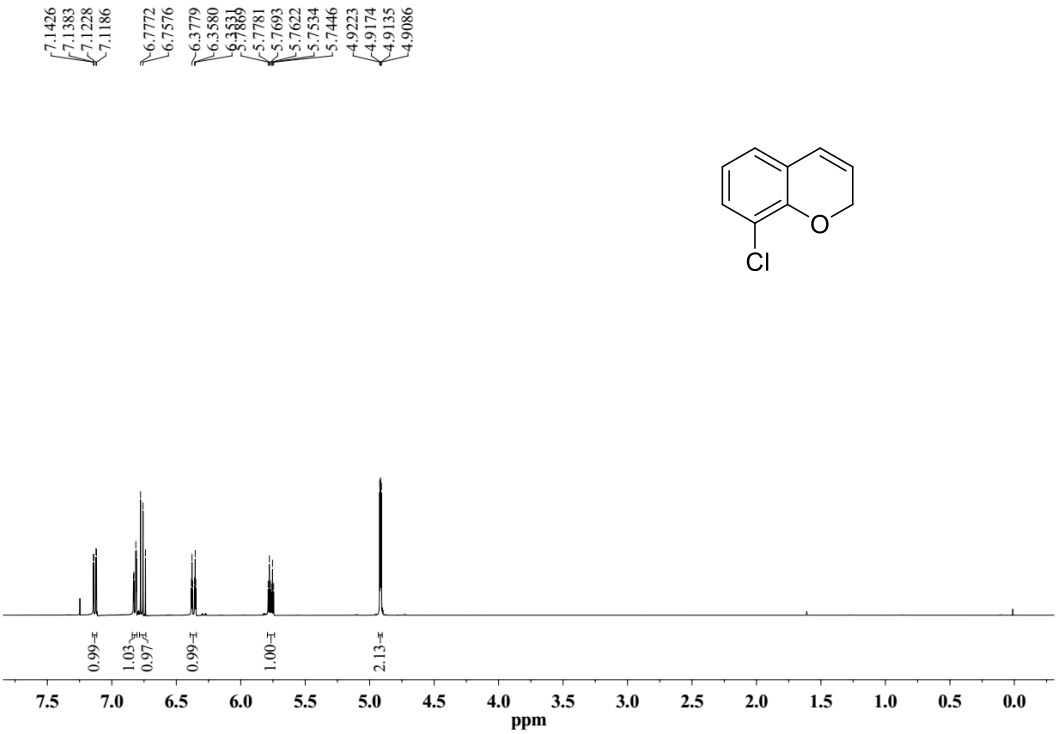


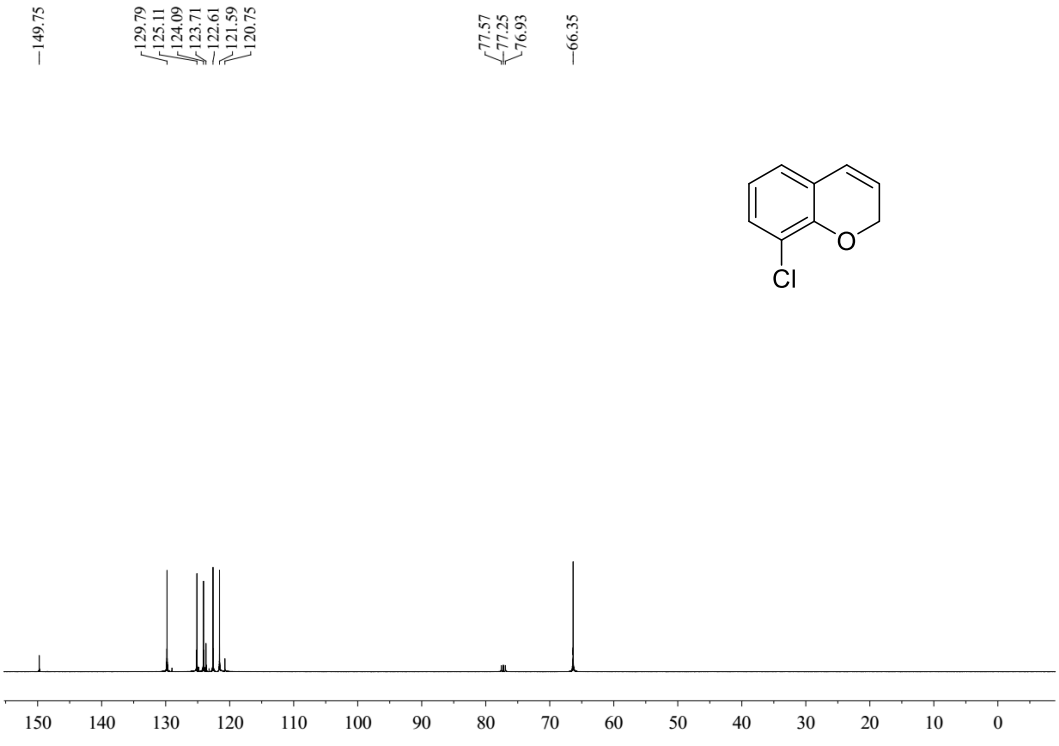




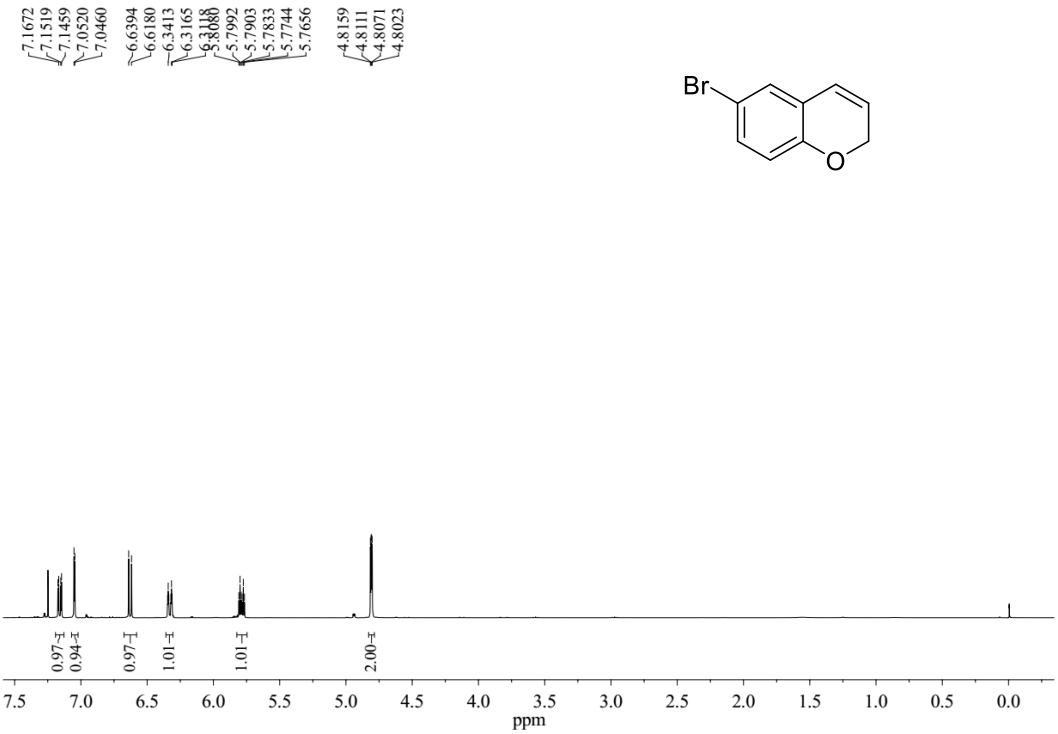


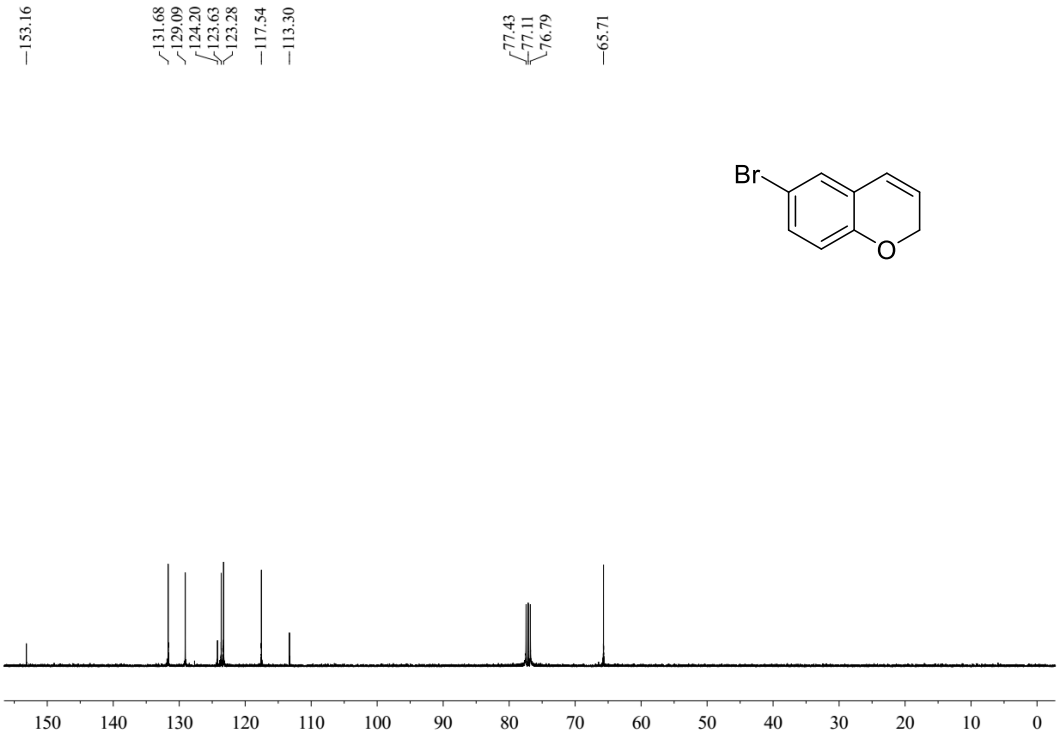
8-chloro-2H-chromene (3g)



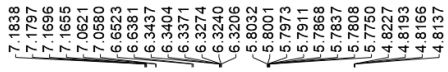


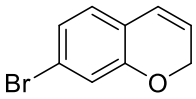
6-bromo-2H-chromene (3h)

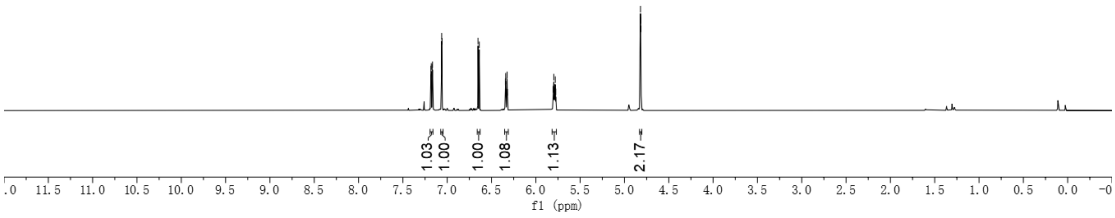


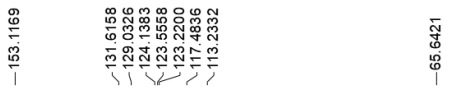


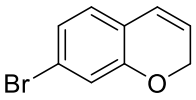
7-bromo-*2H*-chromene (3i)

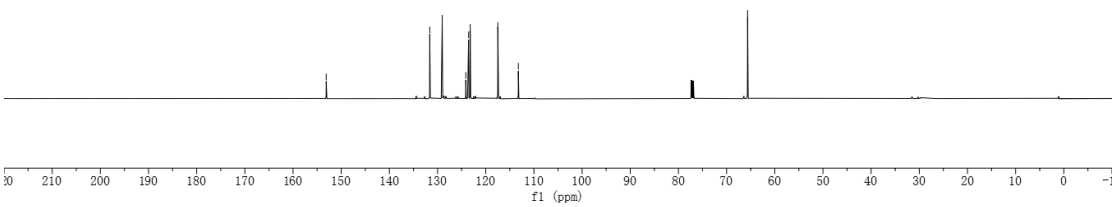




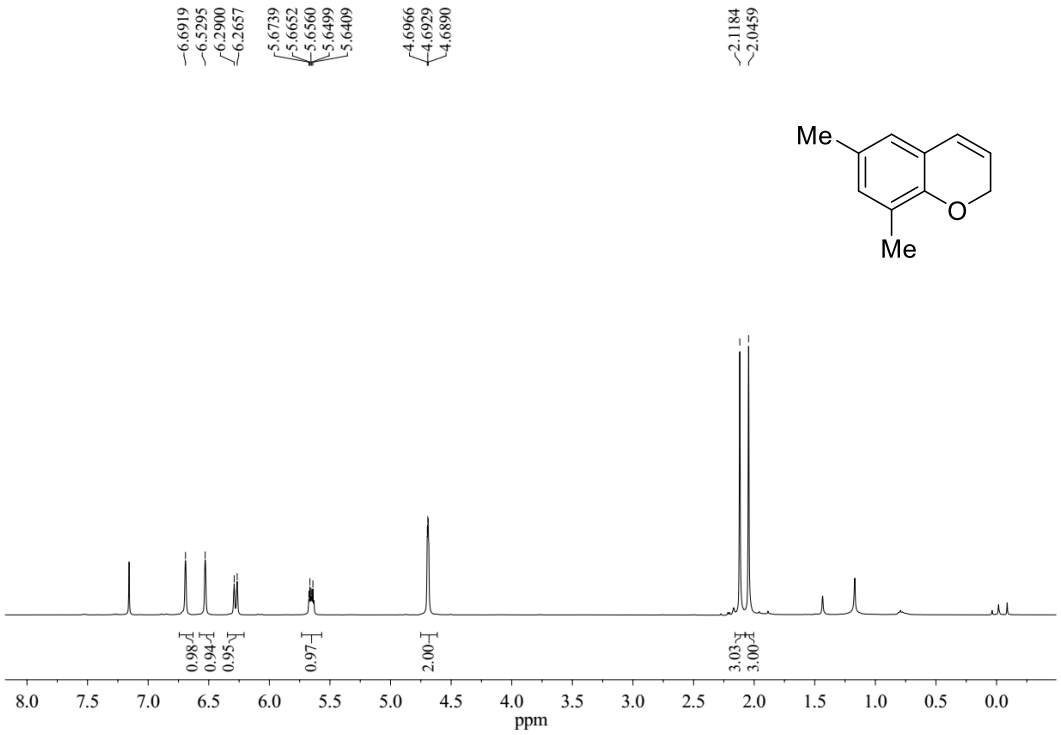


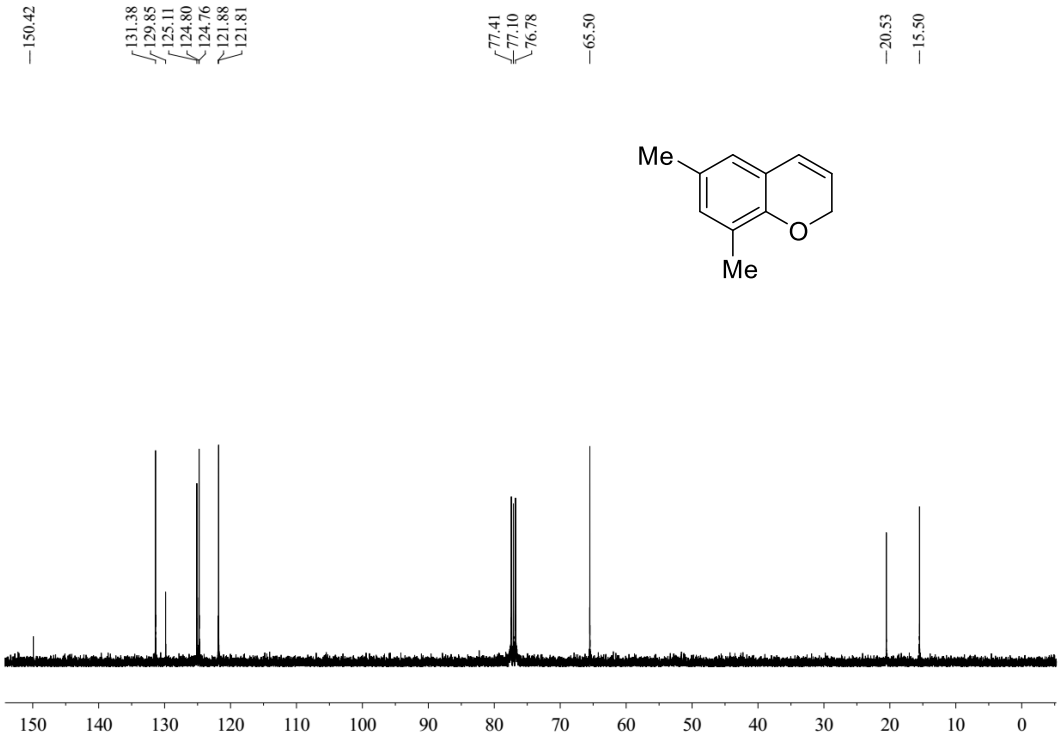




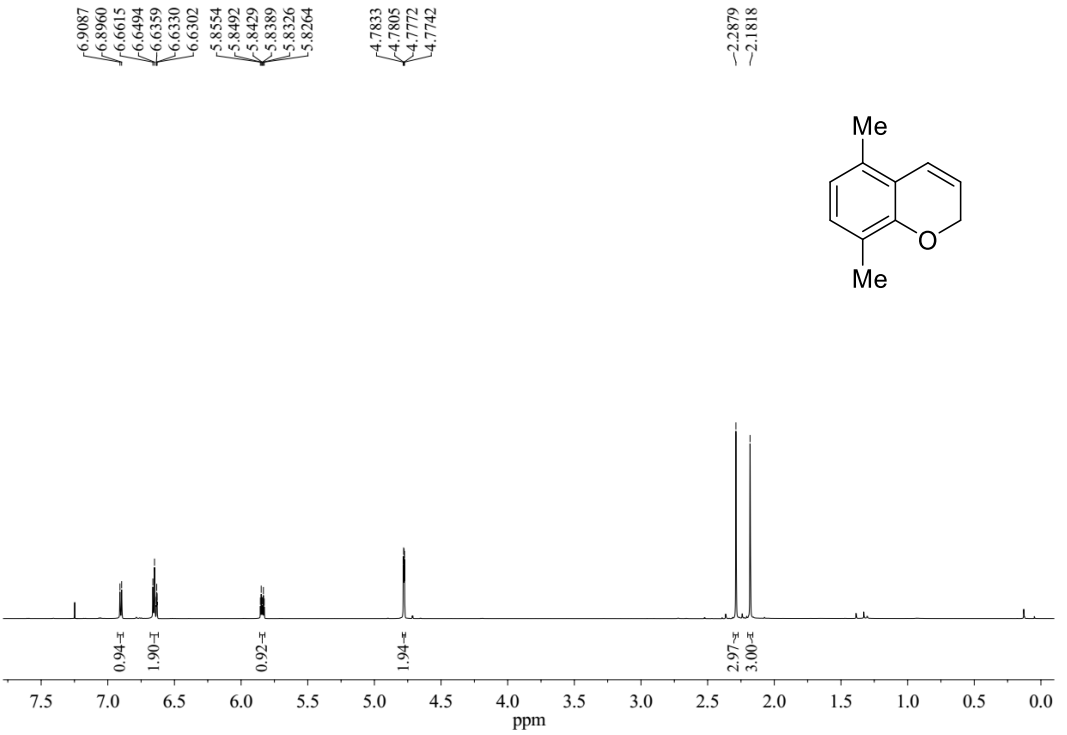


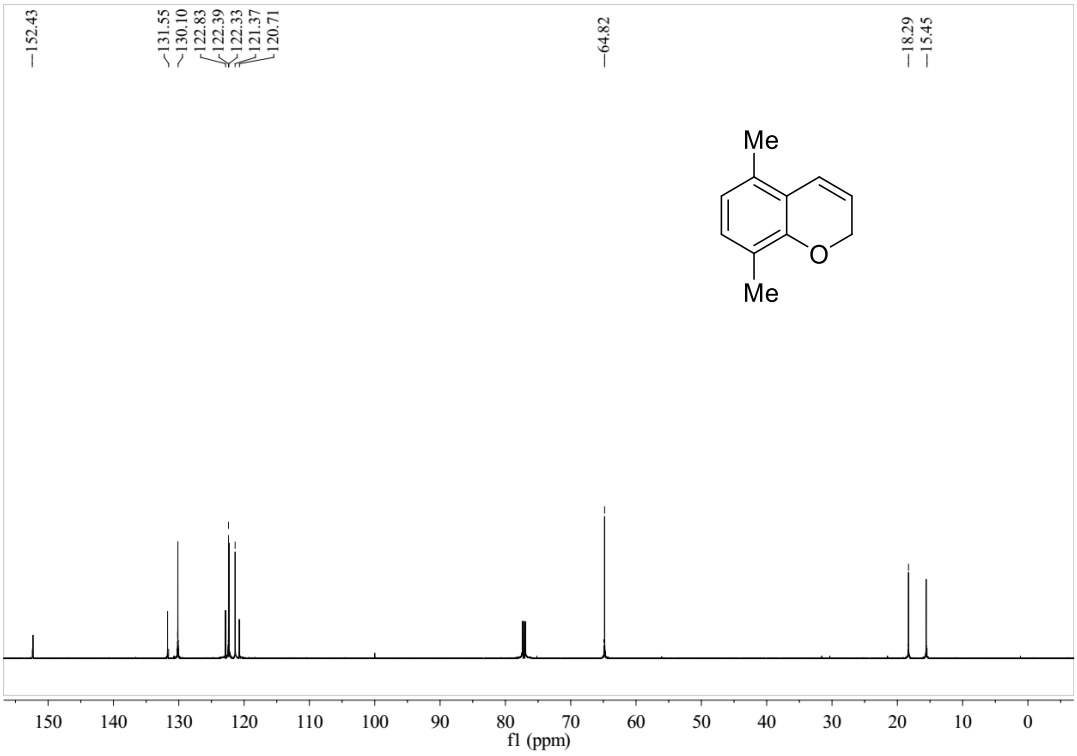
6, 8-dimethyl-2H-chromene (3j)



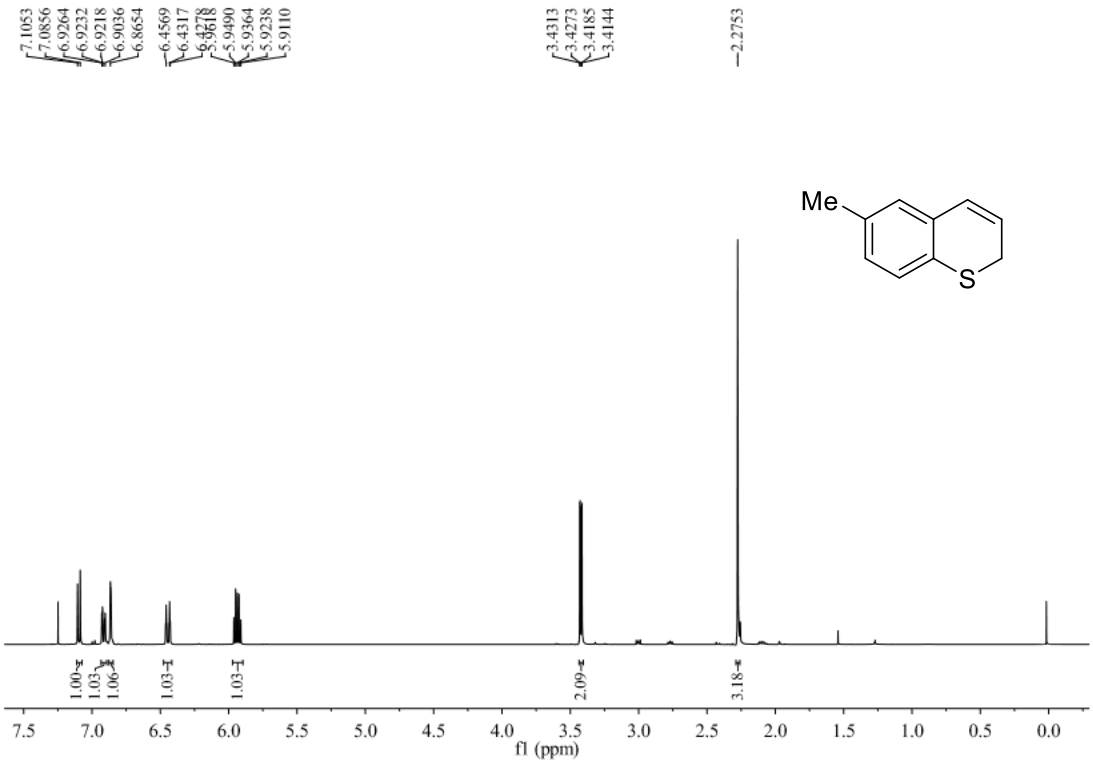


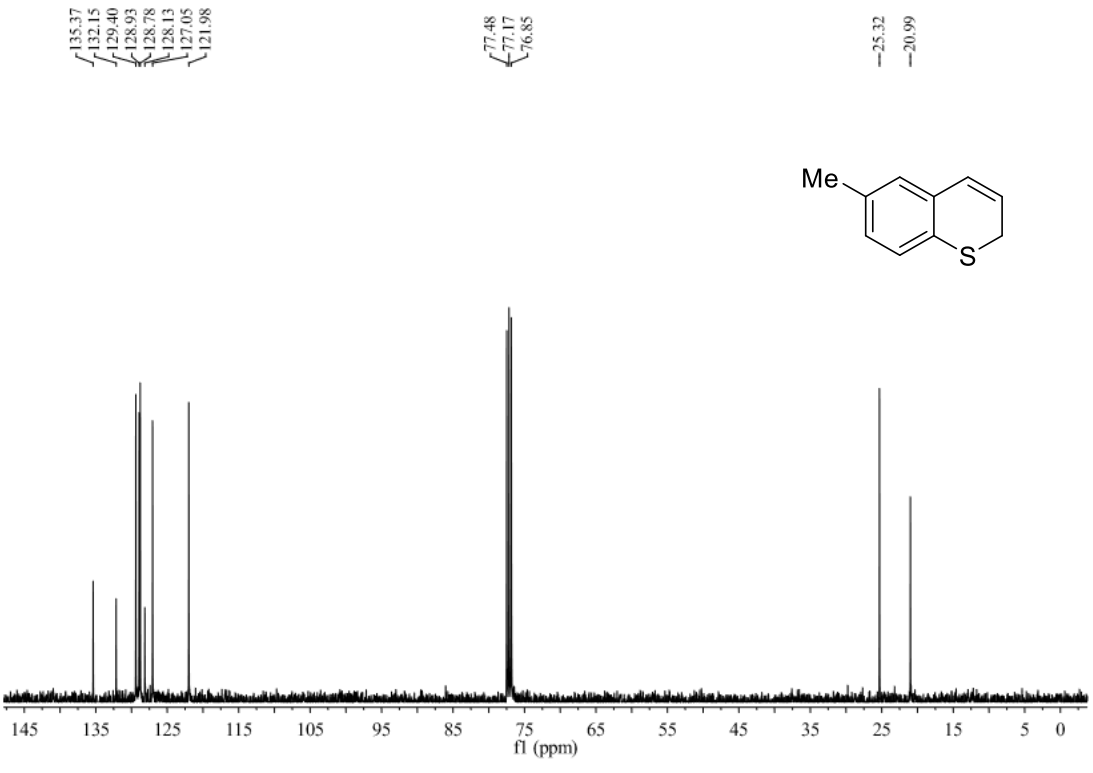
5, 8-dimethyl-2H-chromene (3k)



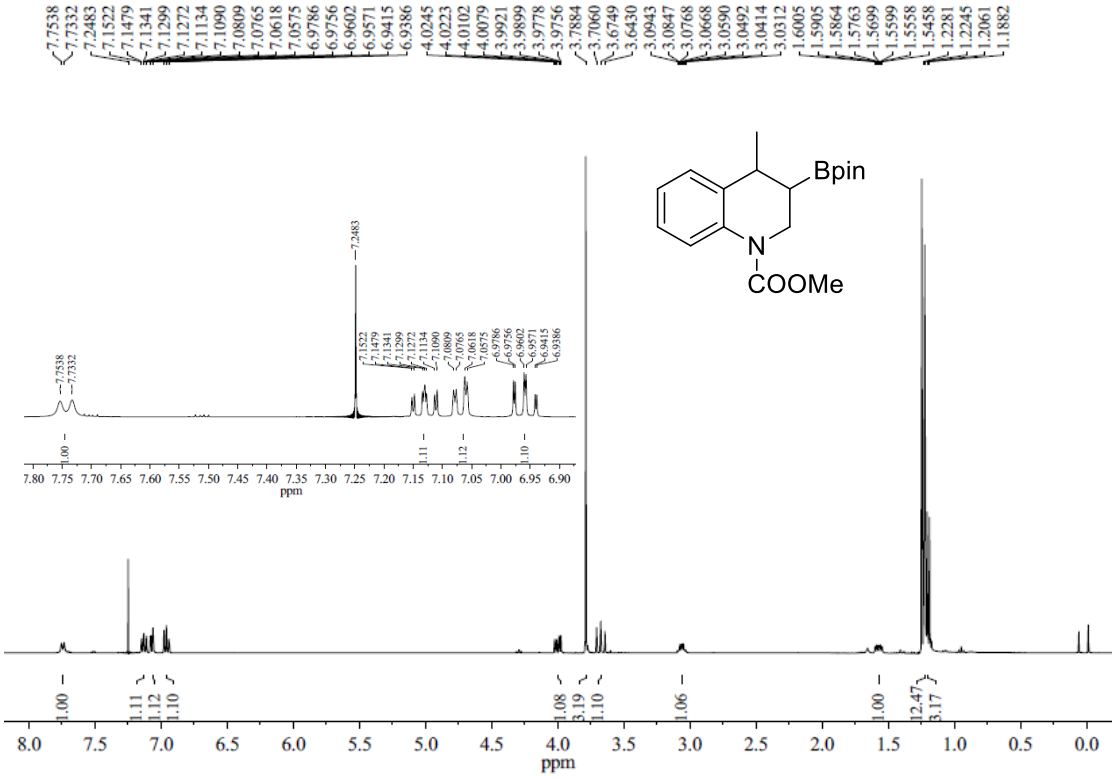


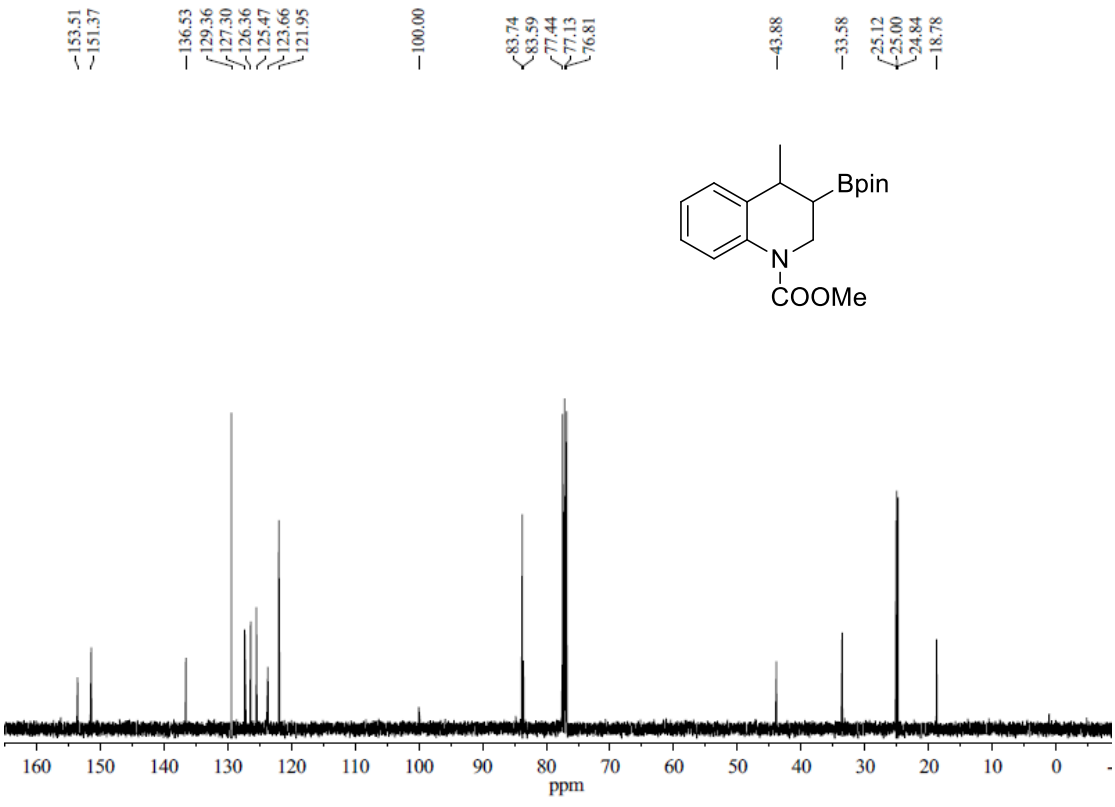
6-methyl-2H-thiochromene (3l)





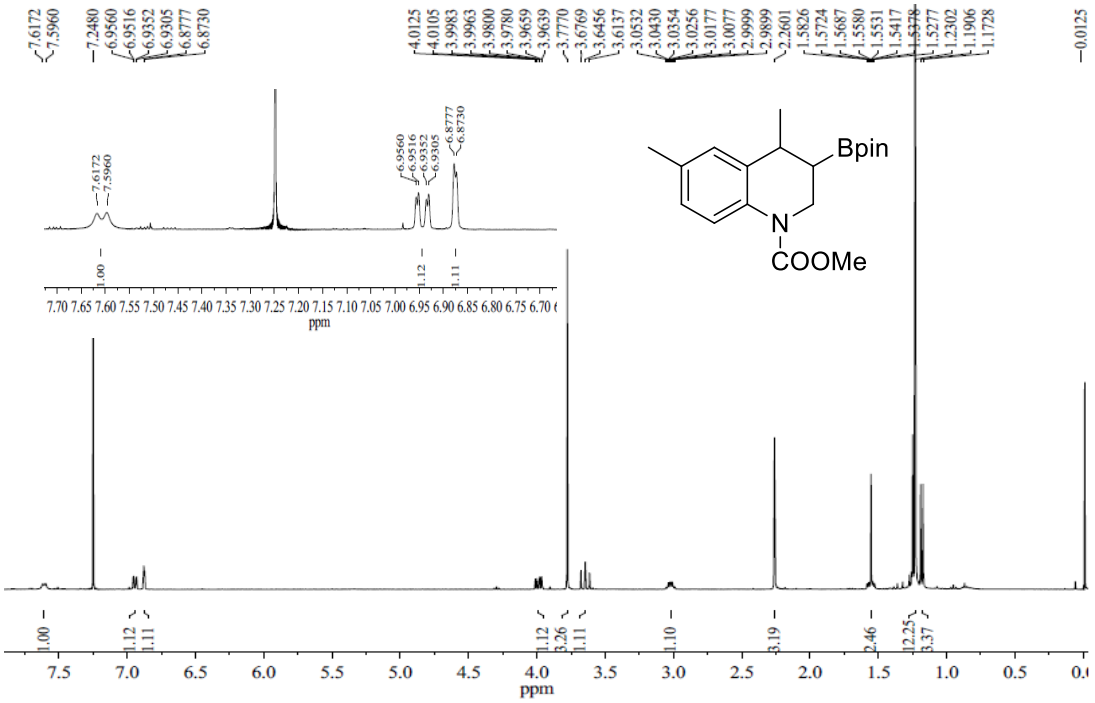
methyl 4-methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3,4-dihydroquinoline-1(*2H*)-carboxylate (2a)

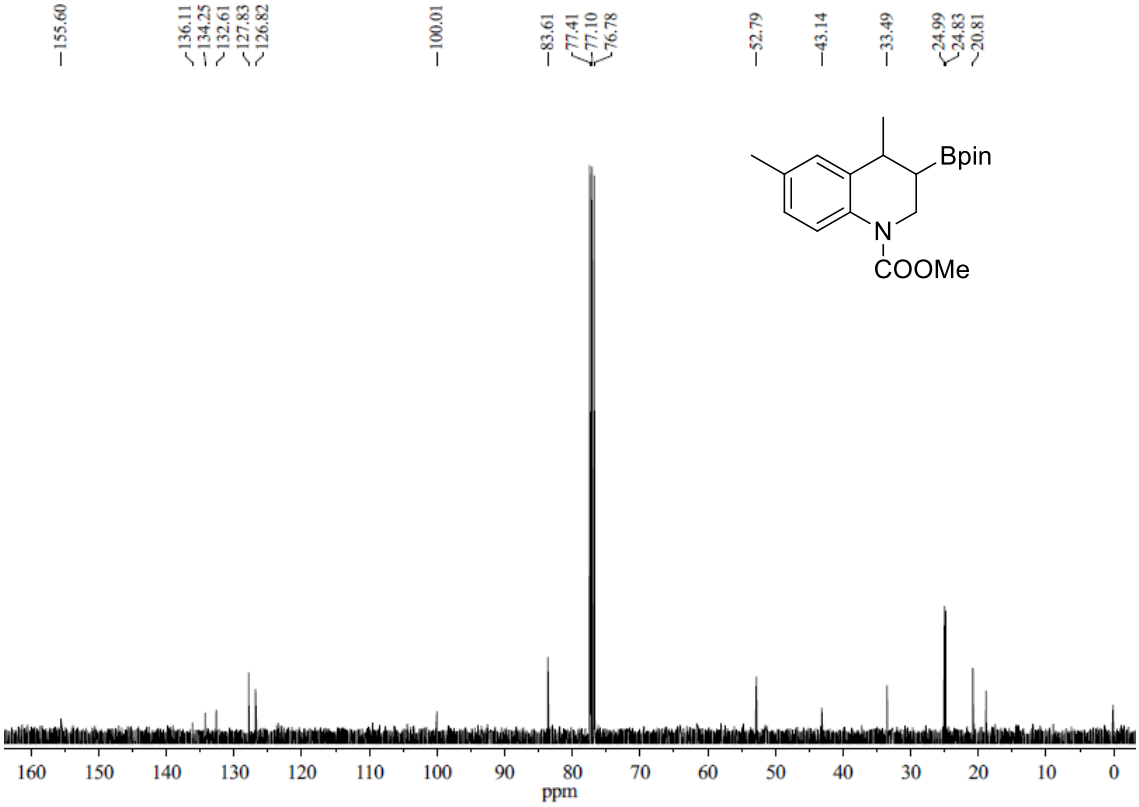




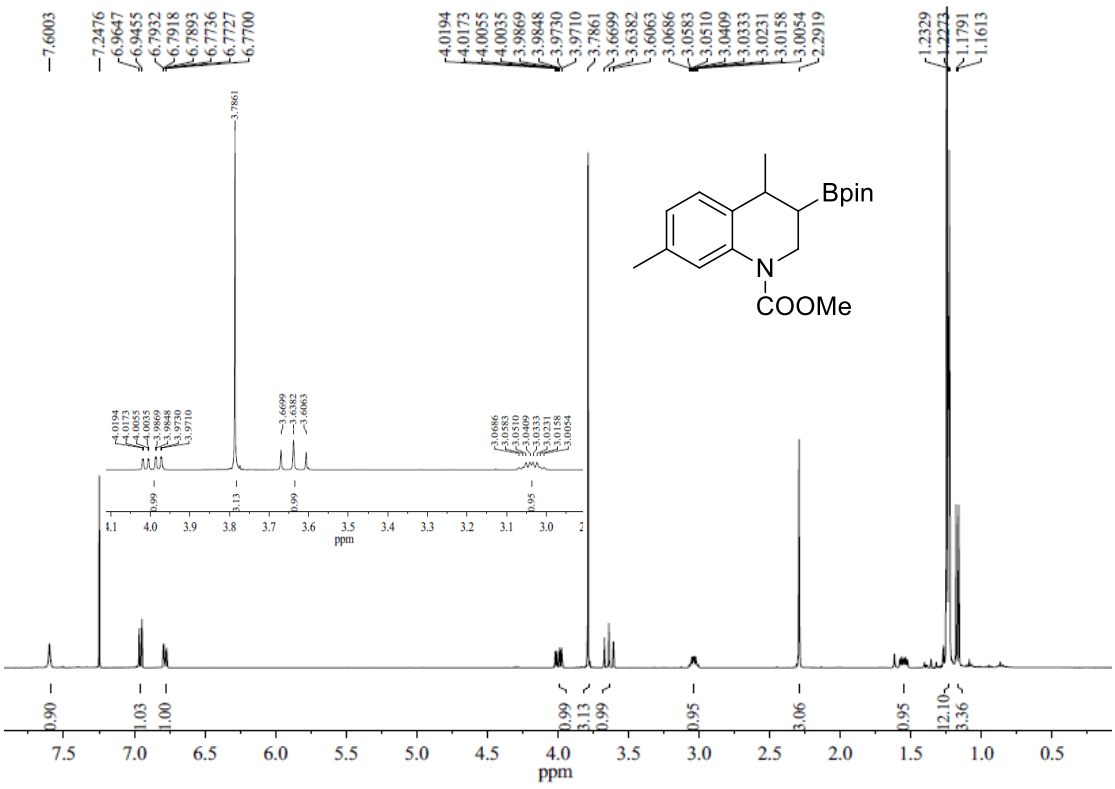
Methyl 4,6-dimethyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3,4-dihydroquinoline-

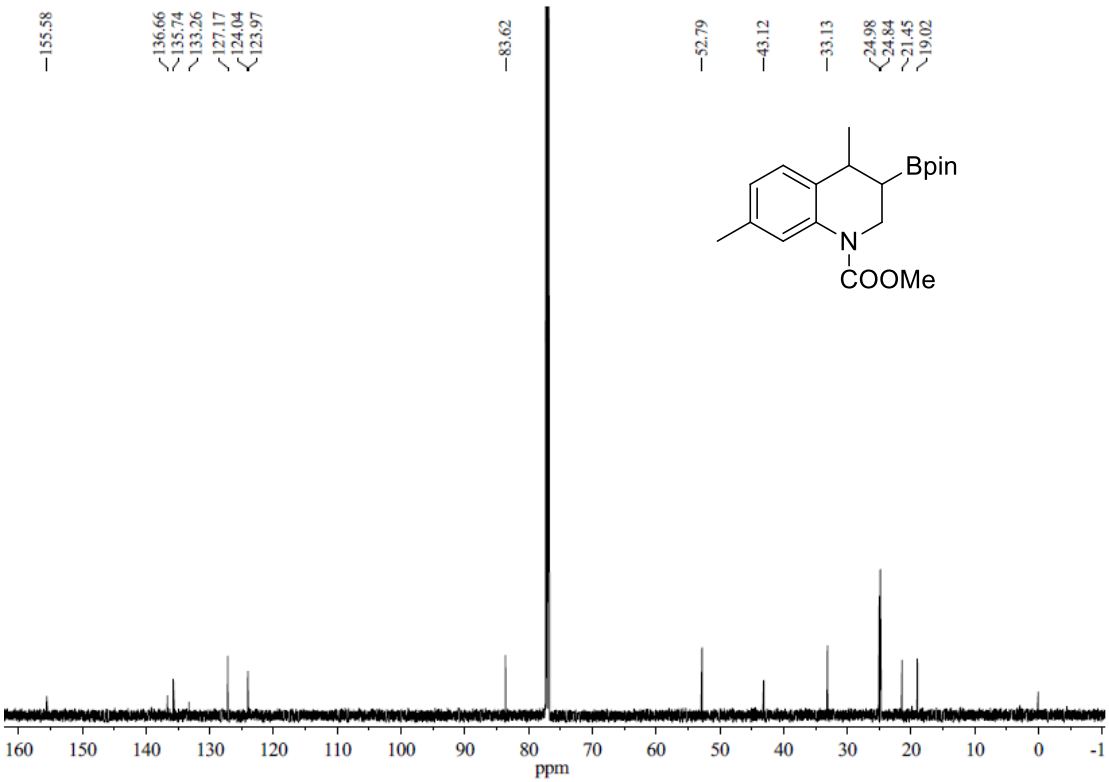
1(*2H*)-carboxylate (2b)



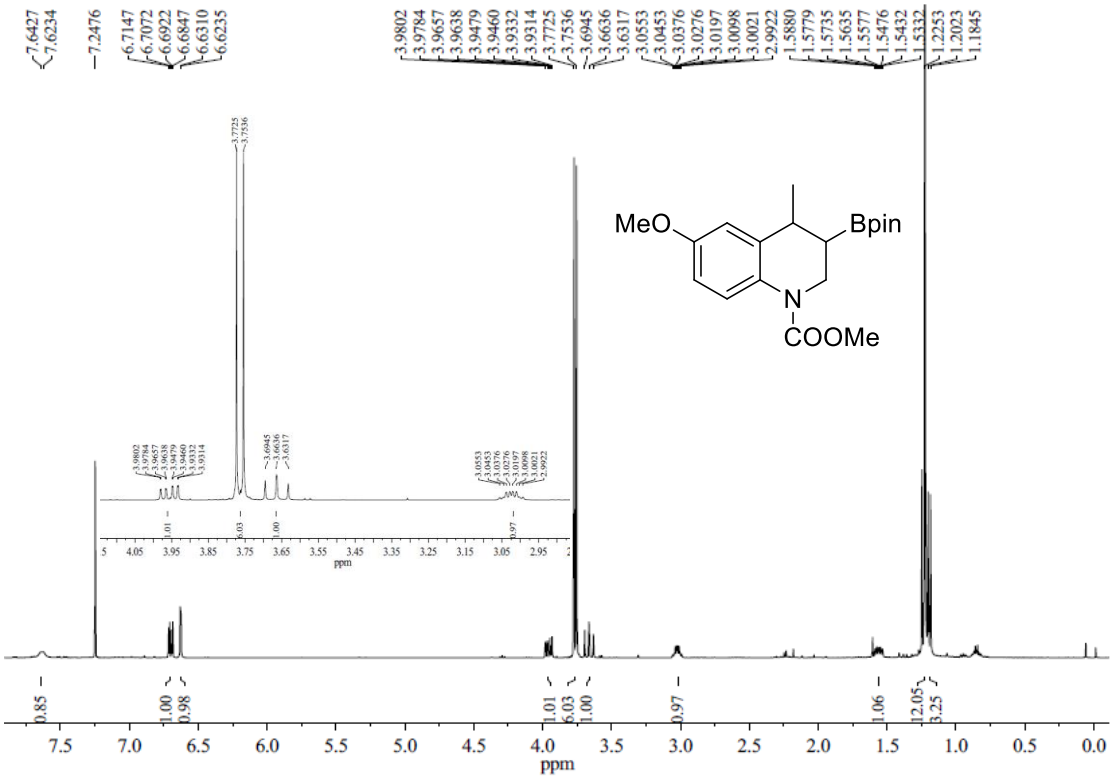


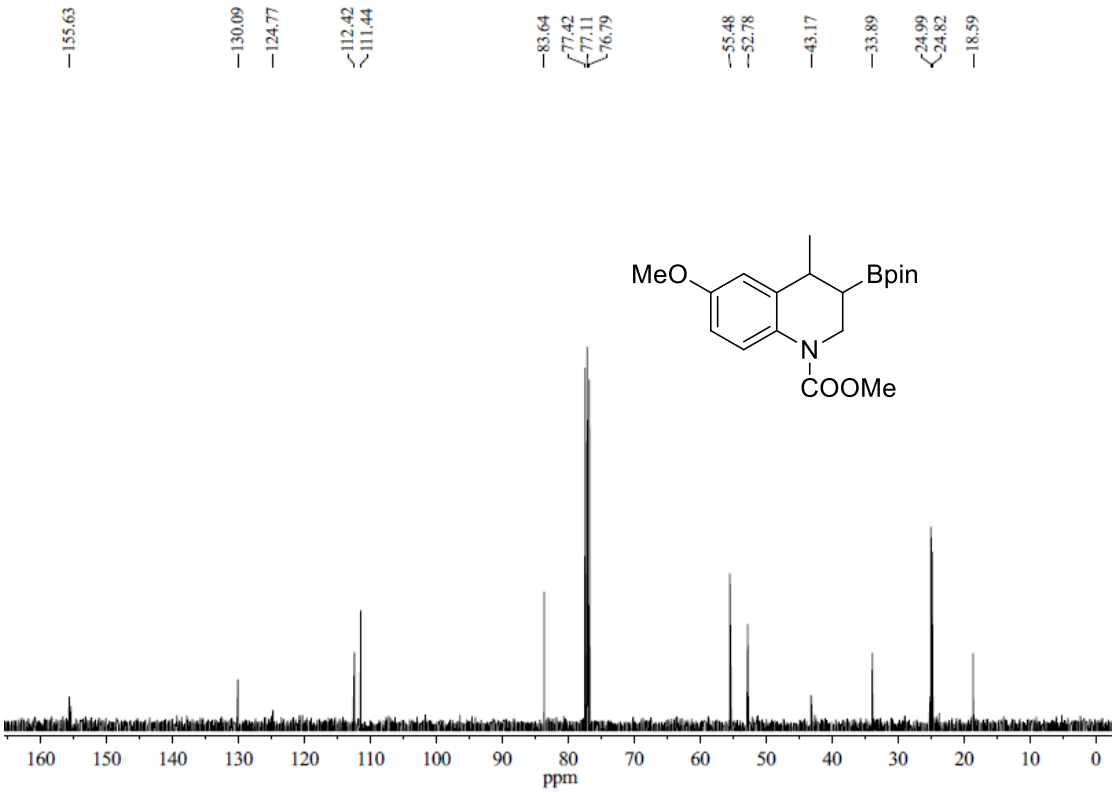
Methyl 4,7-dimethyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3,4-dihydroquinoline-1(2H)-carboxylate (2c)



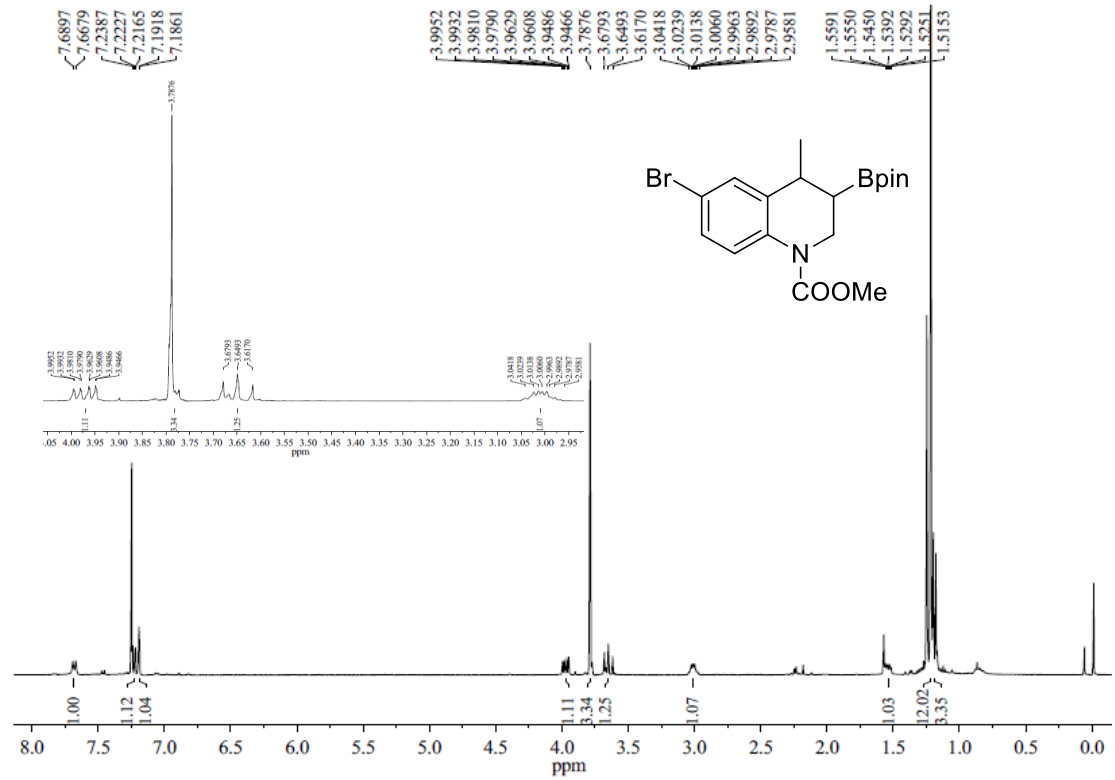


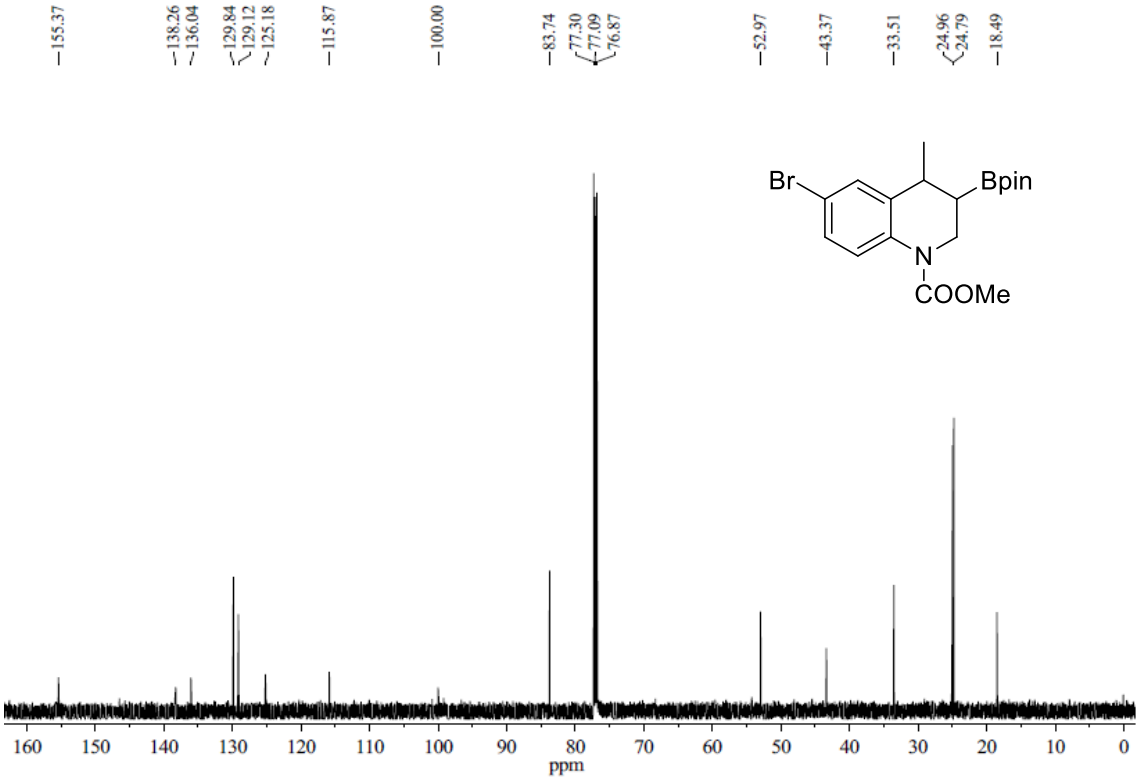
Methyl 6-methoxy-4-methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3,4-dihydroquinoline-1(*2H*)-carboxylate (2d)



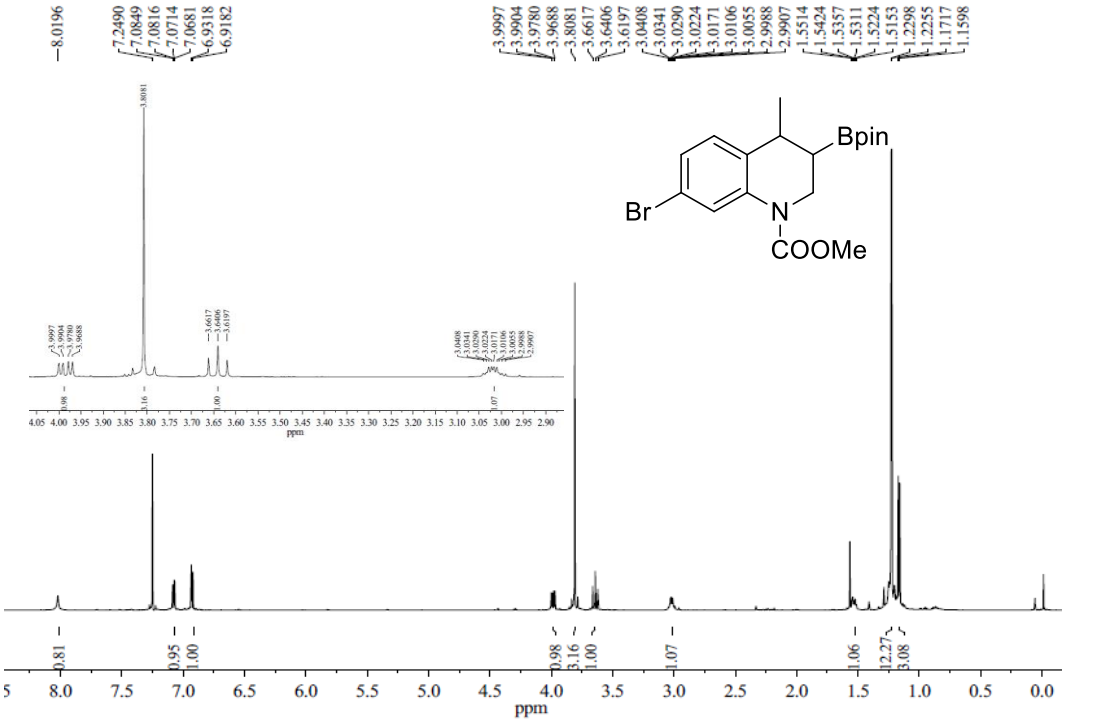


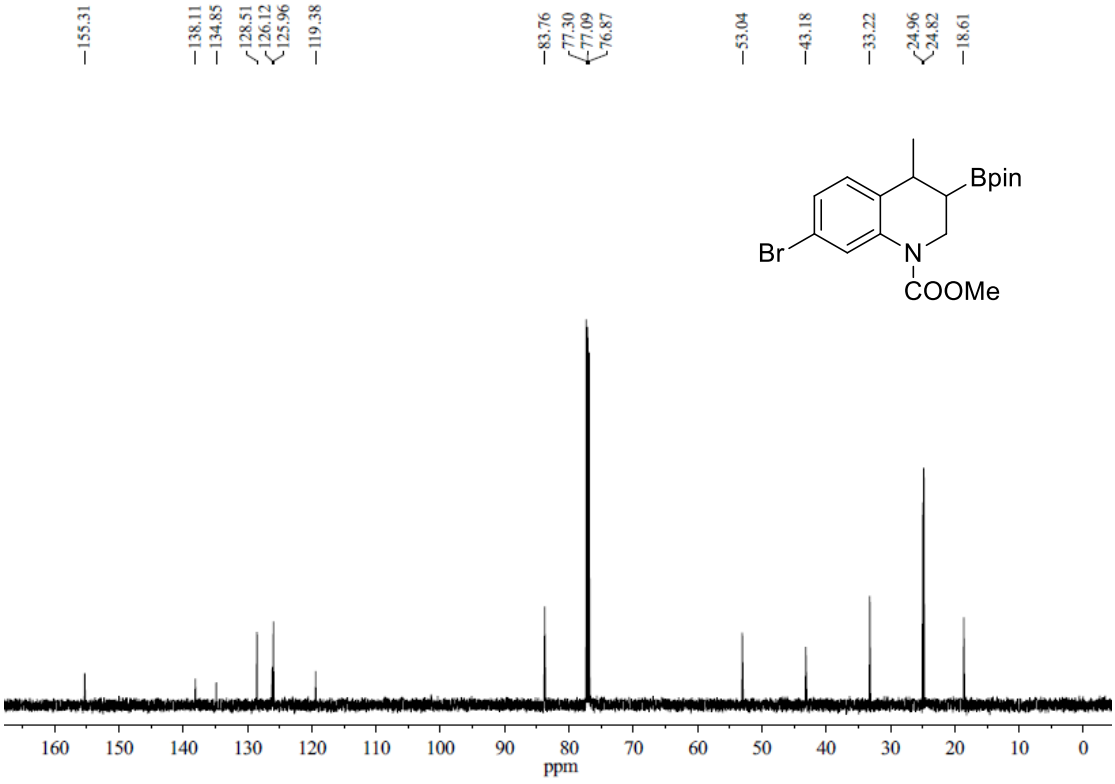
methyl 6-bromo-4-methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3,4-dihydroquinoline-1(*2H*)-carboxylate (2e)



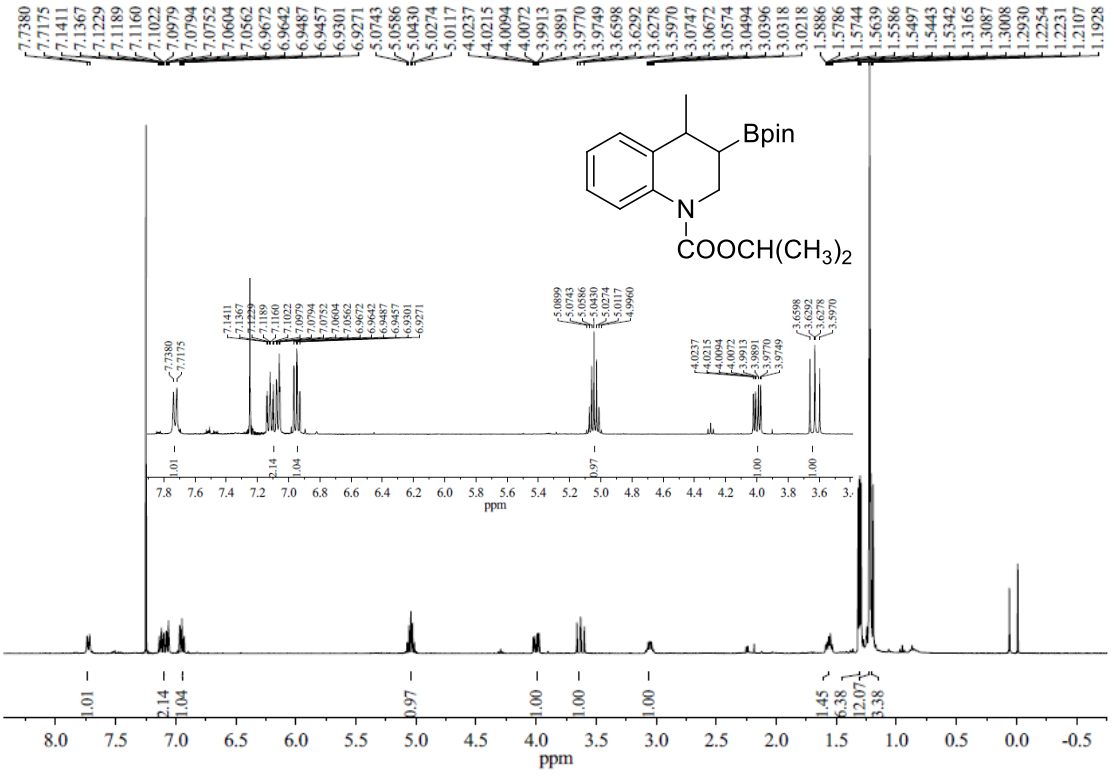


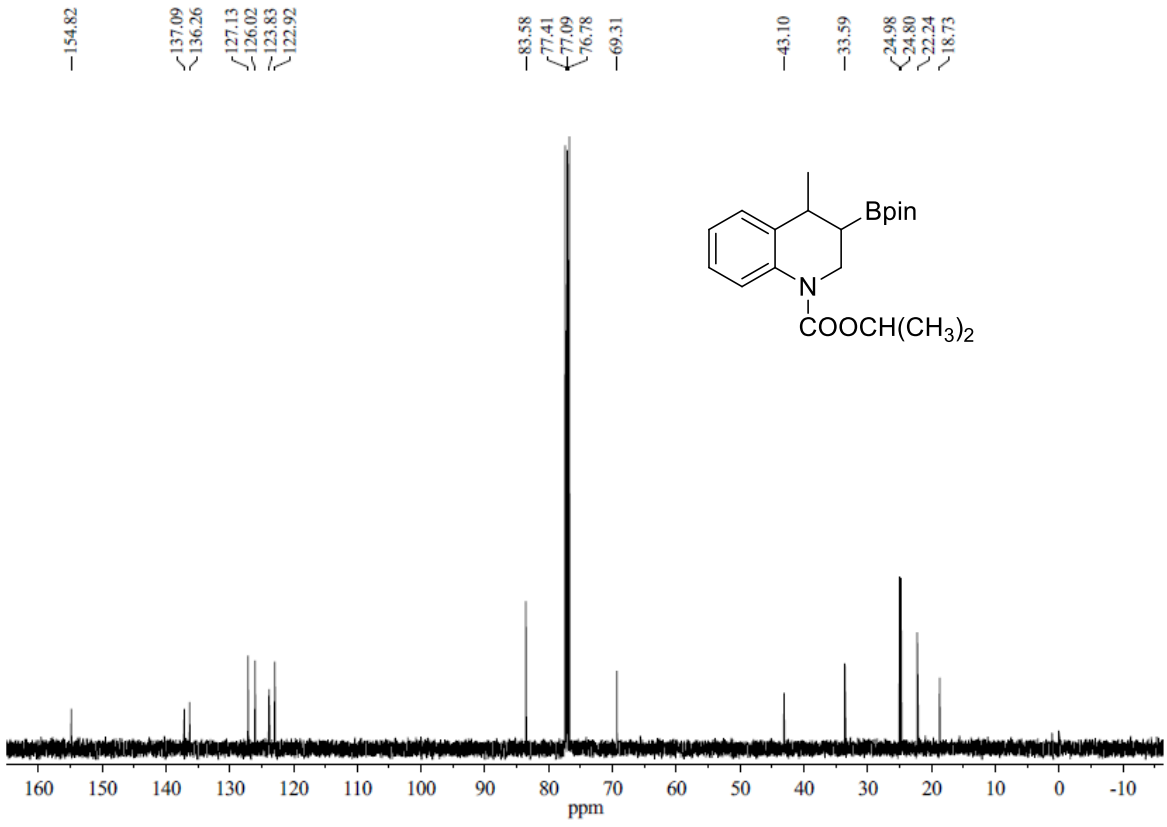
methyl 7-bromo-4-methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3,4-dihydroquinoline-1(2*H*)-carboxylate (2f)



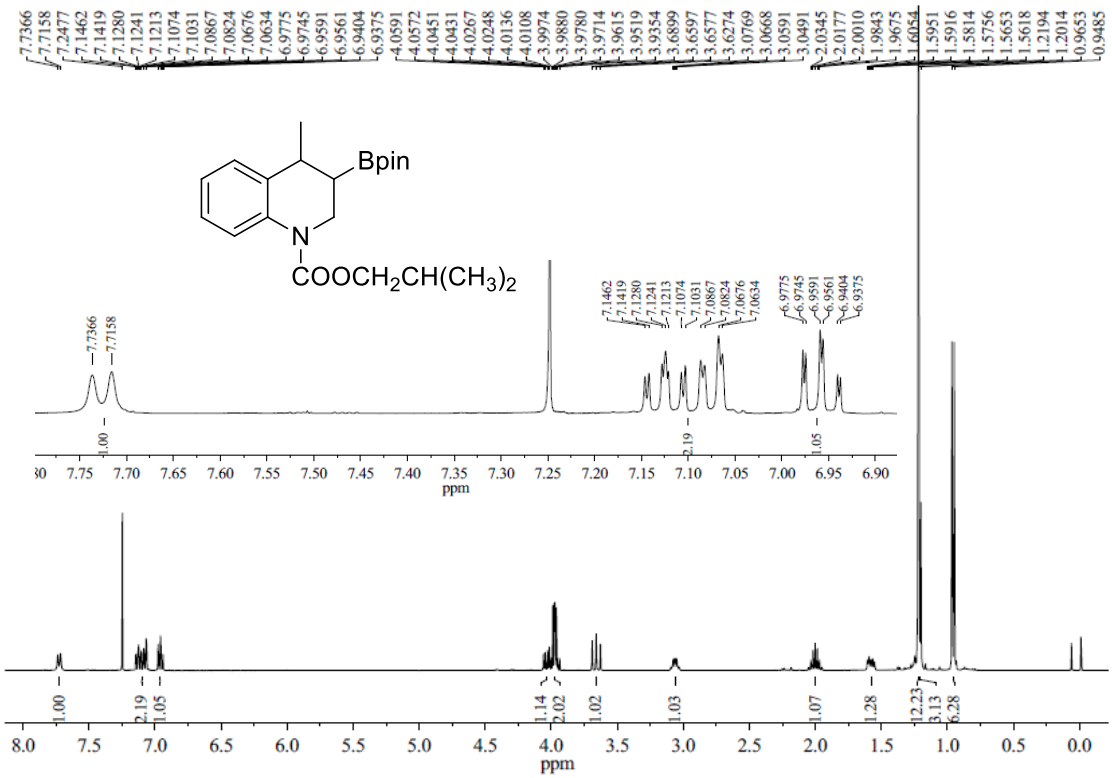


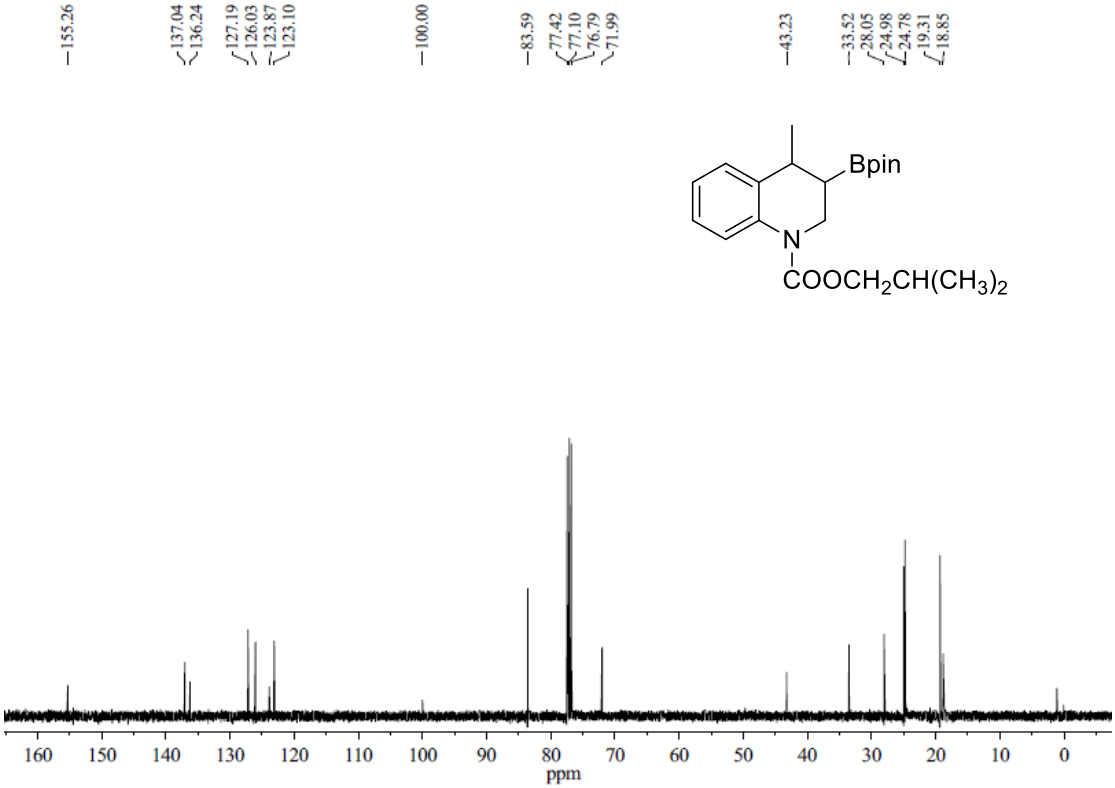
Isopropyl 4-methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3,4-dihydroquinoline-1(*2H*)-carboxylate (2g)



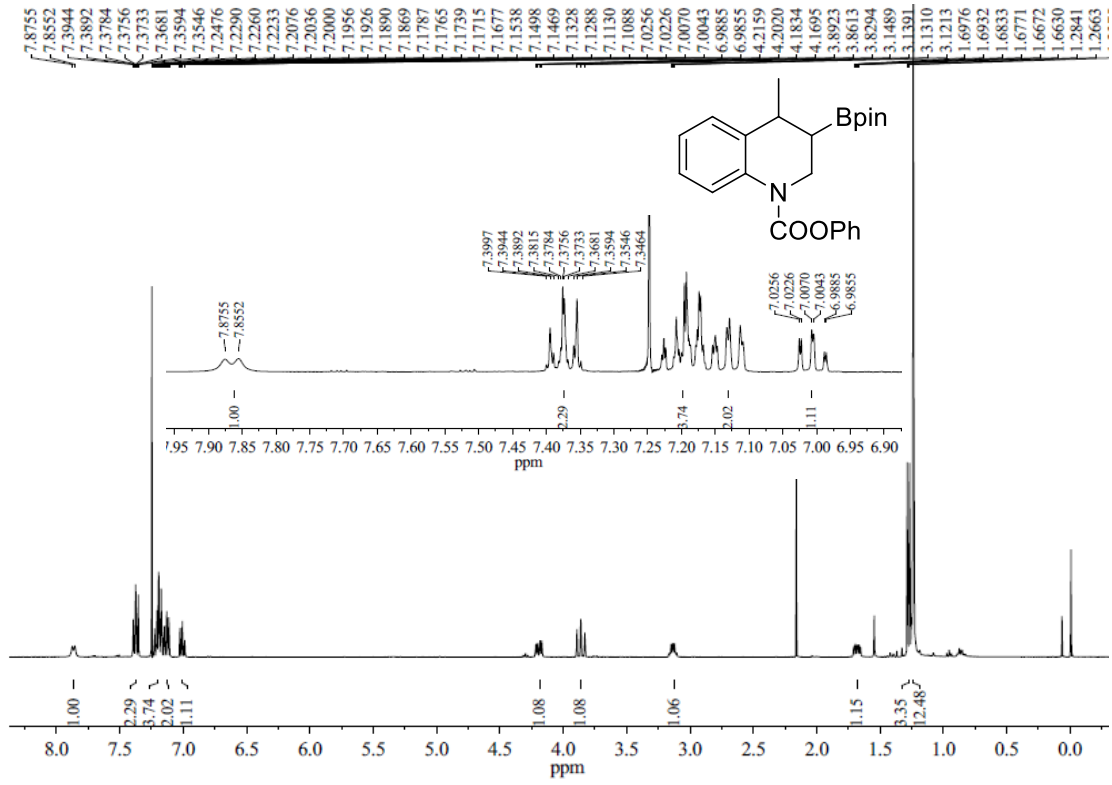


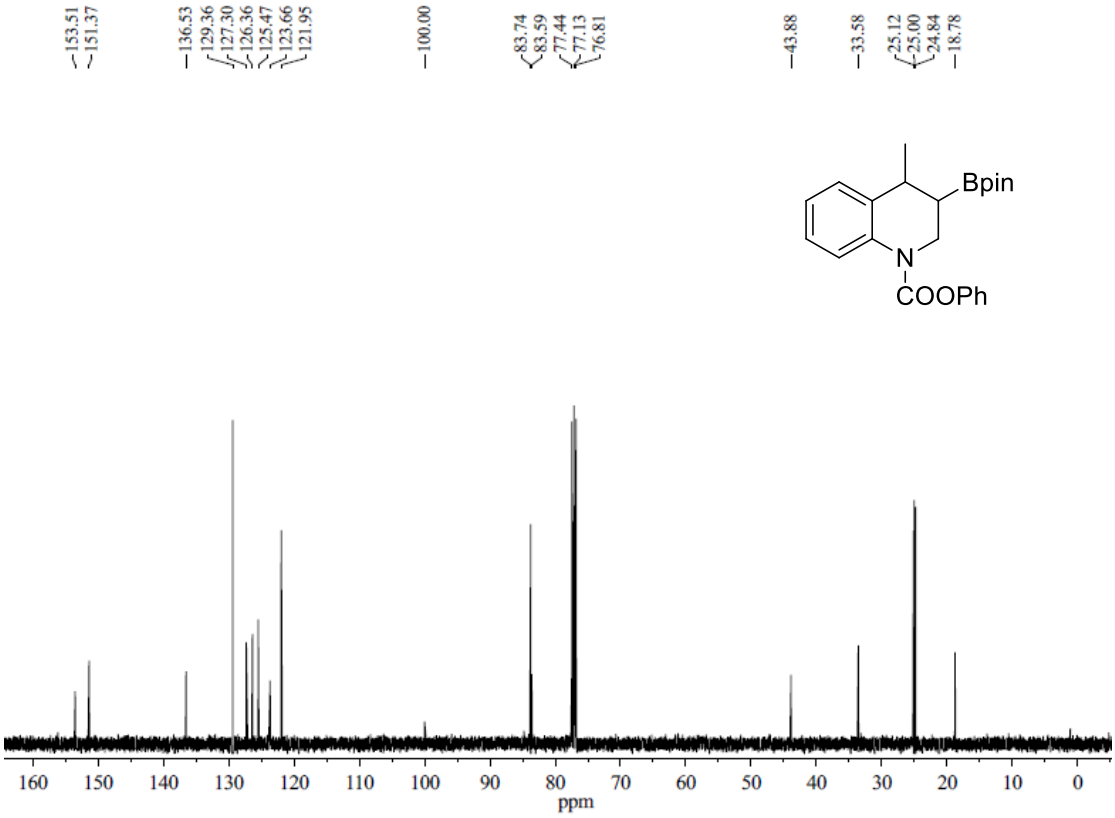
Isobutyl 4-methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3,4-dihydroquinoline-1(*2H*)-carboxylate (2h)



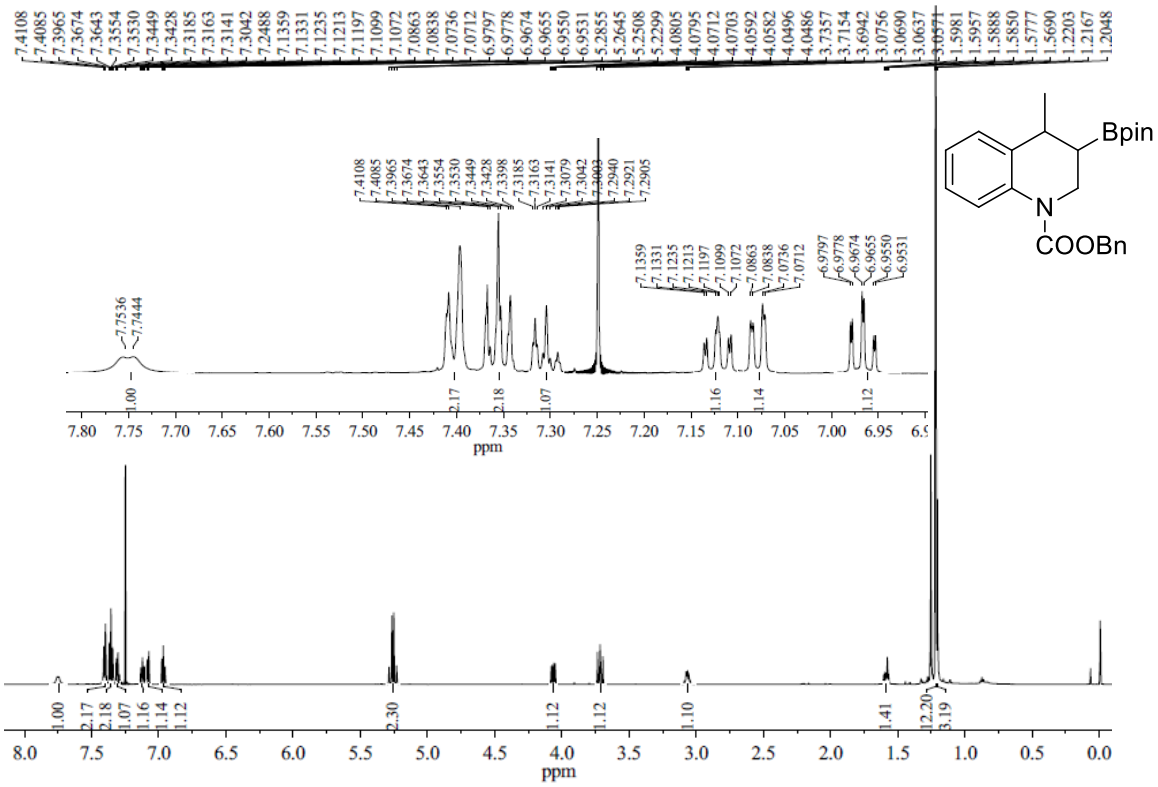


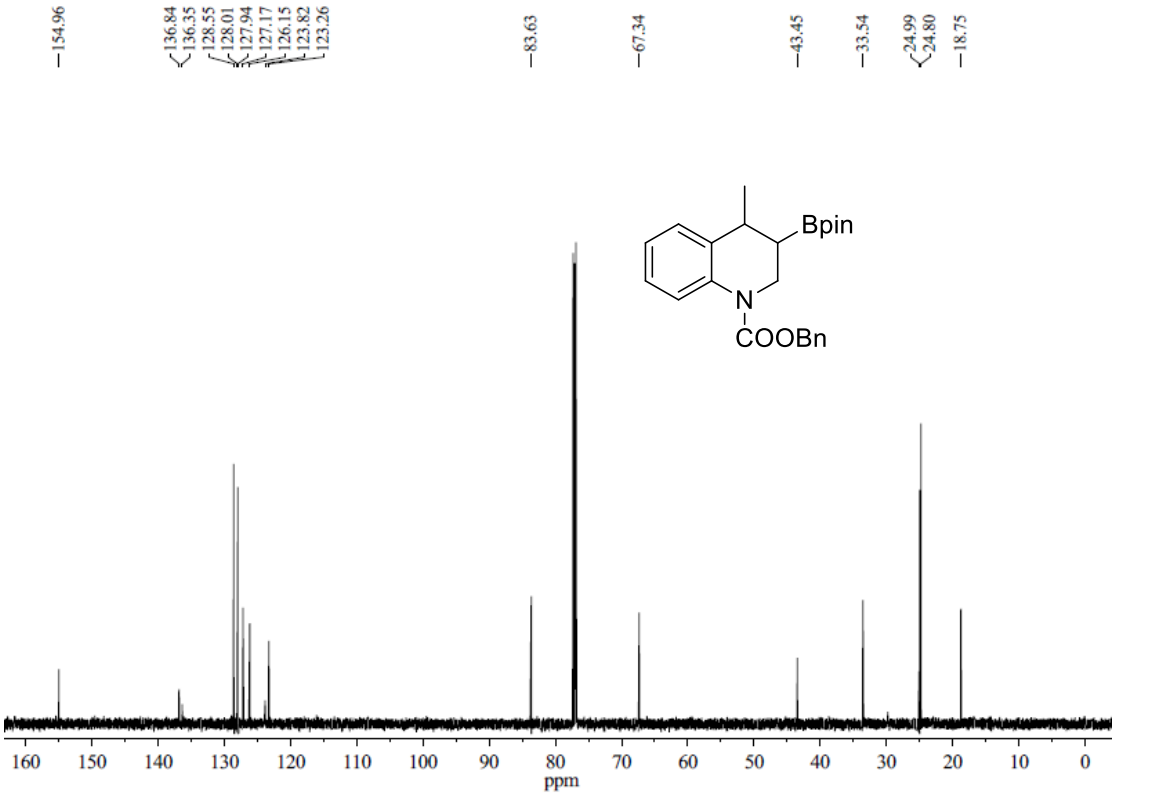
Phenyl 4-methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3,4-dihydroquinoline-1(*2H*)-carboxylate (2i)



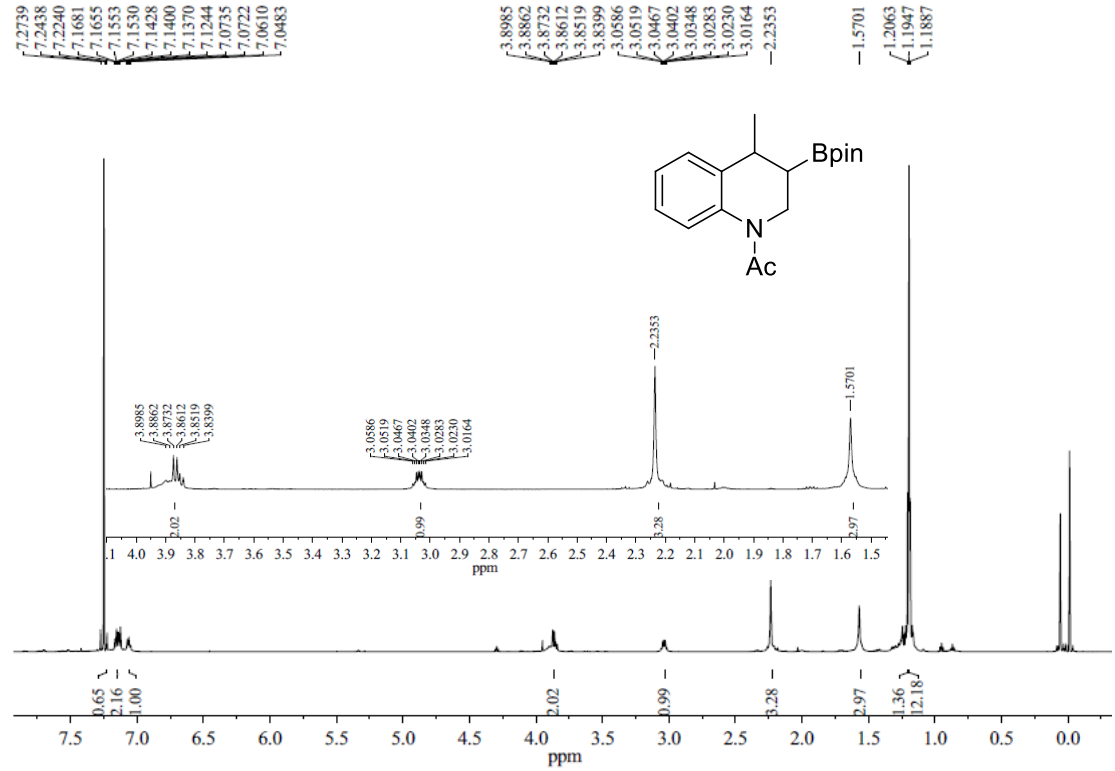


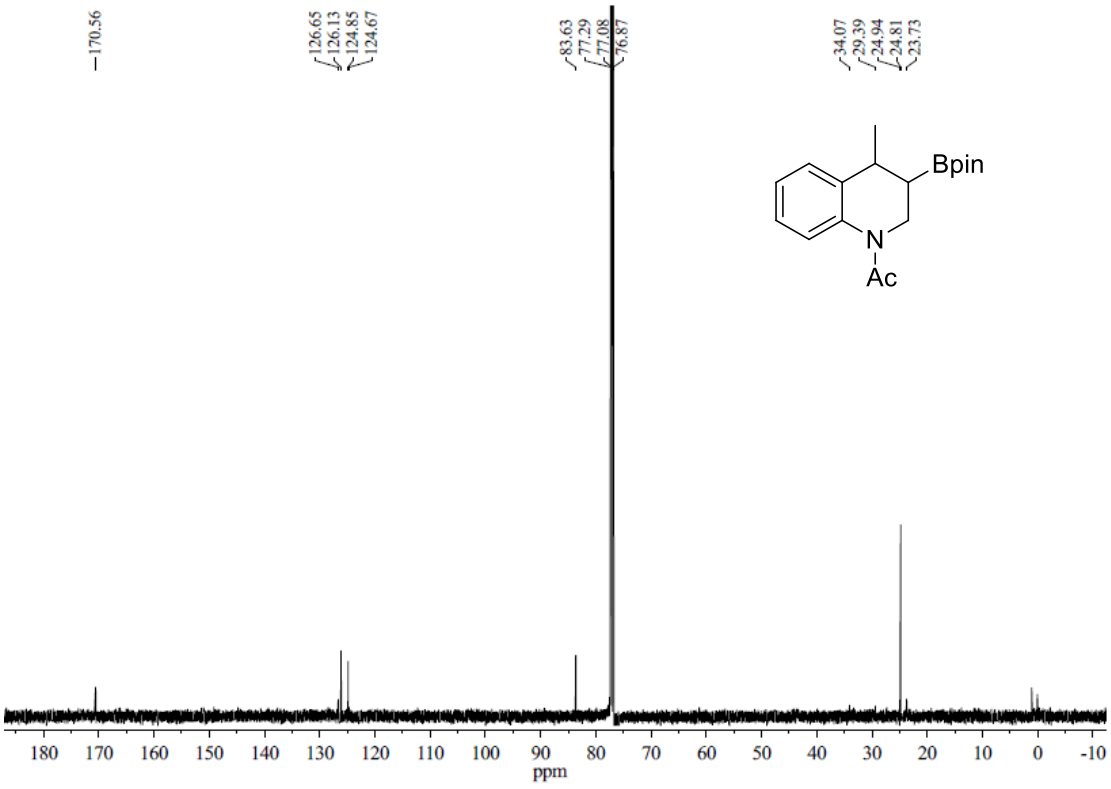
Benzyl 4-methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3,4-dihydroquinoline-1(*2H*)-carboxylate (2j)



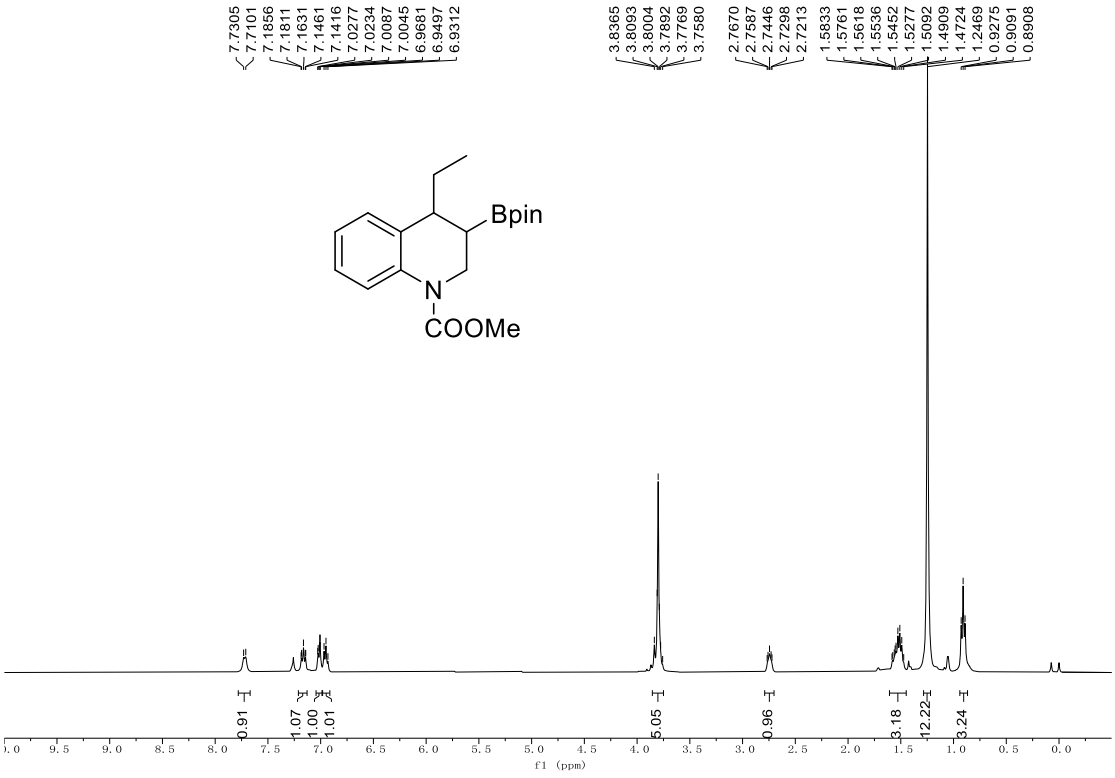


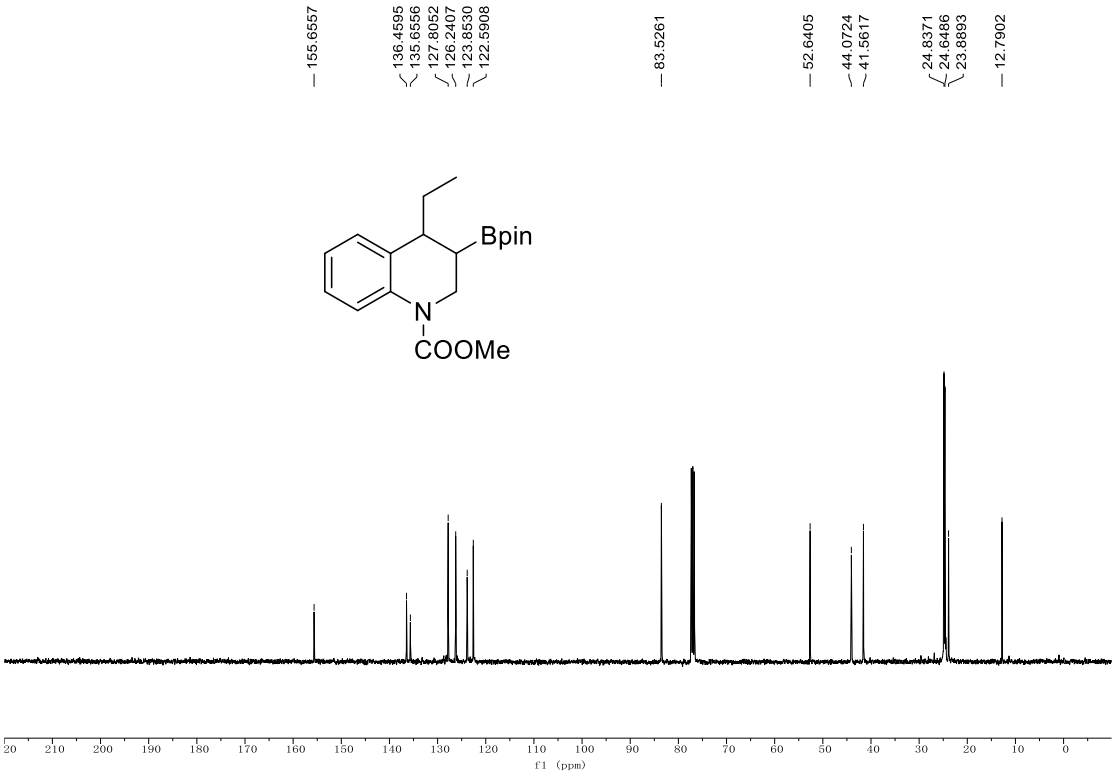
1-(4-methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3,4-dihydroquinolin-1(2H)-yl)ethanone (2k)



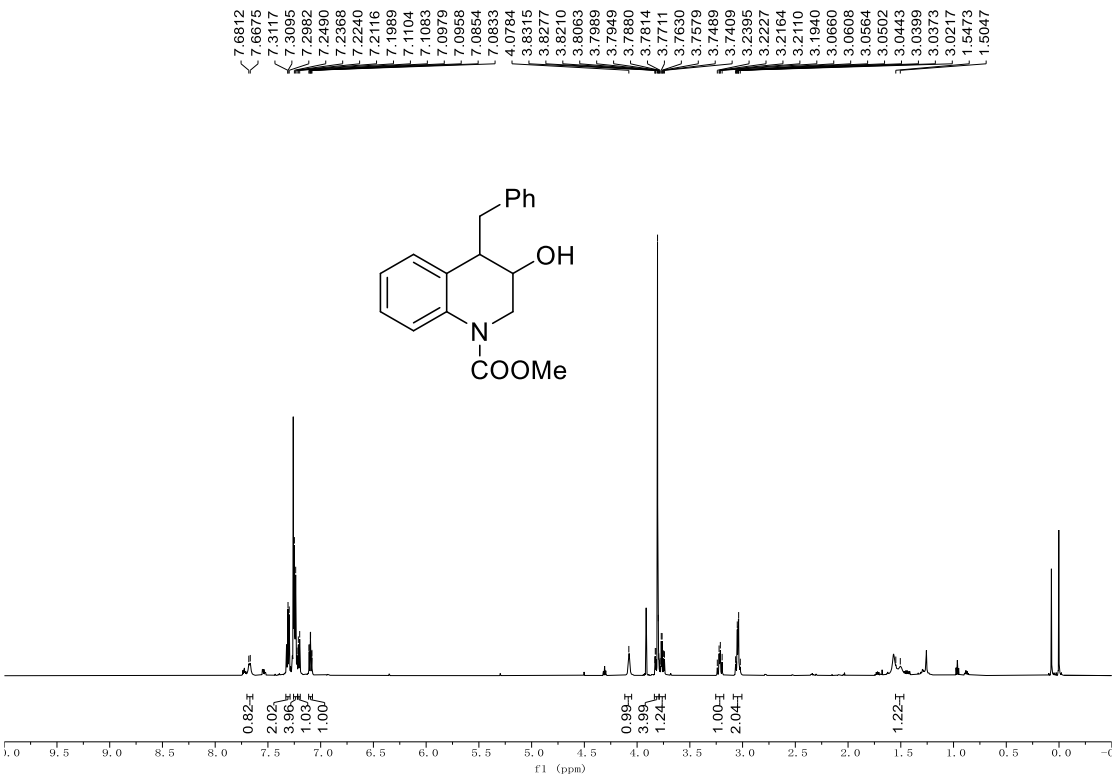


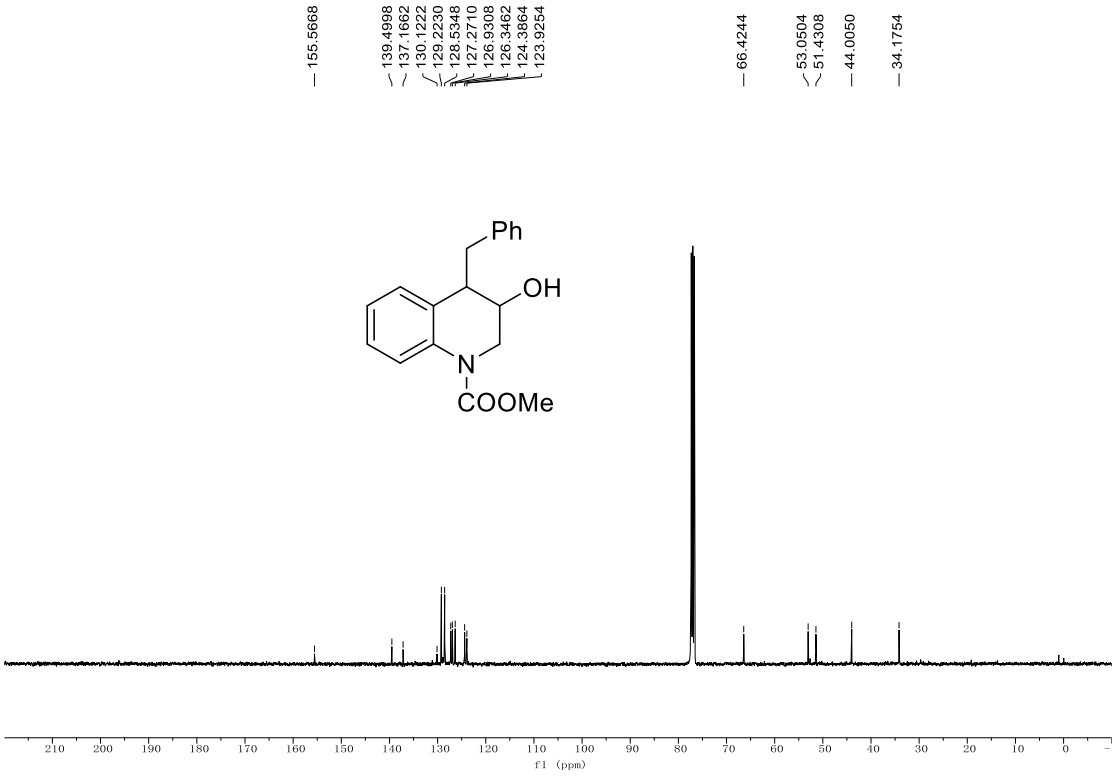
methyl 4-ethyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3,4-dihydroquinoline-1(2H)-carboxylate (2l)



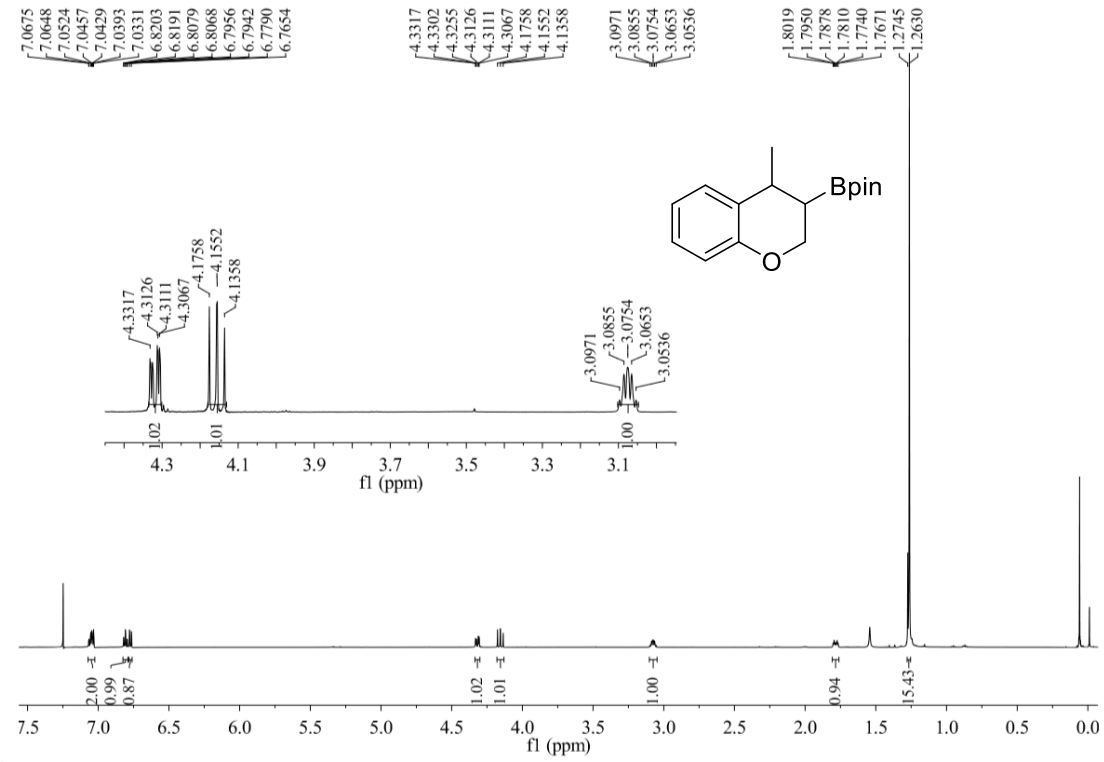


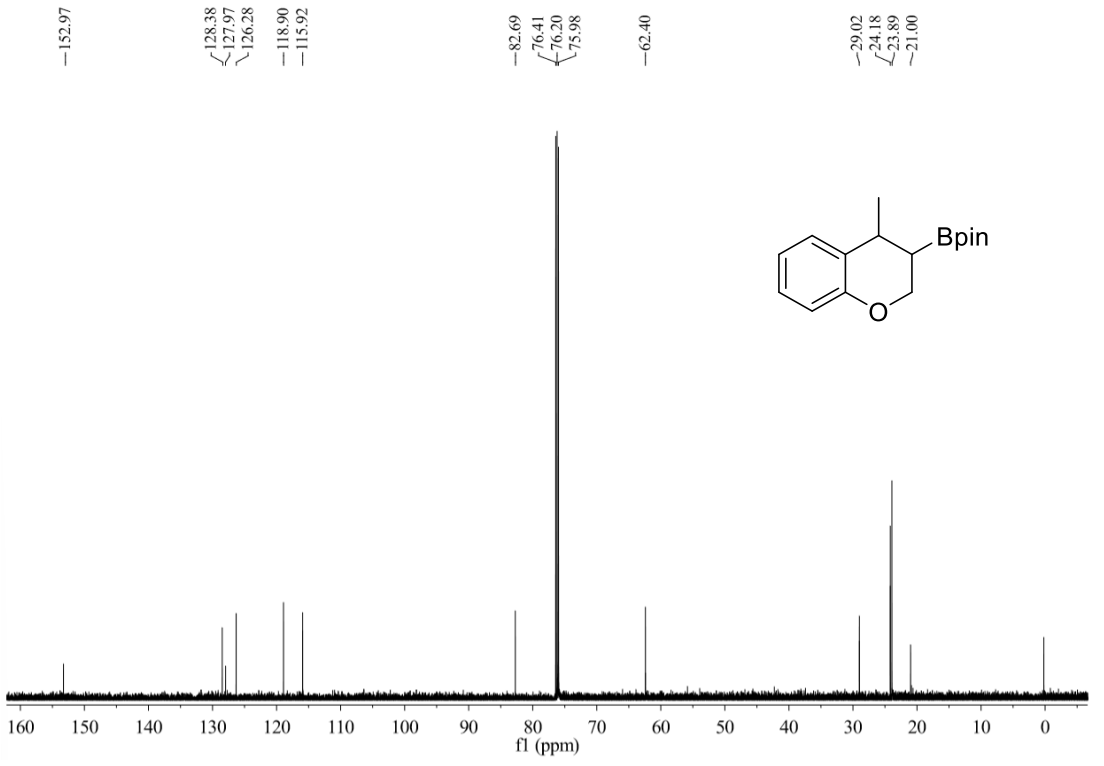
methyl 4-benzyl-3-hydroxy-3,4-dihydroquinoline-1(2H)-carboxylate (2m)



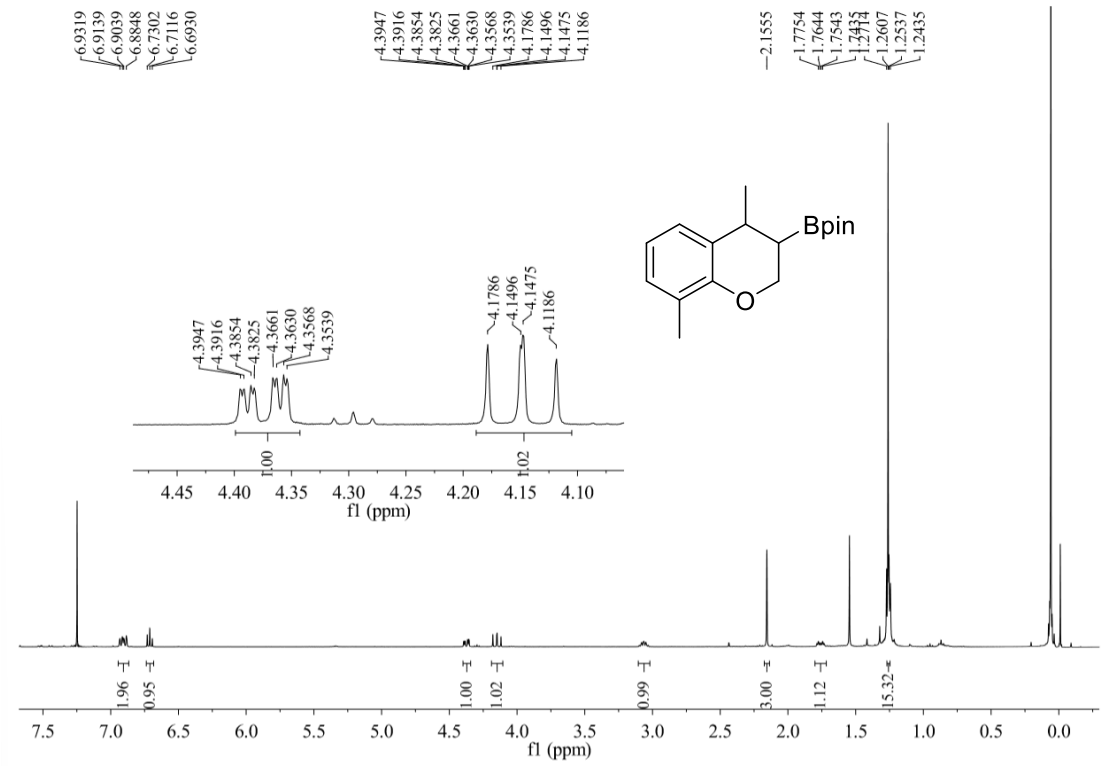


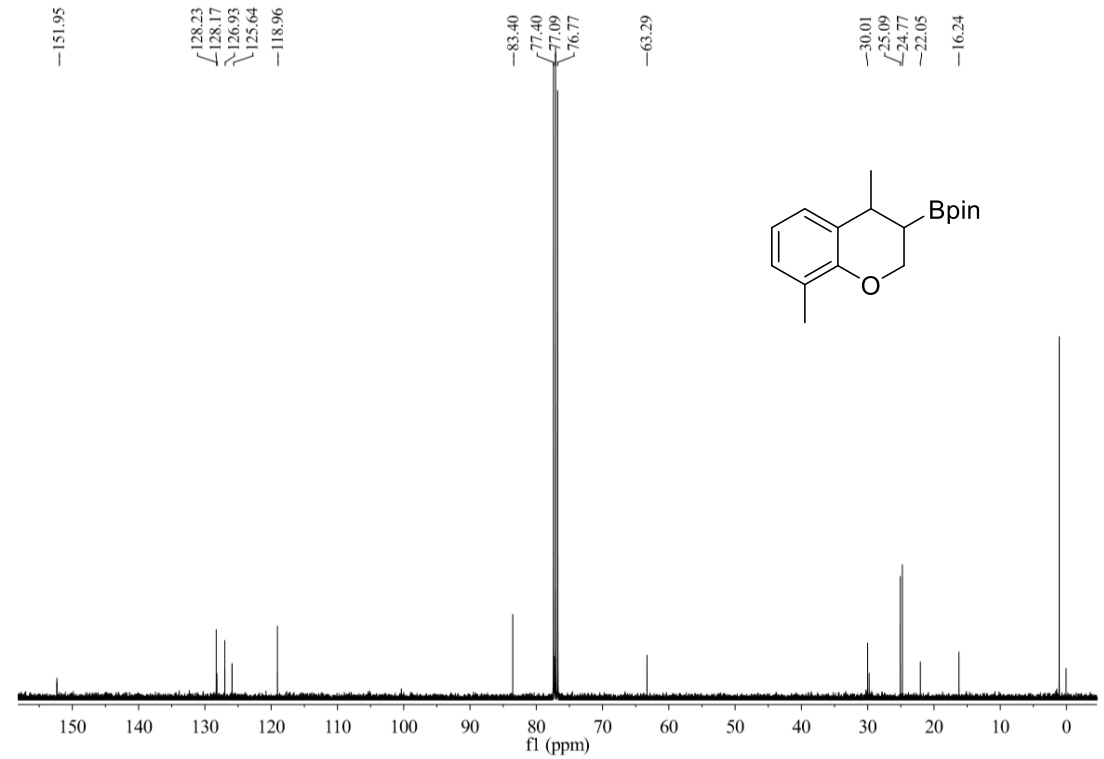
4,4,5,5-tetramethyl-2-(4-methylchroman-3-yl)-1,3,2-dioxaborolane (4a)



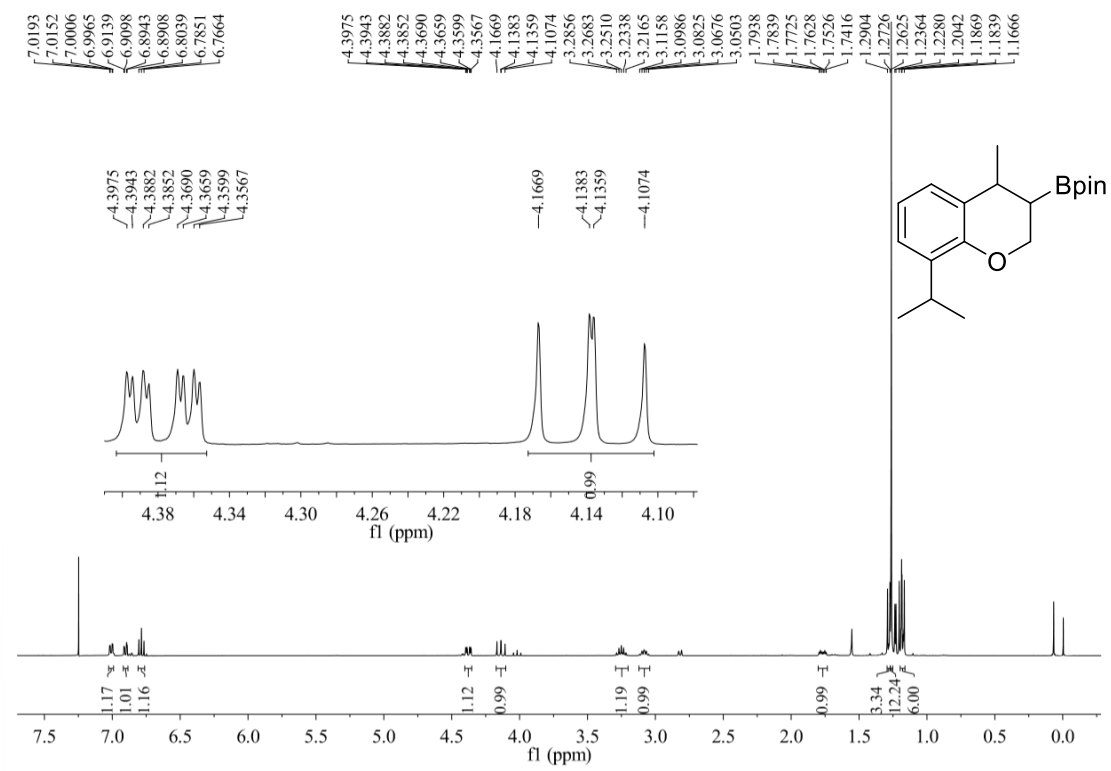


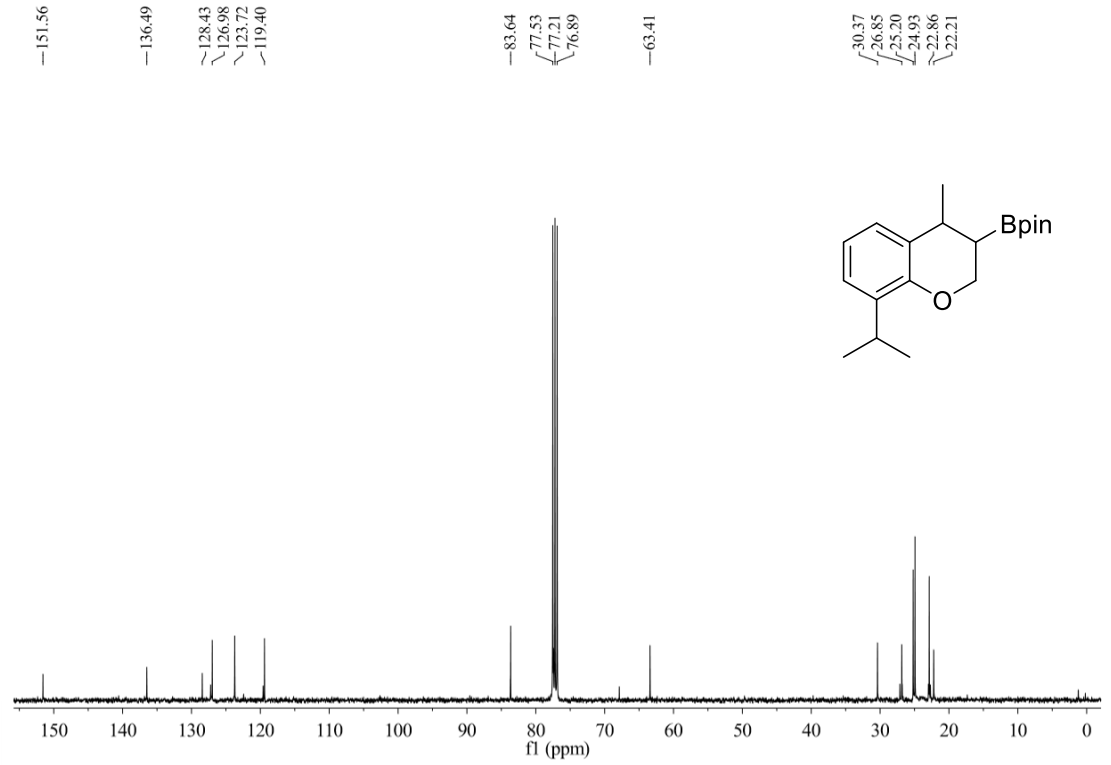
2-(4,8-dimethylchroman-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4b)



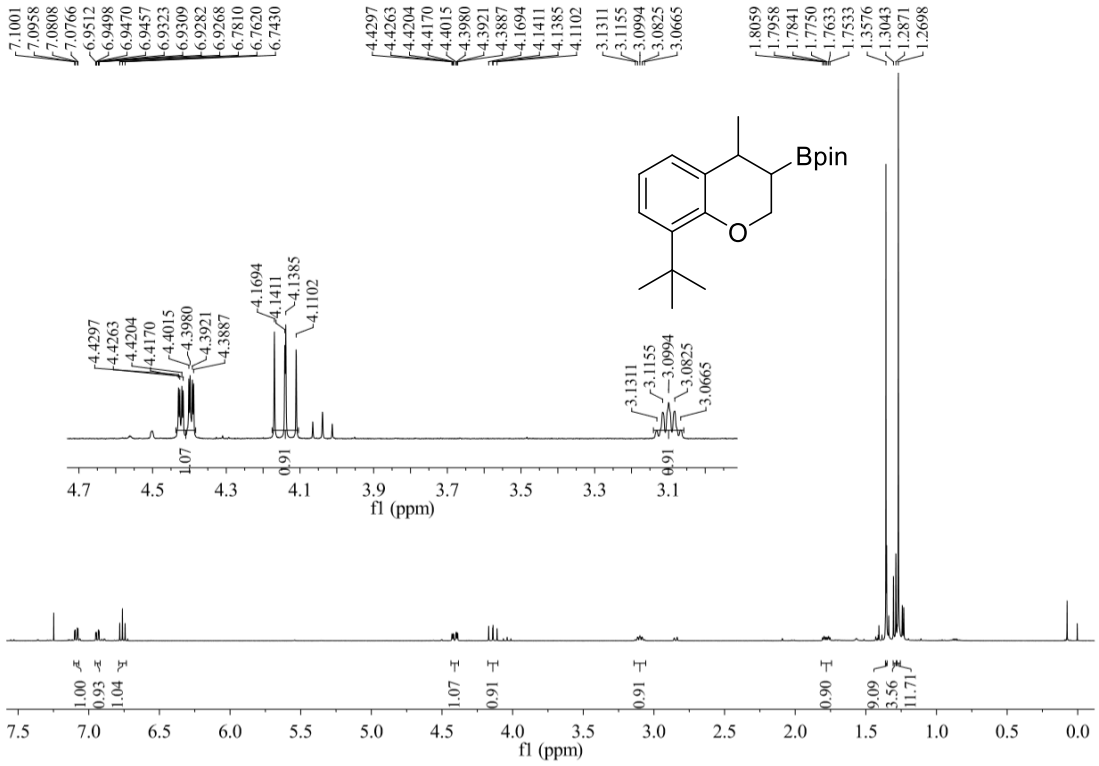


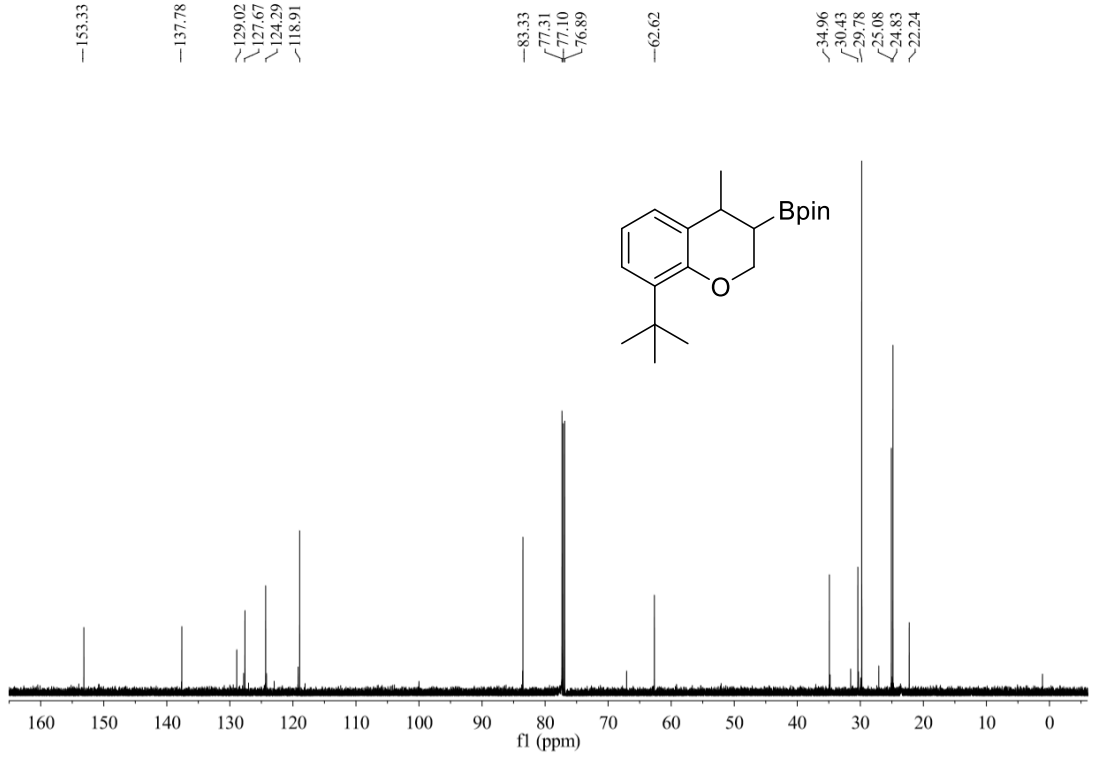
2-(8-isopropyl-4-methylchroman-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4c)



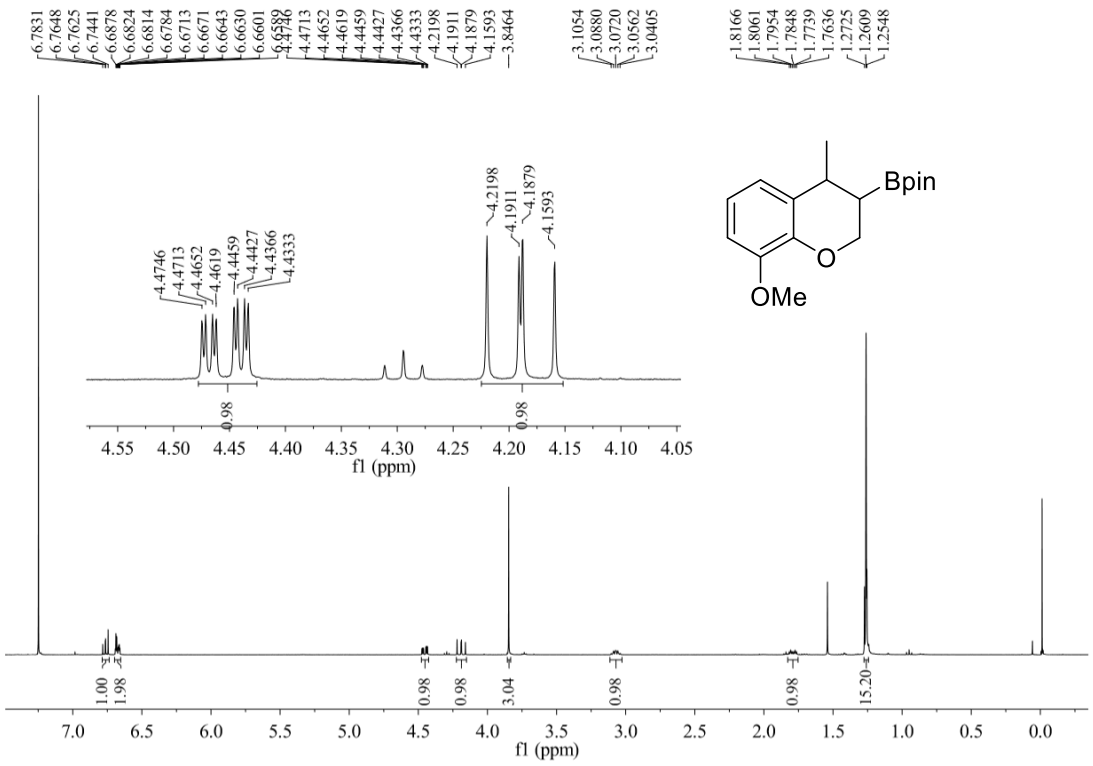


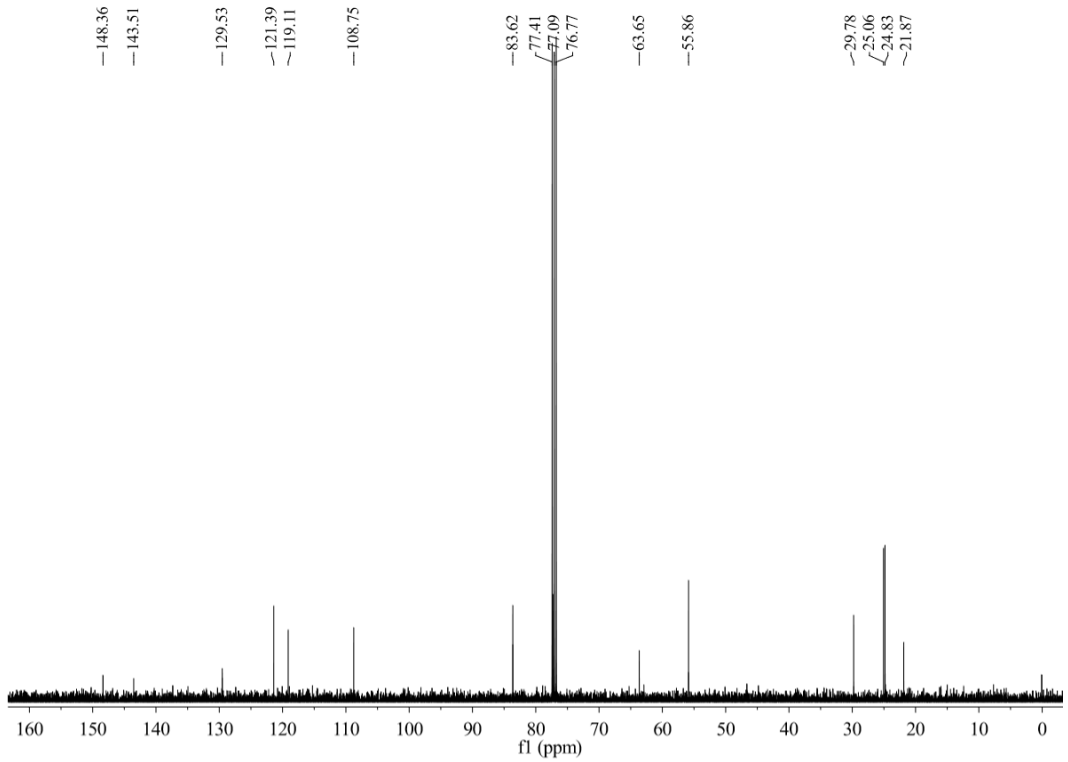
2-(8-(tert-butyl)-4-methylchroman-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4d)



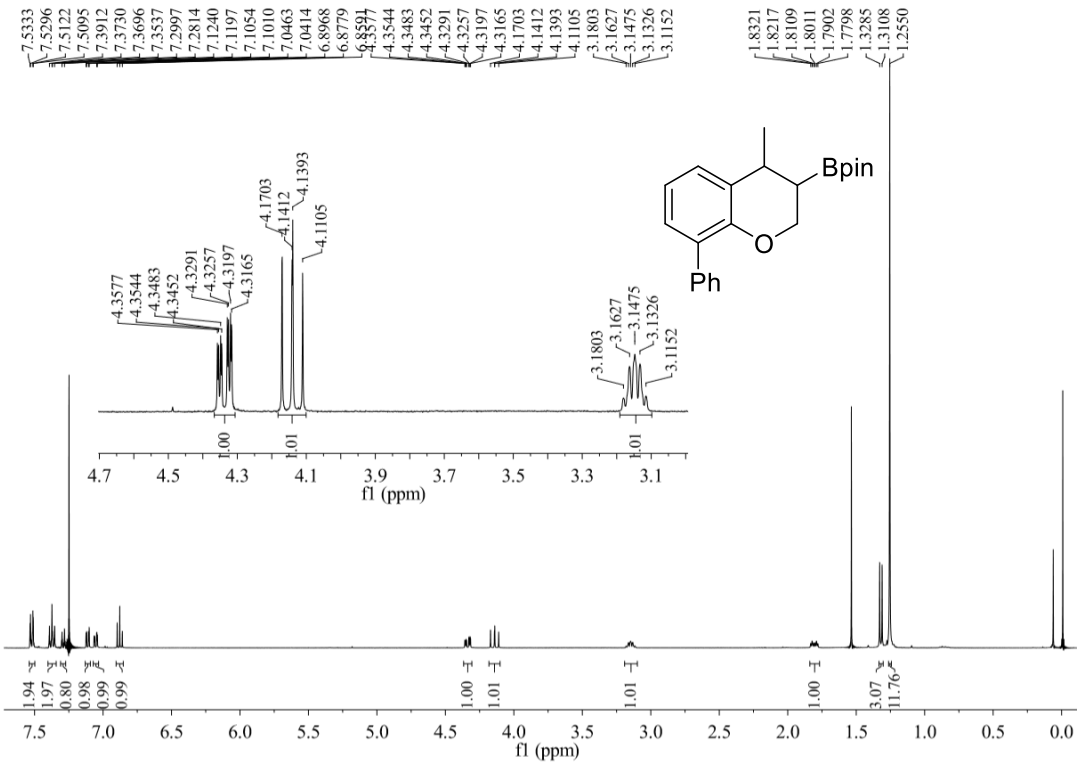


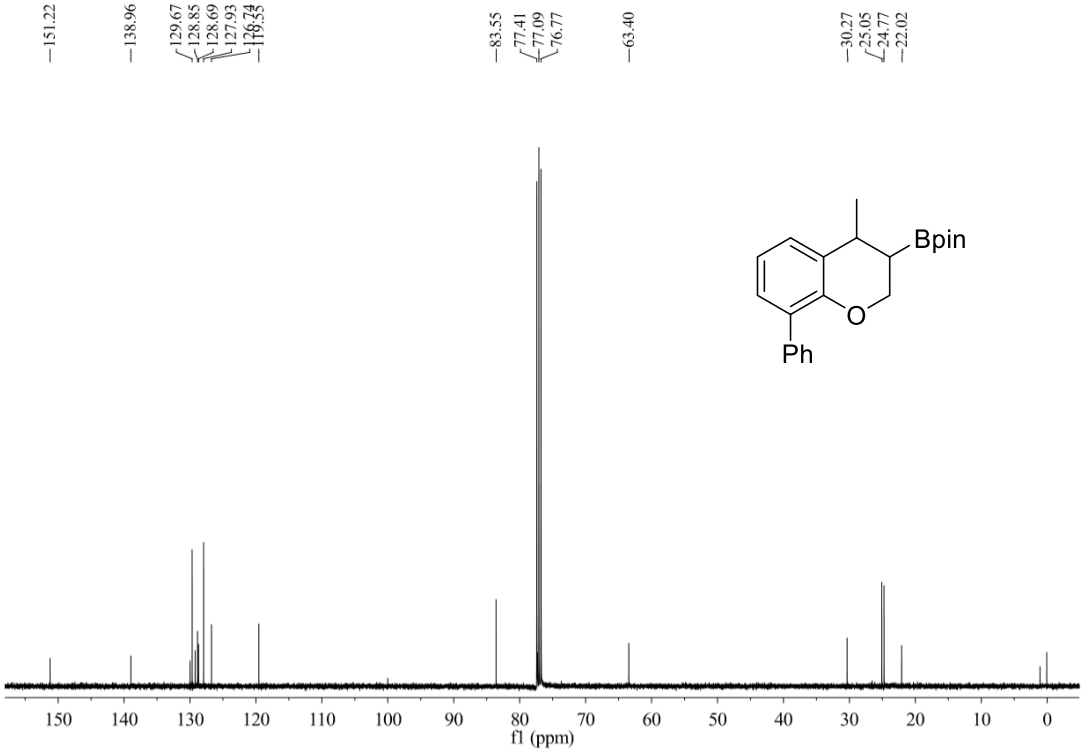
2-(8-methoxy-4-methylchroman-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4e)



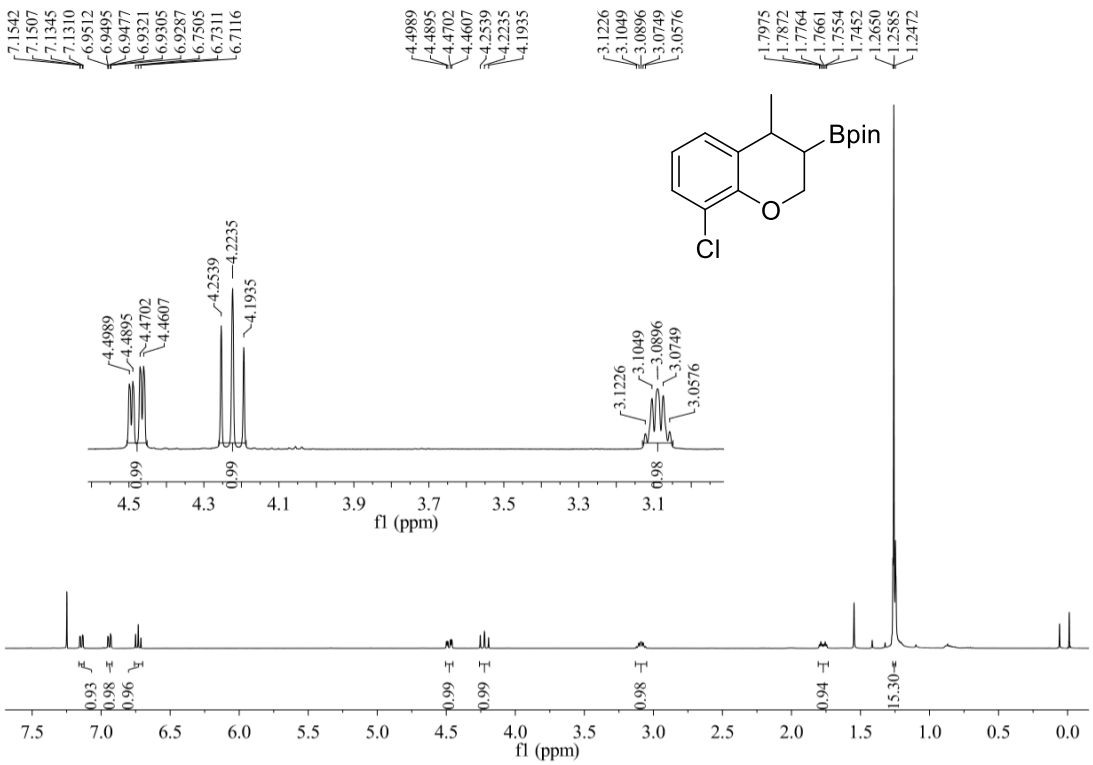


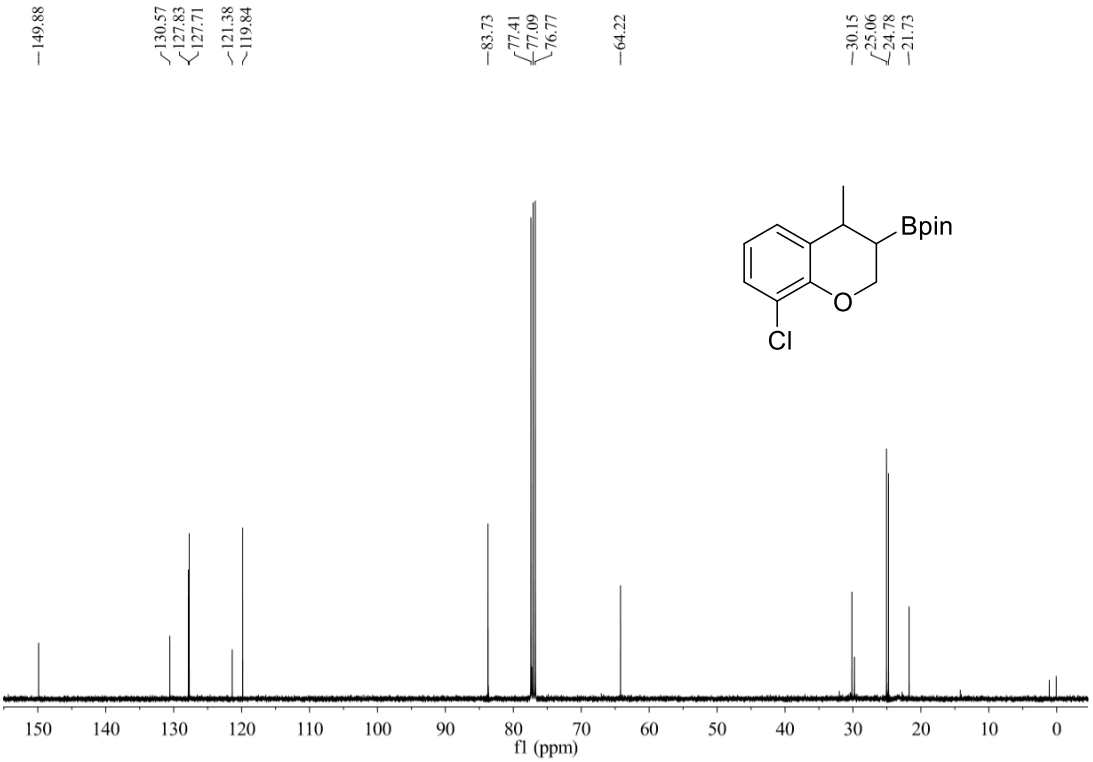
4,4,5,5-tetramethyl-2-(4-methyl-8-phenylchroman-3-yl)-1,3,2-dioxaborolane (4f)



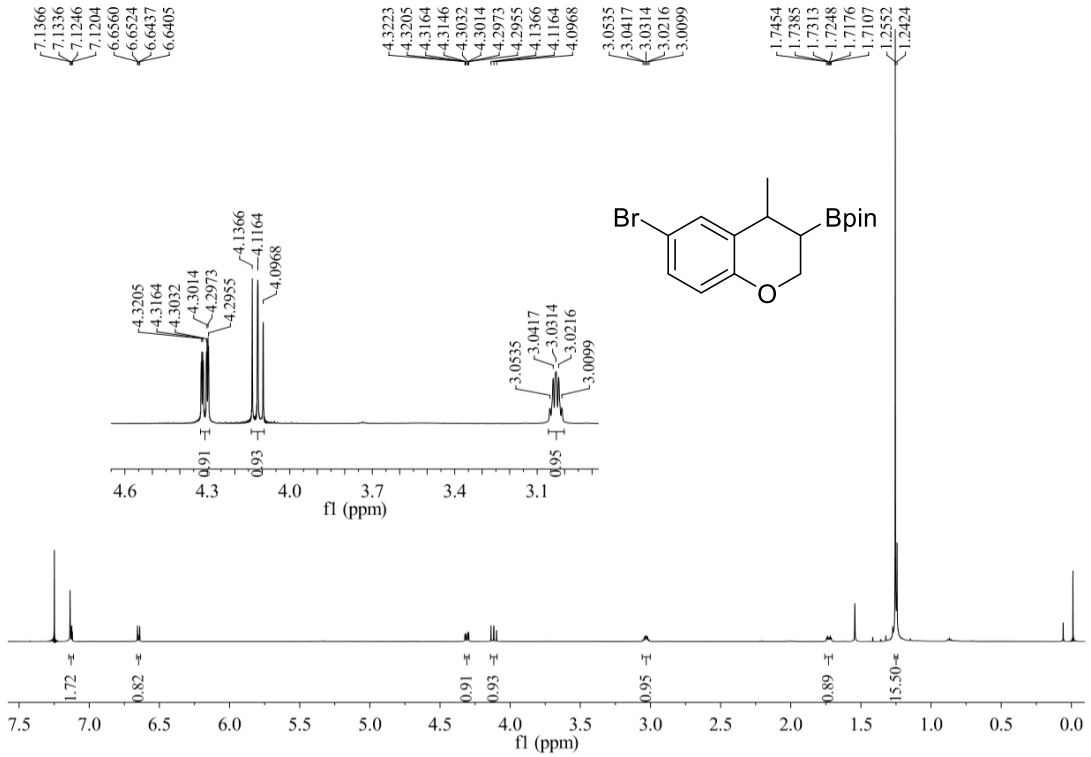


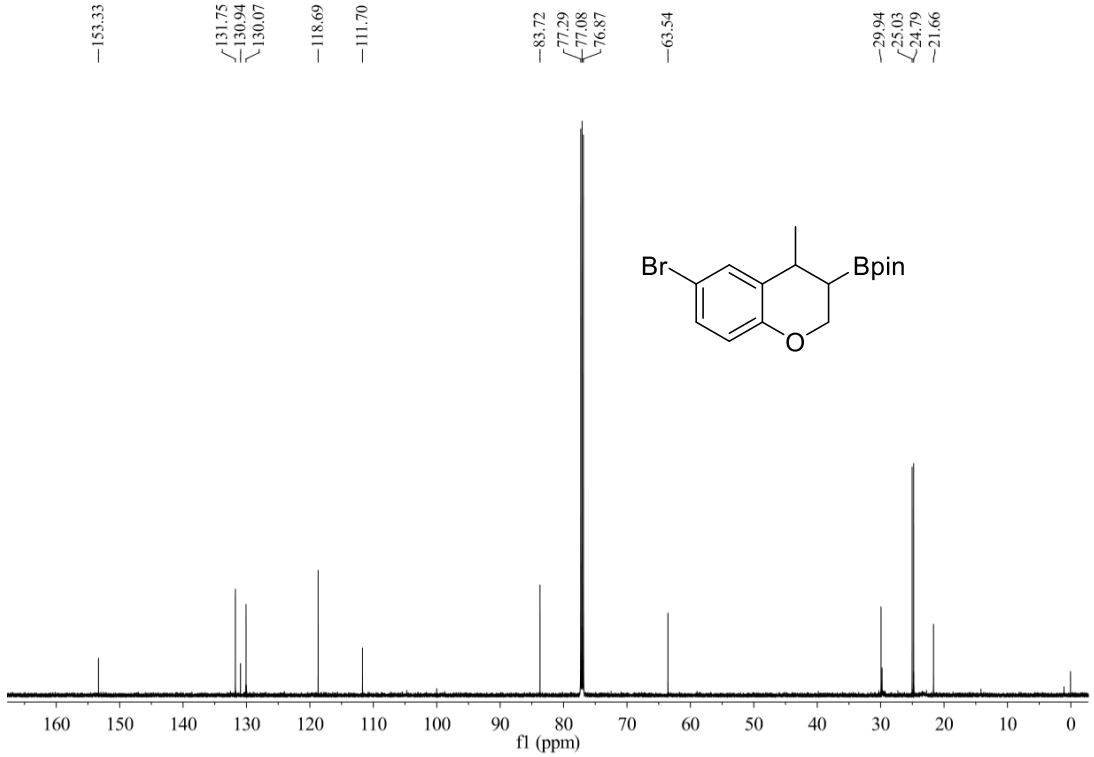
2-(8-chloro-4-methylchroman-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4g)



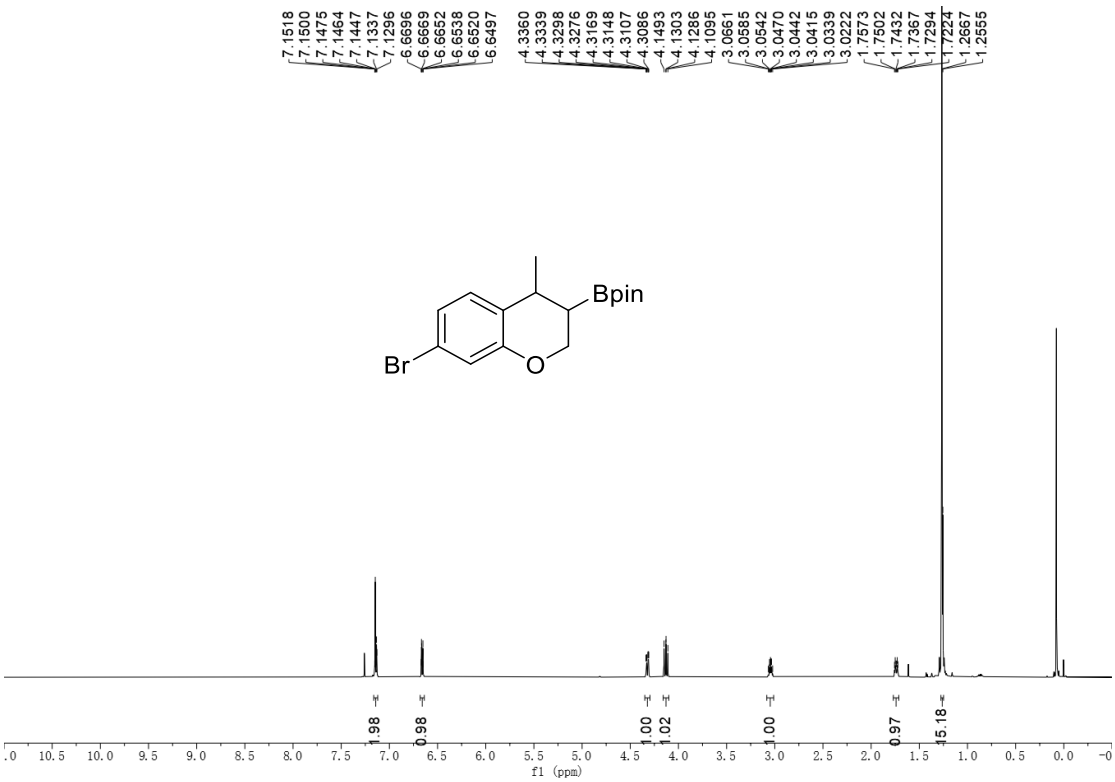


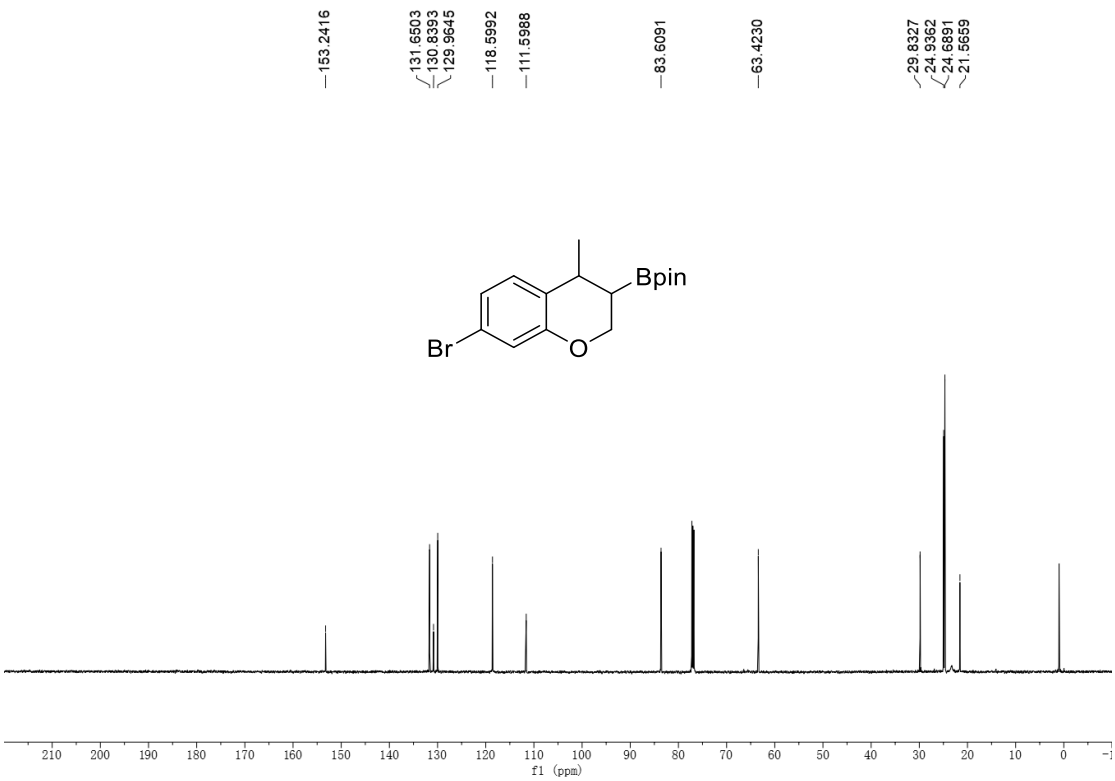
2-(6-bromo-4-methylchroman-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4h)



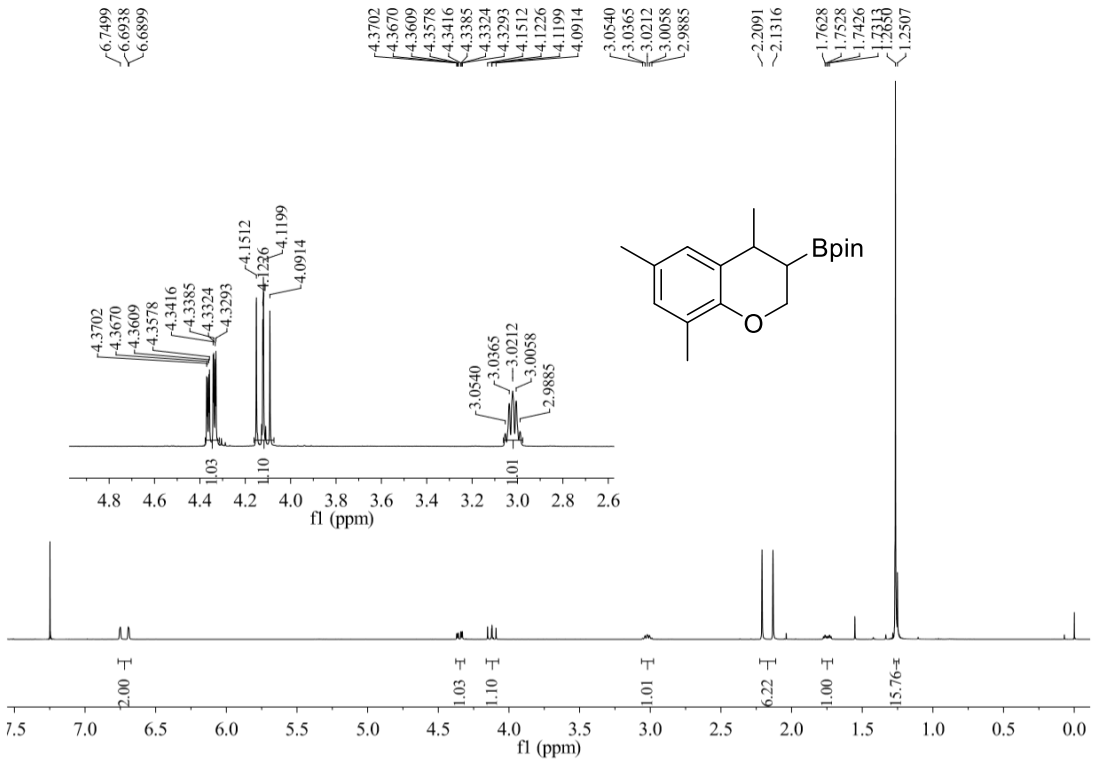


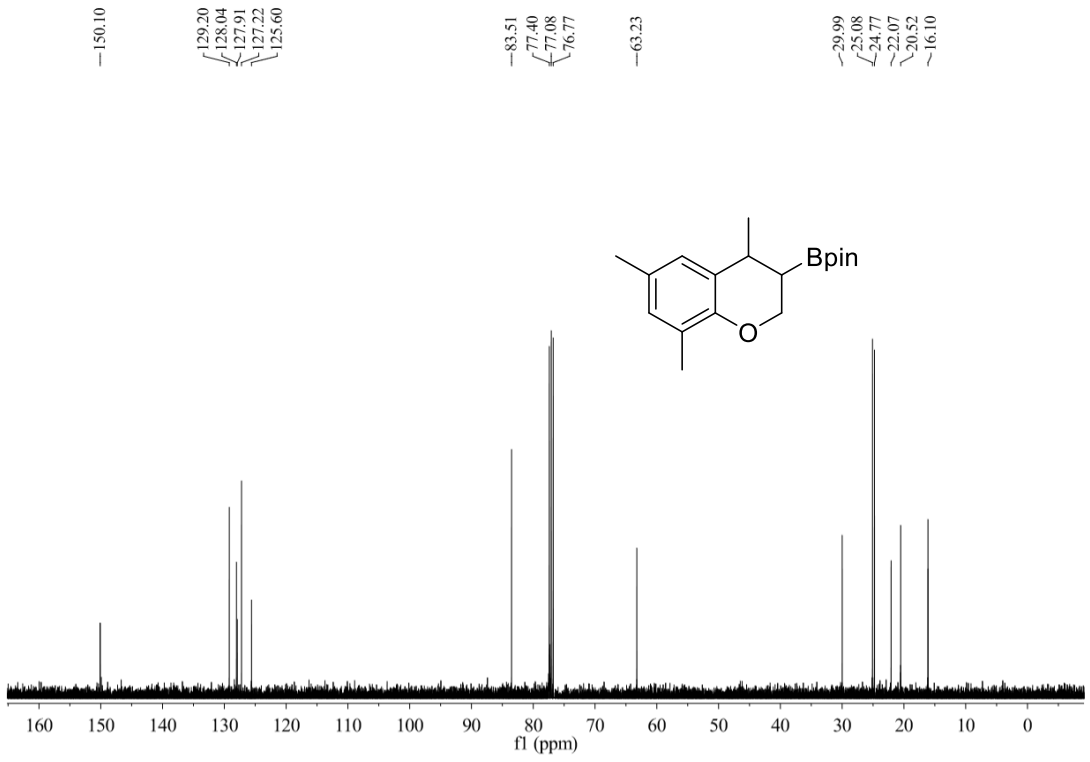
2-(7-bromo-4-methylchroman-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4i)



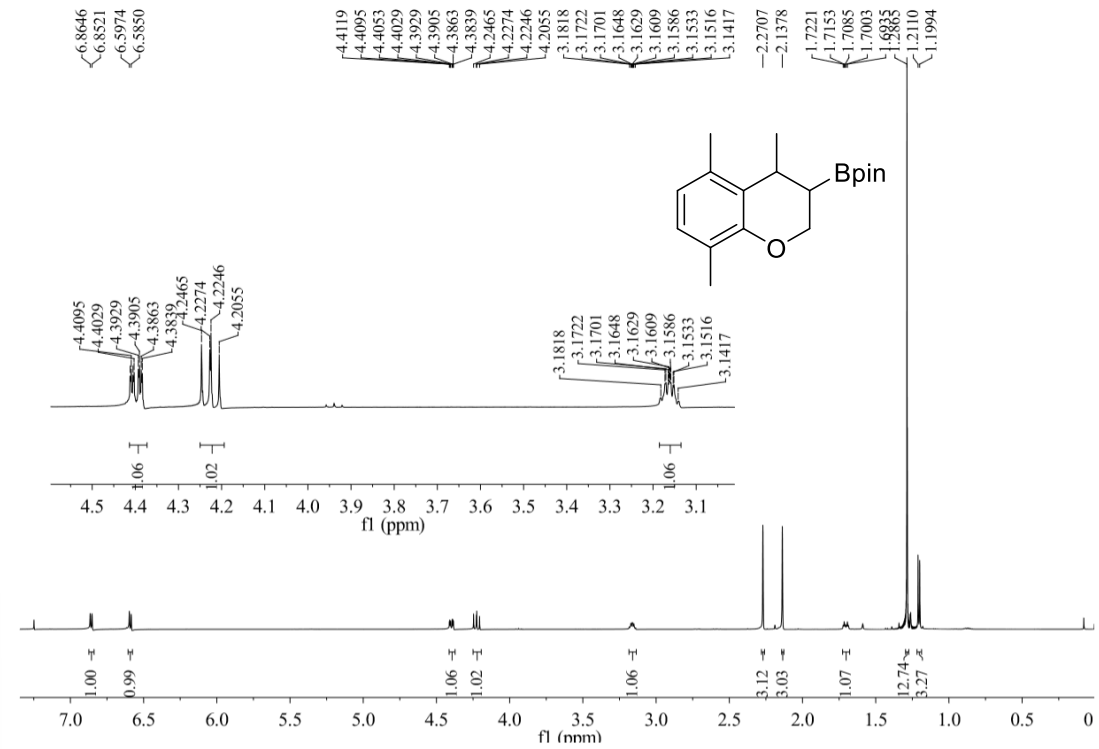


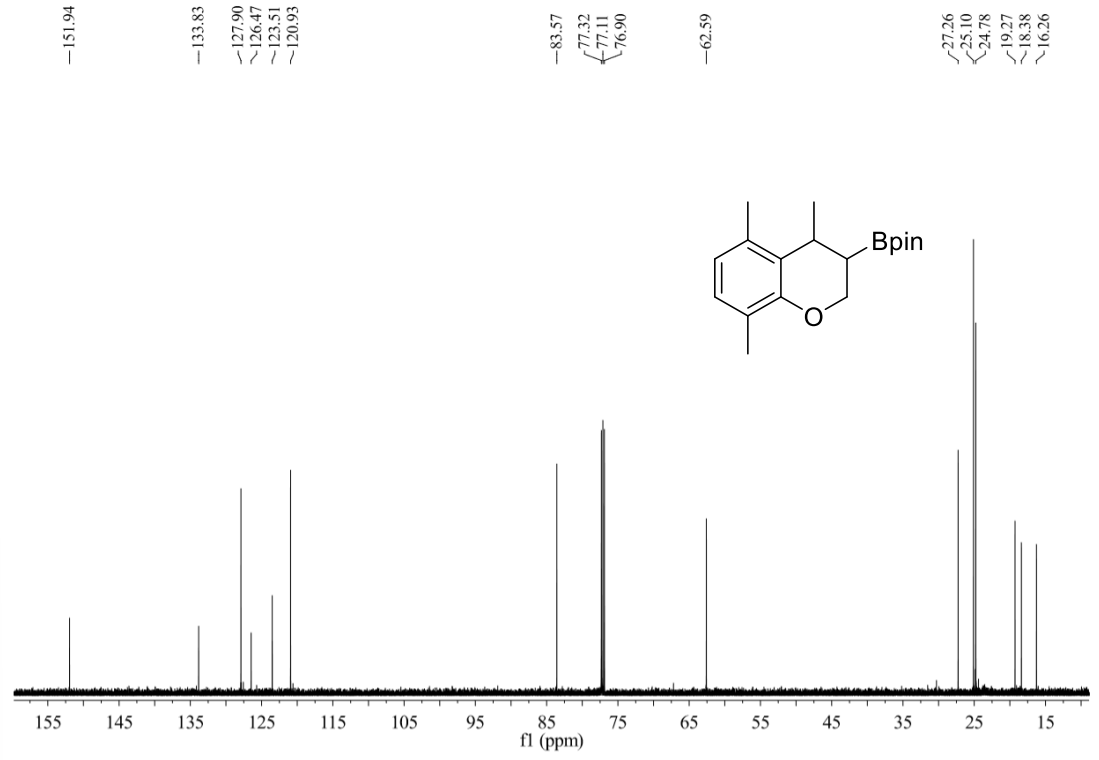
4,4,5,5-tetramethyl-2-(4,6,8-trimethylchroman-3-yl)-1,3,2-dioxaborolane (4j)



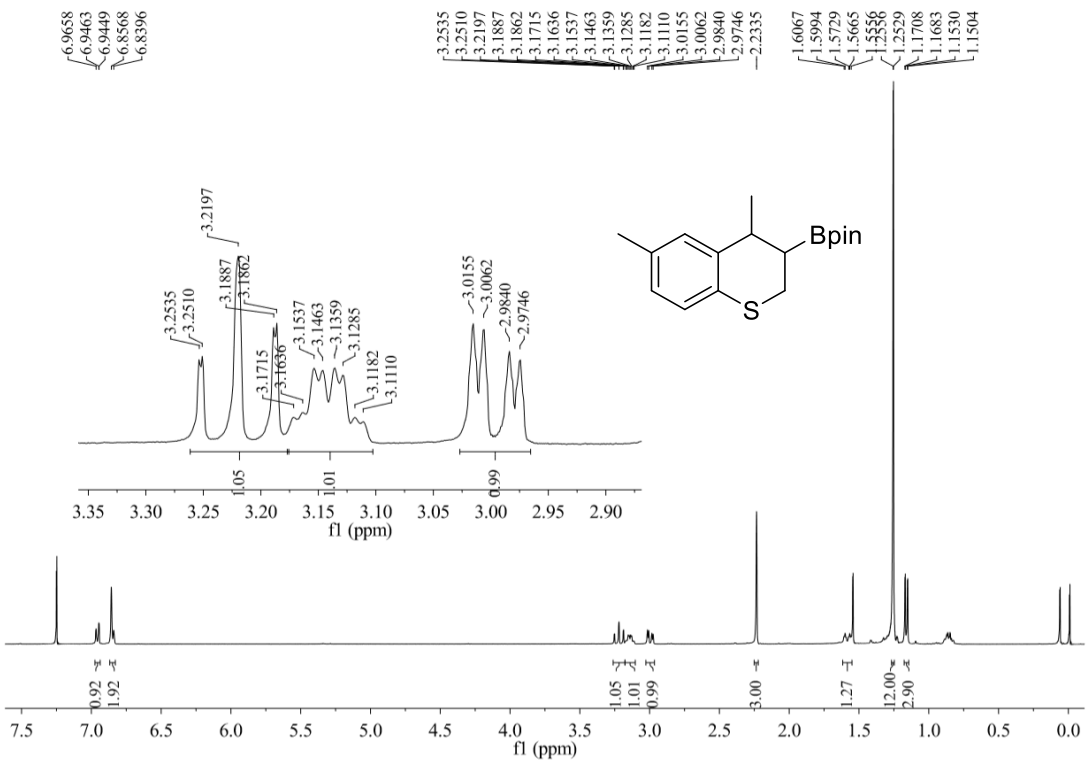


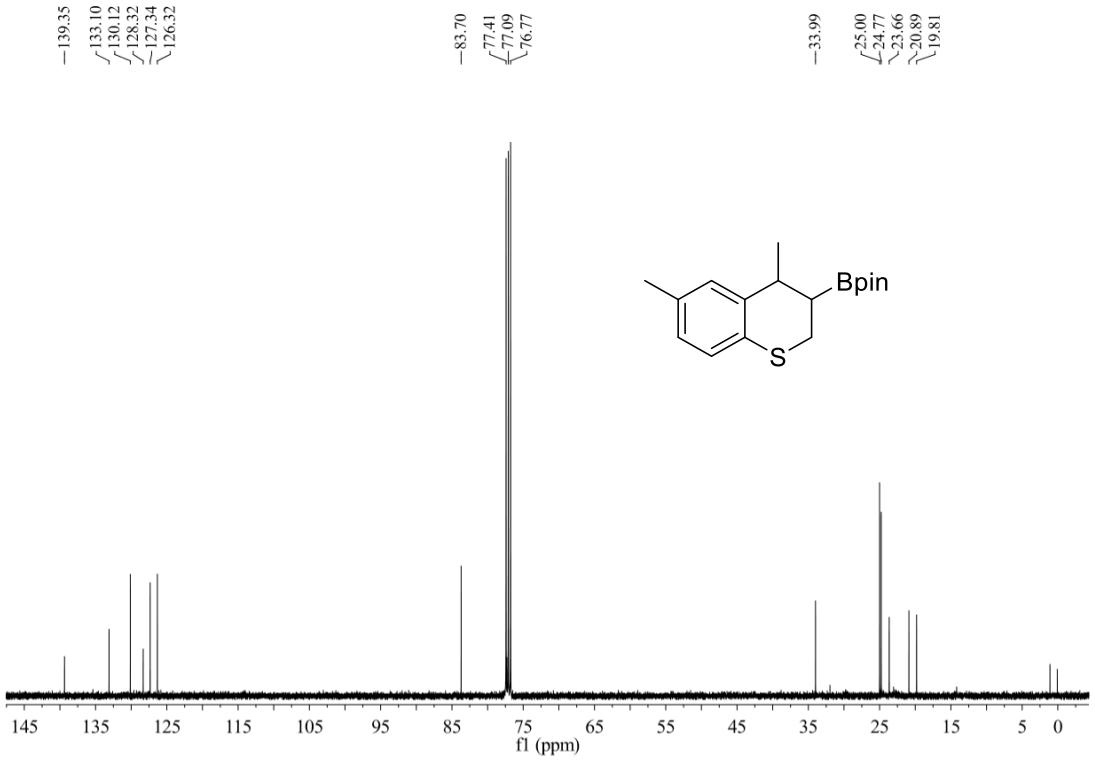
4,4,5,5-tetramethyl-2-(4,5,8-trimethylchroman-3-yl)-1,3,2-dioxaborolane (4k)



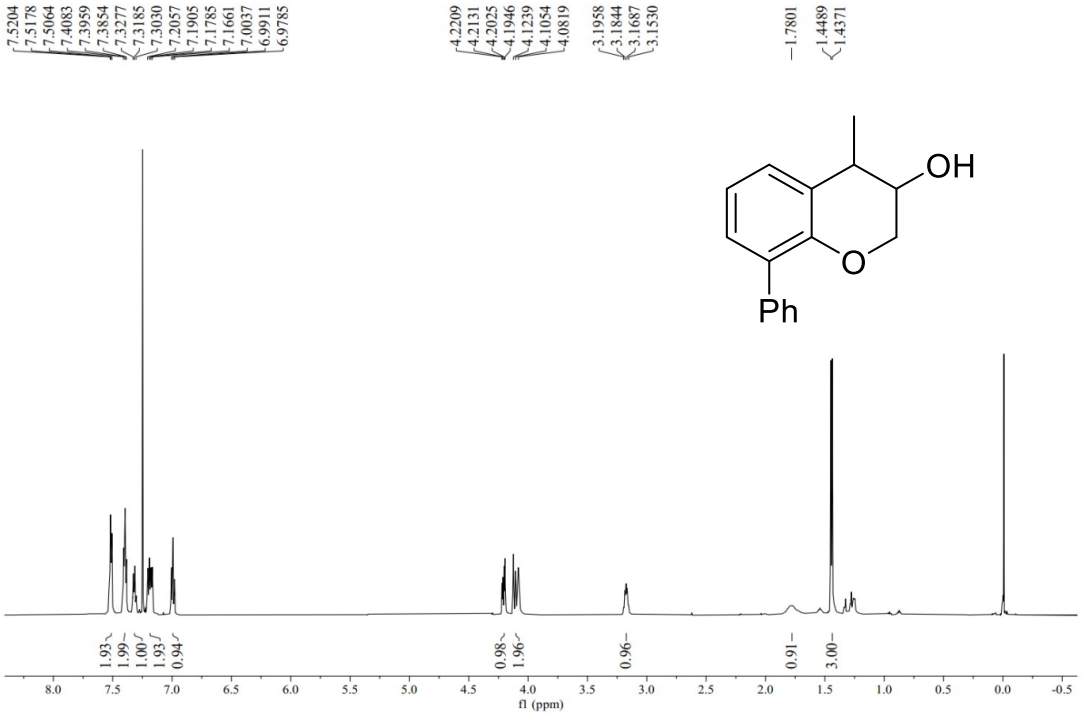


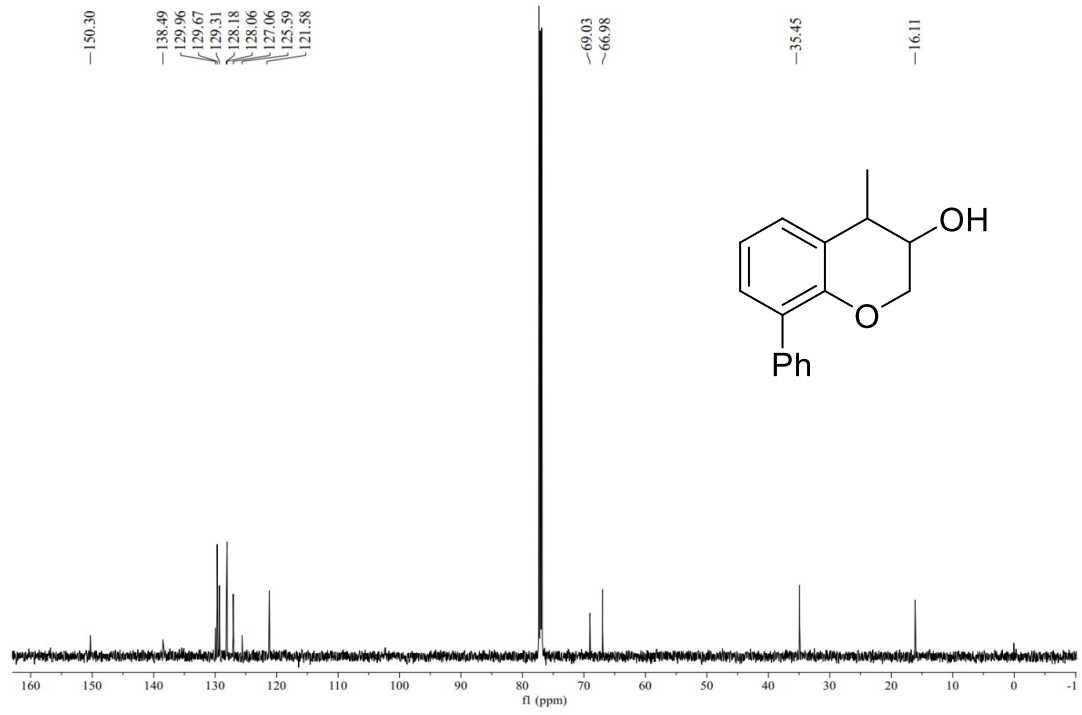
2-(4,6-dimethylthiochroman-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4l)



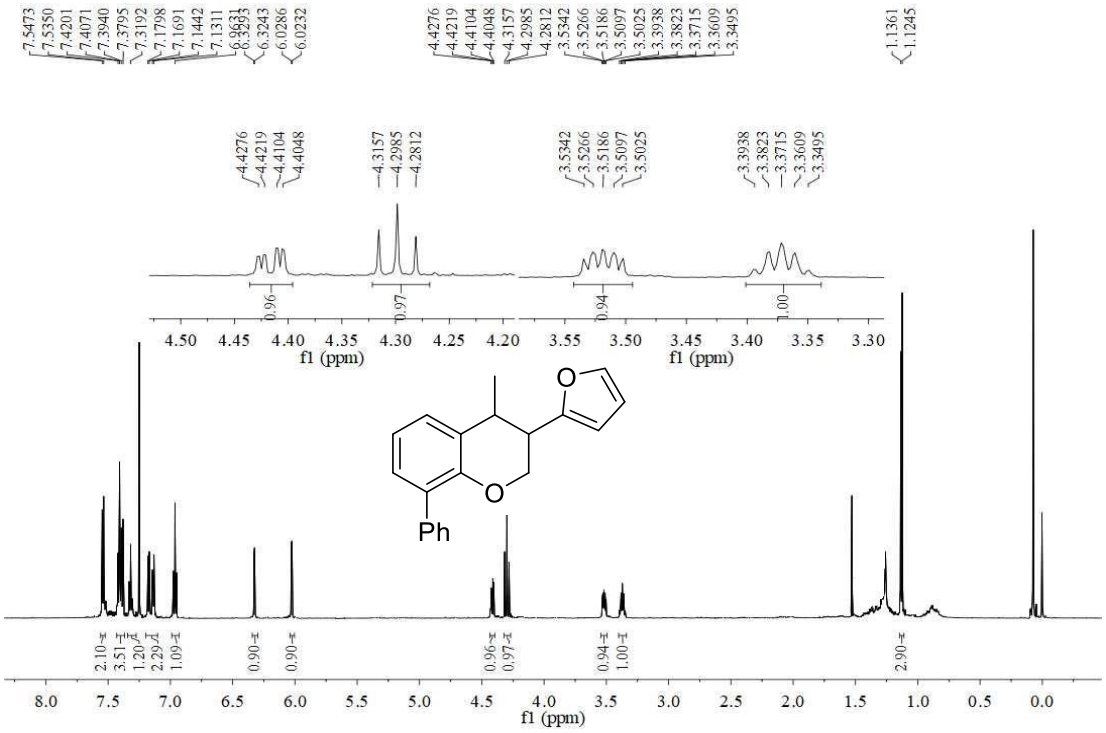


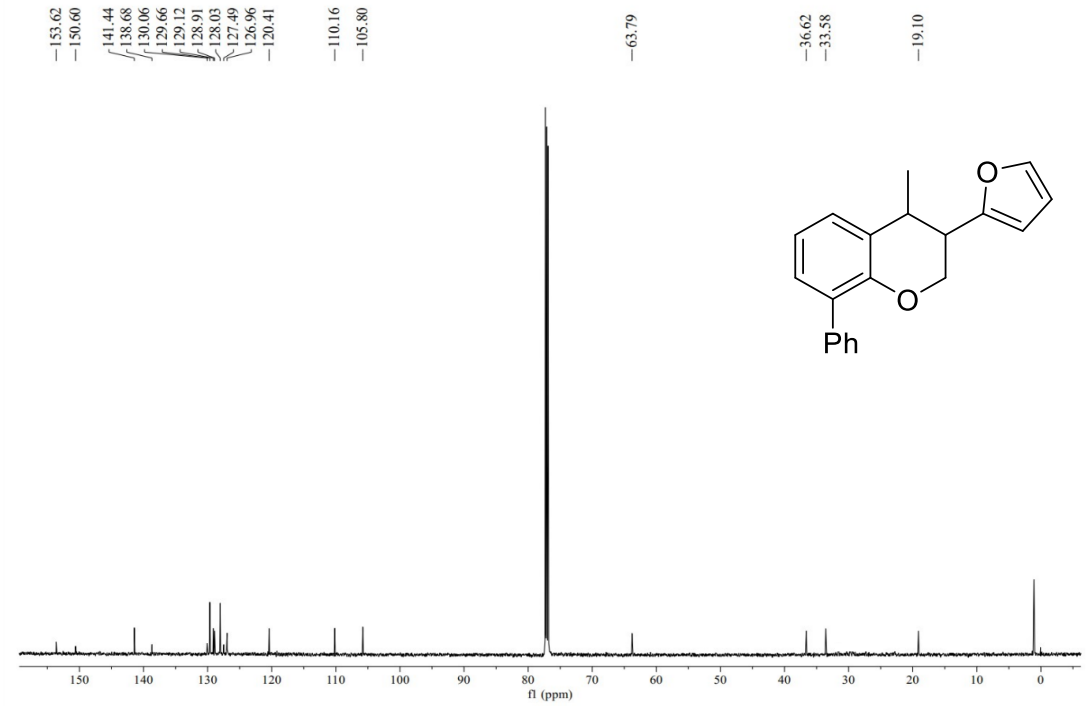
4-methyl-8-phenylchroman-3-ol (5)



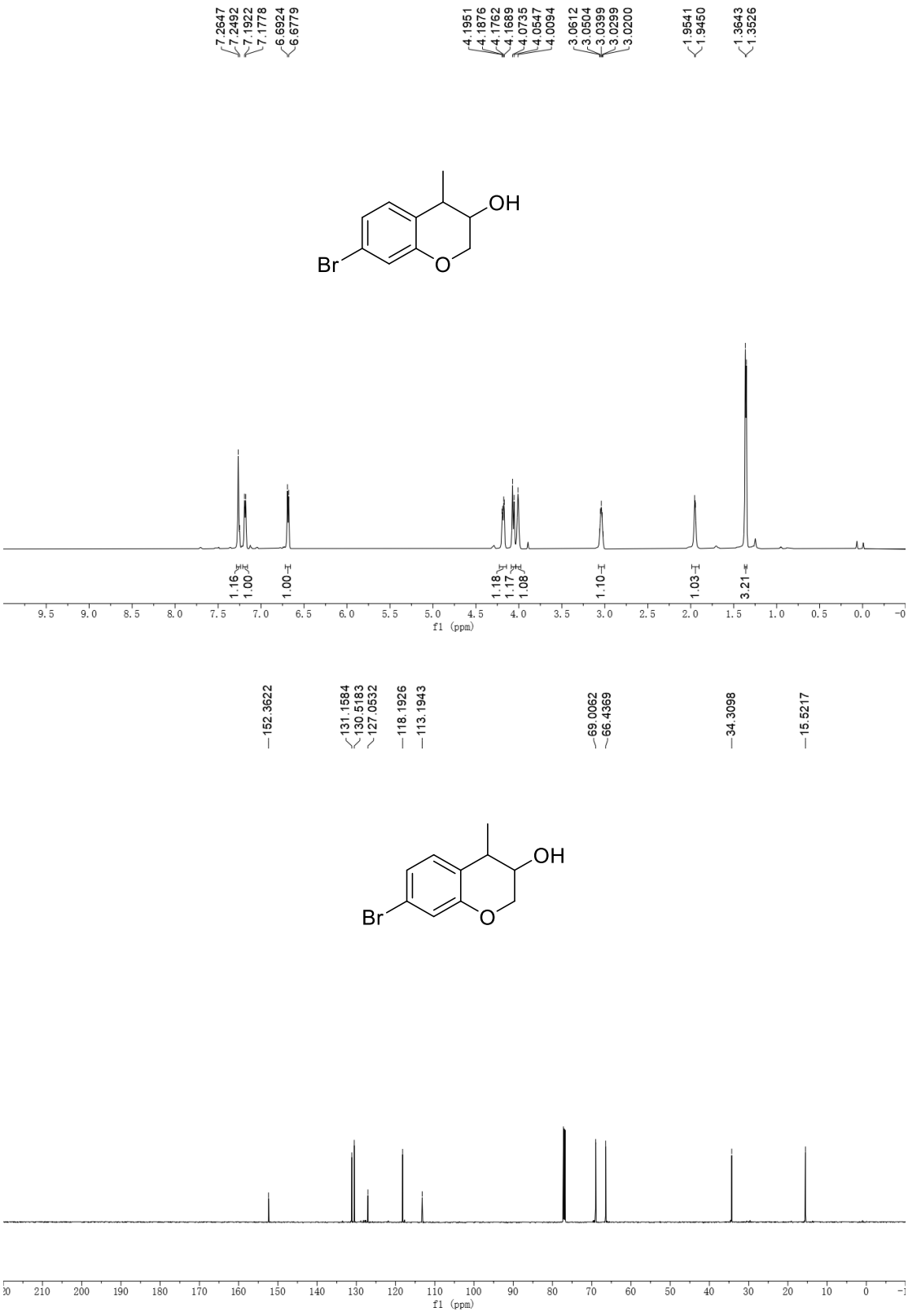


3-(furan-2-yl)-4-methyl-8-phenylchromane (6)

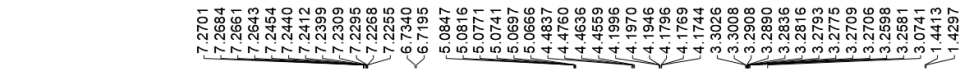


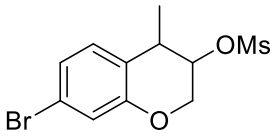


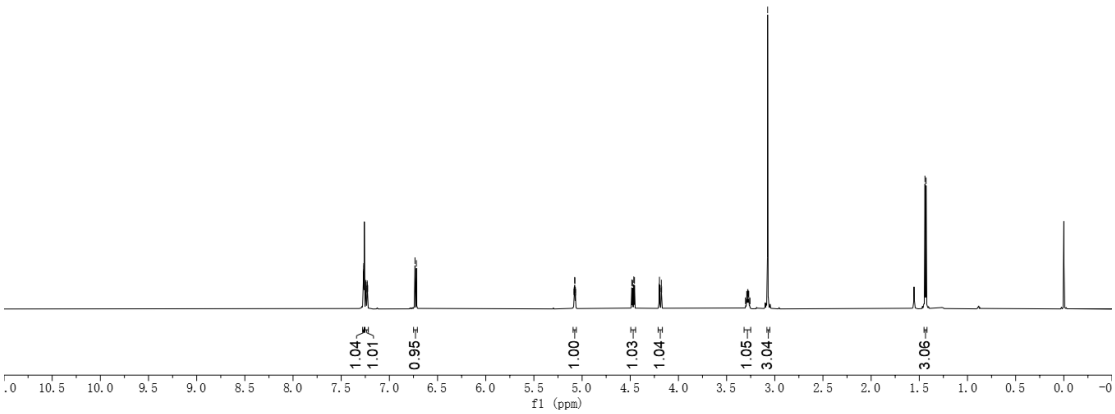
7-bromo-4-methylchroman-3-ol (7)

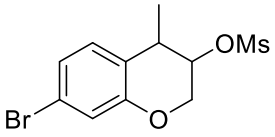


7-bromo-4-methylchroman-3-yl methanesulfonate (8)

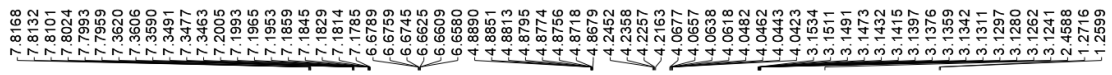


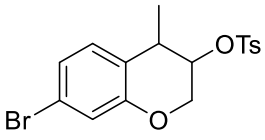


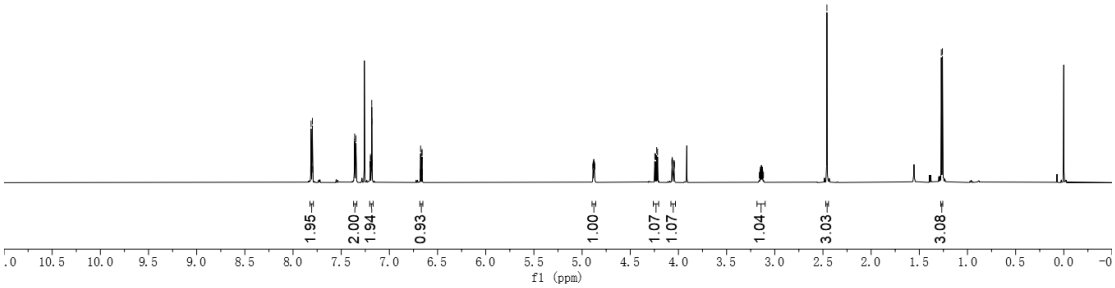


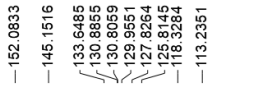


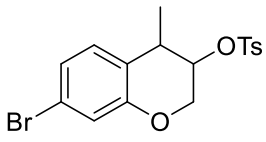
7-bromo-4-methylchroman-3-yl 4-methylbenzenesulfonate (9)





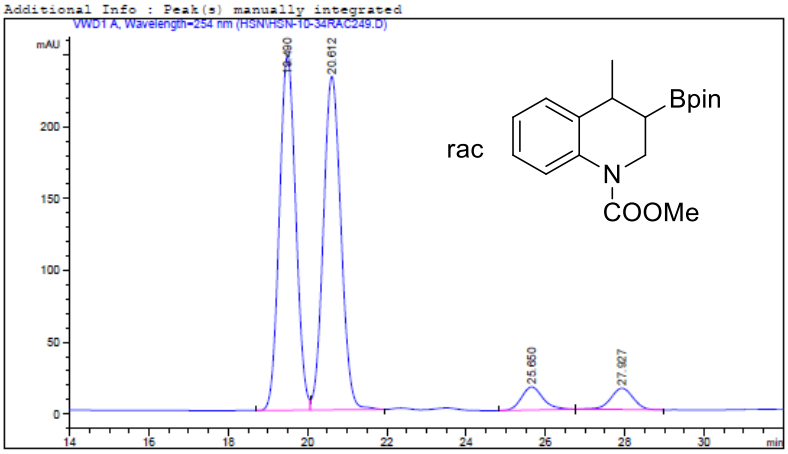






9. SFC and HPLC spectra of all compounds

Additional Info : Peak(s) manually integrated



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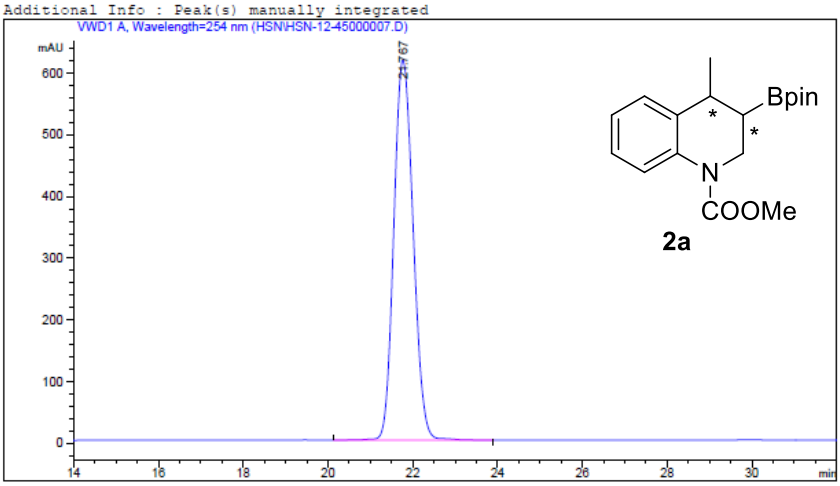
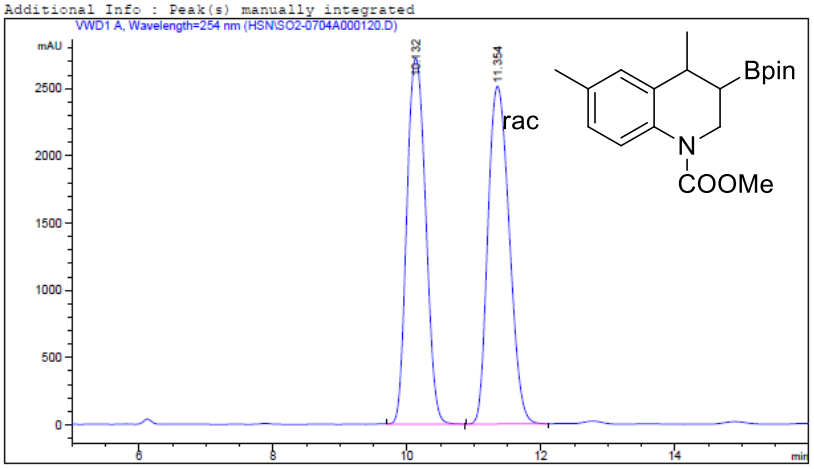
1	19.490	BV	0.4522	7096.04688	246.94789	46.0173
2	20.612	VB	0.4808	7141.59033	232.20294	46.3126
3	25.650	BB	0.5767	602.86121	16.03176	3.9095
4	27.927	BB	0.6071	579.89319	14.80042	3.7606
Totals :				1.54204e4	509.98301	

Additional Info : Peak(s) manually integrated



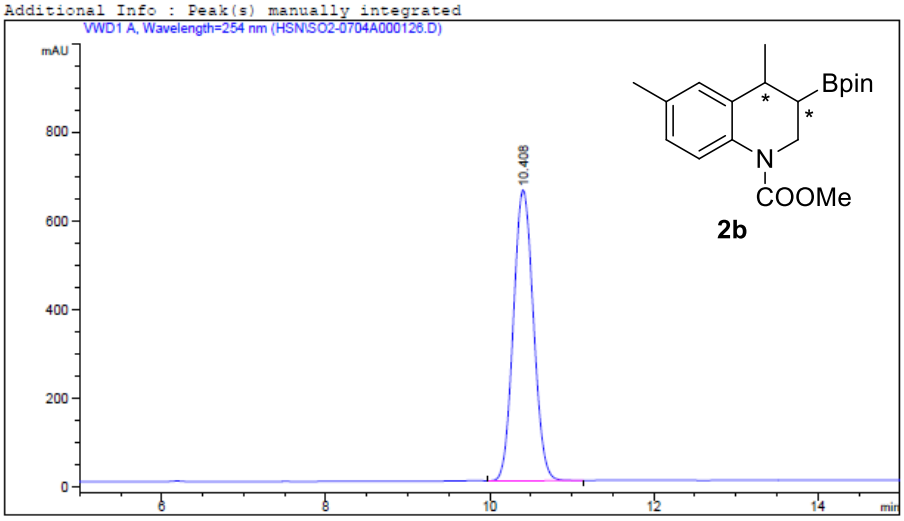
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.767	BB	0.5013	1.94923e4	615.73993	100.0000
Totals :				1.94923e4	615.73993	

Additional Info : Peak(s) manually integrated



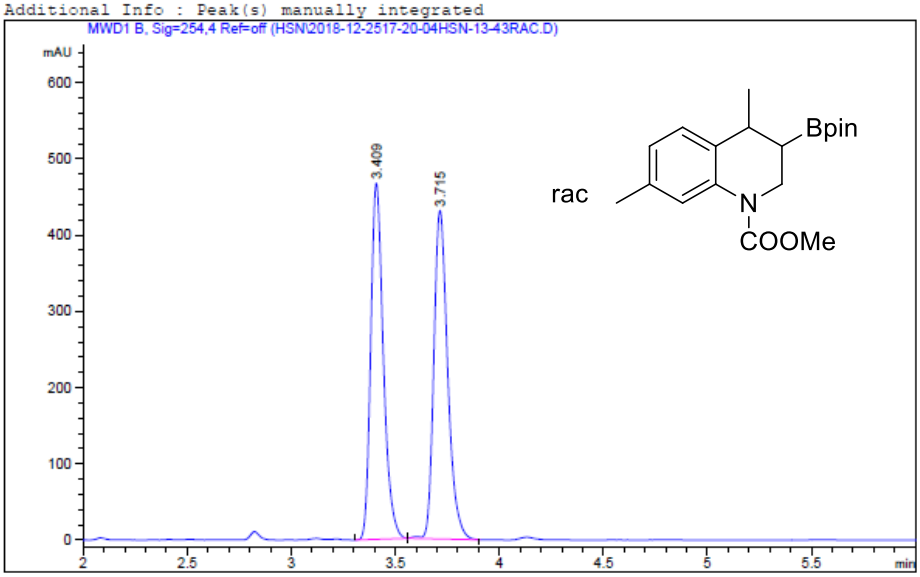
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.132	VB	0.3170	5.32458e4	2723.98438	48.9623
2	11.354	BB	0.3570	5.55028e4	2509.89307	51.0377
Totals :				1.08749e5	5233.87744	

Additional Info : Peak(s) manually integrated



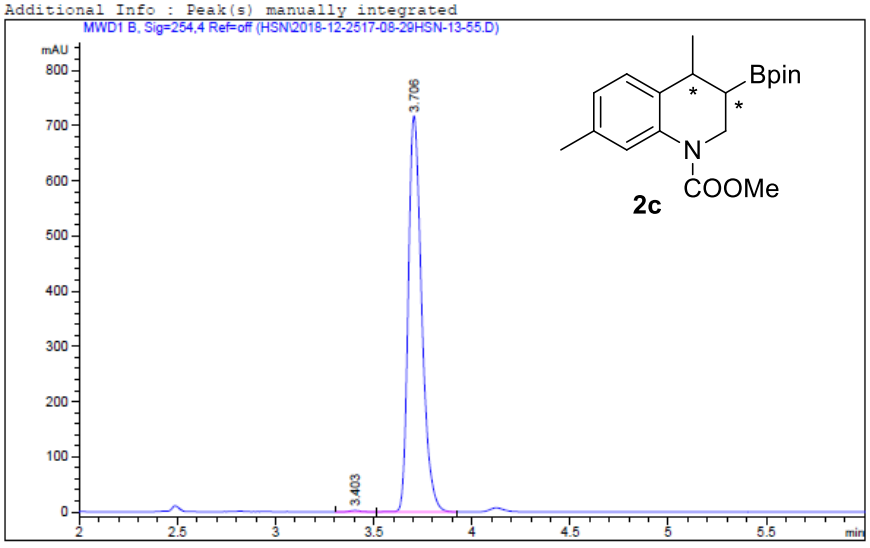
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.408	VB	0.2668	1.11151e4	655.44049	100.0000
Totals :				1.11151e4	655.44049	

Additional Info : Peak(s) manually integrated



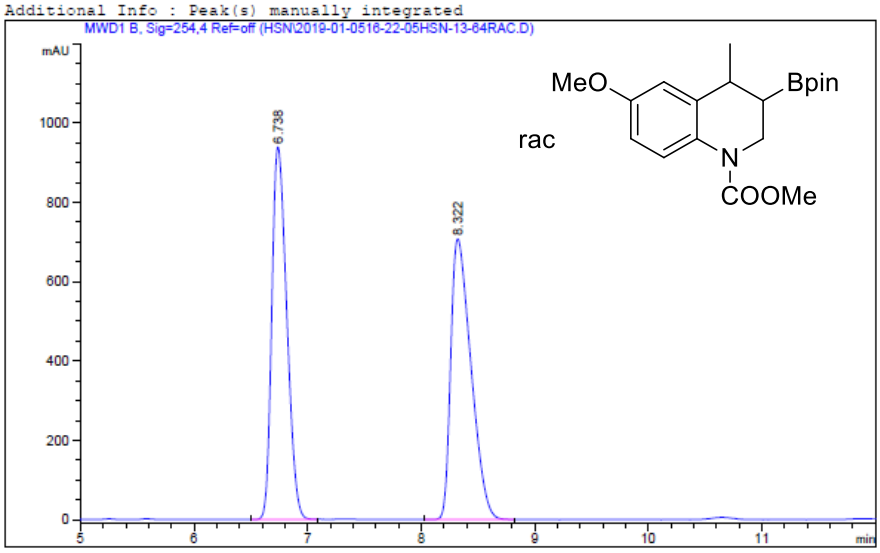
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.409	BB	0.0641	1967.26648	467.29135	49.6653
2	3.715	VB R	0.0708	1993.78064	431.16693	50.3347
Totals :				3961.04712	898.45828	

Additional Info : Peak(s) manually integrated



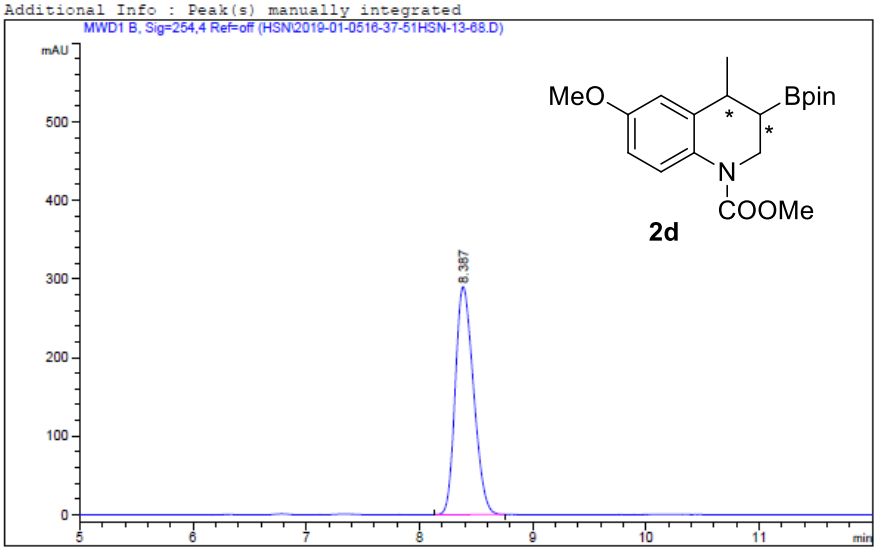
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.403	VV R	0.0557	10.95594	2.59779	0.3205
2	3.706	VB R	0.0734	3407.81396	717.38831	99.6795
Totals :				3418.76990	719.98609	

Additional Info : Peak(s) manually integrated



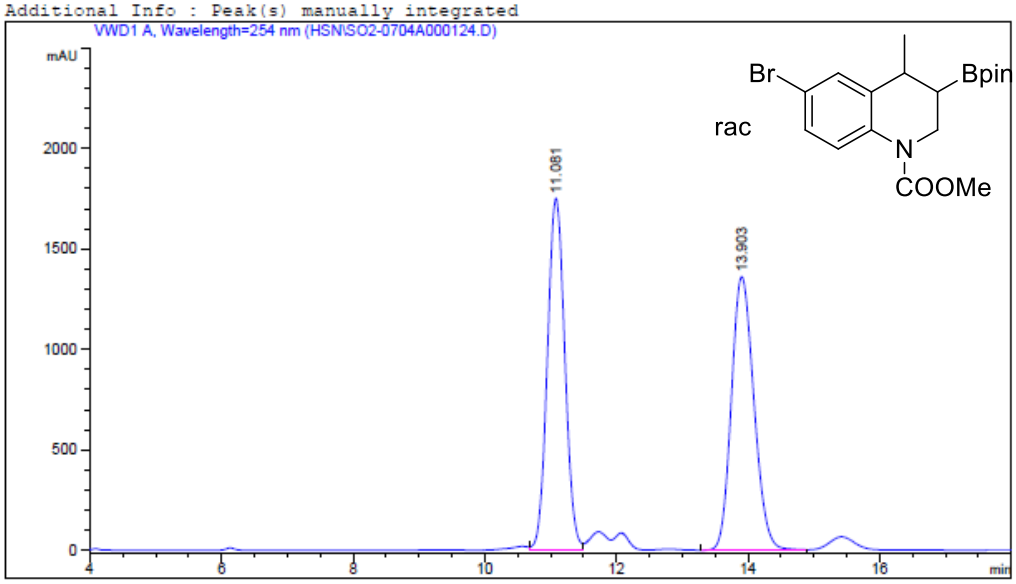
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.738	VV R	0.1416	8583.16992	939.13159	49.5430
2	8.322	VV R	0.1817	8741.52637	707.00177	50.4570
Totals :				1.73247e4	1646.13336	

Additional Info : Peak(s) manually integrated



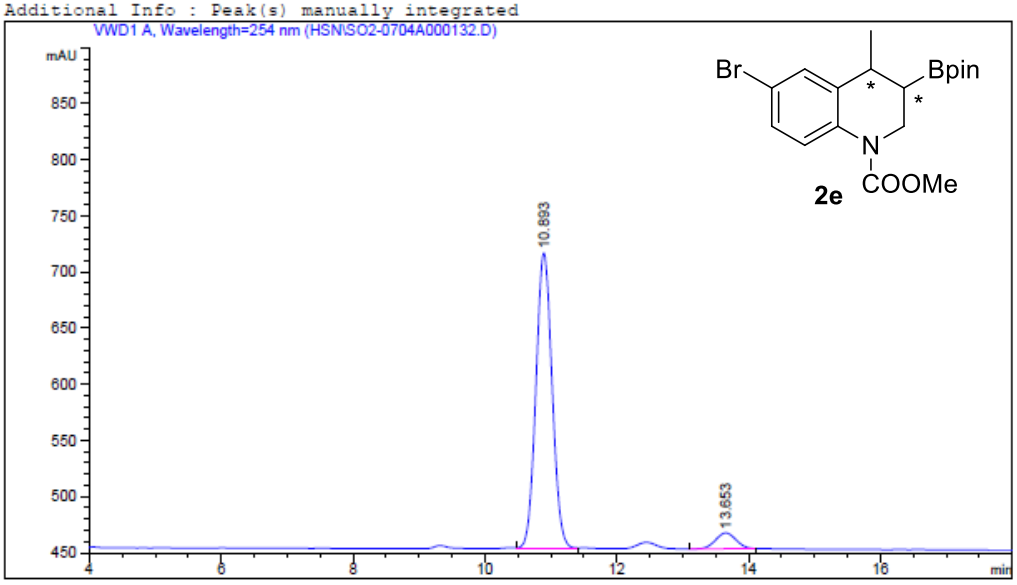
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.387	VV R	0.1688	3248.86035	289.86234	100.0000
Totals :				3248.86035	289.86234	

Additional Info : Peak(s) manually integrated



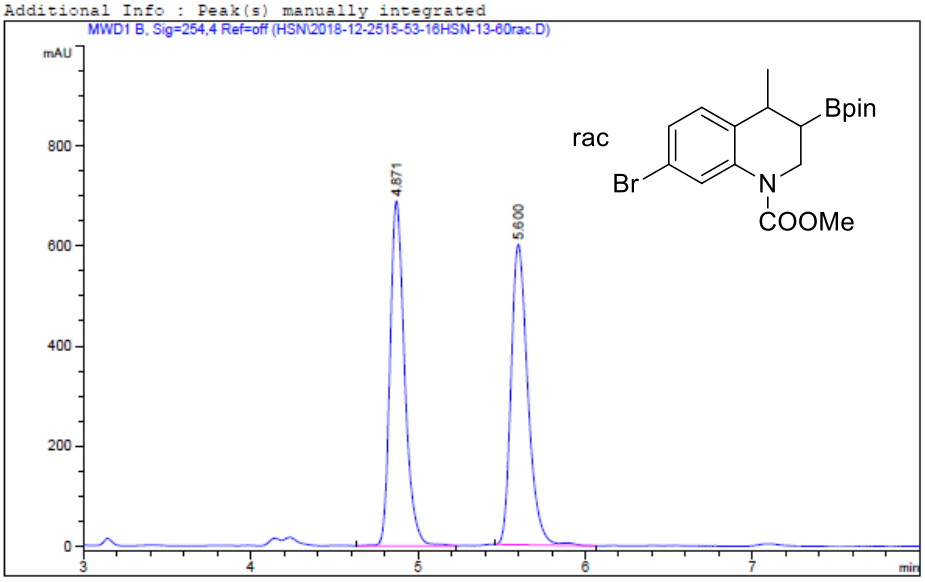
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.081	VV	0.2889	3.22400e4	1750.36707	49.8933
2	13.903	BV	0.3716	3.23779e4	1360.56140	50.1067
Totals :				6.46179e4	3110.92847	

Additional Info : Peak(s) manually integrated



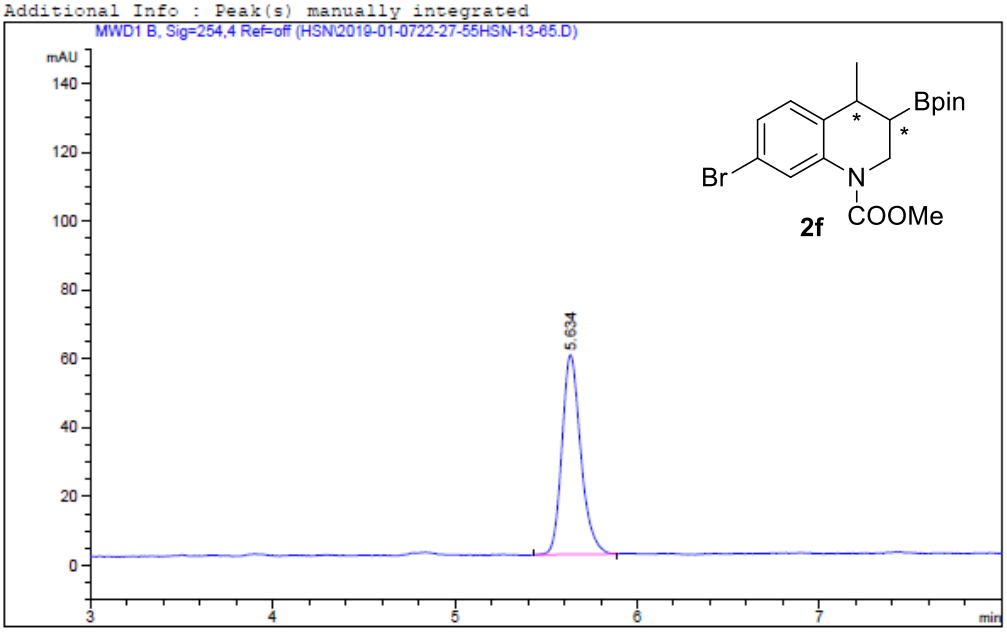
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.893	VV	0.2665	4506.07031	263.50348	93.7045
2	13.653	BB	0.3367	302.73715	14.08760	6.2955
Totals :				4808.80746	277.59108	

Additional Info : Peak(s) manually integrated



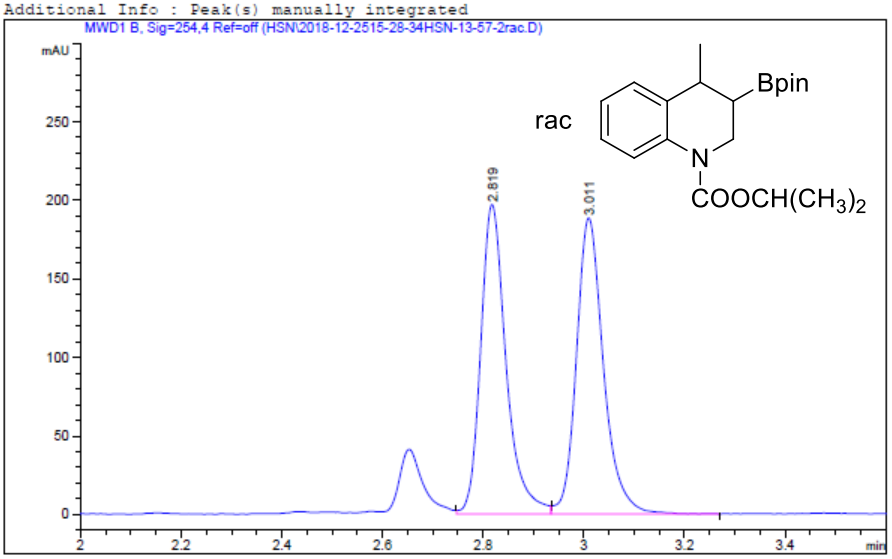
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.871	VV R	0.0920	4161.81787	688.53729	49.8915
2	5.600	BV R	0.1077	4179.91504	599.77081	50.1085
Totals :				8341.73291	1288.30811	

Additional Info : Peak(s) manually integrated



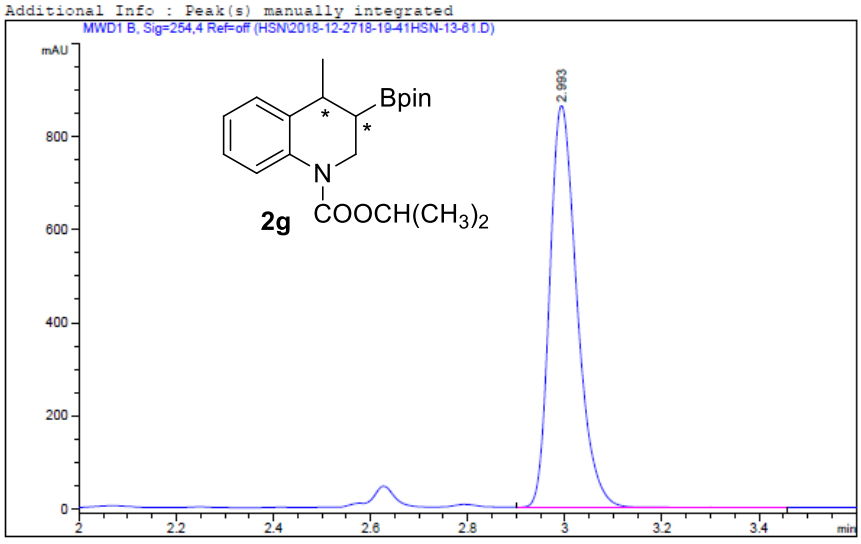
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.634	VV R	0.1034	416.64581	57.93616	100.0000
Totals :				416.64581	57.93616	

Additional Info : Peak(s) manually integrated



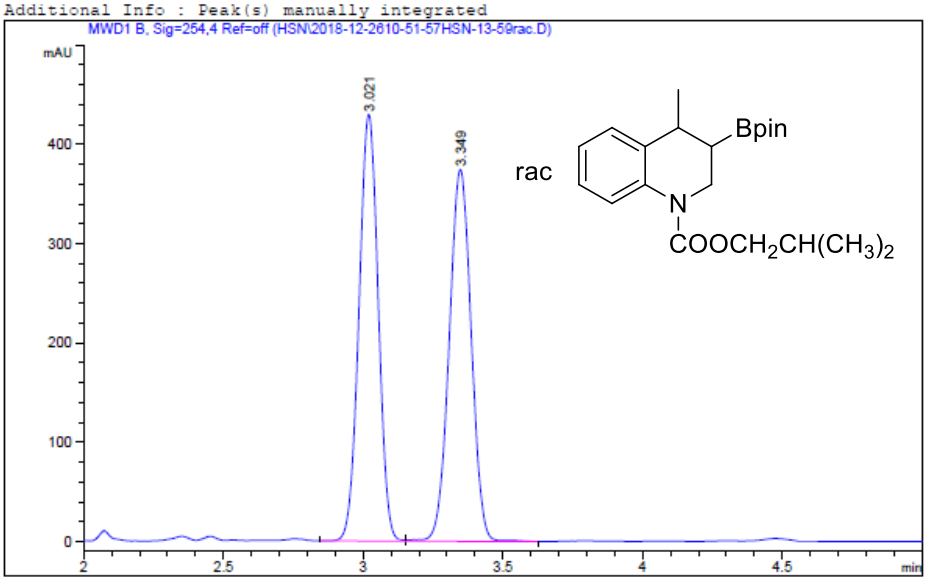
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	2.819	VV	0.0531	693.16724	196.58324	49.4931
2	3.011	VB	0.0579	707.36676	188.03195	50.5069
Totals :				1400.53400	384.61519	

Additional Info : Peak(s) manually integrated



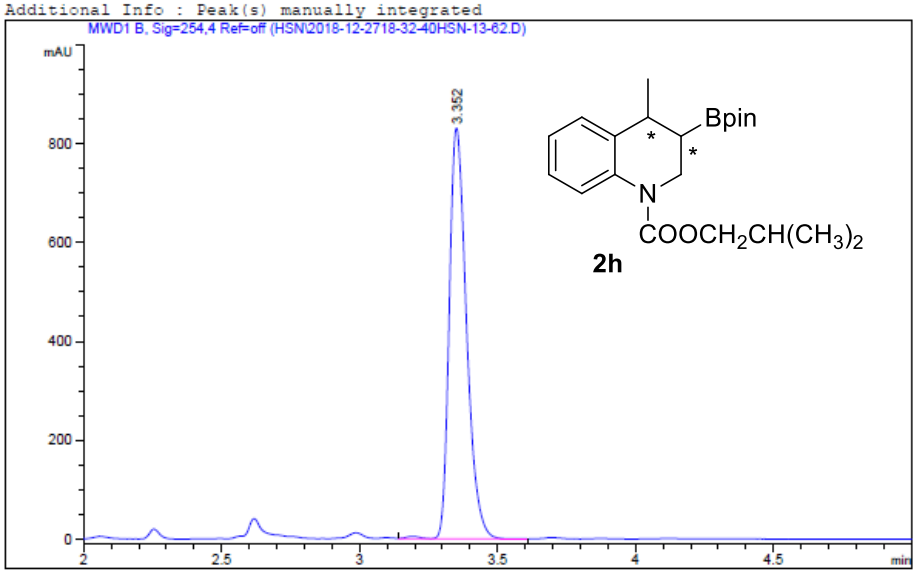
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	2.993	VB	0.0616	3372.90039	862.29388	100.0000
Totals :				3372.90039	862.29388	

Additional Info : Peak(s) manually integrated



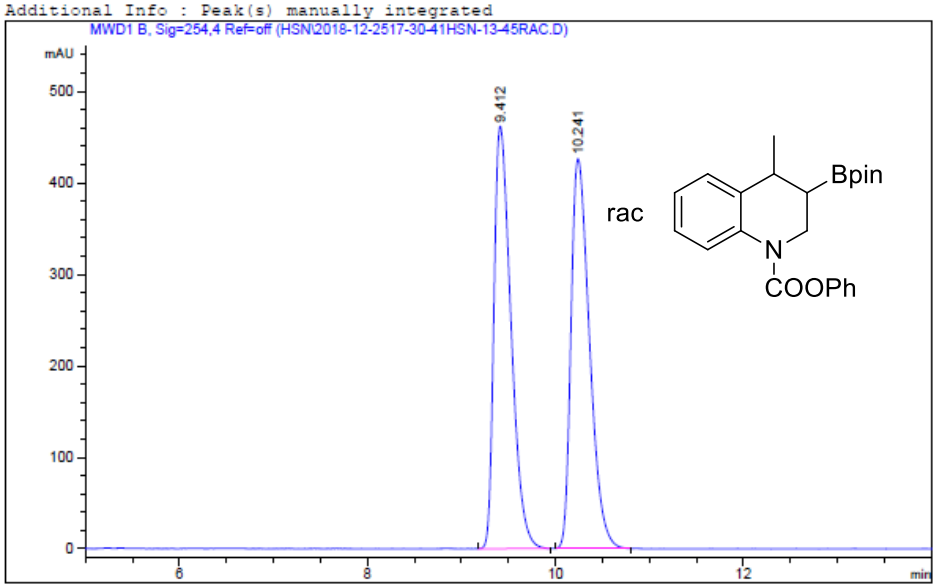
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.021	BV	0.0759	2054.07251	429.06149	50.0031
2	3.349	VB	0.0861	2053.82007	374.08072	49.9969
Totals :				4107.89258	803.14221	

Additional Info : Peak(s) manually integrated



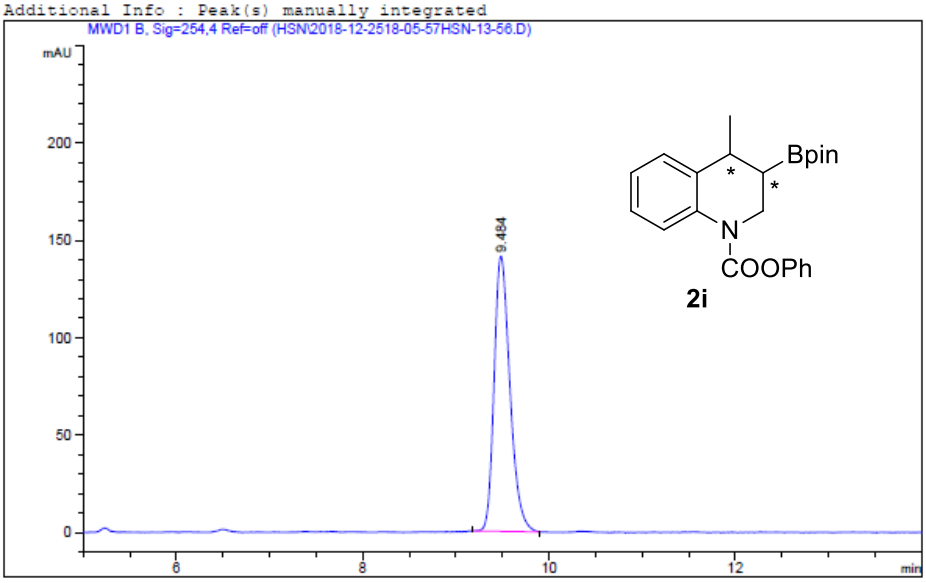
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.352	VB R	0.0666	3618.77612	829.69946	100.0000
Totals :				3618.77612	829.69946	

Additional Info : Peak(s) manually integrated



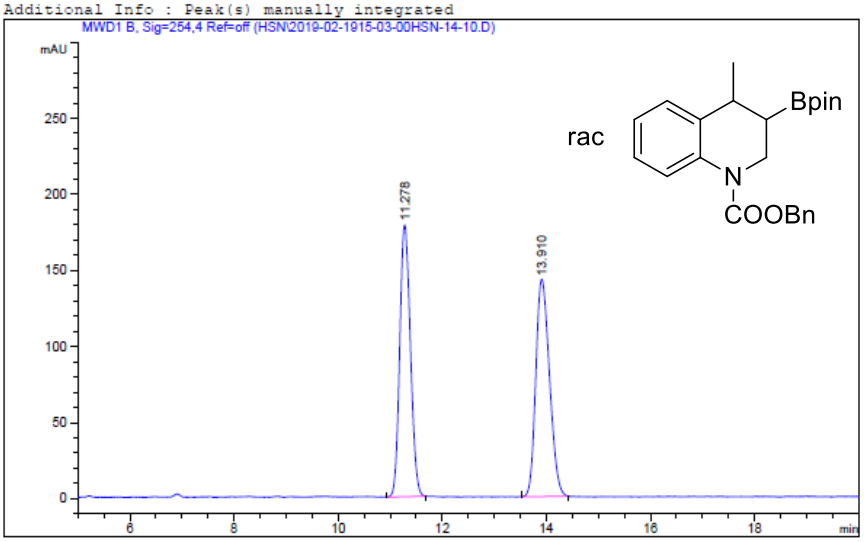
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.412	VV R	0.1877	5805.60254	461.68948	49.9270
2	10.241	VV R	0.2019	5822.57666	426.09579	50.0730
Totals :				1.16282e4	887.78528	

Additional Info : Peak(s) manually integrated



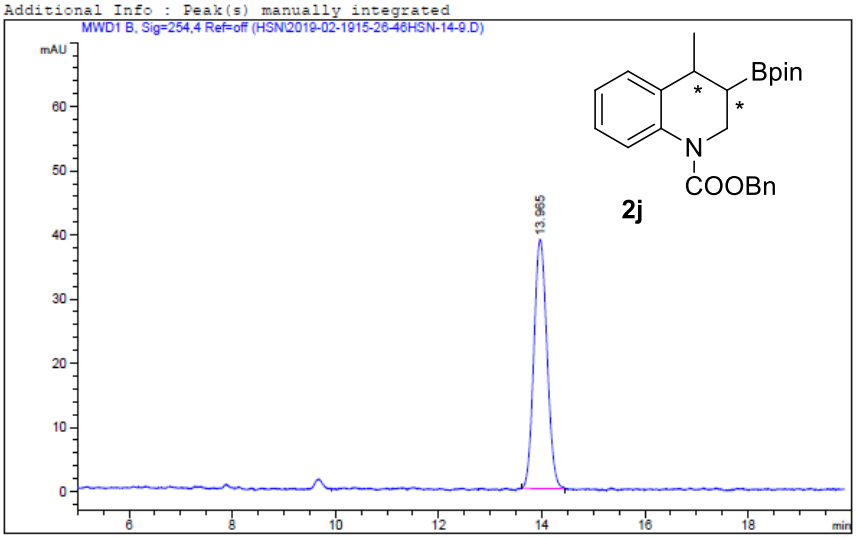
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.484	VV R	0.1749	1668.71838	141.13956	100.0000
Totals :				1668.71838	141.13956	

Additional Info : Peak(s) manually integrated



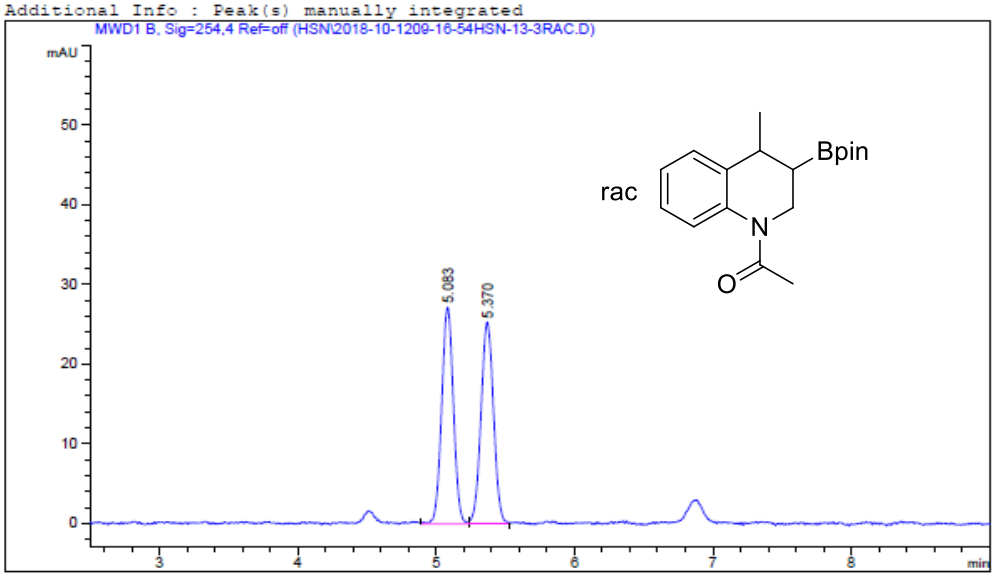
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.278	VV R	0.2023	2536.70386	178.53922	49.3008
2	13.910	VV R	0.2196	2608.66162	142.82715	50.6992
Totals :				5145.36548	321.36636	

Additional Info : Peak(s) manually integrated



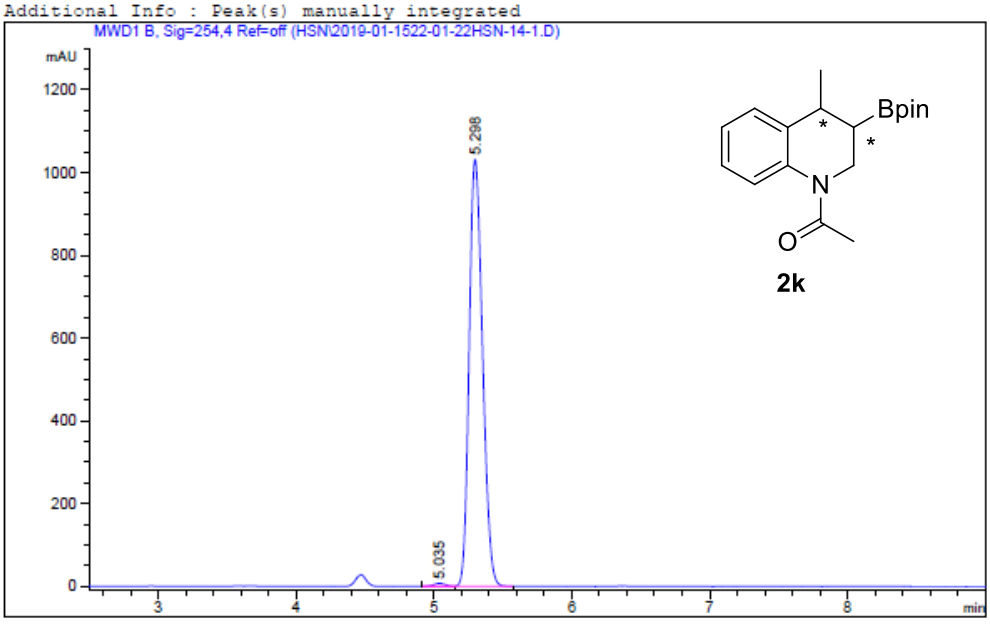
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.965	VV R	0.2102	685.51874	38.87386	100.0000
Totals :				685.51874	38.87386	

Additional Info : Peak(s) manually integrated



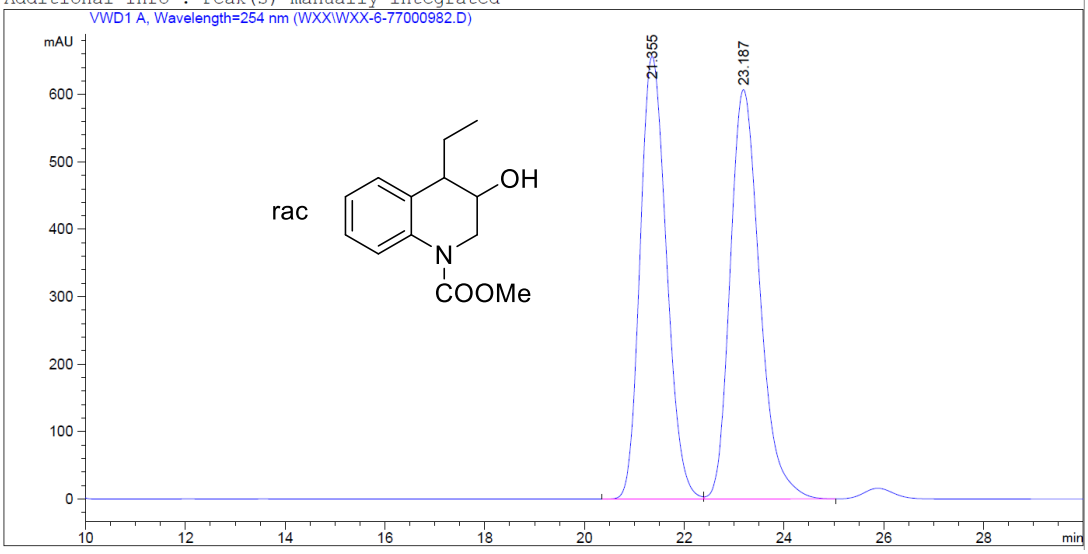
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.083	VV R	0.0920	160.83246	27.20071	50.3413
2	5.370	VV R	0.0910	158.65140	25.34509	49.6587
Totals :				319.48386	52.54580	

Additional Info : Peak(s) manually integrated



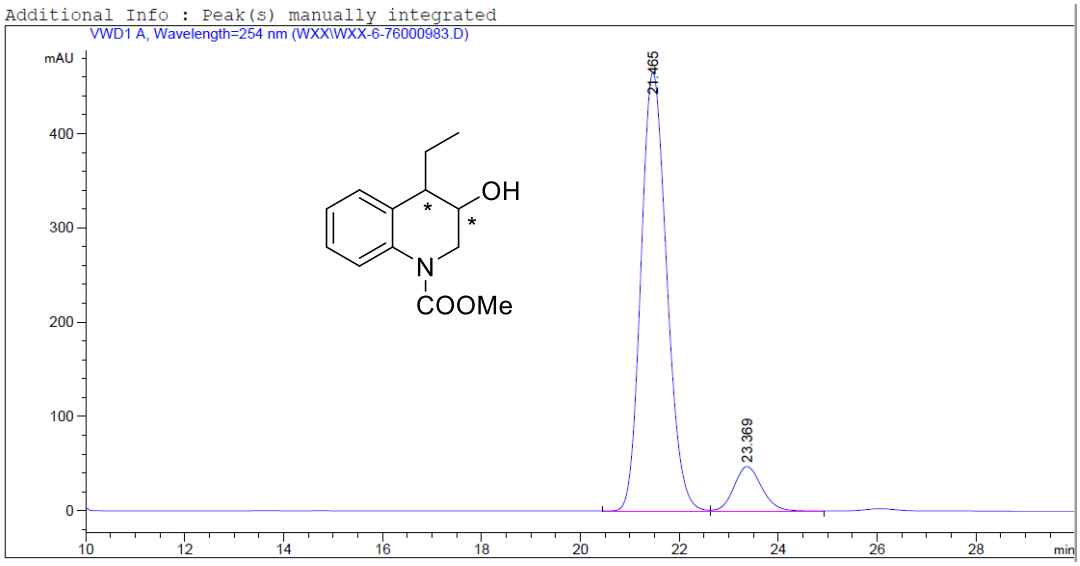
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.035	BV E	0.0754	44.73246	7.40895	0.6396
2	5.298	VV R	0.1066	6948.83594	1031.88977	99.3604
Totals :				6993.56839	1039.29872	

Additional Info : Peak(s) manually integrated



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.355	BV	0.5764	2.41219e4	656.84271	49.0314
2	23.187	VB	0.6418	2.50749e4	607.23981	50.9686
Totals :				4.91968e4	1264.08252	

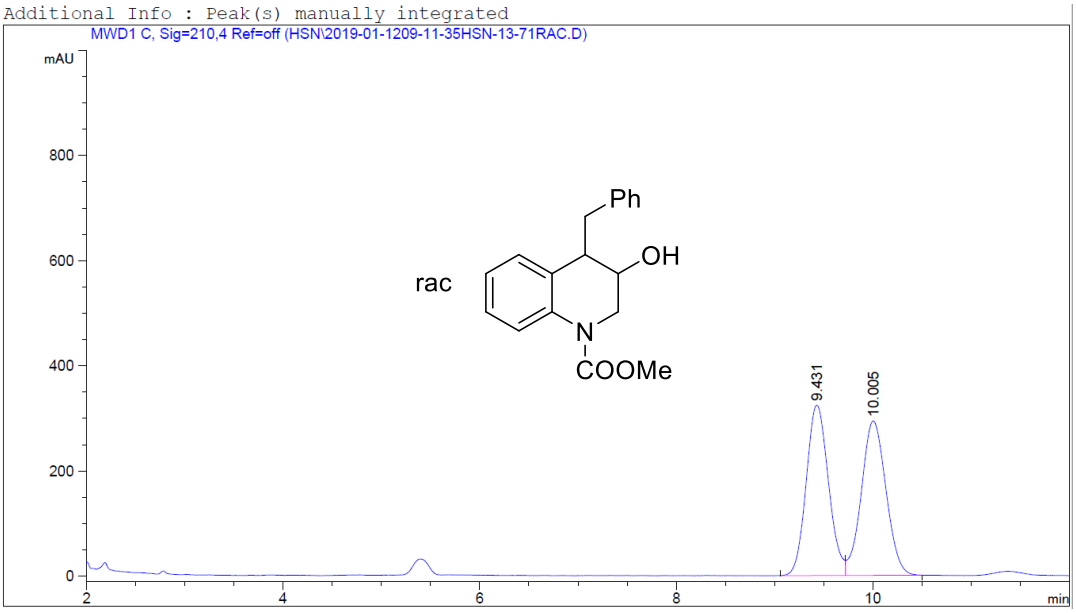
Additional Info : Peak(s) manually integrated



Signal 1: VWD1 A, Wavelength=254 nm

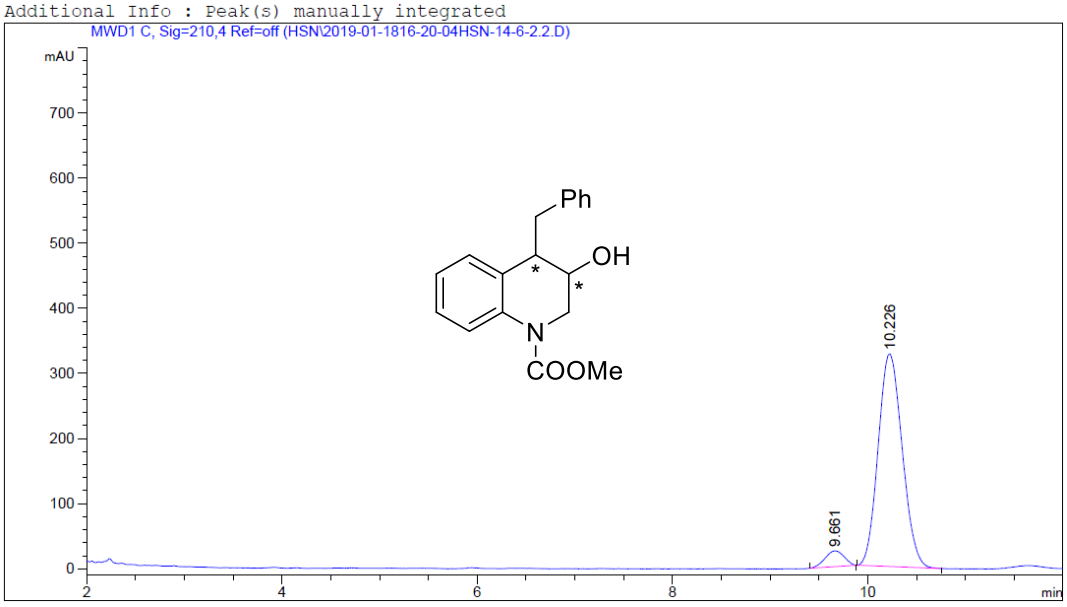
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.465	BV	0.5662	1.67908e4	465.05923	90.2056
2	23.369	VB	0.6013	1823.11743	47.02920	9.7944
Totals :				1.86139e4	512.08844	

Additional Info : Peak(s) manually integrated



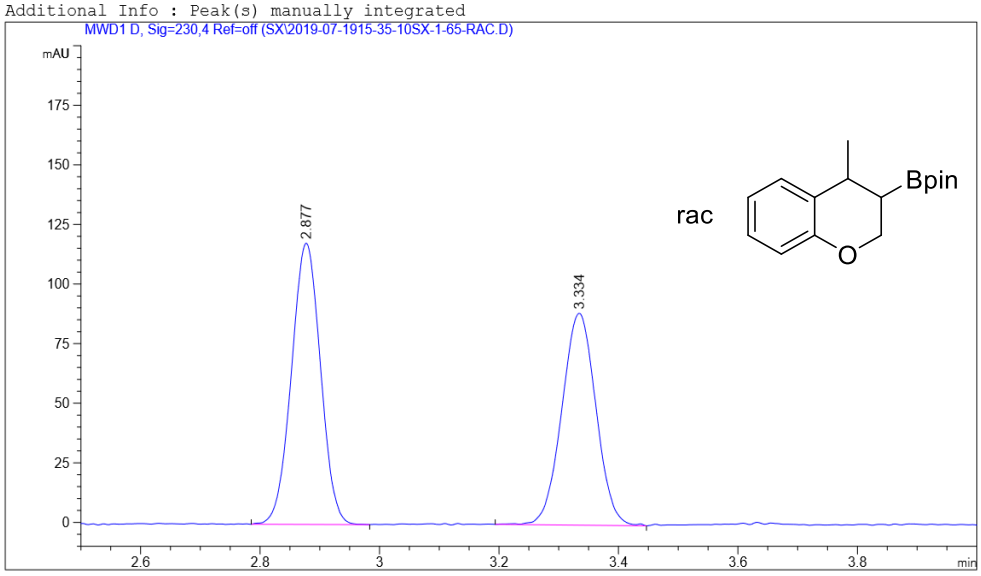
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.431	BV	0.2258	5100.64453	324.57666	49.8497
2	10.005	VV R	0.2411	5131.39355	294.10269	50.1503
Totals :				1.02320e4	618.67935	

Additional Info : Peak(s) manually integrated



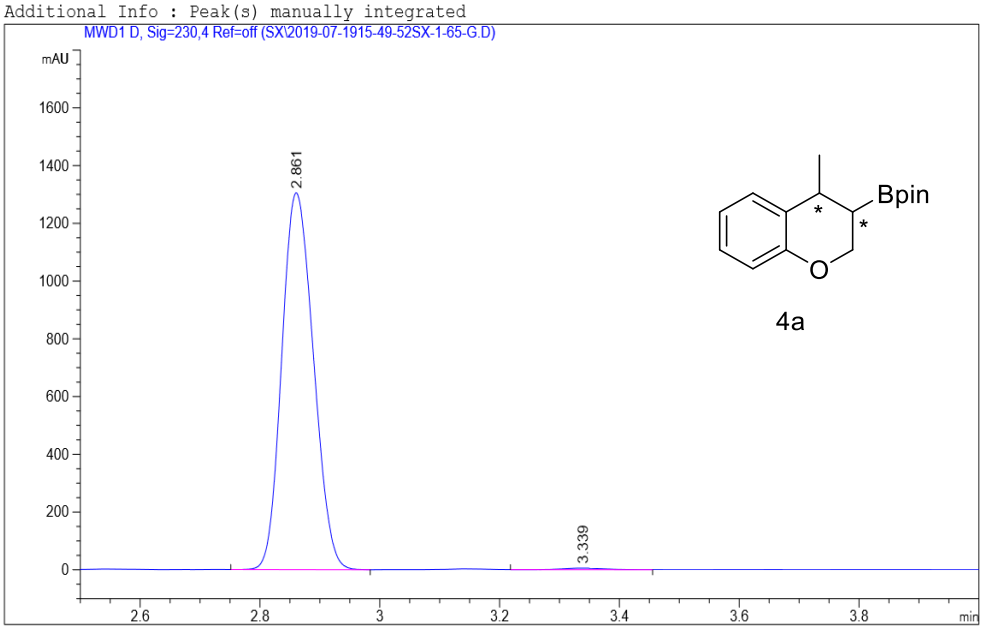
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.661	BB	0.1609	328.60941	24.36417	5.5535
2	10.226	BB	0.2056	5588.53955	326.67313	94.4465
Totals :				5917.14896	351.03730	

Additional Info : Peak(s) manually integrated



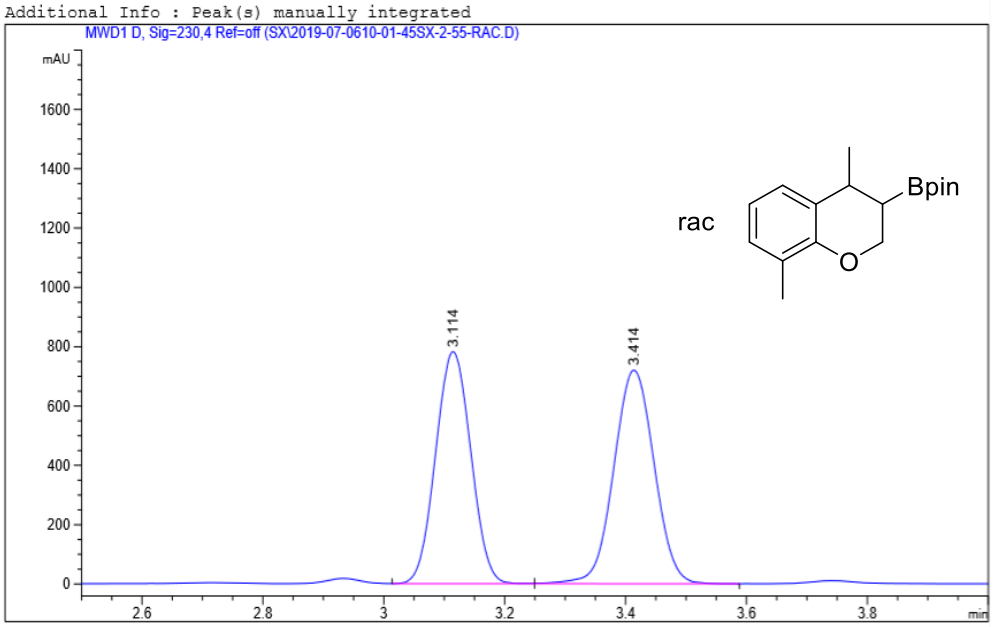
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	2.877	BB	0.0529	398.44870	118.01991	53.0304
2	3.334	VV R	0.0628	352.91077	88.89848	46.9696
Totals :				751.35947	206.91840	

Additional Info : Peak(s) manually integrated



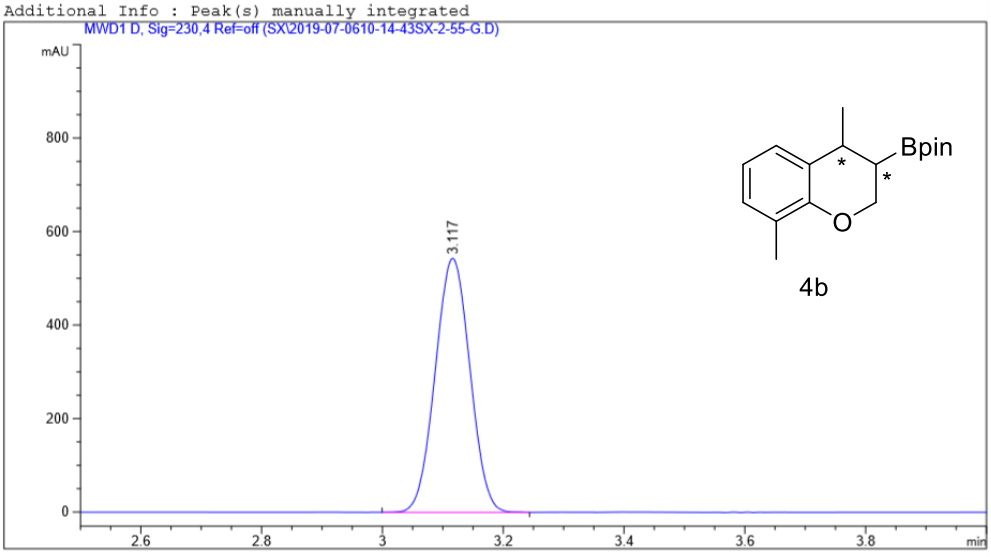
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	2.861	VV R	0.0588	4787.90186	1305.30164	99.4283
2	3.339	VV R	0.0608	27.52984	5.85816	0.5717
Totals :				4815.43170	1311.15979	

Additional Info : Peak(s) manually integrated



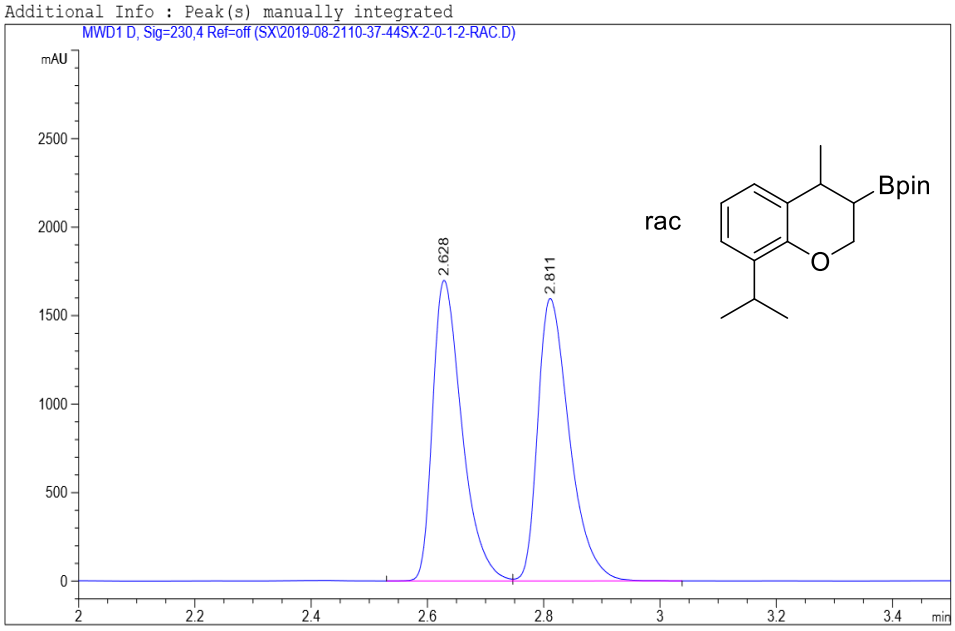
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.114	BV R	0.0642	3167.29956	782.27649	48.6322
2	3.414	VV R	0.0727	3345.45605	720.32324	51.3678
Totals :				6512.75562	1502.59973	

Additional Info : Peak(s) manually integrated



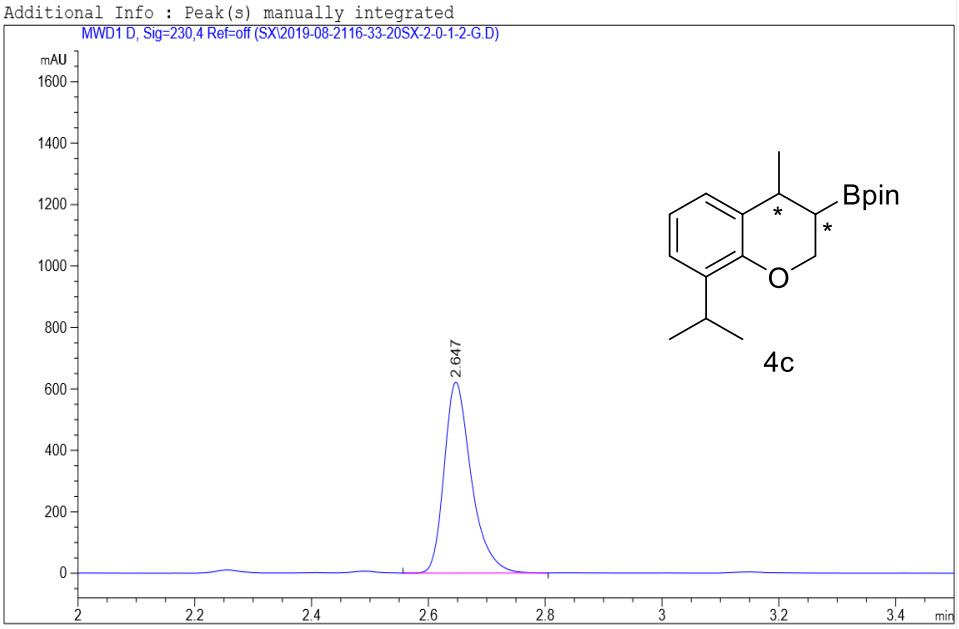
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.117	BV R	0.0636	2169.33716	543.51385	100.0000
Totals :				2169.33716	543.51385	

Additional Info : Peak(s) manually integrated



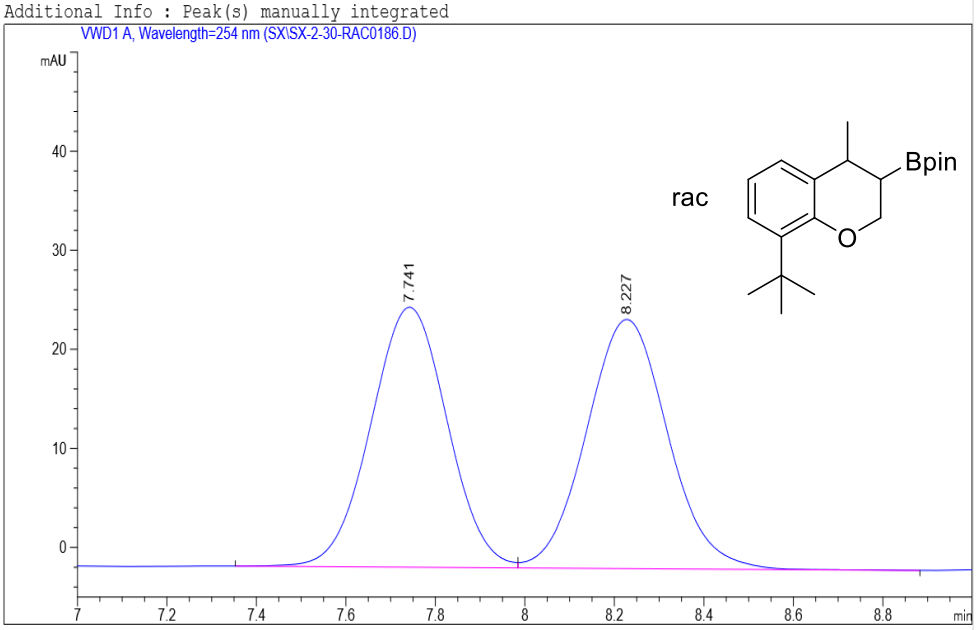
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	2.628	BV	0.0532	5928.97363	1698.82886	49.5415
2	2.811	VB	0.0586	6038.72607	1595.83386	50.4585
Totals :				1.19677e4	3294.66272	

Additional Info : Peak(s) manually integrated



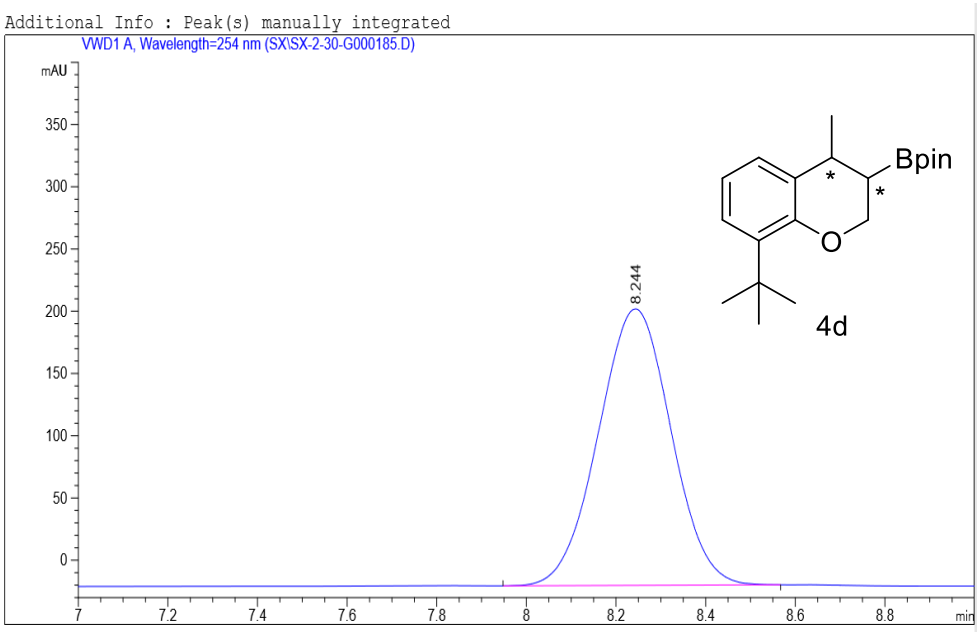
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	2.647	VB R	0.0492	2007.78381	621.51477	100.0000
Totals :				2007.78381	621.51477	

Additional Info : Peak(s) manually integrated



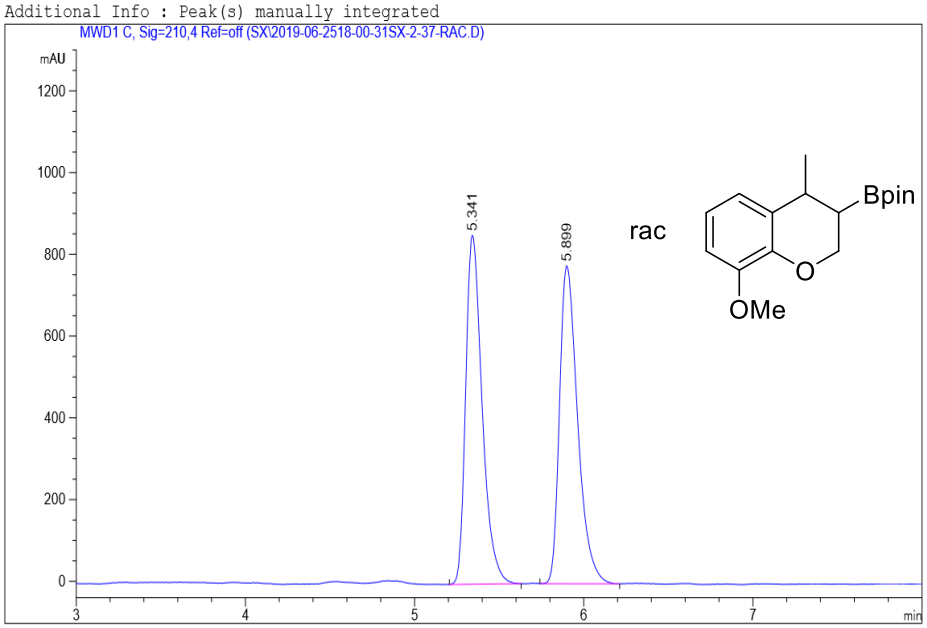
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.741	BV	0.1867	311.91870	26.24359	49.5333
2	8.227	VB	0.1964	317.79617	25.15459	50.4667
Totals :				629.71487	51.39818	

Additional Info : Peak(s) manually integrated



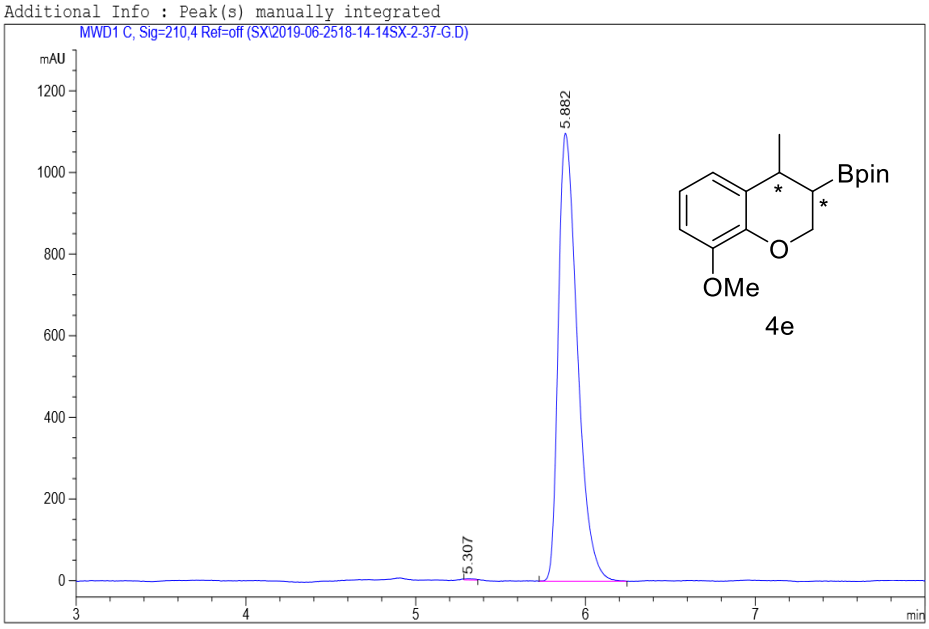
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.244	BB	0.1764	2502.31494	222.10522	100.0000
Totals :				2502.31494	222.10522	

Additional Info : Peak(s) manually integrated



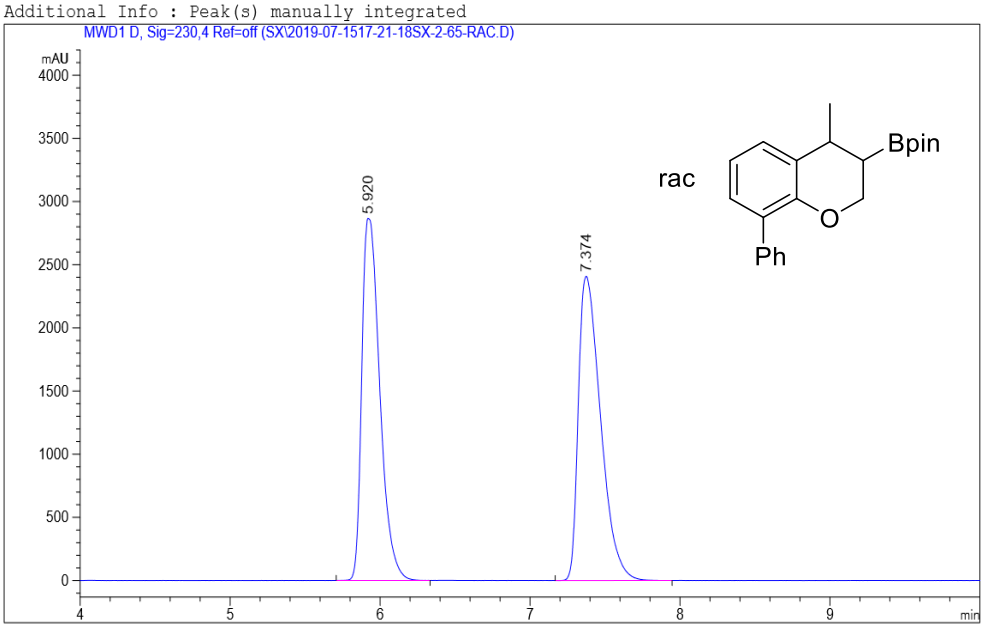
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.341	BV R	0.1037	5754.85791	853.60388	49.8723
2	5.899	VV R	0.1138	5784.32568	777.74994	50.1277
Totals :				1.15392e4	1631.35382	

Additional Info : Peak(s) manually integrated



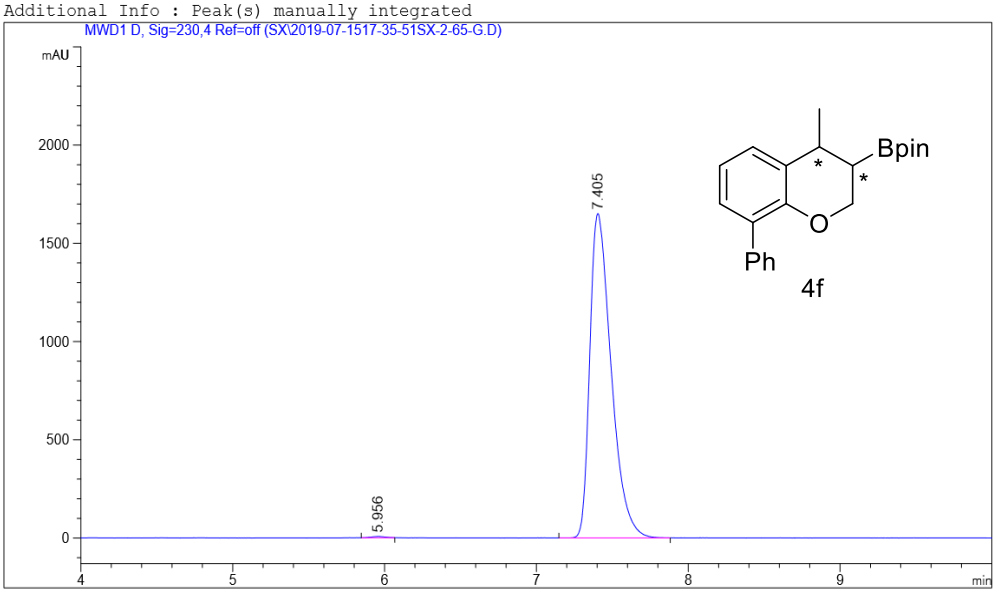
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.307	VV	0.0475	11.11751	2.85231	0.1293
2	5.882	VV R	0.1128	8587.05273	1097.82520	99.8707
Totals :				8598.17025	1100.67751	

Additional Info : Peak(s) manually integrated



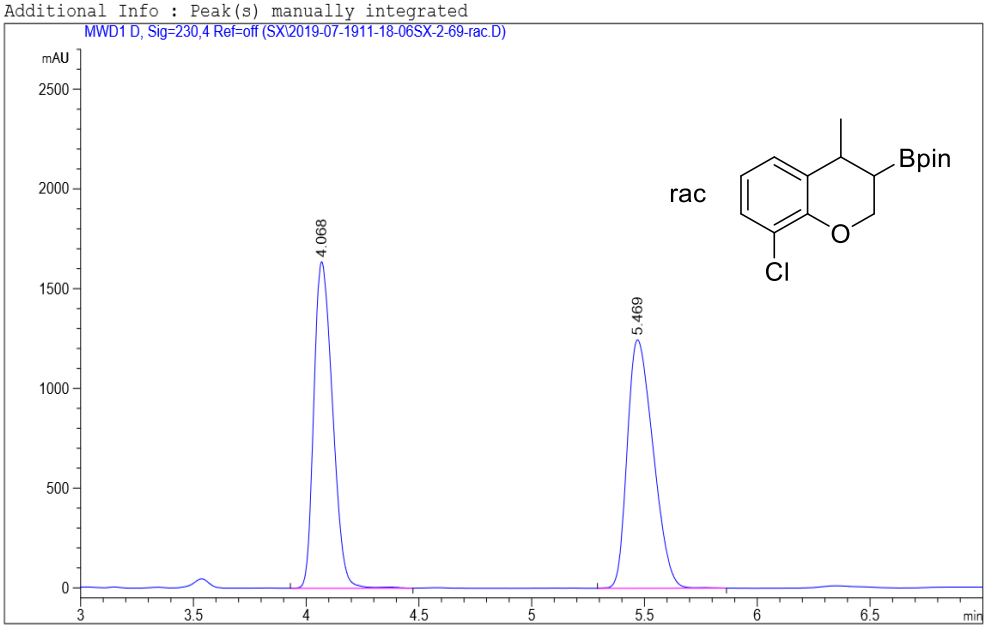
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.920	VV R	0.1102	2.38807e4	2866.53687	49.0752
2	7.374	VV R	0.1566	2.47808e4	2408.00488	50.9248
Totals :				4.86615e4	5274.54175	

Additional Info : Peak(s) manually integrated



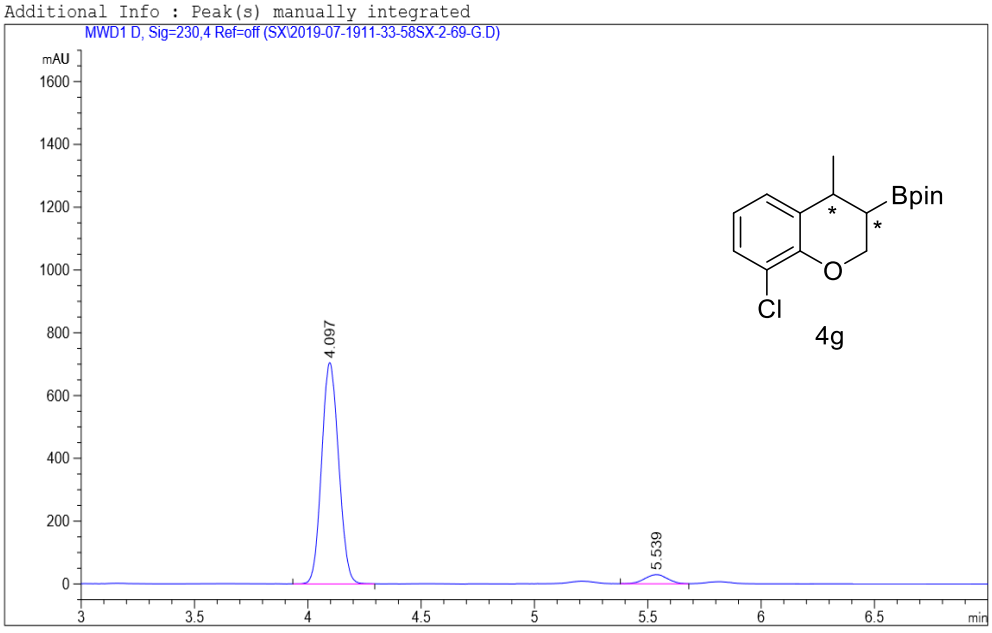
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.956	VV R	0.0820	42.49166	6.69762	0.2635
2	7.405	VV R	0.1492	1.60848e4	1650.57251	99.7365
Totals :				1.61273e4	1657.27013	

Additional Info : Peak(s) manually integrated



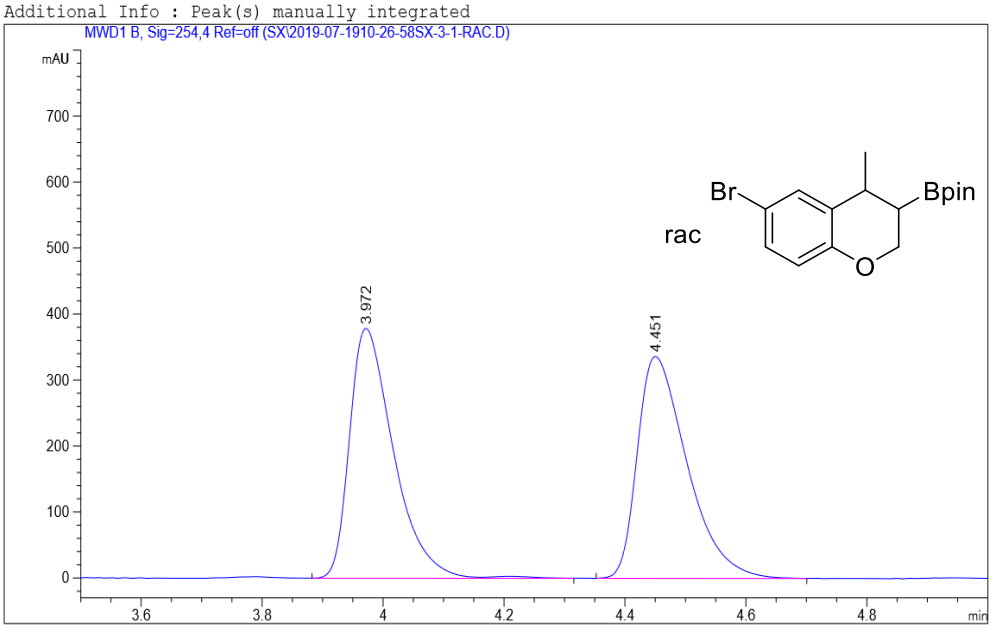
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.068	BV R	0.0916	9446.93262	1636.93909	48.7358
2	5.469	VV R	0.1239	9937.03223	1246.15002	51.2642
Totals :				1.93840e4	2883.08911	

Additional Info : Peak(s) manually integrated



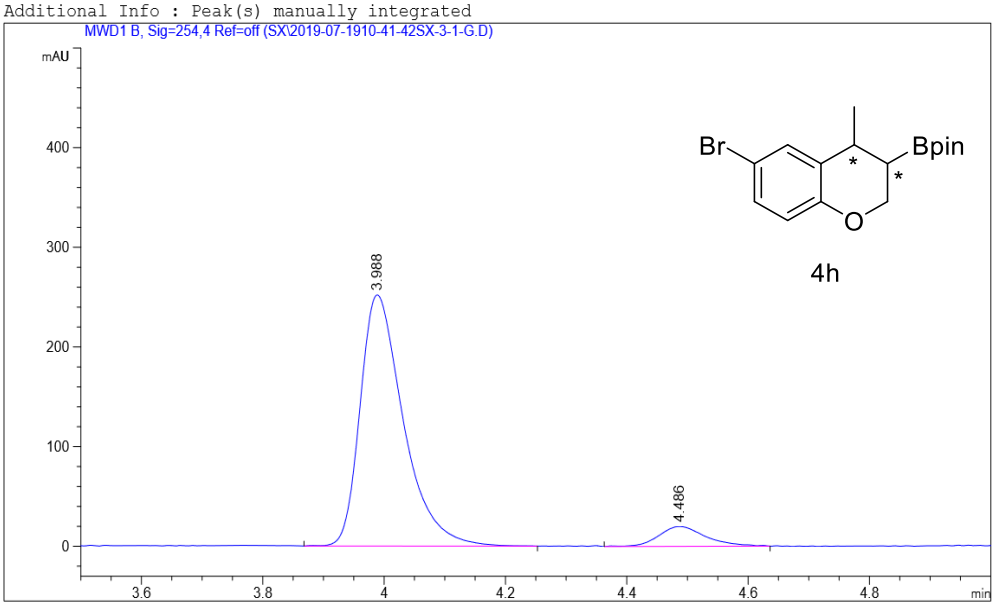
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.097	VV R	0.0826	3689.90381	704.89227	94.7663
2	5.539	VB R	0.0981	203.78479	29.31461	5.2337
Totals :				3893.68860	734.20688	

Additional Info : Peak(s) manually integrated



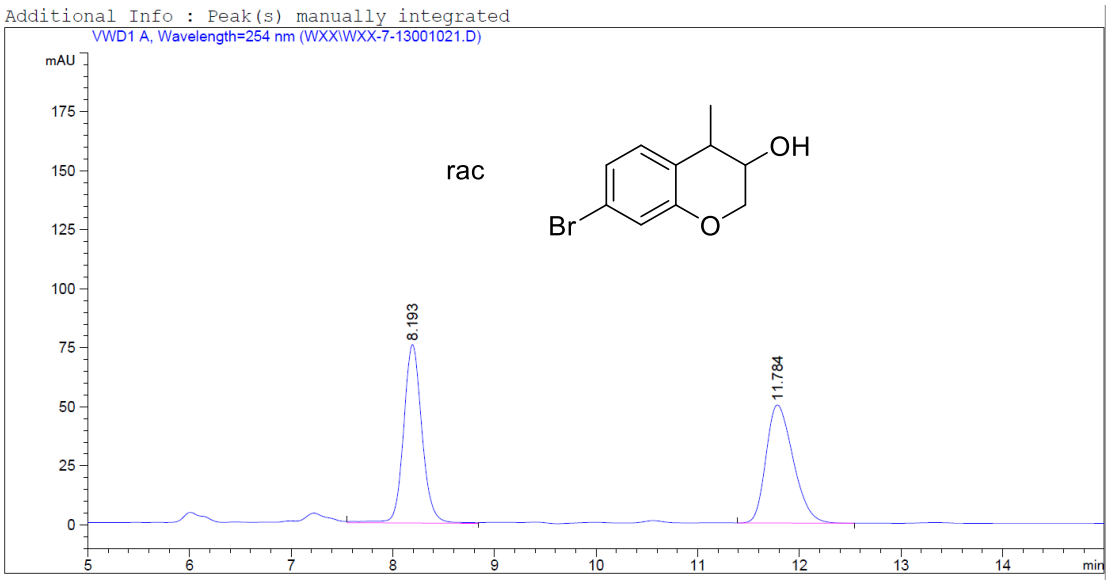
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.972	BV R	0.0771	1916.52222	378.67670	49.9353
2	4.451	BV R	0.0876	1921.49011	336.39191	50.0647
Totals :				3838.01233	715.06860	

Additional Info : Peak(s) manually integrated



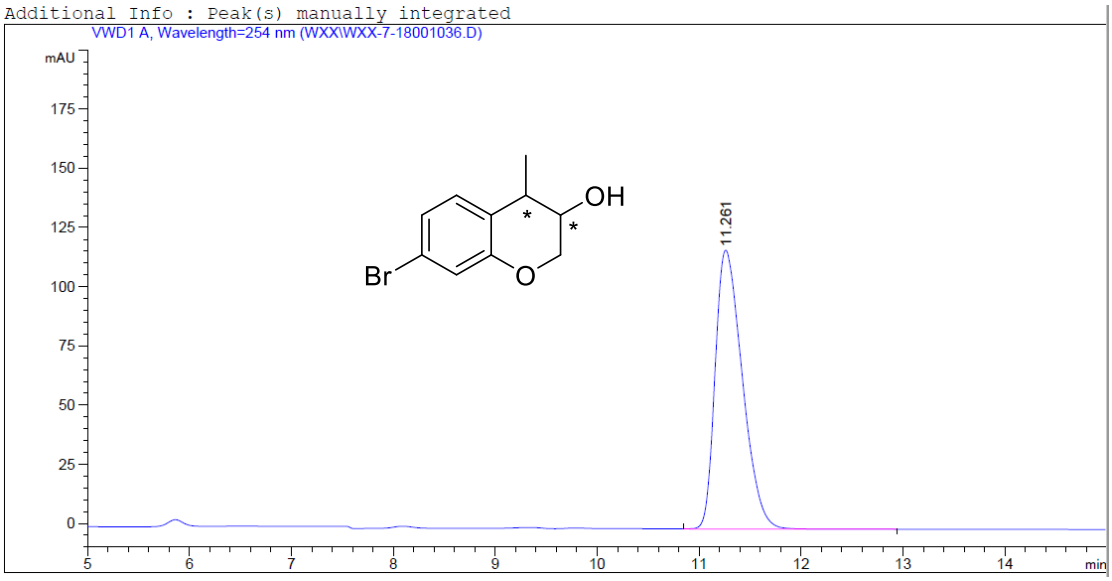
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.988	VV R	0.0743	1248.28442	252.01712	92.0258
2	4.486	VV R	0.0768	108.16631	20.07981	7.9742
Totals :				1356.45074	272.09694	

Additional Info : Peak(s) manually integrated



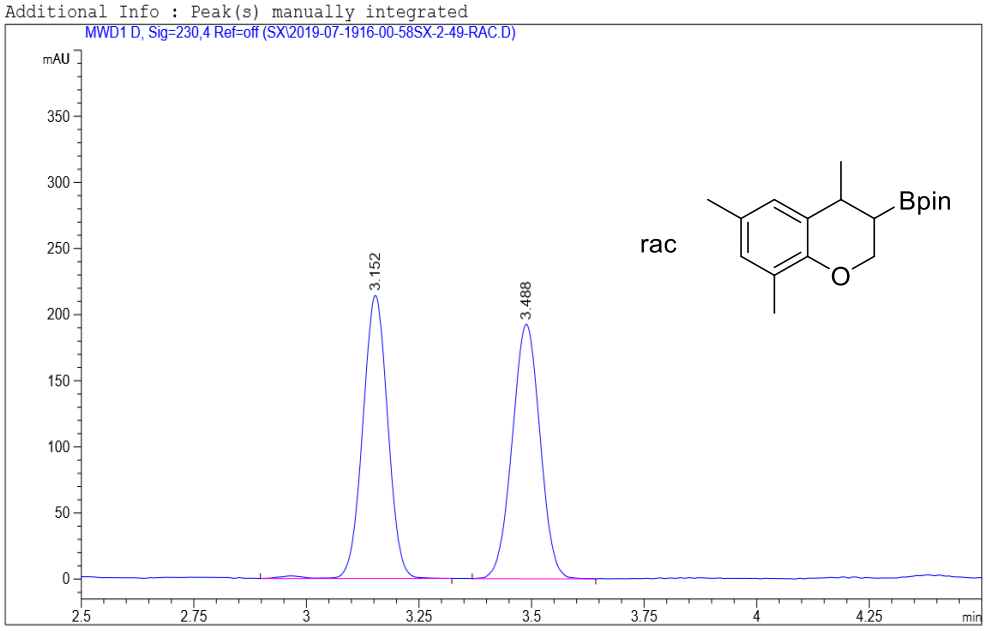
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.193	VV	0.1950	951.65906	75.52600	50.6427
2	11.784	BB	0.2884	927.50610	50.00571	49.3573
Totals :				1879.16516	125.53171	

Additional Info : Peak(s) manually integrated



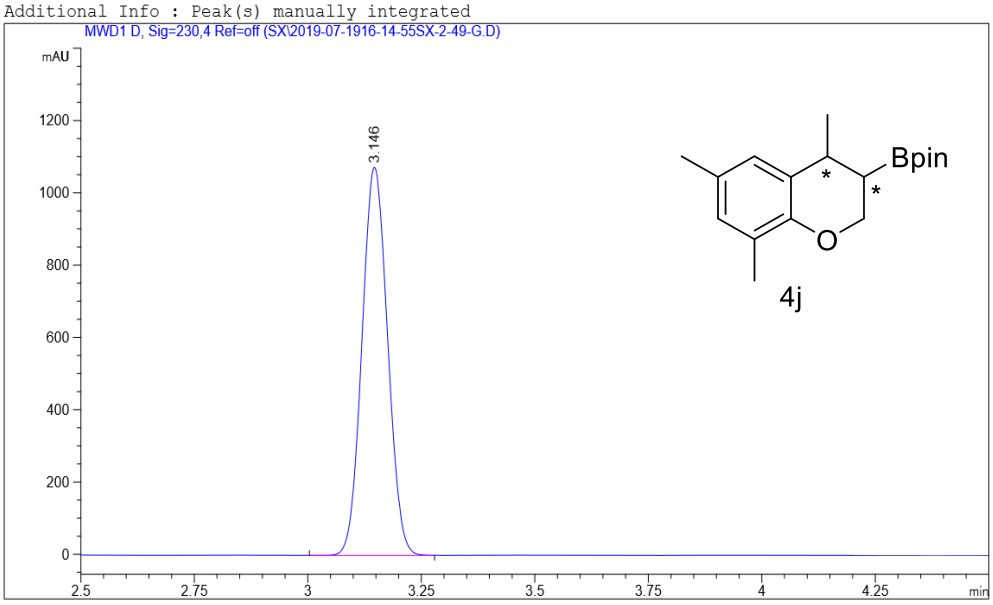
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.261	VB	0.2880	2179.18311	117.69168	100.0000
Totals :				2179.18311	117.69168	

Additional Info : Peak(s) manually integrated



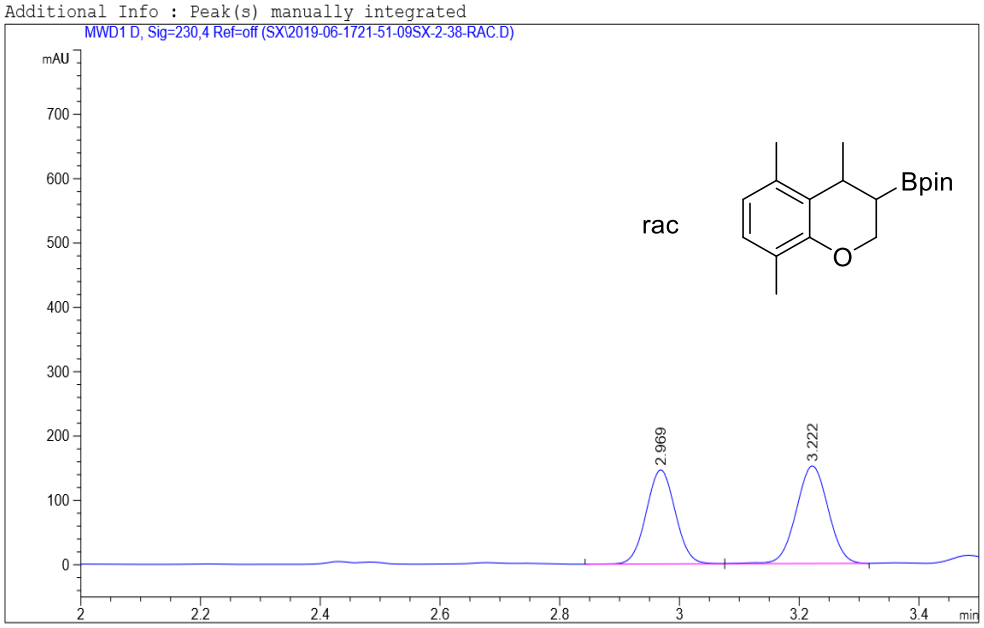
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.152	VV R	0.0603	830.64777	214.20097	50.0507
2	3.488	BV R	0.0677	828.96552	192.53253	49.9493
Totals :				1659.61328	406.73351	

Additional Info : Peak(s) manually integrated



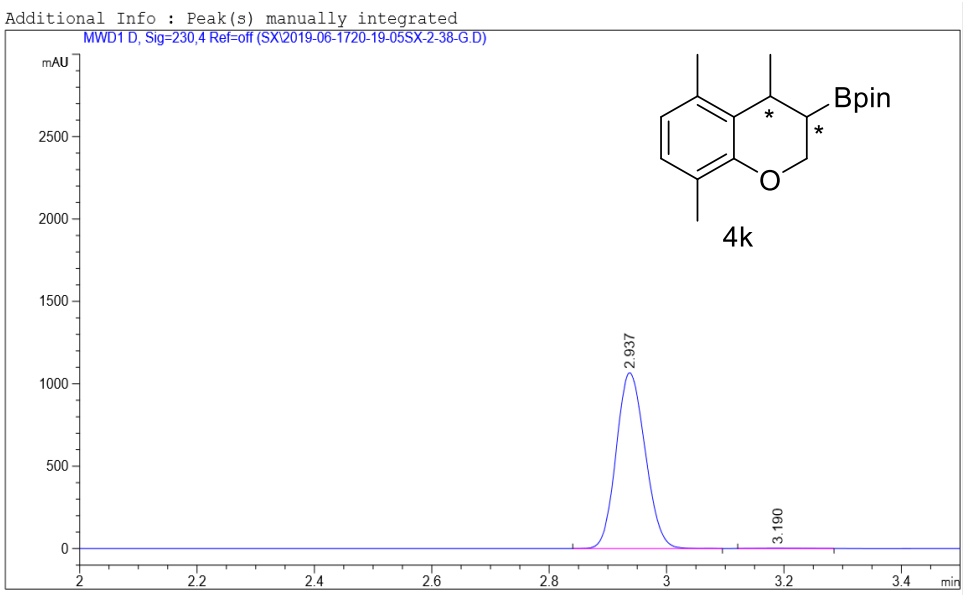
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.146	VV R	0.0612	4207.89600	1073.86365	100.0000
Totals :				4207.89600	1073.86365	

Additional Info : Peak(s) manually integrated



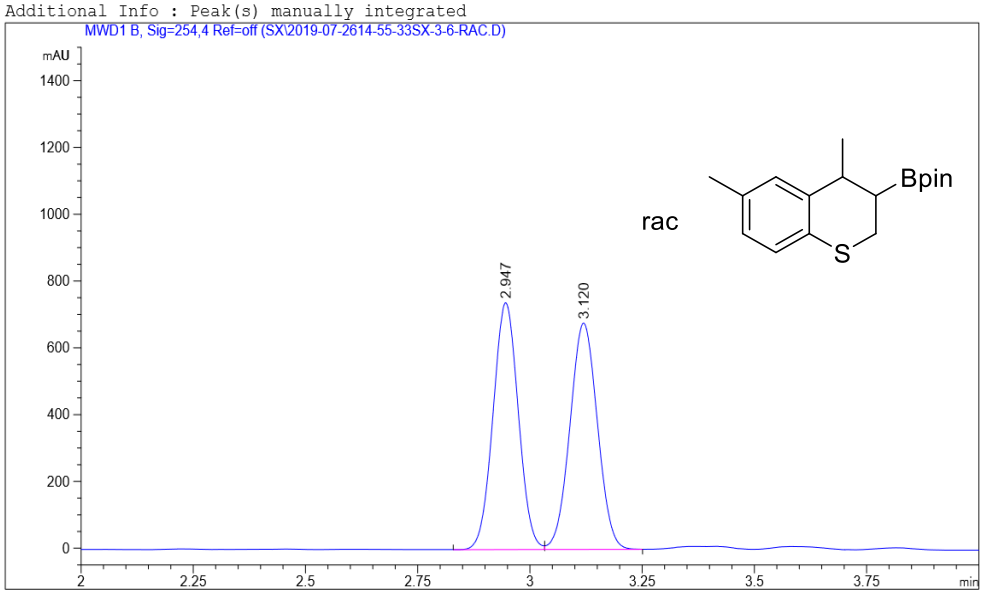
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	2.969	BB	0.0528	491.87753	146.15196	46.7430
2	3.222	VB R	0.0576	560.42511	151.61177	53.2570
Totals :				1052.30264	297.76373	

Additional Info : Peak(s) manually integrated



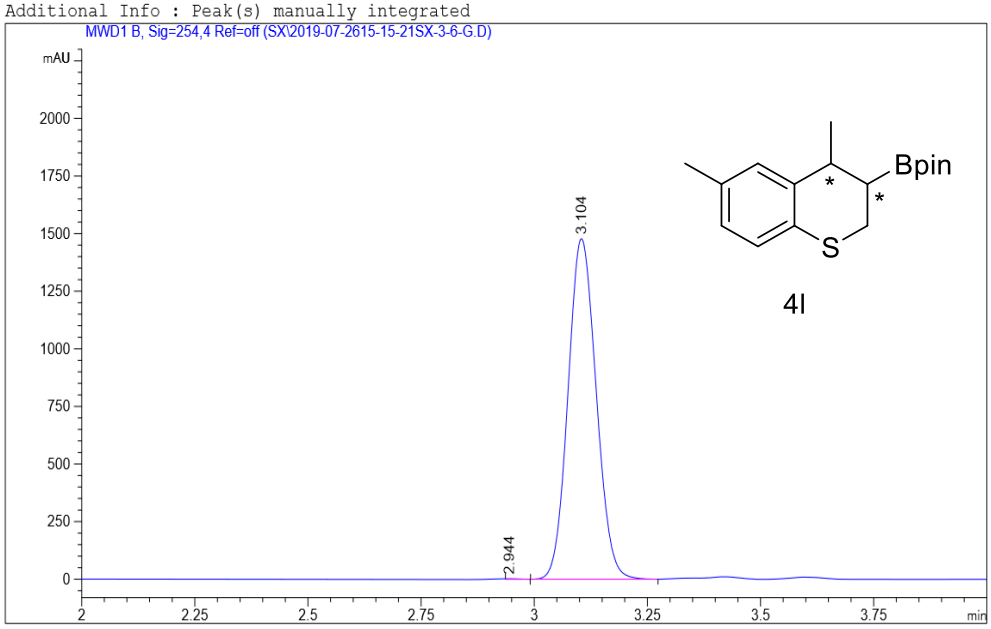
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	2.937	BV R	0.0540	3654.46167	1066.58069	99.7853
2	3.190	BV R	0.0471	7.86413	2.12698	0.2147
Totals :				3662.32580	1068.70766	

Additional Info : Peak(s) manually integrated



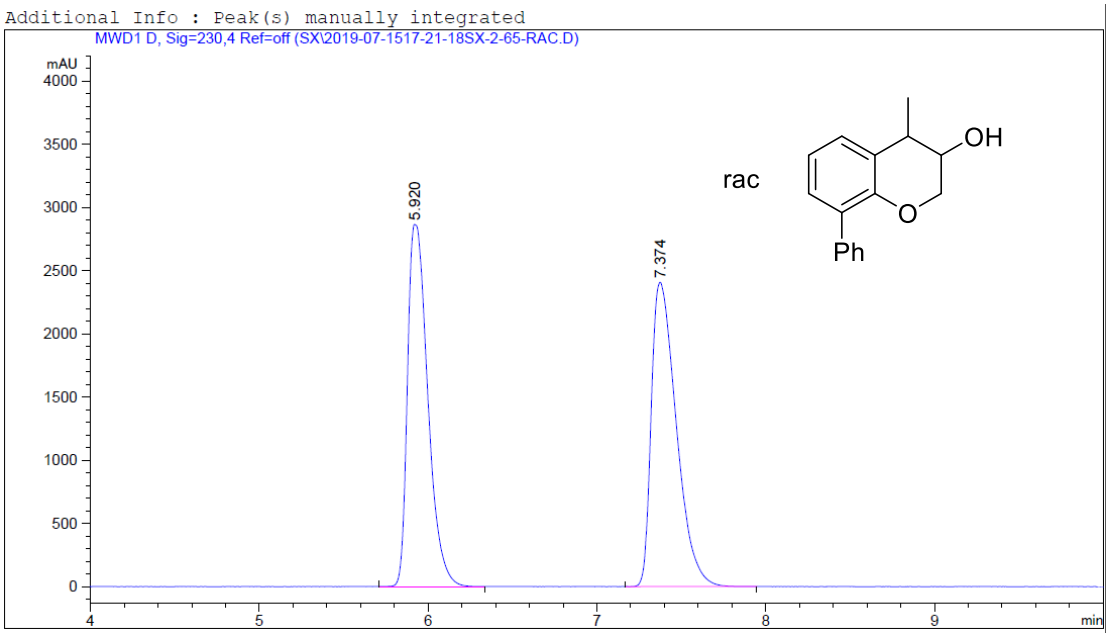
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	2.947	BV	0.0612	2894.19116	739.45544	50.0840
2	3.120	VV R	0.0667	2884.47852	677.69769	49.9160
Totals :				5778.66968	1417.15314	

Additional Info : Peak(s) manually integrated



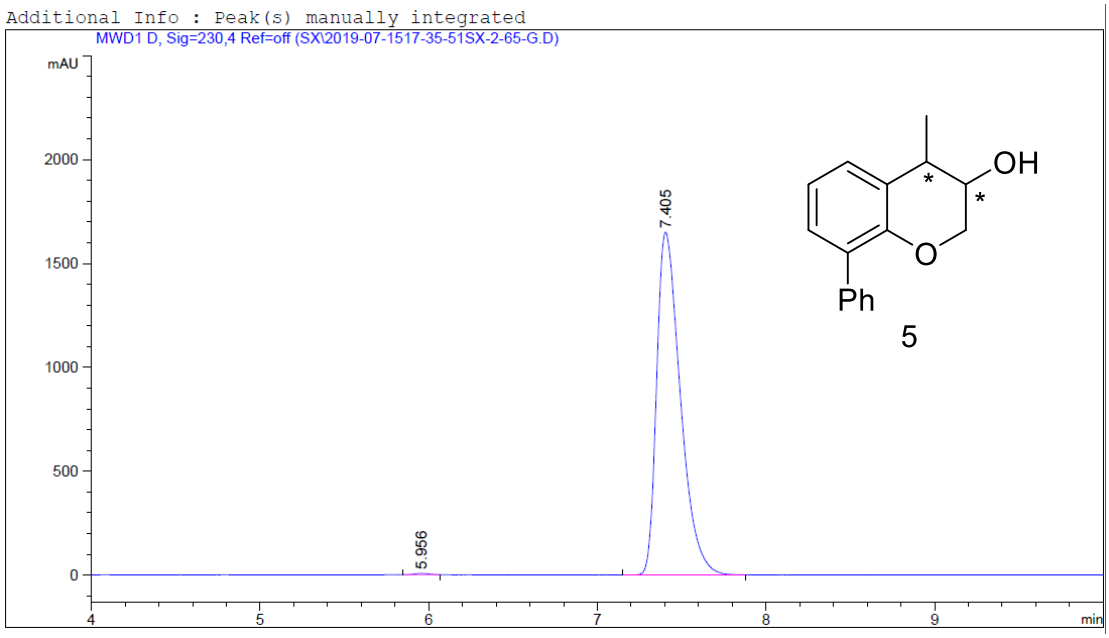
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	2.944	VB	0.0277	4.73446	2.61115	0.0741
2	3.104	BB	0.0679	6386.38184	1478.07861	99.9259
Totals :				6391.11630	1480.68976	

Additional Info : Peak(s) manually integrated



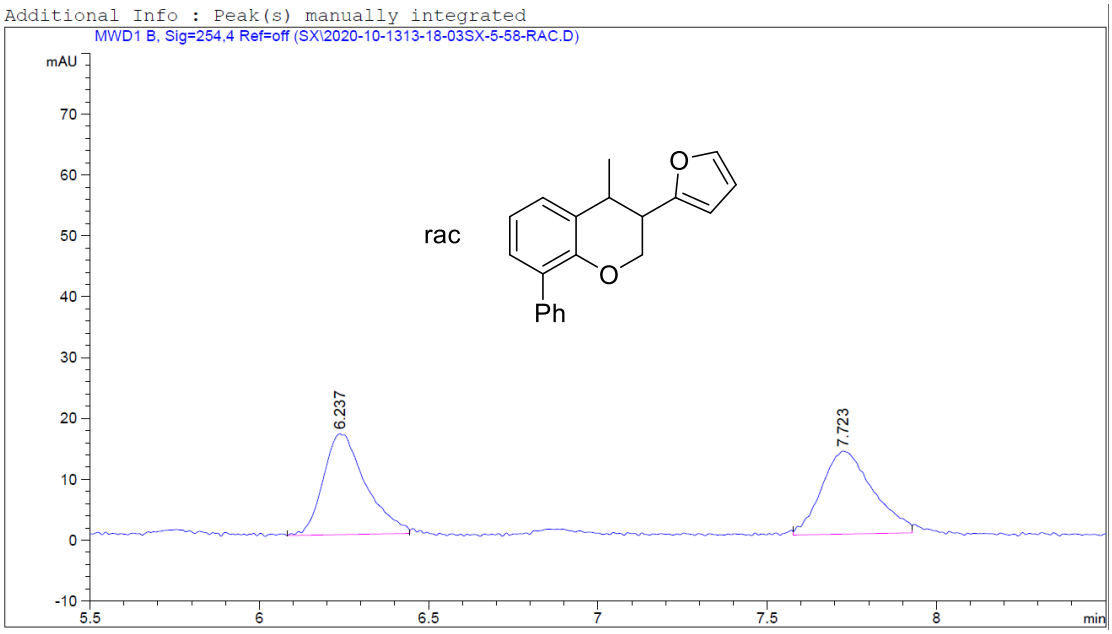
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.920	VV R	0.1102	2.38807e4	2866.53687	49.0752
2	7.374	VV R	0.1566	2.47808e4	2408.00488	50.9248
Totals :				4.86615e4	5274.54175	

Additional Info : Peak(s) manually integrated



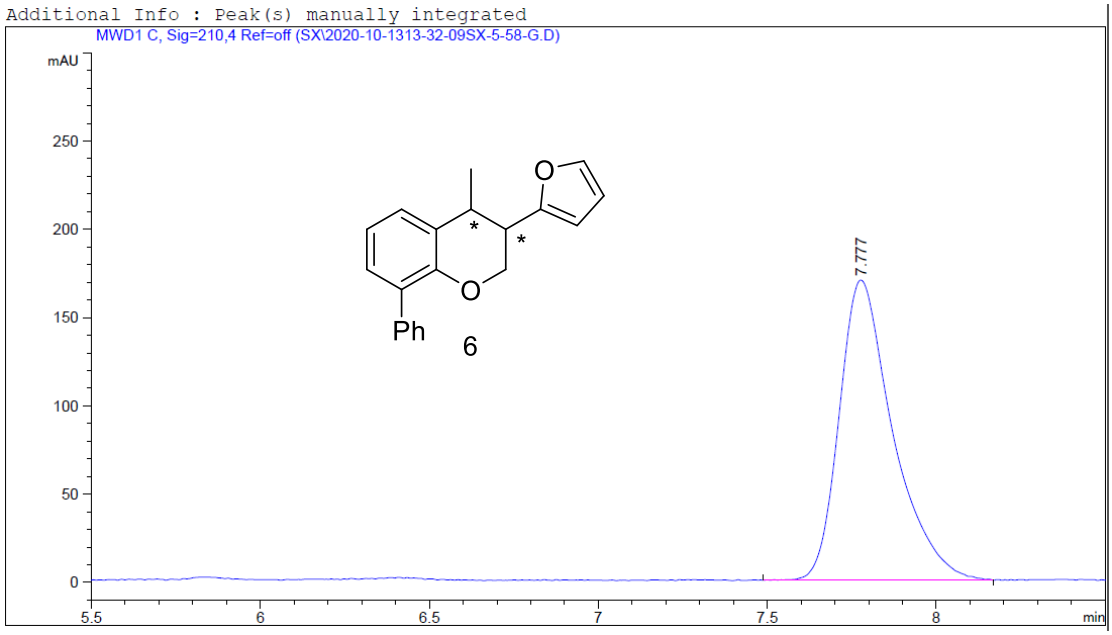
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.956	VV R	0.0820	42.49166	6.69762	0.2635
2	7.405	VV R	0.1492	1.60848e4	1650.57251	99.7365
Totals :				1.61273e4	1657.27013	

Additional Info : Peak(s) manually integrated



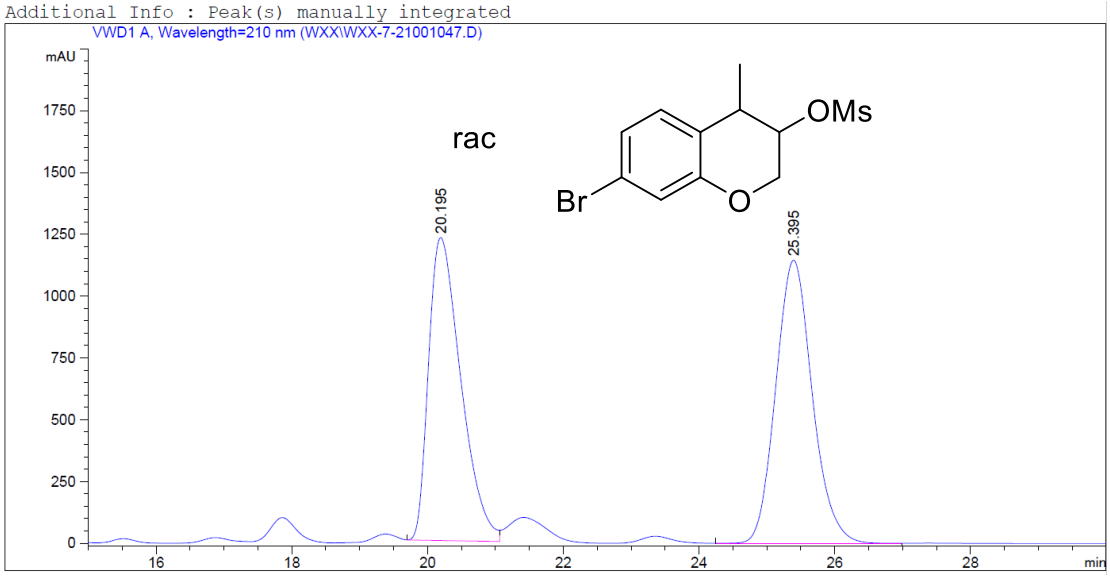
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.237	BV	0.1165	144.47655	16.61224	50.0855
2	7.723	VV	0.1343	143.98346	13.62382	49.9145
Totals :				288.46001	30.23606	

Additional Info : Peak(s) manually integrated



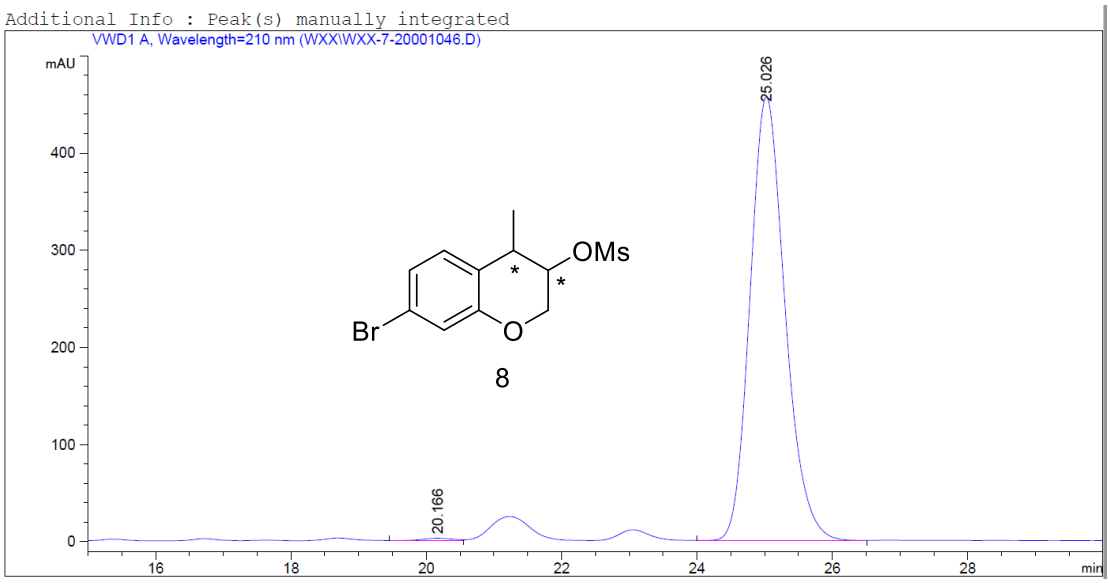
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.777	BB	0.1649	1877.60864	169.98178	100.0000
Totals :				1877.60864	169.98178	

Additional Info : Peak(s) manually integrated



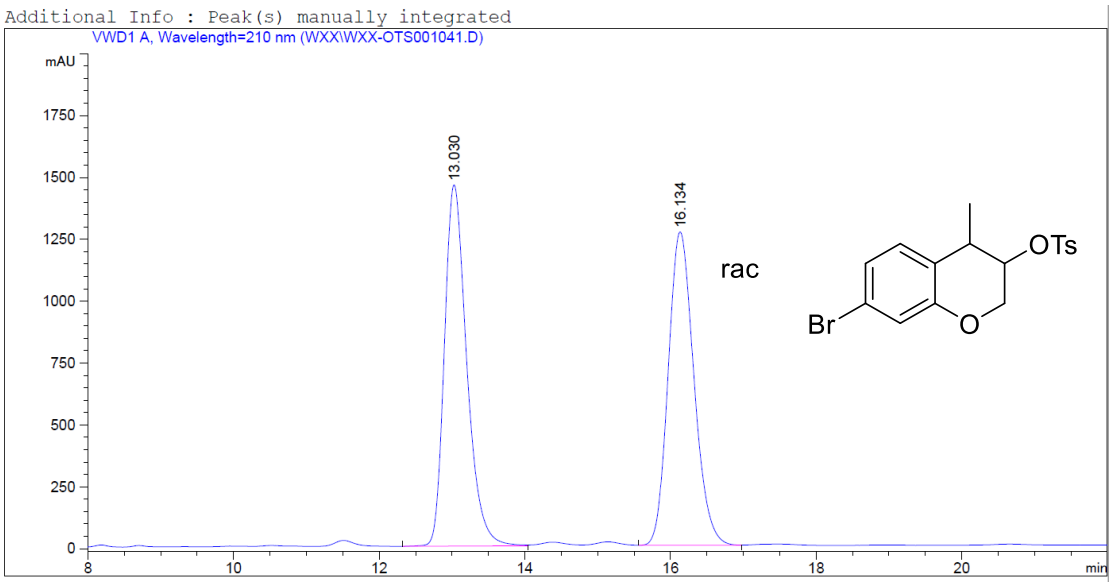
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.195	BV	0.5093	4.04768e4	1225.46301	48.5988
2	25.395	BB	0.5772	4.28108e4	1145.07361	51.4012
Totals :				8.32876e4	2370.53662	

Additional Info : Peak(s) manually integrated



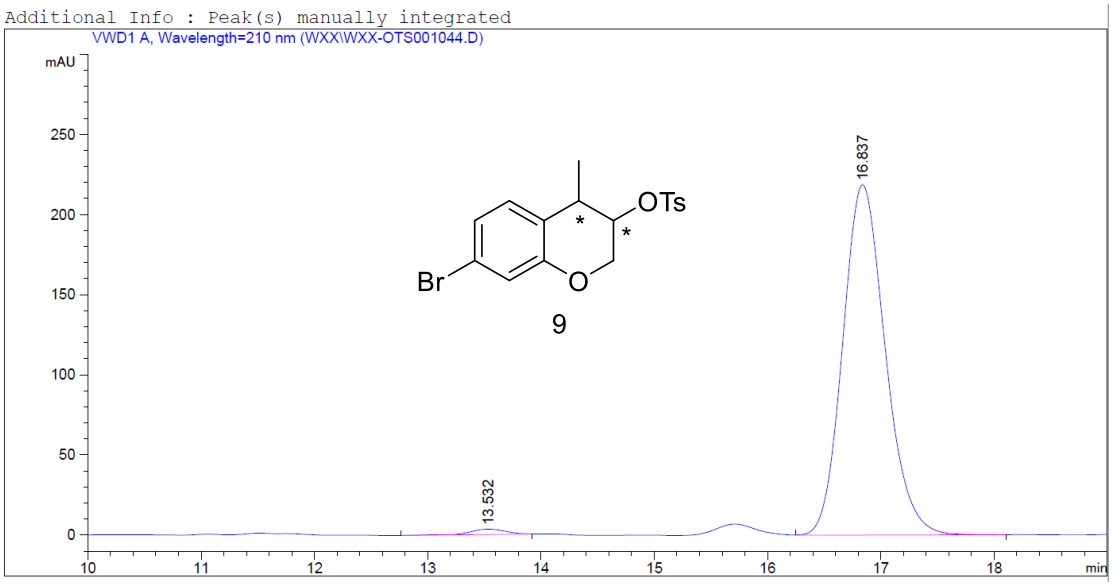
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.166	BV	0.4638	73.27442	2.36959	0.4445
2	25.026	BB	0.5544	1.64112e4	456.56659	99.5555
Totals :				1.64845e4	458.93618	

Additional Info : Peak(s) manually integrated



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.030	BV	0.3250	3.10173e4	1459.29297	50.0124
2	16.134	BV	0.3796	3.10018e4	1266.39172	49.9876
Totals :				6.20191e4	2725.68469	

Additional Info : Peak(s) manually integrated



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.532	BB	0.3401	72.00000	3.33219	1.2506
2	16.837	VB	0.4025	5685.14551	218.52538	98.7494
Totals :				5757.14551	221.85756	

10. Figures of single-crystals

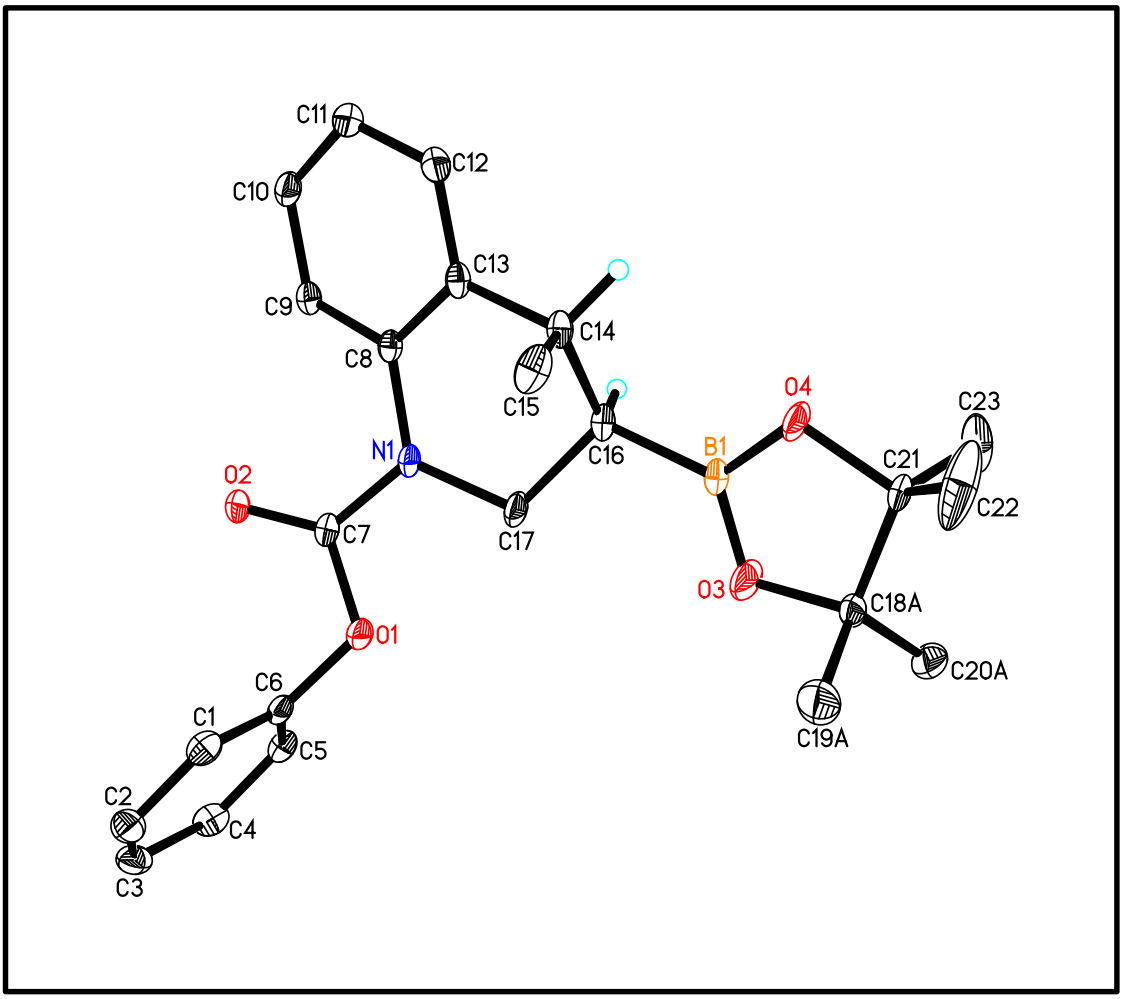


Figure S1. Structure of compound **2i**.

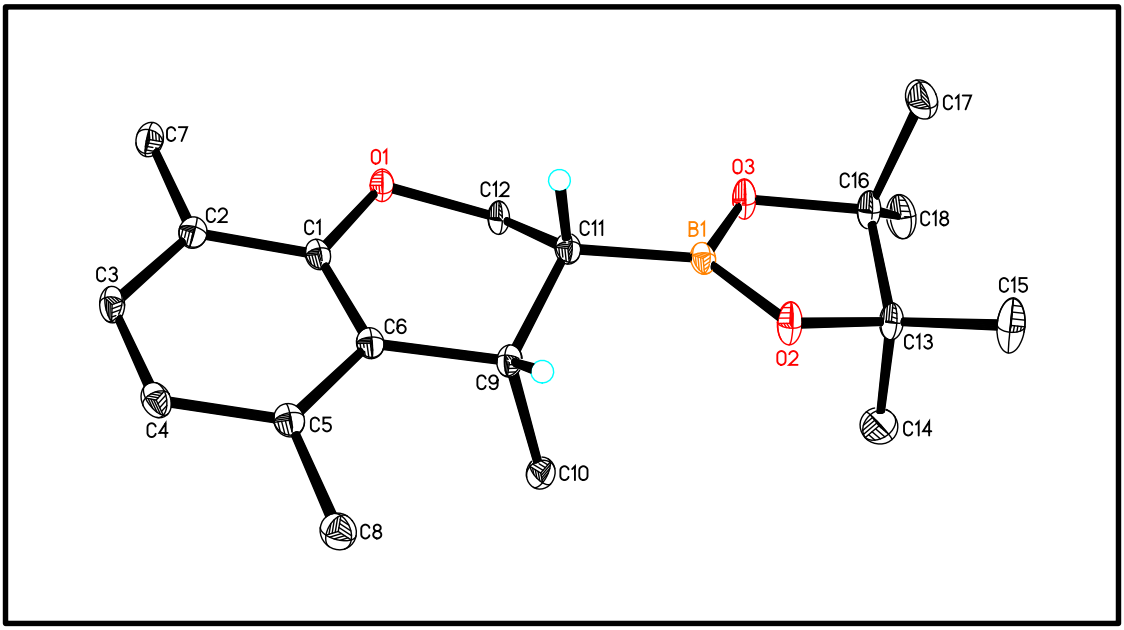


Figure S2. Structure of compound **4j**.