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Electronic Supplementary Information

Nickel(II)-catalyzed asymmetric intramolecular Alder-ene reaction of 1,7-dienes

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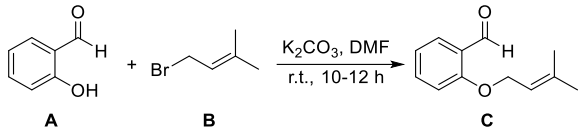
General Remarks

Unless otherwise noted, all commercially available compounds were used without further purification. CH_2Cl_2 and CH_2ClCH_2Cl (DCE) were distilled from CaH_2. Enantiomeric excesses (ee) were determined by HPLC analysis using the corresponding commercial chiral column as stated in the experimental procedures at 23 °C with UV or PDA detector. The chiral HPLC methods were calibrated with the corresponding racemic mixtures. ^{1}H NMR and ^{13}C{^{1}H} NMR were recorded on a Bruker AMX-400 spectrometer in $CDCl_3$. Data for ^{1}H NMR are reported as follows: chemical shift in reference to residual $CHCl_3$ at 7.26 ppm (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, td = triplet of doublets, m = multiplet), coupling constants (*J*) are in Hertz (Hz), and integration. Data for ^{13}C{^{1}H} NMR are reported in terms of chemical shift in reference to the $CDCl_3$ solvent signal (77.16 ppm). ^{19}F{^{1}H} NMR spectra were collected on commercial instruments (376 MHz) with complete proton decoupling. HRMS was recorded on Thermo Scientific Q Exactive hybrid quadrupole-Orbitrap mass spectrometer (ESI Source). IR was recored on Bruker Tensor II spectrometer with Plantium ATR accessory. Optical rotations were measured at 589 nm on a Rudolph Autopol V automatic polarimeter and are reported as follows: $[\alpha]^T_D$ (*c* g/100 mL, in solvent). Unless otherwise indicated, reagents obtained from commercial sources were used without further purification. The chiral *N*,*N*′-dioxide ligands were synthesized by the same procedure in the literature.[1]

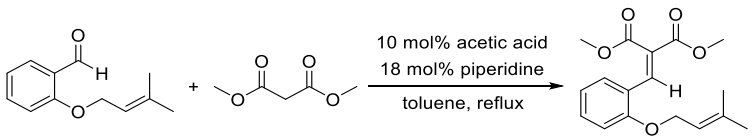
General Procedure for the Synthesis of Substrate

General procedure for the synthesis of **1a−1r** and **1x**.



A **B** **C**

K_2CO_3 (30 mmol, 1.5 equiv) was added in one portion to a stirring solution of 2-hydroxybenzaldehyde **A** (20 mmol, 1.0 equiv) in DMF (60 mL), the resulting mixture was stirred at r.t. (room temperature) for 15 mins. Then prenyl bromide **B** (30 mmol, 1.5 equiv) was added via a syringe over a period of a few minutes and the resulting mixture was stirred at r.t. for 10−12 h (monitored by TLC). The reaction was then diluted with H_2O (20 mL) and extracted with EtOAc (3×20 mL). The organic layer was washed with H_2O (20 mL) and brine (20 mL), then dried over $NaSO_4$, filtered. The solvent was removed in vacuo and the residue was subjected to column chromatography (SiO_2, eluent: petroleum ether/ethyl acetate = 20:1). After drying in vacuo, compound **C** was obtained as a colorless oil.

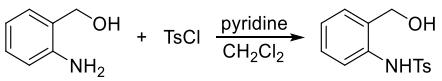


C **D** **1b**

A solution of benzaldehyde **C** (20.0 mmol, 1.0 equiv), dimethyl malonate **D** (20.0 mmol, 1.0 equiv), AcOH (2.0 mmol, 0.1 equiv) and piperidine (3.6 mmol, 0.18 equiv) in toluene (60 mL) was heated at 120 °C for 10 h in a round-bottomed flask fitted with a Dean−Stark apparatus. After the reaction was complete (monitored by TLC), the solvent was removed in vacuo and the residue was subjected to column chromatography (SiO_2, eluent: petroleum ether/ethyl acetate = 50:1). After drying in vacuo, compound **1b** was obtained as a white solid.

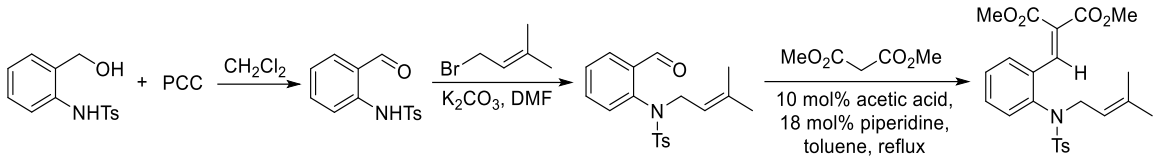
The intermediate bromide of substrate **1d−1g** was prepared according to the literature procedure.[2]
The 2-mercaptobenzaldehyde of substrate **1x** was prepared according to the literature procedure.[3]

General procedure for the synthesis of **1s−1v**.



E **F**

A solution of 2-aminobenzylalcohol **E** (80.0 mmol, 1.0 equiv) and pyridine (96.0 mmol, 1.2 equiv) in dry CH_2Cl_2 (200 mL) was treated dropwise with a solution of TsCl (160.0 mmol, 2.0 equiv) in dry CH_2Cl_2 (50 mL). The mixture was stirred at room temperature until the reaction was complete as confirmed by TLC. The reaction was then diluted with CH_2Cl_2 (50 mL) and washed with water (50 mL) and brine (50 mL). The organic phase was separated, dried over $NaSO_4$, filtered, and evaporated to give a crude product. The product **F** was purified by recrystallization from EtOAc to give a white solid.

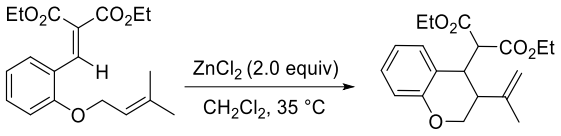


F **G** **1s**

A solution of PCC (80.0 mmol, 2.0 equiv) in dry CH_2Cl_2 (200 mL) was treated dropwise with a solution of *N*-(2-(hydroxymethyl)phenyl)-4-methylbenzenesulfonamide **F** (40.0 mmol, 1.0 equiv) in dry CH_2Cl_2 (25 mL). The mixture was stirred at room temperature until the reaction was complete as confirmed by TLC (2–3 h). The reaction was then diluted with Et_2O (100 mL) and stirred for another 30 mins. The mixture was filtered through silica and washed with Et_2O (3×30 mL), the filtrate was concentrated in vacuo. The residue was subjected to column chromatography (SiO_2, eluent: petroleum ether/ethyl acetate = 4:1). After drying in vacuo, compound **G** was obtained as a white solid. The last two steps were similar to the general procedure for the synthesis of **1a**−**1r**.

Compound **1w** was prepared according to the literature procedure.[4]

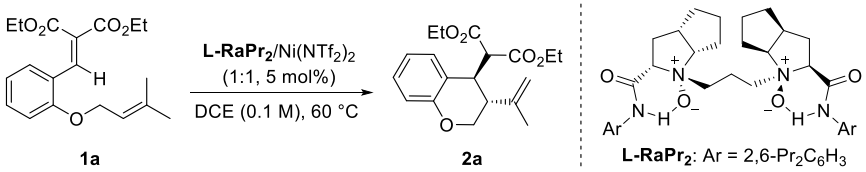
General Procedure for the Racemic Alder-Ene Reaction



1a **2a**

An oven-dried test tube was charged with **1a** (0.1 mmol), $ZnCl_2$ (2.0 equiv, 0.2 mmol) and CH_2Cl_2 (1.0 mL). The reaction mixture was stirred at 35 °C and detected by TLC. After the reaction was completed, the residue was subjected to column chromatography (SiO_2, eluent: petroleum ether/ethyl acetate = 10:1) to afford the racemic product **2a**.

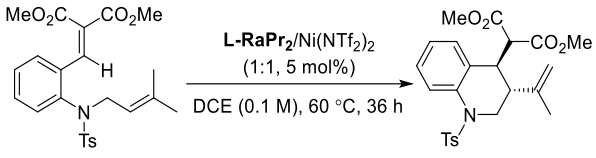
General Procedure for the Asymmetric Alder-Ene Reaction



1a **2a**

An oven-dried test tube was charged with **L-RaPr$_2$** (0.005 mmol, 5 mol%), $Ni(NTf_2)_2$ (0.005 mmol, 5 mol%) and CH_2Cl_2 (1.0 mL) and the resulting solution was stirred at 30 °C for 30 min. After removing the solvent under vacuo, **1a** (0.1 mmol) was weighted into the tube followed by adding DCE (1.0 mL). Then, the reaction mixture was stirred at 60 °C and detected by TLC. After the reaction was completed, the residue was subjected to column chromatography (SiO_2, eluent: petroleum ether/ethyl acetate = 10:1) to afford the enantioenriched product **2a**.

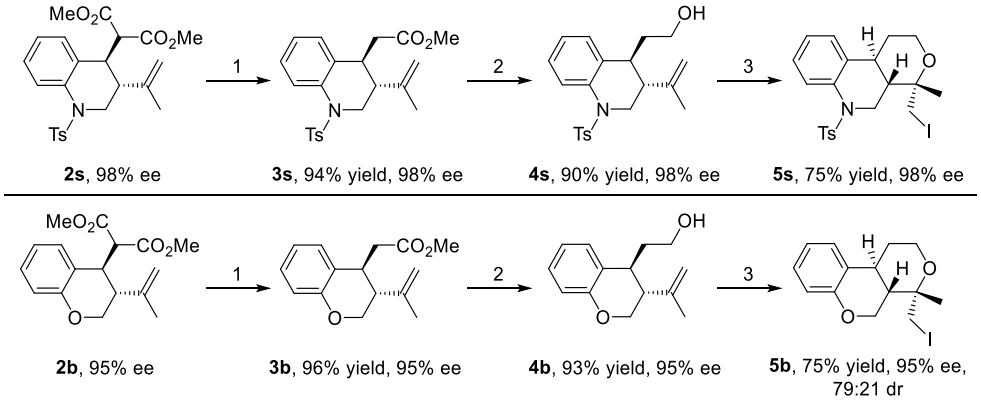
Experimental Procedure for the Gram-scale Reaction and Transformations of the Products



1s, 3.0 mmol, 1.37 g

2s, 1.31 g, 95% yield
98% ee, 96:4 dr

A dry reaction 50 mL round-bottom flask was charged with $Ni(NTf_2)_2$ (0.15 mol, 5 mol%, 93.0 mg), **L-RaPr$_2$** (0.15 mol, 5 mol%, 105.0 mg) and CH_2Cl_2 (30.0 mL) and the resulting solution was stirred at 30 °C for 30 min. After removing the solvent under vacuo, the substrate**1s** (3.0 mmol, 1.37g) were weighted into the round-bottom flask followed by adding DCE (30.0 mL). Then, the reaction mixture was stirred at 60 °C for 36 hours. After the reaction was completed, the reaction mixture was concentrated in vacuo and the residue was subjected to column chromatography (SiO2, eluent: petroleum ether/ethyl acetate = 4:1) to afford the desired product **2s** (1.31 g, 95% yield, 98% ee, 96:4 dr).

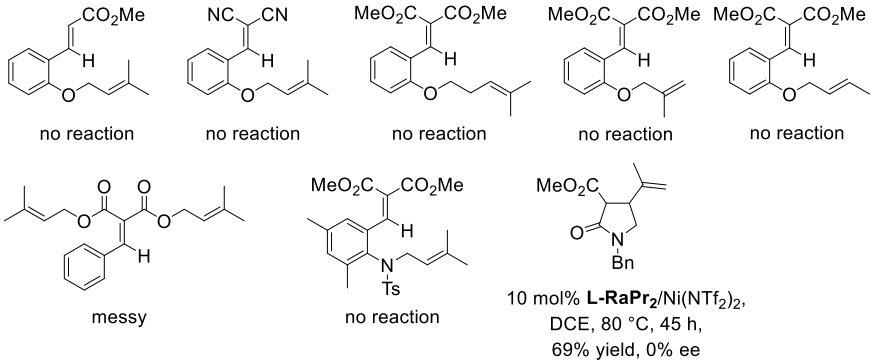


1) An oven-dried test tube was charged with **2s** (0.4 mmol, 183.0 mg) or **2b** (0.6 mmol, 182.4 mg) and DMSO (0.5 M) followed by adding LiCl (2.1 equiv) and H_2O (1.1 equiv). The reaction mixture was stirred at 130 °C for 5 hours and detected by TLC. After the reaction was completed, the reaction was quenched with EtOAc/H_2O (3 mL/3 mL)and extracted with EtOAc (2×10 mL). The organic layer was dried over $NaSO_4$ and filtered. The solvent was removed in vacuo and the residue was subjected to column chromatography (SiO_2, eluent: petroleum ether/ethyl acetate = 4:1 for **3s**, petroleum ether/ethyl acetate = 10:1 for **3b**) to afford the desired product **3s** (150.9 mg, 94% yield, 98% ee) or **3b** (141.6 mg, 96% yield, 95% ee).

2) To a solution of **3s** (0.36 mmol, 144.5 mg) or **3b** (0.4 mmol, 98.7 mg) in CH_2Cl_2 (1.0 mL) was added *i*Bu_2AlH (2.6 equiv) at −40 ºC in N_2 atmosphere. The reaction mixture was stirred at −40 °C for 4 hours and then stirred at room temperature. After the reaction was completed, the reaction was quenched with MeOH (2 mL) and 2 M HCl (2 mL), extracted with CH_2Cl_2 and the organic layer was dried over $NaSO_4$ and filtered. The solvent was removed in vacuo and the residue was subjected to column chromatography (SiO_2, eluent: petroleum ether/ethyl acetate = 4:1 for **4s**, petroleum ether/ethyl acetate = 10:1 for **4b**) to afford the desired product **4s** (120.0 mg, 90% yield, 98% ee) or **4b** (80.9 mg, 93% yield, 95% ee).

3) To a solution of **4s** (0.1 mmol, 37.1 mg) or **4b** (0.26 mmol, 57.6 mg) in CH_2Cl_2 (1.0 mL) was added NIS (1.2 equiv), the mixture was stirred at room temperature for 12 h and detected by TLC. After the reaction was completed, the residue was subjected to column chromatography (SiO_2, eluent: petroleum ether/ethyl acetate = 4:1 for **5s**, petroleum ether/ethyl acetate = 10:1 for **5b**) to afford the desired product **5s** (37.3 mg, 75% yield, 98% ee) or **5b** (66.8 mg, 75% yield, 98% ee, 79:21 dr).

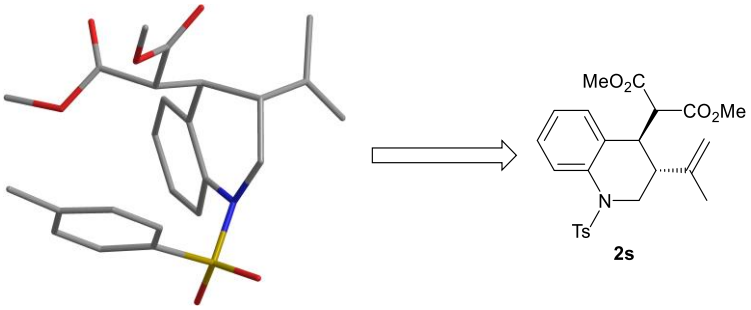
Unsuccessful Substrate Scope



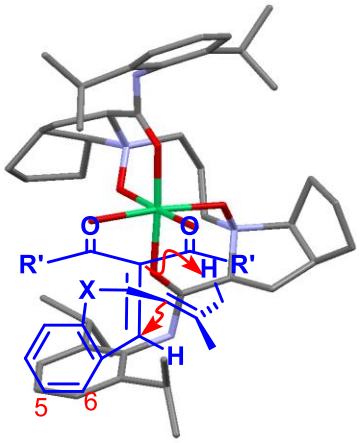
Determination of Absolute Configuration and the X-ray Structure of 2s

The absolute configuration of the optically active product **2s** was determined to be (*R*, *R*) by X-ray crystal analysis.

The single crystal of **2S** was obtained from mixed solvents of CH_2Cl_2 and petroleum ether. CCDC 1889731 contains the supplementary crystallographic data which can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.



The Stereocontrol Model of the Asymmetric Alder-Ene Reaction

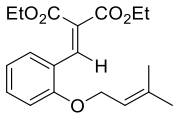


dimethyl alkene
from *Re*-face attack

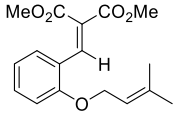
alkylidene malonate
β-Si-face attack

According to our previous work[5] and the absolution configuration of the Alder-ene product, a stereocontrol model was proposed. The alkylidene malonate was activated by chiral *N,N'*-dioxide/nickel complex via a bidentate coordination fashion. Due to the steric hinderance of the amide moiety, *Re*-face of dimethyl alkene approached the β-*Si*-face of the alkylidene malonate, affording the (*R*, *R*) product. When the substrate with 5- and 6-subtitutions, the steric hinderance between the 5- or 6-substituted phenyl group and the amide moiety increased sharply, leading to the decrease of diastereoselectivity.

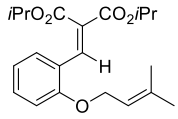
Characterization of the Substrates



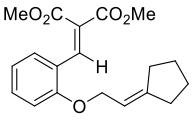
Diethyl 2-{2-[(3-methylbut-2-en-1-yl)oxy]benzylidene}malonate (1a):
Pale yellow oil.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (s, 1H), 7.41 – 7.37 (m, 1H), 7.34 – 7.28 (m, 1H), 6.91 – 6.85 (m, 2H), 5.51 – 5.41 (m, 1H), 4.55 (d, *J* = 6.4 Hz, 2H), 4.31 – 4.23 (m, 4H), 1.76 (s, 3H), 1.71 (s, 3H), 1.31 (t, *J* = 7.2 Hz, 3H), 1.22 (t, *J* = 7.2 Hz, 3H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 166.9, 164.4, 157.5, 138.5, 137.7, 131.9, 129.1, 125.9, 122.7, 120.4, 119.5, 112.3, 65.6, 61.4, 61.4, 25.8, 18.3, 14.2, 13.9.
HRMS (ESI) Calculated for $C_{19}H_{24}O_5$ ([M]+Na^+) = 355.1516, Found 355.1508.
IR (neat): 2982, 1721, 1620, 1598, 1485, 1453, 1375, 1255, 1201, 1163, 1112, 1063, 992, 751 cm^{-1}.



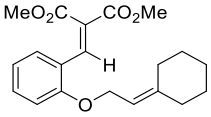
Dimethyl 2-{2-[(3-methylbut-2-en-1-yl)oxy]benzylidene}malonate (1b):
White solid, m.p. = 50 – 53 °C.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (s, 1H), 7.36 – 7.29 (m, 2H), 6.92 – 6.86 (m, 2H), 5.49 – 5.42 (m, 1H), 4.56 (d, *J* = 6.4 Hz, 2H), 3.82 (s, 3H), 3.76 (s, 3H), 1.77 (s, 3H), 1.72 (s, 3H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 167.3, 164.7, 157.5, 139.2, 137.7, 132.1, 128.8, 125.1, 122.5, 120.4, 119.5, 112.4, 65.5, 52.4, 52.4, 25.7, 18.2.
HRMS (ESI) Calculated for $C_{17}H_{20}O_5$ ([M]+Na^+) = 327.1203, Found 327.1195.
IR (neat): 2991, 1717, 1615, 1597, 1488, 1449, 1375, 1260, 1207, 1164, 1112, 1067, 957, 756 cm^{-1}.



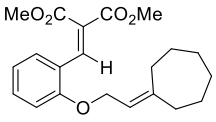
Diisopropyl 2-{2-[(3-methylbut-2-en-1-yl)oxy]benzylidene}malonate (1c):
Yellow solid, m.p. = 40 – 43 °C.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.46 – 7.41 (m, 1H), 7.34 – 7.29 (m, 1H), 6.91 – 6.85 (m, 2H), 5.52 – 5.44 (m, 1H), 5.25 – 5.17 (m, 1H), 5.17 – 5.09 (m, 1H), 4.56 (d, *J* = 6.4 Hz, 2H), 1.78 (d, *J* = 1.4 Hz, 3H), 1.73 (d, *J* = 1.3 Hz, 3H), 1.30 (d, *J* = 6.4 Hz, 6H), 1.25 (d, *J* = 6.0 Hz, 6H).
^{13}C{^{1}H} NMR (101 Mz, $CDCl_3$) δ 166.5, 163.9, 157.5, 137.7, 137.5, 131.7, 129.0, 126.7, 122.8, 120.3, 119.6, 112.3, 68.9, 68.9, 65.5, 25.7, 21.8, 21.5, 18.3.
HRMS (ESI) Calculated for $C_{21}H_{28}O_5$ ([M]+Na^+) = 383.1829, Found 383.1821.
IR (neat): 2979, 1727, 1710, 1624, 1598, 1453, 1342, 1262, 1211, 1103, 1062, 984, 757 cm^{-1}.



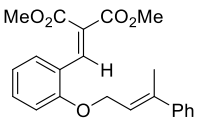
Dimethyl 2-[2-(2-cyclopentylideneethoxy)benzylidene]malonate (1d):
Colorless oil.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (s, 1H), 7.36 – 7.30 (m, 2H), 6.93 – 6.87 (m, 2H), 5.62 – 5.54 (m, 1H), 4.56 (d, *J* = 6.4 Hz, 2H), 3.84 (s, 3H), 3.78 (s, 3H), 2.35 – 2.26 (m, 4H), 1.76 – 1.68 (m, 2H), 1.68 – 1.60 (m, 2H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 167.4, 164.8, 157.6, 149.1, 139.4, 132.0, 128.9, 125.1, 122.5, 120.4, 115.0, 112.4, 67.0, 52.5, 52.5, 33.8, 29.1, 26.3, 26.0.
HRMS (ESI) Calculated for $C_{19}H_{22}O_5$ ([M]+Na^+) = 353.1359, Found 353.1351.
IR (neat): 2951, 1725, 1598, 1487, 1453, 1435, 1262, 1210, 1113, 1066, 985, 752 cm^{-1}.



Dimethyl 2-[2-(2-cyclohexylideneethoxy)benzylidene]malonate (1e):
Corlorless oil.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (s, 1H), 7.36 – 7.30 (m, 2H), 6.92 – 6.86 (m, 2H), 5.44 – 5.37 (m, 1H), 4.60 (d, *J* = 6.4 Hz, 2H), 3.84 (s, 3H), 3.78 (s, 3H), 2.25 – 2.10 (m, 4H), 1.60 – 1.54 (m, 6H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 167.4, 164.8, 157.6, 145.8, 139.4, 132.0, 128.9, 125.0, 122.6, 120.5, 116.1, 112.5, 64.9, 52.5, 52.5, 36.9, 29.3, 28.3, 27.6, 26.6.
HRMS (ESI) Calculated for $C_{20}H_{24}O_5$ ([M]+Na^+) = 367.1516, Found 367.1508.
IR (neat): 2927, 2851, 1724, 1598, 1485, 1452, 1261, 1210, 1066, 984, 751 cm^{-1}.

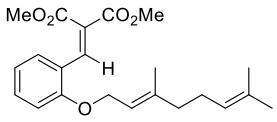


Dimethyl 2-[2-(2-cycloheptylideneethoxy)benzylidene]malonate (1f):
White solid, m.p. = 64 – 66 °C.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (s, 1H), 7.36 – 7.31 (m, 2H), 6.93 – 6.87 (m, 2H), 5.47 (t, *J* = 6.4 Hz, 1H), 4.59 (d, *J* = 6.0 Hz, 2H), 3.84 (s, 3H), 3.78 (s, 3H), 2.35 – 2.26 (m, 4H), 1.65 – 1.58 (m, 4H), 1.55 – 1.49 (m, 4H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 167.3, 164.8, 157.6, 147.0, 139.3, 132.0, 128.9, 125.1, 122.6, 120.4, 119.7, 112.4, 65.4, 52.5, 52.4, 37.6, 30.5, 29.8, 29.1, 28.8, 27.1.
HRMS (ESI) Calculated for $C_{21}H_{26}O_5$ ([M]+Na^+) = 381.1672, Found 381.1665.
IR (neat): 2921, 1720, 1619, 1598, 1489, 1450, 1215, 952, 754 cm^{-1}.

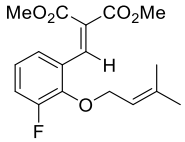


Dimethyl (E)-2-{2-[(3-phenylbut-2-en-1-yl)oxy]benzylidene}malonate (1g):
White solid, m.p. = 72 – 75 °C.

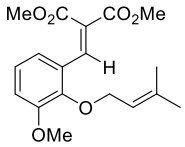
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (s, 1H), 7.45 – 7.41 (m, 2H), 7.38 – 7.31 (m, 4H), 7.30 – 7.25 (m, 1H), 6.98 – 6.90 (m, 2H), 6.06 – 6.00 (m, 1H), 4.81 (d, *J* = 6.0 Hz, 2H), 3.83 (s, 3H), 3.78 (s, 3H), 2.17 – 2.11 (m, 3H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 167.3, 164.8, 157.3, 142.4, 139.2, 139.0, 132.1, 129.1, 128.3, 127.5, 125.8, 125.4, 122.6, 122.5, 120.7, 112.4, 66.1, 52.6, 52.5, 16.5.
HRMS (ESI) Calculated for $C_{22}H_{22}O_5$ ([M]+Na^+) = 389.1359, Found 389.1351.
IR (neat): 2983, 1718, 1628, 1595, 1434, 1358, 1273, 1220, 988, 763 cm^{-1}.



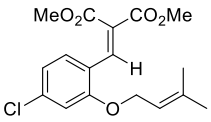
Dimethyl (E)-2-{2-[(3,7-dimethylocta-2,6-dien-1-yl)oxy]benzylidene}malonate (1h):
Colorless oil.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (s, 1H), 7.36 – 7.28 (m, 2H), 6.92 – 6.84 (m, 2H), 5.52– 5.42 (m, 1H), 5.12 – 5.01 (m, 1H), 4.60 (d, *J* = 6.0 Hz, 2H), 3.81 (s, 3H), 3.76 (s, 3H), 2.17 – 2.03 (m, 4H), 1.72 (s, 3H), 1.66 (s, 3H), 1.60 (s, 3H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 167.2, 164.7, 157.5, 140.9, 139.1, 132.0, 131.7, 128.9, 125.2, 123.7, 122.5, 120.5, 119.4, 112.5, 65.6, 52.4, 52.3, 39.4, 26.2, 25.6, 17.7, 16.6.
HRMS (ESI) Calculated for $C_{22}H_{28}O_5$ ([M]+Na^+) = 395.1829, Found 395.1820.
IR (neat): 2985, 1726, 1620, 1598, 1485, 1453, 1372, 1261, 1210, 1066, 985, 751 cm^{-1}.



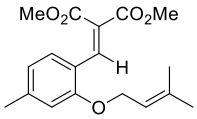
Dimethyl 2-{3-fluoro-2-[(3-methylbut-2-en-1-yl)oxy]benzylidene}malonate (1i):
Colorless oil.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (s, 1H), 7.16 – 7.08 (m, 2H), 7.02 – 6.95 (m, 1H), 5.48 (t, *J* = 7.2 Hz, 1H), 4.60 (d, *J* = 7.2 Hz, 2H), 3.86 (s, 3H), 3.78 (s, 3H), 1.75 (s, 3H), 1.65 (s, 3H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 166.7, 164.4, 155.8 (d, *J* = 247.5 Hz), 145.6 (d, *J* = 11.7 Hz), 140.3, 138.3 (d, *J* = 3.5 Hz), 129.2 (d, *J* = 3.0 Hz), 126.8, 123.9 (d, *J* = 3.4 Hz), 123.7 (d, *J* = 7.9 Hz), 119.2, 118.8 (d, *J* = 19.4 Hz), 70.9 (d, *J* = 5.5 Hz), 52.7 (d, *J* = 2.7 Hz), 52.6 (d, *J* = 2.6 Hz), 25.8, 17.9.
^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ –128.7 (s, 1F).
HRMS (ESI) Calculated for $C_{17}H_{19}FO_5$ ([M]+Na^+) = 345.1109, Found 345.1116.
IR (neat): 2986, 1727, 1577, 1460, 1436, 1369, 1219, 1078, 935, 787, 745 cm^{-1}.



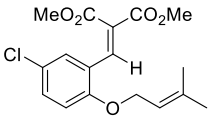
Dimethyl 2-{3-methoxy-2-[(3-methylbut-2-en-1-yl)oxy]benzylidene}malonate (1j):
Yellow oil.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (s, 1H), 7.04 – 6.99 (m, 1H), 6.97 – 6.91 (m, 2H), 5.54 – 5.47 (m, 1H), 4.51 (d, *J* = 7.6 Hz, 2H), 3.87 (s, 3H), 3.85 (s, 3H), 3.78 (s, 3H), 1.74 (s, 3H), 1.64 (s, 3H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 167.1, 164.6, 153.1, 147.3, 139.5, 139.5, 128.3, 125.9, 124.0, 120.1, 119.8, 114.4, 70.1, 55.9, 52.6, 52.5, 25.8, 17.8.
HRMS (ESI) Calculated for $C_{18}H_{22}O_6$ ([M]+Na^+) = 357.1309, Found 357.1302.
IR (neat): 2986, 1725, 1624, 1576, 1436, 1369, 1209, 1062, 956, 785, 739 cm^{-1}.



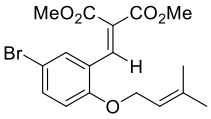
Dimethyl 2-{4-chloro-2-[(3-methylbut-2-en-1-yl)oxy]benzylidene}malonate (1k):
White solid, m.p. = 53 – 56 °C.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (s, 1H), 7.30 – 7.22 (m, 1H), 6.92 – 6.84 (m, 2H), 5.44 (s, 1H), 4.55 (d, *J* = 6.0 Hz, 2H), 3.82 (s, 3H), 3.77 (s, 3H), 1.78 (s, 3H), 1.73 (s, 3H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 166.9, 164.4, 157.9, 138.4, 137.8, 137.5, 129.6, 125.6, 121.1, 120.6, 118.8, 112.9, 65.9, 52.4, 52.3, 25.6, 18.2.
HRMS (ESI) Calculated for $C_{17}H_{19}{}^{34.9689}ClO_5$ ([M]+Na^+) = 361.0813, Found 361.0817.
HRMS (ESI) Calculated for $C_{17}H_{19}{}^{36.9659}ClO_5$ ([M]+Na^+) = 363.0784, Found 363.0784.
IR (neat): 2993, 1719, 1619, 1484, 1410, 1369, 1211, 978, 821 cm^{-1}.



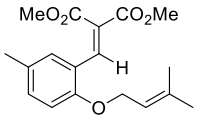
Dimethyl 2-{4-methyl-2-[(3-methylbut-2-en-1-yl)oxy]benzylidene}malonate (1l):
White solid, m.p. = 69 – 73 °C.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (s, 1H), 7.24 – 7.19 (m, 1H), 6.75 – 6.68 (m, 2H), 5.53 – 5.42 (m, 1H), 4.55 (d, *J* = 6.4 Hz, 2H), 3.83 (s, 3H), 3.79 (s, 3H), 2.35 (s, 3H), 1.79 (s, 3H), 1.74 (s, 3H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 167.7, 165.0, 157.6, 143.0, 139.2, 137.7, 128.7, 123.9, 121.4, 119.7, 119.5, 113.2, 65.5, 52.5, 52.4, 25.8, 22.0, 18.3.
HRMS (ESI) Calculated for $C_{18}H_{22}O_5$ ([M]+Na^+) = 341.1359, Found 341.1352.
IR (neat): 2990, 1716, 1603, 1437, 1250, 1206, 1170, 1117, 1067, 1016, 839 cm^{-1}.



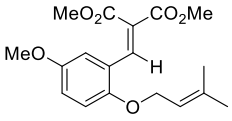
Dimethyl 2-{5-chloro-2-[(3-methylbut-2-en-1-yl)oxy]benzylidene}malonate (1m):
White solid, m.p. = 44 – 47 °C.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (s, 1H), 7.30 – 7.25 (m, 2H), 6.89 – 6.79 (m, 1H), 5.47 – 5.39 (m, 1H), 4.55 (d, *J* = 8.4 Hz, 2H), 3.84 (s, 3H), 3.81 (s, 3H), 1.78 (s, 3H), 1.73 (s, 3H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 166.7, 164.5, 156.0, 138.3, 137.7, 131.5, 128.5, 126.3, 125.4, 123.9, 119.0, 113.6, 66.0, 52.6, 52.5, 31.6, 25.8, 22.7, 18.3, 14.1.
HRMS (ESI) Calculated for $C_{17}H_{19}{}^{34.9689}ClO_5$ ([M]+Na^+) = 361.0813, Found 361.0813.
HRMS (ESI) Calculated for $C_{17}H_{19}{}^{36.9659}ClO_5$ ([M]+Na^+) = 363.0784, Found 363.0780.
IR (neat): 2986, 1726, 1622, 1481, 1410, 1369, 1266, 1212, 1130, 1066, 980, 893, 808 cm^{-1}.



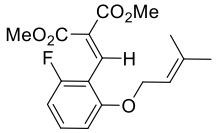
Dimethyl 2-{5-bromo-2-[(3-methylbut-2-en-1-yl)oxy]benzylidene}malonate (1n):
White solid, m.p. = 43 – 47 °C.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (s, 1H), 7.45 – 7.40 (m, 2H), 6.81 – 6.76 (m, 1H), 5.46 – 5.40 (m, 1H), 4.55 (d, *J* = 6.4 Hz, 2H), 3.85 (s, 3H), 3.82 (s, 3H), 1.78 (s, 3H), 1.73 (s, 3H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 166.7, 164.5, 156.5, 138.3, 137.7, 134.4, 131.5, 126.4, 124.5, 119.0, 114.1, 112.6, 65.9, 52.7, 25.8, 18.3.
HRMS (ESI) Calculated for $C_{17}H_{19}{}^{78.9183}BrO_5$ ([M]+Na^+) = 405.0308, Found 405.0308.
HRMS (ESI) Calculated for $C_{17}H_{19}{}^{80.9163}BrO_5$ ([M]+Na^+) = 407.0288, Found 407.0287.
IR (neat): 2950, 1731, 1703, 1586, 1433, 1376, 1285, 1222, 1064, 977, 807, 765 cm^{-1}.



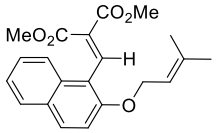
Dimethyl 2-{5-methyl-2-[(3-methylbut-2-en-1-yl)oxy]benzylidene}malonate (1o):
White solid, m.p. = 48 – 50 °C.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (s, 1H), 7.16 – 7.10 (m, 2H), 6.80 (d, *J* = 8.4 Hz, 1H), 5.49 – 5.43 (m, 1H), 4.54 (d, *J* = 6.4 Hz, 2H), 3.84 (s, 3H), 3.78 (s, 3H), 2.25 (s, 3H), 1.78 (s, 3H), 1.72 (s, 3H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 167.4, 164.9, 155.6, 139.4, 137.6, 132.6, 129.7, 129.4, 124.8, 122.3, 119.7, 112.5, 65.8, 52.5, 52.4, 25.8, 20.5, 18.3.
HRMS (ESI) Calculated for $C_{18}H_{22}O_5$ ([M]+Na^+) = 341.1359, Found 341.1352.
IR (neat): 3028, 1749, 1493, 1363, 1266, 1212, 1066, 979, 816, 795 cm^{-1}.



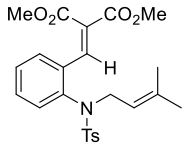
Dimethyl 2-{5-methoxy-2-[(3-methylbut-2-en-1-yl)oxy]benzylidene}malonate (1p):
Yellow solid, m.p. = 42 – 46 °C.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (s, 1H), 6.93 – 6.88 (m, 2H), 6.88 – 6.82 (m, 1H), 5.48 – 5.42 (m, 1H), 4.52 (d, *J* = 6.4 Hz, 2H), 3.84 (s, 3H), 3.81 (s, 3H), 3.73 (s, 3H), 1.78 (s, 3H), 1.72 (s, 3H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 167.3, 164.7, 153.4, 152.0, 139.0, 137.8, 125.3, 123.2, 119.7, 118.1, 114.2, 113.3, 66.5, 55.7, 52.5, 52.5, 25.8, 18.2.
HRMS (ESI) Calculated for $C_{18}H_{22}O_6$ ([M]+Na^+) = 357.1309, Found 357.1301.
IR (neat): 2982, 1721, 1625, 1493, 1360, 1212, 1067, 1037, 982, 796, 702 cm^{-1}.



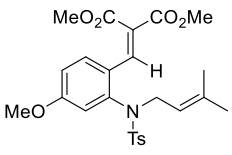
Dimethyl 2-{2-fluoro-6-[(3-methylbut-2-en-1-yl)oxy]benzylidene}malonate (1q):
Yellow oil.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (s, 1H), 7.32 – 7.25 (m, 1H), 6.72 – 6.64 (m, 2H), 5.48 – 5.38 (m, 1H), 4.57 (d, *J* = 6.4 Hz, 2H), 3.85 (s, 3H), 3.73 (s, 3H), 1.78 (s, 3H), 1.72 (s, 3H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 165.9, 165.2, 160.9 (d, *J* = 251.1 Hz), 158.1 (d, *J* = 6.6 Hz), 137.9, 135.2, 131.8 (d, *J* = 11.3 Hz), 128.0 (d, *J* = 2.8 Hz), 119.2, 111.8 (d, *J* = 16.1 Hz), 107.9 (d, *J* = 5.5 Hz), 107.8 (d, *J* = 14.4 Hz), 66.2, 52.6 (d, *J* = 2.7 Hz), 52.1 (d, *J* = 2.8 Hz), 25.8, 18.3.
^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ –109.4 (s, 1F).
HRMS (ESI) Calculated for $C_{17}H_{19}FO_5$ ([M]+Na^+) = 345.1109, Found 345.1114.
IR (neat): 2987, 1718, 1611, 1574, 1460, 1436, 1373, 1255, 1221, 1075, 1046, 777, 740 cm^{-1}.



Dimethyl 2-{{2-[(3-methylbut-2-en-1-yl)oxy]naphthalen-1-yl}methylene}malonate (1r):
Yellow solid, m.p. = 84 – 87 °C.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (s, 1H), 7.82 (dd, *J* = 8.4, 3.6 Hz, 2H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.51 – 7.45 (m, 1H),, 7.36 (t, *J* = 7.6 Hz, 1H), 7.23 (d, *J* = 9.2 Hz, 1H), 5.48 – 5.42 (m, 1H), 4.67 (d, *J* = 6.4 Hz, 2H), 3.90 (s, 3H), 3.52 (s, 3H), 1.76 (s, 3H), 1.72 (s, 3H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 165.8, 165.3, 154.2, 140.8, 137.4, 132.2, 131.6, 129.0, 128.7, 128.4, 127.3, 124.1, 123.6, 119.9, 117.1, 114.5, 66.6, 52.6, 51.8, 25.8, 18.3.
HRMS (ESI) Calculated for $C_{21}H_{22}O_5$ ([M]+Na^+) = 377.1359, Found 377.1352.
IR (neat): 2988, 1739, 1698, 1614, 1507, 1435, 1264, 1072, 1045, 816, 782, 750 cm^{-1}.

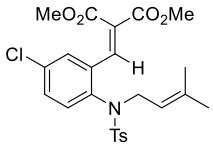


Dimethyl 2-{2-{[4-methyl-N-(3-methylbut-2-en-1-yl)phenyl]sulfonamido}benzylidene}malonate (1s):
White solid, m.p. = 100 – 104 °C.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.62 (d, *J* = 8.4 Hz, 2H), 7.42 – 7.37 (m, 1H), 7.33 – 7.25 (m, 4H), 6.98 – 6.92 (m, 1H), 5.12 – 5.00 (m, 1H), 4.35 – 3.95 (m, 2H), 3.84 (s, 3H), 3.73 (s, 3H), 2.44 (s, 3H), 1.57 (s, 3H), 1.38 (s, 3H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 166.7, 164.1, 143.7, 140.5, 139.0, 138.7, 136.1, 134.8, 130.7, 130.0, 129.6, 128.7, 128.5, 127.9, 127.0, 117.7, 52.6, 52.5, 49.7, 25.6, 21.6, 17.5.
HRMS (ESI) Calculated for $C_{24}H_{27}NO_6S$ ([M]+Na^+) = 480.1451, Found 480.1442.
IR (neat): 3027, 1721, 1595, 1374, 1338, 1253, 1216, 1091, 1065, 875, 708, 572, 551 cm^{-1}.

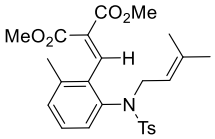


Dimethyl 2-{4-methoxy-2-{[4-methyl-N-(3-methylbut-2-en-1-yl)phenyl]sulfonamido}benzylidene}malonate (1t):
White solid, m.p. = 100 – 103 °C.

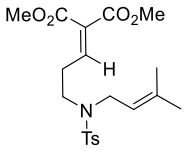
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (s, 1H), 7.65 (d, *J* = 8.0 Hz, 2H), 7.35 (d, *J* = 8.8 Hz, 1H), 7.29 (d, *J* = 8.0 Hz, 2H), 6.83 (dd, *J* = 8.8, 2.0 Hz, 1H), 6.56 – 6.48 (m, 1H), 5.14 – 5.04 (m, 1H), 4.11 (d, *J* = 85.6 Hz, 2H), 3.81 (s, 3H), 3.76 (s, 3H), 3.71 (s, 3H), 2.43 (s, 3H), 1.58 (s, 3H), 1.41 (s, 3H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 167.2, 164.4, 161.4, 143.7, 140.8, 139.7, 138.9, 136.1, 129.7, 129.6, 127.9, 126.7, 124.7, 117.7, 115.5, 114.6, 55.5, 52.5, 49.7, 25.6, 21.6, 17.5.
HRMS (ESI) Calculated for $C_{25}H_{29}NO_7S$ ([M]+Na^+) = 510.1557, Found 510.1550.
IR (neat): 2988, 1729, 1597, 1498, 1369, 1245, 1206, 1158, 1123, 1033, 925, 819, 658, 546 cm^{-1}.



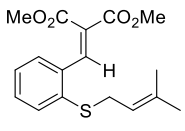
Dimethyl 2-{5-chloro-2-{[4-methyl-N-(3-methylbut-2-en-1-yl)phenyl]sulfonamido}benzylidene}malonate (1u):
Colorless oil.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (s, 1H), 7.61 (d, *J* = 8.0 Hz, 2H), 7.38 (d, *J* = 2.0 Hz, 1H), 7.32 – 7.25 (m, 3H), 6.86 (d, *J* = 8.4 Hz, 1H), 5.08 – 5.00 (m, 1H), 4.21 (s, 1H), 3.98 (s, 1H), 3.84 (s, 3H), 3.78 (s, 3H), 2.44 (s, 3H), 1.58 (s, 3H), 1.41 (s, 3H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 166.0, 163.8, 144.0, 139.1, 138.9, 137.5, 136.4, 135.7, 134.3, 131.0, 130.5, 129.7, 128.6, 128.1, 127.8, 117.4, 52.7, 52.6, 49.6, 25.6, 17.5.
HRMS (ESI) Calculated for $C_{24}H_{26}{}^{34.9689}ClNO_6S$ ([M]+Na^+) = 514.1062, Found 514.1064.
HRMS (ESI) Calculated for $C_{24}H_{26}{}^{36.9659}ClNO_6S$ ([M]+Na^+) = 516.1032, Found 516.1035.
IR (neat): 2987, 1729, 1587, 1477, 1437, 1345, 1251, 1217, 1158, 1064, 874, 814, 708, 665, 579, 546 cm^{-1}.



Dimethyl 2-{2-methyl-6-{[4-methyl-N-(3-methylbut-2-en-1-yl)phenyl]sulfonamido}benzylidene}malonate (1v):
White solid, m.p. = 101 – 104 °C.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (s, 1H), 7.60 (d, *J* = 8.4 Hz, 2H), 7.27 (d, *J* = 7.6 Hz, 2H), 7.16 (d, *J* = 7.6 Hz, 1H), 7.10 (t, *J* = 7.6 Hz, 1H), 6.62 (d, *J* = 7.6 Hz, 1H), 5.13 – 5.07 (m, 1H), 4.07 (d, *J* = 6.8 Hz, 2H), 3.89 (s, 3H), 3.59 (s, 3H), 2.45 (s, 3H), 2.21 (s, 3H), 1.59 (s, 3H), 1.45 (s, 3H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 164.9, 164.3, 146.0, 143.5, 137.5, 137.1, 137.1, 136.5, 136.0, 130.3, 129.7, 129.4, 128.3, 128.1, 126.4, 118.5, 52.7, 52.2, 49.6, 25.7, 21.6, 20.0, 17.7.
HRMS (ESI) Calculated for $C_{25}H_{29}NO_6S$ ([M]+Na^+) = 494.1608, Found 494.1598.
IR (neat): 2988, 1729, 1717, 1338, 1263, 1222, 1158, 1064, 828, 676 cm^{-1}.



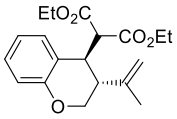
Dimethyl 2-{3-{[4-methyl-N-(3-methylbut-2-en-1-yl)phenyl]sulfonamido}propylidene}malonate (1w):
White solid, m.p. = 43 – 46 °C.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 7.6 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 4.99 (t, *J* = 7.2 Hz, 1H), 3.86 (s, 3H), 3.82 (s, 3H), 3.79 – 3.75 (m, 2H), 3.60 – 3.55 (m, 1H), 3.29 – 3.15 (m, 2H), 2.43 (s, 3H), 2.02 – 1.90 (m, 1H), 1.78 – 1.68 (m, 1H), 1.67 (s, 3H), 1.62 (s, 3H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 166.1, 165.1, 143.3, 137.8, 136.4, 129.7, 127.3, 118.5, 60.2, 53.4, 53.1, 46.4, 44.0, 33.3, 29.1, 25.7, 21.5, 17.8.
HRMS (ESI) Calculated for $C_{20}H_{27}NO_6S$ ([M]+Na^+) = 432.1451, Found 432.1450.
IR (neat): 2982, 1730, 1597, 1440, 1374, 1273, 1220, 1157, 1048, 895, 802, 652, 549 cm^{-1}.



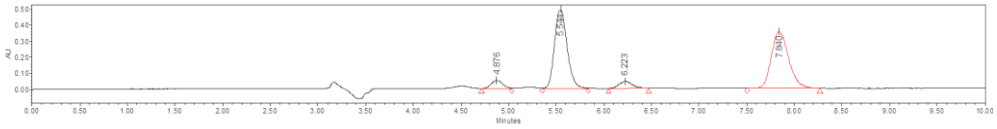
Dimethyl 2-{2-[(3-methylbut-2-en-1-yl)thio]benzylidene}malonate (1x):
Yellow solid, m.p. = 51 – 54 °C.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (s, 1H), 7.44 (d, *J* = 8.0 Hz, 1H), 7.36 – 7.29 (m, 2H), 7.20 (t, *J* = 7.6 Hz, 1H), 5.31 – 5.24 (m, 1H), 3.86 (s, 3H), 3.71 (s, 3H), 3.49 (d, *J* = 7.6 Hz, 2H), 1.70 (s, 3H), 1.54 (s, 3H).

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 166.6, 164.4, 142.0, 137.8, 137.1, 134.9, 131.6, 130.2, 128.3, 127.0, 126.7, 118.8, 52.6, 52.4, 33.2, 25.6, 17.6.
HRMS (ESI) Calculated for $C_{17}H_{20}O_4S$ ([M]+Na^+) = 343.0975, Found 343.0970.
IR (neat): 2984, 1729, 1699, 1621, 1433, 1370, 1256, 1220, 1065, 976, 752 cm^{-1}.

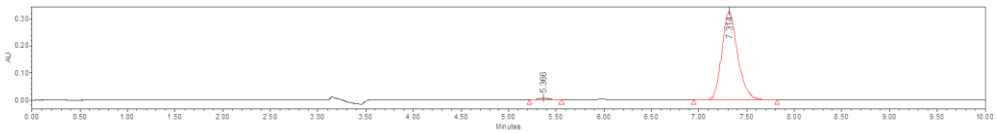
Characterization of the Products



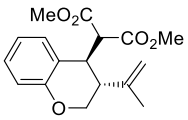
Diethyl 2-[3-(prop-1-en-2-yl)chroman-4-yl]malonate (2a):
11:1 dr, the major diastereomer was isolated as colorless oil in 80% yield, 97% ee, $[\alpha]^{22}_D$ = –100.5 (*c* = 0.39, in CH_2Cl_2).
HPLC: Chiralcel IC, hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 210 nm, t_{r1} = 5.37 min, t_{r2} = 7.31 min.
^1H NMR (400 MHz, $CDCl_3$) δ 7.16 – 7.07 (m, 2H), 6.83 – 6.75 (m, 2H), 4.88 (s, 1H), 4.85 (s, 1H), 4.30 – 4.13 (m, 4H), 4.05 – 3.95 (m, 2H), 3.80 – 3.70 (m, 2H), 2.61 (q, *J* = 4.4 Hz, 1H), 1.79 (s, 3H), 1.26 (t, *J* = 7.2 Hz, 3H), 1.05 (t, *J* = 7.2 Hz, 3H).
$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 168.4, 168.1, 154.3, 143.2, 129.8, 128.3, 120.7, 120.3, 116.7, 113.3, 65.8, 61.7, 61.4, 57.3, 42.2, 37.4, 21.6, 14.1, 13.8.
HRMS (ESI) Calculated for $C_{19}H_{24}O_5$ ([M]+Na^+) = 355.1516, Found 355.1508.
IR (neat): 2980, 1728, 1647, 1608, 1583, 1491, 1450, 1386, 1227, 1174, 1151, 1052, 900, 755, 736 cm^{-1}.



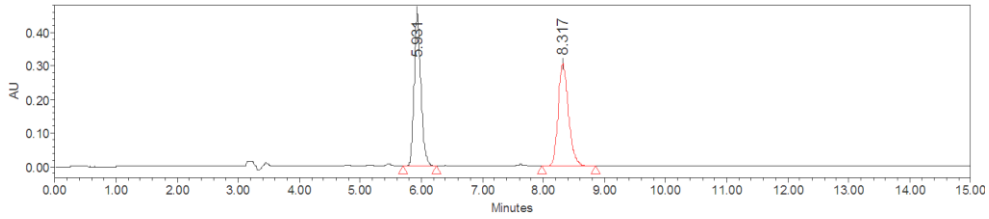
	Retention Time	Area	% Area
1	4.876	415858	4.29
2	5.544	4411539	45.54
3	6.223	424801	4.39
4	7.840	4435045	45.78



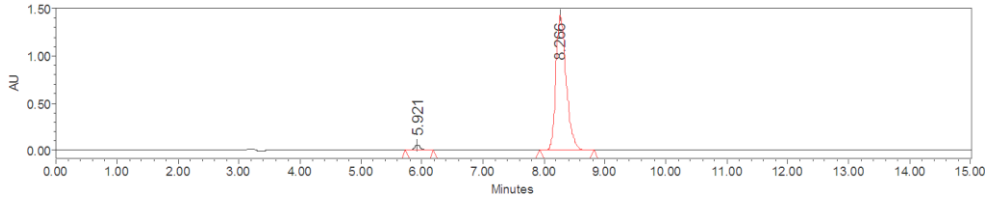
	Retention Time	Area	% Area
1	5.366	51351	1.35
2	7.314	3743670	98.65



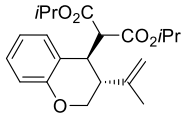
Dimethyl 2-[3-(prop-1-en-2-yl)chroman-4-yl]malonate (2b):
9:1 dr, the major diastereomer was isolated as white solid in 89% yield, m.p. = 40 – 42 °C, ee = 95%, $[\alpha]^{22}_D$ = –108.3 (*c* = 1.41, in CH_2Cl_2).
HPLC: Chiralcel IC, hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 210 nm, t_{r1} = 5.92 min, t_{r2} = 8.27 min.
^1H NMR (400 MHz, $CDCl_3$) δ 7.14 – 7.07 (m, 2H), 6.84 – 6.76 (m, 2H), 4.88 (s, 1H), 4.85 (s, 1H), 4.24 (dd, *J* = 11.6, 3.6 Hz, 1H), 4.17 (dd, *J* = 11.6, 4.8 Hz, 1H), 3.80 – 3.74 (m, 5H), 3.55 (s, 3H), 2.60 (q, *J* = 3.6 Hz, 1H), 1.80 (s, 3H).
$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 168.7, 168.4, 154.3, 143.2, 129.6, 128.4, 120.5, 120.4, 116.8, 113.3, 65.7, 57.1, 52.7, 52.3, 42.0, 37.6, 21.6.
HRMS (ESI) Calculated for $C_{17}H_{20}O_5$ ([M]+Na^+) = 327.1203, Found 327.1196.
IR (neat): 2889, 1741, 1646, 1582, 1491, 1436, 1333, 1305, 1270, 1227, 1199, 1097, 994, 871, 821, 763 cm^{-1}.



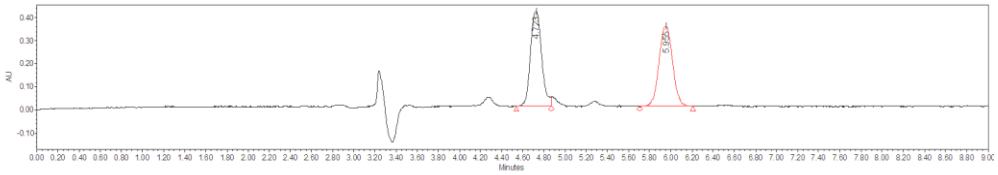
	Retention Time	Area	% Area
1	5.931	3574192	49.89
2	8.317	3590564	50.11



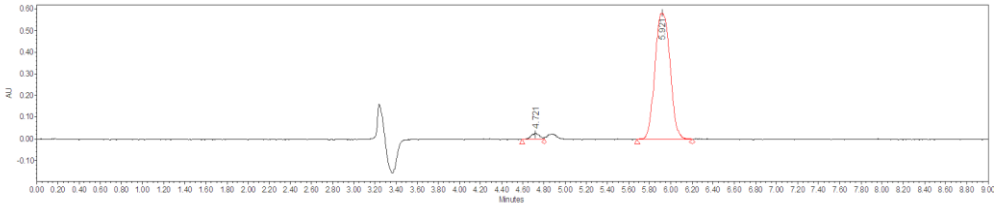
	Retention Time	Area	% Area
1	5.921	447519	2.56
2	8.266	17025242	97.44



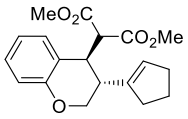
Diisopropyl 2-[3-(prop-1-en-2-yl)chroman-4-yl]malonate (2c):
12:1 dr, the major diastereomer was isolated as colorless oil in 84% yield, ee = 95%, $[\alpha]^{22}_{D}$ = –93.3 (*c* = 1.06, in CH_2Cl_2).
HPLC: Chiralcel IC, hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min, λ = 210 nm, t_{r1} = 4.72 min, t_{r2} = 5.92 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (d, *J* = 7.6 Hz, 1H), 7.12 – 7.06 (m, 1H), 6.82 – 6.74 (m, 2H), 5.11 (hept, *J* = 6.4 Hz, 1H), 4.91 – 4.81 (m, 3H), 4.26 (dd, *J* = 11.2, 3.6 Hz, 1H), 4.16 (dd, *J* = 11.6, 5.2 Hz, 1H), 3.80 – 3.71 (m, 1H), 3.67 (d, *J* = 7.2 Hz, 1H), 2.62 (q, *J* = 4.8 Hz, 1H), 1.80 (s, 3H), 1.26 (t, *J* = 6.0 Hz, 6H), 1.15 (d, *J* = 6.0 Hz, 3H), 0.95 (d, *J* = 6.0 Hz, 3H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 168.2, 167.5, 154.4, 143.3, 130.1, 128.2, 120.9, 120.3, 116.6, 113.4, 69.2, 69.1, 66.0, 57.4, 42.5, 37.3, 21.7, 21.7, 21.6, 21.5, 21.3.
HRMS (ESI) Calculated for $C_{21}H_{28}O_5$ ([M]+Na^+) = 383.1829 Found 383.1831.
IR (neat): 2980, 1723, 1647, 1608, 1583, 1491, 1453, 1374, 1228, 1174, 1098, 901, 828, 755 cm^{-1}.



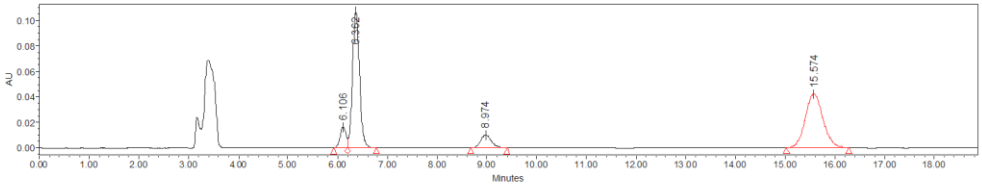
	Retention Time	Area	% Area
1	4.723	3005893	49.61
2	5.955	3052621	50.39



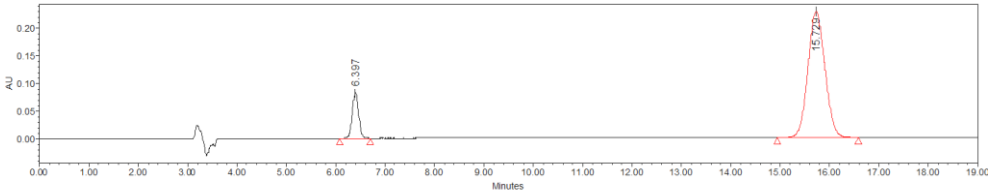
	Retention Time	Area	% Area
1	4.721	144900	2.45
2	5.921	5758420	97.55



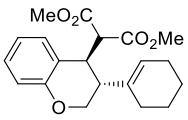
Dimethyl 2-[3-(cyclopent-1-en-1-yl)chroman-4-yl]malonate (2d):
11:1 dr, the major diastereomer was isolated as colorless oil in 77% yield, ee = 76%, $[\alpha]^{20}_{D}$ = –102.2 (*c* = 0.42, in CH_2Cl_2).
HPLC: Chiralcel IC, hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 210 nm, t_{r1} = 6.40 min, t_{r2} = 15.73 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 – 7.02 (m, 2H), 6.83 – 6.74 (m, 2H), 5.47 (s, 1H), 4.26 – 4.16 (m, 2H), 3.76 (s, 3H), 3.75 (s, 2H), 3.56 (s, 3H), 2.66 (s, 1H), 2.35 – 2.27 (m, 2H), 2.27 – 2.19 (m, 2H), 1.81 (p, *J* = 7.4 Hz, 2H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 168.6, 168.5, 154.3, 142.0, 129.7, 128.4, 127.0, 120.5, 120.2, 116.8, 65.2, 57.6, 52.7, 52.4, 37.8, 37.3, 33.9, 32.6, 23.0.
HRMS (ESI) Calculated for $C_{19}H_{22}O_5$ ([M]+Na^+) = 353.1359, Found 353.1356.
IR (neat): 2951, 2845, 1733, 1608, 1583, 1490, 1434, 1313, 1227, 1194, 1148, 1018, 966, 757 cm^{-1}.



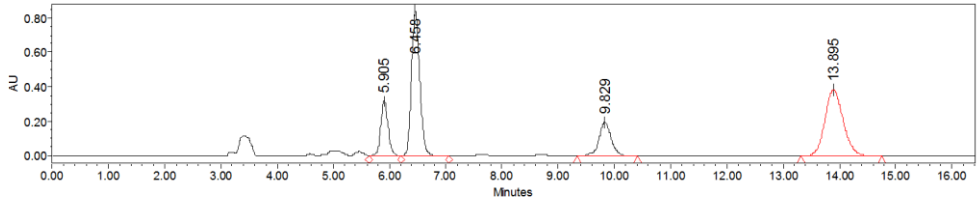
	Retention Time	Area	% Area
1	6.106	132955	5.64
2	6.362	1044978	44.33
3	8.974	145856	6.19
4	15.574	1033677	43.85



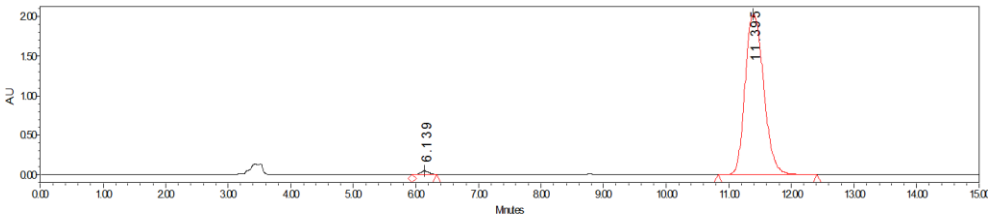
	Retention Time	Area	% Area
1	6.397	736438	11.92
2	15.729	5440805	88.08



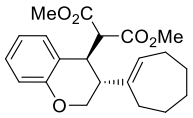
Dimethyl 2-[3-(cyclohex-1-en-1-yl)chroman-4-yl]malonate (2e):
>19:1 dr, the major diastereomer was isolated as colorless oil in 89% yield, ee = 98%, $[\alpha]^{20}_{D}$ = –109.6 (*c* = 0.45, in CH_2Cl_2).
HPLC: Chiralcel IC, hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 210 nm, t_{r1} = 6.14 min, t_{r2} = 11.40 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 – 7.05 (m, 2H), 6.84 – 6.76 (m, 2H), 5.56 (s, 1H), 4.19 (dd, *J* = 11.3, 3.7 Hz, 1H), 4.08 (dd, *J* = 11.3, 5.9 Hz, 1H), 3.81 – 3.72 (m, 5H), 3.55 (s, 3H), 2.52 (q, *J* = 5.2 Hz, 1H), 2.02 – 1.90 (m, 4H), 1.62 – 1.56 (m, 2H), 1.55 – 1.47 (m, 2H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 169.0, 168.5, 154.6, 135.5, 129.4, 128.2, 124.3, 121.2, 120.3, 116.8, 66.5, 56.7, 52.6, 52.3, 42.8, 37.5, 27.2, 25.3, 22.9, 22.2.
HRMS (ESI) Calculated for $C_{20}H_{24}O_5$ ([M]+Na^+) = 367.1516, Found 367.1513.
IR (neat): 2926, 1733, 1607, 1583, 1491, 1434, 1310, 1227, 1193, 1146, 1115, 1022, 997, 756 cm^{-1}.



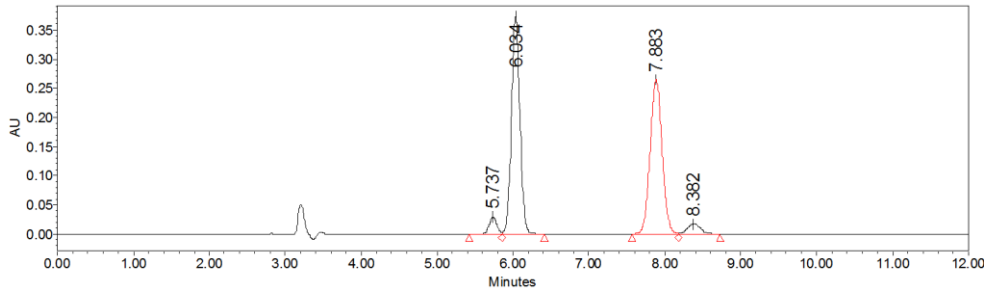
	Retention Time	Area	% Area
1	5.905	2876545	12.61
2	6.458	8485046	37.21
3	9.829	2884186	12.65
4	13.895	8558545	37.53



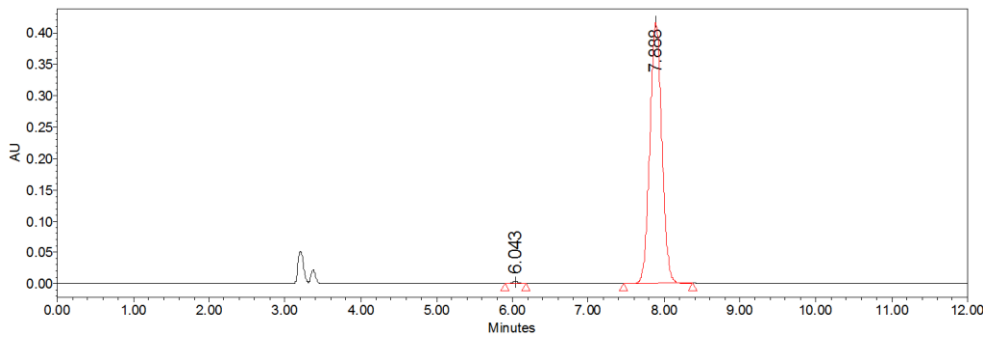
	Retention Time	Area	% Area
1	6.139	435193	1.03
2	11.395	41936033	98.97



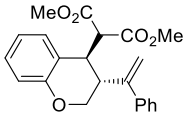
Dimethyl 2-[3-(cyclohept-1-en-1-yl)chroman-4-yl]malonate (2f):
16:1 dr, the major diastereomer was isolated as colorless oil in 90% yield, ee = 99%, $[\alpha]^{21}_{D}$ = –89.2 (*c* = 0.46, in CH_2Cl_2).
HPLC: Chiralcel IC, hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 210 nm, t_{r1} = 6.04 min, t_{r2} = 7.89 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 – 7.06 (m, 2H), 6.83 – 6.75 (m, 2H), 5.74 (t, *J* = 6.6 Hz, 1H), 4.20 (dd, *J* = 11.4, 3.9 Hz, 1H), 4.06 (dd, *J* = 11.4, 6.1 Hz, 1H), 3.80 (d, *J* = 7.0 Hz, 1H), 3.77 (s, 3H), 3.70 (t, *J* = 6.3 Hz, 1H), 3.52 (s, 3H), 2.60 (q, *J* = 5.5 Hz, 1H), 2.17 (t, *J* = 5.5 Hz, 2H), 2.07 – 2.01 (m, 2H), 1.74 – 1.66 (m, 2H), 1.50 – 1.35 (m, 3H), 1.34 – 1.23 (m, 1H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 169.1, 168.5, 154.6, 142.0, 129.7, 129.5, 128.2, 121.1, 120.3, 116.7, 66.4, 56.6, 52.6, 52.2, 44.5, 37.3, 32.7, 31.3, 28.3, 27.0, 26.8.
HRMS (ESI) Calculated for $C_{21}H_{26}O_5$ ([M]+Na^+) = 381.1672, Found 381.1669.
IR (neat): 2918, 2846, 1733, 1608, 1583, 1491, 1450, 1434, 1317, 1227, 1193, 1151, 1007, 756 cm^{-1}.



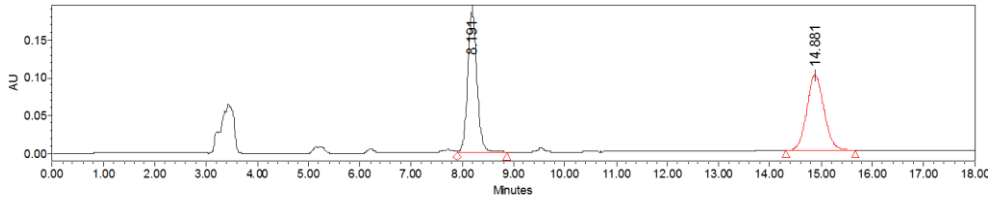
	Retention Time	Area	% Area
1	5.737	207898	3.36
2	6.034	2888126	46.65
3	7.883	2885196	46.60
4	8.382	210247	3.40



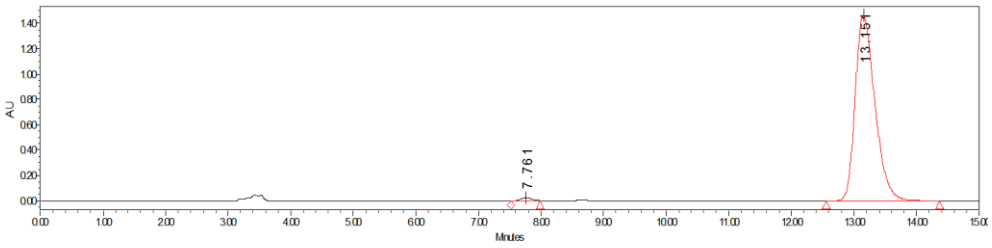
	Retention Time	Area	% Area
1	6.043	22062	0.48
2	7.888	4551968	99.52



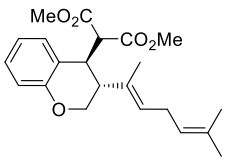
Dimethyl 2-[3-(1-phenylvinyl)chroman-4-yl]malonate (2g):
>19:1 dr, the major diastereomer was isolated as colorless oil in 83% yield, ee = 98%, $[\alpha]^{21}_{D}$ = –223.1 (*c* = 0.49, in CH_2Cl_2).
HPLC: Chiralcel IC, hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 210 nm, t_{r1} = 7.76 min, t_{r2} = 13.15 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.28 (m, 5H), 7.15 – 7.05 (m, 2H), 6.86 – 6.75 (m, 2H), 5.47 (s, 1H), 4.96 (s, 1H), 4.53 – 4.39 (m, 2H), 3.88 – 3.83 (m, 1H), 3.67 (d, *J* = 4.3 Hz, 1H), 3.56 (s, 3H), 3.52 – 3.43 (m, 1H), 3.21 (s, 3H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 169.1, 168.8, 153.9, 146.5, 140.1, 130.5, 128.7, 128.5, 128.3, 126.5, 121.2, 119.8, 116.3, 114.2, 64.8, 53.9, 52.5, 52.1, 39.3, 36.1.
HRMS (ESI) Calculated for $C_{22}H_{22}O_5$ ([M]+Na^+) = 389.1359, Found 389.1360.
IR (neat): 2951, 1731, 1608, 1583, 1491, 1454, 1433, 1225, 1147, 1066, 1039, 1023, 904, 779, 756, 699 cm^{-1}.



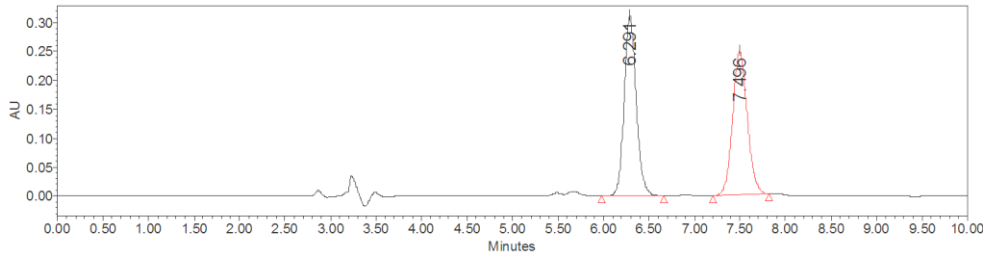
	Retention Time	Area	% Area
1	8.191	2322241	50.19
2	14.881	2304447	49.81



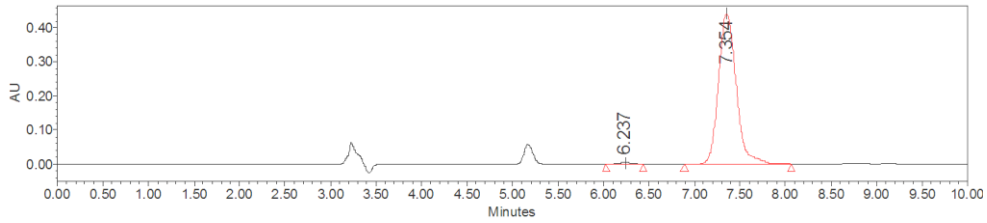
	Retention Time	Area	% Area
1	7.761	274777	0.85
2	13.151	31957080	99.15



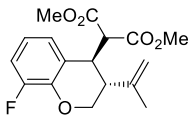
Dimethyl 2-[3-(6-methylhepta-1,5-dien-2-yl)chroman-4-yl]malonate (2h):
5:1 dr, the major diastereomer was isolated as colorless oil in 72% yield, ee = 98%, $[\alpha]^{22}_{D}$ = –143.4 (*c* = 0.30, in CH_2Cl_2).
HPLC: Chiralcel IC, hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min, λ = 210 nm, t_{r1} = 6.24 min, t_{r2} = 7.35 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 – 7.07 (m, 2H), 6.83 – 6.77 (m, 2H), 5.31 (t, *J* = 7.2 Hz, 1H), 5.00 (t, *J* = 7.2 Hz, 1H), 4.20 (dd, *J* = 11.2, 4.0 Hz, 1H), 4.07 (dd, *J* = 11.2, 6.4 Hz, 1H), 3.80 (d, *J* = 6.8 Hz, 1H), 3.77 – 3.74 (m, 4H), 3.52 (s, 3H), 2.69 – 2.62 (m, 3H), 1.66 (s, 6H), 1.56 (s, 3H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 169.1, 168.5, 154.7, 132.4, 131.9, 129.3, 128.1, 127.2, 122.5, 121.3, 120.3, 116.8, 66.9, 56.3, 52.6, 52.2, 44.0, 37.6, 27.1, 25.6, 17.7, 14.8.
HRMS (ESI) Calculated for $C_{22}H_{28}O_5$ ([M]+Na^+) = 395.1829, Found 395.1830.
IR (neat): 2953, 1732, 1608, 1583, 1491, 1452, 1434, 1131, 1228, 1195, 1151, 1118, 1020, 758 cm^{-1}.



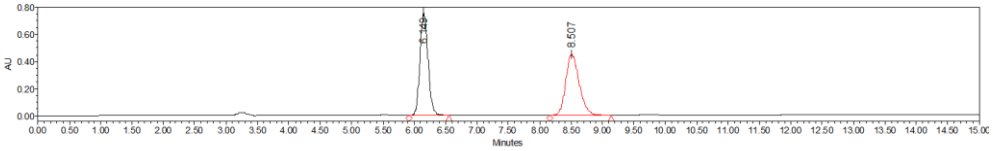
	Retention Time	Area	% Area
1	6.291	2859630	50.59
2	7.496	2792399	49.41



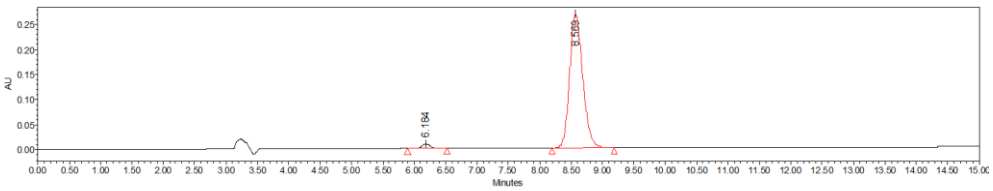
	Retention Time	Area	% Area
1	6.237	49440	0.82
2	7.354	5974004	99.18



Dimethyl 2-[8-fluoro-3-(prop-1-en-2-yl)chroman-4-yl]malonate (2i):
7:1 dr, the major diastereomer was isolated as white solid in 76% yield, m.p. = 56 – 60 °C, ee = 96%, $[\alpha]^{22}_{D}$ = –105.5 (*c* = 0.40, in CH_2Cl_2).
HPLC: Chiralcel IC, hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 210 nm, t_{r1} = 6.18 min, t_{r2} = 8.57 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.97 – 6.85 (m, 2H), 6.77 – 6.70 (m, 1H), 4.90 (s, 1H), 4.86 (s, 1H), 4.34 – 4.24 (m, 2H), 3.82 – 3.74 (m, 5H), 3.56 (s, 3H), 2.63 (q, *J* = 3.3, 2.8 Hz, 1H), 1.80 (s, 3H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 168.5, 168.2, 151.5 (d, *J* = 244.8 Hz), 142.7 (d, *J* = 11.3 Hz), 142.7, 124.5 (d, *J* = 3.6 Hz), 123.1, 119.6 (d, *J* = 7.2 Hz), 114.8 (d, *J* = 17.8 Hz), 113.6, 66.0, 56.9, 52.8 (d, *J* = 3.0 Hz), 52.4 (d, *J* = 2.5 Hz), 41.7, 37.2, 21.6.
^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ –136.8 (s, 1F).
HRMS (ESI) Calculated for $C_{17}H_{19}FO_5$ ([M]+Na^+) = 345.1109, Found 345.1110.
IR (neat): 2955, 1745, 1645, 1588, 1491, 1431, 1272, 1257, 1197, 1145, 1080, 985, 892, 785, 770, 712 cm^{-1}.

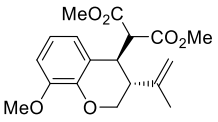


	Retention Time	Area	% Area
1	6.149	6696276	50.07
2	8.507	6678407	49.93

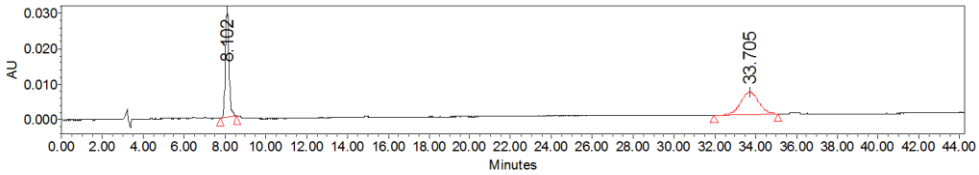


	Retention Time	Area	% Area

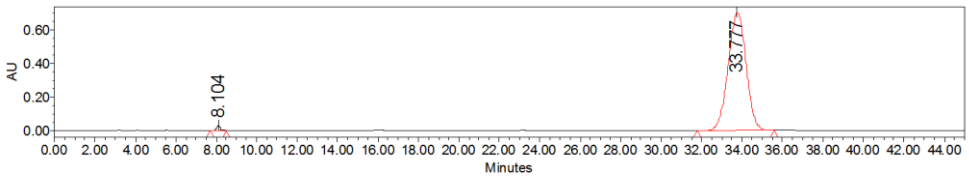
1	6.184	78433	1.99
2	8.569	3864901	98.01



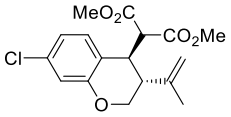
Dimethyl 2-[8-methoxy-3-(prop-1-en-2-yl)chroman-4-yl]malonate (2j):
7.5:1 dr, the major diastereomer was isolated as white solid in 83% yield, m.p. = 32 – 35 °C, ee = 98%, $[\alpha]^{22}_{D}$ = –110.2 (*c* = 0.40, in CH_2Cl_2).
HPLC: Chiralcel IC, hexane/*i*-PrOH = 70/30, flow rate 1.0 mL/min, λ = 210 nm, t_{r1} = 8.10 min, t_{r2} = 33.78 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.80 – 6.68 (m, 3H), 4.88 (s, 1H), 4.85 (s, 1H), 4.30 (d, *J* = 4.2 Hz, 2H), 3.85 (s, 3H), 3.78 (d, *J* = 2.0 Hz, 2H), 3.76 (s, 3H), 3.56 (s, 3H), 2.59 (s, 1H), 1.80 (s, 3H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 168.6, 168.4, 148.2, 143.7, 143.0, 121.3, 121.2, 119.8, 113.4, 110.0, 65.9, 57.2, 55.8, 52.7, 52.3, 41.7, 37.4, 21.7.
HRMS (ESI) Calculated for $C_{18}H_{22}O_6$ ([M]+Na^+) = 357.1309, Found 357.1309.
IR (neat): 2953, 1737, 1643, 1586, 1489, 1434, 1341, 1302, 1258, 1221, 1147, 1115, 994, 885, 733, 627 cm^{-1}.



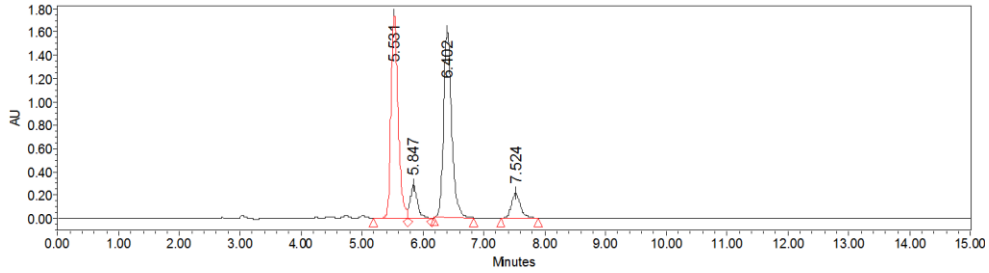
	Retention Time	Area	% Area
1	8.102	387330	50.26
2	33.705	383301	49.74



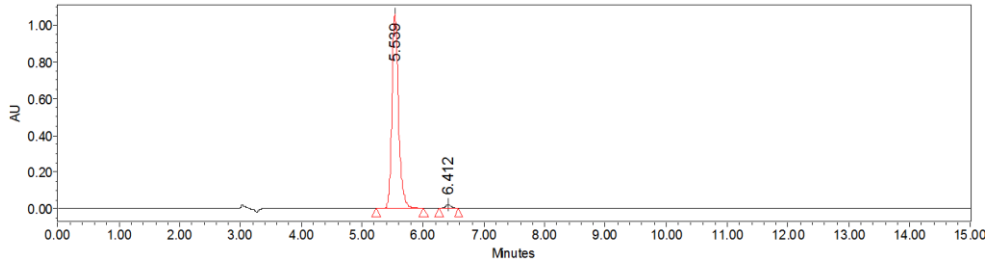
	Retention Time	Area	% Area
1	8.104	408275	0.94
2	33.777	42971566	99.06



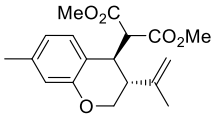
Dimethyl 2-[7-chloro-3-(prop-1-en-2-yl)chroman-4-yl]malonate (2k):
9:1 dr, the major diastereomer was isolated as white solid in 90% yield, m.p. = 36 – 38 °C, ee = 96%, $[\alpha]^{22}_{D}$ = –107.2 (*c* = 0.42, in CH_2Cl_2).
HPLC: Chiralcel IA, hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 210 nm, t_{r1} = 5.54 min, t_{r2} = 6.41 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.03 (d, *J* = 8.1 Hz, 1H), 6.83 – 6.76 (m, 2H), 4.89 (s, 1H), 4.83 (s, 1H), 4.27 – 4.14 (m, 2H), 3.77 (s, 3H), 3.74 – 3.69 (m, 2H), 3.57 (s, 3H), 2.57 (q, *J* = 3.4 Hz, 1H), 1.79 (s, 3H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 168.5, 168.2, 154.9, 142.8, 133.6, 130.6, 120.6, 119.1, 117.0, 113.5, 65.8, 56.9, 52.8, 52.4, 41.7, 37.1, 21.6.
HRMS (ESI) Calculated for $C_{17}H_{19}{}^{34.9689}ClO_5$ ([M]+Na^+) = 361.0813, Found 361.0809.
HRMS (ESI) Calculated for $C_{17}H_{19}{}^{36.9659}ClO_5$ ([M]+Na^+) = 363.0784, Found 363.0777.
IR (neat): 2953, 1745, 1600, 1487, 1429, 1299, 1270, 1226, 1196, 1147, 1130, 1082, 997, 922, 872, 810, 778 cm^{-1}.



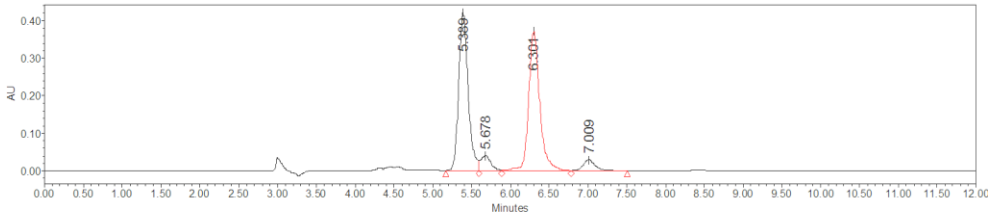
	Retention Time	Area	% Area
1	5.531	14257849	42.60
2	5.847	2270692	6.78
3	6.402	14784296	44.17
4	7.524	2156237	6.44



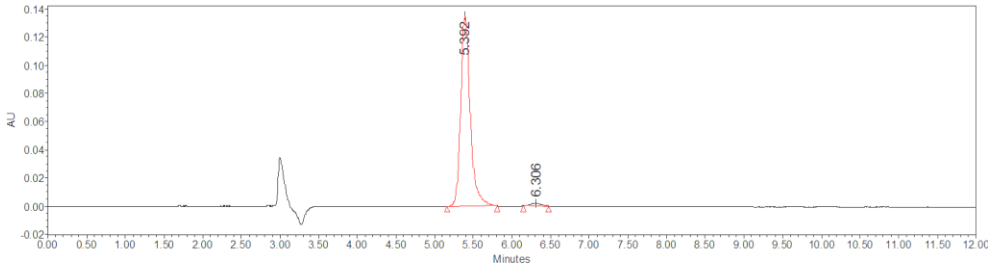
	Retention Time	Area	% Area
1	5.539	8074913	97.94
2	6.412	169730	2.06



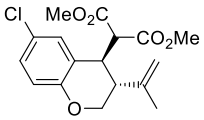
Dimethyl 2-[7-methyl-3-(prop-1-en-2-yl)chroman-4-yl]malonate (2l):
12:1 dr, the major diastereomer was isolated as white solid in 85% yield, m.p. = 38 – 40 °C, ee = 97%, $[\alpha]^{23}_{D}$ = –115.5 (*c* = 0.42, in CH_2Cl_2).
HPLC: Chiralcel IA, hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min, λ = 210 nm, t_{r1} = 5.39 min, t_{r2} = 6.31 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.95 (d, *J* = 8.0 Hz, 1H), 6.66 – 6.58 (m, 2H), 4.87 (s, 1H), 4.85 (s, 1H), 4.23 – 4.13 (m, 2H), 3.78 – 3.70 (m, 5H), 3.58 (s, 3H), 2.55 (q, *J* = 4.0 Hz, 1H), 2.24 (s, 3H), 1.79 (s, 3H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 168.7, 168.5, 154.0, 143.3, 138.5, 129.3, 121.4, 117.4, 117.2, 113.2, 65.5, 57.3, 52.7, 52.4, 41.9, 37.3, 21.7, 21.1.
HRMS (ESI) Calculated for $C_{18}H_{22}O_5$ ([M]+Na^+) = 341.1359, Found 341.1357.
IR (neat): 2955, 1746, 1731, 1572, 1504, 1436, 1303, 1258, 1193, 1151, 1131, 1098, 887, 780, 630, 594 cm^{-1}.



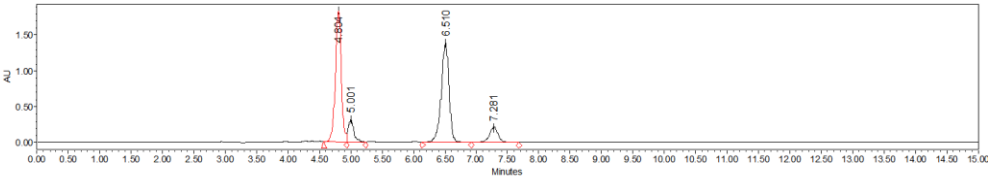
	Retention Time	Area	% Area
1	5.389	3553371	44.90
2	5.678	361752	4.57
3	6.301	3684496	46.56
4	7.009	313824	3.97



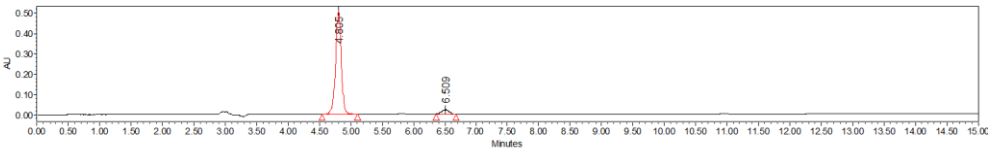
	Retention Time	Area	% Area
1	5.392	1158704	98.52
2	6.306	17428	1.48



Dimethyl 2-[6-chloro-3-(prop-1-en-2-yl)chroman-4-yl]malonate (2m):
3:1 dr, the major diastereomer was isolated as colorless oil in 62% yield, ee = 90%, $[\alpha]^{22}_D$ = –82.8 (*c* = 0.25, in CH_2Cl_2).
HPLC: Chiralcel IA, hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 210 nm, t_{r1} = 4.81 min, t_{r2} = 6.51 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 – 7.04 (m, 2H), 6.77 – 6.70 (m, 1H), 4.89 (s, 1H), 4.83 (s, 1H), 4.26 – 4.15 (m, 2H), 3.78 (s, 3H), 3.75 – 3.68 (m, 2H), 3.61 (s, 3H), 2.56 (q, *J* = 4.0 Hz, 1H), 1.79 (s, 3H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 168.4, 168.1, 152.9, 142.9, 129.2, 128.5, 125.0, 122.0, 118.2, 113.5, 65.6, 57.1, 52.80, 52.5, 41.5, 37.4, 21.6.
HRMS (ESI) Calculated for $C_{17}H_{19}{}^{34.9689}ClO_5$ ([M]+Na^+) = 361.0813, Found 361.0813.
HRMS (ESI) Calculated for $C_{17}H_{19}{}^{36.9659}ClO_5$ ([M]+Na^+) = 363.0784, Found 363.0780.
IR (neat): 2953, 1734, 1647, 1578, 1487, 1434, 1410, 1235, 1195, 1156, 1098, 1020, 900, 818, 635 cm^{-1}.

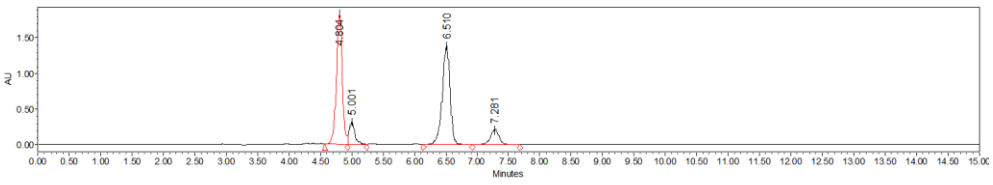


	Retention Time	Area	% Area
1	4.804	11823961	42.51
2	5.001	1955818	7.03
3	6.510	12087874	43.46
4	7.281	1948795	7.01

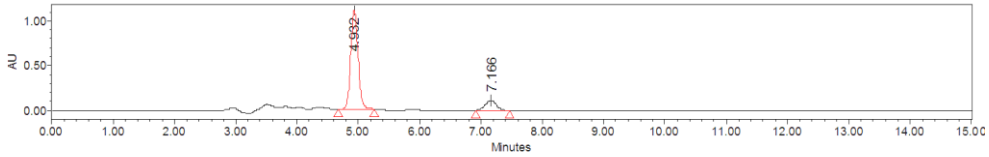


	Retention Time	Area	% Area
1	4.805	3162589	94.92
2	6.509	169289	5.08

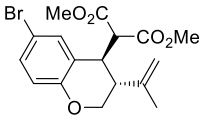
The minor diastereomer was isolated as colorless oil in 17% yield, ee = 75%, $[\alpha]^{20}_D$ = –137.7 (*c* = 0.11, in CH_2Cl_2).
HPLC: Chiralcel IA, hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 210 nm, t_{r1} = 4.93 min, t_{r2} = 7.17 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 – 7.06 (m, 2H), 6.74 (d, *J* = 8.4 Hz, 1H), 4.95 (s, 1H), 4.57 (s, 1H), 4.31 – 4.25 (m, 2H), 4.03 – 3.98 (m, 1H), 3.73 (s, 3H), 3.56 (d, *J* = 6.4 Hz, 1H), 3.38 (s, 3H), 2.72 – 2.63 (m, 1H), 1.80 (s, 3H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 169.0, 168.5, 152.6, 142.5, 129.9, 128.8, 124.4, 122.8, 117.8, 112.3, 64.7, 54.2, 52.7, 52.3, 41.2, 35.8, 23.4.
HRMS (ESI) Calculated for $C_{17}H_{19}{}^{34.9689}ClO_5$ ([M]+Na^+) = 361.0813, Found 361.0813.
HRMS (ESI) Calculated for $C_{17}H_{19}{}^{36.9659}ClO_5$ ([M]+Na^+) = 363.0784, Found 363.0782.
IR (neat): 2952, 1733, 1646, 1487, 1434, 1268, 1147, 1025, 894, 816, 736, 670 cm^{-1}.



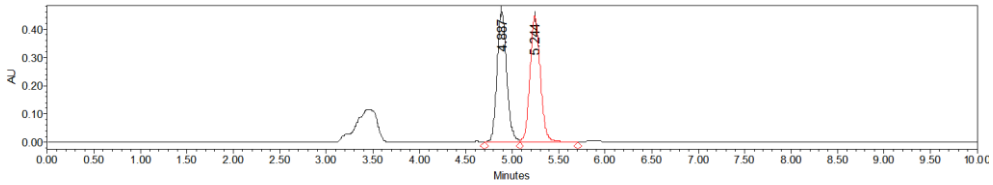
	Retention Time	Area	% Area
1	4.804	11823961	42.51
2	5.001	1955818	7.03
3	6.510	12087874	43.46
4	7.281	1948795	7.01



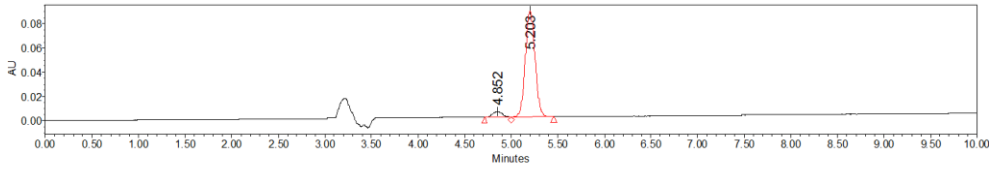
	Retention Time	Area	% Area
1	4.932	9192676	87.46
2	7.166	1317536	12.54



Dimethyl 2-[6-bromo-3-(prop-1-en-2-yl)chroman-4-yl]malonate (2n):
2.5:1 dr, the major diastereomer was isolated as colorless oil in 61% yield, ee = 90%, $[\alpha]^{22}_{D}$ = –63.8 (*c* = 0.28, in CH_2Cl_2).
HPLC: Chiralcel IC, hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 210 nm, t_{r1} = 4.85 min, t_{r2} = 5.20 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 – 7.18 (m, 2H), 6.71 – 6.65 (m, 1H), 4.88 (s, 1H), 4.83 (s, 1H), 4.21 (d, *J* = 4.0 Hz, 2H), 3.78 (s, 3H), 3.73 – 3.69 (m, 2H), 3.62 (s, 3H), 2.54 (q, *J* = 3.2 Hz, 1H), 1.80 (s, 3H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 168.4, 168.1, 153.4, 142.8, 132.2, 131.4, 122.5, 118.7, 113.5, 112.2, 65.5, 57.2, 52.8, 52.5, 41.4, 37.3, 21.7.
HRMS (ESI) Calculated for $C_{17}H_{19}{}^{78.9183}BrO_5$ ([M+Na$^+$]) = 405.0308, Found 405.0307.
HRMS (ESI) Calculated for $C_{17}H_{19}{}^{80.9163}BrO_5$ ([M+Na$^+$]) = 407.0288, Found 407.0285.
IR (neat): 2952, 1733, 1646, 1574, 1483, 1434, 1406, 1234, 1154, 1127, 1019, 900, 816, 612 cm^{-1}.



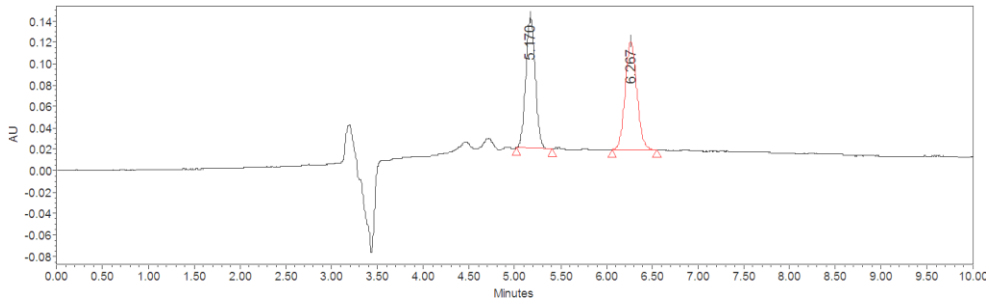
	Retention Time	Area	% Area
1	4.887	3378576	49.68
2	5.244	3422033	50.32



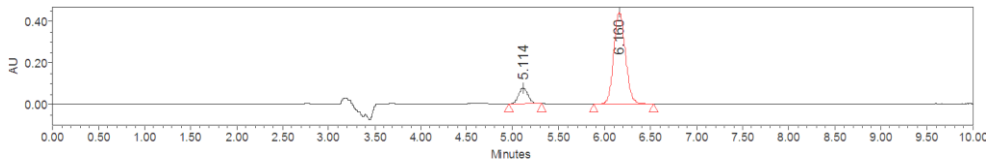
	Retention Time	Area	% Area
1	4.852	32484	4.92
2	5.203	628421	95.08

The minor diastereomer was isolated as colorless oil in 27% yield, ee = 75%, $[\alpha]^{20}_{D}$ = –112.6 (*c* = 0.41, in CH_2Cl_2).
HPLC: Chiralcel IC, hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 220 nm, t_{r1} = 5.11 min, t_{r2} = 6.16 min.

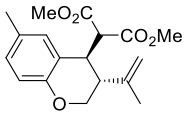
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 – 7.19 (m, 2H), 6.69 (d, *J* = 8.8 Hz, 1H), 4.95 (s, 1H), 4.57 (s, 1H), 4.33 – 4.24 (m, 2H), 4.04 – 3.97 (m, 1H), 3.73 (s, 3H), 3.55 (d, *J* = 6.8 Hz, 1H), 3.39 (s, 3H), 2.71 – 2.64 (m, 1H), 1.80 (s, 3H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 168.9, 168.5, 153.2, 142.4, 132.8, 131.6, 123.4, 118.3, 112.2, 111.5, 64.7, 54.2, 52.7, 52.3, 41.1, 35.8, 23.4.
HRMS (ESI) Calculated for $C_{17}H_{19}{}^{78.9183}BrO_5$ ([M]+Na^+) = 405.0308, Found 405.0307.
HRMS (ESI) Calculated for $C_{17}H_{19}{}^{80.9163}BrO_5$ ([M]+Na^+) = 407.0288, Found 407.0286.
IR (neat): 2951, 1732, 1645, 1576, 1484, 1434, 1239, 1146, 1025, 894, 815, 736, 659 cm^{-1}.



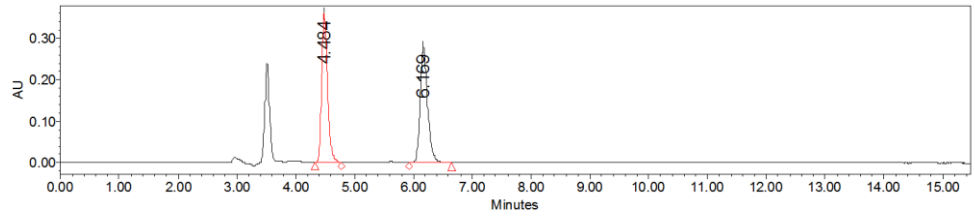
	Retention Time	Area	% Area
1	5.170	874854	49.43
2	6.267	894943	50.57



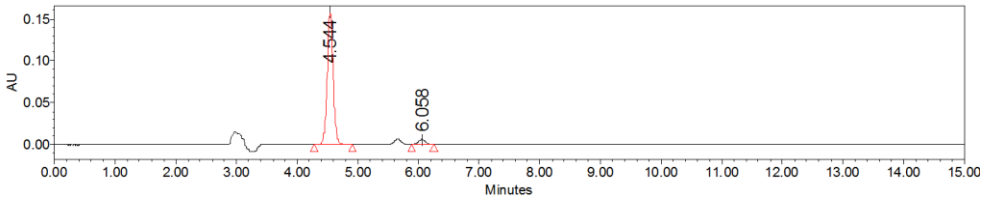
	Retention Time	Area	% Area
1	5.114	554274	12.53
2	6.160	3868469	87.47



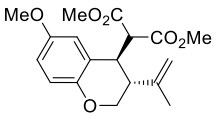
Dimethyl 2-[6-methyl-3-(prop-1-en-2-yl)chroman-4-yl]malonate (2o):
5:1 dr, the major diastereomer was isolated as white solid in 60% yield, m.p. = 32 – 34 °C, ee = 91%, $[\alpha]^{23}_D$ = –94.0 (*c* = 0.34, in CH_2Cl_2).
HPLC: Chiralcel IA, hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 210 nm, t_{r1} = 4.54 min, t_{r2} = 6.06 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.94 – 6.89 (m, 1H), 6.87 (s, 1H), 6.69 (d, *J* = 8.0 Hz, 1H), 4.87 (s, 1H), 4.85 (s, 1H), 4.23 – 4.12 (m, 2H), 3.77 – 3.74 (m, 4H), 3.73 – 3.69 (m, 1H), 3.57 (s, 3H), 2.55 (q, *J* = 4.0 Hz, 1H), 2.21 (s, 3H), 1.80 (s, 3H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 168.7, 168.5, 152.0, 143.4, 129.8, 129.4, 129.2, 120.1, 116.5, 113.2, 65.5, 57.4, 52.6, 52.2, 42.0, 37.5, 21.7, 20.6.
HRMS (ESI) Calculated for $C_{18}H_{22}O_5$ ([M]+Na^+) = 341.1359, Found 341.1358.
IR (neat): 2951, 1740, 1618, 1500, 1434, 1268, 1223, 1196, 1127, 995, 906, 828, 810, 556, 521 cm^{-1}.



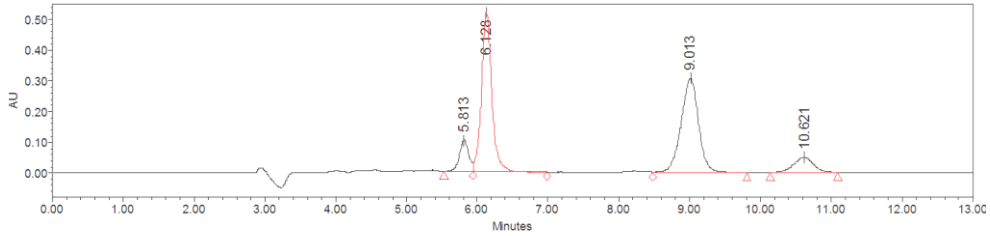
	Retention Time	Area	% Area
1	4.484	2485235	50.08
2	6.169	2477763	49.92



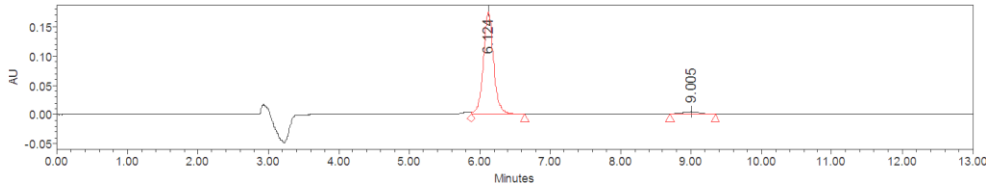
	Retention Time	Area	% Area
1	4.544	1086648	95.56
2	6.058	50499	4.44



Dimethyl 2-[6-methoxy-3-(prop-1-en-2-yl)chroman-4-yl]malonate (2p):
4:1 dr, the major diastereomer was isolated as white solid in 58% yield, m.p. = 28 – 32 °C, ee = 92%, $[\alpha]^{22}_{D}$ = –109.0 (*c* = 0.20, in CH_2Cl_2).
HPLC: Chiralcel IA, hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 220 nm, t_{r1} = 6.12 min, t_{r2} = 9.00 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.75 – 6.69 (m, 2H), 6.69 – 6.66 (m, 1H), 4.89 (d, *J* = 0.8 Hz, 1H), 4.85 (s, 1H), 4.19 (dd, *J* = 11.6, 3.6 Hz, 1H), 4.11 (dd, *J* = 11.6, 5.2 Hz, 1H), 3.80 – 3.77 (m, 1H), 3.77 (s, 3H), 3.74 (d, *J* = 4.2 Hz, 1H), 3.71 (s, 3H), 3.58 (s, 3H), 2.59 (q, *J* = 4.8 Hz, 1H), 1.79 (s, 3H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 168.7, 168.5, 153.2, 148.4, 143.2, 121.1, 117.4, 114.9, 113.7, 113.4, 65.9, 57.1, 55.6, 52.7, 52.4, 42.2, 37.8, 21.6.
HRMS (ESI) Calculated for $C_{18}H_{22}O_6$ ([M]+Na^+) = 357.1309, Found 357.1310.
IR (neat): 2953, 1750, 1645, 1496, 1432, 1327, 1263, 1232, 1152, 1042, 967, 899, 805, 695 cm^{-1}.

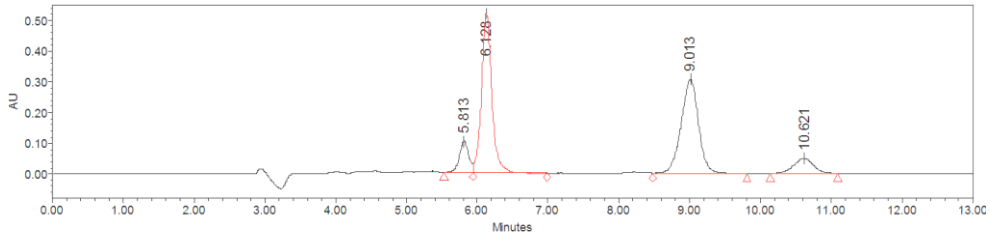


	Retention Time	Area	% Area
1	5.813	933038	7.49
2	6.128	5292465	42.50
3	9.013	5265400	42.28
4	10.621	962974	7.73

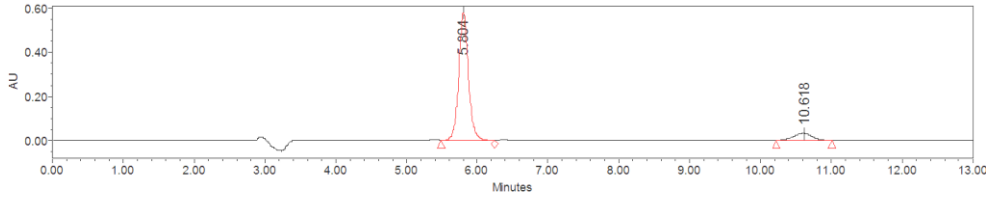


	Retention Time	Area	% Area
1	6.124	1766348	96.08
2	9.005	72059	3.92

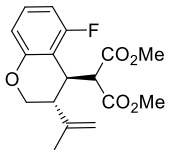
The minor diastereomer was isolated as colorless oil in 15% yield, ee = 80%, $[\alpha]^{22}_{D}$ = –112.4 (*c* = 0.20, in CH_2Cl_2).
HPLC: Chiralcel IA, hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 220 nm, t_{r1} = 5.80 min, t_{r2} = 10.62 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.73 (d, *J* = 1.2 Hz, 2H), 6.65 – 6.63 (m, 1H), 4.93 (s, 1H), 4.56 (s, 1H), 4.28 – 4.21 (m, 2H), 4.03 – 3.98 (m, 1H), 3.72 (s, 6H), 3.59 (d, *J* = 6.8 Hz, 1H), 3.34 (s, 3H), 2.75 – 2.67 (m, 1H), 1.81 (s, 3H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 169.2, 168.9, 152.7, 147.9, 143.0, 121.5, 117.1, 115.8, 114.2, 112.0, 64.5, 55.8, 54.4, 52.6, 52.3, 41.6, 36.3, 23.5.
HRMS (ESI) Calculated for $C_{18}H_{22}O_6$ ([M]+Na^+) = 357.1309, Found 357.1299.
IR (neat): 2951, 1733, 1645, 1499, 1483, 1241, 1211, 1148, 1027, 899, 815, 719 cm^{-1}.



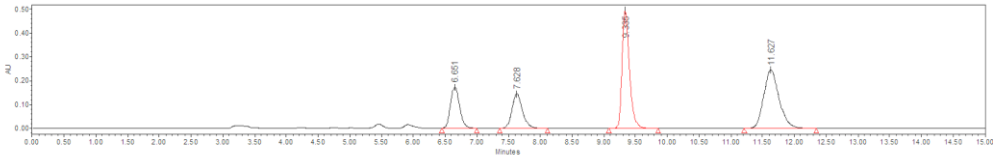
	Retention Time	Area	% Area
1	5.813	933038	7.49
2	6.128	5292465	42.50
3	9.013	5265400	42.28
4	10.621	962974	7.73



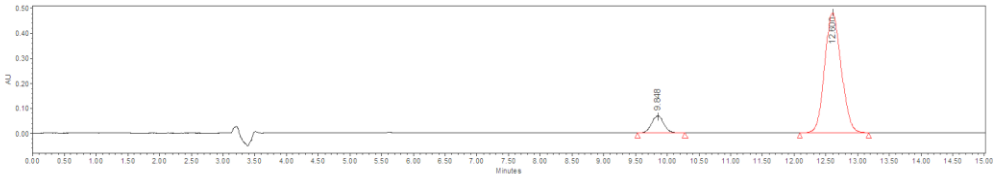
	Retention Time	Area	% Area
1	5.804	5430913	90.02
2	10.618	602059	9.98



Dimethyl 2-[5-fluoro-3-(prop-1-en-2-yl)chroman-4-yl]malonate (2q):
1.5:1 dr, the minor diastereomer was isolated as colorless oil in 32% yield, ee = 81%, $[\alpha]^{22}_{D}$ = –260.6 (*c* = 0.10, in CH_2Cl_2).
HPLC: Chiralcel IC, hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 220 nm, t_{r1} = 9.85 min, t_{r2} = 12.60 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 – 7.05 (m, 1H), 6.65 – 6.53 (m, 2H), 4.99 (s, 1H), 4.59 (s, 1H), 4.37 – 4.22 (m, 3H), 3.75 (s, 3H), 3.54 (d, *J* = 4.8 Hz, 1H), 3.34 (s, 3H), 2.65 (dt, *J* = 11.2, 4.0 Hz, 1H), 1.85 (s, 3H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 168.8, 168.8, 160.9 (d, *J* = 246.2 Hz), 155.1 (d, *J* = 6.9 Hz), 142.5, 128.9 (d, *J* = 10.7 Hz), 112.4, 112.0 (d, *J* = 2.9 Hz), 110.3 (d, *J* = 21.3 Hz), 106.1 (d, *J* = 22.1 Hz), 64.6, 53.0, 52.7, 52.2, 41.2, 30.2, 23.3.
^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ –114.8 (s, 1F).
HRMS (ESI) Calculated for $C_{17}H_{19}FO_5$ ([M]+Na^+) = 345.1109, Found 345.1102.
IR (neat): 2952, 1733, 1621, 1586, 1465, 1435, 1345, 1258, 1229, 1149, 1090, 1059, 1029, 979, 904, 785, 769 cm^{-1}.



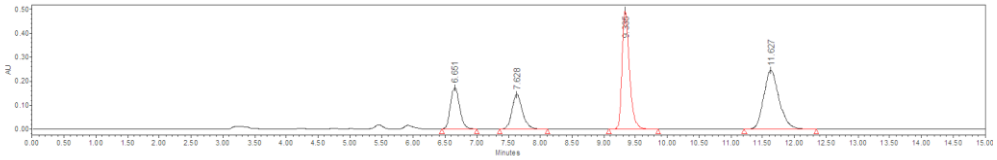
	Retention Time	Area	% Area
1	6.651	1691139	14.48
2	7.628	1705159	14.60
3	9.335	4137961	35.42
4	11.627	4146861	35.50



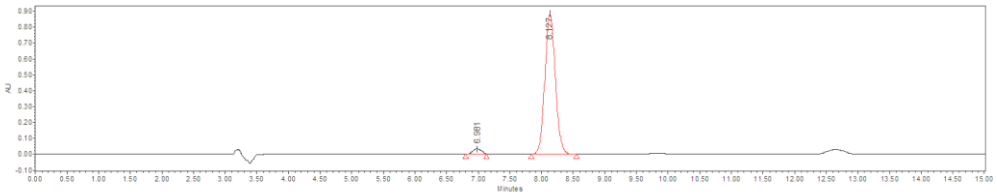
	Retention Time	Area	% Area

1	9.848	930503	9.61
2	12.600	8747393	90.39

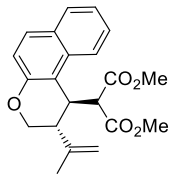
The major diastereomer was isolated as colorless oil in 43% yield, ee = 95%, $[\alpha]^{23}_{D}$ = –64.2 (*c* = 0.28, in CH_2Cl_2).
HPLC: Chiralcel IC, hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 220 nm, t_{r1} = 6.98 min, t_{r2} = 8.13 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 – 7.05 (m, 1H), 6.64 – 6.56 (m, 2H), 4.85 (s, 1H), 4.82 (s, 1H), 4.23 – 4.18 (m, 1H), 4.16 (dd, *J* = 12.0, 3.6 Hz, 1H), 3.93 (dd, *J* = 7.6, 2.8 Hz, 1H), 3.86 (d, *J* = 7.2 Hz, 1H), 3.70 (s, 3H), 3.66 (s, 3H), 2.70 (q, *J* = 3.7 Hz, 1H), 1.82 (s, 3H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 168.5, 168.3, 161.5 (d, *J* = 244.6 Hz), 155.7 (d, *J* = 7.2 Hz), 143.5, 128.6 (d, *J* = 10.9 Hz), 112.9, 112.6 (d, *J* = 3.0 Hz), 109.2 (d, *J* = 19.3 Hz), 106.8 (d, *J* = 22.5 Hz), 65.3, 55.7, 52.5, 52.5, 40.8, 32.3, 21.7.
^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ –115.9 (s, 1F).
HRMS (ESI) Calculated for $C_{17}H_{19}FO_5$ ([M]+Na^+) = 345.1109, Found 345.1104.
IR (neat): 2953, 1735, 1622, 1586, 1466, 1435, 1303, 1237, 1196, 1152, 1105, 1087, 1012, 904, 776 cm^{-1}.



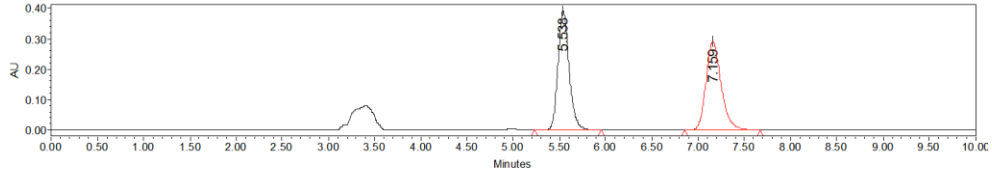
	Retention Time	Area	% Area
1	6.651	1691139	14.48
2	7.628	1705159	14.60
3	9.335	4137961	35.42
4	11.627	4146861	35.50



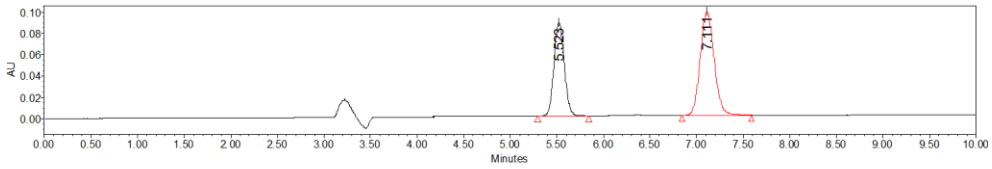
	Retention Time	Area	% Area
1	6.981	259219	2.50
2	8.127	10112577	97.50



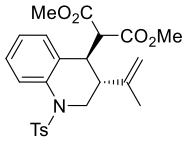
Dimethyl 2-{2-(prop-1-en-2-yl)-2,3-dihydro-1H-benzo[f]chromen-1-y}malonate (2r):
6:1 dr, the major diastereomer was isolated as white solid in 49% yield, m.p. = 74 – 78 °C, ee = 20%, $[\alpha]^{23}_{D}$ = –54.0 (*c* = 0.33, in CH_2Cl_2).
HPLC: Chiralcel IC, hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 210 nm, t_{r1} = 5.52 min, t_{r2} = 7.11 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 8.8 Hz, 1H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.63 (d, *J* = 8.8 Hz, 1H), 7.51 – 7.45 (m, 1H), 7.33 – 7.27 (m, 1H), 7.02 (d, *J* = 9.2 Hz, 1H), 4.99 (s, 1H), 4.81 – 4.76 (m, 1H), 4.63 (s, 1H), 4.46 – 4.35 (m, 2H), 3.78 (s, 3H), 3.57 (d, *J* = 5.6 Hz, 1H), 2.79 – 2.73 (m, 4H), 1.89 (s, 3H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 169.7, 168.7, 151.7, 142.9, 132.8, 129.3, 128.7, 128.0, 126.3, 123.2, 123.2, 118.4, 113.5, 112.1, 64.3, 54.3, 52.7, 51.7, 41.6, 31.7, 23.5.
HRMS (ESI) Calculated for $C_{21}H_{22}O_5$ ([M]+Na^+) = 377.1359, Found 377.1352.
IR (neat): 2950, 1728, 1621, 1600, 1434, 1295, 1226, 1157, 1095, 1028, 907, 818, 760 cm^{-1}.



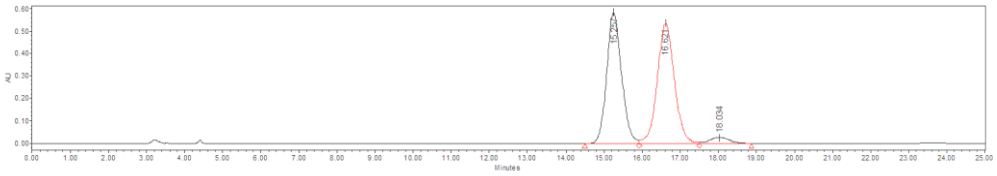
	Retention Time	Area	% Area
1	5.538	3278540	49.91
2	7.159	3290691	50.09



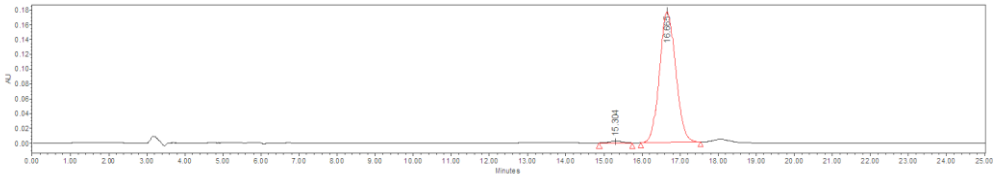
	Retention Time	Area	% Area
1	5.523	675294	39.89
2	7.111	1017420	60.11



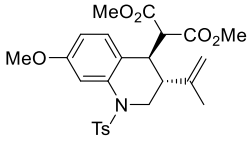
Dimethyl 2-[3-(prop-1-en-2-yl)-1-tosyl-1,2,3,4-tetrahydroquinolin-4-yl]malonate (2s):
>19:1 dr, the major diastereomer was isolated as white solid in 89% yield, m.p. = 74 – 76 °C, ee = 98%, $[\alpha]^{23}_{D}$ = –97.1 (*c* = 0.76, in CH_2Cl_2).
HPLC: Chiralcel IC, hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 210 nm, t_{r1} = 15.30 min, t_{r2} = 16.66 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.4 Hz, 1H), 7.67 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 7.22 – 7.16 (m, 1H), 7.08 (d, *J* = 7.2 Hz, 1H), 6.99 (t, *J* = 7.2 Hz, 1H), 4.76 (s, 1H), 4.67 (s, 1H), 3.92 (dd, *J* = 5.6, 12.8 Hz, 1H), 3.72 (s, 3H), 3.66 (dd, *J* = 13.2, 5.6 Hz, 1H), 3.59 (dd, *J* = 8.8, 5.2 Hz, 1H), 3.41 (s, 3H), 2.94 (d, *J* = 8.8 Hz, 1H), 2.66 (q, *J* = 5.2 Hz, 1H), 2.40 (s, 3H), 1.66 (s, 3H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 168.3, 167.9, 143.9, 143.4, 136.8, 135.9, 129.8, 129.8, 128.0, 127.9, 127.2, 124.2, 123.0, 113.5, 55.5, 52.7, 52.1, 47.7, 43.6, 40.3, 21.6, 20.7.
HRMS (ESI) Calculated for $C_{24}H_{27}NO_6S$ ([M]+Na^+) = 480.1451, Found 480.1446.
IR (neat): 2953, 1733, 1647, 1599, 1490, 1434, 1351, 1245, 1160, 1089, 1027, 966, 899, 841, 813, 759, 676, 652, 574, 540 cm^{-1}.



	Retention Time	Area	% Area
1	15.257	15777750	47.51
2	16.621	16579551	49.93
3	18.034	849980	2.56

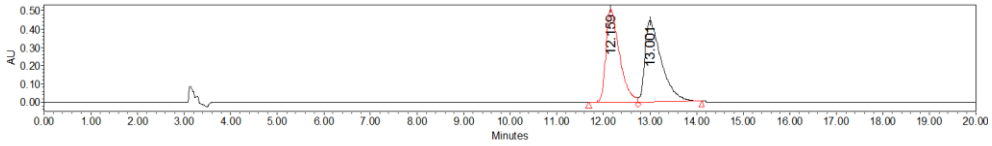


	Retention Time	Area	% Area
1	15.304	57220	1.08
2	16.665	5249005	98.92

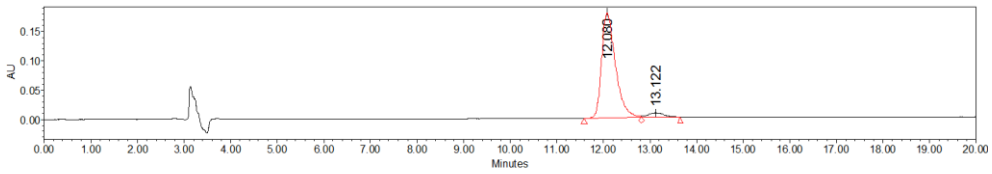


Dimethyl 2-[7-methoxy-3-(prop-1-en-2-yl)-1-tosyl-1,2,3,4-tetrahydroquinolin-4-yl]malonate (2t):
>19:1 dr, the major diastereomer was isolated as colorless oil in 75% yield, ee = 90%, $[\alpha]^{21}_{D}$ = –138.7 (*c* = 0.84, in CH_2Cl_2).
HPLC: Chiralcel IB, hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min, λ = 210 nm, t_{r1} = 12.08 min, t_{r2} = 13.12 min.

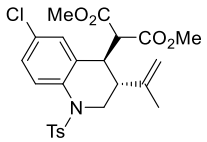
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.4 Hz, 2H), 7.40 (d, *J* = 2.4 Hz, 1H), 7.28 (d, *J* = 8.4 Hz, 2H), 6.97 (d, *J* = 8.4 Hz, 1H), 6.56 (dd, *J* = 8.4, 2.4 Hz, 1H), 4.76 (s, 1H), 4.67 (s, 1H), 3.88 (dd, *J* = 12.8, 5.6 Hz, 1H), 3.78 (s, 3H), 3.74 – 3.65 (m, 4H), 3.54 (dd, *J* = 9.2, 4.8 Hz, 1H), 3.43 (s, 3H), 2.85 (d, *J* = 9.2 Hz, 1H), 2.59 (q, *J* = 5.2 Hz, 1H), 2.41 (s, 3H), 1.66 (s, 3H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 168.4, 167.9, 159.0, 144.0, 143.4, 137.5, 135.7, 130.5, 129.8, 127.2, 119.8, 113.4, 110.6, 108.0, 55.8, 55.3, 52.7, 52.2, 47.5, 43.2, 39.7, 21.6, 20.8.
HRMS (ESI) Calculated for $C_{25}H_{29}NO_7S$ ([M]+Na^+) = 510.1557, Found 510.1554.
IR (neat): 2953, 1735, 1611, 1505, 1434, 1351, 1264, 1161, 1090, 1038, 897, 812, 732, 703, 655, 581, 544 cm^{-1}.



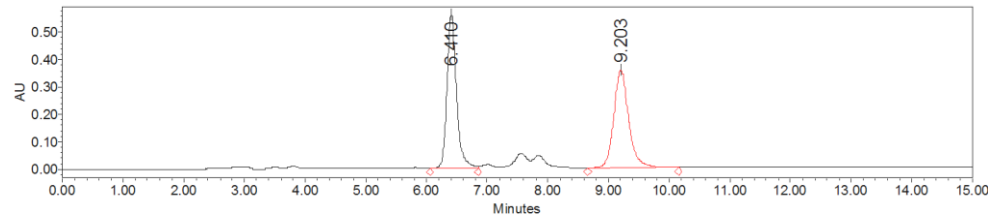
	Retention Time	Area	% Area
1	12.159	10249890	48.49
2	13.001	10889047	51.51



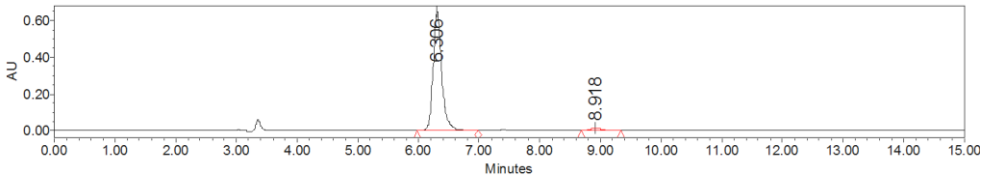
	Retention Time	Area	% Area
1	12.080	3704833	94.92
2	13.122	198431	5.08



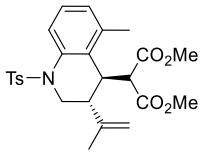
Dimethyl 2-[6-chloro-3-(prop-1-en-2-yl)-1-tosyl-1,2,3,4-tetrahydroquinolin-4-yl]malonate (2u):
6:1 dr, the major diastereomer was isolated as colorless oil in 76% yield, ee = 94%, $[\alpha]^{22}_D$ = –85.6 (*c* = 0.40, in CH_2Cl_2).
HPLC: Chiralcel IA, hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 210 nm, t_{r1} = 6.31 min, t_{r2} = 8.92 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.8 Hz, 1H), 7.66 – 7.61 (m, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.17 (dd, *J* = 8.8, 2.4 Hz, 1H), 7.07 (d, *J* = 2.4 Hz, 1H), 4.77 (s, 1H), 4.65 (s, 1H), 3.84 (dd, *J* = 13.2, 6.0 Hz, 1H), 3.73 (s, 3H), 3.69 (dd, *J* = 13.2, 5.2 Hz, 1H), 3.52 (dd, *J* = 9.2, 4.8 Hz, 1H), 3.47 (s, 3H), 2.78 (d, *J* = 9.2 Hz, 1H), 2.59 (q, *J* = 5.2 Hz, 1H), 2.41 (s, 3H), 1.65 (s, 3H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 168.0, 167.5, 144.2, 142.9, 135.3, 135.3, 129.9, 129.7, 129.6, 129.5, 128.1, 127.2, 124.4, 113.7, 55.3, 52.8, 52.3, 47.3, 43.0, 40.0, 21.6, 20.8.
HRMS (ESI) Calculated for $C_{24}H_{26}{}^{34.9689}ClNO_6S$ ([M]+Na^+) = 514.1062, Found 514.1058.
HRMS (ESI) Calculated for $C_{24}H_{26}{}^{36.9659}ClNO_6S$ ([M]+Na^+) = 516.1032, Found 516.1033.
IR (neat): 2953, 1735, 1648, 1598, 1485, 1434, 1352, 1164, 1089, 1025, 970, 900, 814, 664, 546 cm^{-1}.



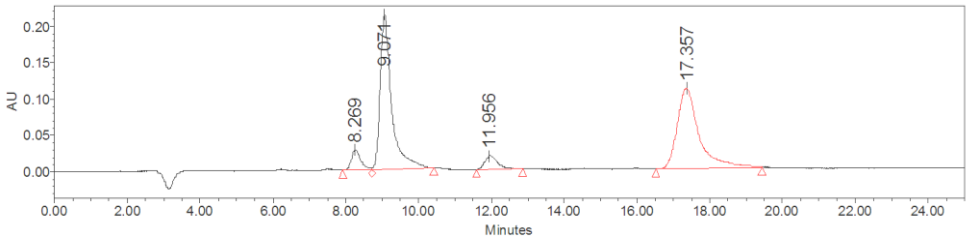
	Retention Time	Area	% Area
1	6.410	6092353	49.88
2	9.203	6120943	50.12



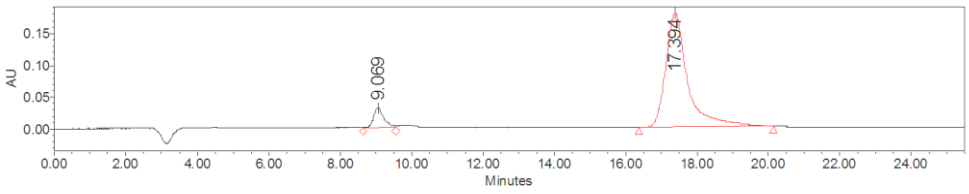
	Retention Time	Area	% Area
1	6.306	6461187	96.97
2	8.918	201783	3.03



Dimethyl 2-[5-methyl-3-(prop-1-en-2-yl)-1-tosyl-1,2,3,4-tetrahydroquinolin-4-yl]malonate (2v):
1:1 dr, the major diastereomer was isolated as colorless oil in 44% yield, ee = 85%, $[\alpha]^{21}_{D}$ = –94.9 (*c* = 0.37, in CH_2Cl_2).
HPLC: Chiralcel ADH, hexane/*i*-PrOH = 85/15, flow rate 1.0 mL/min, λ = 220 nm, t_{r1} = 9.07 min, t_{r2} = 17.39 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.4 Hz, 2H), 7.54 (d, *J* = 8.4 Hz, 1H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.05 (t, *J* = 8.0 Hz, 1H), 6.86 (d, *J* = 7.6 Hz, 1H), 4.94 (s, 1H), 4.76 (s, 1H), 4.20 (dd, *J* = 8.0, 2.8 Hz, 1H), 4.04 – 3.89 (m, 2H), 3.67 (s, 3H), 3.41 (d, *J* = 8.0 Hz, 1H), 3.07 (s, 3H), 2.41 (s, 3H), 2.37 – 2.30 (m, 4H), 1.79 (s, 3H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 168.8, 168.7, 143.8, 142.4, 137.0, 136.9, 136.6, 129.7, 128.7, 127.2, 125.7, 119.2, 111.7, 52.5, 51.9, 51.2, 44.9, 43.2, 35.0, 23.2, 21.6, 20.0.
HRMS (ESI) Calculated for $C_{25}H_{29}NO_6S$ ([M+Na$^+$]) = 494.1608, Found 494.1606.
IR (neat): 2951, 1734, 1646, 1595, 1469, 1434, 1350, 1284, 1246, 1162, 1093, 1035, 813, 655, 575 cm^{-1}.



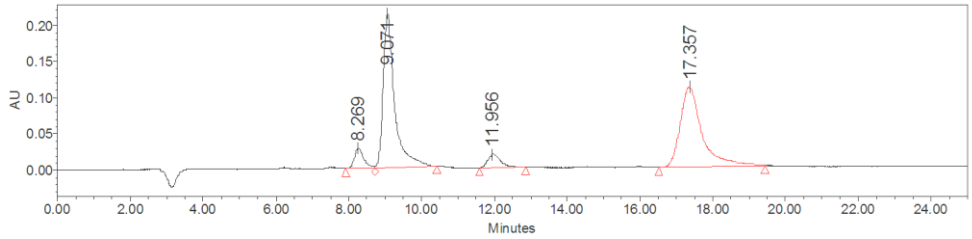
	Retention Time	Area	% Area
1	8.269	488349	4.82
2	9.071	4610161	45.48
3	11.956	465501	4.59
4	17.357	4573107	45.11



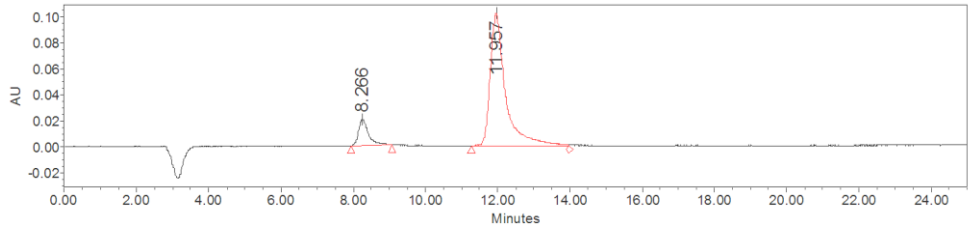
	Retention Time	Area	% Area
1	9.069	627026	7.58
2	17.394	7641357	92.42

The minor diastereomer was isolated as colorless oil in 43% yield, ee = 78%, $[\alpha]^{22}_{D}$ = –46.2 (*c* = 0.19, in CH_2Cl_2).
HPLC: Chiralcel ADH, hexane/*i*-PrOH = 85/15, flow rate 1.0 mL/min, λ = 220 nm, t_{r1} = 8.27 min, t_{r2} = 11.96 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 – 7.77 (m, 2H), 7.54 (d, *J* = 8.4 Hz, 1H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.07 (t, *J* = 8.0 Hz, 1H), 6.87 (d, *J* = 7.2 Hz, 1H), 4.64 (s, 1H), 4.48 (s, 1H), 4.00 (dd, *J* = 12.4, 8.0 Hz, 1H), 3.89 (dd, *J* = 11.2, 2.0 Hz, 1H), 3.76 (s, 3H), 3.50 (dd, *J* = 12.4, 4.0 Hz, 1H), 3.35 (d, *J* = 10.8 Hz, 1H), 3.30 (s, 3H), 2.96 – 2.90 (m, 1H), 2.41 (s, 3H), 2.23 (s, 3H), 1.62 (s, 3H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 168.6, 168.4, 144.5, 143.7, 137.8, 137.0, 136.6, 129.8, 127.7, 127.4, 127.3, 126.5, 120.1, 112.5, 54.2, 52.7, 52.1, 47.2, 45.1, 37.1, 21.6, 21.1, 19.3.
HRMS (ESI) Calculated for $C_{25}H_{29}NO_6S$ ([M+Na$^+$]) = 494.1608, Found 494.1598.

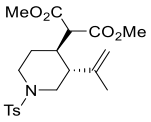
IR (neat): 2952, 1734, 1649, 1596, 1434, 1349, 1261, 1160, 1095, 1029, 984, 812, 781, 736, 664, 578, 544 cm^{-1}.



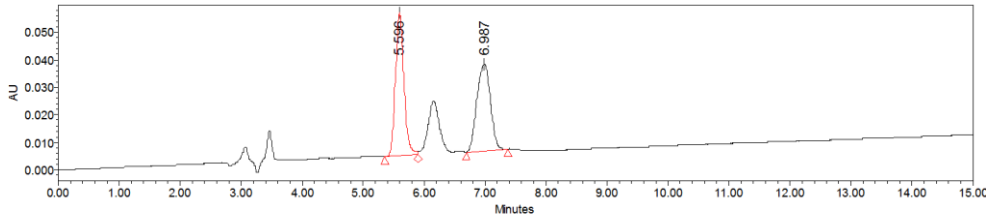
	Retention Time	Area	% Area
1	8.269	488349	4.82
2	9.071	4610161	45.48
3	11.956	465501	4.59
4	17.357	4573107	45.11



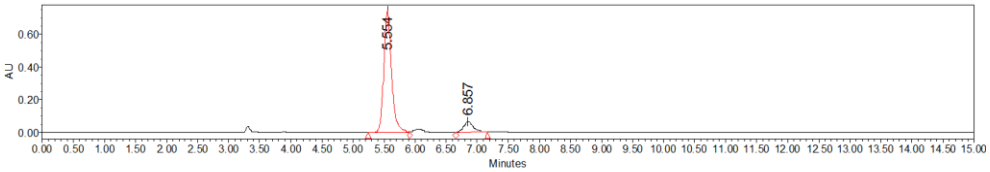
	Retention Time	Area	% Area
1	8.266	368168	10.94
2	11.957	2998212	89.06



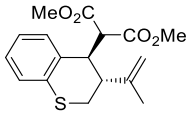
Dimethyl 2-[3-(prop-1-en-2-yl)-1-tosylpiperidin-4-yl]malonate (2w):
6:1 dr, the major diastereomer was isolated as white solid in 80% yield, m.p. = 76 – 80 °C, ee = 81%, $[\alpha]^{23}_{D}$ = –62.0 (*c* = 0.52, in CH_2Cl_2).
HPLC: Chiralcel IA, hexane/*i*-PrOH = 70/30, flow rate 1.0 mL/min, λ = 210 nm, t_{r1} = 5.55 min, t_{r2} = 6.86 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 4.94 (s, 1H), 4.78 (s, 1H), 3.87 – 3.80 (m, 1H), 3.78 – 3.70 (m, 4H), 3.68 (s, 3H), 3.57 (d, *J* = 3.2 Hz, 1H), 2.44 (s, 3H), 2.36 (td, *J* = 11.2, 4.0 Hz, 1H), 2.26 (td, *J* = 12.0, 2.4 Hz, 1H), 2.09 (t, *J* = 11.2 Hz, 1H), 2.04 – 1.89 (m, 2H), 1.73 – 1.62 (m, 4H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 169.3, 168.3, 143.6, 143.2, 133.0, 129.7, 127.7, 114.6, 52.5, 52.2, 51.9, 51.0, 46.5, 46.3, 38.3, 26.8, 21.5, 20.7.
HRMS (ESI) Calculated for $C_{20}H_{27}NO_6S$ ([M]+Na^+) = 432.1451, Found 432.1451.
IR (neat): 2919, 1759, 1734, 1435, 1379, 1336, 1264, 1185, 905, 850, 815, 755, 657, 547 cm^{-1}.



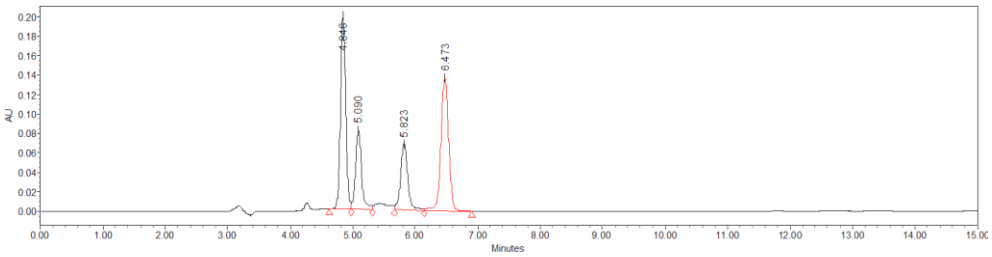
	Retention Time	Area	% Area
1	5.596	509695	51.32
2	6.987	483548	48.68



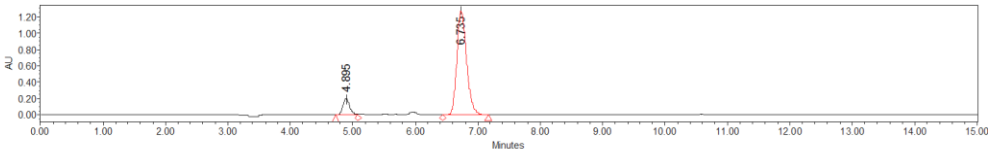
	Retention Time	Area	% Area
1	5.554	6450180	90.48
2	6.857	678572	9.52



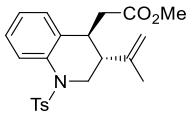
Dimethyl 2-[3-(prop-1-en-2-yl)thiochroman-4-yl]malonate (2x):
4:1 dr, the major diastereomer was isolated as white solid in 71% yield, m.p. = 36 – 38 °C, ee = 80%, $[\alpha]^{23}_{D}$ = –123.5 (*c* = 0.43, in CH_2Cl_2).
HPLC: Chiralcel IC, hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 210 nm, t_{r1} = 4.90 min, t_{r2} = 6.74 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 – 7.11 (m, 1H), 7.11 – 7.06 (m, 1H), 7.06 – 7.03 (m, 1H), 6.99 – 6.94 (m, 1H), 4.85 (s, 1H), 4.72 (q, *J* = 1.2 Hz, 1H), 3.99 (d, *J* = 11.2 Hz, 1H), 3.82 – 3.77 (m, 4H), 3.45 (s, 3H), 3.24 (dd, *J* = 12.8, 6.4 Hz, 1H), 3.04 (ddd, *J* = 12.9, 3.5, 1.0 Hz, 1H), 2.88 – 2.83 (m, 1H), 1.71 (s, 3H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 168.5, 168.2, 144.2, 133.6, 131.7, 131.0, 127.6, 127.1, 124.4, 112.2, 54.6, 52.8, 52.3, 42.6, 41.0, 27.3, 21.4.
HRMS (ESI) Calculated for $C_{17}H_{20}O_4S$ ([M]+Na$^+$) = 343.0975, Found 343.0970.
IR (neat): 2953, 1745, 1724, 1650, 1433, 1290, 1256, 1182, 1142, 1070, 935, 907, 754, 730 cm^{-1}.



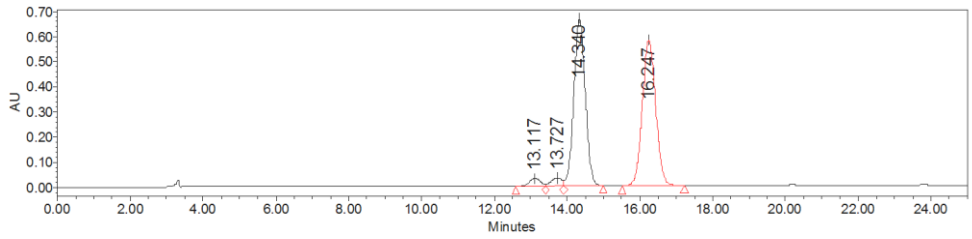
	Retention Time	Area	% Area
1	4.846	1148918	33.69
2	5.090	543183	15.93
3	5.823	545848	16.01
4	6.473	1171980	34.37



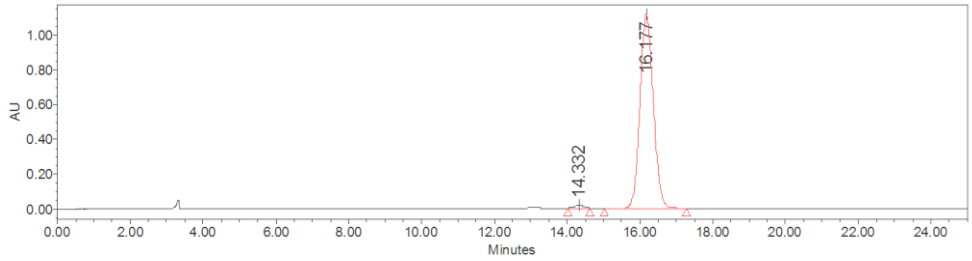
	Retention Time	Area	% Area
1	4.895	1510584	9.90
2	6.735	13746207	90.10



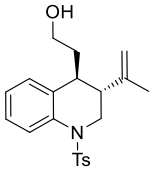
Methyl 2-[3-(prop-1-en-2-yl)-1-tosyl-1,2,3,4-tetrahydroquinolin-4-yl]acetate (3s):
The product was isolated as colorless oil in 94% yield, ee = 98%, $[\alpha]^{22}_{D}$ = –65.3 (*c* = 0.98, in CH_2Cl_2).
HPLC: Chiralcel IC, hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 210 nm, t_{r1} = 14.33 min, t_{r2} = 16.18 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.0 Hz, 1H), 7.53 (d, *J* = 8.0 Hz, 2H), 7.26 – 7.17 (m, 3H), 7.14 – 7.09 (m, 2H), 4.83 (t, *J* = 1.2 Hz, 1H), 4.65 (s, 1H), 4.02 (dd, *J* = 13.6, 4.4 Hz, 1H), 3.59 (s, 3H), 3.39 (dd, *J* = 13.6, 10.4 Hz, 1H), 3.20 – 3.13 (m, 1H), 2.40 (s, 3H), 2.21 (dd, *J* = 15.6, 6.4 Hz, 1H), 2.13 – 2.01 (m, 2H), 1.65 (s, 3H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 172.6, 144.0, 143.3, 136.7, 136.5, 132.8, 129.7, 128.1, 127.2, 126.9, 125.5, 125.0, 114.0, 51.6, 49.4, 45.7, 39.8, 36.0, 19.6.
HRMS (ESI) Calculated for $C_{22}H_{25}NO_4S$ ([M]+Na$^+$) = 422.1397, Found 422.1392.
IR (neat): 2950, 2924, 1733, 1489, 1436, 1349, 1159, 1068, 890, 814, 761, 713, 651 cm^{-1}.



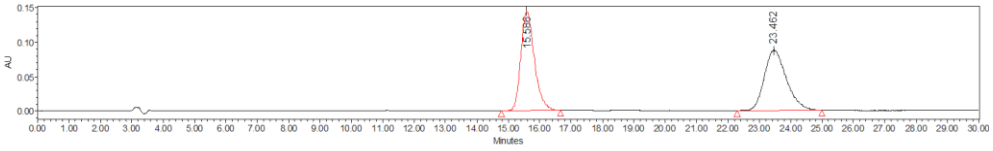
	Retention Time	Area	% Area
1	13.117	639435	2.09
2	13.727	664320	2.17
3	14.340	14563547	47.61
4	16.247	14721007	48.13



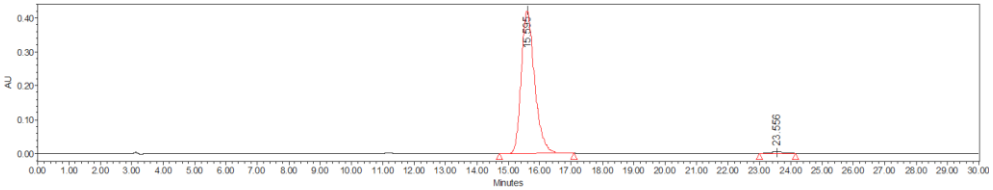
	Retention Time	Area	% Area
1	14.332	320070	1.12
2	16.177	28311228	98.88



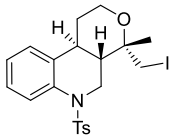
2-[3-(Prop-1-en-2-yl)-1-tosyl-1,2,3,4-tetrahydroquinolin-4-yl]ethan-1-ol (4s):
The product was isolated as colorless oil in 90% yield, ee = 98%, $[\alpha]^{23}_{D}$ = –57.8 (*c* = 1.20, in CH_2Cl_2).
HPLC: Chiralcel IA, hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 210 nm, t_{r1} = 15.60 min, t_{r2} = 23.56 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.0 Hz, 1H), 7.55 (d, *J* = 8.4 Hz, 2H), 7.26 – 7.15 (m, 4H), 7.11 (t, *J* = 7.2 Hz, 1H), 4.85 (s, 1H), 4.69 (s, 1H), 4.06 (dd, *J* = 13.6, 4.4 Hz, 1H), 3.34 (dd, *J* = 13.6, 10.0 Hz, 1H), 3.26 – 3.11 (m, 2H), 2.87 (q, *J* = 6.4 Hz, 1H), 2.38 (s, 3H), 2.23 – 2.13 (m, 1H), 1.68 (s, 3H), 1.58 – 1.38 (m, 2H), 1.24 (s, 1H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 144.5, 143.9, 136.8, 136.8, 133.2, 129.6, 128.8, 127.3, 126.6, 125.3, 124.9, 113.2, 59.6, 49.7, 44.6, 37.2, 36.5, 21.5, 20.5.
HRMS (ESI) Calculated for $C_{21}H_{25}NO_3S$ ([M+Na$^+$) = 394.1447, Found 394.1429.
IR (neat): 2936, 1645, 1597,1487, 1448, 1344, 1159, 1089, 1071, 1043, 966, 896, 813, 759, 734, 712, 659, 572 cm^{-1}.



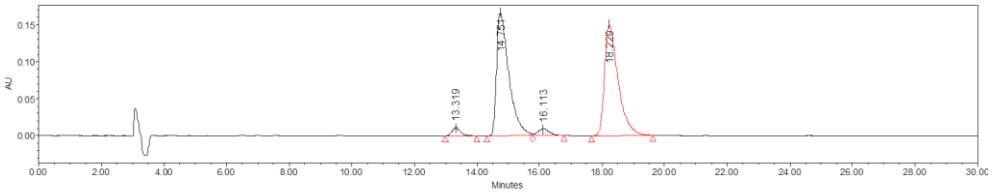
	Retention Time	Area	% Area
1	15.586	4285216	50.08
2	23.462	4271572	49.92



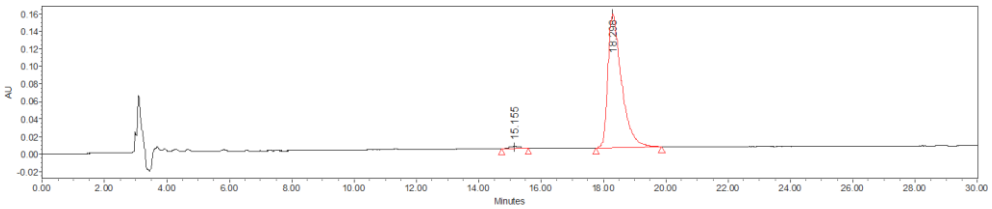
	Retention Time	Area	% Area
1	15.595	12359104	99.10
2	23.556	112520	0.90



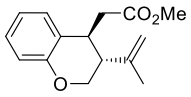
4-(Iodomethyl)-4-methyl-6-tosyl-1,4,4a,5,6,10b-hexahydro-2H-pyrano[3,4-c]quinolone (5s):
The product was isolated as colorless oil in 75% yield, ee = 98%, $[\alpha]^{22}_{D}$ = +17.3 (*c* = 0.59, in CH_2Cl_2).
HPLC: Chiralcel IB, hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 210 nm, t_{r1} = 15.16 min, t_{r2} = 18.30 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.0 Hz, 1H), 7.46 (d, *J* = 8.0 Hz, 2H), 7.26 – 7.20 (m, 3H), 7.19 – 7.10 (m, 2H), 4.12 (dd, *J* = 13.2, 4.8 Hz, 1H), 3.80 (dd, *J* = 12.4, 4.4 Hz, 1H), 3.55 – 3.41 (m, 2H), 3.24 (dd, *J* = 13.2, 11.6 Hz, 1H), 3.10 (d, *J* = 11.2 Hz, 1H), 2.43 – 2.33 (m, 4H), 2.13 – 2.05 (m, 1H), 1.67 – 1.59 (m, 1H), 1.39 – 1.25 (m, 4H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 144.1, 136.2, 136.0, 132.8, 129.7, 127.2, 125.4, 124.8, 72.2, 61.0, 47.2, 43.9, 34.0, 29.6, 27.5, 21.6, 10.3.
HRMS (ESI) Calculated for $C_{21}H_{24}INO_3S$ ([M]+Na^+) = 520.0414, Found 520.0407.
IR (neat): 2935, 1598, 1486, 1449, 1347, 1162, 1125, 1089, 962, 890, 873, 814, 759, 732, 713, 698, 662, 585, 564, 539 cm^{-1}.



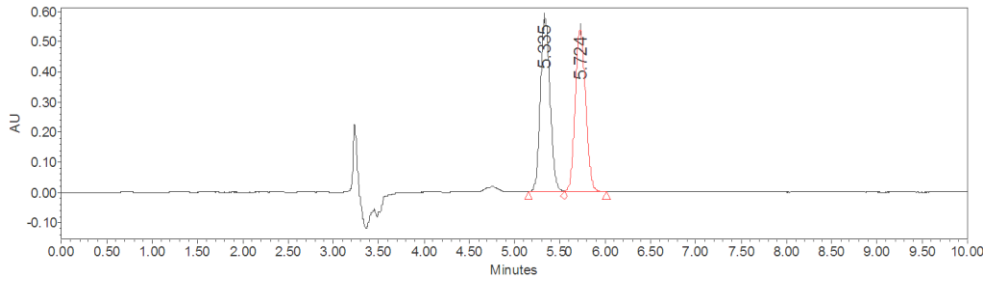
	Retention Time	Area	% Area
1	13.319	222870	2.32
2	14.751	4557055	47.53
3	16.113	248190	2.59
4	18.229	4559938	47.56



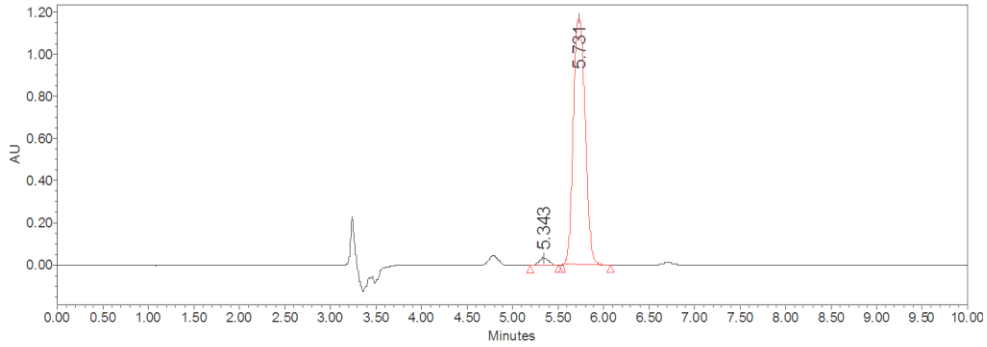
	Retention Time	Area	% Area
1	15.155	44314	0.95
2	18.298	4612460	99.05



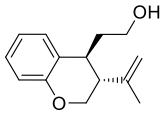
Methyl 2-[3-(prop-1-en-2-yl)chroman-4-yl]acetate (3b):
The product was isolated as colorless oil in 96% yield, ee = 95%, $[\alpha]^{23}_{D}$ = –63.0 (*c* = 0.38, in CH_2Cl_2).
HPLC: Chiralcel IC, hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min, λ = 220 nm, t_{r1} = 5.34 min, t_{r2} = 5.73 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.04 – 6.98 (m, 2H), 6.78 (td, *J* = 7.6, 0.8 Hz, 1H), 6.71 (d, *J* = 8.4 Hz, 1H), 4.85 – 4.83 (m, 1H), 4.76 (s, 1H), 4.08 (dd, *J* = 11.2, 3.2 Hz, 1H), 3.97 (dd, *J* = 11.2, 7.2 Hz, 1H), 3.60 (s, 3H), 3.36 (q, *J* = 6.8 Hz, 1H), 2.60 (d, *J* = 6.0 Hz, 2H), 2.39 (td, *J* = 7.2, 3.2 Hz, 1H), 1.71 (s, 3H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 172.9, 154.2, 143.4, 128.5, 127.7, 124.5, 120.8, 116.8, 113.6, 66.9, 51.7, 44.5, 40.3, 34.5, 21.3.
HRMS (ESI) Calculated for $C_{15}H_{18}O_3$ ([M]+Na^+) = 269.1149, Found 269.1146.
IR (neat): 2950, 1733, 1645, 1607, 1581, 1489, 1435, 1359, 1311, 1225, 1160, 1119, 1052, 1014, 898, 752 cm^{-1}.



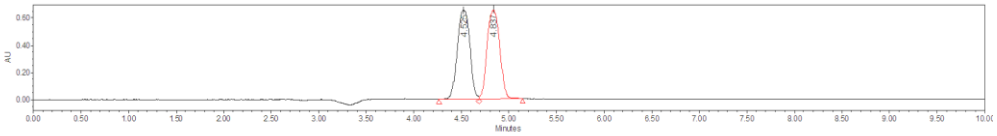
	Retention Time	Area	% Area
1	5.335	4305025	49.84
2	5.724	4332223	50.16



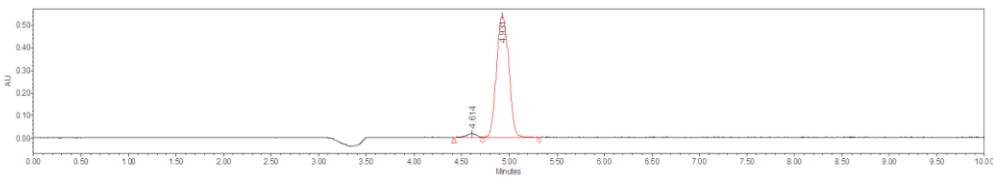
	Retention Time	Area	% Area
1	5.343	237471	2.21
2	5.731	10515595	97.79



2-[3-(Prop-1-en-2-yl)chroman-4-yl]ethan-1-ol (4b):
The product was isolated as colorless oil in 93% yield, ee = 95%, $[\alpha]^{23}_{D}$ = –44.0 (*c* = 0.45, in CH_2Cl_2).
HPLC: Chiralcel IC, hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 210 nm, t_{r1} = 4.61 min, t_{r2} = 4.93 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (d, *J* = 7.6 Hz, 1H), 7.12 – 7.06 (m, 1H), 6.88 (td, *J* = 7.6, 1.2 Hz, 1H), 6.79 (dd, *J* = 8.0, 1.2 Hz, 1H), 4.91 – 4.88 (m, 1H), 4.80 (s, 1H), 4.17 (dd, *J* = 11.2, 3.6 Hz, 1H), 4.10 – 4.03 (m, 1H), 3.78 – 3.66 (m, 2H), 3.07 (q, *J* = 6.0 Hz, 1H), 2.46 – 2.40 (m, 1H), 2.07 – 1.99 (m, 1H), 1.99 – 1.90 (m, 1H), 1.80 (s, 3H), 1.72 (s, 1H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 154.3, 144.3, 129.2, 127.3, 125.1, 120.6, 116.7, 112.8, 66.6, 60.1, 43.9, 38.7, 34.5, 21.8.
HRMS (ESI) Calculated for $C_{14}H_{18}O_2$ ([M]+Na^+) = 241.1199, Found 241.1202.
IR (neat): 2882, 1645, 1606, 1581, 1488, 1450, 1376, 1310, 1225, 1120, 1043, 893, 753 cm^{-1}.

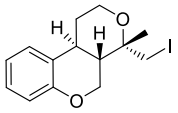


	Retention Time	Area	% Area
1	4.525	5962641	49.80
2	4.837	6010142	50.20

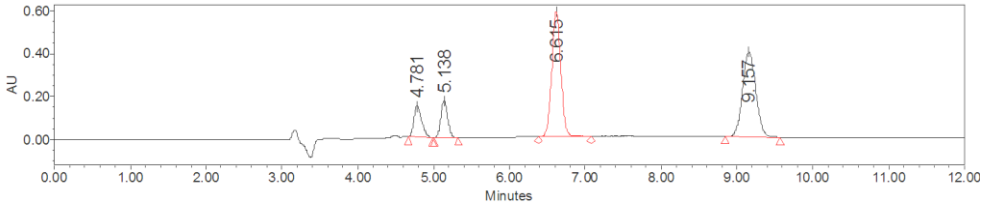


	Retention Time	Area	% Area
1	4.614	128758	2.59

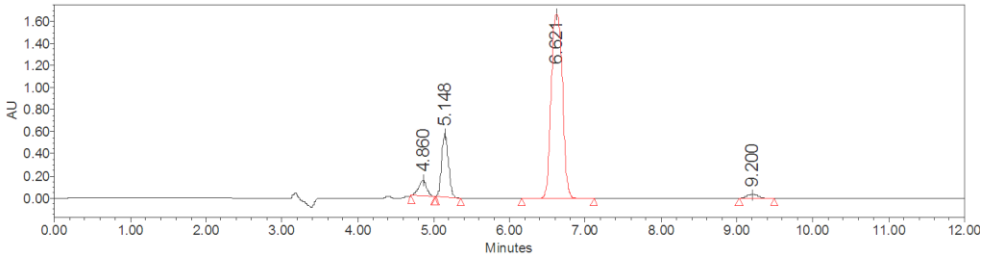
2	4.931	4837704	97.41



4-(Iodomethyl)-4-methyl-1,4a,5,10b-tetrahydro-2H,4H-pyrano[3,4-c]chromene (5b):
79:21 dr, the product was isolated as colorless oil in 75% yield, ee = 97%, $[\alpha]^{22}_{D}$ = +127.8 (*c* = 0.98, in CH_2Cl_2).
HPLC: Chiralcel IC, hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 220 nm, t_{r1} = 4.86 min, t_{r2} = 5.15 min, t_{r3} = 6.62 min, t_{r4} = 9.20 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 – 7.08 (m, 2H), 6.94 – 6.86 (m, 1H), 6.83 – 6.76 (m, 1H), 4.30 (dd, *J* = 10.4, 3.2 Hz, 1H), 3.96 – 3.89 (m, 1H), 3.80 – 3.72 (m, 2H), 3.62 (td, *J* = 12.4, 2.4 Hz, 1H), 3.00 (d, *J* = 10.8 Hz, 1H), 2.92 (td, *J* = 12.0, 4.0 Hz, 1H), 2.30 – 2.20 (m, 1H), 2.14 (td, *J* = 12.0, 3.2 Hz, 1H), 1.53 (qd, *J* = 12.8, 4.8 Hz, 1H), 1.42 – 1.38 (m, 3H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 153.5, 127.9, 126.0, 124.5, 120.6, 116.6, 71.7, 66.8, 61.3, 43.8, 32.9, 29.8, 27.8, 11.1.
HRMS (ESI) Calculated for $C_{14}H_{17}IO_2$ ([M]+Na^+) = 367.0165, Found 367.0173.
IR (neat): 2937, 2860, 1606, 1580, 1488, 1450, 1377, 1314, 1226, 1148, 1090, 1073, 1045, 988, 838, 716 cm^{-1}.



	Retention Time	Area	% Area
1	4.781	1060429	8.99
2	5.138	1102223	9.34
3	6.615	4827682	40.92
4	9.157	4807037	40.75



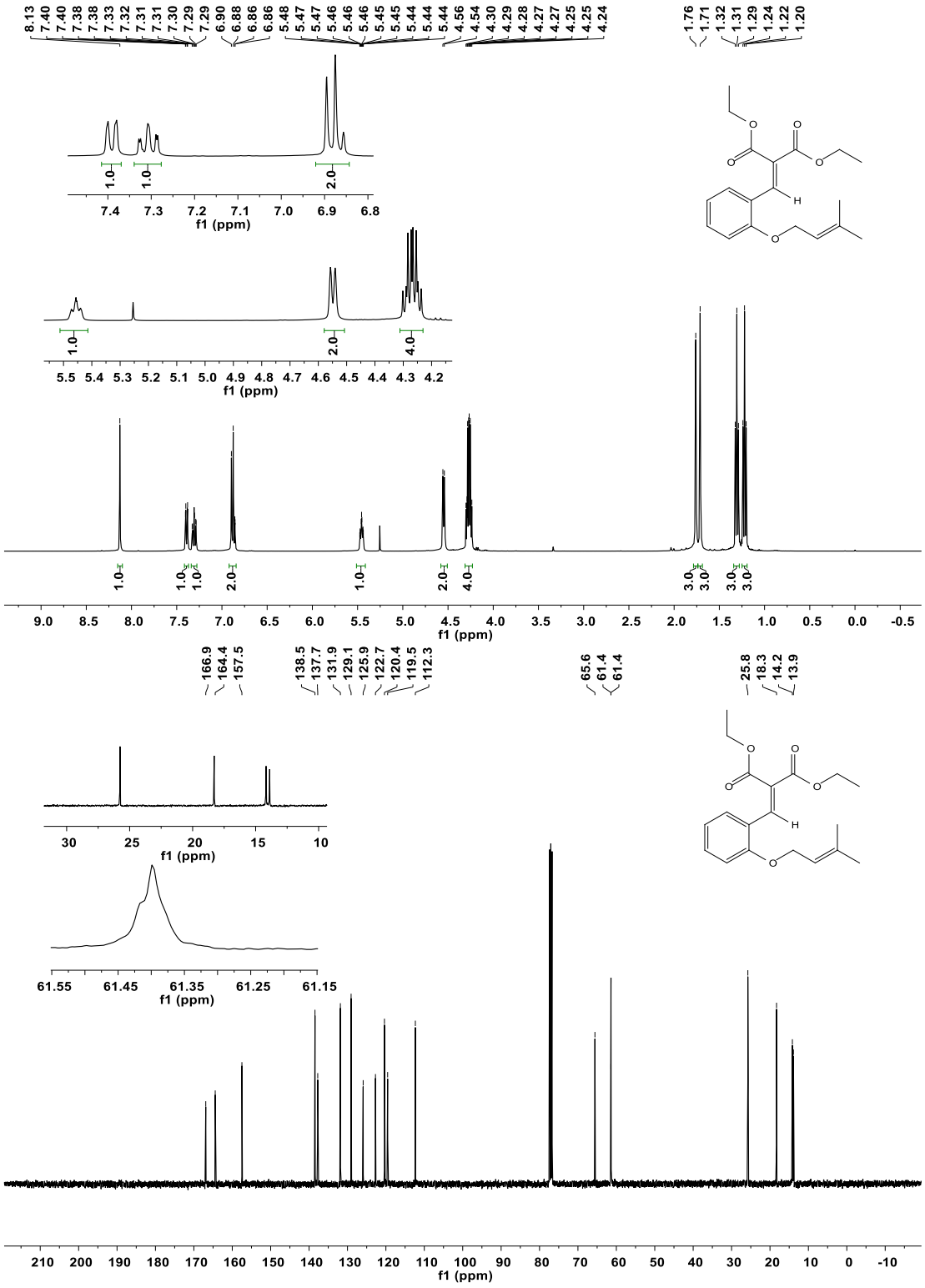
	Retention Time	Area	% Area
1	4.860	1093835	4.89
2	5.148	3637123	16.26
3	6.621	17241922	77.07
4	9.200	398233	1.78

References

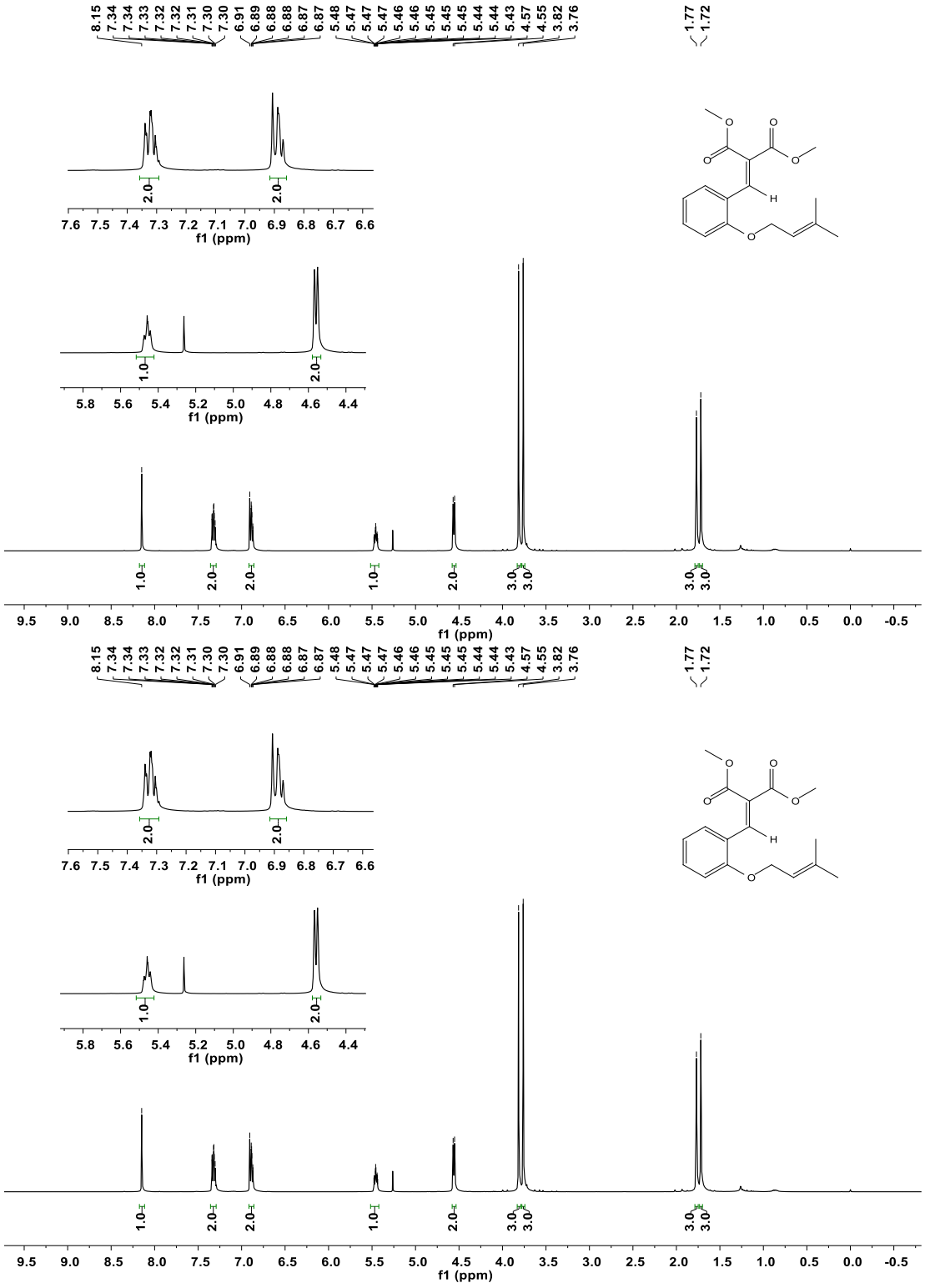
1 Y. H. Wen, X. Huang, J. L. Huang, Y. Xiong, B. Qin and X. M. Feng, *Synlett*, 2005, 2445.
2 R. J. Comito, F. G. Finelli and D. W. C. MacMillan, *J. Am. Chem. Soc.*, 2013, **135**, 9358.
3 M. Li, J. L. Petersen and J. M. Hoover, *Org. Lett.*, 2017, **19**, 638.
4 S. M. Walker, J. T. Williams, A. G. Russell, B. M. Kariuki and J. S. Snaith, *Org. Biomol. Chem.*, 2007, **5**, 2925.
5 X. H. Liu, H. F. Zheng, Y. Xia, L. L. Lin and X. M. Feng, *Acc. Chem. Res.*, 2017, **50**, 2621.

Copies of NMR Spectra for Substrates and Products

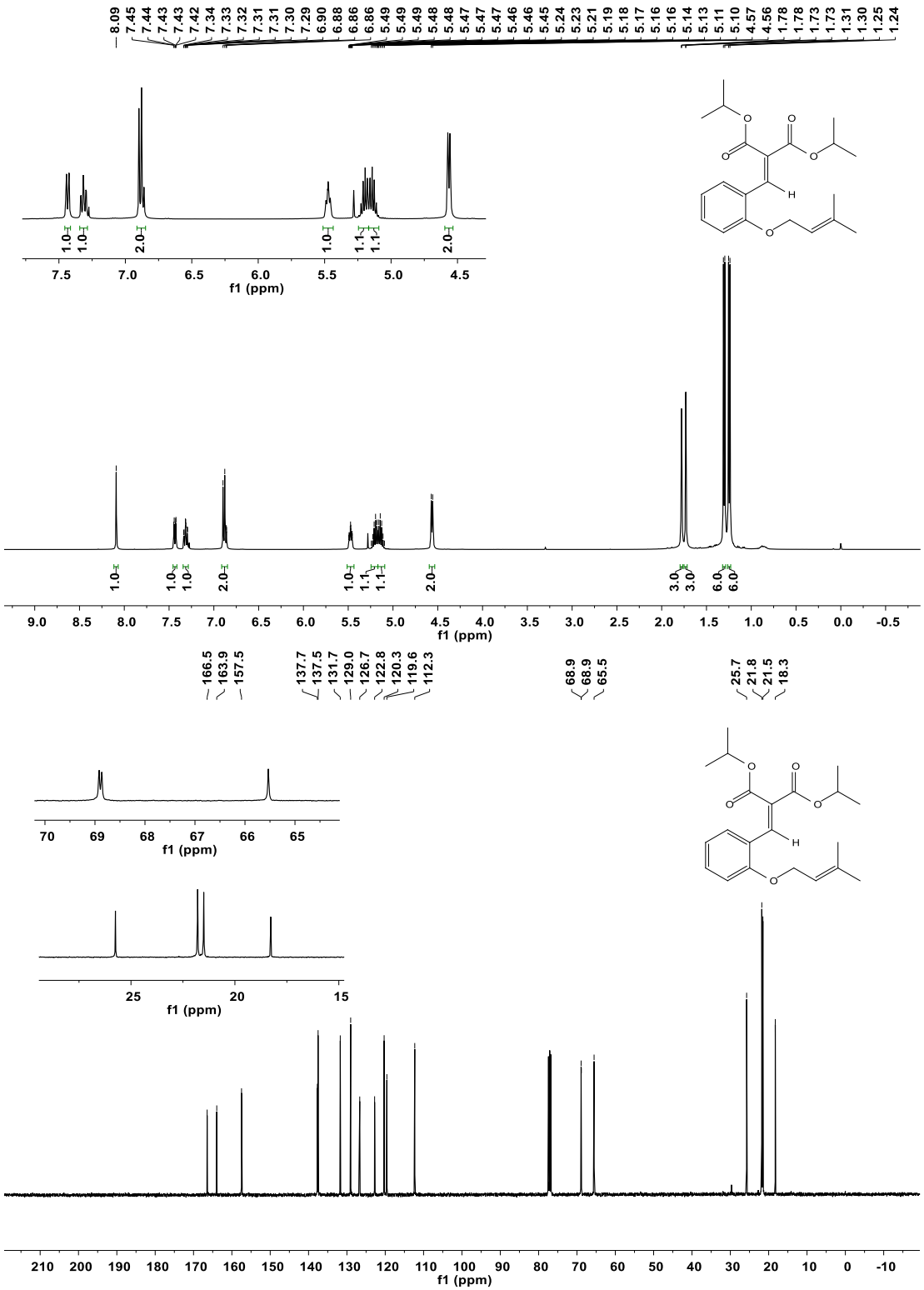
Diethyl 2-{2-[(3-methylbut-2-en-1-yl)oxy]benzylidene}malonate (1a):



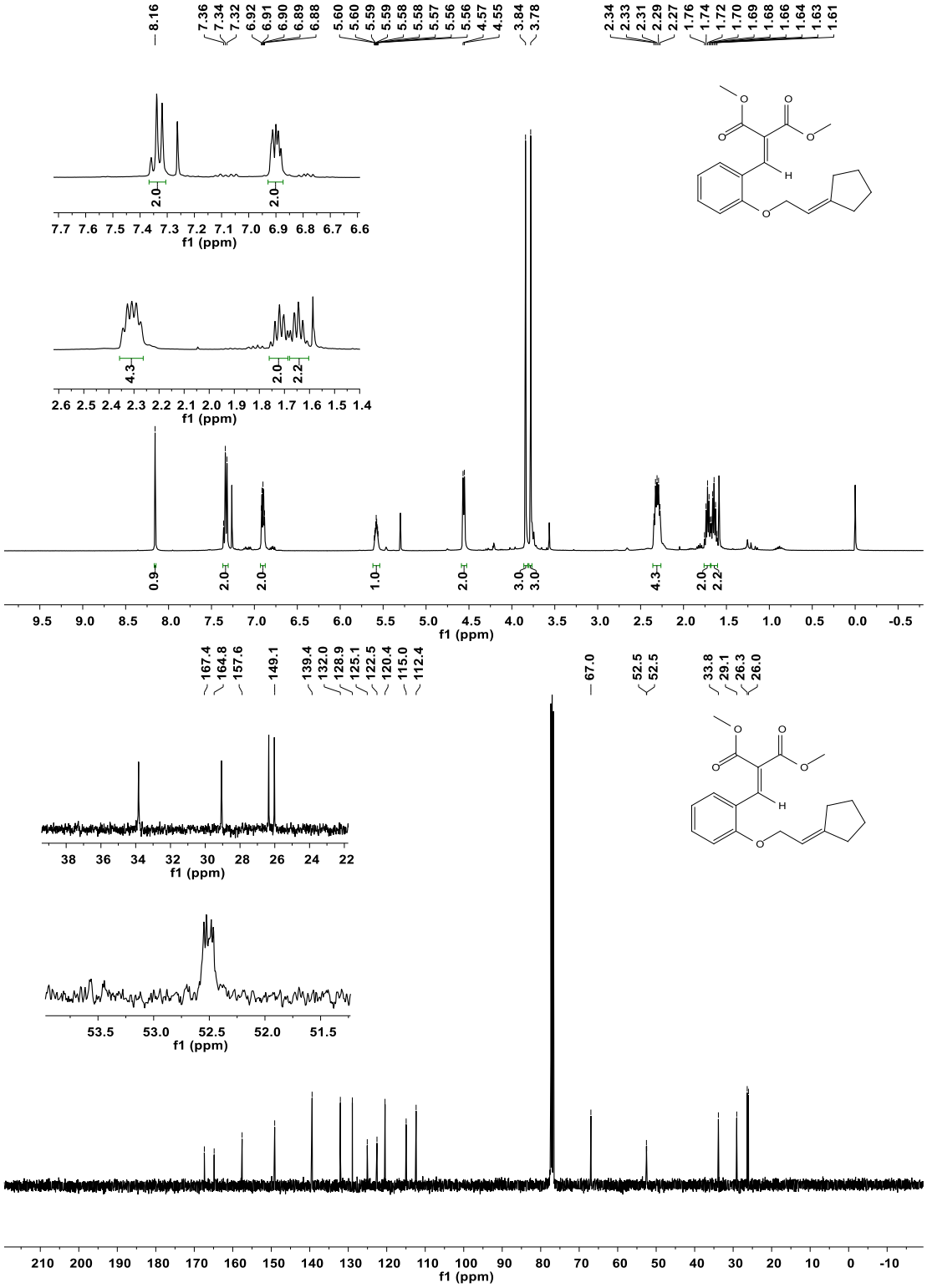
Dimethyl 2-{2-[(3-methylbut-2-en-1-yl)oxy]benzylidene}malonate (1b):



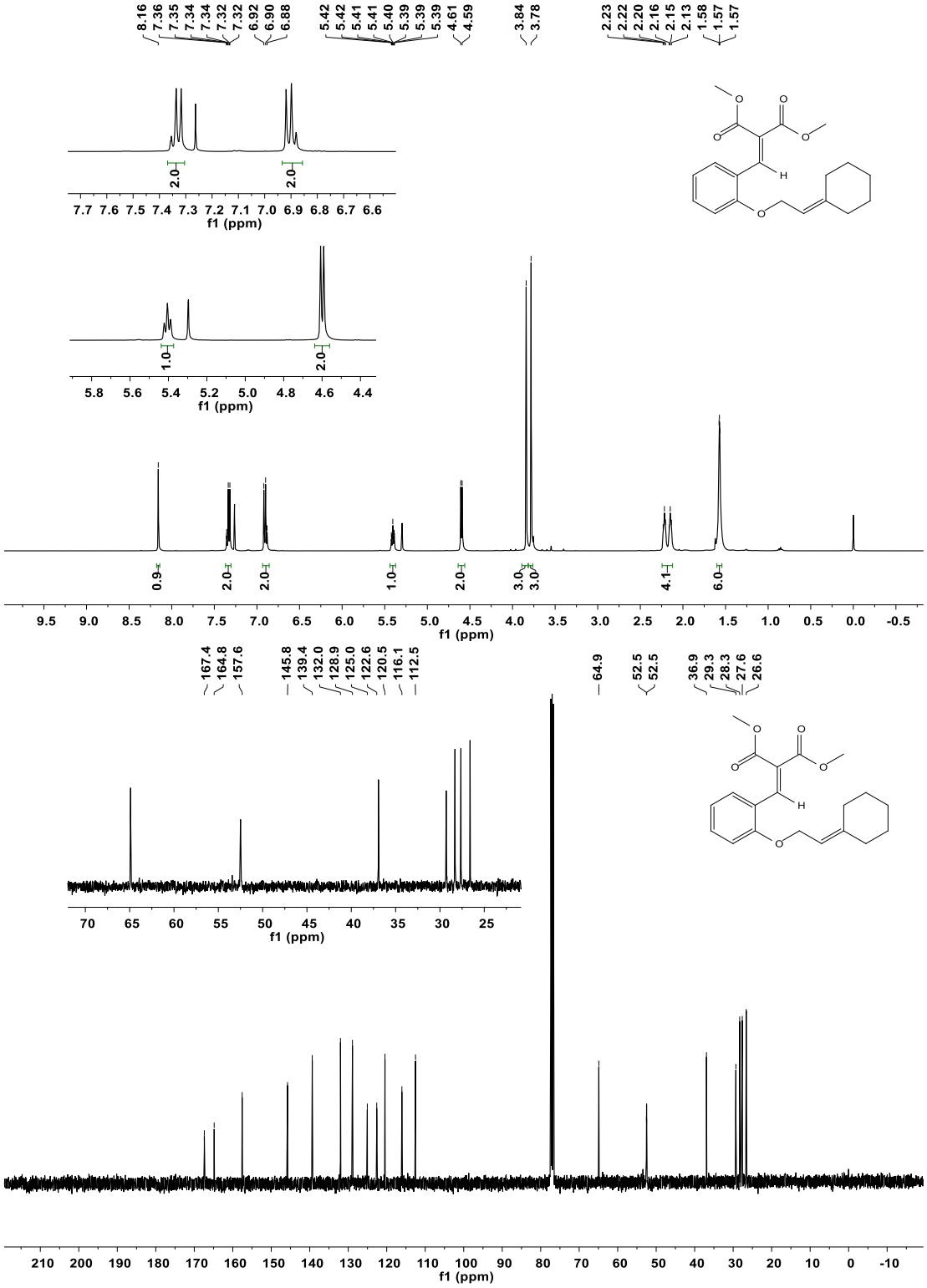
Diisopropyl 2-{2-[(3-methylbut-2-en-1-yl)oxy]benzylidene}malonate (1c):



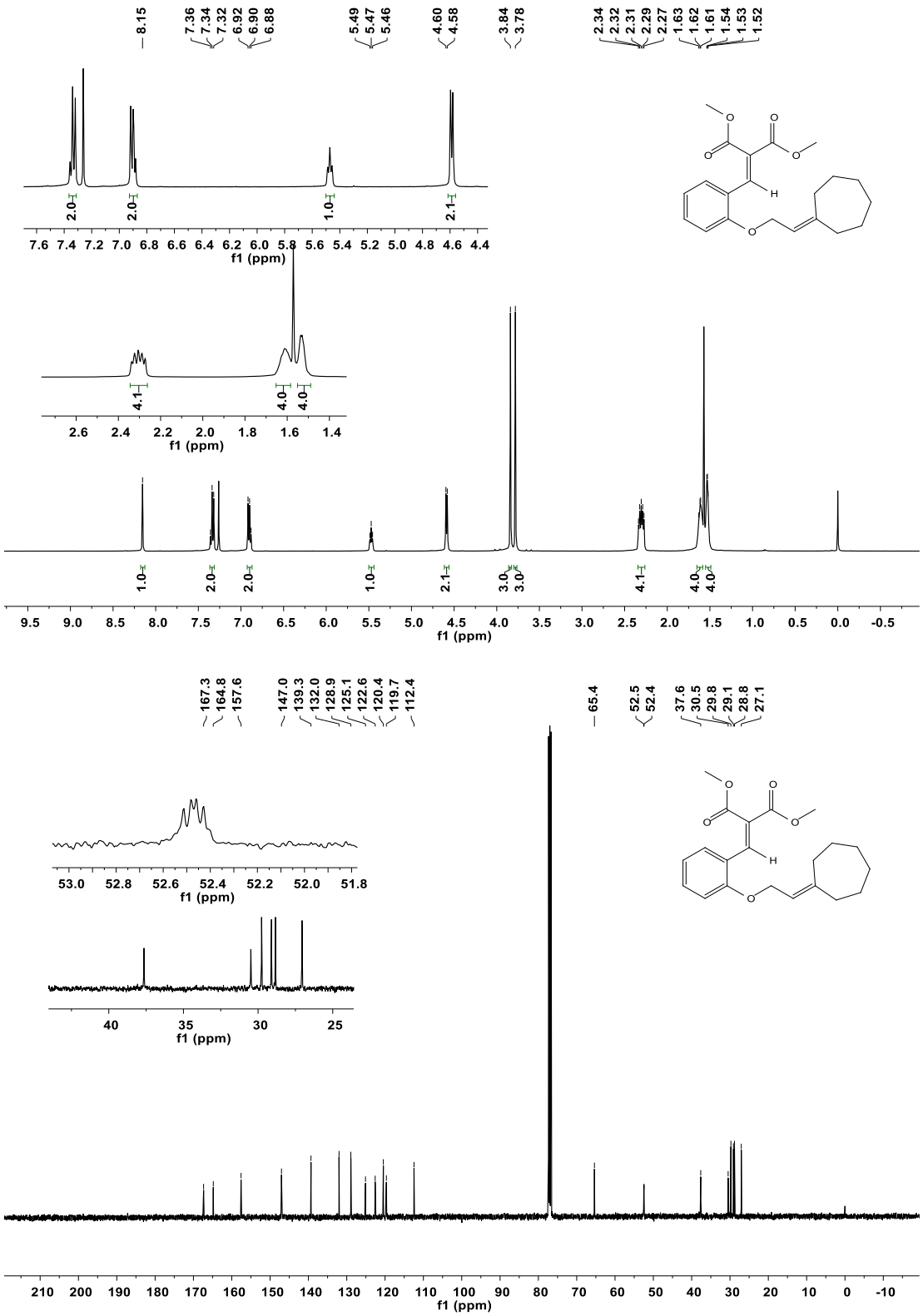
Dimethyl 2-[2-(2-cyclopentylideneethoxy)benzylidene]malonate (1d):



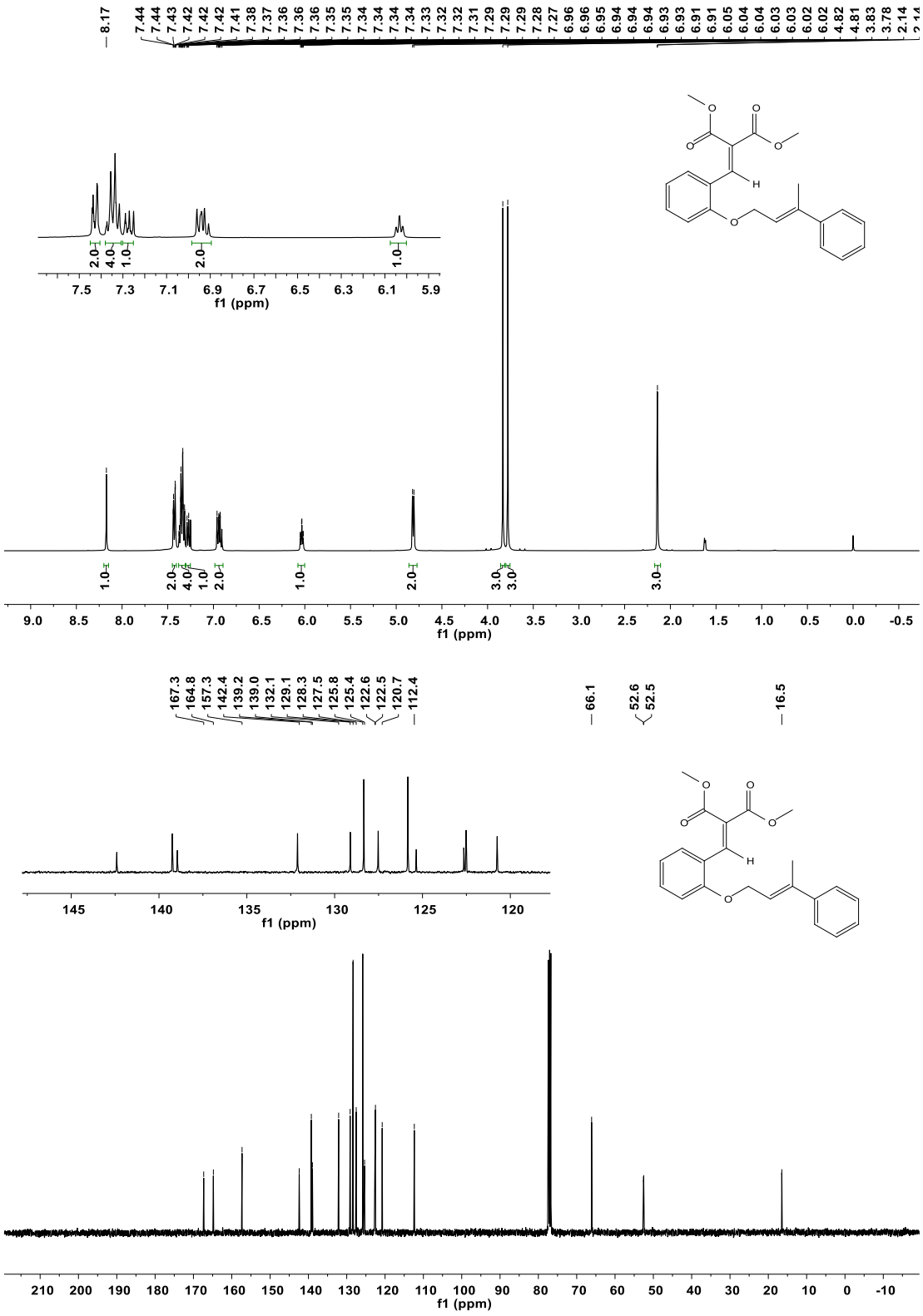
Dimethyl 2-[2-(2-cyclohexylideneethoxy)benzylidene]malonate (1e):



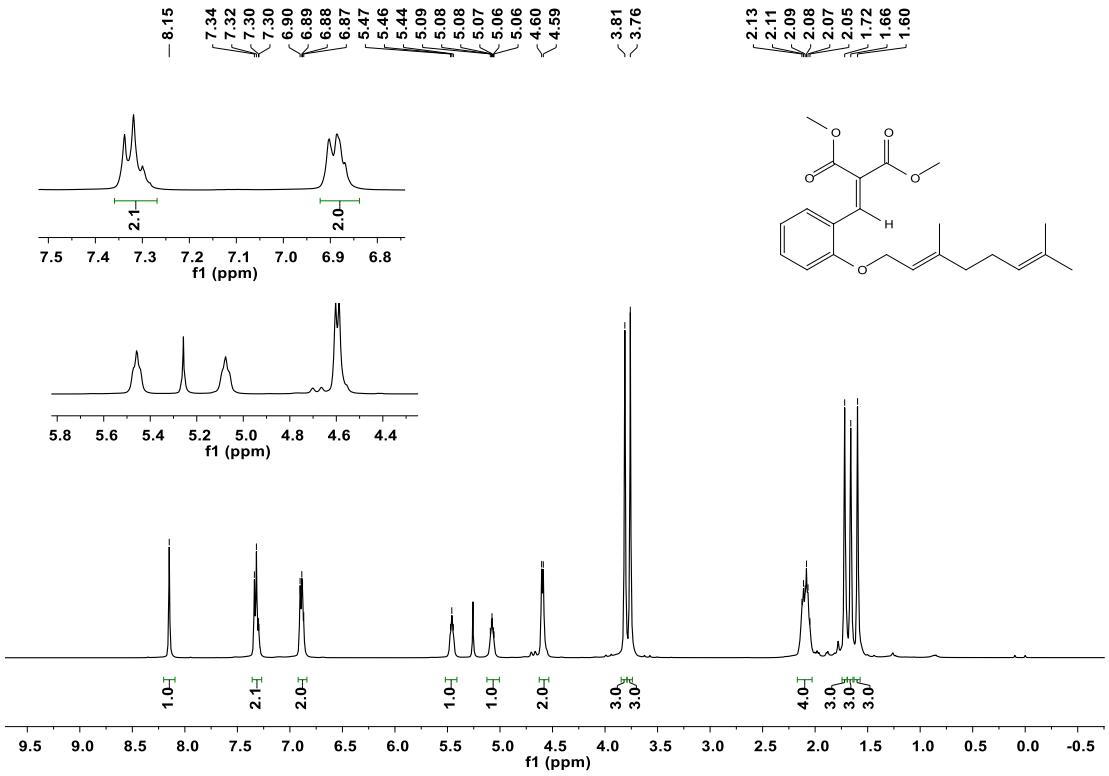
Dimethyl 2-[2-(2-cycloheptylideneethoxy)benzylidene]malonate (1f):

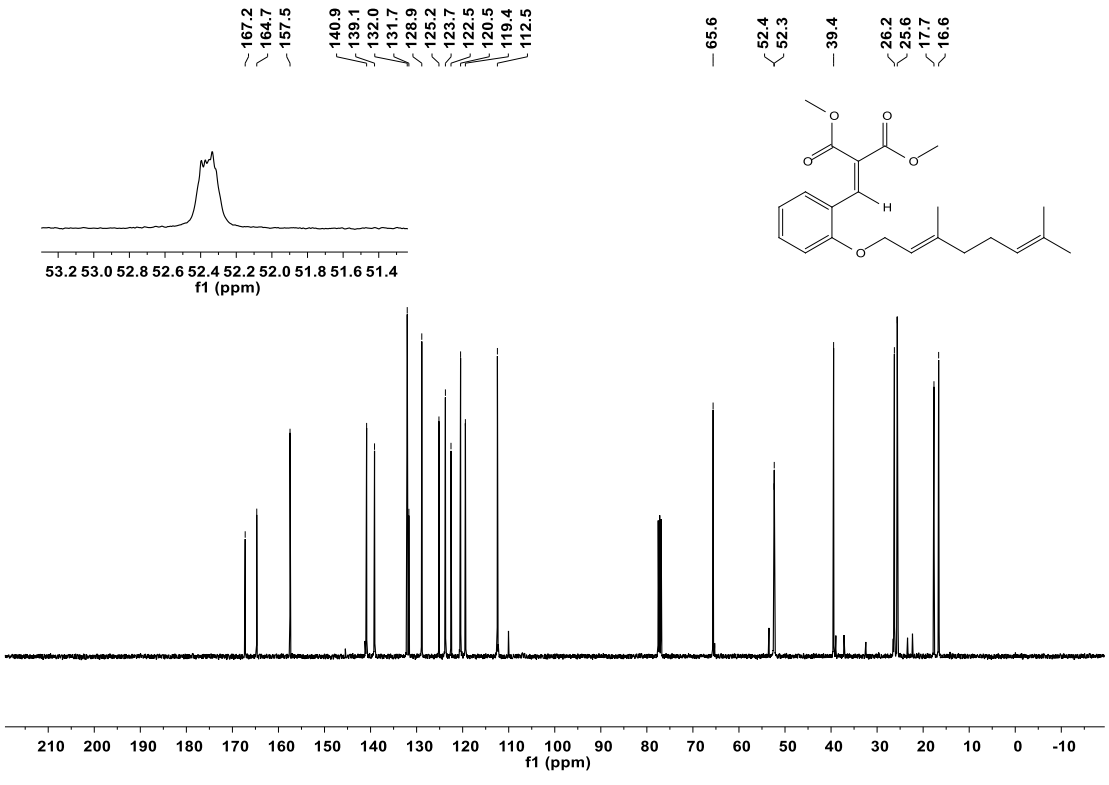


Dimethyl (E)-2-{2-[(3-phenylbut-2-en-1-yl)oxy]benzylidene}malonate (1g):

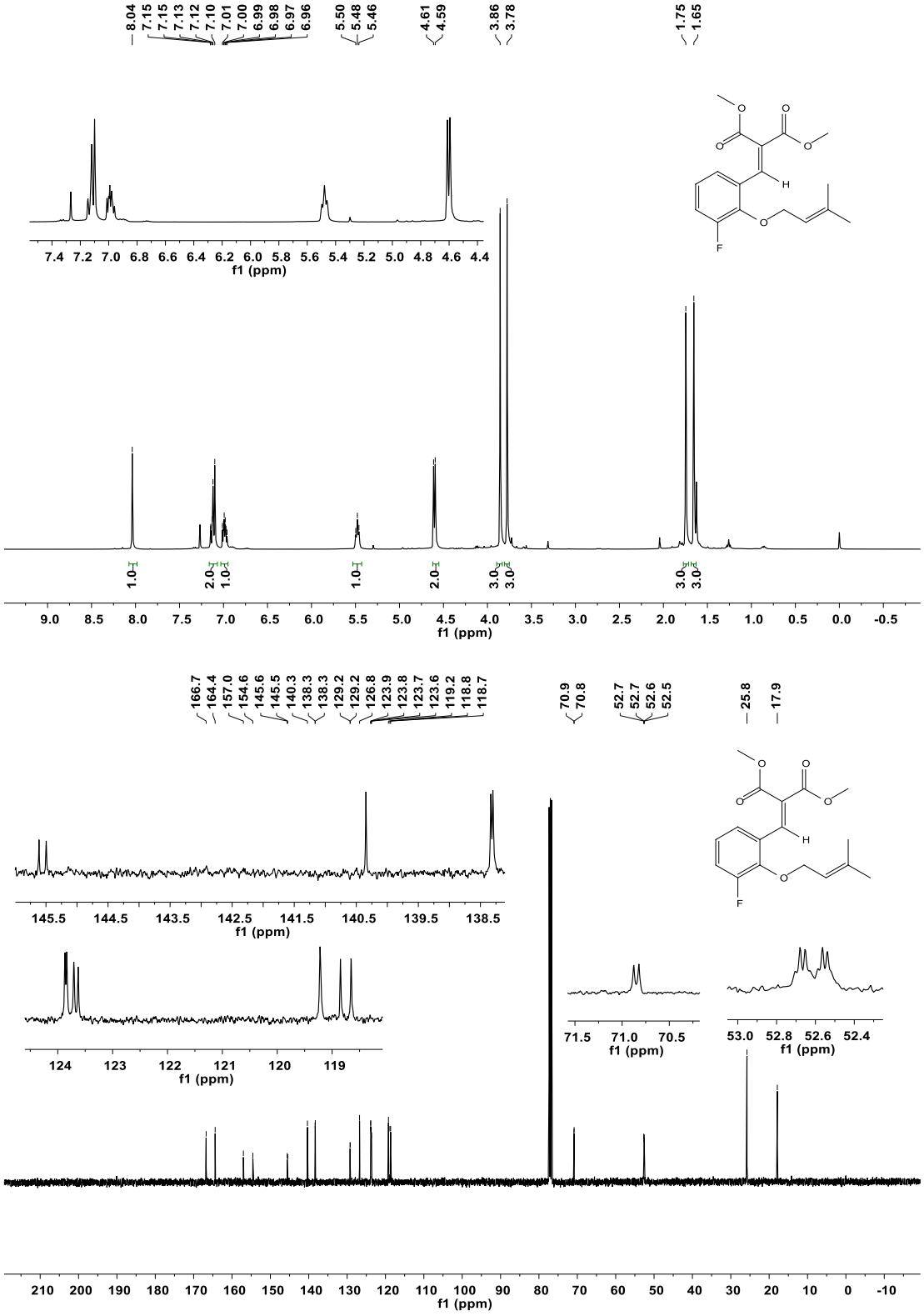


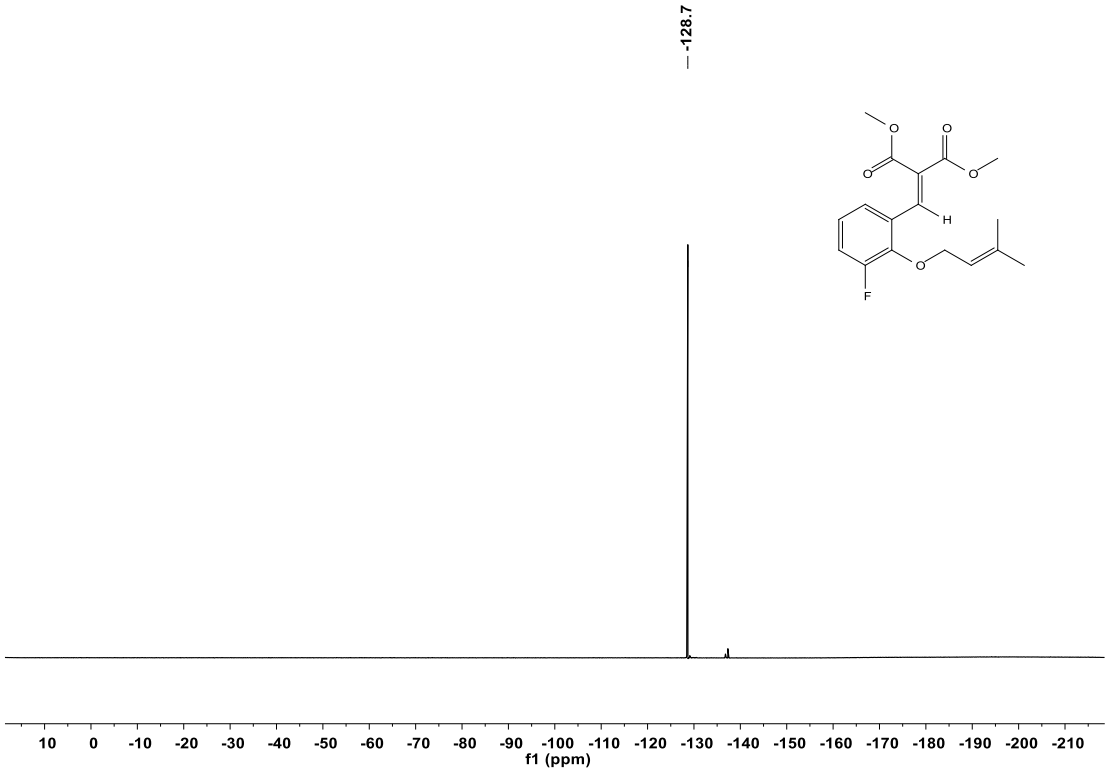
Dimethyl (E)-2-{2-[(3,7-dimethylocta-2,6-dien-1-yl)oxy]benzylidene}malonate (1h):



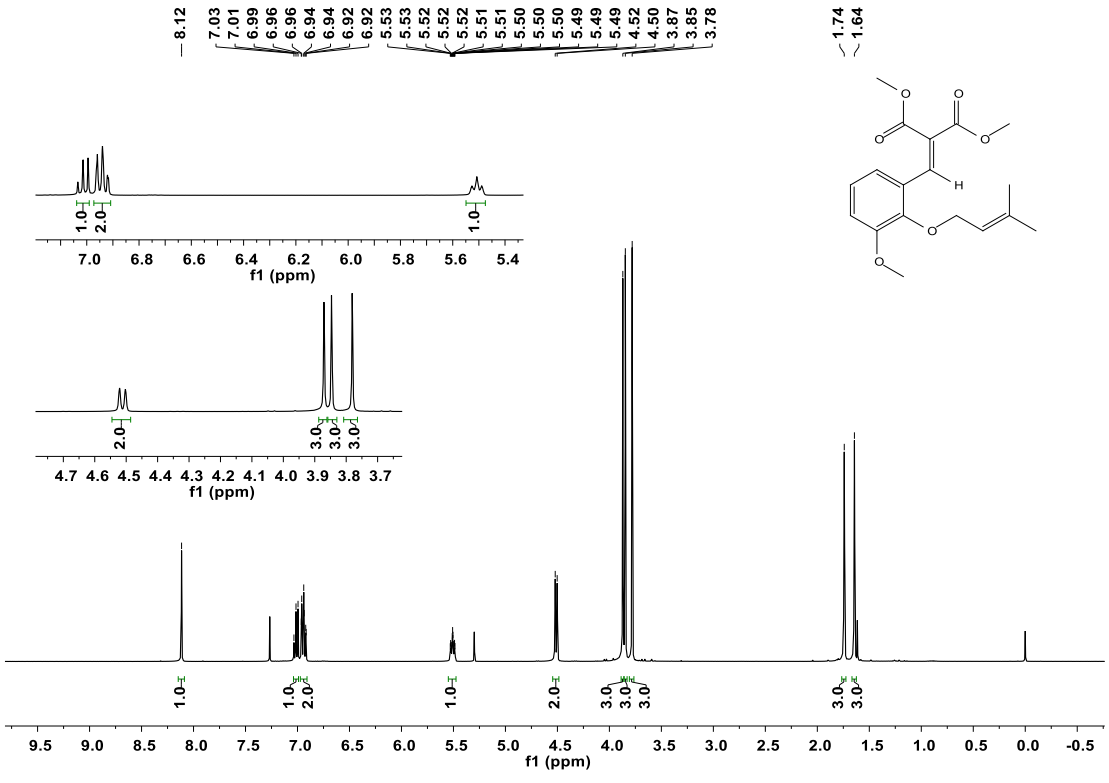


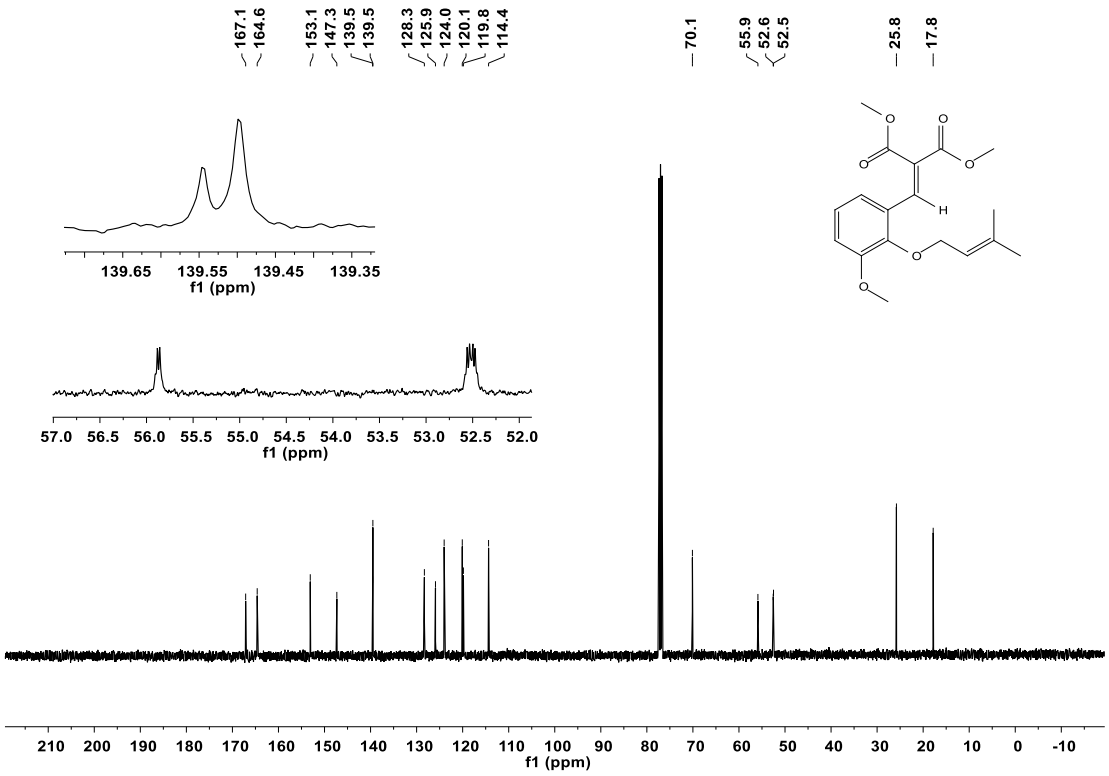
Dimethyl 2-{3-fluoro-2-[(3-methylbut-2-en-1-yl)oxy]benzylidene}malonate (1i):



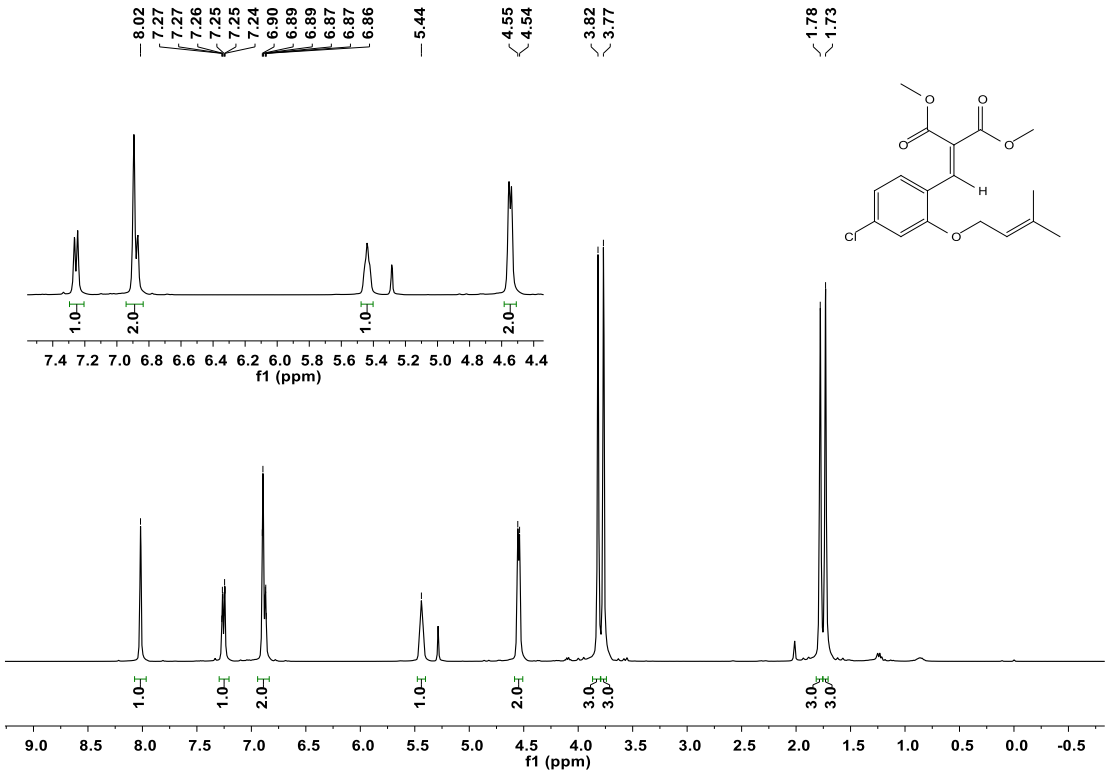


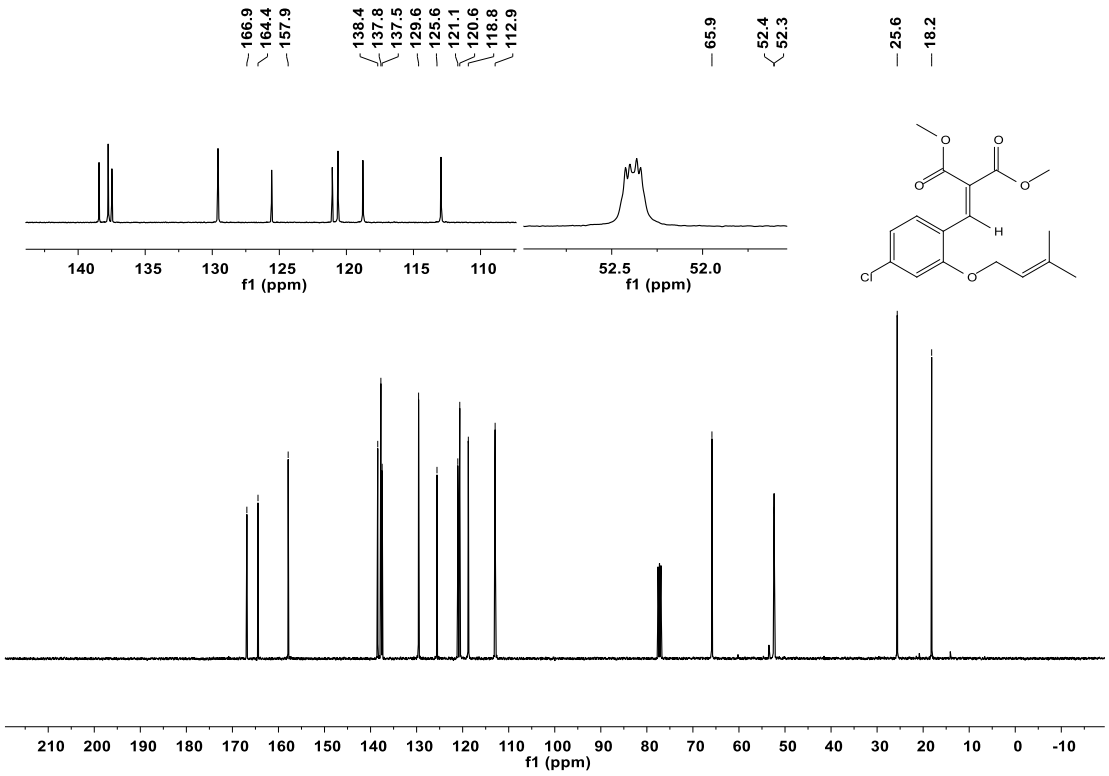
Dimethyl 2-{3-methoxy-2-[(3-methylbut-2-en-1-yl)oxy]benzylidene}malonate (1j):



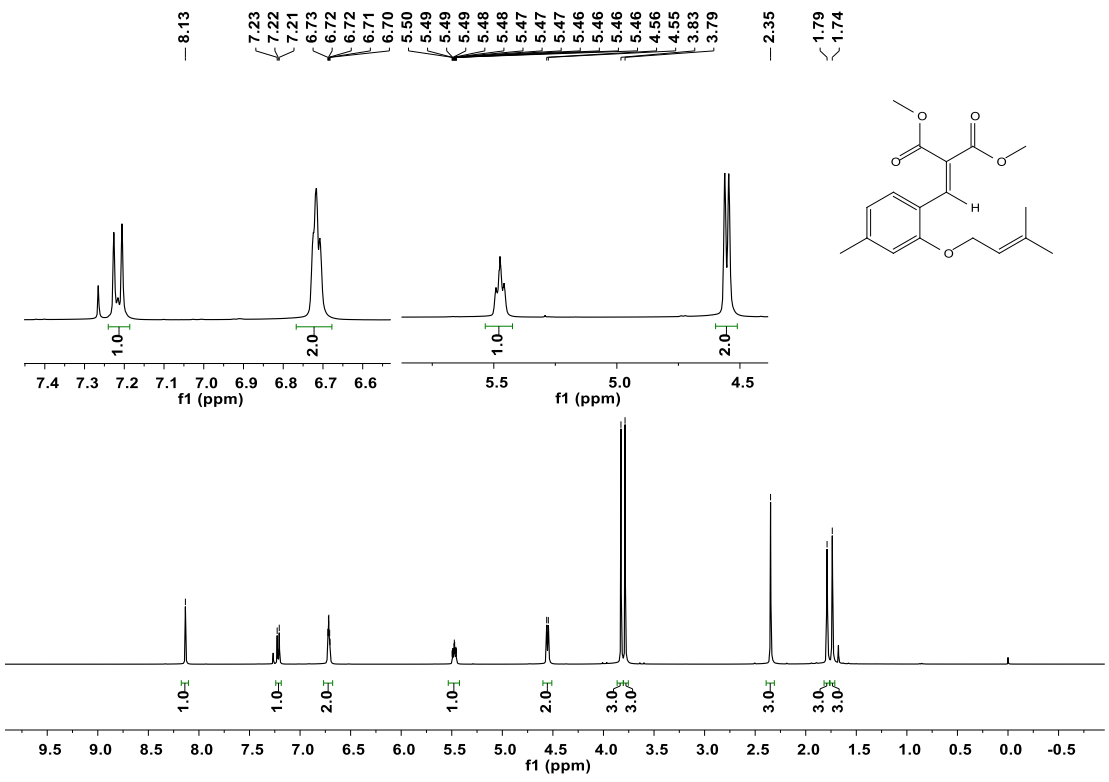


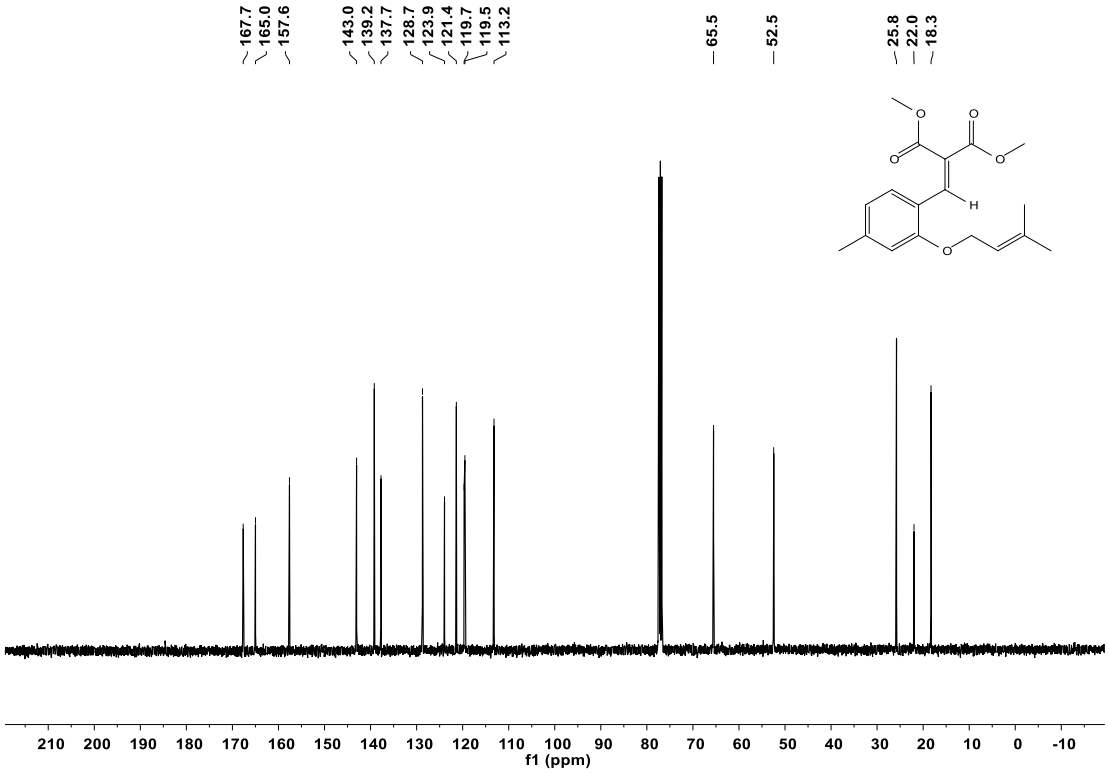
Dimethyl 2-{4-chloro-2-[(3-methylbut-2-en-1-yl)oxy]benzylidene}malonate (1k):



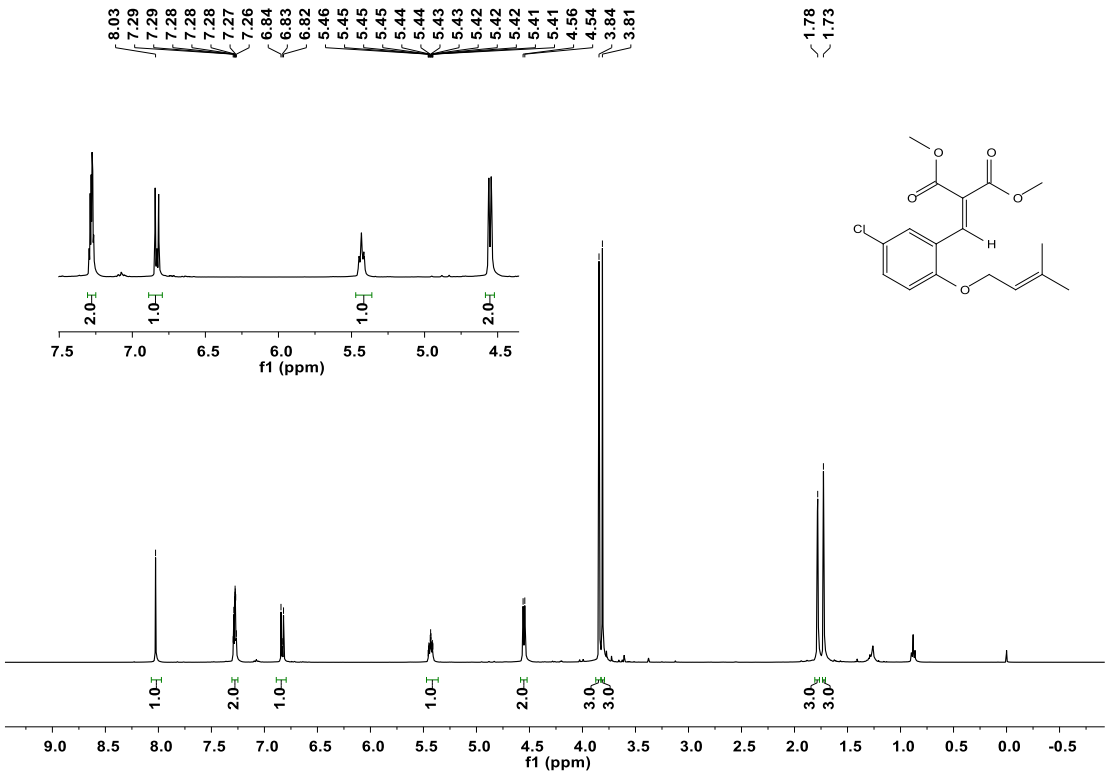


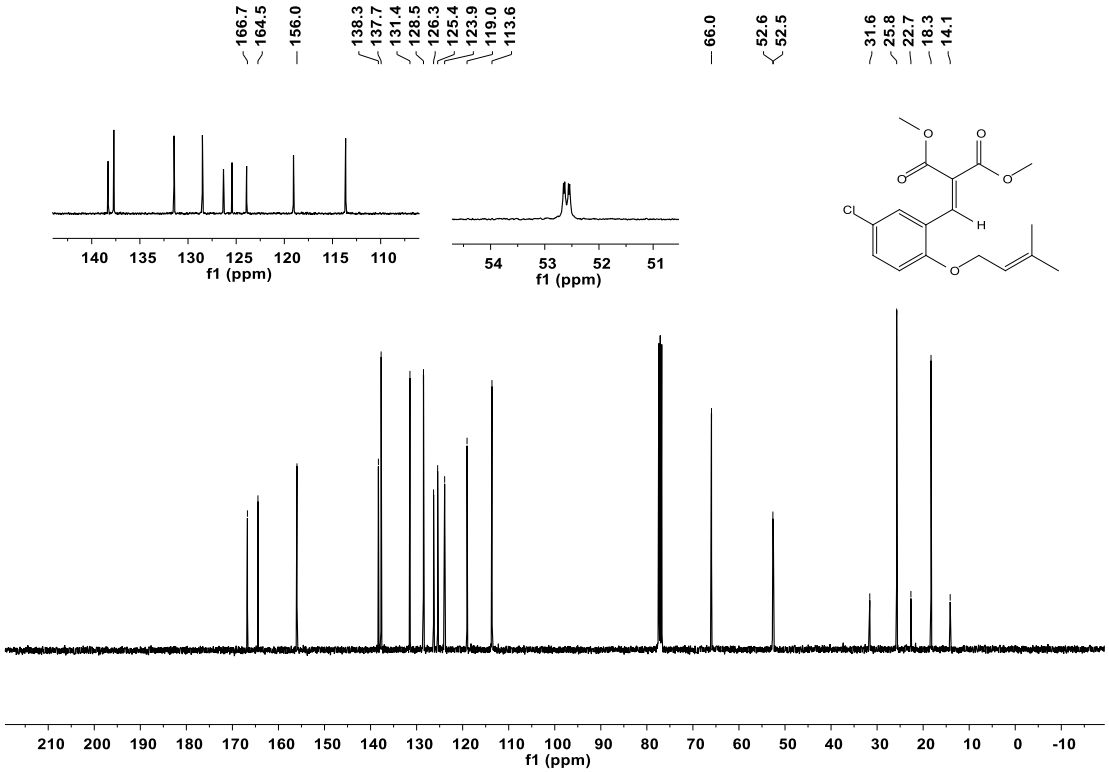
Dimethyl 2-{4-methyl-2-[(3-methylbut-2-en-1-yl)oxy]benzylidene}malonate (1l):



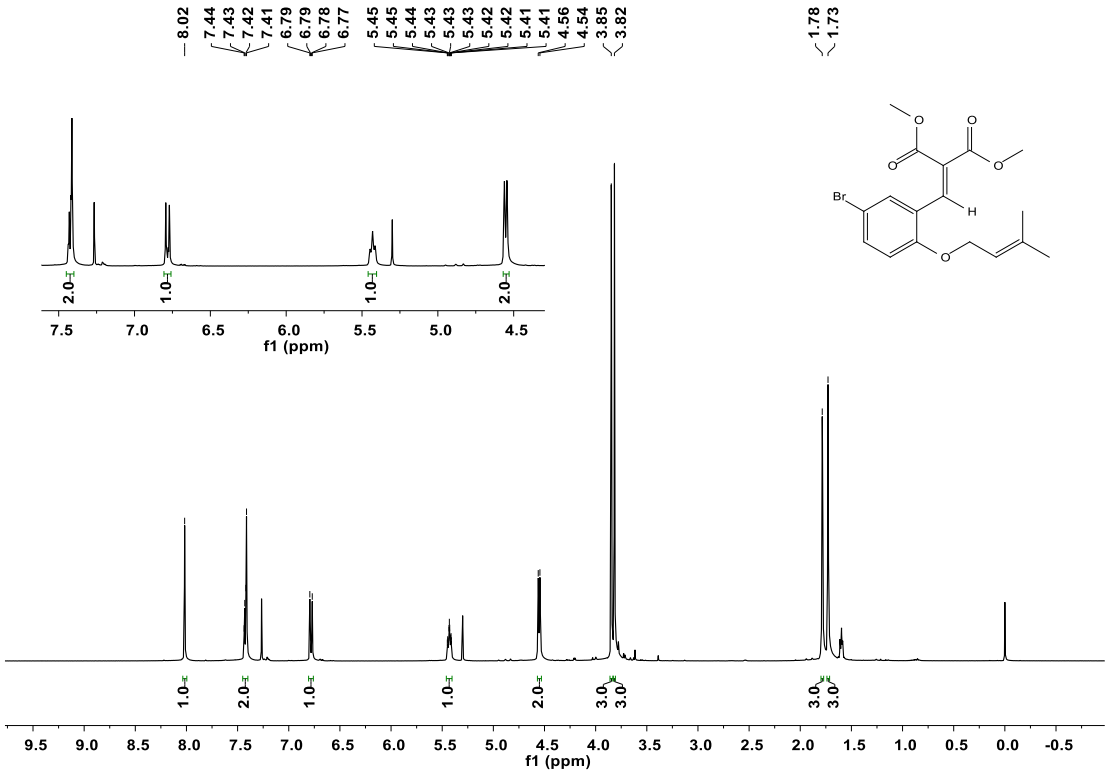


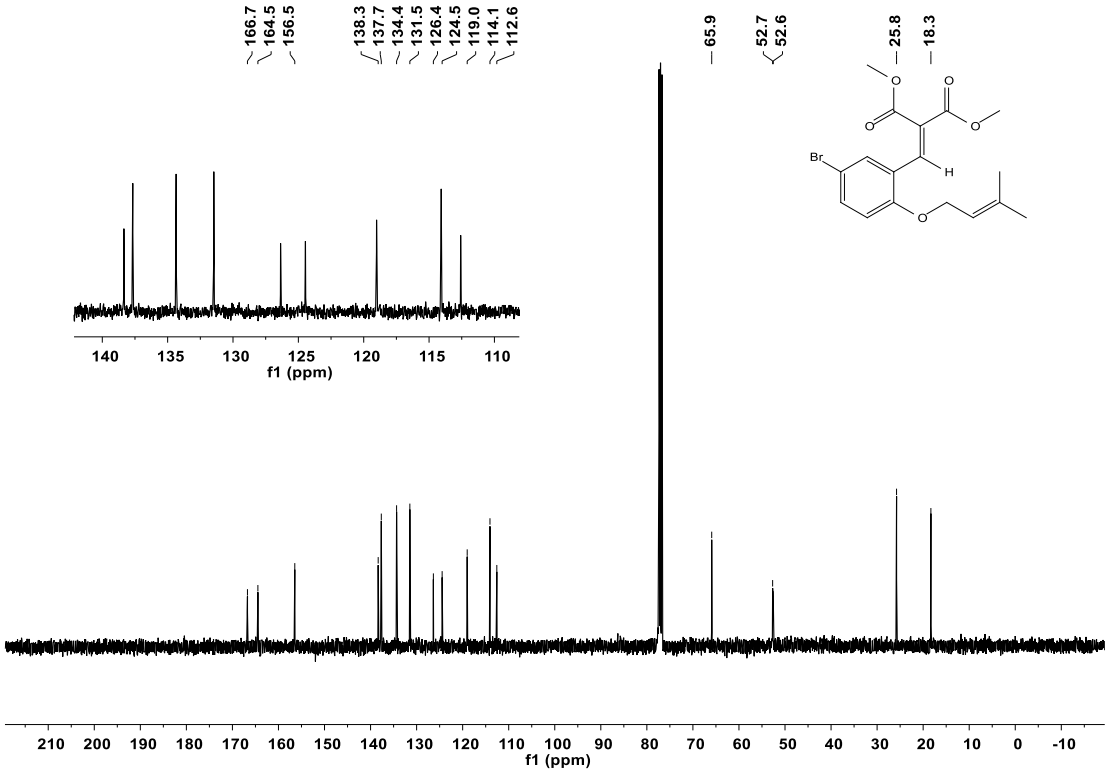
Dimethyl 2-{5-chloro-2-[(3-methylbut-2-en-1-yl)oxy]benzylidene}malonate (1m):



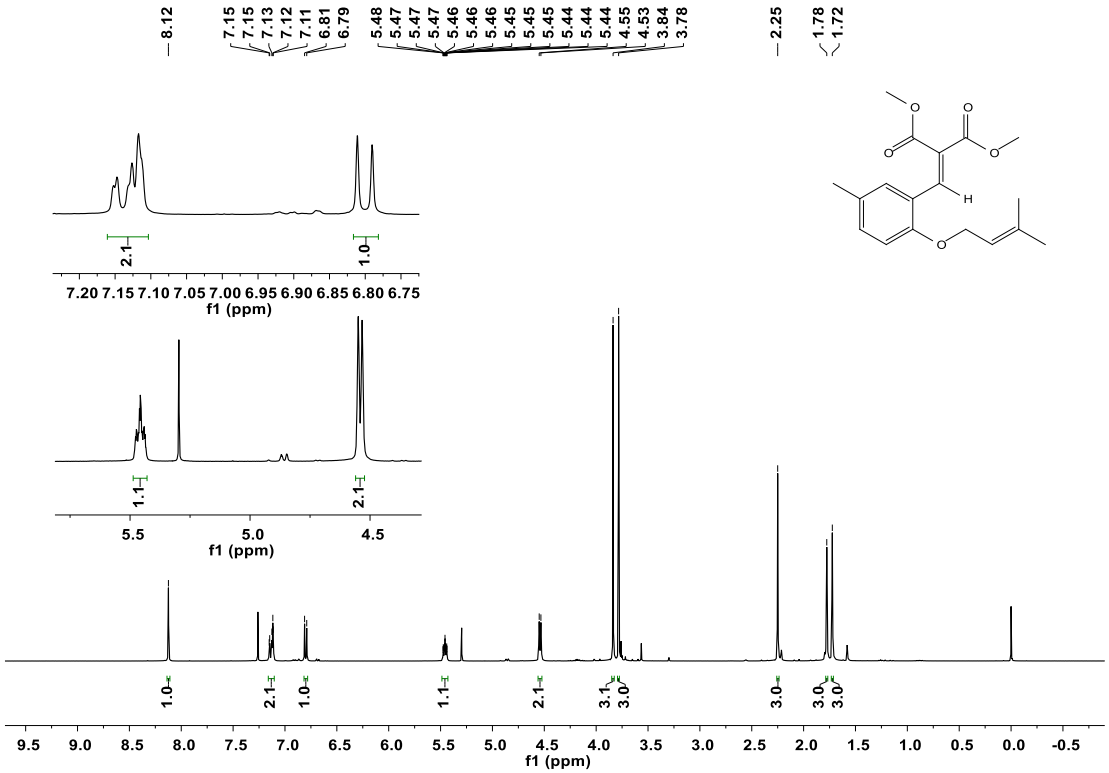


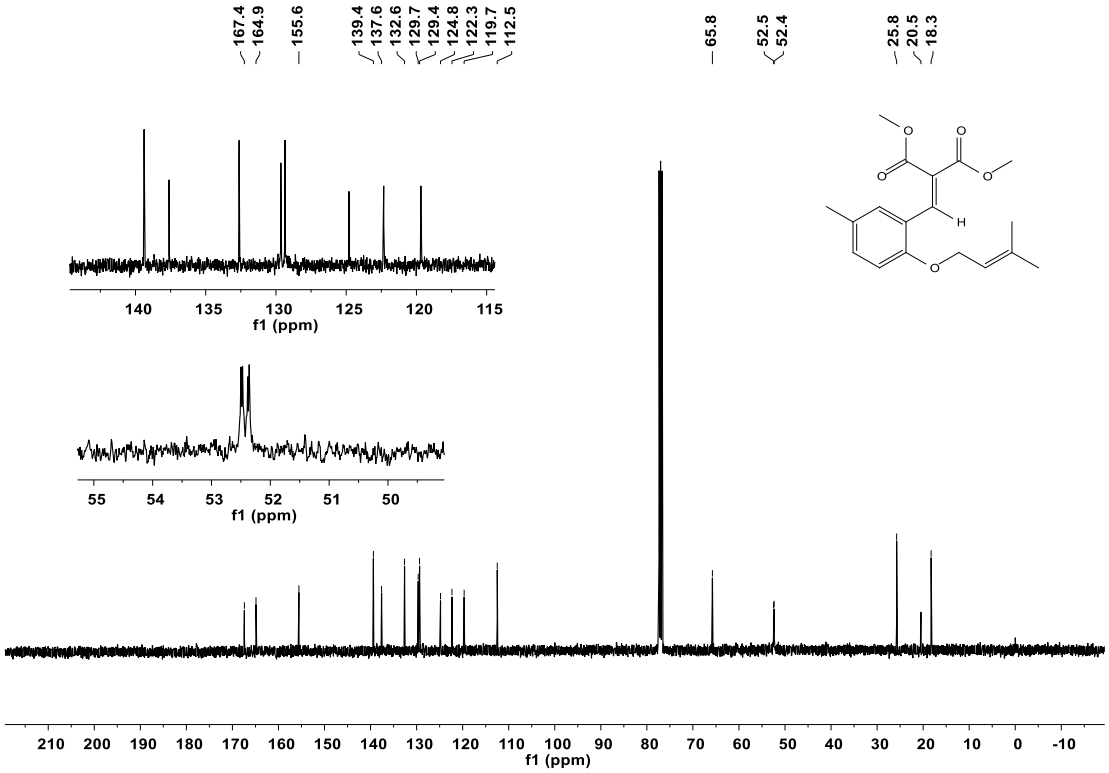
Dimethyl 2-{5-bromo-2-[(3-methylbut-2-en-1-yl)oxy]benzylidene}malonate (1n):



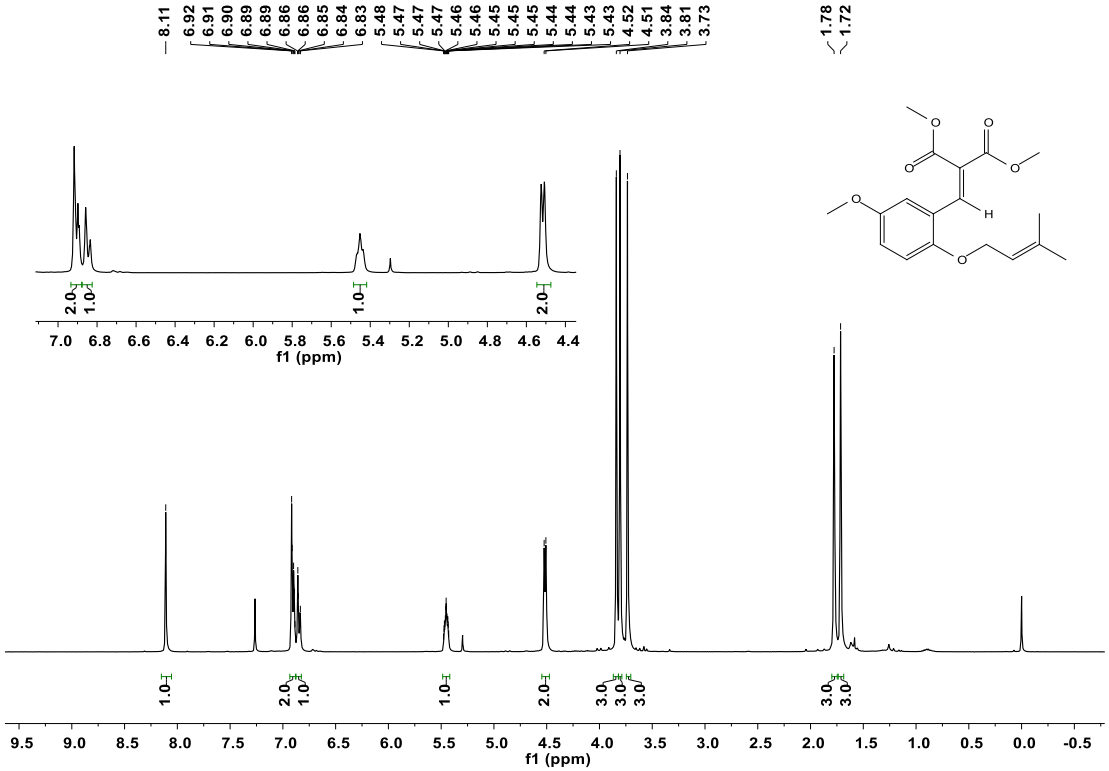


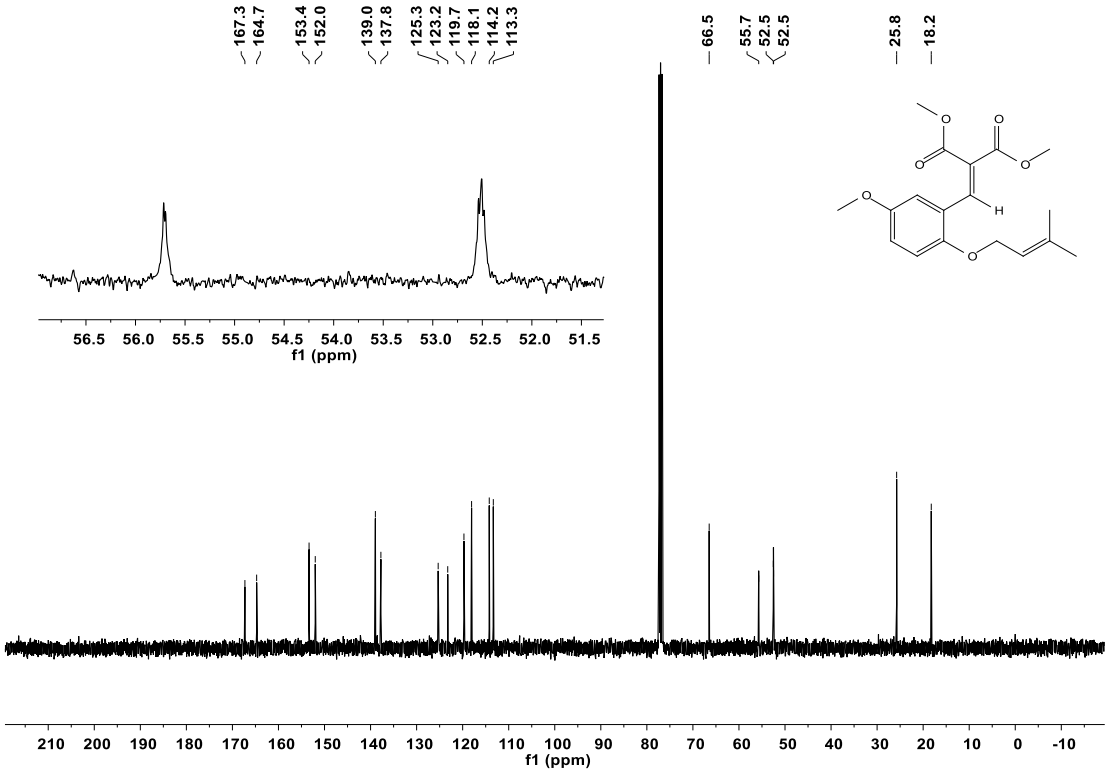
Dimethyl 2-{5-methyl-2-[(3-methylbut-2-en-1-yl)oxy]benzylidene}malonate (1o):



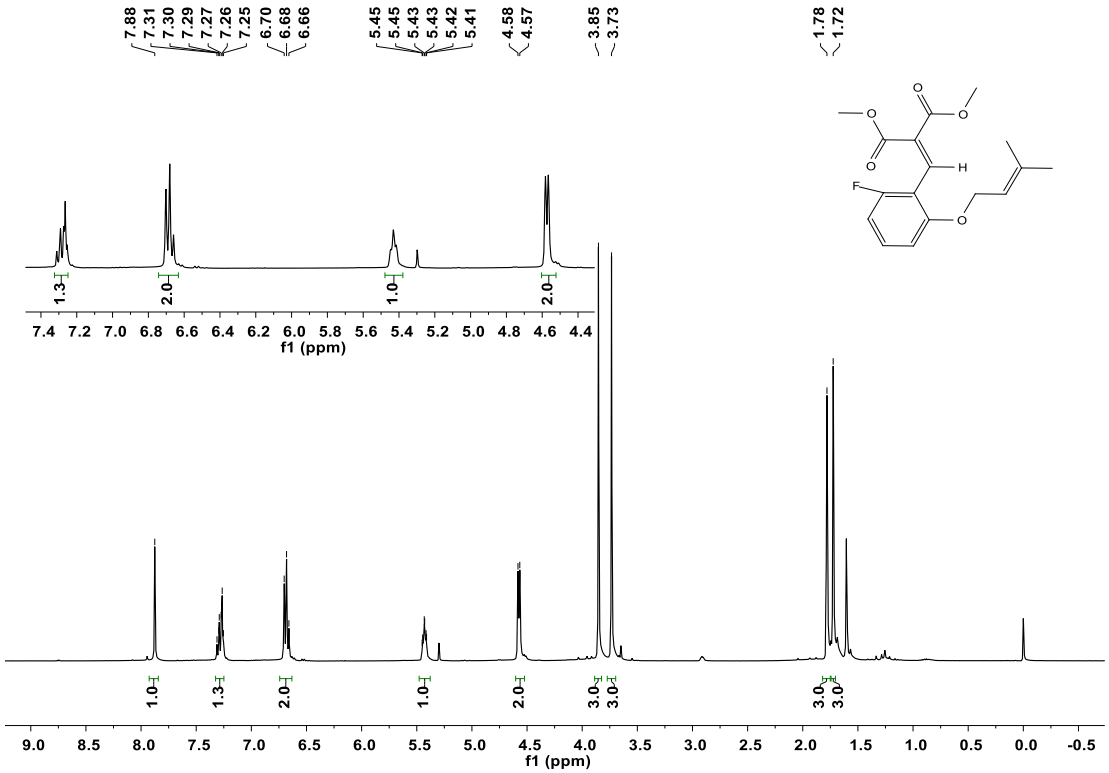


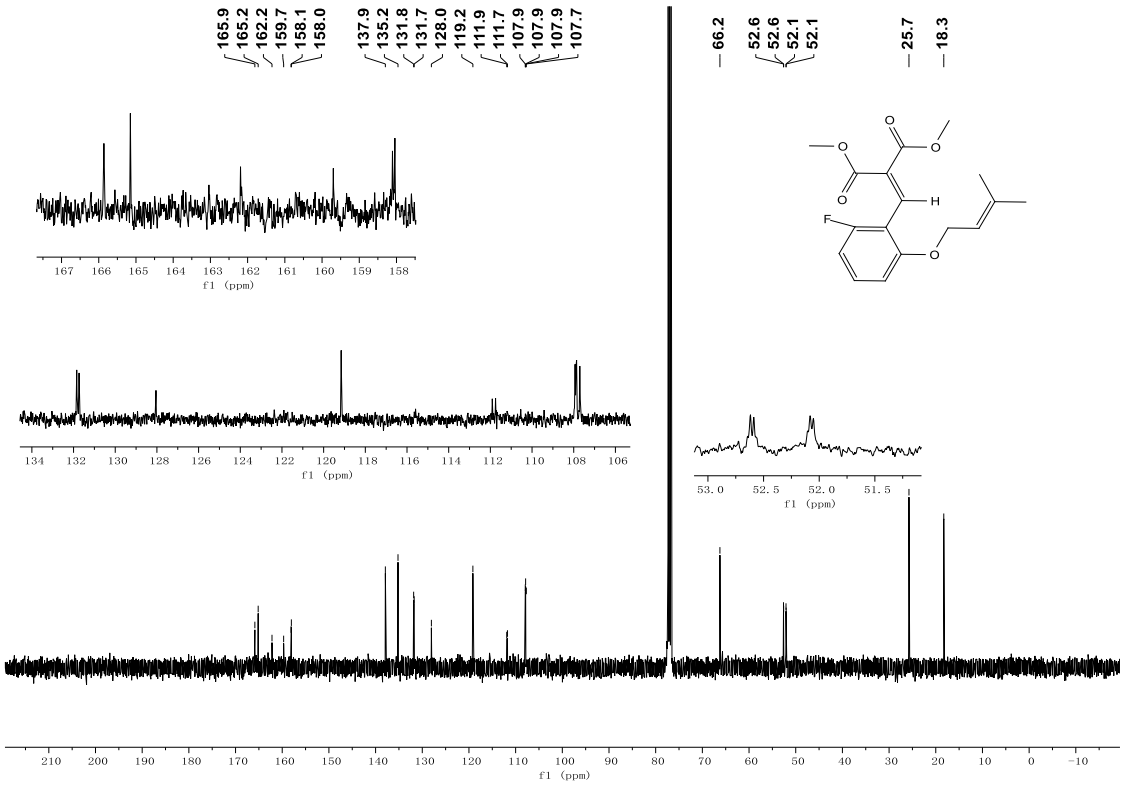
Dimethyl 2-{5-methoxy-2-[(3-methylbut-2-en-1-yl)oxy]benzylidene}malonate (1p):

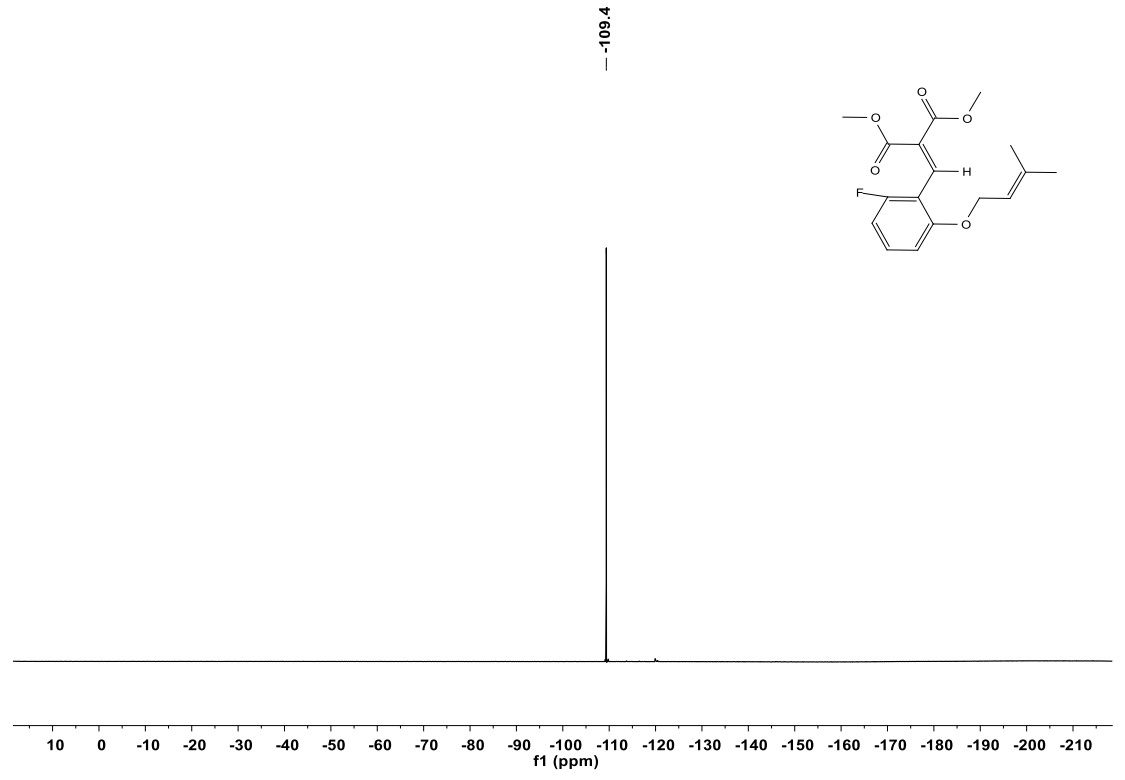




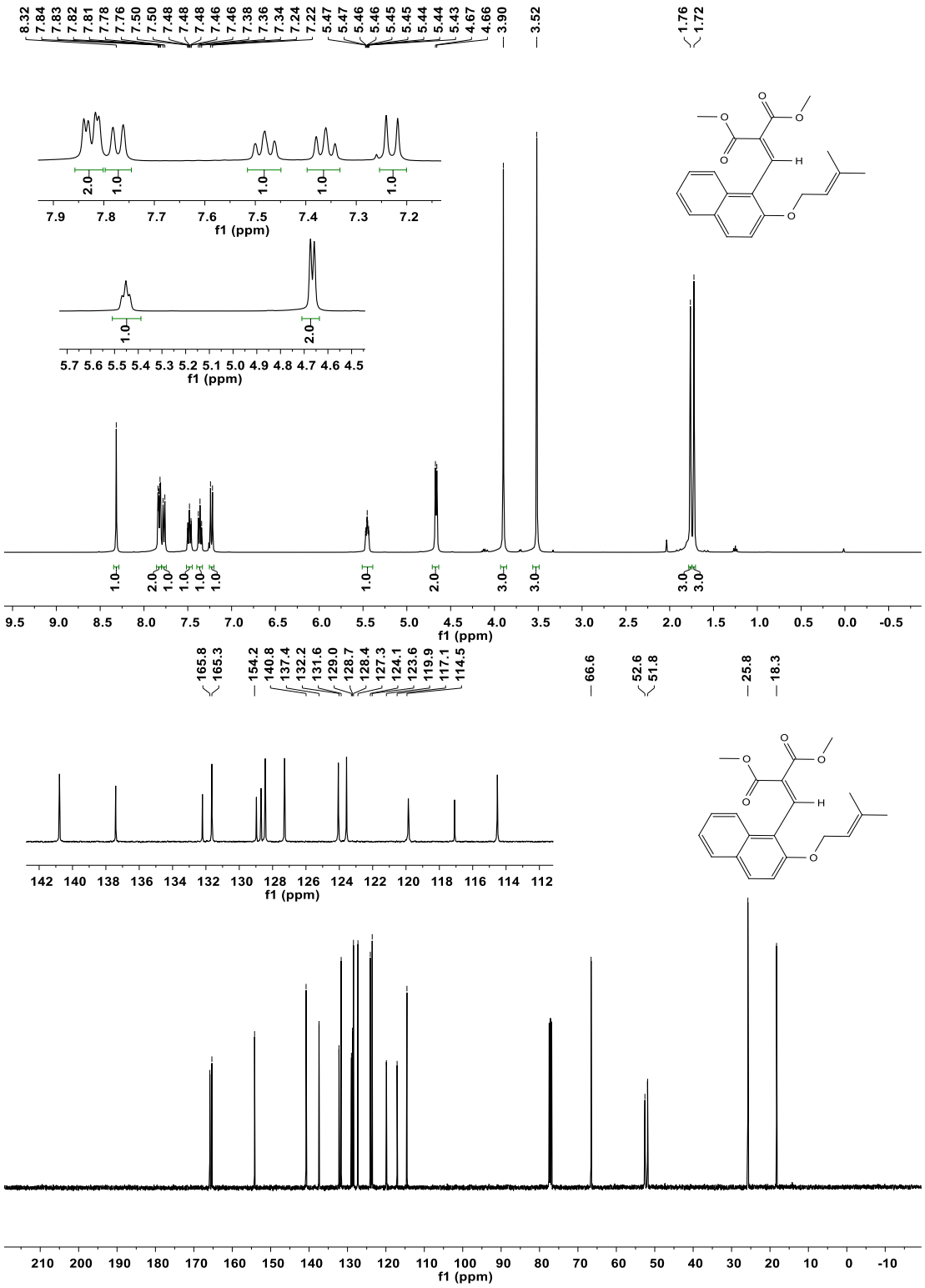
Dimethyl 2-{2-fluoro-6-[(3-methylbut-2-en-1-yl)oxy]benzylidene}malonate (1q):



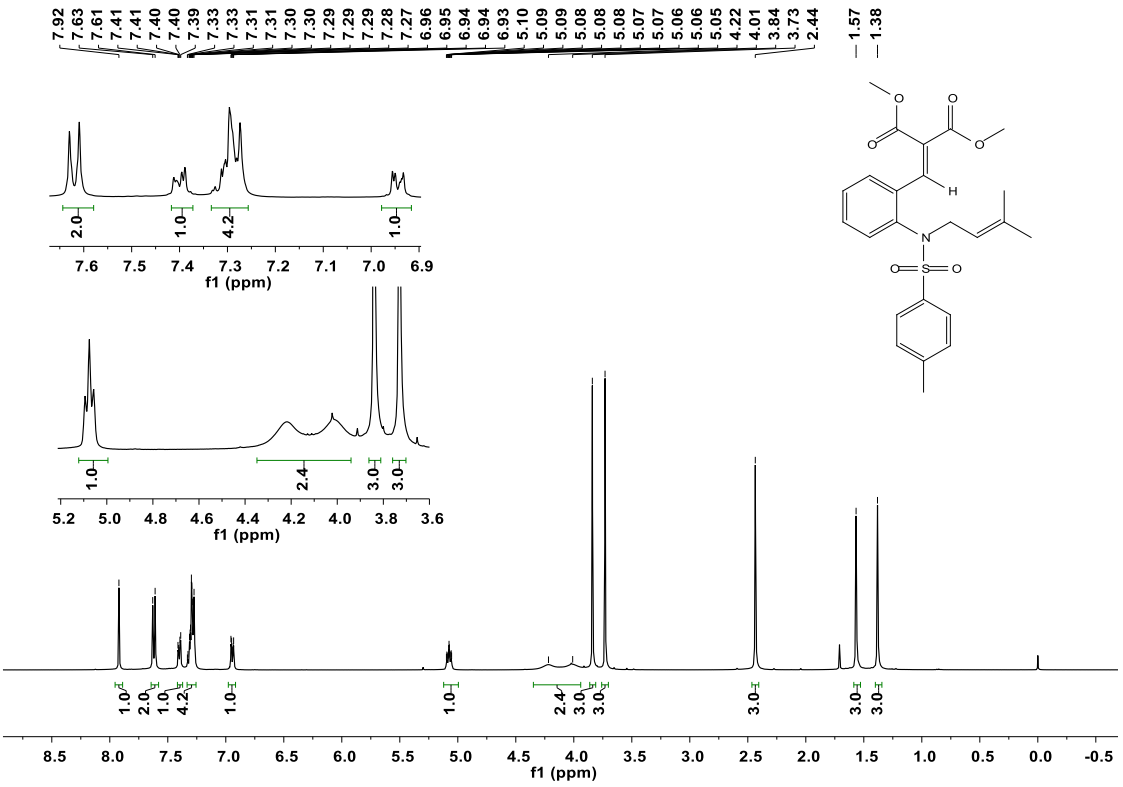

165.9
165.2
162.2
159.7
158.1
158.0
137.9
135.2
131.8
131.7
128.0
119.2
111.9
111.7
107.9
107.9
107.9
107.7
66.2
52.6
52.6
52.1
52.1
25.7
18.3
f1 (ppm)

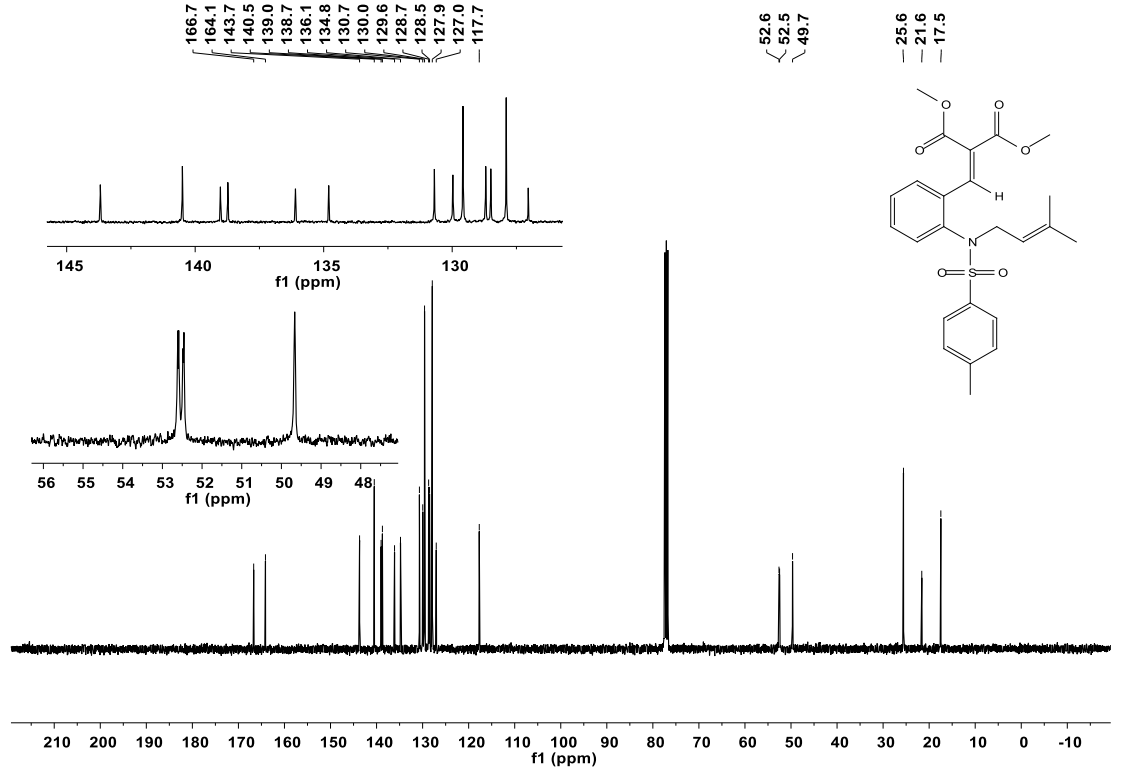

-109.4
f1 (ppm)

Dimethyl 2-{{2-[(3-methylbut-2-en-1-yl)oxy]naphthalen-1-yl}methylene}malonate (1r):

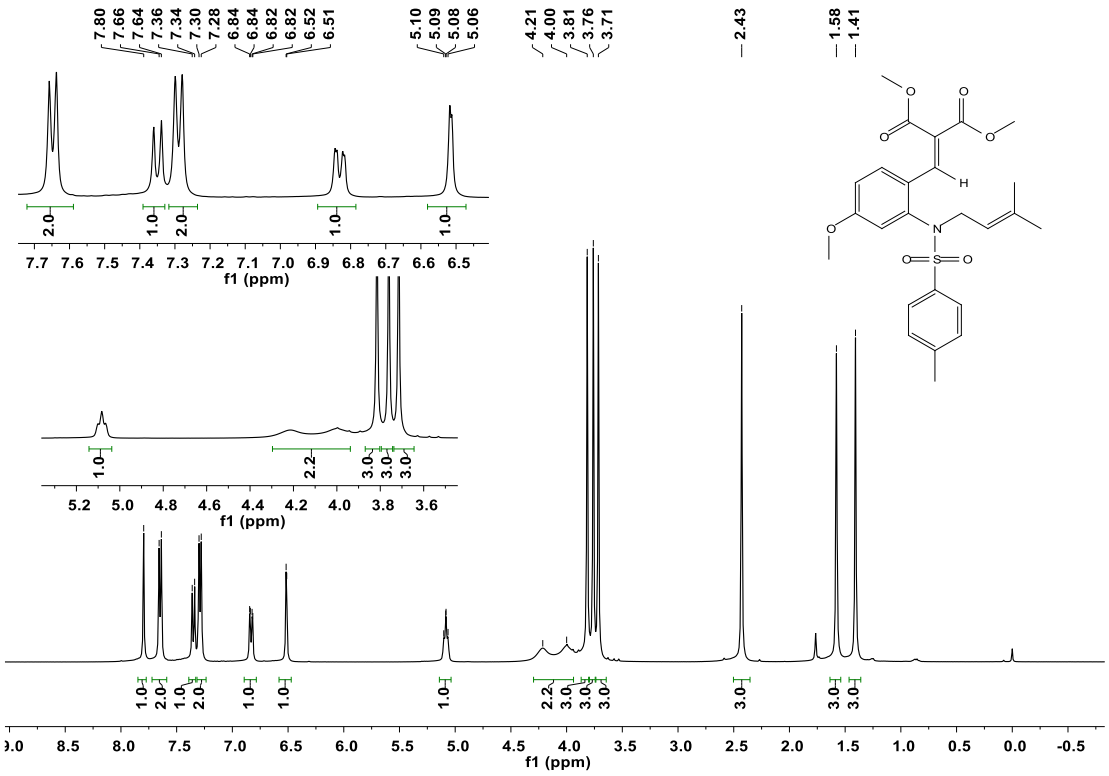


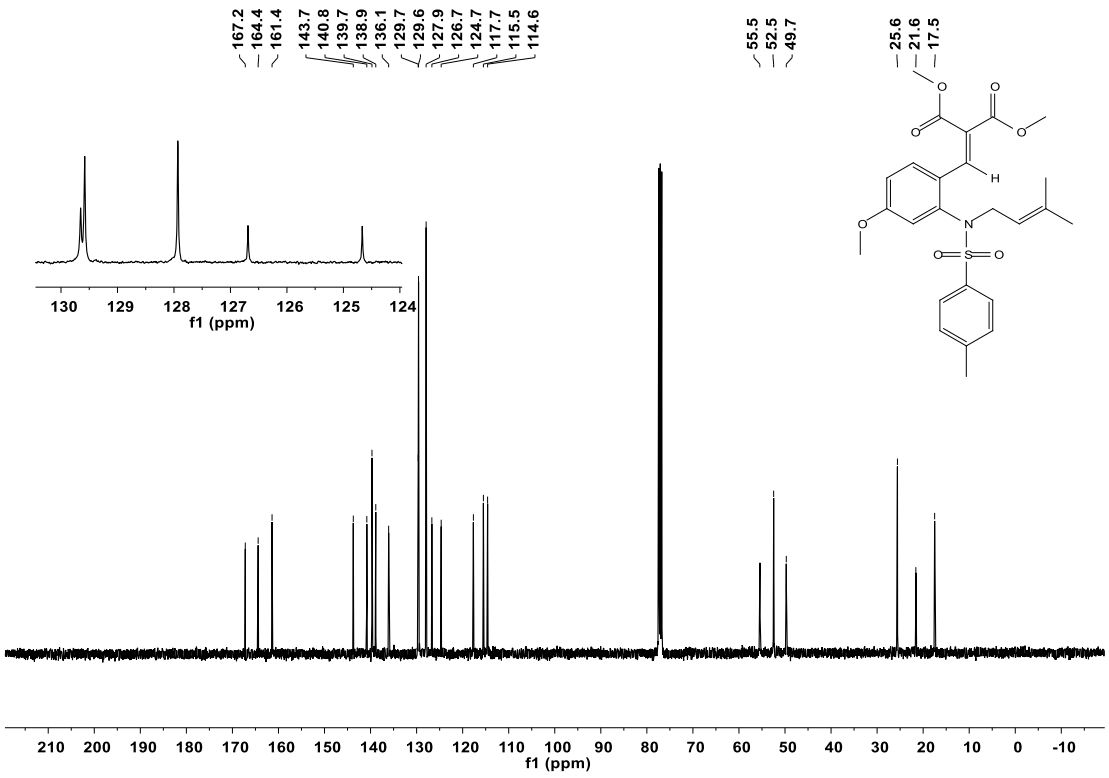
Dimethyl 2-{2-{[4-methyl-N-(3-methylbut-2-en-1-yl)phenyl]sulfonamido}benzylidene}malonate (1s):



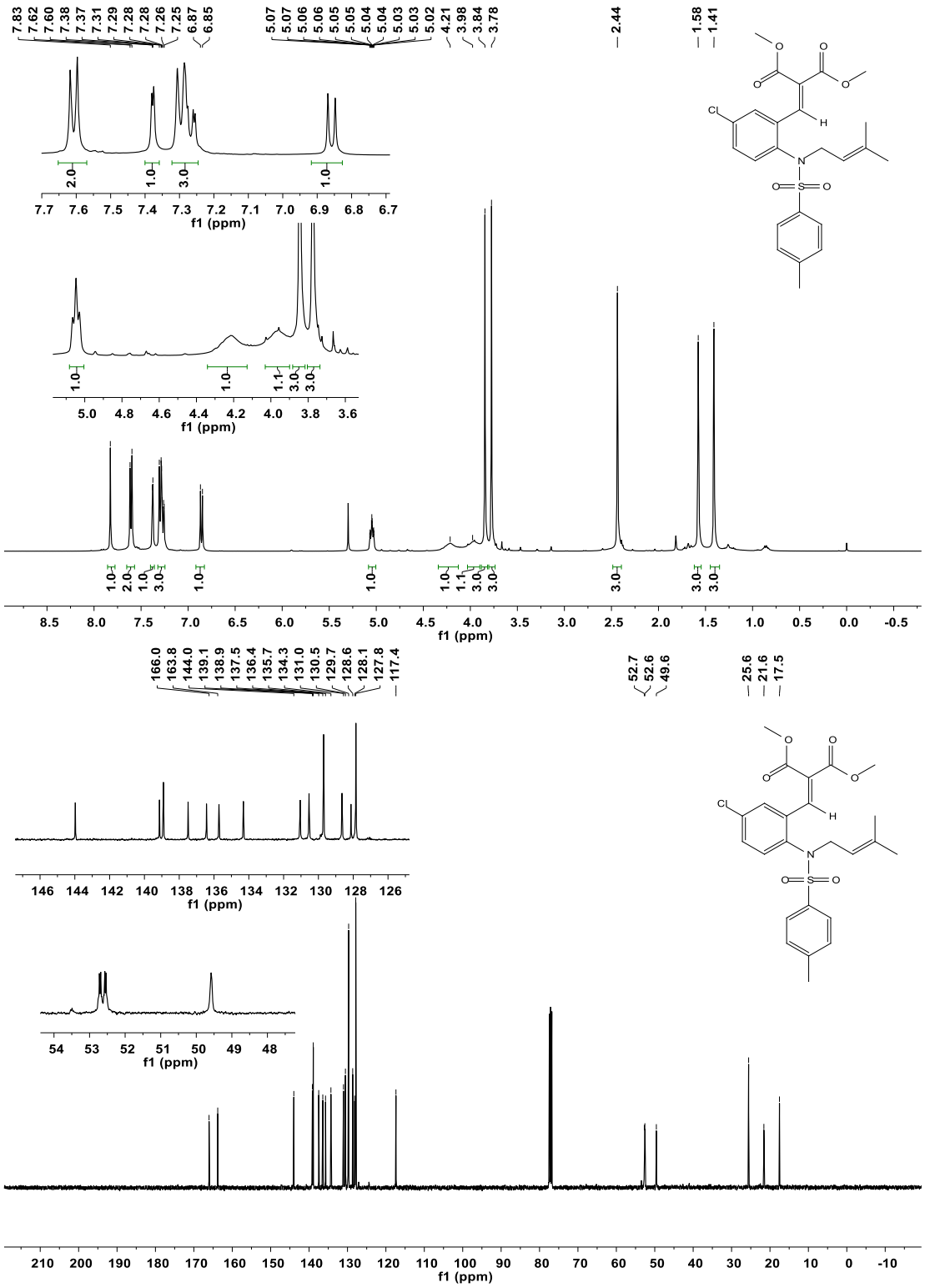


Dimethyl 2-{4-methoxy-2-{[4-methyl-N-(3-methylbut-2-en-1-yl)phenyl]sulfonamido}benzylidene}malonate (1t):

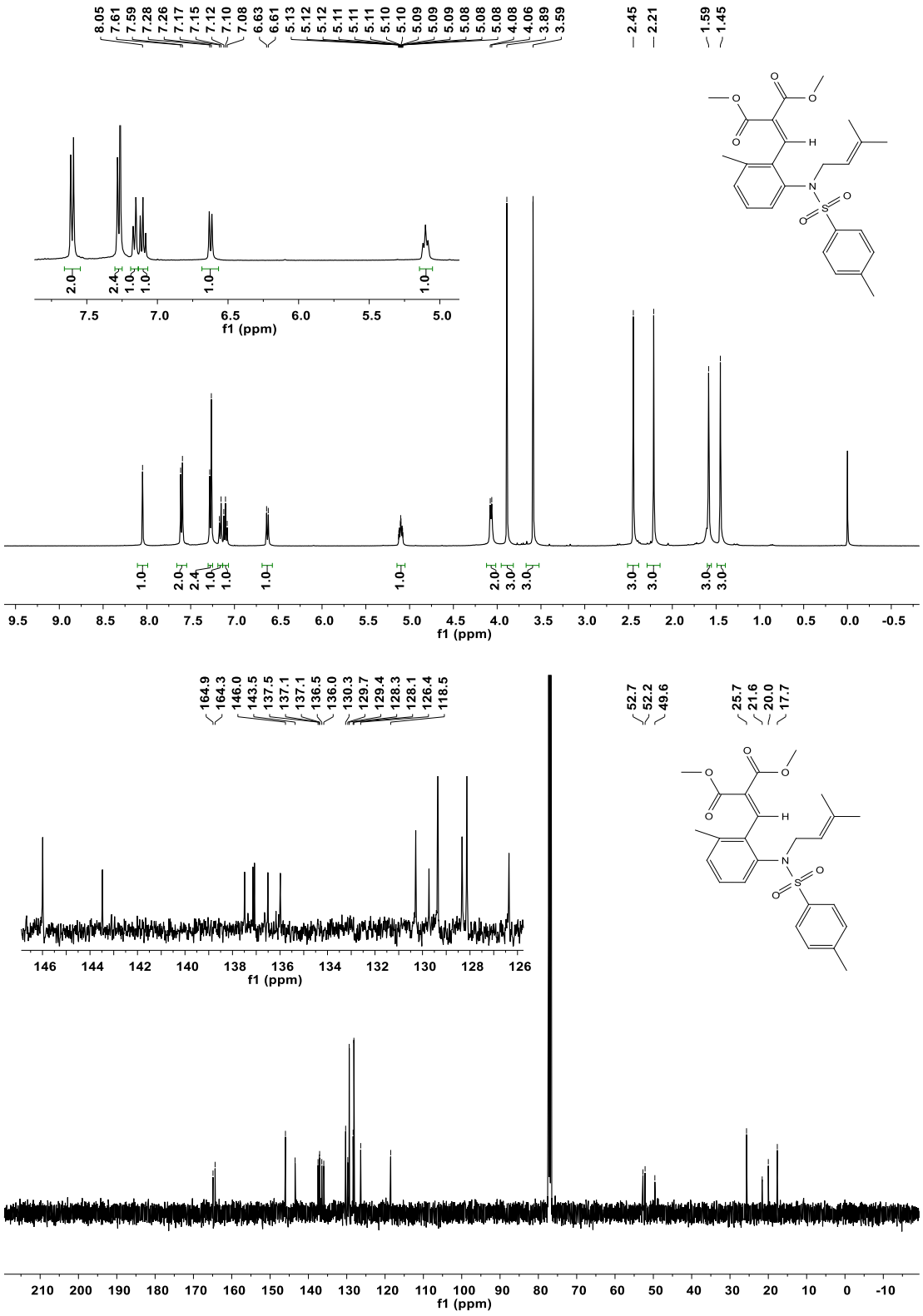




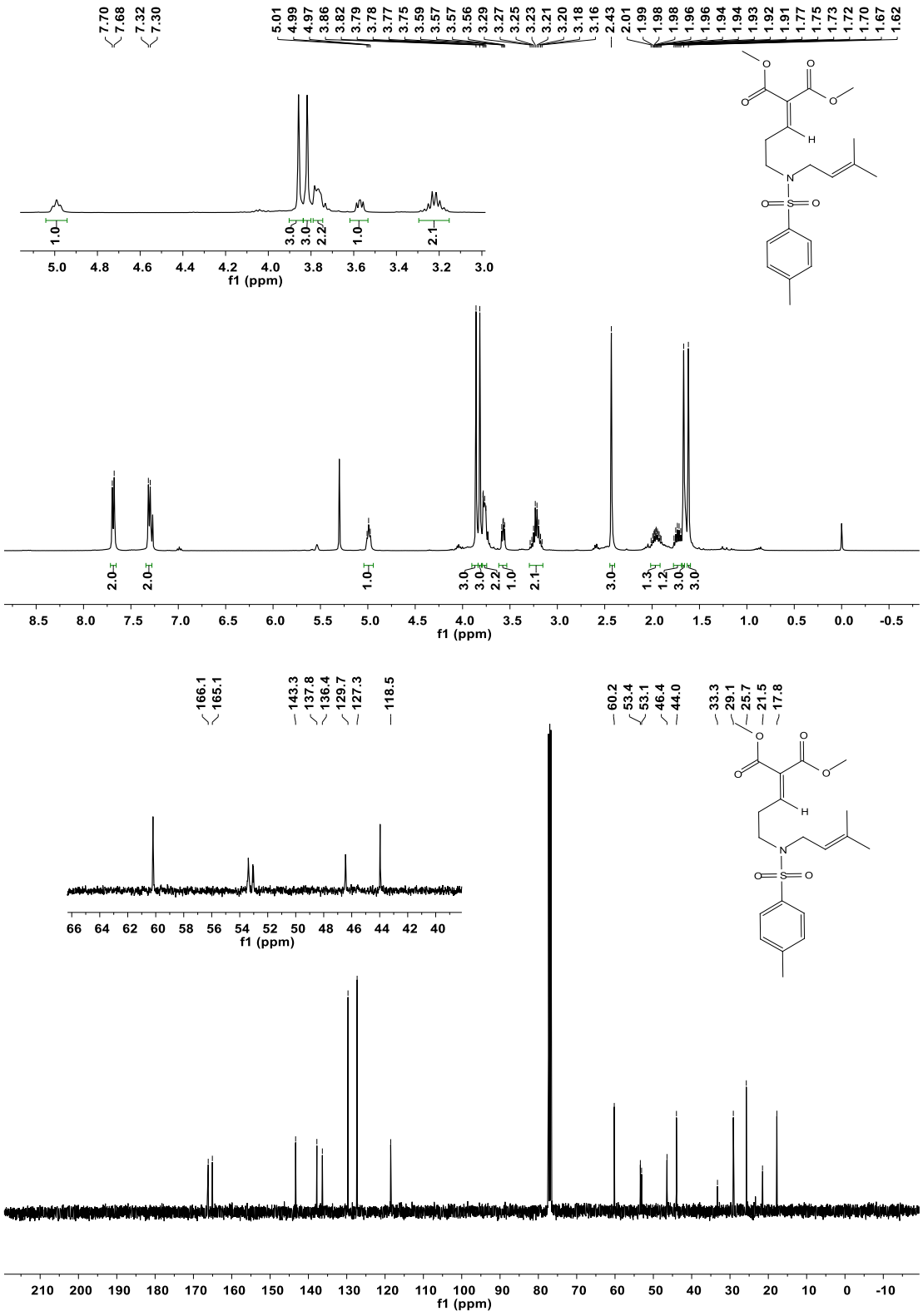
Dimethyl 2-{5-chloro-2-{[4-methyl-N-(3-methylbut-2-en-1-yl)phenyl]sulfonamido}benzylidene}malonate (1u):



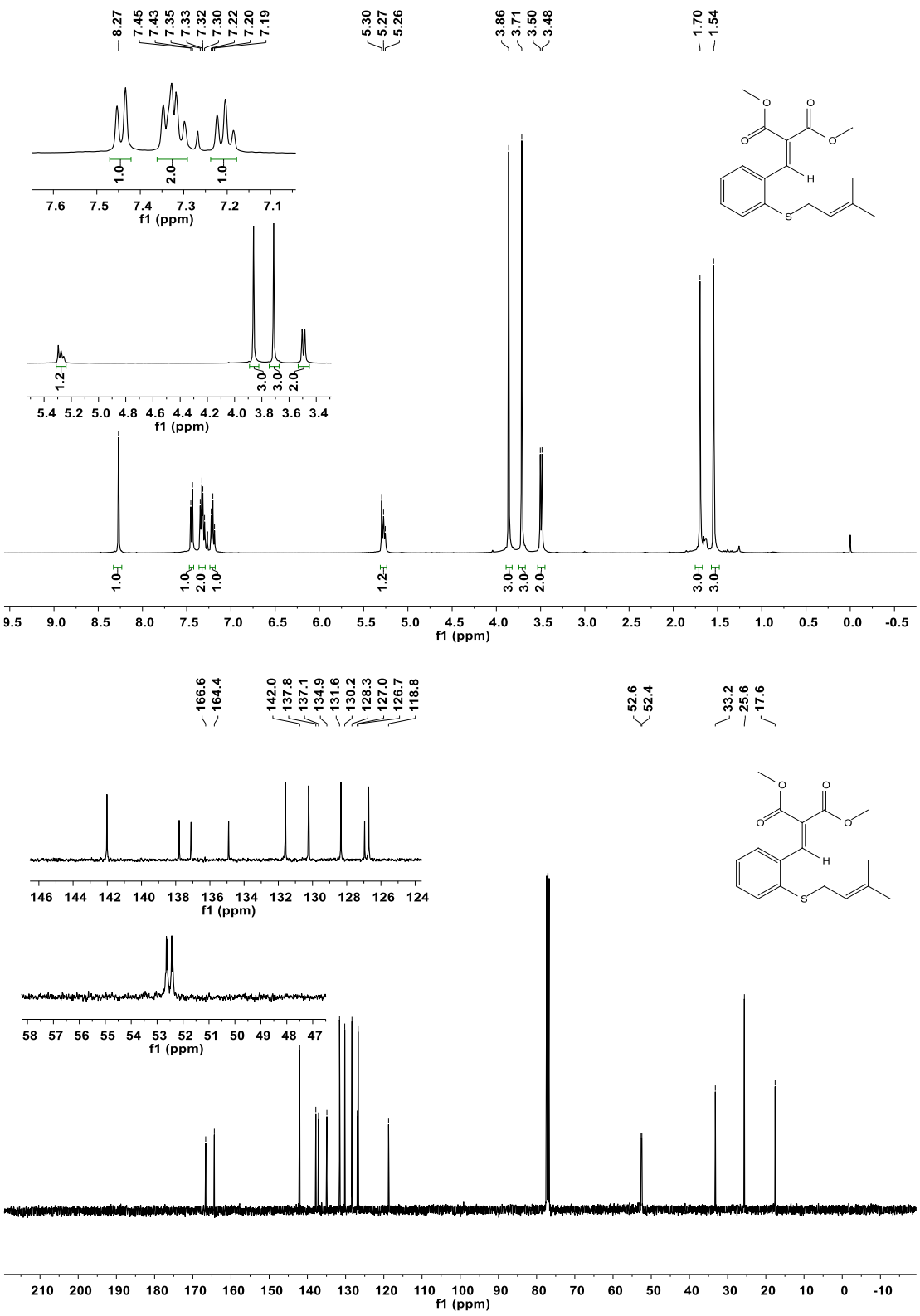
Dimethyl 2-{2-methyl-6-{[4-methyl-N-(3-methylbut-2-en-1-yl)phenyl]sulfonamido}benzylidene}malonate (1v):



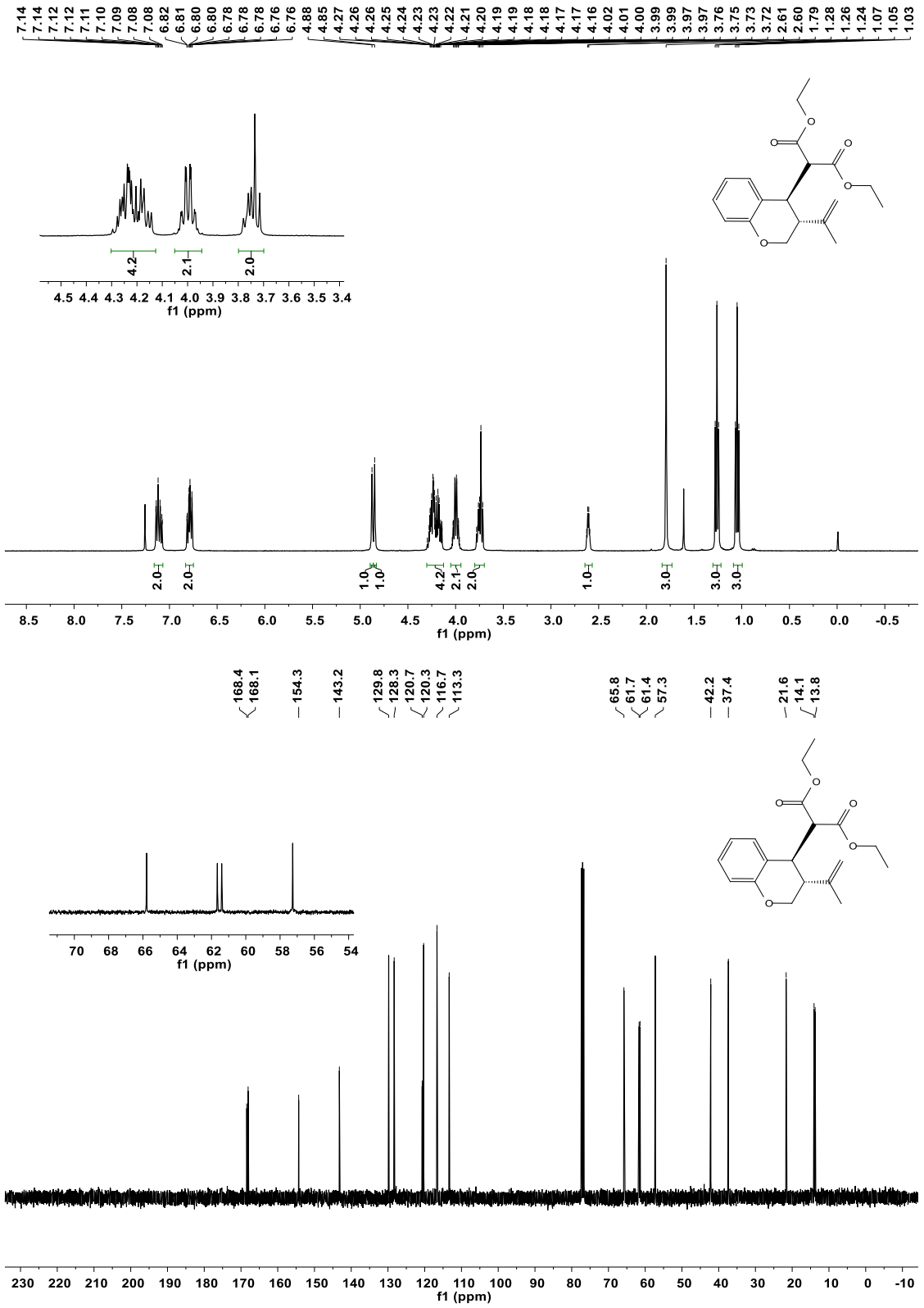
Dimethyl 2-{3-{[4-methyl-N-(3-methylbut-2-en-1-yl)phenyl]sulfonamido}propylidene}malonate (1w):



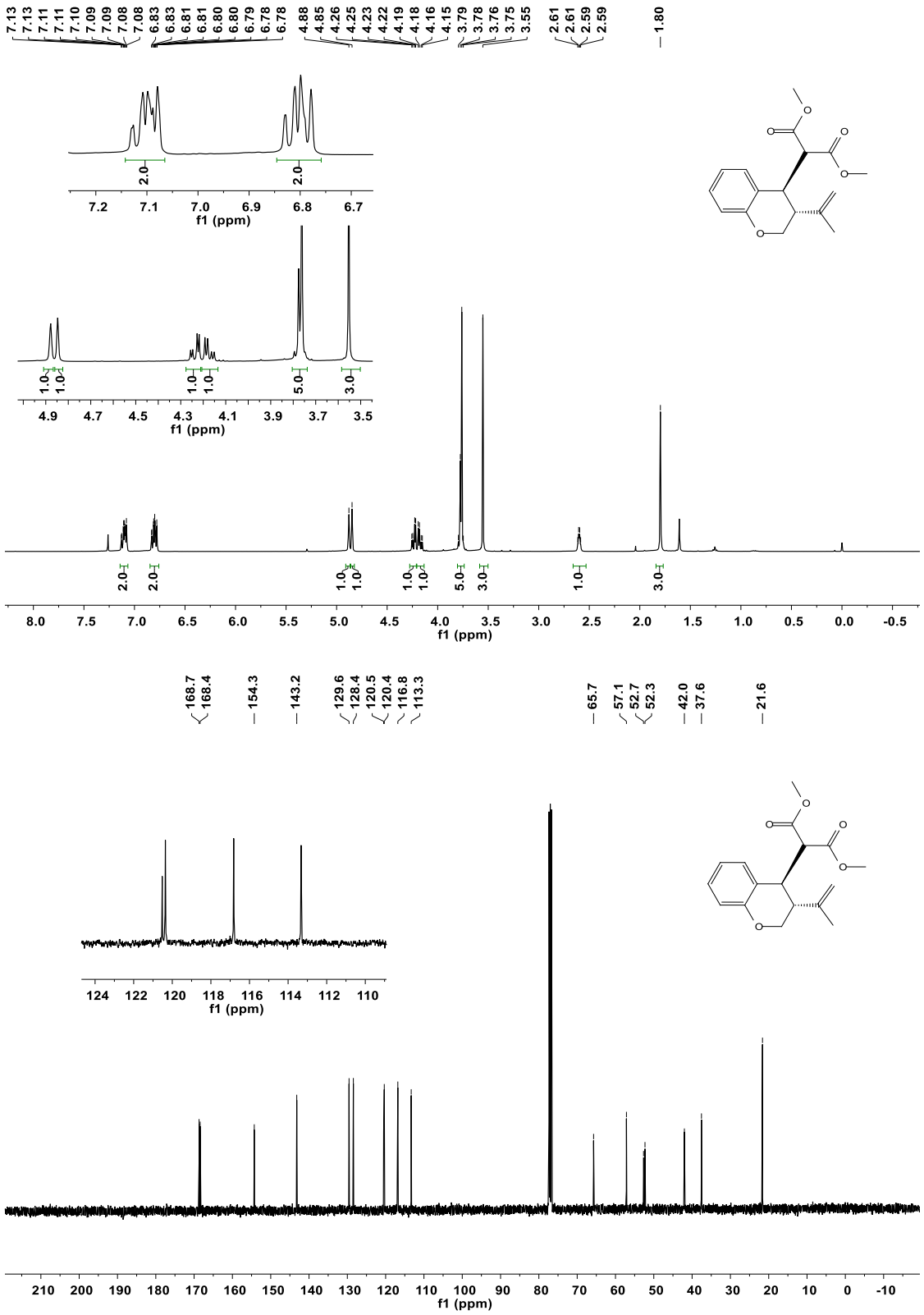
Dimethyl 2-{2-[(3-methylbut-2-en-1-yl)thio]benzylidene}malonate (1x):



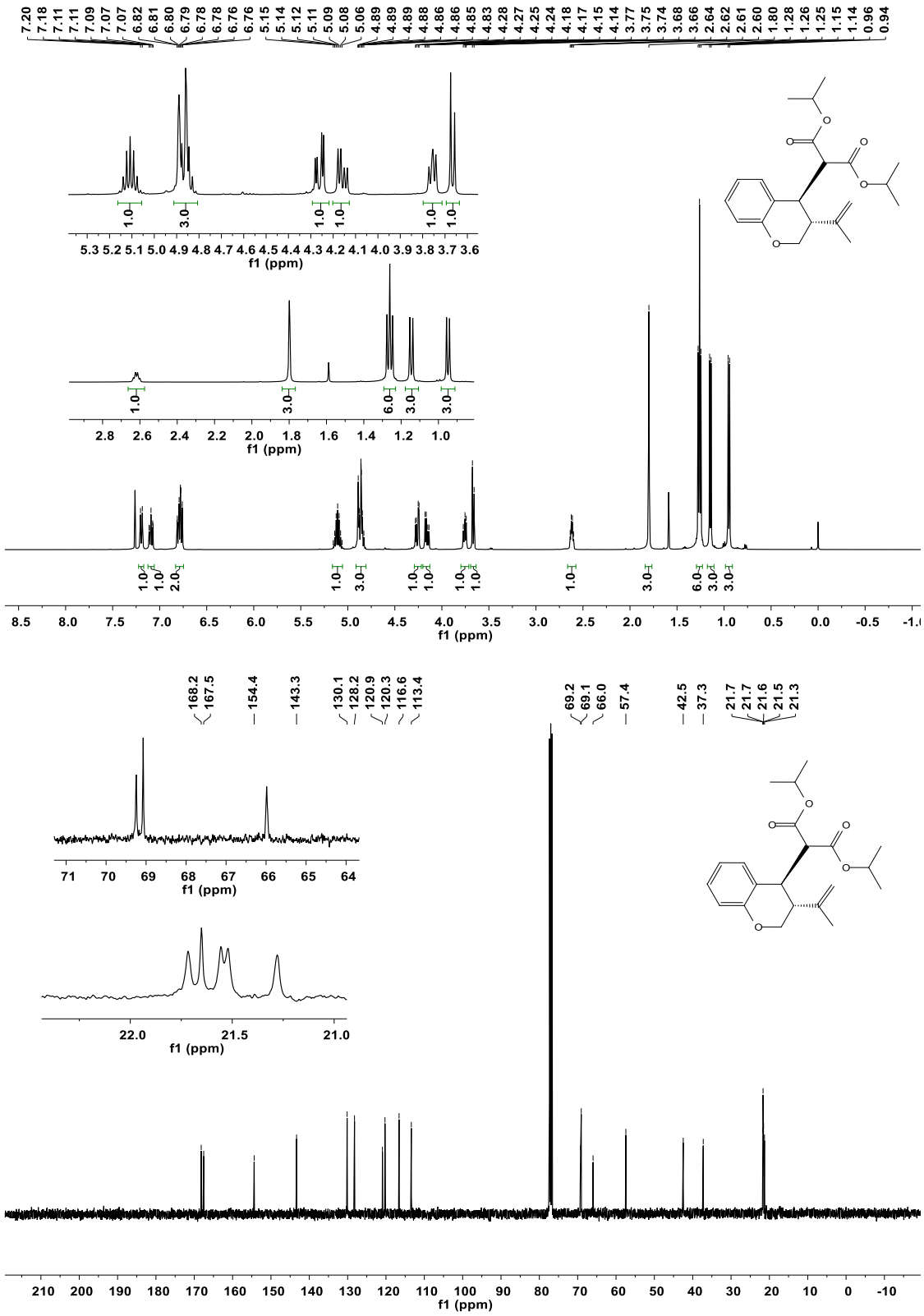
Diethyl 2-[3-(prop-1-en-2-yl)chroman-4-yl]malonate (2a):



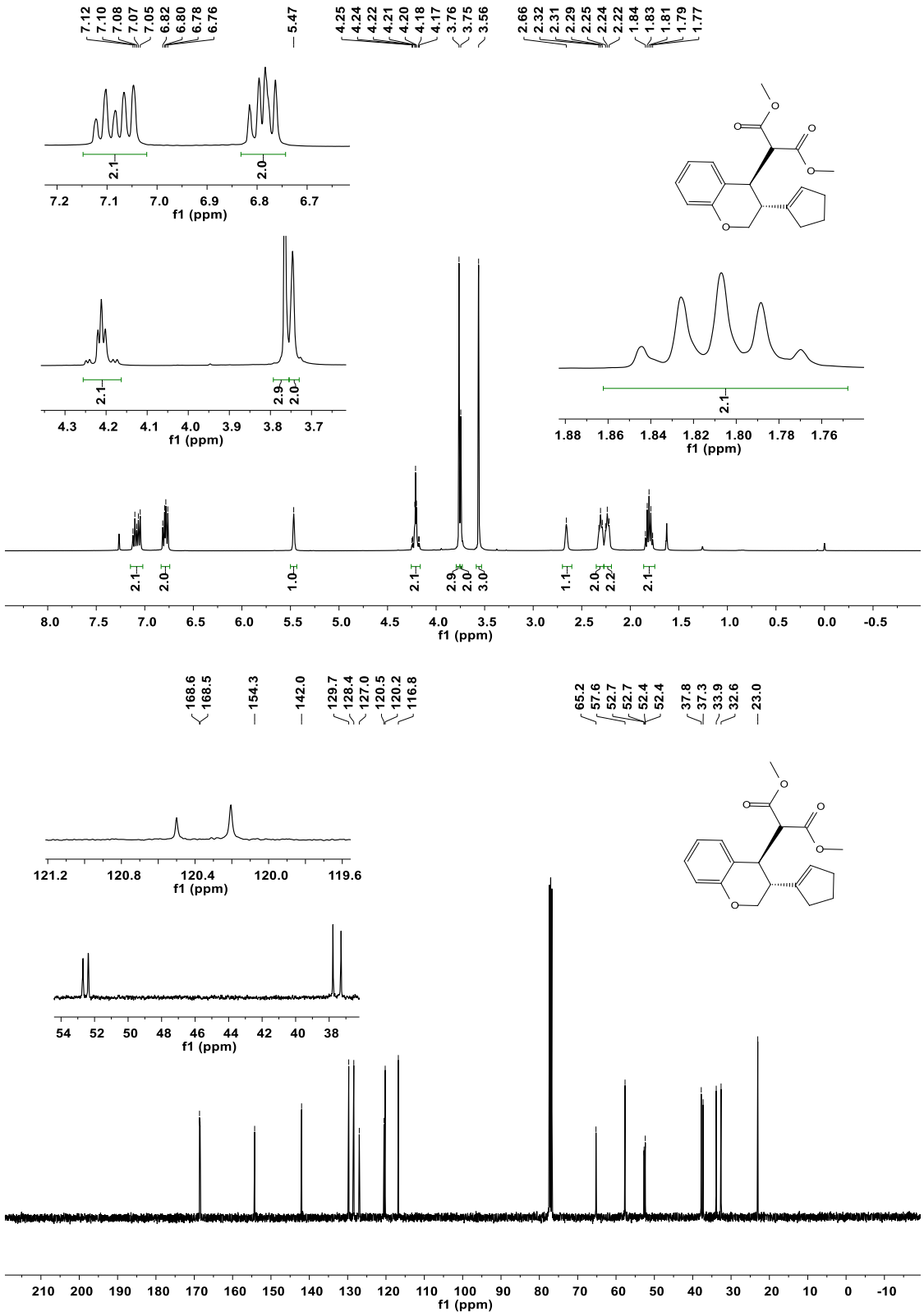
Dimethyl 2-[3-(prop-1-en-2-yl)chroman-4-yl]malonate (2b):



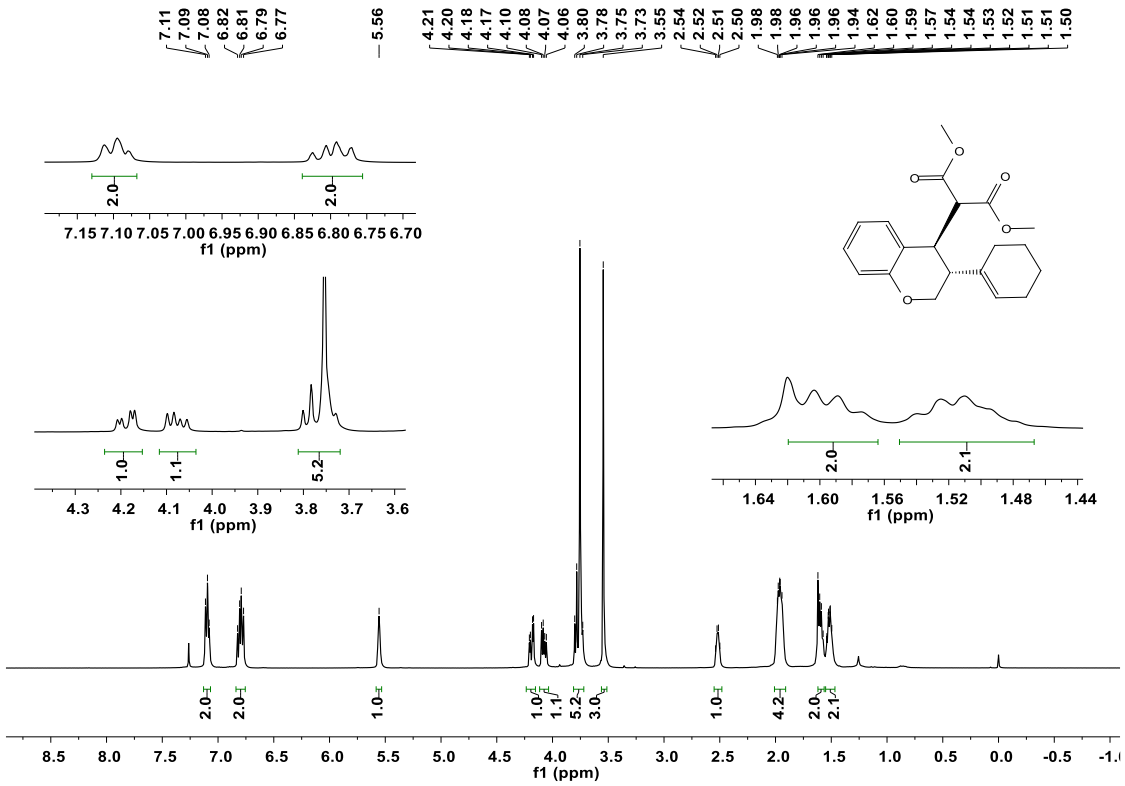
Diisopropyl 2-[3-(prop-1-en-2-yl)chroman-4-yl]malonate (2c):

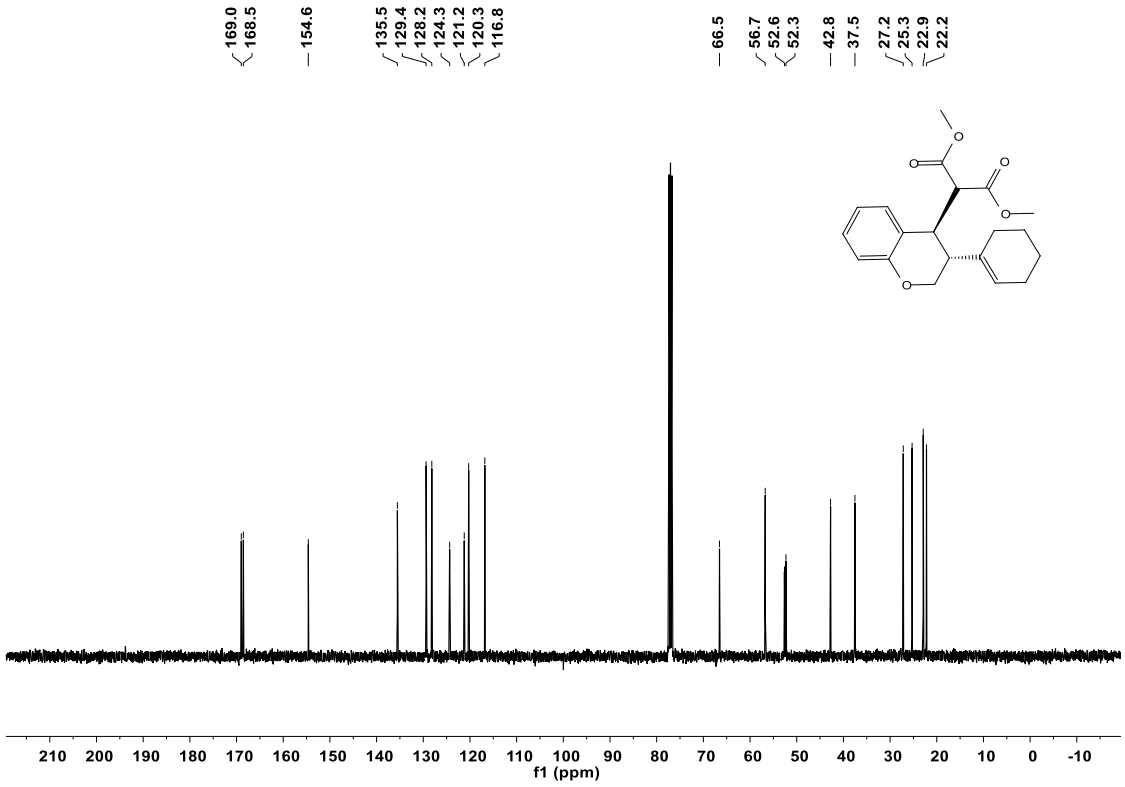


Dimethyl 2-[3-(cyclopent-1-en-1-yl)chroman-4-yl]malonate (2d):

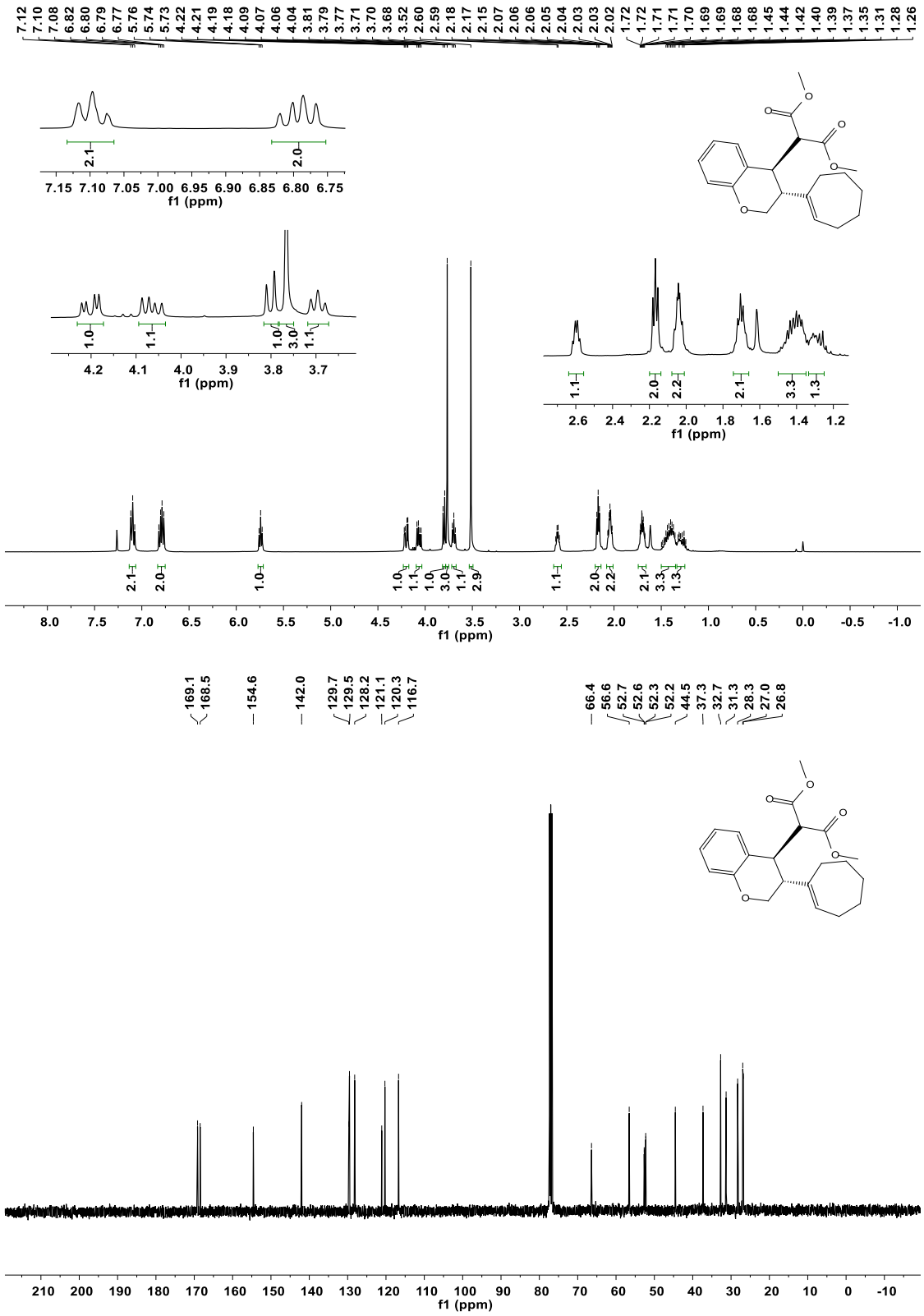


Dimethyl 2-[3-(cyclohex-1-en-1-yl)chroman-4-yl]malonate (2e):

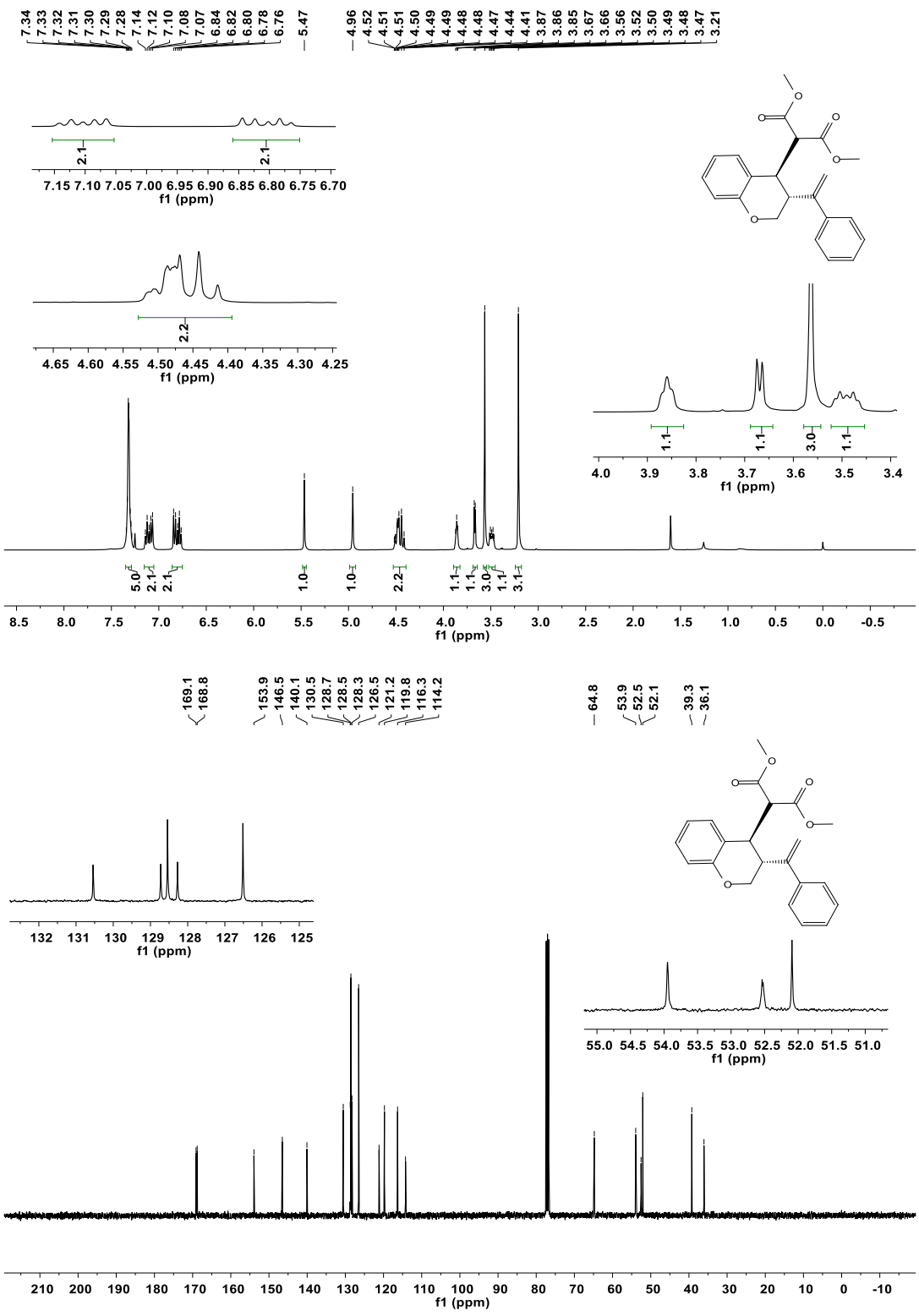




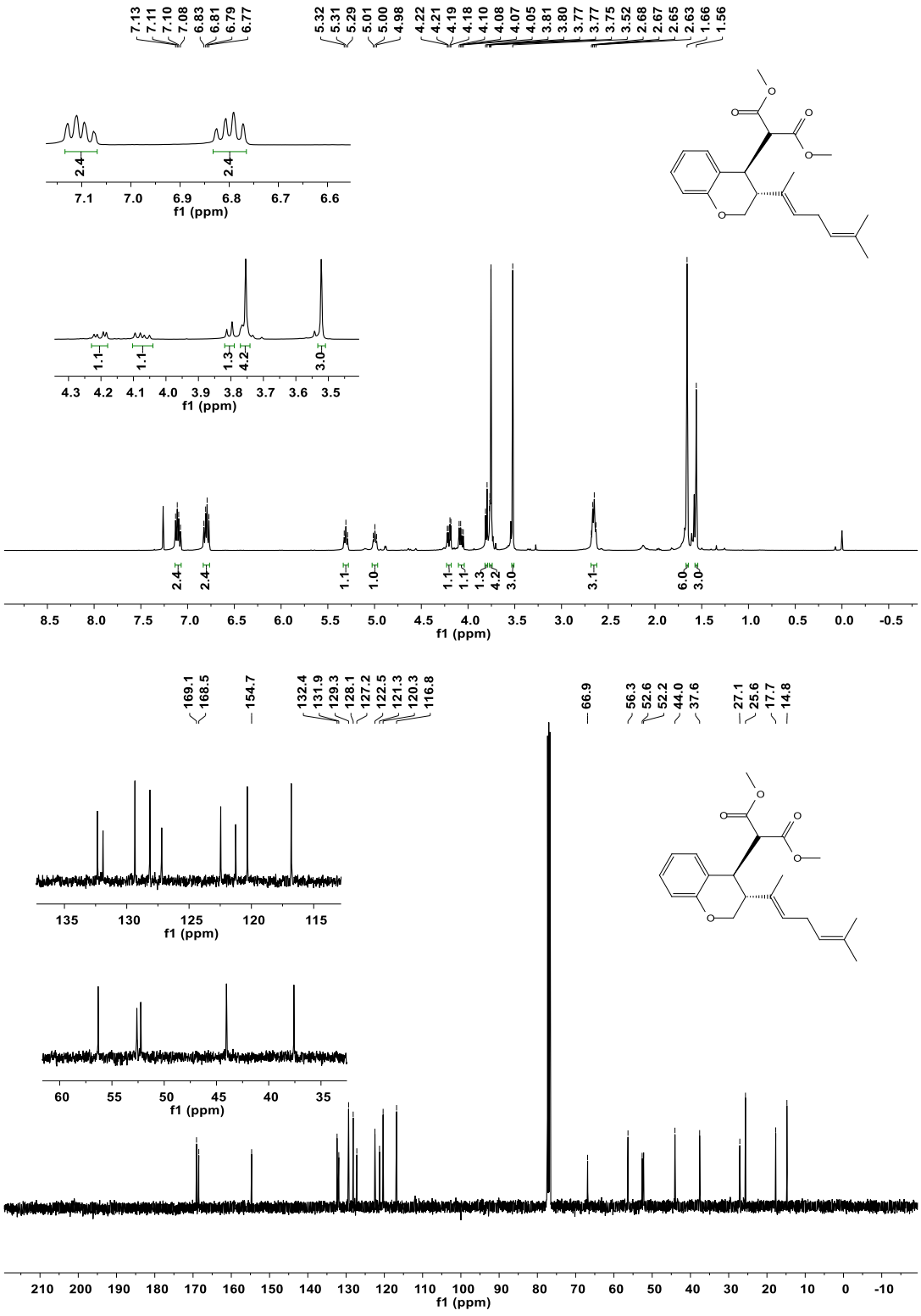
Dimethyl 2-[3-(cyclohept-1-en-1-yl)chroman-4-yl]malonate (2f):



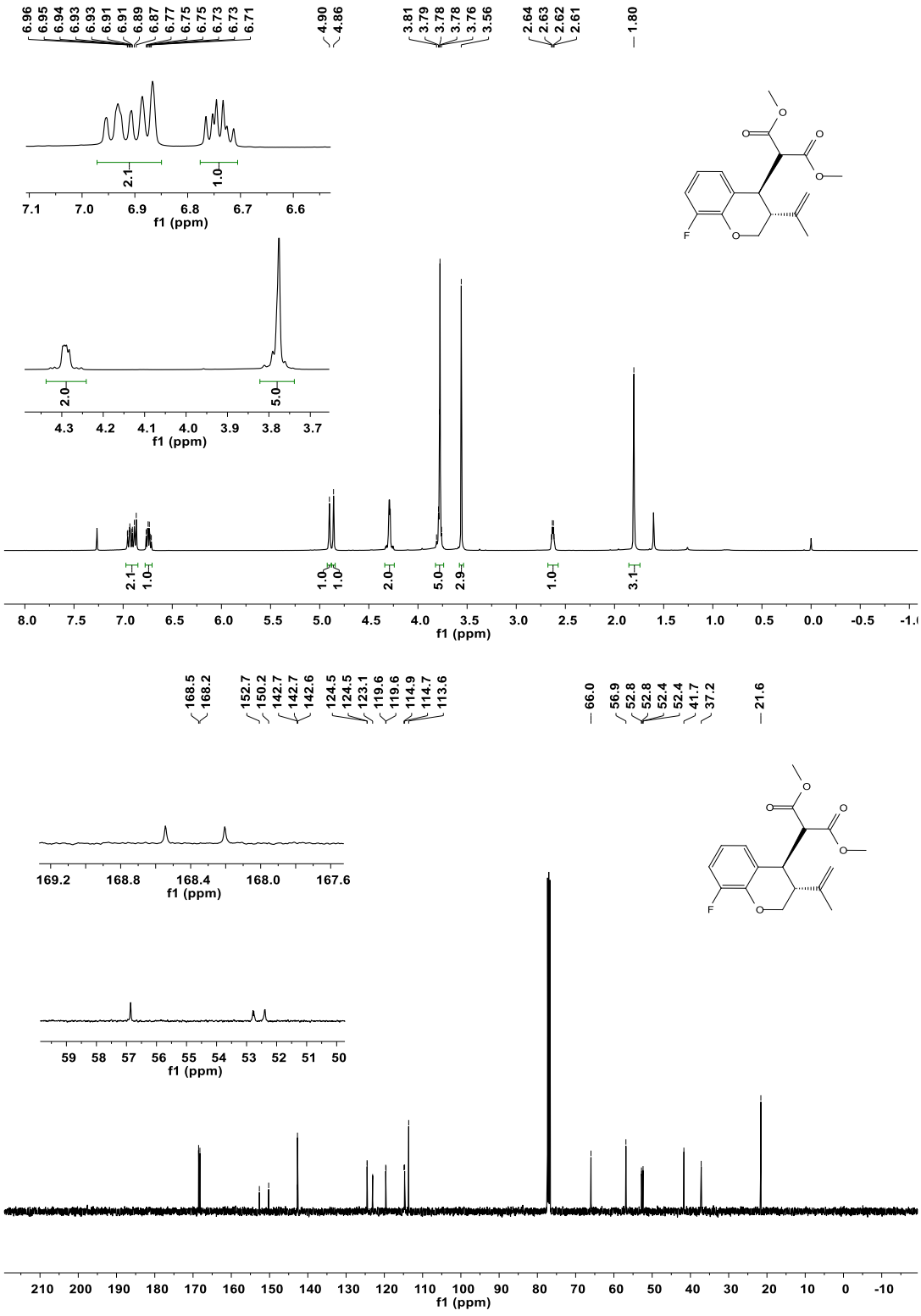
Dimethyl 2-[3-(1-phenylvinyl)chroman-4-yl]malonate (2g):

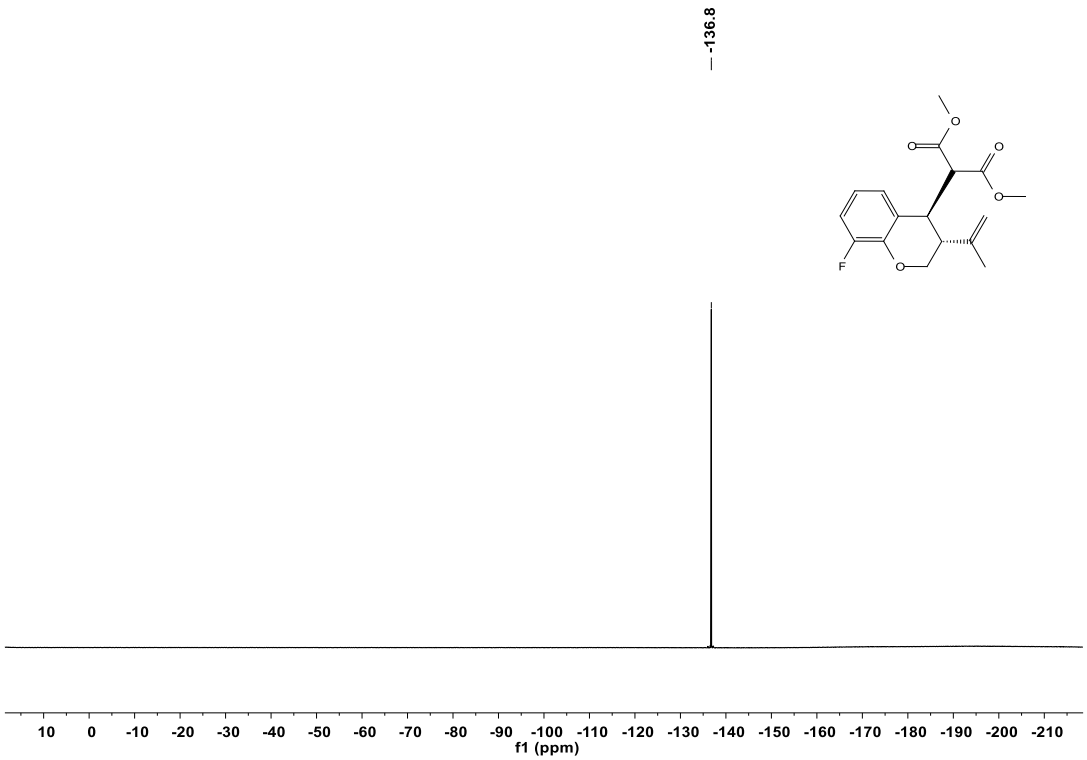


Dimethyl 2-[3-(6-methylhepta-1,5-dien-2-yl)chroman-4-yl]malonate (2h):

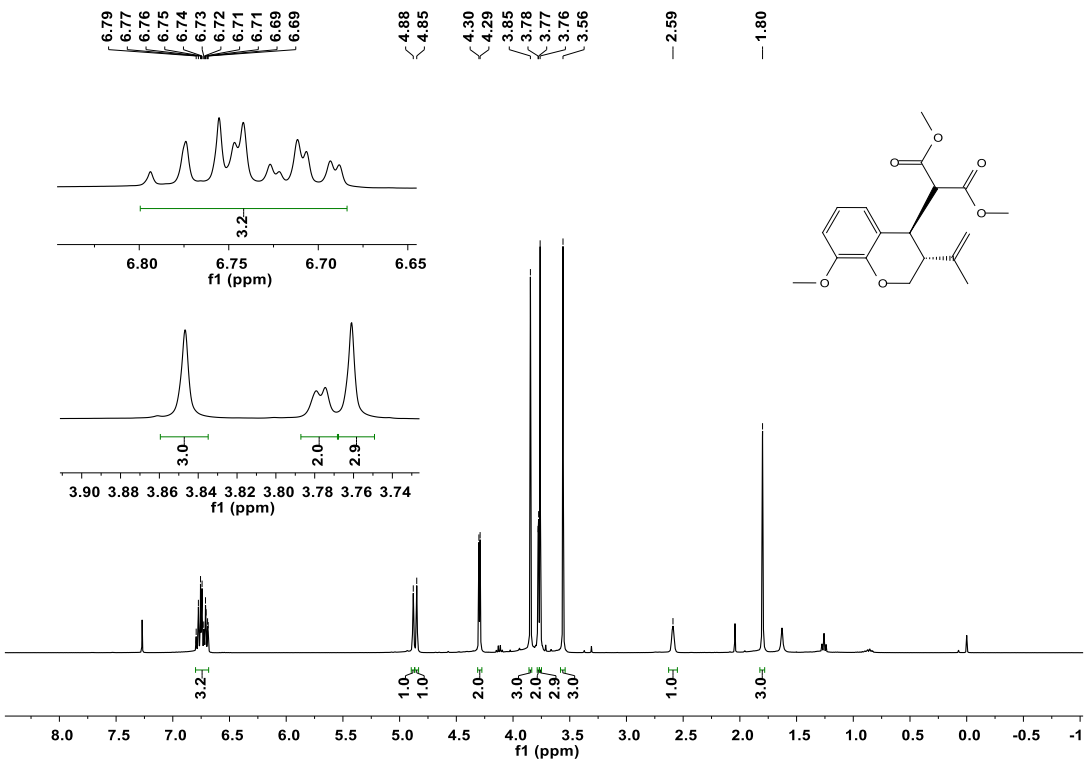


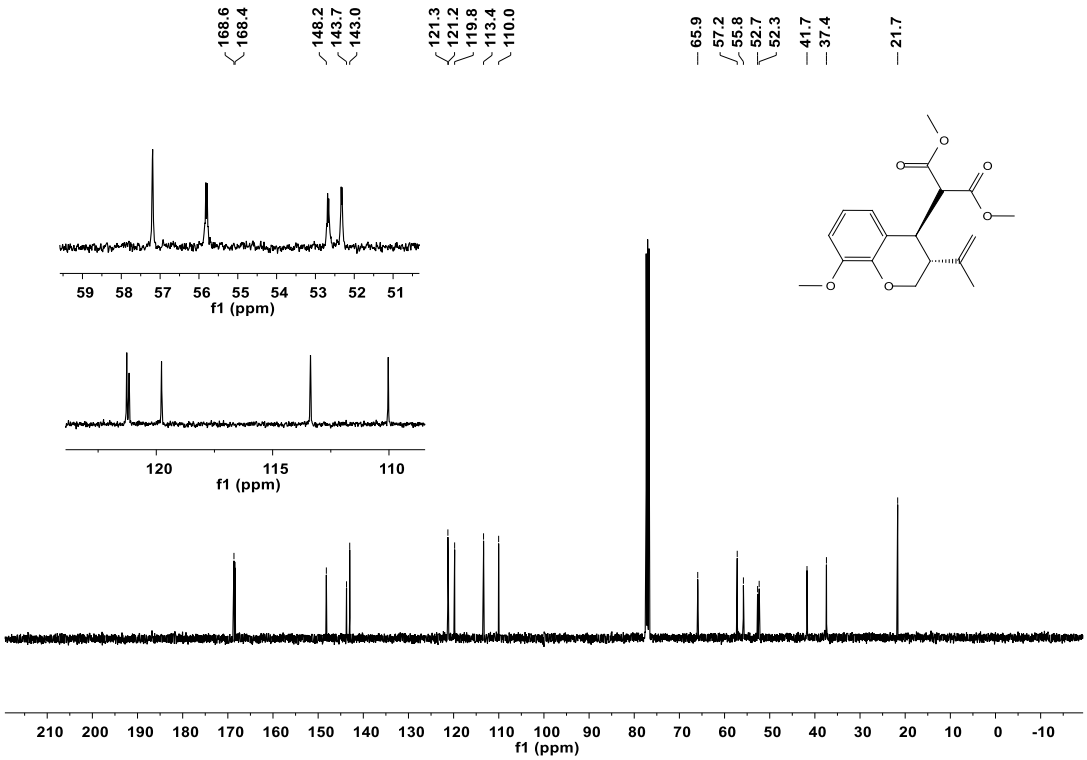
Dimethyl 2-[8-fluoro-3-(prop-1-en-2-yl)chroman-4-yl]malonate (2i):



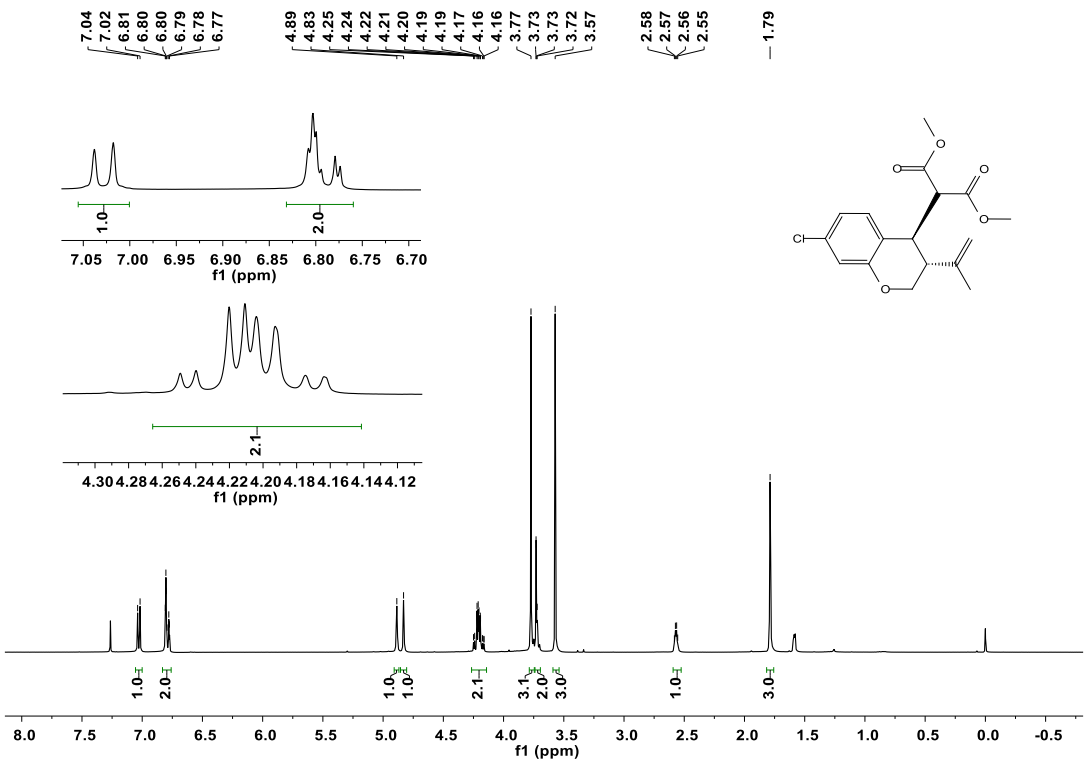


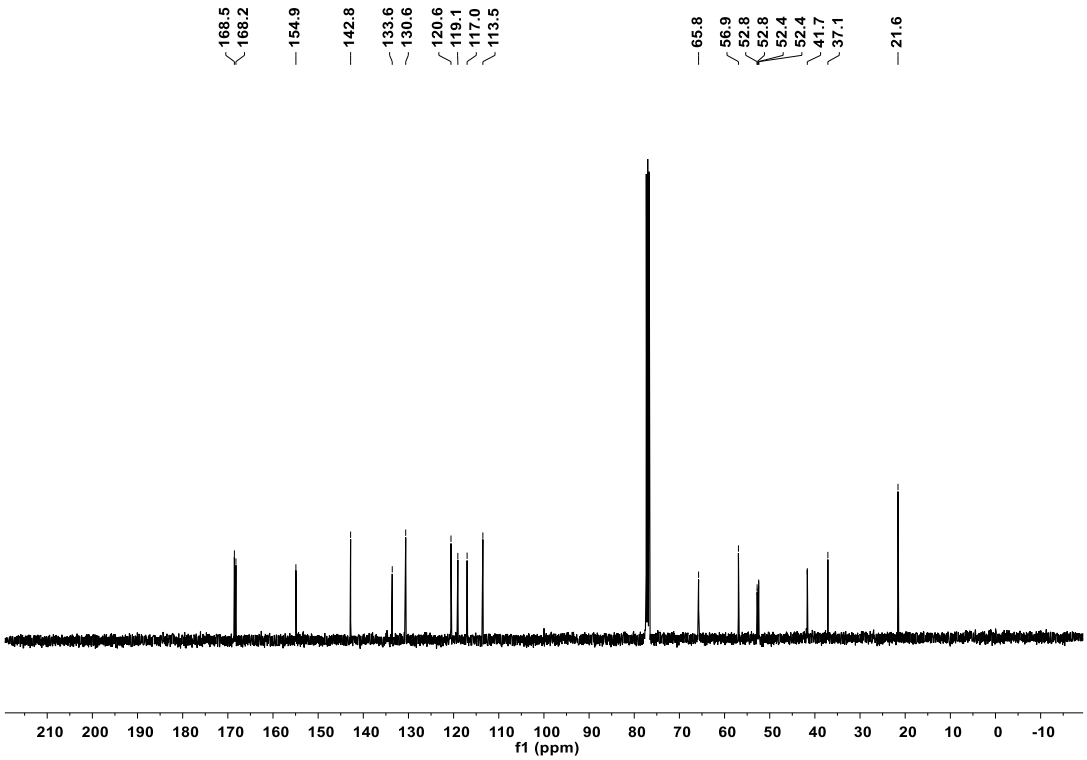
Dimethyl 2-[8-methoxy-3-(prop-1-en-2-yl)chroman-4-yl]malonate (2j):



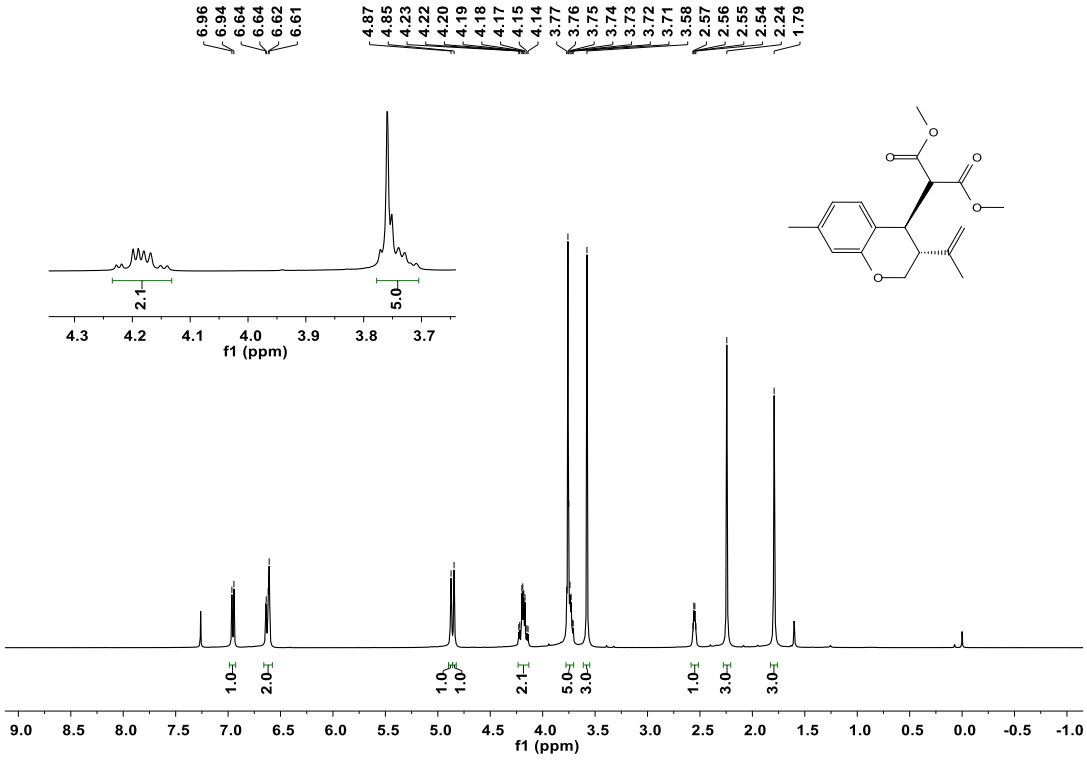


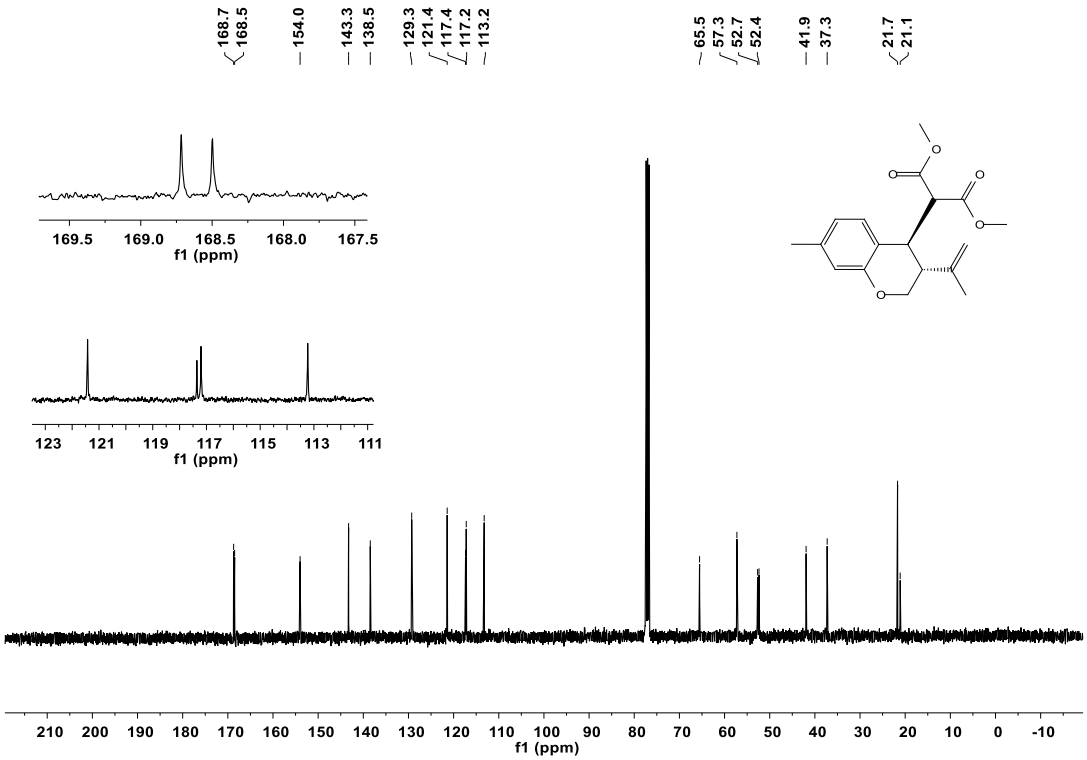
Dimethyl 2-[7-chloro-3-(prop-1-en-2-yl)chroman-4-yl]malonate (2k):



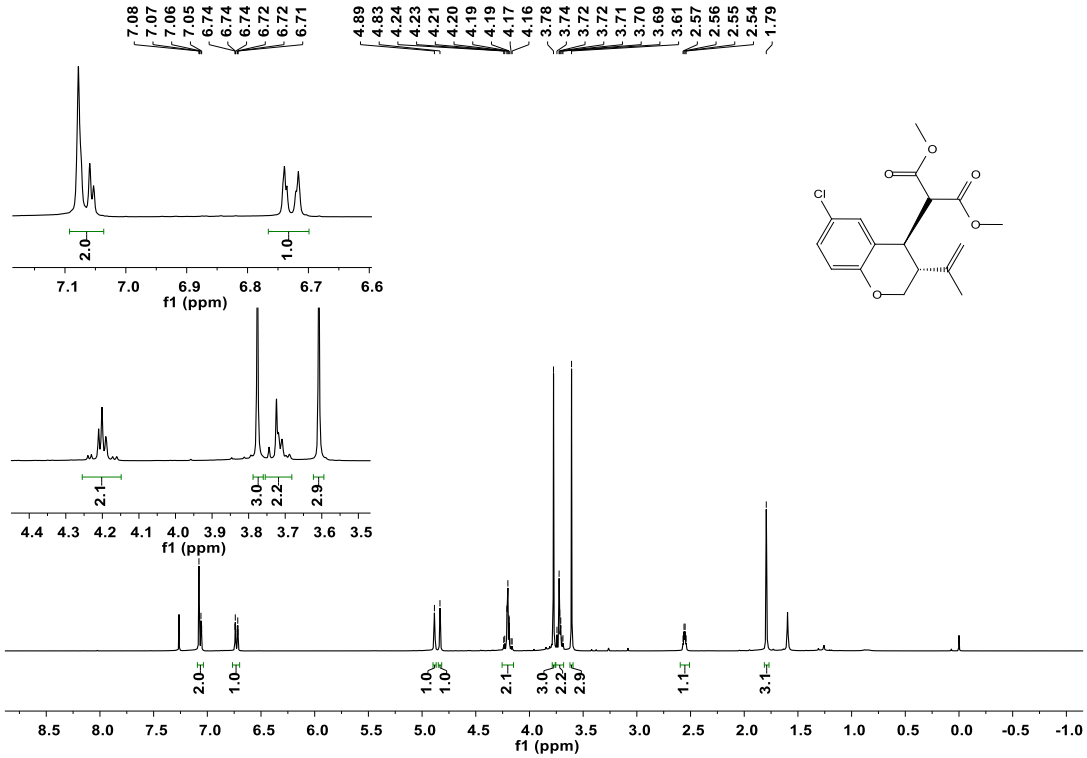


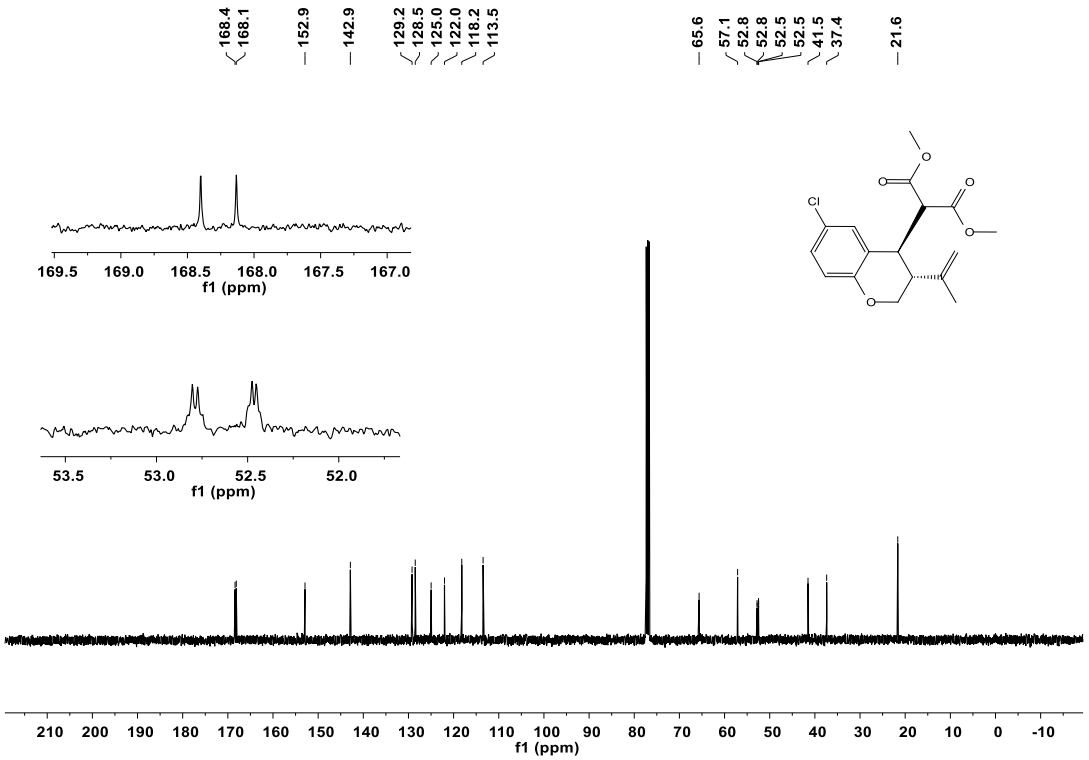
Dimethyl 2-[7-methyl-3-(prop-1-en-2-yl)chroman-4-yl]malonate (2l):



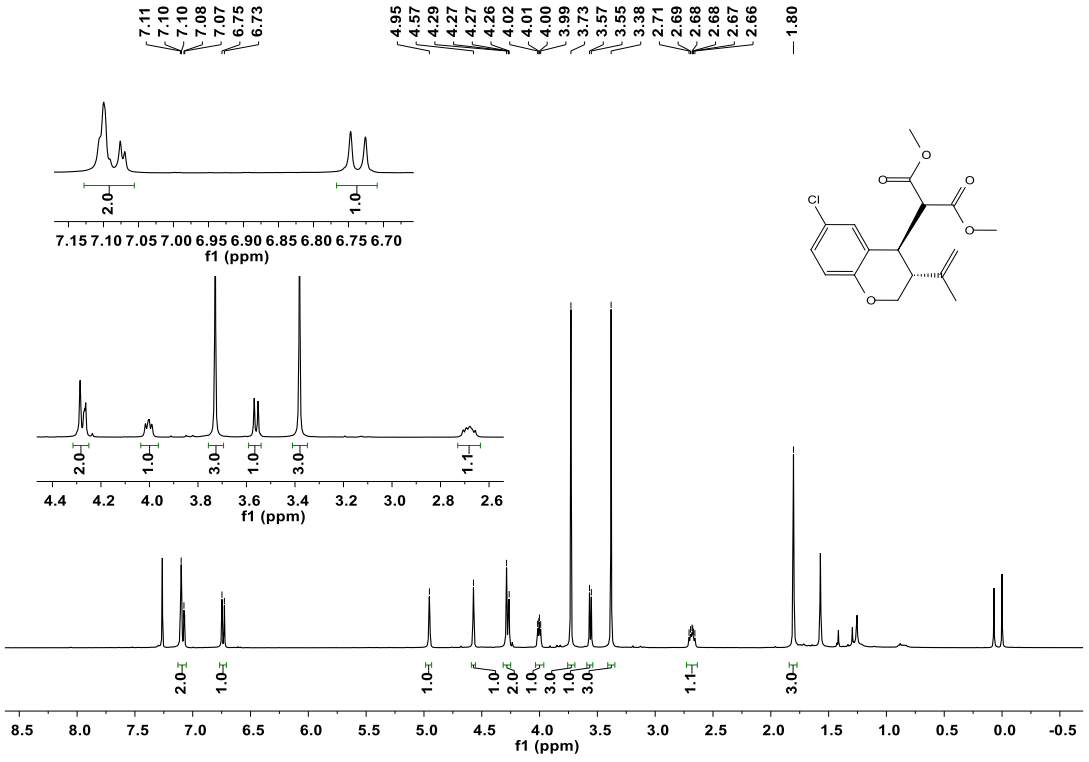


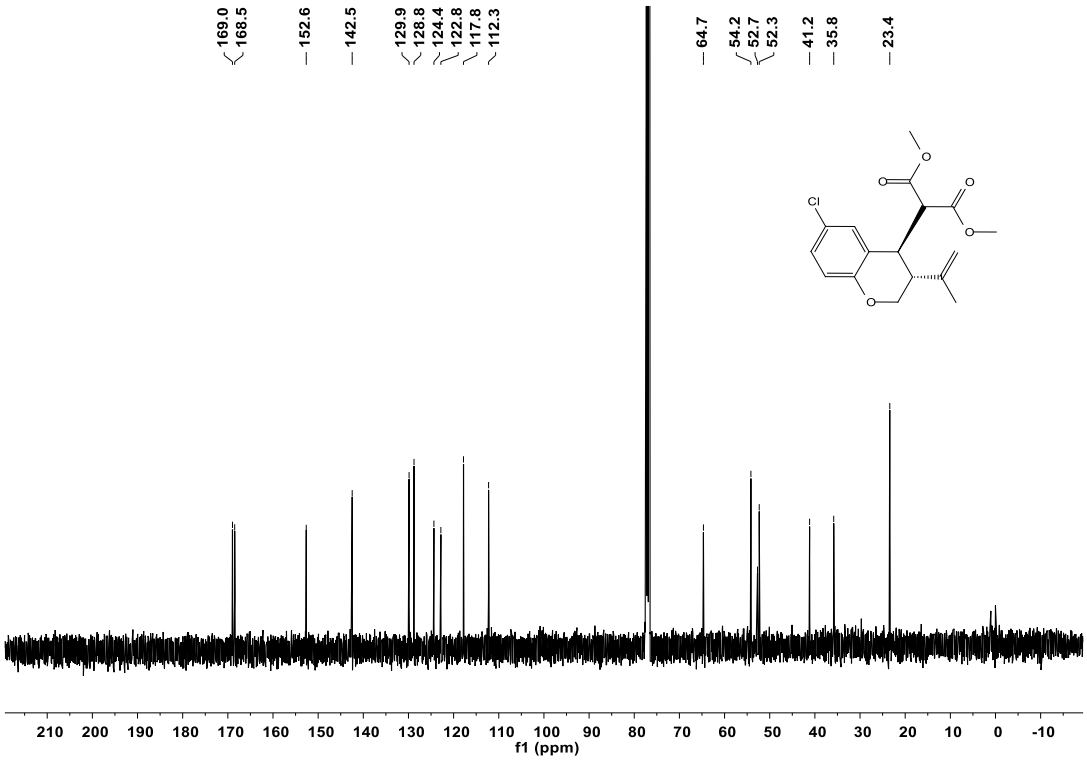
Dimethyl 2-[6-chloro-3-(prop-1-en-2-yl)chroman-4-yl]malonate (2m) (major):



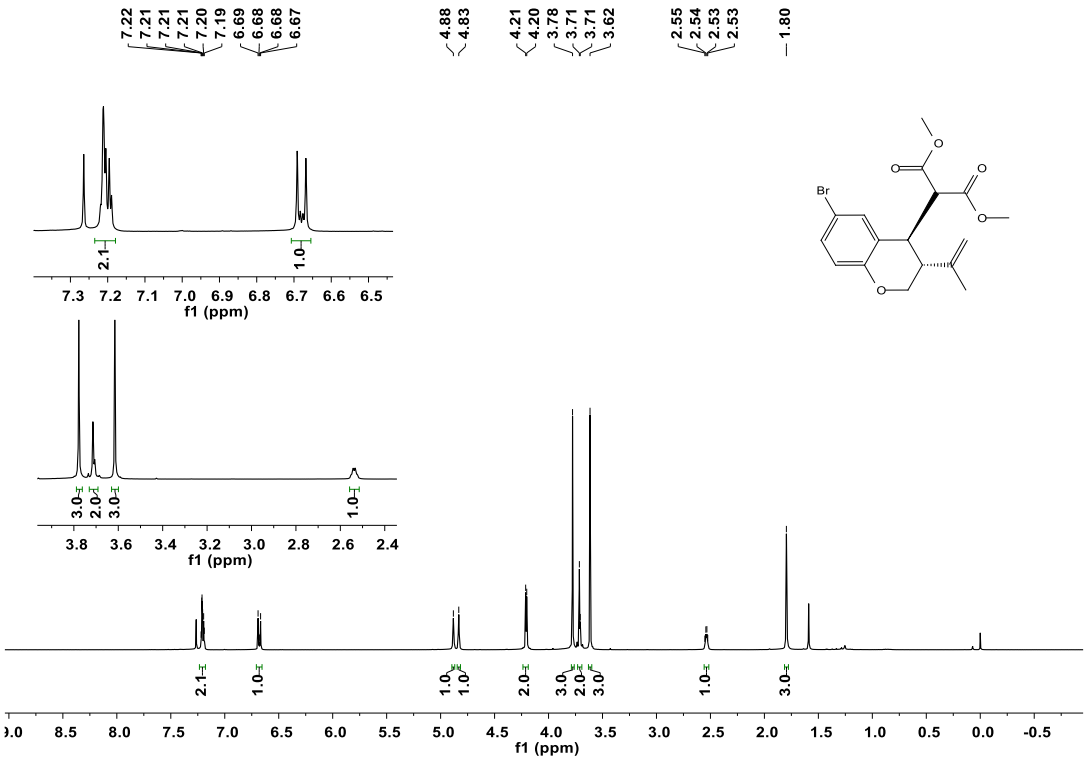


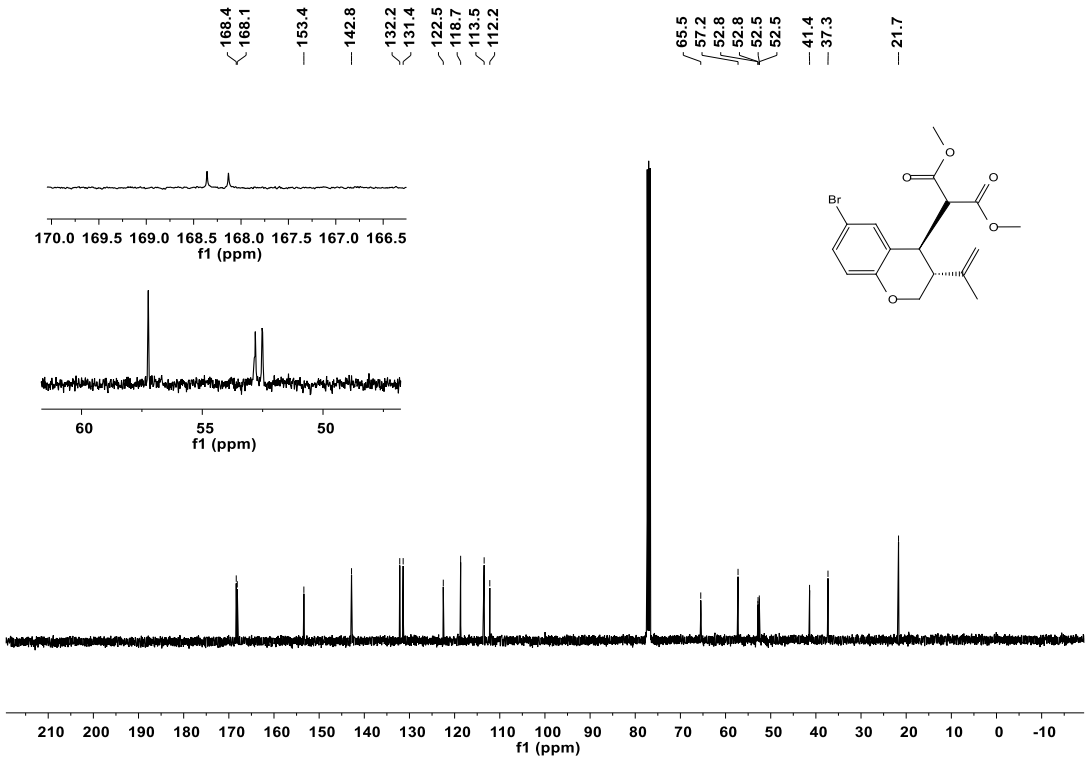
Dimethyl 2-[6-chloro-3-(prop-1-en-2-yl)chroman-4-yl]malonate (2m) (minor):



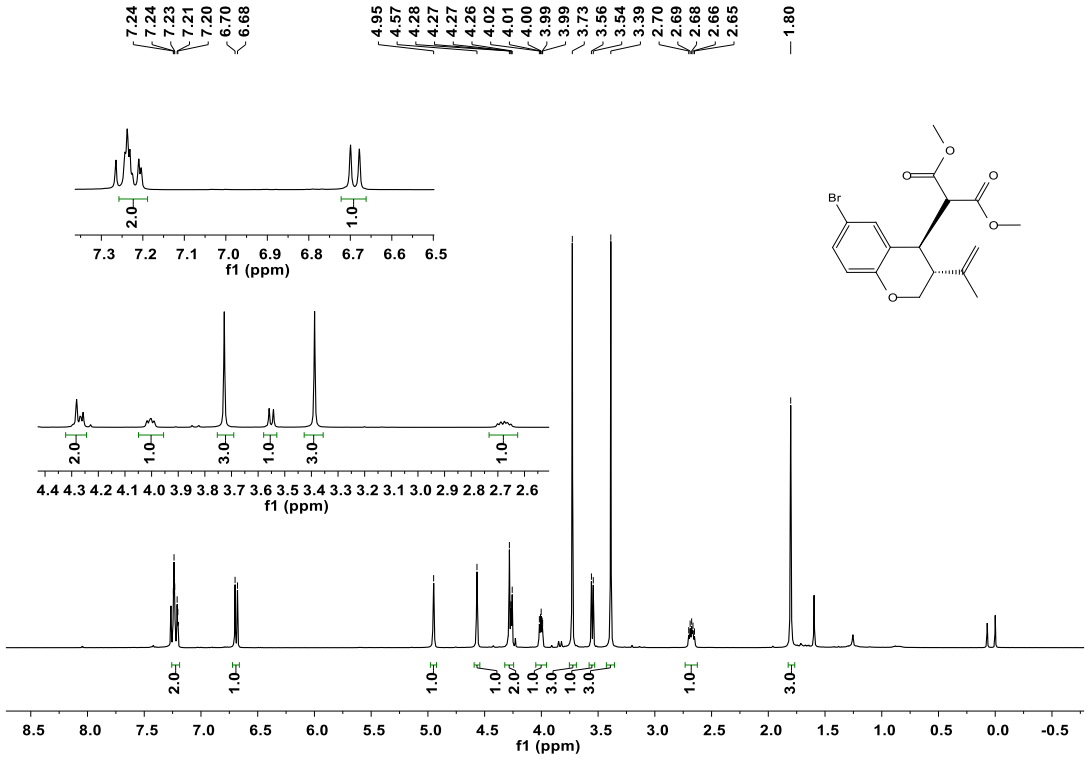


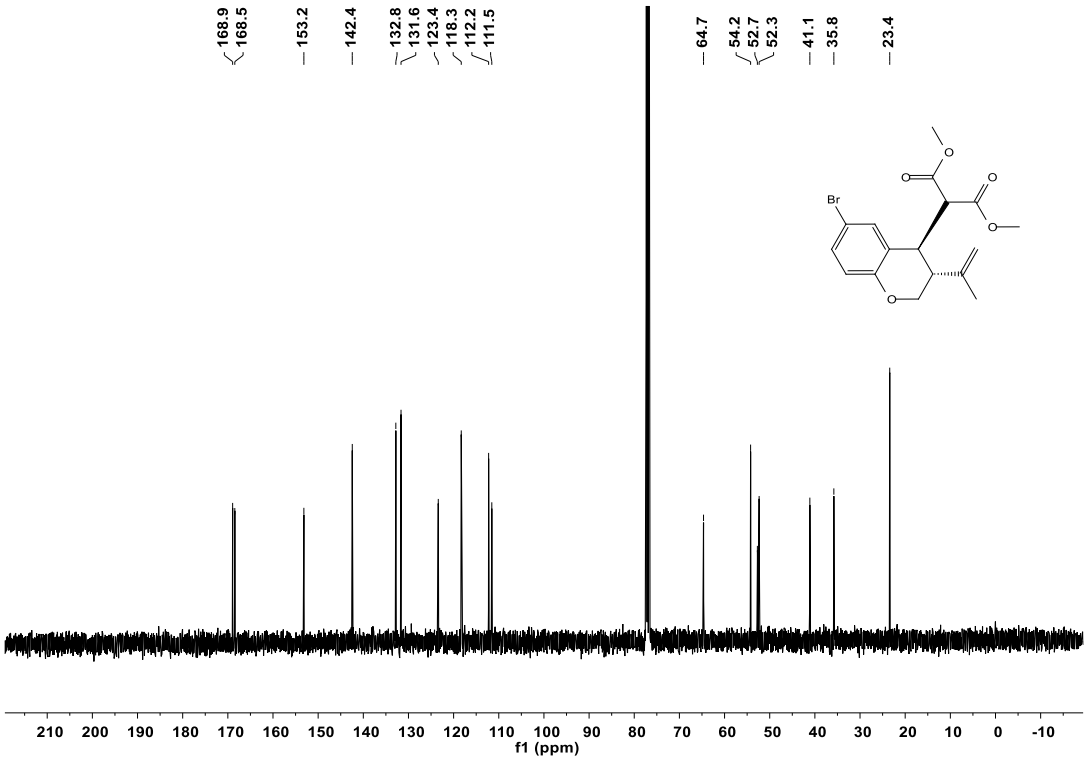
Dimethyl 2-[6-bromo-3-(prop-1-en-2-yl)chroman-4-yl]malonate (2n) (major):



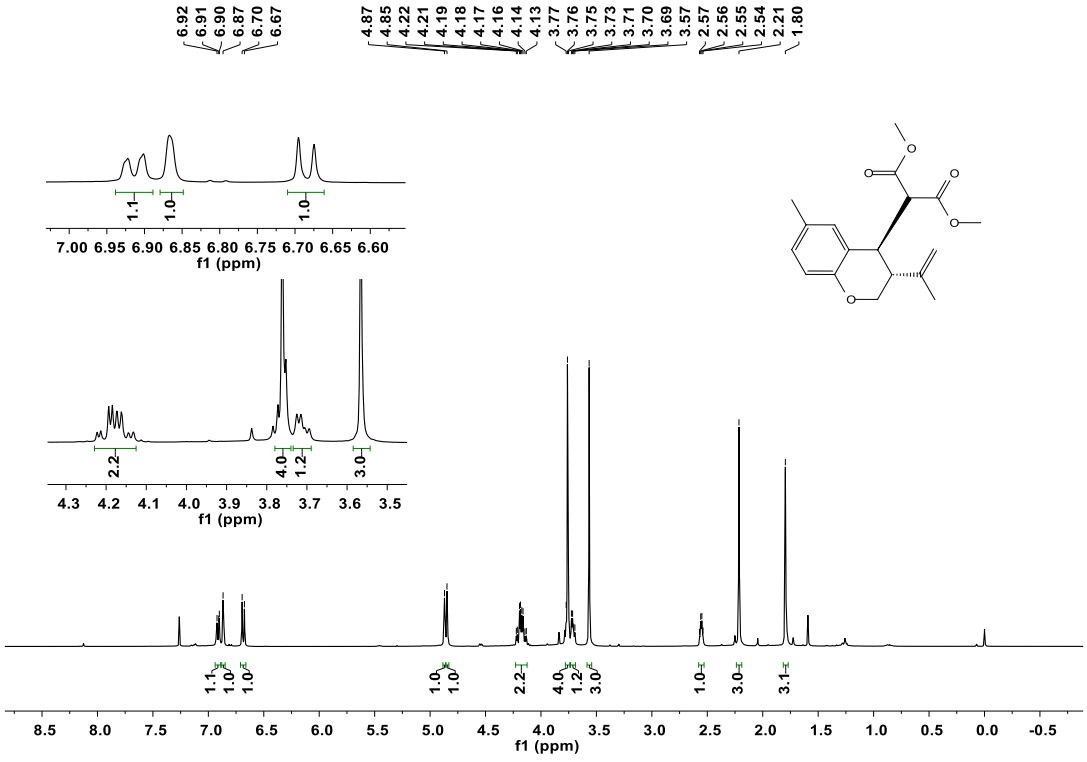


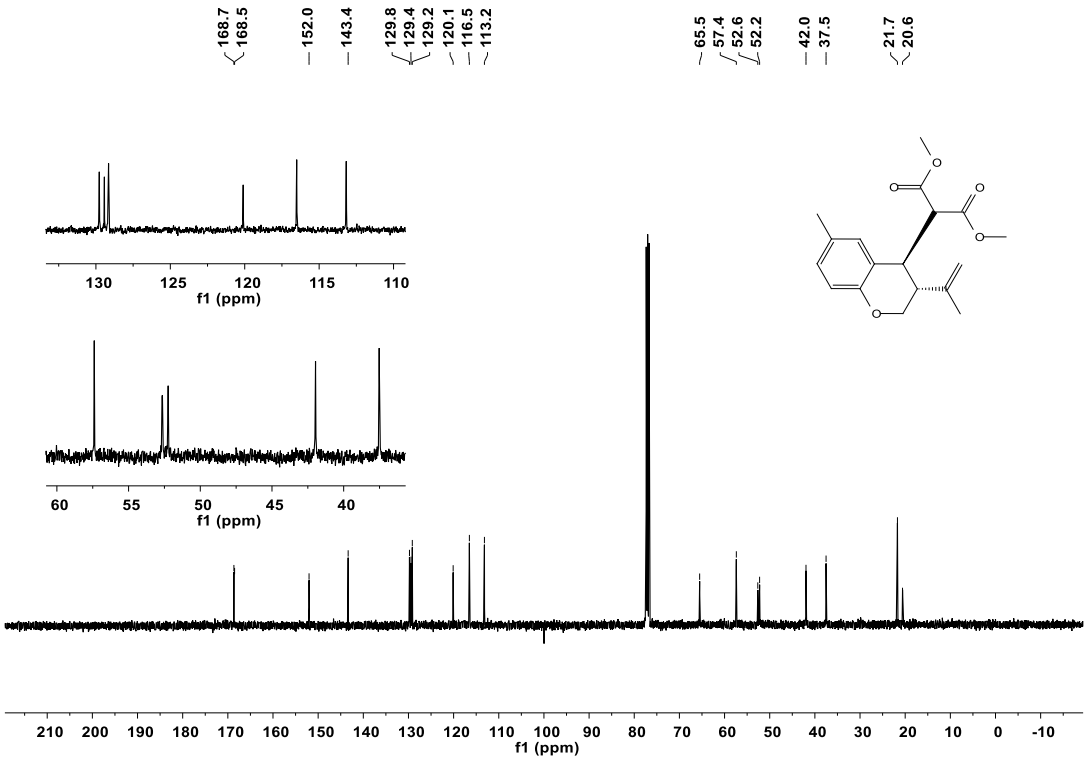
Dimethyl 2-[6-bromo-3-(prop-1-en-2-yl)chroman-4-yl]malonate (2n) (minor):



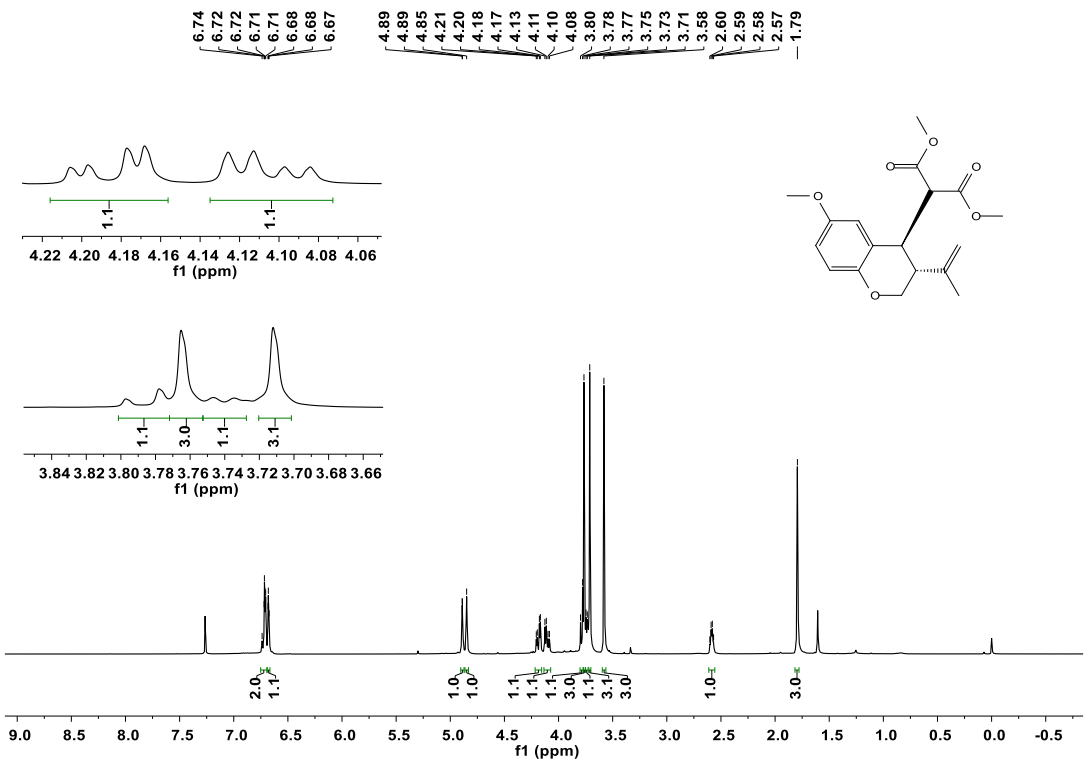


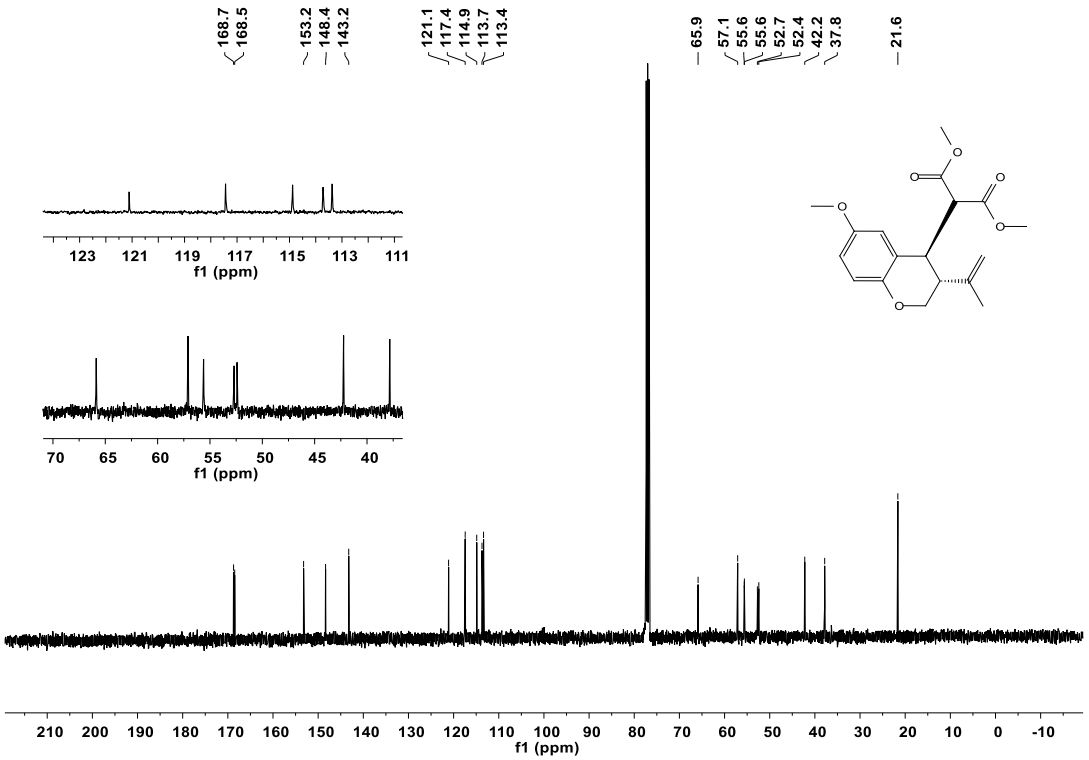
Dimethyl 2-[6-methyl-3-(prop-1-en-2-yl)chroman-4-yl]malonate (2o):



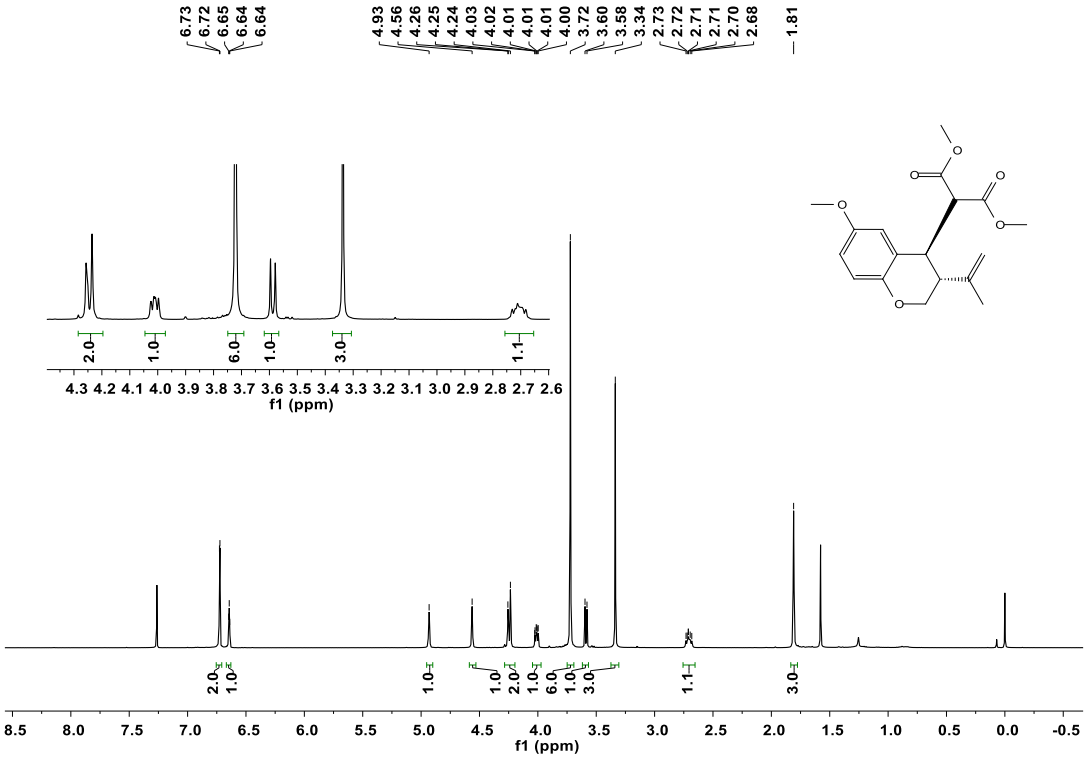


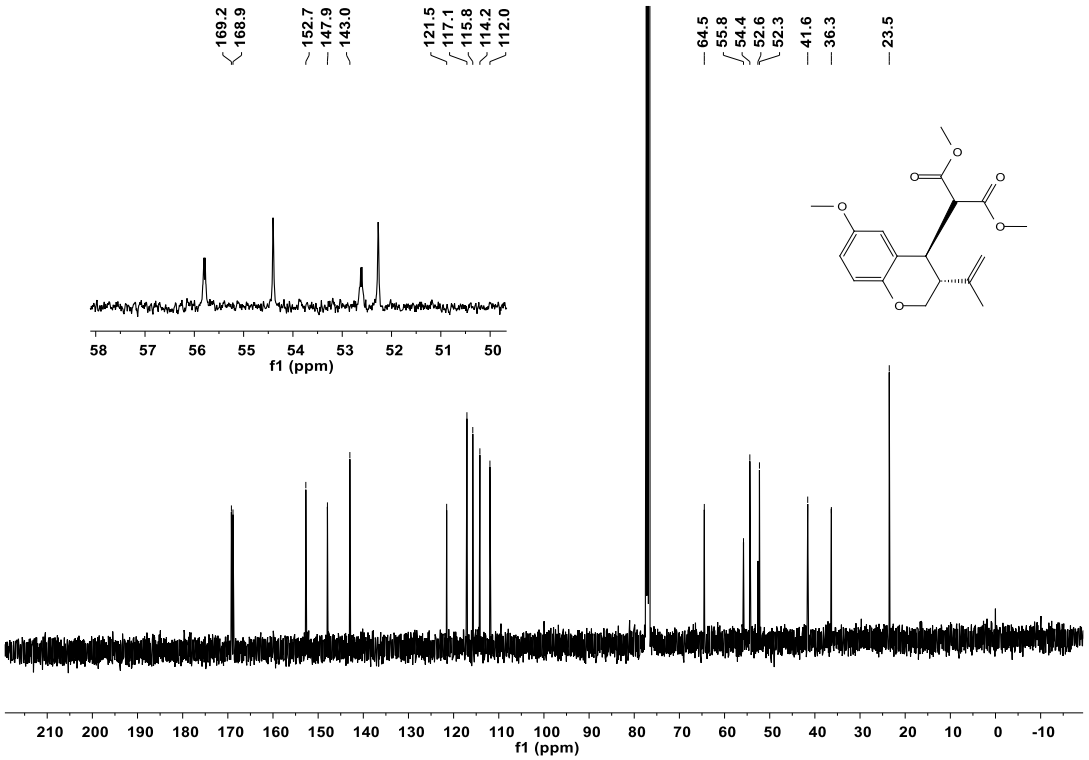
Dimethyl 2-[6-methoxy-3-(prop-1-en-2-yl)chroman-4-yl]malonate (2p) (major):



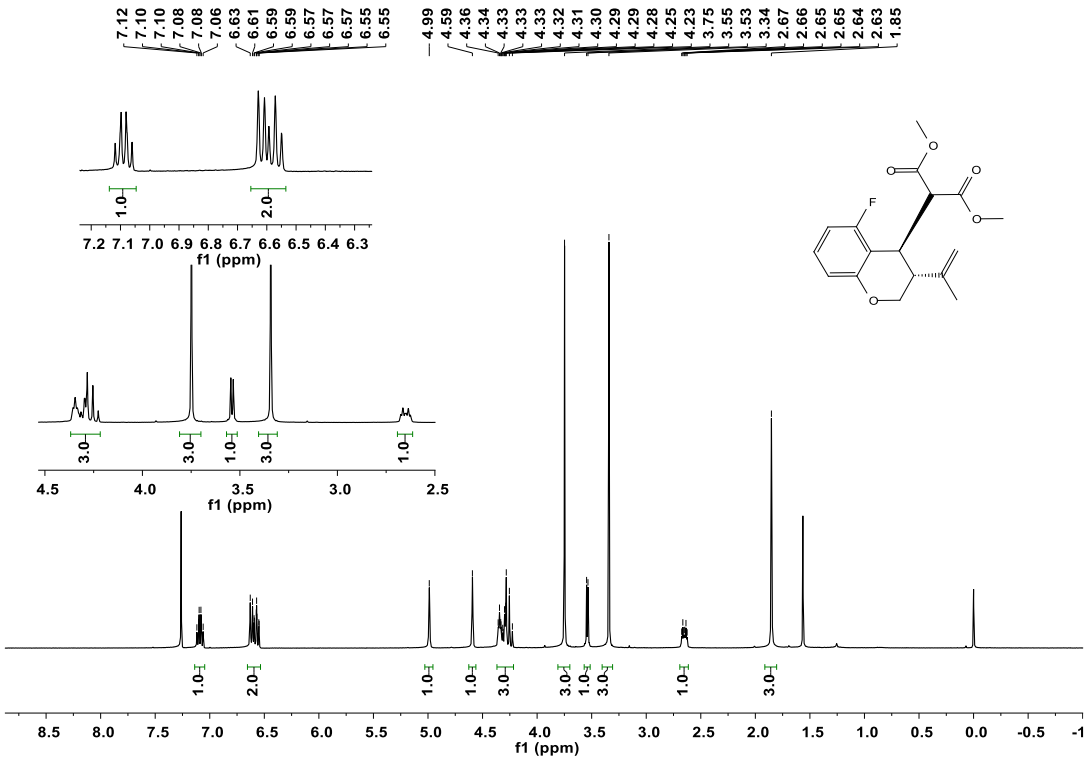


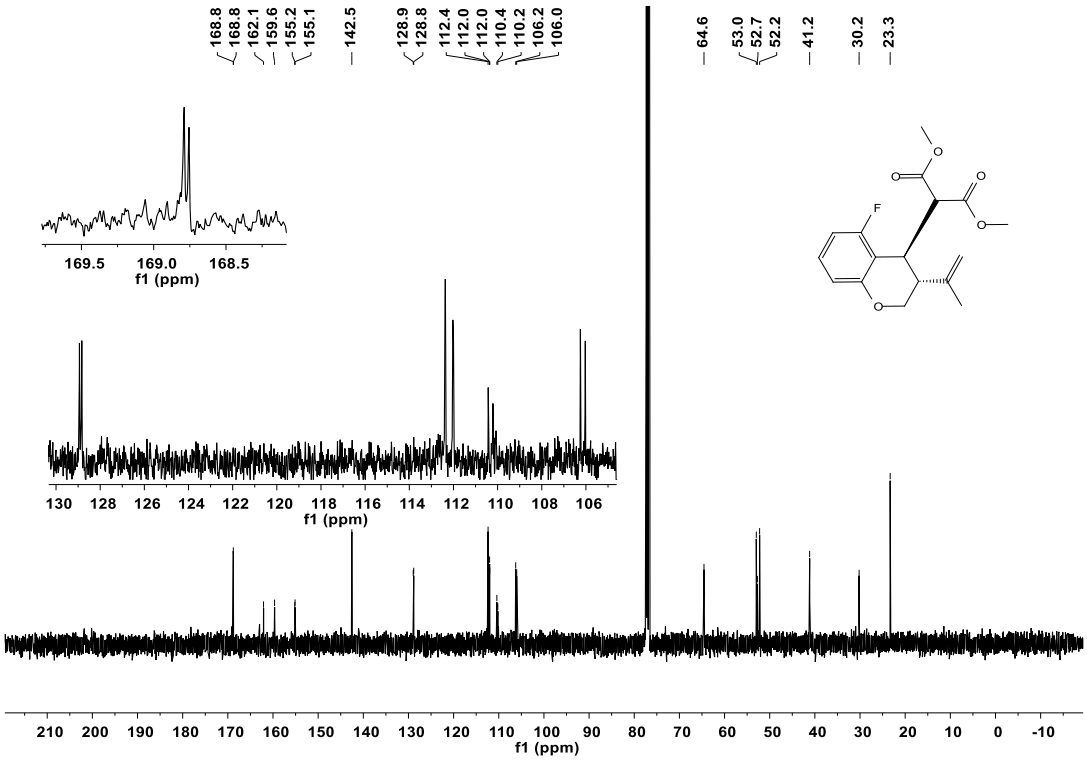
Dimethyl 2-[6-methoxy-3-(prop-1-en-2-yl)chroman-4-yl]malonate (2p) (minor):

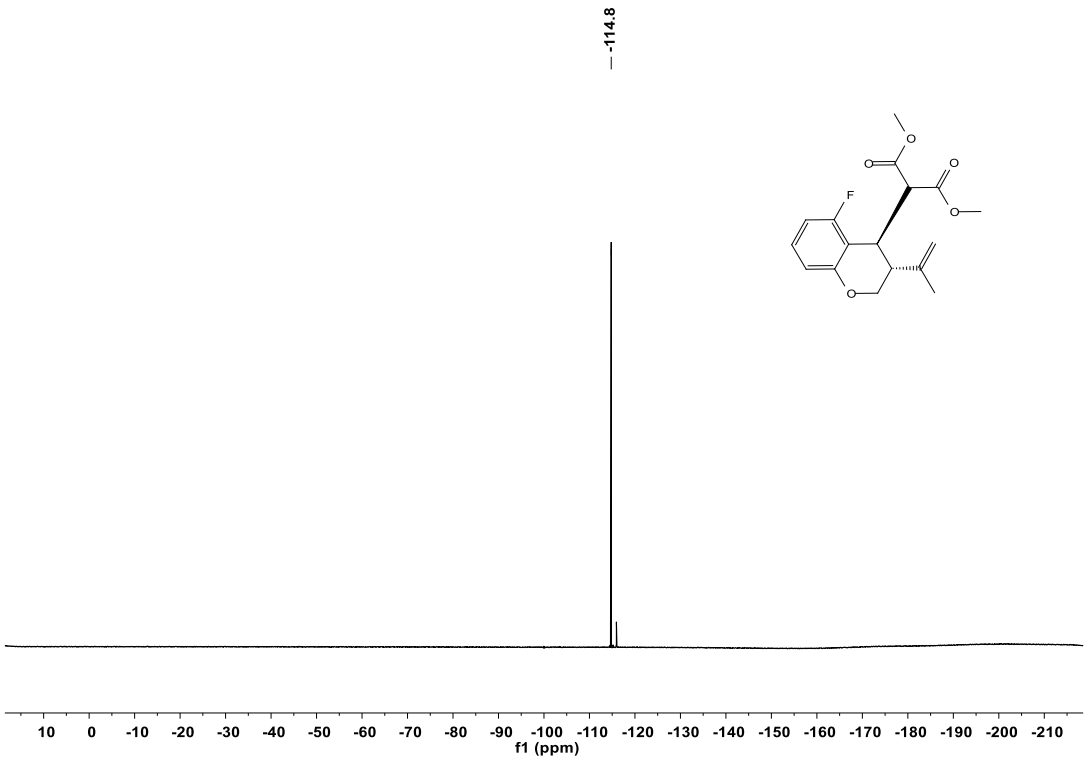




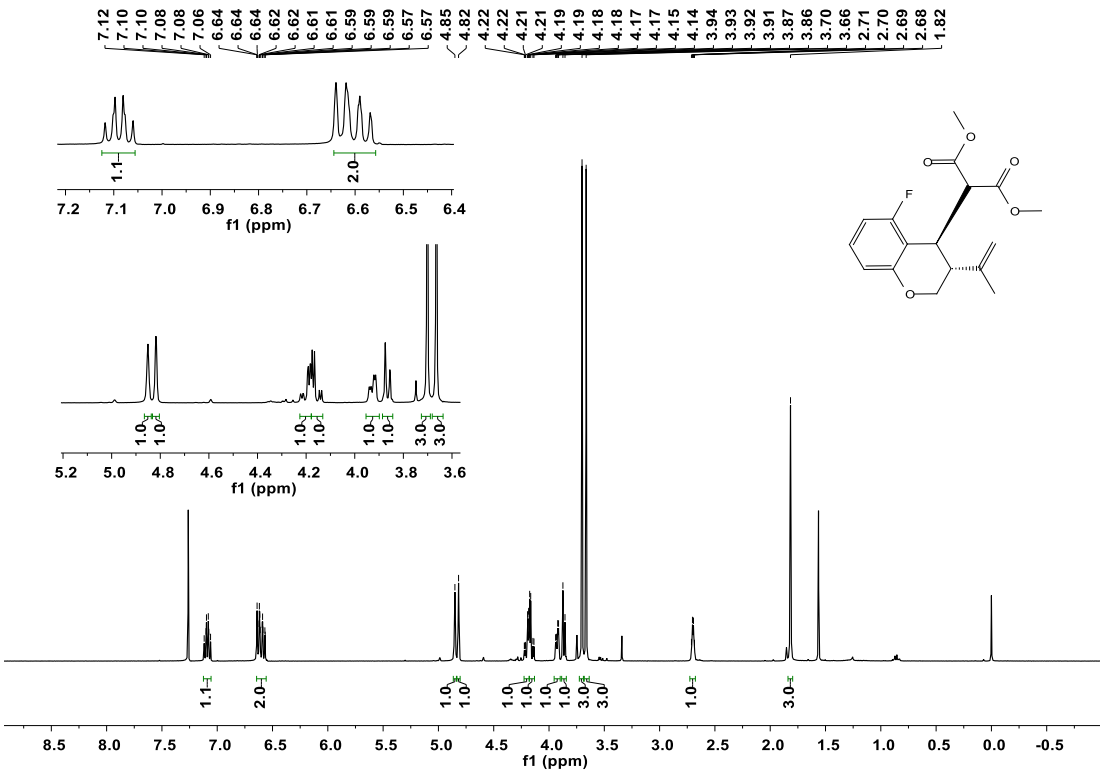
Dimethyl 2-[5-fluoro-3-(prop-1-en-2-yl)chroman-4-yl]malonate (2q) (minor):

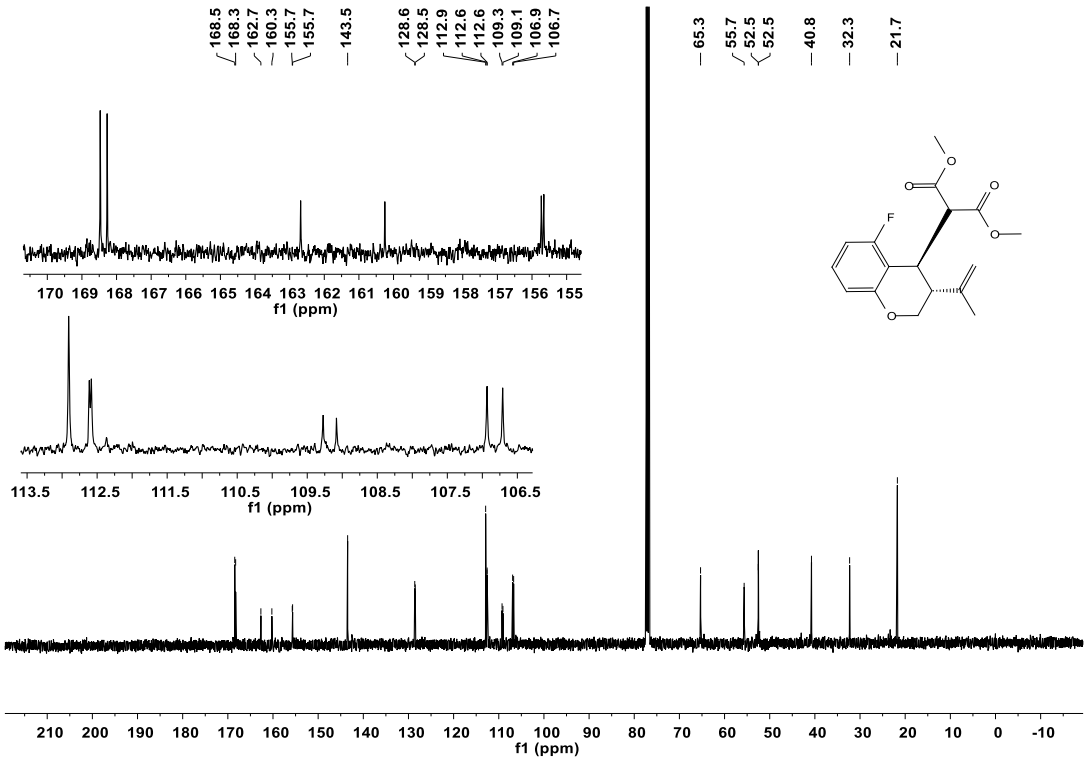


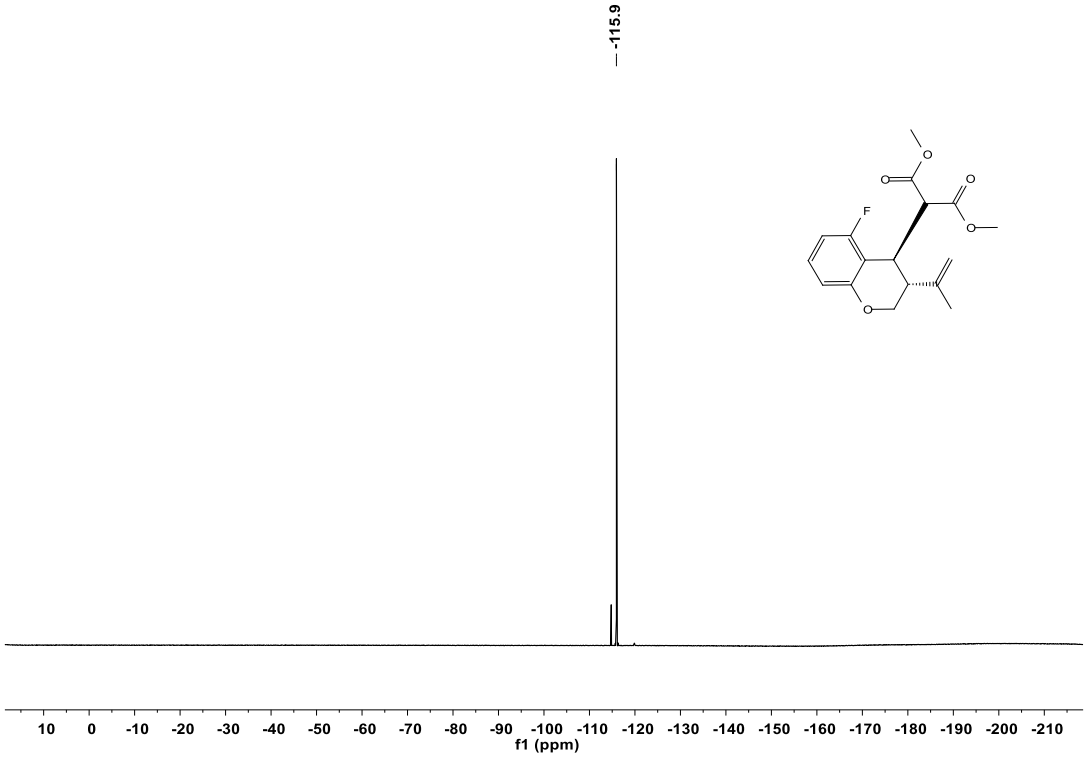

168.8
168.8
162.1
159.6
155.2
155.1
142.5
128.9
128.8
112.4
112.0
112.0
110.4
110.2
106.2
106.0
64.6
53.0
52.7
52.2
41.2
30.2
23.3
169.5
169.0
168.5
f1 (ppm)
130
128
126
124
122
120
118
116
114
112
110
108
106
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)
F
O


-114.8
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)
F
O

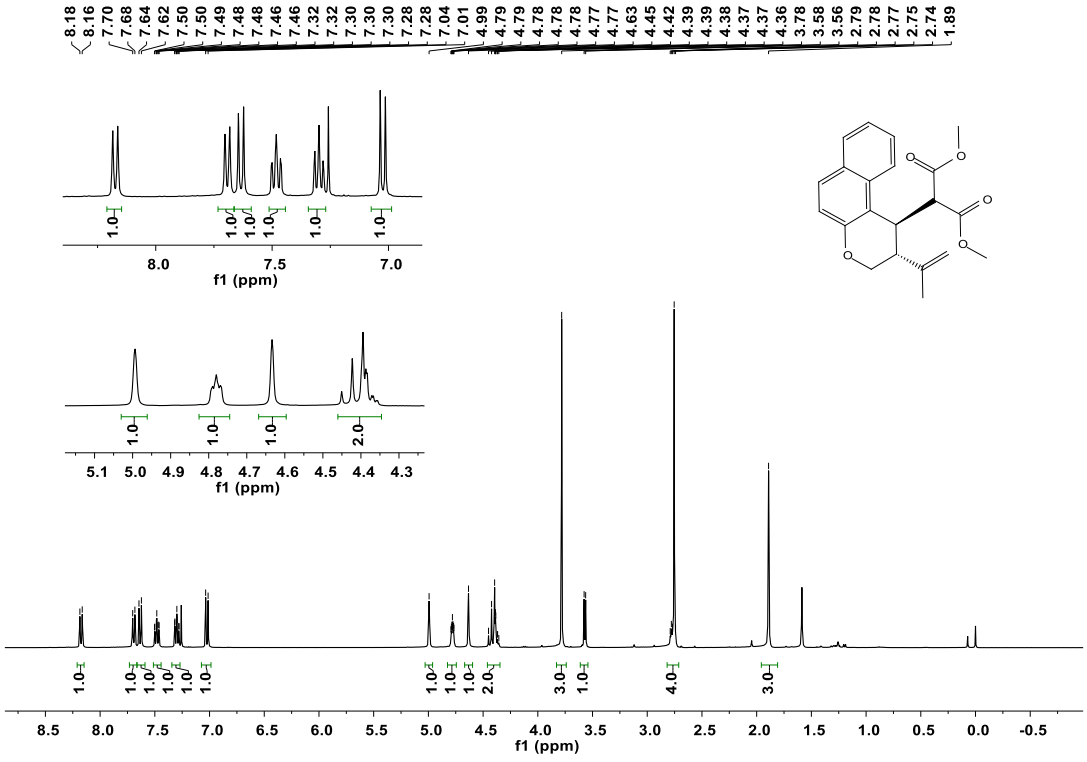
Dimethyl 2-[5-fluoro-3-(prop-1-en-2-yl)chroman-4-yl]malonate (2q) (major):

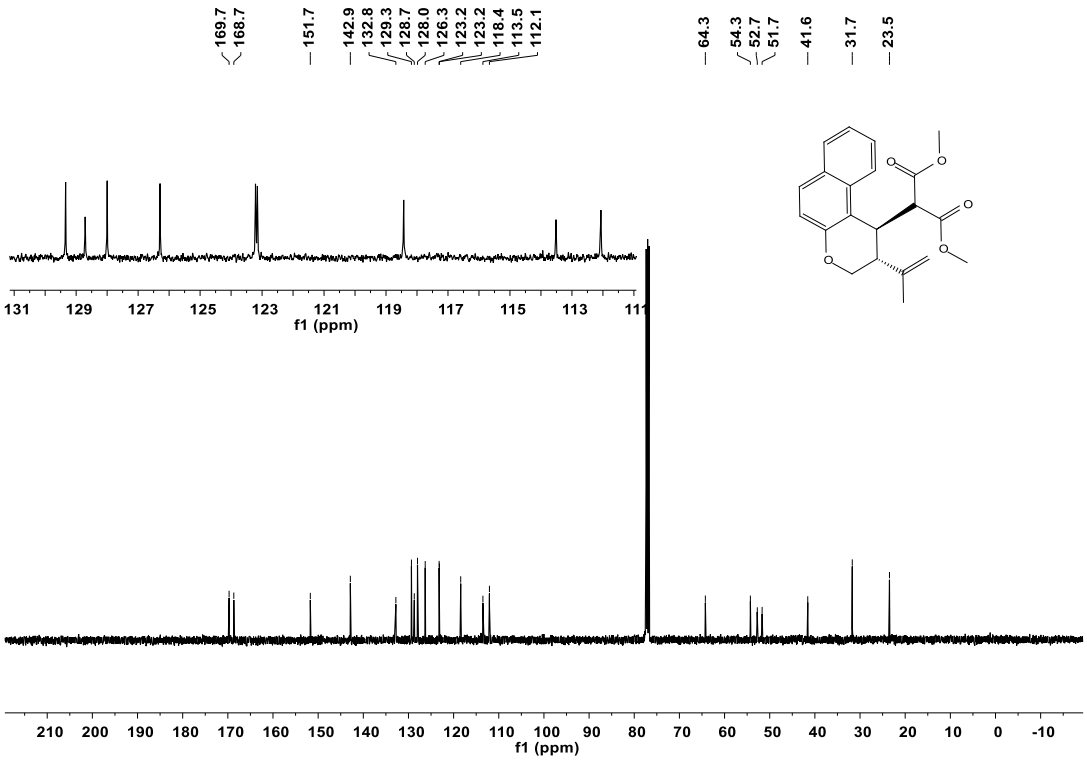




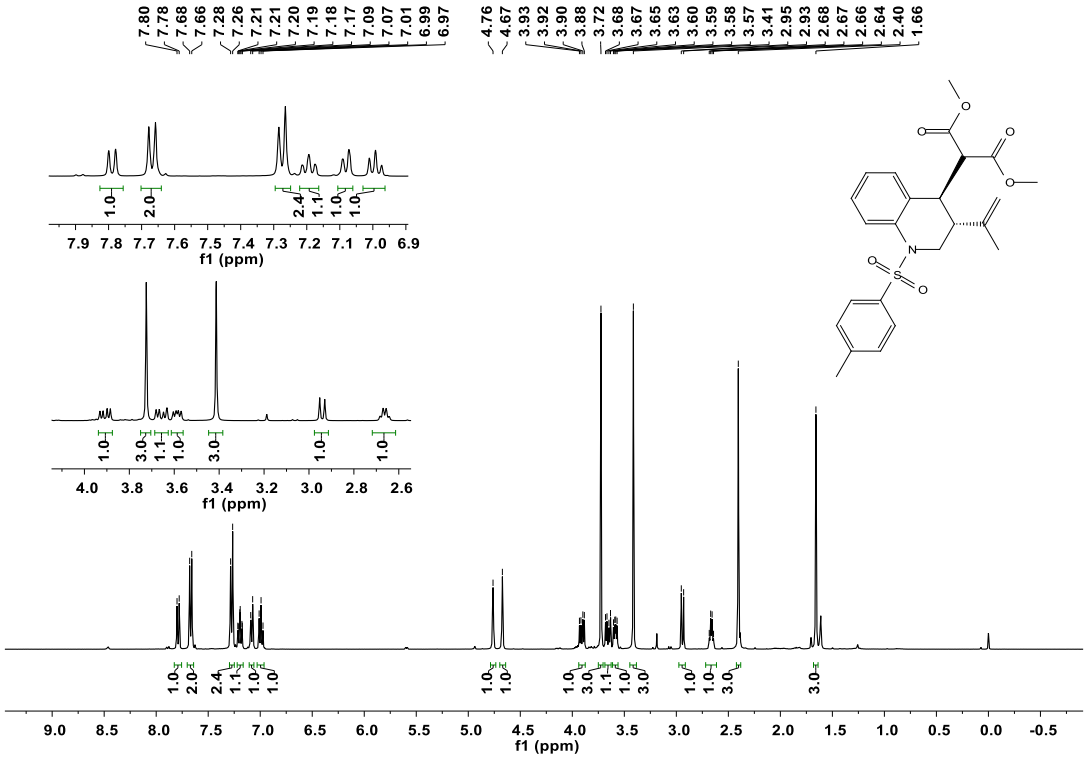


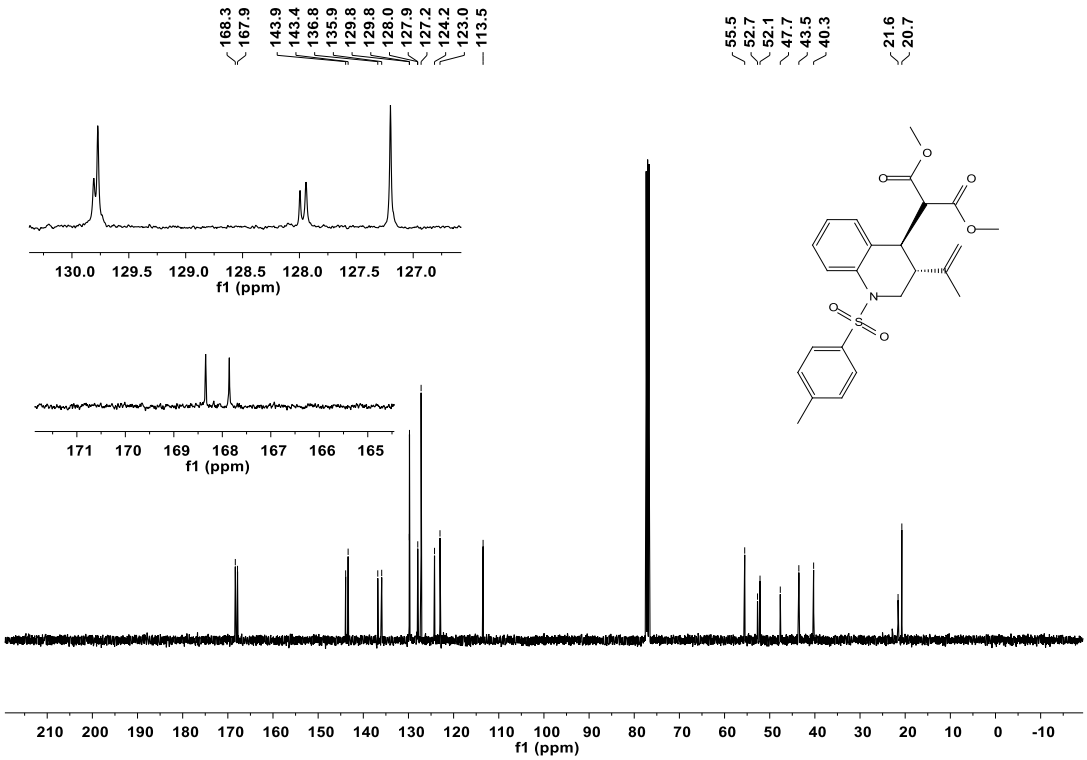
Dimethyl 2-{2-(prop-1-en-2-yl)-2,3-dihydro-1H-benzo[f]chromen-1-y}malonate (2r):



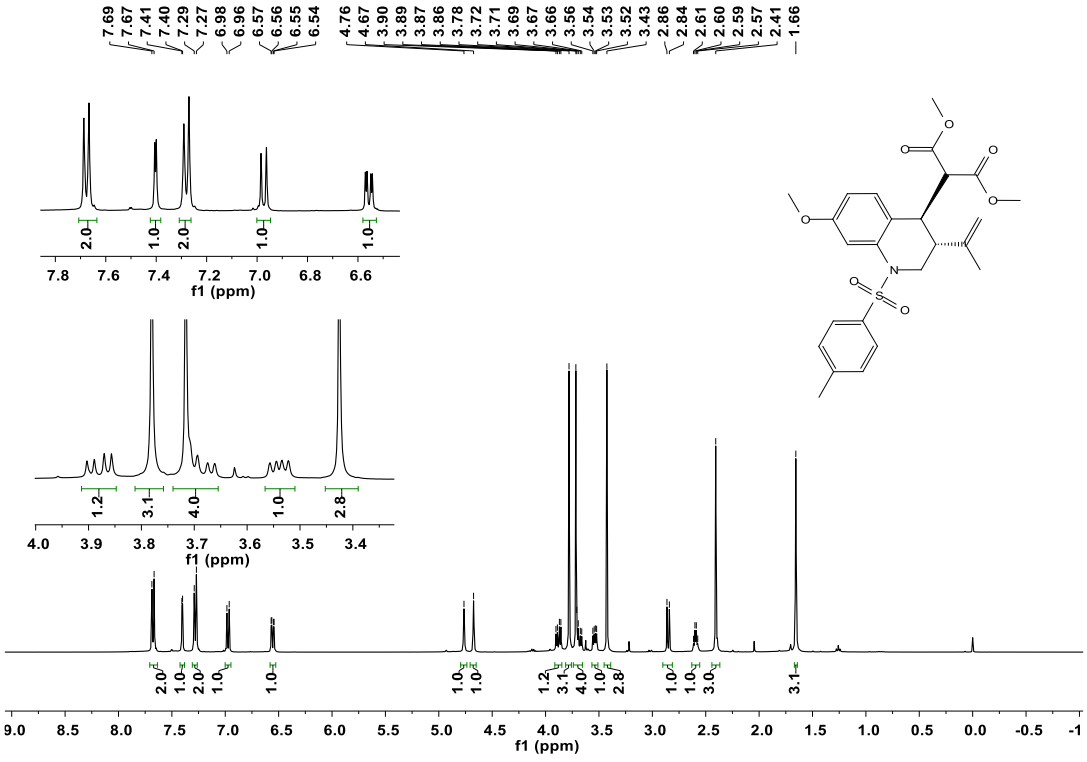


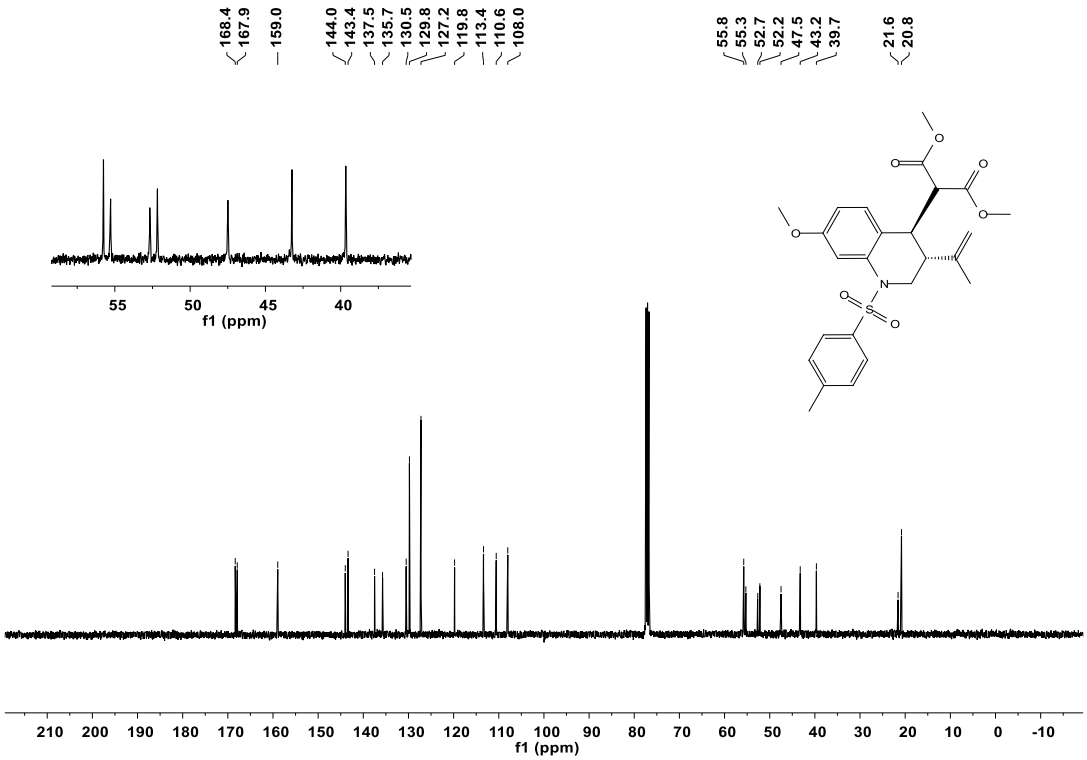
Dimethyl 2-[3-(prop-1-en-2-yl)-1-tosyl-1,2,3,4-tetrahydroquinolin-4-yl]malonate (2s):



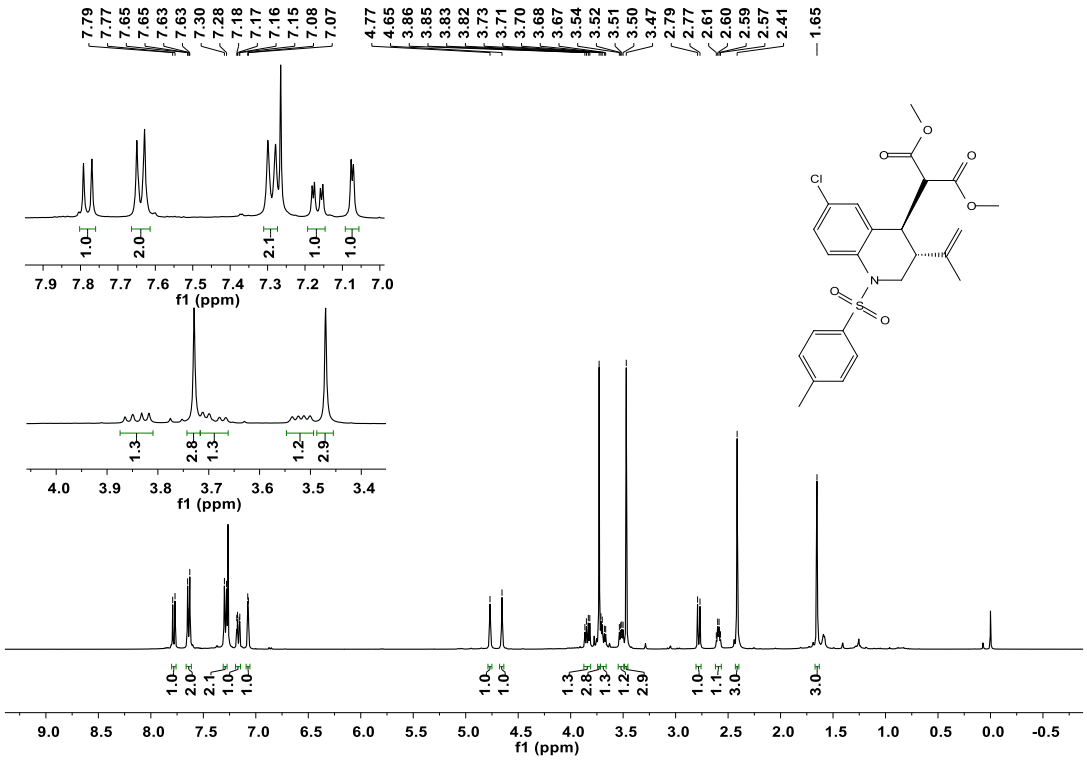


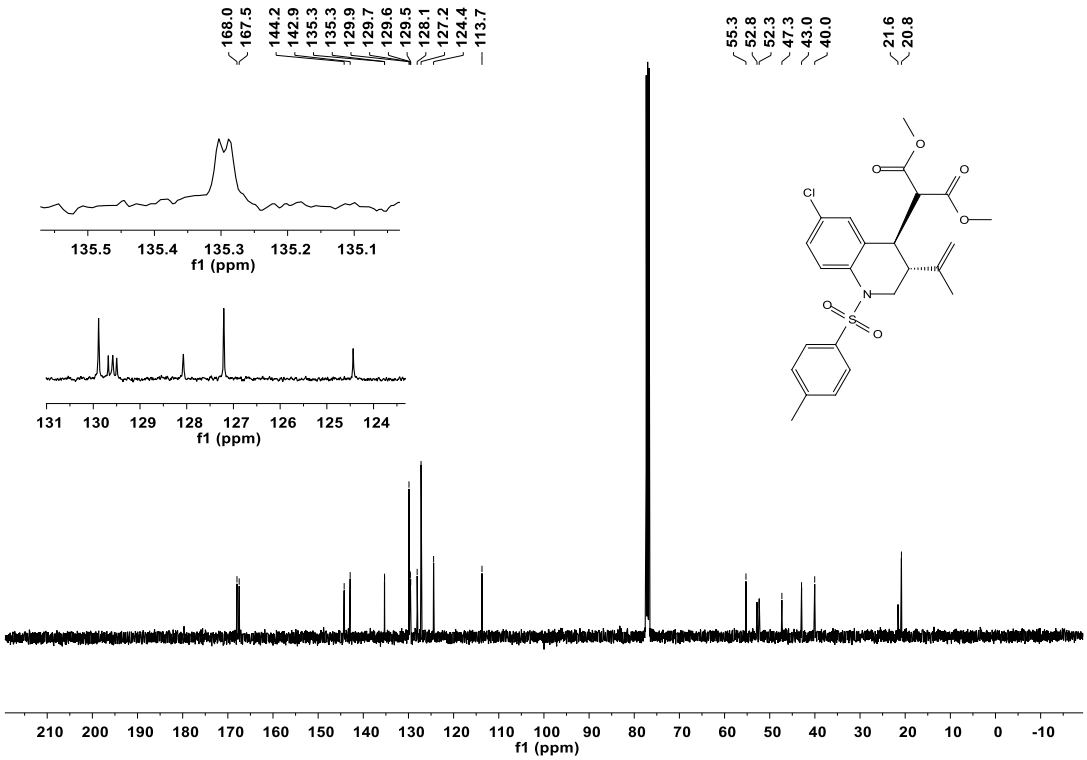
Dimethyl 2-[7-methoxy-3-(prop-1-en-2-yl)-1-tosyl-1,2,3,4-tetrahydroquinolin-4-yl]malonate (2t):



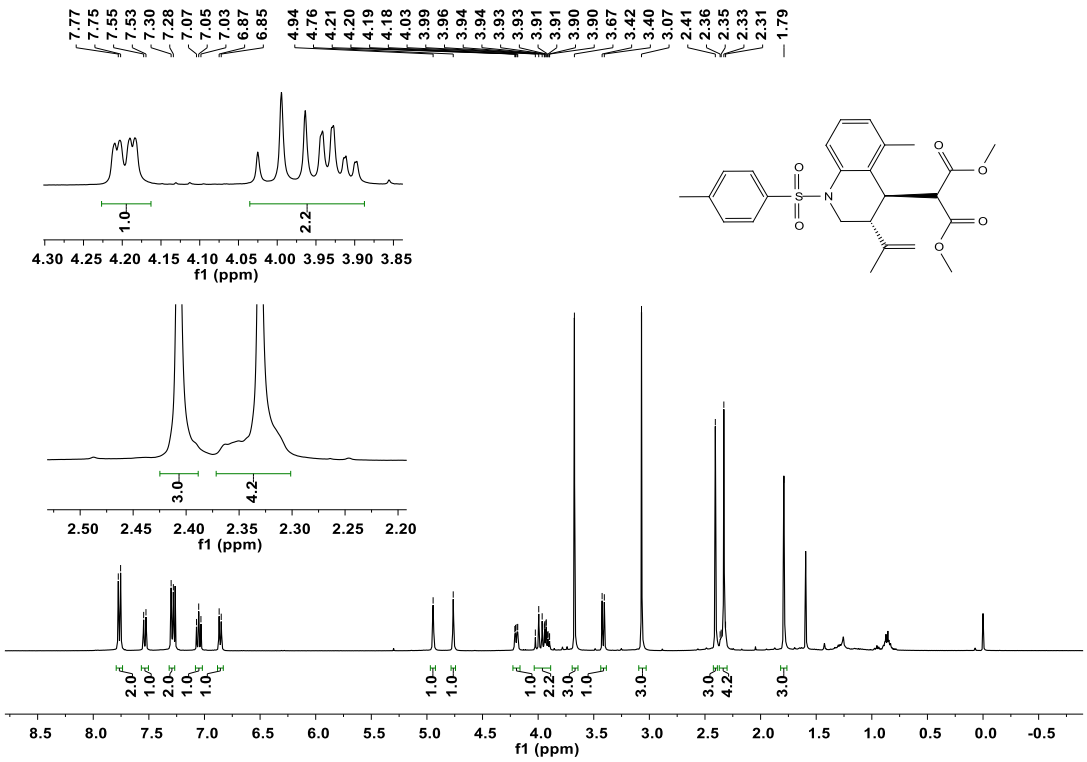


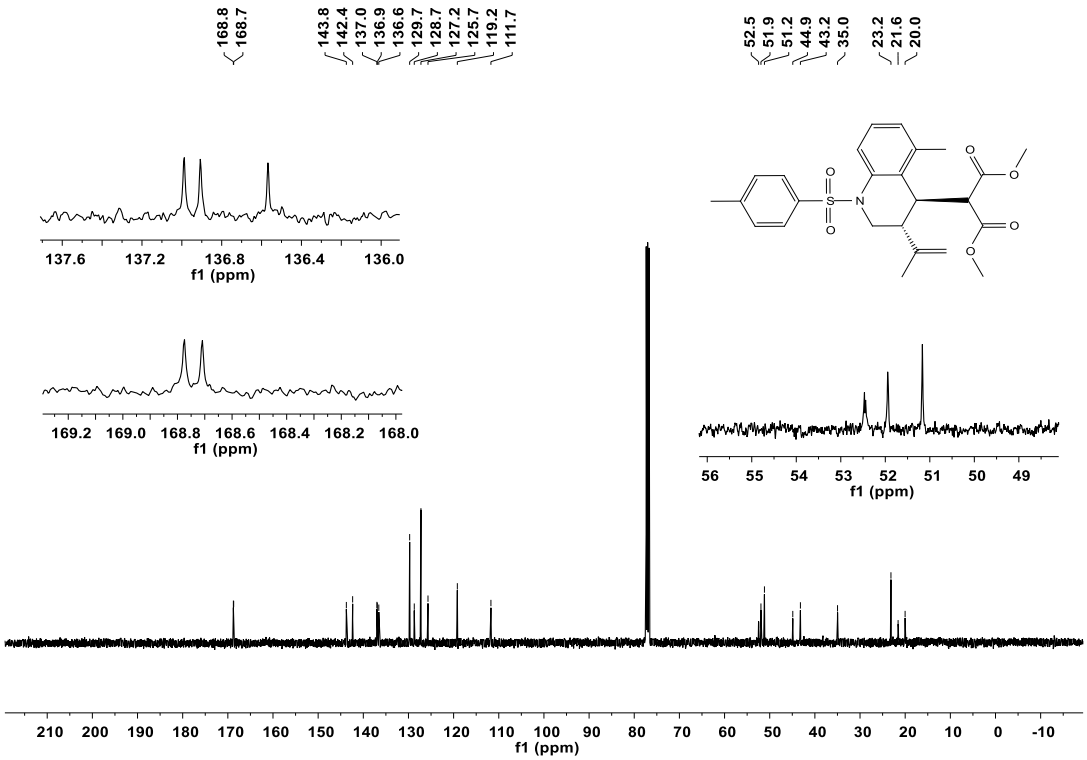
Dimethyl 2-[6-chloro-3-(prop-1-en-2-yl)-1-tosyl-1,2,3,4-tetrahydroquinolin-4-yl]malonate (2u):



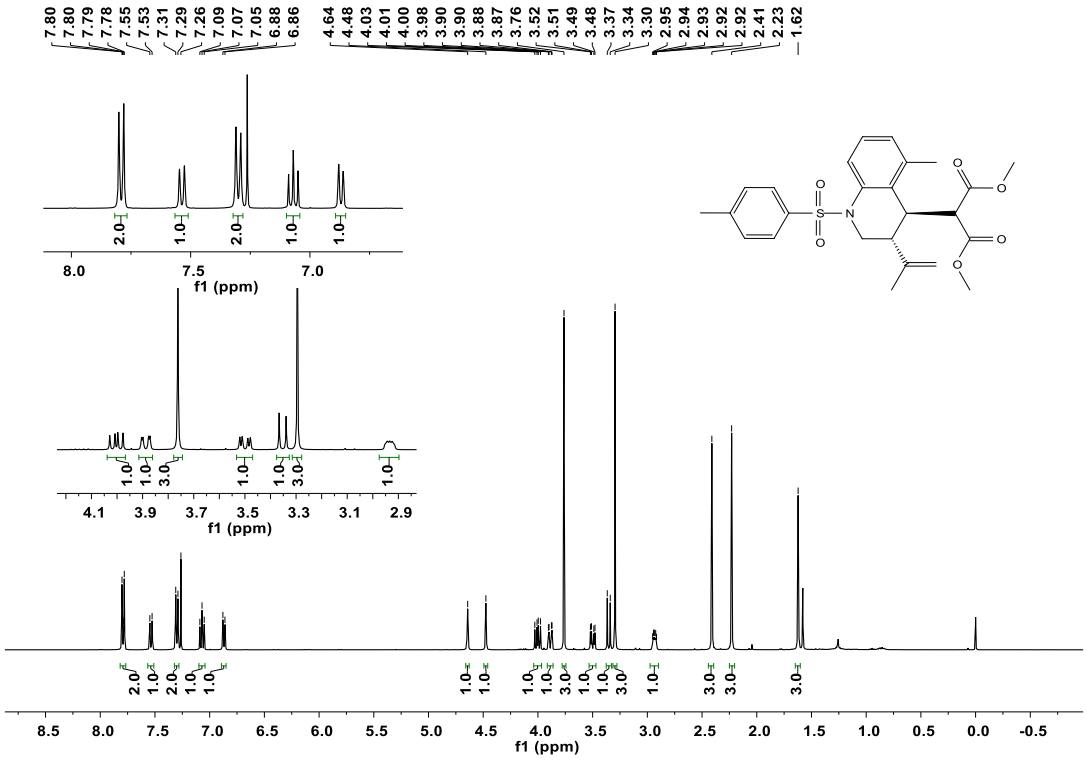


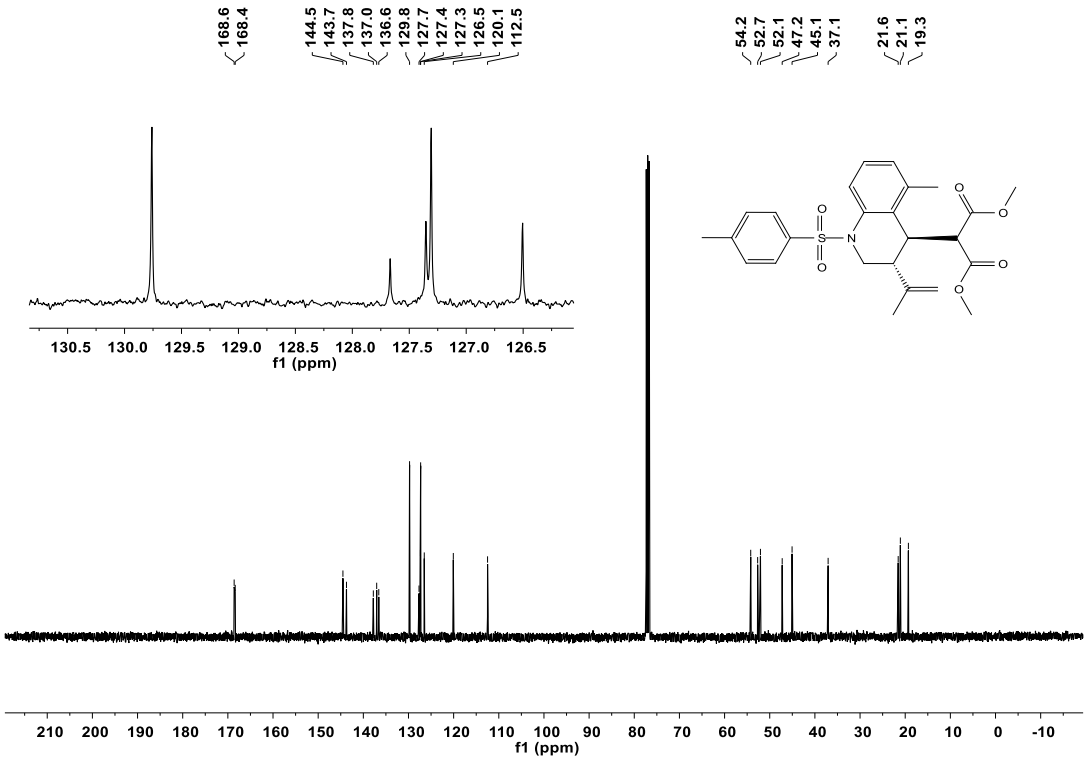
Dimethyl 2-[5-methyl-3-(prop-1-en-2-yl)-1-tosyl-1,2,3,4-tetrahydroquinolin-4-yl]malonate (2v) (major):



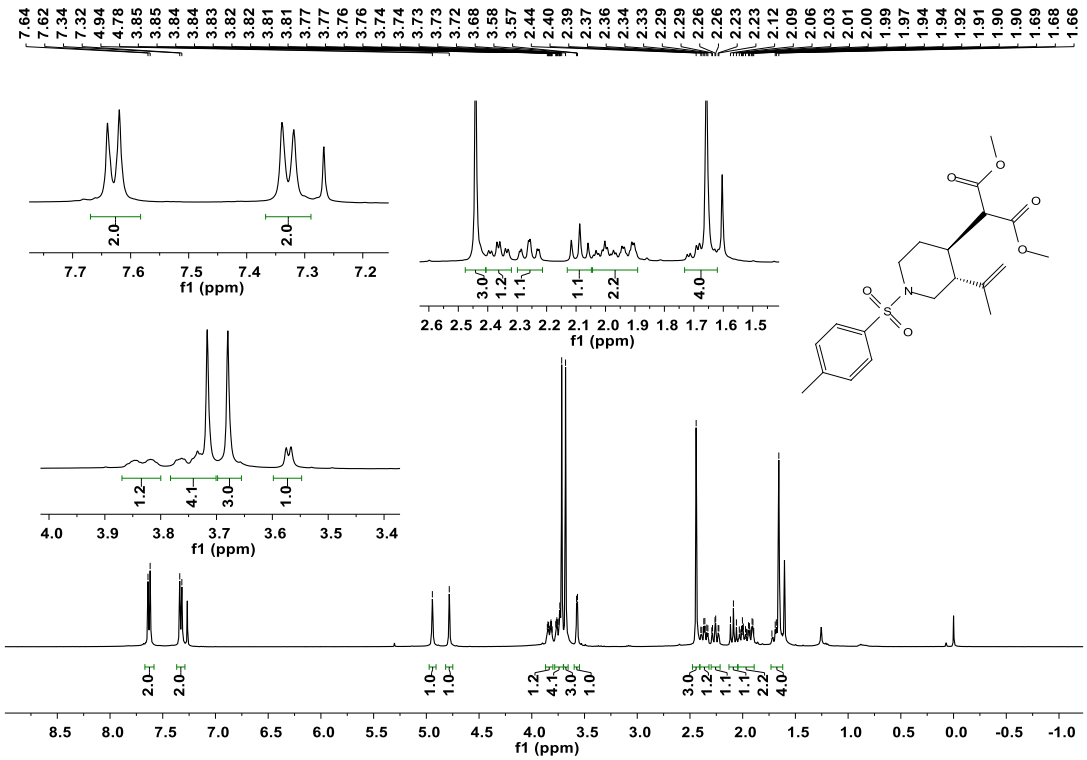


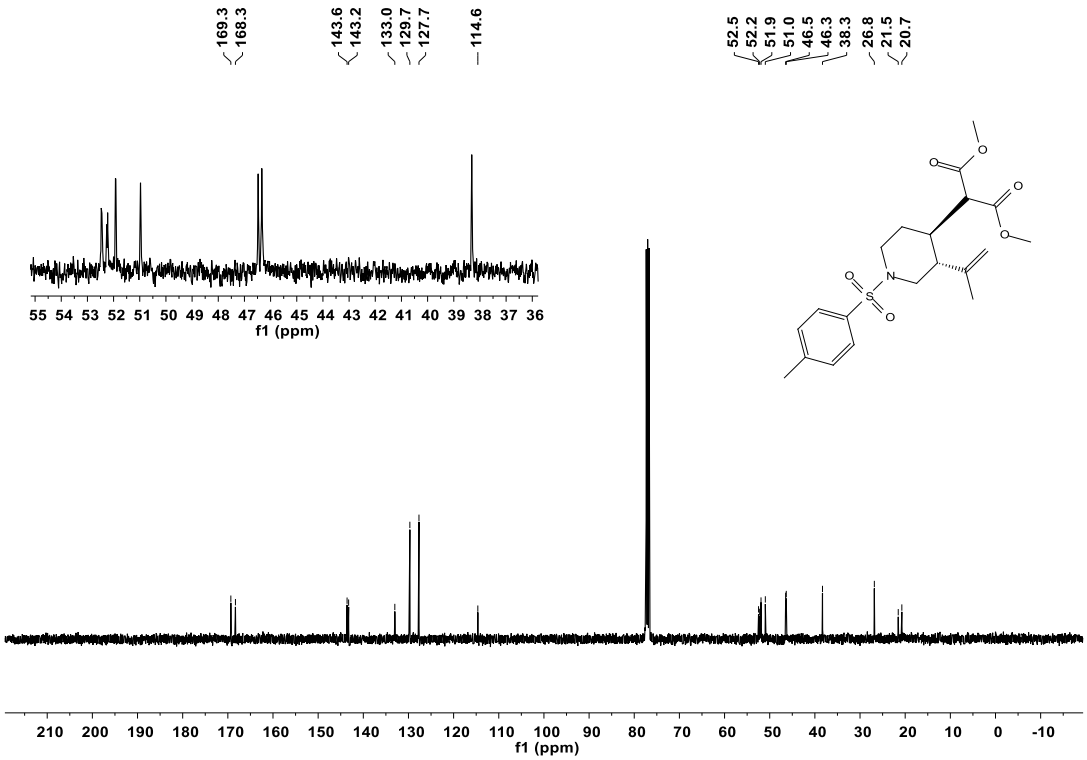
Dimethyl 2-[5-methyl-3-(prop-1-en-2-yl)-1-tosyl-1,2,3,4-tetrahydroquinolin-4-yl]malonate (2v) (minor):



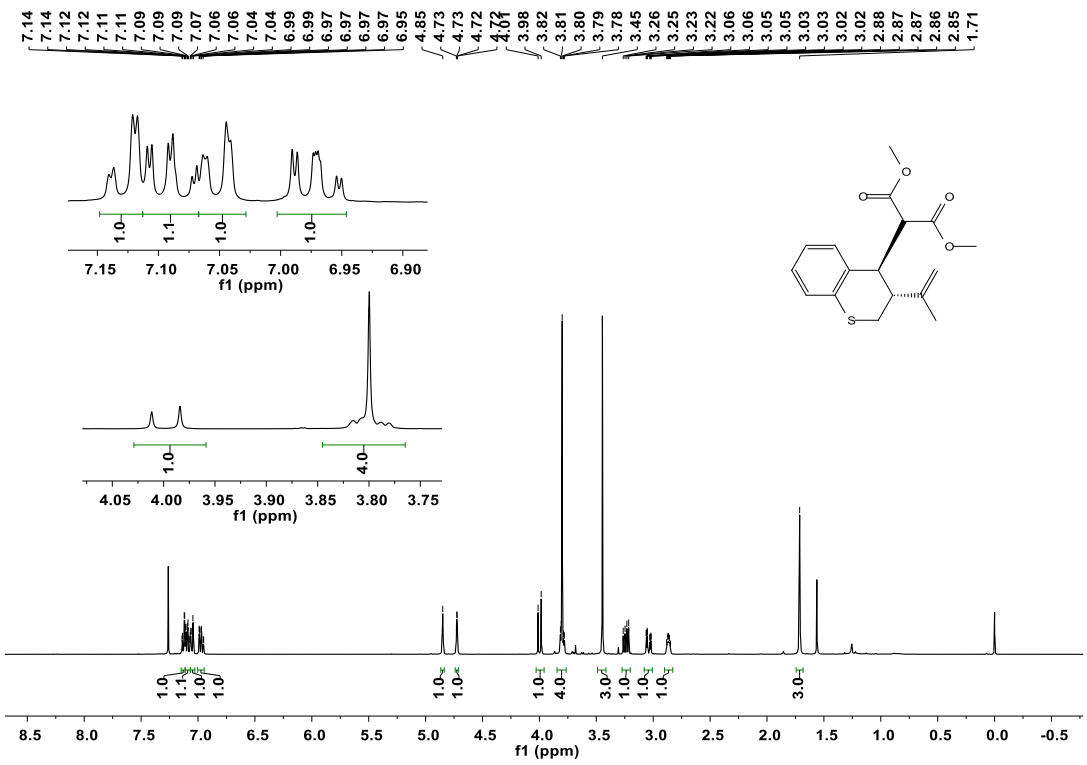


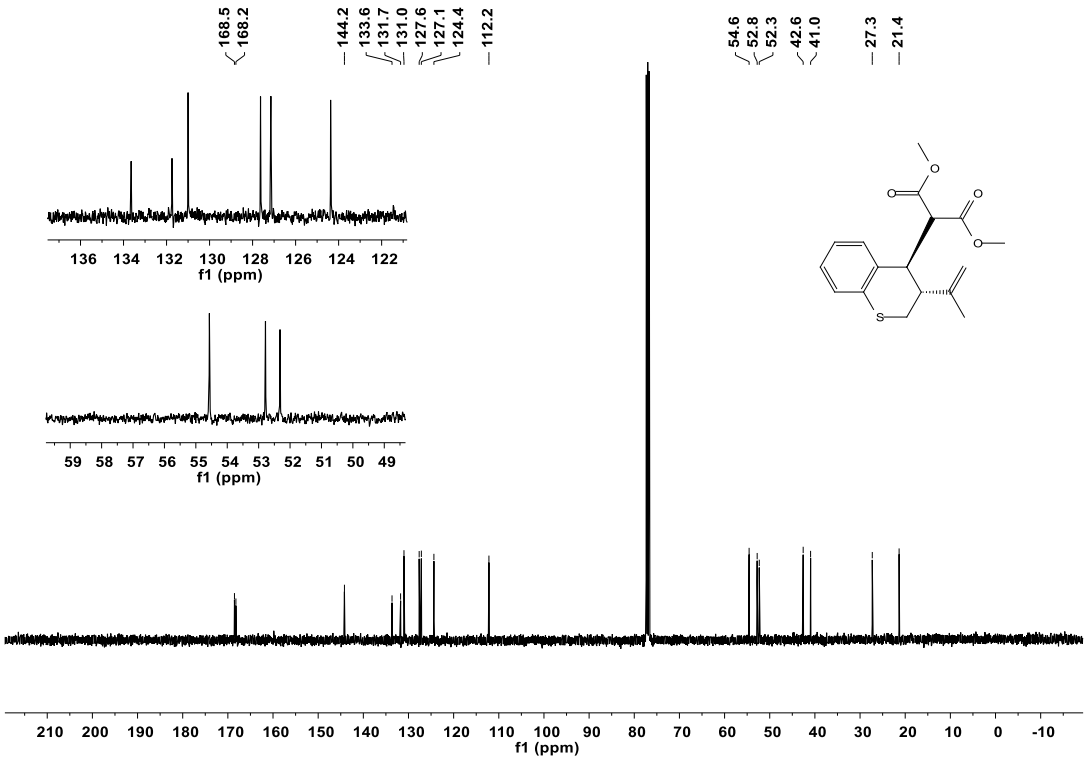
Dimethyl 2-[3-(prop-1-en-2-yl)-1-tosylpiperidin-4-yl]malonate (2w):



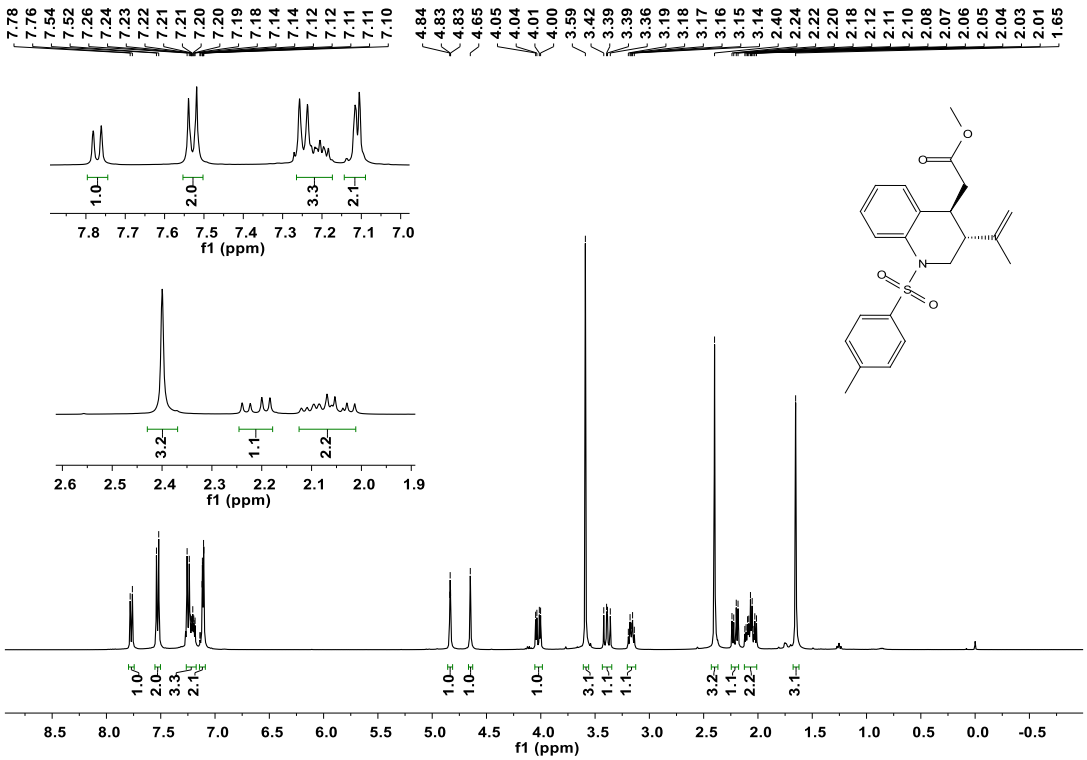


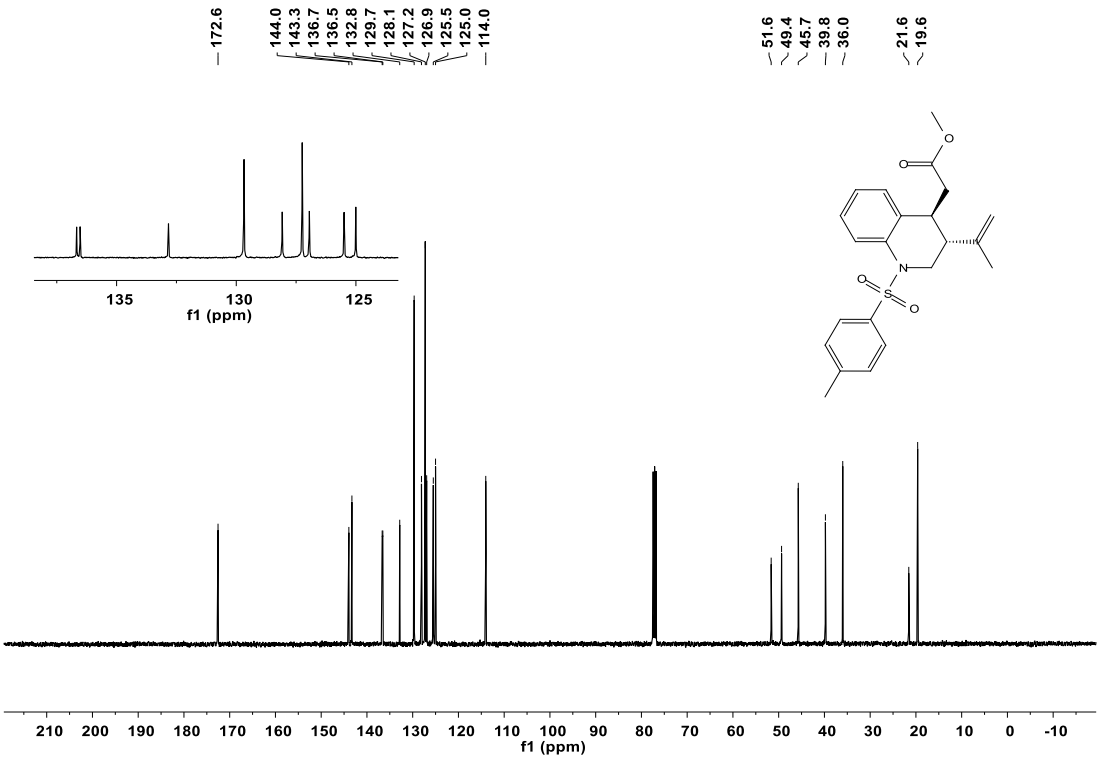
Dimethyl 2-[3-(prop-1-en-2-yl)thiochroman-4-yl]malonate (2x):



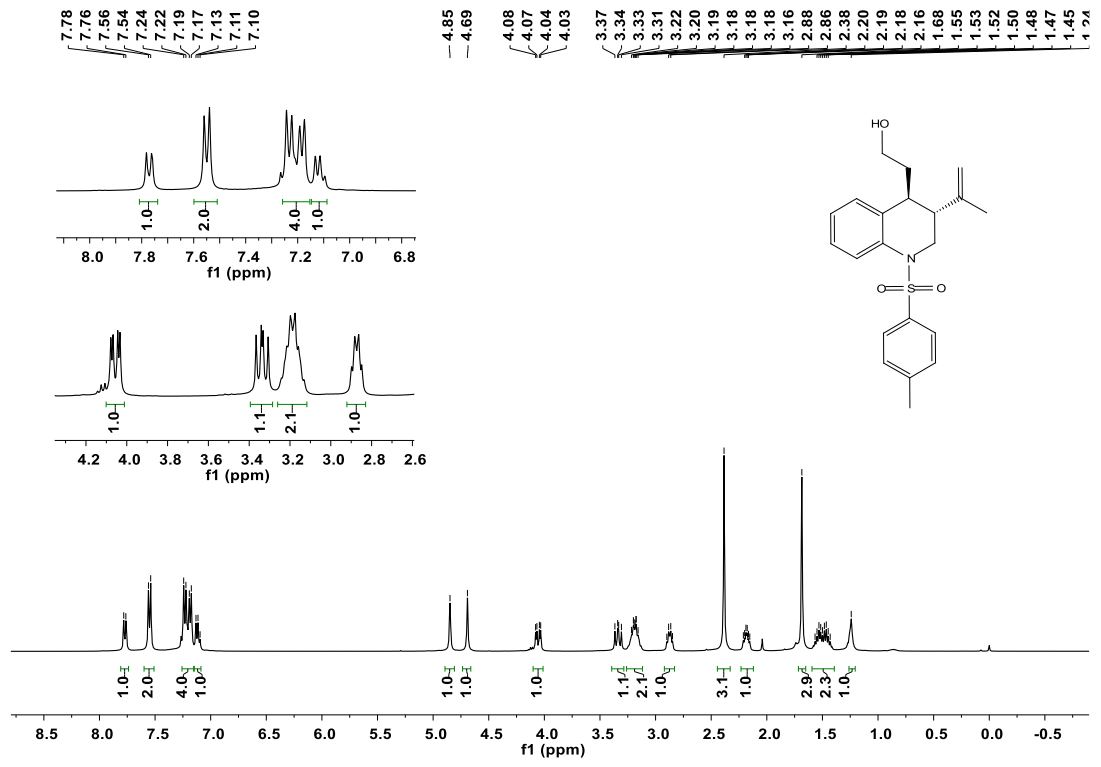


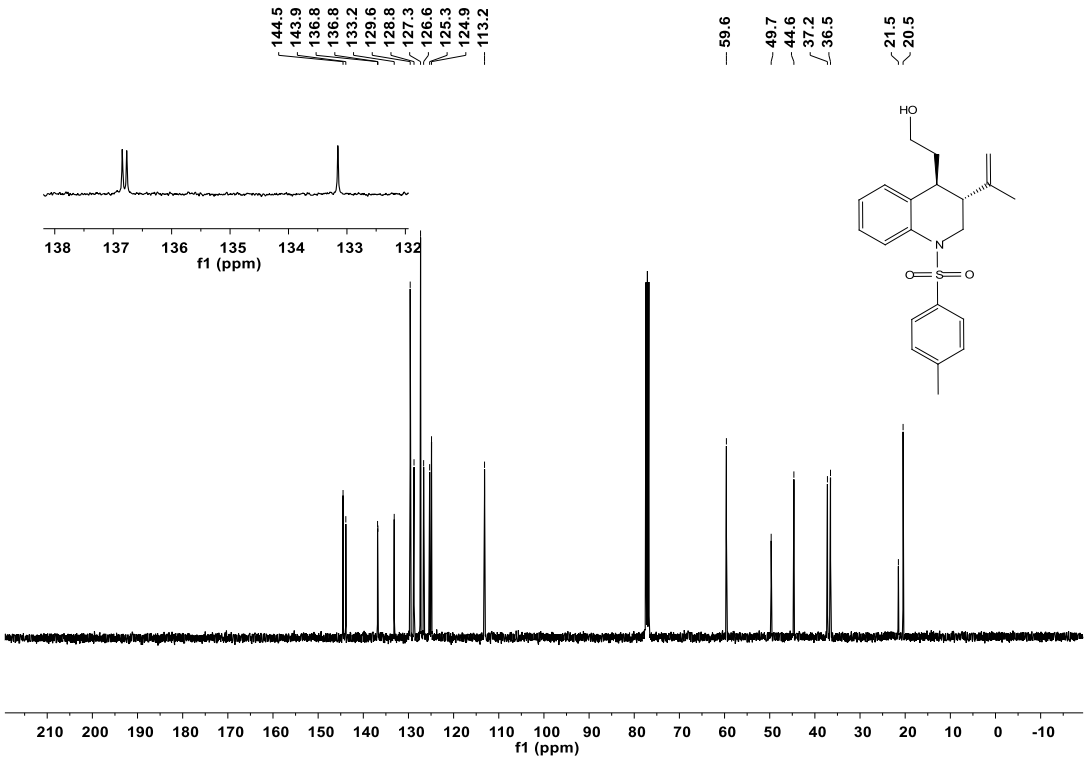
Methyl 2-[3-(prop-1-en-2-yl)-1-tosyl-1,2,3,4-tetrahydroquinolin-4-yl]acetate (3s):



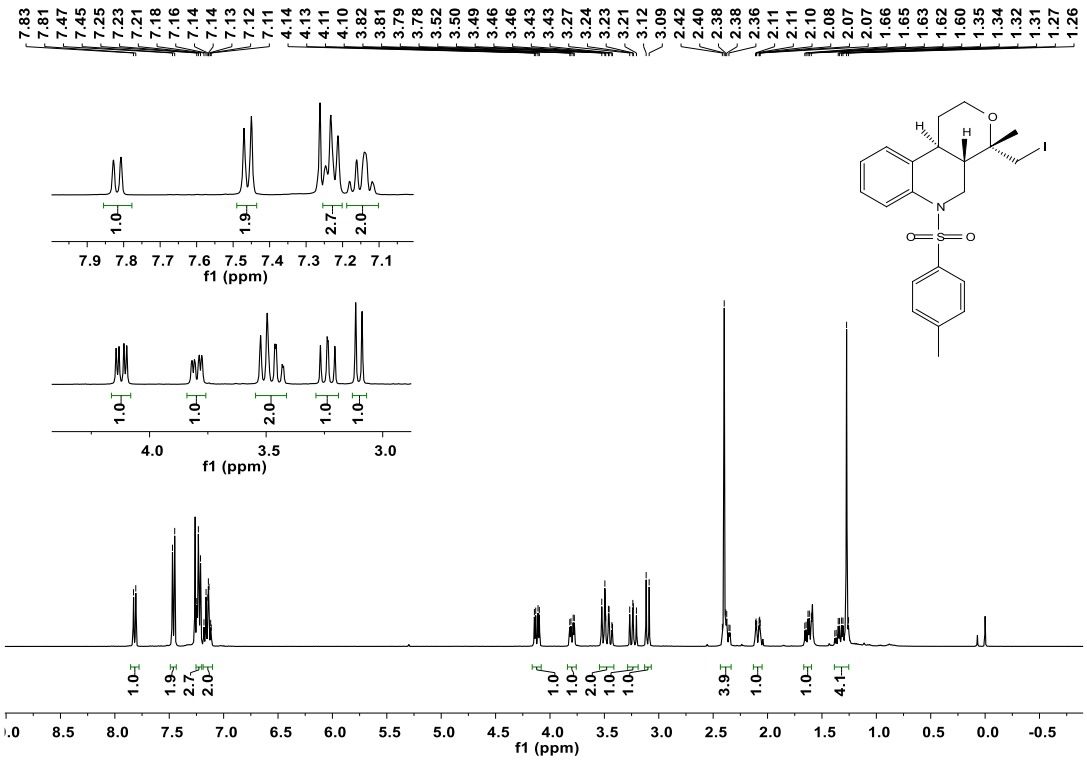


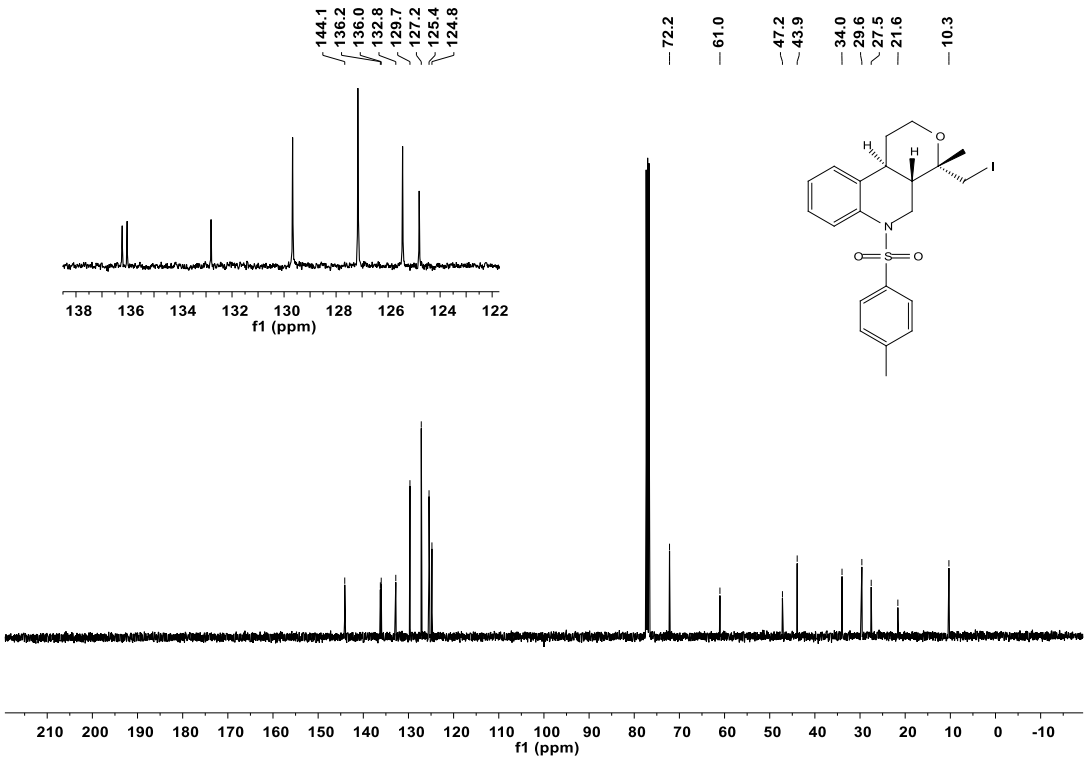
2-[3-(Prop-1-en-2-yl)-1-tosyl-1,2,3,4-tetrahydroquinolin-4-yl]ethan-1-ol (4s):



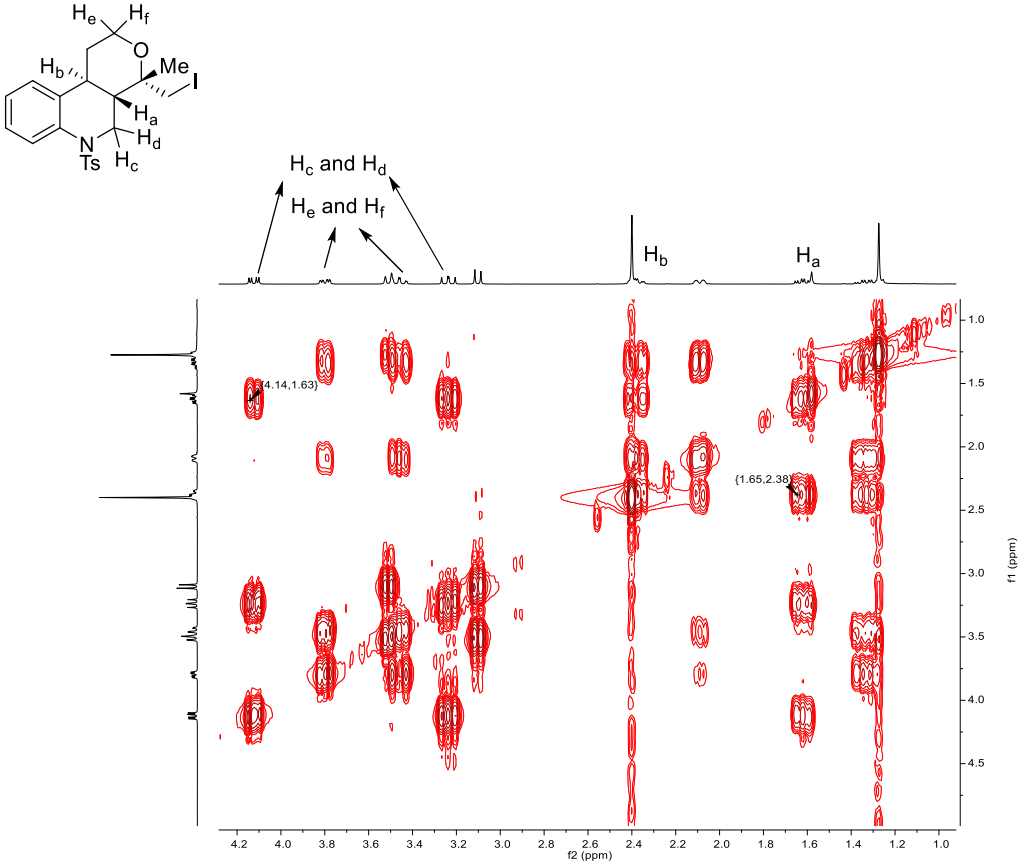


4-(Iodomethyl)-4-methyl-6-tosyl-1,4,4a,5,6,10b-hexahydro-2H-pyrano[3,4-c]quinolone (5s):

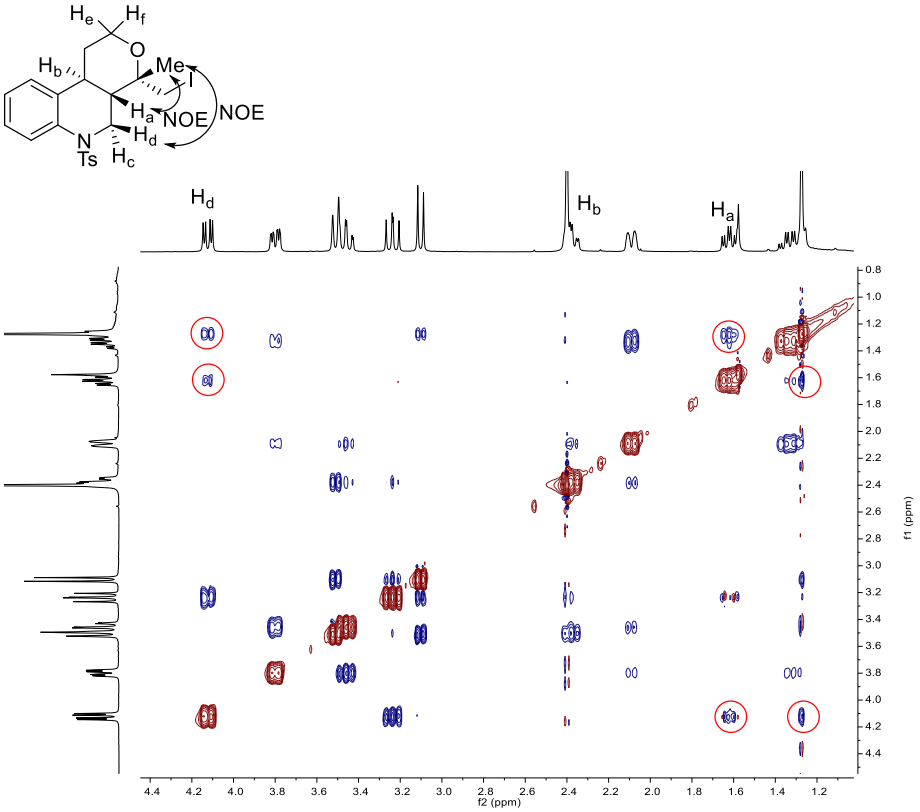




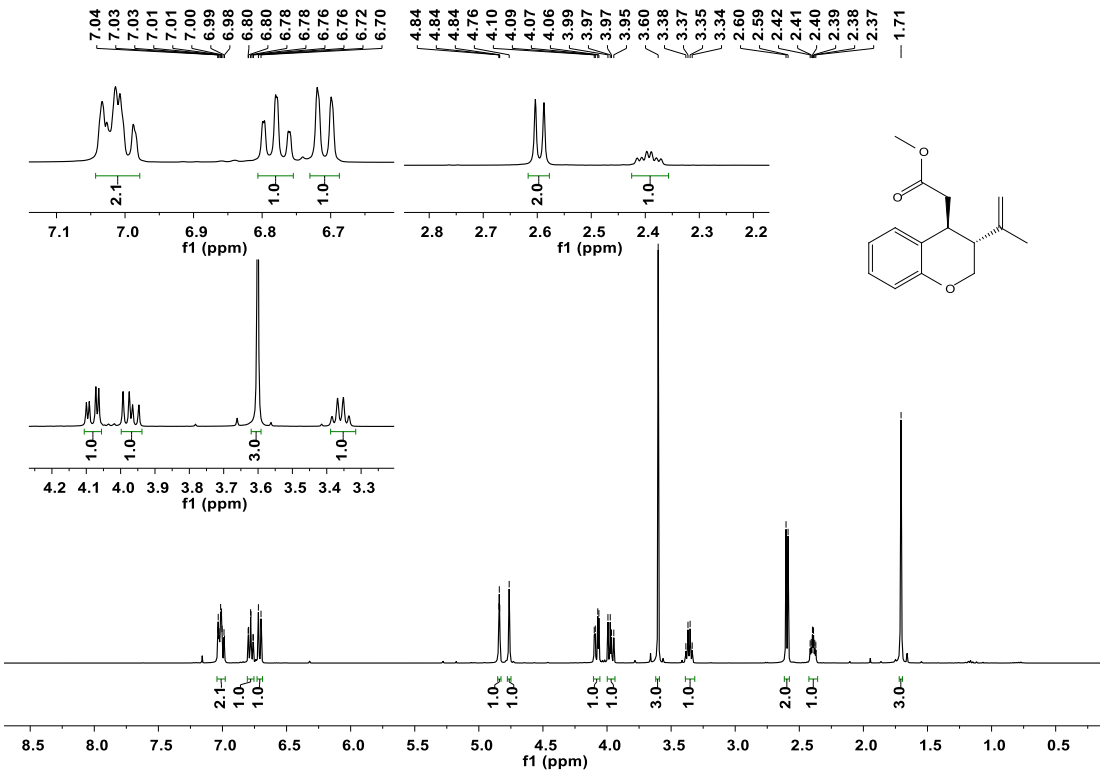
COSY spectra of 5s:

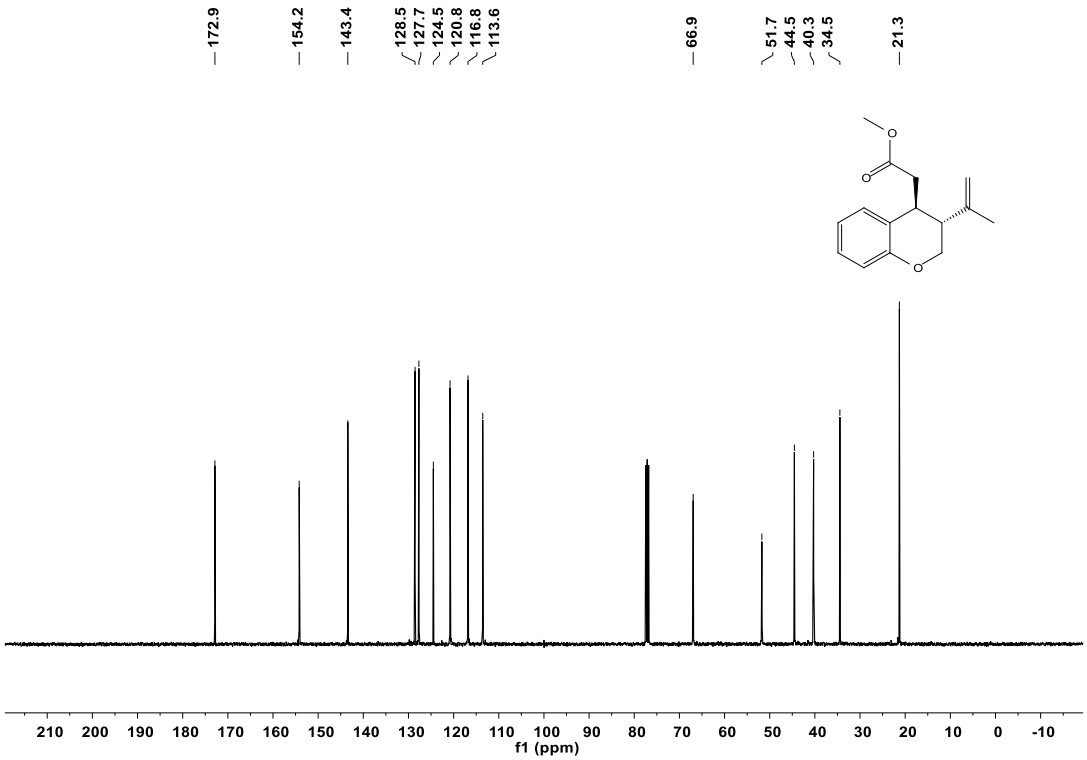


NOESY spectra of 5s:

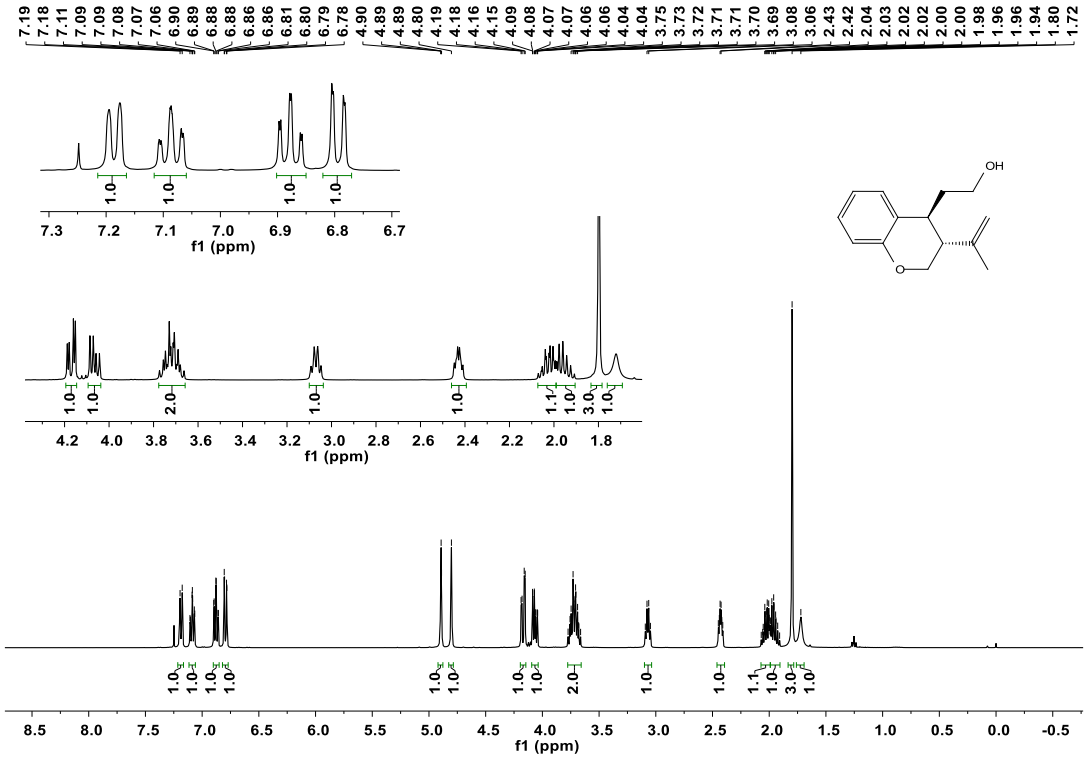


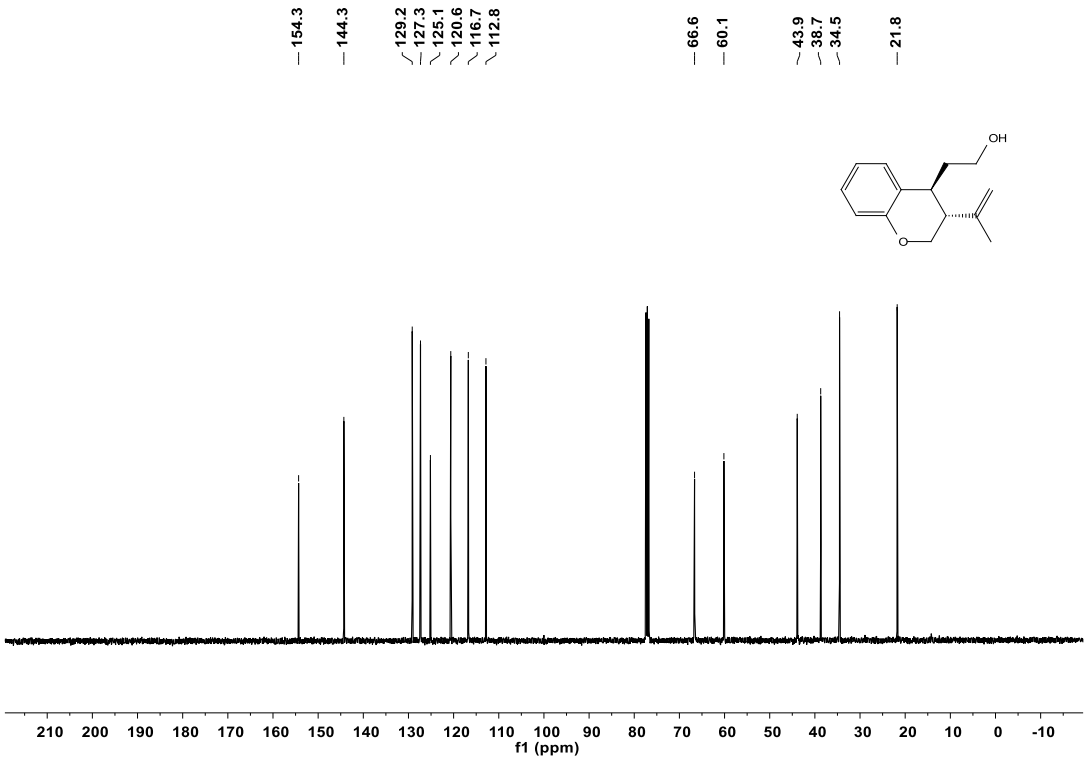
Methyl 2-[3-(prop-1-en-2-yl)chroman-4-yl]acetate (3b):



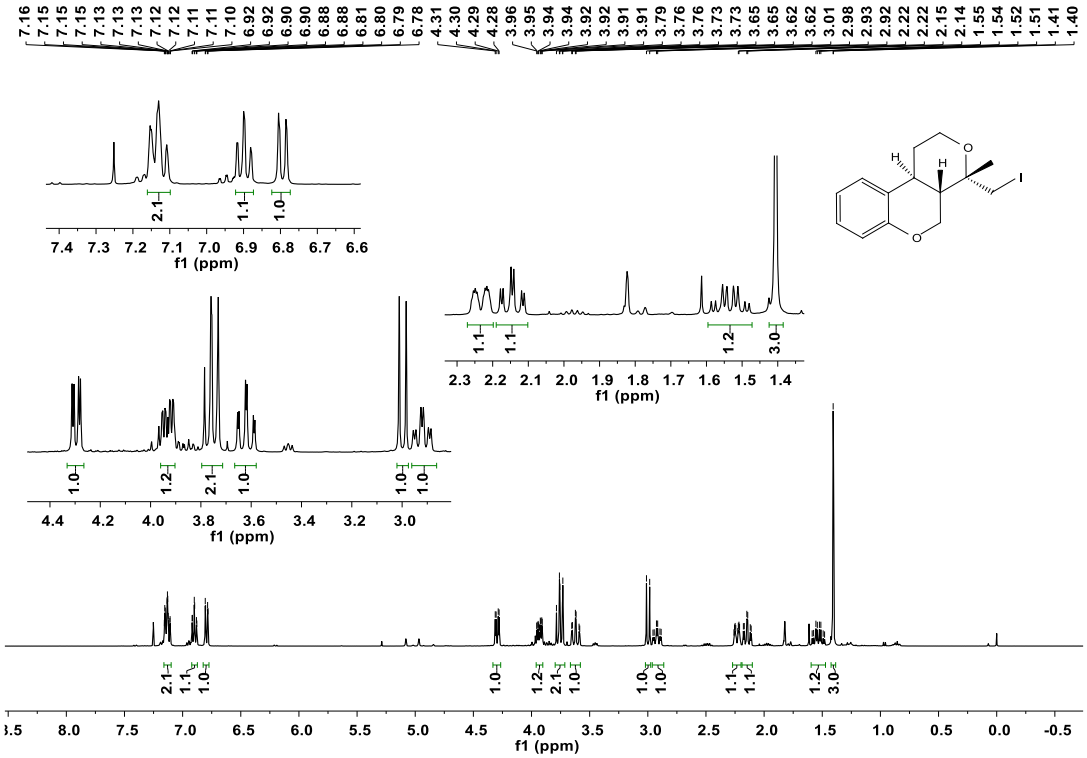


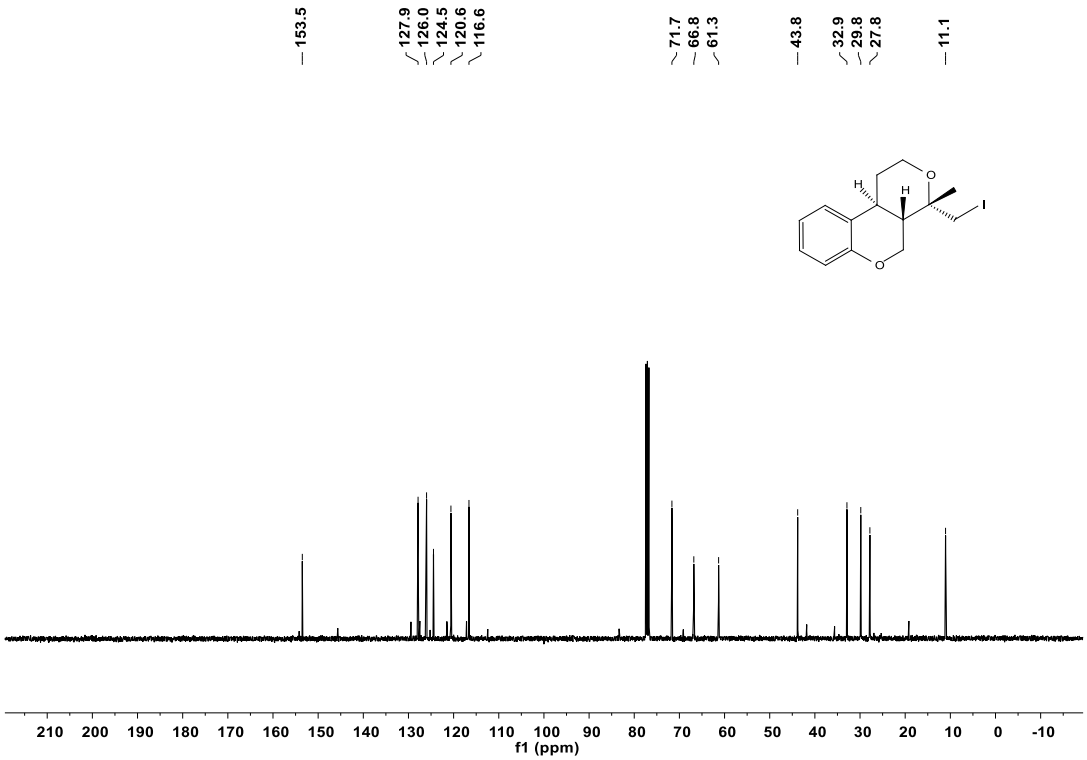
2-[3-(Prop-1-en-2-yl)chroman-4-yl]ethan-1-ol (4b):



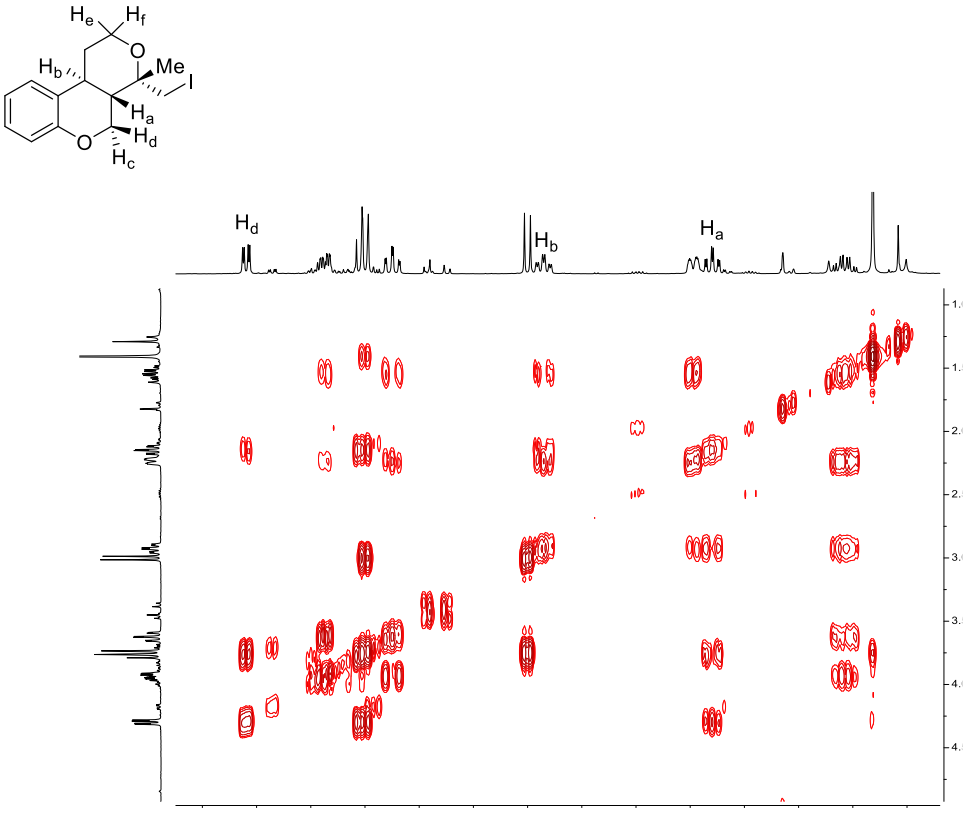


4-(Iodomethyl)-4-methyl-1,4a,5,10b-tetrahydro-2H,4H-pyrano[3,4-c]chromene (5b):





COSY spectra of 5b:



NOESY spectra of 5b: