Supporting Information

Enantioselective Synthesis of Chromanones via a Peptidic Phosphane Catalysed Rauhut–Currier Reaction

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Contents

1. General Methods

Solvents: Except as otherwise indicated, reactions were carried out using oven-dried glassware under nitrogen with dry, freshly distilled solvents. Tetrahydrofuran was distilled from calcium hydride and $LiAlH_4$ in the presence of triphenyl methane. CH_2Cl_2, MeOH, toluene, MeCN and hexane were distilled from calcium hydride. All other solvents were used as obtained from commercial sources.

TLC: All reactions were monitored by thin layer chromatography (TLC) using glass plates precoated with Merck silica gel 60 F254. Visualization was by the quenching of UV fluorescence (λmax = 254 nm) or by staining with ceric ammonium molybdate or potassium permanganate. Retention factors (R_f) are quoted to 0.01.

Chromatography: Flash column chromatography was carried out using slurry-packed Merck 9385 Kieselgel 60 silica gel under a positive pressure of air or nitrogen. Additonally, Combiflash® (Teledyne ISCO), an automated chromatography system, was used for purification of compounds.

Analytical HPLC: Analysis was performed on a Shimadzu XR-LC (CBM-20A) instrument using chiral stationary phases (Chiralpack AI, Chiralcel OD) and *n*-hexane/*iso*-propanol as the solvent system. Retention times (t_r) are reported to the nearest 0.01 min. For comparison, racemic samples were prepared using dicyclohexylphenylphosphane as catalyst.

Optical rotation: Analysis was performed on a Anton Paar (MCP 100) polarimeter.

IR: Infrared (IR) spectra were recorded on a Perkin-Elmer Spectrum One FT-IR spectrometer using a Diamant/KRS5 ATR. All compounds were placed on the reflector as a chloroform solution which was dried building a neat film. Selected absorption maxima (ν_{max}) are reported in wavenumbers (cm^{-1}) and the following abbreviations are used: w, weak; m, medium; s, strong; br, broad.

NMR: Nuclear magnetic resonance spectra were recorded using an internal deuterium lock on Bruker DPX 400 (400MHz), Bruker Avance 400 QNP Ultrashield (400 MHz), Bruker Avance 500 BB ATM (500 MHz) and Bruker Avance 500 Cryo Ultrashield (500 MHz) spectrometers. Chemical shifts (δ) are referenced to the solvent signal and are quoted in ppm to the nearest 0.01 ppm for δH and to the nearest 0.1 ppm for δC. Coupling constants (*J*) are reported in Hertz to the nearest 0.1 Hz.

HRMS: High resolution mass spectrometry was carried out with a Micromass Q-TOF or a Waters LCT Premier Mass Spectrometer using electrospray ionisation [ESI] or electron ionisation [EI].

Melting points: This data was collected on a BÜCHI B-545 using racemic samples.

2. Materials

Catalysts:

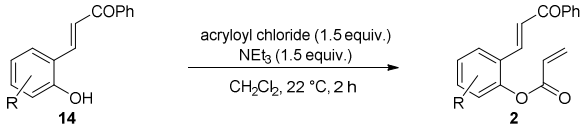
- Phosphanes **8-12** were synthesised according to literature known procedures.[1]

Substrates:

- Chalcones **14a-k** were synthesised either according to literature known aldol condensation (**14a-e, g**) [2] or by Wittig reaction (**14f, h-k**).[3] All other substrates and reagents were purchased from commercial sources and used as obtained without further purification.

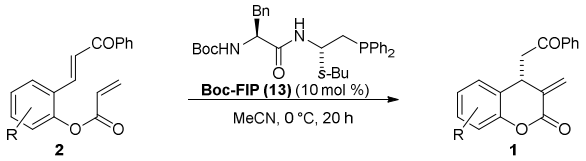
3. General Procedures

3.1 Synthesis of Chalcones **2** (**GP 1**)



To a stirring solution of phenol **14** (5 mmol) in dichloromethane (20 mL) was added triethylamine (7.5 mmol) and acryloyl chloride (7.5 mmol) over 30 seconds at 22 °C.[2] The resulted solution was stirred two hours at 22 °C. Subsequently, the reaction mixture was diluted with ethyl acetate (100 mL), washed twice with 1N aqueous hydrochloric solution (2 x 50 mL) and once with brine (50 mL). The organic phase was dried with magnesium sulfate and the solvent was evaporated. The crude reaction product was purified via column chromatography using *n*-hexane/ethyl acetate as eluent.

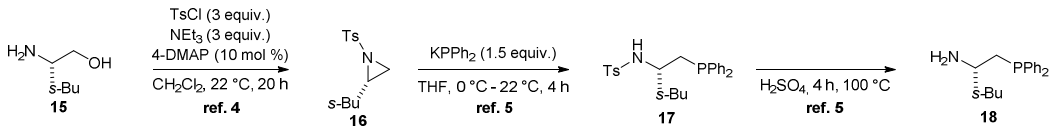
3.2 Synthesis of Chromanones **1** via Rauhut–Currier Reaction (**GP 2**)



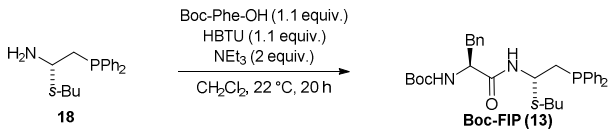
To a stirring solution of the chalcone **2** (0.5 mmol) in acetonitrile (5 mL) was added Boc-FIP (0.05 mmol) at 0 °C. The resulted red solution was stirred at 0 °C for 20 h. Subsequently, this reaction mixture was loaded on 1 g of dry silica and purified via column chromatography using *n*-hexane/ethyl acetate as eluent.

4. Analytical Data

4.1. Boc-FIP



Aminophosphane **18** was synthesized according to known literature protocols. [4,5]



To a stirring solution of amine **18** (1.35 g, 4.73 mmol) in dichloromethane (25 mL) under positive pressure of nitrogen was added triethylamine (1.31 mL, 9.46 mmol), Boc-protected phenylalanine (1.38 g, 5.20 mmol) and HBTU (1.97 g,

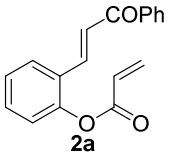
[2]On a 5 mmol scale no cooling was necessary. However, if the reaction is scaled up cooling with an ice bath is recommended.

5.20 mmol), respectively. The resulted suspension was stirred for 20 h at 22 °C. Subsequently, the solution was diluted with ethyl acetate (150 mL) washed twice with 1N aqueous hydrochloric solution (2 x 50 mL) and once with brine (50 mL). The organic phase was dried with magnesium sulfate and the solvent was evaporated. The crude colorless solid was purified via column chromatography using *n*-hexane/ethyl acetate (6:1) as eluent. The peptidic phosphane **13** was obtained as a colorless solid (1.72 g, 3.22 mmol, 68% yield).

R_f = 0.22 (*n*-hexane/EtOAc 4:1); m.p. 154.8-155.6 °C; $[\alpha]_D^{25}$ = +18.0 (*c* = 0.10, $CHCl_3$), IR (ATR): 3358w, 2968w, 1683s, 1652s, 1517s, 1431m, 1366m, 1317m, 1250m, 1170s, 1046m, 1025w, 742m, 695s cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 0.74 - 0.81 (m, 6H), 0.88 - 1.01 (m, 1H), 1.24 1.36 (m, 1H), 1.41 (s, 9H), 1.62 - 1.71 (m, 1H), 1.99 - 2.19 (m, 2H), 3.04 (d, *J* = 6.6 Hz, 2H), 3.88 - 4.00 (m, 1H), 4.11 - 4.22 (m, 1H), 5.02 (br s, 1H), 5.82 (br d, *J* = 9.0 Hz, 1H), 7.19 - 7.48 (m, 15H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ =11.5 (CH_3), 15.0 (CH_3), 24.4 (CH_2), 28.3 (CH_3), 30.8 (CH_2), 37.8 (CH_2), 38.4 (CH), 51.3 (CH), 55.6 (CH), 80.0 (C), 126.8 (CH), 128.50 (CH), 128.6 (CH), 128.9 (CH), 129.4 (CH), 132.5 (CH), 132.7 (CH), 133.0 (CH), 133.2 (CH), 137.1 (C), 138.4 (C), 138.5 (C), 155.4 (C), 170.3 (C) ppm;[3] HRMS (ESI): *m*/*z* calcd for $C_{32}H_{42}N_2O_3P^+$: 533.2928 [M+H^+]; found: 533.2972.

4.2. Chalcones **2**

Compound **2a**:

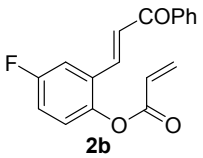


2a

Prepared according to general procedure **GP1** from the phenol **S1a** (1.12 g, 5.0 mmol), compound **2a** (1.11 g, 4.0 mmol, 80% yield) was isolated as a tan solid after column chromatography (eluent *n*-hexane/EtOAc 4:1).

R_f = 0.33 (*n*-hexane/EtOAc 4:1); m.p. 55.2-57.1 °C; IR (ATR): 1742s, 1664m, 1644w, 1604s, 1575m, 1483w, 1448w, 1403m, 1332w, 1319w, 1282m, 1245w, 1213s, 1181m, 1094w, 1070w, 1034w, 1015s cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 6.09 (dd, *J* = 10.5 Hz, 1.1 Hz, 1H), 6.39 (dd, *J* = 17.3 Hz, 10.9 Hz, 1H), 6.67 (dd, *J* = 17.3 Hz, 1.1 Hz, 1H), 7.20 (dd, *J* = 8.8 Hz, 1.1 Hz, 1H), 7.34 – 7.31 (m, 1H), 7.55 - 7.44 (m, 4H), 7.59 (tt, *J* = 7.3 Hz, 1.2 Hz, 1H), 7.79 (dd, *J* = 7.8 Hz, 1.6 Hz, 1H), 7.87 (d, *J* = 15.8 Hz, 1H), 8.00 – 7.98 (m, 2H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 123.3 (CH), 124.3 (CH), 126.4 (CH), 127.8 (CH), 127.8 (C), 128.6 (CH), 128.6 (CH), 131.3 (CH), 132.9 (CH), 133.5 (CH_2), 138.0 (C), 138.1 (CH), 149.6 (C), 164.2 (C), 190.4 (C) ppm; HRMS (ESI): *m*/*z* calcd for $C_{18}H_{15}O_3^+$: 279.1016 [M+H^+]; found: 279.1009.

Compound **2b**:



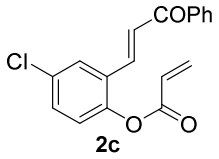
2b

Prepared according to general procedure **GP1** from the phenol **S1b** (1.21 g, 5.0 mmol), compound **2b** (0.74 g, 2.5 mmol, 50% yield) was isolated as a tan solid after column chromatography (eluent *n*-hexane/EtOAc 99:1 - 7:1).

[3]Many of the signals in the carbon NMR have split in pairs which are likely due to the restricted rotation of the peptidic bonds.

R_f = 0.39 (*n*-hexane/EtOAc 4:1); m.p. 122.0-123.3 °C; IR (ATR): 1746m, 1666m, 1607s, 1486m, 1448m, 1429w, 1404w, 1336m, 1272s, 1232s, 1176m, 1140s, 1017s cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 6.10 (dd, *J* = 10.4 Hz, 0.9 Hz, 1H), 6.38 (dd, *J* = 17.4 Hz, 10.4 Hz, 1H), 6.67 (dd, *J* = 17.4 Hz, 1.2 Hz, 1H), 7.19 - 7.13 (m, 2H), 7.52 - 7.46 (m, 4H), 7.60 (tt, *J* = 7.3 Hz, 1.8 Hz, 1H), 7.80 (dd, *J* = 15.9 Hz, 1.2 Hz, 1H), 8.01 – 7.98 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 113.7 (d, *J* = 23.5 Hz, CH), 118.1 (d, *J* = 23.5 Hz, CH), 124.9 (d, J = 33.1 Hz, CH), 124.7 (CH), 127.1 (CH), 128.6 (CH), 128.7 (CH), 129.4 (d, *J* = 785 Hz, C), 133.1 (CH), 133.8 (CH_2), 136.8 (d, *J* = 2.1 Hz, CH), 137.7 (C), 145.5 (d, *J* = 3.2 Hz, C), 160.3 (d, *J* = 245.4 Hz, C-F), 164.2 (C), 189.9 (C) ppm; HRMS (ESI): *m*/*z* calcd for $C_{18}H_{14}O_3F^+$: 297.0921 [*M*+H^+]; found: 297.0931.

Compound **2c**:

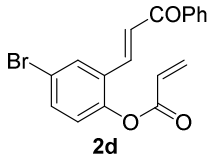


2c

Prepared according to general procedure **GP1** from the phenol **S1c** (1.29 g, 5.0 mmol), compound **2c** (1.20 g, 3.9 mmol. 77% yield) was isolated as a tan solid after column chromatography (eluent *n*-hexane/EtOAc 9:1 - 7:3).

R_f = 0.43 (*n*-hexane/EtOAc 4:1); m.p. 119.2-119.3 °C; IR (ATR): 1747s, 1667m, 1609s, 1579m, 1478m, 1448w, 1404w, 1332m, 1316w, 1294w, 1245s, 1216m, 1175s, 1143w, 1111w, 1017s cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 6.08 (dd, *J* = 10.4 Hz, 0.8 Hz, 1H), 6.35 (dd, *J* = 17.2 Hz, 10.4 Hz, 1H), 6.65 (dd, *J* = 17.2 Hz, 0.8 Hz, 1H), 7.14 (d, *J* = 8.8 Hz, 1H), 7.38 (dd, *J* = 8.8 Hz, 2.4 Hz, 1H), 7.52 - 7.47 (m, 3H), 7.58 (tt, *J* = 7.4 Hz, 1.4 Hz, 1H), 7.73 (d, *J* = 2.4 Hz, 1H), 7.77 (d, *J* = 16.0 Hz, 1H), 8.00 – 7.97 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 124.6 (CH), 125.0 (CH), 127.1 (CH), 127.3 (CH), 128.6 (CH), 128.7 (CH), 129.4 (C), 131.0 (CH), 131.9 (C), 133.2 (CH), 134.0 (CH_2), 136.5 (CH), 137.7 (C), 148.0 (C), 164.0 (C), 189.8 (C) ppm; HRMS (ESI): *m*/*z* calcd for $C_{18}H_{14}O_3{}^{35}Cl^+$: 313.0626 [*M*+$H^+$]; found: 313.0634.

Compound **2d**:

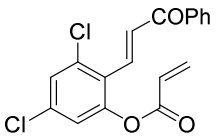


2d

Prepared according to general procedure **GP1** from the phenol **S1d** (1.52 g, 5.0 mmol), compound **2d** (1.27 g, 3.6 mmol, 71% yield) was isolated as a tan solid after column chromatography (eluent *n*-hexane/EtOAc 9:1 - 7:3).

R_f = 0.38 (*n*-hexane/EtOAc 4:1); m.p. 76.5-76.8 °C; IR (ATR): 1746s, 1666m, 1607s, 1578m, 1474w, 1447w, 1401w, 1333w, 1314m, 1278m, 1243s, 1213s, 1175m, 1107w, 1070w, 1033m, 1015s cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 6.09 (dd, *J* = 10.6 Hz, 1.0 Hz, 1H), 6.36 (dd, *J* = 17.4 Hz, 10.2 Hz, 1H), 6.66 (dd, *J* = 17.4 Hz, 1.0 Hz, 1H), 7.09 (d, *J* = 8.5 Hz, 1H), 7.55 - 7.47 (m, 4H), 7.58 (tt, *J* = 7.2 Hz, 1.4 Hz, 1H), 7.77 (d, *J* = 16.0 Hz, 1H), 7.89 (d, *J* = 2.4 Hz, 1H), 8.02 – 7.99 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 119.6 (C), 124.9 (CH), 125.0 (CH), 127.0 (CH), 128.6 (CH), 128.7 (CH), 129.8 (C), 130.3 (CH), 133.2 (CH), 133.9 (CH_2), 136.4 (CH), 137.7 (C), 148.5 (C), 163.9 (C), 189.8 (C) ppm; HRMS (ESI): *m*/*z* calcd for $C_{18}H_{14}O_3{}^{79}Br^+$: 357.0121 [*M*+$H^+$]; found: 357.0131.

Compound **2e**:

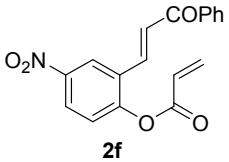


2e

Prepared according to general procedure **GP1** from the phenol **S1e** (1.47 g, 5.0 mmol), compound **2e** (0.76 g, 2.2 mmol, 44% yield) was isolated as a tan solid after column chromatography (eluent *n*-hexane/EtOAc 49:1 - 4:1).

R_f = 0.47 (*n*-hexane/EtOAc 4:1); m.p. 87.4-87.6 °C; IR (ATR): 1749s, 1669s, 1607m, 1587m, 1552w, 1448m, 1392s, 1296m, 1271w, 1214s, 1195m, 1122s, 1090m, 1013m cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 6.12 (dd, *J* = 10.4 Hz, 0.9 Hz, 1H), 6.36 (dd, *J* = 17.4 Hz, 10.4 Hz, 1H), 6.68 (dd, *J* = 17.4 Hz, 0.9 Hz, 1H), 7.19 (d, *J* = 2.1 Hz, 1H), 7.44 (d, *J* = 2.1 Hz, 1H), 7.53 - 7.50 (m, 2H), 7.57 (d, *J* = 16.2 Hz, 1H), 7.62 (tt, *J* = 7.3 Hz, 1.8 Hz, 1H), 7.79 (d, *J* = 16.2 Hz, 1H), 7.98 – 7.96 (m, 2H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 122.6 (CH), 126.2 (C), 126.8 (CH), 128.0 (CH), 128.6 (CH), 128.7 (CH), 129.0 (CH), 133.2 (CH), 134.5 (CH_2), 135.2 (CH), 135.3 (C), 136.2 (C), 137.5 (C), 149.9 (C), 163.4 (C), 190.0 (C) ppm; HRMS (ESI): *m*/*z* calcd for $C_{18}H_{13}O_3{}^{35}Cl_2^+$: 347.0236 [$M$+$H^+$]; found: 347.0247.

Compound **2f**:

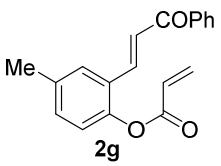


2f

Prepared according to general procedure **GP1** from the phenol **S1f** (1.35 g, 5.0 mmol), compound **2f** (1.36 g, 4.2 mmol, 84% yield) was isolated as a tan solid after column chromatography (eluent *n*-hexane/EtOAc 49:1 - 17:3).

R_f = 0.20 (*n*-hexane/EtOAc 4:1); m.p. 196.7-198.9 °C; IR (ATR): 1749s, 1668m, 1608s, 1579m, 1523w, 1473w, 1448w, 1404m, 1343w, 1291m, 1219s, 1165s, 1135m, 1070w, 1016w cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 6.14 (dd, *J* = 10.4 Hz, 0.9 Hz, 1H), 6.36 (dd, *J* = 17.4 Hz, 10.4 Hz, 1H), 6.70 (dd, *J* = 17.1 Hz, 0.9 Hz, 1H), 7.31 (d, *J* = 15.6 Hz, 1H), 7.38 (dd, *J* = 9.2 Hz, 2.4 Hz, 1H), 7.54 - 7.51 (m, 3H), 7.62 (tt, *J* = 7.3 Hz, 1.2 Hz, 1H), 8.04 – 8.01 (m, 2H), 8.19 – 8.15 (m, 2H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 122.2 (CH), 123.2 (CH), 127.0 (CH), 127.0 (CH), 128.0 (CH), 128.8 (CH), 128.8 (CH), 133.3 (CH), 133.6 (C), 134.3 (CH_2), 137.3 (C), 139.6 (CH), 145.5 (C), 154.1 (C), 163.4 (C), 190.2 (C) ppm; HRMS (ESI): *m*/*z* calcd for $C_{18}H_{14}O_4N^+$: 324.0866 [M+H^+]; found: 324.0880.

Compound **2g**:

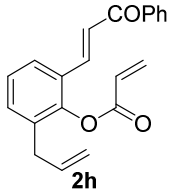


2g

Prepared according to general procedure **GP1** from the phenol **S1g** (1.19 g, 5.0 mmol), compound **2g** (0.58 g, 2.0 mmol, 40% yield) was isolated as a tan solid after column chromatography (eluent *n*-hexane/EtOAc 19:1 - 7:3).

R_f = 0.35 (*n*-hexane/EtOAc 4:1); m.p. 115.7-116.3 °C; IR (ATR): 1746s, 1665m, 1605s, 1490m, 1448w, 1403m, 1290w, 1234w, 1199s, 1145w, 1018s cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 2.41 (s, 3H), 6.08 (dd, *J* = 10.4 Hz, 1.2 Hz, 1H), 6.35 (dd, *J* = 17.4 Hz, 10.4 Hz, 1H), 6.66 (dd, *J* = 17.4 Hz, 1.2 Hz, 1H), 7.09 (d, *J* = 8.2 Hz, 1H), 7.26 (ddd, *J* = 8.2 Hz, 2.1 Hz, 0.6 Hz, 1H), 7.53 - 7.48 (m, 3H), 7.61 - 7.57 (m, 2H), 7.84 (d, *J* = 15.9 Hz, 1H), 8.01 – 7.98 (m, 2H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 20.9 (CH_3), 122.9 (CH), 123.9 (CH), 127.3 (C), 127.4 (CH), 128.1 (CH), 128.5 (CH), 128.6 (CH), 132.1 (CH), 132.8 (CH), 133.3 (CH_2), 136.1 (C), 138.0 (C), 138.3 (CH), 147.5 (C), 164.4 (C), 190.4 (C) ppm; HRMS (ESI): *m*/*z* calcd for $C_{19}H_{17}O_3^+$: 293.1172 [M+H^+]; found: 293.1184.

Compound **2h**:

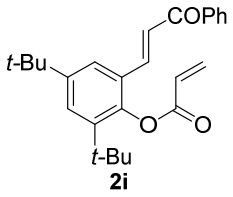


2h

Prepared according to general procedure **GP1** from the phenol **S1h** (1.32 g, 5.0 mmol), compound **2h** (1.02 g, 3.2 mmol, 64% yield) was isolated as brown oil after column chromatography (eluent *n*-hexane/EtOAc 9:1 - 4:1).

R_f = 0.19 (*hexane*/EtOAc 4:1); IR (ATR): 1742s, 1664s, 1640m, 1605s, 1578m, 1491w, 1449w, 1403w, 1332m, 1318w, 1293w, 1266w, 1234s, 1217m, 1166s, 1138m, 1034w, 1017m cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 3.31 - 3.30 (m, 2H), 5.11 - 5.06 (m, 2H), 5.93 - 5.85 (m, 1H), 6.10 (dd, *J* = 10.4 Hz, 1.2 Hz, 1H), 6.39 (dd, *J* = 17.4 Hz, 10.7 Hz, 1H), 6.68 (dd, *J* = 17.4 Hz, 1.2 Hz, 1H), 7.34 (dd, *J* = 7.6 Hz, 1.8 Hz, 1H), 7.51 - 7.46 (m, 3H), 7.58 (tt, *J* = 7.3 Hz, 1.2 Hz, 1H), 7.67 (dd, *J* = 7.3 Hz, 1.8 Hz, 1H), 7.78 (d, *J* = 15.6 Hz, 1H), 7.99 – 7.96 (m, 2H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 34.6 (CH_2), 116.9 (CH_2), 124.3 (CH), 125.9 (CH), 126.6 (CH), 127.0 (CH), 128.4 (C), 128.6 (CH), 128.6 (CH), 132.3 (CH), 132.8 (CH), 133.5 (C), 133.7 (CH_2), 135.3 (CH), 138.0 (C), 138.5 (CH), 148.1 (C), 164.0 (C), 190.4 (C), ppm; HRMS (ESI): *m*/*z* calcd for $C_{21}H_{18}O_3^+$: 318.1250 [M^+]; found: 318.1261.

Compound **2i**:



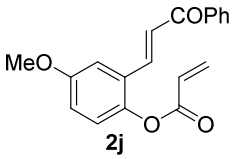
2i

Prepared according to general procedure **GP1** from the phenol **S1i** (1.68 g, 5.0 mmol), compound **2i** (1.66 g, 4.3 mmol, 85% yield) was isolated as a colorless semi solid after column chromatography (eluent *n*-hexane/EtOAc 9:1 - 4:1).

R_f = 0.26 (*n*-hexane/EtOAc 4:1); IR (ATR): 1746m, 1667m, 1645w, 1605s, 1579m, 1447w, 1403w, 1364m, 1332m, 1277s, 1245s, 1213m, 1141w, 1017s cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 6.10 (dd, *J* = 10.4 Hz, 1.2 Hz, 1H), 6.39 (dd, *J* = 17.1 Hz, 10.4 Hz, 1H), 6.67 (dd, *J* = 17.2 Hz, 1.2 Hz, 1H), 7.39 (d, *J* = 15.6 Hz, 1H), 7.49 - 7.46 (m, 2H), 7.52 (d, *J* = 2.4 Hz, 1H), 7.57 (tt, *J* = 7.6 Hz, 1.2 Hz, 1H), 7.61 (d, *J* = 2.1 Hz, 1H), 7.64 (d, *J* = 16.2 Hz, 1H), 7.96 – 7.94 (m, 2H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 30.5 (CH_3), 31.4 (CH_3), 34.8 (C), 35.0 (C), 122.4 (CH), 124.4 (CH), 127.0 (CH), 127.7 (CH), 128.4, 128.5 (CH), 128.6 (CH), 132.6 (CH), 133.6 (CH_2), 138.1 (C), 140.2 (CH), 141.6 (C),

146.2 (C), 148.5 (C), 164.7 (C), 191.2 (C) ppm; HRMS (ESI): *m*/*z* calcd for $C_{26}H_{31}O_3^+$: 391.2268 [*M*+H^+]; found: 391.2281.

Compound **2j**:

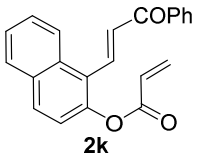


2j

Prepared according to general procedure **GP1** from the phenol **S1j** (1.27 g, 5.0 mmol), compound **2j** (0.46 g, 1.5 mmol, 30% yield) was isolated as a dark green solid after column chromatography (eluent *n*-hexane/EtOAc 19:1 - 4:1).

R_f = 0.31 (*n*-hexane/EtOAc 4:1); m.p. 63.4-63.9 °C; IR (ATR): 1741m, 1663m, 1635w, 1604s, 1578m, 1490s, 1466w, 1447w, 1428w, 1403m, 1339w, 1318w, 1288m, 1243m, 1215w, 1196s, 1139s, 1108w, 1070w, 1035m, 1015s cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.89 (s, 3H), 6.09 (dd, *J* = 10.4 Hz, 1.1 Hz, 1H), 6.40 (dd, *J* = 17.4 Hz, 10.5 Hz, 1H), 6.68 (dd, *J* = 17.2 Hz, 1.1 Hz, 1H), 7.02 (dd, *J* = 8.8 Hz, 2.9 Hz, 1H), 7.14 (d, *J* = 8.8 Hz, 1H), 7.27 (d, *J* = 2.9 Hz, 1H), 7.55 - 7.46 (m, 3H), 7.61 (tt, *J* = 7.4 Hz, 1.2 Hz, 1H), 7.83 (d, *J* = 15.9 Hz, 1H), 8.02 – 8.00 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.8 (CH_3), 112.1 (CH), 117.0 (CH), 124.0 (CH), 124.4 (CH), 127.4 (CH), 128.4 (C), 128.6 (CH), 128.6 (CH), 132.9 (CH), 133.3 (CH_2), 138.0 (C), 138.2 (CH), 143.3 (C), 157.5 (C), 164.6 (C), 190.4 (C) ppm; HRMS (ESI): *m*/*z* calcd for $C_{19}H_{16}O_4{}^{23}Na^+$: 331.0941 [*M*+$Na^+$]; found: 331.0952.

Compound **2k**:



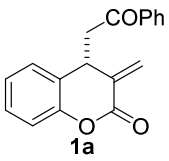
2k

Prepared according to general procedure **GP1** from the phenol **S1k** (1.37 g, 5.0 mmol), compound **2k** (0.87 g, 2.7 mmol, 53% yield) was isolated as brown oil after column chromatography (eluent *n*-hexane/EtOAc 9:1 - 7:3).

R_f = 0.46 (*n*-hexane/EtOAc 4:1); IR (ATR): 1740s, 1664m, 1603s, 1577m, 1510w, 1463w, 1447m, 1402w, 1369m, 1345s, 1287m, 1261w, 1243s, 1205m, 1177s, 1136w, 1078m, 1033w, 1013s cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.06 (dd, *J* = 10.7 Hz, 1.2 Hz, 1H), 6.40 (dd, *J* = 17.4 Hz, 10.7 Hz, 1H), 6.68 (dd, *J* = 17.4 Hz, 1.2 Hz, 1H), 7.32 (d, *J* = 8.9 Hz, 1H), 7.61 – 7.49 (m, 6H), 7.91 – 7.87 (m, 2H), 8.04 – 8.01 (m, 2H), 8.17 – 8.14 (m, 1H), 8.24 (d, *J* = 15.9 Hz, 1H), ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 121.7 (CH), 124.2 (C), 124.6 (CH), 126.1 (CH), 127.5 (CH), 127.5 (CH), 128.7 (CH), 128.7 (CH), 128.7 (CH), 129.4 (CH), 130.8 (CH), 131.9 (C), 132.3 (C), 133.1 (CH), 133.5 (CH_2), 137.3 (CH), 137.7 (C), 146.6 (C), 164.4 (C), 190.0 (C) ppm; HRMS (ESI): *m*/*z* calcd for $C_{21}H_{17}O_3^+$: 329.1172 [*M*+H^+]; found: 329.1186.

4.3 Chromanones **1**

Compound **1a**:



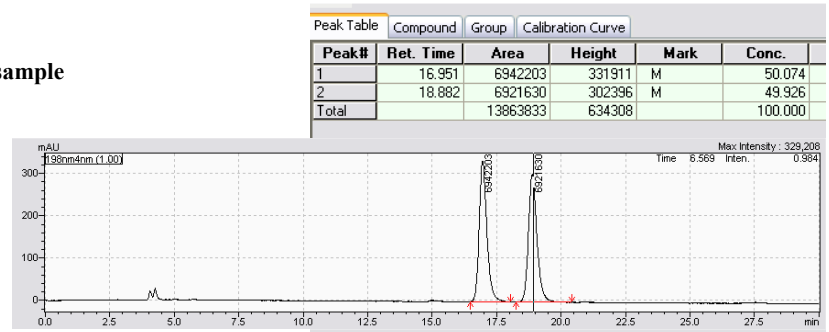
1a

Compound **1a** was prepared according to general procedure **GP2** from chalcone **2a** (139 mg, 0.5 mmol). However, instead of a common column chromatography highly pure product was obtained by diluting the crude reaction mixture with *n*-hexane/EtOAc 4:1 (50 mL) and filtering the mixture through a short silica pad (~20 g silica). Proceeding so, compound **1a** was isolated as red solid (129 mg, 0.46 mmol, 93% yield).

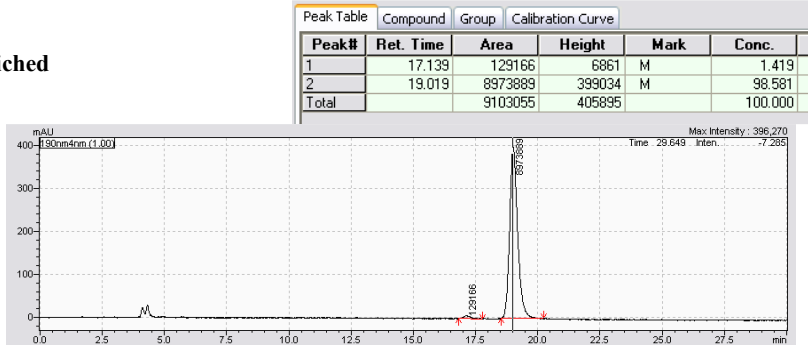
R_f = 0.31 (*n*-hexane/EtOAc 4:1); $[\alpha]_D^{26}$ = +138.0 (*c* = 0.10, $CHCl_3$), m.p. 147.3-147.4 °C; IR (ATR): 1746s, 1683s, 1597w, 1491s, 1458w, 1449w, 1407w, 1367m, 1300m, 1240m, 1220s, 1186m, 1138s, 1104m, 1040m, 1001w cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.31 (dd, *J* = 17.4 Hz, 7.2 Hz, 1H), 3.44 (dd, *J* = 17.4 Hz, 7.2 Hz, 1H), 4.53 (t, *J* = 6.5 Hz, 1H), 5.91 (s, 1H), 6.38 (s, 1H), 7.10-7.06 (m, 2H), 7.29-7.22 (m, 2H), 7.43 - 7.39 (m, 2H), 7.54 (tt, *J* = 7.5 Hz, 1.7 Hz, 1H), 7.85 - 7.83 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 38.2 (CH), 46.1 (CH_2), 117.3 (CH), 124.9 (CH), 125.2 (C), 128.0 (CH), 128.1 (CH), 128.7 (CH), 128.7 (CH), 129.9 (CH_2), 133.6 (C), 135.7 (CH), 136.4 (C), 150.6 (C), 163.3 (C), 196.3 (C) ppm; HRMS (ESI): *m*/*z* calcd for $C_{18}H_{15}O_3^+$: 279.1016 [*M*+H^+]; found: 279.1009.

The *ee* was determined by HPLC on a chiral stationary phase (Chiralpack IA, *n*-hexane/*i*-PrOH 95:5, 1.0 mL/min), t_R = 16.95 min, 18.88 min.

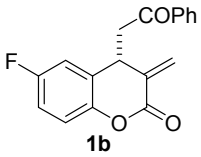
racemic sample



enantioenriched



Compound **1b**:



1b

Prepared according to general procedure **GP2** from chalcone **2b** (148 mg, 0.5 mmol), compound **1b** was isolated as colorless solid (74 mg, 0.25 mmol, 50% yield) after column chromatography (eluent *n*-hexane/EtOAc 4:1).

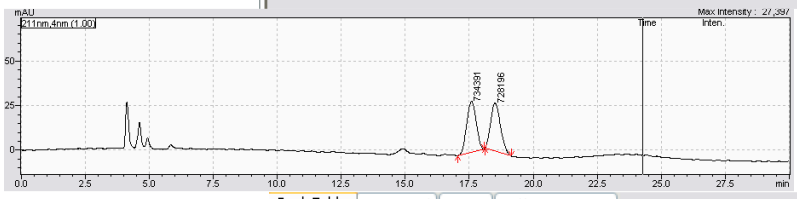
R_f = 0.40 (*n*-hexane/EtOAc 4:1); $[\alpha]_D^{26}$ = +113.0 (*c* = 0.10, $CHCl_3$), m.p. 134.9-137.6 °C; IR (ATR): 1750s, 1683s, 1597w, 1449m, 1437w, 1365m, 1307w, 1267m, 1204s, 1129s, 1002w cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 3.34 (dd, *J* = 17.7 Hz, 6.1 Hz, 1H), 3.44 (dd, *J* = 17.7 Hz, 6.7 Hz, 1H), 4.51 (t, *J* = 6.4 Hz, 1H), 5.93 (s, 1H), 6.42 (s, 1H), 6.97 - 6.93 (m, 1H), 7.06-7.02 (m, 2H), 7.46 – 7.42 (m, 2H), 7.56 (tt, *J* = 7.2 Hz, 1.2 Hz, 1H), 7.88-7.86 (m, 2H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 38.1 (CH), 45.9 (CH_2), 114.7 (d, J = 23.5 Hz, CH), 115.5 (d, *J* = 23.5 Hz, CH), 118.6 (d, *J* = 7.5 Hz, CH), 126.7 (d, *J* = 7.5 Hz, C), 128.0 (CH), 128.8 (CH), 130.2 (CH_2), 133.7 (CH), 135.1 (CH), 136.2 (C), 146.6 (d, *J* = 3.2 Hz, C), 159.2 (d, *J* = 244.4 Hz, C-F), 162.8 (C), 195.9 (C) ppm; HRMS (ESI): *m/z* calcd for $C_{18}H_{14}O_3F^+$: 297.0921 [M+H^+]; found: 297.0930.

The *ee* was determined by HPLC on a chiral stationary phase (Chiralcel OD, *n*-hexane/*i*-PrOH 95:5, 1.0 mL/min), t_R = 17.59 min, 18.51 min.

racemic sample

Peak Table | Compound | Group | Calibration Curve

Peak#	Ret. Time	Area	Height	Mark	Conc.
1	17.587	734391	28474	M	50.212
2	18.509	728196	26996	M	49.788
Total		1462587	55470		100.000

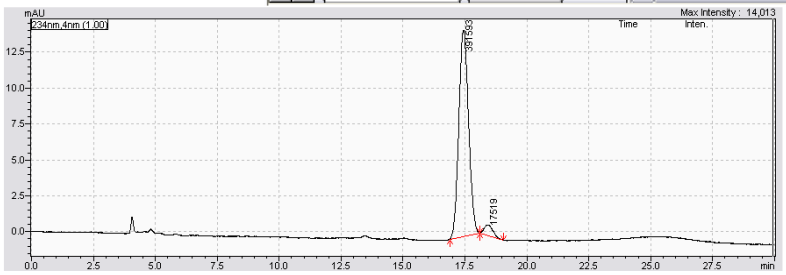


enantioenriched

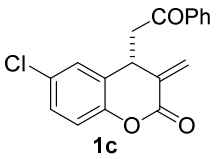
Peak Table | Compound | Group | Calibration Curve

Peak#	Ret. Time	Area	Height	Mark	Conc.
1	17.445	391593	14346	M	95.718
2	18.411	17519	734	M	4.282
Total		409113	15080		100.000

Extracted 234nm | Ch1 254nm



Compound **1c**:



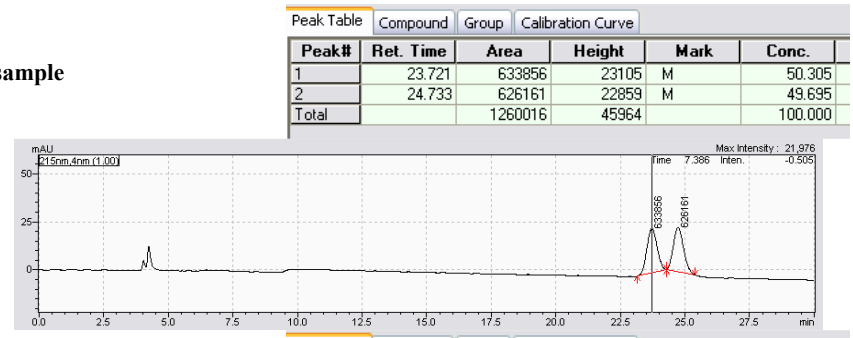
1c

Prepared according to general procedure **GP2** from chalcone **2c** (156 mg, 0.5 mmol), compound **1c** was isolated as colorless solid (120 mg, 0.38 mmol, 77% yield) after column chromatography (eluent *n*-hexane/EtOAc 4:1).

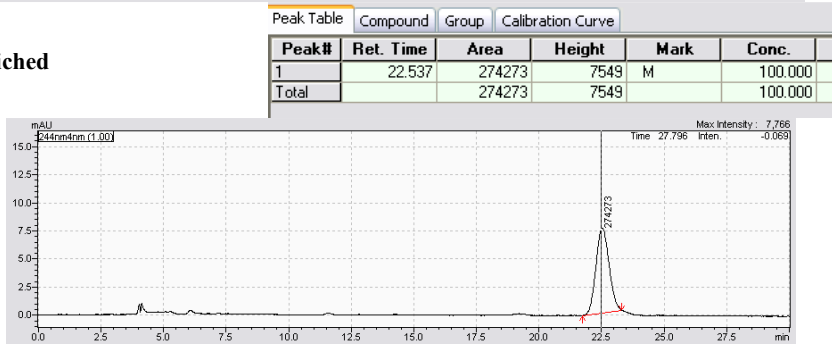
R_f = 0.37 (*n*-hexane/EtOAc 4:1); $[\alpha]_D^{26}$ = +70.0 (*c* = 0.10, $CHCl_3$), m.p. 149.7-151.3 °C; IR (ATR): 1745s, 1682s, 1630w, 1597w, 1484m, 1449m, 1421w, 1366w, 1311w, 1253m, 1224s, 1202m, 1138s, 1114m, 1087m, 1001w cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.33 (dd, *J* = 17.7 Hz, 6.1 Hz, 1H), 3.46 (dd, *J* = 17.7 Hz, 6.7 Hz, 1H), 4.50 (t, *J* = 6.4 Hz, 1H), 5.94 (s, 1H), 6.43 (s, 1H), 6.95 (d, *J* = 8.9 Hz, 1H), 7.22 (dd, *J* = 8.9 Hz, 2.4 Hz, 1H), 7.31 (d, *J* = 2.4 Hz, 1H), 7.46 – 7.43 (m, 3H), 7.57 (tt, *J* = 7.2 Hz, 1.2 Hz, 1H), 7.88 - 7.86 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 37.9 (CH), 46.0 (CH_2), 118.7 (CH), 126.7 (C), 128.0 (CH), 128.0 (CH), 128.8 (CH), 128.8 (CH), 129.8 (C), 130.4 (CH_2), 133.7 (CH), 135.0 (C), 136.2 (C), 149.2 (C), 162.6 (C), 195.8 (C) ppm; HRMS (ESI): *m*/*z* calcd for $C_{18}H_{14}O_3{}^{35}Cl^+$: 313.0626 [$M$+$H^+$]; found: 313.0637.

The *ee* was determined by HPLC on a chiral stationary phase (Chiralcel OD, *n*-hexane/*i*-PrOH 97:3, 1.0 mL/min), t_R = 23.72 min, 24.73 min.

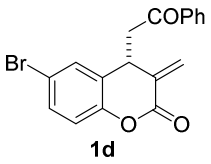
racemic sample



enantioenriched



Compound **1d**:



1d

Prepared according to general procedure **GP2** from chalcone **2d** (177 mg, 0.5 mmol), compound **1d** was isolated as a colorless solid (138 mg, 0.39 mmol, 78% yield) after column chromatography (eluent *n*-hexane/EtOAc 4:1).

R_f = 0.41 (*n*-hexane/EtOAc 4:1); $[\alpha]_D^{26}$ = +32.0 (*c* = 0.10, $CHCl_3$), m.p. 163.0-163.2 °C; IR (ATR): 1746s, 1681s, 1597w, 1481m, 1448w, 1411w, 1365w, 1310m, 1270w, 1252m, 1227s, 1206m, 1134s, 1111s, 1074w cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 3.31 (dd, *J* = 17.7 Hz, 6.4 Hz, 1H), 3.44 (dd, *J* = 17.7 Hz, 6.4 Hz, 1H), 4.48 (t, *J* = 6.4 Hz, 1H), 5.92 (s, 1H), 6.41 (s, 1H), 6.95 (d, *J* = 8.6 Hz, 1H), 7.35 (dd, *J* = 8.6 Hz, 2.4 Hz, 1H), 7.45 – 7.41 (m, 3H), 7.55 (tt, *J* = 7.2 Hz, 1.2 Hz, 1H), 7.87 – 7.84 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 37.8 (CH), 46.1 (CH_2), 117.3 (C), 119.1 (CH), 127.2 (C), 128.1 (CH), 128.8 (CH), 130.5 (CH_2), 130.9 (CH), 131.7 (CH), 133.7 (CH), 134.9 (C), 136.2 (C), 149.7 (C), 162.5 (C), 195.8 (C) ppm; HRMS (ESI): *m*/*z* calcd for $C_{18}H_{14}O_3{}^{79}Br^+$: 357.0121 [*M*+$H^+$]; found: 357.0132.

The *ee* was determined by HPLC on a chiral stationary phase (Chiralcel OD, *n*-hexane/*i*-PrOH 95:5, 1.0 mL/min), t_R = 18.12 min, 19.46 min.

racemic sample

Peak Table | Compound | Group | Calibration Curve

Peak#	Ret. Time	Area	Height	Mark	Conc.
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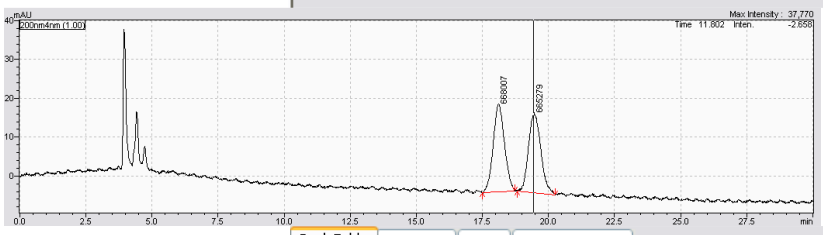
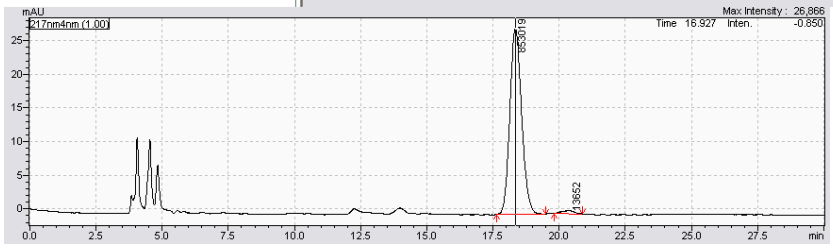
2	19.455	665279	20565	M	49.898
Total		1333286	43152		100.000



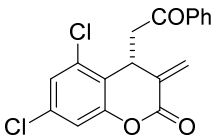
enantioenriched

Peak Table | Compound | Group | Calibration Curve

Peak#	Ret. Time	Area	Height	Mark	Conc.
1	18.346	853019	27652	M	98.425
2	20.425	13652	431	M	1.575
Total		866672	28083		100.000



Compound **1e**:



1e

Compound **1e** was prepared according to general procedure **GP2** from chalcone **2e** (173 mg, 0.5 mmol). However, instead of a common column chromatography highly pure product was obtained by diluting the crude reaction mixture with *n*-hexane/EtOAc 4:1 (50 mL) and filtering the mixture through a short silica pad (~20 g silica). Proceeding so, compound **1e** was isolated as brown oil (121 mg, 0.35 mmol, 70% yield).[4]

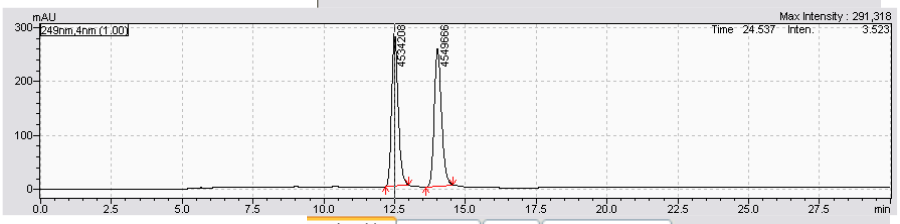
R_f = 0.34 (*n*-hexane/EtOAc 4:1); $[\alpha]_D^{26}$ = –69.0 (*c* = 0.10, $CHCl_3$), m.p. 145.7-146.3 °C; IR (ATR): 1751s, 1683s, 1597w, 1571m, 1449m, 1398w, 1365w, 1301m, 1257w, 1231s, 1207m, 1174s, 1114m, 1087w cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 3.24 (dd, *J* = 17.7 Hz, 3.3 Hz, 1H), 3.67 (dd, *J* = 17.7 Hz, 8.6 Hz, 1H), 4.76 (dd, *J* = 8.9 Hz, 3.1 Hz, 1H), 6.06 (s, 1H), 6.50 (s, 1H), 7.08 (d, *J* = 2.1 Hz, 1H), 7.24 (d, *J* = 2.1 Hz, 1H), 7.49 – 7.45 (m, 2H), 7.60 (tt, *J* = 7.6 Hz, 1.2 Hz, 1H), 7.92 - 7.89 (m, 2H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 35.9 (CH), 43.6 (CH_2), 116.7 (CH), 121.6 (C), 125.5 (CH), 128.1 (CH), 128.8 (CH), 132.2 (CH_2), 133.1 (C), 133.6 (C), 133.7 (CH), 134.3 (C), 136.2 (C), 152.0 (C), 195.8 (C) ppm; HRMS (ESI): *m*/*z* calcd for $C_{18}H_{13}O_3{}^{35}Cl_2^+$: 347.0242 [$M$+$H^+$]; found: 347.0257.

The *ee* was determined by HPLC on a chiral stationary phase (Chiralpack IA, *n*-hexane/*i*-PrOH 95:5, 1.0 mL/min), t_R = 12.49 min, 14.01 min.

racemic sample

Peak Table | Compound | Group | Calibration Curve

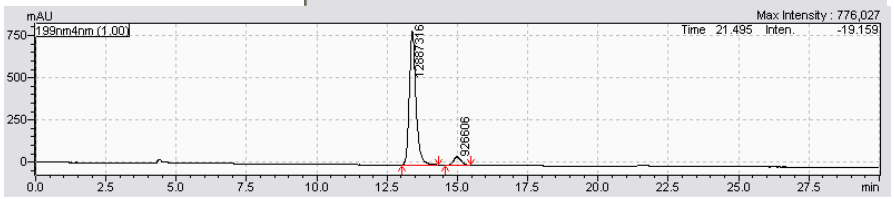
Peak#	Ret. Time	Area	Height	Mark	Conc.
1	12.496	4534208	284875	M	49.915
2	14.012	4549666	254177	M	50.085
Total		9083873	539052		100.000



enantioenriched

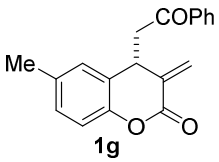
Peak Table | Compound | Group | Calibration Curve

Peak#	Ret. Time	Area	Height	Mark	Conc.
1	13.394	12887316	791545	M	93.292
2	14.988	926606	50808	M	6.708
Total		13813923	842354		100.000



[4]Synthesized using catalyst **11d**.

Compound **1g**:



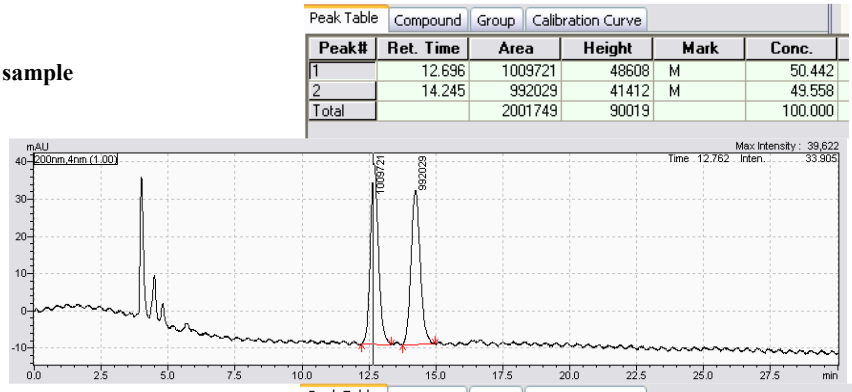
1g

Prepared according to general procedure **GP2** from chalcone **2g** (146 mg, 0.5 mmol), compound **1g** was isolated as colorless solid (133 mg, 0.45 mmol, 91% yield) after column chromatography (eluent *n*-hexane/EtOAc 4:1).

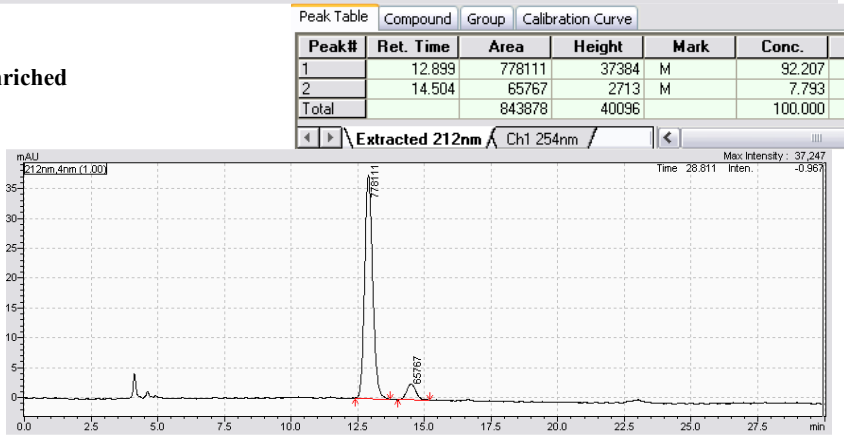
R_f = 0.35 (*n*-hexane/EtOAc 4:1); $[\alpha]_D^{26}$ = +82.0 (*c* = 0.10, $CHCl_3$), m.p. 147.0-148.1 °C; IR (ATR): 1747s, 1684s, 1597w, 1459w, 1407m, 1258w, 1198m, 1134s cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 3.28 (dd, *J* = 17.4 Hz, 6.1 Hz, 1H), 3.43 (dd, *J* = 17.4 Hz, 7.3 Hz, 1H), 4.49 (t, *J* = 6.7 Hz, 1H), 5.90 (s, 1H), 6.38 (s, 1H), 6.97 (d, *J* = 8.2 Hz, 1H), 7.08 – 7.04 (m, 2H), 7.45 – 7.42 (m, 2H), 7.56 (tt, *J* = 7.6 Hz, 1.2 Hz, 1H), 7.87 – 7.85 (m, 2H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 38.2 (CH), 46.0 (CH_2), 117.0 (CH), 124.8 (C), 128.0 (CH), 128.3 (CH), 128.7 (CH), 129.2 (CH), 129.7 (CH_2), 133.5 (CH), 134.5 (C), 135.9 (C), 136.5 (C), 148.5 (C), 163.5 (C), 196.3 (C) ppm; HRMS (ESI): *m*/*z* calcd for $C_{19}H_{17}O_3^+$: 293.1172 [M+H^+]; found: 293.1178.

The *ee* was determined by HPLC on a chiral stationary phase (Chiralcel OD, *n*-hexane/*i*-PrOH 95:5, 1.0 mL/min), t_R = 12.69 min, 14.25 min.

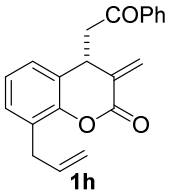
racemic sample



enantioenriched



Compound **1h**:



1h

Prepared according to general procedure **GP2** from chalcone **2h** (151 mg, 0.5 mmol), compound **1h** was isolated as colorless oil (136 mg, 0.42 mmol, 90% yield) after column chromatography (eluent *n*-hexane/EtOAc 4:1).

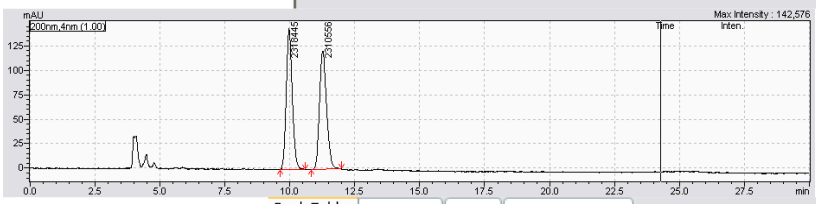
R_f = 0.18 (*n*-hexane/EtOAc 4:1); $[\alpha]_D^{26}$ = +109.0 (*c* = 0.10, $CHCl_3$), m.p. 113.5-114.3 °C; IR (ATR): 1745s, 1684s, 1638m, 1596w, 1580w, 1459w, 1449m, 1406w, 1352m, 1297w, 1258m, 1182s, 1076m, 1001w cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 3.28 (dd, *J* = 17.4 Hz, 6.1 Hz, 1H), 3.43 (dd, *J* = 17.4 Hz, 7.3 Hz, 1H), 3.51 – 3.49 (m, 2H), 4.53 (t, *J* = 6.7 Hz, 1H), 5.13 - 5.08 (m, 1H), 5.92 (s, 1H), 6.03 - 5.95 (m, 1H), 6.37 (s, 1H), 7.04 (t, *J* = 7.6 Hz, 1H), 7.16 – 7.12 (m, 2H), 7.46 – 7.41 (m, 2H), 7.55 (tt, *J* = 7.6 Hz, 1.5 Hz, 1H), 7.87 - 7.85 (m, 2H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 33.7 (CH_2), 38.5 (CH), 45.7 (CH_2), 116.4 (CH_2), 124.7 (CH), 125.3 (C), 126.0 (CH), 128.0 (CH), 128.6 (C), 128.7 (CH), 129.3 (CH), 129.6 (CH_2), 133.5 (CH), 135.8 (C), 135.9 (CH), 136.5 (C), 148.4 (C), 163.2 (C), 196.4 (C) ppm; HRMS (ESI): *m*/*z* calcd for $C_{21}H_{19}O_3^+$: 319.1329 [M+H^+]; found: 319.1334.

The *ee* was determined by HPLC on a chiral stationary phase (Chiralcel OD, *n*-hexane/*i*-PrOH 95:5, 1.0 mL/min), t_R = 9.97 min, 11.26 min.

racemic sample

Peak Table | Compound | Group | Calibration Curve

Peak#	Ret. Time	Area	Height	Mark	Conc.
1	9.968	2318445	143735	M	50.085
2	11.263	2310556	120916	M	49.915
Total		4629001	264652		100.000

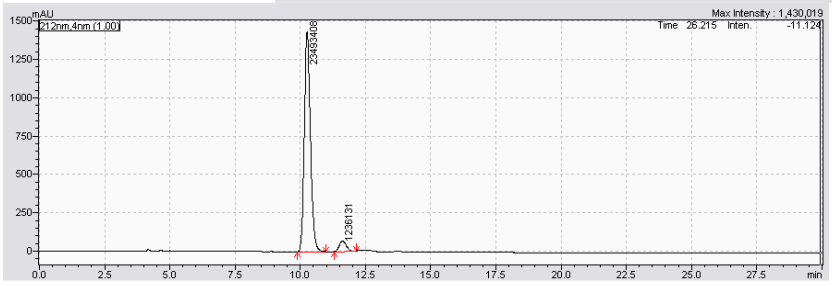


enantioenriched

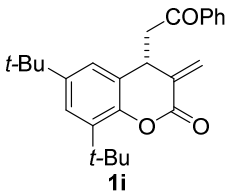
Peak Table | Compound | Group | Calibration Curve

Peak#	Ret. Time	Area	Height	Mark	Conc.
1	10.262	23493408	1433952	M	95.001
2	11.619	1236131	68835	M	4.999
Total		24729539	1502787		100.000

Extracted 212nm | Ch1 254nm



Compound **1i**:



1i

Compound **1i** was prepared according to general procedure **GP2** from chalcone **2i** (195 mg, 0.5 mmol). However, instead of a common column chromatography highly pure product was obtained by diluting the crude reaction mixture with *n*-hexane/EtOAc 4:1 (50 mL) and filtering the mixture through a short silica pad (~20 g silica). Proceeding so, compound **1i** was isolated as colorless oil (195 mg, 0.5 mmol, 99% yield).[5]

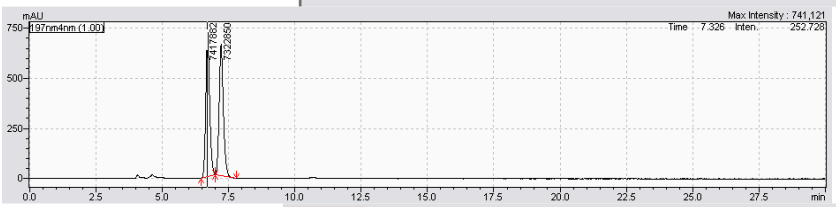
R_f = 0.09 (*n*-hexane/EtOAc 9:1); $[\alpha]_D^{26}$ = +44.0 (*c* = 0.10, $CHCl_3$), IR (ATR): 1746s, 1686s, 1644m, 1598w, 1541m, 1477s, 1448m, 1407w, 1394m, 1363w, 1297m, 1267m, 1250w, 1219w, 1202m, 1179s, 1051w, 1002m cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 3.26 (dd, *J* = 17.7 Hz, 3.3 Hz, 1H), 3.39 (dd, *J* = 17.7 Hz, 8.6 Hz, 1H), 4.48 (m, 1H), 5.90 (s, 1H), 6.33 (s, 1H), 7.09 (d, *J* = 2.4 Hz, 1H), 7.26 (d, *J* = 2.4 Hz, 1H), 7.42 – 7.38 (m, 2H), 7.60 (tt, *J* = 7.5 Hz, 1.3 Hz, 1H), 7.84 - 7.82 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 30.2 (CH_3), 31.4 (CH_3), 34.6 (C), 35.1 (C), 39.6 (CH), 45.2 (CH_2), 122.8 (CH), 123.3 (CH), 125.3 (C), 128.1 (CH), 128.7 (CH), 129.2 (CH_2), 133.4 (CH), 136.0 (C), 136.7 (C), 147.1 (C), 147.2 (C), 163.4 (C), 196.8 (C) ppm; HRMS (ESI): *m*/*z* calcd for $C_{26}H_{31}O_3^+$: 391.2268 [M+H^+]; found: 391.2276.

The *ee* was determined by HPLC on a chiral stationary phase (Chiralcel OD, *n*-hexane/*i*-PrOH 97:3, 1.0 mL/min), t_R = 6.70 min, 7.22 min.

racemic sample

Peak Table | Compound | Group | Calibration Curve

Peak#	Ret. Time	Area	Height	Mark	Conc.
1	6.704	7417882	730764	M	50.322
2	7.215	7322850	657231	M	49.678
Total		14740732	1387994		100.000



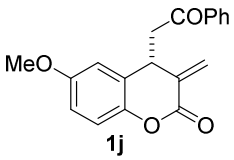
enantioenriched

Peak Table | Compound | Group | Calibration Curve

Peak#	Ret. Time	Area	Height	Mark	Conc.
1	6.632	15538713	1430129	M	96.855
2	7.153	504579	50434	M	3.145
Total		16043292	1480563		100.000

[5]This compound readily decomposes during column chromatography.

Compound **1j**:



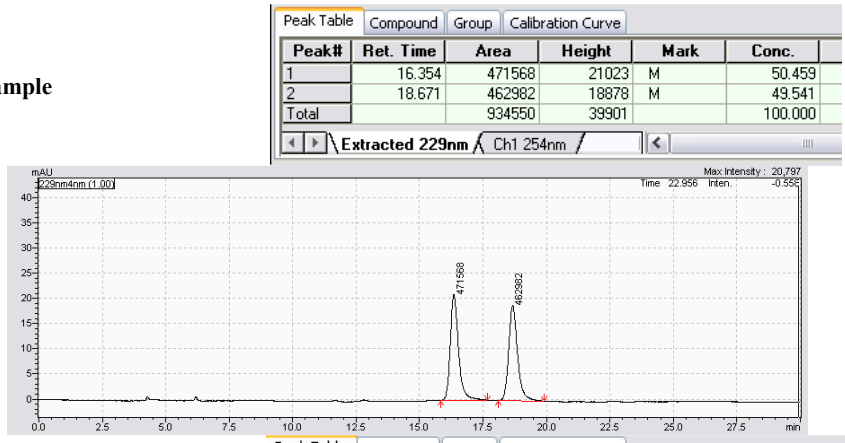
1j

Prepared according to general procedure **GP2** from chalcone **2j** (153 mg, 0.5 mmol), compound **1j** was isolated as a tan solid (104 mg, 0.34 mmol, 68% yield) after column chromatography (eluent *n*-hexane/EtOAc 4:1).

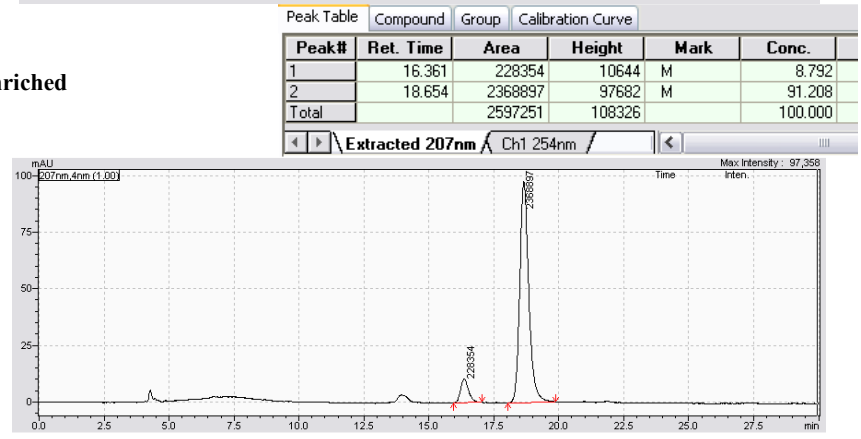
R_f = 0.19 (*n*-hexane/EtOAc 4:1); $[\alpha]_D^{26}$ = +59.0 (*c* = 0.10, $CHCl_3$), m.p. 99.5-100.5 °C; IR (ATR): 1743s, 1684m, 1498s, 1207s, 1137m, 770w, 690w cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 3.29 (dd, *J* = 17.4 Hz, 6.1 Hz, 1H), 3.42 (dd, *J* = 17.4 Hz, 7.1 Hz, 1H), 3.74 (s, 3H), 4.48 (t, *J* = 6.6 Hz, 1H), 5.89 (s, 1H), 6.37 (s, 1H), 6.77 (dt, *J* = 8.8 Hz, 2.9 Hz, 2H), 6.99 (d, *J* = 8.8 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 2H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.84 (d, *J* = 7.3 Hz, 2H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 38.4 (CH), 45.8 (CH_2), 55.6 (CH_3), 112.7 (CH), 114.0 (CH), 118.0 (CH), 125.9 (C), 127.9 (CH), 128.6 (CH), 129.6 (CH_2), 133.5 (CH), 135.7 (C), 136.4 (C), 144.4 (C), 156.3 (C), 163.3 (C), 196.2 (C) ppm; HRMS (ESI): *m*/*z* calcd for $C_{19}H_{17}O_4^+$: 309.1127 [M+H^+]; found: 309.1142.

The *ee* was determined by HPLC on a chiral stationary phase (Chiralpack IA, *n*-hexane/*i*-PrOH 90:10, 1.0 mL/min), t_R = 16.35 min, 18.67 min.

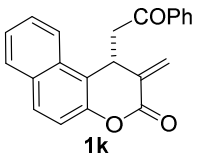
racemic sample



enantioenriched



Compound **1k**:



1k

Prepared according to general procedure **GP2** from chalcone **2k** (170 mg, 0.5 mmol), compound **1k** was isolated as colorless oil (56 mg, 0.17 mmol, 33% yield) after column chromatography (eluent *n*-hexane/EtOAc 4:1).[6]

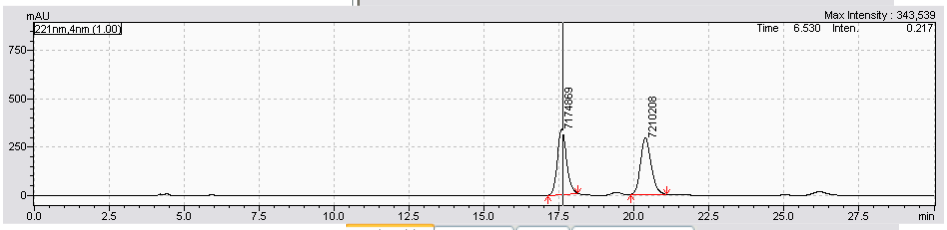
R_f = 0.38 (*n*-hexane/EtOAc 3:1); $[\alpha]_D^{26}$ = –46.0 (*c* = 0.10, $CHCl_3$), IR (ATR): 1748s, 1683s, 1633w, 1597w, 1516w, 1466m, 1449s, 1400w, 1352m, 1313w, 1271m, 1243m, 1222w, 1157s, 1127w, 1079m, 1044w, 1024w, 1002w cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 3.19 (dd, *J* = 17.6 Hz, 2.7 Hz, 1H), 3.70 (dd, *J* = 17.6 Hz, 10.0 Hz, 1H), 5.29 (dd, *J* = 10.0 Hz, 2.7 Hz, 1H), 6.13 (s, 1H), 6.49 (s, 1H), 7.31 - 7.28 (m, 1H), 7.63 – 7.43 (m, 5H), 7.83 (d, *J* = 8.8 Hz, 1H), 7.90 - 7.88 (m, 3H), 7.99 - 7.97 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 34.3 (CH), 44.0 (CH_2), 117.6 (C), 122.1 (CH), 125.4 (CH), 127.7 (CH), 128.1 (CH), 129.1 (CH), 129.6 (CH), 129.9 (C), 131.2 (C), 131.4 (CH_2), 133.6 (CH), 134.9 (C), 136.5 (C), 148.4 (C), 163.1 (C), 196.6 (C) ppm; HRMS (ESI): *m*/*z* calcd for $C_{22}H_{17}O_3^+$: 329.1172 [M+H^+]; found: 329.1180.

The *ee* was determined by HPLC on a chiral stationary phase (Chiralpack IA, *n*-hexane/*i*-PrOH 95:5, 1.0 mL/min), t_R = 17.58 min, 20.38 min.

racemic sample

Peak Table | Compound | Group | Calibration Curve

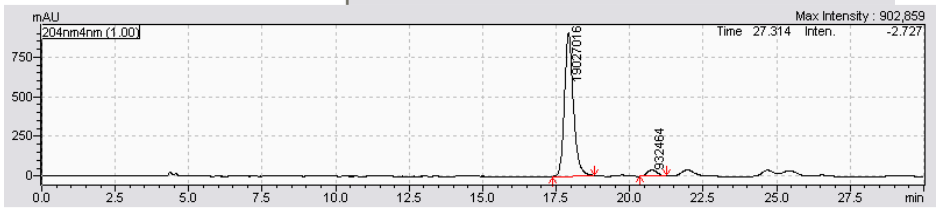
Peak#	Ret. Time	Area	Height	Mark	Conc.
1	17.582	7174869	338206	M	49.877
2	20.378	7210208	293647	M	50.123
Total		14385077	631853		100.000



enantioenriched

Peak Table | Compound | Group | Calibration Curve

Peak#	Ret. Time	Area	Height	Mark	Conc.
1	17.919	19027016	903252	M	95.328
2	20.760	932464	39537	M	4.672
Total		19959480	942790		100.000



[6]Synthesized using catalyst **11d**.

5. Kinetic Studies

The reaction rates were determined by the following NMR experiment:

A freshly prepared solution of chalcone **2** (0.07 mmol) in deuterated dry acetonitrile (0.7 mL) was used to shim and calibrate the NMR mashine (Bruker Avance 500). Subsequently, this solution was poured in to a vial containing the catalyst **11d** (0.007 mmol), shaken for 10-20 seconds and transfered back into the originally used NMR tube. This time point was considered as the start of the reaction t_0. Each NMR measurement consisted of eight scans with 1-2 minutes in between two measurements. The reaction was monitored until around 50% of starting material was converted (usually 2-4 hours).

The individual NMR spectra were processed via Topspin software (Bruker) and analyzed via Dynamics Center add-on. The reaction profile was obtained intergrating the signals of the terminal double bond in the product (for example, see signal 1 in Figure S1).

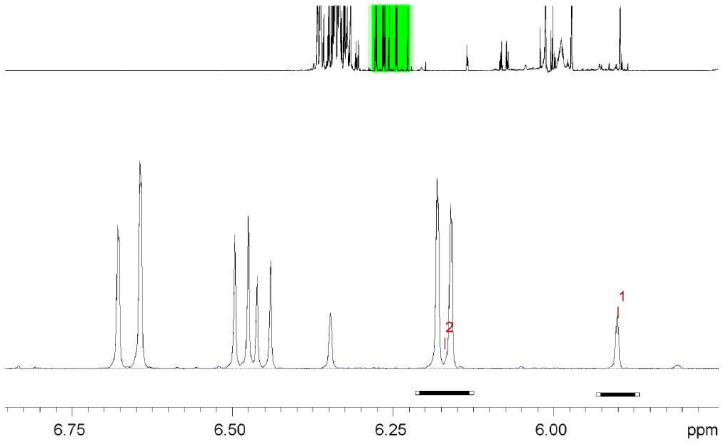


Figure S1. Example of the intergrated signals.

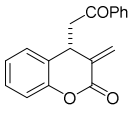
Best fitting exponential regression of the individual reaction profiles and hence, the reaction contants were obtained using Monte Carlo simulation (Dynamics Center add-on of Topspin software). The values are summarized in table S1 and table S2, respectively. The Eyring and the Hammett plots are shown in figure S2 and S3, respectively. In the Eyring plot, the linear regression gave a slope of −33.1±0.8 mol and an intercept of 1534.6±255.8 molK. From this data the entropy of activation $\Delta_rS^{\ddagger}$ and the enthalpy of activation $\Delta_rH^{\ddagger}$ was obtained by the multiplication with the ideal gas constant *R*:

$\Delta_rS^{\ddagger} = -33.1\pm0.8$ mol * $R = -275.1\pm6.7$ J*K^{-1}*mol^{-1}

$\Delta_rH^{\ddagger} = 1534.6\pm255.8$ molK * $R = 12.8\pm2.1$ kJ*mol^{-1}

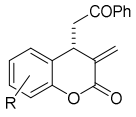
In the Hammett plot, the linear regression gave a slope of +2.0±0.2 which directly corresponds to the Hammett's reaction constant ρ.

Table S1. Reaction Constants at Different Temperatures.

Compound	T [K]	k [s^{-1}]	k(error) [s^{-1}]	T^{-1} / K^{-1}	ln((*h**k)/(T*k_B))
	278	$9.04*10^{-05}$	$1.09*10^{-08}$	0.00359712	–38.69886516
	288	$1.49*10^{-04}$	----------	0.00347222	–38.23450249
	298	$1.47*10^{-04}$	$1.53*10^{-05}$	0.0033557	–38.28214921
	308	$1.82*10^{-04}$	$2.48*10^{-07}$	0.00324675	–38.10158141
	318	$2.09*10^{-04}$	$2.36*10^{-07}$	0.00314465	–37.99520544
	328	$2.89*10^{-04}$	$2.52*10^{-07}$	0.00304878	–37.70207523

k(error) is the statistical error of the Monte Carlo simulation. *h* = Planck constant. k_B = Boltzman constant.

Table S2. Reaction Constants at 298 K Obtained Using Differently Substitueted Substrates.

Compound	R	k [s^{-1}]	k(error) [s^{-1}]	σ_m	σ_p	$(\sigma_m+\sigma_p)/2$	$\log(k_x/k_H)$
	H	$1.35*10^{-04}$	$5.62*10^{-08}$	0.00	0.00	0.00	0.00
	F	$3.86*10^{-04}$	$1.45*10^{-07}$	0.34	0.06	0.20	0.46
	Cl	$5.26*10^{-04}$	$2.54*10^{-07}$	0.37	0.22	0.30	0.59
	Br	$6.86*10^{-04}$	$1.93*10^{-07}$	0.39	0.31	0.35	0.71
	Me	$1.18*10^{-04}$	$6.25*10^{-08}$	–0.06	–0.17	–0.12	–0.06
	MeO	$8.27*10^{-05}$	$2.797*10^{-08}$	0.11	–0.28	–0.09	–0.21

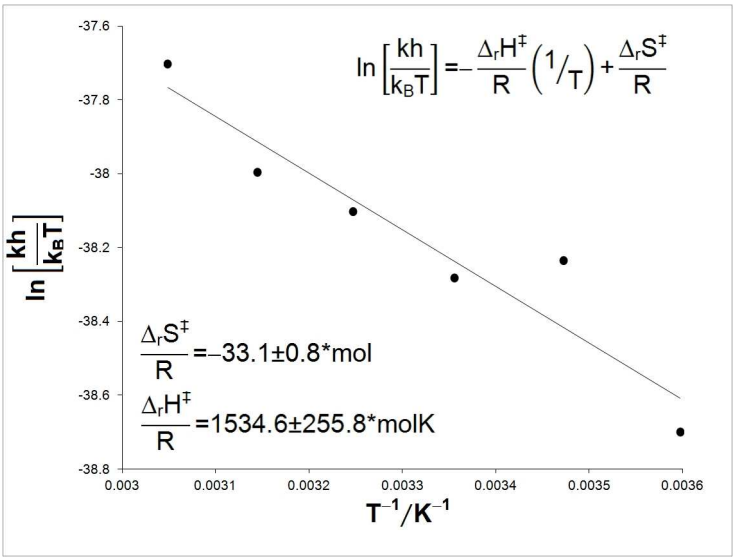


Figure S2. Eyring Plot. R = Ideal gas constant.

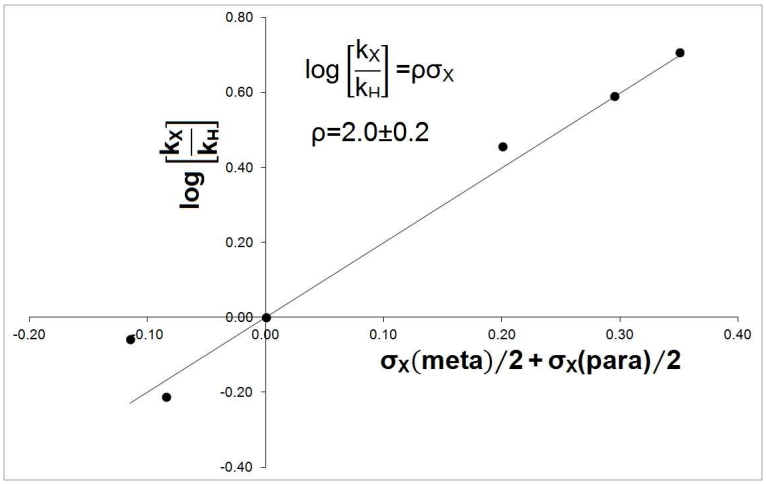
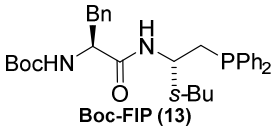


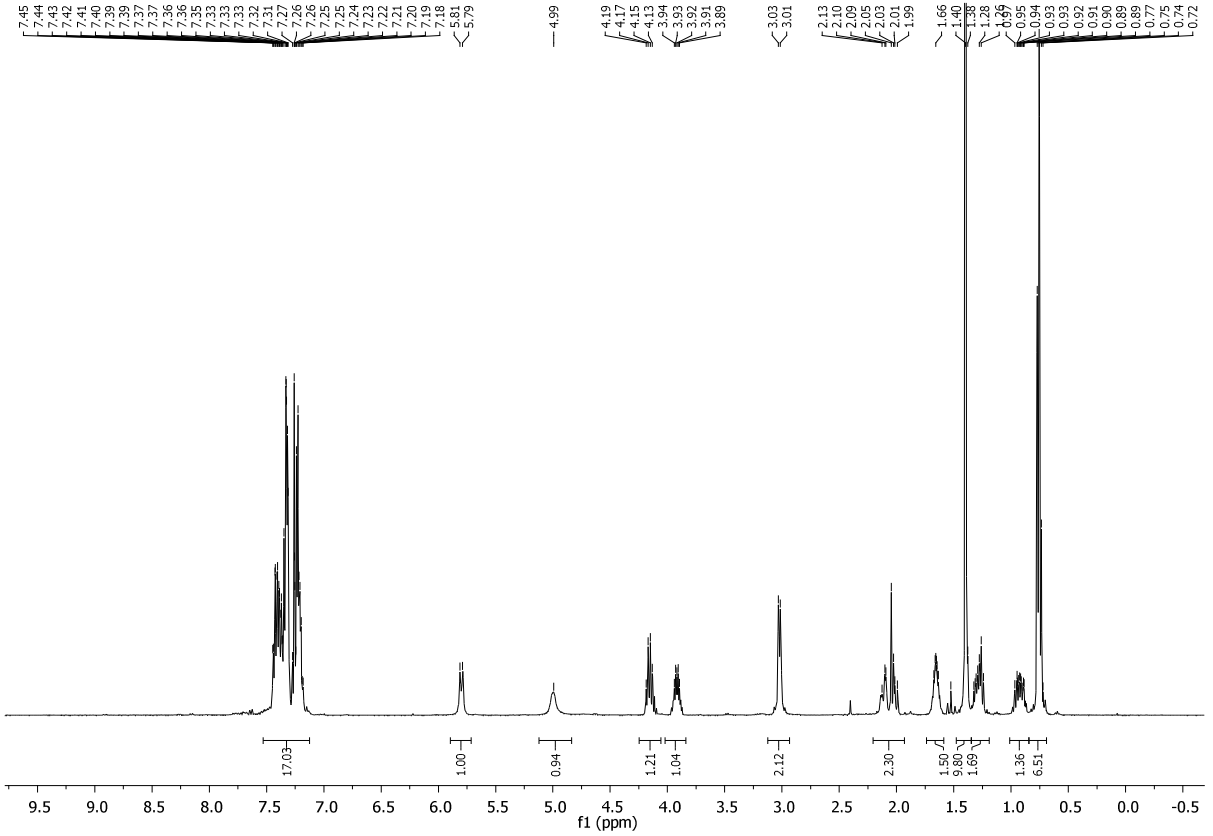
Figure S3 Hammett Plot.

6. NMR Spectra

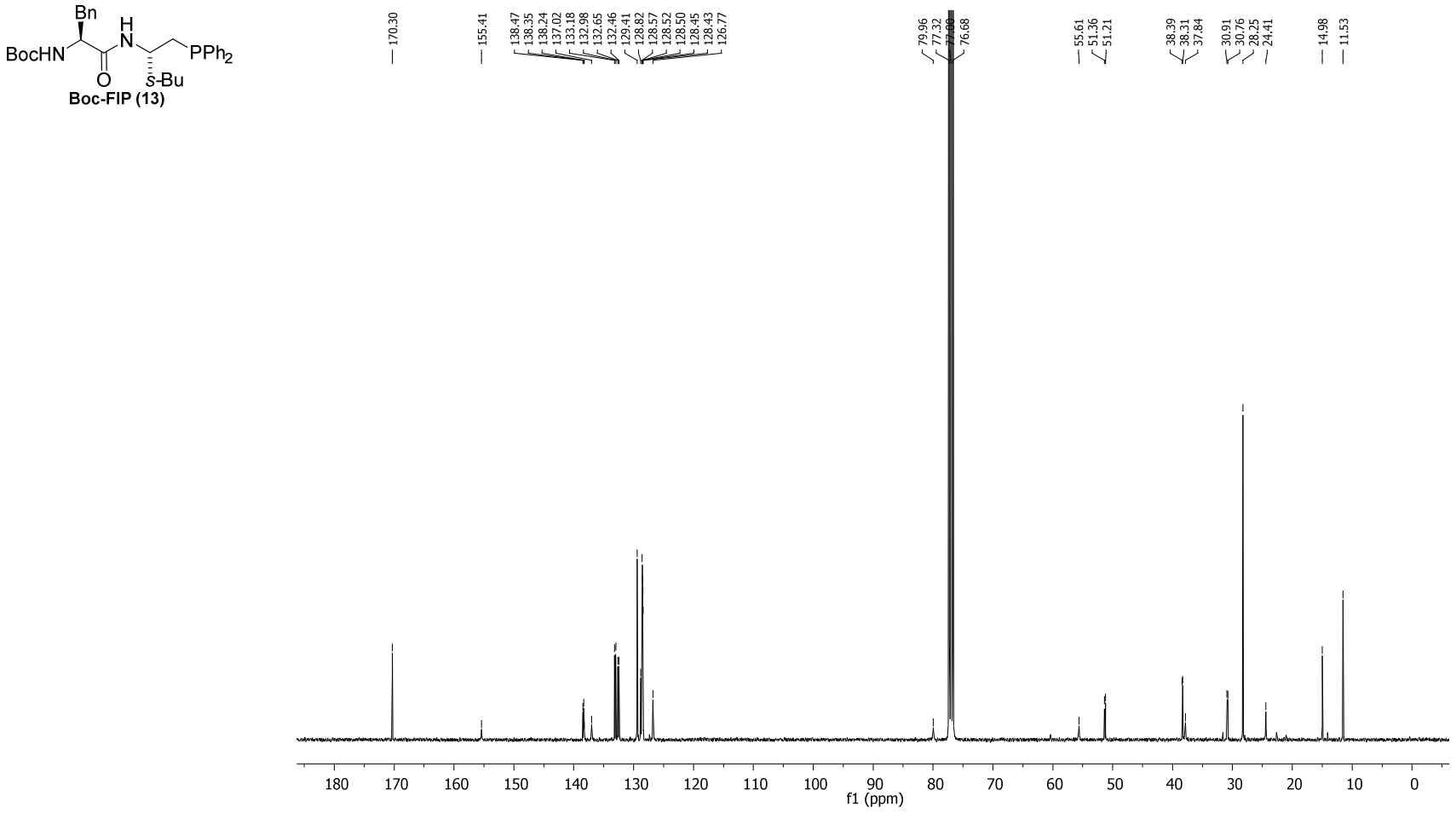
6.1 Boc-FIP



Boc-FIP (13)

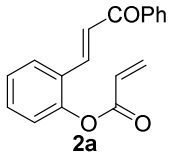


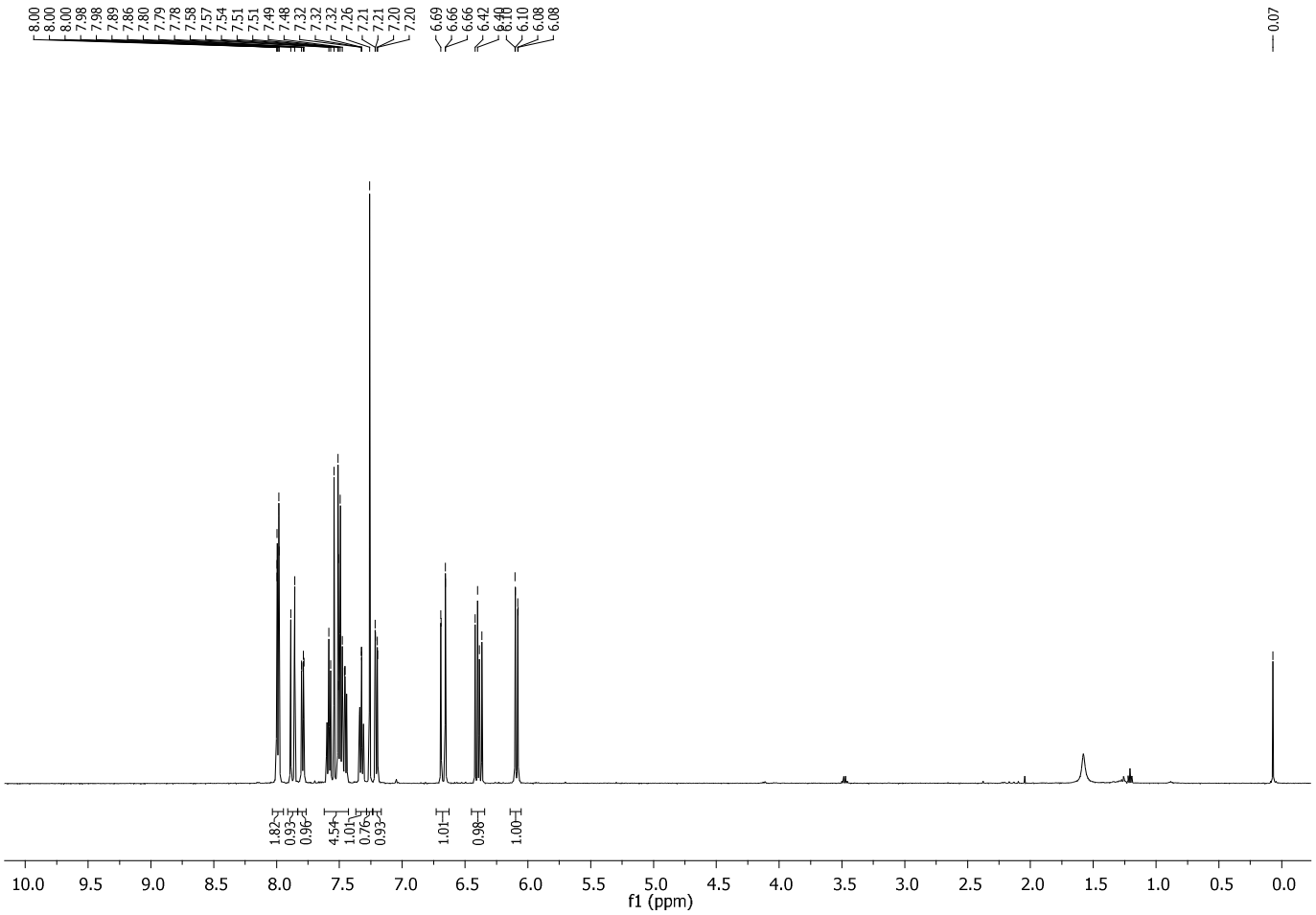
^{1}H NMR, $CDCl_3$, 400 MHz



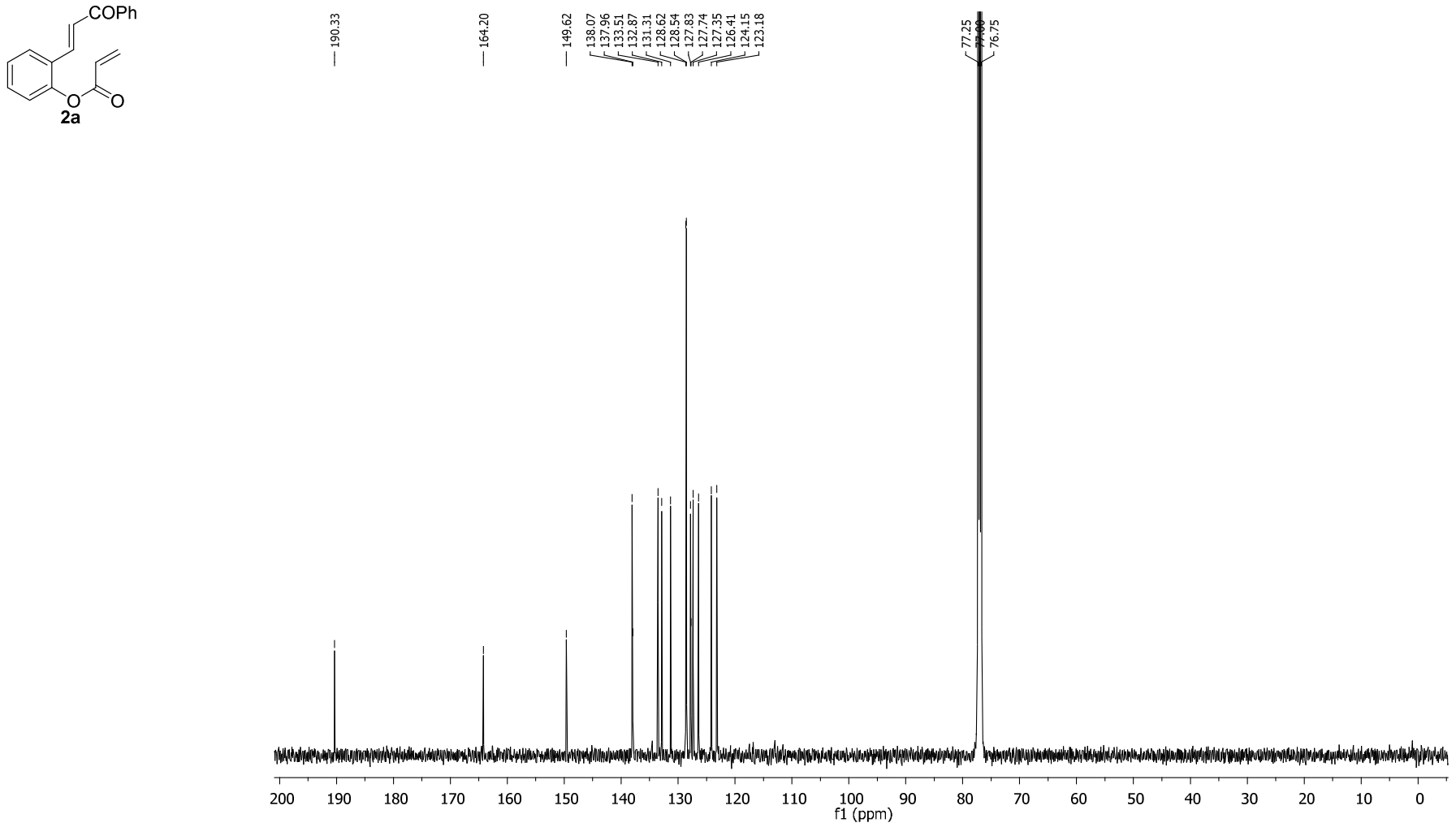
^{13}C NMR, $CDCl_3$, 101 MHz

6.2 Chalcones **2**

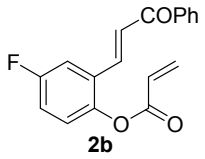




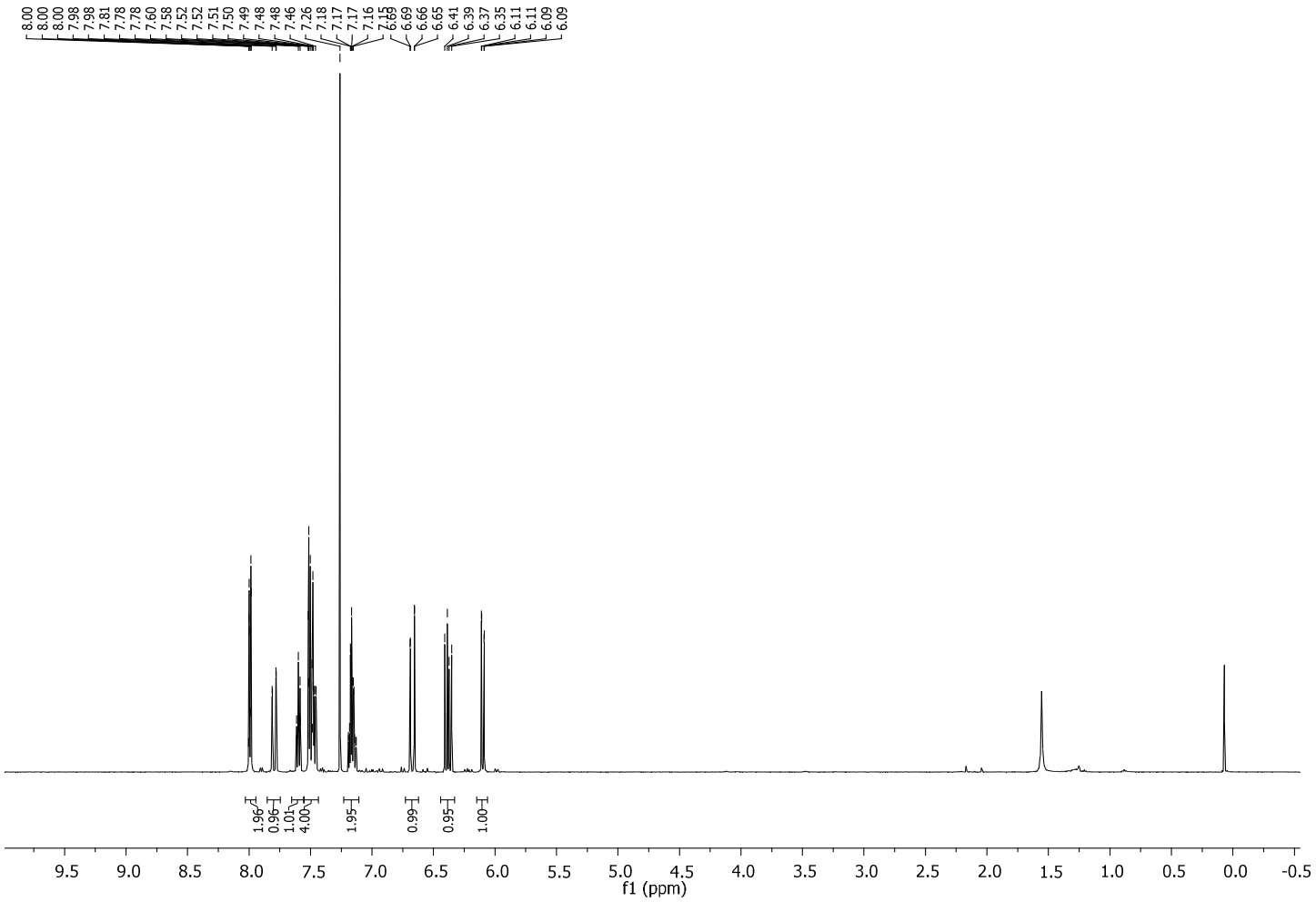
^{1}H NMR, $CDCl_3$, 500 MHz



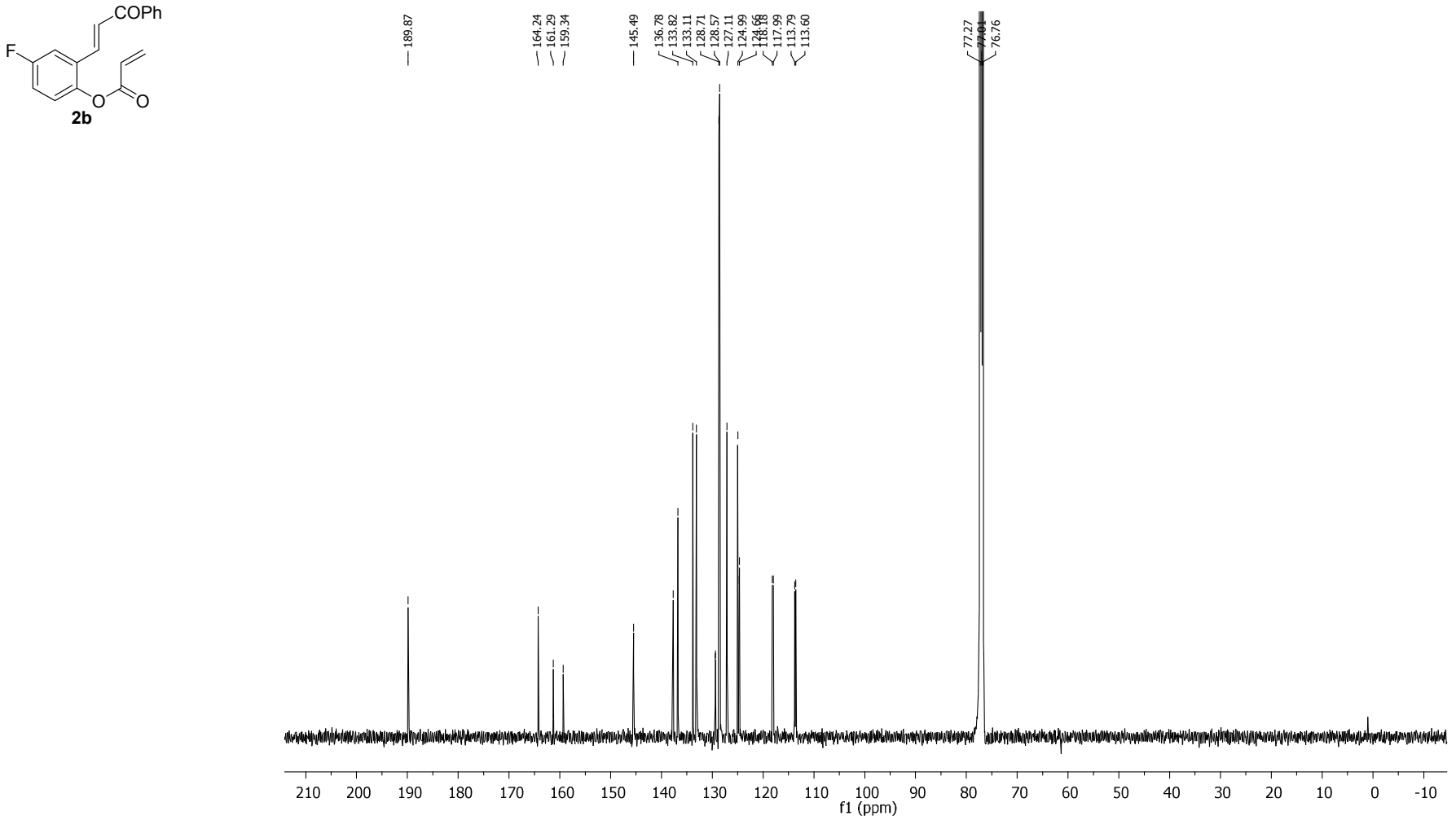
^{13}C NMR, $CDCl_3$, 126 MHz



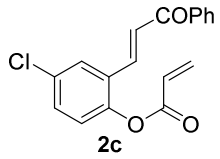
2b



^{1}H NMR, $CDCl_3$, 400 MHz



^{13}C NMR, $CDCl_3$, 101 MHz



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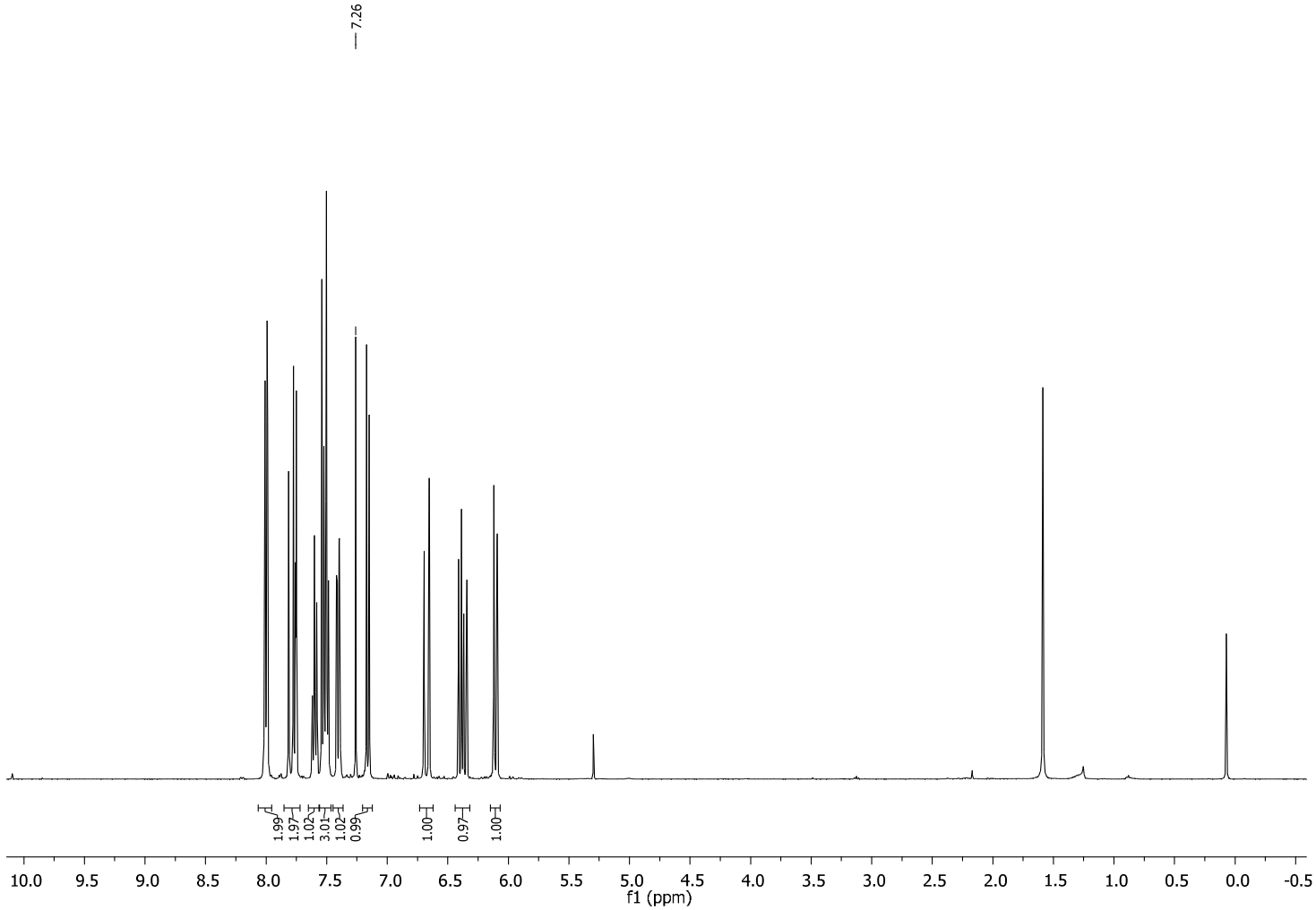
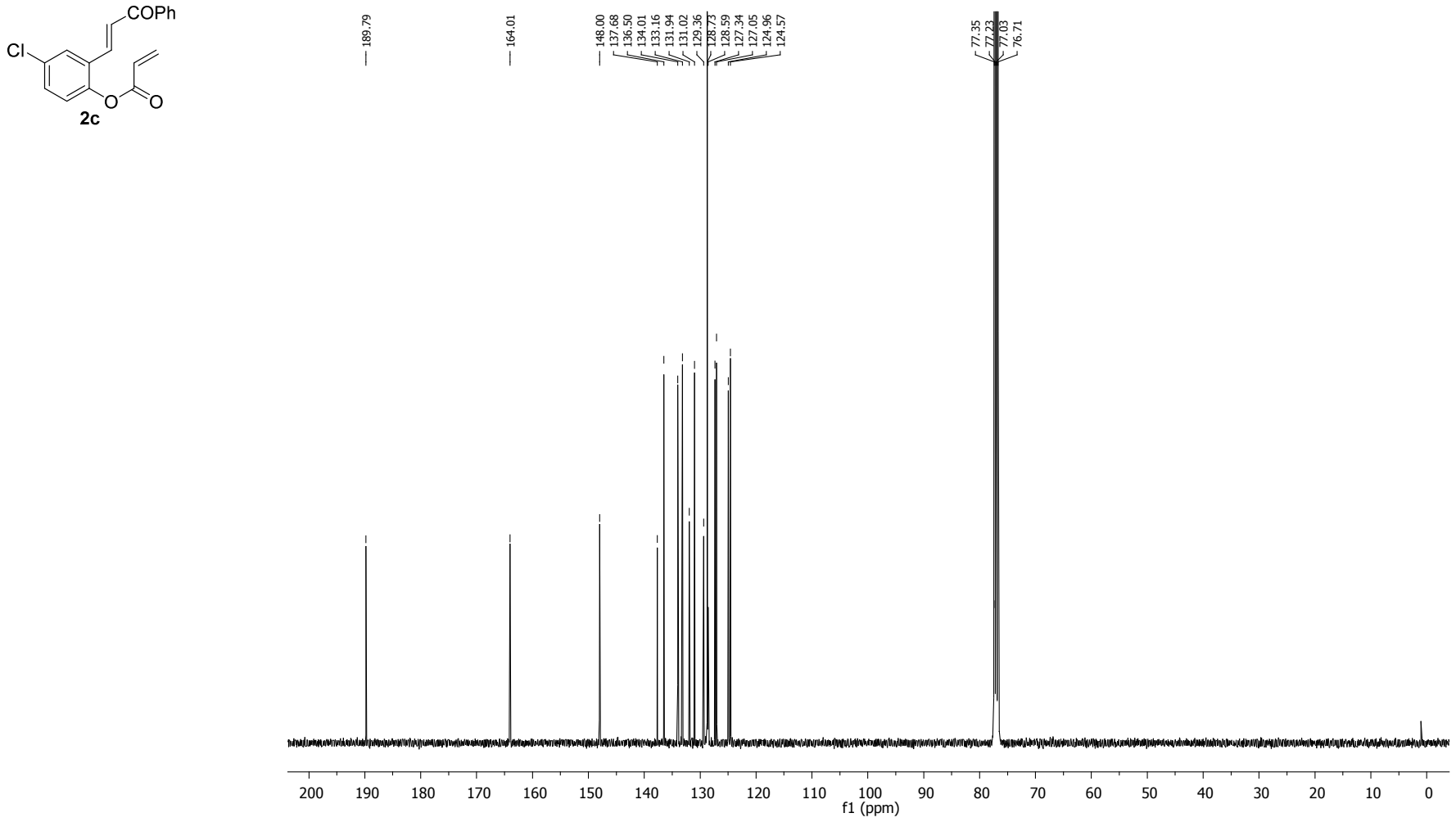
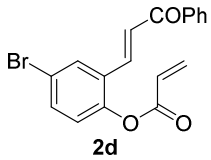


^{1}H NMR, $CDCl_3$, 400 MHz



^{13}C NMR, $CDCl_3$, 101 MHz



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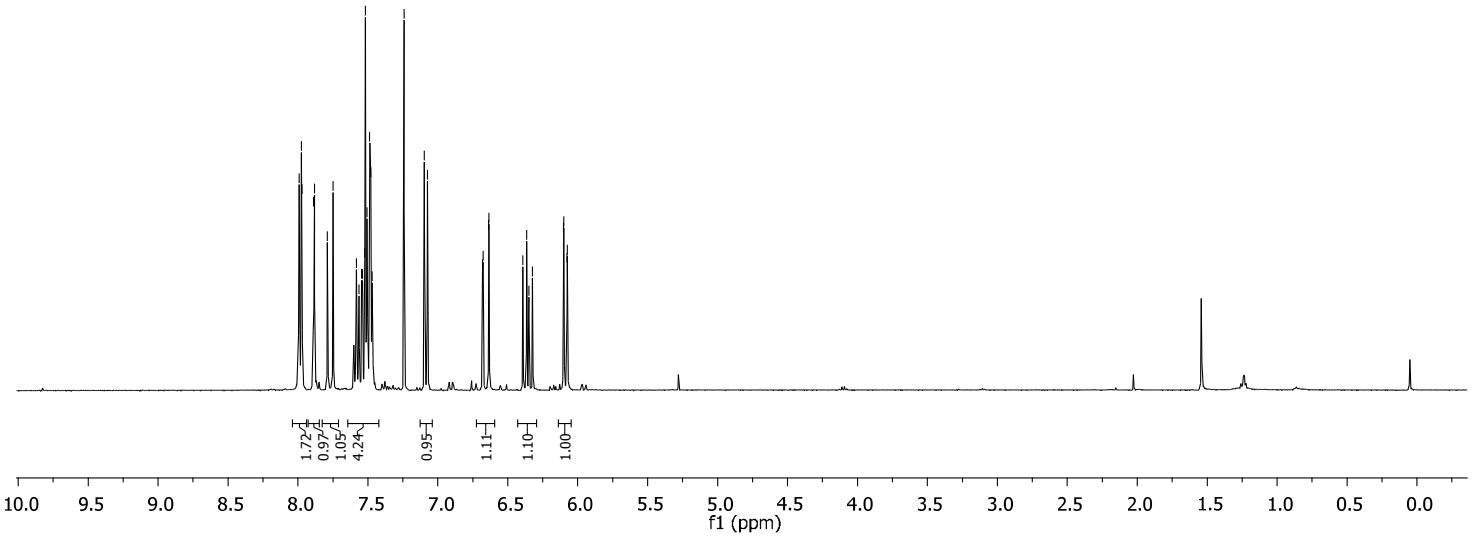
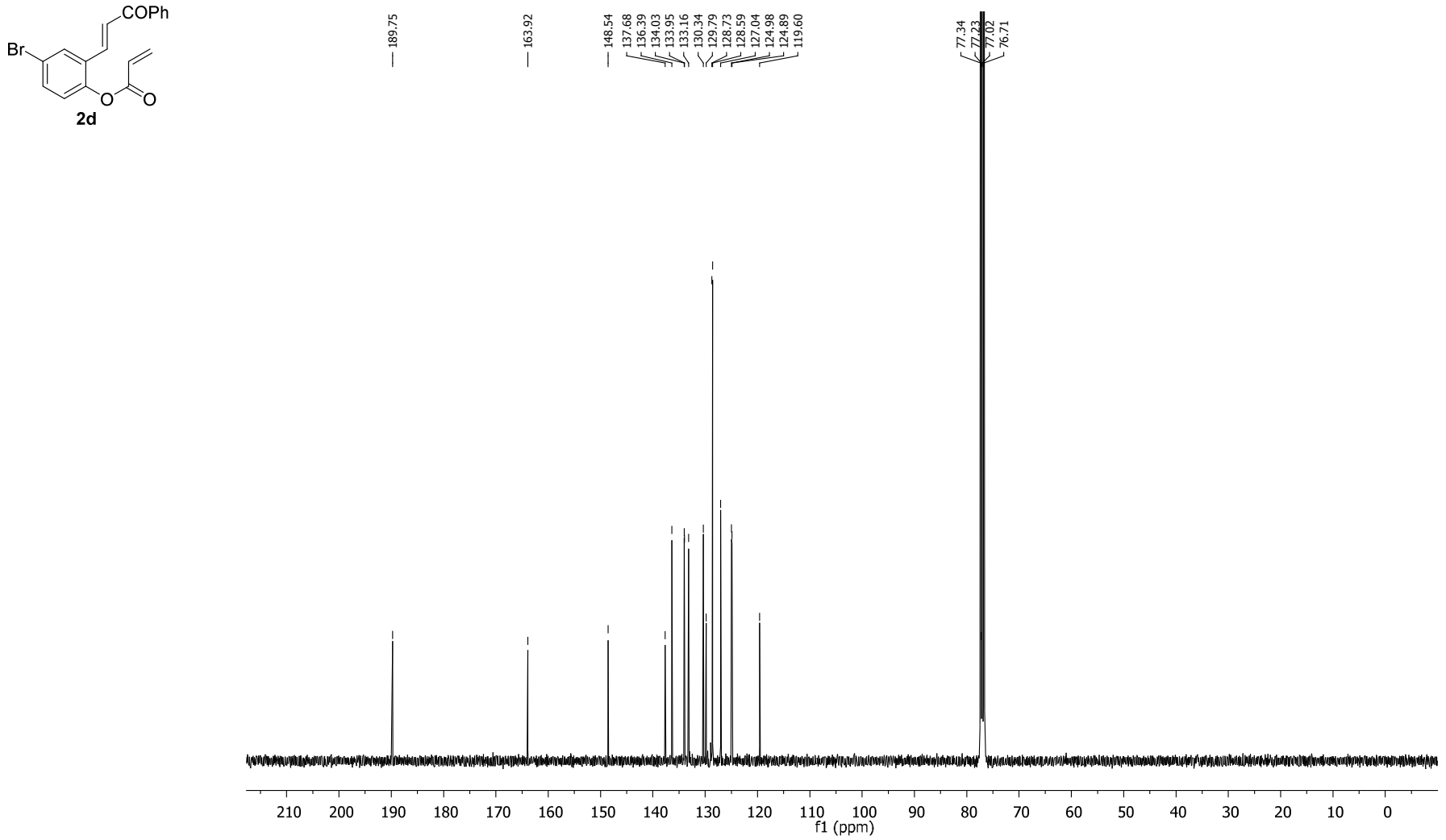
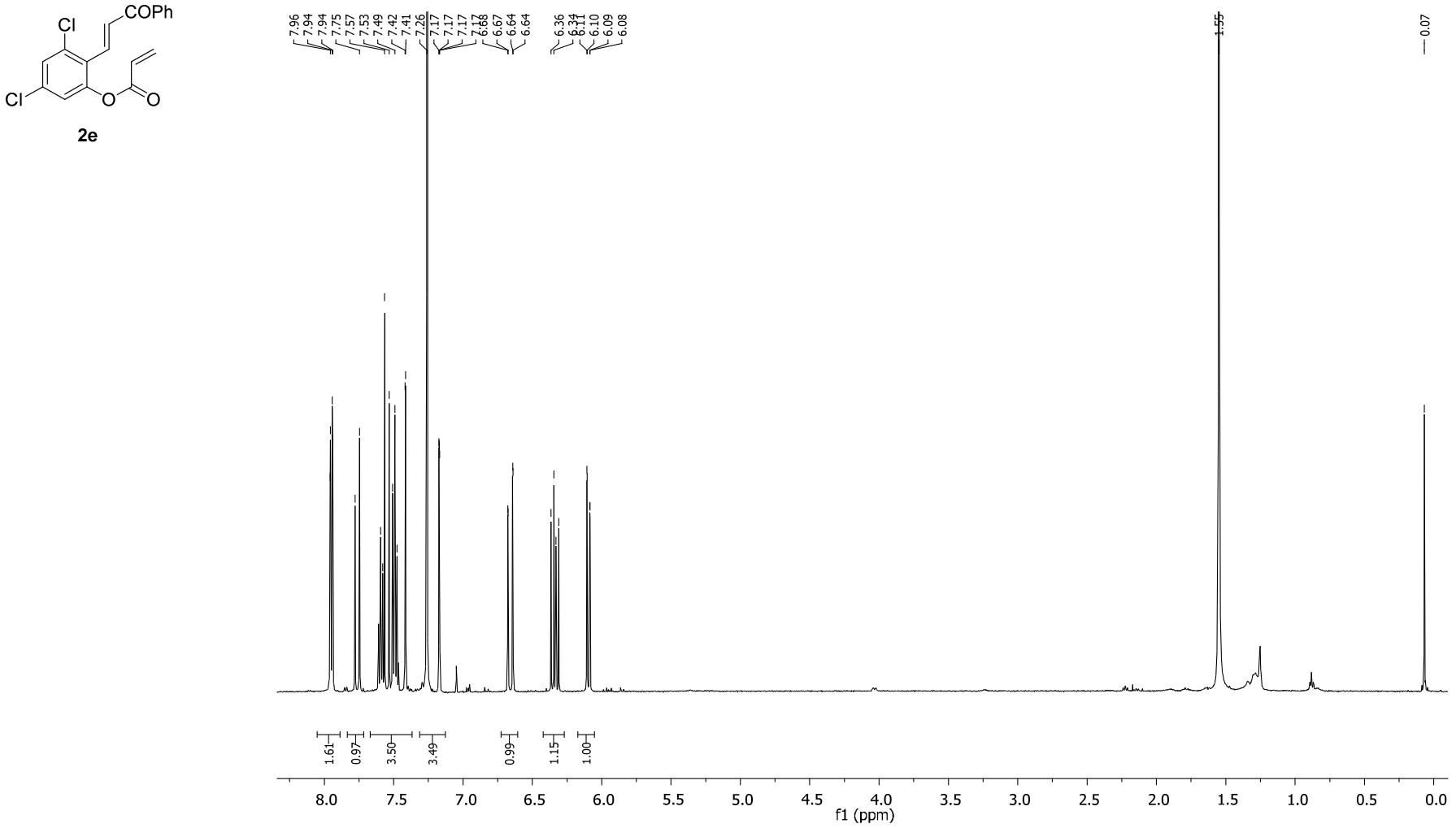


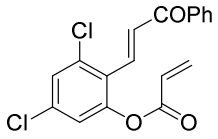
^{1}H NMR, $CDCl_3$, 400 MHz



^{13}C NMR, $CDCl_3$, 101 MHz



^{1}H NMR, $CDCl_3$, 500 MHz



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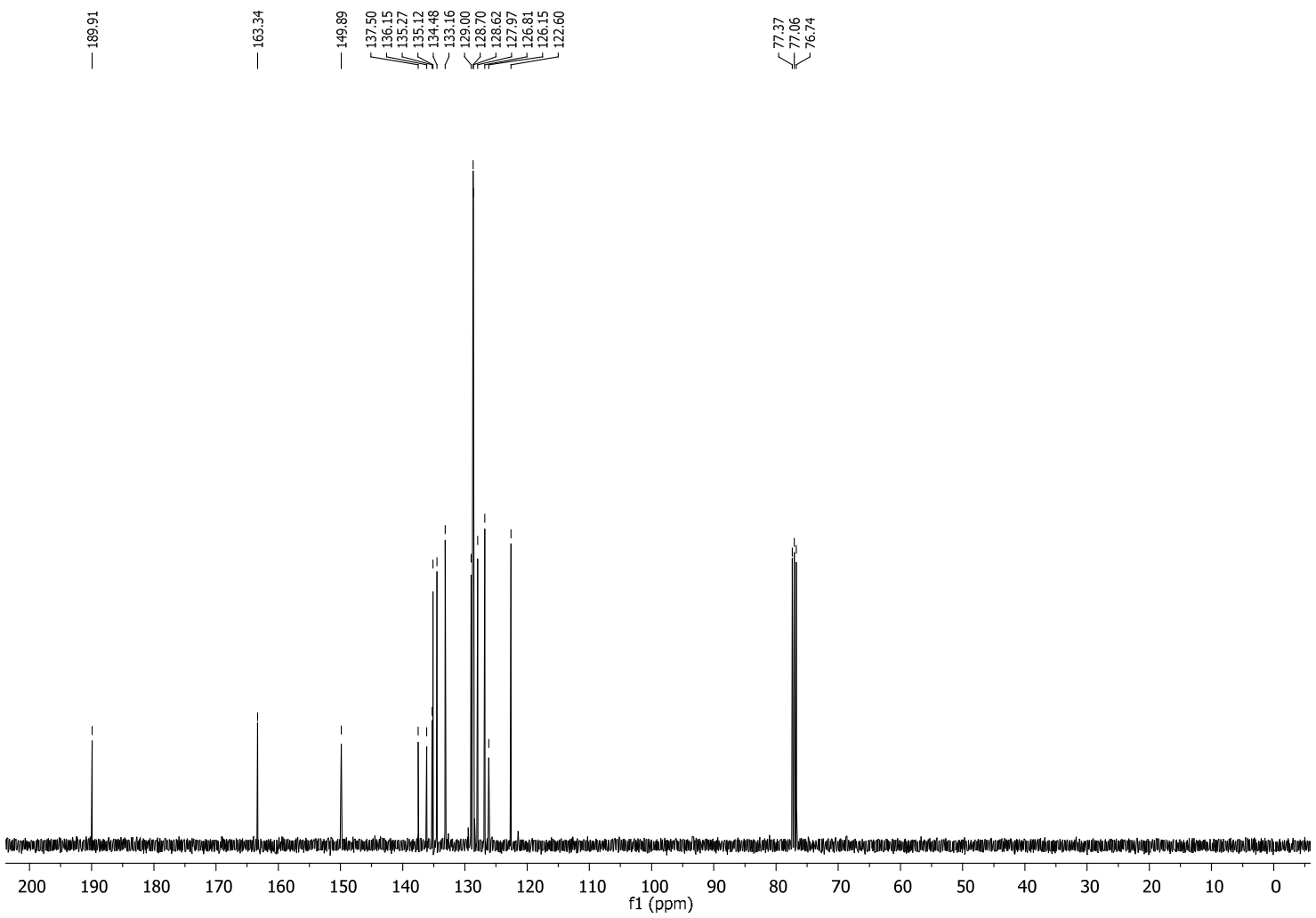
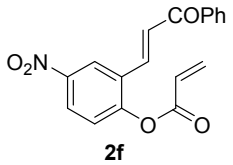


^{13}C NMR, $CDCl_3$, 126 MHz



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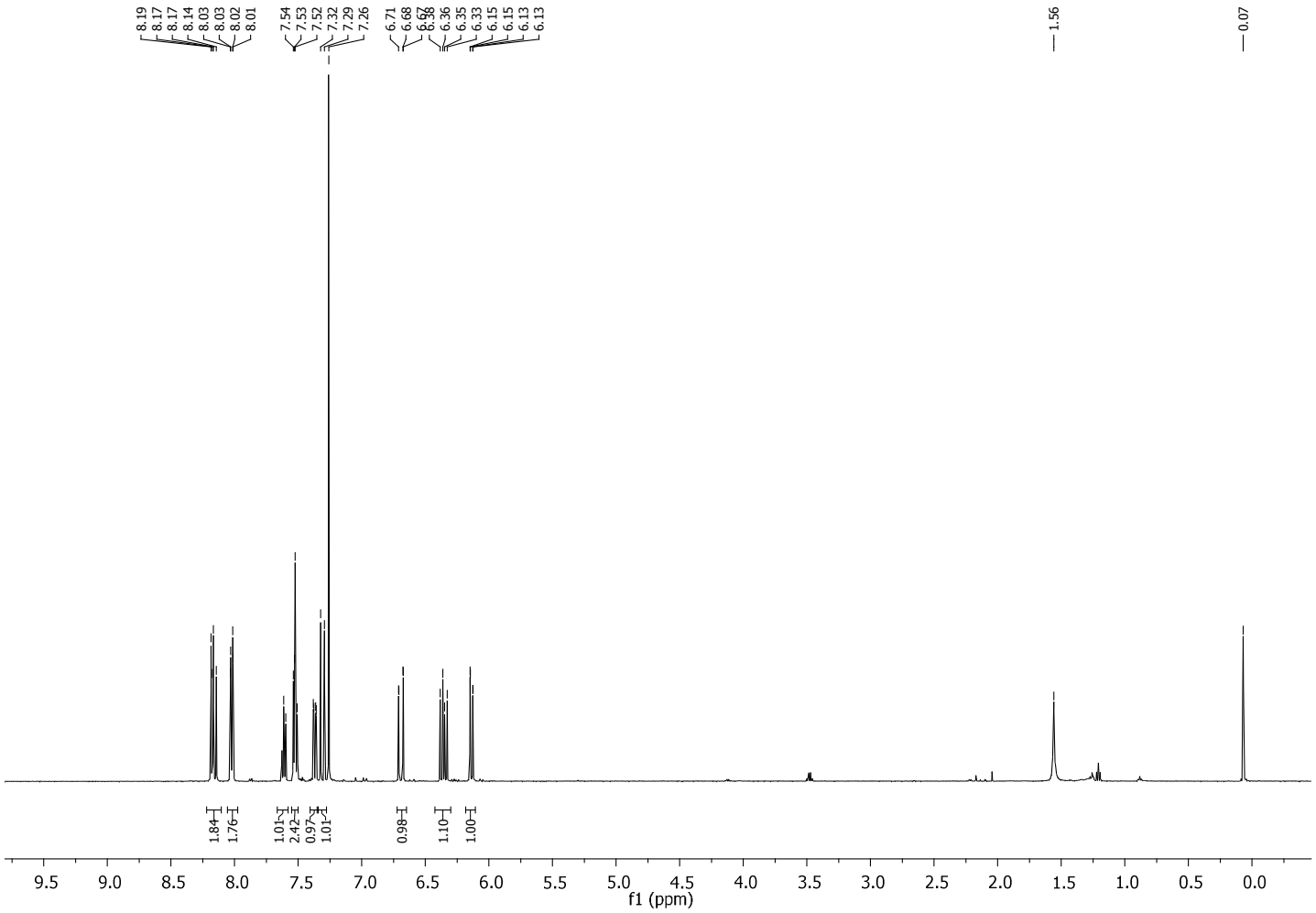
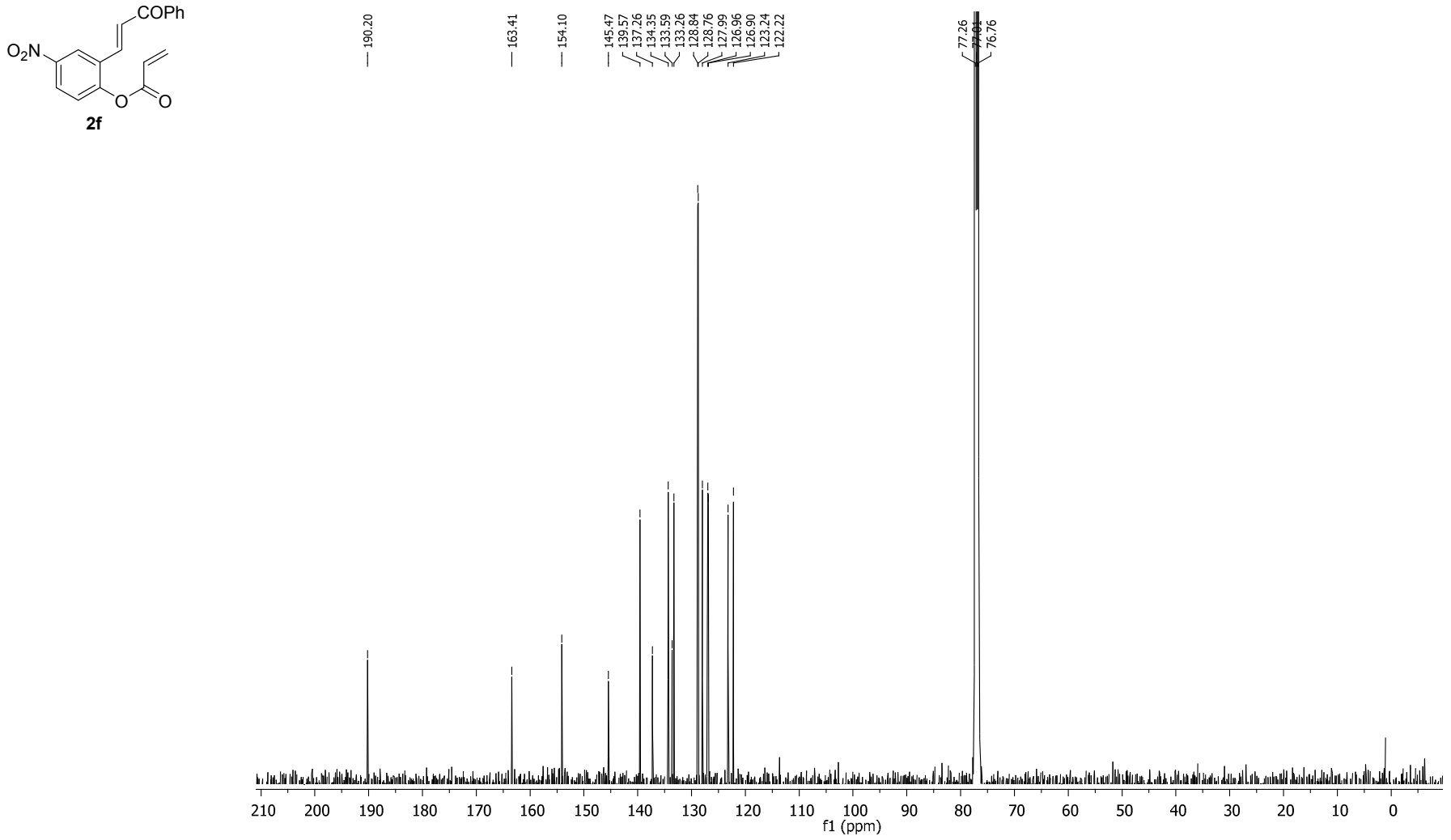
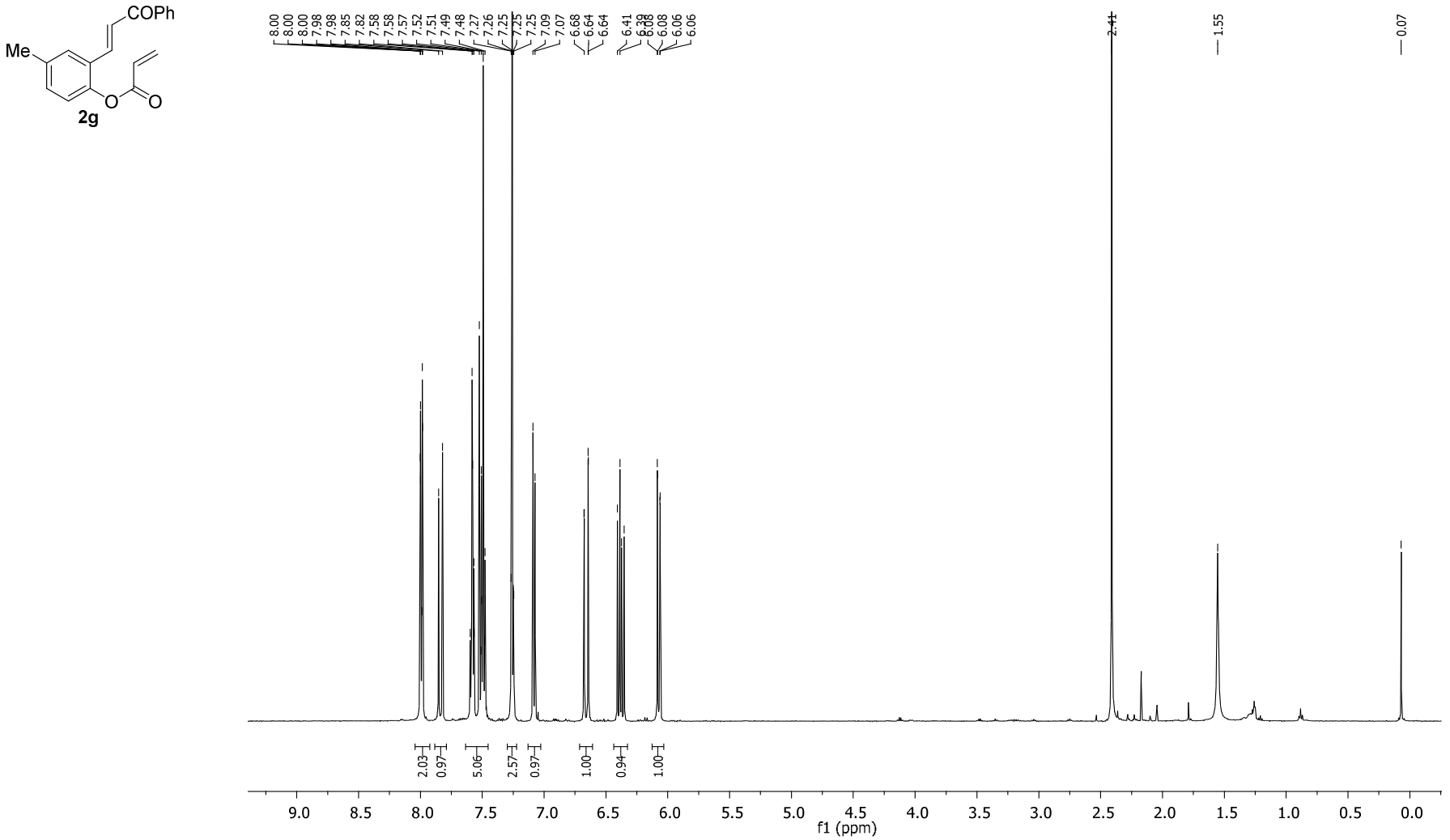


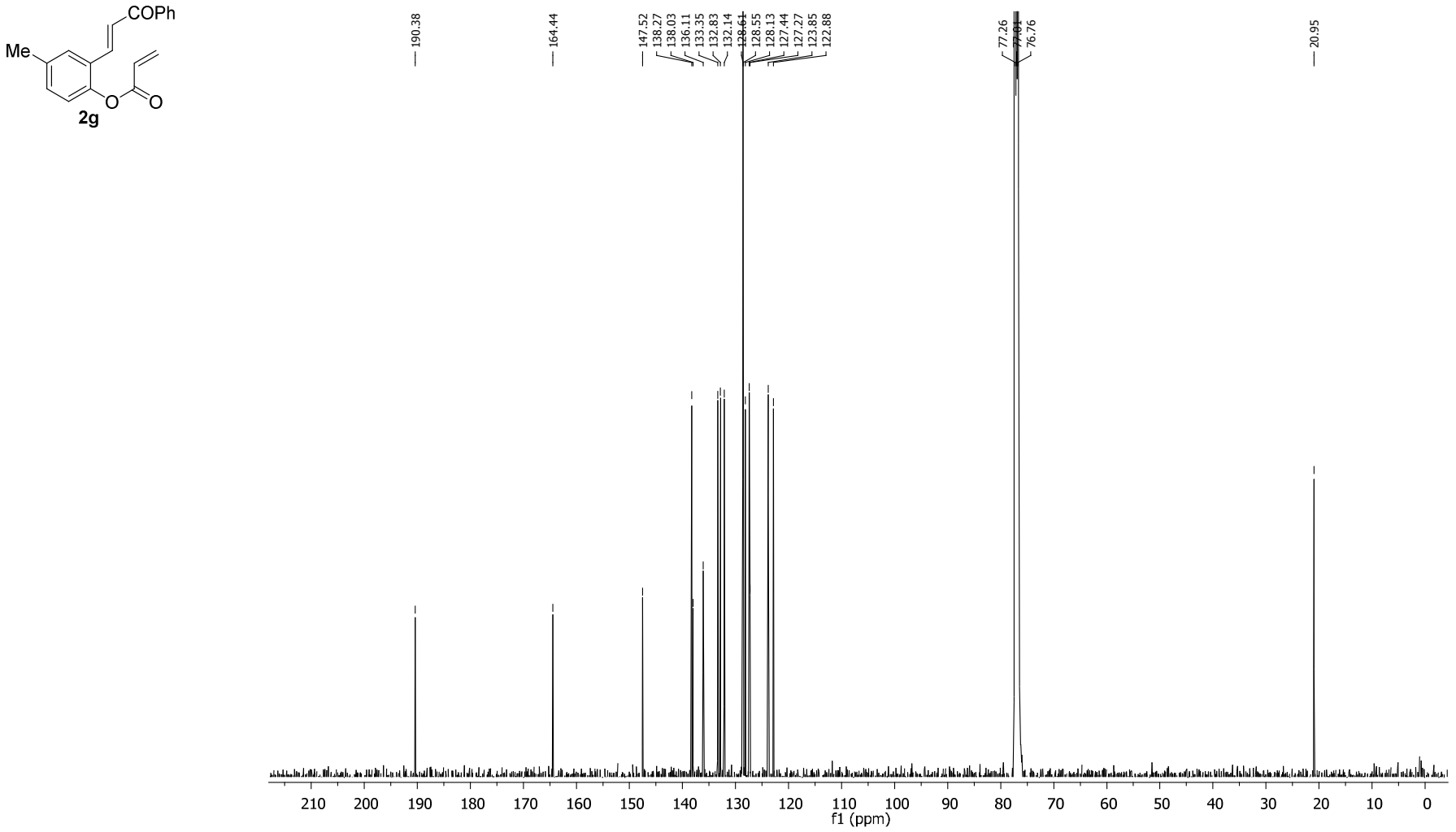
^{1}H NMR, $CDCl_3$, 500 MHz



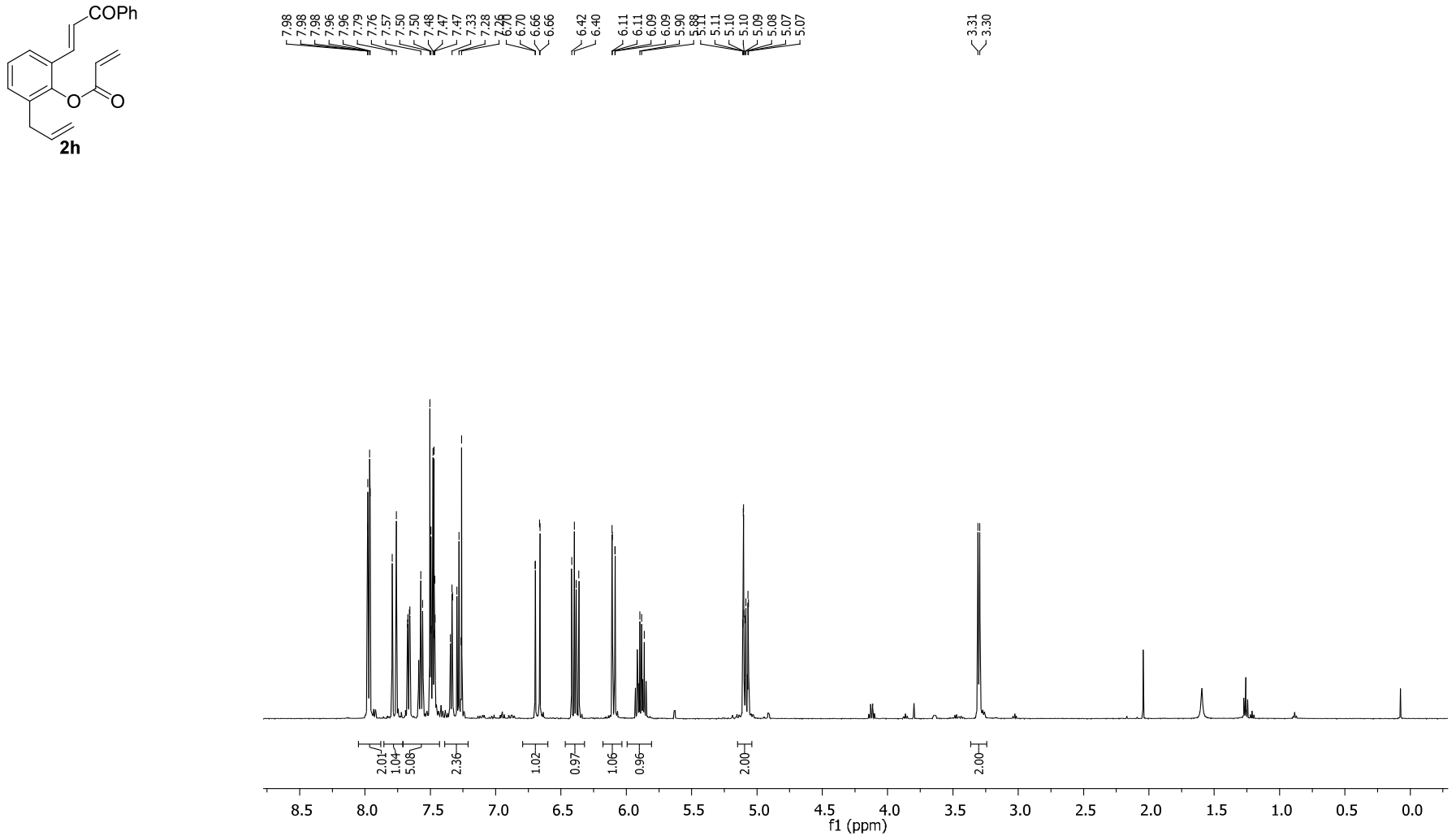
^{13}C NMR, $CDCl_3$, 126 MHz



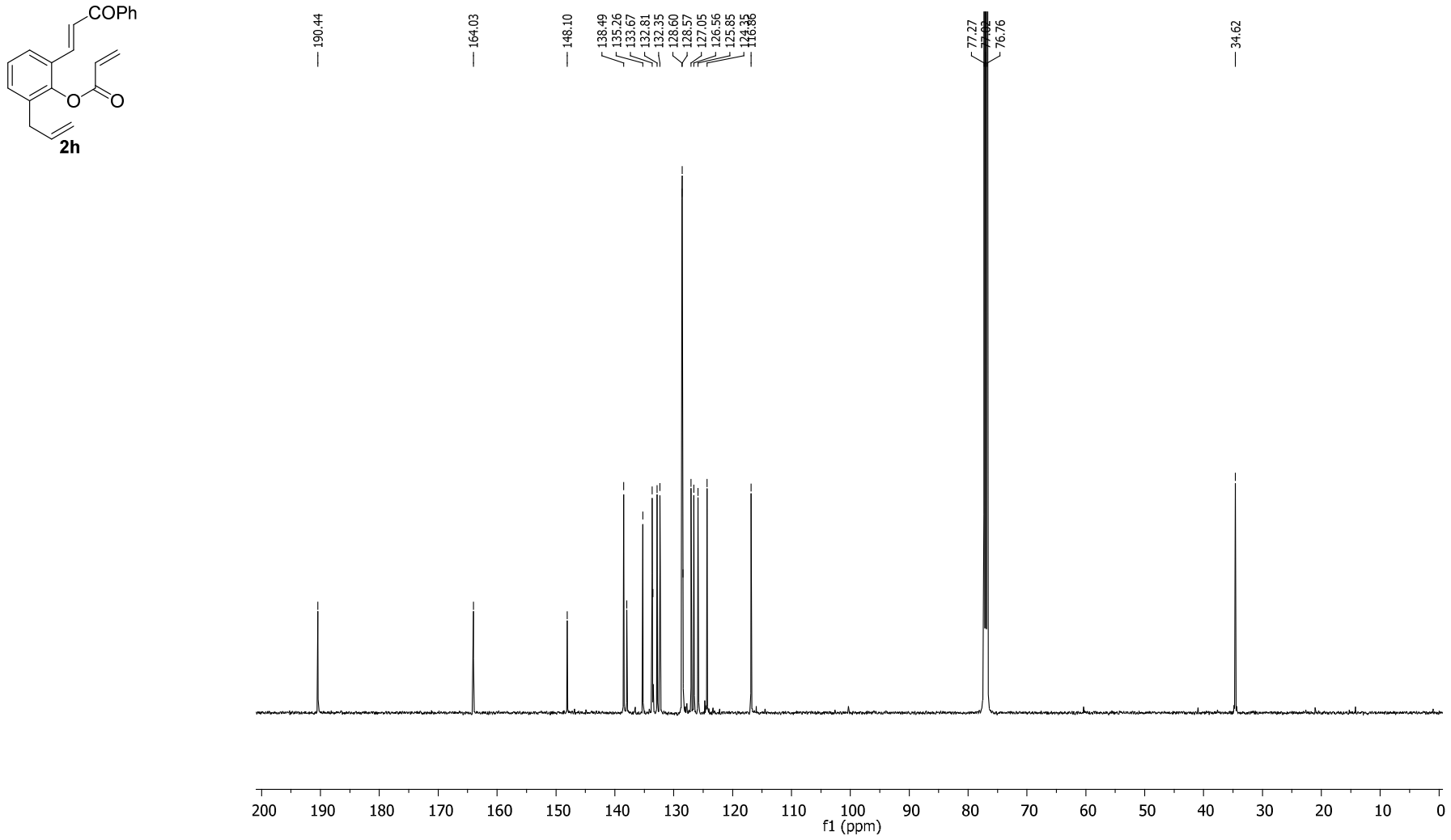
^{1}H NMR, $CDCl_3$, 500 MHz



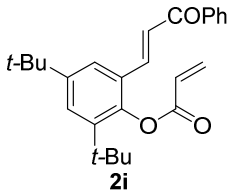
^{13}C NMR, $CDCl_3$, 126 MHz



^{1}H NMR, $CDCl_3$, 500 MHz



^{13}C NMR, $CDCl_3$, 126 MHz



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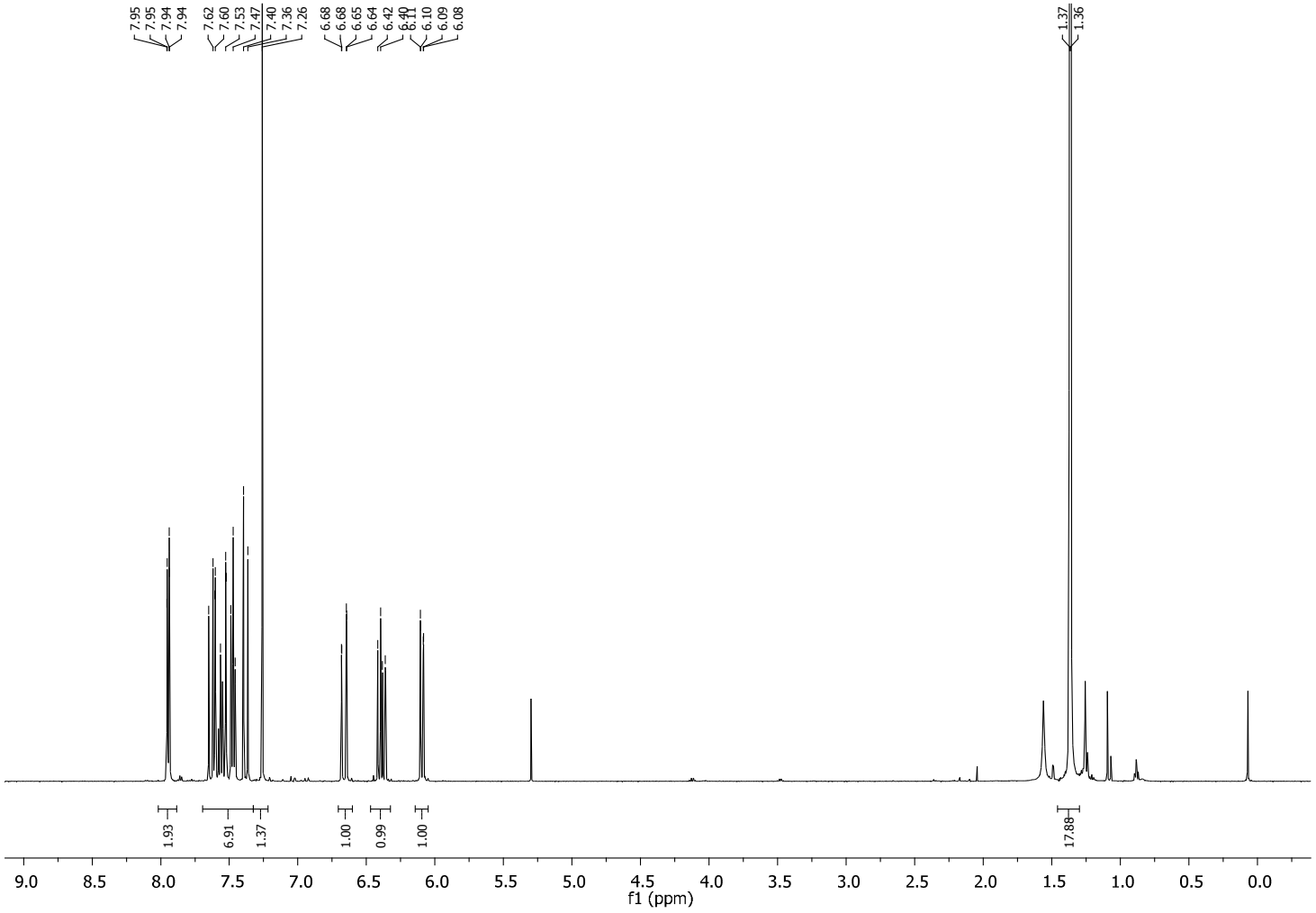
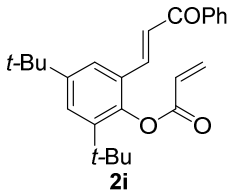


^{1}H NMR, $CDCl_3$, 500 MHz



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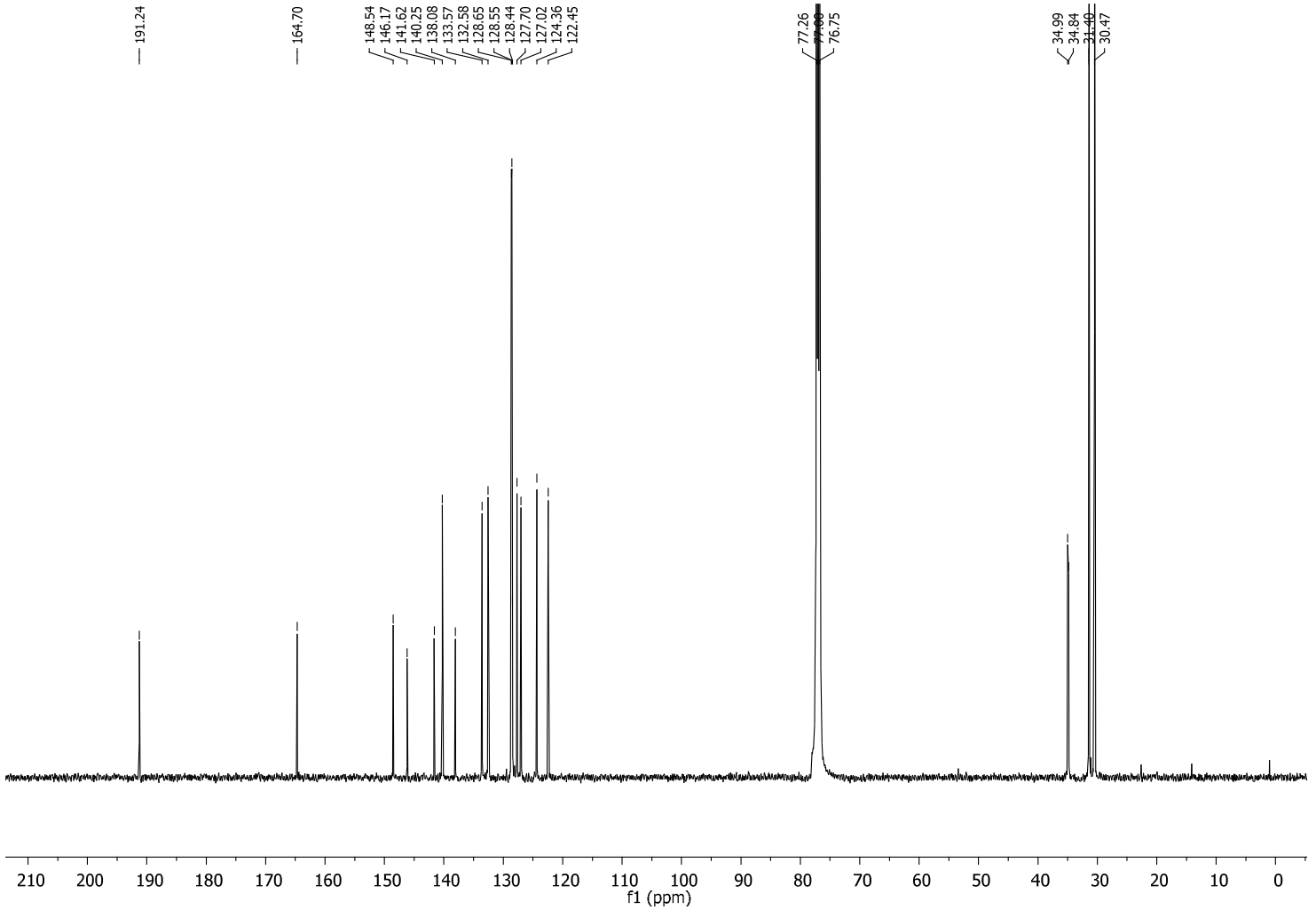
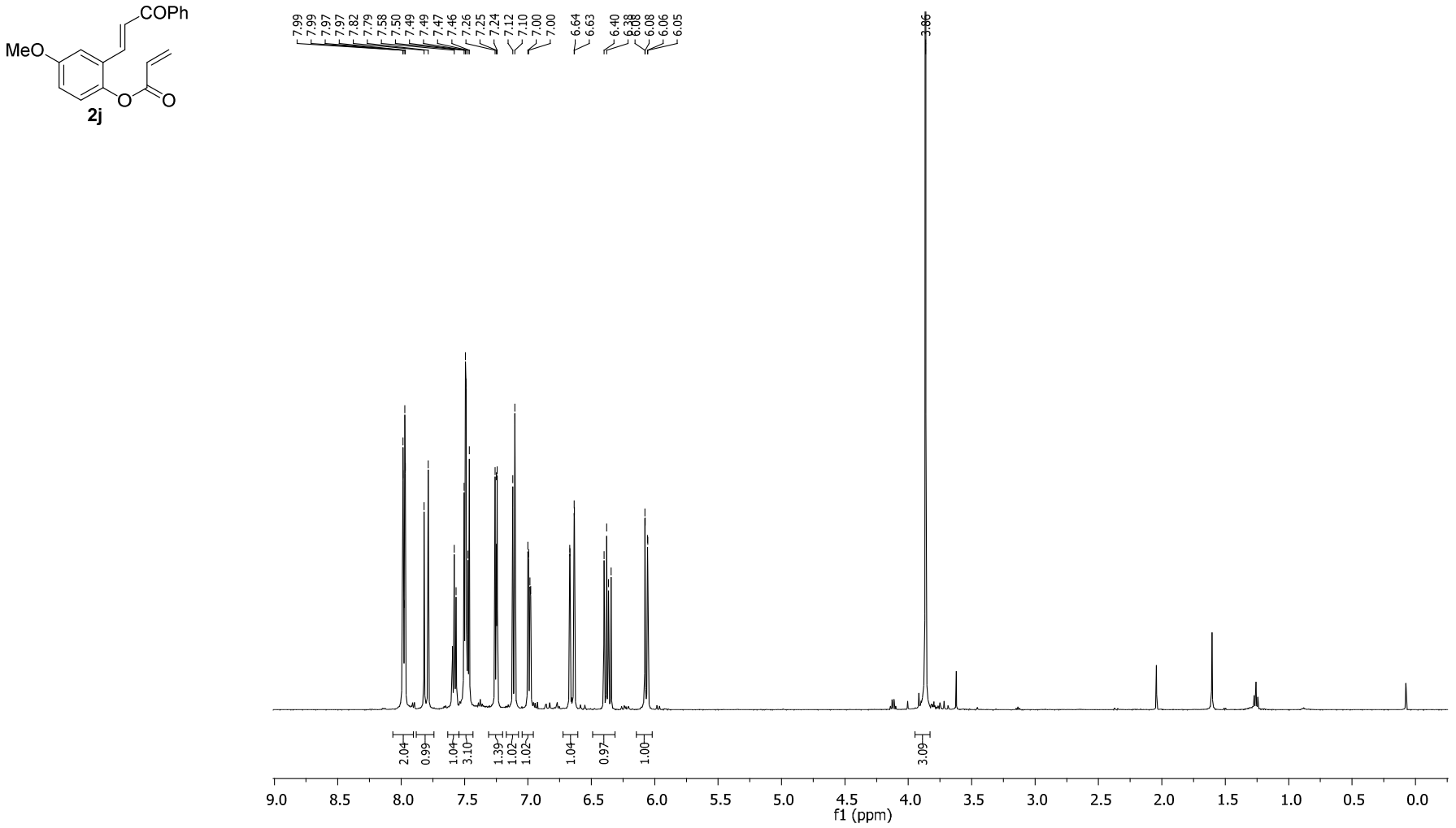
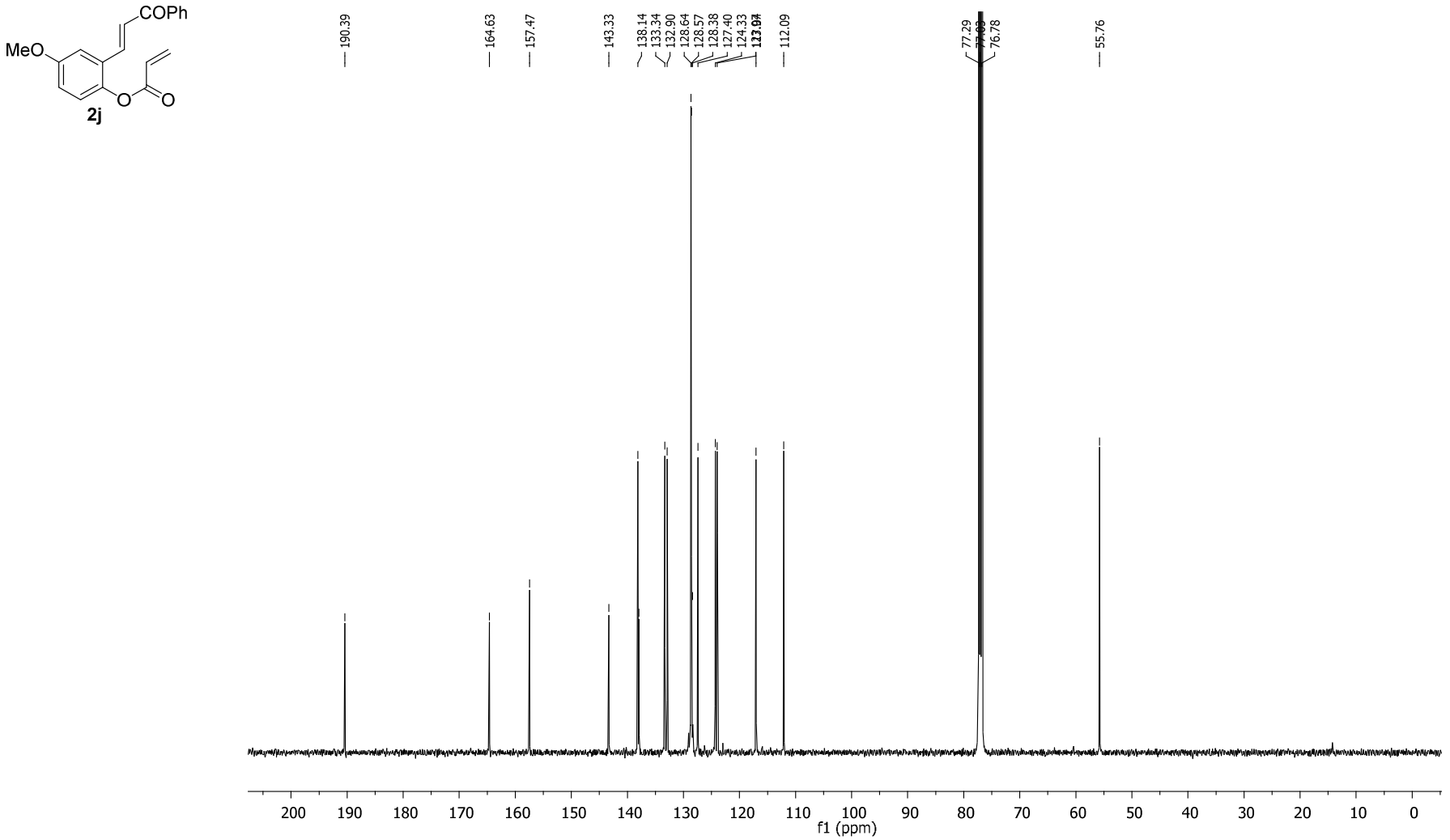


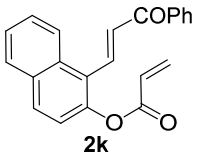
^{13}C NMR, $CDCl_3$, 126 MHz



^{1}H NMR, $CDCl_3$, 400 MHz



^{13}C NMR, $CDCl_3$, 101 MHz



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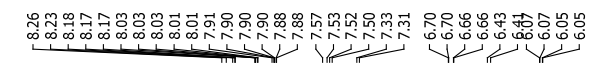
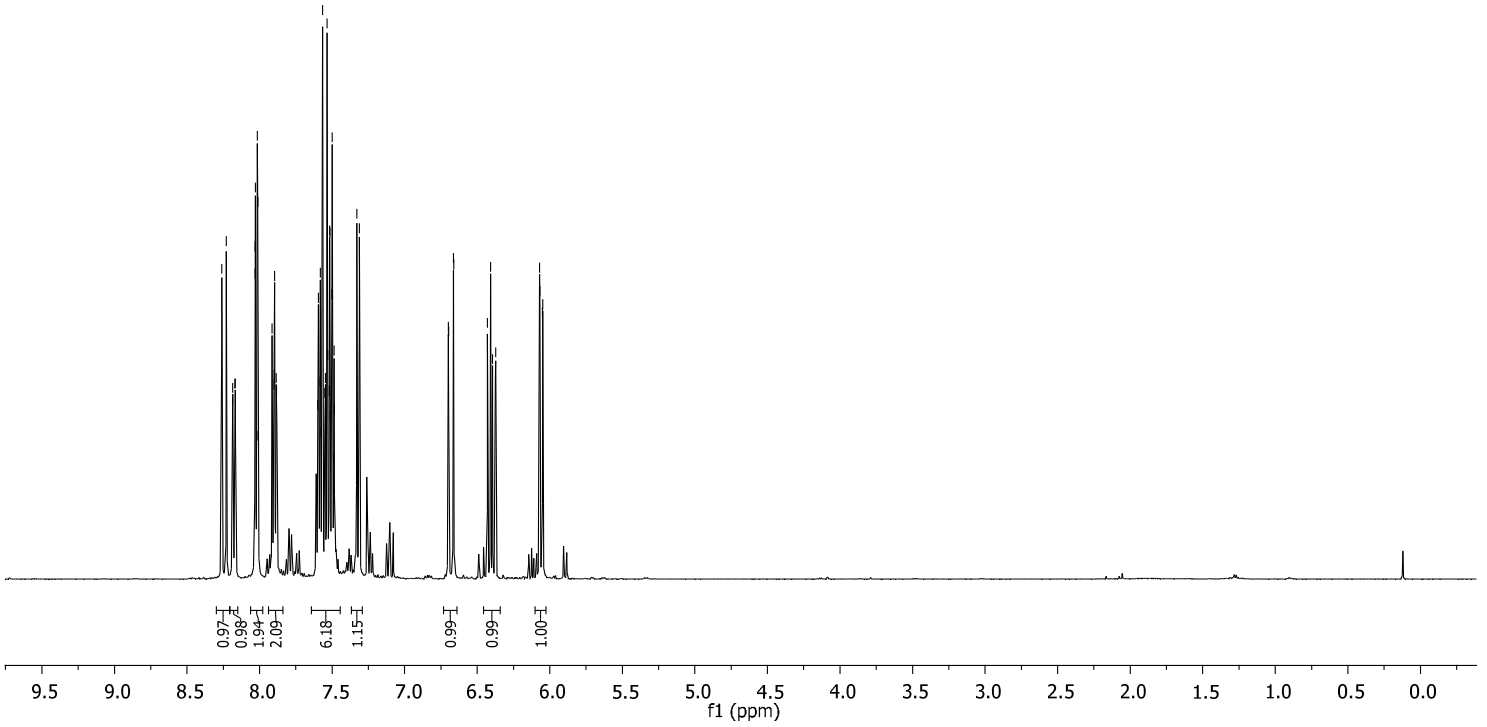
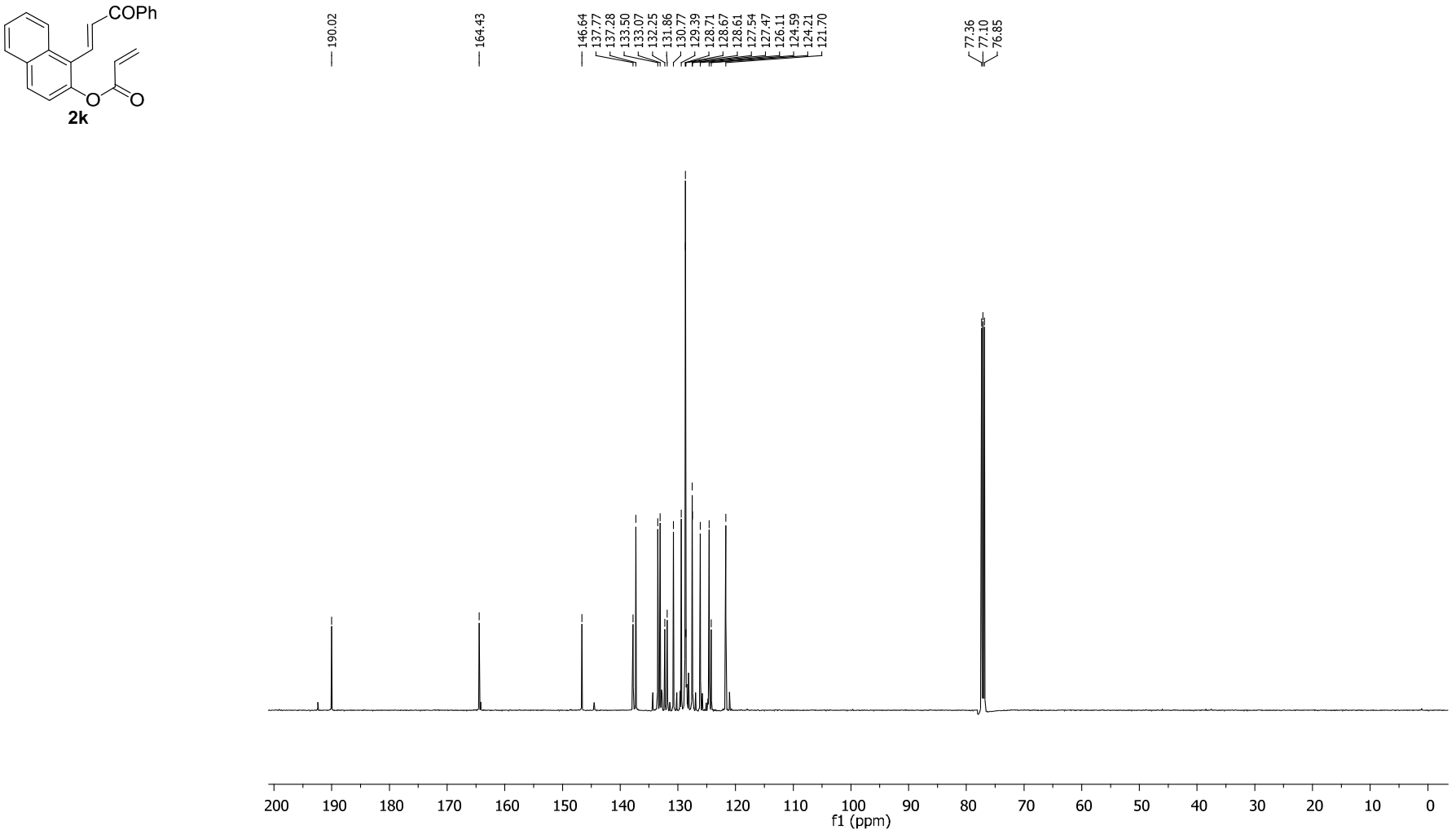


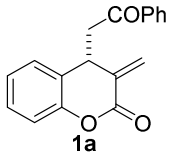


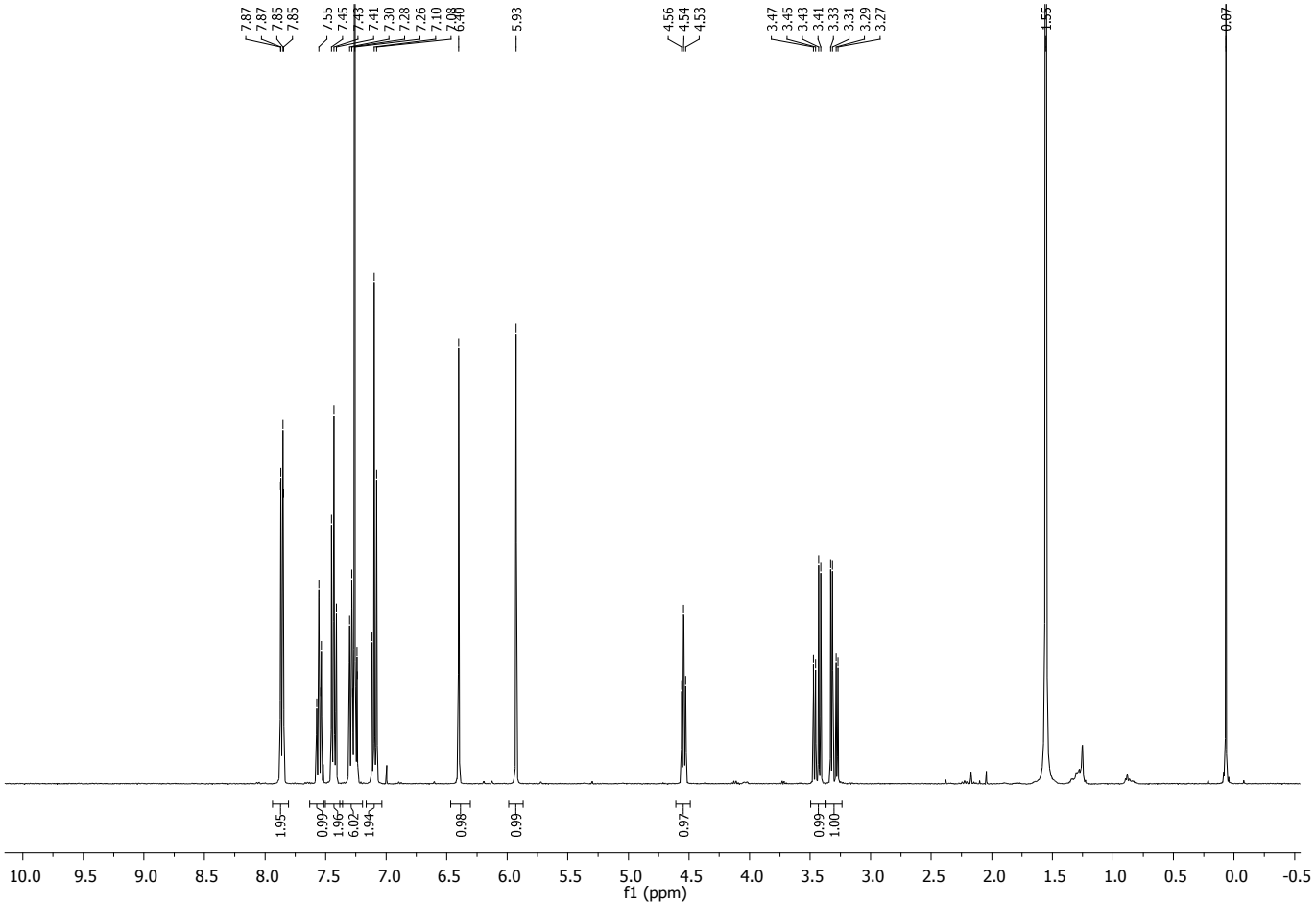
^{1}H NMR, $CDCl_3$, 400 MHz



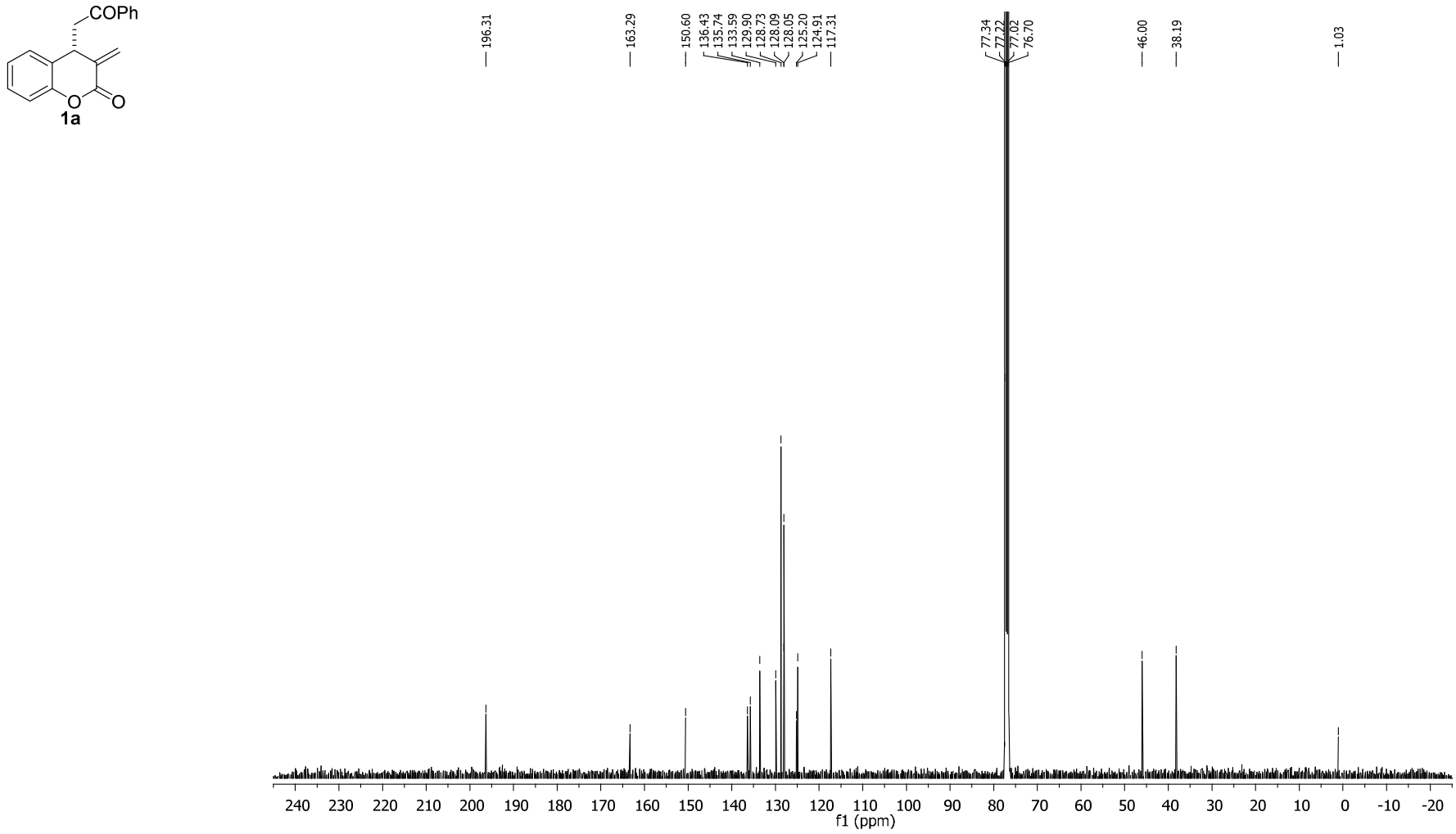
^{13}C NMR, $CDCl_3$, 101 MHz

6.2 Chromanones **1**

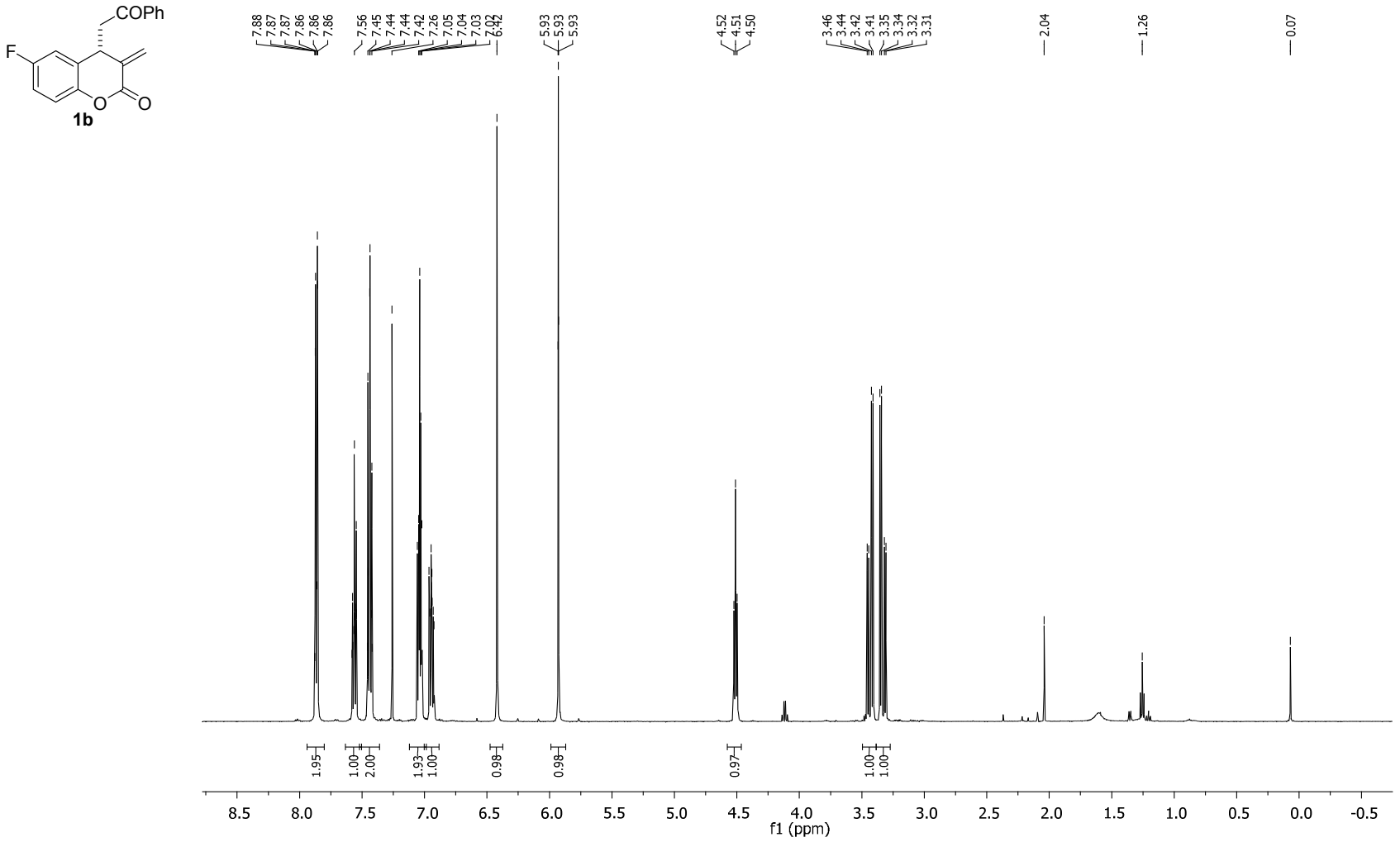




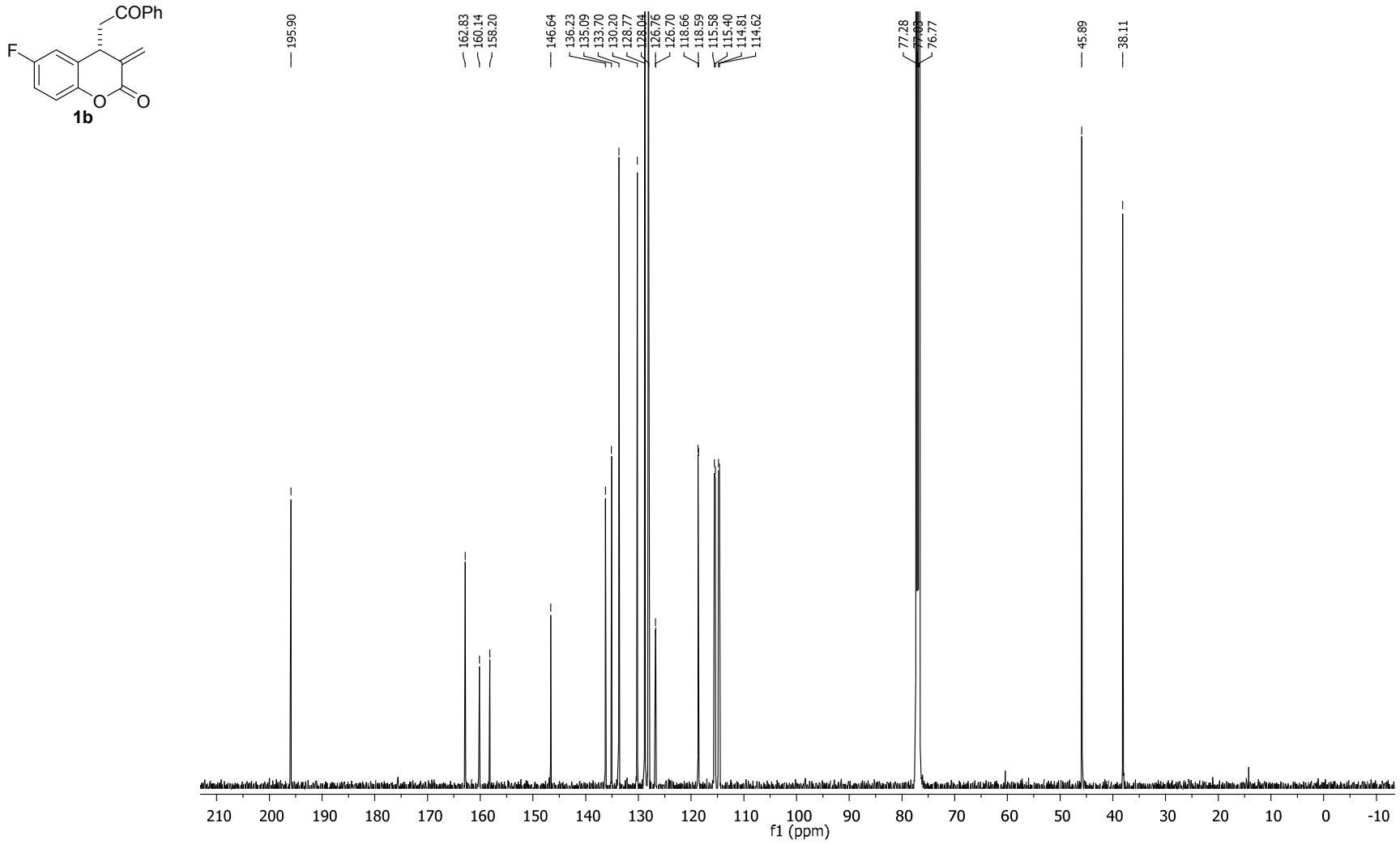
^{1}H NMR, $CDCl_3$, 400 MHz



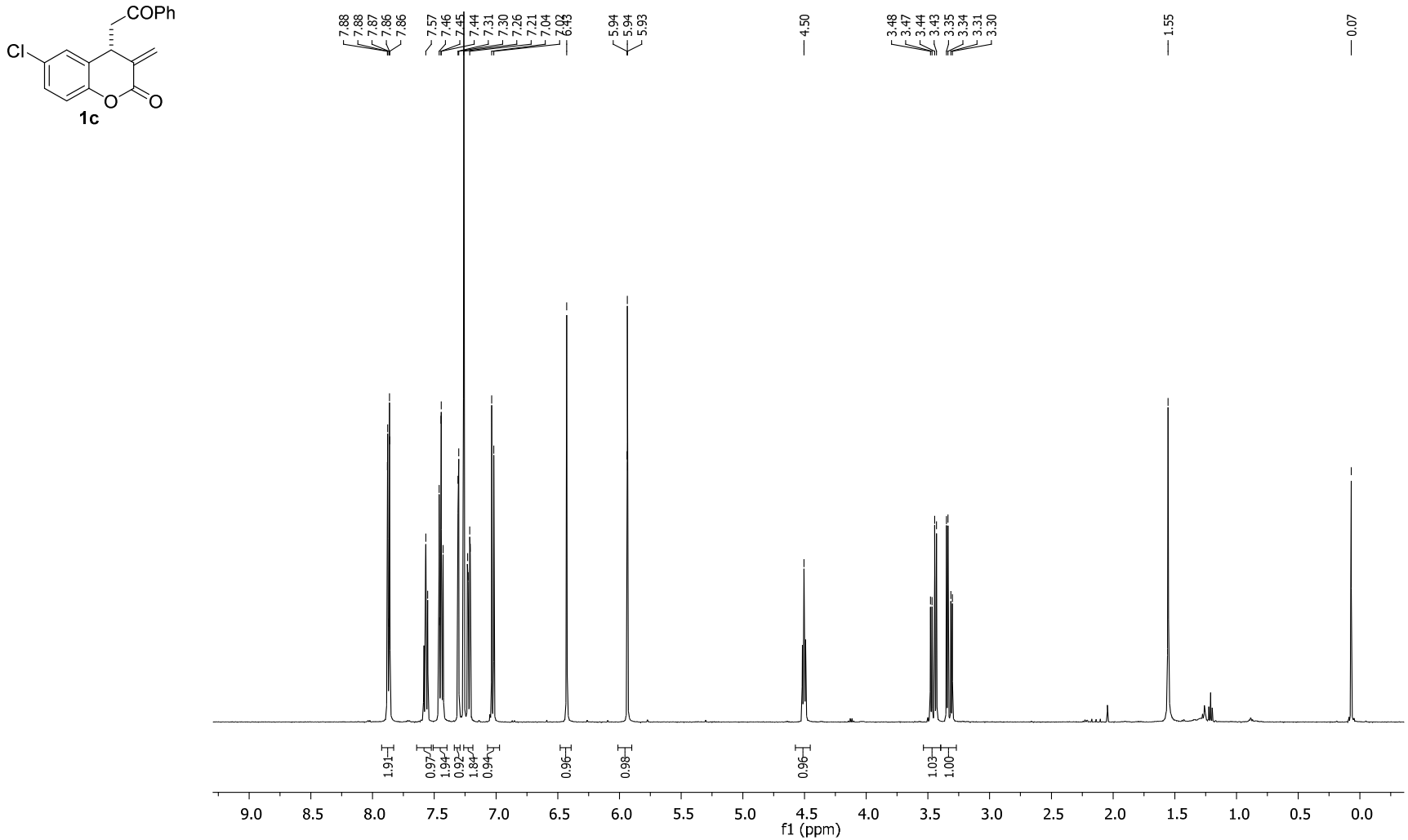
^{13}C NMR, $CDCl_3$, 101 MHz



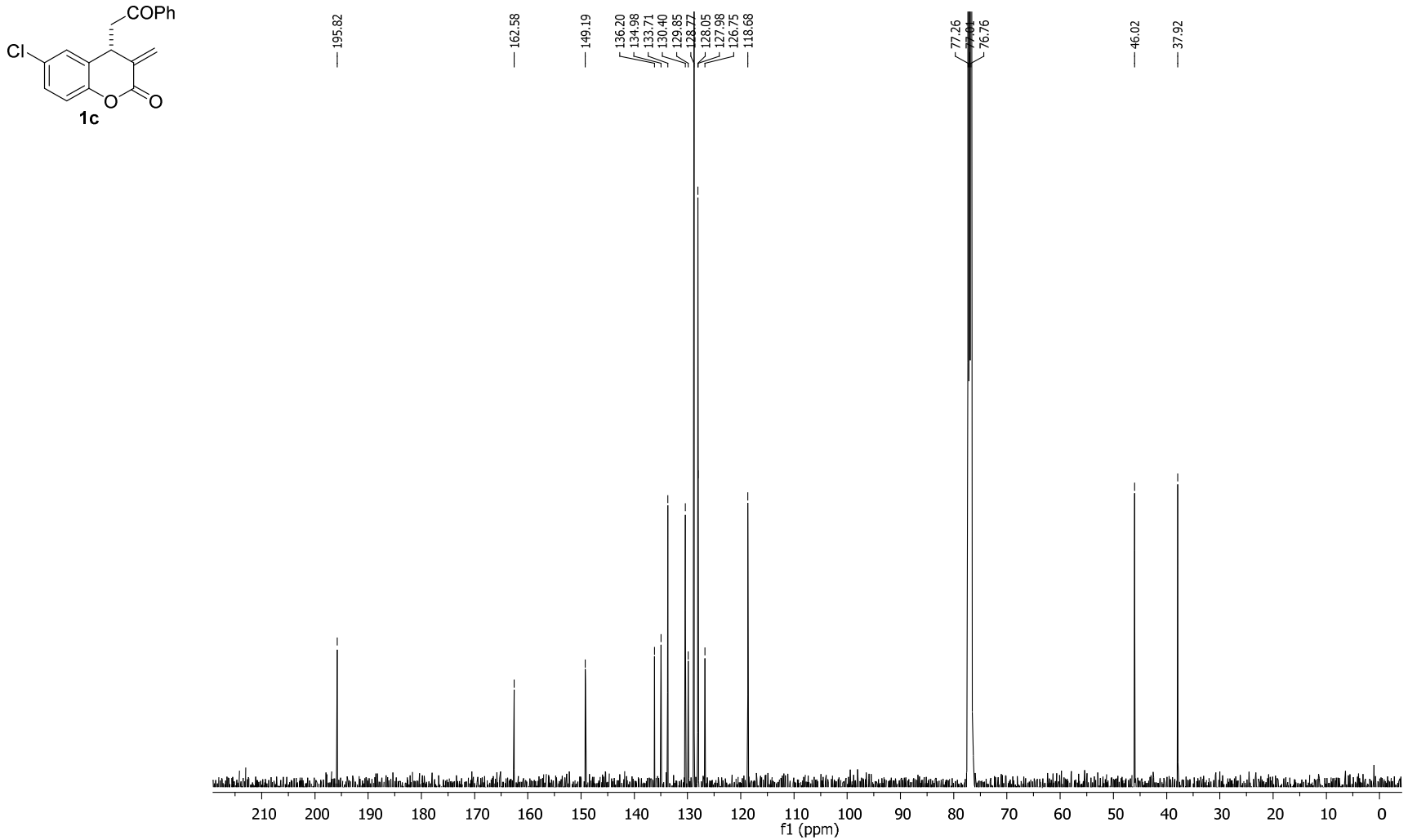
^{1}H NMR, $CDCl_3$, 500 MHz



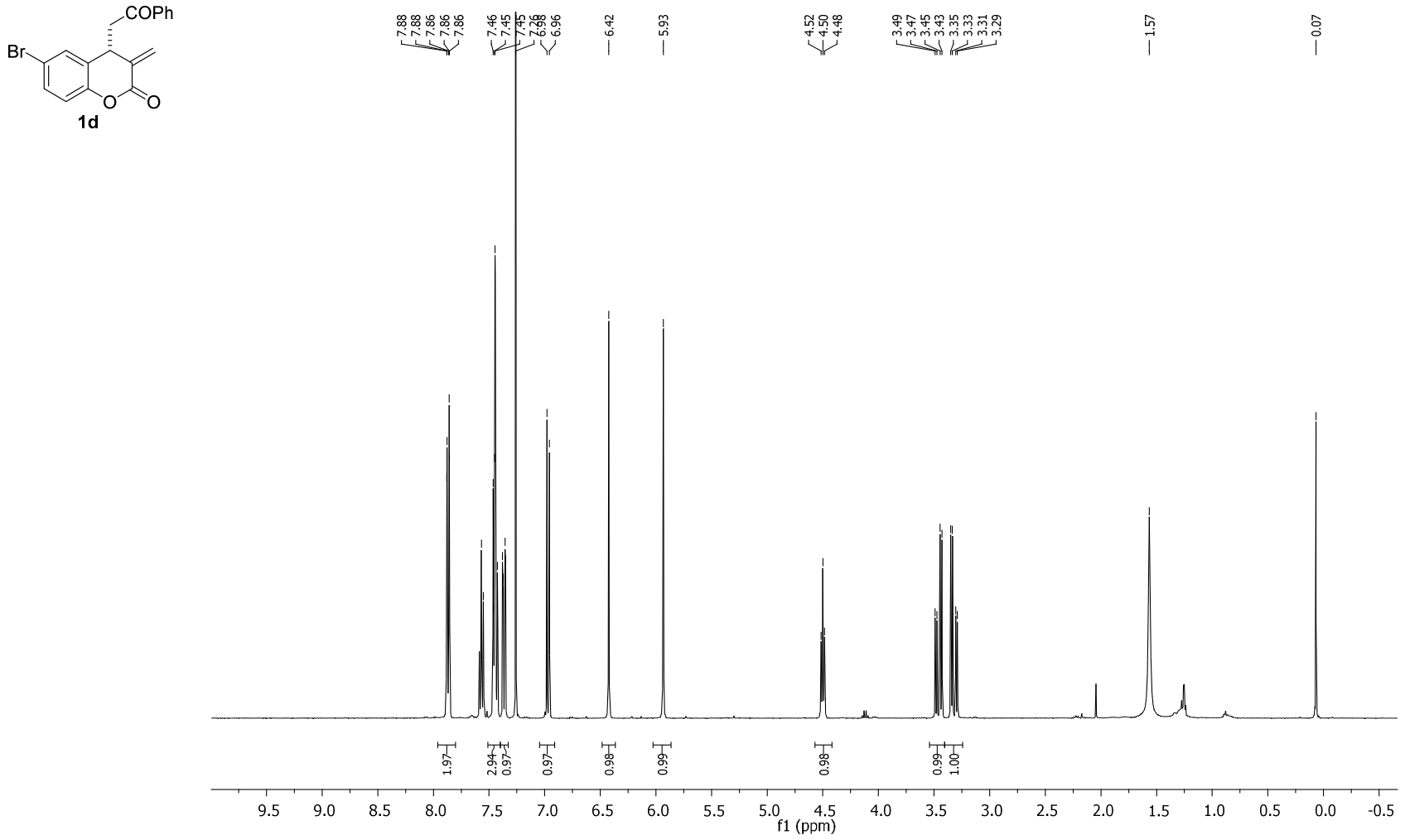
^{13}C NMR, $CDCl_3$, 126 MHz



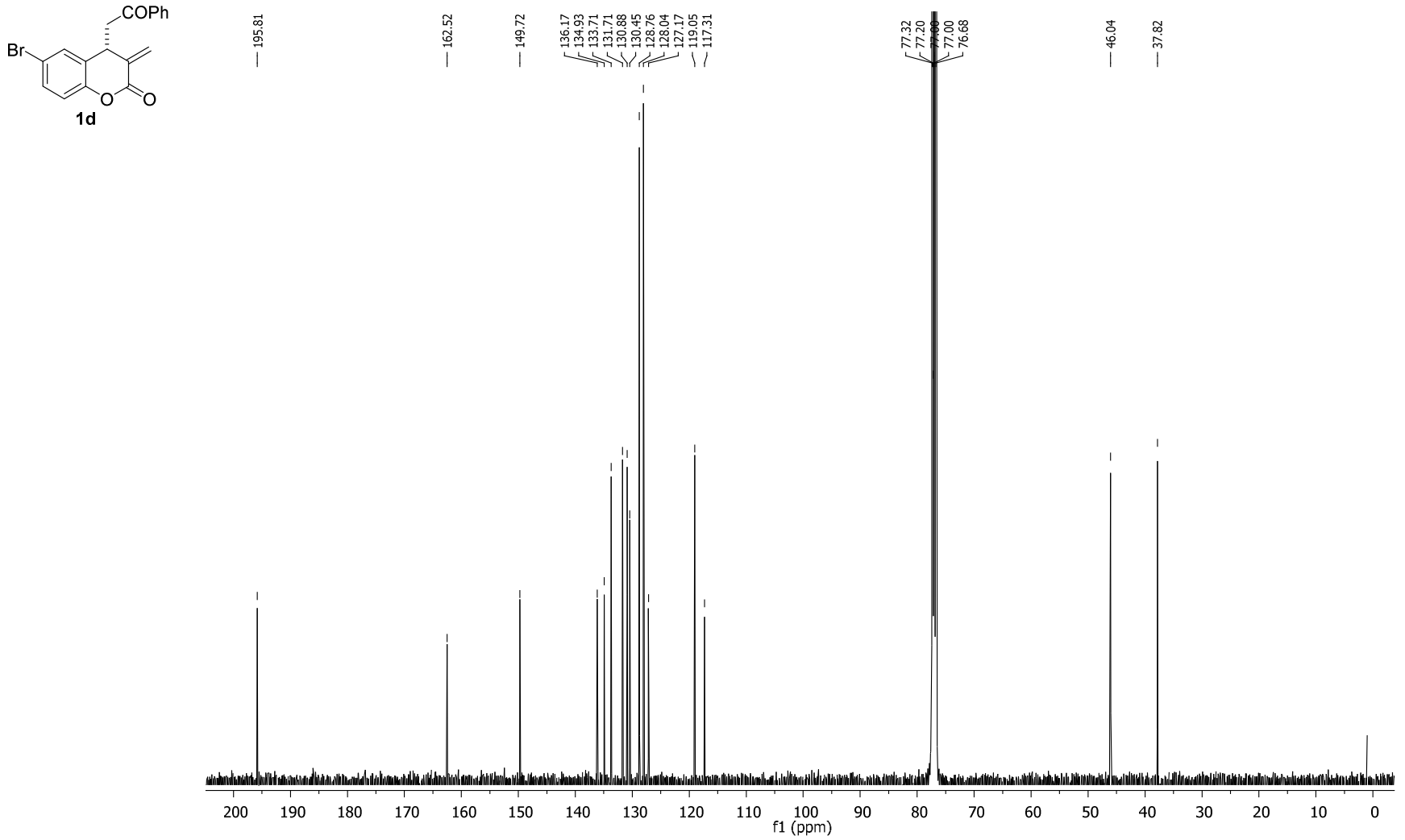
^{1}H NMR, $CDCl_3$, 400 MHz



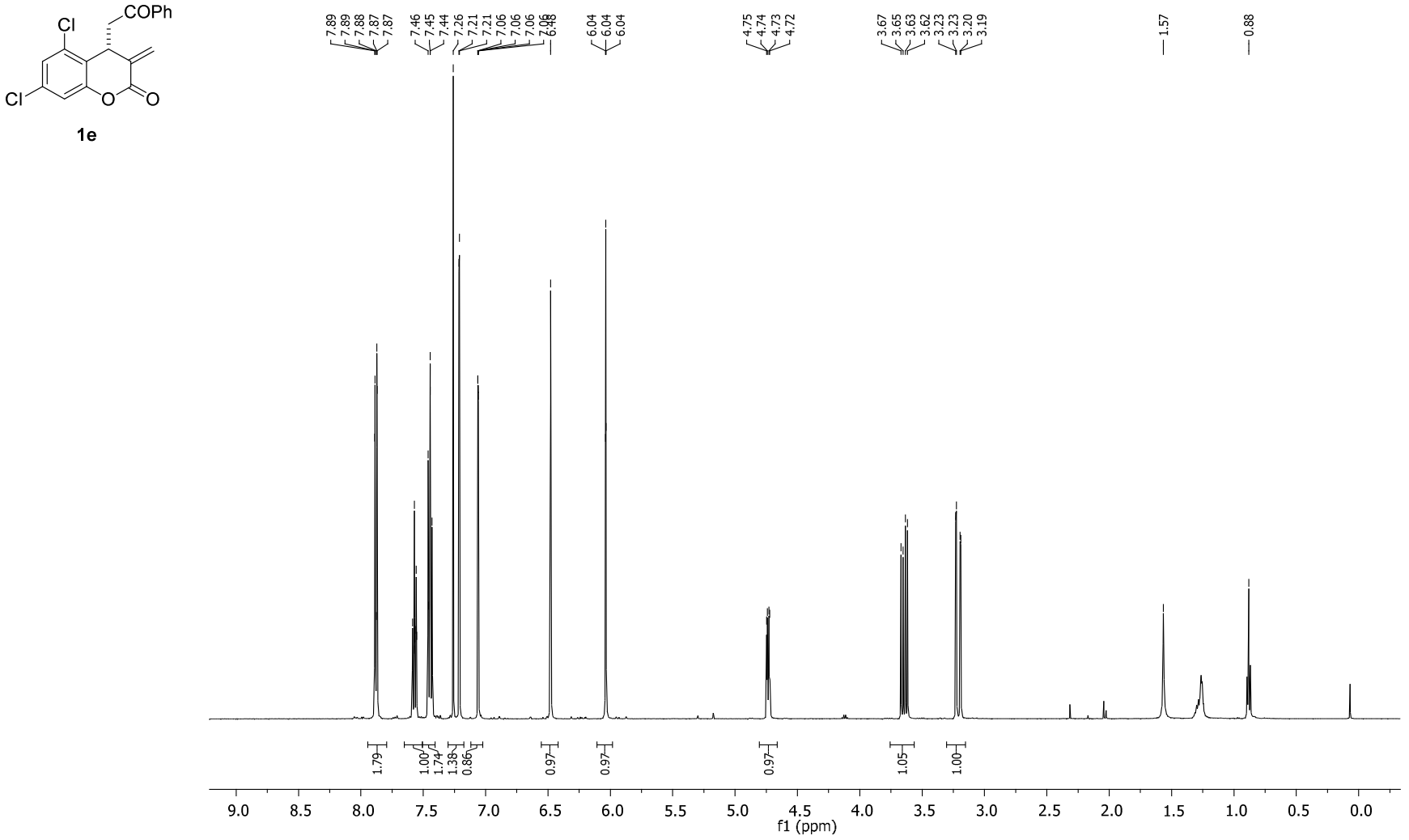
^{13}C NMR, $CDCl_3$, 101 MHz



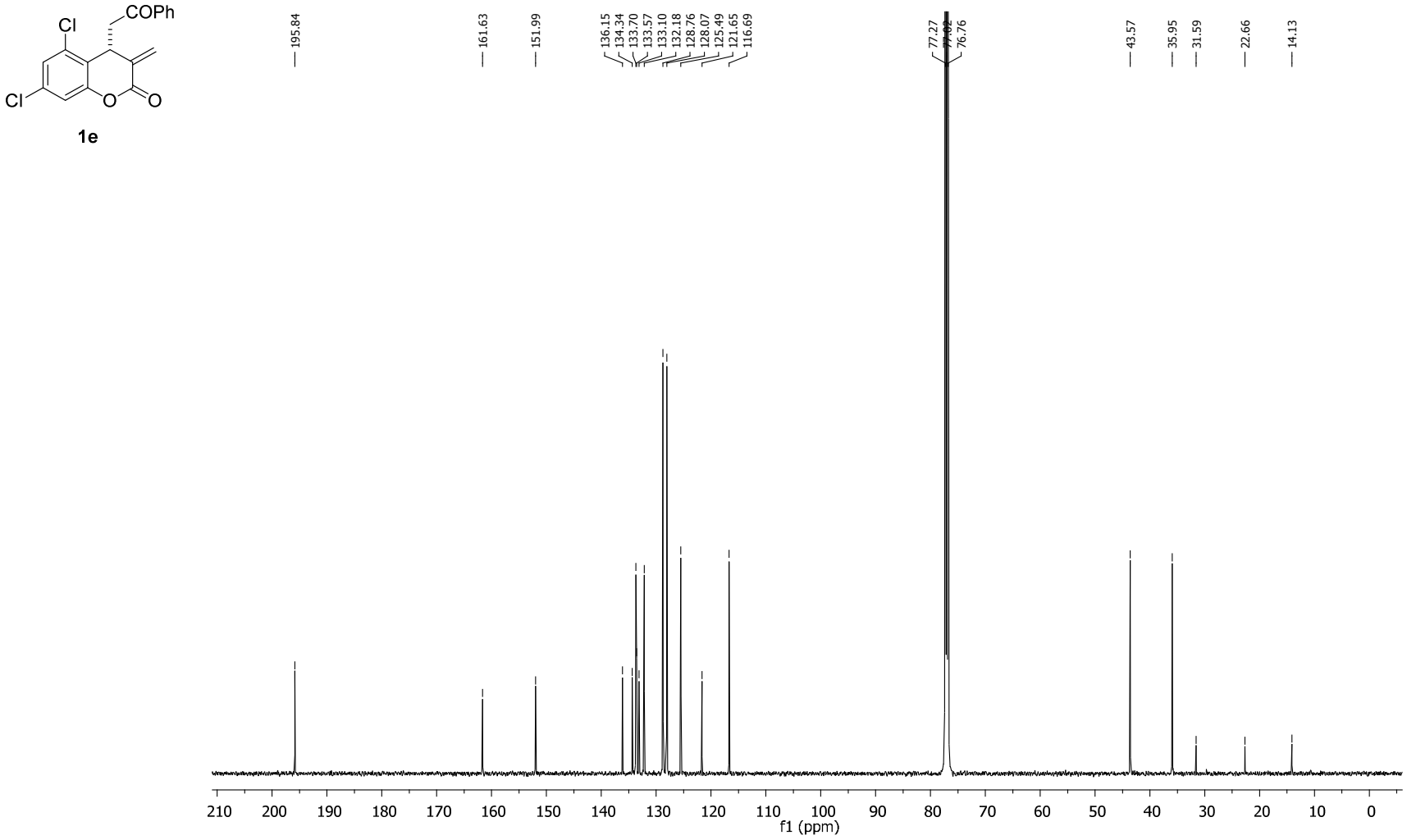
^{1}H NMR, $CDCl_3$, 400 MHz



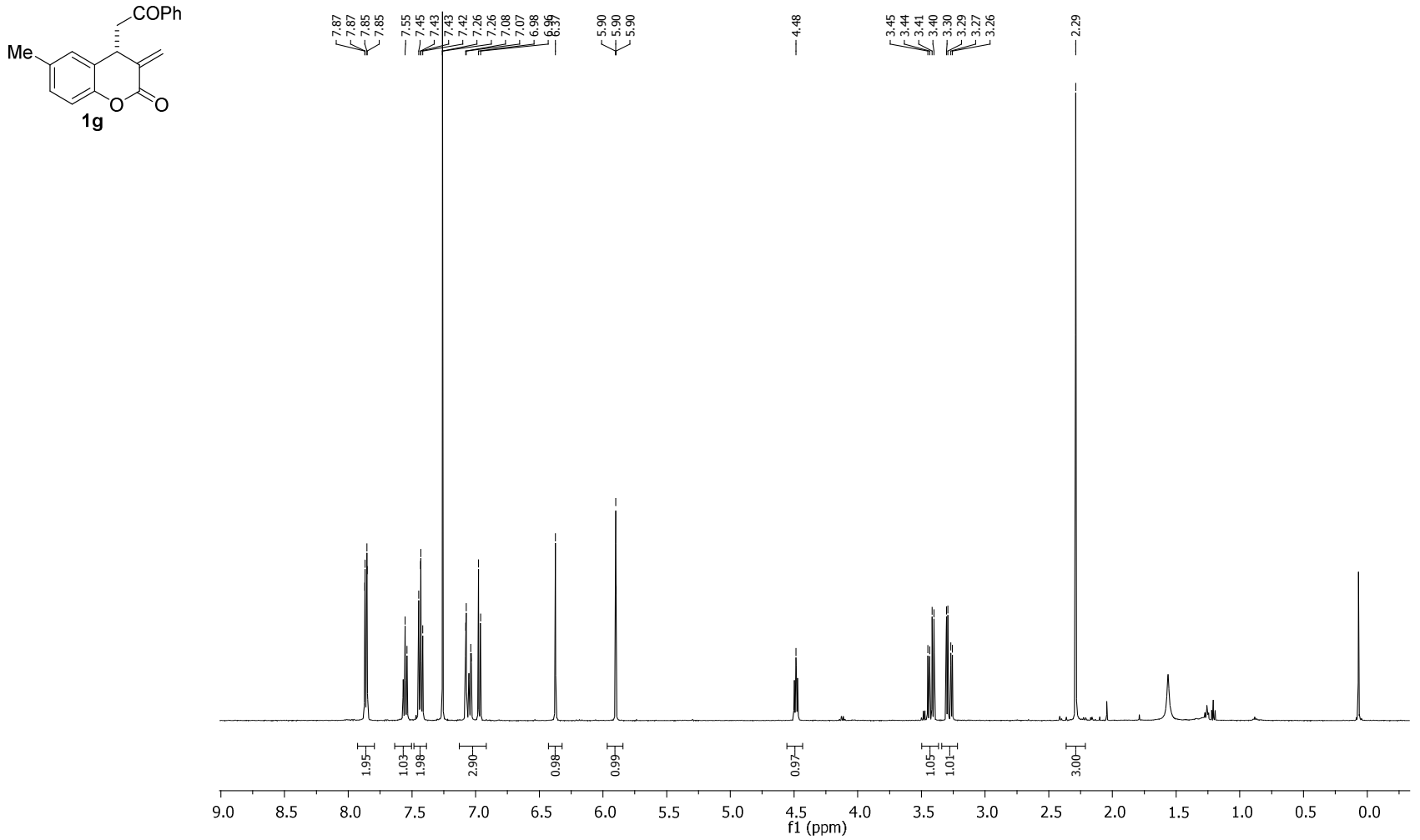
^{13}C NMR, $CDCl_3$, 101 MHz



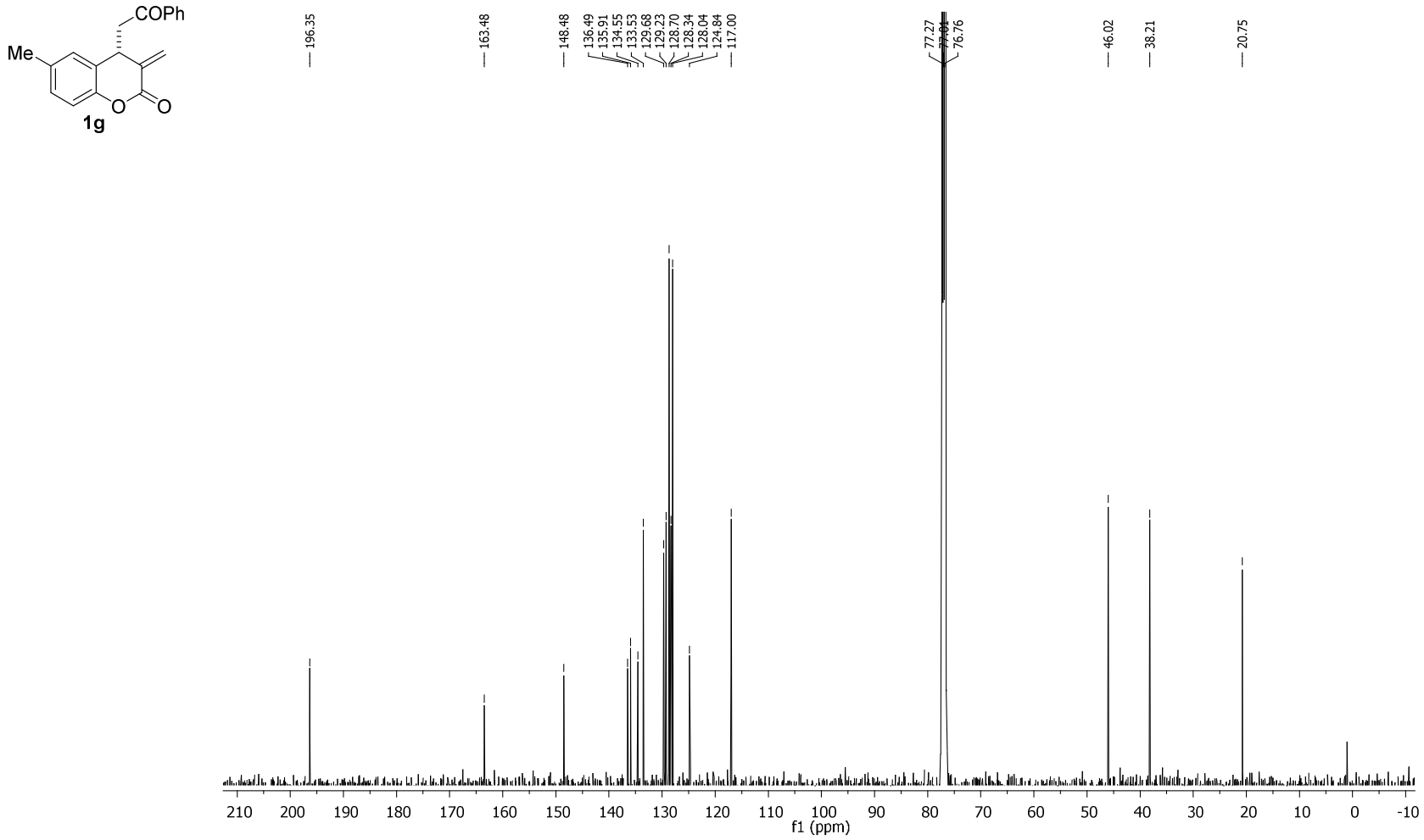
^{1}H NMR, $CDCl_3$, 500 MHz



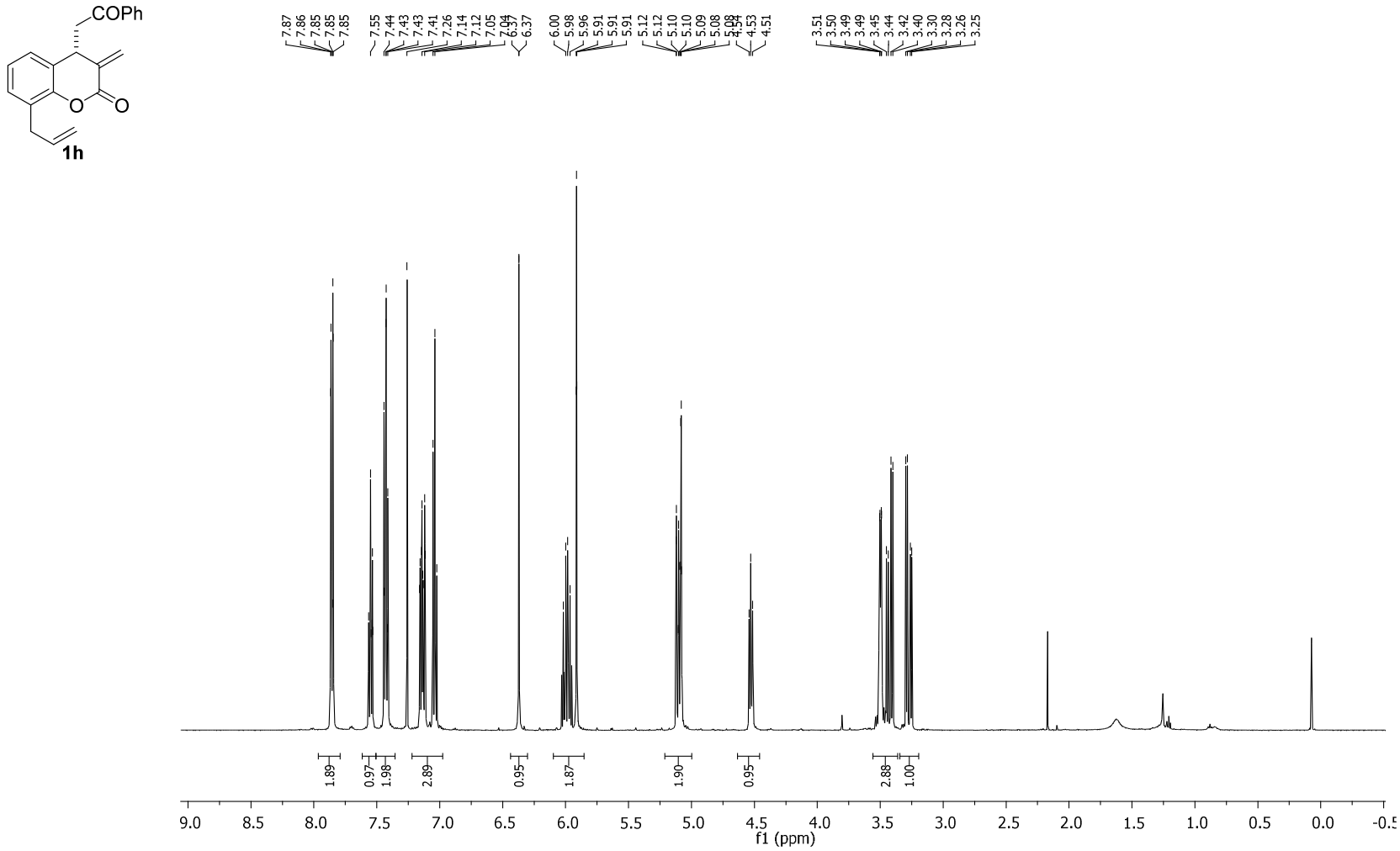
^{13}C NMR, $CDCl_3$, 126 MHz



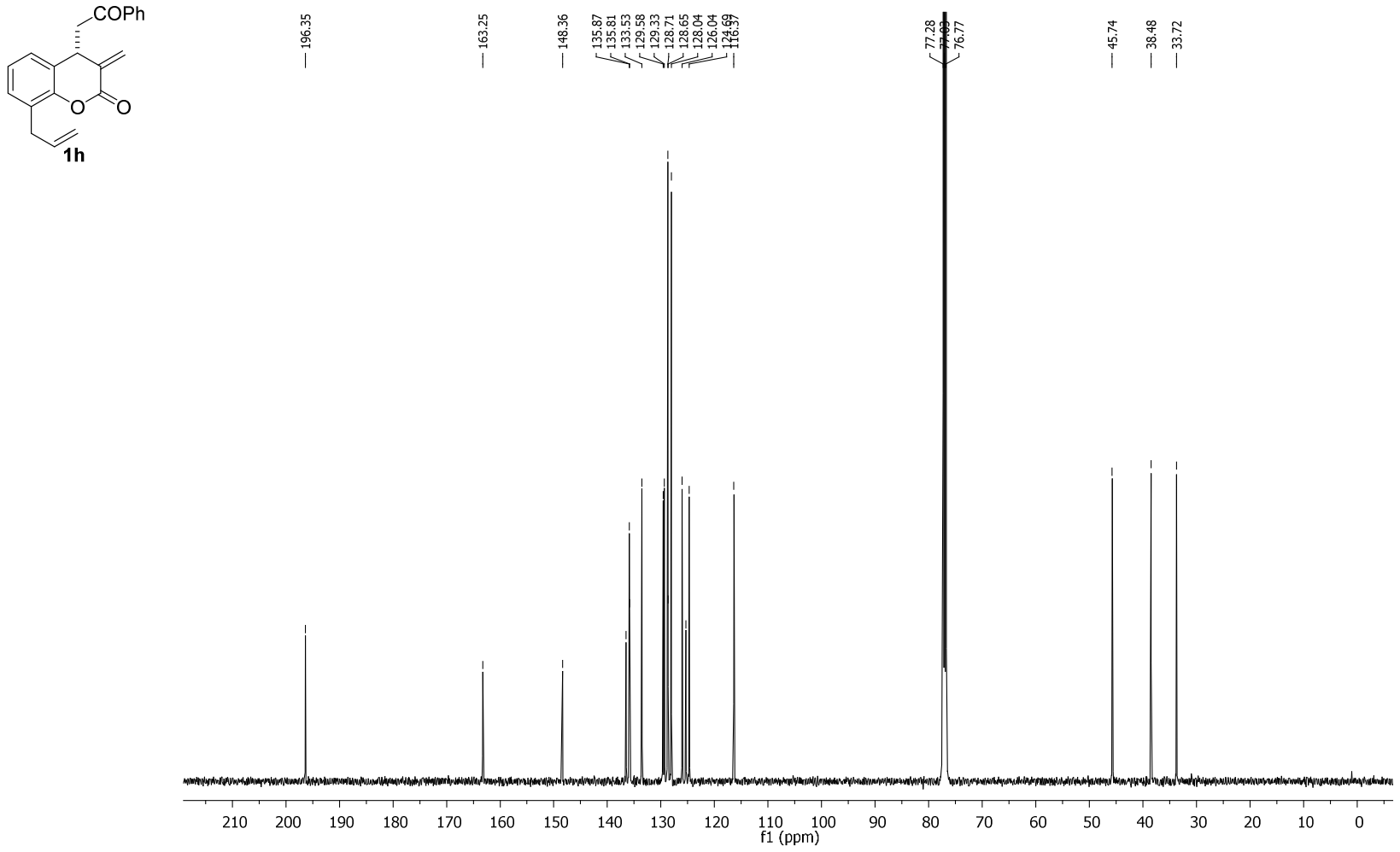
^{1}H NMR, $CDCl_3$, 500 MHz



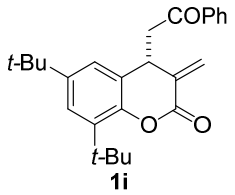
^{13}C NMR, $CDCl_3$, 126 MHz



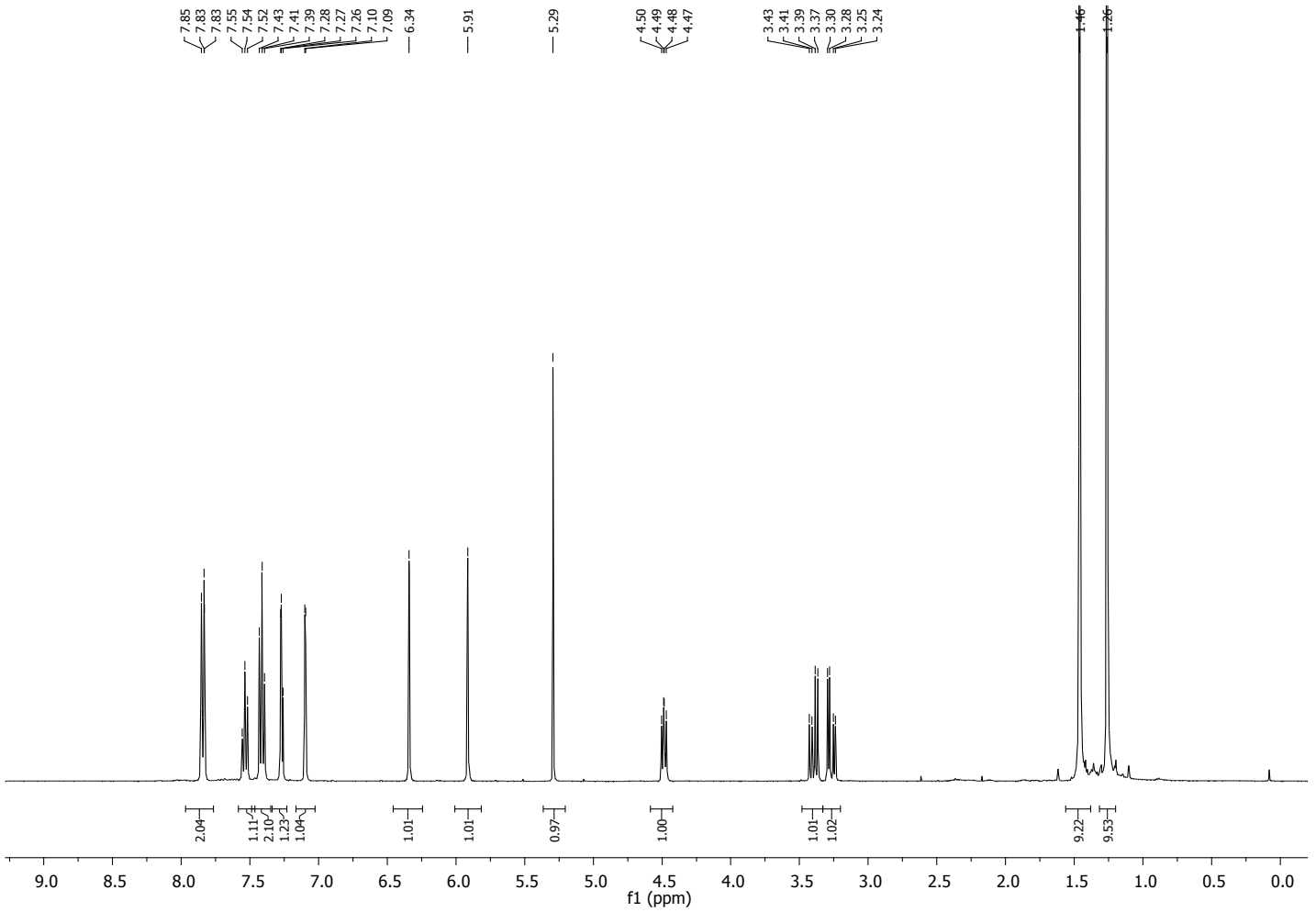
^{1}H NMR, $CDCl_3$, 500 MHz



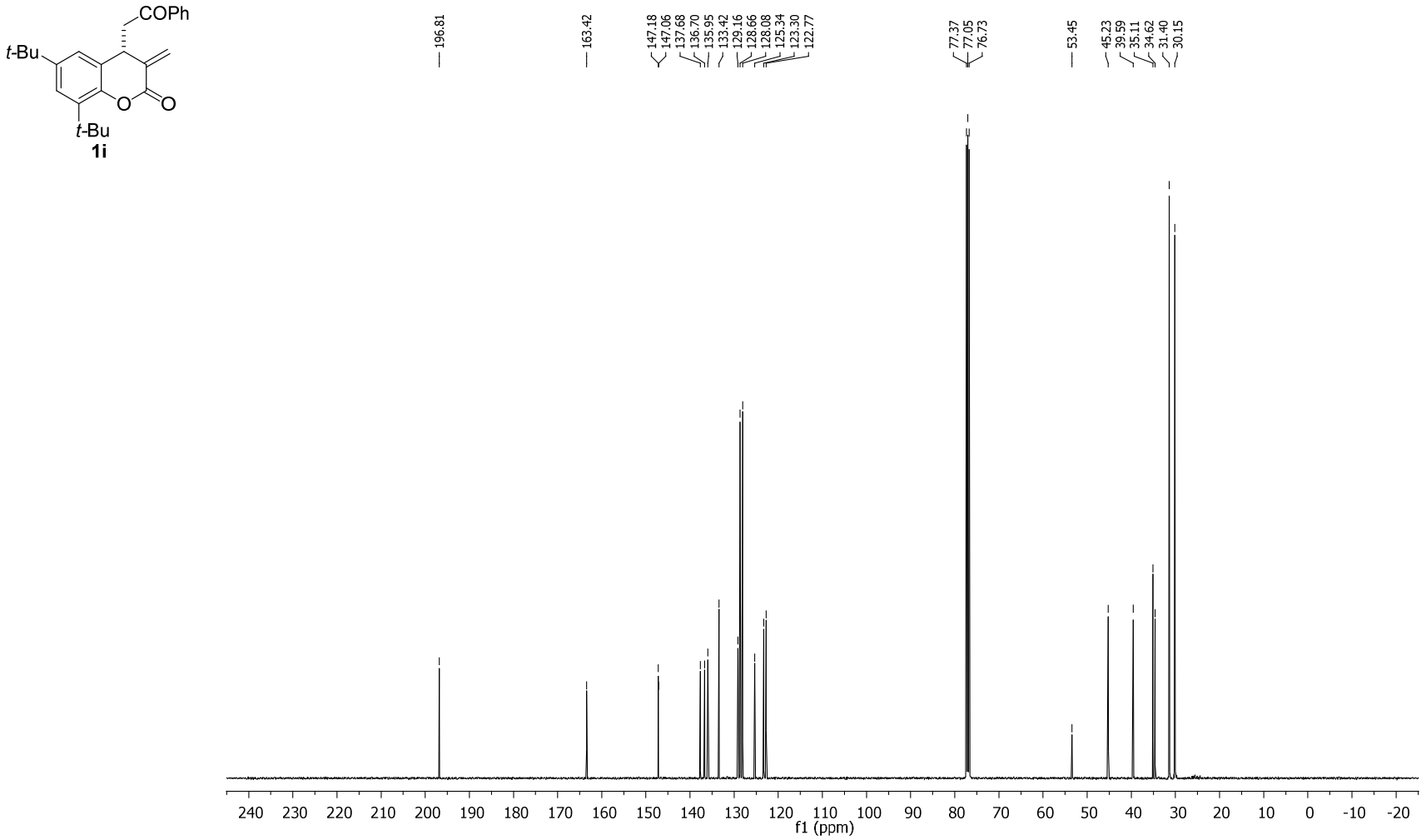
^{13}C NMR, $CDCl_3$, 126 MHz



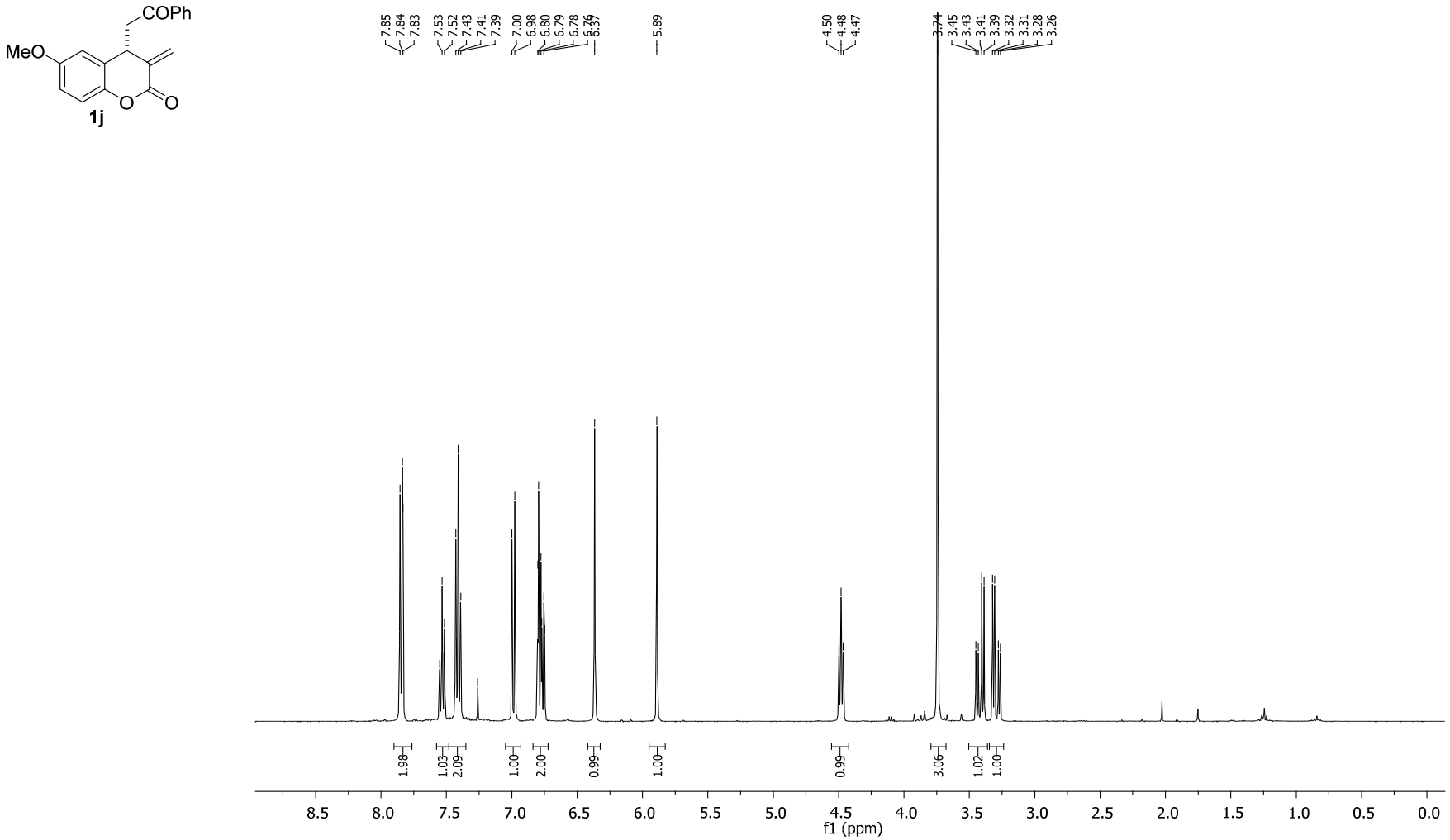
1i



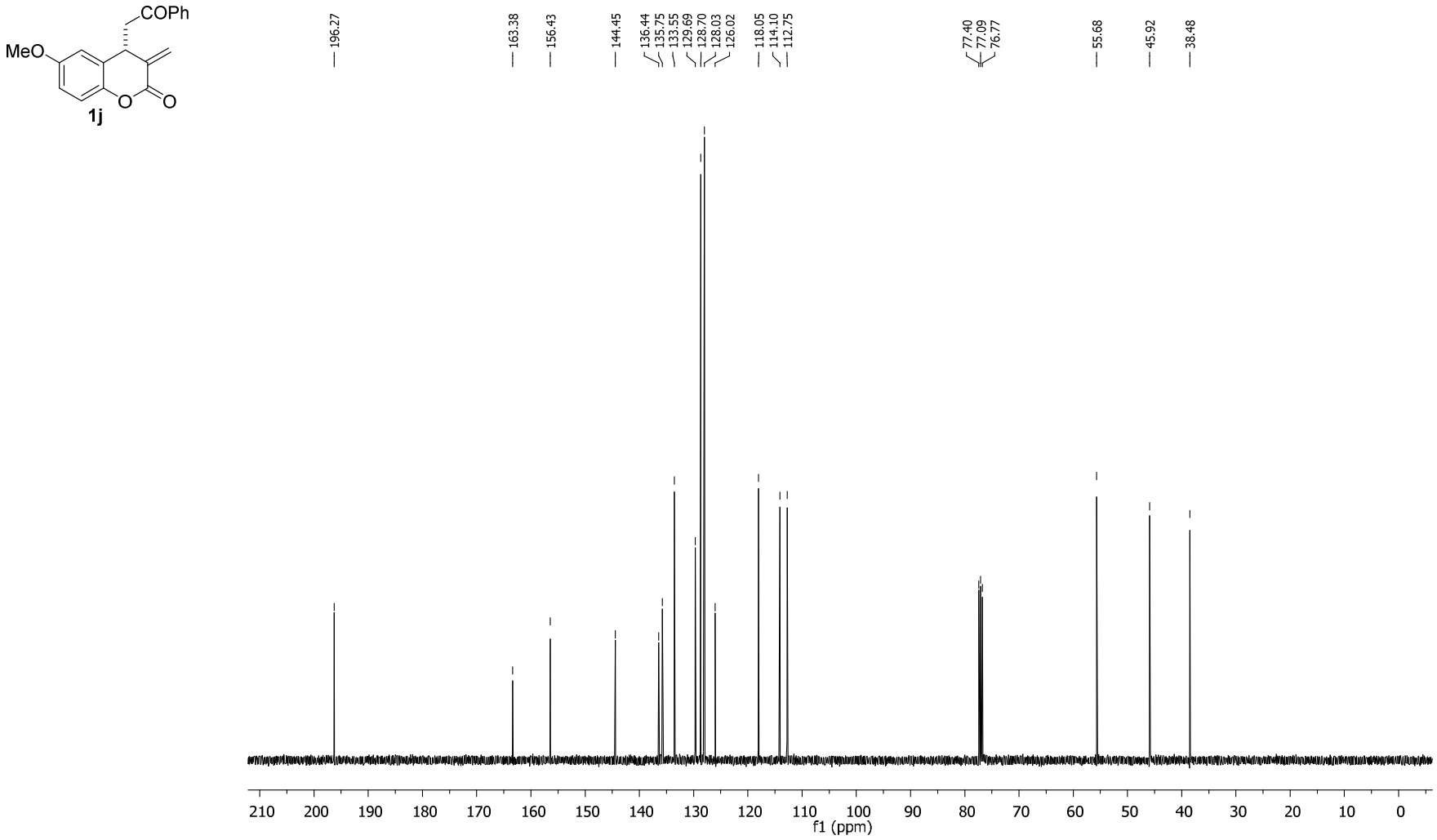
^{1}H NMR, $CDCl_3$, 400 MHz



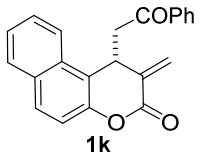
^{13}C NMR, $CDCl_3$, 101 MHz



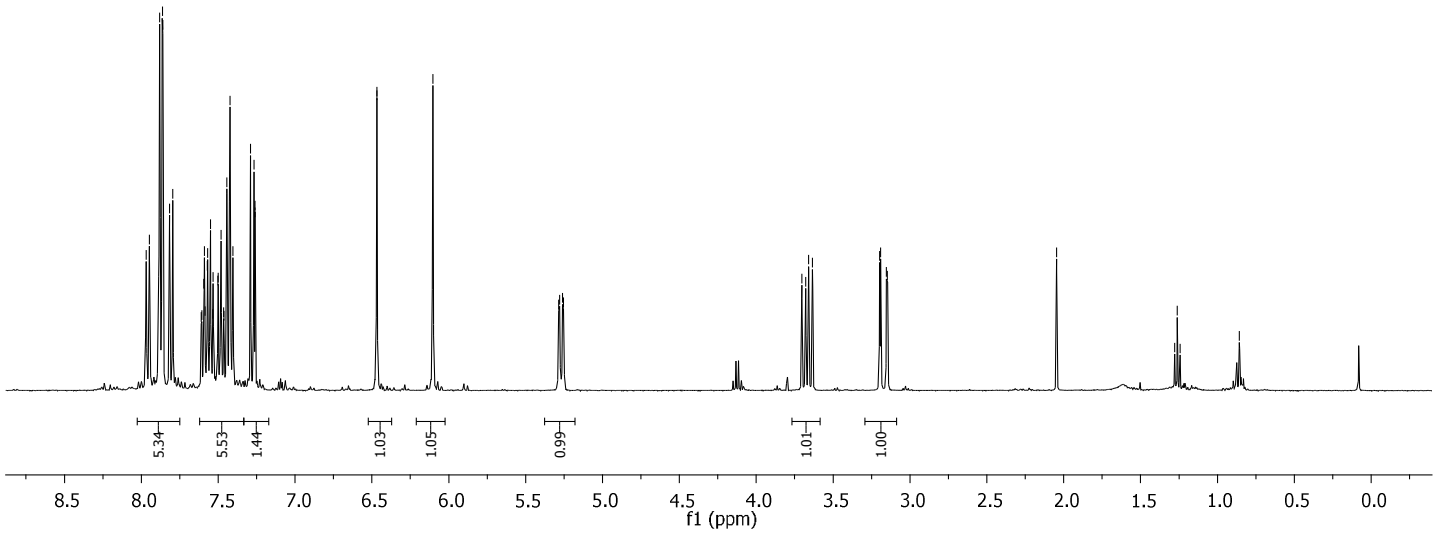
^{1}H NMR, $CDCl_3$, 400 MHz



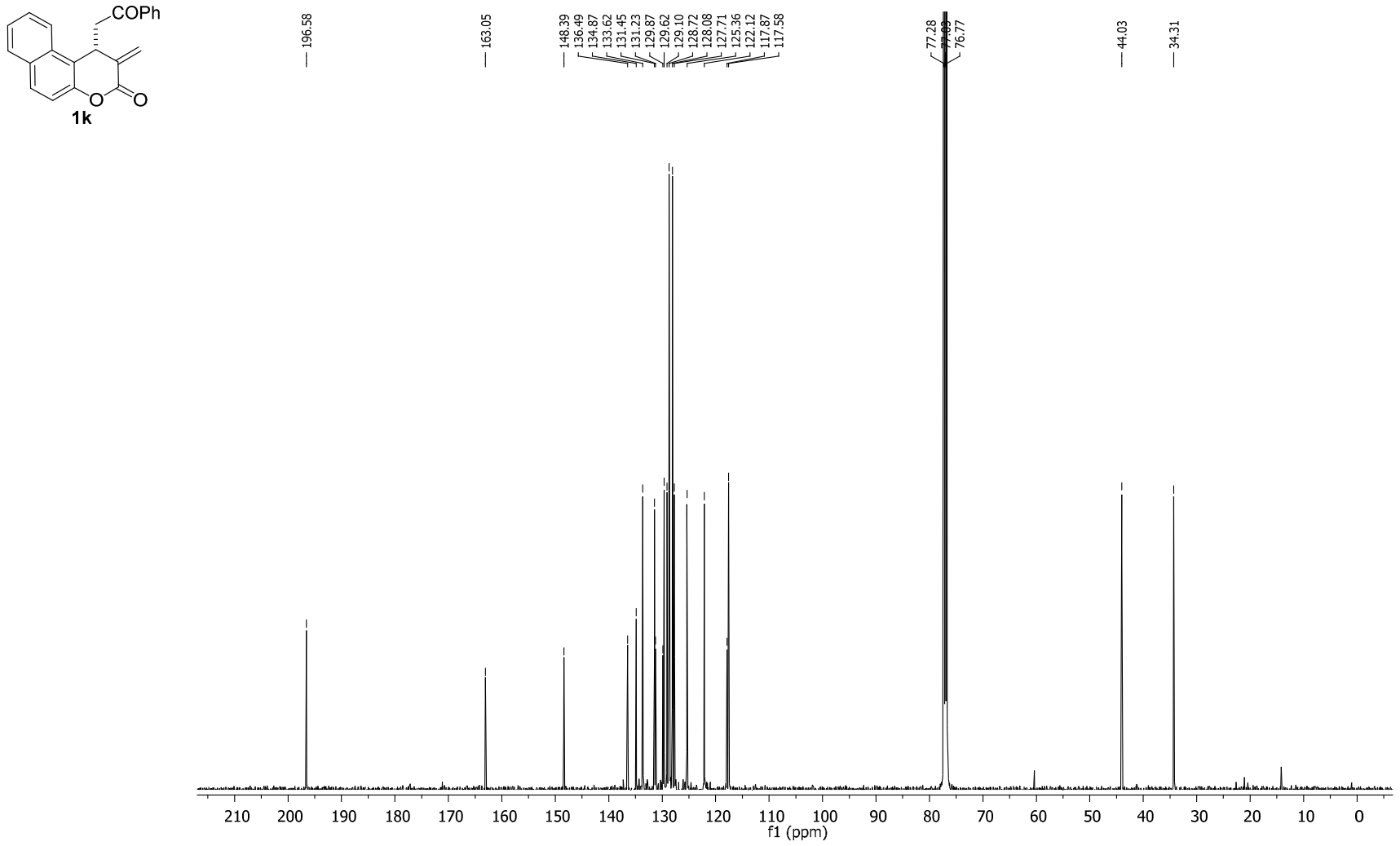
^{13}C NMR, $CDCl_3$, 101 MHz



1k



^{1}H NMR, $CDCl_3$, 400 MHz



^{13}C NMR, $CDCl_3$, 101 MHz

7. References

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