SUPPORTING INFORMATION

Design and Synthesis of Indol-PHOX: A New Class of Modular Phosphine-Oxazoline Ligands for Palladium-Catalyzed Enantioselective Decarboxylative Allylation

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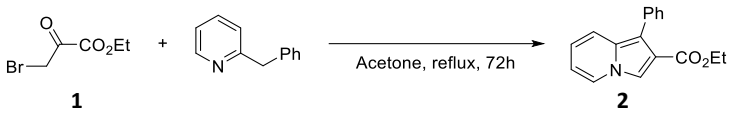
Content

1. General Information

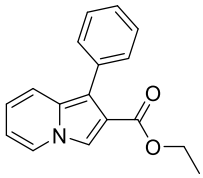
All air and/or water-sensitive reactions were carried out under an argon atmosphere. THF, Et_2O, CH_2Cl_2 and toluene were dried over alumina columns in a solvent purification apparatus (Innovative technology). Reactions were monitored by thin layer chromatography carried out on a precoated silica gel plates (Merck 60F254) and revealed with either an ultra-violet lamp (λ = 254 nm, λ = 356 nm), a potassium permanganate solution or a *p*-anisaldehyde solution. Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded using a Bruker AC400 (400 MHz) or a Bruker AC 500 (500 MHz). Data were reported as follows: chemical shifts (δ), multiplicity (recorded as s, singlet; d, doublet; t, triplet; q, quadruplet; quint, quintuplet; sext, sextuplet; hept, heptuplet; m, multiplet and br, broad), coupling constants and integration. Carbon-13 nuclear magnetic resonance (^{13}C{^{1}H} NMR) spectra were recorded using a Bruker AC400 (101 MHz) or a Bruker AC 500 (126 MHz). The chemical shifts are expressed in parts per million (ppm) relative to the center line of the triplet at 77.16 ppm for $CDCl_3$. Column purifications are performed using VWR Chemicals Silica Gel 60 (40-60 µm) or using the CombiFlash NEXTGEN 300+. Optical rotations were measured on a Jasco P-1010 polarimeter or Perkin-Elmer 241 polarimeter. Hight resolution mass spectrometric (HRMS) analyses were measured on Agilent 6546 LC/QTOF at Chimi ParisTech. The enantiomeric excess was determined by HPLC analysis.

2. Synthesis of Indol-PHOX Ligands **5a – 5f**

Ethyl 1-phenylindolizine-2-carboxylate (2)

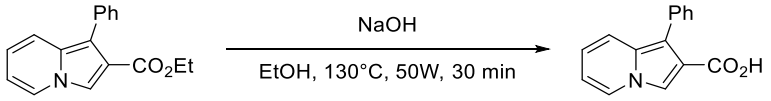


In a round bottom flask was dissolved 2-benzylpyridine (18.9 g, 18.0 mL, 111.7 mmol, 2.0 equiv.) in acetone (200 mL). Ethyl bromopyruvate (**1**) (10.9 g, 7.0 mL, 55.9 mmol, 1.0 equiv.) was added and the mixture was stirred at reflux for 72 h. The reaction mixture was concentrated under vacuum and the black oil was solubilized in dichloromethane, washed twice with a saturated solution of HCl (4N), twice with a solution of NaOH (1N) and once with brine. The organic phases were combined, dried over $MgSO_4$, filtered and concentrated under vacuum. The black oil was purified by column chromatography on silica gel (petroleum ether/CH_2Cl_2/EtOAc gradient from 100:0:0 to 70:24:6) affording **2** as a green oil (6.7 g, 25.2 mmol, 45% yield).



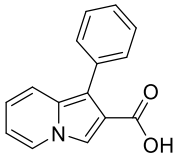
Chemical Formula: $C_{17}H_{15}O_2N$
Molecular Weight: 265.31 g/mol
Column chromatography, eluent petroleum ether/CH_2Cl_2/EtOAc gradient from 100:0:0 to 70:24:6
Green solid, 6.7 g, 45% yield
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (s, 1H), 7.86 (dt, *J* = 7.0, 1.2 Hz, 1H), 7.50 – 7.46 (m, 2H), 7.45 – 7.36 (m, 3H), 7.35 – 7.29 (m, 1H), 6.66 (ddd, *J* = 9.2, 6.5, 1.1 Hz, 1H), 6.55 (td, *J* = 6.7, 1.3 Hz, 1H), 4.25 (q, *J* = 7.1 Hz, 2H), 1.24 (t, *J* = 7.1 Hz, 3H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 165.1, 134.2, 131.3, 130.8, 127.9, 126.6, 125.3, 119.5, 118.5, 117.7, 116.9, 116.1, 112.9, 60.1, 14.3.
HRMS (ESI) m/z $[M+H]^+$ Calculated for $C_{17}H_{16}O_2N$: 266.1176. Found: 266.1177.

1-phenylindolizine-2-carboxylic acid (3)



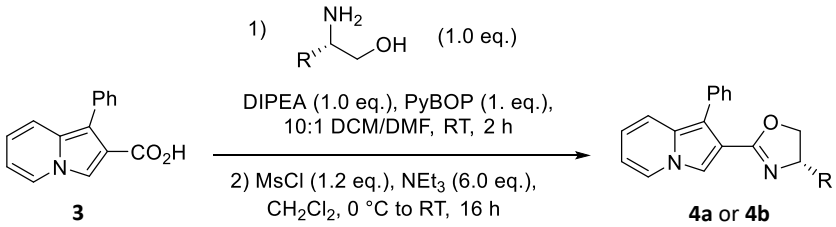
2 **3**

In a microwave tube was added ethyl 1-phenylindolizine-2-carboxylate (**2**) (2.0 g, 7.5 mmol, 1.0 equiv.), NaOH (0.6 g, 15.1 mmol, 2.0 equiv.) and ethanol (12 mL). The mixture was stirred and heated (130 °C, 50W irradiation) for 30 min. Ethanol was removed under vacuum. The solid was dissolved in water and acidified with a solution of HCl (4N) until pH = 1. The suspension was extracted three times with CH_2Cl_2 (100 mL). The organic phases were combined and condensed under vacuum. 1-Phenylindolizine-2-carboxylic acid (**3**) was obtained as a yellow solid (1.78 g, 7.5 mmol, quantitative yield).



Chemical Formula: $C_{15}H_{11}O_2N$
Molecular Weight: 237.26 g/mol
Yellow solid, 1.78 g, quantitative yield
^{1}H NMR (400 MHz, DMSO-d_6) δ 12.19 (s, 1H), 8.30 (d, J = 7.0 Hz, 1H), 8.13 (s, 1H), 7.45 – 7.36 (m, 4H), 7.34 – 7.25 (m, 2H), 6.78 – 6.73 (m, 1H), 6.67 (td, J = 6.8, 1.3 Hz, 1H).
^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6) δ 165.6, 134.0, 130.4, 130.3, 127.7, 126.2, 126.0, 119.2, 118.1, 117.9, 117.3, 114.5, 112.4.
HRMS (ESI) m/z $[M+H]^+$ Calculated for $C_{15}H_{12}O_2N$: 238.0863. Found: 238.0861.

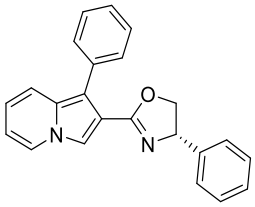
2.a. General method for Indolizino-oxazoline synthesis **4a – 4b**



3 **4a** or **4b**

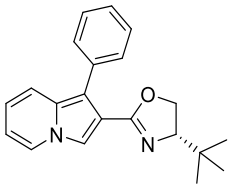
In a round bottom flask were dissolved 1-phenylindolizine-2-carboxylic acid (**3**) (1.0 equiv.) and corresponding amino-alcohol (1.0 equiv.) in CH_2Cl_2 (0.2M). Then pyBOP (1.0 equiv.) followed by DIPEA (1.0 equiv.) were added. The mixture was stirred at room temperature until completion. The mixture was washed with a solution of HCl (1N) and extracted with dichloromethane three times. Organic phases were combined, washed with brine, dried over $MgSO_4$, filtered and concentrated under vacuum. Crude product was filtered on a silica pad (50/50 EtOAc/petroleum ether) and the corresponding amido-alcohol was engaged without further purification in the next step. In a round bottom flask under nitrogen, crude amido-alcohol was dissolved in CH_2Cl_2 (0.2M) and NEt_3 was added (2.5 equiv.). The mixture was cooled down to 0 °C and mesyl chloride was slowly added (1.2 equiv.), then allowed to return to room temperature and stirred for 16 hours. The mixture was washed with HCl (1N), three times with a saturated solution of K_2CO_3 and three times with brine. Organic phase was dried over $MgSO_4$, filtered and concentrated under vacuum. The residue was purified by column chromatography on silica gel to provide **4a** or **4b** (petroleum ether/EtOAc gradient from 100:0 to 75:25).

(*S*)-4-phenyl-2-(1-phenylindolizin-2-yl)-4,5-dihydrooxazole (4a)



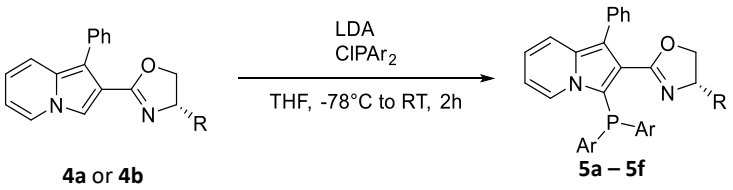
Chemical Formula: $C_{23}H_{18}ON_2$
Molecular Weight: 338.41 g/mol
Column chromatography, eluent petroleum ether/EtOAc gradient from 100:0 to 75:25
Yellow solid, 1.72 g, 86% yield, $[\alpha]^{25}_{D}$ = -37 (*c* 1.1, $CHCl_3$)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.88 (dd, *J* = 7.0, 1.2 Hz, 1H), 7.58 – 7.51 (m, 2H), 7.47 – 7.38 (m, 3H), 7.38 – 7.27 (m, 6H), 6.68 (ddd, *J* = 9.2, 6.5, 1.1 Hz, 1H), 6.55 (td, *J* = 6.7, 1.3 Hz, 1H), 5.32 (dd, J_{HH} = 10.0, 7.9 Hz, 1H), 4.64 (dd, J_{HH} = 10.1, 8.3 Hz, 1H), 4.12 (t, J_{HH} = 8.2 Hz, 1H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 162.4, 143.0, 134.4, 131.2, 130.6, 128.7, 128.0, 127.4, 126.8, 126.4, 125.2, 118.9, 118.4, 115.3, 114.7, 114.6, 112.4, 74.3, 69.9.
HRMS (ESI) m/z $[M+H]^+$ Calculated for $C_{23}H_{18}ON_2$: 339.1492. Found: 339.1493.

(*S*)-4-(*tert*-butyl)-2-(1-phenylindolizin-2-yl)-4,5-dihydrooxazole (4b)



Chemical Formula: $C_{21}H_{22}ON_2$
Molecular Weight: 318.42 g/mol
Column chromatography, eluent petroleum ether/EtOAc gradient from 100:0 to 75:25
Yellow solid, 1.60 g, 60% yield, $[\alpha]^{25}_{D}$ = -107 (*c* 1.2, $CHCl_3$)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (dt, *J* = 7.0, 1.1 Hz, 1H), 7.81 (d, *J* = 0.6 Hz, 1H), 7.56 – 7.49 (m, 2H), 7.47 – 7.37 (m, 3H), 7.33 – 7.27 (m, 1H), 6.66 (ddd, *J* = 9.2, 6.5, 1.1 Hz, 1H), 6.52 (ddd, *J* = 6.5, 1.3 Hz, 1H), 4.18 (dd, J_{HH} = 10.1, 8.6 Hz, 1H), 4.10 (dd, J_{HH} = 8.5, 7.4 Hz, 1H), 3.97 (dd, J_{HH} = 10.1, 7.4 Hz, 1H), 0.93 (s, 9H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 160.7, 134.4, 131.1, 130.1, 127.9, 126.3, 125.2, 118.9, 118.4, 115.0, 115.0, 114.6, 112.2, 76.3, 68.1, 34.2, 26.0.
HRMS (ESI) m/z $[M+H]^+$ Calculated for $C_{21}H_{23}ON_2$: 319.1805. Found: 319.1805.

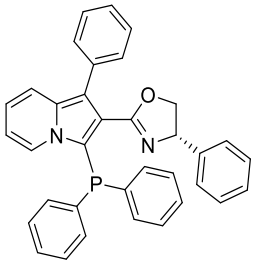
2.b. General procedure for Indolizino-oxazoline diarylphosphine synthesis **5a – 5f**



In a round bottom flask, to a solution of the corresponding indolizino-oxazoline (**4a** or **4b**) (1.0 equiv.) in THF (0.1 M) was added dropwise at -78°C a commercial solution of lithium diisopropylamide (1M in THF/hexanes, 1.1 equiv.) and the mixture was stirred for 30 minutes. Then the corresponding chloro diarylphosphine (1.1 eq.) was added. The mixture was stirred 30 minutes at -78 °C and then 1 hour at 0 °C. The mixture was carefully quenched with a saturated solution of NH_4Cl and concentrated under vacuum. The suspension was dissolved in EtOAc and washed with brine. The organic layers were combined, dried over $MgSO_4$, filtered and concentrated under

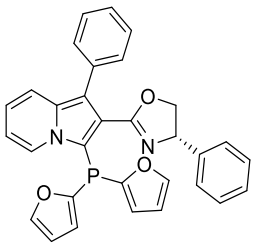
vacuum. The crude was purified by column chromatography on silica gel to provide **5a – 5f** (petroleum ether/ EtOAc gradient from 100:0 to 80:20).

(*S*)-2-(3-(diphenylphosphaneyl)-1-phenylindolizin-2-yl)-4-phenyl-4,5-dihydrooxazole (5a)



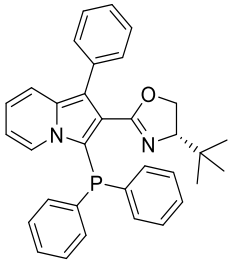
Chemical Formula: $C_{35}H_{27}ON_2P$
Molecular Weight: 522.59 g/mol
Column chromatography, eluent petroleum ether/EtOAc gradient from 100:0 to 80:20
Light pink solid, 1.94 g, 82% yield, $[\alpha]^{25}_{D}$ = -59 (*c* 0.9, $CHCl_3$)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (ddt, *J* = 7.2, 2.3, 1.1 Hz, 1H), 7.67 – 7.53 (m, 3H), 7.53 – 7.39 (m, 6H), 7.38 – 7.28 (m, 7H), 7.25 – 7.17 (m, 3H), 7.13 – 7.10 (m, 2H), 6.83 (ddd, *J* = 9.1, 6.6, 1.0 Hz, 1H), 6.44 (td, *J* = 6.9, 1.4 Hz, 1H), 5.06 (dd, J_{HH} = 10.4, 8.7 Hz, 1H), 4.36 (dd, J_{HH} = 10.4, 8.3 Hz, 1H), 3.93 (t, J_{HH} = 8.5 Hz, 1H).
^{31}P NMR (162 MHz, $CDCl_3$) δ -32.0.
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 162.1 (d, J_{PC} = 0.7 Hz), 142.6, 134.7, 134.2 (d, J_{PC} = 0.9 Hz), 133.8 (d, J_{PC} = 8.0 Hz), 133.8 (d, J_{PC} = 7.8 Hz), 132.6 (d, J_{PC} = 18.7 Hz), 132.6 (d, J_{PC} = 18.7 Hz), 130.1 , 128.7 (d, J_{PC} = 6.4 Hz), 128.7 (d, J_{PC} = 6.3 Hz), 128.5, 128.5 (d, J_{PC} = 1.2 Hz), 127.2, 127.0 (d, J_{PC} = 1.2 Hz), 126.6, 126.3 (d, J_{PC} = 21.6 Hz), 125.8 (d, J_{PC} = 9.8 Hz), 120.4, 118.8, 116.7 (d, J_{PC} = 5.0 Hz), 115.3 (d, J_{PC} = 23.4 Hz), 112.0, 74.5, 70.5.
HRMS (ESI) m/z $[M+H]^+$ Calculated for $C_{35}H_{28}ON_2P$: 523.1934. Found: 523.1935.

(*S*)-2-(3-(di(furan-2-yl)phosphaneyl)-1-phenylindolizin-2-yl)-4-phenyl-4,5-dihydrooxazole (5b)



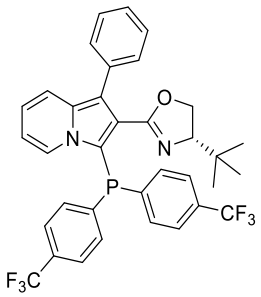
Chemical Formula: $C_{31}H_{23}O_3N_2P$
Molecular Weight: 502.21 g/mol
Column chromatography, eluent petroleum ether/EtOAc gradient from 100:0 to 80:20
Yellow solid, 276 mg, 82% yield, $[\alpha]^{25}_{D}$ = -25 (*c* 1.1, $CHCl_3$)
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (dq, *J* = 7.2, 1.1 Hz, 1H), 7.64 (td, *J* = 1.8, 0.7 Hz, 2H), 7.61 – 7.51 (m, 3H), 7.47 – 7.37 (m, 2H), 7.35 – 7.21 (m, 6H), 6.88 (ddd, *J* = 9.1, 6.5, 1.1 Hz, 1H), 6.76 (dt, *J* = 3.3, 1.0 Hz, 1H), 6.72 (dt, *J* = 3.3, 0.8 Hz, 1H), 6.58 (ddd, *J* = 7.2, 6.5, 1.4 Hz, 1H), 6.45-6.42 (m, 2H), 5.41 (dd, *J* = 10.3, 8.5 Hz, 1H), 4.71 (dd, *J* = 10.3, 8.3 Hz, 1H), 4.15 (dd, *J* = 8.5, 8.3 Hz, 1H).
^{31}P NMR (162 MHz, $CDCl_3$) δ -78.8.
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 162.2 (d, J_{PC} = 0.9 Hz), 148.9 (d, J_{PC} = 3.9 Hz), 148.8 (d, J_{PC} = 1.6 Hz), 147.3 (d, J_{PC} = 2.7 Hz), 147.2 (d, J_{PC} = 3.0 Hz), 142.7, 135.3, 134.1 (d, J_{PC} = 1.5 Hz), 129.9, 128.6, 128.4, 127.4, 127.2 (d, J_{PC} = 1.7 Hz), 127.2, 127.2, 126.8, 126.6, 120.9, 120.8 (d, J_{PC} = 26.2 Hz), 120.5 (d, J_{PC} = 24.2 Hz), 118.5, 116.4 (d, J_{PC} = 7.7 Hz), 113.3 (d, J_{PC} = 27.1 Hz), 112.1, 111.1 (d, J_{PC} = 5.7 Hz), 111.1 (d, J_{PC} = 4.9 Hz), 74.9, 70.8.
HRMS (ESI) m/z $[M+H]^+$ Calculated for $C_{31}H_{24}O_3N_2P$: 503.1522. Found: 503.1520.

(*S*)-4-(tert-butyl)-2-(3-(diphenylphosphaneyl)-1-phenylindolizin-2-yl)-4,5-dihydrooxazole (5c)



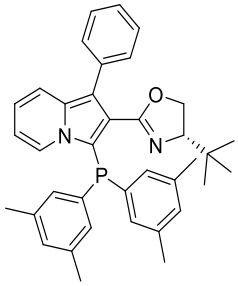
Chemical Formula: $C_{33}H_{31}N_2OP$
Molecular Weight: 502.60 g/mol
Column chromatography, eluent petroleum ether/EtOAc gradient from 100:0 to 80:20
Light pink solid, 215 mg, 80% yield, $[\alpha]^{25}_{D}$ = -79 (*c* 1.1, $CHCl_3$)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (ddt, *J* = 7.2, 2.1, 1.0 Hz, 1H), 7.60 – 7.48 (m, 5H), 7.43 – 7.27 (m, 11H), 6.80 (ddd, *J* = 9.1, 6.5, 1.1 Hz, 1H), 6.38 (ddd, *J* = 7.2, 6.5, 1.4 Hz, 1H), 4.0 – 3.95 (m, 2H), 3.74 (dd, J_{HH} = 10.0, 8.8 Hz, 1H), 0.84 (s, 9H).
^{31}P NMR (162 MHz, $CDCl_3$) δ -32.1.
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 160.6, 134.7, 134.5 (d, J_{PC} = 9.1 Hz), 134.22 (d, J_{PC} = 1.0 Hz), 134.0 (d, J_{PC} = 8.8 Hz), 132.6 (d, J_{PC} = 18.9 Hz), 132.1 (d, J_{PC} = 18.4 Hz), 130.1, 128.7 (d, J_{PC} = 6.4 Hz), 128.7 (d, J_{PC} = 5.9 Hz), 128.4, 128.3, 128.2, 126.8 (d, J_{PC} = 24.4 Hz), 126.5, 125.9 (d, J_{PC} = 8.1 Hz), 120.3, 118.8, 116.5 (d, J_{PC} = 5.5 Hz), 115.5 (d, J_{PC} = 26.4 Hz), 111.8, 76.8, 68.6, 33.9, 26.2 (d, J_{PC} = 1.2 Hz).
HRMS (ESI) m/z $[M+H]^+$ Calculated for $C_{33}H_{32}N_2OP$: 503.2247. Found: 503.2247.

(*S*)-2-(3-(bis(4-(trifluoromethyl)phenyl)phosphaneyl)-1-phenylindolizin-2-yl)-4-(tert-butyl)-4,5-dihydrooxazole (5d)



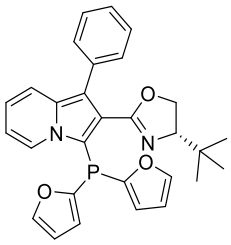
Chemical Formula: $C_{35}H_{29}F_6ON_2P$
Molecular Weight: 638.59 g/mol
Column chromatography, eluent petroleum ether/EtOAc gradient from 100:0 to 80:20
Light orange solid, 154 mg, 64% yield, $[\alpha]^{25}_{D}$ = -46 (*c* 0.9, $CHCl_3$)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (ddt, *J* = 7.2, 2.7, 1.1 Hz, 1H), 7.73 – 7.67 (m, 2H), 7.65 – 7.55 (m, 5H), 7.54 – 7.45 (m, 4H), 7.44 – 7.37 (m, 2H), 7.31 (ddt, *J* = 8.6, 6.6, 1.1 Hz, 1H), 6.87 (ddd, *J* = 9.1, 6.6, 1.1 Hz, 1H), 6.50 (ddd, *J* = 7.2, 6.5, 1.3 Hz, 1H), 3.87 (m, J_{HH} = 9.2, 8.6 Hz, 1H), 3.88 (m, J_{HH} = 10.1, 8.6 Hz, 1H), 3.54 (dd, J_{HH} = 10.1, 9.2 Hz, 1H), 0.81 (s, 9H).
^{31}P NMR (162 MHz, $CDCl_3$) δ -32.2.
^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -62.8.
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 160.2, 139.2 (d, J_{PC} = 11.1 Hz), 138,4 (d, J_{PC} = 10.6 Hz), 135.3 (d, J_{PC} = 0.9 Hz), 133.9 (d, J_{PC} = 0.9 Hz), 133.3 (d, J_{PC} = 19.8 Hz), 133.3 (d, J_{PC} = 18.8 Hz), 131.0 (q, J_{FC} = 32.5 Hz), 130.6 (q, J_{FC} = 32.9 Hz), 130,1, 128,5, 126,9, 126.8 (d, J_{PC} = 19.8 Hz,), 125.6 (dq, J_{PC} = 7.0, J_{FC} = 3.5 Hz), 125.5 (dq, J_{PC} = 6.6, J_{FC} = 3.4 Hz), 125.3 (d, J_{PC} = 11.1 Hz), 124.2 (q, J_{FC} = 272.3 Hz), 121.0, 119.2, 117.3 (d, J_{PC} = 4.7 Hz), 113.4 (d, J_{PC} = 19.1 Hz), 112.7, 76.8, 68.7, 33.9, 26.2.
HRMS (ESI) m/z $[M+H]^+$ Calculated for $C_{35}H_{30}F_6N_2OP$: 639.1994. Found: 639.1994.

(*S*)-2-(3-(bis(3,5-dimethylphenyl)phosphaneyl)-1-phenylindolizin-2-yl)-4-(tert-butyl)-4,5-dihydrooxazole (5e)



Chemical Formula: $C_{37}H_{39}ON_2P$
Molecular Weight: 558.71 g/mol
Column chromatography, eluent petroleum ether/EtOAc gradient from 100:0 to 80:20
White solid, 1.36 g, 66% yield, $[\alpha]^{25}_{D}$ = -55 (*c* 1.0, $CHCl_3$)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (ddt, *J* = 7.2, 2.0, 1.1 Hz, 1H), 7.63 – 7.54 (m, 3H), 7.45 – 7.36 (m, 2H), 7.33 – 7.24 (m, 1H), 7.18 (ddt, *J* = 8.2, 1.7, 0.6 Hz, 2H), 6.98 – 6.93 (m, 3H), 6.90 – 6.87 (m, 1H), 6.79 (ddd, *J* = 9.1, 6.5, 1.1 Hz, 1H), 6.39 (ddd, *J* = 7.2, 6.5, 1.4 Hz, 1H), 4.05 (dd, *J* = 10.3, 8.5 Hz, 1H), 3.98 (dd, *J* = 8.8, 8.5 Hz, 1H), 3.76 (dd, *J* = 10.3, 8.8 Hz, 1H), 2.27 (s, 6H), 2.24(s, 6H), 0.88 (s, 9H).
^{31}P NMR (162 MHz, $CDCl_3$) δ -32.4.
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 160.7, 138.1 (d, J_{PC} = 9.2 Hz), 138.0 (d, J_{PC} = 8.5 Hz), 134.5, 134.4 (d, J_{PC} = 1.7 Hz), 134.4 (d, J_{PC} = 7.9 Hz), 133.6 (d, J_{PC} = 8.6 Hz), 130.7 (d, J_{PC} = 19.5 Hz), 130.4, 129.9, 129.9, 129.7 (d, J_{PC} = 18.4 Hz), 128.3, 126.7 (d, J_{PC} = 25.4 Hz), 126.3, 126.2 (d, J_{PC} = 7.4 Hz), 120.2, 118.6, 116.3 (d, J_{PC} = 28.3 Hz), 116.1 (d, J_{PC} = 5.6 Hz), 111.5, 76.9, 68.6, 33.8, 26.3, 21.6, 21.5.
HRMS (ESI) m/z $[M+H]^+$ Calculated for $C_{37}H_{40}ON_2P$: 559.2873. Found: 559.2873.

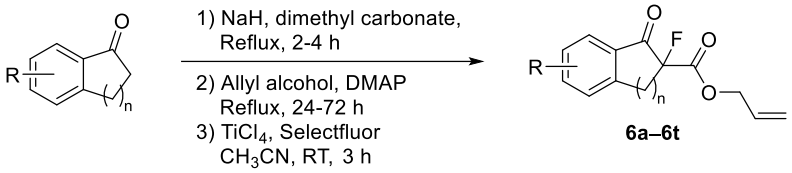
(*S*)-4-(tert-butyl)-2-(3-(di(furan-2-yl)phosphaneyl)-1-phenylindolizin-2-yl)-4,5-dihydrooxazole (5f)



Chemical Formula: $C_{29}H_{27}O_3N_2P$
Molecular Weight: 482.52 g/mol
Column chromatography, eluent petroleum ether/EtOAc gradient from 100:0 to 80:20
Light yellow solid, 208 mg, 70% yield, $[\alpha]^{25}_{D}$ = -65 (*c* 0.9, $CHCl_3$)
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (dq, *J* = 7.2, 1.0 Hz, 1H), 7.62 (ddd, *J* = 10.3, 1.8, 0.7 Hz, 2H), 7.54 (dt, *J* = 9.1, 1.3 Hz, 1H), 7.52 – 7.48 (m, 2H), 7.43 – 7.35 (m, 2H), 7.31 – 7.27 (m, 1H), 6.85 (ddd, *J* = 9.1, 6.6, 1.0 Hz, 1H), 6.80 (ddd, *J* = 3.2, 1.2, 0.7 Hz, 1H), 6.65 (dt, *J* = 3.3, 0.7 Hz, 1H), 6.55 (ddd, *J* = 7.2, 6.5, 1.4 Hz, 1H), 6.44-6.41 (m, 2H), 4.25 (dd, J_{HH} = 9.9, 8.1 Hz, 1H), 4.14 (t, *J* = 8.1 Hz, 1H), 4.08 (dd, *J* = 9.8, 8.1 Hz, 1H), 0.97 (s, 9H).
^{31}P NMR (162 MHz, $CDCl_3$) δ -79.7.
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 160.7 (d, J_{PC} = 0.5 Hz), 149.2 (d, J_{PC} = 11.5 Hz), 149.1 (d, J_{PC} = 16.0 Hz), 147.3 (d, J_{PC} = 2.2 Hz), 147.0 (d, J_{PC} = 3.0 Hz), 135.2, 134.2 (d, J_{PC} = 1.6 Hz), 129.9, 128.2, 127.2 (d, J_{PC} = 1.0 Hz), 127.2 (d, J_{PC} = 37.9 Hz), 126.5, 120.9 (d, J_{PC} = 28.0 Hz), 120.8, 120.1 (d, J_{PC} = 24.0 Hz), 118.4, 116.1 (d, J_{PC} = 7.7 Hz), 113.5 (d, J_{PC} = 29.0 Hz), 111.9, 111.1 (d, J_{PC} = 5.0 Hz), 111.0 (d, J_{PC} = 3.5 Hz), 77.0, 69.0, 34.2, 26.3, 26.2.
HRMS (ESI) m/z $[M+H]^+$ Calculated for $C_{29}H_{28}O_3N_2P$: 483.1832. Found: 483.1832.

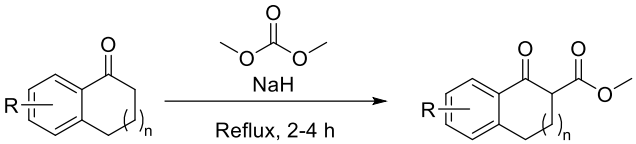
3. General method for the synthesis of compounds **11a – 11t**

The preparation of the enantioselective decarboxylative allylation precursors was achieved in three steps starting from indanone, tetralone and benzo[7]annulone derivatives.



n = 1, R = H, 5-Cl, 4-CF_3, 6-OMe, 5,6-di-MeO, 5,6-di-Me, 2-naphthyl
n = 2, R = H, 7-MeO, 5-MeO, 7-Me, 7-Br, 6-Cl, 7-F, 6-Br, 7-Cl, 2-naphthyl
n = 3, R = H

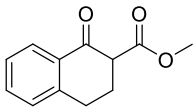
3.a. General method A (**11a – 11l**)[1]



n = 1, 2 **11a–11l**

To a suspension of NaH (60%, suspension in oil, 4.8 g, 120 mmol, 4.0 equiv.) in dimethyl carbonate (30 mL) was added dropwise a solution of 1-tetralone (4.4 g, 30 mmol, 1.0 equiv.) in dimethyl carbonate (30 mL) at room temperature. The reaction mixture was heated to reflux (oil bath) and stirred until the starting material was totally consumed (2-4 h). After cooling to room temperature, water was added and the mixture was extracted with ethyl acetate three times. The combined organic layers were dried with $MgSO_4$, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (petroleum ether/diethyl ether 10 : 0.5) to give methyl β-keto ester **11a**.

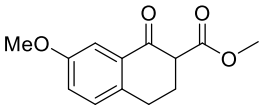
Methyl 1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (11a)[1]



Chemical Formula: $C_{12}H_{12}O_3$
Molecular Weight: 204.23 g/mol
Column chromatography, eluent petroleum ether/diethyl ether 10: 0.5
White solid, 5.0 g, 82% yield
In accordance with the literature: **^{1}H NMR** (400 MHz, $CDCl_3$) (keto: enol = 1.1 :1) Signals corresponding to enol form: *δ* 12.40 (s, 1H), 8.05 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.80 (dd, *J* = 7.4, 1.7 Hz, 1H), 7.50 (td, *J* = 7.5, 1.5 Hz, 1H), 7.20 – 7.15 (m, 1H), 3.78 (s, 3H), 2.83 – 2.79 (m, 2H), 2.54 – 2.45 (m, 1H), 2.40 – 2.33 (m, 1H). Signals corresponding to keto form: *δ* 7.36 – 7.22 (m, 4H), 3.83 (s, 3H), 3.63 (dd, *J* = 10.3, 4.7 Hz, 1H), 3.13 – 2.93 (m, 2H), 2.57 (m, 2H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) Signals corresponding to both forms *δ* 193.6, 173.5, 171.1, 165.5, 144.1, 139.9, 134.4, 132.2, 131.0, 130.4, 129.3, 128.2, 127.9, 127.4, 127.0, 124.8, 97.3, 54.9, 52.8, 52.1, 28.2, 28.1, 26.8, 21.0.

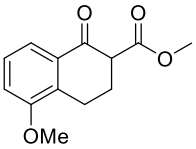
[1] L.-Q. Cui, Z.-L. Dong, K. Liu and C. Zhang, *Org. Lett.*, **2011**, *13*, 6488.

Methyl 7-methoxy-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (11b)[2]



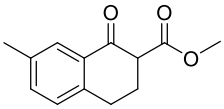
Chemical Formula: $C_{13}H_{14}O_4$
Molecular Weight: 234.25 g/mol
Column chromatography, eluent petroleum ether/diethyl ether 10: 0.5
White solid, 2.3 g, 66% yield
^{1}H NMR (400 MHz, $CDCl_3$) (keto: enol = 1:2) Signals corresponding to enol form *δ* 12.44 (s, 1H), 7.34 (d, *J* = 2.7 Hz, 1H), 7.10 – 7.03 (m, 1H), 6.88 (dd, *J* = 8.3, 2.7 Hz, 1H), 3.84 – 3.80 (m, 6H), 2.75 – 2.71 (m, 2H), 2.58 – 2.51 (m, 2H). Signals corresponding to keto form: 7.51 (d, *J* = 2.8 Hz, 1H), 7.17 – 7.13 (m, 1H), 7.10 – 7.03 (m, 1H), 3.84 – 3.80 (m, 3H), 3.78 (s, 3H), 3.60 (dd, *J* = 10.1, 4.8 Hz, 1H), 3.04 – 2.85 (m, 2H), 2.51 – 2.42 (m, 1H), 2.37 – 2.30 (m, 1H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) Signals corresponding to both forms *δ* 193.3, 173.2, 170.8, 165.1, 158.6, 158.5, 136.4, 132.6, 131.7, 130.9, 130.1, 128.5, 122.5, 117.1, 109.7, 108.9, 97.3, 55.6, 55.6, 54.4, 52.4, 51.8, 27.0, 26.9, 26.8, 20.9.

Methyl 5-methoxy-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (11c)[2]



Chemical Formula: $C_{13}H_{14}O_4$
Molecular Weight: 234.25 g/mol
Column chromatography, eluent petroleum ether/ethyl acetate 9.5: 0.5
Pale yellow oil, 2.2 g, 81% yield
In accordance with the literature: **^{1}H NMR** (400 MHz, $CDCl_3$) (keto: enol = 1.1:1) Signals corresponding to enol form *δ* 12.39 (s, 1H), 7.45 (dd, *J* = 7.8, 1.0 Hz, 1H), 7.32 – 7.22 (m, 1H), 6.93 (dd, *J* = 8.2, 1.0 Hz, 1H), 3.85 (s, 3H), 3.82 (s, 3H), 3.09 (dt, *J* = 17.9, 5.2 Hz, 1H), 2.86 – 2.74 (m, 1H), 2.49 – 2.40 (m, 1H), 2.35 (m, 1H). Signals corresponding to keto form *δ* 7.66 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.32 – 7.22 (m, 1H), 7.04 (dd, *J* = 8.1, 1.1 Hz, 1H), 3.87 (s, 3H), 3.78 (s, 3H), 3.60 (dd, *J* = 10.6, 4.7 Hz, 1H), 2.86 – 2.74 (m, 2H), 2.58 – 2.50 (m, 2H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) Signals corresponding to both forms *δ* 193.6, 173.2, 170.8, 165.2, 156.8, 156.0, 132.8, 131.1, 127.8, 127.2, 127.0, 119.3, 116.9, 114.8, 112.9, 96.9, 55.8, 55.7, 54.2, 52.4, 51.8, 25.7, 21.3, 20.1, 20.0.

Methyl 7-methyl-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (11d)[2]



Chemical Formula: $C_{13}H_{14}O_3$
Molecular Weight: 218.25 g/mol
Column chromatography, eluent petroleum ether/diethyl ether 10: 0.5
White solid, 2.3 g, 68% yield
^{1}H NMR (400 MHz, $CDCl_3$) (keto: enol = 1:1) Signals corresponding to enol form *δ* 12.42 (s, 1H), 7.87 – 7.83 (m, 1H), 7.64 – 7.62 (m, 1H), 7.06 (m, 1H), 3.82 (s, 3H), 2.77 – 2.74 (m, *J* = 8.9, 6.6 Hz, 2H), , 2.52 – 2.42 (m, 1H), 2.36 (s, 3H), 2.34– 2.30 (m, 1H). Signals corresponding to keto form: *δ* 7.31 (dd, *J* = 7.8, 1.9 Hz, 1H), 7.18 – 7.11 (m, 2H), 3.78 (s, 3H), 3.60 (dd, *J* = 10.2, 4.7 Hz, 1H), 3.08 – 2.88 (m, 2H), 2.57 – 2.53 (m, 2H), 2.36 (s, 3H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) Signals corresponding to both forms *δ* 193.8, 173.6, 171.2, 165.8, 141.2, 137.1, 136.9, 136.6, 135.4, 131.9, 131.7, 130.2, 129.2, 128.2, 127.8, 125.3, 97.2, 54.9, 52.8, 52.1, 27.8, 27.7, 27.0, 21.6, 21.4, 21.1.

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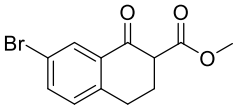
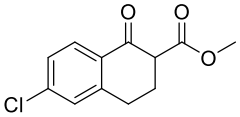
[2] T. Wang, F. Su, S. Yin, B. Zhang, Y. Liu, B. Sun, H. Tian and S. Liang, *Asian J. Org. Chem.*, **2025**, *14*, e202400458.

Methyl 7-bromo-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (11e)[2]



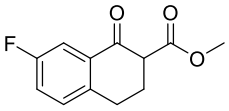
Chemical Formula: $C_{12}H_{11}BrO_3$
Molecular Weight: 281.99 g/mol
Column chromatography, eluent petroleum ether/ethyl acetate 9.5: 0.5
Pale yellow solid, 2.5 g, 78% yield,
^{1}H NMR (400 MHz, $CDCl_3$) (keto: enol = 1:2.5) Signals corresponding to enol form δ 12.32 (s, 1H), 7.92 (d, J = 2.1 Hz, 1H), 7.43 (dd, J = 8.0, 2.1 Hz, 1H), 7.03 – 7.06 (m, 1H), 3.83 (s, 3H), 2.76 – 2.73 (m, 2H), 2.61 – 2.53 (m, 2H). Signals corresponding to keto form: 8.16 (d, J = 2.2 Hz, 1H), 7.60 (dd, J = 8.2, 2.2 Hz, 1H), 7.13 – 7.16 (m, 1H), 3.78 (s, 3H), 3.61 (dd, J = 9.8, 4.8 Hz, 1H), 3.06 – 2.87 (m, 2H), 2.53 – 2.44 (m, 1H), 2.35 (m, 1H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) Signals corresponding to both forms δ 191.9, 172.9, 170.3 163.7, 142.4, 138.2, 136.8, 133.3, 131.9, 130.8, 130.7, 129.1, 127.4, 121.1, 120.5, 97.8, 54.1, 52.6, 51.9, 27.4, 27.2, 26.2, 20.5.

Methyl 6-chloro-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (11f)[2]



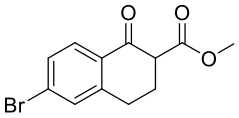
Chemical Formula: $C_{12}H_{11}ClO_3$
Molecular Weight: 238.67 g/mol
Column chromatography, eluent petroleum ether/ethyl acetate 9: 1
White solid, 1.2 g, 88% yield
^{1}H NMR (400 MHz, $CDCl_3$) (only enol form) δ 12.36 (s, 1H), 7.72 (d, J = 8.3 Hz, 1H), 7.28 – 7.23 (m, 1H), 7.17 – 7.16 (m, 1H), 3.83 (s, 3H), 2.79 (dd, J = 8.9, 6.6 Hz, 2H), 2.60 – 2.52 (m, 2H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 173.0, 164.3, 141.3, 136.5, 128.6, 127.7, 127.0, 125.9, 97.1, 51.9, 27.7, 20.5.

Methyl 7-fluoro-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (11g)[2]



Chemical Formula: $C_{12}H_{11}FO_3$
Molecular Weight: 222.22 g/mol
Column chromatography, eluent petroleum ether/ethyl acetate 9.5: 0.5
White solid, 2.5 g, 76% yield
^{1}H NMR (400 MHz, $CDCl_3$) (keto: enol = 1: 5) Signals corresponding to enol form δ 12.33 (s, 1H), 7.48 (dd, J = 9.5, 2.7 Hz, 1H), 7.12 (dd, J = 8.3, 5.4 Hz, 1H), 7.01 (td, J = 8.4, 2.7 Hz, 1H), 3.83 (s, 3H), 2.77 (t, J = 7.8 Hz, 2H), 2.56 (dd, J = 8.8, 6.5 Hz, 2H). Signals corresponding to keto form δ 7.70 (dd, J = 9.0, 2.7 Hz, 1H), 7.24 – 7.18 (m, 2H), 3.78 (s, 3H), 3.64 – 3.59 (m, 1H), 3.10 – 2.90 (m, 2H), 2.53 – 2.45 (m, 1H), 2.39 – 2.32 (m, 1H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 192.2, 173.1, 170.5, 164.0, 161.9 (d, $^1J_{CF}$ = 245.4 Hz), 161.3 (d, $^1J_{CF}$ = 248.5 Hz), 139.5, 134.9, 133.3, 131.8 (d, $^3J_{CF}$ = 7.0 Hz) 130.8 (d, $^3J_{CF}$ = 7.0 Hz), 128.8 (d, $^3J_{CF}$ = 7.0 Hz), 121.4 (d, $^2J_{CF}$ = 22.2 Hz), 117.2 (d, $^2J_{CF}$ = 21.2 Hz), 113.7 (d, $^2J_{CF}$ = 22.2 Hz), 111.4 (d, $^2J_{CF}$ = 24.2 Hz), 97.8, 54.1, 52.6, 51.9, 27.1, 27.0, 26.5, 20.8.
^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -115.73.

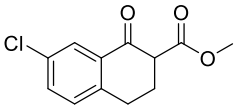
Methyl 6-bromo-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (11h)



Chemical Formula: $C_{12}H_{11}BrO_3$

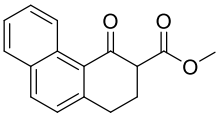
Molecular Weight: 283.12 g/mol
Column chromatography, eluent petroleum ether/ethyl acetate 9.5: 0.5
White solid, 1.2 g, 80% yield
^{1}H NMR (400 MHz, $CDCl_3$) (keto: enol = 1: 6) Signals corresponding to enol form δ 12.35 (s, 1H), 7.65 (d, J = 8.3 Hz, 1H), 7.43 – 7.38 (m, 1H), 7.34 – 7.32 (m, 1H), 3.83 (s, 3H), 2.79 (dd, J = 8.9, 6.7 Hz, 2H), 2.61 – 2.53 (m, 2H). Signals corresponding to keto form δ 7.90 (d, J = 8.3 Hz, 1H), 7.48 – 7.43 (m, 2H), 3.78 (s, 3H), 3.65 – 3.58 (m, 1H), 3.09 – 2.91 (m, 2H), 2.53 – 2.44 (m, 1H), 2.35 (m, 1H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) Signals corresponding to both forms δ 173.0, 164.3, 145.4, 141.4, 136.3, 131.9, 130.7, 130.6, 129.9, 129.6, 129.5, 129.1, 129.0, 126.1, 125.0, 97.2, 54.2, 52.6, 51.9, 27.7, 27.4, 26.3, 20.5.
HRMS (APCI) m/z : Calculated for $C_{12}H_{11}BrO_3H$ $[M+H]^+$: 282.9970. Found 282.9965.

Methyl 7-chloro-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (11i)[2]



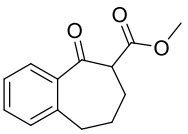
Chemical Formula: $C_{12}H_{11}ClO_3$
Molecular Weight: 238.67 g/mol
Column chromatography, eluent petroleum ether/ethyl acetate 9.5: 0.5
White solid, 2.4 g, 90% yield
^{1}H NMR (400 MHz, $CDCl_3$) (keto: enol = 1: 3) Signals corresponding to enol form δ 12.32 (s, 1H), 7.76 (d, J = 2.2 Hz, 1H), 7.30 – 7.26 (m, 1H), 7.14 – 7.07 (m, 1H), 3.83 (s, 3H), 2.77 (dd, J = 8.9, 6.6 Hz, 2H), 2.59 – 2.53 (m, 2H). Signals corresponding to keto form δ 8.00 (d, J = 2.3 Hz, 1H), 7.45 (dd, J = 8.2, 2.3 Hz, 1H), 7.22 – 7.18 (m, 1H), 3.78 (s, 3H), 3.62 (m, 1H), 3.09 – 2.90 (m, 2H), 2.53 – 2.44 (m, 1H), 2.35 (m, 1H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) Signals corresponding to both forms δ 192.1, 172.9, 170.4, 163.8, 141.9, 137.6, 133.9, 133.3, 133.0, 132.7, 131.6, 130.5, 130.4, 128.8, 127.6, 124.5, 97.8, 54.1, 52.6, 51.9, 27.3, 27.1, 26.3, 20.6.

Methyl 4-oxo-1,2,3,4-tetrahydrophenanthrene-3-carboxylate (11j)



Chemical Formula: $C_{16}H_{14}O_3$
Molecular Weight: 254.28 g/mol
Column chromatography, eluent petroleum ether/ethyl acetate 9: 1
White solid, 1.2 g, 75% yield
^{1}H NMR (400 MHz, $CDCl_3$) (only keto form) δ 9.34 (dq, J = 8.7, 0.9 Hz, 1H), 7.94 (d, J = 8.4 Hz, 1H), 7.84 – 7.77 (m, 1H), 7.63 (ddd, J = 8.6, 6.9, 1.5 Hz, 1H), 7.50 (ddd, J = 8.1, 6.9, 1.2 Hz, 1H), 7.29 (d, J = 8.4 Hz, 1H), 3.80 (s, 3H), 3.77 (dd, J = 10.5, 4.8 Hz, 1H), 3.30 – 3.10 (m, 2H), 2.59 (m, 1H), 2.48 – 2.37 (m, 1H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 195.5, 171.0, 146.1, 134.9, 132.9, 131.5, 129.2, 128.5, 126.9, 126.6, 126.6, 126.3, 56.2, 52.5, 29.5, 26.2.
HRMS (APCI) m/z : Calculated for $C_{16}H_{14}O_3H$ $[M+H]^+$: 255.1021. Found 255.1019.

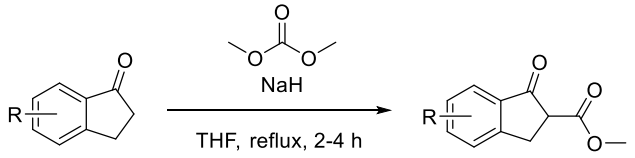
Methyl 5-oxo-6,7,8,9-tetrahydro-5H-benzo[7]annulene-6-carboxylate (11l)[1]



Chemical Formula: $C_{13}H_{14}O_3$
Molecular Weight: 218.25 g/mol
Column chromatography, eluent petroleum ether/ethyl acetate 10: 0.2
Colorless oil, 1.5 g, 70% yield

In accordance with the literature: **^{1}H NMR** (400 MHz, $CDCl_3$) (keto: enol = 1: 2) Signals corresponding to enol form δ 12.61 (s, 1H), 7.65 – 7.60 (m, 1H), 7.38 – 7.29 (m, 2H), 7.24 – 7.19 (m, 1H), 3.83 (s, 3H), 2.64 (t, J = 6.7 Hz, 2H), 2.25 – 1.99 (m, 4H). Signals corresponding to keto form δ 7.75 (dd, J = 7.8, 1.5 Hz, 1H), 7.43 (td, J = 7.5, 1.5 Hz, 1H), 7.38 – 7.29 (m, 1H), 7.24 – 7.19 (m, 1H), 3.76 (s, 3H), 2.98 – 2.92 (m, 2H), 2.25 – 1.99 (m, 4H), 1.89 – 1.78 (m, 1H).
^{13}C{1H} NMR (101 MHz, $CDCl_3$) Signals corresponding to both forms δ 200.7, 173.5, 170.9, 170.6, 141.4, 141.2, 138.1, 135.8, 132.6, 130.2, 130.0, 129.3, 129.1, 127.3, 126.9, 126.5, 100.3, 56.7, 52.4, 51.9, 33.6, 32.9, 31.9, 25.5, 24.5, 21.9.

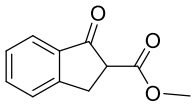
3.b. General method B (**11m – 11t**)[3]



11m–11t

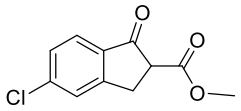
To a solution of NaH (60%, suspension in oil, 1.3 g, 33 mmol, 2.2 equiv.) in abs. THF (33 mL) containing dimethyl carbonate (6.8 g, 75 mmol, 5.0 equiv.) was added dropwise a solution of 1-indanone (1.9 g, 15 mmol, 1.0 equiv.) in abs. THF (15 mL) at room temperature. The reaction mixture was heated to reflux (oil bath) and stirred until the starting material was totally consumed (1-3 h). Ater cooling to room temperature, 1 M HCl aqueous solution was added and the mixture was extracted with ethyl acetate three times. The combined organic layers were dried with $MgSO_4$, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (petroleum ether/ ethyl acetate 9: 1) to give methyl β-keto ester **11m**.

Methyl 1-oxo-2,3-dihydro-1H-indene-2-carboxylate (11m)[3]



Chemical Formula: $C_{11}H_{10}O_3$
Molecular Weight: 190.20 g/mol
Column chromatography, eluent petroleum ether/ethyl acetate 9: 1
Brown oil, 1.9 g, 70% yield
In accordance with the literature: **^{1}H NMR** (400 MHz, $CDCl_3$) (keto: enol = 5: 1) Signals corresponding to enol form δ 10.37 (s, 1H), 7.67 – 7.63 (m, 1H), 7.49 – 7.46 (m, 1H), 7.43 – 7.41 (m, 1H), 7.43 – 7.41 (m, 1H), 3.86 (s, 3H), 3.52 (d, J = 0.7 Hz, 2H). Signals corresponding to keto form δ 7.78 (dd, J = 7.7, 0.5 Hz, 1H), 7.63 (td, J = 7.5, 1.3 Hz, 1H), 7.50 (dt, J = 7.8, 1.0 Hz, 1H), 7.41 – 7.37 (m, 1H), 3.79 (s, 3H), 3.74 (dd, J = 8.3, 4.1 Hz, 1H), 3.57 (m, 1H), 3.42 – 3.34 (m, 1H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) Signals corresponding to both forms δ 199.6, 169.7, 153.7, 135.6, 135.4, 129.6, 128.0, 127.0, 126.7, 124.9, 120.9, 53.3, 52.9, 51.4, 32.7, 30.4.

Methyl 5-chloro-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (11n) [3]

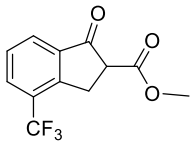


Chemical Formula: $C_{11}H_9ClO_3$
Molecular Weight: 224.64 g/mol
Column chromatography, eluent petroleum ether/ethyl acetate 9: 1

[3] K. Matsuzaki, K. Okuyama, E. Tokunaga, M. Shiro and N. Shibata, *ChemistryOpen*, **2014**, *3*, 233.

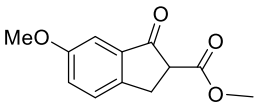
Yellow solid, 1.2 g, 45% yield,
In accordance with the literature: **^{1}H NMR** (400 MHz, $CDCl_3$) (keto: enol = 3.6 : 1) Signals corresponding to enol form *δ* 10.33 (s, 1H), 7.56 (dd, *J* = 8.2, 0.6 Hz, 1H), 7.47 – 7.45 (m, 1H), 7.41 – 7.35 (m, 1H), 3.86 (s, 3H), 3.51 (t, *J* = 0.7 Hz, 2H). Signals corresponding to keto form *δ* 7.71 (dd, *J* = 8.2, 0.6 Hz, 1H), 7.52 – 7.50 (m, 1H), 7.41 – 7.35 (m, 1H), 3.80 (s, 3H), 3.78 – 3.73 (m, 1H), 3.59 – 3.52 (m, 1H), 3.35 (ddq, *J* = 17.5, 8.3, 0.7 Hz, 1H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) Signals corresponding to both forms *δ* 198.0, 169.3, 155.1, 144.8, 142.3, 135.8, 135.5, 133.8, 128.9, 127.5, 126.9, 125.9, 125.3, 121.8, 102.6, 53.3, 53.0, 51.5, 32.5, 30.1.

Methyl 1-oxo-4-(trifluoromethyl)-2,3-dihydro-1H-indene-2-carboxylate (11o)



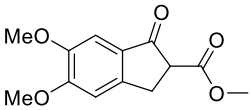
Chemical Formula: $C_{12}H_9F_3O_3$
Molecular Weight: 258.20 g/mol
Column chromatography, eluent petroleum ether/ethyl acetate 9.5: 0.5
White solid, 795 mg, 62% yield,
^{1}H NMR (400 MHz, $CDCl_3$) (keto: enol = 1 : 1.3) Signals corresponding to enol form *δ* 10.28 (s, 1H), 7.82 (d, *J* = 7.6 Hz, 1H), 7.67 (dt, *J* = 7.7, 0.9 Hz, 1H), 7.57 – 7.50 (m, 1H), 3.88 (s, 3H), 3.72 (*J* = 1.8 Hz, 2H), Signals corresponding to keto form *δ* 7.97 (d, *J* = 7.7 Hz, 1H), 7.90 (dt, *J* = 7.6, 1.0 Hz, 1H), 7.57 – 7.50 (m, 1H), 3.82 (s, 3H), 3.81 – 3.78 (m, 1H), 3.77 – 3.70 (m, 1H), 3.58 (dd, *J* = 17.9, 8.3 Hz, 1H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) *δ* 198.2, 169.4, 168.9, 150.9, 140.5, 138.7, 136.9, 132.2 (d, $^3J_{CF}$ = 5.1 Hz), 128.5, 128.3, 127.6, 126.1 (d, $^3J_{CF}$ = 5.1 Hz), 125.6 (q, $^1J_{CF}$ = 274.7 Hz), 125.1 (q, $^1J_{CF}$ = 274.7 Hz), 124.2, 103.3, 77.4, 53.1, 52.9, 51.6, 32.1, 29.3.
HRMS (APCI) m/z : Calculated for $C_{12}H_9F_3O_3H$ $[M+H]^+$: 259.0582. Found 259.0578.

Methyl 6-methoxy-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (11p)[3]



Chemical Formula: $C_{12}H_{12}O_4$
Molecular Weight: 220.22 g/mol
White solid, 1.5 g, 75% yield
Column chromatography, eluent petroleum ether/ethyl acetate 9: 1
In accordance with the literature **^{1}H NMR** (400 MHz, $CDCl_3$) (keto: enol = 7 : 1) Signals corresponding to enol form *δ* 10.38 (br, 1H), 7.35 (dq, *J* = 8.3, 0.7 Hz, 1H), 7.15 (d, *J* = 2.5 Hz, 1H), 7.01 – 6.97 (m, 1H), 3.86 (s, 3H), 3.85 (s, 3H), 3.50 – 3.44 (m, 2H). Signals corresponding to keto form *δ* 7.39 (dt, *J* = 8.2, 0.8 Hz, 1H), 7.24 – 7.18 (m, 2H), 3.83 (d, *J* = 0.7 Hz, 3H), 3.79 (d, *J* = 0.7 Hz, 3H), 3.76 (ddd, *J* = 8.1, 3.9, 0.7 Hz, 1H), 3.51 – 3.43 (m, 1H), 3.30 (dd, *J* = 16.9, 8.1 Hz, 1H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) Signals corresponding to keto form *δ* 199.5, 169.7, 159.9, 146.7, 136.6, 127.4, 125.2, 105.8, 55.8, 54.0, 52.9, 29.8.

Methyl 5,6-dimethoxy-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (11q)[4]

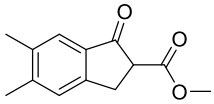


Chemical Formula: $C_{13}H_{14}O_5$
Molecular Weight: 250.25 g/mol
Column chromatography, eluent petroleum ether/ethyl acetate 6: 4
White solid, 1.1 g, 80% yield

[4] A. Granados, P. Sarro and A. Vallribera, *Molecules*, **2019**, *24*, 1141.

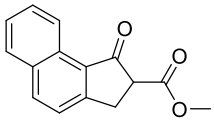
^{1}H NMR (400 MHz, $CDCl_3$) (only keto form) δ 7.17 (s, 1H), 6.90 (s, 1H), 3.97 (s, 3H), 3.90 (s, 3H), 3.78 (s, 3H), 3.72 (dd, *J* = 7.9, 3.6 Hz, 1H), 3.45 (ddd, *J* = 17.0, 3.6, 0.9 Hz, 1H), 3.27 (ddd, *J* = 17.0, 7.9, 0.9 Hz, 1H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 198.0, 170.0, 156.3, 149.9, 149.4, 128.1, 107.4, 104.9, 56.5, 56.3, 53.5, 52.9, 30.2.

Methyl 5,6-dimethyl-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (11r)



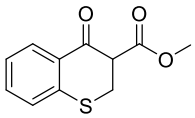
Chemical Formula: $C_{13}H_{14}O_3$
Molecular Weight: 218.25 g/mol
Column chromatography, eluent petroleum ether/ethyl acetate 9: 1
Orange solid, 1.2 g, 75% yield
^{1}H NMR (400 MHz, $CDCl_3$) (only keto form) δ 7.53 (s, 1H), 7.27 (s, 1H), 3.78 (s, 3H), 3.70 (dd, *J* = 8.2, 3.9 Hz, 1H), 3.47 (dd, *J* = 17.3, 3.8 Hz, 1H), 3.28 (dd, *J* = 17.1, 8.2 Hz, 1H), 2.35 (s, 3H), 2.30 (s, 3H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 199.3, 170.0, 151.9, 146.1, 137.0, 133.5, 127.4, 125.1, 53.6, 52.8, 30.0, 20.9, 19.9.
HRMS (APCI) m/z Calculated for $C_{13}H_{14}O_3H$ $[M+H]^+$: 219.1021. Found 219.1018.

Methyl 1-oxo-2,3-dihydro-1H-cyclopenta[a]naphthalene-2-carboxylate (11s)[5]



Chemical Formula: $C_{15}H_{12}O_3$
Molecular Weight: 240.26 g/mol
Column chromatography, eluent petroleum ether/ethyl acetate 8: 2
Yellow solid, 1.3 g, 84% yield
^{1}H NMR (400 MHz, $CDCl_3$) (only keto form) δ 9.07 (d, *J* = 8.3 Hz, 1H), 8.08 (d, *J* = 8.4 Hz, 1H), 7.90 (d, *J* = 8.1 Hz, 1H), 7.68 (ddd, *J* = 8.3, 7.0, 1.4 Hz, 1H), 7.61 – 7.51 (m, 2H), 3.86 (dd, *J* = 7.8, 3.5 Hz, 1H), 3.82 (s, 3H), 3.65 (dd, *J* = 17.6, 3.6 Hz, 1H), 3.45 (dd, *J* = 17.6, 7.8 Hz, 1H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 199.8, 169.9, 157.4, 136.8, 132.9, 129.7, 129.4, 128.4, 127.0, 124.0, 123.8, 53.8, 52.9, 30.7.

Methyl 4-oxothiochromane-3-carboxylate (11t)[6]



Chemical Formula: $C_{11}H_{10}O_3S$
Molecular Weight: 222.26 g/mol
Column chromatography, eluent petroleum ether/ethyl acetate 9: 1
Yellow solid, 300 mg, 45% yield
^{1}H NMR (400 MHz, $CDCl_3$) (only enol form) δ 12.66 (s, 1H), 7.85 (dt, *J* = 7.7, 1.1 Hz, 1H), 7.31 – 7.25 (m, 2H), 7.23 – 7.17 (m, 1H), 3.85 (s, 3H), 3.72 (s, 2H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 171.8, 165.9, 137.3, 131.1, 129.3, 127.4, 126.9, 125.7, 93.8, 52.2, 23.5.

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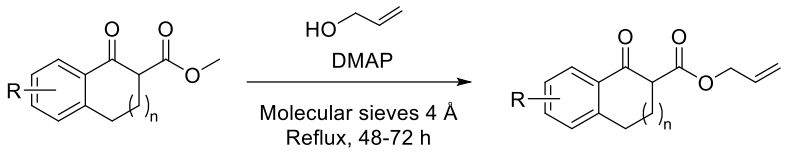
[5] Y. Zhang, Y. Du, Y.-B. Chen, J.-H. Nie, Y. Xiong, B.-D. Cui, X.-Q. Mou, M.-Q. Zou and Y.-Z. Chen, *React. Chem. Eng.*, **2025**, *10*, 306.
[6] I. Matthews, T. Coulter, C. Ghiron, C. Brennan, M. Uddin, L. Pettersson, D. Thrige and P. Huxley, *WO2004048378 A1*, **2004**, Active Biotech AB.

4. General method for the synthesis of compounds **12a-12t**

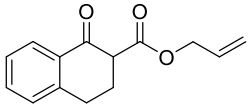
4.a. General method C (**12a – 12l**)[7]



11a–11l **12a–12l**

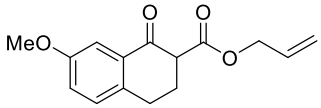
To a solution of β-keto ester **11a** (5.0 g, 24.5 mmol, 1.0 equiv.) in allyl alcohol (122.5 mL, 0.2 M) was added DMAP (4.5 g, 36.8 mmol, 1.5 equiv.) and molecular sieves (4 Å) (12 g). The reaction mixture was stirred and heated to reflux (oil bath) until full conversion (48 – 96 h). The reaction was monitored by ^{1}H NMR analysis. After cooling to room temperature, a saturated aqueous NH_4Cl solution was added and the mixture was extracted with ethyl acetate (3 times). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate 9.8: 0.2) to give allyl β-keto ester **12a.**

Allyl 1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (12a)[7]



Chemical Formula: $C_{14}H_{14}O_3$
Molecular Weight: 230.26 g/mol
Column chromatography, eluent petroleum ether/ethyl acetate 9.8: 0.2
Colorless oil, 3.0 g, 55% yield
In accordance with the literature: **^{1}H NMR** (400 MHz, $CDCl_3$) (keto: enol = 1:12) Signals corresponding to enol form *δ* 12.40 (s, 1H), 7.81 (dd, *J* = 7.5, 1.7 Hz, 1H), 7.39 – 7.22 (m, 2H), 7.22 – 7.12 (m, 1H), 6.08 – 5.86 (m, 1H), 5.43 – 5.19 (m, 2H), 4.80 – 4.63 (m, 2H), 2.82 (m, 2H), 2.61 (m, 2H). Signals corresponding to keto form *δ* 8.06 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.50 – 7.48 (m, 1H), 7.39 – 7.22 (m, 2H), 6.08 – 5.86 (m, 1H), 5.43 – 5.19 (m, 2H), 4.80 – 4.63 (m, 2H), 3.65 (dd, *J* = 10.5, 4.7 Hz, 1H), 3.13 – 2.95 (m, 2H), 2.58 – 2.47 (m, 1H), 2.38 (dq, *J* = 13.5, 5.0 Hz, 1H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) Signals corresponding to enol form *δ* 172.5, 165.5, 139.6, 132.4, 130.7, 130.1, 127.6, 126.7, 124.5, 118.3, 97.0, 65.2, 27.9, 20.7.

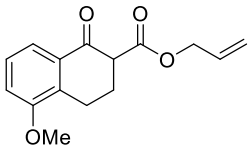
Allyl 7-methoxy-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (12b)



Chemical Formula: $C_{15}H_{16}O_4$
Molecular Weight: 260.29 g/mol
Column chromatography, eluent petroleum ether/ethyl acetate 9.5: 0.5
Colorless oil, 1.3 g, 60% yield
^{1}H NMR (400 MHz, $CDCl_3$) (keto: enol = 1.4: 1) Signals corresponding to enol form *δ* 12.42 (s, 1H), 7.34 (d, *J* = 2.7 Hz, 1H), 7.12 – 7.03 (m, 1H), 6.88 (dd, *J* = 8.2, 2.8 Hz, 1H), 6.07 – 5.87 (m, 1H), 5.43 – 5.19 (m, 2H), 4.77 – 4.61 (m, 2H), 3.83 (s, 3H), 2.76 – 2.72 (m, 2H), 2.62 – 2.55 (m, 2H). Signals corresponding to keto form *δ* 7.51 (d, *J* = 2.8 Hz, 1H), 7.15 (m, 1H), 7.12 – 7.03 (m, 1H), 6.07 – 5.87 (m, 1H), 5.43 – 5.19 (m, 2H), 4.77 – 4.61 (m, 2H), 3.82 (s, 3H), 3.61 (dd, *J* = 10.4, 4.7 Hz, 1H), 3.05 – 2.85 (m, 2H), 2.49 – 2.44 (m, 1H), 2.38 – 2.31 (m, 1H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) Signals corresponding to both forms *δ* 193.2, 172.5, 170.1, 165.4, 158.6, 158.5, 136.4, 132.6, 132.3, 131.9, 131.7, 130.9, 130.1, 128.5, 122.5, 118.6, 118.2, 117.2, 109.6, 108.9, 97.2, 65.9, 65.2, 55.6, 55.6, 54.5, 27.0, 26.8, 20.9.
HRMS (APCI) m/z Calculated for $C_{15}H_{16}O_4Na$ $[M+Na]^+$: 283.0943. Found 283.0943.

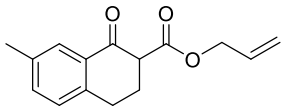
[7] T. Boddaert, Y. Coquerel and J. Rodriguez, *Eur. J. Org. Chem.*, **2011**, *26*, 5061.

Allyl 5-methoxy-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (12c)



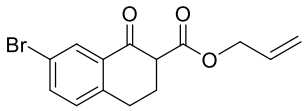
Chemical Formula: $C_{15}H_{16}O_4$
Molecular Weight: 260.29 g/mol
Column chromatography, eluent petroleum ether/ethyl acetate 9.5: 0.5
Pale yellow oil, 1.3 g, 60% yield
^{1}H NMR (400 MHz, $CDCl_3$) (keto: enol = 1.3: 1) Signals corresponding to enol form δ 12.38 (s, 1H), 7.45 (dd, J = 7.8, 1.1 Hz, 1H), 7.35 – 7.20 (m, 1H), 6.94 (dd, J = 8.2, 1.1 Hz, 1H), 6.08 – 5.86 (m, 1H), 5.43 – 5.19 (m, 2H), 4.78 – 4.62 (m, 2H), 3.85 (s, 3H), 2.86 – 2.74 (m, 2H), 2.57 (dd, J = 8.8, 7.1 Hz, 2H). Signals corresponding to keto form δ 7.66 (dd, J = 7.9, 1.1 Hz, 1H), 7.35 – 7.20 (m, 1H), 7.04 (dd, J = 8.1, 1.2 Hz, 1H), 6.08 – 5.86 (m, 1H), 5.43 – 5.19 (m, 2H), 4.78 – 4.62 (m, 2H), 3.87 (s, 3H), 3.62 (dd, J = 10.7, 4.7 Hz, 1H), 3.10 (dt, J = 17.9, 5.1 Hz, 1H), 2.86 – 2.74 (m, 1H), 2.51 – 2.42 (m, 1H), 2.40 – 2.32 (m, 1H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) Signals corresponding to both forms δ 193.5, 172.5, 170.1, 165.5, 156.8, 156.0, 132.9, 132.8, 132.4, 131.9, 131.1, 127.9, 127.2, 127.0, 119.4, 118.6, 118.3, 116.9, 114.8, 112.9, 96.9, 65.9, 65.2, 55.8, 55.8, 54.3, 25.7, 21.4, 20.1, 20.0.
HRMS (APCI) m/z Calculated for $C_{15}H_{16}O_4H$ $[M+H]^+$: 261.1127. Found 261.1125.

Allyl 7-methyl-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (12d)



Chemical Formula: $C_{15}H_{16}O_3$
Molecular Weight: 244.29 g/mol
Column chromatography, eluent petroleum ether/ethyl acetate 9.5: 0.5
Colorless oil, 800 mg, 36% yield
^{1}H NMR (400 MHz, $CDCl_3$) (keto: enol = 1: 1.4) Signals corresponding to enol form δ 12.41 (s, 1H), 7.63 (d, J = 1.8 Hz, 1H), 7.16 – 7.13 (m, 1H), 7.08 – 7.06 (m, 1H), 6.07 – 5.85 (m, 1H), 5.32 – 5.22 (m, 2H), 4.73 (dt, J = 5.6, 1.5 Hz, 2H), 2.84 – 2.71 (m, 2H), 2.63 – 2.55 (m, 2H), 2.36 (s, 3H). Signals corresponding to keto form δ 7.86 (d, J = 1.9 Hz, 1H), 7.31 (dd, J = 7.8, 2.0 Hz, 1H), 7.16 – 7.13 (m, 1H), 6.07 – 5.85 (m, 1H), 5.42 – 5.35 (m, 2H), 4.70 – 4.68 (m, 2H), 3.62 (dd, J = 10.4, 4.7 Hz, 1H), 3.09 – 2.89 (m, 2H), 2.50 (m, 1H), 2.39 – 2.32 (m, 4H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) Signals corresponding to both forms δ 193.7, 172.8, 170.4, 166.1, 141.2, 137.1, 136.9, 136.6, 135.4, 132.7, 132.3, 131.9, 131.8, 130.2, 129.2, 128.2, 127.8, 125.3, 118.9, 118.6, 97.3, 66.2, 65.5, 55.1, 27.8, 27.7, 27.0, 21.6, 21.4, 21.1.
HRMS (APCI) m/z Calculated for $C_{15}H_{16}O_3Na$ $[M+Na]^+$: 267.0997. Found 267.0996.

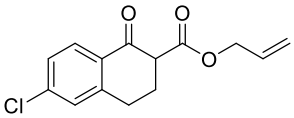
Allyl 7-bromo-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (12e)



Chemical Formula: $C_{14}H_{13}BrO_3$
Molecular Weight: 309.16 g/mol
Column chromatography, eluent petroleum ether/ethyl acetate 9.5: 0.5
White solid, 600 mg, 26% yield
^{1}H NMR (400 MHz, $CDCl_3$) (keto: enol = 1: 2) Signals corresponding to enol form δ 12.31 (s, 1H), 7.93 (d, J = 2.1 Hz, 1H), 7.44 (dd, J = 8.0, 2.1 Hz, 1H), 7.05 (dt, J = 8.0, 1.0 Hz, 1H), 6.06 – 5.87 (m, 1H), 5.43 – 5.22 (m, 2H), 4.74 (dt, J = 5.6, 1.5 Hz, 2H), 2.79 – 2.75 (m, 2H), 2.64 – 2.56 (m, 2H). Signals corresponding to keto form δ 8.17 (d, J = 2.2 Hz, 1H), 7.60 (dd, J = 8.2, 2.2 Hz, 1H), 7.15 (d, J = 8.2 Hz, 1H), 6.06 – 5.87 (m, 1H), 5.43 – 5.22 (m, 2H), 4.71 – 4.67 (m, 2H), 3.63 (dd, J = 10.0, 4.8 Hz, 1H), 3.08 – 2.90 (m, 2H), 2.56 – 2.46 (m, 1H), 2.42 – 2.32 (m, 1H).

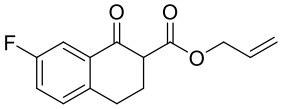
$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) Signals corresponding to both forms δ 192.3, 172.3, 169.7, 164.6, 159.7, 145.4, 141.5, 132.2, 131.9, 131.8, 130.7, 130.6, 129.9, 129.6, 129.4, 129.1, 126.1, 125.1, 118.8, 118.4, 97.2, 66.1, 65.4, 54.4, 27.6, 27.5, 26.3, 20.5.
HRMS (APCI) m/z Calculated for $C_{14}H_{13}BrO_3Na$ $[M+Na]^+$: 330.9946. Found 330.9943.

Allyl 6-chloro-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (12f)



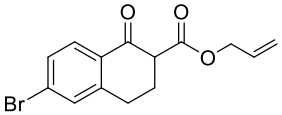
Chemical Formula: $C_{14}H_{13}ClO_3$
Molecular Weight: 264.70 g/mol
Column chromatography, eluent petroleum ether/ethyl acetate 9.5: 0.5
Orange oil, 350 mg, 28% yield
^1H NMR (400 MHz, $CDCl_3$) (keto: enol = 1: 3) Signals corresponding to enol form δ 12.36 (s, 1H), 7.72 (d, J = 8.3 Hz, 1H), 7.33 – 7.23 (m, 1H), 7.18 – 7.17 (m, 1H), 6.04 – 5.93 (m, 1H), 5.43 – 5.22 (m, 2H), 4.73 (dt, J = 5.5, 1.5 Hz, 2H), 2.82 – 2.77 (m, 2H), 2.64 – 2.57 (m, 2H). Signals corresponding to keto form δ 7.99 (d, J = 8.4 Hz, 1H), 7.33 – 7.23 (m, 2H), 5.94 – 5.88 (m, 1H), 5.43 – 5.22 (m, 2H), 4.71 – 4.67 (m, 2H), 3.63 (dd, J = 10.1, 4.7 Hz, 1H), 3.11 – 2.92 (m, 2H), 2.56 – 2.46 (m, 1H), 2.47 – 2.34 (m, 1H).
$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) Signals corresponding to both forms δ 192.1, 172.2, 169.7, 164.5, 145.3, 141.2, 140.4, 136.5, 132.2, 131.8, 130.3, 129.5, 128.8, 128.8, 127.7, 127.6, 126.9, 125.9, 118.7, 118.4, 97.1, 66.0, 65.3, 54.4, 27.7, 27.5, 26.3, 20.5.
HRMS (APCI) m/z : Calculated for $C_{14}H_{13}ClO_3H$ $[M+H]^+$: 265.0631. Found 265.0634.

Allyl 7-fluoro-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (12g)



Chemical Formula: $C_{14}H_{13}FO_3$
Molecular Weight: 248.25 g/mol
Column chromatography, eluent petroleum ether/ethyl acetate 9.5: 0.5
Colorless oil, 320 mg, 20% yield
^1H NMR (400 MHz, $CDCl_3$) (keto: enol = 1: 2) Signals corresponding to enol form δ 12.32 (s, 1H), 7.49 (dd, J = 9.5, 2.8 Hz, 1H), 7.13 (dd, J = 8.3, 5.4 Hz, 1H), 7.01 (td, J = 8.4, 2.7 Hz, 1H), 6.07 – 5.87 (m, 1H), 5.43 – 5.21 (m, 2H), 4.74 (dt, J = 5.6, 1.5 Hz, 2H), 2.78 (dd, J = 9.1, 6.4 Hz, 2H), 2.67 – 2.54 (m, 2H). Signals corresponding to keto form δ 7.71 (dd, J = 9.0, 2.7 Hz, 1H), 7.25 – 7.15 (m, 2H), 6.07 – 5.87 (m, 1H), 5.43 – 5.21 (m, 2H), 4.72 – 4.68 (m, 2H), 3.69 – 3.60 (m, 1H), 3.10 – 2.88 (m, 2H), 2.54 – 2.47 (m, 1H), 2.41 – 2.34 (m, 1H).
$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$)) Signals corresponding to both forms δ 192.2, 172.3, 169.7, 164.3, 161.8 (d, $^1J_{CF}$ = 245.4 Hz), 161.7 (d, $^1J_{CF}$ = 247.5 Hz) 134.9, 134.2, 131.8 (d, $^3J_{CF}$ = 7.1 Hz), 130.8 (d, $^3J_{CF}$ = 7.2 Hz), 130.0 (d, $^3J_{CF}$ = 8.6 Hz), 128.9 (d, $^3J_{CF}$ = 7.9 Hz), 123.7, 119.1, 118.8, 118.5, 118.4, 117.4 (d, $^2J_{CF}$ = 21.7 Hz), 113.7 (d, $^2J_{CF}$ = 22.2 Hz), 111.4 (d, $^2J_{CF}$ = 23.6 Hz), 108.0 (d, $^2J_{CF}$ = 22.7 Hz), 66.1, 65.4, 54.3, 27.1, 27.1, 26.6, 20.8.
$^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$) δ -115.71.
HRMS (APCI) m/z : Calculated for $C_{14}H_{13}FO_3H$ $[M + H]^+$: 249.0927. Found 249.0922.

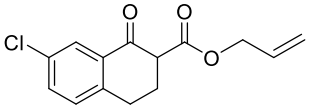
Allyl 6-bromo-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (12h)



Chemical Formula: $C_{14}H_{13}BrO_3$
Molecular Weight: 308.00 g/mol
Column chromatography, eluent petroleum ether/ethyl acetate 9.5: 0.5
Colorless oil, 300 mg, 25% yield

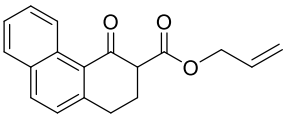
^{1}H NMR (400 MHz, $CDCl_3$) (keto: enol = 1: 2) Signals corresponding to enol form δ 12.34 (s, 1H), 7.65 (d, J = 8.3 Hz, 1H), 7.49 – 7.39 (m, 1H), 7.33 (m, 1H), 6.05 – 5.95 (m, 1H), 5.44 – 5.30 (m, 2H), 4.73 (dt, J = 5.6, 1.5 Hz, 2H), 2.79 (m, 2H), 2.63 – 2.57 (m, 2H). Signals corresponding to keto form δ 7.90 (d, J = 8.3 Hz, 1H), 7.49 – 7.39 (m, 2H), 5.95 – 5.87 (m, 1H), 5.30 – 5.23 (m, 2H), 4.72 – 4.67 (m, 2H), 3.63 (dd, J = 10.1, 4.8 Hz, 1H), 3.10 – 2.92 (m, 2H), 2.57 – 2.44 (m, 1H), 2.40 – 2.33 (m, 1H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) Signals corresponding to both forms δ 192.3, 172.3, 169.7, 164.6, 159.7, 145.4, 141.5, 132.2, 131.9, 131.8, 130.7, 130.6, 129.9, 129.6, 129.4, 129.1, 126.1, 125.1, 118.8, 118.4, 97.2, 66.1, 65.4, 54.4, 27.6, 27.5, 26.3, 20.5.
HRMS (APCI) m/z : Calculated for $C_{14}H_{13}BrO_3H$ $[M + H]^+$: 309.0126. Found 309.0122.

Allyl 7-chloro-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (12i)



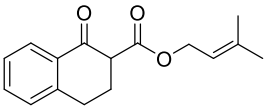
Chemical Formula: $C_{14}H_{13}ClO_3$
Molecular Weight: 264.70 g/mol
Column chromatography, eluent petroleum ether/ethyl acetate 9.5: 0.5
Yellow oil, 300 mg, 23% yield
^{1}H NMR (400 MHz, $CDCl_3$) (keto: enol = 1: 2) Signals corresponding to enol form δ 12.32 (d, J = 2.6 Hz, 1H), 7.77 (d, J = 2.3 Hz, 1H), 7.31 – 7.26 (m, 1H), 7.10 (dt, J = 8.2, 1.1 Hz, 1H), 6.06 – 5.94 (m, 1H), 5.44 – 5.20 (m, 2H), 4.73 (dt, J = 5.6, 1.5 Hz, 2H), 2.80 – 2.75 (m, 2H), 2.64 – 2.54 (m, 2H). Signals corresponding to keto form δ 8.00 (t, J = 1.9 Hz, 1H), 7.45 (dd, J = 8.2, 2.4 Hz, 1H), 7.21 (dd, J = 8.2, 1.1 Hz, 1H), 5.96 – 5.87 (m, 1H), 5.31 – 5.20 (m, 2H), 4.72 – 4.64 (m, 2H), 3.65 – 3.59 (m, 1H), 3.09 – 2.90 (m, 2H), 2.54 – 2.45 (m, 1H), 2.42 – 2.31 (m, 1H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) Signals corresponding to both forms δ 192.0, 172.2, 169.6, 164.1, 141.9, 137.7, 133.9, 133.3, 133.1, 132.7, 132.2, 131.8, 131.6, 130.5, 130.4,128.8, 127.6, 124.5, 118.8, 118.5, 97.8, 66.1, 65.4, 54.3, 27.3, 27.2, 26.3, 20.6.
HRMS (APCI) m/z : Calculated for $C_{14}H_{13}ClO_3H$ $[M + H]^+$: 265.0631. Found 265.0628.

Allyl 4-oxo-1,2,3,4-tetrahydrophenanthrene-3-carboxylate (12j)



Chemical Formula: $C_{18}H_{16}O_3$
Molecular Weight: 280.32 g/mol
Column chromatography, eluent petroleum ether/ethyl acetate 9.5: 0.5
Yellow oil, 200 mg, 10% yield
^{1}H NMR (400 MHz, $CDCl_3$) (keto: enol = 4: 1) Signals corresponding to enol form δ 13.40 (s, 1H), 9.45 – 9.38 (m, 1H), 7.93 – 7.91 (m, 1H), 7.83 – 7.82 (m, 1H), 7.57 – 7.43 (m, 2H), 7.33 (d, J = 2.2 Hz, 1H), 6.09 – 5.99 (m, 1H), 5.43 – 5.29 (m, 2H), 4.78 (dt, J = 5.6, 1.5 Hz, 2H), 3.15 – 3.11 (m, 2H), 2.81 – 2.77 (m, 2H). Signals corresponding to keto form δ 9.34 (dq, J = 8.8, 0.8 Hz, 1H), 7.94 (d, J = 8.5 Hz, 1H), 7.82 – 7.76 (m, 1H), 7.63 (ddd, J = 8.6, 6.8, 1.5 Hz, 1H), 7.57 – 7.43 (m, 1H), 7.30 (d, J = 8.5 Hz, 1H), 5.99 – 5.88 (m, 1H), 5.37 – 5.21 (m, 2H), 4.71 (dq, J = 5.7, 1.2 Hz, 2H), 3.83 – 3.75 (m, 1H), 3.31 – 3.14 (m, 2H), 2.66 – 2.56 (m, 1H), 2.49 – 2.42 (m, 1H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) Signals corresponding to both forms δ 200.6, 195.4, 170.3, 146.9, 145.9, 134.9, 134.3, 132.8, 131.9, 131.5, 129.2, 128.9, 128.7, 128.5, 128.4, 127.1, 126.9, 126.9, 126.8, 126.7, 126.6, 126.3, 125.9, 125.5, 118.5, 118.3, 65.9, 65.3, 56.3, 41.2, 31.7, 30.1, 29.5, 26.2, 23.2, 20.3.
HRMS (APCI) m/z : Calculated for $C_{18}H_{16}O_3H$ $[M + H]^+$: 281.1178. Found 281.1174.

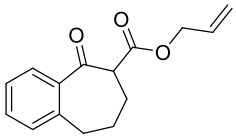
3-methylbut-2-en-1-yl 1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (12k)



Chemical Formula: $C_{16}H_{18}O_3$

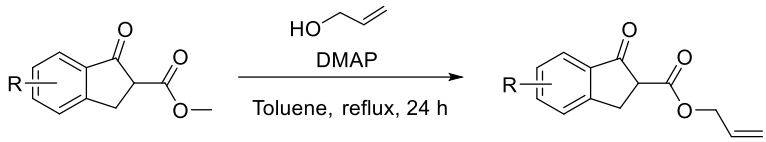
Molecular Weight: 258.32 g/mol
Column chromatography, eluent petroleum ether/ethyl acetate 9.8: 0.2
Pale yellow oil, 120 mg, 10% yield
^{1}H NMR (400 MHz, $CDCl_3$) (keto: enol = 1: 2) Signals corresponding to enol form δ 12.46 (s, 1H), 7.80 (dd, J = 7.5, 1.6 Hz, 1H), 7.37 – 7.26 (m, 2H), 7.18 – 7.15 (m, 1H), 5.47 – 5.30 (m, 1H), 4.73 (dt, J = 7.2, 0.9 Hz, 2H), 2.81 (dd, J = 8.9, 6.6 Hz, 2H), 2.61 – 2.54 (m, 2H), 1.75 (s, 3H), 1.74 (s, 3H). Signals corresponding to keto form δ 8.06 – 8.03 (m, 1H), 7.55 – 7.44 (m, 2H), 7.37 – 7.26 (m, 1H), 5.47 – 5.30 (m, 1H), 4.69 (dt, J = 7.2, 0.9 Hz, 2H), 3.61 (dd, J = 10.3, 4.7 Hz, 1H), 3.06 – 2.98 (m, 2H), 2.54 – 2.46 (m, 1H), 2.40 – 2.31 (m, 1H), 1.79 (s, 3H), 1.77 (s, 3H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) Signals corresponding to both forms δ 193.4, 172.9, 170.4, 165.1, 143.8, 139.6, 139.2, 133.9, 131.9, 130.6, 130.2, 128.9, 127.9, 127.5, 127.0, 126.7, 124.4, 118.8, 118.4, 111.1 97.2, 62.3, 61.6, 54.7, 27.9, 27.8, 26.6, 25.9, 25.9, 20.7, 18.3, 18.2.
HRMS (APCI) m/z : Calculated for $C_{16}H_{18}O_3Na$ $[M + Na]^+$: 281.1154. Found 281.1152.

Allyl 5-oxo-6,7,8,9-tetrahydro-5H-benzo[7]annulene-6-carboxylate (12l)[7]



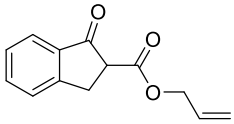
Chemical Formula: $C_{15}H_{16}O_3$
Molecular Weight: 244.29 g/mol
Column chromatography, eluent petroleum ether/ethyl acetate 9.8: 0.2
Pale yellow oil, 890 mg, 80% yield
In accordance with the literature : **^{1}H NMR** (400 MHz, $CDCl_3$) (keto: enol = 1: 3) Signals corresponding to enol form δ 12.59 (s, 1H), 7.66 – 7.61 (m, 1H), 7.38 – 7.29 (m, 2H), 7.24 – 7.19 (m, 1H), 6.01 (m, 1H), 5.42 – 5.21 (m, 2H), 4.75 (dt, J = 5.5, 1.5 Hz, 2H), 2.65 (t, J = 6.9 Hz, 2H), 2.25 – 2.06 (m, 4H). Signals corresponding to keto form δ 7.76 (dd, J = 7.8, 1.5 Hz, 1H), 7.43 (td, J = 7.5, 1.5 Hz, 1H), 7.38 – 7.29 (m, 1H), 7.24 – 7.19 (m, 1H), 5.94 – 5.86 (m, 1H), 5.42 – 5.21 (m, 2H), 4.67 (dq, J = 5.8, 1.2 Hz, 2H), 3.88 – 3.82 (m, 1H), 2.99 – 2.92 (m, 2H), 2.25 – 2.06 (m, 3H), 1.91 – 1.79 (m, 1H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) Signals corresponding to both forms δ 200.6, 172.8, 170.9, 170.4, 141.4, 141.2, 138.2, 135.8, 132.6, 132.4, 132.0, 130.3, 130.0, 129.3, 129.1, 127.3, 126.9, 126.5, 118.7, 118.1, 100.3, 65.9, 65.2, 56.8, 33.7, 33.0, 31.9, 25.5, 24.5, 21.9.

4.b. General method D (**12m – 12t**) [3]



To a solution of β-keto ester **11m** (400 mg, 2.1 mmol, 1.0 equiv.) and DMAP (282 mg, 2.3 mmol, 1.1 equiv.) in toluene (1.6 mL, 1.3 M) was added allyl alcohol (0.43 mL, 6.3 mmol, 3.0 equiv.). The reaction mixture was heated to reflux (oil bath) overnight. A saturated aqueous NH_4Cl solution was added and the mixture was extracted with dichloromethane (3 times). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate 9:1) to give allyl β-keto ester **12m**.

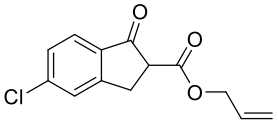
Allyl 1-oxo-2,3-dihydro-1H-indene-2-carboxylate (12m)[3]



Chemical Formula: $C_{13}H_{12}O_3$
Molecular Weight: 216.24 g/mol

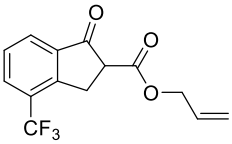
Column chromatography, eluent petroleum ether/ethyl acetate 9: 1
Colorless oil, 250 mg, 55% yield
In accordance with the literature: **^{1}H NMR** (400 MHz, $CDCl_3$) (keto: enol = 5: 1) Signals corresponding to enol form *δ* 10.37 (s, 1H), 7.68 – 7.59 (m, 1H), 7.54 – 7.35 (m, 3H), 6.07 – 6.00 (m, 1H), 5.44 – 5.22 (m, 2H), 4.79 – 4.77 (m, 2H), 3.60 (d, *J* = 4.1 Hz, 2H). Signals corresponding to keto form *δ* 7.78 (d, *J* = 7.7 Hz, 1H), 7.68 – 7.59 (m, 1H), 7.54 – 7.35 (m, 2H), 5.99 – 5.89 (m, 1H), 5.44 – 5.22 (m, 2H), 4.75 – 4.63 (m, 2H), 3.76 (dd, *J* = 8.3, 4.1 Hz, 1H), 3.56 – 3.55 (m, 1H), 3.39 (dd, *J* = 17.3, 8.3 Hz, 1H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) Signals corresponding to both forms *δ* 199.5, 168.9, 153.7, 143.5, 137.0, 135.6, 135.4, 132.5, 131.8, 129.6, 128.0, 127.0, 126.7, 124.9, 120.9, 118.8, 118.3, 102.3, 66.3, 64.8, 53.4, 32.7, 30.4, 1.2.

Allyl 5-chloro-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (12n)[3]



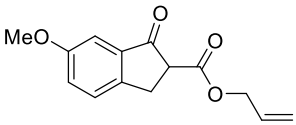
Chemical Formula: $C_{13}H_{11}ClO_3$
Molecular Weight: 250.68 g/mol
Column chromatography, eluent petroleum ether/ethyl acetate 9: 1
Yellow solid, 540 mg, 44% yield
In accordance with the literature: **^{1}H NMR** (400 MHz, $CDCl_3$) (keto: enol = 4: 1) Signals corresponding to enol form *δ* 10.32 (s, 1H), 7.56 (dd, *J* = 8.1, 0.5 Hz, 1H), 7.45 – 7.45 (m, 1H), 7.39 – 7.36 (m, 1H), 6.06 – 5.99 (m, 1H), 5.44 – 5.24 (m, 2H), 4.77 (dt, *J* = 5.7, 1.4 Hz, 2H), 3.58 – 3.56 (m, 2H). Signals corresponding to keto form *δ* 7.70 (d, *J* = 8.2 Hz, 1H), 7.57 – 7.50 (m, 1H), 7.39 – 7.36 (m, 1H), 5.99 – 5.89 (m, 1H), 5.41 – 5.24 (m, 2H), 4.74 – 4.64 (m, 2H), 3.77 (dd, *J* = 8.3, 4.1 Hz, 1H), 3.54 – 3.52 (m, 1H), 3.36 (ddq, *J* = 17.4, 8.3, 0.7 Hz, 1H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) Signals corresponding to both forms *δ* 197.6, 168.2, 154.8, 144.6, 141.9, 135.6, 135.2, 133.5, 132.0, 131.4, 128.6, 127.2, 126.6, 125.6, 125.0, 121.5, 118.6, 118.2, 102.4, 66.2, 64.6, 53.1, 32.2, 29.8.

Allyl 1-oxo-4-(trifluoromethyl)-2,3-dihydro-1H-indene-2-carboxylate (12o)



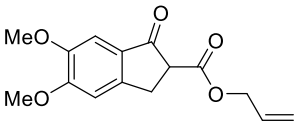
Chemical Formula: $C_{14}H_{11}F_3O_3$
Molecular Weight: 284.23 g/mol
Column chromatography, eluent petroleum ether/ethyl acetate 9: 1
White solid, 170 mg, 20%
^{1}H NMR (400 MHz, $CDCl_3$) (keto: enol = 1: 1) Signals corresponding to enol form *δ* 10.29 (s, 1H), 7.82 (d, *J* = 7.6 Hz, 1H), 7.67 (d, *J* = 7.8 Hz, 1H), 7.58 – 7.48 (m, 1H), 6.08 – 5.88 (m, 1H), 5.45 – 5.24 (m, 2H), 4.79 (dt, *J* = 5.7, 1.4 Hz, 2H), 3.78 – 3.70 (m, 2H). Signals corresponding to keto form *δ* 7.99 – 7.87 (m, 2H), 7.58 – 7.48 (m, 1H), 6.08 – 5.88 (m, 1H), 5.45 – 5.24 (m, 2H), 4.77 – 4.60 (m, 2H), 3.83 – 3.80 (m, 1H), 3.78 – 3.70 (m, 1H), 3.63 – 3.54 (m, 1H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) Signals corresponding to both forms *δ* 198.1, 168.2, 150.9, 140.5, 138.7, 136.9, 132.2, 131.6, 131.3, 128.5, 128.3, 128.2, 127.7, 126.2, 126.1, 124.2, 124.1, 122.4, 119.1, 118.8, 103.3, 66.6, 65.1, 53.0, 32.1, 29.4.
^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) Signals corresponding to both forms *δ* -62.05, -62.30.
HRMS (APCI) m/z : Calculated for $C_{14}H_{11}F_3O_3$ $[M]^+$: 285.0739. Found 285.0733.

Allyl 6-methoxy-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (12p)[3]



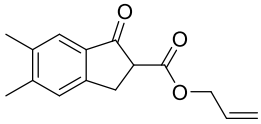
Chemical Formula: $C_{14}H_{14}O_4$
Molecular Weight: 246.26 g/mol
Column chromatography, eluent petroleum ether/ethyl acetate 8: 2
White solid, 100 mg, 10% yield
In accordance with the literature: **^{1}H NMR** (400 MHz, $CDCl_3$)) (keto: enol = 7: 1) Signals corresponding to enol form δ 10.37 (br, 1H), 7.35 (dd, J = 8.3, 0.7 Hz, 1H), 7.15 (d, J = 2.4 Hz, 1H), 7.00 (dd, J = 8.3, 2.5 Hz, 1H), 6.06 – 6.00 (m, 1H), 5.43 – 5.22 (m, 2H), 4.77 (dt, J = 5.5, 1.5 Hz, 2H), 3.86 (s, 3H), 3.51 – 3.44 (m, 2H). Signals corresponding to keto form δ 7.39 (dq, J = 8.1, 0.8 Hz, 1H), 7.24 – 7.18 (m, 2H), 6.02 – 5.90 (m, 1H), 5.43 – 5.22 (m, 2H), 4.76 – 4.63 (m, 2H), 3.83 (s, 3H), 3.77 (dd, J = 8.1, 3.9 Hz, 1H), 3.51 – 3.44 (m, 1H), 3.31 (ddd, J = 16.7, 8.0, 0.8 Hz, 1H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) Signals corresponding to both forms δ 199.4, 169.0, 159.9, 159.3, 146.6, 138.2, 136.6, 135.6, 132.5, 131.8, 127.3, 125.6, 125.1, 118.8, 118.3, 117.4, 105.8, 104.6, 103.2, 66.3, 64.8, 55.8, 54.1, 31.9, 29.8.

Allyl 5,6-dimethoxy-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (12q)



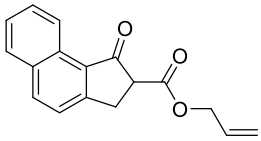
Chemical Formula: $C_{15}H_{16}O_5$
Molecular Weight: 276.29 g/mol
Column chromatography, eluent petroleum ether/ethyl acetate 7: 3
Colorless oil, 300 mg, 30% yield
^{1}H NMR (400 MHz, $CDCl_3$) (only keto form) δ 7.21 (s, 1H), 6.89 (s, 1H), 5.91 – 5.81 (m, 1H), 5.32 – 5.18 (m, 2H), 4.70 (dq, J = 5.9, 1.2 Hz, 2H), 3.99 (s, 3H), 3.91 (s, 3H), 3.70 (dd, J = 17.4, 10.5 Hz, 1H), 3.42 – 3.26 (m, 1H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 197.9, 169.2, 156.2, 149.9, 149.3, 131.8, 128.1, 118.7, 107.4, 104.9, 66.2, 56.4, 56.2, 53.6, 30.2.
HRMS (APCI) m/z : Calculated for $C_{15}H_{16}O_5H$ $[M+H]^+$: 277.1076. Found 277.1072.

Allyl 5,6-dimethyl-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (12r)



Chemical Formula: $C_{15}H_{16}O_3$
Molecular Weight: 244.29 g/mol
Column chromatography, eluent petroleum ether/ethyl acetate 9: 1
Colorless oil, 490 mg, 45% yield
^{1}H NMR (400 MHz, $CDCl_3$) (only keto form) δ 7.54 (s, 1H), 7.27 (s, 1H), 5.98 – 5.89 (m, 1H), 5.43 – 5.20 (m, 2H), 4.77 – 4.63 (m, 2H), 3.72 (dd, J = 8.2, 4.0 Hz, 1H), 3.54 – 3.41 (m, 1H), 3.30 (dd, J = 17.1, 8.1 Hz, 1H), 2.35 (s, 3H), 2.30 (s, 3H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 155.9, 151.8, 145.9, 131.9, 127.4, 125.1, 118.9, 118.7, 66.2, 53.7, 30.0, 20.9, 19.9.
HRMS (APCI) m/z : Calculated for $C_{15}H_{16}O_3H$ $[M+H]^+$: 245.1178. Found 245.1174.

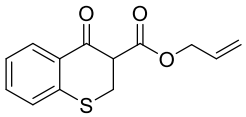
Allyl 1-oxo-2,3-dihydro-1H-cyclopenta[a]naphthalene-2-carboxylate (12s)



Chemical Formula: $C_{17}H_{14}O_3$
Molecular Weight: 266.30 g/mol
Column chromatography, eluent petroleum ether/ethyl acetate 9: 1

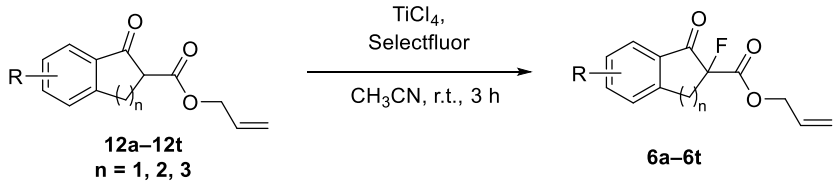
Colorless oil, 200 mg, 20% yield
^{1}H NMR (400 MHz, $CDCl_3$) δ (only keto form) 9.16 (dt, J = 8.4, 1.0 Hz, 1H), 8.05 (d, J = 8.4 Hz, 1H), 7.91 – 7.86 (m, 2H), 7.52 – 7.48 (m, 2H), 6.02 – 5.92 (m, 1H), 5.43 – 5.21 (m, 2H), 4.78 – 4.62 (m, 2H), 3.64 (dd, J = 17.6, 3.7 Hz, 1H), 3.43 (dd, J = 17.6, 7.9 Hz, 1H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 199.7, 169.2, 158.5, 136.8, 132.9, 132.7, 129.4, 128.9, 128.3, 126.9, 124.1, 124.0, 123.73, 118.74, 66.28, 53.8, 30.72.
HRMS (APCI) m/z : Calculated for $C_{17}H_{14}O_3H$ $[M+H]^+$: 267.1021. Found 267.1018.

Allyl 4-oxothiochromane-3-carboxylate (12t)



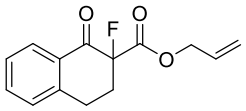
Chemical Formula: $C_{13}H_{12}O_3S$
Molecular Weight: 248.30 g/mol
Column chromatography, eluent petroleum ether/ethyl acetate 9.8: 0.2
Yellow solid, 90 mg, 30% yield
^{1}H NMR (400 MHz, $CDCl_3$)) (keto: enol = 1: 2) Signals corresponding to enol form δ 12.66 (s, 1H), 7.86 – 7.84 (m, 1H), 7.30 – 7.26 (m, 2H), 7.24 – 7.17 (m, 1H), 6.07 – 5.95 (m, 1H), 5.46 – 5.16 (m, 2H), 4.75 (dt, J = 5.7, 1.4 Hz, 2H), 3.75 (s, 2H). Signals corresponding to keto form δ 8.13 (ddd, J = 8.0, 1.6, 0.5 Hz, 1H), 7.40 (ddd, J = 8.0, 7.2, 1.6 Hz, 1H), 7.26 – 7.25 (m, 1H), 7.24 – 7.17 (m, 1H), 5.94 – 5.85 (m, 1H), 5.46 – 5.16 (m, 2H), 4.71 (ddt, J = 7.1, 5.7, 1.4 Hz, 2H), 3.93 (dd, J = 10.1, 3.6 Hz, 1H), 3.64 (dd, J = 13.6, 10.1 Hz, 1H), 3.35 (dd, J = 13.6, 3.7 Hz, 1H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) Signals corresponding to both forms δ 189.7, 171.0, 166.3, 137.3, 133.8, 131.9, 131.6, 131.1, 130.4, 129.9, 129.3, 127.6, 127.5, 126.9, 125.7, 125.4, 118.9, 93.8, 66.4, 65.8, 54.2, 28.9, 23.5.
HRMS (APCI) m/z : Calculated for $C_{13}H_{12}O_3SH$ $[M+H]^+$: 249.0585. Found 249.0579.

5. General method for the synthesis of compounds **6a – 6t**



Compounds **6a – 6t** were prepared according to a published procedure.[8] Neat $TiCl_4$ (119.5 µL, 1.1 mmol, 0.1 equiv, 10 mol%) was added to a 20 °C solution of **12a** (2.5 g, 10.9 mmol, 1.0 equiv.) in acetonitrile (109 mL). After stirring for 5 minutes, SelectFluor™ (4.6 g, 13.1 mmol, 1.2 equiv.) was added in one portion. The reaction mixture was stirred at room temperature for 2 h then quenched by adding H_2O and extracted with Et_2O (3 times). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate 9.8: 0.2) to give the fluorinated allyl β-keto ester **6a**.

Allyl 2-fluoro-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (6a)[8]

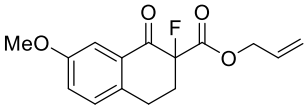


Chemical Formula: $C_{14}H_{13}FO_3$
Molecular Weight: 248.25 g/mol
Column chromatography, eluent petroleum ether/ethyl acetate 9.8: 0.2
Colorless oil, 2.5 g, 93% yield.

[8] J. T. Mohr, T. Nishimata, D. C. Behenna and B. M. Stoltz, *J. Am. Chem. Soc.*, **2006**, 128, *35*, 11348.

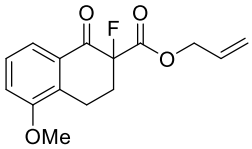
In accordance with the literature : **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.08 (dd, J = 7.9, 1.4 Hz, 1H), 7.55 (td, J = 7.5, 1.5 Hz, 1H), 7.40 – 7.33 (m, 1H), 7.28 (m, 1H), 5.88 (m, 1H), 5.32 – 5.20 (m, 2H), 4.78 – 4.67 (m, 2H), 3.26 – 3.02 (m, 2H), 2.83 – 2.66 (m, 1H), 2.56 (m, 1H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 188.28 ($^{2}J_{C-F}$ = 18.2Hz), 166.9 ($^{2}J_{C-F}$ = 26.0Hz), 142.9, 134.4, 130.6, 130.4, 128.6, 128.3, 127.1, 119.0, 93.04 ($^{1}J_{C-F}$ = 194.2 Hz), 66.4, 31.7 ($^{2}J_{C-F}$ = 22.2Hz), 24.8 ($^{3}J_{C-F}$ = 7.3 Hz).
^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -164.25.

Allyl 2-fluoro-7-methoxy-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (6b)



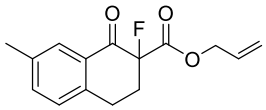
Chemical Formula: $C_{15}H_{15}FO_4$
Molecular Weight: 278.28 g/mol
Column chromatography, eluent petroleum ether/ethyl acetate 8: 2
White solid, 1.0 g, 78% yield
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, J = 2.7 Hz, 1H), 7.19 (d, J = 8.5 Hz, 1H), 7.13 (dd, J = 8.5, 2.8 Hz, 1H), 5.88 (ddt, J = 17.3, 10.4, 5.7 Hz, 1H), 5.34 – 5.20 (m, 2H), 4.79 – 4.66 (m, 2H), 3.84 (s, 3H), 3.12 (m, 1H), 3.01 (m, 1H), 2.80 – 2.65 (m, 1H), 2.60 – 2.48 (m, 1H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 188.6 (d, $^{2}J_{C-F}$ = 18.6 Hz), 167.3 (d, $^{2}J_{C-F}$ = 26.2 Hz), 158.9, 136.0, 131.5, 131.0, 130.2, 123.5, 119.4, 110.1, 93.3 (d, $^{1}J_{C-F}$ = 194.2 Hz), 66.8, 55.7, 32.3 (d, $^{2}J_{C-F}$ = 22.1 Hz), 24.3 (d, $^{3}J_{C-F}$ = 7.2 Hz).
^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -164.11.
HRMS (APCI) m/z Calculated for $C_{15}H_{15}FO_4Na$ $[M+Na]^+$: 301.0852 Found 301.0850.

Allyl 2-fluoro-5-methoxy-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (6c)



Chemical Formula: $C_{15}H_{15}FO_4$
Molecular Weight: 278.28 g/mol
Column chromatography, eluent petroleum ether/ethyl acetate 9.5: 0.5
White solid, 920 mg, 88% yield
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (dd, J = 7.9, 1.1 Hz, 1H), 7.34 (tt, J = 8.1, 0.8 Hz, 1H), 7.08 (dd, J = 8.2, 1.1 Hz, 1H), 5.92 – 5.83 (m, 1H), 5.32 – 5.20 (m, 2H), 4.76 – 4.67 (m, 2H), 3.88 (s, 3H), 3.14 – 2.95 (m, 2H), 2.79 – 2.65 (m, 1H), 2.55 – 2.48 (m, 1H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 189.1, 167.0 (d, $^{2}J_{C-F}$ = 26.2 Hz), 156.7, 132.4, 131.7, 131.0, 127.8, 120.0, 119.3, 115.4, 93.4 (d, $^{1}J_{C-F}$ = 194.7 Hz), 66.7, 55.9, 31.2 (d, $^{2}J_{C-F}$ = 22.0 Hz), 19.1 (d, $^{3}J_{C-F}$ = 7.7 Hz).
^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -164.60.
HRMS (APCI) m/z Calculated for $C_{15}H_{15}FO_4H$ $[M+H]^+$: 279.1033. Found 279.1036.

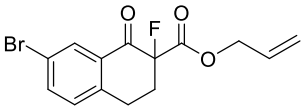
Allyl 2-fluoro-7-methyl-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (6d)



Chemical Formula: $C_{15}H_{15}FO_3$
Molecular Weight: 262.28 g/mol
Column chromatography, eluent petroleum ether/ethyl acetate 9.5: 0.5
Colorless oil, 600 mg, 74% yield
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, J = 1.9 Hz, 1H), 7.37 (dd, J = 7.8, 2.0 Hz, 1H), 7.17 (m, 1H), 5.88 (ddt, J = 17.2, 10.5, 5.7 Hz, 1H), 5.34 – 5.20 (m, 2H), 4.78 – 4.67 (m, 2H), 3.15 (m, 1H), 3.03 (m, 1H), 2.80 – 2.64 (m, 1H), 2.54 (m, 1H), 2.38 (s, 3H).

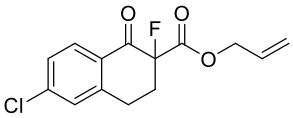
$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 188.7 (d, $^2J_{C-F}$ = 18.6 Hz), 167.2 (d, $^2J_{C-F}$ = 26.6 Hz), 140.3, 137.2, 135.7, 130.9, 130.4, 128.7, 128.5, 119.2, 93.33 (d, $^1J_{C-F}$ = 194.1 Hz), 66.6, 32.03 (d, $^2J_{C-F}$ = 22.1 Hz), 24.51 (d, $^3J_{C-F}$ = 7.3 Hz), 20.9.
$^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$) δ -164.14.
HRMS (APCI) m/z Calculated for : $C_{15}H_{15}FO_3H$ $[M+H]^+$: 263.1083. Found 263.1079.

Allyl 7-bromo-2-fluoro-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (6e)



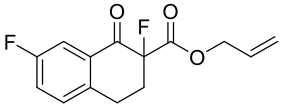
Chemical Formula: $C_{14}H_{12}BrFO_3$
Molecular Weight: 327.15 g/mol
Column chromatography, eluent petroleum ether/dichloromethane 5: 5
White solid, 160 mg, 90% yield
^1H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, J = 2.1 Hz, 1H), 7.66 (dd, J = 8.2, 2.2 Hz, 1H), 7.18 (m, 1H), 5.88 (ddt, J = 17.2, 10.4, 5.7 Hz, 1H), 5.36 – 5.20 (m, 2H), 4.73 (m, 2H), 3.22 – 2.98 (m, 2H), 2.83 – 2.66 (m, 1H), 2.56 (m, 1H).
$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 187.5 (d, $^2J_{C-F}$ = 19.0 Hz), 166.9 (d, $^2J_{C-F}$ = 26.1 Hz), 141.9, 137.5, 132.2, 131.3, 130.8, 130.7, 121.5, 119.6, 93.0 (d, $^1J_{C-F}$ = 196.1 Hz), 66.9, 31.8 (d, $^2J_{C-F}$ = 22.3 Hz), 24.7 (d, $^3J_{C-F}$ = 7.4 Hz).
$^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$) δ -164.40.
HRMS (APCI) m/z Calculated for $C_{14}H_{12}BrFO_3Na$ $[M+Na]^+$: 348.9852. Found 348.9849.

Allyl 6-chloro-2-fluoro-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (6f)



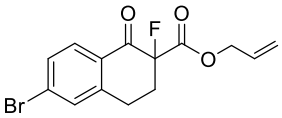
Chemical Formula: $C_{14}H_{12}ClFO_3$
Molecular Weight: 282.70 g/mol
Column chromatography, eluent petroleum ether/ethyl acetate 6: 4
Brown solid, 150 mg, 47% yield
^1H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, J = 8.4 Hz, 1H), 7.40 – 7.32 (m, 1H), 7.32 – 7.28 (m, 1H), 5.93 – 5.84 (m, 1H), 5.32 – 5.24 (m, 2H), 4.79 – 4.65 (m, 2H), 3.19 – 2.99 (m, 2H), 2.82 – 2.66 (m, 1H), 2.64 – 2.49 (m, 1H).
$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 187.7 (d, $^2J_{C-F}$ = 18.3 Hz), 167.0 (d, $^2J_{C-F}$ = 26.5 Hz), 144.7, 141.4, 130.9, 130.3, 129.2, 128.9, 128.1, 119.6, 93.1 (d, $^1J_{C-F}$ = 195.4 Hz), 66.9, 31.8 (d, $^2J_{C-F}$ = 22.3 Hz), 24.9 (d, $^3J_{C-F}$ = 7.3 Hz).
$^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$) δ -164.33.
HRMS (APCI) m/z: Calculated for $C_{14}H_{12}ClFO_3H$ $[M + H]^+$: 283.0537. Found 283.0534.

Allyl 2,7-difluoro-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (6g)



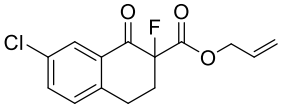
Chemical Formula: $C_{14}H_{12}F_2O_3$
Molecular Weight: 266.24 g/mol
Column chromatography, eluent petroleum ether/ethyl acetate 7: 3
Yellow oil, 280 mg, 88% yield
^1H NMR (400 MHz, $CDCl_3$) δ 7.73 (dt, J = 8.9, 1.8 Hz, 1H), 7.30 – 7.25 (m, 2H), 5.93 – 5.83 (m, 1H), 5.32 – 5.23 (m, 2H), 4.78 – 4.68 (m, 2H), 3.22 – 3.01 (m, 2H), 2.80 – 2.66 (m, 1H), 2.90 – 2.51 (m, 1H).
$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 187.9 (d, $^2J_{C-F}$ = 18.9 Hz), 166.9 (d, $^2J_{C-F}$ = 26.4 Hz), 161.8 (d, $^1J_{C-F}$ = 248.7 Hz), 139.0 (d, $^4J_{C-F}$ = 3.2 Hz), 132.2 (d, $^3J_{C-F}$ = 6.7 Hz), 130.9 (d, $^3J_{C-F}$ = 7.3 Hz), 130.8, 122.2 (d, $^2J_{C-F}$ = 22.3 Hz), 119.4, 114.2 (d, $^2J_{C-F}$ = 22.5 Hz), 93.0 (d, $^1J_{C-F}$ = 195.4 Hz), 66.8, 32.0 (d, $^2J_{C-F}$ = 22.3 Hz), 24.4 (d, $^3J_{C-F}$ = 7.4 Hz).
$^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$) δ -113.78, -164.59.
HRMS (APCI) m/z: Calculated for $C_{14}H_{12}F_2O_3H$ $[M + H]^+$: 267.0833. Found 267.0836.

Allyl 6-bromo-2-fluoro-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (6h)



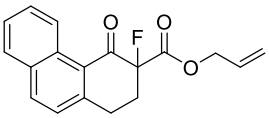
Chemical Formula: $C_{14}H_{12}BrFO_3$
Molecular Weight: 327.15 g/mol
Column chromatography, eluent petroleum ether/ethyl acetate 6: 4
Yellow oil, 176 mg, 66% yield
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, J = 8.4 Hz, 1H), 7.53 – 7.44 (m, 2H), 5.92 5.82 (m, 1H), 5.38 – 5.20 (m, 2H), 4.76 – 4.67 (m, 2H), 3.24 – 2.99 (m, 2H), 2.80 – 2.64 (m, 1H), 2.59 – 2.50 (m, 1H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 187.8 (d, $^2J_{C\text{-}F}$ = 19.2 Hz), 166.9 (d, $^2J_{C\text{-}F}$ = 26.3 Hz), 144.8, 131.9, 131.0, 130.8, 130.3, 130.2, 129.5, 119.6, 93.0 (d, $^1J_{C\text{-}F}$ = 195.9 Hz), 66.9, 31.7 (d, $^2J_{C\text{-}F}$ = 22.3 Hz), 24.8 (d, $^3J_{C\text{-}F}$ = 8.1 Hz).
^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -164.31.
HRMS (APCI) m/z: Calculated for $C_{14}H_{12}BrFO_3H$ $[M + H]^+$: 327.0032. Found 327.0027.

Allyl 7-chloro-2-fluoro-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (6i)



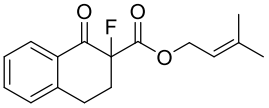
Chemical Formula: $C_{14}H_{12}ClFO_3$
Molecular Weight: 282.70 g/mol
Column chromatography, eluent petroleum ether/ethyl acetate 6: 4
Yellow oil, 180 mg, 58% yield
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, J = 2.3 Hz, 1H), 7.51 (dd, J = 8.2, 2.3 Hz, 1H), 7.26 – 7.23 (m, 1H), 5.93 – 5.83 (m, 1H), 5.34 – 5.22 (m, 2H), 4.77 – 4.68 (m, 2H), 3.22 – 2.98 (m, 2H), 2.82 – 2.65 (m, 1H), 2.60 – 2.51 (m, 1H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 187.7 (d, $^2J_{C\text{-}F}$ = 20.2 Hz), 166.8 (d, $^2J_{C\text{-}F}$ = 30.0 Hz), 141.4, 134.7, 133.8, 131.9, 130.9, 130.5, 128.2, 119.6, 93.0 (d, $^1J_{C\text{-}F}$ = 191.9 Hz), 66.9, 31.8 (d, $^2J_{C\text{-}F}$ = 21.2 Hz), 24.6 (d, $^3J_{C\text{-}F}$ = 7.1 Hz).
^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -164.44.
HRMS (APCI) m/z: Calculated for $C_{14}H_{12}ClFO_3H$ $[M + H]^+$: 283.0537. Found 283.0532.

Allyl 3-fluoro-4-oxo-1,2,3,4-tetrahydrophenanthrene-3-carboxylate (6j)



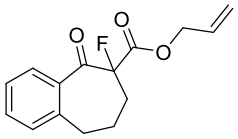
Chemical Formula: $C_{18}H_{15}FO_3$
Molecular Weight: 298.31 g/mol
Column chromatography, eluent petroleum ether/ethyl acetate 8: 2
Colorless oil, 70 mg, 76% yield
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.34 – 9.24 (m, 1H), 8.00 (d, J = 8.4 Hz, 1H), 7.86 – 7.80 (m, 1H), 7.66 (ddd, J = 8.6, 6.9, 1.5 Hz, 1H), 7.54 (ddd, J = 8.1, 6.8, 1.2 Hz, 1H), 7.32 (d, J = 8.4 Hz, 1H), 5.93 – 5.84 (m, 1H), 5.34 – 5.19 (m, 2H), 4.74 (dt, J = 5.7, 1.4 Hz, 2H), 3.45 – 3.18 (m, 2H), 2.93 – 2.76 (m, 1H), 2.60 – 2.60 (m, 1H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 190.2 (d, $^2J_{C\text{-}F}$ = 20.2 Hz), 167.4 (d, $^2J_{C\text{-}F}$ = 26.3 Hz), 145.9, 135.9, 132.9, 131.7, 131.2, 129.7, 128.7, 126.6, 126.6, 126.3, 125.2, 119.3, 94.3 (d, $^1J_{C\text{-}F}$ = 193.2 Hz), 66.7, 31.4 (d, $^2J_{C\text{-}F}$ = 22.2 Hz), 26.5 (d, $^3J_{C\text{-}F}$ = 7.1 Hz).
^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -162.88.
HRMS (APCI) m/z: Calculated for $C_{18}H_{15}FO_3H$ $[M + H]^+$: 299.1083. Found 299.1080.

3-methylbut-2-en-1-yl 2-fluoro-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (6k)



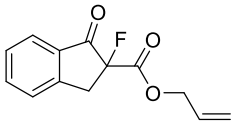
Chemical Formula: $C_{16}H_{17}FO_3$
Molecular Weight: 276.31 g/mol
Column chromatography, eluent petroleum ether/ethyl acetate 9.5: 0.5
Yellow oil, 30 mg, 22% yield
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 – 8.05 (m, 1H), 7.55 (td, J = 7.5, 1.5 Hz, 1H), 7.37 (td, J = 7.6, 1.1 Hz, 1H), 7.30 – 7.26 (m, 1H), 5.33 – 5.29 (m, 1H), 4.79 – 4.65 (m, 2H), 3.24 – 3.02 (m, 2H), 2.79 – 2.66 (m, 1H), 2.58 – 2.50 (m, 1H), 1.73 (s, 3H), 1.66 (s, 3H).
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 188.8 (d, $^2J_{C\text{-}F}$ = 18.9 Hz), 167.5 (d, $^2J_{C\text{-}F}$ = 25.2 Hz), 143.3, 140.8, 134.6, 134.3, 128.9, 128.6, 127.4, 117.6, 93.4 (d, $^1J_{C\text{-}F}$ = 194.0 Hz), 63.3, 32.0 (d, $^2J_{C\text{-}F}$ = 21.4 Hz), 25.9, 25.1 (d, $^3J_{C\text{-}F}$ = 7.1 Hz), 18.2.
^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -164.04.
HRMS (APCI) m/z: Calculated for $C_{16}H_{17}FO_3Na$ $[M + Na]^+$: 299.1059. Found 299.1055.

Allyl 6-fluoro-5-oxo-6,7,8,9-tetrahydro-5H-benzo[7]annulene-6-carboxylate (6l)[8]



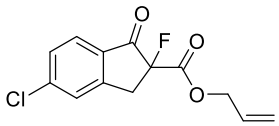
Chemical Formula: $C_{15}H_{15}FO_3$
Molecular Weight: 262.28 g/mol
Column chromatography, eluent petroleum ether/ethyl acetate 9.8: 0.2
Colorless oil, 360 mg, 68% yield
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (dd, J = 7.7, 1.5 Hz, 1H), 7.43 (td, J = 7.5, 1.5 Hz, 1H), 7.31 (td, J = 7.5, 1.2 Hz, 1H), 7.24 – 7.19 (m, 1H), 5.89 (ddt, J = 17.2, 10.4, 5.7 Hz, 1H), 5.37 – 5.22 (m, 2H), 4.71 (m, 2H), 3.11 (m, 1H), 2.94 (m, 1H), 2.73 – 2.53 (m, 1H), 2.30 (m, 1H), 2.15 (m, 1H), 1.98 – 1.86 (m, 1H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 198.8 (d, $^2J_{C\text{-}F}$ = 26.5 Hz), 167.0 (d, $^2J_{C\text{-}F}$ = 25.6 Hz), 140.8, 136.6, 132.5, 131.1, 129.7, 129.5, 126.8, 119.3, 99.1 (d, $^1J_{C\text{-}F}$ = 196.8 Hz), 66.8, 33.5, 32.9 (d, $^2J_{C\text{-}F}$ = 22.0 Hz), 22.5 (d, $^3J_{C\text{-}F}$ = 2.5 Hz).
^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -158.38.

Allyl 2-fluoro-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (6m)[9]



Chemical Formula: $C_{13}H_{11}FO_3$
Molecular Weight: 234.23 g/mol
Column chromatography, eluent petroleum ether/ethyl acetate 9.5: 0.5
White solid, 200 mg, 93% yield
In accordance with the literature : **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.86 – 7.84 (m, 1H), 7.71 (td, J = 7.6, 1.3 Hz, 1H), 7.55 – 7.42 (m, 2H), 5.91 – 5.81 (m, 1H), 5.30 – 5.19 (m, 2H), 4.75 – 4.66 (m, 2H), 3.87 – 3.75 (m, 1H), 3.53 – 3.36 (m, 1H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 195.3 (d, $^2J_{C\text{-}F}$ = 18.1 Hz), 167.1 (d, $^2J_{C\text{-}F}$ = 28.2 Hz), 151.0 (d, $^3J_{C\text{-}F}$ = 3.8 Hz), 136.9, 133.4, 130.9, 128.8, 126.7, 125.8, 119.4, 94.3 (d, $^1J_{C\text{-}F}$ = 202.7 Hz), 66.87, 38.4 (d, $^2J_{C\text{-}F}$ = 23.9 Hz).
^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -164.51.

Allyl 5-chloro-2-fluoro-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (6n)

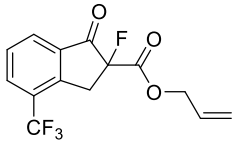


Chemical Formula: $C_{13}H_{10}ClFO_3$

[9] R. A. Craig, S. A. Loskot, J. T. Mohr, D. C. Behenna, A. M. Harned and B. M. Stoltz, *Org. Lett.*, **2015**, *17*, 5160.

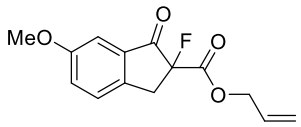
Molecular Weight: 268.67 g/mol
Column chromatography, eluent petroleum ether/ethyl acetate 9.5: 0.5
Yellow solid, 440 mg, 82% yield
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, J = 8.2 Hz, 1H), 7.51 (d, J = 1.6 Hz, 1H), 7.45 (dd, J = 8.3, 1.8 Hz, 1H), 5.90 – 5.81 (m, 1H), 5.33 – 5.20 (m, 2H), 4.75 – 4.66 (m, 2H), 3.78 (dd, J = 17.8, 11.1 Hz, 1H), 3.50 – 3.33 (m, 1H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 193.7 (d, $^{2}J_{C\text{-}F}$ = 19.2 Hz), 166.7 (d, $^{2}J_{C\text{-}F}$ = 28.3 Hz), 152.3, 143.6, 131.8, 130.8, 129.7, 127.0, 126.9, 119.7, 94.6 (d, $^{1}J_{C\text{-}F}$ = 203.8 Hz), 67.0, 38.1 (d, $^{2}J_{C\text{-}F}$ = 24.3 Hz).
^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -163.95.
HRMS (APCI) m/z: Calculated for $C_{13}H_{10}ClFO_3H$ $[M + H]^+$: 269.0381. Found 269.0378.

Allyl 2-fluoro-1-oxo-4-(trifluoromethyl)-2,3-dihydro-1H-indene-2-carboxylate (6o)



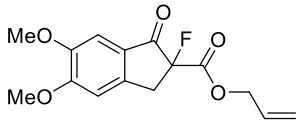
Chemical Formula: $C_{14}H_{10}F_4O_3$
Molecular Weight: 302.22 g/mol
Column chromatography, eluent petroleum ether/ethyl acetate 9: 1
Yellow oil, 130 mg, 82% yield
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 – 7.94 (m, 2H), 7.70 – 7.58 (m, 1H), 5.91 – 5.81 (m, 1H), 5.34 – 5.22 (m, 2H), 4.78 – 4.65 (m, 2H), 4.05 – 3.91 (m, 1H), 3.66 – 3.51 (m, 1H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 194,4 (d, $^{2}J_{C\text{-}F}$ = 17.5 Hz), 166.5 (d, $^{2}J_{C\text{-}F}$ = 28.5 Hz), 148.2, 134.8, 133.3 (d, $^{3}J_{C\text{-}F}$ = 4.6 Hz), 130.7, 129.3, 129.1, 124.8, 122.1, 119.7, 93.7 (d, $^{1}J_{C\text{-}F}$ = 192.8 Hz), 67.1, 37.5 (d, $^{2}J_{C\text{-}F}$ = 24.8 Hz).
$^{19F\{1H\}}$ NMR (376 MHz, $CDCl_3$) δ -62.35, -164.06.
HRMS (APCI) m/z: Calculated for $C_{14}H_{10}F_4O_3H$ $[M + H]^+$: 303.0644. Found 303.0643.

Allyl 2-fluoro-6-methoxy-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (6p)



Chemical Formula: $C_{14}H_{13}FO_4$
Molecular Weight: 264.25 g/mol
Column chromatography, eluent petroleum ether/ethyl acetate 8: 2
Colorless oil, 60 mg, 81% yield
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.37 (m, 1H), 7.29 (dd, J = 8.4, 2.6 Hz, 1H), 7.25 (d, J = 2.5 Hz, 1H), 5.91 – 5.81 (m, 1H), 5.30 – 5.19 (m, 2H), 4.75 – 4.66 (m, 2H), 3.85 (s, 3H), 3.76 – 3.69 (m, 1H), 3.45 – 3.29 (m, 1H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 167.2 (d, $^{2}J_{C\text{-}F}$ = 29.8 Hz), 160.3, 143.9, 134.6, 130.9, 127.4, 126.5, 119.4, 106.6, 95.3 (d, $^{1}J_{C\text{-}F}$ = 199.1 Hz), 66.9, 55.9, 37.9, 37.8 (d, $^{2}J_{C\text{-}F}$ = 23.9 Hz).
^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -164.11.
HRMS (APCI) m/z: Calculated for $C_{14}H_{13}FO_4H$ $[M + H]^+$: 265.0876. Found 265.0875.

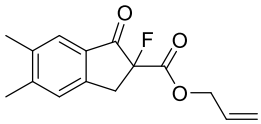
Allyl 2-fluoro-5,6-dimethoxy-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (6q)



Chemical Formula: $C_{15}H_{15}FO_5$
Molecular Weight: 294.28 g/mol
Column chromatography, eluent petroleum ether/ethyl acetate 8: 2
Colorless oil, 200 mg, 94% yield
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (s, 1H), 6.89 (s, 1H), 5.91 – 5.81 (m, 1H), 5.32 – 5.18 (m, 2H), 4.70 (dq, J = 5.9, 1.2 Hz, 2H), 3.99 (s, 3H), 3.91 (s, 3H), 3.70 (dd, J = 17.4, 10.5 Hz, 1H), 3.42 – 3.26 (m, 1H).

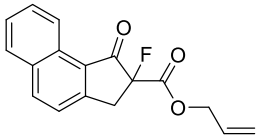
$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 193.4 (d, $^2J_{C-F}$ = 19.2 Hz), 167.4 (d, $^2J_{C-F}$ = 28.3 Hz), 157.3, 150.5, 147.0 (d, $^3J_{C-F}$ = 5.1 Hz), 130.9, 126.2, 119.4, 107.4, 105.6, 95.1 (d, $^1J_{C-F}$ = 203.0 Hz), 66.8, 56.6, 56.3, 38.2 (d, $^2J_{C-F}$ = 24.2 Hz).
$^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$) δ -163.82.
HRMS (APCI) m/z: Calculated for $C_{15}H_{15}FO_5H$ $[M + H]^+$: 295.0982. Found 295.0979.

Allyl 2-fluoro-5,6-dimethyl-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (6r)



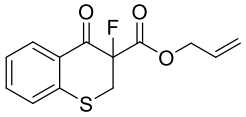
Chemical Formula: $C_{15}H_{15}FO_3$
Molecular Weight: 262.28 g/mol
Column chromatography, eluent petroleum ether/ethyl acetate 8: 2
Colorless oil, 300 mg, 82% yield
^1H NMR (400 MHz, $CDCl_3$) δ 7.60 (s, 1H), 7.26 (s, 1H), 5.90 – 5.81 (m, 1H), 5.34 – 5.16 (m, 2H), 4.74 – 4.65 (m, 2H), 3.71 (dd, *J* = 17.5, 11.0 Hz, 1H), 3.43 – 3.28 (m, 1H), 2.38 (s, 3H), 2.32 (s, 3H).
$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 194.2 (d, $^2J_{C-F}$ = 20.2 Hz), 167.3 (d, $^2J_{C-F}$ = 30.3 Hz), 149.0 (d, $^3J_{C-F}$ = 4.0 Hz), 147.6, 137.9, 131.4, 130.9, 127.3, 125.9, 119.2, 95.0 (d, $^1J_{C-F}$ = 207.0 Hz), 66.6, 37.8 (d, $^2J_{C-F}$ = 24.2 Hz), 21.0, 19.8.
$^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$) δ -164.36.
HRMS (APCI) m/z: Calculated for $C_{15}H_{15}FO_3H$ $[M + H]^+$: 263.1083. Found 263.1081.

Allyl 2-fluoro-1-oxo-2,3-dihydro-1H-cyclopenta[a]naphthalene-2-carboxylate (6s)



Chemical Formula: $C_{17}H_{13}FO_3$
Molecular Weight: 284.29 g/mol
Column chromatography, eluent petroleum ether/ethyl acetate 8: 2
White solid, 80 mg, 45% yield
^1H NMR (400 MHz, $CDCl_3$) δ 9.02 (dd, *J* = 8.3, 1.2 Hz, 1H), 8.16 (d, *J* = 8.4 Hz, 1H), 8.00 – 7.86 (m, 1H), 7.73 (ddd, *J* = 8.4, 7.0, 1.3 Hz, 1H), 7.66 – 7.58 (m, 1H), 7.54 (d, *J* = 8.4 Hz, 1H), 5.92 – 5.82 (m, 1H), 5.33 – 5.19 (m, 2H), 4.81 – 4.65 (m, 2H), 3.90 (dd, *J* = 17.8, 10.7 Hz, 1H), 3.63 – 3.47 (m, 1H).
$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 195.2 (d, $^2J_{C-F}$ = 18.2 Hz), 167.3 (d, $^2J_{C-F}$ = 28.3 Hz), 154.7, 138.3, 133.2, 130.9, 130.1, 129.7, 128.7, 127.9, 127.6, 124.3, 123.4, 119.4, 94.5 (d, $^1J_{C-F}$ = 207.0 Hz), 66.87, 38.6 (d, $^2J_{C-F}$ = 24.2 Hz).
$^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$) δ -163.72.
HRMS (APCI) m/z: Calculated for $C_{17}H_{13}FO_3H$ $[M + H]^+$: 285.0927. Found 285.0922.

Allyl 3-fluoro-4-oxothiochromane-3-carboxylate (6t)

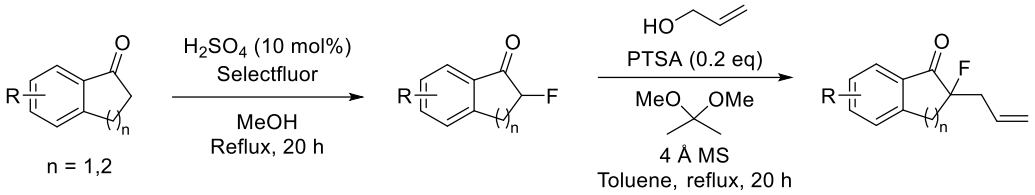


Chemical Formula: $C_{13}H_{11}FO_3S$
Molecular Weight: 266.29 g/mol
Column chromatography, eluent petroleum ether/ethyl acetate 6: 4
White solid, 60 mg, 81% yield
^1H NMR (400 MHz, $CDCl_3$) δ 8.16 (dd, *J* = 8.2, 1.5 Hz, 1H), 7.49 – 7.40 (m, 1H), 7.30 – 7.23 (m, 2H), 5.89 – 5.79 (m, 1H), 5.28 – 5.19 (m, 2H), 4.80 – 4.66 (m, 2H), 3.73 – 3.61 (m, 2H).
$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 185.8 (d, $^2J_{C-F}$ = 17.2 Hz), 165.6 (d, $^2J_{C-F}$ = 30.3 Hz), 140.4, 134.3, 130.6, 130.6, 130.2, 127.4, 125.9, 119.5, 91.4 (d, $^1J_{C-F}$ = 202.0 Hz), 67.22, 33.5 (d, $^2J_{C-F}$ = 25.3 Hz).
$^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$) δ -159.35.

HRMS (APCI) m/z: Calculated for $C_{13}H_{11}FO_3SH$ $[M + H]^+$: 267.0491. Found 267.0483.

6. General method for the synthesis of compounds **7a – 7t**

6.a. Preparation of the racemate



Step 1 **Step 2**

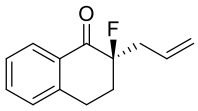
Step 1:[10] In a round-bottom tube containing a solution of the commercially available 1-tetralone (277.8 mg, 1.9 mmol, 1 equiv.) and Selectfluor (807.8 mg, 2.28 mmol, 1.2 equiv.) in MeOH (0.7 M) was added H_2SO_4 conc. (10 µL, 0.19 mmol, 0.01 equiv.) under argon and the tube was equipped with a reflux condenser. The mixture was heated (oil bath) and stirred overnight at 50 °C. After completion of the reaction, the reaction mixture was diluted with CH_2Cl_2 and washed with brine (2 times). Organic layers were combined, dried over $MgSO_4$, filtered and the solvent was evaporated under reduced pressure. The crude product was purified by flash chromatography on silica gel (petroleum ether/EtOAc 9:1) to afford the fluorinated ketone.

Step 2:[11] In a round-bottom tube containing a solution of previously obtained fluorinated ketone (250 mg, 1.2 mmol, 1 equiv.) and allyl alcohol (0.41 mL, 6 mmol, 5 equiv.) in toluene (0.6 M) were added 2,2-dimethoxypropane (0.22 mL, 1.8 mmol, 1.5 equiv.), *p*-toluenesulfonic acid (41.3 mg, 0.24 mmol, 0.2 equiv.) and 4 Å molecular sieves (360 mg). The tube was sealed and heated to reflux (oil bath) for 20 h. The cooled reaction was diluted with CH_2Cl_2 and washed successively with $NaHCO_3$ (aqueous saturated solution) and brine. The combined organic layers were dried over $MgSO_4$, filtered and the solvent was evaporated under reduced pressure. The crude product was purified by flash chromatography on silica gel (petroleum ether/EtOAc 9.8: 0.2).

6.b. Preparation of the chiral compounds **7a-7t**

A dried round-bottom tube was charged with $[Pd_2(dba)_3]$ (3.0 mg, 3.3 µmol, 0.025 equiv.) and the ligand **4f** (4.0 mg, 8.3 µmol, 0.0625 equiv.) under agon. After flushing the system with argon 3 times, MTBE (2.0 mL) was added and the mixture was stirred for 30 minutes at 40 °C. A solution of ketoester (**6b**) (36.7 mg, 0.132 mmol, 1 equiv.) in MTBE (0.6 mL) was added dropwise to the reaction mixture. The resulting solution was stirred for 3 hours at 40°C. Full conversion was observed by NMR (^1H and ^{19}F). The solvent was evaporated in vacuo and the crude product was purified by column chromatography on silica gel (petroleum ether/ diethyl ether 9.9: 0.1). The enantiomeric excess was determined by HPLC analysis.

(*R*)-2-allyl-2-fluoro-3,4-dihydronaphthalen-1(2H)-one (7a) [12]

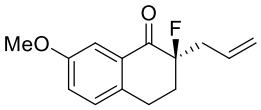


Chemical Formula: $C_{13}H_{13}FO$
Molecular Weight: 204.24 g/mol
Column chromatography, eluent petroleum ether/ethyl acetate 9.9: 0.1

[10] L. Bacheley, R. Molina Betancourt, R. Ravindra, G. Guillamot, P. Phansavath and V. Ratovelomanana-Vidal, *Eur. J. Org. Chem.*, **2023**, *26*, e202300383.
[11] J. M. Cid, J. L. Romera and A. A. Trabanco, *Tetrahedron Lett.*, **2004**, *45*, 1133.
[12] M. Nakamura, A. Hajra, K. Endo and E. Nakamura, *Angew. Chem. Int. Ed.*, **2005**, *44*, 7248.

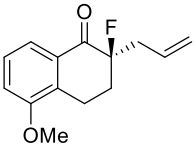
Pale yellow oil, 45 mg, 95% yield, 94% ee, $[\alpha]^{25}_{D}$ = -26,9 (c 0.64, $CHCl_3$) {lit. $[\alpha]^{25}_{D}$ = -30,2 (c 0.64, $CHCl_3$)}[13]
Scale-up experiment: Pale yellow oil, 754 mg, 92% yield, 94% ee
In accordance with the literature: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.06 (dd, J = 7.9, 1.4 Hz, 1H), 7.52 (td, J = 7.5, 1.5 Hz, 1H), 7.39 – 7.32 (m, 1H), 7.28 – 7.22 (m, 1H), 5.95 – 5.84 (m, 1H), 5.27 – 5.10 (m, 2H), 3.17 – 2.95 (m, 2H), 2.78 – 2.50 (m, 2H), 2.48 – 2.29 (m, 2H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 194.2 (d, $^2J_{C\text{-}F}$ = 19.4 Hz), 142.8, 134.2, 131.0, 131.0, 128.9, 128.4, 127.3, 120.0, 95.1 (d, $^1J_{C\text{-}F}$ = 185.1 Hz), 38.1 (d, $^2J_{C\text{-}F}$ = 23.6 Hz), 32.0 (d, $^2J_{C\text{-}F}$ = 22.4 Hz), 26.06 (d, $^3J_{C\text{-}F}$ = 10.0 Hz).
^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -159.97.
HPLC Chiralpak IC, hexane/2-propanol = 90/10, 0.5 mL/min, 254 nm, t_S (S) = 18.56 min (minor), t_R (R) = 20.09 min (major).

(*R*)-2-allyl-2-fluoro-7-methoxy-3,4-dihydronaphthalen-1(2H)-one (7b)



Chemical Formula: $C_{14}H_{15}FO_2$
Molecular Weight: 234.27 g/mol
Column chromatography, eluent petroleum ether/ethyl acetate 9.9: 0.1
Pale yellow oil, 30 mg, 97% yield, 96% ee, $[\alpha]^{25}_{D}$ = -34.8 (c 1.0, $CHCl_3$)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, J = 2.8 Hz, 1H), 7.16 (d, J = 8.5 Hz, 1H), 7.12 – 7.09 (m, 1H), 5.94 – 5.84 (m, 1H), 5.27 – 5.09 (m, 2H), 3.84 (s, 3H), 3.09 – 2.87 (m, 2H), 2.77 – 2.49 (m, 2H), 2.48 – 2.24 (m, 2H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 194.1 (d, $^2J_{C\text{-}F}$ = 17.2 Hz), 158.7, 135.3, 131.7, 130.9, 130.0, 122.8, 119.8, 109.7, 95.1 (d, $^1J_{C\text{-}F}$ = 185.4 Hz), 55.57, 38.0 (d, $^2J_{C\text{-}F}$ = 23.2 Hz), 32.1 (d, $^2J_{C\text{-}F}$ = 22.2 Hz), 25.2 (d, $^3J_{C\text{-}F}$ = 10.1 Hz).
^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -159.90.
HRMS (APCI) m/z: Calculated for $C_{14}H_{15}FO_2H$ $[M + H]^+$: 235.1134. Found 235.1134.
HPLC Chiralpak IC, hexane/2-propanol = 90/10, 0.5 mL/Zmin, 254 nm, t_S (S) = 23.75 min (minor), t_R (R) = 25.00 min (major).

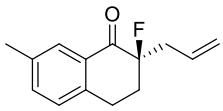
(*R*)-2-allyl-2-fluoro-5-methoxy-3,4-dihydronaphthalen-1(2H)-one (7c)



Chemical Formula: $C_{14}H_{15}FO_2$
Molecular Weight: 234.27 g/mol
Column chromatography, eluent petroleum ether/ethyl acetate 9.9: 0.1
Pale yellow oil**,** 30 mg, 97% yield, 94% ee, $[\alpha]^{25}_{D}$ = -9.70 (c 1.0, $CHCl_3$)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (dd, J = 8.0, 1.2 Hz, 1H), 7.37 – 7.29 (m, 1H), 7.05 (dd, J = 8.1, 1.1 Hz, 1H), 5.95 – 5.84 (m, 1H), 5.26 – 5.11 (m, 2H), 3.88 (s, 3H), 3.18 – 3.05 (m, 1H), 2.86 – 2.73 (m, 1H), 2.73 – 2.46 (m, 2H), 2.44 – 2.29 (m, 2H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 194.7 (d, $^2J_{C\text{-}F}$ = 17.5 Hz), 156.85, 131.71, 131.0 (d, $^4J_{C\text{-}F}$ = 3.6 Hz), 128.5, 127.8, 119.9, 119.7, 114.8, 95.2 (d, $^1J_{C\text{-}F}$ = 185.9 Hz), 55.8, 38.0 (d, $^2J_{C\text{-}F}$ = 23.4 Hz), 31.2 (d, $^2J_{C\text{-}F}$ = 22.3 Hz), 20.3 (d, $^3J_{C\text{-}F}$ = 10.8 Hz).
^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -160.53.
HRMS (APCI) m/z : Calculated for $C_{14}H_{15}FO_2H$ $[M + H]^+$: 235.1134. Found 235.1131.
HPLC Chiralpak IC, hexane/2-propanol = 90/10, 0.5 mL/min, 254 nm, t_S (S) = 24.59 min (minor), t_R (R) = 30.01 min (major).

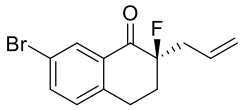
(*R*)-2-allyl-2-fluoro-7-methyl-3,4-dihydronaphthalen-1(2H)-one (7d)

[13] Bélanger, E.; Cantin, K. ; Messe, O.; Paquin, J.-F. *J. Am. Chem. Soc*. **2007**, *129*, 5, 1034.



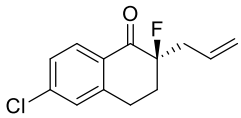
Chemical Formula: $C_{14}H_{15}FO$
Molecular Weight: 218.27 g/mol
Column chromatography, eluent petroleum ether/ethyl acetate 9.9: 0.1
Pale yellow oil, 27 mg, 94% yield, 94% ee, $[\alpha]^{25}_{D}$ = -30,3 (c 1.0, $CHCl_3$)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.84 (m, 1H), 7.34 (dd, *J* = 7.9, 2.0 Hz, 1H), 7.15 (d, *J* = 7.8 Hz, 1H), 5.94 – 5.84 (m, 1H), 5.27 – 5.11 (m, 2H), 3.10 – 2.92 (m, 2H), 2.79 – 2.46 (m, 2H), 2.46 – 2.28 (m, 2H), 2.37 (s, 3H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 194.4 (d, $^2J_{C-F}$ = 17.6 Hz), 139.9, 137.1, 135.3, 131.1 (d, $^3J_{C-F}$ = 3.8 Hz), 130.8, 128.8, 128.4, 119.9, 95.3 (d, $^1J_{C-F}$ = 185.2 Hz), 38.1 (d, $^2J_{C-F}$ = 23.4 Hz), 32.1 (d, $^2J_{C-F}$ = 22.3 Hz), 25.7 (d, $^3J_{C-F}$ = 10.2 Hz), 21.0.
^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -159.85.
HRMS (APCI) m/z: Calculated for $C_{14}H_{15}FOH$ $[M + H]^+$: 219.1185. Found 219.1181.
HPLC Chiralpak IC, hexane/2-propanol = 90/10, 0.5 mL/min, 254 nm, t_S (*S*) = 19.31 min (minor), t_R (*R*) = 20.34 min (major).

(*R*)-2-allyl-7-bromo-2-fluoro-3,4-dihydronaphthalen-1(2H)-one (7e)



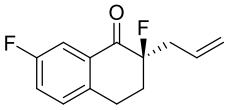
Chemical Formula: $C_{13}H_{12}BrFO$
Molecular Weight: 282.01 g/mol
Column chromatography, eluent petroleum ether/ethyl acetate 9.5: 0.5
Pale yellow oil, 35 mg, 94% yield, 93% ee, $[\alpha]^{25}_{D}$ = -27.9 (c 1.0, $CHCl_3$)
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 2.2 Hz, 1H), 7.62 (dd, *J* = 8.2, 2.2 Hz, 1H), 7.19 – 7.12 (m, 1H), 5.92 – 5.81 (m, 1H), 5.27 – 5.13 (m, 2H), 3.12 – 2.89 (m, 2H), 2.79 – 2.48 (m, 2H), 2.48 – 2.27 (m, 2H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 192.6 (d, $^2J_{C-F}$ = 17.2 Hz), 141.6, 137.0, 132.6, 131.1, 130.7, 121.3, 120.3, 94.8 (d, $^1J_{C-F}$ = 185.8 Hz), 38.2 (d, $^2J_{C-F}$ = 23.5 Hz), 31.8 (d, $^2J_{C-F}$ = 22.8 Hz), 31.7, 25.6 (d, $^3J_{C-F}$ = 9.8 Hz).
^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -160.43.
HRMS (APCI) m/z: Calculated for $C_{13}H_{12}BrFOH$ $[M + H]^+$: 283.0134. Found 283.0130.
HPLC Chiralpak IF, hexane/2-propanol = 90/10, 0.5 mL/min, 254 nm, t_R (*R*) =14.88 min (major), t_S (*S*) = 19.93 min (minor).

(*R*)-2-allyl-6-chloro-2-fluoro-3,4-dihydronaphthalen-1(2H)-one (7f)



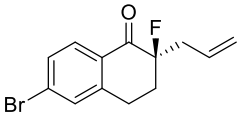
Chemical Formula: $C_{13}H_{12}ClFO$
Molecular Weight: 238.69 g/mol
Column chromatography, eluent petroleum ether/ethyl acetate 9.5: 0.5
Pale yellow oil, 30 mg, 95% yield, 94% ee, $[\alpha]^{25}_{D}$ = -9.90 (c 1.0, $CHCl_3$)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.5 Hz, 1H), 7.34 – 7.31 (m, 1H), 7.27 – 7.26 (m, 1H), 5.92 – 5.82 (m, 1H), 5.26 – 5.12 (m, 2H), 3.17 – 2.90 (m, 2H), 2.78 – 2.48 (m, 2H), 2.47 – 2.27 (m, 2H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 192.8 (d, $^2J_{C-F}$ = 18.2 Hz), 144.45, 140.72, 130.8 (d, $^4J_{C-F}$ = 4.5 Hz), 130.1, 129.5, 128.8, 127.9, 120.2, 94.7 (d, $^1J_{C-F}$ = 286.0 Hz), 38.1 (d, $^2J_{C-F}$ = 23.6 Hz), 31.8 (d, $^2J_{C-F}$ = 22.7 Hz), 25.8 (d, $^2J_{C-F}$ = 9.9 Hz).
^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -160.26.
HRMS (APCI) m/z : Calculated for $C_{13}H_{12}ClFOH$ $[M + H]^+$: 239.0639. Found 239.0643.
HPLC Chiralpak IF, hexane/2-propanol = 90/10, 1 mL/min, 254 nm, t_R (*R*) = 6.82 min (major), t_S (*S*) = 8.80 min (minor).

(*R*)-2-allyl-2,7-difluoro-3,4-dihydronaphthalen-1(2H)-one (7g)



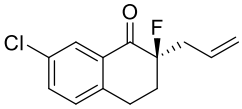
Chemical Formula: $C_{13}H_{12}F_2O$
Molecular Weight: 222.23 g/mol
Column chromatography, eluent petroleum ether/ethyl acetate 9.5: 0.5
Pale yellow oil, 28 mg, 94% yield, 94% ee, $[\alpha]^{25}_D$ = -17.3 (c 1.0, $CHCl_3$)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 – 7.66 (m, 1H), 7.29 – 7.19 (m, 2H), 5.93 – 5.82 (m, 1H), 5.26 – 5.13 (m, 2H), 3.15 – 3.04 (m, 1H), 3.01 – 2.93 (m, 1H), 2.77 – 2.49 (m, 2H), 2.49 – 2.27 (m, 2H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 193.0 (d, $^2J_{C-F}$ = 17.9 Hz), 161.8 (d, $^1J_{C-F}$ = 248.2 Hz), 138.7, 132.6 (d, $^3J_{C-F}$ = 7.3 Hz), 130.8 (d, $^3J_{C-F}$ = 10.1 Hz), 130.7, 121.7 (d, $^2J_{C-F}$ = 22.5 Hz), 120.2, 114.1 (d, $^2J_{C-F}$ = 22.4 Hz), 94.7 (d, $^1J_{C-F}$ = 185.2 Hz), 38.0 (d, $^2J_{C-F}$ = 23.4 Hz), 32.0 (d, $^2J_{C-F}$ = 22.6 Hz), 25.3 (d, $^3J_{C-F}$ = 9.9 Hz).
^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -114.31, -160.56.
HRMS (APCI) m/z : Calculated for $C_{13}H_{12}F_2OH$ $[M + H]^+$: 223.0934. Found 223.0938.
HPLC Chiralpak IF, hexane/2-propanol = 90/10, 1 mL/min, 254 nm, t_R (*R*) = 6.70 min (major), t_S (*S*) = 7.68 min (minor).

(*R*)-2-allyl-6-bromo-2-fluoro-3,4-dihydronaphthalen-1(2H)-one (7h)



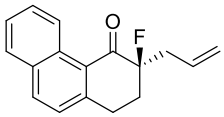
Chemical Formula: $C_{13}H_{12}BrFO$
Molecular Weight: 282.01 g/mol
Column chromatography, eluent petroleum ether/ethyl acetate 9.5: 0.5
Pale yellow oil, 87 mg, 90% yield, 94% ee, $[\alpha]^{25}_D$ = - 3.8 (c 1.0, $CHCl_3$)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.4 Hz, 1H), 7.54 – 7.41 (m, 2H), 5.92 – 5.81 (m, 1H), 5.25 – 5.12 (m, 2H), 3.16 – 2.90 (m, 2H), 2.79 – 2.49 (m, 2H), 2.49 – 2.25 (m, 2H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 192.9 (d, $^2J_{C-F}$ = 18.2 Hz), 144.5, 131.8, 130.8, 130.7, 130.1, 129.9, 129.6, 120.2, 94.5 (d, $^1J_{C-F}$ = 184.8 Hz), 38.0 (d, $^2J_{C-F}$ = 23.2 Hz), 31.8 (d, $^2J_{C-F}$ = 23.2 Hz), 25.7 (d, $^3J_{C-F}$ = 10.1 Hz).
^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -160.29.
HRMS (APCI) m/z : Calculated for $C_{13}H_{12}BrFOH$ $[M + H]^+$: 283.0134. Found 283.0128.
HPLC Chiralpak IF, hexane/2-Propanol = 90/10, 0.5 mL/min, 254 nm, t_R (*R*) = 7.56 min (major), t_S (*S*) = 10.03 min (minor).

(*R*)-2-allyl-7-chloro-2-fluoro-3,4-dihydronaphthalen-1(2H)-one (7i)



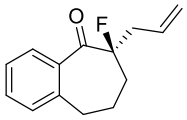
Chemical Formula: $C_{13}H_{12}ClFO$
Molecular Weight: 238.69 g/mol
Column chromatography, eluent petroleum ether/ethyl acetate 9.5: 0.5
Pale yellow oil, 30 mg, 95% yield, 93% ee, $[\alpha]^{25}_D$ = - 34.8 (c 1.0, $CHCl_3$)
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 2.3 Hz, 1H), 7.48 (dd, *J* = 8.2, 2.3 Hz, 1H), 7.22 (dd, *J* = 8.2, 1.0 Hz, 1H), 5.92 – 5.82 (m, 1H), 5.29 – 5.12 (m, 2H), 3.23 – 2.85 (m, 2H), 2.81 – 2.47 (m, 2H), 2.47 – 2.22 (m, 2H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 192.8 (d, $^2J_{C-F}$ = 20.2 Hz), 141.1, 134.2, 133.6, 132.3, 130.7, 130.5, 128.1, 120.3, 94.8 (d, $^1J_{C-F}$ = 184.8 Hz), 38.0 (d, $^2J_{C-F}$ = 23.2 Hz), 31.9 (d, $^2J_{C-F}$ = 22.2 Hz), 25.5 (d, $^3J_{C-F}$ = 10.1 Hz).
^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -160.48.
HRMS (APCI) m/z : Calculated for $C_{13}H_{12}ClFOH$ $[M + H]^+$: 239.0639. Found 239.0636.
HPLC Chiralpak IF, hexane/2-Propanol = 90/10, 1.0 mL/min, 254 nm, t_R (*R*) = 7.36 min (major), t_S (*S*) = 9.58 min (minor).

(*R*)-3-allyl-3-fluoro-2,3-dihydrophenanthren-4(1H)-one (7j)



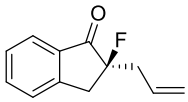
Chemical Formula: $C_{17}H_{15}FO$
Molecular Weight: 254.30 g/mol
Column chromatography, eluent petroleum ether/ethyl acetate 9.5: 0.5
Pale yellow oil, 16 mg, 52% yield, 91% ee, $[\alpha]^{25}_{D}$ = -16.3 (c 1.0, $CHCl_3$)
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.25 (dd, *J* = 8.7, 1.0 Hz, 1H), 7.96 (d, *J* = 8.4 Hz, 1H), 7.86 – 7.80 (m, 1H), 7.65 (ddd, *J* = 8.6, 6.9, 1.5 Hz, 1H), 7.53 (ddd, *J* = 8.0, 6.8, 1.2 Hz, 1H), 7.29 (d, *J* = 8.4 Hz, 1H), 5.98 – 5.89 (m, 1H), 5.24 – 5.10 (m, 2H), 3.39 – 3.09 (m, 2H), 2.87 – 2.34 (m, 4H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 196.4 (d, $^2J_{C-F}$ = 17.2 Hz), 144.7, 135.0, 132.9, 131.7, 131.2, 129.3, 128.5, 126.6, 126.5, 126.3, 125.9, 119.9, 95.4 (d, $^1J_{C-F}$ = 184.8 Hz), 38.7 (d, $^2J_{C-F}$ = 23.2 Hz), 32.0 (d, $^2J_{C-F}$ = 23.2 Hz), 27.51 (d, $^3J_{C-F}$ = 10.1 Hz).
^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -158.50.
HRMS (APCI) m/z : Calculated for $C_{17}H_{15}FOH$ $[M + H]^+$: 255.1185. Found 255.1181.
HPLC Chiralpak IC, hexane/2-Propanol = 90/10, 1 mL/min, 254 nm, t_R (*R*) = 11.22 min (minor), t_S (*S*) = 12.39 min (major).

(*R*)-6-allyl-6-fluoro-6,7,8,9-tetrahydro-5H-benzo[7]annulen-5-one (7l)[12]



Chemical Formula: $C_{14}H_{15}FO$
Molecular Weight: 218.27 g/mol
Column chromatography, eluent petroleum ether/ethyl acetate 9.9: 0.1
Pale yellow oil, 28 mg, 92% yield, 90% ee, $[\alpha]^{25}_{D}$ = -44.4 (c 0.36, $CHCl_3$) {lit. $[\alpha]^{25}_{D}$ = -42,1 (c 0.36, $CHCl_3$)}[13]
In accordance with the literature : **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.46 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.38 (td, *J* = 7.5, 1.5 Hz, 1H), 7.30 – 7.27 (m, 1H), 7.21 – 7.17 (m, 1H), 5.85 – 5.74 (m, 1H), 5.18 – 5.05 (m, 2H), 3.16 – 3.04 (m, 1H), 2.96 – 2.85 (m, 1H), 2.81 – 2.52 (m, 2H), 2.26 – 1.95 (m, 3H), 1.88 – 1.74 (m, 1H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 204.2 (d, $^2J_{C-F}$ = 27.3 Hz), 140.9, 137.9, 131.5, 131.2 (d, $^4J_{C-F}$ = 4.0 Hz), 129.6, 128.8, 126.6, 119.7, 101.9 (d, $^1J_{C-F}$ = 183.8 Hz), 40.8 (d, $^2J_{C-F}$ = 23.2 Hz), 36.4 (d, $^2J_{C-F}$ = 22.2 Hz), 34.5, 23.9 (d, $^2J_{C-F}$ = 3.0 Hz).
^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -154.40.
HPLC Chiralpak OJ, hexane/2-propanol = 99/1, 0.8 mL/min, 254 nm, t_R (*R*) = 12.64 min (major), t_S (*S*) = 15.60 min (minor).

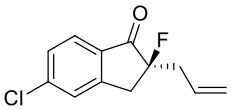
(*S*)-2-allyl-2-fluoro-2,3-dihydro-1H-inden-1-one (7m)[12]



Chemical Formula: $C_{12}H_{11}FO$
Molecular Weight: 190.22 g/mol
Column chromatography, eluent petroleum ether/ethyl acetate 9.9: 0.1
Pale yellow oil, 24 mg, 94% yield, 84% ee, $[\alpha]^{25}_{D}$ = -53.5 (c 0.68, $CHCl_3$) {lit. $[\alpha]^{25}_{D}$ = -59,2 (c 0.68, $CHCl_3$)}[8]
In accordance with the literature : **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80 (dd, *J* = 7.7, 1.2 Hz, 1H), 7.65 (td, *J* = 7.5, 1.3 Hz, 1H), 7.46 – 7.39 (m, 2H), 5.82 – 5.72 (m, 1H), 5.26 – 5.11 (m, 2H), 3.48 – 3.23 (m, 2H), 2.86 – 2.77 (m, 1H), 2.59 – 2.42 (m, 1H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 200.8 (d, $^2J_{C-F}$ = 17.8 Hz), 150.4 (d, $^4J_{C-F}$ = 4.3 Hz), 136.5, 134.2, 130.6 (d, $^3J_{C-F}$ = 7.2 Hz), 128.4, 126.8, 125.2, 120.4, 97.1 (d, $^1J_{C-F}$ = 188.4 Hz), 39.5 (d, $^2J_{C-F}$ = 25.2 Hz), 37.8 (d, $^2J_{C-F}$ = 24.7 Hz).
^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -157.04.

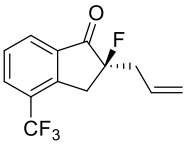
HPLC Chiralpak IC, hexane/2-Propanol = 90/10, 0.5 mL/min, 254 nm, t_S (*S*) = 18.48 min (minor), t_R (*R*) = 19.62 min (major).

(*S*)-2-allyl-5-chloro-2-fluoro-2,3-dihydro-1H-inden-1-one (7n)



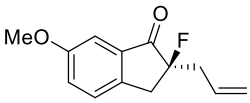
Chemical Formula: $C_{12}H_{10}ClFO$
Molecular Weight: 224.66 g/mol
Column chromatography, eluent petroleum ether/ethyl acetate 9.9: 0.1
Pale yellow oil, 27 mg, 91% yield, 86% ee, $[\alpha]^{25}_D$ = -20.8 (c 1.0, $CHCl_3$)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.2 Hz, 1H), 7.46 – 7.36 (m, 2H), 5.79 – 5.68 (m, 1H), 5.26 – 5.12 (m, 2H), 3.47 – 3.18 (m, 2H), 2.89 – 2.73 (m, 1H), 2.61 – 2.43 (m, 1H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 199.3 (d, $^2J_{C-F}$ = 18.1 Hz), 151.9, 143.1, 132.6, 130.2 (d, $^3J_{C-F}$ = 7.3 Hz), 129.3, 127.1, 126.3, 120.7, 97.0 (d, $^1J_{C-F}$ = 189.6 Hz), 39.4 (d, $^2J_{C-F}$ = 25.3 Hz), 37.5 (d, $^2J_{C-F}$ = 25.1 Hz).
^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -155.98.
HRMS (APCI) m/z : Calculated for $C_{12}H_{10}ClFOH$ $[M + H]^+$: 225.0482. Found 225.0480.
HPLC Chiralpak IC, hexane/2-propanol = 95/5, 0.5 mL/min, 254 nm, t_R (*R*) = 20.45 min (minor), t_S (*S*) = 22.13 min (major).

(*S*)-2-allyl-2-fluoro-4-(trifluoromethyl)-2,3-dihydro-1H-inden-1-one (7o)



Chemical Formula: $C_{13}H_{10}F_4O$
Molecular Weight: 258.22 g/mol
Column chromatography, eluent petroleum ether/ethyl acetate 9.9: 0.1
Pale yellow oil, 23 mg, 66% yield, 86% ee, $[\alpha]^{25}_D$ = -25.6 (c 1.0, $CHCl_3$)
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 – 7.91 (m, 2H), 7.57 (tq, *J* = 7.7, 0.8 Hz, 1H), 5.79 – 5.69 (m, 1H), 5.30 – 5.15 (m, 2H), 3.66Z – 3.38 (m, 2H), 2.89 – 2.80 (m, 1H), 2.66 – 2.50 (m, 1H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 199.6, 147.9, 135.6, 132.9, 129.9 (d, $^3J_{C-F}$ = 7.5 Hz), 128.8, 128.5, 123.6 (q, $^1J_{C-F}$ = 273.8 Hz), 121.1, 119.2, 96.3 (d, $^1J_{C-F}$ = 188.7 Hz), 39.2 (d, $^2J_{C-F}$ = 25.3 Hz), 36.6 (d, $^2J_{C-F}$ = 25.6 Hz).
^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -62.48, -155.78.
HRMS (APCI) m/z : Calculated for $C_{13}H_{10}F_4OH$ $[M + H]^+$: 259.0746. Found 259.0744.
HPLC Chiralpak IC, hexane/2-propanol = 95/5, 0.5 mL/min, 254 nm, t_R (*R*) = 12.88 min (minor), t_S (*S*) = 13.61 min (major).

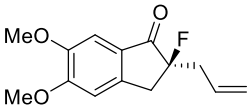
(*S*)-2-allyl-2-fluoro-4-methoxy-2,3-dihydro-1H-inden-1-one (7p)



Chemical Formula: $C_{13}H_{13}FO_2$
Molecular Weight: 220.24 g/mol
Column chromatography, eluent petroleum ether/ethyl acetate 9.9: 0.1
Pale yellow oil, 27 mg, 92% yield, 87% ee, $[\alpha]^{25}_D$ = -40.9 (c 1.0, $CHCl_3$)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.29 (m, 1H), 7.27 – 7.24 (m, 1H), 7.24 – 7.20 (m, 1H), 5.81 – 5.71 (m, 1H), 5.26 – 5.10 (m, 2H), 3.84 (s, 3H), 3.41 – 3.13 (m, 2H), 2.80 (m, 1H), 2.62 – 2.42 (m, 1H).

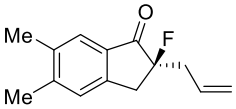
$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 160.0, 143.3, 135.2, 130.6 (d, $^3J_{C-F}$ = 7.2 Hz), 128.5, 127.6, 126.0, 120.4, 106.0, 97.9 (d, $^1J_{C-F}$ = 192.6 Hz), 55.8, 39.7 (d, $^2J_{C-F}$ = 25.4 Hz), 37.2 (d, $^2J_{C-F}$ = 24.6 Hz).
$^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$) δ -156.60.
HRMS (APCI) m/z : Calculated for $C_{13}H_{13}FO_2H$ $[M + H]^+$: 221.0978. Found 221.0974.
HPLC Chiralpak IF, hexane/2-propanol = 90/10, 1.0 mL/min, 254 nm, t_S (*S*) = 7.63 min (major), t_R (*R*) = 8.23 min (minor).

(*S*)-2-allyl-2-fluoro-5,6-dimethoxy-2,3-dihydro-1H-inden-1-one (7q)



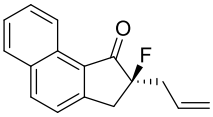
Chemical Formula: $C_{14}H_{15}FO_3$
Molecular Weight: 250.27 g/mol
Column chromatography, eluent petroleum ether/ethyl acetate 9.9: 0.1
Pale yellow oil, 31 mg, 94% yield, 88% ee, $[\alpha]^{25}_D$ = - 30.1 (c 1.0, $CHCl_3$)
^1H NMR (400 MHz, $CDCl_3$) δ 7.20 (s, 1H), 6.83 (s, 1H), 5.81 – 5.70 (m, 1H), 5.26 – 5.10 (m, 2H), 3.98 (s, 3H), 3.91 (s, 3H), 3.39 – 3.14 (m, 2H), 2.86 – 2.77 (m, 1H), 2.65 – 2.44 (m, 1H).
$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 199.2 (d, $^2J_{C-F}$ = 18.2 Hz), 156.9, 150.2, 146.2, 130.9 (d, $^3J_{C-F}$ =8.1 Hz), 126.9, 120.2, 107.5, 105.2, 97.5 (d, $^1J_{C-F}$ = 188.9 Hz), 56.5, 56.3, 39.7 (d, $^2J_{C-F}$ = 25.3 Hz), 37.4 (d, $^2J_{C-F}$ =25.3 Hz).
$^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$) δ -155.78.
HRMS (APCI) m/z : Calculated for $C_{14}H_{15}FO_3H$ $[M + H]^+$: 251.1083. Found 251.1082.
HPLC Chiralpak IF, hexane/2-propanol = 90/10, 1.0 mL/min, 254 nm, t_S (*S*) = 35.05 min (minor), t_R (*R*) = 41.85 min (major).

(*S*)-2-allyl-2-fluoro-5,6-dimethyl-2,3-dihydro-1H-inden-1-one (7r)



Chemical Formula: $C_{14}H_{15}FO$
Molecular Weight: 218.27 g/mol
Column chromatography, eluent petroleum ether/ethyl acetate 9.9: 0.1
Pale yellow oil, 28 mg, 95% yield, 87% ee, $[\alpha]^{25}_D$ = - 33.3 (c 1.0, $CHCl_3$)
^1H NMR (400 MHz, $CDCl_3$) δ 7.49 (s, 1H), 7.13 (s, 1H), 5.74 – 5.63 (m, 1H), 5.16 – 5.02 (m, 2H), 3.32 – 3.07 (m, 2H), 2.81 – 2.65 (m, 1H), 2.52 – 2.36 (m, 1H), 2.28 (s, 3H), 2.24 (s, 3H).
$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 200.5 (d, $^2J_{C-F}$ = 18.2 Hz), 148.5, 147.1, 137.5, 132.3, 130.8 (d, $^3J_{C-F}$ = 7.1 Hz), 127.5, 125.4, 120.2, 97.5 (d, $^1J_{C-F}$ = 188.9 Hz), 39.7 (d, $^2J_{C-F}$ = 26.3 Hz), 37.3 (d, $^2J_{C-F}$ = 24.2 Hz), 21.1, 19.9.
$^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$) δ -156.75.
HRMS (APCI) m/z : Calculated for $C_{14}H_{15}FOH$ $[M + H]^+$: 219.1185. Found 219.1180.
HPLC Chiralpak IC, hexane/2-Propanol = 90/10, 1 mL/min, 254 nm, t_S (*S*) = 13.33 min (minor), t_R (*R*) = 15.38 min (major).

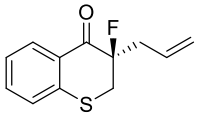
(*S*)-2-allyl-2-fluoro-2,3-dihydro-1H-cyclopenta[a]naphthalen-1-one (7s)



Chemical Formula: $C_{16}H_{13}FO$
Molecular Weight: 240.28 g/mol
Column chromatography, eluent petroleum ether/ethyl acetate 9.5: 0.5
Pale yellow oil, 25 mg, 79% yield, 94% ee, $[\alpha]^{25}_D$ = - 16.2 (c 1.0, $CHCl_3$)
^1H NMR (400 MHz, $CDCl_3$) δ 9.07 (d, *J* = 8.3 Hz, 1H), 8.11 (d, *J* = 8.3 Hz, 1H), 7.90 (d, *J* = 8.1 Hz, 1H), 7.71 (ddd, *J* = 8.4, 6.9, 1.3 Hz, 1H), 7.62 – 7.57 (m, 1H), 7.47 (d, *J* = 8.4 Hz, 1H), 5.85 – 5.75 (m, 1H), 5.29 – 5.08 (m, 2H), 3.57 – 3.33 (m, 2H), 2.97 – 2.83 (m, 1H), 2.70 – 2.50 (m, 1H).

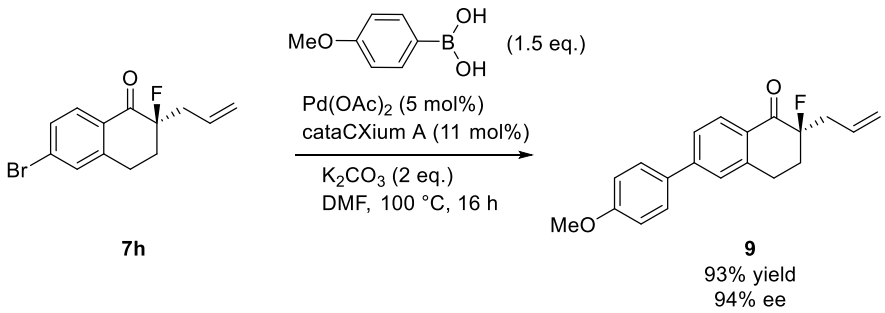
$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 201.0 (d, $^2J_{C-F}$ = 19.2 Hz), 153.8, 137.7, 133.1, 130.9, 130.8, 129.7, 129.6, 128.5, 127.3, 124.4, 123.7, 120.3, 97.5 (d, $^1J_{C-F}$ = 187.9 Hz), 39.7 (d, $^2J_{C-F}$ = 25.3 Hz), 38.1 (d, $^2J_{C-F}$ = 14.2 Hz).
$^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$) δ -156.07.
HRMS (APCI) m/z : Calculated for $C_{16}H_{13}FOH$ $[M + H]^+$: 241.1029. Found 241.1023.
HPLC Chiralpak IC, hexane/2-Propanol = 90/10, 1 mL/min, 254 nm, t_S (*S*) = 9.42 min (minor), t_R (*R*) = 12.39 min (major).

(*R*)-3-allyl-3-fluorothiochroman-4-one (7t)



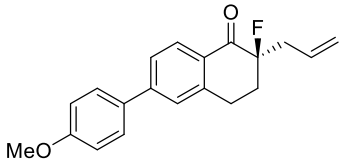
Chemical Formula: $C_{12}H_{11}FOS$
Molecular Weight: 222.28 g/mol
Column chromatography, eluent petroleum ether/ethyl acetate 9.5: 0.5
Pale yellow oil, 10 mg, 48% yield, 92% ee, $[\alpha]^{25}_D$ = -66.9 (c 1.0, $CHCl_3$)
^1H NMR (400 MHz, $CDCl_3$) δ 8.11 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.43 (ddd, *J* = 8.3, 7.1, 1.5 Hz, 1H), 7.26 – 7.20 (m, 2H), 6.02 – 5.80 (m, 1H), 5.36 – 5.21 (m, 2H), 3.62 (ddd, *J* = 13.2, 6.5, 0.9 Hz, 1H), 3.17 (dd, *J* = 13.1, 7.6 Hz, 1H), 2.99 – 2.65 (m, 2H).
$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 191.0 (d, $^2J_{C-F}$ = 17.2 Hz), 140.7, 134.0, 130.6, 130.0, 129.7, 127.1, 125.6, 121.3, 93.7 (d, $^1J_{C-F}$ = 198.9 Hz), 36.7 (d, $^2J_{C-F}$ = 22.2 Hz), 32.9 (d, $^2J_{C-F}$ = 28.2 Hz).
$^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$) δ -159.72.
HRMS (APCI) m/z : Calculated for $C_{12}H_{12}FOSH$ $[M + H]^+$: 223.0593. Found 223.0591.
HPLC Chiralpak IF, hexane/2-Propanol = 90/10, 1 mL/min, 254 nm, t_S (*S*) = 7.99 min (major), t_R (*R*) = 10.95 min (minor).

7. Post-functionalization

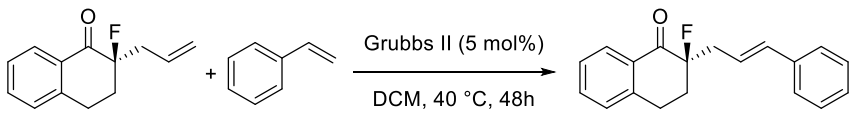


A dried round-bottom 10 mL tube under argon was charged with (*R*)-2-allyl-6-bromo-2-fluoro-3,4-dihydronaphthalen-1(2H)-one (**7h**) (50 mg, 0.18 mmol, 1 equiv.), (4- methoxyphenyl) boronic acid (41.0 mg, 0.27 mmol, 1.5 equiv.), K_2CO_3 (49.8 mg, 0.36 mmol, 2 equiv.), $Pd(OAc)_2$ (2.0 mg, 9 µmol, 0.05 equiv.) and cataCXium A (7.1 mg, 19.8 µmol, 0.11 equiv.). 1.8 mL of DMF were then added. The mixture was stirred at 100 °C for 16 h. The reaction mixture was then quenched with a saturated $NaHCO_3$ aqueous solution and extracted twice with CH_2Cl_2. The organic layers were dried over $MgSO_4$, filtered and concentrated under vacuum. The obtained brown solid was purified by flash column chromatography on silica gel (petroleum ether/EtOAc 9:1). The desired product **9** was obtained as a brown solid (51.9 mg, 93%).

(*R*)-2-allyl-2-fluoro-6-(4-methoxyphenyl)-3,4-dihydronaphthalen-1(2H)-one (9)



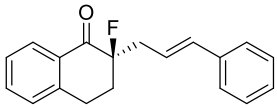
Chemical Formula: $C_{20}H_{19}FO_2$
Molecular Weight: 310.37 g/mol
Column chromatography, eluent petroleum ether/ethyl acetate 9: 1
Brown solid, 52 mg, 93% yield, 94% ee
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, J = 8.2 Hz, 1H), 7.61 – 7.52 (m, 3H), 7.42 (d, J = 1.7 Hz, 1H), 7.04 – 6.96 (m, 2H), 5.97 – 5.86 (m, 1H), 5.30 – 5.13 (m, 2H), 3.87 (s, 3H), 3.24 – 2.97 (m, 2H), 2.80 – 2.51 (m, 2H), 2.51 – 2.32 (m, 2H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 193.7 (d, $^2J_{C\text{-}F}$ = 18.2 Hz), 160.3, 146.5, 143.3, 132.1, 131.1 (d, $^3J_{C\text{-}F}$ = 4.0 Hz), 129.3, 129.1, 128.6, 126.6, 125.6, 119.9, 114.6, 95.1 (d, $^1J_{C\text{-}F}$ = 184.8 Hz), 55.5, 38.2 (d, $^2J_{C\text{-}F}$ = 23.2 Hz), 32.1 (d, $^2J_{C\text{-}F}$ = 22.2 Hz), 26.2 (d, $^3J_{C\text{-}F}$ = 10.1 Hz).
^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -159.73.
HRMS (APCI) m/z : Calculated for $C_{20}H_{19}FO_2H$ $[M + H]^+$: 311.1447. Found 311.1442.
HPLC Chiralpak IF, hexane/2-Propanol = 90/10, 1 mL/min, 254 nm, t_S (S) = 14.87 min (major), t_R (R) = 18.35 min (minor).



7a **10**

A dried round-bottom 50 mL tube under argon was charged with (R)-2-allyl-2-fluoro-3,4-dihydronaphthalen-1(2H)-one (**7a**) (70 mg, 0.34 mmol, 1 equiv.), styrene (106.2 mg, 1.02 mmol, 3 equiv.) and Grubbs II catalyst (14.4 mg, 17 µmol, 0.05 equiv.). 6.8 mL of DCM were then added and the mixture was stirred at 40 °C for 48 h. The solvent was evaporated in vacuo and the obtained dark brown solid was purified by flash column chromatography on silica gel (petroleum ether/EtOAc 9.8: 0.2). The desired product **10** was obtained as a brown solid (67.0 mg, 70%).

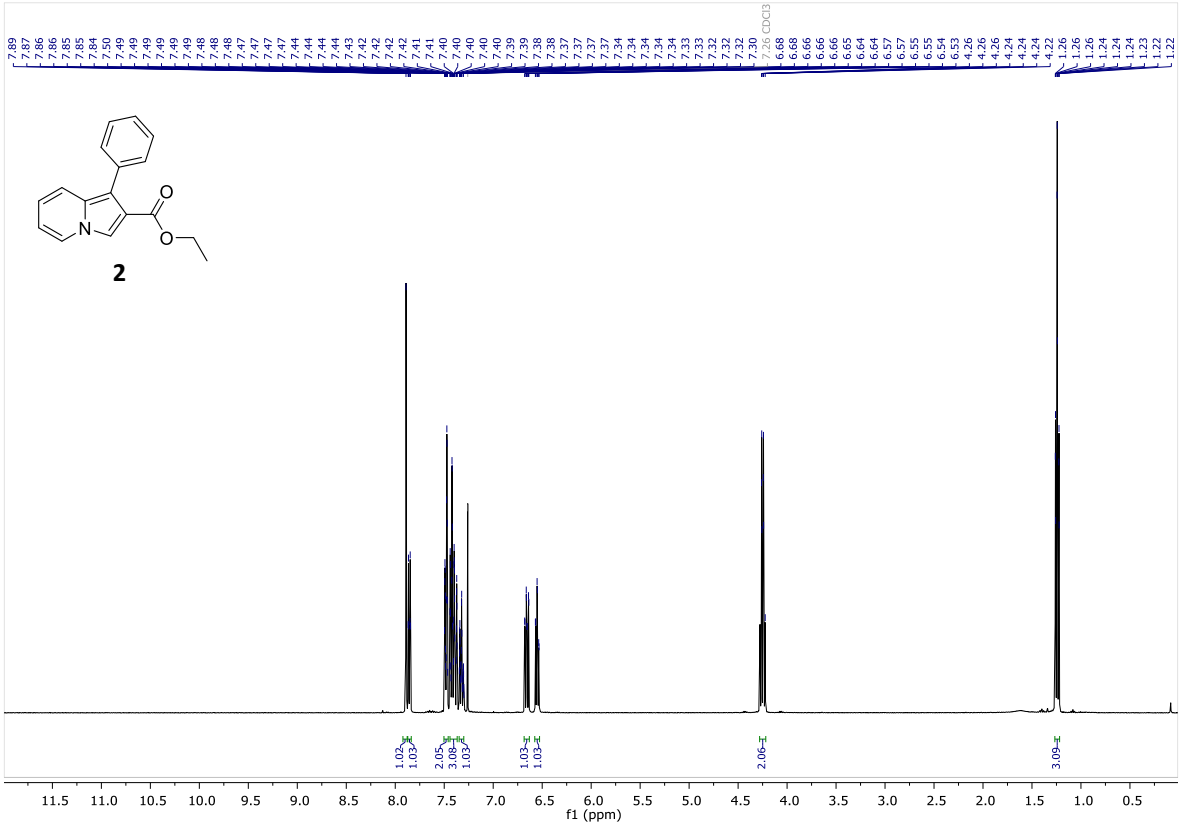
(R)-2-cinnamyl-2-fluoro-3,4-dihydronaphthalen-1(2H)-one (10)



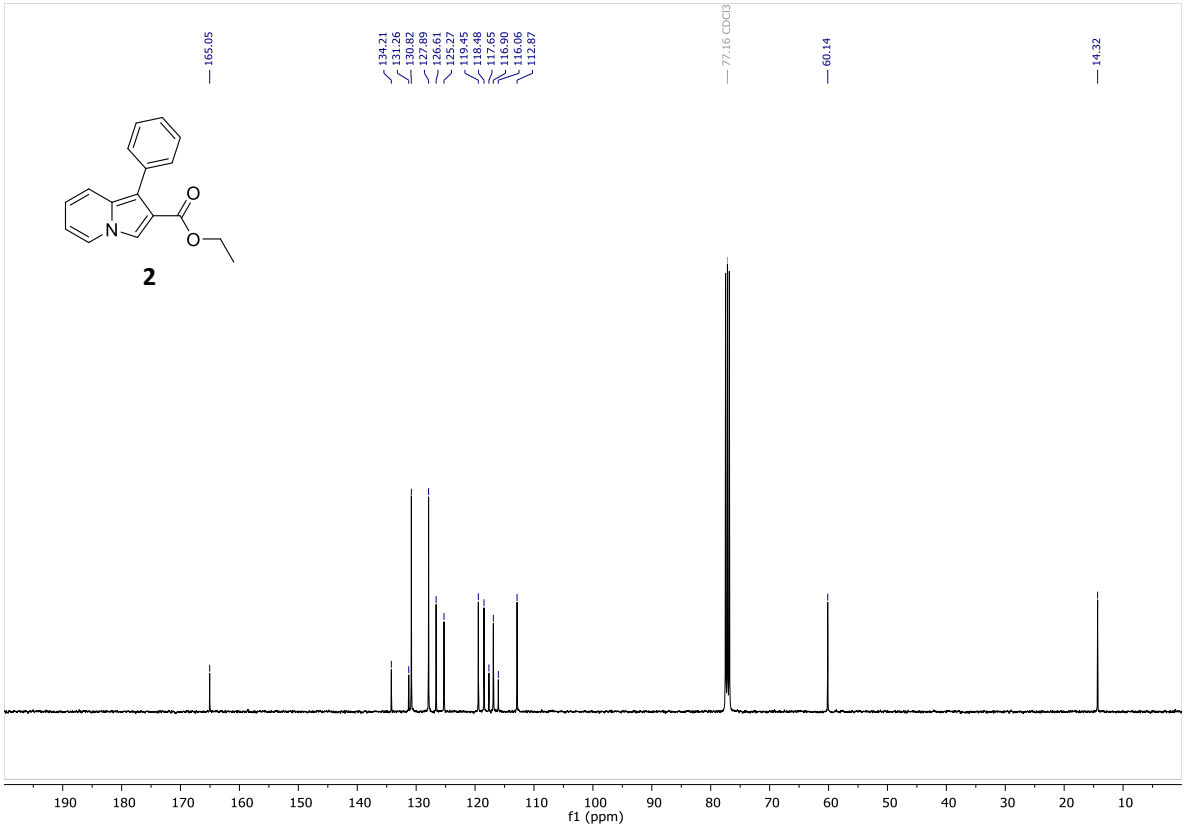
Chemical Formula: $C_{19}H_{17}FO$
Molecular Weight: 280.34 g/mol
Column chromatography, eluent petroleum ether/ethyl acetate 9.8: 0.2
Brown solid, 67.0 mg, 70% yield, 94% ee
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (dd, J = 7.9, 1.5 Hz, 1H), 7.43 (td, J = 7.5, 1.5 Hz, 1H), 7.30 – 7.10 (m, 7H), 6.41 (d, J = 15.8 Hz, 1H), 6.22 – 6.15 (m, 1H), 3.10 – 2.86 (m, 2H), 2.86 – 2.55 (m, 2H), 2.37 – 2.26 (m, 2H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 194.0 (d, $^2J_{C\text{-}F}$ = 27.2 Hz), 142.9, 136.9, 134.8, 134.2, 131.0, 128.8, 128.7, 128.4, 127.7, 127.3, 126.4, 122.5, 122.4, 95.3 (d, $^1J_{C\text{-}F}$ = 184.8 Hz), 37.4 (d, $^2J_{C\text{-}F}$ = 24.2 Hz), 32.0 (d, $^2J_{C\text{-}F}$ = 22.2Hz), 26.0 (d, $^3J_{C\text{-}F}$ = 10.1 Hz).
^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -159.45.
HRMS (APCI) m/z : Calculated for $C_{19}H_{17}FOH$ $[M + H]^+$: 281.1342. Found 281.1344.

8. NMR spectra for compounds **2a – 5f**

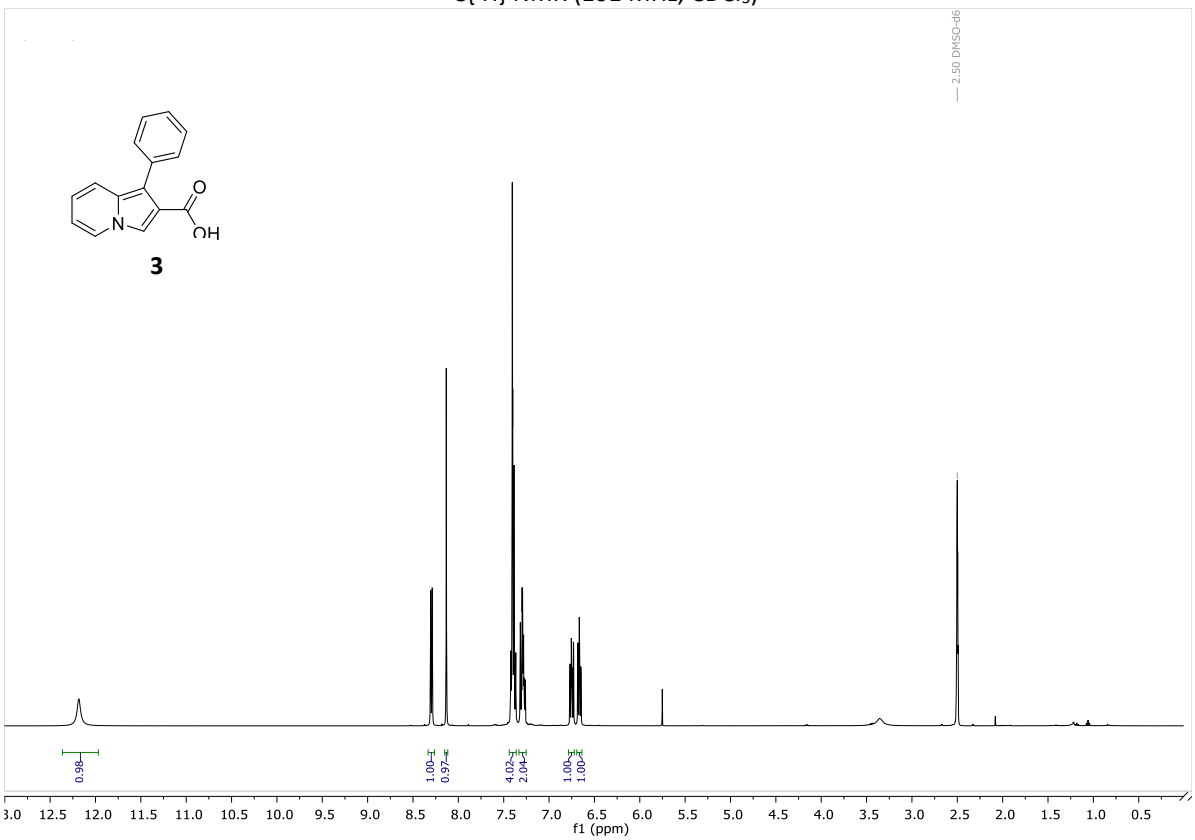
NMR spectra:



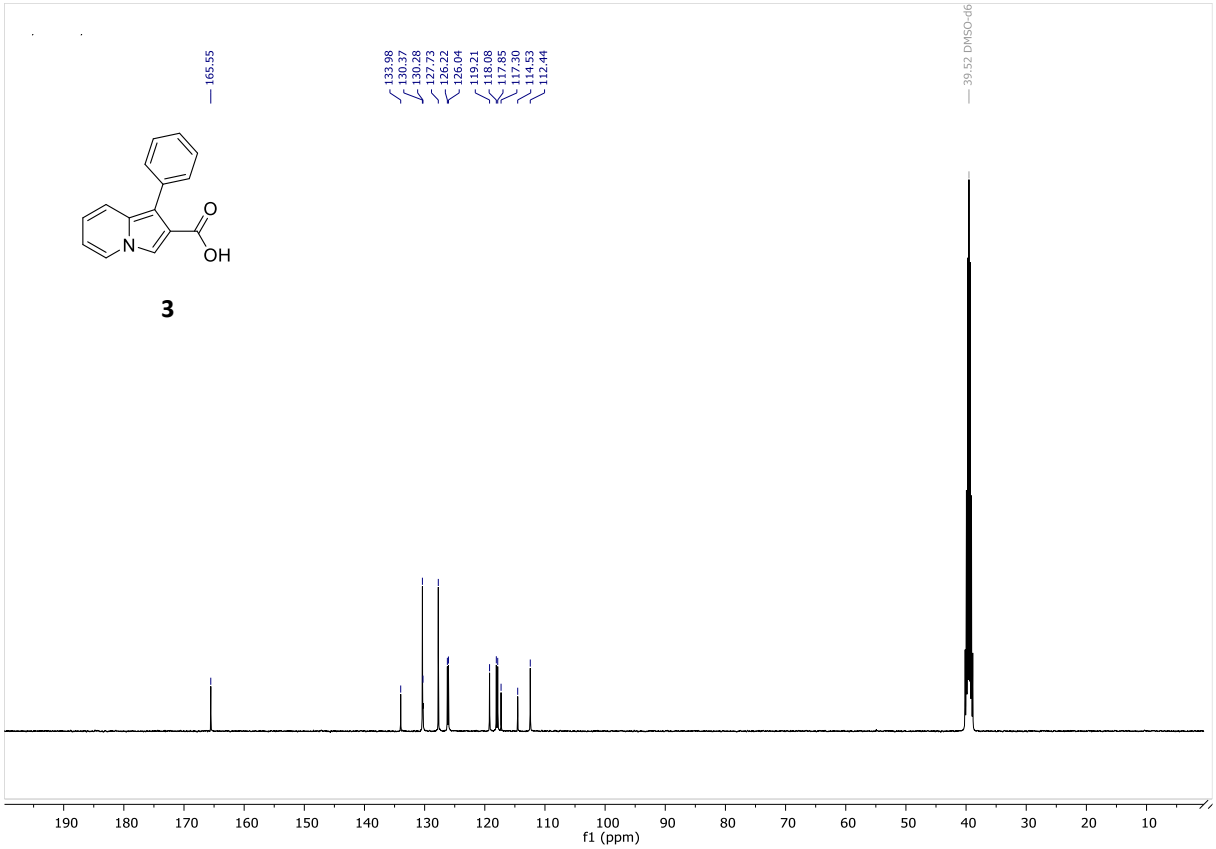
^{1}H NMR (400 MHz, $CDCl_3$)



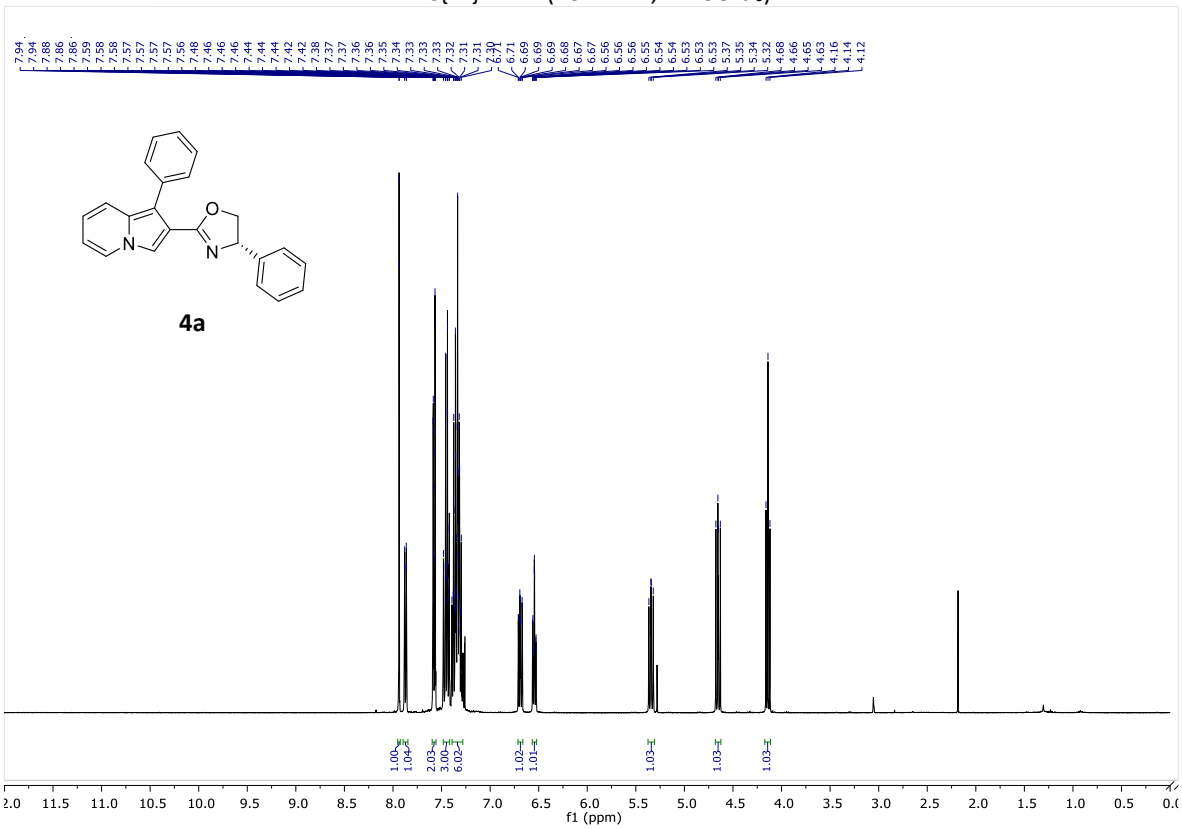
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



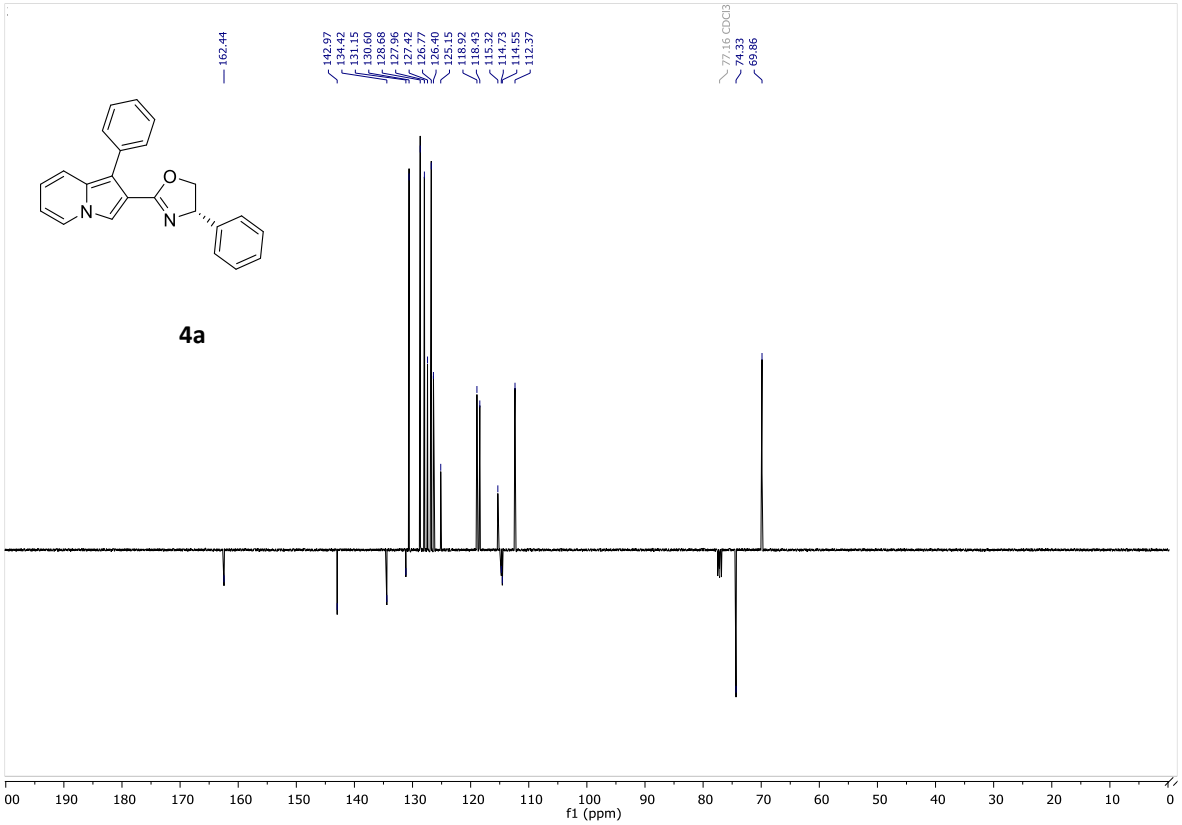
^{1}H NMR (400 MHz, DMSO-d_6)



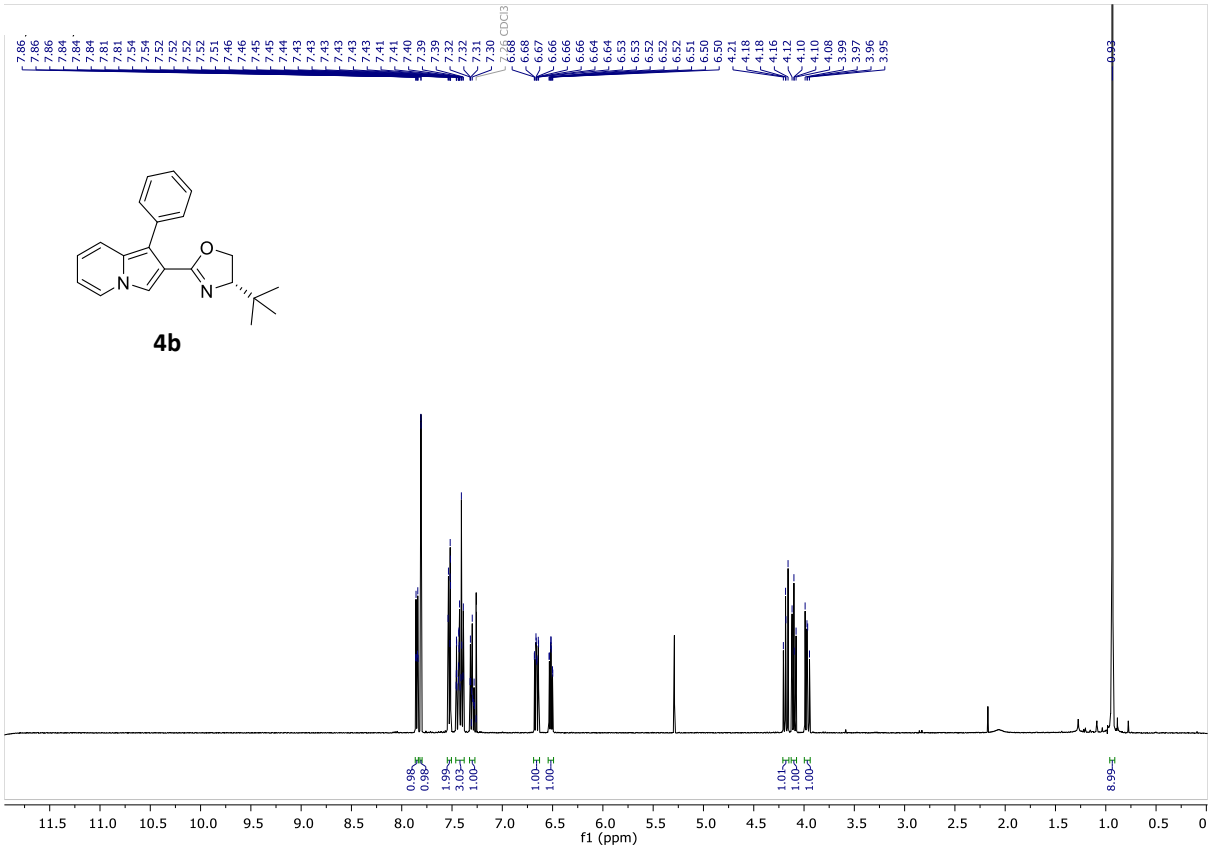
$^{13}C\{^1H\}$ NMR (101 MHz, DMSO-d_6)



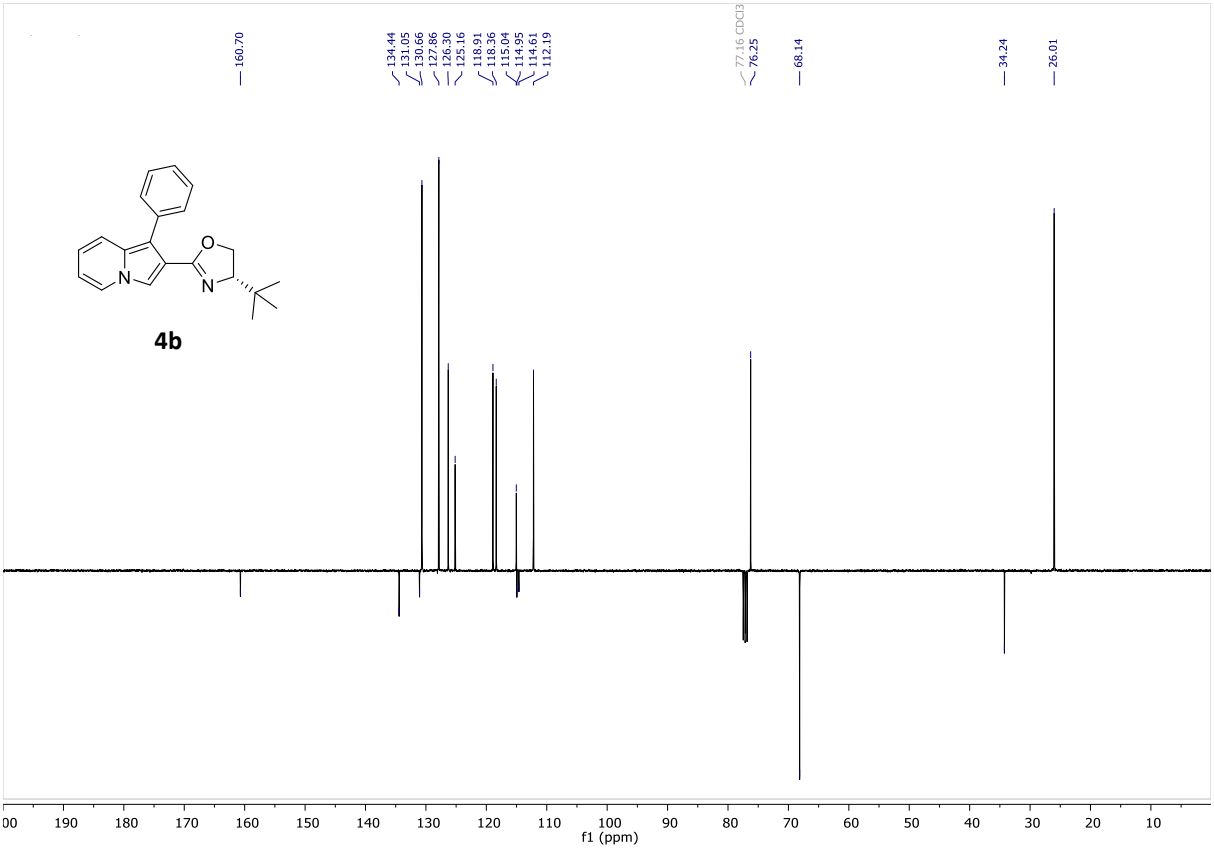
^1H NMR (400 MHz, $CDCl_3$)



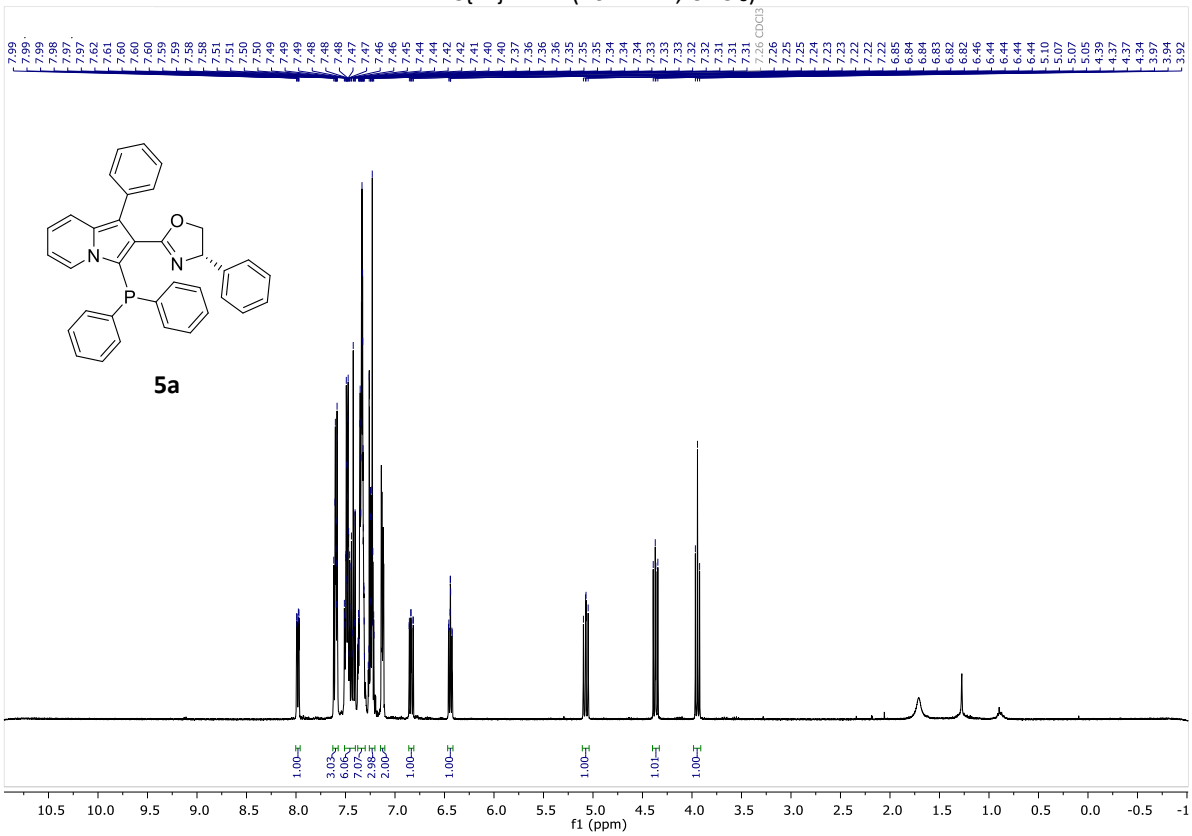
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



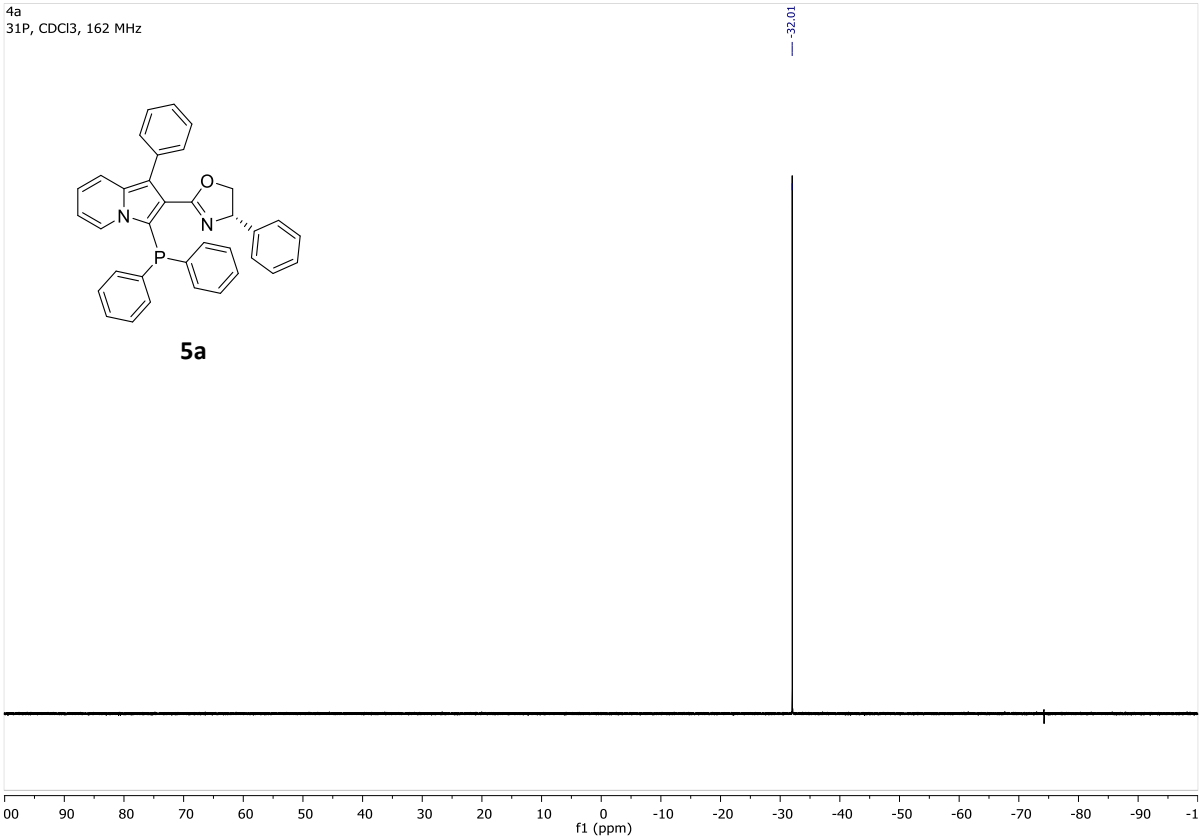
^{1}H NMR (400 MHz, $CDCl_3$)



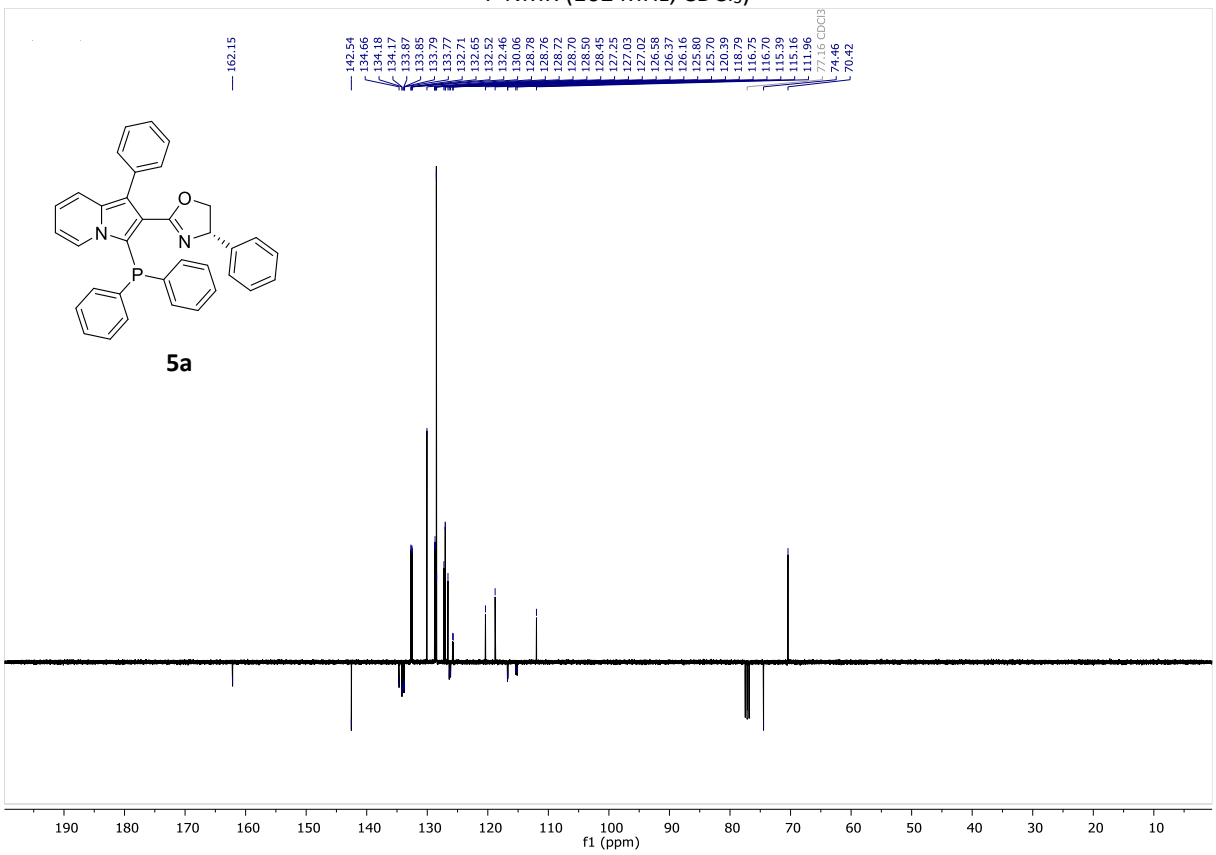
$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$)



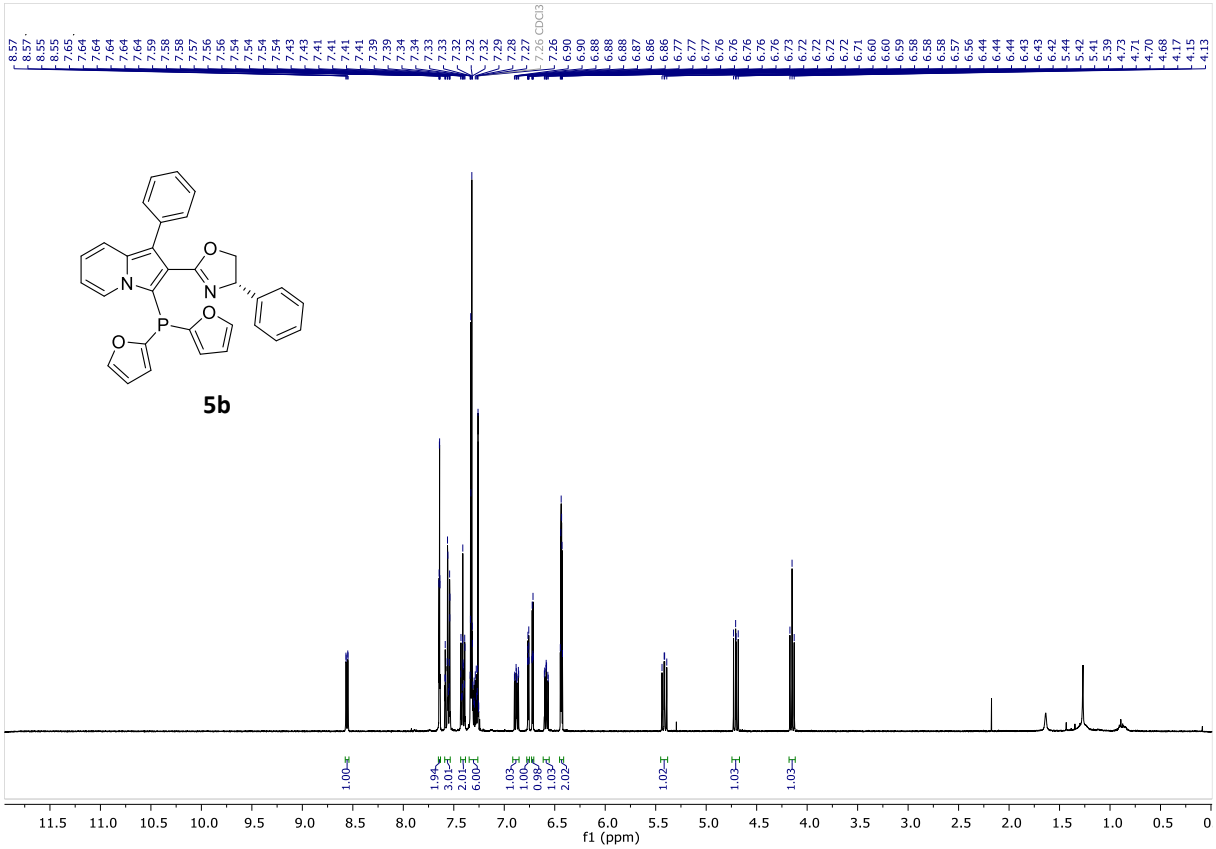
^1H NMR (400 MHz, $CDCl_3$)



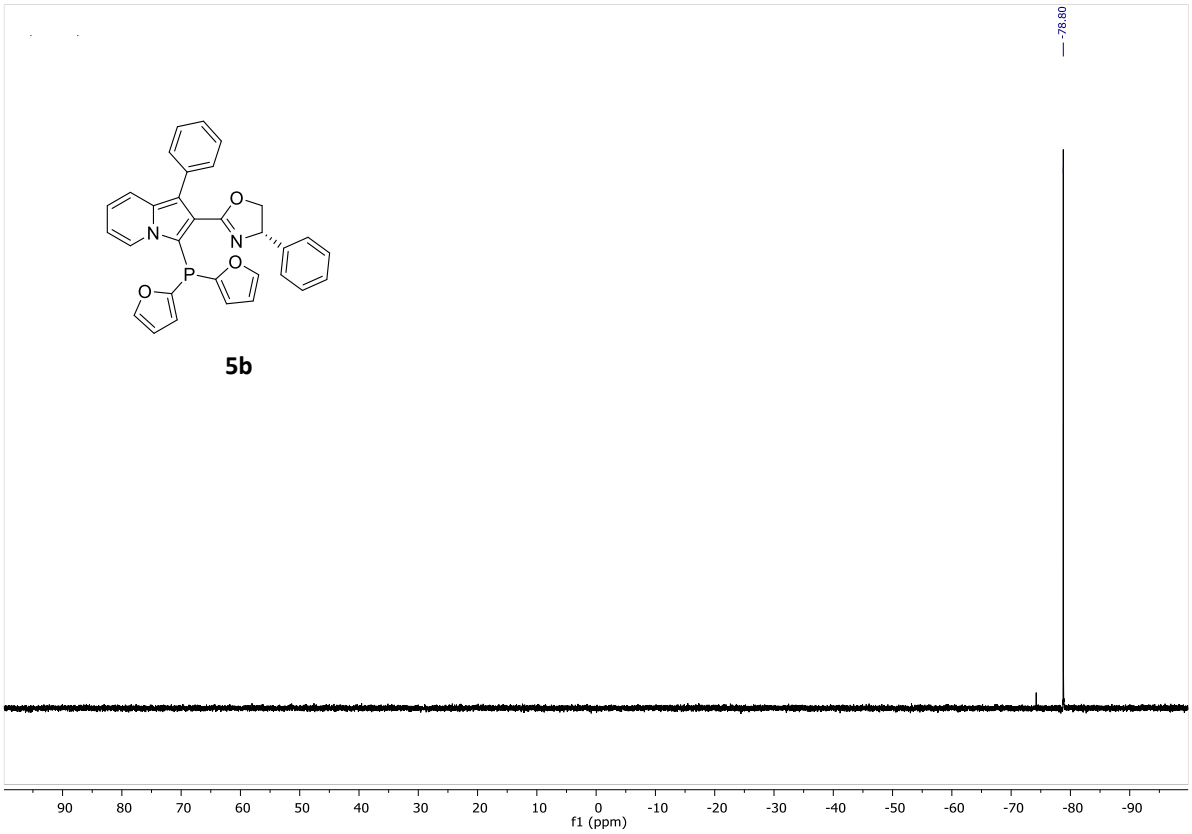
^{31}P NMR (162 MHz, $CDCl_3$)



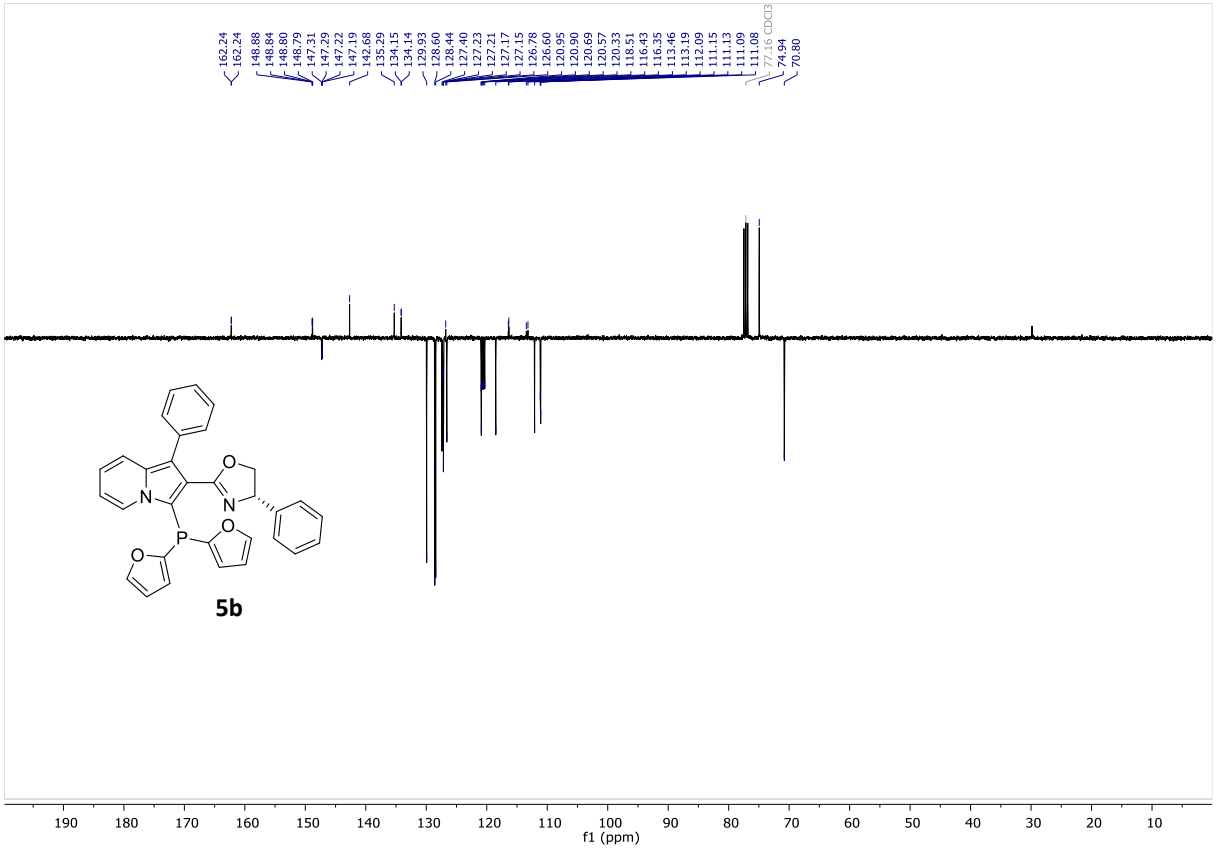
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)



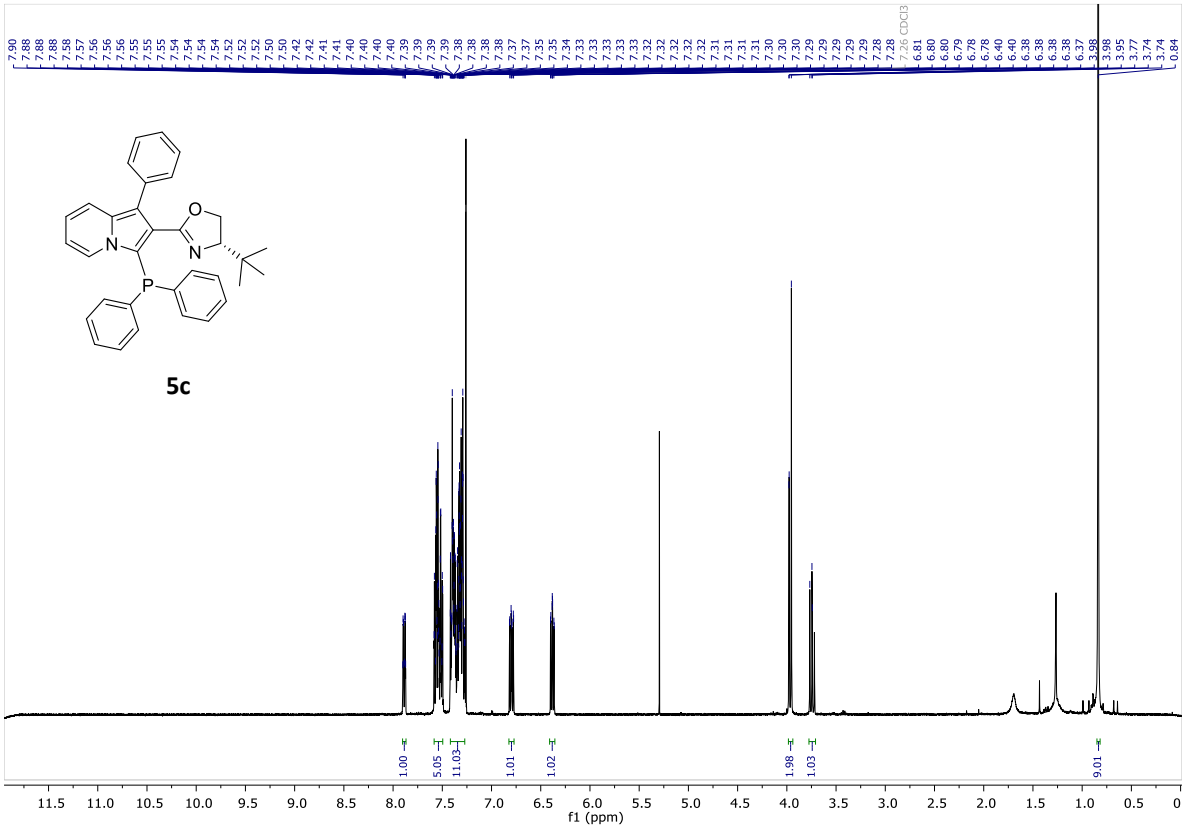
^{1}H NMR (400 MHz, $CDCl_3$)



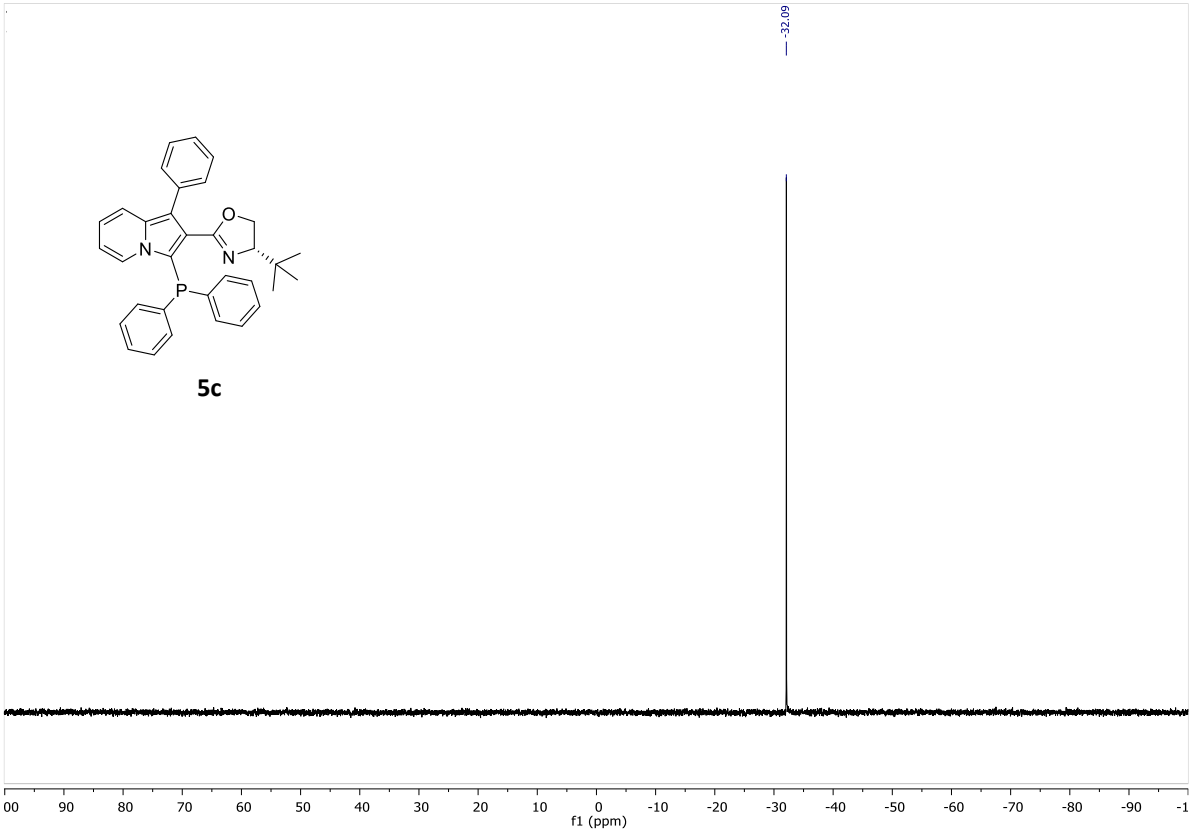
^{31}P NMR (162 MHz, $CDCl_3$)



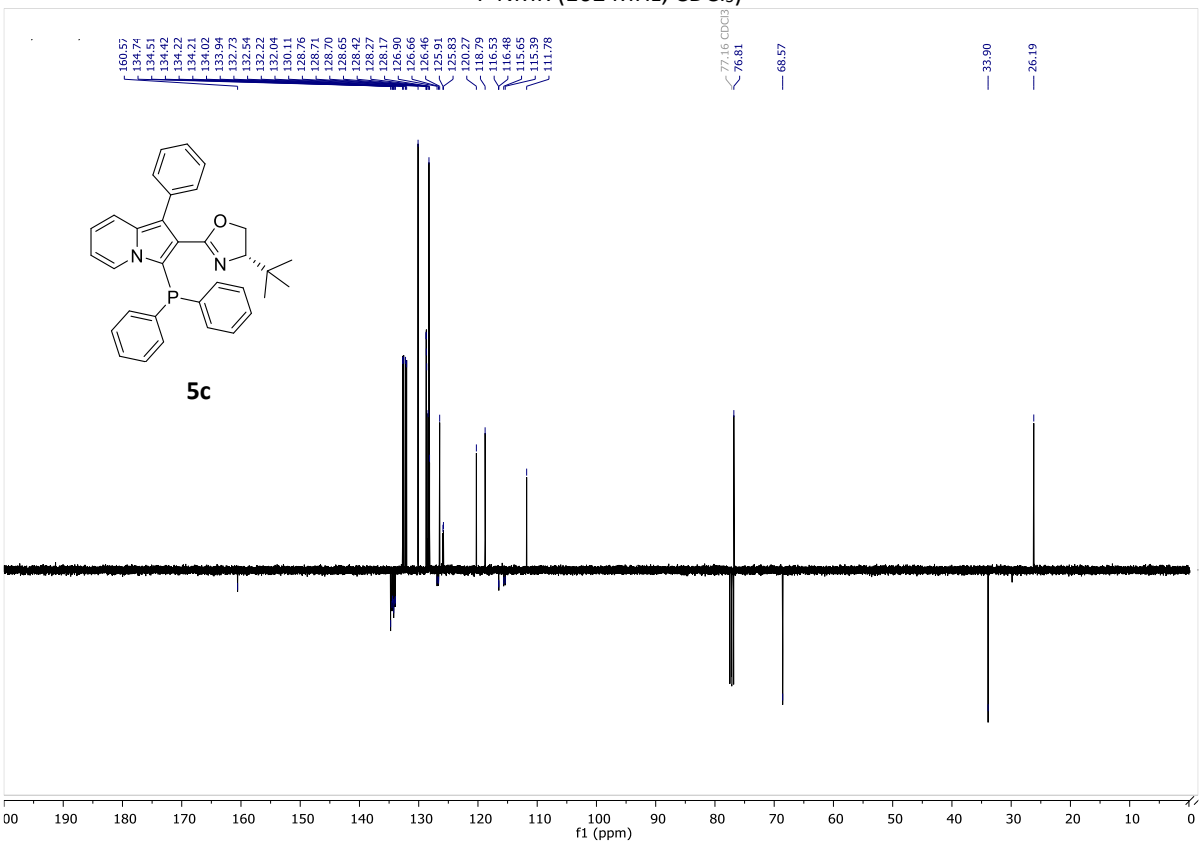
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



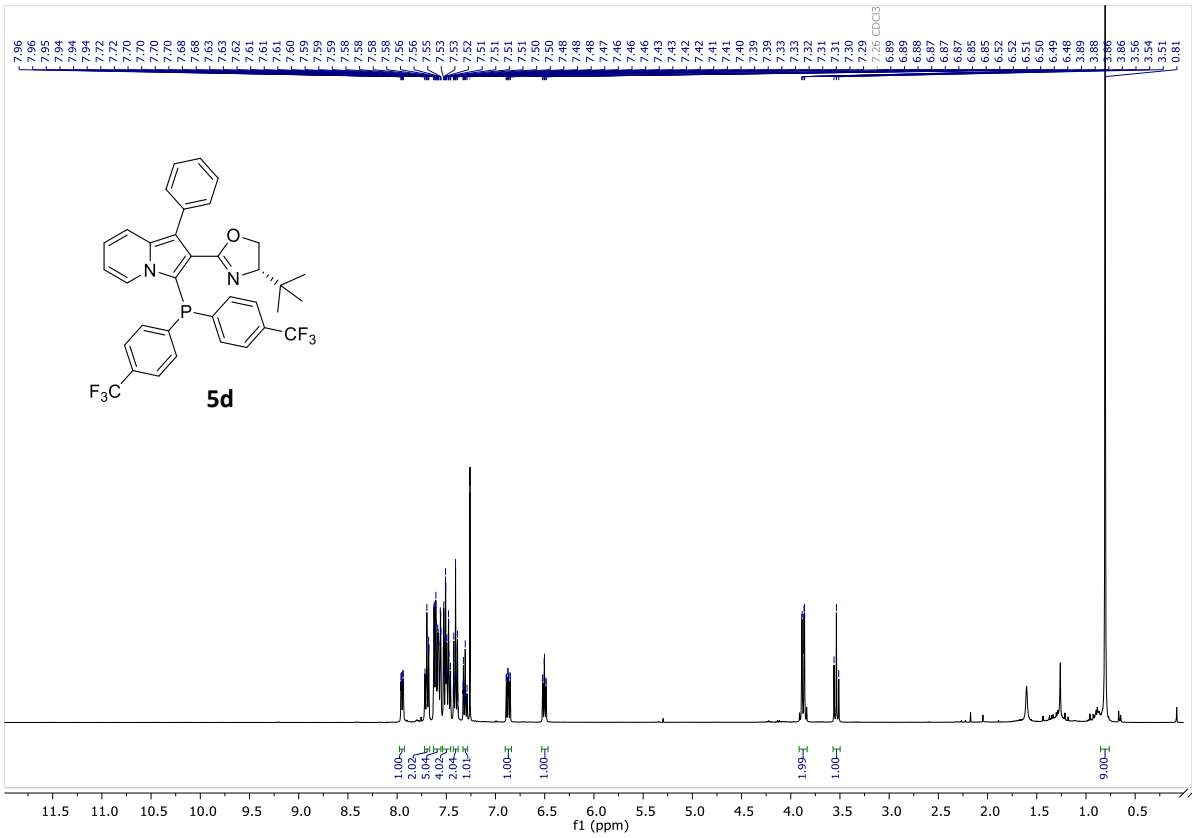
^{1}H NMR (400 MHz, $CDCl_3$)



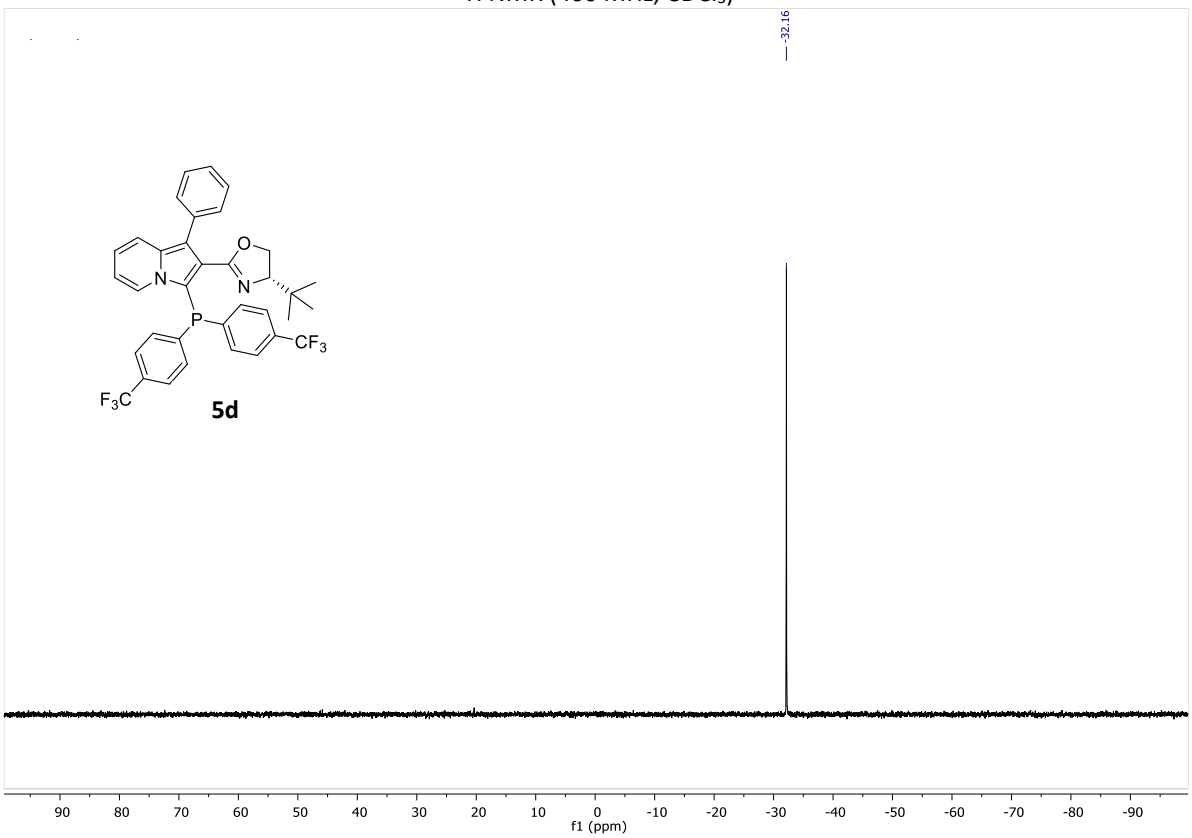
^{31}P NMR (162 MHz, $CDCl_3$)



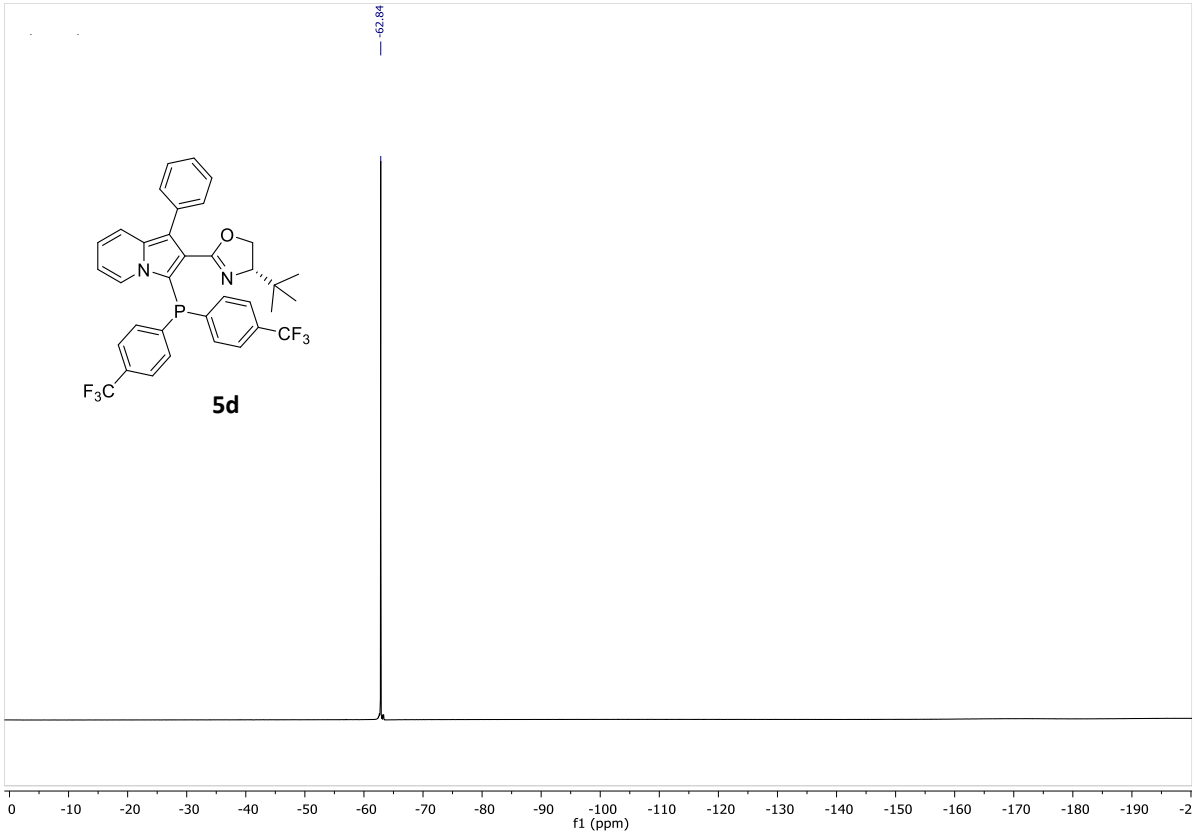
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)



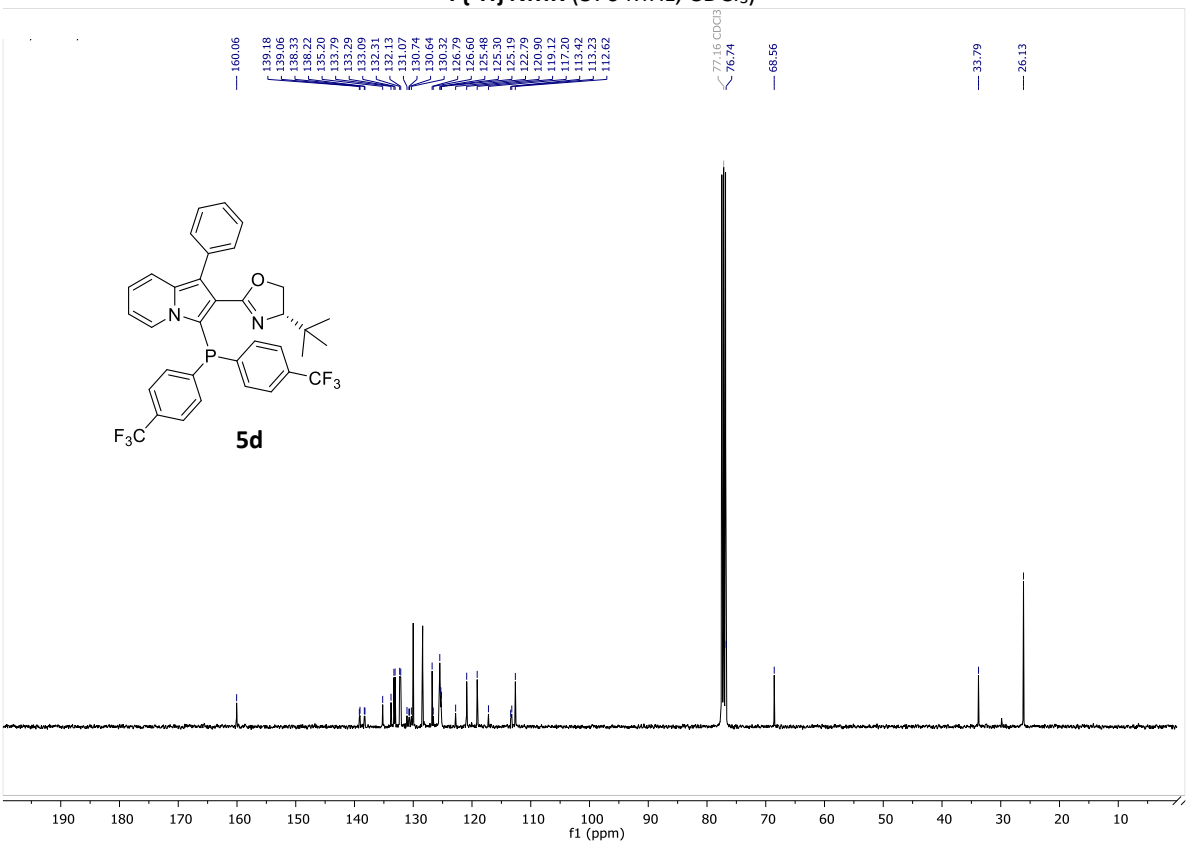
^{1}H NMR (400 MHz, $CDCl_3$)



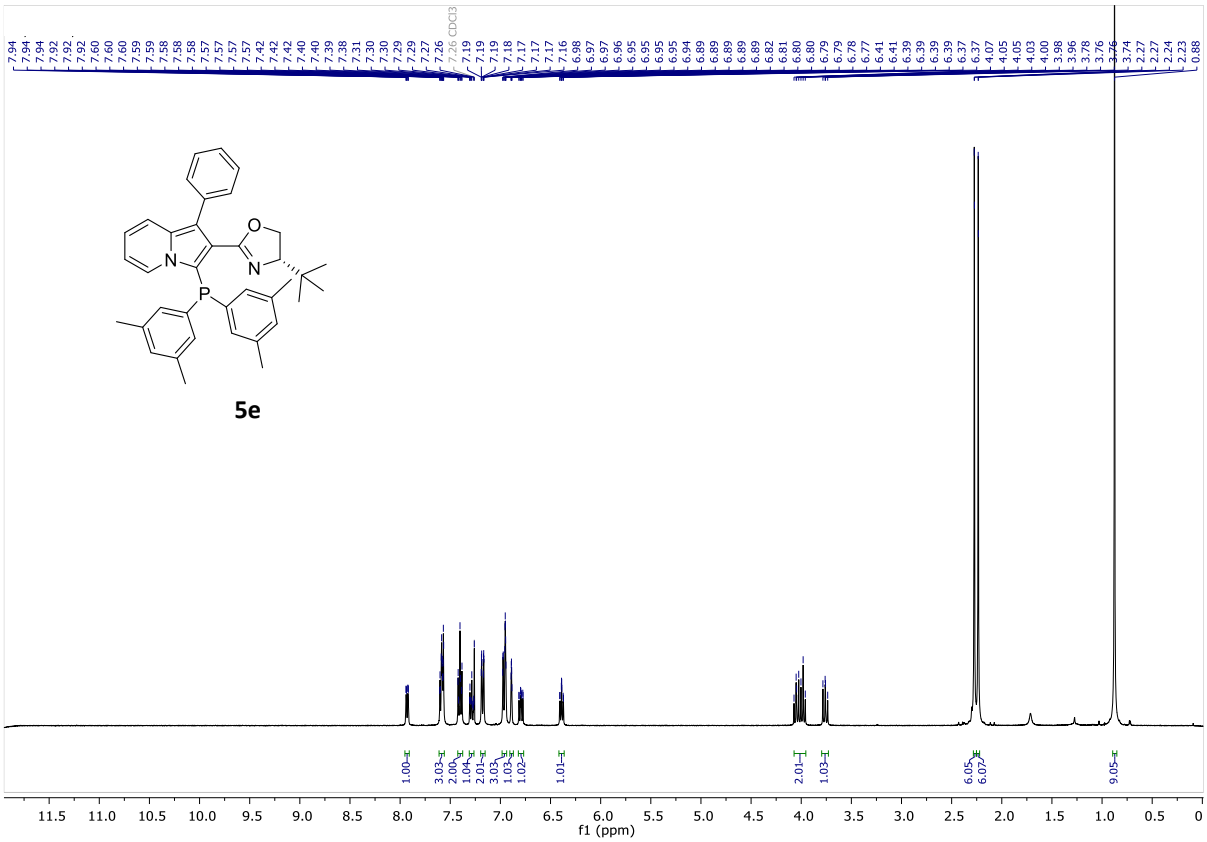
^{31}P NMR (162 MHz, $CDCl_3$)



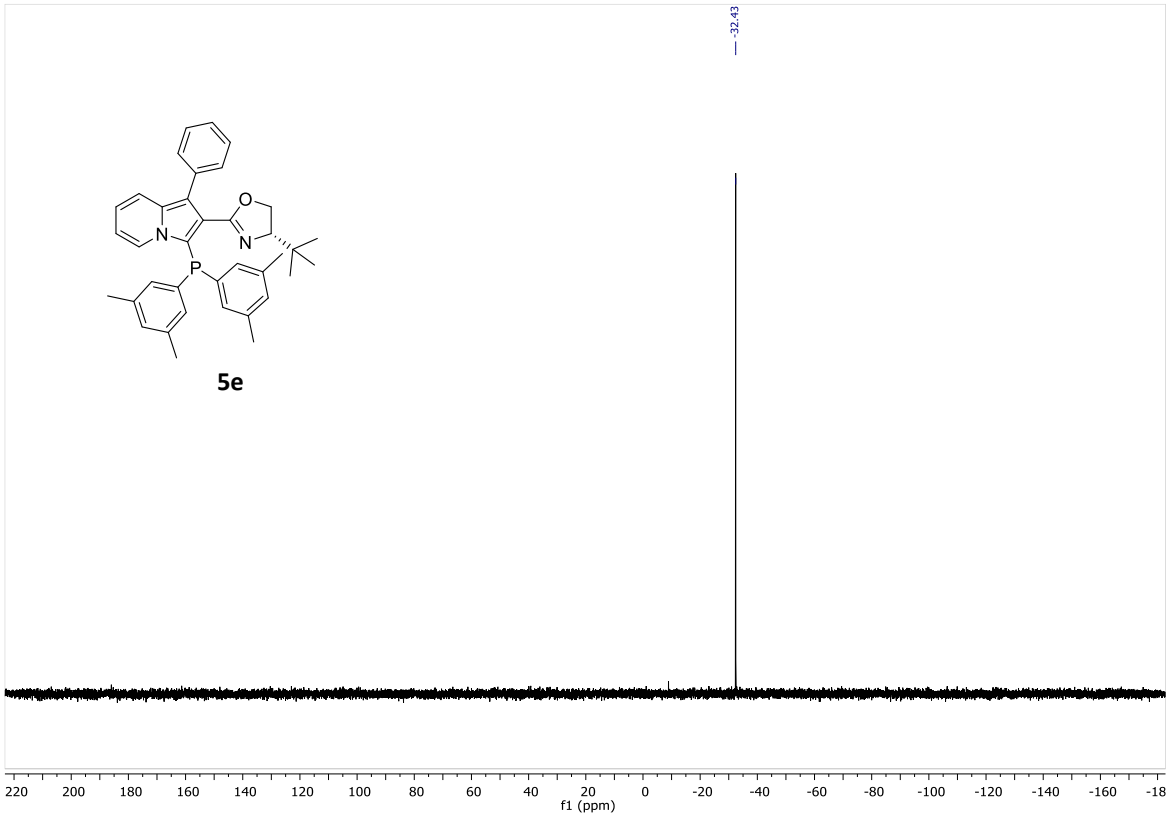
^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$)



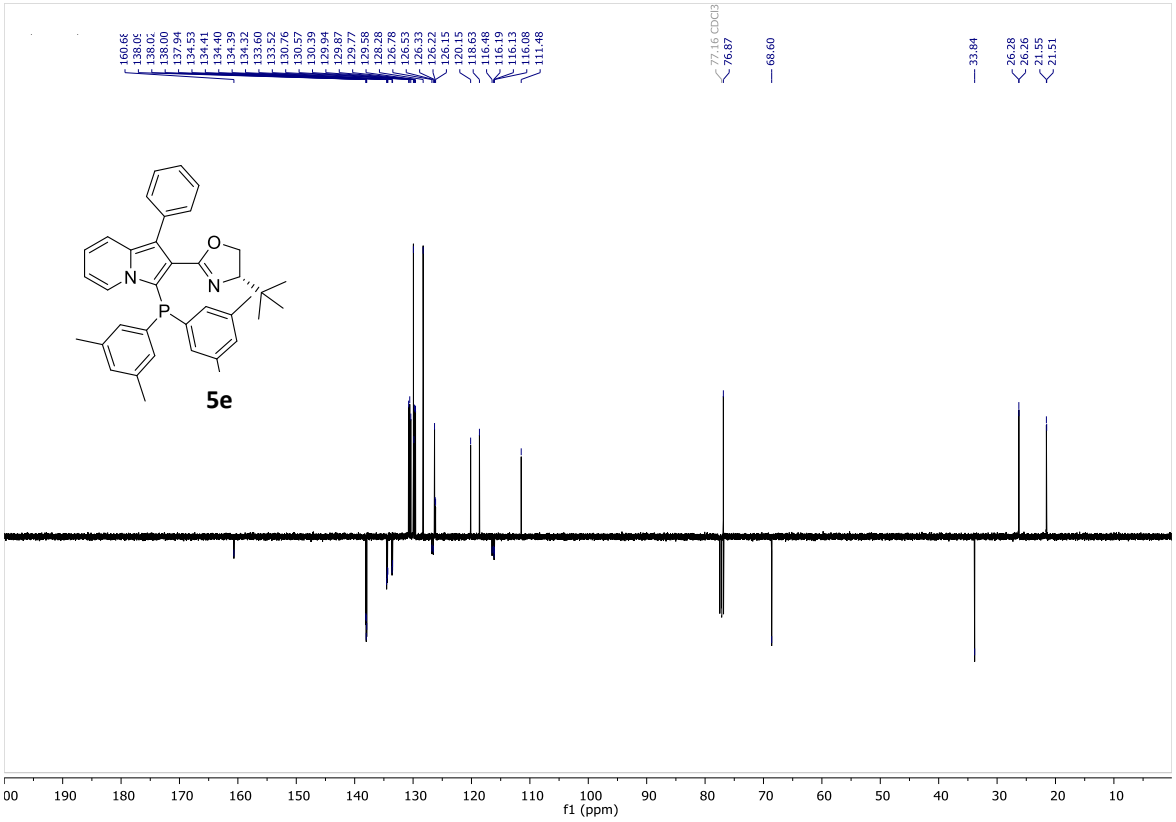
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)



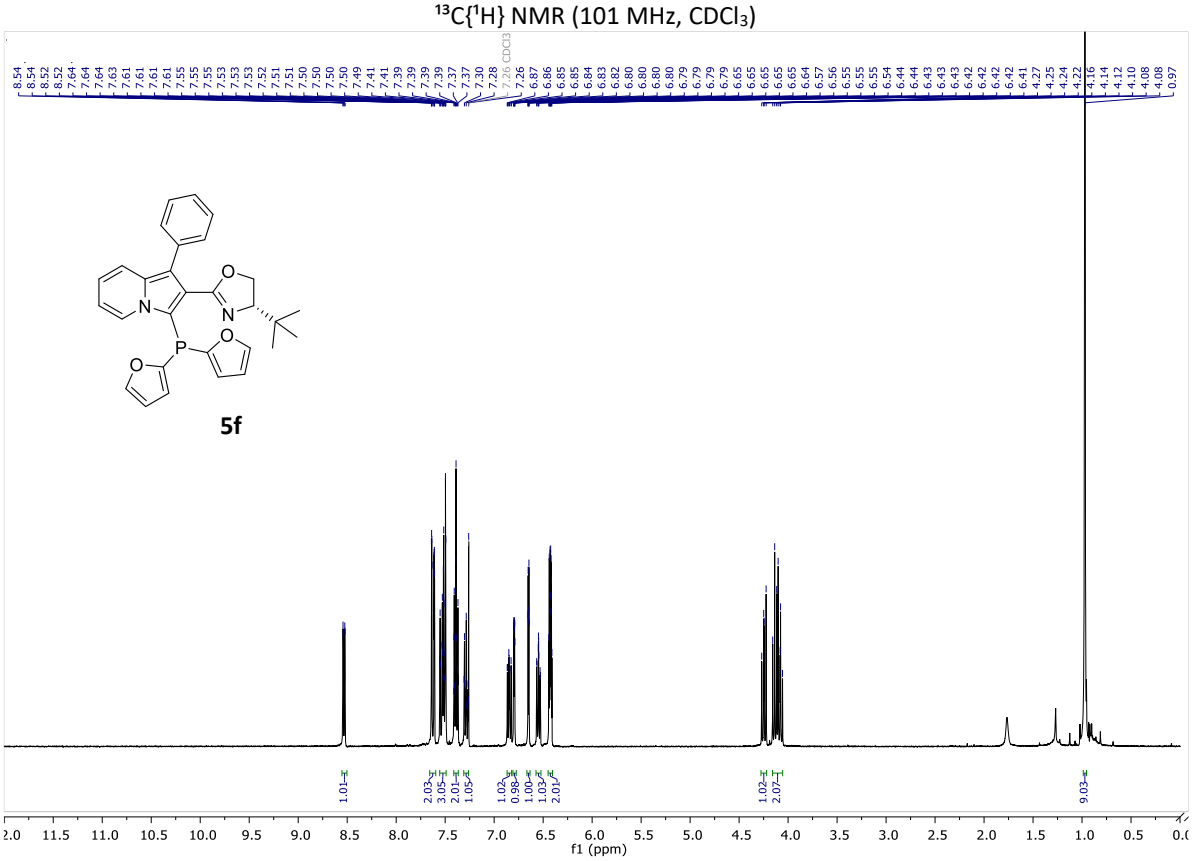
^{1}H NMR (400 MHz, $CDCl_3$)



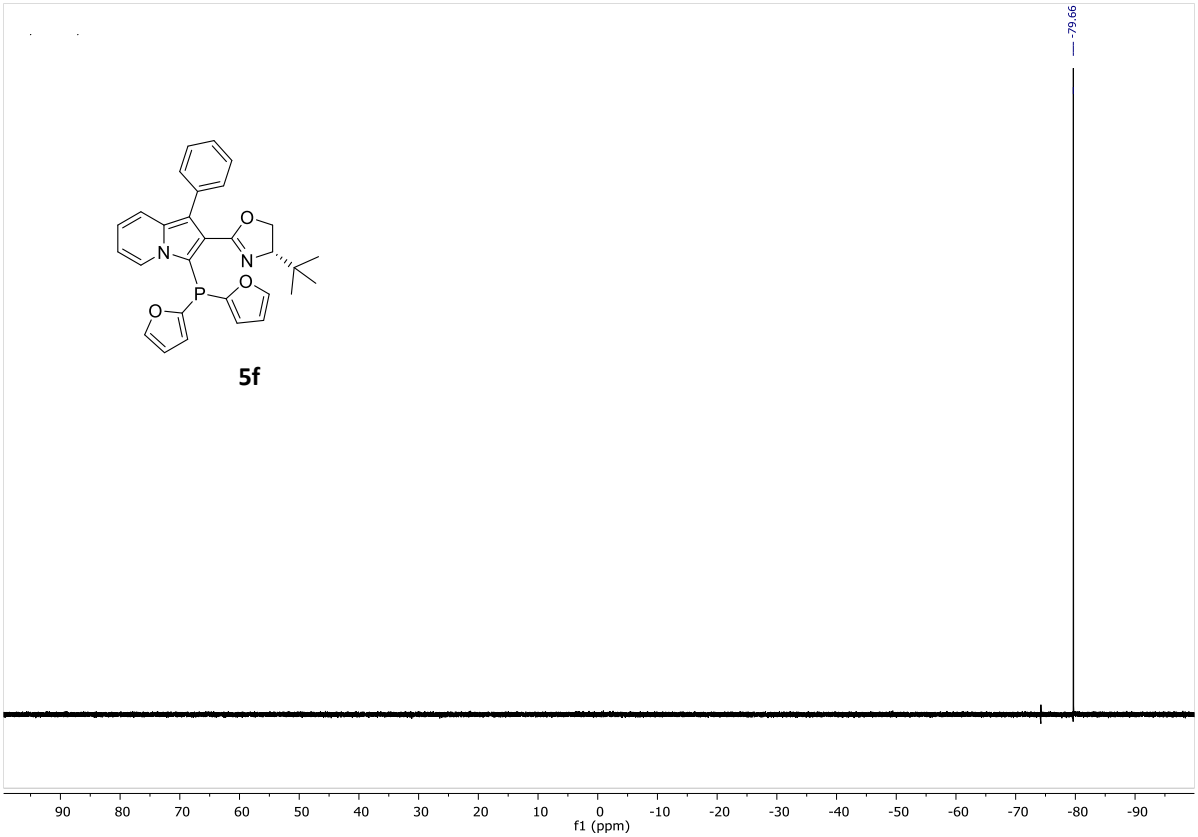
^{31}P NMR (162 MHz, $CDCl_3$)



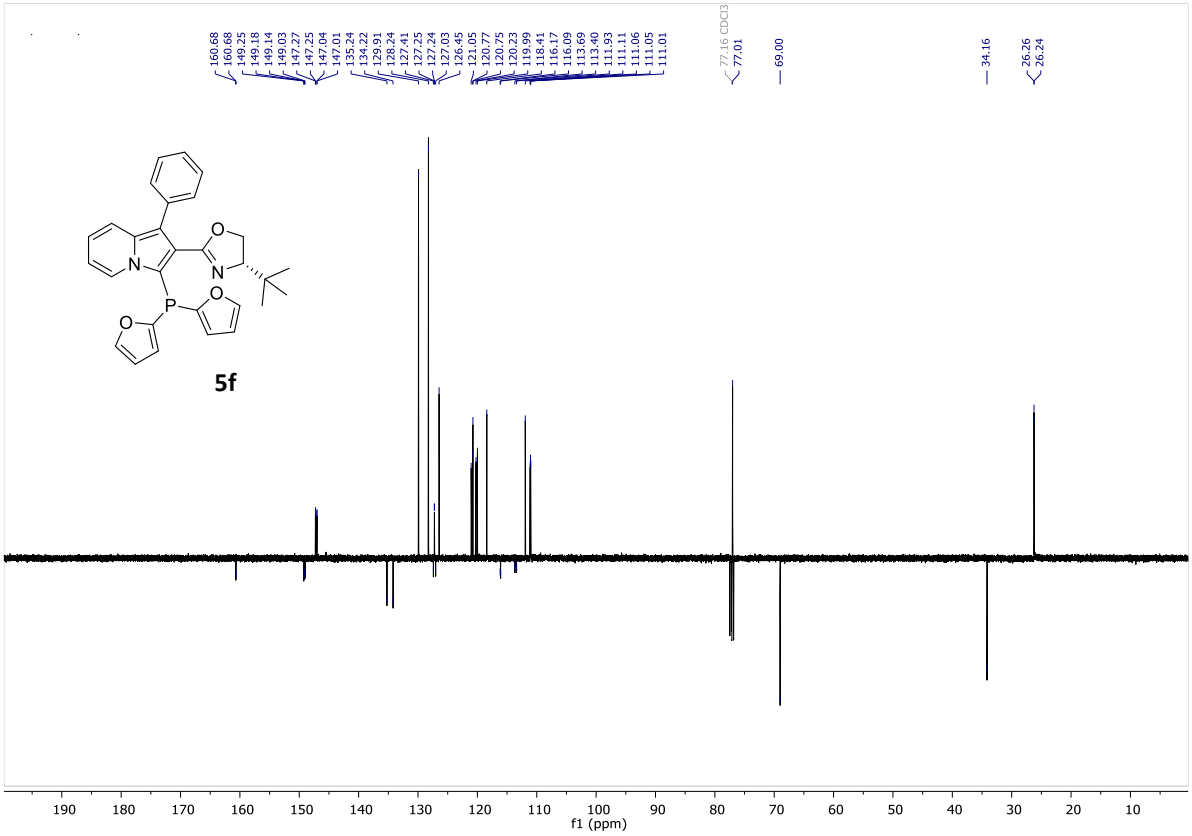
$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$)



^1H NMR (400 MHz, $CDCl_3$)

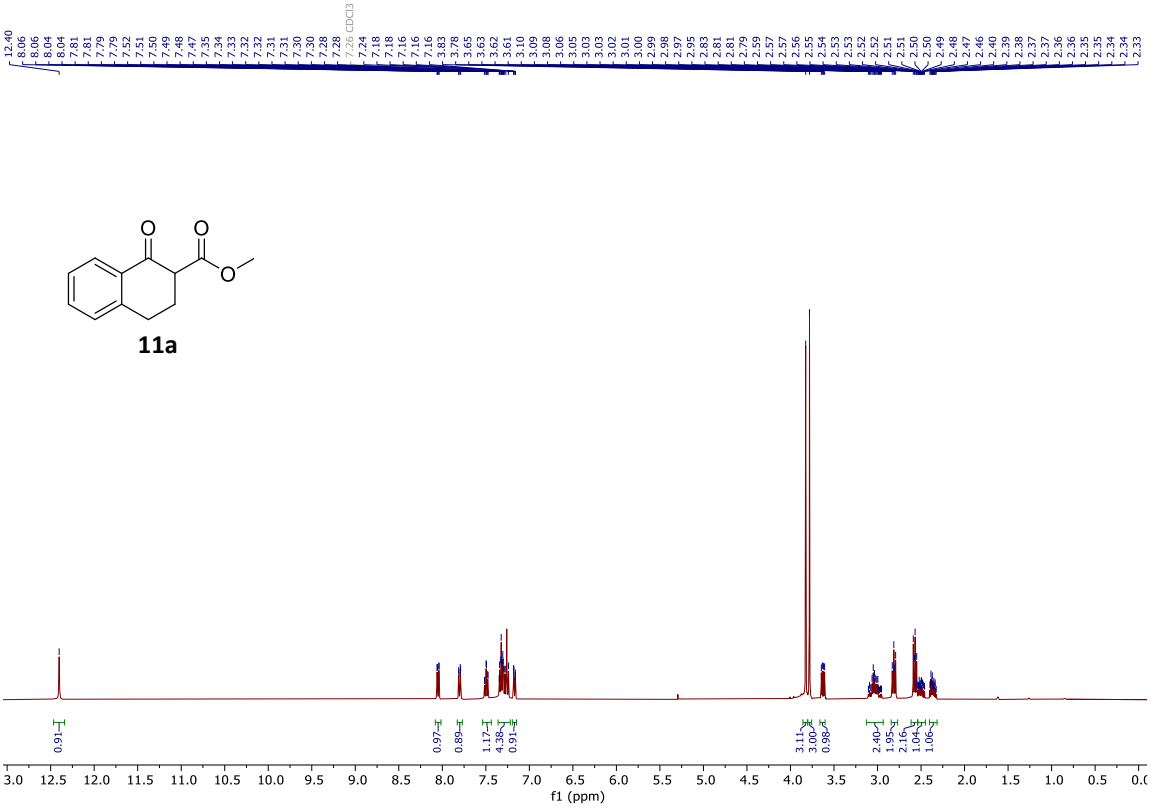


^{31}P NMR (162 MHz, $CDCl_3$)

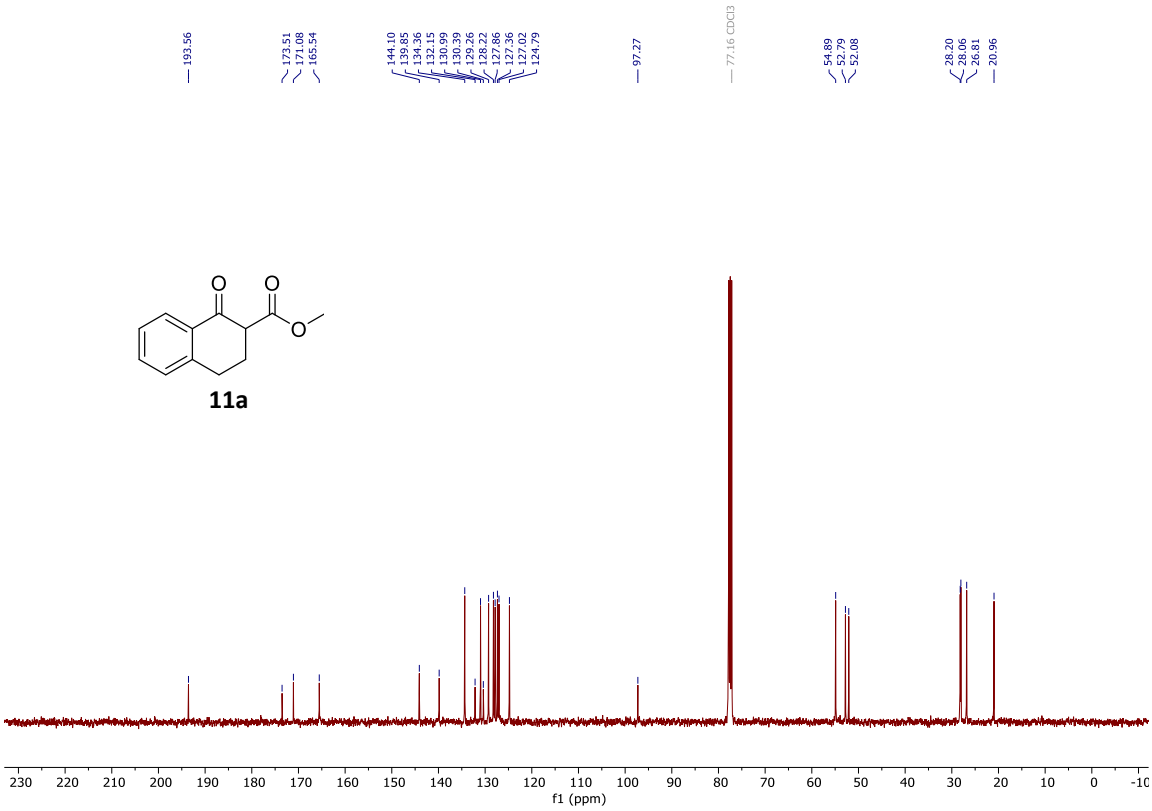


^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)

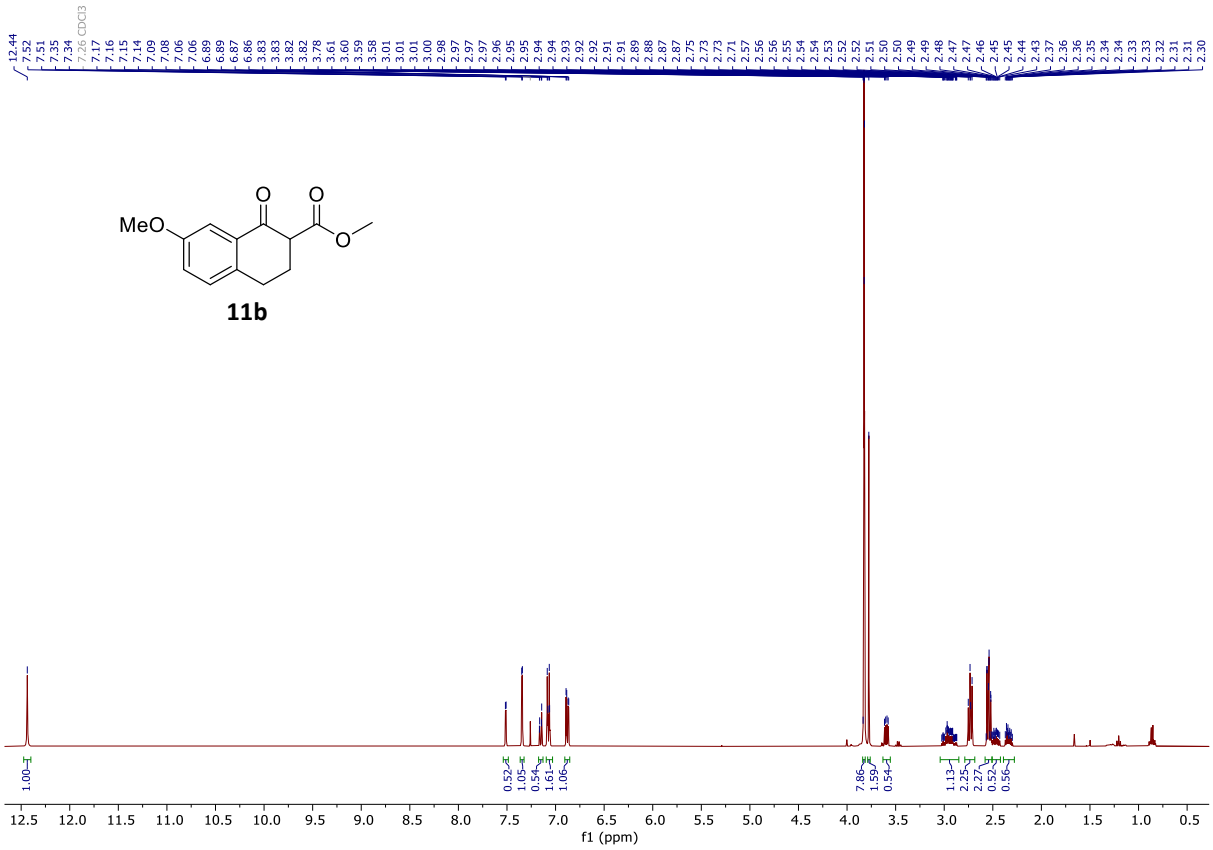
9. NMR spectra for compounds **11a – 11t**



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

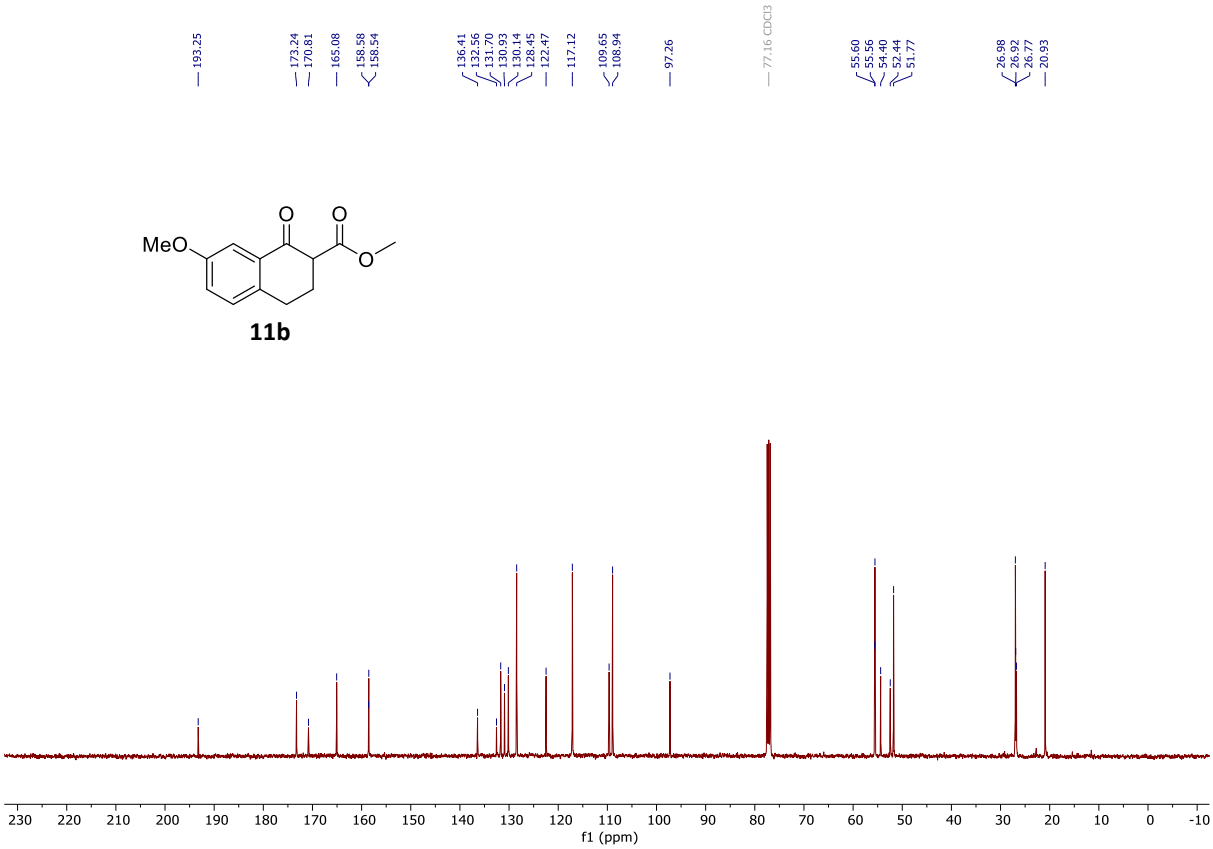


$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$)



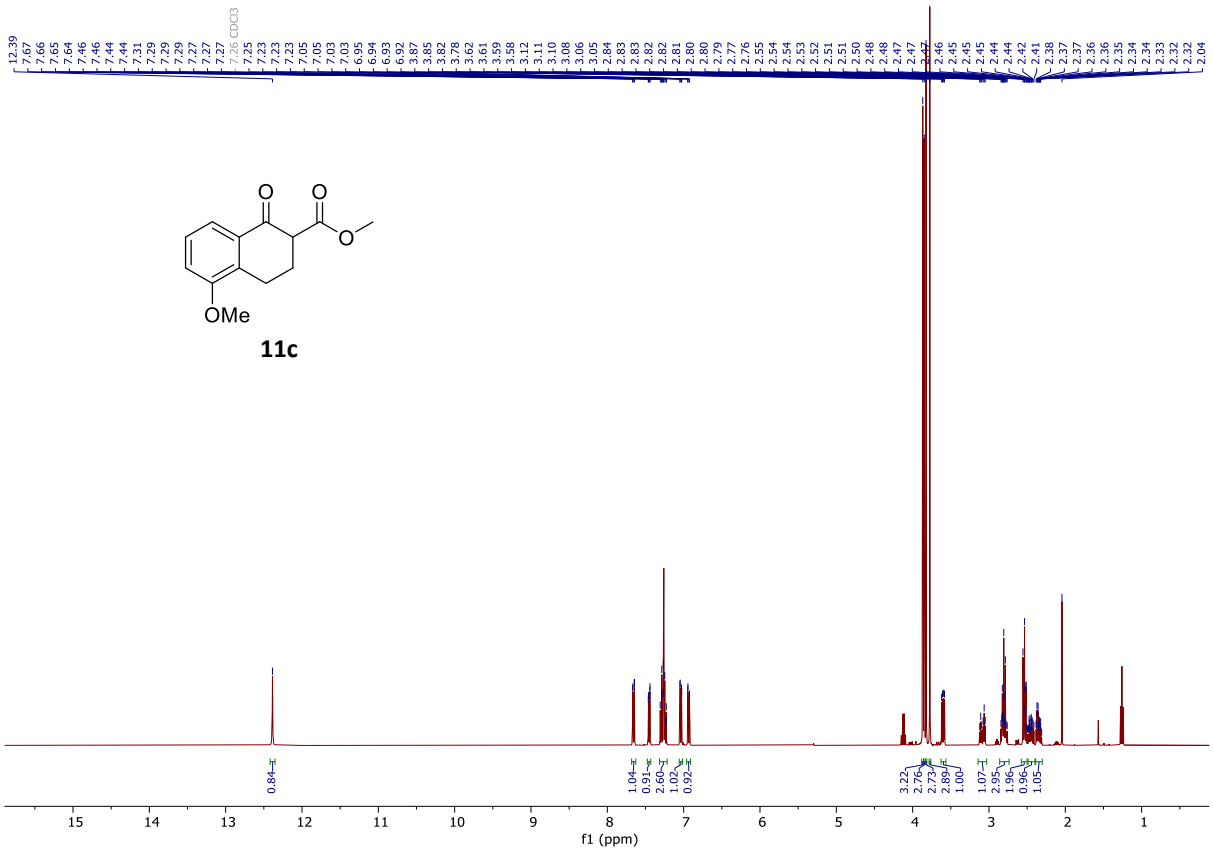
11b

^1H NMR (400 MHz, $CDCl_3$)

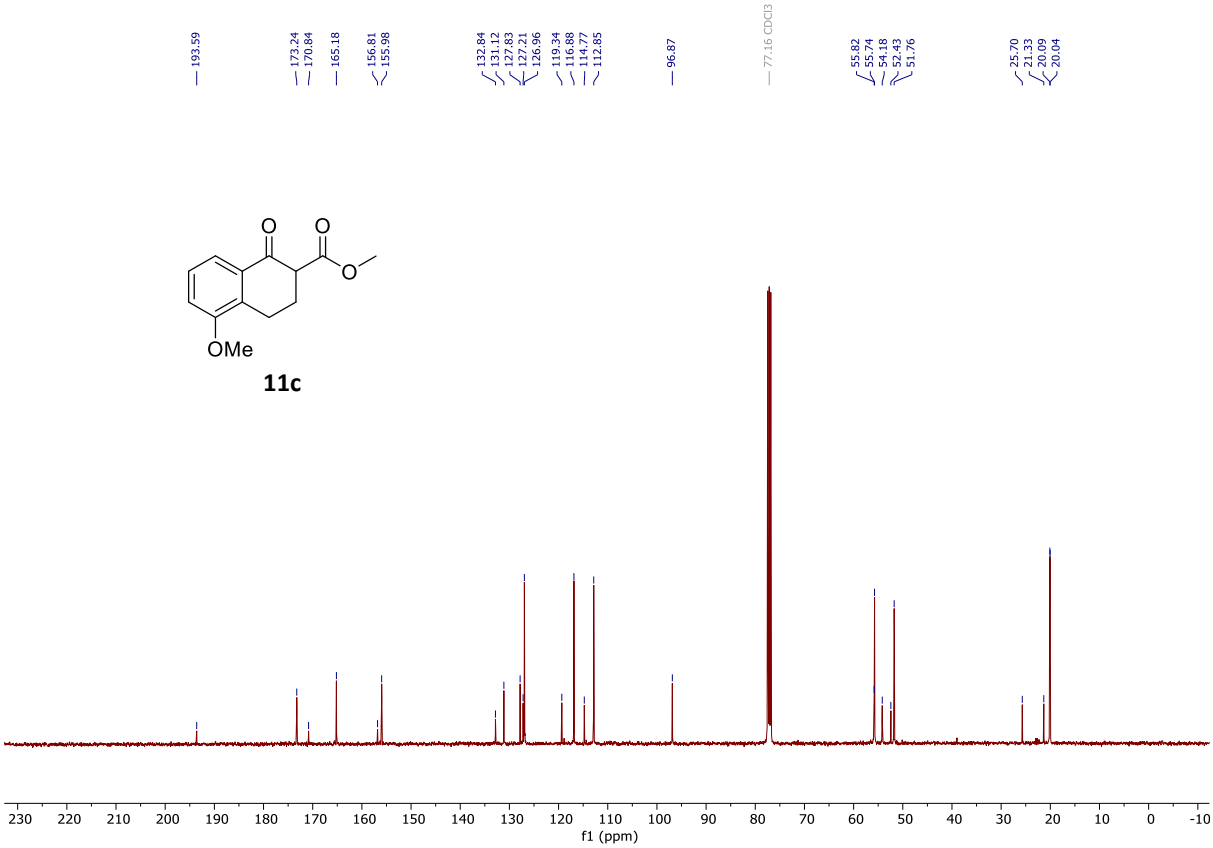


11b

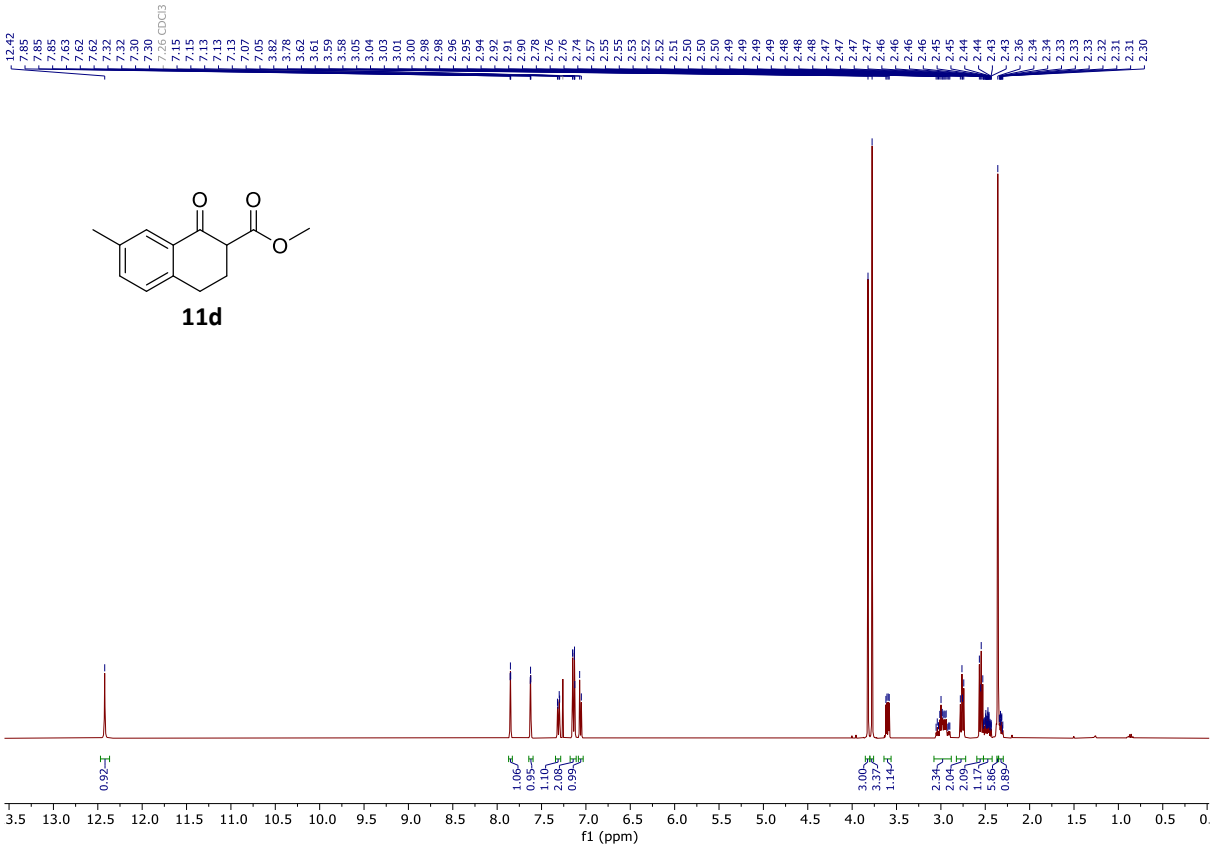
$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$)



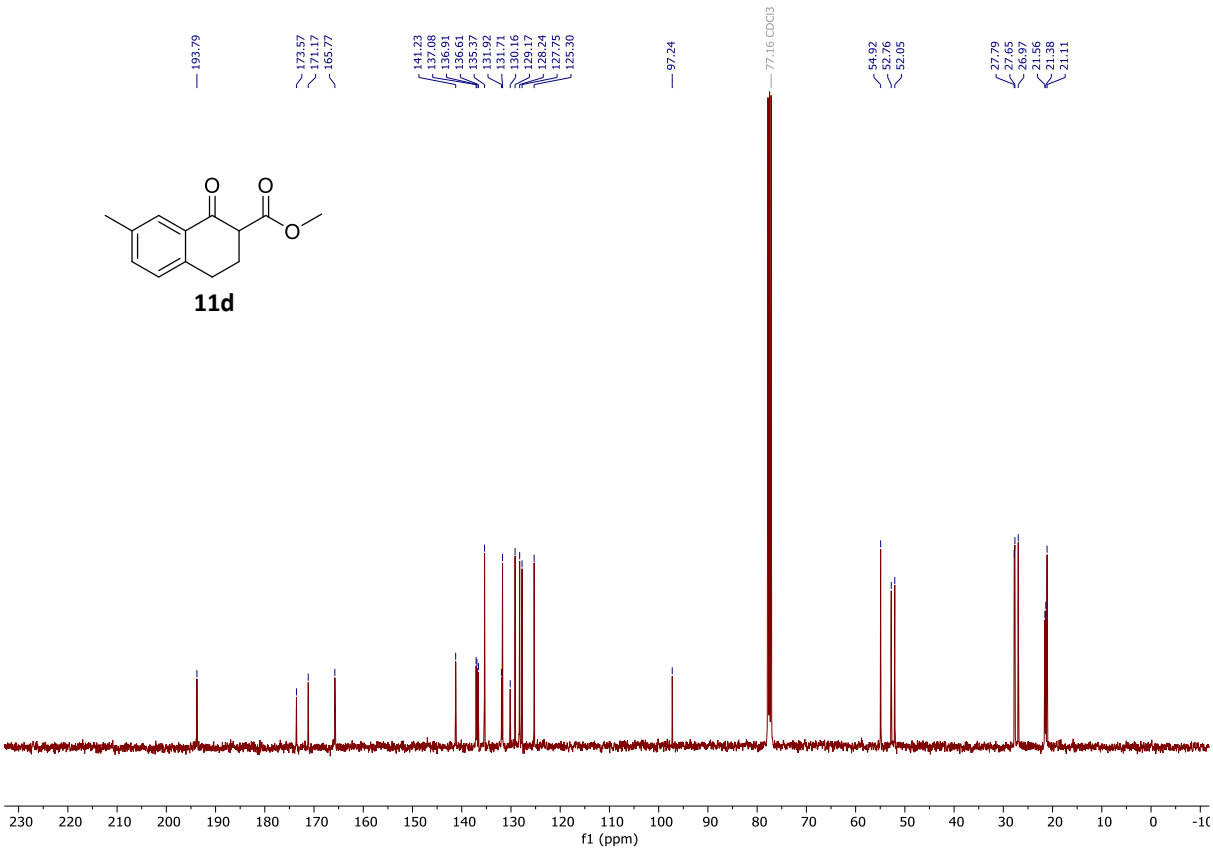
^1H NMR (400 MHz, $CDCl_3$)



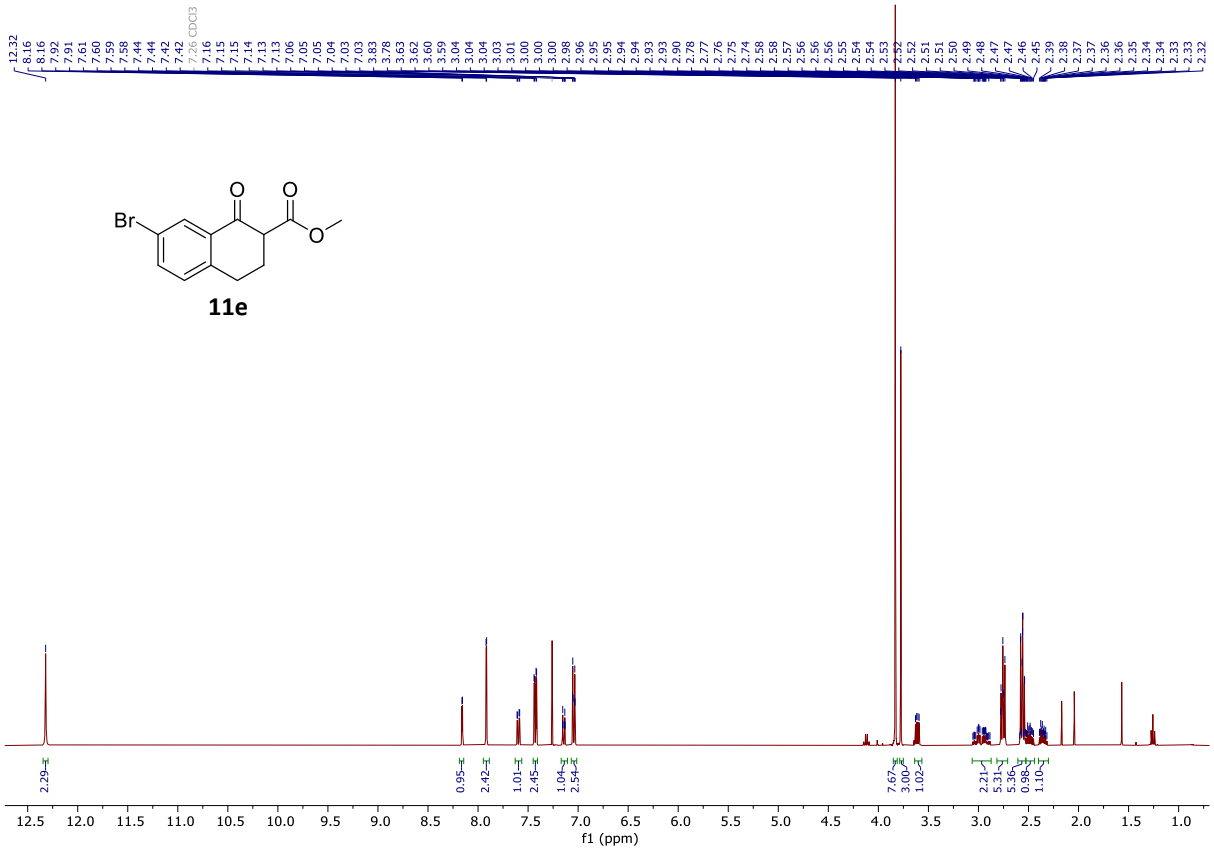
$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$)



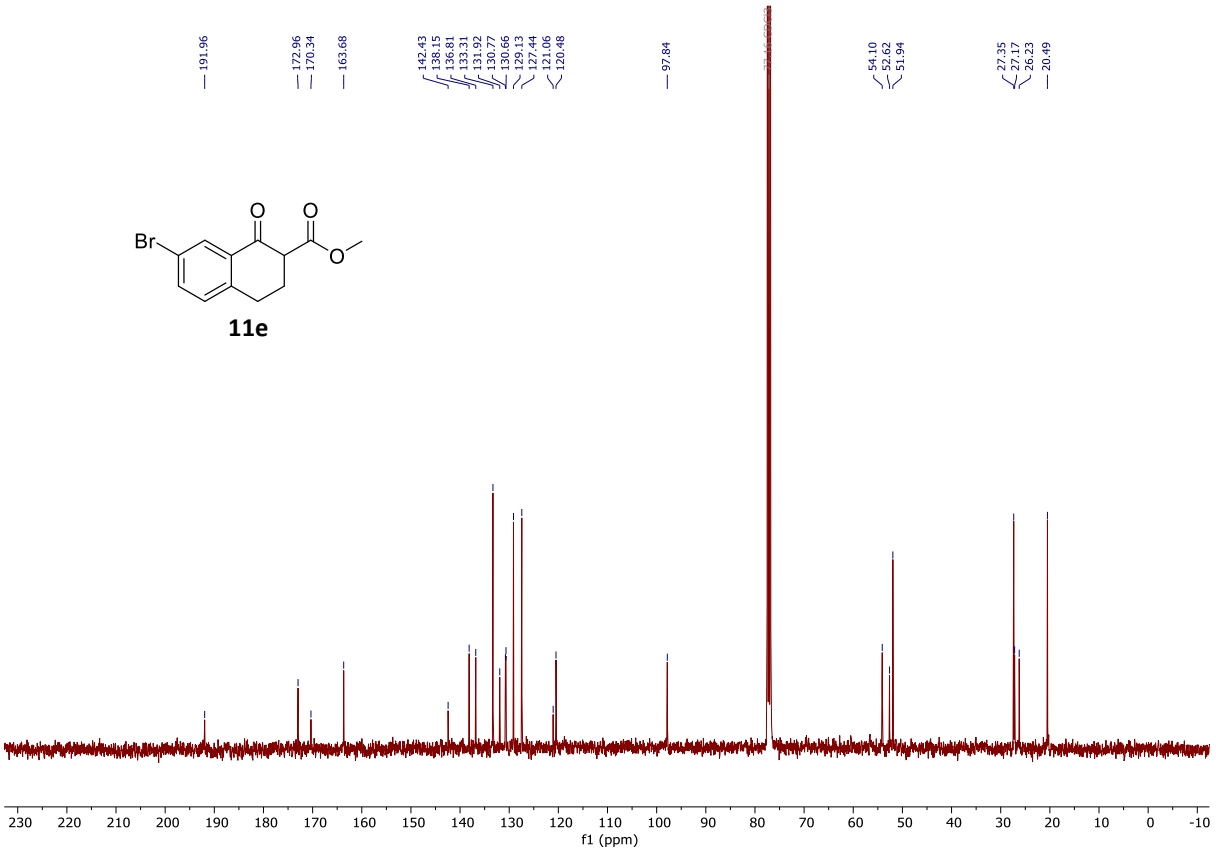
^{1}H NMR (400 MHz, $CDCl_3$)



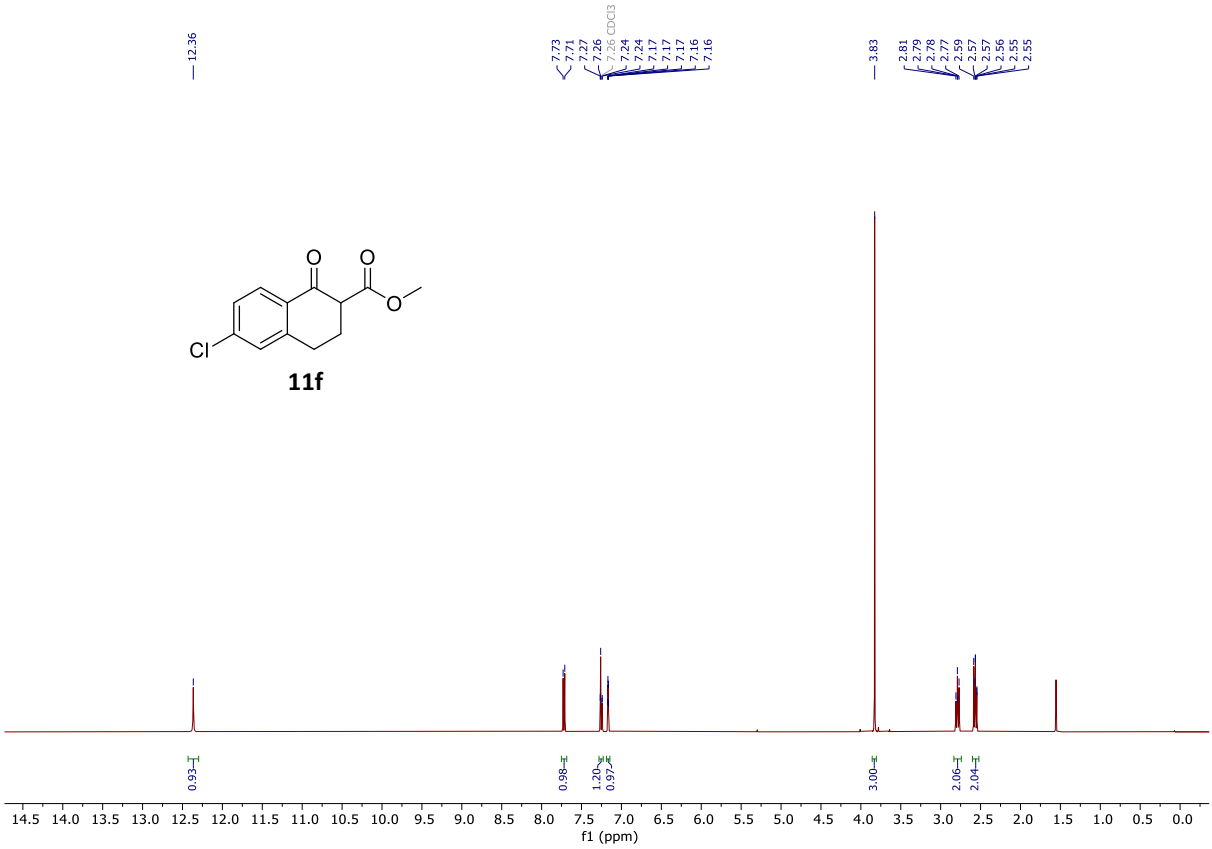
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)



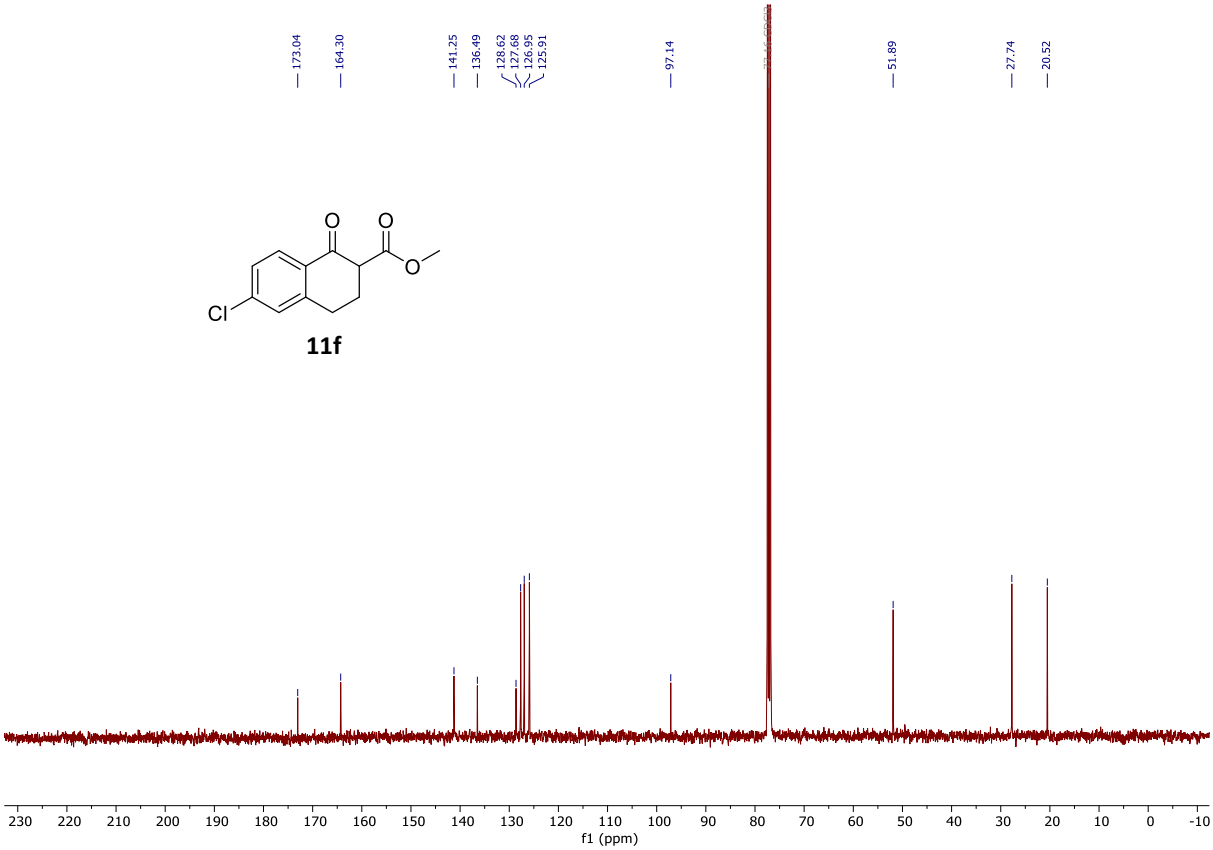
^{1}H NMR (400 MHz, $CDCl_3$)



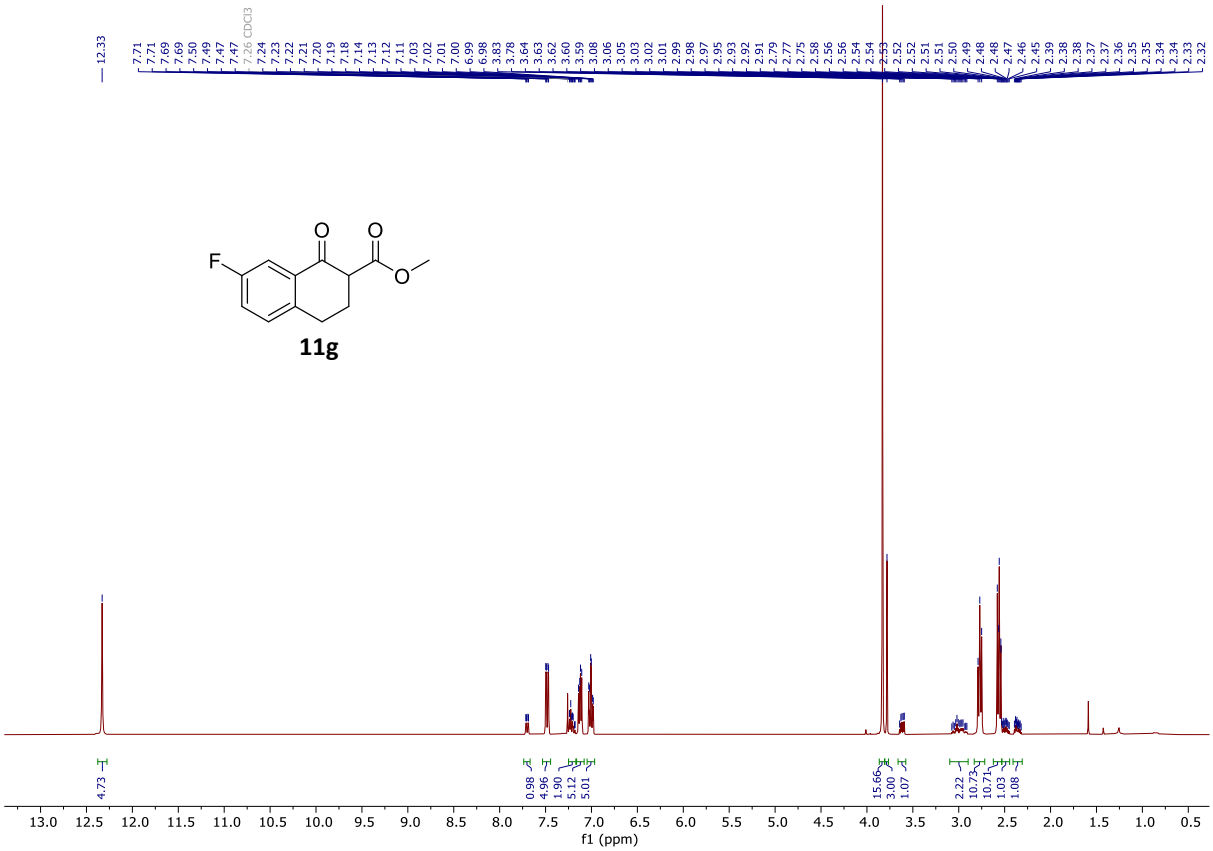
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)



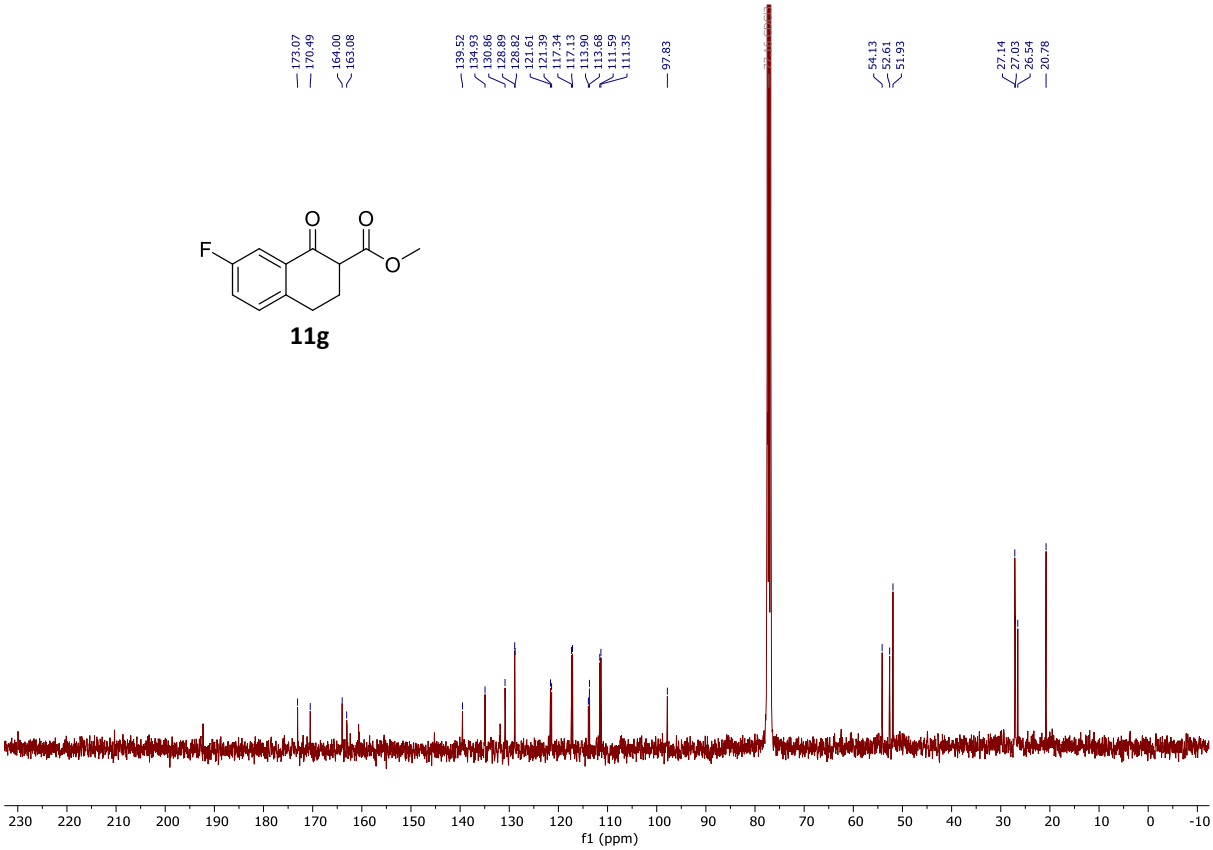
^{1}H NMR (400 MHz, $CDCl_3$)



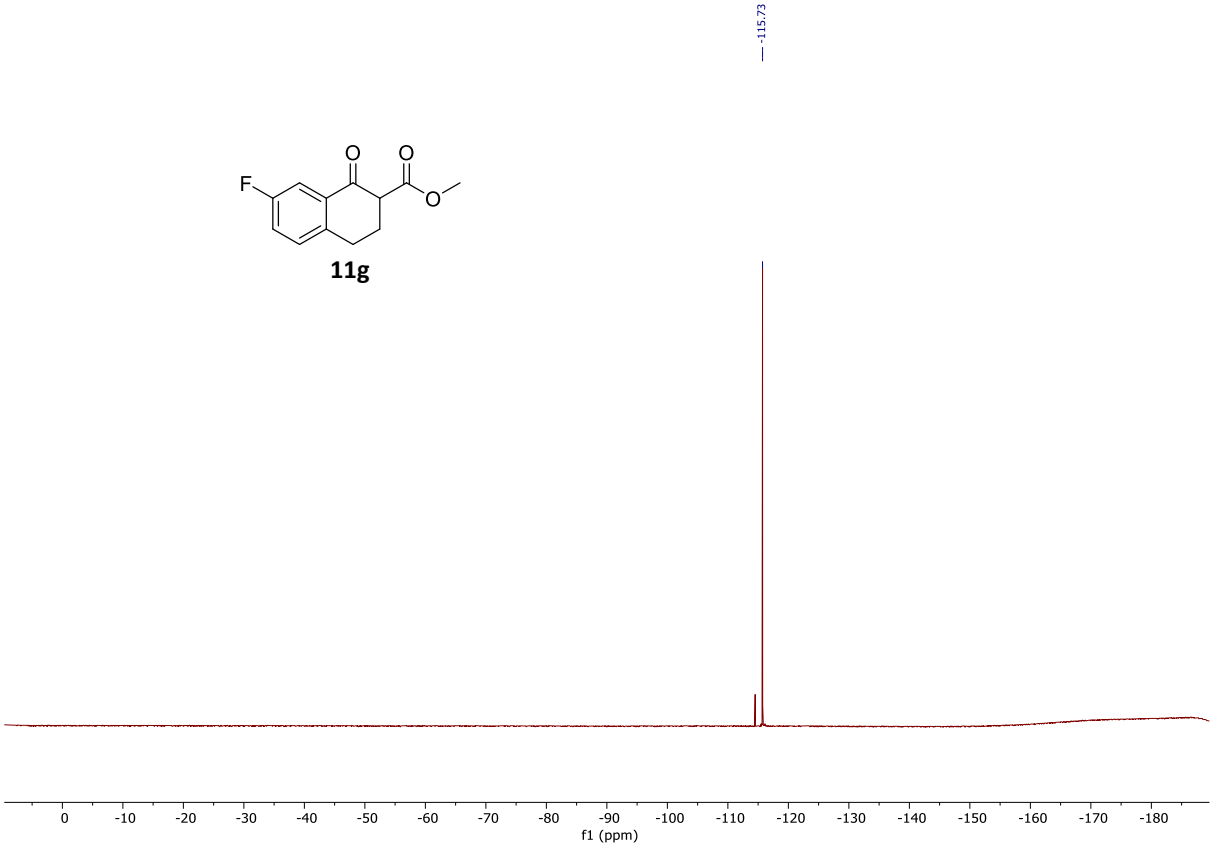
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)



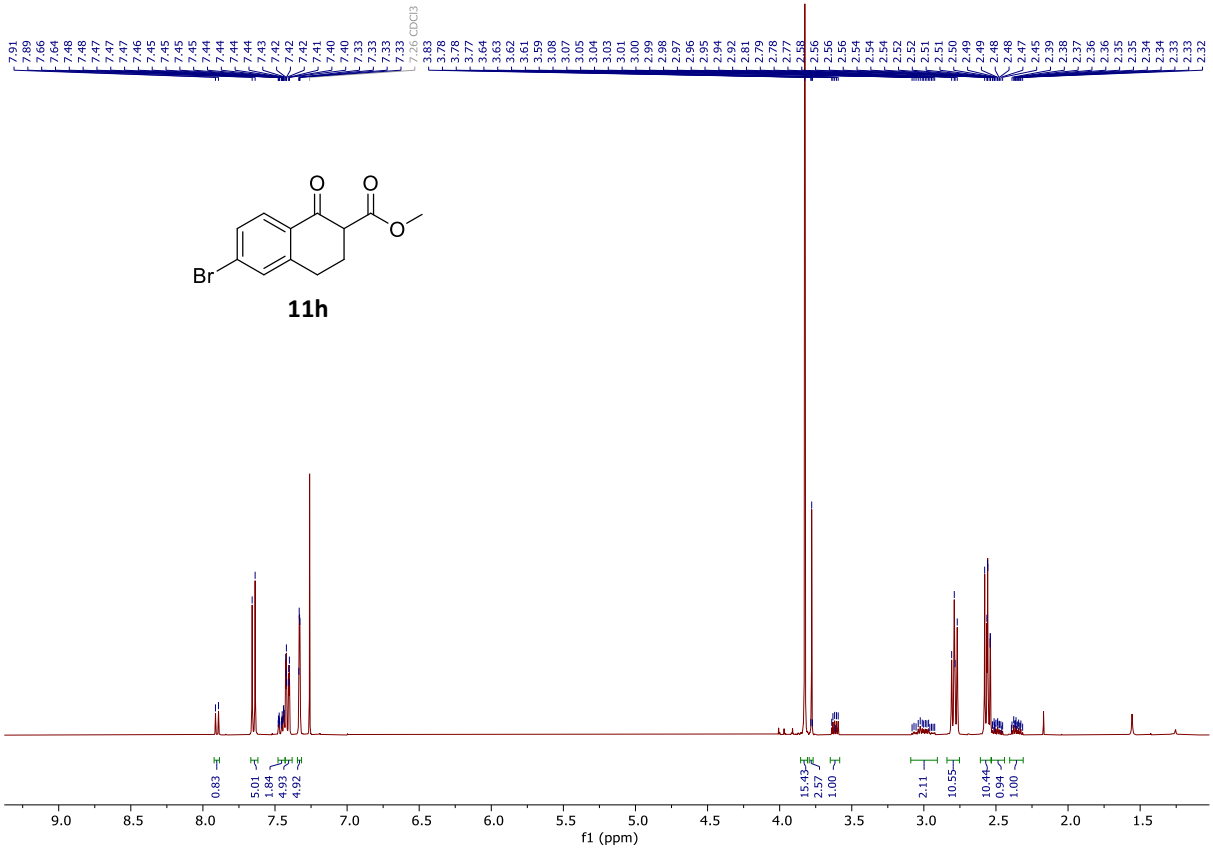
^{1}H NMR (400 MHz, $CDCl_3$)



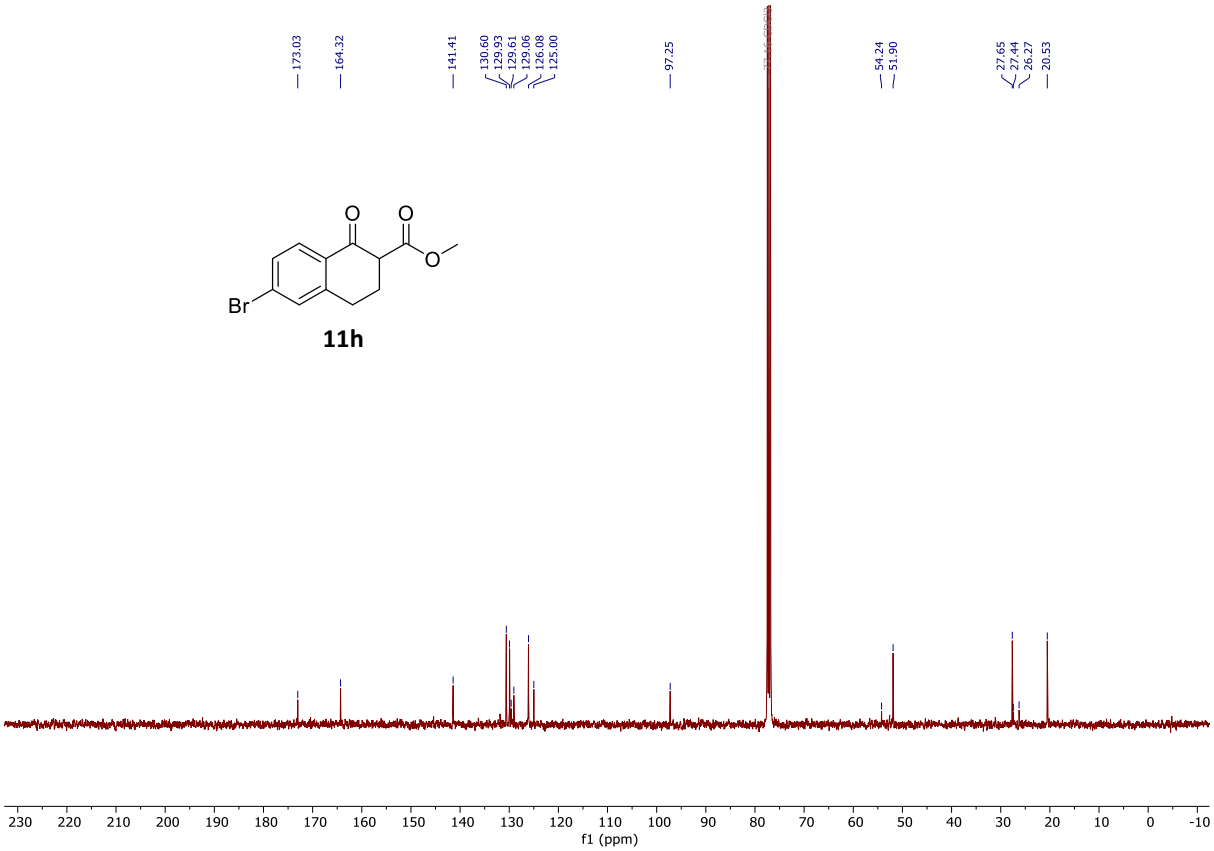
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



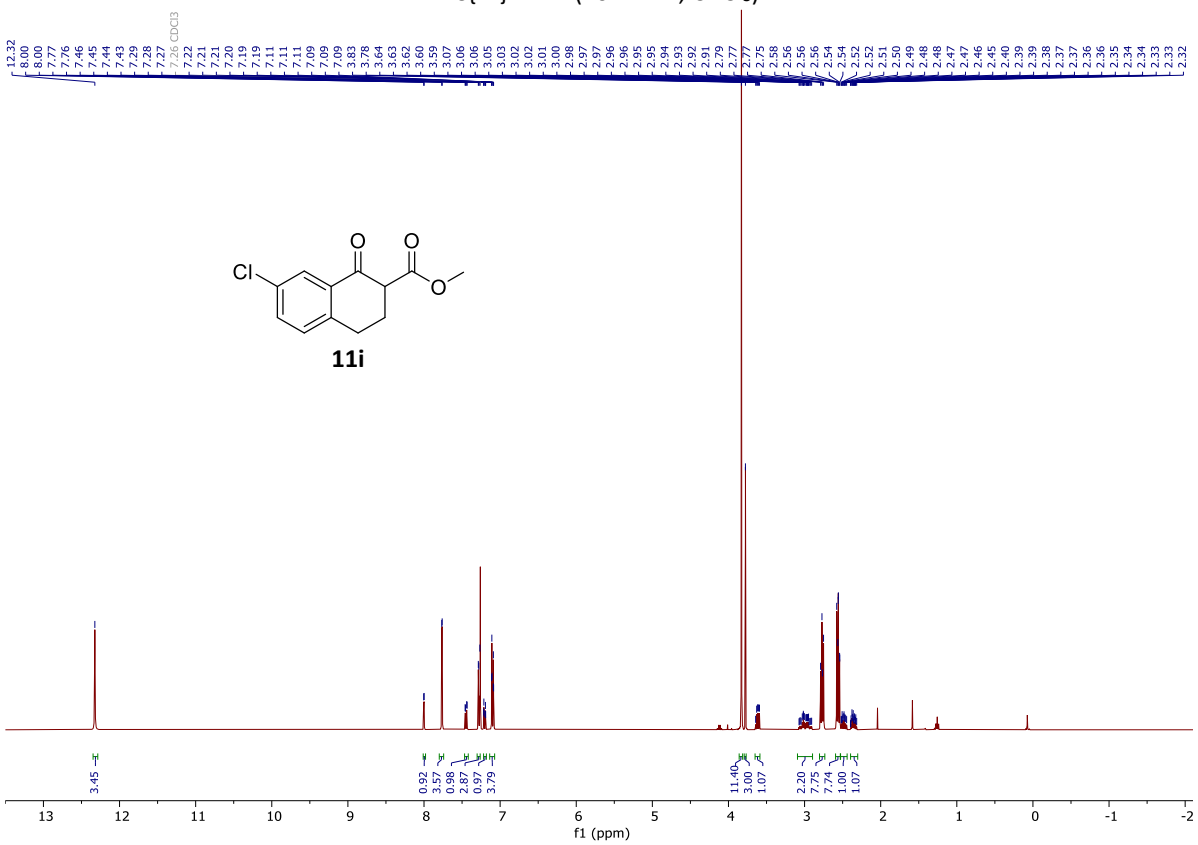
$^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$)



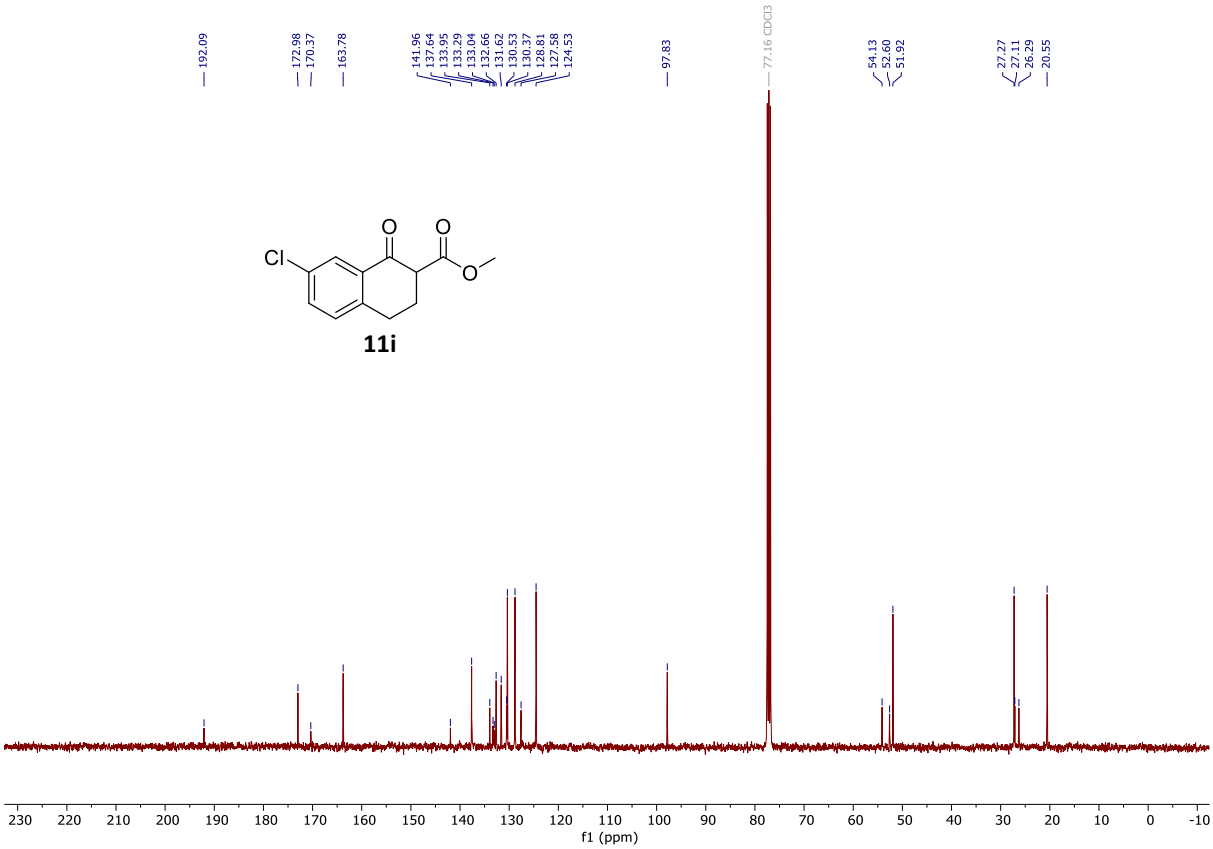
^{1}H NMR (400 MHz, $CDCl_3$)



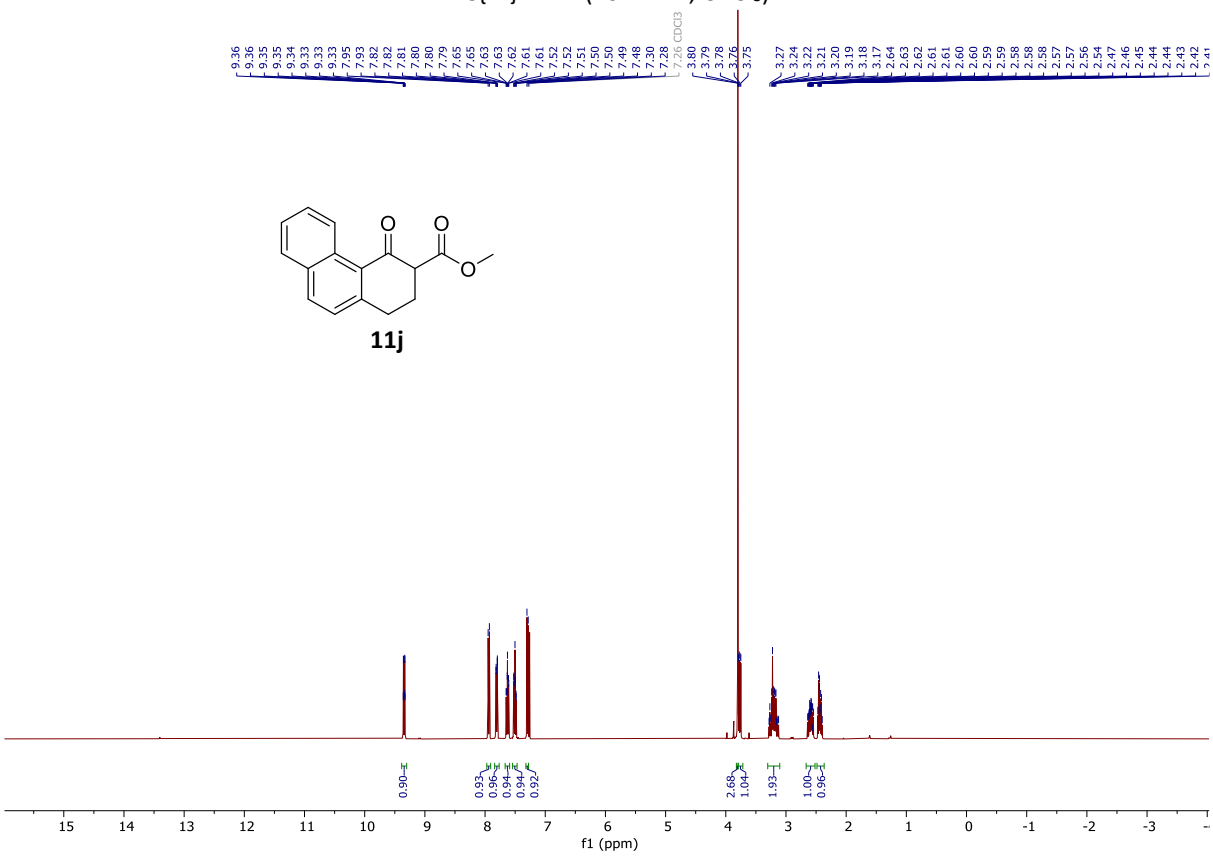
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



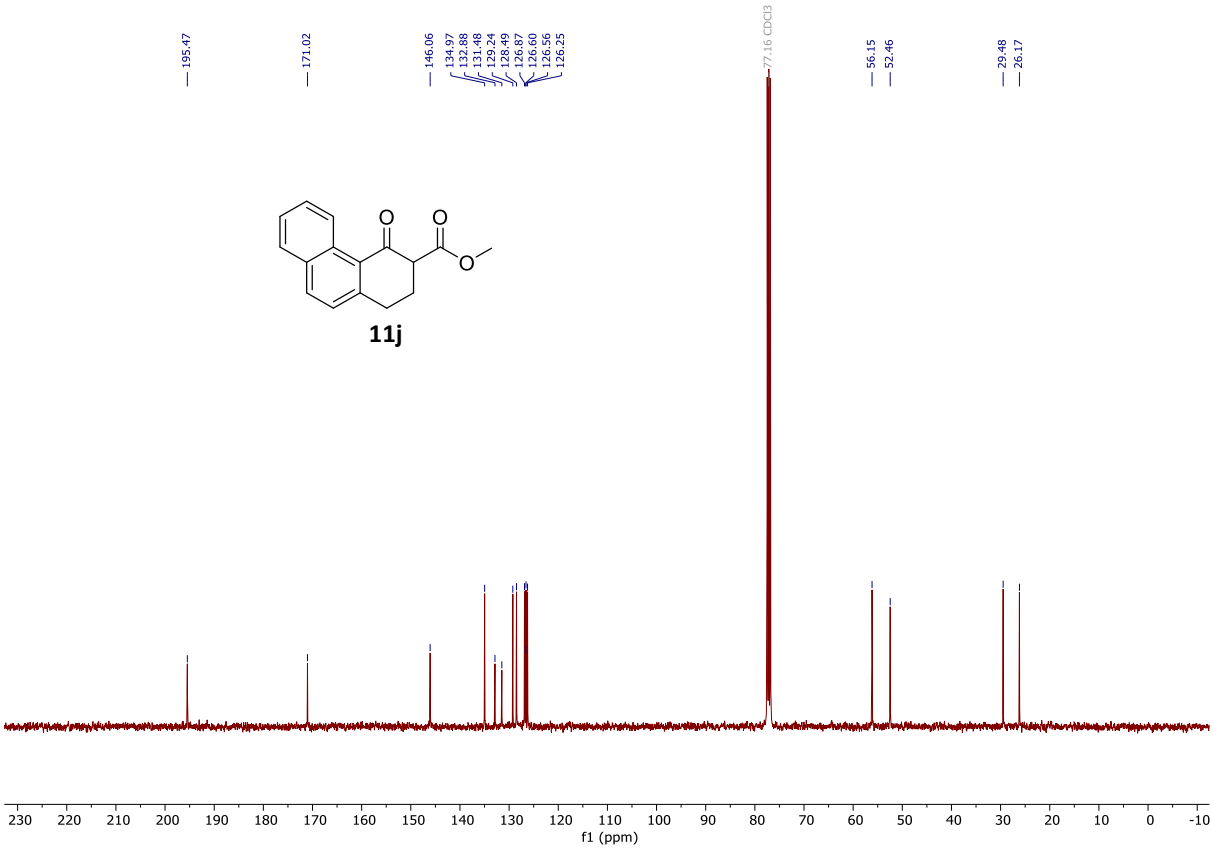
^{1}H NMR (400 MHz, $CDCl_3$)



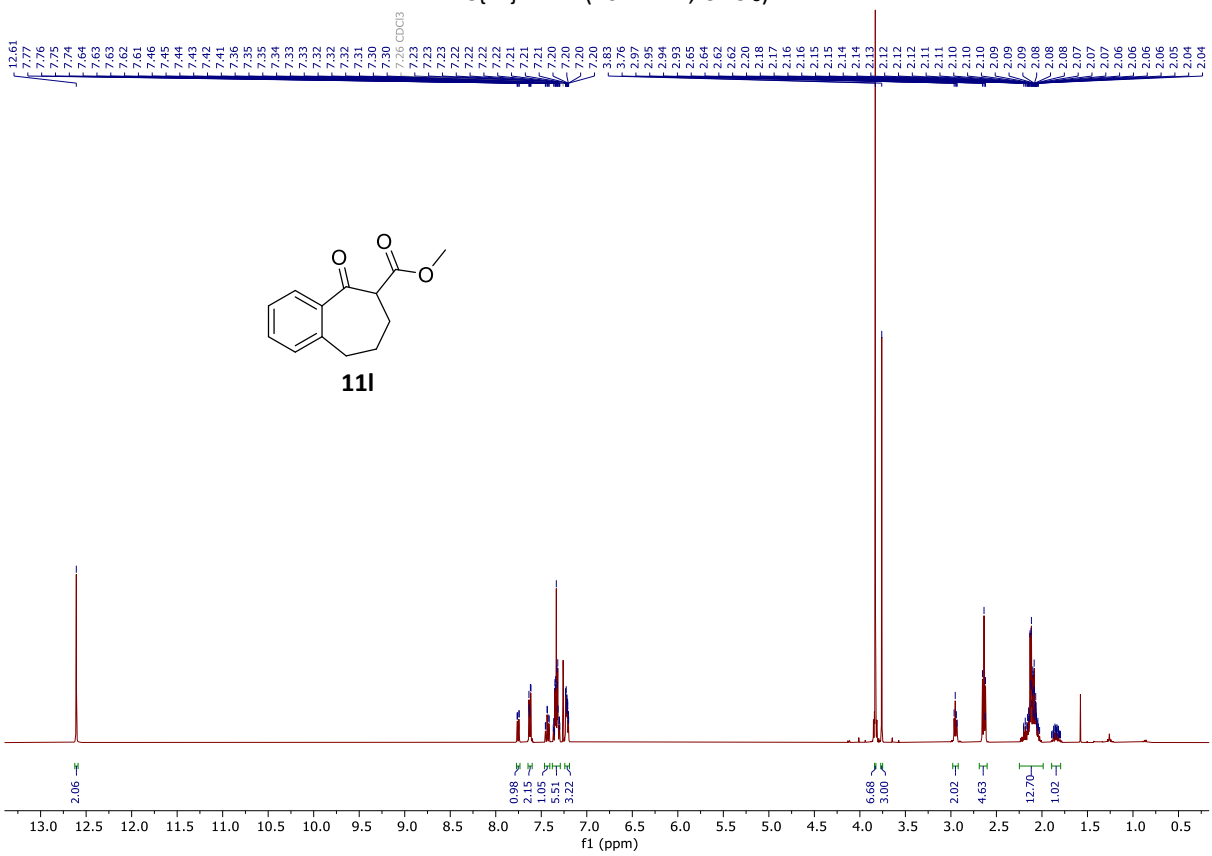
$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$)



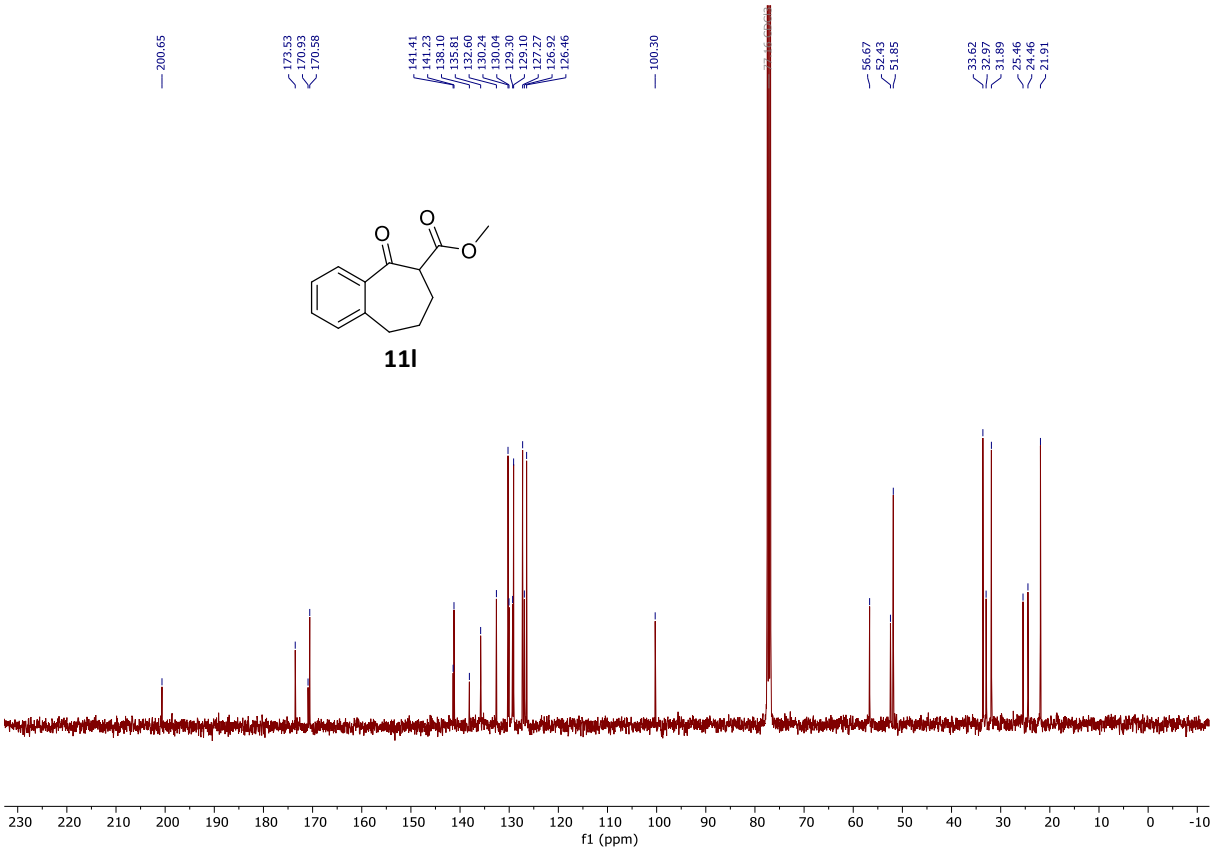
^1H NMR (400 MHz, $CDCl_3$)



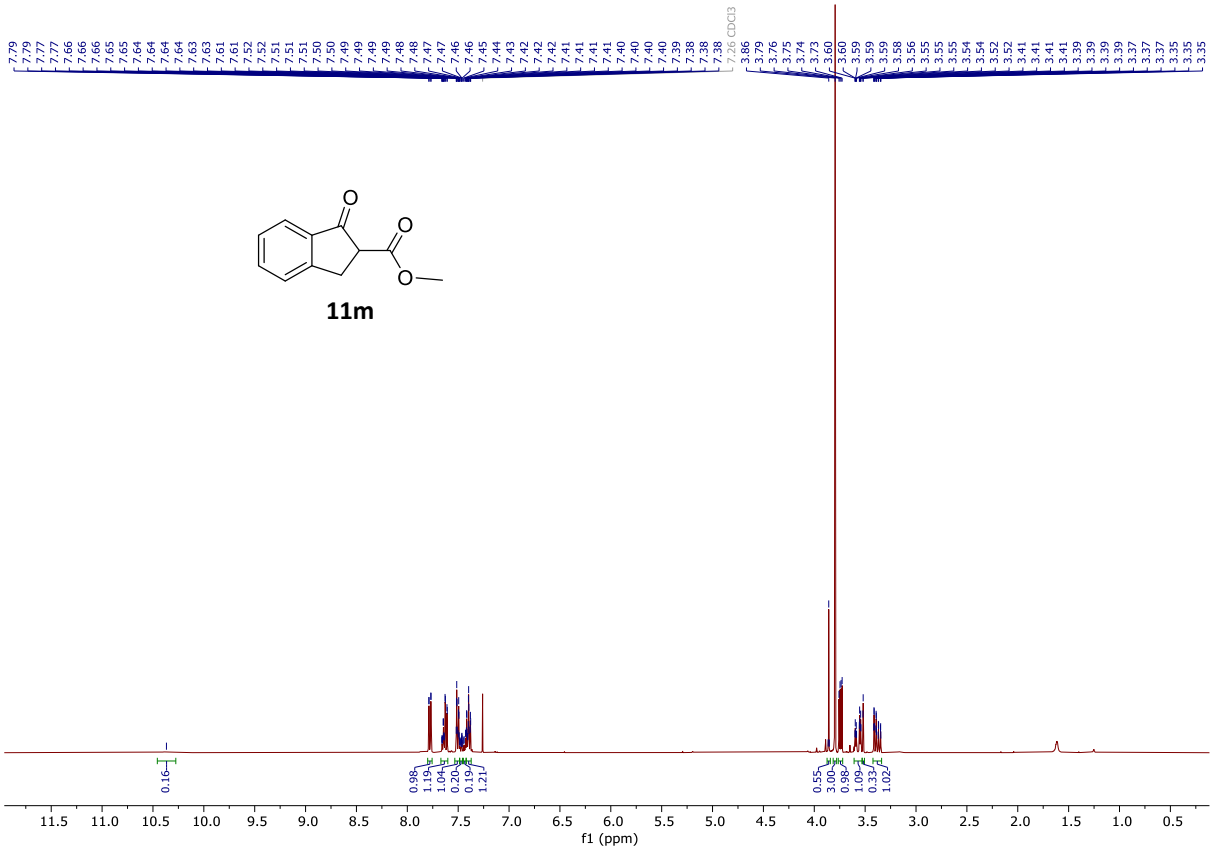
$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$)



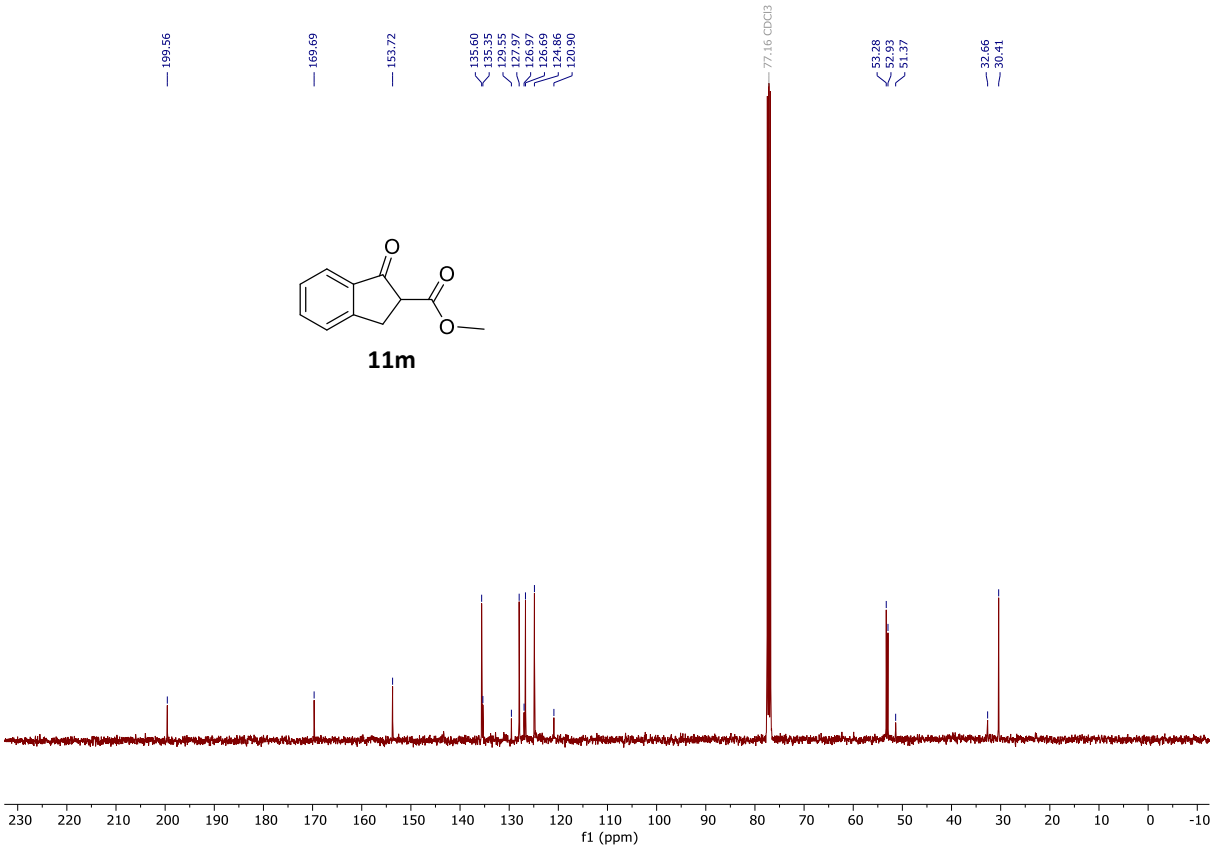
^1H NMR (400 MHz, $CDCl_3$)



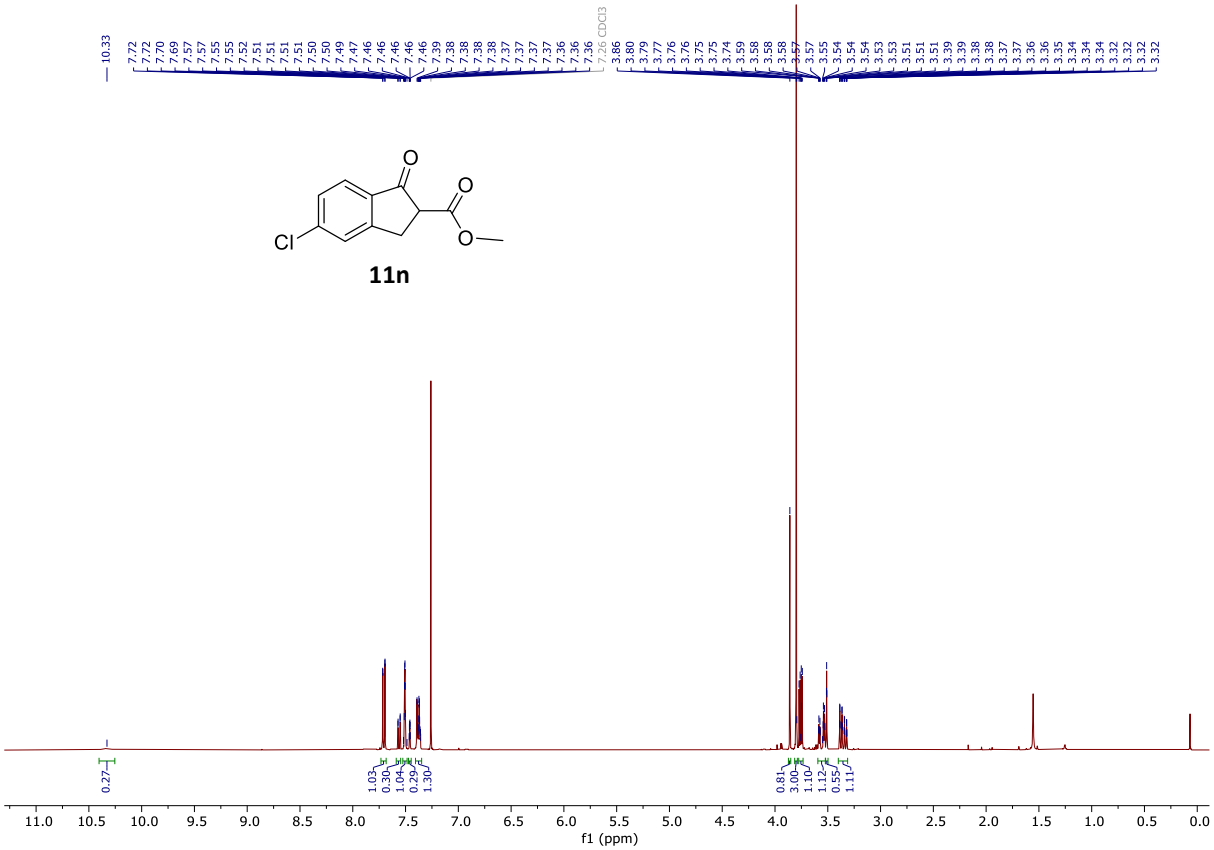
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



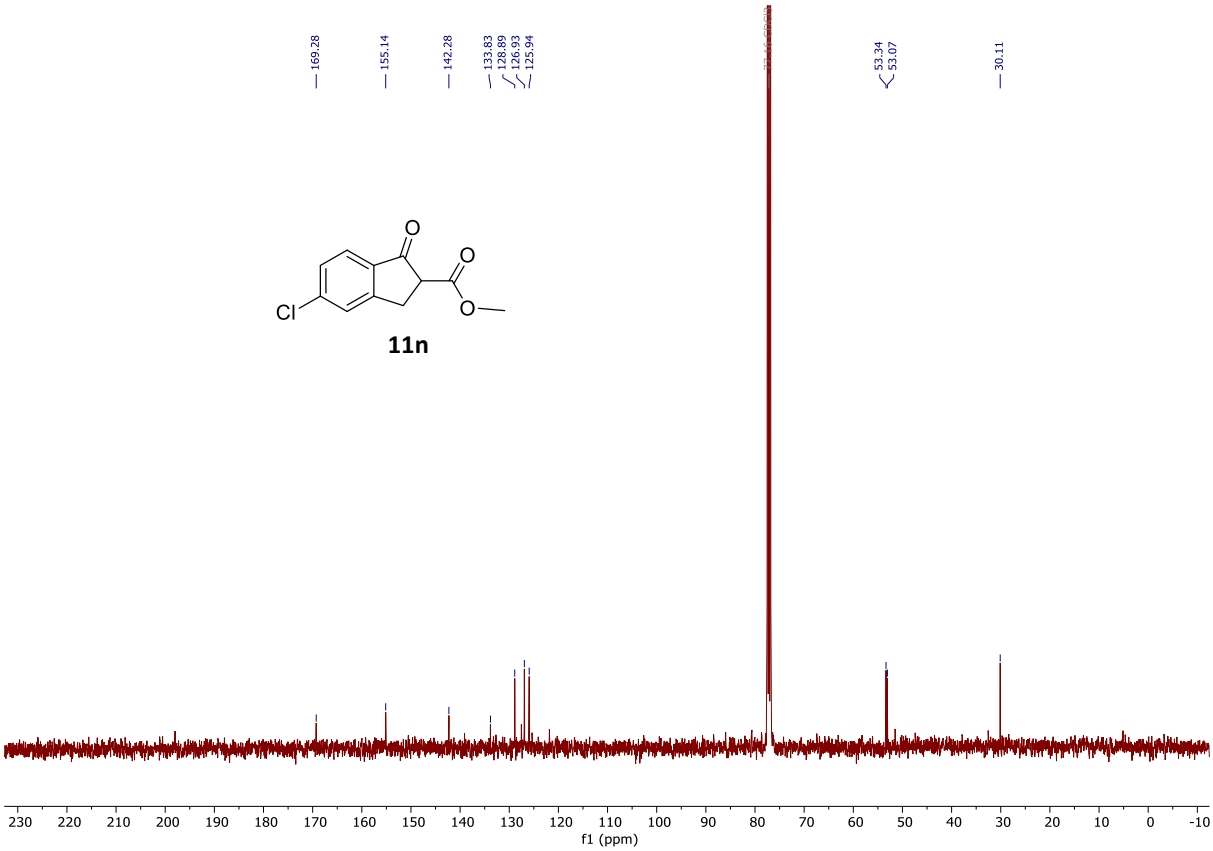
^{1}H NMR (400 MHz, $CDCl_3$)



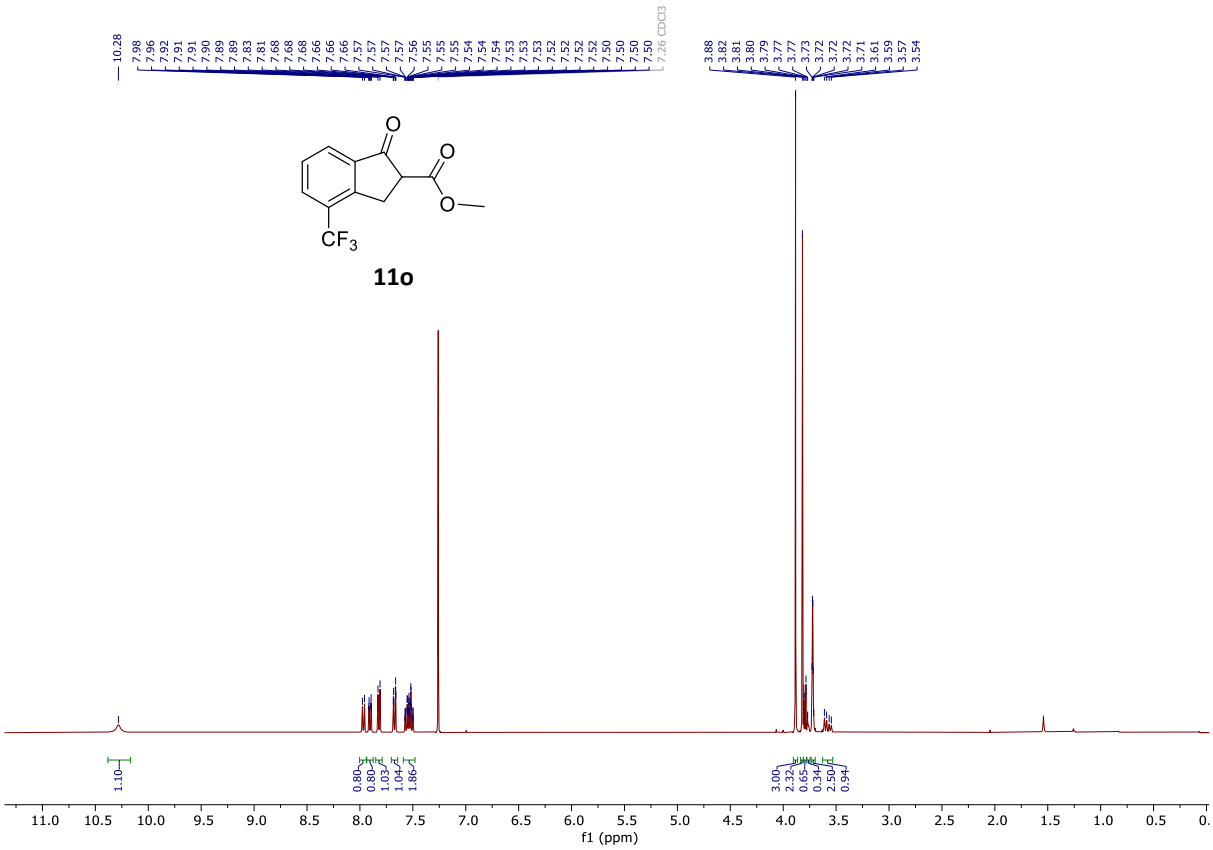
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



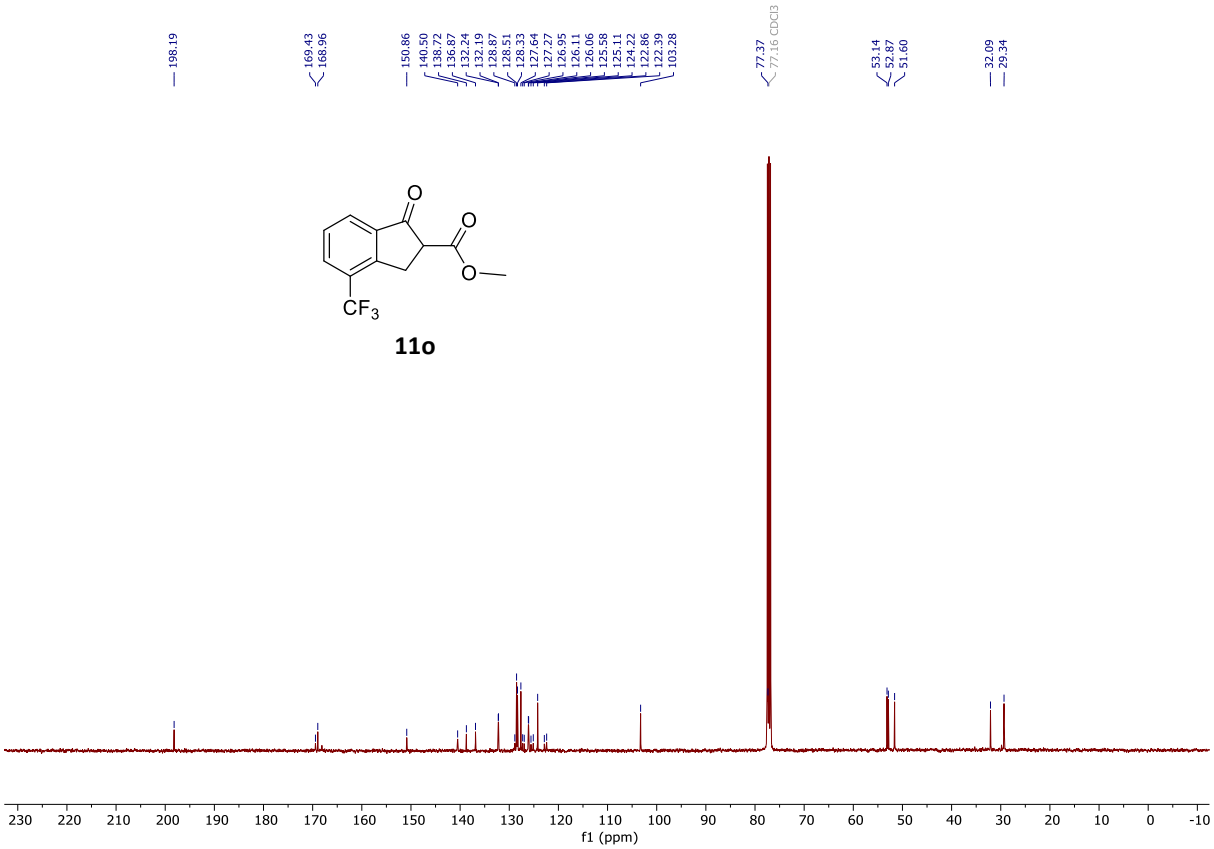
^{1}H NMR (400 MHz, $CDCl_3$)



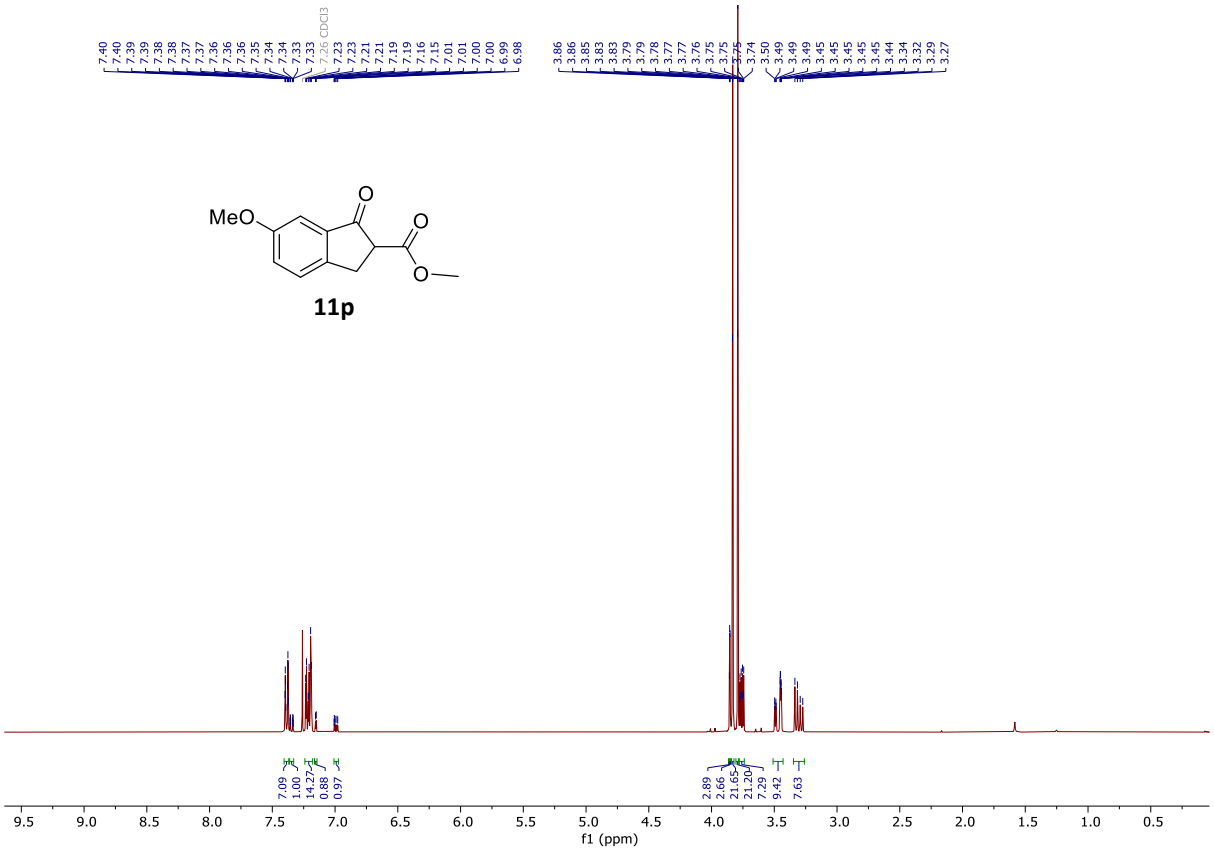
$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$)



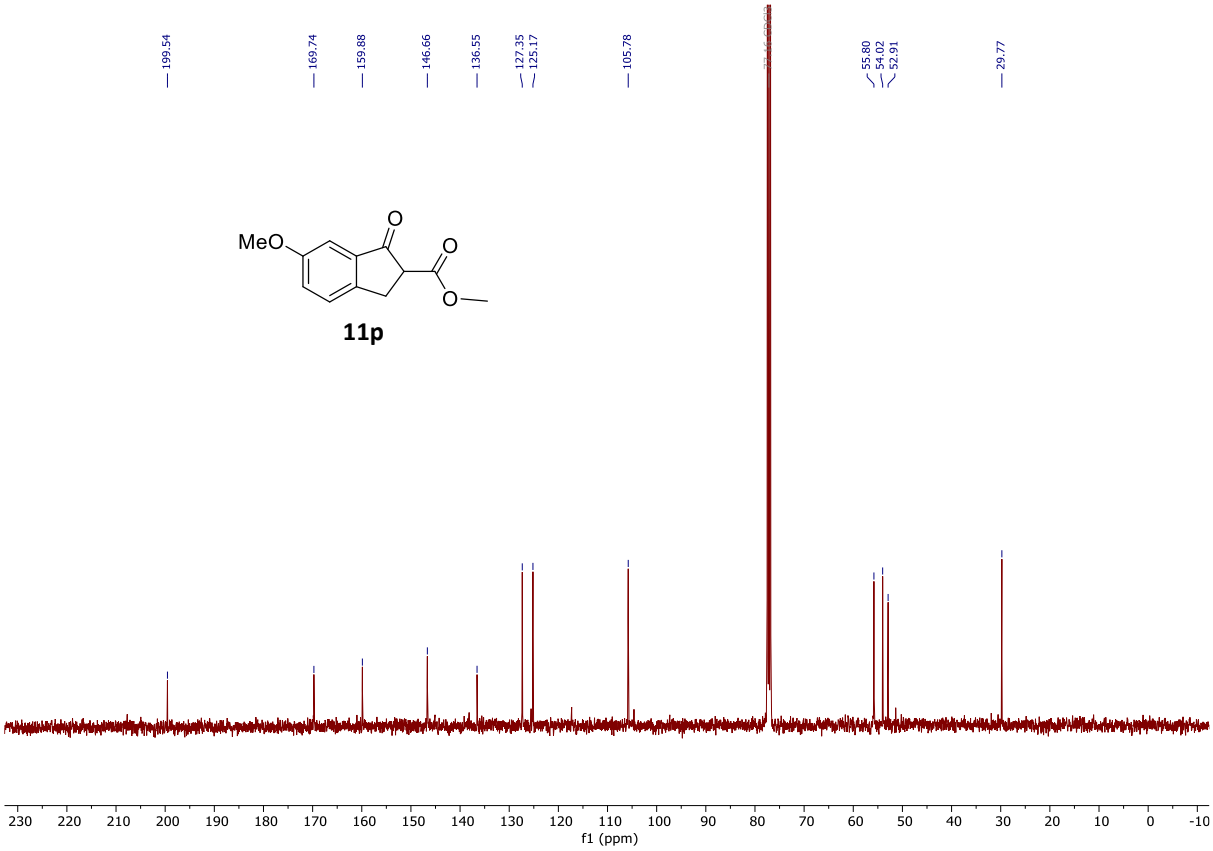
^1H NMR (400 MHz, $CDCl_3$)



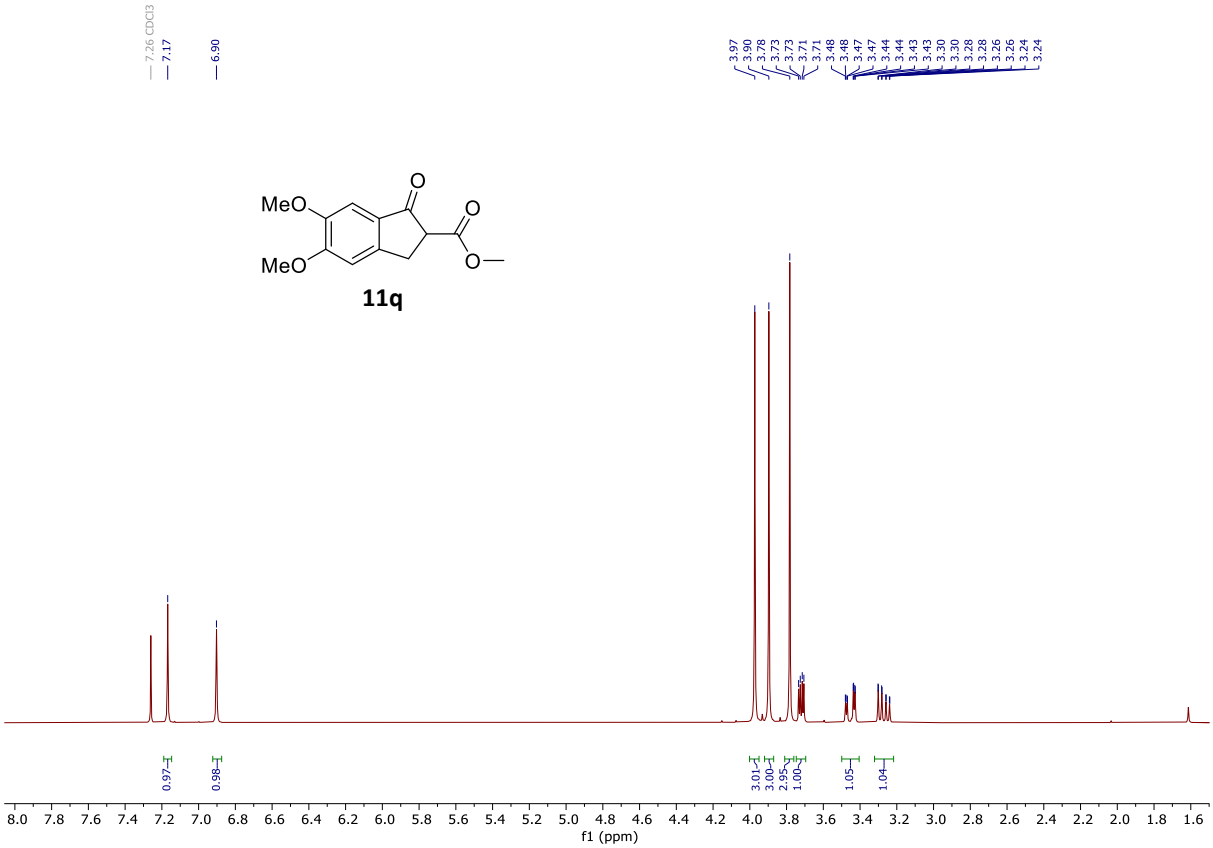
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



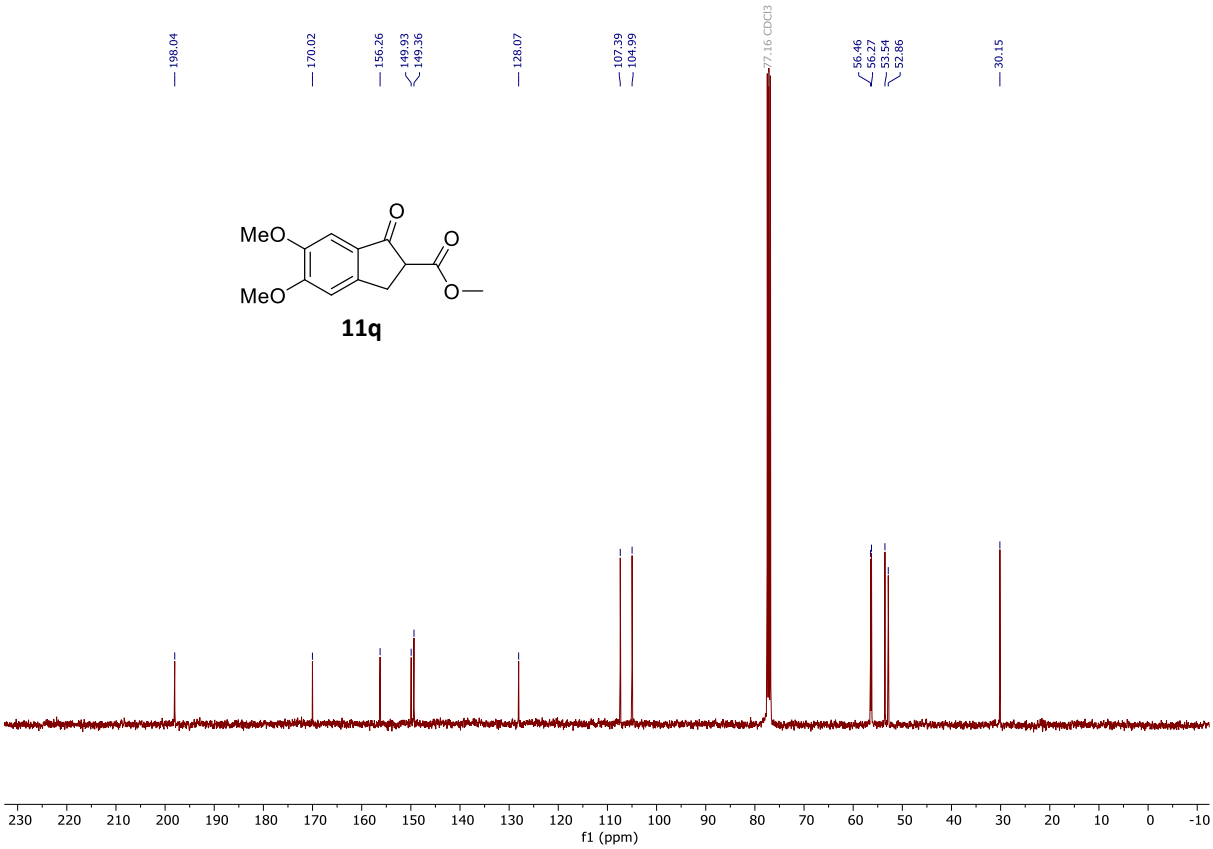
^{1}H NMR (400 MHz, $CDCl_3$)



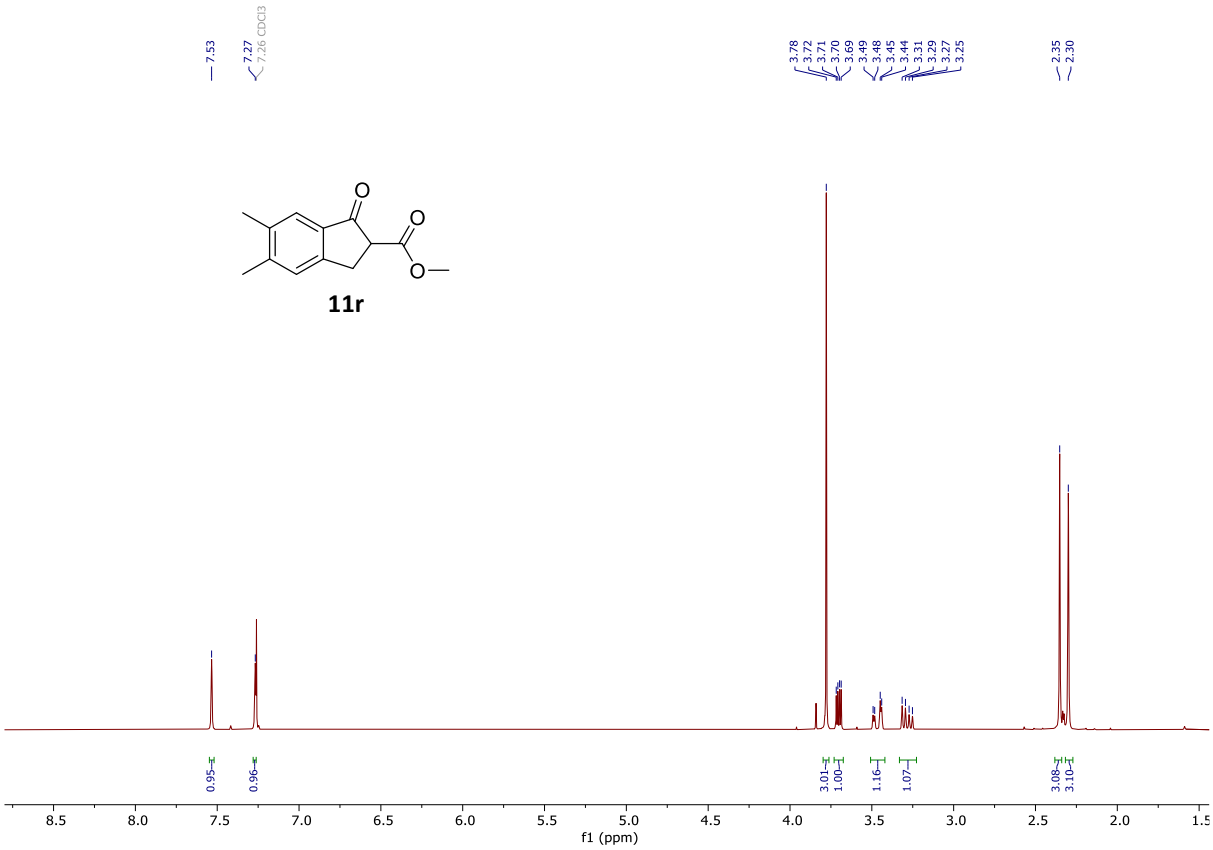
$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$)



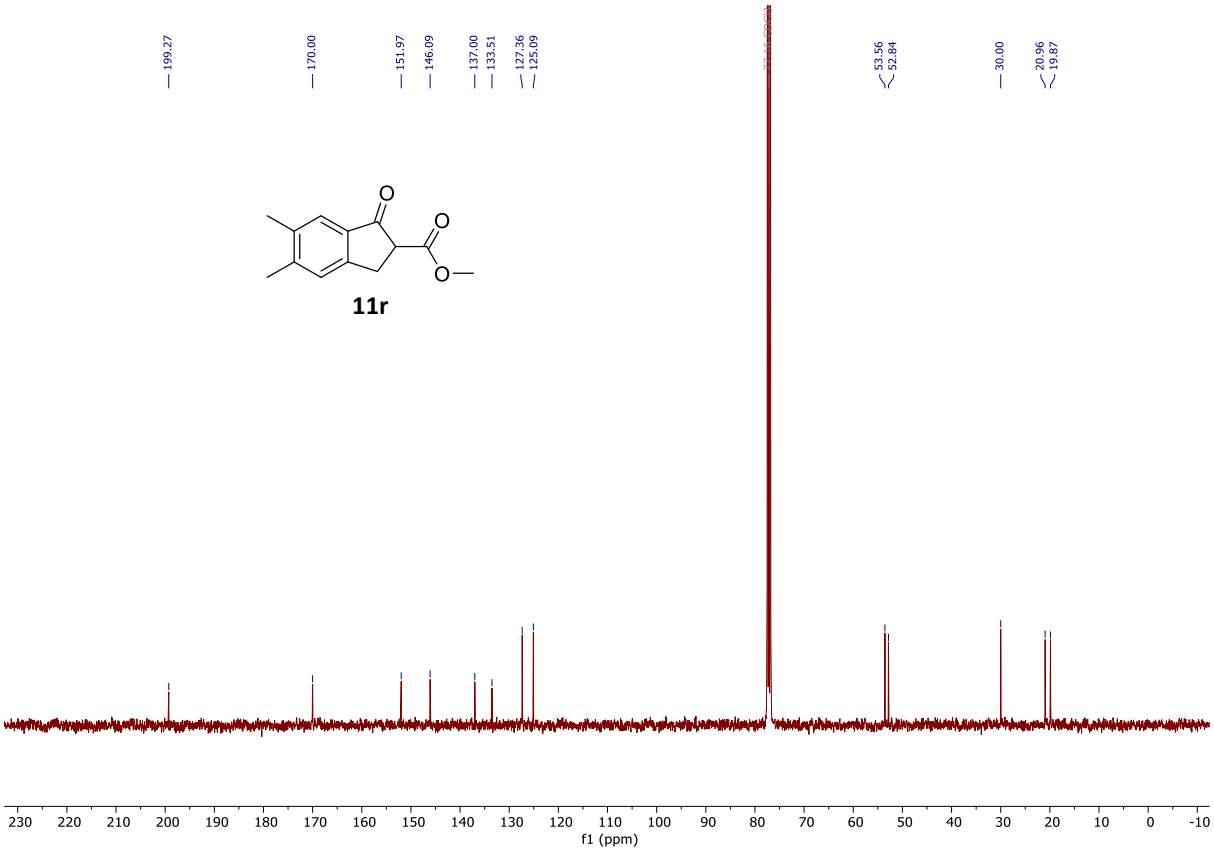
^1H NMR (400 MHz, $CDCl_3$)



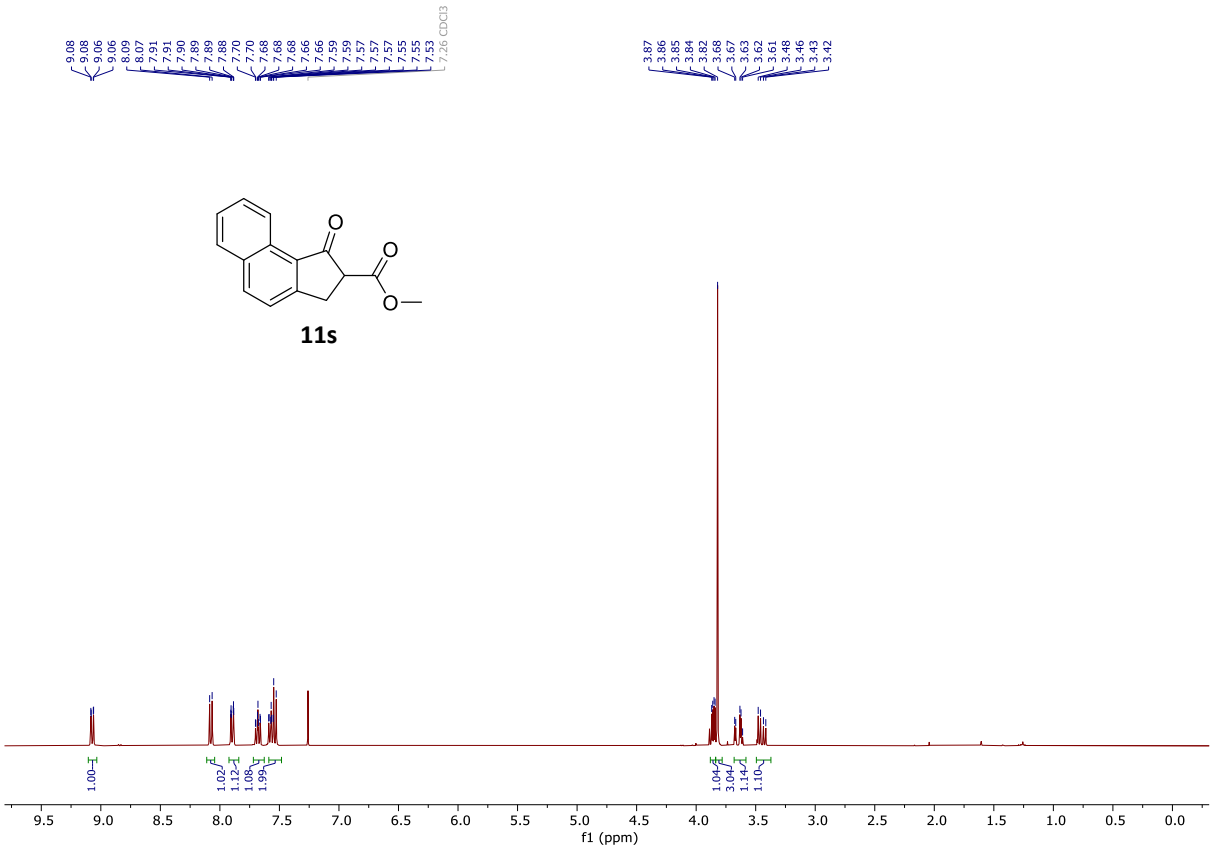
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



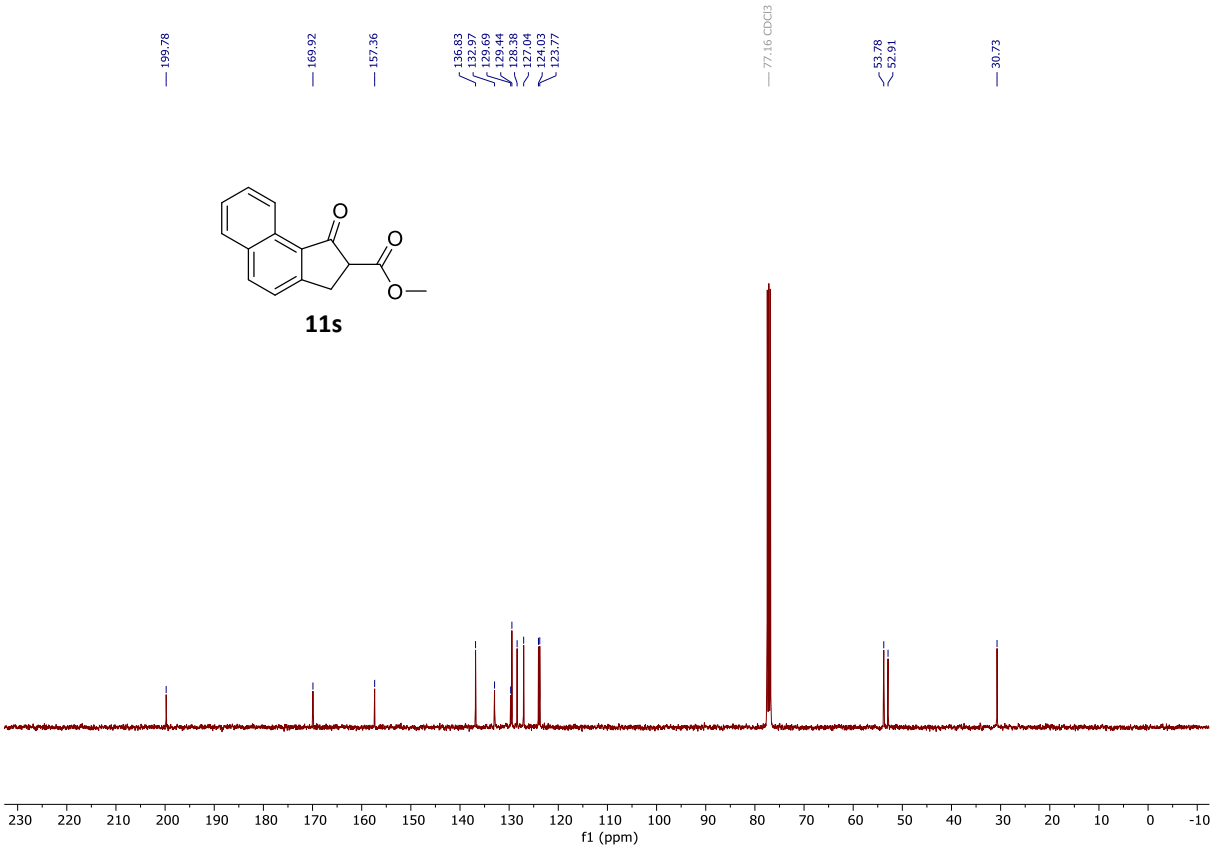
^{1}H NMR (400 MHz, $CDCl_3$)



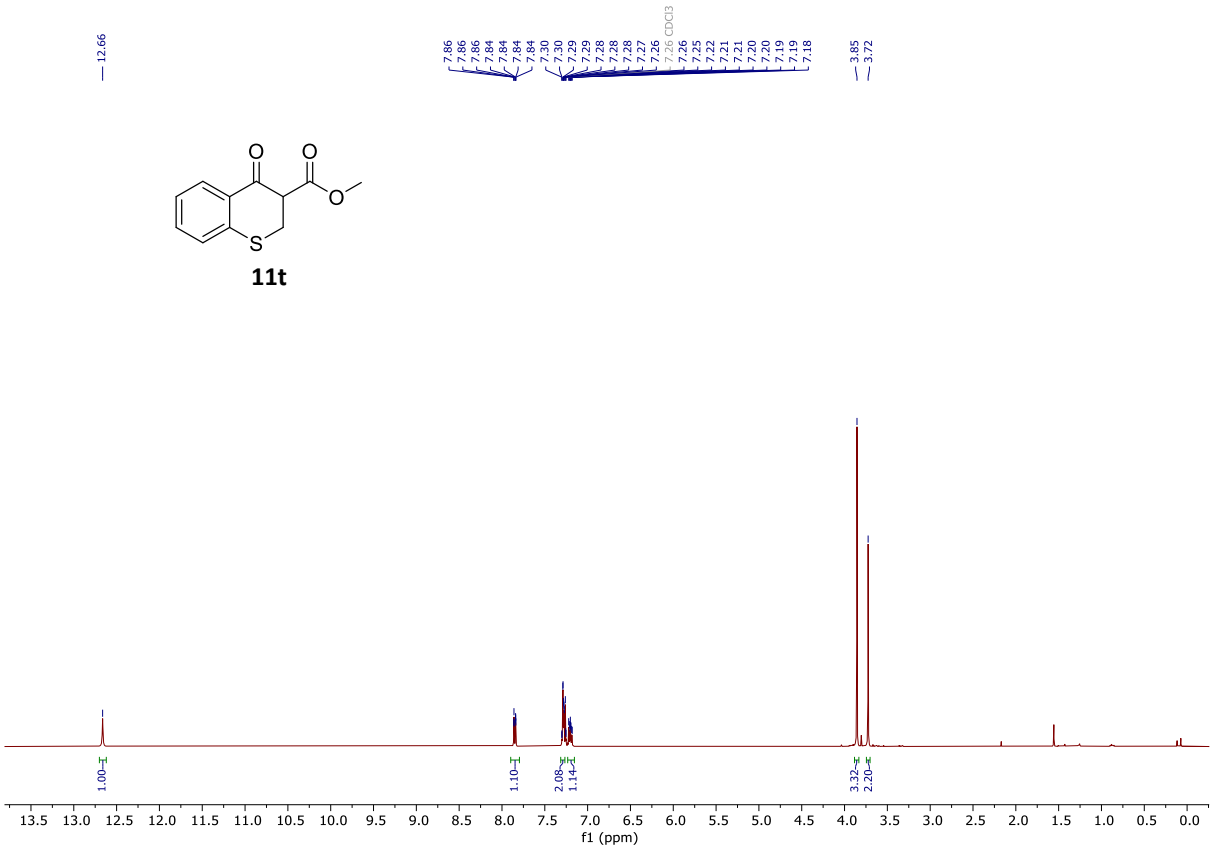
$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$)



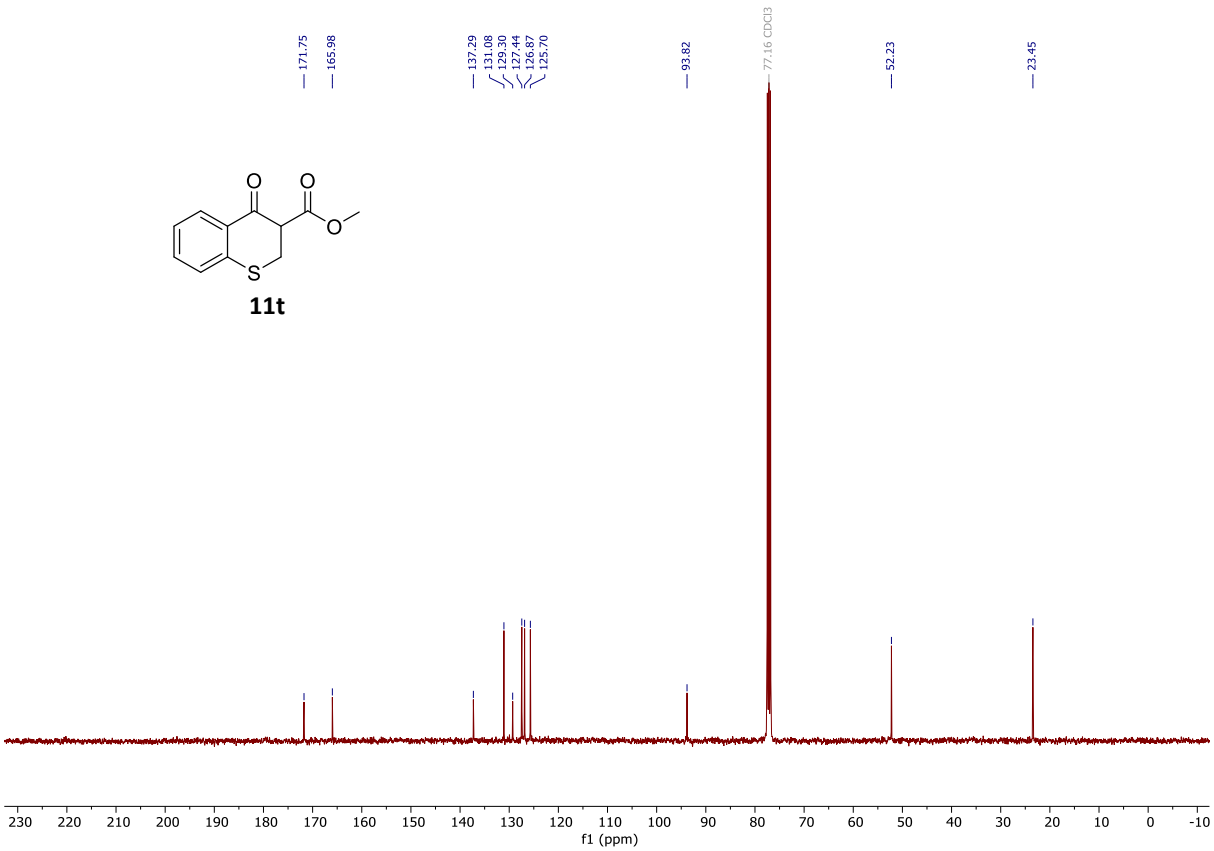
^1H NMR (400 MHz, $CDCl_3$)



$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$)

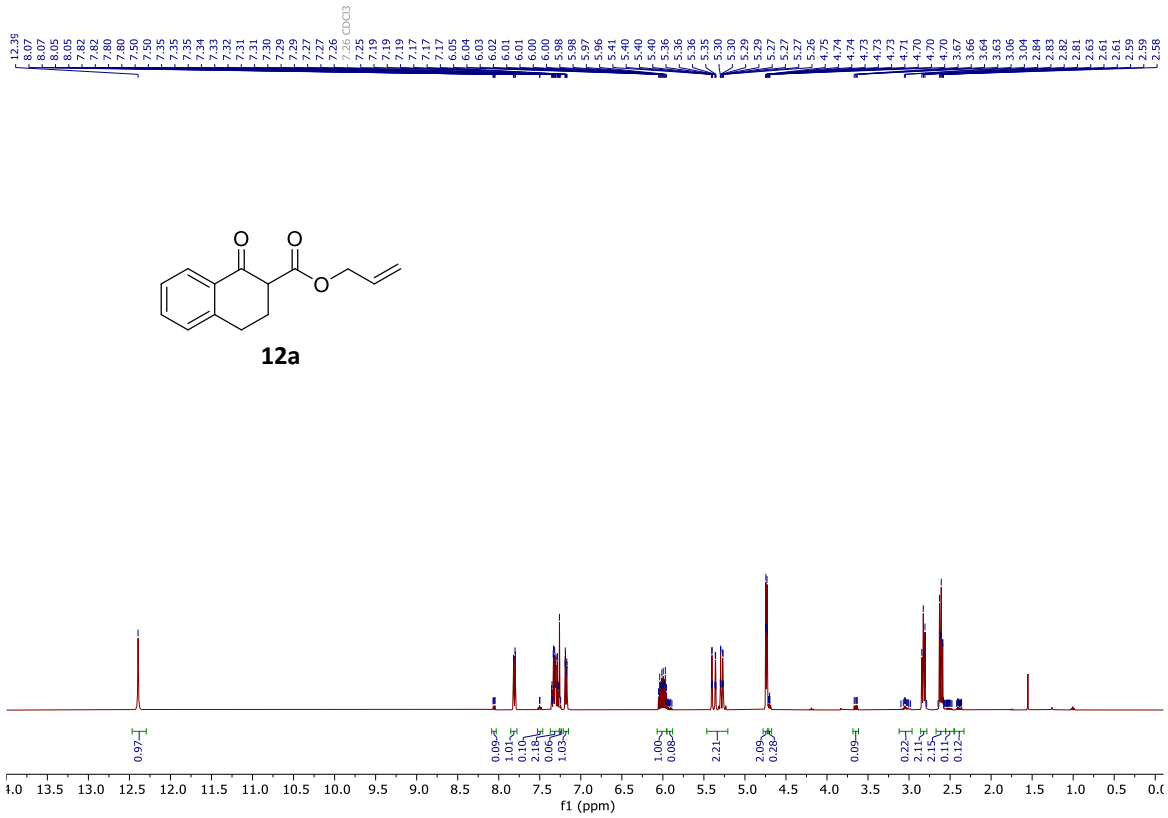


^1H NMR (400 MHz, $CDCl_3$)

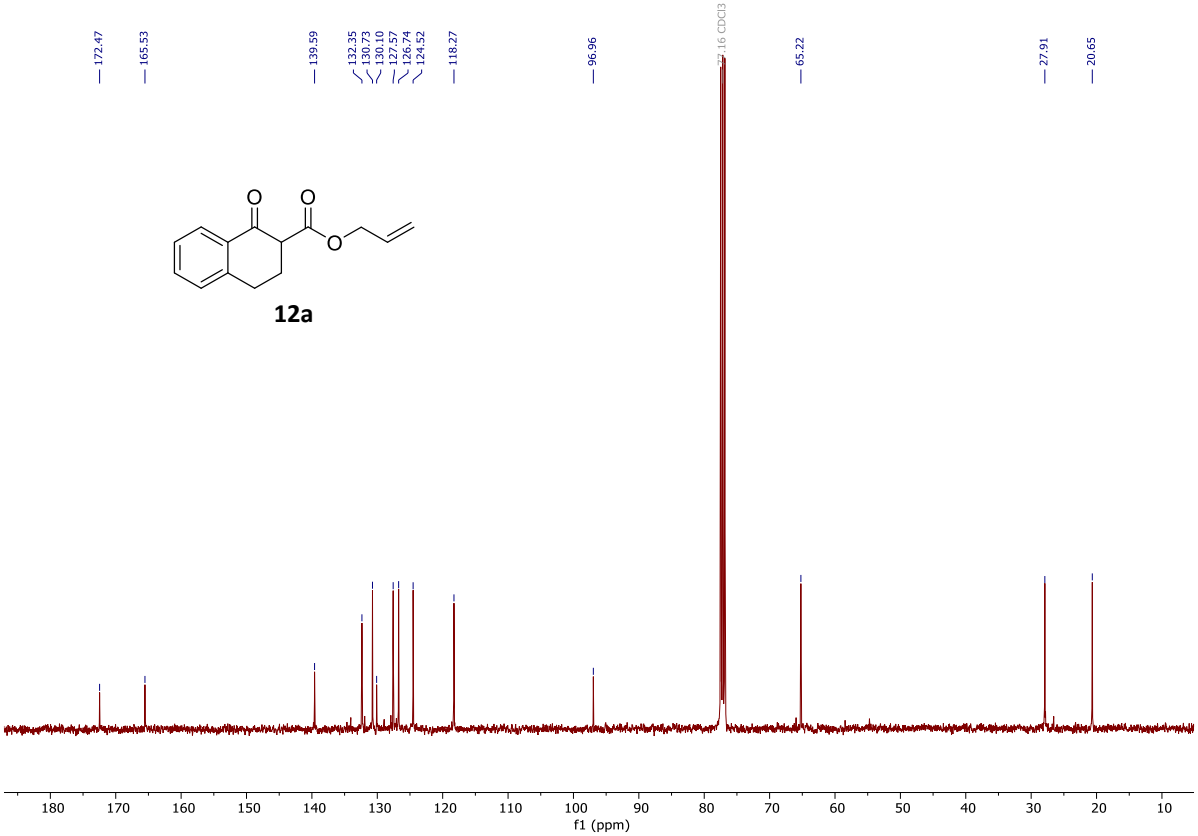


$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)

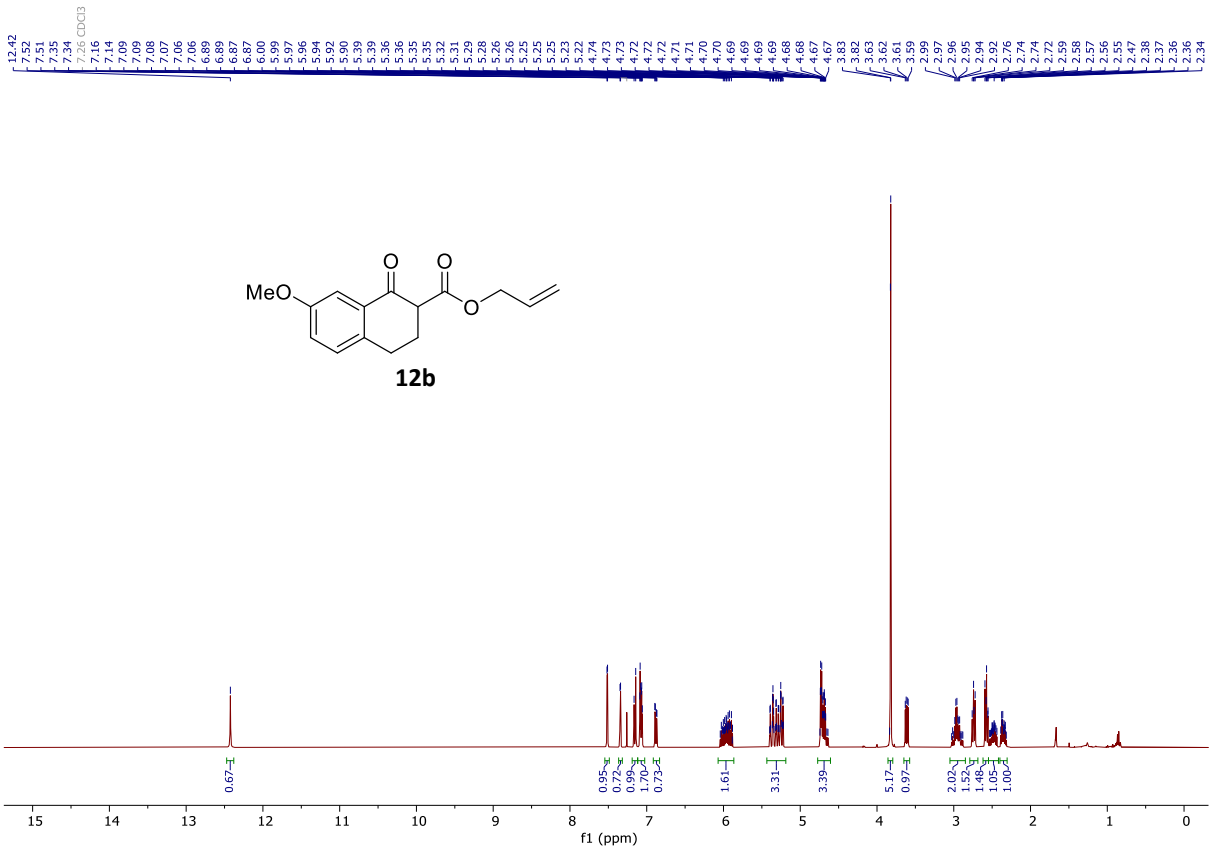
10. NMR spectra for compounds **12a – 12t**



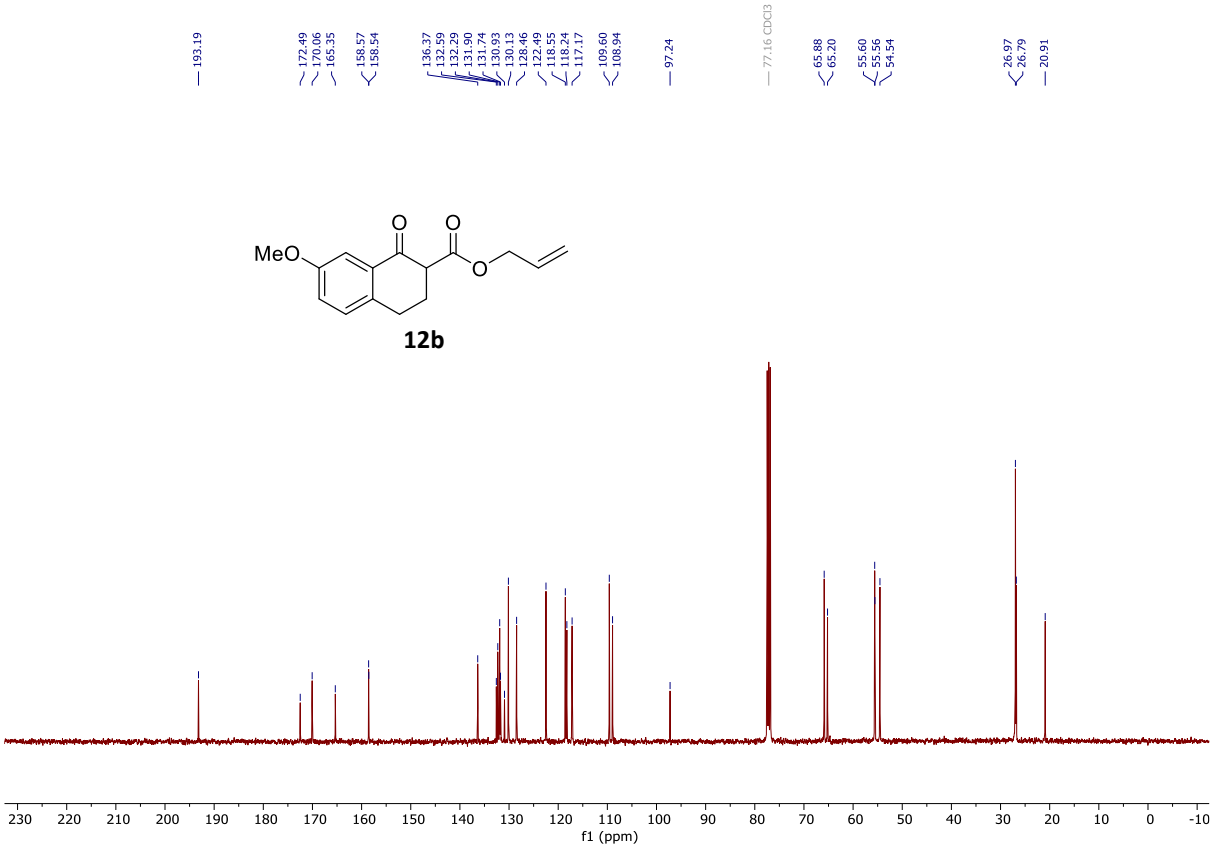
^{1}H NMR (400 MHz, $CDCl_3$)



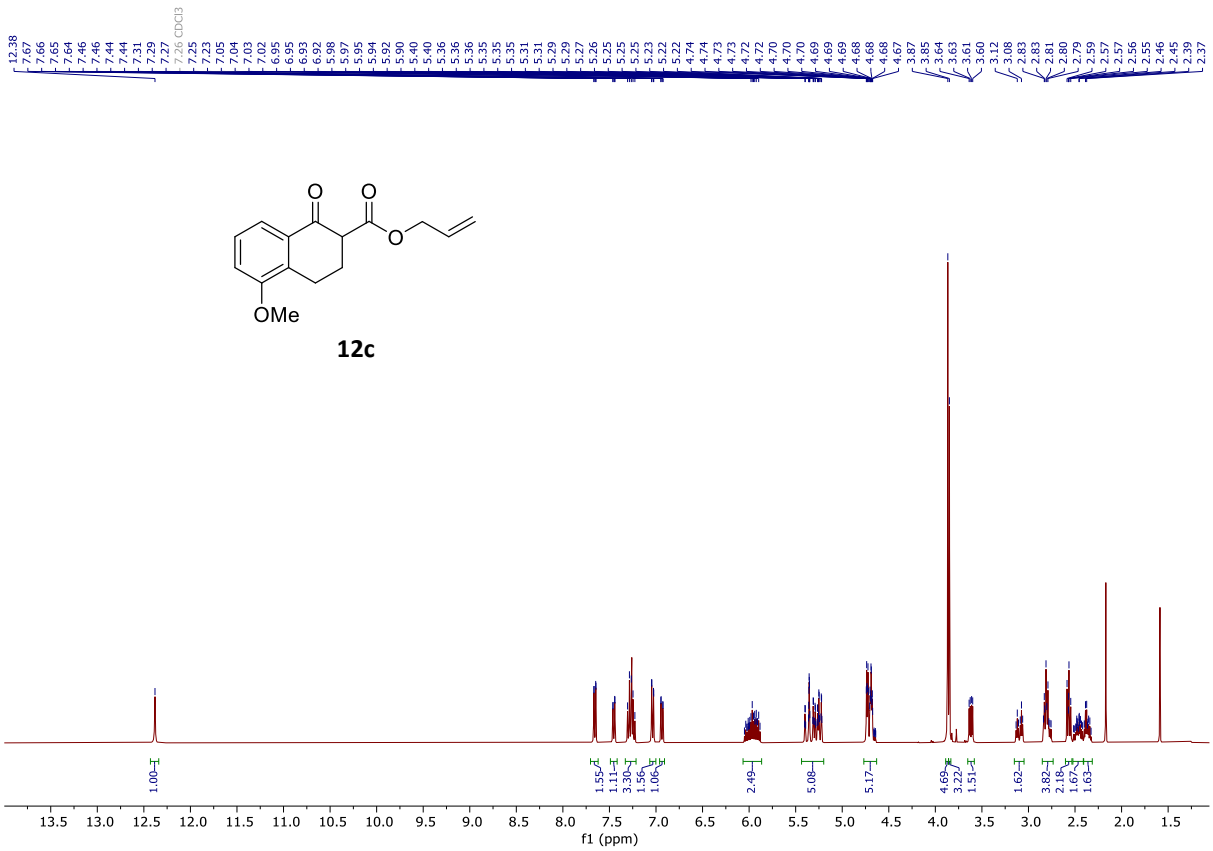
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)



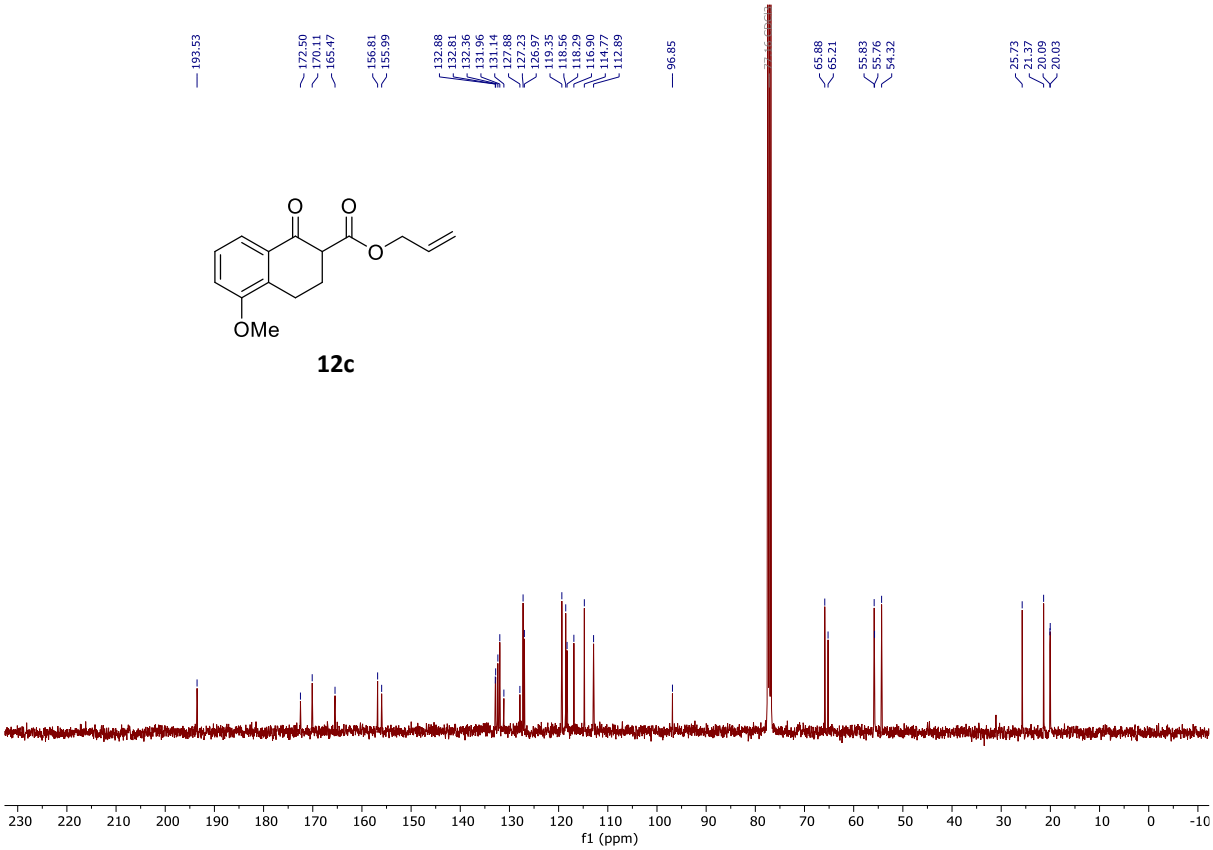
^{1}H NMR (400 MHz, $CDCl_3$)



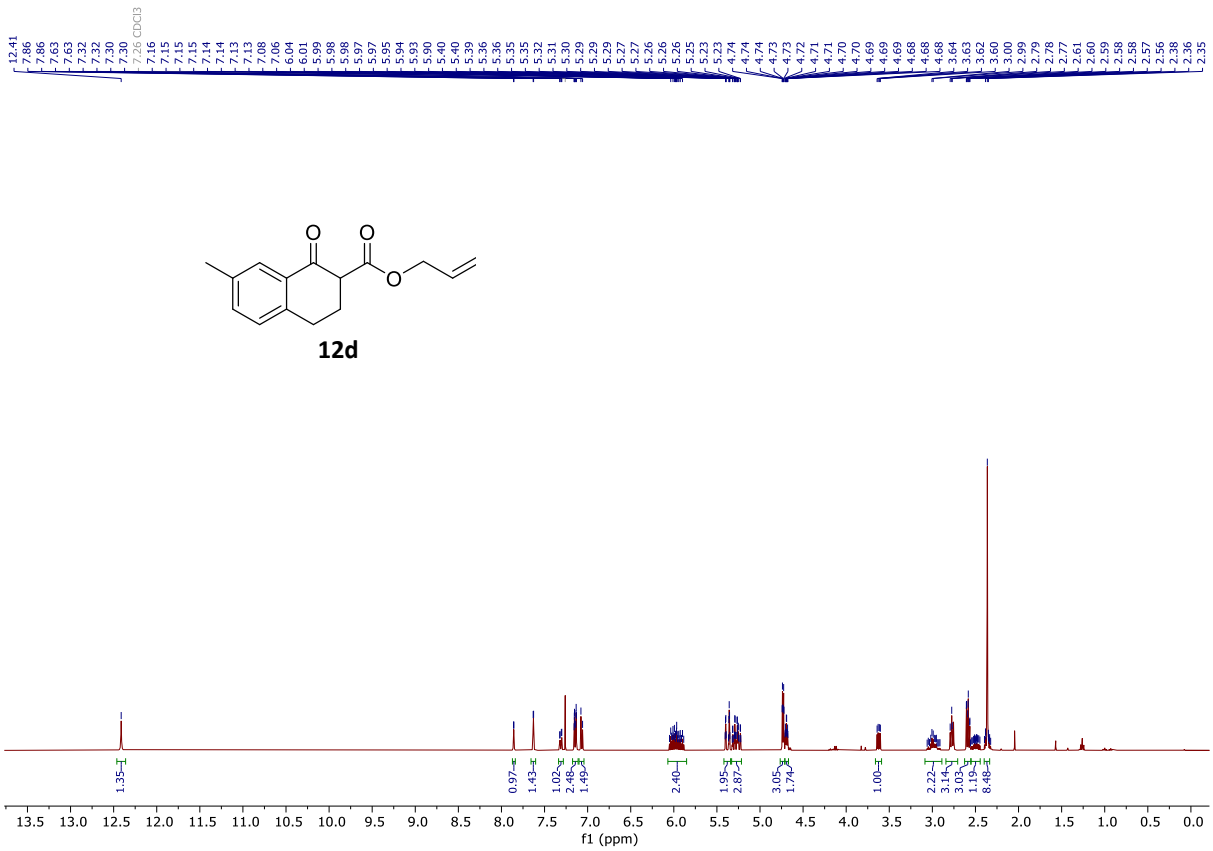
$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$)



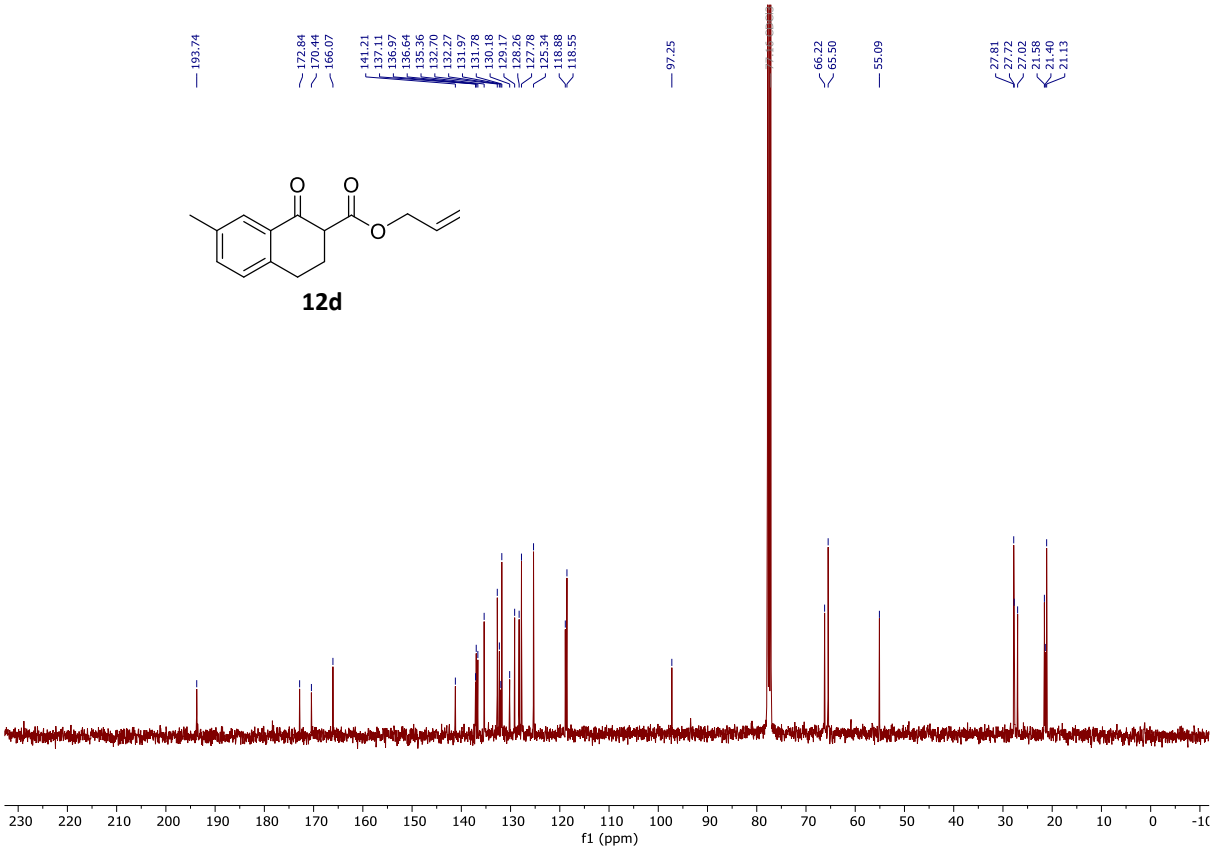
^1H NMR (400 MHz, $CDCl_3$)



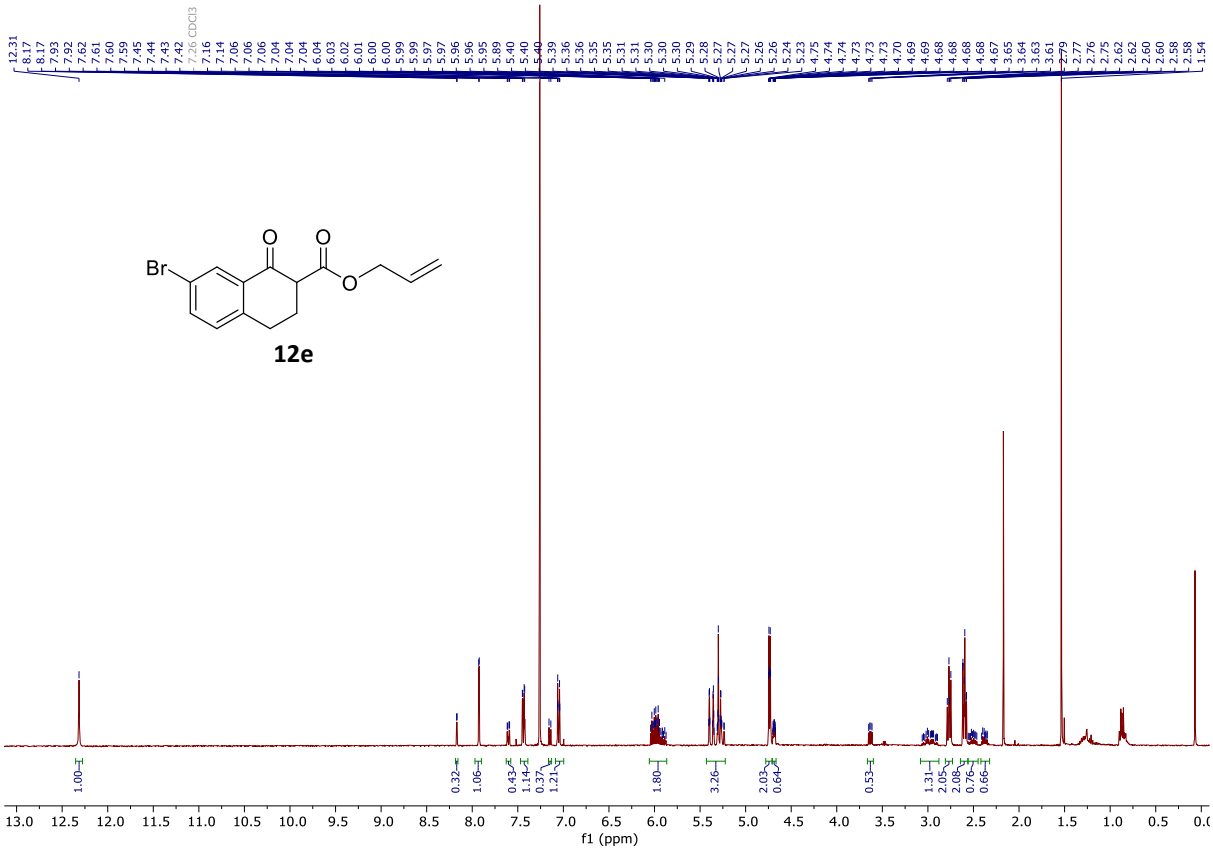
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



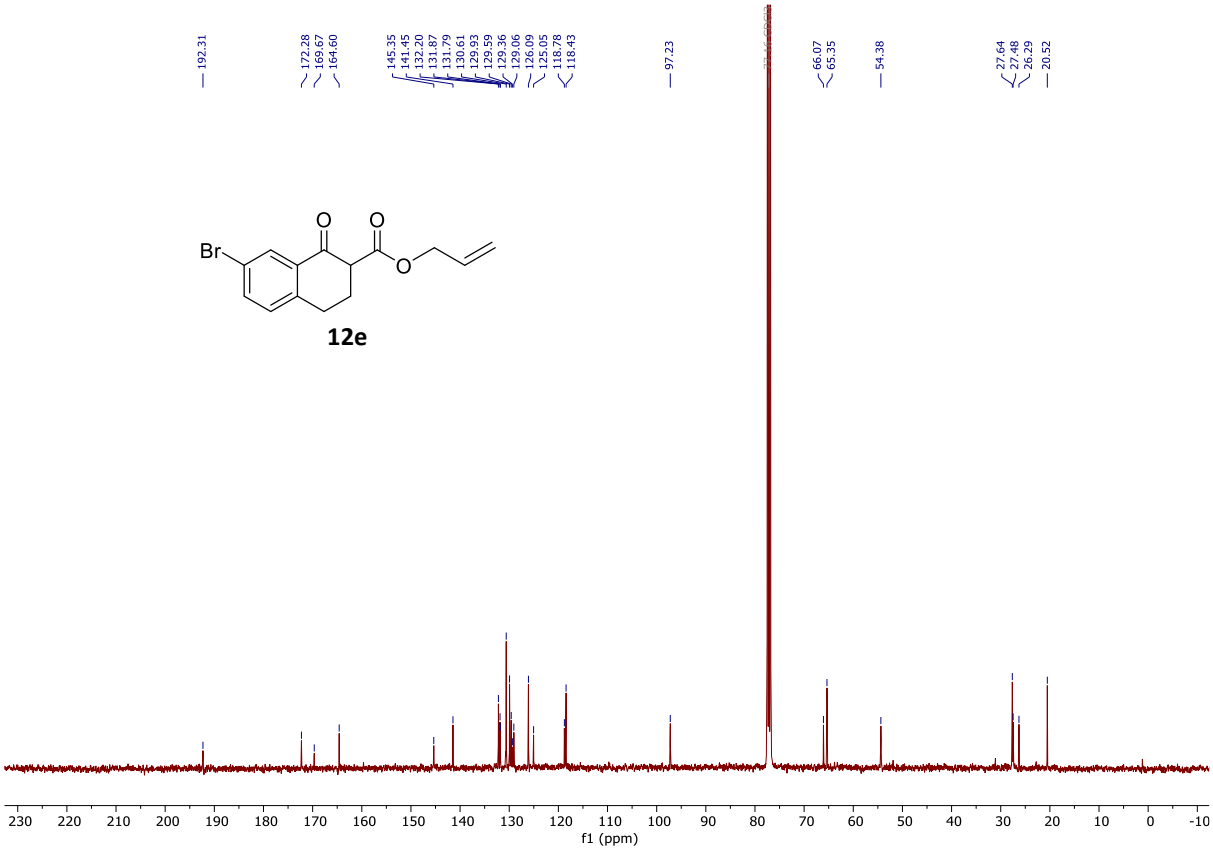
^{1}H NMR (400 MHz, $CDCl_3$)



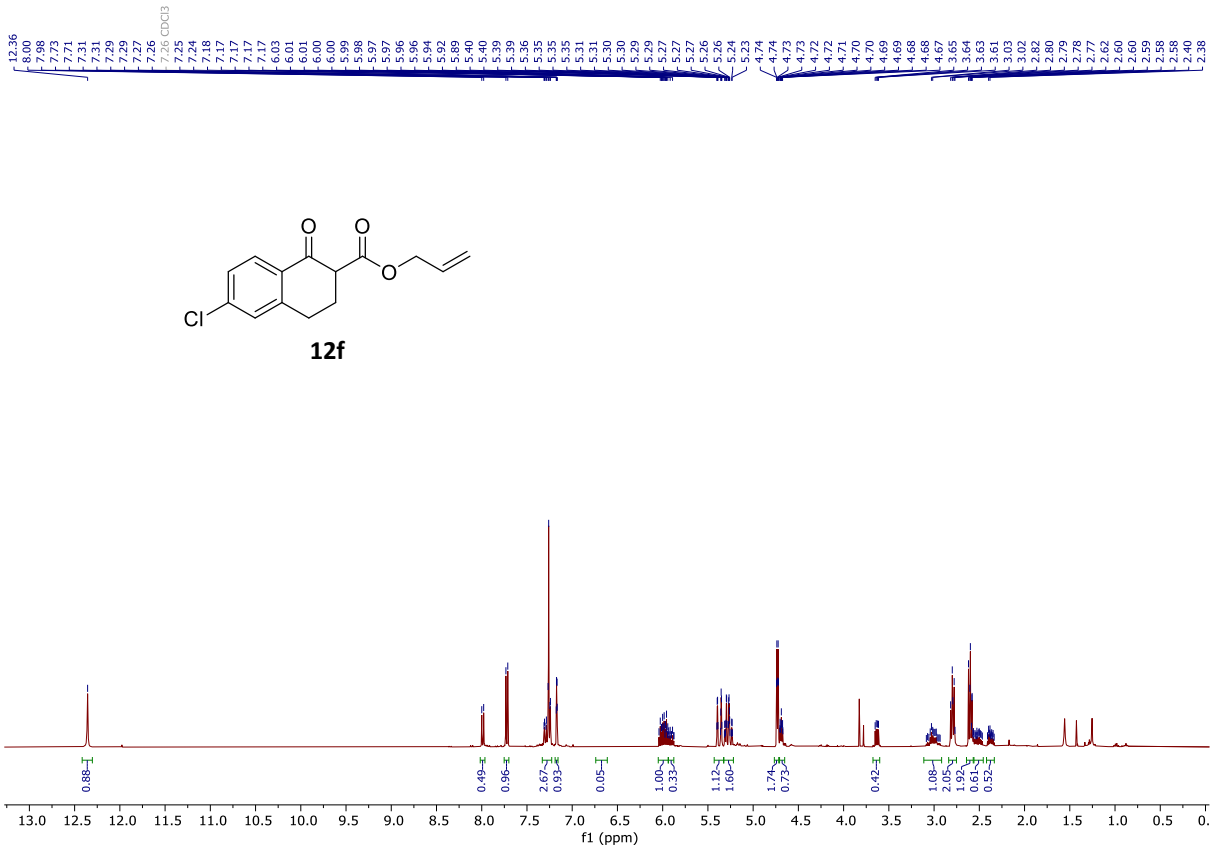
$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$)



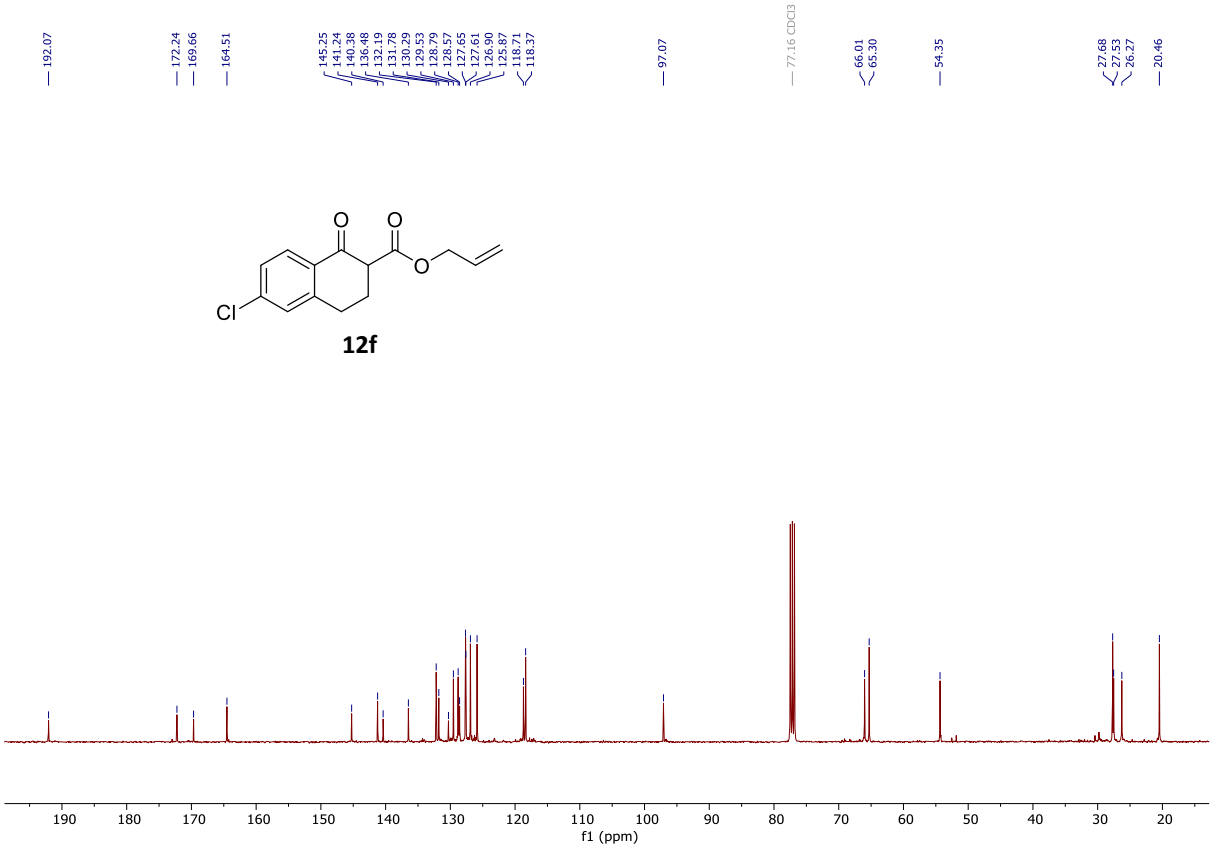
^1H NMR (400 MHz, $CDCl_3$)



$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$)

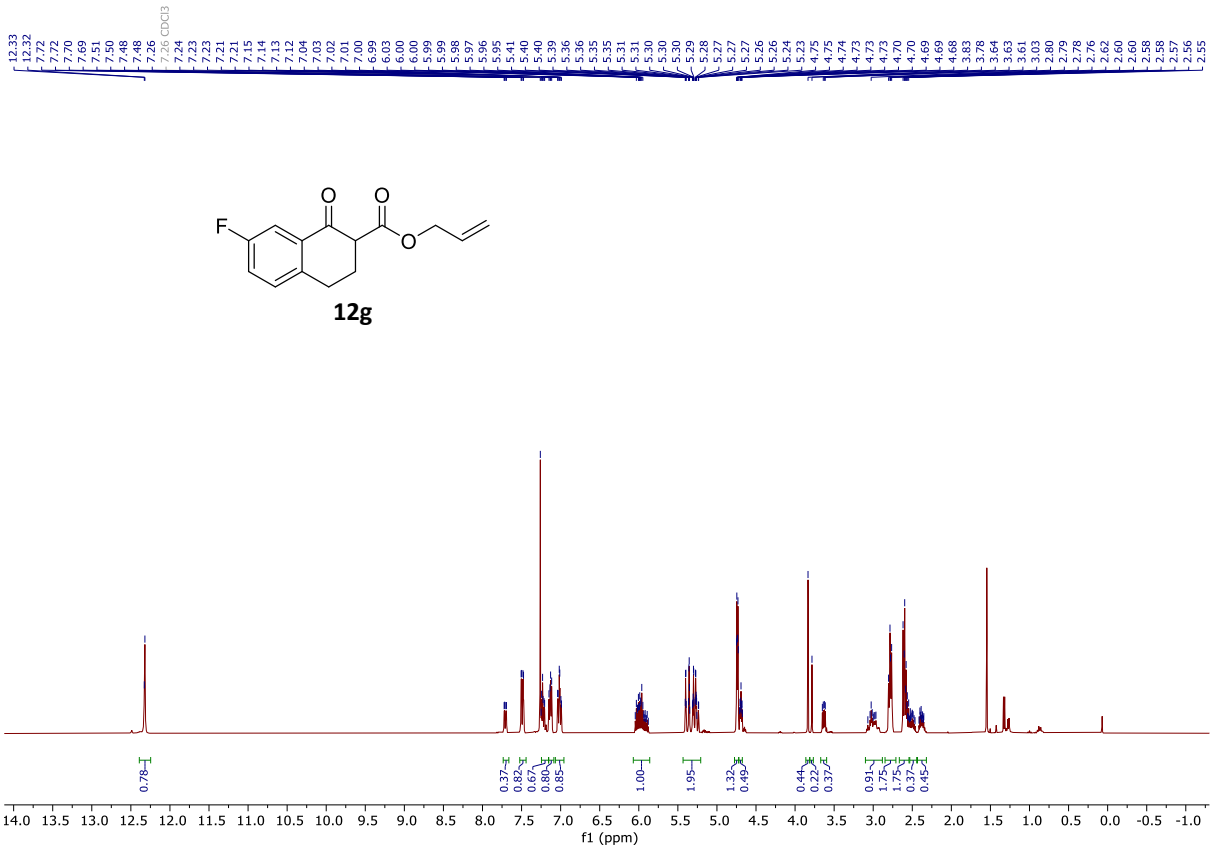


^1H NMR (400 MHz, $CDCl_3$)



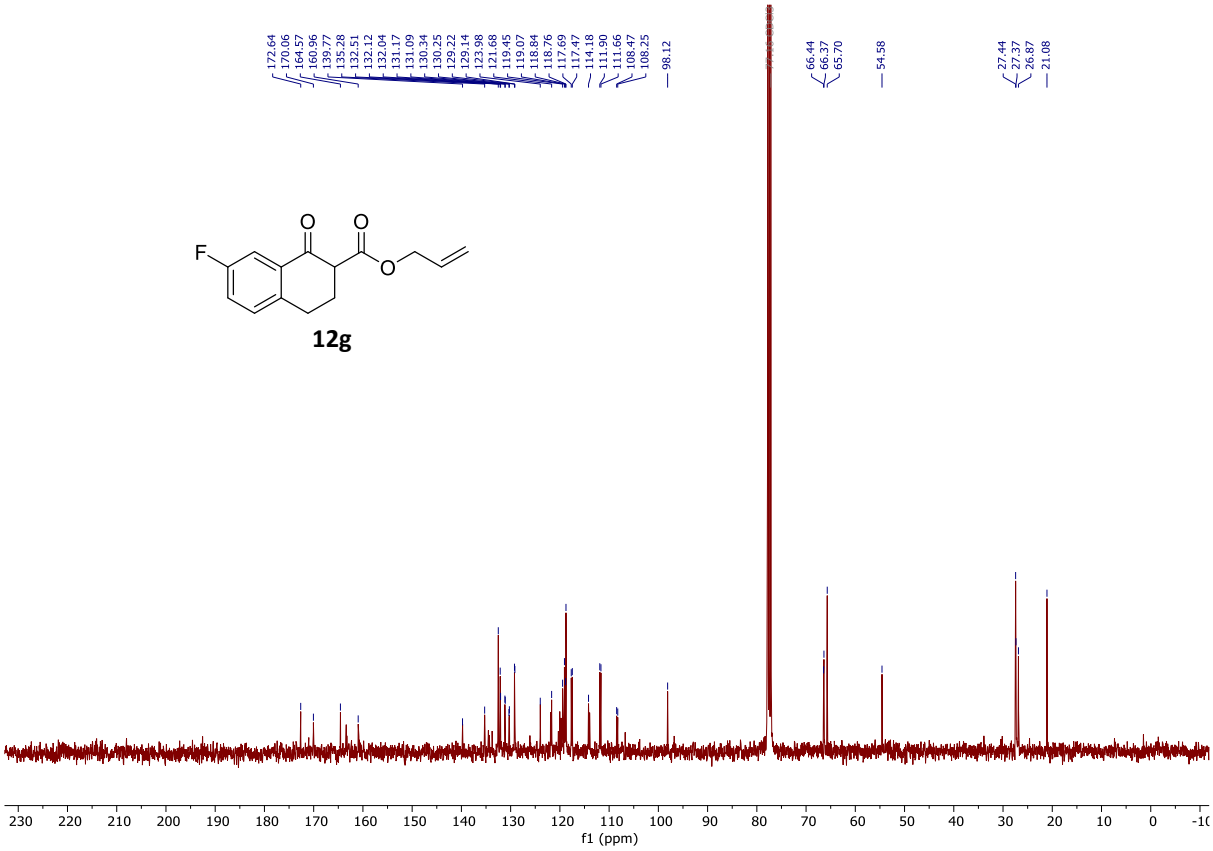
12f

$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)

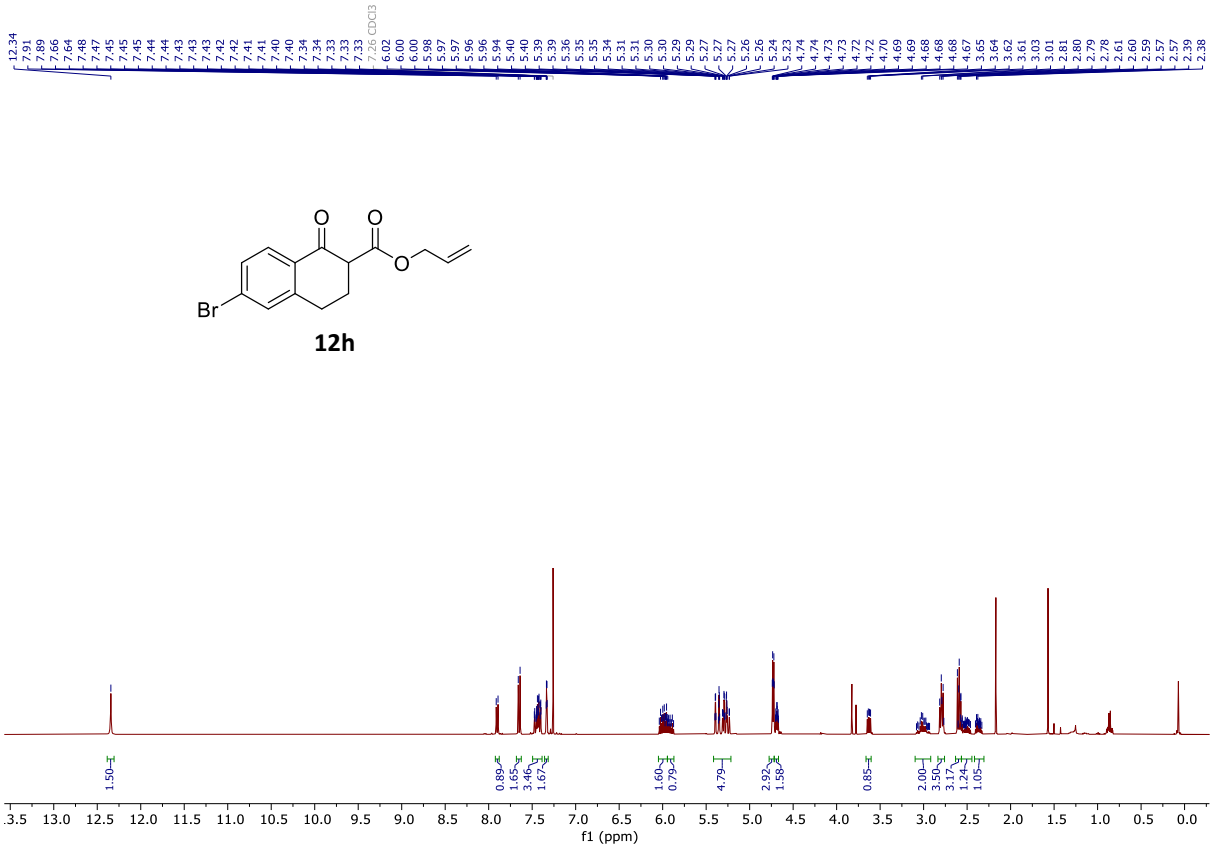


12g

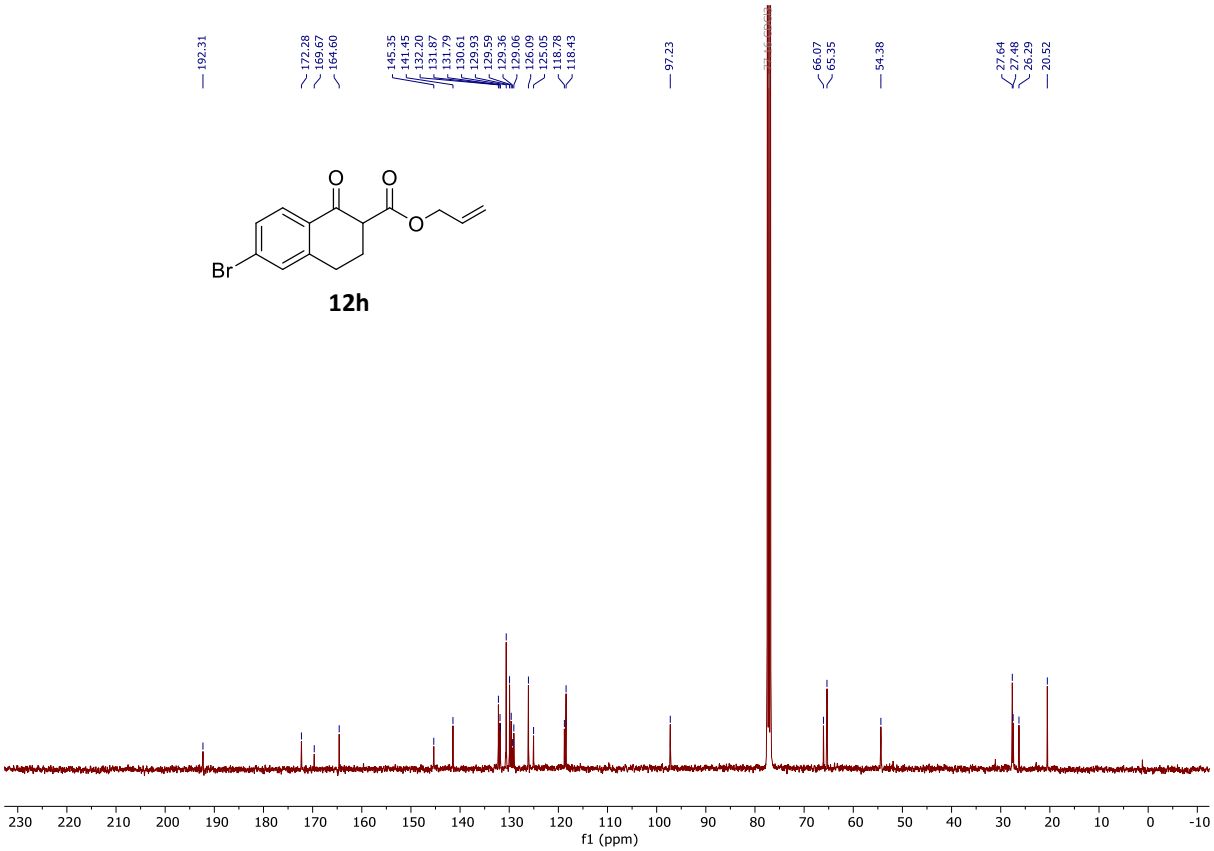
^{1}H NMR (400 MHz, $CDCl_3$)



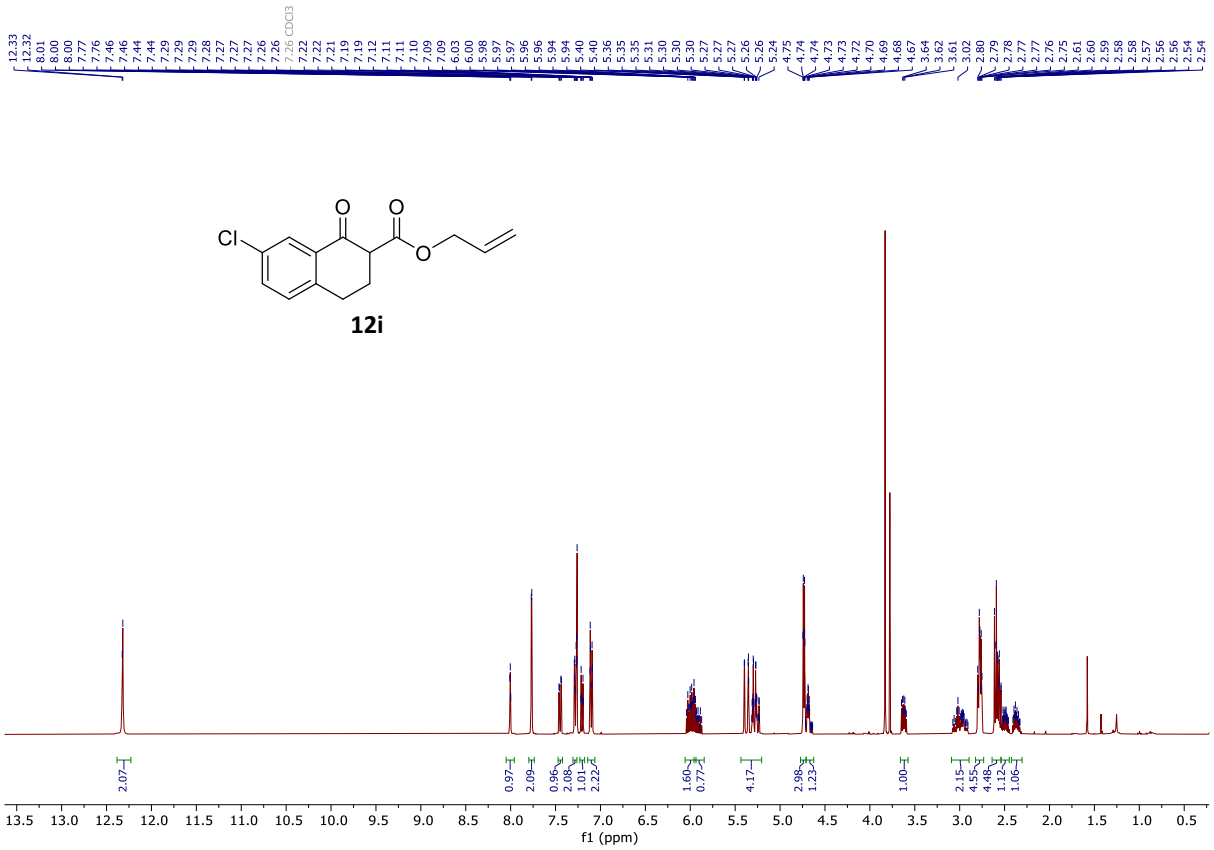
$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$)



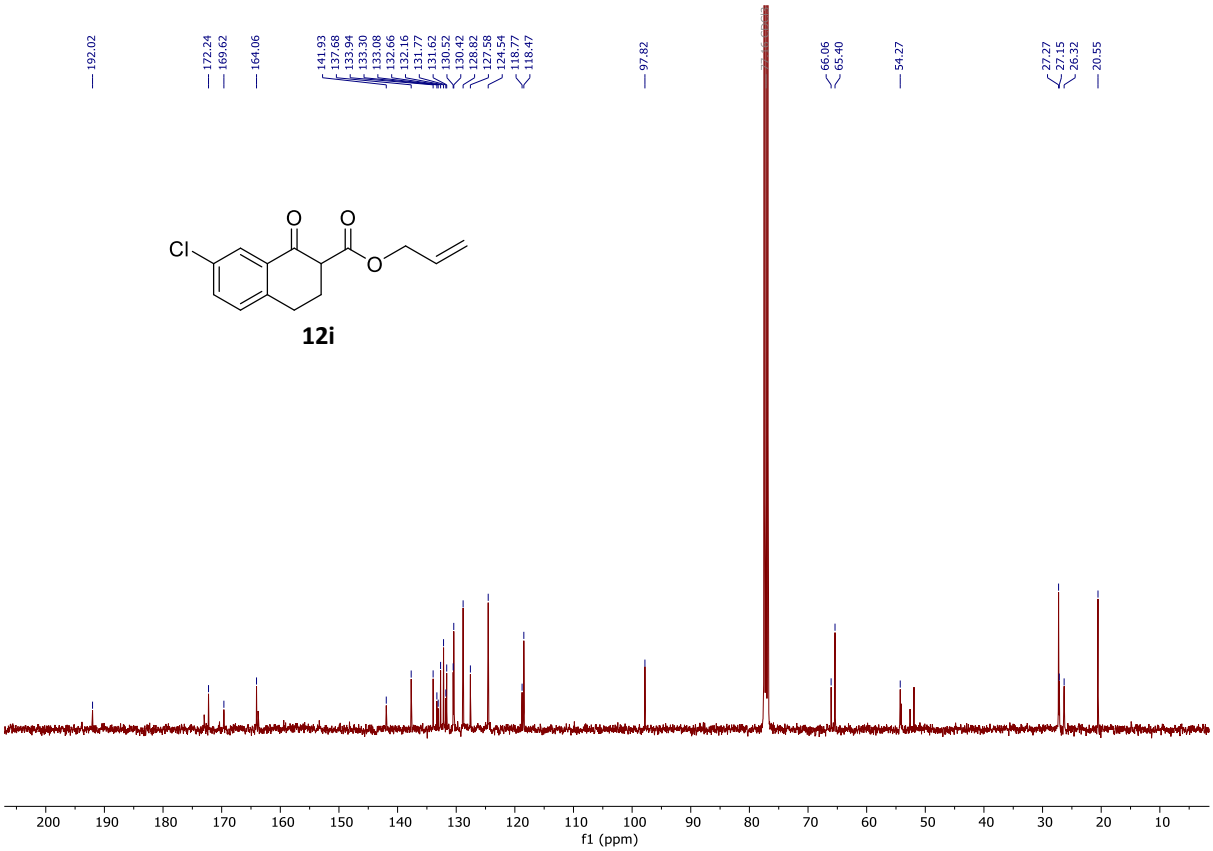
^1H NMR (400 MHz, $CDCl_3$)



$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$)

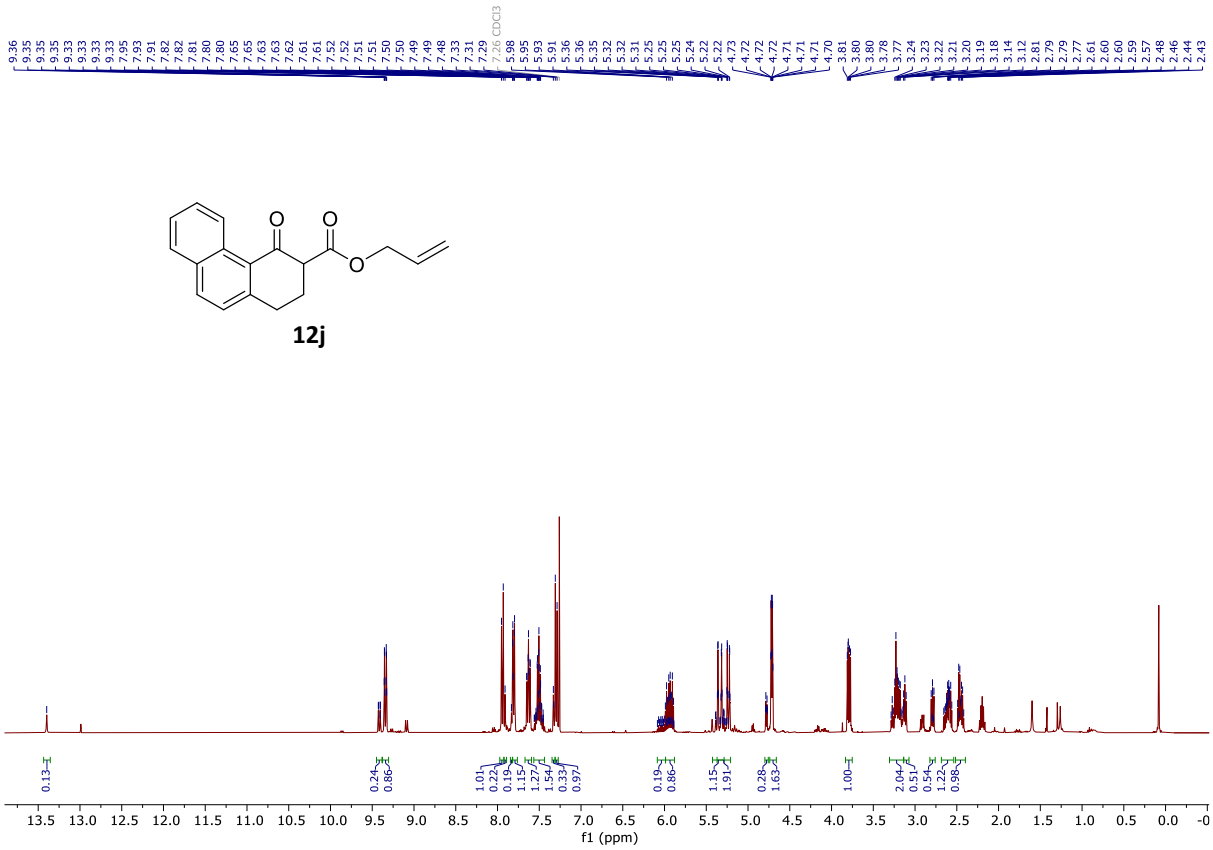


^1H NMR (400 MHz, $CDCl_3$)



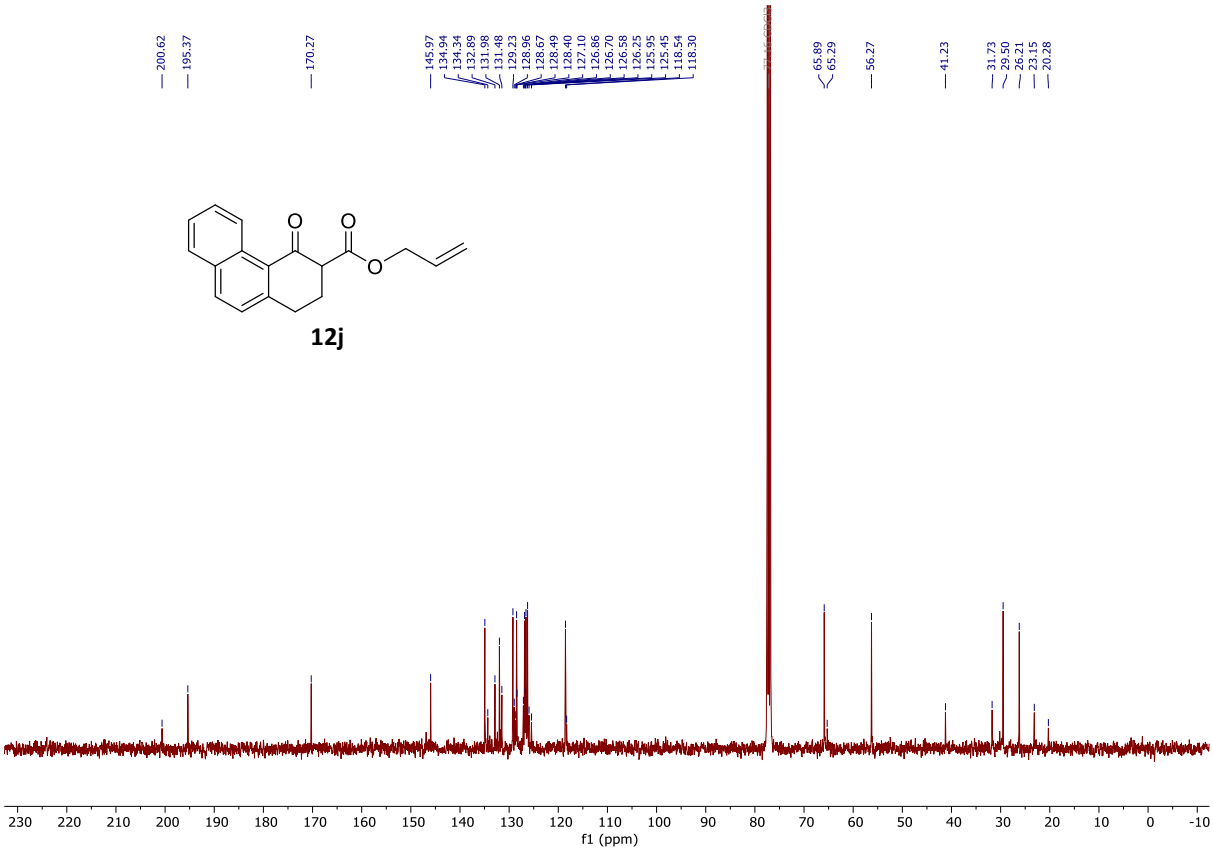
12i

$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)

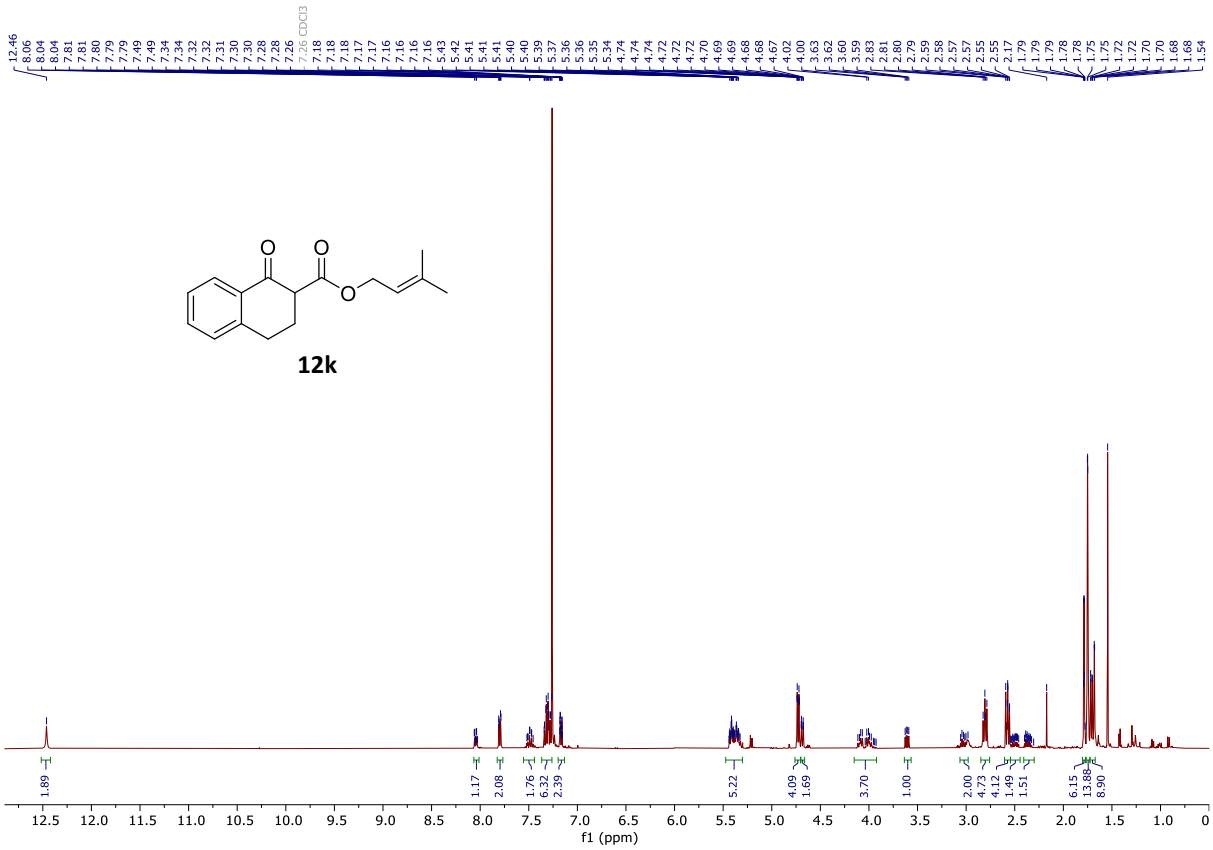


12j

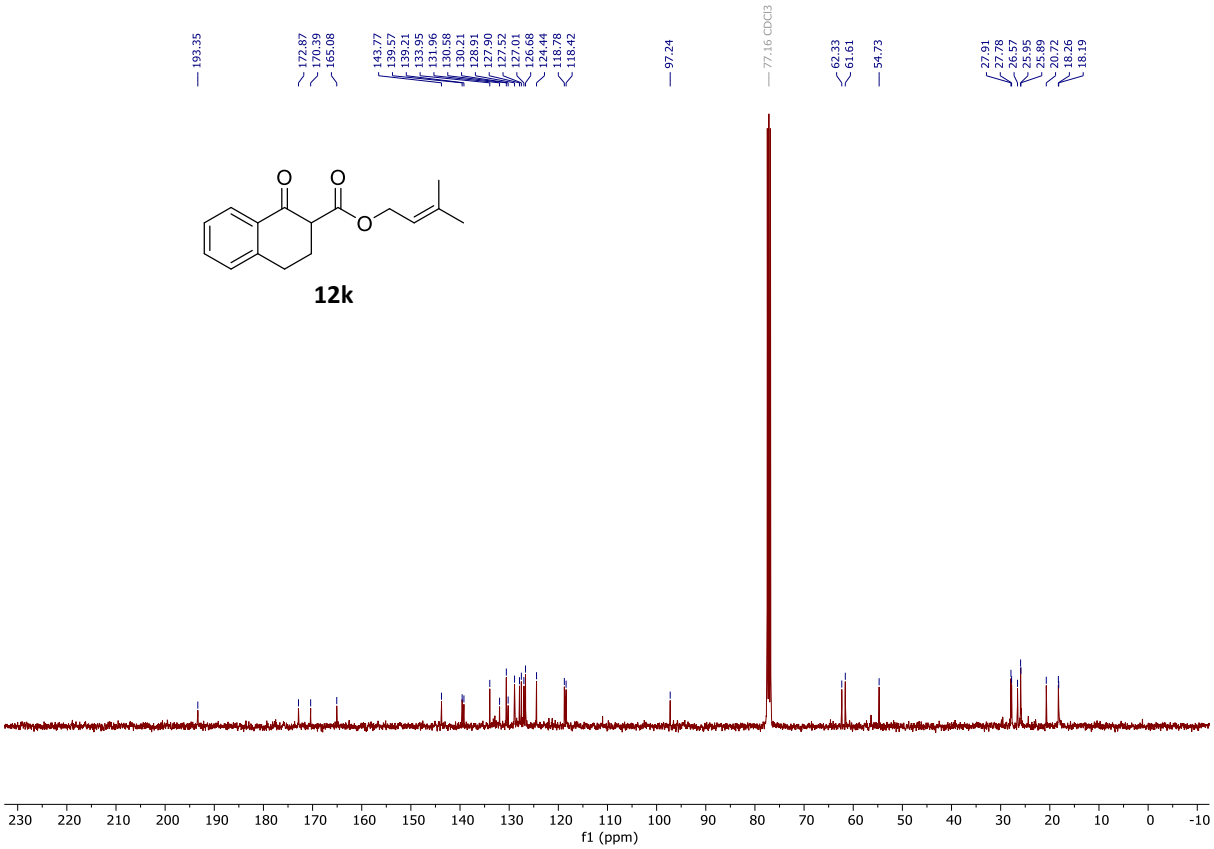
^{1}H NMR (400 MHz, $CDCl_3$)



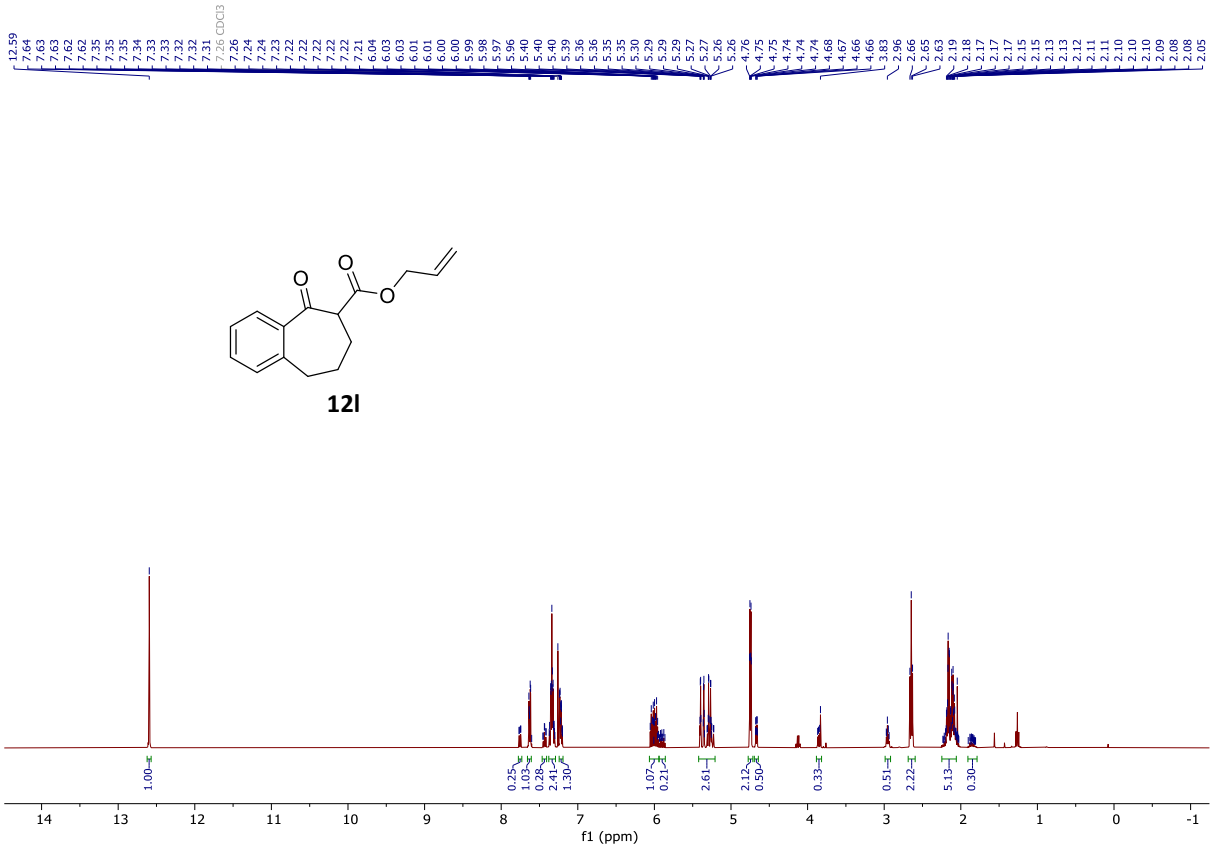
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



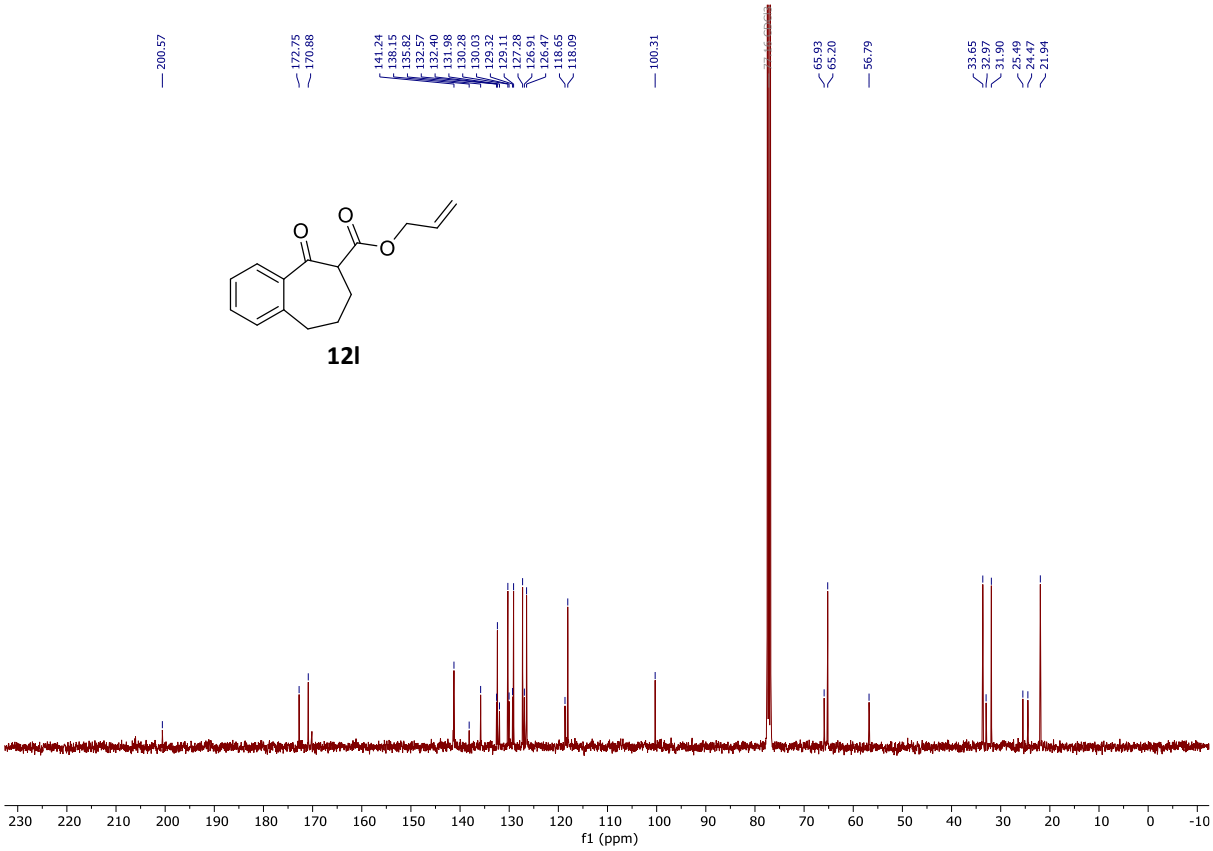
^{1}H NMR (400 MHz, $CDCl_3$)



$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$)

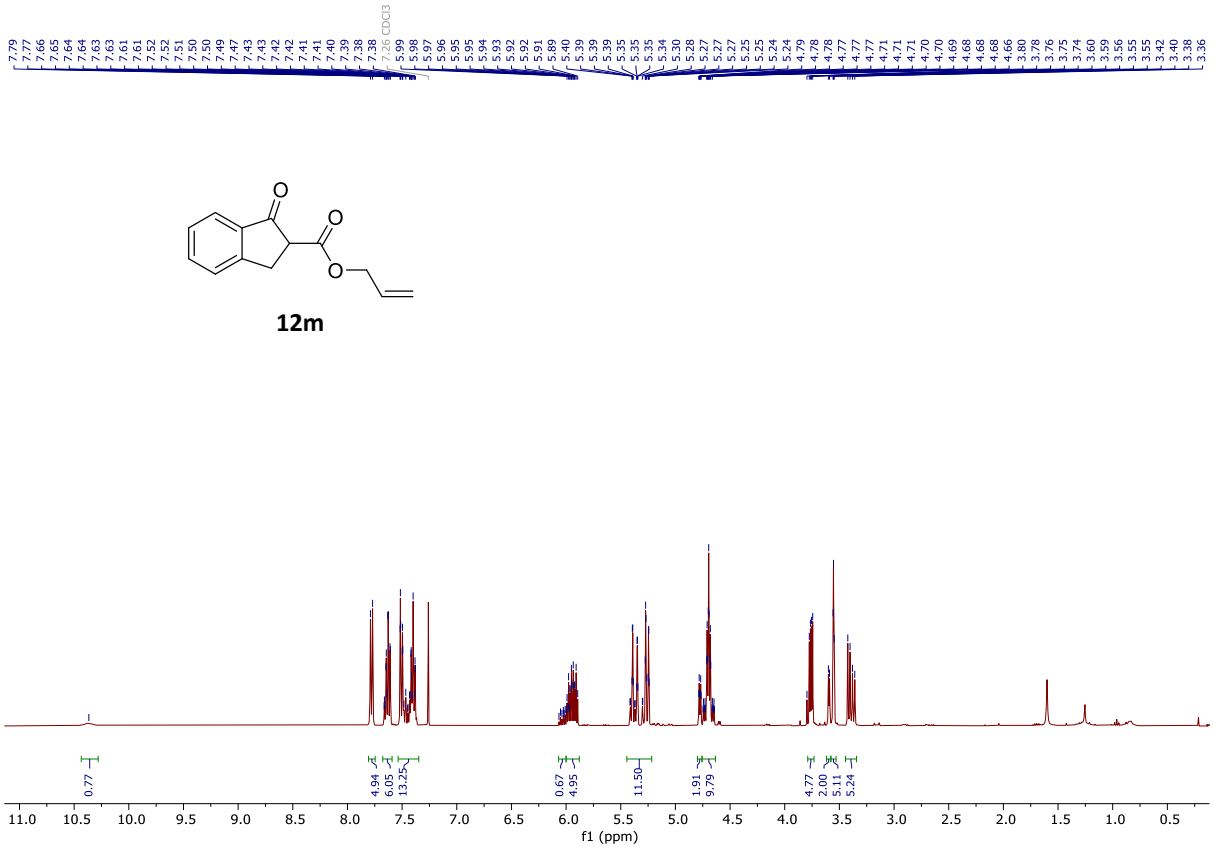


^1H NMR (400 MHz, $CDCl_3$)



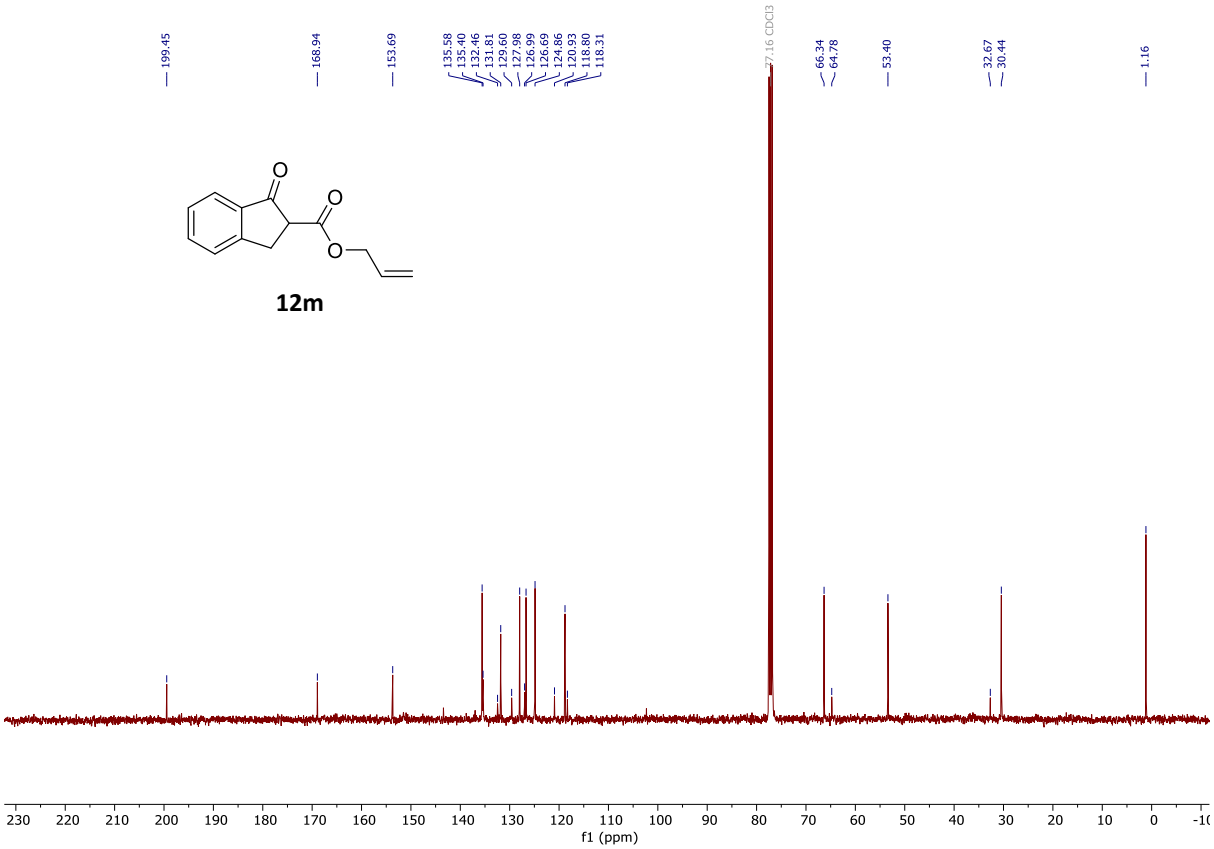
12l

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$)



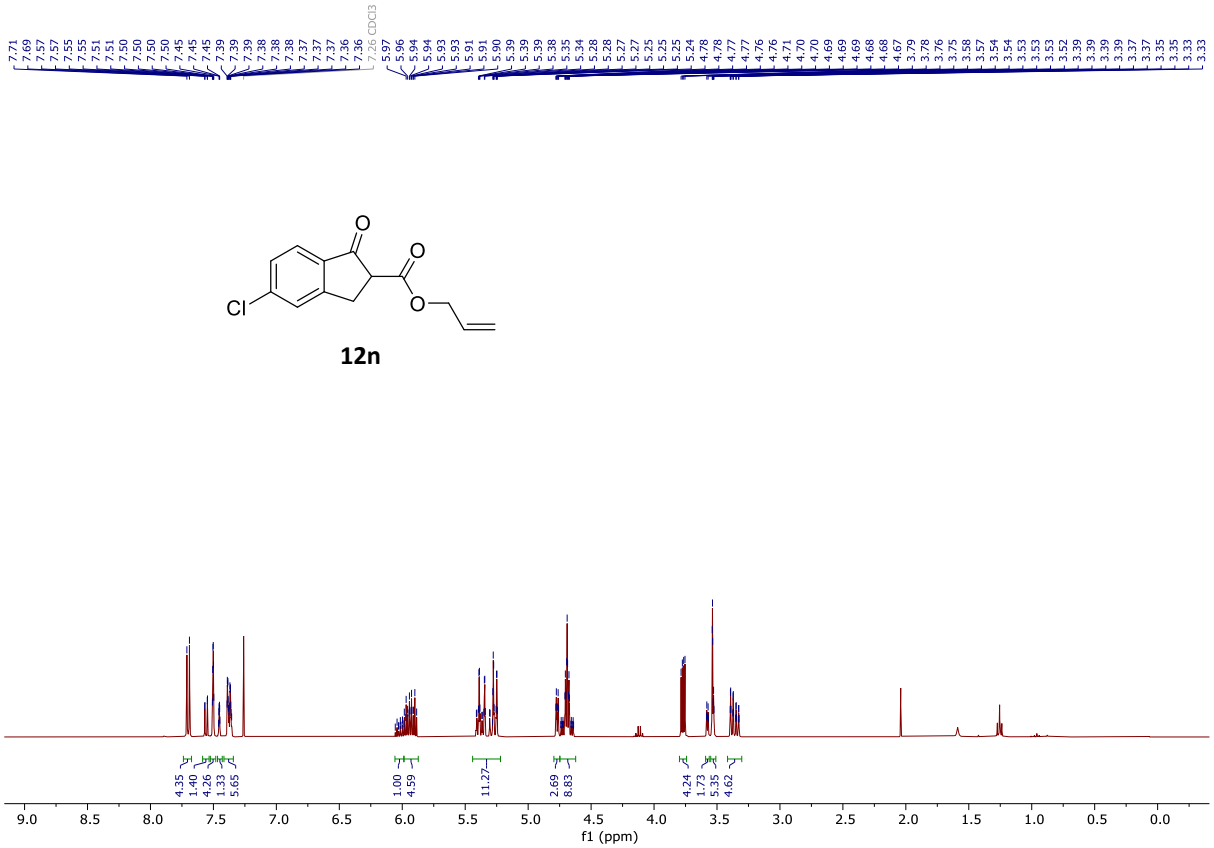
12m

^1H NMR (400 MHz, $CDCl_3$)



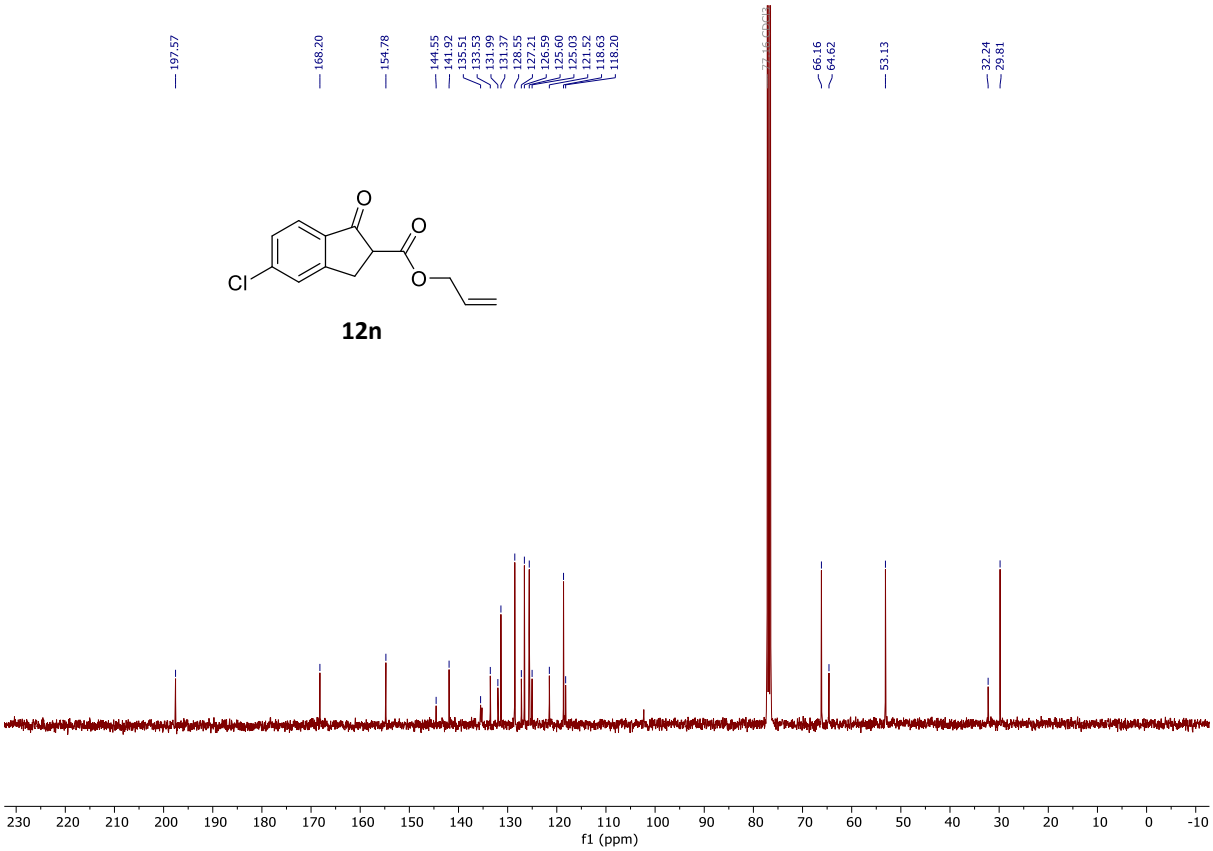
12m

$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



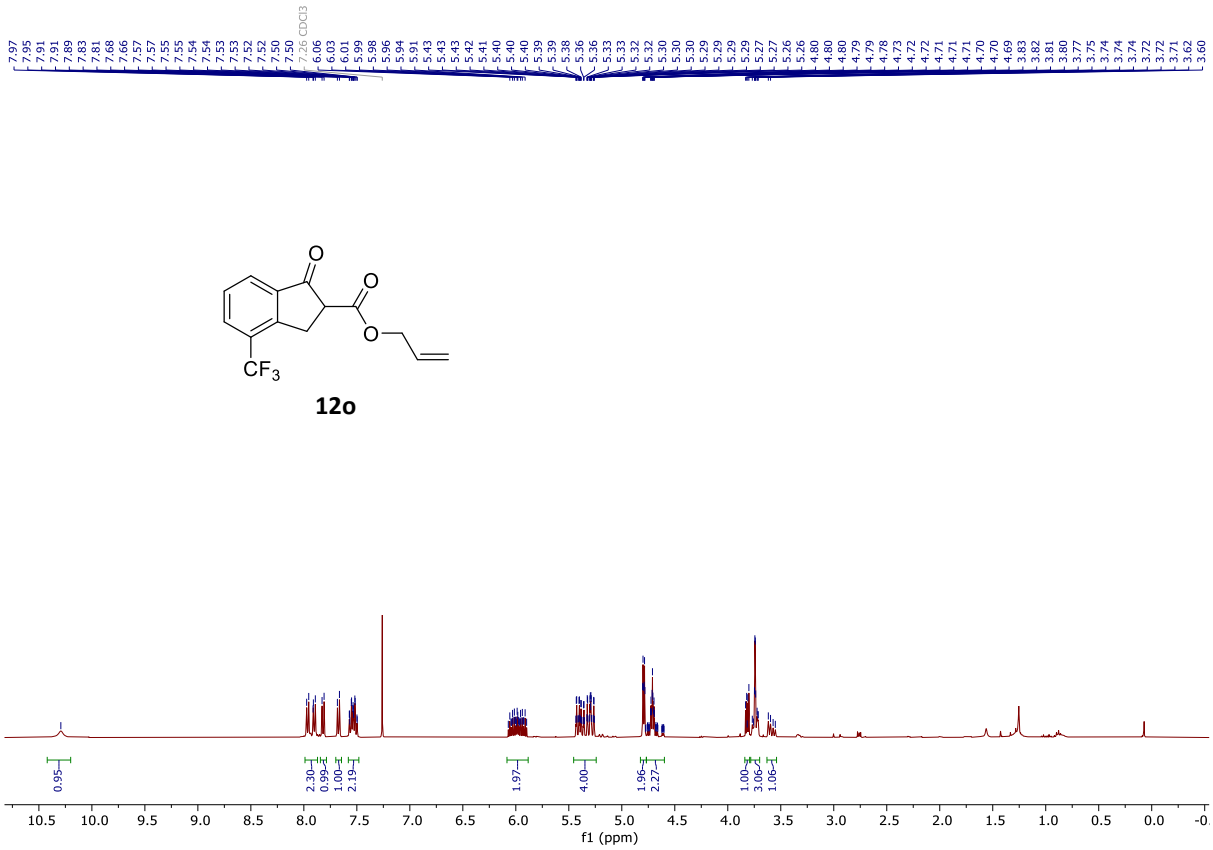
12n

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



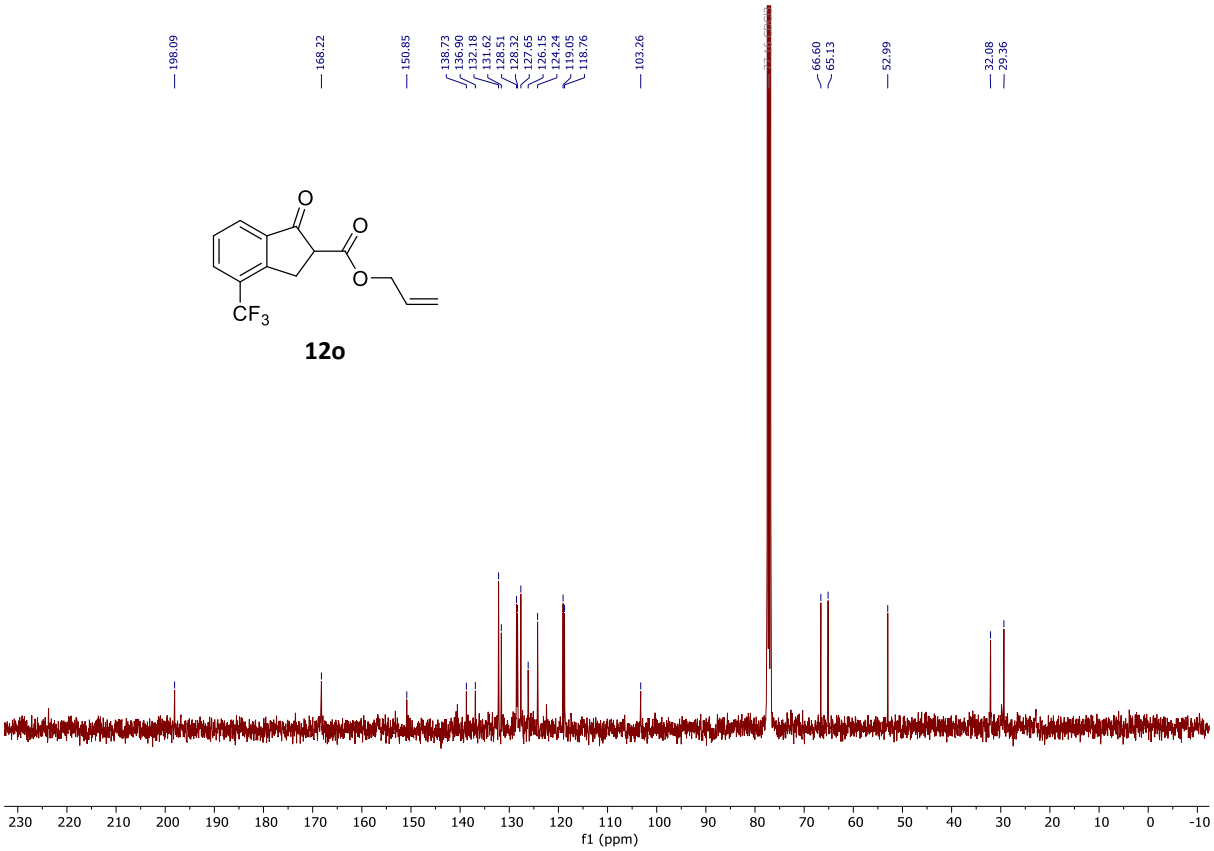
12n

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$)

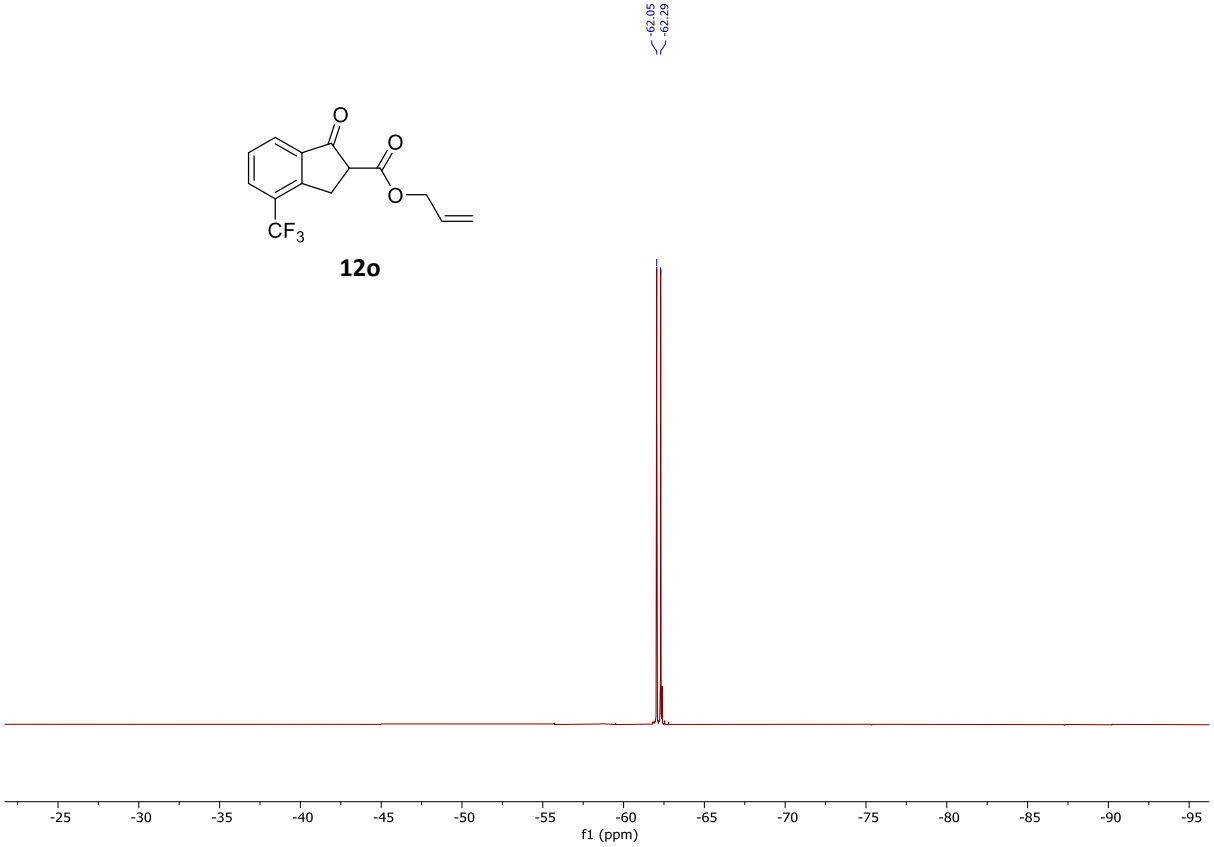


12o

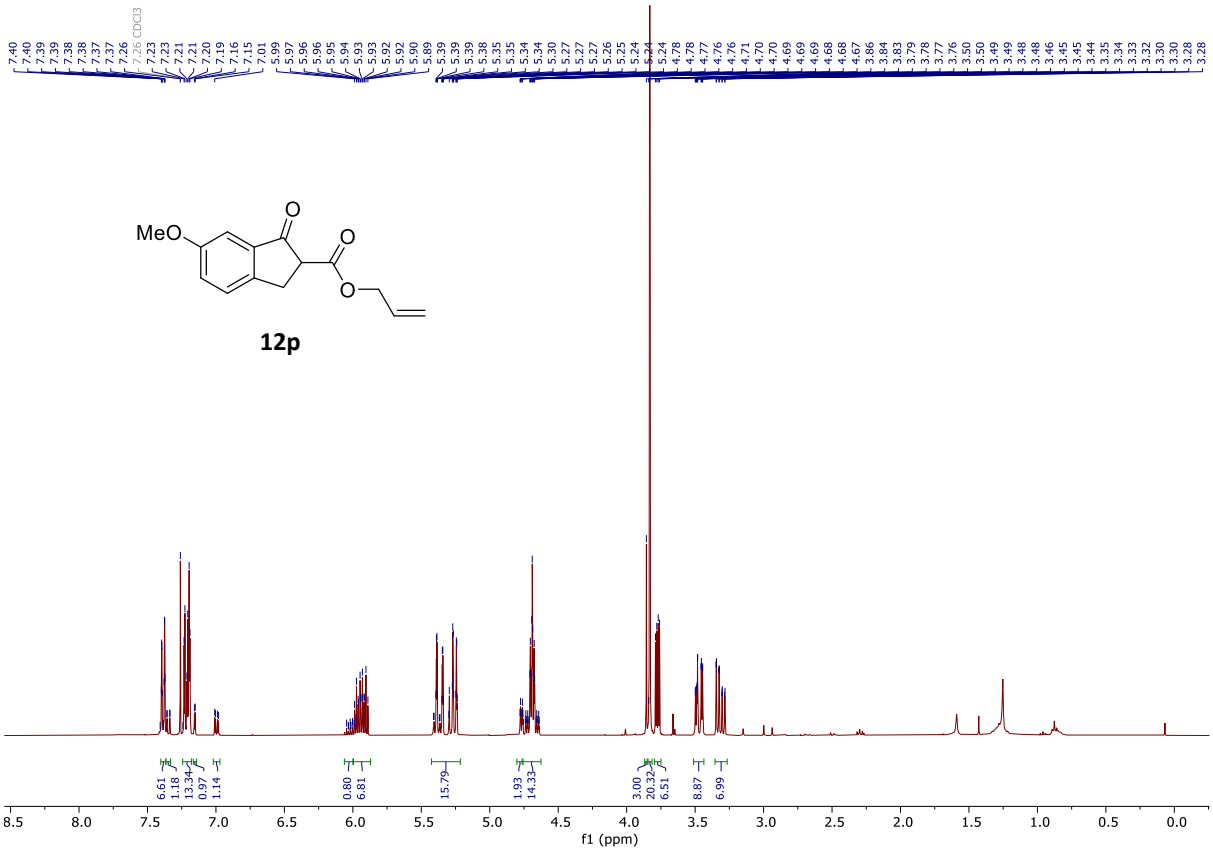
^1H NMR (400 MHz, $CDCl_3$)



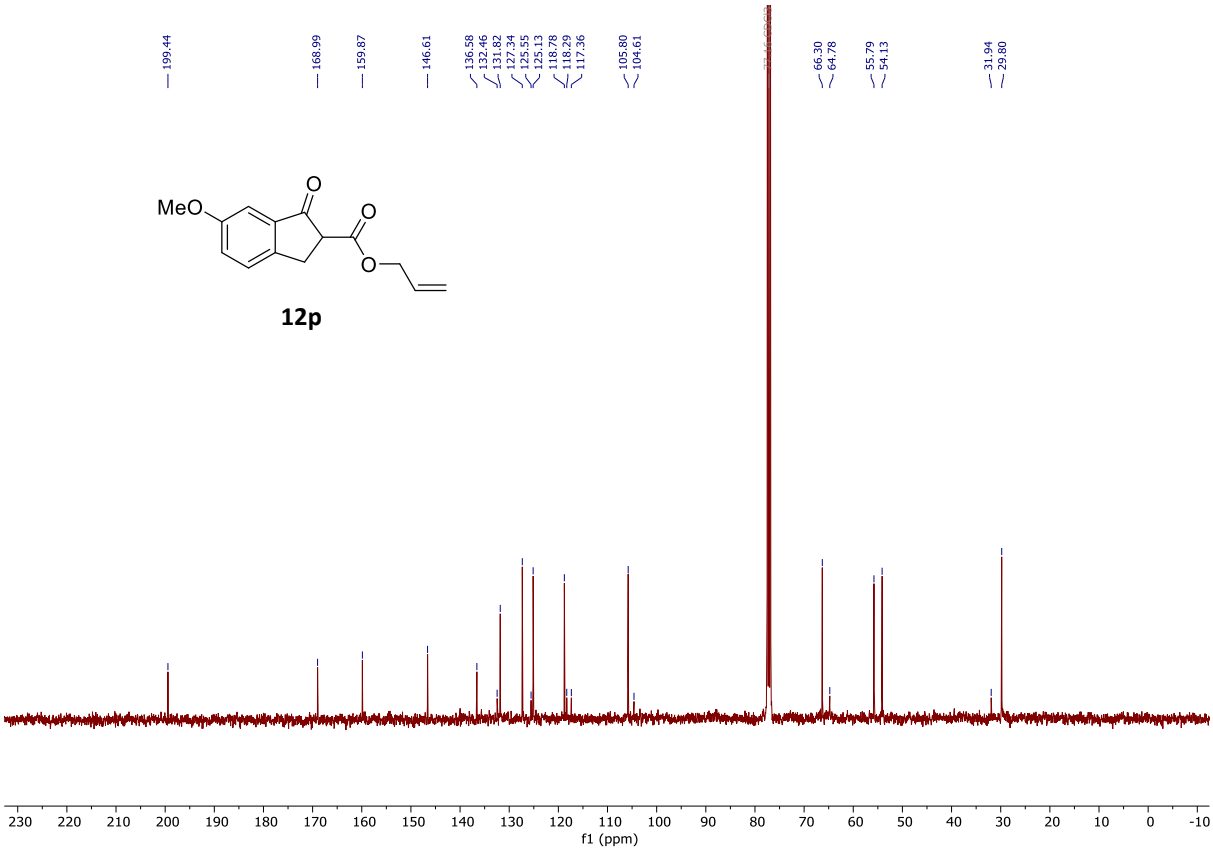
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



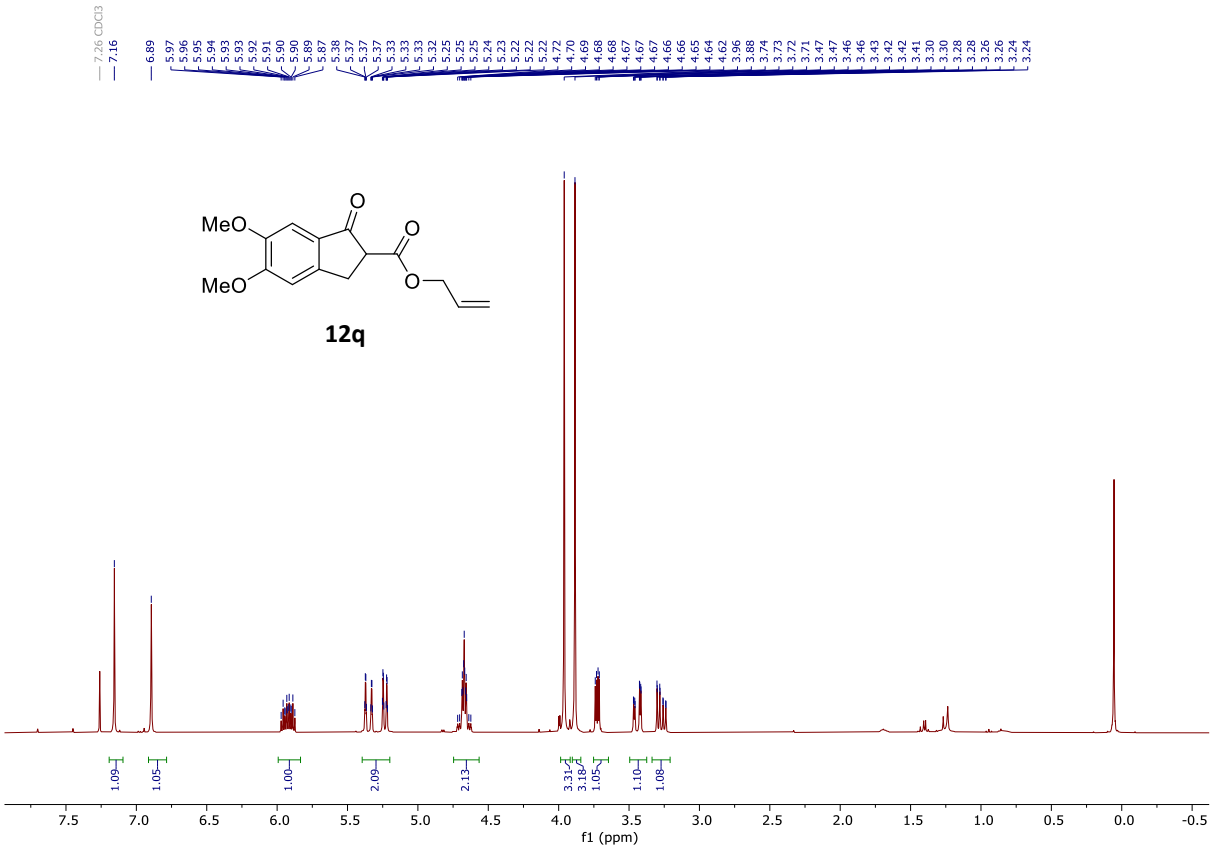
$^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$)



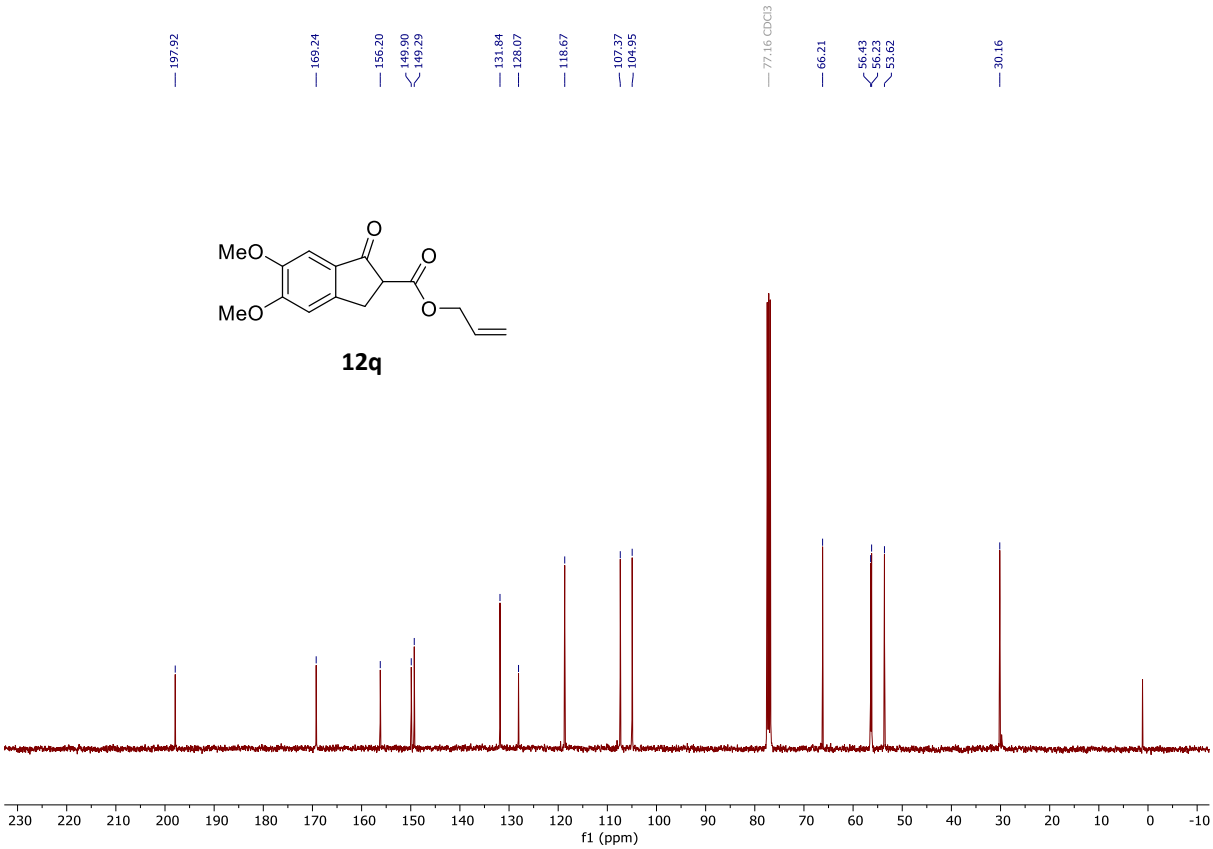
^{1}H NMR (400 MHz, $CDCl_3$)



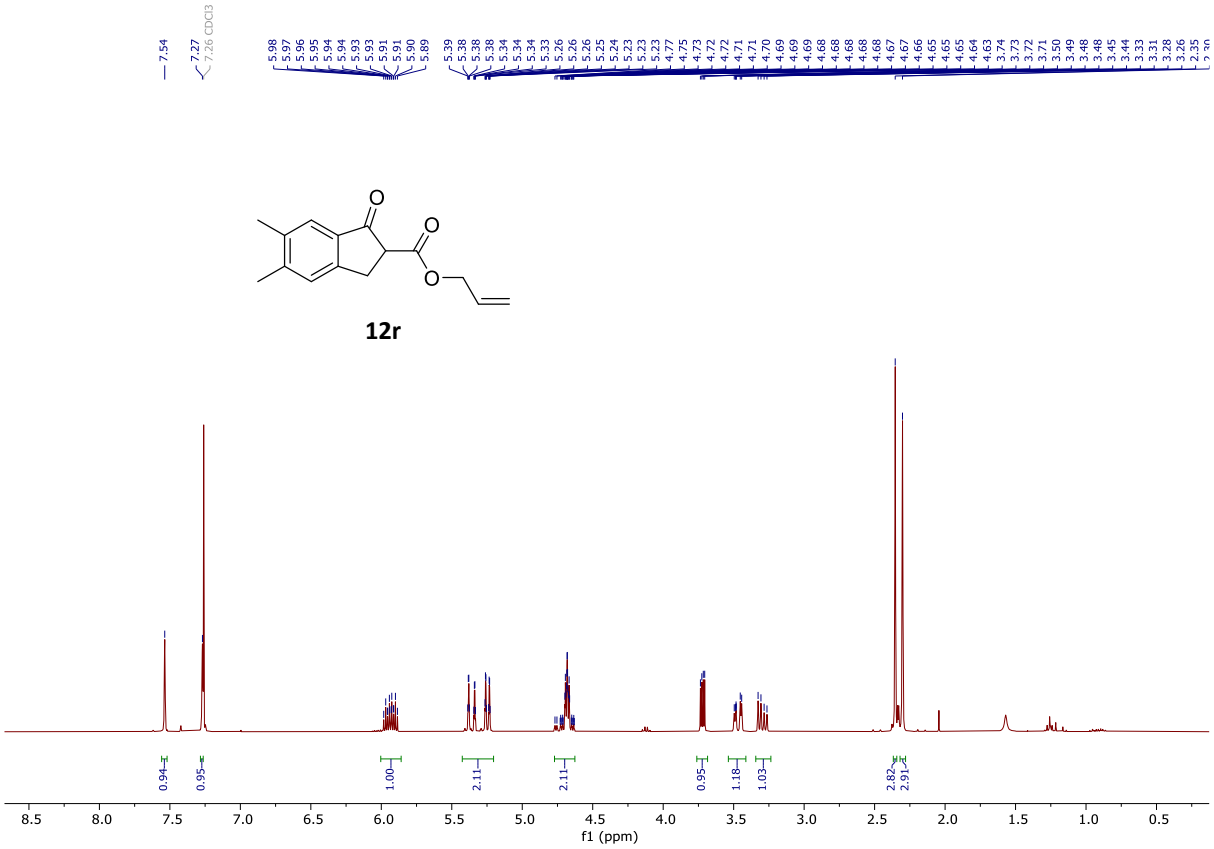
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)



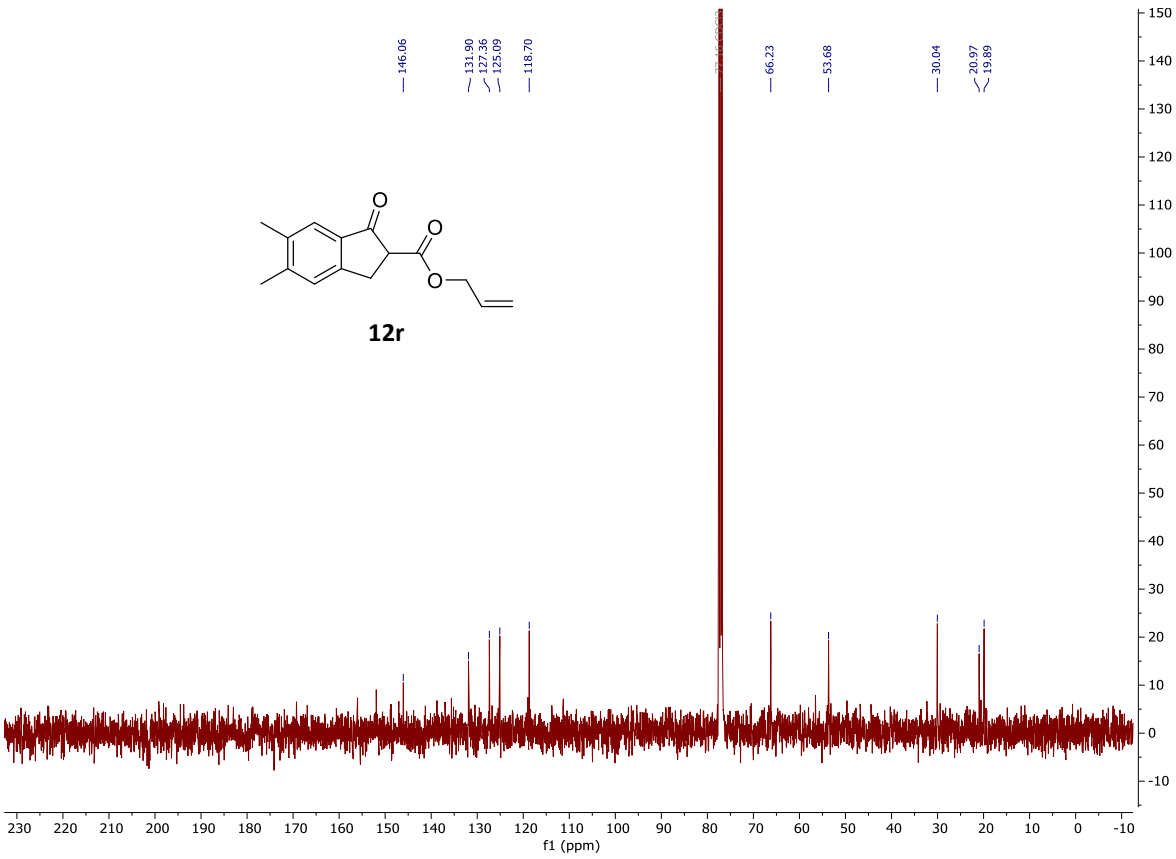
^{1}H NMR (400 MHz, $CDCl_3$)



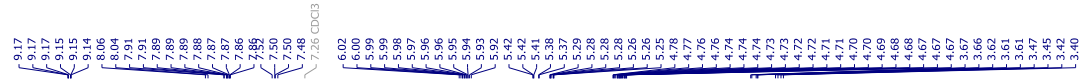
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)

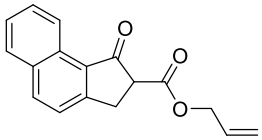


^{1}H NMR (400 MHz, $CDCl_3$)

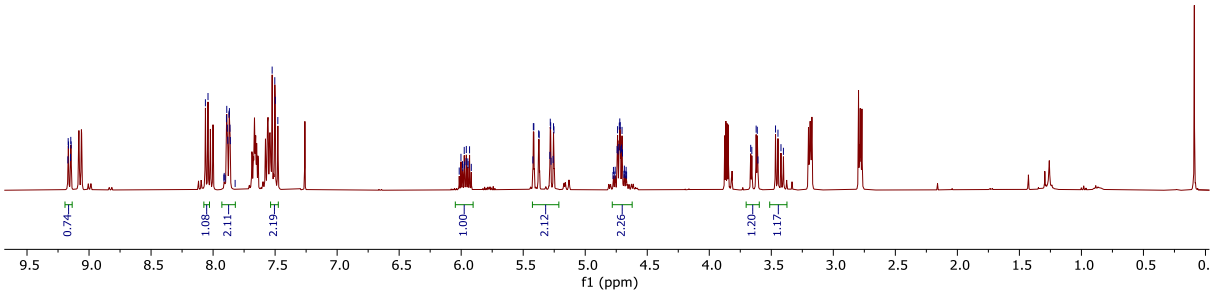


^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)

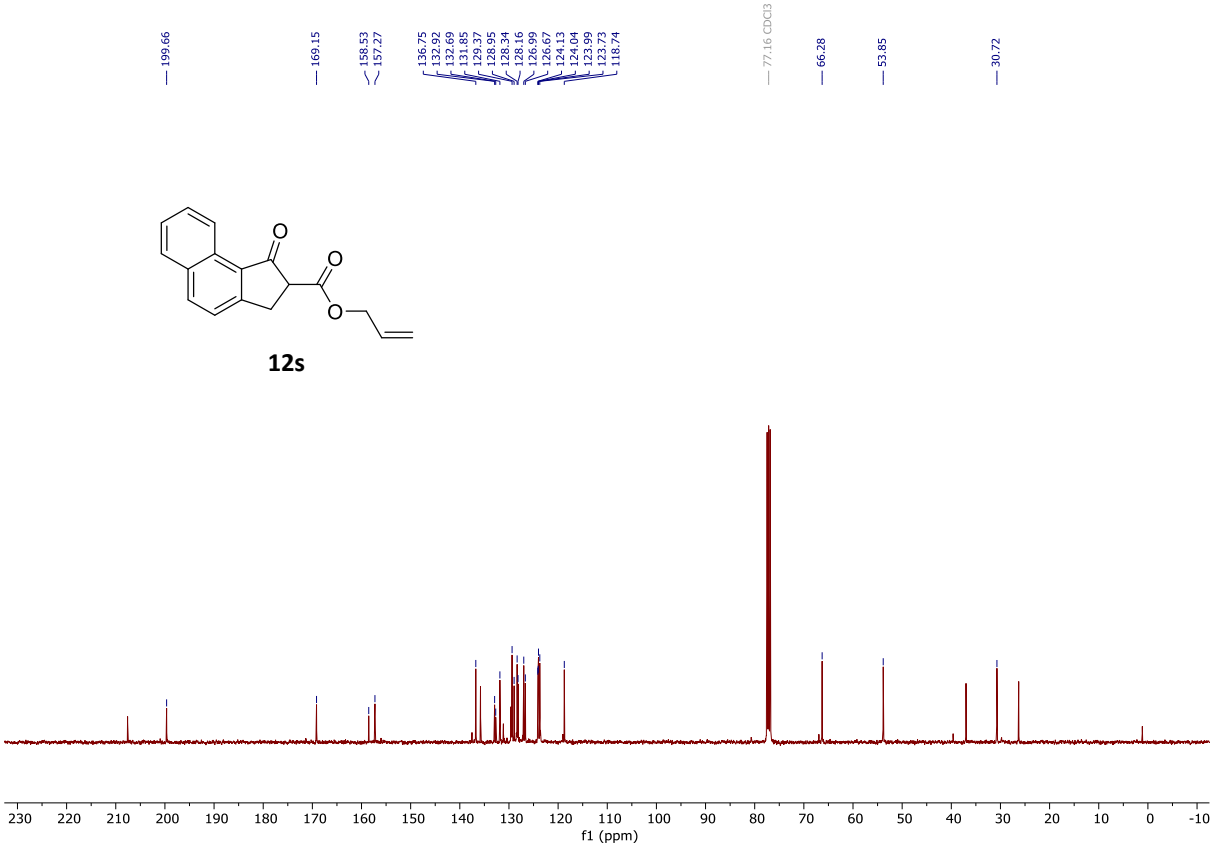




12s

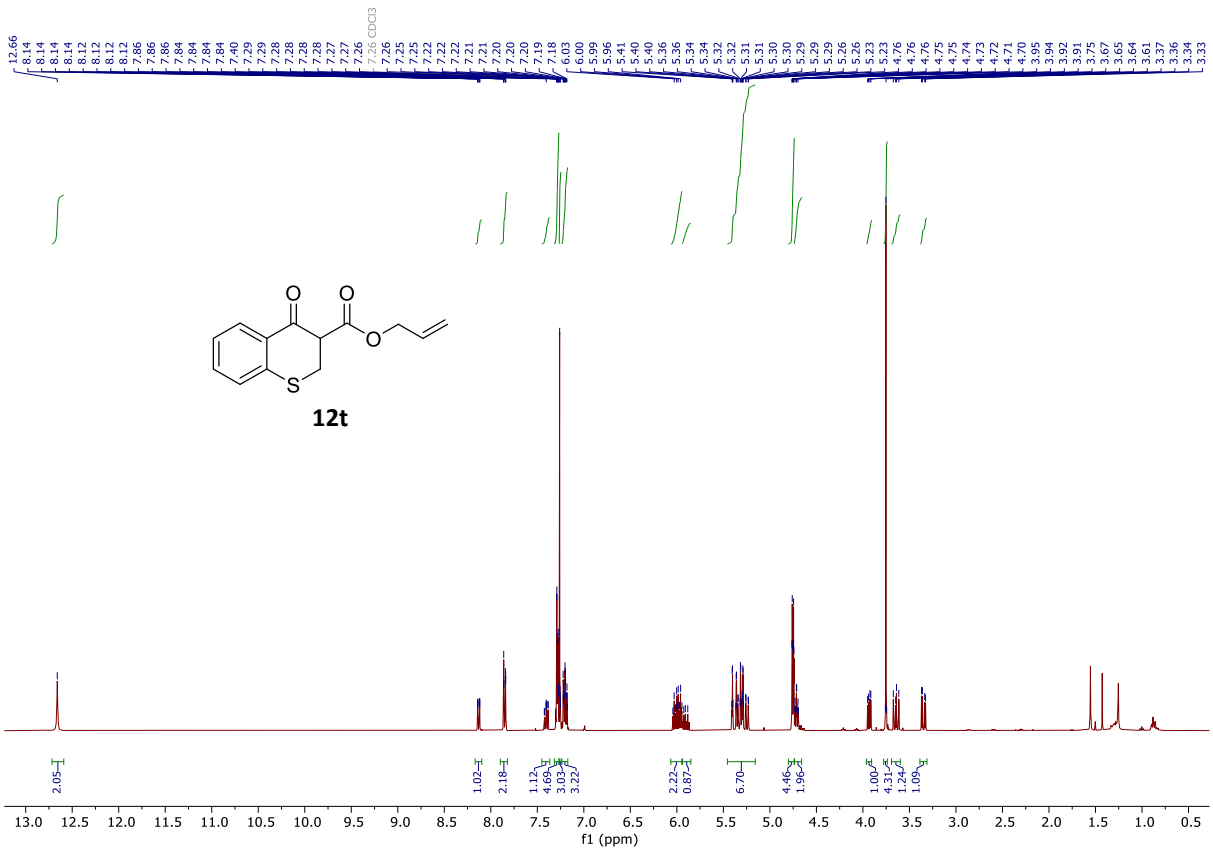


^{1}H NMR (400 MHz, $CDCl_3$)

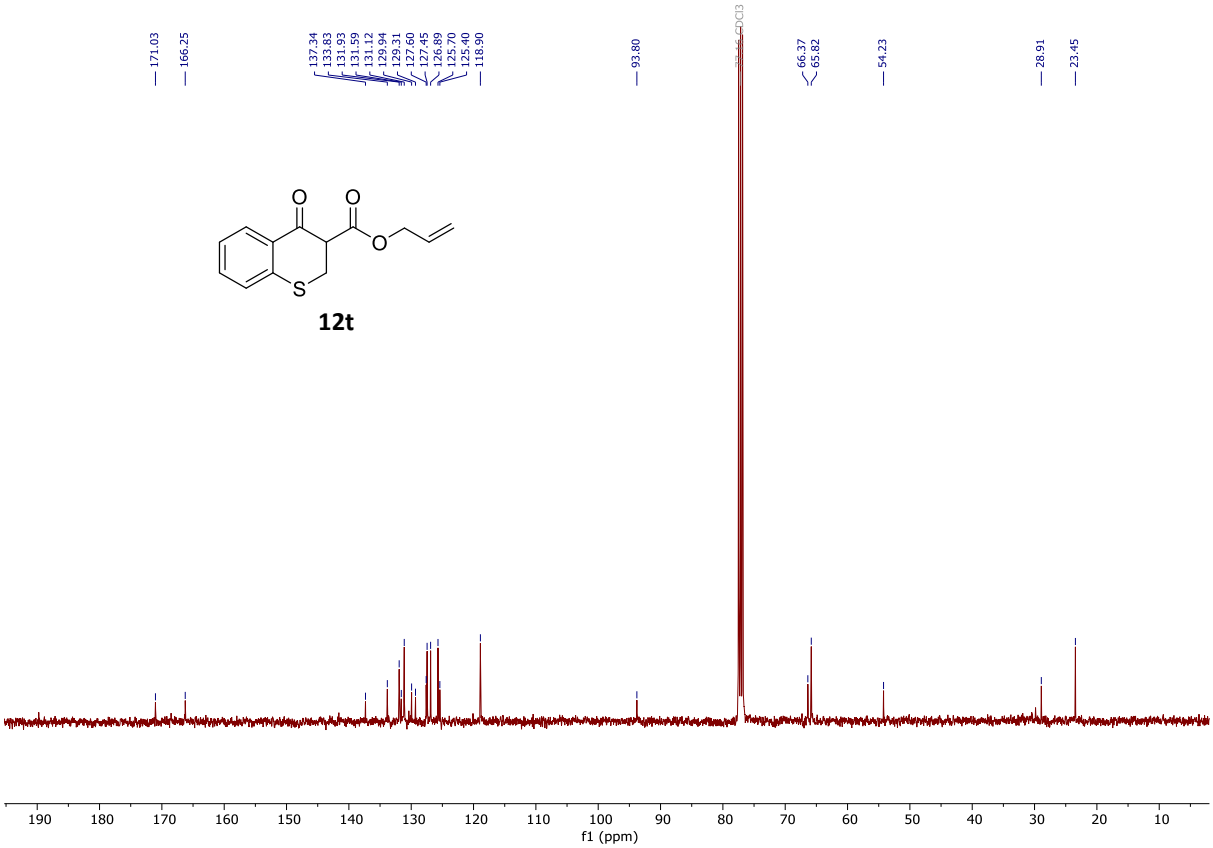


12s

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)

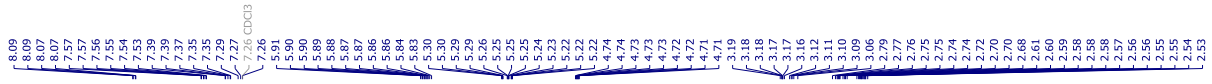


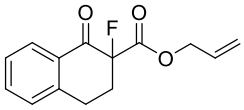
^{1}H NMR (400 MHz, $CDCl_3$)



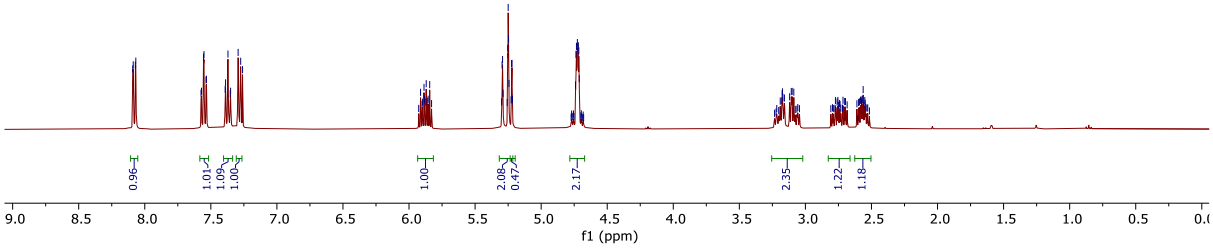
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)

11. NMR spectra for compounds **6a – 6t**

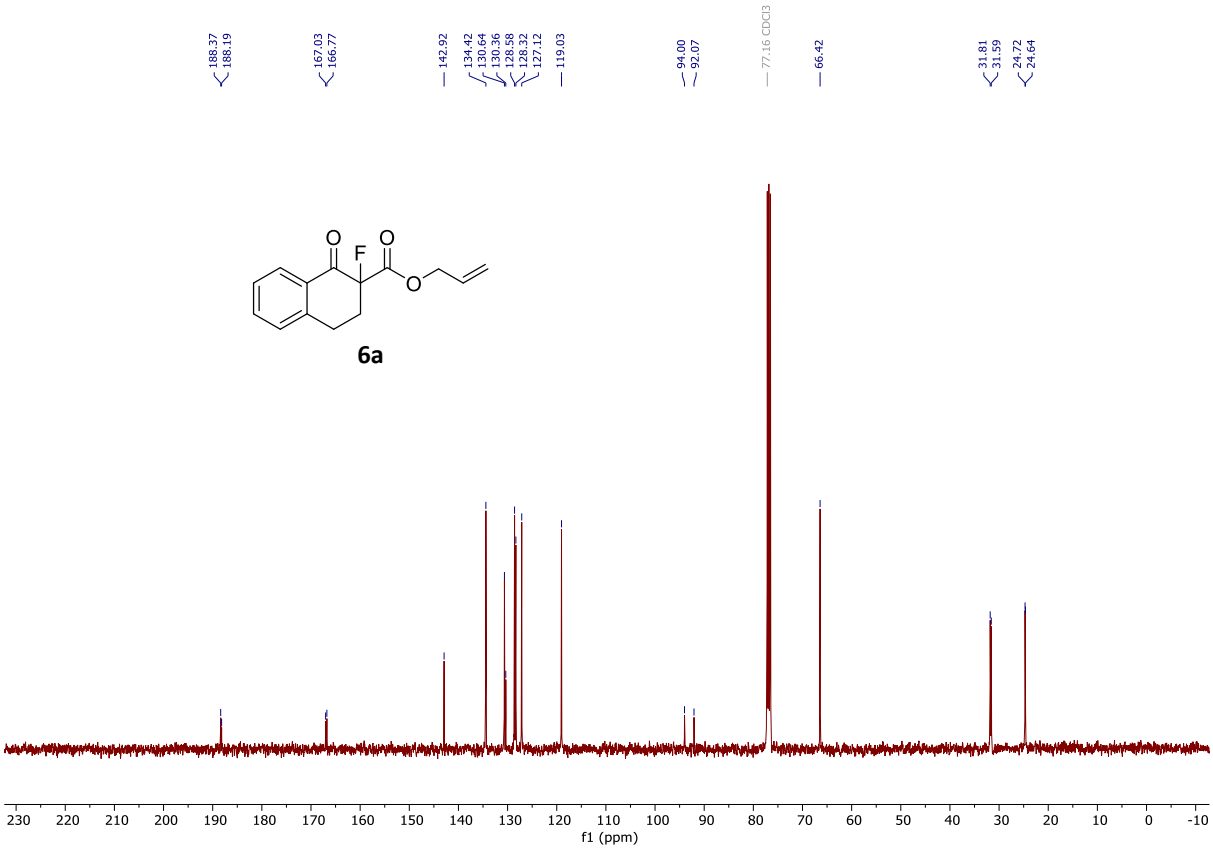




6a

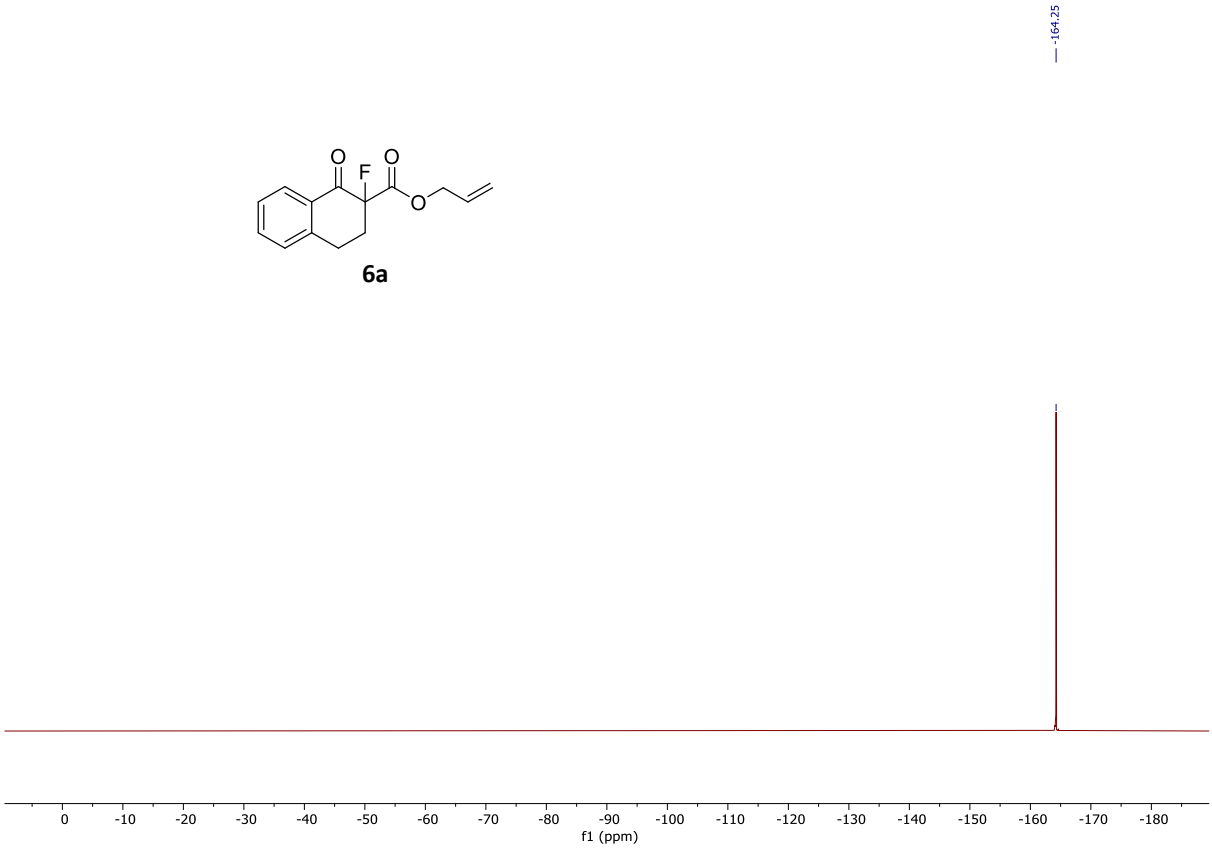


^{1}H NMR (400 MHz, $CDCl_3$)

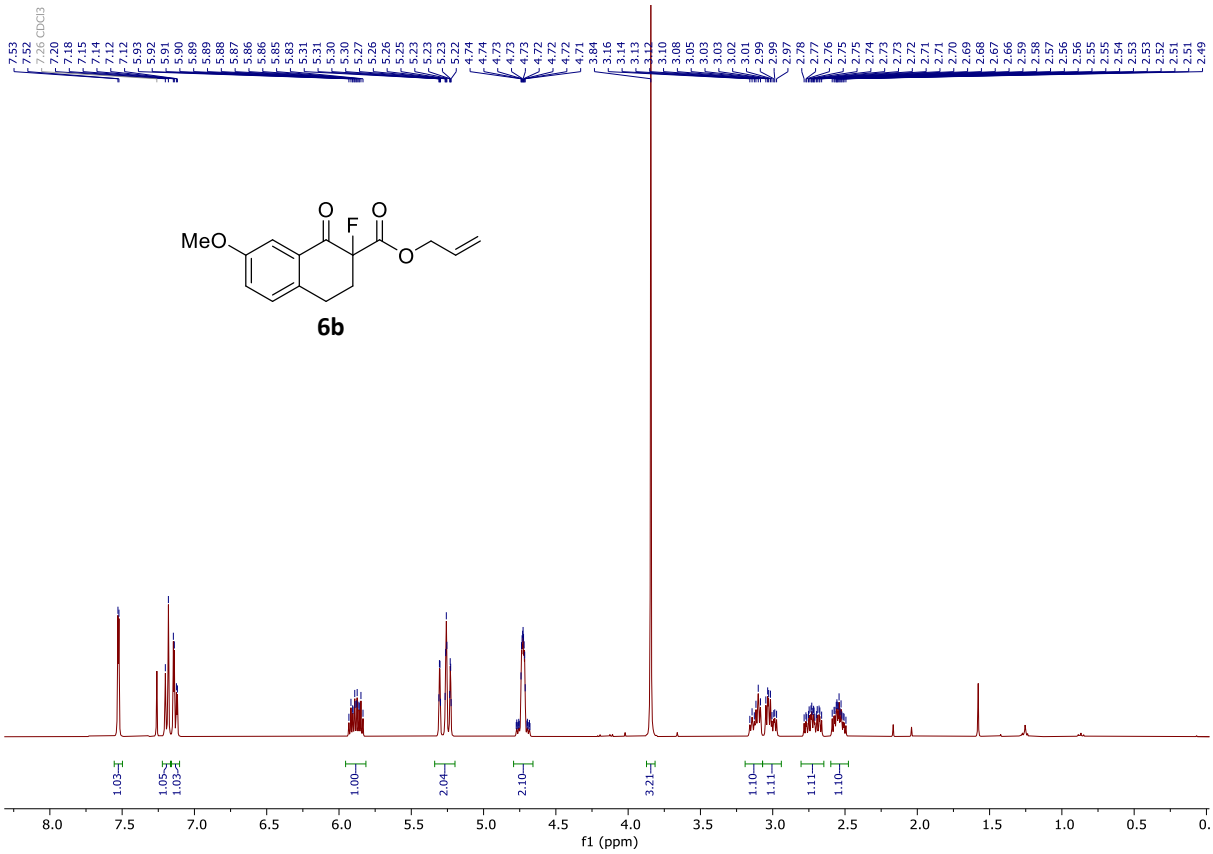


^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)

6a

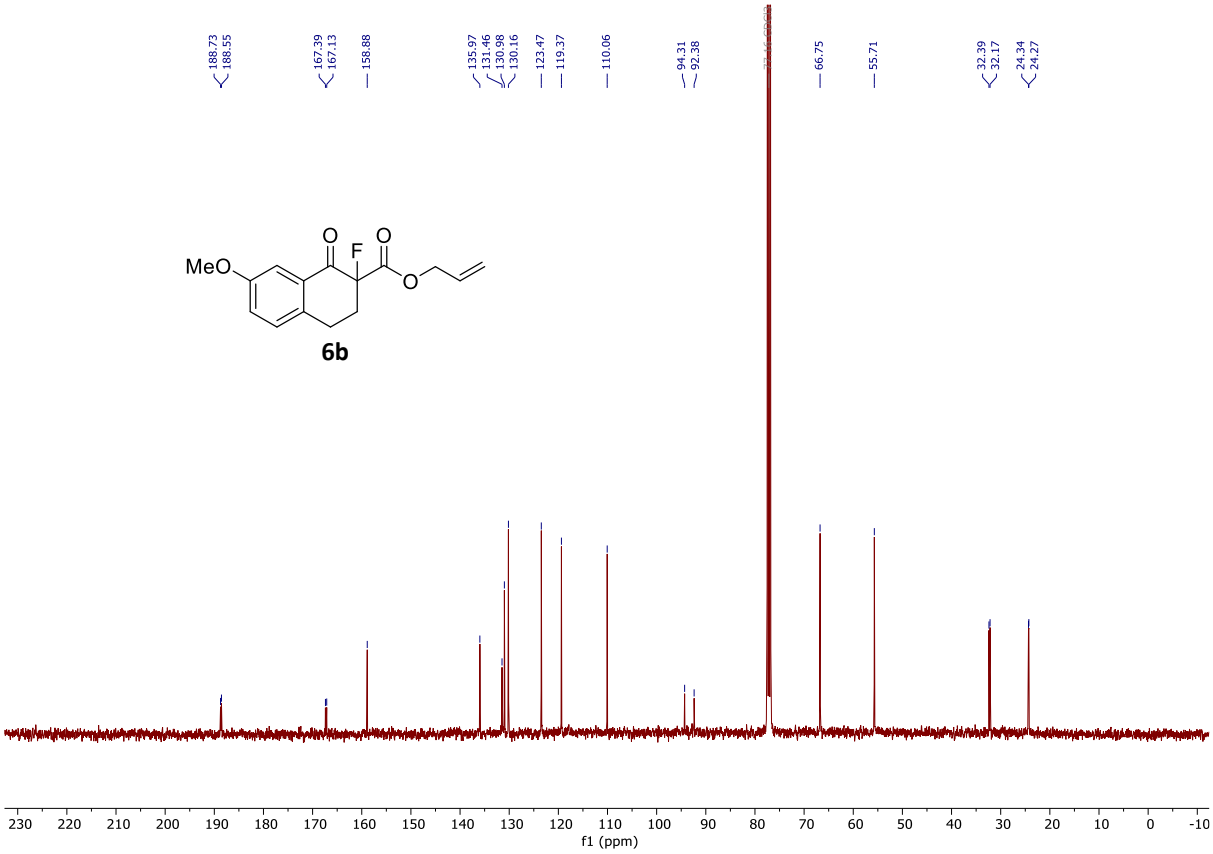


$^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$)

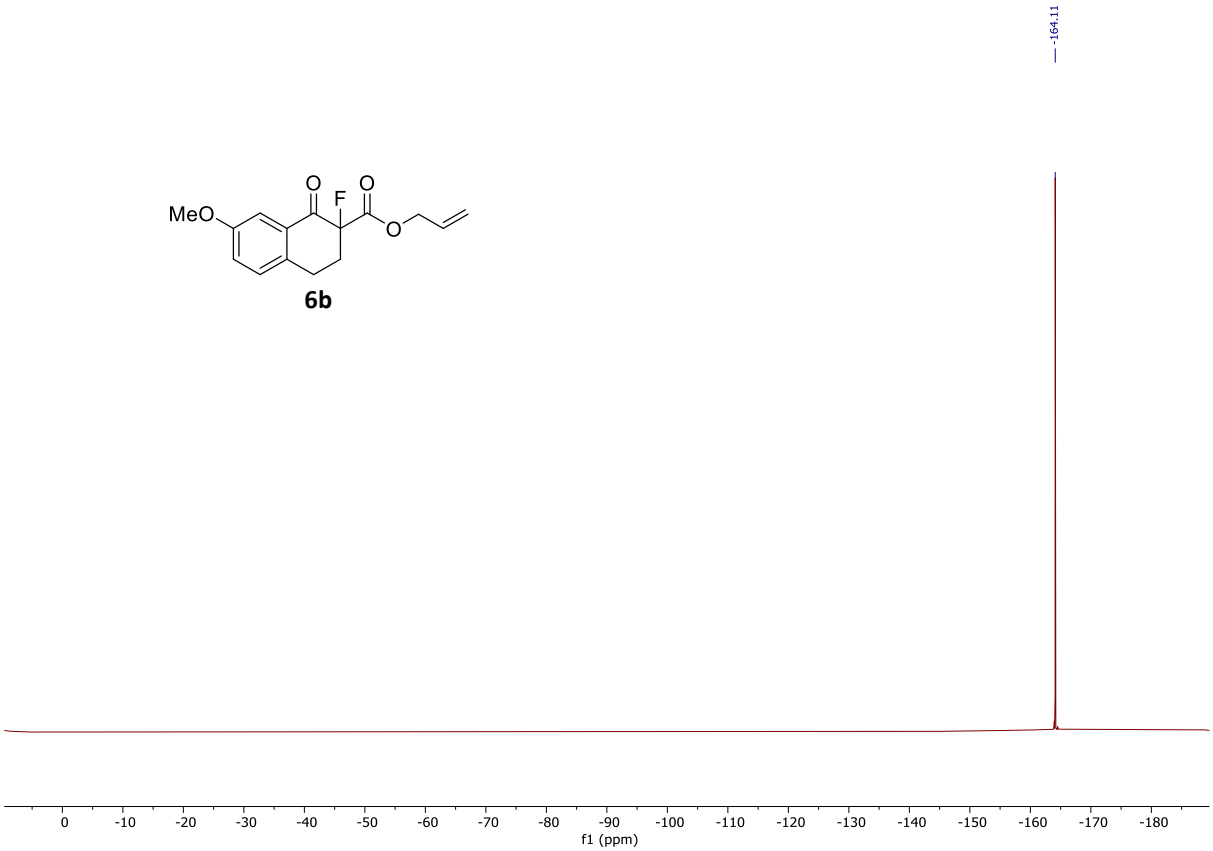


6b

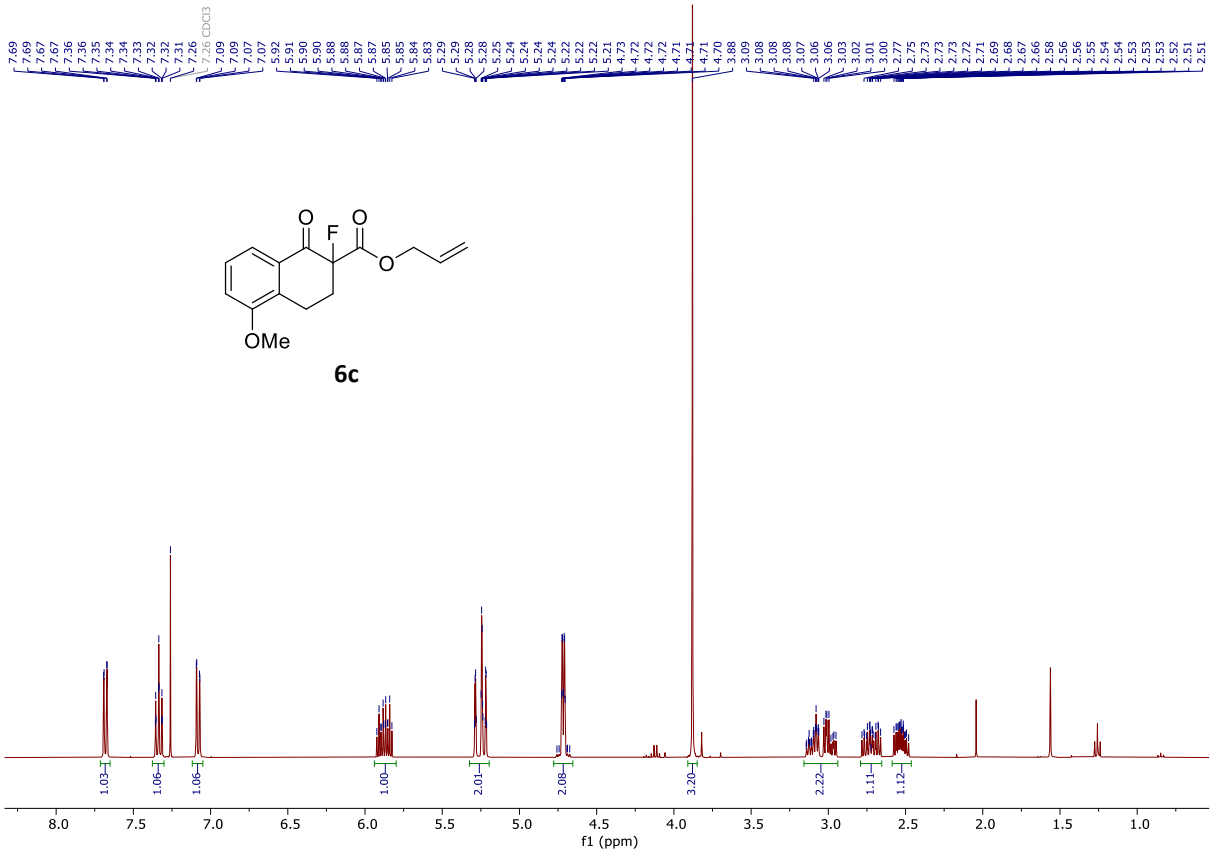
^{1}H NMR (400 MHz, $CDCl_3$)



$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)

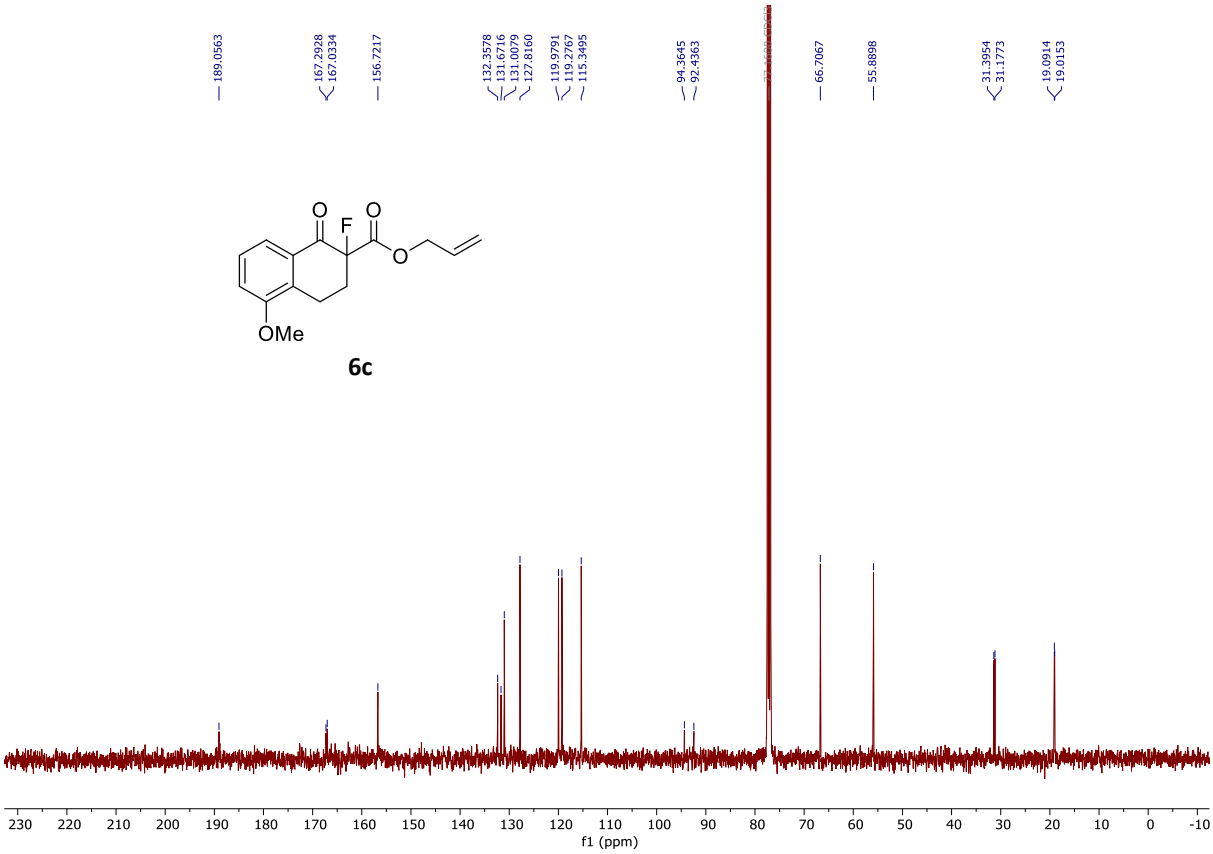


$^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$)



6c

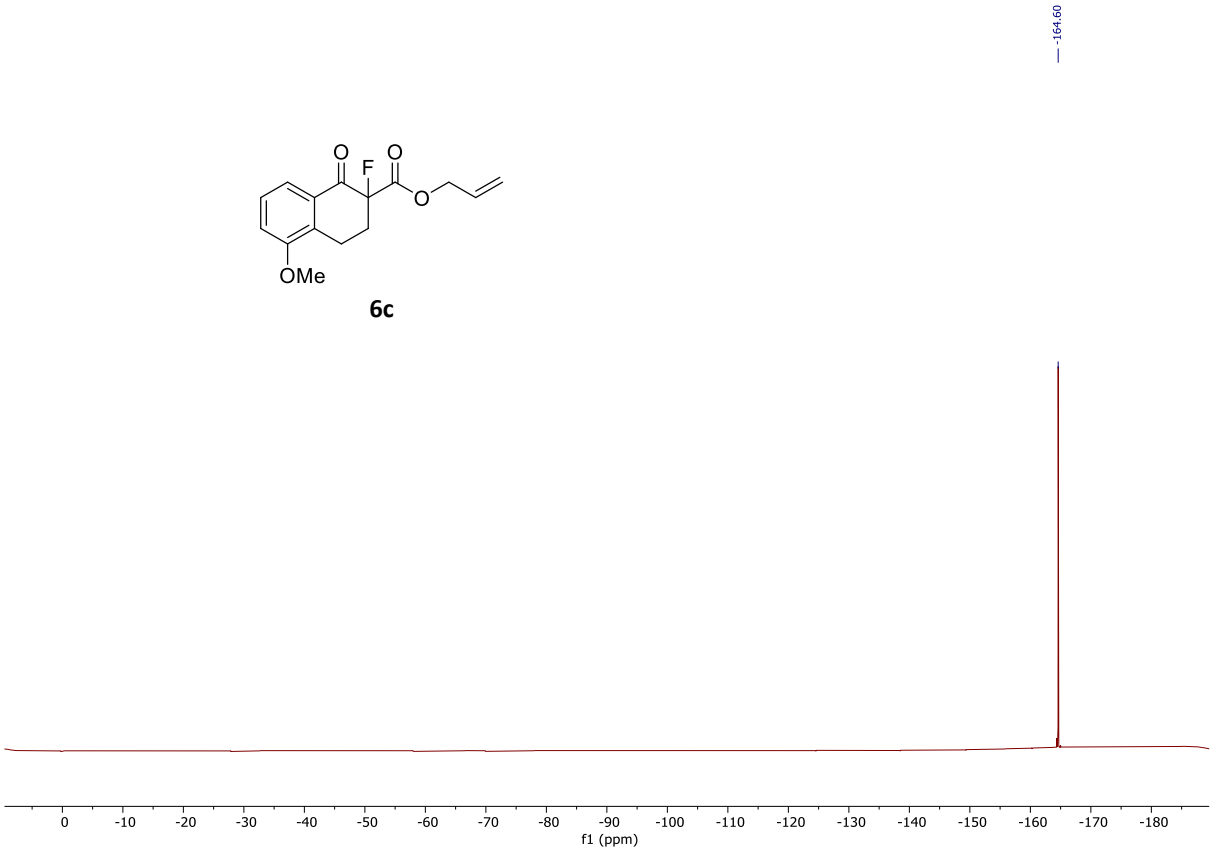
^{1}H NMR (400 MHz, $CDCl_3$)



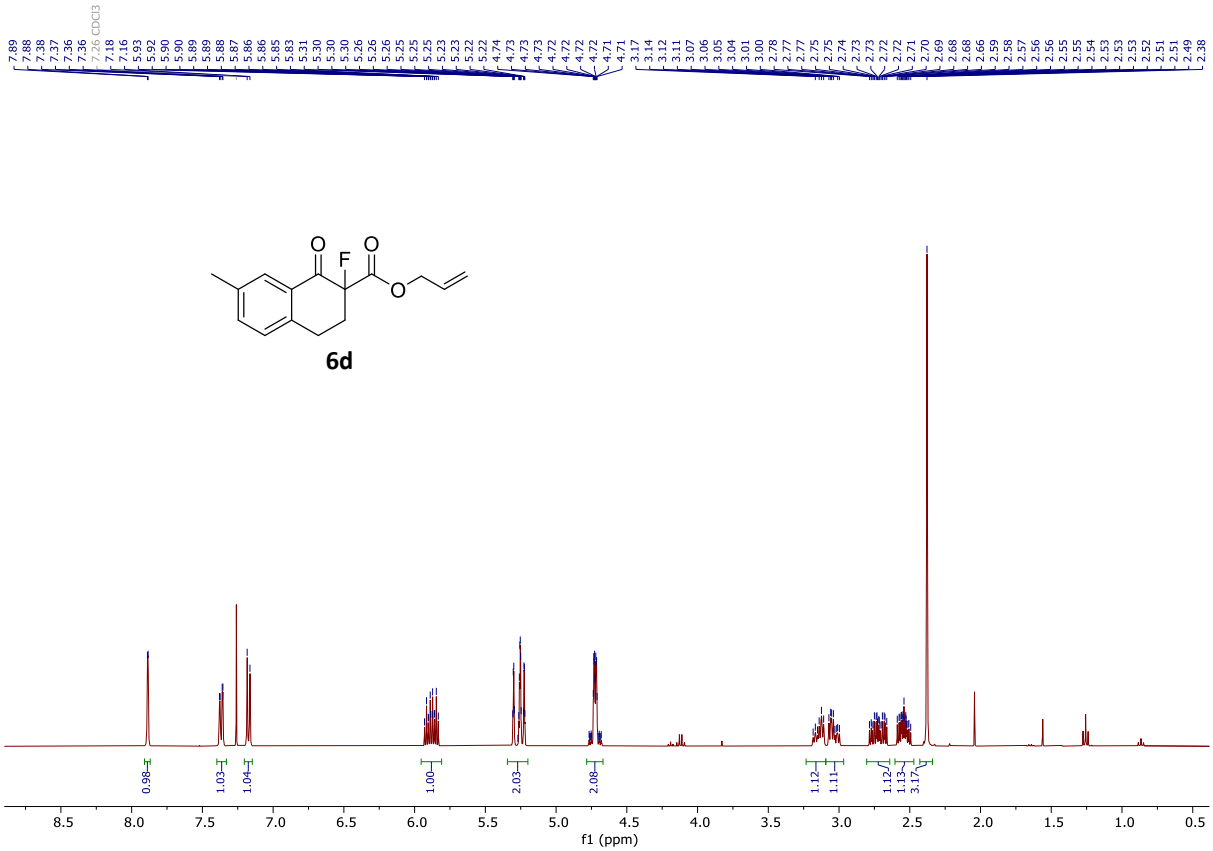
6c

$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)

6c

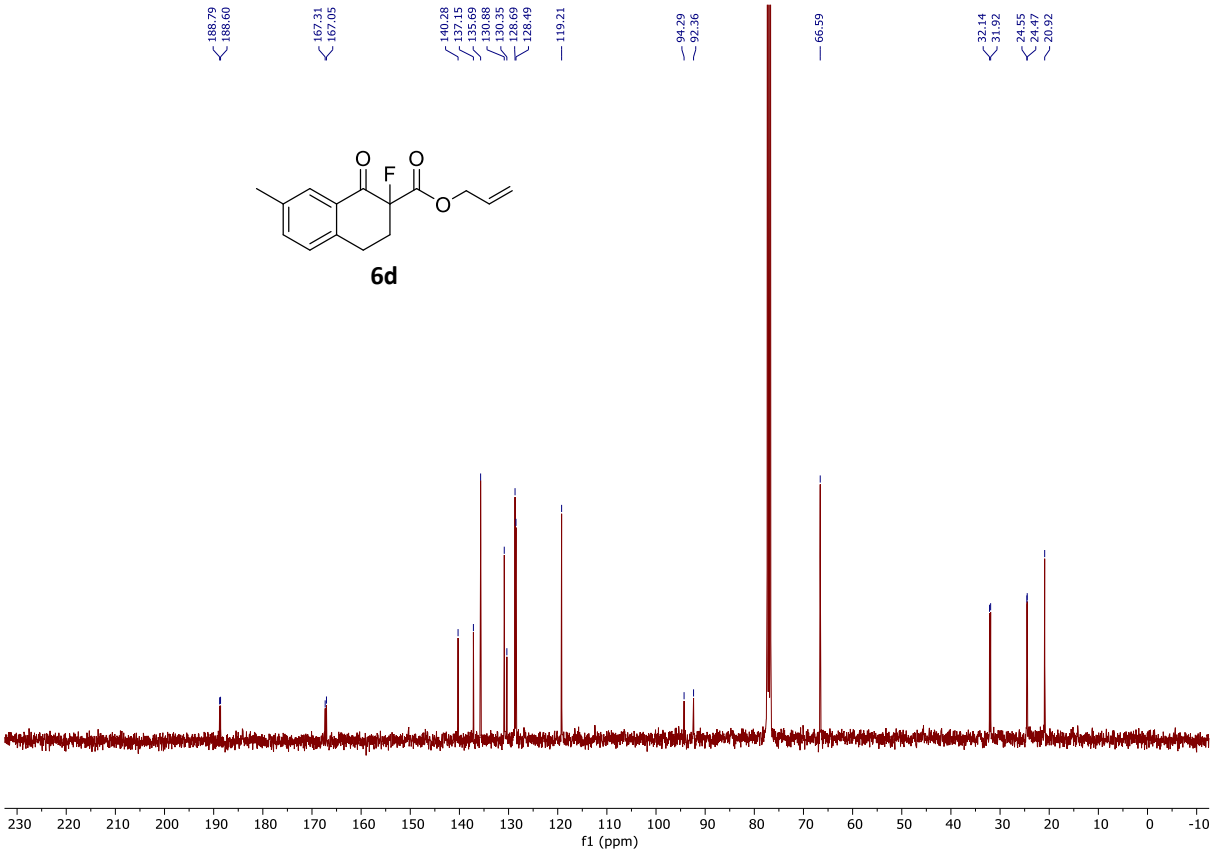


$^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$)

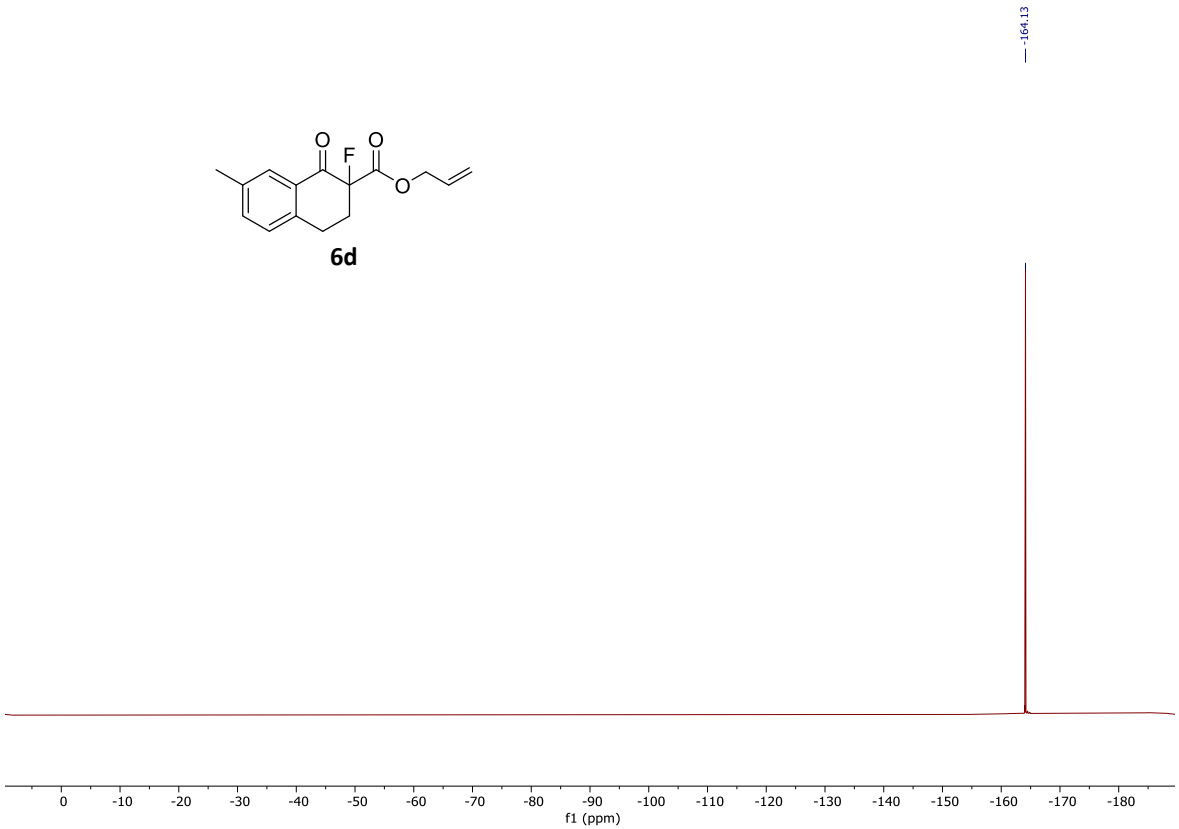


6d

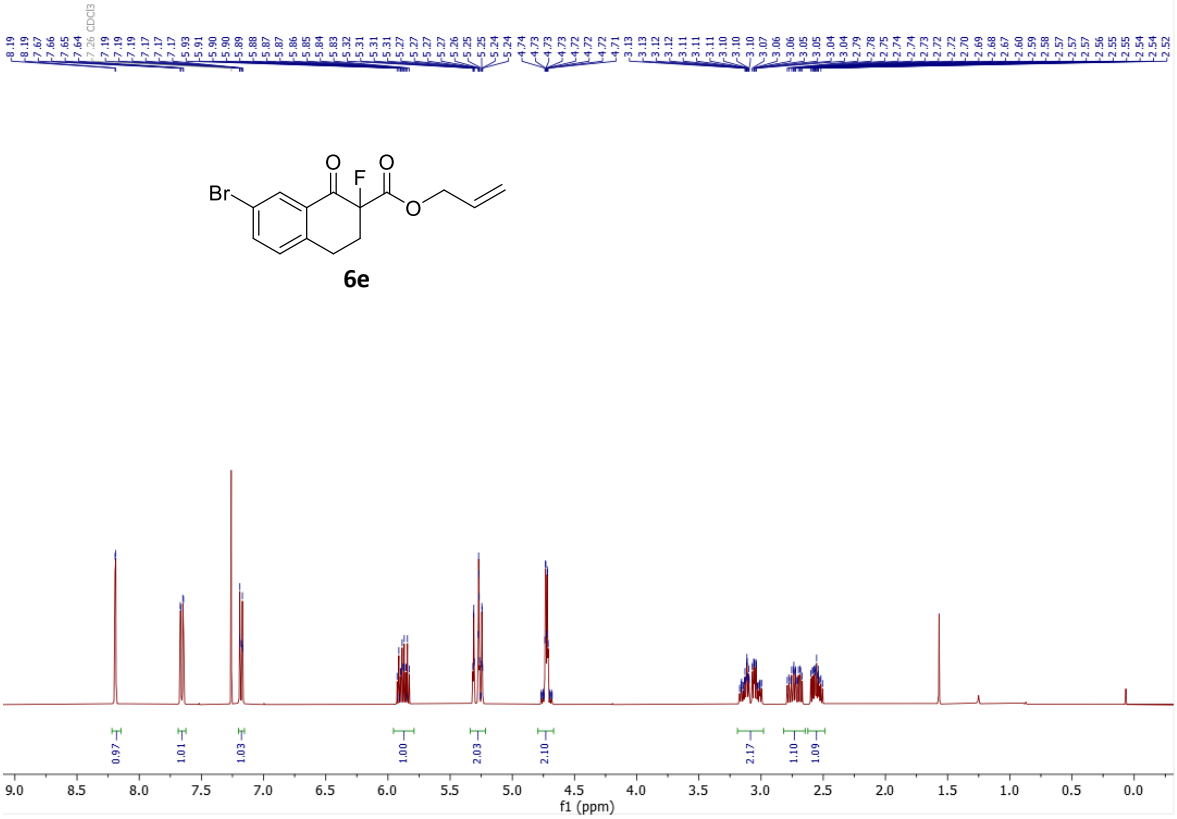
^{1}H NMR (400 MHz, $CDCl_3$)



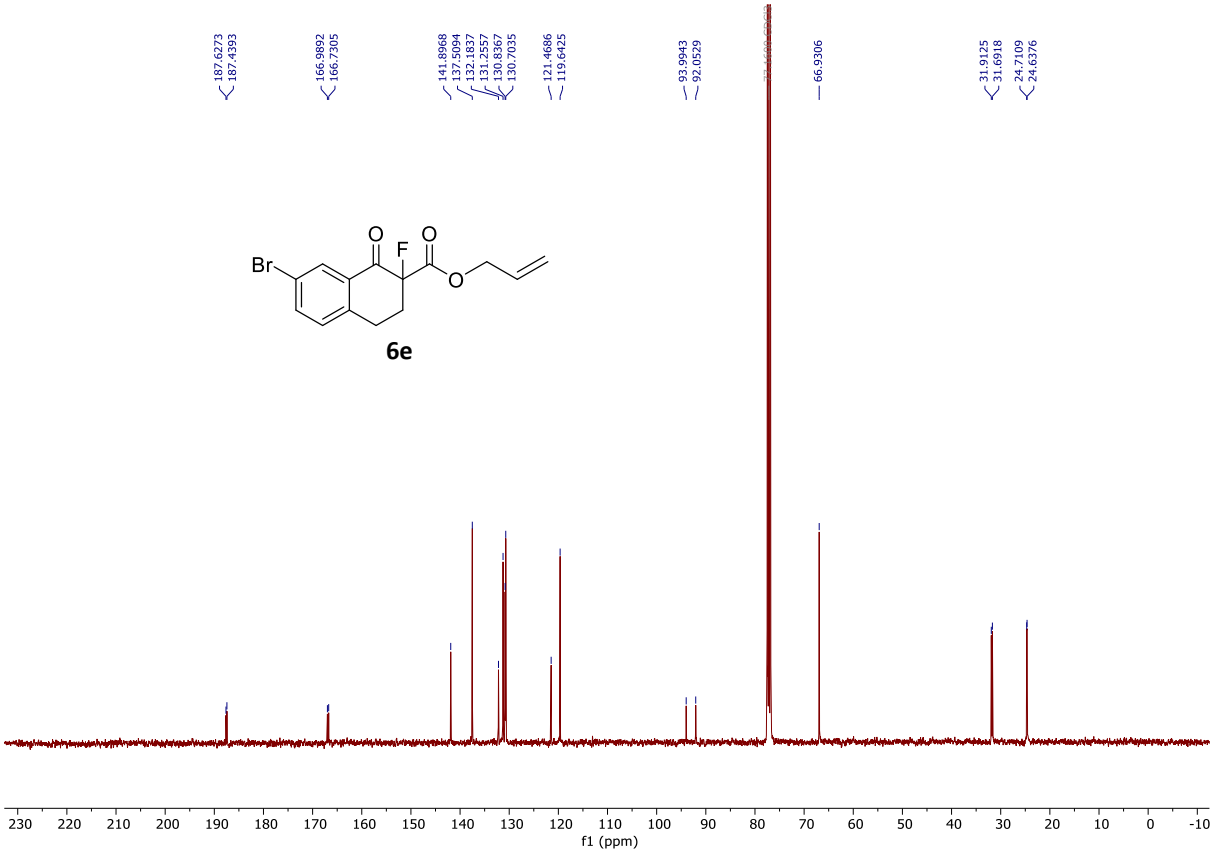
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



$^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$)

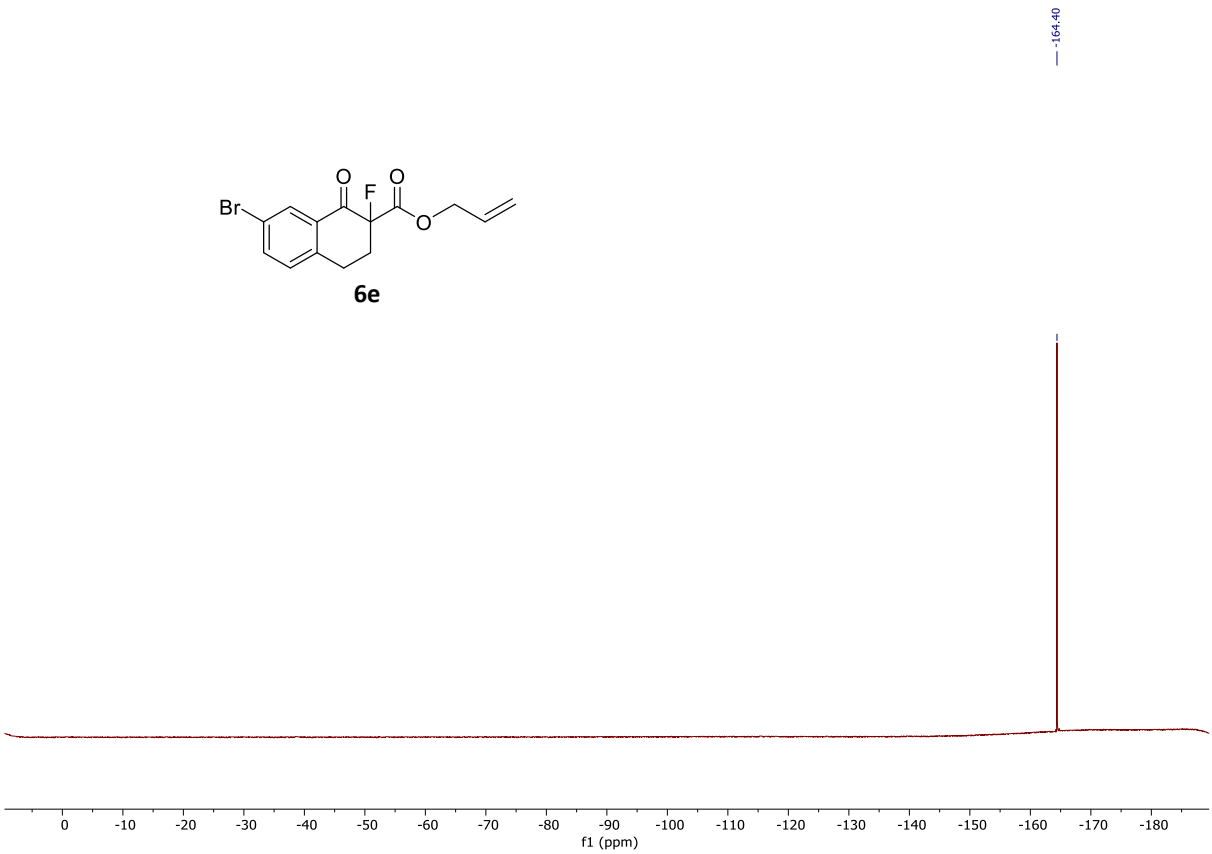


^{1}H NMR (400 MHz, $CDCl_3$)

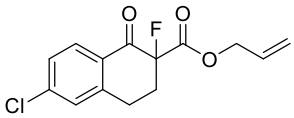


^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)

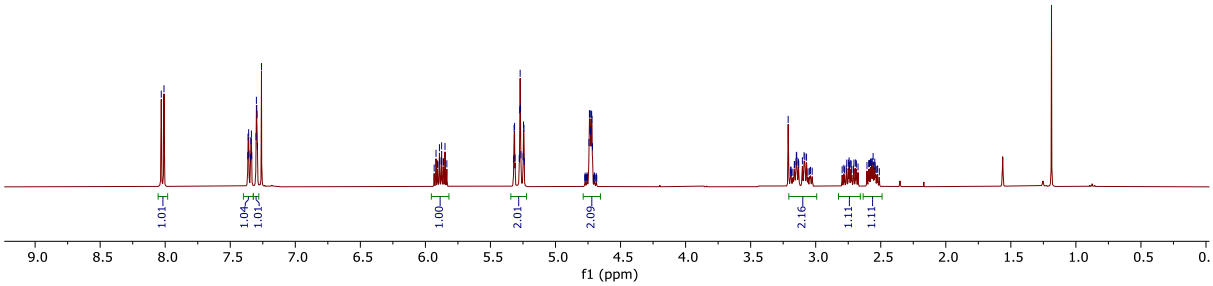
6e



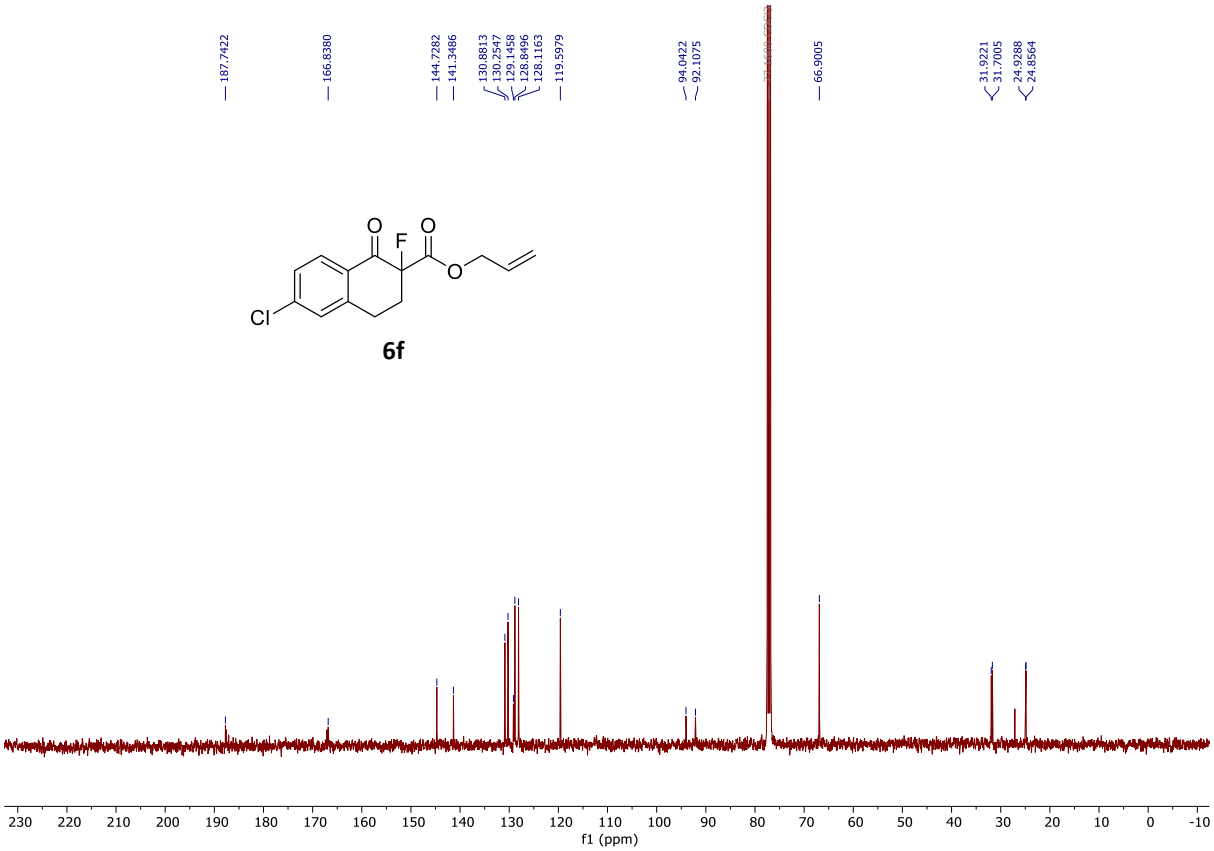
$^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$)



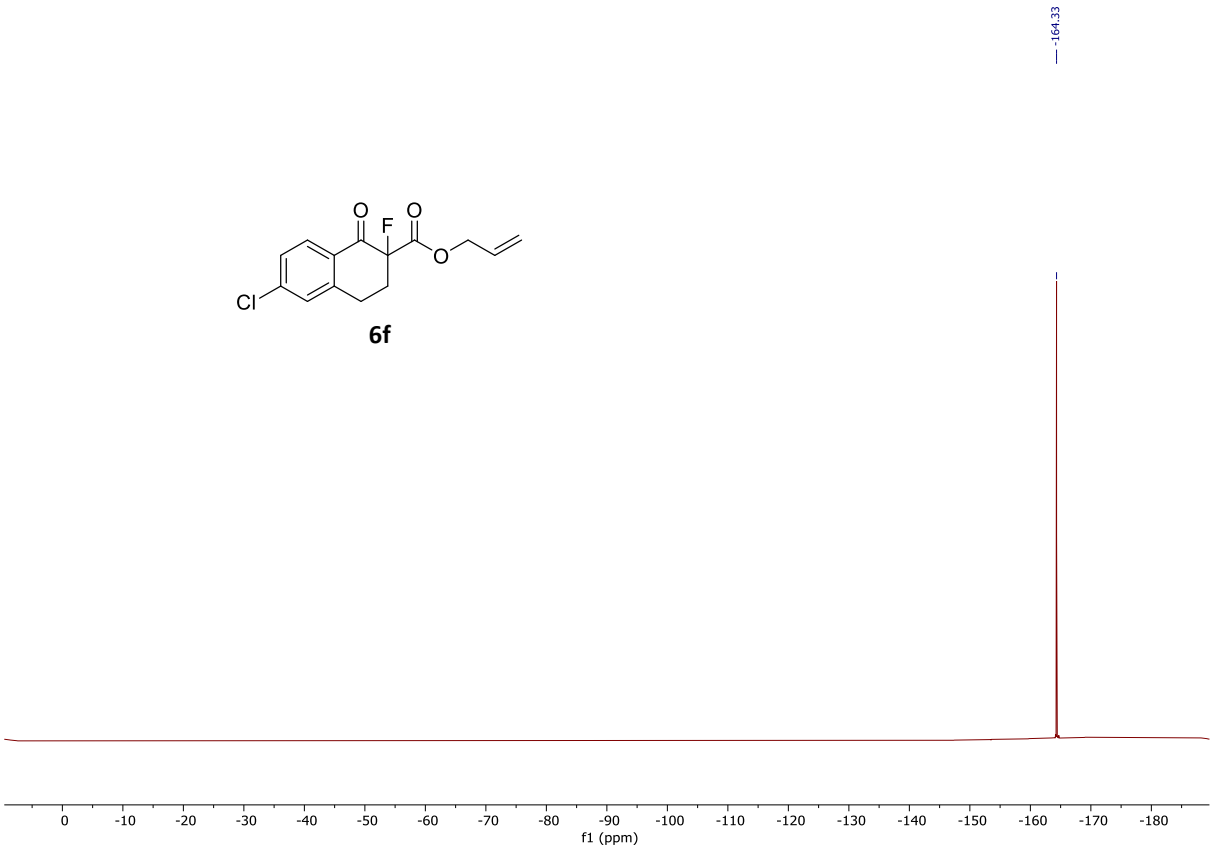
6f



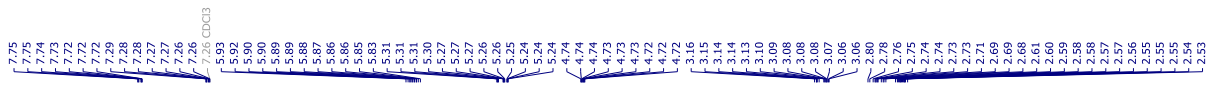
^{1}H NMR (400 MHz, $CDCl_3$)

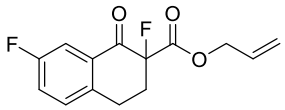


$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



$^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$)





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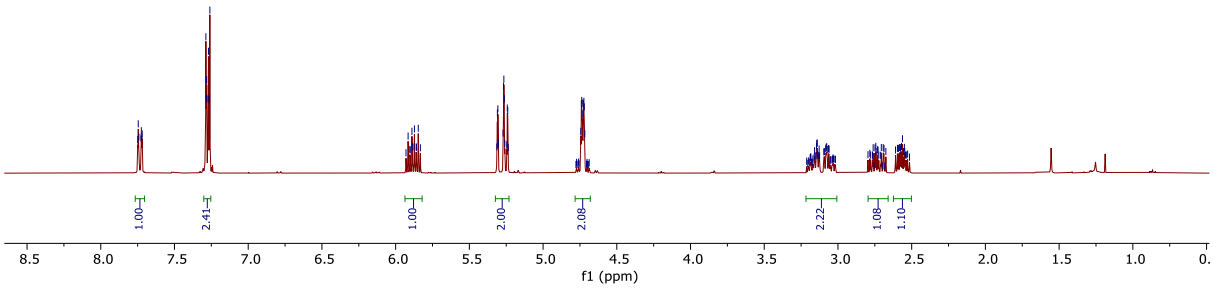
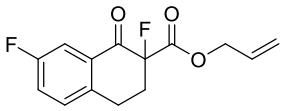
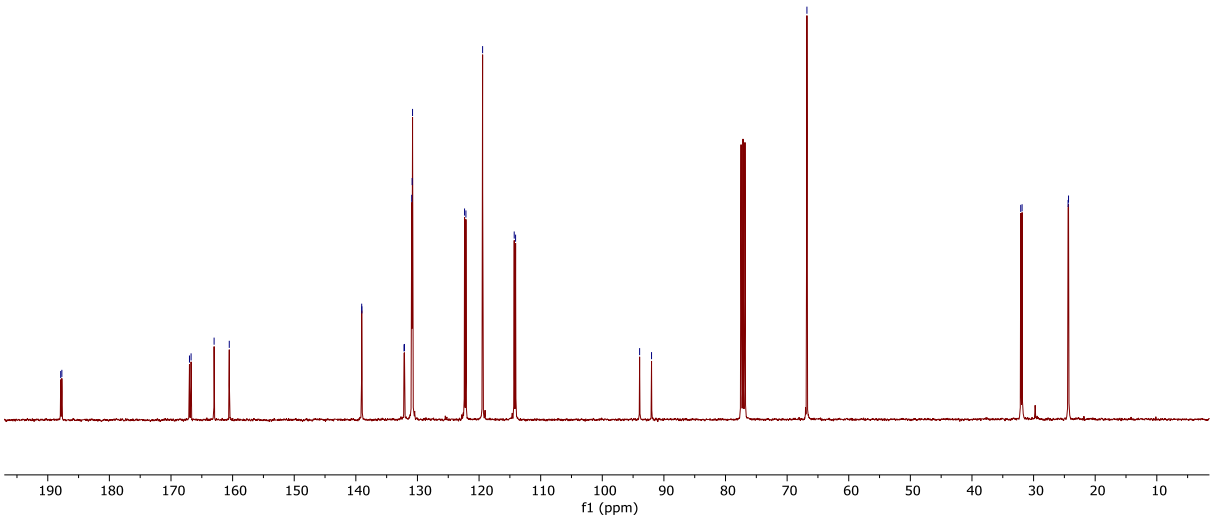


^{1}H NMR (400 MHz, $CDCl_3$)

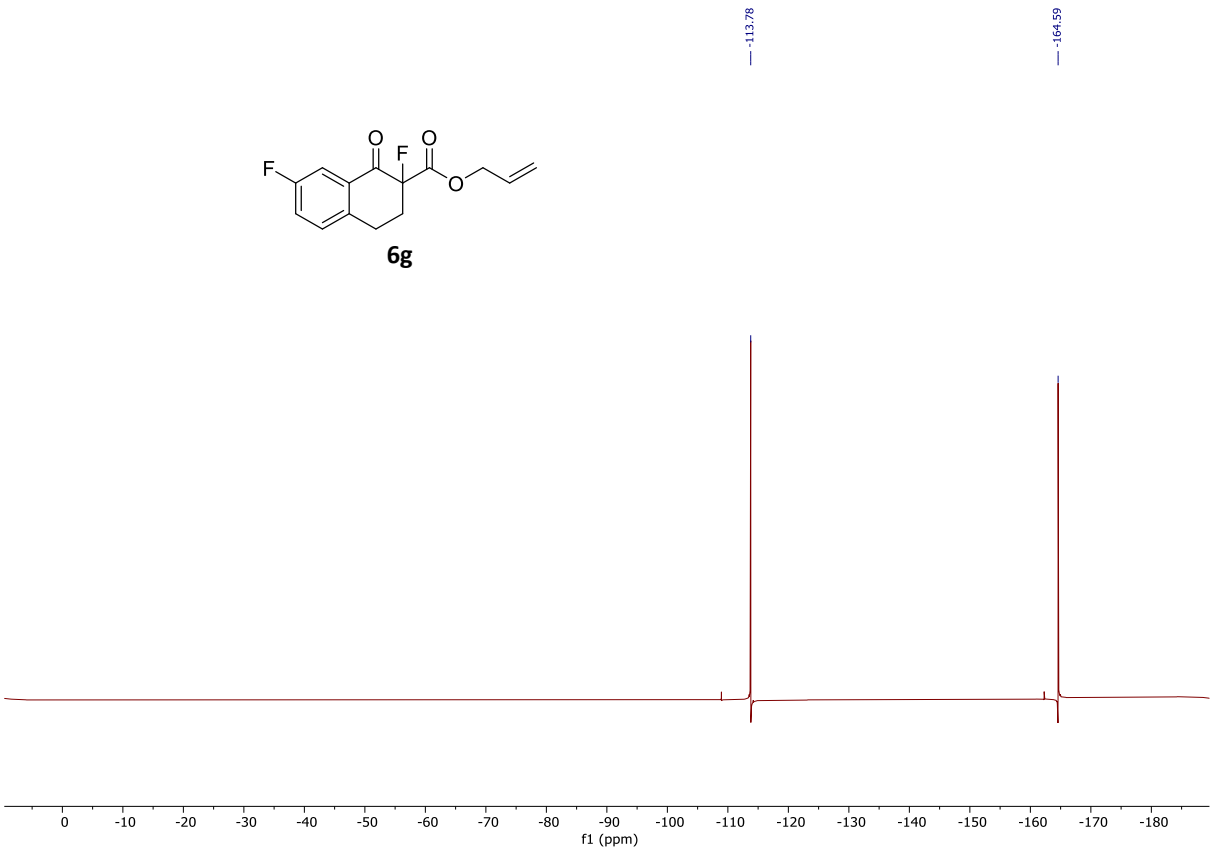


6g

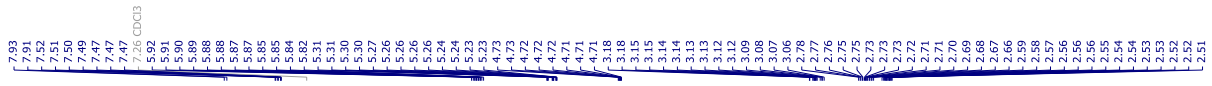


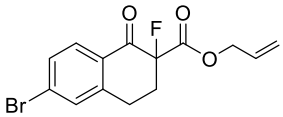
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)

6g

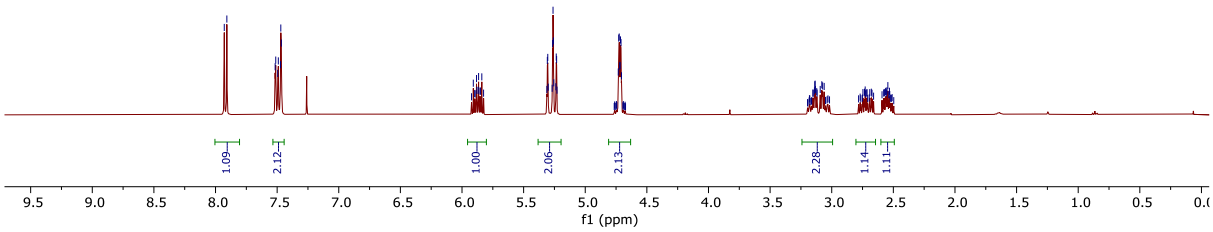


$^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$)

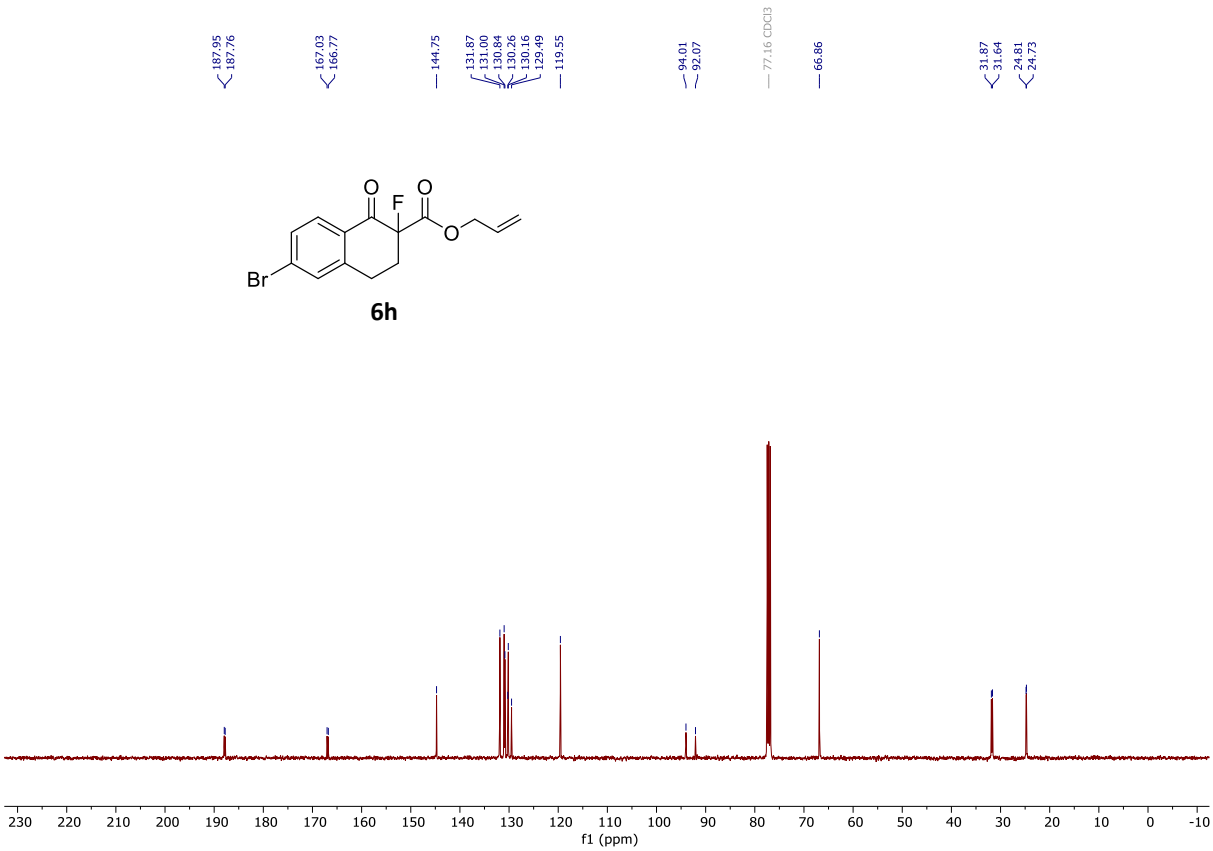




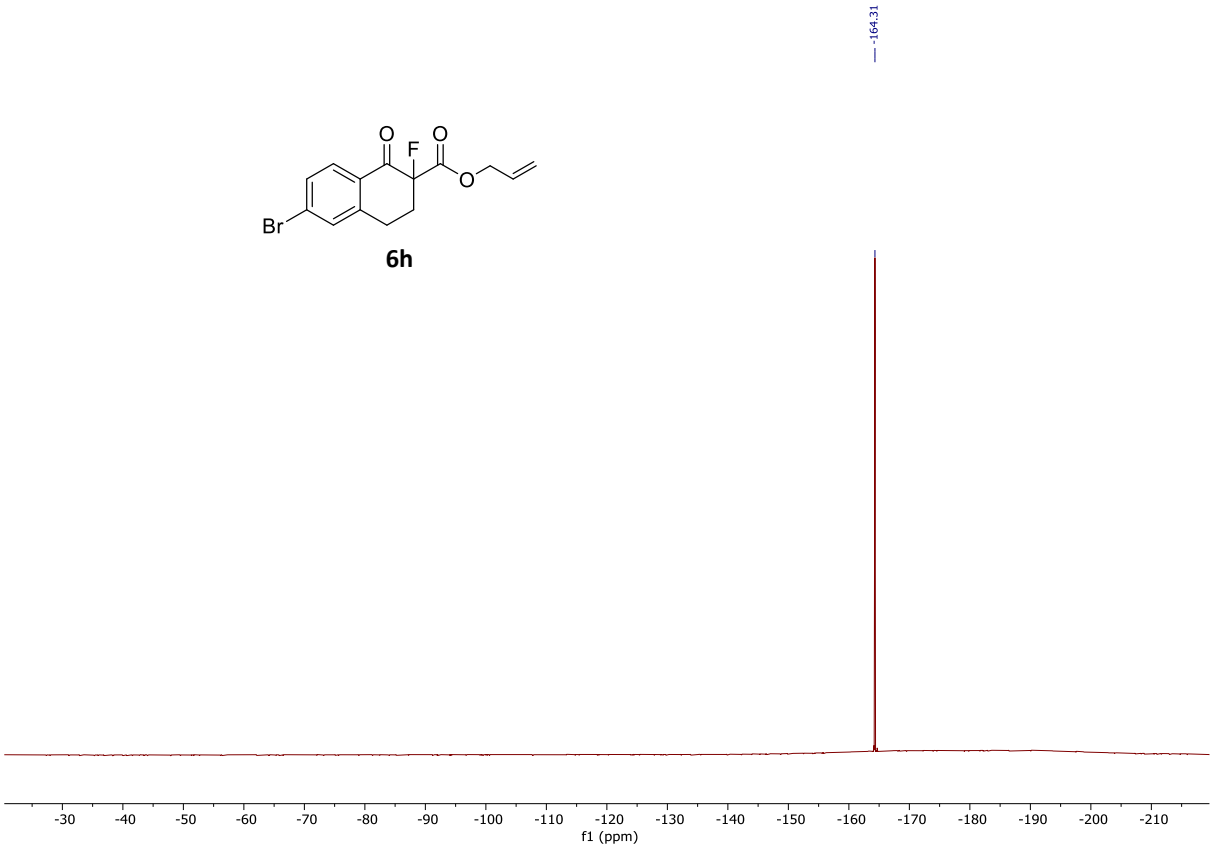
6h



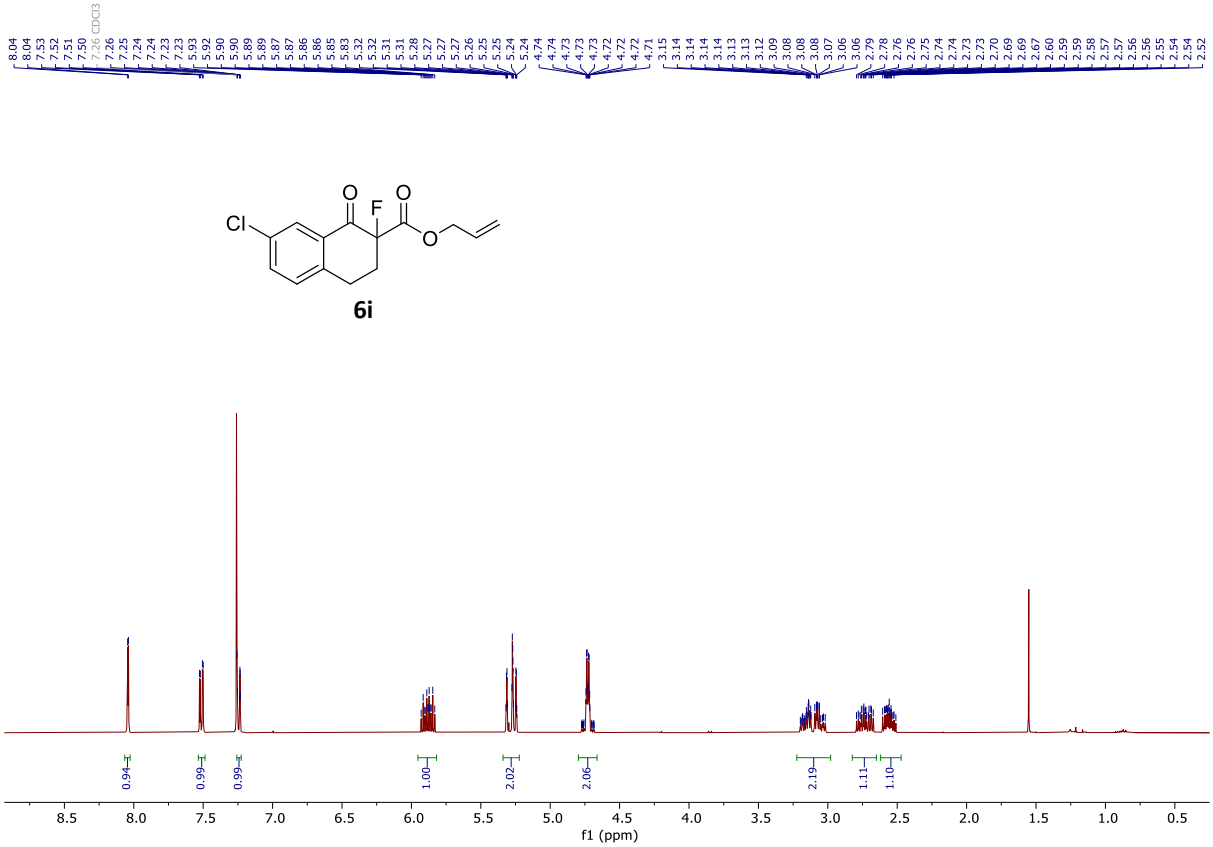
^{1}H NMR (400 MHz, $CDCl_3$)



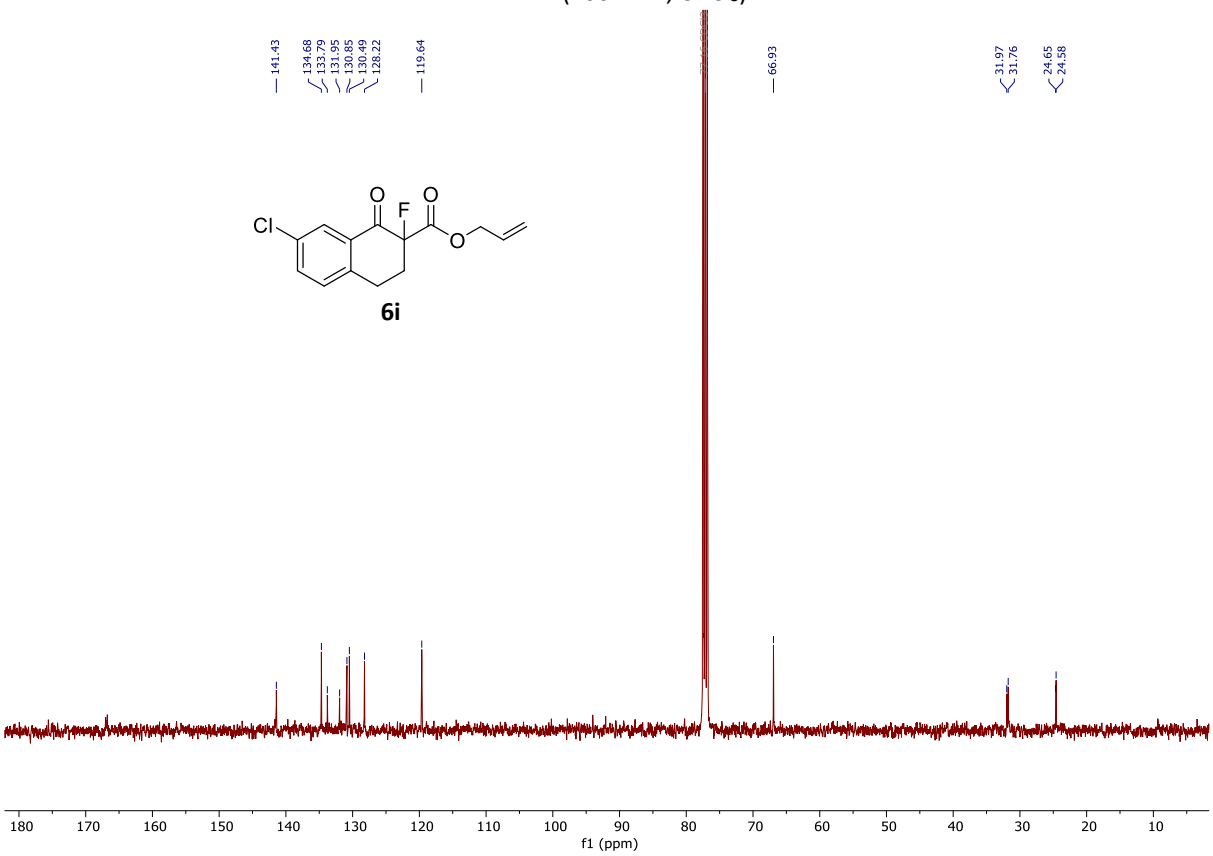
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



$^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$)

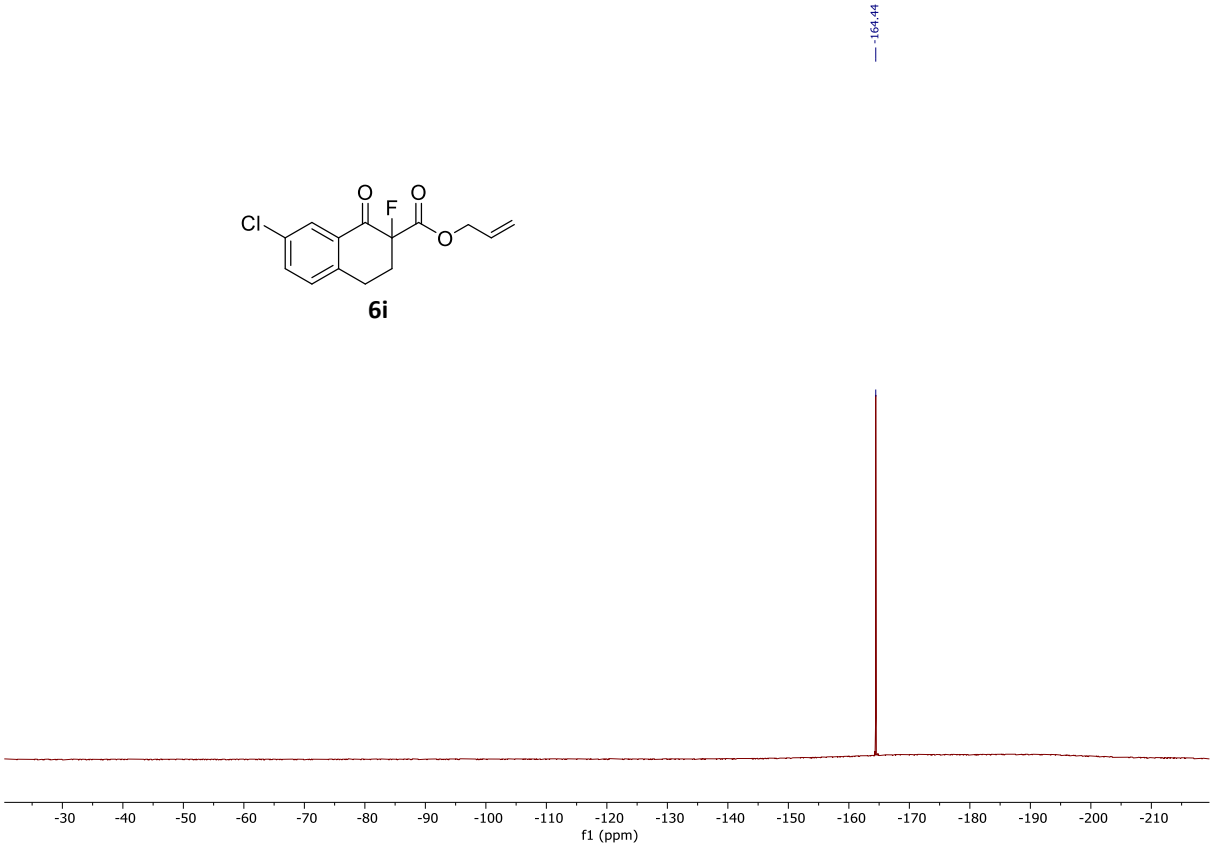


^{1}H NMR (400 MHz, $CDCl_3$)

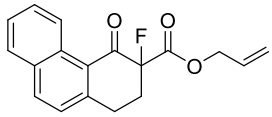


^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)

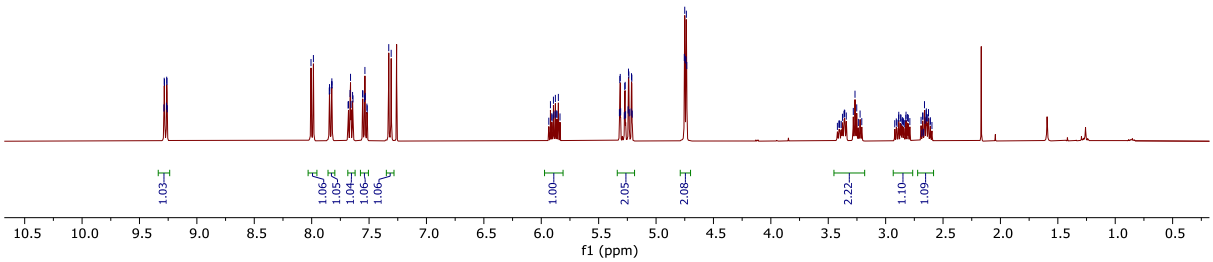
6i



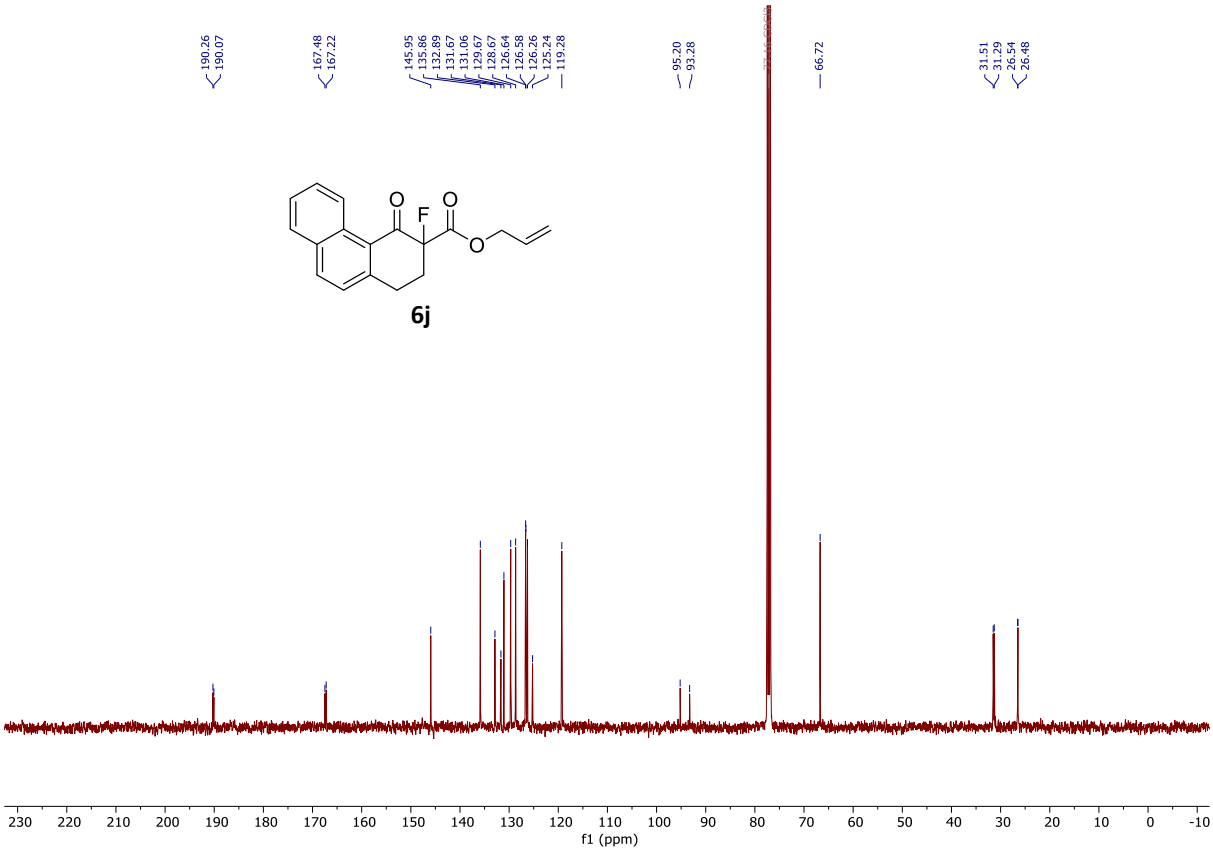
$^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$)



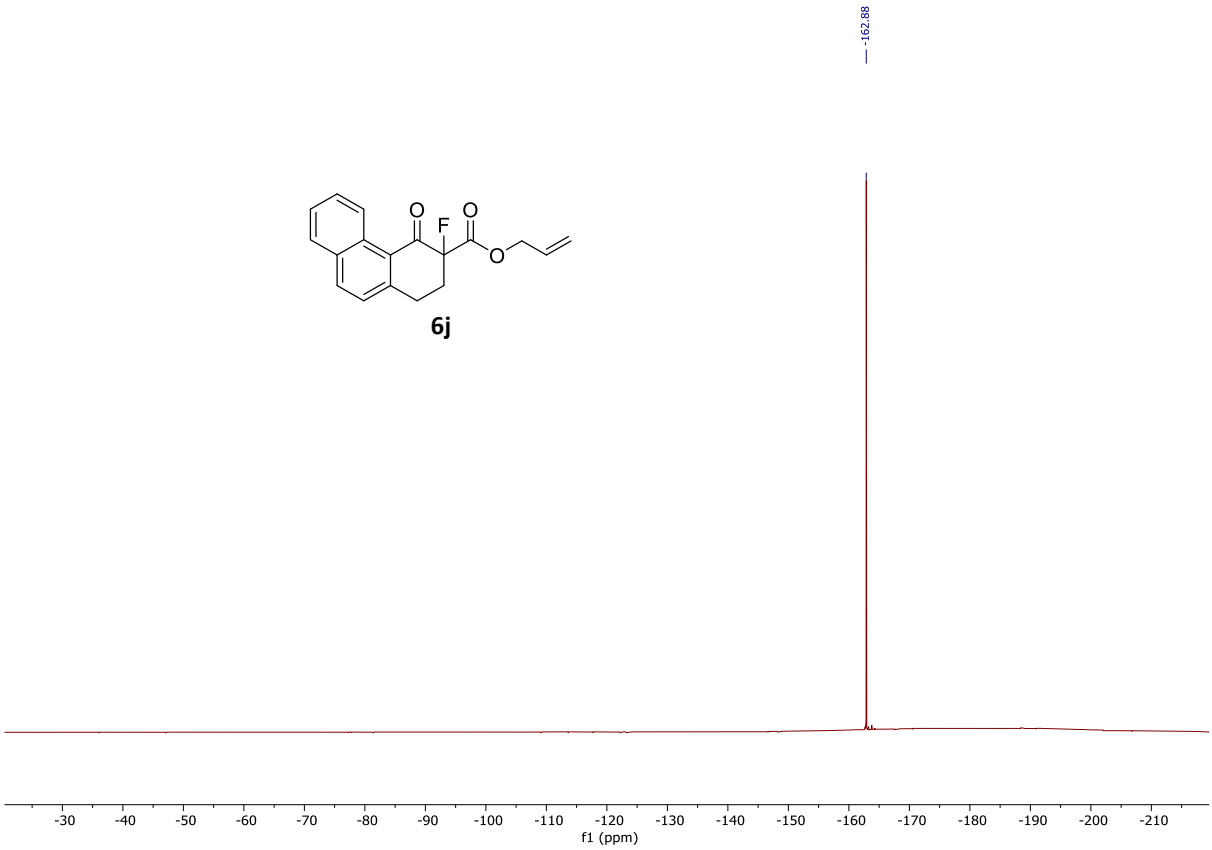
6j



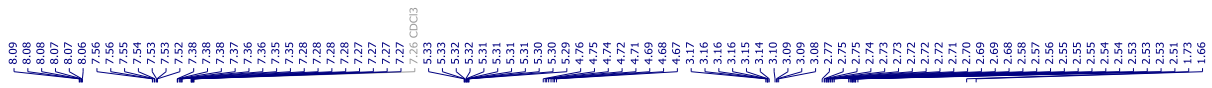
^{1}H NMR (400 MHz, $CDCl_3$)

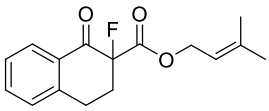


$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)

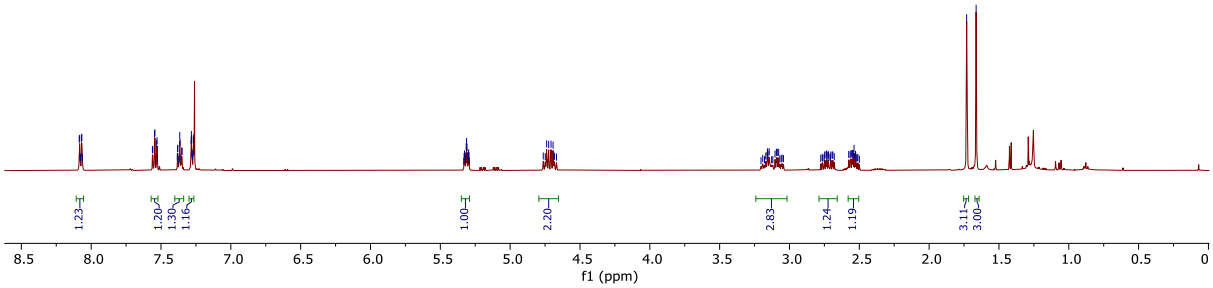


$^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$)

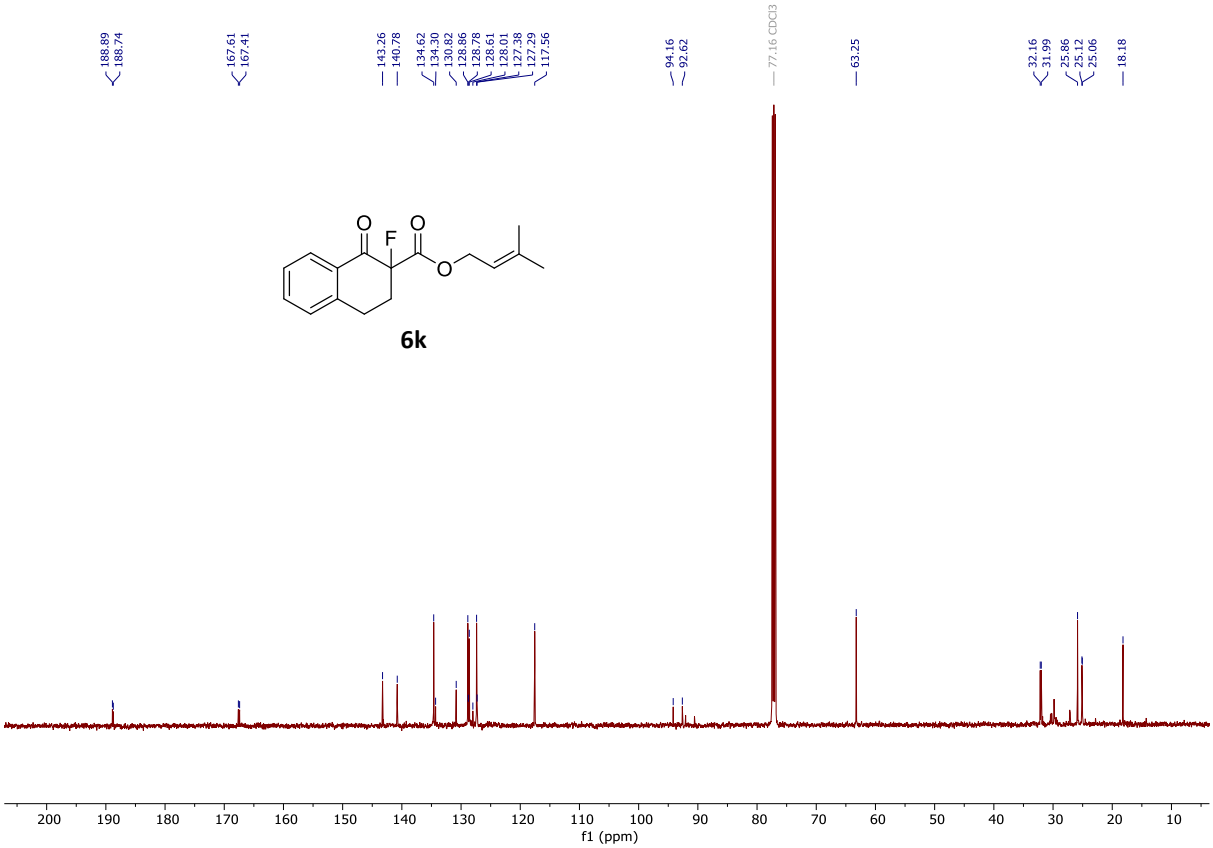




6k



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



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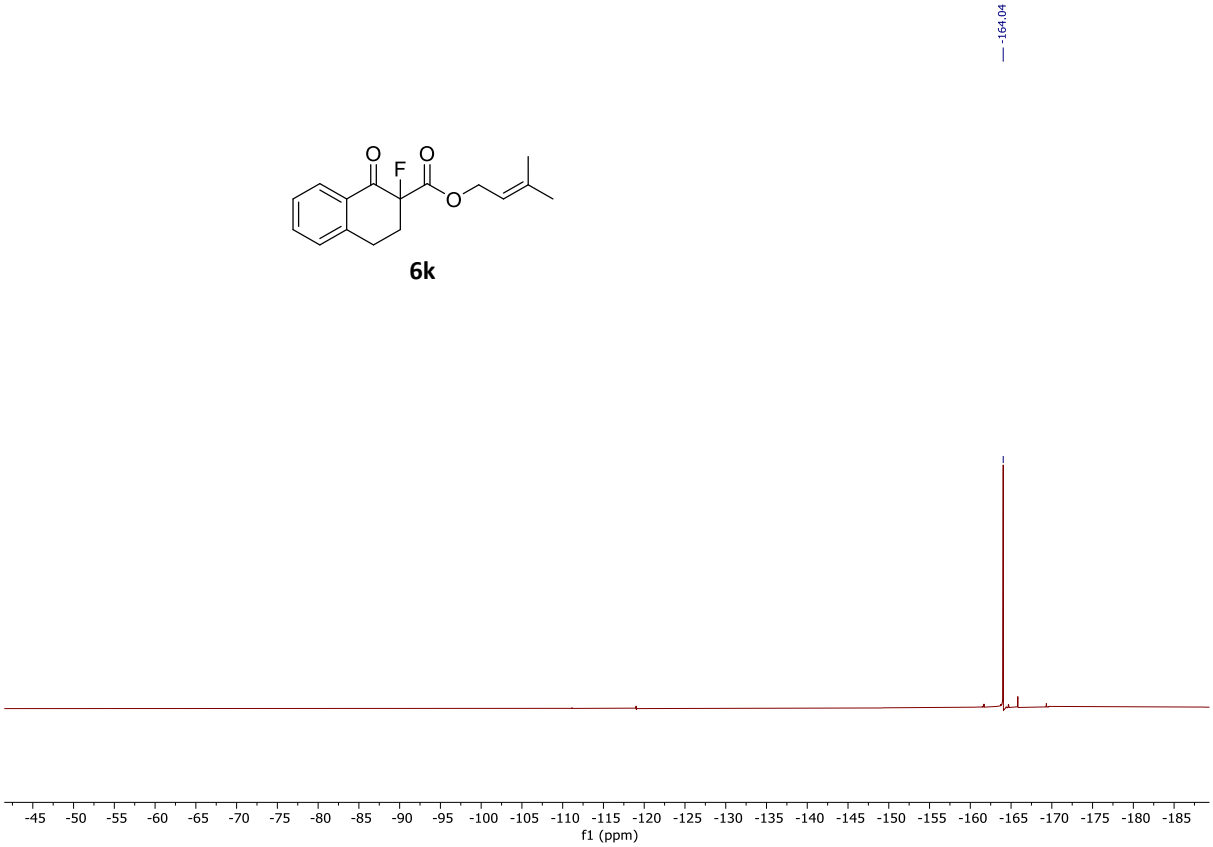
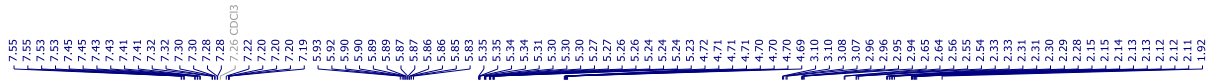
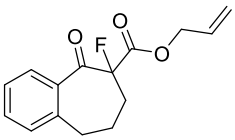
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)

6k



$^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$)





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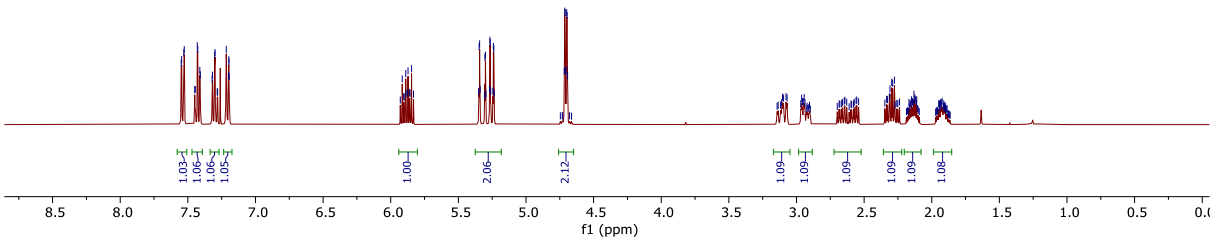
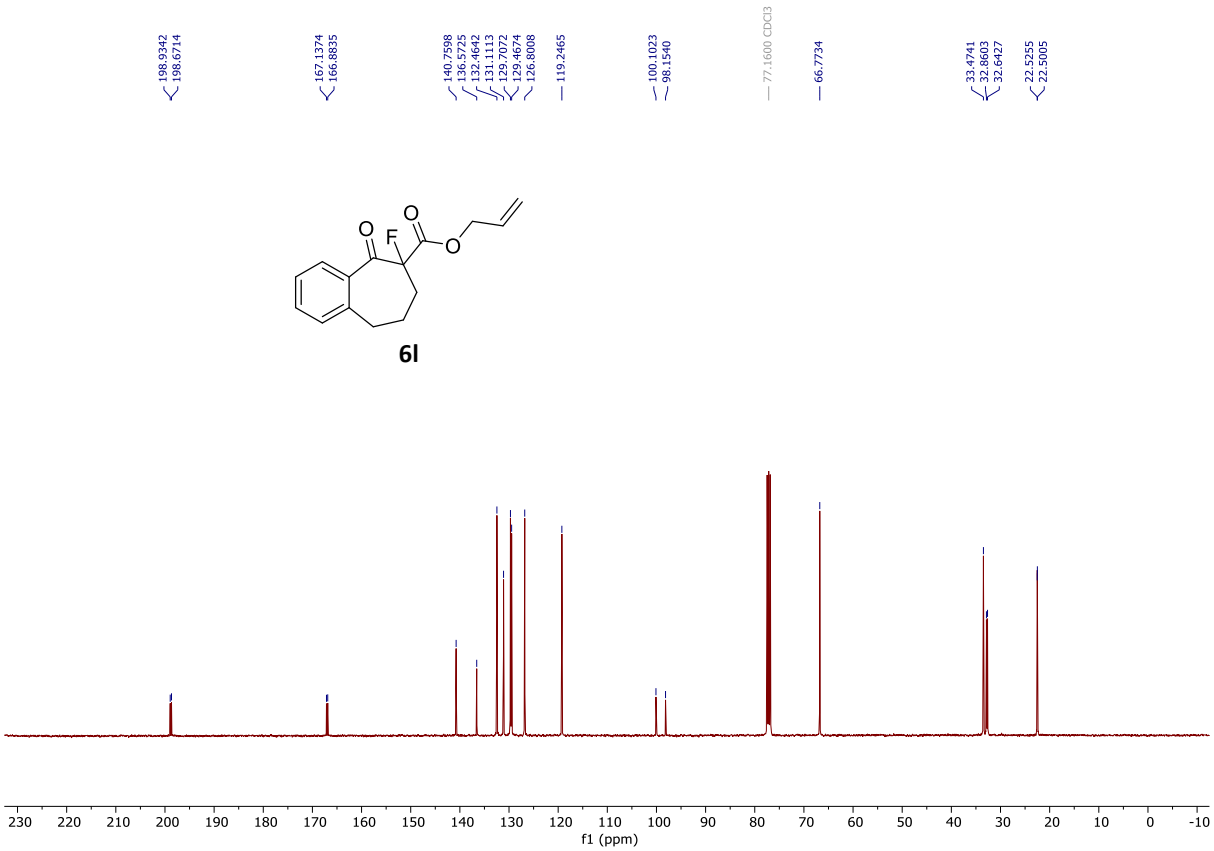
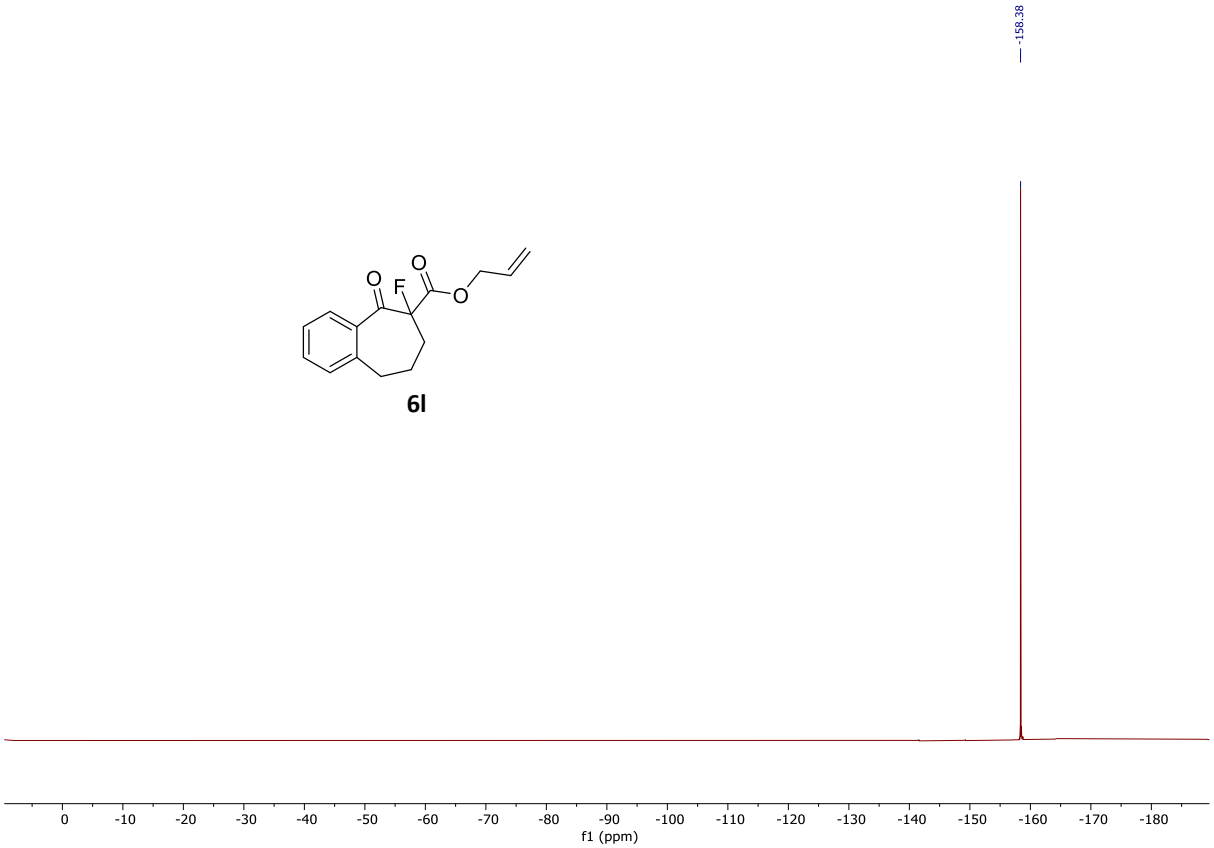


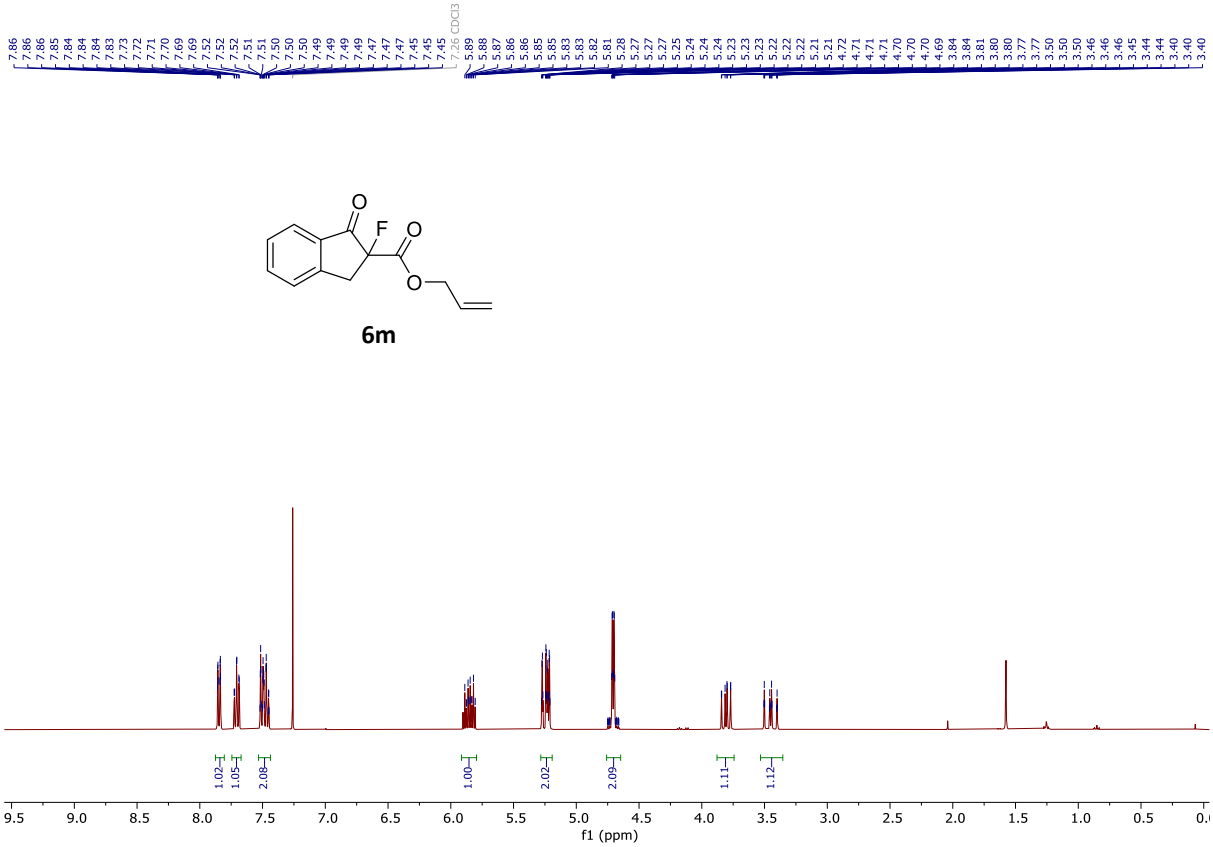
^{1}H NMR (400 MHz, $CDCl_3$)



$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)

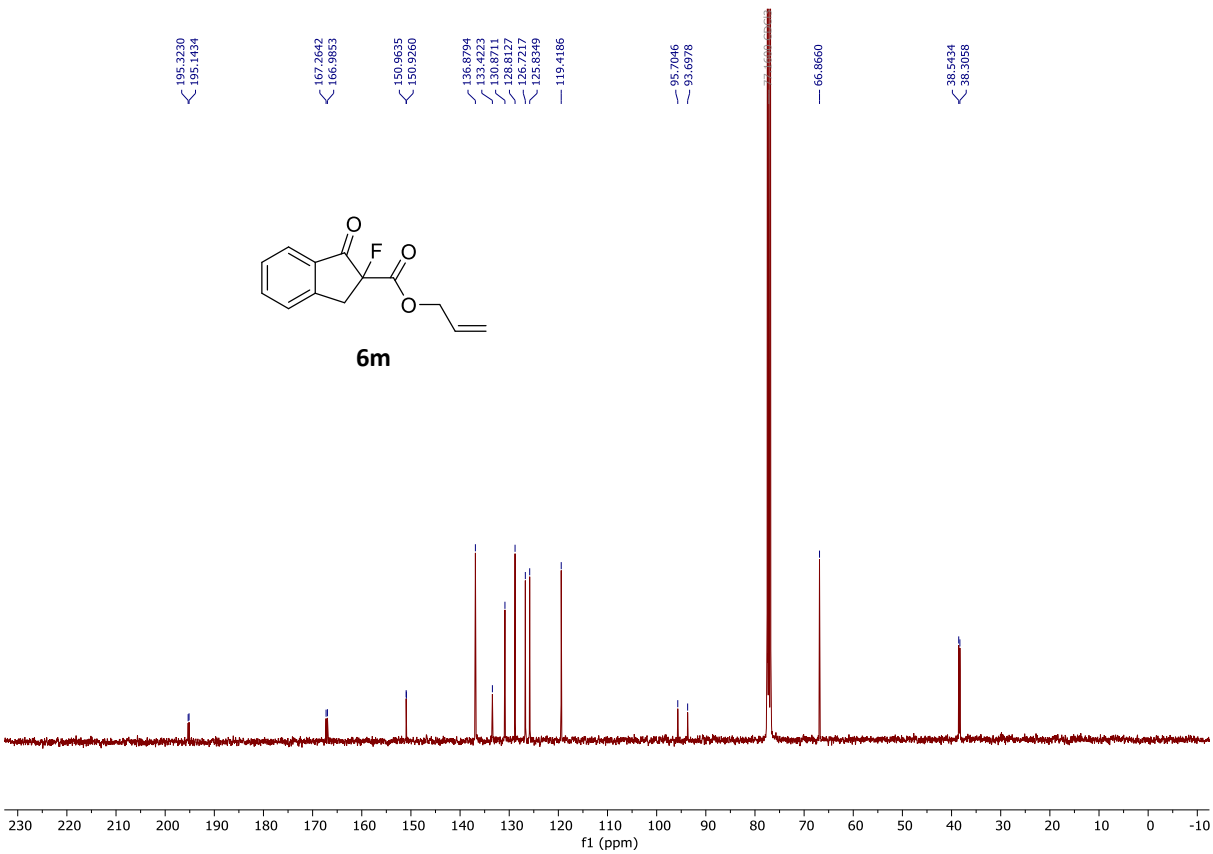


$^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$)



6m

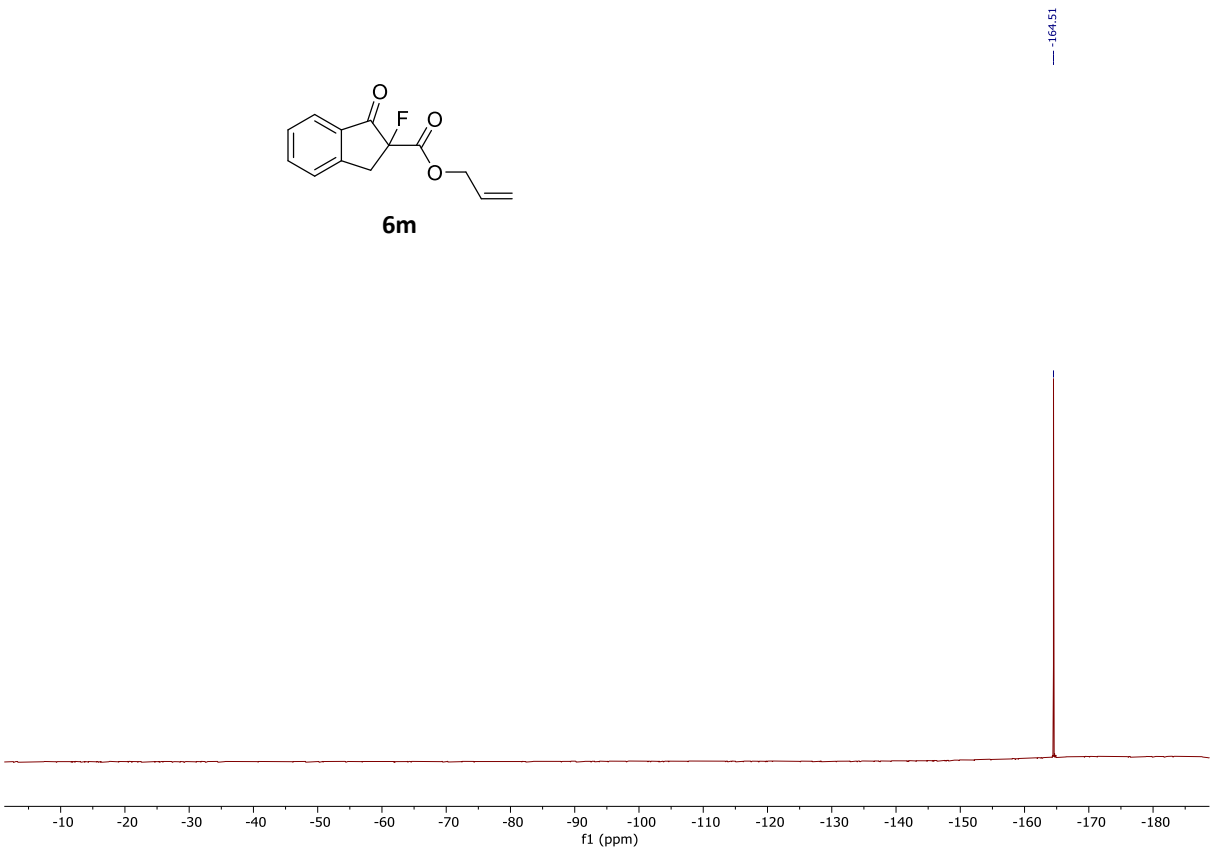
^{1}H NMR (400 MHz, $CDCl_3$)



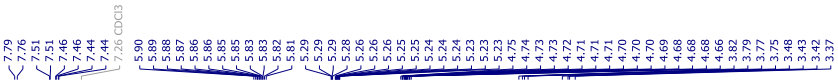
6m

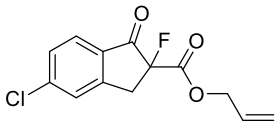
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)

6m



$^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$)





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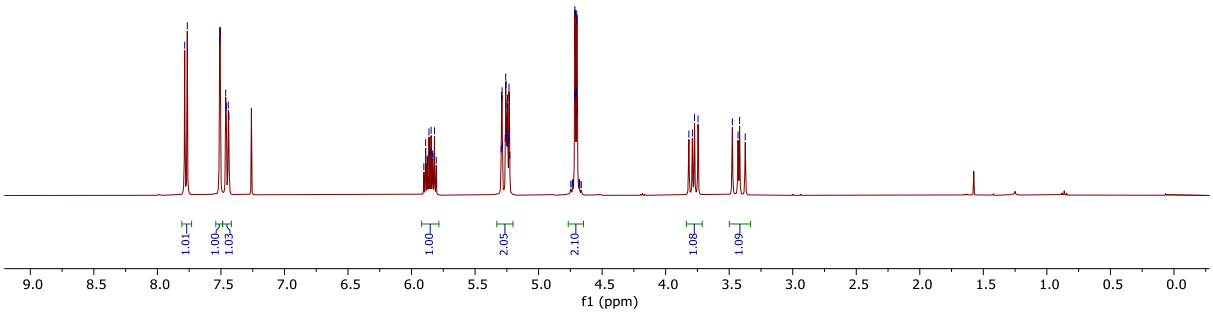
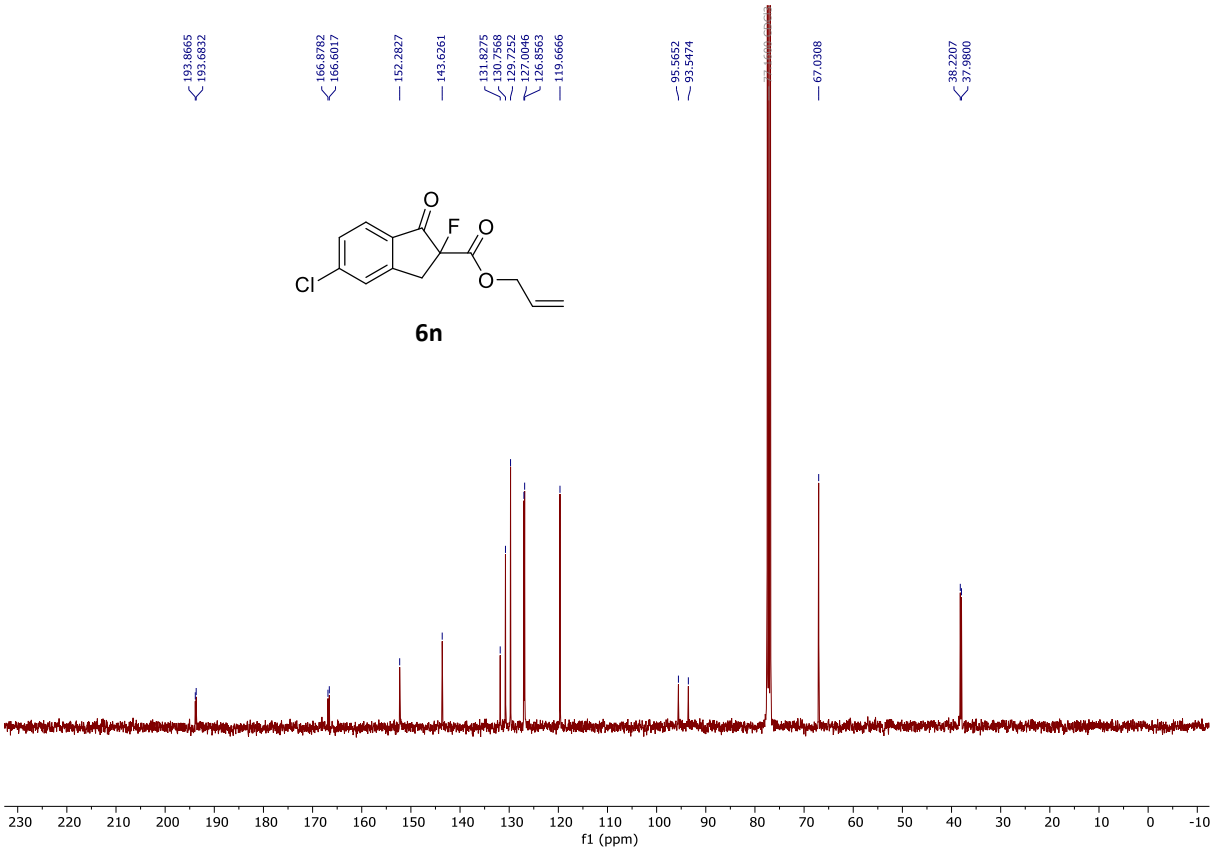
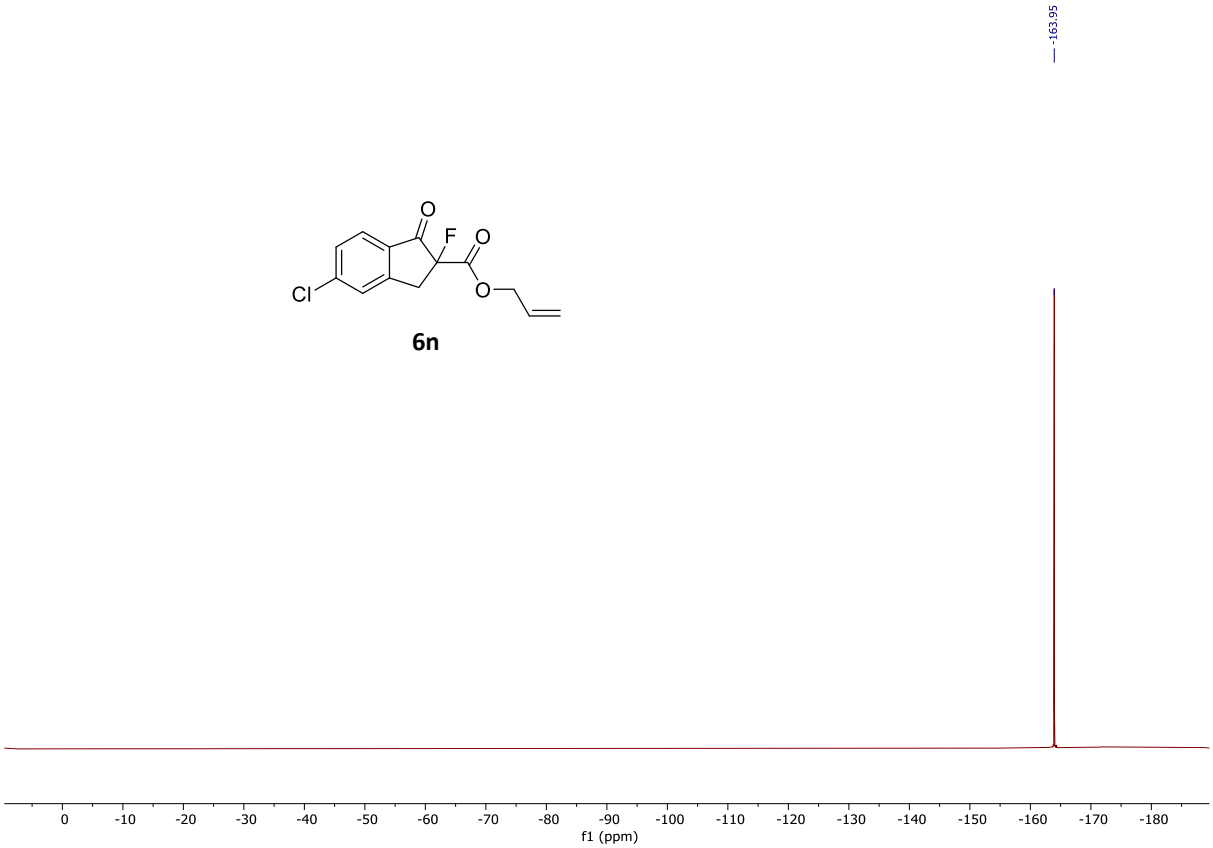


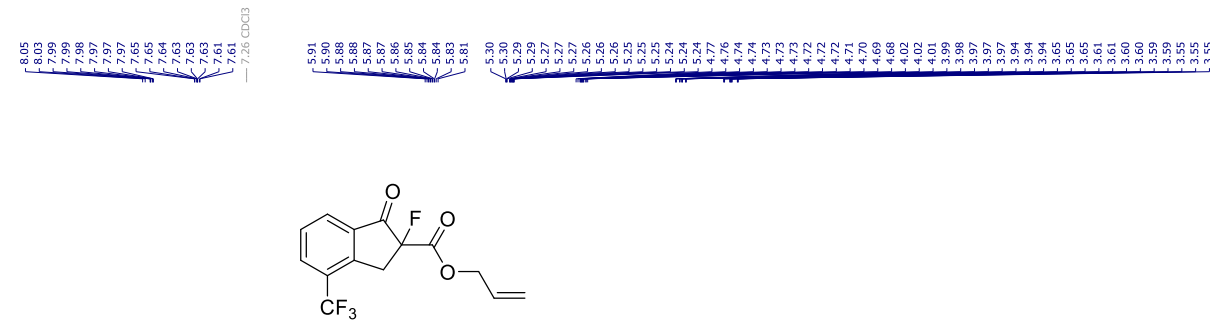
^{1}H NMR (400 MHz, $CDCl_3$)



$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



$^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$)



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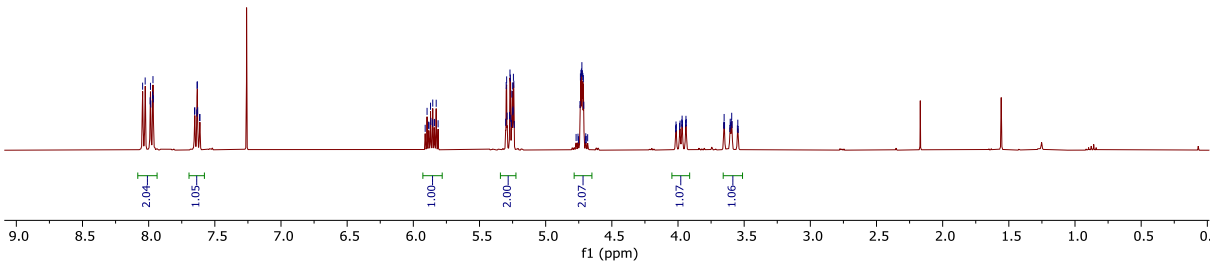
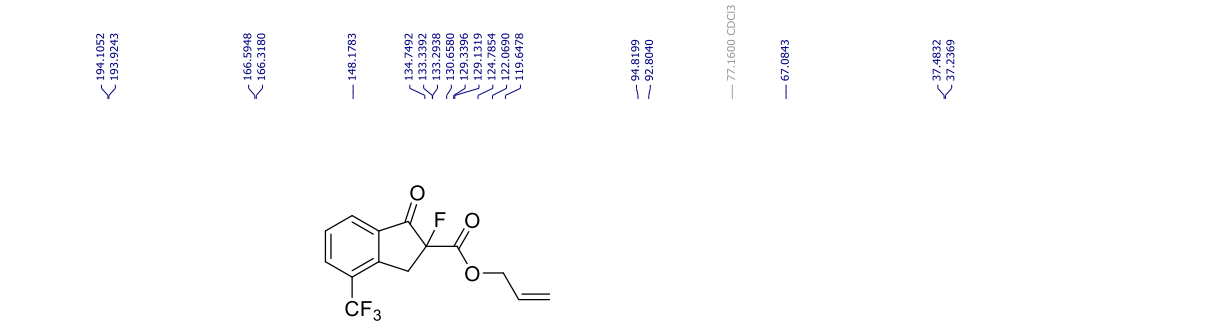


^{1}H NMR (400 MHz, $CDCl_3$)



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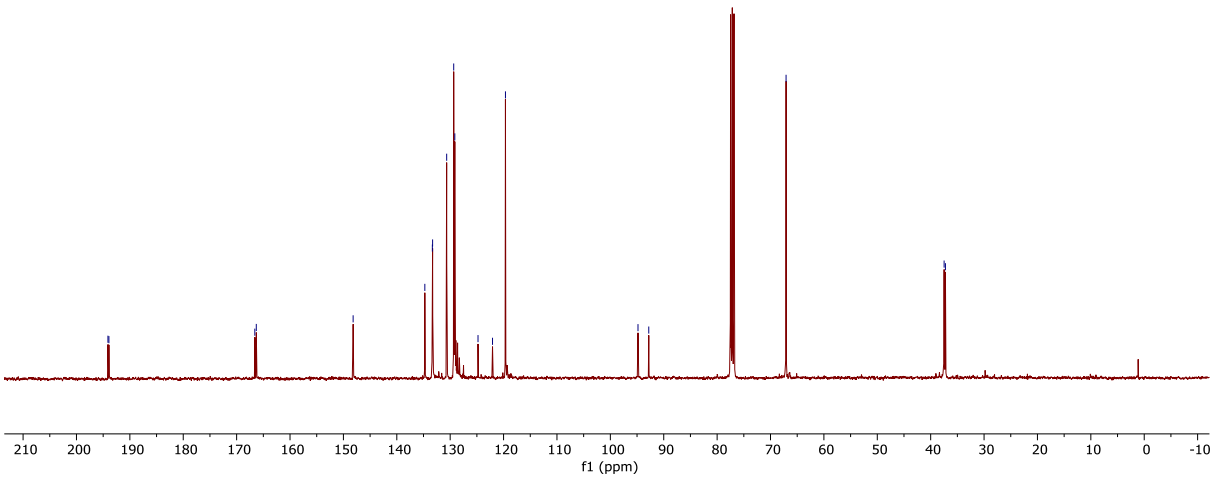
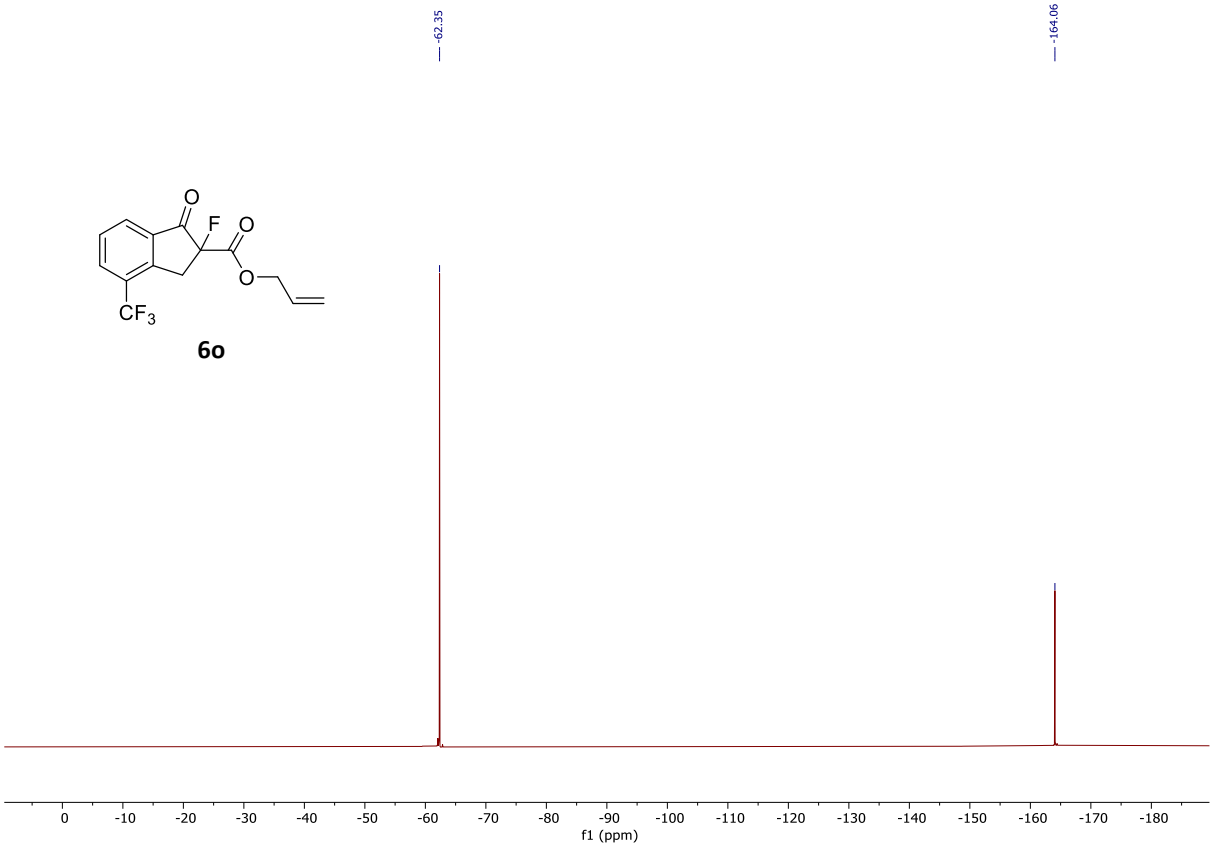
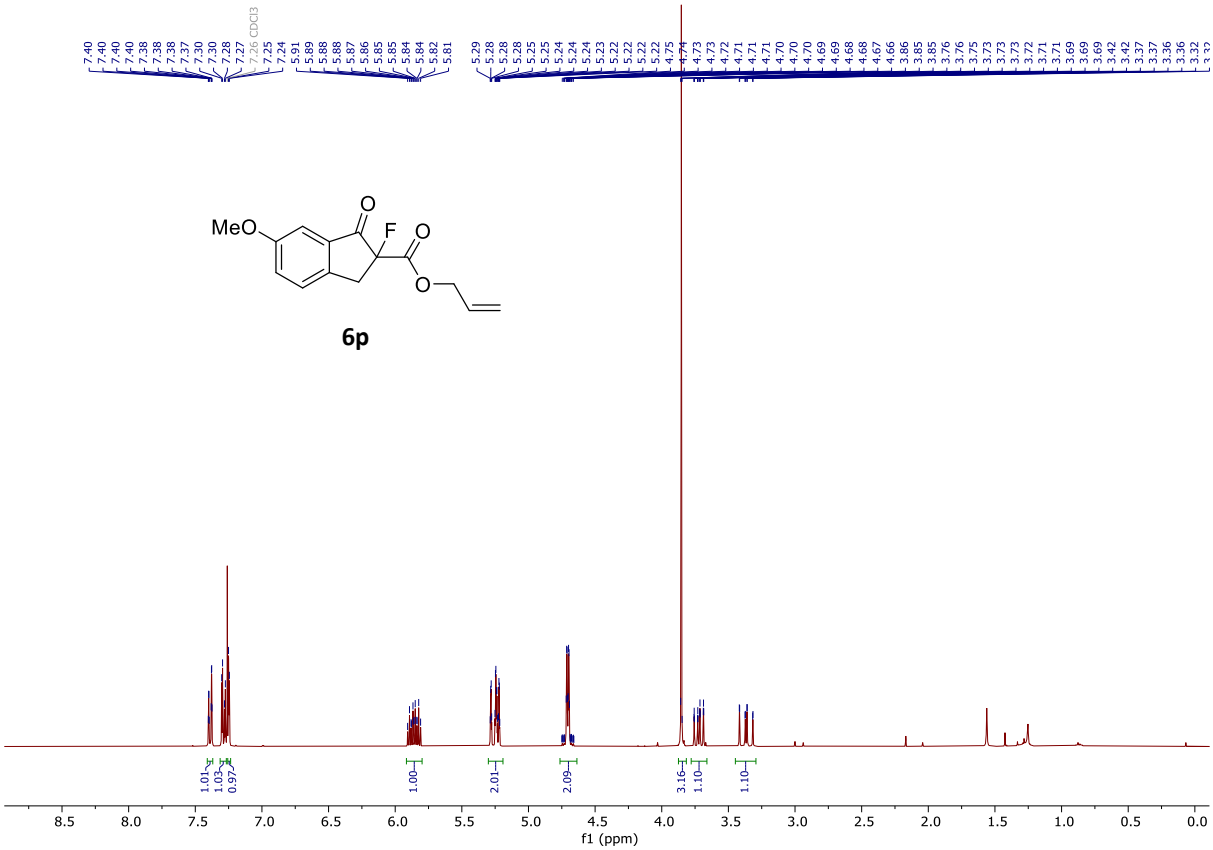


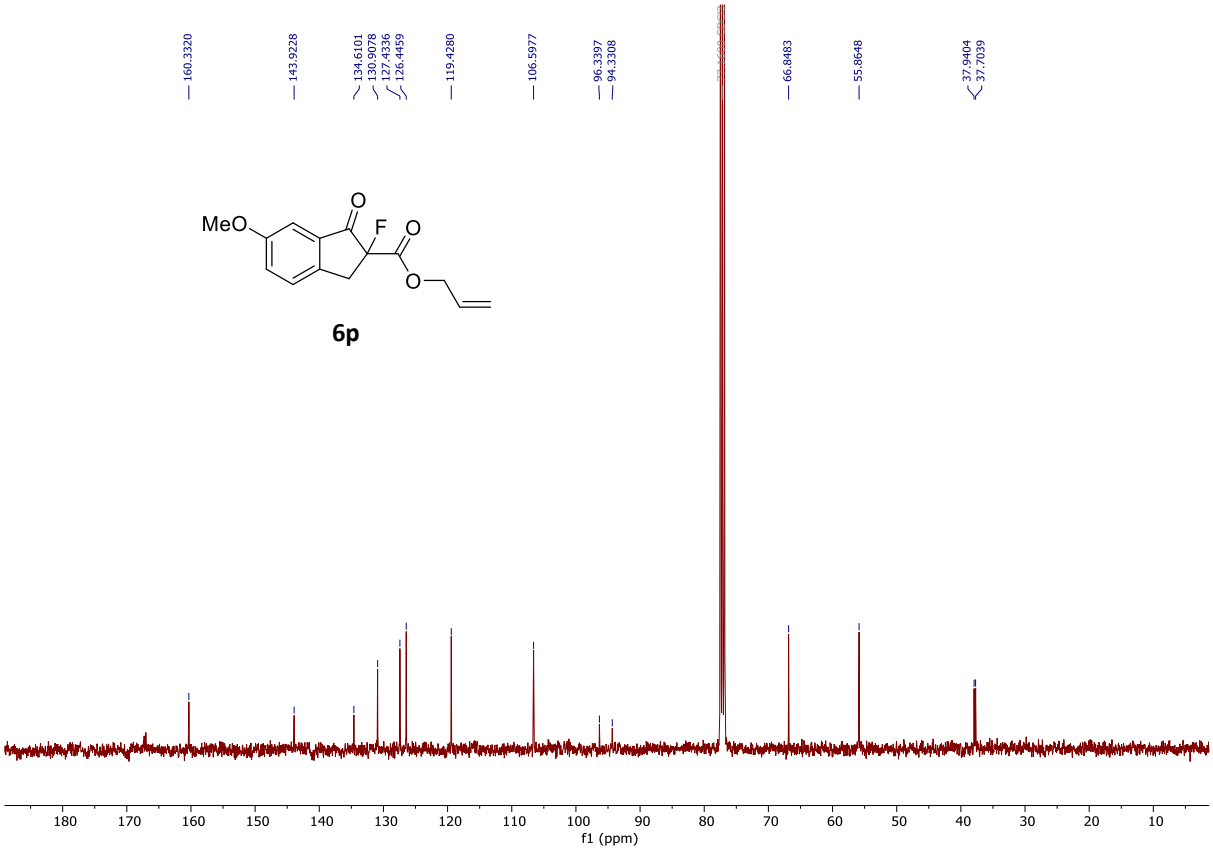
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)



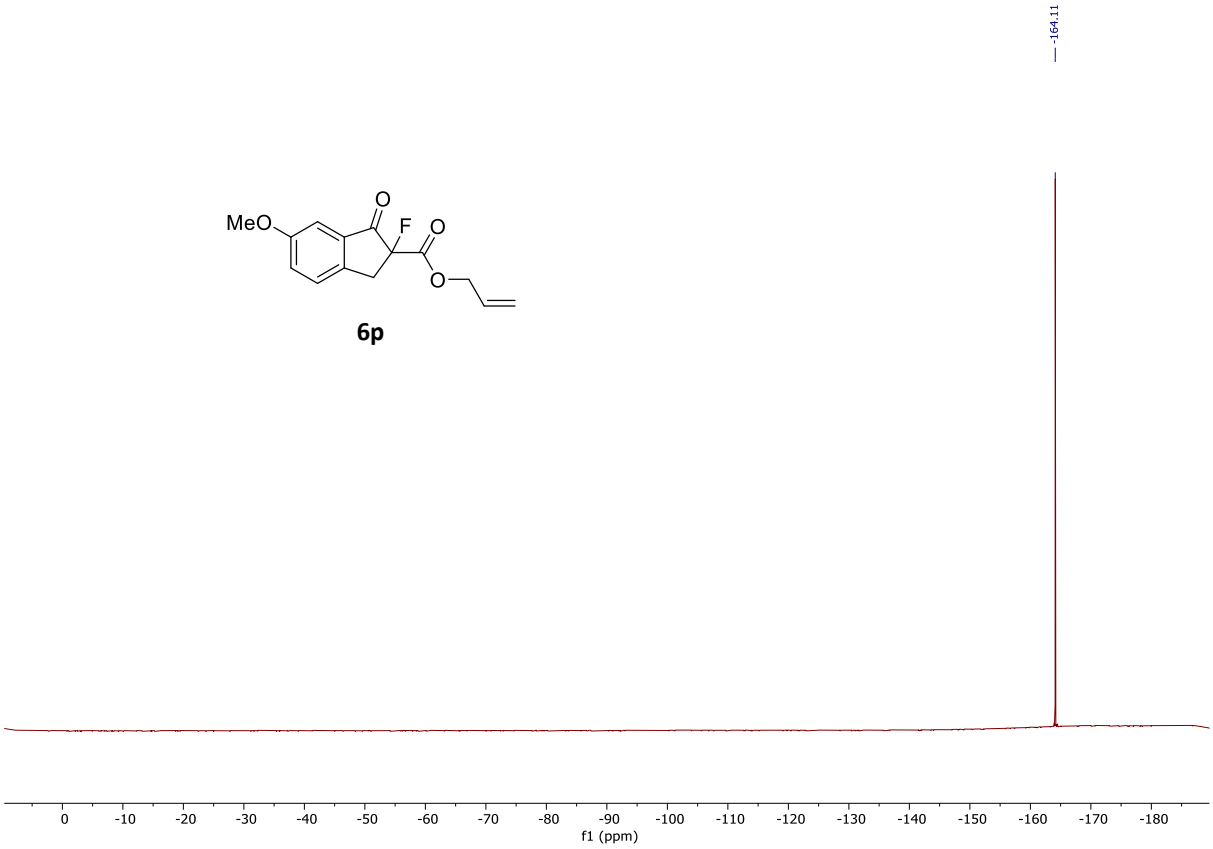
$^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$)



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



$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



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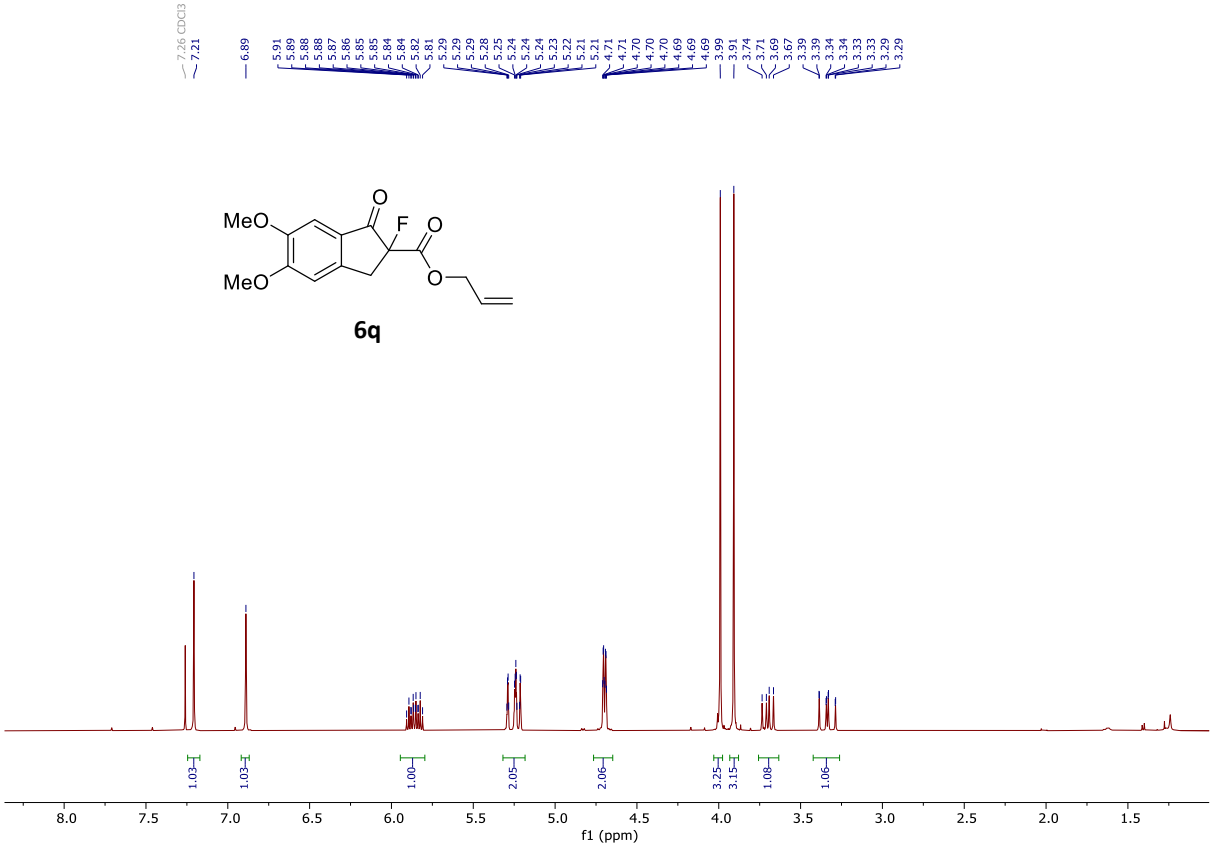
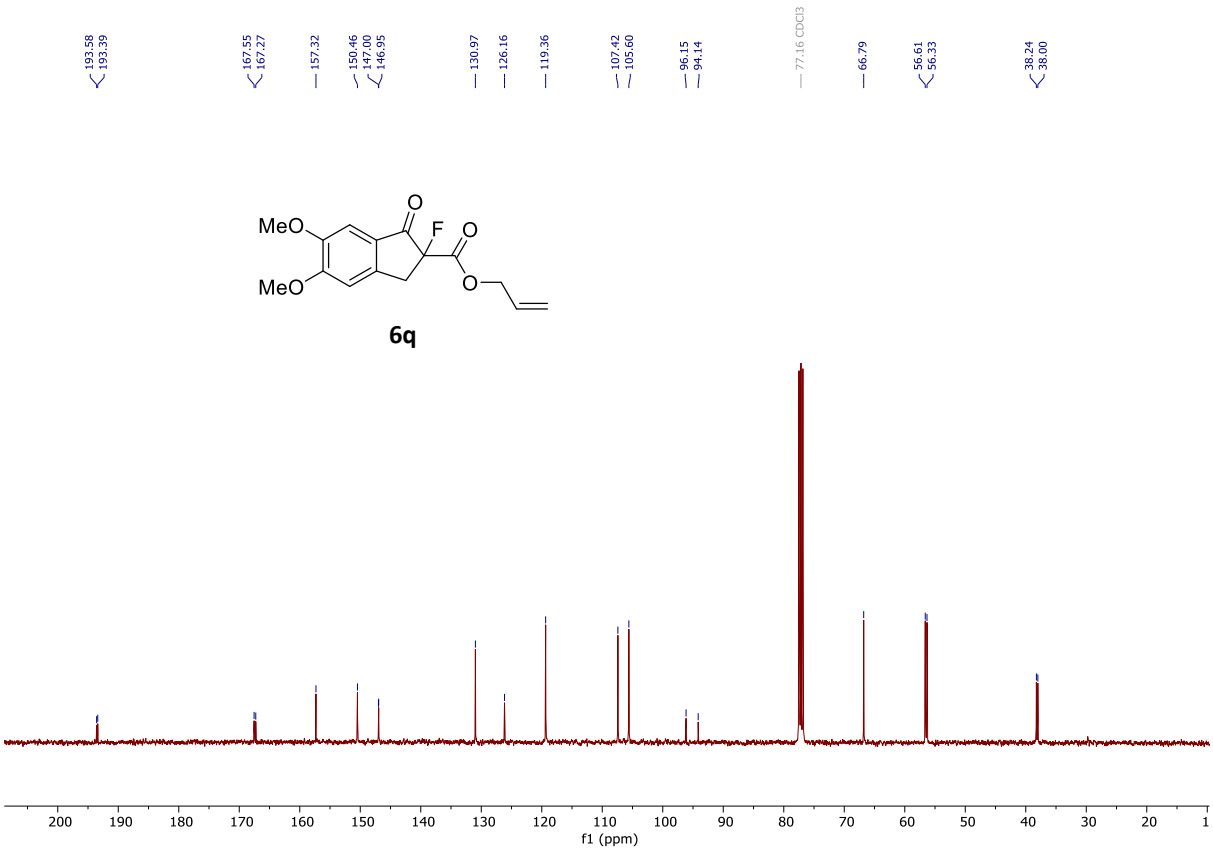
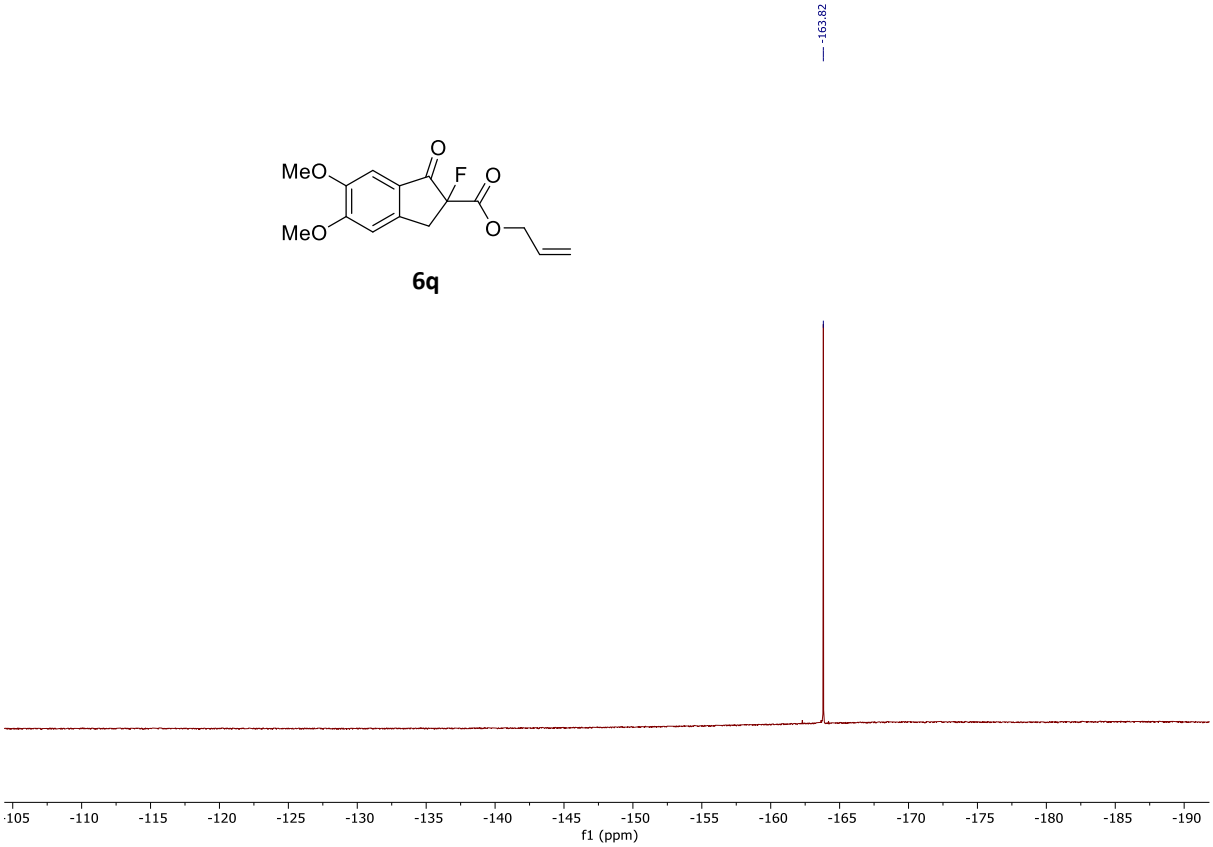


^{1}H NMR (400 MHz, $CDCl_3$)

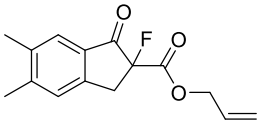


$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)

6q



$^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$)



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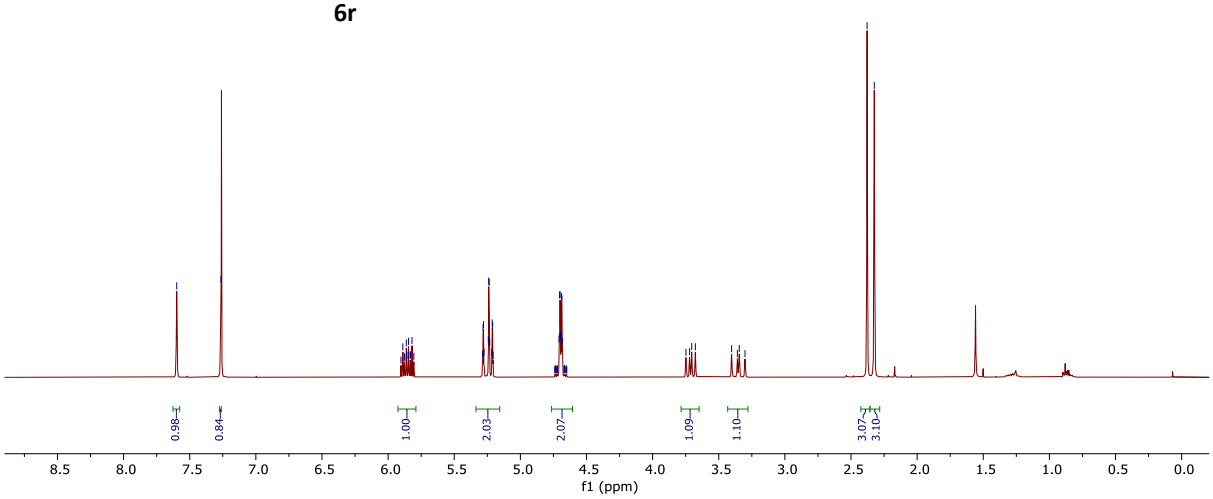
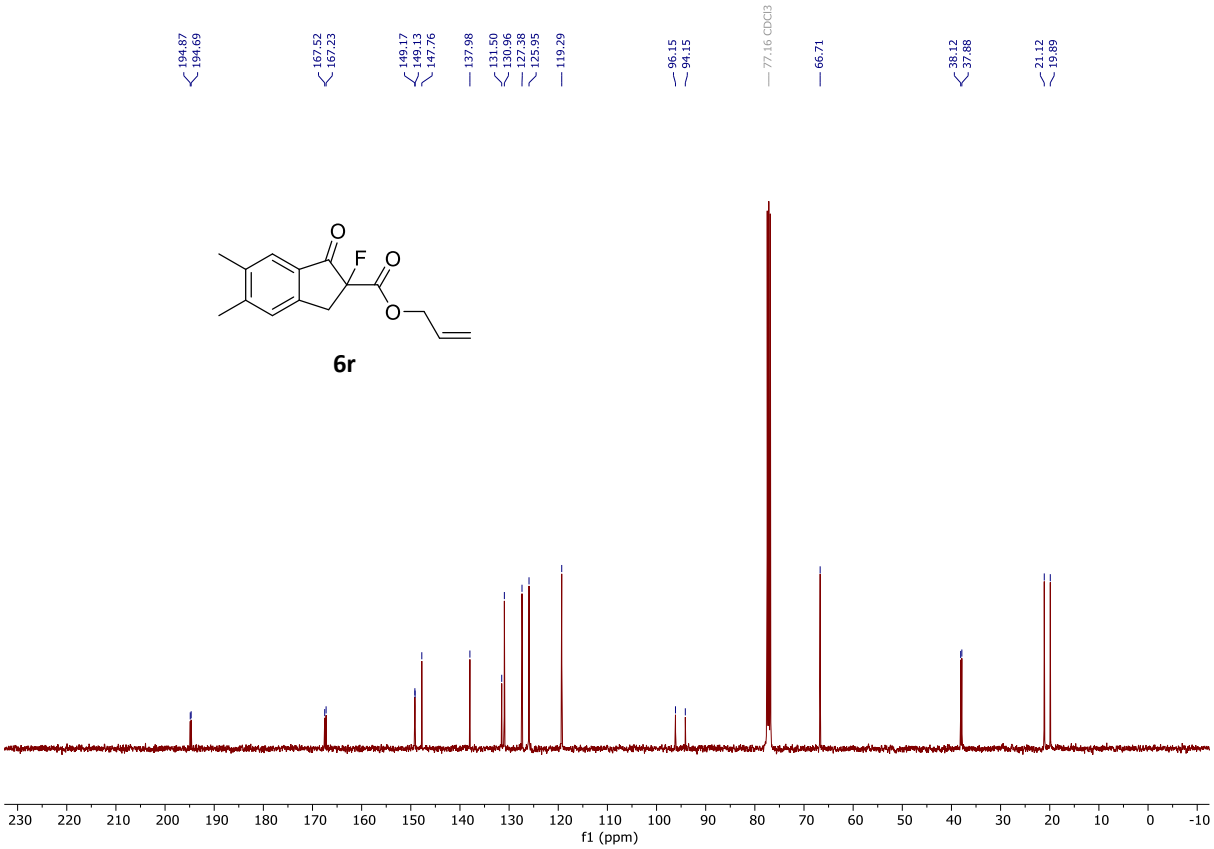
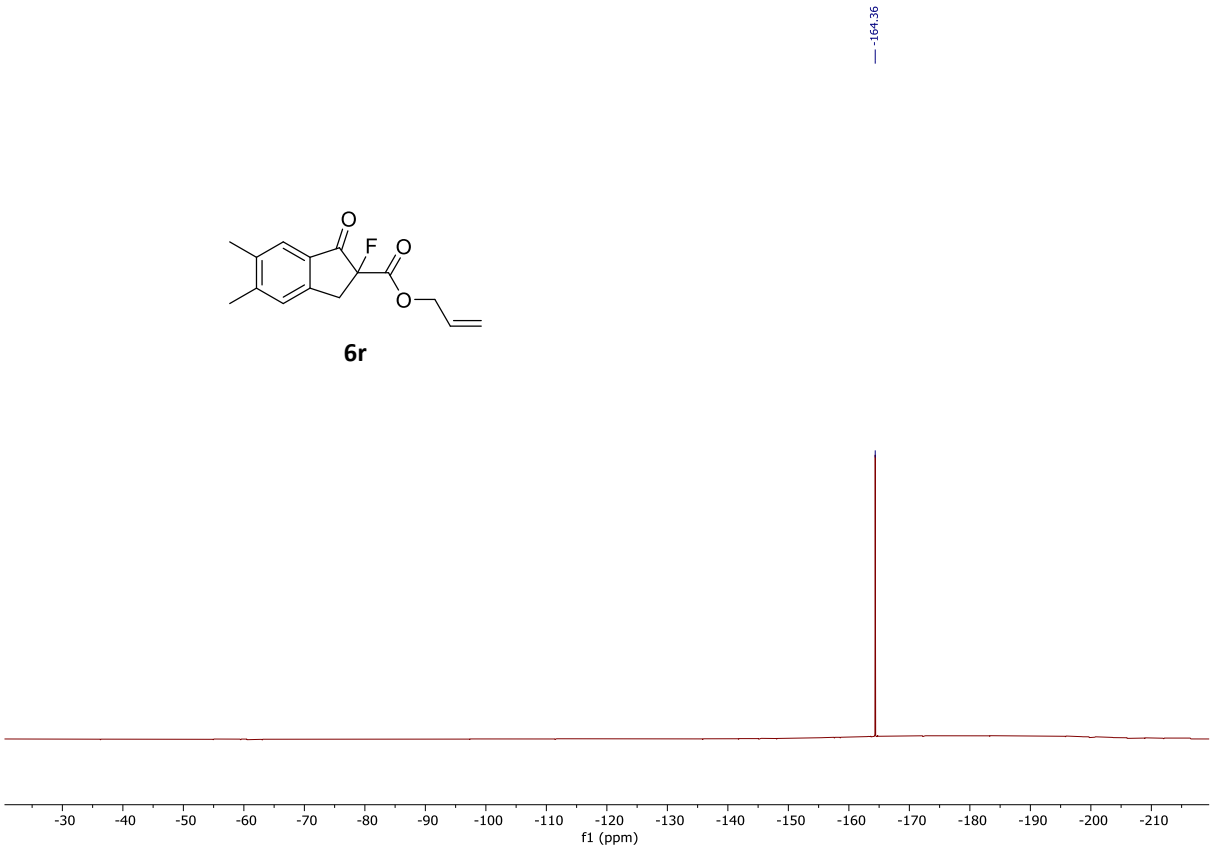


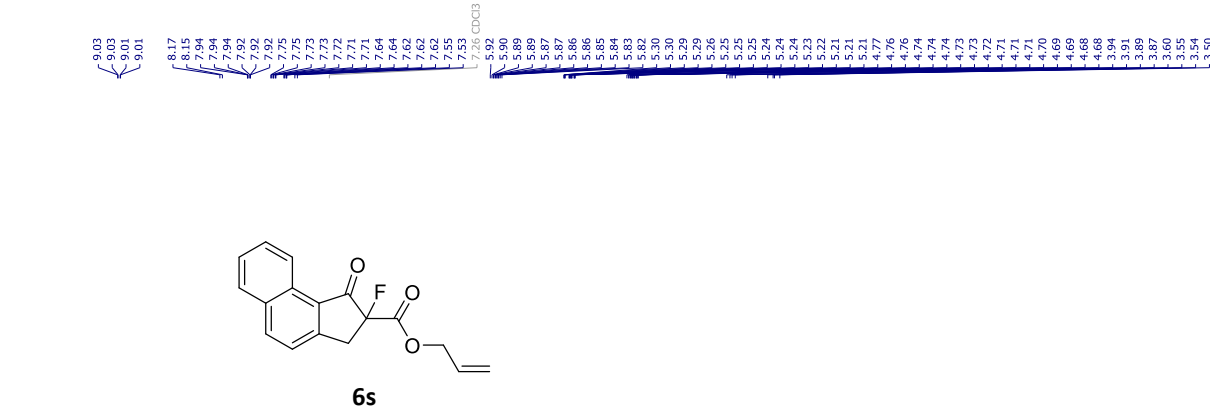
^{1}H NMR (400 MHz, $CDCl_3$)



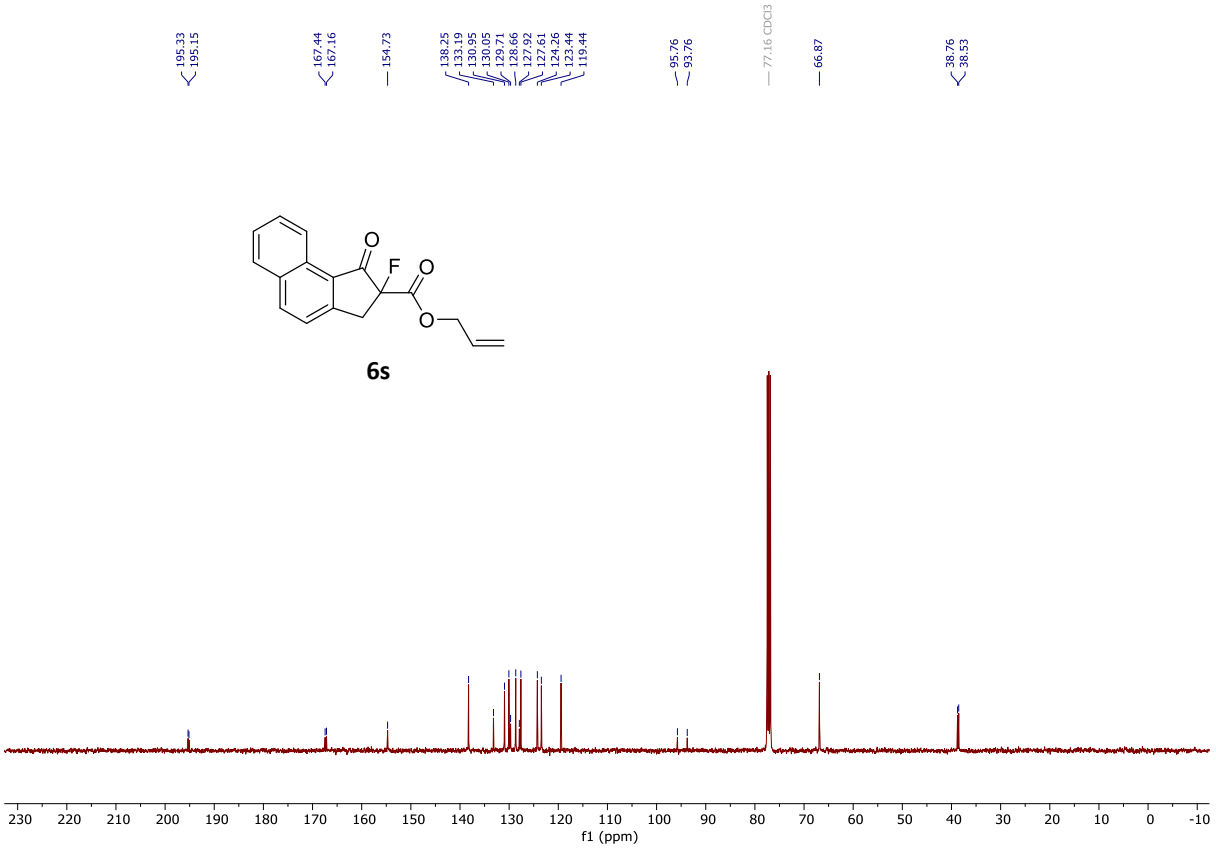
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



$^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$)

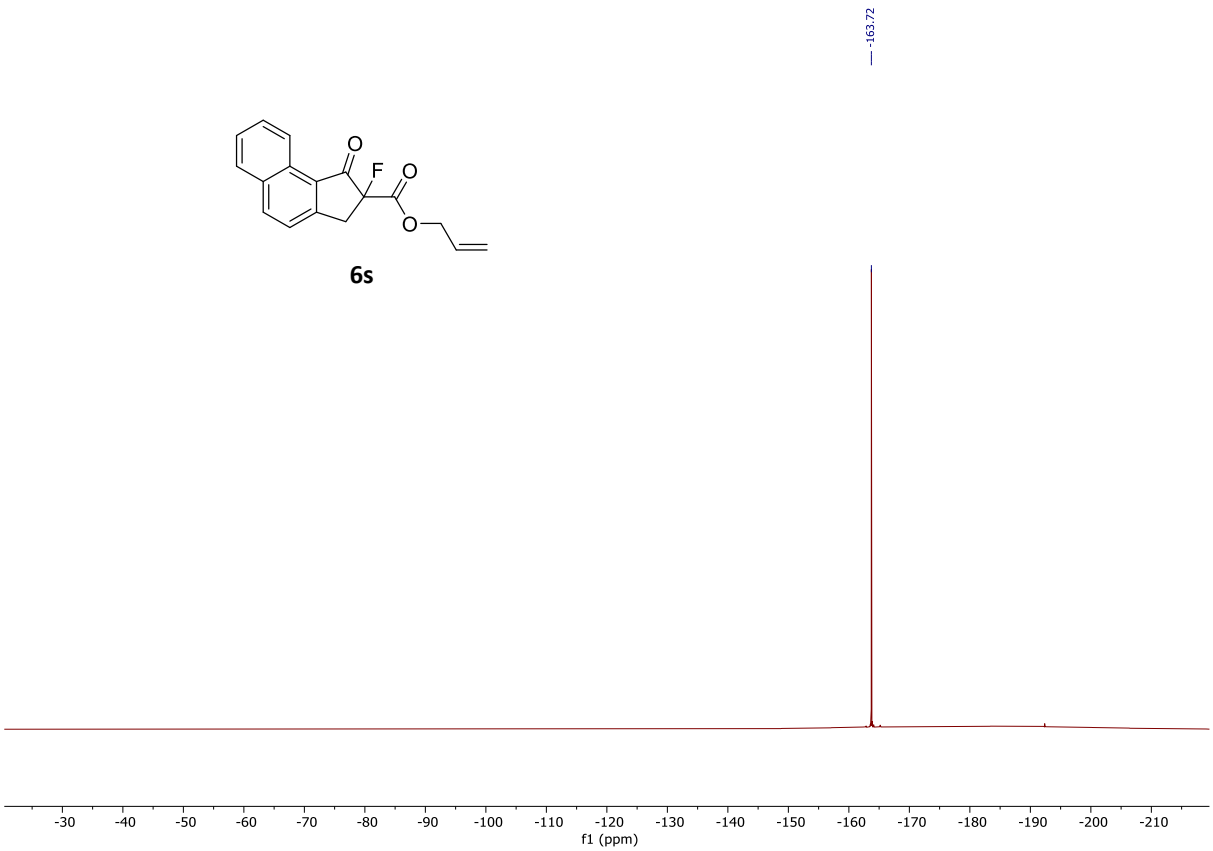


^{1}H NMR (400 MHz, $CDCl_3$)

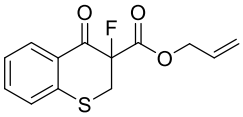


^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)

6s



$^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$)



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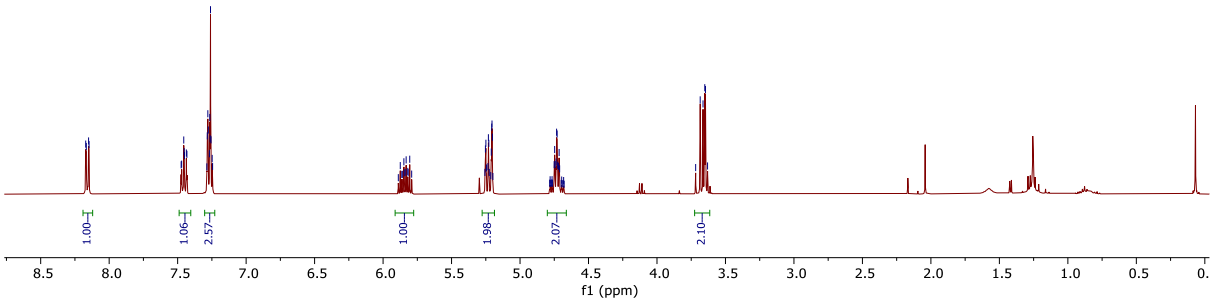
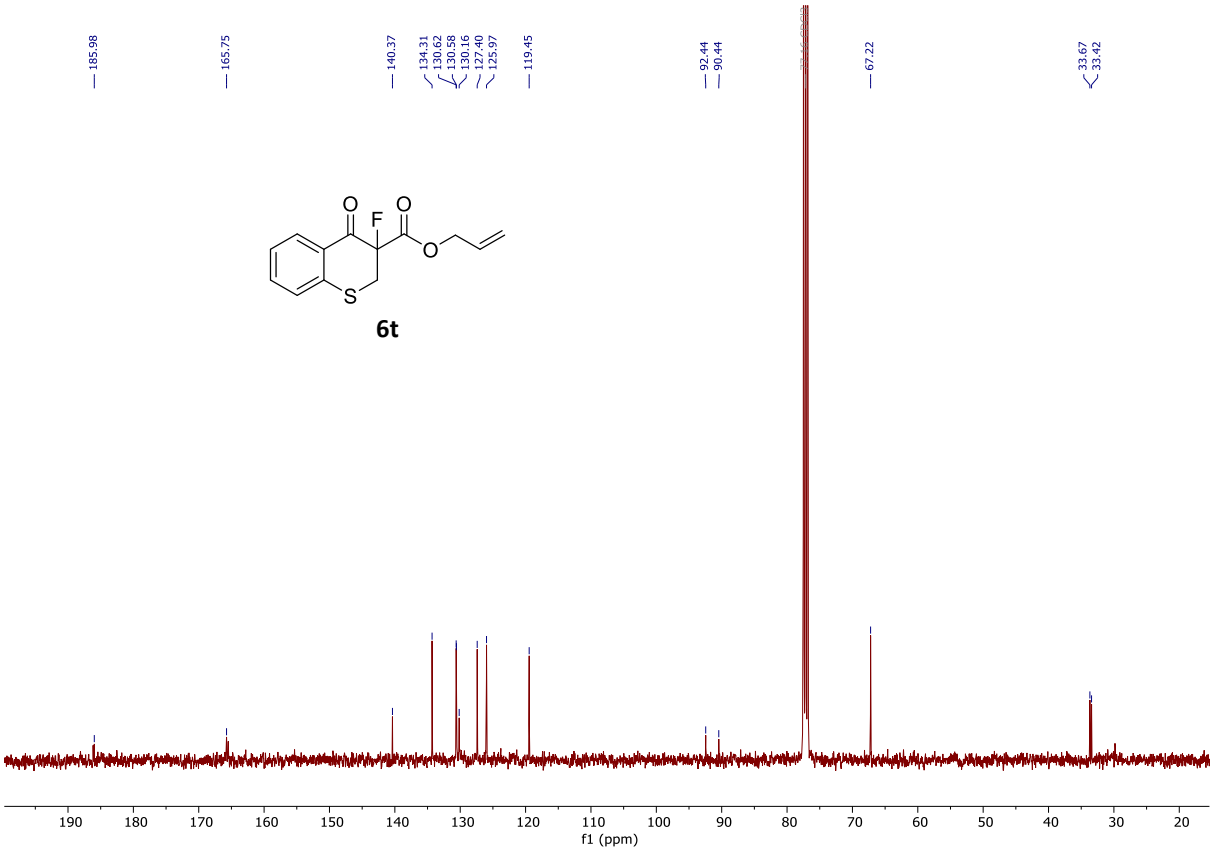
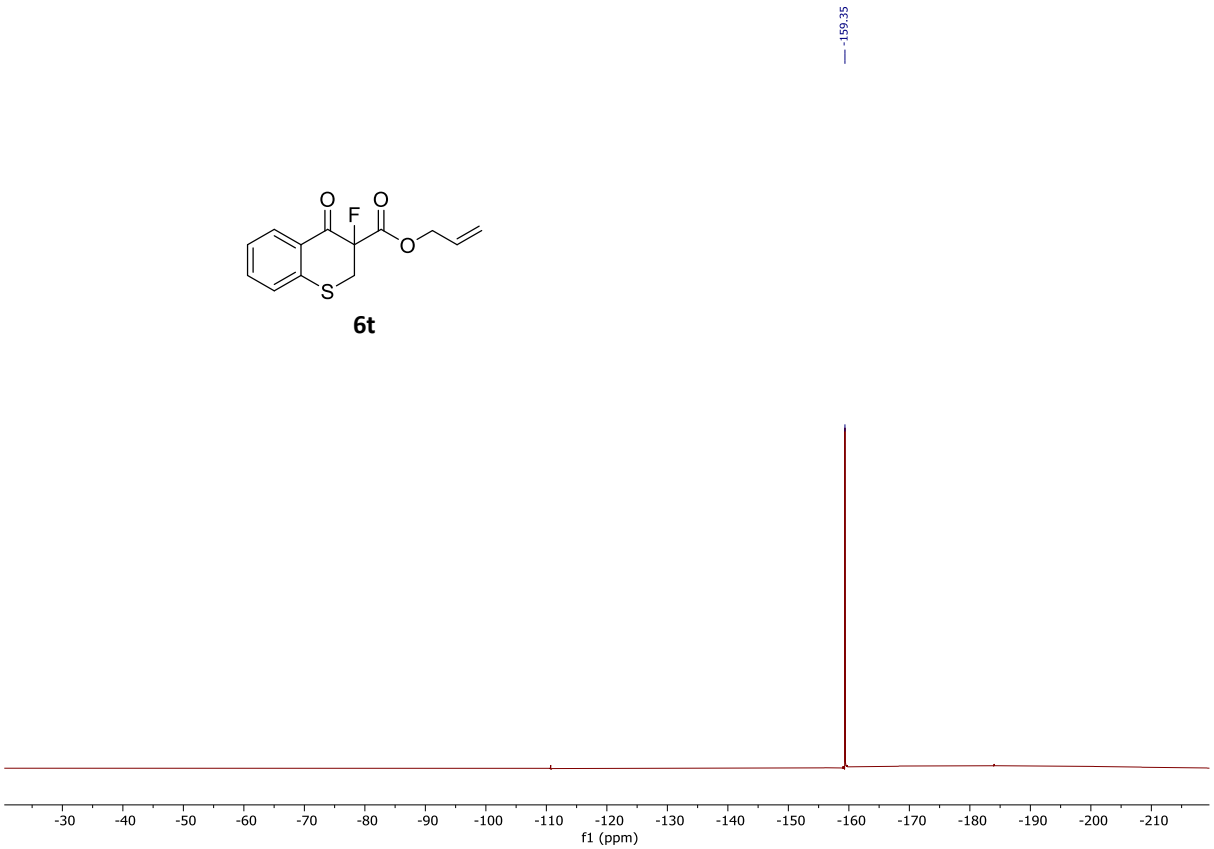


^{1}H NMR (400 MHz, $CDCl_3$)

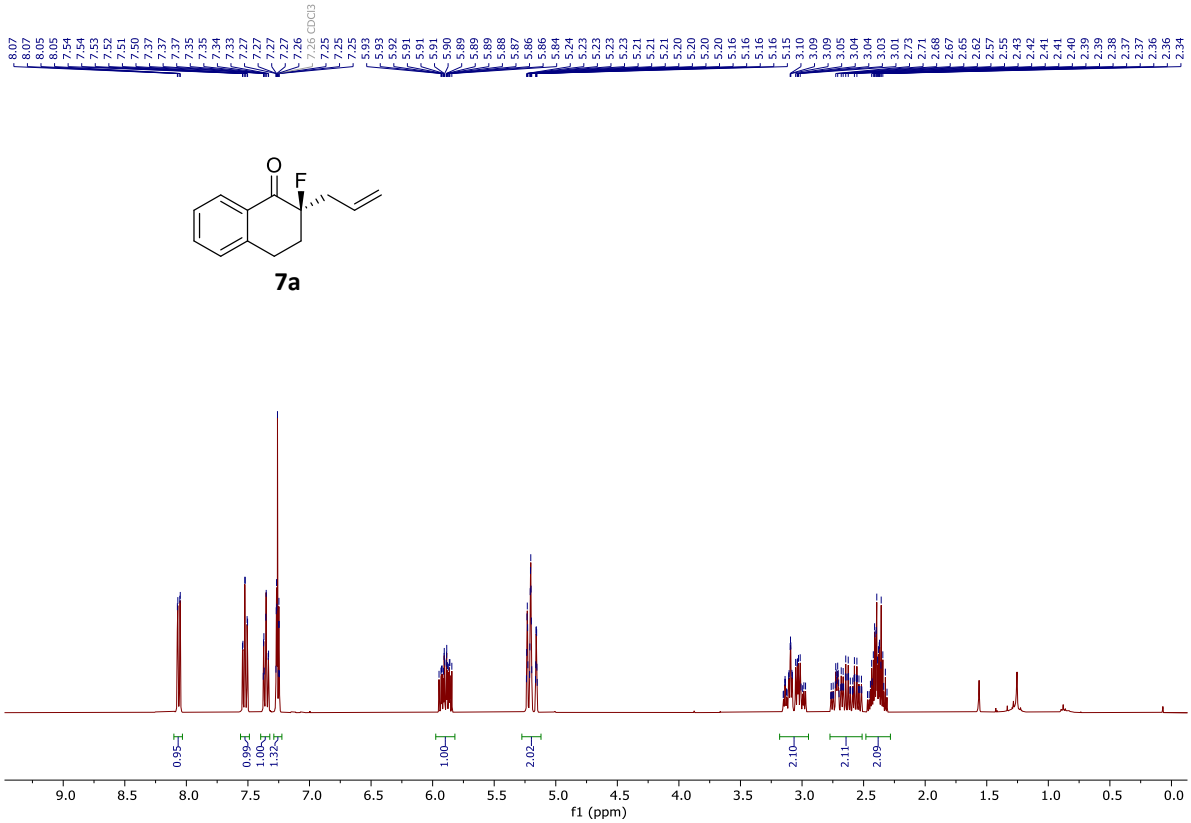


$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)

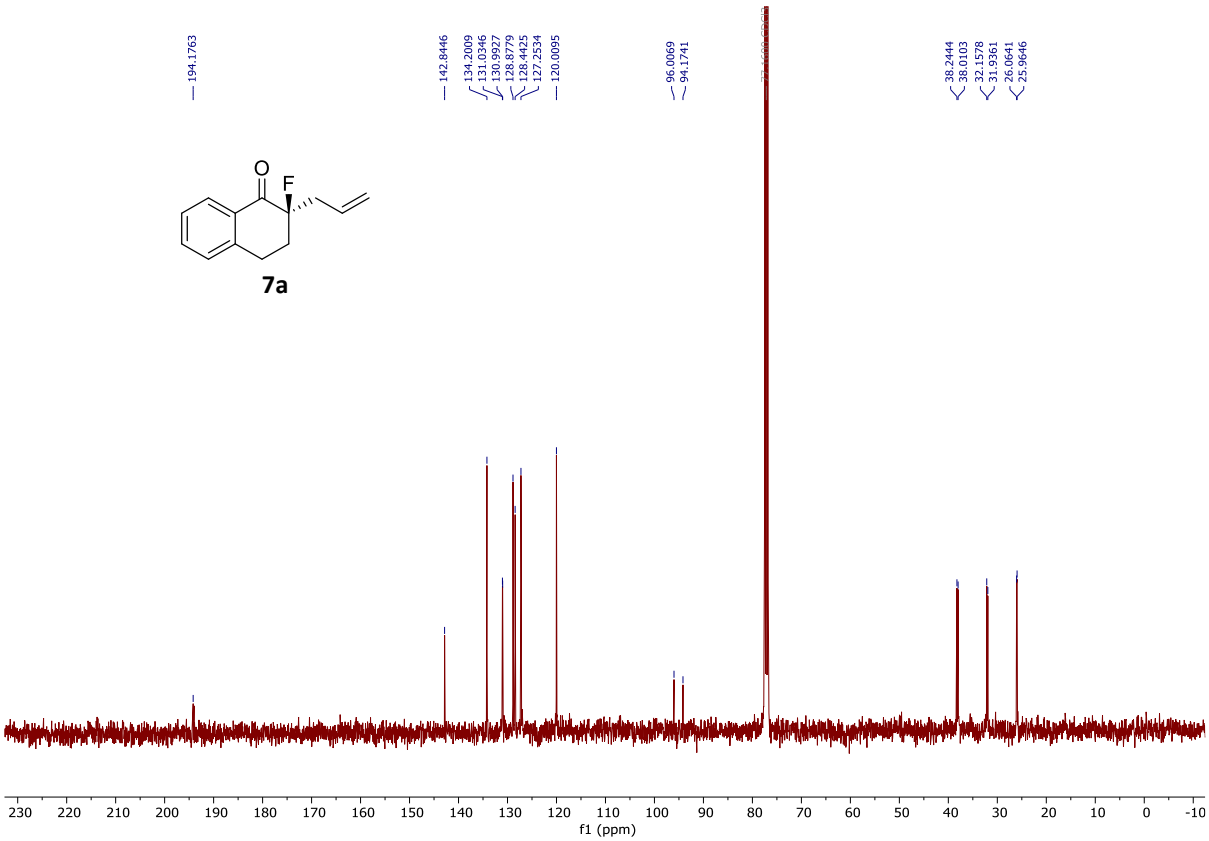


$^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$)

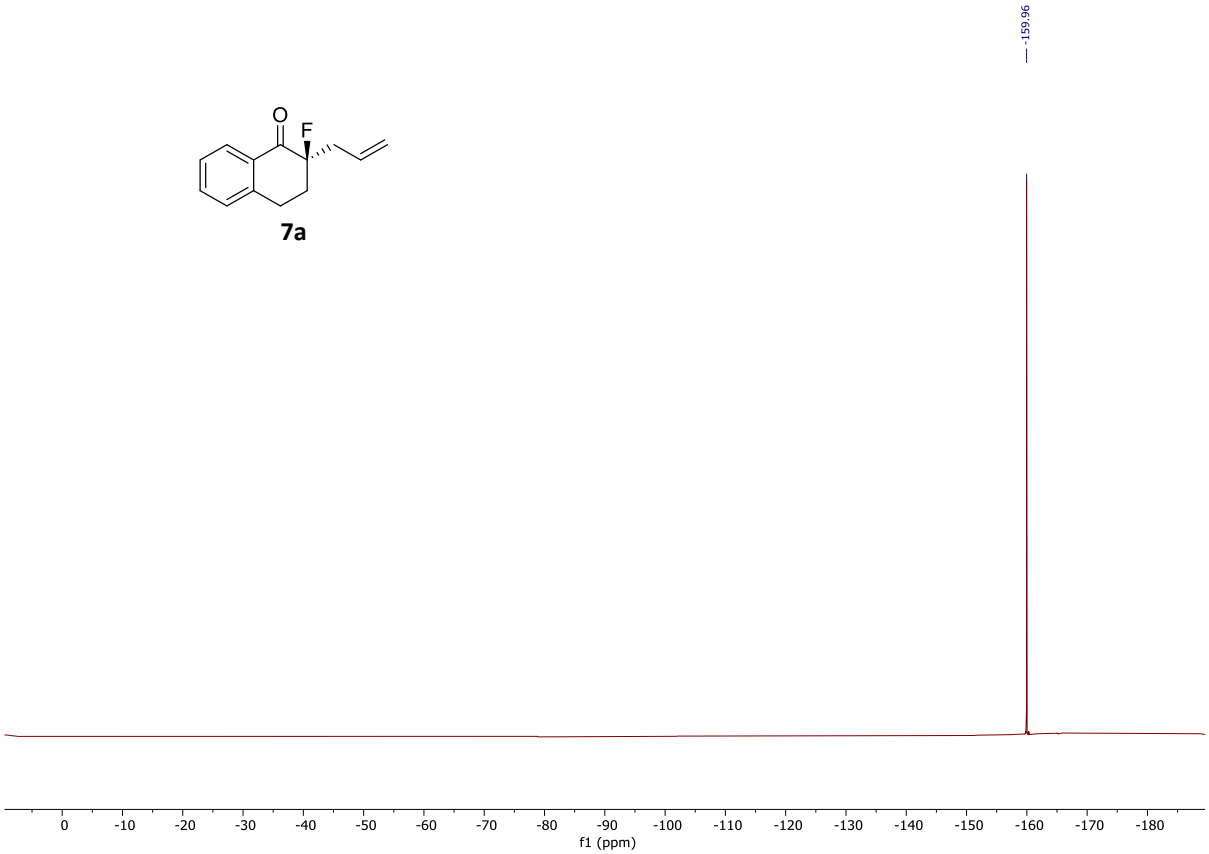
12. NMR spectra for compounds **7a – 7t**



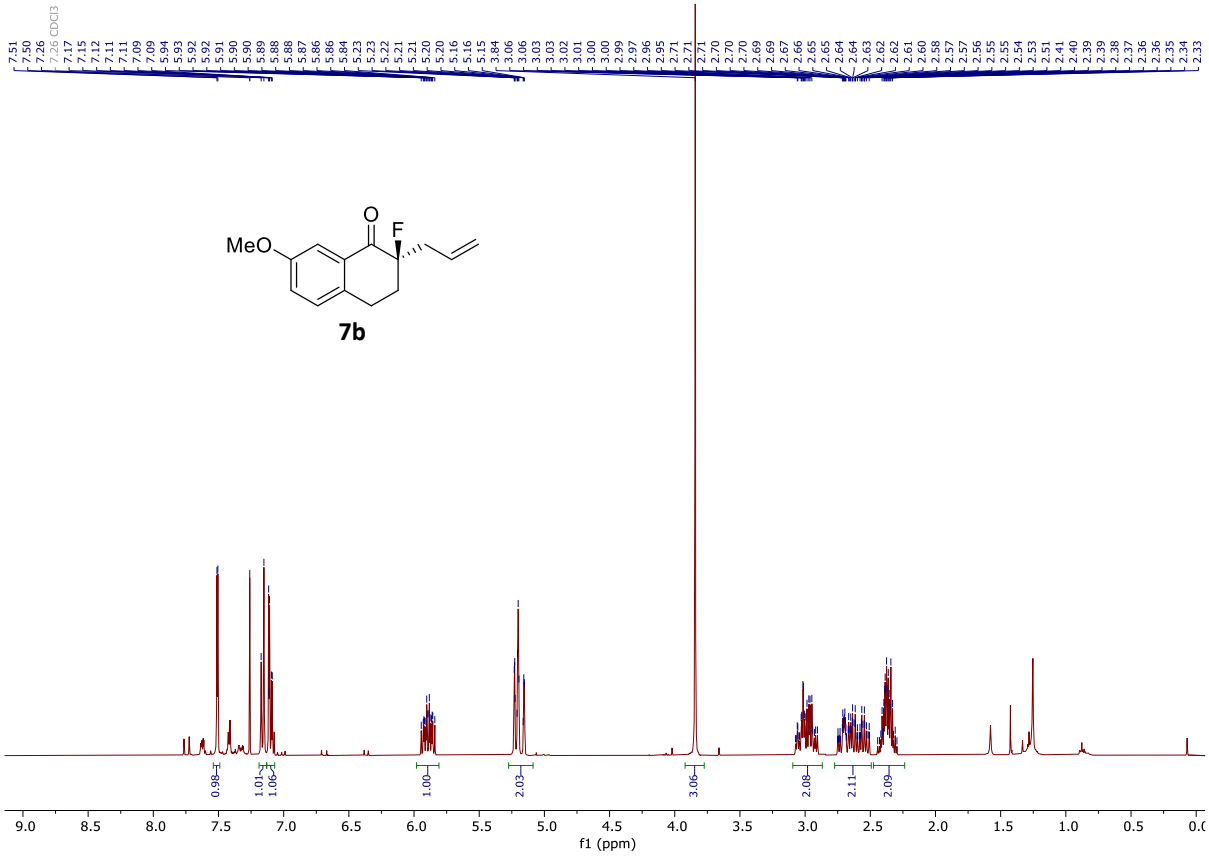
^{1}H NMR (400 MHz, $CDCl_3$)



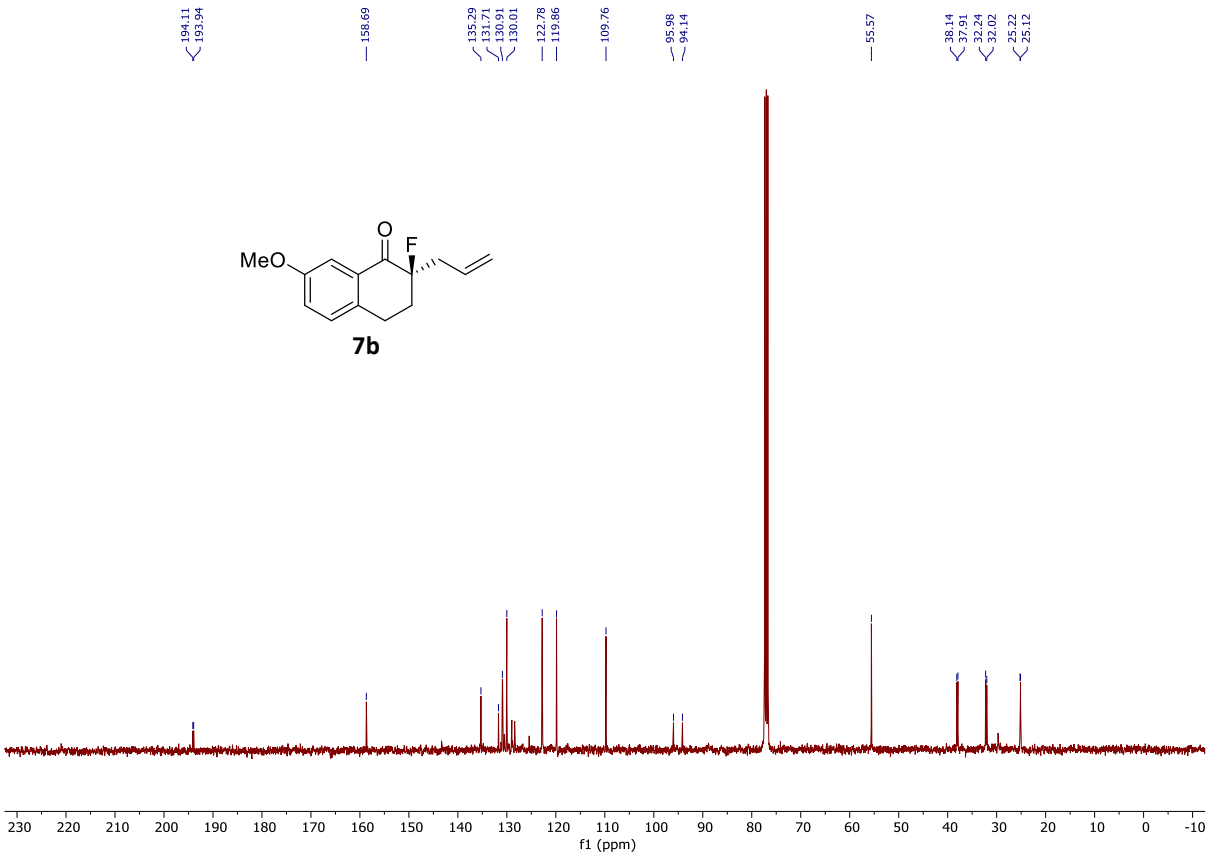
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



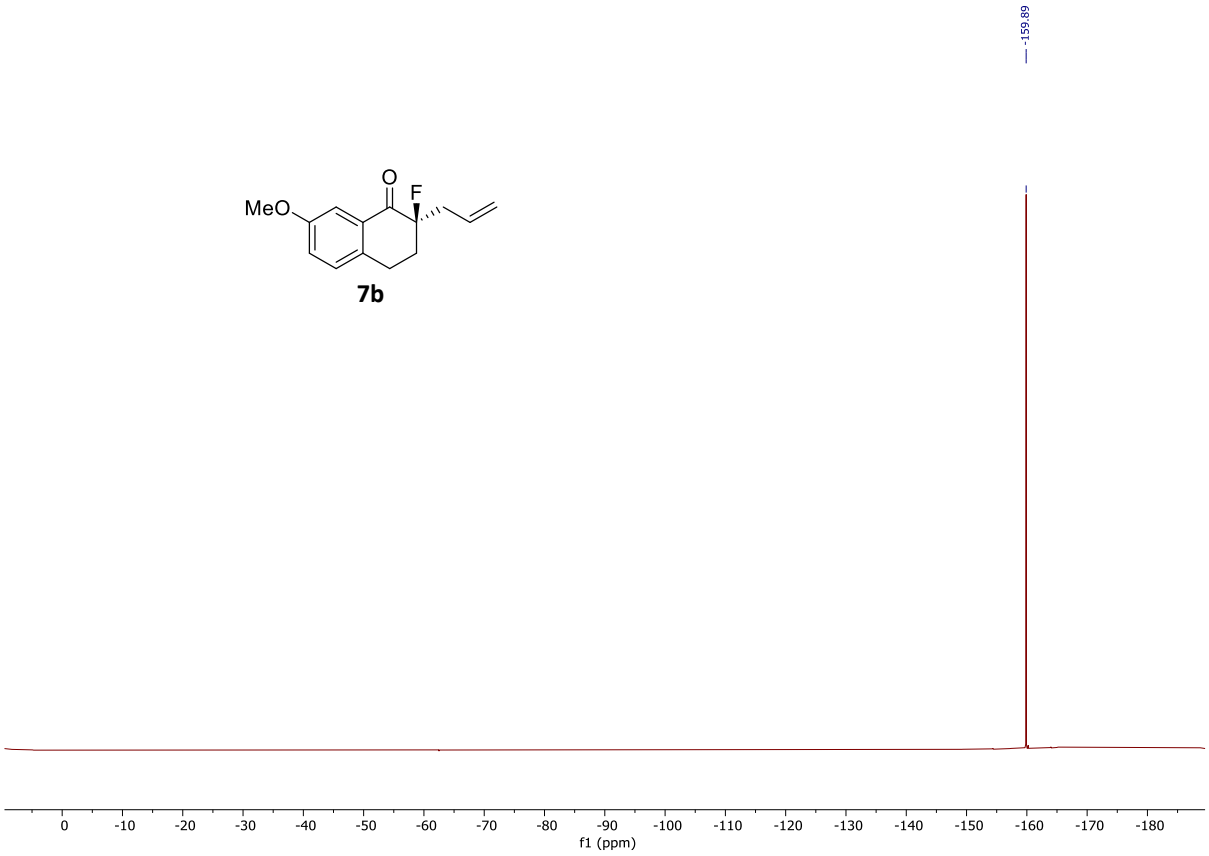
$^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$)



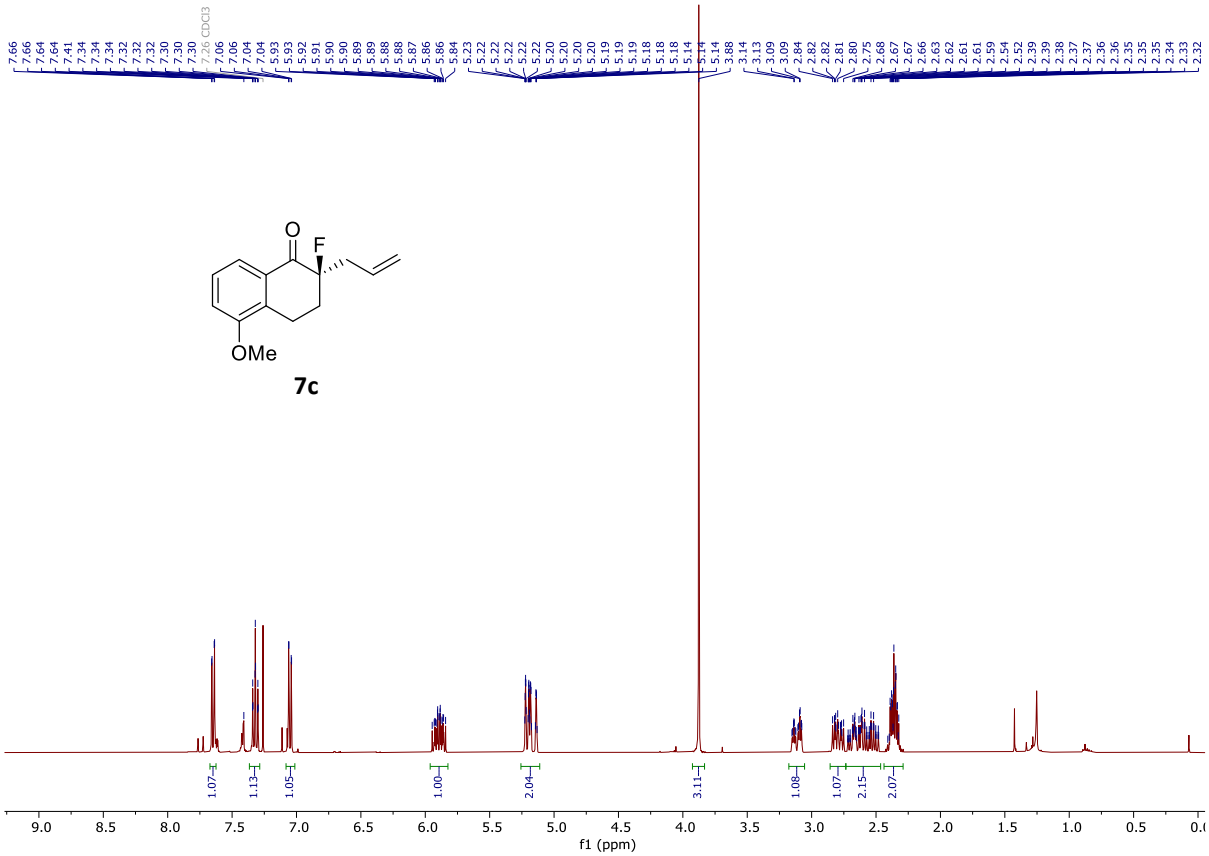
^{1}H NMR (400 MHz, $CDCl_3$)



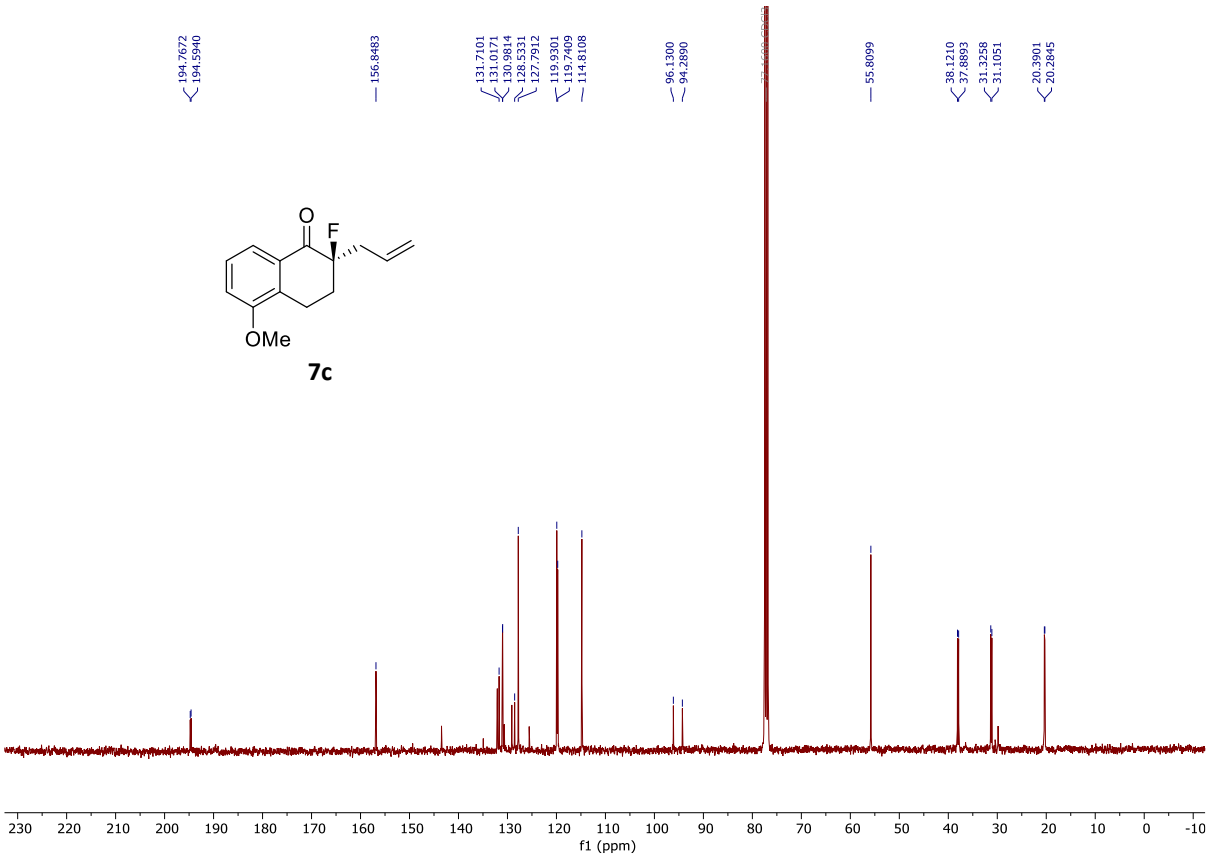
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



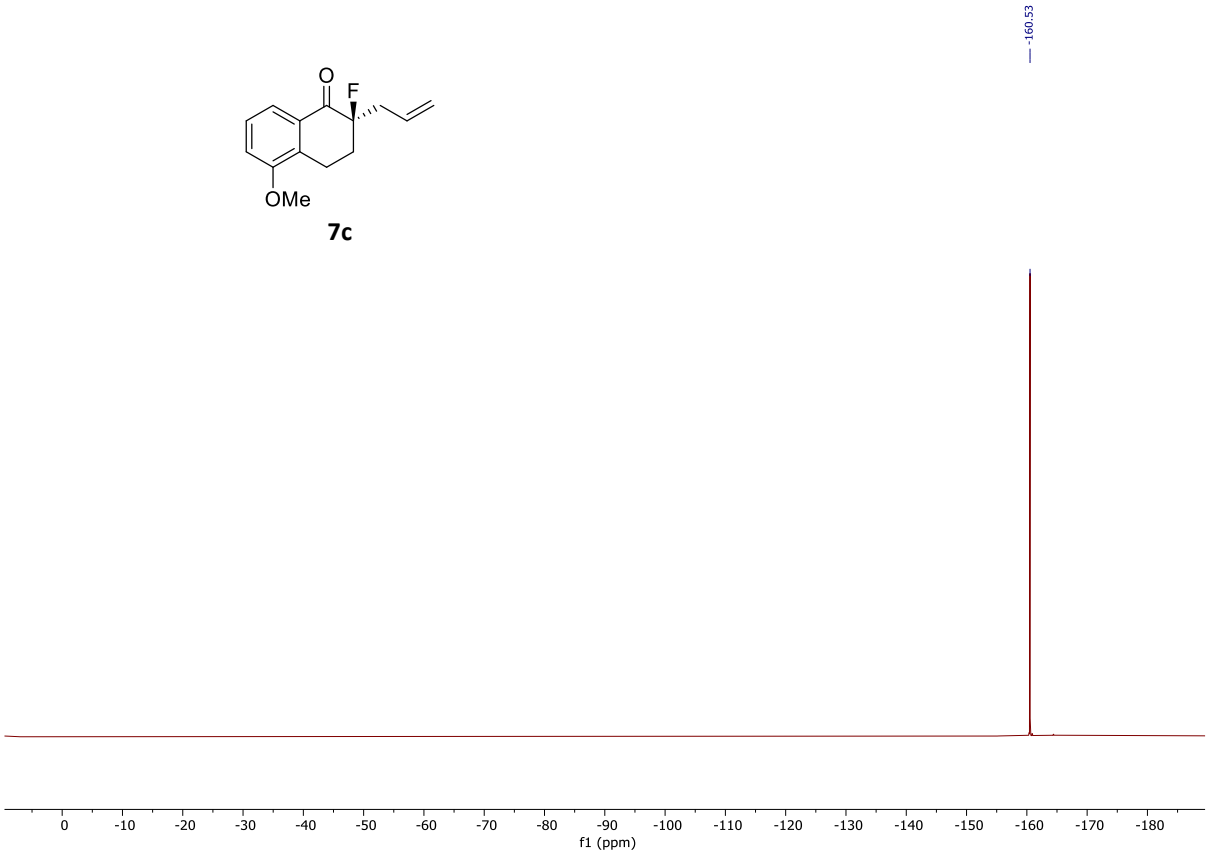
$^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$)



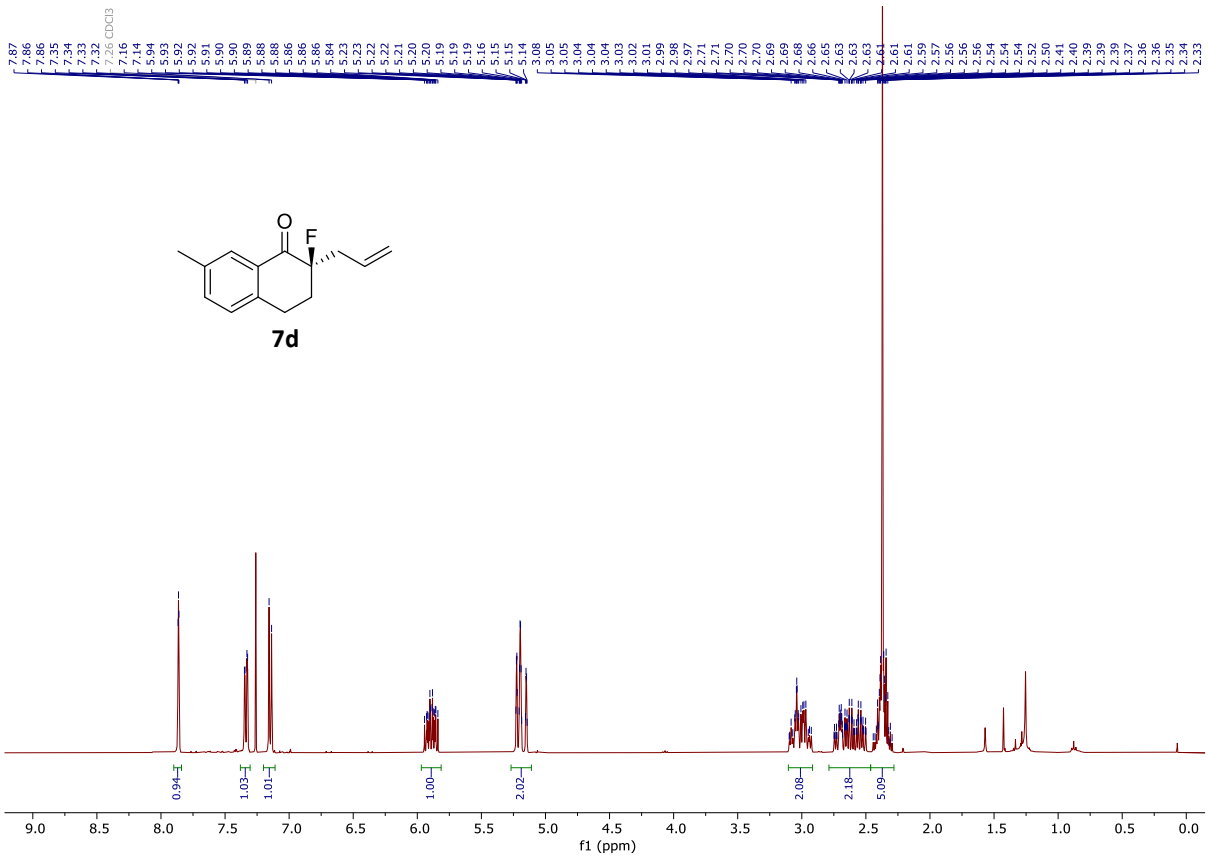
^{1}H NMR (400 MHz, $CDCl_3$



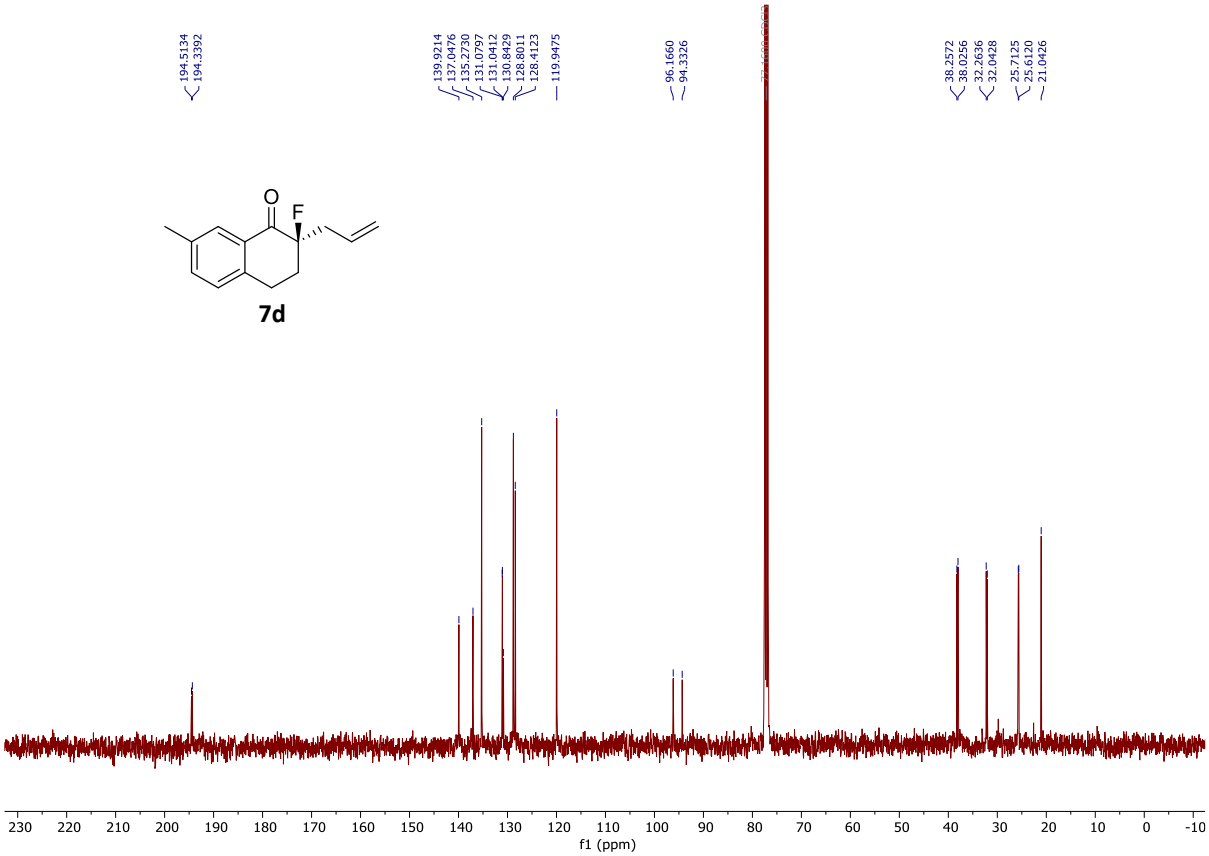
$^{13}C\{^{1}H\}$ NMR $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



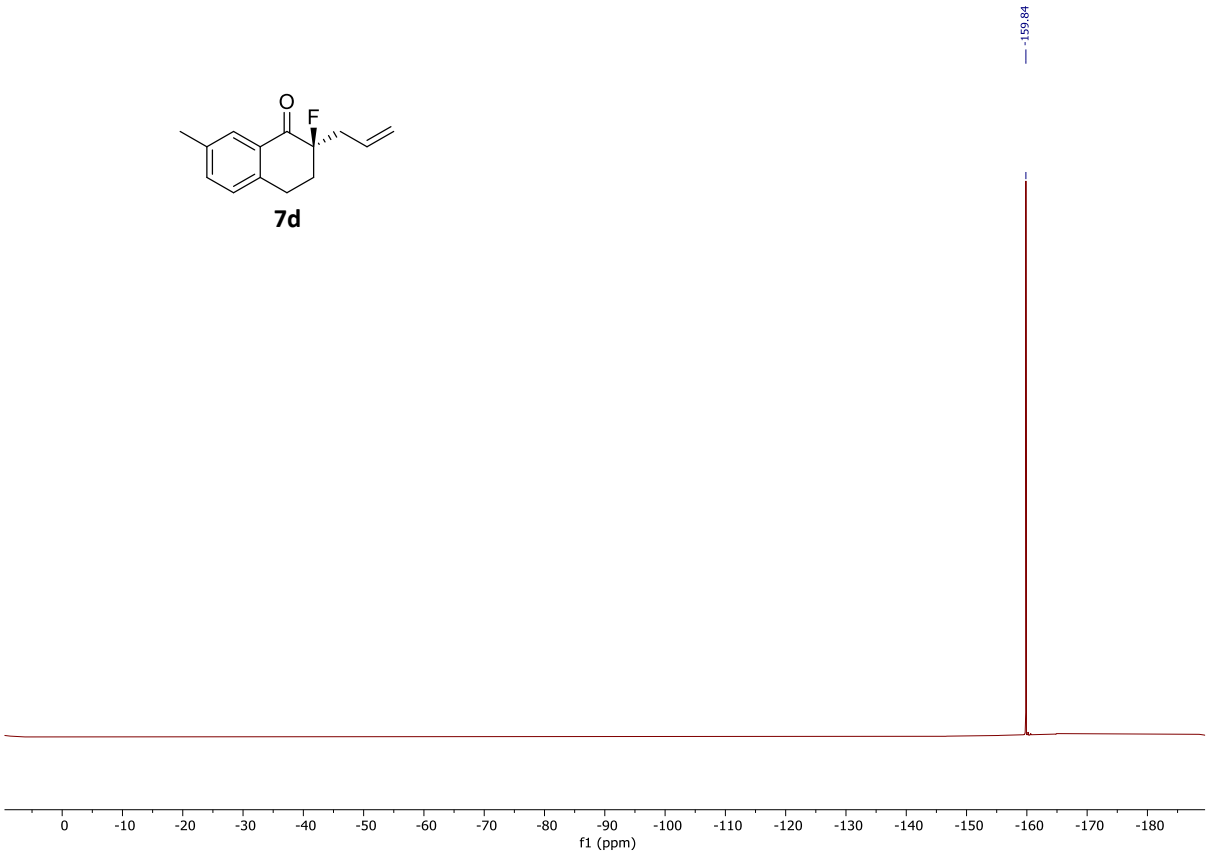
$^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$)



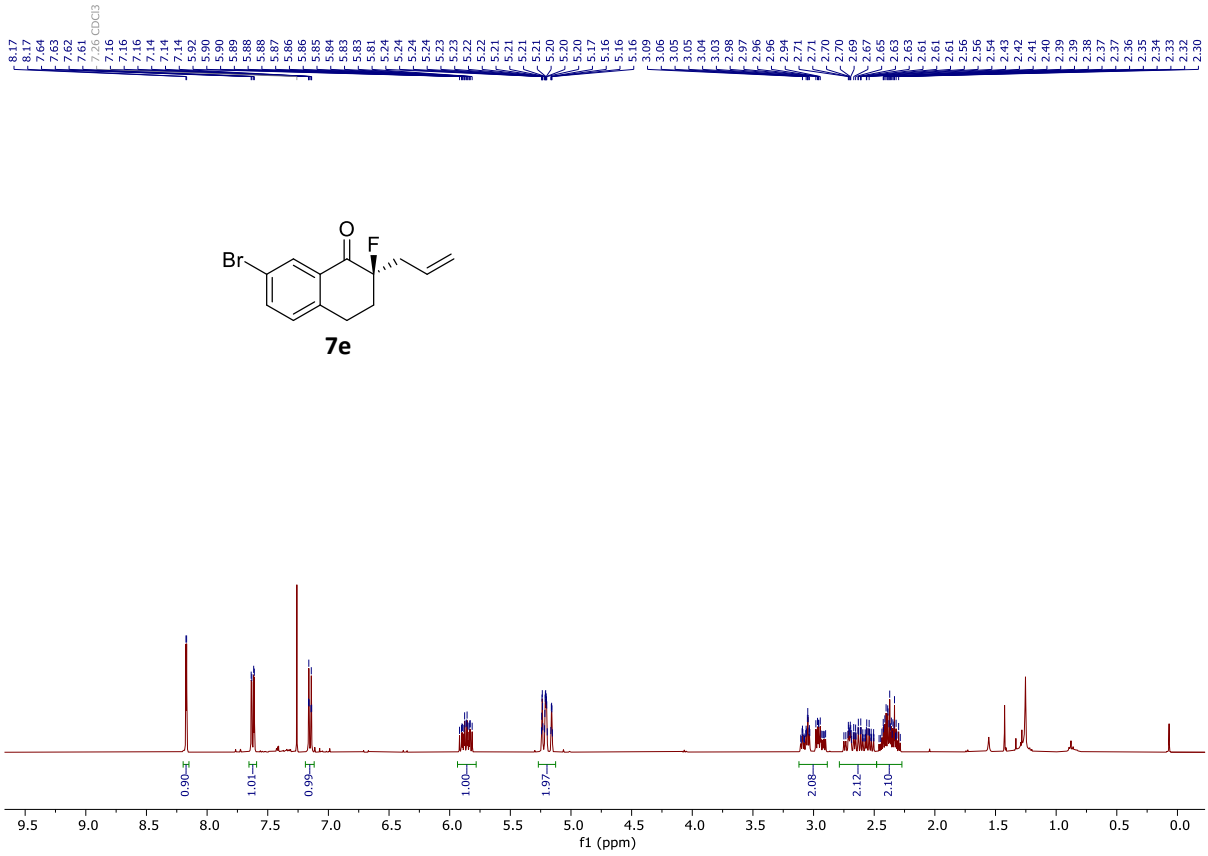
^{1}H NMR (400 MHz, $CDCl_3$)



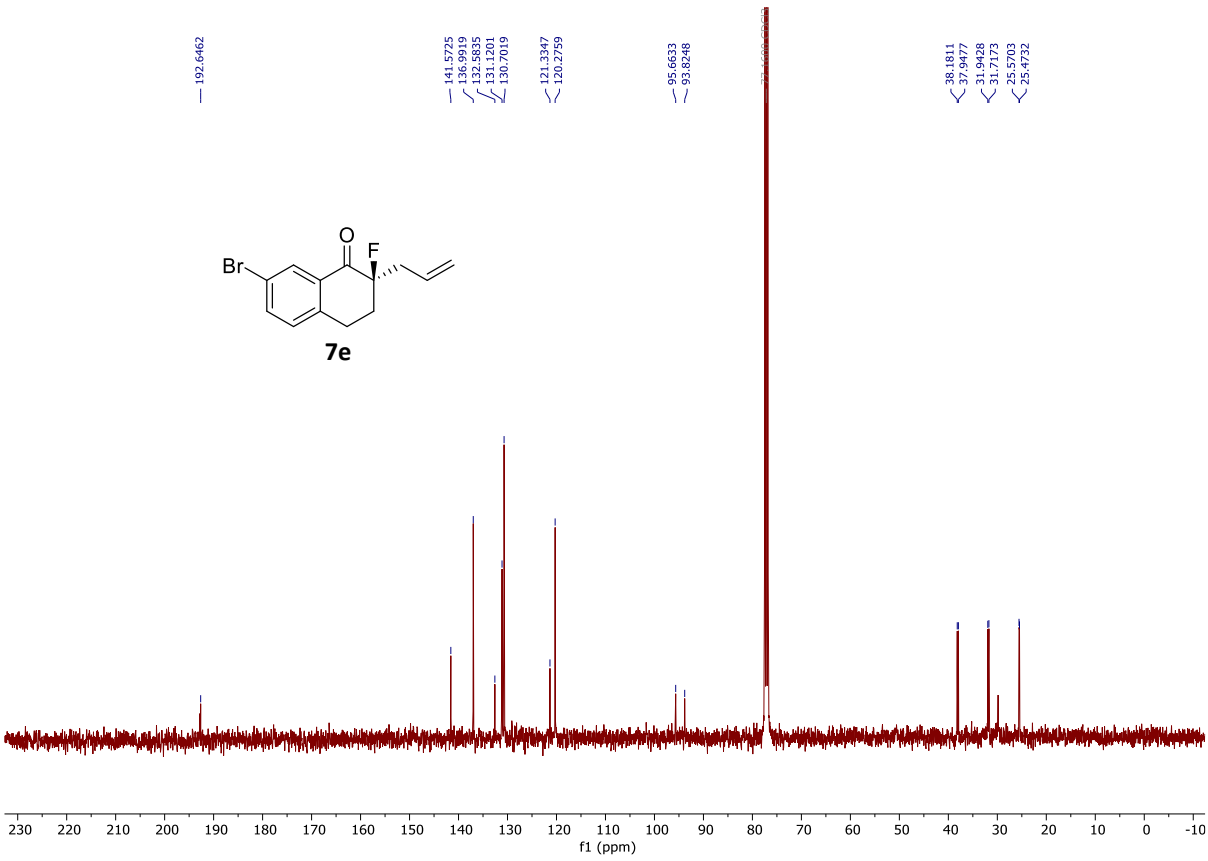
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



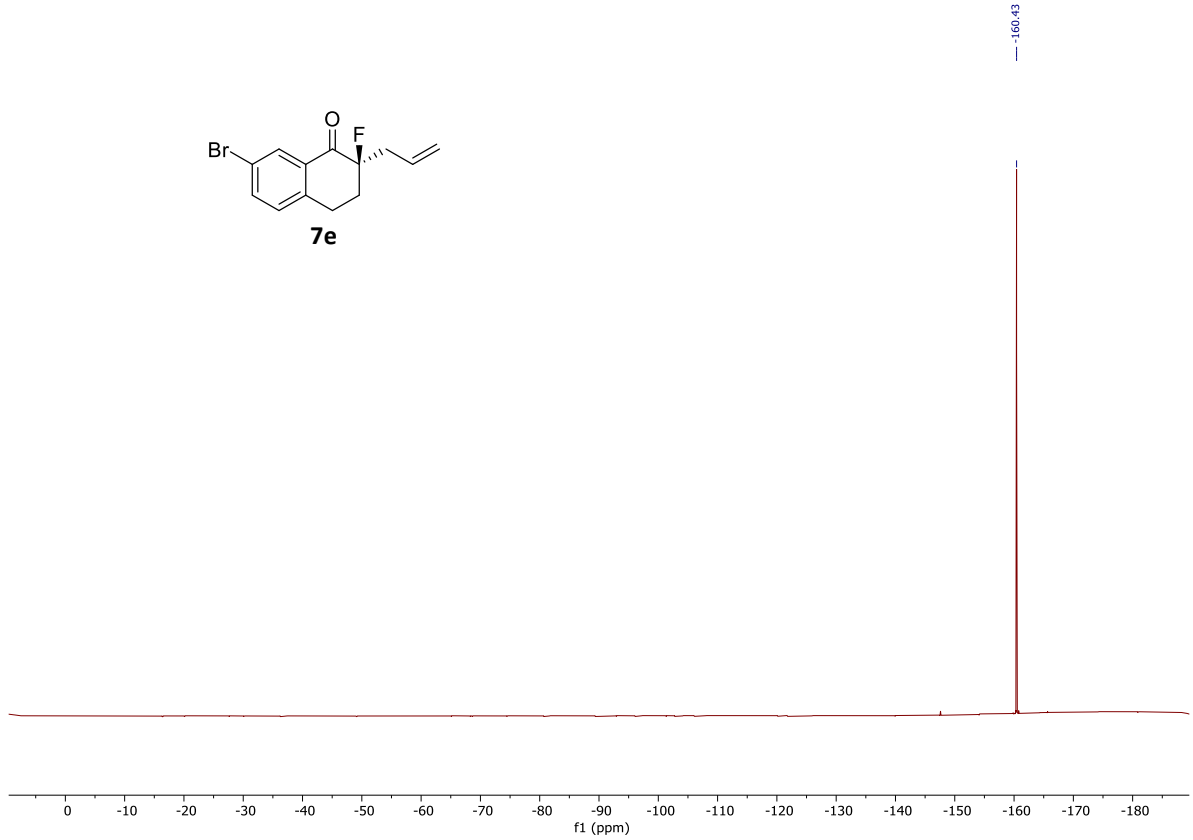
$^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$)



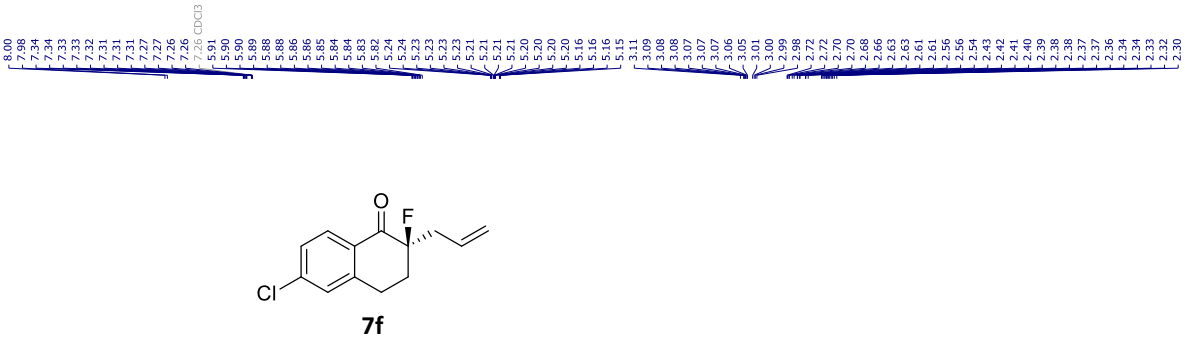
^{1}H NMR (400 MHz, $CDCl_3$)



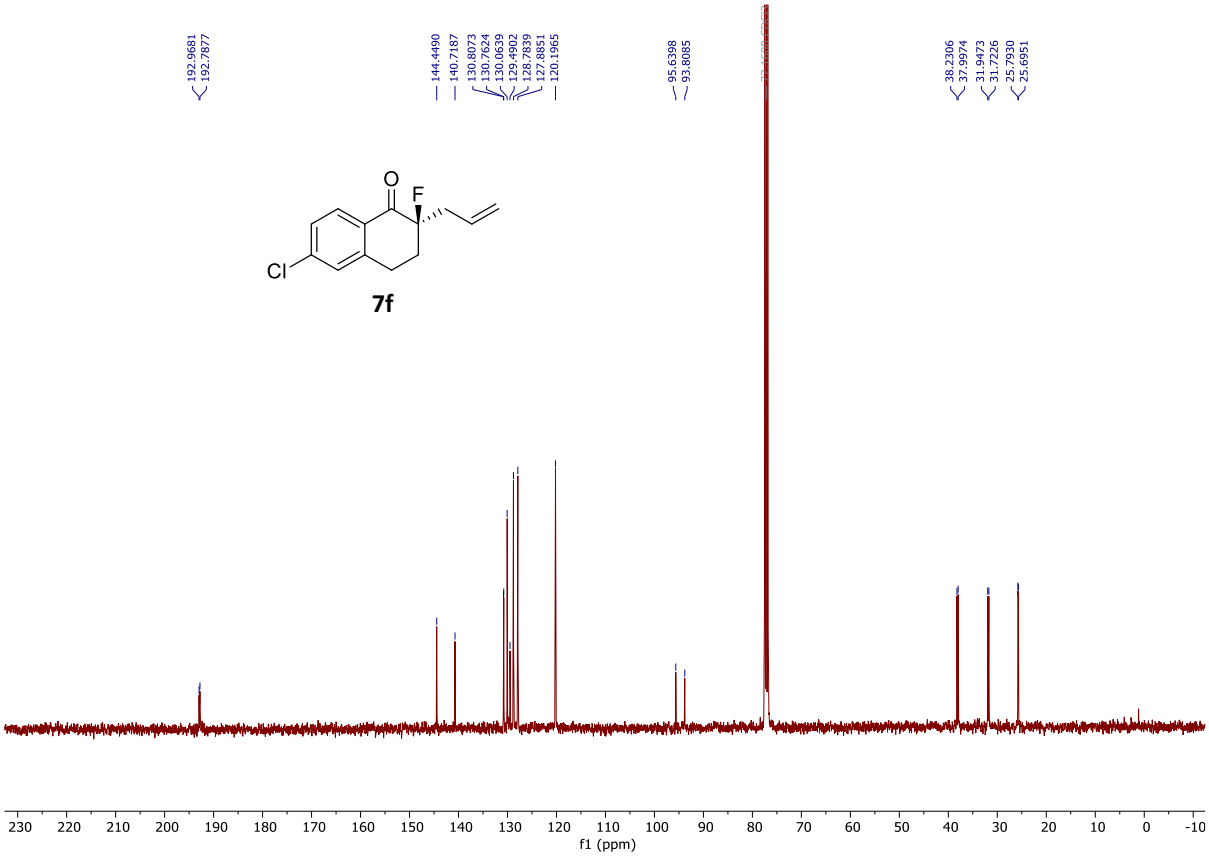
$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$)



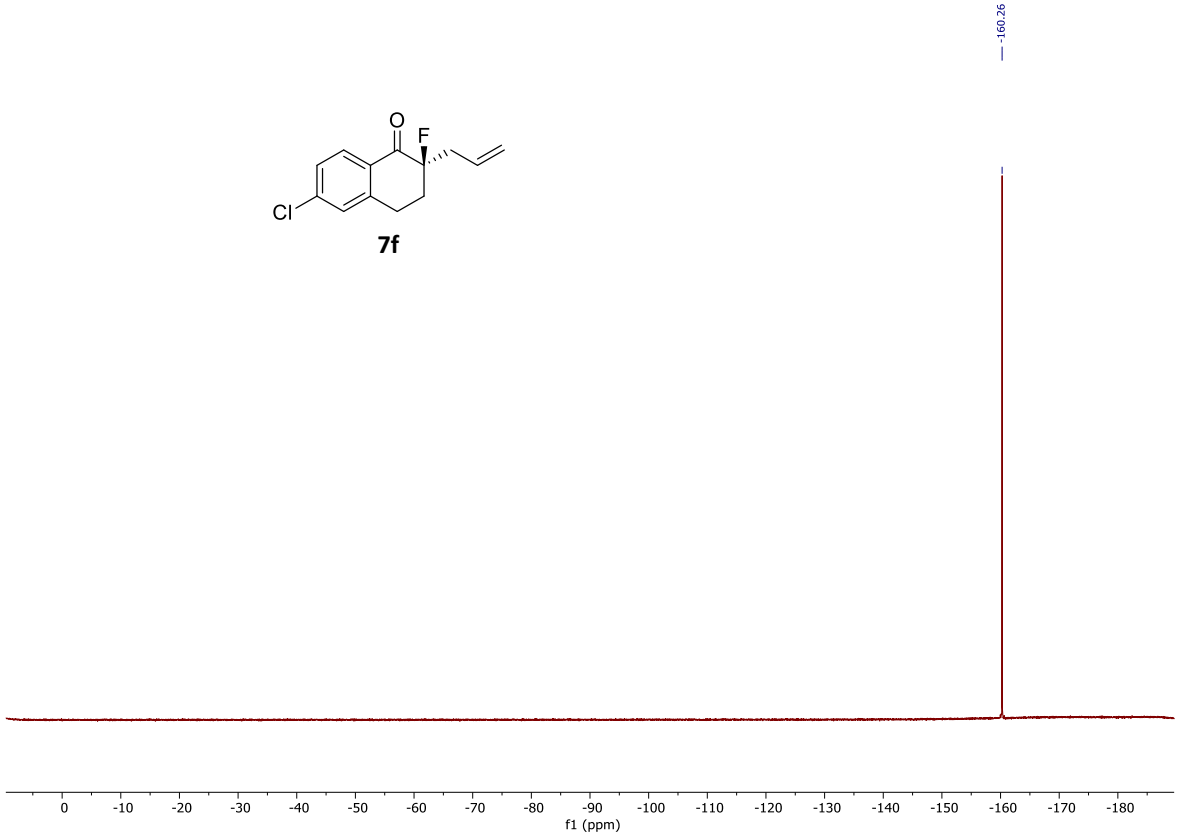
$^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$)



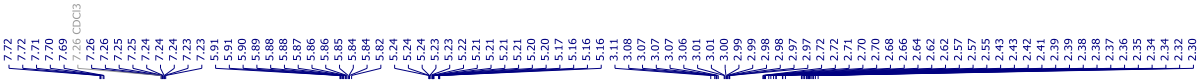
^1H NMR (400 MHz, $CDCl_3$)

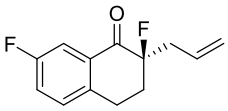


$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$)



$^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$)





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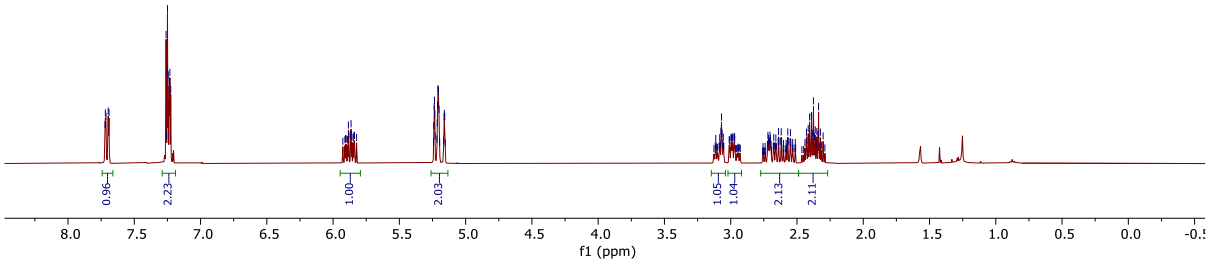
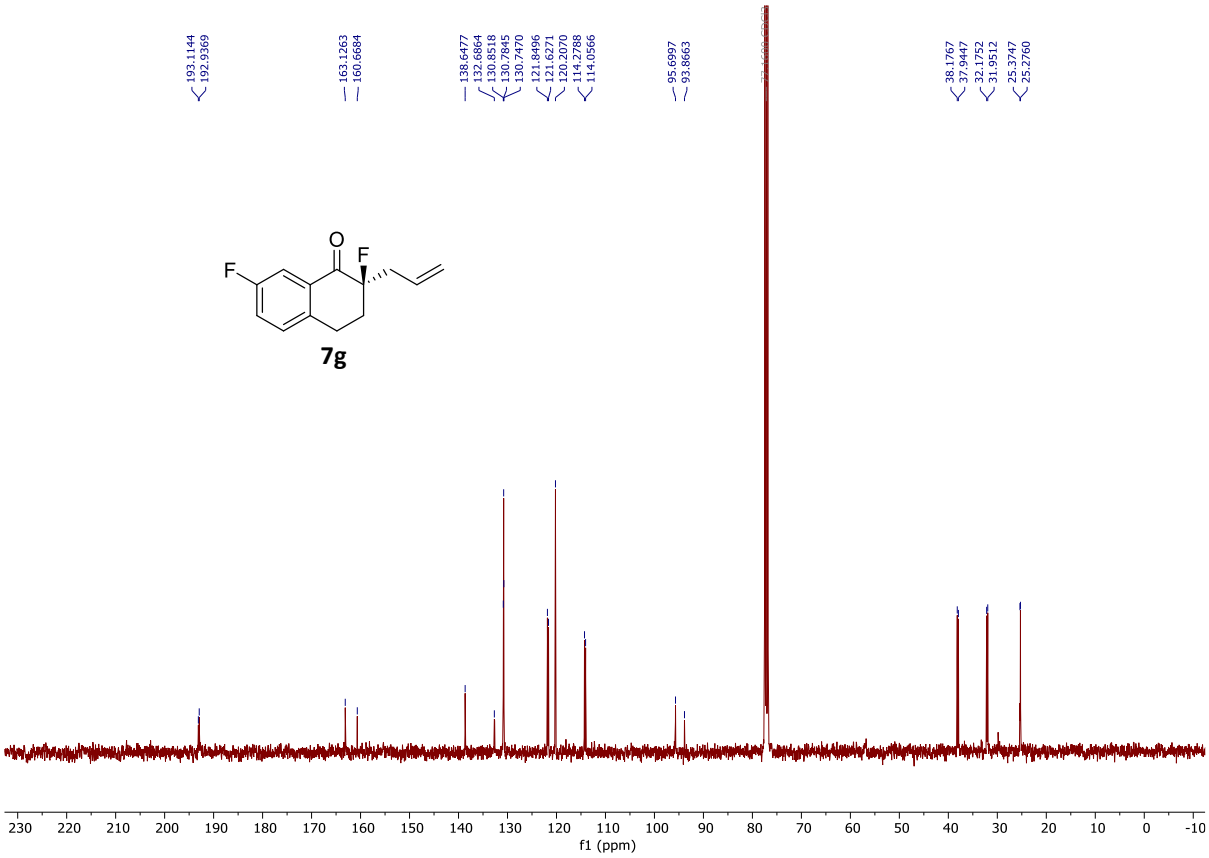
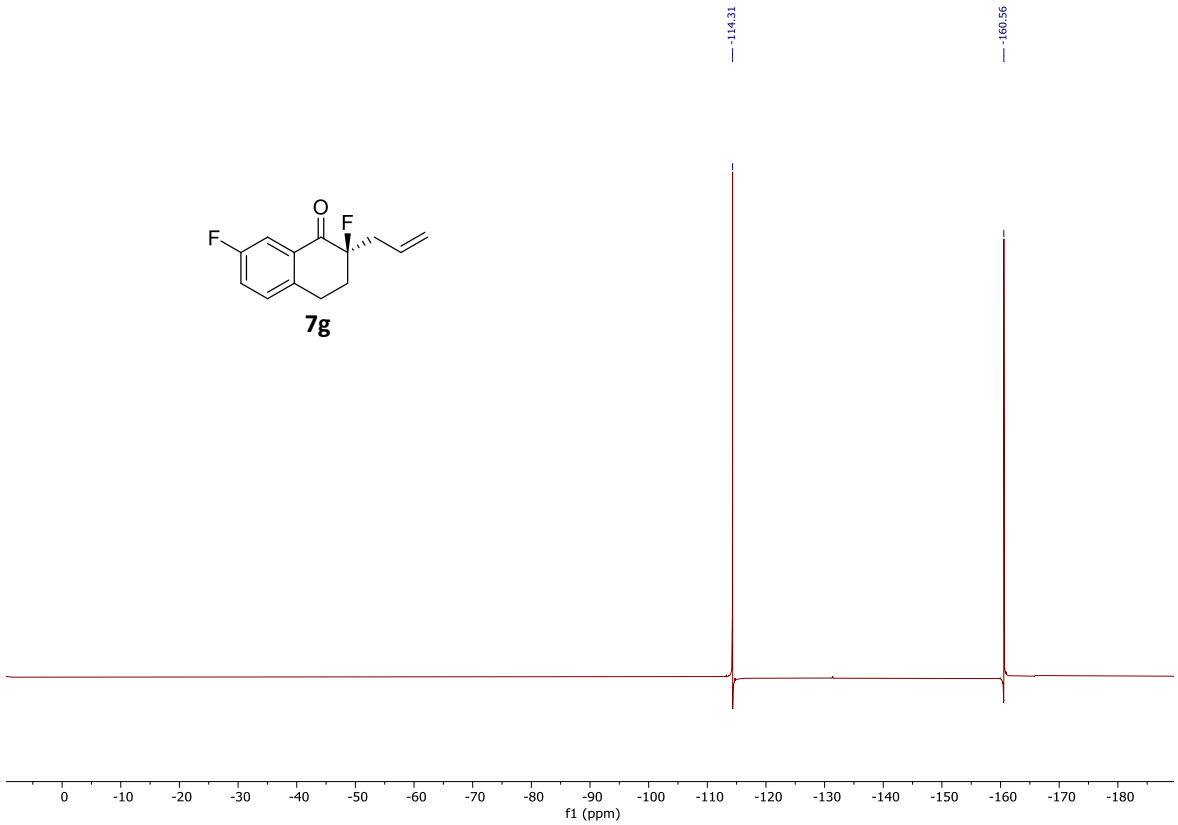


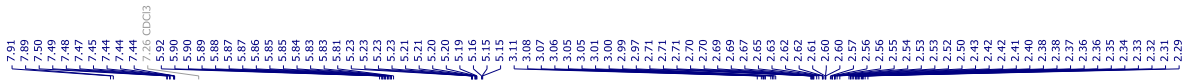
^{1}H NMR (400 MHz, $CDCl_3$)

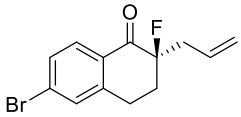


$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



$^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$)





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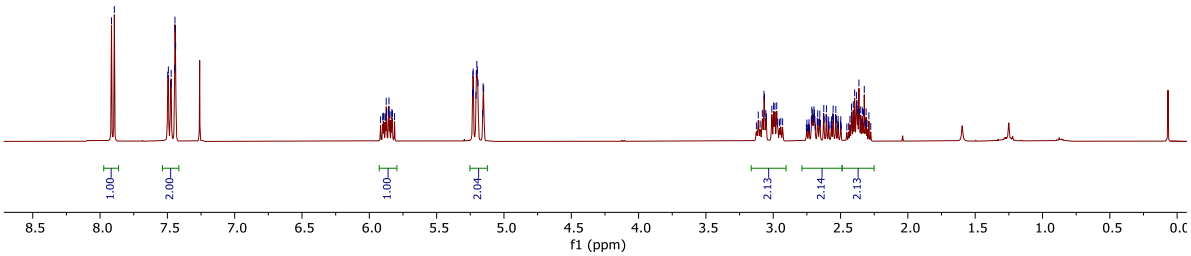
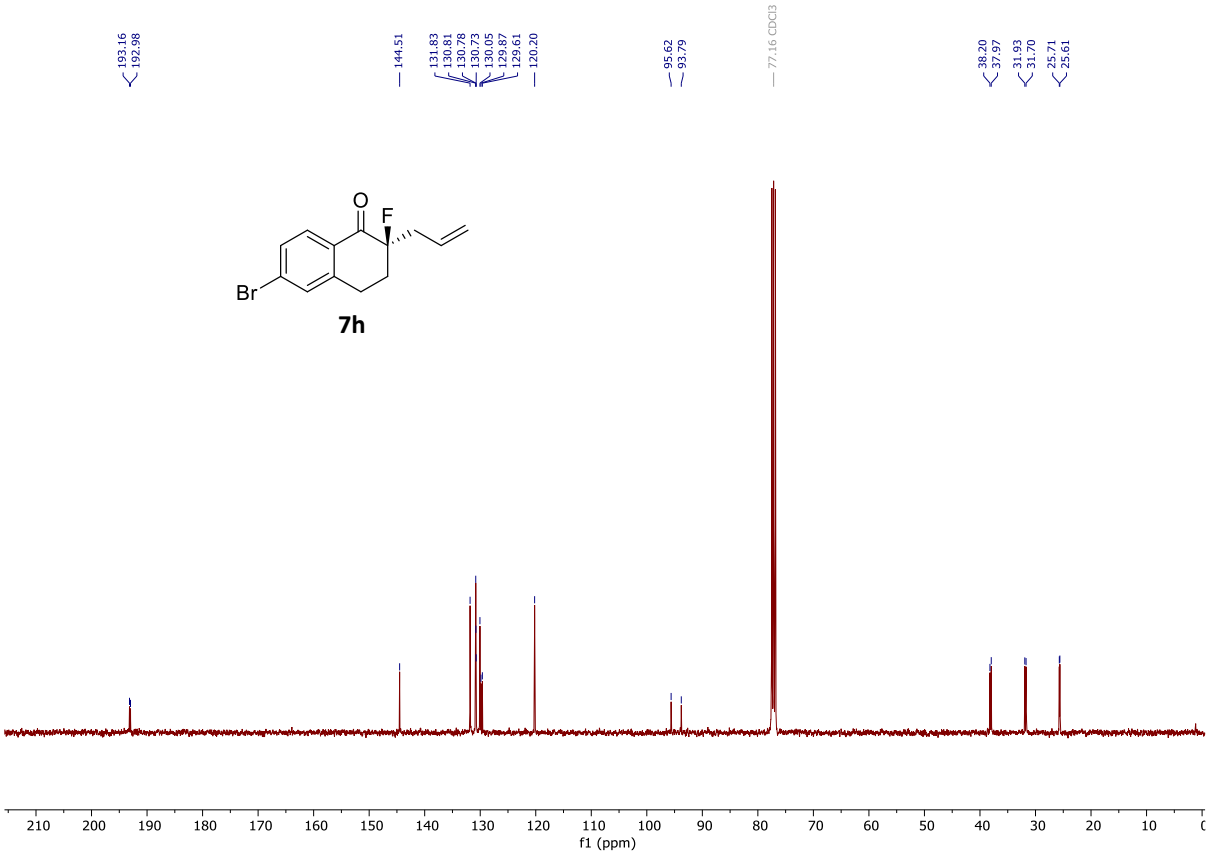


^{1}H NMR (400 MHz, $CDCl_3$)



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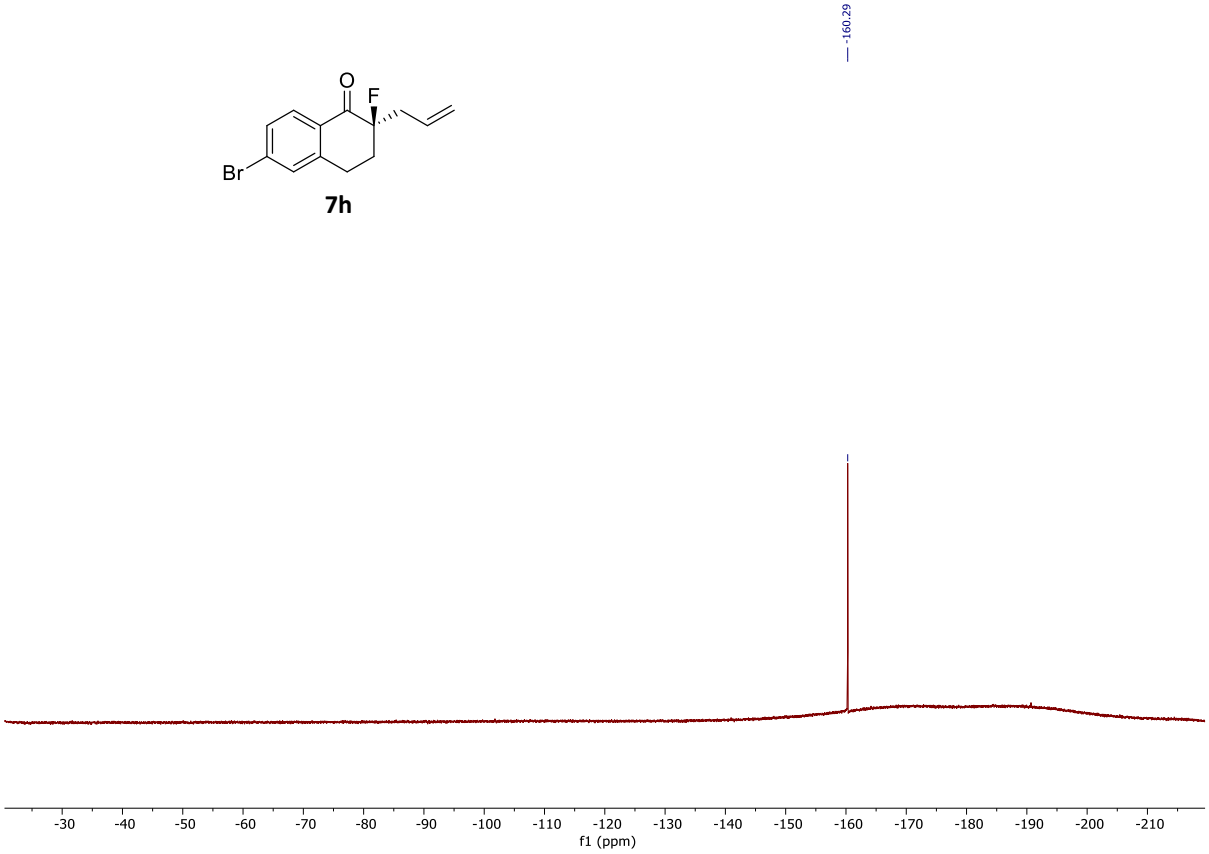
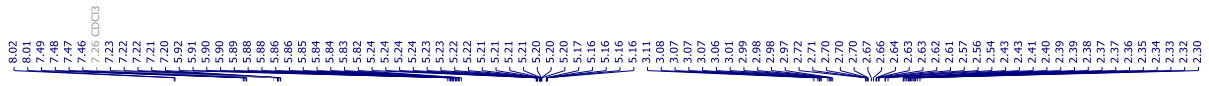
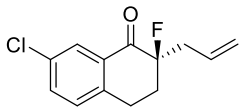
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)

7h



$^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$)





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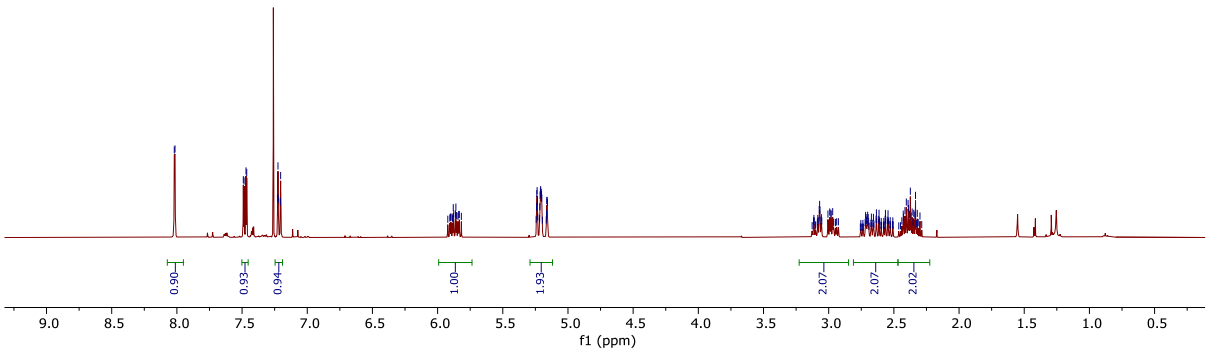
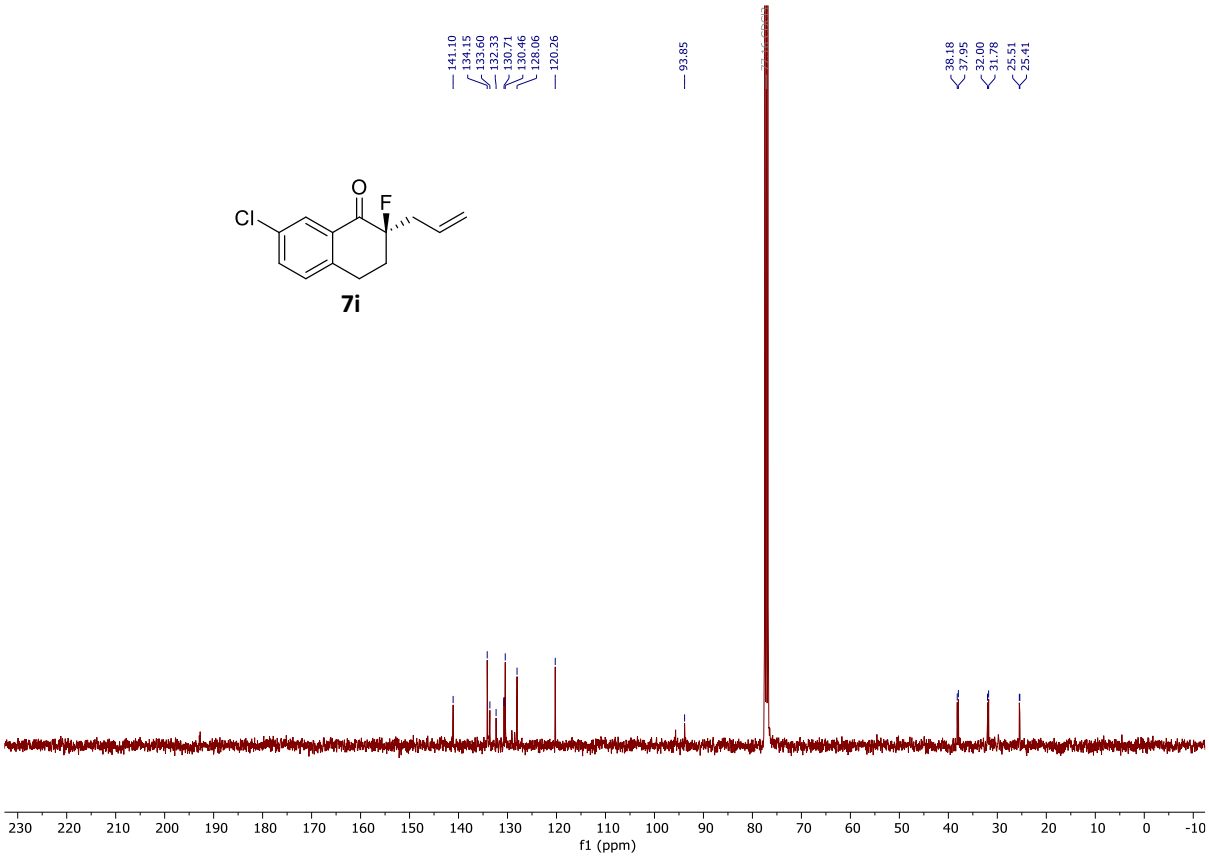
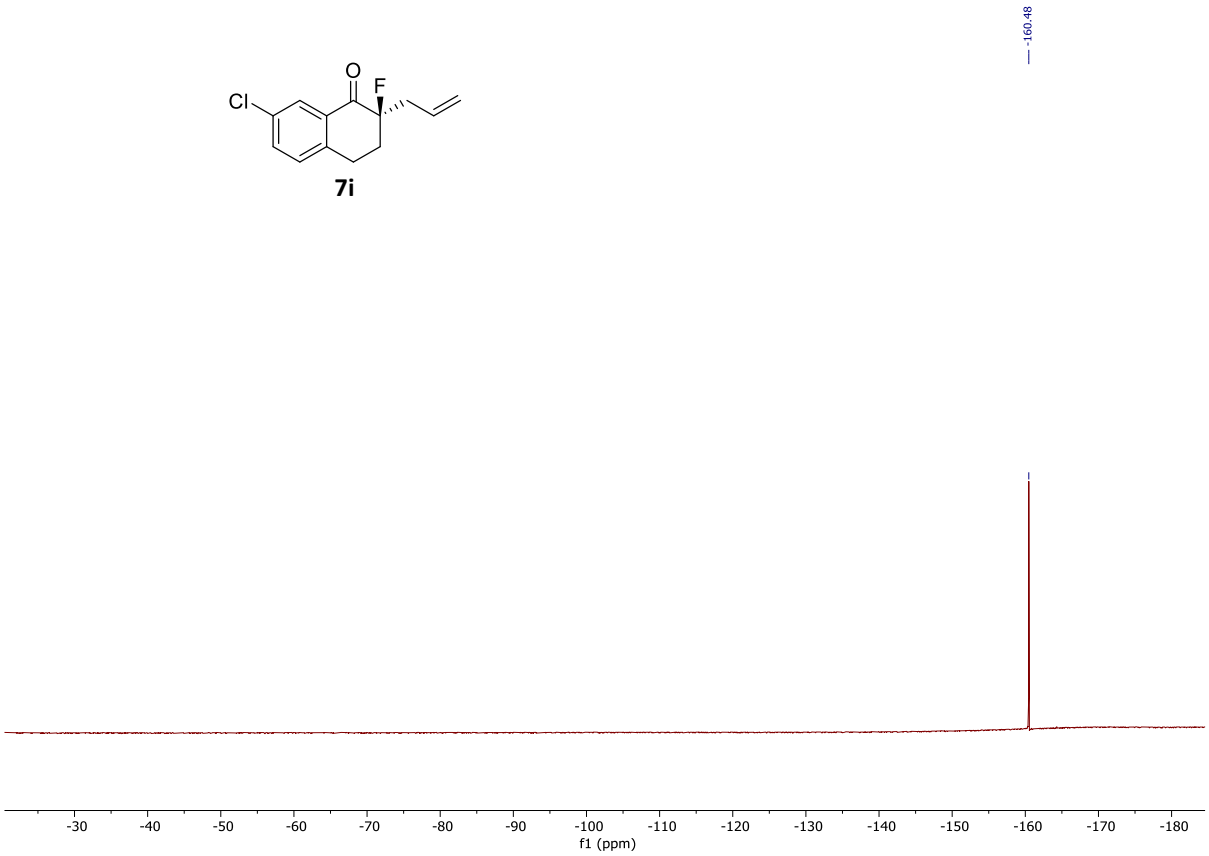


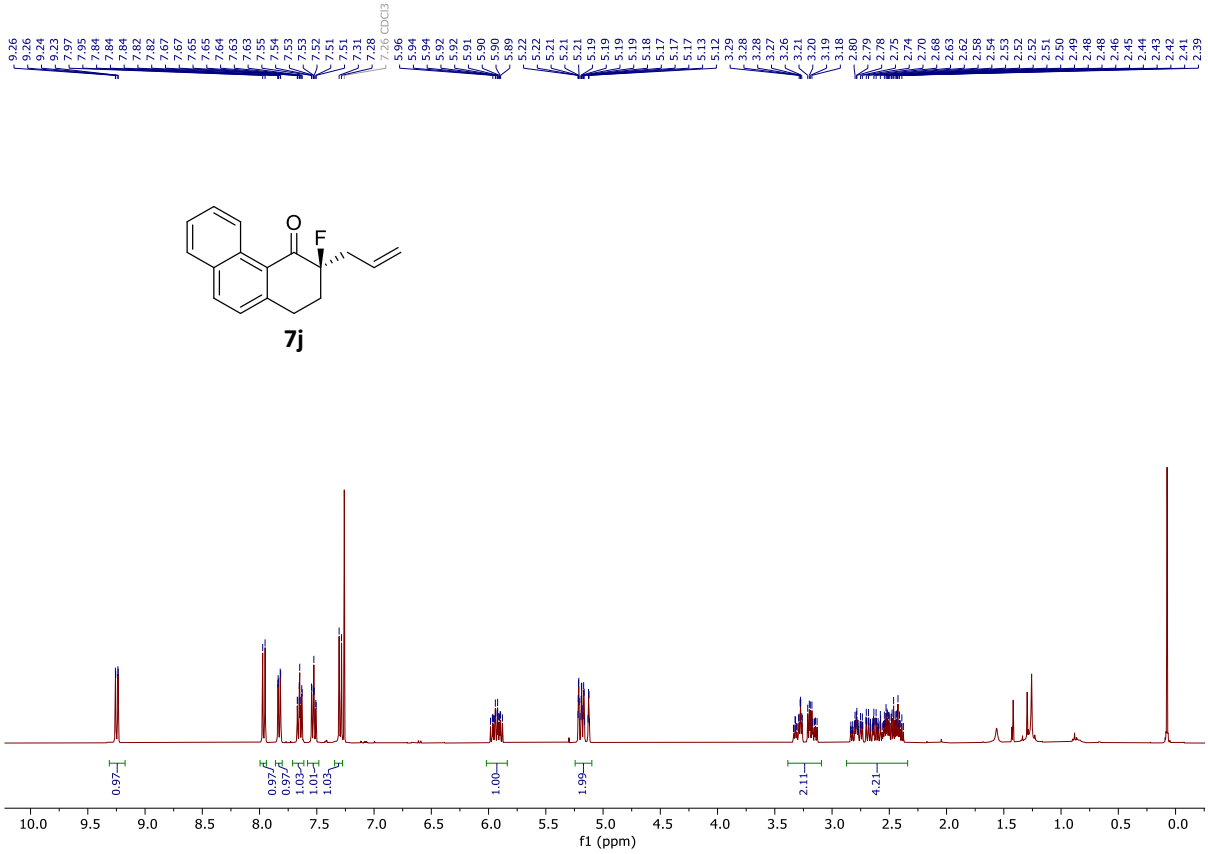
^{1}H NMR (400 MHz, $CDCl_3$)



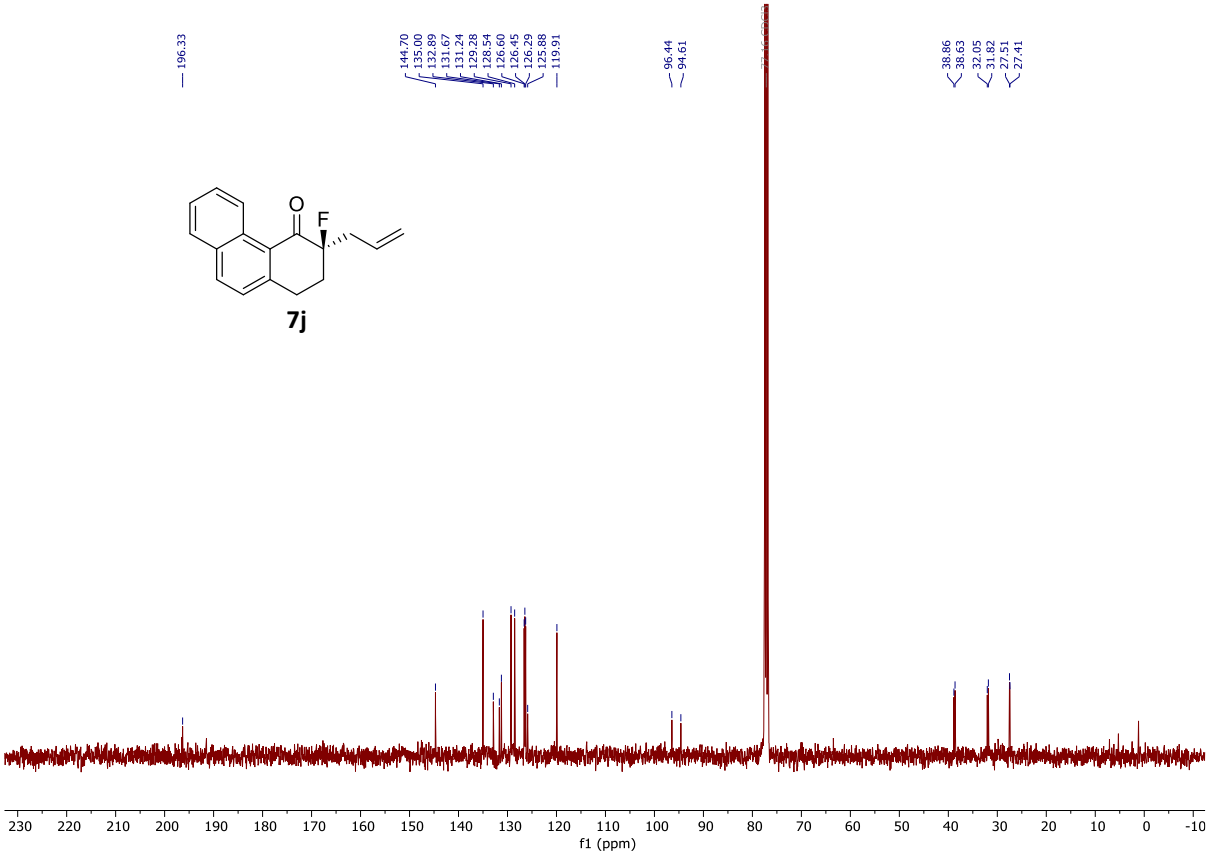
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



$^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$)



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



^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)

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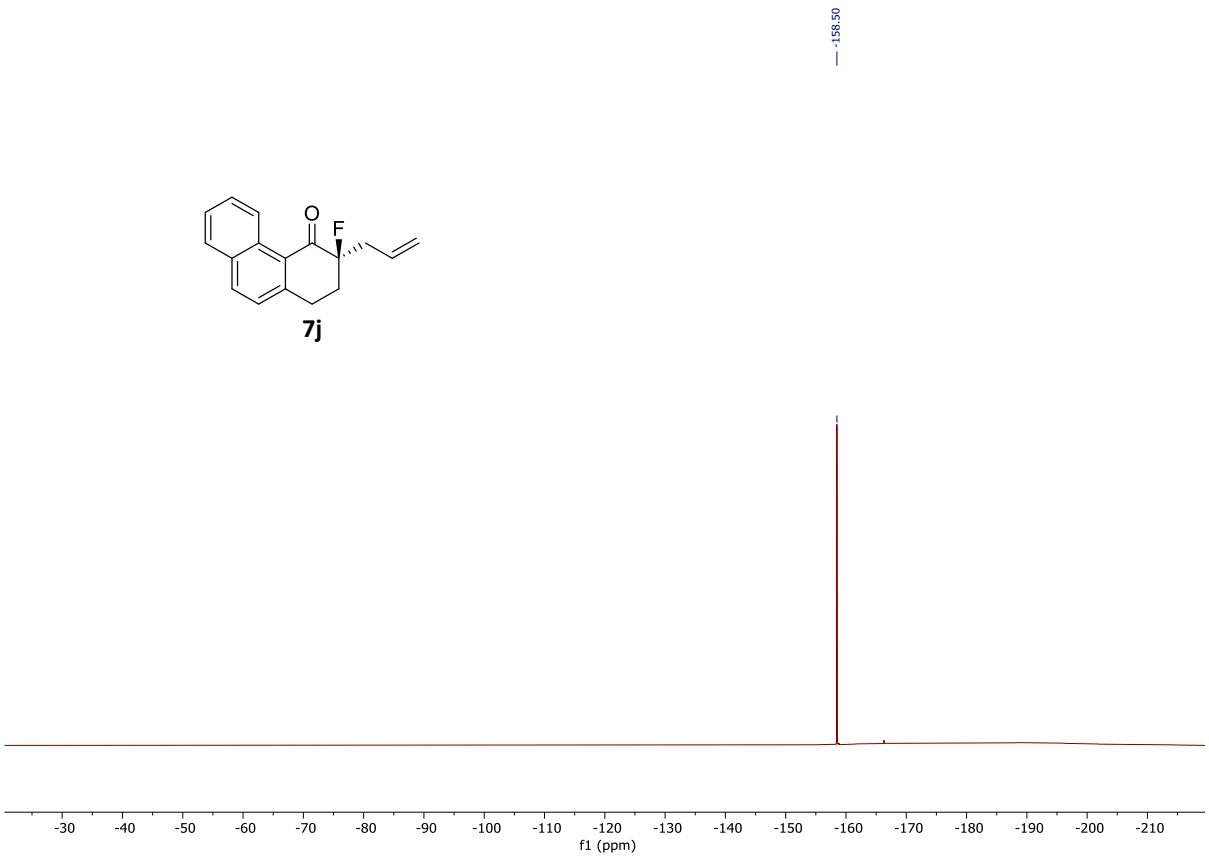
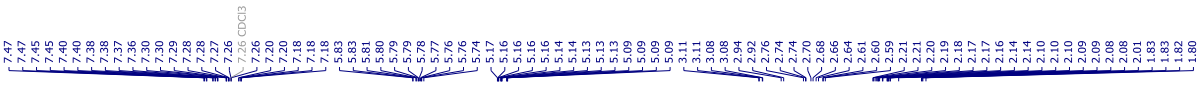
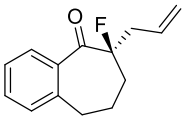


$^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$)





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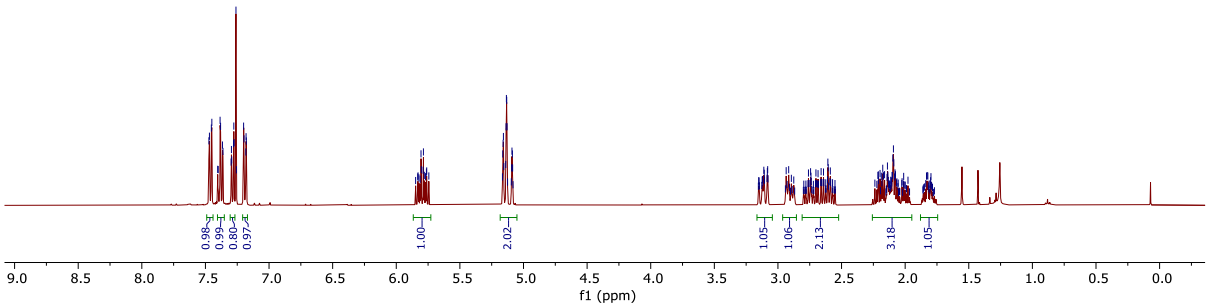
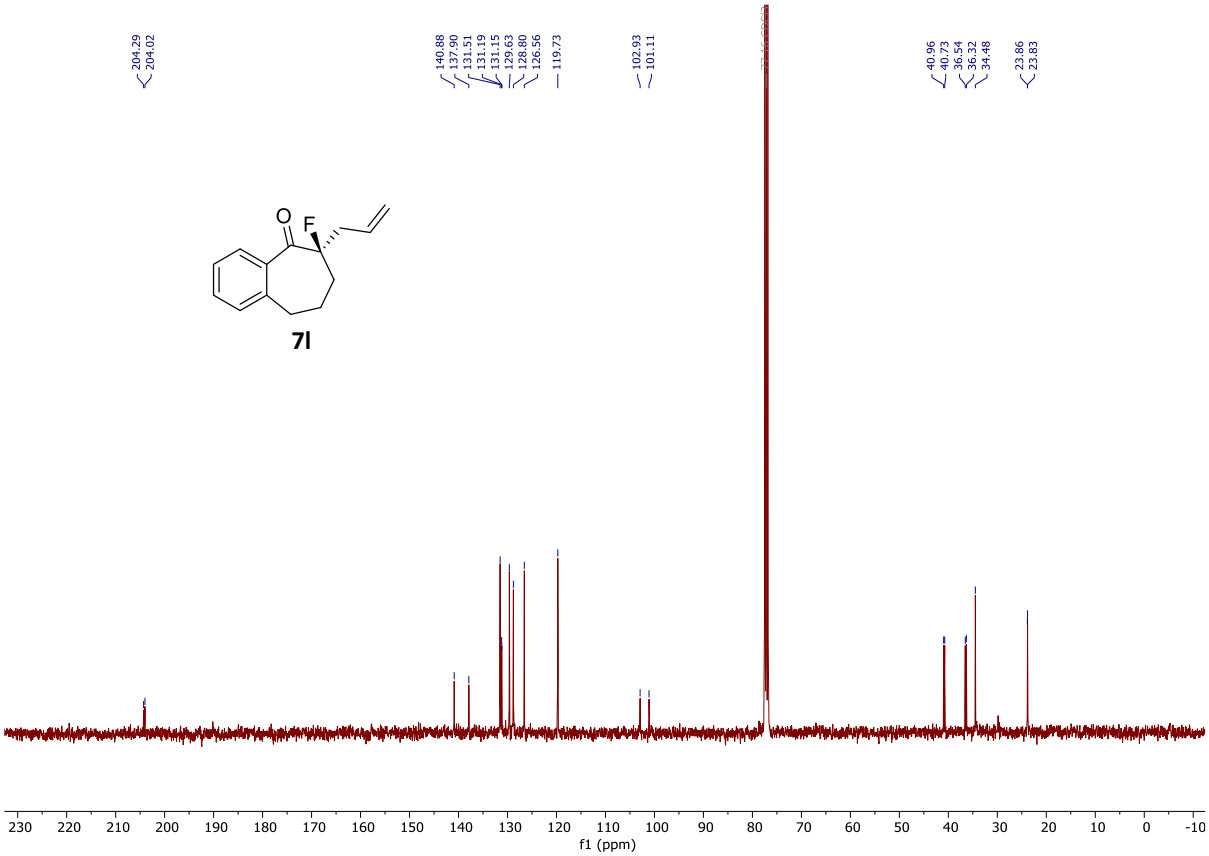
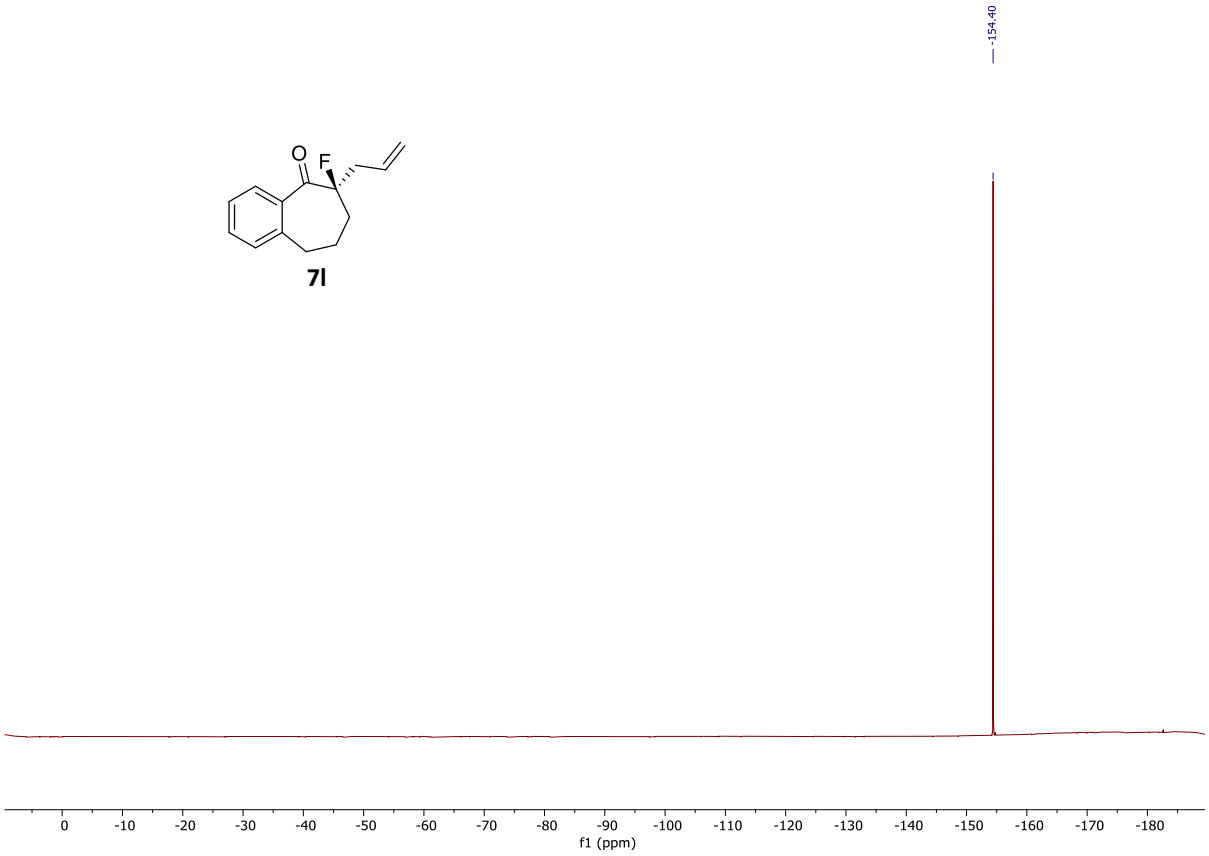


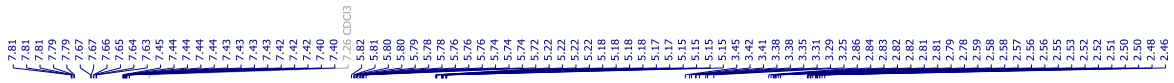
^{1}H NMR (400 MHz, $CDCl_3$)

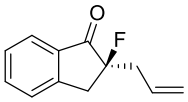


$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



$^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$)





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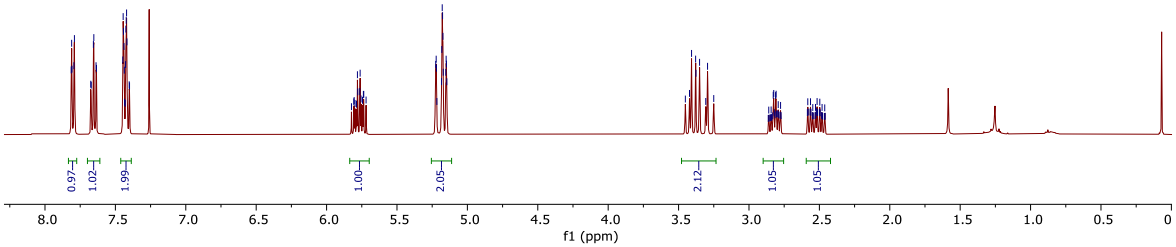
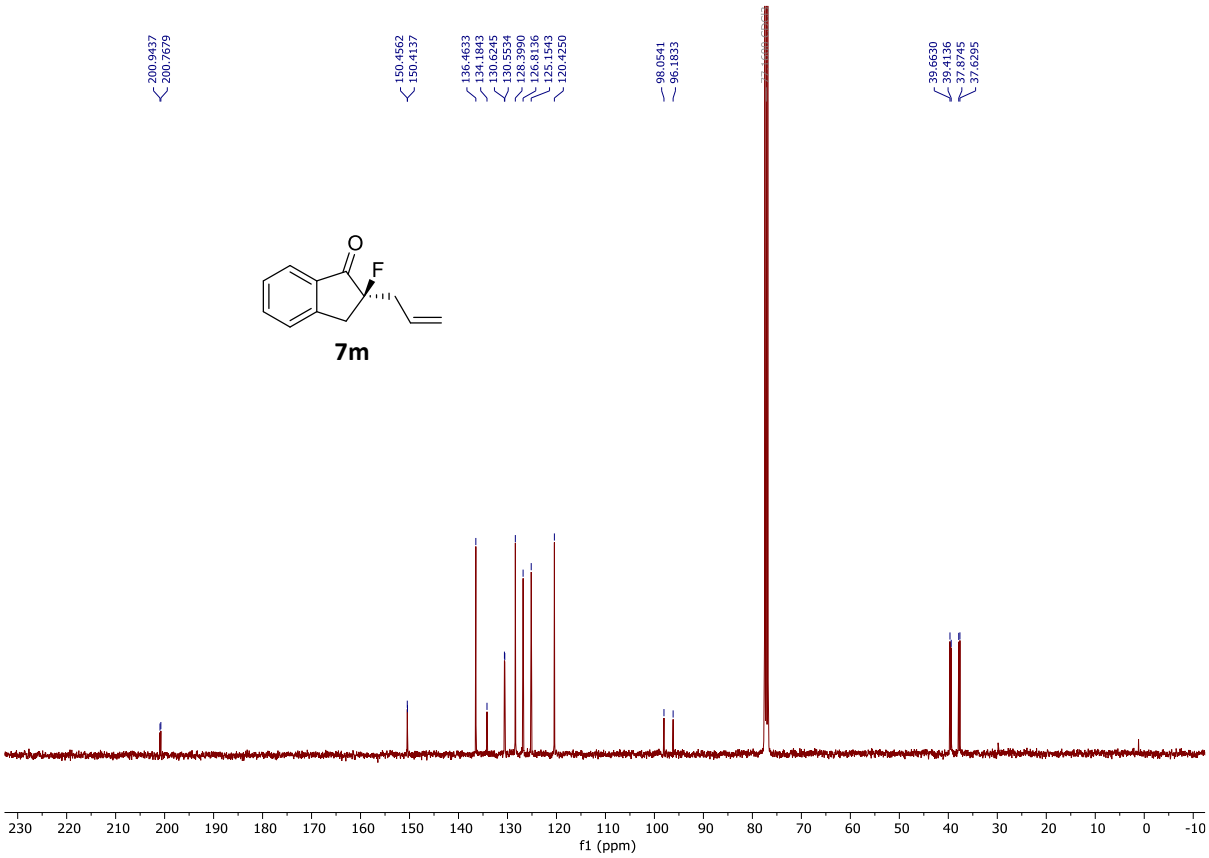
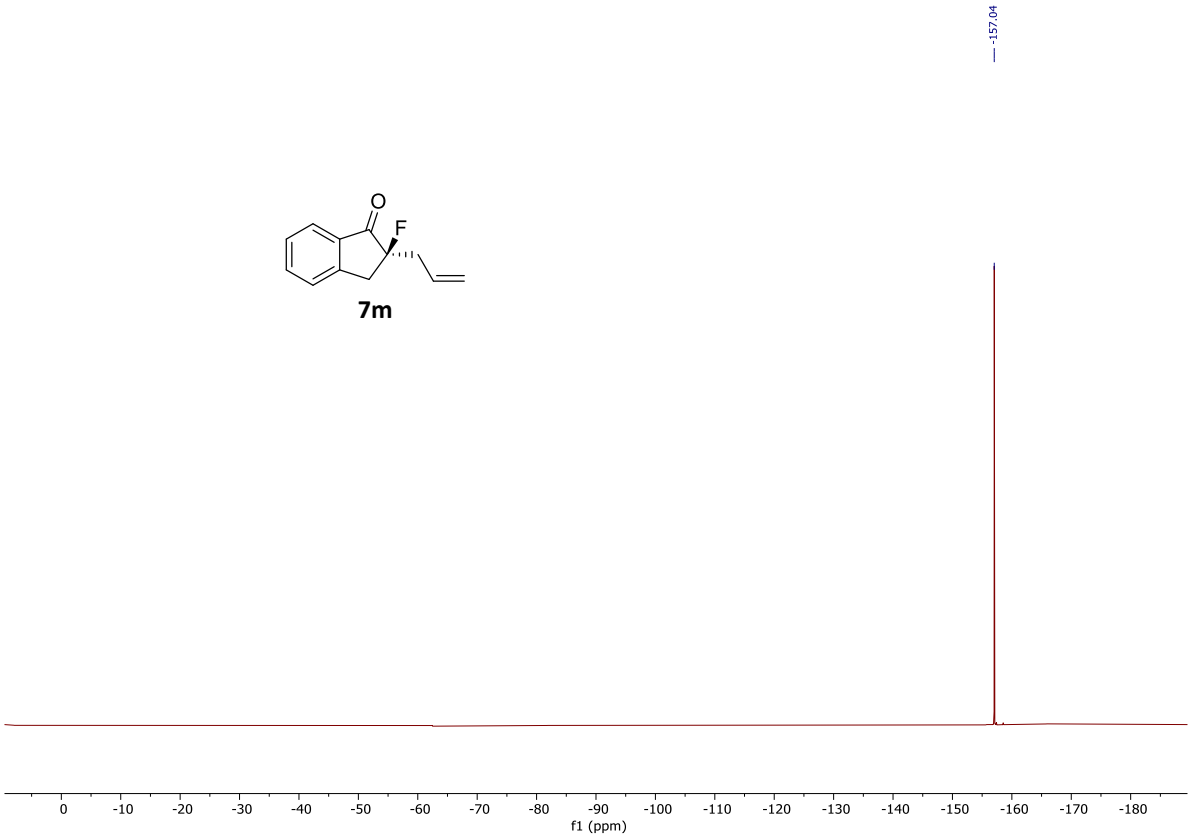


^{1}H NMR (400 MHz, $CDCl_3$)

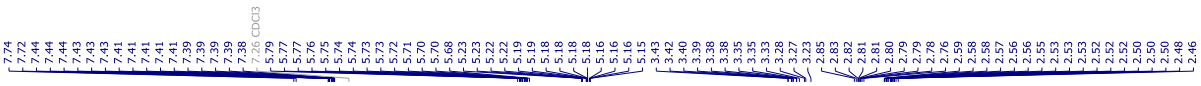


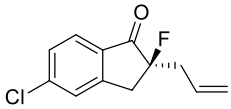
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)

7m



$^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$)





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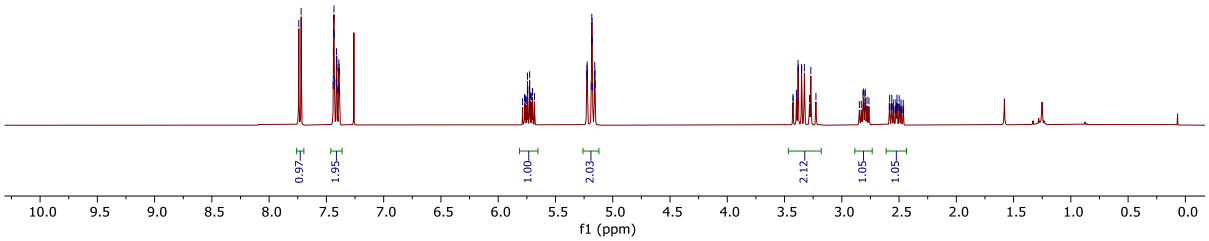
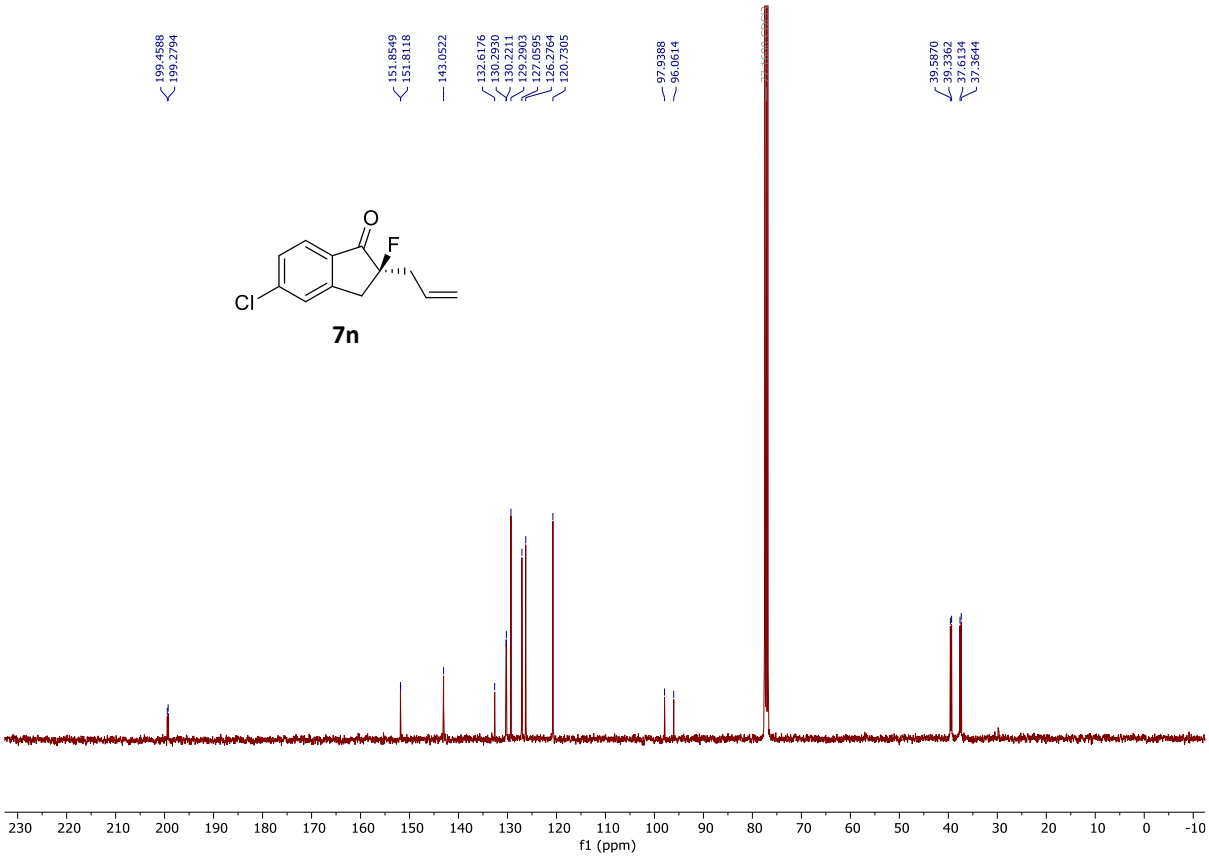
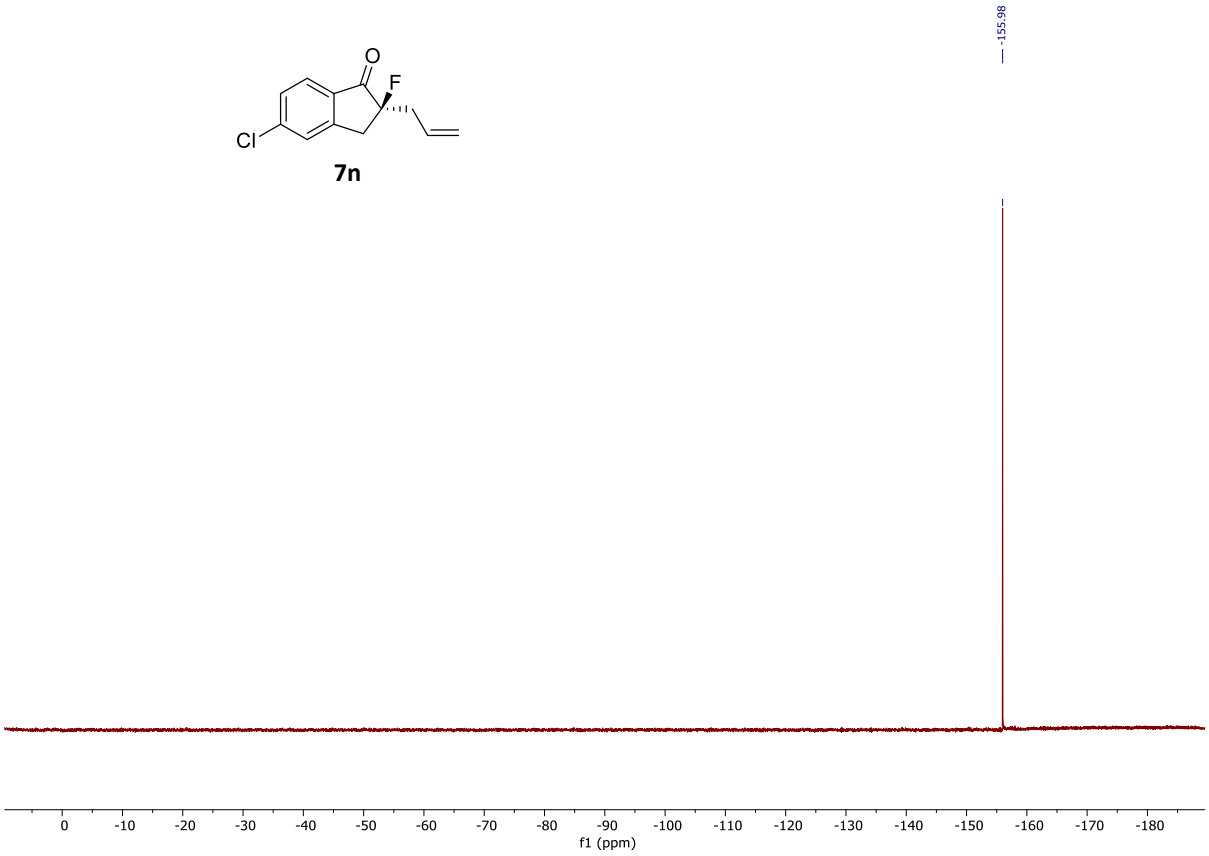


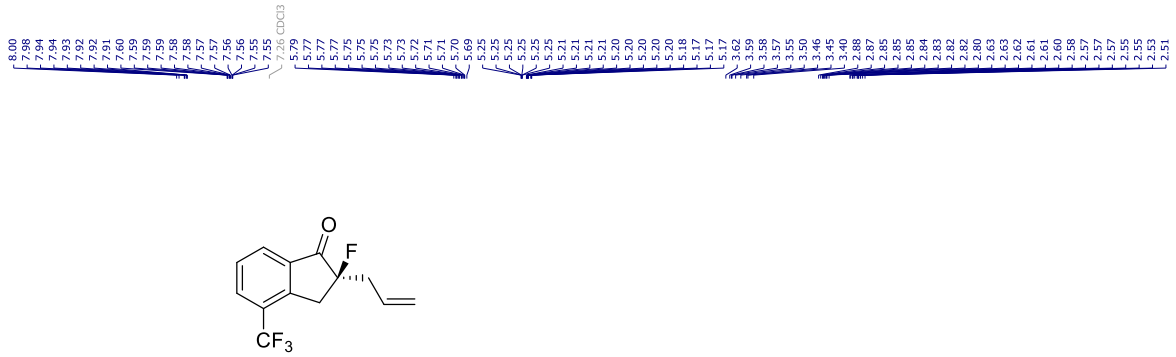
^{1}H NMR (400 MHz, $CDCl_3$)



$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



$^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$)



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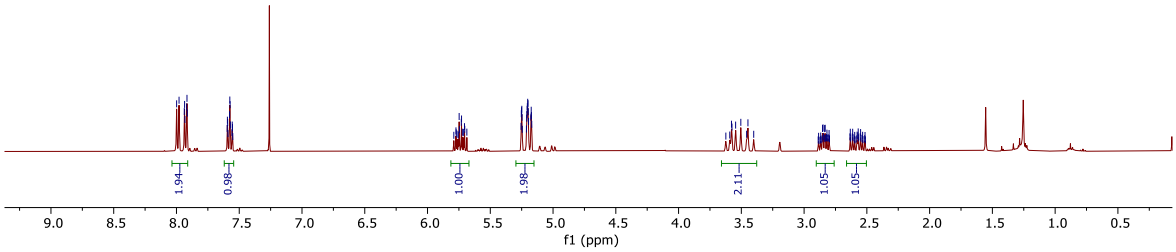
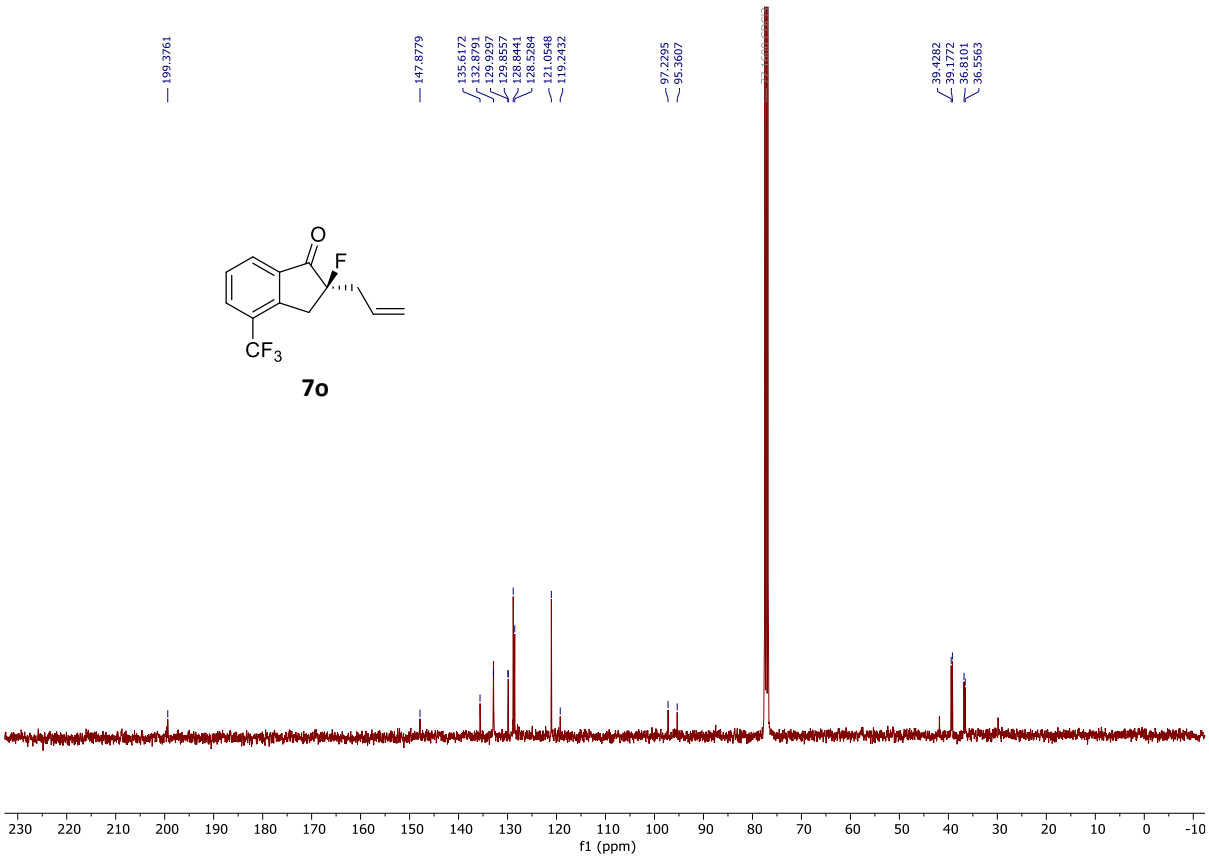


^{1}H NMR (400 MHz, $CDCl_3$)



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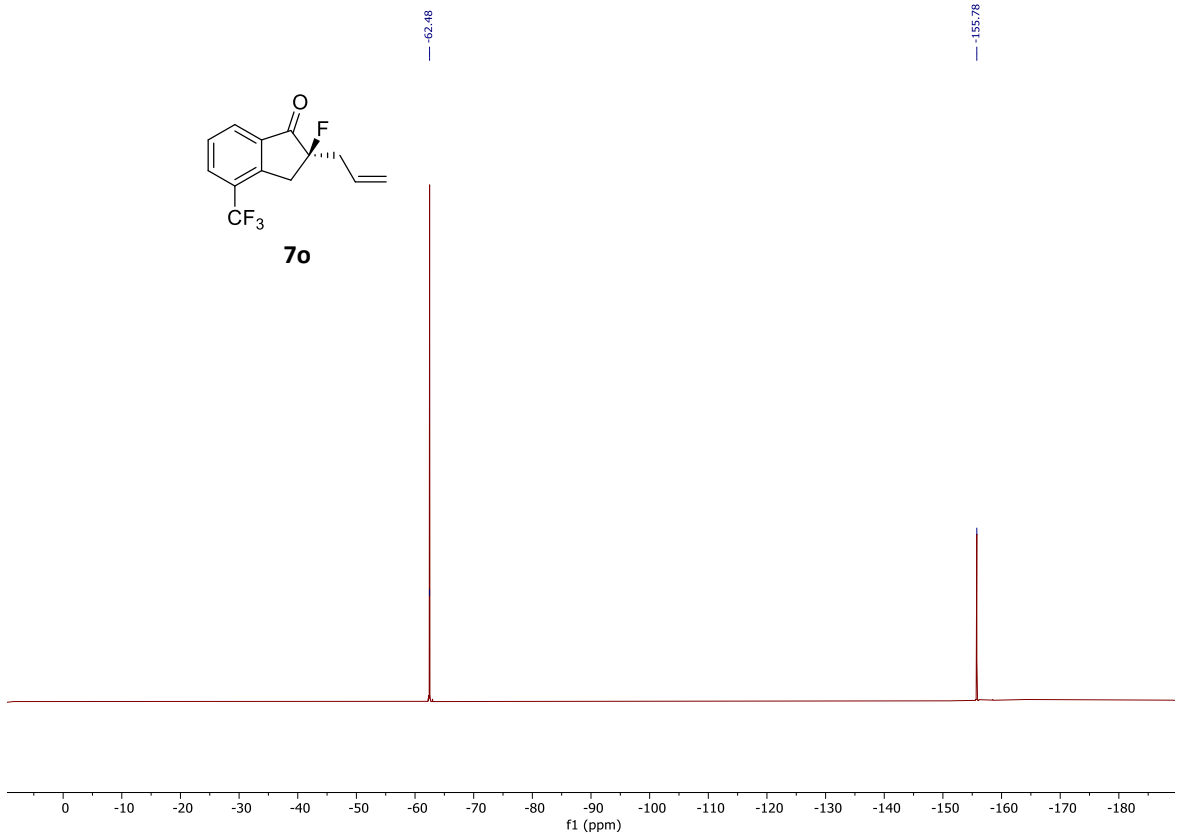
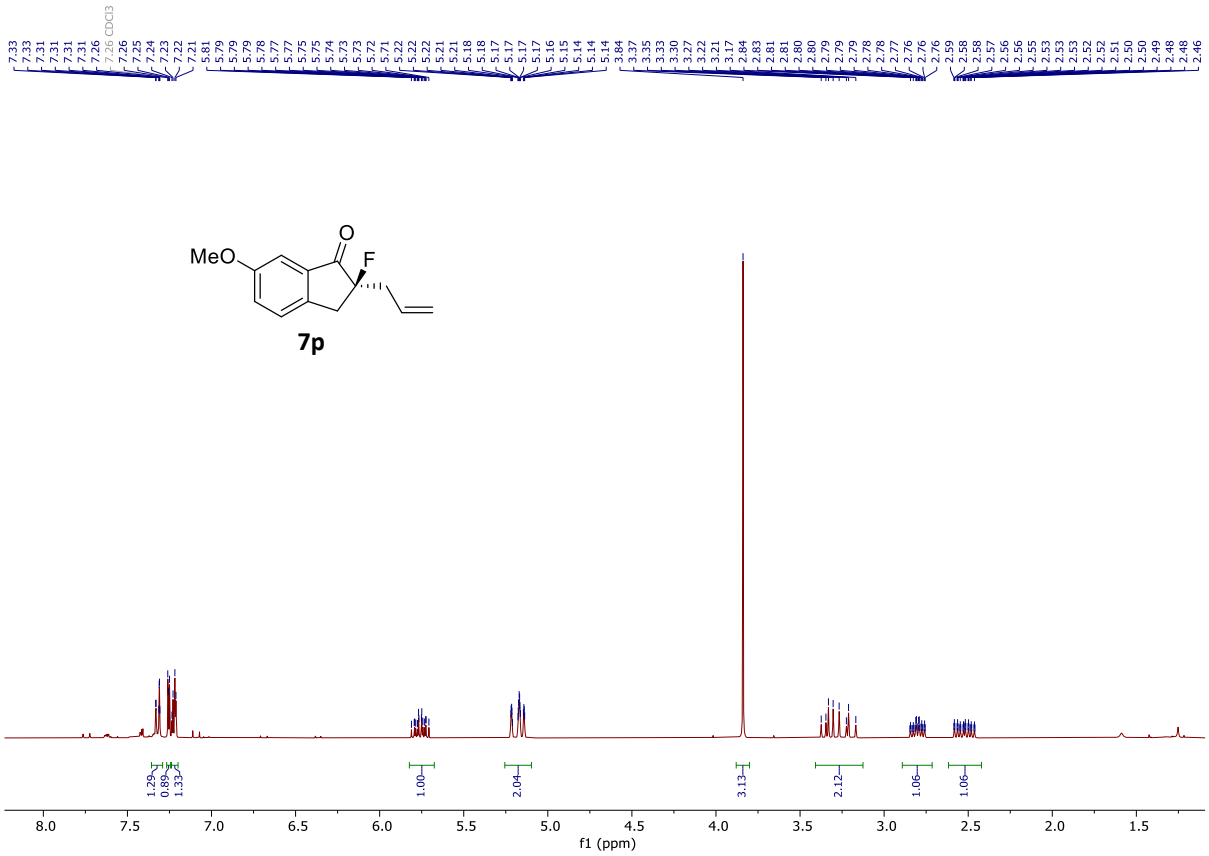
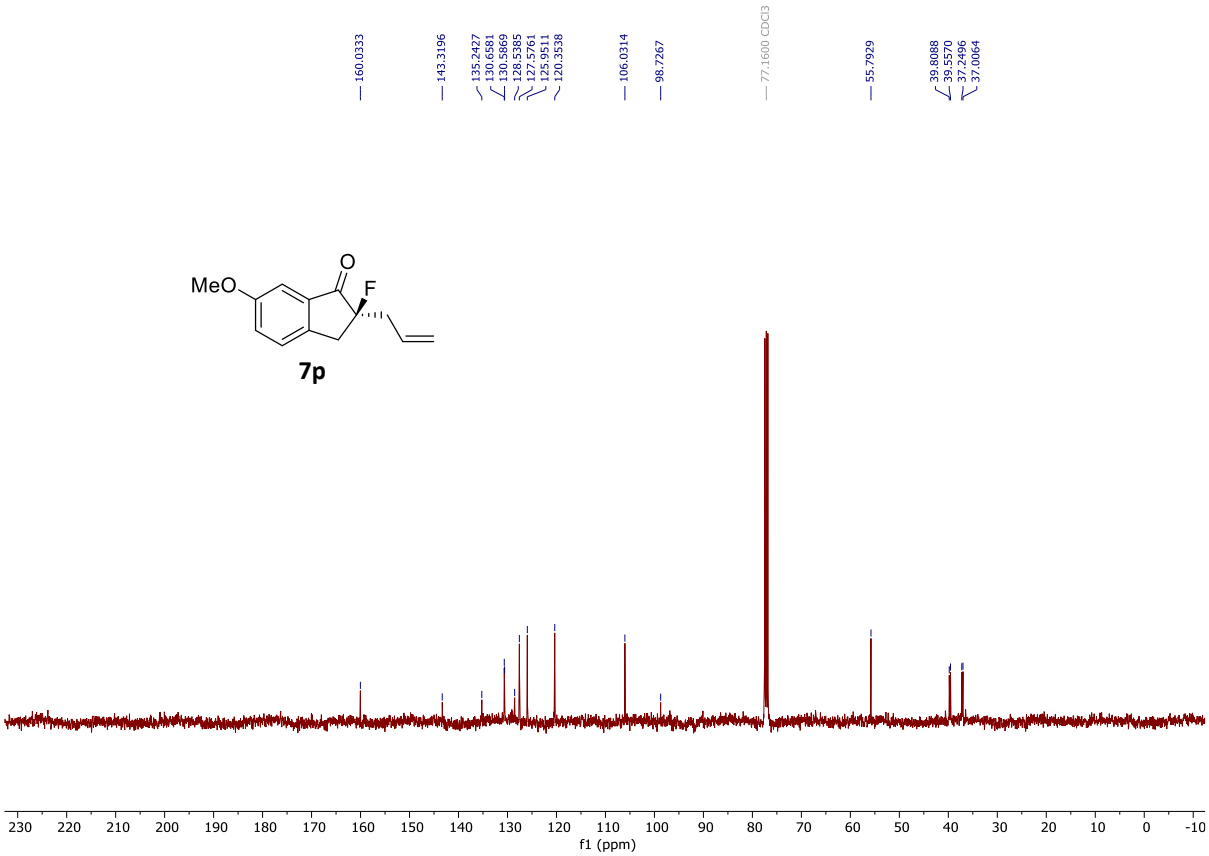
^{13}C{^{1}H} NMR ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)



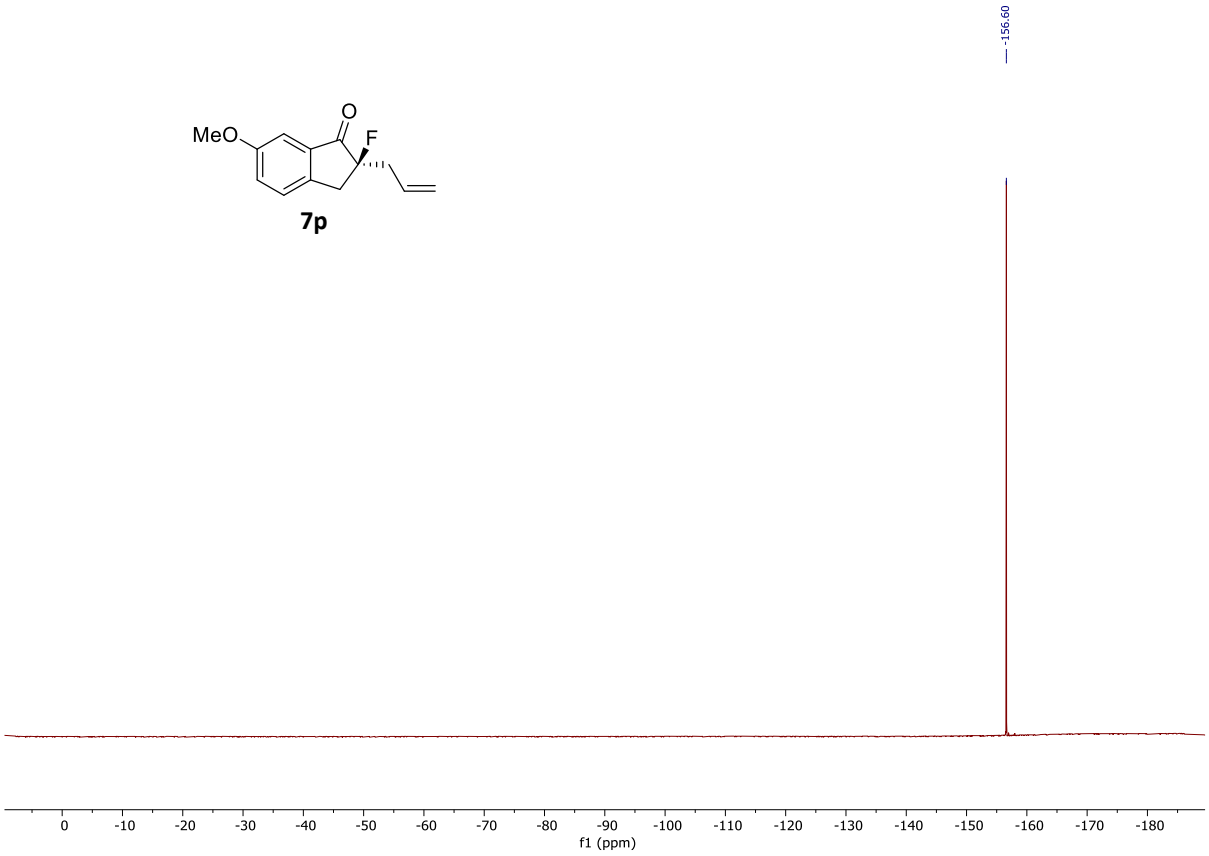
$^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$)



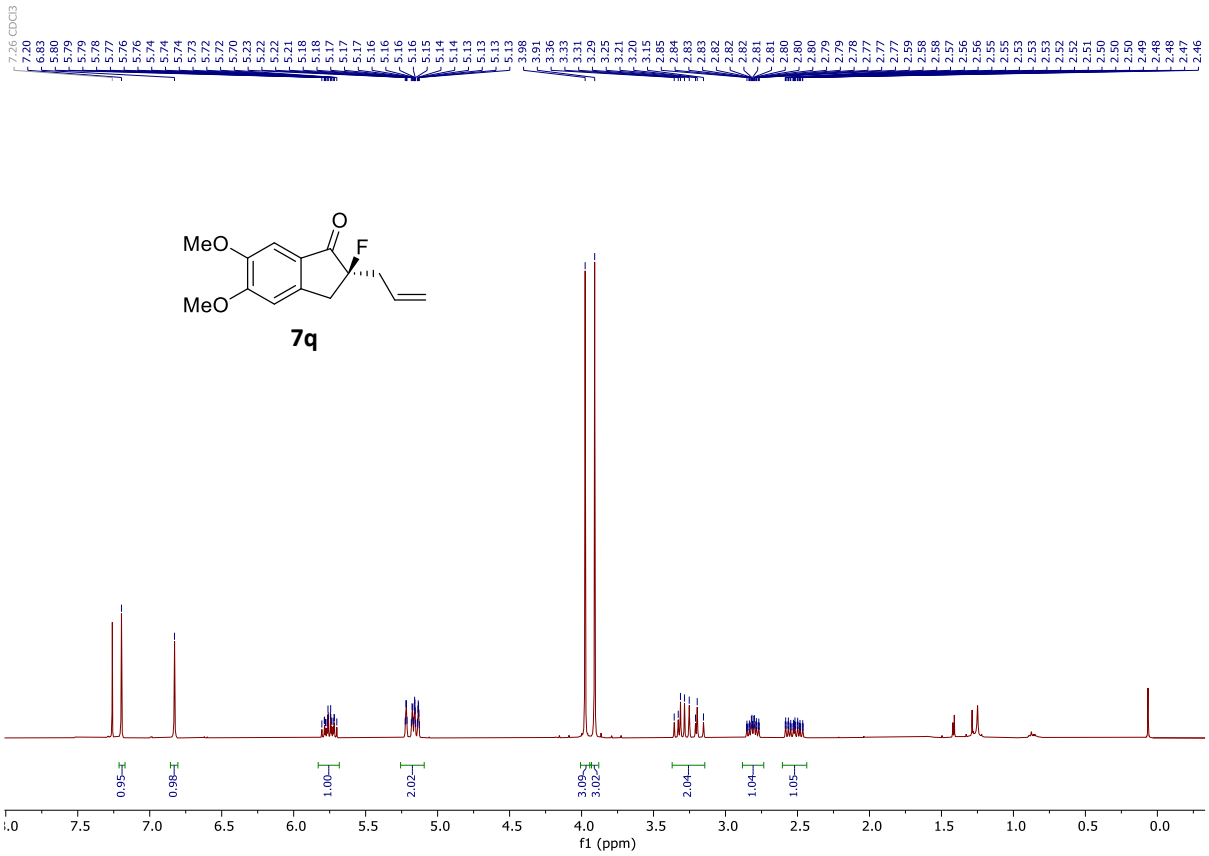
^{1}H NMR (400 MHz, $CDCl_3$)



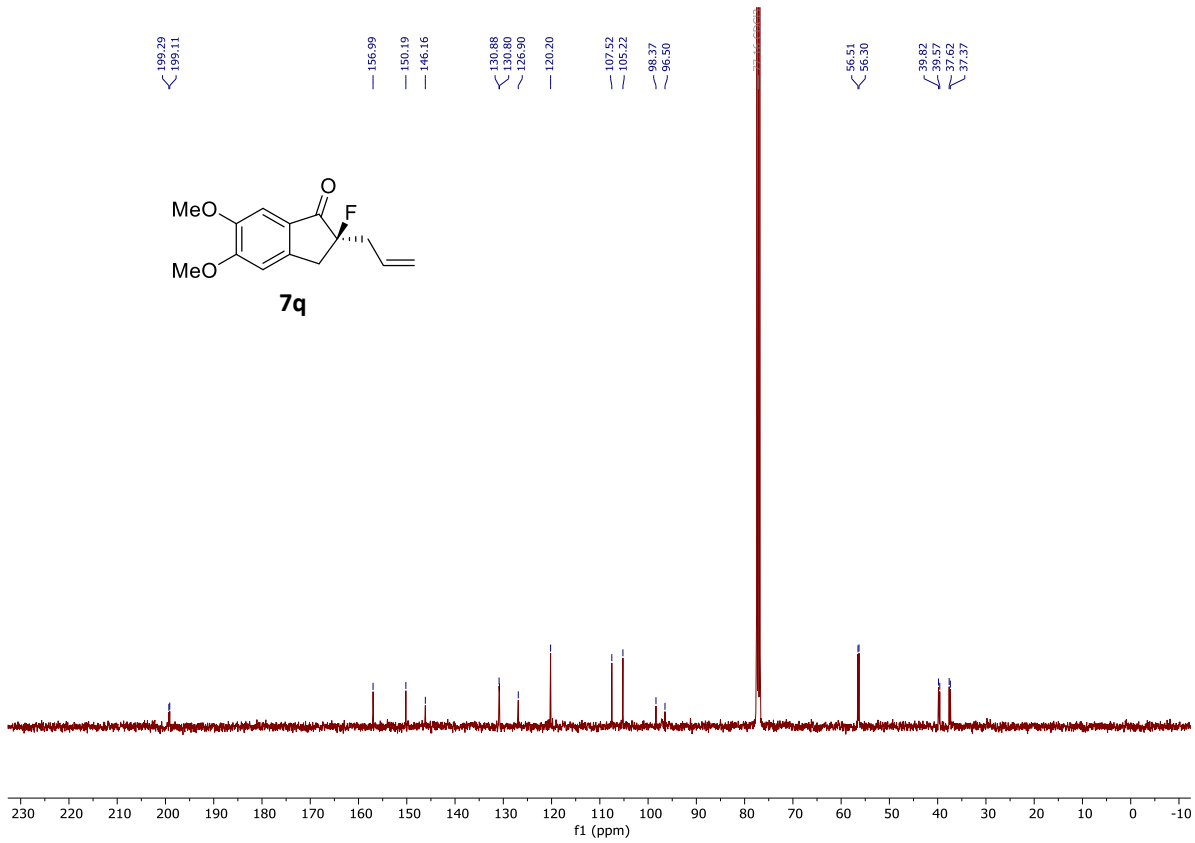
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



$^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$)



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



^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)

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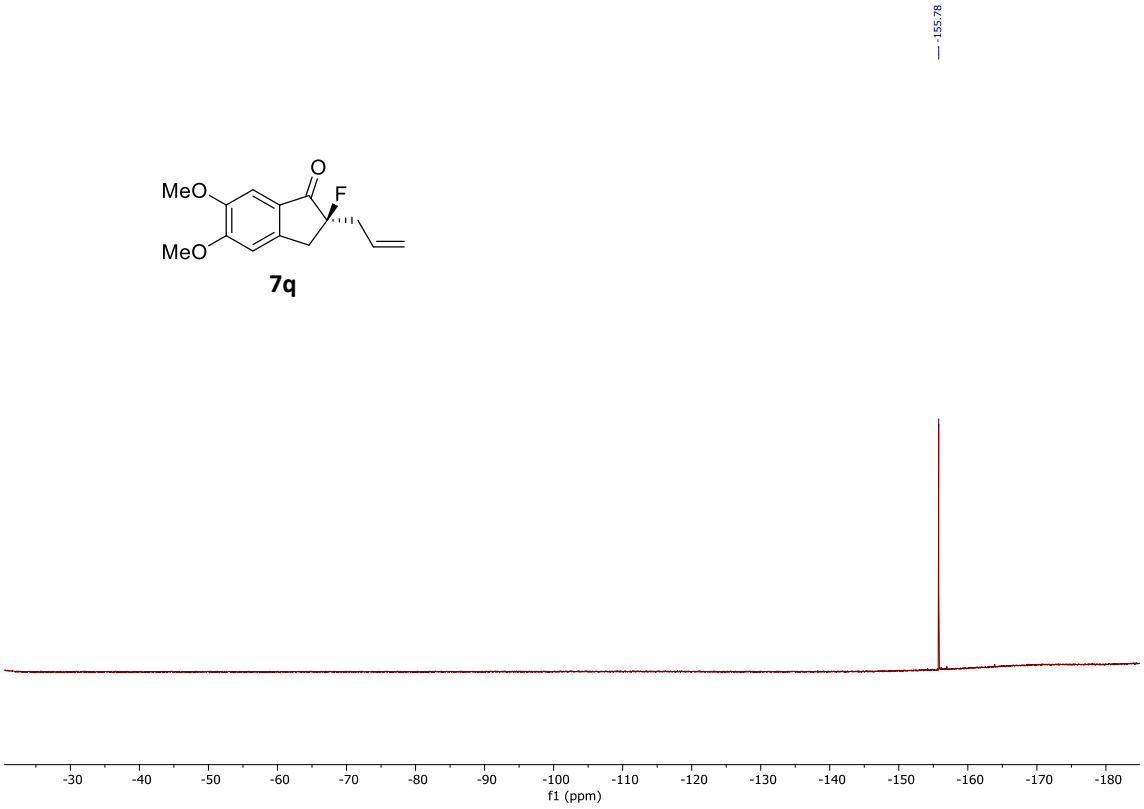
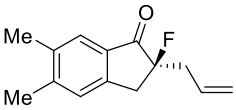


$^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$)



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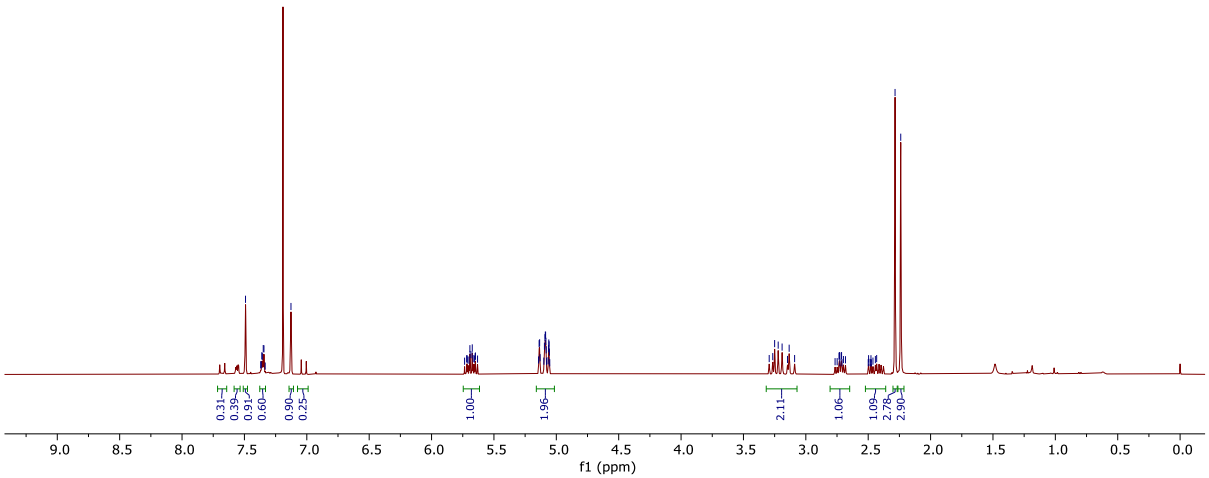
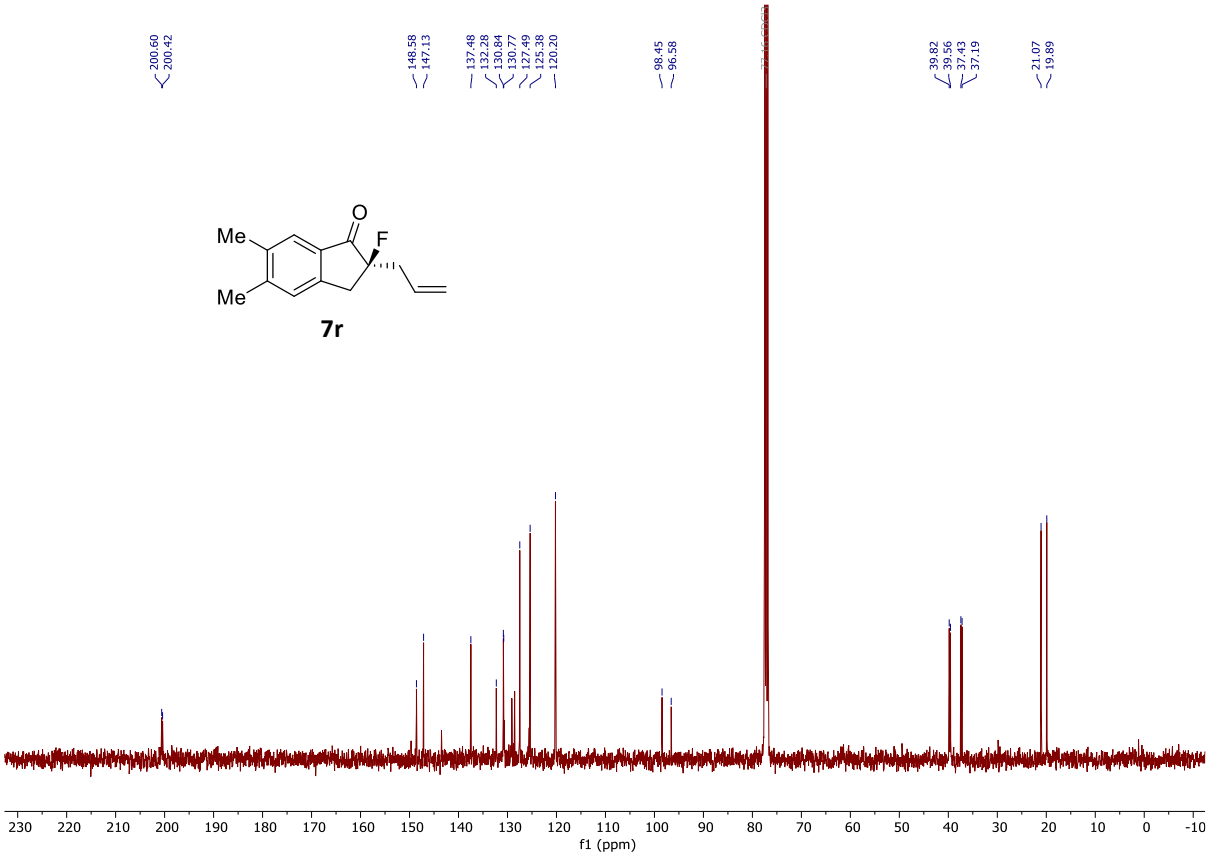
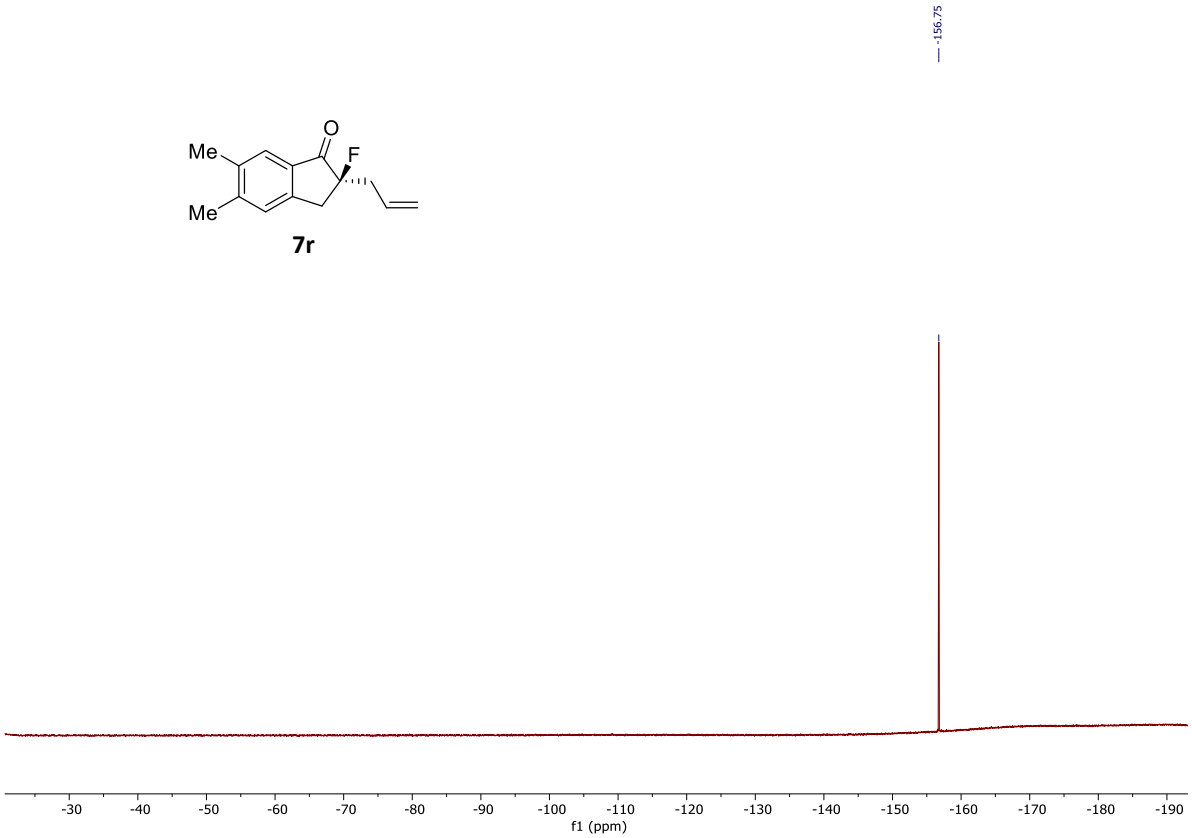


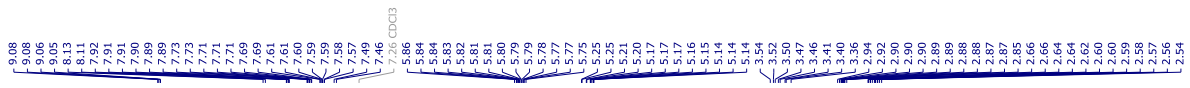
^{1}H NMR (400 MHz, $CDCl_3$)

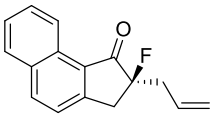


$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



$^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$)





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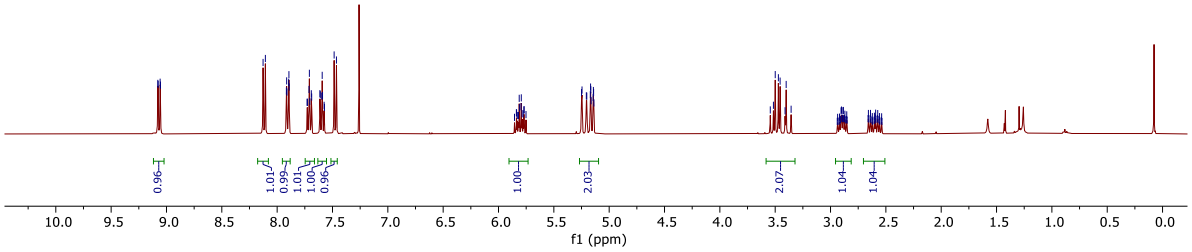
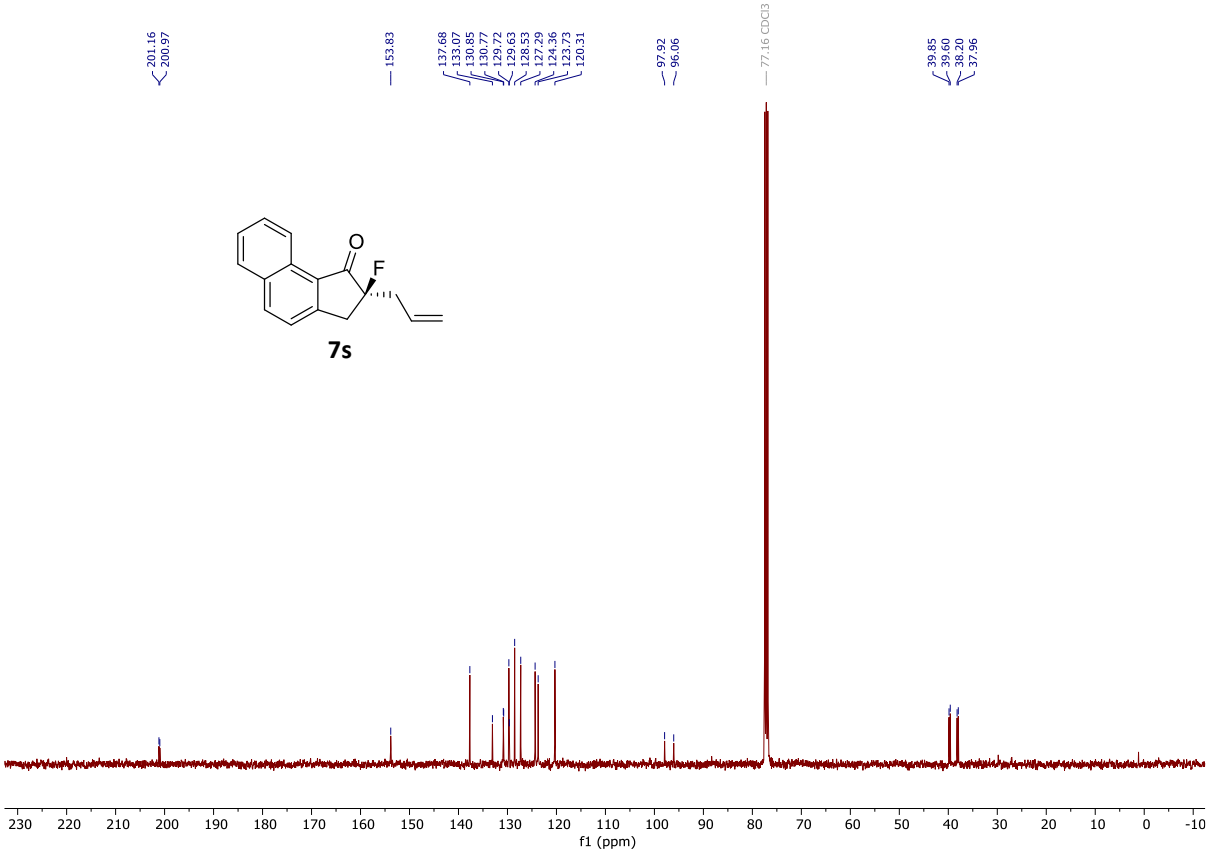


^{1}H NMR (400 MHz, $CDCl_3$)



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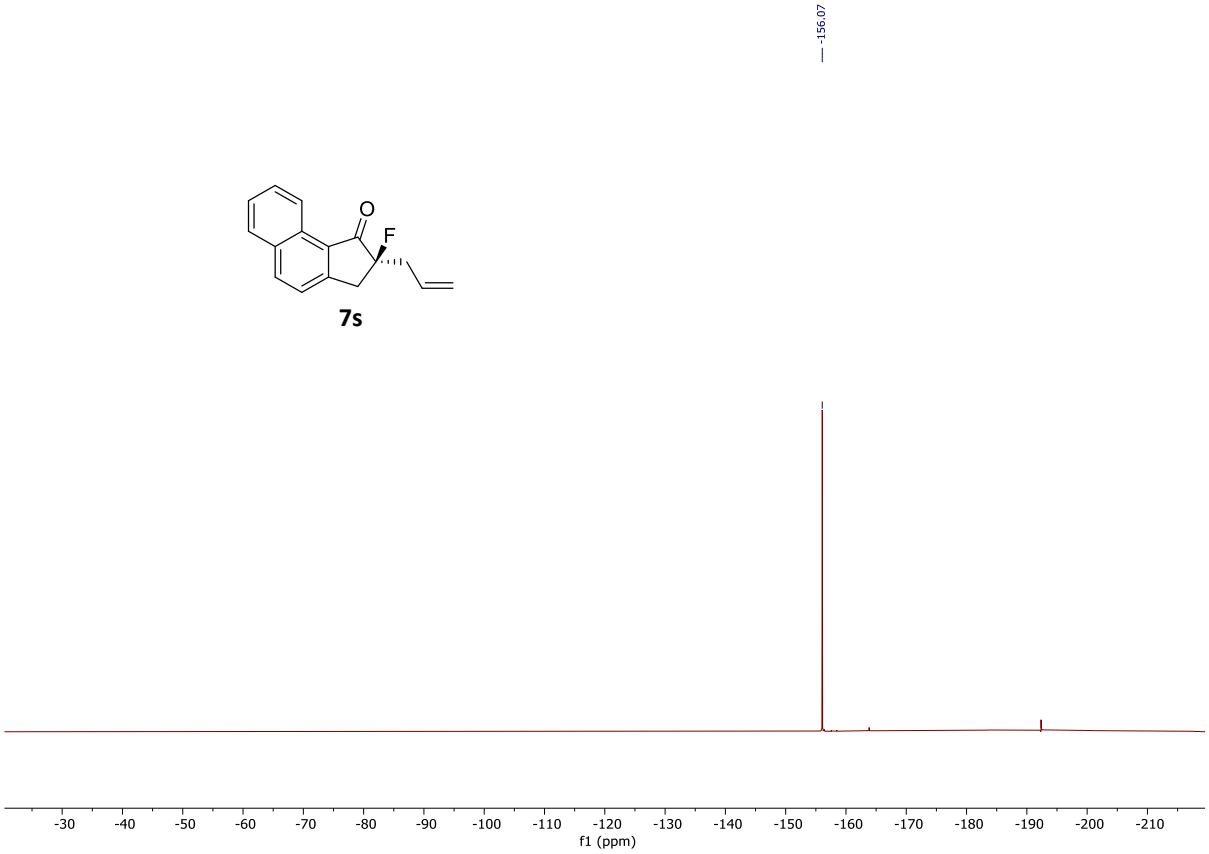
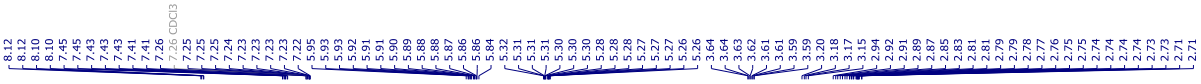
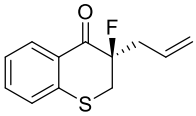
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)

7s

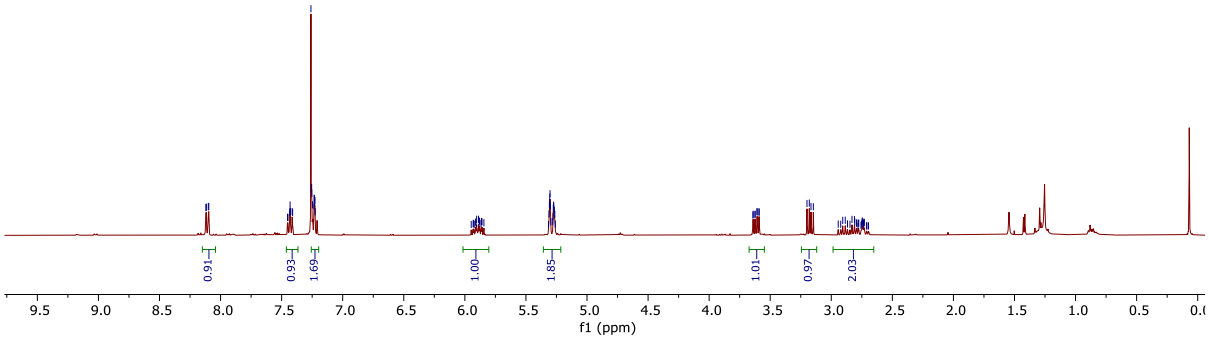


$^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$)

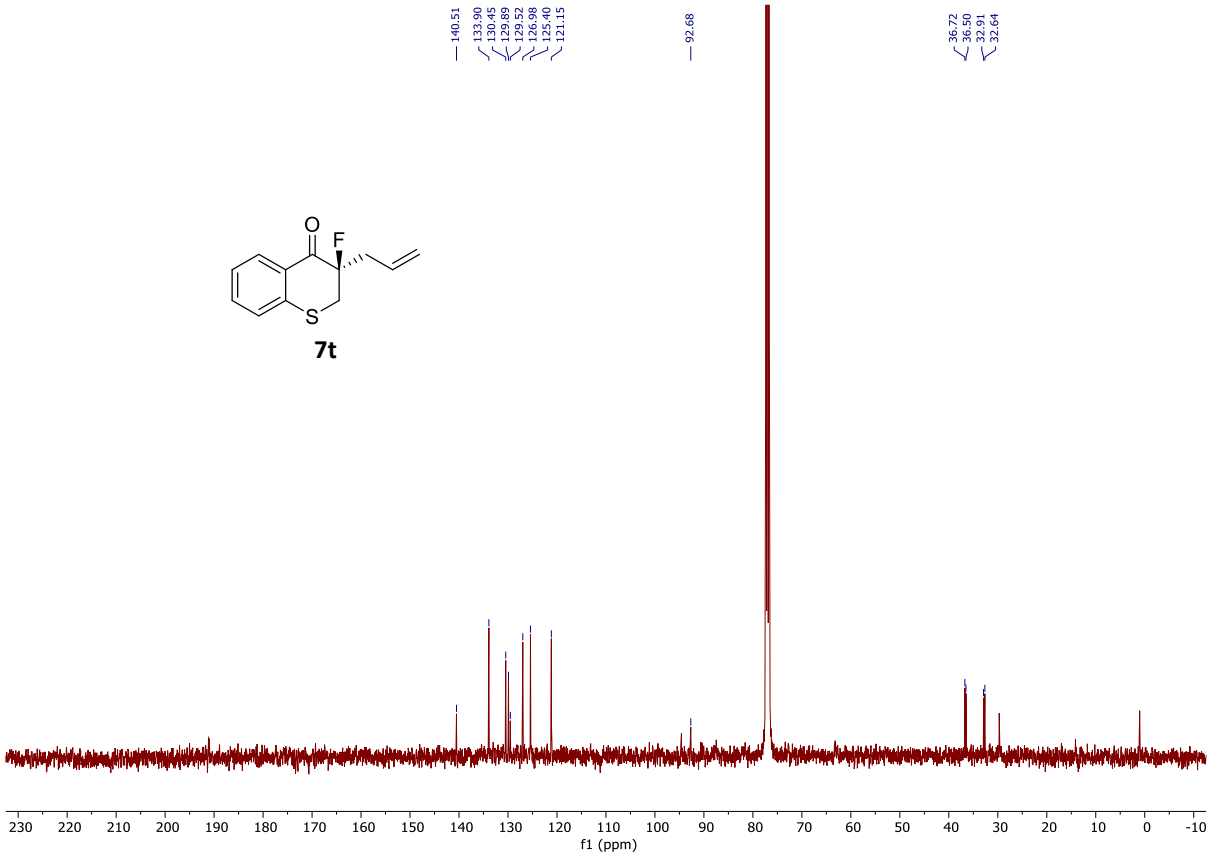




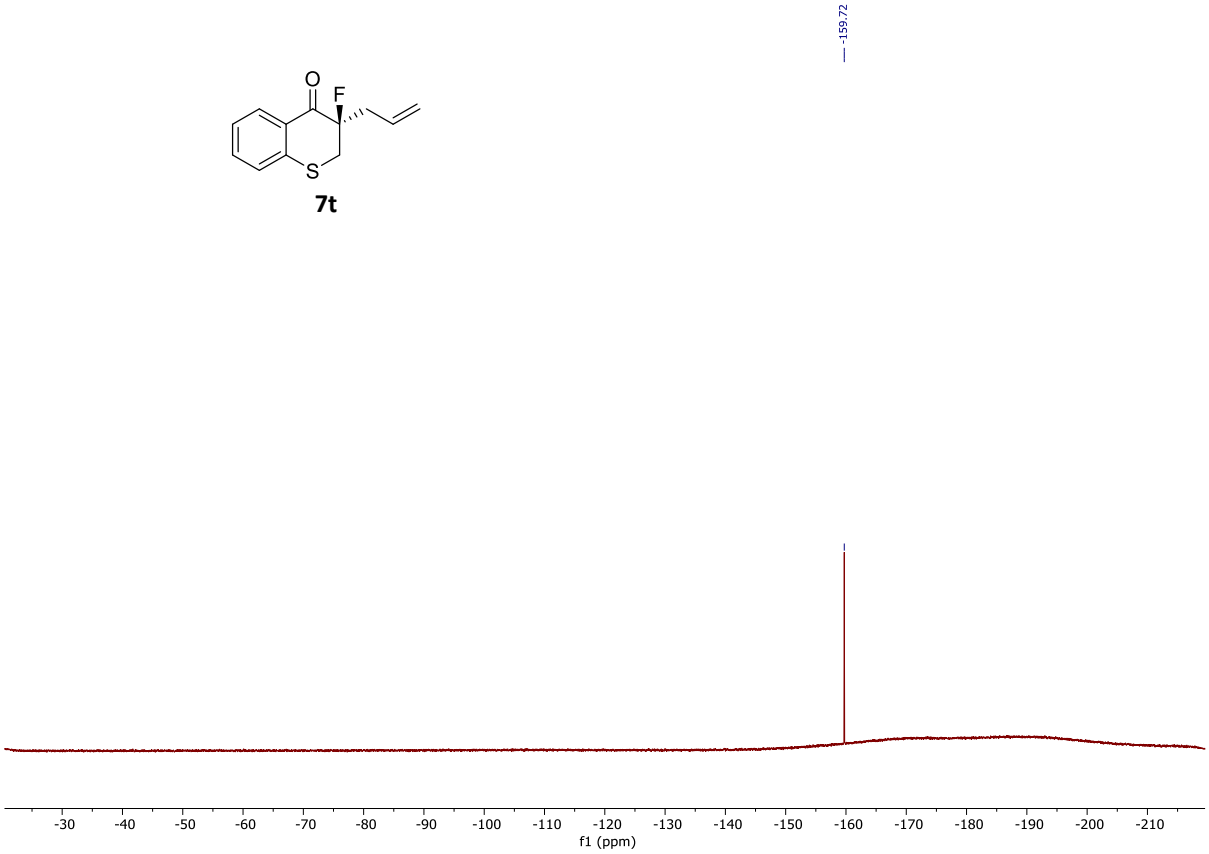
7t



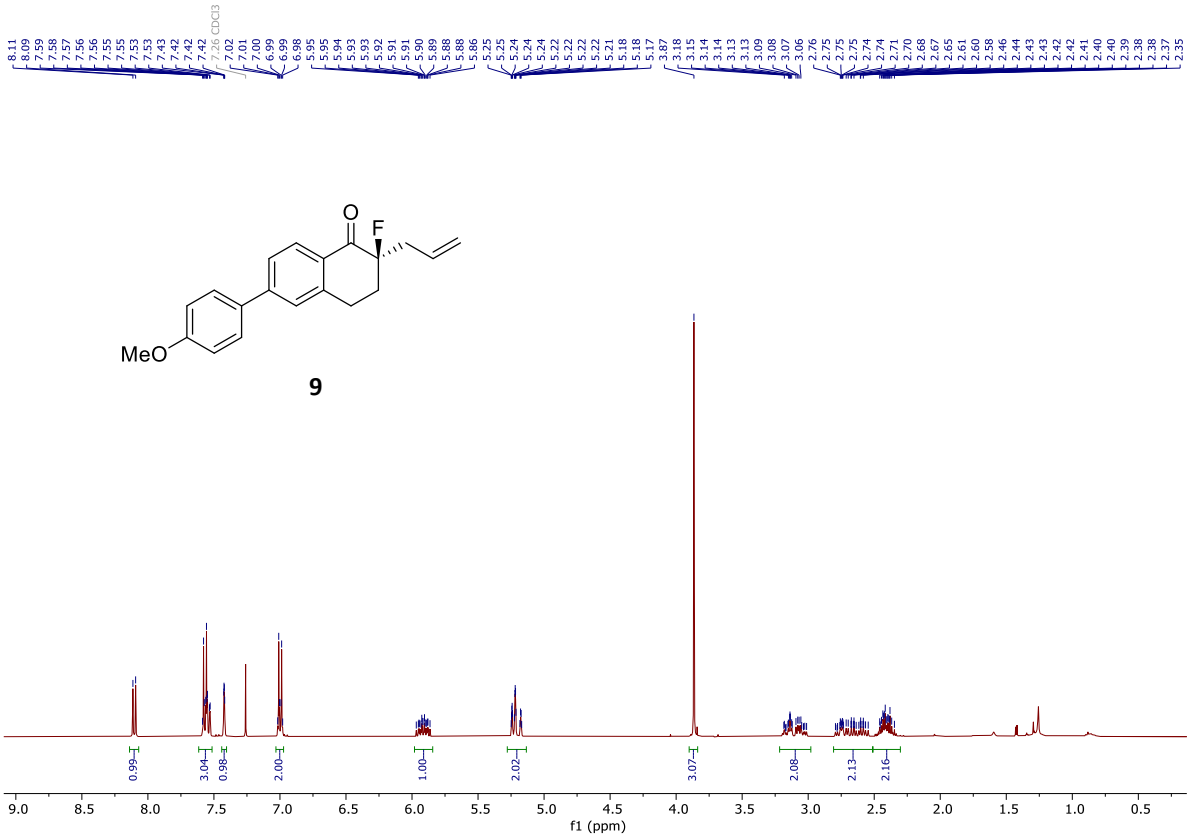
^{1}H NMR (400 MHz, $CDCl_3$)



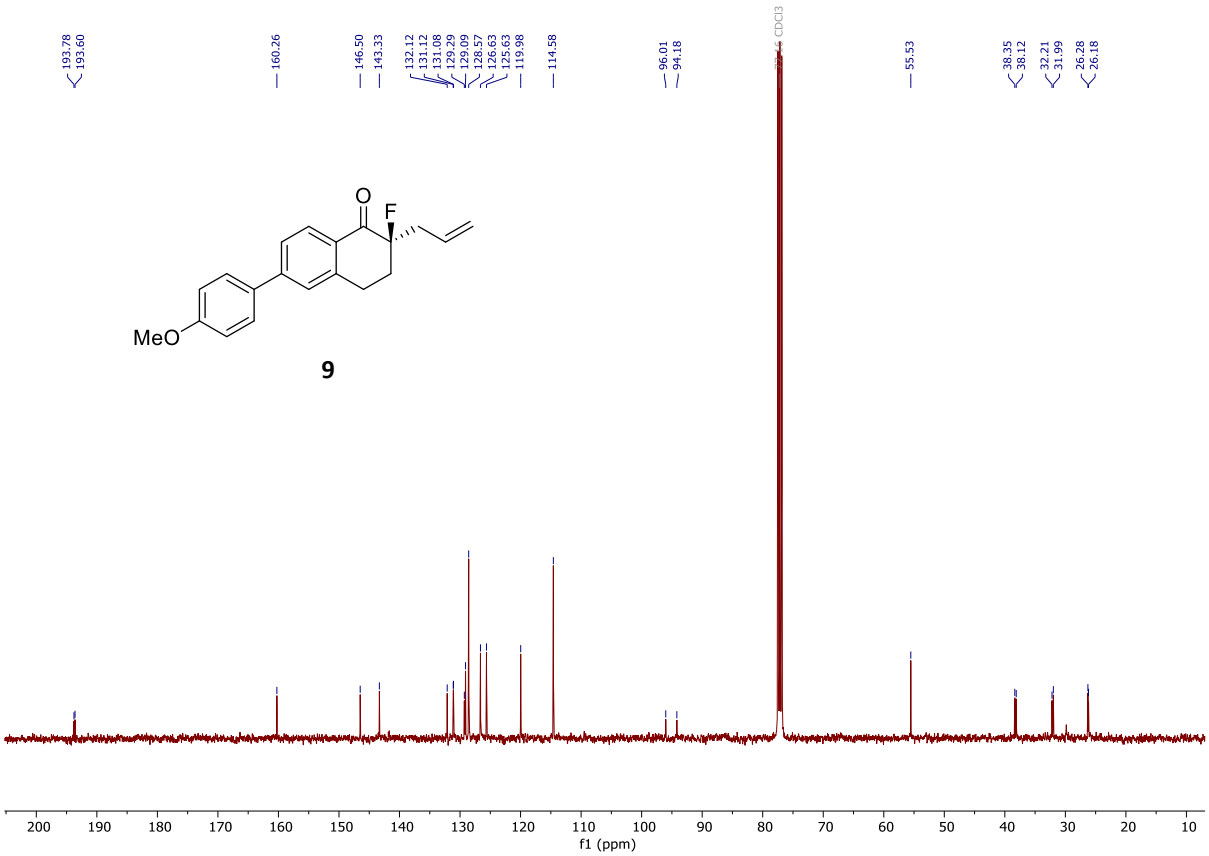
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



$^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$)

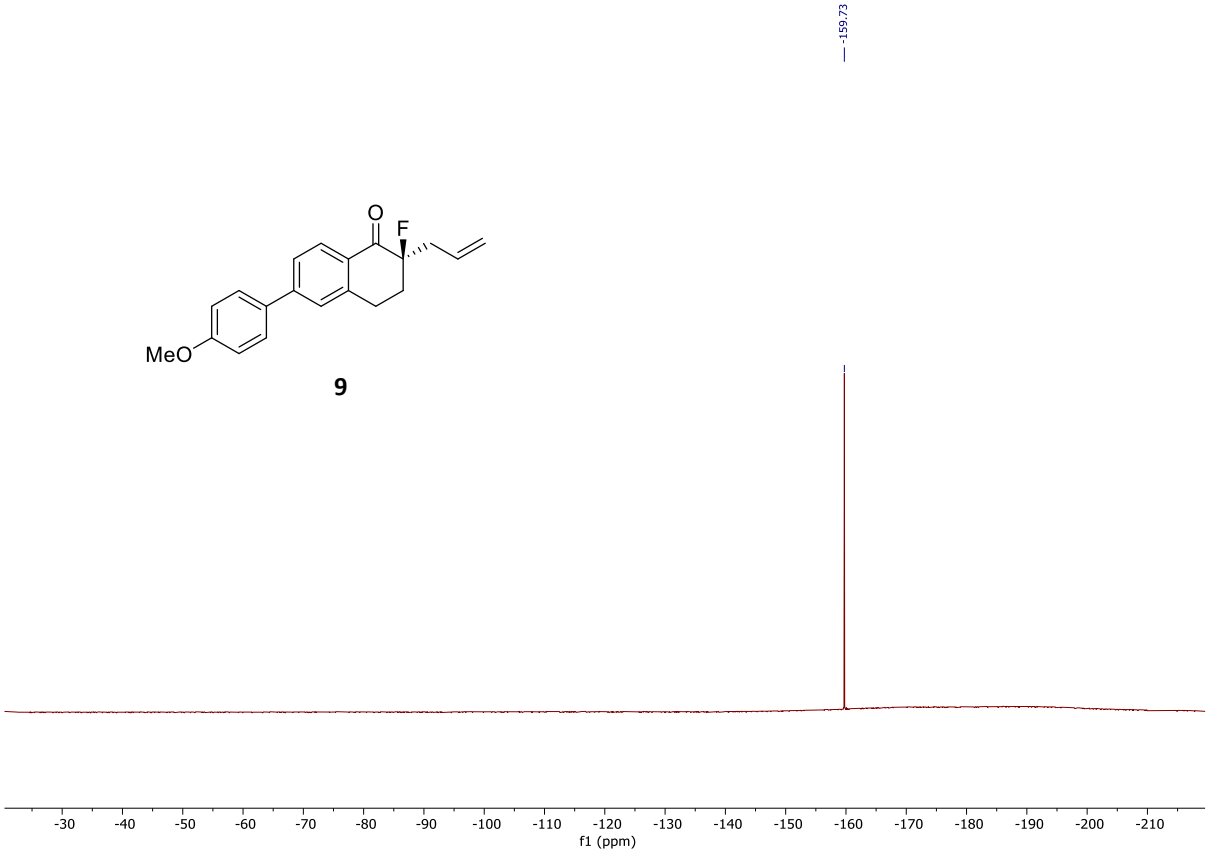


^{1}H NMR (400 MHz, $CDCl_3$)

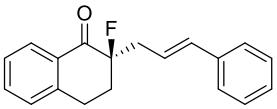


^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)

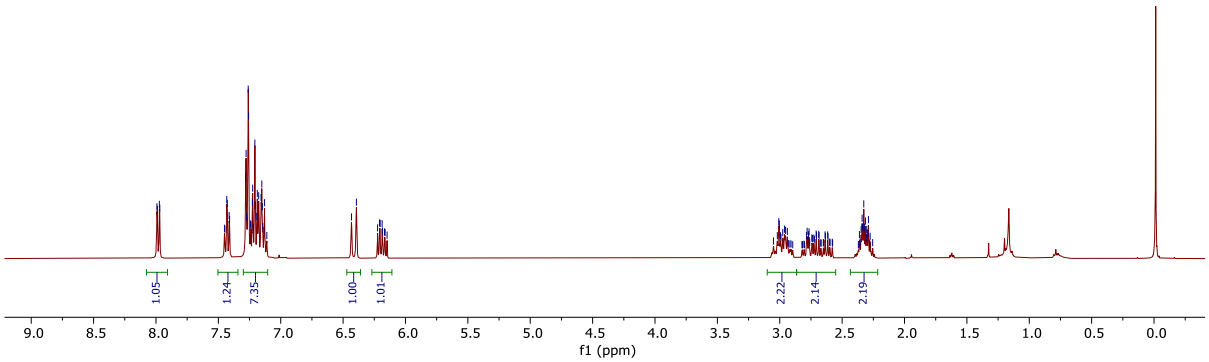
9



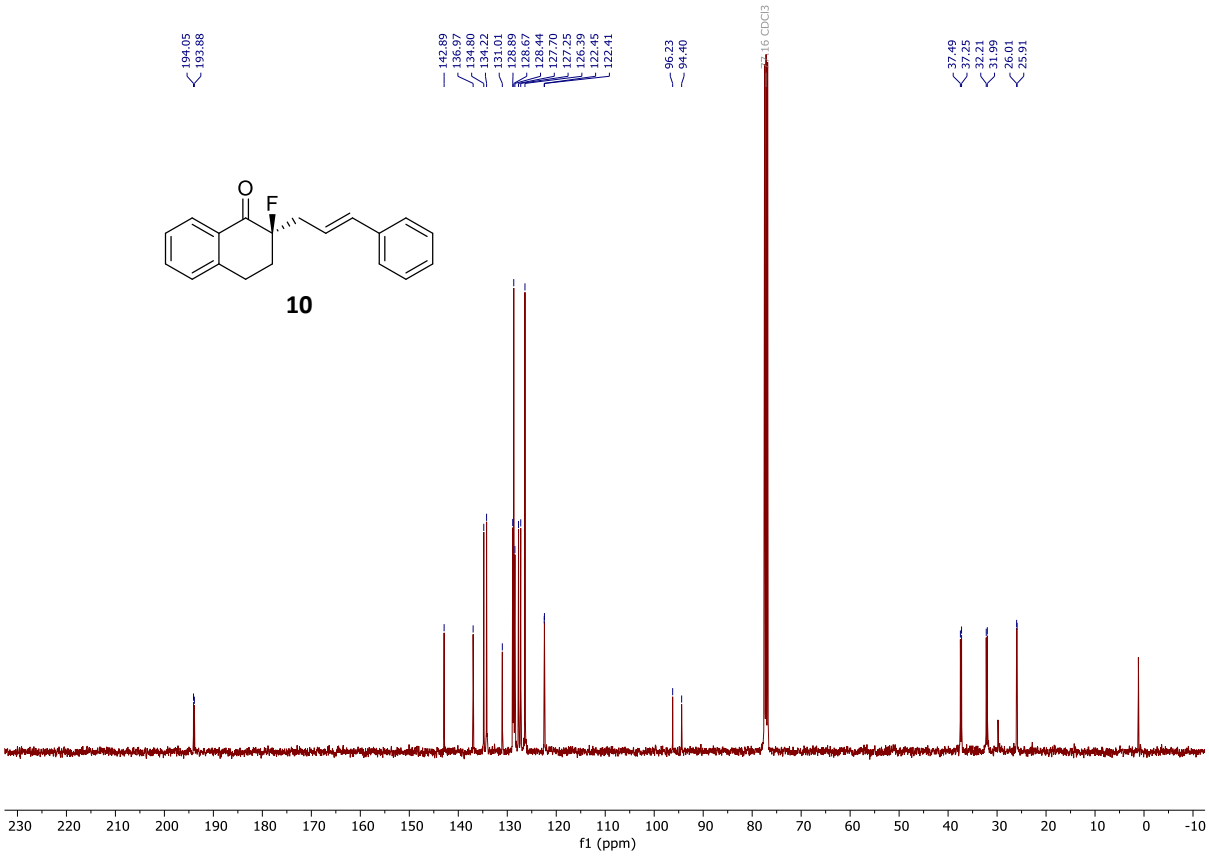
$^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$)



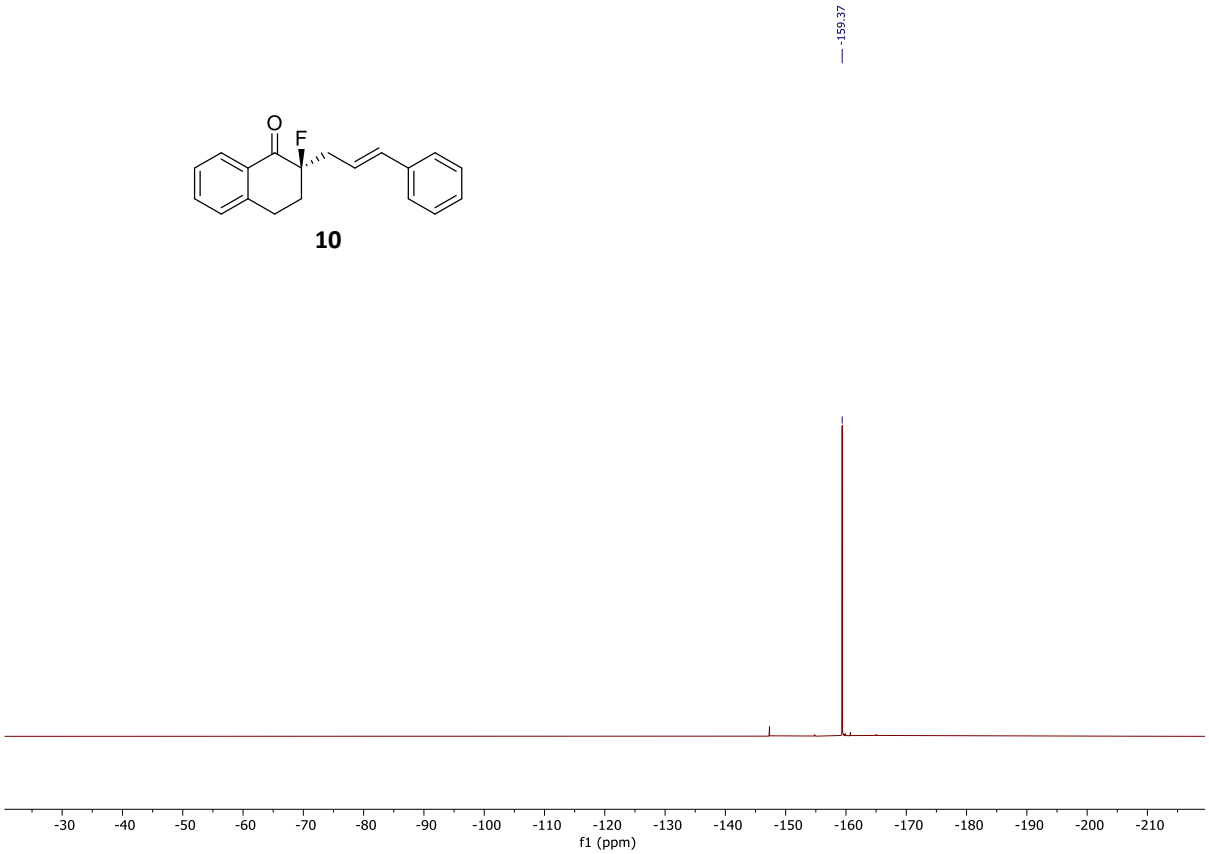
10



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



$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)

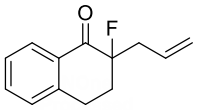


$^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$)

13. HPLC analysis for compounds **7a – 7t**

Eluant : Hexane / iPrOH 90/10

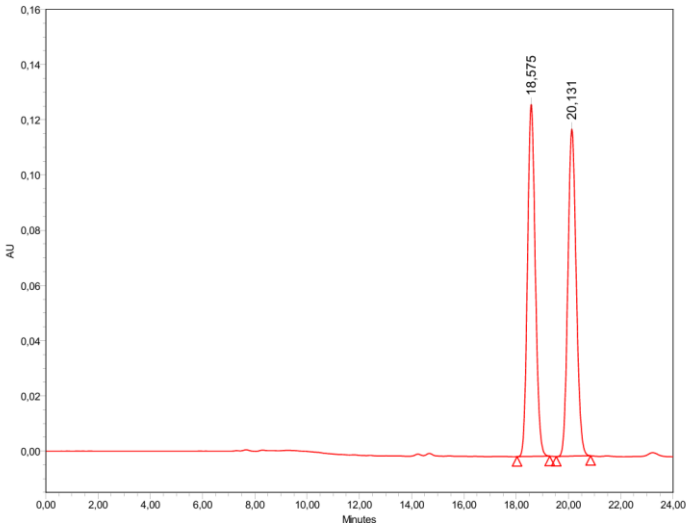
Column : Chiralpak IC



Flow : 0,5 ml /min

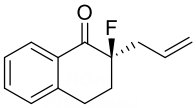
T° : 20°C

	Retention Time (min)	% Area
1	18,575	50,05
2	20,131	49,95



Eluant : Hexane / iPrOH 90/10

Column : Chiralpak IC

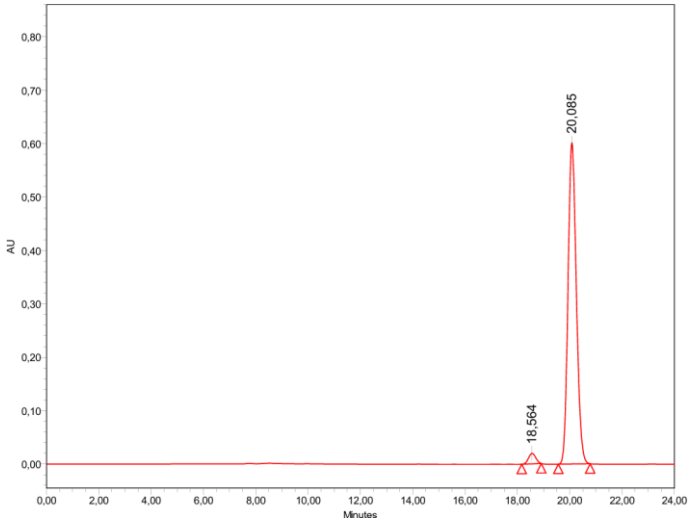


7a

Flow : 0,5 ml /min

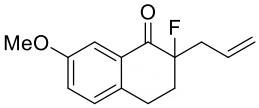
T° : 20°C

	Retention Time (min)	% Area
1	18,564	2,76
2	20,085	97,24



Eluant : Hexane / iPrOH 90/10

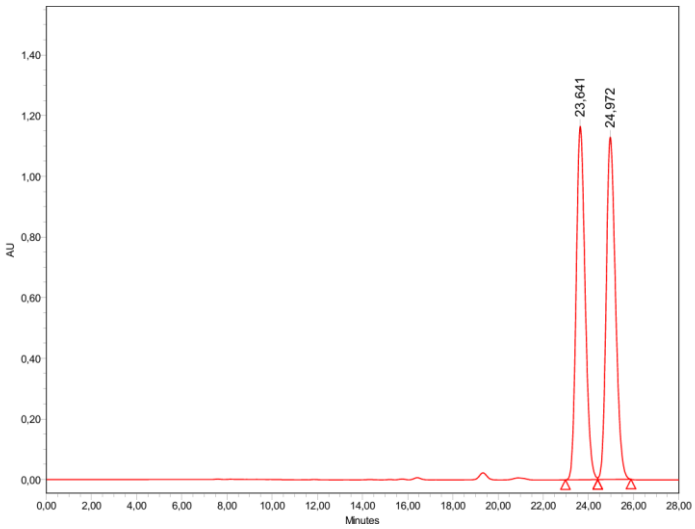
Column : Chiralpak IC



Flow : 0,5 ml /min

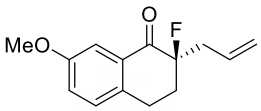
T° : 20°C

	Retention Time (min)	% Area
1	23,641	49,93
2	24,972	50,07



Eluant : Hexane / iPrOH 90/10

Column : Chiralpak IC

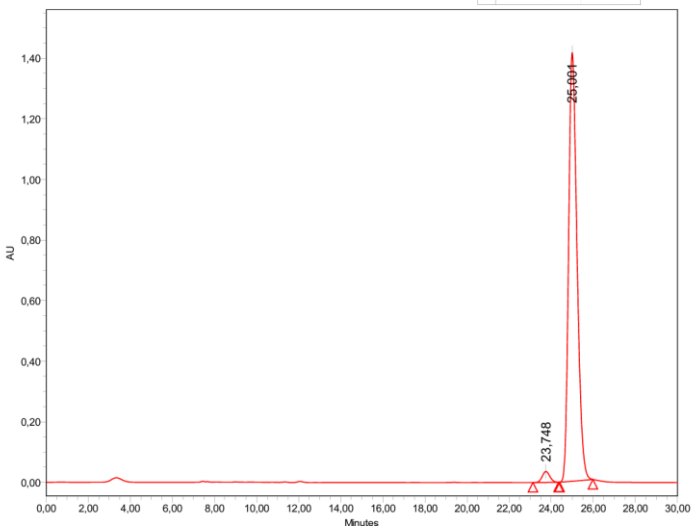


7b

Flow : 0,5 ml /min

T° : 20°C

	Retention Time (min)	% Area
1	23,748	2,26
2	25,001	97,74

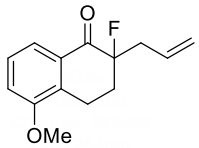


Eluant : Hexane / iPrOH 90/10

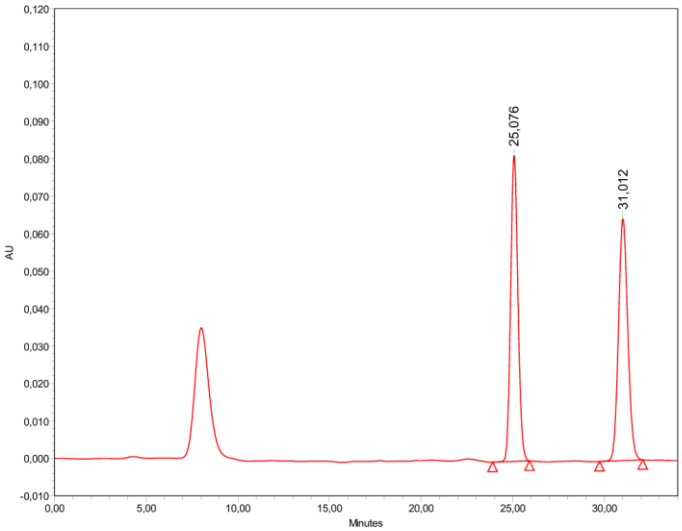
Column : Chiralpak IC

Flow : 0,5 ml /min

T° : 20°C



	Retention Time (min)	% Area
1	25,076	49,77
2	31,012	50,23

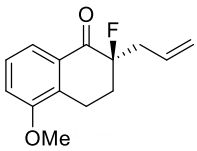


Eluant : Hexane / iPrOH 90/10

Column : Chiralpak IC

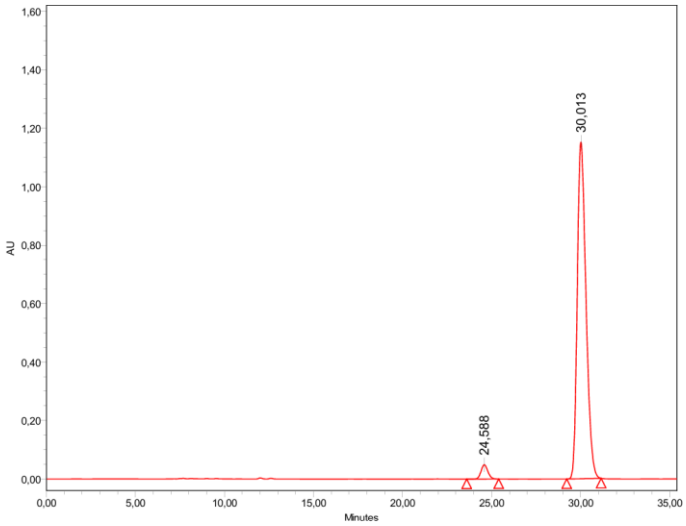
Flow : 0,5 ml /min

T° : 20°C



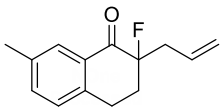
7c

	Retention Time (min)	% Area
1	24,588	3,21
2	30,013	96,79



Eluant : Hexane / iPrOH 90/10

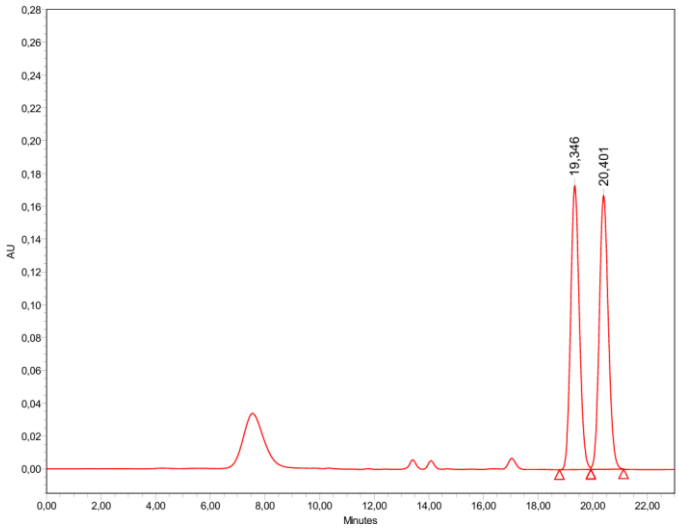
Column : Chiralpak IC



Flow : 0,5 ml /min

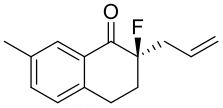
T° : 20°C

	Retention Time (min)	% Area
1	19,346	49,98
2	20,401	50,02



Eluant : Hexane / iPrOH 90/10

Column : Chiralpak IC

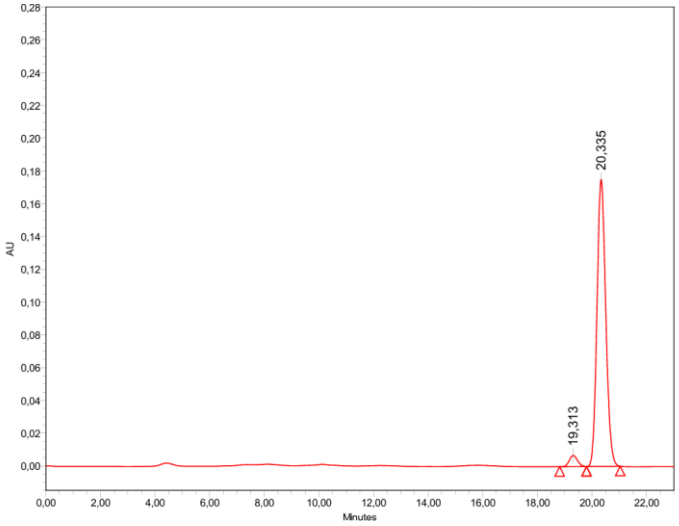


7d

Flow : 0,5 ml /min

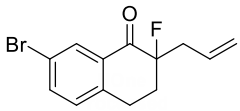
T° : 20°C

	Retention Time (min)	% Area
1	19,313	3,53
2	20,335	96,47



Eluant : Hexane / iPrOH 90/10

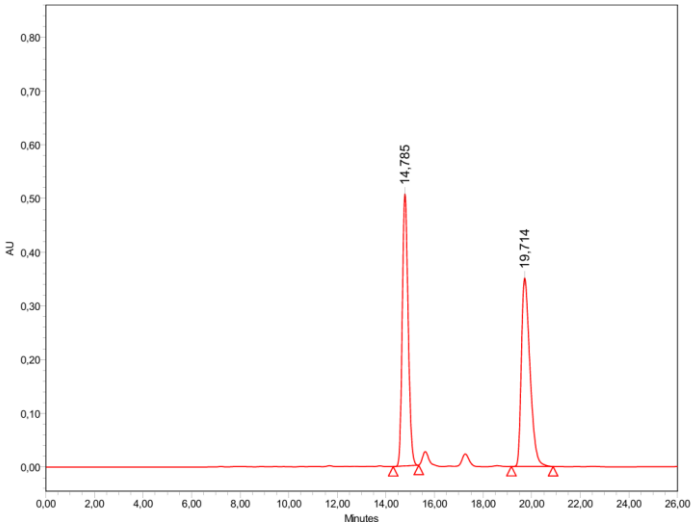
Column : Chiralpak IF



Flow : 0,5 ml /min

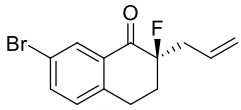
T° : 20°C

	Retention Time (min)	% Area
1	14,785	49,75
2	19,714	50,25



Eluant : Hexane / iPrOH 90/10

Column : Chiralpak IF

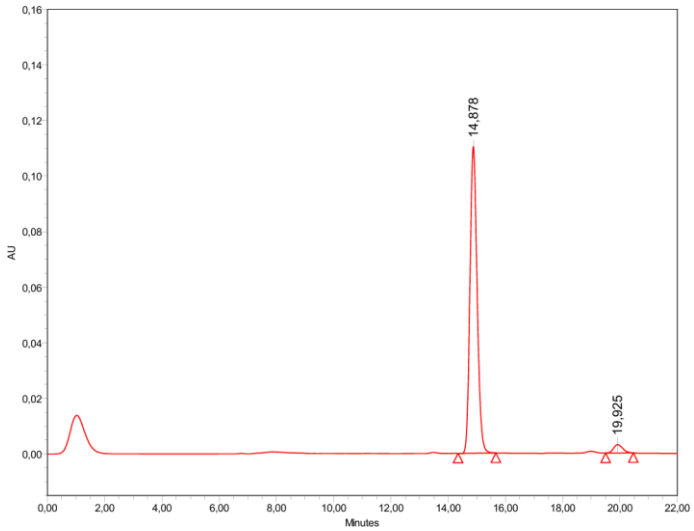


7e

Flow : 0,5 ml /min

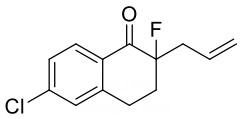
T° : 20°C

	Retention Time (min)	% Area
1	14,878	96,59
2	19,925	3,41



Eluant : Hexane / iPrOH 90/10

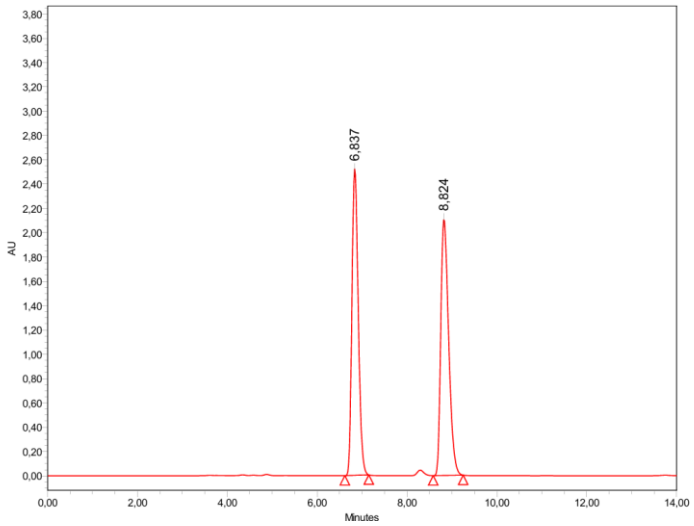
Column : Chiralpak IF



Flow : 1,0 ml /min

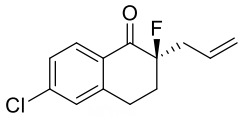
T° : 20°C

	Retention Time (min)	% Area
1	6,837	49,07
2	8,824	50,93



Eluant : Hexane / iPrOH 90/10

Column : Chiralpak IF

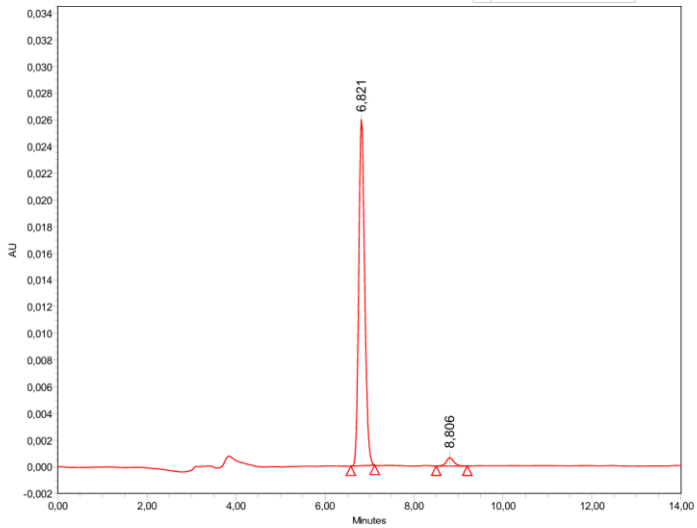


7f

Flow : 1,0 ml /min

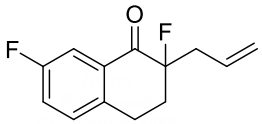
T° : 20°C

	Retention Time (min)	% Area
1	6,821	97,01
2	8,806	2,99



Eluant : Hexane / iPrOH 90/10

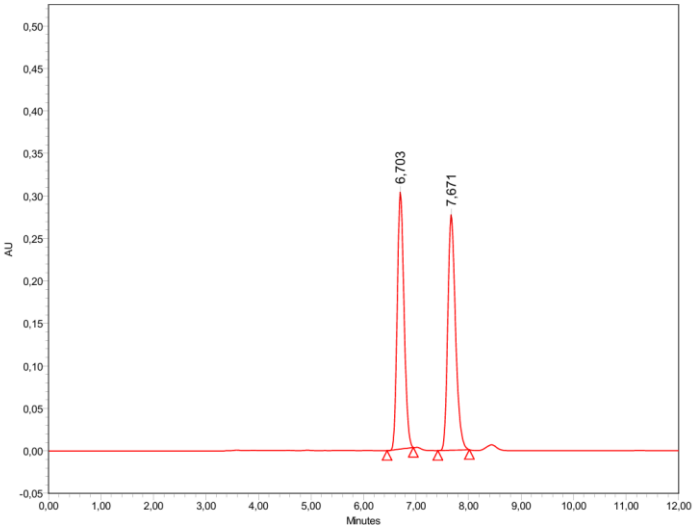
Column : Chiralpak IF



Flow : 1,0 ml /min

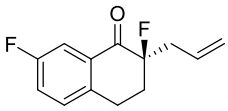
T° : 20°C

	Retention Time (min)	% Area
1	6,703	49,05
2	7,671	50,95



Eluant : Hexane / iPrOH 90/10

Column : Chiralpak IF

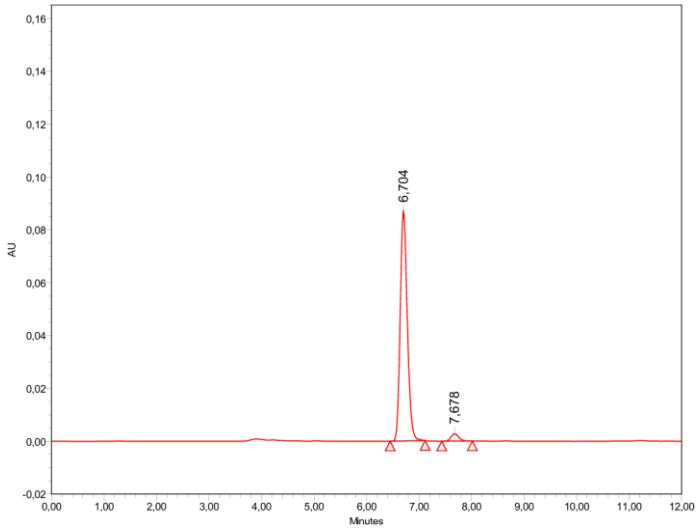


7g

Flow : 1,0 ml /min

T° : 20°C

	Retention Time (min)	% Area
1	6,704	96,64
2	7,678	3,36



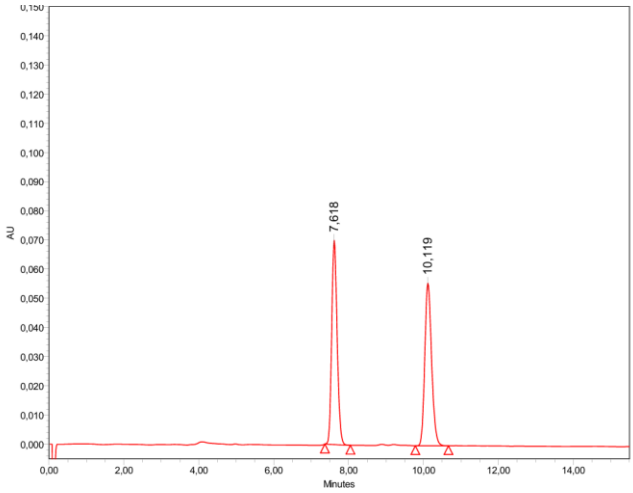
Eluant : Hexane / iPrOH 90/10

Column : Chiralpak IF

Flow : 1,0 ml /min

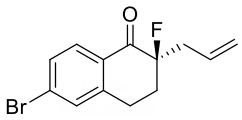
T° : 20°C

	Retention Time (min)	% Area
1	7,618	49,89
2	10,119	50,11



Eluant : Hexane / iPrOH 90/10

Column : Chiralpak IF

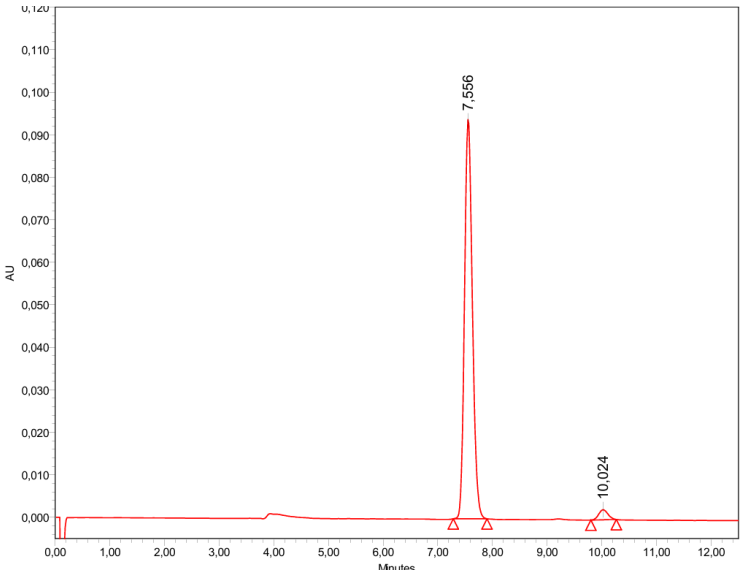


7h

Flow : 1,0 ml /min

T° : 20°C

	Retention Time (min)	% Area
1	7,556	97,15
2	10,024	2,85



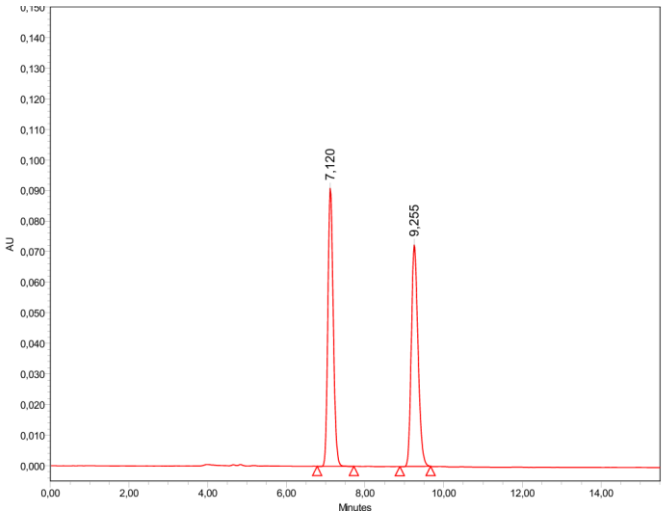
Eluant : Hexane / iPrOH 90/10

Column : Chiralpak IF

Flow : 1,0 ml /min

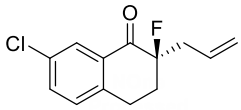
T° : 20°C

	Retention Time (min)	% Area
1	7,120	50,05
2	9,255	49,95



Eluant : Hexane / iPrOH 90/10

Column : Chiralpak IF

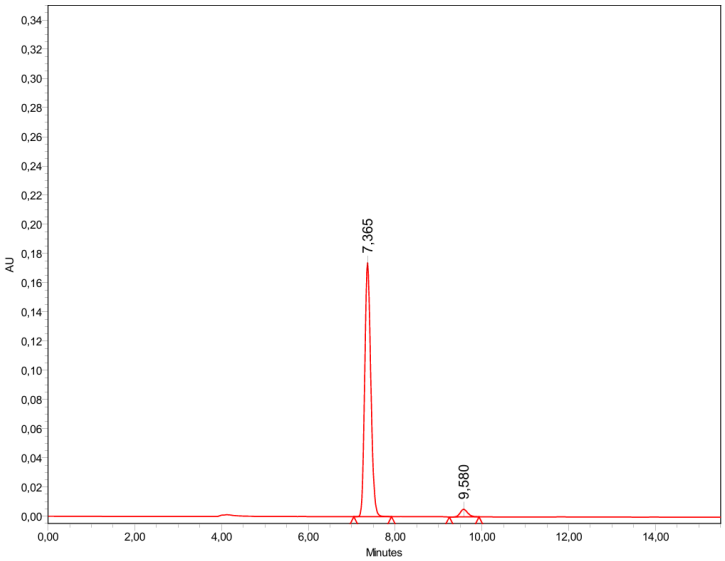


7i

Flow : 1,0 ml /min

T° : 20°C

	Retention Time (min)	% Area
1	7,365	96,49
2	9,580	3,51



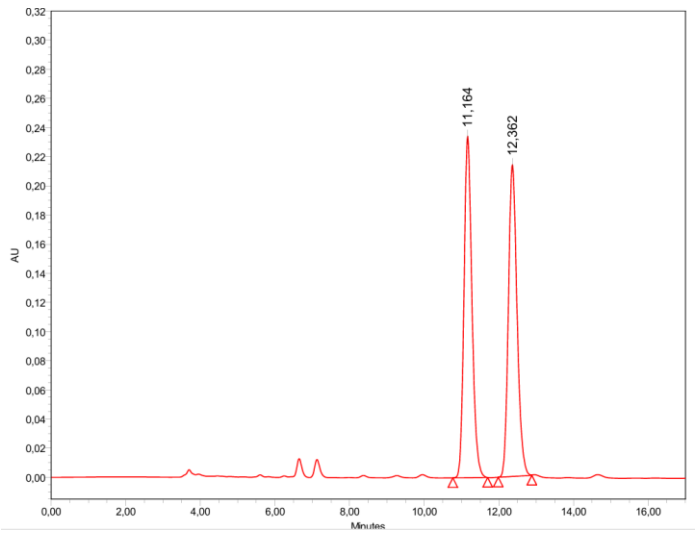
Eluant : Hexane / iPrOH 90/10

Column : Chiralpak IC

Flow : 1,0 ml /min

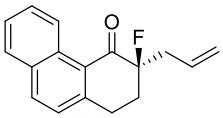
T° : 20°C

	Retention Time (min)	% Area
1	11,164	50,20
2	12,362	49,80



Eluant : Hexane / iPrOH 90/10

Column : Chiralpak IC

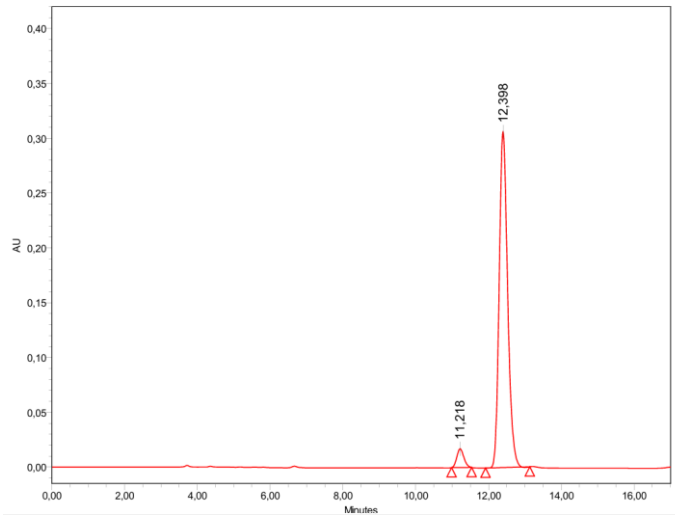


7j

Flow : 1,0 mL/min

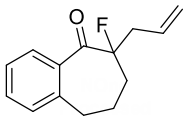
T° : 20°C

	Retention Time (min)	% Area
1	11,218	4,46
2	12,398	95,54



Eluant : Hexane / iPrOH 99/1

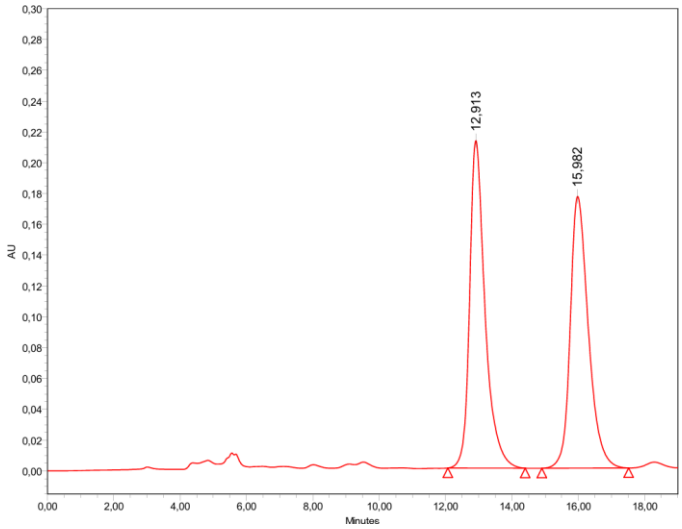
Column : Chiralpak OJ



Flow : 0,8 ml /min

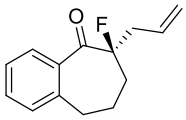
T° : 20°C

	Retention Time (min)	% Area
1	12,913	50,67
2	15,982	49,33



Eluant : Hexane / iPrOH 99/1

Column : Chiralpak OJ

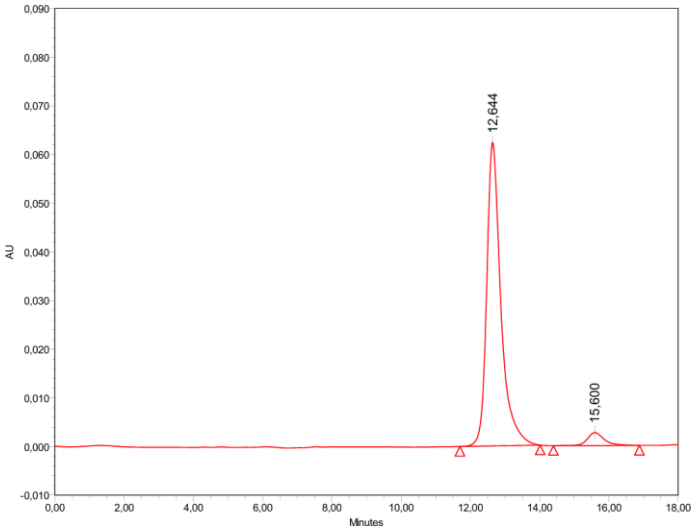


7l

Flow : 0,8 ml /min

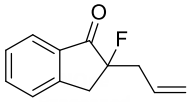
T° : 20°C

	Retention Time (min)	% Area
1	12,644	95,11
2	15,600	4,89



Eluant : Hexane / iPrOH 90/10

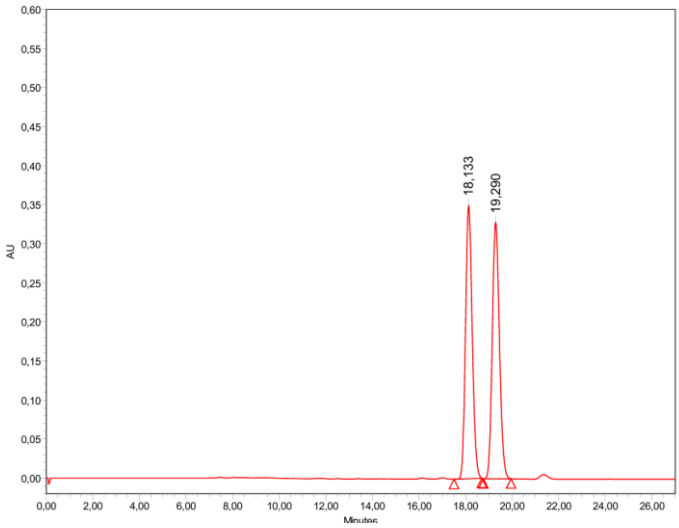
Column : Chiralpak IC



Flow : 0,5 ml /min

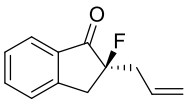
T° : 20°C

	Retention Time (min)	% Area
1	18,133	49,97
2	19,290	50,03



Eluant : Hexane / iPrOH 90/10

Column : Chiralpak IC

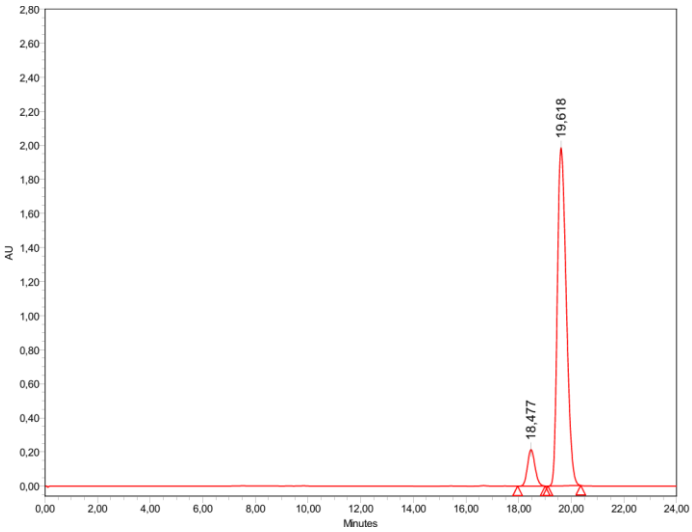


7m

Flow : 0,5 ml /min

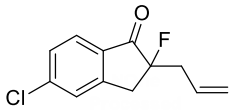
T° : 20°C

	Retention Time (min)	% Area
1	18,477	8,27
2	19,618	91,73



Eluant : Hexane / iPrOH 95/5

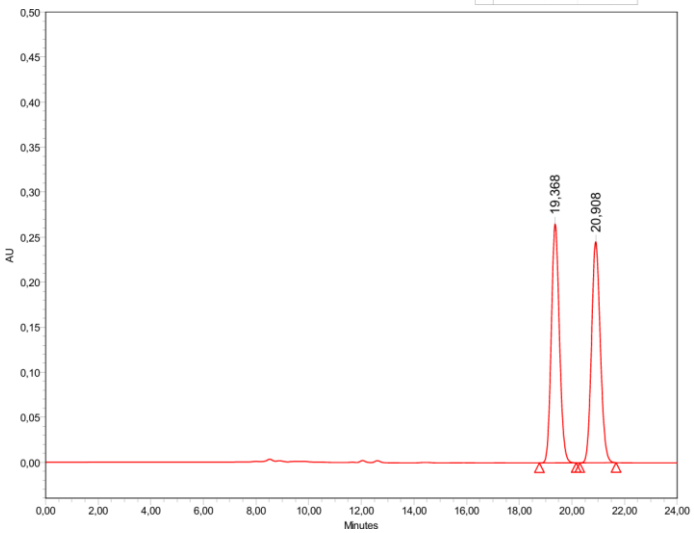
Column : Chiralpak IC



Flow : 0,5 ml /min

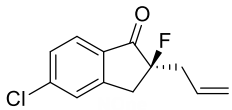
T° : 20°C

	Retention Time (min)	% Area
1	19,368	50,03
2	20,908	49,97



Eluant : Hexane / iPrOH 95/5

Column : Chiralpak IC

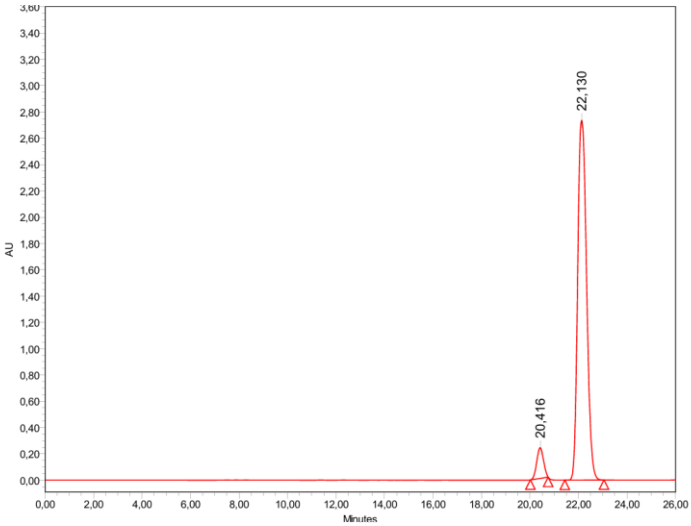


7n

Flow : 0,5 ml /min

T° : 20°C

	Retention Time (min)	% Area
1	20,416	6,08
2	22,130	93,92

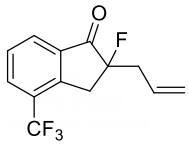


Eluant : Hexane / iPrOH 95/5

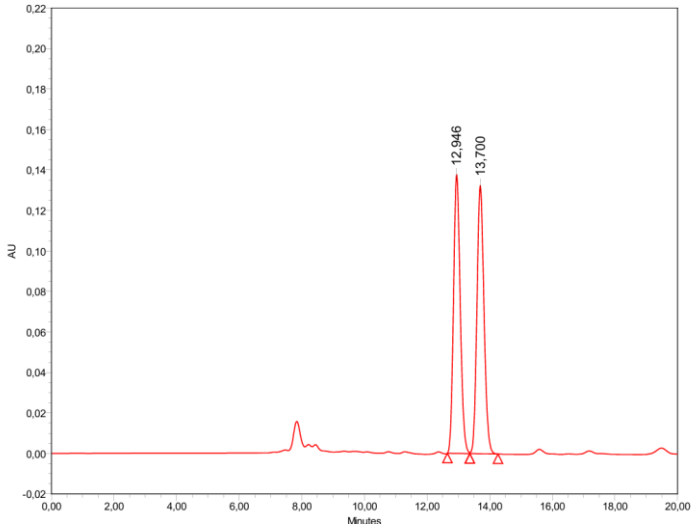
Column : Chiralpak IC

Flow : 0,5 ml /min

T° : 20°C



	Retention Time (min)	% Area
1	12,946	49,74
2	13,700	50,26

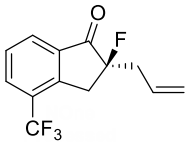


Eluant : Hexane / iPrOH 95/5

Column : Chiralpak IC

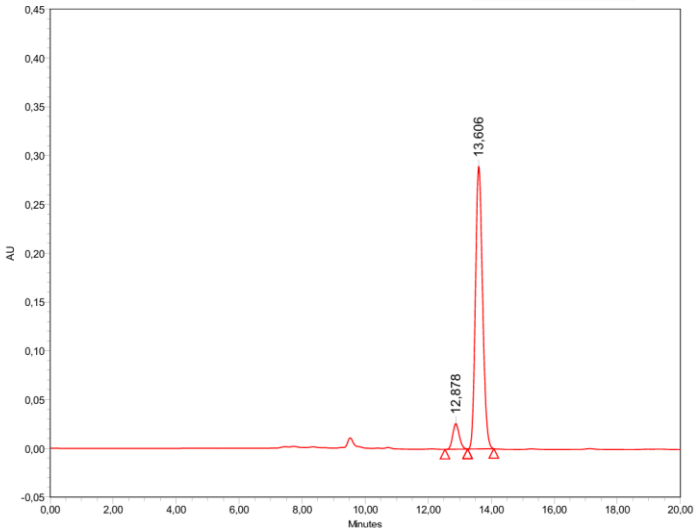
Flow : 0,5 ml /min

T° : 20°C



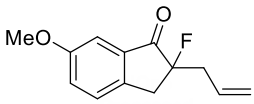
7o

	Retention Time (min)	% Area
1	12,878	7,70
2	13,606	92,30



Eluant : Hexane / iPrOH 90/10

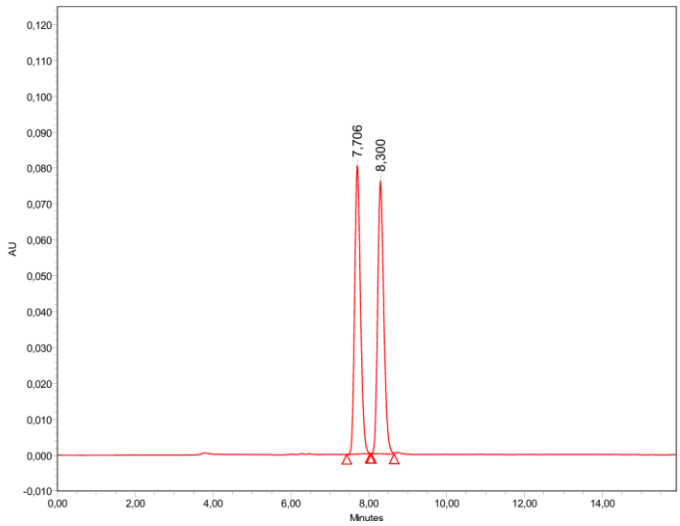
Column : Chiralpak IF



Flow : 1,0 ml /min

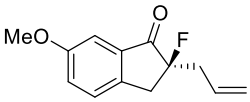
T° : 20°C

	Retention Time (min)	% Area
1	7,706	50,18
2	8,300	49,82



Eluant : Hexane / iPrOH 90/10

Column : Chiralpak IF

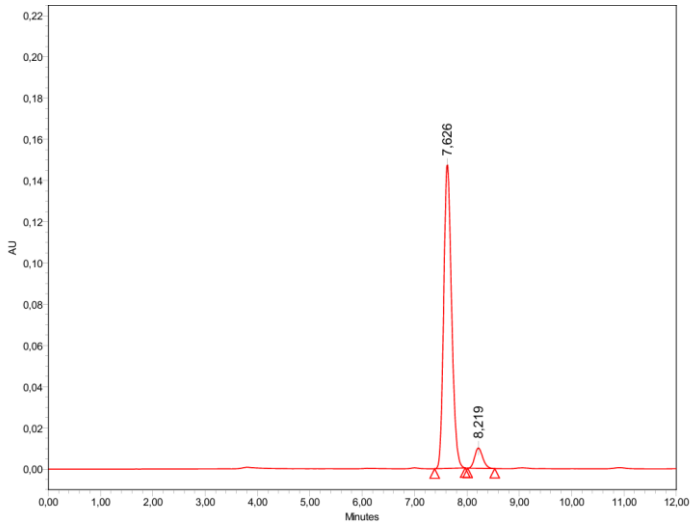


7p

Flow : 1,0 ml /min

T° : 20°C

	Retention Time (min)	% Area
1	7,626	93,60
2	8,219	6,40



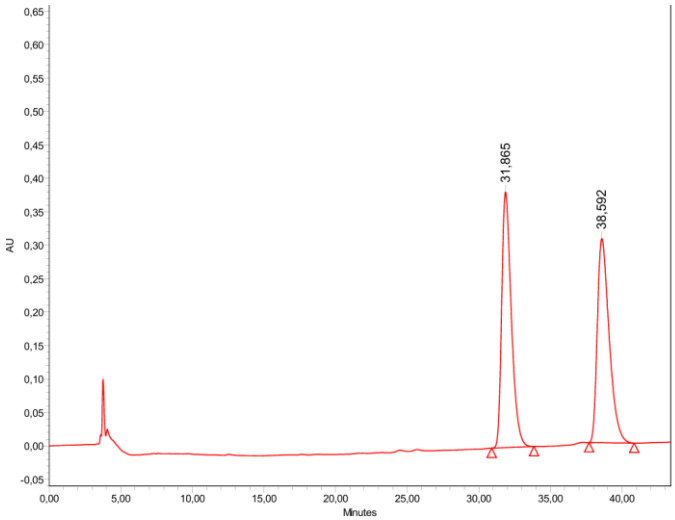
Eluant : Hexane / iPrOH 90/10

Column : Chiralpak IC

Flow : 1,0 ml /min

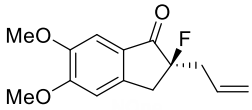
T° : 20°C

	Retention Time (min)	% Area
1	31,865	50,40
2	38,592	49,60



Eluant : Hexane / iPrOH 90/10

Column : Chiralpak IC

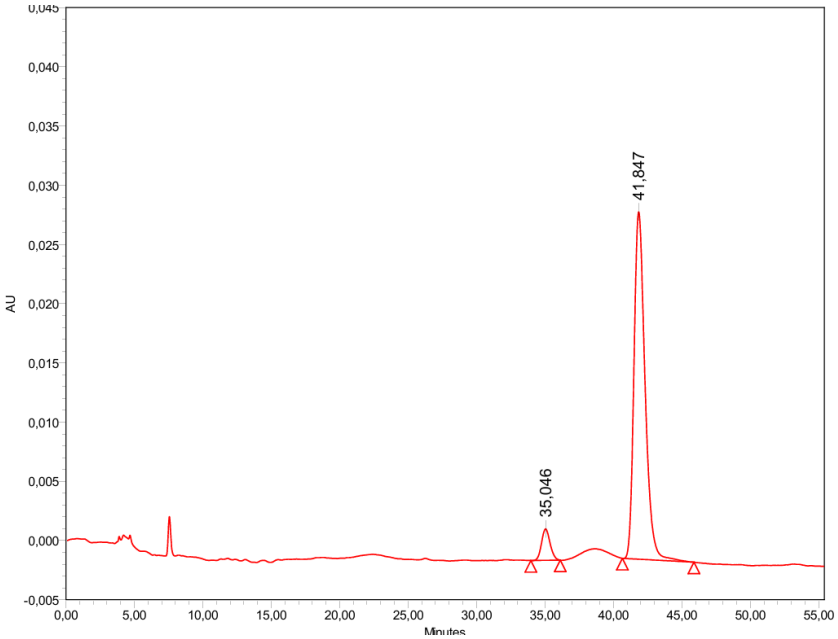


7q

Flow : 1,0 ml /min

T° : 20°C

	Retention Time (min)	% Area
1	35,046	6,54
2	41,847	93,46



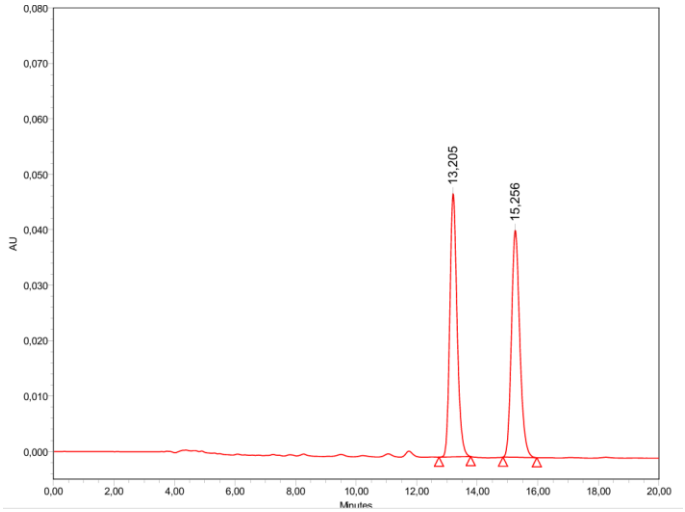
Eluant : Hexane / iPrOH 90/10

Column : Chiralpak IC

Flow : 1,0 ml /min

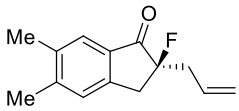
T° : 20°C

	Retention Time (min)	% Area
1	13,205	50,05
2	15,256	49,95



Eluant : Hexane / iPrOH 90/10

Column : Chiralpak IC

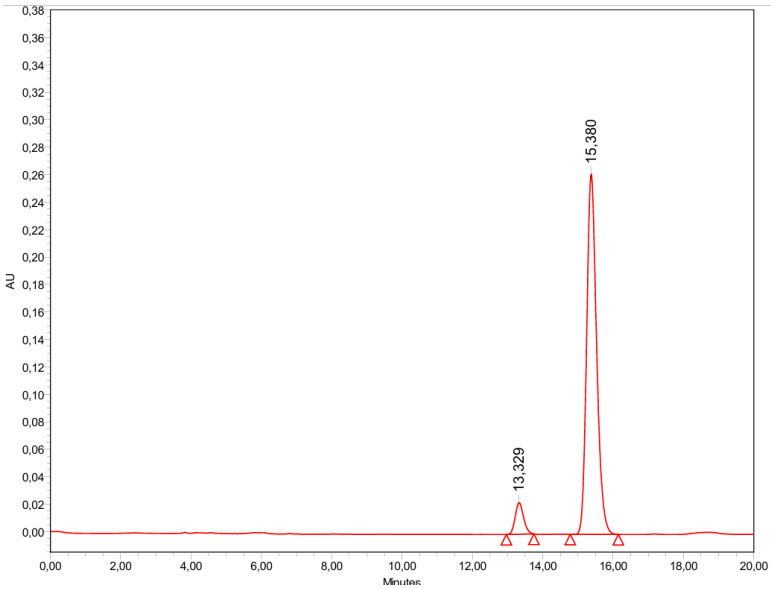


7r

Flow : 1,0 ml /min

T° : 20°C

	Retention Time (min)	% Area
1	13,329	6,92
2	15,380	93,08



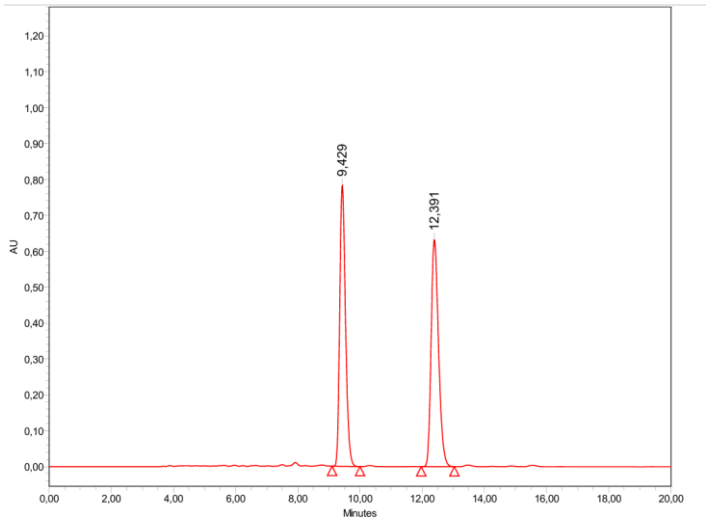
Eluant : Hexane / iPrOH 90/10

Column : Chiralpak IC

Flow : 1,0 ml /min

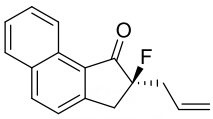
T° : 20°C

	Retention Time (min)	% Area
1	9,429	49,15
2	12,391	50,85



Eluant : Hexane / iPrOH 90/10

Column : Chiralpak IC

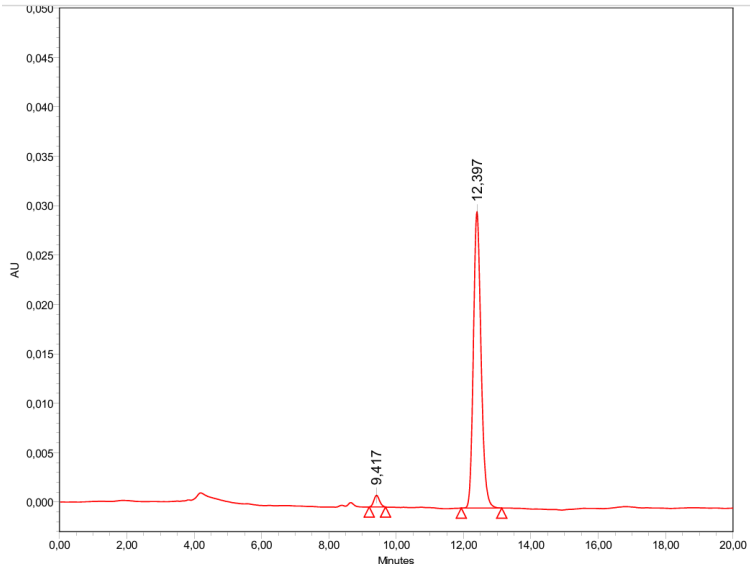


7s

Flow : 1,0 ml /min

T° : 20°C

	Retention Time (min)	% Area
1	9,417	2,81
2	12,397	97,19



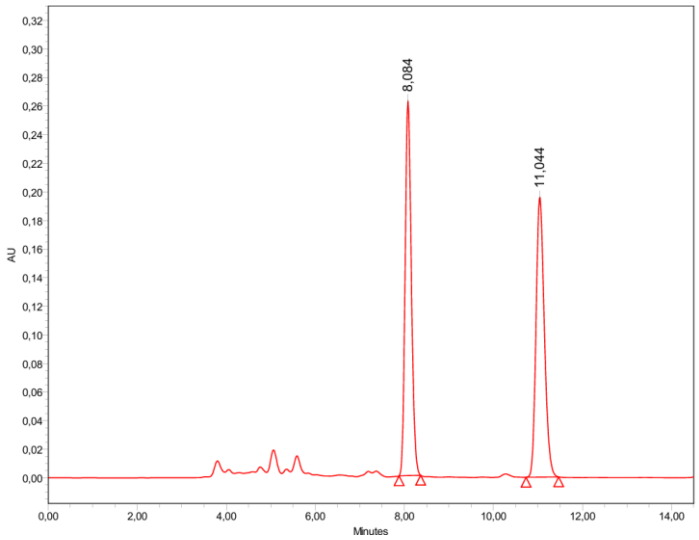
Eluant : Hexane / iPrOH 90/10

Column : Chiralpak IF

Flow : 1,0 mL/min

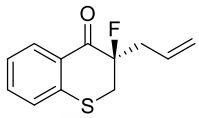
T° : 20°C

	Retention Time (min)	% Area
1	8,084	50,17
2	11,044	49,83



Eluant : Hexane / iPrOH 90/10

Column : Chiralpak IF

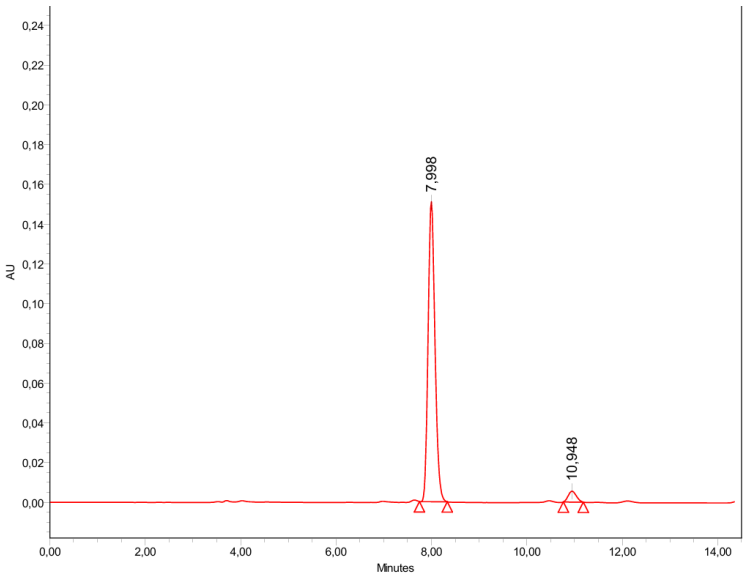


7t

Flow : 1,0 mL/min

T° : 20°C

	Retention Time (min)	% Area
1	7,998	95,95
2	10,948	4,05



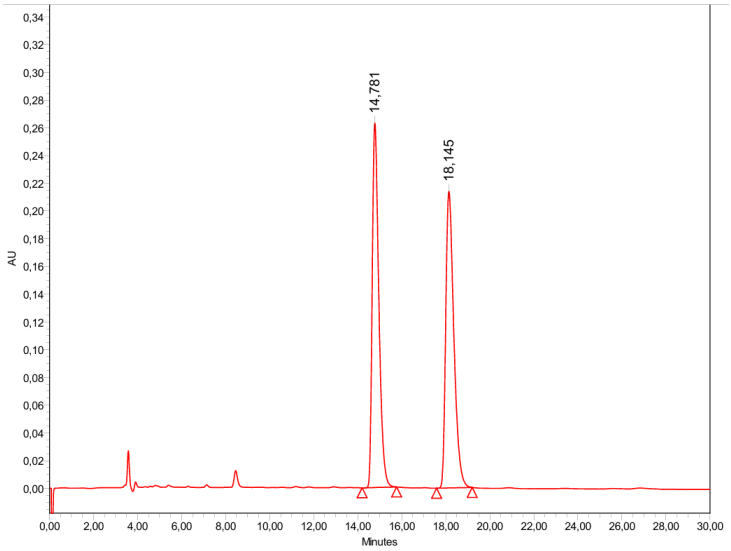
Eluant : Hexane / iPrOH 90/10

Column : Chiralpak

Flow : 1,0 ml /min

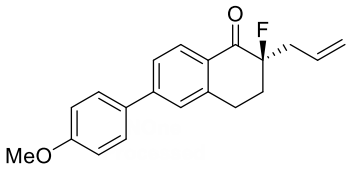
T° : 20°C

	Retention Time (min)	% Area
1	14,781	49,96
2	18,145	50,04



Eluant : Hexane / iPrOH 90/10

Column : Chiralpak

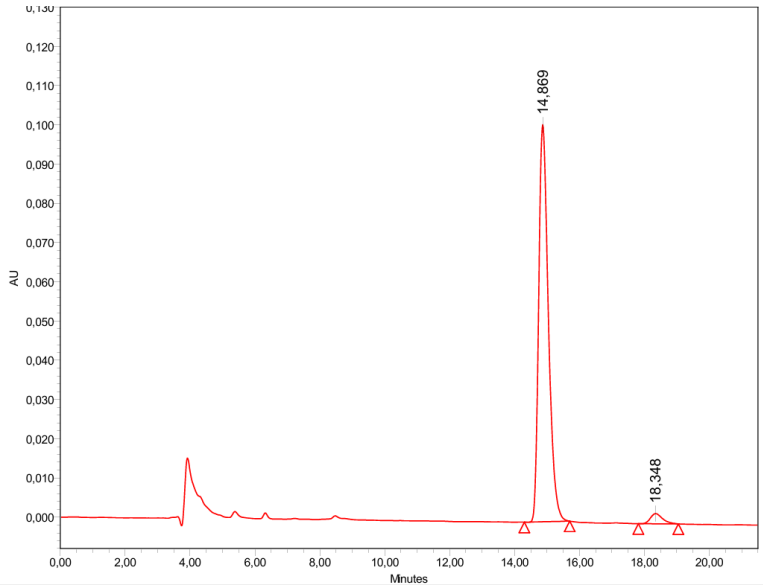


9

Flow : 1,0 ml /min

T° : 20°C

	Retention Time (min)	% Area
1	14,869	96,90
2	18,348	3,10



14. X-Ray Crystallographic Data for Compound **7n**

X-Ray crystal determination: A saturated solution of 15 mg of compound 7n in CH_2Cl_2 was introduced into a 1 mL vial. This vial was then placed in a 10 mL vial containing 2 mL of pentane. The system was closed and placed in the fridge. The vapour diffusion was let to happen (4 °C) for 4 days, leading to long-needle crystals.

A single crystal was selected, mounted and transferred into a cold nitrogen gas stream. Intensity data was collected with a Bruker Kappa APEX II system using micro-source Cu-Kα radiation radiation. Unit-cell parameters determination, data collection strategy, integration and absorption correction were carried out with the Bruker APEX suite of programs. The structure was solved with SHELXT and refined anisotropically by full-matrix least-squares methods with SHELXL using WinGX. Absolute structure was determined by anomalous scattering effects analysis and chemical absolute configuration was then deduced. The structure was deposited at the Cambridge Crystallographic Data Centre with number CCDC 2434440 and can be obtained free of charge via www.ccdc.cam.ac.uk

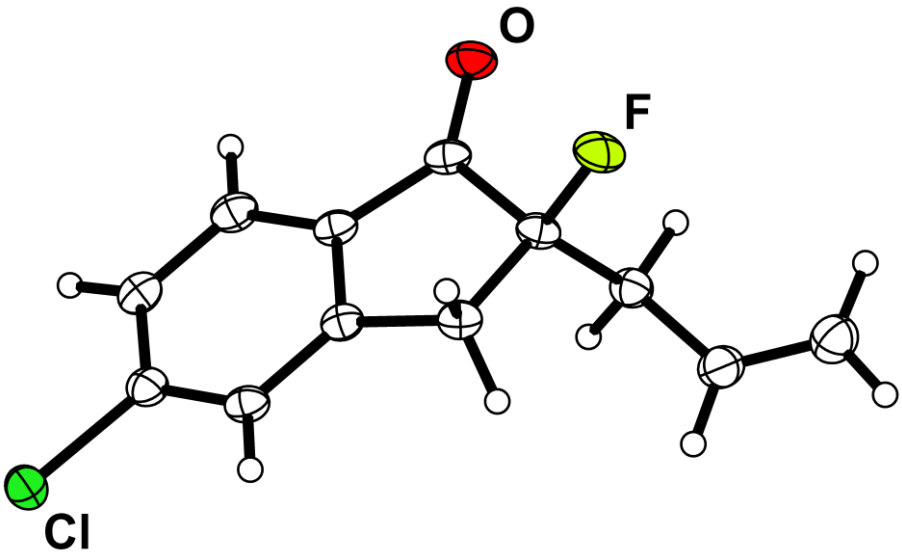


Fig. Ellipsoids are drawn with 30% probability.

Crystal data for 7n . $C_{12}H_{10}ClFO$, orthorhombic P 2_1 2_1 2_1, a = 4.9450 (1) Å, b = 5.8696 (1) Å, c = 36.3744(7) Å, α = β = γ = 90°, V = 1055.77(3) $Å^3$, Z = 4, colourless bar 0.5 × 0.5 × 0.05 mm^3, μ = 3.079 mm^{-1}, min / max transmission = 0.13 / 0.32, T= 200(1) K, λ = 1.54178 Å, θ range = 4.87° to 66.59°, 5802 reflections measured, 1844 independent, R_{int} = 0.0174, completeness = 0.998, 136 parameters, 0 restraints, Flack x = -0.010(6), final R indices R1 [I>2σ(I)] = 0.0268 and wR2 (all data) = 0.0678, GOF on F^2 = 1.123, largest difference peak / hole = 0.15 / -0.19 e·$Å^{-3}$.