Supporting Information

Unexpected Effect of the Fluorine Atom on the Optimal Ligand-to-Palladium Ratio in the Enantioselective Pd-Catalyzed Allylation Reaction of Fluorinated Enol Carbonates

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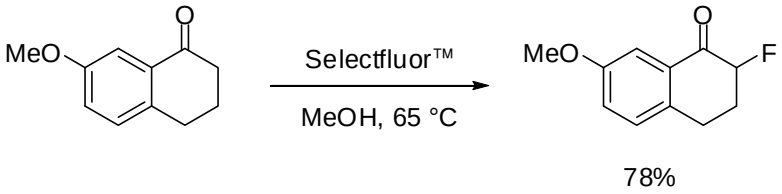
The following includes general experimental procedures, specific details for representative reactions, and isolation and spectroscopic information for the new compounds prepared. ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded on a VARIAN Inova 400 MHz in $CDCl_3$ at ambient temperature using tetramethylsilane (^{1}H NMR) or residual $CHCl_3$ (^{1}H and ^{13}C NMR) as the internal standard, or $CFCl_3$ (^{19}F NMR) as the external standard. Infrared spectra were recorded on a Bomem FT-IR MB-Series spectrometer. High-resolution mass spectra were performed on a LC/MS-TOF Agilent 6210 using electrospray ionization (ESI) or by AIMS Lab (University of Toronto) on an ABI/Sciex QStar mass spectrometer using ESI. Enantiomeric excesses were determined by HPLC analysis with a Hewlett Packard 1200 Series. Optical rotation $[\alpha]_D$ were measured on a Jasco DIP-360 Polarimeter. Melting points were recorded on a Uni-Met capillary melting point apparatus and are uncorrected. (*S*)-*t*-Bu-PHOX was prepared using literature procedure.[1]

[1] Peer, M.; de Jong, J. C.; Kiefer, M.; Langer, T.; Rieck, H.; Schell, H.; Sennhenn, P.; Sprinz, J.; Steinhagen, H.; Wiese, B.; Helmchen, G. *Tetrahedron* **1996**, *52*, 7547.

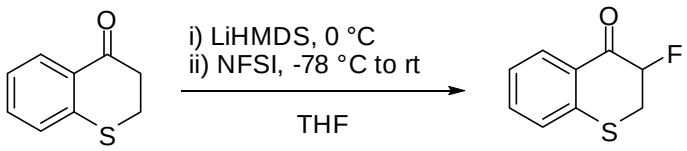
Synthesis of the α-fluoroketones

The fluoroketones were prepared as described previously[2] or as indicated thereafter.



78%

2-Fluoro-7-methoxy-1-tetralone The fluoroketone was prepared following a literature protocol.[3] On a 1.7 mmol scale, the desired product (258 mg, 78%) was isolated as a white solid by flash chromatography using 10% Et_2O/hexane. mp 84-85 ºC; IR (neat) ν = 3018, 2958, 2908, 2843, 1693, 1495, 1320, 1276, 1070, 1002, 870 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, 1H, J = 2.7 Hz), 7.18 (d, 1H, J = 8.5 Hz), 7.11 (dd, 1H, J = 8.5, 2.7 Hz), 5.15 (ddd, 1H, J = 47.9, 12.3, 5.2 Hz), 3.85 (s, 3H), 3.07 (m, 2H), 2.62–2.53 (m, 1H), 2.40–2.28 (m, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -190.8 (m, 1F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.7 (d, $J_{C\text{-}F}$ = 14.5 Hz), 158.9, 135.9, 132.3, 130.2, 123.1, 109.1, 91.6 (d, $J_{C\text{-}F}$ = 187.7 Hz), 55.9, 30.6 (d, $J_{C\text{-}F}$ = 18.6 Hz), 26.5 (d, $J_{C\text{-}F}$ = 11.7 Hz); HRMS-ESI cald for $C_{11}H_{12}FO_2$ $[M+H]^+$ 195.0816, found 195.0823.

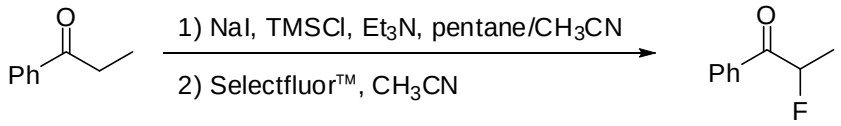


82%

2-Fluoro-thiochroman-4-one To a 0 ºC solution of LiHMDS (4.6 mL, 4.6 mmol, 1.0 M in THF) in THF (6 mL) was added a solution of the thioketone (750 mg, 4.6 mmol) in THF (2 mL) dropwise over 15 minutes and stirred 1.5 h at 0 ºC. The resulting enolate solution was added dropwise over 15 minutes to a

[2] Bélanger, É.; Cantin, K.; Messe, O.; Tremblay, M.; Paquin, J.-F. *J. Am. Chem. Soc.* **2007**, *129*, 1034.
[3] Stavber, S.; Jereb, M.; Zupan, M. *Synthesis* **2002**, 2609.

-78 ºC solution of NFSI (1.58 g, 5.02 mmol) in THF (12 mL). The reaction mixture was allowed to warm to rt overnight. The reaction was transferred into a mixture of CH_2Cl_2 and satd NH_4Cl. The layers were separated, the aqueous layer was extracted with CH_2Cl_2 (3×). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and the solvent was evaporated to give the crude product. The pure product (684 mg, 82%) was isolated as a white solid by flash chromatography using 10% acetone/hexane. mp 82-85 ºC; IR (neat) ν = 3158, 3068, 2933, 2903, 1703, 1591, 1441, 1381, 1270, 1218, 1147, 1122 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, 1H, J = 8.0 Hz), 7.43 (t, 1H, J = 7.6 Hz), 7.30–7.21 (m, 2H), 5.42 (ddd, 1H, J = 47.6, 13.4, 4.8 Hz), 3.60 (dt, 1H, J = 12.9, 2.8 Hz), 3.32–3.25 (m, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -184.4 (ddd, 1F, J = 47.6, 9.2, 2.9 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.7, 134.3, 130.5, 130.2 (d, J_{C-F} = 2.2 Hz), 127.3, 125.8, 90.5, 85.6, 31.1 (d, J_{C-F} = 23.5 Hz); HRMS-ESI cald for $C_9H_{11}NSFO$ $[M+NH_4]^+$ 200.0540, found 200.0540.

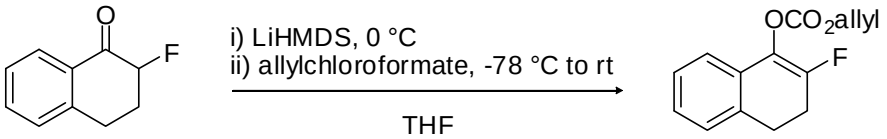


63%

2-Fluoro-1-propriophenone The fluoroketone was prepared following a literature protocol.[4] Spectroscopic data were in agreement with the literature.[3]

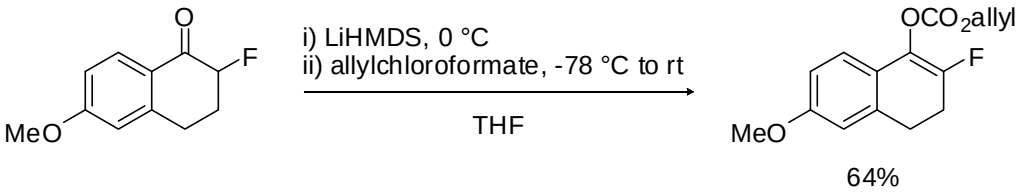
[4] Solladie-Cavallo, A.; Jierry, L.; Bouerat, L.; Taillasson, P. *Tetrahedron : Asymmetry* **2001**, *12*, 883.

Synthesis of the fluorinated allyl enol carbonates

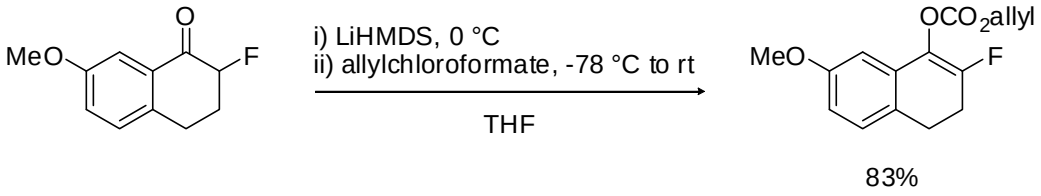


1 (85%)

Allyl-2-fluoro-3,4-dihydronaphthalen-1-yl carbonate (1) (General protocol) To a 0 ºC solution of LiHMDS (3.2 mL, 3.2 mmol, 1.0 M in THF) in THF (4 mL) was added a solution of the fluoroketone (500 mg, 3.0 mmol) in THF (1 mL) dropwise over 15 minutes and was stirred 1.5 h at 0 ºC. The resulting enolate solution was added dropwise over 15 minutes to a -78 ºC solution of allylchloroformate (0.39 ml, 3.65 mmol) in THF (8 ml). The reaction mixture was allowed to warm to rt overnight. The reaction was transferred into a mixture of CH_2Cl_2 and satd NH_4Cl. The layers were separated, the aqueous layer was extracted with CH_2Cl_2 (3×). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and the solvent was evaporated to give the crude product. The pure product (633 mg, 85%) was isolated as a colorless oil by flash chromatography using 5% acetone/hexane. IR (neat) ν = 3072, 3025, 2949, 2897, 2840, 1769, 1707, 1370, 1295, 1246, 1149, 992, 768 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.27–7.11 (m, 4H), 6.06-5.96 (m, 1H), 5.44 (d, 1H, J = 17.2 Hz), 5.34 (d, 1H, J = 10.4 Hz), 4.76 (d, 2H, J = 5.8 Hz), 3.06 (t, 2H, J = 8.3 Hz), 2.73 (m, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -118.9 (m, 1F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.6 (d, J_{C-F} = 2.1 Hz), 151.5 (d, J_{C-F} = 271.3 Hz), 132.5, 131.3, 130.0 (d, J_{C-F} = 1.1 Hz), 128.0 (d, J_{C-F} = 11.9 Hz), 127.7, 127.6 (d, J_{C-F} = 2.3 Hz), 127.0, 120.8 (d, J_{C-F} = 7.1 Hz), 119.7, 69.8, 27.9 (d, J_{C-F} = 7.2 Hz), 24.5 (d, J_{C-F} = 20.1 Hz); HRMS-ESI cald for $C_{14}H_{17}NFO_3$ $[M+NH_4]^+$ 266.1187, found 266.1191.

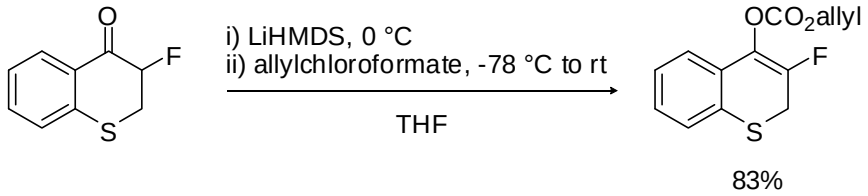


Allyl-2-fluoro-6-methoxy-3,4-dihydronaphthalen-1-yl carbonate Following the general protocol on a 2.57 mmol scale**,** the desired product (457 mg, 64%) was isolated as colorless oil by flash chromatography using 15% Et_2O/hexane. IR (neat) ν = 3087, 2998, 2949, 2902, 2839, 1769, 1709, 1502, 1333, 1252, 1227, 1150, 958 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.08 (d, 1H, *J* = 8.3 Hz), 6.72 (m, 2H), 6.05–5.95 (m, 1H), 5.43 (d, 1H, *J* = 17.2 Hz), 5.34 (d, 1H, *J* = 10.4 Hz), 4.75 (d, 2H, *J* = 5.8 Hz), 3.79 (s, 3H), 3.02 (t, 2H, *J* = 8.2 Hz), 2.71 (m, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -122.6 (m, 1F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.2 (d, $J_{C\text{-}F}$ = 2.5 Hz), 152.6 (d, $J_{C\text{-}F}$ = 2.1 Hz), 149.7 (d, $J_{C\text{-}F}$ = 268.6 Hz), 134.5, 131.3, 127.9 (d, $J_{C\text{-}F}$ = 12.2 Hz), 122.7, 122.0 (d, $J_{C\text{-}F}$ = 7.3 Hz), 119.7, 114.4, 111.4, 69.7, 55.6, 28.2 (d, $J_{C\text{-}F}$ = 7.2 Hz), 24.5 (d, $J_{C\text{-}F}$ = 20.4 Hz); HRMS-ESI cald for $C_{15}H_{19}NFO_4$ $[M+NH_4]^+$ 296.1293, found 296.1288.

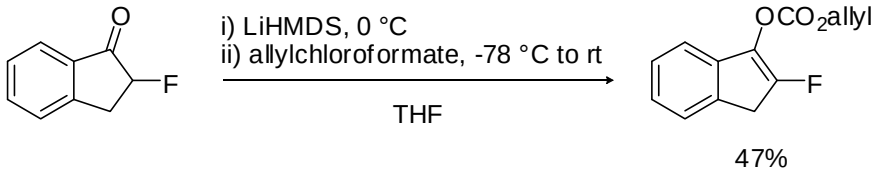


Allyl-2-fluoro-7-methoxy-3,4-dihydronaphthalen-1-yl carbonate Following the general protocol on a 1.33 mmol scale**,** the desired product (309 mg, 83 %) was isolated as colorless oil by flash chromatography using 10 % Et_2O/hexane. IR (neat) ν = 3097, 3030, 2999, 2960, 2894, 2839, 1765, 1705, 1494, 1370, 1295, 1227, 1183, 1044, 998 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.03 (d, 1H, *J* = 8.2 Hz), 6.74 (d, 1H, *J* = 2.5 Hz), 6.68 (dd, 1H, *J* = 8.2, 2.5 Hz), 6.05-5.95 (m, 1H), 4.75 (d, 1H, *J* = 5.7 Hz), 3.78 (s, 3H), 2.98 (t, 2H, J = 8.2 Hz), 2.70 (m, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -118.1 (m, 1F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.0, 153.5, 152.5 (d, $J_{C\text{-}F}$ = 2.1 Hz), 150.3, 131.3, 128.6, 128.0 (d, $J_{C\text{-}F}$ = 12.2 Hz),

124.6, 119.7, 112.1 (d, J_{C-F} = 2.5 Hz), 107.4 (d, J_{C-F} = 7.2 Hz), 69.8, 55.6, 27.0 (d, J_{C-F} = 7.3 Hz), 24.8 (d, J_{C-F} = 19.9 Hz); HRMS-ESI cald for $C_{15}H_{19}NFO_4$ $[M+NH_4]^+$ 296.1293, found 296.1338.

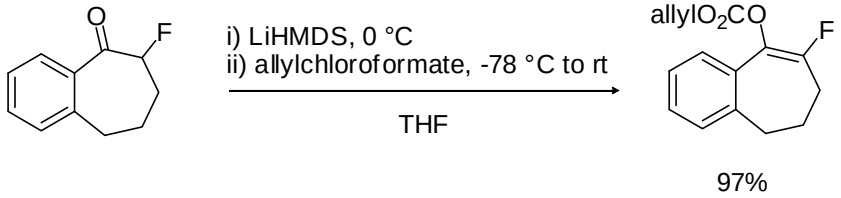


Allyl-3-fluoro-2H-thiochromen-4-yl carbonate Following the general protocol on a 2.74 mmol scale**,** the desired product (603 mg, 83%) was isolated as colorless oil by flash chromatography using 10% Et_2O/hexane. IR (neat) ν = 3064, 3023, 2958, 2895, 2823, 1767, 1704, 1471, 1439, 1365, 1297, 1242, 1165, 1069, 942 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.23–7.13 (m, 4H), 6.04-5.95 (m, 1H), 5.44 (d, 1H, *J* = 17.2 Hz), 5.35 (d, 1H, *J* = 10.4 Hz), 4.76 (d, 2H, *J* = 5.8 Hz), 3.81 (d, 2H, J = 6.9Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.4 (t, 1F, *J* = 6.9 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.3 (d, J_{C-F} = 2.2 Hz), 146.3 (d, J_{C-F} = 276.8 Hz), 131.1, 129.5 (d, J_{C-F} = 14.1 Hz), 129.1, 128.8, 128.5 (d, J_{C-F} = 2.5 Hz), 126.9, 126.3, 122.9 (d, J_{C-F} = 6.7 Hz), 119.9, 70.0, 25.6 (d, J_{C-F} = 25.7 Hz); HRMS-ESI cald for $C_{13}H_{15}NSFO_3$ $[M+NH_4]^+$ 284.0751, found 284.0758.

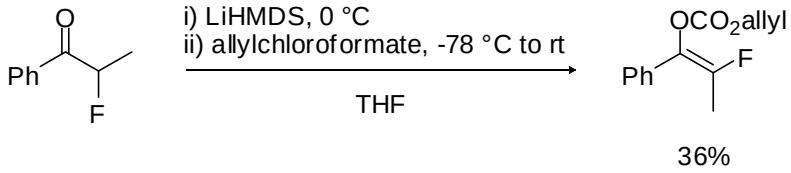


Allyl-2-fluoro-1H-inden-3-yl carbonate Following the general protocol on a 3.33 mmol scale**,** the desired product (367 mg, 47%) was isolated as colorless oil by flash chromatography using 5% Et_2O/hexane. IR (neat) ν = 3082, 3054, 3029, 2953, 2903, 1776, 1691, 1461, 1330, 1243, 1166, 1154, 969 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.32 (m, 2H), 7.24 (m, 2H), 6.08-5.98 (m, 1H), 5.47 (d, 1H, *J* = 17.2 Hz), 5.37 (d, 1H, *J* = 10.4 Hz), 4.80 (d, 2H, *J* = 5.8 Hz), 3.54 (s, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -

132.7 (m, 1F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.2 (d, $J_{C\text{-}F}$ = 282.3 Hz), 151.9 (d, $J_{C\text{-}F}$ = 2.2 Hz), 137.0 (d, $J_{C\text{-}F}$ = 1.2 Hz), 131.9 (d, $J_{C\text{-}F}$ = 8.0 Hz), 131.1, 127.7 (d, $J_{C\text{-}F}$ = 7.7 Hz), 127.3, 125.7 (d, $J_{C\text{-}F}$ = 4.5 Hz), 124.3 (d, $J_{C\text{-}F}$ = 1.1 Hz), 120.1, 118.2 (d, $J_{C\text{-}F}$ = 6.7 Hz), 70.0, 32.8 (d, $J_{C\text{-}F}$ = 17.8 Hz); HRMS-ESI cald for $C_{13}H_{15}NFO_3$ $[M+NH_4]^+$ 252.1031, found 252.1034.

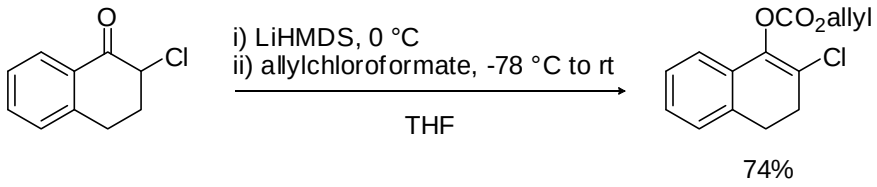


Allyl-8-fluoro-6,7-dihyro-5H-benzo[7]annulen-9-yl carbonate Following the general protocol on a 2.84 mmol scale**,** the desired product (725 mg, 97%) was isolated as colorless oil by flash chromatography using 5% Et_2O/hexane. IR (neat) ν = 3072, 3024, 2945, 2901, 2871, 2850, 1766, 1451, 1373, 1238, 1176, 981, 770 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, 2H, *J* = 7.5 Hz), 7.23 (m, 2H), 7.14 (d, 1H, *J* = 7.1 Hz), 6.02–5.93 (m, 1H), 5.40 (d, 1H, *J* = 17.2 Hz), 5.31 (d, 1H, *J* = 10.5 Hz), 4.71 (d, 2H, *J* = 5.7 Hz), 2.85 (m, 2H), 2.65 (q, 2H, J = 7.0 Hz), 1.99 (m, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -106.3 (t, 1F, *J* = 6.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.6 (d, $J_{C\text{-}F}$ = 256.8 Hz), 153.2 (d, $J_{C\text{-}F}$ = 1.7 Hz) 140.1 (d, $J_{C\text{-}F}$ = 17.4 Hz), 131.4, 131.0 (d, $J_{C\text{-}F}$ = 17.4Hz), 130.3 (d, $J_{C\text{-}F}$ = 1.9 Hz), 129.4, 128.4 (d, $J_{C\text{-}F}$ = 1.4 Hz), 126.8, 125.8 (d, $J_{C\text{-}F}$ = 5.7 Hz), 119.4, 69.5, 34.3, 30.0 (d, $J_{C\text{-}F}$ = 24.1 Hz), 25.7 (d, $J_{C\text{-}F}$ = 10.0 Hz); HRMS-ESI cald for $C_{15}H_{19}NFO_3$ $[M+NH_4]^+$ 280.1344, found 280.1368.



(Z)-allyl-2-fluoro-1-phenylprop-1-enyl carbonate Following the general protocol on a 1.64 mmol scale**,** the desired product (139 mg, 36%) was isolated as colorless oil by flash chromatography using 5% acetone/hexane. IR (neat) ν = 3088, 3063, 3033, 2958, 2928, 1764, 1446, 1388, 1240, 1136, 1040, 985

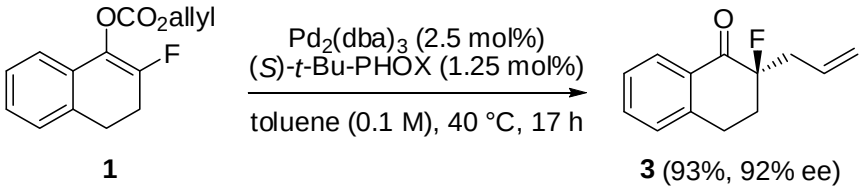
cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43–734 (m, 5H), 5.99-5.89 (m, 1H), 5.37 (d, 1H, *J* = 17.2 Hz), 5.29 (d, 1H, *J* = 10.5 Hz), 4.67 (d, 2H, *J* = 5.7 Hz), 2.13 (d, 3H, *J* = 18.0 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -110.6 (q, 1F, *J* = 18.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.1 (d, $J_{C\text{-}F}$ = 1.7 Hz),151.8, 149.2, 132.2 (d, $J_{C\text{-}F}$ = 2.6 Hz), 131.4 (d, $J_{C\text{-}F}$ = 17.2 Hz), 131.3, 129.1, 128.7, 128.6 (d, $J_{C\text{-}F}$ = 2.8 Hz), 119.4, 69.5, 15.3 (d, $J_{C\text{-}F}$ = 26.2 Hz); HRMS-ESI cald for $C_{13}H_{17}NFO_3$ $[M+NH_4]^+$ 254.1187, found 254.1190.



Allyl-2-chloro-3,4-dihydronaphthalen-1-yl carbonate Following the general protocol on a 3.20 mmol scale of 2-chlorotetralone[5]**,** the desired product (624 mg, 74%) was isolated as colorless oil by flash chromatography using 5% Et_2O/hexane. IR (neat) ν = 3071, 3025, 2947, 2895, 2838, 1768, 1652, 1488, 1364, 1233, 1149, 943, 765 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24–7.14 (m, 4H), 6.06-5.96 (m, 1H), 5.45 (d, 1H, *J* = 17.2 Hz), 5.35 (d, 1H, *J* = 10.4 Hz), 4.77 (d, 2H, *J* = 5.7 Hz), 3.02 (t, 2H, J = 8.2 z), 2.80 (t, 2H, J = 8.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.1, 141.6, 134.5, 131.3, 130.0, 128.5, 127.8, 127.1, 122.9, 121.0, 119.7, 69.8, 31.1, 28.3; HRMS-ESI cald for $C_{14}H_{17}NClO_3$ $[M+NH_4]^+$ 282.0892, found 282.0894.

[5] 2-Chlorotetralone was prepared from α-tetralone using a literature protocol, see Brummond, K. M.; Gesenberg, K. D. *Tetrahedron Lett.* **1999**, *40*, 2231. Spectroscopic data were in agreement with the literature, see Hajra, S.; Bhowmick, M.; Maki, B.; Sinha, D. *J. Org. Chem.* **2007**, *72*, 4872.

Representative procedure for the enantioselective Pd-catalyzed allylation reaction

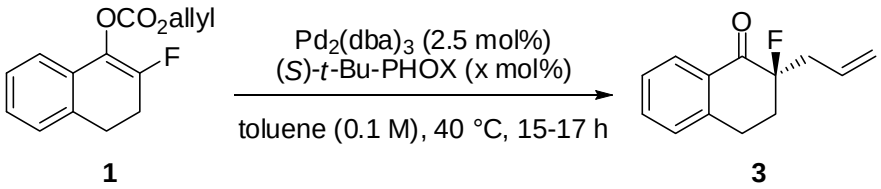


1 **3** (93%, 92% ee)

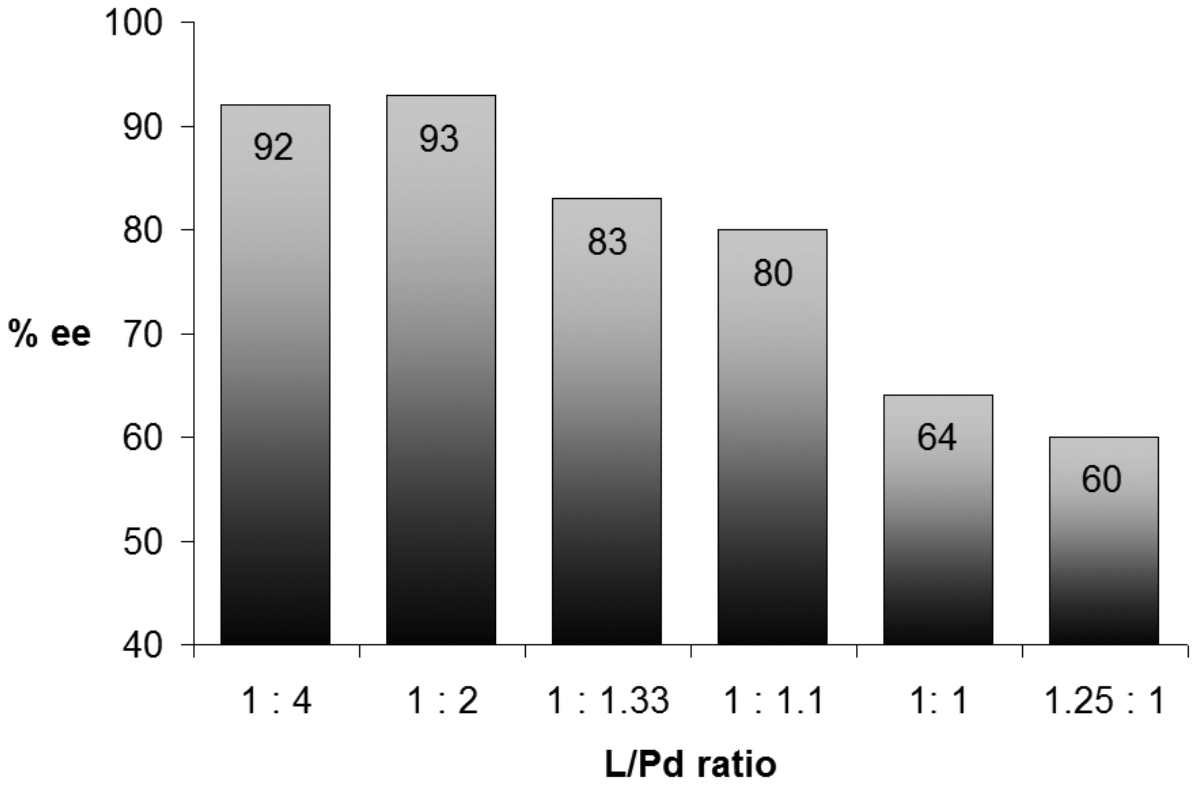
(*R*)-2-Allyl-2-fluoro-1-tetralone (3) (General protocol for the Pd-catalyzed allylation reaction) (Table 1 – entry 1) A 25 ml round-bottom flask under nitrogen was charged with $Pd_2(dba)_3$ (27.7 mg, 0.030 mmol, 2.5 mol%) and (*S*)-*t*-Bu-PHOX (5.9 mg, 0.015 mmol, 1.25 mol%, L/Pd = 1 : 4) followed by toluene (8 mL). After stirring 30 minutes at RT, a solution of the fluorinated allyl enol carbonate **1** (300 mg, 1.2 mmol) in toluene (4 mL) was added and the reaction mixture was heated at 40 ºC for 17 h. H_2O and Et_2O were added and the layers were separated. The aqueous phase was extracted with Et_2O (3×). The combined organic layers were dried over anhydrous Na_2SO_4, and concentrated. The desired product (229 mg, 93%) was isolated as a colorless oil by flash chromatography using 5% Et_2O/hexane. The enantioselectivity was 92% ee (OJ-H, 254 nm, hexane:2-propanol = 99.9:0.1, flow rate 0.5 ml/min, $t_{r\ (minor)}$ = 34.4 min, $t_{r\ (major)}$ = 38.2 min). All spectroscopic data were in agreement with the literature.[2,6] When the reaction was conducted under similar conditions using 3.0 mol% of (*S*)-*t*-Bu-PHOX (L/Pd = 1 : 1.67), the desired product was isolated in 97% yield and 93% ee (Table 1 - entry 2). When the reaction was conducted using 6.25 mol% of (*S*)-*t*-Bu-PHOX (L/Pd = 1.25 : 1), **3** was isolated in 85% yield and 59% ee (Table 1 - entry 3).

[6] Nakamura, M.; Hajra, A.; Endo, K.; Nakamura, E. *Angew. Chem. Int. Ed.* **2005**, *44*, 7248.

Effect of L/Pd ratio on the enantioselectivity for the allylation of allyl enol carbonate 1



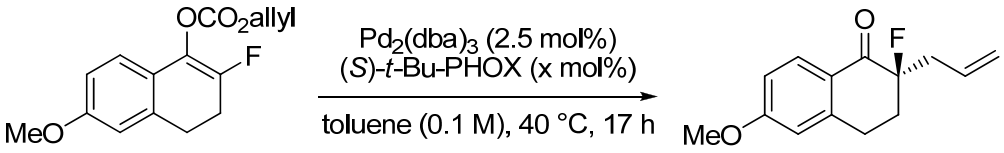
1 **3**



Entry	L/Pd ratio	(*S*)-*t*-Bu-PHOX (mol%)	yield (%)[a,b]	ee (%)[a,c]
1	1 : 4	1.25	93	92
2	1 : 2	2.5	84	93
3	1 : 1.33	3.75	94	83
4	1 : 1.1	4.5	95	80
5	1 : 1	5.0	73	64
6	1.25 : 1	6.25	86	60

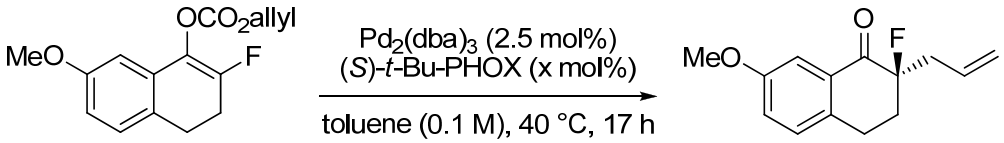
[a] Average of at least 2 independent runs; [b] Isolated yield; [c] Determined by chiral HPLC.

Reaction of Various Fluorinated Allyl Enol Carbonate (Table 1)



1.25 mol% (L/Pd = 1 : 4)	87%, 92% ee
6.25 mol% (L/Pd = 1.25 : 1)	98%, 57% ee

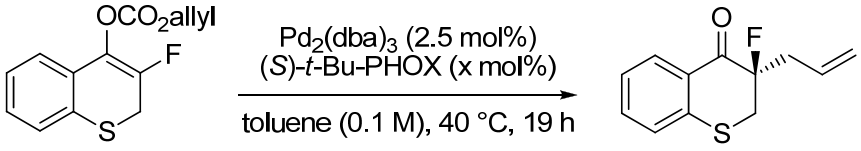
(*R*)-2-Allyl-2-fluoro-6-methoxy-1-tetralone (Table 1 - entry 4) Following the general protocol on a 0.26 mmol scale using 1.25 mol% of (*S*)-*t*-Bu-PHOX (L/Pd = 1 : 4), the desired product (53 mg, 87%) was isolated as a colorless oil by flash chromatography using 10% acetone/hexane. The enantioselectivity was 92% ee (AD-H, 254 nm, hexane:2-propanol = 99:1, flow rate 1.0 ml/min, $t_{r\ (minor)}$ = 17.7 min, $t_{r\ (major)}$ = 19.4 min). All spectroscopic data were in agreement with the literature.[2,6] When the reaction was conducted under similar conditions using 6.25 mol% of (*S*)-*t*-Bu-PHOX (L/Pd = 1.25 : 1), the desired product was isolated in 98% yield and 57% ee (Table 1 - entry 5).



1.25 mol% (L/Pd = 1 : 4)	92%, 94% ee
6.25 mol% (L/Pd = 1.25 : 1)	86%, 54% ee

(*R*)-2-Allyl-2-fluoro-7-methoxy-1-tetralone (Table 1 - entry 6) Following the general protocol on a 0.25 mmol scale using 1.25 mol% of (*S*)-*t*-Bu-PHOX (L/Pd = 1 : 4), the desired product (55 mg, 92%) was isolated as a colorless oil by flash chromatography using 10% Et_2O/hexane. The enantioselectivity was 94% ee (OJ-H, 254 nm, hexane:2-propanol = 99:1, flow rate 0.5 ml/min, $t_{r\ (minor)}$ = 29.1 min, $t_{r\ (major)}$ = 36.2 min). The absolute configurations were assigned based on the established stereochemical outcome of the reaction. $[\alpha]_D^{22}$ -36.9 (c 0.82, $CHCl_3$); IR (neat) ν = 3077, 3008, 2942, 2839, 1698, 1611, 1498,

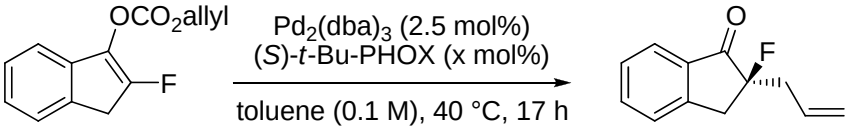
1283, 1251, 1035, 923, 828 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, J = 2.3 Hz, 1H), 7-17–7.09 (m, 2H), 5.89 (m, 1H), 5.19 (m, 2H), 3.84 (s, 3H), 3.07–2.91 (m, 2H), 2.75–2.51 (m, 2H), 2.44–2.30 (m, 2H,); ^{19}F NMR (376 MHz, $CDCl_3$) δ -160.3 (m, 1F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.3 (d, J_{C-F} = 17.6 Hz), 158.9, 135.5, 131.9 (d, J_{C-F} = 1.1 Hz), 131.1 (d, J_{C-F} = 3.9 Hz), 130.2, 123.0, 120.1, 110.0 (d, J_{C-F} = 1.5 Hz), 95.3 (d, J_{C-F} = 184.3 Hz), 55.8, 38.2 (d, J_{C-F} = 23.5 Hz), 32.4 (d, J_{C-F} = 22.3 Hz), 25.4 (d, J_{C-F} = 10.3 Hz); HRMS-ESI cald for $C_{14}H_{16}FO_2$ $[M+H]^+$ 235.1126, found 235.1136. When the reaction was conducted under similar conditions using 6.25 mol% of (*S*)-*t*-Bu-PHOX (L/Pd = 1.25 : 1), the desired product was isolated in 86% yield and 56% ee (Table 1 - entry 7).



1.25 mol% (L/Pd = 1 : 4) 90%, 92% ee
6.25 mol% (L/Pd = 1.25 : 1) 93%, 42% ee

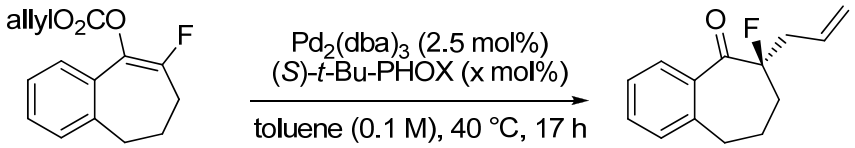
(*R*)-3-allyl-3-fluorothiochroman-4-one (Table 1 - entry 8) Following the general protocol on a 0.30 mmol scale using 1.25 mol% of (*S*)-*t*-Bu-PHOX (L/Pd = 1 : 4), the desired product (59 mg, 90%) was isolated as a colorless oil by flash chromatography using 10% Et_2O/hexane. The enantioselectivity was 92% ee (OJ-H, 254 nm, hexane:2-propanol = 95:5, flow rate 0.8 ml/min, $t_{r\ (minor)}$ = 13.1 min, $t_{r\ (major)}$ = 13.9 min). The absolute configurations were assigned based on the established stereochemical outcome of the reaction. $[\alpha]_D^{22}$ -62.4 (c 1.07, $CHCl_3$); IR (neat) ν = 3079, 3014, 2982, 2917, 1698, 1591, 1460, 1438, 1301, 1274, 1259, 1199, 929 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, 1H, J = 8.0 Hz), 7.43 (t, 1H, J = 7.0 Hz), 7.27–7.21 (m, 2H), 5.95–5.85 (m, 1H), 5.29 (d, 2H, J = 12.2 Hz), 3.62 (dd, 2H, J = 13.1, 6.4 Hz), 3.17 (dd, 2H, J = 13.1, 7.6 Hz), 2.95–2.69 (m, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -160.1 (m, 1F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.3 (d, J_{C-F} = 17.3 Hz), 140.7, 134.1, 130.7, 130.1, 129.7, 127.2, 125.6, 121.4, 93.8 (d, J_{C-F} = 190.2 Hz), 36.8 (d, J_{C-F} = 22.6 Hz), 33.0 (d, J_{C-F} = 28.2 Hz); HRMS-ESI cald for

$C_{12}H_{12}OFS$ $[M+H]^+$ 223.0587, found 223.0592. When the reaction was conducted under similar conditions using 6.25 mol% of (*S*)-*t*-Bu-PHOX (L/Pd = 1.25 : 1), the desired product was isolated in 93% yield and 42% ee (Table 1 - entry 9).



3.0 mol% (L/Pd = 1 : 1.67)	91%, 82% ee
6.25 mol% (L/Pd = 1.25 : 1)	90%, 30% ee

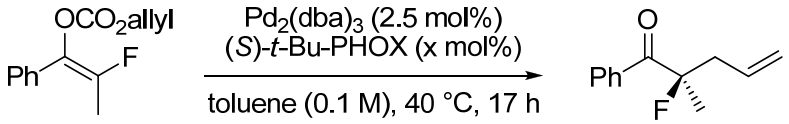
(*S*)-2-allyl-2-fluoro-1-indanone (Table 1 - entry 10) Following the general protocol on a 0.33 mmol scale using 3.0 mol% of (*S*)-*t*-Bu-PHOX (L/Pd = 1 : 1.67), the desired product (57 mg, 91%) was isolated as a colorless oil by flash chromatography using 5% Et_2O/hexane. The enantioselectivity was 82% ee (AD-H, 254 nm, hexane:2-propanol = 99:1, flow rate 0.8 ml/min, $t_{r\ (major)}$ = 9.2 min, $t_{r\ (minor)}$ = 11.7 min). All spectroscopic data were in agreement with the literature.[2,6] When the reaction was conducted under similar conditions using 6.25 mol% of (*S*)-*t*-Bu-PHOX (L/Pd = 1.25 : 1), the desired product was isolated in 90% yield and 30% ee (Table 1 - entry 11).



1.25 mol% (L/Pd = 1 : 4)	83%, 88% ee
6.25 mol% (L/Pd = 1.25 : 1)	87%, 76% ee

(*R*)-2-allyl-2-fluoro-1-benzosuberone (Table 1 - entry 12) Following the general protocol on a 0.29 mmol scale using 1.25 mol% of (*S*)-*t*-Bu-PHOX (L/Pd = 1 : 4), the desired product (49 mg, 83%) was isolated as a colorless oil by flash chromatography using 5% Et_2O/hexane. The enantioselectivity was 88% ee (OJ-H, 254 nm, hexane:2-propanol = 99:1, flow rate 0.8 ml/min, $t_{r\ (major)}$ = 12.3 min, $t_{r\ (minor)}$ =

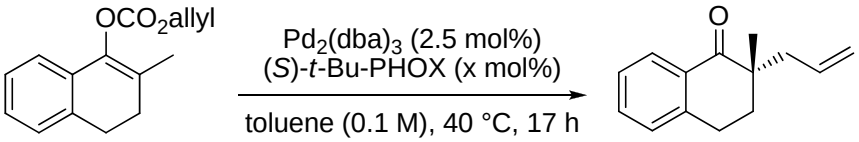
16.5 min). All spectroscopic data were in agreement with the literature.[2,6] When the reaction was conducted under similar conditions using 6.25 mol% of (*S*)-*t*-Bu-PHOX (L/Pd = 1.25 : 1), the desired product was isolated in 87% yield and 76% ee (Table 1 - entry 13).



3.0 mol% (L/Pd = 1 : 1.67)	58%, 34% ee
6.25 mol% (L/Pd = 1.25 : 1)	75%, 36% ee

(*R*)-2-fluoro-2-methyl-1-phenylpent-4-en-1-one (Table 1 - entry 14) Following the general protocol on a 0.29 mmol scale using 3.0 mol% of (*S*)-*t*-Bu-PHOX (L/Pd = 1 : 1.67), the desired product (32 mg, 58%) was isolated as a colorless oil by flash chromatography using 5% Et_2O/hexane. The enantioselectivity was 34% ee (OD-H, 254 nm, hexane:2-propanol = 99.9:0.1, flow rate 0.5 ml/min, $t_{r\,(minor)}$ = 17.8 min, $t_{r\,(major)}$ = 19.8 min). All spectroscopic data were in agreement with the literature.[6] When the reaction was conducted under similar conditions using 6.25 mol% of (*S*)-*t*-Bu-PHOX (L/Pd = 1.25 : 1), the desired product was isolated in 75% yield and 36% ee (Table 1 - entry 15).

Allylation of non-fluorinated allyl enol carbonates

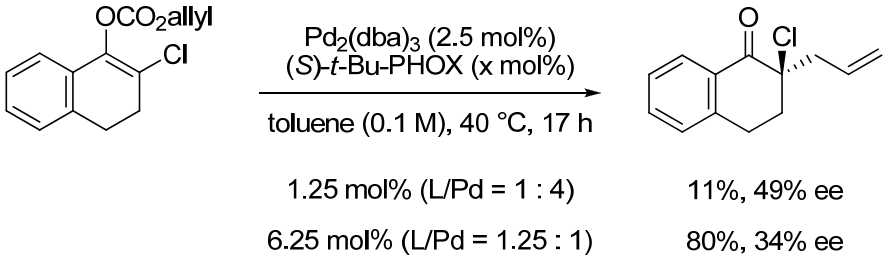


4 **5**

3.0 mol% (L/Pd = 1 : 1.67)	84%, 92% ee
6.25 mol% (L/Pd = 1.25 : 1)	91%, 92% ee

(*S*)-2-allyl-2-methyl-1-tetralone (5) (Scheme 1) Following the general protocol on a 0.30 mmol scale using 3.0 mol% of (*S*)-*t*-Bu-PHOX (L/Pd = 1 : 1.67), the desired product (51 mg, 84%) was isolated as a

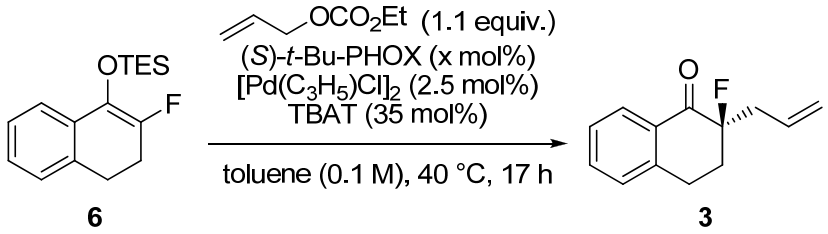
colorless oil by flash chromatography using 5% Et_2O/hexane. The enantioselectivity was 92% ee (OD-H, 254 nm, hexane:2-propanol = 99.9:0.1, flow rate 0.7 ml/min, $t_{r\ (major)}$ = 22.9 min, $t_{r\ (minor)}$ = 25.5 min). All spectroscopic data were in agreement with the literature.[7] When the reaction was conducted under similar conditions using 6.25 mol% of (*S*)-*t*-Bu-PHOX (L/Pd = 1.25 : 1), the desired product was isolated in 91% and 92% ee.



(*R*)-2-Allyl-2-chloro-1-tetralone (Reference 15) Following the general protocol on a 0.29 mmol scale using 1.25 mol% of (*S*)-*t*-Bu-PHOX (L/Pd = 1 : 4), the desired product (7 mg, 11%) was isolated as a colorless oil by flash chromatography using 5% Et_2O/hexane. The enantioselectivity was 49% ee (OD-H, 254 nm, hexane:2-propanol = 99.5:0.5, flow rate 0.5 ml/min, $t_{r\ (major)}$ = 13.4 min, $t_{r\ (minor)}$ = 15.7 min). The absolute configurations were assigned based on the established stereochemical outcome of the reaction. $[\alpha]_D^{22}$ +14.5 (c 0.60, $CHCl_3$); IR (neat) ν = 3076, 2980, 2937, 2844, 1690, 1602, 1455, 1239, 1224, 996, 922, 746 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, 1H, *J* = 7.9 Hz), 7.52 (t, 1H, *J* = 7.4 Hz), 7.35 (t, 1H, *J* = 7.6 Hz), 7.26 (d, 1H, *J* = 7.0 Hz), 5.89 (m, 1H), 5.23 (d, 1H, *J* = 6.0 Hz), 5.20 (s, 1H), 3.35 (m, 1H), 3.01–2.86 (m, 3H), 2.47-2.29 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.0, 143.3, 134.1, 132.6, 130.3, 129.2, 128.9, 127.3, 120.1, 70.0, 43.1, 35.3, 26.0; HRMS-ESI cald for $C_{13}H_{14}OCl$ $[M+H]^+$ 221.0727, found 221.0736. When the reaction was conducted under similar conditions using 6.25 mol% of (*S*)-*t*-Bu-PHOX (L/Pd = 1.25 : 1), the desired product was isolated in 80% yield and 34% ee.

[7] Mohr, J. T.; Behenna, D. C.; Harned, A. M.; Stoltz, B. M. *Angew. Chem. Int. Ed.* **2005**, *44*, 6924.

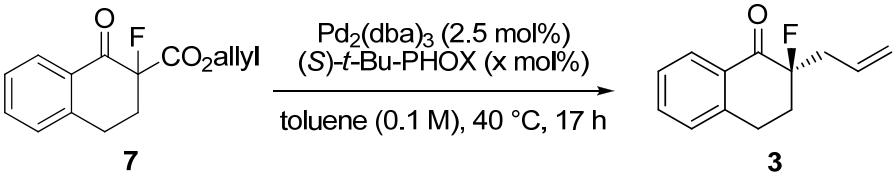
Allylation of alternative fluorinated precursors



6 **3**

1.25 mol% (L/Pd = 1 : 4)	79%, 91% ee
6.25 mol% (L/Pd = 1.25 : 1)	91%, 91% ee

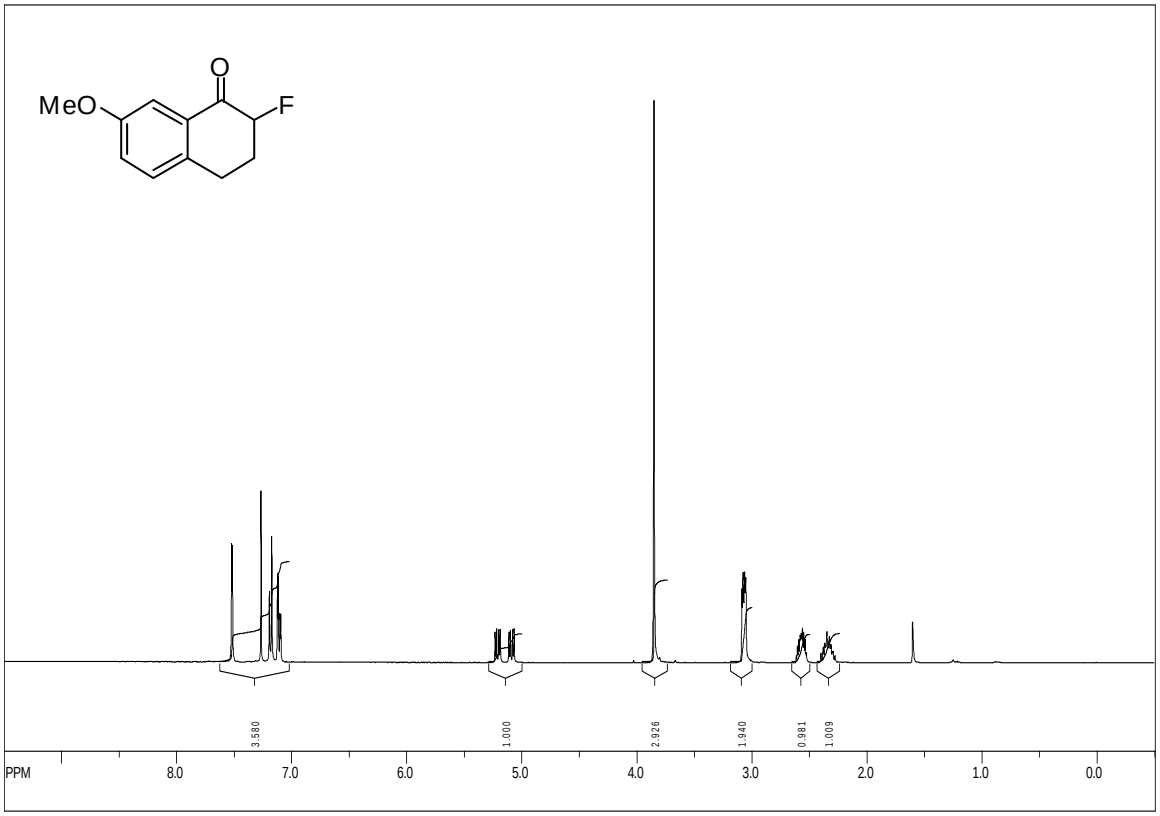
(*R*)-2-Allyl-2-fluoro-1-tetralone (3) (Scheme 2) Following the published protocol[2] on a 0.27 mmol scale of **6** using 1.25 mol% of (*S*)-*t*-Bu-PHOX (L/Pd = 1 : 4)**,** the desired product (44 mg, 79%) was isolated as a colorless oil by flash chromatography using 5% Et_2O/hexane. The enantioselectivity was 91% ee. When the reaction was conducted under similar conditions using 6.25 mol% of (*S*)-*t*-Bu-PHOX (L/Pd = 1.25 : 1), the desired product was isolated in 91% yield and 91% ee.



7 **3**

1.25 mol% (L/Pd = 1 : 4)	50%, 89% ee
6.25 mol% (L/Pd = 1.25 : 1)	94%, 93% ee

(*R*)-2-Allyl-2-fluoro-1-tetralone (3) (Scheme 2) Following the general procedure on a 0.32 mmol scale of **7** using 1.25 mol% (*S*)-*t*-Bu-PHOX (L/Pd = 1 : 4), the desired product (33 mg, 50%) was isolated as a colorless oil by flash chromatography using 5% Et_2O/hexane. The enantioselectivity was 89% ee. When the reaction was conducted under similar conditions using 6.25 mol% of (*S*)-*t*-Bu-PHOX (L/Pd = 1.25 : 1), the desired product was isolated in 94% yield and 93% ee.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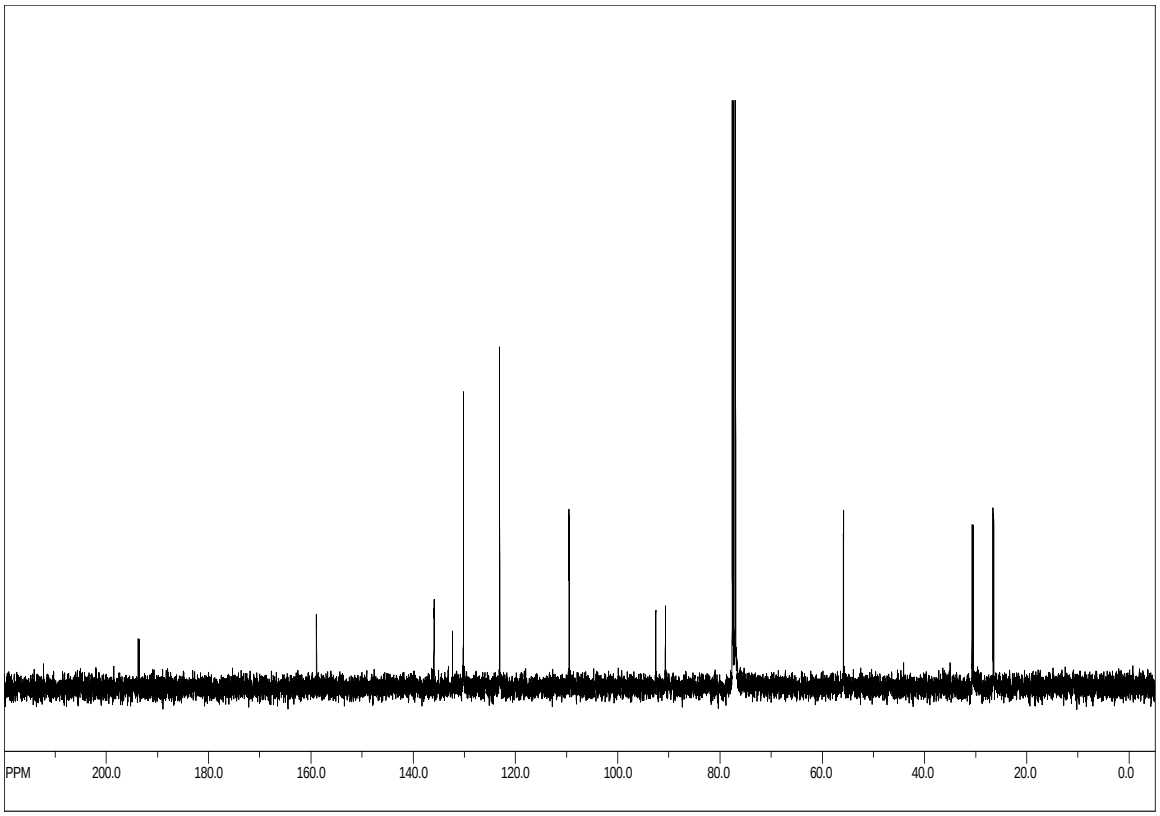
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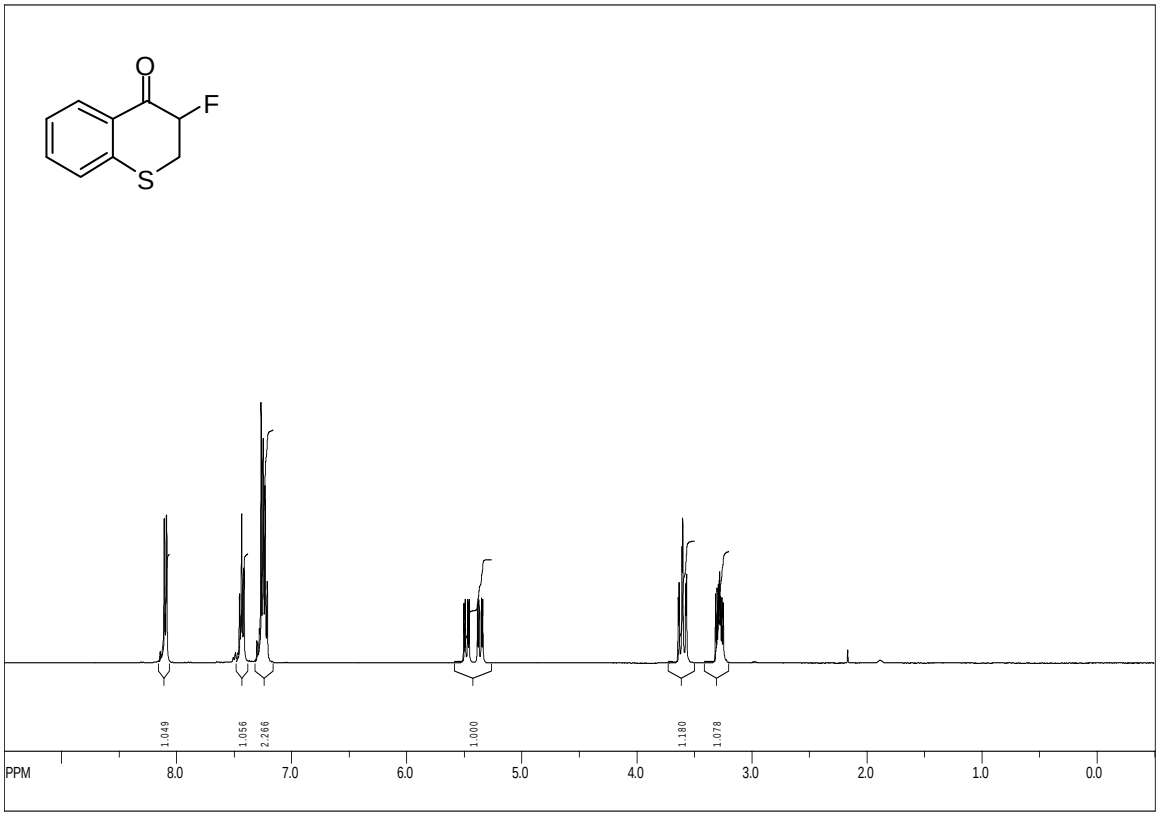
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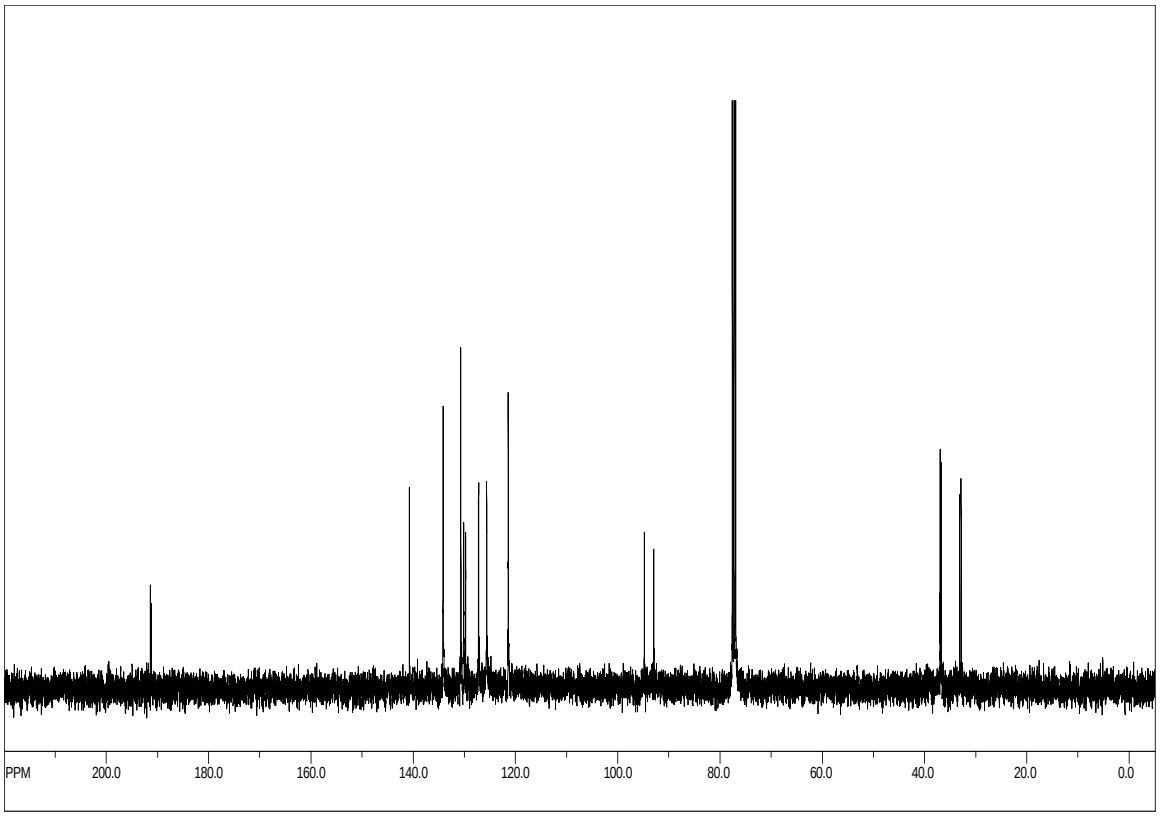
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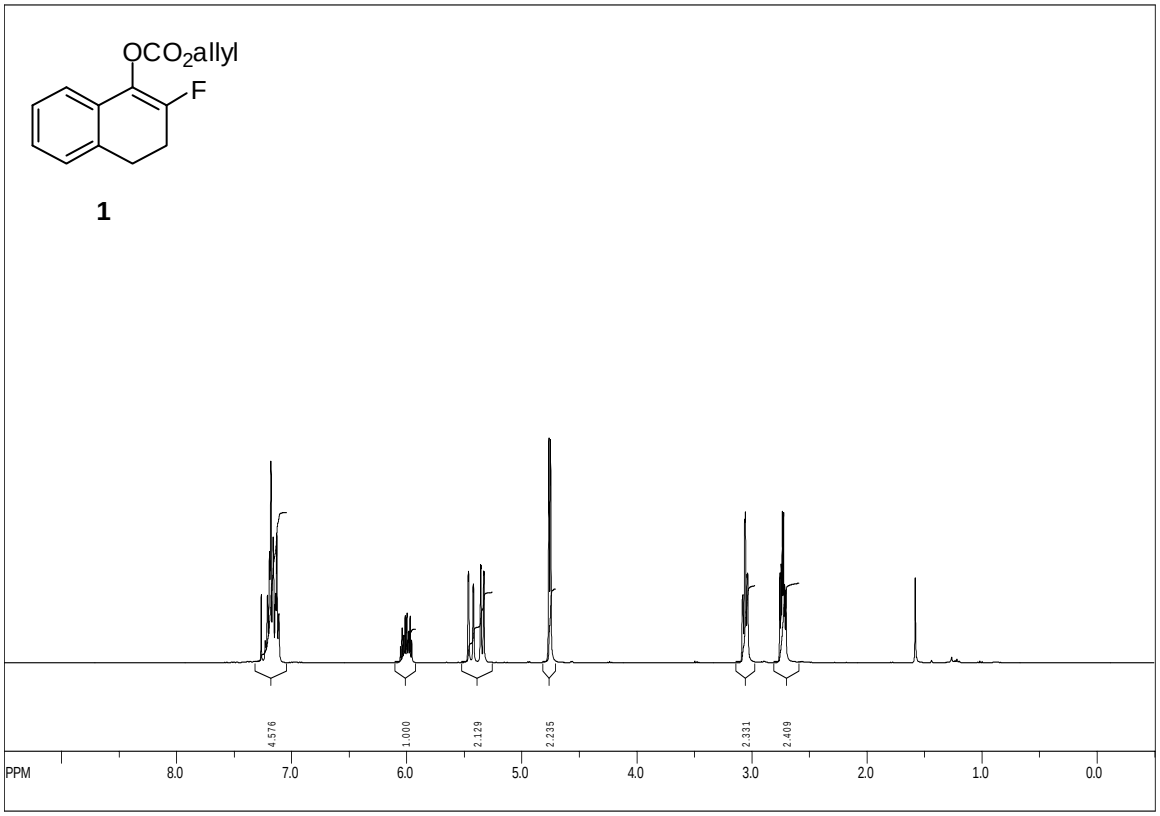
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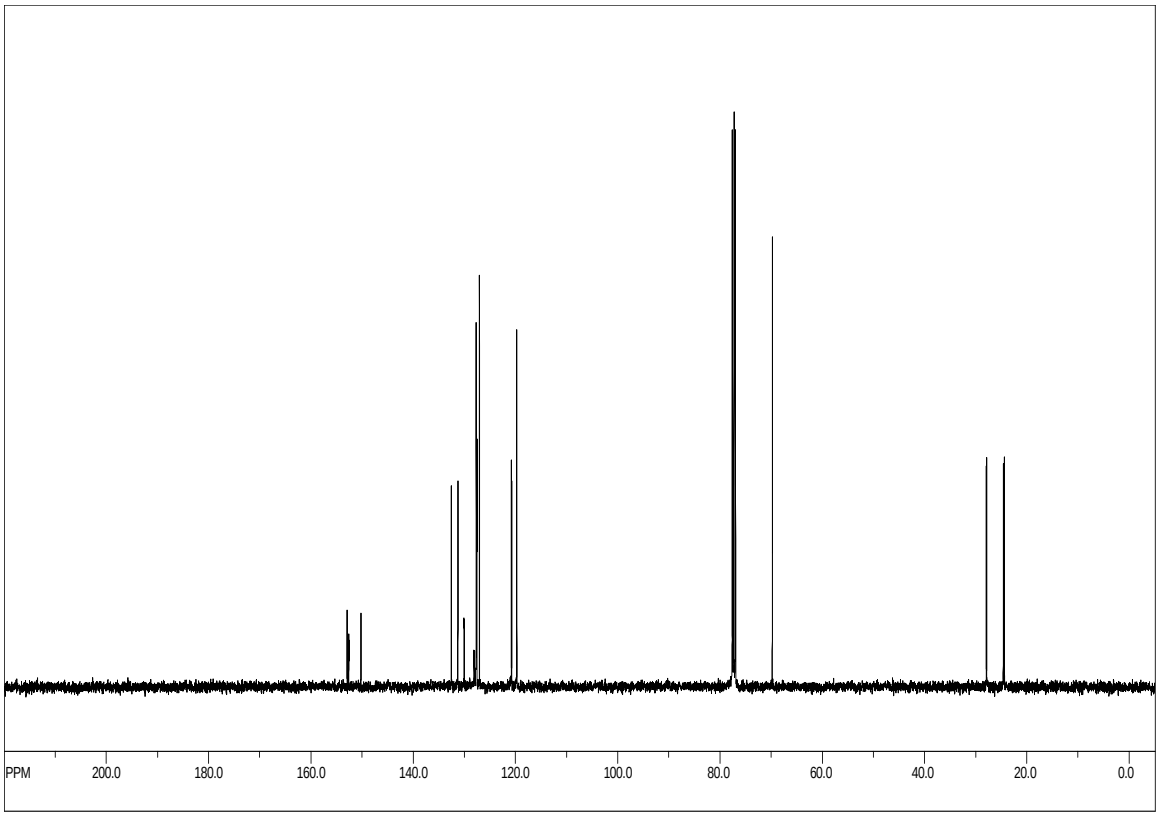
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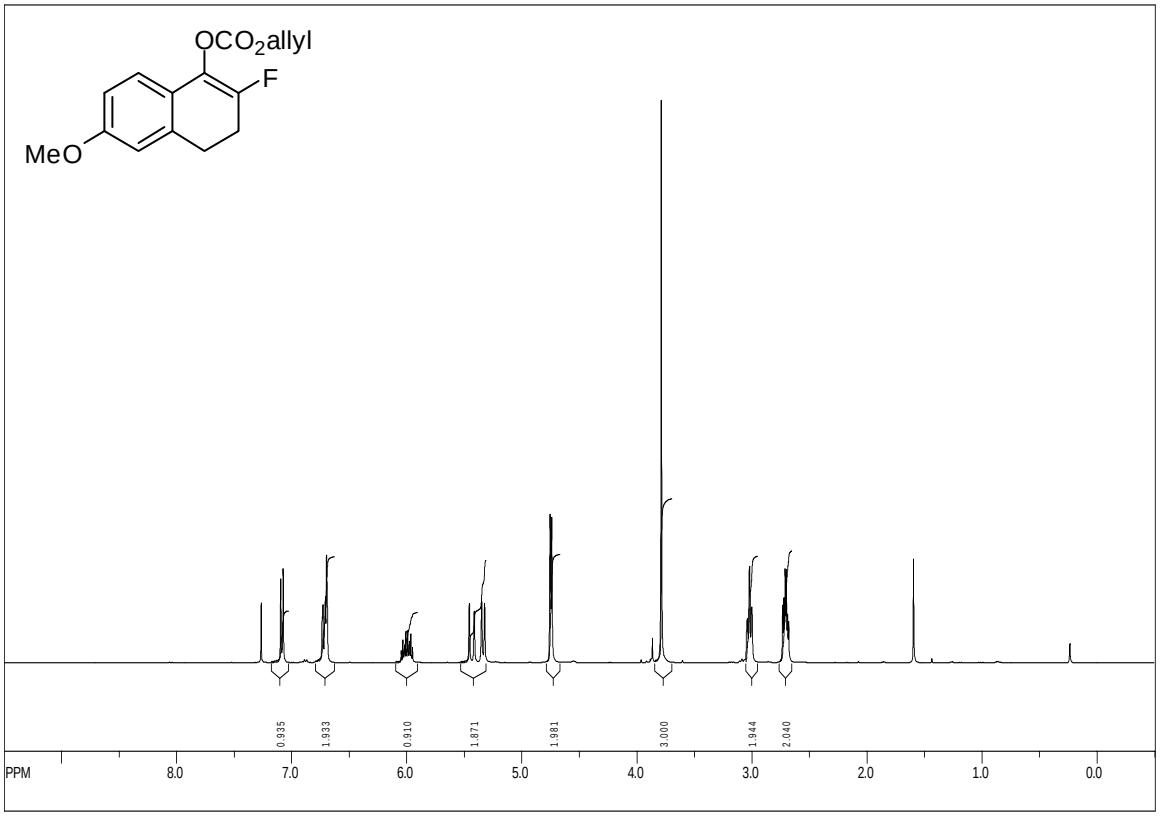
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2.040
PPM
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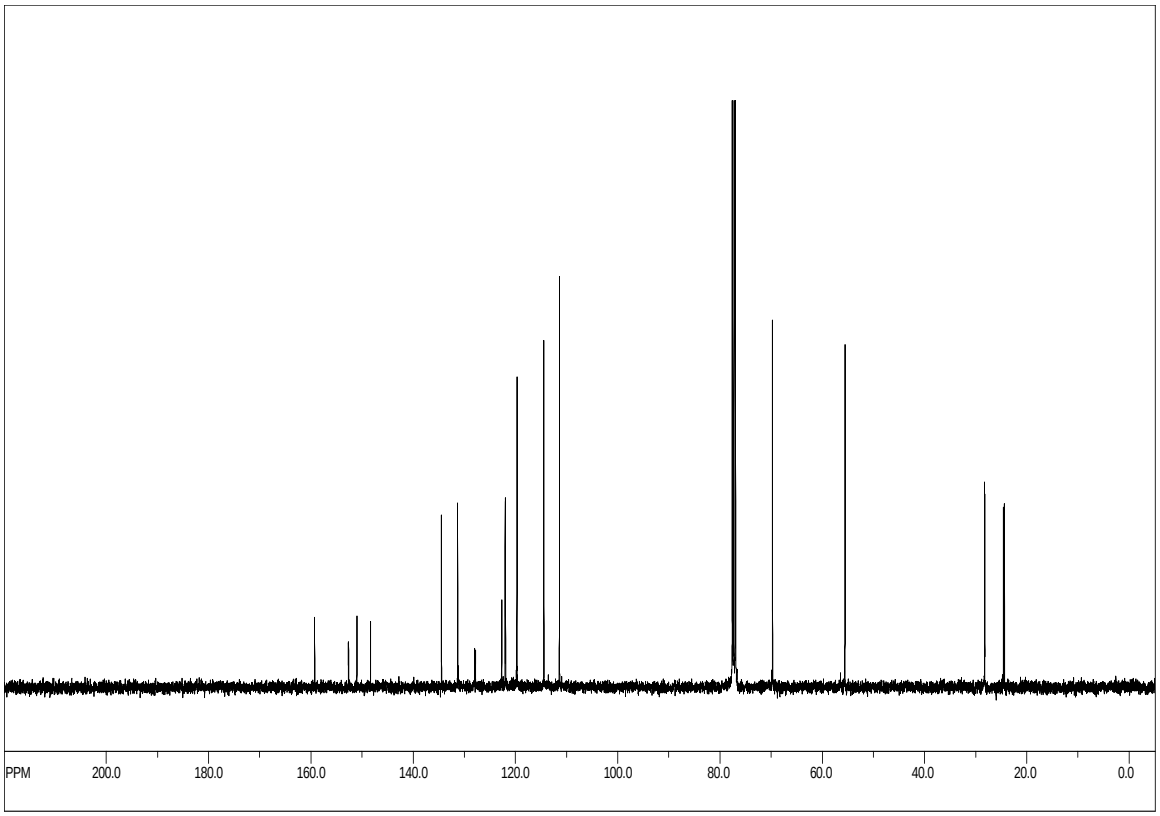
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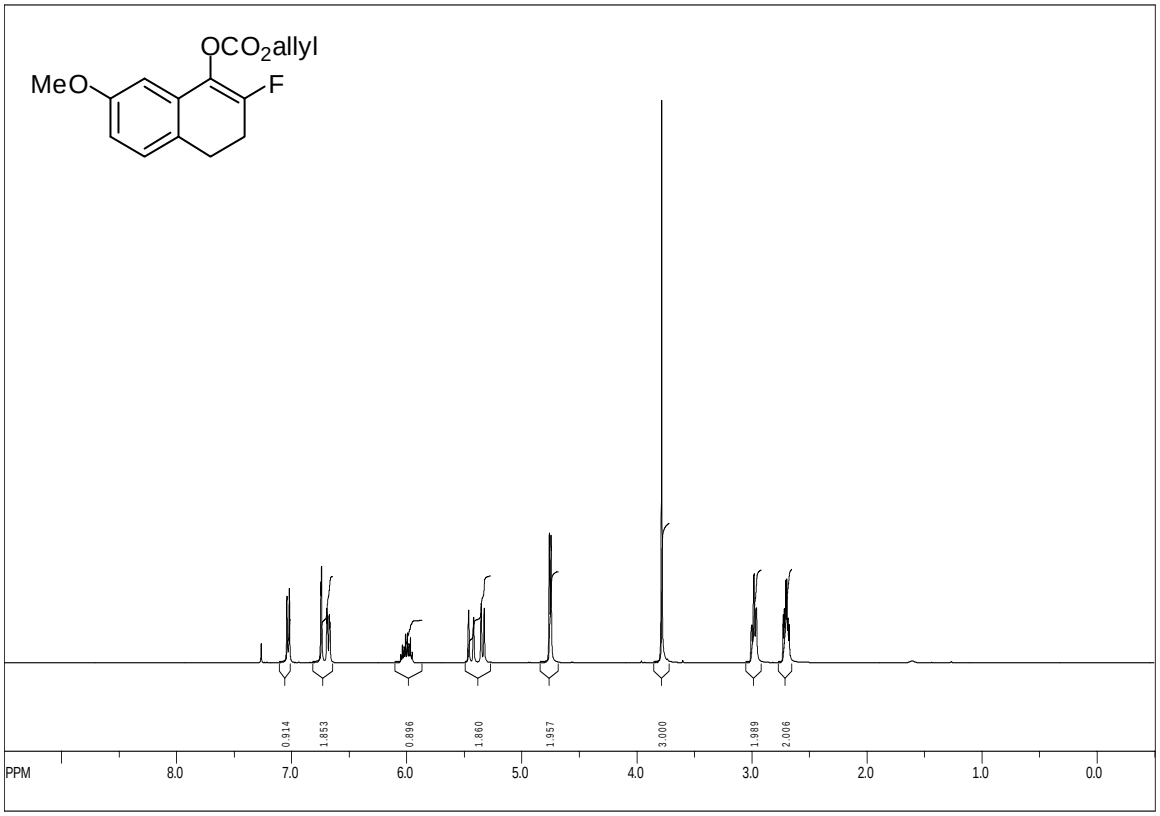
OCO2allyl
MeO
F
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1.853
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1.860
1.957
3.000
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PPM
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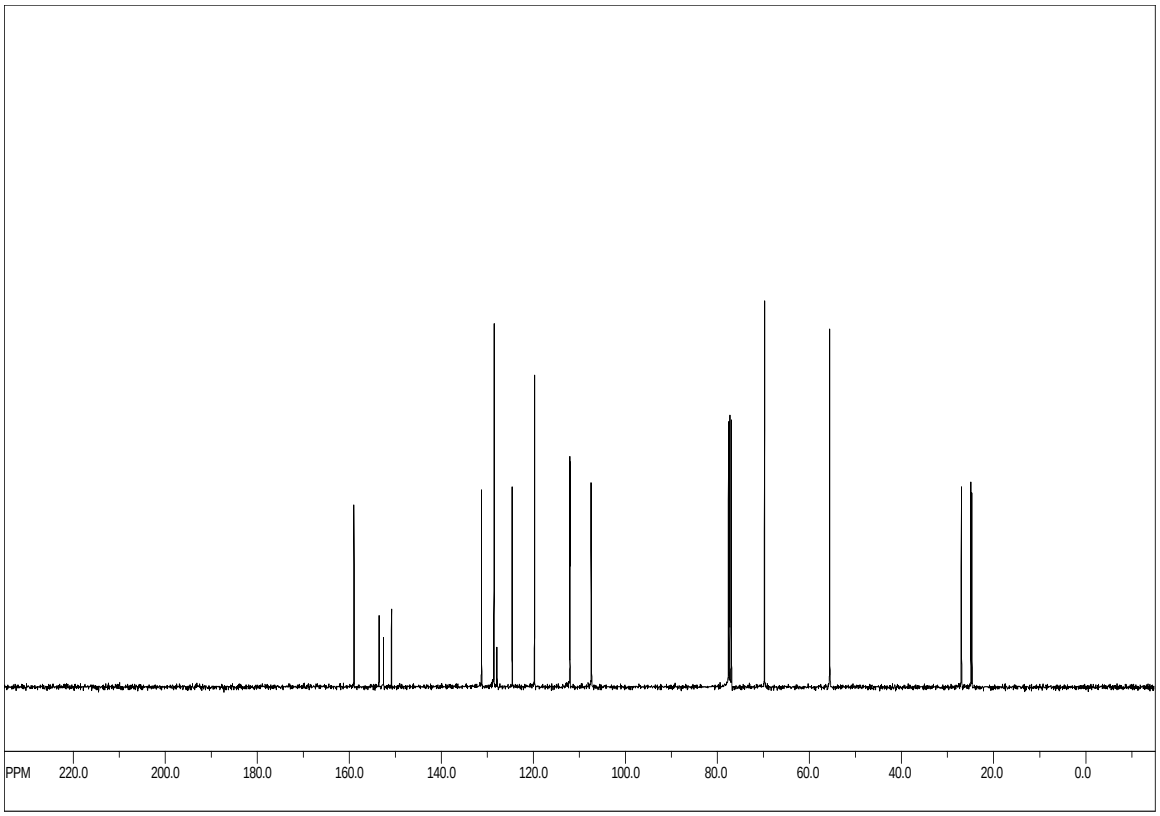
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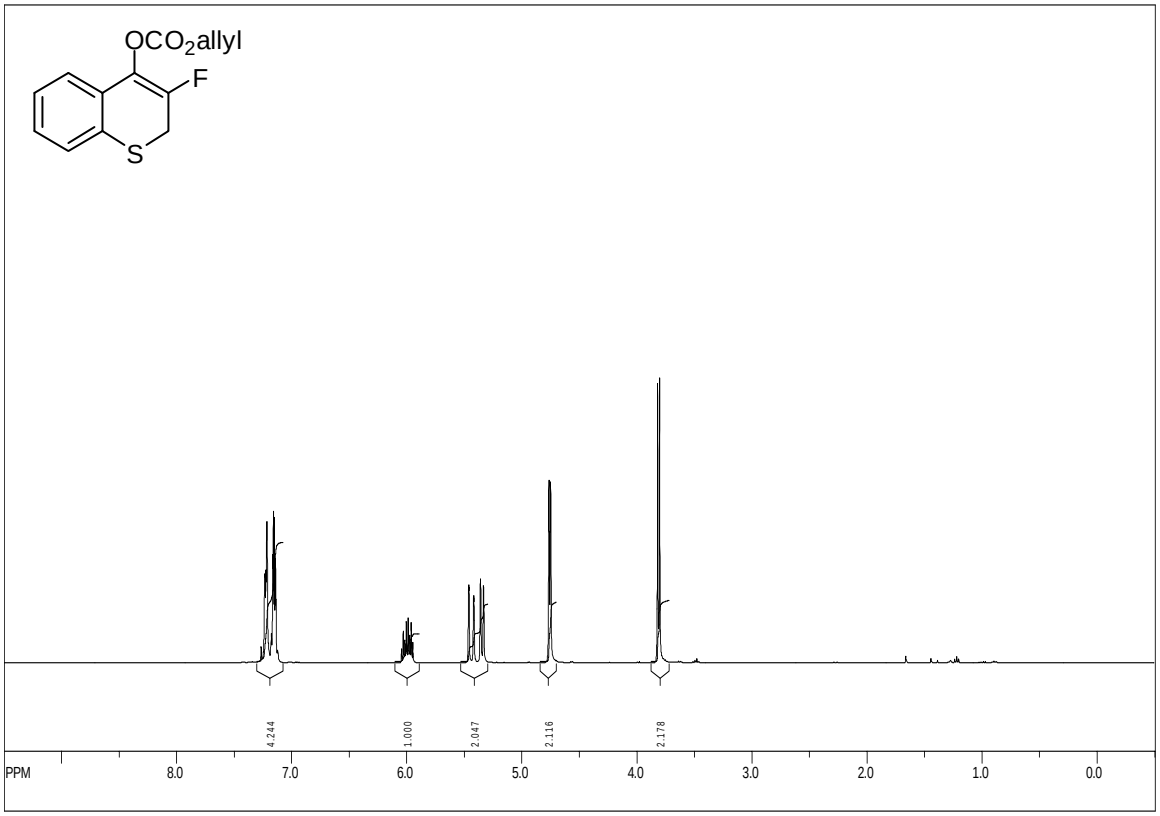
OCO2allyl
F
S
4.244
1.000
2.047
2.116
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PPM
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4.0
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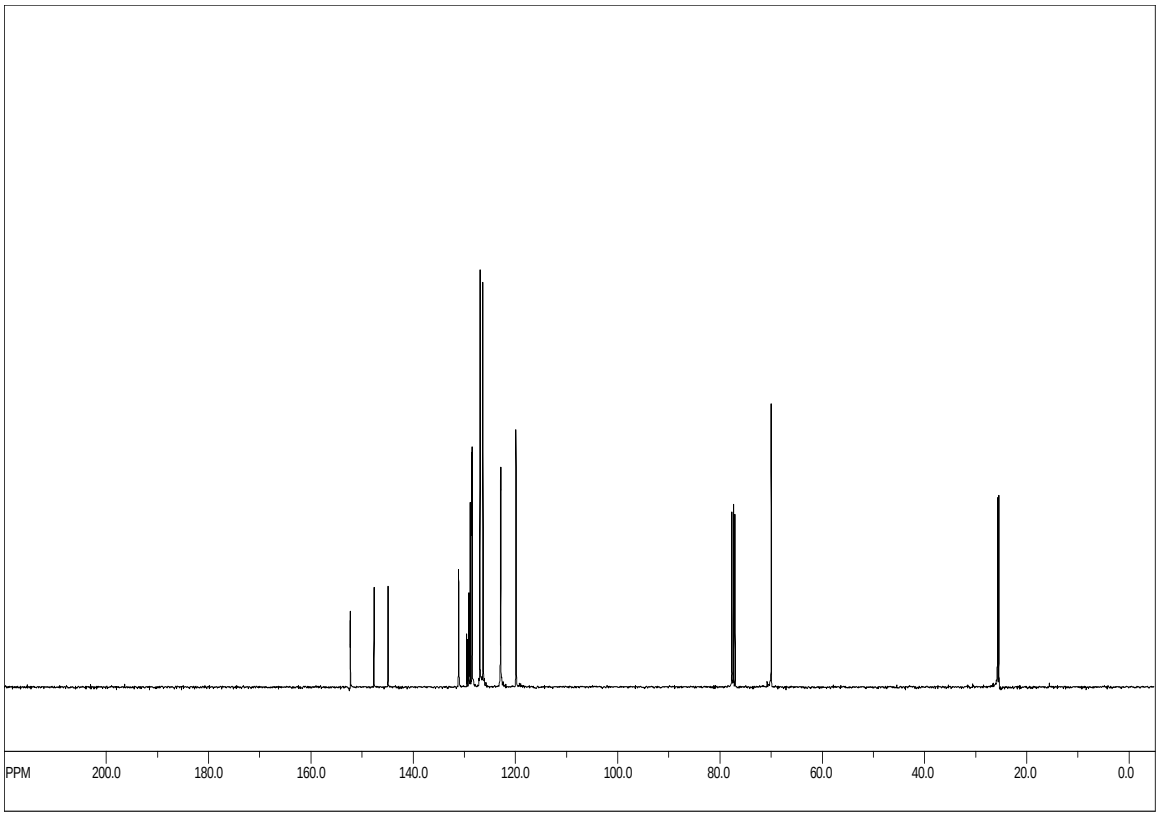
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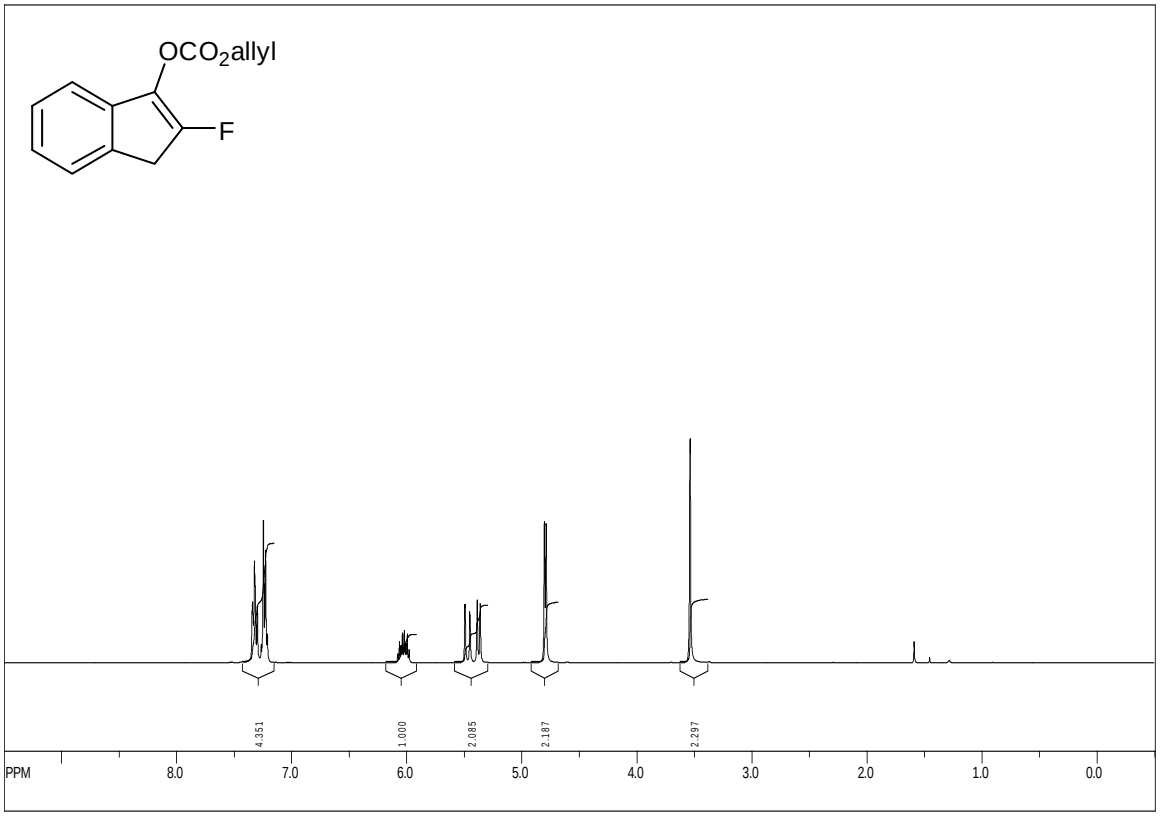
OCO2allyl
F
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2.085
2.187
2.297
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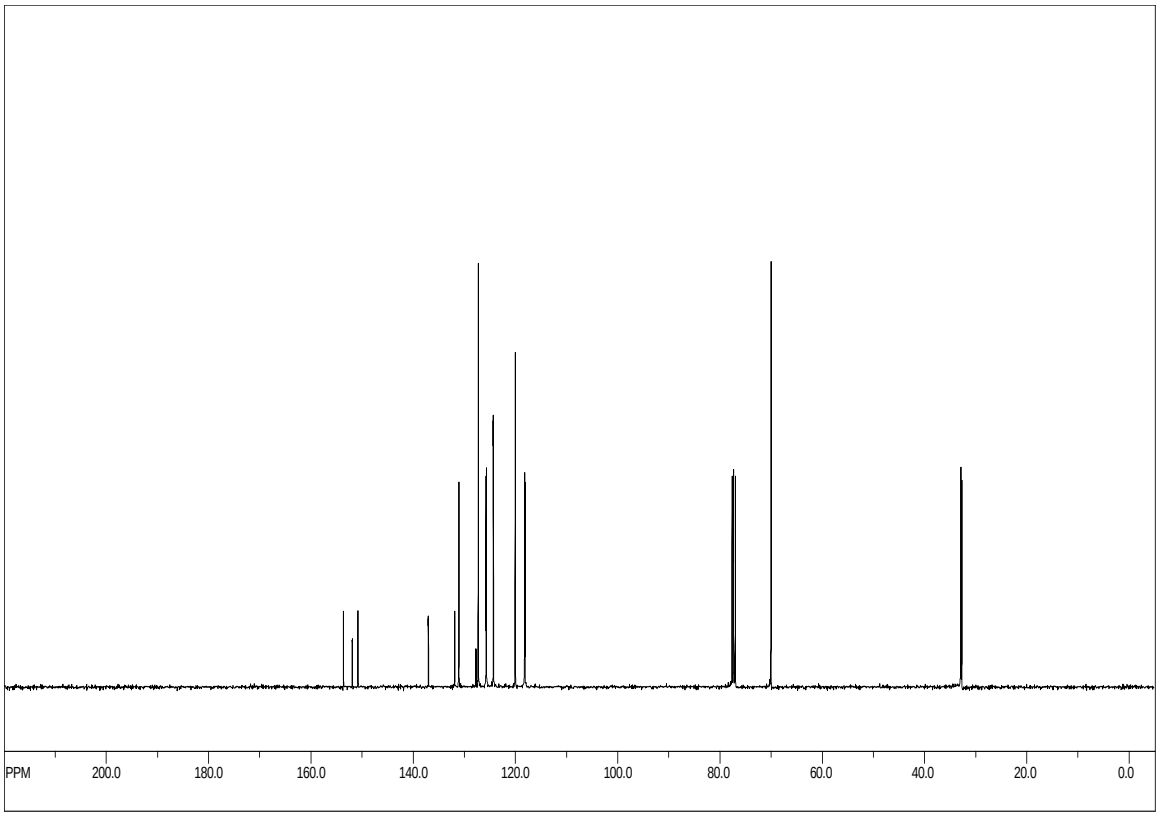
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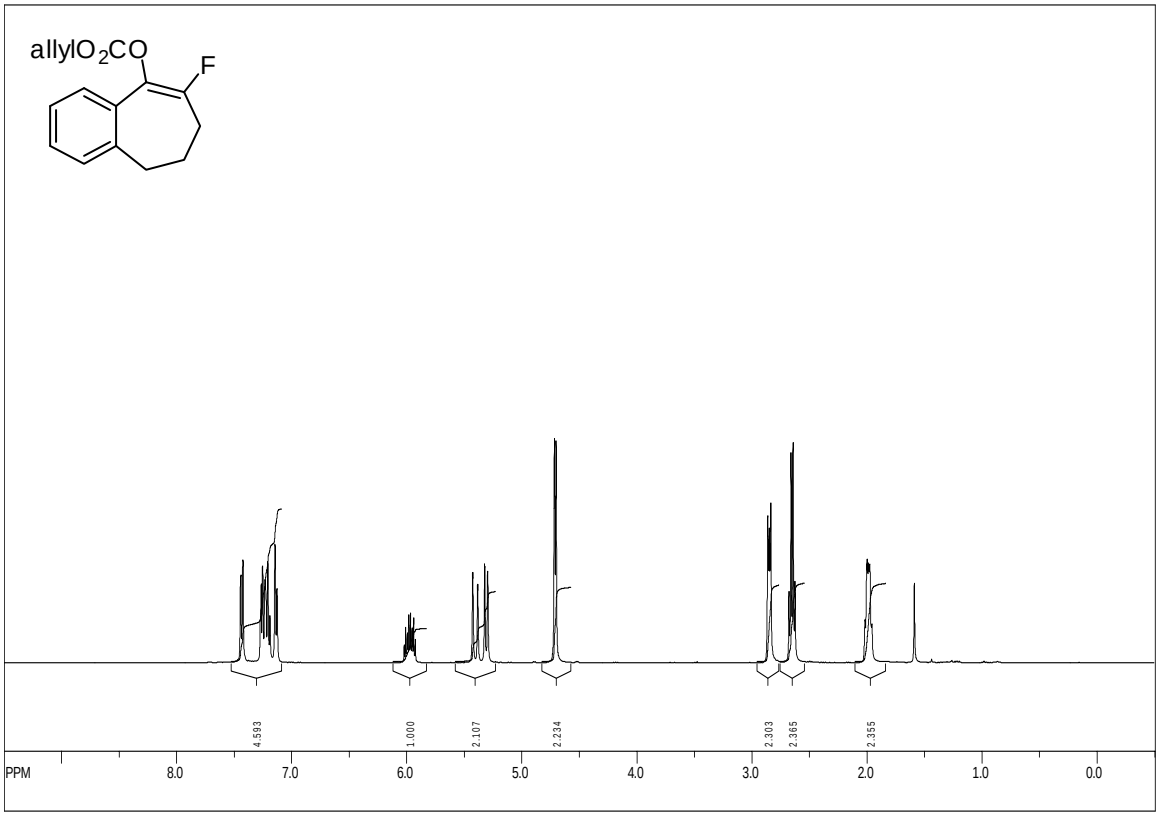
allylO2CO
F
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1.000
2.107
2.234
2.303
2.365
2.355
PPM
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4.0
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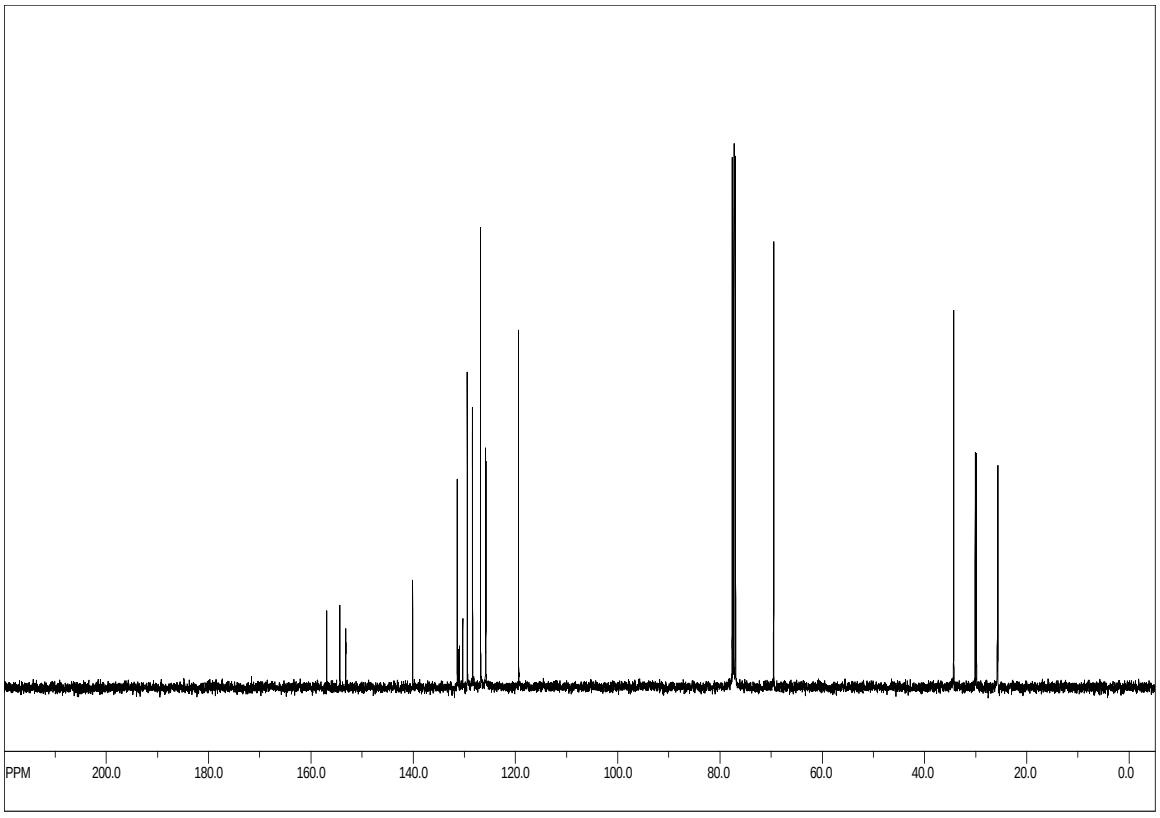
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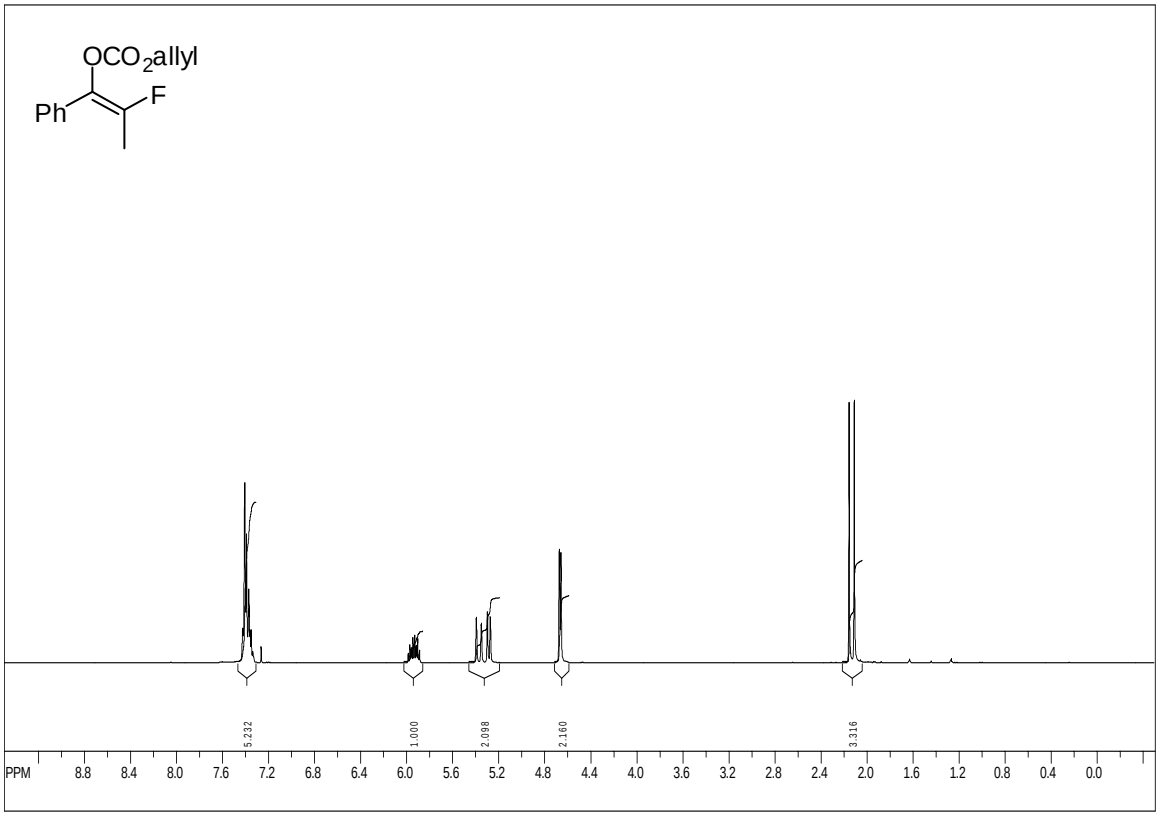
OCO2allyl
Ph
F
5.232
1.000
2.098
2.160
3.316
PPM
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8.4
8.0
7.6
7.2
6.8
6.4
6.0
5.6
5.2
4.8
4.4
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3.6
3.2
2.8
2.4
2.0
1.6
1.2
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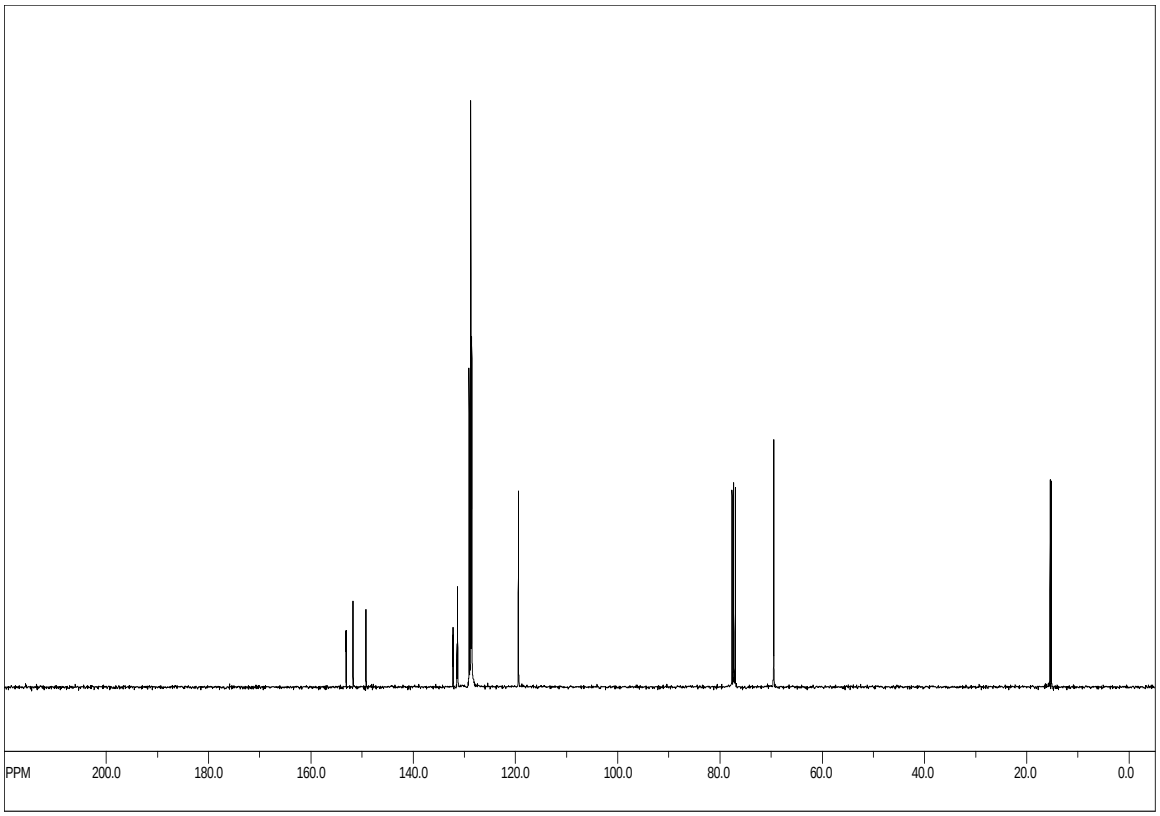
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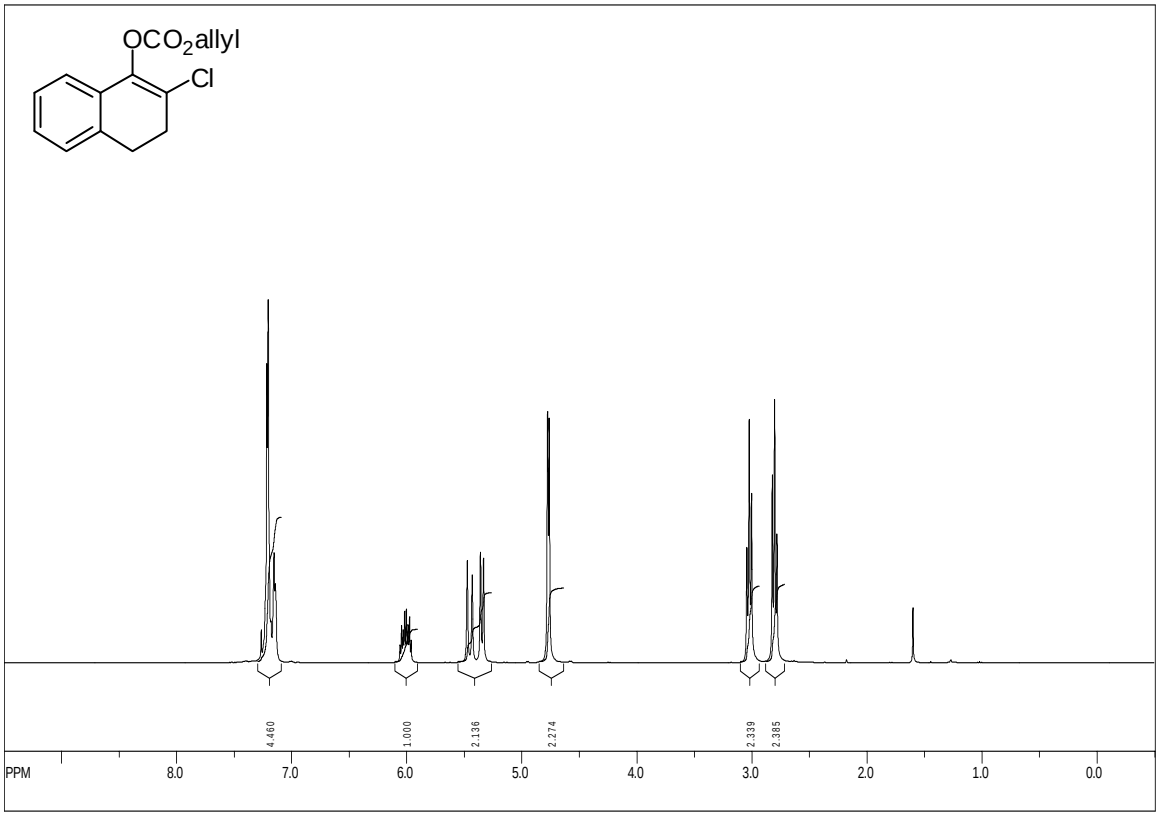
OCO2allyl
Cl
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2.274
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PPM
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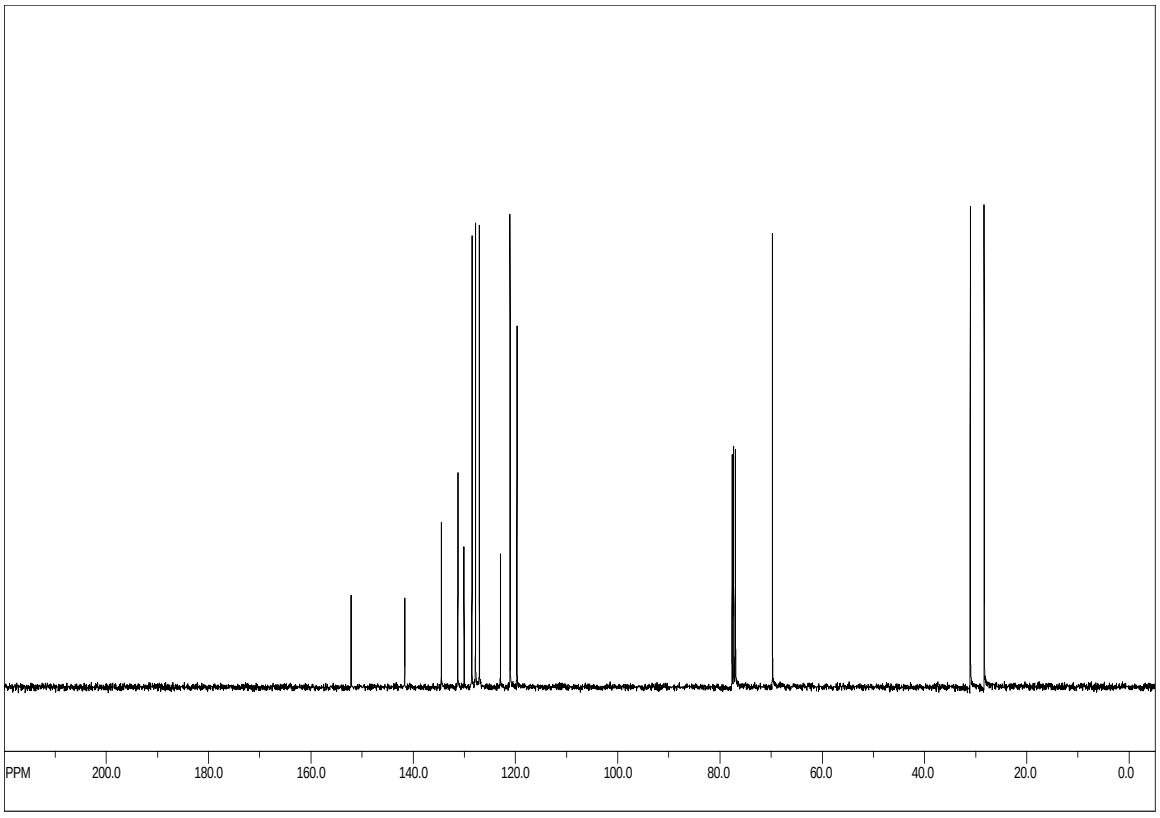
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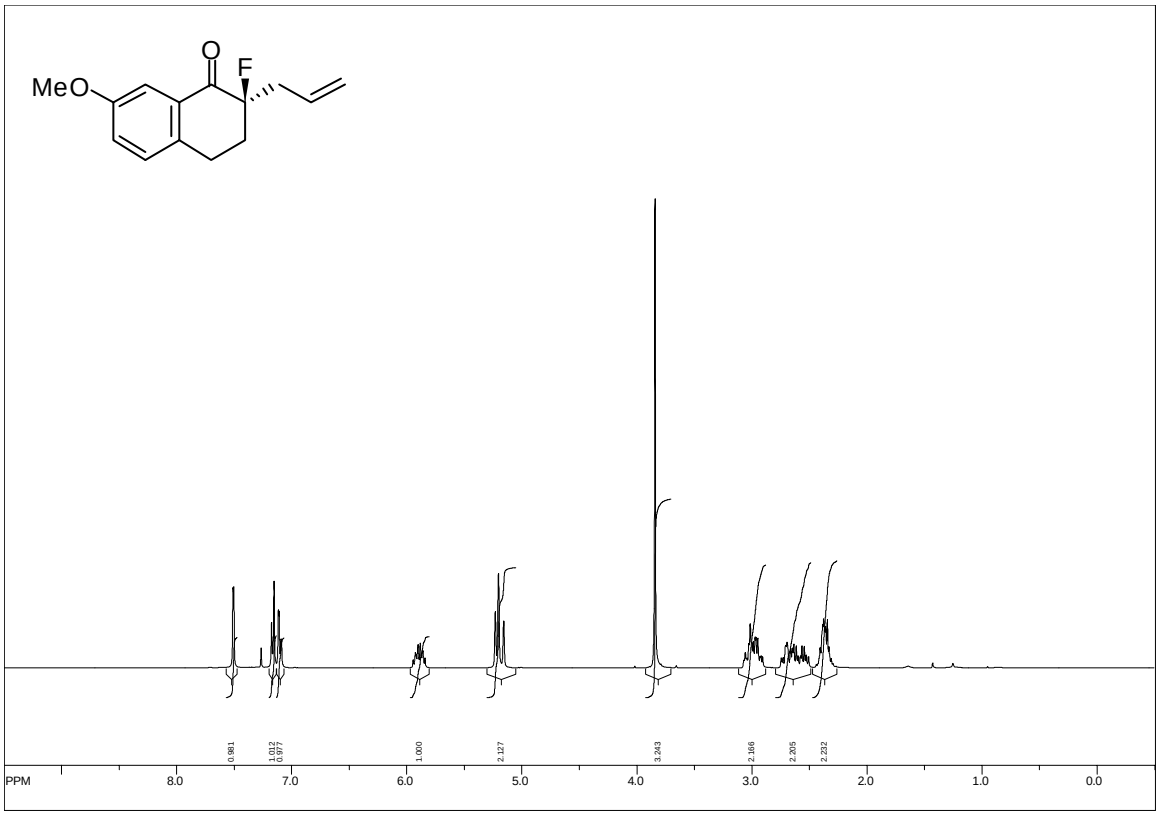
O
F
MeO
0.981
1.012
0.977
1.000
2.127
3.243
2.166
2.205
2.232
PPM
8.0
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6.0
5.0
4.0
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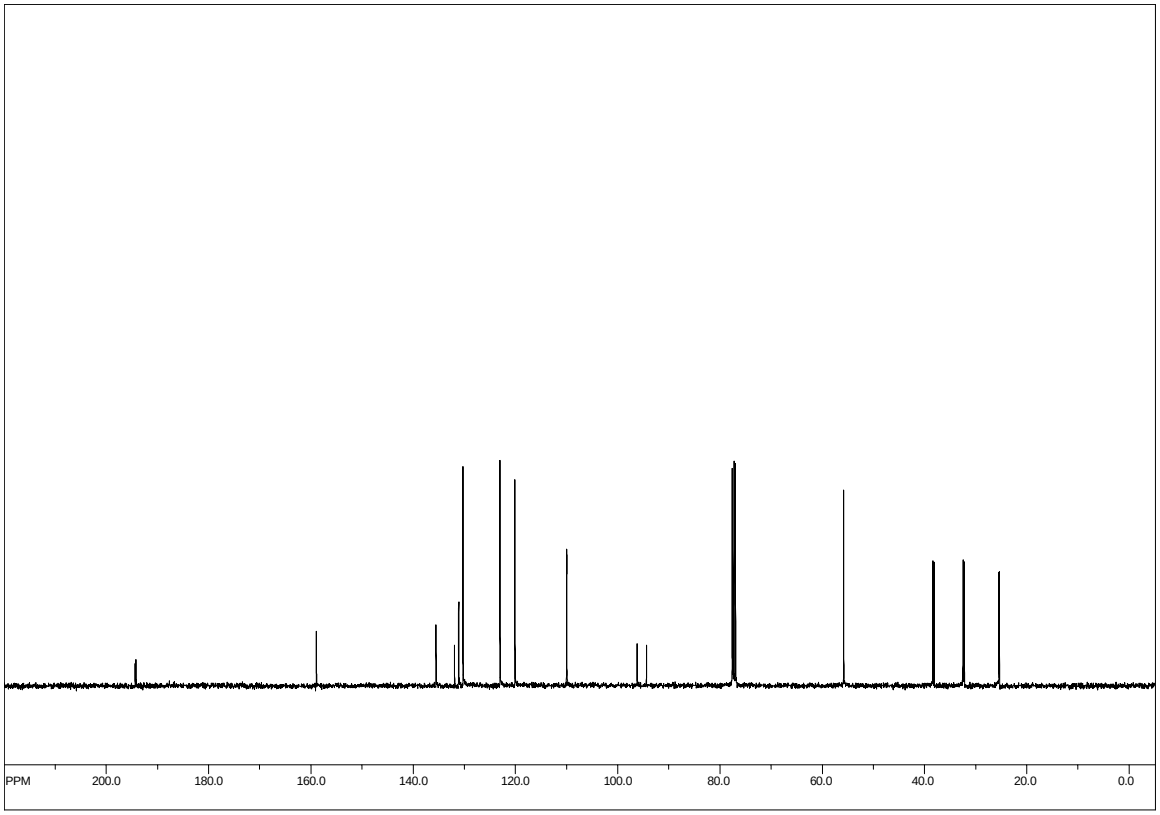
0.0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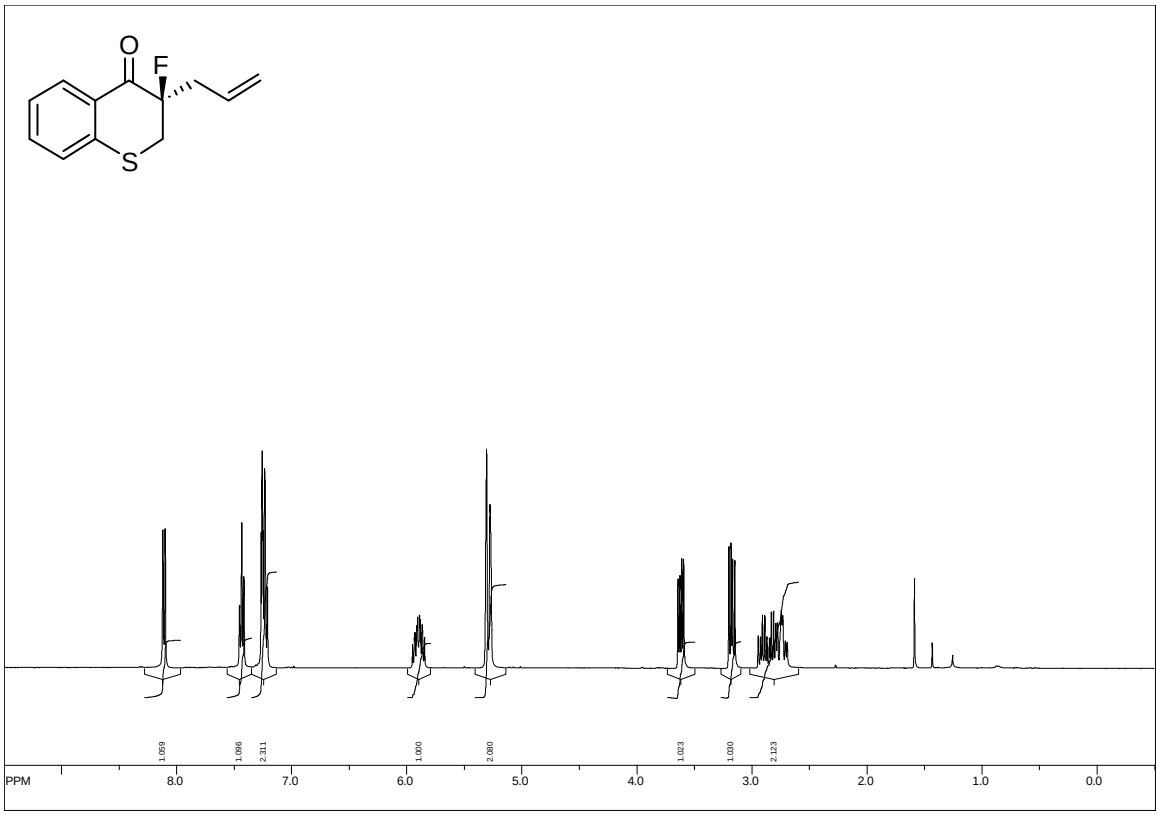
O
F
S
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1.096
2.311
1.000
2.080
1.023
1.030
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PPM
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6.0
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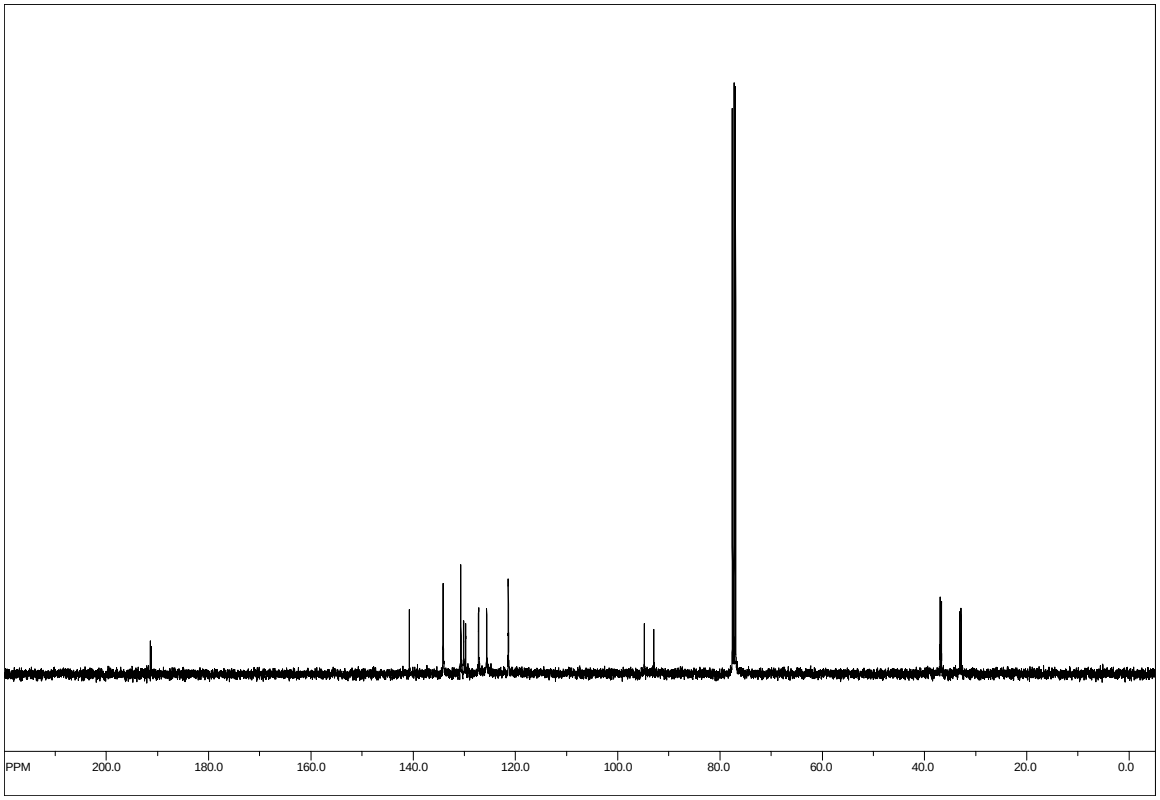
1.0
0.0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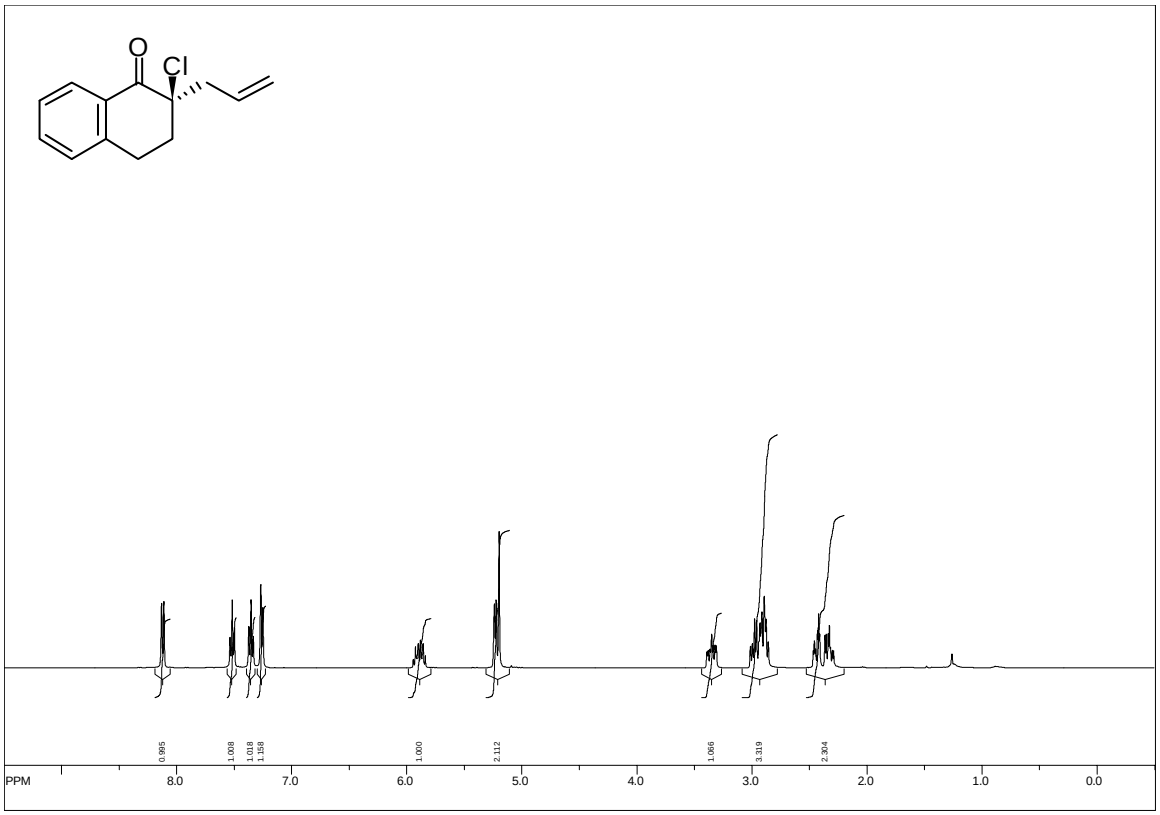
O
Cl
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1.008
1.018
1.936
1.000
2.112
1.066
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PPM
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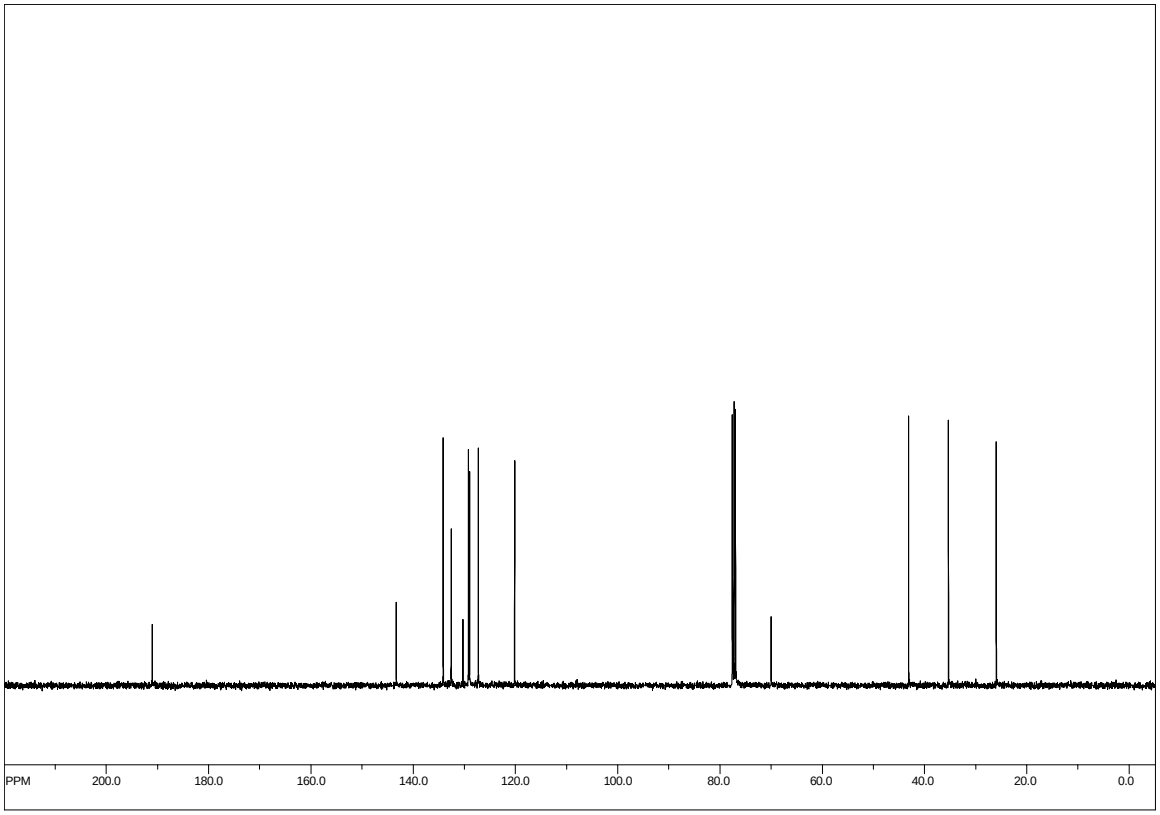
0.0


PPM
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