

Supporting Information

Enantioselective Pd-Catalyzed Allylation Reaction of Fluorinated Silyl Enol Ethers

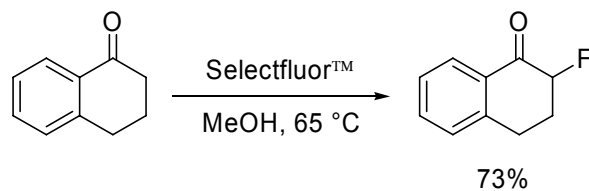
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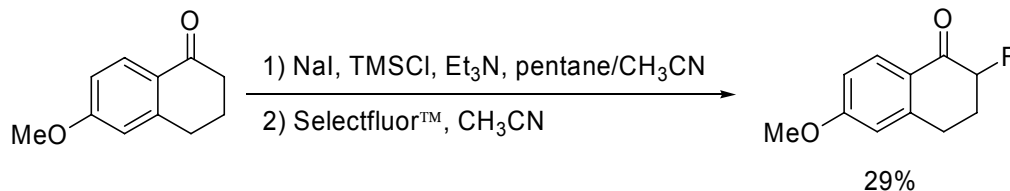
The following includes general experimental procedures, specific details for representative reactions, and isolation and spectroscopic information for the new compounds prepared. ^1H , ^{13}C , and ^{19}F NMR spectra were recorded on a VARIAN Inova 400 MHz in CDCl_3 at ambient temperature using tetramethylsilane (^1H NMR) or residual CHCl_3 (^1H 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. Low-resolution mass spectra were obtained on a Hewlett Packard Series II GC with a HP-5989A EI mass spectrometer. High-resolution mass spectra were performed by AIMS Lab (University of Toronto) and were obtained either by electron impact ionization (EI) on a Micromass 70S-250 sector mass spectrometer or electrospray ionization (ESI) on an ABI/Sciex QStar mass spectrometer. Enantiomeric excesses were determined by HPLC analysis with a Hewlett Packard Series 1100. Optical rotation $[\alpha]_{\text{D}}$ were measured on a Jasco DIP-360 Polarimeter. Melting points were recorded on a Uni-Met capillary melting point apparatus and are uncorrected. Ligands **6-8** were purchased from commercial sources while ligand **9** was prepared using literature procedure.¹

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

Synthesis of the α -fluoroketones



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

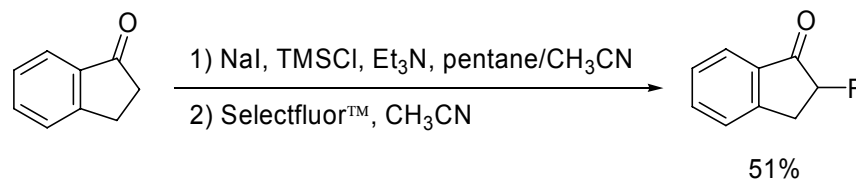


2-Fluoro-6-methoxy-1-tetralone The fluoroketone was prepared using a literature protocol.⁴ On a 2.8 mmol scale, the desired product (162 mg, 29% overall yield) was isolated as a white solid by flash chromatography using 10% acetone/hexane. mp 59-62 °C; IR (neat) $\nu = 2946, 2919, 2942, 1684, 1598, 1334, 1253, 1074, 927, 853 \text{ cm}^{-1}$; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.05 (d 1H, $J = 8.8 \text{ Hz}$), 6.87 (dd, 1H, $J = 8.8, 2.3 \text{ Hz}$), 6.71 (s, 1H), 5.11 (ddd, 1H, $J = 48.0, 12.4, 5.1 \text{ Hz}$), 3.87 (s, 3H), 3.09 (m, 2H), 2.55 (m, 1H), 2.34 (m, 1H); $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -190.8 (m, 1F); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 192.2 (d, $J_{\text{C-F}} = 14.9 \text{ Hz}$), 164.5, 144.8, 130.6, 124.9, 114.0, 112.80, 91.2 (d, $J_{\text{C-F}} = 186 \text{ Hz}$), 55.8, 30.4 (d, $J_{\text{C-F}} = 19.1 \text{ Hz}$), 27.5 (d, $J_{\text{C-F}} = 11.5 \text{ Hz}$); HRMS-ESI calcd for $\text{C}_{11}\text{H}_{12}\text{FO}_2$ $[\text{M}+\text{H}]^+$ 195.0815, found 195.0809.

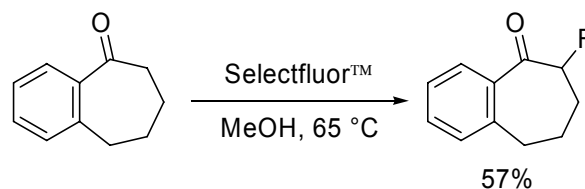
² Stavber, S.; Jereb, M.; Zupan, M. *Synthesis* **2002**, 2609.

³ Stavber, S.; Šket, B.; Zajc, B.; Zupan, M. *Tetrahedron* **1989**, 45, 6003.

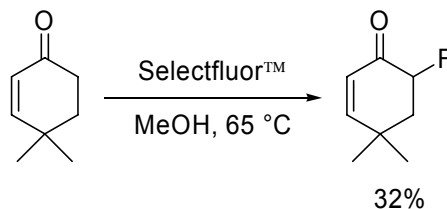
⁴ Solladie-Cavallo, A.; Jierry, L.; Bouerat, L.; Taillasson, P. *Tetrahedron : Asymmetry* **2001**, 12, 883.



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



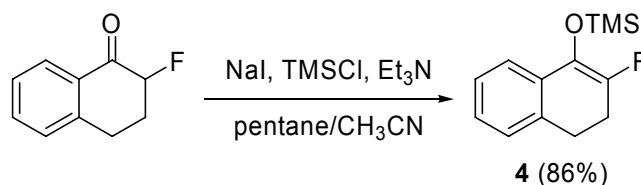
2-Fluoro-1-benzosuberone The fluoroketone was prepared following a literature protocol.² Spectroscopic data were in agreement with the literature.³



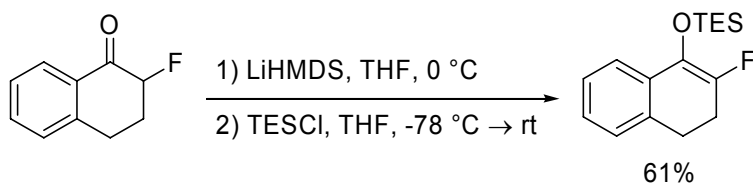
6-Fluoro-4,4-dimethylcyclohex-2-enone The fluoroketone was prepared following a literature protocol.² On a 4.0 mmol scale, the desired product (185 mg, 32%) was isolated as a white solid by flash chromatography using 10% acetone/hexane. mp 100-103 °C; IR (neat) $\nu = 3028, 2965, 2877, 1701, 1473, 1363, 1081, 1045, 910, 832, 800 \text{ cm}^{-1}$; ¹H NMR (400 MHz, CDCl₃) δ 6.67 (d, 1H, $J = 9.1$ Hz), 5.87 (dd, 1H, $J = 10.0, 4.4$ Hz), 5.08 (ddd, 1H, $J = 47.9, 13.2, 5.6$ Hz), 2.26 (m, 1H), 2.07 (m, 1H), 1.27 (s, 3H), 1.22 (s, 3H); ¹⁹F NMR (376 MHz, CDCl₃) δ -196.1 (m, 1F); ¹³C NMR (100 MHz, CDCl₃) δ 194.8 (d, $J_{\text{C-F}} = 14.7$ Hz), 159.9 (d, $J_{\text{C-F}} = 1.7$ Hz), 124.8,

88.3 (d, $J_{C-F} = 188$ Hz), 42.6 (d, $J_{C-F} = 16.8$ Hz), 35.8 (d, $J_{C-F} = 10.8$ Hz), 30.9, 26.5; HRMS-ESI calcd for $C_8H_{12}FO$ $[M+H]^+$ 143.0866, found 143.0867.

Synthesis of the fluorinated silyl enol ethers

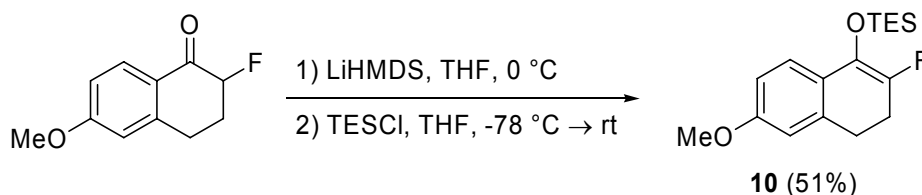


(2-Fluoro-3,4-dihydronaphthalen-1-yloxy)trimethylsilane (4) To a solution of the fluoroketone (500 mg, 3.0 mmol) in dry pentane (6 ml) was added Et_3N (850 μL , 6.1 mmol), TMSCl (770 μL , 6.1 mmol) followed by a solution of anhydrous NaI (911 mg, 6.1 mmol) in dry CH_3CN (15 ml), and the resulting mixture was stirred overnight. The upper layer (pentane) was transferred into another flask. The remaining mixture was extracted with pentane (5 \times). The pentane layers were combined and evaporated. The desired product (616 mg, 86%) was isolated as a colorless oil by flash chromatography using 5% Et_2O /hexane. IR (neat) $\nu = 3069, 2958, 2896, 2842, 1692, 1326, 1253, 1192, 903, 848$ cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.36 (d, 1H, $J = 7.6$ Hz), 7.21 (t, 1H, $J = 7.3$ Hz), 7.10 (m, 2H), 2.96 (dt, 2H, $J = 8.5, 2.1$ Hz), 2.64 (dt, 2H, $J = 8.4, 4.1$ Hz), 0.27 (d, 9H, $J = 1.1$ Hz); ^{19}F NMR (376 MHz, CDCl_3) δ -128.3 (s, 1F); ^{13}C NMR (100 MHz, CDCl_3) δ 146.4 (d, $J_{C-F} = 256$ Hz), 133.4 (d, $J_{C-F} = 3.3$ Hz), 132.0, 129.4 (d, $J_{C-F} = 11.8$ Hz), 126.8, 126.5, 126.4 (d, $J_{C-F} = 2.3$ Hz), 121.5 (d, $J_{C-F} = 7.2$ Hz), 28.3 (d, $J_{C-F} = 7.6$ Hz), 24.4 (d, $J_{C-F} = 21.7$ Hz), 0.20 (d, $J_{C-F} = 2.6$ Hz); GC-MS calcd for $C_{13}H_{17}FOSi$ $[M]^+$ 236, found 236.

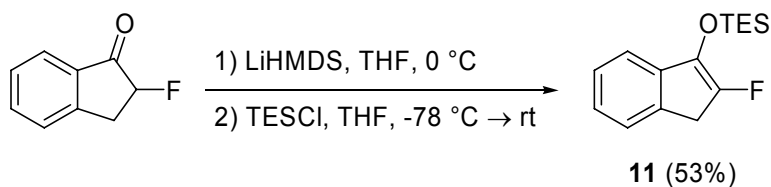


Triethyl(2-fluoro-3,4-dihydronaphthalen-1-yloxy)silane (General protocol for the TES enol ether formation)

To a 0 °C solution of LiHMDS (1.77 mL, 1.67 mmol, 1.06 M in THF) in THF (4 ml) was added the fluoroketone (250 mg, 1.5 mmol) dropwise over 15 minutes. The resulting mixture was stirred 1.5 h at 0 °C, and the enolate solution was added dropwise over 15 minutes to a -78 °C solution of TESCl (310 μ L, 1.82 mmol) in THF (8 ml). The reaction mixture was allowed to warm to rt overnight. The reaction was transferred into a mixture of CH₂Cl₂ and satd NH₄Cl. The layers were separated, the aqueous layer extracted with CH₂Cl₂ (3 \times). The combined organic layers were washed with brine, dried over anhydrous Na₂SO₄, and the solvent was evaporated to give the crude product. The pure product (170 mg, 61%) was isolated as a colorless oil by flash chromatography using 100% pentane. IR (neat) ν = 2956, 2913, 2878, 2841, 1691, 1325, 1205, 1192, 1090, 951 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.41 (d, 1H, J = 7.6 Hz), 7.21 (t, 1H, J = 7.3 Hz), 7.10 (m, 2H), 2.94 (t, 2H, J = 8.4 Hz), 2.62 (td, 2H, J = 8.4, 4.2 Hz), 1.01 (t, 9H, J = 7.9 Hz), 0.77 (q, 6H, J = 7.9 Hz); ¹⁹F NMR (376 MHz, CDCl₃) δ -128.9 (s, 1F); ¹³C NMR (100 MHz, CDCl₃) δ 146.3 (d, J_{C-F} = 256 Hz), 133.5 (d, J_{C-F} = 3.3 Hz), 133.0, 129.6 (d, J_{C-F} = 11.8 Hz), 126.7, 126.4, 126.3 (d, J_{C-F} = 2.3 Hz), 121.5 (d, J_{C-F} = 7.2 Hz), 28.3 (d, J_{C-F} = 7.5 Hz), 25.0 (d, J_{C-F} = 21.9 Hz), 6.7, 5.1 (d, J_{C-F} = 2.2 Hz); HRMS-EI calcd for C₁₆H₂₃FOSi [M]⁺ 278.1502, found 278.1496.

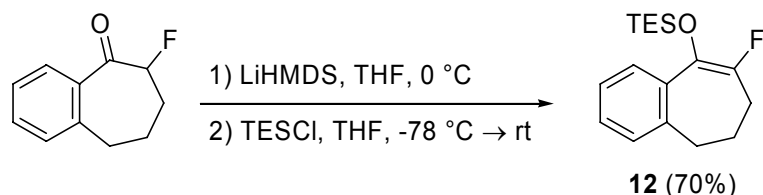


Triethyl(2-fluoro-6-methoxy-3,4-dihydronaphthalen-1-yloxy)silane (10) Following the general procedure on a 1.2 mmol scale, the desired product (197 mg, 51%) was isolated as a colorless oil by flash chromatography using 2% Et₂O/pentane. IR (neat) $\nu = 2956, 2878, 2837, 1693, 1499, 1330, 1251, 954, 745 \text{ cm}^{-1}$; ¹H NMR (400 MHz, CDCl₃) δ 7.31 (d, 1H, $J = 8.4$ Hz), 6.73 (dd, 1H, $J = 8.4, 2.4$ Hz), 6.65 (m, 1H), 3.79 (s, 3H), 2.91 (m, 2H), 2.60 (m, 2H), 1.00 (t, 9H, $J = 7.9$ Hz), 0.76 (q, 6H, $J = 7.9$ Hz); ¹⁹F NMR (376 MHz, CDCl₃) δ -132.1 (s, 1F); ¹³C NMR (100 MHz, CDCl₃) δ 158.4 (d, $J_{\text{C-F}} = 2.3$ Hz), 144.6 (d, $J_{\text{C-F}} = 253$ Hz), 134.8, 129.3 (d, $J_{\text{C-F}} = 11.8$ Hz), 126.3 (d, $J_{\text{C-F}} = 2.8$ Hz), 122.7, (d, $J_{\text{C-F}} = 7.3$ Hz), 113.4, 110.8, 55.2 (d, $J_{\text{C-F}} = 2.5$ Hz), 28.6 (d, $J_{\text{C-F}} = 7.5$ Hz), 24.5 (d, $J_{\text{C-F}} = 22.1$ Hz), 6.7, 5.1 (d, $J_{\text{C-F}} = 2.2$ Hz); HRMS-ESI calcd for C₁₇H₂₆FO₂Si [M+H]⁺ 309.1680, found 309.1684

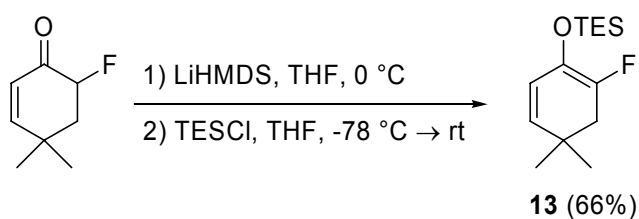


Triethyl(2-fluoro-3H-inden-1-yloxy)silane (11) Following the general procedure on a 1.5 mmol scale, the desired product (221 mg, 53%) was isolated as a colorless oil by flash chromatography using 100% pentane. IR (neat) $\nu = 2958, 2913, 2878, 1681, 1366, 1247, 1170, 959, 852 \text{ cm}^{-1}$; ¹H NMR (400 MHz, CDCl₃) δ 7.27 (m, 3H), 7.17 (m, 1H), 3.40 (d, 2H, $J = 2.2$ Hz), 1.03 (t, 9H, $J = 7.9$ Hz), 0.79 (q, 6H, $J = 7.9$ Hz); ¹⁹F NMR (376 MHz, CDCl₃) δ -146.5 (s, 1F); ¹³C NMR (100 MHz, CDCl₃); 147.9 (d, $J_{\text{C-F}} = 269$ Hz), 140.7 (d, $J_{\text{C-F}} = 3.9$ Hz), 132.7 (d, $J_{\text{C-F}} = 8.4$ Hz),

130.8 (d, $J_{C-F} = 7.6$ Hz), 126.8, 124.8 (d, $J_{C-F} = 4.5$ Hz), 123.7 (d, $J_{C-F} = 1.5$ Hz), 117.9 (d, $J_{C-F} = 7.1$ Hz), 32.0 (d, $J_{C-F} = 19.6$ Hz), 6.7, 5.2 (d, $J_{C-F} = 1.7$ Hz); HRMS-EI calcd for $C_{15}H_{21}FOSi$ $[M]^+$ 264.1346, found 264.1358.



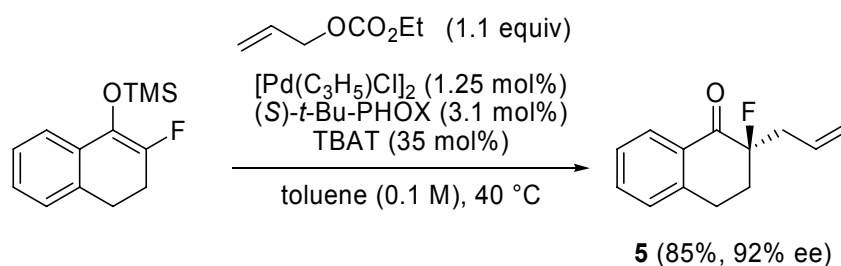
(Z)-Triethyl(6-fluoro-8,9-dihydro-7H-benzo[7]annulen-5-yloxy)silane (12) Following the general procedure on a 0.98 mmol scale, the desired product (202 mg, 70%) was isolated as a colorless oil by flash chromatography using pentane. IR (neat) $\nu = 3068, 2954, 2912, 2877, 1674, 1288, 1183, 911, 742$ cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, 1H, $J = 7.4$ Hz), 7.24 (m, 1H), 7.16 (t, 1H, $J = 6.4$ Hz), 7.09 (d, 1H, $J = 7.4$ Hz), 2.71 (m, 2H), 2.48 (m, 2H), 1.97 (m, 2H), 0.95 (t, 9H, $J = 7.9$ Hz), 0.67 (q, 6H, $J = 7.9$ Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.6 (t, 1F, $J = 9.3$ Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.4 (d, $J_{C-F} = 244$ Hz), 139.6, 134.8 (d, $J_{C-F} = 3.6$ Hz), 132.2 (d, $J_{C-F} = 16.8$ Hz), 128.5 (d, $J_{C-F} = 15.5$ Hz), 127.4 (d, $J_{C-F} = 1.1$ Hz), 127.2 (d, $J_{C-F} = 5.7$ Hz), 126.2, 34.0, 28.9 (d, $J_{C-F} = 25.7$ Hz), 28.0 (d, $J_{C-F} = 8.4$ Hz), 6.9, 5.4 (d, $J_{C-F} = 1.8$ Hz); HRMS-EI calcd for $C_{17}H_{25}FOSi$ $[M]^+$ 292.1659, found 292.1665.



Triethyl(2-fluoro-4,4-dimethylcyclohexa-1,5-dienyloxy)silane (13) Following the general procedure on a 1.4 mmol scale, the desired product (238 mg, 66%) was isolated as a colorless oil

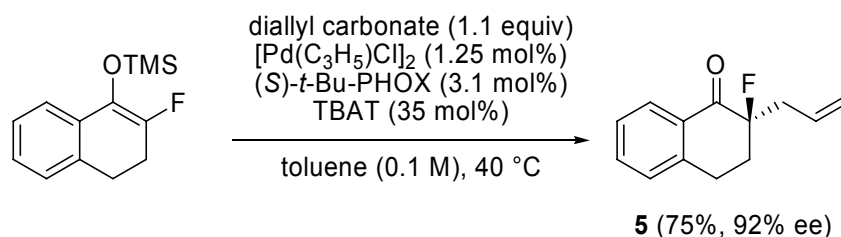
by flash chromatography using 100% pentane. IR (neat) $\nu = 3031, 2964, 2918, 2871, 2825, 1702, 1377, 1253, 1228, 1089, 862, 738 \text{ cm}^{-1}$; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 5.54 (t, 1H, $J = 9.5 \text{ Hz}$), 5.27 (d, 1H, $J = 9.5 \text{ Hz}$), 2.35 (d, 2H, $J = 3.8 \text{ Hz}$), 1.08 (s, 6H), 0.99 (t, 9H, $J = 7.9 \text{ Hz}$), 0.68 (q, 6H, $J = 7.9 \text{ Hz}$); $^{19}\text{F NMR}$ (376 MHz, CDCl_3) $\delta -133.7$ (m, 1F); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 143.7 (d, $J_{\text{C-F}} = 258 \text{ Hz}$), 134.2 (d, $J_{\text{C-F}} = 3.4 \text{ Hz}$), 127.8 (d, $J_{\text{C-F}} = 10.9 \text{ Hz}$), 123.2, 39.0 (d, $J_{\text{C-F}} = 18.0 \text{ Hz}$), 34.8 (d, $J_{\text{C-F}} = 6.7 \text{ Hz}$), 28.3 (d, $J_{\text{C-F}} = 1.5 \text{ Hz}$), 6.7, 5.1 (d, $J_{\text{C-F}} = 1.1 \text{ Hz}$); HRMS-EI calcd for $\text{C}_{14}\text{H}_{25}\text{FOSi}$ $[\text{M}]^+$ 256.1659, found 256.1663.

Enantioselective Pd-catalyzed allylation reaction

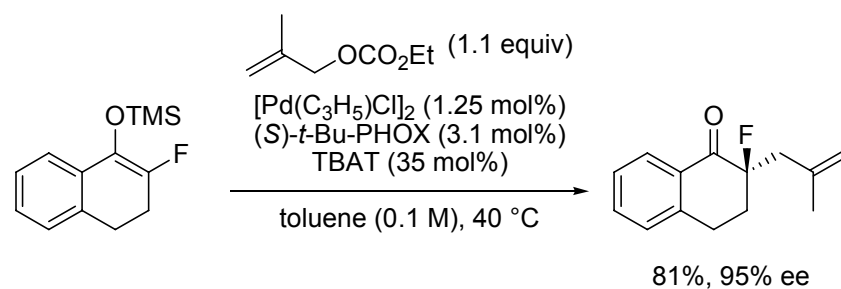


(R)-2-Allyl-2-fluoro-1-tetralone (5) (General protocol for the Pd-catalyzed allylation reaction – 1.25 mol% Pd) (Table 2 – entry 1) Into a 10 ml flask under nitrogen was added TBAT (66.7 mg, 0.124 mmol), (*S*)-*t*-Bu-PHOX (4.3 mg, 11 μmol) and $[\text{Pd}(\text{C}_3\text{H}_5)\text{Cl}]_2$ (1.6 mg, 4.4 μmol) followed by toluene (2 ml). After stirring 30 minutes at rt, a solution of the fluorinated silyl enol ether (83 mg, 0.35 mmol) and allyl ethyl carbonate (50 μL , 0.39 mmol) in toluene (1.5 ml) was added and the reaction mixture was heated at 40 $^\circ\text{C}$ overnight. The reaction was quenched by the addition of H_2O and Et_2O . The layers were separated and the aqueous phase was extracted with Et_2O (3 \times). The combined organic layers were dried over anhydrous Na_2SO_4 , and

the solvent was evaporated. The desired product (61 mg, 85%) was isolated as a colorless oil by flash chromatography using 5% Et₂O/hexane. The enantioselectivity was 92% ee (OJ-H, 254 nm, hexane:2-propanol = 99.9:0.1, flow rate 0.5 ml/min, $t_{r(\text{minor})}$ = 35.7 min, $t_{r(\text{major})}$ = 40.7 min). $[\alpha]_{\text{D}}^{22}$ -30.2 (c 0.64, CHCl₃) {lit.⁵ $[\alpha]_{\text{D}}^{29}$ -32.3 (c 1.08, CH₂Cl₂)}. All other spectroscopic data was in agreement with the literature.⁵



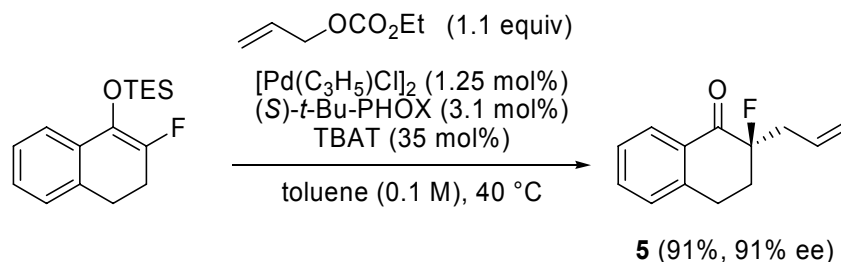
(R)-2-Allyl-2-fluoro-1-tetralone (5) (Table 2 – entry 2) Following the general protocol for 1.25 mol% Pd on a 0.35 mmol scale using diallyl carbonate instead of allyl ethyl carbonate, the desired product was obtained in 75% (55 mg). The enantioselectivity was 92% ee.



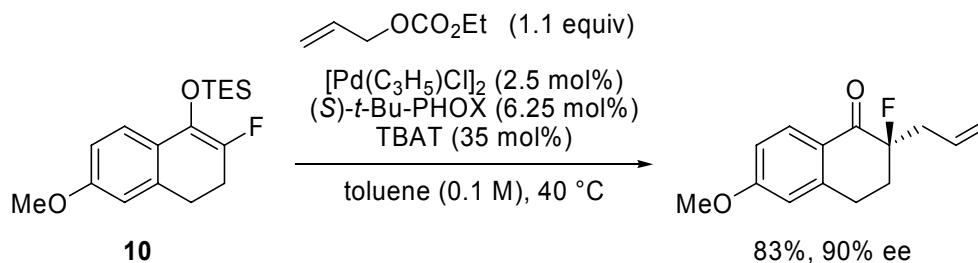
(R)-2-fluoro-2-(2-methylallyl)-1-tetralone (Table 2 – entry 3) Following the general protocol for 1.25 mol% Pd on a 0.38 mmol scale using ethyl 2-methylallyl carbonate instead of allyl ethyl carbonate, the desired product was isolated (67 mg, 81%) by flash chromatography using 5% Et₂O/hexane. The enantioselectivity was 95% ee (OJ-H, 254 nm, hexane:2-propanol = 99.9:0.1,

⁵ Nakamura, M.; Hajra, A.; Endo, K.; Nakamura, E. *Angew. Chem. Int. Ed.* **2005**, *44*, 7248.

flow rate 0.8 ml/min, t_r (major) = 14.6 min, t_r (minor) = 16.0 min). $[\alpha]_D^{22}$ -25.2 (c 0.63, CHCl_3) {lit.⁵ $[\alpha]_D^{29}$ -30.9 (c 1.33, CH_2Cl_2)}. All other spectroscopic data was in agreement with the literature.⁵

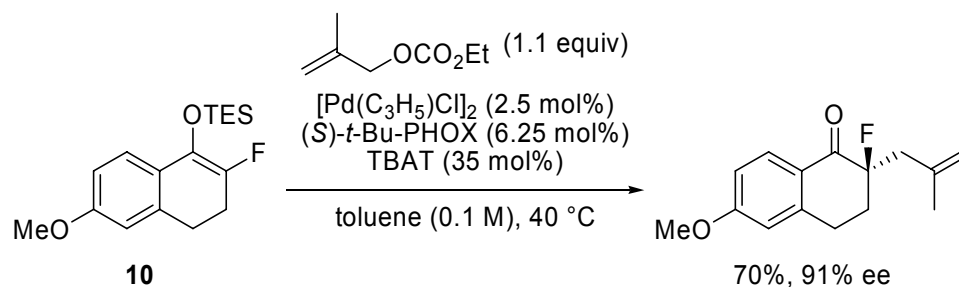


(R)-2-Allyl-2-fluoro-1-tetralone (5) (Table 2 – entry 4) Following the general protocol for 1.25 mol% Pd on a 0.32 mmol scale using the TES enol ether instead of the TMS enol ether, the desired product was isolated in 91% (59 mg). The enantioselectivity was 91% ee.

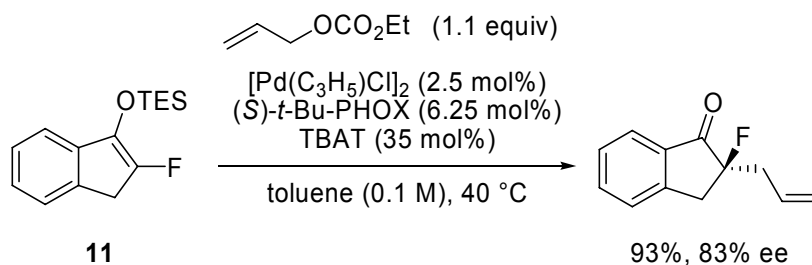


(R)-2-Allyl-2-fluoro-6-methoxy-1-tetralone (General protocol for the Pd-catalyzed allylation reaction – 2.5 mol% Pd) (Table 2 – entry 5) Into a 10 ml flask under nitrogen was added TBAT (45.9 mg, 0.085 mmol), (*S*)-*t*-Bu-PHOX (5.9 mg, 15 μmol) and $[\text{Pd}(\text{C}_3\text{H}_5)\text{Cl}]_2$ (2.2 mg, 6.1 μmol) followed by toluene (2 ml). After stirring 30 minutes at rt, a solution of the fluorinated silyl enol ether **10** (74 mg, 0.24 mmol) and allyl ethyl carbonate (34 μL , 0.26 mmol) in toluene (1.5 ml) was added and the reaction mixture was heated at 40 °C overnight. The reaction was quenched by the addition of H_2O and Et_2O . The layers were separated and the aqueous phase was extracted with Et_2O (3 \times). The combined organic layers were dried over anhydrous Na_2SO_4 , and

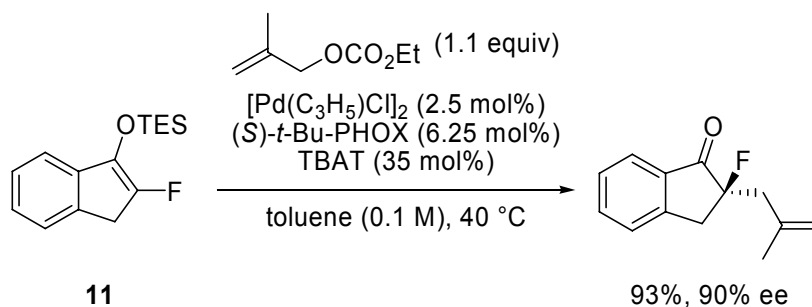
the solvent was evaporated. The desired product (47 mg, 83%) was isolated as a colorless oil by flash chromatography using 10% acetone/hexane. The enantioselectivity was 90% ee (AD-H, 254 nm, hexane:2-propanol = 99:1, flow rate 1.0 ml/min, $t_{r(\text{minor})}$ = 17.6 min, $t_{r(\text{major})}$ = 20.6 min). $[\alpha]_{\text{D}}^{22}$ -20.5 (c 0.52, CHCl_3) {lit.⁵ $[\alpha]_{\text{D}}^{29}$ -24.5 (c 1.25, CH_2Cl_2)}. All other spectroscopic data was in agreement with the literature.⁵



(R)-2-fluoro-6-methoxy-2-(2-methylallyl)-1-tetralone (Table 2 – entry 6) Following the general protocol for 2.5 mol% Pd on a 0.17 mmol scale of **10** using ethyl 2-methylallyl carbonate instead of allyl ethyl carbonate, the desired product (29 mg, 70%) was isolated as a colorless oil by flash chromatography using 7% acetone/hexane. The enantioselectivity was 91% ee (AD-H, 254 nm, hexane:2-propanol = 99:1, flow rate 0.8 ml/min, $t_{r(\text{major})}$ = 21.2 min, $t_{r(\text{minor})}$ = 23.3 min). The absolute configurations were assigned based on the established stereochemical outcome of the reaction. $[\alpha]_{\text{D}}^{22}$ -28.0 (c 0.48, CHCl_3); IR (neat) ν = 3075, 2947, 2843, 1689, 1600, 1264, 1222, 1078, 919 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 8.04 (d, 1H, J = 8.8 Hz), 6.88 (dd, 1H, J = 8.8, 2.3 Hz), 6.69 (m, 1H), 4.98 (s, 1H), 4.79 (s, 1H), 3.87 (s, 3H), 3.02 (m, 2H), 2.71–2.30 (m, 4H), 1.86 (s, 3H); ^{19}F NMR (376 MHz, CDCl_3) δ -156.9 (m, 1F); ^{13}C NMR (100 MHz, CDCl_3) δ 193.2 (d, $J_{\text{C-F}}$ = 17.5 Hz), 164.4, 145.4, 140.7, 131.0 (d, $J_{\text{C-F}}$ = 1.5 Hz), 124.5 (d, $J_{\text{C-F}}$ = 1.0 Hz), 116.2, 114.1, 112.7, 95.8 (d, $J_{\text{C-F}}$ = 184 Hz), 55.8, 41.6 (d, $J_{\text{C-F}}$ = 22.3 Hz), 31.9 (d, $J_{\text{C-F}}$ = 22.7 Hz), 26.8 (d, $J_{\text{C-F}}$ = 10.3 Hz), 24.0 (d, $J_{\text{C-F}}$ = 3.5 Hz); HRMS-ESI calcd for $\text{C}_{15}\text{H}_{18}\text{FO}_2$ $[\text{M}+\text{H}]^+$ 249.1285, found 249.1275.

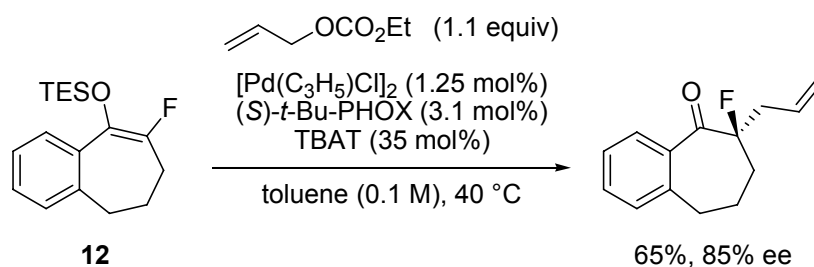


(S)-2-allyl-2-fluoro-1-indanone (Table 2 – entry 7) Following the general protocol for 2.5 mol% Pd on a 0.27 mmol scale of **11**, the desired product (48 mg, 93%) was isolated as a colorless oil by flash chromatography using 5% Et₂O/hexane. The enantioselectivity was 83% ee (AD-H, 254 nm, hexane:2-propanol = 99:1, flow rate 0.8 ml/min, $t_{r(\text{major})}$ = 9.7 min, $t_{r(\text{minor})}$ = 12.1 min). $[\alpha]_{\text{D}}^{22}$ -59.0 (*c* 0.68, CHCl₃) {lit.⁵ $[\alpha]_{\text{D}}^{29}$ -59.2 (*c* 0.62, CH₂Cl₂)}. All other spectroscopic data was in agreement with the literature.⁵

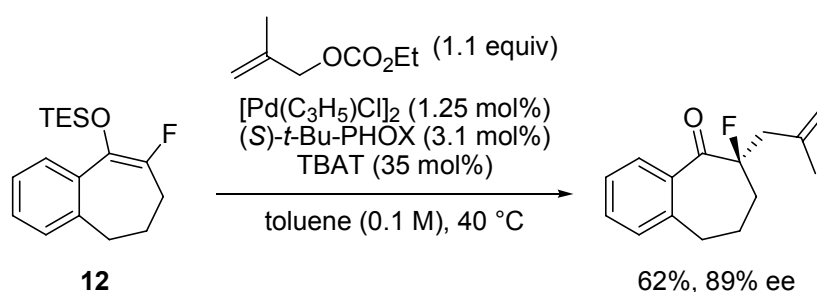


(S)-2-fluoro-2-(2-methylallyl)-1-indanone (Table 2 – entry 8) Following the general protocol on a 0.26 mmol scale of **11** using ethyl 2-methylallyl carbonate instead of allyl ethyl carbonate, the desired product (49 mg, 93 %) was isolated as a colorless oil by flash chromatography using 5% Et₂O/hexane. The enantioselectivity was 90% ee (AD-H, 254 nm, hexane:2-propanol = 99:1, flow rate 0.8 ml/min, $t_{r(\text{major})}$ = 11.3 min, $t_{r(\text{minor})}$ = 12.7 min). The absolute configurations were assigned based on the established stereochemical outcome of the reaction. $[\alpha]_{\text{D}}^{22}$ -64.1 (*c* 0.63, CHCl₃); IR (neat) ν = 3077, 2919, 1728, 1608, 1467, 1306, 902, 731 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.82 (d 1H, *J* = 7.6 Hz), 7.66 (t, 1H, *J* = 7.6 Hz), 7.43 (m, 2H), 4.94 (s, 1H), 4.79 (s,

1H), 3.52 (dd, 1H, $J = 17.7, 12.0$ Hz), 3.29 (dd, 1H, $J = 23.0, 17.6$ Hz), 2.82 (t, 1H, $J = 14.3$ Hz), 2.39 (dd, 1H, $J = 31.8, 14.5$ Hz), 1.80 (s, 3H); ^{19}F NMR (376 MHz, CDCl_3) δ -155.7 (m, 1F); ^{13}C NMR (100 MHz, CDCl_3) δ 201.0 (d, $J_{\text{C-F}} = 18.1$ Hz), 150.7 (d, $J_{\text{C-F}} = 4.2$ Hz), 140.5 (d, $J_{\text{C-F}} = 3.3$ Hz), 136.6, 134.0 (d, $J_{\text{C-F}} = 1.4$ Hz), 128.5, 127.0 (d, $J_{\text{C-F}} = 1.3$ Hz), 125.4 (d, $J_{\text{C-F}} = 1.1$ Hz), 116.2 (d, $J_{\text{C-F}} = 1.0$ Hz), 98.0 (d, $J_{\text{C-F}} = 187$ Hz), 42.6 (d, $J_{\text{C-F}} = 24.5$ Hz), 37.5 (d, $J_{\text{C-F}} = 24.5$ Hz), 24.0 (d, $J_{\text{C-F}} = 2.6$ Hz); HRMS-ESI calcd for $\text{C}_{13}\text{H}_{14}\text{FO}$ $[\text{M}+\text{H}]^+$ 205.1023, found 205.1033.

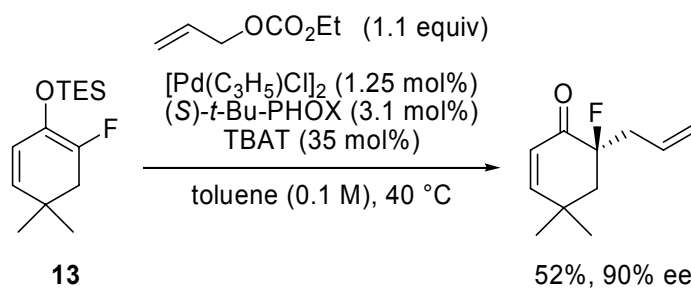


(R)-2-allyl-2-fluoro-1-benzosuberone (Table 2 – entry 9) Following the general protocol for 1.25 mol% Pd on a 0.25 mmol scale of **12**, the desired product was isolated in 65% (36 mg). The enantioselectivity was 85% ee (OJ-H, 254 nm, hexane:2-propanol = 99:1, flow rate 0.8 ml/min, $t_{\text{r (major)}} = 11.8$ min, $t_{\text{r (minor)}} = 17.0$ min). $[\alpha]_{\text{D}}^{22} -42.1$ (c 0.36, CHCl_3) {lit.⁵ $[[\alpha]_{\text{D}}^{29} -51.3$ (c 1.17, CH_2Cl_2)}. All other spectroscopic data was in agreement with the literature.⁵



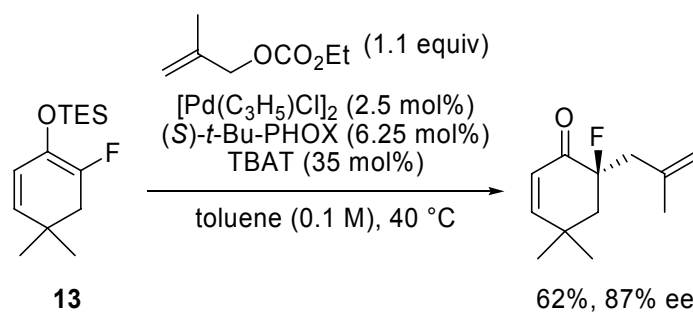
(R)-2-fluoro-2-(2-methylallyl)-1-benzosuberone (Table 2 – entry 10) Following the general protocol for 1.25 mol% Pd on a 0.27 mmol of **12** scale using ethyl 2-methylallyl carbonate

instead of allyl ethyl carbonate, the desired product (39 mg, 62 %) was isolated as a colorless oil by flash chromatography using 5% Et₂O/hexane. The enantioselectivity was 89% ee (OJ-H, 254 nm, hexane:2-propanol = 99:1, flow rate 0.8 ml/min, t_r (major) = 9.7 min, t_r (minor) = 16.2 min). The absolute configurations were assigned based on the established stereochemical outcome of the reaction. $[\alpha]_D^{30}$ -34.5 (c 0.47, CHCl₃); IR(neat) ν = 3073, 3021, 2927, 2864, 1698, 1448, 1281, 900, 741 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.46 (d 1H, J = 7.5 Hz), 7.39 (t, 1H, J = 7.5 Hz), 7.28 (m, 1H), 7.19 (d, 1H, J = 7.5 Hz), 4.91 (s, 1H), 4.75 (s, 1H), 3.14 (m, 1H), 2.91 (m, 1H), 2.80–2.57 (m, 2H), 2.23–1.96 (m, 3H), 1.83–1.76 (m, 4H); ¹⁹F NMR (376 MHz, CDCl₃) δ -153.6 (m, 1F); ¹³C NMR (100 MHz, CDCl₃) δ 204.6 (d, J_{C-F} = 28.3 Hz), 141.1 (d, J_{C-F} = 2.2 Hz), 140.2, 138.0, 131.5, 129.7, 128.8 (d, J_{C-F} = 1.1 Hz), 126.6, 115.9 (d, J_{C-F} = 1.1 Hz), 102.9 (d, J_{C-F} = 183 Hz), 43.8 (d, J_{C-F} = 21.4 Hz), 36.6 (d, J_{C-F} = 22.7 Hz), 34.4 (d, J = 2.0 Hz), 24.3 (d, J = 3.1 Hz), 24.0 (d, J = 2.6 Hz); HRMS-ESI calcd for C₁₅H₁₈FO [M+H]⁺ 233.1336, found 233.1345.



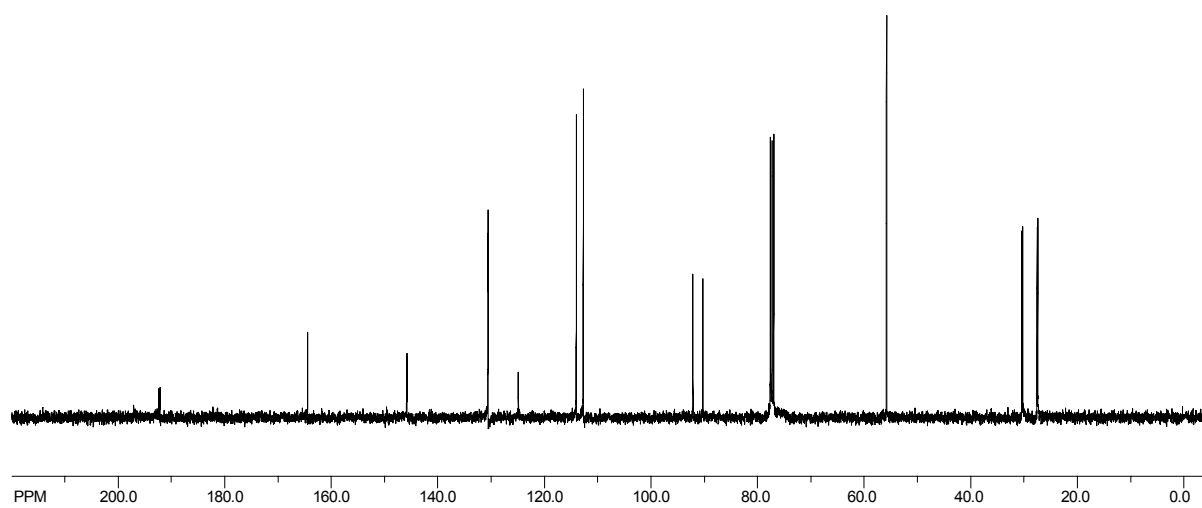
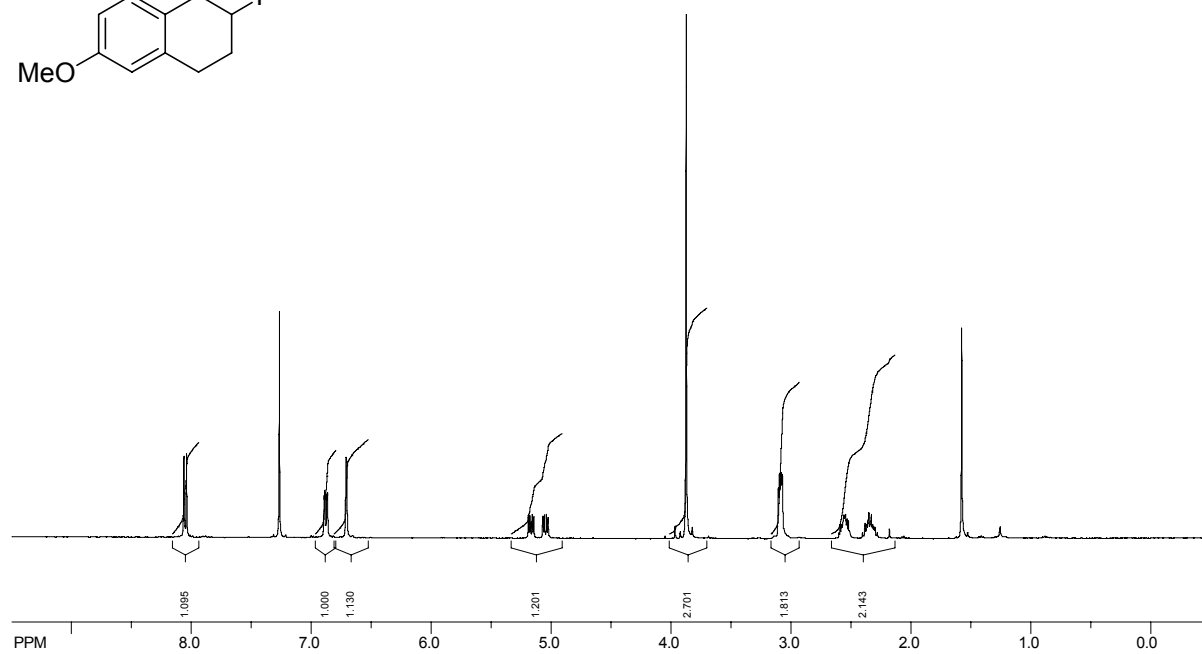
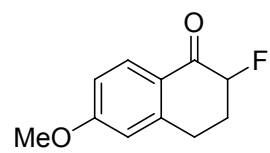
(S)-6-Allyl-6-fluoro-4,4-dimethylcyclohex-2-enone (Table 2 – entry 11) Following the general procedure for 1.25 mol% Pd on a 0.29 mmol scale of **13**, The desired product (27 mg, 52%) was isolated as a colorless oil by flash chromatography using 5% Et₂O/hexane. The enantioselectivity was 90% ee (AD-H, 220 nm, hexane:2-propanol = 99.9:0.1, flow rate 0.8 ml/min, t_r (major) = 15.6 min, t_r (minor) = 24.5 min). The absolute configurations were assigned based on the established

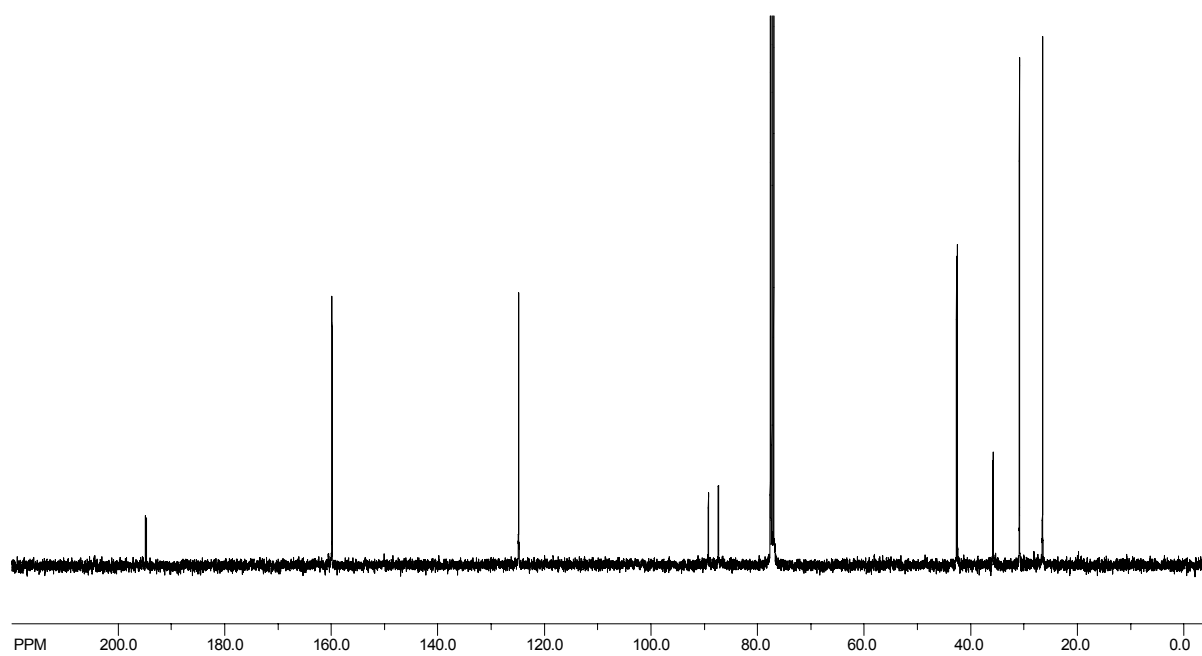
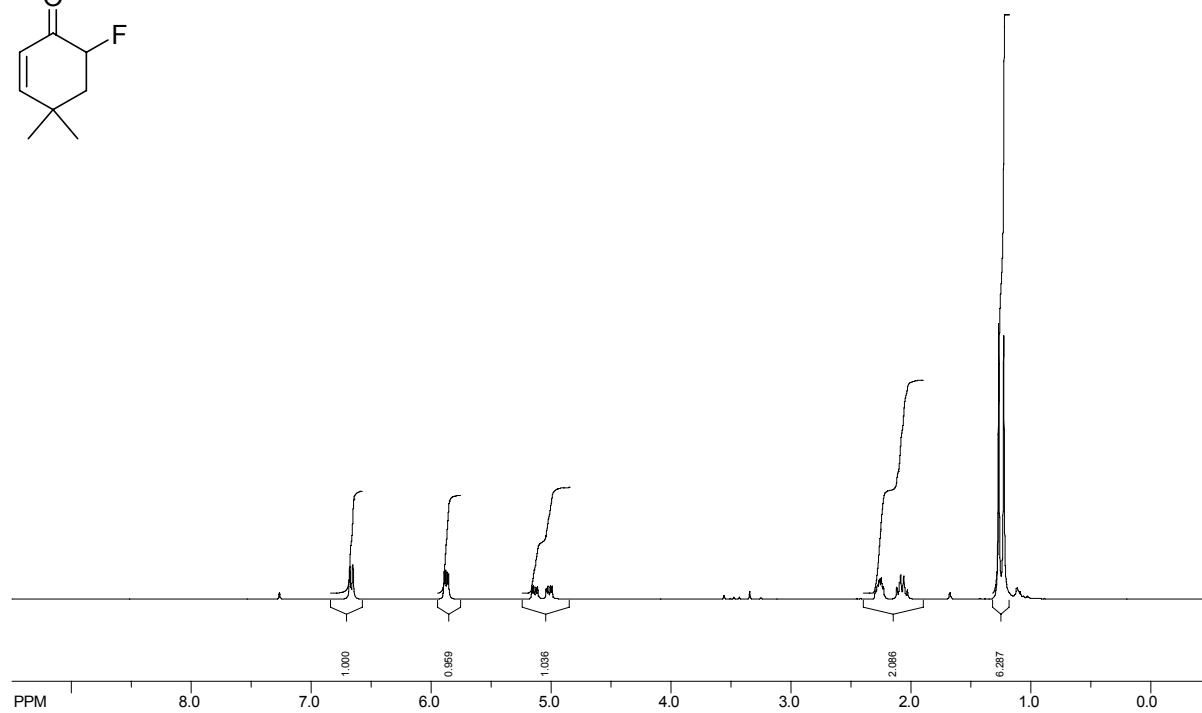
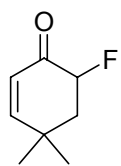
stereochemical outcome of the reaction. $[\alpha]_D^{30} +26.0$ (c, 0.35, CHCl_3); IR (neat) $\nu = 3081, 2963, 2873, 1691, 1432, 1365, 1235, 1127, 994, 851 \text{ cm}^{-1}$; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 6.74 (dd, 1H, $J = 10.2, 1.2 \text{ Hz}$), 5.96 (d, 1H, $J = 10.2 \text{ Hz}$), 5.79 (m, 1H), 5.17 (m, 2H), 2.73 (m, 1H), 2.51 (m, 1H), 2.20 (t, 1H, $J = 15.1 \text{ Hz}$), 1.96 (dd, 1H, $J = 34.6, 15.1 \text{ Hz}$), 1.27 (s, 3H), 1.19 (s, 3H); $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -151.6 (m, 1F); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 193.3 (d, $J_{\text{C-F}} = 19.1 \text{ Hz}$), 160.4, 131.5 (d, $J_{\text{C-F}} = 6.4 \text{ Hz}$), 124.8, 120.1, 93.2 (d, $J_{\text{C-F}} = 177 \text{ Hz}$), 44.2 (d, $J_{\text{C-F}} = 21.0 \text{ Hz}$), 39.9 (d, $J_{\text{C-F}} = 23.8 \text{ Hz}$), 34.1 (d, $J_{\text{C-F}} = 2.7 \text{ Hz}$), 30.2 (d, $J_{\text{C-F}} = 1.1 \text{ Hz}$), 30.0 (d, $J_{\text{C-F}} = 3.6 \text{ Hz}$); HRMS-ESI calcd for $\text{C}_{11}\text{H}_{16}\text{FO}$ $[\text{M}+\text{H}]^+$ 183.1179, found 183.1172.

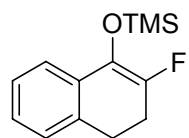


(S)-6-Fluoro-4,4-dimethyl-6-(2-methylallyl)cyclohex-2-enone (Table 2 – entry 12) Following the general procedure for 2.5 mol% Pd on a 0.31 mmol scale of **13** using ethyl 2-methylallyl carbonate instead of allyl ethyl carbonate, the desired product (37 mg, 62%) was isolated as a colorless oil by flash chromatography using 7% Et_2O /hexane. The enantioselectivity of the corresponding ketone was 87% ee (AD-H, 220 nm, hexane:2-propanol = 99.5:0.5, flow rate 0.8 ml/min $t_{\text{r (major)}} = 9.7 \text{ min}$, $t_{\text{r (minor)}} = 11.4 \text{ min}$). The absolute configurations were assigned based on the established stereochemical outcome of the reaction. $[\alpha]_D^{22} +46.1$ (c, 0.41, CHCl_3); IR (neat) $\nu = 3078, 2962, 2868, 1691, 1449, 1365, 1247, 1066, 991, 838 \text{ cm}^{-1}$; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 6.75 (dd, 1H, $J = 10.2, 1.3 \text{ Hz}$), 5.97 (d, 1H, $J = 10.2 \text{ Hz}$), 4.95 (s, 1H), 4.75 (s, 1H),

2.77 (t, 1H, $J = 15.2$ Hz), 2.41 (dd, 1H, $J = 31.4, 14.5$ Hz), 2.23 (m, 1H), 1.89 (dd, 1H, $J = 36.4, 15.2$ Hz), 1.78 (s, 3H), 1.27 (s, 3H), 1.19 (s, 3H); ^{19}F NMR (376 MHz, CDCl_3) $\delta -150.0$ (m, 1F); ^{13}C NMR (100 MHz, CDCl_3) δ 193.1 (d, $J_{\text{C-F}} = 19.5$ Hz), 160.4, 140.6 (d, $J_{\text{C-F}} = 2.4$ Hz), 124.7, 116.3, 93.6 (d, $J_{\text{C-F}} = 177$ Hz), 44.0 (d, $J_{\text{C-F}} = 21.1$ Hz), 42.9 (d, $J_{\text{C-F}} = 22.5$ Hz), 33.9 (d, $J_{\text{C-F}} = 2.1$ Hz), 30.6 (d, $J_{\text{C-F}} = 1.0$ Hz), 28.8 (d, $J_{\text{C-F}} = 3.8$ Hz), 24.2 (d, $J_{\text{C-F}} = 3.1$ Hz); HRMS-ESI calcd for $\text{C}_{12}\text{H}_{18}\text{FO}$ $[\text{M}+\text{H}]^+$ 197.1336, found 197.1335.





**4**