Experimental section

Genaral Methods. Unless otherwise noted, materials were obtained from commercial suppliers and were used without further purification. All manipulations involving air-sensitive materials were performed under argon, with such materials being exposed only to throughly dried and degassed solvents. Anhydrous ether, THF and CH_2Cl_2 were purchased and were used without further purification.

^1H NMR and ^{13}C NMR spectra were recorded with a Varian Gemini-200 (200 MHz) or a Varian VXR-500 (500 MHz) in $CDCl_3$ unless otherwise noted. Chemical shifts were reported in parts per million (ppm) downfield from internal tetramethylsilane (Me_4Si). ^{19}F NMR spectra were recorded with a Varian VXR-500 (470 MHz) in $CDCl_3$ unless otherwise noted. Chemical shifts were reported in ppm downfield from internal hexafluorobenzene (C_6F_6). Data were tabulated in the following order: multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; quint, quintet; sex, sextet; sep, septet; m, multiplet; br, broad peak), number of protons, coupling constants (in hertz). Infrared (IR) spectra were obtained on a JASCO FT/IR-5000 spectrometer as thin films on NaCl plates, and all spectra were reported in wave numbers (cm^{-1}). Optical rotations were measured on a JASCO DIP-140 digital polarimeter. Specific rotations, $[\alpha]_D$, were reported in degree and the concentration (*c*) was given in grams per 100 mL of the indicated solvent. Melting points, mp, were measured on a MRK MEL-TEMP II without correction. Colomn chromatography was conducted with silica gel (BW-200) by using a mixture of hexanes and ethyl acetate (v/v). Gas liquid chromatography (GLC) was performed on a Shimadzu GC-14A chromatograph equipped with a flame ionization detector and nitrogen carrier gas using ULBON HR-20M on Chromosorb W, 30 m x 3 mm.

(*E*)-7-Fluoro-2,2,6-trimethylhept-4-ene-3-one (*E*-6a): Perfluoropropene diethylamine adduct (PPDA; 25 g) was added into a solution of methyl (*R*)-3-hydroxy-2-methylpropionate (11.08 mL, 100 mmol) in CH_2Cl_2 (60 mL) and the mixture was refluxed for 20 h. The solution was poured into ice-water bath and extracted with CH_2Cl_2 three times, washed with brine, and dried over anhydrous $MgSO_4$. After removal of the solvent, the residue was distilled under reduced pressure (28 °C/14 mmHg) to give methyl 3-fluoro-2-methylpropionate **5** (8.41 g, 70.0 mmol) in 70% yield.

To the solution of Wittig reagent (3.54 g, 15.0 mmol) in ether (10 mL), prepared from triethyl phosphite and 1-bromopinacolone at 100 °C for 4 h, was added 9.4 mL of BuLi (1.6 *M* solution in hexanes, 15 mmol) at -30 °C and stirred for 30 min at that temperature. To this ylide solution was added 10 mmol of **5** and stirring was continued for 2 h at -78 °C and then allowed to warm to 0 °C over 4 h. The mixture was quenched with 1 *N* HCl aq (10 mL), extracted with ether (5 mL x 3), washed with sat. $NaHCO_3$ aq and brine, and dried over anhydrous $MgSO_4$. The volatiles were removed under reduced pressure and the residue was purified by column chromatography to give 0.74 g of the desired monofluoromethylated acceptor ***E*-6a** (4.32 mmol) in 43% yield. $[\alpha]_D^{29}$ -9.8 (*c* 1.00, $CHCl_3$); ^1H NMR δ 6.84 (1 H, dd, *J*=15.5, 7.0 Hz), 6.58 (1 H, d, *J*=15.5 Hz), 4.34 (1 H, ddd, *J*=46.8, 8.5, 6.5 Hz), 4.33 (1 H, ddd, *J*=47.1, 8.9, 6.6 Hz), 2.74 (1 H, dsep, *J*=17.5, 6.5 Hz), 1.67 (9 H, s), 1.13 (3 H, d, *J*=7.0 Hz); ^{13}C NMR δ 203.54, 146.38 (d, *J*=5.4 Hz), 124.48, 85.87 (d, *J*=173.1 Hz), 42.77,

37.25 (d, *J*=19.4 Hz), 25.91 (3 C), 14 83 (d, *J*=6.5 Hz); ^{19}F NMR δ -58.45 (dt, *J*=47.4, 16.4 Hz); IR (neat) ν 2970, 1691, 1628, 1478, 1367, 1080, 1014, 986 cm^{-1}. Anal. Calcd for $C_{10}H_{17}FO$: C, 69.73; H, 9.95. Found: C, 69.39; H, 10.03.

(*E*)-7,7-Difluoro-2,2,6-trimethylhept-4-ene-3-one (*E*-6b): The round-bottomed flask containing 2-(trifluoromethyl)propenoic acid **9** (54.6 g, 390 mmol) and phthaloyl dichloride (84.3 mL, 580 mmol) was connected to the Claisen distillation head, and the mixture was heated to 150 °C with collecting the resultant acid chloride, and the temperature was raised eventually to 190 °C to furnish 86.5 g of the acid chloride (545 mmol) in 94% yield.

To a CH_2Cl_2 (200 mL) solution containing this acid chloride (54.4 g, 343 mmol) and 2-phenyl-ethanol (52.1 mL, 411 mmol) was slowly added pyridine (37.8 mL, 446 mmol) at -20°C for 2 h and the mixture was further stirred for 2 h at that temperature. The usual work-up and chromatographic purification produced 77.1 g of the desired methacrylate (316 mmol) in 92% yield. R_f=0.43 (AcOEt: Hexane=1:10) as a colorless oil, ^{1}H NMR δ 7.35-7.25 (5 H, m), 6.68 (1 H, q, *J*=1.7 Hz), 6.42 (1 H, q, *J*=1.1 Hz), 4.46 (2 H, t, *J*=7.1 Hz), 3.02 (2 H, t, *J*=6.9 Hz); ^{13}C NMR δ 160.96, 137.23, 132.68 (q, *J*=5.0 Hz), 131.17 (q, *J*=32.1 Hz), 128.79, 128.40, 126.57, 121.23 (q, *J*=272.5 Hz), 66.12, 34.69; ^{19}F NMR δ 96.06 (s); IR (neat) ν 3030, 2361, 1736, 1456, 1398, 1352, 1247, 1146, 1097, 989, 810, 748, 696 cm^{-1}. Anal. Calcd for $C_{12}H_{11}F_3O_2$: C, 59.02; H, 4.54. Found: C, 58.75; H, 4.49.

29.8 g of this methacrylate (122 mmol) in MeOH (100 mL) was hydrogenated with 10% Pd/C (0.647 g, 0.61 mmol) under atomospheric pressure of hydrogen at room temperature for 12 h. Removal of the catalyst by filtration and chromatographic purification yielded the corresponding saturated ester **10c** (27.6 g, 112 mmol) in 92% yield. R_f=0.49 (AcOEt:Hexane=1:10) as a colorless oil, ^{1}H NMR δ 7.33-7.20 (5 H, m), 4.42-4.35 (2 H, m), 3.18 (1 H, qq, *J*=8.3, 7.3 Hz), 2.97 (2 H, t, *J*= 7.1 Hz), 1.36 (3 H, d, *J*=7.3 Hz); ^{13}C NMR δ 167.59 (q, *J*=2.9 Hz), 137.18, 128.72, 128.34, 126.50, 124.88 (q, *J*=279.3 Hz), 65.84, 44.32 (q, *J*=28.4 Hz), 34.62, 10.60 (q, *J*=2.7 Hz); ^{19}F NMR δ 91.76 (d, *J*=7.6 Hz); IR (neat) ν 2959, 2364, 1748, 1603, 1461, 1335, 1268, 1204, 1124, 1079, 1008, 748, 699 cm^{-1}. Anal. Calcd for $C_{12}H_{13}F_3O_2$: C, 58.54; H, 5.32. Found: C, 58.18; H, 5.00.

To a THF solution (150 mL) containing **10c** (25.6 g, 104 mmol) was slowly added LDA at -78 °C, prepared from diisopropylamine (21.8 g, 156 mmol) and *n*-BuLi (156 mmol) in 100 mL of THF, and the mixture was stirred for further 1 h at the same temperature. The usual work-up and chromatographic purification produced 20.4 g of the desired terminally difluorinated methacrylate (89.4 mmol) in 86% yield. R_f= 0.50 (AcOEt:Hexane=1:10) as a colorless oil, ^{1}H NMR δ 7.33-7.23 (5 H, m), 4.38 (2 H, t, *J*=7.1 Hz), 2.98 (2 H, t, *J*=6.8 Hz), 1.78 (3 H, t, *J*=3.2 Hz); ^{13}C NMR δ 164.23 (dd, *J*=7.7, 5.4 Hz), 158.91 (dd, *J*=307.8, 293.7 Hz), 137.33, 128.48, 127.99, 126.11, 83.92 (dd, *J*=24.1, 7.7 Hz), 65.32, 34.75, 9.18 (d, *J*=1.7 Hz); ^{19}F NMR δ 92.52(1 F, q, *J*=3.1 Hz), 88.41 (1 F, q, *J*=3.1 Hz); IR (neat) ν 3030, 2959, 2364, 2343, 1750, 1722, 1498, 1395, 1332, 1159, 1128, 764, 750, 700 cm^{-1}. Anal. Calcd for $C_{12}H_{12}F_2O_2$: C, 63.71; H, 5.35. Found: C, 63.88; H, 5.70.

To a MeOH (10 mL) solution of the resultant ester (0.68 g, 3.0 mmol) was added 0.41 g of 10% Pd/C (0. 39 mmol) and the whole mixture was stirred for 3 h under hydrogen with 0.5 kgf/cm^2 pressure. Removal of the catalyst by filtration and chromatographic purification yielded the corresponding saturated ester **10b** (0.48 g, 2.1 mmol) in 70% yield. R_f=0.48 (AcOEt:Hexane=1:10) as a colorless oil, ^{1}H NMR δ 7.38-7.20 (5 H, m), 5.98 (1 H, td, *J*=55.0, 4.7 Hz), 4.37 (2 H, t, *J*=6.9 Hz), 2.96 (2 H, t, *J*=6.9 Hz), 2.95-2.80 (1 H, m), 1.25(3 H, d, *J*=7.4 Hz); ^{13}C NMR δ 165.52 (t, *J*=7.2 Hz), 132.70, 124.17, 123.85, 121.99, 111.22 (t, *J*=241.9 Hz), 61.02, 39.63 (t, *J*=22.9 Hz), 30.39, 5.12 (t, *J*=5.2 Hz); ^{19}F NMR δ 42.26 (1 F, ddd, *J*=282.7, 56.0, 8.6 Hz), 35.17 (1 F, ddd, *J*=283.5, 56.0, 17.2 Hz); IR (neat) ν 2959, 2361, 1740, 1461, 1396, 1323, 1258, 1192, 1155, 1075, 993, 749, 700 cm^{-1}. Anal. Calcd for $C_{12}H_{14}F_2O_2$: C, 63.15; H, 6.18. Found: C, 63.26; H, 6.02.

A THF solution of DIBAL (40.1 mmol) was added to 9.15 g (40.1 mmol) of **10b** in 100 mL of Et_2O at -78 °C and the whole mixture was stirrd for 1 h at that temperature. The ylide (60 mmol) was added to this solution, and the mixture was stirred for 5 h from -30 to -10 °C, followed by 30 min stirring at 0 °C. The usual work-up and chromatographic purification furnished 5.26 g of the desired difluoromethylated acceptor ***E*-6b** (27.7 mmol) in 69% yield. R_f=0.47 (AcOEt:Hexane=1:10) as a colorless oil, ^{1}H NMR δ 6.82 (1 H, dd, *J*=15.4, 7.4 Hz), 6.62 (1 H, dd, *J*=15.4, 1.10 Hz), 5.70 (1 H, td, *J*=56.6, 3.8 Hz), 2.89-2.69 (1 H, m), 1.20 (3 H, d, *J*=7.2 Hz), 1.17 (9 H, s); ^{13}C NMR δ 202.86, 141.41 (t, *J*=4.9 Hz), 126.22, 116.86 (t, *J*=243.3 Hz), 42.77, 40.56 (t, *J*=20.6 Hz), 25.75, 12.22; ^{19}F NMR δ 40.51 (1 F, ddd, *J*=278.3, 56.0, 13.8 Hz), 39.08 (1 F, ddd, *J*=278.3, 56.0, 14.7 Hz); IR (neat) ν 2971, 2362, 1693, 1631, 1471, 1395, 1368, 1132, 1074, 993, 942 cm^{-1}. Anal. Calcd for $C_{10}H_{16}F_2O$: C, 63.14; H, 8.48. Found: C, 62.90; H, 8.22.

(*E*)-7,7,7-Trifluoro-2,2,6-trimethylhept-4-en-3-one (*E*-6c): To a ylide solution (12 mmol) prepared as above was added 3,3,3-trifluoro-2-methylpropionaldehyde (1 mL, 10 mmol) was added at -30 °C and stirring was continued for 1 h at 0 °C. The usual work-up and chromatographic purification yielded 1.33 g of the desired trifluoromethylated acceptor ***E*-6c** (6.39 mmol) in 64% yield as a white crystal, mp 33.5-36.0 °C, bp 71 °C/14 mmHg; ^{1}H NMR δ 6.78 (1 H, dd, *J*=15.0, 8.5 Hz), 6.65 (1 H, d, *J*=15.5 Hz), 3.04 (1 H, oct, *J*=7.5 Hz), 1.29 (3 H, d, *J*=7.0 Hz), 1.16 (9 H, s); ^{13}C NMR δ 203.59, 139.61, 127.68, 126.64 (q, *J*=280.0 Hz), 43.27, 41.40 (q, *J*=28.0 Hz), 26.10, 13.22; ^{19}F NMR δ 89.78 (d, *J*=7.5 Hz); IR (neat) ν 2977, 2361, 1693, 1634, 1263, 1176, 1130, 1085, 1023, 1005, 986 cm^{-1}. Anal. Calcd for $C_{10}H_{15}F_3O$: C, 57.68; H, 7.26. Found: C, 57.43; H, 7.01.

(*Z*)-7,7,7-Trifluoro-2,2,6-trimethylhept-4-en-3-one (*Z*-6c): Ethyl diphenylphosphono-acetate (40.429 g, 126.2 mmol) was added to a suspension of sodium hydride (4.244 g, 176.7 mmom) in THF (500 mL) at 0 °C. After 10 min stirring at that temperature, the reaction mixture was cooled to -78 °C and further stirred for 15 min. Then 3,3,3-trifluoro-2-methylpropionaldehyde (17.503 g, 138.8 mmol, freshly distilled with a few drop of BF_3·OEt_2 prior to use) was added, and the resulting mixture was gradually warmed to -10 °C over 1 h. After quenching the reaction mixture with sat. NH_4Cl aq. and the usual work-up, the obtained crude α,β-unsaturated ester was dissolved in a solvent

(THF:H_2O=1:1, 200-300 mL) and sodium hydroxide (15.251 g, 381.3 mmol) was added. After stirring overnight at rt and the usual extractive treatment furnished 21.938 g (130.5 mmol) of *Z*-5,5,5-trifluoro-4-methylpent-2-enoic acid **8** in 94% yield. ^{1}H NMR δ 6.29 (1 H, dd, *J*=11.5, 9.9 Hz), 6.00 (1 H, d, *J*=11.5 Hz), 4.37 (1 H, m), 1.27 (3 H, d, *J*=7.1 Hz); ^{13}C NMR δ 170.81, 144.98 (q, *J*=2.9 Hz), 126.60 (q, *J*=278.7 Hz), 122.19, 37.74 (q, *J*=28.3 Hz), 13.48 (q, *J*=2.8 Hz); ^{19}F NMR δ 89.09 (d, *J*=8.6 Hz); IR (neat) ν 2986, 1702, 1654, 1597, 1438, 1350, 1255, 1175, 1138, 1020, 832 cm^{-1}. The intermediary ethyl *Z*-5,5,5-trifluoro-4-methylpent-2-enoate can be purified and isolated by distillation. bp. 60.0 °C/30 mmHg; ^{1}H NMR δ 6.13 (1 H, dd, *J*=11.5, 9.7 Hz), 5.96 (1 H, d, *J*=11.5 Hz), 4.41 (1 H, m), 4.20 (2 H, q, *J*=7.1 Hz), 1.31 (3 H, t, *J*=7.2 Hz), 1.26 (3 H, d, *J*=7.1 Hz); ^{13}C NMR δ 165.12, 142.06 (q, *J*=3.0 Hz), 126.76 (q, *J*=278.6 Hz), 122.85, 60.36, 37.38 (q, *J*=28.1 Hz), 14.07, 13.43 (q, *J*=2.7 Hz); ^{19}F NMR δ 89.05 (d, *J*=7.6 Hz); IR (neat) ν 2989, 1722, 1656, 1464, 1420, 1384, 1350, 1261, 1198, 1137, 1112, 1070, 1020, 833 cm^{-1}; Anal. Calcd for $C_8H_{11}F_3O_2$: C, 48.98; H, 5.65. Found: C, 49.00; H, 5.29.

A solution of **8** (10.485 g, 62.37 mmol) in CH_2Cl_2 (150 mL) was treated with acetyl chloride (4.879 mL, 68.61 mmol) at 0 ℃, and then triethylamine (9.563 g, 68.61 mmol) was added to the reaction mixture. After 30 min, *n*-hexane (*ca.* 100 mL) was added to the flask, and the resulting salts were removed by filtration. Evaporation of the volatiles afforded basically pure mixed anhydride (12.121 g, 57.7 mmol) and this material was employed without further purification.

A solution of this mixed anhydride (0.478 g, 2.27 mmol) in THF (5 mL) was added a 2.0 mol/L solution of *tert*-BuMgCl in diethyl ether (1.135 mL, 2.27 mmol) at -78 °C. After stirring for 1 h and addition of 1 mol/L HCl aq., the usual work-up followed by distillation gave the desired ***Z*-6** (0.123 g, 0.590 mmol) in 26% total yield from the acid along with 24.9% recovery. bp. 62 °C/14 mmHg; ^{1}H NMR δ 6.57 (1 H, d, *J*=11.8 Hz), 6.03 (1 H, dd, *J*=11.7, 9.8 Hz), 4.16 (1 H, dqqd, *J*=9.9, 8.8, 7.0, 1.2 Hz), 1.24 (3 H, d, *J*=7.1 Hz), 1.16 (9 H, s); ^{13}C NMR δ 205.94, 139.87 (q, *J*=2.9 Hz), 126.87 (q, *J*=281.1 Hz), 125.58, 43.86, 37.60 (q, *J*=27.8 Hz), 26.05, 13.41 (q, *J*=2.8 Hz); ^{19}F NMR δ 88.82 (d, *J*=8.6 Hz); IR (neat) ν 2972, 2911, 2874, 1693, 1625, 1480, 1464, 1417, 1382, 1347, 1258, 1175, 1135, 1113, 1076, 1016, 1004, 918, 862, 824, 805, 741, 709, 668 cm^{-1}. Anal. Calcd for $C_{10}H_{15}F_3O$: C, 57.68; H, 7.26. Found: C, 57.53; H, 7.27.

General Procedure for Michael addition of enolate to variously fluorinated enones: To a THF solution of diisopropylamine (2 equiv, 0.5 *M*) was added at -78 °C 2 equiv of *n*-BuLi and the mixture was stirred for 30 min at that temperature. Appropriate carbonyl compound (2 equiv) was added to this LDA solution at -78 ℃ and the whole was stirred further 1 h at that temperature. An enone (1 equiv) was added to this solution and stirred at -78 ℃ for 1 h. The reaction was quenched with 3 *N* HCl aq. and extracted with ether three times, washed with sat. $NaHCO_3$ aq. and brine, and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure to give the crude products, which was purified by silica gel column chromatography.

3-(1,1,1-Trifluoroprop-2-yl)-2,6,6-trimethyl-1-phenylheptane-1,5-dione (11c): 95% yield as a

colorless oil, 97:3 inseparable diastereomer mixture; R_f=0.38 (AcOEt:Hexane=1:8); IR (neat) ν 2977, 1708, 1678, 1596, 1466, 1366, 1264, 1177, 1119, 1066, 1007, 971, 751, 710 cm^{-1}; Anal. Calcd for $C_{19}H_{25}F_3O_2$: C, 66.65; H, 7.36. Found: C, 66.48; H, 7.40. **Major isomer:** ^{1}H NMR δ 7.93-7.46 (5 H, m), 3.84 (1 H, quint, *J*=6.4 Hz), 3.02 (1 H, tdd, *J*=6.1, 4.2, 3.7 Hz), 2.67 (1 H, dd, *J*=19.3, 4.6 Hz), 2.60 (1 H, dd, *J*=19.1, 6.6 Hz), 2.49 (1 H, dqq, *J*=10.1, 7.1, 3.7 Hz), 1.17 (3 H, d, *J*=6.8 Hz), 1.12 (9 H, s), 1.04 (3 H, d, *J*=7.1 Hz); ^{13}C NMR δ 213.24, 203.18, 136.58, 133.14, 128.67, 128.23 (q, *J*=123.4 Hz), 128.02, 44.06, 41.68, 38.27 (q, *J*=25.0 Hz), 34.56, 33.17, 26.56, 14.77, 9.89 (q, *J*=3.1 Hz); ^{19}F NMR δ 91.66 (d, *J*=10.3 Hz). **Minor isomer:** ^{19}F NMR δ 94.52 (d, *J*=10.7 Hz).

Ethyl 3-(1,1,1-trifluoroprop-2-yl)-6,6-dimethyl-2-(methylthio)-5-oxoheptanoate (12c): Quantitative yield as a colorless oil, 92:8 inseparable diastereomer mixture; R_f=0.32 (AcOEt:Hexane=1:8); IR (neat) ν 2971, 1727, 1710, 1478, 1393, 1368, 1303, 1270, 1174, 1141, 1118, 1068, 1035 cm^{-1}. Anal. Calcd for $C_{15}H_{25}O_3F_3S$: C, 52.62; H, 7.36. Found :C, 52.30; H, 7.32. **Major isomer:** ^{1}H NMR δ 4.21 (2 H, q, *J*=7.1 Hz), 3.24-3.15 (2 H, m), 2.86 (1 H, dd, *J*=18.8, 5.9 Hz), 2.64 (1 H, dd, *J*=18.7, 3.3 Hz), 2.51 (1 H, qqd, *J*=9.9, 7.4, 2.2), 2.09 (3 H, s), 1.30 (3 H, t, *J*=7.1 Hz), 1.18 (9 H, s), 1.06 (3 H, d, *J*=7.2 Hz); ^{13}C NMR δ 213.01, 170.97, 133.59 (q, *J*=280.1 Hz), 61.87, 51.50, 38.64 (q, *J*=25.5 Hz), 34.93, 31.45, 27.34, 27.08, 14.66, 13.90, 9.18; ^{19}F NMR δ 90.73 (d, *J*=9.5 Hz). **Minor isomer:** ^{19}F NMR δ 91.12 (d, *J*=10.3 Hz).

3-(1,1,1-Trifluoroprop-2-yl)-*N*,*N*,2,6,6-pentamethyl-5-oxoheptanamide (13c): 88% yield, 51:49 separable diastereomer mixture; **Major isomer**: R_f=0.36 (AcOEt:Hexane=1:1) as a white crystal, mp 86-87 °C; ^{1}H NMR δ 3.06 (3 H, s), 3.04 (1 H, quint, *J*=7.0 Hz), 2.89 (3 H, s), 2.87 (1 H, quint, *J*=6.0 Hz), 2.76 (1 H, dd, *J*=19.0, 6.0 Hz), 2.58 (1 H, dd, *J*=19.0, 5.0 Hz), 2.46-2.35 (1 H, m), 1.15 (9 H, s), 1.07 (3 H, d, *J*=7.0 Hz), 1.06 (3 H, d, *J*=7.0 Hz); ^{13}C NMR δ 214.06, 174.84, 128.61 (q, *J*=279.0 Hz), 44.39, 38.94 (q, *J*=25.0 Hz), 37.24, 35.95, 34.56, 33.04, 26.99, 14.02, 10.74; ^{19}F NMR δ 91.72 (d, *J*=6.9 Hz); IR (neat) ν 2978, 2364, 2343, 1704, 1632, 1264, 1176, 1157 cm^{-1}. Anal. Calcd for $C_{15}H_{26}O_2NF_3$: C, 58.24; H, 8.47; N, 4.53. Found : C, 58.24, H, 8.41, N, 4.44. **Minor isomer:** R_f=0.45 (AcOEt: Hexane=1:1) as a pale yellow oil; ^{1}H NMR δ 3.18 (3 H, s), 3.04-2.98 (1 H, m), 2.93 (3 H, s), 2.84 (1 H, dd, *J*=18.0, 8.0 Hz), 2.74-2.70 (1 H, m), 2.65 (1 H, ddd, *J*=10.5, 7.0, 3.0 Hz), 2.60 (1 H, dd, *J*=18.0, 3.0 Hz), 1.16 (9 H, s), 1.09 (3 H, d, *J*=7.5 Hz), 1.04 (3 H, d, *J*=7.0 Hz); ^{13}C NMR δ 214.91, 174.64, 128.73 (q, *J*=278.9 Hz), 44.54, 37.14 (q, *J*=10.2 Hz), 37.05, 36.35, 35.86, 34.64, 32.14, 26.65, 12.66, 10.69; ^{19}F NMR δ 89.60 (d, *J*=10.8 Hz); IR (neat) ν 2970, 2875, 2361, 1706, 1640 cm^{-1}. Anal. Calcd for $C_{15}H_{26}O_2NF_3$: C, 58.24; H, 8.47; N, 4.53. Found : C, 58.01, H, 8.11, N, 4.90.

3-(1,1-Difluoroprop-2-yl)-2,6,6-trimethyl-1-phenylheptane-1,5-dione (11b): 81% yield as a colorless oil, 92:8 inseparable diastereomer mixture; R_f=0.43 (AcOEt:Hexane=1:7); IR (neat) ν 2972, 1704, 1680, 1596, 1485, 1368, 1221, 1107, 1065, 989, 754, 709 cm^{-1}; Anal. Calcd for $C_{19}H_{26}F_2O_2$: C, 70.35; H, 8.08. Found: C, 70.28; H, 8.33. **Major isomer:** ^{1}H NMR δ 7.97-7.77 (5 H, m), 5.90 (1 H, td, *J*=56.6, 3.3 Hz), 3.73 (1 H, quint, *J*=6.6 Hz), 2.90 (1 H, quint, *J*=5.2 Hz), 2.65 (1 H, dd, *J*=19.2, 5.1

Hz), 2.57 (1 H, dd, *J*=18.7, 5.5 Hz), 2.20-1.98 (1 H, m), 1.14 (3 H, d, *J*=6.9 Hz), 1.13 (9 H, s), 0.91 (3 H, d, *J*=7.1 Hz); ^{13}C NMR δ 213.32, 202.61, 136.03, 132.78, 128.36, 127.76, 118.53 (t, *J*=241.6 Hz), 43.88, 42.06, 38.67 (t, *J*=18.6 Hz), 34.15, 33.40 (d, *J*=4.0 Hz), 26.51, 13.89, 8.72 (t, *J*=4.9 Hz); ^{19}F NMR δ 42.48 (1 F, ddd, *J*=279.2, 56.9, 12.9 Hz), 37.83 (1 F, ddd, *J*=278.3, 56.9, 20.7 Hz). **Minor isomer:** ^{1}H NMR δ 5.71 (td, 1 H, *J*=56.3, 3.8 Hz), 3.86 (1 H, qd, *J*=6.9, 5.5 Hz); ^{19}F NMR δ 44.46 (1 F, ddd, *J*=280.0, 56.0, 12.9 Hz), 40.28 (1 F, ddd, *J*=280.0, 56.9, 18.1 Hz).

Ethyl 3-(1,1-difluoroprop-2-yl)-6,6-dimethyl-2-(methylthio)-5-oxoheptanoate (12b): 86% yield as a pale yellow oil, 83:15:2 inseparable diastereomer mixture; R_f=0.34 (AcOEt: Hexane=1: 8), IR (neat) ν_2973,1727, 1707, 1479, 1466, 1395, 1368, 1307, 1269, 1155, 1094, 1066, 1030, 1001 cm^{-1}. Anal. Calcd for $C_{15}H_{26}F_2O_3S$: C, 55.53; H, 8.08. Found: C, 55.32; H, 8.14. **Major isomer:** ^{1}H NMR δ 5.76 (1 H, td, *J*=56.3, 2.5 Hz), 4.21 (2 H, q, *J*=7.2 Hz), 3.15 (1 H, d, *J*=10.2 Hz), 3.05-2.80 (2 H, m), 2.64 (1 H, dd, *J*=18.7, 5.8 Hz), 2.10-2.00 (1 H, m), 2.06 (3 H, s), 1.30 (3 H, t, *J*=7.1 Hz), 1.18 (9 H, s), 0.95 (3 H, d, *J*=7.2 Hz); ^{13}C NMR_δ 213.75, 170.96, 118.51 (t, *J*=242.3 Hz), 61.40, 50.67, 44.30, 38.44 (t, *J*=19.3 Hz), 34.35, 31.77, 31.63, 27.00, 14.27, 13.16; ^{19}F NMR δ 44.35 (1 F, ddd, *J*=280.0, 56.0, 12.1 Hz), 35.76 (1 F, ddd, *J*=280.0, 56.0, 23.1 Hz). **2nd Major isomer:** ^{1}H NMR δ 5.74 (1 H, td, *J*=56.0, 4.1 Hz), 3.32 (1 H, d, *J*=9.3 Hz), 2.05 (3 H, s), 1.18 (9 H, s), 1.04 (3 H, d, *J*=7.4 Hz); ^{13}C NMR_δ 171.32, 61.24, 27.45; ^{19}F NMR δ 44.05 (1 F, ddd, *J*=282.6, 56.0, 12.9 Hz), 40.71 (1 F, ddd, *J*=282.6, 56.4, 19.0 Hz). **Minor isomer:** ^{1}H NMR δ 5.81 (1 H, td, *J*=56.5, 3.0 Hz); ^{19}F NMR δ 43.71 (ddd, *J*=279.6, 56.4, 12.5 Hz), 37.38 (ddd, *J*=280.0, 56.4, 22.4 Hz).

3-(1,1-Difluoroprop-2-yl)-*N*,*N*,2,6,6-pentamethyl-5-oxoheptanamide (13b): 74% yield as a pale yellow oil, 50:31:14:5 inseparable diastereomer mixture; R_f=0.31 (AcOEt:Hexane=1:1), IR (neat) ν_2970, 1706, 1641, 1479, 1397, 1148, 1066, 992 cm^{-1}. Anal. Calcd for $C_{15}H_{27}F_2NO_2$: C, 61.83; H, 9.34; N, 4.81. Found: C, 61.88; H, 9.32; N, 4.80. **Major isomer:** ^{1}H NMR δ 5.70 (1 H, td, *J*=56.8, 3.0 Hz), 3.07 (3 H, s), 2.89 (3 H, s), 2.77-2.51 (3 H, m), 2.00 (1 H, m), 1.15 (9 H, s), 1.03 (3 H, d, *J*=6.6 Hz), 0.92 (3 H, d, *J*=7.1 Hz); ^{13}C NMR_δ 214.72, 174.82, 118.93 (t, *J*=240.9 Hz), 44.28, 39.10 (t, *J*=18.2 Hz), 37.38, 37.21, 35.87, 34.35, 33.20, 27.02, 13.49, 9.20; ^{19}F NMR δ 41.92 (1 F, ddd, *J*=279.2, 56.4, 12.2 Hz), 36.98 (1 F, ddd, *J*=278.7, 56.4, 22.6 Hz). **2nd Major isomer:** ^{1}H NMR δ 5.82 (1 H, td, *J*=56.9, 3.1 Hz), 3.14 (3 H, s), 2.92 (3 H, s), 2.25 (1 H, m), 1.14 (9 H, s), 1.07 (3 H, d, *J*=7.1 Hz), 0.97 (3 H, d, *J*=7.1 Hz); ^{13}C NMR δ 215.26, 175.23, 44.47, 37.56, 36.15, 35.24, 33.31, 26.74, 13.91, 9.31; ^{19}F NMR δ 40.81 (1 F, ddd, *J*=276.4, 56.4, 16.9 Hz), 37.80 (1 F, ddd, *J*=275.9, 56.4, 19.7 Hz). **3rd Major isomer:** ^{1}H NMR δ 5.72 (1 H, td, *J*=56.4, 3.9 Hz), ^{19}F NMR δ 44.04 (1 F, ddd, *J*=279.2, 56.4, 13.6 Hz), 39.87 (1 F, ddd, *J*=278.7, 56.4, 18.3 Hz). **Minor isomer:** ^{1}H NMR δ 5.80 (1 H, td, *J*=56.4, 3.2 Hz), ^{19}F NMR δ 44.51 (1 F, ddd, *J*=279.2, 56.4, 18.3 Hz), 38.21 (1 F, ddd, *J*=280.6, 57.8, 17.8 Hz).

3-(1-Fluoroprop-2-yl)-2,6,6-trimethyl-1-phenylheptane-1,5-dione (11a): 50% yield as a pale yellow oil (ca. 20% of starting material was recovered), 82:18 inseparable diastereomer mixture; R_f=0.45 (AcOEt: Hexane=1:10); IR (neat) ν 2969, 1706, 1679, 1478, 1462, 1440, 1336, 1216, 1067,

1002, 981, 751, 705 cm^{-1}. Anal. Calcd for $C_{19}H_{27}FO_2$: C,74.48; H, 8.88. Found: C, 74.44; H, 8.52. **Major isomer:** ^{1}H NMR δ 7.96-7.44 (5 H, m), 4.42 (2 H, dd, *J*=47.5, 5.2 Hz), 3.77 (1 H, qd, *J*=6.9, 5.2 Hz), 2.80-2.73 (1 H, m), 2.63 (1 H, dd, *J*=19.0, 4.4 Hz), 2.53 (1 H, dd, *J*=19.0, 6.3 Hz), 2.02-1.85 (1 H, m), 1.12 (9 H, s), 1.12 (3 H, d, *J*=6.8 Hz), 0.90 (3 H, dd, *J*=6.9, 0.8 Hz); ^{13}C NMR δ 213.68, 203.27, 136.25, 132.81, 128.50, 128.02, 87.22 (d, *J*=168.9 Hz), 44.18, 41.61, 36.32 (d, *J*=17.5 Hz), 35.58 (d, *J*=3.4 Hz), 34.80, 26.81, 13.79 (d, *J*=6.3 Hz), 12.97; ^{19}F NMR δ -60.71 (td, *J*=47.4, 25.0 Hz). **Minor isomer:** ^{1}H NMR δ 3.83 (1 H, qd, *J*=6.9, 4.7 Hz), 1.12 (9 H, s); ^{19}F NMR δ -56.62 (td, *J*=47.3, 21.4 Hz)

Ethyl 3-(1-fluoroprop-2-yl)-6,6-dimethyl-2-(methylthio)-5-oxoheptanoatem (12a): 76% yield as a pale yellow oil, 69:31 inseparable diastereomer mixture; R_f=0.36 (AcOEt: Hexane=1:8), IR (neat) n 2976, 2362, 2344, 1726, 1702, 1478, 1368, 1156, 1031 cm^{-1}; Anal. Calcd for $C_{15}H_{27}O_3SF$: C, 58.79; H, 8.88. Found :C, 58.98; H, 8.87. **Major isomer:** ^{1}H NMR δ 4.73 (1 H, m), 4.18 (2 H, m), 3.45 (d,1 H, *J*=7.0 Hz), 2.92(dd, 1 H, *J*=18.0, 5.0 Hz), 2.74 (1 H, m), 2.74-2.63 (1 H, m), 2.13 (3 H, s), 1.78-1.62 (2 H, m), 1.31-1.28 (6 H, m), 1.15 (9 H, s); ^{13}C NMR δ 214.94, 171.95, 89.64 (d, *J*=164.4 Hz), 61.19, 51.52, 44.40, 38.45 (d, *J*=23.4 Hz), 31.51, 26.73, 21.83, 21.37 14.65, 14.39; ^{19}F NMR δ -60.43 (td, 1 F, *J*=47.3, 24.4 Hz). **Minor isomer:** ^{1}H NMR δ 3.39 (1 H, d, *J*=8.0 Hz), 2.98 (1 H, dd, *J*=19.0, 5.0 Hz), 2.10 (3 H, s), 1.33 (3 H, d, *J*=6.0 Hz), 1.28 (3 H, t, *J*=6.5 Hz), 1.13 (9 H, s); ^{13}C NMR δ 89.64 (d, *J*=164.4 Hz), 52.45, 44.35, 32.56, 21.94, 21.47, 14.29; ^{19}F NMR δ -57.91 (td, *J*=47.3, 22.9 Hz).

3-(1-Fluoroprop-2-yl)-N,N,2,6,6-pentamethyl-5-oxoheptanamide (13a): 79% yield as a pale yellow oil, 34:34:16:16 inseparable diastereomer mixture; R_f=0.30 (AcOEt:Hexane=1:1); IR (neat) ν 2973, 1703, 1642, 1479, 1465, 1396, 1139, 1064 cm^{-1}; Anal. Calcd for $C_{15}H_{28}O_2NF$: C, 65.90; H, 10.32; N, 5.12. Found :C, 65.57; H, 10.13; N, 5.40. **Two major isomers:** ^{1}H NMR δ 4.47-4.13 (1 H, m), 3.12 and 3.09 (3 H, s each), 3.03-2.95 (1 H, m), 2.93 and 2.87 (3 H, s each), 2.80 (1 H, dd, *J*=19.3, 4.2 Hz), 2.78 (1 H, dd, *J*=18.6, 6.4 Hz), 2.63 (1 H, dd, *J*=18.8, 5.4 Hz), 2.45 (1 H, dd, *J*=19.0, 5.9 Hz), 2.33 (1 H, quint, *J*=5.6 Hz), 2.15-1.75 (1 H, m), 1.16 and 1.15 (9 H, s each), 1.07 (3 H, d, *J*=7.1 Hz), 1.01 (3 H, d, *J*=6.9 Hz), 0.92 (3 H, dd, *J*=7.0, 1.0 Hz), 0.90 (3 H, dd, *J*=7.0, 1.2 Hz); ^{13}C NMR δ 214.62 (d, *J*=0.6 Hz) and 213.85 (d, *J*=0.6 Hz), 175.04 and 174.55, 87.46 (d, *J*=168.6 Hz) and 86.77 (d, *J*=168.6 Hz), 43.95 and 43.76, 36.94, 36.73 (d, *J*=0.9 Hz) and 36.66 (d, *J*=1.4 Hz), 36.18 (d, *J*=16.9 Hz) and 35.74 (d, *J*=17.8 Hz), 35.32 and 35.28, 34.95 (d, *J*=0.9 Hz) and 34.41 (d, *J*=0.9 Hz), 26.58 and 26.33, 14.34 and 13.62 (d, *J*=5.7 Hz), 12.42 and 12.35; ^{19}F NMR δ -62.94 (td, *J*=47.6, 26.4 Hz) and -59.07 (td, *J*=47.6, 23.0 Hz). **Two minor isomers:** ^{1}H NMR δ 2.77 (1 H, dd, *J*=19.3, 6.1 Hz), 2.60 (1 H, dd, *J*=15.3, 7.2 Hz), 2.50 (1 H, dd, *J*=17.1, 3.9 Hz), 1.15 and 1.14 (9 H, s each), 1.07 (3 H, d, *J*=7.1 Hz), 1.00 (3 H, d, *J*=6.9 Hz), 0.99 (3 H, d, *J*=6.6 Hz), 0.93 (3 H, dd, *J*=7.5, 1.0 Hz); ^{13}C NMR δ 215.10 and 214.09, 175.30 and 174.78, 86.78 (d, *J*=168.6 Hz) and 86.73 (d, *J*=167.8 Hz), 43.92, 35.34 and 35.30, 34.64 (d, *J*=1.1 Hz) and 34.14 (d, *J*=1.1 Hz), 26.51, 14.54 (d, *J*=6.6 Hz) and 14.19 (d, *J*=7.5 Hz), 12.37 and 12.34; ^{19}F NMR δ -58.84 (td, *J*=47.4, 23.3 Hz) and -56.94 (td, *J*=48.0, 21.0 Hz).