Supplemental Materials for:

Carbon Nucleophiles in the Mitsunobu Reaction. Mono- and Dialkylation of Bis(2,2,2-trifluoroethyl) Malonates

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Table 2. Dehydrative Mono- and Di-alkylations of Bis(2,2,2-trifluoroethyl) Malonates **1** and **2**.^a

	NuH	alcohol	prod	R ¹	R ²	yld(%)
1 ^b	1	HOCH ₂ CH=CH ₂	2 c	H ₂ C=CHCH ₂	H	60
2	1	HOCH ₂ CH=CH ₂ ^c	3 a	H ₂ C=CHCH ₂	H ₂ C=CHCH ₂	92
3	2 a	HOCH ₂ CH=CH ₂	3 b	PhCH ₂ CH ₂ CH ₂	H ₂ C=CHCH ₂	96
4 ^d	1	(<i>E</i>) HOCH ₂ CH=C(H)Ph	2 d	(<i>E</i>) PhCH=CHCH ₂	H	76
5	2 l	(<i>E</i>) HOCH ₂ CH=C(H)SnBu ₃	3 c	H ₂ C=CHCH=CH(CH ₂) ₂	(<i>n</i> Bu) ₃ SnCH=CHCH ₂	86
6	1	HOC(CH ₃)HCH=C(H)CH ₃ ^e	2 e^e	H ₃ CCH=CHC(CH ₃)H	H	54
7	1	HOC(CH ₃)HC≡CH	2 f	(HC≡C)CH(CH ₃)	H	23
8	1	HOC(CH ₃)HCH ₂ CH=CH ₂	2 g	H ₂ C=CHCH ₂ C(CH ₃)H	H	-
9	1	(<i>E</i>) HOCH ₂ CH=CH(CH ₂) ₂ CH ₃	2 h	H ₃ C(CH ₂) ₂ CH=CHCH ₂	H	50 ^f
			2 i	H ₃ C(CH ₂) ₂ CHCH=CH ₂	H	
10 ^d	1	HOCH(CH=CH ₂) ₂	2 j^e	H ₂ C=CHCH=CHCH ₂	H	52

11 ^d	1	CH ₃	2 k	H ₃ C	H	58
12	2 a	HOCH ₂ CH ₂ CH ₂ CH=CH ₂	3 d	PhCH ₂ CH ₂ CH ₂	H ₂ C=CH(CH ₂) ₃	89
13	1	HO(CH ₂) ₂ CH=CHCH=CH ₂	2 l	H ₂ C=CHCH=CH(CH ₂) ₂	H	56
14	1	HO(CH ₂) ₂ CH=CHCH=CH ₂ ^c	3 e	H ₂ C=CHCH=CH(CH ₂) ₂	H ₂ C=CHCH=CH(CH ₂) ₂	75
15	2 l	HO(CH ₂) ₃ CH=CHCH=CH ₂	3 f	H ₂ C=CHCH=CH(CH ₂) ₂	H ₂ C=CHCH=CH(CH ₂) ₃	75
16	1	HO(CH ₂) ₃ CH=CHCH=CH ₂ ^c	3 g	H ₂ C=CHCH=CH(CH ₂) ₃	H ₂ C=CHCH=CH(CH ₂) ₃	63

a) Reaction conditions (unless otherwise noted): A mixture of alcohol (1 equiv.), **1** or **2** (1.1 equiv.), Ph₃P (1.5 equiv.), and ADDP (1.5 equiv.) in dry toluene at room temperature. The course of the reaction is followed by TLC. b) A small amount of dialkylated product **3a** was also obtained. c) **1** (1.0 equiv.), alcohol (2.5 equiv.), Ph₃P (3.5 equiv.), and ADDP (3.75 equiv.) in dry toluene at room temperature. d) This reaction was run at 0 °C; when run at rt, the yield was lower. e) Predominantly E. f) A 2.4 : 1 mixture of **2h** : **2i** is obtained.

Preparation of Bis(2,2,2-trifluoroethyl) Malonate (1). A 250 mL round-bottom flask equipped with a condenser was charged with malonic acid (8.00 g, 76.9 mmol), trifluoroethanol (30.0 mL, 41.2 g, 412 mmol), benzene (40 mL) and conc. sulfuric acid (1 mL). The flask was flushed with nitrogen and the reaction mixture refluxed for 6 hours under nitrogen atmosphere. Afterwards, the reaction mixture was allowed to cool to room temperature, diluted with additional benzene (80 mL), and washed sequentially with 80-100 mL portions of 10% sodium carbonate (3 x 80 mL), water, and brine. The organic layer was dried (anhydrous sodium sulfate) and concentrated yielding the compound **1** (9.7-11.7 g, 47-57%) as a clear oil, which was used without further purification: ¹H NMR (300 MHz, CDCl₃) δ 4.53 (q, *J* = 8.3 Hz, 4H), 3.59 (s, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 164.27, 122.70 (q, *J* = 277.1 Hz), 61.28 (q, *J* = 37.0 Hz), 40.19; ¹⁹F NMR (470 MHz, CDCl₃) δ -74.69 (t, *J* = 8.3 Hz); IR 1754.5 cm⁻¹; MS *m/z* 268 (M⁺), 207, 169 (base), 127, 83, 69; HRMS calcd for C₇H₆F₆O₄ 268.0170 (M⁺), found 268.0177 *m/z*.

Two alternative procedures for the preparation of this compound have been reported: (i) Mozhaev, V. V.; Budde, C. L.; Rich, J. O.; Usyatinsky, A. Y.; Michels, P. C.; Khmelnistky, Y. L.; Clark, D. S.; Dordick, J. S. *Tetrahedron* **1998**, *54*, 3971-3982; and (ii) Lei, Y. X.; Cerioni, G.; Rappoport, Z. *J. Org. Chem.* **2001**, *66*, 8379-8394.

Representative Procedures.

Monoalkylation; Illustrated for the Preparation of 2a. To a solution of **1** (590 mg, 2.2 mmol), 3-phenyl-1-propanol (272 mg, 2.0 mmol), and Ph₃P (786 mg, 3.0 mmol) in dry toluene (10 mL) was added a solution of ADDP (1,1'-(azodicarbonyl)dipiperidine, 756 mg, 3.0 mmol) in dry toluene (10 mL) dropwise. The resulting mixture was stirred at room and the course of the reaction followed by TLC. (Alternatively, in some cases, the reaction is stirred at 0 °C; see Table 2.) Upon complete consumption of starting alcohol, (ca 12-48 h), the reaction mixture was filtered through a short silica column using 20% ethyl acetate/hexanes eluent. The solvents were removed in vacuo and the crude product was further purified by chromatography in silica using 2% ethyl acetate/hexanes eluent to give the monoalkylated product **2a** (648 mg, 84%).

Dialkylation; Illustrated for the Preparation of 3e. To a room temperature solution of **1** (284 mg, 1.1 mmol), (*E*) 3,5-hexadien-1-ol (245 mg, 2.5 mmol), and Ph₃P (865 mg, 3.3 mmol) in dry toluene (10 mL) was added a solution of ADDP (832 mg, 3.3 mmol) in dry toluene (10 mL) dropwise. The resulting mixture was stirred overnight. (Alternatively, in some cases, the reaction is stirred at 0 °C; see Table 2.) Afterwards, the solvents were removed in vacuo and the residue taken up in hot ethyl acetate. A solid (Ph₃PO) crystallizes upon cooling and is removed via filtration and washed with hexane. The combined filtrate and hexane wash is concentrated in vacuo and the residue fractionated by chromatography on silica (260-400 mesh, step gradient from 100% hexanes to 8:92 EtOAc:Hex) afforded the dialkylation product **3e** (345 mg, 75%) as a pale yellow oil.

Characterization Data:

2a: bulb-to-bulb distilled, oven temperature 175-195 °C @ 4-5 torr; ¹H NMR (300 MHz, CDCl₃) δ 7.33-7.16 (m, 5H), 4.53 (q, *J* = 8.3 Hz, 4H), 3.59 (t, *J* = 7.5 Hz, 1H), 2.68 (t, *J* = 7.6 Hz, 2H), 2.07-1.99 (m, 2H), 1.76-1.68 (m, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 167.16, 141.29, 128.62, 128.48, 126.24, 122.70 (q, *J* = 277.1 Hz), 61.14 (q, *J* = 37.0 Hz), 50.98, 35.42, 28.81, 28.24; ¹⁹F NMR (470 MHz, CDCl₃) δ -74.45 (t, *J* = 8.2 Hz); IR 1754 cm⁻¹; MS *m/z* 386 (M⁺, base), 286, 186, 158, 117, 104, 91; HRMS calcd for C₁₆H₁₆F₆O₄ (M⁺) 386.0953, found 386.0955 *m/z*.

2b: bulb-to-bulb distilled, oven temperature 125-140 °C @ 1 torr; ^1H NMR (300 MHz, CDCl_3) δ 7.34-7.19 (m, 5H), 4.55-4.42 (m, 4H), 3.90 (t, $J = 7.9$ Hz, 1H), 3.30 (d, $J = 7.9$ Hz, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 166.65, 136.56, 128.93, 128.84, 127.43, 122.64 (q, $J = 277.1$ Hz), 61.27 (q, $J = 37.4$ Hz), 53.03, 34.55; ^{19}F NMR (470 MHz, CDCl_3) δ -74.52 (m); IR 1756 cm^{-1} ; MS m/z 358 (M^+), 230, 189, 159, 131 (base), 91; HRMS calcd for $\text{C}_{14}\text{H}_{12}\text{F}_6\text{O}_4$ (M^+) 358.0640, found 358.0648 m/z .

2c: bulb-to-bulb distilled, oven temperature 70-80 °C @ 0.55 torr; ^1H NMR (300 MHz, CDCl_3) δ 5.81-5.70 (m, 1H), 5.19-5.10 (m, 2H), 4.52 (q, $J = 8.3$ Hz, 4H), 3.67 (t, $J = 7.5$ Hz, 1H), 2.71 (t, $J = 7.2$ Hz, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 166.71, 132.73, 122.70 (q, $J = 277.1$ Hz), 118.86, 61.20 (q, $J = 37.0$ Hz), 50.89, 32.70; ^{19}F NMR (470 MHz, CDCl_3) δ -74.57--74.61 (m); IR 1756 cm^{-1} ; HRMS calcd for $\text{C}_{10}\text{H}_{10}\text{F}_6\text{O}_4$ (M^+) 308.0483, found 308.0474 m/z .

2d: ^1H NMR (500 MHz, CDCl_3) δ 7.28-7.32 (m, 4H), 7.21-7.25 (m, 1H), 6.51 (d, $J = 15.8$ Hz, 1H), 6.09-6.15 (m, 1H), 4.53 (q, $J = 8.2$ Hz, 4H), 3.74 (t, $J = 7.4$ Hz, 1H), 2.88 (t, $J = 7.3$ Hz, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 166.5, 136.6, 134.0, 128.6, 127.7, 126.3, 123.7, 122.5 (q, $J = 275.8$ Hz), 121.4, 61.1 (q, $J = 37$ Hz), 51.1, 31.9; IR (neat): 1759 cm^{-1} ; MS m/z : 384 (M^+), 256, 157, 124, 117 (base), 91; HRMS calcd for $\text{C}_{16}\text{H}_{14}\text{F}_6\text{O}_4$ (M^+) 384.0796, found 384.0796 m/z .

2e: bulb-to-bulb distilled, oven temperature 70-80 °C @ 0.15 torr; ^1H NMR (300 MHz, CDCl_3) δ 5.59-5.50 (m, 1H), 5.40-5.30 (m, 1H), 4.58-4.40 (m, 4H), 3.48 (d, $J = 8.3$ Hz, 1H), 2.98-2.90 (m, 1H), 1.62 (dd, $J = 6.2, 1.4$ Hz, 3H), 1.10 (d, $J = 6.7$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 166.32, 166.25, 131.26, 127.71, 122.77 (q, $J = 277.1$ Hz), 60.95 (q, $J = 37.0$ Hz), 57.26, 37.67, 18.46, 17.82; ^{19}F NMR (470 MHz, CDCl_3) δ -74.53 (m); IR 1757 cm^{-1} ; MS m/z : 336 (M^+), 208, 193, 109, 81, 69 (base); HRMS calcd for $\text{C}_{12}\text{H}_{14}\text{F}_6\text{O}_4$ (M^+) 336.0796, found 336.0784 m/z .

2f: ^1H NMR (500 MHz, CDCl_3): δ 4.49-4.59 (m, 4H), 3.65 (d, $J = 8.5\text{ Hz}$, 1H), 3.22-3.31 (m, 1H), 2.17 (s, 3H), 1.31 (d, $J = 7.0\text{ Hz}$, 3H); ^{13}C NMR (125 MHz, CDCl_3): δ 165.5, 122.8 (q, $J = 275.8\text{ Hz}$), 83.6, 71.6, 61.5 (q, $J = 36.7\text{ Hz}$), 56.7, 26.5, 18.9; IR (neat): 1757 cm^{-1} ; MS m/z : 320 (M^+), 305, 268, 221, 193 (base), 83; HRMS calcd for $\text{C}_{11}\text{H}_{10}\text{F}_6\text{O}_4$ (M^+) 320.0483, found 320.0483 m/z .

2h (data from a 2.4:1 mixture with **2i**): ^1H NMR (500 MHz, CDCl_3) δ 5.52-5.56 (m 1H), 5.30-5.36 (m, 1H), 4.64 (q, $J = 8.3\text{ Hz}$, 4H), 3.59 (t, $J = 7.5\text{ Hz}$, 1H), 2.63 (t, $J = 7.4\text{ Hz}$, 2H), 1.93 (q, $J = 7.1\text{ Hz}$, 2H), 1.29-1.36 (m, 2H), 0.84 (t, $J = 7.4\text{ Hz}$, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 166.7, 135.2, 123.9, 122.5 (q, $J = 276\text{ Hz}$), 60.9, (q, $J = 36.7\text{ Hz}$), 51.4, 34.4, 31.7, 22.2, 13.4; IR (neat): 1767 cm^{-1} ; MS m/z : 350 (M^+), 281, 222, 179, 82 (base), 67; HRMS calcd for $\text{C}_{12}\text{H}_{12}\text{F}_6\text{O}_4$ (M^+) 350.0953, found 350.0955 m/z .

2j: ^1H NMR (500 MHz, CDCl_3) δ 6.18-6.28 (m, 1H), 6.08-6.17 (m, 1H), 5.54-5.62 (m, 1H), 5.14 (d, $J = 16.8\text{ Hz}$, 1H), 5.06 (d, $J = 10\text{ Hz}$, 1H), 4.50 (q, $J = 8.3\text{ Hz}$, 4H), 3.64 (t, $J = 7.5\text{ Hz}$, 1H), 2.73 (t, $J = 7.3\text{ Hz}$, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 166.5, 136.2, 134.9, 127.6, 122.6 (q, $J = 276\text{ Hz}$), 117.4, 61.1 (q, $J = 37\text{ Hz}$), 51.0, 31.5; IR (neat): 1757 cm^{-1} ; MS m/z : 334 (M^+), 206, 79 (base), 67; HRMS calcd for $\text{C}_{12}\text{H}_{12}\text{F}_6\text{O}_4$ (M^+) 334.0673, found 334.0642 m/z .

2k: ^1H NMR (500 MHz, CDCl_3) δ 4.50-4.54 (m, 4H), 3.67 (dd, $J = 7.2, 14.2\text{ Hz}$, 1H), 1.54 (d, $J = 7.2\text{ Hz}$, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 167.7, 122.5 (q, $J = 275\text{ Hz}$), 121.7, 61.1 (q, $J = 36.7\text{ Hz}$), 45.3, 13.3; IR (neat) 1747 cm^{-1} ; MS m/z : 282 (M^+), 263, 238, 183, 127, 83 (base), 68; HRMS calcd for $\text{C}_8\text{H}_8\text{F}_6\text{O}_4$ (M^+) 282.0327, found 282.0327 m/z .

2l: ^1H NMR (500 MHz, CDCl_3) δ 6.34-6.26 (m, 1 H), 6.11-6.05 (m, 1 H), 5.65-5.59 (m, 1 H), 5.14 (d, $J = 17.0\text{ Hz}$, 1 H), 5.03 (d, $J = 10.1\text{ Hz}$, 1 H), 4.57-4.49 (m, 4 H), 3.59 (t, $J = 7.4\text{ Hz}$, 1 H), 2.21-2.17 (m, 2 H), 2.12-2.07 (m, 2 H); ^{13}C NMR (500 MHz, CDCl_3) δ 167.2, 136.8, 133.3, 131.9, 122.8 (q, $J = 277\text{ Hz}$), 116.5, 61.2 (q, $J = 37.2\text{ Hz}$), 50.3, 29.1, 28.1; FTIR (cm^{-1}) 1761; HRMS analysis (EI, $\text{C}_{13}\text{H}_{14}\text{F}_6\text{O}_4$ = 348.0796) found 348.0787 m/z .

3a: bulb-to-bulb distilled, oven temperature 70-85 °C @ 0.25 torr; ^1H NMR (300 MHz, CDCl_3) δ 5.72-5.58 (m, 2H), 5.18-5.12 (m, 4H), 4.49 (q, $J = 8.3$ Hz, 4H), 2.70 (d, $J = 7.4$ Hz, 4H); ^{13}C NMR (75 MHz, CDCl_3) δ 168.59, 131.05, 122.76 (q, $J = 277$ Hz), 120.43, 61.09 (q, $J = 37.0$ Hz), 57.96, 37.05; ^{19}F NMR (470 MHz, CDCl_3) δ -74.45 (t, $J = 8.2$ Hz); IR 1751 cm^{-1} ; MS m/z 348 (M^+), 307, 277, 220, 207 (base); HRMS calcd for $\text{C}_{13}\text{H}_{14}\text{F}_6\text{O}_4$ (M^+) 348.0796, found 348.0805 m/z .

3b: bulb-to-bulb distilled, oven temperature 130-140 °C @ 0.1 torr; ^1H NMR (300 MHz, CDCl_3) δ 7.34-7.16 (m, 5H), 5.67-5.55 (m, 1H), 5.16-5.09 (m, 2H), 4.50 (q, $J = 8.3$ Hz, 4H), 2.72 (d, $J = 7.4$ Hz, 2H), 2.66 (t, $J = 7.5$ Hz, 2H), 2.06-2.00 (m, 2H), 1.64-1.56 (m, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 168.98, 141.43, 131.13, 128.55, 128.45, 126.18, 122.76 (q, $J = 277$ Hz), 120.12, 60.93 (q, $J = 37.0$ Hz), 57.82, 37.09, 35.86, 31.98, 25.68; ^{19}F NMR (470 MHz, CDCl_3) δ -74.44 (t, $J = 8.3$ Hz); IR 1751 cm^{-1} ; MS m/z 426 (M^+), 298, 285, 117, 104, 91 (base); HRMS calcd for $\text{C}_{19}\text{H}_{20}\text{F}_6\text{O}_4$ (M^+) 426.1266, found 426.1265 m/z .

3c: ^1H NMR (CDCl_3 , 500 MHz) δ 6.32-6.24 (m, 1 H), 6.12 (d, 1 H, $J = 18.7$ Hz), 6.10-6.03 (m, 1 H), 5.77-5.70 (m, 1 H), 5.62 (broad d, 1 H), 5.12 (d, 1 H, $J = 17.0$ Hz), 5.01 (d, 1 H, $J = 10.2$ Hz), 4.50 (q, 4 H, $J = 7.89$ Hz), 2.82 (d, 2 H, $J = 7.04$ Hz), 2.06-2.05 (overlapping m, 4 H), 1.51-1.45 (m, 6 H), 1.32-1.27 (m, 6 H), 0.93-0.86 (m, 15 H); ^{13}C NMR (500 MHz, CDCl_3) δ 169.1, 140.8, 136.9, 136.1, 132.8, 132.3, 122.8 (q, $J = 277$ Hz), 116.1, 61.1 (q, $J = 37.2$ Hz), 57.5, 32.0, 29.3, 27.5, 27.1, 13.9, 9.6; FTIR 1756 cm^{-1} ; HRMS (FAB, $(\text{C}_{24}\text{H}_{44}\text{F}_6\text{O}_4\text{Sn}, (\text{M}^+ \text{ minus } \text{C}_4\text{H}_9) = 621.1412)$ found 621.1453 m/z .

3d: oven temperature 135-150 °C @ 0.1 torr; ^1H NMR (300 MHz, CDCl_3) δ 7.35-7.15 (m, 5H), 5.79-5.70 (m, 1H), 5.06-4.97 (m, 2H), 4.54-4.46 (m, 4H), 2.64 (t, $J = 7.6$ Hz, 2H), 2.09-1.92 (m, 6H), 1.59-1.49 (m, 2H), 1.29-1.19 (m, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 169.48, 141.45, 137.66, 128.57, 128.46, 126.19, 122.77 (q, $J = 277$ Hz), 115.51, 60.84 (q, $J = 37.4$ Hz), 57.75, 35.86, 33.64, 32.06, 31.96, 25.74,

23.21; ^{19}F NMR (470 MHz, CDCl_3) δ -74.45 (t, J = 8.2 Hz); IR 1753 cm^{-1} ; MS m/z 454 (M^+), 386, 286, 117, 104 (base), 91; HRMS calcd for $\text{C}_{21}\text{H}_{24}\text{F}_6\text{O}_4$ (M^+) 454.1579, found 454.1570 m/z .

3e: TLC analysis (30:70 EtOAc:Hex) R_f = 0.62; ^1H NMR (300 MHz, CDCl_3) δ 6.29 (2H, dt, J = 16.9, 10.3 Hz), 6.07 (2H, dd, J = 15.0, 10.5 Hz), 5.67-5.60 (2H, m), 5.13 (2H, d, J = 16.9), 5.02 (2H, d, J = 10.0), 4.51 (4H, q, J = 8.3 Hz), 2.12-1.99 (8H, m); ^{13}C NMR (75 MHz, CDCl_3) δ 169.7, 137.3, 133.1, 132.8, 125.1, 121.4, 116.7, 62.2, 61.8, 61.3, 60.8, 57.7, 32.6, 27.6; IR (ATR-ZnSe) 1753 cm^{-1} ; HRMS analysis (FAB) calcd for $\text{C}_{19}\text{H}_{22}\text{O}_4\text{F}_6$ plus H = 429.1488 found 428.1422 m/z .

3f: TLC analysis (30:70 EtOAc:Hex) R_f = 0.60; ^1H NMR (300 MHz, CDCl_3) δ 6.37-6.23 (2H, m), 6.07 (2H, dd, J = 15.0, 10.5 Hz), 5.69-5.60 (2H, m), 5.12 (2H, d, J = 16.9 Hz), 5.01 (2H, d, J = 10.0 Hz), 4.51 (4H, qd, J = 8.4, 1.4 Hz), 2.24-1.95 (8H, m), 1.37-1.27 (2H, m); ^{13}C NMR (75 MHz, CDCl_3) δ 169.2, 136.9, 136.6, 133.6, 133.5, 132.5, 132.1, 131.9, 124.4, 120.8, 115.9, 115.4, 61.5, 61.0, 60.5, 60.0, 57.3, 32.3, 31.9, 26.9, 23.4; IR (ATR-ZnSe) 1753 cm^{-1} ; HRMS analysis (EI, $\text{C}_{20}\text{H}_{24}\text{F}_6\text{O}_4$ = 442.1586) found 442.1579 m/z .

3g: TLC analysis (30:70 EtOAc:Hex) R_f = 0.63; ^1H NMR (300 MHz, CDCl_3) δ 6.30 (2H, dt, J = 16.9, 10.3 Hz), 6.07 (2H, dd, J = 15.3, 10.5), 5.69-5.59 (2H, m), 5.10 (2H, d, J = 16.9 Hz), 5.99 (2H, d, J = 10.3 Hz), 4.52 (4H, q, J = 8.3 Hz), 2.15-2.08 (4H, m), 1.99-1.93 (4H, m), 1.36-1.24 (4H, m); ^{13}C NMR (75 MHz, CDCl_3) δ 169.9, 137.6, 134.5, 134.2, 132.5, 129.3, 129.2, 129.1, 125.1, 121.5, 115.9, 62.1, 61.6, 61.1, 60.6, 58.3, 32.9, 32.6, 24.1; IR (ATR-ZnSe) 1754 cm^{-1} ; HRMS (FAB, calcd for $\text{C}_{21}\text{H}_{27}\text{F}_6\text{O}_4$ = 456.1735) found 456.1735 m/z .

4 (data from a 2.4 : 2.3 : 1 mixture with **5** and **6**): ^1H NMR (500 MHz, CDCl_3): δ 6.08-6.13 (m, 1H), 5.91-6.08 (m, 1H), 5.54-5.60 (m, 1H), 5.34-5.52 (m, 1H), 4.47-4.58 (m, 4H), 3.62 (t, J = 7.3 Hz, 1H), 2.70 (t, J = 7.2 Hz, 2H), 1.72 (d, J = 6.6 Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3): δ 166.5, 134.4, 130.7, 129.6,

124.2, 122.5 (q, $J = 275.3$ Hz), 60.9 (q, $J = 36.7$ Hz), 51.2, 31.6, 17.9; IR (neat): 1741 cm^{-1} ; MS (m/z): 348 (M^+), 220, 81 (base); HRMS calcd for $C_{12}H_{12}F_6O_4$ 348.0797, found 348.0797 m/z .

Dibenzyl Bis(trifluoroethyl)malonate: m.p. 55-56 °C; ^1H NMR (300 MHz, CDCl_3) δ 7.37-7.18 (m, 10H), 4.34 (q, $J = 8.3$ Hz, 4H), 3.34 (s, 4H); ^{13}C NMR (75 MHz, CDCl_3) δ 168.75, 135.13, 134.02, 133.76, 130.09, 128.84, 128.68, 128.58, 127.65, 122.69 (q, $J = 277$ Hz), 61.31 (q, $J = 37.4$ Hz), 39.90; ^{19}F NMR (470 MHz, CDCl_3) δ -74.14 (t, $J = 8.1$ Hz); IR 1749 cm^{-1} ; MS m/z 448 (M^+), 357, 257, 183, 91 (base); HRMS calcd for $C_{21}H_{18}F_6O_4$ 448.1109, found 448.1100 m/z .