Mild Electrophilic Trifluoromethylation of β -Ketoesters and Silyl Enol Ethers with 5-Trifluoro methylidibenzothiophenium Tetrafluoroborate

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SUPPORTING INFORMATION

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General Experimental

^1H , ^{13}C and ^{19}F NMR spectra were recorded on a 300 MHz (75 MHz for ^{13}C and 282 MHz for ^{19}F) spectrometer in CDCl_3 , and δ (ppm) is quoted relative to the residual signal of CDCl_3 (^1H NMR $\delta_{\text{H}} = 7.27$ ppm). Trichlorofluoromethane served as internal standard ($\delta_{\text{F}} = 0$ ppm) for ^{19}F NMR. Chemical shifts are reported in ppm (d); multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), sext (sextet), m (multiplet) and br (broad). Coupling constants, J , are reported in Hertz. Melting points were uncorrected. Infrared (IR) peaks are reported in cm^{-1} with the indicated relative intensities. Flash chromatography was performed on silica gel (230-400 Mesh). Mass spectrometry data are reported in the form of m/z (intensity relative to base peak = 100).

Spectroscopic characterization

1-oxo-2-trifluoromethyl-indan-2-carboxylic acid methyl ester 5a: Yield 99%; m. p. 64-65 °C; ^1H NMR (300 MHz, CDCl_3) δ 3.53 (d, $J = 17.7$ Hz, 1H), 3.68 (d, $J = 17.7$ Hz, 1H), 3.72 (s, 3H), 7.38-7.47 (m, 2H), 7.48-7.66 (m, 1H), 7.78 (d, $J = 7.9$ Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 34.5, 54.0, 63.4 (q, $^2J_{\text{F-C}} = 25.9$ Hz), 123.8 (q, $^1J_{\text{F-C}} = 283.0$ Hz, CF_3), 126.0, 126.7, 128.9, 134.7, 136.7, 152.0, 166.0, 193.3; ^{19}F NMR (282 MHz, $\text{CDCl}_3/\text{CFCl}_3$) δ -69.82 (s, 3F); IR (film, cm^{-1}): 2958, 2849, 1758, 1726, 1606, 1592, 1465, 1435, 1277, 1181, 1084, 1045, 890, 797; MS (EI) m/z : 258 (M^+); HRMS (EI) m/z Calcd for $\text{C}_{12}\text{H}_9\text{F}_3\text{O}_3$: 258.0504. Found: m/z 258.0505.

1-oxo-2-trifluoromethyl-indan-2-carboxylic acid benzyl ester 5b: Yield 94%; ^1H NMR (300 MHz, CDCl_3) δ 3.51 (d, $J = 17.7$ Hz, 1H), 3.64 (d, $J = 17.7$ Hz, 1H), 5.12 (d, $J = 12.4$ Hz, 1H), 5.18 (d, $J = 12.4$ Hz, 1H), 7.16-7.38 (m, 5H), 7.41-7.58 (m, 2H), 7.59-7.64 (m, 1H), 7.77 (d, $J = 7.5$ Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 34.5, 63.5 (q, $^2J_{\text{F-C}} = 25.9$ Hz), 68.4, 123.9 (q, $^1J_{\text{F-C}} = 283.0$ Hz, CF_3), 126.0, 126.7, 128.1 ($2 \times \underline{\text{CH}}$), 128.8, 128.9 ($2 \times \underline{\text{CH}}$), 129.0, 129.5, 135.0, 136.7, 152.0, 165.4, 193.2; ^{19}F NMR (282 MHz, $\text{CDCl}_3/\text{CFCl}_3$) δ -69.62 (s, 3F); IR (film, cm^{-1}): 2920, 2849, 1756, 1723, 1591, 1455, 1275, 1181, 1036, 889, 792, 695; MS (EI) m/z : 334 (M^+); HRMS (EI) m/z Calcd for $\text{C}_{18}\text{H}_{13}\text{F}_3\text{O}_3$: 334.0817. Found: m/z 334.0818.

1-oxo-2-trifluoromethyl-tetralone-2-carboxylic acid methyl ester 5c: Yield 52%; ^1H NMR (300 MHz, CDCl_3) δ 2.36-2.46 (m, 1H), 2.73-2.80 (m, 1H), 2.94-2.98 (m, 2H), 3.70 (s, 3H), 7.18 (d, $J = 7.5$ Hz, 1H), 7.27-7.32 (m, 1H), 7.44-7.49 (m, 1H), 8.05 (d, $J = 7.9$ Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 25.5, 28.1, 54.1, 62.3 (q, $^2J_{\text{F-C}} = 24.0$ Hz), 124.2 (q, $^1J_{\text{F-C}} = 284.0$ Hz, CF_3), 127.7, 128.9, 129.1, 131.8, 134.7, 142.5, 160.4, 187.4; ^{19}F NMR (282 MHz, $\text{CDCl}_3/\text{CFCl}_3$) δ -69.31 (s,

3F); IR (film, cm^{-1}): 2918, 2849, 1746, 1697, 1600, 1454, 1306, 1227, 1175, 1072, 896, 736; MS (EI) m/z : 272 (M^+); HRMS (EI) m/z Calcd for $\text{C}_{13}\text{H}_{11}\text{F}_3\text{O}_3$: 272.0660. Found: m/z 272.0658.

1-oxo-2-trifluoromethyl-tetralone-2-carboxylic acid benzyl ester 5d: Yield 60%; ^1H NMR (300 MHz, CDCl_3) δ 2.34-2.44 (m, 1H), 2.70-2.85 (m, 3H), 5.04 (d, $J = 12.1$ Hz, 1H), 5.20 (d, $J = 12.1$ Hz, 1H), 7.00-7.47 (m, 8H), 8.04 (d, $J = 7.9$ Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 25.1, 28.1, 62.3 (q, $^2J_{\text{F-C}} = 24.0$ Hz), 68.6, 124.1 (q, $^1J_{\text{F-C}} = 284.0$ Hz, CF_3), 127.7, 128.1 ($2 \times \underline{\text{CH}}$), 128.7, 128.8, 128.9 ($2 \times \underline{\text{CH}}$), 129.1, 131.9, 134.6, 134.8, 142.3, 165.5, 187.4; ^{19}F NMR (282 MHz, $\text{CDCl}_3/\text{CFCl}_3$) δ -69.22 (s, 3F); IR (film, cm^{-1}): 2921, 2850, 1746, 1697, 1600, 1455, 1305, 1278, 1224, 1177, 1071, 1049, 897, 736, 696; MS (CI) m/z : 349 (M^++1); HRMS (EI) m/z Calcd for $\text{C}_{19}\text{H}_{15}\text{F}_3\text{O}_3$: 348.0973. Found: m/z 348.0975.

1-oxo-2-trifluoromethyl-cyclopentan-2-carboxylic acid 1'-naphthylmethyl ester 5e: Yield 36%; ^1H NMR (300 MHz, CDCl_3) δ 1.84-1.97 (m, 2H), 2.34-2.50 (m, 4H), 5.62 (d, $J = 12.4$ Hz, 1H), 5.73 (d, $J = 12.4$ Hz, 1H), 7.43-7.58 (m, 4H), 7.88-7.93 (m, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 18.2, 29.6, 37.2, 62.3 (q, $^2J_{\text{F-C}} = 25.4$ Hz), 65.6, 118.6 (q, $^1J_{\text{F-C}} = 282.0$ Hz, CF_3), 122.1, 124.2, 125.1, 125.8, 126.8, 127.8, 128.8, 128.9, 130.3, 132.7, 164.4, 204.1; ^{19}F NMR (282 MHz, $\text{CDCl}_3/\text{CFCl}_3$) δ -69.27 (s, 3F); IR (film, cm^{-1}): 2920, 2849, 1768, 1745, 1599, 1454, 1298, 1228, 1194, 1117, 993, 799, 776; MS (EI) m/z : 336 (M^+); HRMS (EI) m/z Calcd for $\text{C}_{18}\text{H}_{15}\text{F}_3\text{O}_3$: 336.0973. Found: m/z 336.0975.

3-oxo-2-methyl-2-trifluoromethyl-butyric acid 1'-naphthylmethyl ester 5f: Yield 28%; ^1H NMR (300 MHz, CDCl_3) δ 1.59 (s, 3H), 2.13 (s, 3H), 5.71 (s, 2H), 7.43-7.58 (m, 4H), 7.87-7.97 (m, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 16.0, 27.7, 64.8 (q, $^2J_{\text{F-C}} = 25.3$ Hz), 67.1, 123.6, 124.0 (q, $^1J_{\text{F-C}} = 283.0$ Hz, CF_3), 126.1, 126.5, 127.2, 128.5, 129.2, 130.2, 130.3, 131.8, 134.0, 166.6, 197.3; ^{19}F NMR (282 MHz, $\text{CDCl}_3/\text{CFCl}_3$) δ -68.93 (s, 3F); IR (film, cm^{-1}): 2955, 2927, 1754, 1729,

1512, 1456, 1361, 1286, 1256, 1206, 1116, 1088, 940, 794, 776; MS (EI) m/z : 324 (M^+); HRMS (EI) m/z Calcd for $C_{17}H_{15}F_3O_3$: 324.0973. Found: m/z 324.0976.

1-oxo-2-trifluoromethyl-indan-2-carboxylic acid (1'R, 2'S, 5'R)-(-)-menthyl ester 5g: Yield 97%; 1H NMR (300 MHz, $CDCl_3$) δ 0.63-0.99 (m, 12H), 1.18-1.70 (m, 5H), 1.87-1.96 (m, 1H), 3.52 (d, $J = 17.7$ Hz, 1H), 3.63 (d, $J = 17.7$ Hz, 1H), 4.62-4.72 (m, 1H), 7.36-7.47 (m, 2H), 7.61 (t, $J = 7.5$ Hz, 1H), 7.76 (d, $J = 7.5$ Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 16.2, 21.1, 22.3, 23.4, 26.2, 31.7, 34.3, 34.6, 40.5, 46.9, 63.6 (q, $^2J_{F-C} = 26.0$ Hz), 77.7, 120.2 (q, $^1J_{F-C} = 281.0$ Hz, CF_3), 125.8, 126.6, 128.8, 134.9, 136.5, 152.0, 165.1, 193.4; ^{19}F NMR (282 MHz, $CDCl_3/CFCl_3$) δ -69.49 (s), -69.50 (s); IR (film, cm^{-1}): 2956, 2928, 1751, 1725, 1606, 1591, 1465, 1288, 1274, 1183, 1154, 1085, 1034, 950, 889, 689; MS (CI) m/z : 383 ($M^+ + 1$); HRMS (EI) m/z Calcd for $C_{21}H_{25}F_3O_3$: 382.1756. Found: m/z 382.1751.

2-ethyl-2-trifluoromethyl-1-indanone 8b: Yield 80%; 1H NMR (300 MHz, $CDCl_3$) δ 0.74 (t, $J = 7.2$ Hz, 3H), 1.82-1.89 (m, 1H), 2.01-2.06 (m, 1H), 3.14 (d, $J = 17.7$ Hz, 1H), 3.44 (d, $J = 17.7$ Hz, 1H), 7.32-7.47 (m, 2H), 7.56-7.61 (m, 1H), 7.72 (d, $J = 8.5$ Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 8.3, 25.2, 33.4, 57.3 (q, $^2J_{C-F} = 24.7$ Hz), 125.0, 126.6, 126.7 (q, $^1J_{C-F} = 282.0$ Hz, CF_3), 128.4, 136.1, 136.4, 152.4, 201.1; ^{19}F NMR (282 MHz, $CDCl_3/CFCl_3$) δ -72.33 (s); IR (film, cm^{-1}): 1721, 1607, 1558, 1506, 1466, 1291, 1205, 1157, 981, 875, 738; MS (EI) m/z : 228 (M^+); HRMS (EI) m/z Calcd for $C_{12}H_{11}F_3O$: 228.0762. Found: m/z 228.0765.

2-benzyl-2-trifluoromethyl-1-indanone 8c: Yield 61% (77% in CsF-mediated reaction); m.p. 58-59 °C; 1H NMR (300 MHz, $CDCl_3$) δ 3.04 (d, $J = 13.9$ Hz, 1H), 3.20 (d, $J = 17.7$ Hz, 1H), 3.37 (d, $J = 17.7$ Hz, 1H), 3.58 (d, $J = 13.9$ Hz, 1H), 7.06-7.13 (m, 5H), 7.28-7.33 (m, 2H), 7.46-7.49 (m, 1H), 7.71 (d, $J = 7.5$ Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 32.4, 37.1, 58.0 (q, $^2J_{C-F} =$

23.3 Hz), 124.8, 126.3, 126.4 (q, $^1J_{\text{C-F}} = 283.0$ Hz, CF_3), 127.6, 128.2, 128.7 ($2 \times \underline{\text{CH}}$), 130.7 ($2 \times \underline{\text{CH}}$), 134.3, 136.0, 136.3, 152.4, 200.9; ^{19}F NMR (282 MHz, $\text{CDCl}_3/\text{CFCl}_3$) δ -72.60 (s); IR (film, cm^{-1}): 1722, 1611, 1558, 1464, 1292, 1238, 1204, 1155, 978, 873, 779; MS (EI) m/z : 290 (M^+); HRMS (EI) m/z Calcd for $\text{C}_{17}\text{H}_{13}\text{F}_3\text{O}$: 290.0918. Found: m/z 290.0920.

2-methyl-2-trifluoromethyl-1-tetralone 8d: Yield 53% (88% in CsF-mediated reaction); ^1H NMR (300 MHz, CDCl_3) δ 1.41 (s, 3H), 2.08-2.16 (m, 1H), 2.36-2.46 (m, 1H), 2.94-3.00 (m, 2H), 7.17-7.38 (m, 2H), 7.40-7.49 (m, 1H), 8.02 (d, $J = 7.8$ Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 17.1, 25.0, 29.7, 50.8 (q, $^2J_{\text{C-F}} = 24.0$ Hz), 126.6 (q, $^1J_{\text{C-F}} = 283.0$ Hz, CF_3), 127.5, 128.8, 129.1, 131.5, 134.4, 143.0, 194.0; ^{19}F NMR (282 MHz, $\text{CDCl}_3/\text{CFCl}_3$) δ -73.56 (s); IR (film, cm^{-1}): 1721, 1693, 1607, 1589, 1465, 1315, 1294, 1233, 1157, 1085, 873, 780, 742; MS (EI) m/z : 228 (M^+); HRMS (EI) m/z Calcd for $\text{C}_{12}\text{H}_{11}\text{F}_3\text{O}$: 228.0762. Found: m/z 228.0763

2-trifluoromethyl-1-tetralone 8h: Yield 53%; ^1H NMR (300 MHz, CDCl_3) δ 2.22-2.34 (m, 1H), 2.36-2.53 (m, 1H), 2.88-3.09 (m, 2H), 3.14-3.32 (m, 1H), 7.22-7.40 (m, 2H), 7.40-7.60 (m, 1H), 8.06 (d, $J = 8.3$ Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 23.5, 27.9, 51.3 (q, $^2J_{\text{C-F}} = 25.4$ Hz), 125.4 (q, $^1J_{\text{C-F}} = 280.0$ Hz, CF_3), 127.5, 128.3, 129.2, 132.3, 134.6, 143.4, 189.4; ^{19}F NMR (282 MHz, $\text{CDCl}_3/\text{CFCl}_3$) δ -68.04 (d, $J = 8.7$ Hz); IR (film, cm^{-1}): 1721, 1694, 1609, 1559, 1540, 1507, 1465, 1379, 1292, 1231, 1204, 1155, 1099, 979, 876, 780; MS (EI) m/z : 214 (M^+); HRMS (EI) m/z Calcd for $\text{C}_{11}\text{H}_9\text{F}_3\text{O}$: 214.0605. Found: m/z 214.0606.

Data for compounds **8a**, **8g** and **8i** are in agreement with the literature.¹

References

(1) Umemoto, T.; Ishihara, S. *J. Am. Chem. Soc.* **1993**, *115*, 2156-2164.

¹³C NMR

¹H NMR

¹³C NMR

NMR

¹³C NMR

¹H NMR

¹³C NMR

¹H NMR

¹³C NMR

¹H NMR

¹³C NMR

¹³C NMR

¹H NMR

¹³C NMR

¹H NMR

¹³C NMR