

**New Stable Reagents for the Nucleophilic Trifluoromethylation. 1. Trifluoromethylation of Carbonyl Compounds with N-Formylmorpholine Derivatives.**

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**Supporting Information**

**General :** Aldehydes were purified by distillation or recrystallization prior use. CsF was dried overnight at 250°C then stored at 110°C. TLC : Silica Gel 60 F<sub>254</sub>, detection by UV light and with an ethanolic solution of phosphomolybdic acid. Column chromatography : Silica gel 60M (0.04 – 0.063 mm). NMR : Brüker AC 200 (188 MHz for <sup>19</sup>F) and Brüker DRX 300 (300 MHz for <sup>1</sup>H and 75 MHz for <sup>13</sup>C). CDCl<sub>3</sub> as solvent with TMS as internal reference for <sup>1</sup>H and <sup>13</sup>C and CFCl<sub>3</sub> for <sup>19</sup>F. Mass Spectra : Nermag R10-10H (70eV). Melting point (mp) (uncorrected) : Büchi apparatus.

**Preparation of 3 :** In a vessel fitted with a gastight mechanical stirrer were successively introduced, under nitrogen, dry THF (20mL), N-formylmorpholine (10 mmol) and tetrabutyl ammonium fluoride (2.4 mmol) as a 1M solution in THF previously dried over molecular sieves. The vessel was closed and cooled to -10°C before bubbling an excess (6 eq.) of HCF<sub>3</sub> in the reactor through a septum. Then, N(TMS)<sub>3</sub> (15 mmol), dissolved in dry THF (15 mL) was introduced and the mixture was stirred at -10°C for 1h. After reaction, the reactor was warmed up to room temperature and stirred at this temperature for 15h. Pentane was then added and the solution was washed with water and 6% aqueous NaHCO<sub>3</sub>. After evaporation, the crude mixture was purified by flash chromatography with petroleum ether / acetone (4:1) as eluent.

**Typical trifluoromethylation procedure – Synthesis of 4a :** Benzophenone (1 mmol) was added to a solution of 3 (1 mmol) in DME (1 mL). Then, CsF (0.2 eq.) was added and the mixture was heated to 80°C for 5h. After reaction, the crude mixture was directly deposited on the top of a chromatography column and eluted with petroleum ether / acetone (10:1).

**2,2,2-trifluoro-1-morpholinoethyl trimethylsilyl ether (3) :**

$^1H$  NMR : 4.35 (q,  $J_{HF} = 5.73$ , 1H), 3.64 (t,  $J = 4.8$ , 4H), 2.74 and 2.67 (2dt,  $J = 11.5$ ,  $J = 4.8$ , 4H), 0.15 (s, 9H)

$^{13}C$  NMR : 123.70 (q,  $^1J_{CF} = 286.59$ ), 85.77 (q,  $^2J_{CF} = 32.57$ ), 67.30, 48.24, 0.04

$^{19}F$  NMR : -76.87 (d,  $J = 6.4$ )

Mass spectra : 257 ( $M^{+}\bullet$ ), 188, 168, 73

**2,2,2-trifluoro-1,1-diphenylethyl trimethylsilyl ether (4a) :**

$^1H$  NMR : 7.45-7.46 (massif, 4H), 7.34-7.37 (massif, 6H), -0.002 (s, 9H)

$^{13}C$  NMR : 140.98, 128.32, 128.23 (q,  $^4J_{CF} = 1.5$ ), 127.88, 125.24 (q,  $^1J_{CF} = 287$ ), 82.03 (q,  $^2J_{CF} = 28.3$ ) 1.32

$^{19}F$  NMR : -73.10

Mass spectra : 324 ( $M^{+}\bullet$ ), 255, 213, 185, 165, 105, 77, 73

**9-(trifluoromethyl)-9*H*-fluoren-9-yl trimethylsilyl ether (4b) :**

mp : 41°C

$^1H$  NMR : 7.73 (d,  $J = 7.6$ , 2H), 7.69 (d,  $J = 7.6$ , 2H), 7.50 (t,  $J = 7.6$ , 2H), 7.37 (t,  $J = 7.6$ , 2H), -0.20 (s, 9H)

$^{13}C$  NMR : 141.91, 141.16, 130.64, 128.13, 126.26 (q,  $^4J_{CF} = 1.5$ ), 125.23 (q,  $^1J_{CF} = 284$ ), 120.31, 83.10 (q,  $^2J_{CF} = 32.9$ ), 1.20

$^{19}F$  NMR : -80.26

Mass spectra : 322 ( $M^{+}\bullet$ ), 253, 211, 183, 77, 73

**2,2,2-trifluoro-1,1-di(2-pyridinyl)ethyl trimethylsilyl ether (4c) :**

$^1H$  NMR : 8.54-8.57 (massif, 2H), 7.70-7.81 (massif, 4H), 7.21-7.26 (massif, 2H), 0.06 (s, 9H)

$^{13}C$  NMR : 158.86, 148.68, 136.89, 125.00 (q,  $^1J_{CF} = 288$ ), 123.58, 123.24 (q,  $^4J_{CF} = 1.72$ ), 2.28

$^{19}F$  NMR : -73.55

Mass spectra : 326 ( $M^{+}\bullet$ ), 311, 257, 242, 168, 150, 78, 73, 51

**(E)-1,1,1-trifluoro-2,4-diphenyl-3-buten-2-ol (4d) :**

$^1H$  NMR : 7.63 (d,  $J = 9.5$ , 2H), 7.40-7.43 (massif, 8H), 6.73 (d,  $J = 16.3$ , 1H) 6.59 (d,  $J = 16.3$ , 1H), 0.18 (s, 9H)

<sup>13</sup>C NMR : 138.03, 135.74, 135.30, 128.87, 128.69, 128.61, 127.99, 126.93 (q, <sup>4</sup>J<sub>CF</sub> = 1.1), 126.89, 125.37 (q, <sup>1</sup>J<sub>CF</sub> = 331), 79.98 (q, <sup>2</sup>J<sub>CF</sub> = 28.8), 2.07

<sup>19</sup>F NMR : -77.95

Mass spectra : 350 (M<sup>+</sup>•), 281, 191, 77, 73

**2,2,2-trifluoro-1-phenylethyl trimethylsilyl ether (4e) :**

<sup>1</sup>H NMR : 7.53-7.57 (massif, 2H), 7.42-7.47 (massif, 3H), 5.01 (q, J<sub>HF</sub> = 6.7, 1H), 0.21 (s, 9H)

<sup>13</sup>C NMR : 135.92 (q, <sup>3</sup>J<sub>CF</sub> = 1.15), 129.51, 128.72, 128.01 (q, <sup>4</sup>J<sub>CF</sub> = 1.15), 124.72 (q, <sup>1</sup>J<sub>CF</sub> = 282.2), 73.75 (q, <sup>2</sup>J<sub>CF</sub> = 31.8), 0.04

<sup>19</sup>F NMR : -78.90 (d, J = 7.6)

**2,2,2-trifluoro-1-(3-thienyl)ethyl trimethylsilyl ether (4f) :**

<sup>1</sup>H NMR : 7.40 (broad d, J = 3, 1H), 7.34 (dd, J = 5, J = 3, 1H), 7.18 (broad d, J = 5, 1H), 5.07 (q, J<sub>HF</sub> = 6.5, 1H), 0.16 (s, 9H)

<sup>13</sup>C NMR : 137.05 (q, <sup>3</sup>J<sub>CF</sub> = 1.15), 126.80 (q, <sup>4</sup>J<sub>CF</sub> = 1.15), 126.44, 124.74 (q, <sup>4</sup>J<sub>CF</sub> = 1.15) 124.39 (q, <sup>1</sup>J<sub>CF</sub> = 282), 70.27 (q, <sup>2</sup>J<sub>CF</sub> = 33), 0.06

<sup>19</sup>F NMR : -79.08 (d, J = 7.4)

Mass spectra : 254 (M<sup>+</sup>•), 185, 143, 115, 77, 73, 45

**2,2,2-trifluoro-1-(1-methyl-1*H*-pyrrol-2-yl)ethyl trimethylsilyl ether (4g) :**

<sup>1</sup>H NMR : 6.66 (dd, J = 2.6, J = 2, 1H), 6.27 (qq, J = 4, J = 2, 1H), 6.13 (dd, J = 2.6, J = 4, 1H), 5.08 (q, J<sub>HF</sub> = 7.1, 1H), 3.73 (s, 3H), 0.16 (s, 9H)

<sup>13</sup>C NMR : 125.55, 125.18, 124.56 (q, <sup>1</sup>J<sub>CF</sub> = 282), 111.48 (q, <sup>3</sup>J<sub>CF</sub> = 1.15), 107.6, 68.81 (q, <sup>2</sup>J<sub>CF</sub> = 34), 35.24 (q, <sup>4</sup>J<sub>CF</sub> = 2.3), -0.07

<sup>19</sup>F NMR : -77.66 (d, J = 7.3)

Mass spectra : 251 (M<sup>+</sup>•), 182, 162, 73