Supporting Information for

A New Method for the Synthesis of Difluormethyl Enol Ethers by O-Difluoromethylation of 1,3-Diones with ClCF₂CO₂Et

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Synthesis of Substrates.

1,3-Cyclohexanediione (12.5 mmol) was dissolved in 5 M aqueous NaOH (2.5 ml, 12.5 mmol) at 0 °C. Benzyl bromide (18.8 mmol) was added to the resulting solution in one portion. The ice bath was removed and the mixture was heated at 65 °C for 24 h, then allowed to cool to room temperature. The solid was filtered, and washed with petroleum ether (5 mL × 3), cold water (5 mL × 3) and diethyl ether (5 mL × 3). The product was dried under vacuo.

4-((2,5-Dioxocyclopentyl)methyl)benzonitrile (1d)

Obtained as a white solid in 84% yield (2.2 g). 1H NMR (400 MHz, CD3OD) δ 7.60 (d, J = 8.0 Hz, 2H), 7.40 (d, J = 7.9 Hz, 2H), 3.52 (s, 2H), 2.55 (s, 4H). 13C NMR (101 MHz, CD3OD) δ 146.4 (s), 132.5 (s), 129.6 (s), 119.5 (s), 114.8 (s), 109.0 (s), 27.2 (s). IR (KBr) ν 2923, 2226, 1846, 1604, 1553, 1262, 1238, 1163, 858, 822, 662, 581, 550, 496, 434 cm⁻¹. HRMS (ESI) calcd for C13H11NO2: 214.0863; Found: 214.0860.

2-(4-Methylbenzyl)cyclohexane-1,3-dione (1h)

Obtained as a white solid in 86% yield (2.3 g). 1H NMR (400 MHz, CD3OD) δ 7.06 (d, J = 7.8 Hz, 2H), 6.97 (d, J = 7.8 Hz, 2H), 3.51 (s, 2H), 2.42 (t, J = 5.9 Hz, 4H), 2.24 (s, 3H), 1.99 – 1.89 (m, 2H). 13C NMR (101 MHz, CD3OD) δ 138.5 (s), 134.2 (s), 128.1 (s), 128.0 (s), 115.4 (s), 26.5 (s), 20.6 (s), 19.7 (s). IR (KBr) ν 3131, 2948, 1658, 1513, 1422, 1375, 1322, 1282, 1257, 1174, 1140, 1104, 1066, 1006, 807, 781, 759 cm⁻¹. HRMS (ESI) calcd for C14H16O2: 217.1223; Found: 217.1219.
*O*-Difluoromethylation of 4,4-Dimethylcyclohexane-1,3-dione.

\[ 1s + \text{ClCF}_2\text{CO}_2\text{Et} \xrightarrow{\text{NaOH, DMF, 60 °C}} 3s \]

\[ 3s \text{ 74\%, 7:10} \]

$^{19}$F NMR spectrum of 3s (two regio-isomers) in CDCl$_3$
$^1$H NMR spectrum of 3s (two regio-isomers) in CDCl$_3$

GC-MS of 3s (two regio-isomers)
Copies of $^1$H NMR, and $^{13}$C NMR Spectra for Substrates 1d and 1h

$^1$H NMR spectrum of 1d in CD$_3$OD

$^{13}$C NMR spectrum of 1d in CD$_3$OD
$^1$H NMR spectrum of 1h in CD$_3$OD

$^{13}$C NMR spectrum of 1h in CD$_3$OD
Copies of $^1$H NMR, $^{19}$F NMR and $^{13}$C NMR Spectra for Compounds 3a-r

$^{19}$F NMR spectrum of 3a in CDCl$_3$

$^1$H NMR spectrum of 3a in CDCl$_3$
$^{13}$C NMR spectrum of 3a in CDCl$_3$

$^{19}$F NMR spectrum of 3b in CDCl$_3$
$^{1}$H NMR spectrum of 3b in CDCl$_3$

$^{13}$C NMR spectrum of 3b in CDCl$_3$
$^{19}$F NMR spectrum of 3c in CDCl$_3$

$^1$H NMR spectrum of 3c in CDCl$_3$
$^{13}$C NMR spectrum of 3c in CDCl$_3$

$^{19}$F NMR spectrum of 3d in CDCl$_3$
$^1$H NMR spectrum of 3d in CDCl$_3$

$^{13}$C NMR spectrum of 3d in CDCl$_3$
$^{19}$F NMR spectrum of 3e in CDCl$_3$

$^{1}$H NMR spectrum of 3e in CDCl$_3$
$^{13}$C NMR spectrum of 3e in CDCl$_3$

$^{19}$F NMR spectrum of 3f in CDCl$_3$
$^1$H NMR spectrum of 3f in CDCl$_3$

$^{13}$C NMR spectrum of 3f in CDCl$_3$
$^{19}$F NMR spectrum of 3g in CDCl$_3$

$^1$H NMR spectrum of 3g in CDCl$_3$
$^{13}$C NMR spectrum of 3g in CDCl$_3$

$^{19}$F NMR spectrum of 3h in CDCl$_3$
$^1$H NMR spectrum of 3h in CDCl$_3$

$^{13}$C NMR spectrum of 3h in CDCl$_3$
$^{19}$F NMR spectrum of 3i in CDCl$_3$

$^1$H NMR spectrum of 3i in CDCl$_3$
$^{13}$C NMR spectrum of 3i in CDCl$_3$

$^{19}$F NMR spectrum of 3j in CDCl$_3$
$^1$H NMR spectrum of 3j in CDCl$_3$

$^{13}$C NMR spectrum of 3j in CDCl$_3$
$^{19}\text{F}$ NMR spectrum of $3k$ in CDCl$_3$

![$^{19}\text{F}$ NMR spectrum of $3k$ in CDCl$_3$](image)

$^1\text{H}$ NMR spectrum of $3k$ in CDCl$_3$

![$^1\text{H}$ NMR spectrum of $3k$ in CDCl$_3$](image)
$^{13}$C NMR spectrum of 3k in CDCl$_3$

F NMR spectrum of 3l in CDCl$_3$
$^1$H NMR spectrum of 3l in CDCl$_3$

![H NMR spectrum](image)

$^{13}$C NMR spectrum of 3l in CDCl$_3$

![C NMR spectrum](image)
$^{19}$F NMR spectrum of 3m in CDCl$_3$

$^1$H NMR spectrum of 3m in CDCl$_3$
$^{13}$C NMR spectrum of 3m in CDCl$_3$

$^{19}$F NMR spectrum of 3n in CDCl$_3$
$^1$H NMR spectrum of 3n in CDCl$_3$

$^{13}$C NMR spectrum of 3n in CDCl$_3$
$^{19}$F NMR spectrum of $3o$ in CDCl$_3$

$^1$H NMR spectrum of $3o$ in CDCl$_3$
$^{13}$C NMR spectrum of 3o in CDCl$_3$

$^{19}$F NMR spectrum of 3p in CDCl$_3$
$^1$H NMR spectrum of 3p in CDCl$_3$

$^{13}$C NMR spectrum of 3p in CDCl$_3$

- 198.657
- 168.241
- 114.077
- 107.027
- 50.675
- 41.456
- 28.018
$^{19}$F NMR spectrum of 3q in CDCl$_3$

\[ \text{OCF}_2\text{H} \]

$^1$H NMR spectrum of 3q in CDCl$_3$

\[ \text{OCF}_2\text{H} \]
$^{13}$C NMR spectrum of $3q$ in CDCl$_3$

$^{19}$F NMR spectrum of $3r$ in CDCl$_3$
$^1$H NMR spectrum of 3r in CDCl$_3$

$^{13}$C NMR spectrum of 3r in CDCl$_3$