Regiodivergent Lewis-base promoted O- to C-carboxyl transfer of furanyl carbonates

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SUPPORTING INFORMATION

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1.1 General information

Reactions involving moisture sensitive reagents were carried out under an argon atmosphere using standard vacuum line techniques in addition to freshly distilled solvents. All glassware used was flame dried and cooled under vacuum.

Solvents (THF, CH₂Cl₂, toluene, hexane and Et₂O) were obtained anhydrous and purified by an alumina column (Mbraun SPS-800). Anhydrous CH₃CN was obtained by distillation over calcium hydride. Petrol is defined as petroleum ether 40-60 °C. All other solvents and commercial reagents were used as supplied without further purification unless stated otherwise.

Methylmagnesium bromide and phenylmagnesium bromide were both used as a 3M solution in Et₂O as supplied (Aldrich). Potassium bis(trimethylsilyl)amide (KHMDS) was used as a 0.5M solution in toluene as supplied (Aldrich). Hydrogen chloride was used as a 4M solution in dioxane as supplied (Aldrich). Sodium hydride refers to a 60% wt. dispersion in mineral oil as supplied (Aldrich) and was used unwashed.

Room temperature (rt) refers to 20-25 °C. Temperatures of 0 °C and -78 °C were obtained using ice/water and CO₂(s)/acetone baths respectively. Temperatures of 0 °C to -50 °C for overnight reactions were obtained using an immersion cooler (HAAKE EK 90). Reflux conditions were obtained using an oil bath equipped with a contact thermometer. In vacuo refers to the use of a Büchi Rotavapor R-2000 rotary evaporator with a Vacubrand CVC₂ vacuum controller or a Heidolph Laborota 4001 rotary evaporator with a vacuum controller.

Analytical thin layer chromatography was performed on pre-coated aluminium plates (Kieselgel 60 F₂₅₄ silica). TLC visualisation was carried out with ultraviolet light (254 nm), followed by staining with a 1% aqueous KMnO₄ solution. Flash column chromatography was performed on Kieselgel 60 silica in the solvent system stated.

⁻¹H and ¹³C nuclear magnetic resonance (NMR) spectra were acquired on either a Bruker Avance 300 (300 MHz, ¹H, 75 MHz ¹³C) or a Bruker Avance II 400 (400 MHz, ¹H, 100 MHz ¹³C) spectrometer at ambient temperature in the deuterated solvent stated. All chemical shifts are quoted in parts per million (ppm) relative to the residual solvent as the internal standard. All coupling constants, J, are quoted in Hz. Multiplicities are indicated by: s (singlet), d (doublet), t (triplet), q (quartet), ABq (AB quartet), sept (septet), oct (octet), m (multiplet), dd (doublet of doublets), ddd (doublet of doublet of doublets), dt (doublet of triplets) and td (triplet of doublets). The abbreviation Ar is used to denote aromatic, br to denote broad and app. to denote apparent.

Infrared spectra (νₘₐₓ) were recorded on a Perkin-Elmer Spectrum GX FT-IR spectrometer using either thin films on NaCl plates or KBr discs. Only the characteristic peaks are quoted. Melting points were recorded on an Electrothermal apparatus and are uncorrected.
Mass spectrometry (m/z) data were acquired by electrospray ionisation (ESI), electron impact (EI) or nanospray ionisation (NSI) either at the University of St Andrews or the EPSRC National Mass Spectrometry Service Centre, Swansea. At the University of St Andrews, low and high resolution ESI MS were carried out on a Micromass LCT spectrometer. At the EPSRC National Mass Spectrometry Service Centre, low resolution NSI MS was carried out on a Micromass Quattro II spectrometer and high resolution NSI MS on a Thermofisher LTQ Orbitrap XL spectrometer.

The following furanyl carbonates were made according to the literature procedure:¹

\[
\begin{align*}
R^1 = \text{Ph}, R^2 = \text{Me}, R^3 = \text{Ph}, 5 & \quad R^1 = 4-\text{FC}_6\text{H}_4, R^2 = \text{Me}, R^3 = \text{Ph}, 17 \\
R^1 = \text{Me}, R^2 = \text{Ph}, R^3 = \text{Ph}, 11 & \quad R^1 = 4-\text{FC}_6\text{H}_4, R^2 = \text{Me}, R^3 = \text{CH}_2\text{CCl}_3, 18 \\
R^1 = \text{Ph}, R^2 = \text{Bn}, R^3 = \text{Ph}, 12 & \quad R^1 = 4-\text{FC}_6\text{H}_4, R^2 = \text{Bn}, R^3 = \text{Ph}, 19 \\
R^1 = \text{Ph}, R^2 = \text{Bn}, R^3 = \text{CH}_2\text{CCl}_3, 13 & \quad R^1 = 4-\text{FC}_6\text{H}_4, R^2 = \text{Et}, R^3 = \text{Ph}, 20 \\
R^1 = \text{Ph}, R^2 = \text{Et}, R^3 = \text{Ph}, 14 & \quad R^1 = 4-\text{FC}_6\text{H}_4, R^2 = 4-\text{BrC}_6\text{H}_4, R^3 = \text{Ph}, 21 \\
R^1 = \text{Ph}, R^2 = 4-\text{BrC}_6\text{H}_4, R^3 = \text{Ph}, 15 & \quad R^1 = 4-\text{FC}_6\text{H}_4, R^2 = \text{Allyl}, R^3 = \text{Ph}, 22 \\
R^1 = \text{Ph}, R^2 = \text{Allyl}, R^3 = \text{Ph}, 16
\end{align*}
\]

1.2 General Experimental Procedures

**General procedure A: DMAP-promoted rearrangement.**

To a solution of carbonate (1 equiv.) in THF (~1 mL per 100 mg of carbonate) was added DMAP (10 mol%). The mixture was stirred for 5 min and then concentrated *in vacuo*.

**General procedure B: NHC-promoted rearrangement.**

To a solution of carbonate (1 equiv.) in THF (~1 mL per 100 mg of carbonate) was added the requisite triazolium salt (1 or 10 mol%) and finally KHMDS (0.9 or 9 mol%). The mixture was stirred for 1 min to 5 min and then concentrated *in vacuo*.

1.3 Experimental Procedures and Characterization Data

**phenyl 3-methyl-2-oxo-5-phenyl-2,3-dihydrofuran-3-carboxylate**

Following general procedure A, carbonate 5 (100 mg, 0.34 mmol) and DMAP (4.22 mg, 0.034 mmol) in THF (1 mL) for 5 min gave a ratio of products (α:γ 60:40). Chromatographic purification (eluent Et₂O:petrol 20:80) gave 6 (60.0 mg, 60%) as a colorless solid with spectroscopic data in accordance with the literature.² mp 61 °C {Lit.¹ mp 62-64 °C}; δH (400 MHz, CDCl₃) 1.82 (3H, s, CH₃), 6.03 (1H, s, C(4)H), 7.11-7.12 (2H, m, ArH), 7.24-7.27 (1H, m, ArH), 7.37-7.40 (2H, m, ArH), 7.46-7.48 (3H, m, ArH) and 7.69-7.71 (2H, m, ArH).
phenyl 4-methyl-5-oxo-2-phenyl-2,5-dihydrofuran-2-carboxylate

Following general procedure B, carbonate 5 (200 mg, 0.68 mmol), triazolium BF₄ salt precursor to 8 (14.1 mg, 0.068 mmol) and KHMDS (0.122 mL, 0.061 mmol) in THF (1 mL) for 5 min gave a ratio of products (α:γ 16:84). Chromatographic purification (eluent Et₂O:petrol 20:80) gave 7 (144 mg, 72%) as a colorless oil with spectroscopic data in accordance with the literature.

δ_H (400 MHz, CDCl₃) 1.99 (3H, s, CH₃), 6.98-7.00 (2H, m, ArH), 7.18-7.20 (1H, m, ArH), 7.30-7.34 (2H, m, ArH) 7.39-7.44 (3H, m, ArH) and 7.55-7.58 (3H, m, C(3)H and ArH).

Following general procedure B, carbonate 5 (200 mg, 0.68 mmol), triazolium BF₄ salt precursor to 8 (1.41 mg, 6.80 µmol) and KHMDS (12.2 µL, 6.12 µmol) in THF (1 mL) for 5 min gave a ratio of products (α:γ <2:98). Chromatographic purification (eluent Et₂O:petrol 20:80) gave 7 (170 mg, 85%) as a colorless oil. Data are in accordance with those given previously.

phenyl 3-benzyl-2-oxo-5-phenyl-2,3-dihydrofuran-3-carboxylate

Following general procedure A, carbonate 12 (100 mg, 0.34 mmol) and DMAP (4.22 mg, 0.034 mmol) in THF (1 mL) for 5 min gave a ratio of products (α:γ 64:36). Chromatographic purification (eluent Et₂O:petrol 10:90) gave 23 (45.2 mg, 45%) as a colorless solid with spectroscopic data in accordance with the literature. mp 110-112 °C; δ_H (400 MHz; CDCl₃) 3.49 (1H, ABq, J 13.6, CHH), 3.64 (1H, ABq, J 13.6, CHH), 5.96 (1H, s, C(4)H), 7.04-7.08 (2H, m, ArH), 7.22-7.27 (6H, m, ArH), 7.35-7.40 (5H, m, ArH) and 7.53-7.57 (2H, m, ArH).
phenyl 4-benzyl-5-oxo-2-phenyl-2,5-dihydrofuran-2-carboxylate

Following general procedure B, carbonate 12 (200 mg, 0.54 mmol), triazolium BF₄ salt precursor to 8 (14.7 mg, 0.054 mmol) and KHMDS (0.097 mL, 0.49 mmol) in THF (1 mL) for 5 min gave a ratio of products (α:γ 19:81). Chromatographic purification (eluent Et₂O:petrol 20:80) gave 24 (134 mg, 67%) as a colorless oil; IR (thin film) ν max/cm⁻¹: 1773 (C=O), 1761 (C=O), 1647 (Ar C=C), 1493, 1451, 1189 (C–O), 1053, 1025, 734 and 676; δH (400 MHz, CDCl₃) 3.67 (1H, ABq, J 16.9, 1.6, CHH), 3.72 (1H, ABq, J 16.9, 1.6, CHH), 6.97–7.01 (2H, m, ArH), 7.21–7.38 (9H, m, ArH and C(3)H), 7.41–7.46 (3H, m, ArH) and 7.53–7.56 (2H, m, ArH); δC (100 MHz, CDCl₃) 32.0, 87.9, 121.0, 126.0, 126.7, 127.3, 129.1, 129.2, 129.7, 135.2, 135.4, 136.6, 147.1, 150.3, 166.1 and 171.3; m/z (ESI⁺) 388 (100, [M+NH₄]⁺); HRMS (ESI⁺) C₂₄H₂₂NO₄⁺ ([M+NH₄]⁺) requires 388.1543, found 388.1543 (-0.1 ppm).

Following general procedure B, carbonate 12 (200 mg, 0.54 mmol), triazolium BF₄ salt precursor to 8 (1.47 mg, 5.40 µmol) and KHMDS (9.72 µL, 4.86 µmol) in THF (1 mL) for 1 min gave a ratio of products (α:γ 4:96). Chromatographic purification (eluent Et₂O:petrol 20:80) gave 24 (134 mg, 67%) as a colorless oil. Data are in accordance with those given previously.

3-benzyl-5-phenylfuran-2-yl (1,1,1-trichloro-2-methylpropan-2-yl) carbonate

To a solution of 3-benzyl-5-phenylfuran-2(5H)-one¹ (0.80 g, 3.20 mmol) in THF (15 mL) at 0 °C was added triethylamine (0.89 mL, 6.40 mmol) and 1,1,1-trichloro-2-methylpropan-2-yl carbonochloridate (1.54 g, 6.40 mmol). After 30 min at rt the reaction mixture was poured into 0.5M HCl, and extracted with Et₂O (x 3). The organic fraction was washed with brine, dried (MgSO₄), filtered and concentrated in vacuo. Chromatographic purification (15:85, CH₂Cl₂/petrol) gave carbonate 25 (0.81 g, 55%) as a colorless solid; mp 78-80 °C; IR (KBr) ν max/cm⁻¹: 2954, 1786 (C=O), 1234, 1153 (C=O), 801 and 694; δH (300 MHz; CDCl₃) 2.00 (6H, s, (CH₃)₂), 3.74 (2H, s, CH₂), 6.46 (1H, s, C(4)H), 7.22-7.38 (8H, m, ArH) and 7.56-7.59 (2H, m, ArH); δC (75 MHz, CDCl₃): 21.1, 30.0, 92.0, 104.8, 107.7, 108.6, 123.4, 126.5, 127.5, 128.7, 128.8, 130.2, 129.2, 146.4, 147.4 and 149.1; m/z (ES⁺) 470.1 (39,

S5
[M+NH$_4^+$] and 453.0 (100, [M+H]$^+$); HRMS (ES$^+$) C$_{22}$H$_{10}$O$_4$Cl$_3^+$ required 453.0422, found 453.0422 (+0.1 ppm).

1,1,1-trichloro-2-methylpropan-2-yl 3-benzyl-2-oxo-5-phenyl-2,3-dihydrofuran-3-carboxylate

Following general procedure A, carbonate 25 (91.0 mg, 0.20 mmol) and DMAP (2.40 mg, 0.02 mmol) in THF (0.9 mL) for 15 min gave a ratio of products ($\alpha$:$\gamma$ 62:38). Chromatographic purification (eluent CH$_2$Cl$_2$:petrol 50:50 to 100% CH$_2$Cl$_2$) gave the alpha product 26 (51.0 mg, 56%) as a colorless solid and the gamma product (26.0 mg, 26%) as a pale yellow oil. Data for alpha product 26; mp 132-134 ºC; IR (KBr) $\nu_{max}$/cm$^{-1}$: 2938, 1792 (C=O), 1742 (C=O), 1233, 795 and 765; $\delta$$_H$ (300 MHz, CDCl$_3$) 1.88 (3H, s, CH$_3$), 1.92 (3H, s, CH$_3$), 3.38 (1H, ABq, $J$ 13.6, CH$_2$), 3.50 (1H, ABq, $J$ 13.6, CH$_2$), 5.80 (1H, s, C(4)H), 7.18-7.25 (5H, m, ArH), 7.34-7.36 (3H, m, ArH) and 7.46-7.49 (2H, m, ArH); $\delta$$_C$ (75 MHz, CDCl$_3$): 21.3, 21.4, 40.2, 62.7, 90.8, 101.8, 105.5, 125.3, 127.6, 127.7, 128.6, 128.8, 130.1, 130.3, 134.4, 154.3, 154.5, 165.3 and 172.9; m/z (ES$^+$) 470.1 (100, [M+NH$_4^+$]$^+$) and 453.0 (5, [M+H]$^+$); HRMS (ES$^+$) C$_{22}$H$_{23}$O$_4$NCl$_3^+$ required 470.0687, found 470.0687 (+0 ppm).

1,1,1-trichloro-2-methylpropan-2-yl 4-benzyl-5-oxo-2-phenyl-2,5-dihydrofuran-2-carboxylate

Following general procedure B, carbonate 25 (91.0 mg, 0.20 mmol), triazolium BF$_4$ salt precursor to 8 (5.50 mg, 0.02 mmol) and KHMDS (0.036 mL, 0.18 mmol) in THF (0.9 mL) for 5 min gave a ratio of products ($\alpha$:$\gamma$ 4:96). Chromatographic purification (eluent 100% CH$_2$Cl$_2$) gave 27 (72.8 mg, 80%) as a pale yellow oil; IR (thin film) $\nu_{max}$/cm$^{-1}$: 2923, 1776 (broad, 2 $\times$ C=O), 1452, 1152 (C-O), 1032, 791 and 697; $\delta$$_H$ (300 MHz, CDCl$_3$): 1.80 (3H, s, CH$_3$), 1.88 (3H, s, CH$_3$), 3.60 (1H, ABq, $J$ 16.9, 1.7, CH$_2$), 3.70 (1H, ABq, $J$ 16.9, 1.6, CH$_2$), 7.21-7.24 (3H, m, ArH), 7.27-7.32 (2H, m, ArH), 7.35 (1H, app. t, $J$ 2.0, C(3)H), 7.37-7.41 (3H, m, ArH) and 7.47-7.51 (2H, m, ArH); $\delta$$_C$ (75 MHz, CDCl$_3$): 21.1, 21.4, 31.9, 88.1, 91.1, 105.3, 126.1, 127.2, 128.9, 129.0, 129.0, 129.5, 134.9, 135.2, 136.6, 146.9, 164.8 and
m/z (ES+) 470.1 (100, [M+NH₄]⁺) and 453.0 (8, [M+H]⁺); HRMS (ES+) C₁₂H₂₃O₄NCl₃⁺ required 470.0687, found 470.0679 (-1.7 ppm).

Following general procedure B, carbonate 25 (91.0 mg, 0.20 mmol), triazolium BF₄ salt precursor to 8 (0.55 mg, 2.00 µmol) and KHMDS (3.6 µL, 1.80 µmol) in THF (1 mL) for 1 min gave a ratio of products (α:γ 1:99). Chromatographic purification (eluent 100% CH₂Cl₂) gave 27 (82.8 mg, 91%) as a pale yellow oil. Data are in accordance with those given previously.

2,2,2-trichloroethyl 3-benzyl-2-oxo-5-phenyl-2,3-dihydrofuran-3-carboxylate

Following general procedure A, carbonate 13 (85.0 mg, 0.20 mmol) and DMAP (2.40 mg, 0.02 mmol) in THF (0.9 mL) for 15 min gave a ratio of products (α:γ 54:46). Chromatographic purification (eluent CH₂Cl₂:petrol 50:50 to 100% CH₂Cl₂) gave the alpha product 28 (37.6 mg, 44%) as a colorless solid and the gamma product (31.3 mg, 37%) as a colorless solid. Data for the alpha product 28; Spectroscopic data in accordance with the literature.¹ mp 110-112 °C {Lit.¹ mp 110-112 °C}; δH (300 MHz; CDCl₃) 3.45 (1H, ABq, J 13.6, CH₃H), 3.56 (1H, ABq, J 13.6, CCHH), 4.75 (1H, ABq, J 11.9, OCHH), 4.88 (1H, ABq, J 11.9, OCHH), 5.84 (1H, s, C(4)H), 7.18-7.26 (5H, m, ArH), 7.35-7.39 (3H, m, ArH) and 7.48-7.51 (2H, m, ArH).

2,2,2-trichloroethyl 4-benzyl-5-oxo-2-phenyl-2,5-dihydrofuran-2-carboxylate

Following general procedure B, carbonate 13 (85.0 mg, 0.20 mmol), triazolium BF₄ salt precursor to 8 (5.50 mg, 0.20 mmol) and KHMDS (0.036 mL, 0.018 mmol) in THF (0.9 mL) for 5 min gave a ratio of products (α:γ 5:95). Chromatographic purification (eluent 100% CH₂Cl₂) gave 29 (60.4 mg, 71%) as a colorless solid with spectroscopic data in accordance with the literature.¹ mp 94-96 °C {Lit.¹ mp 94-96 °C}; δH (400 MHz; CDCl₃) 3.62 (1H, ABq, J 16.9, 1.7, CHH), 3.69 (1H, ABq, J 16.9, 1.6, CHH), 4.71 (1H, ABq, J 11.9, OCHH), 4.82 (1H, ABq, J 11.8, OCHH), 7.22-7.24 (2H, m, ArH), 7.27-7.30 (2H, m, C(3)H and ArH), 7.32-7.36 (2H, m, ArH), 7.39-7.41 (3H, m, ArH) and 7.48-7.51 (2H, m, ArH).
Following general procedure B, carbonate 13 (85.0 mg, 0.20 mmol), triazolium BF₄ salt precursor to 8 (0.55 mg, 2.0 µmol) and KHMDS (4.00 µL, 1.80 µmol) in THF (0.9 mL) for 1 min gave a ratio of products (α:γ 1:99). Chromatographic purification (eluent 100% CH₂Cl₂) gave 29 (72.8 mg, 86%) as a colorless solid. Data are in accordance with those given previously.

phenyl 3-ethyl-2-oxo-5-phenyl-2,3-dihydrofuran-3-carboxylate

Following general procedure A, carbonate 14 (61.7 mg, 0.20 mmol) and DMAP (2.40 mg, 0.02 mmol) in THF (0.7 mL) for 5 min gave a ratio of products (α:γ 47:53). Chromatographic purification (eluent CH₂Cl₂:petrol 50:50) gave 30 (20.0 mg, 32%) as a sticky colorless solid with spectroscopic data in accordance with the literature. δH (300 MHz; CDCl₃) 1.05 (3H, t, J 7.5, C₃H₃), 2.30 (2H, q, J 7.5, C₂H₂), 5.96 (1H, s, C(4)H), 7.09 (2H, dd, J 8.6, 1.1, ArH), 7.22-7.26 (1H, m, ArH), 7.37 (2H, t, J 7.9, ArH), 7.44-7.47 (3H, m, ArH) and 7.68-7.71 (2H, m, ArH).

phenyl 4-ethyl-5-oxo-2-phenyl-2,5-dihydrofuran-2-carboxylate

Following general procedure B, carbonate 14 (61.7 mg, 0.20 mmol), triazolium BF₄ salt precursor to 8 (5.50 mg, 0.02 mmol) and KHMDS (0.036 mL, 0.018 mmol) in THF (0.9 mL) for 5 min gave a ratio of products (α:γ 21:79). Chromatographic purification (eluent 100% CH₂Cl₂) gave 31 (33.3 mg, 54%) as a colorless oil; IR (KBr) νmax/cm⁻¹: 2974, 1777 (broad, 2×C=O), 1493, 1191 (C-O), 1027, 965, 736 and 689; δH (400 MHz, CDCl₃) 1.24 (3H, t, J 7.4, CH₃), 2.34-2.49 (2H, m, CH₂), 7.02-7.04 (2H, m, ArH), 7.22-7.26 (1H, m, ArH), 7.34-7.38 (2H, m, ArH), 7.42-7.48 (3H, m, ArH), 7.54 (1H, t, J 1.8, C(3)H) and 7.60-7.63 (2H, m, ArH); δC (100 MHz, CDCl₃): 11.7, 19.0, 87.7, 121.0, 125.9, 126.6, 129.2, 129.6, 129.7, 135.4, 136.9, 145.2, 150.3, 166.2 and 171.6; m/z (ES⁺) 326.1 (100, [M+NH₄]⁺) and 309.1 (12, [M+H]⁺); HRMS (ES⁺) C₁₉H₂₀O₃N⁺ required 326.1387, found 326.1389 (+0.7 ppm).
Following general procedure B, carbonate 14 (61.7 mg, 0.20 mmol), triazolium BF$_4$ salt precursor to 8 (0.55 mg, 2.0 µmol) and KHMDS (4.00 µL, 1.80 µmol) in THF (0.9 mL) for 1 min gave a ratio of products (α:γ 1:99). Chromatographic purification (eluent 100% CH$_2$Cl$_2$) gave 31 (44.0 mg, 71%) as a colorless oil. Data are in accordance with those given previously.

**phenyl 3-(4-bromobenzyl)-2-oxo-5-phenyl-2,3-dihydrofuran-3-carboxylate**

Following general procedure A, carbonate 15 (60.2 mg, 0.134 mmol) and DMAP (1.61 mg, 0.0134 mmol) in THF (1 mL) for 5 min gave a ratio of products (α:γ 53:47). Chromatographic purification (eluent CH$_2$Cl$_2$:petrol 50:50) gave 32 (25.9 mg, 43%) as a colorless solid with spectroscopic data in accordance with the literature.$^1$ mp 150-152 °C (Lit.$^1$ mp 150-152 °C); δ$_{H}$ (400 MHz; CDCl$_3$) 3.46 (1H, ABq, $J$ 13.7, CH$_2$H), 3.58 (1H, ABq, $J$ 13.7, CHH), 5.94 (1H, s, C(4)H), 7.06–7.09 (2H, m, ArH), 7.12–7.16 (2H, m, ArH), 7.26–7.29 (1H, m, ArH), 7.37–7.43 (7H, m, ArH) and 7.56–7.59 (2H, m, ArH).

**phenyl 4-(4-bromobenzyl)-5-oxo-2-phenyl-2,5-dihydrofuran-2-carboxylate**

Following general procedure A, carbonate 15 (60.2 mg, 0.134 mmol), triazolium BF$_4$ salt precursor to 8 (3.65 mg, 0.0134 mmol) and KHMDS (0.024 mL, 0.012 mmol) in THF (1 mL) for 5 min gave a ratio of products (α:γ 10:90). Chromatographic purification (eluent 100% CH$_2$Cl$_2$) gave 33 (48.0 mg, 80%) as a colorless oil; IR ν$_{max}$ (thin film) /cm$^{-1}$ 3107, 3057, 1804 (C=O), 1760 (C=O), 1652, 1591 (C=C), 1490, 1406, 1281, 1188 (C-O), 1126, 1072, 1013, 94, 833, 755 and 688 (C-Br); δ$_{H}$ (400 MHz, CDCl$_3$) 3.62 (1H, ABq, $J$ 16.9, 1.5, CH$_2$H), 3.67 (1H, ABq, $J$ 16.9, 1.5, CHH), 7.00–6.98 (2H, m, ArH), 7.14 (2H, app d, $J$ 8.4, ArH), 7.24–7.20 (1H, m, ArH), 7.38–7.35 (3H, m, ArH and C(3)H), 7.49–7.43 (2H, m, ArH), 7.56–7.54 (5H, m, ArH); δ$_C$ (100 MHz, CDCl$_3$) 31.4, 88.0, 121.0, 121.3, 125.9, 126.7, 129.3, 129.7, 129.8, 130.8, 132.2, 134.7, 135.0, 135.5, 147.4, 150.3, 165.9 and 171.1; $m/z$ MS (ESI$^+$) 449 (100,
\[ \text{[} \text{Br}^\text{79} \text{M} + \text{H}]^+ \text{) and 451 (98, [} \text{Br}^\text{81} \text{M} + \text{H}]^+ \text{); HRMS (ESI+)} \quad \text{C}_{24} \text{H}_{18} \text{BrO}_4^+ \quad \text{([} \text{Br}^\text{79} \text{M} + \text{H}]^+) \text{ requires 449.0383, found 449.0378, (-1.1 ppm).} \]

**phenyl 3-allyl-2-oxo-5-phenyl-2,3-dihydrofuran-3-carboxylate**

![structure](image)

Following general procedure A, carbonate 16 (64.0 mg, 0.20 mmol) and DMAP (2.40 mg, 0.03 mmol) in THF (0.6 mL) for 5 min gave a ratio of products (α:γ 61:39). Chromatographic purification (eluent CH\(_2\)Cl\(_2\):petrol 50:50 then 100% CH\(_2\)Cl\(_2\)) gave the alpha product 34 (34.5 mg, 54%) as a colorless oil and the gamma product (20.5 mg, 32%) as a colorless oil. Data for the alpha product 34; Spectroscopic data in accordance with the literature.\(^1\) δ\(_{\text{H}}\) (400 MHz; CDCl\(_3\)) 2.92 (1H, ABq, J 13.9, J 7.9, CH\(_{\text{H}}\)), 3.05 (1H, ABq, J 13.9, J 6.8, CH\(_{\text{H}}\)), 5.20-5.22 (1H, m, =CH\(_{\text{H}}\)), 5.28 (1H, app. dd, J 17.0, 1.4, =CHH), 5.75-5.85 (1H, m, CH=CH\(_2\)), 5.98 (1H, s, C(4)H), 7.08-7.10 (2H, m, Ar\(_{\text{H}}\)), 7.22-7.26 (1H, m, Ar\(_{\text{H}}\)), 7.35-7.39 (2H, m, Ar\(_{\text{H}}\)), 7.43-7.46 (3H, m, Ar\(_{\text{H}}\)) and 7.67-7.69 (2H, m, Ar\(_{\text{H}}\)).

**phenyl 4-allyl-5-oxo-2-phenyl-2,5-dihydrofuran-2-carboxylate**

![structure](image)

Following general procedure B, carbonate 16 (64.0 mg, 0.20 mmol), triazolium BF\(_4\) salt precursor to 8 (5.50 mg, 0.02 mmol) and KHMDS (0.036 mL, 0.018 mmol) in THF (0.7 mL) for 5 min gave a ratio of products (α:γ 31:69). Chromatographic purification (eluent 100% CH\(_2\)Cl\(_2\)) gave the alpha product (15.3 mg, 24%) as a colorless oil and the gamma product 35 (32.1 mg, 50%) as a colorless oil. Data for the gamma product 35; Spectroscopic data in accordance with the literature.\(^1\) δ\(_{\text{H}}\) (400 MHz; CDCl\(_3\)) 3.08-3.19 (2H, m, CH\(_2\)), 5.21 (1H, t, J 1.3, =CH\(_{\text{H}}\)), 5.23-5.25 (1H, m, =CHH), 5.85-5.98 (1H, m, CH=CH\(_2\)), 7.02-7.04 (2H, m, Ar\(_{\text{H}}\)), 7.22-7.26 (1H, m, Ar\(_{\text{H}}\)), 7.34-7.38 (2H, m, Ar\(_{\text{H}}\)), 7.43-7.48 (3H, m, Ar\(_{\text{H}}\)), 7.58 (1H, t, J 1.7, C(3)H) and 7.59-7.62 (2H, m, Ar\(_{\text{H}}\)).

Following general procedure B, carbonate 16 (64.0 mg, 0.20 mmol), triazolium BF\(_4\) salt precursor to 8 (0.55 mg, 2.00 µmol) and KHMDS (3.6 µL, 1.80 µmol) in THF (0.7 mL) for 1 min gave a ratio of products (α:γ 6:94). Chromatographic purification (eluent 100% CH\(_2\)Cl\(_2\))
gave 35 (52.0 mg, 81%) as a colorless oil. Data are in accordance with those given previously.

**Phenyl 5-(4-fluorophenyl)-3-methyl-2-oxo-2,3-dihydrofuran-3-carboxylate**

![Chemical structure of 36]

Following general procedure A, carbonate 17 (100 mg, 0.32 mmol) and DMAP (3.92 mg, 0.032 mmol) in THF (1 mL) for 5 min gave a ratio of products (α:γ 71:29). Chromatographic purification (eluent CH₂Cl₂:petrol 70:30) gave alpha product 36 (52.0 mg, 52%) as a colorless solid with spectroscopic data in accordance with the literature.

1°mp 42-44 °C \(\text{Lit.}^1\) mp 42-44 °C; \(\delta_H\) (400 MHz, CDCl₃) 1.71 (3H, s, C₃H₃), 5.86 (1H, s, C(4)H), 7.00-7.09 (4H, m, ArH), 7.14-7.18 (1H, m, ArH), 7.27-7.31 (2H, m, ArH), 7.57-7.61 (2H, m, ArH).

**Phenyl 2-(4-fluorophenyl)-4-methyl-5-oxo-2,5-dihydrofuran-2-carboxylate**

![Chemical structure of 37]

Following general procedure B, carbonate 17 (100 mg, 0.32 mmol), triazolium BF₄ salt precursor to 8 (8.75 mg, 0.032 mmol) and KHMDS (0.058 mL, 0.029 mmol) in THF (1 mL) for 5 min gave a ratio of products (α:γ 12:88). Chromatographic purification (eluent 100% CH₂Cl₂) gave gamma product 37 (67.0 mg, 67%) as a colorless oil; \(\nu_{\text{max}}\) (thin film) 3532, 3084, 2960 (C-H), 1770 (C=O), 1660, 1603, 1509; \(\delta_H\) (400 MHz, CDCl₃) 1.95 (3H, d, \(J_{1,6}\)), 6.93-6.95 (2H, m, ArH), 7.03-7.08 (2H, m, ArH), 7.14-7.18 (1H, m, ArH), 7.26-7.30 (2H, m, ArH), 7.48-7.53 (3H, m, C(3)H and ArH); \(\delta_C\) (100 MHz, CDCl₃) 10.9, 87.0, 116.2 (d, \(J_{22.2}\)), 121.0, 126.7, 128.0 (d, \(J_{8.3}\)), 129.7, 131.3, 131.3, 146.3, 150.2, 163.2 (d, \(J_{248.2}\), 166.0, 171.9; \(m/z\) (NSI⁺) 330 ([M+NH₄]⁺, 100%); HRMS (NSI⁺) C₁₈H₁₇O₄NF⁺ ([M+NH₄]⁺) requires 330.1136; found 330.1137 (+0.3 ppm).

Following general procedure B, carbonate 17 (100 mg, 0.32 mmol), triazolium BF₄ salt precursor to 8 (0.875 mg, 3.2 µmol) and KHMDS (5.77 µL, 2.9 µmol) in THF (1 mL) for 1 min gave a ratio of products (α:γ 10:90). Chromatographic purification (eluent 100% CH₂Cl₂) gave 37 (71.0 mg, 71%) as a colorless oil. Data are in accordance with those given previously.
2,2,2-trichloroethyl 5-(4-fluorophenyl)-3-methyl-2-oxo-2,3-dihydrofuran-3-carboxylate

Following general procedure A, carbonate 18 (36.8 mg, 0.10 mmol) and DMAP (1.22 mg, 0.01 mmol) in THF (0.4 mL) for 5 min gave a ratio of products (α:γ 67:33). Chromatographic purification (eluent CH₂Cl₂:petrol 40:60) gave 38 (22.0 mg, 60%) as a colorless oil with spectroscopic data in accordance with the literature.¹ δH (500 MHz, CDCl₃) 1.69 (3H, s, CH₃), 4.67 (1H, ABq, J 11.9, CH₂), 4.80 (1H, ABq, J 11.9, CH₂), 5.77 (1H, s, C(4)H), 7.04-7.08 (2H, m, ArH), 7.54-7.57 (2H, m, ArH).

2,2,2-trichloroethyl 2-(4-fluorophenyl)-4-methyl-5-oxo-2,5-dihydrofuran-2-carboxylate

Following general procedure B, carbonate 18 (36.8 mg, 0.10 mmol), triazolium BF₄ salt precursor to 8 (2.73 mg, 0.01 mmol) and KHMDS (0.018 mL, 0.009 mmol) in THF (0.4 mL) for 5 min gave a ratio of products (α:γ 15:85). Chromatographic purification (eluent CH₂Cl₂:petrol 70:30) gave 39 (28.0 mg, 76%) as a colorless solid with spectroscopic data in accordance with the literature.¹ mp 84-86 °C {Lit.¹ mp 84-86 °C}; δH (500 MHz, CDCl₃) 1.94 (3H, d, J 1.5, CH₃), 4.69-4.74 (2H, m, CH₂), 7.02-7.05 (2H, m, ArH), 7.43-7.44 (1H, m, C(3)H), 7.46-7.49 (2H, m, ArH).

Phenyl 3-benzyl-5-(4-fluorophenyl)-2-oxo-2,3-dihydrofuran-3-carboxylate
Following general procedure A, carbonate 19 (50.0 mg, 0.13 mmol) and DMAP (1.58 mg, 0.013 mmol) in THF (1 mL) for 5 min gave a ratio of products (α:γ 71:29). Chromatographic purification (eluent CH₂Cl₂:petrol 50:50) gave 40 (28.0 mg, 56%) as a colorless solid with spectroscopic data in accordance with the literature.¹ mp 108-110 °C; δ (400 MHz, CDCl₃) 3.41 (1H, ABq, J 13.6, PhCH₂H), 3.55 (1H, ABq, J 13.6, PhCH₂H), 5.82 (1H, s, C(4)H), 6.98-7.02 (4H, m, ArH), 7.16-7.20 (6H, m, ArH), 7.28-7.32 (2H, m, ArH), 7.44-7.47 (2H, m, ArH).

**Phenyl 4-benzyl-2-(4-fluorophenyl)-5-oxo-2,5-dihydrofuran-2-carboxylate**

Following general procedure B, carbonate 19 (50 mg, 0.13 mmol), triazolium BF₄⁻ salt precursor to 8 (3.52 mg, 0.013 mmol) and KHMDS (0.023 mL, 0.012 mmol) in THF (1 mL) for 5 min gave a ratio of products (α:γ 20:80). Chromatographic purification (eluent CH₂Cl₂:petrol 70:30) gave 41 (28.0 mg, 56%) as a colorless solid; mp 78-80 °C; ν (KBr) 3087, 2924 (C-H), 1776 (C=O), 1655, 1602, 1509; δ (400 MHz, CDCl₃) 3.57-3.67 (2H, m, C(2)H₂Ph), 6.90-6.92 (2H, m, ArH), 7.03-7.07 (2H, m, ArH), 7.15-7.31 (9H, m, ArH and C(3)H), 7.44-7.48 (2H, m, ArH); δ (100 MHz, CDCl₃) 32.0, 87.4, 116.2 (d, J 21.9), 121.0, 126.7, 127.3, 128.0 (d, J 8.6), 128.9, 129.1, 129.7, 131.0 (d, J 3.0), 135.7, 136.4, 146.8, 150.2, 163.3 (d, J 248.3), 165.9 and 171.1; m/z (NSI⁺) 406 ([M+NH₄]⁺, 75%); HRMS (NSI⁺) C₂₄H₂₁O₄NF⁺ ([M+NH₄]⁺) requires 406.1449; found 406.1449 (-0.0 ppm).

Following general procedure B, carbonate 19 (50.0 mg, 0.13 mmol), triazolium BF₄⁻ salt precursor to 8 (0.352 mg, 1.29 µmol) and KHMDS (0.023 mL, 0.012 mmol) in THF (1 mL) for 1 min gave a ratio of products (α:γ 7:93). Chromatographic purification (eluent CH₂Cl₂:petrol 70:30) gave 41 (39.0 mg, 78%) as a colorless solid. Data are in accordance with those given previously.

**Phenyl 3-ethyl-5-(4-fluorophenyl)-2-oxo-2,3-dihydrofuran-3-carboxylate**

Following general procedure A, carbonate 20 (32.6 mg, 0.100 mmol) and DMAP (1.22 mg, 0.01 mmol) in THF (0.3 mL) for 5 min gave a ratio of products (α:γ 48:52). Chromatographic
purification (eluent CH$_2$Cl$_2$:petrol 50:50) gave 42 (15.0 mg, 46%) as a colorless solid with spectroscopic data in accordance with the literature.$^1$ mp 62-64 °C {Lit.$^1$ mp 62-64 °C}; δ$_H$ (400 MHz, CDCl$_3$) 0.98 (3H, t, $J$ 7.5, CH$_3$), 2.22 (2H, q, $J$ 7.5, CH$_2$CH$_3$), 5.82 (1H, s, C(4)H), 7.01-7.10 (4H, m, ArH), 7.15-7.19 (1H, m, ArH), 7.28-7.33 (2H, m, ArH), 7.59-7.63 (2H, m, ArH).

**phenyl 4-ethyl-2-(4-fluorophenyl)-5-oxo-2,5-dihydrofuran-2-carboxylate**

Following general procedure B, carbonate 20 (32.6 mg, 0.100 mmol), triazolium BF$_4$ salt precursor to 8 (2.73 mg, 0.01 mmol) and KHMD$S$ (0.018 mL, 0.009 mmol) in THF (0.3 mL) for 5 min gave a ratio of products ($\alpha$:$\gamma$ 20:80). Chromatographic purification (eluent CH$_2$Cl$_2$:petrol 70:30) gave 43 (20.0 mg, 61%) as a colorless solid; mp 44-46 °C; ν$_{\text{max}}$ (KBr) 3074, 2985 (C-H), 2944, 1769 (C=O), 1601, 1592, 1509; δ$_H$ (400 MHz, CDCl$_3$) 1.18 (3H, t, $J$ 7.5, CH$_3$), 2.30-2.38 (2H, CH$_2$CH$_3$), 6.94-6.97 (2H, ArH), 7.05-7.09 (2H, ArH), 7.16-7.20 (1H, ArH), 7.27-7.31 (2H, ArH), 7.44 (1H, CH(3)H), 7.51-7.55 (2H, ArH); δ$_C$ (100 MHz, CDCl$_3$) 11.7, 19.0, 87.2, 116.2 (d, $J$ 21.8), 121.0, 126.7, 128.0 (d, $J$ 8.5), 129.7, 131.3 (d, $J$ 3.3), 137.3, 144.9, 150.3, 163.2 (d, $J$ 248.2), 166.2 and 171.4; m/z (NSI$^+$) 344 ([M+NH$_4]^+$, 100%); HRMS (NSI$^+$) C$_{19}$H$_{19}$O$_4$NF$^+$ ([M+NH$_4]^+$) requires 344.1293; found 344.1294 (+0.4 ppm).

Following general procedure B, carbonate 20 (32.6 mg, 0.1 mmol), triazolium BF$_4$ salt precursor to 8 (0.27 mg, 1 µmol) and KHMD$S$ (1.8 µL, 0.9 µmol) in THF (0.3 mL) for 1 min gave a ratio of products ($\alpha$:$\gamma$ 4:96). Chromatographic purification (eluent CH$_2$Cl$_2$:petrol 70:30) gave 43 (27.0 mg, 83%) as a colorless solid. Data are in accordance with those given previously.

**phenyl 5-methyl-2-oxo-3-phenyl-2,3-dihydrofuran-3-carboxylate**

Following general procedure A, carbonate 11 (29.4 mg, 0.1 mmol) and DMAP (1.22 mg, 0.01 mmol) in THF (0.3 mL) for 5 min gave a ratio of products ($\alpha$:$\gamma$ 57:43). Chromatographic purification (eluent CH$_2$Cl$_2$:petrol 50:50) gave 44 (14.0 mg, 48%) as a colorless solid with
spectroscopic data in accordance with the literature.\textsuperscript{1} mp 56-58 °C \{Lit.\textsuperscript{1} mp 56-58 °C\}; $\delta_{\text{H}}$ (400 MHz, CDCl$_3$) 2.11 (3H, d, $J$ 1.5, CH$_3$), 5.72 (1H, q, $J$ 1.5, C(4)H), 6.97-7.00 (2H, m, ArH), 7.14-7.18 (1H, m, ArH), 7.26-7.38 (5H, m, ArH), 7.49-7.52 (2H, m, ArH).

\textbf{phenyl 2-methyl-5-oxo-4-phenyl-2,5-dihydrofuran-2-carboxylate}

\begin{center}
\includegraphics[width=0.2\textwidth]{45.png}
\end{center}

Following general procedure B, carbonate 11 (29.4 mg, 0.1 mmol), triazolium BF$_4$ salt precursor to 8 (2.73 mg, 0.01 mmol) and KHMDS (0.018 mL, 0.009 mmol) in THF (0.3 mL) for 5 min gave a ratio of products ($\alpha$:$\gamma$ 1:99). Chromatographic purification (eluent CH$_2$Cl$_2$:petrol 70:30) gave 45 (25.0 mg, 85%) as a colorless oil with spectroscopic data in accordance with the literature.\textsuperscript{1} $\delta_{\text{H}}$ (400 MHz, CDCl$_3$) 1.87 (3H, s, C(3)H), 7.01-7.05 (2H, m, ArH), 7.17-7.21 (1H, m, ArH), 7.29-7.39 (5H, m, ArH), 7.59 (1H, s, C(3)H), 7.83-7.86 (2H, m, ArH).

Following general procedure B, carbonate 11 (29.4 mg, 0.1 mmol), triazolium BF$_4$ salt precursor to 8 (0.27 mg, 1 µmol) and KHMDS (1.8 µL, 0.9 µmol) in THF (0.3 mL) for 1 h gave exclusively the $\gamma$ product. Chromatographic purification (eluent CH$_2$Cl$_2$:petrol 70:30) gave 45 (26.0 mg, 88%) as a colorless oil. Data are in accordance with those given previously.

\textbf{1.4 References and Notes:}


1.5 $^1$H and $^{13}$C NMR Spectra for Novel Compounds
S17
$^{1}H$ CDCl$_3$, 400 MHz
$^1$H, CDCl$_3$, 400 MHz