A simple and efficient synthesis of functionalized cyclic carbonate monomers using a versatile pentafluorophenyl ester intermediate.

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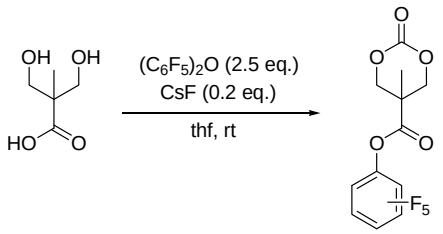
Supplemental Information

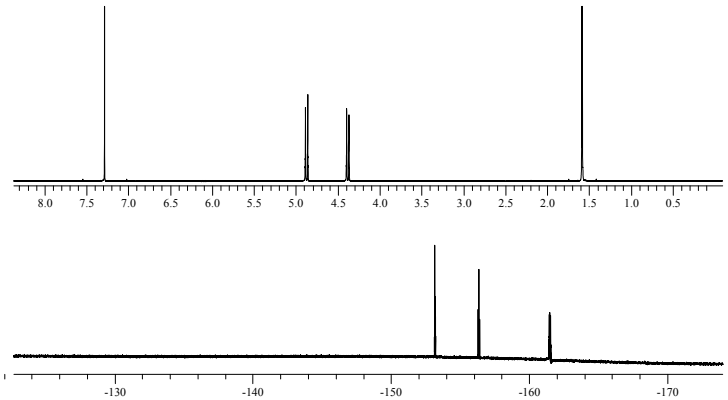
Materials: Reagents were available commercially from Aldrich and used as received unless otherwise noted. 2,2-Bis(hydroxymethyl)propionic acid (bis-MPA) and 2,2-bis(hydroxymethyl)butanoic acid (bis-MBA) were obtained from Perstorp (Sweden). Bis(pentafluorophenyl)carbonate (PFC) was obtained from Central Glass Co., Ltd. (Japan). 1-(3,5-bis(trifluoromethyl)phenyl)-3-cyclohexyl-2-thiourea (TU) was prepared as previously reported in Pratt *et al. Macromolecules* **2006**, *39*, 7863. Benzyl 2,2-bis(hydroxymethyl)propanoate (Bn-MPA) was prepared as previously reported in Pratt *et al. Chem. Commun.* **2008**, 114. TU and 4-pyrene-1-butanol (99%) were dried by stirring in dry THF with CaH_2, filtering, and removing the solvent *in vacuo*. 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (98%) was stirred over CaH_2, vacuum distilled, then stored over molecular sieves (3 Å).

Methods: Melting points of small molecules were determined with a capillary tube melting point apparatus and are uncorrected. ^{19}F-, ^{1}H- and $\{^{1}H\}^{13}C$-NMR spectra were obtained on a Bruker Avance 400 instrument using $CDCl_3$ solutions unless noted otherwise. Gel permeation chromatography (GPC) was performed in THF at 30 °C using a Waters chromatograph equipped with four 5 μm Waters columns (300 mm x 7.7 mm) connected in series with increasing pore size (10, 100, 1000, 10^5, 10^6 Å), a Waters 410 differential refractometer for refractive index (RI) detection and a 996 photodiode array detector, and calibrated with polystyrene standards (750 - (2 x 10^6) g/mol).

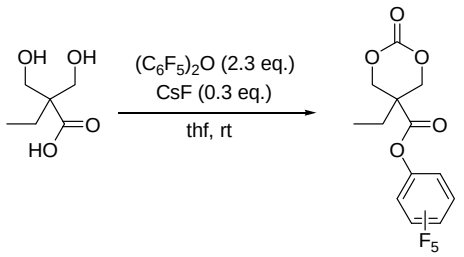
Synthesis: Preparation of pentafluorophenyl 5-methyl-2-oxo-1,3-dioxane-5-carboxylate (MTC-OPhF_5) (**1**).



A 100 mL round bottom flask was charged with 2,2-bis(hydroxymethyl)propionic acid (bis-MPA) (3.00 g, 22 mmol), bis-(pentafluorophenyl)carbonate (PFC) (21.70 g, 55 mmol, 2.5 eq.), CsF (0.7 g, 4.6 mmol, 0.2 eq.), and 70 mL of anhydrous tetrahydrofuran (THF). Initially the reaction was heterogeneous, but after one hour a clear homogeneous solution was formed that was allowed to stir for 20 hours. The solvent was removed *in vacuo*. The residue was re-dissolved in methylene chloride and, after 10 min, a byproduct precipitated and could be quantitatively recovered. This byproduct was identified as pentafluorophenol by ^{19}F NMR and GCMS (observed m/z: 184). The filtrate was extracted with sodium bicarbonate and water and was dried with $MgSO_4$. The solvent was evaporated *in vacuo* and the product was recrystallized from ethyl acetate/hexane mixture to give MTC-OPhF_5 as a white crystalline powder. Yield: 5.50 g (75 % yield). GCMS single peak, calc'd m/z for $C_{12}H_7F_5O_5$: 326, found: 326. ^1H NMR (400 MHz, $CDCl_3$): δ 4.85 (d, J = 10.8 Hz, 2H, CH_aH_b), 4.36 (d, J = 10.8 Hz, 2H, CH_aH_b), 1.55 (s, 3H, CCH_3). ^{19}F NMR (376 MHz, $CDCl_3$) ($CFCl_3$=0 ppm): δ -154.0~154.1 (m, 2F), -157.3 (t, 1F, J = 2Hz), -162.4~162.5 (m, 2F). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 167.9, 146.8, 142.2~136.7(m, 5C), 128.0, 72.4(2C), 41.0, 17.5.

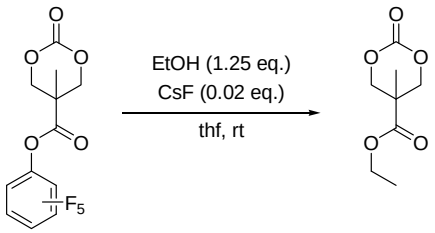


Preparation of pentafluorophenyl 5-ethyl-2-oxo-1,3-dioxane-5-carboxylate (ETC-OPhF_5).

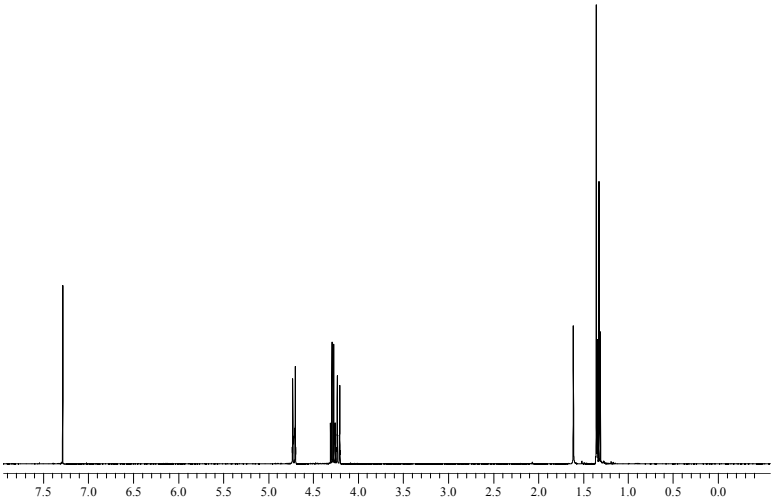


To a 100 mL round bottom flask, 2,2-bis(hydroxymethyl)butanoic acid (bis-MBA) (3.0 g, 20 mmol) was combined with bis(pentafluorophenyl)carbonate (18.4 g, 47 mmol, 2.3 eq.) and cesium fluoride (0.92 g, 6.0 mmol, 0.3 eq.) in anhydrous tetrahydrofuran (29 mL) and stirred for 20 hours at room temperature. The reaction was concentrated (bath temperature: 30 °C, pressure: ~100 mm Hg) and redissolved in methylene chloride. Upon sitting (~10 min) the pentafluorophenol byproduct fell out of solution and could be recovered. After removal of the byproduct by filtration, the mother liquid was washed with aqueous sodium bicarbonate (3 x 50mL) (pH of aqueous layer ~8) and brine (1 x 50mL). The organic layer was separated and dried over anhydrous sodium sulfate. After filtration, the solution was concentrated to give the crude product. The crude was dissolved in ethyl acetate (6 mL) at 65 °C. n-Hexane (24 mL) was added to the solution at the same temperature after which the solution was slowly cooled to room temperature. After stirring the solution over night, the crystal was separated by filtration (5.1 g, 75% isolated yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.86 (d, 2H, J = 11 Hz), 4.44 (d, 2H, J = 11 Hz), 1.94 (q, 2H, J = 8 Hz), 1.08 (t, 3H, J = 8 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) ($CFCl_3$=0 ppm): δ -153.7~-153.8 (m, 2F), -157.2~-157.3 (m, 1F), -162.4~-162.5(m, 2F). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.3, 147.1, 140.9, 140.2, 138.1, 124.2, 71.6, 45.4, 25.4, 8.2.

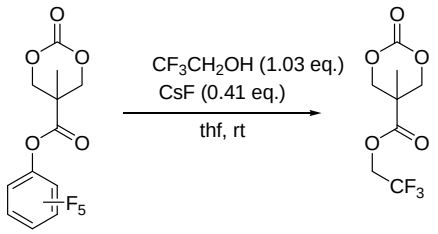
Preparation of ethyl 5-methyl-2-oxo-1,3-dioxane-5-carboxylate (MTC-OEt) (**2a**).



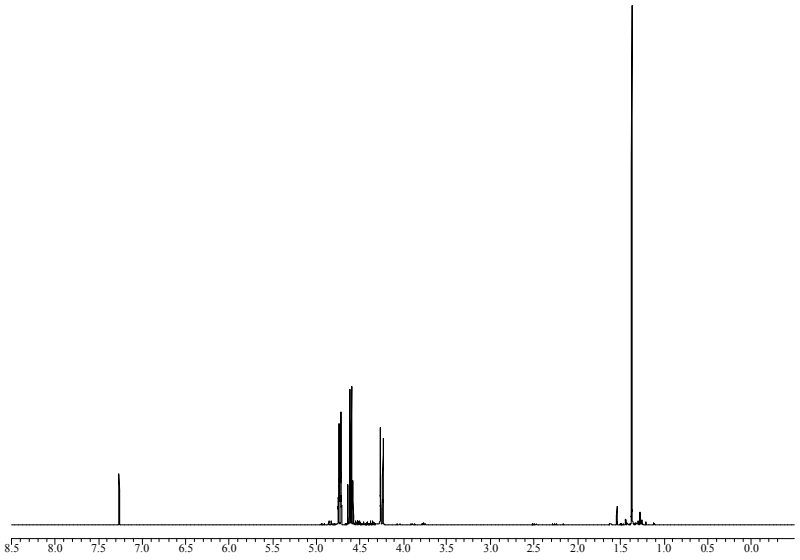
A round bottom flask was charged with an anhydrous THF solution of MTC-$OPhF_5$ (0.056 g, 0.17 mmol), ethanol (0.1 g, 0.22 mmol, 1.25 eq.), and CsF (0.005 g, 0.034 mmol, 0.02 eq.). The reaction was allowed to stir overnight, after which NMR analysis on the crude product showed about 95% conversion to the ethyl ester carbonate. The solvent was removed and the mixture was re-dissolved in methylene chloride. The solution was allowed to stand for approximately 10min, at which time the pentafluorophenol byproduct precipitated and could be quantitatively recovered. The organic phase was treated with saturated $NaHCO_3$ (200 mL), brine (200 mL), and water (200 mL), and dried over $MgSO_4$. The solvent was evaporated *in vacuo*, and the residue was recrystallized from ethyl acetate to give white crystals. Yield: 56%. GCMS single peak, calc'd m/z for $C_8H_{12}O_5$: 188, found: 188. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.68 (d, 2H, C*H*$_2$OCOO), 4.25 (q, 1H, OC*H*$_2$CH$_3$), 4.19 (d, 2H, C*H*$_2$OCOO), 1.32 (s, 3H, C*H*$_3$), 1.29 (t, 3H, C*H*$_3$CH$_2$O). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.0, 147.5, 72.9, 62.1, 39.9, 17.3, 13.8.



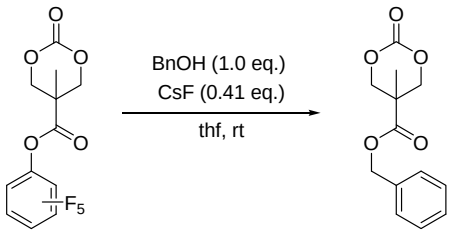
Synthesis of 2,2,2-trifluoroethyl 5-methyl-2-oxo-1,3-dioxane-5-carboxylate (MTC-OTFE) (**2b**)



A THF solution (2 mL) of 2,2,2-trifluoroethanol (233 μL, 3.20 mmol, 1.03 eq.) was slowly added to a mixture of MTC-OPhF_5 (1.0g, 3.1 mmol) and CsF (193 mg, 1.27 mmol, 0.41 eq.) in anhydrous THF (4 mL) at room temperature. The reaction mixture was stirred for 17 hours before the solvent was removed under vacuum. The residue was then dissolved in methylene chloride, the insoluble material was filtered, and the filtrate was dried and concentrated *in vacuo* to give the product MTC-OTFE as a clear oil (616 mg, 81.7 %). GCMS single peak, calc'd m/z for $C_8H_9F_3O_5$: 242, found: 243. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.74 (d, *J* = 11.2 Hz, 2H, C$H_a$$H_b$O), 4.61 (q, *J* = 8.3 Hz, 2H, C$H_2$$CF_3$), 4.25 (d, *J* = 11.2 Hz, 2H, $CH_a$$H_b$O), 1.39 (s, 3H, C$H_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.8, 147.1, 122.4, 72.5, 61.1, 40.4, 17.0.



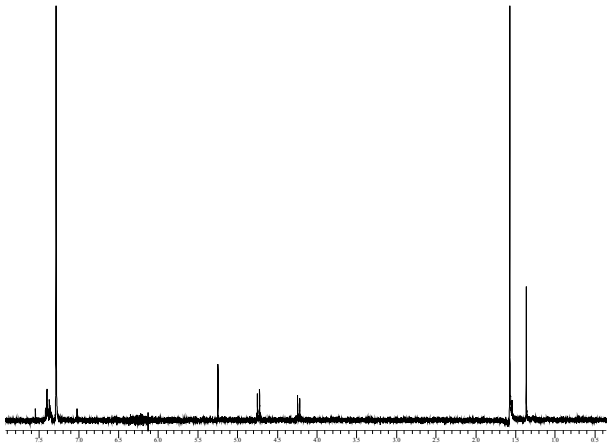
Preparation of benzyl 5-methyl-2-oxo-1,3-dioxane-5-carboxylate (MTC-OBn) (**2c**).



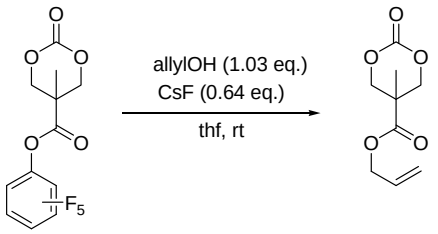
Condition A: A round bottom flask was charged with MTC-OPhF_5 (0.50 g, 1.5 mmol), CsF (0.09 g, 0.62 mmol, 0.41 eq.), benzyl alcohol (0.17 g, 1.5 mmol, 1.0 eq.), and 10 mL of anhydrous THF. The reaction mixture was stirred for 90 hours, filtered to remove pentafluorophenol byproduct, and the solvent was evaporated *in vacuo*. The reaction mixture was dissolved in methylene chloride. After about 30 min, more of the pentafluorophenol byproduct had precipitated and was again removed by filtration. The organic phase was then treated with saturated $NaHCO_3$ (50 mL), brine (50 mL), water (50 mL), dried over $MgSO_4$, and concentrated *in vacuo*. The crude product was purified by recrystallization from ethyl acetate/hexanes at 4 °C overnight to give white crystals. Yield: 51%.

Condition B (higher CsF loading): A round bottom flask was charged with MTC-OPhF_5 (0.50 g, 1.5 mmol), CsF (0.30 g, 2.0 mmol, 1.33 eq.), benzyl alcohol (0.17 g, 1.5 mmol, 1.0 eq.), and 10 mL of anhydrous THF. The reaction mixture was stirred for 24 hours, filtered to remove pentafluorophenol byproduct, and the solvent was evaporated *in vacuo*. The reaction mixture was dissolved in methylene chloride. After about 30 min, more of the pentafluorophenol byproduct had precipitated and was again removed by filtration. The organic phase was then treated with saturated $NaHCO_3$ (200 mL), brine (200 mL), water (200 mL), dried over $MgSO_4$, and concentrated *in vacuo*. The crude product was purified by column chromatography (silica, 1:1 ethyl acetate/hexanes) to give a crystalline solid, m.p. 67 °C to 69 °C. Yield: 68%. GCMS single peak, calc'd m/z for $C_{13}H_{14}O_5$: 250, found: 250. ^{1}H NMR (400 MHz, $CDCl_3$): δ

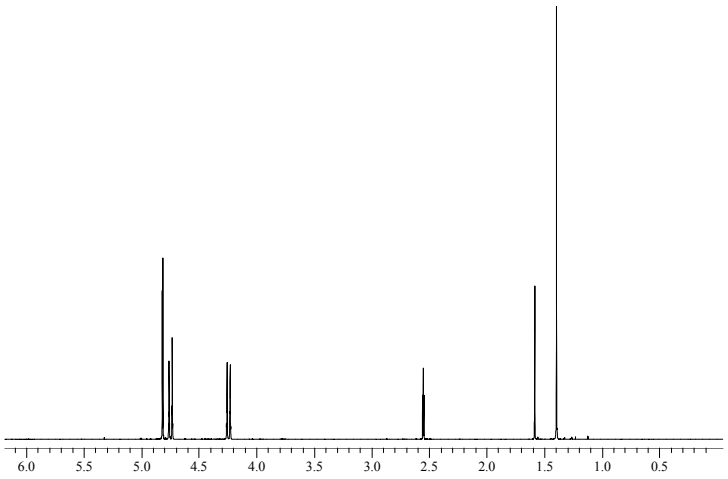
7.45 (m, 5H, ArH), 5.3 (s, 2H, $ArCH_2$), 4.70 (d, J = 10.8Hz, 2H, CH_aH_b), 4.25 (d, J = 10.8Hz, 2H, CH_aH_b), 1.35 (s, 3H, CCH_3).



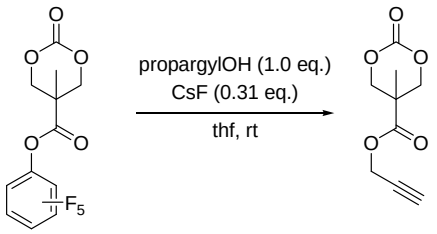
Preparation of allyl 5-methyl-2-oxo-1,3-dioxane-5-carboxylate (MTC-OCH_2CHCH_2 (**2d**).



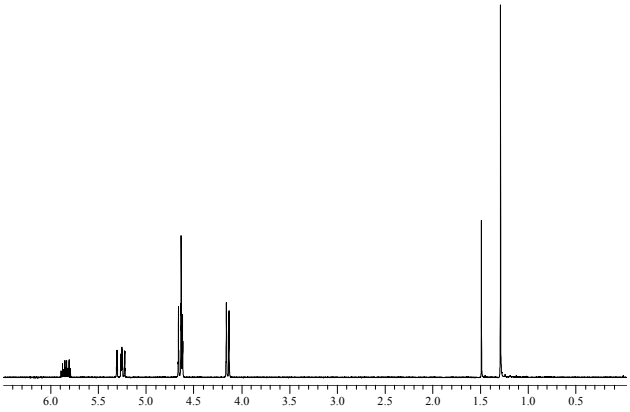
A round bottom flask was charged with MTC-$OPhF_5$ (1.18 g, 3.6 mmol), CsF (0.35 g, 2.3 mmol, 0.64 eq.), allyl alcohol (0.219 g, 3.7 mol, 1.03 eq.), and 10 mL of anhydrous THF. The mixture was stirred for 24 hours, filtered to remove pentafluorophenol byproduct, and the solvent was evaporated *in vacuo*. The crude product was dissolved in methylene chloride, and the solution was allowed to stand for about 30min, during which time more pentafluorophenol byproduct precipitated. The pentafluorophenol byproduct was removed by filtration. The organic phase was treated sequentially with saturated $NaHCO_3$ (200 mL), brine (200 mL), and water (200 mL), then dried over $MgSO_4$ and concentrated. Purification of the product by column chromatography (silica, 1:1 ethyl acetate/hexanes) provided the desired material as an oil that slowly solidified to a white solid, m.p. 64 ºC to 66 °C. Yield: 65%. GCMS single peak, calc'd m/z for $C_9H_{12}O_5$: 200; found: 200. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 5.80-5.90 (m, 1H CH), 4.65 (t, 2H, $COOCH_2$), 4.60 (d, J = 10.8 Hz, 2H, CH_aH_b), 4.24 (d, J = 10.8 Hz, 2H, CH_aH_b), 1.38 (s, 3H, CCH_3).



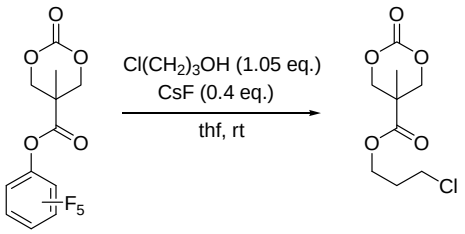
Preparation of propargyl 5-methyl-2-oxo-1,3-dioxane-5-carboxylate (MTC-OCH_2CCH) (**2e**).



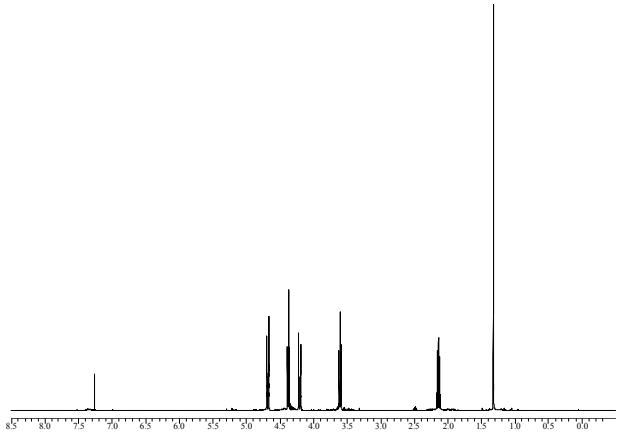
A round bottom flask was charged with MTC-$OPhF_5$ (0.70 g, 2.1 mmol), CsF (0.10 g, 0.66 mmol, 0.31 eq.), propargyl alcohol (0.29 g, 2.1 mmol, 1.0 eq.), and 10 mL of anhydrous THF. The mixture was stirred for 24 hours at ambient temperature, filtered to remove pentafluorophenol, and the solvent was evaporated *in vacuo*. The reaction mixture was dissolved in methylene chloride, allowed to stand for about 30min, and filtered to remove additional pentafluorophenol byproduct that was quantitatively recovered. The organic phase was then treated with saturated $NaHCO_3$ (200 mL), brine (200 mL), water (200 mL), dried over $MgSO_4$ and was concentrated. The crude product was purified by column chromatography (silica, 1:1 ethyl acetate/hexanes) to a clear oil that slowly solidified to a white solid, m.p. 70 to 72 °C. Yield: 65%. GCMS single peak, calc'd m/z for $C_9H_{10}O_5$: 198, found: 198. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.80 (d, J = 2.4 Hz, 2H, OCH_2CCH), 4.72 (d, J = 10.8 Hz, 2H, CH_aH_b), 4.24 (d, J = 10.8 Hz, 2H, CH_aH_b), 2.55 (t, J = 2.4 Hz, 1H, OCH_2CCH), 1.38 (s, 3H, CCH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.8, 147.7, 76.8, 76.4, 73.2, 53.9, 40.6, 17.8.



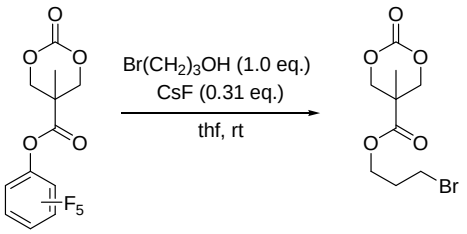
Preparation of 3-chloropropyl 5-methyl-2-oxo-1,3-dioxane-5-carboxylate (MTC-$OCH_2CH_2CH_2Cl$) (**2f**).



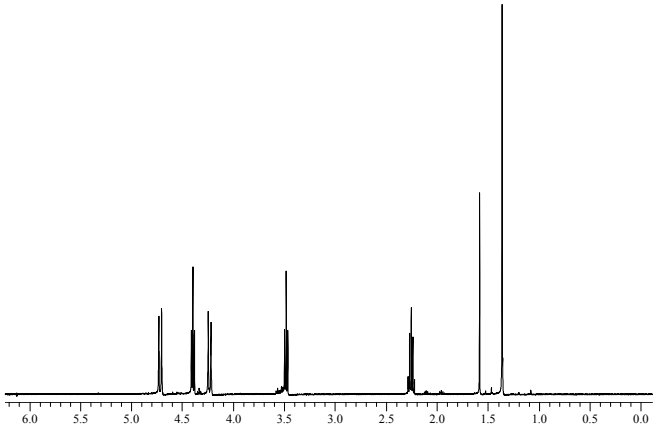
A round bottom flask was charged with MTC-$OPhF_5$ (0.98 g, 3.0 mmol), CsF (0.18 g, 1.20 mmol, 0.40 eq.), 3-chloro-1-propanol (0.298 g, 3.1 mmol, 1.05 eq.), and 10 mL anhydrous THF. The reaction mixture was stirred for 40 hours, filtered to remove pentafluorophenol byproduct, and the solvent was evaporated *in vacuo*. The reaction mixture was dissolved in methylene chloride, allowed to stand for about 30 min, and filtered to remove more pentafluorophenol by-product by precipitation. After filtration, the organic phase was then treated with saturated $NaHCO_3$ (50 mL), brine (50 mL), water (50 mL), dried over $MgSO_4$ and concentrated. The crude product was purified by column chromatography (silica, 1:1 ethyl acetate/hexanes) to a clear, colorless oil. Yield: 0.45 g (63%). GCMS single peak, calc'd m/z for $C_9H_{13}ClO_5$: 236, found: 236. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.68 (d, J = 11.2 Hz, 2H, CH_aH$_b$), 4.37 (t, J = 6.2 Hz, 2H, OCH_2CH$_2$), 4.21 (d, J = 11.2 Hz, 2H, CH$_a$$H_b$), 3.61 (t, J = 6.2 Hz, 2H, CH_2Cl), 2.14 (quin, J = 6.2 Hz, 2H, CH$_2$CH_2CH$_2$), 1.33 (s, 3H, CCH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.4, 147.8, 73.4, 63.4, 41.2, 40.7, 31.5, 17.9.



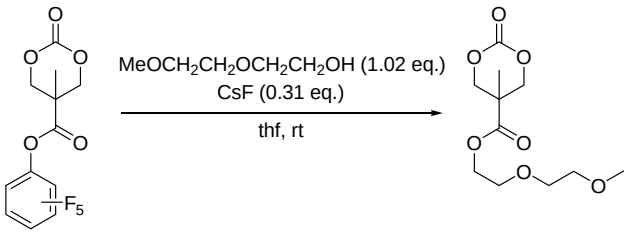
Preparation of 3-bromopropyl 5-methyl-2-oxo-1,3-dioxane-5-carboxylate (MTC-$OCH_2CH_2CH_2Br$) (**2g**).



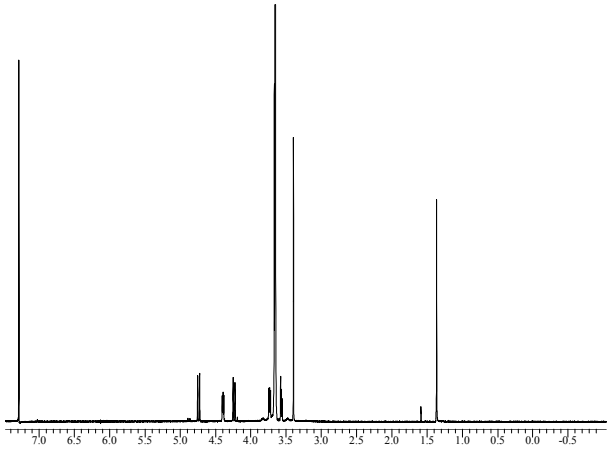
A round bottom flask was charged with MTC-$OPhF_5$ (0.7 g, 2.1 mmol), CsF (0.10 g, 0.66 mmol, 0.31 eq.), 3-bromopropanol (0.298 g, 2.1 mmol, 1.0 eq.), and 10 mL anhydrous THF. The reaction mixture was stirred for 24 hours, filtered to remove pentafluorophenol byproduct, and the solvent was evaporated *in vacuo*. The reaction mixture was dissolved in methylene chloride, allowed to stand for about 30 min, and filtered to remove more pentafluorophenol by-product by precipitation. After filtration, the organic phase was then treated with saturated $NaHCO_3$ (200 mL), brine (200 mL), water (200 mL), dried over $MgSO_4$ and concentrated. The crude product was purified by column chromatography (silica, 1:1 ethyl acetate/hexanes) to a clear, colorless oil. Yield: 70%. GCMS single peak, calc'd m/z for $C_9H_{13}BrO_5$: 280, found: 281. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.70 (d, J = 10.8 Hz, 2H, CH_aH$_b$), 4.40 (t, J = 6.0 Hz, 2H, OCH_2CH$_2$), 4.22 (d, J = 10.8 Hz, 2H, CH$_a$$H_b$), 3.50 (t, J = 6.0 Hz, 2H, CH_2Cl), 2.08 (quin, J = 6.0 Hz, 2H, CH$_2$CH_2CH$_2$), 1.27 (s, 3H, CCH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.0, 147.3, 72.9, 63.9, 40.2, 31.0, 28.9, 17.3.



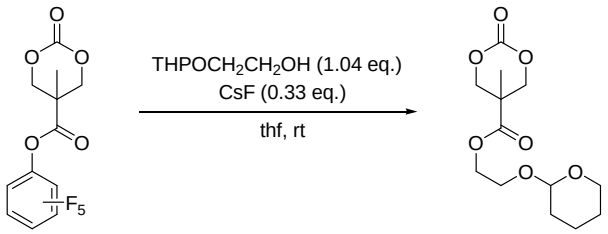
Preparation of 2-(2-methoxyethoxy)ethyl 5-methyl-2-oxo-1,3-dioxane-5-carboxylate (MTC-$OCH_2CH_2OCH_2CH_2OMe$) (**2h**).



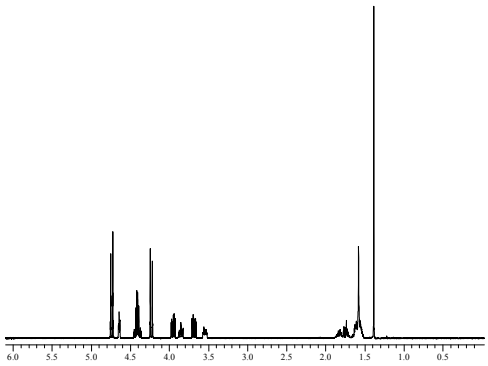
A round bottom flask was charged with MTC-$OPhF_5$ (0.86 g, 2.65 mmol), CsF (0.14 g, 0.92 mmol, 0.31 eq.), diethylene glycol monomethyl ether (0.43 g, 2.7 mmol, 1.02 eq.), and 10 mL of anhydrous THF. The reaction mixture was stirred for 24 hours, filtered to remove pentafluorophenol byproduct, and the solvent was evaporated *in vacuo*. The residue was dissolved in methylene chloride, allowed to stand about 30 min, and the additional precipitated pentafluorophenol byproduct was removed by filtration. The filtrate was concentrated and then dissolved in diethyl ether. The product separated out of the diethyl ether and was removed in a separation funnel and used without further purification. The product was isolated as a liquid. Yield: ~50%. ^{1}H NMR (400MHz, $CDCl_3$): δ 4.73-4.70 (d, 2H, -C*H*$_2$OCOOC*H*$_2$$CCH_3$-), 4.38-4.36 (t, 2H, PEG-CH_2C*H*$_2$-OCO), 4.22-4.20 (d, 4H, -C*H*$_2$OCOOC*H*$_2$$CCH_3$-), 3.65 (m, 4H, OC*H2*C*H2* PEG), 3.38 (s, 3H, OCH2CH2OC*H*$_3$ PEG), 1.38 (s, 3H, CC*H*$_3$$CH_2CCOOCH_2$).



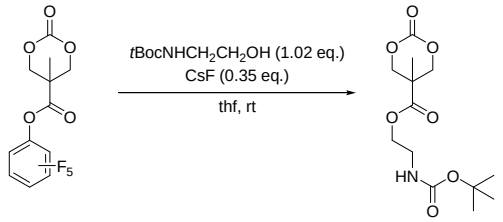
Preparation of 2-(tetrahydro-2H-pyran-2-yloxy)ethyl 5-methyl-2-oxo-1,3-dioxane-5-carboxylate (MTC-OCH_2CH_2OTHP) (**2i**).



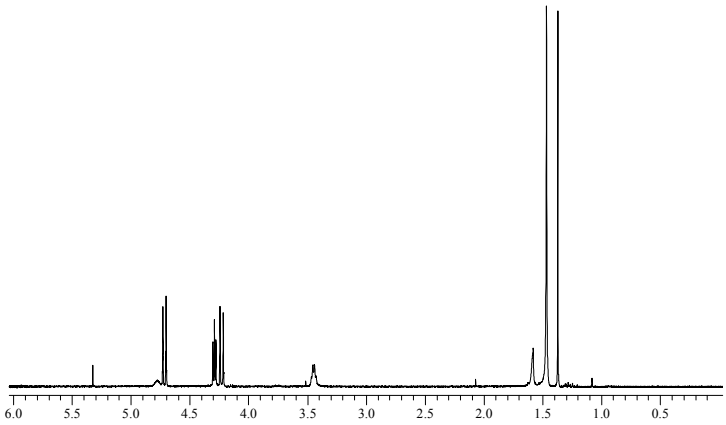
A round bottom flask was charged with MTC-$OPhF_5$ (0.95 g, 2.8 mmol), CsF (0.14 g, 0.92 mmol, 0.33 eq.), 2-(tetrahydro-2H-pyran-2-yloxy)ethanol (0.43 g, 2.9 mmol, 1.04 eq.) and 10 mL of anhydrous THF. The mixture was stirred for 24 hours, filtered to remove pentafluorophenol byproduct, and the solvent was evaporated. The reaction mixture was dissolved in CH_2Cl_2, allowed to stand for 30min, and filtered to remove additional precipitated pentafluorophenol. The organic phase was then treated with saturated $NaHCO_3$ (200 mL), brine (200 mL), water (200 mL), and dried over $MgSO_4$. After removing the solvent *in vacuo*, the crude product was purified by column chromatography (silica, 1:1 ethyl acetate/hexanes) to a colorless oil. Yield: 65%. GCMS single peak, calc'd m/z for $C_{13}H_{20}O_7$: 288, found: 287. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.70 (d, 2H, C*H*$_2$OCOO), 4.61 (t, 1H, OC*H*O), 4.38 (m, 2H, OCOC*H*$_2$CH$_2$), 4.20 (d, 2H, C*H*$_2$OCOO), 3.92 (m, 1H, C*H*$_a$H$_b$OCH), 3.82 (m, 1H, OC*H*$_a$H$_b$CH$_2$CH$_2$), 3.65 (m, 1H, CH$_a$*H*$_b$OCH), 3.51 (m, 1H, OCH$_a$*H*$_b$CH$_2$CH$_2$), 1.85-1.65 (m, 2H, CHC*H*$_2$), 1.61-1.47 (m, 4H, CH$_2$C*H*$_2$C*H*$_2$CH$_2$), 1.35 (s, 3H, C*H*$_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.9, 147.4, 98.7, 72.9, 65.0, 64.7, 62.1, 40.1, 30.3, 25.2, 19.2, 17.5.



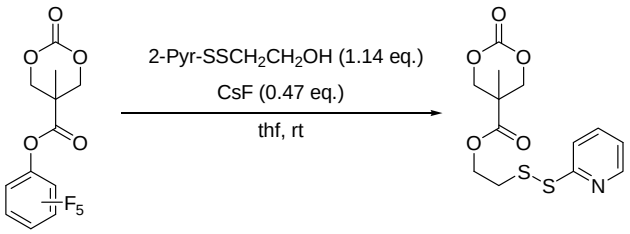
Preparation of 2-(tert-butoxycarbonylamino)ethyl 5-methyl-2-oxo-1,3-dioxane-5-carboxylate (MTC-OCH_2CH_2NHBoc) (**2j**).



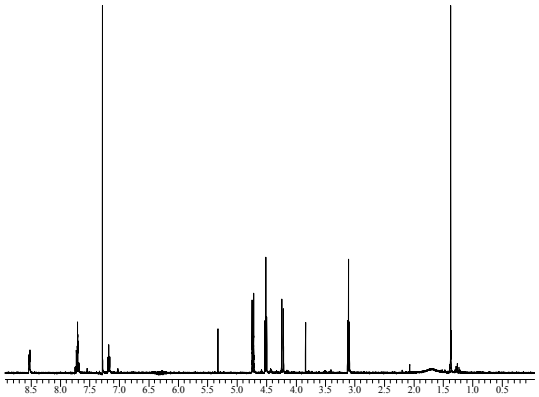
A round bottom flask was charged with MTC-$OPhF_5$ (0.86 g, 2.65 mmol), CsF (0.14 g, 0.92 mmol, 0.35 eq.), *N*-Boc-ethanolamine (0.43 g, 2.7 mmol, 1.02 eq.), and 10 mL of anhydrous THF. The reaction mixture was stirred for 24 hours, filtered to remove pentafluorophenol byproduct, and the solvent was evaporated *in vacuo*. The reaction mixture was redissolved in methylene chloride. After about 30 min, more of the pentafluorophenol byproduct precipitated and was removed by filtration. The organic phase was then treated with saturated $NaHCO_3$ (200 mL), brine (200 mL), water (200 mL), dried over $MgSO_4$ and concentrated. Purification of the crude product by column chromatography (silica, 1:1 ethyl acetate/hexanes) provided the product as a solid, m.p. 52 °C to 55 °C. Yield: 65%. GCMS single peak, calc'd m/z for $C_{13}H_{15}NO_7$: 303, calc'd m/z for $C_8H_{13}NO_5$: 203, found: 204. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.88 (br, 1H, N*H*), 4.69 (d, J = 10.8 Hz, 2H, CH_aH$_b$), 4.26 (t, J = 5.2 Hz, 2H, OCH_2CH$_2$), 4.21 (d, J = 10.8 Hz, 2H, CH$_a$$H_b$), 3.42 (m, 2H, CH$_2CH_2$NH), 1.44 (s, 9H, C(C$H_3$)$_3$), 1.34 (s, 3H, CC$H_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.5, 156.3, 148.0, 80.1, 73.4, 65.8, 40.6, 39.8, 28.7, 17.8.



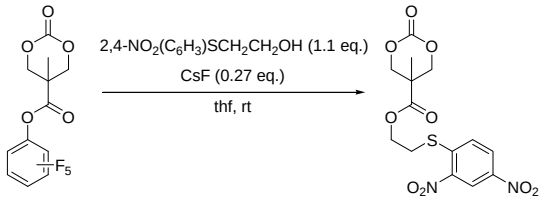
Preparation of 2-(pyridin-2-yl-disulfanyl)ethyl 5-methyl-2-oxo-1,3-dioxane-5-carboxylate (MTC-OCH_2CH_2SS(2-Py)) (**2k**).



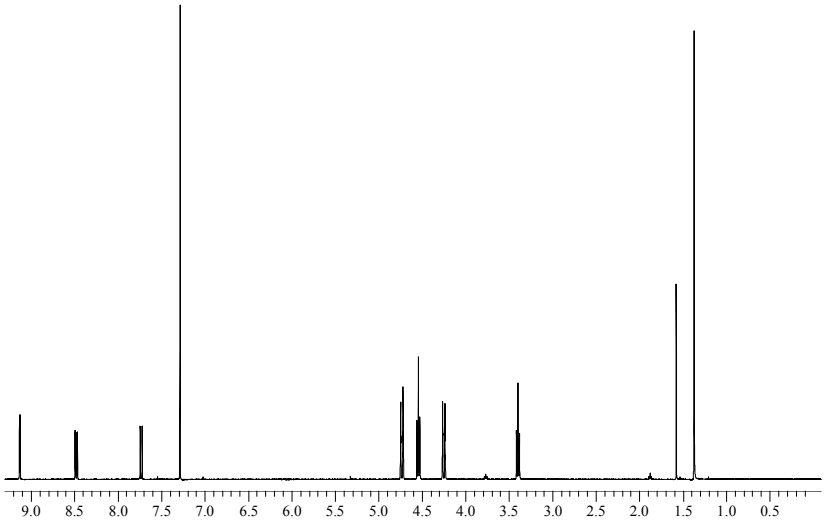
A round bottom flask was charged with MTC-$OPhF_5$ (0.25 g, 0.7 mmol), CsF (0.05 g, 0.33 mmol, 0.47 eq.), S-2-pyridyl-S'-2-hydroxyethyl disulfide (0.15g, 0.8 mmol, 1.14 eq.), and 10 mL of anhydrous THF. The mixture was stirred for 24 hours and filtered to remove pentafluorophenol byproduct. The solvent was then evaporated *in vacuo*. The reaction mixture was dissolved in CH_2Cl_2, allowed to stand 30 min, and filtered to remove additional precipitated pentafluorophenol. The organic phase was treated with saturated $NaHCO_3$ (200 mL), brine (200 mL), water (200 mL), dried over $MgSO_4$ and concentrated. The crude product was purified by column chromatography (silica, 1:1 ethyl acetate/hexanes) to an oil that slowly solidified to a white solid, mp 64-65°C. Yield: 65%. GCMS single peak, calc'd m/z for $C_{13}H_{15}NO_5S_2$: 329, calc'd m/z for $C_8H_{12}O_5S$: 220 (with loss of pyridyl thione), found: 220. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.49 (m, 1H, Ar*H*), 7.67 (m, 2H, Ar*H*), 7.14 (m, 1H, Ar*H*), 4.70 (d, J = 10.8 Hz, 2H, CH_aH_b), 4.49 (t, J = 6.4 Hz, 2H, $COOCH_2$), 4.21 (d, J = 10.8 Hz, 2H, CH_aH_b), 3.08 (t, J = 6.4 Hz, 2H, SCH_2), 1.35 (s, 3H, CCH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.3, 159.5, 150.2, 147.8, 137.6, 121.5, 120.4, 73.3, 64.1, 40.7, 37.3, 18.0.



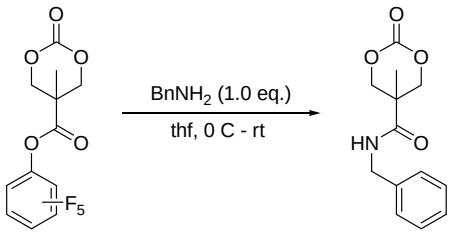
Preparation of 2-(2,4-dinitrophenylthio)ethyl 5-methyl-2-oxo-1,3-dioxane-5-carboxylate (MTC-OCH_2CH_2S-2,4-dinitroPh) (**2l**).



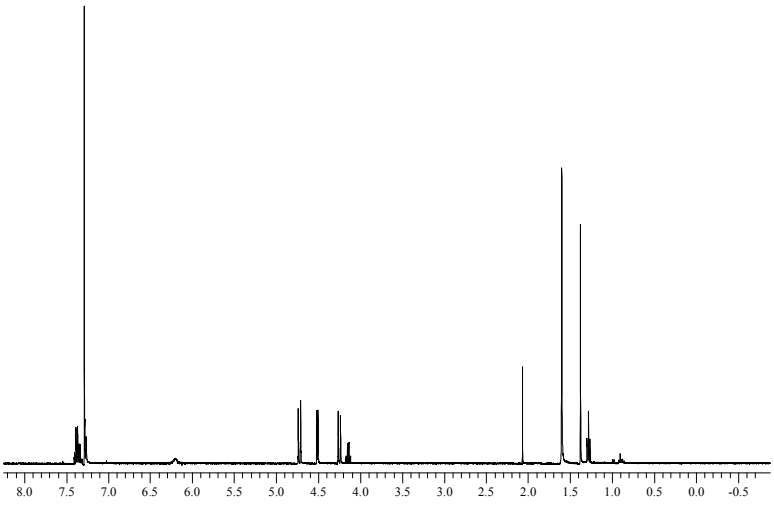
A round bottom flask was charged with MTC-$OPhF_5$ (2.40 g, 7.43 mmol), CsF (0.31 g, 2.04 mmol, 0.27 eq.), 2-(2,4-dinitrophenylthio)ethanol (2.00 g, 8.19 mmol, 1.1 eq.), and 35 mL of anhydrous THF. The mixture was stirred for 24 hours, filtered to remove pentafluorophenol byproduct, and the solvent was evaporated *in vacuo*. The residue was dissolved in methylene chloride, allowed to stand about 30 min, and filtered to remove additional precipitated pentafluorophenol byproduct. The organic phase was then treated with saturated $NaHCO_3$ (200 mL), brine (200 mL), water (200 mL), dried over $MgSO_4$, and concentrated *in vacuo*. The crude product was purified by column chromatography (silica, 1:1 ethyl acetate/hexanes) to provide the desired product as an oil that slowly solidified to a yellow solid. Yield: 90%. ^{1}H NMR (400MHz in $CDCl_3$): δ 9.25 (s, 1H, ArH), 8.45 (d, 1H, ArH), 7.70 (d, 1H, ArH), 4.70 (d, J = 10.8Hz, 2H, CH_aH_b), 4.55 (t, 2H, $COOCH_2$), 4.25 (d, J = 10.8Hz, 2H, CH_aH_b), 3.40 (t, 2H, SCH_2), 1.35 (s, 3H, CCH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.3, 147.3, 145.3, 144.7, 144.4, 127.6, 126.9, 121.9, 72.9, 62.3, 40.6, 30.7, 17.3.



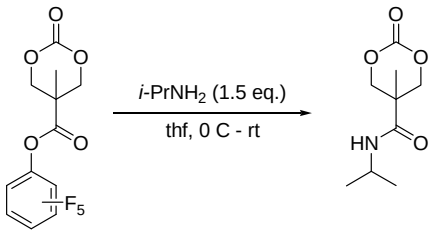
Preparation of *N*-benzyl-5-methyl-2-oxo-1,3-dioxane-5-carboxamide (MTC-NHBn) (**2m**).



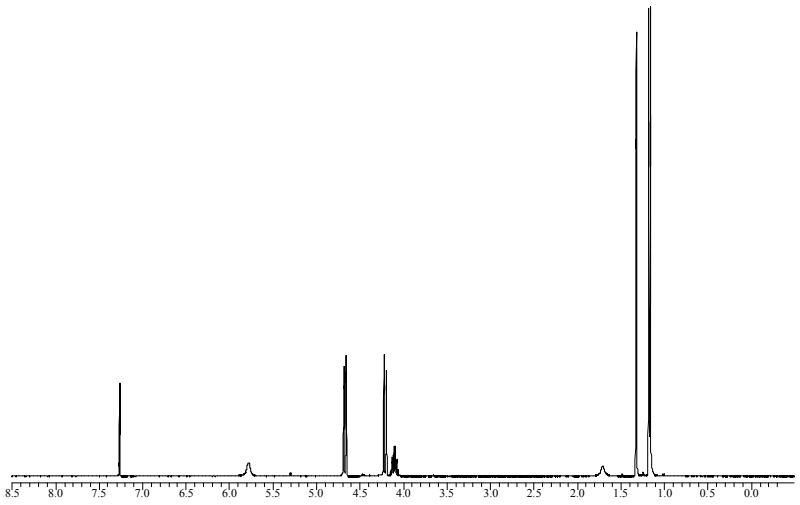
To an anhydrous THF solution of MTC-OPhF_5 (0.25 g, 0.76 mmol), benzyl amine (0.08 g, 0.76 mmol, 1.0 eq.) dissolved in THF was added dropwise at 0 ºC. ^{1}H NMR after 5 min reaction time showed 60% conversion at 0 ºC. The reaction was allowed to proceed overnight and slowly warm to room temperature. The ^{1}H NMR of the reaction mixture showed quantitative conversion of the ester to the amide with no residual benzyl amine and no side reactions. The reaction mixture was concentrated, dissolved in methylene chloride, a non-solvent for the pentafluorophenol, and filtered. The product was concentrated and crystallized from ethyl acetate/hexane mixtures. Yield: 70%. GCMS single peak, calc'd m/z for $C_{13}H_{15}NO_4$: 249, found: 249. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30-7.45 (m, 5H, ArH), 4.70 (d, J = 10.8Hz, 2H, CH_aH_b), 4.50 (d, 2H, $ArCH_2N$), 1.35 (s, 3H, CCH_3).



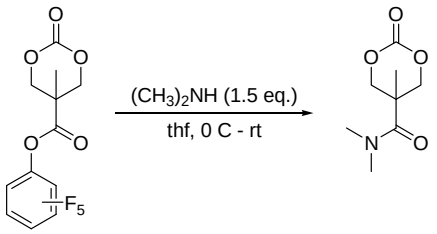
Preparation of *N*-isopropyl-5-methyl-2-oxo-1,3-dioxane-5-carboxamide (MTC-NHiPr) (**2n)**



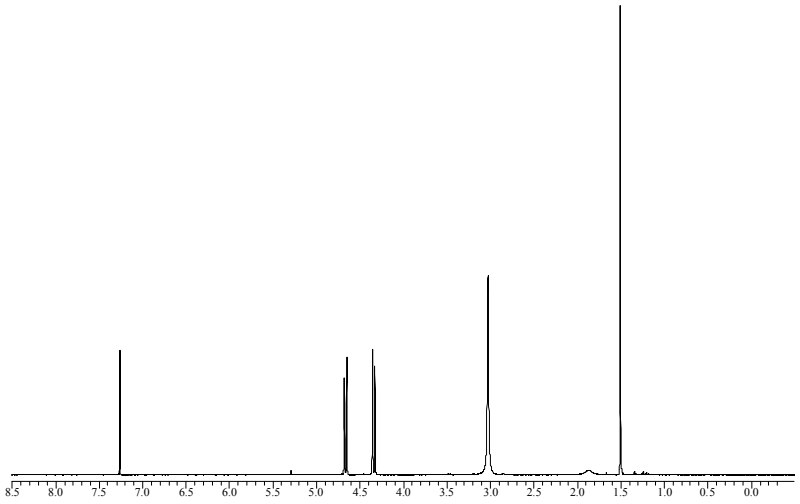
A solution of isopropylamine (200 μL, 2.31 mmol, 1.5 eq.) in anhydrous THF (2 mL) was gently added dropwise to an anhydrous THF solution (4 mL) including MTC-$OPhF_5$ (500 mg, 1.54 mmol) at 0 ºC and the reaction mixture was stirred for 30 minutes before the reaction mixture was allowed to warm to room temperature. After an additional 16 hours stirring, the solvent was removed under vacuum, methylene chloride was added to the residue, and the insoluble material was filtered. The dried filtrate was concentrated under vacuum and the residue was recrystallized from a mixture of ethyl acetate and diethyl ether to provide the product MTC-NHiPr as a white solid (234 mg, 76%). GCMS single peak, calc'd m/z for $C_9H_{15}NO_4$: 201, found: 201. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.78 (b, 1H, N*H*), 4.67 (d, *J* = 11.2 Hz, 2H, CH_aH$_b$O), 4.21 (d, *J* = 11.2 Hz, 2H, CH$_a$$H_b$O), 4.15-4.05 (m, 1H, C*H*), 1.32 (s, 3H, CH_3), 1.17 (d, *J* = 6.4 Hz, 6H, CHCH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.0, 147.6, 73.9, 42.1, 39.7, 22.3, 17.7.



Preparation of *N,N*-dimethyl-5-methyl-2-oxo-1,3-dioxane-5-carboxamide (MTC-NMe_2) (**2o**)

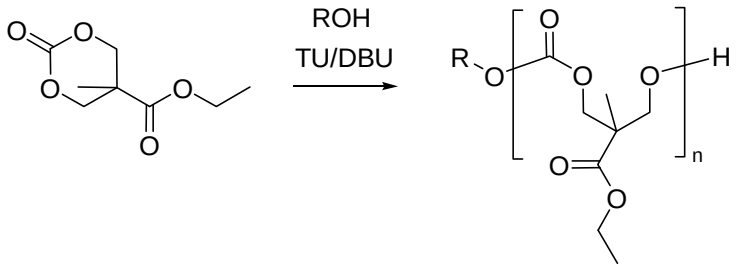


The synthesis was conducted by the same procedure and the same stoichiometry used for MTC-NiP (**2n**), using 2.0 M THF solution of dimethylamine as the amine in place of isopropylamine. The crude product MTC-NMe_2 was also purified by recrystallization (EtOAc/Et_2O) to yield a white solid (184 mg, 64%). GCMS single peak, calc'd m/z for $C_8H_{13}NO_4$: 187, found: 187. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.66 (d, J = 10.8 Hz, 2H, CH_aH$_b$O), 4.33 (d, J = 10.8 Hz, 2H, CH$_a$$H_b$O), 3.03 (s, 6H, NC$H_3$), 1.51 (s, 3H, C$H_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.8, 148.1, 73.6, 39.8, 37.5, 17.6.



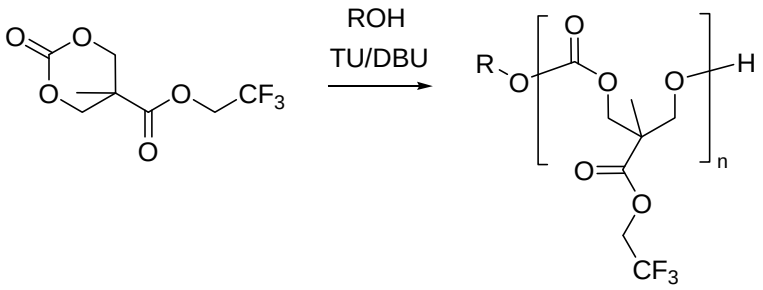
Polymerization examples

Synthesis of poly(ethyl 5-methyl-2-oxo-1,3-dioxane-5-carboxylate) (**3a**).



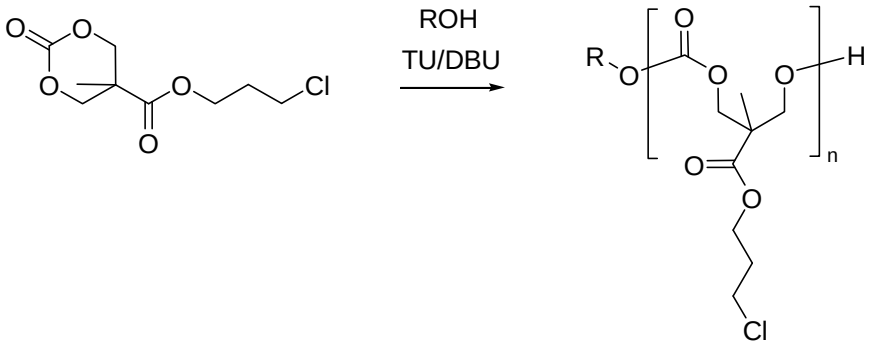
MTC-OEt (191 mg, 1.01 mmol), Bn-MPA (2.1 mg, 0.01 mmol), and TU (17.1 mg, 0.05 mmol) were dissolved in methylene chloride (1.0 mL), and this solution was transferred to a vial containing DBU (7.8 mg, 0.05 mmol) to start polymerization at room, temperature ($[M]_0/[I]_0$ = 108). After 2.0 h stirring, benzoic acid (8.6 mg, 0.07 mmol) was added into the mixture and stirred for 30 minutes (conversion ~92%). The solution was then precipitated into cold methanol and centrifuged. The precipitates were then dried in vacuum. Yield: 164 mg (86%), ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41-7.30 (m, 5H; *Ph*), 5.16 (s, 2H; C*H*$_2$), 4.41-4.11 (m, ~528H; C*H*$_2$ and C*H*$_2$OCOO $_{\text{polymer}}$), 3.71 (s, 4H; C*H*$_2$), 1.31-1.17 (m, ~517H; C*H*$_3$ $_{\text{polymer}}$), GPC (THF): M_n 17100, PDI 1.27.

Synthesis of poly(2,2,2-trifluoroethyl 5-methyl-2-oxo-1,3-dioxane-5-carboxylate) (**3b**)



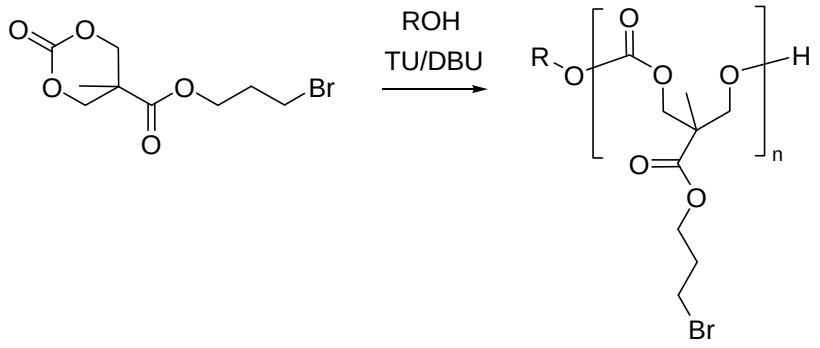
MTC-OTFE (244 mg, 1.0 mmol), Bn-MPA (4.2 mg, 0.02 mmol), and TU (18.3 mg, 0.05 mmol) were dissolved in methylene chloride (1 mL), and this solution was transferred to a vial containing DBU (7.2 mg, 0.05 mmol) to start polymerization at room, temperature ($[M]_0/[I]_0$ = 54). After 2.5 h stirring, benzoic acid (12.7 mg, 0.1 mmol) was added into the mixture and stirred for 30 minutes (conversion ~91%). The solution was then precipitated into cold methanol and collected by centrifugation. The precipitates were then dried under vacuum. Yield: 189 mg (76%), ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39-7.28 (m, 5H; *Ph*), 5.16 (s, 2H; C*H*$_2$), 4.61-4.46 (m, ~73H; C*H*$_2$ polymer), 4.40-4.20 (m, ~138H; C*H*$_2$OCOO polymer), 3.75 (s, 4H; C*H*$_2$), 1.37-1.16 (m, ~112H; C*H*$_3$ polymer), GPC (THF): M_n 11500, PDI 1.26.

Synthesis of poly(3-chloropropyl 5-methyl-2-oxo-1,3-dioxane-5-carboxylate) (**3c**).



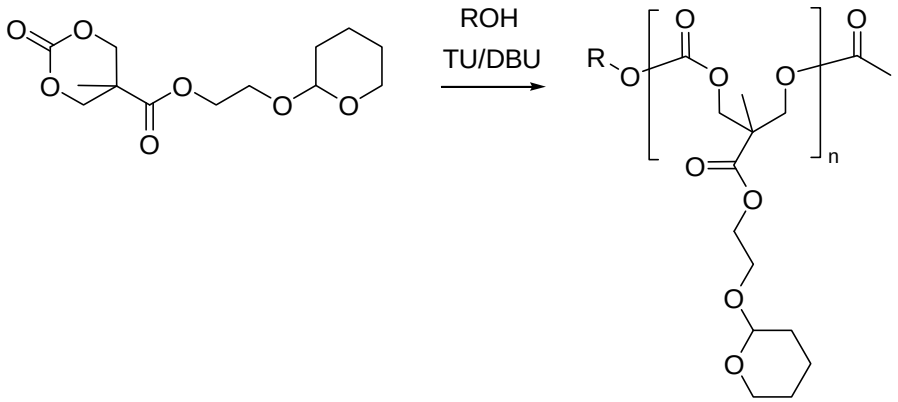
MTC-$OCH_2CH_2CH_2Cl$ (236 mg, 1.0 mmol), Bn-MPA (2.2 mg, 0.01 mmol), and TU (19.4 mg, 0.05 mmol) were dissolved in methylene chloride (1.0 mL), and this solution was transferred to a vial containing DBU (8.0 mg, 0.05 mmol) to start polymerization at room, temperature ($[M]_0/[I]_0$ = 102). After 5.0 h stirring, benzoic acid (13.4 mg, 0.11 mmol) was added into the mixture and stirred for 30 min (conversion ~91%). The solution was then precipitated in cold methanol and centrifuged. The precipitates were then dried in vacuum. Yield: 153 mg (64%), ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41-7.29 (m, 5H; *Ph*), 5.16 (s, 2H; C*H*$_2$), 4.37-4.22 (m, ~155H; C*H*$_2$O and C*H*$_2$OCOO polymer), 3.71 (s, 4H; C*H*$_2$OH $_{\text{end group}}$), 3.63-3.56 (m, ~52H; C*H*$_2$Cl $_{\text{polymer}}$), 2.15-2.06 (m, ~58H; C*H*$_{2\ \text{polymer}}$), 1.33-1.19 (m, ~85H; C*H*$_{3\ \text{polymer}}$), GPC (THF): M_n 4400, PDI 1.32.

Synthesis of poly(3-bromopropyl 5-methyl-2-oxo-1,3-dioxane-5-carboxylate) (**3d**).



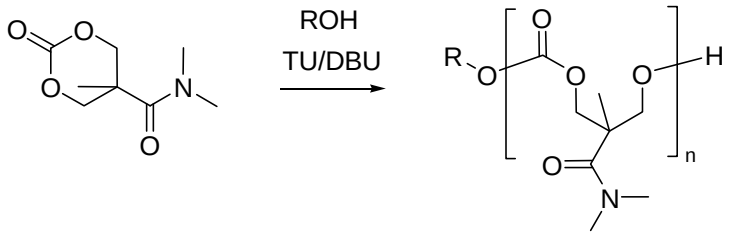
MTC-$OCH_2CH_2CH_2Br$ (291 mg, 1.04 mmol), Bn-MPA (2.3 mg, 0.01 mmol), and TU (17.9 mg, 0.05 mmol) were dissolved in methylene chloride (1.0 mL), and this solution was transferred to a vial containing DBU (7.1 mg, 0.05 mmol) to start polymerization at room, temperature ($[M]_0/[I]_0$ = 101). After 2.0 h stirring, benzoic acid (15.2 mg, 0.12 mmol) was added into the mixture and stirred for 30 minutes (conversion ~91%). The solution was then precipitated into isopropanol and centrifuged. The precipitates were then dried in vacuum. Yield: 244 mg (84%), ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40-7.28 (m, 5H; *Ph*), 5.17 (s, 2H; C*H*$_2$), 4.51-4.12 (m, ~230H; C*H*$_2$ and C*H*$_2$OCOO $_{\text{polymer}}$), 3.71 (s, 4H; C*H*$_2$OH $_{\text{end group}}$), 3.50-3.39 (m, ~70H: C*H*$_2$Br $_{\text{polymer}}$), 2.26-2.12 (m, ~71H; C*H*$_2$ $_{\text{polymer}}$), 1.31-1.23 (m, ~105H; C*H*$_3$ $_{\text{polymer}}$), GPC (THF): M_n 7300, PDI 1.42.

Synthesis of poly(2-(tetrahydro-2H-pyran-2-yloxy)ethyl 5-methyl-2-oxo-1,3-dioxane-5-carboxylate) (**3e**).



MTC-OCH_2CH_2OTHP (292 mg, 1.01 mmol), Bn-MPA (2.3 mg, 0.01 mmol), and TU (19.4 mg, 0.05 mmol) were dissolved in methylene chloride (1.0 mL), and this solution was transferred to a vial containing DBU (9.0 mg, 0.06 mmol) to start polymerization at room, temperature ($[M]_0/[I]_0$ = 99). After 2.0 h stirring, acetic anhydride (23.2 mg, 0.23 mmol) was added into the mixture and stirred overnight (conversion ~91%). The solution was then precipitated into the mixture of hexane and diethyl ether (1:2) and centrifuged. The precipitates were then dried in vacuum. Yield: 176 mg (60%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41-7.28 (m, 5H; *Ph*), 5.16 (s, 2H; C*H*$_2$), 4.66-4.59 (m, ~66H; C*H* $_{\text{polymer}}$), 4.37-4.23 (m, ~394H; C*H*$_2$OCO and C*H*$_2$OCOO $_{\text{polymer}}$), 3.93-3.47 (m. ~270H; CH_2CH_2O $_{\text{polymer}}$), 2.04 (s, 6H; C*H*$_{3\ \text{end group}}$), 1.87-1.46 (m, ~245H; C*H*$_{2\ \text{polymer}}$), 1.32-1.22 (m, ~105H; C*H*$_{3\ \text{polymer}}$), GPC (THF): M_n 6600, PDI 1.24.

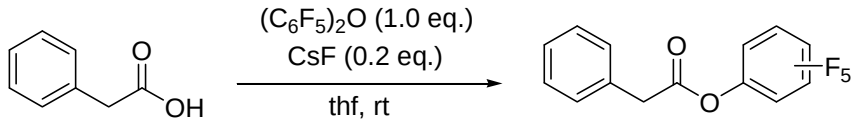
Synthesis of poly(*N,N*-dimethyl-5-methyl-2-oxo-1,3-dioxane-5-carboxamide) (**3f**).



MTC-NMe_2 (93 mg, 0.5 mmol), 1-pyrenebutanol (2.2 mg, 8.0 μmol), and TU (6.6 mg, 17.8 μmol) were dissolved in methylene chloride (1 mL), and this solution was transferred to a vial containing DBU (4.4 mg, 28.9 μmol) to start polymerization at room, temperature ($[M]_0/[I]_0$ = 63). Polymerization took 5-6 days. Benzoic acid (7.1 mg, 57.8 μmol) was added into the mixture and stirred for 30 minutes (conversion ~82%). The solution was then precipitated into cold diethyl ether and filtered. The precipitates were then dried in vacuum. Yield: 68 mg (71%), ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.31-7.82 (m, 9H; pyrene), 4.59-4.21 (m, ~134H; C*H*$_2$OCOO polymer), 3.61 (t, 2H; C*H*$_2$O), 3.40 (t, 2H; C*H*$_2$), 3.03-2.92 (br, ~188H; NC*H*$_3$ polymer), 1.97 (m, 2H; C*H*$_2$), 1.67-1.60 (br, 2H; C*H*$_2$), 1.40-1.28 (m, ~96H; C*H*$_3$), GPC (DMF): M_n 10500, PDI 1.32.

Model reaction #1: Formation of pentafluorophenyl ester

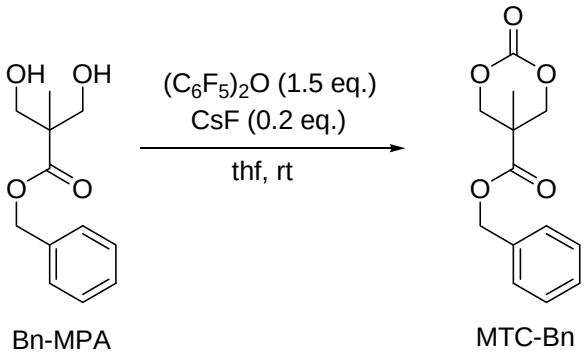
Synthesis of pentafluorophenyl 2-phenylacetate.



Phenylacetic acid (0.168 g, 0.426 mmol) and bis(pentafluorophenyl)carbonate (0.58 g, 0.426 mmol, 1.0 eq.) were dissolved in 2 mL of anhydrous THF in a round bottom flask. CsF (0.2 g, 0.09 mmol, 0.21 eq.) was added and allowed to stir overnight. The solvent was removed and the mixture was re-dissolved in methylene chloride. . The organic phase was then treated with saturated $NaHCO_3$ (200 mL), brine (200 mL), water (200 mL), dried over $MgSO_4$ and concentrated. The product was isolated as a clear liquid. GCMS single peak, calc'd m/z for $C_{14}H_7O_2F_5$: 302, found: 302. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 (m, 5H, ArH), 3.99 (s, 2H, $ArCH_2$). ^{19}F-NMR (400 MHz, $CDCl_3$): 153.3, 158.6, 162.9.

Model reaction #2: Formation of cyclic carbonate from 1,3-diol

Preparation of MTC-Bn.



Bn-MPA MTC-Bn

In a 20 mL glass vial, Bn-MPA (500 mg, 2.25 mmol), bis(pentafluorophenyl) carbonate (1.32 g, 3.35 mmol, 1.5 eq.), cesium fluoride (67 mg, 0.44 mmol, 0.2 eq.), and dry THF (5 mL) were added and stirred for 16 hours at room temperature. After the solvent was evaporated from the inhomogeneous mixture methylene chloride (15 mL) was added to the residue, and the insoluble material was filtered. The filtrate was then washed with saturated aqueous $NaHCO_3$ (2 × 20 mL), dried over $MgSO_4$, filtered and evaporated to give MTC-Bn as a white solid (402 mg, 71.6%).