Convenient Formation of DPM Esters Using Diphenylmethyl Trichloroacetimidate

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Supporting information

Table of Contents

General Methods S2
Experimental Procedures and Tabulated Characterization data S3-S10
$^1$H and $^{13}$C spectra S11-S70
Chiral HPLC Data S71-S76
General Methods:

**General Information.** All anhydrous reactions were run under a positive pressure of argon or nitrogen. All syringes, needles, and reaction flasks required for anhydrous reactions were dried in an oven and cooled under an N₂ atmosphere or in a desiccator. Dichloromethane and THF were dried by passage through an alumina column following the method of Grubbs (Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, **15**, 1518). Triethylamine was distilled from CaH₂. All other reagents and solvents were purchased from commercial sources and used without further purification.

**Analysis and Purification.** Analytical thin layer chromatography (TLC) was performed on precoated glass backed plates (silica gel 60 F₂₅₄; 0.25 mm thickness). The TLC plates were visualized by UV illumination and by staining. Solvents for chromatography are listed as volume:volume ratios. Flash column chromatography was carried out on silica gel (40-63 μm). Melting points were recorded using an electrothermal melting point apparatus and are uncorrected. Optical rotations were measured at the sodium D line (589 nm) on a digital polarimeter and reported in reagent grade solvent. Enantiopurity was determined using chiral phase HPLC with 0.46 × 25 cm columns. Elemental analyses were performed on an elemental analyzer with a thermal conductivity detector and 2 meter GC column maintained at 50 °C.

**Identity.** Proton (¹H NMR) and carbon (¹³C NMR) nuclear magnetic resonance spectra were recorded at 300 MHz and 75 MHz respectively. The chemical shifts are given in parts per million (ppm) on the delta (δ) scale. Coupling constants are reported in hertz (Hz). The spectra were recorded in solutions of deuterated chloroform (CDCl₃), with residual chloroform (δ 7.26 ppm for ¹H NMR, δ 77.23 ppm for ¹³C NMR) as the internal reference. Data are reported as follows: (s = singlet; d = doublet; t = triplet; q = quartet; p = pentet; dd = doublet of doublets; dt = doublet of triplets; td = triplet of doublets; tt = triplet of triplets; qd = quartet of doublets; ddd = doublet of doublet of doublets; br s = broad singlet). Where applicable, the number of protons attached to the corresponding carbon atom was determined by DEPT 135 NMR. Infrared (IR) spectra were obtained as thin films on NaCl plates by dissolving the compound in CH₂Cl₂ followed by evaporation or as KBr pellets.
General procedure for esterification using diphenylmethyl imidate and cinnamic acid as an example:

Cinnamic acid (0.200 g, 1.35 mmol) and diphenylmethyl trichloroacetimidate (0.580 g, 1.76 mmol) were added to a flame dried round bottom flask. Dry dichloromethane (5.4 mL) was then added and the reaction was stirred under argon for 18 h. Triethylamine (0.5 mL) was then added the reaction mixture was preadsorbed on silica gel. Purification by silica gel chromatography using 1% triethylamine/5% ethyl acetate/94% hexanes provided 0.401 g (93%) of the diphenylmethyl cinnamate 13 as a white solid.

Procedures for Purification of Esters:

**Method A.** Triethylamine was added and the reaction mixture was preadsorbed on silica gel and purified by silica gel chromatography using the listed solvent system.

**Method B.** The reaction mixture was preadsorbed on silica gel and purified by silica gel chromatography using the listed solvent system.

**Method C.** After the stirring the reaction mixture for 18 h, methanol (~5 ml) was added to the reaction and the mixture was stirred for 2 hours. The reaction mixture was then preadsorbed on silica gel and purified by silica gel chromatography using the listed solvent system.

Purified by method A (1% triethylamine/1% ethyl acetate/98% hexanes solvent system).

**Benzhydryl dodecanoate (4).** White solid (0.37 g, 84%); mp = 60-62°C; TLC Rf = 0.91 (10% ethyl acetate/90% hexanes); IR (KBr) 2845, 2837, 1694, 1240, 900 cm\(^{-1}\); \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.36-7.26 (m, 10H), 6.91 (s, 1H), 2.43 (t, \(J\) = 7.5 Hz, 2H), 1.70-1.65 (m, 2H), 1.26 (br s, 16H), 0.90 (t, \(J\) = 7.2 Hz Hz, 3H); \(^13\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 173.0, 140.6, 128.7, 128.1, 127.3, 76.8, 34.8, 32.2, 29.9, 29.8, 29.7, 29.6, 29.5, 29.4, 25.2, 22.9, 14.4; Anal. Calcd for C\(_{25}\)H\(_{34}\)O\(_2\): C, 81.92; H, 9.35. Found: C, 82.25; H, 9.12.

Purified by method B (1% ethyl acetate/99% hexanes solvent system).

**Benzhydryl 3,3-dimethylbutanoate (7).** Clear oil (0.67 g, 92%); TLC Rf = 0.79 (10% ethyl acetate/90% hexanes); IR (thin film) 3033, 2959, 2870, 1734, 1227, 1127 cm\(^{-1}\); \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.37-7.26 (m, 10H), 6.90 (s, 1H), 2.32 (s, 2H), 0.99 (s, 9H); \(^13\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 171.4, 140.6, 128.6, 127.9, 127.4, 76.7, 48.2, 31.1, 29.8. Anal. Calcd for C\(_{19}\)H\(_{22}\)O\(_2\): C, 80.82; H, 7.85. Found: C, 81.11; H, 8.03.

Purified by method A (1% triethylamine/5% ethyl acetate/94% hexanes solvent system).

**Benzhydryl cyclopropanecarboxylate (8).** Clear colorless oil (0.52 g, 89%); TLC Rf = 0.25 (5% ethyl acetate/95% hexanes); IR (thin film) 3064, 3032, 2939, 1729, 1391, 1260, 1164 cm\(^{-1}\); \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.35-7.26 (m, 10H), 6.89 (s, 1H), 1.80-1.71 (m, 1H), 1.08-1.03 (m, 2H), 0.93-0.86 (m, 2H); \(^13\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 174.1, 140.6, 128.8, 128.1, 127.3, 77.0, 13.5, 8.9. Anal. Calcd for C\(_{17}\)H\(_{16}\)O\(_2\): C, 80.93; H, 6.39. Found: C, 81.34; H, 6.47.

Purified by method A (1% triethylamine/5% ethyl acetate/94% hexanes solvent system).
**Benzhydryl 2,2-diphenylacetate (9).** White solid (0.27 g, 76%); mp = 107-108°C; TLC Rf = 0.50 (10% ethyl acetate/90% hexanes); IR (KBr) 3061, 3086, 3030, 2950, 1715, 1120, cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 7.32-7.19 (m, 20H), 6.92 (s, 1H), 5.16 (s, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 171.5, 140.1, 138.6, 129.0, 128.7, 128.6, 128.1, 127.5, 127.3, 77.9, 57.5. Anal. Calcd for C₂₇H₂₂O₂: C, 85.69; H, 5.86. Found: C, 86.06; H, 5.66.

Purified by method B (5% ethyl acetate/95% hexanes solvent system).

**Benzhydryl adamantane-1-carboxylate(10)**

White solid (0.34 g, 59%); mp = 131-134°C; TLC Rf = 0.64 (10% ethyl acetate/90% hexanes); IR (KBr) 3032, 2907, 2852, 1728, 1226, 1071 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 7.35-7.25 (m, 10H), 6.84 (s, 1H), 2.04 (br s, 3H), 1.96 (br s, 6H), 1.73 (br s, 6H); ¹³C NMR (75 MHz, CDCl₃) δ 176.5, 140.8, 128.6, 128.5, 127.9, 127.4, 127.1, 76.3, 41.0, 38.9, 36.6, 28.1. Anal. Calcd for C₂₄H₂₆O₂: C, 83.20; H, 7.56. Found: C, 83.17; H, 7.85.

Purified by method A (1% triethylamine/5% ethyl acetate/94% hexanes solvent system).

**(S)-benzhydryl 3,3,3-trifluoro-2-methoxy-2-phenylpropanoate (11).** Clear colorless oil (0.46 g, 59%); [α]₂⁰D = +13.9 (c = 1.00, CHCl₃); TLC Rf = 0.50 (10% ethyl acetate/90% hexanes); IR (thin film) 3066, 3034, 2950, 2849, 1749, 1246, 1122 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 7.40-7.21 (m, 15H), 7.09 (s, 1H), 3.49 (d, J = 1.2 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 165.9, 140.2, 139.4, 139.3, 132.6, 129.9, 129.6, 129.0, 128.8, 128.7, 128.6, 128.5, 128.4, 128.1, 128.0, 127.8, 127.6, 127.3, 123.9 (q, J = 286.8 Hz), 85.0 (q, J = 27.5 Hz), 79.4, 55.84, 55.83; Anal. Calcd for C₂₃H₁₉F₃O₃: C, 68.99; H, 4.78. Found: C, 68.61; H, 4.40.

Purified by method A (1% triethylamine/5% ethyl acetate/94% hexanes solvent system).

**(E)-Benzhydryl but-2-enoate (12).** Clear colorless oil (0.85 g, 79%); TLC Rf = 0.50 (10% ethyl acetate/90% hexanes); IR (thin film) 3089, 3064, 3033, 2973, 2943, 2851, 2254, 1953, 1700, 1656, 1254, 1173, 867, 700 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 7.38-7.24 (m, 10H), 7.03-5.94 (m, 1H), 1.90 (dd, J = 1.8, 6.9 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 165.6, 145.8, 140.8, 128.9, 127.5, 123.0, 76.9, 6.39. Anal. Calcd for C₁₇H₁₆O₂: C, 80.93; H, 6.39. Found: C, 80.72; H, 6.60.

Purified by method A (1% triethylamine/10% ethyl acetate/89% hexanes solvent system).

**Lit. ref. for characterization data:** Magens, S.; Plietker, B. J. Org. Chem. 2010, 75, 3715.

**(E)-Benzhydryl cinnamate (13).** White solid (0.401 g, 93%); mp = 74-77°C; TLC Rf = 0.57 (10% ethyl acetate/90% hexanes); ¹H NMR (300 MHz, CDCl₃) δ 7.78 (d, J = 16.2 Hz, 1H), 7.57-7.54 (m, 2H), 7.44-7.26 (m, 13H), 7.05 (s, 1H), 6.58 (d, J = 0.6, 15.9 Hz, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 166.2, 145.7, 140.5, 134.5, 130.7, 129.1, 128.8, 128.4, 128.2, 127.4, 118.2, 77.2.

Purified by method A (1% triethylamine/5% ethyl acetate/94% hexanes solvent system).
Benzhydryl 3-phenylpropionate (14). White solid (0.55 g, 85%); mp = 98-100°C; TLC Rf = 0.54 (10% ethyl acetate/90% hexanes); IR (KBr) 3030, 2210, 1959, 1692, 1490, 1301, 1157, 863 cm\(^{-1}\); \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.62-7.58 (m, 2H), 7.48-7.26 (m, 13H), 7.01 (s, 1H); \(^1\)3C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 153.4, 139.5, 133.3, 130.9, 128.83, 128.80, 128.4, 127.5, 119.8, 87.2, 80.9, 78.8. Anal. Calcd for C\(_{22}\)H\(_{16}\)O\(_2\): C, 84.59; H, 5.16. Found: C, 84.54; H, 5.34.

Purified by method B (5% ethyl acetate/95% hexanes solvent system).

Benzhydryl undec-10-ynoate (15). Colorless crystals (0.30 g, 79%); mp = 40-41°C; TLC Rf = 0.46 (10% ethyl acetate/90% hexanes); IR (KBr) 3293, 2931, 2917, 2851, 1739 cm\(^{-1}\); \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.36-7.26 (m, 10H), 6.89 (s, 1H), 2.42 (t, \(J = 7.2\) Hz, 2H), 2.17 (dt, \(J = 6.9, 2.7\) Hz, 2H), 1.95-1.93 (m, 2H), 1.68-1.63 (m, 1H), 1.53-1.46 (m, 2H), 1.38-1.29 (m, 8H); \(^1\)3C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 172.9, 140.6, 128.7, 128.1, 127.3, 84.9, 76.8, 68.4, 34.8, 29.3, 29.2, 29.1, 28.9, 25.2, 18.6. Anal. Calcd for C\(_{24}\)H\(_{28}\)O\(_2\): C, 82.72; H, 8.10. Found: C, 82.40; H, 7.81.

Purified by method B (5% ethyl acetate/95% hexanes solvent system).

Benzhydryl pent-4-ynoate (16). Clear yellow oil (0.47 g, 88%); TLC Rf = 0.33 (5% ethyl acetate/95% hexanes); IR (thin film) 3294, 3088, 3064, 3032, 2924, 2120, 1739, 1247, 1160, 978, 699 cm\(^{-1}\); \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.37-7.26 (m, 10), 6.91 (s, 1H), 2.71-2.66 (m, 2H), 2.58-2.51 (m, 2H), 1.96 (t, \(J = 2.4\) Hz, 1H); \(^1\)3C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 170.7, 140.1, 128.6, 128.0, 127.2, 82.5, 77.2, 69.4, 33.6, 14.4. Anal. Calcd for C\(_{18}\)H\(_{16}\)O\(_2\): C, 81.79; H, 6.10. Found: C, 81.44; H, 6.33.

Purified by method A (1% triethylamine/10% ethyl acetate/89% hexanes solvent system).

Benzhydryl benzoate (17). White solid (2.58 g, 99%); mp = 88-89°C; TLC Rf = 0.42 (10% ethyl acetate/90% hexanes); IR (KBr) 3090, 3031, 2948, 1712, 1267, 1189 cm\(^{-1}\); \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 8.17-8.13 (m, 2H), 7.60-7.55 (m, 1H), 7.50-7.26 (m, 12H), 7.13 (s, 1H); \(^1\)3C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 165.8, 140.5, 133.4, 130.4, 130.0, 128.8, 128.7, 128.2, 127.4, 77.7. Anal. Calcd for C\(_{20}\)H\(_{16}\)O\(_2\): C, 83.31; H, 5.59. Found: C, 83.37; H, 5.74.

Purified by method A (1% triethylamine/5% ethyl acetate/95% hexanes solvent system).

Benzhydryl 2-bromobenzoate (18). Clear colorless oil (3.55 g, 97%); TLC Rf = 0.44 (10% ethyl acetate/90% hexanes); IR (thin film) 3087, 3063, 3031, 2939, 1728, 1236 cm\(^{-1}\); \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.91-7.88 (m, 1H), 7.69-7.66 (m, 1H), 7.48-7.26 (m, 12H), 7.13 (s, 1H); \(^1\)3C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 165.3, 140.1, 134.8, 133.0, 132.2, 131.8, 128.9, 128.3, 127.6, 127.5, 122.2, 78.7. Anal. Calcd for C\(_{20}\)H\(_{15}\)BrO\(_2\): C, 65.41; H, 4.12. Found: C, 65.29; H, 4.24.

Purified by method A (1% triethylamine/4% ethyl acetate/94% hexanes solvent system).

Benzhydryl 2-methoxybenzoate (19). Clear colorless oil (0.23 g, 74%); TLC Rf = 0.21 (10% ethyl acetate/90% hexanes); IR (thin film) 3062, 3030, 2939, 2837, 2340, 2037, 1953, 1717, 1601, 1293, 1128, 1079, 854, 617, 600 cm\(^{-1}\); \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.94-7.91 (m, 1H), 7.52-7.44 (m, 4H),
7.37-7.25 (m, 7H), 7.10 (s, 1H), 7.02-6.97 (m, 2H), 3.92 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 165.3, 159.8, 140.8, 134.0, 132.2, 128.7, 128.0, 127.4, 120.3, 120.0, 112.3, 77.5, 56.1. Anal. Calcd for C$_{21}$H$_{18}$O$_3$: C, 79.22; H, 5.70. Found: C, 78.93; H, 5.61.

Purified by method A (1% triethylamine/5% ethyl acetate/94% hexanes solvent system).

**Lit. ref. for characterization data:** Muzart, J.; Pale, P.; Pete, J. P.; Riahi, A. Bull Chem. Soc. Fr. 1988 4, 731.

**Benzhydryl but-3-enoate (20).** Clear colorless oil (0.35 g, 76%); TLC R$_f$ = 0.44 (10% ethyl acetate/90% hexanes); IR (thin film) 3064, 3031, 2983, 2938, 1740, 1642, 1543, 1030 cm$^{-1}$; $^1$H NMR (300 MHz, CDCl$_3$) δ 7.35-7.26 (m, 10H), 6.90 (s, 1H), 6.02-5.90 (m, 1H), 5.22-5.15 (m, 2H), 3.23-3.20 (m, 2H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 170.7, 140.5, 130.4, 128.9, 128.3, 127.4, 119.1, 77.3, 39.6.

Purified by method A (1% triethylamine/5% ethyl acetate/94% hexanes solvent system).

**Benzhydryl 2-bromododecanoate (21).** Clear colorless oil (0.40 g, 83%); TLC R$_f$ = 0.78 (10% ethyl acetate/90% hexanes); IR (thin film) 3064, 3032, 2924, 2854, 1741, 1495, 1454, 1257, 1144, 1080, 600 cm$^{-1}$; $^1$H NMR (300 MHZ CDCl$_3$) δ 7.38-7.26 (m, 10H), 6.89 (s, 1H), 4.31 (t, J = 7.5 Hz, 1H), 2.07-2.00 (m, 2H), 1.23 (br s, 16H), 0.88 (t, J = 6.3 Hz, 3H); $^{13}$C NMR (75 MHZ CDCl$_3$) δ 169.0, 139.8, 139.7, 128.8, 128.7, 128.4, 127.4, 127.3, 78.5, 46.4, 35.2, 32.2, 29.8, 29.7, 29.6, 29.1, 27.4, 23.0, 14.4. Anal. Calcd for C$_{25}$H$_{33}$O$_2$Br: C, 67.41; H, 7.47. Found: C, 67.60; H, 7.66.

Purified by method C (1% triethylamine/5% ethyl acetate/94% hexanes solvent system).


**2(S,5R,6R)-Benzhydryl 6-(2-phenoxyacetamido)-3,3-dimethyl-7-oxo-4-thia-1-aza-bicyclo[3.2.0]heptane-2-carboxylate (22).** White solid (0.19 g, 63%); [a]$^\text{D}$ = +123.3 (c = 1.47, CHCl$_3$); TLC R$_f$ = 0.45 (15% ethyl acetate/85% toluene); IR (KBr) 3387, 3061, 3031, 2970, 2930, 2867, 1787, 1744, 1692, 1598, 1519, 1494, 1205 cm$^{-1}$; $^1$H NMR (300 MHz, CDCl$_3$) δ 7.36-7.30 (m, 13H), 7.10-6.91 (m, 4H), 5.74 (dd, J = 4.2, 9.3 Hz, 1H), 5.61 (d, J = 4.2 Hz, 1H), 4.56-4.55 (m, 3H), 1.58 (s, 3H), 1.27 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 173.2, 168.1, 166.9, 157.1, 139.3, 139.2, 130.0, 128.9, 128.8, 128.7, 128.5, 127.8, 127.2, 122.6, 115.0, 78.7, 70.6, 68.2, 67.3, 65.2, 58.5, 32.5, 26.7.

Purified by method A (1% triethylamine/20% dichloromethane/79% hexanes solvent system).

**S6**

**(S)-Benzhydryl 2-(2-methoxynaphthalen-6-yl)propanoate ((+)-23).** White solid (1.38 g, 89%); mp = 132-134°C; [a]$^\text{D}$ = +55.7 (c = 1.10, CHCl$_3$); TLC R$_f$ = 0.42 (20% ethyl acetate/80% hexanes); IR (KBr) 3059, 3000, 2942, 2359, 1723, 1604, 1162, 705 cm$^{-1}$; $^1$H NMR (300 MHz, CDCl$_3$) δ 7.30-7.04 (m, 12H), 6.84 (s, 1H), 4.01-3.93 (m, 4H), 1.59 (d, J = 6.9 Hz, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 173.7, 157.8, 140.4, 140.3, 135.7, 133.9, 129.5, 129.1, 128.7, 128.5, 128.1, 127.9, 127.4, 127.3 126.9, 126.7, 126.3, 119.2, 105.8, 77.4, 55.5, 45.9, 18.6. Anal. Calcd for C$_{27}$H$_{24}$O$_3$: C, 81.79; H, 6.10. Found: C, 81.54; H, 6.11. The enantiomeric ratio was
determined by HPLC using a chiral column (OD-H), n-hexane:i-PrOH = 99:1, 1 mL/min; \( t_R = 11.4 \) min compared to a racemic sample which showed two peaks \( t_R = 9.7 \) and 11.4 min.

Purified by method A (1% triethylamine/5% ethyl acetate/94% hexanes solvent system).

### Benzhydryl 2-acetoxybenzoate (24).
White solid (0.30 g, 90%); mp = 103-105°C; TLC \( R_f = 0.26 \) (10% ethyl acetate/90% hexanes); IR (KBr) 3032, 2932, 1771, 1715, 1196 cm\(^{-1}\); \( ^1\)H NMR (300 MHz, CDCl\(_3\)) \( \delta \) 8.12 (dd, \( J = 1.8, 7.8 \) Hz, 1H), 7.60-7.54 (m, 1H), 7.40-7.26 (m, 11H), 7.12-7.09 (m, 2H), 2.05 (s, 3H); \( ^13\)C NMR (75 MHz, CDCl\(_3\)) \( \delta \) 169.9, 163.8, 150.9, 140.0, 134.2, 132.2, 128.8, 128.3, 127.5, 126.3, 124.2, 123.7, 77.9, 20.9. Anal. Calcd for C\(_{22}\)H\(_{18}\)O\(_4\): C, 76.29; H, 5.24. Found: C, 76.22; H, 5.46.

Purified by method A (1% triethylamine/30% ethyl acetate/69% hexanes solvent system).

### (±)-Diphenylmethyl-2-hydroxy-2-phenylacetate (25).
White solid (0.58 g, 92%); mp = 113-114°C; TLC \( R_f = 0.65 \) (30% ethyl acetate/70% hexanes). IR (KBr) 3221, 2815, 2800, 1699, 1240 cm\(^{-1}\); \( ^1\)H NMR (300 MHz, CDCl\(_3\)) \( \delta \) 7.42-7.18 (m, 13H), 6.91-6.87 (m, 3H), 5.28 (d, \( J = 5.4 \) Hz, 1H), 3.45 (d, \( J = 5.7 \) Hz, 1H); \( ^13\)C NMR (75 MHz, CDCl\(_3\)) \( \delta \) 173.0, 139.5, 139.4, 138.3, 128.9, 128.83, 128.79, 128.6, 128.5, 128.1, 127.6, 127.0, 126.5, 79.0, 73.3. Anal. Calcd for C\(_{21}\)H\(_{18}\)O\(_3\): C, 79.22; H, 5.70. Found: C, 79.53; H, 5.40.

Purified by method A (1% triethylamine/10% ethyl acetate/89% hexanes solvent system).

### (±)-Benzhydryl 3-hydroxy-3-phenylpropanoate (26).
White solid (0.36 g, 79%); mp = 62-68°C; TLC \( R_f = 0.54 \) (40% ethyl acetate/60% hexanes); IR (KBr) 3430, 3085, 3058, 3028, 2927, 1721, 1263, 1163 cm\(^{-1}\); \( ^1\)H NMR (300 MHz, CDCl\(_3\)) \( \delta \) 7.38-7.26 (m, 15H), 6.92 (s, 1H), 5.17 (dd, \( J = 4.2, 8.4 \) Hz, 1H), 3.12-3.08 (br s, 1H), 2.96-2.81 (m, 2H); \( ^13\)C NMR (75 MHz, CDCl\(_3\)) \( \delta \) 171.6, 142.8, 140.12, 140.06, 128.8, 128.33, 128.28, 128.1, 127.44, 127.35, 126.0, 77.7, 70.6, 43.9. Anal. Calcd for C\(_{22}\)H\(_{20}\)O\(_3\): C, 79.50; H, 6.06. Found: C, 79.40; H, 5.88.

Purified by method A (1% triethylamine/5% ethyl acetate/95% hexanes solvent system).

### tert-butyl (R)-1-((Benzhydryloxy)carbonyl)ethylcarbamate (27).
White solid (0.29 g, 76%); mp = 97-98°C; [\( \alpha \)]\(_D\) = +11.79 (c = 1.0, CHCl\(_3\)); TLC \( R_f = 0.47 \) (10% ethyl acetate/90% hexanes); IR (KBr) 3340, 3063, 3003, 2979, 2935,1715, 1705, 1395, 1280 cm\(^{-1}\); \( ^1\)H NMR (300 MHz, CDCl\(_3\)) \( \delta \) 7.35-7.26 (m, 10H), 6.89 (s, 1H), 5.06 (br s, 1H) 4.48-4.43 (m, 1H), 1.43-1.40 (m, 12H); \( ^13\)C NMR (75 MHz, CDCl\(_3\)) \( \delta \) 172.6, 155.3, 140.0, 139.9, 128.8, 128.7, 128.3, 127.3, 127.2, 80.0, 78.0, 49.6, 28.6, 18.7. Anal. Calcd for C\(_{21}\)H\(_{25}\)NO\(_4\): C, 71.26; H, 7.09. Found: C, 71.26; H, 7.23. The enantiomeric ratio was determined by HPLC using a chiral column (OD-H), n-hexane:i-PrOH = 99:1, 1 mL/min; \( t_R = 12.8 \) min compared to a racemic sample which showed two peaks \( t_R = 12.6 \) and 14.4 min.

Purified by method B (10% acetone/90% hexanes solvent system).
Benzhydryl picolinate (28). White solid (0.21 g, 71%); mp = 101-103°C; TLC Rf = 0.23 (20% acetone/80% hexanes); IR (KBr) 3052, 1744, 1130 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 8.80 (dq, J = 0.9, 4.8 Hz, 1H), 8.19 (dt, J = 1.1, 7.8 Hz, 1H), 7.85 (dt, J = 1.8, 7.8 Hz, 1H), 7.50-7.44 (m, 5H), 7.39-7.27 (m, 6H), 7.22 (s, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 164.3, 150.3, 148.3, 140.0, 137.1, 128.8, 128.2, 127.5, 127.1, 125.4, 78.2; Anal. Calcd for C₁₉H₁₅NO₂: C, 78.87; H, 5.23; N, 4.84. Found: C, 78.89; H, 5.36; N, 5.16.


Benzhydryl 3-(benzyloxy)thiophene-2-carboxylate (29). Light pink solid (0.26 g, 75%); mp = 91-95°C; TLC Rf = 0.29 (60% dichloromethane/40% hexanes); IR (KBr) 3065, 3033, 1710, 1685, 1540, 1058 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 7.50-7.22 (m, 16H), 7.01 (s, 1H), 6.87 (d, J = 5.4 Hz, 1H), 5.24 (s, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 161.2, 161.1, 140.9, 136.5, 131.3, 128.9, 128.7, 128.4, 128.0, 127.7, 127.3, 117.5, 111.0, 77.1, 73.7. Anal. Calcd for C₂₅H₂₀O₃S: C, 74.98; H, 5.03; Found: C, 74.76; H, 5.38.

Diphenylmethyl trichloroacetimidate (0.300 g, 0.913 mmol) was dissolved in 2 mL of toluene and heated to reflux. After ~24 h the reaction was allowed to cool to room temperature and preabsorbed on silica gel. Purification by silica gel chromatography (5% ethyl acetate/95% hexanes) provided 138 mg (46% yield) of N-benzhydryl-trichloroacetamide as an off-white solid.

N-Benzhydryl-trichloroacetamide (5). mp = 121-123°C; TLC Rf = 0.65 (10% ethyl acetate/90% hexanes); ¹H NMR (300 MHz, CDCl₃) δ 7.32-7.11 (m, 11H), 6.09 (d, J = 7.8 Hz, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 161.0, 139.9, 129.1, 128.3, 127.4, 92.8, 59.1; Anal Calcd for C₁₅H₁₂Cl₃NO: C, 54.82; H, 3.68; N, 4.26; Found: C, 55.14; H, 3.73; N, 4.66.


Diphenylmethyl imidate (0.301 g, 0.91 mmol) was dissolved in 3.6 ml dichloromethane and camphor sulfonic acid (43 mg, 0.18 mmol) was added. The mixture was stirred at rt for 18 h. The reaction mixture was then preabsorbed on silica gel and purified by silica gel chromatography (5% ethyl acetate/95% hexanes) which provided 0.149 g (90%) of the ether as a white solid.

Diphenylmethyl ether (6). White solid (0.149 g, 90%); mp = 107-108°C; TLC Rf = 0.77 (5% ethyl acetate/95% hexanes); ¹H NMR (300 MHz, CDCl₃) δ 7.44-7.26 (m, 20H), 5.46 (s, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 142.5, 128.7, 127.8, 127.6, 80.3.
Racemization of (+)-23:
Ester (+)-23 (0.472 g, 1.18 mmol) was dissolved in 5 mL tetrahydrofuran. DBU (0.21 mL, 1.42 mmol) was added and the reaction mixture was heated to reflux. After ~18 h the reaction was allowed to cool to room temperature and the solvent was removed under reduced pressure. The residue was dissolved in 10 mL ethyl acetate and washed with 1M HCl (2 x 20 mL) followed by 20 mL brine. The organic layer was dried over magnesium sulfate and concentrated. Purification by silica gel chromatography (10% ethyl acetate/90% hexanes) gave 0.453 g (96%) of racemized ester (±)-23 as a white solid. The characterization data for this compound matched those reported for ester (+)-23 except the optical rotation was 0°. Analysis by chiral HPLC (OD-H column, n-hexane:i-PrOH = 99:1, 1 mL/min) showed two peaks of equal ratio, $t_R = 9.7$ and 11.4 min.

Racemization of (+)-27:
Ester (+)-27 (70 mg, 0.19 mmol) was dissolved in 1.5 mL toluene. DBU (30 mg, 0.19 mmol) was then added and the reaction mixture was heated to reflux. After ~18 h the reaction was allowed to cool to room temperature and the solvent was removed under reduced pressure. The residue was dissolved in 10 mL ethyl acetate and washed with 1M HCl (2 x 20 mL) followed by 20 mL brine. The organic layer was dried over magnesium sulfate and concentrated to give crude product. Purification by column chromatography (10% ethyl acetate/90% hexanes) gave 50 mg (72%) of racemized ester (±)-27 as a white solid. The characterization data for this compound matched those reported for ester (+)-27 except the optical rotation was 0°. Analysis by chiral HPLC (OD-H column, n-hexane:i-PrOH = 99:1, 1 mL/min) showed two peaks of equal ratio, $t_R = 12.6$ and 14.4 min.

Ester (+)-23 (0.198 g, 0.52 mmol) and 10% palladium on carbon (55 mg, 0.52 mmol) were placed in a flame-dried flask. Dry methanol (2.5 mL) was then added. The flask was evacuated and then filled with hydrogen gas using a balloon. After 75 min the reaction mixture was vacuum filtered through a bed of Celite with methanol. The filtrate was concentrated and then purified by silica gel chromatography (30% ethyl acetate/70% hexanes) to give 0.101 g (83%) of the carboxylic acid 34 as a white solid. **(S)-2-(2-Methyl-naphthalene-6-yl)propanoic acid** (34). White solid (0.100 g, 83%); mp = 153-155°C; $[\alpha]_{D}^{20} = +56.9$ (c = 1.0, CHCl3); TLC $R_f = 0.11$ (30% ethyl acetate/70% hexanes); $^1$H NMR (300 MHz, CDCl3) δ 7.70 (dd, $J = 2.4$, 8.4 Hz, 3H), 7.41 (dd, $J = 3.9$, 8.7 Hz, 1H), 7.16-7.10 (m, 2H), 3.91-3.85 (m, 4H), 1.60 (d, $J = 7.2$, Hz, 3H); $^{13}$C NMR (75 MHz, CDCl3) δ 181.3, 157.9, 135.1, 134.0, 129.5, 129.1, 127.5, 126.40, 126.36, 119.3, 105.8, 55.5, 45.5, 18.3. The enantiomeric ratio was determined by HPLC using a chiral column (OD-H), n-hexane:i-PrOH = 97:3, 1 mL/min; $t_R = 15.1$ min compared to a racemic sample which showed two peaks $t_R = 12.9$ and 15.4 min. Racemic (±)-34 was prepared following the same procedure as (+)-34, only with racemic starting material prepared from the racemization of ester 23.
Esterification of salycyclic acid 30:
Salicylic acid 30 (300 mg, 2.17 mmol) and diphenylmethyl trichloroacetimidate 2 (930 mg, 2.83 mmol) were added to a flame dried round bottom flask. Dry dichloromethane (8.7 mL) was then added and the reaction stirred under argon for 18 h. Triethylamine (0.5 mL) was then added and the reaction mixture was preadsorbed on silica gel. Purification by silica gel chromatography using a solvent gradient of 0%:5%:10%:20%:30%:50% ethyl acetate / hexanes buffered with 1% triethylamine afforded 31 (510 mg, 77%) as a colorless oil, 32 (150 mg, 15%) as a white sticky solid and 33 (20 mg, 3%) as a white solid.

Benzhydryl 2-hydroxybenzoate (31):
Colorless oil (510 mg, 77%); TLC $R_f = 0.66$ (20% ethyl acetate/80% hexanes); IR (thin film) 3189, 3090, 3066, 3033, 1674, 1400, 1211, 1158 cm$^{-1}$; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 10.67 (s, 1H), 8.07-8.03 (m, 1H), 7.51-7.29 (m, 11H), 7.13 (s, 1H), 7.00-6.90 (m, 2H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 169.6, 162.3, 140.0, 136.3, 130.3, 129.0, 128.6, 127.5, 119.6, 118.1, 112.8, 78.2. Anal. Calcd for C$_{20}$H$_{16}$O$_3$: C, 78.93; H, 5.30. Found: C, 78.94; H, 5.30.

Benzhydryl 2-(benzhydryloxy)benzoate (32):
White sticky solid (150 mg, 15%); TLC $R_f = 0.72$ (50% ethyl acetate/50% hexanes); IR (KBr) 3064, 3031, 2929, 1724, 1600, 1247, 1164, 1070 cm$^{-1}$; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.90-7.87 (m, 1H), 7.45-7.21 (m, 21H), 7.15 (s, 1H), 6.96-6.91 (m, 2H), 6.38 (s, 1H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 166.1, 157.4, 141.0, 140.7, 133.6, 132.4, 128.9, 128.7, 128.1, 128.0, 127.6, 127.3, 121.3, 120.6, 114.9, 82.0, 78.0. Anal. Calcd for C$_{33}$H$_{26}$O$_3$: C, 84.23; H, 5.57. Found: C, 84.49; H, 5.66.

2-(Benzhydryloxy)benzoic acid (33):
White solid (20 mg, 3%); TLC $R_f = 0.57$ (20% ethyl acetate/80% hexanes); IR (KBr) 3386, 1693, 1667, 1249 cm$^{-1}$; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 8.20 (dd, $J = 1.5$, 7.8 Hz, 1H), 7.44-7.32 (m, 12H), 7.12-7.07 (m, 1H), 6.99-6.96 (m, 1H), 6.47 (s, 1H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 165.6, 157.0, 139.0, 135.0, 134.0, 129.4, 129.0, 127.0, 122.6, 118.5, 114.7, 84.8. Anal. Calcd for C$_{20}$H$_{16}$O$_3$: C, 78.93; H, 5.30. Found: C, 78.76; H, 5.37.
Chiral HPLC Data

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AAA-2-63
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AAA-2-65
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