Catalytic Enantioselective Construction of All-Carbon Quaternary Stereocenters: Synthetic and Mechanistic Studies of the C-Acylation of Silyl Ketene Acetals

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Supporting Information

I. General

THF, toluene, Et₂O, and CH₂Cl₂ were purified by passage through a neutral alumina column. Ac₂O was distilled from phosphorus pentoxide. [Me₄N]OAc (Alfa Aesar) was purified by recrystallization from 2:1 CH₃CN/CH₂Cl₂ and dried under vacuum at 150 °C. *n*-BuLi (Alfa Aesar) was titrated with diphenylacetic acid (Aldrich) prior to each use. Methylene chloride-*d*₂ (Cambridge Isotope Laboratories) was distilled from CaH₂.

2-Phenylbutyric acid (Aldrich), 4-methoxyphenylacetic acid (Avocado), (4-trifluoromethylphenyl)acetic acid (Avocado), thiophene-2-acetic acid (Avocado), (S)-(+)-2-(6-methoxynaphthalene)propionic acid (TCI), 2-phenylpropionic acid (Aldrich), NEt₃ (EM Science), *N,N*-dimethylformamide (Aldrich), zinc dust (Mallinckrodt), mercury (II) chloride (Alfa Aesar), bromoethane (Alfa Aesar), pentane (Burdick & Jackson), hydrochloric acid (Fisher), sulfuric acid (Fisher), MgSO₄ (Fisher), iodoethane (Alfa Aesar), 2-bromopropane (Avocado), diisopropylamine (Aldrich), Me₃SiCl (Avocado), TBSCl (Pfizer), Et₂O (Mallinckrodt), isopropanol (Fluka), oxalyl chloride (Aldrich), *t*-butanol (Aldrich), 2,2-dimethylpropanol (Avocado), CH₃CN (Aldrich), methanol (Mallinckrodt), phenylacetic acid (Aldrich), (*E*)-styrylacetic acid (Aldrich), 4-methoxyphenylacetic acid (Avocado), 4-trifluoromethylphenylacetic acid (Avocado), *o*-tolylacetic acid (Avocado), naphthalene-1-acetic acid (Avocado), thiophene-2-acetic acid (Avocado), thiophene-3-acetic acid (Avocado), 1-methyl-3-indoleacetic acid (Aldrich), 1,3,2-dioxathiolane 2,2-dioxide (Aldrich), 1,4-dioxane (Aldrich), isobutylene oxide (TCI), chloroform (Mallinckrodt), bromine (Fluka), FeBr₃ (Strem), AgSbF₆ (Strem), tetrabutylammonium chloride (TCI), absolute EtOH (Pharmco), and 3-oxo-1-indancarboxylic acid (Aldrich) were used as received.

Catalyst 1 was prepared as previously reported.¹

All experiments were conducted under an argon or nitrogen atmosphere in oven-dried glassware with magnetic stirring, unless otherwise specified.

II. Preparation of Carboxylic Acids

These reactions have not been optimized.

4-Methyl-2-phenylpentanoic acid [14320-58-2]. This was prepared according to the procedure of Padwa and Doyle.²

¹H NMR (500 MHz, CDCl₃) δ 7.26-7.37 (m, 5H), 3.67 (app t, 1H, J=8.0), 1.96 (ddd, 1H, J=14.0, J=8.0, J=6.0), 1.71 (ddd, 1H, J=14.0, J=7.5, J=6.5), 1.50 (app sept, 1H, J=6.5), 0.92 (d, 6H, J=7.0). ¹³C NMR (125 MHz, CDCl₃) δ 180.9, 138.8, 128.9, 128.3, 127.7, 49.7, 42.2, 26.0, 22.8, 22.4.

3-Methyl-2-phenylbutyric acid [3508-94-9]. This was prepared according to the procedure of Mosher,³ using phenylacetic acid (11.3 g, 83.1 mmol) and 2-bromopropane (11.5 mL, 122 mmol). Product: tan solid (14.5 g, 98%).

¹H NMR (500 MHz, CDCl₃) δ 12.0 (s, 1H), 7.26-7.36 (m, 5H), 3.15 (d, 1H, J=10.5), 2.34 (m, 1H), 1.09 (d, 3H, J=6.5), 0.72 (d, 3H, J=7.0). ¹³C NMR (125 MHz, CDCl₃) δ 180.6, 137.9, 128.8, 128.7, 127.7, 60.2, 31.7, 21.7, 20.3.

2-(4-Methoxyphenyl)butyric acid [29644-99-3]. A solution of *n*-BuLi (in hexanes; 24.8 mL, 66.2 mmol) was added via syringe to a solution of 4-methoxyphenylacetic acid (5.00 g, 30.1 mmol) in THF (80 mL) at -78 °C. The resulting mixture was warmed to room temperature and stirred for 45 min. Neat bromoethane (9.00 mL, 120 mmol) was then added via syringe, and the resulting solution was stirred for 12 h. The reaction mixture was then quenched by the addition of HCl (1N; 100 mL) and extracted with Et₂O (3 x 100 mL). The combined extracts were dried (Na₂SO₄) and concentrated to a yellow oil (5.07 g, 87%).

¹H NMR (300 MHz, CDCl₃) δ 7.25 (ddd, 2H, J=8.4, J=3.0, J=1.8), 6.87 (ddd, 2H, J=8.7, J=3.0, J=2.1), 3.80 (s, 3H), 3.41 (dd, 1H, J=7.8, J=7.5), 2.09 (dq, 1H, J=13.8, J=7.5), 1.79 (dq, 1H, J=13.5, J=7.8), 0.90 (app t, 3H, J=7.2). ¹³C NMR (125 MHz, CDCl₃) δ 180.9, 159.1, 130.6, 129.3, 114.2, 55.4, 52.6, 26.5, 12.3.

2-(2-Thienyl)butyric acid [54955-40-7]. This was prepared according to the procedure of Padwa and Doyle.²

¹H NMR (500 MHz, CDCl₃) δ 12.0 (s, 1H), 7.26 (m, 1H), 7.01 (m, 2H), 3.83 (app t, 1H, J=7.5), 2.17 (m, 1H), 1.92 (m, 1H), 1.01 (t, 3H, J=7.0). ¹³C NMR (125 MHz, CDCl₃) δ 179.3, 140.7, 127.3, 127.0, 125.4, 48.6, 27.8, 12.1.

Indan-1-carboxylic acid [14381-42-1]. Mercury (II) chloride (0.192 g, 0.709 mmol) was added to a solution of zinc dust (7.52 g, 115 mmol) in water (5.0 mL). Hydrochloric acid (0.3 mL) was added, and the resulting slurry was stirred for 15 min, filtered, and washed with water. This solid was added to a flask containing 3-oxo-1-indancarboxylic acid (2.50 g, 14.2 mmol) dissolved in a 2.5/1 solution of toluene/water. Concentrated hydrochloric acid (10 mL) was added, and the reaction mixture was refluxed for 12 h. Then, the mixture was extracted with Et₂O (3 x 100 mL), and the combined extracts were dried (MgSO₄) and concentrated to a yellow oil (2.13 g, 93%).

¹H NMR (300 MHz, CDCl₃) δ 7.45 (m, 1H), 7.18-7.29 (m, 3H), 4.10 (dd, 1H, J=8.4, J=6.3), 3.11 (m, 1H), 2.94 (m, 1H), 2.30-2.52 (m, 2H). ¹³C NMR (125 MHz, CDCl₃) δ 181.3, 144.9, 140.7, 128.5, 127.3, 125.7, 125.4, 50.7, 32.4, 29.4.

(E)-4-phenyl-2-ethyl-3-butenic acid [52216-97-4]. A solution of *n*-BuLi (in hexanes; 14.2 mL, 41.1 mmol) was added via syringe to a -78 °C solution of (*E*)-styrylacetic acid (3.03 g, 18.7 mmol) in THF (50 mL). This mixture was stirred for 40 min at -78 °C, and then neat bromoethane (4.20 mL, 56.1 mmol) was added via syringe. The resulting solution was stirred for 12 h, and then the reaction was quenched by the addition of saturated NH₄Cl (100 mL). The mixture was extracted with Et₂O (3 x 100 mL), washed with saturated NaCl (2 x 50 mL), dried (Na₂SO₄), and concentrated to a yellow solid (3.36 g, 94%).

¹H NMR (300 MHz, CDCl₃) δ 7.21-7.40 (m, 5H), 6.50 (d, 1H, J=15.9), 6.19 (dd, 1H, J=15.9, J=9.0), 3.11 (m, 1H), 1.91 (app sept, 1H, J=7.2), 1.71 (app sept, 1H, J=7.5), 0.99 (dd, 3H, J=7.8, J=7.2). ¹³C NMR (125 MHz, CDCl₃) δ 180.6, 136.9, 133.0, 128.7, 127.8, 126.9, 126.5, 51.2, 26.0, 11.8.

III. Preparation of Esters

These reactions have not been optimized.

Oxalyl chloride (10.6 mL, 122 mmol) was added over 5 min to a $-78\text{ }^{\circ}\text{C}$ solution of 2-phenylbutyric acid (8.00 g, 48.7 mmol) and *N,N* dimethylformamide (3 drops) in CH_2Cl_2 (40 mL). The resulting mixture was stirred at $-78\text{ }^{\circ}\text{C}$ for 2 h, and then it was warmed to room temperature and concentrated. CH_2Cl_2 (40 mL) was then added to the unpurified acid chloride, and the resulting solution was cooled to $0\text{ }^{\circ}\text{C}$. To this solution was added 2-methyl-2-propanol (5.13 mL, 53.6 mmol) and then NEt_3 (3 mL). The reaction mixture was slowly warmed to room temperature and then stirred for 15 h. Saturated NH_4Cl (50 mL) was added, and then the reaction mixture was extracted with CH_2Cl_2 (3 x 50 mL). The combined organic layers were washed with saturated NaHCO_3 (2 x 100 mL) and water (2 x 50 mL), dried over MgSO_4 , filtered, and concentrated, to yield an orange oil. Purification by vacuum distillation ($83\text{--}85\text{ }^{\circ}\text{C}$, 1 mm Hg) furnished the target compound as a clear, colorless liquid (6.06 g, 52%).

^1H NMR (500 MHz, C_6D_6) δ 7.32 (dd, 2H, $J=6.0$, $J=0.5$), 7.13 (m, 2H), 7.04 (tt, 1H, $J=7.5$, $J=1.5$), 3.35 (t, 1H, $J=7.5$), 2.12 (d app t, 1H, $J=13.5$, $J=7.5$), 1.70 (d app t, 1H, $J=13.5$, $J=7.5$), 1.29 (s, 9H), 0.83 (app t, 3H $J=7.5$). ^{13}C NMR (125 MHz, CDCl_3) δ 173.5, 139.9, 128.5, 128.0, 127.0, 80.6, 54.6, 28.1, 27.0, 12.4. FTIR (thin film) 3030, 2969, 2933, 2876, 1729, 1454, 1148, 1078, 749, 698 cm^{-1} . HRMS (EI, m/z) calcd. for $\text{C}_{14}\text{H}_{20}\text{O}_2$ (M^+) 220.1457, found 220.1458.

[2294-71-5]. Methanol (123 mL) and sulfuric acid (0.81 mL, 15.2 mmol) were added to a solution of 2-phenylbutyric acid (25.0 g, 152 mmol) in benzene (300 mL). The reaction mixture was refluxed for 14 h, and then it was cooled to room temperature, diluted with water (200 mL), and extracted with Et_2O (3 x 200 mL). The combined extracts were washed successively with saturated NaHCO_3 (2 x 200 mL) and saturated NaCl (2 x 200 mL), dried (MgSO_4), and concentrated to a yellow liquid. Purification by vacuum distillation ($118\text{ }^{\circ}\text{C}$, 1 mm Hg) furnished a clear, colorless liquid (23.0 g, 85%).

^1H NMR (500 MHz, CDCl_3) δ 7.25-7.35 (m, 5H), 3.67 (s, 3H), 3.50 (app t, 1H, $J=8.0$), 2.15 (dq, 1H, $J=15.5$, $J=8.0$), 1.84 (dq, 1H, $J=14.5$, $J=7.0$), 0.93 (app t, 3H, $J=7.5$). ^{13}C NMR (125 MHz, CDCl_3) δ 174.7, 139.4, 128.8, 128.2, 127.5, 53.6, 52.1, 27.0, 12.4.

2,2-Dimethylpropanol (9.9 mL, 91.4 mmol), concentrated sulfuric acid (6 drops), and MgSO_4 (3 scoops) were added to a solution of 2-phenylbutyric acid (5.00 g, 30.5 mmol) in toluene (30 mL). The reaction mixture was refluxed for 12 h, and then the reaction was quenched by the addition of saturated NaHCO_3 (100 mL). The reaction mixture was extracted with Et_2O (2 x 100 mL), and the combined extracts were dried (MgSO_4) and concentrated to a yellow oil (6.54 g, 91%).

^1H NMR (500 MHz, CDCl_3) δ 7.19-7.38 (m, 5H), 3.83 (d, 1H, $J=11.0$), 3.79 (d, 1H, $J=10.5$), 3.52 (app t, 1H, $J=7.5$), 2.18 (m, 1H), 1.87 (m, 1H), 0.95 (t, 3H, $J=7.5$), 0.90 (s, 9H). ^{13}C NMR (125 MHz, CDCl_3) δ 174.2, 139.5, 128.7, 128.3, 127.4, 74.0, 54.1, 31.7, 26.7, 26.6, 12.5. FTIR (thin film) 3031, 2963, 2875, 1735, 1455, 1368, 1164, 995, 698 cm^{-1} . HRMS (EI, m/z) calcd. for $\text{C}_{15}\text{H}_{22}\text{O}_2$ (M^+) 234.1614, found 234.1613.

[135806-11-0]. Isopropanol (5 mL), concentrated sulfuric acid (4 drops), toluene (25 mL), and MgSO_4 (3 scoops) were added to 2-phenylbutyric acid (10.0 g, 60.9 mmol). The reaction mixture was refluxed for 12 h, and then the reaction was quenched by the addition of saturated NaHCO_3 (100 mL). The reaction mixture was extracted with Et_2O (3 x 100 mL), and the combined extracts were washed with saturated NaHCO_3 (2 x 100 mL), dried (MgSO_4), and concentrated to a light-yellow oil (6.19 g, 49%).

^1H NMR (500 MHz, CDCl_3) δ 7.33 (m, 4H), 7.27 (m, 1H), 5.04 (app sept, 1H, $J=6.5$), 3.44 (dd, 1H, $J=7.5$, $J=7.0$), 2.13 (dq, 1H, $J=14.5$, $J=7.0$), 1.81 (dq, 1H, $J=15.0$, $J=8.0$), 1.26 (d, 3H, $J=6.5$), 1.17 (d, 3H, $J=6.5$), 0.94 (app t, 3H, $J=7.5$). ^{13}C NMR (125 MHz, CDCl_3) δ 174.2, 140.1, 129.2, 128.6, 127.7, 68.5, 54.5, 27.6, 22.5, 22.3, 12.9.

Oxalyl chloride (10.6 mL, 122 mmol) was added over 5 min to a $-78\text{ }^\circ\text{C}$ solution of 2-phenylbutyric acid (8.00 g, 48.7 mmol) and N,N dimethylformamide (3 drops) in CH_2Cl_2 (40 mL). The resulting mixture was stirred at $-78\text{ }^\circ\text{C}$ for 2 h, and then it was warmed to room temperature and concentrated. CH_2Cl_2 (40 mL) was added to the unpurified acid chloride, and the resulting solution was cooled to $0\text{ }^\circ\text{C}$. To this solution was added t -butanol (5.13 mL, 53.6 mmol) and then NEt_3 (3 mL). The reaction mixture was slowly warmed to room temperature and then stirred for 15 h. Saturated NH_4Cl (50 mL) was added, and then the reaction mixture was extracted with CH_2Cl_2 (3 x 50

mL). The combined organic layers were washed with saturated NaHCO_3 (2 x 100 mL) and water (2 x 50 mL), dried over MgSO_4 , filtered, and concentrated to yield an orange oil. Purification by vacuum distillation (83–85 °C, 1 mm Hg) furnished the target compound as a clear, colorless liquid (6.06 g, 52%).

^1H NMR (500 MHz, C_6D_6) δ 7.32 (dd, 2H, $J=6.0$, $J=0.5$), 7.13 (m, 2H), 7.04 (tt, 1H, $J=7.5$, $J=1.5$), 3.35 (t, 1H, $J=7.5$), 2.12 (d app t, 1H, $J=13.5$, $J=7.5$), 1.70 (d app t, 1H, $J=13.5$, $J=7.5$), 1.29 (s, 9H), 0.83 (app t, 3H, $J=7.5$). ^{13}C NMR (125 MHz, CDCl_3) δ 173.5, 139.9, 128.5, 128.0, 127.0, 80.6, 54.6, 28.1, 27.0, 12.4. FTIR (thin film) 3030, 2969, 2933, 2876, 1729, 1454, 1148, 1078, 749, 698 cm^{-1} . HRMS (EI, m/z) calcd. for $\text{C}_{14}\text{H}_{20}\text{O}_2$ (M^+) 220.1457, found 220.1458.

[65757-64-4]. Isopropanol (25 mL), sulfuric acid (6 drops), and MgSO_4 (3 scoops) were added to 2-phenylpropionic acid (5.00 g, 33.3 mmol). After refluxing for 72 h, the reaction mixture was cooled to room temperature, and the reaction was quenched by the addition of saturated NaHCO_3 . The mixture was extracted with Et_2O (3 x 100 mL), and the combined extracts were washed successively with saturated NaHCO_3 (2 x 50 mL) and water (2 x 50 mL), dried (Na_2SO_4), and concentrated to a clear, colorless oil (4.95 g, 77%).

^1H NMR (300 MHz, CDCl_3) δ 7.24–7.32 (m, 5H), 5.00 (app sept, 1H, $J=6.0$), 3.67 (q, 1H, $J=7.2$), 1.49 (d, 3H, $J=7.2$), 1.22 (d, 3H, $J=6.0$), 1.14 (d, 3H, $J=6.3$). ^{13}C NMR (125 MHz, CDCl_3) δ 174.7, 141.5, 129.2, 128.1, 127.7, 68.6, 46.4, 22.5, 22.2, 19.3.

[124888-45-5]. Oxalyl chloride (2.84 mL, 32.5 mmol) was added over 5 min to a –78 °C solution of 4-methyl-2-phenylpentanoic acid (2.50 g, 13.0 mmol) and N,N -dimethylformamide (2 drops) in CH_2Cl_2 (35 mL). The resulting mixture was stirred at –78 °C for 2.5 h, and then it was warmed to room temperature and concentrated. CH_2Cl_2 (20 mL) was added to the unpurified acid chloride, and the resulting solution was cooled to 0 °C. To this solution was added isopropanol (20 mL) and then NEt_3 (2.2 mL). The reaction mixture was slowly warmed to room temperature and then stirred for 12 h. Saturated NH_4Cl (50 mL) was added, and then the reaction mixture was extracted with Et_2O (3 x 100 mL). The combined organic layers were washed successively with saturated NaHCO_3 (2 x 100 mL) and saturated brine (2 x 50 mL), dried (Na_2SO_4), filtered, and concentrated to a light-yellow oil. Purification by flash chromatography (5% Et_2O /95% pentane) provided a clear, colorless oil (1.90 g, 62%).

^1H NMR (300 MHz, CDCl_3) δ 7.21-7.35 (m, 5H), 4.99 (app sept, 1H, $J=6.3$), 3.61 (dd, 1H, $J=7.5$, $J=7.2$), 1.97 (ddd, 1H, $J=13.5$, $J=9.0$, $J=6.3$), 1.65 (dt, 1H, $J=13.8$, $J=6.9$), 1.48 (app sept, 1H, $J=6.6$), 1.22 (d, 3H, $J=6.3$), 1.13 (d, 3H, $J=6.6$), 0.92 (d, 6H, $J=6.6$). ^{13}C NMR (75 MHz, CDCl_3) δ 173.9, 139.8, 128.7, 128.1, 127.2, 68.0, 50.1, 42.7, 26.1, 22.8, 22.6, 22.0, 21.8.

[13027-70-8]. Oxalyl chloride (2.09 mL, 24.0 mmol) was added over 5 min to a -78°C solution of 3-methyl-2-phenylbutyric acid (1.71 g, 9.59 mmol) and *N,N*-dimethylformamide (2 drops) in CH_2Cl_2 (20 mL). The resulting mixture was stirred at -78°C for 2 h, and then it was warmed to room temperature and concentrated. CH_2Cl_2 (10 mL) was added to the unpurified acid chloride, and the resulting solution was cooled to 0°C . To this solution was added isopropanol (10 mL) and then NEt_3 (2.67 mL). The reaction mixture was slowly warmed to room temperature and then stirred for 12 h. Saturated NaHCO_3 (50 mL) was added, and then the reaction mixture was extracted with Et_2O (3 x 75 mL). The combined organic layers were washed with saturated NaHCO_3 (2 x 75 mL), dried (Na_2SO_4), filtered, and concentrated, to yield a light-yellow oil (1.80 g, 85%).

^1H NMR (500 MHz, CDCl_3) δ 7.36 (m, 2H), 7.31 (td, 2H, $J=7.0$, $J=2.0$), 7.25 (tt, 1H, $J=7.0$, $J=1.5$), 5.00 (app sept, 1H, $J=6.5$), 3.11 (d, 1H, $J=11.0$), 2.35 (m, 1H), 1.24 (d, 3H, $J=6.0$), 1.16 (d, 3H, $J=6.0$), 1.07 (d, 3H, $J=6.5$), 0.72 (d, 3H, $J=6.5$). ^{13}C NMR (125 MHz, CDCl_3) δ 173.7, 138.8, 128.7, 128.6, 127.3, 68.0, 60.7, 32.2, 22.1, 21.8, 21.6, 20.5.

[68641-85-0]. Isopropanol (15 mL), concentrated sulfuric acid (6 drops), and MgSO_4 (3 scoops) were added to 2-(6-methoxynaphthalen-2-yl)propionic acid (1.92 g, 8.34 mmol). The reaction mixture was refluxed for 12 h, and then the reaction was quenched by the addition of saturated NaHCO_3 (100 mL). The mixture was extracted with Et_2O (3 x 100 mL), and the combined extracts were washed successively with saturated NaHCO_3 (2 x 100 mL) and saturated brine (2 x 100 mL), dried (Na_2SO_4), and concentrated to a white solid (2.05 g, 90%).

^1H NMR (500 MHz, CDCl_3) δ 7.71 (dd, 2H, $J=9.0$, $J=4.5$), 7.67 (d, 1H, $J=1.0$), 7.42 (dd, 1H, $J=8.5$, $J=2.0$), 7.14 (dt, 2H, $J=9.0$, $J=2.5$), 5.01 (app sept, 1H, $J=6.0$), 3.92 (s, 3H), 3.81 (q, 1H, $J=7.0$), 1.57 (d, 3H, $J=7.0$), 1.23 (d, 3H, $J=6.5$), 1.13 (d, 3H, $J=6.0$). ^{13}C NMR (125 MHz, CDCl_3) δ 174.9, 158.3, 136.7, 134.3, 130.0, 129.6, 127.7, 127.0, 126.6, 119.6, 106.2, 68.7, 56.0, 46.3, 22.5, 22.3, 19.3.

Isopropanol (10 mL), concentrated sulfuric acid (5 drops), toluene (10 mL), and MgSO_4 (3 scoops) were added to 2-(4-methoxyphenyl)butyric acid (1.02 g, 5.25 mmol). The reaction mixture was refluxed for 12 h, after which the reaction was quenched by the addition of saturated NaHCO_3 (100 mL). The mixture was extracted with Et_2O (3 x 75 mL), and the combined extracts were washed successively with saturated NaHCO_3 (2 x 100 mL) and saturated brine (2 x 100 mL), dried (MgSO_4), and concentrated to a yellow oil (0.875 g, 71%).

^1H NMR (300 MHz, CDCl_3) δ 7.22 (ddd, 2H, $J=9.0$, $J=3.0$, $J=2.1$), 6.85 (ddd, 2H, $J=9.0$, $J=3.0$, $J=2.1$), 4.99 (app sept, 1H, $J=6.3$), 3.79 (s, 3H), 3.35 (app t, 1H, $J=7.5$), 2.05 (dq, 1H, $J=15.0$, $J=7.5$), 1.74 (dq, 1H, $J=14.7$, $J=7.2$), 1.22 (d, 3H, $J=6.3$), 1.14 (d, 3H, $J=6.3$), 0.89 (app t, 3H, $J=7.5$). ^{13}C NMR (125 MHz, C_6D_6) δ 173.8, 159.6, 132.3, 129.6, 114.6, 67.9, 55.0, 53.6, 27.7, 22.1, 21.9, 12.7. FTIR (thin film) 2967, 2936, 2876, 1728, 1611, 1513, 1465, 1374, 1303, 1251, 1172, 1108, 1037, 831 cm^{-1} . HRMS (EI, m/z) calcd. for $\text{C}_{14}\text{H}_{20}\text{O}_3$ (M^+) 236.1407, found 236.1412.

Isopropanol (15 mL), sulfuric acid (5 drops), and MgSO_4 (3 scoops) were added to (4-trifluoromethylphenyl)acetic acid (3.00 g, 12.9 mmol) in a Schlenk tube. The mixture was heated for 36 h at 100 $^\circ\text{C}$, and then the reaction was quenched by the addition of saturated NaHCO_3 . The reaction mixture was extracted with Et_2O (3 x 100 mL), and the combined extracts were washed successively with saturated NaHCO_3 (2 x 100 mL) and water (2 x 100 mL), dried (Na_2SO_4), and concentrated to a white crystalline solid (2.72 g, 86%).

^1H NMR (300 MHz, CDCl_3) δ 7.58 (d, 2H, $J=8.1$), 7.40 (d, 2H, $J=8.1$), 5.02 (sept, 1H, $J=6.3$), 3.64 (s, 2H), 1.23 (d, 6H, $J=6.3$). ^{13}C NMR (125 MHz, CDCl_3) δ 171.0, 139.0, 130.3, 130.0 (q, $J=32.2$), 126.1 (q, $J=4.0$), 124.9 (q, $J=271.8$), 69.3, 42.1, 22.4. FTIR (thin film) 2988, 1719, 1559, 1457, 1327, 1230, 1180, 1109, 1070, 1021, 905, 835 cm^{-1} . HRMS (ESI, m/z) calcd. for $\text{C}_{12}\text{H}_{13}\text{F}_3\text{O}_2\text{Na}$ ($\text{M}+\text{Na}$) $^+$ 269.0760, found 269.0768. mp = 33-34 $^\circ\text{C}$.

A solution of *n*-BuLi (in hexanes; 3.12 mL, 8.53 mmol) was added via syringe to a -78 $^\circ\text{C}$ solution of diisopropylamine (1.20 mL, 8.53 mmol) in THF (10 mL). The mixture was stirred at -78 $^\circ\text{C}$ for 30 min, and then a solution of isopropyl 4-

trifluoromethylphenylacetate (2.00 g, 8.12 mmol) in THF (20 mL) was added via cannula. The mixture was stirred for 45 min at -78°C , and then iodoethane (0.715 g, 8.93 mmol) was added. The mixture was allowed to warm to room temperature and stirred for 12 h. The reaction was then quenched by the addition of HCl (1 M; 50 mL), and the mixture was extracted with Et_2O (3 x 100 mL). The combined extracts were washed successively with 1M HCl (1 x 50 mL), saturated NaHCO_3 (2 x 50 mL), and water (2 x 50 mL), and then they were dried (MgSO_4) and concentrated to a dark-orange oil. Purification by flash chromatography (10% Et_2O /90% pentane) provided a clear, colorless oil (1.86 g, 83%).

^1H NMR (500 MHz, CDCl_3) δ 7.58 (d, 2H, $J=8.0$), 7.44 (d, 2H, $J=8.0$), 5.01 (app sept, 1H, $J=6.0$), 3.48 (app t, 1H, $J=7.5$), 2.11 (dq, 1H, $J=14.5$, $J=7.0$), 1.79 (dq, 1H, $J=14.5$, $J=7.0$), 1.24 (d, 3H, $J=6.5$), 1.15 (d, 3H, $J=6.5$), 0.91 (app t, 3H, $J=7.5$). ^{13}C NMR (125 MHz, CDCl_3) δ 173.5, 144.0, 130.0 (q, $J=32.2$), 129.0, 126.1 (q, $J=3.5$), 124.9 (q, $J=271.8$), 68.9, 54.2, 27.5, 22.4, 22.2, 12.7. FTIR (thin film) 2981, 2939, 2880, 1731, 1619, 1459, 1376, 1327, 1170, 1126, 1069, 1020, 841 cm^{-1} . HRMS (EI, m/z) calcd. for $\text{C}_{14}\text{H}_{17}\text{F}_3\text{O}_2$ (M^+) 274.1175, found 274.1177.

Isopropanol (35 mL), concentrated sulfuric acid (6 drops), and MgSO_4 (3 scoops) were added to 2-(2-thienyl)butyric acid (4.12 g, 24.2 mmol). The reaction mixture was refluxed for 12 h, after which the reaction was quenched by the addition of saturated NaHCO_3 (50 mL). The mixture was extracted with Et_2O (3 x 100 mL), and the combined extracts were washed with saturated NaHCO_3 (2 x 100 mL), dried (Na_2SO_4), and concentrated to a brown oil. Purification by flash chromatography (8% Et_2O /92% pentane $\rightarrow$ 12% Et_2O /88% pentane) afforded the pure product (1.47 g, 29%). Several later fractions that were contaminated with a close-eluting impurity were discarded.

^1H NMR (500 MHz, CDCl_3) δ 7.19 (dd, 1H, $J=4.0$, $J=2.5$), 6.94 (m, 2H), 5.04 (app sept, 1H, $J=6.0$), 3.74 (dd, 1H, $J=7.5$, $J=8.0$), 2.10 (dq, 1H, $J=15.0$, $J=7.5$), 1.86 (dq, 1H, $J=14.5$, $J=7.5$), 1.25 (d, 3H, $J=6.5$), 1.22 (d, 3H, $J=6.0$), 0.96 (app t, 3H, $J=7.0$). ^{13}C NMR (125 MHz, CDCl_3) δ 172.6, 141.8, 126.5, 125.2, 124.4, 68.4, 49.1, 28.2, 21.8, 21.7, 12.1. FTIR (thin film) 3108, 3073, 2979, 2935, 2877, 1732, 1457, 1375, 1259, 1179, 1108, 957, 827 cm^{-1} . HRMS (ESI, m/z) calcd. for $\text{C}_{11}\text{H}_{16}\text{O}_2\text{S}$ (M^+) 212.0866, found 212.0861.

[214461-31-1]. Isopropanol (20 mL), concentrated sulfuric acid (6 drops), and MgSO_4 (3 scoops) were added to indan-1-carboxylic acid (2.13 g, 13.1 mmol). The reaction mixture was refluxed for 12 h, after which the reaction was quenched by the addition of

saturated NaHCO_3 (100 mL). The mixture was extracted with Et_2O (3 x 100 mL), and the combined extracts were washed with saturated NaHCO_3 (2 x 100 mL), dried (Na_2SO_4), and concentrated to an orange oil. Purification by flash chromatography (5% Et_2O /95% pentane) provided a clear, colorless oil (1.91 g, 71%).

^1H NMR (500 MHz, CDCl_3) δ 7.45 (d, 1H, $J=7.0$), 7.21-7.29 (m, 3H), 5.11 (app sept, 1H, $J=6.0$), 4.05 (dd, 1H, $J=8.0$, $J=7.0$), 3.15 (m, 1H), 2.96 (m, 1H), 2.49 (m, 1H), 2.36 (m, 1H), 1.32 (d, 3H, $J=6.5$), 1.31 (d, 3H, $J=6.5$). ^{13}C NMR (125 MHz, CDCl_3) δ 173.6, 144.3, 141.2, 127.6, 126.5, 124.8 (2), 68.2, 50.5, 31.9, 28.7, 22.1, 22.0.

Isopropanol (28 mL), concentrated sulfuric acid (10 drops), and MgSO_4 (4 scoops) were added to (E)-4-phenyl-2-ethyl-3-butynoic acid (2.85 g, 15.0 mmol), and the resulting mixture was refluxed for 12 h. The reaction was quenched by the addition of saturated NaHCO_3 (100 mL), and the mixture was extracted with Et_2O (3 x 125 mL), washed with saturated NaHCO_3 (2 x 100 mL), dried (Na_2SO_4) and concentrated to a gold oil. Purification by flash chromatography (5% Et_2O /95% pentane) provided a light-yellow oil (1.74 g, 50%).

^1H NMR (500 MHz, CDCl_3) δ 7.38 (m, 2H), 7.32 (td, 2H, $J=8.5$, $J=2.0$), 7.24 (tt, 1H, $J=7.0$, $J=2.0$), 6.48 (d, 1H, $J=15.5$), 6.22 (dd, 1H, $J=16.0$, $J=9.0$), 5.05 (app sept, 1H, $J=6.0$), 3.03 (m, 1H), 1.88 (dq, 1H, $J=14.5$, $J=7.0$), 1.66 (dq, 1H, $J=15.0$, $J=7.5$), 1.27 (d, 3H, $J=7.0$), 1.25 (d, 3H, $J=6.5$), 0.96 (app t, 3H, $J=7.0$). ^{13}C NMR (125 MHz, CDCl_3) δ 174.4, 137.7, 132.7, 129.2, 128.5, 128.2, 127.0, 68.5, 52.2, 26.8, 22.6, 22.5, 12.4. FTIR (thin film) 2978, 2935, 2877, 1728, 1452, 1374, 1264, 1176, 1107, 967, 744, 695 cm^{-1} . HRMS (EI, m/z) calcd. for $\text{C}_{15}\text{H}_{20}\text{O}_2$ (M^+) 232.1458, found 232.1457.

IV. Preparation of Silyl Ketene Acetals

These reactions have not been optimized. A small variation in the E/Z ratio of the products was observed on some occasions.

General procedure 2. A solution of *n*-BuLi (in hexanes; 6.50 mL, 17.8 mmol) was added via syringe to a $-78\text{ }^{\circ}\text{C}$ solution of diisopropylamine (2.49 mL, 17.8 mmol) in THF (20 mL). The mixture was stirred at $-78\text{ }^{\circ}\text{C}$ for 30 min, and then a solution of the ester (3.50 g, 17.0 mmol) in THF (10 mL) was added via cannula. The mixture was stirred at $-78\text{ }^{\circ}\text{C}$ for 60 min, and then Me_3SiCl (2.37 mL, 18.7 mmol) was added, resulting in a clear, light-yellow solution, which was warmed to room temperature and stirred for 3 h. The THF was then removed, pentane was added, and the resulting mixture was filtered. The solvent was removed, and the resulting yellow liquid was purified by fractional distillation ($132\text{ }^{\circ}\text{C}$, 2 mm Hg), which afforded a clear, colorless liquid as a 1.6/1 mixture of isomers (2.81 g, 59%).

^1H NMR (300 MHz, C_6D_6) major isomer: δ 6.99-7.49 (m, 5H), 4.34 (sept, 1H, $J=6.3$), 2.61 (q, 2H, $J=7.5$), 1.16 (d, 6H, $J=6.3$), 1.04 (m, 3H), -0.07 (s, 9H); minor isomer: δ 6.99-7.49 (m, 5H), 4.06 (sept, 1H, $J=6.0$), 2.53 (q, 2H, $J=7.2$), 1.04 (m, 3H), 0.91 (d, 6H, $J=6.0$), 0.21 (s, 9H). ^{13}C NMR (75 MHz, CDCl_3) δ 150.0, 149.1, 140.8, 140.4, 130.2, 130.0, 128.4, 126.0, 125.9, 106.0, 105.2, 71.7, 69.7, 24.6, 23.9, 22.4, 22.2, 14.5, 14.1, 0.65, 0.27. FTIR (neat) 3056, 2958, 2870, 1660, 1599, 1364, 1253, 1197, 1134, 1013, 963, 847, 761, 698 cm^{-1} . HRMS (EI, m/z) calcd. for $\text{C}_{16}\text{H}_{26}\text{O}_2\text{Si}$ (M^+) 278.1697, found 278.1691.

[96695-11-3]. General procedure 2 was followed, using *n*-BuLi (2.35 M in hexanes; 9.57 mL, 22.5 mmol), diisopropylamine (3.15 mL, 22.5 mmol), ester (4.00 g, 22.5 mmol), and Me_3SiCl (2.85 mL, 22.5 mmol) in THF (32 mL). The product, a light-yellow oil, was isolated as a 1.4/1 mixture of isomers (3.66 g, 65%), which was pure according to ^1H NMR.

^1H NMR (500 MHz, C_6D_6) major isomer: δ 7.00-7.50 (m, 5H), 3.36 (s, 3H), 2.59 (q, 2H, $J=7.5$), 1.09 (t, 3H, $J=7.5$), -0.07 (s, 9H); minor isomer: δ 7.00-7.50 (m, 5H), 3.14 (s, 3H), 2.50 (q, 2H, $J=7.5$), 1.04 (t, 3H, $J=7.5$), 0.18 (s, 9H). ^{13}C NMR (125 MHz, CDCl_3) δ 152.8, 151.7, 140.8, 139.9, 130.1, 129.8, 128.6, 128.5, 126.1 (2), 103.5, 103.0, 57.5, 56.1, 24.4, 24.1, 15.0, 14.0, 0.54, 0.24.

General procedure 2 was followed, using *n*-BuLi (in hexanes; 4.73 mL, 13.4 mmol), diisopropylamine (1.88 mL, 13.4 mmol), ester (3.00 g, 12.8 mmol), and Me₃SiCl (1.79 mL, 14.1 mmol) in THF (22 mL). Purification by chromatography on adsorption alumina (pentane) inside a glovebox afforded a 1.1/1 mixture of isomers as a clear, colorless oil (1.92 g, 49%).

¹H NMR (300 MHz, C₆D₆) major isomer: δ 6.99-7.47 (m, 5H), 3.50 (s, 2H), 2.56 (q, 2H, J=7.5), 1.36 (s, 9H), 0.99 (t, 3H, J=7.5), -0.92 (s, 9H); minor isomer: δ 6.99-7.47 (m, 5H), 3.32 (s, 2H), 2.52 (q, 2H, J=7.5), 1.04 (s, 9H), 1.03 (t, 3H, J=7.2), 0.24 (s, 9H). ¹³C NMR (125 MHz, CDCl₃) δ 151.8, 151.4, 140.9, 139.9, 130.3, 130.1, 128.4, 128.3, 126.1, 126.0, 104.5, 103.2, 80.5, 79.3, 32.4, 32.2, 27.1, 27.0, 24.6, 24.1, 14.9, 14.0, 0.62, 0.33. FTIR (neat) 3056, 2958, 2870, 1660, 1599, 1364, 1197, 1134, 1013, 963, 847, 761, 698 cm⁻¹. HRMS (EI, *m/z*) calcd. for C₁₈H₃₀O₂Si (M) + 306.2010, found 306.2004.

A solution of *n*-BuLi (in hexanes; 4.41 mL, 11.3 mmol) was added via syringe to a -78 °C solution of diisopropylamine (1.58 mL, 11.3 mmol) in THF (20 mL). The mixture was stirred at -78 °C for 45 min, and then a solution of the ester (2.50 g, 11.3 mmol) in THF (20 mL) was added via cannula. The mixture was stirred at -78 °C for 90 min, and then Me₃SiCl (1.43 mL, 11.3 mmol) was added, resulting in a clear, light-yellow solution, which was warmed to room temperature and stirred for 3 h. The THF was then removed, pentane was added, and the resulting mixture was filtered. The solvent was removed, and the resulting yellow liquid was purified by fractional distillation (88-91 °C, 1.0 mm Hg), which afforded a clear, colorless oil (1.80 g, 55%; 1.5/1 mixture of isomers).

¹H NMR (500 MHz, C₆D₆) major isomer: δ 6.99-7.47 (m, 5H), 2.56 (q, 2H, J=7.5), 1.36 (s, 9H), 0.99 (t, 3H, J=7.5), -0.92 (s, 9H); minor isomer: δ 6.99-7.47 (m, 5H), 2.52 (q, 2H, J=7.5), 1.04 (s, 9H), 1.03 (t, 3H, J=7.2), 0.24 (s, 9H). ¹³C NMR (125 MHz, CDCl₃) δ 149.2, 149.1, 140.9, 140.3, 130.4, 130.3, 126.1, 125.9, 109.7, 108.7, 80.5, 79.0, 55.7, 55.2, 29.8, 29.5, 24.6, 14.0, 1.0, 0.6. FTIR (CH₂Cl₂) 2967, 2876, 1658, 1642, 1598, 1367, 1218, 1148, 1093, 987 cm⁻¹. HRMS (EI, *m/z*) calcd. for C₁₃H₂₀O₂Si (M-C₄H₈) + 236.1227, found 236.1222.

General procedure 2 was followed, using *n*-BuLi (in hexanes; 6.26 mL, 16.4 mmol), diisopropylamine (2.30 mL, 16.4 mmol), ester (3.00 g, 15.6 mmol), and Me₃SiCl (2.18 mL, 17.2 mmol) in THF (35 mL). The product, a light-yellow oil, was isolated as a 1.8/1 mixture of isomers (3.74 g, 91%), which was pure according to ¹H NMR.

¹H NMR (500 MHz, C₆D₆) major isomer: 7.52 (m, 2H), 7.21 (m, 3H), 4.34 (sept, 1H, J=6.0), 2.08 (s, 3H), 1.14 (d, 6H, J=6.0), -0.03 (s, 9H); minor isomer: δ 7.61 (m, 2H), 7.03 (m, 3H), 4.15 (sept, 1H, J=6.5), 2.03 (s, 3H), 0.97 (d, 6H, J=6.0), 0.20 (s, 9H). ¹³C NMR (125 MHz, C₆D₆) δ 150.4, 149.5, 142.0, 141.5, 129.4, 129.2, 128.3, 128.2, 125.8, 125.7, 98.8, 98.4, 71.5, 70.3, 22.3, 22.2, 17.2, 16.6, 0.58, 0.30. FTIR (neat) 3055, 2975, 2930, 1661, 1599, 1494, 1443, 1382, 1373, 1253, 1206, 1134, 1107, 1067, 1027, 957, 900, 848, 762 cm⁻¹. HRMS (EI, *m/z*) calcd. for C₁₅H₂₄O₂Si (M⁺) 264.1540, found 264.1539.

General procedure 2 was followed, using *n*-BuLi (in hexanes; 2.30 mL, 6.73 mmol), diisopropylamine (0.943 mL, 6.73 mmol), ester (1.50 g, 6.40 mmol), and Me₃SiCl (0.893 mL, 7.04 mmol) in THF (20 mL). The product, a light-yellow oil, was isolated as a 3.3/1 mixture of isomers (1.82 g, 93%), which was pure according to ¹H NMR.

¹H NMR (500 MHz, C₆D₆) major isomer: δ 7.44-7.54 (m, 2H), 7.19-7.30 (m, 2H), 7.06-7.13 (m, 1H), 4.11 (sept, 1H, J=6.0), 2.59 (d, 2H, J=7.2), 1.80 (m, 1H), 1.02 (d, 6H, J=6.3), 1.01 (d, 6H, J=6.9), 0.32 (s, 9H); minor isomer: δ 7.44-7.54 (m, 2H), 7.19-7.30 (m, 2H), 7.06-7.13 (m, 1H), 4.45 (sept, 1H, J=6.3), 2.52 (d, 2H, J=7.2), 1.80 (m, 1H), 1.26 (d, 6H, J=6.0), 1.00 (d, 6H, J=6.5), 0.01 (s, 9H). ¹³C NMR (125 MHz, C₆D₆) δ 151.1, 150.1, 141.4, 141.0, 130.5, 130.1, 128.7, 128.4, 126.0, 125.9, 103.2, 102.4, 71.8, 69.7, 40.5, 39.5, 27.9, 27.8, 23.3, 23.2, 22.5, 22.3, 0.91, 0.33. FTIR (neat) 3056, 2956, 2868, 1654, 1465, 1383, 1372, 1253, 1206, 1133, 1105, 1005, 994, 882, 848, 757 cm⁻¹. HRMS (EI, *m/z*) calcd. for C₁₈H₃₀O₂Si (M⁺) 306.2010, found 306.2013.

General procedure 2 was followed, using *n*-BuLi (in hexanes; 2.05 mL, 5.24 mmol), diisopropylamine (0.734 mL, 5.24 mmol), ester (1.10 g, 4.99 mmol), and Me₃SiCl (0.697 mL, 5.49 mmol) in THF (20 mL). The product, a light-yellow oil, was isolated as a 1.3/1 mixture of isomers (1.39 g, 95%), which was pure according to ¹H NMR.

^1H NMR (500 MHz, C_6D_6) major isomer: δ 7.10-7.30 (m, 5H), 4.38 (sept, 1H, $J=6.5$), 3.34 (sept, 1H, $J=7.0$), 1.20 (d, 6H, $J=6.0$), 1.14 (d, 6H, $J=7.0$), -0.06 (s, 9H); minor isomer: δ 7.10-7.30 (m, 5H), 4.05 (sept, 1H, $J=6.5$), 3.17 (sept, 1H, $J=7.0$), 1.14 (d, 6H, $J=7.0$), 0.93 (d, 6H, $J=6.5$), 0.27 (s, 9H). ^{13}C NMR (125 MHz, C_6D_6) δ 149.2, 148.4, 139.3, 138.9, 132.1, 132.0, 128.2, 128.0, 126.6, 126.5, 110.2, 109.7, 71.3, 69.4, 29.6, 29.0, 22.8, 22.5, 22.3, 22.2, 0.64, 0.19. FTIR (neat) 3055, 2962, 2931, 2871, 1665, 1494, 1466, 1382, 1360, 1253, 1207, 1107, 1062, 972, 906, 848, 753, 701 cm^{-1} . HRMS (EI, m/z) calcd. for $\text{C}_{17}\text{H}_{28}\text{O}_2\text{Si}$ (M^+) 292.1853, found 292.1852.

General procedure 2 was followed, using *n*-BuLi (in hexanes; 2.36 mL, 5.78 mmol), diisopropylamine (0.810 mL, 5.78 mmol), ester (1.50 g, 5.51 mmol), and Me_3SiCl (0.769 mL, 6.06 mmol) in THF (35 mL). The product, a white solid, was isolated as a 1.5/1 mixture of isomers (1.45 g, 76%), which was pure according to ^1H NMR.

^1H NMR (300 MHz, C_6D_6) major isomer: δ 7.01-8.05 (m, 6H), 4.49 (sept, 1H, $J=6.0$), 3.46 (s, 3H), 2.29 (s, 3H), 1.29 (d, 6H, $J=6.6$), 0.05 (s, 9H); minor isomer: δ 7.01-8.05 (m, 6H), 4.26 (sept, 1H, $J=6.0$), 3.46 (s, 3H), 2.24 (s, 3H), 1.07 (d, 6H, $J=6.0$), 0.33 (s, 9H). ^{13}C NMR (125 MHz, C_6D_6) δ 158.2, 158.1, 150.6, 149.8, 137.3, 136.9, 130.0, 129.9, 129.1, 128.9, 126.5, 126.4, 119.4, 119.3, 106.3, 106.2, 71.8, 70.4, 55.1, 22.3, 17.4, 16.7, 0.67, 0.35. FTIR (thin film) 2972, 2930, 1653, 1604, 1485, 1464, 1373, 1254, 1199, 1121, 1065, 1035, 895 cm^{-1} . HRMS (EI, m/z) calcd. for $\text{C}_{20}\text{H}_{28}\text{O}_3\text{Si}$ (M^+) 344.1808, found 344.1821. mp = 51-54°C.

General procedure 2 was followed, using *n*-BuLi (in hexanes; 1.61 mL, 4.44 mmol), diisopropylamine (0.622 mL, 4.44 mmol), ester (1.00 g, 4.23 mmol), and Me_3SiCl (0.591 mL, 4.65 mmol) in THF (30 mL). The product, a light-yellow oil, was isolated as a 1.5/1 mixture of isomers (1.98 g, 75%), which was pure according to ^1H NMR.

^1H NMR (300 MHz, C_6D_6) major isomer: δ 7.44 (m, 2H), 6.87 (m, 2H), 4.14 (sept, 1H, $J=6.3$), 3.36 (s, 3H), 2.60 (q, 2H, $J=7.5$), 1.13 (t, 3H, $J=7.5$), 1.01 (d, 6H, $J=6.3$), 0.28 (s, 9H); minor isomer: δ 7.44 (m, 2H), 6.87 (m, 2H), 4.40 (sept, 1H, $J=6.3$), 3.36 (s, 3H), 2.67 (q, 2H, $J=7.5$), 1.22 (d, 6H, $J=6.0$), 1.13 (t, 3H, $J=7.5$), 0.02 (s, 9H). ^{13}C NMR (125 MHz, C_6D_6) δ 158.4, 158.3, 149.6, 148.7, 132.9, 132.6, 131.2, 131.0, 113.9, 105.5, 104.8, 71.5, 69.7, 55.1, 55.0, 24.7, 24.0, 22.4, 22.3, 14.5, 14.2, 0.69, 0.35. FTIR (neat) 3036, 2967, 2933, 2874, 1661, 1610, 1512, 1465, 1383, 1287, 1253, 1203, 1178, 1132, 1106, 1040, 989, 848 cm^{-1} . HRMS (EI, m/z) calcd. for $\text{C}_{17}\text{H}_{28}\text{O}_3\text{Si}$ (M^+) 308.1802, found 308.1809.

General procedure 2 was followed, using *n*-BuLi (in hexanes; 1.58 mL, 4.21 mmol), diisopropylamine (0.590 mL, 4.21 mmol), ester (1.10 g, 4.01 mmol), and Me₃SiCl (0.559 mL, 4.41 mmol) in THF (25 mL). The product, an orange oil, was isolated as a 1.6/1 mixture of isomers (1.07 g, 62%), which was pure according to ¹H NMR.

¹H NMR (300 MHz, C₆D₆) major isomer: δ 7.24-7.43 (m, 4H), 4.03 (sept, 1H, J=6.3), 2.41 (q, 2H, J=7.2), 0.95 (t, 3H, J=7.5), 0.85 (d, 6H, J=6.3), 0.17 (s, 9H); minor isomer: δ 7.24-7.43 (m, 4H), 4.29 (sept, 1H, J=6.3), 2.49 (q, 2H, J=7.2), 1.10 (d, 6H, J=6.0), 0.95 (t, 3H, J=7.5), -0.15 (s, 9H). ¹³C NMR (125 MHz, C₆D₆) δ 150.8, 150.1, 144.8, 144.3, 130.1, 129.8, 129.0, 128.6, 127.6, 127.4, 125.2 (q, J=4.0), 125.1 (q, J=4.0), 104.7 (q), 104.0 (q), 71.8, 70.1, 23.9, 23.3, 22.2, 22.0, 14.3, 14.0, 0.44, 0.70. FTIR (neat) 2964, 2929, 2874, 1657, 1649, 1613, 1384, 1327, 1254, 1213, 1165, 1125, 1068, 990, 844 cm⁻¹. HRMS (EI, *m/z*) calcd. for C₁₇H₂₅F₃O₂Si (M⁺) 346.1570, found 346.1571.

A solution of *n*-BuLi (in hexanes; 1.98 mL, 4.95 mmol) was added via syringe to a -78 °C solution of diisopropylamine (0.694 mL, 4.95 mmol) in THF (10 mL). The mixture was stirred at -78 °C for 30 min, and then a solution of the ester (1.00 g, 4.71 mmol) in THF (10 mL) was added via cannula. The mixture was stirred at -78 °C for 45 min, and then a solution of TBSCl (0.851 g, 5.65 mmol) in THF (5 mL) was added, resulting in a clear, light-yellow solution, which was warmed to room temperature and stirred for 3 h. The THF was then removed, pentane was added, and the mixture was filtered. Purification by chromatography on adsorption alumina (pentane) inside a glovebox afforded a clear, colorless oil (1.06 g, 69%) as a 10/1 mixture of isomers.

¹H NMR (500 MHz, C₆D₆) major isomer: δ 6.99 (ddd, 1H, J=3.5, J=1.0, J=0.5), 6.94 (dd, 1H, J=5.5, J=1.5), 6.89 (ddd, 1H, J=5.0, J=3.5, J=0.5), 4.39 (sept, 1H, J=6.0), 2.64 (q, 2H, J=7.5), 1.24 (d, 6H, J=6.0), 1.23 (t, 3H, J=7.5), 0.97 (s, 6H), 0.14 (s, 9H); minor isomer: δ 7.02 (ddd, 1H, J=3.5, J=1.5, J=0.5), 6.92 (m, 1H), 6.86 (ddd, 1H, J=5.0, J=3.5, J=0.5), 4.35 (sept, 1H, J=6.0), 2.59 (q, 2H, J=7.5), 1.19 (t, 3H, J=7.5), 1.12 (d, 6H, J=6.0), 0.98 (s, 6H), 0.12 (s, 9H). ¹³C NMR (125 MHz, C₆D₆) δ 149.7, 149.3, 142.8, 142.5, 126.8, 126.5, 124.8, 124.4, 123.3, 122.9, 102.5, 101.5, 72.1, 71.2, 27.0, 26.5, 26.1, 23.4, 22.1, 21.5, 18.6, 14.3, -3.7, -4.1. FTIR (neat) 2960, 2931, 2859, 1646, 1463, 1373, 1255, 1235, 1200, 1128, 1104, 1050, 975, 915, 831, 783, 685 cm⁻¹. HRMS (EI, *m/z*) calcd. for C₁₇H₃₀O₂SSi (M⁺) 326.1730, found 326.1728.

General procedure 2 was followed, using *n*-BuLi (in hexanes; 3.67 mL, 9.77 mmol), diisopropylamine (1.37 mL, 9.77 mmol), ester (1.90 g, 9.30 mmol), and Me₃SiCl (1.29 mL, 10.2 mmol) in THF (25 mL). The product, a light-yellow oil, was isolated as a 1.4/1 mixture of isomers (2.05 g, 80%), which was pure according to ¹H NMR.

¹H NMR (300 MHz, C₆D₆) major isomer: δ 7.93 (d, 1H, J=8.1), 6.98-7.22 (m, 3H), 4.28 (sept, 1H, J=6.3), 2.66-2.82 (m, 4H), 1.09 (d, 6H, J=6.0), 0.20 (s, 9H); minor isomer: δ 8.90 (d, 1H, J=7.8), 6.98-7.22 (m, 3H), 4.37 (sept, 1H, J=6.0), 2.66-2.82 (m, 4H), 1.15 (d, 6H, J=6.0), 0.15 (s, 9H). ¹³C NMR (125 MHz, C₆D₆) δ 147.7, 147.6, 145.6, 145.1, 141.6, 141.5, 127.0, 125.9, 125.7, 125.3, 125.2, 124.2, 123.8, 107.1, 106.7, 71.2, 70.7, 30.9, 30.8, 28.2, 28.0, 22.4, 22.2, 0.75, 0.70. FTIR (neat) 3066, 3019, 2974, 2932, 2850, 1679, 1599, 1460, 1383, 1372, 1286, 1253, 1205, 1140, 1109, 1003, 862, 848, 754 cm⁻¹. HRMS (EI, *m/z*) calcd. for C₁₆H₂₄O₂Si (M⁺) 276.1540, found 276.1543.

General procedure 2 was followed, using *n*-BuLi (in hexanes; 1.37 mL, 3.89 mmol), diisopropylamine (0.545 mL, 3.89 mmol), ester (0.861 g, 3.71 mmol), and Me₃SiCl (0.518 mL, 4.08 mmol) in THF (20 mL). The product, a light-yellow oil, was isolated as a 1.1/1 mixture of isomers (0.870 g, 77%), which was pure according to ¹H NMR.

¹H NMR (300 MHz, C₆D₆) major isomer: δ 7.37 (d, 1H, J=16.2), 7.44 (m, 2H), 7.13 (m, 2H), 6.97 (m, 1H), 6.47 (d, 1H, J=16.2), 4.32 (sept, 1H, J=6.3), 2.52 (q, 2H, J=7.2), 1.21 (t, 3H, J=7.50), 1.06 (d, 6H, J=6.0), 0.14 (s, 9H); minor isomer: δ 7.54 (d, 1H, J=16.2), 7.44 (m, 2H), 7.13 (m, 3H), 6.48 (d, 1H, J=16.2), 4.23 (sept, 1H, J=6.3), 2.43 (q, 2H, J=7.5), 1.19 (t, 3H, J=7.80), 1.07 (d, 6H, J=6.3), 0.13 (s, 9H). ¹³C NMR (125 MHz, C₆D₆) δ 152.1, 152.0, 140.2, 129.3, 128.7, 127.1, 126.7, 125.4, 126.4, 123.5, 123.3, 106.8, 105.2, 71.8, 70.2, 22.3, 22.2, 19.9, 19.5, 14.4, 14.2, 0.55, 0.38. FTIR (neat) 3079, 3039, 2974, 2933, 2874, 1630, 1596, 1494, 1452, 1373, 1332, 1254, 1195, 1120, 1038, 967, 866, 848, 750, 692 cm⁻¹. HRMS (EI, *m/z*) calcd. for C₁₈H₂₈O₂Si (M⁺) 304.1853, found 304.1850.

A solution of *n*-BuLi (3.24 M in hexanes; 2.56 mL, 8.28 mmol) was added via syringe to a -78 °C solution of diisopropylamine (1.16 mL, 8.28 mmol) in THF (20 mL). The mixture was stirred at -78 °C for 35 min, and then a solution of the lactone (1.50 g, 7.89

mmol) in THF (10 mL) was added via cannula. The mixture was stirred at $-78\text{ }^{\circ}\text{C}$ for 60 min, and then chlorotributylsilane (2.75 mL, 10.3 mmol) was added, resulting in a clear, light-yellow solution, which was warmed to room temperature and stirred for 12 h. The THF was then removed, and the residue was taken up in pentane and filtered. The solvent was removed, and the resulting yellow oil was used without further purification (2.46 g, 80%).

^1H NMR (500 MHz, C_6D_6) δ 7.59 (m, 2H), 7.33 (m, 2H), 7.01 (ddt, 1H, $J=7.5$, $J=7.0$, $J=1.5$), 2.55 (s, 2H), 1.44 (m, 6H), 1.35 (m, 6H), 1.20 (s, 6H), 0.88 (t, 9H, $J=7.5$), 0.82 (m, 6H). ^{13}C NMR (125 MHz, C_6D_6) δ 153.1, 136.9, 128.3, 124.2, 123.1, 81.7, 81.0, 43.4, 28.5, 26.7, 25.4, 14.4, 13.8. FTIR (neat) 2958, 2925, 2872, 1665, 1602, 1376, 1277, 1169, 985, 823 cm^{-1} . HRMS (EI, m/z) calcd. for $\text{C}_{24}\text{H}_{40}\text{O}_2\text{Si}$ (M^+) 388.2793, found 388.2790.

A solution of *n*-BuLi (2.92 M in hexanes; 2.84 mL, 8.28 mmol) was added via syringe to a $-78\text{ }^{\circ}\text{C}$ solution of diisopropylamine (1.16 mL, 8.28 mmol) in THF (20 mL). The mixture was stirred at $-78\text{ }^{\circ}\text{C}$ for 35 min, and then a solution of the lactone (1.50 g, 7.89 mmol) in THF (10 mL) was added via cannula. The mixture was stirred at $-78\text{ }^{\circ}\text{C}$ for 60 min, and then chlorodimethylphenylsilane (1.46 mL, 8.68 mmol) was added, resulting in a clear, light-yellow solution, which was warmed to room temperature and stirred for 12 h. The THF was then removed, and the residue was taken up in pentane and filtered. The solvent was removed, and the resulting yellow oil was used without further purification (2.19 g, 86%).

^1H NMR (500 MHz, C_6D_6) δ 7.58 (m, 4H), 7.28 (m, 2H), 6.99-7.19 (m, 4H), 2.49 (s, 2H), 1.07 (s, 6H), 0.46 (s, 6H). ^{13}C NMR (125 MHz, C_6D_6) δ 153.2, 134.2, 133.7, 130.6, 130.0, 128.9, 128.8, 124.7, 123.7, 83.1, 81.7, 43.8, 28.8, -0.19 . FTIR (neat) 3084, 2976, 1677, 1604, 1454, 1257, 1118, 1054, 952, 831 cm^{-1} . HRMS (EI, m/z) calcd. for $\text{C}_{20}\text{H}_{24}\text{O}_2\text{Si}$ (M^+) 324.1540, found 324.1543.

A solution of *n*-BuLi (2.65 M in hexanes; 0.592 mL, 1.57 mmol) was added via syringe to a $-78\text{ }^{\circ}\text{C}$ solution of diisopropylamine (0.220 mL, 1.57 mmol) in THF (10 mL). The mixture was stirred at $-78\text{ }^{\circ}\text{C}$ for 30 min, and then a solution of the lactone (0.300 g, 1.57 mmol) in THF (5 mL) was added via cannula. The mixture was stirred at $-78\text{ }^{\circ}\text{C}$ for 60 min, and then chlorotriisopropylsilane (0.336 mL, 1.57 mmol) was added, resulting in a clear, light-yellow solution, which was warmed to room temperature and stirred for 12 h. The THF was then removed, and the residue was taken up in pentane and filtered. The solvent was removed, and the resulting yellow oil was used without further purification (0.370 g, 68%).

^1H NMR (500 MHz, C_6D_6) δ 7.59 (dd, 2H, $J=7.5$, $J=3.0$), 7.33 (m, 2H), 7.01 (ddt, 1H, $J=7.5$, $J=7.0$, $J=1.0$), 2.54 (s, 2H), 1.22 (sept, 3H, $J=7.0$), 1.16 (s, 6H), 1.12 (d, 18H, $J=7.0$). ^{13}C NMR (125 MHz, C_6D_6) δ 153.2, 137.4, 128.8, 124.7, 123.6, 81.7, 81.4, 44.1, 29.0, 18.4, 13.4. FTIR (neat) 3056, 3032, 2945, 2893, 2867, 1662, 1600, 1501, 1464, 1374, 1279, 1169, 1110, 1100, 1068, 1005, 985, 883, 821 cm^{-1} . HRMS (EI, m/z) calcd. for $\text{C}_{21}\text{H}_{34}\text{O}_2\text{Si}$ (M^+) 346.2323, found 346.2315.

A solution of *n*-BuLi (2.92 M in hexanes; 2.84 mL, 8.28 mmol) was added via syringe to a $-78\text{ }^{\circ}\text{C}$ solution of diisopropylamine (1.16 mL, 8.28 mmol) in THF (20 mL). The mixture was stirred at $-78\text{ }^{\circ}\text{C}$ for 30 min, and then a solution of the lactone (1.50 g, 7.89 mmol) in THF (10 mL) was added via cannula. The mixture was stirred at $-78\text{ }^{\circ}\text{C}$ for 60 min, and then 1-chloro-1-methylsilacyclobutane (1.26 mL, 10.3 mmol) was added, resulting in a clear, light-yellow solution, which was warmed to room temperature and stirred for 2 h. The THF was then removed, and the residue was taken up in pentane and filtered. The solvent was removed, and the resulting clear oil was isolated as a mixture (3.4/1 product/starting material, based on ^1H NMR) that was used without further purification (1.17 g, 54%).

^1H NMR (300 MHz, C_6D_6) δ 7.55 (m, 2H), 7.29 (m, 2H), 7.00 (tt, 1H, $J=7.2$, $J=1.5$), 2.53 (s, 2H), 2.00 (m, 2H), 1.55 (m, 4H), 1.15 (s, 6H), 0.30 (s, 3H). ^{13}C NMR (75 MHz, C_6D_6) δ 152.9, 136.5, 128.4, 124.3, 123.4, 82.7, 81.4, 43.4, 28.4, 19.4, 14.4, -0.37 . FTIR (neat) 2973, 2933, 1666, 1601, 1500, 1449, 1275, 1122, 985, 870, 793 cm^{-1} . HRMS (EI, m/z) calcd. for $\text{C}_{16}\text{H}_{22}\text{O}_2\text{Si}$ (M^+) 274.1384, found 274.1384.

V. Catalytic Asymmetric C-Acylation of Silyl Ketene Acetals

General. Although several of the silyl ketene acetals were purified inside of a glovebox by chromatography on Florisil or adsorption alumina (Section IV), this level of purity is not essential for the catalytic enantioselective C-acylations—we have used unpurified silyl ketene acetals, and they furnish the same ee. Most of the C-acylations were set up inside of a glovebox, due to the moisture sensitivity of the silyl ketene acetals (some of the time, we obtained lower yields when reactions were set up outside of a glovebox).

General Procedure B (with a glovebox). A solution of catalyst (0.05 equiv) in toluene/CH₂Cl₂ (2:1) was added to a 4-mL vial that contained the silyl ketene acetal (1.0 equiv). The resulting solution was stirred for 5 min at room temperature, and then Ac₂O (1.3 equiv) was added. The vial was capped and removed from the glovebox, and the reaction mixture was stirred for 24 h at room temperature. The product was then purified (without workup) by flash chromatography (5→25% Et₂O/pentane). The catalyst was recovered by eluting with CH₂Cl₂ and then 10% Et₃N/90% EtOAc. The ee of the product was determined either by chiral HPLC or by chiral GC.

General Procedure C (without a glovebox). The catalyst (0.05 equiv) was added to a 4-mL vial (with a puncturable teflon-lined cap) that contained a solution of the silyl ketene acetal (1.0 equiv) in toluene/CH₂Cl₂ (2:1). The resulting solution was stirred for 5 min at room temperature, after which Ac₂O (1.3 equiv) was added. The reaction mixture was stirred for 24–36 h at room temperature, and then the product was purified (without workup) by flash chromatography (5→25% Et₂O/pentane). The catalyst was recovered by eluting with CH₂Cl₂ and then 10% Et₃N/90% EtOAc. The ee of the product was determined either by chiral HPLC or by chiral GC.

Table 1, entry 1. General procedure B was followed, using silyl ketene acetal (0.150 g, 0.599 mmol), Ac₂O (0.0735 mL, 0.779 mmol), (+)-**4** (0.0205 g, 0.0300 mmol), and 0.60 mL of toluene/CH₂Cl₂ (2:1), which furnished 89% (0.118 g, 0.536 mmol) of a clear, colorless oil, which was shown by chiral GC (Chiraldex G-TA, 20 m x 0.25 mm, 110 °C, 1.0 mL/min, retention times of enantiomers: 18.6 min (minor), 19.7 min (major)) to have 70% ee.

For run 2, general procedure C was followed, with silyl ketene acetal (0.153 g, 0.613 mmol), Ac₂O (0.0752 mL, 0.797 mmol), and (–)-**4** (0.0210 g, 0.0306 mmol) in 0.61 mL of toluene/CH₂Cl₂ (2:1), which furnished 85% of the product (0.115 g, 0.522 mmol), which was shown by chiral GC to have 70% ee.

¹H NMR (500 MHz, CDCl₃) δ 7.27–7.38 (m, 5H), 3.81 (s, 3H), 2.38 (m, 1H), 2.19 (m, 1H), 2.08 (s, 3H), 0.86 (app t, 3H, J=7.0). ¹³C NMR (125 MHz, CDCl₃) δ 203.8, 171.9,

137.2, 128.9, 128.2, 127.9, 69.4, 52.6, 28.3, 27.9, 9.8. FTIR (neat) 3061, 2953, 2883, 1715 (br), 1496, 1438, 1435, 1355, 1234, 1204, 1127, 700 cm^{-1} . HRMS (ESI, m/z) calcd. for $\text{C}_{13}\text{H}_{16}\text{O}_3\text{Na}$ ($\text{M}+\text{Na}$)⁺ 243.0992, found 243.0988. $[\alpha]^{23}_{\text{D}} = -66^\circ$ ($c=0.35$, CH_2Cl_2 ; for product with 70% ee).

Table 1, entry 2. General procedure B was followed, using silyl ketene acetal (0.150 g, 0.489 mmol), Ac_2O (0.0600 mL, 0.636 mmol), (+)-4 (0.0168 g, 0.0245 mmol), and 0.49 mL of toluene/ CH_2Cl_2 (2:1), which furnished 72% (0.0975 g, 0.353 mmol) of a clear, colorless oil, which was shown by chiral HPLC (Daicel CHIRALCEL OJ, 4.6 mm x 25 cm, hexane/isopropanol 90:10, 1.0 mL/min, retention times of enantiomers: 9.5 min (major), 7.4 min (minor)) to have 79% ee.

For run 2, general procedure C was followed, with silyl ketene acetal (0.150 g, 0.489 mmol), Ac_2O (0.0600 mL, 0.636 mmol), and (–)-4 (0.0168 g, 0.0245 mmol) in 0.49 mL of toluene/ CH_2Cl_2 (2:1), which furnished 77% of the product (0.104 g, 0.376 mmol), which was shown by chiral HPLC to have 79% ee.

^1H NMR (500 MHz, CDCl_3) δ 7.30 (m, 5H), 3.90 (d, 1H, $J=10.5$), 3.86 (d, 1H, $J=10.5$), 2.38 (m, 1H), 2.21 (m, 1H), 2.08 (s, 3H), 0.92 (s, 9H), 0.86 (app t, 3H, $J=7.5$). ^{13}C NMR (125 MHz, CDCl_3) δ 203.7, 171.4, 137.4, 128.8, 128.2, 127.8, 75.2, 69.5, 31.5, 28.4, 28.0, 26.7, 9.8. FTIR (neat) 2962, 2883, 1715 (br), 1496, 1465, 1368, 1232, 1127, 986, 755, 700 cm^{-1} . HRMS (ESI, m/z) calcd. for $\text{C}_{17}\text{H}_{24}\text{O}_3\text{Na}$ ($\text{M}+\text{Na}$)⁺ 299.1618, found 299.1616. $[\alpha]^{22}_{\text{D}} = -54^\circ$ ($c=0.59$, CH_2Cl_2 ; for product with 79% ee).

Table 1, entry 3. General procedure B was followed, using silyl ketene acetal (0.150 g, 0.539 mmol), Ac_2O (0.0661 mL, 0.701 mmol), (+)-4 (0.0185 g, 0.0269 mmol), and 0.54 mL of toluene/ CH_2Cl_2 (2:1), which furnished 90% (0.120 g, 0.483 mmol) of a clear, colorless oil, which was shown by chiral GC (Chiraldex G-TA, 20 m x 0.25 mm, 110 $^\circ\text{C}$, 1.0 mL/min, retention times of enantiomers: 21.2 min (major), 20.0 min (minor)) to have 84% ee.

For run 2, general procedure C was followed, with silyl ketene acetal (0.150 g, 0.539 mmol), Ac_2O (0.0661 mL, 0.701 mmol), and (–)-4 (0.0185 g, 0.0269 mmol) in 0.54 mL of toluene/ CH_2Cl_2 (2:1), which furnished 94% of the product (0.126 g, 0.507 mmol), which was shown by chiral GC to have 86% ee.

^1H NMR (500 MHz, CDCl_3) δ 7.26–7.37 (m, 5H), 5.18 (app sept, 1H, $J=6.5$), 2.35 (m, 1H), 2.15 (m, 1H), 2.06 (s, 3H), 1.28 (d, 3H, $J=6.0$), 1.27 (d, 3H, $J=6.0$), 0.84 (app t, 3H, $J=7.0$). ^{13}C NMR (125 MHz, CDCl_3) δ 203.9, 170.8, 158.9, 129.4, 128.9, 114.0, 69.1, 68.5,

55.4, 28.2, 27.6, 21.7, 9.5. FTIR (neat) 3061, 2981, 2939, 2883, 1734, 1714, 1497, 1448, 1386, 1354, 1234, 1103, 833, 700 cm^{-1} . HRMS (ESI, m/z) calcd. for $\text{C}_{15}\text{H}_{20}\text{O}_3\text{Na}$ ($\text{M}+\text{Na}$)⁺ 271.1305, found 271.1309. $[\alpha]_{\text{D}}^{22} = -69^\circ$ ($c=0.58$, CH_2Cl_2 ; for product with 84% ee).

Table 1, entry 4. General procedure B was followed, using silyl ketene acetal (0.150 g, 0.513 mmol), Ac_2O (0.0629 mL, 0.667 mmol), (+)-4 (0.0176 g, 0.0257 mmol), and 0.51 mL of toluene/ CH_2Cl_2 (2:1), which furnished 44% (0.0590 g, 0.225 mmol) of a clear, colorless oil, which was shown by chiral GC (Chiraldex G-TA, 20 m x 0.25 mm, 110 $^\circ\text{C}$, 1.0 mL/min, retention times of enantiomers: 24.5 min (minor), 25.5 min (major)) to have 93% ee.

For run 2, general procedure C was followed, with silyl ketene acetal (0.152 g, 0.519 mmol), Ac_2O (0.0640 mL, 0.678 mmol), and (–)-4 (0.0179 g, 0.0260 mmol) in 0.52 mL of toluene/ CH_2Cl_2 (2:1), which furnished 49% of the product (0.0670 g, 0.255 mmol), which was shown by chiral GC to have 92% ee.

^1H NMR (500 MHz, CDCl_3) δ 7.27–7.38 (m, 5H), 2.33 (dq, 1H, $J=14.0$, $J=7.5$), 2.13 (dq, 1H, $J=14.0$, $J=7.5$), 2.08 (s, 3H), 1.51 (s, 9H), 0.86 (app t, 3H, $J=7.5$). ^{13}C NMR (125 MHz, CDCl_3) δ 204.0, 170.2, 137.4, 128.7, 128.3, 127.6, 82.6, 69.7, 28.5, 28.1, 27.9, 9.5. FTIR (thin film) 2978, 1737, 1713, 1495, 1370, 1248, 1156, 1126, 841, 700 cm^{-1} . HRMS (ESI, m/e) calcd. for $\text{C}_{16}\text{H}_{22}\text{NaO}_3$ ($\text{M}+\text{Na}^+$) 285.1461, found 285.1457. $[\alpha]_{\text{D}}^{20} = -70^\circ$ ($c=0.70$, CHCl_3 ; for product with 91% ee).

Table 2, entry 1. General procedure B was followed, using silyl ketene acetal (0.150 g, 0.567 mmol), Ac_2O (0.0700 mL, 0.737 mmol), (+)-4 (0.0195 g, 0.0284 mmol), and 0.57 mL of toluene/ CH_2Cl_2 (2:1), which furnished 54% (0.0720 g, 0.307 mmol) of a clear, colorless oil, which was shown by chiral HPLC (Daicel CHIRALCEL OJ, 4.6 mm x 25 cm, hexane/isopropanol 90:10, 1.0 mL/min, retention times of enantiomers: 17.1 min (major), 21.9 min (minor)) to have 69% ee.

For run 2, general procedure B was followed, with silyl ketene acetal (0.138 g, 0.520 mmol), Ac_2O (0.0638 mL, 0.676 mmol), and (–)-4 (0.0179 g, 0.0260 mmol) in 0.52 mL of toluene/ CH_2Cl_2 (2:1), which furnished 53% of the product (0.064 g, 0.273 mmol), which was shown by chiral HPLC to have 69% ee.

^1H NMR (300 MHz, CDCl_3) δ 7.26–7.38 (m, 5H), 5.13 (app sept, 1H, $J=6.3$), 2.10 (s, 3H), 1.74 (s, 3H), 1.27 (d, 3H, $J=6.6$), 1.25 (d, 3H, $J=6.3$). ^{13}C NMR (125 MHz, CDCl_3) δ 205.6, 172.1, 139.4, 129.3, 128.3, 128.0, 70.0, 65.4, 28.1, 22.3, 22.2, 22.1. FTIR (neat) 3062, 2983, 2936, 1734, 1716, 1600, 1497, 1457, 1448, 1375, 1355, 1256, 1101, 1076, 1031, 929, 887

cm⁻¹. HRMS (ESI, *m/z*) calcd. for C₁₄H₁₈O₃Na (M+Na)⁺ 257.1148, found 257.1155. [α]_D²³ = -47.1° (c=0.70, CHCl₃; for product with 69% ee).

Table 2, entry 3. General procedure B was followed, using silyl ketene acetal (0.130 g, 0.424 mmol), Ac₂O (0.0520 mL, 0.551 mmol), (+)-4 (0.0146 g, 0.0272 mmol), and 0.42 mL of toluene/CH₂Cl₂ (2:1), which furnished 79% (0.0921 g, 0.333 mmol) of a clear, colorless oil, which was shown by chiral HPLC (Daicel CHIRALCEL OJ, 4.6 mm x 25 cm, hexane/isopropanol 99:1, 0.7 mL/min, retention times of enantiomers: 7.1 min (minor), 7.9 min (major)) to have 85% ee.

For run 2, general procedure B was followed, with silyl ketene acetal (0.130 g, 0.539 mmol), Ac₂O (0.0520 mL, 0.551 mmol), and (-)-4 (0.0146 g, 0.0272 mmol) in 0.42 mL of toluene/CH₂Cl₂ (2:1), which furnished 85% of the product (0.0994 g, 0.360 mmol), which was shown by chiral HPLC to have 84% ee.

¹H NMR (500 MHz, CDCl₃) δ 7.47 (m, 2H), 7.34 (m, 2H), 7.27 (tt, 1H, *J*=6.5, *J*=1.5), 5.18 (app sept, 1H, *J*=6.5), 2.27 (dd, 1H, *J*=14.5, *J*=6.5), 2.09 (dd, 1H, *J*=14.5, *J*=6.0), 2.05 (s, 3H), 1.49 (app sept, 1H, *J*=6.5), 1.30 (d, 3H, *J*=6.0), 1.28 (d, 3H, *J*=6.5), 0.86 (d, 3H, *J*=7.0), 0.70 (d, 3H, *J*=7.0). ¹³C NMR (125 MHz, CDCl₃) δ 203.2, 170.8, 137.6, 128.7, 128.4, 127.6, 69.2, 68.4, 43.9, 27.5, 25.2, 24.3, 23.9, 21.8, 21.7. FTIR (neat) 2959, 2872, 1714 (br), 1497, 1375, 1218, 1104, 701, 575 cm⁻¹. HRMS (ESI, *m/z*) calcd. for C₁₇H₂₄O₃Na (M+Na)⁺ 299.1618, found 299.1616. [α]_D²³ = -63° (c=0.25, CH₂Cl₂; for product with 85% ee).

Table 2, entry 4. General procedure B was followed, using silyl ketene acetal (0.162 g, 0.553 mmol), Ac₂O (0.0678 mL, 0.719 mmol), (+)-4 (0.0190 g, 0.0277 mmol), and 0.55 mL of toluene/CH₂Cl₂ (2:1), which furnished 46% (0.0682 g, 0.260 mmol) of a clear, colorless oil, as a 12:1 mixture of C-acyl:O-acyl isomers. The C-acylated product was shown by chiral GC (Chiraldex G-TA, 20 m x 0.25 mm, 105 °C, 1.0 mL/min, retention times of enantiomers: 37.7 min (minor), 39.8 min (major)) to have 97% ee.

For run 2, general procedure C was followed, with silyl ketene acetal (0.160 g, 0.547 mmol), Ac₂O (0.0671 mL, 0.711 mmol), and (-)-4 (0.0188 g, 0.0274 mmol) in 0.55 mL of toluene/CH₂Cl₂ (2:1), which furnished 52% of the product (0.0750 g, 0.286 mmol) as a 12:1 mixture of C-acyl:O-acyl isomers. The C-acylated product was shown by chiral GC to have 97% ee.

¹H NMR (500 MHz, CDCl₃) δ 7.06-7.37 (m, 5H), 5.25 (app sept, 1H, *J*=6.5), 2.90 (app sept, 1H, *J*=6.5), 1.99 (s, 3H), 1.33 (app t, 6H, *J*=6.5), 1.00 (d, 3H, *J*=7.0), 0.75 (d, 3H, *J*=7.0). ¹³C NMR (125 MHz, CDCl₃) δ 203.3, 170.0, 136.5, 128.7, 128.6, 127.6, 72.7, 69.3, 32.8, 28.7,

22.1, 22.0, 19.7, 18.5. FTIR (neat) 3063, 3031, 2969, 2938, 2877, 1734, 1710, 1653, 1540, 1457, 1387, 1236, 1199, 1167, 1104, 700 cm^{-1} . HRMS (ESI, m/z) calcd. for $\text{C}_{16}\text{H}_{22}\text{O}_3\text{Na}$ ($\text{M}+\text{Na}$) $^{+}$ 285.1461, found 285.1459. $[\alpha]_{\text{D}}^{21} = -75^{\circ}$ ($c=0.45$, CH_2Cl_2 ; for product with 97% ee).

Table 3, entry 2. General procedure B was followed, using silyl ketene acetal (0.150 g, 0.435 mmol), Ac_2O (0.0534 mL, 0.566 mmol), (+)-4 (0.0149 g, 0.0218 mmol), and 0.44 mL of toluene/ CH_2Cl_2 (2:1), which furnished 93% (0.127 g, 0.403 mmol) of a white solid, which was shown by chiral HPLC (Daicel CHIRALCEL OJ, 4.6 mm x 25 cm, hexane/isopropanol 90:10, 1.0 mL/min, retention times of enantiomers: 22.3 min (major), 28.8 min (minor)) to have 91% ee.

For run 2, general procedure C was followed, with silyl ketene acetal (0.168 g, 0.488 mmol), Ac_2O (0.0596 mL, 0.634 mmol), and (–)-4 (0.0168 g, 0.0244 mmol) in 0.49 mL of toluene/ CH_2Cl_2 (2:1), which furnished 90% of the product (0.137 g, 0.436 mmol), which was shown by chiral HPLC to have 88% ee.

^1H NMR (500 MHz, CDCl_3) δ 7.75 (app t, 3H, $J=9.0$), 7.38 (dd, 1H, $J=8.5$, $J=1.5$), 7.17 (dd, 1H, $J=9.0$, $J=2.5$), 7.14 (d, 1H, $J=2.5$), 5.19 (app sept, 1H, $J=6.5$), 3.92 (s, 3H), 2.15 (s, 3H), 1.86 (s, 3H), 1.31 (d, 3H, $J=6.0$), 1.29 (d, 3H, $J=6.5$). ^{13}C NMR (125 MHz, CDCl_3) δ 205.3, 171.7, 158.2, 133.9, 133.8, 129.8, 128.8, 127.2, 126.3, 126.1, 119.3, 105.5, 69.5, 64.6, 55.5, 27.5, 21.8, 21.7, 21.6. FTIR (thin film) 2983, 2938, 1734, 1716, 1653, 1636, 1607, 1559, 1540, 1506, 1457, 1387, 1375, 1255, 1199, 1101, 1032, 922 cm^{-1} . HRMS (ESI, m/z) calcd. for $\text{C}_{19}\text{H}_{22}\text{O}_4\text{Na}$ ($\text{M}+\text{Na}$) $^{+}$ 337.1410, found 337.1400. $[\alpha]_{\text{D}}^{22} = -49^{\circ}$ ($c=0.29$, CH_2Cl_2 ; for product with 91% ee). mp = 63–64 $^{\circ}\text{C}$.

Table 3, entry 3. General procedure B was followed, using silyl ketene acetal (0.150 g, 0.486 mmol), Ac_2O (0.0596 mL, 0.632 mmol), (+)-4 (0.0167 g, 0.0243 mmol), and 0.49 mL of toluene/ CH_2Cl_2 (2:1), which furnished 86% (0.116 g, 0.417 mmol) of a clear, colorless oil, which was shown by chiral GC (Chiraldex G-TA, 20 m x 0.25 mm, 120 $^{\circ}\text{C}$,

1.0 mL/min, retention times of enantiomers: 105.5 min (major), 99.7 min (minor)) to have 90% ee.

For run 2, general procedure C was followed, with silyl ketene acetal (0.150 g, 0.486 mmol), Ac₂O (0.0596 mL, 0.632 mmol), and (–)-4 (0.0167 g, 0.0243 mmol) in 0.49 mL of toluene/CH₂Cl₂ (2:1), which furnished 80% of the product (0.108 g, 0.388 mmol), which was shown by chiral GC to have 89% ee.

¹H NMR (500 MHz, CDCl₃) δ 7.29 (ddd, 2H, J=9.0, J=5.0, J=3.0), 6.88 (ddd, 2H, J=9.0, J=5.0, J=3.0), 5.17 (app sept, 1H, J=6.5), 3.80 (s, 3H), 2.32 (m, 1H), 2.14 (m, 1H), 2.05 (s, 3H), 1.28 (d, 3H, J=6.0), 1.26 (d, 3H, J=6.5), 0.83 (app t, 3H, J=7.5). ¹³C NMR (125 MHz, CDCl₃) δ 203.9, 170.8, 158.9, 129.4, 128.9, 114.0, 69.1, 68.4, 55.3, 28.1, 27.6, 21.8, 21.7, 9.4. FTIR (neat) 2980, 2938, 2839, 1734, 1712, 1610, 1514, 1465, 1375, 1254, 1234, 1186, 1102, 1035, 828 cm⁻¹. HRMS (ESI, *m/z*) calcd. for C₁₆H₂₂O₄Na (M+Na)⁺ 301.1410, found 301.1406. [α]_D²² = –89° (c=0.99, CH₂Cl₂; for product with 90% ee).

Table 3, entry 4. General procedure B was followed, using silyl ketene acetal (0.130 g, 0.375 mmol), Ac₂O (0.0567 mL, 0.601 mmol), (+)-4 (0.0159 g, 0.0231 mmol), and 0.46 mL of toluene/CH₂Cl₂ (2:1), which furnished 96% (0.114 g, 0.360 mmol) of a clear, colorless oil, which was shown by chiral GC (Chiraldex G-TA, 20 m x 0.25 mm, 130 °C, 1.0 mL/min, retention times of enantiomers: 11.2 min (major), 10.5 min (minor)) to have 92% ee.

For run 2, general procedure B was followed, with silyl ketene acetal (0.131 g, 0.378 mmol), Ac₂O (0.0567 mL, 0.601 mmol), and (–)-4 (0.0159 g, 0.0231 mmol) in 0.46 mL of toluene/CH₂Cl₂ (2:1), which furnished 96% of the product (0.115 g, 0.364 mmol), which was shown by chiral GC to have 91% ee.

¹H NMR (500 MHz, CDCl₃) δ 7.63 (d, 2H, J=9.0), 7.53 (d, 2H, J=9.0), 5.19 (app sept, 1H, J=6.5), 2.38 (m, 1H), 2.18 (m, 1H), 2.10 (s, 3H), 1.31 (d, 3H, J=6.5), 1.28 (d, 3H, J=6.5), 0.84 (app t, 3H, J=7.5). ¹³C NMR (125 MHz, CDCl₃) δ 202.7, 170.1, 141.03, 141.01, 129.9 (q, J=32.6), 125.6 (q, J=4.0), 124.1 (q, J=270.5), 69.7, 69.1, 28.4, 27.8, 21.8, 21.7, 9.3. FTIR (neat) 2983, 2940, 1734, 1716, 1653, 1617, 1540, 1457, 1386, 1328, 1235, 1168, 1127, 1102, 1071, 1018, 832 cm⁻¹. HRMS (ESI, *m/z*) calcd. for C₁₆H₁₉F₃O₃Na (M+Na)⁺ 339.1179, found 339.1166. [α]_D²² = –43° (c=0.41, CH₂Cl₂; for product with 92% ee).

Table 3, entry 5. General procedure B was followed (reaction time: 36 h), using silyl ketene acetal (0.155 g, 0.475 mmol), Ac₂O (0.0582 mL, 0.617 mmol), (+)-**4** (0.0163 g, 0.0238 mmol), and 0.48 mL of toluene/CH₂Cl₂ (2:1), which furnished 66% (0.0787 g, 0.309 mmol) of a clear, colorless oil, which was shown by chiral HPLC (Daicel CHIRALCEL OJ, 4.6 mm x 25 cm, hexane/isopropanol 90:10, 1.0 mL/min, retention times of enantiomers: 6.9 min (major), 12.3 min (minor)) to have 72% ee.

For run 2, general procedure B was followed (reaction time: 36 h), with silyl ketene acetal (0.0700 g, 0.215 mmol), Ac₂O (0.0263 mL, 0.279 mmol), and (–)-**4** (0.0074 g, 0.0108 mmol) in 0.22 mL of toluene/CH₂Cl₂ (2:1), which furnished 70% of the product (0.0383 g, 0.151 mmol), which was shown by chiral HPLC to have 73% ee.

For run 3, general procedure C was followed (reaction time: 36 h), with silyl ketene acetal (0.155 g, 0.475 mmol), Ac₂O (0.0582 mL, 0.617 mmol), and (–)-**4** (0.0163 g, 0.0238 mmol) in 0.48 mL of toluene/CH₂Cl₂ (2:1), which furnished 54% of the product (0.0650 g, 0.255 mmol), which was shown by chiral HPLC to have 73% ee.

¹H NMR (500 MHz, CDCl₃) δ 7.31 (dd, 1H, J=5.0, J=1.5), 7.0 (dd, 1H, J=5.5, J=4.0), 6.95 (dd, 1H, J=7.0, J=1.0), 5.19 (app sept, 1H, J=6.5), 2.33 (m, 1H), 2.22 (m, 1H), 2.07 (s, 3H), 1.30 (d, 3H, J=6.0), 1.28 (d, 3H, J=6.5), 0.80 (app t, 3H, J=7.5). ¹³C NMR (125 MHz, CDCl₃) δ 201.1, 170.0, 138.9, 126.7, 126.6, 126.5, 69.9, 66.9, 30.5, 26.6, 21.8, 21.6, 9.1. FTIR (neat) 3108, 2980, 2938, 2880, 1741, 1716, 1457, 1375, 1355, 1233, 1103, 832, 703 cm⁻¹. HRMS (ESI, *m/z*) calcd. for C₁₃H₁₈O₃SNa (M+Na)⁺ 277.0869, found 277.0867. [α]_D²² = –77° (c=0.23, CH₂Cl₂; for product with 72% ee).

Table 3, entry 6. General procedure B was followed, using silyl ketene acetal (0.150 g, 0.543 mmol), Ac₂O (0.0666 mL, 0.706 mmol), (+)-**4** (0.0186 g, 0.0271 mmol), and 0.54 mL of CH₂Cl₂, which furnished 82% (0.110 g, 0.447 mmol) of a clear, colorless oil, which was shown by chiral HPLC (Daicel CHIRALCEL OJ, 4.6 mm x 25 cm, hexane/isopropanol 90:10, 1.0 mL/min, retention times of enantiomers: 8.1 min (major), 9.6 min (minor)) to have 82% ee.

For run 2, general procedure C was followed, with silyl ketene acetal (0.155 g, 0.561 mmol), Ac₂O (0.0688 mL, 0.728 mmol), and (–)-**4** (0.0193 g, 0.0281 mmol) in 0.56 mL of CH₂Cl₂, which furnished 82% of the product (0.113 g, 0.459 mmol), which was shown by chiral HPLC to have 80% ee.

^1H NMR (500 MHz, CDCl_3) δ 7.53 (m, 1H), 7.23-7.30 (m, 3H), 5.09 (app sept, 1H, $J=6.5$), 2.95-3.07 (m, 2H), 2.73 (ddd, 1H, $J=15.5$, $J=8.5$, $J=7.0$), 2.55 (ddd, 1H, $J=13.0$, $J=8.0$, $J=4.5$), 2.21 (s, 3H), 1.29 (d, 3H, $J=6.5$), 1.25 (d, 3H, $J=6.0$). ^{13}C NMR (125 MHz, CDCl_3) δ 203.3, 170.7, 144.9, 139.4, 128.7, 126.8, 126.6, 125.0, 72.6, 69.5, 33.2, 31.0, 26.6, 21.8, 21.7. FTIR (thin film) 3071, 2982, 2935, 2854, 1734, 1716, 1603, 1458, 1386, 1375, 1356, 1233, 1106, 1074, 830, 766 cm^{-1} . HRMS (ESI, m/z) calcd. for $\text{C}_{15}\text{H}_{18}\text{O}_3\text{Na}$ ($\text{M}+\text{Na}$) $^+$ 269.1148, found 269.1140. $[\alpha]^{22}_{\text{D}} = -35^\circ$ ($c=0.29$, CH_2Cl_2 ; for product with 82% ee).

Eq 5. General procedure B was followed, using silyl ketene acetal (0.130 g, 0.427 mmol), Ac_2O (0.0524 mL, 0.555 mmol), (+)-4 (0.0147 g, 0.0214 mmol), and 0.427 mL of toluene/ CH_2Cl_2 (2:1) to produce 80% (0.0938 g, 0.342 mmol) of a clear, colorless oil, which was shown by chiral HPLC (Daicel CHIRALPAK AD, 4.6 mm x 25 cm, hexane/isopropanol 99:1, 0.7 mL/min, retention times of enantiomers: 10.0 min (minor), 10.6 min (major)) to have 54% ee (reaction time: 80 h).

For run 2, general procedure B was followed, with silyl ketene acetal (0.130 g, 0.427 mmol), Ac_2O (0.0524 mL, 0.555 mmol), and (-)-4 (0.0147 g, 0.0214 mmol) in 0.43 mL of toluene/ CH_2Cl_2 (2:1), which furnished 81% of the product (0.0944 g, 0.344 mmol), which was shown by chiral HPLC to have 53% ee.

^1H NMR (500 MHz, CDCl_3) δ 7.42 (m, 2H), 7.34 (m, 2H), 7.27 (m, 1H), 6.81 (d, 1H, $J=17.0$), 6.38 (d, 1H, $J=16.5$), 5.16 (app sept, 1H, $J=6.0$), 2.15-2.20 (m, 4H), 2.04-2.11 (m, 1H), 1.28 (app t, 6H, $J=6.5$), 0.85 (app t, 3H, $J=7.5$). ^{13}C NMR (125 MHz, CDCl_3) δ 202.4, 171.0, 136.8, 132.4, 128.8, 128.2, 126.7, 126.0, 69.4, 66.5, 28.5, 27.3, 21.8, 21.7, 8.9. FTIR (neat) 3027, 2974, 2938, 1734, 1713, 1457, 1449, 1375, 1234, 1103, 972, 748 cm^{-1} . HRMS (EI, m/z) calcd. for $\text{C}_{17}\text{H}_{22}\text{O}_3$ (M^+) 274.1563, found 274.1572. $[\alpha]^{22}_{\text{D}} = -12^\circ$ ($c=0.21$, CH_2Cl_2 ; for product with 54% ee).

VI. Mechanistic Studies

Eq 6. A solution of the silyl ketene acetal (0.020 g, 0.066 mmol) and 1,4-dioxane (internal standard; 0.0011 mL, 0.013 mmol) in CD_2Cl_2 (0.80 mL) was added to a screwcap NMR tube. Immediately prior to data acquisition, Ac_2O (0.0062 mL, 0.066 mmol) was added. The reaction was monitored by ^1H NMR spectroscopy after reaction times of 5 min, 30 min, 3.5 h, 30 h, 60 h, and 100 h. All of the spectra showed only unreacted starting materials.

Eq 6. A stock solution of the silyl ketene acetal was prepared by the addition of CD_2Cl_2 (1.0 mL) and 1,4-dioxane (internal standard; 6.0 μL) to the silyl ketene acetal (42.0 mg, 0.138 mmol). Another stock solution was prepared by the addition of CD_2Cl_2 (1 mL) to $\text{Me}_4\text{N}[\text{OAc}]$ (5.3 mg, 0.040 mmol). To a screwcap NMR tube was added 0.35 mL of the stock solution of the silyl ketene acetal, then CD_2Cl_2 (0.40 mL), and then 62 μL of the stock solution of $\text{Me}_4\text{N}[\text{OAc}]$. After ~ 10 min, neat Ac_2O (6.1 μL , 0.064 mmol) was added. A ^1H NMR spectrum after 2 min indicated $\sim 80\%$ conversion to product (versus 1,4-dioxane).

Eq 7. A solution of catalyst (0.10 equiv) in CH_2Cl_2 was added to a 4-mL vial that contained the silyl ketene acetal (1.0 equiv). The resulting solution was stirred for 5 min at room temperature, and then Ac_2O (1.0 equiv) was added. The vial was capped and removed from the glove box. The reaction mixture was stirred for 24-72 h at room temperature, and then it was passed through a plug of silica. The ee of the product was determined by chiral GC.

Eq 8. A solution of Me_4NF (3.1 mg, 0.0331 mmol) in CH_2Cl_2 (1 mL) was added to a solution of the silyl ketene acetal (10.0 mg, 0.0331 mmol) in CH_2Cl_2 (1 mL). The reaction was stirred for two min, after which a deep-green solution of the SbF_6 salt of acetylated (-)-**4** (0.0320 g, 0.0331 mmol)⁴ in CH_2Cl_2 (2 mL) was added. A color change from deep green to purple (the catalyst is purple in solution) was observed. The reaction mixture was passed through a plug of silica gel with CH_2Cl_2 as the eluant. The product was shown by chiral GC (Chiraldex G-TA, 20 m x 0.25 mm, 150 $^\circ\text{C}$, 1.0 mL/min, retention times of enantiomers: 9.48 min (major), 12.9 min (minor)) to have 86% ee.

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500 MHz, CDCl₃

500 MHz, CDCl₃

500 MHz, CDCl₃

500 MHz, CDCl₃

300 MHz, CDCl₃

500 MHz, CDCl₃

500 MHz, CDCl₃

500 MHz, CDCl₃

500 MHz, CDCl₃

500 MHz, CDCl₃