Supporting Information

General Methods. All reactions were carried out under a nitrogen atmosphere with oven-dried glassware. The progress of all reactions was monitored by thin-layer chromatography to ensure the reactions had reached completion. All manipulations involving dicyclohexylborane and dialkylzinc reagents were carried out using an inert atmosphere in a Vacuum Atmosphere drybox with an attached MO-40 Dritrain or by using the standard Schlenk or vacuum line techniques. Dichloromethane, diethyl ether, toluene, and hexanes were dried through alumina columns. All aldehydes and trichloroacetonitrile were dried through recrystallization and sublimed prior to use and stored under N₂. Unless otherwise specified, all chemicals were obtained from Acros, Aldrich, or GFS Chemicals, and all solvents were purchased from Fischer Scientific. All aldehydes and terminal alkynes are commercially available. The ¹H NMR and ¹³C{¹H} NMR spectra were obtained on a Bruker AM-500 Fourier transform NMR spectrometer at 500 and 125 MHz, respectively. Chemical shifts are reported in units of parts per million downfield from tetramethylsilane, and all coupling constants are reported in Hertz. The infrared spectra were obtained using a Perkin-Elmer 1600 series spectrometer. Thin-layer chromatography was performed on Whatman precoated silica gel 60 F-254 plates and visualized by ultra-violet light or by staining with ceric ammonium molybdate stain. Silica gel (230-400 mesh, Silicycle) was used for air-flashed chromatography. Analysis of enantiomeric excess was performed using a Hewlett-Packard 10550 Series HPLC and a Chiralcel OD-H column. Absolute configuration was determined by comparison of optical rotation to literature data for known compounds.

(S)-1-Phenyl-5-trityloxypent-2-en-1-ol (2). General Procedure A. To a stirred solution of Cy₂BH (0.75 mmol) in toluene (1 mL), prepared according to Oppolzer’s procedure⁵⁸ (flask A), was added a solution of trityl protected 3-butyne-1-ol (234 mg, 0.75 mM in toluene) dropwise. The homogenous reaction mixture was stirred for 30 min at room temperature. To a separate flask (B) at -30 °C was added 0.5 mL toluene and (−)-MIB (4.8 mg, 0.02 mmol), followed by benzaldehyde (51 µL, 0.5 mmol), then Et₂Zn (1.0 mL, 1.0 M) or Me₂Zn (0.5 mL, 2.0 M) in toluene. The contents of flask (A) were then transferred dropwise to flask (B) over 1 h with a syringe pump. The reaction was stirred at -30 °C for 3.5 h and quenched with saturated NH₄Cl solution. The organic layers were extracted with diethyl ether, washed with H₂O, and dried over MgSO₄. The filtrate was concentrated in vacuo and the residue was chromatographed on silica (10% ethyl acetate in hexanes) to afford the title compound in 75% yield (158 mg, 0.38 mmol) as a colorless oil. [α]D¹⁰ = +14.8 (c = 1.05, CHCl₃, 90% ee); ¹H NMR (CDCl₃, 500 MHz): δ 1.85 (s, 1H), 2.36 (dt, 2H, J = 6.4, 6.3 Hz), 3.13 (t, 2H, J = 6.6 Hz), 5.15 (d, 1H, J = 6.0 Hz), 5.70-5.81 (m, 2H), and 7.19-7.42 (m, 20H) ppm; ¹³C{¹H} NMR (CDCl₃, 125 MHz): δ 32.7, 62.7, 74.8, 86.2, 125.9, 126.6, 127.3, 127.5, 128.2, 128.4, 129.0, 133.8, 142.9, and 144.0 ppm; IR (neat) 3372, 3060, 2922, 1597, 1491, 1448, 1220 cm⁻¹. HRMS-CI m/z 443.2007 [(M + Na)+; calcd for C₃₀H₂₈O₂Na: 443.1987].

(R)-1-Phenyl-5-trityloxypent-2-en-1-ol (3). The product was prepared by General Procedure A using 267 mg (1.5 mmol) Cy₂BH, 469 mg (1.5 mmol) 3-trityloxy-1-butyne, 5.0 mL (2.0 mmol, 1.0 M in toluene) Et₂Zn, 9.6 mg (0.04 mmol) (+)-MIB, and
102 µL (1.0 mmol) benzaldehyde. The crude product was purified by column chromatography (10% ethyl acetate in hexanes) to give the title compound as a colorless oil in 74% yield (312 mg, 0.74 mmol). \([\alpha]_D^{20} = -13.6 \ (c = 1.07 , \text{CHCl}_3, 90 \% \text{ ee}); 1^H \text{ NMR (CDCl}_3, 500 MHz): \delta \ 1.80 \ (s, 1H), 2.28 \ (dt, 2H, J = 6.4, 6.2 Hz), 3.04 \ (t, 2H, J = 6.6 Hz), 5.06 \ (d, 1H, J = 6.0 Hz), 5.62-5.72 \ (m, 2H), 7.11-7.26 \ (m, 14H), \text{ and } 7.34 \ (d, 6H, J = 7.2 Hz) \text{ ppm}; ^{13}C\{^1H\} \text{ NMR (CDCl}_3, 125 MHz): \delta \ 33.0, 63.0, 75.0, 86.5, 126.9, 127.5, 127.7, 128.4, 128.7, 129.2, 134.1, 143.1, \text{ and } 144.3 \text{ ppm}; \text{ IR (neat): } 3359, 3085, 3052, 3030, 2925, 2870, 1958, 1817, 1668, 1597, 1491, 1448, 1380, 1318, 1221 \text{ cm}^{-1}. \text{ HRMS-CI m/z 443.1988 } (\text{M + Na}^+); \text{ calcd for C}_{30}H_{28}O_2Na: 443.1987].

(S)-1-(4-Trifluoromethylphenyl)-5-trityloxypent-2-en-1-ol (4). The product was prepared by General Procedure A using 1.36 g (7.5 mmol) Cy$_2$BH, 2.34 g (5.0 mmol) 3-trityloxy-1-butyne, 5.0 mL (10.0 mmol, 2.0 M in toluene) Me$_2$Zn, 47.8 mg (0.2 mmol) (−)-MIB, and 686 µL (5.0 mmol) p-trifluoromethylbenzaldehyde. The crude product was purified by column chromatography (5-10% ethyl acetate in hexanes) to give the title compound as a colorless oil in 67% yield (1.6 g, 3.3 mmol). \([\alpha]_D^{20} = +15.6 \ (c = 1.49 , \text{CHCl}_3, 96 \% \text{ ee}); 1^H \text{ NMR (CDCl}_3, 500 MHz): \delta \ 1.95 \ (br s, 1H), 2.26 \ (dt, 2H, J = 6.5, 6.4 Hz), 3.06 \ (t, 2H, J = 6.5 Hz), 5.09 \ (d, 1H, J = 6.9 Hz), 5.58 \ (dd, 1H, J = 15.4, 6.9 Hz), 5.70 \ (dt, 1H, J = 15.4, 6.8 Hz), 7.12 \ (t, 3H, J = 7.4 Hz), 7.16 \ (t, 6H, J = 7.6 Hz), 7.32 \ (d, 6H, J = 7.2 Hz), 7.36 \ (d, 2H, J = 8.1 Hz), \text{ and } 7.46 \ (d, 2H, J = 8.2 Hz) \text{ ppm}; ^{13}C\{^1H\} \text{ NMR (CDCl}_3, 125 MHz): \delta \ 31.6, 62.8, 74.5, 86.5, 125.31, 125.34, 126.4, 126.9, 127.7, 128.6, 130.4, 133.5, 144.2, \text{ and } 146.9 \text{ ppm}; \text{ IR (neat): } 3368, 3059, 3032, 2932, 2856, 1958, 1814, 1702, 1671, 1619, 1597, 1490, 1322 \text{ cm}^{-1}. \text{ HRMS-CI m/z 511.1847 } (\text{M + Na}^+); \text{ calcd for C}_{31}H_{27}F_3O_2Na: 511.1861].

(S)-1-(2-Bromophenyl)-5-trityloxypent-2-en-1-ol (5). The product was prepared by General Procedure A using 134 mg (0.75 mmol) Cy$_2$BH, 234 mg (0.75 mmol) 3-trityloxy-1-butyne, 1.0 mL (1.0 mmol, 1.0 M in toluene) Et$_2$Zn, 4.8 mg (0.02 mmol) (−)-MIB, and 58 µL (0.50 mmol) o-bromobenzaldehyde. The crude product was purified by column chromatography (10% ethyl acetate in hexanes) to give the title compound as a colorless oil in 75% yield (187 mg, 0.37 mmol). \([\alpha]_D^{20} = -23.3 \ (c = 1.17 , \text{CHCl}_3, 99 \% \text{ ee}); 1^H \text{ NMR (CDCl}_3, 500 MHz): \delta \ 2.05 \ (br d, 1H, J = 2.9 Hz), 2.34 \ (dt, 2H, J = 6.6, 6.6 Hz), 3.12 \ (t, 2H, J = 6.5 Hz), 5.54 \ (br d, 1H, J = 5.3 Hz), 5.68 \ (dd, 1H, J = 15.4, 6.2 Hz), 5.83 \ (dt, 1H, J = 15.3, 6.8 Hz), 7.09-7.12 \ (m, 1H), 7.18-7.22 \ (m, 3H), 7.24-7.29 \ (m, 7H), 7.39-7.41 \ (m, 6H), \text{ and } 7.49-7.54 \ (m, 2H) \text{ ppm}; ^{13}C\{^1H\} \text{ NMR (CDCl}_3, 125 MHz): \delta \ 32.8, 62.6, 74.5, 86.5, 125.31, 125.34, 126.4, 126.9, 127.7, 128.6, 130.4, 133.5, 144.2, \text{ and } 146.9 \text{ ppm}; \text{ IR (neat): } 3354, 3059, 3032, 2932, 2856, 1958, 1814, 1702, 1671, 1619, 1597, 1490, 1322 \text{ cm}^{-1}. \text{ HRMS-CI m/z 521.1106 } (\text{M + Na}^+); \text{ calcd for C}_{31}H_{27}BrO_2Na: 511.1861].

(S)-1-(4-Chlorophenyl)-5-trityloxypent-2-en-1-ol (6). The product was prepared by General Procedure A using 134 mg (0.75 mmol) Cy$_2$BH, 234 mg (0.75 mmol) 3-trityloxy-1-butyne, 1.0 mL (1.0 mmol, 1.0 M in toluene) Et$_2$Zn, 4.8 mg (0.02 mmol) (−)-MIB, and 70.3 mg (0.50 mmol) p-chlorobenzaldehyde. The crude product was purified by column chromatography (10% ethyl acetate in hexanes) to give the title compound as a colorless oil in 76% yield (173 mg, 0.38 mmol). \([\alpha]_D^{20} = -4.18 \ (c = 0.67,
$^1$H NMR (CDCl$_3$, 500 MHz): $\delta$ 1.82 (br s, 1H), 2.35 (dt, 2H, $J = 6.5, 6.4$ Hz), 3.13 (t, 2H, $J = 6.5$ Hz), 5.14 (d, 1H, $J = 6.6$ Hz), 5.67 (dd, 1H, $J = 15.4, 6.7$ Hz), 5.77 (dt, 1H, $J = 15.4, 6.7$ Hz), 7.22-7.30 (m, 13H), and 7.41-7.43 (m, 6H) ppm; $^{13}$C($^1$H) NMR (CDCl$_3$, 125 MHz): $\delta$ 33.0, 62.9, 74.4, 86.6, 126.9, 127.6, 127.7, 128.6, 128.7, 129.9, 133.8, 141.5, and 144.2 ppm; IR (neat) 3404, 3058, 2926, 1668, 1596, 1490, 1448, 1220 cm$^{-1}$. HRMS-CI m/z 477.1575 [(M + Na)$^+$]; calcd for C$_{30}$H$_{27}$ClO$_2$Na: 477.1597.

(5)-1-(4-Fluorophenyl)-5-trityloxypent-2-en-1-ol (7). The product was prepared by General Procedure A using 134 mg (0.75 mmol) Cy$_2$BH, 234 mg (0.75 mmol) 3-trityloxy-1-butyne, 1.0 mL (1.0 mmol, 1.0 M in toluene) Et$_2$Zn, 4.8 mg (0.02 mmol) (−)-MIB, and 54 μL (0.50 mmol) p-flurobenzaldehyde. The crude product was purified by column chromatography (10% ethyl acetate in hexanes) to give the title compound as a colorless oil in 71% yield (156 mg, 0.36 mmol). $[\alpha]_D^{20} = +13.3$ (c = 1.29, CHCl$_3$, 94% ee); $^1$H NMR (CDCl$_3$, 500 MHz): $\delta$ 1.79 (br s, 1H), 2.28 (dt, 2H, $J = 6.5, 6.5$ Hz), 3.06 (t, 2H, $J = 6.5$ Hz), 5.05 (d, 1H, $J = 6.4$ Hz), 5.61 (dd, 1H, $J = 15.4, 6.5$ Hz), 5.69 (dt, 1H, $J = 15.4, 6.5$ Hz), 6.91 (t, 2H, $J = 8.7$ Hz), 7.12-7.23 (m, 11H), and 7.33 (d, 6H, $J = 7.2$ Hz) ppm; $^{13}$C($^1$H) NMR (CDCl$_3$, 125 MHz): $\delta$ 32.7, 62.6, 74.1, 86.2, 114.9, 115.0, 126.6, 127.5, 127.6, 127.7, 128.4, 129.3, 133.7, and 144.0 ppm; IR (neat) 3368, 3058, 3032, 2924, 2870, 1603, 1508, 1491, 1448, 1222 cm$^{-1}$. HRMS-CI m/z 461.1873 [(M + Na)$^+$]; calcd for C$_{30}$H$_{27}$FO$_2$Na: 461.1893.

1-Cyclohexyl-5-trityloxypent-2-en-1-ol (8). The product was prepared by General Procedure A using 134 mg (0.75 mmol) Cy$_2$BH, 234 mg (0.75 mmol) 3-trityloxy-1-butyne, 0.5 mL (1.0 mmol, 2.0 M in toluene) Me$_2$Zn, 4.8 mg (0.02 mmol) (−)-MIB, and 60 μL (0.50 mmol) cyclohexanecarboxaldehyde. The crude product was purified by column chromatography (5% ethyl acetate in hexanes) to give the title compound as a colorless oil in 66% yield (140 mg, 0.33 mmol). $[\alpha]_D^{20} = -5.4$ (c = 1.00, CHCl$_3$, 93% ee); $^1$H NMR (CDCl$_3$, 500 MHz): $\delta$ 0.95-0.98 (m, 2H), 1.18-1.26 (m, 4H), 1.65-1.84 (m, 5H), 1.85 (br d, 1H, $J = 12.8$ Hz), 2.34 (dt, 2H, $J = 6.5, 6.4$ Hz), 3.12 (t, 2H, $J = 6.5$ Hz), 3.77 (br t, 1H, $J = 6.6$ Hz), 5.52 (dd, 1H, $J = 15.4, 7.3$ Hz), 5.64 (dt, 1H, $J = 15.4, 6.7$ Hz), 7.20-7.22 (m, 3H), 7.27 (t, 6H, $J = 7.5$ Hz), and 7.44 (d, 6H, $J = 7.2$ Hz) ppm; $^{13}$C($^1$H) NMR (CDCl$_3$, 125 MHz): $\delta$ 26.08, 26.15, 26.5, 28.6, 28.8, 33.1, 43.7, 63.2, 77.6, 126.9, 127.7, 128.7, 129.5, 133.4, and 144.3 ppm; IR (neat) 3382, 3058, 3032, 2923, 2851, 2359, 1957, 1597, 1490, 1448, 1219 cm$^{-1}$. HRMS-CI m/z 449.2479 [(M + Na)$^+$]; calcd for C$_{30}$H$_{33}$O$_2$Na: 449.2457.

2-Methyl-8-trityloxyoct-5-en-4-ol (9). The product was prepared by General Procedure A using 534 mg (3.0 mmol) Cy$_2$BH, 938 mg (3.0 mmol) 3-trityloxy-1-butyne, 4.0 mL (4.0 mmol, 1.0 M in toluene) Et$_2$Zn, 19.0 mg (0.08 mmol) (−)-MIB, and 215 μL (2.0 mmol) isovaleraldehyde. The crude product was purified by column chromatography (10% ethyl acetate in hexanes) to give the title compound as a colorless oil in 54% yield (436 mg, 1.1 mmol). $[\alpha]_D^{20} = +5.6$ (c = 0.43, CHCl$_3$, 99% ee); $^1$H NMR (CDCl$_3$, 500 MHz): $\delta$ 0.89 (d, 3H, $J = 2.7$ Hz), 0.91 (d, 3H, $J = 2.7$ Hz), 1.26-1.33 (m, 2H—OH underneath), 1.42-1.48 (m, 1H), 1.68-1.73 (m, 1H), 2.33 (dt, 2H, $J = 6.6, 6.5$ Hz), 3.11 (t, 2H, $J = 6.6$ Hz), 4.11 (dt, 1H, $J = 7.0, 6.8$ Hz), 5.51 (dd, 1H, $J = 15.4, 7.0$ Hz), 5.66 (dt, 1H, $J = 15.4, 6.8$ Hz), 7.22 (q, 3H, $J = 7.4$ Hz), 7.28 (t, 6H, $J = 7.6$ Hz), and
7.43 (d, 6H, J = 7.4 Hz) ppm; \(^{13}\text{C}\{\text{\textsuperscript{1}H}\} \text{NMR (CDCl}_3, 125 \text{MHz}): \delta 22.8, 23.2, 24.8, 33.3, 63.4, 71.5, 86.7, 127.1, 128.0, 128.6, 128.8, 128.9, 135.6, and 144.6 ppm; IR (neat) 3353, 3057, 3022, 2954, 1596, 1490, 1448, 1383, 1220 cm\(^{-1}\). HRMS-Cl \text{m/z} 423.2311 [(M + Na)\(^+\)]; calcd for C\(_{28}\)H\(_{32}\)O\(_2\)Na: 423.2300.

**1-Trityloxytridec-3-en-5-ol (10).** The product was prepared by General Procedure A using 41 mg (0.23 mmol) Cy\(_2\)BH, 72 mg (0.23 mmol) 3-trityloxy-1-butyne, 0.3 mL (0.3 mmol, 1.0 M in toluene) Et\(_2\)Zn, 1.4 mg (0.006 mmol) , and 26 \(\mu\)L (0.15 mmol) nonylaldehyde. The crude product was purified by column chromatography (10% ethyl acetate in hexanes) to give the title compound as a colorless oil in 68% yield (46 mg, 0.10 mmol). \([\alpha]_D^{20} = +6.25 (c = 0.48, \text{CHCl}_3, 78\% \text{ ee}); \text{\textsuperscript{1}H NMR (CDCl}_3, 500 MHz): \delta 0.80 (t, 3H, J = 6.9 Hz), 1.18-1.29 (m, 13H), 1.36-1.46 (m, 2H), 2.26 (dt, 2H, J = 6.6, 6.6 Hz), 3.04 (t, 2H, J = 6.7 Hz), 3.95 (dt, 1H, J = 6.6, 6.5 Hz), 5.44 (dd, 1H, J = 15.4, 6.9 Hz), 5.58 (dt, 1H, J = 15.4, 6.8 Hz), 7.15 (t, 3H, J = 7.3 Hz), 7.21 (t, 6H, J = 7.5 Hz), and 7.36 (d, 6H, J = 7.4 Hz) ppm; \text{\textsuperscript{13}\text{C}\{\text{\textsuperscript{1}H}\} \text{NMR (CDCl}_3, 125 MHz): \delta 13.8, 22.4, 25.2, 29.0, 29.27, 29.34, 31.6, 32.8, 37.1, 63.0, 72.8, 86.2, 126.6, 127.5, 128.2, 128.4, 134.8, and 144.1 ppm; IR (neat) 3351, 3059, 3032, 2925, 2854, 1490, 1448, 1221 cm\(^{-1}\). HRMS-Cl \text{m/z} 479.2920 [(M + Na)\(^+\)]; calcd for C\(_{32}\)H\(_{40}\)O\(_2\)Na: 479.2926.**

\((S)-2,2,2\text{-Trichloro-}\text{-N-[3-phenyl-1-(2-trityloxyethyl)allyl]acetamide (11). General Procedure B.} \text{DBU (2.4 \(\mu\)L, 0.016 mmol) was added to a stirred solution of (S)-1-phenyl-5-trityloxypent-2-en-1-ol (2) (33.5 mg, 0.08 mmol) in 2 mL dry ether. The reaction flask was cooled to \(-5^\circ\text{C}, and Cl}_3\text{CCN (12.0 \(\mu\)L, 0.12 mmol) was added dropwise. After stirring for 1 h and gradually warming from \(-5^\circ\text{C} to r.t., the reaction was filtered quickly through a plug of silica gel, rinsing thoroughly with ether. The filtrate was concentrated in vacuo and 5 mL of dry toluene was added. The reaction was refluxed 17 h under a N\(_2\) atmosphere, then the toluene was removed in vacuo to afford 32 mg of the title compound (0.06 mmol, 70% yield) as a white solid after recrystallization from hexanes. \ m.p.: 82-86^\circ\text{C}; [\alpha]_D^{20} = -15.1 (c = 0.35, \text{CHCl}_3); \text{\textsuperscript{1}H NMR (CDCl}_3, 500 MHz, \delta 1.85 -1.89 (m, 1H), 2.04 -2.08 (m, 1H), 3.26 -3.30 (m, 2H), 4.68 -4.71 (m, 1H), 5.89 (dd, 1H, J = 15.9, 6.3 Hz), 6.41 (d, 1H, J = 16.0 Hz), and 7.14-7.37 (m, 21H) ppm; \text{\textsuperscript{13}\text{C}\{\text{\textsuperscript{1}H}\} \text{NMR (CDCl}_3, 125 MHz): \delta 33.7, 51.7, 60.0, 87.4, 126.3, 126.7, 126.9, 127.5, 127.7, 128.2, 128.4, 131.4, 136.0, 143.3, and 161.0 ppm; IR (KBr) 3423, 3063, 3031, 2924, 2367, 2344, 1690, 1508, 1448 \text{ cm}\(^{-1}\); HRMS-ESI \text{m/z} 586.1109 [(M + Na)\(^+\)]; calcd for C\(_{32}\)H\(_{28}\)Cl\(_3\)NO\(_2\)Na: 586.1083.**

\((R)-2,2,2\text{-Trichloro-}\text{-N-[3-phenyl-1-(2-trityloxyethyl)allyl]acetamide (12). The product was prepared by General Procedure B using 57 \(\mu\)L (0.38 mmol) DBU, 48 \(\mu\)L (0.48 mmol) Cl\(_3\)CCN, and 134 mg (0.32 mmol) (R)-1-phenyl-5-trityloxypent-2-en-1-ol (3). The crude product was purified by recrystallization from hexanes to give the title compound as a white solid in 72% yield (130 mg, 0.23 mmol). \ m.p.: 82-86^\circ\text{C}; [\alpha]_D^{20} = +34.3 (c = 1.21, \text{CHCl}_3); \text{\textsuperscript{1}H NMR (500 MHz, CDCl}_3): \delta 1.92-1.98 (m, 1H), 2.10-2.17 (m, 1H), 3.31-3.37 (m, 2H), 4.75-4.79 (m, 1H), 5.96 (dd, 1H, J = 15.9, 6.3 Hz), 6.48 (d, 1H, J = 15.9 Hz), 7.20-7.30 (m, 14H), 7.40 (br d, 1H, J = 7.8 Hz), and 7.43 (d, 6H, J = 8.1 Hz) ppm; \text{\textsuperscript{13}\text{C}\{\text{\textsuperscript{1}H}\} \text{NMR (125 MHz, CDCl}_3): \delta 34.0, 52.0, 60.3, 80.8, 87.6, 126.6, 127.0, 127.2, 127.8, 127.9, 128.5, 128.7, 131.7, 136.2, 143.5, and 161.2 ppm; IR (KBr)
(S)-2,2,2-Trichloro-N-[3-(4-trifluoromethylphenyl)-1-(2-trityloxyethyl)allyl]acetamide (13). The product was prepared by General Procedure B using 6.0 µL (0.04 mmol) DBU, 30 µL (0.30 mmol) C6H5CCN, and 100 mg (0.20 mmol) (S)-1-(4-trifluoromethylphenyl)-5-trityloxypent-2-en-1-ol (4). The crude product was purified by recrystallization from hexanes to give the title compound as a white solid in 69% yield (88 mg, 0.14 mmol). m.p.: 92-95 °C; [α]D20 = -36.9 (c = 1.18, CHCl3); 1H NMR (500 MHz, CDCl3): δ 1.85-1.90 (m, 1H), 2.06-2.10 (m, 1H), 3.23-3.26 (m, 1H), 3.29-3.33 (m, 1H), 4.69-4.71 (m, 1H), 5.94 (dd, 1H, J = 15.9, 6.1 Hz), 6.39 (d, 1H, J = 15.9 Hz), 7.13 (t, 3H), 7.19 (t, 6H), 7.23 (d, 2H, J = 8.4 Hz), 7.35 (d, 6H, J = 7.3 Hz), and 7.45 (d, 3H, J = 8.4 Hz) ppm; 13C{1H} NMR (125 MHz, CDCl3): δ 33.9, 52.2, 60.4, 88.0, 125.62, 125.65, 127.0, 127.5, 128.2, 128.9, 130.0, 130.4, 140.0, 143.6, 147.2, and 161.6 ppm; IR (KBr) 3342, 3298, 3055, 3030, 2955, 2873, 2365, 2345, 1708, 1685, 1616, 1596, 1521, 1489, 1448, 1324, 1280, 1222 cm−1; HRMS-CI m/z 654.0988 [(M + Na)+] calcd for C33H27Cl3F3NO2Na: 654.0957.

(S)-2,2,2-Trichloro-N-[3-(2-bromophenyl)-1-(2-trityloxyethyl)allyl]acetamide (14). The product was prepared by General Procedure B using 16.6 µL (0.11 mmol) DBU, 13 µL (0.13 mmol) C6H5CCN, and 45 mg (0.089 mmol) (S)-1-(2-bromophenyl)-5-trityloxypent-2-en-1-ol (5). The crude product was purified by recrystallization from hexanes to give the title compound as a white solid in 71% yield (41 mg, 0.064 mmol). m.p.: 97-101 °C; [α]D20 = -39.7 (c = 0.60, CHCl3); 1H NMR (500 MHz, CDCl3): δ 1.93-1.98 (m, 1H), 2.11-2.17 (m, 1H), 3.33-3.39 (m, 2H), 4.81-4.83 (m, 1H), 5.94 (dd, 1H, J = 15.9, 5.5 Hz), 6.82 (d, 1H, J = 15.9 Hz), 7.09 (t, 1H, J = 7.8 Hz), 7.18-7.22 (m, 4H), 7.26 (t, 6H, J = 7.4 Hz), 7.30 (d, 1H, J = 7.7 Hz), 7.43 (d, 6H, J = 7.4 Hz), 7.48 (br d, 1H, J = 6.3 Hz), and 7.53 (d, 1H, J = 6.3 Hz) ppm; 13C{1H} NMR (125 MHz, CDCl3): δ 34.0, 52.0, 60.6, 80.8, 124.0, 127.4, 127.6, 127.9, 128.2, 128.9, 129.2, 130.2, 130.4, 133.2, 136.5, 143.7, and 161.6 ppm; IR (KBr) 3311, 3266, 3081, 3051, 3022, 2925, 2873, 2365, 2345, 1708, 1685, 1616, 1596, 1521, 1489, 1448, 1324, 1280, 1222 cm−1; HRMS-CI m/z 664.0156 [(M + Na)+] calcd for C32H27BrCl3NO2Na: 664.0188.

(S)-2,2,2-Trichloro-N-[3-(4-chlorophenyl)-1-(2-trityloxyethyl)allyl]acetamide (15). The product was prepared by General Procedure B using 2.7 µL (0.018 mmol) DBU, 13.2 µL (0.13 mmol) C6H5CCN, and 40 mg (0.088 mmol) (S)-1-(4-chlorophenyl)-5-trityloxypent-2-en-1-ol (5). The crude product was purified by recrystallization from hexanes to give the title compound as a white solid in 70% yield (36 mg, 0.060 mmol). m.p.: 182-184 °C; [α]D20 = -2.75 (c = 0.40, CHCl3); 1H NMR (500 MHz, CDCl3): δ 1.91-1.97 (m, 1H), 2.11-2.18 (m, 1H), 3.29-3.39 (m, 2H), 4.73-4.78 (m, 1H), 5.91 (dd, 1H, J = 15.9, 6.2 Hz), 6.40 (d, 1H, J = 15.9 Hz), 7.15 (d, 2H, J = 8.5 Hz), 7.20-7.29 (m, 11H), and 7.44 (d, 7H, J = 7.4 Hz) ppm; 13C{1H} NMR (125 MHz, CDCl3): δ 33.8, 52.0, 60.2, 80.8, 87.8, 127.2, 127.7, 127.8, 127.9, 128.6, 128.7, 130.4, 134.4, 134.8, 143.5 and 161.3 ppm; IR (KBr) 3430, 3058, 3028, 2923, 2850, 2369, 2346, 1716, 1701, 1635, 1560, 1501, 1449, 1383, 1264 cm−1; HRMS-CI m/z 620.0711 [(M + Na)+] calcd for C32H27Cl3NO2Na: 620.0694.
(S)-2,2,2-Trichloro-N-[3-(4-fluorophenyl)-1-(2-trityloxyethyl)allyl]acetamide (16). The product was prepared by General Procedure B using 1.7 µL (0.011 mmol) DBU, 8.3 µL (0.83 mmol) CH_{2}CCN, and 24 mg (0.055 mmol) (S)-1-(4-fluorophenyl)-5-trityloxypent-2-en-1-ol (7). The crude product was purified by recrystallization from hexanes to give the title compound as a white solid in 81% yield (26 mg, 0.045 mmol). m.p.: 79-81 °C; [α]_D^{20} = -31.4 (c = 0.21, CHCl_3); ^1H NMR (500 MHz, CDCl_3): δ 1.92-1.97 (m, 1H), 2.11-2.17 (m, 1H), 3.30-3.38 (m, 2H), 4.73-4.76 (m, 1H), 5.85 (dd, 1H, J = 15.9, 6.3 Hz), 6.42 (d, 1H, J = 15.9 Hz), 6.97 (t, 2H, J = 8.6 Hz), 7.19-7.29 (m, 11H), and 7.43 (d, 7H, J = 7.3 Hz) ppm; ^13C{^1H} NMR (125 MHz, CDCl_3): δ 33.9, 52.0, 60.2, 81.0, 87.7, 115.3, 115.5, 126.8, 127.2, 127.8, 127.9, 128.07, 128.14, 128.7, 130.5, 143.5, and 161.2 ppm; IR (KBr) 3350, 3057, 3032, 2927, 2877, 2369, 2345, 1701, 1601, 1508, 1448, 1228 cm^{-1}; HRMS -CI m/z 604.1014 [(M + Na)^+]; calcd for C_{32}H_{27}Cl_3FNO_2Na: 604.0989.

2,2,2-Trichloro-N-[3-cyclohexyl-1-(2-trityloxyethyl)allyl]acetamide (17). General Procedure C. DBU (62 µL, 0.41 mmol) was added to a stirred solution of 1-cyclohexyl-5-trityloxypent-2-en-1-ol (8) (146 mg, 0.34 mmol) in 2.0 mL of dry dichloromethane. The reaction flask was cooled to 0 °C, and Cl_3CCN (51 µL, 0.51 mmol) was added dropwise. After stirring for 1 h and gradually warming from 0 °C to r.t., the reaction was quenched with a small amount of sat. NH_4Cl. The reaction mixture was then filtered quickly through a plug of silica gel and NaSO_4, rinsing thoroughly with dichloromethane. The filtrate was concentrated in vacuo, dissolved in 5.0 mL of p-xylene, and K_2CO_3 (10 mg) was added. The reaction was refluxed 20 h under a N_2 atmosphere and then filtered. The solvent was removed in vacuo to afford 128 mg of the title compound (0.22 mmol, 66% yield) after recrystallization from hexanes. m.p.: 80-82 °C; [α]_D^{20} = -19.6 (c = 0.69, CHCl_3); ^1H NMR (500 MHz, CDCl_3): δ 0.88-0.92 (m, 2H), 1.04-1.09 (m,1H), 1.11 -1.20 (m, 2H), 1.51 -1.57 (m, 3H), 1.60 -1.63 (m, 2H), 1.73 -1.82 (m, 2H), 1.90-1.97 (m, 1H), 3.17-3.22 (m, 2H), 4.45-4.49 (m, 1H), 5.11 (dd, 1H, J = 15.6, 6.2 Hz), 5.44 (dd, 1H, J = 15.6, 6.5 Hz), 7.10 (br d, 1H), 7.11-7.17 (m, 3H), 7.22 (t, 6H, J = 7.9 Hz), and 7.35 (d, 6H, J = 7.2 Hz) ppm; ^13C{^1H} NMR (125 MHz, CDCl_3): δ 26.2, 26.3, 32.9, 33.0, 34.4, 40.4, 51.9, 60.5, 87.7, 125.1, 127.3, 128.1, 128.9, 138.9, 143.9, and 161.1 ppm; IR (KBr) 3451, 3058, 2917, 2843, 2354, 2339, 1694, 1605, 1553, 1501, 1442, 1375, 1323, 1271, 1227 cm^{-1}; HRMS -CI m/z 592.1535 [(M + Na)^+]; calcd for C_{32}H_{34}Cl_3NO_2Na: 592.1553.

2,2,2-Trichloro-N-[5-methyl-1-(2-trityloxyethyl)hex-2-enyl]acetamide (18). The product was prepared by General Procedure C using 45 µL (0.30 mmol) DBU, 38 µL (0.38 mmol) CH_{2}CCN, 100 mg (0.25 mmol) 2-methyl-8-trityloxyoct-5-en-4-ol (9), and 8 mg K_2CO_3. The crude product was purified by recrystallization from hexanes to give the title compound as a white solid in 74% yield (101 mg, 0.19 mmol). m.p.: 101-103 °C; [α]_D^{20} = -13.3 (c = 1.17, CHCl_3); ^1H NMR (500 MHz, CDCl_3): δ 0.73 (d, 3H, J = 1.1 Hz), 0.74 (d, 3H, J = 1.1 Hz), 0.78-0.82 (m, 1H), 1.44-1.49 (m, 1H), 1.73-1.77 (m, 2H), 1.91-1.97 (m, 1H), 3.22 (t, 2H, J = 5.1 Hz), 4.46 (m, 1H), 5.11 (dd, 1H, J = 15.4, 6.2 Hz), 5.46 (dt, 1H, J = 14.5, 7.2 Hz), 7.15 (t, 3H, J = 7.3 Hz), 7.22 (t, 7H, J = 7.5 Hz), and 7.35 (d, 6H, J = 7.3 Hz) ppm; ^13C{^1H} NMR (125 MHz, CDCl_3): δ 22.4, 22.5, 28.3, 34.3, 41.7, 52.0, 60.5, 87.8, 93.3, 127.3, 128.1, 128.6, 128.9, 132.0, 143.9, and 161.2 ppm; IR
2,2,2-Trichloro-N-[1-(2-trityloxyethyl)undec-2-enyl]acetamide (19). The product was prepared by General Procedure C using 45 µL (0.30 mmol) DBU, 38 µL (0.38 mmol) Cl₃CCN, 100 mg (0.25 mmol) 1-trityloxytridec-3-en-5-ol (10), and 8 mg K₂CO₃. The crude product was purified by recrystallization from hexanes to give the title compound as a white solid in 68% yield (103 mg, 0.17 mmol). m.p.: 92-93 °C; [α]D²⁰ = -3.2 (c = 1.18, CHCl₃); ¹H NMR (500 MHz, CDCl₃): δ 0.81 (t, 3H, J = 6.8 Hz), 1.17-1.21 (m, 12H), 1.73-1.77 (m, 1H), 1.84 -1.86 (m, 2H), 1.90 -1.96 (m, 1H), 3.20 (m, 2H), 4.46 (m, 1H), 5.13 (dd, 1H, J = 15.4, 6.0 Hz), 5.48 (dt, 1 H, J = 15.3, 6.6 Hz), 7.14-7.17 (m, 4H), 7.22 (t, 6H, J = 7.4 Hz), and 7.35 (d, 6H, J = 7.3 Hz) ppm; ¹³C{¹H} NMR (125 MHz, CDCl₃): δ 14.1, 22.7, 29.0, 29.1, 29.2, 29.4, 31.9, 32.1, 34.0, 51.7, 60.2, 87.5, 92.8, 127.08, 127.11, 127.9, 128.7, 133.1, 143.7, and 161.0 ppm; IR (KBr) 3288, 3088, 3056, 3029, 2925, 2853, 1710, 1686, 1596, 1532, 1490, 1448, 1386, 1289, 1252, 1222 cm⁻¹; HRMS-CI m/z 622.2057 [(M + Na)⁺; calcd for C₃₄H₄₀Cl₃NO₂Na: 622.2022].

(R)-2,2,2-Trichloro-N-[1-(2-hydroxyethyl)-3-phenylallyl]acetamide (20).

General Procedure D. Et₂AlCl (530 µL, 1.8M in toluene) was added dropwise to a stirred solution of (R)-2,2,2-trichloro-N-[3-phenyl-1-(2-trityloxyethyl)allyl]acetamide (12) (36.0 mg, 0.064 mmol) in 3.0 mL dry dichloromethane. After stirring for 20 min at room temperature, the reaction was quenched with saturated NaHCO₃. The organic layer was extracted with dichloromethane, washed with H₂O, and dried over MgSO₄. The filtrate was concentrated in vacuo, and the residue was chromatographed on silica (30% EtOAc in hexanes) to afford the title compound in 88% yield (18.5 mg, 0.057 mmol) as a colorless oil. [α]D²⁰ = +34.2 (c = 0.53, CHCl₃); ¹H NMR (500 MHz, CDCl₃): δ 1.78-1.83 (m, 1H), 1.92 (br s, 1H), 2.05 -2.11 (m, 1H), 3.77 -3.85 (m, 2H), 4.75-4.78 (m, 1H), 6.07 (dd, 1H, J = 15.9, 6.0 Hz), 6.55 (d, 1H, J = 15.9 Hz), 7.19 (t, 1H, J = 7.3 Hz), 7.25 (t, 2H, J = 7.5 Hz), 7.31 (d, 2H, J = 7.4 Hz), and 7.56 (br d, 1H, J = 6.2 Hz) ppm; ¹³C{¹H} NMR (125 MHz, CDCl₃): δ 36.1, 51.4, 59.4, 126.6, 126.9, 128.0, 128.6, 132.0, 136.1, and 161.8 ppm; IR (neat) 3316, 3025, 2943, 2926, 2919, 2861, 1694, 1517, 1448, 1251 cm⁻¹.

(S)-2,2,2-Trichloro-N-[3-(2-bromophenyl)-1-(2-hydroxyethyl)allyl]acetamide (21). The product was prepared by General Procedure D using 330 µL (0.59 mmol) Et₂AlCl and 25 mg (0.039 mmol) (S)-2,2,2-trichloro-N-[3-(2-bromophenyl)-1-(2-trityloxyethyl)allyl]acetamide (14). The crude product was purified by column chromatography (30% EtOAc in hexanes) to give the title compound as a colorless oil in 91% yield (14.3 mg, 0.036 mmol). [α]D²⁰ = -55.0 (c = 0.38, CHCl₃); ¹H NMR (500 MHz, CDCl₃): δ 1.80-1.85 (m, 1H), 1.93 (br s, 1H), 2.08-2.13 (m, 1H), 3.80-3.87 (m, 2H), 4.79-4.83 (m, 1H), 6.07 (dd, 1H, J = 15.9, 5.4 Hz), 6.90 (d, 1H, J = 16.0 Hz), 7.05 (t, 1H, J = 7.7 Hz), 7.20 (t, 1H, J = 7.4 Hz), 7.42 (d, 1H, J = 7.8 Hz), 7.48 (d, 1H, J = 8.0 Hz), and 7.70 (br d, 1H, J = 6.9 Hz) ppm; ¹³C{¹H} NMR (125 MHz, CDCl₃): δ 35.7, 51.2, 59.4, 89.0, 123.8, 127.1, 127.5, 129.2, 130.1, 130.4, 133.0, 136.2, and 161.8 ppm; IR (neat) 3318, 2924, 1694, 1514, 1466, 1435, 1260 cm⁻¹.
(S)-2,2,2-Trichloro-N-[3-(4-fluorophenyl)-1-(2-hydroxyethyl)allyl]acetamide (22). The product was prepared by General Procedure D using 920 µL (1.65 mmol) Et₂AlCl and 64 mg (0.11 mmol) (S)-2,2,2-trichloro-N-[3-(4-fluorophenyl)-1-(2-trityloxyethyl)allyl]acetamide (16). The crude product was purified by column chromatography (20-30% EtOAc in hexanes) to give the title compound as a colorless oil in 95% yield (35 mg, 0.10 mmol). [α]_D^20 = -60.6 (c = 0.52, CHCl₃); ¹H NMR (500 MHz, CDCl₃): δ 1.85-1.90 (m, 1H), 2.05 (br s, 1H), 2.11-2.16 (m, 1H), 3.84-3.92 (m, 2H), 4.80-4.82 (m, 1H), 6.10 (dd, 1H, J = 15.9, 6.0 Hz), 6.58 (d, 1H, J = 15.9 Hz), 7.01 (t, 2H, J = 8.6 Hz), 7.26-7.36 (m, 2H), and 7.71 (br d, J = 6.6 Hz) ppm; ¹³C{¹H} NMR (125 MHz, CDCl₃): δ 36.0, 51.5, 59.4, 80.8, 115.5, 115.7, 126.7, 128.0, 128.1, 130.8, 132.3, 161.5, 161.8, and 163.5 ppm; IR (neat) 3314, 3036, 2953, 2921, 1694, 1602, 1506, 1229, 1158 cm⁻¹; HRMS -CI m/z 338.9991 [M⁺]; calcd for C₁₃H₁₃Cl₃FNO₂: 338.9996.

2,2,2-Trichloro-N-[5-methyl-1-(2-hydroxyethyl)-hex-2-enyl]acetamide (23). The product was prepared by General Procedure D using 1.4 mL (2.55 mmol) Et₂AlCl and 94 mg (0.17 mmol) 2,2,2-trichloro-N-[5-methyl-1-(2-trityloxyethyl)hex-2-enyl]acetamide (18). The crude product was purified by column chromatography (20% EtOAc in hexanes) to give the title compound as a colorless oil in 92% yield (47 mg, 0.16 mmol). [α]_D^20 = -38.7 (c = 1.00, CHCl₃); ¹H NMR (500 MHz, CDCl₃): δ 0.83 (d, 6H, J = 6.6 Hz), 1.57-1.61 (m, 1H), 1.66-1.71 (m, 1H), 1.89 (t, 2H, J = 6.9 Hz), 1.92-1.98 (m, 1H), 2.27 (br s, 1H), 3.71-3.79 (m, 2H), 4.53-4.55 (m, 1H), 5.38 (dd, 1H, J = 15.4, 5.9 Hz), 5.64 (dt, 1H, J = 15.4, 7.1 Hz), and 7.46 (br d, 1H, J = 5.8 Hz) ppm; ¹³C{¹H} NMR (125 MHz, CDCl₃): δ 22.17, 22.23, 28.1, 36.3, 41.6, 51.2, 59.3, 92.8, 128.4, 132.2, and 161.7 ppm; IR (neat) 3424, 3329, 2953, 2869, 2356, 2325, 1694, 1519, 1467, 1384, 1367, 1263 cm⁻¹; HRMS-ESI m/z 324.0313 [(M + Na)⁺]; calcd for C₁₁H₁₈Cl₃NO₂Na: 324.0301.

2,2,2-Trichloro-N-[1-(2-hydroxyethyl)undec-2-enyl]acetamide (24). The product was prepared by General Procedure D using 680 µL (1.23 mmol) Et₂AlCl and 49 mg (0.082 mmol) 2,2,2-trichloro-N-[1-(2-trityloxyethyl)undec-2-enyl]acetamide (19). The crude product was purified by column chromatography (15-20% EtOAc in hexanes) to give the title compound as a colorless oil in 89% yield (26.1 mg, 0.073 mmol). [α]_D^20 = -15.1 (c = 0.45, CHCl₃); ¹H NMR (500 MHz, CDCl₃): δ 0.81 (t, 3H, J = 6.7 Hz), 1.20 (m, 10H), 1.30 (t, 2H, J = 6.7 Hz), 1.63-1.69 (m, 1H), 1.91-1.96 (m, 1H), 1.97-2.01 (m, 2H), 2.05 (br s, 1H), 3.73 (m, 2H), 4.52-4.55 (m, 1H), 5.37 (dd, 1H, J = 15.4, 5.9 Hz), 5.65 (dt, 1H, J = 15.4, 6.7 Hz), and 7.29 (br d, 1H, J = 6.5 Hz) ppm; ¹³C{¹H} NMR (125 MHz, CDCl₃): δ 14.1, 22.6, 29.0, 29.1, 29.3, 29.4, 31.9, 32.3, 36.6, 51.0, 59.2, 127.3, 133.6, and 161.7 ppm; IR (neat) 3465, 3424, 3308, 2926, 2853, 1697, 1519, 1467, 1261 cm⁻¹; HRMS-CI m/z 380.0928 [(M + Na)⁺]; calcd for C₁₅H₂₆Cl₃NO₂Na: 380.0927.

7-Methyl-3-(2,2,2-trichloro-acetylamino)oct-4-enoic acid (32). General Procedure E. A solution of 2,2,2-trichloro-N-[5-methyl-1-(2-hydroxyethyl)hex-2-enyl]acetamide (23) (33.6 mg, 0.11 mmol) in 1 mL acetone and 1 mL dichloromethane was cooled to 0 °C, and 94 µL Jones’ reagent was added dropwise. After stirring at 0 °C for 3 min, the reaction was warmed to r.t. The reaction was stirred at r.t. 20 min, filtered through Celite, and the acetone was removed in vacuo. The remaining aqueous solution
was extracted with dichloromethane, and the organic layer was washed with sat. NaHCO₃. This aqueous layer was then acidified to pH 2 with 2 M HCl. The resulting aqueous layer was extracted with dichloromethane, and the combined organic layers were dried over MgSO₄. The crude product was purified by column chromatography (1% MeOH in dichloromethane to 1% MeOH, 0.5% AcOH in dichloromethane) to afford the title compound in 95% yield (33.2 mg, 0.105 mmol) as a white solid. 

\[ \alpha \] D²⁰ = -7.4 (c = 0.57, CHCl₃); ¹H NMR (500 MHz, CDCl₃): δ 0.86 (d, 6H, \( J = 6.2 \) Hz), 1.58-1.67 (m, 1H), 1.94 (t, 2H, \( J = 6.7 \) Hz), 2.79 (br d, 2H, \( J = 7.2 \) Hz), 4.75 (m, 1H), 5.49 (dd, 1H, \( J = 15.3, 6.1 \) Hz), 5.73 (dt, 1H, \( J = 15.2, 6.9 \) Hz), and 7.59 (br d, 1H, \( J = 8.3 \) Hz) ppm; ¹³C{¹H} NMR (125 MHz, CDCl₃): δ 22.1, 22.2, 28.0, 37.8, 41.4, 49.2, 127.0, 133.5, 161.1 and 176.1 ppm; IR (neat) 3336, 3025, 2955, 2919, 2861, 1710, 1517, 1466, 1408, 1367, 1290, 1261 cm⁻¹; HRMS-CI m/z 316.0269 [(M + H)⁺; calcd for C₁₁H₁₇Cl₃NO₃: 316.0274].

(S)-5-(2-Bromophenyl)-3-(2,2,2-trichloro-acetylamino)pent-4-enoic acid (28).

The product was prepared by General Procedure E using 7.5 mg (0.019 mmol) (S)-2,2,2-trichloro-N-[3-(2-bromophenyl)-1-(2-hydroxyethyl)allyl]acetamide (21), 1 mL acetone, and 16 µL Jones’ reagent. The crude product was purified by column chromatography (1% MeOH, 0.5% AcOH in dichloromethane) to give the title compound as a white solid in 100% yield (7.9 mg, 0.019 mmol). 

\[ \alpha \] D²⁰ = -9.4 (c = 0.16, CHCl₃); ¹H NMR (500 MHz, CDCl₃): δ 2.93 (d, 2H, \( J = 4.9 \) Hz), 4.99-5.02 (m, 1H), 6.19 (dd, 1H, \( J = 15.9, 5.6 \) Hz), 7.00 (d, 1H, \( J = 15.9 \) Hz), 7.13 (t, 1H, \( J = 7.7 \) Hz), 7.47 (d, 1H, \( J = 7.8 \) Hz), 7.54 (d, 1H, \( J = 8.0 \) Hz), and 7.76 (br d, 1H, \( J = 8.3 \) Hz) ppm; ¹³C{¹H} NMR (125 MHz, CDCl₃): δ 37.2, 49.1, 127.2, 127.5, 128.3, 128.5, 129.5, 131.6, 133.0, 154.3, 167.9, and 173.7 ppm; IR (neat) 3323, 2921, 2854, 1780, 1718, 1710, 1689, 1660, 1589, 1526, 1464, 1407, 1253 cm⁻¹; HRMS-CI m/z 413.9059 [(M + H)⁺; calcd for C₁₃H₁₂BrCl₃NO₃: 413.9066].

(S)-5-(4-Chlorophenyl)-3-(2,2,2-trichloro-acetylamino)pent-4-enoic acid (29).

The product was prepared by General Procedure E using 7.0 mg (0.02 mmol) (S)-2,2,2-trichloro-N-[3-(4-chlorophenyl)-1-(2-hydroxyethyl)allyl]acetamide and 17 µL Jones’ reagent. The crude product was purified by column chromatography (1% MeOH, 0.5% AcOH in dichloromethane) to give the title compound as a white solid in 93% yield (6.9 mg, 0.019 mmol). 

\[ \alpha \] D²⁰ = -12.0 (c = 0.25, CHCl₃); ¹H NMR (500 MHz, CDCl₃): δ 2.81-2.86 (m, 2H), 4.87-4.89 (m, 1H), 6.14 (dd, 1H, \( J = 15.9, 6.5 \) Hz), 6.53 (d, 1H, \( J = 15.9 \) Hz), 7.22 (s, 4H), and 7.67 (br d, 1H, \( J = 8.2 \) Hz) ppm; ¹³C{¹H} NMR (125 MHz, CDCl₃): δ 37.3, 49.4, 92.6, 126.1, 127.9, 128.9, 131.9, 134.0, 134.3, 161.3, 173.2 ppm; IR (neat) 3321, 2921, 2854, 1780, 1718, 1710, 1689, 1660, 1589, 1526, 1464, 1407, 1253 cm⁻¹; HRMS-CI m/z 413.9059 [(M + H)⁺; calcd for C₁₃H₁₂BrCl₃NO₃: 413.9066].

(S)-5-(4-Fluorophenyl)-3-(2,2,2-trichloro-acetylamino)pent-4-enoic acid (30).

The product was prepared by General Procedure E using 10.0 mg (0.03 mmol) (S)-2,2,2-trichloro-N-[3-(4-fluorophenyl)-1-(2-hydroxyethyl)allyl]acetamide and 26 µL Jones’ reagent. The crude product was purified by column chromatography (1% MeOH, 0.5% AcOH in dichloromethane) to give the title compound as a white solid in 98% yield (10.4 mg, 0.029 mmol). 

\[ \alpha \] D²⁰ = -7.9 (c = 0.53, CHCl₃); ¹H NMR (500 MHz, CDCl₃): δ 2.85-2.94 (m, 2H), 4.92-4.95 (m, 1H), 6.14 (dd, 1H, \( J = 15.9, 6.5 \) Hz), 6.61 (d, 1H, \( J = 15.9 \) Hz), 7.01 (t, 2H, \( J = 8.6 \) Hz), 7.32-7.35 (m, 2H), and 7.70 (br d, 1H, \( J = 8.3 \) Hz) ppm; IR
(neat) 3330, 2918, 2850, 1710, 1601, 1509, 1405, 1230 cm$^{-1}$; HRMS-CI m/z 353.9857 [(M + H)$^+$; calcd for C$_{13}$H$_{21}$ClF$_3$NO$_3$: 353.9867].

3-(2,2,2-trichloro-acetylamino)tridec-4-enoic acid (33). The product was prepared by General Procedure E using 9.6 mg (0.027 mmol) 2,2,2-trichloro-N-[1-(2-hydroxyethyl)undec-2-enyl]acetamide (24) and 23 µL Jones’ reagent. The crude product was purified by column chromatography (1% MeOH in dichloromethane to 1% MeOH, 0.5% AcOH in dichloromethane) to give the title compound as a white solid in 96% yield (9.7 mg, 0.026 mmol). $\alpha$$_D$$^20$ = -13.2 (c = 0.28, CHCl$_3$); $^{1}$H NMR (500 MHz, CDCl$_3$): $\delta$ 0.88 (t, 3H, J = 6.9 Hz), 1.26-1.31 (m, 10 H), 1.35-1.37 (m, 2H), 2.04 (dt, 2H, J = 7.2, 6.9 Hz), 2.77 (m, 2H), 4.74 (m, 1H), 5.50 (dd, 1H, J = 15.4, 5.8 Hz), 5.75 (dt, 1H, J = 15.4, 6.7 Hz), and 7.53 (br d, 1H, J = 7.3 Hz) ppm; $^{13}$C{$_1$$^1$H} NMR (125 MHz, CDCl$_3$): $\delta$ 14.1, 22.7, 28.9, 29.1, 29.3, 29.4, 29.7, 31.9, 32.2, 49.3, 92.6, 126.0, 134.8, 161.1, and 176.1 ppm; IR (neat) 3336, 3072, 3039, 2924, 2854, 2357, 1709, 1514, 1461, 1437, 1407, 1378, 1290, 1261, 1232 cm$^{-1}$; HRMS -CI m/z 371.0813 [M$^+$; calcd for C$_{15}$H$_{24}$Cl$_3$NO$_3$: 371.0822].

3-(2,2,2-Trichloro-acetylamino)-5-(4-trifluoromethylphenyl)pent-4-enoic acid (27). General Procedure F. A solution of (S)-2,2,2-trichloro-N-[3-(4-trifluoromethylphenyl)-1-(2-trityloxyethyl)allyl]acetamide (27) (35.5 mg, 0.056 mmol) in 1.0 mL acetone and 1.0 mL dichloromethane was cooled to 0 °C, and 50 µL Jones’ reagent was added dropwise. After stirring at 0°C for 3 min, the reaction was warmed to r.t. The reaction was stirred at r.t. 4 h, filtered through Celite, and then the organic solvent was removed in vacuo. The remaining aqueous solution was extracted with dichloromethane. After washing the organic layer with sat. NaHCO$_3$, the resulting aqueous layer was acidified to pH 2 with 2M HCl and extracted with dichloromethane. The combined organic layers were dried over MgSO$_4$, and the crude product was purified by column chromatography (1% MeOH in dichloromethane to 1% MeOH, 0.5 % AcOH in dichloromethane) to afford the title compound in 97% yield (22.0 mg, 0.054 mmol) as a white solid. $\alpha$$_D$$^20$ = -34.1 (c = 0.17, CHCl$_3$); $^{1}$H NMR (500 MHz, CDCl$_3$): $\delta$ 2.80-2.89 (m, 2H), 4.89 -4.92 (m, 1H), 6.26 (dd, 1H, J = 15.9, 6.4 Hz), 6.61 (d, 1H, J = 15.9 Hz), 7.39 (d, 2H, J = 8.1 Hz), 7.50 (d, 2H, J = 8.1 Hz), and 7.72 (br d, 1H, J = 8.5 Hz) ppm; $^{13}$C{$_1$$^1$H} NMR (125 MHz, CDCl$_3$): $\delta$ 29.7, 49.3, 92.7, 125.6, 125.7, 126.9, 128.2, 128.9, 131.6, 161.4, and 173.9 ppm; IR (neat) 3336, 3072, 3039, 2924, 2854, 2357, 1709, 1514, 1461, 1437, 1407, 1378, 1290, 1261, 1232 cm$^{-1}$; HRMS -CI m/z 402.9742 [M$^+$; calcd for C$_{14}$H$_{11}$Cl$_3$F$_3$NO$_3$: 402.9757].

(S)-3-(2,2,2-Trichloro-acetylamino)-5-(4-trifluoromethylphenyl)pent-4-enoic acid (25). The product was prepared by General Procedure E using 27 mg (0.048 mmol) (R)-2,2,2-trichloro-N-[1-(2-trityloxyethyl)-3-phenylallyl]acetamide (12) and 41 µL Jones’ reagent. The crude product was purified by column chromatography (1% MeOH in dichloromethane to 1% MeOH, 0.5% AcOH in dichloromethane) to afford the title compound in 95% yield (15.2 mg, 0.045 mmol). $\alpha$$_D$$^20$ = +37.0 (c = 0.40, CHCl$_3$); $^{1}$H NMR (500 MHz, CDCl$_3$): $\delta$ 2.85 (m, 2H), 4.92 (m, 1H), 6.20 (dd, 1H, J = 15.9, 6.5 Hz), 6.61 (d, 1H, J = 15.9 Hz), 7.23 (t, 1H, J = 7.3 Hz), 7.29 (t, 2H, J = 7.4 Hz), 7.33 (d, 2H, J = 7.3 Hz), and 7.71 (br d, 1H, J = 8.3 Hz) ppm; $^{13}$C{$_1$$^1$H} NMR (125 MHz, CDCl$_3$): $\delta$ 37.9, 49.5, 92.6, 125.4, 126.7, 128.3, 128.7, 133.0, 135.7, 161.3, and
5-Cyclohexyl-3-(2,2,2-trichloro-acetylamino)pent-4-enoic acid (31). The product was prepared by General Procedure F using 37 mg (0.065 mmol) 2,2,2-trichloro-\(N\)-[3-cyclohexyl-1-(2-trityloxyethyl)allyl]acetamide (17) and 57 \(\mu\)L Jones’ reagent. The crude product was purified by column chromatography (1% MeOH in dichloromethane to 1% MeOH, 0.5% AcOH in dichloromethane) to give the title compound as a white solid in 97% yield (21.6 mg, 0.063 mmol). \([\alpha]_{D}^{20} = -14.6 \) (c = 0.39, CHCl\(_3\)); \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 0.98-1.26 (m, 6H), 1.60-1.69 (m, 4H), 1.93 (m, 1H), 2.74 (m, 2H), 4.70 (m, 1H), 5.42 (dd, 1H, \(J = 15.6, 6.1\) Hz), 5.66 (dd, 1H, \(J = 15.5, 6.6\) Hz), and 7.50 (br d, 1H, \(J = 7.7\) Hz) ppm; \(^{13}\)C\{\(^1\)H\} NMR (125 MHz, CDCl\(_3\)): \(\delta\) 25.9, 26.0, 279.7, 32.5, 32.6, 38.0, 40.3, 49.4, 92.7, 123.6, 140.3, 161.0, and 175.7 ppm; IR (neat) 3324, 2924, 2851, 1709, 1518, 1449, 1411, 1261 cm\(^{-1}\); HRMS-ESI m/z 342.0419 [(M + H\(^+\)); calcd for C\(_{13}\)H\(_{19}\)Cl\(_3\)NO\(_3\): 342.0431].

Conditions for the Determination of Enantiomeric Excess

Chiral HPLC analyses were performed using a Chiralcel OD-H column. The conditions for the resolution of the racemates are described below.

1-Phenyl-5-trityloxypent-2-en-1-ol (2): \(t_1 = 10.6\) min, \(t_2 = 17.8\) min (Hexane / 2-propanol: 92/8, 1.0 mL/min).

1-(4-Trifluoromethylphenyl)-5-trityloxypent-2-en-1-ol (4): \(t_1 = 9.1\) min, \(t_2 = 26.6\) min (Hexane / 2-propanol: 92/8, 1.0 mL/min).

1-(2-Bromophenyl)-5-trityloxypent-2-en-1-ol (5): \(t_1 = 40.2\) min, \(t_2 = 43.3\) min (Hexane / 2-propanol: 90/10, 0.2 mL/min).

1-(4-Chlorophenyl)-5-trityloxypent-2-en-1-ol (6): \(t_1 = 9.1\) min, \(t_2 = 12.4\) min (Hexane / 2-propanol: 95/5, 1.0 mL/min).

1-(4-Fluorophenyl)-5-trityloxypent-2-en-1-ol (7): \(t_1 = 10.3\) min, \(t_2 = 23.5\) min (Hexane / 2-propanol: 95/5, 1.0 mL/min).

1-Cyclohexyl-5-trityloxypent-2-en-1-ol (8): \(t_1 = 23.4\) min, \(t_2 = 37.5\) min (Hexane / 2-propanol: 95/5, 0.5 mL/min).

2-Methyl-8-trityloxyoct-5-en-4-ol (9): \(t_1 = 33.2\) min, \(t_2 = 43.9\) min (Hexane / 2-propanol: 99/1, 0.5 mL/min).

1-Trityloxytridec-3-en-5-ol (10): \(t_1 = 28.9\) min, \(t_2 = 51.0\) min (Hexane / 2-propanol: 99/1, 0.5 mL/min).
NMR Spectra