Electronic Supplementary Material (ESI) for Chemical Communications

Rhodium Catalyzed Regio- and Enantioselective Amination of Racemic Secondary Allylic Trichloroacetimidates with *N*-Methyl Anilines

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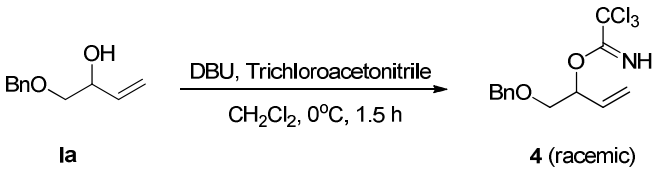
Table of Contents

Supporting Information

Methods and Reagents. All reactions were performed in oven-dried Schlenk flasks fitted with glass stoppers under positive argon pressure. Organic solutions were concentrated by rotary evaporation below 40 ^{o}C at 25 torr. Analytical thin-layer chromatography (TLC) and gas chromatography (GC) were routinely used to monitor the progress of the reactions. TLC was performed using pre-coated glass plates with 230-400 mesh silica gel impregnated with a fluorescent indicator (250 nm). Visualization was accomplished using UV light, potassium permanganate, or phosphomolybdic acid. Monitoring by GC was performed using an HP-1 (30m x 0.320mm) column and temperature gradient of 100-250^{o}C over 10 min. Flash chromatography was performed on silica gel flash chromatography columns or a Teledyne Isco CombiFlash R_f system utilizing normal phase pre-column cartridges and gold high performance columns. The ee's were determined by HPLC using a Diacel Chiralcel 4.6 x 250 mm OD-H or Diacel Chiralcel OJ-3 4.6 x 150 mm column fitted with guard columns with flow rates and mobile phases as indicated. Dry solvents were obtained from a SG Waters solvent system utilizing activated alumina columns under an argon pressure or purchased from Sigma-Aldrich in sure-seal bottles. The rhodium catalysts and chiral diene ligands were handled and transferred to Schlenk flasks within a glove box under a nitrogen atmosphere. All chemicals and reagents were obtained from commercial vendors and used without further purification.

Instrumentation. All proton (^{1}H) nuclear magnetic resonance spectra were recorded on a 400 MHz spectrometer. All carbon (^{13}C) nuclear magnetic resonance spectra were recorded on a 100 MHz NMR spectrometer. Chemical shifts are expressed in parts per million (δ scale) and are referenced to residual $CHCl_3$ (^{1}H: δ 7.24 ppm, ^{13}C: δ 77.23 ppm) or MeOH (^{1}H: δ 3.31 ppm, ^{13}C: δ 49.15 ppm) in the NMR solvent. Data are presented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, and bs = broad singlet), integration, and coupling constant in hertz (Hz). Infrared (IR) spectra were reported in cm^{-1}. High resolution TOF mass spectrometry utilizing electrospray ionization in positive or negative modes was performed to confirm the identity of the compounds.

Procedure for Preparation of Allylic Trichloroacetimidates 4, 6-15 and 26

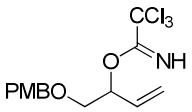


1a **4** (racemic)

A 50 mL flask was charged with allylic alcohol **1a** (1.24g, 6.97 mmol) and 17 ml of anhydrous dichloromethane and was cooled to 0°C. Trichloroacetonitrile (2.10 ml, 20.9 mmol, 3 equiv.) was added to the flask followed by dropwise addition of DBU (0.52 mL, 3.49 mmol, 0.5 equiv.). After stirring for 3 h at 0°C, the reaction was concentrated and loaded onto a pre-equilibrated 25g Teledyne Isco silica load cartridge followed by elution onto a pre-equilibrated 40g column providing allylic trichloroacetimidate **4** (2.25g, 92%) as a brown oil.

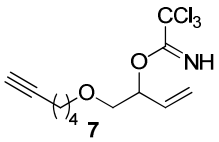
^{1}H NMR spectrum is matched with the literature compound.[4]

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.35 (s, NH), 7.34-7.30 (m, 4H), 7.30-7.25 (m, 1H), 5.95-5.85 (m, 1H), 5.66-5.58 (m, 1H), 5.44 (dt, *J* = 17.3, 1.3 Hz, 1H), 5.28 (dt, *J* = 10.7, 1.2 Hz, 1H), 4.60 (s, 2H), 3.72-3.69 (m, 2H).
IR (film, cm^{-1}): ν = 3342, 3088, 3064, 3030, 2897, 2861, 1664, 1496, 1454, 1362, 1286, 1205, 1075, 987, 930, 873, 793, 735, 697.



6

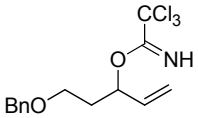
^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.35 (bs, NH), 7.24 (d, *J* = 8.7 Hz, 2H), 6.85 (d, *J* = 8.7 Hz, 2H), 5.93-5.85 (m, 1H), 5.62-5.58 (m, 1H), 5.43 (dt, *J* = 17.3, 1.4 Hz, 1H), 5.27 (dt, *J* = 10.7, 1.3 Hz, 1H), 4.52 (s, 2H), 3.78 (s, 3H), 3.70-3.62 (m, 2H).
^{13}C NMR ($CDCl_3$, 100 MHz): δ = 162.1, 159.4, 132.8, 130.3, 129.4, 118.2, 114.0, 91.9, 78.4, 73.2, 71.0, 55.5.
IR (film, cm^{-1}): ν = 3342, 3001, 2933, 2907, 2862, 2837, 1733, 1665, 1613, 1586, 1514, 1464, 1362, 1301, 1248, 1173, 1081, 1036, 989, 931, 849, 822.
HRMS (TOF ES+): calc. for $C_{14}H_{16}Cl_3NO_3Na$ $(M+Na)^+$: 374.0093; found: 374.0095.



7

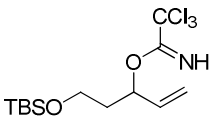
^{1}H NMR spectrum is matched with the literature compound.[5]

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.30 (s, NH), 5.89-5.82 (m, 1H), 5.54-5.51 (m, 1H), 5.40 (dt, *J* = 13.8, 1.0 HZ, 1H), 5.23 (dt, *J* = 8.6, 1.0 Hz, 1H), 3.64-3.57 (m, 2H), 3.56-3.49 (m, 2H), 2.17-2.12 (m, 2H), 1.73-1.66 (m, 5H).
IR (film, cm^{-1}): ν = 3343, 2950, 2920, 2862, 1664, 1647, 1434, 1345, 1286, 1123, 1074, 987, 973, 930, 872, 813, 793, 743.



8

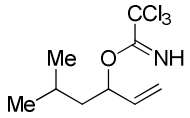
^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.30 (bs, NH), 7.32-7.25 (m, 5H), 5.91-5.83 (m, 1H), 5.59-5.55 (m, 1H), 5.35 (dt, *J* = 17.3, 1.3 Hz, 1H), 5.21 (dt, *J* = 10.6, 1.2 Hz, 1H), 4.48 (s, 2H), 3.60-3.56 (m, 2H), 2.08-2.01 (m, 2H).
^{13}C NMR ($CDCl_3$, 100 MHz): δ = 161.9, 138.4, 135.6, 128.6, 127.9, 127.8, 117.0, 91.9, 76.7, 73.3, 66.0, 34.8.
IR (film, cm^{-1}): ν = 3343, 3087, 3064, 3030, 2953, 2924, 2860, 2796, 1952, 1872, 1735, 1662, 1495, 1454, 1422, 1413, 1360, 1299, 1285, 1204, 1074, 1028, 977, 925, 805.
HRMS (TOF ES+): calc. for $C_{14}H_{16}Cl_3NO_2Na$ $(M+Na)^+$: 358.0144; found: 358.0149.



9

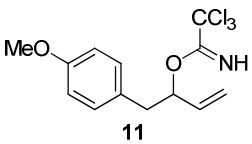
^{1}H NMR spectrum is matched with the literature compound.[4]

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.29 (s, NH), 5.91-5.83 (m, 1H), 5.54-5.49 (m, 1H), 5.34 (dt, *J* = 17.0, 2.4 Hz, 1H), 5.19 (dt, *J* = 10.6, 1.2 Hz, 1H), 3.74-3.70 (m, 2H), 2.00-1.90 (m, 2H), 0.86 (s, 9H), 0.02 (s, 6H).
IR (film, cm^{-1}): ν = 3349, 2955, 2929, 2857, 1664, 1471, 1286, 1255, 1100, 980, 832, 795, 776, 647.



10

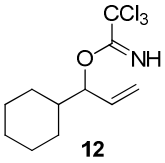
^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.26 (bs, NH), 5.89-5.80 (m, 1H), 5.46-5.41 (m, 1H), 5.33 (dt, *J* = 17.3, 1.3, 1H), 5.18 (dt, *J* = 10.6, 1.2 Hz, 1H), 1.82-1.73 (m, 2H), 1.49-1.42 (m, 1H), 0.93 (d, *J* = 3.6 Hz, 3H), 0.92 (d, *J* = 3.7 Hz, 3H).
^{13}C NMR ($CDCl_3$, 100 MHz): δ = 162.2, 136.2, 116.7, 92.1, 78.2, 43.6, 24.7, 23.2, 22.4.
IR (film, cm^{-1}): ν = 3348, 3087, 2958, 2934, 2871, 1766, 1722, 1661, 1469, 1424, 1387, 1368, 1336, 1299, 1285, 1172, 1129, 1074, 978, 924, 853, 827.
HRMS (TOF ES+): calc. for $C_9H_{15}Cl_3NO$ $(M+H)^+$: 258.0219; found: 258.0221.



11

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.26 (bs, NH), 7.16 (d, *J* = 8.6 Hz, 2H), 6.80 (d, *J* = 8.6 Hz, 2H), 5.89-5.81 (m, 1H), 5.55-5.50 (m, 1H), 5.31 (dt, *J* = 17.3, 1.3 Hz, 1H), 5.19 (dt, *J* = 10.6, 1.2 Hz, 1H), 3.76 (s, 3H), 3.04 (dd, *J* = 14.0, 7.2 Hz, 1H), 2.92 (dd, *J* = 14.0, 5.9 Hz, 1H).
^{13}C NMR ($CDCl_3$, 100 MHz): δ = 161.9, 158.5, 135.2, 130.9, 128.9, 117.3, 113.8, 91.9, 80.2, 55.4, 40.0.

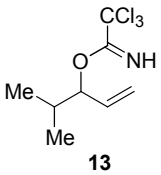
IR (film, cm^{-1}): ν = 3341, 2998, 2851, 2836, 1743, 1662, 1646, 1613, 1585, 1514, 1465, 1442, 1344, 1302, 1248, 1178, 1080, 1037, 988, 928, 823.
HRMS (TOF ES+): calc. for $C_{13}H_{14}Cl_3NO_2Na$ $(M+Na)^+$ calc.: 343.9988; found: 343.9990.



12

^{1}H NMR spectrum is matched with the literature compound.[4]

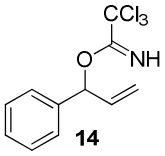
^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.21 (s, NH), 5.84-5.75 (m, 1H), 5.30 (dt, *J* = 17.3, 1.2 Hz, 1H), 5.22 (dt, *J* = 10.6, 1.2 Hz, 1H), 5.15 (t, *J* = 6.3 Hz, 1H), 1.88-1.63 (m, 6H), 1.24-1.09 (m, 5H).
IR (film, cm^{-1}): ν = 3346, 2926, 2853, 1661, 1450, 1340, 1302, 1286, 1073, 980, 930, 889, 824, 792.



13

^{1}H NMR spectrum is matched with the literature compound.[4]

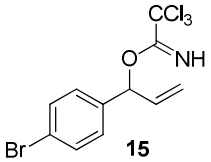
^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.23 (s, NH), 5.86-5.77 (m, 1H), 5.33 (dt, *J* = 17.2, 1.4 Hz, 1H), 5.24 (dt, *J* = 10.6, 1.4 Hz, 1H), 5.16 (t, *J* = 6.0 Hz, 1H), 2.05-1.97 (m, 1H), 0.99 (d, *J* = 7.0 Hz, 3H), 0.97 (d, *J* = 7.0 Hz, 3H).
IR (film, cm^{-1}): ν = 3347, 2965, 2934, 2876, 1662, 1469, 1303, 1287, 1076, 984, 926, 826, 794.



14

^{1}H NMR spectrum is matched with the literature compound.[4]

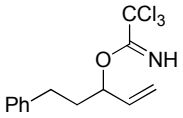
^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.35 (s, NH), 7.43-7.28 (m, 5H), 6.35 (d, *J* = 5.7 Hz, 1H), 6.10-6.02 (m, 1H), 5.40 (dt, *J* = 15.8, 1.4 Hz, 1H), 5.28 (dt, *J* = 10.5, 1.3 Hz, 1H).
IR (film, cm^{-1}): ν = 3346, 2926, 2853, 1661, 1450, 1340, 1302, 1286, 1073, 980, 930, 933, 889, 824, 792.



15

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.37 (s, NH), 7.50-7.45 (m, 2H), 7.30-7.27 (m, 2H), 6.29 (d, *J* = 5.6 Hz, 1H), 6.05-5.97 (m, 1H), 5.39 (dt, *J* = 17.1, 1.3 Hz, 1H), 5.29 (dt, *J* = 10.4, 1.2 Hz, 1H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 161.4, 137.6, 135.4, 131.9, 128.9, 122.4, 117.9, 91.6, 80.0.
IR (film, cm^{-1}): ν = 3341, 3088, 3021, 2989, 2932, 1741, 1664, 1594, 1488, 1410, 1338, 1317, 1281, 1232, 1197, 1070, 1011, 984, 931, 833.
HRMS (TOF ES+): calc. for $C_{11}H_9BrCl_3NONa$ $(M+Na)^+$ calc.: 377.8831; found: 377.8834

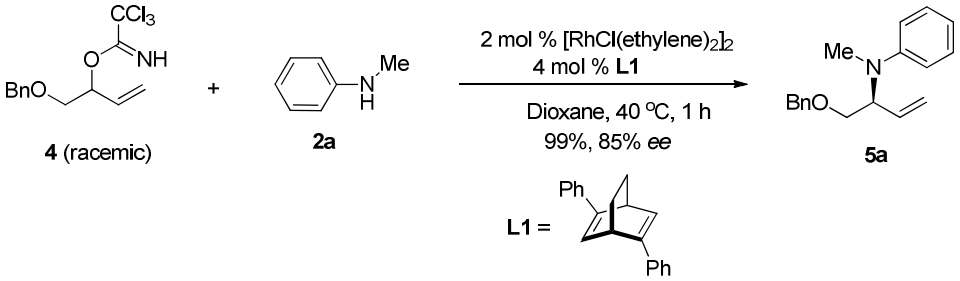


26

^{1}H NMR spectrum is matched with the literature compound.[4]

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.30 (s, NH), 7.29-7.25 (m, 2H), 7.20-7.16 (m, 3H), 5.92-5.84 (m, 1H), 5.40-5.35 (m, 1H), 5.37 (dt, *J* = 17.3, 1.3 Hz, 1H), 5.23 (dt, *J* = 10.6, 1.2 Hz, 1H), 2.82-2.67 (m, 2H), 2.13-2.02 (m, 2H).
IR (film, cm^{-1}): ν = 3343, 3085, 3026, 2928, 2861, 1661, 1496, 1455, 1285, 1074, 974, 928, 884, 824, 793, 748, 697.

General Procedure for Regio- and Enantioselective Amination of Racemic Allylic Trichloroacetimidates with $[RhCl(ethylene)]_2$/ L1



A 10 mL oven-dried Schlenk flask was charged with $[RhCl(ethylene)_2]_2$ (1.1 mg, 2.8 μmol, 2 mol%) and (1*S*,4*S*)-2,5-diphenylbicyclo[2.2.2]octa-2,5-diene (**L1**) (1.5 mg, 5.6 μmol, 4 mol%) in a glove box. The flask was sealed, removed from the glove box, and dioxane (0.35 mL) was added to the Schlenk and stirred for 15 min resulting in a bright-red solution. A separate 10 mL Schlenk flask was charged with allylic imidate **4** (45 mg, 0.14 mmol, 1.0 equiv), dioxane (0.35 mL) and aniline **2a** (23 μL, 0.21 mmol, 1.5 equiv). The rhodium catalyst solution was then added to the flask containing the solution of **4** and **2a**. The mixture was immediately placed in an oil bath at 40°C and stirred under argon. The progress of the reaction was monitored by GC at 1 h. The crude reaction was purified by adsorbing directly onto a dry 5g Teledyne Isco silica cartridge using vacuum followed by elution onto a pre-equilibrated 24g silica flash column (0 → 10% ethyl acetate/hexane) providing allylic amine **5a** (37 mg, 99%, branched/linear > 84:1) as pale yellow oil.

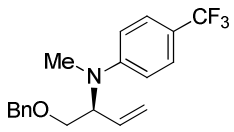
^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.33-7.22 (m, 7H), 6.82 (d, *J* = 8.7 Hz, 2H), 6.75 (t, *J* = 7.2 Hz, 1H), 5.94-5.86 (m, 1H), 5.26 (d, *J* = 1.8 Hz, 1H), 5.23 (d, *J* = 7.5, 1.6 Hz, 1H), 4.62-4.57 (m, 1H), 4.55 (d, *J* = 12.3 Hz, 1H), 4.51 (d, *J* = 12.3 Hz, 1H), 3.74-3.66 (m, 2H), 3.50 (s, 1H), 2.83 (s, 9H).

IR (film, cm^{-1}): ν =2858, 2815, 1596, 1503, 1453, 1359, 1312, 1289, 1209, 1094, 1028, 990, 921, 745, 712, 691.
[α]$^{20}_{D}$: +17.43, c =, $CHCl_3$
HPLC: 2.5mg/mL in 50/50 IPA/Hex, 2 μL injection, 4.6 x 250mm Chiralcel OD-H, 0.6 mL/min., 1% IPA in hexanes, 254 nm, major 21.03 min., minor 13.15 min., 85% ee

*Note: When reactions were scaled and required concentration with catalyst prior to purification, significant isomerization from the branched amine **5a** to the linear amine product was observed during isolation. To avoid isomerization, the following procedure was used on a 0.5 g scale to prepare **5a**:*

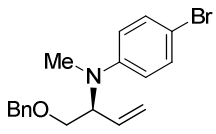
The progress of the reaction was monitored by GC at 1 h. The crude reaction was allowed to equilibrate to room temperature, filtered through a silica pad with 20% ethyl acetate in hexanes and concentrated. The crude oil was purified by adsorbing in dichloromethane onto a dry 25g Teledyne Isco silica cartridge using vacuum followed by elution onto a pre-equilibrated 40g silica flash column (0 → 20% ethyl acetate/hexane) providing allylic amine **5a** (410 mg, 99%, branched/linear > 23:1) as pale yellow oil.

[α]$^{20}_{D}$ +15.91:, c = 1, $CHCl_3$
HPLC: 2.5mg/mL in 50/50 IPA/Hex, 2 μL injection, 4.6 x 250mm Chiralcel OD-H, 0.6 mL/min., 1% IPA in hexanes, 254 nm, major 20.05 min., minor 12.93 min., 87% ee



5b

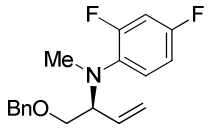
^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.43 (d, J = 8.5 Hz, 2H), 7.31-7.22 (m, 5H), 6.77 (d, *J* = 8.8 Hz, 2H), 5.87-5.79 (m, 1H), 5.25 (dt, *J* = 10.7, 1.6 Hz, 1H), 5.18 (dt, *J* = 17.4, 1.6 Hz, 1H), 4.64-4.60 (m, 1H), 4.52 (d, *J* = 12.0 Hz, 1H), 4.49 (d, *J* = 12.0 Hz, 1H), 3.69-3.67 (m, 2H), 2.84 (s, 3H).
^{13}C NMR ($CDCl_3$, 100 MHz): δ = 152.7, 138.1, 134.1, 128.6, 127.9, 127.8, 126.6, 126.6, 126.5, 126.5, 117.5, 112.1, 73.4, 70.1, 60.0, 32.6.
IR (film, cm^{-1}): ν = 3088, 3066, 3029, 2946, 2890, 2860, 2838, 1615, 1529, 1455, 1385, 1329, 1201, 1164, 1108, 1071, 987, 928, 818.
HRMS (TOF ES+): calc. for $C_{19}H_{21}F_3NO$ $(M+H)^+$: 336.1575; found: 336.1581.
[α]$^{20}_{D}$ = +14.24:, c = 1, $CHCl_3$
HPLC: 2.5mg/mL in 50/50 IPA/Hex, 2 μL injection, 4.6 x 150mm Chiralcel OJ-3, 1 mL/min., 2.5% IPA in hexanes, 254 nm, major 10.28 min., minor 8.21 min., 93% ee



5c

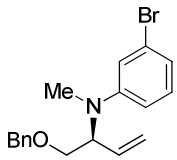
^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.33-7.22 (m, 7H), 6.64 (d, *J* = 9.1 Hz, 2H), 5.84-5.76 (m, 1H), 5.21 (dt, *J* = 10.7, 1.5 Hz, 1H), 5.16 (dt, *J* = 17.4, 1.4 Hz, 1H), 4.51 (d, *J* = 12.1 Hz, 1H), 4.48 (d, *J* = 12.0 Hz, 1H), 3.67-3.60 (m, 2H), 2.75 (s, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 156.6, 138.1, 134.4, 131.9, 128.6, 127.9, 127.8, 117.4, 115.0, 73.3, 70.1, 60.4, 32.6.
IR (film, cm^{-1}): ν = 3085, 3064, 3030, 2861, 1865, 1736, 1673, 1639, 1591, 1495, 1454, 1380, 1361, 1309, 1272, 1251, 1208, 1110, 1028, 993, 924, 807.
HRMS (TOF ES+): calc. for $C_{18}H_{21}BrNO$ $(M+H)^+$: 346.0807; found: 346.0814.
$[\alpha]^{20}_D$: +9.70, c = 1, $CHCl_3$
HPLC: 2 mg/mL in 50/50 IPA/Hex, 2 µL injection, 4.6 x 250mm Chiralcel OD-H, 0.6 mL/min., 1% IPA in hexanes, 254 nm, major 12.5 min., minor 11.4 min., 83% ee



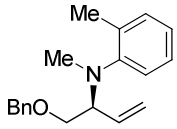
5d

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.33-7.23 (m, 5H), 6.95-6.89 (m, 1H), 6.79-6.71 (m, 2H), 5.90-5.81 (m, 1H), 5.21 (dt, *J* = 10.7, 1.4 Hz, 1H), 5.20 (dt, *J* = 17.2, 1.6 Hz, 1H), 4.48 (s, 2H), 4.12-4.07 (m, 1H), 3.69 (ddd, *J* = 10.0, 7.3, 1.1 Hz, 1H), 3.57 (dd, *J* = 10.0, 5.8 Hz, 1H), 2.71 (s, 3H).
^{13}C NMR ($CDCl_3$, 100 MHz): δ = 157.5 (dd, $J_{C\text{-}F}$ = 241, 11.4 Hz), 155.8 (dd, $J_{C\text{-}F}$ = 246, 11.7 Hz), 138.4, 136.9 (dd, $J_{C\text{-}F}$ = 9.0, 3.5 Hz), 135.0, 128.5, 127.8, 122.0 (dd, $J_{C\text{-}F}$ = 9.1, 4.4 Hz), 117.8, 110.6 (dd, $J_{C\text{-}F}$ = 21.3, 3.5 Hz), 104.6 (t, $J_{C\text{-}F}$ = 26 Hz), 73.2, 70.5, 63.7, 63.6, 34.6.
IR (film, cm^{-1}): ν = 3083, 3031, 2947, 2859, 2805, 1592, 1505, 1454, 1361, 1268, 1141, 1114, 1095, 994, 964, 927, 848.
HRMS (TOF ES+): calc. for $C_{18}H_{20}F_2NO$ $(M+H)^+$: 304.1513; found: 304.1514.
$[\alpha]^{20}_D$: +19.57, c = 1, $CHCl_3$
HPLC: 2.5mg/mL in 50/50 IPA/Hex, 2 µL injection, 4.6 x 150mm Chiralcel OJ-3, 1 mL/min., 1% IPA in hexanes, 254 nm, major 7.60 min., minor 9.08 min., 91% ee



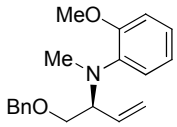
5e

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.32-7.22 (m, 9H), 6.64 (d, *J* = 9.0 Hz, 2H), 5.84-5.76 (m, 1H), 5.21 (dt, *J* = 10.7, 1.4 Hz, 1H), 5.16 (dt, *J* = 17.4, 1.3 Hz, 1H), 4.51 (d, *J* = 12.0 Hz, 1H), 4.47 (d, *J* = 12.0 Hz, 1H), 4.50-4.46 (m, 1H), 3.67-3.60 (m, 2H), 2.75 (s, 3H).
^{13}C NMR ($CDCl_3$, 100 MHz): δ = 151.8, 134.3, 130.6, 130.4, 128.6, 127.9, 127.8, 119.6, 117.4, 116.0, 114.9, 111.8, 73.3, 70.2, 60.2, 32.6.
IR (film, cm^{-1}): ν = 3086, 3065, 3029, 2882, 2861, 2816, 1639, 1591, 1554, 1489, 1453, 1430, 1361, 1325, 1265, 1210, 1095, 1077, 1028, 983, 927, 914, 833.
HRMS (TOF ES+): calc. for $C_{18}H_{21}BrNO$ $(M+H)^+$: 346.0807; found: 346.0833.
$[\alpha]^{20}_D$: +14.90, c = 1, $CHCl_3$
HPLC: 2 mg/mL in 50/50 IPA/Hex, 2 µL injection, 4.6 x 250mm Chiralcel OD-H, 0.6 mL/min., 1% IPA in hexanes, 254 nm, major 31.3 min., minor 13.2 min., 89% ee



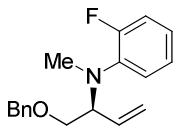
5f

^{1}H NMR (CDCl$_3$, 400 MHz): δ = 7.30-7.24 (m, 5H), 7.16-7.07 (m, 3H), 6.94 (td, *J* = 7.2, 1.5 Hz, 1H), 5.95-5.87 (m, 1H), 5.26-5.21 (m, 2H), 4.46 (d, *J* = 12.0 Hz, 1H), 4.44 (d, *J* = 12.1 Hz, 1H), 3.80-3.76 (m, 1H), 3.70-3.66 (m, 1H), 3.60-3.55 (m, 1H), 2.66 (s, 3H), 2.29 (s, 3H).
^{13}C NMR (CDCl$_3$, 100 MHz): δ = 151.7, 138.5, 136.0, 133.3, 131.3, 128.5, 127.8, 127.7, 126.2, 123.0, 122.0, 117.5, 73.3, 70.7, 64.0, 36.0, 18.7.
IR (film, cm^{-1}): ν = 3064, 3027, 2945, 2855, 2798, 1598, 1491, 1453, 1361, 1254, 1204, 1101, 1051, 1028, 993, 923, 848.
HRMS (TOF ES+): calc. for $C_{19}H_{24}NO$ $(M+H)^+$: 282.1858; found: 282.1864.
[α]$^{20}_D$:+5.70, c = 1, $CHCl_3$
HPLC: 2.5mg/mL in 50/50 IPA/Hex, 2 µL injection, 4.6 x 150mm Chiralcel OJ-3, 1 mL/min., 1% IPA in hexanes, 254 nm, major 7.44 min., minor 6.30 min., 89% ee



5g

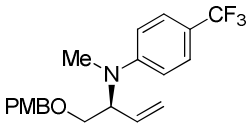
^{1}H NMR (CDCl$_3$, 400 MHz): δ = 7.31-7.24 (m, 5H), 6.96-6.82 (m, 4H), 5.99-5.90 (m, 1H), 5.20 (d, *J* = 10.7 Hz, 1H), 5.16 (d, *J* = 17.5 Hz, 1H), 4.47 (s, 2H), 4.29-4.24 (m, 1H), 3.82, (s, 3H), 3.74 (dd, *J* = 9.7, 6.2 Hz, 1H), 3.63 (dd, *J* = 9.7, 7.0 Hz, 1H), 2.71 (s, 3H).
^{13}C NMR (CDCl$_3$, 100 MHz): δ = 152.7, 141.6, 138.6, 136.0, 128.5, 127.8, 127.7, 122.4, 120.9, 120.7, 117.5, 111.5, 73.1, 70.6, 62.2, 55.6, 34.6.
IR (film, cm^{-1}): ν = 3063, 3030, 2943, 2855, 2800, 1638, 1593, 1499, 1454, 1360, 1234, 1182, 1098, 1054, 1028, 996, 918.
HRMS (TOF ES+): calc. for $C_{19}H_{24}NO_2$ $(M+H)^+$: 298.1807; found: 298.1803.
[α]$^{20}_D$: +19.18, c = 1, $CHCl_3$
HPLC: 2.5mg/mL in 50/50 IPA/Hex, 2 µL injection, 4.6 x 150mm Chiralcel OJ-3, 1 mL/min., 2.5% IPA in hexanes, 254 nm, major 6.94 min., minor 8.59 min., 85% ee



5h

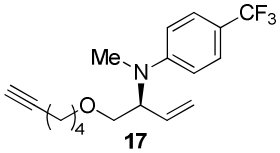
^{1}H NMR (CDCl$_3$, 400 MHz): δ = 7.32-7.23 (m, 5H), 7.01- 6.93 (m, 3H), 6.86-6.83 (m, 1H), 5.94-5.85 (m, 1H), 5.24-5.20 (m, 2H), 4.48 (s, 2H), 4.30-4.28 (m, 1H), 3.75-3.71 (m, 1H), 3.64-3.60 (m, 1H), 2.76 (s, 3H).
^{13}C NMR (CDCl$_3$, 100 MHz): δ = 154.3, 138.4, 135.1, 128.5, 127.8, 127.7, 124.3, 121.2, 120.7, 117.6, 116.4, 116.2, 73.2, 70.5, 63.0, 62.9, 33.9.
IR (film, cm^{-1}): ν = 3084, 3065, 3030, 2948, 2858, 2806, 1610, 1501, 1454, 1360, 1311, 1256, 1210, 1098, 1039, 1028, 993, 924.
HRMS (TOF ES+): calc. for $C_{18}H_{21}FNO$ $(M+H)^+$: 286.1607; found: 286.1606.

$[\alpha]^{20}_D$: +28.79, c = 1, $CHCl_3$
HPLC: 2.5 mg/mL in 50/50 IPA/Hex, 2 µL injection, 4.6 x 150mm Chiralcel OJ-3, 1 mL/min., 1% IPA in hexanes, 254 nm, major 8.45 min., minor 11.18 min., 91% ee



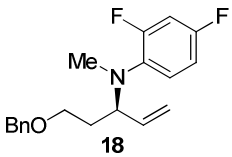
16

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.42 (d, *J* = 8.7 Hz, 2H), 7.14 (d, *J* = 8.7 Hz, 2H), 6.83 (d, *J* = 8.6 Hz, 2H), 6.75 (d, *J* = 8.8 Hz, 2H), 5.85-5.77 (m, 1H), 5.22 (dt, *J* = 10.7, 1.5 Hz, 1H), 5.16 (dt, 17.4, 1.6 Hz, 1H), 4.61-4.57 (m, 1H), 4.43 (d, *J* = 11.7 Hz, 1H), 4.42 (d, *J* = 11.7 Hz, 1H), 3.78 (s, 3H), 3.67-3.60 (m, 2H), 2.82 (s, 3H).
^{13}C NMR ($CDCl_3$, 100 MHz): δ = 159.5, 152.7, 134.1, 130.1, 129.5, 126.6, 126.5, 117.4, 114.0, 112.1, 73.0, 69.7, 59.9, 55.5, 32.6.
IR (film, cm^{-1}): ν = 3093, 3063, 3034, 3005, 2953, 2906, 2856, 2837, 1889, 1764, 1715, 1664, 1614, 1528, 1514, 1466, 1385, 1361, 1327, 1248, 1200, 1163, 1104, 1069, 1035, 985, 927, 818.
HRMS (TOF ES+): calc. for $C_{20}H_{23}F_3NO_2$ $(M+H)^+$: 366.1681; found: 366.1672.
$[\alpha]^{20}_D$: +14.07, c = 1, $CHCl_3$
HPLC: 2 mg/mL in 50/50 IPA/Hex, 2 µL injection, 4.6 x 250mm Chiralcel OD-H, 0.6 mL/min., 1% IPA in hexanes, 254 nm, major 19.78 min., minor 15.14 min., 94% ee



17

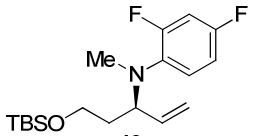
^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.41 (d, *J* = 8.6 Hz, 2H), 6.76 (d, *J* = 8.8 Hz, 2H), 5.86-5.78 (m, 1H), 5.23 (dt, *J* = 10.6, 1.5 Hz, 1H), 5.17 (dt, *J* = 17.3, 1.8 Hz, 1H), 4.57-4.52 (m, 1H), 3.65-3.60 (m, 2H), 3.50-3.45 (m, 2H), 2.85 (s, 3H), 2.14-2.10 (m, 2H), 1.76-1.72 (m, 3H), 1.69-1.62 (m, 2H).
^{13}C NMR ($CDCl_3$, 100 MHz): δ = 152.7, 134.2, 126.6, 126.5, 117.3, 112.0, 78.6, 77.4, 76.0, 69.9, 59.9, 32.6, 29.2, 16.0, 3.6.
IR (film, cm^{-1}): ν = 3091, 2922, 2865, 1769, 1723, 1615, 1572, 1529, 1478, 1434, 1386, 1329, 1247, 1200, 1164, 1113, 1071, 989, 930, 820.
HRMS (TOF ES+): calc. for $C_{18}H_{23}NOF_3$ $(M+H)^+$: 326.1732; found: 326.1726.
$[\alpha]^{20}_D$: +17.05, c = 1, $CHCl_3$
HPLC: 2.5mg/mL in 50/50 IPA/Hex, 2 µL injection, 4.6 x 150mm Chiralcel OJ-3, 1 mL/min., 1% IPA in hexanes, 254 nm, major 10.02 min., minor 6.61 min., 89% ee



18

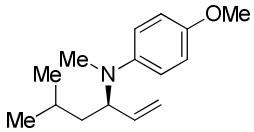
^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.29-7.24 (m, 5H), 6.90-6.88 (m, 1H), 6.78-6.71 (m, 2H), 5.84-5.76 (m, 1H), 5.13 (dt, *J* = 10.4, 1.3 Hz, 1H), 5.04 (dt, *J* = 17.3, 1.4 Hz, 1H), 4.40 (s, 2H), 3.98-3.93 (m, 1H), 3.51 (t, = 6.6 Hz, 2H), 2.64 (s, 3H), 2.04-1.95 (m, 1H), 1.88-1.79 (m, 1H).
^{13}C NMR ($CDCl_3$, 100 MHz): δ = 157.8 (dd, $J_{C\text{-}F}$ = 252, 11.4 Hz), 155.8 (dd, $J_{C\text{-}F}$ = 245, 11.5 Hz), 138.6, 137.0, 136.7 (dd, $J_{C\text{-}F}$ = 8.9, 3.4 Hz), 128.5, 127.9, 127.7, 121.7 (dd, $J_{C\text{-}F}$ = 9.1, 4.5

Hz), 117.0, 110.6 (dd, $J_{C\text{-}F}$ = 21.1, 3.7 Hz), 104.6 (t, $J_{C\text{-}F}$ = 25.1 Hz), 73.2, 67.7, 61.4, 61.4, 33.9, 31.6.
IR (film, cm^{-1}): ν = 3079, 3066, 3031, 2948, 2861, 2803, 1592, 1506, 1454, 1421, 1364, 1269, 1245, 1215, 1141, 1113, 1097, 1028, 996, 968, 925, 848, 804.
HRMS (TOF ES+): calc. for $C_{19}H_{22}F_2NO$ $(M+H)^+$: 318.1669; found: 318.1668.
[α]$^{20}_D$: +26.96, c = 1, $CHCl_3$
HPLC: 2.5mg/mL in 50/50 IPA/Hex, 2 μL injection, 4.6 x 150mm Chiralcel OJ-3, 0.6 mL/min., 2.5% IPA in hexanes, 254 nm, major 7.14 min., minor 8.22 min., 88% ee



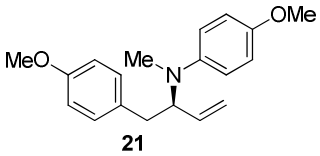
19

^{1}H NMR ($CDCl_3$, 400 MHz): 4:1 mixture of rotamers δ = 6.90-6.71 (m, 3H), 5.86-5.74 (m, 1H), 5.37-5.32 (m, 0.2H), 5.26-5.04 (m, 2H), 3.96-3.92 (m, 0.8H), 3.64-3.60 (m, 2H), 2.64 (s, 2.4H), 2.04 (s, 0.6H), 1.93-1.84 (m, 1H), 1.78-1.67 (m, 1H), 0.86 (s, 3H), 0.83 (s, 6H), 0.02 (s, 2H), -0.02 (s, 2H), -0.05 (s, 2H).
^{13}C NMR ($CDCl_3$, 100 MHz): δ = 170.4, 157.4 (dd, $J_{C\text{-}F}$ = 241, 12.5 Hz), 153.4 (dd, $J_{C\text{-}F}$ = 240, 11.7 Hz), 137.1, 136.8, 136.7, 136.6, 121.7 (dd, $J_{C\text{-}F}$ = 9.1, 4.5 Hz), 116.9, 116.7, 110.5 (dd, $J_{C\text{-}F}$ = 21.1, 3.6 Hz), 104.7 (t, $J_{C\text{-}F}$ = 26 Hz), 103.8, 77.4, 72.2, 61.0, 60.3, 59.2, 37.4, 34.4, 34.1, 26.1, 21.4, 18.4, -5.3.
IR (film, cm^{-1}): ν = 3080, 2953, 2930, 2856, 2801, 1741, 1592, 1508, 1471, 1370, 1269, 1245, 1180, 1141, 1095, 1040, 1010, 993, 969, 926, 836, 814.
HRMS (TOF ES+): calc. for $C_{18}H_{30}F_2NOSi$ $(M+H)^+$: 342.2065; found: 342.2062.
[α]$^{20}_D$: +22.27, c = 1, $CHCl_3$
HPLC: 2.5mg/mL in 50/50 IPA/Hex, 2 μL injection, 4.6 x 150mm Chiralcel OJ-3, 0.3 mL/min., 1% IPA in hexanes, 254 nm, major 6.28 min., minor 6.53 min., 87% ee



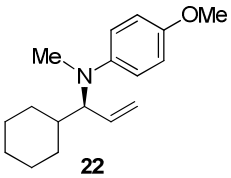
20

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 6.80 (dt, *J* = 9.3, 2.6 Hz, 2H), 6.75 (dt, *J* = 9.3, 2.5 Hz, 2H), 5.80-5.72 (m, 1H), 5.08 (dt, *J* = 10.5, 1.5 Hz, 1H), 5.05 (dt, *J* = 17.2, 1.6 Hz, 1H), 4.18-4.13 (m, 1H), 3.74 (s, 3H), 2.67 (s, 3H), 1.63-1.55 (m, 2H), 1.41-1.34 (m, 1H), 0.90 (d, *J* = 6.4 Hz, 3H), 0.86 (d, *J* = 6.4 Hz, 3H).
^{13}C NMR ($CDCl_3$, 100 MHz): δ = 151.9, 145.5, 137.9, 115.7, 115.6, 114.8, 59.8, 55.9, 41.2, 32.4, 25.0, 23.2, 22.7.
IR (film, cm^{-1}): ν = 3072, 2954, 2934, 2909, 2869, 2832, 2800, 1638, 1510, 1467, 1384, 1366, 1286, 1244, 1181, 1132, 1101, 1040, 991, 951, 920, 815.
HRMS (TOF ES+): calc. for $C_{15}H_{24}NO$ $(M+H)^+$: 234.1858; found: 234.1858.
[α]$^{20}_D$: +56.97, c = 1, $CHCl_3$
HPLC: 2 mg/mL in 50/50 IPA/Hex, 2 μL injection, 4.6 x 250mm Chiralcel OD-H, 0.3 mL/min., 100% hexanes, 254 nm, major 61.6 min., minor 70.6 min., 91% ee



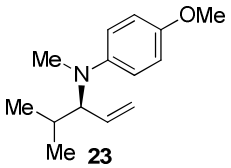
21

^{1}H NMR ($CDCl_3$, 400 MHz): 7.07 (d, *J* = 8.6 Hz, 2H), 6.77 (d, *J* = 8.9 Hz, 4H), 6.70 (d, *J* = 9.2 Hz, 2H), 5.87-5.79 (m, 1H), 5.11 (dt, *J* = 10.6, 1.5 Hz, 1H), 5.05 (dt, *J* = 17.3, 1.6 Hz, 1H), 4.32-4.29 (m, 1H), 3.75 (s, 3H), 3.73 (s, 3H), 2.94-2.87 (m, 1H), 2.83-2.78 (m, 1H), 2.74 (s, 3H).
^{13}C NMR ($CDCl_3$, 100 MHz): δ = 158.1, 152.2, 145.1, 136.8, 131.4, 130.2, 116.5, 116.3, 114.6, 113.9, 111.2, 64.6, 55.9, 55.4, 37.2, 33.1.
IR (film, cm^{-1}): ν = 3064, 3033, 2997, 2933, 2908, 2834, 1735, 1661, 1611, 1583, 1510, 1464, 1441, 1420, 1300, 1245, 1178, 1107, 1037, 990, 975, 922, 817.
HRMS (TOF ES+): calc. for $C_{19}H_{24}NO_2$ $(M+H)^+$: 298.1807; found: 298.1830.
$[\alpha]^{20}_D$: +18.50, c = 1, $CHCl_3$
HPLC: 2.5mg/mL in 50/50 IPA/Hex, 2 µL injection, 4.6 x 150mm Chiralcel OJ-3, 0.75 mL/min., 2.5% IPA in hexanes, 254 nm, major 25.3 min., minor 28.4 min., 87% ee



22

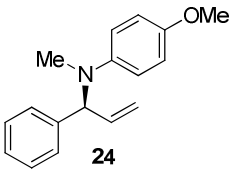
^{1}H NMR ($CDCl_3$, 400 MHz): δ = 6.78 (d, *J* = 9.2 Hz, 2H), 6.71 (d, *J* = 9.2 Hz, 2H), 5.80-5.71 (m, 1H), 5.07 (ddd, *J* = 10.3, 1.8, 0.8 Hz, 1H), 4.97 (ddd, *J* = 17.2, 1.8, 0.8 Hz, 1H), 3.73 (s, 3H), 3.67-3.63 (m, 1H), 2.68 (s, 3H), 1.84-1.53 (m, 7H), 1.26-1.10 (m, 3H), 0.93-0.84 (m, 2H).
^{13}C NMR ($CDCl_3$, 100 MHz): δ = 151.6, 145.8, 135.5, 117.0, 115.4, 114.7, 68.7, 55.9, 39.5, 32.6, 31.2, 30.8, 26.8, 26.4.
IR (film, cm^{-1}): ν = 3069, 3038, 2924, 2851, 1745, 1662, 1636, 1578, 1510, 1464, 1450, 1365, 1313, 1278, 1244, 1180, 1090, 1040, 992, 975, 920, 813.
HRMS (TOF ES+): calc. for $C_{17}H_{26}NO$ $(M+H)^+$: 260.2014; found: 260.2007.
$[\alpha]^{20}_D$: +24.94, c = 1, $CHCl_3$
HPLC: 2 mg/mL in ethanol, 12 µL injection, 4.6 x 150mm Chiralcel OJ-3, 1 mL/min., 2.5% IPA in hexanes, 254 nm, major 4.5 min., minor 3.8 min., 96% ee



23

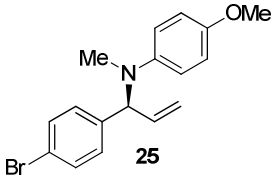
^{1}H NMR ($CDCl_3$, 400 MHz): δ = 6.80-6.77 (m, 2H), 6.74-6.71 (m, 2H), 5.81-5.72 (m, 1H), 5.10-5.07 (m, 1H), 5.02-4.97 (m, 1H), 3.74 (s, 3H), 3.57-3.52 (m, 1H), 2.68 (s, 3H), 1.90-1.53 (m, 1H), 0.93 (d, *J* = 2.1 Hz, 3H), 0.91 (d, *J* = 2.0 Hz, 3H).
^{13}C NMR ($CDCl_3$, 100 MHz): δ = 151.7, 145.8, 135.7, 128.7, 124.9, 116.9, 115.6, 114.7, 70.0, 55.9, 32.7, 30.2, 20.6, 20.5.
IR (film, cm^{-1}): ν = 3077, 2956, 2905, 2870, 2832, 2805, 1636, 1607, 1577, 1511, 1466, 1385, 1366, 1277, 1244, 1181, 1086, 1040, 975, 918, 814.
HRMS (TOF ES+): calc. for $C_{14}H_{22}NO$ $(M+H)^+$: 220.1701; found: 220.1703.
$[\alpha]^{20}_D$: +40.40, c = 1, $CHCl_3$

HPLC: 2.5mg/mL in 50/50 IPA/Hex, 2 µL injection, 4.6 x 150mm Chiralcel OJ-3, 0.6 mL/min., 1% IPA in hexanes, 254 nm, major 5.43 min., minor 4.98 min., 95% ee



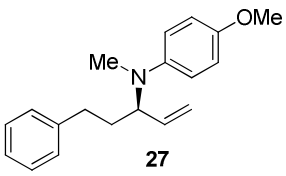
24

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.34-7.29 (m, 5H), 6.80 (d, *J* = 9.3 Hz, 2H), 6.77 (d, *J* = 9.3 Hz, 2H), 6.14-6.06 (m, 1H), 5.28 (d, *J* = 10.2 Hz, 1H), 5.24 (d, *J* = 6.4 Hz, 1H), 5.18 (d, *J* = 17.2 Hz, 1H), 3.74 (s, 3H), 2.66 (s, 3H).
^{13}C NMR ($CDCl_3$, 100 MHz): δ = 151.7, 145.8, 135.7, 128.7, 124.9, 116.9, 115.6, 114.7, 70.0, 55.9, 32.7, 30.2, 20.6, 20.5.
IR (film, cm^{-1}): ν = 3065, 2955, 2906, 2870, 2832, 2805, 1510, 1466, 1385, 1366, 1278, 1244, 1181, 1085, 1040, 994, 974, 920, 814.
HRMS (TOF ES+): calc. for $C_{17}H_{20}NO$ $(M+H)^+$: 254.1545; found: 254.1552.
$[\alpha]^{20}_D$: +45.50, c = 1, $CHCl_3$
HPLC: 2.5mg/mL in 50/50 IPA/Hex, 2 µL injection, 4.6 x 150mm Chiralcel OJ-3, 1 mL/min., 5% IPA in hexanes, 254 nm, major 9.58 min., minor 11.6 min., 93% ee



25

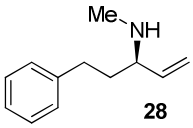
^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.45 (d, *J* = 8.5 Hz, 2H), 7.19 (d, *J* = 8.6 Hz, 2H), 6.83 (d, *J* = 9.5 Hz, 2H), 6.79 (d, *J* = 9.4 Hz, 2H), 6.12-6.03 (m, 1H), 5.32 (dt, *J* = 10.3, 1.4 Hz, 1H), 5.21 (dt, *J* = 17.0, 1.4 Hz, 1H), 5.18 (s, 1H), 3.78 (s, 3H), 2.68 (s, 3H).
^{13}C NMR ($CDCl_3$, 100 MHz): δ = 152.6, 144.8, 140.0, 135.8, 131.6, 129.8, 121.2, 118.4, 116.7, 114.7, 67.0, 55.9, 35.2.
IR (film, cm^{-1}): ν = 3043, 2990, 2949, 2903, 2831, 2805, 1741, 1588, 1508, 1485, 1402, 1368, 1276, 1241, 1179, 1119, 1071, 1037, 1009, 927, 862, 814.
HRMS (TOF ES+): calc. for $C_{17}H_{19}BrNO$ $(M+H)^+$: 332.0650; found: 332.0643.
$[\alpha]^{20}_D$: -41.59, c = 1 $CHCl_3$
HPLC: 2.5 mg/mL in 50/50 IPA/Hex, 2 µL injection, 4.6 x 250mm Chiralcel OD-H, 0.6 mL/min., 5% IPA in hexanes, 254 nm, major 8.80 min., minor 8.13 min., 86% ee



27

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.27-7.23 (m, 2H), 7.19-7.12 (m, 3H), 6.81-6.79 (m, 2H), 6.73-6.71 (m, 2H), 5.48-5.75 (m, 1H), 5.15-5.06 (m, 2H), 4.10-4.05 (m, 1H), 3.75 (s, 3H), 2.73 (s, 3H), 2.68-2.56 (m, 2H), 2.05-1.93 (m, 1H), 1.92-1.85 (m, 1H).
^{13}C NMR ($CDCl_3$, 100 MHz): δ = 152.1, 145.4, 142.2, 137.4, 128.7, 128.5, 126.0, 116.1, 116.0, 114.8, 61.4, 56.0, 33.8, 33.0, 32.5.

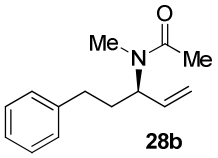
IR (film, cm^{-1}): ν = 3062, 3026, 2999, 2944, 2860, 2831, 2803, 1638, 1603, 1509, 1454, 1379, 1243, 1180, 1117, 1038, 921, 815.
HRMS (TOF ES+): calc. for $C_{19}H_{24}NO$ $(M+H)^+$: 282.1858; found: 282.1854.
[α]$^{20}_D$ +33.95:, c = 1, $CHCl_3$
HPLC: 2 mg/mL in 50/50 IPA/Hex, 2 μL injection, 4.6 x 250mm Chiralcel OD-H, 0.6 mL/min., 1% IPA in hexanes, 254 nm, major 12.69 min., minor 14.31 min., 84% ee



28

Secondary allylic amine **28** was prepared using a modified literature procedure.[1] A round bottom flask was charged with 387 mg (1.37 mmol) of **27** and 16 mL of acetonitrile. The flask was cooled to 0^{o}C and ammonium cerium (IV) nitrate (3 equiv., 2.26 g, 4.12 mmol) in 8 mL of distilled water was added slowly to the flask which immediately became a deep purple solution and returned to a yellow solution at the end of the addition. At 1 h, saturated aqueous sodium bicarbonate solution was added to attain a pH of 5-6, followed by addition of anhydrous sodium sulfite until a brown solution with insoluble light brown sludge was visible. The brown solution was collected and the brown solids were washed with ethyl acetate (4 x 25 mL). The combined organics were dried over sodium sulfate, filtered and concentrated. Purification by loading onto a 5 g Isco load cartridge and elution (5-20% MeOH/dichloromethane/1% TEA) onto a 24 g column yielded **28** as a light yellow oil (206 mg, 85%).

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.26-7.22 (m. 2H), 7.17-7.12 (m, 3H), 5.74-5.65 (m, 1H), 5.32 (dd, *J* = 10.2, 1.3 Hz, 1H), 5.24 (dd, *J* = 17.1, 0.72 Hz, 1H), 3.17-3.12 (m, 1H), 2.69-2.61 (m, 1H), 2.59-2.51 (m, 1H), 2.45 (s, 3H), 2.05-1.96 (m, 1H), 1.88-1.78 (m, 1H).
^{13}C NMR ($CDCl_3$, 100 MHz): δ = 141.3, 136.6, 128.7, 128.6, 126.2, 120.5, 63.5, 35.4, 32.8, 32.0.
IR (film, cm^{-1}): ν = 3316, 3062, 3026, 2935, 2852, 2789, 1945, 1865, 1804, 1742, 1639, 1603, 1495, 1475, 1453, 1414, 1314, 1136, 1114, 1030, 994, 917.
HRMS (TOF ES+): calc. for $C_{12}H_{18}N$ $(M+H)^+$: 176.1439; found: 176.1446.
[α]$^{20}_D$:, c = +3.32, MeOH

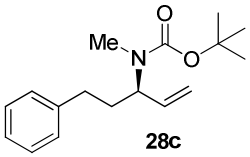


28b

A flask was charged with 57 mg (0.33 mmol) of **28** and 1.5 mL of anhydrous pyridine. Acetic anhydride (2 equiv., 0.061 mL, 0.65 mmol) and 4-dimethylaminopyridine (5 mol%, 2 mg, 0.016 mmol) was added to the flask. After stirring for 15 h, the reaction was diluted with saturated sodium bicarbonate and extracted with dichloromethane. The organics were washed with saturated aqueous sodium chloride, dried over magnesium sulfate and concentrated. The crude material was adsorbed onto an Isco 5g load cartridge and purified on a 24 g column (0-100% ethyl acetate/hexanes) yielding **28b** as a clear oil (67 mg, 95%).

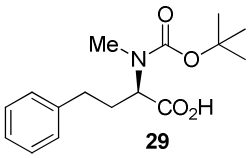
^{1}H NMR ($CDCl_3$, 400 MHz): 1:1 mixture of rotamers δ = 7.29-7.23 (m, 2H), 7.20-7.13 (m, 3H), 5.76-5.68 (m, 1H), 5.30-5.23 (m, 0.5H), 5.19-5.05 (m, 2H), 4.15-4.08 (m, 0.5H), 2.78 (s, 1.5H), 2.73 (s, 1.5H), 2.65-2.50 (m, 2H), 2.07 (s, 1.5H), 2.03-1.94 (m, 1H), 1.89 (s, 1.5H), 1.89-1.80 (m, 1H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 171.3, 171.1, 141.9, 140.7, 136.7, 136.1, 128.8, 128.5, 128.5, 128.4, 126.5, 126.1, 116.8, 116.5, 58.7, 54.2, 33.3, 32.8, 32.4, 32.3, 30.4, 27.3, 22.4, 21.6.
IR (film, cm^{-1}): ν = 3084, 3062, 3026, 2978, 2941, 2862, 1951, 1874, 1739, 1636, 1495, 1454, 1428, 1398, 1360, 1327, 1252, 1125, 1076, 1006, 924.
HRMS (TOF ES+): calc. for $C_{14}H_{20}NO$ $(M+H)^+$: 218.1545; found: 218.1553.
$[\alpha]^{20}_D$:, c = +16.60, $CHCl_3$



28c

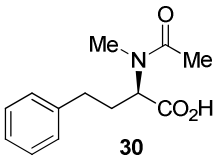
A flask was charged with 172 mg (0.98 mmol) of **28**, 2.5 mL of THF and 2.5 mL of distilled water. Potassium carbonate (2 equiv., 271 mg, 1.96 mmol) was added to the flask followed by 236 mg (1.1 equiv., 1.08 mmol) of di-*tert*-butyl dicarbonate. After stirring for 15 h, the reaction was diluted with saturated sodium bicarbonate and extracted with dichloromethane. The organic layers were washed with brine, dried over sodium sulfate and concentrated. The crude material was adsorbed onto an Isco 5g load cartridge and purified on a 12 g column (0-50% ethyl acetate/hexanes) yielding **28c** as a clear oil (232 mg, 86%).
^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.28-7.24 (m, 2H), 7.18-7.15 (m, 3H), 5.79-5.71 (m, 1H), 5.14-5.06 (m, 2H), 2.69 (bs, 3H), 2.57 (bs, 1H), 1.88-1.82 (m, 2H), 1.44 (bs, 9H).
^{13}C NMR ($CDCl_3$, 100 MHz): δ = 156.3, 137.3, 128.6, 126.1, 116.2, 85.4, 79.7, 33.2, 32.7, 28.7, 27.6.
IR (film, cm^{-1}): ν =3085, 3026, 3004, 2976, 2931, 2865, 1810, 1758, 1687, 1584, 1496, 1478, 1454, 1389, 1365, 1328, 1255, 1166, 1134, 1072, 976, 921, 875.
HRMS (TOF ES+): calc. for $C_{17}H_{25}NO_2Na$ $(M+Na)^+$: 298.1783; found: 298.1779.
$[\alpha]^{20}_D$:, c = +11.77, MeOH



29

29 was prepared following a literature procedure.[2] A flask was charged with 50 mg (0.18 mmol) of **28c**, 0.6 mL of carbon tetrachloride, 0.6 mL of acetonitrile and 0.8 mL of distilled water. The biphasic mixture was stirred vigorously and 155 mg (4 equiv., 0.73 mmol) of sodium periodate was added and allowed to dissolve. $RuCl_3$ hydrate (1.5mg, 4 mol%, 7μmol) was added and stirring was continued for 15 h. The reaction was diluted with distilled water and extracted with dichloromethane. The organics were dried over sodium sulfate, filtered and concentrated yielding **29** as brown oil (49 mg, 92%).

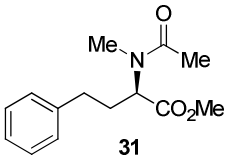
^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1:1 mixture of rotamers 9.57 (s, 0.65H), 7.27-7.24 (m, 2H), 7.18-7.16 (m, 3H), 4.38-4.31 (m, 0.5H), 3.92-3.87 (m, 0.5H), 2.90 (s, 1.5H), 2.81 (s, 1.5H), 2.68-2.64 (m, 2H), 2.36-2.20 (m, 1H), 2.00-1.86 (m, 1H), 1.51-1.40 (m, 9H).
^{13}C NMR ($CDCl_3$, 100 MHz): δ = 200.3, 200.0, 141.1, 128.5, 126.4, 66.2, 65.2, 53.6, 32.7, 32.4, 32.2, 31.3, 30.8, 28.9, 28.6, 28.5, 28.1, 8.6.
IR (film, cm^{-1}): ν = 3596-2716 br, 3085, 3061, 2975, 2929, 2868, 2716, 1948, 1736, 1688, 1603, 1495, 1479, 1454, 1391, 1366, 1325, 1252, 1153, 1085, 1030, 983, 866.
HRMS (TOF ES-): calc. for $C_{16}H_{22}NO_4$ $(M-H)^-$: 292.1549; found: 292.1553.
$[\alpha]^{20}_D$: +9.79, c = 1 MeOH



30

30 was prepared following a literature procedure.[2] A flask was charged with 32 mg (0.15 mmol) of **30b**, 0.5 mL of carbon tetrachloride, 0.5 mL of acetonitrile and 0.7 mL of distilled water. The biphasic mixture was stirred vigorously and 126 mg (4 equiv., 0.59 mmol) of sodium periodate was added and allowed to dissolve. $RuCl_3$ hydrate (1.2mg, 4 mol%, 6 μmol) was added and stirring was continued for 1 hour. The reaction was diluted with distilled water and extracted with dichloromethane. The organics were dried over sodium sulfate, filtered and concentrated yielding **30** as brown oil (34 mg, 98%).

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1:1 mixture of rotamers δ = 9.45 (s, 0.5H), 7.30-7.25 (m, 2H), 7.21-7.14 (m, 3H), 5.15-5.11 (m, 0.5H), 4.67-4.63 (m, 0.5H), 2.88 (s, 3H), 2.74-2.61 (m, 1H), 2.59-2.51 (m, 1H), 2.38-2.30 (m, 1H), 2.13 (s, 1.5H), 2.10 (s, 1.5H), 2.04-1.90 (m, 1H).
^{13}C NMR ($CDCl_3$, 100 MHz): δ = 174.4, 172.8, 172.4, 140.9, 140.8, 140.0, 129.0, 128.9, 128.8, 128.6, 128.5, 126.7, 126.5, 126.3, 64.8, 59.5, 56.8, 34.5, 33.0, 32.8, 32.6, 32.0, 31.6, 30.4, 30.2, 28.9, 27.7, 22.0, 21.7, 21.5.
δ = **IR (film, cm^{-1}):** ν = 3677-2259 br, 3084, 3060, 3027, 3001, 2930, 2861, 1728, 1644, 1601, 1495, 1454, 1404, 1322, 1241, 1212, 1173, 1127, 1086, 1029, 1018, 912.
HRMS (TOF ES-): calc. for $C_{13}H_{16}NO_3$ $(M-H)^-$: 234.1130; found: 234.1131.
$[\alpha]^{20}_D$: +8.14, c = 1 MeOH



31

Compound **31** was prepared following a modified literature procedure.[3] A round bottom flask was charged with 40 mg (0.18 mmol) of **28b**, 1.5 mL of dichloromethane, and 0.37 mL of 2.5 M methanolic NaOH (5 equiv., 0.92 mmol). The flask was cooled to -78°C and subjected to ozonolysis for 30 min. The crude reaction was adsorbed onto a 5g Isco load cartridge followed by elution onto a 12g silica column (0-100% EA/Hexanes) resulting in 31 mg (68%) of **33** as a clear oil.

^{1}H NMR ($CDCl_3$, 400 MHz): 3:1 mixture of rotamers δ = 7.30-7.15 (m, 5H), 5.26-5.22 (m, 0.75H), 4.22-4.19 (m, 0.25H), 3.71 (s, 0.75H), 3.67 (s, 2.25H), 2.87 (s, 2.25H), 2.84 (s, 0.75H), 2.66-2.56 (m, 1H), 2.55-2.51 (m, 1H), 2.33-2.26 (m, 1H), 2.10 (s, 2.25H), 2.01-1.97 (m, 1H), 1.84 (s, 0.75H).
^{13}C NMR ($CDCl_3$, 100 MHz): δ = 172.0, 171.9, 171.7, 171.4, 141.0, 139.9, 128.9, 128.6, 128.5, 126.8, 126.3, 59.3, 56.0, 52.7, 52.4, 32.8, 32.5, 31.8, 30.4, 28.6, 22.1, 21.6.
IR (film, cm^{-1}): ν = 3027, 2952, 2932, 1737, 1650, 1495, 1454, 1434, 1399, 1364, 1327, 1247, 1211, 1169, 1126, 1089, 1013, 912.
HRMS (TOF ES+): calc. for $C_{14}H_{19}NO_3$ $(M+Na)^+$: 272.1263; found: 272.1261.
$[\alpha]^{20}_D$:, c = +11.19, MeOH

HPLC: 2.5 mg/mL in 50/50 IPA/Hex, 2 μL injection, 4.6 x 150mm Chiralcel OJ-3, 0.3 mL/min., 8% IPA in hexanes, 210 nm, minor rotamer: major 20.17 min., minor 21.21 min., 83% ee, major rotamer: major 43.69 min., minor 45.07 min., 84% ee

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(3) Trost, B. M.; Bunt, R. C.; Lemoine, R. C.; Calkins, T. L. *J. Am. Chem. Soc.* **2000**, *122*, 5968.
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