

Rhodium-Catalyzed Regioselective Amination of Secondary Allylic Trichloroacetimidates with Unactivated Aromatic Anilines

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Table of Contents

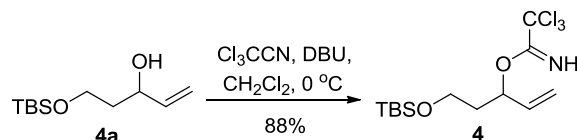
Methods and Reagents	Page S-1
General Procedures	Page S-2, S-4, S-14
Analytical Data of All Compounds	Page S-2 – S-20

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 °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 achieved using UV light, potassium permanganate, or ceric ammonium molybdate. Monitoring by GC was performed using an HP-1 (30m x 0.320mm) column and temperature gradient of 100- 250°C over 10 minutes. Flash chromatography was performed on glass flash chromatography columns or a Teledyne Isco CombiFlash Rf system utilizing normal phase pre-column cartridges and gold high performance columns. Dry tetrahydrofuran was obtained from a SG Waters solvent system utilizing activated alumina columns under an argon pressure. The rhodium catalysts were handled and transferred to Schlenk flasks within a glove box under a nitrogen atmosphere. Enantiomeric excess was measured by chiral HPLC using Diacel Chiralcel OD-H (0.46cm x 25 cm) column. All commercially available phosphites were distilled prior to use. All other chemicals were obtained from commercial vendors and used without further purification.

Instrumentation. All proton (^1H) nuclear magnetic resonance spectra were recorded on 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 ^1H in the NMR solvent (CDCl_3 : δ 7.24 ppm, δ 77.23 ppm; C_6D_6 : δ 7.16 ppm, δ 128.39 ppm). 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 mode was performed to confirm the identity of the compounds.

General Procedure for the Preparation of Branched Allylic Trichloroacetimidates 4- 12



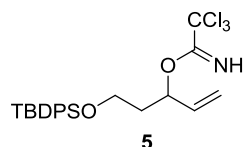
A 100 mL oven-dried Schlenk flask was charged with **4a** (1.94 g, 8.96 mmol, 1 equiv) and dry dichloromethane (50 mL). Trichloroacetonitrile (2.70 mL, 26.9 mmol, 3 equiv) was added. The resulting solution was cooled to 0°C, and DBU was added (0.33 mL, 2.24 mmol, 0.25 equiv). The reaction mixture was allowed to warm to room temperature and stir overnight. The mixture was concentrated *in vacuo*, and the resulting residue was purified by silica gel flash chromatography (30/1 hexane/ethyl acetate + 1% triethylamine) to provide **4** (2.84 g, 88%) as a clear oil.

¹H NMR (CDCl₃, 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), 2.03-1.87 (m, 2H), 0.86 (s, 9H), 0.03 (s, 6H).

¹³C NMR (CDCl₃, 100 MHz): δ = 161.9, 135.8, 116.7, 76.5, 59.1, 37.7, 26.1, 18.5, -5.2.

IR (film, cm⁻¹): ν = 3349, 2955, 2929, 2857, 1664, 1471, 1286, 1255, 1100, 980, 832, 795, 776, 647.

HRMS (TOF ESI+): calc. for $\text{C}_{13}\text{H}_{24}\text{Cl}_3\text{NO}_2\text{SiNa (M+Na)}^+$: 382.0543; found: 382.0542.

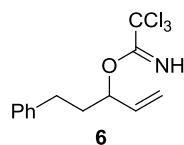


¹H NMR (CDCl₃, 400 MHz): δ = 8.30 (s, NH), 7.65-7.62 (m, 4H), 7.42-7.32 (m, 6H), 5.92-5.84 (m, 1H), 5.66-5.61 (m, 1H), 5.34 (dt, *J* = 17.3, 1.3 Hz, 1H), 5.19 (dt, *J* = 10.6, 1.2 Hz, 1H), 3.83-3.72 (m, 2H), 2.07-1.93 (m, 2H), 1.02 (s, 9H).

¹³C NMR (CDCl₃, 100 MHz): δ = 161.9, 135.8, 135.7, 133.9, 133.8, 129.8, 127.8, 116.7, 76.5, 59.9, 37.5, 27.0, 19.4.

IR (film, cm⁻¹): ν = 3344, 3071, 2958, 2930, 2857, 1663, 1472, 1427, 1298, 1286, 1111, 1091, 979, 823, 795, 737, 702, 647.

HRMS (TOF ESI+): calc. for $C_{23}H_{28}Cl_3NO_2SiNa$ ($M+Na$)⁺: 506.0853; found: 506.0859.

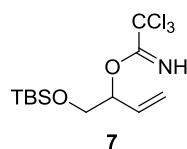


¹H NMR (CDCl₃, 400 MHz): δ = 8.30 (s, NH), 7.29-7.25 (m, 2H), 7.20-7.16 (m, 3H), 5.92-5.84 (m, 1H), 5.40-5.35 (m, 1H), 5.37 (dt, *J* = 17.3, 1.3 Hz, 1H), 5.23 (dt, *J* = 10.6, 1.2 Hz, 1H), 2.82-2.67 (m, 2H), 2.17-1.97 (m, 2H).

¹³C NMR (CDCl₃, 100 MHz): δ = 162.0, 141.5, 135.6, 128.7, 128.6, 126.2, 117.2, 78.8, 36.2, 31.5.

IR (film, cm⁻¹): ν = 3343, 3085, 3026, 2928, 2861, 1661, 1496, 1455, 1285, 1074, 974, 928, 884, 824, 793, 748, 697.

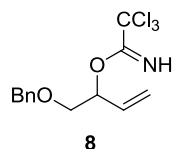
HRMS (TOF ESI+): calc. for $\text{C}_{13}\text{H}_{14}\text{Cl}_3\text{NONa}$ ($\text{M}+\text{Na}$)⁺: 306.0219; found: 306.0225.



¹H NMR (CDCl₃, 400 MHz): δ = 8.31 (s, NH), 5.93-5.84 (m, 1H), 5.43-5.40 (m, 1H), 5.41 (dt, J = 17.4, 1.3 Hz, 1H), 5.26 (dt, J = 10.7, 1.2 Hz, 1H), 3.83-3.74 (m, 2H), 0.86 (s, 9H), 0.05 (s, 3H), 0.04 (s, 3H).

¹³C NMR (CDCl₃, 100 MHz): δ = 162.2, 133.0, 118.1, 80.0, 64.6, 26.0, 18.5, -5.1, -5.2.

IR (film, cm⁻¹): ν = 3349, 2954, 2929, 2858, 1664, 1471, 1462, 1287, 1255, 1130, 1078, 993, 933, 835, 795, 777.

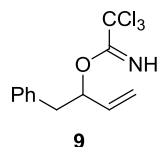


¹H NMR (CDCl₃, 400 MHz): δ = 8.35 (s, NH), 7.34-7.30 (m, 4H), 7.30-7.25 (m, 1H), 5.95-5.85 (m, 1H), 5.66-5.58 (m, 1H), 5.44 (dt, J = 17.3, 1.3 Hz, 1H), 5.28 (dt, J = 10.7, 1.2 Hz, 1H), 4.60 (s, 2H), 3.72-3.69 (m, 2H).

¹³C NMR (CDCl₃, 100 MHz): δ = 162.1, 138.2, 132.7, 128.6, 127.9, 127.8, 118.3, 78.3, 73.5, 71.3.

IR (film, cm⁻¹): ν = 3342, 3088, 3064, 3030, 2897, 2861, 1664, 1496, 1454, 1362, 1286, 1205, 1075, 987, 930, 873, 793, 735, 697.

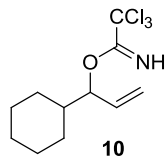
HRMS (TOF ESI⁺): calc. for C₁₂H₂₂Cl₃NO₂SiNa (M+Na)⁺: 343.9988; found: 343.9984



¹H NMR (CDCl₃, 400 MHz): δ = 8.26 (s, NH), 7.30-7.25 (m, 4H), 7.22-7.18 (m, 1H), 5.91-5.83 (m, 1H), 5.60-5.55 (m, 1H), 5.32 (dt, J = 17.2, 1.3 Hz, 1H), 5.20 (dt, J = 10.6, 1.2 Hz, 1H), 3.11 (dd, J = 13.9, 7.4 Hz, 1H), 2.99 (dd, 13.9, 5.8 Hz, 1H).

¹³C NMR (CDCl₃, 100 MHz): δ = 161.9, 136.9, 135.1, 129.9, 128.4, 126.8, 117.3, 80.0, 40.8.

IR (film, cm⁻¹): ν = 3342, 3087, 3064, 3029, 2948, 2925, 1661, 1496, 1455, 1343, 1301, 1285, 1073, 984, 930, 859, 837, 793, 751, 698.

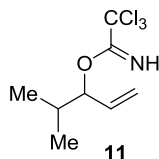


¹H NMR (CDCl₃, 400 MHz): δ = 8.21 (s, NH), 5.84-5.75 (m, 1H), 5.30 (dt, J = 17.3, 1.2 Hz, 1H), 5.22 (dt, J = 10.6, 1.2 Hz, 1H), 5.15 (t, J = 6.3 Hz, 1H), 1.88-1.62 (m, 6H), 1.27-1.02 (m, 5H).

¹³C NMR (CDCl₃, 100 MHz): δ = 162.2, 134.4, 117.7, 92.2, 83.7, 42.0, 28.8, 28.3, 26.6, 26.2, 26.1.

IR (film, cm⁻¹): ν = 3346, 2926, 2853, 1661, 1450, 1340, 1302, 1286, 1073, 980, 930, 933, 889, 824, 792.

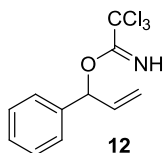
HRMS (TOF ESI+): calc. for C₁₁H₁₇Cl₃NO (M+H)⁺: 284.0376; found 284.0383



¹H NMR (CDCl₃, 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), 2.07-1.95 (m, 1H), 0.99 (d, J = 7.0 Hz, 3H), 0.97 (d, J = 7.0 Hz, 3H).

¹³C NMR (CDCl₃, 100 MHz): δ = 162.3, 134.1, 117.8, 84.2, 32.3, 18.4, 17.9.

IR (film, cm⁻¹): ν = 3347, 2965, 2934, 2876, 1662, 1469, 1303, 1287, 1076, 984, 926, 826, 794.



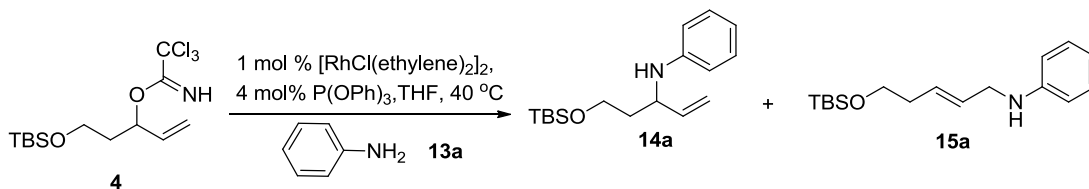
¹H NMR (CDCl₃, 400 MHz): δ = 8.36 (s, NH), 7.43-7.28 (m, 5H), 6.35 (d, J = 5.7 Hz, 1H), 6.10-6.02 (m, 1H), 5.40 (dt, J = 15.8, 1.4 Hz, 1H), 5.28 (dt, J = 10.5, 1.3 Hz, 1H).

¹³C NMR (CDCl₃, 100 MHz): δ = 161.4, 138.6, 135.9, 128.7, 128.4, 127.0, 117.3, 91.7, 80.7.

IR (film, cm⁻¹): ν = 3346, 2926, 2853, 1661, 1450, 1340, 1302, 1286, 1073, 980, 930, 933, 889, 824, 792.

HRMS (TOF ESI+): calc. for C₁₁H₁₁Cl₃NO (M+H)⁺: 277.9925; found: 277.9906

General Procedure for Amination of Secondary Allylic Trichloroacetimidates with 1 mol% [RhCl(ethylene)₂]₂:



A 10 mL Schlenk flask was charged with [RhCl(ethylene)₂]₂ (0.54 mg, 1.4 μ mol, 1 mol%) in a glove box. The flask was sealed and removed from the glove box, and THF (0.35 mL) was added to the Schlenk under argon followed by triphenylphosphite (1.5 μ L, 5.5 μ mol, 4 mol%). The rhodium-phosphite complex solution was allowed to stir at 25 °C for 15 min. A separate 10 mL Schlenk flask was charged with **4** (50 mg, 0.14 mmol, 1 equiv), THF (0.35 mL) and aniline **13a** (38 μ L, 0.42 mmol, 3 equiv). The rhodium catalyst solution was then added to the flask containing the **4** and **13a** solution. The reaction mixture was stirred at 40 °C under argon. Reaction progress was monitored by GC. After 30 min, the crude reaction was concentrated *in vacuo*, loaded in dichloromethane onto an ISCO load cartridge, and dried under

vacuum. Elution onto an ISCO 12g silica column (0 $\rightarrow$ 2.5% ethyl acetate/hexane) provided **14a** and **15a** (40 mg, 96%, **14a/15a** >99:1) as pale yellow oil.

Compound 14a:

^1H NMR (CDCl₃, 400 MHz): δ = 7.13 (dd, J = 7.3, 2.0 Hz, 1H), 7.11 (dd, J = 7.3, 1.9 Hz, 1H), 6.63 (t, J = 7.3 Hz, 1H), 6.58 (d, J = 1.0 Hz, 1H), 6.56 (d, J = 0.96 Hz, 1H), 5.80-5.72 (m, 1H), 5.21 (dt, J = 17.2, 1.4 Hz, 1H), 5.12 (dt, J = 10.3, 1.4 Hz, 1H), 4.34 (s, NH), 4.03-3.99 (m, 1H), 3.82-3.77 (m, 1H), 3.74-3.68 (m, 1H), 1.88-1.73 (m, 2H), 0.90 (s, 9H), -0.04 (s, 6H).

^{13}C NMR (CDCl₃, 100 MHz): δ = 148.0, 139.7, 129.2, 117.0, 115.5, 113.4, 60.6, 54.3, 38.0, 26.1, 18.4, -5.2.

IR (film, cm⁻¹): ν = 3340, 3085, 3061, 3024, 2941, 2860, 2812, 1663, 1597, 1503, 1453, 1378, 1348, 1306, 1211, 1193, 1076, 1031, 990, 922, 796, 746, 692.

HRMS (ESI): calc. for C₁₇H₃₀NOSi (M+H): 292.2103; found: 292.2097

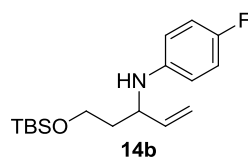
Compound 15a:

^1H NMR (CDCl₃, 400 MHz): δ = 7.18 (dd, J = 7.4, 2.1 Hz, 1H), 7.15 (dd, J = 7.3, 2.0 Hz, 1H), 6.69 (t, J = 7.3 Hz, 1H), 6.61 (d, J = 1.1 Hz, 1H), 6.59 (d, J = 0.96 Hz, 1H), 5.67-5.54 (m, 2H), 3.75 (d, J = 5.8 Hz, 2H), 3.65 (t, J = 6.6 Hz, 2H), 2.34 (q, J = 6.6 Hz, 2H), 0.89 (s, 9H), -0.05 (s, 6H).

^{13}C NMR (CDCl₃, 100 MHz): δ = 148.4, 129.6, 129.4, 128.8, 117.7, 113.2, 62.8, 41.4, 31.5, 26.2, 18.6, -5.0.

IR (film, cm⁻¹): ν = 3401, 3052, 3020, 2954, 2928, 2885, 2856, 1727, 1604, 1505, 1314, 1255, 1096, 929, 836, 777, 748, 691.

HRMS (ESI): calc. for C₁₇H₃₀NOSi (M+H): 292.2103; found: 292.2097

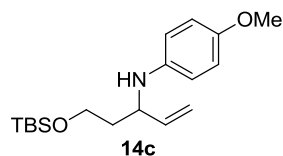


^1H NMR (CDCl₃, 400 MHz): δ = 6.82 (t, J = 8.8 Hz, 2H), 6.49 (dd, J = 9.0, 4.5 Hz, 2H), 5.77-5.69 (m, 1H), 5.21 (dt, J = 17.2 Hz, 1.4 Hz, 1H), 5.12 (dt, J = 10.3 Hz, 1.3 Hz, 1H), 4.25 (s, NH), 3.95-3.91 (m, 1H), 3.82-3.77 (m, 1H), 3.74-3.68 (m, 1H), 1.87-1.72 (m, 2H), 0.90 (s, 9H), 0.04 (s, 6H).

^{13}C NMR (CDCl₃, 100 MHz): δ = 156.8, 144.2, 139.7, 115.7, 115.5, 114.2, 60.6, 55.1, 38.0, 26.1, 18.4, -5.2.

IR (film, cm⁻¹): ν = 3405, 2953, 2929, 2857, 1509, 1471, 1255, 1220, 1096, 918, 835, 816, 775.

HRMS (ESI): calc. for C₁₇H₂₉NOSiF (M+H): 310.2002; found: 310.2000.

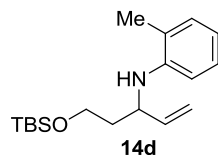


^1H NMR (CDCl₃, 400 MHz): δ = 6.73 (d, J = 9.0 Hz, 2H), 6.54 (d, J = 8.9 Hz, 2H), 5.78-5.70 (m, 1H), 5.20 (dt, J = 17.2 Hz, 1.4 Hz, 1H), 5.10 (dt, J = 10.3 Hz, 1.2 Hz, 1H), 4.01 (s, NH), 3.94-3.89 (m, 1H), 3.81-3.76 (m, 1H), 3.73-3.68 (m, 1H), 3.71 (s, 3H), 1.85-1.72 (m, 2H), 0.89 (s, 9H), 0.04 (s, 6H).

^{13}C NMR (CDCl_3 , 100 MHz): δ = 151.9, 142.2, 140.3, 115.3, 114.9, 114.7, 60.6, 56.0, 55.2, 38.2, 26.1, 18.4, -5.2.

IR (film, cm^{-1}): ν = 3397, 2952, 2929, 2856, 1510, 1470, 1236, 1094, 1041, 916, 835, 816, 775.

HRMS (ESI): calc. for $\text{C}_{18}\text{H}_{32}\text{NO}_2\text{Si}$ ($\text{M}+\text{H}$): 322.2202; found: 322.2198.

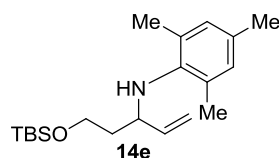


^1H NMR (CDCl_3 , 400 MHz): δ = 7.07-7.00 (m, 2H), 6.61-6.57 (m, 2H), 5.81-5.73 (m, 1H), 5.20 (dt, J = 17.2 Hz, 1.2 Hz, 1H), 5.11 (dt, J = 10.2 Hz, 1.1 Hz, 1H), 4.07-4.05 (m, 1H), 4.00 (s, NH), 3.83-3.79 (m, 1H), 3.76-3.70 (m, 1H), 2.13 (s, 3H), 1.90-1.80 (m, 2H), 0.88 (s, 9H), 0.03 (s, 6H).

^{13}C NMR (CDCl_3 , 100 MHz): δ = 147.9, 139.7, 129.2, 117.0, 115.4, 113.3, 60.5, 54.3, 38.0, 26.1, 18.4, -5.2.

IR (film, cm^{-1}): ν = 3423, 2953, 2928, 2856, 1606, 1587, 1512, 1471, 1449, 1315, 1255, 991, 916, 834, 776, 744.

HRMS (ESI): calc. for $\text{C}_{18}\text{H}_{32}\text{NOSi}$ ($\text{M}+\text{H}$): 306.2253; found: 306.2249.

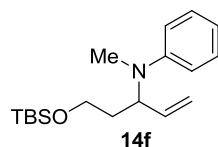


^1H NMR (CDCl_3 , 400 MHz): δ = 6.76 (s, 2H), 5.70-5.61 (m, 1H), 4.95-4.94 (m, 1H), 4.92-4.90 (m, 1H), 3.79-3.64 (m, 3H), 2.97 (s, NH), 2.19 (s, 6H), 2.18 (s, 3H), 1.90-1.82 (m, 1H), 1.75-1.67 (m, 1H), 0.87 (s, 9H), 0.01 (s, 6H).

^{13}C NMR (CDCl_3 , 100 MHz): δ = 142.4, 140.5, 130.8, 129.5, 115.4, 60.1, 57.5, 39.2, 26.2, 20.8, 19.2, 18.4, -5.2.

IR (film, cm^{-1}): ν = 3386, 3077, 2952, 2928, 2897, 2856, 1482, 1472, 1253, 1231, 1095, 989, 916, 835, 774.

HRMS (ESI): calc. for $\text{C}_{20}\text{H}_{36}\text{NOSi}$ ($\text{M}+\text{H}$): 334.2566; found: 334.2562.

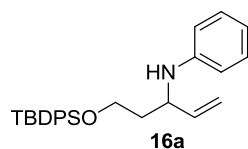


^1H NMR (CDCl_3 , 400 MHz): δ = 7.20-7.14 (m, 2H), 6.81-6.79 (m, 2H), 6.66 (tt, J = 7.2, 1.0 Hz, 1H), 5.86-5.77 (m, 1H), 5.14-5.07 (m, 2H), 4.56-4.51 (m, 1H), 3.64-3.56 (m, 2H), 2.72 (s, 3H), 1.94-1.79 (m, 2H), 0.86 (s, 9H), 0.02 (s, 6H).

^{13}C NMR (CDCl_3 , 100 MHz): δ = 150.8, 137.5, 129.2, 116.6, 115.8, 113.4, 60.1, 56.6, 34.7, 31.8, 26.1, 18.4, -5.2.

IR (film, cm^{-1}): ν = 2953, 2928, 2884, 2857, 1598, 1504, 1471, 1253, 1095, 990, 835, 775, 747.

HRMS (ESI): calc. for $\text{C}_{18}\text{H}_{32}\text{NOSi}$ ($\text{M}+\text{H}$): 306.2253; found: 306.2250.

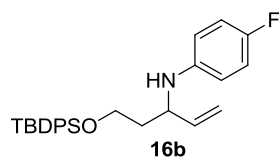


¹H NMR (CDCl₃, 400 MHz): δ = 7.67-7.62 (m, 4H), 7.41-7.29 (m, 6H), 7.13 (dd, J = 8.5, 7.3 Hz, 2H), 6.65 (tt, J = 7.3, 1.0 Hz, 1H), 6.58 (dd, J = 8.6, 1.0 Hz, 2H), 5.79-5.71 (m, 1H), 5.22 (dt, J = 17.1, 1.4 Hz, 1H), 5.11 (dt, J = 10.3, 1.3 Hz, 1H), 4.21 (s, NH), 4.15-4.07 (m, 1H), 3.87-3.81 (m, 1H), 3.76-3.71 (m, 1H), 1.90-1.87 (m, 1H), 1.86-1.79 (m, 1H), 1.06 (s, 9H).

¹³C NMR (CDCl₃, 100 MHz): δ = 147.9, 139.8, 135.8, 133.6, 129.8, 129.2, 127.9, 117.1, 115.3, 113.4, 61.4, 53.9, 38.1, 27.1, 19.3.

IR (film, cm⁻¹): ν = 3409, 2952, 2930, 2857, 1601, 1505, 1427, 1316, 1105, 1092, 822, 743, 700.

HRMS (ESI): calc. for C₂₇H₃₄NOSi (M+H): 416.2410; found: 416.2404.

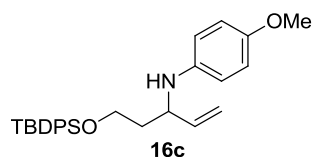


¹H NMR (CDCl₃, 400 MHz): δ = 7.66-7.61 (m, 4H), 7.43-7.29 (m, 6H), 6.83 (t, J = 8.8 Hz, 2H), 6.49 (dd, J = 9.0, 4.4 Hz, 2H), 5.77-5.68 (m, 1H), 5.20 (dt, J = 17.2, 1.4 Hz, 1H), 5.11 (dt, J = 10.3, 1.3 Hz, 1H), 4.11 (s, NH), 4.04-4.02 (m, 1H), 3.87-3.81 (m, 1H), 3.76-3.71 (m, 1H), 1.88-1.85 (m, 1H), 1.82-1.78 (m, 1H), 1.05 (s, 9H).

¹³C NMR (CDCl₃, 100 MHz): δ = 144.1, 139.7, 135.7, 133.6, 133.5, 129.8, 127.9, 115.7, 115.5, 114.2, 61.3, 54.6, 38.1, 27.1, 19.3.

IR (film, cm⁻¹): ν = 3409, 2930, 2889, 2857, 1509, 1427, 1220, 818, 775, 736, 700, 688.

HRMS (ESI): calc. for C₂₇H₃₃NOFSi (M+H): 434.2315; found: 434.2317.

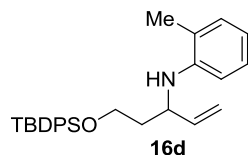


¹H NMR (CDCl₃, 400 MHz): δ = 7.66-7.61 (m, 4H), 7.43-7.29 (m, 6H), 6.73 (d, J = 9.0 Hz, 2H), 6.53 (d, J = 9.0 Hz, 2H), 5.77-5.69 (m, 1H), 5.20 (dt, J = 17.2, 1.3 Hz, 1H), 5.09 (dt, J = 10.3, 1.1 Hz, 1H), 4.04-4.00 (m, 1H), 3.91 (s, NH), 3.86-3.80 (m, 1H), 3.76-3.71 (m, 1H), 3.72 (s, 3H), 1.85-1.79 (m, 2H), 1.05 (s, 9H).

¹³C NMR (CDCl₃, 100 MHz): δ = 151.9, 142.1, 140.2, 135.7, 133.7, 133.5, 129.8, 127.8, 115.4, 115.0, 114.8, 61.5, 55.9, 54.7, 38.2, 26.9, 19.4.

IR (film, cm⁻¹): ν = 3399, 2930, 2896, 2857, 1509, 1471, 1463, 1427, 1236, 1108, 1040, 819, 737, 701, 688.

HRMS (ESI): calc. for C₂₈H₃₆NO₂Si (M+H): 446.2511; found: 446.2515.

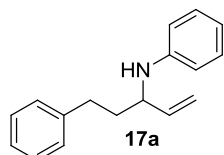


¹H NMR (CDCl₃, 400 MHz): δ = 7.67-7.62 (m, 4H), 7.45-7.29 (m, 6H), 7.15-7.0 (m, 2H), 6.70-6.60 (m, 2H), 5.84-5.75 (m, 1H), 5.22 (dt, *J* = 17.2, 1.4 Hz, 1H), 5.12 (dt, *J* = 10.3, 1.3 Hz, 1H), 4.25-4.21 (m, 1H), 3.89-3.85 (m, 1H), 3.83-3.76 (m, 1H), 3.6 (s, NH), 2.08 (s, 3H), 1.95-1.86 (m, 2H), 1.07 (s, 9H).

¹³C NMR (CDCl₃, 100 MHz): δ = 145.6, 140.0, 135.7, 133.9, 133.7, 130.2, 129.8, 127.8, 127.1, 121.9, 116.8, 115.2, 111.0, 61.0, 52.9, 38.7, 27.1, 19.4, 17.8.

IR (film, cm⁻¹): ν = 3427, 2956, 2930, 2892, 2856, 1605, 1587, 1510, 1427, 1105, 821, 739, 700, 687.

HRMS (ESI): calc. for C₂₈H₃₆NOSi (M+H): 430.2566; found: 430.2565.

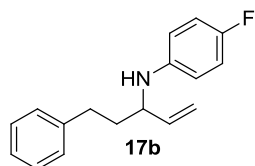


¹H NMR (CDCl₃, 400 MHz): δ = 7.29-7.25 (m, 2H), 7.20-7.10 (m, 5H), 6.66 (t, *J* = 7.2 Hz, 1H), 6.55 (dd, *J* = 8.6, 1.0 Hz, 2H), 5.80-5.72 (m, 1H), 5.21 (dt, *J* = 17.2, 1.3 Hz, 1H), 5.14 (dt, *J* = 10.3, 1.2 Hz, 1H), 3.83 (bs, 1H), 3.61 (s, NH), 2.74 (t, *J* = 7.6 Hz, 2H), 1.93-1.87 (m, 2H).

¹³C NMR (CDCl₃, 100 MHz): δ = 147.7, 141.8, 139.8, 129.3, 128.7, 128.6, 126.1, 117.4, 115.6, 113.5, 55.5, 37.4, 32.3.

IR (film, cm⁻¹): ν = 3403, 3083, 3052, 3024, 2977, 2921, 2856, 1599, 1503, 1454, 1428, 1315, 1254, 992, 918, 746, 691.

HRMS (ESI): calc. for C₁₇H₂₀NO (M+H): 238.1596; found: 238.1599.

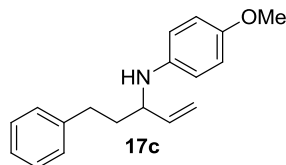


¹H NMR (CDCl₃, 400 MHz): δ = 7.29-7.24 (m, 2H), 7.20-7.15 (m, 3H), 6.83 (t, *J* = 8.8 Hz, 2H), 6.45 (dd, *J* = 9.0, 4.4 Hz, 2H), 5.76-5.68 (m, 1H), 5.18 (dt, *J* = 17.2, 1.3 Hz, 1H), 5.14 (dt, *J* = 10.3, 1.2 Hz, 1H), 3.74 (q, *J* = 6.1 Hz, 1H), 3.49 (s, NH), 2.73 (t, *J* = 6.9 Hz, 2H), 1.91-1.85 (m, 2H).

¹³C NMR (CDCl₃, 100 MHz): δ = 141.7, 139.8, 128.6, 126.2, 115.9, 115.5, 114.4, 103.7, 56.1, 37.4, 32.5.

IR (film, cm⁻¹): ν = 3412, 3083, 3061, 3026, 3003, 2977, 2922, 2857, 1507, 1454, 1313, 1218, 992, 920, 817, 778, 749, 699.

HRMS (ESI): calc. for C₁₇H₁₉NF (M+H): 256.1502; found: 256. 500.

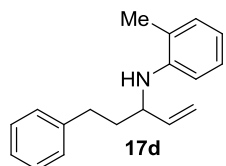


¹H NMR (CDCl₃, 400 MHz): δ = 7.29-7.25 (m, 2H), 7.20-7.16 (m, 3H), 6.73 (d, J = 8.8 Hz, 2H), 6.51 (d, J = 8.8 Hz, 2H), 5.78-5.69 (m, 1H), 5.20 (d, J = 17.2 Hz, 1H), 5.13 (d, J = 10.3 Hz, 1H), 3.75 (q, J = 6.7 Hz, 1H), 3.73 (s, 3H), 3.36 (s, NH), 2.73 (t, J = 7.7 Hz, 2H), 1.91-1.85 (m, 2H).

¹³C NMR (CDCl₃, 100 MHz): δ = 152.1, 141.9, 141.7, 140.2, 128.7, 128.6, 126.1, 115.7, 115.0, 114.9, 56.4, 55.9, 37.5, 32.3.

IR (film, cm⁻¹): ν = 3395, 3081, 3061, 3025, 2998, 2932, 2856, 2830, 1602, 1508, 1463, 1453, 1441, 1231, 1178, 1036, 992, 817, 816, 747, 699.

HRMS (ESI): calc. for C₁₈H₂₂NO (M+H): 268.1701; found: 268.1694.

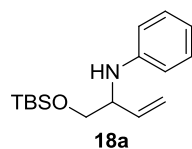


¹H NMR (CDCl₃, 400 MHz): δ = 7.30-7.26 (m, 2H), 7.21-7.17 (m, 3H), 7.08-7.03 (m, 2H), 6.62 (td, J = 7.4, 1.0 Hz, 1H), 6.52 (d, J = 7.9 Hz, 1H), 5.84-5.75 (m, 1H), 5.21 (dt, J = 17.2, 1.4 Hz, 1H), 5.13 (dt, J = 10.3, 1.2 Hz, 1H), 3.90 (q, J = 6.5 Hz, 1H), 3.47 (s, NH), 2.73 (t, J = 7.5 Hz, 2H), 2.11 (s, 3H), 1.98-1.94 (m, 2H).

¹³C NMR (CDCl₃, 100 MHz): δ = 145.4, 141.8, 140.2, 130.2, 128.6, 127.1, 126.2, 121.8, 116.9, 115.5, 110.8, 55.3, 37.6, 32.4, 17.7.

IR (film, cm⁻¹): ν = 3434, 3025, 2920, 2854, 1605, 1586, 1509, 1497, 1478, 1447, 1314, 1257, 990, 916, 744, 698, 682.

HRMS (ESI): calc. for C₁₈H₂₂N (M+H): 252.1752; found: 252.1746.

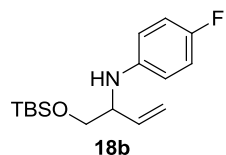


¹H NMR (CDCl₃, 400 MHz): δ = 7.15 (dd, J = 7.8, 6.6 Hz, 2H), 6.69 (tt, J = 7.3, 1.0 Hz, 1H), 6.38 (dd, J = 10.6, 1.1 Hz, 2H), 5.86-5.77 (m, 1H), 5.31 (dt, J = 17.3, 1.4 Hz, 1H), 5.19 (dt, J = 10.3, 1.3 Hz, 1H), 4.19 (s, NH), 3.87 (bs, 1H), 3.75 (dd, J = 9.9, 4.5 Hz, 1H), 3.64 (dd, J = 9.9, 6.0 Hz, 1H), 0.90 (s, 9H), 0.06 (s, 3H), 0.05 (s, 3H).

¹³C NMR (CDCl₃, 100 MHz): δ = 148.0, 137.8, 129.2, 117.0, 116.7, 114.0, 65.9, 57.9, 26.1, 18.5, -5.1, -5.2.

IR (film, cm⁻¹): ν = 3397, 2953, 2928, 2884, 2857, 1602, 1503, 1471, 1316, 1254, 1101, 992, 835, 812, 776, 747, 690.

HRMS (ESI): calc. for C₁₆H₂₈NOSi (M+H): 278.1940; found: 278.1944.



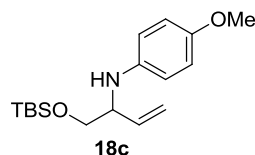
¹H NMR (CDCl₃, 400 MHz): δ = 6.84 (t, J = 8.9, 2H), 6.57 (dd, J = 9.1, 4.5 Hz, 2H), 5.82-5.74 (m, 1H), 5.29 (dt, J = 17.3, 1.4 Hz, 1H), 5.18 (dt, J = 10.3, 1.3 Hz, 1H), 4.02 (s, NH), 3.81-3.77

(m, 1H), 3.74 (dd, $J = 9.7, 4.3$ Hz, 1H), 3.61 (dd, $J = 9.8, 6.1$ Hz, 1H), 0.89 (s, 9H), 0.06 (s, 3H), 0.05 (s, 3H).

^{13}C NMR (CDCl_3 , 100 MHz): $\delta = 157.3, 154.9, 144.4, 137.8, 116.9, 115.7, 115.5, 115.1, 115.0, 65.8, 58.7, 26.0, 18.5, -5.1$.

IR (film, cm^{-1}): $\nu = 3394, 2953, 2929, 2884, 2857, 1509, 1471, 1463, 1255, 1220, 1097, 835, 818, 776$.

HRMS (ESI): calc. for $\text{C}_{16}\text{H}_{27}\text{NOFSi}$ ($\text{M}+\text{H}$): 296.1846; found: 296.1854.

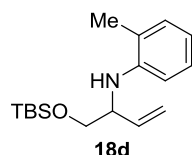


^1H NMR (CDCl_3 , 400 MHz): $\delta = 6.73$ (d, $J = 9.0$, 2H), 6.61 (d, $J = 9.0$ Hz, 2H), 5.83-5.74 (m, 1H), 5.28 (dt, $J = 17.3, 1.4$ Hz, 1H), 5.16 (dt, $J = 10.3, 1.3$ Hz, 1H), 3.79-3.75 (m, 1H), 3.73 (dd, $J = 11.1, 1.2$ Hz, 1H), 3.72 (s, 3H), 3.59 (dd, $J = 9.8, 6.2$ Hz, 1H), 2.14 (s, NH), 0.88 (s, 9H), 0.05 (s, 3H), 0.04 (s, 3H).

^{13}C NMR (CDCl_3 , 100 MHz): $\delta = 152.4, 142.2, 138.2, 116.7, 115.6, 114.8, 65.9, 59.1, 55.9, 26.1, 18.5, -5.1, -5.2$.

IR (film, cm^{-1}): $\nu = 3385, 2952, 2929, 2898, 2857, 2831, 1510, 1470, 1463, 1243, 1232, 1100, 1041, 835, 819, 777$.

HRMS (ESI): calc. for $\text{C}_{17}\text{H}_{30}\text{NO}_2\text{Si}$ ($\text{M}+\text{H}$): 308.2046; found: 308.2053.

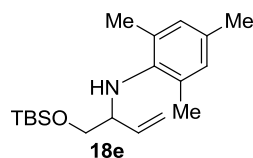


^1H NMR (CDCl_3 , 400 MHz): $\delta = 7.09$ -7.04 (m, 2H), 6.67-6.62 (m, 2H), 5.87-5.78 (m, 1H), 5.31 (dt, $J = 17.3, 1.4$ Hz, 1H), 5.20 (dt, $J = 10.3, 1.3$ Hz, 1H), 3.95-3.90 (m, 1H), 3.79 (dd, $J = 9.8, 4.4$ Hz, 1H), 3.68 (dd, $J = 9.8, 6.1$ Hz, 1H), 2.17 (s, 3H), 0.91 (s, 9H), 0.08 (s, 3H), 0.07 (s, 3H).

^{13}C NMR (CDCl_3 , 100 MHz): $\delta = 146.0, 138.1, 130.2, 127.0, 122.7, 117.2, 116.7, 111.5, 66.0, 57.7, 26.0, 18.4, 17.7, -5.2$.

IR (film, cm^{-1}): $\nu = 3402, 2953, 2928, 2884, 2857, 1606, 1586, 1509, 1471, 1462, 1313, 1254, 1102, 918, 834, 812, 776, 744$.

HRMS (ESI): calc. for $\text{C}_{17}\text{H}_{30}\text{NOSi}$ ($\text{M}+\text{H}$): 292.2097; found: 292.2098.

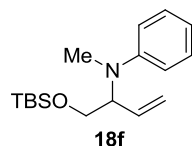


^1H NMR (CDCl_3 , 400 MHz): $\delta = 6.77$ (s, 2H), 5.91-5.83 (m, 1H), 5.12 (dt, $J = 17.2, 1.7$ Hz, 1H), 5.02 (dt, $J = 10.3, 1.1$ Hz, 1H), 3.79 (dd, $J = 9.7, 3.7$ Hz, 1H), 3.67 (dd, $J = 9.7, 2.9$ Hz, 1H), 3.63-3.59 (m, 1H), 2.22 (s, 6H), 2.20 (s, 3H), 0.91 (s, 9H), 0.06 (s, 3H), 0.05 (s, 3H).

^{13}C NMR (CDCl_3 , 100 MHz): $\delta = 142.2, 138.5, 130.8, 129.7, 129.5, 115.8, 66.0, 61.3, 26.0, 20.7, 18.9, 18.5, -5.1, -5.2$.

IR (film, cm⁻¹): ν = 2953, 2928, 2857, 1483, 1471, 1462, 1443, 1251, 1098, 992, 952, 833, 812, 775.

HRMS (ESI): calc. for C₁₉H₃₄NOSi (M+H): 320.2410; found: 320.2413.

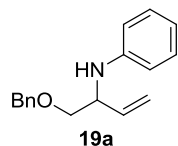


¹H NMR (CDCl₃, 400 MHz): δ = 7.24-7.18 (m, 2H), 6.80-6.77 (m, 2H), 6.69 (tt, J = 7.2, 1.0 Hz, 1H), 5.93-5.85 (m, 1H), 5.23 (d, J = 1.8 Hz, 1H), 5.19 (dt, J = 7.0, 1.8 Hz, 1H), 4.43-4.38 (m, 1H), 3.84-3.76 (m, 2H), 2.82 (s, 3H), 0.84 (s, 9H), 0.02 (s, 3H), 0.01 (s, 3H).

¹³C NMR (CDCl₃, 100 MHz): δ = 150.7, 135.1, 129.2, 116.8, 116.6, 113.2, 63.6, 62.4, 32.8, 25.9, 18.3, -5.4.

IR (film, cm⁻¹): ν = 2952, 2928, 2884, 2856, 1597, 1503, 1471, 1462, 1108, 835, 814, 774, 746, 690.

HRMS (ESI): calc. for C₁₇H₃₀NOSi (M+H): 292.2097; found: 292.2099.

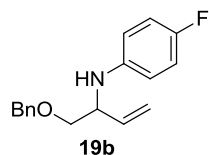


¹H NMR (CDCl₃, 400 MHz): δ = 7.39-7.29 (m, 5H), 7.17 (dd, J = 13.9, 7.3 Hz, 2H), 6.71 (t, J = 7.3 Hz, 1H), 6.64 (dd, J = 7.6, 1.9 Hz, 2H), 5.91-5.83 (m, 1H), 5.34 (dt, J = 17.3, 1.3 Hz, 1H), 5.22 (dt, J = 10.3, 1.2 Hz, 1H), 4.59 (d, J = 12.1 Hz, 1H), 4.55 (d, J = 12.1 Hz, 1H), 4.16 (s, NH), 4.09-4.05 (m, 1H), 3.63 (dd, J = 9.5, 4.5 Hz, 1H), 3.57 (dd, J = 9.6, 6.2 Hz, 1H).

¹³C NMR (CDCl₃, 100 MHz): δ = 147.8, 138.2, 137.6, 129.2, 128.6, 127.9, 127.8, 117.8, 116.7, 114.0, 73.4, 72.7, 56.0.

IR (film, cm⁻¹): ν = 3396, 3085, 3051, 3026, 2897, 2857, 1600, 1503, 1453, 1431, 1360, 1100, 1076, 1027, 992, 922, 870, 747, 692.

HRMS (ESI): calc. for C₁₇H₂₀NO (M+H): 254.1545; found: 254.1545.

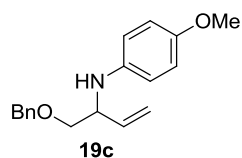


¹H NMR (CDCl₃, 400 MHz): δ = 7.39-7.29 (m, 5H), 6.86 (t, J = 6.7 Hz, 2H), 6.59-6.54 (m, 2H), 5.87-5.78 (m, 1H), 5.32 (dt, J = 17.3, 1.3 Hz, 1H), 5.21 (dt, J = 10.3, 1.2 Hz, 1H), 4.58 (d, J = 12.1 Hz, 1H), 4.53 (d, J = 12.1 Hz, 1H), 4.07 (s, NH), 3.99-3.95 (m, 1H), 3.63 (dd, J = 9.6, 4.3 Hz, 1H), 3.53 (dd, J = 9.6, 6.5 Hz, 1H).

¹³C NMR (CDCl₃, 100 MHz): δ = 157.3, 155.0, 144.1, 138.1, 137.5, 128.6, 128.0, 127.9, 116.9, 115.7, 115.5, 115.0, 114.9, 73.4, 72.7, 56.8.

IR (film, cm⁻¹): ν = 3398, 2898, 2858, 1602, 1508, 1453, 1360, 1313, 1215, 1095, 1076, 1027, 992, 922, 819, 736, 696.

HRMS (ESI): calc. for C₁₇H₁₉FNO (M+H): 272.1458; found: 272.1451

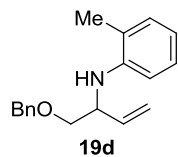


¹H NMR (CDCl₃, 400 MHz): δ = 7.36-7.27 (m, 5H), 6.74 (d, J = 9.0 Hz, 2H), 6.60 (d, J = 9.0 Hz, 2H), 5.87-5.79 (m, 1H), 5.31 (dt, J = 17.3, 1.3 Hz, 1H), 5.18 (dt, J = 10.3, 1.2 Hz, 1H), 4.56 (d, J = 12.0 Hz, 1H), 4.52 (d, J = 12.0 Hz, 1H), 3.98-3.94 (m, 1H), 3.72 (s, 3H), 3.60 (dd, J = 9.5, 4.5 Hz, 1H), 3.53 (dd, J = 9.5, 6.4 Hz, 1H).

¹³C NMR (CDCl₃, 100 MHz): δ = 152.7, 141.8, 138.2, 137.9, 128.6, 128.0, 127.9, 116.9, 115.7, 115.0, 114.9, 73.4, 72.8, 57.2, 56.0.

IR (film, cm⁻¹): ν = 3387, 2931, 2902, 2857, 2832, 1601, 1509, 1463, 1453, 1233, 1178, 1097, 1036, 992, 818, 736, 697.

HRMS (ESI): calc. for C₁₈H₂₂NO₂ (M+H): 284.1651; found: 284.1657.

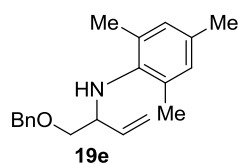


¹H NMR (CDCl₃, 400 MHz): δ = 7.38-7.29 (m, 5H), 7.10-7.05 (m, 2H), 6.69-6.62 (m, 2H), 5.93-5.84 (m, 1H), 5.35 (d, J = 17.3 Hz, 1H), 5.23 (d, J = 10.4 Hz, 1H), 4.60 (d, J = 12.0 Hz, 1H), 4.58 (d, J = 12.0 Hz, 1H), 4.12-4.09 (m, 1H), 3.68-3.60 (m, 2H).

¹³C NMR (CDCl₃, 100 MHz): δ = 145.8, 138.2, 137.8, 130.2, 128.6, 127.9, 127.8, 127.0, 122.6, 118.8, 117.4, 116.7, 111.4, 73.3, 72.7, 55.9, 17.7.

IR (film, cm⁻¹): ν = 3405, 2895, 2857, 1605, 1586, 1508, 1477, 1448, 1359, 1313, 1262, 1102, 1050, 1026, 989, 920, 744, 715, 697.

HRMS (ESI): calc. for C₁₈H₂₂NO (M+H): 268.1701; found: 268.1706.

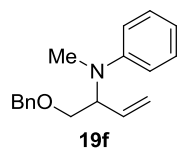


¹H NMR (CDCl₃, 400 MHz): δ = 7.37-7.27 (m, 5H), 6.80 (s, 2H), 6.01-5.92 (m, 1H), 5.21 (dt, J = 17.3, 1.3 Hz, 1H), 5.10 (dt, J = 10.3, 1.2 Hz, 1H), 4.59 (d, J = 12.1 Hz, 1H), 4.53 (d, J = 12.1 Hz, 1H), 3.77-3.74 (m, 1H), 3.63-3.56 (m, 2H), 3.50 (s, 1H), 2.23 (s, 9H).

¹³C NMR (CDCl₃, 100 MHz): δ = 142.2, 138.4, 131.0, 129.8, 129.6, 128.5, 127.7, 115.8, 73.6, 73.2, 60.0, 20.7, 18.8.

IR (film, cm⁻¹): ν = 3380, 3004, 2939, 2913, 2856, 1508, 1482, 1452, 1357, 1233, 1099, 1038, 1027, 1012, 991, 852, 733, 696.

HRMS (ESI): calc. for C₂₀H₂₆NO (M+H): 296.2014; found: 296.2024.

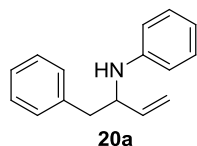


¹H NMR (CDCl₃, 400 MHz): δ = 7.35-7.21 (m, 7H), 6.81 (d, J = 8.7 Hz, 2H), 6.73 (t, J = 7.2 Hz, 1H), 5.94-5.86 (m, 1H), 5.26 (d, J = 1.8 Hz, 1H), 5.22 (dt, J = 7.5, 1.6 Hz, 1H), 4.61-4.57 (m, 1H), 4.55 (d, J = 12.3 Hz, 1H), 4.51 (d, J = 12.3 Hz, 1H), 3.74-3.66 (m, 2H), 3.50 (s, 1H), 2.83 (s, 9H).

¹³C NMR (CDCl₃, 100 MHz): δ = 150.5, 138.4, 135.1, 129.2, 128.5, 127.8, 127.8, 117.1, 113.5, 73.3, 70.5, 60.3, 32.7.

IR (film, cm⁻¹): ν = 2858, 2815, 1596, 1503, 1453, 1359, 1312, 1289, 1209, 1094, 1028, 990, 921, 745, 712, 691.

HRMS (ESI): calc. for C₁₈H₂₂NO (M+H): 268.1701; found: 268.1699.

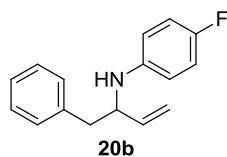


¹H NMR (CDCl₃, 400 MHz): δ = 7.32-7.28 (m, 2H), 7.23-7.20 (m, 3H), 7.16-7.12 (m, 2H), 6.68 (tt, J = 7.3, 1.0 Hz, 1H), 6.59 (dd, J = 7.8, 1.0 Hz, 2H), 5.85-5.77 (m, 1H), 5.19 (dt, J = 17.2, 1.4 Hz, 1H), 5.12 (dt, J = 10.3, 1.3 Hz, 1H), 4.15-4.12 (m, 1H), 3.70 (s, NH), 2.92 (d, J = 6.6 Hz, 2H).

¹³C NMR (CDCl₃, 100 MHz): δ = 147.5, 139.4, 137.8, 129.6, 129.3, 128.6, 126.7, 117.6, 115.6, 113.7, 56.7, 42.1.

IR (film, cm⁻¹): ν = 3406, 3083, 3052, 3025, 2978, 2919, 2851, 1599, 1503, 1453, 1429, 1315, 1287, 1252, 992, 919, 747, 692.

HRMS (ESI): calc. for C₁₆H₁₈N (M+H): 224.1439; found: 224.1445.

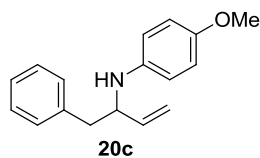


¹H NMR (CDCl₃, 400 MHz): δ = 7.32-7.28 (m, 2H), 7.25-7.19 (m, 3H), 6.84 (t, J = 8.8 Hz, 2H), 6.50 (dd, J = 9.0, 4.4 Hz, 2H), 5.83-5.74 (m, 1H), 5.16 (dt, J = 17.2, 1.4 Hz, 1H), 5.12 (dt, J = 10.3, 1.3 Hz, 1H), 4.06-4.04 (m, 1H), 3.57 (s, NH), 2.92 (dd, J = 13.7, 6.4 Hz, 1H), 2.88 (dd, J = 9.5, 2.6 Hz, 1H).

¹³C NMR (CDCl₃, 100 MHz): δ = 157.2, 154.8, 143.8, 139.4, 137.7, 129.6, 128.6, 126.8, 115.8, 115.7, 115.6, 114.7, 114.6, 57.5, 42.1.

IR (film, cm⁻¹): ν = 3409, 1506, 1454, 1217, 991, 921, 817, 766, 751, 699.

HRMS (ESI): calc. for C₁₆H₁₇NF (M+H): 242.1345; found: 242.1347.

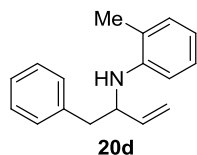


¹H NMR (CDCl₃, 400 MHz): δ = 7.31-7.27 (m, 2H), 7.24-7.19 (m, 3H), 6.75 (d, J = 9.0 Hz, 2H), 6.56 (d, J = 9.0 Hz, 2H), 5.84-5.75 (m, 1H), 5.17 (dt, J = 17.2, 1.4 Hz, 1H), 5.11 (dt, J = 10.3, 1.3 Hz, 1H), 4.04 (q, J = 6.6 Hz, 1H), 3.72 (s, 3H), 3.45 (s, NH), 2.90 (d, J = 6.6 Hz, 2H).

^{13}C NMR (CDCl_3 , 100 MHz): δ = 152.3, 141.6, 139.8, 138.0, 129.6, 128.6, 126.7, 115.6, 115.3, 114.9, 57.8, 55.9, 42.1.

IR (film, cm^{-1}): ν = 3396, 1508, 1463, 1453, 1233, 1178, 1036, 992, 919, 817, 749, 700.

HRMS (ESI): calc. for $\text{C}_{17}\text{H}_{20}\text{NO}$ ($\text{M}+\text{H}$): 254.1545; found: 254.1550.



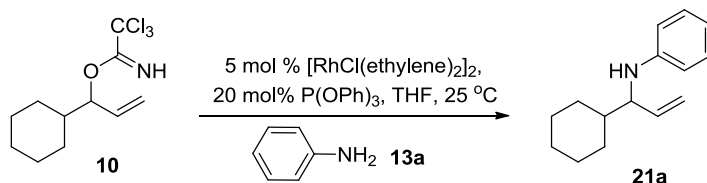
^1H NMR (CDCl_3 , 400 MHz): δ = 7.32-7.28 (m, 2H), 7.24-7.21 (m, 3H), 7.07 (t, J = 7.8 Hz, 2H), 7.02-6.99 (m, 1H), 6.64-6.60 (m, 2H), 5.90-5.82 (m, 1H), 5.21 (dt, J = 17.2, 1.4 Hz, 1H), 5.14 (dt, J = 10.3, 1.3 Hz, 1H), 4.15 (s, 1H), 3.57 (s, NH), 3.01 (dd, J = 13.7, 6.2 Hz, 1H), 2.92 (dd, J = 13.6, 7.2 Hz, 1H), 2.01 (s, 3H).

^{13}C NMR (CDCl_3 , 100 MHz): δ = 145.5, 139.8, 137.8, 130.2, 129.6, 128.6, 127.1, 126.8, 122.3, 117.1, 115.4, 111.2, 56.8, 42.3, 17.6.

IR (film, cm^{-1}): ν = 3423, 1604, 1586, 1509, 1478, 1447, 1313, 1258, 1051, 989, 918, 744, 699.

HRMS (ESI): calc. for $\text{C}_{17}\text{H}_{20}\text{N}$ ($\text{M}+\text{H}$): 238.1596; found: 238.1607.

General Procedure for Amination of Secondary Allylic Trichloroacetimidates with 5 mol% $[\text{RhCl}(\text{ethylene})_2]_2$:



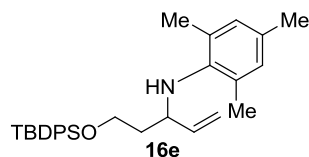
A 10 mL Schlenk flask was charged with $[\text{RhCl}(\text{ethylene})_2]_2$ (2.7 mg, 7.0 μmol , 5 mol%) in a glove box. The flask was sealed and removed from the glove box, and THF (0.35 mL) was added to the Schlenk under argon followed by triphenylphosphite (7.4 μL , 28.0 μmol , 20 mol%). The rhodium-phosphite complex solution was allowed to stir at 25 $^\circ\text{C}$ for 15 min. A separate 10 mL Schlenk flask was charged with **10** (40 mg, 0.14 mmol, 1 equiv), THF (0.35 mL) and aniline **13a** (38 μL , 0.42 mmol, 3 equiv). The rhodium catalyst solution was then added to the flask containing the **10** and **13a** solution. The reaction mixture was stirred at 25 $^\circ\text{C}$ under argon. Reaction progress was monitored by GC. After 30 min, the crude reaction was concentrated *in vacuo*, loaded in dichloromethane onto an ISCO load cartridge, and dried under vacuum. Elution onto an ISCO 24g silica column (0 $\rightarrow$ 40% ethyl acetate/hexane) provided **21a** (30 mg, 96%, branched/linear >53:1) as pale yellow oil.

^1H NMR (CDCl_3 , 400 MHz): δ = 7.13 (dd, J = 7.3, 2.2 Hz, 1H), 7.11 (dd, J = 7.3, 2.2 Hz, 1H), 6.64 (t, J = 6.3 Hz, 1H), 6.58 (d, J = 1.0 Hz, 1H), 6.56 (d, J = 0.92 Hz, 1H), 5.74-5.66 (m, 1H), 5.15 (dt, J = 14.9, 1.4 Hz, 1H), 5.12 (dt, J = 9.0, 1.4 Hz, 1H), 3.67-3.61 (m, 1H, NH), 1.85-1.65 (m, 5H), 1.53-1.44 (m, 1H), 1.29-1.01 (m, 5H).

^{13}C NMR (CDCl_3 , 100 MHz): δ = 148.1, 138.5, 129.3, 117.1, 116.0, 113.4, 61.2, 42.9, 29.7, 29.5, 26.7, 26.6, 26.5.

IR (film, cm⁻¹): ν = 3314, 3081, 3051, 3018, 2922, 2850, 1725, 1600, 1502, 1503, 1448, 1429, 1317, 1251, 1065, 992, 916, 745, 690.

HRMS (ESI): calc. for C₁₅H₂₂N (M+H)⁺: 216.1752; found: 216.1751.

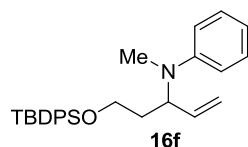


¹H NMR (CDCl₃, 400 MHz): δ = 7.69-7.65 (m, 4H), 7.45-7.35 (m, 6H), 6.80 (s, 2H), 5.70-5.61 (m, 1H), 4.97-4.95 (m, 1H), 4.93 (bs, 1H), 3.89-3.81 (m, 2H), 3.77-3.71 (m, 1H), 2.89 (s, NH), 2.22 (s, 9H), 2.01-1.91 (m, 1H), 1.77-1.69 (m, 1H), 1.06 (s, 9H).

¹³C NMR (CDCl₃, 100 MHz): δ = 142.2, 140.3, 135.8, 134.0, 130.8, 129.7, 129.6, 129.5, 127.8, 115.4, 61.1, 57.3, 39.1, 27.0, 20.7, 19.3, 19.2.

IR (film, cm⁻¹): ν = 2930, 2895, 2857, 1482, 1472, 1427, 1107, 1090, 917, 822, 737, 700, 687.

HRMS (ESI): calc. for C₃₀H₄₀NOSi (M+H): 458.2879; found: 458.2877.

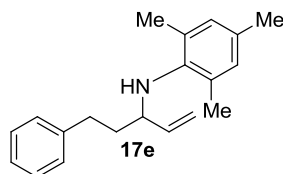


¹H NMR (CDCl₃, 400 MHz): δ = 7.77-7.67 (m, 2H), 7.59-7.57 (m, 2H), 7.46-7.30 (m, 6H), 7.26-7.21 (m, 2H), 6.89-6.86 (m, 2H), 6.76-6.70 (m, 1H), 5.90-5.82 (m, 1H), 5.18-5.10 (m, 2H), 4.75-4.70 (m, 1H), 3.75-3.65 (m, 2H), 2.71 (s, 3H), 1.98-1.88 (m, 2H), 1.07 (s, 9H).

¹³C NMR (CDCl₃, 100 MHz): δ = 150.7, 137.5, 135.7, 133.9, 133.8, 129.8, 129.7, 129.2, 127.9, 127.8, 116.7, 115.7, 113.5, 60.8, 56.6, 34.5, 31.8, 27.0, 19.3.

IR (film, cm⁻¹): ν = 2953, 2930, 2887, 2856, 1597, 1574, 1503, 1471, 1427, 1106, 1087, 822, 742, 700, 688.

HRMS (ESI): calc. for C₂₈H₃₆NOSi (M+H): 430.2566; found: 430.2561.

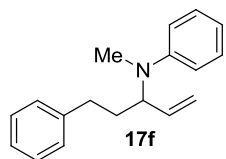


¹H NMR (CDCl₃, 400 MHz): δ = 7.30-7.26 (m, 2H), 7.20-7.17 (m, 3H), 6.78 (s, 2H), 5.75-5.67 (m, 1H), 5.03-4.96 (m, 2H), 3.55 (q, J = 7.8 Hz, 1H), 2.88 (s, NH), 2.75-2.71 (m, 2H), 2.21 (s, 3H), 2.18 (s, 6H), 2.03-1.96 (m, 1H), 1.87-1.83 (m, 1H).

¹³C NMR (CDCl₃, 100 MHz): δ = 142.2, 142.1, 140.4, 130.9, 129.6, 129.4, 128.6, 128.5, 126.0, 115.7, 60.0, 37.9, 32.6, 20.7, 19.1.

IR (film, cm⁻¹): ν = 3062, 3025, 2939, 2916, 2856, 1482, 1453, 1230, 1011, 989, 916, 853, 743, 698.

HRMS (ESI): calc. for C₂₀H₂₆N (M+H): 280.2065; found: 280.2063.

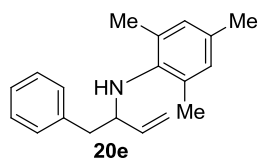


¹H NMR (CDCl₃, 400 MHz): δ = 7.29-7.14 (m, 7H), 6.78-6.70 (m, 3H), 5.89-5.80 (m, 1H), 5.19-5.11 (m, 2H), 4.34 (m, 1H), 2.81 (s, 3H), 2.70-2.59 (m, 2H), 2.08-1.96 (m, 2H).

¹³C NMR (CDCl₃, 100 MHz): δ = 150.7, 142.0, 137.3, 129.2, 128.6, 128.5, 126.0, 116.7, 115.9, 113.3, 59.6, 33.9, 33.0, 31.6.

IR (film, cm⁻¹): ν = 3083, 3060, 3024, 3003, 2941, 2863, 2811, 1596, 1502, 1453, 9990, 919, 745, 691.

HRMS (ESI): calc. for C₁₈H₂₂N (M+H): 252.1752; found: 252.1759.

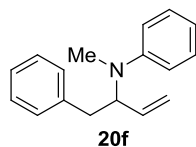


¹H NMR (CDCl₃, 400 MHz): δ = 7.30-7.26 (m, 2H), 7.22-7.19 (m, 3H), 6.78 (s, 2H), 5.74-5.65 (m, 1H), 4.93-4.87 (m, 2H), 3.83 (q, *J* = 7.7 Hz, 1H), 3.01 (dd, *J* = 13.2, 5.4 Hz, 1H), 2.96 (s, NH), 2.79 (dd, *J* = 13.2, 7.9 Hz, 1H), 2.20 (s, 3H), 2.15 (s, 6H).

¹³C NMR (CDCl₃, 100 MHz): δ = 141.9, 139.7, 138.6, 131.2, 129.8, 129.6, 128.4, 126.4, 115.5, 61.5, 42.7, 20.8, 19.1.

IR (film, cm⁻¹): ν = 3371, 3026, 2939, 2915, 1482, 1453, 1373, 1300, 1230, 1156, 990, 917, 853, 737, 698.

HRMS (ESI): calc. for C₁₉H₂₄N (M+H): 266.1909; found: 266.1924.

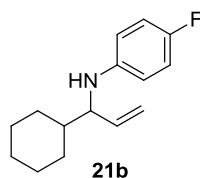


¹H NMR (CDCl₃, 400 MHz): δ = 7.28-7.15 (m, 7H), 6.76-6.67 (m, 3H), 5.92-5.84 (m, 1H), 5.17-5.09 (m, 2H), 4.61-4.56 (m, 1H), 3.05-2.91 (m, 2H), 2.82 (s, 3H).

¹³C NMR (CDCl₃, 100 MHz): δ = 150.4, 139.1, 136.6, 129.3, 129.2, 128.5, 126.3, 116.9, 116.3, 113.5, 62.3, 38.3, 32.3.

IR (film, cm⁻¹): ν = 3084, 3061, 3024, 3002, 2979, 2938, 1595, 1573, 1502, 1453, 1118, 1097, 1030, 990, 920, 745, 691.

HRMS (ESI): calc. for C₁₇H₂₀N (M+H): 238.1596; found: 239.1608.

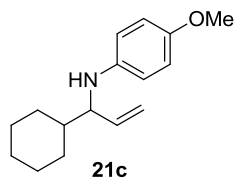


¹H NMR (CDCl₃, 400 MHz): δ = 6.82 (t, *J* = 8.8 Hz, 1H), 6.49 (dd, *J* = 9.1, 4.4 Hz, 1H), 5.75-5.62 (m, 1H), 5.14 (d, *J* = 2.0 Hz, 1H), 5.11 (dd, *J* = 3.8, 1.5 Hz, 1H), 3.53 (bs, 2H), 1.84-1.62 (m, 5H), 1.48-1.44 (m, 1H), 1.25-1.03 (m, 5H).

^{13}C NMR (CDCl_3 , 100 MHz): δ = 156.9, 154.5, 144.4, 116.1, 115.7, 115.5, 114.3, 114.2, 62.0, 42.9, 29.7, 29.5, 26.7, 26.5, 26.4.

IR (film, cm^{-1}): ν = 3422, 2923, 2851, 1507, 1449, 1315, 1289, 993, 917, 816.

HRMS (ESI): calc. for $\text{C}_{15}\text{H}_{21}\text{NF}$ ($\text{M}+\text{H}$) $^+$: 234.1658; found: 234.1655.

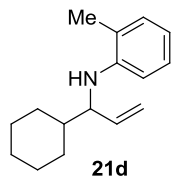


^1H NMR (CDCl_3 , 400 MHz): δ = 6.73 (d, J = 8.8 Hz, 2H), 6.53 (d, J = 8.8 Hz, 2H), 5.72-5.64 (m, 1H), 5.15-5.10 (m, 2H), 3.71 (s, 3H), 3.53 (t, J = 6.5 Hz, 1H), 3.41 (s, NH), 1.85-1.64 (m, 5H), 1.51-1.44 (m, 1H), 1.28-1.00 (m, 5H).

^{13}C NMR (CDCl_3 , 100 MHz): δ = 151.9, 142.4, 138.9, 115.9, 115.0, 114.8, 62.3, 55.9, 42.9, 29.7, 29.5, 26.7, 26.6, 26.5.

IR (film, cm^{-1}): ν = 3405, 2922, 2850, 2831, 1509, 1481, 1463, 1448, 1232, 1178, 1038, 994, 915, 815.

HRMS (ESI): calc. for $\text{C}_{16}\text{H}_{24}\text{NO}$ ($\text{M}+\text{H}$) $^+$: 246.1858; found: 246.1855.

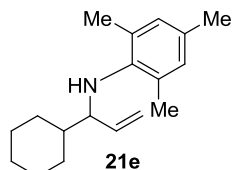


^1H NMR (CDCl_3 , 400 MHz): δ = 7.08-7.01 (m, 2H), 6.61-6.54 (m, 2H), 5.77-5.68 (m, 1H), 5.15 (d, J = 9.2, 1.5 Hz, 1H), 5.13-5.11 (m, 1H), 3.70 (s, 1H), 3.56 (bs, NH), 2.14 (s, 3H), 1.88-1.74 (m, 5H), 1.69-1.55 (m, 1H), 1.27-1.05 (m, 5H).

^{13}C NMR (CDCl_3 , 100 MHz): δ = 145.8, 138.6, 130.2, 127.1, 121.7, 116.5, 115.8, 110.7, 60.8, 42.9, 29.6, 26.7, 26.6, 26.5, 17.8.

IR (film, cm^{-1}): ν = 3442, 2922, 1605, 1586, 1509, 1477, 1447, 1315, 1302, 1288, 1254, 1051, 984, 916, 794, 743, 713.

HRMS (ESI): calc. for $\text{C}_{16}\text{H}_{24}\text{N}$ ($\text{M}+\text{H}$) $^+$: 230.1909; found: 230.1910.

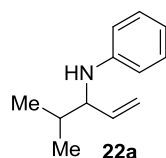


^1H NMR (CDCl_3 , 400 MHz): δ = 6.75 (s, 2H), 5.63-5.54 (m, 1H), 4.87 (dd, J = 10.2, 1.8 Hz, 1H), 4.77 (dd, J = 16.9, 1.8 Hz, 1H), 3.33 (dd, J = 8.4, 5.9 Hz, 1H), 2.18 (s, 9H), 1.95-1.65 (m, 5H), 1.49-1.45 (m, 1H), 1.31-1.01 (m, 5H).

^{13}C NMR (CDCl_3 , 100 MHz): δ = 142.5, 138.7, 130.5, 129.6, 129.2, 115.8, 65.7, 43.2, 30.4, 29.3, 26.9, 26.6, 20.7, 19.3.

IR (film, cm^{-1}): ν = 3349, 2921, 2851, 1483, 1301, 1246, 1231, 1152, 989, 976, 914, 852.

HRMS (ESI): calc. for $\text{C}_{18}\text{H}_{28}\text{N}$ ($\text{M}+\text{H}$) $^+$: 258.2222; found: 258.2226.

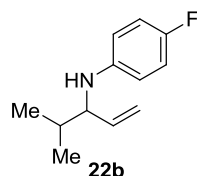


^1H NMR (CDCl_3 , 400 MHz): δ = 7.16-7.11 (m, 2H), 6.67-6.63 (m, 1H), 6.60-6.57 (m, 2H), 5.76-5.67 (m, 1H), 5.15 (td, J = 15.7, 1.4 Hz, 2H), 3.69-3.62 (m, 2H), 1.90-1.82 (m, 1H), 0.99 (d, J = 6.8 Hz, 3H), 0.96 (d, J = 6.8 Hz, 3H),

^{13}C NMR (CDCl_3 , 100 MHz): δ = 148.1, 138.1, 129.3, 117.2, 116.2, 113.5, 61.6, 32.6, 19.0, 18.7.

IR (film, cm^{-1}): ν = 3416, 2959, 2940, 2929, 2902, 2872, 1600, 1503, 1428, 1317, 1272, 1178, 1154, 916, 866, 746, 690.

HRMS (ESI): calc. for $\text{C}_{12}\text{H}_{18}\text{N}$ ($\text{M}+\text{H}$) $^+$: 176.1439; found: 176.1438.

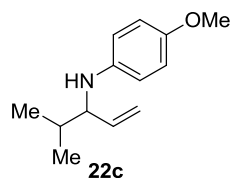


^1H NMR (CDCl_3 , 400 MHz): δ = 6.86-6.80 (m, 2H), 6.53-6.48 (m, 1H), 5.72-5.64 (m, 1H), 5.17 (d, J = 3.0 Hz, 1H), 5.13 (dd, J = 2.8, 1.6 Hz, 1H), 3.55-3.53 (m, 2H), 1.87-1.79 (m, 1H), 0.97 (d, J = 6.8 Hz, 3H), 0.94 (d, J = 6.8 Hz, 3H),

^{13}C NMR (CDCl_3 , 100 MHz): δ = 156.8, 154.6, 144.4, 138.0, 116.4, 115.8, 115.6, 114.3, 114.2, 62.4, 32.7, 19.0, 18.7.

IR (film, cm^{-1}): ν = 3424, 2960, 2873, 1507, 1466, 1315, 1218, 994, 918, 816, 773, 749.

HRMS (ESI): calc. for $\text{C}_{12}\text{H}_{17}\text{NF}$ ($\text{M}+\text{H}$) $^+$: 194.1345; found: 194.1341.

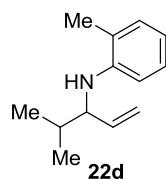


^1H NMR (CDCl_3 , 400 MHz): δ = 6.76-6.72 (m, 2H), 6.57-6.53 (m, 1H), 5.73-5.65 (m, 1H), 5.17 (t, J = 1.6 Hz, 1H), 5.15-5.12 (m, 1H), 3.71 (s, 3H), 3.54 (t, J = 5.4 Hz, 1H), 3.40 (s, NH), 1.88-1.79 (m, 1H), 0.98 (d, J = 6.8 Hz, 3H), 0.94 (d, J = 6.8 Hz, 3H),

^{13}C NMR (CDCl_3 , 100 MHz): δ = 152.0, 142.3, 138.4, 116.2, 115.0, 114.8, 62.6, 56.0, 32.6, 19.1, 18.7.

IR (film, cm^{-1}): ν = 3404, 2932, 1509, 1463, 1229, 1178, 1038, 994, 916, 815, 756.

HRMS (ESI): calc. for $\text{C}_{13}\text{H}_{20}\text{NO}$ ($\text{M}+\text{H}$) $^+$: 206.1545; found: 206.1547.

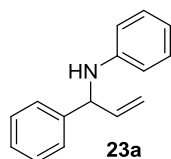


¹H NMR (CDCl₃, 400 MHz): δ = 7.09-7.03 (m, 2H), 6.62-6.55 (m, 2H), 5.79-5.71 (m, 1H), 5.20 (t, J = 1.6 Hz, 1H), 5.17-5.14 (m, 1H), 3.74-3.69 (m, 1H), 3.55 (s, NH), 2.16 (s, 3H), 1.95-1.87 (m, 1H), 1.01 (d, J = 6.8 Hz, 3H), 0.97 (d, J = 6.8 Hz, 3H),

¹³C NMR (CDCl₃, 100 MHz): δ = 145.8, 138.2, 130.2, 127.2, 121.8, 116.7, 116.1, 110.8, 61.2, 32.7, 19.0, 18.8, 17.7.

IR (film, cm⁻¹): ν = 3442, 2958, 1605, 1586, 1510, 1477, 1464, 1446, 1315, 1303, 1252, 1051, 992, 917, 744, 714.

HRMS (ESI): calc. for C₁₃H₂₀N (M+H)⁺: 190.1596; found: 190.1589.

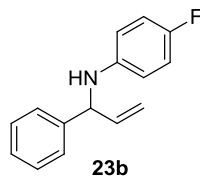


¹H NMR (CDCl₃, 400 MHz): δ = 7.35-7.21 (m, 5H), 7.11-7.06 (m, 2H), 6.64 (t, J = 7.3 Hz, 1H), 6.56 (d, J = 8.6 Hz, 2H), 6.07-5.98 (m, 1H), 5.28 (bs, 1H), 5.24-5.19 (m, 1H), 4.91 (t, J = 4.4 Hz, 1H), 4.02 (bs, NH),

¹³C NMR (CDCl₃, 100 MHz): δ = 147.4, 142.0, 139.2, 129.3, 128.9, 127.6, 127.3, 117.8, 116.2, 113.7, 61.0.

IR (film, cm⁻¹): ν = 3409, 3082, 3051, 3024, 1599, 1500, 1451, 1428, 1313, 1266, 1243, 1179, 1028, 991, 923, 746, 690.

HRMS (ESI): calc. for C₁₅H₁₆N (M+H)⁺: 210.1288; found: 210.1283

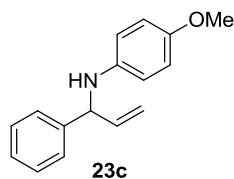


¹H NMR (CDCl₃, 400 MHz): δ = 7.35-7.25 (m, 5H), 6.82 (t, J = 8.8 Hz, 2H), 6.50 (dd, J = 8.7, 4.4 Hz, 2H), 6.01-5.96 (m, 1H), 5.27 (dt, J = 18.8, 1.4 Hz, 1H), 5.21 (dt, J = 10.2, 1.3 Hz, 1H), 4.84 (d, J = 5.9 Hz, 1H), 3.95 (bs, NH),

¹³C NMR (CDCl₃, 100 MHz): δ = 157.2, 154.9, 143.7, 141.9, 139.2, 128.9, 127.7, 127.3, 116.3, 115.8, 115.6, 114.6, 114.5, 61.6.

IR (film, cm⁻¹): ν = 3413, 1508, 1452, 1402, 1312, 1218, 927, 818, 780, 749, 700.

HRMS (ESI): calc. for C₁₅H₁₅NF (M+H)⁺: 228.1193; found: 228.1189.

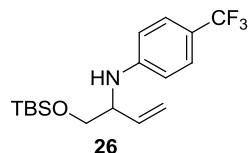


¹H NMR (CDCl₃, 400 MHz): δ = 7.39-7.24 (m, 5H), 6.73 (D, J = 9.0 Hz, 2H), 6.55 (d, J = 8.9 Hz, 2H), 6.06-5.98 (m, 1H), 5.26 (dt, J = 17.1, 1.4 Hz, 1H), 5.20 (dt, J = 10.2, 1.3 Hz, 1H), 4.85 (d, J = 6.0 Hz, 1H), 3.80 (bs, NH), 3.71 (s, 3H).

^{13}C NMR (CDCl_3 , 100 MHz): δ = 152.2, 142.3, 141.6, 139.6, 128.9, 127.6, 127.3, 116.1, 115.0, 114.8, 61.9, 55.9.

IR (film, cm^{-1}): ν = 3396, 2830, 1509, 1463, 1452, 1405, 1240, 1230, 1178, 1036, 992, 924, 817, 764, 746, 700.

HRMS (ESI): calc. for $\text{C}_{16}\text{H}_{18}\text{NO}$ ($\text{M}+\text{H}$) $^+$: 240.1389; found: 240.1388.



^1H NMR (CDCl_3 , 400 MHz): δ = 7.35 (d, J = 8.5, 2H), 6.61 (d, J = 8.5 Hz, 2H), 5.81-5.76 (m, 1H), 5.27 (dt, J = 17.3, 1.4 Hz, 1H), 5.20 (dt, J = 10.4, 1.3 Hz, 1H), 4.51 (d, J = 5.8 Hz, NH), 3.92-3.86 (m, 1H), 3.77 (dd, J = 10.4, 4.4 Hz, 1H), 3.63 (dd, J = 10.0, 5.8 Hz, 1H), 0.88 (s, 9H), 0.06 (s, 3H), 0.05 (s, 3H).

^{13}C NMR (CDCl_3 , 100 MHz): δ = 150.5, 136.8, 126.7, 119.2, 118.9, 117.2, 113.0, 65.7, 57.5, 26.0, 18.5, -5.1, -5.2.

IR (film, cm^{-1}): ν = 3421, 2954, 2931, 2884, 2858, 1617, 1531, 1483, 1472, 1325, 1257, 1186, 1159, 1107, 1066, 835, 825, 778.

HRMS (ESI): calc. for $\text{C}_{17}\text{H}_{27}\text{NOF}_3\text{Si}$ ($\text{M}+\text{H}$): 346.1819; found: 346.1814.