Supporting Information

Intramolecular Hydroamination of Alkynes Catalyzed by Pd(PPh₃)₄/Triphenylphosphine under Neutral Conditions

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General Information. ^1H NMR spectra are reported as follows: chemical shift in ppm (δ) relative to the chemical shift of CDCl_3 at 7.24 ppm, integration, multiplicities (s = singlet, d = doublet, t = triplet, m = multiplet), and coupling constants (Hz). ^{13}C NMR spectra reported in ppm (δ) relative to the central line of triplet for CDCl_3 at 77 ppm. IR bands are reported in cm^{-1} . Chemicals and reagents were purchased from commercial suppliers and used without further purification unless otherwise mentioned. Column chromatography was carried out employing Silica gel 60 N (spherical, neutral, 100~210 μm). Analytical thin-layer chromatography (TLC) was performed on 0.2 mm precoated plate Kieselgel 60 F₂₅₄. Moisture sensitive reactions were conducted under an argon atmosphere using standard Schlenk techniques.

Preparation of Starting Materials

The starting materials were prepared in multiple steps by following the known protocols with some modifications in each step.¹ Scheme 1 shows the synthetic route for the substrates **1a**, **1b** and **1f**.

Scheme 1. Preparation of Starting Materials

Preparation of 6-Phenyl-hex-5-yn-1-ol (8) (Sonogashira reaction)²: To 5-hexyn-1-ol **7** (4.02 g, 41.0 mmol), Pd(PPh₃)₄ (0.47 g, 0.41 mmol) and CuI (0.16 g, 0.82 mmol) in Et₃N (180 mL) was added freshly distilled iodobenzene (4.6 mL, 41.0 mmol) under argon. After stirring for 1.5 h at 50 °C, the mixture was filtered and concentrated. Purification of the crude mixture by silica gel column chromatography (hexane/ethyl acetate, 4/1) gave alcohol **8** (6.22 g, 35.7 mmol, 87%).

Preparation of Azide (9)³: Methanesulfonyl chloride (1.9 mL, 24.0 mmol) was added dropwise to alcohol **8** (3.48 g, 20 mmol) and Et₃N (4.2 mL, 30.0 mmol) in CH₂Cl₂ (50 mL) at 0 °C and stirred for 2 h. The mixture was poured into a separatory funnel containing ice-cold 1N HCl (50 mL) and extracted with CH₂Cl₂ (25 mL x 3). The combined organic phases were washed with saturated NaHCO₃, dried over MgSO₄ and concentrated in vacuo to give the crude mesylate, which was used in the next step without further purification. The crude mesylate was treated with NaN₃ (1.95 g, 30.0 mmol) in DMF (20 mL) at 55 °C for 5 h then diluted with Et₂O (100 mL) and H₂O (15 mL). The mixture was extracted with Et₂O (30 mL x 3). Purification of the crude product by silica gel column chromatography afforded azide **9** (3.75 g, 18.8 mmol, 94%) as a pale yellow oil.

Reduction of Azide (9) with LiAlH₄: Azide **9** (3.39 g, 17.0 mmol) in Et₂O (30 mL) was added to a solution of LiAlH₄ (0.65 g, 17.0 mmol) in Et₂O (140 mL) at 0 °C. The mixture was stirred for 3 h and was carefully quenched by addition of aqueous NaHCO₃. The mixture was extracted with Et₂O (50 mL x 3), washed with brine, dried over MgSO₄, filtered and concentrated to give the amine **10** in a nearly pure form.

Preparation of *N*-Nonaflyl-(6-phenyl-hex-5-ynyl)-amine (1a): To a solution of the crude amine **10** (1.30 g, 7.5 mmol) in CH₂Cl₂ (15 mL) was added Et₃N (1.6 mL, 11.2 mmol) at 0 °C. Nonafluorobutanesulfonyl fluoride (1.4 mL, 8.2 mmol) was then added dropwise. The reaction mixture was stirred for 1 h and then allowed to warm to room temperature. Water (30 mL) was added and the mixture was extracted with CH₂Cl₂ (15 mL x 3). Purification of the residue by silica gel column chromatography gave **1a** (3.07 g, 6.75 mmol, 90%) as pale yellow oil.

Preparation of *N*-Triflyl-(6-phenyl-hex-5-ynyl)-amine (1b): To a solution of the crude amine **10** (1.30 g, 7.5 mmol) in CH₂Cl₂ (15 mL) was added Et₃N (1.6 mL, 11.2 mmol) at -78 °C. Trifluoromethanesulfonic anhydride (1.4 mL, 8.2 mmol) was then added dropwise. The

reaction mixture was stirred for 1 h and then allowed to warm to room temperature. Water (30 mL) was added and the mixture was extracted with CH_2Cl_2 (15 mL x 3). Purification of the residue by silica gel column chromatography gave **1a** (1.95 g, 6.37 mmol, 85%) as pale yellow oil.

Preparation of *N*-Benzyl-(6-phenyl-hex-5-ynyl)-amine (1f)³: KOH (0.67 g, 12.0 mmol), amine **10** (1.04 g, 6.0 mmol) and benzyl bromide (0.78 mL, 6.6 mmol) were refluxed for 30 minutes in ethanol/water 1:1 (60 mL). The solution was extracted at basic pH (NH_4OH) with CH_2Cl_2 (50 mL x 3). Purification by silica gel column chromatography (hexane/ethyl acetate 20/1 ~ 10/1) gave **1f** (1.42 g, 5.4 mmol, 90%).

Analytical Data

The ^1H NMR and ^{13}C NMR spectra of the substrates **1a** and **1b** were identical with those reported in the literature.⁴

***N*-Triflyl-6-(4-methoxyphenyl)-5-hexynylamine (1c)**: ^1H NMR (400MHz, CDCl_3) δ 1.69-1.62 (m, 2H), 1.83-1.76 (m, 2H), 2.45 (t, $J = 6.5$ Hz, 2H), 3.40-3.35 (m, 2H), 3.79 (s, 3H), 4.81 (br s, 1H), 6.82-6.78 (m, 2H), 7.32-7.28 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 18.9, 25.3, 29.4, 44.1, 55.3, 81.3, 87.2, 113.8, 115.6, 121.2, 132.8, 159.1. IR (neat) 3319, 2939, 2841, 1606, 1510, 1456, 607 cm^{-1} . GCMS Calcd for $\text{C}_{14}\text{H}_{16}\text{F}_3\text{NO}_3\text{S}$ (M^+) 335.1. Found 335.0.

***N*-Triflyl-6-(4-trifluoromethylphenyl)-5-hexynylamine (1d)**: ^1H NMR (400MHz, CDCl_3) δ 1.87-1.67 (m, 4H), 2.51 (t, $J = 6.5$ Hz, 2H), 3.42-3.37 (m, 2H), 4.82 (br s, 1H), 7.48 (d, $J = 8.0$ Hz, 2H), 7.55 (d, $J = 8.0$ Hz, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 18.8, 25.0, 29.3, 44.0, 80.3, 91.6, 118.0, 121.2, 125.1, 127.4, 129.3, 131.8. IR (KBr) 3309, 2931, 1618, 1440, 1326, 842 cm^{-1} . GCMS Calcd for $\text{C}_{14}\text{H}_{13}\text{F}_6\text{NO}_2\text{S}$ (M^+) 373.1. Found 373.0.

***N*-Triflyl-5-undecynylamine (1e)**: ^1H NMR (400MHz, CDCl_3) δ 0.90 (t, $J = 7.0$ Hz, 3H), 1.39-1.26 (m, 4H), 1.61-1.44 (m, 4H), 1.78-1.69 (m, 2H), 2.17-2.11 (m, 2H), 2.26-2.19 (m, 2H), 3.38-3.33 (m, 2H), 4.87 (br s, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 13.9, 18.1, 18.6, 22.2, 25.5, 28.7, 29.2, 31.1, 44.1, 78.9, 81.6, 118.0. IR (neat) 3317, 2935, 2862, 1434, 1373, 1232, 609 cm^{-1} .

¹. GCMS Calcd for C₁₂H₂₀F₃NO₂S (M⁺) 299.1. Found 299.0.

***N*-Benzyl-6-phenyl-5-hexynylamine (1f):** ¹H NMR (400MHz, CDCl₃) δ 1.72-1.50 (m, 4H), 2.31 (t, *J* = 6.5 Hz, 2H), 2.44 (t, *J* = 6.5 Hz, 2H), 3.55 (s, 2H), 7.38-7.17 (m, 10H). ¹³C NMR (100 MHz, CDCl₃) δ 19.1, 26.1, 26.3, 52.6, 58.2, 80.7, 90.2, 124.0, 126.7, 127.4, 128.1, 128.3, 128.7, 131.5, 139.8. IR (KBr) 3028, 2931, 2862, 1596, 1450, 1361, 1026, 738 cm⁻¹. GCMS Calcd for C₁₉H₂₁N (M⁺) 263.2. Found 263.0.

***N*-Triflyl-7-phenyl-6-heptynylamine (1g):** ¹H NMR (400MHz, CDCl₃) δ 1.71-1.49 (m, 6H), 2.43 (t, *J* = 6.5 Hz, 2H), 3.35-3.30 (m, 2H), 4.74 (br s, 1H), 7.38-7.23 (m, 5H). ¹³C NMR (100 MHz, CDCl₃) δ 13.3, 19.5, 22.1, 23.8, 38.5, 75.1, 83.7, 115.4, 117.9, 121.8, 122.3, 125.6. IR (neat) 3319, 2941, 2864, 1373, 1193, 609 cm⁻¹. GCMS Calcd for C₁₄H₁₆F₃NO₂S (M⁺) 319.1. Found 319.0.

***N*-Nonaflyl-2-[(*E*)-2-phenylethenyl]pyrrolidine (2a)⁴:** ¹H NMR (400MHz, CDCl₃) δ 2.31-1.91 (m, 4H), 3.79-3.58 (m, 2H), 4.72 (dt, *J* = 7.5, 4.0 Hz, 1H), 6.09 (dd, *J* = 16.0, 7.5 Hz, 1H), 6.55 (d, *J* = 16.0 Hz, 1H), 7.37-7.21 (m, 5H). ¹³C NMR (75 MHz, CDCl₃) δ 29.7, 33.1, 49.7, 63.6, 126.58, 126.59, 127.8 (for 3 coalescence peaks), 128.0, 128.3, 128.6, 132.1, 136.0. IR (KBr) 3026, 2989, 1598, 1490, 1382, 1203, 748 cm⁻¹. Anal. Calcd for C₁₆H₁₄F₉NO₂S (455.34): C, 42.20; H, 3.10; N, 3.08; S, 7.04. Found: C, 42.06; H, 3.29; N, 2.96; S, 7.43. HRMS (ESI) Calcd for C₁₆H₁₄F₉NO₂S (M⁺+Na) 478.0494. Found 478.0494. Registry No. 666705-75-5.

***N*-Triflyl-2-[(*E*)-2-phenylethenyl]pyrrolidine (2b)⁴:** ¹H NMR (400MHz, CDCl₃) δ 2.13-1.90 (m, 3H), 2.29-2.19 (m, 1H), 3.72-3.56 (m, 2H), 4.66 (dt, *J* = 7.5, 4.0 Hz, 1H), 6.07 (dd, *J* = 16.0, 7.5 Hz, 1H), 6.55 (d, *J* = 16.0 Hz, 1H), 7.37-7.22 (m, 5H). ¹³C NMR (75 MHz, CDCl₃) δ 24.4, 33.1, 49.4, 63.3, 126.6, 127.54, 127.58, 128.0, 128.6, 132.2, 136.0. IR (KBr) 2986, 1380, 1201, 1170, 1091, 1064, 748 cm⁻¹. Anal. Calcd for C₁₃H₁₄F₃NO₂S (305.32): C, 51.14; H, 4.62; N, 4.59; S, 10.50. Found: C, 51.28; H, 4.78; N, 4.62; S, 10.23. HRMS (ESI) Calcd for C₁₃H₁₄F₃NO₂S (M⁺+Na) 328.0590. Found 328.0590. Registry No. 666705-68-6.

***N*-Triflyl-2-[(*E*)-2-(4-methoxyphenyl)ethenyl]pyrrolidine (2c):** ¹H NMR (400MHz, CDCl₃) δ 2.30-1.90 (m, 4H), 3.73-3.57 (m, 2H), 3.81 (s, 3H), 4.68-4.63 (m, 1H), 5.95 (dd, *J* = 16.0, 7.5 Hz, 1H), 6.51 (d, *J* = 16.0 Hz, 1H), 6.85 (d, *J* = 8.5 Hz, 2H), 7.30 (d, *J* = 8.5 Hz, 2H), ¹³C NMR

(75 MHz, CDCl₃) δ 24.4, 33.1, 49.3, 55.3, 63.5, 114.0, 125.3, 127.8, 128.7, 131.71, 131.73, 159.5. IR (neat) 2956, 1608, 1380, 1249, 1064 cm⁻¹. HRMS (ESI) Calcd for C₁₄H₁₆F₃NO₃S (M⁺+Na) 358.0695. Found 358.0695.

***N*-Triflyl-2-[(*E*)-2-(4-trifluoromethylphenyl)ethenyl]pyrrolidine (2d):** ¹H NMR (400MHz, CDCl₃) δ 2.14-1.91 (m, 3H), 2.32-2.22 (m, 1H), 3.74-3.57 (m, 2H), 4.67 (dt, *J* = 7.5, 4.0 Hz, 1H), 6.17 (dd, *J* = 16.0, 7.5 Hz, 1H), 6.58 (d, *J* = 16.0 Hz, 1H), 7.44 (d, *J* = 8.0 Hz, 2H), 7.55 (d, *J* = 8.0 Hz, 2H). ¹³C NMR (75 MHz, CDCl₃) δ 24.4, 33.0, 49.5, 63.0, 122.3, 125.52, 125.57, 125.6, 126.7, 130.3, 130.9, 139.4. IR (KBr) 2999, 2920, 1616, 1454, 1388, 1226, 1028 cm⁻¹. HRMS (ESI) Calcd for C₁₄H₁₃F₆NO₂S (M⁺+Na) 396.0463. Found 396.0462.

***N*-Triflyl-2-[(*E*)-2-pentylethenyl]pyrrolidine (*trans*-2e):** ¹H NMR (400MHz, CDCl₃) δ 0.87 (t, *J* = 6.5 Hz, 3H), 1.39-1.19 (m, 6H), 2.19-1.76 (m, 6H), 3.65-3.46 (m, 2H), 4.45 (dt, *J* = 7.5, 4.0 Hz, 1H), 5.34 (dd, *J* = 15.5, 7.5 Hz, 1H), 5.64 (dt, *J* = 15.5, 6.5 Hz, 1H). ¹³C NMR (75 MHz, CDCl₃) δ 14.0, 22.4, 24.3, 28.5, 31.3, 32.0, 33.0, 49.2, 63.3, 118.0, 128.1, 134.1. IR (neat) 2958, 2929, 1390, 1226, 1153, 1064 cm⁻¹. HRMS (ESI) Calcd for C₁₂H₂₀F₃NO₂S (M⁺+Na) 322.1065. Found 322.1059.

***N*-Triflyl-2-[(*Z*)-2-pentylethenyl]pyrrolidine (*cis*-2e):** ¹H NMR (400MHz, CDCl₃) δ 0.88 (t, *J* = 7.0 Hz, 3H), 1.40-1.23 (m, 4H), 1.83-1.49 (m, 6H), 2.03-2.09 (m, 2H), 3.17-3.23 (m, 1H), 3.73-3.76 (m, 1H), 4.60 (br m, 1H), 5.72-5.42 (m, 2H). ¹³C NMR (75 MHz, CDCl₃) δ 13.9, 18.5, 22.1, 25.3, 29.7, 31.1, 32.0, 42.9, 56.0, 117.7, 122.0, 135.0. IR (neat) 2933, 2862, 1388, 1184, 1147, 941 cm⁻¹. HRMS (ESI) Calcd for C₁₂H₂₀F₃NO₂S (M⁺+Na) 322.1065. Found 322.1059.

***N*-Benzyl-2-[(*E*)-2-phenylethenyl]pyrrolidine (2f)^{5,6}:** ¹H NMR (300MHz, CDCl₃) δ 1.90-1.66 (m, 3H), 2.22-1.94 (m, 2H), 3.02-2.92 (m, 2H), 3.13 (d, *J* = 12.8 Hz, 1H), 4.06 (d, *J* = 12.8 Hz, 1H), 6.19 (dd, *J* = 15.9, 8.5 Hz, 1H), 6.55 (d, *J* = 15.9 Hz, 1H), 7.42-7.18 (m, 10H). ¹³C NMR (75 MHz, CDCl₃) δ 22.1, 31.7, 53.3, 58.3, 67.8, 126.2, 126.7, 127.3, 128.1, 128.5, 128.9, 131.6, 132.5, 137.1, 139.3. IR (neat) 3026, 2925, 1494, 1452, 987, 744 cm⁻¹. HRMS (ESI) Calcd for C₁₉H₂₁N (M⁺+Bn) 354.2216. Found 354.2217. Registry No. 234092-63-8.

***N*-Triflyl-2-[(*E*)-2-phenylethenyl]piperidine (2g)⁶:** ¹H NMR (400MHz, CDCl₃) δ 1.79-1.52 (m, 4H), 1.99-1.85 (m, 2H), 3.29 (m, 1H), 3.83 (br d, *J* = 14.0 Hz, 1H), 4.82 (br s, 1H), 6.21 (dd, *J* = 16.0, 5.0 Hz, 1H), 6.58 (dd, *J* = 16.0, 1.5 Hz, 1H), 7.40-7.23 (m, 5H). ¹³C NMR (100 MHz, CDCl₃) δ 18.6, 25.3, 29.6, 43.2, 56.2, 118.3, 121.5, 126.5, 128.1, 128.6, 133.2, 136.0. IR (neat) 3028, 2949, 1386, 1056, 609 cm⁻¹. HRMS (EI) Calcd for C₁₄H₁₆F₃NO₂S (M⁺+Na) 342.0746. Found 342.0747. Registry No. 503622-58-0.

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