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Supporting Information

Iridium-Catalyzed, Ligand-Controlled Directed Alkynylation and

Alkenylation of Arene with Terminal Alkyne

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Materials and Methods

Unless otherwise noted, all reactions were assembled on a Schlenk vacuum line or in a glovebox using oven-dried glassware and were stirred with Teflon-coated magnetic stirring bars. All the ligands were purchased from Strem Chemicals and were used as received. $[Ir(cod)_2]OTf^1$ was prepared according to literature methods. Triisopropylsilylacetylene, 1-(3-Dimethylaminopropyl)-3-ethylcarbodiimide Hydrochloride (EDCI) and 4-dimethylaminopyridine (DMAP) were purchased from Alfa Aesar and were used as received. Chloroform was distilled from CaH₂. All other solvents and reagents were used as received. All work-up and purification procedures were carried out with reagent grade solvents in air. Reaction temperatures above 25 °C refer to temperatures of an aluminum heating block or a silicon oil bath, which were controlled by an electronic temperature modulator from IKA. NMR spectra were acquired on NMR spectrometer with 400 MHz for ¹H NMR and 126 MHz for ¹³C NMR at the NMR facility at Center of Basic Molecular Science (CBMS). Chemical shifts (δ) are reported in ppm relative to the residual solvent signal (δ = 7.26 for ¹H NMR and $\delta = 77.16$ for ¹³C NMR). Data for ¹H NMR spectra are reported as follows: chemical shift (multiplicity, coupling constants, number of hydrogens). Abbreviations are as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br (broad). Infrared (IR) spectra were recorded on a Bruker FT-IR alpha (ATR mode) spectrophotometer. GC data were obtained on a Shimazu 2010 Plus GC system containing an Rxi®-5ms capillary column. High-resolution mass spectral data was performed on a Thermo Scientific Q Exactive (positive mode) at the Mass Spectrometry Facility, CBMS.

General procedure for C-H alkynylation

In an Ar-filled glovebox, 0.10 mmol of benzamide, 5.6 mg of $[Ir(cod)_2]OTf$ (0.010 mmol) and 5.4 mg of ligand L3 (0.012 mmol) were weighed into a one-dram screw-capped vial. A stir bar was added, and the substrate was dissolved in CHCl₃ (1.0 mL). The resulting solution was treated with triisopropylsilylacetylene (54.7 mg, 0.30 mmol). The vial was capped with a Teflon-lined screw cap, and the resulting solution was then removed from the glovebox, placed in a pre-heated aluminum block at 80 °C for 24 h. The reaction mixture was directly purified by column chromatography on silica gel with EtOAc/hexanes mixture as eluent.

General procedure for C-H alkenylation

In an Ar-filled glovebox, 0.10 mmol of benzamide, 5.4 mg of $[Ir(cod)_2]OTf (0.010 mmol)$ and 14.2 mg of ligand **L6** (0.012 mmol) were weighed into a one-dram screw-capped vial. A stir bar was added, and the substrate was dissolved in CHCl₃ (1.0 mL). The resulting solution was treated with triisopropylsilylacetylene (54.7 mg, 0.30 mmol). The vial was capped with a Teflon-lined screw cap, and the resulting solution was then removed from the glovebox, placed in a pre-heated aluminum block at 80 °C for 48 h. The reaction mixture was directly purified by column chromatography on silica gel with EtOAc/hexanes mixture as eluent.

General method for the synthesis of substrates

$$\bigcap_{R} O + CH_{3}NH_{2} HCI \xrightarrow{EDCI, DMAP, Et_{3}N, DCM}$$

1a to **1n** and **1p**: In a 100 ml round-bottomed flask, 5.0 mmol of benzoic acid, methylamine hydrochloride (405.2 mg, 6.0 mmol), EDCI (1.44 g, 7.5 mmol), and DMAP (61.1 mg, 0.5 mmol) were added. A stir bar was added, and the solid was dissolved in CH₂Cl₂ (20 mL). The resulting solution was treated with triethylamine (1.52 g, 15.0 mmol) and stirred at room temperature for 12 h. The reaction mixture was concentrated and extracted with EtOAc. The separated organic layer was dried over anhydrous MgSO₄. After evaporation of the solvent under reduced pressure, components of the residue were purified by column chromatography on silica gel with EtOAc/hexanes mixture as eluent.



10: In a 100 ml round-bottomed flask, 5.0 mmol acid, 1.2 equiv. methylamine hydrochloride, 1.5 equiv. EDCI, 10 mol% DMAP were added see above for changes. A stir bar was added, and the solids were dissolved in CH₂Cl₂ (20 mL). The resulting solution was stirred at room temperature for 12 h. The reaction mixture was concentrated and extracted with EtOAc. The separated organic layer was dried over anhydrous MgSO₄. After evaporation of the solvent under reduced pressure, components of the residue were purified by column chromatography on silica gel with

EtOAc/hexanes mixture as eluent.



1a-D₅²: To a stirred solution of 2,3,4,5,6-pentadeuteriobromobenzene (810 mg, 5.00 mmol) in anhydrous THF (20 mL), a solution of *n*-BuLi in *n*-hexane (2.4 mL, 2.4 M, 5.6 mmol) was added dropwise at -78 $\$ for 10 min. The mixture was stirred at the same temperature for 30 min, and then CO₂ was bubbled through the mixture at -78 $\$ for 10 min. The mixture was allowed to warm to ambient temperature, quenched with H₂O (20 mL), acidified to pH=1 with 1 M HCl, and extracted with EtOAc (3 \times 30 mL). The combined organic phase was dried over MgSO₄, filtered and the solvents were removed in vacuum to give the product. **1a**-D₅ was prepared from the 2,3,4,5,6-pentadeuteriobenzoyl acid according to the general method.







¹H NMR (400 MHz, CDCl₃) of **5**















¹H NMR (400 MHz, CDCl₃) of **10**

Characterization of substrates:

1a: ¹**H NMR** (400 MHz, CDCl₃) δ 7.76 (d, J = 7.2 Hz, 2H), 7.48 (t, J = 7.3 Hz, 1H), 7.41 (t, J = 7.4 Hz, 2H), 6.24 (s, 1H), 3.01 (d, J = 4.9 Hz, 3H). ¹³**C NMR (101 MHz, CDCl₃)** δ 168.39, 134.79, 131.46, 128.67, 126.95, 26.96. ESI-HR calcd for C₈H₁₀NO⁺ ([M+H]⁺) 136.0757, found 136.0753. **IR** v (cm⁻¹) 3309, 1637, 1544, 695. **M. P.** 84 °C.

1b: ¹**H NMR** (400 MHz, CDCl₃) δ 7.37 – 7.27 (m, 2H), 7.19 (m, 2H), 5.80 (s, 1H), 2.98 (d, J = 4.9 Hz, 3H), 2.44 (s, 3H). ¹³**C NMR** (101 MHz, CDCl₃) δ 170.92, 136.67, 136.16, 131.11, 129.91, 126.78, 125.81, 26.75, 19.89. **ESI-HR** calcd for C₉H₁₂NO⁺ ([M+H]⁺) 150.0913, found 150.0911. **IR** v (cm⁻¹) 3292, 1634, 1540, 735. **M. P.** 81 °C.

∽_N∽CH₃ H

1c: ¹**H NMR** (400 MHz, CDCl₃) δ 7.57 – 7.44 (m, 2H), 7.39 (td, J = 8.1, 6.0 Hz, 1H), 7.18 (tdd, J = 8.3, 2.6, 0.9 Hz, 1H), 6.26 (s, 1H), 3.01 (d, J = 4.9 Hz, 3H). ¹³**C NMR** (101 MHz, CDCl₃) δ 167.10, 162.90 (d, J = 247.6 Hz), 137.04 (d, J = 6.8 Hz), 130.35 (d, J = 7.9 Hz), 122.41 (d, J = 3.0 Hz), 118.49 (d, J = 21.3 Hz), 114.43 (d, J = 22.9 Hz), 27.05. **ESI-HR** calcd for C₈H₉FNO⁺ ([M+H]⁺) 154.0663, found 154.0659. **IR** v (cm⁻¹) 3325, 1638, 1542, 732. **M. P.** 92 °C.

N-CH₃

1d: ¹**H NMR** (400 MHz, CDCl₃) δ 7.75 (t, J = 1.8 Hz, 1H), 7.62 (dt, J = 7.7, 1.1 Hz, 1H), 7.49 – 7.41 (m, 1H), 7.39 – 7.31 (m, 1H), 6.53 – 6.13 (m, 1H), 3.00 (t, J = 4.9 Hz, 3H). ¹³**C NMR** (101 MHz, CDCl₃) δ 167.06, 136.56, 134.87, 131.51, 130.00, 127.38, 125.07, 27.05. **ESI-HR** calcd for C₈H₉ClNO⁺ ([M+H]⁺) 170.0367, found 170.0366. **IR** v (cm⁻¹) 3308, 1635, 1547, 733. **M. P.** 96 °C.



1e: ¹**H NMR** (400 MHz, CDCl₃) δ 7.90 (t, J = 1.7 Hz, 1H), 7.67 (d, J = 7.8 Hz, 1H), 7.61 (d, J = 8.0 Hz, 1H), 7.30 (t, J = 7.9 Hz, 1H), 6.32 (d, J = 113.3 Hz, 1H), 3.01 (d, J = 4.8 Hz, 3H). ¹³**C NMR** (101 MHz, CDCl₃) δ 166.94, 136.76, 134.43, 130.26, 130.25, 125.57, 122.86, 27.06. **ESI-HR** calcd for C₈H₉BrNO⁺ ([M+H]⁺) 213.9862, found 213.9861. **IR** v (cm⁻¹) 3306, 1633, 1545, 738. **M. P.** 82 °C.



1f: ¹**H NMR** (400 MHz, CDCl₃) δ 8.09 (s, 1H), 7.82 (d, J = 7.9 Hz, 1H), 7.71 (d, J = 7.8 Hz, 1H), 7.17 (t, J = 7.8 Hz, 1H), 6.08 (s, 1H), 3.01 (d, J = 4.9 Hz, 3H). ¹³**C NMR** (101 MHz, CDCl₃) δ 166.93, 140.34, 136.76, 136.12, 130.33, 126.25, 94.36, 27.09. **ESI-HR** calcd for C₈H₉INO⁺ ([M+H]⁺) 261.9723, found 261.9718. **IR** v (cm⁻¹) 3307, 1635, 1557, 734. **M. P.** 107 °C.



1g: ¹**H NMR** (400 MHz, CDCl₃) δ 7.63 (d, J = 8.6 Hz, 2H), 7.59 – 7.53 (m, 2H), 6.14 (s, 1H), 3.01 (d, J = 4.9 Hz, 3H). ¹³**C NMR** (101 MHz, CDCl₃) δ 167.37, 133.63, 131.94, 128.61, 126.16, 27.04. **ESI-HR** calcd for C₈H₉BrNO⁺ ([M+H]⁺) 213.9862, found 213.9860. **IR** v (cm⁻¹) 3342, 1637, 1556, 733. **M. P.** 162 °C.



1h: ¹**H NMR** (400 MHz, CDCl₃) δ 7.72 (d, J = 8.2 Hz, 2H), 7.37 (d, J = 8.2 Hz, 2H), 6.16 (s, 1H), 4.77 (s, 2H), 3.01 (d, J = 4.9 Hz, 3H), 0.94 (s, 9H), 0.10 (s, 6H). ¹³**C NMR** (101 MHz, CDCl₃) δ 168.24, 145.21, 133.36, 126.94, 126.10, 64.65, 26.96, 26.06, 18.55, -5.13. **ESI-HR** calcd for C₁₅H₂₆NO₂Si⁺ ([M+H]⁺) 280.1727, found 280.1722. **IR** v (cm⁻¹) 3324, 1634, 1549, 834. **M. P.** 63 °C.



1i: ¹**H NMR** (400 MHz, CDCl₃) δ 7.99 (d, J = 8.3 Hz, 2H), 7.84 (d, J = 8.4 Hz, 2H), 6.38 (d, J = 64.7 Hz, 1H), 3.03 (d, J = 4.9 Hz, 3H), 2.63 (s, 3H). ¹³**C NMR** (101 MHz, CDCl₃) δ 197.57, 167.36, 139.26, 138.67, 128.67, 127.31, 27.10, 26.93. **ESI-HR** calcd for C₁₀H₁₂NO₂⁺ ([M+H]⁺) 178.0863, found 178.0861. **IR** v (cm⁻¹) 3391, 1678, 1643, 1546, 764. **M. P.** 138 °C.



1j: ¹**H NMR** (400 MHz, CDCl₃) δ 8.20 – 7.97 (m, 2H), 7.92 – 7.71 (m, 2H), 6.35 (d, J = 86.9 Hz, 1H), 3.94 (s, 3H), 3.03 (d, J = 4.9 Hz, 3H). ¹³**C NMR** (101 MHz, CDCl₃) δ 167.48, 166.45, 138.68, 132.79, 129.99, 127.04, 52.52, 27.09. **ESI-HR** calcd for C₁₀H₁₂NO₃⁺ ([M+H]⁺) 194.0812, found 194.0814. **IR** v (cm⁻¹) 3365, 1723, 1635, 1550, 750. **M. P.** 133 °C.

1k: ¹**H NMR** (400 MHz, CDCl₃) δ 7.87 (d, J = 8.1 Hz, 2H), 7.69 (d, J = 7.6 Hz, 2H), 6.33 (d, J = 106.1 Hz, 1H), 3.04 (dd, J = 4.9, 1.4 Hz, 3H). ¹³**C NMR** (101 MHz, CDCl₃) δ 167.13, 138.02,

133.26 (q, J = 32.7 Hz), 127.47, 125.73 (q, J = 3.7 Hz), 125.06 (q, J = 272.3 Hz), 27.09. **ESI-HR** calcd for C₉H₉F₃NO⁺ ([M+H]⁺) 204.0631, found 204.0635. **IR** v (cm⁻¹) 3297, 1646, 1558, 748. **M. P.** 153 °C.



11: ¹**H NMR** (400 MHz, CDCl₃) δ 7.77 (d, J = 8.6 Hz, 2H), 7.13 (d, J = 8.6 Hz, 2H), 6.37 (s, 1H), 2.98 (d, J = 4.8 Hz, 3H), 2.30 (s, 3H). ¹³**C NMR** (101 MHz, CDCl₃) δ 169.16, 167.50, 153.09, 132.39, 128.41, 121.82, 26.99, 21.25. **ESI-HR** calcd for C₁₀H₁₂NO₃⁺ ([M+H]⁺) 194.0812, found 194.0818. **IR** v (cm⁻¹) 3324, 1755, 1647, 1558, 749. **M. P.** 148 °C.



1m: ¹**H NMR** (400 MHz, CDCl₃) δ 7.59 (s, 1H), 7.52 (t, J = 4.3 Hz, 1H), 7.29 (t, J = 6.2 Hz, 2H), 6.37 (s, 1H), 2.99 (dd, J = 4.8, 0.8 Hz, 3H), 2.37 (s, 3H). ¹³**C NMR** (101 MHz, CDCl₃) δ 168.57, 138.50, 134.77, 132.16, 128.52, 127.76, 123.89, 26.93, 21.47. **ESI-HR** calcd for C₉H₁₂NO⁺ ([M+H]⁺) 150.0913, found 150.0919. **IR** v (cm⁻¹) 3311, 1636, 1542, 749. **M. P.** 59 °C.



1n: ¹**H NMR** (400 MHz, CDCl₃) δ 7.67 (s, 1H), 7.47 – 7.40 (m, 1H), 7.40 – 7.33 (m, 1H), 6.18 (s, 1H), 3.01 (d, J = 4.9 Hz, 3H). ¹³**C NMR** (101 MHz, CDCl₃) δ 165.69 (d, J = 2.4 Hz), 162.68 (d, J = 252.7 Hz), 138.22 (d, J = 7.3 Hz), 125.99 (d, J = 3.3 Hz), 123.07 (d, J = 9.2 Hz), 122.05 (d, J = 24.5 Hz), 113.49 (d, J = 22.8 Hz), 27.17. **ESI-HR** calcd for C₈H₈BrFNO⁺ ([M+H]⁺) 231.9768, found 231.9780. **IR** v (cm⁻¹) 3326, 1637, 1579, 749. **M. P.** 117 °C.



10: ¹**H NMR** (400 MHz, CDCl₃) δ 6.60 (t, J = 3.7 Hz, 1H), 5.68 (s, 1H), 3.27 (dt, J = 13.4, 6.6 Hz, 2H), 2.29 – 2.19 (m, 2H), 2.18 – 2.11 (m, 2H), 1.77 – 1.47 (m, 6H), 0.93 (t, J = 7.4 Hz, 3H). ¹³**C NMR** (101 MHz, CDCl₃) δ 168.77, 133.46, 133.22, 41.38, 25.47, 24.48, 23.06, 22.32, 21.72, 11.55. **ESI-HR** calcd for C₁₀H₁₈NO⁺ ([M+H]⁺) 168.1383, found 168.1390. **IR** v (cm⁻¹) 3309, 1657, 1617, 749. **M. P.** 67 °C.



1p: ¹**H NMR** (400 MHz, CDCl₃) δ 7.83 – 7.72 (m, 2H), 7.60 – 7.53 (m, 2H), 7.53 – 7.48 (m, 1H), 7.44 (t, J = 7.5 Hz, 2H), 7.37 – 7.29 (m, 2H), 6.71 (t, J = 6.1 Hz, 1H), 4.95 – 4.81 (m, 1H), 4.33 (s, 2H), 4.11 (t, J = 9.0 Hz, 1H), 4.06 – 3.98 (m, 2H), 3.98 – 3.69 (m, 5H). ¹³**C NMR** (101 MHz, CDCl₃) δ 168.38, 166.94, 154.48, 137.47, 136.78, 133.64, 132.16, 128.84, 127.21, 126.35, 119.20, 72.10, 68.71, 64.25, 49.80, 47.87, 42.65. **ESI-HR** calcd for C₂₁H₂₂N₃O₅⁺ ([M+H]⁺) 396.1554, found 396.1561. **IR** v (cm⁻¹) 3338, 1749, 1653, 1517, 750. **M. P.** 203 °C.

Characterization of products:



3a: Following the general procedure, amide **1a** (13.5 mg, 0.100 mmol) was converted to the alkynylation product **3a**. Purification by silica gel chromatography gave 28.1 mg (89% yield) of **3a** as a white solid. ¹**H** NMR (400 MHz, CDCl₃) δ 8.12 (dd, J = 7.3, 1.3 Hz, 1H), 7.94 – 7.65 (m, 1H), 7.60 – 7.50 (m, 1H), 7.47 – 7.33 (m, 2H), 3.00 (d, J = 4.8 Hz, 3H), 1.16 (dd, J = 16.4, 3.8 Hz, 21H). ¹³**C** NMR (101 MHz, CDCl₃) δ 166.62, 135.39, 134.39, 130.49, 130.30, 129.14, 119.62, 105.85, 98.56, 26.78, 18.75, 11.38. **ESI-HR** calcd for C₁₉H₃₀NOSi⁺ ([M+H]⁺) 316.2091, found 316.2094. **IR** v (cm⁻¹) 3297, 2153, 1653, 1541, 751. **M. P.** 61 °C.



3b: Following the general procedure, amide **1b** (14.9 mg, 0.100 mmol) was converted to the alkynylation product **3b**. Purification by silica gel chromatography gave 29.3 mg (89% yield) of **3b** as a white solid. ¹**H NMR** (400 MHz, CDCl₃) δ 7.32 (d, J = 7.4 Hz, 1H), 7.21 – 7.11 (m, 2H), 5.84 (s, 1H), 2.97 (d, J = 4.9 Hz, 3H), 2.33 (s, 3H), 1.10 (s, 21H). ¹³**C NMR** (101 MHz, CDCl₃) δ 169.38, 139.73, 135.93, 130.65, 130.62, 128.77, 120.69, 104.64, 94.55, 26.72, 19.60, 18.80, 11.44. **ESI-HR** calcd for C₂₀H₃₂NOSi⁺ ([M+H]⁺) 330.2248, found 330.2247. **IR** v (cm⁻¹) 3269, 2152, 1636, 1567, 750. **M. P.** 209 °C.



3c: Following the general procedure, amide **1c** (14.9 mg, 0.100 mmol) was converted to the alkynylation product **3c**. Purification by silica gel chromatography gave 30.6 mg (93% yield) of **3c** as a white solid. ¹**H NMR** (400 MHz, CDCl₃) δ 7.94 (s, 1H), 7.80 (s, 1H), 7.43 (d, J = 7.8 Hz, 1H), 7.19 (dd, J = 7.8, 1.0 Hz, 1H), 2.99 (d, J = 4.8 Hz, 3H), 2.38 (s, 3H), 1.21 – 1.06 (m, 21H). ¹³**C NMR** (101 MHz, CDCl₃) δ 166.77, 139.59, 135.10, 134.41, 131.33, 130.86, 116.67, 106.10, 97.62, 26.79, 21.53, 18.77, 11.40. **ESI-HR** calcd for C₂₀H₃₂NOSi⁺ ([M+H]⁺) 330.2248, found 330.2239. **IR** v (cm⁻¹) 3307, 2148, 1654, 1540, 751. **M. P.** 88 °C.



3d: Following the general procedure, amide **1d** (15.3 mg, 0.100 mmol) was converted to the alkynylation product **3d**. Purification by silica gel chromatography gave 23.6 mg (71% yield) of **3d** as a white solid. ¹**H NMR** (400 MHz, CDCl₃) δ 8.02 – 7.77 (m, 2H), 7.53 (dd, J = 8.5, 5.5 Hz, 1H), 7.17 – 6.99 (m, 1H), 3.00 (d, J = 4.8 Hz, 3H), 1.24 – 1.05 (m, 21H). ¹³**C NMR** (101 MHz, CDCl₃) δ 165.18 (d, J = 1.9 Hz), 162.79 (d, J = 251.5 Hz), 137.82 (d, J = 7.6 Hz), 136.51 (d, J = 7.9 Hz), 118.04 (d, J = 22.3 Hz), 117.50 (d, J = 24.3 Hz), 115.74 (d, J = 3.6 Hz), 104.87, 98.59 (d, J = 1.4 Hz), 26.89, 18.76, 11.38. **ESI-HR** calcd for C₁₉H₂₉FNOSi⁺ ([M+H]⁺) 334.1997, found 334.1994. **IR** v (cm⁻¹) 3295, 2151, 1656, 1543, 745. **M. P.** 71 °C.



3e: Following the general procedure, amide **1e** (17.0 mg, 0.100 mmol) was converted to the alkynylation product **3e**. Purification by silica gel chromatography gave 23.4 mg (67% yield) of **3e** as a white solid. ¹**H NMR** (400 MHz, CDCl₃) δ 8.12 (d, J = 2.2 Hz, 1H), 7.79 (s, 1H), 7.47 (d, J = 8.3 Hz, 1H), 7.36 (dd, J = 8.3, 2.3 Hz, 1H), 3.00 (d, J = 4.8 Hz, 3H), 1.20 – 1.10 (m, 21H). ¹³**C NMR** (101 MHz, CDCl₃) δ 165.27, 136.84, 135.58, 135.54, 130.69, 130.50, 118.03, 104.76, 99.91, 26.90, 18.75, 11.37. **ESI-HR** calcd for C₁₉H₂₉CINOSi⁺ ([M+H]⁺) 350.1701, found 350.1704. **IR** v (cm⁻¹) 3297, 2153, 1655, 1543, 730. **M. P.** 78 °C.



3f: Following the general procedure, amide **1f** (21.4 mg, 0.100 mmol) was converted to the alkynylation product **3f**. Purification by silica gel chromatography gave 34.8 mg (88% yield) of **3f** as a white solid. ¹**H NMR** (400 MHz, CDCl₃) δ 8.27 (d, J = 2.0 Hz, 1H), 7.76 (s, 1H), 7.51 (dd, J = 8.2, 2.1 Hz, 1H), 7.39 (d, J = 8.2 Hz, 1H), 2.99 (d, J = 4.8 Hz, 3H), 1.18 – 1.10 (m, 21H). ¹³**C NMR** (101 MHz, CDCl₃) δ 165.18, 136.88, 135.62, 133.60, 133.38, 123.62, 118.48, 104.81, 100.10, 26.89, 18.74, 11.36. **ESI-HR** calcd for C₁₉H₂₉BrNOSi⁺ ([M+H]⁺) 394.1196, found 394.1197. **IR** v (cm⁻¹) 3295, 2152, 1654, 1542, 730. **M. P.** 95 °C.

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3g: Following the general procedure, amide **1g** (26.1 mg, 0.100 mmol) was converted to the alkynylation product **3f**. Purification by silica gel chromatography gave 39.9 mg (90% yield) of **3g** as a light yellow solid. ¹**H NMR** (400 MHz, CDCl₃) δ 8.45 (d, J = 1.3 Hz, 1H), 7.71 (dd, J = 8.1, 1.5 Hz, 2H), 7.23 (d, J = 8.1 Hz, 1H), 2.98 (d, J = 4.8 Hz, 3H), 1.33 – 1.00 (m, 21H). ¹³**C NMR** (101 MHz, CDCl₃) δ 165.12, 139.46, 139.22, 136.61, 135.49, 119.05, 104.93, 100.35, 95.11, 26.89, 18.75, 11.35. **ESI-HR** calcd for C₁₉H₂₉INOSi⁺ ([M+H]⁺) 442.1058, found 442.1056. **IR** v (cm⁻¹) 3307, 2149, 1654, 1541, 748. **M. P.** 105 °C.



3h: Following the general procedure, amide **1h** (19.3 mg, 0.100 mmol) was converted to the alkynylation product **3h**. Purification by silica gel chromatography gave 33.5 mg (90% yield) of **3h** as a yellow oil. ¹**H NMR** (400 MHz, CDCl₃) δ 8.15 (d, J = 8.7 Hz, 1H), 7.72 (s, 1H), 7.16 (dd, J = 8.7, 2.4 Hz, 1H), 2.99 (d, J = 4.8 Hz, 3H), 2.30 (s, 3H), 1.18 – 1.11 (m, 21H). ¹³**C NMR** (101 MHz, CDCl₃) δ 168.90, 165.84, 151.99, 133.05, 132.02, 126.97, 122.75, 121.02, 104.81, 99.69, 26.83, 21.18, 18.74, 11.35. **ESI-HR** calcd for C₂₁H₃₂NO₃Si⁺ ([M+H]⁺) 374.2146, found 374.2136. **IR** v (cm⁻¹) 3307, 2150, 1769, 1653, 1541, 751.



3i: Following the general procedure, amide **1i** (27.9 mg, 0.100 mmol) was converted to the alkynylation product **3i**. Purification by silica gel chromatography gave 32.2 mg (70% yield) of **3i** as a white solid. ¹**H NMR** (400 MHz, CDCl₃) δ 8.11 (d, J = 8.2 Hz, 1H), 7.89 (d, J = 25.3 Hz, 1H), 7.52 (s, 1H), 7.34 (d, J = 8.1 Hz, 1H), 4.74 (s, 2H), 3.00 (M, 3H), 1.16 (dd, J = 11.5, 4.2 Hz, 21H), 0.94 (s, 9H), 0.10 (s, 6H). ¹³**C NMR** (101 MHz, CDCl₃) δ 166.47, 144.40, 133.69, 131.65, 130.43, 126.47, 119.49, 106.27, 98.35, 63.99, 26.75, 25.99, 18.76, 18.47, 11.39, -5.19. **ESI-HR** calcd for

C₂₆H₄₆NO₂Si₂⁺ ([M+H]⁺) 460.3062, found 460.3061. **IR** v (cm⁻¹) 3308, 2147, 1666, 1540, 751. **M. P.** 84 °C.



3j: Following the general procedure, amide **1j** (21.4 mg, 0.100 mmol) was converted to the alkynylation product **3j**. Purification by silica gel chromatography gave 31.8 mg (81% yield) of **3j** as a yellow solid. ¹**H NMR** (400 MHz, CDCl₃) δ 8.00 (d, J = 8.5 Hz, 1H), 7.73 (S, 1H), 7.66 (d, J = 2.0 Hz, 1H), 7.55 (dd, J = 8.5, 2.0 Hz, 1H), 2.99 (d, J = 4.8 Hz, 3H), 1.19 – 1.08 (m, 21H). ¹³C **NMR** δ 165.73, 136.62, 134.19, 132.43, 131.99, 124.81, 121.34, 104.30, 100.43, 26.86, 18.75, 11.34. **ESI-HR** calcd for C₁₉H₂₉BrNOSi⁺ ([M+H]⁺) 394.1196, found 394.1197. **IR** v (cm⁻¹) 3304, 2154, 1650, 1582, 880. **M. P.** 83 °C.



3k: Following the general procedure, amide **1k** (20.3 mg, 0.100 mmol) was converted to the alkynylation product **3k**. Purification by silica gel chromatography gave 30.5 mg (80% yield) of **3k** as a yellow solid. ¹**H NMR** (400 MHz, CDCl₃) δ 8.22 (d, J = 8.3 Hz, 1H), 7.75 (s, 1H), 7.73 – 7.54 (m, 2H), 3.02 (d, J = 4.8 Hz, 3H), 1.19 – 1.12 (m, 21H). ¹³**C NMR** (101 MHz, CDCl₃) δ 165.47, 138.52, 132.64 (q, J = 33.1 Hz), 131.08 (m, two overlapping peaks), 125.59 (q, J = 3.6 Hz), 123.59 (q, 272.8 Hz), 120.48, 104.12, 100.75, 26.95, 18.76, 11.35. **ESI-HR** calcd for C₂₀H₂₉F₃NOSi⁺ ([M+H]⁺) 384.1965, found 384.1959. **IR** v (cm⁻¹) 3282, 2163, 1649, 1558, 752. **M. P.** 65 °C.



3I: Following the general procedure, amide **1I** (17.7 mg, 0.100 mmol) was converted to the alkynylation product **3I**. Purification by silica gel chromatography gave 33.1 mg (92% yield) of **3I** as a yellow oil. ¹**H NMR** (400 MHz, CDCl₃) δ 8.19 (d, J = 8.2 Hz, 1H), 8.07 (d, J = 1.4 Hz, 1H), 7.93 (dd, J = 8.2, 1.6 Hz, 1H), 7.74 (s, 1H), 3.01 (d, J = 4.8 Hz, 3H), 2.62 (s, 3H), 1.19 – 1.09 (m, 21H). ¹³**C NMR** (101 MHz, CDCl₃) δ 196.89, 165.77, 138.99, 138.35, 134.07, 130.80, 128.49, 120.23, 104.70, 99.93, 26.91 (*two overlapping peaks*), 18.76, 11.35. **ESI-HR** calcd for C₂₁H₃₂NO₂Si⁺ ([M+H]⁺) 358.2197, found 358.2194. **IR** v (cm⁻¹) 3294, 2155, 1691, 1653, 1542, 750.



3m: Following the general procedure, amide **1m** (19.3 mg, 0.100 mmol) was converted to the alkynylation product **3m**. Purification by silica gel chromatography gave 32.8 mg (88% yield) of **3m** as a yellow oil. ¹**H NMR** (400 MHz, CDCl₃) δ 8.16 (d, J = 8.6 Hz, 2H), 8.03 (dd, J = 8.2, 1.5 Hz, 1H), 7.78 (S, 1H), 3.94 (s, 3H), 3.01 (d, J = 4.8 Hz, 3H), 1.18 – 1.09 (m, 21H). ¹³**C NMR** (101 MHz, CDCl₃) δ 165.86, 165.82, 139.06, 135.45, 132.03, 130.53, 129.73, 119.99, 104.65, 99.76, 52.64, 26.91, 18.76, 11.35. **ESI-HR** calcd for C₂₁H₃₂NO₃Si⁺ ([M+H]⁺) 374.2146, found 374.2143. **IR** v (cm⁻¹) 3293, 2155, 1729, 1652, 1542, 750.



3n: Following the general procedure, amide **1n** (23.2 mg, 0.100 mmol) was converted to the alkynylation product **3n**. Purification by silica gel chromatography gave 21.8 mg (53% yield) of **3n** as a white solid. ¹H NMR (400 MHz, CDCl₃) δ 8.08 (dd, J = 1.8, 1.2 Hz, 1H), 7.71 (s, 1H), 7.37 (dd, J = 8.0, 2.0 Hz, 1H), 3.00 (d, J = 4.8 Hz, 3H), 1.19 – 1.10 (m, 21H). ¹³C NMR (101 MHz, CDCl₃) δ 164.25 (d, J = 2.9 Hz), 163.98 (d, J = 256.8 Hz), 138.04, 129.21 (d, J = 3.4 Hz), 123.19 (d, J = 9.8 Hz), 121.25 (d, J = 25.0 Hz), 108.09 (d, J = 17.6 Hz), 107.08 (d, J = 4.8 Hz), 97.32, 26.99, 18.70, 11.29. **ESI-HR** calcd for C₁₉H₂₈BrFNOSi⁺ ([M+H]⁺) 412.1102, found 412.1101. **IR** v (cm⁻¹) 3293, 2162, 1652, 1558, 750. **M. P.** 89 °C.



3o: Following the general procedure, amide **1o** (16.7 mg, 0.100 mmol) was converted to the alkynylation product **3o**. Purification by silica gel chromatography gave 31.7 mg (91% yield) of **3o** as a white solid. ¹**H NMR** (400 MHz, CDCl₃) δ 7.18 (s, 1H), 3.28 (dd, J = 13.7, 6.6 Hz, 2H), 2.37 (d, J = 43.5 Hz, 4H), 1.66 – 1.50 (m, 6H), 1.08 (s, 21H), 0.92 (t, J = 7.4 Hz, 3H). ¹³**C NMR** (101 MHz, CDCl₃) δ 167.87, 139.93, 121.02, 106.74, 99.05, 41.53, 32.37, 26.47, 23.02, 22.09, 21.90, 18.77, 11.71, 11.36. **ESI-HR** calcd for C21H38NOSi+ ([M+H]⁺) 348.2717, found 348.2718. **IR** v (cm⁻¹) 3306, 2138, 1644, 1540, 750.



3p: Following the general procedure, amide **1p** (39.5 mg, 0.100 mmol) was converted to the alkynylation product **3p**. Purification by silica gel chromatography gave 48.0 mg (83% yield) of **3p**

as a white solid. ¹**H** NMR (400 MHz, CDCl₃) δ 8.14 (t, J = 6.1 Hz, 1H), 8.07 – 7.98 (m, 1H), 7.63 – 7.54 (m, 3H), 7.47 – 7.40 (m, 2H), 7.36 – 7.29 (m, 2H), 4.96 – 4.81 (m, 1H), 4.33 (s, 2H), 4.10 (t, J = 8.9 Hz, 1H), 4.06 – 3.99 (m, 2H), 3.98 – 3.86 (m, 2H), 3.81 – 3.71 (m, 3H), 1.26 – 1.10 (m, 21H). ¹³C NMR (101 MHz, CDCl₃) δ 167.21, 166.87, 154.24, 137.31, 136.98, 134.78, 134.27, 131.16, 130.27, 129.18, 126.28, 120.12, 119.09, 105.35, 99.67, 71.97, 68.72, 64.26, 49.81, 48.15, 42.97, 18.83, 11.37. **ESI-HR** calcd for C₃₂H₄₂N₃O₅Si⁺ ([M+H]⁺) 576.2888, found 576.2899. **IR** v (cm⁻¹) 3295, 2154, 1749, 1652, 1516, 750. **M. P.** 171 °C.



3s: Following the general procedure, amide **1a** (6.8 mg, 0.050 mmol) and alkyne **2d** (21.1 mg, 0.150 mmol) were converted to the alkynylation product **3s**. Purification by silica gel chromatography gave 5.1 mg (37% yield) of **3s** as a white solid. ¹**H NMR** (400 MHz, CDCl₃) δ 8.11 (dd, J = 7.6, 1.5 Hz, 1H), 7.67 (s, 1H), 7.54 (dd, J = 7.3, 1.6 Hz, 1H), 7.41 (m, 2H), 3.01 (t, J = 5.4 Hz, 3H), 1.01 (s, 9H), 0.25 – 0.20 (m, 6H). ¹³**C NMR** (101 MHz, CDCl₃) δ 166.69, 135.74, 134.07, 130.51, 130.30 , 129.28, 119.43, 104.58, 100.18, 26.72, 26.23, 16.78, -4.48. **ESI-HR** calcd for C₁₆H₂₄NOSi⁺ ([M+H]⁺) 274.1622, found 274.1618. **IR** v (cm⁻¹) 3307, 2158, 1651, 1541, 776. **M. P.** 62 °C.



3t: Following the general procedure, amide **1a** (6.8 mg, 0.050 mmol) and alkyne **2e** (39.7 mg, 0.150 mmol) were converted to the alkynylation product **3t**. Purification by silica gel chromatography gave 11.3 mg (56% yield) of **3t** as a white solid. ¹**H NMR** (400 MHz, CDCl₃) δ 8.12 (d, J = 7.1 Hz, 1H), 7.82 (d, J = 6.3 Hz, 4H), 7.68 (d, J = 6.7 Hz, 1H), 7.57 – 7.35 (m, 9H), 2.76 (d, J = 4.5 Hz, 3H),

1.17 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 166.64, 136.14, 135.68, 134.30, 132.71, 130.57, 130.37, 130.06, 129.68, 128.16, 119.19, 107.45, 97.32, 27.27, 26.75, 18.87. **ESI-HR** calcd for C₂₆H₂₈NOSi⁺ ([M+H]⁺) 398.1935, found 398.1938. **IR** ν (cm⁻¹) 3306, 2159, 1646, 1540, 757. **M. P.** 146 °C.



4a: Following the general procedure, amide **1a** (13.5 mg, 0.100 mmol) was converted to the alkenylation product **4a**. Purification by silica gel chromatography gave 20.5 mg (65% yield) of **4a** as a yellow solid. ¹**H NMR** (400 MHz, CDCl₃) δ 7.55 (d, J = 7.8 Hz, 1H), 7.47 (d, J = 7.6 Hz, 1H), 7.39 (t, J = 7.5 Hz, 1H), 7.29 (d, J = 7.4 Hz, 1H), 7.23 (d, J = 19.4 Hz, 1H), 6.36 (d, J = 19.3 Hz, 1H), 5.77 (s, 1H), 2.97 (d, J = 4.9 Hz, 3H), 1.19 – 1.06 (m, 21H). ¹³**C NMR** (101 MHz, CDCl₃) δ 170.18, 143.61, 137.26, 135.40, 130.19, 128.62, 127.86, 127.76, 126.51, 26.85, 18.80, 11.11. **ESI-HR** calcd for C₁₉H₃₂NOSi⁺ ([M+H]⁺) 318.2248, found 318.2246. **IR** v (cm⁻¹) 3281, 1637, 1541, 750. **M. P.** 80 °C.



4b: Following the general procedure, amide **1b** (14.9 mg, 0.100 mmol) was converted to the alkenylation product **4b**. Purification by silica gel chromatography gave 5.8 mg (18% yield) of **4b** as a yellow solid. ¹**H NMR** (400 MHz, CDCl₃) δ 7.42 (d, J = 7.8 Hz, 1H), 7.25 – 7.20 (m, 1H), 7.10 (d, J = 7.5 Hz, 1H), 7.00 (d, J = 19.3 Hz, 1H), 6.34 (d, J = 19.3 Hz, 1H), 5.61 (d, J = 3.9 Hz, 1H), 2.98 (d, J = 4.9 Hz, 3H), 2.33 (s, 3H), 1.18 – 1.05 (m, 21H). ¹³C **NMR** (101 MHz, CDCl₃) δ 170.63, 143.20, 136.37, 136.31, 134.97, 129.58, 129.03, 127.67, 122.90, 26.54, 19.27, 18.78, 11.10. **ESI-HR** calcd for C₂₀H₃₄NOSi⁺ ([M+H]⁺) 332.2404, found 332.2405. **IR** v (cm⁻¹) 3256, 1634, 1559, 750. **M. P.** 171 °C.



4c: Following the general procedure, amide **1c** (14.9 mg, 0.100 mmol) was converted to the alkenylation product **4c**. Purification by silica gel chromatography gave 30.9 mg (93% yield) of **4c** as a light yellow solid.¹**H NMR** (400 MHz, CDCl₃) δ 7.45 (d, J = 8.0 Hz, 1H), 7.31 (s, 1H), 7.25 – 7.09 (m, 2H), 6.30 (d, J = 19.4 Hz, 1H), 5.71 (s, 1H), 3.11 – 2.84 (m, 3H), 2.35 (s, 3H), 1.26 – 1.03 (m, 21H). ¹³**C NMR** (101 MHz, CDCl₃) δ 170.31, 143.51, 137.91, 135.26, 134.51, 130.98, 128.32, 127.41, 126.48, 26.84, 21.14, 18.81, 11.12. **ESI-HR** calcd for C₂₀H₃₄NOSi⁺ ([M+H]⁺) 332.2404, found 332.2398. **IR** v (cm⁻¹) 3292, 1637, 1541, 750. **M. P.** 96 °C.



4d: Following the general procedure, amide **1d** (15.3 mg, 0.100 mmol) was converted to the alkenylation product **4d**. Purification by silica gel chromatography gave 21.4 mg (64% yield) of **4d** as a white solid. ¹**H NMR** (400 MHz, CDCl₃) δ 7.28 – 7.19 (m, 2H), 7.13 – 7.07 (m, 1H), 6.94 (d, J = 19.9 Hz, 1H), 6.41 (d, J = 19.9 Hz, 1H), 5.80 (s, 1H), 2.93 (d, J = 4.9 Hz, 2H), 1.19 – 1.06 (m, 15H). ¹³**C NMR** (101 MHz, CDCl₃) δ 169.28 (d, J = 3.2 Hz), 160.34 (d, J = 250.2 Hz), 137.64 (d, J = 2.4 Hz), 136.48, 135.17 (d, J = 5.8 Hz), 128.59 (d, J = 9.0 Hz), 125.50 (d, J = 13.3 Hz), 123.67 (d, J = 3.6 Hz), 117.48 (d, J = 23.4 Hz), 26.91, 18.75, 10.97. **ESI-HR** calcd for C₁₉H₃₁FNOSi⁺ ([M+H]⁺) 336.2153, found 336.2154. **IR** v (cm⁻¹) 3274, 1637, 1558, 750. **M. P.** 85 °C.

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4e: Following the general procedure, amide **1e** (17.0 mg, 0.100 mmol) was converted to the alkenylation product **4e**. Purification by silica gel chromatography gave 11.2 mg (32% yield) of **4e** as a white solid. ¹**H NMR** (400 MHz, CDCl₃) δ 7.49 (d, J = 8.4 Hz, 1H), 7.46 (d, J = 2.2 Hz, 1H), 7.35 (dd, J = 8.4, 2.0 Hz, 1H), 7.15 (d, J = 19.3 Hz, 1H), 6.35 (d, J = 19.3 Hz, 1H), 5.74 (s, 1H), 2.97 (d, J = 4.9 Hz, 3H), 1.18 – 1.03 (m, 21H). ¹³**C NMR** (101 MHz, CDCl₃) δ 168.72, 142.32, 136.65, 135.74, 133.70, 130.28, 129.59, 127.97, 127.76, 26.91, 18.79, 11.12. **ESI-HR** calcd for C₁₉H₃₁ClNOSi⁺ ([M+H]⁺) 352.1858, found 352.1853. **IR** v (cm⁻¹) 3274, 1637, 1558, 750. **M. P.** 79 °C.



4f: Following the general procedure, amide **1f** (21.4 mg, 0.100 mmol) was converted to the alkenylation product **4f**. Purification by silica gel chromatography gave 18.4 mg (46% yield) of **4f** as a yellow solid. ¹**H NMR** (400 MHz, CDCl₃) δ 7.60 (d, J = 1.8 Hz, 1H), 7.50 (dd, J = 8.4, 1.6 Hz, 1H), 7.42 (d, J = 8.4 Hz, 1H), 7.14 (d, J = 19.4 Hz, 1H), 6.36 (d, J = 19.3 Hz, 1H), 5.76 (s, 1H), 2.96 (d, J = 4.9 Hz, 3H), 1.21 – 1.05 (m, 21H). ¹³**C NMR** (101 MHz, CDCl₃) δ 168.58, 142.37, 136.89, 136.16, 133.21, 130.64, 129.70, 128.16, 121.66, 26.91, 18.79, 11.10. **ESI-HR** calcd for C₁₉H₃₁BrNOSi⁺ ([M+H]⁺) 396.1353, found 396.1345. **IR** v (cm⁻¹) 3270, 1636, 1557, 751. **M. P.** 116 °C.



4g: Following the general procedure, amide **1g** (26.1 mg, 0.100 mmol) was converted to the alkenylation product **4g**. Purification by silica gel chromatography gave 19.0 mg (43% yield) of **4g** as a yellow solid. ¹**H NMR** (400 MHz, CDCl₃) δ 7.79 (d, J = 1.6 Hz, 1H), 7.70 (dd, J = 8.3, 1.1 Hz, 1H), 7.28 (d, J = 8.4 Hz, 1H), 7.13 (d, J = 19.3 Hz, 1H), 6.36 (d, J = 19.3 Hz, 1H), 5.75 (s, 1H), 2.96

(d, J = 4.9 Hz, 3H), 1.20 – 1.06 (m, 21H). ¹³C NMR (101 MHz, CDCl₃) δ 168.44, 142.46, 139.12, 137.05, 136.70, 136.46, 129.78, 128.20, 92.94, 26.91, 18.79, 11.10. ESI-HR calcd for C₁₉H₃₁INOSi⁺ ([M+H]⁺) 444.1214, found 444.1199. IR v (cm⁻¹) 3271, 1637, 1557, 750. M. P. 150 °C.



4h: Following the general procedure, amide **1h** (19.3 mg, 0.100 mmol) was converted to the alkenylation product **4h**. Purification by silica gel chromatography gave 16.2 mg (43% yield) of **4h** as a yellow solid. ¹**H** NMR (400 MHz, CDCl₃) δ 7.49 (d, J = 8.3 Hz, 1H), 7.24 (d, J = 2.1 Hz, 1H), 7.20 (d, J = 19.3 Hz, 1H), 7.02 (dd, J = 8.3, 2.1 Hz, 1H), 6.35 (d, J = 19.3 Hz, 1H), 5.74 (s, 1H), 2.96 (d, J = 4.9 Hz, 3H), 2.32 (s, 3H), 1.21 – 1.06 (m, 21H). ¹³C NMR (101 MHz, CDCl₃) δ 169.43, 169.41, 152.07, 142.63, 139.08, 133.08, 129.88, 129.23, 121.15, 119.36, 26.92, 21.26, 18.78, 11.10. **ESI-HR** calcd for C₂₁H₃₄NO₃Si⁺ ([M+H]⁺) 376.2302, found 376.2292. **IR** v (cm⁻¹) 3292, 1758, 1646, 1541, 751. **M. P.** 106 °C.



4i: Following the general procedure, amide **1i** (27.9 mg, 0.100 mmol) was converted to the alkenylation product **4i**. Purification by silica gel chromatography gave 18.2 mg (39% yield) of **4i** as a light yellow solid. ¹**H NMR** (400 MHz, CDCl₃) δ 7.53 (d, J = 8.4 Hz, 1H), 7.47 (d, J = 7.9 Hz, 1H), 7.29 – 7.20 (m, 2H), 6.37 (d, J = 19.3 Hz, 1H), 5.72 (s, 1H), 4.77 (s, 1H), 2.97 (d, J = 4.9 Hz, 2H), 1.22 – 1.05 (m, 11H), 0.95 (s, 5H), 0.11 (s, 3H). ¹³**C NMR** (101 MHz, CDCl₃) δ 170.10, 143.84, 143.83, 137.35, 133.85, 128.56, 127.91, 125.22, 123.88, 64.52, 26.88, 26.05, 18.81, 18.53, 11.11, -5.11. **ESI-HR** calcd for C₂₆H₄₈NO₂Si₂⁺ ([M+H]⁺) 462.3218, found 462.3201. **IR** v (cm⁻¹) 3292, 1647, 1541, 750. **M. P.** 108 °C.



4j: Following the general procedure, amide **1j** (21.4 mg, 0.100 mmol) was converted to the alkenylation product **4j**. Purification by silica gel chromatography gave 19.1 mg (48% yield) of **4j** as a white solid. ¹**H NMR** (400 MHz, CDCl₃) δ 7.66 (d, J = 1.7 Hz, 1H), 7.41 (dd, J = 8.2, 1.8 Hz, 1H), 7.35 (d, J = 8.2 Hz, 1H), 7.15 (d, J = 19.3 Hz, 1H), 6.37 (d, J = 19.3 Hz, 1H), 5.73 (s, 1H), 2.96 (d, J = 4.9 Hz, 3H), 1.24 – 1.05 (m, 21H). ¹³**C NMR** (101 MHz, CDCl₃) δ 169.21, 142.15, 139.21, 134.11, 130.77, 130.63, 129.44, 129.41, 124.66, 26.91, 18.79, 11.10. **ESI-HR** calcd for C₁₉H₃₁BrNOSi⁺ ([M+H]⁺) 396.1353, found 396.1341. **IR** v (cm⁻¹) 3274, 1646, 1578, 750. **M. P.** 126 °C.



4k: Following the general procedure, amide **1k** (20.3 mg, 0.100 mmol) was converted to the alkenylation product **4k**. Purification by silica gel chromatography gave 18.6 mg (48% yield) of **4k** as a white solid. ¹**H NMR** (400 MHz, CDCl₃) δ 7.77 (s, 1H), 7.62 – 7.48 (m, 2H), 7.20 (d, J = 19.4 Hz, 1H), 6.45 (d, J = 19.4 Hz, 1H), 5.76 (s, 1H), 2.99 (d, J = 4.9 Hz, 3H), 1.23 – 1.06 (m, 21H). ¹³**C NMR** (101 MHz, CDCl₃) δ 168.84, 141.84, 138.27, 137.72, 132.15 (q, J = 32.5 Hz), 131.04, 128.15, 124.22 (q, J = 3.7 Hz), 123.69 (q, J = 273.7 Hz), 123.14 (q, J = 3.7 Hz), 26.76, 18.62, 10.95. **ESI-HR** calcd for C₂₀H₃₁F₃NOSi⁺ ([M+H]⁺) 386.2122, found 386.2113. **IR** v (cm⁻¹) 3274, 1645, 1558, 749. **M. P.** 114 °C.



41: Following the general procedure, amide **11** (17.7 mg, 0.100 mmol) was converted to the alkenylation product **41**. Purification by silica gel chromatography gave 14.9 mg (42% yield) of **41** as a yellow oil. ¹**H NMR** (400 MHz, CDCl₃) δ 8.11 (d, J = 1.4 Hz, 1H), 7.83 (dd, J = 7.9, 1.6 Hz, 1H), 7.55 (d, J = 7.9 Hz, 1H), 7.21 (d, J = 19.4 Hz, 1H), 6.47 (d, J = 19.3 Hz, 1H), 5.78 (s, 1H), 2.99 (d, J = 4.9 Hz, 3H), 2.63 (s, 2H), 1.24 – 1.05 (m, 21H). ¹³**C NMR** (101 MHz, CDCl₃) δ 197.78, 169.35, 142.48, 139.28, 138.36, 137.61, 130.50, 128.11, 127.52, 126.18, 26.96, 26.89, 18.79, 11.11. **ESI-HR** calcd for C₂₁H₃₄NO₂Si⁺ ([M+H]⁺) 360.2353, found 360.2341. **IR** v (cm⁻¹) 3291, 1686, 1647, 1557, 750.



4m: Following the general procedure, amide **1m** (19.3 mg, 0.100 mmol) was converted to the alkenylation product **4m**. Purification by silica gel chromatography gave 17.5 mg (47% yield) of **4m** as a colorless oil. ¹**H** NMR (400 MHz, CDCl₃) δ 8.20 (s, 1H), 7.92 (dd, J = 8.0, 1.4 Hz, 1H), 7.51 (d, J = 8.0 Hz, 1H), 7.19 (d, J = 19.4 Hz, 1H), 6.47 (d, J = 19.4 Hz, 1H), 5.78 (s, 1H), 3.94 (s, 3H), 2.98 (d, J = 4.9 Hz, 3H), 1.20 – 1.07 (m, 21H). ¹³**C** NMR (101 MHz, CDCl₃) δ 169.44, 166.63, 142.34, 139.23, 137.35, 131.69, 130.30, 128.65, 127.87, 127.64, 52.53, 26.89, 18.80, 11.11. **ESI-HR** calcd for C₂₁H₃₄NO₃Si⁺ ([M+H]⁺) 376.2302, found 376.2296. **IR** v (cm⁻¹) 3274, 1726, 1647, 1558, 750.



4n: Following the general procedure, amide **1n** (23.2 mg, 0.100 mmol) was converted to the alkenylation product **4n**. Purification by silica gel chromatography gave 24.3 mg (59% yield) of **4n** as a light yellow solid. ¹**H NMR** (400 MHz, CDCl₃) δ 7.41 (d, J = 0.4 Hz, 1H), 7.28 (dd, J = 10.0, 2.0 Hz, 1H), 6.85 (d, J = 19.9 Hz, 1H), 6.41 (d, J = 19.9 Hz, 1H), 5.80 (s, 1H), 2.93 (d, J = 4.9 Hz, 3H), 1.20 – 1.05 (m, 21H). ¹³**C NMR** (101 MHz, CDCl₃) δ 167.76 (d, J = 3.4 Hz), 160.14 (d, J = 255.1 Hz), 138.64 (d, J = 2.9 Hz), 136.17 (d, J = 5.8 Hz), 135.48, 126.88 (d, J = 3.7 Hz), 124.65 (d, J = 13.3 Hz), 120.90 (d, J = 26.5 Hz), 120.90 (d, J = 10.2 Hz), 26.97, 18.72, 10.93. **ESI-HR** calcd for C₁₉H₃₀BrFNOSi⁺ ([M+H]⁺) 414.1259, found 414.1267. **IR** v (cm⁻¹) 3272, 1641, 1558, 750. **M**. **P**. 124 °C.



4o: Following the general procedure, amide **1o** (16.7 mg, 0.100 mmol) was converted to the alkenylation product **4o**. Purification by silica gel chromatography gave 24.2 mg (69% yield) of **4o** as a yellow solid. ¹**H NMR** (400 MHz, CDCl₃) δ 6.88 (d, J = 19.3 Hz, 1H), 5.82 (d, J = 19.3 Hz, 1H), 5.54 (s, 1H), 3.29 (dt, J = 14.0, 6.3 Hz, 2H), 2.29 (d, J = 54.8 Hz, 4H), 1.73 – 1.63 (m, 4H), 1.54 (td, J = 14.4, 7.1 Hz, 2H), 1.16 – 0.98 (m, 21H), 0.94 (t, J = 7.4 Hz, 3H). ¹³**C NMR** (101 MHz, CDCl₃) δ 171.79, 144.02, 135.69, 134.54, 123.68, 41.44, 27.99, 24.53, 23.06, 22.24, 22.22, 18.83, 11.66, 11.10. **ESI-HR** calcd for C₂₁H₄₀NOSi⁺ ([M+H]⁺) 350.2874, found 350.2877. **IR** v (cm⁻¹) 3272, 1635, 1621, 750. **M. P.** 101 °C.



4p: Following the general procedure, amide **1p** (39.5 mg, 0.100 mmol) was converted to the alkenylation product **4p**. Purification by silica gel chromatography gave 33.4 mg (58% yield) of **4p** as a yellow solid. ¹**H NMR** (400 MHz, CDCl₃) δ 7.63 – 7.52 (m, 3H), 7.41 (t, J = 7.6 Hz, 1H), 7.34 (t, J = 7.5 Hz, 3H), 7.29 – 7.22 (m, 3H), 6.48 (dd, J = 13.8, 6.0 Hz, 1H), 6.38 (d, J = 19.3 Hz, 1H), 4.94 – 4.76 (m, 1H), 4.30 (d, J = 1.7 Hz, 2H), 4.08 (tt, J = 8.8, 4.4 Hz, 1H), 4.05 – 3.98 (m, 2H), 3.92 – 3.82 (m, 2H), 3.78 – 3.66 (m, 3H), 1.19 – 1.05 (m, 21H). ¹³**C NMR** (101 MHz, CDCl₃) δ 170.41, 166.87, 154.30, 142.96, 137.59, 137.41, 136.75, 134.14, 130.69, 128.75, 127.84, 127.46, 126.63, 126.29, 119.06, 71.89, 68.65, 64.21, 49.75, 47.88, 42.74, 18.81, 11.10. **ESI-HR** calcd for C₃₂H₄₄N₃O₅Si⁺ ([M+H]⁺) 578.3045, found 578.3048. **IR** v (cm⁻¹) 3307, 1749, 1653, 1516, 750. **M**. **P**. 185 °C.

4s: Following the general procedure, amide **1a** (6.8 mg, 0.050 mmol) and alkyne **2d** (21.1 mg, 0.150 mmol) were converted to the alkenylation product **4s**. Purification by silica gel chromatography gave 4.6 mg (33% yield) of **4s** as a white solid. ¹**H NMR** (400 MHz, CDCl₃) δ 7.56 (d, J = 7.8 Hz, 1H), 7.51 – 7.44 (m, 1H), 7.39 (t, J = 7.6 Hz, 1H), 7.29 (t, J = 6.8 Hz, 1H), 7.17 (d, J = 19.1 Hz, 1H), 6.44 (d, J = 19.1 Hz, 1H), 5.72 (s, 1H), 2.99 (d, J = 4.9 Hz, 3H), 0.92 (s, 9H), 0.11 (s, 6H). ¹³**C NMR** (101 MHz, CDCl₃) δ 170.17, 142.82, 136.96, 135.41, 131.30, 130.23, 127.94, 127.78, 126.56, 26.86, 26.63, 16.89, -5.93. **ESI-HR** calcd for C₁₆H₂₆NOSi⁺ ([M+H]⁺) 276.1778, found 276.1776. **IR** v (cm⁻¹) 3293, 1638, 1540, 753. **M. P.** 73 °C.



4t: Following the general procedure, amide **1a** (6.8 mg, 0.050 mmol) and alkyne **2e** (39.7 mg, 0.150 mmol) were converted to the alkenylation product **4t**. Purification by silica gel chromatography gave 9.7 mg (49% yield) of **4t** as a white solid. ¹**H NMR** (400 MHz, CDCl₃) δ 7.69 – 7.61 (m, 5H), 7.50 – 7.35 (m, 8H), 7.31 (t, J = 7.5 Hz, 1H), 7.17 – 7.08 (m, 1H), 6.90 – 6.79 (m, 1H), 5.51 (d, J = 36.9 Hz, 1H), 2.74 (d, J = 4.9 Hz, 3H), 1.12 (d, J = 13.0 Hz, 9H). ¹³**C NMR** (101 MHz, CDCl₃) δ 169.74, 146.65, 136.62, 136.36, 135.70, 134.42, 130.25, 129.47, 128.33, 128.07, 127.87, 127.44, 126.56, 27.96, 26.72, 18.55. **ESI-HR** calcd for C₂₆H₃₀NOSi⁺ ([M+H]⁺) 400.2091, found 400.2096. **IR** v (cm⁻¹) 3284, 1637, 1539, 739. **M. P.** 101 °C.

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