Supporting Information

Iridium-Catalyzed, Ligand-Controlled Directed Alkynylation and Alkenylation of Arene with Terminal Alkyne

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Table of Contents

Materials and Methods ........................................................................................................................................... S2
General procedure for C-H alkynylation ................................................................................................................ S2
General procedure for C-H alkenylation ................................................................................................................ S3
General method for the synthesis of substrates ....................................................................................................... S3
Deuterium labelling experiments ........................................................................................................................ S4
Characterization of substrates: .......................................................................................................................... S9
Characterization of products: ............................................................................................................................. S14
References ........................................................................................................................................................... S30
Copies of NMR spectra ....................................................................................................................................... S31
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 was prepared according to literature methods. Triisopropylsilylacetylene, 1-(3-Dimethylaminopropyl)-3-ethylcarbodiimide Hydrochloride (EDCI) and 4-dimethylaninopyridine (DMAP) were purchased from Alfa Aesar and were used as received. 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 ^1^H NMR and 126 MHz for ^1^3C 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 ^1^H NMR and δ = 7.16 for ^1^3C NMR). Data for ^1^H 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

1a to 1n: 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.

1o: 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-D$_5^2$: 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 °C for 10 min. The mixture was stirred at the same temperature for 30 min, and then CO$_2$ was bubbled through the mixture at -78 °C for 10 min. The mixture was allowed to warm to ambient temperature, quenched with H$_2$O (20 mL), acidified to pH=1 with 1 M HCl, and extracted with EtOAc (3 × 30 mL). The combined organic phase was dried over MgSO$_4$, filtered and the solvents were removed in vacuum to give the product. 1a-D$_5$ was prepared from the 2,3,4,5,6-pentadeuteriobenzoyl acid according to the general method.

**Deuterium labelling experiments**

[Diagram showing the reaction between 1a and 2a]
H NMR (400 MHz, CDCl₃) of 3a

H NMR (400 MHz, CDCl₃) of 5

GC-MS of vinyl silane-D₂

H₂ acceptor m/z⁺ 186

H₂ acceptor m/z⁺ 185
$^1$H NMR (400 MHz, CDCl₃) of 7

GC-MS of vinyl silane-D₁

1a-D₅ + 2a-D → standard conditions

Alkylation

$^1$H NMR (400 MHz, CDCl₃) of 9
GC-MS of vinyl silane-D$_3$

\[
\begin{align*}
\text{H NMR (400 MHz, CDCl$_3$) of 4a} \\
\text{H NMR (400 MHz, CDCl$_3$) of 6}
\end{align*}
\]

standard conditions
Alkenylation
70% D
20% D
6, 58%

standard conditions
Alkenylation
>95% D
8, 68%
$^1$H NMR (400 MHz, CDCl$_3$) of 8

![](image1.png)

$^1$H NMR (400 MHz, CDCl$_3$) of 10

![](image2.png)
Characterization of substrates:

\[
\begin{align*}
\text{O} & \quad \text{N-CH}_3 \\
\end{align*}
\]

1a: \( ^1H \) NMR (400 MHz, CDCl\(_3\)) \( \delta \) 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, CDCl\(_3\)) \( \delta \) 168.39, 134.79, 131.46, 128.67, 126.95, 26.96. \text{ESI-HR} \text{calcd for C}_{8}H_{10}NO}^{+} ([M+H]^+) 136.0757, found 136.0753. \text{IR } \nu (\text{cm}^{-1}) 3309, 1637, 1544, 695. \text{M. P.} 84 \degree C.

\[
\begin{align*}
\text{O} & \quad \text{N-CH}_3 \\
\end{align*}
\]

1b: \( ^1H \) NMR (400 MHz, CDCl\(_3\)) \( \delta \) 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, CDCl\(_3\)) \( \delta \) 170.92, 136.67, 136.16, 131.11, 129.91, 126.78, 125.81, 26.75, 19.89. \text{ESI-HR} \text{calcd for C}_{9}H_{12}NO}^{+} ([M+H]^+) 150.0913, found 150.0911. \text{IR } \nu (\text{cm}^{-1}) 3292, 1634, 1540, 735. \text{M. P.} 81 \degree C.

\[
\begin{align*}
\text{O} & \quad \text{N-CH}_3 \\
\end{align*}
\]

1c: \( ^1H \) NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.57 – 7.44 (m, 2H), 7.39 (td, \( J = 8.1, 6.0 \) Hz, 1H), 7.18 (td, \( J = 8.3, 2.6, 0.9 \) Hz, 1H), 6.26 (s, 1H), 3.01 (d, \( J = 4.9 \) Hz, 3H). \( ^{13}C \) NMR (101 MHz, CDCl\(_3\)) \( \delta \) 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. \text{ESI-HR} \text{calcd for C}_{8}H_{9}FNO}^{+} ([M+H]^+) 154.0663, found 154.0659. \text{IR } \nu (\text{cm}^{-1}) 3325, 1638, 1542, 732. \text{M. P.} 92 \degree C.
1d: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 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, CDCl$_3$) $\delta$ 167.06, 136.56, 134.87, 131.51, 130.00, 127.38, 125.07, 27.05. ESI-HR calcd for C$_8$H$_9$ClNO$^+$ ([M+H]$^+$) 170.0367, found 170.0366. IR $\nu$ (cm$^{-1}$) 3308, 1635, 1547, 733. M. P. 96 °C.

1e: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 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, CDCl$_3$) $\delta$ 166.94, 136.76, 134.43, 130.26, 130.25, 125.57, 122.86, 27.06. ESI-HR calcd for C$_8$H$_9$BrNO$^+$ ([M+H]$^+$) 213.9862, found 213.9861. IR $\nu$ (cm$^{-1}$) 3306, 1633, 1545, 738. M. P. 82 °C.

1f: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 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, CDCl$_3$) $\delta$ 166.93, 140.34, 136.76, 136.12, 130.33, 126.25, 94.36, 27.09. ESI-HR calcd for C$_8$H$_9$INO$^+$ ([M+H]$^+$) 261.9723, found 261.9718. IR $\nu$ (cm$^{-1}$) 3307, 1635, 1557, 734. M. P. 107 °C.

1g: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 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, CDCl$_3$) $\delta$ 167.37, 133.63, 131.94, 128.61, 126.16, 27.04. ESI-HR calcd for C$_8$H$_9$BrNO$^+$ ([M+H]$^+$) 213.9862, found 213.9860. IR $\nu$ (cm$^{-1}$) 3342, 1637, 1556, 733. M. P. 162 °C.
\[
\text{TBSO-} \text{O} \text{N-CH}_{3}
\]

\text{1h: } ^{1}H \text{ NMR (400 MHz, CDCl}_{3} \text{)} \delta 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). 

\text{13C NMR (101 MHz, CDCl}_{3} \text{)} \delta 168.24, 145.21, 133.36, 126.94, 126.10, 64.65, 26.96, 26.06, 18.55, -5.13. \text{ ESI-HR calcd for } C_{15}H_{26}NO_{2}Si^{+} ([M+H]^{+}) 280.1727, \text{ found } 280.172. \text{ IR } \nu (\text{cm}^{-1}) 3324, 1634, 1549, 834. \text{ M. P. } 63^\circ C.

\[
\text{H}_{3}C \text{O} \text{N-CH}_{3}
\]

\text{1i: } ^{1}H \text{ NMR (400 MHz, CDCl}_{3} \text{)} \delta 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). \text{13C NMR (101 MHz, CDCl}_{3} \text{)} \delta 197.57, 167.36, 139.26, 138.67, 128.67, 127.31, 27.10, 26.93. \text{ ESI-HR calcd for } C_{10}H_{12}NO_{2}^{+} ([M+H]^{+}) 178.0863, \text{ found } 178.0861. \text{ IR } \nu (\text{cm}^{-1}) 3391, 1678, 1643, 1546, 764. \text{ M. P. } 138^\circ C.

\[
\text{H}_{3}C \text{O} \text{N-CH}_{3}
\]

\text{1j: } ^{1}H \text{ NMR (400 MHz, CDCl}_{3} \text{)} \delta 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). \text{13C NMR (101 MHz, CDCl}_{3} \text{)} \delta 167.48, 166.45, 138.68, 132.79, 129.99, 127.04, 52.52, 27.09. \text{ ESI-HR calcd for } C_{10}H_{12}NO_{3}^{+} ([M+H]^{+}) 194.0812, \text{ found } 194.0814. \text{ IR } \nu (\text{cm}^{-1}) 3365, 1723, 1635, 1550, 750. \text{ M. P. } 133^\circ C.

\[
\text{F}_{3}C \text{O} \text{N-CH}_{3}
\]

\text{1k: } ^{1}H \text{ NMR (400 MHz, CDCl}_{3} \text{)} \delta 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). \text{13C NMR (101 MHz, CDCl}_{3} \text{)} \delta 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** ν (cm⁻¹) 3297, 1646, 1558, 748. **M. P.** 153 °C.

![Chemical Structure 1]

**1l: ¹H 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). **¹³C 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** ν (cm⁻¹) 3324, 1755, 1647, 1558, 749. **M. P.** 148 °C.

![Chemical Structure 1](image1)

**1m: ¹H 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). **¹³C NMR** (101 MHz, CDCl₃) δ 168.57, 138.50, 134.77, 128.52, 127.76, 123.89, 26.93, 21.47. **ESI-HR** calcd for C₉H₁₂NO⁺ ([M+H]+'') 150.0913, found 150.0919. **IR** ν (cm⁻¹) 3311, 1636, 1542, 749. **M. P.** 59 °C.

![Chemical Structure 1](image2)

**1n: ¹H 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). **¹³C 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 C₉H₈BrFNO⁺ ([M+H]+'') 231.9768, found 231.9780. **IR** ν (cm⁻¹) 3326, 1637, 1579, 749. **M. P.** 117 °C.
1o: ¹H 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). ¹³C 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: ¹H 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). ¹³C 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. \[^{1}H\text{ NMR}\ (400 \text{ MHz, CDCl}_3)\ \delta 8.12\ (dd, J = 7.3, 1.3 \text{ Hz, 1H}), 7.94 - 7.65\ (m, 1H), 7.60 - 7.50\ (m, 1H), 7.47 - 7.33\ (m, 2H), 3.00\ (d, J = 4.8 \text{ Hz, 3H}), 1.16\ (dd, J = 16.4, 3.8 \text{ Hz, 21H}).\]

\[^{13}C\text{ NMR}\ (101 \text{ MHz, CDCl}_3)\ \delta 166.62, 135.39, 134.39, 130.49, 130.30, 129.14, 119.62, 105.85, 98.56, 26.78, 18.75, 11.38.\ ESI-\text{HR}\ \text{calcd for C}_{19}\text{H}_{30}\text{NOSi}^+ ([M+H]^+) 316.2091, \ \text{found 316.2094.}\]

\[^{13}C\text{ NMR}\ \text{IR} \nu (\text{cm}^{-1})\ (3297, 2153, 1653, 1541, 751. \text{ M. P. 61 } \text{C}.\]

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. \[^{1}H\text{ NMR}\ (400 \text{ MHz, CDCl}_3)\ \delta 7.32\ (d, J = 7.4 \text{ Hz, 1H}), 7.21 - 7.11\ (m, 2H), 5.84\ (s, 1H), 2.97\ (d, J = 4.9 \text{ Hz, 3H}), 2.33\ (s, 3H), 1.10\ (s, 21H).\]

\[^{13}C\text{ NMR}\ (101 \text{ MHz, CDCl}_3)\ \delta 169.38, 139.73, 135.93, 130.65, 130.62, 128.77, 120.69, 104.64, 94.55, 26.72, 19.60, 18.80, 11.44.\ ESI-\text{HR}\ \text{calcd for C}_{20}\text{H}_{32}\text{NOSi}^+ ([M+H]^+) 330.2248, \ \text{found 330.2247.}\ \text{IR} \nu (\text{cm}^{-1})\ (3269, 2152, 1636, 1567, 750. \text{ M. P. 209 } \text{C}.\]
3c: Following the general procedure, amide 1c (14.9 mg, 0.100 mmol) was converted to the alkylation product 3c. Purification by silica gel chromatography gave 30.6 mg (93% yield) of 3c as a white solid. \(^1H\) NMR (400 MHz, CDCl\(_3\)) \(\delta\) 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, CDCl\(_3\)) \(\delta\) 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. \textbf{ESI-HR} calcd for C\(_{20}\)H\(_{32}\)NOSi\(^+\) ([M+H]\(^+\)) 330.2248, found 330.2239. \textbf{IR} \(\nu\) (cm\(^{-1}\)) 3307, 2148, 1654, 1540, 751. \textbf{M. P.} 88 °C.

3d: Following the general procedure, amide 1d (15.3 mg, 0.100 mmol) was converted to the alkylation product 3d. Purification by silica gel chromatography gave 23.6 mg (71% yield) of 3d as a white solid. \(^1H\) NMR (400 MHz, CDCl\(_3\)) \(\delta\) 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, CDCl\(_3\)) \(\delta\) 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. \textbf{ESI-HR} calcd for C\(_{19}\)H\(_{29}\)FNOSi\(^+\) ([M+H]\(^+\)) 334.1997, found 334.1994. \textbf{IR} \(\nu\) (cm\(^{-1}\)) 3295, 2151, 1656, 1543, 745. \textbf{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, CDCl\(_3\)) \(\delta 8.12 \text{ (d, } J = 2.2 \text{ Hz, } 1\text{H}), 7.79 \text{ (s, } 1\text{H}), 7.47 \text{ (d, } J = 8.3 \text{ Hz, } 1\text{H}), 7.36 \text{ (dd, } J = 8.3, 2.3 \text{ Hz, } 1\text{H}), 3.00 \text{ (d, } J = 4.8 \text{ Hz, } 3\text{H}), 1.20 - 1.10 \text{ (m, } 21\text{H}). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta 165.27, 136.84, 135.58, 135.54, 130.69, 130.50, 118.03, 104.76, 99.91, 26.90, 18.75, 11.37. \text{ ESI-HR calcd for } C_{19}H_{29}ClNOSi^+ ([M+H]^+) 350.1701, \text{ found 350.1704. IR } \nu \text{ (cm}^{-1}) 3297, 2153, 1655, 1543, 730. \text{ M. P. 78 \textdegree 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, CDCl\(_3\)) \(\delta 8.27 \text{ (d, } J = 2.0 \text{ Hz, } 1\text{H}), 7.76 \text{ (s, } 1\text{H}), 7.51 \text{ (dd, } J = 8.2, 2.1 \text{ Hz, } 1\text{H}), 7.39 \text{ (d, } J = 8.2 \text{ Hz, } 1\text{H}), 2.99 \text{ (d, } J = 4.8 \text{ Hz, } 3\text{H}), 1.18 - 1.10 \text{ (m, } 21\text{H}). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta 165.18, 136.88, 135.62, 133.60, 133.38, 123.62, 118.48, 104.81, 100.10, 26.89, 18.74, 11.36. \text{ ESI-HR calcd for } C_{19}H_{29}BrNOSi^+ ([M+H]^+) 394.1196, \text{ found 394.1197. IR } \nu \text{ (cm}^{-1}) 3295, 2152, 1654, 1542, 730. \text{ M. P. 95 \textdegree C.}
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, CDCl$_3$) 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, CDCl$_3$) δ 165.12, 139.46, 139.22, 136.61, 119.05, 104.93, 100.35, 95.11, 26.89, 18.75, 11.35. ESI-HR calcd for C$_{19}$H$_{29}$INOSi$^+$ ([M+H]$^+$) 442.1058, found 442.1056. IR ν (cm$^{-1}$) 3307, 2149, 1654, 1541, 748. M. P. 105 ℃.

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, CDCl$_3$) δ 8.15 (d, J = 8.7 Hz, 1H), 7.72 (s, 1H), 7.16 (d, 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, CDCl$_3$) 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 C$_{21}$H$_{32}$NO$_3$Si$^+$ ([M+H]$^+$) 374.2146, found 374.2136. IR ν (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, CDCl$_3$) 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, CDCl$_3$) 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
C_{26}H_{28}NO_{2}Si_{2}^{+} ([M+H]^{+}) 460.3062, found 460.3061. IR ν (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, CDCl_{3}) 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). ^{13}C 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 C_{19}H_{29}BrNOSi^{+} ([M+H]^{+}) 394.1196, found 394.1197. IR ν (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, CDCl_{3}) 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, CDCl_{3}) 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 C_{20}H_{38}F_{3}NOSi^{+} ([M+H]^{+}) 384.1965, found 384.1959. IR ν (cm^{-1}) 3282, 2163, 1649, 1558, 752. M. P. 65 °C.
3l: Following the general procedure, amide 1l (17.7 mg, 0.100 mmol) was converted to the alkylation product 3l. Purification by silica gel chromatography gave 33.1 mg (92% yield) of 3l as a yellow oil. ¹H 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). ¹³C 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 C₂₁H₂₃NO₂Si⁺ ([M+H]⁺) 358.2197, found 358.2194. IR ν (cm⁻¹) 3249, 2155, 1691, 1653, 1542, 750.

3m: Following the general procedure, amide 1m (19.3 mg, 0.100 mmol) was converted to the alkylation product 3m. Purification by silica gel chromatography gave 32.8 mg (88% yield) of 3m as a yellow oil. ¹H 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). ¹³C 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 C₂₁H₂₃NO₂Si⁺ ([M+H]⁺) 374.2146, found 374.2143. IR ν (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. $^1$H NMR (400 MHz, CDCl$_3$) 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). $^{13}$C NMR (101 MHz, CDCl$_3$) 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 C$_{19}$H$_{28}$BrFNOSi$^+$ ([M+H]$^+$) 412.1102, found 412.1101. IR ν (cm$^{-1}$) 3293, 2162, 1652, 750. M. P. 89 ℃.

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, CDCl$_3$) 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, CDCl$_3$) 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 C$_{21}$H$_{38}$NOSi$^+$ ([M+H]$^+$) 348.2717, found 348.2718. IR ν (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, CDCl$_3$) 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, 9H).

$^{13}$C NMR (101 MHz, CDCl$_3$) 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 C$_{32}$H$_{42}$N$_3$O$_5$Si$^+$ ([M+H]$^+$) 576.2888, found 576.2899. IR ν (cm$^{-1}$) 3295, 2154, 1749, 1652, 1516, 750. M. P. 171 ℃.

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, CDCl$_3$) 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, CDCl$_3$) 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 C$_{16}$H$_{24}$NOSi$^+$ ([M+H]$^+$) 274.1622, found 274.1618. IR ν (cm$^{-1}$) 3307, 2158, 1651, 1541, 776. M. P. 62 ℃.

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, CDCl$_3$) 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). $^{13}$C NMR (101 MHz, CDCl$_3$) 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, 18.75, 18.87. ESI-HR calcd for C$_{26}$H$_{28}$NOSi$^+$ ([M+H]$^+$) 398.1935, found 398.1938. IR ν (cm$^{-1}$) 3306, 2159, 1646, 1540, 757. M. P. 146 ºC.

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, CDCl$_3$) 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, CDCl$_3$) 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 C$_{19}$H$_{32}$NOSi$^+$ ([M+H]$^+$) 318.2248, found 318.2246. IR ν (cm$^{-1}$) 3281, 1637, 1541, 750. M. P. 80 ºC.

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, CDCl$_3$) 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). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 170.63, 143.20, 136.37, 136.31, 134.97, 129.58, 129.03, 127.67, 122.90, 26.85, 19.27, 18.78, 11.10. ESI-HR calcd for C$_{20}$H$_{34}$NOSi$^+$ ([M+H]$^+$) 332.2404, found 332.2405. IR ν (cm$^{-1}$) 3256, 1634, 1559, 750. M. P. 171 ºC.
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, CDCl$_3$) 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, 2H), 3.11 (s, 1H), 1.26 – 1.03 (m, 21H). $^{13}$C NMR (101 MHz, CDCl$_3$) 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 C$_{20}$H$_{34}$NOSi$^+$ ([M+H]$^+$) 332.2404, found 332.2398. IR ν (cm$^{-1}$) 3292, 1637, 1541, 750. M. P. 96 ℃.

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, CDCl$_3$) 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, CDCl$_3$) 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 C$_{19}$H$_{31}$FNOSi$^+$ ([M+H]$^+$) 336.2153, found 336.2154. IR ν (cm$^{-1}$) 3274, 1637, 1558, 750. M. P. 85 ℃.
**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, CDCl$_3$) 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, CDCl$_3$) 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 C$_{19}$H$_{31}$ClNOSi$^+$ ([M+H]$^+$) 352.1858, found 352.1853. IR ν (cm$^{-1}$) 3274, 1637, 1558, 750. M. P. 79 ℃.

![Structure of 4e](image)

**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, CDCl$_3$) 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 = 19.3 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, CDCl$_3$) 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 C$_{19}$H$_{31}$BrNOSi$^+$ ([M+H]$^+$) 396.1353, found 396.1345. IR ν (cm$^{-1}$) 3270, 1636, 1557, 751. M. P. 116 ℃.

![Structure of 4f](image)

**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, CDCl$_3$) 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). \[^{13}\text{C} \text{NMR}\] (101 MHz, CDCl\(_3\)) \(\delta\) 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 C\(_{19}\)H\(_{31}\)NO\(_4\)Si\(^+\) ([M+H]\(^+\)) 444.1214, found 444.1199. IR \(\nu\) (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. \[^{1}\text{H} \text{NMR}\] (400 MHz, CDCl\(_3\)) \(\delta\) 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). \[^{13}\text{C} \text{NMR}\] (101 MHz, CDCl\(_3\)) \(\delta\) 169.43, 169.41, 152.07, 142.63, 139.08, 133.08, 129.88, 121.15, 119.36, 26.92, 18.78, 11.10. ESI-HR calcd for C\(_{21}\)H\(_{34}\)NO\(_3\)Si\(^+\) ([M+H]\(^+\)) 376.2302, found 376.2292. IR \(\nu\) (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. \[^{1}\text{H} \text{NMR}\] (400 MHz, CDCl\(_3\)) \(\delta\) 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), 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). \[^{13}\text{C} \text{NMR}\] (101 MHz, CDCl\(_3\)) \(\delta\) 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 C\(_{26}\)H\(_{48}\)NO\(_2\)Si\(_2\)\(^+\) ([M+H]\(^+\)) 462.3218, found 462.3201. IR \(\nu\) (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, CDCl$_3$) $\delta$ 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, CDCl$_3$) $\delta$ 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 caled for C$_{19}$H$_{31}$BrNOSi$^+$ ([M+H]$^+$) 396.1353, found 396.1341. IR $\nu$ (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, CDCl$_3$) $\delta$ 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, CDCl$_3$) $\delta$ 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 caled for C$_{20}$H$_{31}$F$_3$NOSi$^+$ ([M+H]$^+$) 386.2122, found 386.2113. IR $\nu$ (cm$^{-1}$) 3274, 1645, 1558, 749. M. P. 114 °C.

S26
Following the general procedure, amide 1l (17.7 mg, 0.100 mmol) was converted to the alkenylation product 4l. Purification by silica gel chromatography gave 14.9 mg (42% yield) of 4l as a yellow oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 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, CDCl$_3$) $\delta$ 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 C$_{21}$H$_{34}$NO$_2$Si$^+$ ([M+H]$^+$) 360.2353, found 360.2341. IR $\nu$ (cm$^{-1}$) 3291, 1686, 1647, 1557, 750.

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, CDCl$_3$) $\delta$ 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, CDCl$_3$) $\delta$ 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 C$_{21}$H$_{34}$NO$_3$Si$^+$ ([M+H]$^+$) 376.2302, found 376.2296. IR $\nu$ (cm$^{-1}$) 3274, 1726, 1647, 1558, 750.
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. ¹H 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). ¹³C 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 C₁₉H₂₉BrFNOSi⁺ ([M⁺H⁺]⁺) 414.1259, found 414.1267. IR ν (cm⁻¹) 3272, 1641, 1558, 750. M. P. 124 °C.

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. ¹H 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). ¹³C 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 C₂₁H₄₉NOSi⁺ ([M⁺H⁺]⁺) 350.2874, found 350.2877. IR ν (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, CDCl$_3$) 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, CDCl$_3$) 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 C$_{32}$H$_{44}$N$_3$O$_5$Si$^+$ ([M+H]$^+$) 578.3045, found 578.3048. IR ν (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, CDCl$_3$) 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, CDCl$_3$) 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 C$_{16}$H$_{36}$NOSi$^+$ ([M+H]$^+$) 276.1778, found 276.1776. IR ν (cm$^{-1}$) 3293, 1638, 1540, 753. M. P. 73 °C.
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, CDCl$_3$) $\delta$ 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, CDCl$_3$) $\delta$ 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 C$_{26}$H$_{30}$NOSi $^{+}$ ([M+H]$^{+}$) 400.2091, found 400.2096.

IR ν (cm$^{-1}$) 3284, 1637, 1539, 739. M. P. 101 ºC.

References


Copies of NMR spectra
TIPS

N
CH₃

-167.87
-139.98
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41.43
33.73
29.47
24.02
22.08
21.50
19.07
17.71
11.36
10.26
Ph⁻¹Bu⁻¹Ph

\[ \text{O} \quad \text{N} \quad \text{CH}_3 \]

S64