Supporting Information for:

Modular synthesis and transition metal-free alkynylation/alkenylation of Castagnoli-Cushman-derived N,O- and N,S-heterocyclic vinyl chlorides

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2. Experimental Section

All experiments involving air and moisture-sensitive reagents were carried out under an inert atmosphere of nitrogen and using freshly distilled solvents. Freshly purchased DMF was stored under 4 Å molecular sieves for several days prior to use. THF was distilled from sodium benzophenone ketyl. All amines and enals were newly purchased and used without further purification. Column chromatography was performed on silica gel (230-400 mesh). Thin-layer chromatography (TLC) was performed using Silicycle SiliaplateTM glass backed plates (250 µm thickness, 60 Å porosity, F-254 indicator) and visualized using UV (254 nm) or CAM, p-anisaldehyde, or KMnO₄ stain. All reported temperatures were internal to a reaction vessel. Unless otherwise indicated, ¹H, ¹³C, and DEPT-135 spectra were acquired using CDCl₃ as solvent, at room temperature. Chemical shifts are quoted in parts per million (ppm). HRMS-EI⁺ data were obtained using either electronspray ionization (ESI) or electron impact (EI) techniques. High-resolution ESI was obtained on an LTQ-FT (ion trap; analyzed using Excalibur). High resolution EI was obtained on an Autospec (magnetic sector; analyzed using MassLynx).

Brine solutions are saturated solutions of aqueous sodium chloride. The lactam precursors utilized in these studies were prepared using our recently reported protocol.¹

General Procedure A: Vilsmeier-Haack functionalization²

To a solution of DMF (40 mmol, 4 equiv) in CH₂Cl₂ (50 mL) at 0 °C was added dropwise, phosphorus oxychloride (20 mmol, 2 equiv). The resulting pale yellow mixture was refluxed for 60 min. A solution of the lactam ester (10 mmol, 1 equiv) in CH₂Cl₂ (50 mL) was added slowly under reflux. After complete addition of the lactam, the mixture was cooled to room temperature (for the morpholinone esters) or 0 °C (for the thiomorpholinone esters) and stirred for the indicated time period (TLC and LC-MS monitoring was used to follow the extent of the reaction). Upon completion, the mixture was poured into a large flask containing crushed ice. After stirring at room temperature for 60 min, the layers were separated (the majority of the product stays in the DCM layer). Powdered K₂CO₃ was added slowly to the aqueous layer and the flask was swirled after each addition (Caution: it bubbles vigorously). The addition/swirling was continued until persistent cloudiness was observed. The neutralized/slightly basic mixture was extracted two times with CH₂Cl₂. The combined organic layers (three in total, one before and two after addition of K₂CO₃) were washed with brine and dried over Na₂SO₄ for 30 min. The mixture was filtered and
concentrated under reduced pressure to give the desired product as an oily salt, which was immediately subjected to flash chromatography on silica with 1% Et₃N.

**General Procedure B (Transition metal-free alkynylation with terminal alkynes)**

To an oven-dried, septum-capped 2-neck-round bottom flask equipped with a stir bar, was added the chloroenal (0.5 mmol, 1.0 equiv) in 2-MeTHF (5 mL) under an argon atmosphere. The desired alkyne (1.2 equiv) was added. After completely degassing the flask, LiTMP (147.2 mg, 2 equiv) was added. The mixture was then stirred at room temperature for the desired length of time (as indicated by TLC and LC-MS). Upon completion, the mixture was quenched with methanol. The combined organics were concentrated to ~5 mL and directly subjected to flash chromatography on silica, pretreated with Et₃N.

**General Procedure C (Transition metal-free alkenylation with styrenes)**

Potassium tert-butoxide (56 mg, 2.0 equiv) and 1,10-phenanthroline (7 mg, 15 mol%) were transferred into a dried Schlenk tube. The sealed tube was evacuated and filled with argon three times. A solution of vinyl chloride 4a (0.25 mmol) in 5 mL anhydrous 2-MeTHF was added via syringe and the mixture was stirred for 5 seconds at room temperature. The tube was placed in a preheated oil bath at 90 °C and it was stirred for 18 h (GC-MS and TLC monitoring). After cooling down, the reaction mixture was filtered through a short silica plug and the silica was washed with ethyl acetate. The organic solvents were evaporated under reduced pressure and the product was purified by flash column chromatography on silica gel, pretreated with triethylamine.

**General Procedure D (Wittig olefination and Diels-Alder reaction)**

Wittig Olefination: To a 25 mL two-neck round-bottomed flask containing a magnetic stir bar under a N₂ atmosphere was added benzyltriphenylphosphonium bromide + sodium amide (240 mg, 0.5 mmol) and 2-MeTHF (10 mL). After stirring at room temperature for 30 min, then aldehyde (0.5 mmol) was added as a solution in 2-MeTHF (5 mL) and stirring was resumed at this temperature for 12 h (GC-MS and TLC monitoring). It flask was then cooled to 0 °C and the contents were quenched by the addition of sat. NH₄Cl(aq) solution (10 mL). The reaction mixture was extracted with EtOAc (3 × 20 mL) and the combined organic layers were dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The crude mixture was purified by gradient
flash chromatography (eluting with 9:1 to 4:1 hexanes/EtOAc) to furnish the conjugated diene as a yellowish liquid in ~90:10 dr.

**Hexannulation:** A vial was flame-dried, evacuated and flushed with nitrogen. A solution of tetracyanoethylene (128 mg, 1.0 mmol, 2 equiv) in 2-MeTHF (5 mL) was added to the vial followed by a solution of crude 1,3-diene (0.5 mmol) in 2-MeTHF (5 mL). The mixture was stirred for 12 h at room temperature. The crude mixture was concentrated under reduced pressure and purified by flash chromatography on silica (pretreated with 1% Et₃N), eluting with hexane/EtOAc.

**Scheme 1 results**

Compound 4a1: Prepared in 10 mmol scale using **General Procedure A**. Temp = room temperature, time = 22 h, Purification: Flash chromatography on silica (pretreated with 1% Et₃N) eluting with hexane/EtOAc (80:20). Yield = 9.416 g, 74%. 

\[
\begin{align*}
\text{\textsuperscript{1}H NMR (400 MHz, Chloroform-}d) & \text{ \delta 9.70 (s, 1H), 7.67 (d, } J = 8.1 \text{ Hz, 2H), 7.40 – 7.22 (m, 2H), 6.88 (d, } J = 8.2 \text{ Hz, 2H), 6.63 (d, } J = 15.8 \text{ Hz, 1H), 6.21 (dd, } J = 15.9, 6.5 \text{ Hz, 1H), 5.01 (s, 1H), 4.89 (d, } J = 6.5 \text{ Hz, 1H), 3.62 (s, 3H).} \\
\text{\textsuperscript{13}C NMR (101 MHz, CDCl}_3) & \text{ \delta 180.4, 167.7, 142.2, 138.5, 135.2, 134.1, 132.8, 131.5, 130.3, 128.8, 127.2, 122.4, 119.6, 91.8, 74.6, 62.6, 52.7. HRMS calc for C}_{21}\text{H}_{17}\text{ClNO}_4, 508.9891, \text{ found 509.9899.}
\end{align*}
\]
Compound 4a2: Prepared in 1 mmol scale using **General Procedure A**. Temp = room temperature, time = 22 h, Purification: Flash chromatography on silica (pretreated with 1% Et₃N)
eluting with hexane/EtOAc (80:20). Yield = 403.3 mg, 77%. $^1$H NMR (400 MHz, Chloroform-$d$) δ 9.68 (s, 1H), 7.77 (d, $J = 7.5$ Hz, 2H), 7.40 – 7.30 (m, 5H), 6.95 (d, $J = 7.5$ Hz, 2H), 6.52 (s, 1H), 5.18 (d, $J = 1.5$ Hz, 1H), 3.65 (s, 3H), 1.97 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 180.38, 168.19, 142.62, 138.69, 138.51, 138.36, 136.29, 129.15, 128.65, 128.39, 127.38, 126.90, 91.76, 72.80, 68.36, 52.79, 15.46. HRMS calc for C$_{22}$H$_{19}$ClNO$_4$, 523.0047, found 523.0041.
Compound 4a3: Prepared in 1 mmol scale using General Procedure A. Temp = room temperature, time = 22 h, Purification: Flash chromatography on silica (pretreated with 1% Et3N) eluting with hexane/EtOAc (70:30). Yield = 347.6 mg, 84%. $^1$H NMR (400 MHz, Chloroform-$d$) δ 9.64 (s, 1H), 7.40 – 7.29 (m, 5H), 7.15 (d, $J = 6.7$ Hz, 2H), 6.83 (d, $J = 6.7$ Hz, 2H), 6.59 (d, $J = 15.7$ Hz, 1H), 6.24 (dd, $J = 15.8$, 7.2 Hz, 1H), 4.98 (d, $J = 1.6$ Hz, 1H), 4.85 (d, $J = 1.6$ Hz, 1H), 3.77 (s, 3H), 3.68 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 179.92, 168.13, 158.85, 135.45, 135.23, 134.14, 131.38, 128.78, 128.64, 127.64, 126.95, 126.92, 122.79, 114.58, 74.52, 64.74, 55.58, 52.74. HRMS calc for C$_{22}$H$_{20}$ClNO$_5$, 413.1030, found 413.1036.
Compound **4a4**: Prepared in 1 mmol scale using **General Procedure A**. Temp = room temperature, time = 22 h, Purification: Flash chromatography on silica (pretreated with 1% Et₃N) eluting with hexane/EtOAc (70:30). Yield = 372.3 mg, 87%. ¹H NMR (400 MHz, Chloroform-d) δ 9.64 (s, 1H), 7.41 – 7.29 (m, 2H), 7.31 – 7.22 (m, 3H), 7.17 (d, J = 7.5 Hz, 2H), 6.86 (d, J = 7.5 Hz, 2H), 6.52 (s, 1H), 5.11 (d, J = 1.5 Hz, 1H), 4.75 (d, J = 1.5 Hz, 1H), 3.83 (s, 3H), 3.74 (s, 3H), 1.99 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 179.88, 168.64, 158.83, 136.46, 135.67, 134.94, 132.07, 131.43, 129.13, 128.96, 128.39, 128.34, 127.36, 127.27, 114.55, 73.01, 69.37, 55.60, 52.81, 15.29. HRMS calc for C₂₃H₂₂ClNO₅, 427.1187, found 427.1182.
Compound 4a5: Prepared in 1 mmol scale using General Procedure A. Temp = room temperature, time = 22 h, Purification: Flash chromatography on silica (pretreated with 1% Et3N) eluting with hexane/EtOAc (85:15). Yield = 306.3 mg, 77%, 90:10 dr. 1H NMR (400 MHz, Chloroform-d) δ 9.71 (s, 1H), 7.45 – 7.37 (m, 5H), 7.25 (d, 2H), 7.01 (d, 2H), 6.65 (dd, J = 15.8, 1.3 Hz, 1H), 6.28 (dd, J = 15.8, 7.0 Hz, 1H), 5.02 (d, J = 1.5 Hz, 1H), 4.91 (dt, J = 7.0, 1.5 Hz, 1H), 3.75 (s, 3H), 2.38 (s, 3H). 13C NMR (101 MHz, CDCl3) δ 180.23, 168.12, 139.97, 137.50, 135.43, 134.10, 130.05, 128.80, 128.68, 126.93, 125.79, 122.81, 74.67, 64.42, 52.73, 21.14. HRMS calc for C22H20ClNO4, 397.1081, found 397.1085.
Compound 4a6: Prepared in 5 mmol scale using **General Procedure A**. Temp = room temperature, time = 22 h, Purification: Flash chromatography on silica (pretreated with 1% Et3N) eluting with hexane/EtOAc (80:20). Yield = 1.71 g, 80%. 1H NMR (400 MHz, Chloroform-d) δ 9.64 (s, 1H), 7.29 (d, 2H), 6.98 (d, J = 8.7 Hz, 2H), 6.88 (d, 2H), 6.80 (dd, 2H), 6.5 (d, J = 14.6 Hz, 1H), 6.11 (m, 1H), 4.95 - 4.60 (m, 2H), 3.84 - 3.52 (m, 6H), 2.41 (m, 3H). 13C NMR (101 MHz, CDCl3) δ 180.6, 168.3, 140.9, 138.6, 134.8, 132.8, 129.2, 128.0, 127.5, 120.6, 114.0, 74.7, 64.1, 54.3, 52.9, 21.4. HRMS calc for C23H22ClNO5, 427.1187, found 427.1183.
Compound 4a7: Prepared in 1 mmol scale using General Procedure A. Temp = room temperature, time = 22 h, Purification: Flash chromatography on silica (pretreated with 1% Et3N) eluting with hexane/EtOAc (50:50). Yield = 426.3 mg, 87%. 1H NMR (400 MHz, Chloroform-d) δ 9.67 (s, 1H), 7.37 – 7.26 (m, 8H), 7.01 – 6.88 (m, 2H), 6.88 – 6.77 (m, 4H), 6.21 (d, J = 10.0 Hz, 1H), 4.92 – 4.86 (m, 1H), 4.83 (dd, J = 10.1, 1.8 Hz, 1H), 3.82 (s, 3H), 3.68 (s, 3H). 13C NMR (101 MHz, CDCl3) δ 179.73, 168.24, 159.03, 146.54, 140.32, 137.89, 135.73, 134.21, 129.04, 128.64, 128.60, 128.48, 128.44, 127.98, 127.54, 120.80, 114.42, 75.29, 61.95, 55.62, 52.82. HRMS calc for C28H24ClNO5, 489.1343, found 489.1348.
Compound 4a8: Prepared using **General Procedure A**. Temp = room temperature, time = 22 h, Purification: Flash chromatography on silica (pretreated with 1% Et3N) eluting with hexane/EtOAc (80:20). Yield = 280 mg, 73%. $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 9.70 (s, 1H), 7.41 - 7.11 (m, 10H), 6.65 (d, $J = 15.8$ Hz, 1H), 6.27 (dd, $J = 15.8$ Hz, 1H), 5.11 (d, $J = 12.6$ Hz, 1H), 4.74 (d, $J = 12.8$ Hz, 1H), 3.66 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 180.5, 167.9, 142.4, 135.9, 134.2, 129.7, 128.8, 127.3, 126.8, 125.7, 124.8, 122.6, 74.4, 64.2, 52.2. HRMS calc for C$_{21}$H$_{18}$ClNO$_4$, 383.0924, found 383.0929.
Compound 4a9: Prepared using **General Procedure A**. Temp = room temperature, time = 22 h, Purification: Flash chromatography on silica (pretreated with 1% Et$_3$N) eluting with hexane/EtOAc (80:20). Yield = 352 mg, 78%. $^1$H NMR (400 MHz, Chloroform-$d$) δ 9.75 (s, 1H), 7.52 (d, $J$ = 4.6 Hz, 2H), 7.42 – 7.23 (m, 7H), 6.69 (d, $J$ = 15.9 Hz, 1H), 6.24 (dd, $J$ = 15.9, 6.3 Hz, 1H), 5.06 (s, 1H), 4.96 (d, $J$ = 6.3 Hz, 1H), 3.59 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 180.6, 167.6, 143.1, 135.2, 134.1, 133.4, 132.0, 131.7, 130.8, 128.8, 126.9, 124.8, 123.5, 122.1, 121.9, 119.6, 74.6, 63.8, 52.6. HRMS calc for C$_{22}$H$_{17}$ClF$_3$NO$_4$, 451.0798, found 451.0793.
Compound 4a10: Prepared using General Procedure A. Temp = room temperature, time = 22 h, Purification: Flash chromatography on silica (pretreated with 1% Et$_3$N) eluting with hexane/EtOAc (75:25). Yield = 265.7 mg, 70%. $^1$H NMR (400 MHz, CDCl$_3$) δ 9.57 (s, 1H), 7.25 (d, $J$ = 8.3 Hz, 1H), 6.82 (d, $J$ = 8.3 Hz, 1H), 6.50 (d, $J$ = 15.8 Hz, 1H), 5.97 (dd, $J$ = 15.8, 7.5 Hz, 1H), 4.85 (s, 1H), 4.69 (d, $J$ = 7.5 Hz, 1H), 4.66 – 4.50 (m, 1H), 3.89 (s, 3H), 3.81 (s, 3H), 1.26 (d, $J$ = 6.7 Hz, 3H), 1.11 (d, $J$ = 6.7 Hz, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 179.35, 168.47, 159.89, 136.46, 133.89, 132.57, 129.98, 128.21, 128.10, 128.05, 122.18, 118.67, 114.12, 75.22, 55.93, 55.37, 52.76, 50.64, 21.31, 20.40. HRMS calc for C$_{19}$H$_{22}$ClNO$_5$, 379.1187, found 379.1193.
Compound 4a11: Prepared using **General Procedure A**. Temp = room temperature, time = 22 h, Purification: Flash chromatography on silica (pretreated with 1% Et$_3$N) eluting with hexane/EtOAc (50:50). Yield = 304 mg, 77%. $^1$H NMR (400 MHz, Chloroform-\textit{d}) $\delta$ 9.59 (s, 1H), 8.19 (d, $J$ = 8.4 Hz, 2H), 7.50 (d, $J$ = 8.5 Hz, 2H), 6.63 (d, $J$ = 15.8 Hz, 1H), 6.30 (dd, $J$ = 15.8, 7.0 Hz, 1H), 4.92 (s, 1H), 4.79 (d, $J$ = 7.0 Hz, 1H), 4.62 (m, 1H), 3.77 (s, 3H), 1.27 (d, $J$ = 6.8 Hz, 3H), 1.14 (d, $J$ = 6.7 Hz, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 179.64, 168.24, 147.57, 141.78, 131.02, 130.18, 129.30, 127.44, 124.15, 77.41, 77.09, 76.77, 74.66, 55.47, 53.01, 50.60, 21.25, 20.45. HRMS calc for C$_{18}$H$_{19}$ClN$_2$O$_6$, 394.0932, found 394.0938.
Compound 4a12: Prepared using General Procedure A. Temp = room temperature, time = 22 h, Purification: Flash chromatography on silica (pretreated with 1% Et3N) eluting with hexane/EtOAc (75:25). Yield = 316.5 mg, 87%. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.54 (s, 1H), 7.40 – 7.16 (m, 5H), 6.37 (s, 1H), 4.95 (d, $J = 1.3$ Hz, 1H), 4.74 – 4.57 (m, 1H), 4.53 (d, $J = 1.3$ Hz, 1H), 3.77 (s, 3H), 1.93 (s, 3H), 1.32 (d, $J = 6.9$ Hz, 3H), 1.14 (d, $J = 6.9$ Hz, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 179.26, 168.93, 136.53, 133.83, 129.03, 128.30, 128.17, 127.15, 73.17, 60.70, 52.88, 50.81, 20.49, 20.38, 15.36. HRMS calc for C$_{19}$H$_{22}$ClNO$_4$, 363.1237, found 363.1233.
Compound 4a13: Prepared using **General Procedure A**. Temp = 40 °C for 18 h. Purification: Flash chromatography on silica (pretreated with 1% Et₃N) eluting with hexane/EtOAc (80:20). Yield = 290 mg, 86%. ¹H NMR (400 MHz, Chloroform-d) δ 9.65 (s, 1H), 7.33 - 7.12 (m, 5H), 5.52 (d, J = 18.2 Hz, 1H), 4.99 (d, J = 18.2 Hz, 1H), 3.77 (s, 3H), 1.55 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 179.9, 169.3, 137.3, 132.7, 129.4, 128.5, 128.1, 127.7, 126.0, 76.9, 61.2, 58.9, 52.8, 31.0. HRMS calc for C₁₇H₂₀ClNO₄, 337.1081, found 337.1085.
Compound 4a14: Prepared using General Procedure A. Temp = 40 °C for 18 h. Purification: Flash chromatography on silica (pretreated with 1% Et$_3$N) eluting with hexane/EtOAc (80:20). Yield = 309 mg, 84%. $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 9.66 (s, 1H), 7.23 (t, $J = 8.0$ Hz, 1H), 6.89 – 6.76 (m, 3H), 5.53 (d, $J = 1.8$ Hz 1H), 5.07 (d, $J = 1.8$ Hz, 1H), 3.77 (s, 3H), 3.73 (s, 3H), 1.57 (s, 9H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 179.96, 169.32, 160.11, 138.87, 135.93, 132.73, 130.20, 118.22, 113.10, 112.18, 77.56, 77.24, 77.02, 76.92, 61.28, 58.43, 55.29, 52.88, 31.02. HRMS calc for C$_{18}$H$_{22}$ClNO$_5$, 367.1187, found 367.1182.
Compound 4a15: Prepared using **General Procedure A**. Temp = 40 °C for 18 h. Purification: Flash chromatography on silica (pretreated with 1% Et$_3$N) eluting with hexane/EtOAc (80:20). Yield = 291.4 mg, 90%. $^1$H NMR (400 MHz, Chloroform-$d$) δ 9.60 (s, 1H), 7.36 – 7.27 (m, 5H), 5.18 (d, $J = 1.4$ Hz, 1H), 4.87 (d, $J = 1.4$ Hz, 1H), 4.69 (m, 1H), 3.80 (s, 3H), 1.18 (d, $J = 6.8$ Hz, 3H), 1.05 (d, $J = 6.8$ Hz, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 179.16, 168.70, 138.91, 129.13, 128.34, 126.05, 77.42, 77.11, 76.79, 75.98, 57.59, 52.93, 50.92, 21.07, 20.27. HRMS calc for C$_{16}$H$_{18}$ClNO$_4$, 323.0924, found 323.0928.
Compound 4a16: Prepared using General Procedure A. Temp = 23 °C for 18 h. Purification: Flash chromatography on silica (pretreated with 1% Et3N) eluting with hexane/EtOAc (80:20). Yield = 304.9 mg, 82%. $^1$H NMR (400 MHz, CDCl₃) δ 9.59 (s, 1H), 7.45 – 7.25 (m, 6H), 7.23 – 7.09 (m, 4H), 5.13 (d, $J = 15.6$ Hz, 1H), 4.80 (d, $J = 1.7$ Hz, 1H), 4.71 (d, $J = 1.6$ Hz, 1H), 4.06 (d, $J = 15.7$ Hz, 1H), 3.45 (s, 3H). $^{13}$C NMR (101 MHz, CDCl₃) δ 179.02, 167.60, 137.97, 136.72, 134.93, 129.30, 129.27, 128.99, 128.93, 128.46, 128.08, 126.91, 75.27, 61.70, 52.58, 52.51. HRMS calc for C$_{20}$H$_{18}$ClNO$_4$, 371.0924, found 371.0928.
Compound **4a17**: Prepared using **General Procedure A**. Temp = 40 °C for 18 h. Purification: Flash chromatography on silica (pretreated with 1% Et$_3$N) eluting with hexane/EtOAc (50:50). Yield = 318 mg, 90%. $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 9.61 (s, 1H), 7.21 (d, 2H), 6.84 (d, 2H), 5.12 (d, $J$ = 18.2 Hz, 1H), 4.89 (d, $J$ = 18.2 Hz, 1H), 3.58 (m, 1H), 3.85 (s, 6H), 1.04 (d, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 179.7, 169.6, 160.3, 138.7, 131.4, 128.5, 114.1, 75.9, 58.2, 56.9, 53.8, 51.0, 21.3, 21.1. HRMS calc for C$_{17}$H$_{20}$ClNO$_5$, 353.1030, found 353.1036.
Compound 4a18: Prepared using **General Procedure A**. Temp = 40 °C for 18 h. Purification: Flash chromatography on silica (pretreated with 1% Et₃N) eluting with hexane/EtOAc (70:30). Yield = 322 mg, 92%. $^1$H NMR (400 MHz, Chloroform-d) δ 9.50 (s, 1H), 7.34 – 7.17 (m, 3H), 7.17 – 7.10 (m, 2H), 5.11 (d, J = 1.3 Hz, 1H), 4.85 (d, J = 1.3 Hz, 1H), 4.62 (tt, J = 9.3, 7.3 Hz, 1H), 3.72 (s, 3H), 1.81 – 1.24 (m, 8H). $^{13}$C NMR (101 MHz, CDCl₃) δ 178.88, 168.55, 138.36, 130.19, 129.09, 128.27, 125.85, 75.95, 60.63, 58.29, 52.87, 29.76, 29.17, 23.05, 22.76. HRMS calc for C₁₈H₂₀ClNO₄, 349.1081, found 349.1087.
Electronic Supplementary Information for RSC Advances; Beng and coworkers

[Diagram of chemical structures and spectra with normalized intensity and chemical shift in ppm]

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Scheme 2 results

Compound 4b1: Prepared using General Procedure A. Temp = 23 °C for 18 h. Purification: Flash chromatography on silica (pretreated with 1% Et₃N) eluting with hexane/EtOAc (80:20). Yield = 296.3 mg, 81%, 83:17 dr, oily substance. ¹H NMR (400 MHz, Chloroform-d) δ 9.81 (s, 1H), 7.44 – 7.28 (m, 5H), 6.49 (dd, J = 32.9, 15.7 Hz, 1H), 6.16 (dd, J = 15.8, 6.8 Hz, 1H), 4.94 (ddd, J = 6.9, 2.9, 1.1 Hz, 1H), 4.85 (p, J = 6.7 Hz, 1H), 3.88 (dd, J = 2.8, 1.0 Hz, 1H), 3.71 (s, 3H), 1.42 – 1.16 (m, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 185.50, 185.04, 169.41, 142.36, 135.60, 133.81, 132.67, 128.81, 128.77, 128.66, 128.53, 128.39, 126.87, 126.84, 126.39, 122.49, 102.48, 56.85, 56.37, 53.06, 52.89, 52.56, 47.89, 44.58, 22.34, 21.32, 20.71, 19.59. HRMS calc for C₁₈H₂₀ClNO₃S 365.0852, found 365.0855.

![Chemical structure of compound 4b1 with 83:17 dr (trans:cis)]
Compound 4b2: Prepared using General Procedure A. Temp = 23 °C for 18 h. Purification: Flash chromatography on silica (pretreated with 1% Et₃N) eluting with hexane/EtOAc (50:50). Yield = 353.3 mg, 86%, 95:5 dr, oily substance. ¹H NMR (400 MHz, Chloroform-δ) δ 9.83 (d, J = 1.0 Hz, 1H), 8.23 – 8.09 (m, 2H), 7.56 – 7.42 (m, 2H), 6.57 (dd, J = 15.9, 1.2 Hz, 1H), 6.33 (dd, J = 15.9, 6.3 Hz, 1H), 5.02 (ddd, J = 6.4, 2.9, 1.3 Hz, 1H), 4.88 (p, J = 6.7 Hz, 1H), 3.95 (dd, J = 2.8, 1.0 Hz, 1H), 3.72 (s, 3H), 1.44 – 1.20 (m, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 185.13, 169.09, 147.44, 142.13, 142.03, 130.93, 130.47, 127.51, 124.08, 123.98, 102.82, 56.46, 53.03, 52.96, 44.21, 22.28, 20.71. HRMS calc for C₁₈H₁₉ClN₂O₅S 410.0703, found 410.0709.
Compound 4b3: Prepared using **General Procedure A**. Temp = 23 °C for 18 h. Purification: Flash chromatography on silica (pretreated with 1% Et3N) eluting with hexane/EtOAc (60:40). Yield = 304.8 mg, 77%, 95:5 dr, oily substance. 

1H NMR (400 MHz, Chloroform-d) δ 9.86 (s, 1H), 7.38 – 7.25 (m, 2H), 6.94 – 6.81 (m, 2H), 6.49 (d, J = 15.8 Hz, 1H), 6.05 (dd, J = 15.8, 7.1 Hz, 1H), 4.95 – 4.79 (m, 2H), 3.87 (d, J = 2.7 Hz, 1H), 3.82 (s, 3H), 3.74 (s, 3H), 1.33 (d, J = 6.8 Hz, 3H), 1.26 (d, J = 6.8 Hz, 3H). 13C NMR (101 MHz, CDCl3) δ 185.13, 169.56, 159.98, 142.30, 132.17, 128.24, 128.12, 124.20, 114.18, 102.48, 57.06, 55.42, 52.97, 52.89, 44.88, 22.42, 20.73. HRMS calc for C19H22ClNO4S 395.0958, found 395.0952.
Compound 4b4: Prepared using **General Procedure A**. Temp = 23 °C for 18 h. Purification: Flash chromatography on silica (pretreated with 1% Et3N) eluting with hexane/EtOAc (90:10). Yield = 325.3 mg, 83%, 90:10 dr, oily substance. $^1$H NMR (400 MHz, Chloroform-$d$) δ 9.85 (s, 1H), 7.44 – 7.32 (m, 5H), 6.48 (dd, $J = 15.8$, 1.3 Hz, 1H), 6.14 (dd, $J = 15.8$, 6.2 Hz, 1H), 5.00 – 4.78 (m, 2H), 3.98 – 3.87 (m, 1H), 3.75 (s, 3H), 1.99 – 1.73 (m, 8H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 185.12, 169.56, 132.68, 128.78, 128.56, 126.85, 125.92, 102.93, 62.63, 57.27, 52.91, 44.25, 30.97, 29.40, 23.06, 23.04. HRMS calc for C$_{20}$H$_{22}$ClNO$_3$S 391.1009, found 391.1003.
Compound 4b5: Prepared using **General Procedure A**. Temp = 23 °C for 18 h. Purification: Flash chromatography on silica (pretreated with 1% Et3N) eluting with hexane/EtOAc (75:25). Yield = 342.3 mg, 80%, 95:5 dr, oily substance. 1H NMR (400 MHz, Chloroform-d) δ 9.96 (s, 1H), 7.46 – 7.30 (m, 10H), 6.48 (dd, J = 15.8, 1.3 Hz, 1H), 6.04 – 5.89 (m, 2H), 4.79 (ddd, J = 6.4, 2.8, 1.4 Hz, 1H), 3.66 (s, 3H), 2.93 (d, J = 2.8 Hz, 1H), 1.77 (d, J = 7.1 Hz, 3H). 13C NMR (101 MHz, CDCl3) δ 185.86, 167.60, 140.99, 137.01, 135.86, 133.72, 129.25, 128.68, 127.42, 126.89, 122.43, 58.56, 56.94, 53.05, 46.52, 17.26. HRMS calc for C23H22ClNO3S 427.1009, found 427.1005.
Compound **4b6**: Prepared using **General Procedure A**. Temp = 23 °C for 18 h. Purification: Flash chromatography on silica (pretreated with 1% Et3N) eluting with hexane/EtOAc (75:25). Yield = 311.5 mg, 82%, 95:5 dr, oily substance. 1H NMR (400 MHz, Chloroform-d) δ 9.80 (s, 1H), 7.31 (dd, J = 8.1, 6.8 Hz, 2H), 7.26 – 7.15 (m, 3H), 6.23 (s, 1H), 4.96 (p, J = 6.7 Hz, 1H), 4.73 – 4.67 (m, 1H), 3.93 – 3.88 (m, 1H), 3.70 (s, 3H), 1.91 (d, J = 1.3 Hz, 3H), 1.33 (d, J = 6.7 Hz, 3H), 1.24 (d, J = 6.6 Hz, 3H). 13C NMR (101 MHz, CDCl3) δ 184.9, 169.6, 143.6, 136.7, 134.4, 128.9, 128.7, 128.3, 127.1, 101.6, 62.1, 53.4, 52.9, 40.7, 21.5, 20.9, 15.7. HRMS calc for C19H22ClNO3S 379.1009, found 379.1003.
Compound 4b7: Prepared using **General Procedure A**. Temp = 23 °C for 18 h. Purification: Flash chromatography on silica (pretreated with 1% Et3N) eluting with hexane/EtOAc (75:25). Yield = 294.7 mg, 78%, 95:5 dr, oily substance. $^1$H NMR (400 MHz, CDCl$_3$) δ 9.70 (s, 1H), 7.36 – 7.25 (m, 5H), 6.23 (s, 1H), 4.62 (d, 1H), 3.83 (d, 1H), 3.65 (s, 3H), 3.26 – 3.11 (m, 1H), 1.79 (s, 3H), 1.07 – 0.91 (m, 4H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 184.73, 169.90, 146.16, 136.56, 132.99, 129.10, 128.41, 128.40, 128.32, 128.30, 127.20, 103.00, 69.29, 52.93, 40.53, 36.70, 15.16, 10.04, 9.90. HRMS calc for C$_{19}$H$_{20}$ClNO$_3$S 377.0852, found 377.0856.
Compound 4b8: Prepared using General Procedure A. Temp = room temperature, time = 6 h, Purification: Flash chromatography on silica (pretreated with 1% Et3N) eluting with hexane/EtOAc (50:50). Yield = 314 mg, 71%, oily substance. $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 9.99 (s, 1H), 7.34 (m, 7H), 7.25 (d, $J = 7.2$ Hz, 2H), 6.46 (s, 1H), 4.88 (d, 1H), 3.96 (d, $J = 2.5$ Hz, 1H), 3.83 (s, 3H), 3.72 (s, 3H), 1.91 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 185.4, 170.4, 159.2, 142.6, 137.3, 136.5, 133.3, 131.5, 129.5, 129.1, 114.9, 102.5, 72.6, 55.5, 53.1, 40.1, 17.6. HRMS calc for C$_{23}$H$_{20}$ClNO$_4$S, 443.0958, found 443.0965.
Compound 4b9: Prepared using **General Procedure A**. Temp = room temperature, time = 6 h, Purification: Flash chromatography on silica (pretreated with 1% Et3N) eluting with hexane/EtOAc (50:50). Yield = 330 mg, 68%, oily substance. $^1$H NMR (400 MHz, Chloroform-d) $\delta$ 9.86 (s, 1H), 7.42 – 7.31 (m, 2H), 7.31 – 7.18 (m, 5H), 6.68 – 6.59 (m, 2H), 6.48 (s, 1H), 4.91 (t, $J = 1.9$ Hz, 1H), 3.96 (dd, $J = 2.3$, 1.0 Hz, 1H), 3.76 (s, 3H), 3.38 (q, $J = 7.1$ Hz, 4H), 1.93 (d, $J = 1.3$ Hz, 3H), 1.20 (t, $J = 7.1$ Hz, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 185.05, 169.89, 147.41, 143.62, 136.77, 133.56, 132.57, 129.34, 129.13, 128.32, 127.16, 111.07, 101.70, 70.93, 52.91, 44.49, 40.18, 15.99, 12.62. HRMS calc for C$_{26}$H$_{29}$ClN$_2$O$_3$S, 484.1587, found 484.1582.
Compound 4b10: Prepared using **General Procedure A.** Temp = room temperature, time = 6 h, Purification: Flash chromatography on silica (pretreated with 1% Et₃N) eluting with hexane/EtOAc (50:50). Yield = 317 mg, 79%, oily substance. $^1$H NMR (400 MHz, Chloroform-$d$) δ 9.84 (s, 1H), 7.31 – 7.02 (m, 10H), 5.25 (d, $J = 16.0$ Hz, 1H), 4.95 (s, 1H), 4.12 (d, $J = 15.9$ Hz, 1H), 3.44 (s, 3H), 2.23 (dd, $J = 16.2$, 5.6 Hz, 1H). $^{13}$C NMR (400 MHz, CDCl₃) δ 187.2, 171.7, 150.4, 139.1, 135.7, 129.2, 128.2, 127.5, 126.9, 106.2, 63.6, 53.8, 51.8, 42.6. HRMS calc for C$_{20}$H$_{18}$ClNO$_3$S, 387.0696, found 387.0691.
Compound 4b11: Prepared using **General Procedure A**. Temp = room temperature, time = 6 h, Purification: Flash chromatography on silica (pretreated with 1% Et3N) eluting with hexane/EtOAc (50:50). Yield = 300 mg, 72%, oily substance. ¹H NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 9.90 (s, 1H, 7.28 – 7.12 (m, 5H), 6.90 – 6.72 (m, 3H), 5.27 (d, \(J = 16.1\) Hz, 1H), 5.12 (d, \(J = 2.4\) Hz, 1H), 4.35 (d, \(J = 16.1\) Hz, 1H), 3.75 – 3.58 (m, 7H). ¹³C NMR (101 MHz, CDCl₃) \(\delta\) 185.0, 167.1, 159.6, 145.15, 137.7, 134.92, 130.06, 129.88, 129.55, 128.76, 128.43, 128.18, 127.98, 127.44, 127.01, 119.14, 114.49, 113.77, 112.68, 102.23, 65.84, 56.50, 52.81, 44.03. HRMS calc for C₂₃H₂₆ClNO₄S, 417.0802, found 417.0806.
Compound 4b12: Prepared using **General Procedure A**. Temp = 23 °C for 18 h. Purification: Flash chromatography on silica (pretreated with 1% Et₃N) eluting with hexane/EtOAc (75:25). Yield = 254.3 mg, 75%, 80:20 dr, oily substance. ¹H NMR (400 MHz, Chloroform-d) δ 9.92 (s, 1H), 7.44 – 7.22 (m, 3H), 7.19 – 7.12 (m, 2H), 5.36 (d, J = 2.5 Hz, 1H), 4.96 (p, J = 6.7 Hz, 1H), 3.89 – 3.83 (m, 4H), 1.31 (d, J = 6.8 Hz, 3H), 1.01 (d, J = 6.8 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 184.98, 169.52, 140.98, 128.78, 128.46, 128.36, 127.20, 126.18, 100.89, 59.75, 59.60, 53.80, 53.45, 52.86, 48.38, 43.91, 33.53, 22.35, 21.63, 20.68, 19.59. HRMS calc for C₁₆H₁₈ClNO₃S, 339.0696, found 339.0691.
Compound 4b13: Prepared using General Procedure A. Temp = 23 °C for 18 h. Purification: Flash chromatography on silica (pretreated with 1% Et₃N) eluting with hexane/EtOAc (75:25). Yield = 281.9 mg, 76%, 80:20 dr, oily substance. ¹H NMR (400 MHz, Chloroform-d) δ 9.85 (s, 1H), 7.06 (d, J = 8.2 Hz, 2H), 6.81 (d, J = 8.2 Hz, 2H), 5.29 (d, J = 2.7 Hz, 1H), 4.92 (p, J = 6.8 Hz, 1H), 3.74 – 3.69 (m, 7H), 1.28 (d, J = 6.7 Hz, 3H), 1.03 (d, J = 6.7 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 185.24, 184.91, 169.60, 159.48, 144.06, 133.10, 128.54, 127.44, 114.09, 113.77, 100.76, 59.31, 59.15, 55.35, 55.23, 53.79, 53.44, 52.79, 48.49, 44.17, 22.37, 21.67, 20.66, 19.60. HRMS calc for C₁₇H₂₀ClNO₄S, 369.0802, found 369.0807.
Compound 4b14: Prepared using **General Procedure A**. Temp = 23 °C for 18 h. Purification: Flash chromatography on silica (pretreated with 1% Et₃N) eluting with hexane/EtOAc (75:25). Yield = 272.5 mg, 77%, 95:5 dr, oily substance. ¹H NMR (400 MHz, Chloroform-δ) δ 10.01 (s, 1H), 7.43 – 7.29 (m, 3H), 7.25 – 7.18 (m, 2H), 5.77 (d, J = 4.7 Hz, 1H), 3.97 (dd, J = 4.7, 0.8 Hz, 1H), 3.76 (s, 3H), 1.61 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 185.70, 169.99, 145.04, 139.43, 129.04, 128.29, 126.12, 63.41, 62.68, 52.98, 49.28, 31.49. HRMS calc for C₁₇H₂₀ClNO₃S, 353.0852, found 353.0859.
Compound 4b15: Prepared using **General Procedure A**. Temp = 23 °C for 18 h. Purification: Flash chromatography on silica (pretreated with 1% Et₃N) eluting with hexane/EtOAc (75:25). Yield = 280.4 mg, 83%, 90:10 dr, oily substance. $^1$H NMR (400 MHz, Chloroform-d) δ 9.88 (s, 1H), 7.45 – 7.27 (m, 3H), 7.23 – 7.09 (m, 2H), 5.39 (d, $J$ = 3.0 Hz, 1H), 3.91 – 3.68 (m, 1H), 3.72 (s, 3H), 3.06 (tt, $J$ = 6.2, 4.6 Hz, 1H), 1.01 – 0.84 (m, 4H). $^{13}$C NMR (101 MHz, CDCl₃) δ 184.71, 169.99, 146.43, 139.28, 129.01, 128.54, 126.00, 102.34, 67.09, 65.99, 52.89, 43.41, 36.96, 10.02, 9.85. FTIR (KBr): 3011.0, 2952.3, 2856.8, 1734.9, 1632.9, 1586.1, 1539.2, 1496.1, 1434.9, 1403.9, 1355.2, 1315.4, 1253.1, 1217.5, 1169.1, 1070.1, 1031.9, 990.8, 970.3, 911.0, 892.4, 832.8, 805.3, 769.7, 751.5. HRMS calc for C₁₆H₁₆ClNO₃S, 337.0539, found 337.0533.
Scheme 3 results

Compound 5a: Prepared in 0.5 mmol scale using General Procedure B. Purification: Flash chromatography on silica (pretreated with 1% Et$_3$N) eluting with hexane/EtOAc (95:5). Yield = 221 mg, 79%, 95:5 dr. $^1$H NMR (400 MHz, Chloroform-d) δ 9.68 (s, 1H), 7.41 – 7.22 (m, 6H), 7.15 – 7.06 (m, 2H), 6.89 – 6.78 (m, 2H), 6.56 (d, $J = 15.8$ Hz, 1H), 6.27 (dd, $J = 15.8$, 7.7 Hz, 1H), 4.99 (d, $J = 1.7$ Hz, 1H), 4.73 (dt, $J = 7.6$, 1.4 Hz, 1H), 3.78 (t, $J = 3.3$ Hz, 7H), 0.91 (d, $J = 4.3$ Hz, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 180.60, 168.30, 158.60, 138.54, 136.50, 135.62, 133.9, 128.7, 128.5, 127.8, 126.9, 123.5, 114.3, 104.5, 95.2, 74.8, 62.4, 55.6, 52.8, 18.4, 11.0. HRMS calc for C$_{33}$H$_{41}$NO$_5$Si, 559.2754, found 559.2759.
Compound 5b: Prepared in 0.5 mmol scale using **General Procedure B.** Purification: Flash chromatography on silica (pretreated with 1% Et$_3$N) eluting with hexane/EtOAc (95:5). Yield = 243.9 mg, 85%, 95:5 dr. $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 9.97 (s, 1H), 7.45 – 7.30 (m, 5H), 7.30 – 7.17 (m, 4H), 6.88 (d, 2H), 6.44 (s, 1H), 4.73 (t, $J = 1.8$ Hz, 1H), 3.96 (dd, $J = 2.4$, 1.0 Hz, 1H), 3.80 (s, 3H), 3.74 (s, 3H), 1.93 (s, 3H), 0.91 (s, 21H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 186.53, 169.89, 159.01, 139.01, 134.42, 129.27, 129.09, 128.81, 128.70, 128.63, 128.61, 128.31, 127.12, 114.21, 111.16, 105.21, 96.56, 67.61, 55.58, 52.86, 39.43, 18.63, 18.53, 16.00, 11.03. HRMS calc for C$_{34}$H$_{43}$NO$_5$Si, 573.2911, found 573.2914.
Compound 5c: Prepared in 0.5 mmol scale using **General Procedure B**. Purification: Flash chromatography on silica (pretreated with 1% Et₃N) eluting with hexane/EtOAc (95:5). Yield = 195.8 mg, 72%, 95:5 dr. ¹H NMR (400 MHz, Chloroform-δ) δ 9.72 (s, 1H), 7.46 – 7.35 (m, 2H), 7.39 – 7.31 (m, 1H), 7.34 – 7.23 (m, 2H), 7.14 (d, J = 8.3 Hz, 1H), 7.14 – 7.02 (m, 3H), 6.59 (dd, J = 15.9, 1.0 Hz, 1H), 6.29 (dd, J = 15.8, 7.3 Hz, 1H), 5.02 (d, J = 1.6 Hz, 1H), 4.79 (dt, J = 7.3, 1.5 Hz, 1H), 3.75 (s, 3H), 2.41 – 2.26 (m, 1H), 2.33 (s, 3H), 1.15 – 1.04 (m, 2H), 1.02 – 0.85 (m, 22H). ¹³C NMR (101 MHz, CDCl₃) δ 180.79, 168.20, 141.02, 138.94, 136.84, 135.64, 133.81, 129.69, 128.76, 128.51, 126.89, 125.92, 123.58, 104.31, 95.23, 74.81, 62.12, 52.75, 21.02, 18.44, 11.06. HRMS calc for C₃₃H₄₁NO₄Si, 543.2805, found 543.2810.
Compound 5d: Prepared in 0.5 mmol scale using **General Procedure B**. Purification: Flash chromatography on silica (pretreated with 1% Et$_3$N) eluting with hexane/EtOAc (95:5). Yield = 225.5 mg, 78%, 95:5 dr. $^1$H NMR (400 MHz, Chloroform-d) δ 9.72 (s, 1H), 7.52 (dq, $J = 8.5$, 1.9, 1.4 Hz, 2H), 7.42 – 7.30 (m, 2H), 7.32 – 7.22 (m, 3H), 7.22 – 7.09 (m, 2H), 6.56 (s, 1H), 5.21 (d, $J = 1.4$ Hz, 1H), 4.80 (q, $J = 1.4$ Hz, 1H), 3.67 (s, 3H), 2.02 (d, $J = 1.3$ Hz, 3H), 1.18 – 1.07 (m, 21H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 180.49, 168.20, 142.56, 136.36, 133.08, 129.16, 128.64, 128.38, 127.35, 124.65, 122.18, 105.92, 92.39, 72.86, 68.36, 52.77, 18.73, 15.45, 11.35. HRMS calc for C$_{33}$H$_{40}$ClNO$_4$Si, 577.2415, found 577.2410.
Compound 5e: Prepared in 0.25 mmol scale using **General Procedure B.** Purification: Flash chromatography on silica (pretreated with 1% Et$_3$N) eluting with hexane/EtOAc (90:10). Yield = 103.2 mg, 81%, 95:5 dr. $^1$H NMR (400 MHz, CDCl$_3$) δ 9.55 (s, 1H), 7.43 – 7.31 (m, 2H), 7.30 – 7.18 (m, 2H), 6.39 (s, 1H), 4.95 (d, $J = 1.4$ Hz, 1H), 4.73 (p, $J = 6.7$ Hz, 1H), 4.45 (d, $J = 1.4$ Hz, 1H), 3.78 (s, 3H), 1.93 (s, 3H), 1.28 (s, 3H), 1.26 (s, 3H), 1.23 – 1.13 (m, 21H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 179.77, 168.87, 137.77, 136.78, 135.28, 135.25, 129.68, 129.01, 128.29, 128.06, 127.02, 104.67, 94.61, 73.46, 58.62, 52.82, 51.74, 20.71, 20.43, 18.68, 15.27, 11.27. HRMS calc for C$_{33}$H$_{43}$NO$_4$Si, 509.2961, found 509.2966.
Compound 5f: Prepared in 0.25 mmol scale using **General Procedure B.** Purification: Flash chromatography on silica (pretreated with 1% Et3N) eluting with hexane/EtOAc (98:2). Yield = 129.6 mg, 73%, 95:5 dr. 1H NMR (400 MHz, Chloroform-d) δ 9.76 (s, 1H), 7.47 – 7.27 (m, 7H), 7.18 (d, 2H), 6.62 (d, J = 15.8 Hz, 1H), 6.27 (dd, J = 15.8, 6.8 Hz, 1H), 5.06 (d, J = 1.7 Hz, 1H), 4.83 (dt, J = 6.8, 1.6 Hz, 1H), 3.73 (s, 3H), 1.26 – 1.09 (m, 24H), 0.96 – 0.89 (m, 18H). 13C NMR (101 MHz, CDCl3) δ 181.22, 167.92, 143.19, 139.88, 135.44, 133.91, 132.76, 128.84, 128.80, 128.64, 126.96, 126.92, 124.94, 124.85, 123.15, 121.64, 106.36, 104.77, 94.99, 91.65, 74.89, 61.59, 52.80, 18.71, 18.46, 11.34, 11.10. HRMS calc for C33H59NO4Si2, 709.3983, found 709.3988.
Compound 5g: Prepared in 0.25 mmol scale using General Procedure B. Purification: Flash chromatography on silica (pretreated with 1% Et3N) eluting with hexane/EtOAc (90:10). Yield = 114.4 mg, 71%, 95:5 dr. 1H NMR (400 MHz, Chloroform-d) δ 9.72 (s, 1H), 7.45 – 7.30 (m, 4H), 7.34 – 7.19 (m, 3H), 7.21 (d, 2H), 6.49 (s, 1H), 5.17 (d, J = 1.9 Hz, 1H), 4.66 (d, J = 1.9 Hz, 1H), 3.80 – 3.67 (m, 5H), 2.62 (t, J = 6.8 Hz, 2H), 2.14 – 1.92 (m, 5H), 1.04 – 0.86 (m, 21H). 13C NMR (101 MHz, CDCl3) δ 181.11, 168.28, 143.14, 140.13, 136.52, 132.26, 129.12, 128.63, 128.33, 127.21, 124.41, 121.56, 104.67, 95.07, 88.90, 80.87, 72.96, 66.15, 52.74, 43.75, 31.46, 18.48, 16.98, 15.37, 11.05. HRMS calc for C38H46ClNO4Si, 643.2885, found 643.2881.
Compound 5h: Prepared in 0.25 mmol scale using **General Procedure B**. Purification: Flash chromatography on silica (pretreated with 1% Et$_3$N) eluting with hexane/EtOAc (80:20). Yield = 85.4 mg, 71%, 95:5 dr. $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 9.72 (s, 1H), 7.69 – 7.41 (m, 8H), 7.20 – 7.02 (m, 2H), 6.98 – 6.48 (m, 1H), 6.41 – 6.02 (m, 2H), 5.08 – 4.75 (m, 2H), 3.76 – 3.51 (s, 3H), 2.32 – 2.01 (m, 2H), 1.89 – 1.52 (m, 4H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 180.3, 168.2, 142.1, 136.0, 130.2, 128.1, 127.8, 126.2, 120.2, 92.2, 85.2, 74.2, 62.5, 52.4, 28.2, 24.3, 23.8, 22.8, 22.4. HRMS calc for C$_{29}$H$_{26}$ClN$_4$O$_4$, 487.1550, found 487.1556.
Compound 5i: Prepared in 0.25 mmol scale using **General Procedure B**. Purification: Flash chromatography on silica (pretreated with 1% Et3N) eluting with hexane/EtOAc (80:20). Yield = 92.0 mg, 76%, 95:5 dr. $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 9.71 (s, 1H), 7.51 – 7.40 (m, 4H), 7.40 – 7.27 (m, 3H), 7.11 (d, $J$ = 8.5 Hz, 2H), 6.55 (s, 1H), 5.19 (d, $J$ = 1.5 Hz, 1H), 4.79 (d, $J$ = 1.5 Hz, 1H), 3.80 – 3.69 (m, 5H), 2.63 (t, $J$ = 6.8 Hz, 2H), 2.08 (q, $J$ = 6.6 Hz, 2H), 2.01 (s, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 180.44, 168.18, 142.16, 136.38, 133.06, 132.60, 132.20, 131.26, 129.16, 128.62, 128.41, 128.37, 128.34, 127.34, 124.79, 122.34, 89.70, 80.62, 72.82, 68.41, 52.71, 43.76, 31.39, 16.95, 15.4. HRMS calc for C$_{26}$H$_{33}$Cl$_2$NO$_4$, 483.1004, found 483.1008.
Compound 5j: Prepared in 0.50 mmol scale using General Procedure B. Purification: Flash chromatography on silica (pretreated with 1% Et3N) eluting with hexane/EtOAc (80:20). Yield = 154.5 mg, 69%, 95:5 dr. \(^1\)H NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 9.72 (s, 1H), 7.70 – 7.21 (m, 7H), 7.22 – 7.04 (m, 2H), 6.78 – 6.52 (d, 1H), 6.41 – 6.03 (d, 1H), 5.02 – 4.88 (m, 2H), 3.87 – 3.51 (s, 3H), 1.62 – 1.42 (t, 1H), 0.98 – 0.72 (m, 4H). \(^1\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 180.5, 168.8, 141.2, 138.2, 136.5, 135.4, 134.2, 133.1, 129.8, 127.2, 126.8, 125.2, 122.7, 96.1, 74.2, 63.8, 52.9, 9.7, 0.1. HRMS calc for C\(_{26}\)H\(_{22}\)ClN\(_4\), 447.1237, found 447.1244.
Compound 5k: Prepared in 0.50 mmol scale using **General Procedure B**. Purification: Flash chromatography on silica (pretreated with 1% Et3N) eluting with hexane/EtOAc (90:10). Yield = 179.3 mg, 72%, 95:5 dr. 1H NMR (400 MHz, Chloroform-d) δ 9.73 (s, 1H), 7.65 – 7.60 (m, 4H), 7.50 – 7.36 (m, 5H), 7.29 – 7.26 (m, 5H), 6.61 (s, 1H), 5.21 (d, J = 1.5 Hz, 1H), 4.87 (s, 1H), 3.71 (s, 3H), 2.04 (s, 3H). 13C NMR (101 MHz, CDCl3) δ 180.4, 168.4, 142.0, 140.1, 139.9, 136.5, 129.2, 129.0, 128.7, 128.4, 128.0, 127.8, 127.3, 127.1, 125.5, 120.3, 115.4, 72.9, 68.7, 52.8, 15.5. HRMS calc for C30H24ClNO4, 497.1394, found 497.1399.
Compound 5l: Prepared in 0.25 mmol scale using **General Procedure B**. Purification: Flash chromatography on silica (pretreated with 1% Et3N) eluting with hexane/EtOAc (95:5). Yield = 98.8 mg, 67%, 95:5 dr. 1H NMR (400 MHz, Chloroform-d) δ 9.97 (s, 1H), 7.45 – 7.30 (m, 5H), 7.30 – 7.17 (m, 4H), 6.88 (d, 2H), 6.44 (s, 1H), 4.73 (t, $J = 1.8$ Hz, 1H), 3.96 (dd, $J = 2.4$, 1.0 Hz, 1H), 3.80 (s, 3H), 3.74 (s, 3H), 1.93 (s, 3H), 0.91 (s, 21H). 13C NMR (101 MHz, CDCl3) δ 186.53, 169.89, 159.01, 139.01, 136.82, 134.42, 129.27, 129.09, 128.81, 128.70, 128.63, 128.61, 128.31, 127.12, 114.21, 111.16, 105.21, 96.56, 67.61, 55.58, 52.86, 39.43, 18.63, 18.53, 16.00, 11.03. HRMS calc for C34H33NO4SSi, 589.2682, found 589.2688.
Compound 5m: Prepared in 0.25 mmol scale using General Procedure B. Purification: Flash chromatography on silica (pretreated with 1% Et₃N) eluting with hexane/EtOAc (90:10). Yield = 108.8 mg, 69%, 95:5 dr. $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 9.92 (s, 1H), 7.43 – 7.20 (m, 7H), 6.57 (dd, $J = 8.8, 4.0$ Hz, 2H), 6.46 (s, 1H), 4.74 (t, $J = 1.7$ Hz, 1H), 3.97 – 3.91 (m, 1H), 3.77 (s, 3H), 3.36 (q, $J = 7.1$ Hz, 4H), 1.98 (s, 3H), 1.22 – 1.05 (m, 6H), 0.93 (s, 21H). $^{13}$C NMR (101 MHz, CDCl₃) $\delta$ 186.41, 169.94, 147.14, 139.59, 137.04, 134.72, 134.21, 129.16, 129.12, 128.27, 127.00, 111.28, 111.05, 110.07, 104.75, 96.73, 67.92, 52.81, 44.48, 39.45, 18.56, 18.54, 16.07, 12.62, 11.10. HRMS calc for C$_{37}$H$_{50}$N$_2$O$_3$Si, 630.3311, found 630.3314.
Compound 5n: Prepared in 0.50 mmol scale using General Procedure B. Purification: Flash chromatography on silica (pretreated with 1% Et₃N) eluting with hexane/EtOAc (90:10). Yield = 183.3 mg, 70%, 90:10 dr. ¹H NMR (400 MHz, CDCl₃) δ 9.97 (s, 1H), 7.43 – 7.25 (m, 5H), 6.22 (s, 1H), 4.63 (d, J = 3.0 Hz, 1H), 3.83 (d, J = 3.0 Hz, 1H), 3.66 (s, 3H), 3.19 (tt, J = 7.0, 4.4 Hz, 1H), 1.83 (s, 3H), 1.07 – 0.95 (m, 25H). ¹³C NMR (101 MHz, CDCl₃) δ 186.11, 170.05, 140.71, 136.86, 134.25, 134.13, 132.24, 132.14, 132.07, 132.05, 129.77, 129.13, 128.67, 128.59, 128.55, 128.51, 128.30, 127.73, 127.05, 112.11, 105.60, 96.58, 65.49, 52.87, 39.50, 36.67, 18.78, 15.51, 11.37, 10.37, 9.48. HRMS calc for C₃₀H₄₁NO₃SSi, 523.2576, found 523.2581.
Compound 5o: Prepared in 0.50 mmol scale using **General Procedure B**. Purification: Flash chromatography on silica (pretreated with 1% Et$_3$N) eluting with hexane/EtOAc (90:10). Yield = 197.2 mg, 68%, 90:10 dr. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.88 (s, 1H), 7.38 – 7.22 (m, 5H), 6.20 (s, 1H), 4.64 (d, $J = 2.1$ Hz, 1H), 3.77 (d, $J = 2.1$ Hz, 1H), 3.70 – 3.45 (m, 4H), 1.97 (s, 3H), 1.77 – 1.69 (m, 4H), 1.51 – 1.41 (m, 6H), 1.15 – 1.03 (m, 21H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 186.41, 169.73, 139.29, 136.96, 129.03, 128.82, 128.30, 127.03, 110.32, 104.77, 96.26, 52.82, 40.54, 33.63, 33.61, 27.24, 24.89, 24.63, 18.81, 16.15, 11.34. HRMS calc for C$_{34}$H$_{49}$N$_2$O$_3$Si, 579.3202, found 579.3208.
Scheme 4 results

Compound 6a: Prepared in 0.25 mmol scale using **General Procedure C**. Purification: Flash chromatography on silica (pretreated with 1% Et$_3$N) eluting with hexane/EtOAc (80:20). Yield = 103.8 mg, 83%, 95:5 dr. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.78 (s, 1H), 7.79 (d, $J =$ 14.2 Hz, 1H), 7.53 – 7.02 (m, 13H), 6.99 (d, $J =$ 14.2 Hz, 1H), 6.73 (d, $J =$ 12.5 Hz, 1H), 6.49 (dd, $J =$ 12.6, 1.3 Hz, 1H), 5.08 (dd, $J =$ 5.8, 1.3 Hz, 1H), 4.78 (d, $J =$ 1.3 Hz, 1H), 3.75 (s, 3H), 2.22 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 180.58, 180.49, 167.98, 138.59, 134.15, 129.59, 128.89, 128.87, 127.28, 127.23, 126.99, 126.62, 122.71, 122.40, 74.75, 74.72, 64.19, 63.98, 52.82, 52.77, 21.40. HRMS calc for C$_{30}$H$_{26}$ClNO$_4$, 499.1550, found 499.1555.
Compound 6b: Prepared in 0.25 mmol scale using **General Procedure C**. Purification: Flash chromatography on silica (pretreated with 1% Et$_3$N) eluting with hexane/EtOAc (80:20). Yield = 93.6 mg, 72%, 95:5 dr. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.79 (s, 1H), 7.49 – 7.32 (m, 11H), 7.32 – 7.07 (m, 4H), 6.77 (d, $J = 14.5$ Hz, 1H), 6.16 (dd, $J = 14.5, 6.7$ Hz, 1H), 5.12 (d, $J = 1.5$ Hz, 1H), 4.92 (dd, $J = 6.7, 1.5$ Hz, 1H), 3.68 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 180.54, 167.95, 141.85, 138.59, 135.95, 135.51, 135.37, 134.14, 133.67, 132.71, 132.23, 129.05, 128.88, 128.80, 128.52, 127.92, 127.85, 127.43, 127.00, 125.69, 122.65, 74.75, 64.11, 52.77. HRMS calc for C$_{30}$H$_{26}$Cl$_2$N$_2$O$_4$, 499.1550, found 499.1555.
Compound 6c: Prepared in 0.25 mmol scale using **General Procedure C**. Purification: Flash chromatography on silica (pretreated with 1% Et₃N) eluting with hexane/EtOAc (50:50). Yield = 100.6 mg, 78%, 95:5 dr. \(^1\)H NMR (400 MHz, CDCl₃) δ 9.79 (s, 1H), 7.70 (d, \(J = 14.1\) Hz, 1H), 7.40 (d, \(J = 8.1\) Hz, 2H), 7.48 – 7.28 (m, 6H), 7.21 – 7.14 (m, 4H), 6.89 – 6.81 (m, 2H), 6.72 (d, \(J = 15.7\) Hz, 1H), 6.30 (dd, \(J = 15.5, 6.7\) Hz, 1H), 5.01 (dd, \(J = 6.7, 1.6\) Hz, 1H), 4.97 (d, \(J = 1.6\) Hz, 1H).
1H), 3.81 (s, 3H), 3.72 (s, 3H). $^1$H NMR (101 MHz, CDCl$_3$) $\delta$ 180.58, 180.52, 167.96, 160.04, 141.69, 138.60, 134.15, 129.85, 129.79, 128.90, 128.87, 128.78, 127.63, 127.42, 127.28, 127.00, 125.71, 122.68, 119.41, 113.66, 112.03, 74.76, 64.15, 55.39, 52.77. HRMS calc for C$_{30}$H$_{26}$ClNO$_5$, 515.1500, found 515.1504.
Compound 6d: Prepared in 0.25 mmol scale using General Procedure C. Purification: Flash chromatography on silica (pretreated with 1% Et3N) eluting with hexane/EtOAc (75:25). Yield = 109.8 mg, 81%, 95:5 dr. 1H NMR (400 MHz, CDCl3) δ 9.78 (s, 1H), 7.79 (d, J = 14.5 Hz, 1H), 7.59 – 7.27 (m, 10H), 7.23 – 7.03 (m, 3H), 6.91 (d, J = 14.5 Hz, 1H), 6.71 (d, J = 15.8 Hz, 1H), 6.30 (dd, J = 15.8, 6.7 Hz, 1H), 4.98 (dd, J = 6.7, 1.6 Hz, 1H), 4.88 (d, J = 1.6 Hz, 1H), 3.71 (s, 3H), 1.39 (s, 9H). 13C NMR (101 MHz, CDCl3) δ 180.56, 167.96, 151.35, 141.45, 138.59, 136.61, 135.42, 134.23, 134.21, 134.12, 129.72, 128.88, 128.86, 128.76, 127.27, 127.00, 126.53, 126.46, 125.82, 125.73, 122.73, 122.43, 74.73, 64.18, 52.77, 34.56, 31.38. HRMS calc for C33H32ClNO4, 541.2020, found 541.2026.
Compound 6e: Prepared in 0.25 mmol scale using General Procedure C. Purification: Flash chromatography on silica (pretreated with 1% Et₃N) eluting with hexane/EtOAc (60:40). Yield = 88.8 mg, 71%, 95:5 dr. ¹H NMR (400 MHz, Chloroform-đ) δ 9.73 (s, 1H), 7.67 – 7.48 (m, 4H),
7.48 – 7.34 (m, 4H), 7.37 – 7.22 (m, 4H), 7.25 – 7.16 (m, 2H), 7.20 – 7.12 (m, 2H), 6.59 (s, 1H), 5.21 (d, $J = 1.5$ Hz, 1H), 4.84 (d, $J = 1.5$ Hz, 1H), 3.79 (s, 1H), 3.70 (s, 3H), 2.04 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 180.36, 168.35, 141.97, 136.99, 136.46, 136.28, 131.50, 129.85, 129.18, 128.86, 128.69, 128.38, 128.08, 127.45, 127.33, 127.31, 126.68, 125.37, 72.90, 68.61, 52.74, 15.45. HRMS calc for C$_{30}$H$_{26}$ClNO$_4$, 499.1550, found 499.1555.
Electronic Supplementary Information for RSC Advances; Beng and coworkers

![Normalized intensity vs. chemical shift](kb-10-127A2-f2.013.esp)

![Normalized intensity vs. chemical shift](kb-10-127A2-f2.003.esp)

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Scheme 5 results

To a 25 mL-round-bottomed flask equipped with a magnetic stir bar was added EtOAc (5 mL) and 10% Pd/C (100 mg) at room temperature. A solution of chloroenal 4a9 (113 mg, 0.25 mmol) in EtOAc (5 mL) was added. The flask was degassed and placed under an inert atmosphere of nitrogen. After complete addition of the chloroenal, the nitrogen line was cut off. A balloon of H2 was attached and the reaction mixture was stirred at room temperature. After complete consumption (based on GC-MS and TLC monitoring), the mixture was filtered through Celite and concentrated under reduced pressure to afford the product as an oil. Purification: Flash chromatography on silica (pretreated with 1% Et3N) eluting with hexane/EtOAc (85:15). Yield = 90.2 mg, 89%, 95:5 dr. 1H NMR (400 MHz, Chloroform-d) δ 7.42 – 7.29 (m, 6H), 7.14 – 6.71 (m, 3H), 5.63 (s, 1H), 4.82 (d, J = 1.7 Hz, 1H), 4.46 – 4.35 (m, 1H), 3.45 (s, 3H), 2.97 – 2.76 (m, 2H), 2.15 – 2.00 (m, 5H). 13C NMR (101 MHz, CDCl3) δ 169.14, 146.53, 140.69, 136.43, 132.11, 131.79, 131.48, 129.77, 128.72, 128.55, 128.43, 126.39, 125.65, 122.94, 117.40, 115.40, 110.74, 110.70, 101.99, 77.48, 77.16, 76.84, 75.26, 54.11, 51.91, 32.50, 30.99, 17.61. HRMS calc for C22H22F3NO3, 405.1552, found 405.1557.
To a 25 mL-round-bottomed flask equipped with a magnetic stir bar was added EtOAc (5 mL) and 10% Pd/C (100 mg) at room temperature. A solution of ynenal 5c (0.25 mmol) in EtOAc (5 mL) was added. The flask was degassed and placed under an inert atmosphere of nitrogen. After complete addition of the chloroenal, the nitrogen line was cut off. A balloon of H₂ was attached and the reaction mixture was stirred at room temperature. After complete consumption (based on GC-MS and TLC monitoring), the mixture was filtered through Celite and concentrated under reduced pressure to afford the product as an oil. Purification: Flash chromatography on silica (pretreated with 1% Et₃N) eluting with hexane/EtOAc (90:10). Yield = 124.6 mg, 93%, 95:5 dr. 

$^1$H NMR (400 MHz, CDCl₃) δ 7.31 – 7.26 (m, 5H), 6.96 (d, $J = 8.0$ Hz, 2H), 6.77 (d, $J = 8.0$ Hz, 2H), 4.51 (d, $J = 1.4$ Hz, 1H), 4.13 (ddd, $J = 10.7, 3.6, 1.5$ Hz, 1H), 3.23 (s, 3H), 3.12 – 3.02 (m, 1H), 2.88 (ddd,
$J = 13.0, 11.3, 5.7 \text{ Hz}, 1\text{H}$), 2.24 – 2.08 (m, 5H), 2.08 – 1.98 (m, 4H), 1.88 – 1.82 (m, 1H), 0.98 – 0.90 (m, 23H), 0.58 (ddd, $J = 14.5, 12.8, 5.5 \text{ Hz}, 1\text{H}$). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 169.87, 145.50, 142.00, 133.40, 130.73, 129.09, 128.56, 128.48, 126.05, 122.00, 116.10, 74.74, 59.67, 51.41, 33.76, 33.27, 22.93, 20.72, 18.81, 18.69, 15.87, 10.85, 8.90. HRMS calc for C$_{33}$H$_{49}$NO$_3$Si, 535.3482, found 535.3488.
Scheme 6 results

Compound 7a: Prepared in 0.50 mmol scale using **General Procedure D**. Purification: Flash chromatography on silica (pretreated with 1% Et$_3$N) eluting with hexane/EtOAc (85:15). Yield = 264.0 mg, 88%, 90:10 dr. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.56 – 7.16 (m, 14H), 6.75 (d, $J$ = 8.3 Hz, 1H), 6.29 (dd, $J$ = 15.9, 6.7 Hz, 1H), 5.83 – 5.76 (m, 1H), 5.13 (d, $J$ = 1.5 Hz, 1H), 4.72 (d, $J$ = 1.5 Hz, 1H), 3.91 (s, 3H), 3.87 (d, $J$ = 10.6 Hz, 1H), 2.23 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 168.26, 166.86, 153.55, 153.08, 141.28, 137.12, 136.63, 134.65, 134.53, 132.21, 129.86, 129.39, 129.33, 129.26, 129.23, 128.93, 128.61, 127.15, 126.77, 125.27, 118.76, 116.22, 114.85, 113.11, 112.66, 110.67, 86.66, 85.77, 67.20, 66.99, 54.04, 21.39. HRMS calc for C$_{35}$H$_{26}$ClN$_5$O$_5$, 599.1724, found 599.1729.
Compound 7b: Prepared in 0.50 mmol scale using **General Procedure D**. Purification: Flash chromatography on silica (pretreated with 1% Et3N) eluting with hexane/EtOAc (65:35). Yield = 270.6 mg, 93%, 90:10 dr. \(^1\)H NMR (400 MHz, CDCl3) \(\delta\) 7.61 – 7.30 (m, 7H), 7.03 – 6.93 (m, 3H), 6.77 (d, \(J = 15.9\) Hz, 1H), 6.12 (dd, \(J = 15.9, 7.0\) Hz, 1H), 5.13 (d, \(J = 1.8\) Hz, 1H), 4.70 – 4.63 (m, 1H), 4.06 – 3.98 (m, 1H), 3.88 – 3.76 (m, 7H), 1.21 (d, \(J = 6.5\) Hz, 3H), 1.10 (d, \(J = 6.5\) Hz, 3H). \(^13\)C NMR (101 MHz, CDCl3) \(\delta\) 167.52, 166.59, 160.89, 154.10, 153.85, 136.24, 133.98, 132.38, 129.16, 128.85, 128.16, 127.02, 118.38, 115.20, 114.89, 114.74, 113.97, 113.23, 113.04, 112.60, 85.78, 78.65, 59.75, 58.27, 55.53, 53.69, 52.55, 20.70, 20.13. HRMS calc for C\(_{32}\)H\(_{28}\)ClN\(_5\)O\(_4\), 581.1830, found 581.1837.
Compound 10: Prepared in 0.50 mmol scale using General Procedure D but the Diels-Alder reaction was conducted at 60 °C for 2 h. Purification: Flash chromatography on silica (pretreated with 1% Et₃N) eluting with hexane/EtOAc (80:20). Yield = 203.7 mg, 79%. ¹H NMR (400 MHz, Chloroform-d) δ 7.70 – 7.50 (m, 6H), 7.54 – 7.44 (m, 2H), 7.43 – 7.34 (m, 2H), 6.78 (s, 1H), 5.27 (d, J = 1.5 Hz, 1H), 5.16 (s, 1H), 4.09 (p, J = 8.3 Hz, 1H), 3.92 (s, 3H), 2.02 – 1.94 (m, 1H), 1.72 – 1.57 (m, 3H), 1.46 – 1.25 (m, 4H). ¹³C NMR (101 MHz, CDCl₃) δ 167.73, 166.69, 154.91, 153.84, 134.49, 133.84, 132.36, 129.75, 129.44, 129.32, 128.86, 126.42, 115.29, 114.51, 114.51, 113.84, 113.16, 112.52, 78.65, 62.68, 60.95, 53.91, 31.00, 30.11, 22.93, 22.73. HRMS calc for C₃₁H₂₅N₃O₃, 515.1957, found 515.1954.
Compound 11: Prepared in 0.50 mmol scale using General Procedure D but the Diels-Alder partner was bromomaleic anhydride (2 equiv) and the reaction was conducted at 90 °C for 12 h. Purification: Flash chromatography on silica (pretreated with 1% Et3N) eluting with hexane/EtOAc (50:50). Yield = 220.6 mg, 83%. 1H NMR (400 MHz, CDCl3) δ 7.49 – 7.10 (m, 12H), 6.96 – 6.82 (m, 3H), 6.77 (d, J = 8.3 Hz, 1H), 6.25 (dd, J = 15.9, 6.7 Hz, 1H), 5.01 – 4.98 (m, 2H), 3.36 (s, 3H), 2.29 (s, 3H). 13C NMR (101 MHz, CDCl3) δ 168.4, 167.9, 164.4, 142.8, 137.12, 136.6, 136.4, 136.2, 133.6, 132.7, 129.6, 128.8, 128.7, 128.2, 127.5, 127.2, 126.9, 126.7, 124.7, 122.3, 118.7, 114.0, 75.2, 62.9, 52.1, 20.9. HRMS calc for C33H25NO6, 531.1682, found 531.1688.
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