

## SUPPORTING INFORMATION

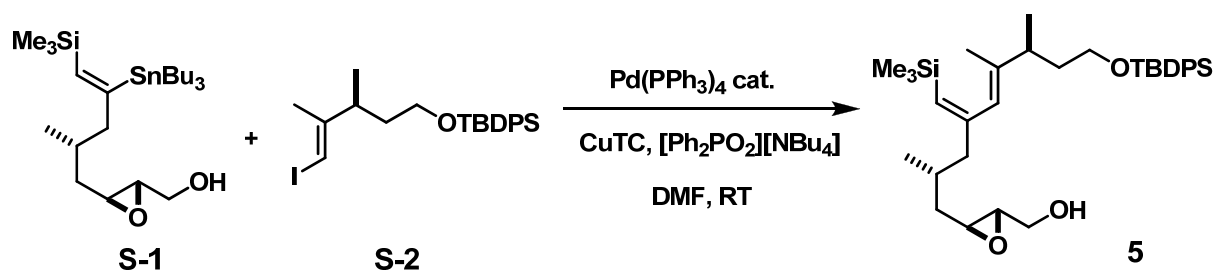
### A versatile protocol for Stille-Migita cross coupling reactions

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**General:** All reactions were carried out in flame-dried glassware under Ar. The solvents were purified by distillation over the drying agents indicated and were transferred under Ar: THF, Et<sub>2</sub>O (Mg-anthracene), DMF (Desmodur®, dibutyltin dilaurate). Flash chromatography: Merck silica gel 60 (230-400 mesh) or CombiFlash Companion (Teledyne Isco). NMR: Spectra were recorded on Bruker DPX 300, AV 400, or DMX 600 spectrometers in the solvents indicated; chemical shifts ( $\delta$ ) are given in ppm relative to TMS, coupling constants ( $J$ ) in Hz. The solvent signals were used as references and the chemical shifts converted to the TMS scale (CDCl<sub>3</sub>:  $\delta_C \equiv 77.0$  ppm; residual CHCl<sub>3</sub> in CDCl<sub>3</sub>:  $\delta_H \equiv 7.26$  ppm; CD<sub>2</sub>Cl<sub>2</sub>:  $\delta_C \equiv 54.0$  ppm; residual CH<sub>2</sub>Cl<sub>2</sub> in CD<sub>2</sub>Cl<sub>2</sub>:  $\delta_H \equiv 5.32$  ppm). <sup>11</sup>B NMR chemical shifts are given relative to external BF<sub>3</sub>·Et<sub>2</sub>O ( $\equiv 0$  ppm). IR: Nicolet Magna IR-750 or Perkin-Elmer spectrometer, wavenumbers ( $\tilde{\nu}$ ) in cm<sup>-1</sup>. MS (EI): Finnigan MAT 8200 (70 eV), Finnigan MAT 8400, ESI-MS: Bruker ESQ 3000, accurate mass determinations: Bruker APEX III FT-MS (7 T magnet). Melting points: Büchi melting point apparatus B-540 (corrected). Elemental analyses: H. Kolbe, Mülheim/Ruhr. Unless stated otherwise, all commercially available compounds (Fluka, Lancaster, Aldrich) were used as received. Compound **12** was identified by comparison with a commercially available authentic sample.

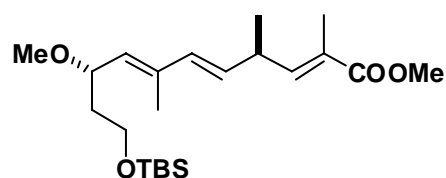


**Representative Procedure: Preparation of Diene 5.** A degassed solution of stannane **S-1** (1.3 g, 2.51 mmol) and vinyl iodide **S-2** (1.25 g, 2.61 mmol) in DMF (15 mL) was added to a

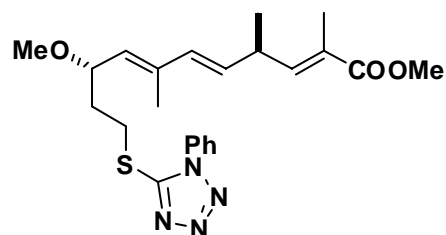
Schlenk tube containing flame-dried  $[\text{Ph}_2\text{PO}_2^-][\text{NBu}_4^+]$  (1.2 g, 2.76 mmol). Copper-thiophene carboxylate complex (CuTC, 717 mg, 3.76 mmol) was then introduced followed by  $\text{Pd}(\text{PPh}_3)_4$  (289 mg, 0.25 mmol). The reaction mixture was then stirred for 30 min before the reaction mixture was quenched with water (10 mL). The aqueous phase was extracted with  $\text{Et}_2\text{O}$  (2 x 20 mL), the combined organic layers were dried over  $\text{Na}_2\text{SO}_4$  and evaporated, and the residue was purified by flash chromatography (hexanes: *tert*-butyl methyl ether, 5:1) to afford product **5** as a colorless oil (1.08 g, 71%).  $[\alpha]_D^{25} = -7.1$  (*c* 1.0,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ ): 7.80-7.78 (m, 4H), 7.35-7.23 (m, 6H), 5.84 (br s, 1H), 5.50 (br s, 1H), 3.72-3.66 (m, 2H), 3.48 (ddd,  $J = 12.3, 5.2, 2.9$  Hz, 1H), 3.29 (ddd,  $J = 11.4, 7.0, 4.2$  Hz, 1H), 2.72 (qd,  $J = 13.4, 7.0$  Hz, 1H), 2.53 (m, 1H), 2.31 (dd,  $J = 7.0, 7.0$  Hz, 1H), 2.20 (dd,  $J = 13.4, 6.5$  Hz, 1H), 1.98 (dd,  $J = 13.4, 7.7$  Hz, 1H), 1.81-1.73 (m, 2H), 1.58-1.50 (m, 1H), 1.50 (d,  $J = 1.0$  Hz, 3H), 1.21 (ddd,  $J = 13.4, 7.8, 5.2$  Hz, 1H), 1.19 (s, 9H), 0.97 (d,  $J = 7.0$  Hz, 3H), 0.87 (m, 1H), 0.86 (d,  $J = 6.5$  Hz, 3H), 0.15 (s, 9H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta = 156.0, 141.9, 136.7, 135.0, 130.6, 127.1, 63.4, 62.4, 59.4, 54.9, 51.3, 39.7, 39.6, 38.9, 30.3, 27.7, 20.6, 20.0, 14.8, 0.5$ ; IR (film):  $\tilde{\nu} = 3438, 2956, 2930, 2858, 1590, 1427, 1106, 858, 832, 700$ ; HRMS (ESI):  $m/z$ : calcd for  $\text{C}_{35}\text{H}_{54}\text{NaO}_3\text{Si}_2 + \text{Na}$ : 601.3509 [ $M^+ + \text{Na}$ ]; found: 601.3506.

Unless stated otherwise, all other compounds were prepared analogously. Their analytical and spectroscopic data are compiled below:

**Compound 1.** Colorless oil (98 mg, 84%).  $[\alpha]_D^{20} = +7.5$  (*c* 1.0,  $\text{CHCl}_3$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 6.60$  (dd,  $J = 9.7, 1.4$  Hz, 1H), 6.06 (d,  $J = 15.8$  Hz, 1H), 5.55 (dd,  $J = 15.7, 6.9$  Hz, 1H), 5.26 (d,  $J = 9.1$  Hz, 1H), 4.23-4.16 (m, 1H), 3.74 (s, 3H), 3.72-3.67 (m, 1H), 3.61-3.57 (m, 1H), 3.27-3.22 (m, 4H), 1.87 (s, 3H), 1.80-1.75 (m, 4H), 1.63-1.57 (m, 1H), 1.15 (d,  $J = 6.8$  Hz, 3H), 0.89 (s, 9H), 0.04 (d,  $J = 5.3$  Hz, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 168.4, 144.8, 135.9, 133.2, 131.8, 130.7, 126.0, 73.7, 58.9, 55.7, 51.4, 38.4, 35.9, 25.5, 19.9, 17.9, 17.1, 12.5, 12.1, -5.7$ ; IR (film):  $\tilde{\nu} = 2953, 2929, 2857, 1716, 1435, 1252, 1090, 960, 834, 774, 750$ ; HRMS (ESI):  $m/z$ : calcd for  $\text{C}_{22}\text{H}_{40}\text{O}_4\text{Si} + \text{Na}$ : 419.25881 [ $M^+ + \text{Na}$ ]; found: 419.25884.

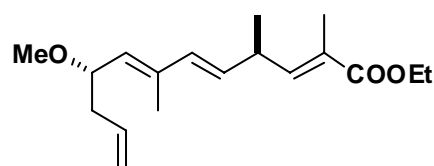


**Compound 2.** Colorless oil (106 mg, 87%).  $[\alpha]_D^{20} = +1.65$  (*c* 0.9,  $\text{CHCl}_3$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta = 7.55$ -7.45 (m, 5H), 6.48 (dd,  $J = 9.7, 1.4$  Hz, 1H), 6.00 (d,  $J = 15.8$  Hz, 1H), 5.53 (dd,  $J = 15.8, 6.8$  Hz, 1H), 5.18 (d,  $J = 8.9$  Hz, 1H), 4.09-4.05 (m, 1H), 3.62 (s, 3H), 3.40-3.30 (m, 2H), 3.12 (s, 3H), 2.01-1.80 (m, 2H), 1.77 (s, 3H), 1.69 (s, 3H), 1.30-1.20 (m, 1H), 1.06 (d,  $J = 6.8$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta = 169.26, 155.2, 145.5, 138.0, 133.9, 132.7, 131.5, 130.9, 130.6, 127.3, 124.7, 76.4, 56.6, 52.3, 37.0, 35.8, 30.4, 20.8, 13.6, 13.1$ ; IR (film):  $\tilde{\nu} = 2927, 1712, 1648, 1597, 1499, 1386,$

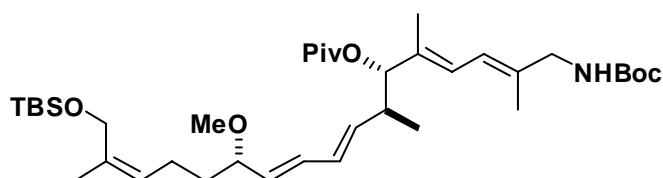


1239, 1088, 967, 760, 750, 693; HRMS (ESI):  $m/z$ : calcd for  $C_{23}H_{30}N_4O_3S+Na$ : 465.19309 [ $M^++Na$ ]; found: 465.19304.

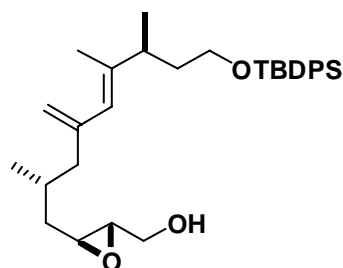
**Compound 3.** Colorless oil (175 mg, 80%).  $[\alpha]_D^{20} = -25.8$  ( $c = 1.2$ ,  $CHCl_3$ );  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta = 6.60$  (d,  $J = 9.7$  Hz, 1H), 6.08 (d,  $J = 15.7$  Hz, 1H), 5.77 (m, 1H), 5.57 (dd,  $J = 15.7, 6.8$  Hz, 1H), 5.28 (d,  $J = 9.0$  Hz, 1H), 5.05 (m, 2H), 4.19 (q,  $J = 7.1$  Hz, 2H), 4.04 (m, 1H), 3.28 (m, 1H), 3.24 (s, 3H), 2.37 (m, 1H), 2.23 (m, 1H), 1.87 (s, 3H), 1.77 (s, 3H), 1.29 (t,  $J = 7.1$  Hz, 3H), 1.16 (d,  $J = 6.7$  Hz, 3H);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ ):  $\delta = 168.4, 144.8, 136.5, 134.6, 133.5, 131.5$  (2x), 126.8, 117.0, 76.9, 60.6, 56.1, 40.1, 36.4, 20.4, 14.4, 13.1, 12.6; IR (film):  $\tilde{\nu} = 2977, 2929, 2873, 1711, 1643, 1448, 1367, 1263, 1240, 1098, 966, 750$   $cm^{-1}$ ; HRMS (ESI):  $m/z$ : calcd for  $C_{18}H_{28}O_3+Na$ : 315.193066 [ $M^++Na$ ]; found: 315.192829.



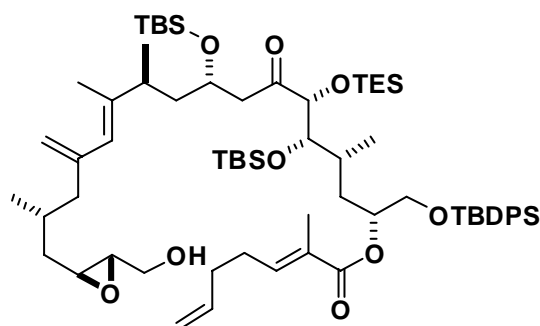
**Product 4.** Pale yellow oil (23 mg, 56%).  $[\alpha]_D^{20} = +34$  ( $c = 1.5$ ,  $CH_2Cl_2$ );  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta = 6.15$  (d,  $J = 11.2$  Hz, 1H), 6.07-5.95 (m, 3H), 5.46 (dd,  $J = 14.4, 8.5$  Hz, 1H), 5.32 (dd,  $J = 14.6, 8.2$  Hz, 1H), 5.11 (td,  $J = 7.4, 1.0$  Hz, 1H), 4.91 (d,  $J = 8.7$  Hz, 1H), 4.52 (brs, 1H), 4.07 (s, 2H), 3.67 (d,  $J = 5.1$  Hz, 2H), 3.42 (m, 1H), 3.14 (s, 3H), 2.51-2.45 (m, 1H), 2.03-1.96 (m, 2H), 1.68 (s, 3H), 1.67 (d,  $J = 1.0$  Hz, 3H), 1.66 (s, 3H), 1.59-1.53 (m, 1H), 1.44-1.36 (m, 1H), 1.39 (s, 9H), 1.09 (s, 9H), 0.87 (d,  $J = 6.9$  Hz, 3H), 0.84 (s, 9H), 0.00 (s, 6H);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ ):  $\delta = 176.9, 155.6, 135.7, 135.5, 134.9, 132.4, 131.9, 130.1, 125.5, 123.9, 120.1, 81.7, 81.1, 61.4, 55.6, 39.6, 38.5, 35.5, 28.0, 26.8, 25.6, 23.1, 20.7, 18.0, 16.7, 14.6, 12.0, -5.6$ ; IR (film):  $\tilde{\nu} = 3375, 2929, 2857, 1723, 1461, 1365, 1251, 1162, 1097, 991, 837, 775, 666$   $cm^{-1}$ ; HRMS (ESI):  $m/z$ : calcd for  $C_{38}H_{67}NO_5Si+Na$ : 684.4627 [ $M^++Na$ ]; found: 684.4630.



**Compound 6.** Yellow oil (90 mg, 79%).  $[\alpha]_D^{25} = -3.6$  (0.95,  $CH_2Cl_2$ );  $^1H$  NMR (400 MHz,  $C_6D_6$ ):  $\delta = 7.80-7.77$  (m, 4H), 7.25-7.22 (m, 6H), 5.65 (br s, 1H), 5.00-4.99 (m, 1H), 4.88 (br s, 1H), 3.71-3.62 (m, 2H), 3.46 (br d,  $J = 12.0$  Hz, 1H), 3.28 (br d,  $J = 12.0$  Hz, 1H), 2.70 (ddd,  $J = 7.5, 5.6, 2.2$  Hz, 1H), 2.51 (ddd,  $J = 4.9, 4.2, 2.8$  Hz, 1H), 2.39 (qd,  $J = 13.4, 6.6$  Hz, 1H), 2.08 (dd,  $J = 13.4, 6.6$  Hz, 1H), 1.87 (dd,  $J = 13.4, 7.8$  Hz, 1H), 1.75-1.66 (m, 2H), 1.62 (d,  $J = 1.2$  Hz, 3H), 1.62-1.55 (m, 2H), 1.47 (ddd,  $J = 11.4, 6.6, 5.0$  Hz, 1H), 1.19 (s, 9H), 1.09 (ddd,  $J = 13.9, 8.6, 5.4$  Hz, 1H), 1.02 (d,  $J = 6.6$  Hz, 3H), 0.97 (d,  $J = 6.9$  Hz, 3H);  $^{13}C$  NMR (100 MHz,  $C_6D_6$ ):  $\delta = 145.4, 142.9, 136.5, 135.1, 129.2, 128.5, 126.5, 115.4, 63.3, 62.4, 59.2, 54.9, 46.8, 40.7, 39.5, 38.6, 30.6, 27.7, 20.5, 20.2, 20.1, 14.7$ ; IR (film):  $\tilde{\nu} = 2956, 2921, 2855, 1428, 1110, 705$ ; HRMS (ESI):  $m/z$ : calcd for  $C_{32}H_{46}NaO_3Si+Na$ : 529.3106 [ $M^++Na$ ]; found: 529.3106.



**Compound 7.** A degassed solution of the stannane shown in Table 1, entry 7 (51 mg, 113  $\mu\text{mol}$ )<sup>1</sup> and the vinyl iodide shown in Table 1, entry 7 (65 mg, 57  $\mu\text{mol}$ )<sup>1</sup> in DMF (0.6 mL) was



added to a Schlenk tube containing flame-dried  $[\text{Ph}_2\text{PO}_2][\text{NBu}_4]$  (105 mg, 230  $\mu\text{mol}$ ). Copperthiophene carboxylate complex (CuTC, 33 mg, 170  $\mu\text{mol}$ ) was then introduced followed by  $\text{Pd}(\text{PPh}_3)_4$  (46 mg, 40  $\mu\text{mol}$ ). The resulting mixture was stirred for 30 min before the reaction

was quenched with water (1 mL). The aqueous phase was extracted with  $\text{Et}_2\text{O}$  (2 x 2 mL), the combined organic layers were dried over  $\text{Na}_2\text{SO}_4$  and evaporated, and the residue was purified by flash chromatography (hexanes:*tert*-butyl methyl ether, 4:1) to afford product **7** as a pale yellow oil (58.6 mg, 89%).  $[\alpha]_D^{20} = +12.3$  ( $c = 0.4$ ,  $\text{CHCl}_3$ );  $^1\text{H NMR}$  (400 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta = 7.81$  (tt,  $J = 1.8, 6.6$  Hz, 4H), 7.26 (m, 6H), 7.01 (tq,  $J = 7.4, 1.1$  Hz, 1H), 5.78 (s, 1H), 5.70 (ddt,  $J = 16.9, 10.3, 6.4$  Hz, 1H), 5.53 (m, 1H), 5.02 (ddt,  $J = 17.7, 1.7, 1.4$  Hz, 1H), 4.98 (ddt,  $J = 11.0, 1.8, 1.2$  Hz, 1H), 4.96 (s, 1H), 4.94 (s, 1H), 4.42 (m, 1H), 4.34 (d,  $J = 4.6$  Hz, 1H), 3.96 (dd,  $J = 4.5, 4.3$  Hz, 1H), 3.89 (dd,  $J = 10.7, 5.5$  Hz, 2H), 3.51 (ddd,  $J = 12.1, 5.4, 2.9$  Hz, 1H), 3.34 (ddd,  $J = 12.3, 6.8, 4.7$  Hz, 1H), 3.15 (dd,  $J = 17.7, 5.2$  Hz, 1H), 2.85 (dd,  $J = 18.2, 7.2$  Hz, 1H), 2.81 (ddd,  $J = 7.2, 6.4, 2.1$  Hz, 1H), 2.58 (ddd,  $J = 7.2, 6.7, 2.7$  Hz, 1H), 2.52 (dq,  $J = 13.8, 6.7$  Hz, 1H), 2.16 (m, 1H), 2.14 (m, 1H), 2.08 (m, 3H), 2.04 (m, 2H), 1.94 (s(d),  $J = 0.9$  Hz, 3H), 1.94 (m, 1H), 1.84 (s(d),  $J = 1.3$  Hz, 3H), 1.81 (m, 1H), 1.78 (m, 1H), 1.71 (m, 1H), 1.55 (m, 1H), 1.36 (ddd,  $J = 13.2, 8.4, 4.0$  Hz, 1H), 1.18 (s, 9H), 1.10 (m, 1H), 1.08 (d,  $J = 6.7$  Hz, 3H), 1.06 (d,  $J = 6.8$  Hz, 3H), 1.03 (s, 9H), 1.02 (s, 9H), 0.89 (t,  $J = 7.8$  Hz, 9H), 0.86 (d,  $J = 6.7$  Hz, 3H), 0.7 (q,  $J = 7.8$  Hz, 6H), 0.45 (s, 3H), 0.20 (s, 3H), 0.17 (s, 3H), 0.16 (s, 3H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta = 208.1, 167.5, 144.8, 143.2, 141.4, 137.8, 136.0, 135.9, 133.8, 129.9, 125.6, 115.3, 114.9, 81.8, 78.6, 72.5, 66.9, 66.3, 62.0, 58.8, 54.3, 48.7, 46.3, 39.8, 39.0, 35.8, 32.9, 32.4, 30.2, 30.0, 29.6, 28.4, 28.3, 28.2, 28.1, 26.0, 26.6, 26.3, 22.7, 19.7, 19.5, 19.4, 18.5, 18.4, 18.3, 18.2, 17.3, 16.3, 16.2, 16.1, 15.6, 15.0, 13.9, 13.7, 12.9, 10.0, 7.2, 5.4, -3.8, -4.1, -4.3, -4.5$ ; IR (film)  $\tilde{\nu} = 3390, 2927, 2876, 1711, 1608, 1514, 1462, 1425, 1390, 1252, 11125, 834, 702, 691$   $\text{cm}^{-1}$ ; HRMS (ESI<sup>+</sup>):  $m/z$ : calcd for:  $\text{C}_{67}\text{H}_{114}\text{O}_9\text{Si}_4+\text{Na}$ : 1197.74376 [ $M^++\text{Na}$ ]; found: 1197.74369.

**Product 8:** A Schlenk flask was charged with commercial tetra-*n*-butylammonium diphenylphosphinate (85 mg, 0.19 mmol), which was melted and allowed to re-cool to ambient temperature under high vacuum ( $10^{-4}$  Torr) twice. Thereafter,  $\text{Pd}(\text{PPh}_3)_4$  (7 mg, 6  $\mu\text{mol}$ ) and copper thiophene-2-carboxylate (35 mg, 0.19 mmol)<sup>2</sup> were introduced and the

<sup>1</sup> A. Fürstner, L. C. Bouchez, J.-A. Funel, V. Liepins, F.-H. Porée, R. Gilmour, F. Beaufils, D. Laurich, M. Tamiya, *Angew. Chem. Int. Ed.* **2007**, *46*, 9265.

<sup>2</sup> G. D. Allred, L. S. Liebeskind, *J. Am. Chem. Soc.* **1996**, *118*, 2748.

mixture was suspended in DMF (0.5 mL) before a degassed solution of the triflate shown in Table 1, entry 8 (82 mg, 0.12 mmol)<sup>3</sup> in DMF (0.5 mL) was added, followed by slow addition of a degassed solution of the stannane shown in Table 1, entry 8 (49 mg, 0.12 mmol)<sup>3</sup> in DMF (0.5 mL) over a period of 15 min. Once the addition was complete, stirring was continued for another 15 min before the reaction was quenched with water (2 mL), diluted with EtOAc (10 mL) and filtered through a short pad of Celite<sup>®</sup>. The filtrate was washed with water and brine (5 mL each) before the organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and evaporated. Purification of the residue by preparative TLC (SiO<sub>2</sub>, EtOAc/hexane, 1:2) gave product **8** as a

colorless foam (60 mg, 65%, 86% based on recovered starting material) and a second fraction containing unreacted triflate (21 mg). m.p. 70-75°C;  $[\alpha]_D^{20} = -51.2^\circ$  (c = 1.1, CH<sub>2</sub>Cl<sub>2</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25°C):  $\delta = 7.24$  (t, *J* = 8.0 Hz, 1H), 7.19 (d, *J* = 8.5 Hz, 1H), 7.12 (t, *J* = 8.1 Hz, 1H), 6.99 (d, *J* = 2.6 Hz, 1H), 6.86 (dd, *J* = 8.6, 2.6 Hz, 1H), 6.82 (d, *J* = 7.4 Hz, 1H), 6.76-6.68 (m, 3H), 6.66 (d, *J* = 8.0 Hz, 1H), 6.54 (d, *J* = 5.2 Hz, 1H), 5.77 (s, 1H), 5.60 (d, *J* = 5.2 Hz, 1H), 3.87 (s, 3H), 3.76 (m, 1H), 3.73 (s, 3H), 3.65 (s, 3H), 3.64 (d, *J* = 15.5 Hz, 1H), 3.43 (s, 3H), 3.38 (dd, *J* = 15.0, 1.9 Hz, 1H), 2.98-2.71 (m, 4H), 2.35 (t, *J* = 7.5 Hz, 2H), 1.03 (m, 21H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25°C):  $\delta = 159.9, 159.7, 159.0, 155.9, 148.8, 143.9, 142.5, 141.3, 141.2, 140.8, 133.6, 131.3, 131.3, 129.9, 129.2, 128.3, 125.5, 119.4, 117.6, 114.1, 113.5, 112.6, 110.2, 109.7, 108.9, 107.1, 81.2, 70.3, 59.2, 56.7, 55.4, 55.1, 55.0, 54.8, 49.8, 28.0, 19.7, 18.6, 11.3$ ; IR (KBr):  $\tilde{\nu} = 2942, 2864, 2836, 2170, 1718, 1603, 1480, 1464, 1384, 1289, 1264, 883, 678$ ; MS (EI): *m/z* (%): 745 (2) [*M*<sup>+</sup>], 714 (4), 550 (100); HRMS (ESI<sup>+</sup>): *m/z*: calcd for C<sub>46</sub>H<sub>55</sub>NO<sub>6</sub>Si+Na: 768.3691 [*M*<sup>+</sup>+Na]; found: 768.3690 [*M*<sup>+</sup>+Na].

**Compound 9.** Colorless syrup (135 mg, 76%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 7.42$ -7.37 (m, 2H), 7.34-7.29 (m, 2H), 7.26-7.20 (m, 1H), 6.56 (d, *J* = 15.9 Hz, 1H), 6.15 (dd, *J* = 7.3, 15.9 Hz, 1H), 6.14 (dd, *J* = 8.1, 15.9 Hz, 1H), 6.07 (d, *J* = 15.9 Hz, 1H), 5.66 (s, 1H), 4.21-4.15 (m, 2H), 4.10-4.05 (d, *J* = 8.5 Hz, 1H), 3.55 (s, 3H), 3.32 (s, 3H), 3.19 (dd, *J* = 2.3, 9.9 Hz, 1H), 2.61-2.51 (m, 1H), 2.26 (d, *J* = 1.0 Hz, 3H), 1.60-1.50 (m, 1H), 1.19 (d, *J* = 6.8 Hz, 3H), 1.02-0.96 (m, 2H), 0.84 (d, *J* = 7.1 Hz, 3H), 0.03 (s, 9H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta = 167.4, 152.4, 138.0, 136.8, 134.0, 132.0, 129.2, 128.6, 127.6, 126.4, 118.3, 86.4, 81.1, 61.8, 61.5, 56.5, 42.7, 40.1, 18.7, 17.4, 13.9, 9.8, -1.5$ ; IR (film):  $\tilde{\nu} = 3027, 2955, 2902, 2829, 1709, 1634, 1611, 1495, 1449, 1372, 1354, 1249, 1238, 1152, 1122, 1092, 972, 860, 837, 749, 693$ ; MS (EI): *m/z* (%): 394 (2), 249 (5), 248 (4), 217 (5), 187 (7), 148 (11), 147

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(100), 115 (10), 75 (32), 73 (14); HRMS (ESI+):  $m/z$ : calcd for  $C_{27}H_{42}SiO_4+Na$ : 481.27501 [ $M^++Na$ ]; found: 481.27486.

**Compound 10.** Yellow oil (391 mg, 77%);  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  = 7.74 (d,  $J$  = 8 Hz, 2H), 7.30 (d,  $J$  = 8 Hz, 2H), 6.12-5.94 (m, 2H), 5.64 (dt,  $J$  = 15, 7 Hz, 1H), 5.42 (dt,  $J$  = 15, 7 Hz, 1H), 4.31 (t,  $J$  = 6 Hz, 1H, NH), 3.66-3.58 (m, 4H), 2.43 (s, 3H), 2.26 (m, 2H), 0.88 (s, 9H), 0.04 (s, 6H);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ ):  $\delta$  = 143.4, 137.1, 133.7, 132.4, 130.6, 129.7, 127.2, 125.2, 62.7, 45.2, 36.2, 25.9, 21.5, 18.3, -5.3; IR (film):  $\tilde{\nu}$  = 3283, 3025, 2954, 2928, 2857, 1660, 1599, 1472, 1329, 1255, 1161, 1095, 1044, 989, 836, 814, 777, 665, 552; MS (EI):  $m/z$  (%): 338 (41), 228 (46), 93 (100), 73 (34); HRMS (ESI+):  $m/z$ : calcd for  $C_{20}H_{33}NO_3SSi+Na$ : 418.1843 [ $M^++Na$ ]; found: 418.1841.

**Compound 11.** Colorless oil (250 mg, 85%).  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  = 7.26 (d,  $J$  = 8 Hz, 2H), 6.83 (d,  $J$  = 8 Hz, 2H), 6.32 (d,  $J$  = 16 Hz, 1H), 6.08 (dt,  $J$  = 16, 7 Hz, 1H), 3.80 (s, 3H), 3.63 (t,  $J$  = 6 Hz, 2H), 2.21 (dt,  $J$  = 7, 7 Hz, 2H), 1.59-1.48 (m, 4H), 0.90 (s, 9H), 0.55 (s, 6H);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  = 158.7, 130.8, 129.3, 128.8, 127.0, 113.9, 63.1, 55.3, 32.8, 32.4, 26.0, 25.8, 18.4, -5.3; IR (film):  $\tilde{\nu}$  = 2932, 2857, 1608, 1511, 1463, 1248, 1174, 1100, 1038, 964, 837, 776; MS (EI):  $m/z$  (%): 320 (<5) [ $M^+$ ], 263 (100), 187 (17), 121 (57), 75 (33); HRMS (ESI+):  $m/z$ : calcd for  $C_{19}H_{32}O_2Si+Na$ : 321.2250 [ $M^++Na$ ]; found: 321.2246.

