

General Procedure for the Synthesis of Vinylogous Amides

To a round bottom flask was added 5 mmol (0.56 grams) of 1,3-cyclohexanedione and 1.0 equiv of the chosen primary amine. Anhydrous toluene or benzene (distilled from CaH_2) was then added and the reaction heated to reflux under a water-cooled condenser. Reaction progress was monitored by TLC (EtOAc) and upon completion (approx. 3 h) cooled to room temperature. Removal of the solvent under vacuum produced a yellow-orange to white solid. The solid was dissolved in dichloromethane, extracted with water (2 x 50 mL) and brine (1 x 50 mL), and dried over sodium sulfate. Column chromatography on silica gel (gradient eluent: ethyl acetate in hexane 20-100% followed by 50% ethyl acetate in dichloromethane) allowed for purification of the compounds.

General Procedure for the Reaction of Vinylogous Amides with α , β -Unsaturated Iminiums

The desired starting enal (0.25 – 1 mmol) was filtered through silica gel and dissolved in anhydrous EtOAc (distilled from CaH_2). The solution was cooled to $-10\text{ }^\circ\text{C}$ (ice in acetone), and 2.0 equiv of piperidine and acetic anhydride were added dropwise via syringe. The iminium mixture was then sealed under nitrogen and heated at $85\text{ }^\circ\text{C}$ (sand bath) for 30 min to 1 h. The warm iminium solution was then transferred quickly via cannula to a solution of the appropriate vinylogous amide (0.5 equiv) in anhydrous toluene (EtOAc:toluene usually 2:3). The reaction mixture was again sealed under a blanket of nitrogen in a sealed tube and heated to $150\text{ }^\circ\text{C}$ in a sand bath for 18-96 h. Reaction progress was monitored by TLC (66% ethyl acetate in hexane). With the reaction complete, the mixture was concentrated under reduced pressure, and the desired cyclized product was isolated using silica gel flash column chromatography (gradient eluent: ethyl acetate in hexane, 5-50%).

Procedure for Removal of Chiral Inducer

The cyclized product *ent*-7 was dissolved in a minimal amount of THF and 1.2 equiv TBAF (1M solution in THF) was added dropwise. The solution was stirred at room temperature and reaction progress monitored by TLC (EtOAc). Upon completion the solution was concentrated under reduced pressure and a short silica gel column (elution

with EtOAc) was used to purify the product. To a sealed tube was added the deprotected alcohol (10-30 mg), 50 mol percent Pd (5% on C), 0.5 mL EtOH (distilled from CaH₂ and stored over molecular sieves), and 6 to 15 equiv ammonium formate. The tube was sealed and heated at 90 °C. When the reaction was complete (TLC with EtOAc as eluent), the reaction was filtered and concentrated under reduced pressure. Isolation of the product was completed by flash silica gel chromatography (gradient eluent: ethyl acetate in hexane, 20-50%).

Characterizations for Isolated Products:

For Compound 4

R_f = 0.35 (75% EtOAc in hexane)

Major isomer: ¹H NMR (300 MHz, CDCl₃) δ 0.85 (t, 3H, J = 7.3 Hz), 1.72 (d, 3H, J = 7.3 Hz), 1.20-2.06 (m, 5 H), 2.33-2.68 (m, 5H), 3.63-3.67 (m, 1H), 5.07-5.27 (m, 2 H), 6.68-6.71 (m, 1 H), 7.24-7.39 (m, 5 H);

¹³C NMR (75 MHz, CDCl₃) δ 14.1, 17.2, 19.9, 21.9, 27.5, 35.9, 37.5, 39.0, 53.4, 56.9, 110.8, 113.8, 120.8, 126.4, 127.5, 127.6, 128.0, 128.7, 141.7, 159.9, 192.1;

Minor isomer: ¹H NMR (300 MHz, CDCl₃) δ 0.60 (t, 3H, J = 7.3 Hz), 1.67 (d, 3H, J = 7.3 Hz), 1.20-2.06 (m, 5 H), 2.33-2.68 (m, 5H), 3.87-3.83 (m, 1H), 5.07-5.27 (m, 2 H), 6.68-6.71 (m, 1 H), 7.24-7.39 (m, 5 H);

¹³C NMR (75 MHz, CDCl₃) δ 13.7, 16.8, 19.5, 21.7, 28.1, 35.9, 37.5, 39.0, 55.5, 57.9, 111.3, 113.5, 120.9, 126.4, 127.5, 127.6, 128.0, 128.7, 140.0, 159.2, 192.1;

IR (thin film) cm⁻¹ 2954 (s), 2870 (m), 1612 (s), 1519 (s), 1446 (s), 1409 (m), 1378 (w), 1339 (m), 1303 (m), 1171 (s);

mass spectrum (EI): m/e (%relative intensity) 280 (2) M-CH₃⁺, 152 (20), 207 (5), 148 (50), 105 (100), 91 (20), 77 (20);

m/e calcd for C₂₀H₂₅NO 295.1936, measd 295.1939

Compound 5

R_f = 0.52 (EtOAc)

Isomer A: ¹H NMR (500 MHz, CDCl₃) δ 0.10 (s, 3 H), 0.13 (s, 3 H), 0.86 (t, 3 H, J = 3.5 Hz), 0.95 (s, 9 H), 0.98 (m, 2 H), 1.75 (m, 2 H), 1.92 - 2.05 (m, 2 H), 2.29 - 2.48 (m, 2 H), 2.65 (dt, 1 H, J = 5, 16 Hz), 2.80 - 2.90 (m, 1 H), 3.73 (m, 1 H), 3.75 (ddd, 1 H, J = 3, 6, 9.5 Hz), 4.06 (m, 1 H), 4.25 (dd, 1 H, J = 6, 10 Hz), 5.11 (m, 2 H), 6.68 (d, 1 H, J = 10 Hz), 7.19 (d, 2 H, J = 7 Hz), 7.28 (m, 3 H);

¹³C NMR (75 MHz, CDCl₃) δ -5.6, -5.5, 16.8, 17.4, 18.1, 21.9, 25.7, 17.8, 35.8, 38.1, 54.0, 62.6, 63.2, 111.0, 113.9, 120.6, 126.9, 128.0, 128.5, 128.7, 137.0, 138.2, 161.7, 192.2;

Isomer B: ¹H NMR (500 MHz, CDCl₃) δ 0.003 (s, 3 H), 0.046 (s, 3 H), 0.30 (m, 1H), 0.86 (t, 3 H, J = 3.5 Hz), 0.82 (s, 9 H), 1.22 (m, 2 H), 1.32 (m, 1 H), 1.92 - 2.05 (m, 2 H), 2.29 - 2.48 (m, 2 H), 2.56 (ddd, 1 H, J = 5, 10, 15 Hz), 2.80 - 2.90 (m, 1 H), 3.89 (ddd, 1

H, J = 3, 6, 9.5 Hz), 4.05 (m, 1 H), 5.11 (m, 2 H), 5.23 (dd, 1 H, J = 6, 10 Hz), 6.67 (d, 1 H, J = 10 Hz), 7.34 (m, 2 H), 7.37 (m, 3 H);

^{13}C NMR (75 MHz, CDCl_3) δ -5.6, -5.5, 13.6, 14.2, 17.8, 21.8, 25.7, 28.3, 35.7, 37.5, 53.3, 63.7, 63.2, 111.0, 113.1, 121.3, 126.9, 128.0, 128.5, 128.7, 137.0, 138.2, 161.0, 192.2;

IR (thin film) cm^{-1} 3052 (s), 2953 (s), 1726 (m), 1609 (s), 1451 (s);

mass spectrum (EI): m/e (%relative intensity) 425 (3) M^+ , 383 (24), 382 (68), 235 (59), 179 (42), 148 (63), 115 (21), 73 (100);

m/e calcd for $\text{C}_{26}\text{H}_{39}\text{NO}_2\text{Si}$ 425.2750, measd 425.2746

Compound 7

R_f = 0.514 (66% EtOAc in hexane)

^1H NMR (300 MHz, CDCl_3) δ -0.38 (s, 3 H), -0.01 (s, 3 H), 0.04 (m, 1 H), 0.47 (t, 3 H, J = 7.2 Hz), 0.60 (s, 9 H), 0.84 (m, 1 H), 1.03 (m, 1 H), 1.25 (m, 1 H), 1.52 (m, 1 H), 1.71 (m, 1 H), 1.95 (m, 1 H), 1.98 (m, 1 H), 2.17 (dt, 1 H, J = 4.8, 24 Hz), 2.36 (dt, 1 H, J = 4.5, 15.9 Hz), 4.10 (m, 1 H), 5.06 (d, 1 H, J = 9.45 Hz), 5.20 (d, 1 H, J = 9.45 Hz), 5.31 (dd, 1 H, J = 6, 9 Hz), 6.48 (d, 1 H, 9.3 Hz), 7.18 (m, 3 H), 7.40 (m, 7 H);

^{13}C NMR (75 MHz, CDCl_3) δ -5.3, -5.0, 13.7, 16.8, 17.8, 21.4, 25.5, 27.8, 35.5, 36.6, 53.5, 68.5, 75.0, 111.2, 112.9, 121.7, 127.3, 127.8, 128.1, 128.3, 128.4, 129.8, 137.5, 140.9, 159.1, 192.2;

IR (thin film) cm^{-1} 3030 (m), 2955 (m), 1614 (s), 1443 (s);

mass spectrum (EI): m/e (%relative intensity) 501 (3) M^+ , 458 (42), 311 (100), 280 (84), 221 (35), 212 (70), 179 (18), 91 (20), 73 (99);

m/e calcd for $\text{C}_{32}\text{H}_{43}\text{NO}_2\text{Si}$ 501.3063, measd 501.3068;

$[\alpha]_D^{23}$ = (-) 641 (c = 2.0, EtOH)

Compound *ent*-7

R_f = 0.514 (66% EtOAc in hexane)

^1H NMR (300 MHz, CDCl_3) δ -0.38 (s, 3 H), -0.01 (s, 3 H), 0.04 (m, 1 H), 0.47 (t, 3 H, J = 7.2 Hz), 0.60 (s, 9 H), 0.84 (m, 1 H), 1.03 (m, 1 H), 1.25 (m, 1 H), 1.52 (m, 1 H), 1.71 (m, 1 H), 1.95 (m, 1 H), 1.98 (m, 1 H), 2.17 (dt, 1 H, J = 4.8, 24 Hz), 2.36 (dt, 1 H, J = 4.5, 15.9 Hz), 4.10 (m, 1 H), 5.06 (d, 1 H, J = 9.45 Hz), 5.20 (d, 1 H, J = 9.45 Hz), 5.31 (dd, 1 H, J = 6, 9 Hz), 6.48 (d, 1 H, 9.3 Hz), 7.18 (m, 3 H), 7.40 (m, 7 H);

^{13}C NMR (75 MHz, CDCl_3) δ -5.3, -5.0, 13.7, 16.8, 17.8, 21.4, 25.5, 27.8, 35.5, 36.6, 53.5, 53.6, 68.5, 75.0, 111.2, 112.9, 121.7, 127.3, 127.8, 128.1, 128.3, 128.4, 129.8, 137.5, 140.9, 159.1, 192.2;

IR (thin film) cm^{-1} 3030 (m), 2955 (m), 1614 (s), 1443 (s);

mass spectrum (EI): m/e (%relative intensity) 501 (3) M^+ , 458 (42), 311 (100), 280 (84), 221 (35), 212 (70), 179 (18), 91 (20), 73 (99);

m/e calcd for $\text{C}_{32}\text{H}_{43}\text{NO}_2\text{Si}$ 501.3063, measd 501.3068;

$[\alpha]_D^{23}$ = (+) 521 (c = 0.30, EtOH)

Compound 9

R_f = 0.35 (66% EtOAc in hexane)

^1H NMR (300 MHz, CDCl_3) δ -0.11 (m, 1 H), 0.45 (t, 3 H, $J = 7.2$ Hz), 0.93 (m, 1 H), 1.06 (m, 1 H), 1.23 (m, 1 H), 1.53 (m, 1 H), 1.88 (s, 3 H), 1.90 (m, 1 H), 1.95 (m, 1 H), 2.18 (m, 1 H), 2.35 (dt, 1 H, $J = 4.8, 15.9$ Hz), 4.08 (m, 1 H), 5.33 (d, 1 H, $J = 11.3$ Hz), 5.38 (dd, 1 H, $J = 6, 9.1$ Hz), 6.32 (d, 1 H, $J = 11.3$ Hz), 6.52 (d, 1 H, $J = 9.1$ Hz), 7.25 (m, 3 H), 7.39 (m, 7 H);
 ^{13}C NMR (75 MHz, CDCl_3) δ 13.6, 14.2, 16.7, 21.0, 21.4, 22.7, 27.6, 29.4, 29.6, 29.7, 31.9, 35.6, 36.6, 53.2, 65.5, 72.6, 111.7, 113.2, 121.7, 127.2, 127.8, 128.2, 128.6, 128.9, 136.6, 137.1, 169.7, 192.5, 211.1;
 IR (thin film) cm^{-1} 3303 (w), 2925 (s), 1746 (m), 1614 (m), 1522 (m), 1443 (m), 1236 (s);
 mass spectrum (EI): m/e (%relative intensity) 429 (2) M^+ , 386 (42), 280 (21), 239 (24), 212 (38), 197 (100), 180 (23), 179 (82), 148 (48), 105 (32), 91 (48);
 m/e calcd for $\text{C}_{28}\text{H}_{31}\text{NO}_3$ 429.2304, measd 429.2295;
 $[\alpha]_{\text{D}}^{23} = (+) 465$ ($c = 0.11$, EtOH)

Compound 15

$R_f = 0.43$ (66% EtOAc in hexane)

mp ($^{\circ}\text{C}$) = 149-151

Major isomer: ^1H NMR (300 MHz, CDCl_3) δ -0.38 (s, 3 H), 0.004 (s, 3 H), 0.23 (d, 3 H, $J = 6.2$ Hz), 0.62 (s, 9 H), 1.49 (m, 1 H), 1.74 (m, 1 H), 1.98 (m, 1 H), 2.08 (m, 1 H), 2.17 (m, 1 H), 2.35 (m, 1 H), 4.24 (quintet, 1 H, $J = 6.2$ Hz), 5.07 (d, 1 H, $J = 9.6$ Hz), 5.14 (d, 1 H, $J = 9.6$ Hz), 5.26 (dd, 1 H, $J = 6.2, 9.3$ Hz), 6.45 (d, 1 H, $J = 9.3$ Hz), 7.20 (m, 3 H), 7.40 (m, 7 H);

Minor isomer: ^1H NMR (300 MHz, CDCl_3) δ 0.38 (s, 3 H), 0.004 (s, 3 H), 0.23 (d, 3 H, $J = 6.2$ Hz), 0.62 (s, 9 H), 1.49 (m, 1 H), 1.74 (m, 1 H), 1.98 (m, 1 H), 2.08 (m, 1 H), 2.17 (m, 1 H), 2.35 (m, 1 H), 4.44 (quintet, 1 H, $J = 6.2$ Hz), 4.94 (d, 1 H, $J = 6.15$ Hz), 5.03 (d, 1 H, $J = 6.15$ Hz), 5.30 (dd, 1 H, $J = 6.2, 9.3$ Hz), 6.45 (d, 1 H, $J = 9.3$ Hz), 7.20 (m, 3 H), 7.40 (m, 7 H);

^{13}C NMR (75 MHz, CDCl_3) δ -5.9, -4.0, 20.1, 21.4, 25.5, 27.7, 35.7, 49.8, 68.3, 74.0, 114.5, 121.0, 127.3, 127.8, 128.1, 128.3, 128.5, 129.8, 137.7, 140.9;

IR (thin film) cm^{-1} 3031 (m), 2954 (m), 1641 (s), 1438 (s), 1172 (s);

mass spectrum (EI): m/e (%relative intensity) 473 (2) M^+ , 458 (11), 311 (26), 353 (27), 352 (100), 221 (18), 75 (10), 73 (41);

m/e calcd for $\text{C}_{30}\text{H}_{39}\text{NO}_2\text{Si}$ 473.2750, measd 473.2750;

$[\alpha]_{\text{D}}^{23} = (-) 569$ ($c = 0.13$, EtOH)

Compound 16

$R_f = 0.34$ (50% EtOAc in hexane)

mp ($^{\circ}\text{C}$) = 168

Major isomer: ^1H NMR (300 MHz, CDCl_3) δ 0.02 (s, 6 H), 0.62 (s, 9 H), 1.10 (m, 2 H), 1.40 (m, 4 H), 1.62 (m, 6 H), 2.02-2.17 (m, 4 H), 2.36 (dt, 1 H, $J = 5, 16$ Hz), 4.13 (dd, 1 H, $J = 5, 5.5$ Hz), 5.08 (d, 1 H, $J = 5$ Hz), 5.12 (dd, 1 H, $J = 5.5, 9.5$ Hz), 5.16 (d, 1 H, $J = 5$ Hz), 6.53 (d, 1 H, $J = 9.5$ Hz), 7.20 (m, 3 H), 7.26 (m, 2 H), 7.37 (m, 3 H), 7.43 (m, 2 H);

^{13}C NMR (75 MHz, CDCl_3) δ -5.3, -4.0, 17.8, 21.8, 25.5, 25.8, 26.1, 26.2, 26.6, 28.3, 35.5, 45.4, 58.8, 68.7, 73.8, 110.0, 112.0, 122.7, 127.1, 127.3, 127.4, 127.5, 127.7, 127.8, 127.9, 128.1, 128.2, 128.4, 129.3, 129.6, 138.3, 140.9, 161.2, 192.0;

Minor isomer: ^1H NMR (300 MHz, CDCl_3) δ 0.09 (s, 6 H), 0.78 (s, 9 H), 1.10 (m, 2 H), 1.40 (m, 4 H), 1.62 (m, 6 H), 2.02-2.17 (m, 4 H), 2.36 (dt, 1 H, $J = 5, 16$ Hz), 4.13 (dd, 1 H, $J = 5, 5.5$ Hz), 5.08 (d, 1 H, $J = 5$ Hz), 5.10 (dd, 1 H, $J = 5.5, 9.5$ Hz), 5.16 (d, 1 H, $J = 5$ Hz), 6.57 (d, 1 H, $J = 9.5$ Hz), 7.20 (m, 3 H), 7.26 (m, 2 H), 7.37 (m, 3 H), 7.43 (m, 2 H);

^{13}C NMR (75 MHz, CDCl_3) δ -4.9, -3.7, 18.0, 22.7, 25.5, 25.8, 26.1, 26.2, 26.6, 29.7, 36.0, 44.5, 61.2, 72.2, 74.8, 112.6, 114.1, 120.9, 127.1, 127.3, 127.4, 127.5, 127.7, 127.8, 127.9, 128.1, 128.2, 128.4, 129.3, 129.6, 137.8, 141.0, 161.7, 192.6;

IR (thin film) cm^{-1} 3031 (w), 2925 (s), 2852 (s), 1614 (s), 1529 (s), 1438 (s), 1171 (s), 1094 (s), 1068 (s);

mass spectrum (EI): m/e (%relative intensity) 541 (5) M^+ , 458 (32), 320 (55), 312 (100), 221 (38), 91 (20), 73 (85);

m/e calcd for $\text{C}_{35}\text{H}_{47}\text{NO}_2\text{Si}$ 541.3376, measd 541.337;

$[\alpha]_{\text{D}}^{23} = (-) 330$ ($c = 0.1$, CH_2Cl_2)

Compound 17

$R_f = 0.45$ (66% EtOAc in hexane)

mp ($^{\circ}\text{C}$) = 88-90

Major isomer: ^1H NMR (300 MHz, CDCl_3) δ -0.33 (s, 3 H), 0.04 (s, 3 H), 0.66 (s, 9 H), 0.87 (m, 1 H), 1.67 (m, 1 H), 1.85 (m, 1 H), 1.99 (m, 1 H), 2.24 (m, 1 H), 2.58 (m, 1 H), 5.22 (m, 1 H), 5.33 (d, 1 H, $J = 9.3$ Hz), 5.44 (dd, 1 H, $J = 6.3, 9.3$ Hz), 6.47 (d, 1 H, $J = 9.3$ Hz), 6.87 (m, 3 H), 7.01 (m, 3 H), 7.26 (m, 6 H), 7.35 (m, 1 H), 7.46 (m, 2 H);

Minor isomer: ^1H NMR (300 MHz, CDCl_3) δ -0.33 (s, 3 H), 0.04 (s, 3 H), 0.66 (s, 9 H), 0.87 (m, 1 H), 1.67 (m, 1 H), 1.85 (m, 1 H), 1.99 (m, 1 H), 2.24 (m, 1 H), 2.58 (m, 1 H), 5.13 (m, 1 H), 5.33 (d, 1 H, $J = 9.3$ Hz), 5.44 (dd, 1 H, $J = 6.3, 9.3$ Hz), 6.53 (d, 1 H, $J = 9.3$ Hz), 6.87 (m, 3 H), 7.01 (m, 3 H), 7.26 (m, 6 H), 7.35 (m, 1 H), 7.46 (m, 2 H);

^{13}C NMR (75 MHz, CDCl_3) δ -5.2, -3.9, 17.8, 21.7, 25.5, 35.6, 58.3, 68.6, 74.2, 111.1, 115.0, 119.9, 124.5, 126.2, 127.4, 127.7, 127.8, 127.9, 128.5, 128.9, 130.2, 136.1, 140.9, 143.8, 160.3, 192.2;

IR (thin film) cm^{-1} 3155 (m), 2930 (s), 1794 (m), 1605 (s), 1471 (s);

mass spectrum (EI): m/e (%relative intensity) 535 (1) M^+ , 478 (1), 315 (27), 314 (95), 221 (32), 179 (16), 91 (48), 75 (26), 73 (100);

m/e calcd for $\text{C}_{35}\text{H}_{41}\text{NO}_2\text{Si}$ 535.2907, measd 535.2896;

$[\alpha]_{\text{D}}^{23} = (-) 438$ ($c = 0.28$, EtOH)

Compound 18

$R_f = 0.55$ (66% EtOAc in hexane)

^1H NMR (300 MHz, CDCl_3) δ -0.33 (s, 3 H), 0.04 (s, 3 H), 0.12 (m, 1 H), 0.59 (m, 1 H), 0.64 (s, 9 H), 0.85 (m, 3 H), 1.14 (m, 1 H), 1.37 (m, 1 H), 1.58 (m, 1 H), 1.70 (m, 1 H), 1.85 (m, 1 H), 1.96 (m, 1 H), 2.10 (m, 1 H), 2.28 (dt, 1 H, $J = 5.1, 16.5$ Hz), 2.53 (m, 1 H), 4.09 (dd, 1 H, $J = 3.3, 10.8$ Hz), 4.96 (d, 1 H, $J = 9$ Hz), 5.33 (d, 1 H, $J = 9$ Hz), 6.15 (s, 1 H), 7.20 (m, 3 H), 7.28 (m, 2 H), 7.37 (m, 3 H), 7.43 (m, 2 H);

^{13}C NMR (75 MHz, CDCl_3) δ -5.26, -3.96, 21.5, 25.5, 25.9, 26.0, 28.0, 29.4, 29.7, 30.1, 35.4, 60.5, 68.1, 73.5, 108.9, 112.1, 127.1, 127.9, 128.1, 128.3, 128.4, 129.6, 131.3, 138.2, 140.9, 192.1;

IR (thin film) cm^{-1} 2926 (s), 2854 (m), 1611 (m), 1538 (m), 1270 (m);

mass spectrum (EI): m/e (%relative intensity) 513 (1) M^+ , 341 (3), 308 (20), 293 (28), 292 (100), 221 (30), 75 (21), 73 (57);

m/e calcd for $C_{33}H_{43}NO_2Si$ 513.3063, measd 513.3072;

$[\alpha]_D^{23} = (+) 492$ ($c = 0.165$, EtOH)

Compound 19

$R_f = 0.42$ (66% EtOAc in hexane)

mp ($^{\circ}C$) = 189-195

Major isomer: 1H NMR (300 MHz, $CDCl_3$) δ -0.30 (s, 3 H), 0.04 (s, 3 H), 0.23, 0.67 (s, 9 H), 1.71 (m, 1 H), 1.90 (m, 1 H), 2.03 (m, 1 H), 2.17 (s, 3 H), 2.24 (m, 1 H), 2.28 (m, 1 H), 2.65 (dt, 1 H, $J = 4.8, 15.6$ Hz), 5.20 (d, 1 H, $J = 9$ Hz), 5.38 (q, 1 H, $J = 9$ Hz), 5.46 (d, 1 H, $J = 6.4$ Hz), 6.44 (d, 1 H, $J = 9$ Hz), 6.77 (m, 4 H), 6.94 (m, 3 H), 7.21 (d, 1 H, $J = 6.4$ Hz), 7.25 (m, 5 H), 7.46 (m, 2 H);

Minor isomer: 1H NMR (300 MHz, $CDCl_3$) δ -0.30 (s, 3 H), 0.04 (s, 3 H), 0.23, 0.67 (s, 9 H), 1.71 (m, 1 H), 1.90 (m, 1 H), 2.03 (m, 1 H), 2.17 (s, 3 H), 2.24 (m, 1 H), 2.28 (m, 1 H), 2.65 (dt, 1 H, $J = 4.8, 15.6$ Hz), 5.10 (d, 1 H, $J = 9$ Hz), 5.38 (q, 1 H, $J = 9$ Hz), 5.26 (d, 1 H, $J = 6.4$ Hz), 6.38 (d, 1 H, $J = 9$ Hz), 6.77 (m, 4 H), 6.94 (m, 3 H), 7.21 (d, 1 H, $J = 6.4$ Hz), 7.25 (m, 5 H), 7.46 (m, 2 H);

^{13}C NMR (75 MHz, $CDCl_3$) δ -5.26, -3.96, 19.1, 21.7, 15.5, 18.2, 35.6, 55.6, 68.5, 74.2, 112.5, 120.0, 124.9, 125.7, 126.1, 127.2, 127.4, 127.6, 128.0, 128.3, 129.7, 135.5, 140.9, 141.6, 192.1;

IR (thin film) cm^{-1} 3062 (w), 2950 (m), 1615 (s), 1530 (s), 1436 (s);

mass spectrum (EI): m/e (%relative intensity) 549 (1) M^+ , 329 (30), 328 (100), 311 (11), 221 (46), 165 (10), 127 (13), 105 (29), 73 (67);

m/e calcd for $C_{36}H_{43}NO_2Si$ 549.3063, measd 549.3059;

$[\alpha]_D^{23} = (+) 646$ ($c = 0.12$, EtOH)

Compound 20

$R_f = 0.39$ (66% EtOAc in hexane)

mp ($^{\circ}C$) = 73-75

1H NMR (300 MHz, $CDCl_3$) δ 0.22 (d, 3 H, $J = 6.3$ Hz), 1.52 (m, 1 H), 1.77 (m, 1 H), 1.89 (s, 3 H), 1.94 (m, 2 H), 2.19 (ddd, 1 H, $J = 4.6, 7.5, 16.4$ Hz), 2.36 (ddd, 1 H, $J = 4.6, 6.6, 16.2$ Hz), 4.21 (m, 1 H), 5.32 (d, 1 H, $J = 9.3$), 5.34 (dd, 1 H, $J = 6.3, 10.6$ Hz), 6.33 (d, 1 H, $J = 10.6$ Hz), 6.50 (d, 1 H, $J = 9.3$ Hz), 7.25 (m, 3 H), 7.41 (m, 7 H);

^{13}C NMR (75 MHz, $CDCl_3$) δ 20.0, 21.0, 21.3, 27.6, 35.6, 44.5, 65.3, 72.6, 114.8, 121.0, 127.1, 128.2, 128.8, 129.0, 137.1, 169.6, 192.6;

IR (thin film) cm^{-1} 3034 (m), 2945 (m), 1746 (s), 1617 (s), 1438 (s), 1236 (s);

mass spectrum (EI): m/e (%relative intensity) 401 (4) M^+ , 386 (40), 252 (67), 239 (21), 197 (100), 179 (79), 148 (45), 105 (25), 91 (40), 77 (17), 73 (20);

m/e calcd for $C_{26}H_{27}NO_3$ 401.1991, measd 401.1985;

$[\alpha]_D^{23} = (+) 656$ ($c = 0.135$, EtOH)

Compound 22

$R_f = 0.36$ (EtOAc)

mp ($^{\circ}C$) = 150 (dec)

^1H NMR (300 MHz, CDCl_3) δ -0.34 (s, 3 H), -0.13 (s, 3H), 0.27 (d, 3 H, J = 6 Hz), 0.64 (s, 9 H), 2.00 (m, 2 H), 2.20 (m, 1 H), 2.26 (m, 1 H), 4.39 (quintet, 1 H, J = 6 Hz), 4.78 (d, 1 H, J = 9 Hz), 5.20 (d, 1 H, J = 9.3 Hz), 5.23 (dd, 1 H, J = 6, 9 Hz), 6.16 (d, 1 H, J = 9.3 Hz), 7.19 (m, 2 H), 7.29 (m, 1 H), 7.33 (m, 2 H), 7.36 (m, 1 H), 7.40 (m, 2 H), 7.46 (m, 2 H);

^{13}C NMR (75 MHz, CDCl_3) δ -5.33, -4.04, 17.8, 21.3, 25.5, 26.0, 33.8, 52.0, 69.9, 73.9, 112.1, 116.5, 118.5, 126.9, 128.1, 128.4, 128.5, 128.7, 129.8, 137.1, 140.8, 171.2, 198.0;

IR (thin film) cm^{-1} 2926 (m), 2855 (m), 1658 (m), 1552 (s), 1471 (s), 1316 (m);

mass spectrum (EI): m/e (%relative intensity) 459 (1) M^+ , 353 (19), 239 (20), 238 (97), 222 (19), 221 (82), 91 (17), 73 (100), 57 (27);

m/e calcd for $\text{C}_{29}\text{H}_{37}\text{NO}_2\text{Si}$ 459.2594, measd 459.2584;

$[\alpha]_{\text{D}}^{23} = (+)$ 426 (c = 0.35, CH_2Cl_2)

Compound 24

R_f = 0.71 (66% EtOAc in hexane)

mp ($^{\circ}\text{C}$) = 61-68

Major isomer: ^1H NMR (300 MHz, CDCl_3) δ -0.38 (s, 3 H), -0.01 (s, 3H), 0.15 (m, 1 H), 0.49 (t, 3 H, J = 7.2 Hz), 0.64 (s, 9 H), 0.77 (s, 3 H), 0.85 (m, 3 H), 4.12 (m, 1 H), 5.04 (d, 1 H, J = 9 Hz), 5.17 (d, 1 H, J = 9 Hz), 5.34 (dd, 1 H, J = 6, 9.4 Hz), 5.90 (s, 1 H), 6.32 (d, 1 H, J = 9.4 Hz), 7.13 (m, 2 H), 7.27 (m, 4 H), 7.39 (m, 3 H), 7.50 (m, 1 H);

Minor isomer: ^1H NMR (300 MHz, CDCl_3) δ -0.38 (s, 3 H), -0.01 (s, 3H), 0.15 (m, 1 H), 0.49 (t, 3 H, J = 7.2 Hz), 0.64 (s, 9 H), 0.77 (s, 3 H), 0.85 (m, 3 H), 4.12 (m, 1 H), 4.70 (d, 1 H, J = 7.65 Hz), 4.98 (dd, 1 H, J = 6, 9.4 Hz), 5.31 (d, 1 H, J = 7.65 Hz), 5.58 (s, 1 H), 6.32 (d, 1 H, J = 9.4 Hz), 7.13 (m, 2 H), 7.27 (m, 4 H), 7.39 (m, 3 H), 7.50 (m, 1 H);

^{13}C NMR (75 MHz, CDCl_3) δ -4.16, 13.6, 16.6, 20.4, 25.5, 25.7, 29.7, 37.0, 52.9, 68.5, 74.6, 97.0, 115.6, 121.4, 127.4, 127.6, 128.2, 128.4, 128.7, 129.7, 159.5;

IR (thin film) cm^{-1} 3031 (m), 2928 (m), 1688 (s), 1515 (m), 1255 (m);

mass spectrum (EI): m/e (%relative intensity) 515 (1) M^+ , 446 (12), 312 (17), 311 (60), 280 (30), 221 (30), 212 (27), 91 (13), 75 (18), 73 (100);

m/e calcd for $\text{C}_{32}\text{H}_{41}\text{NO}_3\text{Si}$ 515.2856, measd 515.2853;

$[\alpha]_{\text{D}}^{23} = (+)$ 116 (c = 0.06, EtOH)

Compound 27

R_f = 0.08 (EtOAc)

^1H NMR (500 MHz, CDCl_3) δ 0.96 (t, 3 H, J = 7 Hz), 1.38 – 1.50 (m, 5 H), 1.90 (m, 1 H), 1.94 (quintet, 2 H, J = 6.5 Hz), 2.21 (ddd, 1 H, J = 5.5, 10, 16 Hz), 2.28 (t, 2 H, J = 6.5 Hz), 2.34 (t, 2 H, J = 6.5 Hz), 2.51 (dt, 1 H, J = 5, 16 Hz), 3.23 (m, 1 H), 4.26 (s, 1 H);

^{13}C NMR (75 MHz, CDCl_3) δ 14.1, 18.3, 18.9, 21.8, 27.1, 29.5, 36.5, 37.9, 51.3, 77.2, 105.0, 158.4, 194.3;

IR (thin film) cm^{-1} 3250 (br), 2953 (s), 2925 (s), 2851 (s), 1574 (m), 1519 (s);

mass spectrum (EI): m/e (%relative intensity) 193 (48) M^+ , 178 (11), 164 (16), 151 (83), 150 (100), 136 (25), 122 (50), 94 (22);

m/e calcd for $\text{C}_{12}\text{H}_{19}\text{NO}$ 193.1467, measd 193.1468;

$[\alpha]_{\text{D}}^{23} = (-)$ 45 (c = 0.20, EtOH)

























