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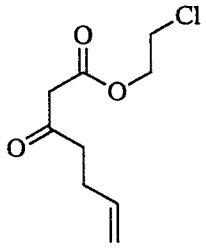
J4905-1

SPECTRAL DATA

The symbols s', d', t' used in ^{13}C NMR data represent zero, one, two, or three attached hydrogens respectively.
"α" and "β" refer to C(5) stereochemistry, the substituent being above the plane of the paper for the β series.

SPECTRAL DATA FOR COMPOUNDS IN SCHEME 1

Precursor to compound 3



FTIR ($CHCl_3$ cast) 1749, 1718 cm^{-1};

^1H NMR ($CDCl_3$, 200 MHz) δ 5.81 (dd t, *J* = 16.8, 10.4, 6.4 Hz, 1 H), 5.09-5.03 (m, 1 H), 5.09-4.98 (m, 1 H), 4.40 (t, *J* = 6.4 Hz, 2 H), 3.60 (t, *J* = 6.4 Hz, 2 H), 3.52 (s, 2 H), 2.68 (t, *J* = 7.2 Hz, 2 H), 2.32-2.40 (m, 2 H);

^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 201.15, 166.33, 136.22, 115.00, 64.23, 48.42, 41.46, 41.09, 26.87;

exact mass *m/z* calcd for $C_9H_{13}ClO_3$ 204.05531, found 204.0553.

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Compound 3

FTIR ($CHCl_3$ cast) 1715, 1674, 1621, 1586 cm^{-1};

^1H NMR ($CDCl_3$, 200 MHz) δ 2.25-2.37 (m, 2 H), 2.42-2.52 (m, 2 H), 4.33-4.41 (m, 2 H), 4.51-4.62 (m, 2 H), 4.88- 5.05 (m, including s at δ 4.93, 3 H), 5.77 (ddt, *J* = 17.2, 10.1, 6.5 Hz, 1 H);

^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 28.83 (t'), 41.45 (t'), 65.40 (t'), 68.16 (t'), 78.38 (d'), 114.41 (t'), 137.76 (d'), 168.32 (s'), 196.40 (s');

exact mass *m/z* calcd for $C_9H_{12}O_3$ 168.0787, found 168.0785.

Compound 4

^1H NMR ($CDCl_3$, 400 MHz) signals corresponding to *Z*-isomer only δ 2.80-2.92 (m, 2 H), 4.14-4.24 (m, 2 H), 4.28-4.40 (m, 2 H), 4.76 (t, *J* = 7.2 Hz, 1 H), 4.92-5.01 (dm, *J* = 10.0 Hz, 1 H), 5.07 (ddd, *J* = 17.2, 3.9, 1.9 Hz, 1 H), 5.87 (ddt, *J* = 17.2, 10.0, 6.2 Hz, 1 H);

Compound 5

X-Ray structure determined.

FTIR ($CHCl_3$ cast) 1733, 1560 cm^{-1};

^1H NMR ($CDCl_3$, 400 MHz) δ 2.12-2.20 (m, 1 H)(, 2.33-2.42 (m, 1 H), 2.56 (d, *J* = 8.0 Hz, 1 H), 2.78 (d, *J* = 8.0 Hz, 1 H), 2.96-3.05 (m, 1 H), 3.70 (s, 3 H), 3.83 (dd, *J* = 10.0, 5.0 Hz, 1 H), 3.86-4.03 (m, 4 H), 5.00-5.05 (dm, *J* = 8.0 Hz, 2 H), 5.33 (d, *J* = 10.0 Hz, 1 H), 5.52-5.63 (m, 1 H);

^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 32.02 (t'), 44.46 (d'), 47.99 (t'), 48.66 (d'), 52.68 (q'), 65.76 (t'), 65.83 (t'), 85.04 (d'), 107.11 (s'), 118.11 (t'), 133.25 (d'), 169.60 (s'), 202.38 (s');

exact mass *m/z* calcd for $C_{13}H_{17}NO_7$ 299.1005, found 299.1001.

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Anal. Calcd for $C_{13}H_{17}NO_7$: C 52.17, H 5.73, N 4.68. Found: C 52.25, H 5.78, N 4.68.

Compound 6 & 6β (Mixture of both isomers)

FTIR (CH_2Cl_2 cast) 3530, 1736 cm^{-1};

^1H NMR ($CDCl_3$, 400 MHz) δ 5.77-5.58 (m, 1 H), 5.08-4.90 (m, 3 H), 4.15 (dt, *J* = 12.0, 4.5 Hz, 0.67 H), 4.08-3.82 (m, 4.66 H), 3.70 (s) and 3.64 (s) (3 H), 3.54 (dd, *J* = 8.4, 4.4 Hz, 0.67 H), 2.67-2.44 (m) and 2.10-1.75 (m) (6 H);

^{13}C NMR ($CDCl_3$, 100.6 MHz) δ (major) 170.8 (s'), 136.8 (d'), 116.2 (t'), 107.3 (s'), 84.6 (d'), 68.3 (d'), 65.4 (t'), 65.2 (t'), 52.0 (q'), 43.0 (d'), 41.5 (d'), 39.3 (t'), 27.3 (t'), (minor) 171.6 (s'), 134.6 (d'), 117.5 (t'), 108.1 (s'), 84.4 (d'), 67.9 (d'), 65.8 (t'), 65.1 (t'), 52.3 (q'), 45.1 (d'), 42.8 (d'), 35.6 (t'), 32.2 (t');

exact mass *m/z* calcd for $C_{13}H_{19}NO_7$ 301.11615, found 301.11637.

Compound 7β (i.e., minor isomer)

X-Ray structure determined.

FTIR (CH_2Cl_2 cast) 1738 cm^{-1};

^1H NMR ($CDCl_3$, 400 MHz) δ 5.70-5.57 (m, 1 H), 5.10-4.90 (m, 3 H), 4.05-3.79 (m, 6 H), 3.70 (s, 3 H), 2.34-2.21 (m, 1 H), 2.13-2.02 (m, 1 H), 1.98-1.75 (m, 3 H), 0.91 (s, 9 H), 0.07 (s, 3 H), 0.04 (s, 3 H);

^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 172.0 (s'), 135.0 (d'), 117.4 (t'), 107.6 (s'), 85.0 (d'), 67.2 (d'), 65.3 (t'), 64.7 (t'), 52.1 (q'), 43.6 (d'), 42.9 (d'), 37.4 (t'), 31.9 (t'), 25.5 (q'), 17.8 (s'), -4.8 (q'), -4.9 (q');

exact mass *m/z* calcd for $C_{15}H_{24}NO_7Si$ (M-*t*-Bu) 358.13220, found 358.13268 (M-*t*-Bu); exact mass HRFAB (NOBA) *m/z* calcd for $C_{18}H_{33}NO_6SiNa$ (M+Na) 438.1924, found 438.1934.

Compound 7 (i.e., major isomer)
FTIR (CH_2Cl_2 cast) 1741 cm^{-1};

^1H NMR ($CDCl_3$, 400 MHz) δ 5.65-5.50 (m, 1 H), 5.03-4.87 (m, 3 H), 4.10-4.03 (m, 1 H), 4.03-3.84 (m, 4 H), 3.61 (s, 3 H), 3.52 (dd, *J* = 12.3, 4.4 Hz, 1 H), 2.62-2.50 (m, 1 H), 2.48-2.36 (m, 1 H), 1.85 (dt, *J* = 14.8, 8.6 Hz, 1 H), 1.77 (d, *J* = 8.5 Hz, 2 H), 0.88 (s, 9 H), 0.08 (s, 3 H), 0.07 (s, 3 H);

^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 170.7 (s'), 137.0 (d'), 115.9 (t'), 107.5 (s'), 84.8 (d'), 68.7 (d'), 65.5 (t'), 65.3 (t'), 51.9 (q'), 44.9 (d'), 42.6 (d'), 40.4 (t'), 27.0 (t'), 25.7 (q'), 18.0 (s'), -4.7 (q');

exact mass *m/z* calcd for $C_{19}H_{33}NO_7Si$ 415.20261, found 415.20252.

Anal. Calcd for $C_{19}H_{33}NO_7Si$: C 54.92, H 8.00, N 3.37, O 26.95. Found: C 55.039, N 8.110, N 3.236.

Compound 8β
FTIR (CH_2Cl_2 cast) 3550 cm^{-1};

^1H NMR ($CDCl_3$, 400 MHz) δ 5.90-5.62 (m, 1 H), 5.14-4.98 (m, 2 H), 4.91 (d, *J* = 1.3 Hz, 1 H), 4.13-3.98 (m, 4 H), 3.85-3.68 (m, 3 H), 2.69-2.50 (m, 2 H), 2.40-2.23 (m, 2 H), 1.97-1.78 (m, 3 H), 0.90 (s, 9 H), 0.07 (s, 3 H), 0.06 (s, 3 H);

^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 136.3 (d'), 116.6 (t'), 106.6 (s'), 86.0 (d'), 68.4 (d'), 65.1 (t'), 64.9 (t'), 59.0 (t'), 41.2 (d'), 40.7 (d'), 40.4 (t'), 31.7 (t'), 25.7 (q'), 17.9 (s'), -4.3 (q'), -4.8 (q');

exact mass *m/z* calcd for $C_{14}H_{24}NO_6Si$ (M-*t*-Bu) 330.13730, found 330.13706; exact mass HRFAB (NOBA) *m/z* calcd for $C_{18}H_{33}NO_6SiNa$ (M+Na) 410.1975, found 410.1974.

Anal. Calcd for $C_{18}H_{33}NO_6Si$: C 55.79, H 8.58, N 3.61. Found: C 55.48, H 8.60, N 3.44.

Compound 8

FTIR (CH_2Cl_2 cast) 3544, 3442 cm^{-1};

^1H NMR ($CDCl_3$, 400 MHz) δ 5.96-5.77 (m, 1 H), 5.18-4.97 (m, 2 H), 4.58 (d, *J* = 9.3 Hz, 1 H), 4.10-4.01 (m, 1 H), 4.01-3.87 (m, 4 H), 3.80-3.63 (m, 2 H), 2.70-2.57 (m, 1 H), 2.54-2.40 (m, 1 H), 2.37-2.25 (m, 1 H), 2.12-1.88 (m, 2 H), 1.88-1.70 (m, 2 H), 0.89 (s, 9 H), 0.07 (s, 3 H), 0.06 (s, 3 H).

^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 138.5 (d'), 115.7 (t'), 106.9 (s'), 86.6 (d'), 69.0 (d'), 65.0 (t'), 60.0 (t'), 42.0 (d'), 40.4 (d'), 40.2 (t'), 25.6 (q'), 17.9 (s'), -4.6 (q'), -4.9 (q').

exact mass *m/z* calcd for $C_{14}H_{24}NO_6Si$ (M-*t*-Bu) 330.13730, found 330.13697; exact mass *m/z* calcd for $C_{18}H_{33}NO_6Si$ 387.2077, found 387.2074;

Anal. Calcd for $C_{18}H_{33}NO_6Si$: C 55.78, H 8.58, N 3.61. Found: C 56.12, H 8.76, N 3.79.

Compound 9β

FTIR (CH_2Cl_2 cast) 3347, 1551 cm^{-1};

^1H NMR ($CDCl_3$, 400 MHz) δ 5.25-5.15 (m) and 4.90-4.80 (m) [1 H], 4.10-3.76 (m, 6 H), 3.53 (dd, *J* = 12.5, 2.9 Hz) and 3.45 (dd, *J* 12.4, 3.9 Hz), [1 H], 3.00 (d, *J* = 4.9 Hz) and 2.45 (dd, *J* = 3.7, 1.5 Hz), [1 H], 2.54-2.42 (m) and 2.20-2.10 (m) [1 H], 2.04-1.44 (m, 4 H), 0.91 (s, 9 H), 0.06 (s, 6 H).

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^{13}C NMR ($CDCl_3$, 75.5 MHz) major δ 107.7 (s'), 91.3 (d'), 86.1 (d'), 69.5 (d'), 65.4 (t'), 64.7 (t'), 60.4 (t'), 38.4 (t'), 35.7 (d'), 34.1 (d'), 29.7 (t'), 25.7 (q'), 17.9 (s'), -4.0 (q'), -4.8 (q').

exact mass *m/z* calcd for $C_{17}H_{30}NO_6Si$ (M-OH) 372.18423, found 372.18404; exact mass *m/z* calcd for $C_{13}H_{22}NO_7Si$ (M-*t*-Bu) 332.11655, found 332.11652; exact mass HRFAB (NOBA) *m/z* calcd for $C_{17}H_{31}NO_7SiNa$ (M+Na) 412.1768, found 412.1766.

Compound 9

FTIR (CH_2Cl_2 cast) cm^{-1}; 3371, 1550 cm^{-1}

^1H NMR ($CDCl_3$, 400 MHz) δ 5.40 (br s, 0.75 H), 5.05 (d, *J* = 12.5) and 5.03 (d, *J* = 12.5) [1 H], 4.78-7.67 (m, 0.25 H), 4.21-3.85 (m, 6 H), 3.75-3.55 (m, 0.5 H), 3.30-3.20 (m, 0.75 H), 2.70-2.40 (m, 2.5 H), 2.35-2.18 (m, 0.27 H), 2.05-1.93 (m, 0.25 H), 1.85-1.72 (m, 2.75 H), 1.60-1.43 (m, 0.75 H), 1.38-1.16 (m, 0.25 H), 0.84 (s, 9 H), 0.07 (s) and 0.04 (s) [6 H].

^{13}C NMR ($CDCl_3$, 75.5 MHz) major δ 108.0 (s'), 97.1 (d'), 85.5 (d'), 67.9 (d'), 65.7 (t'), 65.6 (t'), 65.1 (t'), 39.5 (t'), 35.1 (d'), 33.0 (d'), 25.7 (q'), 24.1 (t'), 18.0 (s'), -4.7 (q'), -4.8 (q').

exact mass *m/z* calcd for $C_{13}H_{22}NO_7Si$ (M-*t*-Bu) 332.11655, found 332.11577; exact mass HRFAB (NOBA) *m/z* calcd for $C_{17}H_{31}NO_7SiNa$ (M+Na) 412.1768, found 412.1774.

Compound 10β

FTIR (CH_2Cl_2 cast) 1742 cm^{-1};

^1H NMR ($CDCl_3$, 400 MHz) δ 5.76 (dd, *J* = 6.6, 3.5 Hz, 1 H), 4.82 (d, *J* = 8.8 Hz, 1 H), 4.08-3.70 (m, 6 H), 3.59 (dd, *J* = 12.5, 3.1 Hz, 1 H), 2.93-2.79 (m, 1 H), 2.30-2.17 (m, 1 H), 2.03 (dd, *J* = 14.2, 5.7 Hz, 1 H), 1.87 (dd, *J* = 14.2, 3.7 Hz, 1 H), 1.82-1.63 (m, 2 H), 1.23 (s, 9 H), 0.90 (s, 9 H), 0.08 (s, 6 H).

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^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 176.9 (s'), 107.4 (s'), 93.3 (d'), 85.9 (d'), 69.2 (d'), 65.3 (t'), 64.8 (t'), 64.4 (t'), 39.1 (d'), 38.8 (t'), 38.7 (t'), 34.1 (d'), 28.7 (s'), 27.0 (q'), 25.6 (q'), 18.0 (s'), -4.2 (q'), -4.5 (q').

exact mass *m/z* calcd for $C_{17}H_{30}NO_6Si$ (M-*t*-Bu) 372.18423, found 372.18496; exact mass HRFAB (NOBA) *m/z* calcd for $C_{22}H_{39}NO_8SiNa$ (M+Na) 496.2343, found 496.2343.

Compound 10

FTIR (CH_2Cl_2 cast) 1746 cm^{-1};

^1H NMR ($CDCl_3$, 400 MHz) δ 5.59 (dd, *J* = 9.9, 2.6 Hz, 1 H), 5.07 (d, *J* = 12.4 Hz, 1 H), 4.17-4.09 (m, 1 H), 4.01-3.87 (m, 4 H), 3.74-3.65 (m, 2 H), 2.56-2.48 (m, 1 H), 2.34-2.27 (m, 1 H), 1.88-1.78 (m, 3 H), 1.52-1.38 (m, 1 H), 1.23 (s, 9 H), 0.88 (s, 9 H), 0.074 (s, 6 H).

^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 176.9 (s'), 108.0 (s'), 94.8 (d'), 85.4 (d'), 67.9 (d'), 66.3 (t'), 65.6 (t'), 65.1 (t'), 39.6 (t'), 39.1 (d'), 38.7 (s'), 34.6 (d'), 27.0 (q'), 25.7 (q'), 24.7 (t'), 18.1 (s'), -4.8 (q').

exact mass *m/z* calcd for $C_{17}H_{30}NO_6Si$ (M-*t*-BuCO) 372.18423, found 372.18318; exact mass HRFAB (NOBA) *m/z* calcd for $C_{22}H_{39}NO_8SiNa$ (M+Na) 496.2343, found 496.2336.

Compound 11β

FTIR (CH_2Cl_2 cast) 1739 cm^{-1};

^1H NMR ($CDCl_3$, 400 MHz) δ 5.79 (dd, *J* = 8.4, 3.4 Hz, 1 H), 4.39 (dd, *J* = 11.8, 5.9 Hz, 1 H), 4.03-3.85 (m, 5 H), 3.45 (dd, *J* = 11.8, 3.3 Hz, 1 H), 2.93 (d, *J* = 8.0 Hz, 1 H), 2.07-1.86 (m, 3 H), 1.86-1.73 (m, 1 H), 1.73-1.64 (m, 2 H), 1.36 (br s, 2 H, NH_2), 1.22 (s, 9 H), 0.86 (s, 9 H), 0.05 (s, 3 H), 0.04 (s, 3 H).

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^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 177.0 (s'), 110.0 (s'), 93.7 (d'), 70.2 (d'), 64.8 (t'), 64.7 (t'), 64.6 (t'), 51.6 (d'), 38.8 (d'), 38.7 (t'), 37.7 (d'), 37.3 (t'), 29.0 (s'), 27.0 (q'), 25.7 (q'), 17.9 (s'), -4.2 (q'), -4.5 (q').

exact mass *m/z* calcd for $C_{22}H_{41}NO_6Si$ 443.27030, found 443.27126.

Compound 11

FTIR (CH_2Cl_2 cast) 1744 cm^{-1};

^1H NMR ($CDCl_3$, 400 MHz) δ 5.60 (dd, *J* = 9.9, 2.6 Hz, 1 H), 4.48 (d, *J* = 11.4 Hz, 1 H), 4.09-3.93 (m, 5 H), 3.56 (dd, *J* = 11.8, 2.7 Hz, 1 H), 3.09 (d, *J* = 11.8 Hz, 1 H), 2.22-2.12 (m, 1 H), 1.87-1.76 (m, 2 H), 1.70-1.52 (m, 2 H), 1.35 (br s, 2 H, NH_2), 1.22 (s, 9 H), 0.87 (s, 9 H), 0.053 (s, 6 H).

^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 177.0 (s'), 109.8 (s'), 95.4 (d'), 68.9 (d'), 66.8 (t'), 65.5 (t'), 65.1 (t'), 50.4 (d'), 39.8 (d'), 38.7 (t'), 38.3 (d'), 38.1 (t'), 27.0 (q'), 25.8 (q'), 25.0 (s'), 18.1 (s'), -4.7 (q'), -4.8 (q').

exact mass *m/z* calcd for $C_{22}H_{41}NO_6Si$ 443.27030, found 443.27039.

Compound 12β

FTIR (CH_2Cl_2 cast) 3365, 1735 cm^{-1};

^1H NMR ($CDCl_3$, 400 MHz) δ 5.98-5.82 (m, 1 H), 5.75-5.60 (m, 1 H), 5.48-5.10 (m, 2 H), 4.92-4.5 (m, 3 H), 4.25-4.00 (m, 3 H), 4.00-3.73 (m, 4 H), 3.60-3.48 (m, 1 H), 2.10-1.89 (m, 2 H), 1.89-1.60 (m, 4 H), 1.22 (s, 9 H), 0.88 (s, 9 H), 0.05 (s, 6 H).

^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 177.1 (s'), 156.4 (s'), 133.0 (d'), 117.5 (t'), 108.8 (s'), 94.2 (d'), 70.1 (d'), 65.6 (t'), 64.9 (t'), 51.3 (d'), 40.3 (d'), 38.7 (t'), 37.3 (t'), 35.7 (d'), 29.4 (s'), 27.0 (q'), 25.6 (q'), 17.9 (s'), -4.5 (q'), -4.8 (q').

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exact mass *m/z* calcd for $C_{22}H_{36}NO_8Si$ (M-*t*-Bu) 470.22101, found 470.22222; exact mass HRFAB (NOBA) *m/z* calcd for $C_{26}H_{45}NO_8SiNa$ (M+Na) 550.2812, found 550.2823.

Compound 12

FTIR (CH_2Cl_2 cast) 3317, 1742 cm^{-1};

^1H NMR ($CDCl_3$, 400 MHz) δ 5.98-5.84 (m, 1 H), 5.66-5.53 (m, 1 H), 5.46-5.10 (m, 2 H), 4.73-4.36 (m, 3 H), 4.28-4.14 (m, 1 H), 4.14-3.84 (m, 6 H), 3.60-3.50 (m, 1 H), 2.27-2.14 (m, 1 H), 1.88-1.70 (m, 3 H), 1.70-1.55 (m, 1 H), 1.53-1.38 (m, 1 H), 1.22 (s, 9 H), 0.89 (s, 9 H), 0.05 (s, 6 H).

^{13}C NMR ($CDCl_3$, 75.5 MHz) major δ 177.1 (s'), 156.3 (s'), 133.0 (d'), 117.7 (t'), 108.9 (t'), 95.1 (d'), 68.6 (d'), 66.2 (t'), 65.6 (t'), 65.4 (t'), 65.2 (t'), 50.9 (d'), 39.6 (d'), 38.7 (s'), 38.3 (t'), 37.1 (d'), 27.0 (q'), 25.8 (q'), 24.7 (t'), 18.1 (s'), -4.8 (q').

exact mass *m/z* calcd for $C_{22}H_{36}NO_8Si$ (M-*t*-Bu) 470.22101, found 470.22089; exact mass HRFAB (NOBA) *m/z* calcd for $C_{26}H_{45}NO_8SiNa$ (M+Na) 550.2812, found 550.2819.

Compound 13β

FTIR (CH_2Cl_2 cast) 3513, 3449, 3332, 1728 cm^{-1};

^1H NMR ($CDCl_3$, 400 MHz) δ 5.98-5.83 (m, 1 H), 5.67-5.54 (m, 1 H), 5.44-5.10 (m, 2 H), 4.73-4.47 (m, 3 H), 4.30-3.90 (m, 6 H), 3.84-3.68 (m, 2 H), 3.64-3.53 (m, 1 H), 2.36-2.22(m, 1 H), 2.05-1.72 (m, 3 H), 1.72-1.47 (m, 2 H), 1.21 (s, 9 H).

^{13}C NMR ($CDCl_3$, 75.5 MHz) major δ 176.8 (s'), 156.2 (s'), 132.8 (d'), 117.7 (t'), 109.8 (s'), 94.5 (d'), 70.4 (d'), 66.0 (s'), 65.6 (t'), 65.4 (t'), 51.0 (d'), 40.3 (d'), 38.6 (t'), 35.0 (d'), 34.9 (t'), 29.7 (s'), 26.9 (q').

exact mass *m/z* calcd for $C_{15}H_{22}NO_6$ (M-*t*-BuCOO) 312.14471, found 312.14407; exact mass HRFAB (NOBA) *m/z* calcd for $C_{20}H_{31}NO_8Na$ (M+Na) 436.1947, found 436.1955.

Compound 13

FTIR (CH_2Cl_2 cast) 3440, 3364, 1725 cm^{-1};

^1H NMR ($CDCl_3$, 400 MHz) δ 5.96-5.82 (m, 1 H), 5.65-5.55 (m, 1 H), 5.46-5.12 (m, 2 H), 4.73-4.38 (m, 3 H), 4.30-4.16 (m, 1 H), 4.16-3.84 (m, 6 H), 3.65-3.54 (m, 1 H), 2.43-2.31 (m, 1 H), 2.02-1.93 (m, 1 H), 1.93-1.57 (m, 4 H), 1.54-1.40 (m, 1 H), 1.23 (s, 9 H).

^{13}C NMR ($CDCl_3$, 75.5 MHz) major δ 177.1 (s'), 156.4 (s'), 132.9 (d'), 117.7 (t'), 108.8 (s'), 95.2 (d'), 67.8 (d'), 65.3 (t'), 65.6 (t'), 65.3 (t'), 50.8 (d'), 38.8 (d'), 38.6 (s'), 37.6 (t'), 36.9 (d'), 26.9 (q'), 24.5 (s').

exact mass *m/z* calcd for $C_{15}H_{22}NO_7$ (M-*t*-Bu) 328.13962, found 328.13923; low resolution mass *m/z* calcd for $C_{20}H_{31}NO_8$ (M) 413.2, found 413.2; exact mass HRFAB (NOBA) *m/z* calcd for $C_{20}H_{31}NO_8Na$ (M+Na) 436.1947, found 436.1953.

Compound 14

FTIR (CH_2Cl_2 cast) 3342, 1719 cm^{-1};

^1H NMR ($CDCl_3$, 400 MHz) δ 5.98-5.83 (m, 1 H), 5.70-5.60 (m, 1 H), 5.41-5.15 (m, 2 H), 4.85-4.52 (m, 3 H), 4.50-4.39 (m, 1 H), 4.18-3.84 (m, 5 H), 3.70-3.60 (m, 1 H), 2.89-2.78 (m, 2 H), 2.66-2.54 (m, 1 H), 2.11-1.75 (m, 3 H), 1.22 (s, 9 H).

^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 205.2 (s'), 176.7 (s'), 156.3 (s'), 132.6 (d'), 117.9 (t'), 108.7 (s'), 92.9 (d'), 66.0 (t'), 65.9 (t'), 65.3 (t'), 64.7 (t'), 51.9 (d'), 46.8 (t'), 46.4 (d'), 38.7 (t'), 36.0 (d'), 28.4 (s'), 26.9 (q').

exact mass *m/z* calcd for $C_{20}H_{29}NO_8$ 411.18930, found 411.18786; *m/z*

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calcd for $C_{16}H_{20}NO_8$ (M-*t*-Bu) 354.11890, found 354.11855.

Compound 15

X-Ray structure obtained.

FTIR (CH_2Cl_2 cast) 3479, 3356, 1732 cm^{-1};

^1H NMR ($CDCl_3$, 400 MHz) δ 6.00-5.84 (m, 1 H), 5.67-5.54 (m, 1 H), 5.47-5.11 (m, 2 H), 4.72-3.91 (m, 10 H), 3.60-3.50 (m, 1 H), 2.30-2.20 (m, 1 H), 2.20-2.01 (m, 3 H), 1.63-1.47 (m, 1 H), 1.23 (s, 9 H), 0.17 (s, 9 H).

^{13}C NMR ($CDCl_3$, 75.5 MHz) major δ 176.9 (s'), 156.1 (s'), 132.8 (d'), 117.8 (t'), 108.9 (s'), 105.1 (s'), 94.6 (d'), 90.3 (s'), 70.6 (s'), 65.9 (t'), 65.7 (t'), 65.5 (t'), 65.4 (t'), 50.3 (d'), 44.5 (d'), 40.1 (t'), 38.6 (t'), 35.1 (d'), 29.6 (s'), 26.9 (q'), -0.23 (q').

exact mass *m/z* calcd for $C_{25}H_{39}NO_8Si$ 509.24451, found 509.24618; *m/z* calcd for $C_{25}H_{37}NO_7Si$ (M-H_2O) 491.23392, found 491.23376.

Compound 16

FTIR (CH_2Cl_2 cast) 3444, 1744 cm^{-1};

^1H NMR ($CDCl_3$, 400 MHz) δ 6.00-5.82 (m, 1 H), 5.66-5.56 (m, 1 H), 5.45-5.10 (m, 2 H), 4.81-4.51 (m, 3 H), 4.29-4.10 (m, 2 H), 4.10-3.97 (m, 1 H), 3.97-3.74 (m, 3 H), 3.57-3.45 (m, 1 H), 2.14-1.98 (m, 3 H), 1.98-1.84 (m, 2 H), 1.67-1.57 (m, 1 H), 1.24 (s, 9 H), 0.87 (s, 9 H), 0.17 (s, 15 H).

^{13}C NMR ($CDCl_3$, 75.5 MHz) major δ 177.0 (s'), 156.3 (s'), 133.0 (d'), 117.6 (t'), 108.0 (s'), 106.5 (s'), 94.8 (d'), 92.3 (s'), 71.1 (s'), 66.5 (t'), 65.6 (t'), 65.3 (t'), 64.7 (t'), 50.5 (d'), 45.6 (d'), 42.6. (t'), 38.7 (t'), 35.3 (d'), 29.3 (s'), 27.0 (q'), 25.7 (q'), 18.2 (s'), -0.37 (q'), -2.8 (q'), -3.0 (q').

exact mass *m/z* calcd for $C_{27}H_{44}NO_8Si_2$ (M-*t*-Bu) 566.26056, found 566.25978; low resolution mass *m/z* calcd for $C_{31}H_{53}NO_8Si_2$ 623.3, found 623.0; exact mass HRFAB (NOBA) *m/z* calcd for $C_{31}H_{53}NO_8Si_2Na$ (M+Na) 646.3207, found 646.3211.

Compound 17

FTIR (CH_2Cl_2 cast) 3440, 1720 cm^{-1};

^1H NMR ($CDCl_3$, 400 MHz) δ 6.00-5.85 (m, 1 H), 5.50-4.54 (m, 5 H), 4.33-3.32 (m, 7 H), 2.66-1.15 (m, 8 H), 0.88 (s, 9 H), 0.26-0.07 (m, 15 H).

^{13}C NMR ($CDCl_3$, 75.5 MHz) major δ 156.4 (s'), 133.0 (d'), 117.5 (t'), 108.0 (s'), 106.8 (s'), 91.7 (s'), 91.1 (d'), 71.4 (s'), 65.6 (t'), 65.5 (t'), 65.1 (t'), 64.7 (t'), 50.0 (d'), 42.5 (t'), 39.6 (d'), 35.8 (d'), 28.6 (t'), 25.7 (q'), 18.2 (s'), -0.32 (q'), -2.8 (q'), -3.0 (q').

exact mass *m/z* calcd for $C_{26}H_{43}NO_6Si_2$ (M-H_2O) 521.26288, found 521.26210; low resolution mass *m/z* calcd for $C_{26}H_{45}NO_7Si_2$ 539.27344, found 539.4; exact mass HRFAB (NOBA) *m/z* calcd for $C_{26}H_{45}NO_7Si_2Na$ (M+Na) 562.2632, found 562.2623.

Compound 18

FTIR (CH_2Cl_2 cast) 3441, 3340, 1739 cm^{-1};

^1H NMR ($CDCl_3$, 400 MHz) δ 6.00-5.85 (m, 1 H), 5.35-5.17 (m, 2 H), 4.85-4.50 (m, 4 H), 4.29-3.76 (m, 6 H), 2.96-2.77 (m, 1 H), 2.62-2.23 (m, 3 H), 2.17-1.96 (m, 2 H), 0.86 (s, 9 H), 0.18 (s, 15 H).

^{13}C NMR ($CDCl_3$, 75.5 MHz) major δ 170.1 (s'), 156.2 (s'), 132.7 (d'), 117.8 (t'), 107.4 (s'), 105.7 (s'), 93.3 (s'), 69.8 (s'), 69.0 (t'), 65.7 (t'), 65.1 (t'), 64.9 (t'), 50.0 (d'), 44.7 (t'), 42.0 (d'), 34.7 (d'), 30.3 (t'), 25.5 (q'), 18.0 (s'), -0.51 (q'), -3.0 (q'), -3.0 (q').

exact mass *m/z* calcd for $C_{25}H_{40}NO_7Si_2$ (M-CH_3) 522.23431, found 522.23261; low resolution mass *m/z* calcd for $C_{26}H_{43}NO_7Si_2$ 537.257, found 537.2; exact mass HRFAB (NOBA) *m/z* calcd for $C_{26}H_{43}NO_7Si_2Na$ (M+Na) 560.2476, found 560.2471.

Compound 19

FTIR (CH_2Cl_2 cast) 3336, 1731 cm^{-1};

^1H NMR ($CDCl_3$, 400 MHz) δ 6.41 (s) and 6.40 (s) [1 H], 5.99-5.03 (m, 1 H), 5.38-5.17 (m, 2 H), 5.03 (d, *J* = 10.1 Hz) and 4.85 (d, *J* = 10.1 Hz) [1 H], 4.67-4.34 (m, 4 H), 4.20-4.07 (m, 1 H), 4.07-3.72 (m, 4 H), 3.00-2.82 (m, 1 H), 2.44 (d, *J* = 14.9 Hz, 1 H), 1.91 (d, *J* = 14.9 Hz) and 1.86 (d, *J* = 14.9 Hz) [1 H], 0.86 (s, 9 H), 0.20 (s, 12 H), 0.072 (s, 3 H).

^{13}C NMR ($CDCl_3$, 75.5 MHz) major δ 164.0 (s'), 157.4 (s'), 156.1 (s'), 123.6 (d'), 118.0 (t'), 116.0 (s'), 106.8 (s'), 102.9 (s'), 94.5 (s'), 70.0 (s'), 67.0 (t'), 65.9 (t'), 65.1 (t'), 56.1 (d'), 47.4 (t'), 35.8 (d'), 25.5 (q'), 18.2 (s'), -0.44 (q'), -3.1 (q'), -3.4 (q').

exact mass *m/z* calcd for $C_{26}H_{41}NO_7Si_2$ 535.24219, found 535.24079.

Compound 20

FTIR (CH_2Cl_2 cast) 3389, 3322, 1727 cm^{-1};

^1H NMR ($CDCl_3$, 400 MHz) δ 6.28 (s, 1 H), 4.79-4.64 (m, 1 H), 4.51-4.38 (m, 1 H), 4.12-3.84 (m, 4 H), 2.78 (s, 2 H), 2.12 (AB q, *J* = 14.6, Δυ = 275.3 Hz, 2 H), 0.88 (s, 9 H), 0.21 (s, 12 H), 0.090 (s, 3 H).

^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 164.6 (s'), 159.6 (s'), 115.0 (d'), 107.8 (s'), 103.5 (s'), 94.1 (s'), 70.3 (s'), 67.4 (t'), 65.4 (t'), 65.1 (t'), 57.9 (d'), 47.6 (t'), 36.3 (d'), 25.5 (q'), 18.2 (s'), -0.38 (q'), -3.1 (q'), -3.3 (q').

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exact mass *m/z* calcd for $C_{22}H_{37}NO_5Si_2$ 451.22104, found 451.22165.

Compound 21

FTIR (CH_2Cl_2 cast) 3465, 3354, 3223, 2169, 1696, 1634, 1601 cm^{-1};

^1H NMR ($CDCl_3$, 400 MHz) δ 5.87 (s, 1 H), 4.94 (AB q, *J* = 13.3, Δυ = 21.2 Hz, 2 H), 4.20-4.02 (m, 6 H), 2.27 (AB q, *J* = 13.5, Δυ = 12.2 Hz, 2 H), 0.85 (s, 9 H), 0.21 (s, 3 H), 0.19 (s, 3 H), 0.18 (s, 9 H).

^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 165.6 (s'), 154.3 (s'), 141.3 (s'), 105.8 (d'), 105.3 (s'), 103.6 (s'), 98.0 (s'), 91.7 (s'), 67.4 (s'), 65.3 (t'), 65.2 (t'), 65.0 (t'), 45.7 (t'), 25.5 (q'), 18.1 (s'), -0.38 (q'), -3.0 (q'), -3.0 (q').

exact mass *m/z* calcd for $C_{22}H_{35}NO_5Si_2$ 449.20538, found 449.20485.

Compound 22

FTIR (CH_2Cl_2 cast) 3410, 3301, 1725 cm^{-1};

^1H NMR ($CDCl_3$, 400 MHz) δ 6.30 (br s, 1 H, NH), 6.23 (s, 1 H), 4.92 (AB q, *J* = 14.7, Δυ = 9.1 Hz, 2 H), 4.11-3.98 (m, 4 H), 3.73 (s, 3 H), 2.28 (AB q, *J* = 13.7, Δυ = 73.1 Hz, 2 H), 0.85 (s, 9 H), 0.23 (s, 3 H), 0.18 (s, 9 H), 0.15 (s, 3 H).

^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 163.9 (s'), 153.9 (s'), 151.8 (s'), 131.0 (s'), 113.0 (d'), 104.3 (s'), 103.6 (s'), 93.5 (s'), 67.9 (t'), 67.5 (t'), 65.3 (t'), 65.2 (t'), 53.0 (q'), 46.1 (t'), 25.4 (q'), 18.1 (s'), -0.51 (q'), -3.1 (q').

exact mass *m/z* calcd for $C_{23}H_{34}NO_7Si_2$ (M-CH_3) 492.18738, found 492.18590; low resolution mass *m/z* calcd for $C_{24}H_{37}NO_7Si_2$ 507.21, found 507.4; exact mass HRFAB (NOBA) *m/z* calcd for $C_{24}H_{37}NO_7Si_2Na$ (M+Na) 530.2006, found 530.1989.

Compound 25

J4905-15

FTIR (CH_2Cl_2 cast) 3270, 2114, 1720 cm^{-1};

^1H NMR ($CDCl_3$, 400 MHz) δ 9.58 (s, 1 H), 7.49 (s, 1 H, NH), 6.43 (s, 1 H), 4.20-4.00 (m, 4 H), 3.76 (s, 3 H), 3.69 (s, 3 H), 2.64 (s, 1 H), 2.35 (AB q, J = 13.7, Δυ = 23.7 Hz, 2 H), 0.86 (s, 9 H), 0.22 (s, 3 H), 0.17 (s, 3 H).

^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 187.7 (d'), 166.9 (s'), 154.1 (s'), 146.2 (s'), 143.5 (s'), 123.6 (s'), 116.7 (d'), 104.4 (s'), 82.8 (s'), 76.5 (s'), 70.0 (s'), 65.5 (t'), 53.4 (q'), 51.7 (q'), 49.8 (t'), 25.6 (q'), 18.2 (s'), -3.0 (q'), -3.2 (q').

exact mass *m/z* calcd for $C_{22}H_{31}NO_8Si$ 465.18188, found 465.18268.

Compound 26

FTIR (CH_2Cl_2 cast) 3402, 3274, 2175, 2115, 1732, 1655 cm^{-1};

^1H NMR ($CDCl_3$, 400 MHz) δ 6.34 (s, 1 H), 6.14 (s, 1 H), 5.86 (s, 1 H), 4.12-4.00 (m, 4 H), 3.74 (s, 3 H), 2.76 (s, 1 H), 2.32 (AB q, J = 13.9, Δυ = 135.9 Hz, 2 H), 0.87 (s, 9 H), 0.23 (s, 3 H), 0.20 (s, 3 H), 0.15 (s, 9 H).

^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 163.0 (s'), 154.2 (s'), 149.8 (s'), 133.3 (s'), 120.6 (s'), 114.0 (d'), 104.2 (s'), 99.7 (s'), 91.8 (s'), 82.1 (s'), 77.2 (d'), 67.8 (s'), 67.7 (d'), 65.5 (t'), 65.5 (t'), 52.9 (q'), 46.6 (t'), 25.6 (q'), 18.2 (s'), -0.26 (q'), -2.9 (q'), -3.1 (q').

exact mass *m/z* calcd for $C_{26}H_{37}NO_7Si_2$ 531.21088, found 531.21006.

Compound 27

X-Ray structure determined.

FTIR (CH_2Cl_2 cast) 3291, 2118, 1732, 1662 cm^{-1};

^1H NMR ($CDCl_3$, 400 MHz) δ 6.19 (s, 1 H), 6.12 (br s, 1 H, NH), 5.82

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(d, J = 2.2 Hz, 1 H), 4.22-4.00 (m, 4 H), 3.77 (s, 3 H), 2.65 (s, 1 H), 2.52 (d, J = 2.2 Hz, 1 H), 2.30 (AB q, J = 13.3, $\Delta\upsilon$ = 113.1 Hz, 2 H), 0.91 (s, 9 H), 0.27 (s, 3 H), 0.26 (s, 3 H).

^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 162.7 (s'), 154.2 (s'), 151.6 (s'), 132.1 (s'), 121.4 (s'), 112.2 (d'), 104.7 (s'), 81.6 (s'), 78.5 (s'), 76.1 (d'), 74.0 (d'), 67.2 (s'), 66.6 (d'), 65.9 (t'), 65.7 (t'), 53.3 (q'), 46.8 (t'), 25.6 (q'), 18.2 (s'), -2.8 (q'), -2.9 (q').

exact mass m/z calcd for $C_{23}H_{29}NO_7Si$ 459.17133, found 459.17124.

C-(9) Epimer of 27

FTIR (CH_2Cl_2 cast) 3298, 2120, 1729 cm^{-1};

^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.37 (s, 1 H), 6.19 (br s, 1 H, NH), 5.83 (d, J = 2.2 Hz, 1 H), 4.17-4.00 (m, 4 H), 3.75 (s, 3 H), 2.79 (s, 1 H), 2.50 (d, J = 2.2 Hz, 1 H), 2.33 (AB q, J = 14.1, $\Delta\upsilon$ = 152.7 Hz, 2 H), 0.85 (s, 9 H), 0.23 (s, 3 H), 0.19 (s, 3 H).

^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 162.8 (s'), 154.2 (s'), 149.6 (s'), 133.2 (s'), 120.3 (s'), 113.9 (d'), 104.2 (s'), 82.0 (s'), 79.1 (s'), 77.5 (d'), 74.4 (d'), 67.9 (s'), 66.9 (d'), 65.6 (t'), 65.4 (t'), 53.1 (q'), 46.6 (t'), 25.5 (q'), 18.3 (s'), -3.0 (q'), -3.2 (q').

exact mass m/z calcd for $C_{23}H_{29}NO_7Si$ 459.17133, found 459.17205.

Compound 28

FTIR (CH_2Cl_2 cast) 3288, 2181, 1723 cm^{-1};

^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.14 (s, 1 H), 6.00 (br s, 1 H, NH), 5.94 (s, 1 H), 4.17-4.00 (m, 4 H), 3.78 (s, 3 H), 2.27 (AB q, J = 13.3, $\Delta\upsilon$ = 95.1 Hz, 2 H), 0.91 (s, 9 H), 0.26 (s, 3 H), 0.25 (s, 3 H).

^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 162.6 (s'), 154.4 (s'), 151.5 (s'),

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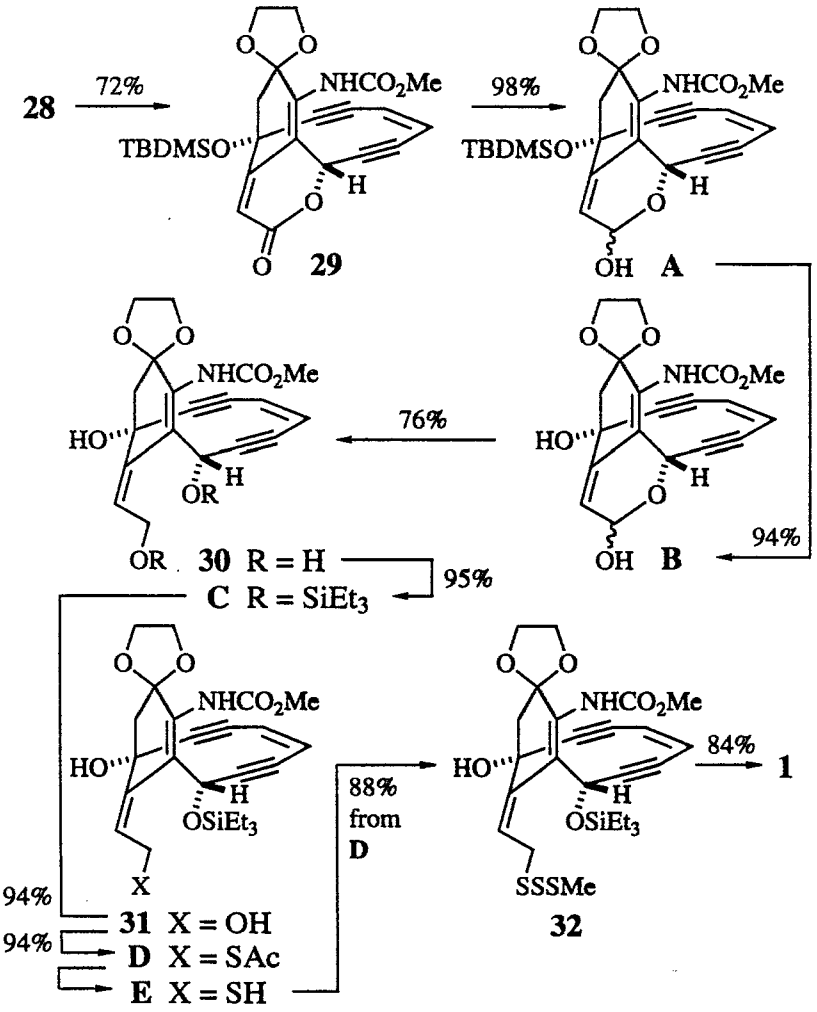
132.2 (s'), 111.9 (d'), 104.7 (s'), 91.8 (s'), 88.7 (s'), 68.8 (s'), 67.8 (d'), 65.9 (t'), 65.7 (t'), 53.5 (q'), 46.9 (t'), 25.6 (q'), 18.2 (s'), 6.7 (s'), 4.6 (s'), -2.9 (q'), -3.1 (q').

exact mass *m/z* calcd for $C_{23}H_{27}I_2NO_7Si$ 710.96466, found 710.96434.

SPECTRAL DATA FOR COMPOUNDS IN SCHEME 2

Expanded version of Scheme 2



Footnotes to expanded version of Scheme 2

28→29: (Z)-1,2-bis(trimethylstannyl)ethene, $Pd(PPh_3)_4$, 60 °C.

29→A: DIBAL.

A→B: TBAF.

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B→30: $NaBH_4$.

30→C: Et_3SiOTf, 2,6-lutidine.

C→31: 3:6:1 AcOH, THF, H_2O.

31→D: diisopropyl azodicarboxylate, Ph_3P, AcSH.

D→E: DIBAL-H.

E→32: *N*-(methyldithio)phthalimide.

32→1: TsOH, H_2O.

Compound 29

FTIR (CH_2Cl_2 cast) 3288, 1728 cm^{-1};

^1H NMR ($CDCl_3$, 400 MHz) δ 6.14 (s, 1 H), 6.12 (br s, 1 H), 5.93 (d, J = 9.6 Hz, 1 H), 5.88 (br s, 1 H, NH), 5.84 (dd, J = 9.6, 1.8 Hz, 1 H), 4.25-3.90 (m, 4 H), 3.78 (s, 3 H), 2.36 (AB q, J = 13.2, Δυ = 61.1 Hz, 2 H), 0.94 (s, 9 H), 0.26 (s, 6 H).

^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 162.5 (s'), 154.4 (s'), 154.0 (s'), 128.1 (s'), 124.6 (d'), 123.4 (d'), 110.9 (d'), 104.8 (s'), 99.2 (s'), 96.3 (s'), 91.0 (s'), 87.9 (s'), 69.3 (s'), 68.7 (d'), 65.9 (t'), 65.3 (t'), 53.3 (q'), 45.5 (t'), 25.6 (q'), 18.1 (s'), -3.0 (q'), -3.0 (q').

exact mass *m/z* calcd for $C_{25}H_{29}NO_7Si$ 483.17133, found 483.17034.

Compound A

FTIR (CH_2Cl_2 cast) 3299, 1729 cm^{-1};

^1H NMR ($CDCl_3$, 400 MHz) δ 6.02 (d, J = 2.2 Hz) and 5.97 (d, J = 2.5 Hz) [1 H], 5.89 (d, J = 2.9 Hz) and 5.86 (d, J = 2.9 Hz) [1 H], 5.78 (dd, J = 2.7, 1.6 Hz) and 5.76 (dd, J = 2.7, 1.8 Hz) [1 H], 5.68 (br s, 1 H, NH), 5.66-5.59 (m, 1 H), 5.55-5.49 (m, 1 H), 4.20-3.86 (m, 4 H), 3.73 (s, 3 H), 3.21 (d, J = 10.6 Hz) and 2.84 (d, J = 10.2 Hz) [1 H, OH], 2.40 (d, J = 13.4 Hz) and 2.39 (d, J = 13.4 Hz) [1 H], 2.26 (d, J = 13.4 Hz) and 2.25 (d, J = 13.4 Hz) [1 H], 0.92 (s, 9 H), 0.32-0.18 (m, 6 H).

J4905-19

exact mass *m/z* calcd for $C_{25}H_{31}NO_7Si$ 485.18694, found 485.18630.

Compound B

FTIR (CH_2Cl_2 cast) 3388, 1717 cm^{-1};

^1H NMR ($CDCl_3$, 400 MHz) δ 7.06 (br s, 1 H, NH), 6.05-5.76 (m, 3 H), 5.65-5.27 (m, 3 H), 4.18-3.84 (m, 4 H), 3.63 (s, 3 H), 2.44 (1/2 ABX, J_{AB} = 13.4, J_{AX} = 5.9 Hz, 1 H), 2.12 (1/2 ABX, J_{AB} = 13.4, J_{BX} = 8.2 Hz, 1 H).

exact mass *m/z* calcd for $C_{19}H_{15}NO_6$ (M-H_2O) 353.08994, found 353.08885; exact mass HRFAB (NOBA) *m/z* calcd for $C_{19}H_{17}NO_7Na$ (M+Na) 394.0903, found 394.0902.

Compound 30

FTIR (CH_2Cl_2 cast) 3384, 1717 cm^{-1};

^1H NMR ($CDCl_3$, 400 MHz) δ 6.72 (br s, 1 H, NH), 6.43 (dd, *J* = 8.3, 6.9 Hz, 1 H), 5.85 (dd, *J* = 9.5, 1.0 Hz, 1 H), 5.82 (d, *J* = 9.5 Hz, 1 H), 5.60 (s, 1 H), 4.66 (br s, 1 H, OH), 4.32 (dd, *J* = 13.0, 8.3 Hz, 1 H), 4.21 (dd, *J* = 13.0, 6.9 Hz, 1 H), 4.10-3.88 (m, 4 H), 3.77 (s, 3 H), 3.12 (br s, 1 H, OH), 2.57 (br s, 1 H, OH), 2.45 (AB q, *J* = 14.4, Δυ = 96.0 Hz, 2 H).

exact mass HRFAB (NOBA) *m/z* calcd for $C_{19}H_{19}NO_7Na$ (M+Na) 396.1059, found 396.1043.

Compound C

FTIR (CH_2Cl_2 cast) 3404, 1715 cm^{-1};

^1H NMR ($CDCl_3$, 400 MHz) δ 6.11 (dd, *J* = 8.0, 5.4 Hz, 1 H), 5.86 (d, *J* = 9.4 Hz, 1 H), 5.81 (br s, 1 H, NH), 5.80 (dd, *J* = 9.4, 1.5 Hz, 1 H), 5.74 (br s, 1 H), 4.41 (dd, *J* = 14.5, 8.0 Hz, 1 H), 4.36 (dd, *J* = 14.5, 3.3 Hz, 1 H), 4.16-3.85 (m, 4 H), 3.74 (s, 3 H), 2.36 (AB q, *J* = 13.3, Δυ = 145.8 Hz, 2 H), 2.35 (s, 1 H, OH), 1.06-0.90 (m, 18 H), 0.79-0.55 (m, 12 H).

exact mass *m/z* calcd for $C_{31}H_{47}O_7NSi_2$ 601.28912, found 601.28946.

Compound 31

FTIR (CH_2Cl_2 cast) 3378, 1716 cm^{-1};

^1H NMR ($CDCl_3$, 400 MHz) δ 6.29 (t, *J* = 6.7 Hz, 1 H), 5.96 (br, 1 H, NH), 5.87 (d, *J* = 9.3 Hz, 1 H), 5.82 (dd, *J* = 9.3, 1.4 Hz, 1 H), 5.79 (br s, 1 H), 4.28 (t, *J* = 6.7 Hz, 2 H), 4.10-3.85 (m, 4 H), 3.73 (s, 3 H), 2.46 (t, *J* = 7.0 Hz, 1 H, OH), 2.45 (s, 1 H, OH), 2.38 (AB q, *J* = 13.6, Δυ = 154.7 Hz, 2 H), 1.01 (t, *J* = 8.0 Hz, 9 H), 0.83-0.69 (m, 6 H).

exact mass *m/z* calcd for $C_{25}H_{31}O_7NSi$ 487.20264, found 487.20079.

Compound D

FTIR (CH_2Cl_2 cast) 3404, 1735, 1690 cm^{-1};

^1H NMR ($CDCl_3$, 400 MHz) δ 6.03 (dd, *J* = 8.9, 6.5 Hz, 1 H), 5.95 (br s, 1 H, NH), 5.85 (d, *J* = 9.1 Hz, 1 H), 5.81 (dd, *J* = 9.1, 1.3 Hz, 1 H), 5.80 (br, 1 H),4.10-3.85 (m, 6 H), 3.74 (s, 3 H), 2.36 (s, 1 H, OH), 2.34 (AB q, *J* = 13.5, Δυ = 162.8 Hz, 2 H), 2.33 (s, 3 H), 1.00 (t, *J* = 8.0 Hz, 9 H), 0.80-0.69 (m, 6 H).

exact mass *m/z* calcd for $C_{27}H_{35}O_7NSIS$ 545.19037, found 545.19001.

Compound 32

FTIR (CH_2Cl_2 cast) 3403, 1737 cm^{-1};

^1H NMR ($CDCl_3$, 400 MHz) δ 6.29 (dd, *J* = 9.9, 4.8 Hz, 1 H), 5.95 (br s, 1 H, NH), 5.86 (d, *J* = 9.1 Hz, 1 H), 5.81 (dd, *J* = 9.1, 1.4 Hz, 1 H), 5.80 (br s, 1 H), 4.11-3.86 (m, 5 H), 3.73 (dd, *J* = 11.3, 4.7 Hz, 1 H), 3.73 (s, 3 H), 2.55 (s, 3 H), 3.43 (s, 1 H, OH), 2.41 (AB q, *J* = 13.3, Δυ = 135.1 Hz, 2 H), 1.00 (t, *J* = 8.0 Hz, 9 H), 0.86-0.66 (m, 6 H).

exact mass HRFAB (NOBA) *m/z* calcd for $C_{26}H_{35}NO_6SiS_3Na$ (M+Na) 604.1294, found 604.1290.

Compound 1 [(±)-calicheamicinone]

FTIR (CH_2Cl_2 cast) 3358, 1713, 1674 cm^{-1};

^1H NMR ($CDCl_3$, 400 MHz) δ 6.95 (br s, 1 H, NH), 6.48 (dd, *J* = 9.3, 6.6 Hz, 1 H), 6.02 (dd, *J* = 6.7, 1.2 Hz, 1 H), 5.91 (dd, *J* = 9.4, 1.2 Hz, 1 H), 5.88 (d, *J* = 9.4 Hz, 1 H), 4.12 (dd, *J* = 14.1, 9.3 Hz, 1 H), 3.86 (dd, *J* 14.1, 6.6 Hz, 1 H), 3.78 (s, 3 H), 3.02 (AB q, *J* = 16.9, Δυ = 143.9 Hz, 2 H), 3.21 (br s, 1 H), 2.68 (s, 1 H), 2.54 (s, 3 H).

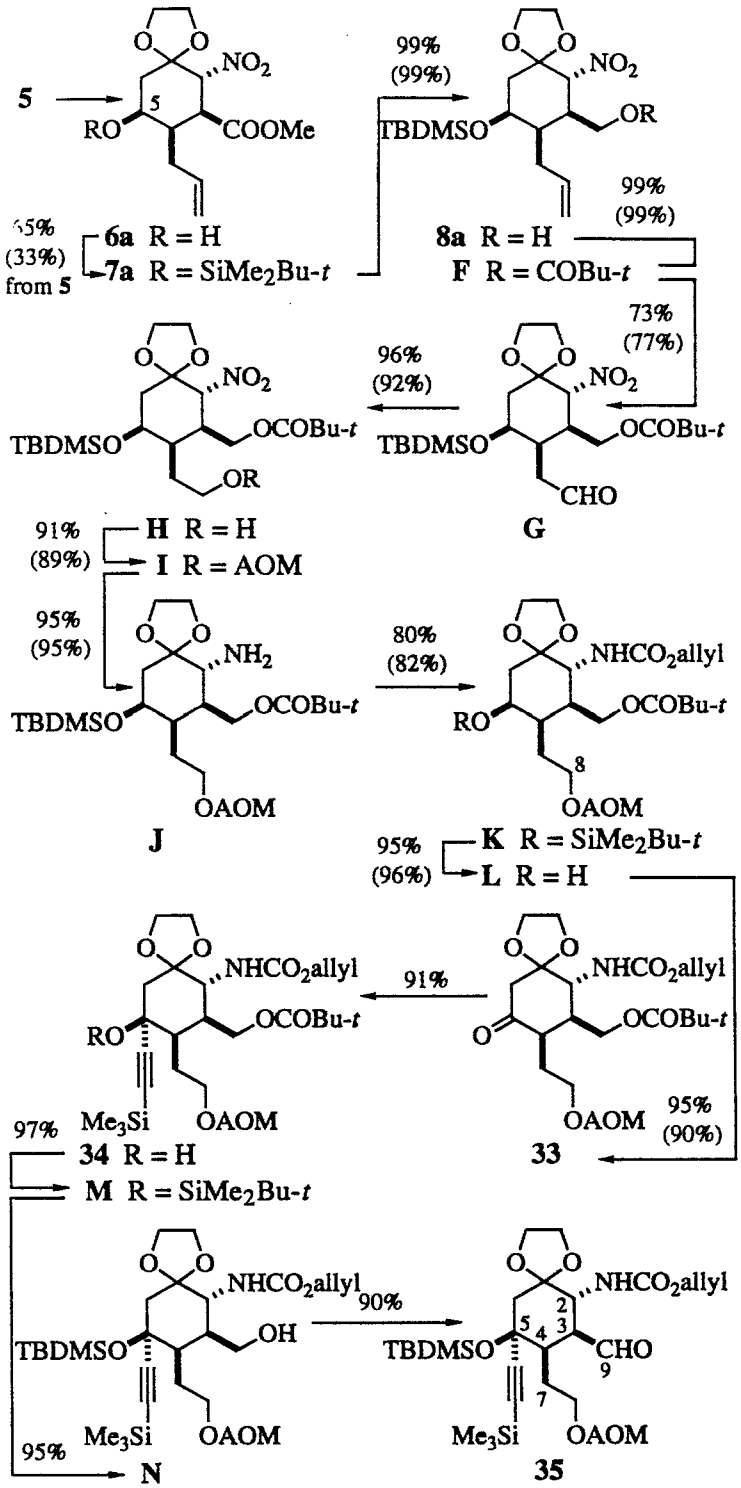
^{13}C NMR ($CDCl_3$, 125 MHz) δ 191.1 (s'), 154.6 (s'), 137.5 (s'), 130.6 (s'), 126.2 (d'), 124.4 (d'), 123.7 (d'), 100.2 (s'), 100.0 (s'), 88.0 (s'), 84.9 (s'), 72.6 (s'), 64.7 (d'), 53.4 (q'), 52.3 (t'), 38.7 (t'), 22.6 (q').

exact mass HRFAB (NOBA) *m/z* calcd for $C_{18}H_{17}NO_5S_3Na$ (M+Na) 446.0167, found 446.0162.

J4985-22

SPECTRAL DATA FOR SECOND ROUTE

Second route (part 1) [Expanded version of Scheme 3][a]



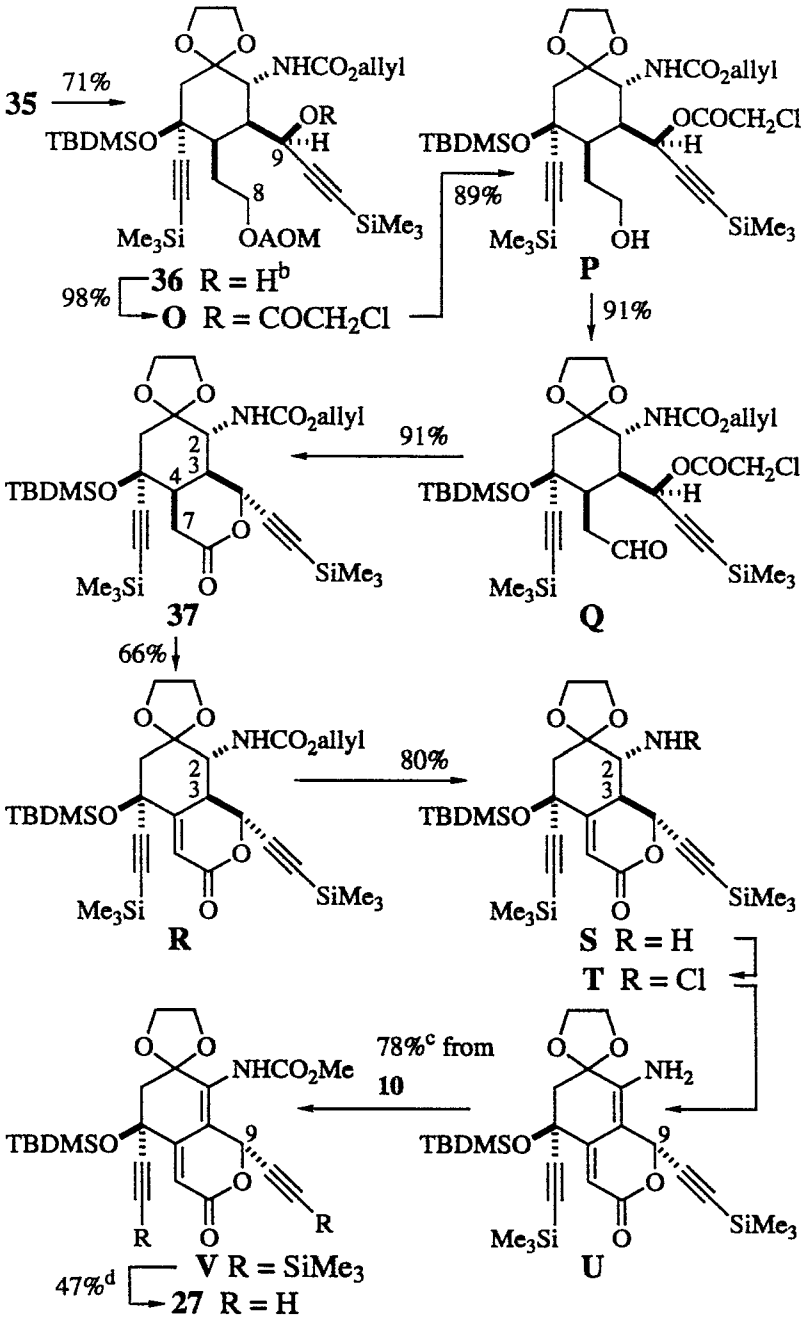
Footnotes for part 1 of expanded version of Scheme 3

[a]AOM = *p*-methoxyphenoxymethyl; yields in brackets refer to the 5α series (the reactions were done under similar conditions to those used for the 5β series shown). All compounds are racemic but are represented by a single enantiomer. Diagram **6a** is the enantiomeric representation of **6**, **7a** of **7**, and **8a** of **8**.

5→6a & **6aα**:	$NaBH_4$.
6a,6aα→7a:	*t*-$BuMe_2SiOTf$, 2,6-lutidine.
6a,6aα→7aα:	*t*-$BuMe_2SiOTf$, 2,6-lutidine.
7a→8a:	DIBAL-H.
8a→F:	*t*-BuCOCl, DMAP.
F→G:	OsO_4; $NaIO_4$.
G→H:	$NaBH_4$.
H→I:	*p*-methoxyphenoxymethyl chloride, *i*-Pr_2NEt.
I→J:	$NiCl_2$; $NaBH_4$; ultrasound.
J→K:	allyloxycarbonyl chloride, pyridine.
K→L:	TBAF.
L→33:	Collins oxidation.
33→34:	1:1.4 $Me_3SiC{\equiv}CLi$, $CeCl_3$; THF, -78 °C.
34→M:	*t*-$BuMe_2SiOTf$, 2,6-lutidine.
M→N:	DIBAL-H.
N→35:	Collins oxidation.

J4905-24

Second route (part 2)[a]
[Expanded version of Scheme 3]



Footnotes for part 2 of expanded version of Scheme 3

[a]AOM = *p*-methoxyphenoxymethyl. [b]Oxidation (PCC) and reduction ($NaBH_4$, *ca.* 90% overall) converts the undesired isomer into an 11.6:1 isomer mixture in favor of **36**. [c]Both **U** and **V** are

inseparable mixtures of C(9) epimers (8:1 in favor of **U** and **V**, respectively). [d]The C(9) epimer of **27**, isolated in 39% yield, can be converted into **27** (see text of the paper).

35→36: 1:1.3 $Me_3SiC{\equiv}CLi$, $CeCl_3$, THF, -78 °C; **36** obtained in 71% isolated yield and its C(9) epimer in 18% yield. The epimer can be converted into **36**, as described in footnote *b* above.

36→O: $ClCH_2COCl$, DMAP.

O→P: CAN.

P→Q: Collins.

Q→37: aqueous NH_3; Collins oxidation.

37→R: LDA, PhSeBr, -78 °C; dimethyldioxirane.

R→S: $Pd(PPh_3)_4$, dimedone; structure of **S** confirmed by X-ray analysis.

S→T: *t*-BuOCl.

T→U: DABCO, room temperature; **U** obtained as an 8:1 mixture of C(9) epimers, of which only the required (major) isomer is shown in the Scheme.

U→V: triphosgene, MeOH; **V** obtained as an 8:1 mixture of C(9) epimers.

V→27: TBAF; the C(9) epimer, isolated in 39% yield from **V** can be converted into **27**, as described in the text of the paper.

Compound Fα

FTIR (CH_2Cl_2 cast) 1733 cm^{-1};

^1H NMR ($CDCl_3$, 400 MHz) δ 5.80-5.64 (m, 1 H), 5.15-5.02 (m, 2 H), 4.76 (d, *J* = 3.7 Hz, 1 H), 4.30 (dd, *J* = 11.0, 5.8 Hz, 1 H), 4.12-3.85 (m, 5 H), 3.80-3.68 (m, 1 H), 2.90-2.78 (m, 1 H), 2.56-2.41 (m, 1 H), 2.35-2.20 (m, 2 H), 1.98-1.82 (m, 2 H), 1.21 (s, 9 H), 0.90 (s, 9 H), 0.06 (s, 3 H), 0.05 (s, 3 H).

^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 177.6 (s'), 135.4 (d'), 117.1 (t'), 106.7 (s'), 85.3 (d'), 68.0 (d'), 64.9 (t'), 60.6 (t'), 41.1 (d'),

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40.0 (t'), 37.7 (d'), 31.6 (t'), 27.0 (q'), 25.6 (q'), 17.8 (s'), -4.4 (q'), -4.9 (q').

exact mass *m/z* calcd for $C_{19}H_{32}NO_7Si$ (M-*t*-Bu) 414.19479, found 414.19321; exact mass HRFAB (NOBA) *m/z* calcd for $C_{23}H_{41}NO_7SiNa$ (M+Na) 494.2550, found 494.2559.

Compound F

FTIR (CH_2Cl_2 cast) 1733 cm^{-1};

^1H NMR ($CDCl_3$, 400 MHz) δ 5.85-5.70 (m, 1 H), 5.12-4.91 (m, 2 H), 4.75 (d, *J* = 8.2 Hz, 1 H), 4.29-4.14 (m, 2 H), 4.14-3.88 (m, 5 H), 2.84-2.68 (m, 1 H), 2.49-2.35 (m, 1 H), 2.35-2.23 (m, 1 H), 2.15-1.96 (m, 2 H), 1.83 (dd, *J* = 13.8, 8.3 Hz, 1 H), 1.19 (s, 9 H), 0.90 (s, 9 H), 0.07 (s, 3 H), 0.05 (s, 3 H).

^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 177.8 (s'), 137.5 (d'), 116.1 (t'), 106.7 (s'), 86.7 (d'), 69.0 (s'), 65.2 (t'), 65.0 (t'), 62.6 (t'), 41.1 (d'), 40.0 (t'), 39.8 (d'), 38.7 (t'), 27.1 (q'), 25.7 (q'), 18.0 (s'), -4.5 (q'), -4.8 (q').

exact mass *m/z* calcd for $C_{19}H_{32}NO_7Si$ (M-*t*-Bu) 414.19479, found 414.19495; exact mass HRFAB (NOBA) *m/z* calcd for $C_{23}H_{41}NO_7SiNa$ (M+Na) 494.2550, found 494.2537.

Compound Gα

FTIR (CH_2Cl_2 cast) 1729 cm^{-1};

^1H NMR ($CDCl_3$, 400 MHz) δ 9.72 (dd, *J* = 2.2, 1.1 Hz, 1 H), 4.71 (dd, *J* = 2.9, 1.2 Hz, 1H), 4.19 (dd, *J* = 11.3, 5.6 Hz, 1 H), 4.15-3.85 (m, 5 H), 3.78-3.67 (m, 1 H), 3.07-2.93 (m, 1 H), 2.90-2.78 (m, 1 H), 2.68-2.55 (m, 1 H), 2.44-2.32 (m, 2 H), 2.02-1.90 (m, 1 H), 1.20 (s, 9 H), 0.87 (s, 9 H), 0.07 (s, 3 H), 0.05 (s, 3 H).

^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 200.5 (d'), 177.8 (s'), 106.6 (s'), 85.4 (d'), 68.6 (d'), 65.2 (t'), 65.1 (t'), 61.2 (t'), 43.0 (t'),

40.5 (t'), 39.8 (d'), 38.8 (s'), 36.3 (d'), 27.1 (q'), 25.7 (q'), 17.9 (s'), -4.2 (q'), -4.6 (q').

exact mass *m/z* calcd for $C_{18}H_{30}NO_8Si$ (M-*t*-Bu) 416.17407, found 416.17344; exact mass HRFAB (NOBA) *m/z* calcd for $C_{22}H_{39}NO_8SiNa$ (M+Na) 496.2343, found 496.2360.

Compound G

FTIR (CH_2Cl_2 cast) 1731 cm^{-1};

^1H NMR ($CDCl_3$, 400 MHz) δ 9.72 (d, *J* = 1.1 Hz, 1 H), 4.66 (d, *J* = 11.2 Hz, 1 H), 4.20-4.07 (m, 2 H), 4.07-3.86 (m, 5 H), 3.01-2.87 (m, 2 H), 2.78-2.65 (m, 1 H), 2.41 (dd, *J* = 17.1, 4.5 Hz, 1 H), 1.90 (dd, *J* = 13.5, 4.0 Hz, 1 H), 1.75 (dd, *J* = 13.5, 11.2 Hz, 1 H), 1.18 (s, 9 H), 0.85 (s, 9 H), 0.07 (s, 3 H), 0.04 (s, 3 H).

^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 199.5 (d'), 177.3 (s'), 107.2 (s'), 86.0 (d'), 68.4 (d'), 65.5 (t'), 65.2 (t'), 62.6 (t'), 40.2 (t'), 38.7 (s'), 37.8 (d'), 37.6 (t'), 36.8 (d'), 26.9 (q'), 25.6 (q'), 17.9 (s'), -4.9 (q'), -5.0 (q').

exact mass *m/z* calcd for $C_{18}H_{30}NO_8Si$ (M-*t*-Bu) 416.17407, found 416.17398; exact mass HRFAB (NOBA) *m/z* calcd for $C_{22}H_{39}NO_8SiNa$ (M+Na) 496.2343, found 496.2328.

Anal. Calcd for $C_{22}H_{39}NO_8Si$: C 55.79, H 8.30, N 2.96. Found: C 56.00, H 8.34, N 2.84.

Compound Hα

FTIR (CH_2Cl_2 cast) 3500, 1732 cm^{-1};

^1H NMR ($CDCl_3$, 400 MHz) δ 4.72 (d, *J* = 3.5 Hz, 1 H), 4.36 (dd, *J* = 11.2, 5.5 Hz, 1 H), 4.17-3.83 (m, 5 H), 4.82-3.65 (m, 3 H), 2.93-2.80 (m, 1 H), 2.43-2.22 (m, 2 H), 1.99-1.80 (m, 2 H), 1.66-1.45 (m, 1 H), 1.60 (s, 1 H, OH), 1.22 (s, 9 H), 0.90 (s, 9 H), 0.08 (s, 3 H), 0.07 (s, 3 H).

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^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 178.0 (s'), 106.7 (s'), 85.5 (d'), 68.6 (d'), 65.0 (t'), 61.2 (t'), 61.1 (t'), 40.3 (t'), 39.0 (d'), 38.8 (d'), 30.4 (t'), 27.1 (q'), 25.7 (q'), 17.9 (s'), -4.4 (q'), -4.7 (q').

exact mass *m/z* calcd for $C_{18}H_{32}NO_8Si$ (M-*t*-Bu) 418.18973, found 418.18841; exact mass HRFAB (NOBA) *m/z* calcd for $C_{22}H_{41}NO_8SiNa$ (M+Na) 498.2499, found 498.2508.

Compound H

FTIR (CH_2Cl_2 cast) 3500, 1731 cm^{-1};

^1H NMR ($CDCl_3$, 400 MHz) δ 4.69 (d, *J* = 10.9 Hz, 1 H), 4.26-4.07 (m,3 H), 4.07-3.87 (m, 3 H), 3.75-3.51 (m, 2 H), 2.94-2.78 (m, 1 H), 2.58 (br s, 1 H, OH), 2.33-2.20 (m, 1 H), 2.03-1.86 (m, 2 H), 1.85-1.60 (m, 2 H), 1.19 (s, 9 H), 0.91 (s, 9 H), 0.11 (s, 6 H).

^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 177.7 (s'), 107.2 (s'), 86.4 (d'), 69.7 (d'), 65.3 (t'), 65.2 (t'), 62.6 (t'), 61.9 (t'), 39.9 (t'), 39.0 (d'), 38.7 (s'), 26.9 (q'), 25.7 (q'), 18.0 (s'), -4.8 (q'), -5.0 (q').

exact mass *m/z* calcd for $C_{18}H_{32}NO_8Si$ (M-*t*-Bu) 418.18973, found 418.18973; exact mass HRFAB (NOBA) *m/z* calcd for $C_{22}H_{41}NO_8SiNa$ (M+Na) 498.2499, found 498.2500.

Compound Iα

FTIR (CH_2Cl_2 cast) 1732 cm^{-1};

^1H NMR ($CDCl_3$, 400 MHz) δ 6.97-6.87 (m, 2 H), 6.85-6.76 (m, 2 H), 5.12 (AB q, *J* = 6.9, Δυ = 11.3 Hz, 2 H), 4.68 (dd, *J* = 4.0, 0.9 Hz, 1 H), 4.29 (dd, *J* = 11.1, 4.4 Hz, 1 H), 4.10-3.85 (m, 5 H), 3.82-3.65 (m, 3 H), 3.77 (s, 3 H), 2.82-2.73 (m, 1 H), 2.40-2.30 (m, 1 H), 2.26 (dd, *J* = 13.5, 9.2 Hz, 1 H), 2.02-1.86 (m, 2 H), 1.57-1.46 (m, 1 H), 1.19 (s, 9 H), 0.88 (s, 9 H), 0.06 (s, 3 H),

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0.04 (s, 3 H).

^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 177.8 (s'), 154.6 (s'), 151.2 (s'), 117.2 (d'), 114.6 (d'), 106.7 (s'), 93.9 (t'), 85.4 (d'), 68.7 (d'), 66.7 (t'), 65.0 (t'), 65.0 (t'), 61.0 (t'), 55.6 (q'), 40.3 (t'), 38.8 (d'), 38.7 (s'), 38.5 (d'), 27.5 (t'), 27.1 (q'), 25.7 (q'), 17.9 (s'), -4.3 (q'), -4.7 (q').

exact mass *m/z* calcd for $C_{30}H_{49}NO_{10}Si$ 611.31256, found 611.31224.

Compound I

FTIR (CH_2Cl_2 cast) 1732 cm^{-1};

^1H NMR ($CDCl_3$, 400 MHz) δ 6.98-6.87 (m, 2 H), 6.87-6.73 (m, 2 H), 5.12 (AB q, J = 7.2, Δυ = 4.4 Hz, 2 H), 4.69 (d, J = 8.5 Hz, 1 H), 4.19 (d, J = 5.6 Hz, 2 H), 4.08-3.85 (m, 5 H), 3.85-3.57 (m, 2 H), 3.77 (s, 3 H), 2.64 (br s, 1 H), 2.22 (br s, 1 H), 2.05-1.92 (m, 1 H), 1.92-1.73 (m, 2 H), 1.73-1.58 (m, 1 H), 1.17 (s, 9 H), 0.87 (s, 9 H), 0.04 (s, 3 H), 0.03 (s, 3 H).

^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 177.7 (s'), 154.5 (s'), 151.1 (s'), 117.1 (d'), 114.6 (d'), 106.6 (s'), 93.5 (t'), 86.5 (d'), 69.0 (d'), 67.4 (t'), 65.1 (t'), 65.0 (t'), 62.9 (t'), 55.6 (q'), 39.7 (t'), 39.4 (d'), 38.7 (s'), 32.7 (d'), 27.0 (q'), 25.7 (q'), 17.9 (s'), -4.7 (q'), -4.9 (q').

exact mass *m/z* calcd for $C_{30}H_{49}NO_{10}Si$ 611.31256, found 611.31105.

Compound Jα

FTIR (CH_2Cl_2 cast) 3449, 3386, 1725 cm^{-1};

^1H NMR ($CDCl_3$, 400 MHz) δ 7.01-6.90 (m, 2 H), 6.87-6.75 (m, 2 H), 5.13 (AB q, J = 6.9, Δυ = 7.3 Hz, 2 H), 4.31 (dd, J = 11.2, 7.3 Hz, 1 H), 4.10 (dd, J = 11.3, 7.3 Hz, 1 H), 4.00-3.84 (m, 4 H), 3.80-3.62 (m, 3 H), 3.76 (s, 3 H), 2.87 (d, J = 5.7 Hz, 1 H), 2.27 (br s, 1 H), 2.07-1.76 (m, 2 H), 1.90 (dd, J = 13.4, 7.9 Hz, 1 H),

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1.68 (dd, J = 13.4, 3.9 Hz, 1 H), 1.63-1.49 (m, 1 H), 1.36 (br s, 2 H, NH_2), 1.17 (s, 9 H), 0.87 (s, 9 H), 0.02 (s, 3 H), 0.01 (s, 3 H).

^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 178.2 (s'), 154.5 (s'), 151.4 (s'), 117.3 (d'), 114.5 (d'), 110.0 (s'), 93.9 (t'), 69.4 (d'), 67.2 (t'), 65.0 (t'), 64.2 (t'), 63.4 (t'), 55.6 (q'), 52.5 (d'), 39.9 (d'), 38.6 (t'), 38.2 (t'), 38.0 (d'), 27.1 (q'), 27.1 (s'), 25.7 (q'), 17.9 (s'), -4.5 (q'), -4.8 (q').

exact mass m/z calcd for $C_{30}H_{51}NO_8Si$ 581.33838, found 581.33746.

Compound J

FTIR (CH_2Cl_2 cast) 3451, 3385 cm^{-1};

^1H NMR ($CDCl_3$, 400 MHz) δ 7.00-6.88 (m, 2 H), 6.84-6.72 (m, 2 H), 5.11 (s, 2 H), 4.55 (dd, J = 11.4, 4.7 Hz, 1 H), 4.10-3.70 (m, 7 H), 3.76 (s, 3 H), 3.66-3.54 (m, 1 H), 2.66 (d, J = 11.3 Hz, 1 H), 2.02-1.82 (m, 3 H), 1.80 (dd, J = 13.4, 4.2 Hz, 1 H), 1.63 (dd, J = 13.1, 11.5 Hz, 1 H), 1.68-1.51 (m, 1 H), 1.18 (s, 11 H), 0.86 (s, 9 H), 0.03 (s, 3 H), 0.01 (s, 3 H).

^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 178.0 (s'), 154.5 (s'), 151.3 (s'), 117.4 (d'), 114.4 (d'), 109.3 (s'), 93.9 (t'), 70.5 (d'), 69.1 (t'), 65.1 (t'), 64.0 (t'), 55.5 (q'), 52.8 (q'), 41.0 (d'), 38.6 (t'), 38.3 (t'), 27.1 (q'), 25.7 (q'), 18.0 (s'), -4.8 (q'), -4.9 (q').

exact mass m/z calcd for $C_{30}H_{51}NO_8Si$ 581.33838, found 481.33639.

Compound Kα

FTIR (CH_2Cl_2 cast) 3446, 1729 cm^{-1};

^1H NMR ($CDCl_3$, 400 MHz) δ 7.00-6.89 (m, 2 H), 6.89-6.73 (m, 2 H), 6.00-5.84 (m, 1 H), 5.33-5.17 (m, 2 H), 5.12 (s, 2 H), 4.87 (d, J = 9.7 Hz, 1 H, NH), 4.55 (d, J = 5.5 Hz, 2 H), 4.24 (dd, J = 11.3,

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6.3 Hz, 1 H), 4.13-3.72 (m, 7 H), 3.76 (s, 3 H), 3.69 (t, J = 6.4 Hz, 2 H), 2.63-2.43 (m, 1 H), 1.95-1.82 (m, 1 H), 1.82-1.57 (m, 4 H), 1.17 (s, 9 H), 0.86 (s, 9 H), 0.00 (s, 3 H), -0.02 (s, 3 H).

^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 178.0 (s'), 156.1 (s'), 154.6 (s'), 151.3 (s'), 132.8 (d'), 117.5 (t'), 117.3 (d'), 114.6 (d'), 108.4 (s'), 94.1 (t'), 68.6 (d'), 67.3 (s'), 65.6 (t'), 65.0 (t'), 64.7 (t'), 62.9 (t'), 55.6 (q'), 52.1 (d'), 39.7 (d'), 38.7 (t'), 37.8 (d'), 37.6 (t'), 27.1 (q'), 26.3 (s'), 25.6 (q'), 17.8 (s'), -4.7 (q'), -5.0 (q').

exact mass *m/z* calcd for $C_{34}H_{55}NO_{10}Si$ 665.35950, found 665.36017.

Compound K

FTIR (CH_2Cl_2 cast) 3347, 1727 cm^{-1};

^1H NMR ($CDCl_3$, 400 MHz) δ 7.00-6.90 (m, 2 H), 6.86-6.75 (m, 2 H), 6.00-5.81 (m, 1 H), 5.35-5.17 (m, 2 H), 5.12 (s, 2 H), 4.66 (d, *J* = 10.2 Hz, 1 H, NH), 4.62-4.48 (m, 2 H), 4.28 (dd, *J* = 11.4, 4.4 Hz, 1 H), 4.12-3.73 (m, 8 H), 3.77 (s, 3 H), 3.69-3.54 (m, 1 H), 2.04-1.88 (m, 3 H), 1.82-1.70 (m, 2 H), 1.70-1.53 (m, 1 H), 1.17 (s, 9 H), 0.86 (s, 9 H), 0.04 (s, 3 H), 0.03 (s, 3 H).

^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 177.9 (s'), 156.1 (s'), 154.5 (s'), 151.3 (s'), 132.8 (d'), 117.7 (t'), 117.4 (d'), 114.5 (d'), 108.3 (s'), 93.8 (t'), 70.2 (d'), 68.8 (t'), 65.6 (t'), 65.4 (t'), 65.0 (t'), 63.5 (t'), 55.5 (q'), 52.5 (d'), 40.6 (d'), 38.8 (t'), 38.6 (t'), 38.5 (d'), 27.1 (q'), 25.7 (q'), 22.6 (s'), 18.0 (s'), -4.9 (q'), -5.0 (q').

exact mass *m/z* calcd for $C_{34}H_{55}O_{10}NSi$ 665.35950, found 665.36039.

Compound Lα

FTIR (CH_2Cl_2 cast) 3520, 3352, 1725 cm^{-1};

^1H NMR ($CDCl_3$, 400 MHz) δ 7.00-6.88 (m, 2 H), 6.86-6.79 (m, 2 H),

5.97-5.81 (m, 1 H), 5.36-5.17 (m, 2 H), 5.12 (s, 2 H), 4.70 (d, *J* = 10.2 Hz, 1 H, NH), 4.65-4.48 (m, 2 H), 4.25 (dd, *J* = 11.5, 5.1 Hz, 1 H), 4.15-3.85 (m, 7 H), 3.77 (s, 3 H), 3.69 (t, *J* = 6.4 Hz, 2 H), 3.44 (d, *J* = 8.9 Hz, 1 H, OH), 2.48-2.35 (m, 1 H), 2.18-2.07 (m, 1 H), 1.96-1.75 (m, 3 H), 1.50-1.37 (m, 1 H), 1.17 (s, 9 H).

^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 178.1 (s'), 156.1 (s'), 154.7 (s'), 151.3 (s'), 132.7 (d'), 117.9 (t'), 117.4 (d'), 114.6 (d'), 109.3 (s'), 94.0 (t'), 68.8 (d'), 67.1 (t'), 65.8 (t'), 65.5 (t'), 65.3 (t'), 63.4 (t'), 55.6 (q'), 52.8 (d'), 40.1 (d'), 38.7 (t'), 37.3 (d'), 34.7 (t'), 27.1 (q'), 26.2 (s').

exact mass *m/z* calcd for $C_{28}H_{41}NO_{10}$ 551.27307, found 551.27185.

Compound L

FTIR (CH_2Cl_2 cast) 3450, 3354, 1725 cm^{-1};

^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.98-6.88 (m, 2 H), 6.88-6.76 (m, 2 H), 5.99-5.80 (m, 1 H), 5.35-5.18 (m, 1 H), 5.16 (AB q, *J* = 7.0, Δυ = 11.6 Hz, 2 H), 4.68 (d, *J* = 9.9 Hz, 1 H, NH), 4.62-4.45 (m, 2 H), 4.33-4.18 (m, 1 H), 4.10-3.70 (m, 8 H), 3.77 (s, 3 H), 3.68-3.56 (m, 1 H), 2.97 (d, *J* = 5.1 Hz, 1 H, OH), 2.22-2.13 (m, 1 H), 2.13-2.00 (m, 1 H), 2.00-1.83 (m, 2 H), 1.81-1.62 (m, 2 H), 1.16 (s, 9 H).

^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 178.0 (s'), 156.2 (s'), 154.7 (s'), 151.0 (s'), 132.7 (d'), 117.7 (t'), 117.3 (d'), 114.6 (d'), 108.2 (t'), 93.8 (t'), 68.9 (d'), 68.6 (t'), 65.7 (t'), 65.4 (t'), 65.0 (t'), 63.2 (t'), 55.5 (q'), 52.5 (d'), 40.8 (d'), 39.1 (d'), 38.6 (t'), 38.2 (t'), 27.1 (q'), 22.4 (s').

exact mass *m/z* calcd for $C_{28}H_{41}NO_{10}$ 551.27307, found 551.27210.

Compound 33

FTIR (CH_2Cl_2 cast) 3351, 1724 cm^{-1};

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^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.98-6.87 (m, 2 H), 6.87-6.76 (m, 2 H), 6.02-5.82 (m, 1 H), 5.38-5.16 (m, 2 H), 5.07 (AB q, J = 7.0, Δυ = 11.6 Hz, 2 H), 4.73 (br s, 1 H), 4.59 (d, J = 5.4 Hz, 2 H), 4.28-4.15 (m, 2 H), 4.15-3.85 (m, 5 H), 3.77 (s, 3 H), 3.75-3.56 (m, 2 H), 2.88-2.69 (m, 2 H), 2.50 (dd, J = 15.1, 1.2 Hz, 1 H), 2.36-2.22 (m, 1 H), 2.11-1.94 (m, 1 H), 1.88-1.71 (m, 1 H), 1.16 (s, 9 H).

^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 206.5 (s'), 178.0 (s'), 156.1 (s'), 154.6 (s'), 151.1 (s'), 132.6 (d'), 117.9 (t'), 117.3 (d'), 114.6 (d'), 108.7 (s'), 93.9 (t'), 66.1 (t'), 65.9 (t'), 65.8 (t'), 65.2 (t'), 62.5 (t'), 55.6 (q'), 53.0 (d'), 47.3 (t'), 40.2 (d'), 38.7 (t'), 27.0 (q'), 26.0 (s').

exact mass m/z calcd for $C_{28}H_{39}NO_{10}$ 549.25739, found 549.25836.

Compound 34

FTIR (CH_2Cl_2 cast) 3446, 1727 cm^{-1};

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.00-6.90 (m, 2 H), 6.86-6.75 (m, 2 H), 6.00-5.82 (m, 1 H), 5.34-5.15 (m, 2 H), 5.15 (AB q, J = 6.9 Hz, Δυ = 14.6 Hz, 2 H), 4.84 (d, J = 9.3 Hz, 1 H, NH), 4.55 (d, J = 5.3 Hz, 2 H), 4.44-4.31 (m, 1 H), 4.09-3.71 (m, 7 H), 3.77 (s, 3 H), 3.71-3.61 (m, 1 H), 3.26 (br s, 1 H, OH), 2.58-2.44 (m, 1 H), 2.25-2.14 (m, 1 H), 2.16 (dd, J = 14.1, 1.5 Hz, 1 H), 2.07-1.92 (m, 1 H), 1.86 (d, J = 14.1 Hz, 1 H), 1.83-1.78 (m, 1 H), 1.17 (s, 9 H), 0.16 (s, 9 H).

^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 177.8 (s'), 156.1 (s'), 154.6 (s'), 151.1 (s'), 132.6 (d'), 117.6 (t'), 117.4 (d'), 114.5 (s'), 109.0 (s'), 107.0 (s'), 93.9 (t'), 88.3 (s'), 68.8 (s'), 68.4 (t'), 65.6 (t'), 65.2 (t'), 64.4 (t'), 62.5 (t'), 55.5 (q'), 51.8 (d'), 43.5 (d'), 41.7 (t'), 40.4 (t'), 38.6 (d'), 27.0 (q'), 23.5 (s'), -0.26 (q').

exact mass m/z calcd for $C_{26}H_{42}NO_{10}Si$ (M-$CH_3OC_6H_4O$) 524.26794, found

524.26726; exact mass HRFAB (NOBA) *m/z* calcd for $C_{33}H_{49}NO_{10}SiNa$ (M+Na) 670.3023, found 670.3020.

Compound M

FTIR (CH_2Cl_2 cast) 3449, 1729 cm^{-1};

^1H NMR ($CDCl_3$, 400 MHz) δ 7.00-6.90 (m, 2 H), 6.87-6.76 (m, 2 H), 6.00-5.82 (m, 1 H), 5.37-5.15 (m, 2 H), 5.11 (s, 2 H), 4.83 (d, *J* = 8.6 Hz, 1 H, NH), 4.55 (d, *J* = 5.3 Hz, 2 H), 4.46-4.28 (m, 1 H), 4.10-3.69 (m, 7 H), 3.77 (s, 3 H), 3.69-3.57 (m, 1 H), 2.55-2.40 (m, 1 H), 2.11-1.94 (m, 2 H), 1.84 (AB q, *J* = 14.0 Hz, Δυ = 74.6 Hz, 2 H), 1.78-1.57 (m, 1 H), 1.18 (s, 9 H), 0.83 (s, 9 H), 0.18 (s, 3 H), 0.15 (s, 3 H), 0.14 (s, 9 H).

^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 177.9 (s'), 156.2 (s'), 154.6 (s'), 151.5 (s'), 132.8 (d'), 117.7 (t'), 117.5 (d'), 114.6 (d'), 108.9 (s'), 107.2 (s'), 94.1 (t'), 90.6 (s'), 70.7 (s'), 68.9 (t'), 65.7 (t'), 65.2 (t'), 64.5 (t'), 63.2 (t'), 55.6 (q'), 52.1 (d'), 44.2 (d'), 43.2 (t'), 40.0 (d'), 38.7 (t'), 27.2 (q'), 25.8 (q'), 24.1 (s'), 18.2 (s'), -0.37 (q'), -2.6 (q'), -2.8 (q').

exact mass *m/z* calcd for $C_{39}H_{63}NO_{10}Si$ 761.39905, found 761.40023.

Compound N

FTIR (CH_2Cl_2 cast) 3493, 3445, 2168, 1725 cm^{-1};

^1H NMR ($CDCl_3$, 400 MHz) δ 7.00-6.89 (m, 2 H), 6.89-6.75 (m, 2 H), 5.98-5.80 (m, 1 H), 5.37-5.09 (m, 2 H), 5.15 (AB q, *J* = 6.9, Δυ = 11.0 Hz, 2 H), 4.82 (d, *J* = 9.8 Hz, 1 H, NH), 4.66-4.47 (m, 2 H), 4.14-4.04 (m, 1 H), 4.04-3.51 (m, 8 H), 3.77 (s, 3 H), 3.34-3.20 (m, 1 H), 2.40-2.11 (m, 2 H), 2.05 (dd, *J* = 13.9, 1.6 Hz, 1 H), 1.91-1.70 (m, 2 H), 1.78 (d, *J* = 13.9 Hz, 1 H), 0.83 (s, 9 H), 0.19 (s, 3 H), 0.16 (s, 9 H), 0.16 (s, 3 H).

^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 156.5 (s'), 154.8 (s'), 151.0 (s'), 132.8 (d'), 117.7 (t'), 117.6 (d'), 114.7 (d'), 108.9 (s'), 107.5

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(s'), 94.0 (t'), 90.7 (s'), 70.8 (s'), 69.9 (t'), 65.7 (t'), 65.1 (t'), 64.5 (t'), 61.2 (t'), 55.6 (q'), 52.3 (d'), 44.4 (d'), 42.8 (t'), 42.2 (d'), 25.8 (q'), 22.9 (t'), 18.1 (s'), -0.31 (q'), -2.6 (q'), -2.8 (q').

exact mass *m/z* calcd for $C_{33}H_{52}NO_9Si_2$ (M-CH_3) 662.31805, found 662.31612; exact mass HRFAB (NOBA) *m/z* calcd for $C_{34}H_{55}NO_9Si_2Na$ (M+Na) 700.3313, found 300.3319.

Compound 35

FTIR (CH_2Cl_2 cast) 3351, 2165, 1725 cm^{-1};

^1H NMR ($CDCl_3$, 400 MHz) δ 9.80 (br s, 1 H), 7.00-6.88 (m, 2 H), 6.88-6.75 (m, 2 H), 5.97-5.78 (m, 1 H), 5.37-5.16 (m, 2 H), 5.10 (s, 2 H), 4.82 (br s, 1 H), 4.57 (d, *J* = 5.2 Hz, 2 H), 4.28 (t, *J* = 8.1 Hz, 1 H), 4.08-3.83 (m, 4 H), 3.83-3.61 (m, 2 H), 3.76 (s, 3 H), 2.93-2.76 (m, 1 H), 2.34-2.05 (m, 2 H), 2.03 (AB q, *J* = 14.4, Δυ = 57.9 Hz, 2 H), 1.88-1.66 (m, 1 H), 0.83 (s, 9 H), 0.18 (s, 3 H), 0.17 (s, 3 H), 0.16 (s, 9 H).

^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 202.2 (d'), 155.9 (s'), 154.6 (s'), 151.3 (s'), 132.6 (d'), 117.8 (t'), 117.4 (d'), 114.5 (d'), 108.1 (s'), 106.6 (s'), 93.8 (t'), 91.1 (s'), 70.9 (s'), 67.5 (t'), 65.1 (t'), 64.3 (t'), 55.6 (t'), 52.7 (q'), 50.8 (d'), 44.1 (t'), 42.9 (d'), 25.8 (q'), 25.6 (t'), 18.2 (s'), -0.41 (q'), -2.8 (q'), -2.9 (q').

exact mass *m/z* calcd for $C_{34}H_{53}NO_9Si$ 675.32587, found 675.32628.

Compound 36

FTIR (CH_2Cl_2 cast) cm^{-1}; 3435, 3407, 2174, 1696 cm^{-1}

^1H NMR ($CDCl_3$, 400 MHz) δ 7.03-6.80 (m, 2 H), 6.80-6.75 (m, 2 H), 6.00-5.83 (m, 1 H), 5.43-5.15 (m, 2 H), 5.15 (AB q, *J* = 6.7, Δυ = 25.9 Hz, 2 H), 4.99 (d, *J* = 9.3 Hz, 1 H, NH), 4.69 (dd, *J* = 5.0, 4.3 Hz, 1 H), 4.66-4.48 (m, 2 H), 4.20-4.05 (m, 2 H), 4.05-3.78

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(m, 6 H), 3.76 (s, 3 H), 2.50-2.33 (m, 1 H), 2.33-2.18 (m, 1 H), 2.18-2.05 (m, 1 H), 2.02 (dd, J = 13.9, 1.9 Hz, 1 H), 1.98-1.87 (m, 1 H), 1.81 (d, J = 13.9 Hz, 1 H), 0.83 (s, 9 H), 0.19 (s, 3 H), 0.17 (s, 9 H), 0.16 (s, 3 H), 0.15 (s, 9 H).

^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 157.4 (s'), 154.6 (s'), 151.6 (s'), 132.6 (d'), 118.2 (t'), 117.7 (d'), 114.6 (d'), 108.8 (s'), 107.7 (s'), 105.6 (s'), 94.4 (s'), 91.0 (s'), 90.7 (s'), 70.6 (s'), 70.2 (t'), 66.2 (t'), 65.1 (t'), 64.6 (t'), 62.9 (d'), 55.7 (q'), 52.3 (d'), 45.8 (d'), 44.4 (d'), 42.7 (t'), 25.8 (q'), 23.8 (t'), 18.1 (s'), -0.12 (q'), -0.32 (q'), -2.6 (q'), -2.8 (q').

exact mass HRFAB (NOBA) m/z calcd for $C_{39}H_{63}NO_9Si_3Na$ 796.3708, found 796.3695.

C(9) epimer of 36

FTIR (CH_2Cl_2 cast) 3435, 3407, 2174, 1696 cm^{-1};

^1H NMR ($CDCl_3$, 400 MHz) δ 7.03-6.90 (m, 2 H), 6.87-6.76 (m, 2 H), 6.00-5.85 (m, 1 H), 5.40-5.08 (m, 4 H), 4.90 (d, J = 9.9 Hz, 1 H), 4.73-4.45 (m, 3 H), 4.19-3.67 (m, 8 H), 3.76 (s, 3 H), 2.58-2.45 (m, 1 H), 2.42-2.28 (m, 1 H), 2.14 (br s, 1 H, OH), 1.91 (AB q, J = 13.8, Δν = 83.9 Hz, 2 H), 1.90-1.78 (m, 1 H), 0.82 (s, 9 H), 0.18 (s, 3 H), 0.16 (s, 9 H), 0.15 (s, 3 H), 0.13 (s, 9 H);

^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 156.7 (s'), 154.5 (s'), 151.3 (s'), 132.8 (d'), 117.7 (t'), 117.5 (d'), 114.5 (d'), 108.9 (s'), 107.5 (s'), 106.9 (s'), 93.9 (t'), 91.1 (s'), 89.0 (s'), 70.5 (s'), 69.6 (t'), 65.9 (t'), 65.1 (t'), 64.6 (t'), 63.5 (t'), 55.4 (q'), 52.0 (d'), 47.4 (d'), 45.4 (d'), 42.5 (t'), 25.7 (q'), 22.9 (t'), 18.0 (q'), -0.28 (q'), -0.48 (q'), -2.7 (q'), -2.9 (q').

exact mass HRFAB (NOBA) m/z calcd for $C_{39}H_{63}NO_9Si_3Na$ (M+Na) 796.3708, found 796.3716.

Ketone derived by oxidation of C(9) epimer of 36

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FTIR (CH_2Cl_2 cast) 3360, 1739, 1681 cm^{-1};

^1H NMR ($CDCl_3$, 400 MHz) δ 6.98-6.90 (m, 2 H), 6.84-6.75 (m, 2 H), 6.03-5.80 (m, 1 H), 5.48-5.14 (m, 2 H), 5.06 (s, 2 H), 4.73-4.42 (m, 3 H), 4.28 (t, *J* = 11.3 Hz, 1 H), 4.11-3.78 (m, 4 H), 3.76 (s, 3 H), 3.71-3.58 (m, 1 H), 3.58-3.46 (m, 1 H), 3.46-3.32 (m, 1 H), 2.45-2.24 (m, 1 H), 2.08-1.75 (m, 3 H), 0.83 (s, 9 H), 0.23 (s, 9 H), 0.19 (s, 9 H), 0.18 (s, 3 H), 0.16 (s, 3 H).

^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 185.6 (s'), 155.7 (s'), 154.5 (s'), 151.6 (s'), 133.0 (d'), 117.6 (d'), 117.5 (t'), 114.5 (d'), 108.3 (s'), 107.3 (s'), 102.1 (s'), 98.7 (s'), 94.1 (t'), 91.4 (s'), 70.6 (s'), 68.5 (t'), 65.6 (t'), 65.3 (t'), 64.9 (t'), 55.7 (d'), 55.6 (q'), 50.9 (d'), 45.8 (d'), 42.9 (t'), 25.8 (q'), 23.4 (t'), 18.1 (s'), -0.29 (q'), -0.76 (q'), -2.7 (q'), -2.8 (q').

exact mass HRFAB (NOBA) *m/z* calcd for $C_{39}H_{61}NO_9Si_3Na$ (M+Na) 794.3552, found 794.3546.

Compound o

FTIR (CH_2Cl_2 cast) 3386, 1771, 1726 cm^{-1};

^1H NMR ($CDCl_3$, 400 MHz) δ 7.03-6.90 (m, 2 H), 6.85-6.78 (m, 2 H), 5.98-5.78 (m, 1 H), 5.79 (d, *J* = 4.0 Hz, 1 H), 5.37-5.14 (m, 2 H), 5.14 (AB q, *J* = 6.9, Δυ = 39.2 Hz, 2 H), 4.75 (d, *J* = 10.3 Hz, 1 H, NH), 4.58-4.40 (m, 2 H), 4.20-3.85 (m, 5 H), 3.94 (AB q, *J* = 15.6, Δυ = 131.2 Hz, 2 H), 3.85-3.78 (m, 1 H), 3.77 (s, 3 H), 3.63-3.53 (m, 1 H), 2.57-2.43 (m, 1 H), 2.43-2.31 (m, 1 H), 2.15-1.92 (m, 2 H), 2.00 (dd, *J* = 13.8, 1.8 Hz, 1 H), 1.80 (d, *J* = 13.8 Hz, 1 H), 0.85 (s, 9 H), 0.19 (s, 3 H), 0.18 (s, 12 H), 0.15 (s, 9 H).

^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 166.7 (s'), 156.2 (s'), 154.6 (s'), 151.5 (s'), 132.8 (d'), 117.9 (t'), 117.4 (d'), 114.6 (d'), 108.7 (s'), 107.5 (s'), 100.5 (s'), 94.0 (s'), 93.9 (s'), 91.2 (s'), 70.4 (s'), 69.3 (t'), 66.0 (t'), 65.3 (t'), 65.0 (d'), 64.8 (t'),

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55.7 (q'), 51.5 (d'), 44.5 (d'), 43.9 (d'), 42.9 (t'), 41.0 (t'), 25.8 (q'), 23.6 (t'), 18.2 (s'), -0.32 (q'), -2.7 (q'), -2.8 (q').

exact mass HRFAB (NOBA) *m/z* calcd for $C_{41}H_{64}ClNO_{10}Si_3Na$ 872.3424, found 872.3391.

Compound P

FTIR (CH_2Cl_2 cast) 3444, 1771, 1726 cm^{-1};

^1H NMR ($CDCl_3$, 400 MHz) δ 5.96-5.80 (m, 1 H), 5.82 (d, *J* = 3.8 Hz, 1 H), 5.38-5.10 (m, 2 H), 4.77 (d, *J* = 10.3 Hz, 1 H, NH), 4.59-4.35 (m, 2 H), 4.17 (AB q, *J* = 15.3, Δυ = 27.9 Hz, 2 H), 4.11-3.72 (m, 6 H), 3.72-3.60 (m, 1 H), 2.60-2.40 (m, 2 H), 2.16-1.90 (m, 2 H), 1.81 (d, *J* = 13.8 Hz, 1 H), 1.52 (br s, 1 H, OH), 0.88 (s, 9 H), 0.22 (s, 3 H), 0.20 (s, 3 H), 0.17 (s, 9 H), 0.15 (s, 9 H).

^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 166.5 (s'), 156.2 (s'), 132.8 (d'), 117.9 (t'), 108.6 (s'), 107.5 (s'), 100.4 (s'), 94.2 (s'), 91.2 (s'), 70.5 (t'), 65.9 (t'), 65.3 (t'), 65.1 (d'), 64.7 (t'), 63.5 (t'), 51.5 (d'), 44.7 (d'), 44.1 (d'), 42.9 (t'), 41.2 (t'), 27.1 (t'), 25.8 (q'), 18.2 (s'), 0.37 (q'), -2.7 (q'), -2.8 (q').

exact mass *m/z* calcd for $C_{33}H_{56}ClNO_8Si_3$ 713.30023, found 713.29980.

Compound Q

FTIR (CH_2Cl_2 cast) 3441, 1773, 1729 cm^{-1};

^1H NMR ($CDCl_3$, 400 MHz) δ 9.71 (t, *J* = 1.5 Hz, 1 H), 5.98-5.80 (m, 1 H), 5.77 (d, *J* = 4.0 Hz, 1 H), 5.38-5.13 (m, 2 H), 4.77 (d, *J* = 10.2 Hz, 1 H, NH), 4.58-4.36 (m, 2 H), 4.13 (AB q, *J* = 15.6, Δυ = 54.1 Hz, 2 H), 4.17-3.84 (m, 5 H), 3.84-3.73 (m, 1 H), 3.47-3.32 (m, 1 H), 2.91-2.68 (m, 2 H), 2.68-2.54 (m, 1 H), 2.61 (dt, *J* = 12.4, 3.6 Hz, 1 H), 2.08 (dd, *J* = 14.0, 1.6 Hz, 1 H), 1.74 (d, *J* = 14.0 Hz, 1 H), 0.83 (s, 9 H), 0.20 (s, 6 H), 0.19 (s, 9 H), 0.16 (s, 9 H).

^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 201.2 (d'), 166.3 (s'), 156.1 (s'), 132.7 (d'), 118.0 (t'), 107.9 (s'), 107.2 (s'), 99.7 (s'), 94.3 (s'), 91.8 (s'), 70.1 (s'), 66.0 (t'), 65.4 (t'), 64.8 (t'), 64.7 (d'), 51.4 (d'), 43.5 (d'), 43.0 (t'), 42.6 (d'), 41.1 (t'), 38.9 (t'), 25.9 (q'), 18.2 (s'), -0.38 (q'), -2.6 (q'), -2.8 (q').

exact mass *m/z* calcd for $C_{29}H_{45}ClNO_8Si_3$(M-*t*-C_4H_9) 654.2141, found 654.21380; exact mass HRFAB (NOBA) *m/z* calcd for $C_{33}H_{54}ClNO_8Si_3Na$ (M+Na) 734.2744, found 734.2750.

Compound 37

FTIR (CH_2Cl_2 cast) 3344, 1747 cm^{-1};

^1H NMR ($CDCl_3$, 400 MHz) δ 6.00-5.80 (m, 1 H), 5.40-5.19 (m, 3 H), 4.80 (br s, 1 H, NH), 4.58 (d, *J* = 5.5 Hz, 2 H), 4.10-3.80 (m, 5 H), 3.04-2.85 (m, 1 H), 2.85-2.70 (m, 1 H), 2.55 (dd, *J* = 18.9, 10.2 Hz, 1 H), 2.40-2.23 (m, 1 H), 2.04 (AB q, *J* = 13.5, Δυ = 72.4 Hz, 2 H), 0.88 (s, 9 H), 0.20 (s, 6 H), 0.18 (s, 18 H).

^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 169.1 (s'), 156.2 (s'), 132.6 (d'), 117.9 (t'), 107.4 (s'), 106.9 (s'), 101.3 (s'), 69.4 (t'), 69.3 (d'), 66.0 (t'), 65.4 (t'), 64.7 (t'), 50.6 (d'), 42.8 (t'), 40.7 (d'), 40.2 (d'), 28.1 (t'), 25.8 (q'), 18.2 (s'), -0.32 (q'), -0.37 (q'), -2.8 (q'), -2.9 (q').

exact mass *m/z* calcd for $C_{27}H_{42}NO_7Si$ (M-*t*-Bu) 576.22693, found 576.22687; exact mass HRFAB (NOBA) *m/z* calcd for $C_{31}H_{51}NO_7Si_3Na$ (M+Na) 656.2871, found 656.2887.

Compound R

FTIR (CH_2Cl_2 cast) 3440, 1736 cm^{-1};

^1H NMR ($CDCl_3$, 400 MHz, 50°C) δ 6.22 (s, 1 H), 6.00-5.84 (m, 1 H), 5.37-5.14 (m, 3 H), 4.95 (br s, 1 H, NH), 4.60 (d, *J* = 5.6 Hz, 2 H), 4.21-3.80 (m, 5 H), 2.98 (d, *J* = 12.0 Hz, 1 H), 2.10 (AB q, *J* = 13.6, Δυ = 258.5 Hz, 2 H), 0.94 (s, 9 H), 0.25 (s, 3 H), 0.24

(s, 3 H), 0.20 (s, 9 H), 0.14 (s, 9 H).

^{13}C NMR ($CDCl_3$, 100.6 MHz) major δ 162.4 (s'), 158.0 (s'), 155.9 (s'), 132.5 (d'), 118.2 (t'), 112.5 (d'), 106.9 (s'), 103.7 (s'), 101.1 (s'), 93.5 (s'), 91.3 (s'), 69.1 (s'), 66.9 (t'), 66.2 (t'), 65.6 (t'), 65.0 (t'), 56.7 (d'), 49.3 (t'), 42.7 (d'), 25.8 (q'), 18.3 (s'), -0.32 (q'), -0.42 (q'), -2.7 (q'), -3.0 (q').

exact mass *m/z* calcd for $C_{31}H_{49}NO_7Si_3$ 631.28168, found 631.28020.

Compound S

X-Ray structure determined.

FTIR (CH_2Cl_2 cast) 3393, 3325, 1731 cm^{-1};

^1H NMR ($CDCl_3$, 400 MHz) δ 6.15 (s, 1 H), 5.80 (s, 1 H), 4.18-3.92 (m, 4 H), 2.81 (AB q, J = 12.2, Δυ = 13.3 Hz, 2 H), 2.04 (AB q, J = 13.3, Δυ = 316.4 Hz, 2 H), 1.30 (br s, 2 H, NH_2), 0.92 (s, 9 H), 0.24 (s, 3 H), 0.22 (s, 3 H), 0.18 (s, 9 H), 0.13 (s, 9 H).

^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 163.0 (s'), 160.3 (s'), 111.3 (d'), 107.6 (s'), 103.8 (s'), 102.0 (s'), 93.2 (s'), 90.7 (s'), 69.4 (s'), 66.9 (d'), 65.5 (t'), 65.2 (t'), 58.2 (d'), 49.7 (t'), 43.8 (d'), 25.8 (q'), 18.3 (s'), -0.26 (q'), -0.39 (q'), -2.6 (q'), -3.0 (q').

exact mass *m/z* calcd for $C_{27}H_{45}NO_5Si_3$ 547.26056, found 547.26030.

Compound V

FTIR (CH_2Cl_2 cast) cm^{-1}; 3401, 1731, 1655 cm^{-1}

^1H NMR ($CDCl_3$, 300 MHz) δ (two isomers in 8:1 ratio) 6.30 (s) and 6.16 (s), [1 H], 6.21 (br s) and 6.14 (br s) [1 H], 5.81 (br s) and 5.24 (br s) [1 H], 4.20-3.91 (m, 4 H), 3.74 (s) and 3.68 (s) [3 H], 2.33 (d, J = 13.3 Hz, 1 H), 2.16 (d, J = 13.3 Hz) and 2.06 (d, J = 13.3 Hz) [1 H], 0.88 (s, 9 H), 0.30-0.09 (m, 24 H).