PHORBOXAZOLE SYNTHETIC STUDIES. 2. CONSTRUCTION OF A C(20-28) SUBTARGET; A FURTHER EXTENSION OF THE PETASIS-FERRIER REARRANGEMENT.

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Experimental Section

Materials and Methods. All reactions were carried out under argon with dry, freshly distilled solvents, vacuum-flamed glassware, and magnetic stirring, unless otherwise stated. Diethyl ether (Et_2O) and tetrahydrofuran (THF) were distilled from sodium/benzophenone; benzene and toluene were distilled from sodium, and dichloromethane (CH_2Cl_2) from calcium hydride. Triethylamine and pyridine were distilled from calcium hydride and stored over KOH. n-Butyllithium was standardized by titration with diphenylacetic acid.

All reactions were monitored by thin layer chromatography (TLC) using 0.25-mm E. Merck precoated silica gel plates. Flash chromatography was performed with the indicated solvents and E. Merck silica gel 60 (particle size 0.040-0.063 mm). Yields refer to chromatographically and spectroscopically pure compounds, except as otherwise indicated.

All melting points were obtained on a Thomas-Hoover apparatus and are corrected. Infrared spectra were recorded on a Perkin-Elmer Model 283B spectrophotometer. Proton and carbon NMR spectra were recorded on a Bruker AM-500 spectrometer. Chemical shifts are reported in δ values relative to tetramethylsilane. Optical rotations were measured with a Perkin-Elmer Model 241 polarimeter in the solvent indicated. High resolution mass spectra were obtained at the University of Pennsylvania Mass Spectrometry Center on either a VG Micromass 70/70H or VG ZAB-E spectrometer. Microanalyses were performed by the University of Pennsylvania elemental analysis center.

(+)-**6:** Obtained as a clear oil: $[\alpha]_D^{20}$ = +20.1° (*c* 1.86, $CHCl_3$); IR ($CHCl_3$) 3310 (s), 3100 (v br), 3020 (s), 3010 (s), 2890 (m), 2400 (w), 2110 (w), 1715 (s), 1460 (m), 1340 (m), 1315 (m), 1295 (m), 1205 (s), 1135 (s), 1025 (m) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 4.53 (dd, *J* = 7.7, 2.2 Hz, 1 H), 2.77 (app quint, *J* = 7.5 Hz, 1 H), 2.51 (d, *J* = 2.2 Hz, 1 H), 1.31 (d, *J* = 7.2 Hz, 3 H) ; ^{13}C NMR (125 MHz, $CDCl_3$) δ 179.7, 81.9, 74.6, 63.9, 46.1, 13.6; high resolution mass spectrum (CI) *m/z* 146.0821 [$(M+NH_4)^+$; calcd for $C_6H_{12}O_3N$: 146.0817].

(-)-**13:** Obtained as a clear oil: $[\alpha]_D^{20}$ = -4.9° (*c* 1.68, $CHCl_3$); IR ($CHCl_3$) 2965 (s), 2930 (s), 2880 (m), 2855 (s), 1735 (s), 1590 (w), 1460 (m), 1425 (m), 1380 (m), 1350 (m), 1210 (s), 1105 (s), 975 (s), 690 (m) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.63-7.58 (m, 4 H), 7.41-7.31 (m, 6 H), 5.54 (t, *J* = 5.5 Hz, 1 H), 3.85 (t, *J* = 6.0 Hz, 2 H), 3.42 (ddd, *J* = 10.9, 8.3, 3.0 Hz, 1 H), 2.43 (dq, *J* = 10.3, 7.3 Hz,1 H), 2.12 - 1.95 (m, 2 H), 1.79-1.73 (m, 1 H), 1.52-1.47 (m, 1 H), 1.24 (d, *J* = 7.3 Hz, 3 H), 1.04 (s, 9 H), 0.99 (t, *J* = 7.4 Hz, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.5, 135.5, 133.6, 129.7, 127.7, 101.0, 81.8, 58.7, 40.9, 38.0, 26.8, 26.6, 19.2, 12.7, 9.3; high resolution mass spectrum (CI) *m/z* 425.2131 [$(M-H)^+$; calcd for $C_{25}H_{33}O_4Si$: 425.2148].

(-)-**11:** Obtained as a clear oil: $[\alpha]_D^{20}$ = -52.6° (*c* 0.39, C_6H_6); IR ($CHCl_3$) 3070 (w), 2965 (s), 2940 (s), 2880 (s), 2860 (s), 1685 (w), 1460 (m), 1425 (m), 1190 (m), 1105 (s), 990 (m), 700 (s) cm^{-1}; ^1H NMR (500 MHz, C_6D_6) δ 7.77-7.72 (m, 4 H), 7.22-7.18 (m, 6 H), 4.96 (t, *J* = 5.2 Hz, 1 H), 4.64 (dq, *J*= 6.8, 1.8 Hz, 1 H), 3.99-3.93 (m, 2H), 3.04 (ddd, *J* = 10.6, 8.1, 2.8 Hz, 1 H), 2.22-2.17 (m, 3 H), 1.70 (dd, *J*= 6.7, 2.0 Hz, 3 H), 1.58-1.52 (m, 1 H), 1.39-1.32 (m, 1 H), 1.17 (s, 9 H), 0.93 (t, *J*= 7.4 Hz, 3 H), 0.70, (d, *J* = 6.7 Hz, 3 H); ^{13}C NMR (125 MHz, C_6D_6) δ 155.3, 135.9, 134.3, 129.9, 128.2, 101.7, 100.0, 83.2, 60.0, 39.0, 37.8, 27.1, 26.3, 19.4, 12.1, 9.9, 9.4; high resolution mass spectrum (CI) *m/z* 437.2513 [$(M-H)^+$; calcd for $C_{27}H_{37}O_3Si$: 437.2512].

(+)-**12:** A solution of (-)-**11** (57 mg, 0.130 mmol) in CH_2Cl_2 (2.6 mL) was cooled to -78 °C and treated with Me_2AlCl (1.0 M in hexane, 130 μL, 0.130 mmol). The resultant solution was stirred for 10 min, placed in a -10 °C bath, stirred for 1 h, treated with triethylamine (1 mL) and saturated aqueous $NaHCO_3$ (10 mL), diluting with CH_2Cl_2. The aqueous layer was extracted with CH_2Cl_2 (2 x 10 mL), and the organic solution was washed with brine (20 mL), dried over $MgSO_4$, filtered, and concentrated in vacuo. Flash chromatography (5 to 10% ethyl

acetate/hexanes) provided (+)-**12** (32.8 mg, 58% yield) as a clear oil: $[\alpha]_D^{20}$ = +7.7° (*c* 0.75, $CHCl_3$); IR ($CHCl_3$) 3070 (w), 2965 (s), 2935 (s), 2880 (s), 2855 (s), 1705 (s), 14555 (m), 1430 (w), 1380 (w), 1340 (w), 1205 (w), 1100 (s), 690 (s) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.67-7.61 (m, 4 H), 7.41-7.33 (m, 6 H), 3.90 (ddd, *J* = 9.0, 9.0, 5.2 Hz, 1 H), 3.89 (ddd, *J* = 10.2, 6.4, 4.1 Hz, 1 H), 3.39 (ddd, *J* = 10.5, 9.4, 2.2 Hz, 1 H), 3.06 (ddd, *J* = 10.6, 8.3, 2.7 Hz, 1 H), 2.34-2.28 (m, 2 H), 2.00-1.92 (m, 1 H), 1.75-1.68 (m, 2 H), 1.50-1.42 (m, 1 H), 1.02 (s, 9 H), 0.97 (d, *J* = 8.7 Hz, 3 H), 0.95 (d, *J* = 8.7 Hz, 3 H), 0.92 (t, *J* = 7.4 Hz, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 210.6, 135.5, 134.0, 129.6, 127.6, 83.6, 79.5, 60.1, 50.0, 49.7, 37.2, 27.0, 26.9, 19.2, 9.5, 9.4; high resolution mass spectrum (CI) *m/z* 439.2671 [$(M+H)^+$; calcd for $C_{27}H_{39}O_3Si$: 439.2668].(+)-**18:** Obtained as a clear oil: $[\alpha]_D^{20}$ = +6.5° (*c* 0.49, $CHCl_3$); IR ($CHCl_3$) 3500 (br), 3015 (m), 2960 (s), 2945 (s), 2865 (s), 1750 (m), 1710 (s), 1465 (m), 1430 (m), 1390 (m), 1110 (s), 1075 (s), 820 (m), 700 (m) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.65-7.60 (m, 4 H), 7.44-7.35 (m, 6 H), 4.52 (br, 1 H), 4.18 (ddd, *J* = 10.1, 4.6, 2.3 Hz, 1 H), 3.95-3.85 (m, 2 H), 2.68 (dq, *J* = 7.2, 4.6 Hz, 1 H), 1.80-1.72 (m, 1 H), 1.64-1.60 (m, 1 H), 1.18 (d, *J* = 7.2 Hz, 3 H), 1.04 (s, 9 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 177.1, 135.5, 132.6, 130.0, 127.7, 72.8, 63.5, 44.3, 34.2, 26.7, 19.0, 11.5; high resolution mass spectrum (ESI) *m/z* 409.1796 [$(M+Na)^+$; calcd for $C_{22}H_{30}O_4SiNa$: 409.1811].

(+)-**20:** A solution of hydroxyacid (+)-**18** (2.77 g, 7.12 mmol) in CH_2Cl_2 (7 mL) was cooled to 0°C, and hexamethyldisilazane (1.78 mL, 7.89 mmol) was added. The resultant mixture was stirred overnight at room temperature, concentrated in vacuo, and used without further purification.

To the crude bis-TMS compound was added 2,6 di-*t*-butyl-4-methylpyridine (146 mg, 0.712 mmol) and a solution of aldehyde **19** in CH_2Cl_2 (60 mL) via cannula. The resulting solution was cooled to -78 °C, and trimethylsilyltriflate (440 μL, 2.90 mmol) was added. The resultant solution was stirred at -78 °C for 6 h, and treated with pyridine (1 mL), then concentrated in vacuo. Flash chromatography on 10:1 silica:H_2O (10% ethyl acetate/hexanes) provided (+)-**20** (2.74 g, 66% yield) as a clear oil: $[\alpha]_D^{20}$ = +19° (*c* 0.50, $CHCl_3$); IR ($CHCl_3$) 3085 (w), 2945 (s), 2890 (m), 2870 (s), 1745 (s), 1465 (m), 1430 (m), 1380 (m), 1350 (m), 1340 (m), 1220 (s), 1115 (s), 980 (s), 700 (m) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.64-7.59 (m, 4 H), 7.40-7.33 (m, 6 H), 5.76 (s, 1 H), 4.20 (ddd, *J* = 8.7, 3.8, 3.8 Hz, 1 H), 3.85 (ddd, *J* = 10.1, 10.1, 4.1 Hz, 1 H), 3.77 (ddd, *J* = 10.0,

5.0, 5.0 Hz, 1 H), 2.65 (dq, *J* = 7.2, 3.9 Hz, 1 H), 1.83-1.78 (m, 1 H), 1.73-1.68 (m, 1 H), 1.25 (d, *J* = 7.4 Hz, 3 H), 1.08 (s, 21 H), 1.04 (s, 9 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.0, 135.5, 133.5, 129.8, 127.8, 99.2, 91.6, 89.4, 74.1, 59.4, 39.6, 33.9, 26.9, 19.2, 18.5, 12.0, 11.0; high resolution mass spectrum (CI) *m/z* 579.3297 [$(M+H)^+$; calcd for $C_{34}H_{51}O_4Si_2$: 579.3326].

C(26) Epimer: $[\alpha]_D^{20}$ = -22.9° (*c* 0.59, $CHCl_3$); IR ($CHCl_3$) 2945 (s), 2890 (m), 2865 (s), 1750 (s), 1665 (w), 1460 (m), 1200 (s), 1110 (s), 990 (s), 875 (m), 690 (s), 660 (s) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66-7.60 (m, 4 H), 7.42-7.35 (m, 6 H), 6.01 (s, 1 H), 4.64 (ddd, *J* = 8.9, 4.4, 4.4 Hz,1 H), 3.76-3.69 (m, 2 H), 2.90 (dq, *J* = 7.2, 4.6 Hz, 1 H), 1.85-1.77 (m, 1 H), 1.77-1.71 (m, 1 H), 1.21 (d, *J* = 7.4, 3 H), 1.04 (s, 9 H), 1.01 (s, 21 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.4, 135.5, 133.5, 129.7, 127.7, 100.0, 90.4, 89.7, 70.4, 60.5, 39.8, 33.8, 26.9, 19.1, 18.5, 11.9, 10.9; high resolution mass spectrum (CI) *m/z* 579.3309 [$(M+H)^+$; calcd for $C_{34}H_{51}O_4Si_2$: 579.3326].

(+)-**25:** Obtained as a clear oil: $[\alpha]_D^{20}$ = +5.5° (*c* 0.58, $CHCl_3$); IR ($CHCl_3$) 2940 (s), 2860 (s), 1755 (s), 1745 (s), 1460 (m), 1430 (w), 1390 (m), 1370 (m), 1350 (s), 1210 (s), 1160 (s), 1100 (s), 1050 (s), 990 (s), 670 (m) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65-7.60 (m, 4 H), 7.40-7.31 (m, 6 H), 5.87 (dd, *J* = 2.5, 1.4 Hz, 1 H), 5.31 (d, *J* = 1.4, 1 H), 4.02-3.98 (m, 1H), 3.81 (ddd, *J* = 14.5, 4.5, 1.1 Hz, 1 H), 3.72 (ddd, *J* = 10.4, 5.1, 5.1 Hz, 1 H), 2.13 (d, *J* = 0.8 Hz, 3 H), 1.94-1.86 (m, 1 H), 1.70-1.64 (m, 2 H), 1.07 (s, 21 H),1.04 (s, 9 H), 1.00 (dd, *J* = 6.8, 1.2 Hz, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.9, 135.5, 133.7, 129.6, 127.7, 100.7, 95.3, 90.1, 86.8, 75.5, 59.7, 35.6, 34.9, 26.9, 21.0, 19.2, 18.5, 11.1, 5.2; high resolution mass spectrum (ESI) *m/z* 645.3387 [$(M+Na)^+$; calcd for $C_{36}H_{54}O_5Si_2Na$: 645.3408]. Anal. Calcd for $C_{36}H_{54}O_5Si_2$, C, 69.41; H, 8.74. Found: C, 69.14; H, 8.77.

(+)-**26:** Obtained as a clear oil: $[\alpha]_D^{20}$ = +68° (*c* 0.54, $CHCl_3$); IR ($CHCl_3$) 2960 (s), 2880 (s), 1460 (m), 1425 (m), 1355 (m), 1305 (m), 1205 (s), 1130 (s), 1105 (s), 1010 (m), 760 (br, s), 660 (s), 610 (m) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93-7.87 (d, *J* = 8.2 Hz, 2 H), 7.69-7.60 (m, 5 H), 7.54 (t, *J* = 7.8 Hz, 2 H), 7.41-7.37 (m, 6H), 6.41 (s, 1 H), 4.79-4.72 (m, 1 H), 4.50 (s, 1H), 3.82-3.73 (m, 2 H), 2.66 (dq, *J* = 7.3, 2.7 Hz, 1 H), 1.86-1.82 (m, 1 H), 1.73-1.69 (m, 1 H), 1.21 (d, *J* = 7.1 Hz, 3 H), 1.07 (s, 9 H) 1.06 (s, 21 H); ^{13}C NMR (125 MHz,

$CDCl_3$) δ 137.3, 135.6, 133.9, 133.6, 129.6, 129.0, 127.7, 127.6, 101.1, 93.7, 88.2, 87.8, 73.3, 59.7, 35.2, 28.8, 26.9, 19.2, 18.5, 13.1, 11.0; high resolution mass spectrum (ESI) *m/z* 727.3305 [$(M+Na)^+$; calcd for $C_{40}H_{56}O_5SSi_2Na$: 727.3285].

(+)-**15:** A deoxygenated solution of sulfone (+)-**26** (347 mg, 0.492 mmol) in THF (4 mL) was cooled to -78 °C, was treated with nBuLi (1.5 M in hexane, 361 μL, 0.541 mmol), and the resultant solution was stirred for 45 minutes. In another flask, a deoxygenated solution of 1,1 chloroiodoethane (365 μL, 3.93 mmol) in THF (1 mL) was treated with *i*PrMgCl (1.9 M in hexane, 2.33 μL, 4.43 mmol) over 40 min. This solution was added via a cannula to the lithiated sulfone solution, stirred at -78 °C for 70 min, and warmed to -10 °C over 30 min. A saturated aqueous $NaHCO_3$ solution (50 mL) and ether (50 mL) were added. The aqueous layer was extracted with ether (3 x 20 mL), and the organic solution was washed with brine (30 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo. Flash chromatography (basic Al_2O_3 with 10% H_2O, 0 to 30% pentane/ether) provided (+) **15** (2.76 g, 95% yield) as a clear oil: *Z* Isomer: $[\alpha]_D^{20}$ = +39.8 ° (*c* 0.48, C_6H_6); IR ($CHCl_3$) 2930 (s), 2865 (s), 1690 (w), 1455 (m), 1425 (m), 1360 (m), 1350 (m), 1330 (m), 1190 (m), 1110 (s), 995 (s), 880 (m), 820 (m), 735 (m), 735 (m), 700 (m) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.76- 7.70 (m, 4 H), 7.28 - 7.21 (m, 6 H), 5.36 (s, 1 H), 4.46 (q, *J* = 6.7 Hz, 1 H), 3.92 (ddd, *J* = 8.7, 4.3, 2.7 Hz, 1 H), 3.79 (ddd, *J* = 13.6, 8.5, 5.0 Hz, 1 H), 3.64 (ddd, *J* = 10.6, 5.6, 5.2 Hz, 1 H), 1.82 (dq, *J* = 7.0, 2.7 Hz, 1 H) 1.79 - 1.73 (m, 1 H), 1.61 (d, *J* = 6.7 Hz, 3 H), 1.52 - 1.45 (m, 1 H), 1.12 (s, 9 H), 1.11 - 1.09 (m, 21 H), 1.07 (d, *J* = 7.0 Hz, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.9, 134.9, 133.0, 129.0, 127.1, 102.8, 102.2, 91.5, 85.5, 75.9, 59.3, 36.9, 34.4, 26.1, 18.4, 17.7, 12.6, 10.4, 8.7; high resolution mass spectrum (ESI) *m/z* 591.3669 [$(M+H)^+$; calcd for $C_{36}H_{55}O_3Si_2$: 591.3690].

E Isomer: $[\alpha]_D^{20}$ = +48.9 ° (*c* 0.54, C_6H_6); IR ($CHCl_3$) 2940 (s), 2860 (s), 1685 (w), 1455 (m), 1425 (m), 1360 (m), 1345 (m), 1190 (m), 1110 (s), 1000 (m), 880 (m), 815 (m), 730 (m), 690 (m) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.76- 7.72 (m, 4 H), 7.29 - 7.23 (m, 6 H), 5.38 (s, 1 H), 5.11 (q, *J* = 7.1 Hz, 1 H), 3.87 (ddd, *J* = 8.3, 3.9, 2.6 Hz, 1 H), 3.79 (ddd, *J* = 15.0, 4.9, 4.9 Hz, 1 H), 3.68 (ddd, *J* = 10.6, 5.6, 5.0 Hz, 1 H), 2.28 (dq, *J* = 7.0, 2.6 Hz, 1 H) 1.72 - 1.63 (m, 1 H), 1.53 - 1.48 (m, 1 H), 1.28 (d, *J* = 7.1 Hz, 3 H), 1.14 (s, 9 H), 1.11 - 1.09 (m, 21 H), 1.08 (d, *J* = 7.0 Hz, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.1, 134.9, 133.1, 129.0, 127.1, 102.7,

102.2, 92.0, 85.4, 75.3, 59.5, 34.4, 31.5, 26.1, 18.4, 17.7, 11.1, 10.4, 9.1; high resolution mass spectrum (CI) *m/z* 591.3669 [$(M+H)^+$; calcd for $C_{36}H_{55}O_3Si_2$: 591.3690].

(+)-**16:** A solution of the 1:1 mixture of *E* and *Z* enol ethers **15** (274 mg, 0.463 mmol) in CH_2Cl_2 (10 mL) was cooled to -78 °C and treated with Me_2AlCl (1.0M in hexane, 500 μL, 0.500 mmol). The resultant solution was stirred for 10 min, placed in a water bath, stirred for 3 min, and treated with triethylamine (1 mL) and saturated aqueous $NaHCO_3$ (20 mL), diluting with CH_2Cl_2. The aqueous layer was extracted with CH_2Cl_2 (3 x 20), and the organic solution was washed with brine (50 mL), dried over $MgSO_4$, filtered, and concentrated in vacuo. Flash chromatography (5% ethyl acetate/hexanes) provided (+)-**16** (249 mg, 91% yield) as a clear oil: $[\alpha]_D^{20}$ = +30° (*c* 0.76, $CHCl_3$); IR ($CHCl_3$) 3080 (w), 2970 (s), 2955 (s), 2900 (m), 2875 (s), 2190 (w), 1715 (s), 1465 (m), 1440 (m), 1390 (m), 1345 (m), 1115 (s), 1095 (s), 1085 (s), 1065 (s), 700 (s) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.66-7.60 (m, 4 H), 7.42-7.32 (m, 6 H), 3.85 (d, *J* = 10.8 Hz, 1H), 3.85-3.80 (m, 2 H), 3.77-3.72 (m, 1 H), 2.70 (dq, *J* = 10.8, 6.7 Hz, 1 H), 2.38 (dq, *J* = 7.2, 2.4 Hz, 1 H), 1.94-1.88 (m, 1 H), 1.65-1.59 (m, 1 H), 1.13 (d, *J* = 7.2 Hz, 3 H), 1.11 (d, *J* = 6.7 Hz, 3 H), 1.08 (s, 21 H) 1.02 (s, 9 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 211.0, 135.5, 133.7, 129.6, 127.7, 104.7, 87.4, 75.9, 74.2, 60.1, 49.3, 46.6, 34.7, 26.9, 19.2, 18.6, 11.2, 11.1, 9.7; high resolution mass spectrum (CI) *m/z* 591.3677 [$(M+H)^+$; calcd for $C_{36}H_{55}O_3Si_2$: 591.3690].

(+)-**29:** Obtained as a clear oil: $[\alpha]_D^{20}$ = +46° (*c* 0.86, $CHCl_3$); IR ($CHCl_3$) 2975 (s), 2885 (s), 1720 (s), 1465 (m), 1390 (m), 1315 (m), 1285 (s), 1115 (s), 1100 (s), 1065 (m), 1030 (m), 975 (m), 820 (m), 700 (s); ^1H NMR (500 MHz, $CDCl_3$) δ 8.06 (dd, *J* = 8.2, 1.2 Hz, 2 H), 7.66-7.62 (m, 4 H), 7.58 (t, *J* = 5.8 Hz, 1 H), 7.45 (t, *J* = 7.9 Hz, 2 H), 7.40-7.32 (m, 6H), 4.89 (dd, *J* =11.1, 4.9 Hz, 1 H), 3.85-3.79 (m, 1 H), 3.81 (d, *J* = 10.4 Hz, 1 H), 3.79-3.72 (m, 2 H), 2.19-2.12 (m, 1 H), 2.10 (dq, *J* = 10.8, 6.5 Hz, 1 H), 1.88 (dq, *J* = 8.9, 5.0 Hz, 1 H), 1.68-1.61 (m, 1 H), 1.08 (s, 21 H), 1.07-1.03 (m, 12 H), 0.96 (d, *J* = 7.0 Hz, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.8, 135.6, 133.9, 133.0, 130.4, 129.6, 128.4, 1277.7, 105.2, 86.2, 78.7, 75.1, 73.5, 60.4, 36.4, 36.1, 35.5, 26.9, 19.3, 18.6, 13.9, 11.2, 6.6; high resolution mass spectrum (CI) *m/z* 697.4101 [$(M+H)^+$; calcd for $C_{43}H_{61}O_4Si_2$: 697.4108].

(+)-**4:** Obtained as a clear oil: $[\alpha]_D^{20}$ = +66.7° (*c* 0.57, $CHCl_3$); IR ($CHCl_3$) 3300 (m), 2980 (m), 2930 (m), 2930 (m), 2815 (m), 1725 (m), 1715 (m), 1600 (m), 1460 (m), 1450 (m), 1390 (m), 1380 (m), 1310 (m), 1275 (s), 1110 (s), 1090 (s), 1070 (m), 1045 (m), 1020 (m), 975 (m), 635 (m) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 9.78 (t, *J* = 1.5 Hz, 1 H), 8.04 (dd, *J* = 7.1, 1.4 Hz, 2 H), 7.57 (t, *J* = 7.5 Hz, 1 H), 7.45 (t, *J* = 7.6 Hz, 2 H), 4.95 (dd, *J* = 11.1, 4.8 Hz, 1 H), 4.15 (ddd, *J* = 8.6, 3.7, 1.9 Hz, 1 H), 3.94 (dd, *J* = 10.6, 2.2 Hz, 1 H), 2.81 (ddd, *J* = 16.8, 9.0, 1.9 Hz, 1 H), 2.51 (d, *J* = 2.2 Hz, 1 H), 2.39 (ddd, *J* = 16.8, 4.1, 1.9 Hz, 1 H), 2.24 (ddq, *J* = 7.1, 4.8, 1.9 Hz, 1H), 2.19 (ddq, *J* = 11.1, 11.1, 6.7 Hz, 1H), 1.05 (d, *J* = 6.6 Hz, 3 H), 1.02 (d, *J* = 7.0 Hz, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.7, 165.7, 133.2, 130.0, 129.6, 128.5, 80.9, 77.6, 74.0, 73.6, 72.9, 46.3, 35.8, 35.8, 13.5, 6.6; high resolution mass spectrum (CI) *m/z* 301.1446 [$(M+H)^+$; calcd for $C_{18}H_{21}O_4$: 301.1440].