Supporting Information

for

Synthesis of Tetrahydrofurans by a Tandem Hydrogen Atom Abstraction/Radical Nucleophilic Displacement Sequence

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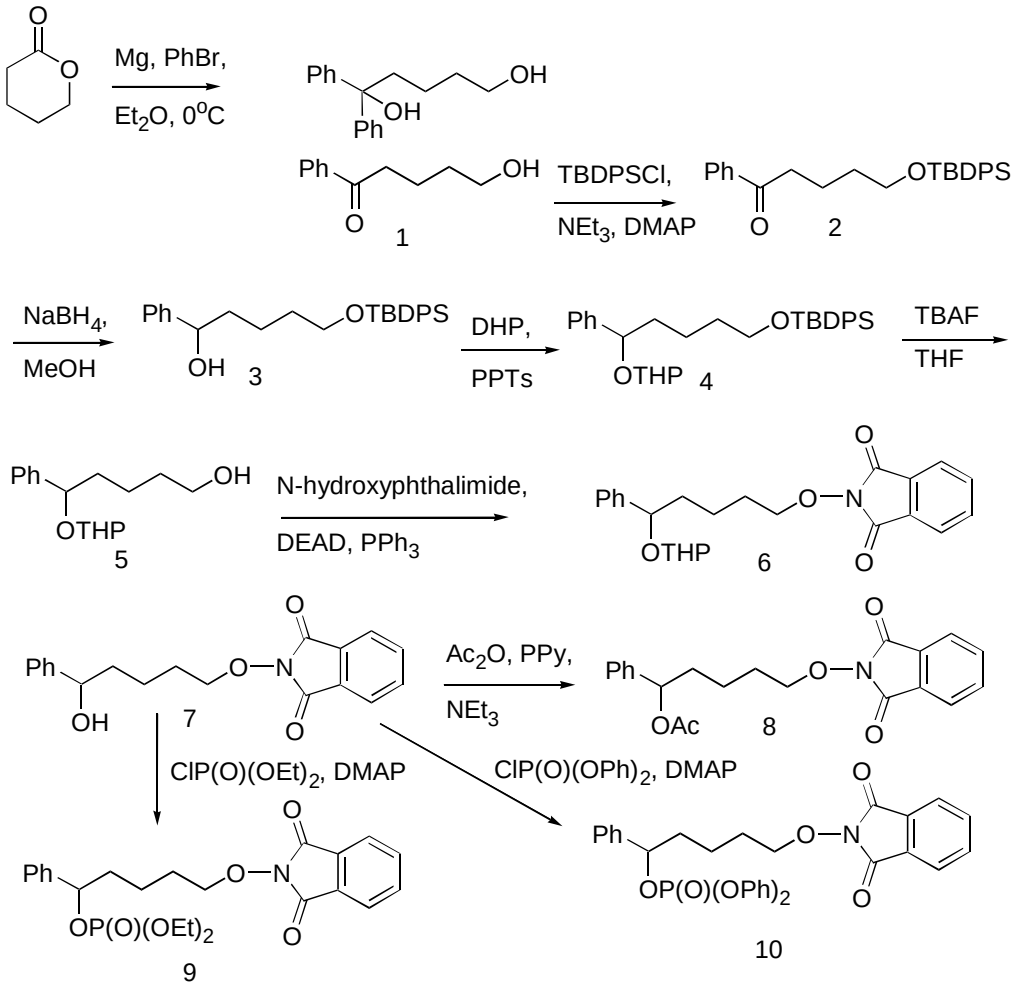
Preparation of Radical Precursors



2. TBDPSCl (1.75 ml, 6.67 mmol) in CH_2Cl_2 (5.0 mL) was added to a solution of **1**[1] (1.08 g, 6.07 mmol), DMAP (0.06 g, 0.486 mmol) and NEt_3 (0.97 mL, 6.98 mmol) in CH_2Cl_2 (15 mL) at room temperature and the resulting reaction mixture was stirred overnight at room temperature before CH_2Cl_2 (50 mL) was added. The CH_2Cl_2 layer was washed with saturated NH_4Cl solution (40 mL), water (20 mL) and brine (20 mL), then

dried (Na_2SO_4) and concentrated to dryness. Column chromatography on silica gel (Hexane/EtOAc 10:1) gave **2** (2.02 g, 80%) as an oil. ^{1}H NMR δ 7.94 (d, 2 H), 7.68 (dd, 4 H), 7.47-7.37 (m, 9 H), 3.72 (t, *J* = 6.2 Hz, 2 H), 2.96 (t, *J* = 7.5 Hz, 2 H), 1.86 (m, 2 H), 1.66 (m, 2 h), 1.06 (s, 9 H); ^{13}C NMR δ 200.5, 137.2, 135.8, 134.2, 133.1, 129.8, 128.7, 128.2, 127.8, 63.7, 38.5, 32.2, 27.1, 20.9, 19.4; Anal. Calcd for $C_{27}H_{32}O_2Si$: C, 77.84, H, 7.74. Found: C, 77.57; H, 7.82.

3. $NaBH_4$ (29 mg, 0.75 mmol) was added at room temperature to a solution of **2** (0.208 g, 0.5 mmol) in methanol (2.5 mL) and the resulting reaction mixture was stirred for 30 min before saturated NH_4Cl solution (10 mL) was added. The resulting mixture was extracted with EtOAc (3 x 15 mL) and the combined extracts were washed with water (10 mL) and brine (10 mL), then dried (Na_2SO_4) and concentrated to dryness. Column chromatography on silica gel (Hexane/EtOAc 5:1) gave **3** (0.195 g, 94%) as a colorless oil. ^{1}H NMR δ 7.72 (m, 4 H), 7.49-7.31 (m, 11 H), 4.66 (t, *J* = 6.7 Hz, 2 H), 3.70 (t, *J* = 6.2 Hz, 2 H), 2.03 (br. s, 1 H), 1.79 (m, 2 H), 1.64 (m, 2 H), 1.44 (m, 2 H), 1.10 (s, 9 H); ^{13}C NMR δ 145.0, 135.7, 134.2, 129.7, 128.6, 127.8, 127.6, 126.1, 74.7, 63.9, 38.9, 32.5, 27.0, 22.2, 19.4; Anal. Calcd for $C_{27}H_{34}O_2Si.1/4H_2O$: C, 76.64; H, 8.22. Found: C, 76.75; H, 8.25.

4. PPTs (0.11 g, 40 mol%, 0.44 mmol) was added at room temperature to a solution of **3** (0.459 g, 1.10 mmol) and dihydropyran (0.20 mL, 2.20 mmol) in CH_2Cl_2 (10 mL). The resulting reaction mixture was stirred at room temperature overnight before it was diluted with EtOAc (50 mL). The organic layer was washed subsequently with saturated $NaHCO_3$ solution (10 mL), water (10 mL) and brine (10 ml), then dried (Na_2SO_4) and concentrated to dryness. Column chromatography on silica gel (Hexane/EtOAc 5/1) gave **4** (0.528 g, 96%) as a colorless oil. ^{1}H NMR δ 7.70 (m, 4 H), 7.46-7.30 (m, 11 H), 4.88 (t, *J* = 3.3 Hz), 4.47 (t, *J* = 3.4 Hz) (1 H), 4.73 (dd, *J* = 7.8, 5.4 Hz), 4.61 (t, *J* = 6.4 Hz) (1 H), 4.00 (m), 3.58 (m), 3.34 (m) (2 H), 3.70 (t, *J* = 6.1 Hz), 3.68 (t, *J* = 6.4 Hz) (2 H), 1.90 (m, 2 H), 1.76 (m, 2 H), 1.67-1.44 (m, 8 H), 1.16 (s, 9 H); ^{13}C NMR δ 143.8, 142.8, 135.7, 134.2, 129.7, 128.5, 128.2, 127.8, 127.1 (d), 126.6, 98.2, 95.2, 79.1, 77.2, 64.0,

63.9, 62.4, 62.0, 38.3, 37.2, 32.7, 30.9, 27.0, 25.8, 25.6, 22.7, 22.0, 19.6, 19.4; Anal. Calcd for $C_{32}H_{42}O_3Si$: C, 76.45; H, 8.42. Found: C, 76.77; H, 8.59.

5. TBAF (2.024 mL, 2.024 mmol) was added dropwise at room temperature to a solution of **4** (0.508 g, 1.012 mmol) in THF (12 mL). The resulting reaction mixture was stirred at room temperature for 2 h before it was diluted with EtOAc (50 mL). The organic layer was washed subsequently with saturated NH_4Cl solution (10 mL), water (10 mL) and brine (10 mL), then dried (Na_2SO_4) and concentrated to dryness. Column chromatography on silica gel (Hexane/EtOAc 1/1) gave **5** (0.261 g, 98%) as a colorless oil. ^{1}H NMR δ 7.36-7.21 (, 5 H), 4.82 (t, *J* = 5.2 Hz), 4.38 (t, *J* = 4.2 Hz), (1 H), 4.67 (dd, *J* = 7.8, 5.7 Hz), 4.55 (t, *J* = 6.4 Hz) (1 H), 3.91 (m), 3.48 (m), 3.25 (m) (2 H), 3.56 (t, *J* = 6.4 Hz), 3.53 (t, *J* = 6.5 Hz) (2 H), 2.34 (s, 1 H), 1.82 (m, 2 H), 1.71 (m, 2 H), 1.61-1.34 (m, 8 H); ^{13}C NMR δ 143.5, 142.4, 128.4, 128.1, 127.5, 127.0, 126.9, 126.5, 98.0, 95.6, 79.0, 77.2, 62.6, 62.5, 61.9, 38.0, 36.9, 32.7, 32.6, 30.8, 30.7, 25.5, 25.4, 22.2, 21.7, 19.7, 19.2; Anal. Calcd for $C_{16}H_{24}O_3$.1/4 H_2O: C, 71.48; H, 9.18. Found: C, 71.82; H, 9.14.

6. DEAD (0.275 mL, 1.70 mmol) was added dropwise at room temperature to a solution of **5** (0.25 g, 0.947 mmol), *N*-hydroxyphthalimide (0.218 g, 1.42 mmol) and PPh_3 (0.38 g, 1.42 mmol) in THF (15 mL). The resulting reaction mixture was stirred at room temperature for 24 h before it was diluted with EtOAc (50 mL) and water (10 mL). The water layer was extracted with EtOAc (3 x 15 mL). The combined EtOAc layers were washed subsequently with saturated $NaHCO_3$ solution (2 x 10 mL), water (10 mL) and brine (10 ml), then dried (Na_2SO_4) and concentrated to dryness. Column chromatography on silica gel (Hexane/EtOAc 1/1) gave **6** (0.388 g, 100%) as a colorless oil. ^{1}H NMR δ 7.79 (dd, 2 H), 7.70 (dd, 2 H), 7.36 –7.19 (m, 5 H), 4.83 (t, *J* = 3.3 Hz), 4.37 (t, *J* = 3.6 Hz) (1 H), 4.68 (dd, *J* = 7.8, 5.4 Hz), 4.58 (t, *J* = 6.4 Hz) (1 H), 4.16 (t, *J* = 6.8 Hz), 4.14 (t, *J* = 6.8 Hz) (2 H), 3.91 (m), 3.48 (m), 3.26 (m) (2 H), 1.91-1.68 (m, 6 H), 1.58-1.39 (m, 6 H); ^{13}C NMR δ 163.6, 143.4, 142.4, 125.0, 134.5, 129.0, 128.4, 128.2, 127.5, 127.0, 126.5, 124.1, 123.5, 98.1, 95.3, 78.7, 78.4 (d), 76.9, 62.4, 62.0, 38.0, 36.7, 30.8, 28.2, 25.6, 25.5, 22.2, 21.5, 19.6, 19.3.

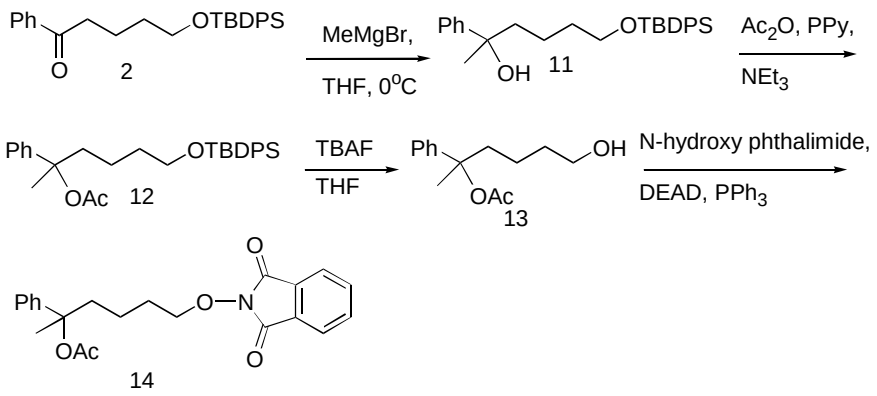
7. PPTs (44.7 mg, 0.18 mmol) was added at room temperature to a solution of **6** (0.368 g, 0.9 mmol) in ethanol (14 mL). The resulting reaction mixture was heated to 55°-60 °C for 4 h before it was cooled to room temperature and the solvent was removed under vacuum. The residue was taken up in EtOAc (75 mL) and washed subsequently with saturated $NaHCO_3$ solution (10 mL), water (10 mL) and brine (10 mL), then dried (Na_2SO_4) and concentrated to dryness. Column chromatography on silica gel (Hexane/EtOAc 1/1) gave **7** (0.28 g, 96%) as a white solid (mp 66-67 °C). ^{1}H NMR δ 7.79 (dd, 2 H), 7.71 (dd, 2 H), 7.35-7.21 (m, 5 H), 4.68 (dd, *J* = 7.5, 5.4 Hz, 1 H), 4.16 (t, *J* = 6.5 Hz, 2 H), 2.43 (br. s, 1 H), 1.80 (m, 4 H), 1.60-1.47 (m, 2 H); ^{13}C NMR δ 163.8, 144.9, 134.6, 129.0, 128.5, 127.5, 126.0, 123.6, 78.4, 74.2, 38.7, 28.0, 22.0; Anal. Calcd for $C_{19}H_{29}NO_4$: C, 70.14; H, 5.88. Found: 70.78; H, 6.03.

8. 4-(1-Pyrrolidinyl)pyridine (0.16 g, 1.07 mmol) was added at room temperature to a solution of **7** (0.692 g, 2.13 mmol) and Ac_2O (0.613 mL, 8.52 mmol) in NEt_3 (15.0 mL). The resulting reaction mixture was stirred at room temperature overnight before it was diluted with EtOAc (100 mL) and saturated NH_4Cl solution (20 mL). The organic layer was washed with 2N HCl to pH to 6-7, then washed subsequently with water (15 mL), saturated $NaHCO_3$ solution (10 mL), water (10 mL) and brine (10 mL), then dried (Na_2SO_4) and concentrated to dryness. Column chromatography on silica gel (Hexane/EtOAc 1/1) gave **8** (0.704 g, 90%) as a white solid (mp 92-94 °C). ^{1}H NMR δ 7.83 (dd, 2 H), 7.73 (dd, 2 H), 7.34-7.26 (m, 5 H), 5.75 (dd, *J* = 7.6, 6.1 Hz, 1 H), 4.17 (t, *J* = 6.6 Hz, 2 H), 2.08 (s, 3 H), 2.00 (m, 1 H), 1.90-1.76 (m, 3 H), 1.54 (m, 2 H); ^{13}C NMR δ 170.6, 163.8, 140.7, 134.6, 129.1, 128.6, 128.1, 126.7, 123.7, 78.3, 76.0, 36.1, 28.0, 21.8, 21.5; Anal. Calcd for $C_{21}H_{21}NO_5$: C, 68.65; H, 5.76. Found: C, 68.75; H, 5.80.

9. Diethyl chlorophosphate (0.112 g, 0.651 mmol) in CH_2Cl_2 (1.0 mL) was added at room temperature to a solution of **7** (0.141 g, 0.434 mmol) and DMAP (0.08 g, 0.651 mmol) in CH_2Cl_2 (8.0 mL). The resulting reaction mixture was stirred at room temperature for 24 h before it was diluted with EtOAc (50 mL). The organic layer was washed subsequently with saturated NH_4Cl solution (10 mL), water (10 mL) and brine (10 ml), then dried (Na_2SO_4) and concentrated to dryness. Column chromatography on silica gel

(Hexane/EtOAc 1/1) gave **9** (0.104 g, 52%, 100% based on recovered **7**) as a colorless oil. ^{1}H NMR δ 7.80 (dd, 2 H), 7.73 (dd, 2 H), 7.37-7.26 (m, 5 H), 5.27 (dd, *J* = 13.7, 7.3 Hz, 1 H), 4.14 (t, *J* = 6.6 Hz, 2 H), 4.08 (m, 1 H), 3.96 (m, 1 H), 3.85 (m, 2 H), 2.03 (m, 1 H), 1.89 (m, 1 H), 1.79 (m, 2 H), 1.62 (m, 1 H), 1.47 (m, 1 H), 1.22 (dt, *J* = 7.1, 0.8 Hz, 3 H), 1.11 (dt, *J* = 7.1, 0.8 Hz, 3 H); ^{13}C NMR δ 163.7, 140.6, 134.6, 132.3, 132.2, 129.1, 128.6, 128.4, 126.6, 123.6, 80.5 (d), 78.3, 63.7 (t), 37.7 (d), 27.9, 21.6, 16.1 (t); ^{31}P NMR δ -1.08; Anal. Calcd for $C_{23}H_{28}NO_7P.1/4H_2O$: C, 59.29; H, 6.16. Found: C, 59.02; H, 6.08.

10. Same procedure as for **9** with replacement of diethyl chlorophosphate by diphenyl chlorophosphate. 63%. ^{1}H NMR δ 7.81 (dd, 2 H), 7.72 (dd, 2 H), 7.33-7.06 (m, 13 H), 6.97 (dd, 2 H), 5.54 (dd, *J* = 13.5, 7.3 Hz, 1 H), 4.09 (t, *J* = 6.6 Hz, 2 H), 2.08 (m, 1 H), 1.95 (m, 1 H), 1.74 (m, 2 H), 1.47 (m, 2 H); ^{13}C NMR δ 163.7, 150.7 (t), 139.6, 134.6, 129.8, 129.7, 129.1, 128.6, 126.7, 125.4, 125.2, 123.6, 120.4, 120.3, 120.2, 120.1, 82.6 (d), 78.1, 37.4 (d), 27.8, 21.4; ^{31}P NMR δ -11.89; Anal. Calcd for $C_{31}H_{28}NO_7P$: C, 66.78; H, 5.06. Found: C, 66.64; H, 5.08.



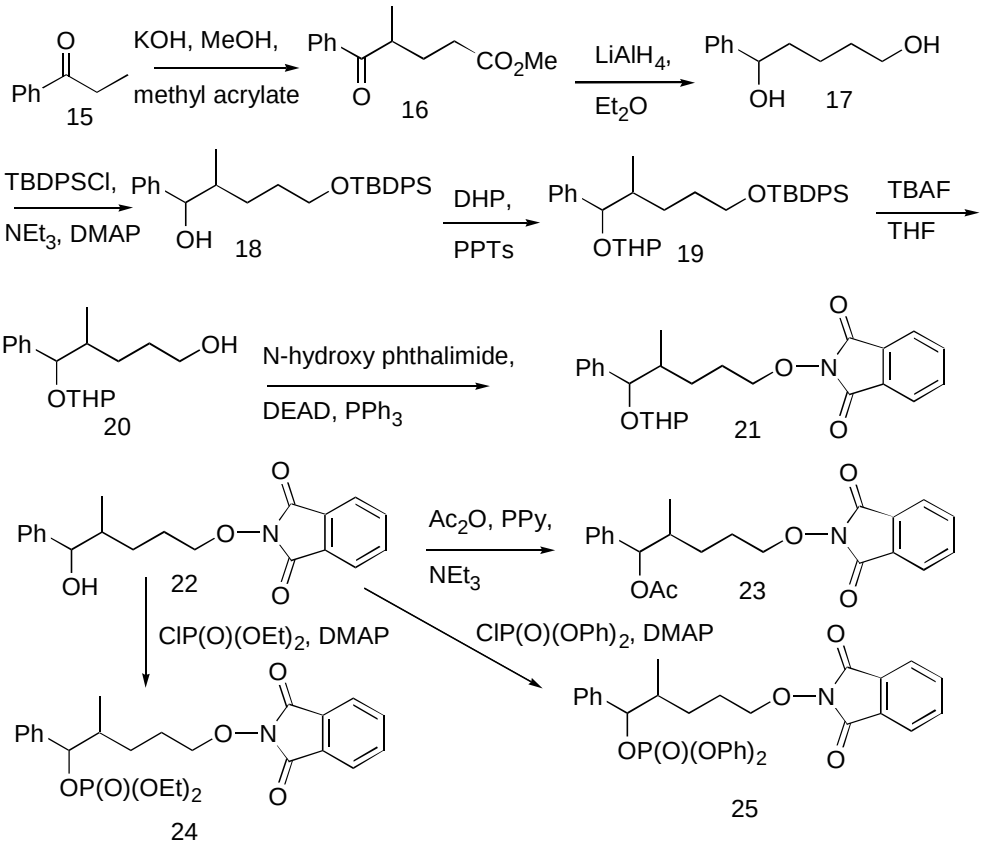
11. MeMgBr (0.424 mL, 3.0 M in Et_2O, 1.27 mmol) was added dropwise at 0 °C to a solution of **2** (0.352 g, 0.847 mmol) in THF (6.0 mL). The reaction mixture was stirred at this temperature for 30 min before EtOAc (50 mL) and HCl (0.5 N, 10 mL) was added to quench the reaction. The water layer was extracted with EtOAc (3 x 10 mL) and the combined extracts were washed subsequently with saturated $NaHCO_3$ solution (10 mL),

water (10 mL) and brine (10 ml), then dried (Na_2SO_4) and concentrated to dryness. Column chromatography on silica gel (Hexane/EtOAc 5/1) gave **11** (0.25 g, 71%) as a colorless oil. ^{1}H NMR δ 7.64 (dd, 4 H), 7.45-7.24 (m, 4 H), 3.62 (t, *J* = 6.4 Hz, 2 H), 1.79 (M, 2 H), 1.68 (br. s, 1 H), 1.55 (s, 3 H), 1.32 (m, 2 H), 1.28 (m, 2 H), 1.03 (s, 9 H); ^{13}C NMR δ 148.1, 135.8, 134.2, 129.7, 128.3, 127.8, 126.7, 125.0, 74.9, 63.9, 44.0, 32.9, 30.3, 27.0, 20.5, 19.4; Anal. Calcd for $C_{28}H_{36}O_2Si$: C, 77.73; H, 8.39. Found: C, 77.25; H, 8.45.

12. Same procedure as for **8**. 97%. ^{1}H NMR δ 7.66 (dd, 4 H), 7.44-7.26 (m, 11 H), 3.64 (t, *J* = 6.2 Hz, 2 H), 2.07 (s, 3 H), 2.00 (m, 2 H), 1.85 (s, 3 H), 1.52 (m, 2 H), 1.30 (m, 2 H), 1.05 (s, 9 H); ^{13}C NMR δ 169.8, 145.2, 135.8, 134.2, 129.7, 128.3, 127.8, 127.0, 124.7, 84.2, 63.7, 42.5, 32.8, 27.0, 25.0, 22.4, 20.3, 19.4; Anal. Calcd for $C_{30}H_{38}O_3Si$: C, 75.90; H, 8.07. Found: C, 75.74; H, 8.16.

13. Same procedure as for **5**. 86%. ^{1}H NMR δ 7.34-7.20 (m, 5 H), 3.53 (dt, *J* = 6.5, 1.4 Hz, 2 H), 2.05 (s, 3 H), 2.03 (m, 2 H), 1.82 (s, 3 H), 1.47 (m, 2 H), 1.26 (m, 2 H); ^{13}C NMR δ 169.9, 145.0, 128.3, 127.0, 124.6, 84.1, 62.6, 42.3, 32.8, 25.0, 22.4, 20.1; Anal. Calcd for $C_{14}H_{20}O_3.1/4H_2O$: C, 69.83; H, 8.58. Found: C, 69.97; H, 8.49.

14. Same procedure as for **6**. 52% White solid (mp 119-121 ^{o}C). ^{1}H NMR δ 7.82 (dd, 2 H), 7.74 (dd, 2 H), 7.32-7.19 (m, 5 H), 4.14 (t, *J* = 6.6 Hz, 2 H), 2.07 (s, 3 H), 2.04 (m, 2 H), 1.85 (s, 3 H), 1.74 (m, 2 H), 1.41 (m, 2 H); ^{13}C NMR δ 169.9, 163.8, 145.1, 134.6, 129.1, 128.4, 127.0, 124.7, 123.7, 84.0, 78.4, 42.3, 28.4, 25.0, 22.5, 20.1; Anal. Calcd for $C_{22}H_{23}NO_5.1/4H_2O$: C, 68.47; H, 6.14. Found: C, 68.68; H, 6.10.



16 and 17. were prepared according to the literature methods.[2,3]

18. Same procedure as for **2**. 100%. ^{1}H NMR δ 7.70-7.64 (m, 4 H), 7.43-7.26 (m, 11 H), 4.51 (d, *J* = 5.9 Hz), 4.44 (d, *J* = 6.8 Hz) (1 H), 3.68 (t, *J* = 6.4 Hz), 3.62 (t, *J* = 6.4 Hz), (2 H), 1.90-1.40 (m, 5 H), 1.06 (s), 1.03 (s) (9 H), 0.93 (d, *J* = 6.7 Hz), 0.76 (d, *J* = 6.8 Hz) (3 H); ^{13}N MR δ 143.9, 143.6, 135.8, 135.0, 134.3, 129.8, 126.6, 79.1, 78.4, 64.4, 64.2, 40.2, 40.1, 30.4, 30.2, 29.4, 28.6, 27.1, 26.8, 19.4, 15.8, 14.7; Anal. Calcd for $C_{28}H_{36}O_2Si$: C, 77.73; H, 8.39. Found: C, 77.84; H, 8.34.

19. Same procedure as for **4**. 60%. ^{1}H NMR δ 7.70-7.62 (m, 4 H), 7.41-7.23 (m, 11 H), 4.78 (br s), 4.40 (m) (1 H), 4.47 (d, *J* = 6.8 Hz), 4.42 (d, *J* = 7.4 Hz), 4.32 (d, *J* = 6.3 Hz), 4.26 (d, *J* = 7.1 Hz) (1 H), 3.94 (m), 3.46 (m), 3.21 (m) (2 H), 3.69 (t, *J* = 6.5 Hz), 3.66 (t, *J* = 6.2 Hz), 3.58 (t, *J* = 6.4 Hz) (2 H), 2.02-1.37 (m, 5 H), 1.06 (s), 1.03 (s), 1.02 (s) (9 H), 0.92 (d, *J* = 6.7 Hz), 0.72 (d, *J* =6.6 Hz), 0.70 (d, *J* = 6.7 Hz) (3 H); ^{13}C NMR δ

142.7, 142.5, 141.6, 141.5, 141.3, 135.8, 134.3, 129.7, 128.2, 127.9, 127.8, 127.5, 127.0, 126.9 (d), 99.5, 99.2, 95.1, 84.3, 84.0, 81.7, 81.3, 64.6, 64.3, 62.2, 62.1, 62.0, 39.8, 39.5, 39.2, 31.0, 30.7, 30.4, 30.3, 29.4 (d), 29.1, 27.1, 25.8, 25.7, 19.5, 19.4, 16.0, 15.8, 15.6, 15.4; Anal. Calcd for $C_{33}H_{44}O_3Si$: C, 76.70; H, 8.58. Found: C, 76.53; H, 8.65.

20. Same procedure as for **5**. 95%. ^{1}H NMR δ 7.34-7.22 (m, 5 H), 4.78(t, *J* = 3.3 Hz), 4.37 (t, *J* = 3.3 Hz), 4.33 (t, *J* =- 3.6 Hz) (1 H), 4.50 (d, *J* = 6.5 Hz), 4.42 (d, *J* = 7.6 Hz), 4.32 (d, *J* = 6.4 Hz), 4.26 (d, *J* = 7.1 Hz) (1 H), 3.92 (m), 3.42 (m), 3.18 (m) (2 H), 3.62 (m), 3.53 (m) (2 H), 1.94-1.41 (m, 5 H), 1.01 (d, *J* = 6.7 Hz), 0.94 (d, *J* = 6.7 Hz), 0.72 (d, J = 6.8 Hz) (3 H); ^{13}C NMR δ 142.6, 142.3, 141.1, 128.2, 128.0, 127.8, 127.6, 127.5, 127.3, 127.0, 99.5, 99.3, 95.7, 95.6, 84.3, 83.9, 81.8, 81.1, 63.3, 63.2, 62.9, 62.6, 62.1 (d), 39.7, 39.3, 39.2, 31.0, 30.7, 30.6 (d), 30.5, 30.3, 29.1, 28.8, 28.7, 25.7, 25.6, 19.9, 19.7, 19.3, 16.2, 15.8, 15.7, 15.5; Anal. Calcd for $C_{17}H_{26}O_3$: C, 73.34; H, 9.41. Found: C, 73.07; H, 9.56.

21. Same procedure as for **6**. 77%. ^{1}H NMR δ 7.85-7.80 (m, 2 H), 7.75-7.72 (m, 2 H), 7.31-7.21 (m, 5 H), 4.79 (t, *J* = 3.2 Hz), 4.37 (m) (1 H), 4.50 (d, *J* = 6.5 Hz), 4.42 (d, *J* = 7.6 Hz), 4.36 (d, *J* = 6.4 Hz), 4.26 (d, *J*= 7.0 Hz) (1 H), 4.19 (m), 4.10 (m) (2 H), 3.93 (m), 3.46 (m), 3.21 (m) (2 H), 2.00-1.10 (m, 5 H), 1.03 (d, *J* = 6.7 Hz), 0.95 (d, *J* = 6.7 Hz), 0.75 (d, *J* = 6.8 Hz) (3 H); ^{13}C NMR δ 163.8, 142.2, 142.3, 141.2, 141.1, 134.6, 129.1, 128.2, 128.0 (d), 127.8, 127.6, 127.4, 127.3, 127.0 (d), 123.6, 99.5, 99.4, 95.2 (d), 84.3, 83.8, 81.5, 81.0, 79.1, 79.0, 78.9, 78.8, 62.4, 62.2, 62.0, 39.7, 39.5, 39.3, 30.9, 30.7, 29.0, 28.8, 28.6, 28.5, 26.1, 26.0, 25.8, 25.6, 19.5, 19.3, 16.1, 15.6, 15.3; Anal. Calcd for $C_{25}H_{29}NO_5$: C, 70.90; H, 6.90. Found: C, 70.38; H, 6.92.

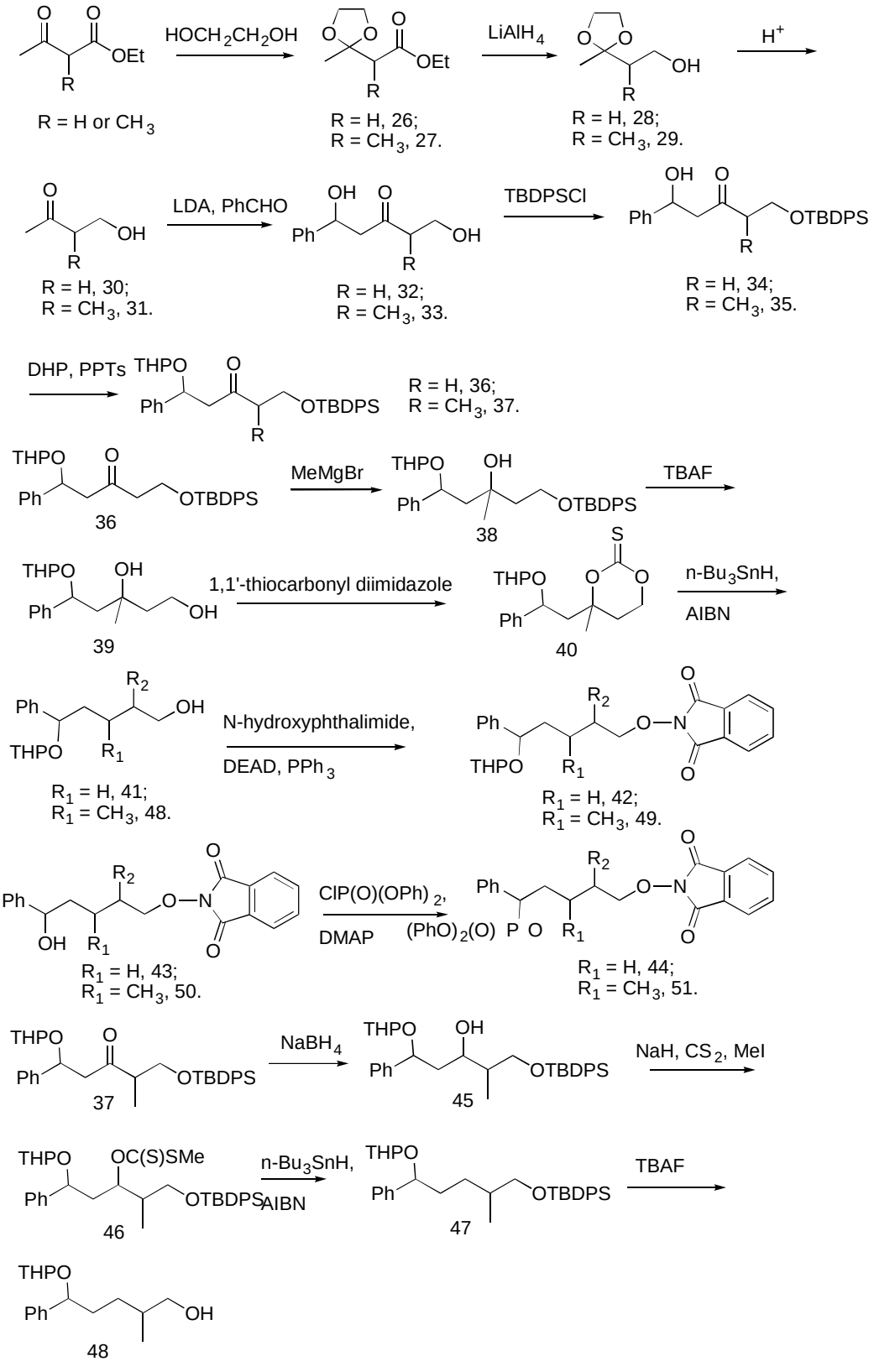
22. Same procedure as for **7**. 83%. ^{1}H NMR δ 7.83-7.80 (m, 2 H), 7.75-7.72 (m, 2 H), 7.32-7.24 (m, 5 H), 4.61 (d, *J* = 5.3 Hz), 4.42 (d, *J* = 7..2 Hz) (1 H), 4.20 (m), 4.15 (t, *J* = 6.6 Hz) (2 H), 2.20 (br. s, 1 H), 1.87 (m, 2 H), 1.80-1.58 (m), 1.46-1.22 (m) (3 H), 0.93 (d, *J* = 6.7 Hz), 0.76 (d, *J* = 6.8 Hz) (3 H); ^{13}C NMR δ 163.9, 143.6, 134.6, 129.1, 128.4, 128.3, 127.6, 127.4, 126.9, 126.5, 123.7, 79.0 (d), 78.8, 40.0 (d), 29.1, 28.4, 26.1, 25.7,

16.0, 14.4; Anal. Calcd for $C_{20}H_{21}NO_4.1/4H_2O$: C: 68.95; H, 6.22. Found: C, 68.63; H, 6.05.

23. Same procedure as for **8**. 100%. ^{1}H NMR δ 7.82 (m, 2 H), 7.73 (m, 2 H), 7.31-7.23 (m, 5 H), 5.64 (d, *J* = 6.3 Hz), 5.53 (d, *J* = 7.7 Hz) (1 H), 4.18 (t, *J* = 6.4 Hz), 4.11 (t, *J* = 6.6 Hz) (2 H), 2.09 (s), 2.07 (s) (3 H), 2.04 (m), 1.95-1.66 (m), 1.59-1.18 (m) (5 H), 0.95 (d, *J* = 6.7 Hz), 0.80 (d, *J* = 6.8 Hz) (3 H); ^{13}C NMR δ 170.5, 163.8, 139.6, 134.6, 129.1, 128.4, 127.9, 127.8, 127.2, 126.9, 123.6, 80.0, 79.3, 78.7, 78.6, 38.4, 38.2, 28.8, 28.4, 25.9, 21.3, 15.7, 15.0; Anal. Calcd for $C_{22}H_{23}NO_5$: C, 69.28; H, 6.08. Found: C, 69.13; H, 6.04.

24. Same procedure as for **9**. 60%. ^{1}H NMR δ 7.81 (m, 2 H), 7.72 (m, 2 H), 7.32-7.22 (m, 5 H), 5.12 (dd, *J* = 8.0, 6.2 Hz), 5.03 (t, *J* = 7.6 Hz) (1 H), 4.18 (t, *J* = 6.5 Hz), 4.11 (t, *J* = 6.6 Hz) (2 H), 4.09 (m, 1 H), 3.93 (m, 1 H), 3.80 (m, 2 H), 2.10-1.65 (m), 1.52 (m), 1.34 (m) (5 H), 1.20 (dt, *J* = 7.0, 0.8 Hz), 1.09 (dt, *J* = 6.9, 0.9 Hz) (3 H), 1.00 (d, *J* = 6.7 Hz), 0.79 (d, *J* = 6.8 Hz) (3 H); ^{13}C NMR δ 163.7, 139.6, 139.4, 134.6, 129.1, 128.3, 128.1, 127.3, 127.1, 123.6, 84.6 (d), 84.3 (d), 78.8, 78.6, 63.7 (t), 39.8 9d), 39.6 (d), 28.5, 28.2, 25.9, 25.7, 16.1 9d), 15.3, 14.9; ^{31}P NMR δ -0.86, -1.02.

25. Same procedure as for **10**. 77%. ^{1}H NMR δ 7.82-7.79 (m, 2 H), 7.74-7.71 (m, 2 H), 7.32-7.07 (m, 13 H), 6.93 (m, 2 H), 5.40 (dd, *J* = 7.8, 6.2 Hz), 5.28 (t, *J* = 7.5 Hz) (1 H), 4.05 (m, 2 H), 2.06 (m, 1 H), 1.88-1.63 (m, 2 H), 1.48 (m), 1.26 (m) (2 H), 0.96 (d, *J* = 6.7 Hz), 0.77 (d, *J* = 6.8 Hz) (3 H); ^{13}C NMR δ 163.8, 150.8, 150.7, 150.6, 138.5, 138.3, 134.6, 129.8, 129.7, 129.0 (d), 128.5, 128.4, 127.4, 127.1, 125.3, 125.2, 123.6, 120.4, 120.3, 120.2, 120.1, 86.7, 86.6, 86.3, 86.2, 78.6, 78.5, 39.8, 39.7, 39.5, 39.4, 28.3, 28.1, 25.8, 25.6, 15.2, 14.8; ^{31}P NMR δ -11.65, -11.83; Anal. Calcd for $C_{32}H_{30}NO_7P.1/4H_2O$: C, 66.72; H, 5.34. Found: C, 66.71; H, 5.33.


HOCH2CH2OH
LiAlH4
H+
R = H or CH3
R = H, 26;
R = CH3, 27.
R = H, 28;
R = CH3, 29.
LDA, PhCHO
TBDPSCl
R = H, 30;
R = CH3, 31.
R = H, 32;
R = CH3, 33.
R = H, 34;
R = CH3, 35.
DHP, PPTs
R = H, 36;
R = CH3, 37.
MeMgBr
TBAF
36
38
1,1'-thiocarbonyl diimidazole
n-Bu3SnH,
AIBN
39
40
N-hydroxyphthalimide,
DEAD, PPh3
R1 = H, 41;
R1 = CH3, 48.
R1 = H, 42;
R1 = CH3, 49.
ClP(O)(OPh)2,
DMAP
(PhO)2(O) P
R1 = H, 43;
R1 = CH3, 50.
R1 = H, 44;
R1 = CH3, 51.
NaBH4
NaH, CS2, MeI
37
45
n-Bu3SnH,
AIBN
46
47
48

32 and **33** were prepared according to the literature method.[4]

34. Same procedure as **2**. 41%. ^{1}H NMR δ 7.66 (dd, 4 H), 7.44-7.26 (m, 11 H), 5.18 (dd, *J* = 8.0, 4.3 Hz, 1 H), 3.96 (t, *J* = 6.1 Hz, 2 H), 2.92 (dd, *J* = 23.2, 17.7 Hz, 1 H), 2.90 (d, *J* = 1.6 Hz, 1 H), 2.65 (t, *J* = 6.1 Hz, 2 H), 1.05 (s, 9 H); ^{13}C NMR δ 210.6, 142.9, 135.7, 133.4, 130.0, 128.7, 127.9, 127.8, 125.8, 70.0, 59.7, 46.3, 27.0; Anal. Calcd for $C_{27}H_{32}O_3Si$: C, 74.96; H, 7.46. Found: C, 74.49; H, 7.44.

35. Same procedure as for **2**. 42%. ^{1}H NMR δ 7.66 (m, 4 H), 7.45-7.25 (m, 11 H), 5.20 (m, 1 H), 3.84 (t, *J* = 10.0 Hz, 1 H), 3.71 (dd, *J* = 10.0, 5.2 Hz, 1 H), 2.96 (m, 2 H), 2.82 (m, 1 H), 1.07 (s), 1.06 (s), (9 H), 1.03 (d, *J* = 3.0 Hz, 3 H); ^{13}C NMR δ 214.5, 214.4, 143.0, 135.7, 133.2, 130.0, 128.6, 128.0, 127.7, 125.9, 125.8, 70.0 (d), 66.3, 66.1, 51.4, 50.9, 49.4, 49.2, 27.0; Anal. Calcd for $C_{28}H_{34}O_3Si$: C, 75.29; H, 7.67. Found: C, 75.16; H, 7.69.

36. Same procedure as for **4**. 95%. ^{1}H NMR δ 7.68 (m, 4 H), 7.44-7.26 (m, 11 H), 5.27 (dd, *J* = 8.8, 4.6 Hz), 5.11 (dd, *J* = 8.8, 4.1 Hz) (1 H), 4.91 (t, *J* = 3.2 Hz), 4.43 (t, *J* = 3.3 Hz) (1 H), 3.97 (d, *J* = 6.4 Hz), 3.94 (t, *J* = 6.4 Hz) (2 H), 3.88 (m), 3.48 (m), 3.24 (dt, *J* = 11.3, 5.0 Hz) (2 H), 3.13 (ddd, *J* = 16.5, 8.8, 4.2 Hz, 1 H), 3.73 (m, 2 H), 2.64 (m, 1 H), 1.82-1.37 (m, 6 H), 1.04 (s, 9 H); ^{13}C NMR δ 207.5, 207.3, 143.0, 141.2, 135.7, 133.6, 129.9, 128.7, 128.5, 128.0, 127.9, 127.5, 126.5, 99.4, 75.7, 73.1, 62.2, 62.1, 59.6, 51.9, 51.7, 46.9, 46.7, 30.7, 30.6, 27.0, 25.6, 25.5, 19.4, 19.3; Anal. Calcd for $C_{32}H_{40}O_4Si$: C, 74.38; H, 7.80. Found: C, 74.31; H, 7.76.

37. Same procedure as for **4**. 93%. ^{1}H NMR δ 7.65 (m, 4 H), 7.43-7.26 (m, 11 H), 5.29 (m), 5.15 (dd, *J* = 8.9, 4.1 Hz), 5.13 (dd, *J* = 8.5, 4.4 Hz) (1 H), 4.94 (dd, *J* = 7.5, 3.5 Hz), 4.44 (dd, *J* = 7.2, 3.5 Hz) (1 H), 3.89 (m), 3.21 (m) (3 H), 3.68 (m, 1 H), 3.50 (m, 1 H), 2.76 (m, 2 H), 1.83-1.36 (m, 6 H), 1.10-1.00 (m, 12 H); ^{13}C NMR δ 211.0, 210.5, 143.3, 143.2, 141.4 (d), 135.7, 133.4, 129.9, 128.6, 128.4, 127.9, 127.4, 127.2, 126.5, 126.4, 99.7, 99.5, 94.5, 77.6, 77.2, 76.8, 75.8, 75.6, 72.9, 72.7, 65.9, 62.2, 62.1, 61.8, 51.2, 50.8,

50.6, 50.4, 49.8, 49.5, 49.4, 30.7, 30.6, 26.9, 25.6, 25.5, 19.3, 19.1, 12.8; Anal. Calcd for $C_{33}H_{42}O_4Si$: C, 74.68; H, 7.98. Found: C, 74.72; H, 8.03.

38. Same procedure as for **11**. 2 Isomers 92%. Anal. Calcd for $C_{33}H_{44}O_4Si$: C, 74.39; H, 8.32. Found: C, 74.53; H, 8.50. Isomer 1 ^{1}H NMR δ 7.77-7.68 (m, 4 H), 7.45-7.28 (m, 11 H), 5.20 (dd, *J* = 10.9, 2.5 Hz), 5.14 (dd, *J* = 10.7, 2.4 Hz) (1 H), 4.42 (t, *J* = 2.6 Hz), 4.38 (t, *J* = 8.7 Hz) (2 H), 4.04 (m, 1 H), 3.94 (m, 2 H), 3.52 (m, 1 H), 2.16 (m, 2 H), 1.88 (m, 2 H), 1.78 (m, 2 H), 1.67 (m, 1H), 1.53 (m, 3 H), 1.45 (s), 1.31 (s) (3 H), 1.11 (s), 1.05 (s) (9 H); ^{13}C NMR δ 142.3, 142.2, 135.6, 133.8, 133.7, 129.8, 129.7, 128.6, 127.8, 127.7, 126.8, 96.4, 96.2, 94.7, 75.6, 75.4, 72.0, 71.9, 63.8, 63.7, 63.0, 61.4, 60.7, 49.2, 49.0, 45.3, 42.9, 30.9, 28.3, 27.0, 26.9, 26.8, 25.6, 25.4, 20.3, 20.2, 19.8, 19.2. Isomer 2 ^{1}H NMR δ 7.74 (m, 4 H), 7.48-7.28 (m, 11 H), 4.94-4.82 (m, 2 H), 4.15 (m, 1 H), 3.94 (m, 2 H), 3.52 (m, 1 H), 3.21 (m, 1 H), 2.22 (m 1 H), 1.99-1.63 (m, 5 H), 1.51 (m, 4 H), 1.35 (s), 1.30 (s) (3 H), 1.12 (s), 1.08 (s) (9 H); ^{13}C NMR δ 144.2, 144.0, 135.6, 133.4, 133.2, 129.9, 129.8, 128.2, 127.8(d), 27.3, 127.2, 126.6, 99.4 (d), 79.0, 78.8, 71.9, 62.2, 61.4, 60.9, 49.4, 44.4, 43.0, 30.8, 28.0, 27.3, 26.9, 25.3, 19.3, 19.1.

39. Same procedure as for **5**. 89%. ^{1}H NMR δ 7.28 (m, 5 H), 5.21 (dd, *J* = 11.0, 2.2 Hz), 5.18 (dd, *J* = 7.8, 2.2 Hz) (1 H), 4.58 (s), 4.46 (s) (1 H), 4.34 (m), 3.98(m) (1 H), 3.83 (m, 1 H), 3.82 (br. s), 3.70 (br.s) (1 H), 3.47 (m, 1 H), 2.24 (dd, *J* = 14.8, 11.5 Hz), 2.07 (dd, *J* = 14.8, 11.2 Hz) (1 H), 1.75-1.46 (m, 9 H), 1.46 (s), 1.30 (s) (3 H); ^{13}C NMR δ 141.8, 141.6, 128.7, 128.0, 127.9, 126.7, 96.9, 96.7, 76.0, 75.5, 74.2, 73.6, 64.2, 59.9, 59.5, 49.8, 48.5, 44.1, 41.2, 31.0, 29.8, 27.9, 26.3, 25.2, 20.4.

40. 1,1'-Thiocarbonyl diimidazole (0.10 g, 0.562 mmol) and DMAP (0.137 g, 1.12 mmol) were added successively to a solution of **39** (0.11 g, 0.374 mmol) in dry CH_3CN (10 mL) at 0^{o}C. The resulting reaction mixture was then heated to reflux for 5 h before it was cooled down and diluted with EtOAc (50 mL) and saturated NH_4Cl solution (10 ml). The water layer was extracted with EtOAc (3 x 10 mL). The combined extracts were washed subsequently with HCl soluton (0.5 N, 15 mL), water (10 mL), saturated $NaHCO_3$ solution (10 mL), water (10 mL) and brine (10 mL), then dried (Na_2SO_4) and

concentrated to dryness. Column chromatography on silica gel (Hexane/EtOAc 1/1) gave **40** (0.0812 g, 65%) as a colorless oil. ^{1}H NMR δ 7.36-7.26 (m, 5 H), 4.93 (dd, *J* = 9.4, 3.2 Hz, 1 H), 4.47 (m, 2 H), 4.21 (m, 1 H), 3.88 (m, 1 H), 2.62 (m, 1 H), 2.35 (m), 2.08(m) (3 H), 1.86-1.36 (m, 6 H), 1.68 (s), 1.59 (s) (3 H); ^{13}C NMR δ 190.8, 141.5, 128.9, 128.2, 126.8, 126.6, 97.5, 97.1, 86.3, 74.0, 73.2, 66.9, 66.4, 65.1, 64.6, 48.6, 47.7, 31.8, 31.4, 31.2, 30.0, 27.0, 25.4, 21.3, 20.9.

41. n-Bu_3SnH (0.205 mL, 0.765 mmol) and AIBN (0.128 mmol) in degassed PhH (2.0 mL) were added to a refluxing solution of **40** (0.0856 g, 0.255 mmol) in PhH (8.0 mL) over 15 min. The resulting reaction mixture was heated to reflux for a further 3 h before it was cooled to room temperature and a solution of CH_3ONa in CH_3OH (2.0 mL, 1.0 M) and THF (2.0 mL) were added. The mixture was stirred overnight before it was diluted with saturated NH_4Cl solution (15 mL) and EtOAc (50 mL). The water layer was extracted with EtOAc (3 x 10 mL) and the combined extracts were washed subsequently with water (10 mL), and brine (10 ml), then dried (Na_2SO_4) and concentrated to dryness. Column chromatography on silica gel (Hexane/EtOAc gradient eluent 9/1 to 1/1) gave **41** (0.050 g, 71%) as a colorless oil. ^{1}H NMR δ 7.37-7.21 (m, 5 H), 4.81 (m, 1 H), 4.37 (dd, *J* = 4.5, 2.8 Hz), 4.33 (dd, *J* = 5.4, 2.7 Hz) (1 H), 3.93 (m, 1 H), 3.70 (m, 2 H), 3.46 (m, 1 H), 2.00-1.25 (m, 10 H), 1.02-0.90 (m, 3 H).

42. Same procedure as for **6**. 43%. ^{1}H NMR δ 7.84 (m, 2 H), 7.74 (m, 2 H), 7.38-7.19 (m, 5 H), 4.81 (m, 1 H), 4.63 (m), 4.40 (m) (1 H), 4.22 (m, 2 H), 3.94 (m), 3.23 (m) (1 H), 3.49 (m, 1 H), 1.95-1.33 (m, 10 H), 1.07-0.98 (m, 3 H); ^{13}C NMR δ 163.8, 144.2, 143.5, 142.3, 135.1, 134.6, 129.2, 128.6, 128.3, 127.7, 127.6, 127.3, 127.2, 127.0, 126.9, 126.6, 124.3, 123.7, 99.1, 98.5, 95.5, 95.4, 77.9, 77.8, 77.1, 77.0, 75.4, 75.0, 62.7, 62.5, 62.2, 62.1, 46.3, 45.8, 45.4, 44.6, 35.6, 35.5, 35.2, 34.8, 30.9, 30.8, 29.9, 26.9, 26.8, 25.7, 25.6, 20.2, 20.1, 19.8, 19.6, 19.4; Anal. Calcd for $C_{25}H_{29}NO_5$: C, 70.90; H, 6.90. Found: C, 71.00; H, 6.86.

43. Same procedure as for **7**. 85%. ^{1}H NMR δ 7.84 (m, 2 H), 7.75 (m, 2 H), 7.38-7.25 (m, 5 H), 4.82 (m, 1 H), 4.26 (m, 2 H), 2.27 (br. s 1 H), 2.17-1.85 (m, 2 H), 1.83-1.45 (m, 3

H), 1.08 (d, *J* = 6.6 Hz), 1.03 (d, *J* = 6.5 Hz) (3 H); ^{13}C NMR δ 163.9, 145.7, 145.0, 134.6, 129.0, 128.6 (d), 127.6, 127.5, 126.0, 125.8, 123.7, 77.0, 76.9, 72.3, 46.8, 46.7, 35.6, 34.7, 29.9, 26.8, 26.7, 20.4, 19.8; Anal. Calcd for $C_{20}H_{21}NO_4$: C, 70.78; H, 6.24. Found: C, 70.82; H, 6.42.

44. Same procedure as for **10**. 91%. ^{1}H NMR δ 7.82 (m, 2 H), 7.74 (m, 2 H), 7.36-7.15 (m, 13 H), 5.60 (m, 1 H), 4.14 (m, 2 H), 2.17 (m), 1.95 (m), 1.81 (m) (3 H), 1.65 (m, 2 H), 0.98 (d, *J* = 5.4 Hz, 3 H); ^{13}C NMR δ 163.7, 150.7 (t), 140.2, 139.3, 134.6, 129.8, 129.7, 129.1 (d), 128.7 (d), 127.1, 126.8, 125.3, 125.1, 123.6, 120.3, 120.2, 120.1, 81.5, 81.4, 80.9, 80.8, 76.8, 76.6, 45.5, 45.4, 44.5, 44.4, 35.3, 34.8, 26.7, 26.5, 19.6, 19.0; ^{31}P NMR δ -11.82, -12.00; Anal. Calcd for $C_{32}H_{30}NO_7P$: C, 67.24; H, 5.29. Found: C, 67.66; H, 5.70.

45. Same procedure as for **3**. 2 Isomers 89%. Anal. Calcd for $C_{33}H_{44}O_4Si.1/4H_2O$: C, 73.77; H, 8.35. Found: C, 73.87; H, 8.35. Isomer 1 ^{1}H NMR δ 7.68 (m, 4 H), 7.44-7.29 (m, 11 H), 5.01 (m, 1 H), 4.47 (br. s, 1 H), 4.09-3.90 (m, 2 H), 3.75-3.58 (m, 2 H), 3.54 (m, 1 H), 2.14-1.57 (m, 9 H), 1.07 (s, 9 H), 0.94 (d, *J* = 6.9 Hz, 3 H); ^{13}C NMR δ 141.8, 135.8, 133.9, 133.8, 129.8, 128.6, 127.9, 127.8, 127.1, 95.3, 77.8, 73.4, 71.7, 66.9, 66.7, 62.5, 42.9, 42.0, 41.1, 30.6, 27.0, 25.5, 19.6, 19.4, 13.1, 11.0. Isomer 2 ^{1}H NMR δ 7.68 (m, 4 H), 7.46-7.26 (m, 11 H), 5.18-4.80 (m), 4.46 (m), 4.07 (m), 3.85-3.50 (m), 3.27 (m) (7 H), 2.18-1.43 (m, 9 H), 1.07 (m, 9 H), 0.98-0.84 (m, 3 H).

46. NaH (0.123 g, 60% in paraphin, 3.073 mmol) was added at room temperature to a solution of **45** (0.545 g, 1.024 mmol) in THF (12 mL). The reaction mixture was stirred at room temperature for 1.5 h before CS_2 (0.184 mL, 3.073 mmol) was added. Then CH_3I (0.255 mL, 4.10 mmol) was added over 1 h. The resulting reaction mixture was stirred at room tempereature for 20 h. before it was quenched by addition of saturated NH_4Cl solution (10 mL) dropwise and then EtOAc (60 mL). The water layer was extracted with EtOAc (3 x 15 mL) and the combined extracts were washed subsequently with water (15 mL) and brine (15 mL), then dried (Na_2SO_4) and concentrated to dryness. Column chromatography on silica gel (Hexane/EtOAc 5/1) gave **46** (0.588 g, 92%) as a colorless

oil. ^{1}H NMR δ 7.64 (m, 4 H), 7.42-7.25 (m, 11 H), 5.94 (m), 5.83 (dt, *J* = 10.1, 3.4 Hz) (1 H), 4.82 (m, 1 H), 4.39 (m, 1 H), 3.94 (m, 1 H), 3.58 (ddd, *J* = 20.1, 10.0, 6.8 Hz, 1 H), 3.51 (m, 2 H), 2.51 (s), 2.48 (s) (3 H), 2.44 (m), 2.33-2.05 (m) (2 H), 1.88 (m), 1.57 (m), 1.29 (m) (7 H), 1.04 (s), 0.97 (s) (9 H), 0.96-0.86 (m, 3 H); ^{13}C NMR δ 214.7 (d), 141.3, 141.0, 135.8, 133.8, 133.7, 133.6 (d), 129.7, 128.7, 128.0, 127.8, 127.6, 127.4, 95.3, 95.0, 82.9, 82.0, 74.3, 74.0, 65.5, 65.2, 62.6, 62.3, 38.8, 38.4, 38.0, 37.4, 30.8, 29.9, 27.0, 26.9, 25.7, 19.6, 19.3, 18.8, 11.8.

47. AIBN (32.3 mg, 0.180 mmol) was added to a solution of **46** (0.5605 g, 0.901 mmol) and n-Bu_3SnH (0.363 mL, 1.352 mmol) in PhH (10.0 mL) at room temperature and the resulting reaction mixture was brought to reflux for 2 h. After cooling the solvent was removed under vacuum and the residue was dissolved in methanol (4 mL) and treated with $NaBH_4$ (51.4 mg, 1.352 mmol) at room temperature. After 5 min the methanol was removed under vacuum and the residue was partitioned between EtOAc (60 mL) and saturated NH_4Cl solution (15 mL). The aqueous layer was extracted with EtOAc (3 x 15 mL) and the combined extracts were washed subsequently with water (15 mL) and brine (15 mL), then dried (Na_2SO_4) and concentrated to dryness. Column chromatography on silica gel (Hexane/EtOAc 100/0 then 10/1) gave **47**, a mixture of 2 isomers (0.44 g, 95%) as a colorless oil. Anal. Calcd for $C_{33}H_{44}O_3Si.1/4H_2O$: C, 76.03; H, 8.60. Found: C, 75.77; H, 8.61. Isomer 1 ^{1}H NMR δ 7.69 (m, 4 H), 7.44-7.26 (m, 11 H), 4.68 (t, *J* = 7.2 Hz, 1 H), 4.44 (t, *J* = 3.3 Hz, 1 H), 3.98(m,, 1 H), 3.50 (m, 3 H), 2.01-1.35 (m, 9 H), 1.08(s), 1.06 (s) (9 H), 0.95 (d, *J* = 6.6 Hz), 0.93 (d, *J* = 5.1 Hz) (3 H); ^{13}C NMR δ 142.8, 135.8, 134.2, 129.6, 128.5, 127.7, 127.6, 127.2, 95.3, 77.6, 69.0, 62.4, 35.9, 30.9, 29.7, 27.0, 25.8, 19.7, 19.5, 16.9. Isomer 2 ^{1}H NMR δ 7.69 (m, 4 H), 7.44-7.26 (m,11 H), 4.84 (dd, *J* = 5.7, 2.8 Hz), 4.42 (t, *J* = 3.6 Hz) (1 H), 4.66 (t, *J* = 7.0 Hz), 4.54 (dt, *J* = 6.4, 2.4 Hz) (1 H), 4.33 (t, *J* = 6.7 Hz), 3.93 (m) (1 H), 3.59-3.42 (m), 3.28 (m) (3 H), 1.95-1.30 (m, 9 H), 1.07 (s, 9 H), 1.02-0.90 (m, 3 H).

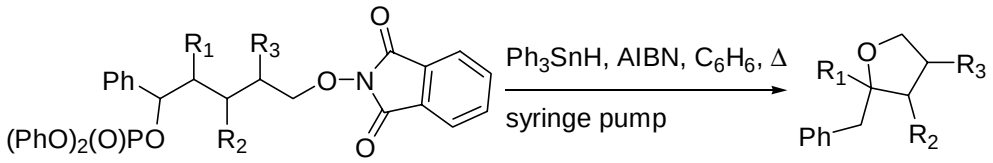
48. Same procedure as for **5**. 2 Isomers 76%. Anal Calcd for $C_{17}H_{26}O_3$: C, 73.34; H, 9.41. Found: C, 72.84; H, 9.66. Isomer 1 ^{1}H NMR δ 7.35-7.25 (m, 5 H), 4.66 (m, 1 H), 4.37 (t, *J* = 3.0 Hz, 1 H), 3.93 (m, 1 H), 3.44 (m, 3 H), 1.95-1.32 (m), 1.09 (m) (9 H), 0.90 (d, *J* =

6.7 Hz), 0.88 (d, *J* = 6.5 Hz) (3 H); ^{13}C NMR δ 142.7, 142.5, 128.5, 127.6, 127.1, 127.0, 96.0, 95.7, 77.8, 77.6, 63.0, 62.8, 35.9, 35.8, 35.7, 31.0, 29.4, 29.3, 25.7, 20.0, 19.9, 16.8. Isomer 2 ^{1}H NMR δ 7.37-7.21 (m, 5 H), 4.82 (t, *J* = 3.3 Hz), 4.37 (t, *J* = 3.2 Hz) (1 H), 4.67 (m), 4.56 (m) (1 H), 3.93 (m), 3.55-3.34 (m), 3.26 (dt, *J* = 11.2, 4.7 Hz) (4 H), 1.95-1.00 (m, 9 H), 0.92-0.86 (m, 3 H); ^{13}C NMR δ 143.7, 143.6, 142.7, 128.5, 128.3, 127.6, 127.1, 127.0, 126.7, 126.6, 98.3, 98.2, 96.0, 95.7, 79.4, 79.3, 77.8, 68.2, 63.0, 62.9, 62.1, 35.9 (d), 35.8, 35.7, 34.6 (d), 31.0, 30.8, 29.4, 29.3, 28.9, 28.0, 25.7, 25.6, 20.0 (d), 19.4, 17.7, 16.7.

49. Same procedure as for **6**. 83%. ^{1}H NMR δ 7.82 (m, 2 H), 7.73 (m, 2 h), 7.38-7.24 (m, 5 H), 4.85 (m), 4.39 (t, *J* = 3.2 Hz) (1 H), 4.67 (m), 4.58 (dt, *J* = 10.8, 6.1 Hz) (1 H), 4.05 (m, 1 H), 3.93 (m), 3.50 (m), 3.27 (dt, *J* = 11.1, 4.5 Hz) (3 H), 1.98-1.39 (m, 6 H), 1.09 (d, *J* = 6.8 Hz), 1.06 (d, *J* = 7.5 Hz), 1.05 (d, *J* = 6.7 Hz), 1.04 (d, *J* =7.0 Hz) (3 H); ^{13}C NMR δ 163.7, 143.6, 143.5, 142.6, 142.5, 134.6, 129.2, 128.5, 128.3, 127.6, 127.1, 126.7, 126.6, 123.6, 98.2, 95.4, 83.6, 83.5, 79.1, 79.0, 62.5, 62.1, 35.7, 35.5, 34.4, 34.2, 32.6, 30.8, 29.7, 29.0, 25.7, 25.6, 19.7, 19.4, 16.9, 16.8; Anal. Calcd for $C_{25}H_{29}NO_5$: C, 70.90; H, 6.90. Found: C, 71.06; H, 7.10.

50. Same procedure as for **7**. 83%. ^{1}H NMR δ 7.81 (m, 2 H), 7.73 (m, 2 H), 7.37-7.24 (m, 5 H), 4.69 (br.q), 4.00 (m, 2 H), 2.40 (br s), 2.32 (br s) (1 H), 1.97 (m), 1.88 (m), 1.63 (m), 1.46 (m), 1.25 (m) (5 H), 1.04 (d, *J* = 6.8 Hz, 3 H); ^{13}C NMR δ 163.8, 145.0, 134.6, 129.1, 128.6, 127.6, 126.0 (d), 123.6, 83.4 (d), 74.9, 74.4, 36.4, 36.3, 32.6, 32.3, 29.4, 29.2, 16.8, 16.7; Anal. Calcd for $C_{20}H_{21}NO_4$: C, 70.78; H, 6.24. Found: C, 71.21; H, 6.65.

51. Same procedure as for **10**. 97%. ^{1}H NMR δ 7.80 (m, 2 H), 7.72 (m, 2 H), 7.35-7.05 (13 H), 6.97 (d, 2 H), 5.52 (dd, *J* = 13.1, 5.8 Hz, 1 H), 3.96 (ddd, *J* = 10.0, 7.7, 1.5 Hz, 1 H), 3.88 (t, *J* = 7.7 Hz, 1 H), 2.18-1.88 (m, 3 H), 1.61-1.40 (m, 1 H), 1.35-1.12 (m, 1 H), 1.00 (dd, *J* = 6.7, 2.1 Hz, 3 H); ^{13}C NMR δ 163.6, 150.8, 150.7, 150.6, 139.6, 134.6, 129.8, 129.7, 129.1, 128.6, 126.7, 125.4, 125.2, 123.6, 120.4, 120.3, 120.2, 83.2, 35.1 (q), 32.3 (d), 28.8, 28.7, 16.8.



52: $R_1 = R_2 = R_3 = H$
53: $R_1 = Me$, $R_2 = R_3 = H$
54: $R_1 = R_3 = H$, $R_2 = Me$
55: $R_1 = R_2 = H$, $R_3 = Me$

General Procedure for the Hydrogen Abstraction/Cyclisation Sequence:
A solution of Ph_3SnH (1.3 eq) and AIBN (50 mol%) in degassed PhH (0.002 M in Ph_3SnH) or in degassed CH_3CN and PhH (v/v 1/1) (0.002 M in Ph_3SnH) was added with a syringe pump (0.49 mL/h) under Ar to a refluxing solution of the phosphate in degassed PhH (0.001 M in phosphate). Stirring was continued for another 2 h after the addition finished before the solvent was removed under vacuum. In each case inspection the crude reaction mixture was inspected by ^{1}H NMR spectroscopy before it was subjected to preparative TLC (Hexane/EtOAc 10/1) to afford the product.

52.[5] 95% when $ClP(O)(OPh)_2$ was used. 60% when $ClP(O)(OEt)_2$**.** ^{1}H NMR δ 7.34-7.22 (m, 5 H), 4.09 (m, 1 H), 3.91 (q, *J* = 8.0 Hz, 1 H), 3.77 (dt, *J* = 8.0, 6.5 Hz, 1 H), 2.95 (dd, *J* = 13.6, 6.4 Hz, 1 H), 2.77 (dd, *J* = 13.6, 6.5 Hz, 1 H), 1.88 (m, 3 H), 1.58 (m, 1 H); ^{13}C NMR δ 139.1, 129.4, 128.4, 126.3, 80.2, 68.0, 42.1, 31.1, 25.7.

53.[6] 90% when $ClP(O)(OPh)_2$ was used. 85% when $ClP(O)(OEt)_2$**.** ^{1}H NMR δ 7.31-7.21 (m, 5 H), 3.85 (m, 1 H), 3.79 (m, 1 H), 2.80 (s, 2 H), 1.97-1.82 (m, 3 H), 1.76 (m), 1.63 (m) (1 H), 1.19 (s, 3 H); ^{13}C NMR δ 138.6, 130.5, 128.0, 126.2, 82.9, 67.5, 47.0, 36.3, 26.5, 26.1.

54. 90%. ^{1}H NMR δ 7.27 (m, 5 H), 4.04 (dt, *J* = 8.1, 5.5 Hz), 3.97 (dt, *J* = 14.7, 8.0 Hz) (1 H), 3.83 (m), 3.74 (ddd, *J* = 14.1, 8.5, 5.6 Hz), 3.59 (dt, *J* = 7.3, 5.0 Hz) (2 H), 2.90-2.70 (m, 2 H), 2.27 (m), 2.08 (m), 1.89 (m), 1.67-1.47 (m) (3 H), 1.03 (d, *J* = 7.0 Hz), 0.97 (d, *J* = 6.5 Hz), (3 H); ^{13}C NMR δ 139.9, 139.3, 129.5, 129.2, 128.5 (d), 126.3,

126.2, 86.5, 82.5, 67.0, 66.4, 40.7, 38.8, 37.1, 35.7, 34.8, 34.1, 17.5, 14.7. Anal. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.52; H, 9.23.

55. 92%. ^{1}H NMR δ 7.24 (m, 5 H), 4.21 (m), 4.10 (m) (1 H), 4.02 (dd, *J* = 8.2, 6.9 Hz), 3.90 (t, *J* = 7.8 Hz) (1 H), 3.38 (t, *J* = 8.0 Hz), 3.28 (dd, *J* = 8.2, 7.0 Hz) (1 H), 3.00 (dd, *J* = 9.9, 4.8 Hz), 2.94 (dd, *J* = 10.2, 4.8 Hz) (1 H), 2.80 (dd, *J* = 10.2, 5.1 Hz), 2.74 (dd, *J* = 9.9, 4.8 Hz) (1 H), 2.30 (m), 2.08 (m) (1 H), 1.81 (m), 1.54 (m) (1 H), 1.26-1.10 (m, 1 H), 1.03 (d, *J* = 6.6 Hz), 1.00 (d, *J* = 6.8 Hz) (3 H);^{13}C NMR δ 139.2, 129.4 (d), 128.5, 126.3, 81.0, 79.7, 75.3, 74.8, 42.5, 40.8, 39.3, 34.5, 33.3, 18.2, 18.0. . Anal. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 82.04; H, 9.19.

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