Lewis Acid Catalyzed Intramolecular Diels-Alder Reactions of Acyclic (*Z*)-Substituted 1,3-Dienes

Neal A. Yakelis and William R. Roush*

Department of Chemistry, University of Michigan, Ann Arbor, MI 48109

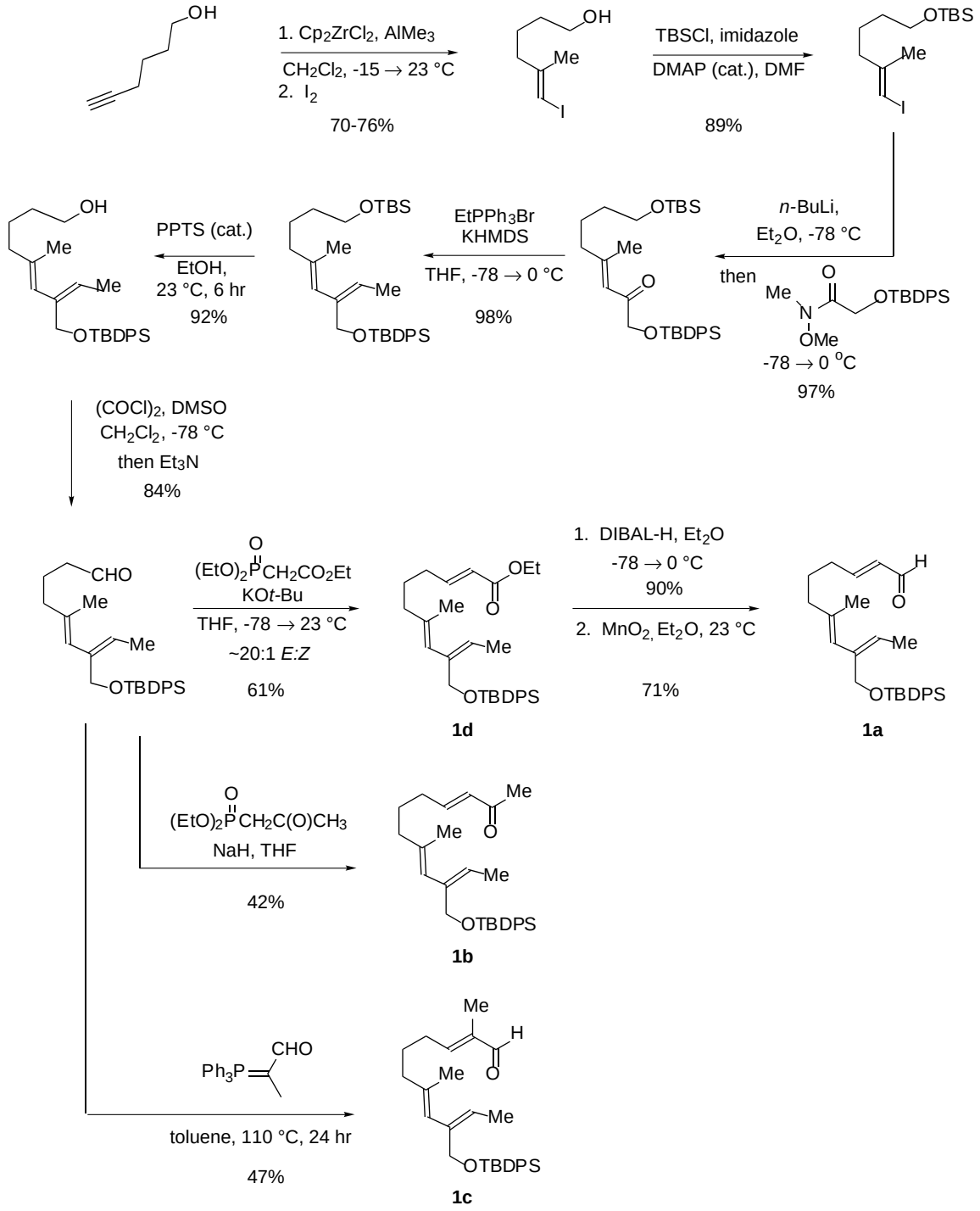
Email Address: roush@umich.edu

SUPPORTING INFORMATION

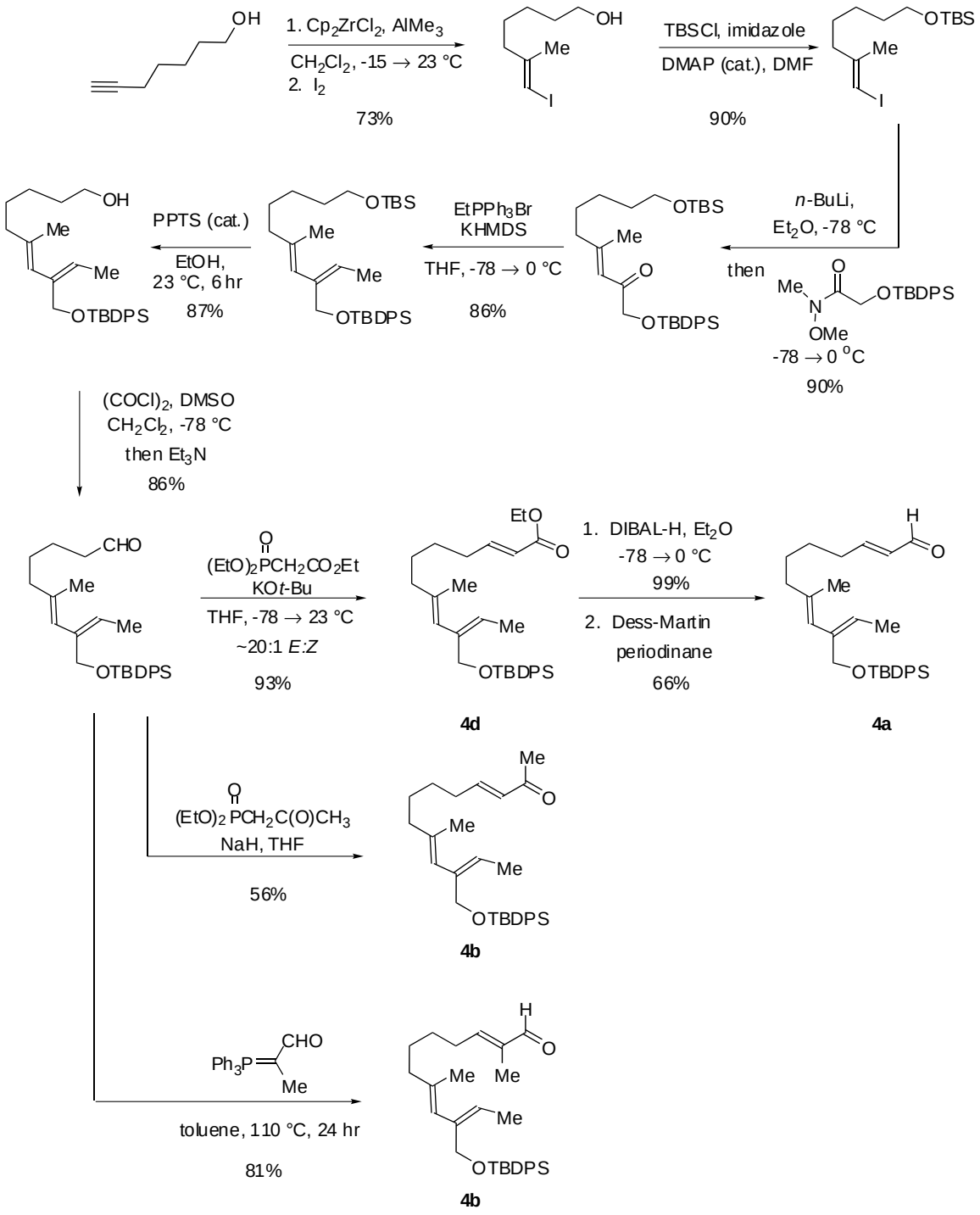
Summaries of the syntheses of trienes **1a-c**, **4a-c**, and **7a,b**; representative procedure for the Lewis acid catalyzed intramolecular Diels-Alder reactions of **1a-c**, **4a-c**, and **7a,b**; tabulated spectroscopic data for cycloadducts **2a-c**, **3a**, **3c**, **5a-c**, **6a**, **6c**, and **8a,b**; and summaries of cycloadduct stereochemical assignments (17 pages).

Summaries of the Syntheses of Trienes 1a-c, 4a-c, and 7a,b

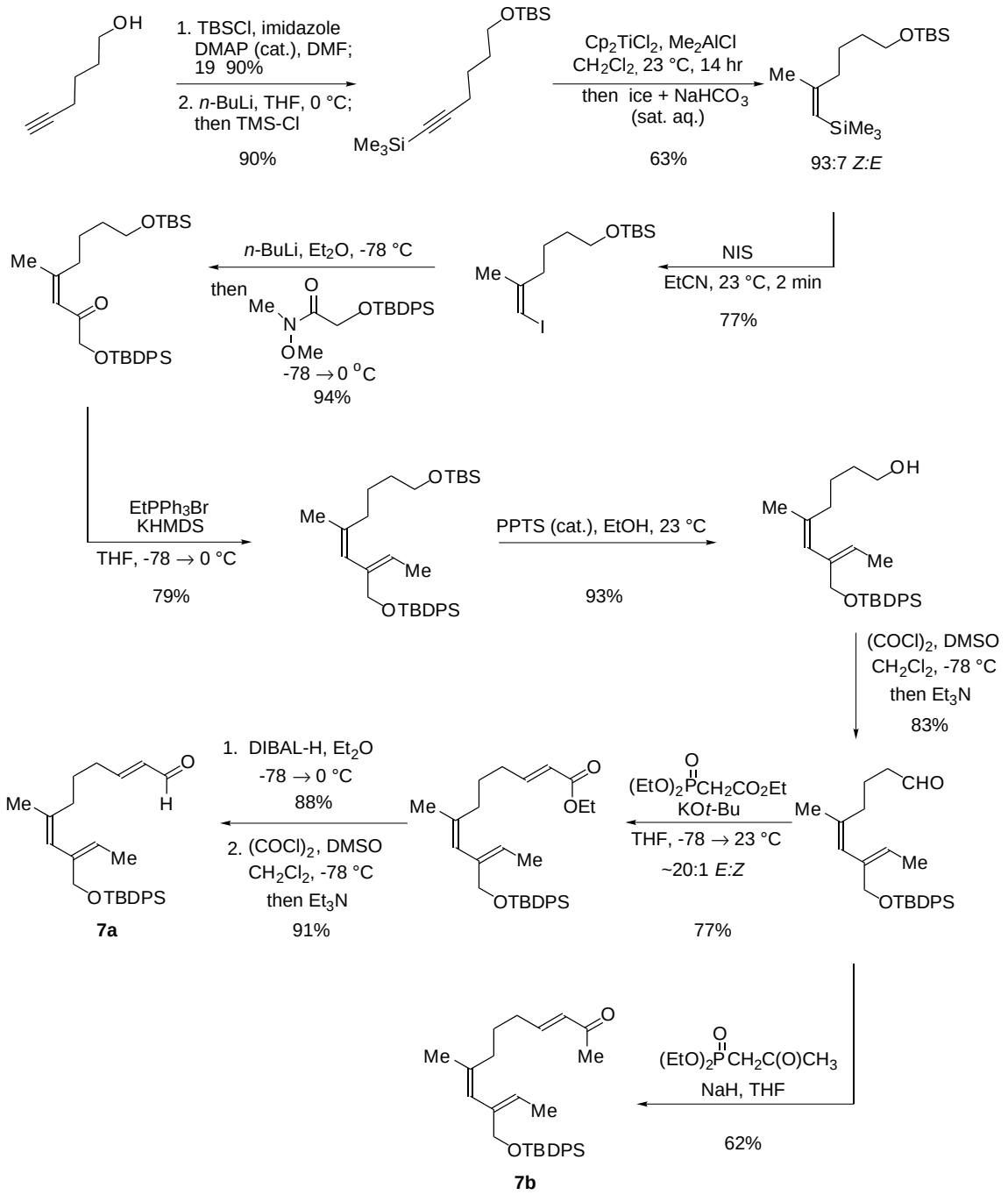
Scheme 1. Synthesis of trienes **1a-c** from 5-hexyn-1-ol.



Scheme 2. Synthesis of trienes **4a-c** from 6-heptyn-1-ol.

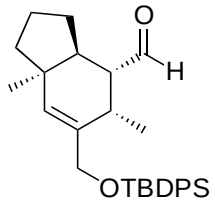


Scheme 3. Synthesis of trienes **7a,b** from 5-hexyn-1-ol.



Representative Procedure for the Lewis Acid Catalyzed IMDA reactions

A solution of **7a** (54 mg, 0.12 mmol) in anhydrous CH_2Cl_2 (4 mL) was cooled to -78 ℃ under an atmosphere of dry nitrogen. A 1.0 M solution of methyl aluminum dichloride in hexanes (Aldrich) (73 μL, 73 μmol) was added dropwise via microliter syringe. Since a prior trial experiment had shown that product formation did not begin until the reaction temperature reached approximately -30 °C, the yellow solution was warmed immediately to -20 °C. After two hours (-20 → -15 °C), the reaction was diluted with 10 mL diethyl ether and quenched with a saturated solution of Rochelle's salt (aq) (5 mL). The resulting mixture was extracted with ether (2 x 25 mL), and the combined organic extracts were washed with brine, dried over $MgSO_4$, filtered, and concentrated. After silica gel flash chromatography of the crude product (40:1 hexanes:EtOAc), the Diels-Alder adduct **8a** was isolated as a clear oil (45 mg, 83 % yield).

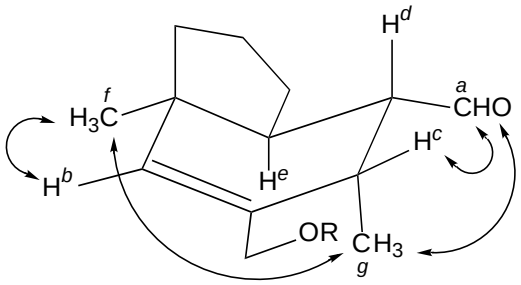


8a

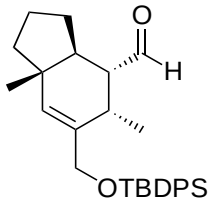
(3a*R*,4*S*,5*S*,7a*R*)-6-([(*tert*-butyldiphenylsilyl)oxy]methyl)-5,7a-dimethyl-2,3,3a,4,5,7a-hexahydro-1*H*-indene-4-carbaldehyde (8a)

R_f 0.49 (9:1 hexanes:EtOAc)**;** ^{1}H NMR (C_6D_6, 500 MHz) δ 9.46 (d, *J* = 1.3 Hz, 1 H), 7.82-7.79 (m, 4 H), 7.26-7.23 (m, 6 H), 5.53 (s, 1 H), 4.15 (A of AB, d, *J* = 13.2 Hz, 1 H), 4.06 (B of AB, d, *J* = 13.2 Hz, 1 H), 2.40 (qd, *J* = 7.0, 3.1 Hz, 1 H), 2.04 (m, 3 H), 1.46 (m, 2 H), 1.39-1.25 (m, 3 H), 1.19 (s, 9 H), 0.91 (s, 3 H), 0.75 (d, *J* = 7.0 Hz, 3 H) ; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 206.0, 135.8, 135.8, 131.8, 129.9, 127.9, 127.8, 76.9, 66.1, 56.9, 43.3, 40.4, 39.3, 31.3, 30.1, 29.3, 27.1, 23.4, 19.5, 15.3; IR (neat) 3071, 3049, 2957, 2932, 2858, 2711, 1959, 1892, 1819, 1722, 1589, 1472, 1461, 1428, 1390, 1373, 1262, 1186, 1112, 1065, 998, 940, 872, 823, 740, 702 cm^{-1}; HRMS (CI, NH_3) for $C_{29}H_{42}NO_2Si$ $[M+NH_4]^+$ calcd. 464.2985, found 464.2964.

^{1}H NMR nOe structure assignment for **8a**:



H	δ (C_6D_6)	*J*=
a	9.46	1 Hz
b	5.53	—
c	2.40	3, 7 Hz
d	1.46	(m)
e	1.46	(m)
f	0.91	—
g	0.75	7 Hz

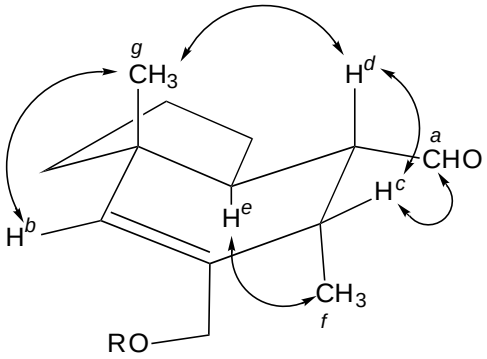


2a

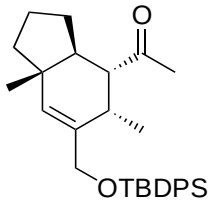
(3a*R*,4*S*,5*S*,7a*R*)-6-([(*tert*-butyldiphenylsilyl)oxy]methyl)-5,7a-dimethyl-2,3,3a,4,5,7a-hexahydro-1*H*-indene-4-carbaldehyde (2a)

R_f 0.39 (9:1 hexanes:EtOAc); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 9.80 (d, *J* = 2.5 Hz, 1 H), 7.69-7.65 (m, 4 H), 7.45-7.35 (m, 6 H), 5.83 (s, 1 H), 4.20 (A of AB, d, *J* = 12.4 Hz, 1 H), 4.04 (B of AB, d, *J* = 12.4 Hz, 1 H), 2.91 (qd, *J* = 7.0, 6.1 Hz, 1 H), 2.61 (ddd, *J* = 11.8, 6.1, 2.6 Hz, 1 H), 1.99 (m, 1 H), 1.89 (m, 1 H), 1.79-1.72 (m, 2 H), 1.76 (m, 1 H), 1.33-1.22 (m, 2 H), 1.06 (s, 9 H), 0.98 (d, *J* = 7.0 Hz, 3 H), 0.77 (s, 3 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 205.6, 138.2, 135.6, 135.5, 133.7, 132.1, 129.6, 129.6, 127.6, 127.6, 66.0, 51.3, 43.0, 41.5, 35.5, 32.1, 26.9, 23.8, 21.0, 20.9, 19.3, 15.4; IR (neat) 3071, 3049, 2959, 2858, 2714, 1958, 1891, 1822, 1723, 1654, 1590, 1472, 1462, 1428, 1374, 1239, 1112, 1048, 1007, 959, 938, 864, 823, 740, 702, 614, 504 cm^{-1}; HRMS (CI, NH_3) for $C_{29}H_{42}NO_2Si$ $[M+NH_4]^+$ calcd. 464.2985, found 464.2973. *Anal.* Calcd. for $C_{29}H_{38}O_2Si$: C, 77.97; H, 8.57. Found: C 78.13; H 8.70.

^{1}H NMR nOe structure assignment for **2a**:



H	δ ($CDCl_3$)	*J*=
a	9.80	3 Hz
b	5.83	—
c	2.91	6, 7 Hz
d	2.61	3, 6, 12 Hz
e	1.99	(m)
f	0.98	7 Hz
g	0.77	—

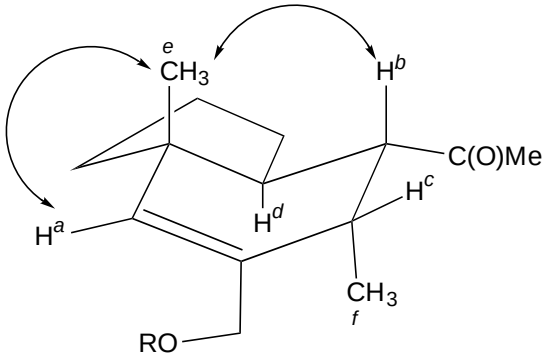


2b

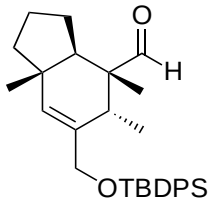
(3a*S*,4*S*,5*S*,7a*R*)-1-[6-([(*tert*-butyldiphenylsilyl)oxy]methyl)-5,7a-dimethyl-2,3,3a,4,5,7a-hexahydro-1*H*-inden-4-yl]ethanone (2b)

R_f 0.36 (9:1 hexanes:EtOAc); ^{1}H NMR (CD_3OD, 500 MHz) δ 7.58-7.55 (m, 4 H), 7.35-7.27 (m, 6 H), 5.69 (s, 1 H), 4.12 (A of AB, d, *J* = 12.3 Hz, 1 H), 3.96 (B of AB, d, *J* = 12.3 Hz, 1 H), 2.80 (dd, *J* = 11.7, 6.1 Hz, 1 H), 2.75 (qd, *J* = 6.8, 6.2 Hz, 1 H), 1.99 (s, 3 H), 1.88 (m, 1 H), 1.64-1.56 (m, 3 H), 1.32 (m, 1 H), 1.15 (m, 1 H), 0.94 (s, 9 H), 0.66 (s, 3 H), 0.60 (d, *J* = 7.0 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 210.8, 138.3, 135.8, 134.1, 132.5, 129.9, 127.8, 66.6, 52.2, 42.9, 42.0, 36.0, 33.1, 29.9, 27.1, 24.4, 21.3, 19.5, 15.2, 14.4; IR (neat) 3070, 3048, 2956, 2931, 2896, 2858, 1713, 1589, 1472, 1462, 1428, 1384, 1358, 1308, 1180, 1141, 1127, 1112, 1085, 1052, 1006, 823, 740, 702, 668, 610 cm^{-1}; HRMS (CI, NH_3) for $C_{30}H_{44}NO_2Si$ $[M+NH_4]^+$ calcd. 478.3141, found 478.3145. *Anal.* Calcd. for $C_{30}H_{40}O_2Si$: C, 78.21; H, 8.75. Found: C 78.00; H 8.83.

^{1}H NMR nOe structure assignment for **2b**:



H	δ (CD_3OD)	*J*=
a	5.69	—
b	2.80	6, 12 Hz
c	2.75	6 Hz
d	1.88	(m)
e	0.66	—
f	0.60	7 Hz

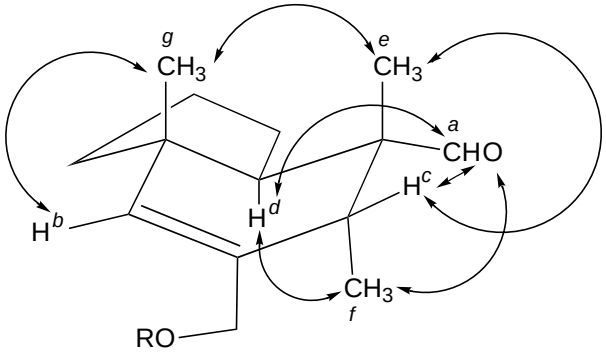


2c

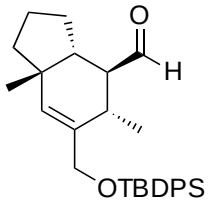
(3a*R*,4*S*,5*R*,7a*S*)-6-([(*tert*-butyldiphenylsilyl)oxy]methyl)-4,5,7a-trimethyl-2,3,3a,4,5,7a-hexahydro-1*H*-indene-4-carbaldehyde (2c)

^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.45 (s, 1 H), 7.69-7.66 (m, 4 H), 7.45-7.36 (m, 6 H), 5.92 (s, 1 H), 4.20 (A of AB, d, *J* = 12.7 Hz, 1 H), 4.06 (B of AB, d, *J* = 12.7 Hz, 1 H), 2.37 (q, *J* = 7.3 Hz, 1 H), 1.96 (dd, *J* = 13.5, 6.7 Hz, 1 H), 1.80-1.72 (m, 2 H), 1.69-1.61 (m, 1 H), 1.49-1.30 (m, 1 H), 1.25 (m, 2 H), 1.08 (s, 3 H), 1.05 (s, 9 H), 1.00 (d, *J* = 7.3 Hz, 3 H), 0.94 (s, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 206.9, 137.4, 135.8, 135.8, 133.9, 133.4, 129.9, 127.9, 127.8, 76.9, 66.4, 50.1, 45.3, 42.9, 39.9, 38.9, 29.9, 27.1, 21.3, 20.8, 19.5, 16.6, 15.4; IR (neat) 3070, 3044, 2958, 2928, 2856, 2698, 1726, 1590, 1461, 1428, 1378, 1130, 1112, 1050, 824, 739, 701 cm^{-1}; HRMS (CI, NH_3) for $C_{30}H_{41}O_2Si$ $[M+H]^+$ calcd. 461.2876, found 461.2877.

^{1}H NMR nOe structure assignment for **2c**:



H	δ ($CDCl_3$)	*J*=
a	9.45	—
b	5.92	—
c	2.37	7 Hz
d	1.96	7, 13 Hz
e	1.08	—
f	1.00	7 Hz
g	0.94	—

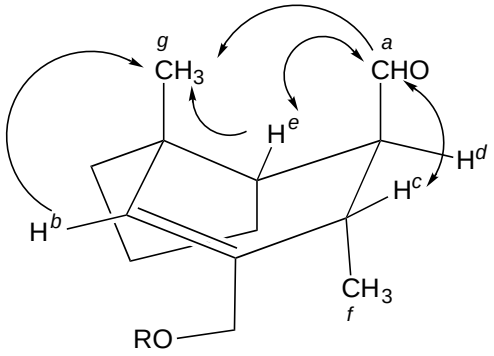


3a

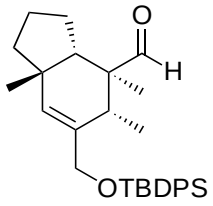
(3a*S*,4*R*,5*S*,7a*S*)-6-([(*tert*-butyldiphenylsilyl)oxy]methyl)-5,7a-dimethyl-2,3,3a,4,5,7a-hexahydro-1*H*-indene-4-carbaldehyde (3a)

^{1}H NMR (C_6D_6, 400 MHz) δ 9.25 (d, *J* = 4.2 Hz, 1 H), 7.82-7.79 (m, 4 H), 7.26-7.23 (m, 6 H), 5.51 (s, 1 H), 4.24 (A of AB, d, *J* = 12.7 Hz, 1 H), 4.08 (B of AB, d, *J* = 12.7 Hz, 1 H), 2.45 (dq, *J* = 8.0, 7.3 Hz, 1 H), 1.84 (ddd, *J* = 9.5, 8.4, 4.1 Hz, 1 H), 1.66 (m, 1 H), 1.68-1.64 (m 1 H), 1.52-1.44 (2 H), 1.38-1.30 (m, 3 H), 1.19 (s, 9 H), 0.91 (d, *J* = 7.1 Hz, 3 H), 0.89 (s, 3 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 205.6, 161.5, 135.8, 135.8, 132.0, 129.9, 129.8, 127.9, 127.8, 66.2, 58.8, 43.4, 43.2, 39.5, 29.9, 29.0, 28.4, 27.0, 22.4, 17.6; IR (neat) 3071, 3043, 2957, 2926, 2855, 2690, 1955, 1888, 1821, 1726, 1586, 1462, 1428, 1378, 1360, 1261, 1159, 1112, 1071, 1047, 1002, 938, 877, 824, 740, 701 cm^{-1}; HRMS (CI, NH_3) for $C_{29}H_{42}NO_2Si$ $[M+NH_4]^+$ calcd. 464.2985, found 464.2977.

^{1}H NMR nOe structure assignment for **3a**:



H	δ (C_6D_6)	*J*=
a	9.25	4 Hz
b	5.51	—
c	2.45	7, 8 Hz
d	1.84	4, 8, 10 Hz
e	1.66	(m)
f	0.91	7 Hz
g	0.89	—

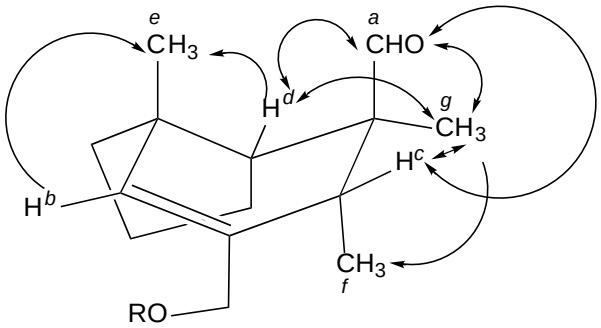


3c

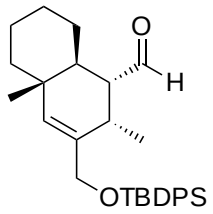
(3a*S*,4*R*,5*R*,7a*S*)-6-([(*tert*-butyldiphenylsilyl)oxy]methyl)-4,5,7a-trimethyl-2,3,3a,4,5,7a-hexahydro-1*H*-indene-4-carbaldehyde (3c)

R_f 0.43 (9:1 hexanes:EtOAc); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 9.35 (s, 1 H), 7.70-7.67 (m, 4 H), 7.44-7.36 (m, 6 H), 5.53 (s, 1 H), 4.21 (A of AB, d, *J* = 13.1 Hz, 1 H), 4.10 (B of AB, d, *J* = 13.1 Hz, 1 H), 2.48 (q, *J* = 7.4 Hz, 1 H), 2.12 (dd, *J* = 9.5, 6.5 Hz, 1 H), 1.87-1.81 (m, 1 H), 1.67-1.43 (m, 5 H), 1.06 (s, 9 H), 1.03 (s, 3 H), 1.01 (d, *J* = 7.1 Hz, 3 H), 0.97 (s, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 207.4, 136.6, 135.8, 135.8, 134.0, 132.5, 129.8, 127.9, 127.8, 66.6, 51.8, 48.7, 42.4, 34.1, 29.9, 29.7, 29.0, 27.1, 24.2, 19.5, 16.2, 14.6; IR (neat) 3072, 3049, 2956, 2929, 2856, 2698, 1958, 1889, 1819, 1726, 1589, 1462, 1428, 1390, 1372, 1362, 1261, 1112, 1068, 1034, 1006, 1000, 941, 891, 824, 739, 701 cm^{-1}; HRMS (CI, NH_3) for $C_{30}H_{41}O_2Si$ $[M+H]^+$ calcd. 461.2876, found 461.2873.

^{1}H NMR nOe structure assignment for **3c**:



H	δ ($CDCl_3$)	*J*=
a	9.35	—
b	5.53	—
c	2.48	7 Hz
d	2.12	7, 9 Hz
e	1.03	—
f	1.01	7 Hz
g	0.97	—

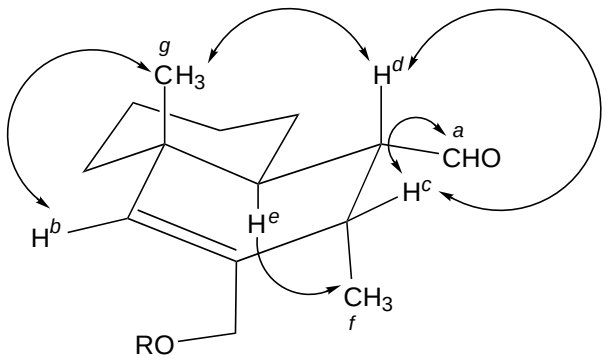


5a

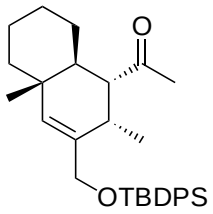
(1*S*,2*S*,4a*S*,8a*R*)-3-([(*tert*-butyldiphenylsilyl)oxy]methyl)-2,4a-dimethyl-1,2,4a,5,6,7,8,8a-octahydronaphthalene-1-carboxaldehyde (5a)

R_f 0.43 (9:1 hexanes:EtOAc); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 9.78 (d, *J* = 4.6 Hz, 1 H), 7.68-7.65 (m, 4 H), 7.44-7.36 (m, 6 H), 5.39 (s, 1 H), 4.18 (A of AB, d, *J* = 12.7 Hz, 1 H), 4.03 (B of AB, d, *J* = 12.7 Hz, 1 H), 2.66 (qd, *J* = 6.9, 6.0 Hz, 1 H), 2.44 (ddd, *J* = 12.2, 6.0, 4.6 Hz, 1 H), 1.90 (ddt, *J* = 12.3, 12.2, 2.9 Hz, 1 H), 1.58-1.52 (m, 3 H), 1.45 (m, 1 H), 1.38-1.20 (m, 3 H), 1.05 (s, 9 H), 1.05 (d, *J* = 6.9 Hz, 3 H), 0.89 (s, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 207.8, 136.8, 135.8, 135.8, 134.9, 133.9, 129.9, 127.9, 127.8, 66.0, 51.2, 39.0, 38.9, 35.5, 32.3, 29.9, 27.1, 26.9, 24.3, 21.5, 19.6, 19.5, 15.1; IR (neat) 3071, 3049, 2930, 2858, 2715, 1721, 1590, 1472, 1446, 1428, 1383, 1263, 1189, 1151, 1113, 1056, 999, 866, 824, 702, 740, 614 cm^{-1}; HRMS (CI, NH_3) for $C_{30}H_{44}NO_2Si$ $[M+NH_4]^+$ calcd. 478.3141, found 478.3148. *Anal.* Calcd. for $C_{30}H_{40}O_2Si$: C, 78.21; H, 8.75. Found: C 78.55; H 8.90.

^{1}H NMR nOe structure assignment for **5a**:



H	δ ($CDCl_3$)	*J*=
a	9.78	5 Hz
b	5.39	—
c	2.66	6 Hz
d	2.44	5, 6, 12 Hz
e	1.99	3, 12, 12 Hz
f	1.05	7 Hz
g	0.89	—

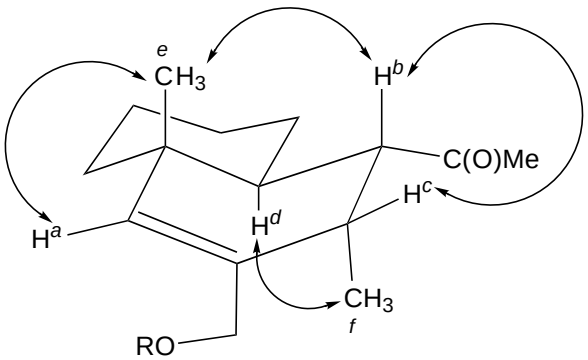


5b

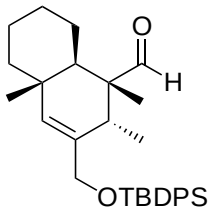
(1*S*,2*S*,4a*S*,8a*R*)-1-[3-([(*tert*-butyldiphenylsilyl)oxy]methyl)-2,4a-dimethyl-1,2,4a,5,6,7,8,8a-octahydronaphthalen-1-yl]-1-ethanone (5b)

R_f 0.42 (9:1 hexanes:EtOAc); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.69-7.55 (m, 4 H), 7.44-7.36 (m, 6 H), 5.35 (s, 1 H), 4.20 (A of AB, d, *J* = 13.5 Hz, 1 H), 4.05 (B of AB, d, *J* = 13.5 Hz, 1 H), 2.83 (dd, *J* = 11.8, 5.8 Hz, 1 H), 2.60 (qd, *J* = 7.0, 5.8 Hz, 1 H), 1.74 (m, 2 H), 1.64 (dd, *J* = 11.8, 11.8 Hz 1 H), 1.53-1.48 (m, 3 H), 1.41-1.28 (m, 2 H), 1.23-1.17 (m, 1 H), 1.06 (s, 9 H), 0.90 (s, 3 H), 0.76 (d, *J* = 7.1 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 210.7, 136.6, 135.8, 135.8, 135.8, 135.1, 134.1, 134.0, 129.9, 127.8, 127.8, 66.6, 52.2, 39.2, 39.0, 35.5, 31.9, 31.5, 27.1, 26.9, 23.3, 21.5, 19.7, 19.5, 15.2; IR (neat) 3070, 3048, 2929, 2857, 1959, 1888, 1822, 1713, 1669, 1589, 1472, 1446, 1428, 1385, 1359, 1296, 1259, 1219, 1189, 1143, 1112, 1055, 1090, 1055, 1006, 970, 952, 939, 882, 864, 823, 740, 702, 609 cm^{-1}; HRMS (CI, NH_3) for $C_{31}H_{43}O_2Si$ $[M+H]^+$ calcd. 475.3032, found 475.3046.

^{1}H NMR nOe structure assignment for **5b**:



H	δ ($CDCl_3$)	*J*=
a	5.35	—
b	2.83	6, 11 Hz
c	2.60	6 Hz
d	1.64	12, 12 Hz
e	0.90	—
f	0.76	7 Hz

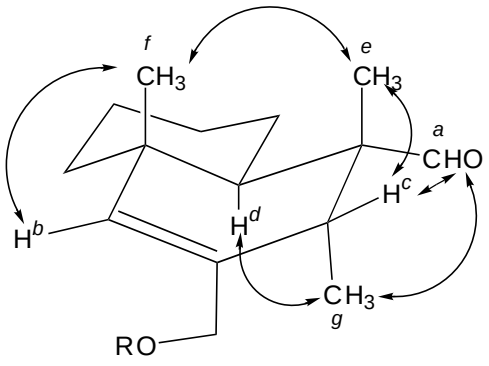


5c

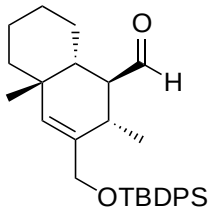
(1*R*,2*R*,4a*R*,8a*R*)-3-([(*tert*-butyldiphenylsilyl)oxy]methyl)-1,2,4a-trimethyl-1,2,4a,5,6,7,8,8a-octahydronaphthalene-1-carboxaldehyde (5c)

R_f 0.32 (9:1 hexanes:EtOAc); ^{1}H NMR (C_6D_6, 500 MHz) δ 9.41 (s, 1 H), 7.80-7.76 (m, 4 H), 7.26-7.23 (m, 6 H), 5.43 (s, 1 H), 4.11 (A of AB, d, *J* = 12.6 Hz, 1 H), 4.01 (B of AB, d, *J* = 12.8 Hz, 1 H), 2.03 (q, *J* = 7.2 Hz, 1 H), 1.91 (m, 1 H), 1.62 (m, 1 H), 1.44-1.37 (m, 2 H), 1.30-1.19 (m, 5 H), 1.17 (s, 9 H), 1.09 (s, 3 H), 0.91 (s, 3 H), 0.86 (d, *J* = 7.2 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 209.2, 198.1, 135.9, 135.8, 134.2, 129.9, 127.9, 127.8, 66.3, 42.5, 42.1, 39.7, 35.5, 29.9, 27.4, 27.1, 22.8, 21.7, 20.4, 19.5, 16.8, 16.0; IR (neat) 3071, 3049, 2925, 2854, 2708, 1726, 1589, 1462, 1428, 1378, 1259, 1188, 1112, 1081, 1060, 998, 883, 823, 738, 701 cm^{-1}; HRMS (CI, NH_3)for $C_{31}H_{46}NO_2Si$ $[M+NH_4]^+$ calcd. 492.3298, found 492.3306.

^{1}H NMR nOe structure assignment for **5c**:



H	δ (C_6D_6)	*J*=
a	9.41	—
b	5.43	—
c	2.03	7 Hz
d	1.91	(m)
e	1.09	—
f	0.91	—
g	0.86	7 Hz

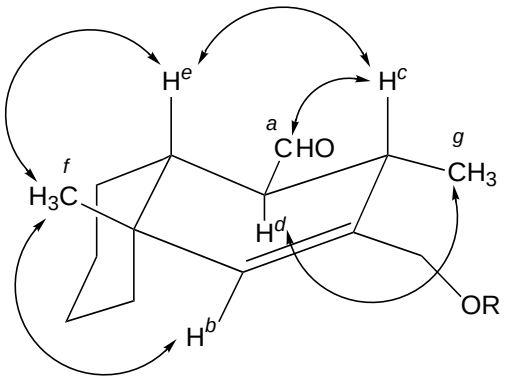


6a

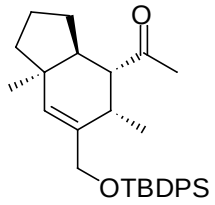
(1*R*,2*S*,4a*S*,8a*S*)-3-([(*tert*-butyldiphenylsilyl)oxy]methyl)-2,4a-dimethyl-1,2,4a,5,6,7,8,8a-octahydronaphthalene-1-carboxaldehyde (6a)

R_f 0.43 (9:1 hexanes:EtOAc); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 9.45 (d, *J* = 5.4 Hz, 1 H), 7.69-7.66 (m, 4 H), 7.44-7.35 (m, 6 H), 5.38 (s, 1 H), 4.25 (A of AB, d, *J* = 12.8 Hz, 1 H), 4.07 (B of AB, d, *J* = 12.8 Hz, 1 H), 2.56 (dq, *J* = 10.0, 7.0 Hz, 1 H), 2.41 (dddd, *J* = 11.5, 10.0, 5.4, 1.8 Hz, 1 H), 1.76 (m, 1 H), 1.51-1.26 (m, 7 H), 1.08 (s, 3 H), 1.05 (s, 9 H), 0.97 (d, *J* = 7.0 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 205.7, 135.8, 135.8, 134.8, 134.0, 129.9, 129.8, 127.9, 127.8, 66.1, 55.1, 38.6, 34.9, 34.1, 30.6, 27.0, 25.9, 25.0, 21.8, 20.6, 19.5, 17.5; IR (neat) 3070, 2930, 2858, 2695, 1725, 1589, 2462, 2428, 1360, 1261, 1194, 1135, 1112, 1064, 1007, 934, 888, 824, 740, 702 cm^{-1}; HRMS (CI, NH_3) for $C_{30}H_{44}NO_2Si$ $[M+NH_4]^+$ calcd. 478.3141, found 478.3129. *Anal.* Calcd. for $C_{30}H_{40}O_2Si$: C, 78.21; H, 8.75. Found: C 78.21; H 8.90.

^{1}H NMR nOe structure assignment for **6a**:



H	δ ($CDCl_3$)	*J*=
a	9.45	5 Hz
b	5.38	—
c	2.56	7, 10 Hz
d	2.41	5, 10, 12 Hz
e	1.76	(m)
f	1.08	—
g	0.97	7 Hz

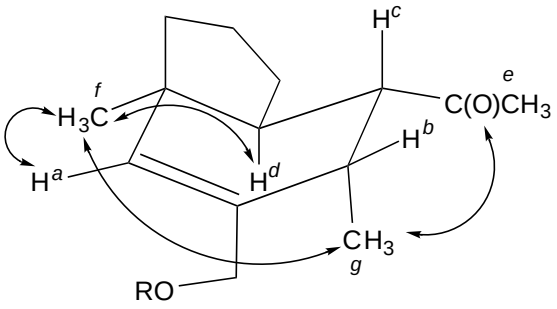


8b

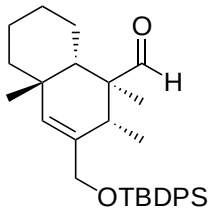
(3a*R*,4*S*,5*S*,7a*R*)-1-[6-([(*tert*-butyldiphenylsilyl)oxy]methyl)-5,7a-dimethyl-2,3,3a,4,5,7a-hexahydro-1*H*-inden-4-yl]ethanone (8b)

R_f 0.46 (9:1 hexanes:EtOAc); ^{1}H NMR (d_6-acetone, 500 MHz) δ 7.74-7.71 (m, 4 H), 7.48-7.41 (m, 6 H), 5.57 (s, 1 H), 4.29 (A of AB, d, *J* = 13.2 Hz, 1 H), 4.16 (B of AB, d, *J* = 13.2 Hz, 1 H), 2.63 (qd, *J* = 6.9, 4.4 Hz, 1 H), 2.59 (dd, *J* = 11.9, 4.4 Hz, 1 H), 2.13 (m, 1 H), 2.08 (s, 3 H), 1.64-1.52 (m, 2 H), 1.49-1.42 (m, 2 H), 1.19-1.11 (m, 2 H), 1.07 (s, 9 H), 1.01 (s, 3 H), 0.69 (d, *J* = 6.9 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 211.1, 137.9, 135.8, 135.8, 133.9, 131.7, 129.9, 127.9, 127.8, 66.4, 58.8, 43.2, 40.1, 39.6, 32.0, 31.6, 30.0, 29.3, 27.1, 23.2, 19.5, 15.0; IR (neat) 3071, 3049, 2957, 2932, 2858, 1960, 1894, 1822, 1710, 1672, 1589, 1472, 1461, 1428, 1380, 1351, 1283, 1258, 1186, 1151, 1127, 1112, 1088, 1061, 998, 940, 874, 823, 740, 702, 690 cm^{-1}; HRMS (CI, NH_3) for $C_{30}H_{44}NO_2Si$ $[M+NH_4]^+$ calcd. 478.3141, found 478.3132. *Anal.* Calcd. for $C_{30}H_{40}O_2Si$: C, 78.21; H, 8.75. Found: C 78.32; H 8.81.

^{1}H NMR nOe structure assignment for **8b**:



H	δ (d_6-acetone)	*J*=
a	5.57	—
b	2.63	4, 7 Hz
c	2.59	4, 11 Hz
d	2.13	(m)
e	2.08	—
f	1.01	—
g	0.69	7 Hz



6c

(1*S*,2*R*,4a*R*,8a*S*)-3-([(*tert*-butyldiphenylsilyl)oxy]methyl)-1,2,4a-trimethyl-1,2,4a,5,6,7,8,8a-octahydronaphthalene-1-carboxaldehyde (6c) could not be isolated as a completely pure compound after extensive purification procedures (silica chromatography and multiple HPLC runs). It was observed in the reaction crude as a minor product. Spectral data that was deciphered from partially purified material: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 9.32 (s, 1H), 7.71-7.66 (m, 4 H), 7.43-7.35 (m, 6 H), 5.36 (s, 1 H), 4.25 (A of AB, d, *J* = 12.7 Hz, 1 H), 4.07 (B of AB, d, *J* = 12.7 Hz, 1 H), 2.69 (q, *J* = 7.5 Hz, 1 H), 2.37-2.29 (m, 2 H).