Synthesis of Enantiomerically Enriched Allenes by (−)-Sparteine-Mediated Lithiation of Alkynyl Carbamates

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SUPPORTING INFORMATION

1. General Experimental:

^{1}H NMR spectra and ^{13}C NMR spectra were recorded on a Bruker AM 300 (300 MHz, ^{1}H; 75 MHz, ^{13}C). Chemical shifts are reported in ppm (δ); multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quartet), qn (quintet), sext (sextet), sept (septet) and m (multiplet). The numbering of the compounds can differ from the IUPAC name. Mass spectroscopy and elemental analysis were performed at the University of Münster. Analytical thin-layer chromatography was performed on Merck silica gel plates (Silica gel 60 F_{254}). Visualization was accomplished with UV light and CAM-solution. Column chromatography was carried out using Merck silica gel 60 (230-400 mesh). Analytical capillary gas chromatography (GC) was performed using the folowing gas chromatograph, fitted with a flame ionization detector: Hewlett Packard Series 5890 Series II. The following columns were used: HP 1 (25 m); HP 1701 (25 m). IR absorption spectra were recorded using a Nicolet 5 DXC. The optical rotations were measured using a Perkin-Elmer 241. All solvents were dried and distilled according to standard procedures. All reactions were performed under an argon atmosphere in dried glassware.

2. Deprotonation of 3 and substitution with electrophiles. – General procedure:

a) Deprotonation/substitution without crystallization of the lithium ion pair **5**:

To a solution of (–)-sparteine (0.29 ml, 1.1 mmol) and alkynyl carbamate **3** (1.0 mmol) in dry toluene (5 ml) at –78 °C, *n*butyllithium in hexane (1.6 M, 0.69 ml, 1.1 mmol) was added. After stirring for 30 min (no crystallization occurred), the electrophile (3.0 mmol) was added dropwise. Stirring was continued for 2 h at –78 °C, and then a mixture of methanol (3 mmol) and diethyl ether (5 ml), followed by 2 N aq. HCl (5 ml) was added. The aq. phase was extracted with diethyl ether (3 x 15 ml) and dried over Na_2SO_4/$NaHCO_3$. After evaporation of the solvent in vacuo, the residue was purified by flash column chromatography on silica gel.

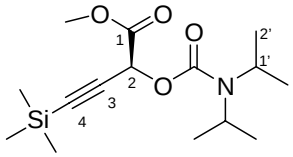
For carboxylation, gaseous CO_2 (liberated from dry ice) was introduced via a gas inlet for 15 min. Stirring was continued for 1 h and the reaction mixture was quenched with 2 N aq. HCl (5 ml). After drying over $MgSO_4$, the solvent was evaporated. The esterfication of the crude product was performed by addition of an ethereal solution of diazomethane.

b) Deprotonation/substitution with crystallization of the lithium ion pair **5**:

To a solution of (–)-sparteine (0.29 ml, 1.3 mmol) and alkynyl carbamate **3** (1.0 mmol) in dry pentane (3 ml) at –78 °C, *n*butyllithium in hexane (1.6 M, 0.81 ml, 1.3 mmol) was added. After stirring for 4 h, the electrophile (10 equiv.) was added very rapidly. Stirring was continued for 2 h at –78 °C, and then a mixture of methanol (3 mmol) and diethyl ether (5 ml), followed by 2 N aq. HCl (5 ml) was added. The aq. phase was extracted with diethyl ether (3 x 15 ml) and dried over Na_2SO_4/$NaHCO_3$. After evaporation of the solvent in vacuo, the residue was purified by flash column chromatography on silica gel.

For carboxylation, gaseous CO_2 (liberated from dry ice) was introduced via a gas inlet for 15 min. Stirring was continued for 1 h and the reaction mixture was quenched with 2 N aq. HCl (5 ml). After drying over $MgSO_4$, the solvent was evaporated. The esterfication of the crude product was performed by addition of an ethereal solution of diazomethane.

(*S*)-2-(*N*,*N*-Diisopropylcarbamoyloxy)-4-(trimethylsilyl)-but-3-ynoic acid methyl ester (6a)



R_f = 0.48 (Et_2O/PE=1/1); t_R= 14.43 min (HP1); shift experiment: 5 mg + 10 mg $Eu(hfc)_3$ in $CDCl_3$, $\Delta\delta$ (OCH_3)= 0.20 ppm; IR (neat): ν [cm^{-1}] = 2980, 2950, 2920, 2880 (C-H), 2170 (C≡C), 1755 (CO_2Me), 1690 (NC=O), 840 (C-Si); ^{1}H-NMR (300 MHz): δ = 0.17 (s, 9 H, $SiMe_3$), 1.25 (d, $^3J_{2',1'}$ = 6.92 Hz, 12 H, 2'-H_3), 3.82 (s, 3 H, OCH_3), 3.94 (m, 2 H, 1'-H_1), 5.80 (s, 1 H, 1-H_1); ^{13}C-NMR (75 MHz): δ = 0.00 ($SiMe_3$), 20.12 (C-2'), 46.48 (C-1'), 53.34 (OCH_3), 63.46 (C-1), 92.87 (C-3), 97.36 (C-2), 154.07 (NC=O), 167.51 (CO_2CH_3); $C_{15}H_{27}NO_4Si$ (313.47): calcd. C 57.48, H 8.68, N 4.47; found C 57.60, H 8.61, N 4.54.

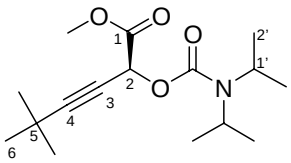
a) Deprotonation/substitution without crystallization of the lithium ion pair **5**:

240 mg (77 %) colourless oil; $[\alpha]_D^{22}$ = +10.3 (c = 1.04 in CH_2Cl_2, 17 % *ee*).

b) Deprotonation/substitution with crystallization of the lithium ion pair **5**:

224 mg (72 %) colourless oil; $[\alpha]_D^{22}$ = +40.9 (c = 1.02 in CH_2Cl_2, 85 % *ee*).

(*S*)-2-(*N*,*N*-Diisopropylcarbamoyloxy)-5,5-dimethyl-hex-3-ynoic acid methyl ester (6b)



R_f = 0.56 (Et_2O/PE=1/1); t_R= 14.12 min (HP1); shift experiment: 5 mg + 20 mg Eu(hfc)$_3$ in $CDCl_3$, Δδ (OCH_3)= 0.21 ppm; IR (neat): ν [cm^{-1}] = 2951, 2910, 2858 (C-H), 2230 (C≡C), 1765 (CO_2Me), 1683 (NC=O); ^{1}H-NMR (300 MHz): δ = 1.22 (m, 21 H, 6-H_3 and 2'-H_3), 3.79 (s, 3 H, OCH_3), 3.97 (m, 2 H, 1'-H_1), 5.74 (s, 1 H, 2-H_1); ^{13}C-NMR (75 MHz): δ = 20.98 (C-2'), 27.85 (C-5), 30.94 (C-6), 46.48 (C-1'), 53.14 (OCH_3), 63.35 (C-2), 71.52 (C-4), 96.17 (C-3), 154.30 (NC=O), 168.23 (CO_2CH_3); $C_{16}H_{27}NO_4$ (297.39): calcd. C 64.62, H 9.15, N 4.71; found C 64.36, H 9.12, N 4.82.

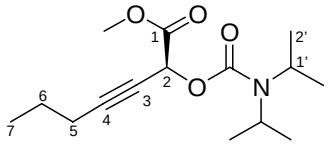
a) Deprotonation/substitution without crystallization of the lithium ion pair **5**:

232 mg (78 %) colourless oil; $[\alpha]_D^{22}$ = +14.5 (c = 1.03 in CH_2Cl_2, 23 % *ee*).

b) Deprotonation/substitution with crystallization of the lithium ion pair **5**:

230 mg (77 %) colourless oil; $[\alpha]_D^{22}$ = +40.2 (c = 1.23 in CH_2Cl_2, 76 % *ee*).

(*S*)-2-(*N*,*N*-Diisopropylcarbamoyloxy)-hept-3-ynoic acid methyl ester (6c)



R_f = 0.38 (Et_2O/PE=1/1); t_R= 15.16 min (HP1); shift experiment: 7 mg + 7 mg Eu(hfc)$_3$ in $CDCl_3$, Δδ (OCH_3)= 0.11 ppm; IR (neat): ν [cm^{-1}] = 2973, 2934, 2875 (C-H), 2243 (C≡C), 1776 (O=CCH_3), 1703 (NC=O); ^{1}H-NMR (300 MHz): δ = 0.98 (t, $^3J_{7,6}$ = 7.3 Hz, 3 H, 7-H_3), 1.25 (d, $^3J_{2',1'}$ = 6.5 Hz, 12 H, 2'-H_3), 1.55 (sext, $^3J_{6,7}$ = $^3J_{6,5}$ = 7.3 Hz, 2 H, 6-H_2), 2.22 (dt, $^3J_{5,6}$ = 7.3 Hz, $^5J_{5,2}$ = 2.2 Hz, 2 H, 5-H_2), 3.80 (s, 3 H, OCH_3), 3.93 (m, 2 H, 1'-H_1), 5.74 (t, $^5J_{2,5}$ = 2.2 Hz, 1 H, 2-H_1); ^{13}C-NMR (75 MHz): δ = 13.62 (C-7), 21.09, 22.02 (C-6, C-4, C-2'), 46.68 (C-1'), 53.09 (OCH_3), 63.37 (C-1), 73.19 (C-3), 88.16 (C-2),154.22 (NC=O), 168.08 (CO_2CH_3); $C_{15}H_{25}NO_4$ (283.26): calcd. C 63.58, H 8.89, N 4.94; found C 63.44, H 8.90, N 4.78.

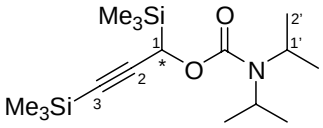
a) Deprotonation/substitution without crystallization of the lithium ion pair **5**:

82 % (233 mg) colourless oil; $[\alpha]_D^{22}$ = +0.4 (c = 1.18 in CH_2Cl_2, 2 % *ee*).

b) Deprotonation/substitution with crystallization of the lithium ion pair **5**:

No crystallization occurred.

(+)-1,3-Bis(trimethylsilyl)-prop-2-ynyl *N,N*-diisopropylcarbamate (6d)



R_f = 0.62 (Et_2O/PE=1/1); t_R= 13.71 min (HP1); IR (neat): ν [cm^{-1}] = 3010, 2958, 2939 (C-H), 2324 (C≡C), 1712 (NC=O), 868 (C-Si); ^{1}H-NMR (300 MHz): δ = 0.12 and 0.13 (s, 9 H, $SiMe_3$), 0.12 (d, $^3J_{2',1'}$ = 6.91 Hz, 12 H, 2'-H_3), 3.88 (m, 2 H, 1'-H_1), 5.17 (s, 1 H, 1-H_1); ^{13}C-NMR (75 MHz): δ = –3.74 and 0.00 ($SiMe_3$), 21.25 (C-2'), 46.14 (C-1'), 59.16 (C-1), 92.00 (C-3), 103.71 (C-2), 155.71 (NC=O); $C_{16}H_{33}NO_2Si_2$ (327.61): calcd. C 58.66, H 10.15, N 4.28; found C 58.61, H 10.06, N 4.47.

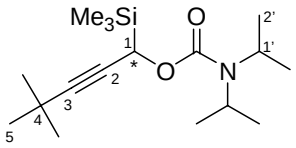
a) Deprotonation/substitution without crystallization of the lithium ion pair **5**:

262 mg (80 %) colourless oil; $[\alpha]_D^{22}$ = +20.4 (c = 0.98 in CH_2Cl_2).

b) Deprotonation/substitution with crystallization of the lithium ion pair **5**:

218 mg (67 %) colourless oil; $[\alpha]_D^{22}$ = +79.2 (c = 1.01 in CH_2Cl_2).

(+)-4,4-Dimethyl-1-(trimethylsilyl)-pent-2-ynyl *N,N*-diisopropylcarbamate (6e)



R_f = 0.58 (Et_2O/PE=1/3); t_R= 13.46 min (HP1); shift experiment: 10 mg + 15 mg Eu(hfc)$_3$ in $CDCl_3$, Δδ ($SiMe_3$)= 0.03 ppm, Δδ (5-H_3)= 0.05 ppm; IR (neat): ν [cm^{-1}] = 2973, 2934, 2908, 2868 (C-H), 2230 (C≡C), 1697 (NC=O), 854 (C-Si); ^{1}H-NMR (300 MHz): δ = 0.14 (s, 9 H, $SiMe_3$), 1.19 (s, 9 H, 5-H_3), 1.21 (d, $^3J_{2',1'}$ = 6.8 Hz, 12 H, 2'-H_3), 3.91 (m, 2 H, 1'-H_1), 5.16

(s, 1 H, 1-H_1); ^{13}C-NMR (75 MHz): δ = –3.23 ($SiMe_3$), 21.65 (C-2‘), 28.14 (C-4), 31.61 (C-5), 46.64 (C-1‘), 59.21 (C-1), 76.56 (C-3), 96.83 (C-2), 156.56 (NC=O); $C_{17}H_{33}NO_2Si$ (311.54): calcd. C 65.54, H 10.68, N 4.50; found C 65.29, H 10.95, N 4.64.

a) Deprotonation/substitution without crystallization of the lithium ion pair **5**:

286 mg (86 %) colourless oil; $[\alpha]_D^{22}$ = +25.1 (c = 1.07 in CH_2Cl_2, 31 % *ee*).

b) *In situ* trapping of the lithium ion pairs **5** with $ClSiMe_3$ in the toluene:

249 mg (80 %) colourless oil; $[\alpha]_D^{22}$ = +19.3 (c = 1.04 in CH_2Cl_2, 22 % *ee*).

c) Lithio-destannylation and substitution with $ClSiMe_3$:

To a solution of 138 mg (0.34 mmol, > 95 % *ee*) of 4,4-dimethyl-1-(trimethylstannyl)-pent-2-ynyl *N*,*N*-diisopropylcarbamate **(7g)** and 0.17 ml (0.51 mmol) (–)-sparteine in dry toluene (5 ml) at –78 °C, ^{n}butyllithium in hexane (1.6 M, 0.28 ml, 0.45 mmol) was added. After stirring for 30 min, 0.13 ml (1.02 mmol) chlorotrimethylsilane was added. Stirring was continued for 2 h at –78 °C, and then a mixture of methanol (3 mmol) and diethyl ether (5 ml), followed by 2 N aq. HCl (5 ml) was added. The aq. phase was extracted with diethyl ether (3 x 15 ml), dried over Na_2SO_4/$NaHCO_3$. After evaporation of the solvent in vacuo, the residue was purified by flash column chromatography on silica gel.

65 mg (61 %) colourless oil; $[\alpha]_D^{22}$ = +39.6 (c = 0.79 in CH_2Cl_2, 40 % *ee*).

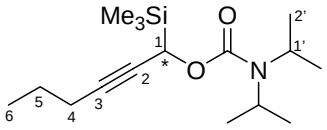
d) Deprotonation/substitution with crystallization of the lithium ion pair **5** – 3 mmol $ClSiMe_3$:

230 mg (74 %) colourless oil; $[\alpha]_D^{22}$ = +26.5 (c = 1.05 in CH_2Cl_2, 30 % *ee*).

e) Deprotonation/substitution with crystallization of the lithium ion pair **5** – 10 mmol $ClSiMe_3$:

198 mg (64 %) colourless oil; $[\alpha]_D^{22}$ = +72.8 (c = 1.00 in CH_2Cl_2, 93 % *ee*).

(+)-1-(Trimethylsilyl)-hex-2-ynyl *N*,*N*-diisopropylcarbamate (6f)



R_f = 0.50 (Et_2O/PE=1/3); t_R= 14.29 min (HP1); shift experiment: 10 mg + 20 mg $Eu(hfc)_3$ in $CDCl_3$, Δδ ($SiMe_3$)= 0.04 ppm; IR (neat): ν [cm^{-1}] = 2967, 2936, 2905, 2875 (C-H), 2225

(C≡C), 1703 (NC=O); ^{1}H-NMR (300 MHz): δ = 0.15 (s, 9 H, $SiMe_3$), 0.96 (t, $^3J_{6,5}$ = 7.28 Hz, 3 H, 6-H_3), 1.21 (d, $^3J_{2',1'}$ = 6.92 Hz, 12 H, 2'-H_3), 1.51 (qt, $^3J_{5,6}$ = $^3J_{5,4}$ = 7.28 Hz, 2 H, 5-H_2), 2.02 (tt, $^3J_{4,5}$ = 6.92 Hz, $^5J_{4,1}$ = 2.38 Hz, 2 H, 4-H_2), 3.69 and 4.17 (m, 2 H, 1'-H_1), 5.12 (t, $^5J_{1,4}$ = 2.38 Hz, 2 H, 1-H_1); ^{13}C-NMR (75 MHz): δ = -3.33 ($SiMe_3$), 13.69 (C-6), 21.44, 22.32, 22.69 (C-5, C-4, C-2'), 46.45 (C-1'), 59.13 (C-1), 78.10 (C-3), 87.88 (C-2), 156.33 (NC=O); $C_{16}H_{31}NO_2Si$ (297.51): calcd. C 64.59, H 10.50, N 4.71; found C 64.27, H 10.65, N 4.29.

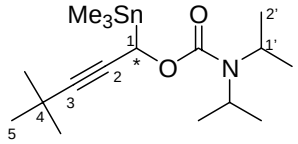
a) Deprotonation/substitution without crystallization of the lithium ion pair **5**:

178 mg (60 %) yellow oil; $[\alpha]_D^{22}$ = +5.0 (c = 1.0 in CH_2Cl_2, 6 % *ee*).

b) Deprotonation/substitution with crystallization of the lithium ion pair **5**:

No crystallization occurred.

(+)-4,4-Dimethyl-1-(trimethylstannyl)-pent-2-ynyl *N*,*N*-diisopropylcarbamate (6g)

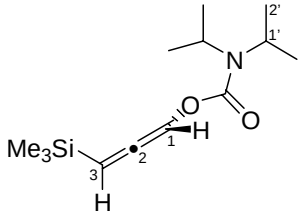


166 mg (41 %) colourless oil; R_f = 0.55 (Et_2O/PE=1/3); t_R= 14.72 min (HP1); shift experiment: 10 mg + 20 mg Eu(hfc)$_3$ in $CDCl_3$, Δδ (5-H_3)= 0.11 ppm; $[\alpha]_D^{22}$ = +26.7 (c = 1.18 in CH_2Cl_2, > 95 % *ee*); IR (neat): ν [cm^{-1}] = 2973, 2927, 2868 (C-H), 2223 (C≡C), 1677 (NC=O); ^{1}H-NMR (300 MHz): δ = 0.19 (s, 9 H, $SnMe_3$), 1.20 (d, $^3J_{2',1'}$ = 6.9 Hz, 12 H, 2'-H_3), 1.22 (s, 9 H, 5-H_3), 3.90 (m, 2 H, 1'-H_1), 5.15 (s, 1 H, 1-H_1); ^{13}C-NMR (75 MHz): δ = –8.10 ($SnMe_3$), 21.40 (C-2'), 28.16 (C-4), 31.62 (C-5), 46.26 (C-1'), 59.12 (C-1), 78.02 (C-3), 98.45 (C-2), 156.17 (NC=O); $C_{17}H_{33}NO_2Sn$ (402.16): calcd. C 50.77, H 8.27, N 3.48; found C 50.74, H 8.47, N 3.17.

3. General procedure for the syntheses of allenes 8:

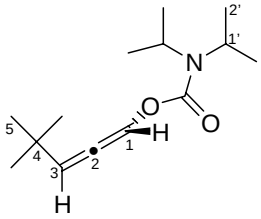
Into a solution of (–)-sparteine (0.29 ml, 1.3 mmol) and alkynyl carbamate **3** (1.0 mmol) in dry pentane (3 ml) at –78 °C was added ^{n}butyllithium in hexane (1.6 M, 0.81 ml, 1.3 mmol). After stirring for 4 h, a precooled (–78 °C) 1 M ClTi(O^iPr)$_3$-solution in toluene (4 ml) was injected very rapidly and fast stirring was continued for 10 min. Then a 1 M glacial acetic acid in diethyl ether (4 ml) was added and after 10 min, the reaction was quenched with 2 N aq. HCl-solution at –78 °C and extracted three times with diethyl ether. The combined organic layers were washed with sat. aq. $NaHCO_3$-solution, dried over Na_2SO_4. Removal of the solvents and purification by flash column chromatography furnished the desired allenes **8**.

(*aR*)-3-(Trimethylsilyl)-propa-1,2-dienyl *N,N*-diisopropylcarbamate (8a)



222 mg (87 %) yellow oil; R_f = 0.76 (Et_2O/PE=1/1); t_R= 12.68 min (HP1); chiral GC (chiral stationary phase: Beta-Dex 120, Supelco, USA): 108 °C, t_{R1} = 102.58 min and t_{R2} = 106.02 min; $[\alpha]_D^{22}$ = −123.5 (c = 1.02 in CH_2Cl_2, 88 % *ee*); IR (Film): ν [cm^{-1}] = 2968, 2937, 2907 (C-H), 1956 (C=C=C), 1715 (NC=O), 847 (C-Si); ^{1}H-NMR (300 MHz): δ = 0.11 (s, 9 H, $SiMe_3$), 1.19 and 1.20 (d, $^3J_{2',1'}$ = 6.91 Hz, 12 H, 2'H_3), 3.89 (m, 2 H, 1'-H_1), 5.85 (d, $^4J_{3,1}$ = 6.56 Hz, 1 H, 3-H_1), 7.37 (d, $^4J_{1,3}$ = 6.56 Hz, 1 H, 1-H_1); ^{13}C-NMR (75 MHz): δ = –1.31 ($SiMe_3$), 20.96 (C-2'), 46.17 (C-1'), 101.19 (C-3), 110.33 (C-1), 153.29 (NC=O), 204.41 (C-2); $C_{13}H_{25}NO_2Si$ (255.43): calcd. C 61.13, H 9.87, N 5.48; found C 61.20, H 9.98, N 5.54.

(*aR*)-4,4-Dimethyl-penta-1,2-dienyl *N,N*-diisopropylcarbamate (8b)

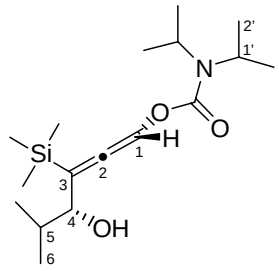


192 mg (80 %) yellow oil; R_f = 0.55 (Et_2O/PE=1/3); t_R= 12.31 min (HP1); $[\alpha]_D^{22}$ = −76.3 (c= 1.02 in CH_2Cl_2, 84 % *ee*); chiral GC (chiral stationary phase: Beta-Dex 120, Supelco, USA): 108 °C, t_{R1}= 93.14 min and t_{R2} = 99.60 min; IR (neat): ν [cm^{-1}] = 3068, 2936, 2904, 2871 (C-H), 1972 (C=C=C), 1709 (NC=O); ^{1}H-NMR (300 MHz): δ = 1.08 (s, 9 H, 5-H_3), 1.23 (d, $^3J_{2',1'}$ = 6.91 Hz, 12 H, 2'-H_3), 3.91 (m, 2 H, 1'-H_1), 5.79 (d, $^4J_{3,1}$ = 5.60 Hz, 1 H, 3-H_1), 7.44 (d, $^4J_{1,3}$ = 5.60 Hz, 1 H, 1-H_1); ^{13}C-NMR (75 MHz): δ = 21.43 (C-2'), 29.97 (C-5), 33.57 (C-4), 46.41 (C-1'), 113.44 (C-3), 117.07 (C-1), 153.60 (NC=O), 190.98 (C-2); $C_{14}H_{25}NO_2$ (239.35): calcd. C 70.25, H 10.53, N 5.85; found C 70.35, H 10.75, N 5.94.

4. General procedure for the syntheses of allenyl carbinols 11:

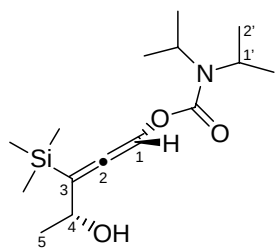
Into a solution of (–)-sparteine (0.29 ml, 1.3 mmol) and alkynyl carbamate **3** (1.0 mmol) in dry pentane (3 ml) at −78 °C was added ^{n}butyllithium in hexane (1.6 M, 0.81 ml, 1.3 mmol). After stirring for 4 h, a precooled (−78 °C) 1 M $ClTi(O^{i}Pr)_3$-solution in toluene (4 ml) was injected very rapidly and fast stirring was continued for 10 min. Then the aldehyde (4 mmol) was added and stirring was continued for 2 hours. The reaction was quenched with 2 N aq. HCl-solution at −78 °C and extracted three times with diethyl ether. The combined organic layers were dried over Na_2SO_4. Removal of the solvents and purification by flash column chromatography furnished the desired allenyl carbinol **11**.

(*aR*,*R*)-4-Hydroxy-5-methyl-3-(trimethylsilyl)-hexa-1,2-dienyl *N*,*N*-diisopropyl-carbamate (11a)



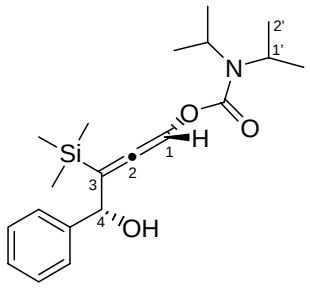
249 mg (76 %) yellow oil; R_f = 0.25 (Et_2O/PE=1/1); t_R= 17.10 min (HP1); $[\alpha]_D^{22}$ = − 64.3 (c = 1.01 in CH_2Cl_2, > 95 % *ee*); shift-experiment: 8 mg + 24 mg $Eu(hfc)_3$ in $CDCl_3$, Δδ (6-H_3)= 0.19 ppm; IR (neat): ν [cm^{-1}] = 3467 (OH), 2969, 2901, 2875 (C-H), 1946 (C=C=C), 1690 (C=O), 847 (C-Si); ^{1}H-NMR (300 MHz): δ = 0.17 (s, 9 H, $SiMe_3$), 0.87 and 1.03 (d, $^3J_{6,5}$ = 6.67 Hz, 6 H, 6-H_3), 1.22 (d, $^3J_{2',1'}$ = 6.92 Hz, 12 H, 2'-CH_3), 1.75 – 2.05 (br. s, 1 H, OH), 1.84 (dsept, $^3J_{5,6}$ = 6.67 Hz, $^3J_{5,4}$ = 4.05 Hz, 1 H, 5-H_1), 3.81 (m, 2 H, 1'-H_1), 4.05 (dd, $^5J_{4,1}$ = 2.15 Hz, $^3J_{4,5}$ = 4.05 Hz, 1 H, 4-H_1), 7.53 (s, 1 H, 1-H_1); ^{13}C-NMR (75 MHz): δ = –1.03 ($SiMe_3$), 15.13, 20.15 (C-6), 21.01 (C-2'), 33.08 (C-5), 46.10 (C-1'), 75.80 (C-4), 113.97 (C-1), 120.32 (C-3), 153.49 (NC=O), 196.53 (C-2); $C_{17}H_{33}NO_3Si$ (327.53): calcd. C 62.34, H 10.16, N 4.28; found C 62.15, H 10.45, N 4.61.

(*aR*,*R*)-4-Hydroxy-3-(trimethylsilyl)-penta-1,2-dienyl *N*,*N*-diisopropylcarbamate (11b)



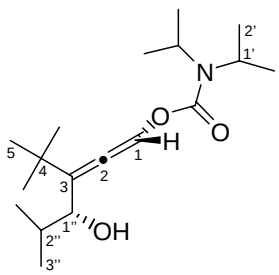
218 mg (73 %) colourless oil; R_f = 0.31 (Et_2O/PE=1/1); t_R= 15.76 min (HP1); $[\alpha]_D^{22}$ = –61.6° (c = 1.08, CH_2Cl_2, 93 % *ee*); chiral HPLC (chiral stationary phase: CHIRA-Grom-2, 8 µm, GROM Analytik + HPLC GmbH, Herrenberg, Germany): isopropanol/hexane =1/150, 0.3 ml/min, t_{R1} = 10.88 min and t_{R2} = 12.80 min; IR (neat): ν [cm^{-1}] = 3456 (OH), 3072, 2972, 2935, 2899 (C-H), 1953 (C=C=C), 1703 (NC=O), 841 (C-Si); ^{1}H-NMR (300 MHz): δ = 0.17 (s, 9 H, $SiMe_3$), 1.22 (d, $^3J_{2',1'}$ = 6.9 Hz, 12 H, 2'-H_3), 1.35 (d, $^3J_{5,4}$ = 6.4 Hz, 3 H, 5-H_3), 2.09 (br s, 1 H, OH), 3.94 (m, 2 H, 1'-H_1), 4.41 (dq, $^3J_{4,5}$ = 6.4 Hz, $^5J_{4,1}$ = 1.9 Hz, 1 H, 4-H_1), 7.46 (d, $^5J_{1,4}$ = 1.9 Hz, 1 H, 1-H_1); ^{13}C-NMR (75 MHz): δ = 0.00 ($SiMe_3$), 21.83 (C-2'), 25.23 (C-5), 47.29 (C-1'), 68.59 (C-4), 114.41 (C-1), 123.17 (C-3), 154.30 (NC=O), 196.90 (C-2); $C_{15}H_{29}NO_3Si$ (299.49): calcd. C 60.16, H 9.76, N 4.68; found C 60.21, H 10.12, N 4.78.

(*aR*,*R*)-4-Hydroxy-4-phenyl-3-(trimethylsilyl)-buta-1,2-dienyl *N*,*N*-diisopropylcarbamate (11c)



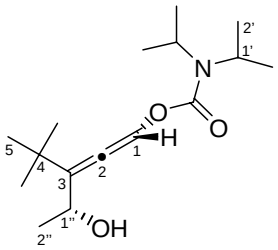
311 mg (86 %) yellow oil; R_f = 0.32 (Et_2O/PE=1/1); IR (neat): ν [cm^{-1}] = 3401 (OH), 3065, 3039, 2973, 2933, 2994, 2875 (C-H), 1947 (C=C=C), 1696 (NC=O), 854 (C-Si), 762, 703 (Ph); $[\alpha]_D^{22}$ = –226.5°(c = 1.02, CH_2Cl_2, > 95 % *ee*); enantiomeric excess was determined by an ^{1}H NMR shift experiment of the corresponding acetate **13c**; ^{1}H-NMR (300 MHz): δ = 0.00 (s, 9 H, $SiMe_3$), 1.29 (d, $^3J_{2',1'}$ = 6.7 Hz, 12 H, 2'-H_3), 3.14 (br s, 1 H, OH), 3.98 (m, 2 H, 1'-H_1), 5.28 (s, 1 H, 4-H_1), 7.45 – 7.45 (m, 5 H, Ph), 7.56 (d, $^5J_{1,4}$ = 1.9 Hz, 1 H, 1-H_1); ^{13}C-NMR (75 MHz): δ = 0.00 ($SiMe_3$), 22.26 (C-2'), 47.90 (C-1'), 75.23 (C-4), 115.77 (C-1), 122.29 (C-3), 128.65, 129.17, 129.59, 143.66 (Ph), 154.73 (NC=O), 197.63 (C-2); $C_{20}H_{31}NO_3Si$ (361.56): calcd. C 66.44, H 8.64, N 3.87; found C 66.60, H 8.60, N 3.81.

(*aS*,*R*)-3-*tert*-Butyl-4-hydroxy-5-methyl-hexa-1,2-dienyl *N*,*N*-diisopropylcarbamate (11d)



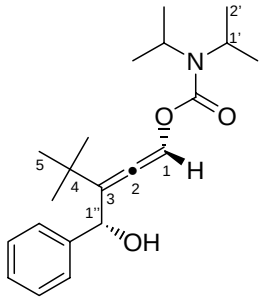
249 mg (80 %) colourless oil; R_f = 0.11 (Et_2O/PE=1/3); t_R= 17.01 min (HP1); $[\alpha]_D^{22}$ = +26.6 (c = 1.26 in CH_2Cl_2); IR (neat): ν [cm^{-1}] = 3448 (OH), 3072, 2963, 2937, 2905, 2872 (C-H), 1964 (C=C=C), 1709 (OC=O); ^{1}H-NMR (300 MHz): δ = 0.94 and 0.99 (d, $^3J_{3'',2''}$ = 6.68 Hz, 6 H, 3''-H_3), 1.14 (s, 12 H, 5-H_3), 1.23 (d, $^3J_{2',1'}$ = 6.68 Hz, 12 H, 2'-H_3), 1.84 (dsept, $^3J_{2'',3''}$ = $^3J_{2'',1''}$ = 6.92 Hz, 1 H, 2''-H_1), 3.82 (d, $^3J_{1'',2''}$ = 6.91 Hz, 1 H, 1''-H_1), 4.17 (m, 2 H, 1'-H_1), 7.63 (s, 1 H, 1-H_1); ^{13}C-NMR (75 MHz): δ = 17.59, 20.52 (C-3''), 21.56 (C-2'), 29.80 (C-5), 34.11 (C-2''), 35.13 (C-4), 46.50 (C-1'), 74.71 (C-1''), 116.01 (C-1), 132.11 (C-3), 153.81 (NC=O), 188.90 (C-2); $C_{18}H_{33}NO_3$ (311.46): calcd. C 69.41, H 10.68, N 4.50; found C 69.50, H 10.89, N 4.61.

(*aS*,*R*)-3-(1-Hydroxy-ethyl)-4,4-dimethyl-penta-1,2-dienyl *N*,*N*-diisopropyl-carbamate (11e)



229 mg (80 %) colourless oil; R_f = 0.36 (Et_2O/PE=1/1); t_R= 15.71 min (HP1); enantiomeric excess was determined by an ^{1}H NMR shift experiment of the corresponding acetate **13e**; $[\alpha]_D^{22}$ = +23.6 (c = 1.05, CH_2Cl_2, 93 % *ee*); IR (neat): ν [cm^{-1}] = 3441 (OH), 3071, 2970, 2935, 2872 (C-H), 1959 (C=C=C), 1703 (NC=O); ^{1}H-NMR (300 MHz): δ = 1.16 (s, 9 H, 5-H_3), 1.24 (d, $^3J_{1',2'}$ = 6.7 Hz, 12 H, 2'-H_3), 1.37 (d, $^3J_{5,4}$ = 6.3 Hz, 3 H, 2''-H_3), 1.92 (br. s, 1 H, OH), 3.95 (m, 2 H, 1'-H_1), 4.39 (q, $^3J_{4,5}$ = 6.3 Hz, 1 H, 1'-H_1), 7.60 (s, 1 H, 1-H_1); ^{13}C-NMR (75 MHz): δ = 22.65 (C-2'), 25.51 (C-2''), 29.77 (C-5), 35.10 (C-4), 46.58 (C-1'), 65.47 (C-1''), 116.17 (C-1), 134.60 (C-3), 153.81 (NC=O), 188.52 (C-2); $C_{16}H_{29}NO_3$ (283.41): calcd. C 67.81, H 10.31, N 4.94; found C 67.60; H 10.57; N 4.68.

(*aS*,*R*)-3-(Hydroxy-phenyl-methyl)-4,4-dimethyl-penta-1,2-dienyl *N*,*N*-diisopropylcarbamate (11f)

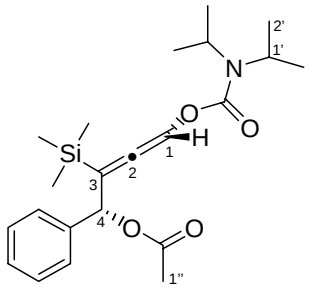


326 mg (86 %) white solid; mp. 91.8 °C; R_f = 0.25 (Et_2O/PE = 1/1); t_R = 20.62 min (HP1); $[\alpha]_D^{22}$ = –203.8 (c = 1.11, CH_2Cl_2, > 95 % *ee*); enantiomeric excess was determined by an ^{1}H NMR shift experiment of the corresponding acetate **13f**; IR (KBr): ν [cm^{-1}] = 3410 (OH), 3045 (C-$H_{arom.}$), 3020 – 2820 (C-$H_{aliph.}$), 1950 (C=C=C), 1680 (NC=O), 756, 693 (Ph); ^{1}H-NMR (300 MHz): δ = 1.07 (s, 9 H, 5-H_3), 1.25 (d, $^3J_{2',1'}$ = 6.9 H, 12 H, 2'-H_3), 2.52 (d, $^3J_{OH,1''}$ = 7.3 Hz, 1 H, OH), 4.09 and 3.79 (m, 2 H, 1'-H_1), 5.25 (d, $^3J_{1'',OH}$ = 7.3 Hz, 1 H, 1''-H_1), 7.49 – 7.17 (m, 5 H, Ph), 7.70 (d, $^5J_{1,4}$ = 1.4 Hz, 1 H, 1-H_1); ^{13}C-NMR (75 MHz): δ = 21.63 (C-2'), 30.17 (C-5), 35.22 (C-4), 47.45 (C-1'), 71.96 (C-1''), 117.32 (C-1), 127.71, 128.17, 128.70 (Ph), 132.77 (C-3), 143.37 (*ipso*-Ph), 153.72 (NC=O), 189.32 (C-2); $C_{21}H_{31}NO_3$ (345.48): found C 73.01, H 9.04, N 4.05; found C 73.19, H 9.23, N 4.01.

5. General procedure for the acetylation of the allenyl carbinol 11:

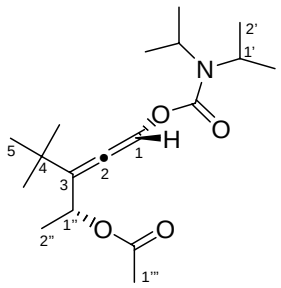
Into a solution of the allenyl carbinol (1 equiv.) in abs. pyridine (3.5 ml/mmol) and abs. dichloromethane (3.5 ml/mmol) at 0 °C was added DMAP (1.5 equiv.) and acetic anhydride (3 equiv.). After stirring for 4 hours at rt, the reaction mixture was quenched with sat. ammonium chloride solution, extracted three times with diethyl ether. The combined extracts were dried over magnesium sulfate, concentrated and purified by flash column chromatography.

(*aR*,*R*)-Acetic acid 4-(*N*,*N*-diisopropylcarbamoyloxy)-1-phenyl-2-(trimethylsilyl)-buta-2,3-dienyl ester (13c)



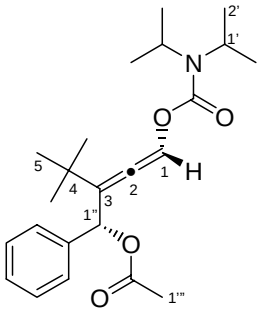
yellow oil; R_f = 0.50 (Et_2O/PE=1/1); t_R= 25.31 min (HP1701); shift experiment: 5 mg + 15 mg Eu(hfc)$_3$ in C_6D_6; Δδ ($SiMe_3$)= 0.03 ppm, Δδ (O_2CCH_3)= 0.29 ppm, Δδ (Ph)= 0.31 ppm or 0.12 ppm; ^{1}H-NMR (300 MHz): δ = 0.04 (s, 9 H, $SiMe_3$), 1.24 (d, $^3J_{2',1'}$ = 6.9 H, 12 H, 2'-H_3), 2.08 (s, 3 H, 1''-H_3), 3.91 (m, 2 H, 1'-H_1), 6.31(d, $^5J_{4,1}$ = 2.0 Hz, 1 H, 4-H_1), 7.42 – 7.26 (m, 5 H, Ph), 7.60 (d, $^5J_{1,4}$ = 2.0 Hz, 1 H, 1-H_1); ^{13}C-NMR (75 MHz): δ = 0.00 ($SiMe_3$), 22.34 (C-2', C-1''), 46.12 (C-1'), 76.49 (C-4), 114.78 (C-1), 118.19 (C-3), 129.19, 129.55, 129.62 (Ph), 139.80 (*ipso*-Ph), 154.54 (NC=O), 171.01 (OC=O), 200.28 (C-2); HRMS (+ES) m/z calcd. for $[C_{22}H_{33}NO_4SiNa]^+$ 426.2077, found for $[M]^+$ 426.2112.

(*aS*,*R*)-Acetic acid 2-*tert*-butyl-4-(*N*,*N*-diisopropylcarbamoyloxy)-1-methyl-buta-2,3-dienyl ester (13e)



colourless oil; R_f = 0.21 (Et_2O/PE=1/1); shift-experiment: 5 mg + 15 mg Eu(hfc)$_3$ in C_6D_6, Δδ (5-H_3)= 0.03 ppm, Δδ (O_2CCH_3)= 0.07 ppm; ^{1}H-NMR (300 MHz): δ = 1.07 (s, 9 H, 5-H_3), 1.17 (d, $^3J_{2',1'}$ = 6.7 Hz, 12 H, 2'-H_3), 1.29 (d, $^3J_{2'',1''}$ = 6.4 H, 3 H, 2''-H_3), 1.97 (s, 3 H, 1'''-H_3), 3.87 (m, 2 H, 1-H_1), 5.45 (dq, $^3J_{1'',2''}$ = 6.4 Hz, $^5J_{1'',1}$ = 0.7 Hz, 1 H, 1''-H_1), 7.58 (d, $^5J_{1,1''}$ = 0.7 Hz, 1 H, 1-H_1); ^{13}C-NMR (75 MHz): δ = 19.79, 21.33, 21.70 (C-2', C-2'', C-1'''), 29.70 (C-5), 35.30 (C-4), 46.95 (C-1'), 67.74 (C-1''), 115.66 (C-1), 129.04 (C-3), 153.67 (NC=O), 170.69 (OC=O), 191.96 (C-2); $C_{18}H_{31}NO_4$ (325.22): calcd. C 66.43, H 69.60, N 4.30; found C 66.48, H 9.67, N 4.17.

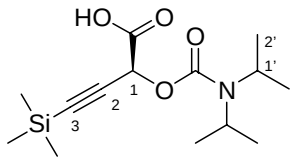
(*aS*,*R*)-Acetic acid 2-*tert*-butyl-4-(*N*,*N*-diisopropylcarbamoyloxy)-1-phenyl-buta-2,3-dienyl ester (13f)



colourless oil; R_f = 0.51 (Et_2O/PE=1/1); shift experiment: 5 mg + 15 mg Eu(hfc)$_3$ in C_6D_6; Δδ (5-H_3)= 0.02 ppm, Δδ (O_2CCH_3)= 0.34 ppm, Δδ(Ph)= 0.09 ppm or 0.11 ppm; ^{1}H-NMR (300 MHz): δ = 1.08 (s, 9 H, 5-H_3), 1.22 (d, $^3J_{2',1'}$= 6.9 Hz, 12 H, 2'-H_3), 2.05 (s, 3 H, 1'''-H_3), 4.13 and 3.73 (m, 2 H, 1'-H_1), 6.33 (s, 1 H, 1''-H_1), 7.49 – 7.20 (m, 5 H, Ph), 7.65 (d, $^5J_{1,1''}$= 1.2 Hz, 1 H, 1-H_1); ^{13}C-NMR (75 MHz): δ = 21.56 (C-2'), 21.60 (C-1'''), 30.03 (C-5), 35.43 (C-4), 46.53 (C-1'), 73.39 (C-1''), 116.09 (C-1), 128.29, 128.38 and 128.61 (Ph), 139.45 (*ipso*-Ph), 153.66 (NC=O), 170.25 (OC=O) 192.04 (C-2); HRMS (+ES) m/z calcd. for $[C_{23}H_{33}NO_4Na]^+$ 410.2307, found for $[M]^+$ 410.2350.

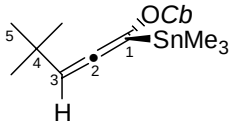
6. Spectroscopic data of the compounds 7, 9, and 12 used for X-ray analysis

(*S*)-2-(*N*,*N*-Diisopropylcarbamoyloxy)-4-(trimethylsilyl)-but-3-ynoic acid (7)



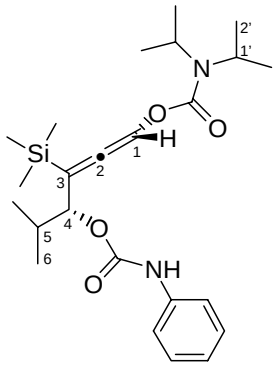
white solid; mp. 165.5 °C; R_f = 0.10 (Et_2O/PE = 1/1 with 0.5 % acetic acid); $[\alpha]_D^{22}$ = +43.1 (c=1.03 in CH_2Cl_2); IR (Film): ν [cm^{-1}] = 3454 (OH), 3055, 2975, 2938 (C-H), 2176 (C≡C), 1742, 1692 (CO_2H, NC=O), 848 (C-Si); ^{1}H-NMR (300 MHz): δ = 0.18 (s, 9 H, $SiMe_3$), 1.24 (d, $^3J_{2', 1'}$ = 5.96 Hz, 12 H, 2'-H_3), 3.91 (m, 2 H, 1-H_1), 5.79 (s, 1 H, 1-H_1), 9.66 (br. s, 1 H, O=COH); ^{13}C-NMR (75 MHz): δ = 0.00 ($SiMe_3$), 21.04 (C-2'), 46.72 (C-1'), 63.72 (C-1), 93.46 (C-3), 96.87 (C-2), 154.44 (NC=O), 171.05 (OC=O); $C_{14}H_{25}NO_4Si$ (299.44): calcd. C 56.16, H 8.42, N 4.68; found C 56.00, H 8.34, N 4.53.

(*aS*)-4,4-Dimethyl-1-(trimethylstannyl)-penta-1,2-dienyl *N*,*N*-diisopropylcarbamate (9)



white solid; mp. 38.8 °C; R_f = 0.89 (Et_2O/PE=1/1); t_R= 15.30 min (HP1); $[\alpha]_D^{22}$ = +36.1 (c = 1.15 in CH_2Cl_2, 85 % *ee*); shift experiment: 5 mg + 20 mg $Eu(hfc)_3$ in $CDCl_3$; Δδ (3-H_1)= 0.04 ppm; IR (Film): ν [cm^{-1}] = 2997, 2962, 2932, 2904, 2868 (C-H), 1934 (C=C=C), 1684 (NC=O); ^{1}H-NMR (300 MHz): δ = 0.17 (s, 9 H, $SnMe_3$), 1.06 (s, 9 H, 5-H_3), 1.21 (d, $^3J_{2',1'}$ = 6.61 Hz, 12 H, 2'-H_3), 3.78 and 4.04 (m, 2 H, 1'-H_1), 5.44 (s, 1 H, 3-H_1); ^{13}C-NMR (75 MHz): δ = -6.30 ($SnMe_3$), 20.76 (C-2'), 29.89 (C-5), 32.51 (C-4), 46.14 (C-1'), 109.29 (C-3), 123.56 (C-1), 154.95 (NC=O), 194.55 (C-2); $C_{17}H_{33}NO_2Sn$ (402.17): calcd. C 50.77, H 8.27, N 3.48; found C 51.12, H 8.14, N 3.43.

(*aR*,*R*)-Phenylcarbamic acid 4-(*N*,*N*-diisopropylcarbamoyloxy)-1-(1-methylethyl)-2-(trimethylsilyl)-buta-2,3-dienyl ester (12)



12 was obtained by stirring of **11a** (1.0 equiv.) with phenyl isocyanate (1.3 equiv.) in abs. pyridine (0.02 ml/mmol) and abs. toluene (5 ml/mmol) at rt for 92 hours. Yellow oil; R_f = 0.68 (Et_2O/PE=1/1); t_R= 23.94 min (HP1); $[\alpha]_D^{22}$ = +77.4 (c=1.05 in CH_2Cl_2); IR (KBr): ν [cm^{-1}] = 3298 (N-H), 3078, 2968, 2884 (C-H), 1949 (C=C=C), 1742, 1687 (NC=O), 854 (C-Si) 760, 696 (Ph); ^{1}H-NMR (300 MHz): δ = 0.18 (s, 9 H, $SiMe_3$), 0.97 and 1.01 (d, $^3J_{6,5}$ = 6.8 Hz, 6 H, 6-H_3), 1.23 (d, $^3J_{2',1'}$ = 6.8 Hz, 12 H, 2'-H_3), 2.02 (dsept, $^3J_{5,6}$ = 6.8 Hz, $^3J_{5,4}$ = 5.2 Hz, 1 H, 5-H_1), 3.92 (m, 2 H, 1'-H_1), 5.23 (dd, $^3J_{4,5}$ = 5.2 Hz, $^3J_{4,1}$ = 1.7 Hz, 1 H, 4-H_1), 6.78 (br. s, 1 H, N-H), 7.43 – 6.99 (m, 5 H, Ph), 7.49 (d, $^5J_{1,4}$ = 1.7 Hz, 1 H, 1-H_1); ^{13}C-NMR (75 MHz): δ = 0.00 ($SiMe_3$), 17.69, 20.63 (C-6), 22.12 (C-2'), 33.26 (C-5), 47.77 (C-1'), 79.21 (C-4), 114.14 (C-1), 117.20 (C-3), 119.90, 124.32, 130.01, 139.18 (Ph), 154.24, 154.57 (NC=O and O*Cb*), 200.91 (C-2); $C_{24}H_{38}N_2O_4Si$ (446.65): calcd. C 64.54, H 8.58, N 6.27; found C 64.60, H 8.70, N 6.24.

7. Informations about X-ray analysis of 7, 9, and 12

X-ray crystal structure analysis of **7**: formula $C_{14}H_{275}NO_4Si$, *M* = 299.44, colourless crystal 0.40 x 0.40 x 0.25 mm, *a* = 9.240(2), *b* = 10.123(1), *c* = 9.826(3) Å, β = 96.19(2)°, *V* = 913.7(4) $Å^3$, ρ_{calc} = 1.088 g cm^{-3}, μ = 12.33 cm^{-1}, empirical absorption correction via ψ scan data (0.638 ≤ *T* ≤ 0.748), *Z* = 2, monoclinic, space group $P2_1$ (No. 4), λ = 1.54178 Å, *T* = 223 K, ω/2θ scans, 2080 reflections collected (±*h*, -*k*, -*l*), [(sinθ)/λ] = 0.62 $Å^{-1}$, 1966 independent (R_{int} = 0.021) and 1905 observed reflections [$I \geq 2\ \sigma(I)$], 212 refined parameters, *R* = 0.041, wR^2 = 0.126, max. residual electron density 0.34 (-0.21) e $Å^{-3}$, Flack parameter 0.02(4), hydrogens calculated and refined as riding atoms.

X-ray crystal structure analysis of **9**: formula $C_{17}H_{33}NO_2Sn$, *M* = 402.13, colourless crystal 0.35 x 0.20 x 0.20 mm, *a* = 6.423(1), *b* = 10.039(1), *c* = 16.417(1) Å, α = 97.88(1), β = 93.46(1), γ = 95.28(1)°, *V* = 1041.3(2) $Å^3$, ρ_{calc} = 1.283 g cm^{-3}, μ = 12.31 cm^{-1}, absorption correction via SORTAV (0.673 ≤ *T* ≤ 0.791), *Z* = 2, triclinic, space group *P*1 (No. 1), λ = 0.71073 Å, *T* = 198 K, ω and φ scans, 11985 reflections collected (±*h*, ±*k*, ±*l*), [(sinθ)/λ] =

0.67 $Å^{-1}$, 7716 independent (R_{int} = 0.028) and 7068 observed reflections [$I \geq 2\ \sigma(I)$], 379 refined parameters, R = 0.027, wR^2 = 0.059, max. residual electron density 0.33 (-0.51) e $Å^{-3}$, Flack parameter -0.02(3), hydrogens calculated and refined as riding atoms.

X-ray crystal structure analysis of **12**: formula $C_{24}H_{38}N_2O_4Si$, M = 446.65, colourless crystal 0.30 x 0.30 x 0.10 mm, , a = 9.701(1), b = 11.928(1), c = 13.887(1) Å, α = 86.64(1), β = 72.63(1), γ = 67.02(1)°, V = 1408.9(2) $Å^3$, ρ_{calc} = 1.053 g cm^{-3}, μ = 9.53 cm^{-1}, empirical absorption correction via ψ scan data (0.763 ≤ T ≤ 0.911), Z = 2, triclinic, space group $P\bar{1}$ (No. 1), λ = 1.54178 Å, T = 223 K, $\omega/2\theta$ scans, 5980 reflections collected ($\pm h, \pm k, -l$), [$(\sin\theta)/\lambda$] = 0.62 $Å^{-1}$, 5980 independent and 4672 observed reflections [$I \geq 2\ \sigma(I)$], 584 refined parameters, R = 0.060, wR^2 = 0.164, max. residual electron density 0.38 (-0.34) e $Å^{-3}$, Flack parameter 0.03(4), hydrogens calculated and refined as riding atoms.

Data sets were collected with Enraf-Nonius CAD4, Nonius MACH3 and KappaCCD diffractometers, the later two equipped with a rotating anode generator Nonius FR591. Programs used: data collection EXPRESS (Nonius B.V., 1994) and COLLECT (Nonius B.V., 1998), data reduction MolEN (K. Fair, Enraf-Nonius B.V., 1990) and Denzo-SMN (Z. Otwinowski, W. Minor, *Methods in Enzymology*, **1997**, *276*, 307-326), absorption correction for CCD data SORTAV (R.H. Blessing, *Acta Cryst.* **1995**, *A51*, 33-37; R.H. Blessing, *J. Appl. Cryst.* **1997**, *30*, 421-426), structure solution SHELXS-86 and SHELXS-97 (G.M. Sheldrick, *Acta Cryst.* **1990**, *A46*, 467-473), structure refinement SHELXL-93 and SHELXL-97 (G.M. Sheldrick, Universität Göttingen, 1997), graphics own programs (M. Brüggemann, Universität Bonn, 2000).

(*S*)-2-(*N*,*N*-Diisopropylcarbamoyloxy)-4-(trimethylsilyl)-but-3-ynoic acid (7)

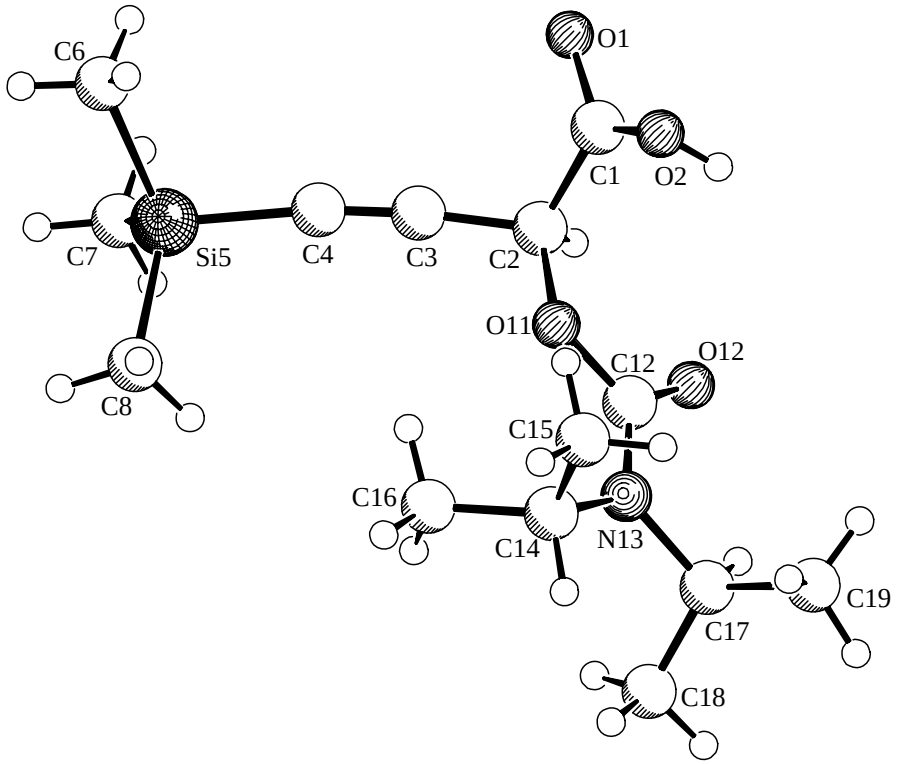


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Table 1. Crystal data and structure refinement for **7**.

Identification code	HOP1513
Empirical formula	C_{14} H_{25} N O_4 Si
Formula weight	299.44
Temperature	223(2) K
Wavelength	1.54178 Å
Crystal system, space group	monoclinic, $P2_1$ (No.4)
Unit cell dimensions	a = 9.240(2) Å b = 10.123(1) Å β = 96.19(2)°. c = 9.826(3) Å
Volume	913.7(4) $Å^3$
Z, Calculated density	2, 1.088 Mg/m^3
Absorption coefficient	1.233 mm^{-1}
F(000)	324
Crystal size	0.40 x 0.40 x 0.25 mm
Theta range for data collection	4.53 to 74.11°.
Limiting indices	-11<=h<=11, -12<=k<=0, -12<=l<=0
Reflections collected / unique	2080 / 1966 [R(int) = 0.0206]

Completeness to theta = 74.11	100.0 %
Max. and min. transmission	0.7480 and 0.6383
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1966 / 1 / 212
Goodness-of-fit on F^2	1.004
Final R indices [I>2σ(I)]	R1 = 0.0408, wR^2 = 0.1258
R indices (all data)	R1 = 0.0422, wR^2 = 0.1280
Absolute structure parameter	0.02(4)
Extinction coefficient	0.046(4)
Largest diff. peak and hole	0.341 and -0.209 eÅ^{-3}

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for **7**.
U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
C(1)	4888(2)	9408(3)	14080(2)	48(1)
O(1)	6306(2)	9547(3)	14159(3)	74(1)
O(2)	4091(2)	10095(3)	14612(3)	80(1)
C(2)	4409(2)	8191(2)	13226(2)	46(1)
C(3)	4992(2)	8166(3)	11895(2)	49(1)
C(4)	5338(3)	8128(3)	10761(2)	56(1)
Si(5)	5646(1)	8005(1)	8946(1)	67(1)
C(6A)	6770(40)	9566(15)	8508(19)	101(5)
C(6B)	6010(70)	9620(30)	8340(20)	94(8)
C(7)	6895(5)	6591(4)	8761(5)	87(1)
C(8)	3820(5)	7594(9)	8033(4)	134(3)
O(11)	2853(2)	8203(2)	12958(2)	54(1)
C(12)	2117(2)	7324(3)	13652(2)	47(1)
O(12)	2722(2)	6690(2)	14596(2)	67(1)
N(13)	714(2)	7256(2)	13186(2)	55(1)
C(14)	12(3)	8069(4)	12043(3)	67(1)
C(15)	-37(4)	9510(4)	12410(5)	86(1)
C(16)	640(5)	7829(7)	10709(3)	101(2)
C(17)	-221(4)	6349(4)	13909(4)	78(1)
C(18)	-902(10)	5331(7)	12993(9)	164(3)
C(19A)	-1070(50)	7130(30)	14960(50)	119(9)
C(19B)	-1390(20)	7110(20)	14440(40)	102(6)

Table 3. Bond lengths [Å] and angles [°] for **7**.

C(1)-O(2)	1.176(3)
C(1)-O(1)	1.312(3)
C(1)-C(2)	1.529(4)
C(2)-O(11)	1.433(2)
C(2)-C(3)	1.468(3)
C(3)-C(4)	1.193(3)
C(4)-Si(5)	1.840(3)
Si(5)-C(6B)	1.78(2)
Si(5)-C(7)	1.860(4)
Si(5)-C(8)	1.870(5)
Si(5)-C(6A)	1.96(3)
O(11)-C(12)	1.349(3)
C(12)-O(12)	1.214(3)
C(12)-N(13)	1.329(3)
N(13)-C(14)	1.484(4)
N(13)-C(17)	1.492(3)
C(14)-C(15)	1.504(6)
C(14)-C(16)	1.509(5)
C(17)-C(18)	1.465(8)
C(17)-C(19B)	1.47(2)
C(17)-C(19A)	1.58(2)
O(2)-C(1)-O(1)	125.4(3)
O(2)-C(1)-C(2)	124.2(2)
O(1)-C(1)-C(2)	110.31(19)
O(11)-C(2)-C(3)	107.05(17)
O(11)-C(2)-C(1)	108.64(18)
C(3)-C(2)-C(1)	113.00(19)
C(4)-C(3)-C(2)	174.0(2)
C(3)-C(4)-Si(5)	173.1(2)
C(6B)-Si(5)-C(4)	108.4(7)
C(6B)-Si(5)-C(7)	122.1(18)
C(4)-Si(5)-C(7)	108.00(18)
C(6B)-Si(5)-C(8)	103.6(19)
C(4)-Si(5)-C(8)	104.73(18)
C(7)-Si(5)-C(8)	108.6(3)
C(6B)-Si(5)-C(6A)	21.1(12)
C(4)-Si(5)-C(6A)	107.4(5)
C(7)-Si(5)-C(6A)	104.4(8)
C(8)-Si(5)-C(6A)	123.0(10)
C(12)-O(11)-C(2)	116.88(17)
O(12)-C(12)-N(13)	126.0(2)
O(12)-C(12)-O(11)	121.3(2)
N(13)-C(12)-O(11)	112.74(19)
C(12)-N(13)-C(14)	124.2(2)
C(12)-N(13)-C(17)	117.5(2)
C(14)-N(13)-C(17)	118.2(2)
N(13)-C(14)-C(15)	112.2(3)
N(13)-C(14)-C(16)	113.0(3)
C(15)-C(14)-C(16)	112.9(4)
C(18)-C(17)-C(19B)	107.6(14)
C(18)-C(17)-N(13)	111.9(4)
C(19B)-C(17)-N(13)	109.5(8)
C(18)-C(17)-C(19A)	123.0(19)
C(19B)-C(17)-C(19A)	21.0(13)
N(13)-C(17)-C(19A)	111.1(10)

Table 4. Anisotropic displacement parameters ($Å^2$ x 10^3) for **7**.
The anisotropic displacement factor exponent takes the form:
$-2\pi^2 [h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U11	U22	U33	U23	U13	U12
C(1)	44(1)	59(1)	40(1)	-4(1)	4(1)	9(1)
O(1)	47(1)	80(1)	94(1)	-44(1)	7(1)	0(1)
O(2)	60(1)	97(2)	84(1)	-31(1)	16(1)	15(1)
C(2)	42(1)	52(1)	45(1)	3(1)	1(1)	3(1)
C(3)	49(1)	48(1)	49(1)	-8(1)	1(1)	-1(1)
C(4)	64(1)	54(1)	51(1)	-11(1)	7(1)	2(1)
Si(5)	89(1)	65(1)	46(1)	-9(1)	13(1)	12(1)
C(6A)	141(14)	73(4)	95(6)	20(4)	47(8)	6(8)
C(6B)	140(20)	64(8)	84(8)	3(5)	37(12)	-22(11)
C(7)	91(2)	81(2)	90(2)	-34(2)	22(2)	0(2)
C(8)	103(3)	219(8)	72(2)	-39(3)	-25(2)	47(4)
O(11)	42(1)	63(1)	55(1)	23(1)	-2(1)	-4(1)
C(12)	52(1)	47(1)	42(1)	5(1)	4(1)	-1(1)
O(12)	71(1)	69(1)	60(1)	25(1)	2(1)	0(1)
N(13)	48(1)	60(1)	58(1)	11(1)	3(1)	-8(1)
C(14)	47(1)	83(2)	68(1)	14(2)	-11(1)	-4(1)
C(15)	74(2)	72(2)	112(3)	30(2)	8(2)	11(2)
C(16)	93(2)	151(4)	54(1)	8(2)	-14(1)	0(3)
C(17)	65(2)	73(2)	98(2)	23(2)	15(2)	-15(1)
C(18)	188(7)	105(4)	200(8)	9(5)	24(6)	-81(5)
C(19A)	142(16)	105(9)	125(17)	49(11)	87(13)	37(11)
C(19B)	72(7)	115(9)	128(14)	47(9)	51(8)	-5(6)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for **7**.

	x	y	z	U(eq)
H(2)	3739	9677	15224	119
H(2A)	4720	7383	13746	56
H(6A1)	6989	9511	7566	151
H(6Å2)	7670	9600	9114	151
H(6Å3)	6205	10357	8628	151
H(6B1)	5131	10152	8311	141
H(6B2)	6311	9558	7427	141
H(6B3)	6774	10026	8949	141
H(7A)	7809	6744	9322	130
H(7B)	7074	6508	7810	130
H(7C)	6454	5785	9054	130
H(8A)	3332	6965	8572	201
H(8B)	3941	7212	7147	201
H(8C)	3240	8392	7907	201
H(14)	-1014	7773	11895	81
H(15A)	-443	9607	13274	130
H(15B)	-641	9980	11700	130
H(15C)	941	9871	12491	130
H(16A)	1599	8227	10748	152
H(16B)	8	8219	9964	152
H(16C)	718	6886	10557	152
H(17)	502	5838	14513	94
H(18A)	-1598	5739	12310	246
H(18B)	-1400	4698	13520	246
H(18C)	-159	4880	12542	246
H(19A)	-1520	7906	14525	178
H(19B)	-397	7391	15742	178
H(19C)	-1818	6563	15273	178
H(19D)	-2000	7503	13682	153
H(19E)	-970	7796	15044	153
H(19F)	-1973	6523	14942	153

(*aS*)-4,4-Dimethyl-1-(trimethylstannyl)-penta-1,2-dienyl *N*,*N*-diisopropylcarbamate (9)

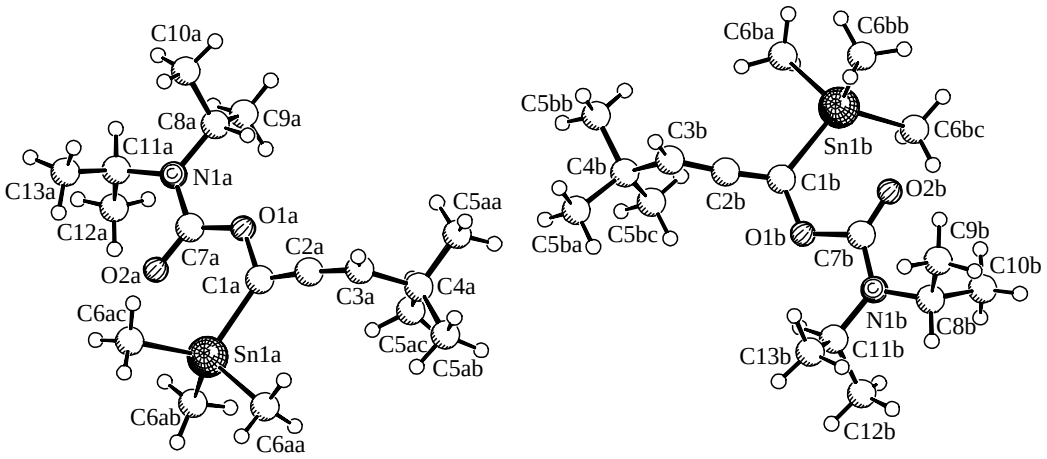

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Table 1. Crystal data and structure refinement for **9**.

Identification code	HOP1622
Empirical formula	C_{17} H_{33} N O_2 Sn
Formula weight	402.13
Temperature	198(2) K
Wavelength	0.71073 Å
Crystal system, space group	triclinic, P1 (No. 1)
Unit cell dimensions	a = 6.423(1) Å α = 97.88(1)°. b = 10.039(1) Å β = 93.46(1)°. c = 16.417(1) Å γ = 95.28(1)°.
Volume	1041.3(2) $Å^3$
Z, Calculated density	2, 1.283 Mg/m^3
Absorption coefficient	1.231 mm^{-1}
F(000)	416
Crystal size	0.35 x 0.20 x 0.20 mm
Theta range for data collection	1.26 to 28.27°.
Limiting indices	-8<=h<=8, -13<=k<=13, -21<=l<=17
Reflections collected / unique	11985 / 7716 [R(int) = 0.0279]
Completeness to theta = 28.27	98.5 %
Max. and min. transmission	0.7908 and 0.6725
Refinement method	Full-matrix least-squares on F^2

Data / restraints / parameters	7716 / 3 / 379
Goodness-of-fit on F^2	1.042
Final R indices [I>2σ(I)]	R1 = 0.0272, wR^2 = 0.0586
R indices (all data)	R1 = 0.0321, wR^2 = 0.0610
Absolute structure parameter	-0.02(3)
Largest diff. peak and hole	0.330 and -0.508 $eÅ^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for **9**.
U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
C(1A)	-9534(12)	13424(8)	9367(5)	51(2)
C(2A)	-8863(7)	13741(5)	8658(3)	56(1)
C(3A)	-8048(8)	14153(5)	7980(4)	61(1)
C(4A)	-5810(16)	13935(11)	7770(7)	59(3)
C(5AA)	-5917(12)	13013(10)	6977(5)	108(3)
C(5AB)	-4696(17)	15338(11)	7687(9)	157(7)
C(5AC)	-4732(14)	13383(11)	8419(6)	134(4)
Sn(1A)	-9394(1)	14895(1)	10441(1)	35(1)
C(6AA)	-7671(13)	16551(8)	9998(6)	49(3)
C(6AB)	-7704(12)	14372(9)	11489(5)	51(2)
C(6AC)	-12384(12)	15531(10)	10693(7)	60(3)
O(1A)	-10600(9)	12102(6)	9274(4)	48(2)
C(7A)	-11657(12)	11781(7)	9893(5)	34(2)
O(2A)	-11664(10)	12520(7)	10558(4)	56(2)
N(1A)	-12868(10)	10593(7)	9726(4)	39(2)
C(8A)	-12876(15)	9752(9)	8905(5)	49(2)
C(9A)	-11544(17)	8569(11)	8943(7)	71(3)
C(10A)	-15086(15)	9316(11)	8550(6)	75(3)
C(11A)	-14007(17)	10068(10)	10401(7)	51(3)
C(12A)	-12530(15)	9802(11)	11097(6)	60(3)
C(13A)	-15817(15)	10824(11)	10617(8)	65(3)
C(1B)	3010(11)	9605(7)	4424(5)	40(2)
C(2B)	1420(5)	9578(3)	4854(2)	27(1)
C(3B)	-258(6)	9471(4)	5246(3)	38(1)
C(4B)	-480(15)	8937(10)	6077(6)	55(3)
C(5BA)	-1361(15)	10101(8)	6641(5)	103(3)
C(5BB)	-2176(14)	7780(10)	5941(6)	94(3)
C(5BC)	1504(11)	8562(8)	6413(4)	93(2)
Sn(1B)	3347(1)	7958(1)	3448(1)	33(1)
C(6BA)	1622(15)	6258(9)	3876(7)	55(3)
C(6BB)	6433(14)	7391(10)	3288(7)	64(3)
C(6BC)	1830(12)	8309(9)	2321(5)	55(2)
O(1B)	4423(8)	10799(6)	4574(3)	37(1)
C(7B)	5653(11)	11081(9)	3925(6)	38(2)
O(2B)	5452(10)	10368(7)	3282(4)	43(1)
N(1B)	6865(10)	12258(7)	4160(4)	35(2)
C(8B)	8084(14)	12840(10)	3542(6)	35(2)
C(9B)	6741(15)	13076(10)	2798(6)	54(2)
C(10B)	9797(12)	11905(11)	3264(6)	57(2)
C(11B)	6886(13)	13079(8)	4965(5)	41(2)
C(12B)	9120(11)	13475(9)	5366(5)	58(3)
C(13B)	5726(16)	14293(10)	4903(6)	60(3)

Table 3. Bond lengths [Å] and angles [°] for **9**.

C(1A)-C(2A)	1.333(9)
C(1A)-O(1A)	1.420(9)
C(1A)-Sn(1A)	2.131(8)
C(2A)-C(3A)	1.356(7)
C(3A)-C(4A)	1.526(11)
C(4A)-C(5AC)	1.437(13)
C(4A)-C(5AA)	1.485(12)
C(4A)-C(5AB)	1.547(14)
Sn(1A)-C(6AC)	2.125(8)
Sn(1A)-C(6AB)	2.131(8)
Sn(1A)-C(6AA)	2.146(9)
O(1A)-C(7A)	1.316(10)
C(7A)-O(2A)	1.234(10)
C(7A)-N(1A)	1.347(9)
N(1A)-C(8A)	1.489(10)
N(1A)-C(11A)	1.493(11)
C(8A)-C(10A)	1.504(12)
C(8A)-C(9A)	1.532(13)
C(11A)-C(13A)	1.480(15)
C(11A)-C(12A)	1.509(14)
C(1B)-C(2B)	1.277(8)
C(1B)-O(1B)	1.419(9)
C(1B)-Sn(1B)	2.175(8)
C(2B)-C(3B)	1.291(5)
C(3B)-C(4B)	1.542(10)
C(4B)-C(5BC)	1.459(11)
C(4B)-C(5BB)	1.501(12)
C(4B)-C(5BA)	1.560(12)
Sn(1B)-C(6BC)	2.127(8)
Sn(1B)-C(6BB)	2.133(9)
Sn(1B)-C(6BA)	2.170(10)
O(1B)-C(7B)	1.408(10)
C(7B)-O(2B)	1.184(10)
C(7B)-N(1B)	1.350(10)
N(1B)-C(11B)	1.458(10)
N(1B)-C(8B)	1.468(10)
C(8B)-C(9B)	1.511(13)
C(8B)-C(10B)	1.560(13)
C(11B)-C(13B)	1.498(11)
C(11B)-C(12B)	1.536(9)

C(2A)-C(1A)-O(1A)	112.2(7)
C(2A)-C(1A)-Sn(1A)	121.5(5)
O(1A)-C(1A)-Sn(1A)	125.6(5)
C(1A)-C(2A)-C(3A)	174.6(6)
C(2A)-C(3A)-C(4A)	122.0(6)
C(5AC)-C(4A)-C(5AA)	111.2(9)
C(5AC)-C(4A)-C(3A)	110.4(8)
C(5AA)-C(4A)-C(3A)	108.1(7)
C(5AC)-C(4A)-C(5AB)	109.5(9)
C(5AA)-C(4A)-C(5AB)	110.8(9)
C(3A)-C(4A)-C(5AB)	106.9(9)
C(6AC)-Sn(1A)-C(1A)	112.3(4)
C(6AC)-Sn(1A)-C(6AB)	113.6(4)
C(1A)-Sn(1A)-C(6AB)	114.3(3)
C(6AC)-Sn(1A)-C(6AA)	106.3(4)
C(1A)-Sn(1A)-C(6AA)	99.3(3)
C(6AB)-Sn(1A)-C(6AA)	109.8(3)
C(7A)-O(1A)-C(1A)	117.0(7)
O(2A)-C(7A)-O(1A)	124.1(7)
O(2A)-C(7A)-N(1A)	121.6(8)
O(1A)-C(7A)-N(1A)	114.2(7)
C(7A)-N(1A)-C(8A)	120.1(7)
C(7A)-N(1A)-C(11A)	119.1(8)
C(8A)-N(1A)-C(11A)	120.6(7)
N(1A)-C(8A)-C(10A)	110.6(8)

N(1A)-C(8A)-C(9A)	111.6(8)
C(10A)-C(8A)-C(9A)	113.2(8)
C(13A)-C(11A)-N(1A)	112.4(9)
C(13A)-C(11A)-C(12A)	117.7(9)
N(1A)-C(11A)-C(12A)	112.2(8)
C(2B)-C(1B)-O(1B)	116.5(6)
C(2B)-C(1B)-Sn(1B)	120.7(5)
O(1B)-C(1B)-Sn(1B)	122.6(5)
C(1B)-C(2B)-C(3B)	175.4(5)
C(2B)-C(3B)-C(4B)	126.9(5)
C(5BC)-C(4B)-C(5BB)	112.7(8)
C(5BC)-C(4B)-C(3B)	112.0(6)
C(5BB)-C(4B)-C(3B)	107.5(7)
C(5BC)-C(4B)-C(5BA)	113.2(7)
C(5BB)-C(4B)-C(5BA)	106.2(8)
C(3B)-C(4B)-C(5BA)	104.7(7)
C(6BC)-Sn(1B)-C(6BB)	111.8(4)
C(6BC)-Sn(1B)-C(6BA)	108.8(4)
C(6BB)-Sn(1B)-C(6BA)	105.9(4)
C(6BC)-Sn(1B)-C(1B)	110.3(3)
C(6BB)-Sn(1B)-C(1B)	117.1(3)
C(6BA)-Sn(1B)-C(1B)	102.1(3)
C(7B)-O(1B)-C(1B)	116.6(7)
O(2B)-C(7B)-N(1B)	130.0(8)
O(2B)-C(7B)-O(1B)	120.8(8)
N(1B)-C(7B)-O(1B)	109.1(8)
C(7B)-N(1B)-C(11B)	124.5(7)
C(7B)-N(1B)-C(8B)	118.5(8)
C(11B)-N(1B)-C(8B)	116.7(7)
N(1B)-C(8B)-C(9B)	113.0(7)
N(1B)-C(8B)-C(10B)	109.9(7)
C(9B)-C(8B)-C(10B)	109.8(7)
N(1B)-C(11B)-C(13B)	110.5(7)
N(1B)-C(11B)-C(12B)	112.2(7)
C(13B)-C(11B)-C(12B)	111.7(8)

Table 4. Anisotropic displacement parameters ($Å^2$ x 10^3) for **9**.
The anisotropic displacement factor exponent takes the form:
$-2\pi^2 [h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U11	U22	U33	U23	U13	U12
C(1A)	56(4)	38(3)	57(4)	2(3)	31(3)	-21(3)
C(2A)	56(3)	48(2)	58(3)	2(2)	9(2)	-13(2)
C(3A)	58(3)	57(3)	66(4)	10(3)	5(3)	-8(2)
C(4A)	59(4)	60(6)	53(5)	7(4)	16(4)	-23(4)
C(5AA)	89(5)	142(7)	79(6)	-37(5)	27(4)	0(5)
C(5AB)	153(10)	65(5)	257(17)	13(8)	137(11)	-26(6)
C(5AC)	112(7)	200(10)	101(7)	40(7)	1(5)	52(7)
Sn(1A)	33(1)	30(1)	42(1)	4(1)	7(1)	-2(1)
C(6AA)	49(5)	26(4)	71(8)	7(5)	17(5)	-6(4)
C(6AB)	49(4)	52(4)	55(5)	21(3)	9(3)	1(3)
C(6AC)	27(3)	71(6)	82(6)	10(5)	13(3)	2(4)
O(1A)	56(3)	34(3)	49(4)	0(3)	18(3)	-19(2)
C(7A)	47(4)	21(3)	30(4)	-4(3)	5(3)	-7(3)
O(2A)	71(4)	41(3)	50(4)	-2(3)	29(3)	-22(3)
N(1A)	35(4)	35(4)	44(5)	8(4)	3(3)	-12(3)
C(8A)	65(5)	49(5)	25(4)	-7(4)	5(4)	-23(4)
C(9A)	79(6)	56(6)	79(8)	9(5)	24(5)	2(4)
C(10A)	104(7)	72(6)	48(6)	7(5)	-3(5)	12(5)
C(11A)	67(6)	35(4)	49(5)	8(4)	13(4)	-21(4)
C(12A)	80(5)	63(6)	40(5)	29(4)	1(4)	-3(4)
C(13A)	69(6)	55(5)	76(8)	16(5)	29(5)	3(4)
C(1B)	50(3)	27(2)	41(3)	2(2)	8(2)	-5(2)
C(2B)	31(2)	23(2)	25(2)	3(1)	0(1)	-2(1)
C(3B)	33(2)	39(2)	39(2)	-3(2)	11(2)	-4(2)
C(4B)	73(5)	57(5)	32(4)	-3(4)	24(4)	-17(4)
C(5BA)	151(7)	79(4)	73(5)	-15(4)	67(5)	-16(5)
C(5BB)	112(6)	83(6)	81(5)	24(4)	19(4)	-50(5)
C(5BC)	102(5)	136(6)	45(3)	51(4)	0(3)	-21(4)
Sn(1B)	31(1)	29(1)	39(1)	3(1)	5(1)	-2(1)
C(6BA)	49(6)	43(6)	74(8)	17(5)	5(5)	-2(5)
C(6BB)	54(5)	54(5)	85(7)	2(5)	15(4)	15(4)
C(6BC)	57(4)	56(4)	46(4)	-7(3)	-13(3)	2(3)
O(1B)	43(3)	35(3)	31(3)	2(2)	10(2)	-11(2)
C(7B)	29(3)	47(5)	42(5)	22(4)	10(3)	0(3)
O(2B)	55(3)	39(3)	31(3)	-3(3)	5(2)	-11(2)
N(1B)	50(4)	27(4)	26(4)	5(3)	9(3)	-4(3)
C(8B)	38(4)	36(4)	31(4)	13(3)	5(3)	-5(3)
C(9B)	66(4)	48(5)	47(5)	12(4)	10(4)	2(4)
C(10B)	42(4)	74(6)	58(6)	15(5)	18(4)	4(4)
C(11B)	47(4)	29(4)	46(5)	7(4)	1(4)	-6(4)
C(12B)	51(4)	59(5)	52(5)	3(4)	-22(4)	-32(4)
C(13B)	63(4)	47(5)	64(6)	-18(4)	8(4)	14(4)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for **9**.

	x	y	z	U(eq)
H(3A)	-8895	14589	7626	73
H(5A1)	-6786	12174	7021	162
H(5Å2)	-4501	12805	6850	162
H(5Å3)	-6536	13451	6535	162
H(5A4)	-5343	15674	7209	235
H(5A5)	-3209	15258	7611	235
H(5A6)	-4831	15969	8187	235
H(5A7)	-3228	13669	8437	201
H(5A8)	-4963	12394	8314	201
H(5A9)	-5271	13710	8948	201
H(6A1)	-8121	16561	9418	73
H(6Å2)	-6169	16446	10049	73
H(6Å3)	-7937	17403	10325	73
H(6A4)	-7422	15169	11912	76
H(6A5)	-6375	14049	11326	76
H(6A6)	-8539	13657	11712	76
H(6A7)	-12263	16518	10830	90
H(6A8)	-12905	15119	11159	90
H(6A9)	-13365	15250	10205	90
H(8A)	-12208	10341	8529	59
H(9A1)	-10092	8919	9125	106
H(9Å2)	-11587	8035	8394	106
H(9Å3)	-12102	7996	9333	106
H(10A)	-15721	8622	8849	112
H(10B)	-15072	8946	7966	112
H(10C)	-15905	10096	8602	112
H(11A)	-14655	9149	10148	62
H(12A)	-11493	9220	10876	90
H(12B)	-13327	9353	11491	90
H(12C)	-11812	10661	11377	90
H(13A)	-15314	11693	10949	98
H(13B)	-16746	10297	10934	98
H(13C)	-16588	10981	10111	98
H(3B)	-1485	9751	4996	46
H(5B1)	-363	10914	6706	154
H(5B2)	-1570	9826	7183	154
H(5B3)	-2703	10293	6390	154
H(5B4)	-2535	7524	6474	141
H(5B5)	-1681	7007	5602	141
H(5B6)	-3420	8054	5657	141
H(5B7)	2565	9342	6474	140
H(5B8)	1963	7818	6037	140
H(5B9)	1315	8274	6952	140
H(6B1)	775	5710	3411	82
H(6B2)	701	6592	4296	82
H(6B3)	2610	5703	4114	82
H(6B4)	6835	6858	3718	96
H(6B5)	7421	8206	3326	96
H(6B6)	6461	6850	2745	96
H(6B7)	541	7693	2194	83
H(6B8)	2767	8150	1876	83
H(6B9)	1483	9246	2374	83
H(8B)	8808	13732	3808	42
H(9B1)	7616	13527	2428	80
H(9B2)	5648	13647	2977	80
H(9B3)	6087	12207	2507	80
H(10D)	10775	11851	3738	86
H(10E)	10563	12278	2835	86
H(10F)	9130	10999	3046	86
H(11B)	6117	12518	5332	49
H(12D)	9866	14114	5057	87

H(12E)	9865	12664	5359	87
H(12F)	9055	13899	5937	87
H(13D)	6510	14906	4588	90
H(13E)	5576	14761	5458	90
H(13F)	4335	14006	4622	90

(*aR*,*R*)-Phenylcarbamic acid 4-(*N*,*N*-diisopropylcarbamoyloxy)-1-(1-methylethyl)-2-(trimethylsilyl)-buta-2,3-dienyl ester (12)

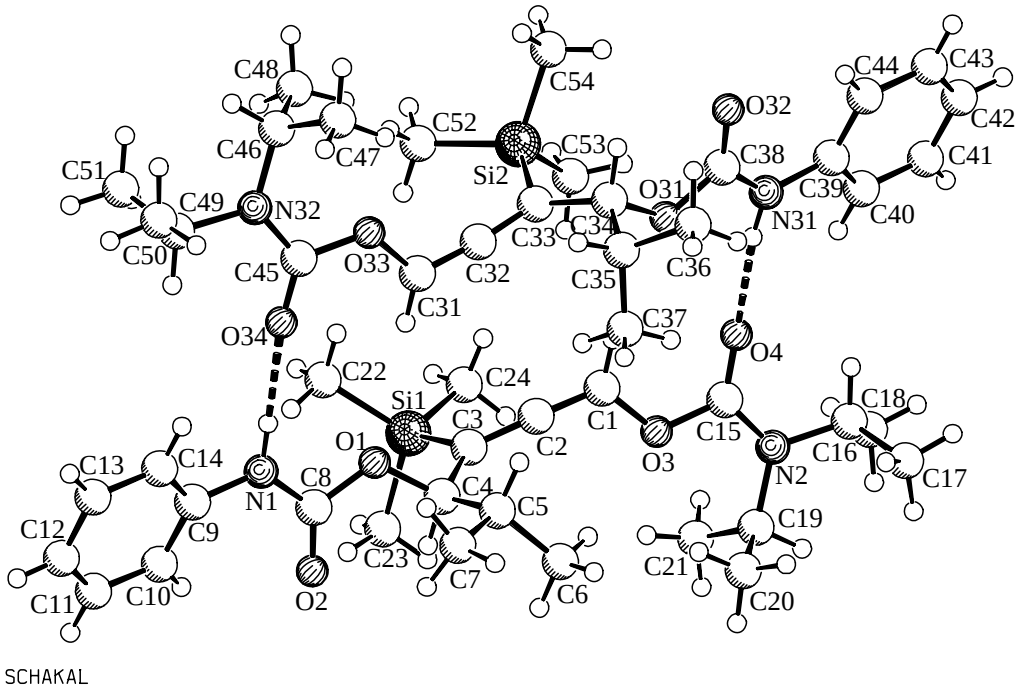

Table 1. Crystal data and structure refinement for **12**.

Identification code	HOP1253
Empirical formula	C_{24} H_{38} N_2 O_4 Si
Formula weight	446.65
Temperature	223(2) K
Wavelength	1.54178 Å
Crystal system, space group	triclinic, P1 (No.1)
Unit cell dimensions	a = 9.701(1) Å α = 86.64(1)°. b = 11.928(1) Å β = 72.63(1)°. c = 13.887(1) Å γ = 67.02(1)°.
Volume	1408.9(2) $Å^3$
Z, Calculated density	2, 1.053 Mg/m^3
Absorption coefficient	0.953 mm^{-1}
F(000)	484

Crystal size	0.30 x 0.30 x 0.10 mm
Theta range for data collection	3.34 to 74.51°.
Limiting indices	-12<=h<=11, -14<=k<=14, -17<=l<=0
Reflections collected / unique	5980 / 5980 [R(int) = 0.0000]
Completeness to theta = 74.51	99.7 %
Max. and min. transmission	0.9107 and 0.7630
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5980 / 3 / 584
Goodness-of-fit on F^2	1.008
Final R indices [I>2σ(I)]	R1 = 0.0596, wR^2 = 0.1638
R indices (all data)	R1 = 0.0855, wR^2 = 0.1780
Absolute structure parameter	0.03(4)
Extinction coefficient	0.0031(8)
Largest diff. peak and hole	0.378 and -0.341 $eÅ^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for **12**.
U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Si(1)	6869(2)	4910(1)	3758(1)	66(1)
C(1)	7248(4)	2946(4)	1545(3)	49(1)
C(2)	6540(4)	3435(4)	2452(3)	50(1)
C(3)	5858(4)	4037(4)	3347(3)	52(1)
C(4)	4261(5)	4108(4)	4013(3)	55(1)
C(5)	3464(6)	3489(7)	3575(4)	91(2)
C(6)	2915(10)	4192(13)	2715(6)	159(5)
C(7)	2064(10)	3369(10)	4404(7)	125(3)
O(1)	4478(3)	3620(2)	4952(2)	54(1)
C(8)	3452(4)	4286(3)	5823(3)	50(1)
O(2)	2514(5)	5312(3)	5824(2)	84(1)
N(1)	3649(4)	3636(3)	6608(2)	51(1)
C(9)	2706(4)	3984(4)	7629(3)	50(1)
C(10)	1850(5)	5203(4)	7988(3)	61(1)
C(11)	940(7)	5458(5)	8986(4)	77(1)
C(12)	863(8)	4540(7)	9611(4)	92(2)
C(13)	1719(8)	3353(7)	9267(4)	88(2)
C(14)	2649(6)	3070(4)	8260(3)	64(1)
O(3)	6898(3)	3657(2)	752(2)	54(1)
C(15)	7723(4)	3159(3)	-208(3)	44(1)
O(4)	8790(4)	2160(3)	-374(2)	64(1)
N(2)	7234(4)	3892(3)	-890(2)	53(1)
C(16)	7997(6)	3468(5)	-1963(3)	69(1)
C(17)	6851(10)	3275(7)	-2429(5)	98(2)
C(18)	8707(9)	4322(8)	-2549(5)	96(2)
C(19)	5877(6)	5094(4)	-640(4)	69(1)
C(20)	4332(7)	4959(7)	-133(5)	97(2)
C(21)	6164(10)	6008(5)	-96(6)	100(2)
C(22)	7478(11)	4293(11)	4882(6)	136(4)
C(23)	5432(10)	6541(7)	4052(8)	123(3)
C(24)	8585(8)	4832(7)	2693(5)	87(2)
Si(2)	11311(2)	-104(1)	2446(1)	70(1)
C(31)	7403(5)	508(4)	4437(3)	62(1)
C(32)	8320(6)	141(4)	3528(4)	62(1)
C(33)	9379(5)	-260(4)	2644(3)	57(1)
C(34)	9170(5)	-948(4)	1854(3)	56(1)
C(35)	7581(6)	-1039(5)	2039(4)	72(1)
C(36)	7724(9)	-2021(7)	1273(6)	98(2)
C(37)	6307(7)	104(7)	2017(7)	103(2)
O(31)	9519(3)	-359(2)	926(2)	57(1)
C(38)	10637(5)	-1066(4)	104(3)	54(1)
O(32)	11352(5)	-2155(3)	100(3)	80(1)
N(31)	10804(4)	-350(3)	-656(3)	56(1)
C(39)	11850(5)	-702(4)	-1654(3)	54(1)
C(40)	11984(6)	226(5)	-2266(4)	65(1)
C(41)	12967(7)	-37(6)	-3253(4)	82(2)
C(42)	13819(7)	-1234(6)	-3623(5)	88(2)
C(43)	13701(7)	-2153(6)	-3019(4)	81(2)
C(44)	12707(6)	-1914(4)	-2020(4)	66(1)
O(33)	7599(4)	-316(3)	5199(2)	68(1)
C(45)	6887(5)	125(4)	6176(3)	52(1)
O(34)	5860(4)	1156(3)	6402(2)	63(1)
N(32)	7418(4)	-683(3)	6814(3)	58(1)
C(46)	8786(6)	-1863(4)	6490(5)	71(1)
C(47)	8458(8)	-2752(5)	5939(6)	91(2)
C(48)	10285(6)	-1704(5)	5920(7)	102(2)
C(49)	6686(7)	-308(5)	7909(4)	75(1)
C(50)	6024(10)	-1203(8)	8463(5)	105(2)

C(51)	7862(11)	-162(8)	8376(6)	110(2)
C(52)	11381(13)	434(11)	3633(7)	143(4)
C(53)	11635(10)	934(10)	1478(8)	135(4)
C(54)	12838(8)	-1651(8)	2053(10)	143(4)

Table 3. Bond lengths [Å] and angles [°] for **12**.

Si(1)-C(24)	1.842(6)
Si(1)-C(22)	1.846(7)
Si(1)-C(23)	1.879(8)
Si(1)-C(3)	1.890(5)
C(1)-C(2)	1.286(5)
C(1)-O(3)	1.391(4)
C(2)-C(3)	1.319(5)
C(3)-C(4)	1.522(6)
C(4)-O(1)	1.437(5)
C(4)-C(5)	1.514(7)
C(5)-C(6)	1.525(12)
C(5)-C(7)	1.546(8)
O(1)-C(8)	1.365(4)
C(8)-O(2)	1.207(5)
C(8)-N(1)	1.317(5)
N(1)-C(9)	1.421(5)
C(9)-C(14)	1.365(6)
C(9)-C(10)	1.396(6)
C(10)-C(11)	1.378(7)
C(11)-C(12)	1.369(9)
C(12)-C(13)	1.359(10)
C(13)-C(14)	1.396(7)
O(3)-C(15)	1.362(4)
C(15)-O(4)	1.213(5)
C(15)-N(2)	1.316(5)
N(2)-C(16)	1.471(5)
N(2)-C(19)	1.491(6)
C(16)-C(18)	1.513(9)
C(16)-C(17)	1.534(9)
C(19)-C(21)	1.515(9)
C(19)-C(20)	1.522(9)
Si(2)-C(53)	1.815(8)
Si(2)-C(52)	1.833(9)
Si(2)-C(54)	1.843(8)
Si(2)-C(33)	1.892(5)
C(31)-C(32)	1.291(7)
C(31)-O(33)	1.405(5)
C(32)-C(33)	1.313(6)
C(33)-C(34)	1.512(7)
C(34)-O(31)	1.445(5)
C(34)-C(35)	1.532(6)
C(35)-C(37)	1.445(9)
C(35)-C(36)	1.567(9)
O(31)-C(38)	1.360(5)
C(38)-O(32)	1.210(5)
C(38)-N(31)	1.331(6)
N(31)-C(39)	1.422(5)
C(39)-C(40)	1.378(7)
C(39)-C(44)	1.391(6)
C(40)-C(41)	1.387(7)
C(41)-C(42)	1.377(9)
C(42)-C(43)	1.361(10)
C(43)-C(44)	1.403(7)
O(33)-C(45)	1.354(5)
C(45)-O(34)	1.226(5)
C(45)-N(32)	1.328(5)
N(32)-C(46)	1.485(6)
N(32)-C(49)	1.485(7)
C(46)-C(48)	1.513(8)
C(46)-C(47)	1.521(9)
C(49)-C(50)	1.512(9)
C(49)-C(51)	1.537(8)

C(24)-Si(1)-C(22)	110.4(4)
C(24)-Si(1)-C(23)	109.3(4)
C(22)-Si(1)-C(23)	110.0(5)

C(24)-Si(1)-C(3)	108.2(2)
C(22)-Si(1)-C(3)	111.7(3)
C(23)-Si(1)-C(3)	107.0(3)
C(2)-C(1)-O(3)	118.0(3)
C(1)-C(2)-C(3)	173.8(4)
C(2)-C(3)-C(4)	122.1(4)
C(2)-C(3)-Si(1)	117.8(3)
C(4)-C(3)-Si(1)	119.9(3)
O(1)-C(4)-C(5)	111.2(4)
O(1)-C(4)-C(3)	106.5(3)
C(5)-C(4)-C(3)	116.2(4)
C(4)-C(5)-C(6)	110.7(7)
C(4)-C(5)-C(7)	110.7(5)
C(6)-C(5)-C(7)	110.3(6)
C(8)-O(1)-C(4)	117.5(3)
O(2)-C(8)-N(1)	127.7(4)
O(2)-C(8)-O(1)	122.3(4)
N(1)-C(8)-O(1)	110.0(3)
C(8)-N(1)-C(9)	126.1(3)
C(14)-C(9)-C(10)	120.4(4)
C(14)-C(9)-N(1)	117.3(4)
C(10)-C(9)-N(1)	122.4(4)
C(11)-C(10)-C(9)	118.5(5)
C(12)-C(11)-C(10)	121.0(5)
C(13)-C(12)-C(11)	120.5(5)
C(12)-C(13)-C(14)	119.6(5)
C(9)-C(14)-C(13)	120.0(5)
C(15)-O(3)-C(1)	117.7(3)
O(4)-C(15)-N(2)	126.3(3)
O(4)-C(15)-O(3)	121.6(3)
N(2)-C(15)-O(3)	112.1(3)
C(15)-N(2)-C(16)	118.3(3)
C(15)-N(2)-C(19)	123.9(3)
C(16)-N(2)-C(19)	117.6(3)
N(2)-C(16)-C(18)	111.4(5)
N(2)-C(16)-C(17)	110.8(5)
C(18)-C(16)-C(17)	112.0(5)
N(2)-C(19)-C(21)	112.7(5)
N(2)-C(19)-C(20)	112.1(4)
C(21)-C(19)-C(20)	114.6(6)
C(53)-Si(2)-C(52)	109.1(5)
C(53)-Si(2)-C(54)	109.8(5)
C(52)-Si(2)-C(54)	109.8(5)
C(53)-Si(2)-C(33)	112.4(3)
C(52)-Si(2)-C(33)	110.1(3)
C(54)-Si(2)-C(33)	105.6(3)
C(32)-C(31)-O(33)	118.1(4)
C(31)-C(32)-C(33)	173.8(5)
C(32)-C(33)-C(34)	122.5(4)
C(32)-C(33)-Si(2)	116.8(4)
C(34)-C(33)-Si(2)	120.3(3)
O(31)-C(34)-C(33)	105.7(3)
O(31)-C(34)-C(35)	109.2(4)
C(33)-C(34)-C(35)	118.5(4)
C(37)-C(35)-C(34)	114.6(5)
C(37)-C(35)-C(36)	110.3(6)
C(34)-C(35)-C(36)	110.2(5)
C(38)-O(31)-C(34)	117.8(3)
O(32)-C(38)-N(31)	127.5(4)
O(32)-C(38)-O(31)	124.3(4)
N(31)-C(38)-O(31)	108.3(3)
C(38)-N(31)-C(39)	127.5(4)
C(40)-C(39)-C(44)	120.2(4)
C(40)-C(39)-N(31)	116.8(4)
C(44)-C(39)-N(31)	123.0(4)
C(39)-C(40)-C(41)	120.5(5)
C(42)-C(41)-C(40)	119.7(5)
C(43)-C(42)-C(41)	120.0(5)
C(42)-C(43)-C(44)	121.5(5)
C(39)-C(44)-C(43)	118.0(5)

C(45)-O(33)-C(31)	118.3(3)
O(34)-C(45)-N(32)	126.4(4)
O(34)-C(45)-O(33)	121.4(4)
N(32)-C(45)-O(33)	112.2(3)
C(45)-N(32)-C(46)	123.7(4)
C(45)-N(32)-C(49)	116.9(4)
C(46)-N(32)-C(49)	119.1(4)
N(32)-C(46)-C(48)	112.8(4)
N(32)-C(46)-C(47)	112.7(4)
C(48)-C(46)-C(47)	113.0(6)
N(32)-C(49)-C(50)	110.9(5)
N(32)-C(49)-C(51)	111.0(5)
C(50)-C(49)-C(51)	111.0(5)

Table 4. Anisotropic displacement parameters ($Å^2$ x 10^3) for **12**. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U11	U22	U33	U23	U13	U12
Si(1)	66(1)	94(1)	39(1)	0(1)	-13(1)	-35(1)
C(1)	51(2)	50(2)	36(2)	7(1)	-14(2)	-9(2)
C(2)	46(2)	54(2)	41(2)	6(2)	-12(2)	-12(2)
C(3)	48(2)	61(2)	35(2)	5(2)	-11(2)	-9(2)
C(4)	45(2)	62(2)	42(2)	-3(2)	-6(2)	-10(2)
C(5)	64(3)	139(5)	70(3)	-33(3)	5(2)	-53(3)
C(6)	86(5)	327(16)	87(5)	10(7)	-40(4)	-95(7)
C(7)	105(5)	174(8)	108(6)	-28(5)	11(4)	-95(6)
O(1)	53(1)	46(1)	39(1)	3(1)	-1(1)	-4(1)
C(8)	48(2)	40(2)	42(2)	0(1)	-3(2)	-4(2)
O(2)	97(3)	48(2)	49(2)	4(1)	-1(2)	15(2)
N(1)	49(2)	42(2)	42(2)	2(1)	-1(1)	-6(1)
C(9)	47(2)	54(2)	42(2)	-4(2)	-4(2)	-20(2)
C(10)	62(2)	63(2)	50(2)	-10(2)	-1(2)	-25(2)
C(11)	76(3)	84(3)	55(3)	-21(3)	1(2)	-29(3)
C(12)	88(4)	127(5)	49(3)	-17(3)	15(3)	-54(4)
C(13)	105(4)	109(5)	52(3)	17(3)	-2(3)	-61(4)
C(14)	72(3)	67(3)	48(2)	4(2)	-5(2)	-31(2)
O(3)	59(2)	47(1)	36(1)	0(1)	-13(1)	-2(1)
C(15)	50(2)	42(2)	35(2)	1(1)	-13(1)	-11(2)
O(4)	73(2)	49(2)	40(1)	1(1)	-8(1)	1(1)
N(2)	61(2)	49(2)	41(2)	5(1)	-21(1)	-8(2)
C(16)	85(3)	78(3)	32(2)	4(2)	-17(2)	-22(2)
C(17)	143(6)	122(5)	59(3)	11(3)	-41(4)	-74(5)
C(18)	98(4)	141(6)	62(3)	18(3)	-19(3)	-66(4)
C(19)	77(3)	54(2)	59(2)	16(2)	-27(2)	-6(2)
C(20)	65(3)	106(5)	90(4)	26(4)	-29(3)	-2(3)
C(21)	137(6)	49(3)	95(4)	8(3)	-32(4)	-22(3)
C(22)	141(7)	256(12)	73(4)	46(6)	-58(4)	-129(8)
C(23)	115(6)	104(5)	141(7)	-50(5)	-17(5)	-41(4)
C(24)	88(4)	111(4)	70(3)	0(3)	-14(3)	-53(3)
Si(2)	64(1)	81(1)	67(1)	3(1)	-16(1)	-32(1)
C(31)	58(2)	51(2)	52(2)	7(2)	-7(2)	-2(2)
C(32)	61(2)	59(2)	54(2)	8(2)	-13(2)	-16(2)
C(33)	57(2)	50(2)	51(2)	4(2)	-7(2)	-14(2)
C(34)	56(2)	55(2)	49(2)	12(2)	-11(2)	-19(2)
C(35)	67(3)	88(3)	64(3)	10(2)	-11(2)	-40(3)
C(36)	108(5)	100(4)	99(5)	-8(4)	-29(4)	-54(4)
C(37)	68(3)	104(4)	131(6)	-18(4)	-18(4)	-32(3)
O(31)	57(2)	46(1)	47(1)	3(1)	-1(1)	-8(1)
C(38)	49(2)	47(2)	53(2)	-6(2)	-7(2)	-13(2)
O(32)	95(2)	44(2)	64(2)	-2(1)	-5(2)	-4(2)
N(31)	54(2)	46(2)	48(2)	-3(1)	-1(2)	-9(2)
C(39)	46(2)	62(2)	47(2)	-8(2)	-5(2)	-21(2)
C(40)	65(3)	66(3)	55(2)	-5(2)	-1(2)	-27(2)
C(41)	88(4)	93(4)	59(3)	0(3)	0(3)	-43(3)
C(42)	83(4)	107(4)	60(3)	-23(3)	11(3)	-44(3)
C(43)	67(3)	84(3)	68(3)	-34(3)	8(2)	-20(3)
C(44)	62(2)	62(2)	61(3)	-19(2)	-2(2)	-19(2)
O(33)	71(2)	47(2)	53(2)	8(1)	-10(1)	4(1)
C(45)	49(2)	46(2)	55(2)	9(2)	-16(2)	-11(2)
O(34)	63(2)	46(1)	55(2)	4(1)	-12(1)	0(1)
N(32)	57(2)	51(2)	63(2)	19(2)	-25(2)	-15(2)
C(46)	62(2)	48(2)	94(4)	22(2)	-32(2)	-10(2)
C(47)	94(4)	49(2)	120(5)	10(3)	-33(4)	-18(2)
C(48)	56(3)	65(3)	164(7)	23(4)	-27(4)	-7(2)
C(49)	89(3)	83(3)	65(3)	21(2)	-35(3)	-37(3)
C(50)	127(6)	140(6)	77(4)	38(4)	-40(4)	-79(5)
C(51)	142(6)	118(5)	112(6)	18(4)	-72(5)	-70(5)

C(52)	160(8)	211(11)	104(6)	-24(6)	-14(6)	-133(8)
C(53)	115(6)	192(9)	150(8)	67(7)	-54(6)	-111(7)
C(54)	63(4)	117(6)	233(12)	-33(7)	-55(6)	-6(4)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for **12**.

	x	y	z	U(eq)
H(1)	7978	2132	1422	59
H(4)	3558	4982	4158	66
H(5)	4234	2660	3300	109
H(6A)	2218	5026	2960	238
H(6B)	2361	3806	2467	238
H(6C)	3817	4189	2170	238
H(7A)	1413	4149	4783	187
H(7B)	2454	2760	4858	187
H(7C)	1446	3122	4092	187
H(100)	4380(60)	2850(50)	6530(40)	61
H(10)	1894	5836	7560	73
H(11)	363	6275	9240	92
H(12)	213	4731	10284	110
H(13)	1685	2726	9705	106
H(14)	3236	2250	8016	77
H(16)	8866	2665	-1998	82
H(17A)	6277	2853	-1969	147
H(17B)	7433	2790	-3065	147
H(17C)	6119	4061	-2547	147
H(18A)	7874	5089	-2597	144
H(18B)	9343	3955	-3223	144
H(18C)	9357	4472	-2202	144
H(19)	5796	5431	-1299	82
H(20A)	4193	4418	-557	145
H(20B)	3473	5753	-37	145
H(20C)	4344	4620	518	145
H(21A)	5899	5892	623	149
H(21B)	5515	6829	-210	149
H(21C)	7261	5888	-352	149
H(22A)	8097	3422	4757	204
H(22B)	6555	4438	5459	204
H(22C)	8104	4693	5022	204
H(23A)	5967	7048	4139	184
H(23B)	4600	6601	4670	184
H(23C)	4986	6816	3500	184
H(24A)	9163	5225	2905	131
H(24B)	8236	5245	2134	131
H(24C)	9260	3984	2479	131
H(31)	6627	1305	4586	75
H(34)	9981	-1789	1761	67
H(35)	7306	-1331	2724	86
H(36A)	6819	-2237	1509	146
H(36B)	8672	-2742	1222	146
H(36C)	7770	-1691	614	146
H(37A)	6281	719	2456	155
H(37B)	5321	-3	2248	155
H(37C)	6464	362	1331	155
H(300)	10120(70)	410(50)	-500(40)	67
H(40)	11405	1043	-2012	78
H(41)	13051	599	-3668	99
H(42)	14483	-1416	-4293	105
H(43)	14300	-2967	-3276	97
H(44)	12622	-2554	-1610	79
H(46)	8957	-2242	7120	85
H(47A)	7455	-2779	6316	136
H(47B)	9281	-3559	5879	136
H(47C)	8428	-2484	5269	136
H(48A)	10304	-1549	5223	154
H(48B)	11180	-2440	5937	154
H(48C)	10332	-1019	6234	154

H(49)	5805	496	7982	90
H(50A)	5324	-1308	8136	157
H(50B)	5448	-892	9159	157
H(50C)	6876	-1982	8450	157
H(51A)	8754	-934	8296	164
H(51B)	7357	86	9089	164
H(51C)	8218	453	8037	164
H(52A)	12427	397	3550	214
H(52B)	11124	-79	4166	214
H(52C)	10628	1270	3811	214
H(53A)	10691	1672	1588	202
H(53B)	11893	546	817	202
H(53C)	12495	1138	1513	202
H(54A)	13858	-1640	1980	214
H(54B)	12824	-1919	1411	214
H(54C)	12635	-2208	2560	214