Palladium Complex-catalysed Carbocyclization–distannylation, –disilylation and –silastannylation of Bis-dienes using Distannanes, Disilanes and Silylstannanes

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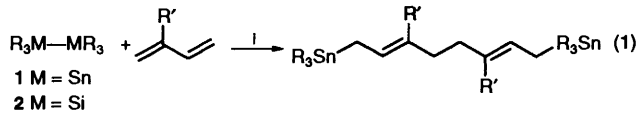
Bis-dienes **4** react with distannanes **1**, disilanes **2**, and silylstannanes **3** in the presence of a catalytic amount of a palladium complex to afford carbocyclization–distannylation, –disilylation and –silastannylation products in high yields. Reaction of distannanes **1a, b** with bis-dienes **4a, b** as well as reaction of disilane **2b** with bis-diene **4d** proceeded regio- and stereo-selectively to afford a single product: *trans*-(*E*),(*Z*) isomers. Regio- and stereo-selective reaction was also realized with the disilane **2b** and bis-diene **4e** to provide only *trans*-(*E*),(*E*) isomer. In other cases, the reactions proceeded regioselectively, but the stereoselectivity was modest. The X-ray crystal structures of the cyclopropanes **10** and **11** have been determined.

Transition-metal-mediated carbocyclizations of substrates containing two or more elements of unsaturation are important as new catalytic strategies for construction of common organic ring systems. Enyne,[1] diynes,[2] and bis-dienes[3] are mainly employed in the transformations.

On the other hand, transition-metal-catalysed insertions of unsaturated compounds into Sn–Sn,[4] Si–Si,[5] Si–Sn,[6] and Ge–Ge[5b] σ-bonds are of current interest, since the reactions provide potent one-step transformations to afford a variety of Group-14-atom compounds.[7] In this context, we have recently developed 1,4-disilylation[8] and 1,4-silastannylation[9] of 1,3-dienes using disilanes **2** and silylstannanes **3** in the presence of transition-metal catalyst. During the course of these studies, we found a highly regio- and stereo-selective intermolecular dimerization–distannylation[10] and dimerization–disilylation[11] of 1,3-dienes using distannanes **1** and disilanes **2** [eqn. (1)]. As the catalyst precursor, $Pd(dba)_2$ (dba = dibenzylideneacetone) showed high catalytic activity even at room temperature.[10,11] Such a highly active catalyst system had never been reported before.

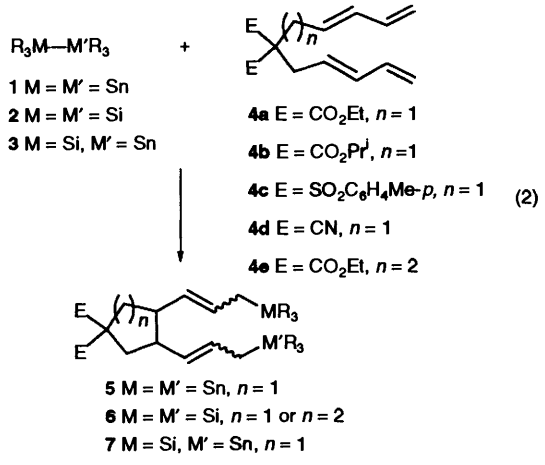


Reagents and conditions: i, $Pd(dba)_2$ (5 mol%) at room temperature

In this paper, we report carbocyclization–distannylation, –disilylation, and –silastannylation of bis-diene **4** using distannanes **1**, disilanes **2**, and silylstannanes **3** catalysed by the palladium(0) complex [eqn. (2)]. This is the first example to show that these Group-14-atom compounds (**1**–**3**) are utilized in carbocyclization reactions. In the present reaction, allylic stannane or allylic silane side chains were introduced regioselectively at the terminal positions with the concomitant carbocyclization. These reactions proceeded at room temperature in the presence of a catalytic amount of $Pd(dba)_2$. Quite recently, Tamao *et al.* reported similar dimerization–disilylation of bis-dienes using a fluoro-substituted disilane.[12] Their work prompted us to report our independent results involving the reactions with disilanes **2** as well as with distannanes **1** and silylstannanes **3**.

Results and Discussion

Reactions with Distannanes.—Distannanes **1** smoothly reacted with bis-dienes **4** in the presence of a catalytic amount (5 mol%) of $Pd(dba)_2$ to afford the carbocyclization–distannylation products **5** [eqn. (3)]. The results are listed in Table 1. Hexamethyldistannane **1a** and ethoxycarbonyl-substituted bis-diene **4a** provided the carbocyclization–distannylation product in excellent yield (entry 1). The reaction proceeded highly regio- and stereo-selectively to afford a single product **5a**. The ^{13}C NMR spectrum of product **5a** shows two Me_3Sn resonances of equal intensity at δ −10.33 and −10.00 with $^{117,119}Sn$ satellites: for both the resonances, $^1J_{Sn-C}$ = 310 and 322 Hz.†



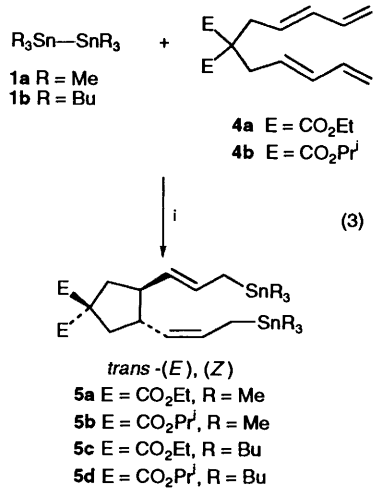
Reagents and conditions: i, $Pd(dba)_2$ (5 mol%) at room temp. to 80 °C, for 20 h

Table 1 Palladium-catalysed carbocyclization–distannylation of bis-dienes using distannanes[a]

Entry	Distannane **1**	Bis-diene **4**	Product **5**	Yield/%[b]
1	**1a**	**4a**	**5a**	90
2	**1a**	**4b**	**5b**	92
3	**1b**[c]	**4a**	**5c**	89
4	**1b**[c]	**4b**	**5d**	89

[a] A mixture of distannane **1** (0.60 mmol), bis-diene **4** (0.50 mmol), $Pd(dba)_2$ (0.025 mmol) as catalyst precursor and toluene (2.0 cm^3) was stirred at room temperature under argon for 20 h. [b] Isolated yield. [c] Treated at 80 °C.

† The ratio of the coupling constants 310/322 = 0.963 coincides with 0.956, the magnetic-moment rate of ^{117}Sn and ^{119}Sn.



Reagents and conditions: i, $Pd(dba)_2$ (5 mol%) at room temp. to 80 °C for 20 h

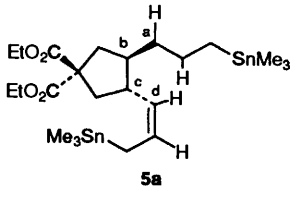
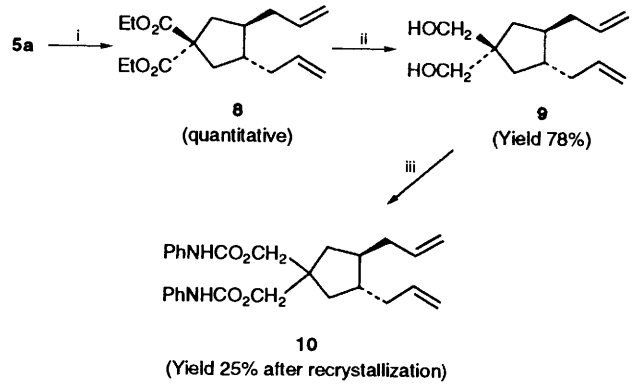


Fig. 1 Notation of compound **5a** for its HMBC spectrum

Olefin proton resonances of compound **5a** consist of two sets of absorptions in 1:1 ratio, and each has (*E*) or (*Z*) vicinal olefin couplings: δ 5.03 (1 H, dd, *J* 15 and 7 Hz), 5.46 (1 H, dt, *J* 15 and 7 Hz), 4.87 (1 H, dd, *J* 10 and 9 Hz), 5.52 (1 H, dt, *J* 10 and 7 Hz). These results indicate that the allylic stannane side chains have both (*E*) and (*Z*) configurations in 1:1 ratio. Furthermore, long-range C^b–H^d correlations (for the notation, see Fig. 1) observed in 2D heteronuclear multiple bond coherence (HMBC)[13] spectrum confirmed that the (*E*)- and (*Z*)-allylic stannane side chains were introduced in the same molecule and that the product **5a** is not an equimolar mixture of (*E*),(*E*) and (*Z*),(*Z*) isomers.

Since *trans* and *cis* stereochemistry of disubstituted cyclopentanes could not be elucidated by NMR spectroscopy,[14] the stereochemistry regarding the allylic stannane side chains was determined by X-ray crystallography as follows. Product **5a** is a liquid compound. Therefore, the transformations in Scheme 1 were performed to obtain single crystals for X-ray analysis. From the stannane **5a**, protonation–destannylation[15] proceeded quantitatively by treatment with hydrochloric acid in ethanol at room temperature, and only the allyl rearrangement compound **8** was obtained as a single product. Then, the ester functionality of compound **8** was reduced with $LiAlH_4$ and the corresponding alcohol **9** was obtained. Finally, reaction with phenyl isocyanate afforded the corresponding urethane **10**. Recrystallization from heptane gave single crystals suitable for X-ray analysis. The molecular structure of **10** is shown in Fig. 2. The structure clearly shows that compound **10** has the *trans* configuration, indicating that the parent substrate **5a** also has a *trans*-structure regarding the allylic stannane side chains. Eventually, the stannane **5a** was determined to have the *trans*-(*E*),(*Z*) structure.

As the catalyst precursor, $Pd(dba)_2$ gave the highest catalytic activity. However, palladium complexes such as $Pd(PPh_3)_4$, $PdCl_2(PhCN)_2$, and $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ did not show any catalytic activity. A naked palladium(0) complex without an electron donating ligand may be most favourable. This catalytic behaviour is the same as was observed in the *intermolecular* dimerization–disilylation of 1,3-dienes with distannanes **1** [eqn. (1) with M = Sn].[10] Therefore, similar catalytic cycle might operate in these two reactions.



Scheme 1 *Reagents and conditions:* i, HCl in EtOH at room temp. for 2 h; ii, $LiAlH_4$ in THF at 65 °C for 4 h; iii, PhN=C=O at room temp. for 30 min, then recrystallization from heptane

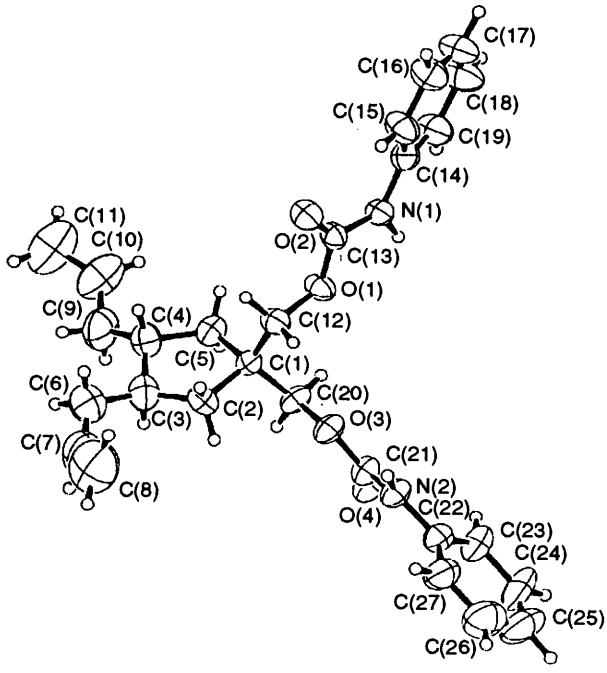
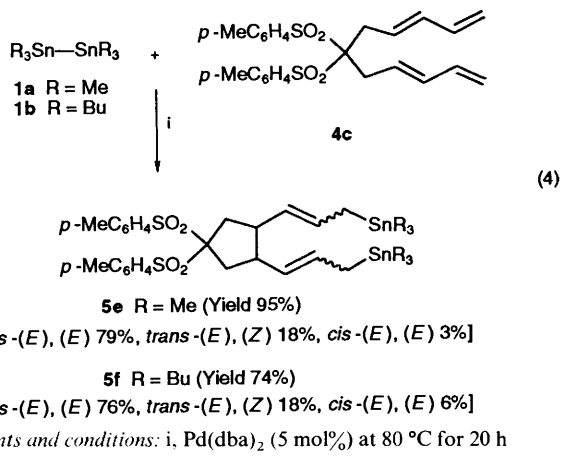


Fig. 2 ORTEP drawing of compound **10** showing 30% probability ellipsoids and the crystallographic numbering scheme

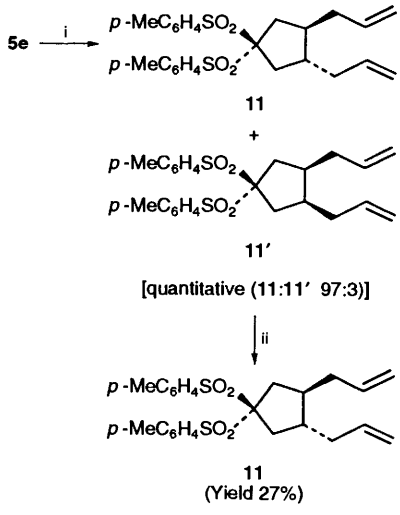
Isopropoxycarbonyl-substituted bis-diene **4b** also reacted with hexamethyldistannane **1a** to give the corresponding product **5b** in high yield (entry 2). ^{13}C and ^1H NMR spectra of compound **5b** showed the product has both (*E*)- and (*Z*)-allylic stannane side chains in 1:1 ratio. Similar treatment of compound **5b** to that in Scheme 1 afforded bis-urethane **10**, the same product as derived from substrate **5a**. Thus, compound **5b** was determined also to have a *trans*-(*E*),(*Z*) structure, as has compound **5a** [eqn. (3)]. Hexabutyldistannane **1b** reacted with bis-dienes **4a** and **4b** to afford the corresponding *trans*-(*E*),(*Z*) products (**5c** and **5d**) in high yields [eqn. (3), entries 3 and 4]. The butylstannane **1b** was less reactive than the methylstannane **1a**. Upon raising of the reaction temperature to 80 °C, the products were obtained in high yields.

From the distannane **1a** and toluene-*p*-sulfonyl-substituted bis-diene **4c**, the carbocyclization–distannylation product **5e**



Reagents and conditions: i, $Pd(dba)_2$ (5 mol%) at 80 °C for 20 h

was obtained in 95% total yield at 80 °C [eqn. (4)]. The reaction proceeded highly regioselectively, but in this case the stereoselectivity was modest. The reaction provided a mixture of three stereoisomers: one major and two minor isomers, which were easily distinguished by their ^{13}C and ^{1}H NMR spectra. The (*E*),(*E*)-isomer was the major one. With compound **5e**, a similar protonation–destannylation reaction to that in Scheme 1 proceeded quantitatively and gave two products (**11** and **11′**, Scheme 2). Further recrystallization from



Scheme 2 *Reagents and conditions:* i, HCl in THF at room temp. for 2 h; ii, recrystallization from EtOH

ethanol successfully removed the minor isomer **11′** and provided single crystals of compound **11**, whose structure was determined by X-ray crystallography. The molecular structure of **11** is shown in Fig. 3. Molecule **11** was on a crystallographic two-fold axis and had a *trans*-configuration, indicating that the major isomer of the parent compound **5e** also has a *trans* structure regarding the allylic stannane side chains. The ^{13}C NMR spectrum measured with nuclear Overhauser enhancement (NOE) suppression and long pulse delay (30 s) revealed that compound **5e** contains *trans*-(*E*),(*E*), *trans*-(*E*),(*Z*), and *cis*-(*E*),(*E*) isomers in 79, 18, and 3%, respectively [eqn. (4)]. Hexabutyldistannane **1b** also reacted with bis-diene **4c** and afforded bis-stannane **5f** in 74% total yield as a mixture of three isomers: *trans*-(*E*),(*E*) 76%, *trans*-(*E*),(*Z*) 18%, and *cis*(*E*),(*E*) 6% [eqn. (4)].

Reaction with Disilanes.—Disilanes **2** reacted with the bis-dienes **4** in the presence of $Pd(dba)_2$ at room temperature.

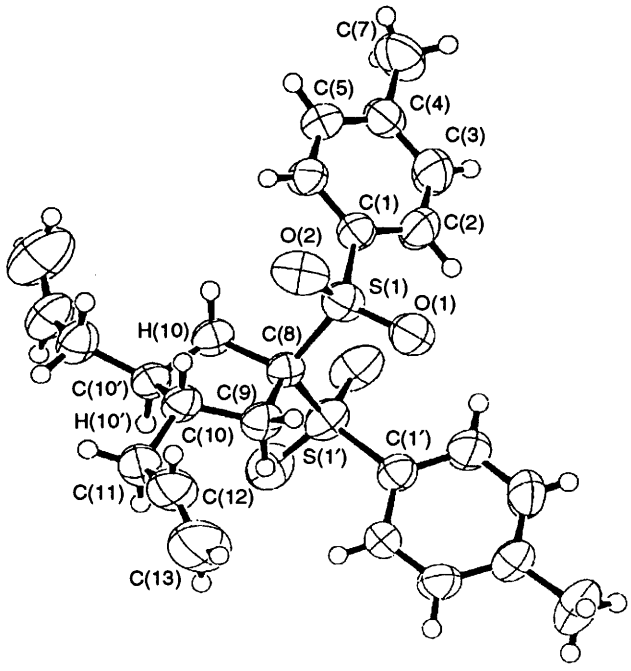
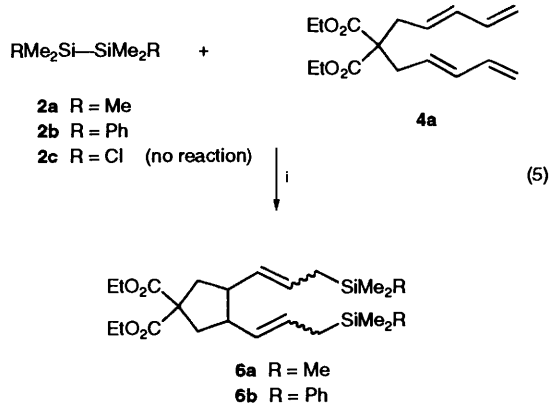


Fig. 3 ORTEP drawing of compound **11** showing 30% probability ellipsoids and the crystallographic numbering scheme

The reaction proceeded highly regioselectively to introduce the silyl group at the terminal position, but stereoselectivity was modest [eqn. (5), Table 2]. Hexamethyldisilane **2a** gave



Reagents and conditions: i, $Pd(dba)_2$ (5 mol%) at room temp. for 20 h

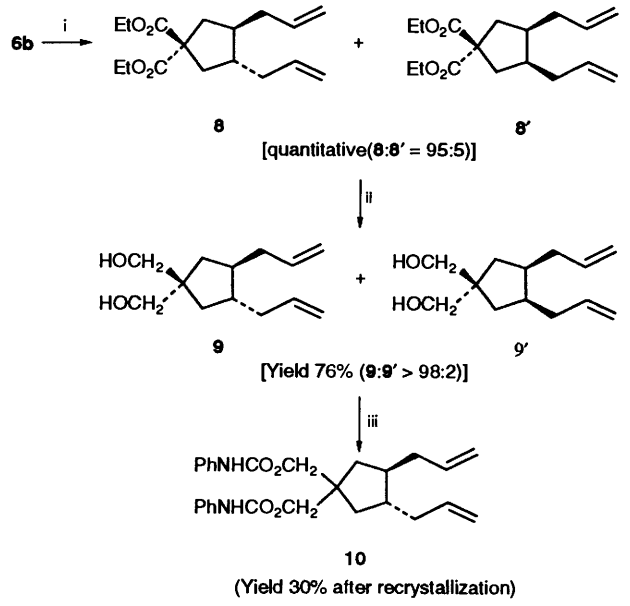
the carbocyclization–disilylation products **6a** in high total yields (entries 1, 2). The reaction can be performed at room temperature in 1,4-dioxane or dimethylformamide (DMF) as solvent, although in tetrahydrofuran (THF) the conversion of the reaction was low and the yield of compound **6a** was reduced markedly (20% for the reaction of disilane **2a** with bis-diene **4a**). 1,2-Diphenyltetramethyldisilane **2b** also reacted with bis-diene **4a** and gave the corresponding products **6b** in 82% total yield (entry 3). Each product was a mixture of three stereoisomers: one major and two minor products, which were easily distinguished by ^{13}C and ^{1}H NMR spectroscopy.

In order to determine the structure, the derivatization of bis-silanes **6a** and **6b** was performed by the following transformations (Scheme 3) similar to Scheme 1. From compound **6b**, protonation–desilylation[16] proceeded quantitatively by treatment with BF_3·AcOH complex at room temperature, and only two isomers of the allyl rearrangement products **8** and **8′** were obtained (Scheme 3). Then the ester functionalities of compounds **8** and **8′** were reduced with

Table 2 $Pd(dba)_2$-catalysed carbocyclization–disilylation of **4a** using disilanes[a]

Entry	Disilane	Solvent	Product	Total yield of **6**[b]	Product distribution		
					trans-(*E*),(*E*)	*trans*-(*E*),(*Z*)	*cis*-(*E*),(*E*)
1	**2a**	1,4-Dioxane	**6a**	96	63	22	15
2	**2a**	DMF	**6a**	84	65	16	19
3	**2b**	1,4-Dioxane	**6b**	82	25	70	5

[a] A mixture of **2** (0.60 mmol), **4a** (0.50 mmol), $Pd(dba)_2$ (0.025 mmol) and solvent (2.0 cm^3) was stirred for 20 h at room temp. under Ar. [b] Isolated yield.

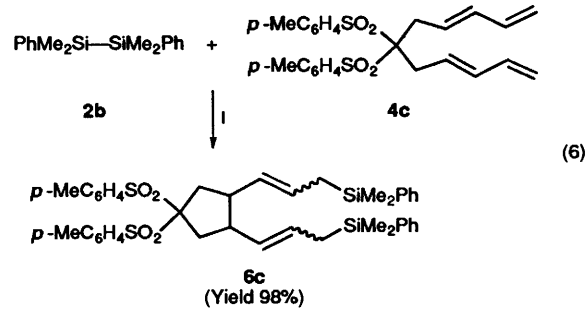


Scheme 3 *Reagents and conditions:* i, BF_3·AcOH in $CHCl_3$ at room temp. for 10 min; ii, $LiAlH_4$ in THF at 65 °C for 4 h; iii, PhN=C=O at room temp. for 30 min

$LiAlH_4$ and the corresponding alcohols (**9** and **9'**; **9**:**9'** > 98:2) were obtained. Finally, reaction with phenyl isocyanate afforded the corresponding urethane. Recrystallization from heptane successfully removed the minor isomer. As compared by GLC and NMR data, major isomers, **8** and **9**, and the urethane **10**, were confirmed to be the same compounds as were derived in Scheme 1 from **5a**. Therefore, these results clearly indicate that the two allylic silane side chains of major product **6** are disposed *trans*. Furthermore, the existence of (*E*) and (*Z*) allylic silane side chains were confirmed by coupling constants of the olefin protons as well as by ^{13}C NMR spectra. Peak integrations of the ^{13}C NMR spectra measured with NOE suppression and long (30 s) pulse delay gave product distributions of the three stereoisomers as follows: *trans*-(*E*),(*E*) 63%, *trans*-(*E*),(*Z*) 22%, and *cis*(*E*),(*E*) 15% for compound **6a** as prepared in 1,4-dioxane (entry 1). For compound **6a** prepared in DMF, the product distribution was *trans*-(*E*),(*E*) 65%, *trans*-(*E*),(*Z*) 16%, and *cis*-(*E*),(*E*) 19% (entry 2). When diphenyltetramethyldisilane **2b** was employed as the disilane, the percentage of the *trans*-(*E*),(*Z*) isomer in the product **6b** increased: *trans*-(*E*),(*E*) 25%, *trans*-(*E*),(*Z*) 70%, *cis*-(*E*),(*E*) 5% (entry 3). The chloro-substituted disilane, 1,2-dichlorotetramethyldisilane **2c**, did not afford any carbocyclization–disilylation product under the standard conditions, although the disilane and the bis-diene were consumed.

In the reaction with disilanes, $Pd(dba)_2$ also showed the highest catalytic activity. Palladium complexes containing phosphorous ligands, such as $Pd(PPh_3)_4$, and $Pd(dba)_2$ combined with $P(OPr^i)_3$ (P/Pd = 2) were totally inert as catalyst precursors. The phosphorous ligands may saturate the catalyst centre.

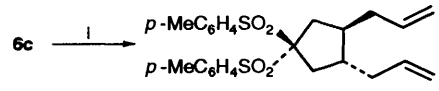
In the reaction of bis-diene **4c** with 1,2-diphenyltetramethyldisilane **2b**, the product **6c** was obtained in 98% isolated yield [eqn. (6)]. The product **6c** was a mixture of three stereoisomers



(6)

trans-(*E*),(*E*) 36%, *trans*-(*E*),(*Z*) 59%, *cis*-(*E*),(*E*) 5%]

Reagents and conditions: i, $Pd(dba)_2$ (5 mol%) at room temp. for 20 h



(7)

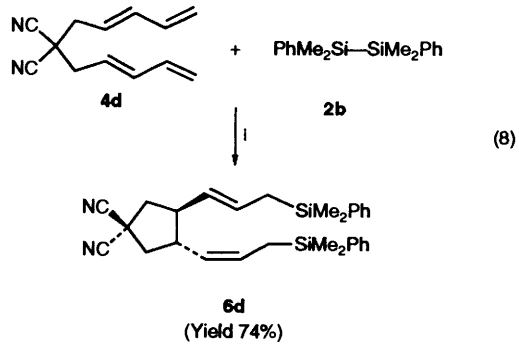
11

Reagents and conditions: i, BF_3·AcOH in $CHCl_3$ for 10 min, then recrystallization from EtOH

judging from its ^{13}C and ^1H NMR spectra. The protonation–desilylation reaction with BF_3·AcOH similar to Scheme 2 proceeded quantitatively to give two isomers. Recrystallization from ethanol successfully removed the minor isomer and afforded pure isomer **11** in 29% yield [eqn. (7)]. GLC and NMR analyses clearly showed that this pure compound is the same compound as that derived from bis-stannane **5e** in Scheme 2, indicating that compound **6c** has a *trans*-configuration regarding the two allylic silane side chains. Finally, quantitative ^{13}C NMR analysis showed that compound **6c** contains *trans*-(*E*),(*E*), *trans*-(*E*),(*Z*), and *cis*-(*E*),(*E*) isomers in 36, 59 and 5%, respectively. Unlike the ethoxycarbonyl-substituted bis-diene **4a**, toluene-*p*-sulfonyl-substituted bis-diene **4c** did not react with hexamethyldisilane **2a** at all. As phenyl-substituted disilane **2b** smoothly reacted with bis-diene **4c** at room temperature, some activating effect of the phenyl functionality is evident. Such a marked effect of the phenyl substituent on the silicon atom is reminiscent of that observed in platinum-catalysed 1,4-disilylation of 1,3-dienes using disilanes including compounds **2a** and **2b**.[8]

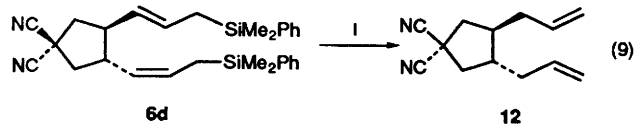
Cyano-substituted bis-diene **4d** was also employed in the reaction. In this case, the reaction proceeded stereo- and regioselectively to afford *a single product* **6d** in 74% yield. The ^1H

NMR spectrum of product **6d** showed two sets of olefin resonances, having (*E*) or (*Z*) vicinal coupling constants, in a 1:1 ratio: δ 5.11 (1 H, dt, *J* 15 and 7 Hz) and δ 5.23 (1 H, dt, *J* 10 and 7 Hz). Other NMR features were very similar to those of compounds **5a–d**. Therefore, we concluded that compound **6d** has the *trans*-(*E*),(*Z*) structure as shown in eqn. (8). In the ^{13}C NMR spectrum of compound



Reagents and conditions: i, $Pd(dba)_2$ (5 mol%) in toluene at room temp. for 20 h

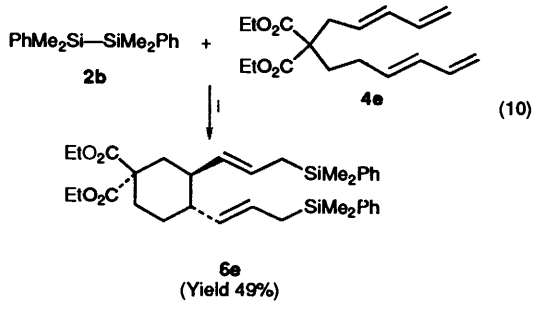
6d two non-equivalent cyano carbon atoms (δ_C 116.95 and 117.07) appeared. However, after the protonation–desilylation reaction [eqn. (9)] which converted (*E*) and (*Z*) allylic silane



Reagents and conditions: i, BF_3·AcOH in $CHCl_3$ at room temp. for 10 min

side chains into the same allyl group, the two non-equivalent cyano carbon resonances became a single peak (δ_C 116.92). With compounds **5a–d**, the same phenomenon was observed with respect to carbonyl carbon resonances after the protonation–destannylation reactions. Accordingly, the stereochemistry of the product **12** and its substrate **6d** must be *trans* as shown in eqns. (8) and (9).

With bis-diene **4e**, the carbocyclization–disilylation took place and six-membered product **6e** was obtained in 49% isolated yield [eqn. (10)]. The reaction proceeded highly regio-



Reagents and conditions: i, $Pd(dba)_2$ (5 mol%) in 1,4-dioxane at room temp. for 20 h

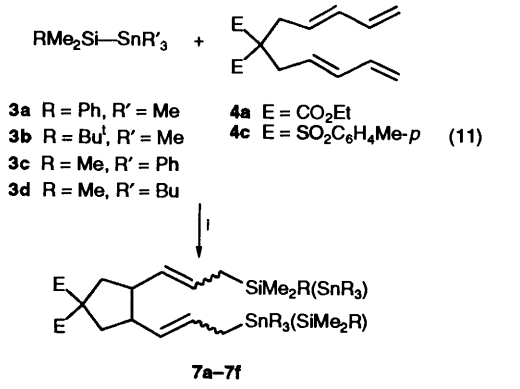
and stereo-selectively to afford a single *trans*-(*E*),(*E*) isomer. The structure was confirmed unambiguously by ^1H and ^{13}C NMR spectroscopy.

Reaction with Silylstannanes.—We attempted to achieve a reaction between silylstannanes **3** and the bis-dienes **4** [eqn. (11)]. However, in the presence of $Pd(dba)_2$, disproportionation of silylstannanes **3** occurred to give a mixture of distannane **1**,

Table 3 $PdCl_2$(cod)-catalysed carbocyclization–silastannylation of bis-dienes using silylstannanes[a]

			7	
Entry	Silylstannane	Bis-diene	Total yield/%[c]	*trans*/*cis*
1	**3a**	**4a**	77	96/4
2	**3b**	**4a**	62	91/9
3	**3c**	**4a**	53	75/25
4	**3d**	**4a**	42	74/26
5[b]	**3a**	**4c**	97	92/8
6[b]	**3c**	**4c**	95	72/28

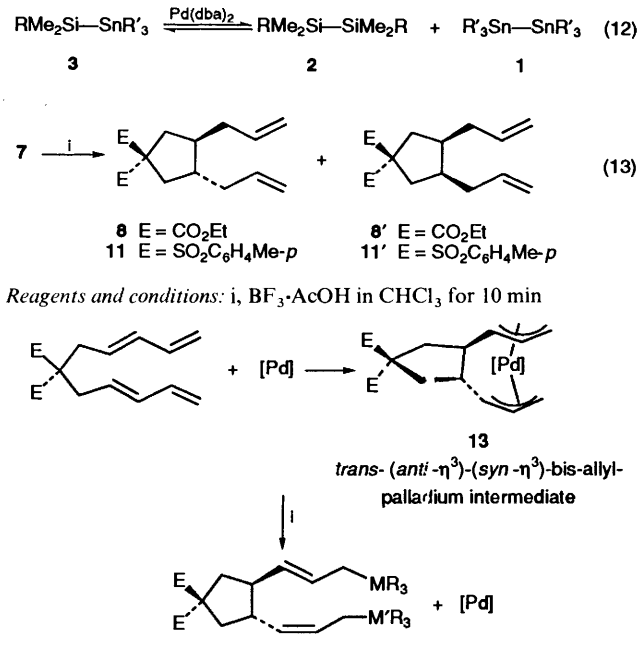
[a] A mixture of silylstannane **3** (0.60 mmol), bis-diene **4** (0.50 mmol), $PdCl_2$(cod) (0.025 mmol) as catalytic precursor and toluene (2.0 cm^3) was stirred at room temp. for 24 h. [b] THF (2.0 cm^3) was used as the solvent in place of toluene. [c] Isolated yield of stereoisomers.



Reagents and conditions: i, $PdCl_2$(cod) (5 mol%) in toluene or THF at room temp. for 24 h

disilane **2**, and silylstannane **3** products [eqn. (12)]. Therefore, $Pd(dba)_2$ could not be used as the catalyst, providing a mixture of the carbocyclization–distannylation (**5**) and –disilylation (**6**) and –silastannylation (**7**) products. However, $PdCl_2$(cod) (cod = cycloocta-1,5-diene) did not catalyse such disproportionation and afforded only the carbocyclization–silastannylation products **7** regioselectively to introduce the silyl and stannyl groups at the terminal positions. However, stereoselectivity was poor. ^{13}C and ^1H NMR spectra of compounds **7** were complicated and showed that (*E*)-allylic silane, (*Z*)-allylic silane, (*E*)-allylic stannane, and (*Z*)-allylic stannane substituents were involved in compounds **7**. Furthermore, occurrence of *trans* and *cis* isomers made the analysis more difficult. Thus, full determination of the product distribution was too difficult. However, protonation–destannylation–desilylation of compounds **7** afforded only two isomers (**8** and **8'**; **11** and **11'**) [eqn. (13)]. In Table 3, total yield and the *trans*/*cis* ratio of compounds **7** are listed for the reaction of bis-dienes **4a** and **4c** with silastannanes **3a–d**.

Concluding Remarks.—Product distribution in the palladium-catalysed carbocyclization–distannylation, –disilylation, –silastannylation of the bis-dienes was affected by the substrates employed. When the reaction proceeded regio- and stereo-selectively to afford the five-membered products (**5a–d**, **6d**), the stereochemistry of the product was *trans*-(*E*),(*Z*). Thus, in these selective cases, a common intermediate such as *trans*-(*anti*-η^3)-(*syn*-η^3)-bis-allyl palladium species (**13**, in Scheme 4) may be involved in the catalytic cycle. A similar bis-η^3-allyl nickel species has been proposed as an intermediate for nickel-catalysed intramolecular cycloaddition of bis-dienes.[17] Bis-(η^3-allyl)palladium intermediates have been postulated in many low-valent palladium-catalysed intermolecular dimerizations



Scheme 4 *Reagent:* i, R_3M–$M'R_3$

or teromerizations of 1,3-dienes.[18] In other cases using bis-dienes **4a–d**, *syn–anti* isomerization[19] of intermediates **13** prior to stannylation and/or silylation might have caused the low stereoselectivity.

Experimental

Materials.—Reagents and solvents were dried and purified before use.[20] Hexamethyldisilane **2a** was purchased from Aldrich. Hexamethyldistannane **1a**,[21] hexabutyldistannane **1b**[22] and silylstannanes **3**[6b] were prepared by the literature methods. 1,2-Dichlorotetramethyldisilane was prepared by the methods reported by Kumada and his co-workers.[23] 1,2-Diphenyltetramethyldisilane **2b** was prepared from dichlorotetramethyldisilane by reaction with phenyllithium. The following catalyst precursors were prepared by published methods: $Pd(dba)_2$,[24] $Pd(PPh_3)_4$,[25] $PdCl_2(PhCN)_2$,[26] $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$,[27] $PdCl_2(cod)$.[28]

Analytical Procedure.—Identification of the products was made with ^1H and ^{13}C NMR and mass spectra. The NMR spectra were recorded with JEOL GX-270, EX-270, or α-400 spectrometers. Samples were dissolved in $CDCl_3$, and the chemical-shift-values were expressed relative to Me_4Si as internal standard. The mass spectra were measured on a Shimadzu QP-1000 (GC–MS) equipped with a PAC 1100S computer system. High-resolution mass spectra were obtained with a Shimadzu 9020-DF and a JEOL JMS-SX102A (25 eV). GLC analysis was made on a Shimadzu GC-8APF equipped with an integrator (C-R6A) with a column (3 mm i.d. × 3 m) packed with Apieson Grease L (5% on Uniport HP, 60/80 mesh), Silicon OV-17 (2% on Uniport HP, 60/80 mesh) and Silicon SE-30 (2% on Uniport HP, 60/80 mesh). TLC analysis was made on a Merck Kieselgel 60 F_{254} (Art. 5725). Elemental analyses were performed at the Microanalytical Centre of Kyoto University.

Preparation of Bis-dienes.—*Bis-diene* **4a**. Diethyl malonate 1.90 g (12 mmol) was added to a solution of sodium ethoxide, prepared by reaction of sodium (0.9 g, 39 mmol) in absolute ethanol (30 cm^3). The solution was stirred at 50 °C for 15 min. Then, (*E*)-penta-2,4-dienyl bromide[29] (3.70 g, 25 mmol) was added dropwise to the solution. Diethyl ether (100 cm^3) was added to the reaction mixture. The organic layer was washed with water, and dried over anhydrous magnesium sulfate. A clear oil (2.35 g, 68%) was obtained by distillation (76 °C/0.5 mmHg), δ_H 1.23 (6 H, t), 2.65 (4 H, d, *J* 7), 4.18 (4 H, q), 5.00 (2 H, d, *J* 10), 5.11 (2 H, d, *J* 15), 5.53 (2 H, dt, *J* 7 and 15), 6.08 (2 H, dd, *J* 10 and 15) and 6.28 (2 H, dt, *J* 10 and 15); δ_C 14.04, 35.92, 57.67, 61.15, 116.26, 127.82, 135.03, 136.53 and 170.55.

Bis-diene **4b**. Diisopropyl malonate (4.24 g, 23 mmol) was used in the above preparation as for **4a**, to afford compound **4b** (4.16 g, 58%); bp 80 °C/0.03 mmHg; δ_H 1.19 (12 H, d, *J* 7), 2.61 (4 H, d, *J* 7), 4.98 (2 H, d, *J* 10), 5.00–5.04 (2 H, m), 5.08 (2 H, d, *J* 15), 5.51 (2 H, dt, *J* 15 and 7), 6.05 (2 H, dd, *J* 15 and 10) and 6.25 (2 H, dt, *J* 15 and 10); δ_C 21.59, 35.87, 57.37, 68.65, 116.22, 127.91, 134.98, 136.56 and 170.12.

Bis-diene **4c**. A suspension of bis-(toluene-*p*-sulfonyl)-methane[30] (14.34 g, 44 mmol) in diethyl ether (100 cm^3) was added to sodium ethoxide solution, which was prepared by the reaction of sodium (1.17 g, 51 mmol) in ethanol (30 cm^3). After this mixture had been stirred for 15 min, (*E*)-penta-2,4-dienyl bromide[29] (6.77 g, 46 mmol) was added dropwise. The solution was stirred overnight. Then, water (30 cm^3) was added to the reaction mixture, and the organic layer was separated. Evaporation of volatiles gave a pale yellow solid. The solid (5.35 g, 14 mmol) was dissolved in DMF (7 cm^3) and the solution was added dropwise to solution of sodium hydride (15 mmol) in DMF (2 cm^3). The purple solution was stirred for 90 min at 40 °C. Then, further (*E*)-penta-2,4-dienyl bromide (2.35 g, 16 mmol) was added dropwise to this solution, which was stirred for 3 h. After extraction with diethyl ether followed by evaporation of the extract, a pale orange solid was obtained by recrystallization from ethanol (3.85 g, 60%); $\delta_H(CDCl_3)$ 2.46 (6 H, s), 3.00 (4 H, d), 5.08 (2 H, d, *J* 10), 5.15 (2 H, d, *J* 15), 5.81 (2 H, dt, *J* 15 and 7), 6.07 (2 H, dd, *J* 10 and 15), 6.29 (2 H, dt, *J* 15 and 10), 7.35 (4 H, d, *J* 7) and 7.90 (4 H, d, *J* 7); δ_C 21.75 (q), 33.24 (t), 90.25 (s), 117.33 (t), 125.29 (d), 129.21 (d), 131.65 (d), 133.97 (s), 136.31 (d), 136.47 (d) and 145.83 (s).

Bis-diene **4d**. Malononitrile (0.685 g, 10 mmol) was added dropwise to a solution of sodium hydride (0.870 g, 23 mmol) in dimethyl sulfoxide (3 cm^3). After the mixture had been stirred for an additional hour, (*E*)-penta-2,4-dienyl bromide[29] (3.147 g, 21 mmol) was added dropwise to the solution. After being stirred for 4 h, the reaction mixture was poured into ice–water (14 cm^3). The organic layer was extracted with diethyl ether and the extract was dried over anhydrous magnesium sulfate. An oil (0.741 g, 36%) was obtained by distillation (bp 88 °C/0.1 mmHg), $\delta_H(CDCl_3)$ 2.72 (4 H, d, *J* 7), 5.21 (2 H, d, *J* 10), 5.29 (2 H, d, *J* 15), 5.71 (2 H, dt, *J* 15 and 7) and 6.27–6.44 (4 H, m); δ_C 37.66 (s), 39.82 (t), 114.90 (s), 119.54 (t), 122.80 (d), 135.39 (d) and 138.45 (d).

Bis-diene **4e**. Diethyl malonate (6.29 g, 39 mmol) was added dropwise to sodium ethoxide solution, prepared by the reaction of sodium (0.941 g, 41 mmol) in ethanol (30 cm^3). After the mixture had been stirred for 90 min at 40 °C, (*E*)-hexa-3,5-dienyl bromide[29] (5.75 g, 36 mmol) was added dropwise. The solution was stirred overnight. The organic layer was extracted with diethyl ether and the extract was dried over anhydrous magnesium sulfate. A liquid (4.55 g, 48%) was obtained by distillation at 82 °C/0.5 mmHg. Then, the monoalkylated diethyl malonate (4.55 g, 19 mmol) was added to sodium ethoxide solution, prepared by sodium (0.54 g, 23 mmol) and ethanol (20 cm^3). The solution was stirred for 6 h at 30–40 °C. (*E*)-Penta-2,4-dienyl bromide[29] (3.59 g, 24 mmol) was added dropwise to this solution, and the whole was stirred for 6 h. The reaction mixture was poured into ice–water (75 cm^3). The organic layer was extracted with diethyl ether. After the extract had been dried over anhydrous magnesium sulfate, a liquid (3.33 g, 57%) was obtained by distillation at 90 °C/0.2 mmHg,

$\delta_H(CDCl_3)$ 1.23 (6 H, t), 1.92–2.06 (4 H, m), 2.67 (2 H, d), 4.17 (4 H, q), 4.96 (1 H, d, *J* 10), 5.00 (1 H, d, *J* 10), 5.07 (1 H, d, *J* 15), 5.11 (1 H, d, *J* 15), 5.52 (1 H, dt, *J* 15 and 7), 5.64 (1 H, dt, *J* 15 and 7), 6.04 (1 H, dd, *J* 15 and 10), 6.08 (1 H, dd, *J* 15 and 10), 6.27 (1 H, dt, *J* 15 and 10) and 6.28 (1 H, dt, *J* 15 and 10).

General Procedure.—A typical reaction procedure is described for the synthesis of compound **5a**. A mixture of hexamethyldistannane **1a** (165 mg, 0.50 mmol), bis-diene **4a** (175 mg, 0.60 mmol), $Pd(dba)_2$ (14 mg, 0.025 mmol), and toluene (2.0 cm^3) was placed under an argon flow in a 20 cm^3 flask and was stirred for 20 h at room temperature. After the reaction had gone to completion, the mixture was passed through a short Florisil column (8 mm i.d. × 50 mm) with toluene (2 cm^3) as eluent to give a clear solution. The product was isolated by medium-pressure chromatography (silica gel: Wakogel 300, 45–75 μm; 1.5% ethyl acetate–hexane as eluent) followed by Kugelrohr distillation in 90% yield.

Compound **8**. Hydrochloric acid (35%; 2.0 cm^3) was added to a solution of compound **5a** (311 mg, 0.50 mmol) in ethanol (4.0 cm^3). The solution was stirred at room temperature for 2 h before being neutralized by aq. sodium hydrogen carbonate. After extraction with ether, the organic layer was separated, and dried over sodium sulfate. Evaporation of volatiles gave compound **8** quantitatively. The same compound **8** was obtained from the reaction of bis-silane **6b** (281 mg, 0.50 mmol) with BF_3·AcOH (0.55 mmol) in chloroform (2.0 cm^3), δ_H 1.19 (6 H, t), 1.57–1.69 (2 H, m), 1.80 (2 H, dd, *J* 15 and 10), 1.79–1.92 (2 H, m), 2.18–2.31 (2 H, m), 2.43 (2 H, dd, *J* 15 and 7), 4.12 (4 H, q), 4.93 (2 H, d, *J* 10), 4.98 (2 H, d, *J* 15) and 5.73 (2 H, ddt, *J* 15, 10 and 7); δ_C 13.94 (q), 37.61 (t), 39.76 (t), 44.00 (d), 58.25 (s), 61.19 (t), 115.63 (t), 136.78 (d) and 172.60 (s).

Compound **9**. A solution of compound **8** (146 mg, 0.50 mmol) in THF (1.0 cm^3) was added to a mixture of lithium aluminium hydride (72 mg, 1.90 mmol) in THF (2.0 cm^3). The mixture was stirred for 4 h at 65 °C. After cooling, the mixture was poured into ice–water. The organic layer was washed successively with 10% aq. HCl and saturated aq. sodium chloride. Pure product **9** (81 mg, 78%) was obtained by Kugelrohr distillation (110 °C/0.5 mmHg), $\delta_H(CDCl_3)$ 1.04 (2 H, dd, *J* 15 and 10), 1.48–1.65 (2 H, m), 1.78 (2 H, dd, *J* 15 and 7), 1.89 (2 H, dd, *J* 15 and 7), 2.10 (2 H, s), 2.30–2.43 (2 H, m), 3.55–3.61 (4 H, m), 4.96 (2 H, d, *J* 10), 5.04 (2 H, d, *J* 15) and 5.77 (2 H, ddt, *J* 15, 10 and 7).

Compound **10**. A mixture of compound **9** (81 mg, 0.39 mmol) and phenyl isocyanate (0.50 cm^3) was stirred for 30 min. By evaporation of excess of phenyl isocyanate, a solid was obtained. Careful crystallization from heptane afforded single crystals suitable for X-ray structure analysis; δ_H 1.16 (2 H, dd, *J* 15 and 10), 1.62–1.69 (2 H, m), 1.84 (2 H, dd, *J* 15 and 7), 1.87 (2 H, dt, *J* 15 and 7), 2.37 (2 H, dd, *J* 15 and 7), 4.06 (4 H, s), 4.98 (2 H, d, *J* 10), 5.03 (2 H, d, *J* 15), 5.77 (2 H, ddt, *J* 15, 10 and 7), 6.69 (2 H, s) and 7.03–7.38 (10 H, m); δ_C 37.55, 38.27, 43.46, 43.62, 68.65, 115.70, 118.76, 123.42, 128.96, 136.91, 137.78 and 153.79; *m/z* (EI) 448 (M^+, 2.1%), 400 (27), 303 (21), 256 (22) and 212 (100) (Found: C, 72.1; H, 7.1. Calc. for $C_{27}H_{32}N_2O_4$: C, 72.30; H, 7.19%).

Compound **11**. A THF (3.0 cm^3) solution of compound **5e** (216 mg, 0.30 mmol) was treated with hydrochloric acid (35%; 1.0 cm^3). The mixture was stirred for 2 h. After extraction with diethyl ether, the organic layer was washed successively with saturated aq. ammonium fluoride and water. A crude solid was obtained by evaporation. Careful recrystallization from ethanol afforded single crystals suitable for X-ray structure analysis; $\delta_H(CDCl_3)$ 1.63–1.67 (2 H, m), 1.82–1.93 (2 H, m), 2.19 (2 H, dd, *J* 15 and 10), 2.25 (2 H, m), 2.46 (6 H, s), 2.63 (2 H, dd, *J* 15 and 7), 5.00 (2 H, d, *J* 15), 5.03 (2 H, d, *J* 10), 5.67 (2 H, ddt, *J* 15, 10 and 7), 7.37 (4 H, d, *J* 8) and 7.91 (4 H, d, *J* 8); δ_C 21.72, 36.30, 37.98, 43.78, 91.29, 116.65, 129.34, 131.37, 133.66, 135.69 and 145.60; *m/z* (EI) 458 (M^+, 7.9%), 425 (4.6), 394 (2.7), 324 (22), 303 (17), 139 (79) and 91 (100); HRMS (EI) (Found: M^+, 458.1593. Calc. for $C_{25}H_{30}O_4S_2$: M, 458.1585).

X-Ray Crystallography.—All data were collected on a Rigaku AFC-7R diffractometer with Mo-Kα radiation (λ = 0.710 69 Å). The cell dimensions were determined by least-squares refinement on diffractometer angles for 25 automatically centred reflections. All structures were solved and refined using the teXsan® crystallographic software package on an IRIS Indigo computer. Scattering factors for neutral atoms were from Cromer and Waber,[31] and anomalous dispersion[32] was used. Atomic coordinates, anisotropic displacement parameters of the non-hydrogen atoms, and tables of bond lengths and angles have been deposited as supplementary material at the Cambridge Crystallographic Data Centre.‡

(a) *Structure of compound* **10**. Fine needle crystals were grown by slow cooling of a heptane solution. $C_{27}H_{32}N_2O_4$, M = 448.56, monoclinic, a = 10.785(6), b = 9.45(1), c = 25.542(5) Å, β = 99.95(3)°, V = 2563(2) $Å^3$ at 23 ± 1 °C, space group $P2_1/n$ (No. 14), Z = 4, D_c = 1.16 g cm^{-3}. Crystal dimensions: 0.1 × 0.15 × 0.9 mm, μ(Mo-Kα) = 0.8 cm^{-1}.

ω-Scan modes with scan width = 1.21 + 0.30 tan θ, ω scan speed 32° min^{-1}, graphite-monochromated Mo-Kα radiation at 23 ± 1 °C; 4279 reflections measured ($1.5 \leqslant \theta \leqslant 25.0°$, $\pm h$, k, l), giving 1524 with $I > 1.5\ \sigma(I)$. Decay and absorption correction were not applied.

The structure was solved by direct methods using SHELX86.[33] Full-matrix least-squares refinement with all non-hydrogen atoms anisotropic and hydrogen atoms in calculated positions for which temperature factors were 1.2-times that of the connecting atoms. The weighting scheme was $w = 1/\sigma^2(F_o)$. Final R- and R_w-values are 0.077, 0.052 ($R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma|F_o|^2]^{\frac{1}{2}}$).

(b) *Structure of compound* **11**. Prismatic crystals were grown by slow cooling of an ethanolic solution. $C_{25}H_{30}O_4S_2$, M = 458.63, monoclinic, a = 17.306(1), b = 10.483(1), c = 13.9189(9) Å, β = 105.178(5)°, V = 2437.1(3) $Å^3$ at 23 ± 1 °C, space group $C2/c$ (No. 15), Z = 4, D_c = 1.25 g cm^{-3}. Crystal dimensions: 0.05 × 0.21 × 0.15 mm, μ(Mo-Kα) = 2.5 cm^{-1}.

ω–2θ Scan modes with scan width = 0.84 + 0.30 tan θ, ω scan speed 32° min^{-1}, graphite-monochromated Mo-Kα radiation at 23 ± 1 °C; 3057 reflections measured ($1.5 \leqslant \theta \leqslant 27.5°$, $\pm h$, k, l), giving 1457 with $I > 3.0\ \sigma(I)$. Decay and absorption correction were not applied. A correction for secondary extinction was applied.

The structure was solved by direct methods by SHELX86.[33] Full-matrix least-squares refinement with all non-hydrogen atoms anisotropic and hydrogen atoms isotropic except for some vinyl hydrogens which are fixed in calculated positions. The weighting scheme was $w = 1/\sigma^2(F_o)$. Final R- and R_w-values are 0.053, 0.056.

Compound **5a**. $\delta_H(CDCl_3)$ 0.01 (9 H, s, $^2J_{Sn\text{-}H}$ 53 and 51), 0.05 (9 H, $^2J_{Sn\text{-}H}$ 53 and 51), 1.20 (3 H, t), 1.21 (3 H, t), 1.52–1.66 (2 H, m), 1.69–1.95 (4 H, m), 2.11–2.24 (1 H, m), 2.38–2.53 (3 H, m), 4.12 (2 H, q), 4.16 (2 H, q), 4.87 (1 H, dd, *J* 10 and 9), 5.03 (1 H, dd, *J* 15 and 7), 5.46 (1 H, dt, *J* 15 and 7) and 5.52 (1 H, dt, *J* 10 and 7); $\delta_C(CDCl_3)$ −10.33 (q, $^1J_{Sn\text{-}C}$ 322 and 310), −10.00 (q, $^1J_{Sn\text{-}C}$ 322 and 310), 12.80 (t, $^1J_{Sn\text{-}C}$ 322 and 310), 14.01 (q), 16.16 (t, $^1J_{Sn\text{-}C}$ 296 and 309), 40.77 (t), 40.83 (t), 43.78 (d), 50.03 (d), 58.30 (s), 61.18 (t), 126.39 (d), 126.81 (d), 129.22 (d, $^2J_{Sn\text{-}C}$ 53), 129.26 (d, $^2J_{Sn\text{-}C}$ 53), 172.68 and 172.77 (s); *m/z*

‡ *Supplementary Publication:* see 'Instructions for Authors' (1995), in the January issue.

(EI) 457 ($M^+ - SnMe_3$) (Found: C, 44.8; H, 6.9. Calc. for $C_{23}H_{42}O_4Sn_2$: C, 44.56; H, 6.83%).

Compound **5b**. $\delta_H(CDCl_3)$ 0.04 (9 H, s, $^2J_{Sn-H}$ 53 and 51), 0.08 (9 H, s, $^2J_{Sn-H}$ 53 and 51), 1.20 (6 H, d, *J* 7), 1.19–1.22 (6 H, m), 1.55–1.96 (6 H, m), 2.08–2.27 (1 H, m), 2.37–2.54 (3 H, m), 4.88 (1 H, dd, *J* 10 and 7), 4.97–5.08 (3 H, m) and 5.42–5.58 (2 H, m); $\delta_C(CDCl_3)$ −10.32 (q, $^1J_{Sn-C}$ 323 and 309), −10.00 (q, $^1J_{Sn-C}$ 323 and 309), 12.80 (t, $^1J_{Sn-C}$ 286 and 307), 16.18 (t, $^1J_{Sn-C}$ 307 and 316), 21.48 (q), 21.50 (q), 40.71 (t), 40.79 (t), 43.74 (d), 50.04 (d), 58.37 (s), 68.44 (d), 68.46 (d), 126.46 (d), 126.94 (d), 129.15 (d, $^2J_{Sn-C}$ 48), 129.23 (d, $^2J_{Sn-C}$ 47), 172.21 (s) and 172.30 (s); HRMS (EI) (Found: M^+, 650.1442. Calc. for $C_{25}H_{46}O_4{}^{120}Sn_2$: M, 650.1440; Found: C, 46.6; H, 7.1. Calc. for $C_{25}H_{46}O_4Sn_2$: C, 46.34; H, 7.16%).

Compound **5c**. $\delta_H(CDCl_3)$ 0.38 (6 H, t), 0.32 (18 H, t), 0.69–2.15 (46 H, m), 3.65 (2 H, q), 3.66 (2 H, q), 4.36 (1 H, dd, *J* 10 and 8), 4.54 (1 H, dd, *J* 15 and 8) and 4.95–5.09 (2 H, m); $\delta_C(CDCl_3)$ 9.14 (t, $^1J_{Sn-C}$ 312 and 298), 9.27 (t, $^1J_{Sn-C}$ 312 and 298), 10.96 (t, $^1J_{Sn-C}$ 250 and 236), 13.67 (q), 14.01 (q), 14.04 (q), 14.37 (t, $^1J_{Sn-C}$ 258 and 241), 27.33 (t, $^2J_{Sn-C}$ 50), 27.37 (t, $^2J_{Sn-C}$ 50), 29.19 (t, $^3J_{Sn-C}$ 21), 40.75 (t), 40.94 (t), 43.75 (d), 50.16 (d), 58.46 (s), 61.15 (t), 61.20 (t), 126.23 (d), 126.56 (d), 129.71 (d, $^2J_{Sn-C}$ 44), 129.86 (d, $^2J_{Sn-C}$ 45), 172.68 (s) and 172.79 (s) (Found: C, 56.5; H, 9.0. Calc. for $C_{41}H_{78}O_4Sn_2$: C, 56.44; H, 9.01%).

Compound **5d**. $\delta_H(C_6D_6)$ 0.74–0.83 (30 H, m), 1.12–2.50 (46 H, m), 4.81 (1 H, dd, *J* 10 and 9), 4.92–5.03 (3 H, m) and 5.40–5.54 (2 H, m); $\delta_C(C_6D_6)$ 9.06 (t, $^1J_{Sn-C}$ 312 and 299), 9.19 (t, $^1J_{Sn-C}$ 312 and 299), 10.88 (t, $^1J_{Sn-C}$ 250 and 236), 13.67 (q), 13.69 (q), 14.29 (t, $^1J_{Sn-C}$ 252), 21.46 (q), 27.31 (t, ^2J 50), 27.34 (t, ^2J 50), 29.12 (t, $^3J_{Sn-C}$ 21), 29.15 (t, $^3J_{Sn-C}$ 21), 40.62 (t), 40.84 (t), 43.65 (d), 50.16 (d), 58.42 (s), 68.35 (d), 68.42 (d), 126.29 (d), 126.61 (d), 129.59 (d), 129.76 (d), 172.18 (s) and 172.31 (s); HRMS (EI) (Found: M^+, 900.4294. Calc. for $C_{43}H_{82}O_4{}^{118}Sn^{120}Sn$: 900.4251; Found: C, 57.55; H, 9.25. Calc. for $C_{43}H_{82}O_4Sn_2$: C, 57.35; H, 9.18%).

Compound **5e**. $\delta_H(CDCl_3)$ *trans*-(*E*),(*E*) 0.01 (18 H, s, $^2J_{Sn-H}$ 54 and 51), 1.59 (4 H, d, $^2J_{Sn-H}$ 57 and 7), 2.37 (6 H, s), 2.04–2.62 (6 H, m), 4.87 (2 H, dd, *J* 15 and 7), 5.39 (2 H, dt, *J* 15 and 7), 7.25–7.33 (4 H, m) and 7.83–7.90 (4 H, m); $\delta_C(CDCl_3)$ *trans*-(*E*),(*E*) −10.33 (q, $^1J_{Sn-C}$ 324 and 306), 16.15 (t, $^1J_{Sn-C}$ 301 and 286), 21.62 (q), 38.70 (t), 49.00 (d), 91.23 (s), 125.13 (d), 129.20 (d), 130.97 (d, $^2J_{Sn-C}$ 52), 131.25 (d), 133.52 (s) and 145.51 (s); δ_C *trans*-(*E*),(*Z*) −10.26 (q, $^1J_{Sn-C}$ 324 and 306), −9.98 (q, $^1J_{Sn-C}$ 301 and 286), 12.8 (t), 16.15 (t, $^1J_{Sn-C}$ 301 and 286), 21.62 (q), 38.4 (t), 43.4 (d), 49.7 (d) and 92.0 (s); δ_C *cis*-(*E*),(*E*) 37.9 (t), 47.0 (d) and 93.7 (s).

Compound **5f**. $\delta_H(CDCl_3)$ *trans*-(*E*),(*E*) 0.81–0.94 (18 H, m), 1.23–2.63 (46 H, m), 2.44 (6 H, s), 4.92 (2 H, dd, *J* 15 and 7) and 5.39–5.64 (2 H, m); $\delta_C(CDCl_3)$ *trans*-(*E*),(*E*) 9.08 (t, $^1J_{Sn-C}$ 314 and 300), 13.66 (q), 14.39 (t, $^1J_{Sn-C}$ 253 and 240), 21.60 (q), 27.26 (t, $^2J_{Sn-C}$ 51), 29.08 (t, $^3J_{Sn-C}$ 20), 38.80 (t), 49.27 (d), 91.39 (s), 125.03 (d), 129.18 (d), 131.31 (d), 131.58 (d, $^2J_{Sn-C}$ 45), 133.78 (s) and 145.43 (s); δ_C *trans*-(*E*),(*Z*) 9.26 (t), 43.48 (d), 49.99 (d) and 91.56 (s); δ_C *cis*-(*E*),(*E*) 47.2 (d) and 93.9 (s).

Compound **6a**. δ_H *trans*-(*E*),(*E*) −0.02 (18 H, s), 1.26 (6 H, t, *J* 7), 1.41 (4 H, d, *J* 7), 1.85–1.95 (2 H, m), 2.10–2.30 (2 H, m), 2.40–2.53 (2 H, m), 4.19 (4 H, q, *J* 7), 5.05 (2 H, dd, *J* 15 and 7) and 5.36 (2 H, dt, *J* 15 and 7); δ_H *trans*-(*E*),(*Z*), *cis*-(*E*),(*E*) −0.03 (18 H, s), 1.26 (6 H, t, *J* 7), 1.41 (4 H, d, *J* 7), 1.85–1.97 (2 H, m), 2.08–2.25 (2 H, m), 2.34–2.50 (2 H, m), 4.19 (4 H, q, *J* 7), 5.00–5.20 (2 H, m) and 5.28–5.46 (2 H, m); δ_C *trans*-(*E*),(*E*) −2.06 (q), 14.03 (q), 22.73 (t), 40.72 (t), 49.54 (d), 58.24 (s), 61.26 (t), 127.12 (d), 129.81 (d) and 172.77 (s); δ_C *trans*-(*E*),(*Z*) −1.9 (q), 14.0 (q), 19.0 (t), 22.7 (t), 39.7 (t), 43.9 (d), 50.2 (d), 58.5 (s), 61.2 (t), 126.8 (2 C, d), 129.6 (d), 129.8 (d) and 173.0 (s); δ_C *cis*-(*E*),(*E*) −1.7 (q), 14.0 (q), 22.8 (t), 40.8 (t), 47.0 (d), 59.1 (s), 61.2 (t), 126.9 (d), 128.9 (d) and 172.7 (s); *m*/*z* (EI) 438 (M^+, 1.5%), 423 (5.4), 393 (3.8), 365 (2.8), 324 (59), 251 (3.9), 178 (29), 78 (92) and 73 (100%); HRMS (EI) (Found: M^+, 438.2613. Calc. for $C_{23}H_{42}O_4Si_2$: M, 438.2621).

Compound **6b**. δ_H *trans*-(*E*),(*Z*) 0.34 (6 H, s), 0.38 (6 H, s), 1.34 (6 H, t, *J* 7), 1.66–1.75 (4 H, m), 2.20–2.64 (6 H, m), 4.29 (4 H, q, *J* 7), 4.81 (1 H, dd, *J* 10 and 7), 4.83 (1 H, dd, *J* 15 and 7), 5.10 (1 H, dt, *J* 15 and 7), 5.14 (1 H, dt, *J* 10 and 7), 5.49 (2 H, dt, *J* 15 and 7) and 7.28–7.54 (10 H, m); δ_H *trans*-(*E*),(*E*), *cis*-(*E*),(*E*) 0.33–0.38 (12 H, m), 1.30–1.39 (6 H, m), 1.66–1.75 (4 H, m), 2.20–2.64 (6 H, m), 4.25–4.35 (4 H, m), 5.15–5.23 (2 H, m), 5.45–5.54 (2 H, m) and 7.28–7.54 (10 H, m); δ_C *trans*-(*E*),(*Z*) −3.4 (q), −3.1 (q), 14.0 (q), 18.1 (t), 21.9 (t), 39.5 (d), 41.7 (t), 43.8 (d), 50.2 (d), 58.4 (s), 61.3 (t), 126.6 (q), 126.7 (t), 128.5 (d), 128.6 (s), 129.8 (d), 130.4 (d), 133.7 (d), 138.7 (s), 172.7 (s) and 172.8 (s); δ_C *trans*-(*E*),(*E*) −3.4 (q), 14.1 (q), 21.9 (t), 40.6 (t), 49.5 (d), 58.2 (s), 61.3 (t), 126.4 (d), 128.5 (d), 128.6 (d), 130.2 (d), 133.7 (d), 138.8 (s) and 172.7 (s); δ_C *cis*-(*E*),(*E*) −3.2 (q), 14.1 (q), 21.4 (t), 39.6 (t), 47.0 (d), 59.0 (s), 61.3 (t), 126.3 (d), 128.5 (d), 128.6 (d), 129.5 (d), 133.7 (d), 138.8 (s) and 172.5 (s); *m*/*z* (EI) 562 (M^+, 3.8%), 498 (25), 441 (40), 400 (100), 374 (67), 299 (39), 253 (16), 225 (35), 207 (28), 201 (20), 189 (47), 179 (32), 173 (29), 149 (100), 135 (70), 84 (100) and 86 (100); HRMS (EI) (Found: M^+, 562.2936. Calc. for $C_{33}H_{46}O_4Si_2$: M, 562.2934).

Compound **6c**. δ_H *trans*-(*E*),(*Z*) 0.22 (6 H, s), 0.24 (6 H, s), 1.55–1.60 (4 H, m), 2.09–2.28 (5 H, m), 2.42 (6 H, s), 2.51–2.61 (1 H, m), 4.80–4.91 (2 H, m), 5.22 (1 H, dt, *J* 15 and 7), 5.34 (1 H, dt, *J* 10 and 7), 7.25–7.40 (10 H, m), 7.42–7.50 (4 H, m) and 7.83–7.93 (4 H, m); δ_H *trans*-(*E*),(*E*) 0.22 (12 H, s), 1.55–1.60 (4 H, m), 2.09–2.28 (5 H, m), 2.35 (6 H, s), 2.51–2.61 (1 H, m), 4.80–4.91 (2 H, m), 5.20 (2 H, dt, *J* 15 and 7), 7.25–7.40 (10 H, m), 7.42–7.50 (4 H, m) and 7.83–7.93 (4 H, m); δ_H *cis*-(*E*),(*E*) 0.20 (6 H, s), 1.55–1.60 (4 H, m), 2.09–2.28 (5 H, m), 2.39 (6 H, s), 2.51–2.61 (1 H, m), 4.95–5.08 (2 H, m), 5.20 (2 H, dt, *J* 15 and 7), 7.25–7.40 (10 H, m), 7.42–7.50 (4 H, m) and 7.83–7.93 (4 H, m); δ_C *trans*-(*E*),(*Z*) −3.52 (q), −3.29 (q), 18.10 (t), 21.65 (1), 21.86 (t), 31.22 (t), 38.50 (t), 43.40 (d), 49.77 (d), 91.48 (s), 127.66 (d), 127.75 (d), 128.26 (d), 128.94 (d), 129.25 (d), 131.27 (d), 133.52 (d), 138.51 (s), 143.28 (s) and 145.60 (s); δ_C *trans*-(*E*),(*E*) −3.44 (q), 21.57 (t), 38.47 (t), 49.04 (d), 91.38 (s), 127.75 (d), 127.94 (d), 128.94 (d), 129.34 (d), 131.27 (d), 133.52 (d), 138.3 (s), 143.3 (s) and 145.6 (s); δ_C *cis*-(*E*),(*E*) −3.36 (q), 14.06 (t), 21.70 (t), 38.36 (t), 47.00 (d), 93.85 (s), 127.7 (d), 127.9 (d), 129.0 (d), 129.3 (d), 131.3 (d), 133.5 (d), 138.3 (s), 143.3 (s) and 145.6 (s); *m*/*z* (EI) 726 (M^+, 0.7%), 696 (0.7), 687 (0.9), 649 (1.2), 641 (0.6), 605 (1.0), 429 (4.1), 355 (4.1), 300 (2.3), 234 (9.8), 213 (9.1), 147 (19), 135 (100), 119 (16), 103 (25), 91 (53), 77 (68), 63 (31) and 51 (72).

Compound **6d**. δ_H −0.048 (q), −0.054 (q), 0.01 (q), 0.02 (q), 1.22 (dd, *J* 7 and 15), 1.36 (t, *J* 7), 1.45 (dd, *J* 10 and 15), 1.52 (dd, *J* 10 and 15), 1.65 (dd, *J* 7 and 15), 1.75 (dd, *J* 10 and 15), 2.07 (dd, *J* 10 and 15), 2.18–2.33 (2 H, m), 4.64–4.72 (2 H, m), 5.11 (1 H, dt, *J* 15 and 7), 5.23 (1 H, dt, *J* 10 and 7) and 7.00–7.24 (10 H, m); δ_C −3.82 (q), −3.59 (q), −3.48 (q), −3.08 (q), 18.65 (t), 21.94 (t), 31.14 (s), 43.19 (d), 44.39 (t), 44.87 (t), 49.42 (d), 116.95 (s), 117.07 (s), 126.53 (d), 126.99 (d), 127.71 (d), 127.88 (d), 128.63 (d), 129.06 (d), 129.24 (d), 133.50 (d), 133.60 (d), 137.88 (s) and 138.24 (s); *m*/*z* (EI) 468 (M^+, 2.0%), 453 (0.5), 429 (1.3), 402 (3.0), 333 (4.2), 255 (2.4), 197 (17), 149 (12), 135 (100) and 84 (100); HRMS (EI) (Found: M^+, 468.2421. Calc. for $C_{29}H_{36}N_2Si_2$: 468.2417).

Compound **6e**. δ_H −0.01 (6 H, s), 0.02 (6 H, s), 1.00 (3 H, t, *J* 7), 1.01 (1 H, m), 1.02 (3 H, t, *J* 7), 1.22 (1 H, t, *J* 13), 1.38 (4 H, t, *J* 7), 1.44 (1 H, dd, *J* 13 and 3), 1.46–1.52 (1 H, m), 1.64 (1 H, dddd, *J* 18, 13, 7 and 3), 2.04 (1 H, dt, *J* 13 and 3), 2.10 (1 H, dd, *J* 13 and 3), 3.92 (2 H, q, *J* 7), 3.96–4.04 (2 H, m), 4.83 (2 H, dd, *J* 15 and 7), 5.06 (1 H, dt, *J* 15 and 7), 5.11 (1 H, dt, *J* 15 and 7) and 7.06–7.30 (10 H, m); δ_C −3.36 (q), 13.96 (q), 14.03 (q),

21.66 (t), 21.71 (t), 29.82 (t), 30.62 (t), 39.95 (t), 43.01 (d), 45.46 (d), 54.92 (s), 60.89 (t), 61.19 (t), 125.06 (d), 125.52 (d), 127.61 (d), 128.81 (d), 133.19 (d), 133.55 (d), 133.64 (d), 138.93 (s), 171.00 (s) and 172.39 (s); *m/z* (EI) 576 (M^+, 5.3%), 548 (1.5), 531 (0.9), 503 (1.7), 498 (2.5), 441 (3.0), 400 (4.1), 307 (4.7), 191 (0.7), 135 (12), 119 (13) and 84 (100); HRMS (EI) (Found: M^+, 576.3101. Calc. for $C_{34}H_{48}O_4Si_2$ M^+, 576.3091).

Compound **12**. δ_H 1.89–1.95 (2 H, m), 1.97–2.01 (2 H, m), 2.02–2.09 (2 H, m), 2.28–2.38 (2 H, m), 2.55 (2 H, dd, *J* 15 and 7), 5.00–5.15 (4 H, m) and 5.65–5.80 (2 H, m); δ_C 31.64 (s), 37.44 (t), 43.41 (d), 44.18 (t), 116.92 (s), 117.56 (t) and 135.02 (d).

Compound **7a**. $\delta_C(CDCl_3)$ −10.42, −10.38, −10.31, −10.04, −3.55, −3.53, −3.48, −3.40, −3.38, −3.33, −3.29, 12.75, 13.95, 13.97, 16.05, 16.09, 17.95, 21.77, 22.55, 31.49, 40.52, 40.57, 40.59, 40.80, 40.83, 43.63, 43.90, 49.29, 49.46, 49.93, 50.06, 58.12, 58.31, 58.34, 61.12, 61.18, 126.07, 126.12, 126.21, 126.26, 126.71, 126.96, 127.58, 127.61, 127.63, 128.79, 128.84, 129.24, 129.27, 129.47, 129.95, 130.39, 130.61, 133.51, 133.53, 138.64, 138.72, 138.75, 172.50, 172.51, 172.58 and 172.60.

Compound **7b**. $\delta_C(CDCl_3)$ −10.40, −10.33, −10.29, −10.02, −6.61, −6.55, −6.52, −6.47, −6.38, 12.80, 13.99, 14.02, 14.06, 16.07, 16.65, 16.67, 18.74, 18.77, 22.59, 26.51, 26.56, 31.53, 40.54, 40.58, 40.77, 40.86, 43.69, 49.36, 49.50, 50.06, 50.14, 58.14, 58.36, 61.19, 61.23, 126.30, 127.03, 127.18, 127.24, 127.34, 128.94, 129.24, 129.27, 129.50, 129.69, 129.88, 172.60, 172.68 and 172.71.

Compound **7c**. $\delta_C(CDCl_3)$ −2.05, −1.99, −1.85, 12.73, 14.00, 16.13, 22.65, 39.38, 39.58, 40.06, 40.67, 43.76, 46.78, 46.85, 50.12, 58.33, 58.97, 61.14, 126.85, 126.97, 127.32, 127.64, 128.06, 128.42, 128.61, 128.67, 128.87, 129.41, 129.58, 136.77, 137.03, 137.29, 138.38, 138.47, 138.53, 172.43 and 172.55.

Compound **7d**. $\delta_C(CDCl_3)$ −2.08, −1.96, −1.81, 6.78, 6.89, 9.10, 9.15, 9.23, 11.32, 11.42, 13.69, 14.01, 14.29, 14.35, 18.91, 22.80, 22.84, 26.94, 27.32, 27.71, 29.01, 29.15, 29.30, 39.74, 39.78, 40.68, 40.87, 43.88, 46.98, 47.04, 49.44, 49.49, 50.02, 58.20, 59.06, 61.23, 61.28, 125.69, 126.42, 126.64, 126.74, 126.80, 126.95, 128.95, 129.34, 129.91, 129.94, 130.14, 172.53, 172.77, 172.80 and 173.02.

Compound **7e**. $\delta_C(CDCl_3)$ −10.32, −10.27, −10.19, −9.96, −3.55, −3.53, −3.43, −3.35, −3.30, 12.94, 14.04, 16.13, 16.19, 21.74, 21.83, 21.87, 22.54, 31.47, 37.64, 37.96, 38.39, 38.46, 38.79, 43.26, 46.91, 47.05, 48.97, 49.09, 49.78, 91.51, 91.67, 94.02, 124.24, 124.81, 124.90, 127.24, 127.41, 127.64, 127.66, 127.72, 128.00, 128.12, 128.46, 128.48, 128.58, 128.66, 128.68, 128.88, 128.92, 128.99, 129.04, 129.54, 130.62, 131.11, 131.18, 131.25, 131.30, 133.53, 134.22, 134.39, 134.50, 135.85, 136.55, 136.66, 138.44 and 138.61.

Compound **7f**. $\delta_C(CDCl_3)$ −2.16, −2.14, −2.02, −1.92, 14.00, 15.16, 16.01, 16.05, 21.45, 21.52, 21.54, 22.50, 22.53, 22.66, 25.46, 31.41, 37.53, 37.65, 38.28, 38.39, 46.78, 46.93, 48.85, 91.24, 93.75, 127.49, 127.52, 127.57, 127.64, 127.70, 127.76, 127.90, 128.05, 128.28, 128.42, 128.45, 128.47, 128.51, 128.54, 128.60, 128.66, 128.79, 128.84, 128.90, 128.93, 128.97, 129.10, 129.17, 129.22, 131.09, 131.18, 133.41, 133.50, 133.58, 133.65, 133.71, 134.19, 135.70, 136.64, 136.69, 136.74, 136.85, 136.89, 137.15, 138.00, 138.04, 138.06, 138.19, 138.23, 138.31, 145.22, 145.34, 145.36, 145.38, 145.44 and 145.48.

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