

# The Effect of the Ring Size of the Dithiolato Leaving Group on the Orientation of $\beta$ -Elimination in the Nickel-catalysed Alkenation of Cyclic Dithioacetals with $\text{Me}_3\text{SiCH}_2\text{MgCl}$

Ken-Tsung Wong,<sup>a</sup> Zhi-Jie Ni<sup>b</sup> and Tien-Yau Luh<sup>\*,a,b</sup>

<sup>a</sup> Department of Chemistry, National Taiwan University, Taipei, Taiwan 10764, Republic of China

<sup>b</sup> Department of Chemistry, The Chinese University of Hong Kong, Shatin, N.T., Hong Kong

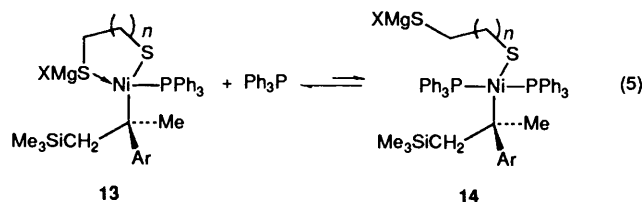
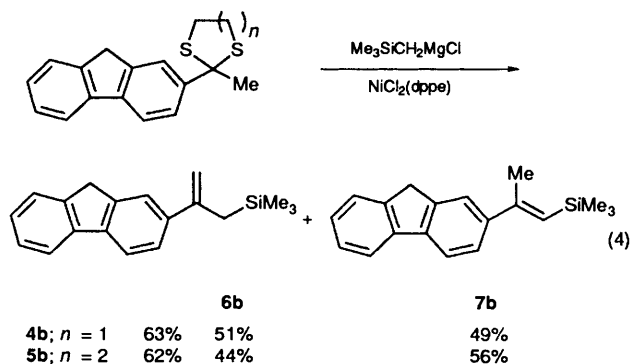
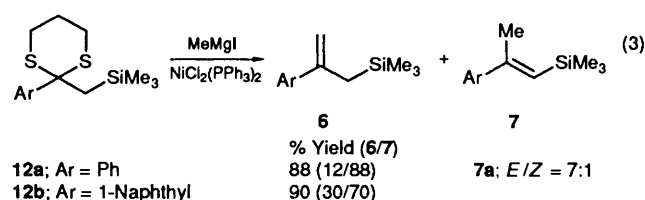
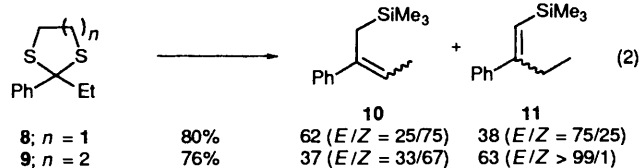
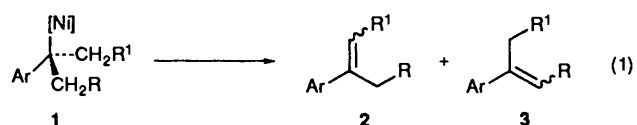
The product distribution (allyl- vs. vinyl-silanes) of the reactions of dithioacetals derived from alkyl aryl ketones with  $\text{Me}_3\text{SiCH}_2\text{MgCl}$  surprisingly depends on ring size of the cyclic dithioacetals, the five-membered ring substrates affording allylsilane as the major product while the six-membered analogues yield vinylsilanes predominantly. These results indicate that the leaving group, dithiolato moiety, may remain coordinated to the metal centre during the course of the catalytic process.

The nickel-catalysed cross couplings of a C–X bond with Grignard reagents is useful in organic synthesis.<sup>1</sup> The mechanism for these reactions may involve an oxidative addition of the C–X bond with the nickel species followed by an association of the Grignard reagent and reductive elimination leading to carbon–carbon bond formation. In general, the selectivity of the reaction is relatively insensitive to the nature of X. However, when X is a bidentate ligand, chelation may occur and X may bind more strongly to the metal centre. As such, the stereoelectronic effect of X may determine the selectivity of the reaction. Our recent discovery concerning the nickel-catalysed alkenation of dithioacetals with Grignard reagents<sup>2,3</sup> may serve as a useful model to test the validity of this viewpoint. The intermediate **1** may undergo competitive  $\beta$ -elimination of an Ni–H species leading to an isomeric mixture of **2** and **3**. We felt that the regioselectivity of this elimination step might depend on the environment around the nickel atom. We report here the surprising ring size effect on the selectivity of the nickel-catalysed cross coupling reactions of dithioacetals with  $\text{Me}_3\text{SiCH}_2\text{MgCl}$ .

Treatment of the dithiolane **4** or dithiane **5** with  $\text{Me}_3\text{SiCH}_2\text{MgCl}$  in the presence of a catalytic amount of  $\text{NiCl}_2(\text{PPh}_3)_2$  in refluxing diethyl ether–benzene gave a mixture of **6** and **7** in good yields. The results are summarized in Table 1. The ratio of **6** to **7** was determined by measuring the relative integrations of the absorptions due to the olefinic protons or those of the methyl protons in the trimethylsilyl groups in the <sup>1</sup>H NMR spectra. The assignments of stereochemistry of **7** were based on NOE experiments. These two isomers were readily separated by preparative gas chromatography.

As can be seen from Table 1, the five-membered dithiolanes **4** favoured the formation of **6** while the six-membered analogues **5** gave predominantly **7**. An electron withdrawing group on the aromatic ring seems to favour slightly the formation of **6**. In addition, the sterically hindered substrate **5a** yielded preferentially **7a**, even five-membered analogues **4a** affording a significant amount of **7a**. The reaction of 2-ethyl-2-phenyl-dithiolane **8** and 2-ethyl-2-phenyldithiane **9** also afforded a mixture of allylsilanes **10** and vinylsilanes **11** (eqn. 2) and the ratio of **10** and **11** fell in line with the results shown in Table 1. It is noted that both **10** and **11** contained *E* and *Z* isomers.

There was no equilibration between **6** and **7** under the reaction conditions employed. Thus, in the presence of a 86:14 mixture of **6b** and **7b**, the reaction of **5h** with  $\text{Me}_3\text{SiCH}_2\text{MgCl}$



\* To whom correspondence should be addressed at National Taiwan University.

**Table 1** Product distribution of the reactions of dithioacetals with  $\text{Me}_3\text{SiCH}_2\text{MgCl}$ 

Substrate	Ar	Yield 6/7 (%)	
		Substrate 4	Substrate 5
a	1-Naphthyl	69 (62/38) <sup>a</sup>	81 (18/82) <sup>b</sup>
b	Fluoren-2-yl	72 (90/10)	91 (32/68)
c	C <sub>6</sub> H <sub>4</sub> -4-OMe	85 (73/27)	78 (14/86)
d	C <sub>6</sub> H <sub>4</sub> -4-Me	77 (86/14)	70 (23/77)
e	C <sub>6</sub> H <sub>4</sub> -4-Ph	81 (89/11)	73 (34/66)
f	Ph	82 (85/15)	78 (25/75)
g	C <sub>6</sub> H <sub>4</sub> -3-OMe	64 (86/14)	71 (40/60)
h	C <sub>6</sub> H <sub>4</sub> -4-F	85 (80/20)	78 (32/68)
i	C <sub>6</sub> H <sub>4</sub> -3-CF <sub>3</sub>	75 (87/13)	68 (41/59)

<sup>a</sup> **7a** *E/Z* = 8/1. <sup>b</sup> **7a** *E/Z* = 4/1.

under the same conditions gave a 33:67 mixture of **6h** and **7h**. The ratio of **6b** to **7b** remained unchanged.

It is envisaged that  $\beta$ -elimination of intermediate **1** ( $\text{R} = \text{Me}_3\text{Si}$ ,  $\text{R}' = \text{H}$ ) may occur in either direction giving **6** or **7**. Based on this assumption, the reaction of dithioacetal **12** with  $\text{MeMgI}$  would give the same intermediate; hence, the distribution of **6** and **7** from this reaction would be the same as those from the reaction of **5** with  $\text{Me}_3\text{SiCH}_2\text{MgCl}$ . Indeed, the reaction of **12a** with  $\text{MeMgI}$  under similar conditions afforded a mixture of **6f** and **7f** (eqn. 3) and the ratios of **6f** to **7f** are compatible with those from the reactions of **5f**. The reaction of **12b** behaved similarly.

These observations suggested that the leaving group, dithiolato anion, may remain coordinated to the nickel during the course of the catalytic process with the conformation of the sulphur moiety in **13** being crucial to the product distribution. In order to test the validity of this conjecture, we carried out the reaction using  $\text{NiCl}_2(\text{dppe})$  as the catalyst. The bidentate ligand, dppe [1,2-bis(diphenylphosphino)ethane], would chelate to the nickel during the course of the catalytic reaction and, therefore, may decrease the amount of coordination of both sulphur moieties in the dithiolato ligand. If so, the discrepancy in selectivity between **6** and **7** might be eliminated. Indeed the reactions of either **4b** or **5b** under these conditions afforded mixtures of **6b** and **7b** in similar ratios (eqn. 4), with the reactions becoming much less selective.

The presence of an excess of  $\text{Ph}_3\text{P}$  did not affect the selectivity of **6** and **7**. Thus, the reaction of **4h** with  $\text{Me}_3\text{SiCH}_2\text{MgCl}$  in the presence of 5 equiv. of  $\text{Ph}_3\text{P}$  and 6 mol% of  $\text{NiCl}_2(\text{PPh}_3)_2$  under usual conditions gave in 74% yield a 77:23 mixture of **6h** and **7h**. The product distribution was comparable with that under normal conditions without added  $\text{Ph}_3\text{P}$ . This result indicated that the intermolecular association of  $\text{Ph}_3\text{P}$  with **13** to form **14** is unfavourable and therefore the intermediate **13** determines the selectivity of the orientation of  $\beta$ -elimination.

In summary, we have demonstrated for the first time the influence of the leaving group on the regioselectivity of  $\beta$ -elimination in the nickel-catalysed cross coupling reaction of dithioacetals with  $\text{Me}_3\text{SiCH}_2\text{MgCl}$ . These results further suggest that, during the course of this catalytic process, the leaving group, dithiolato moiety remained coordinated to the metal centre. With an appropriate choice of substrates, the selective formation of an allylsilane or a vinylsilane can be moderately well controlled.

## Experimental

**General Procedure for  $\text{NiCl}_2(\text{PPh}_3)_2$  Catalysed Reactions of Dithioacetals with  $\text{Me}_3\text{SiCH}_2\text{MgCl}$  or  $\text{MeMgI}$ .**—A mixture of dithioacetal (1 equiv.) and  $\text{NiCl}_2(\text{PPh}_3)_2$  (0.1 equiv.) was treated under  $\text{N}_2$  with the Grignard reagent in diethyl ether (5 equiv.). The mixture was refluxed for 16 h and then poured into saturated aq.  $\text{NH}_4\text{Cl}$ . The organic layer was separated and the aqueous layer was extracted twice ( $2 \times 20 \text{ cm}^3$ ) with diethyl ether. The combined organic portions were washed twice ( $2 \times 20 \text{ cm}^3$ ) with 10% aq.  $\text{NaOH}$  and with water ( $20 \text{ cm}^3$ ), and were dried ( $\text{MgSO}_4$ ). The solvent was removed under reduced pressure and the residue was chromatographed on silica gel (hexane) to give a mixture of **6** and **7**. The ratio of **6** to **7** was determined by the integration of the vinyl protons or of the trimethylsilyl groups in the  $^1\text{H}$  NMR spectra. Analytical samples of **6** and **7** were obtained by preparative gas chromatography (6 ft SE30).

**Reaction of 2-methyl-2-(1-naphthyl)-1,3-dithiane 5a with  $\text{Me}_3\text{SiCH}_2\text{MgCl}$ .** In a manner similar to that described in the general procedure, a solution of **5a** (276 mg, 1.06 mmol) and  $\text{NiCl}_2(\text{PPh}_3)_2$  (65.4 mg, 0.1 mmol) was treated with  $\text{Me}_3\text{SiCH}_2\text{MgCl}$  (1.0 mol  $\text{dm}^{-3}$ ; 5.0  $\text{cm}^3$ , 5.0 mmol) in benzene to give an 18:82 mixture of **6a** and **7a** (*E:Z* = 4:1) (207 mg, 81%). **6a**:  $\delta_{\text{H}}$  -0.14 (s, 9 H), 2.11 (d, *J*\* 1.1, 2 H), 4.98 (d, *J* 2.2, 1 H), 5.19 (d, *J* 1.6, 1 H) and 7.28–8.14 (m, 7-H); *m/z* 240 (100) and 166 (73); (Found:  $\text{M}^+$ , 240.1343. Calc. for  $\text{C}_{16}\text{H}_{20}\text{Si}$ : *M*, 240.1334). (*E*)-**7a**:  $\delta_{\text{H}}$  0.24 (s, 9 H), 2.23 (d, *J* 1.2, 3 H), 5.58 (s, 1 H) and 7.27–7.98 (m, 7 H); *m/z* 240 (100) and 160 (97); (Found:  $\text{M}^+$ , 240.1342. Calc. for  $\text{C}_{16}\text{H}_{20}\text{Si}$ : *M*, 240.1334). (*Z*)-**7a**:  $\delta_{\text{H}}$  -0.41 (s, 9 H), 2.23 (d, *J* 1.2, 3-H), 5.87 (d, *J* 1.3, 1 H) and 7.35–7.91 (m, 7 H); *m/z* 240 (100) and 160 (37); (Found:  $\text{M}^+$ , 240.1329. Calc. for  $\text{C}_{16}\text{H}_{20}\text{Si}$ : *M*, 240.1334).

**Reaction of 2-(fluoren-2-yl)-2-methyl-1,3-dithiane 5b with  $\text{Me}_3\text{SiCH}_2\text{MgCl}$ .** In a manner similar to that described in the general procedure, **5b** (298 mg, 1.0 mmol) and  $\text{NiCl}_2(\text{PPh}_3)_2$  (65.4 mg, 0.1 mmol) were treated with  $\text{Me}_3\text{SiCH}_2\text{MgCl}$  (1.0 mol  $\text{dm}^{-3}$ ; 5.0  $\text{cm}^3$ , 5.0 mmol) in benzene to give a 32:68 mixture of **6b** and **7b** (253.4 mg, 91%). **6b**: M.p. 78–79 °C;  $\delta_{\text{H}}$  -0.11 (s, 9 H), 2.06 (s, 2 H), 3.88 (s, 2 H), 4.87 (s, 1 H), 5.16 (d, *J* 1.3, 1 H) and 7.26–7.73 (m, 7 H); *m/z* 278 (26), 263 (22) and 73 (100); (Found:  $\text{M}^+$ , 278.1482. Calc. for  $\text{C}_{19}\text{H}_{22}\text{Si}$ : *M*, 278.1491). **7b**: M.p. 106–107 °C;  $\delta$  0.02 (s, 9 H), 2.25 (s, 3 H), 3.88 (s, 2 H), 5.97 (s, 1 H) and 7.27–7.77 (m, 7 H); *m/z* 278 (100) and 263 (25); (Found:  $\text{M}^+$ , 278.1490. Calc. for  $\text{C}_{19}\text{H}_{22}\text{Si}$ : *M*, 278.1491).

**Reaction of 2-(4-methoxyphenyl)-2-methyl-1,3-dithiane 5c with  $\text{Me}_3\text{SiCH}_2\text{MgCl}$ .** In a manner similar to that described in the general procedure, **5c** (244 mg, 1.0 mmol) and  $\text{NiCl}_2(\text{PPh}_3)_2$  (65.4 mg, 0.1 mmol) were treated with  $\text{Me}_3\text{SiCH}_2\text{MgCl}$  (1.5 mol  $\text{dm}^{-3}$ ; 3.5  $\text{cm}^3$ , 5.1 mmol) in benzene to give a 14:86 mixture of **6c** and **7c** (172 mg, 78%). **6c**:  $\delta_{\text{H}}$  -0.12 (s, 9 H), 1.96 (s, 2 H), 3.79 (s, 3 H), 4.75 (s, 1 H), 5.03 (d, *J* 1.5, 1 H), 6.81 (d, *J* 8.8, 2 H) and 7.31 (d, *J* 8.8, 2 H); *m/z* 220 (100) and 205 (44); (Found:  $\text{M}^+$ , 220.1267. Calc. for  $\text{C}_{13}\text{H}_{20}\text{OSi}$ : *M*, 220.1283). **7c**:  $\delta$  0.16 (s, 9 H), 2.17 (s, 3 H), 3.79 (s, 3 H), 5.82 (s, 1 H), 6.81 (d, *J* 8.7, 2 H) and 7.40 (d, *J* 8.7, 2 H); *m/z* 220 (100), 205 (75) and 73 (25); (Found:  $\text{M}^+$ , 220.1267. Calc. for  $\text{C}_{13}\text{H}_{20}\text{OSi}$ : *M*, 220.1283).

**Reaction of 2-methyl-2-(4-methylphenyl)-1,3-dithiane 5d with  $\text{Me}_3\text{SiCH}_2\text{MgCl}$ .** In a manner similar to that described in the general procedure, **5d** (224 mg, 1.0 mmol) and  $\text{NiCl}_2(\text{PPh}_3)_2$  (65.4 mg, 0.1 mmol) were treated with  $\text{Me}_3\text{SiCH}_2\text{MgCl}$  (1.0 mol  $\text{dm}^{-3}$ ; 5.0  $\text{cm}^3$ , 5.0 mmol) in benzene to give a 23:77 mixture of **6d** and **7d** (142 mg, 70%). **6d**:  $\delta_{\text{H}}$  -0.12 (s, 9 H), 1.98 (s, 2 H), 2.31 (s, 3 H), 4.80 (s, 1 H), 5.08 (d, *J* 1.4, 1 H), 7.09 (d, *J* 8.0, 2 H) and 7.27 (d, *J* 8.0, 2 H); *m/z* 204 (100) and 189 (42); (Found:  $\text{M}^+$ , 204.1329. Calc. for  $\text{C}_{13}\text{H}_{20}\text{Si}$ : *M*, 204.1334). **7d**:

\* *J* Values are given in Hz throughout.

$\delta_{\text{H}}$  0.16 (s, 9 H), 2.17 (s, 3 H), 2.32 (s, 3 H), 5.86 (s, 1 H), 7.10 (d, *J* 8.0, 2 H) and 7.34 (d, *J* 8.0, 2 H); *m/z* 204 (100) and 189 (68); (Found:  $\text{M}^+$ , 204.1333. Calc. for  $\text{C}_{13}\text{H}_{20}\text{Si}$ : *M*, 204.1334).

*Reaction of 2-(biphenyl-4-yl)-2-methyl-1,3-dithiane 5e with  $\text{Me}_3\text{SiCH}_2\text{MgCl}$ .* In a manner similar to that described in the general procedure, **5e** (286 mg, 1.0 mmol) and  $\text{NiCl}_2(\text{PPh}_3)_2$  (65.4 mg, 0.1 mmol) were treated with  $\text{Me}_3\text{SiCH}_2\text{MgCl}$  (1.0 mol  $\text{dm}^{-3}$ ; 5.0  $\text{cm}^3$ , 5.0 mmol) in benzene to give a 33:46 mixture of **6e** and **7e** (195 mg, 73%). **6e**: *M.p.* 80–82 °C;  $\delta_{\text{H}}$  –0.84 (s, 9 H), 2.04 (s, 2 H), 4.88 (s, 1 H), 5.19 (s, 1 H) and 7.31–7.62 (m, 9 H); *m/z* 266 (100), 251 (34), 194 (21) and 73 (97); (Found:  $\text{M}^+$ , 266.1499. Calc. for  $\text{C}_{18}\text{H}_{22}\text{Si}$ : *M*, 266.1491). **7e**: *M.p.* 94–95 °C;  $\delta_{\text{H}}$  0.19 (s, 9 H), 2.23 (d, *J* 0.7, 3 H), 5.97 (d, *J* 0.7, 1 H) and 7.28–7.61 (m, 9 H); *m/z* 266 (100), 251 (80) and 73 (20); (Found:  $\text{M}^+$ , 266.1498. Calc. for  $\text{C}_{18}\text{H}_{22}\text{Si}$ : *M*, 266.1491).

*Reaction of 2-methyl-2-phenyl-1,3-dithiane 5f with  $\text{Me}_3\text{SiCH}_2\text{MgCl}$ .* In a manner similar to that described in the general procedure, a mixture of **5f** (225 mg, 1.07 mmol) and  $\text{NiCl}_2(\text{PPh}_3)_2$  (32 mg, 0.05 mmol) was treated with  $\text{Me}_3\text{SiCH}_2\text{MgCl}$  (1.0 mol  $\text{dm}^{-3}$ ; 5  $\text{cm}^3$ , 5.0 mmol) in benzene to give a 25:75 mixture of **6f**<sup>5</sup> and **7f**<sup>6</sup> (159 mg, 78%). **6f**:  $\delta_{\text{H}}$  –0.12 (s, 9 H), 2.00 (s, 2 H), 4.85 (d, *J* 0.9, 1 H), 5.11 (d, *J* 1.7, 1 H) and 7.2–7.4 (m, 5 H);  $\delta_{\text{C}}$  –1.5, 26.1, 110.0, 126.3, 127.6, 128.1, 142.8 and 142.6; *m/z* 190 (100), 175 (36) and 73 (60); (Found:  $\text{M}^+$ , 190.1172. Calc. for  $\text{C}_{12}\text{H}_{18}\text{Si}$ : *M*, 190.1177). **7f**:  $\delta_{\text{H}}$  0.18 (s, 9 H), 2.20 (s, 3 H), 5.90 (s, 1 H) and 7.18–7.47 (m, 5 H); *m/z* 190 (28), 175 (90), 135 (100) and 73 (15); (Found:  $\text{M}^+$ , 190.1168. Calc. for  $\text{C}_{12}\text{H}_{18}\text{Si}$ : *M*, 190.1177).

*Reaction of 2-(3-methoxyphenyl)-2-methyl-1,3-dithiane 5g with  $\text{Me}_3\text{SiCH}_2\text{MgCl}$ .* In a manner similar to that described in the general procedure, **5g** (244 mg, 1.0 mmol) and  $\text{NiCl}_2(\text{PPh}_3)_2$  (65.4 mg, 0.1 mmol) were treated with  $\text{Me}_3\text{SiCH}_2\text{MgCl}$  (1.5 mol  $\text{dm}^{-3}$ ; 3.5  $\text{cm}^3$ , 5.1 mmol) in benzene to give a 40:60 mixture of **6g** and **7g** (156 mg, 71%). **6g**:  $\delta_{\text{H}}$  –0.12 (s, 9 H), 1.98 (s, 2 H), 3.80 (s, 3 H), 4.84 (s, 1 H), 5.11 (d, *J* 1.4, 1 H) and 6.75–7.20 (m, 4 H); *m/z* 220 (100) and 205 (20); (Found:  $\text{M}^+$ , 220.1273. Calc. for  $\text{C}_{13}\text{H}_{20}\text{OSi}$ : *M*, 220.1283). **7g**:  $\delta_{\text{H}}$  0.17 (s, 9 H), 2.18 (s, 3 H), 3.81 (s, 3 H), 5.89 (s, 1 H), 6.76–7.22 (m, 4 H); *m/z* 220 (100) and 205 (83); (Found:  $\text{M}^+$ , 220.1277. Calc. for  $\text{C}_{13}\text{H}_{20}\text{OSi}$ : *M*, 220.1283).

*Reaction of 2-(4-fluorophenyl)-2-methyl-1,3-dithiane 5h with  $\text{Me}_3\text{SiCH}_2\text{MgCl}$ .* In a manner similar to that described in the general procedure, **5h** (234 mg, 1.0 mmol) and  $\text{NiCl}_2(\text{PPh}_3)_2$  (65.4 mg, 0.1 mmol) were treated with  $\text{Me}_3\text{SiCH}_2\text{MgCl}$  (1.5 mol  $\text{dm}^{-3}$ ; 3.5  $\text{cm}^3$ , 5.1 mmol) in benzene to give a 32:68 mixture of **6h** and **7h** (163 mg, 78%). **6h**:  $\delta_{\text{H}}$  –0.13 (s, 9 H), 1.96 (s, 2 H), 4.82 (d, *J* 1.1, 1 H), 5.04 (d, *J* 1.7, 1 H), 6.95 (t, *J* 8.7, 2 H) and 7.34 (dd, *J* 8.7, 5.2, 2 H); *m/z* 208 (40), 193 (15) and 73 (100); (Found:  $\text{M}^+$ , 208.1094. Calc. for  $\text{C}_{12}\text{H}_{17}\text{FSi}$ : *M*, 208.1083). **7h**:  $\delta_{\text{H}}$  0.17 (s, 9 H), 2.17 (s, 3 H), 5.83 (s, 1 H), 6.97 (t, *J* 8.7, 2 H) and 7.40 (dd, *J* 8.7, 5.3, 2 H); *m/z* 208 (40), 193 (100) and 73 (15). (Found:  $\text{M}^+$ , 208.1094. Calc. for  $\text{C}_{12}\text{H}_{17}\text{FSi}$ : *M*, 208.1083).

*Reaction of 2-methyl-2-(3-trifluoromethylphenyl)-1,3-dithiane with  $\text{Me}_3\text{SiMgCl}$ .* In a manner similar to that described in the general procedure, **5i** (285 mg, 1.0 mmol) and  $\text{NiCl}_2(\text{PPh}_3)_2$  (65.4 mg, 0.1 mmol) were treated with  $\text{Me}_3\text{SiCH}_2\text{MgCl}$  (1.5 mol  $\text{dm}^{-3}$ ; 3.5  $\text{cm}^3$ , 5.1 mmol) in benzene to give a 41:59 mixture of **6i** and **7i** (181 mg, 68%). **6i**:  $\nu_{\text{max}}/\text{cm}^{-1}$  2953, 1612, 1429, 1331, 1279, 1164, 1127, 853 and 804;  $\delta_{\text{H}}$  –0.12 (s, 9 H), 2.01 (s, 2 H), 4.93 (d, *J* 1.3, 1 H), 5.16 (d, *J* 1.2, 1 H) and 7.35–7.61 (m, 4 H); *m/z* 258 (33), 243 (33), 166 (100), 109 (52) and 73 (67); (Found:  $\text{M}^+$ , 258.1046. Calc. for  $\text{C}_{13}\text{H}_{17}\text{F}_3\text{Si}$ : *M*, 258.1052). **7i**:  $\delta_{\text{H}}$  0.20 (s, 9 H), 2.21 (s, 3 H), 5.95 (s, 1 H) and 7.36–7.66 (m, 4 H); *m/z* 258 (15) and 243 (100); (Found:  $\text{M}^+$ , 258.1052. Calc. for  $\text{C}_{13}\text{H}_{17}\text{F}_3\text{Si}$ : *M*, 258.1052).

*Reaction of 2-methyl-2-(2-naphthyl)-1,3-dithiolane 4a with  $\text{Me}_3\text{SiCH}_2\text{MgCl}$ .* In a manner similar to that described in the general procedure, **4a** (246 mg, 1.0 mmol) and  $\text{NiCl}_2(\text{PPh}_3)_2$

(45 mg, 0.06 mmol) were allowed to react with  $\text{Me}_3\text{SiCH}_2\text{MgCl}$  (1.0 mol  $\text{dm}^{-3}$ ; 5.0  $\text{cm}^3$ , 5.0 mmol) in benzene to give a 62:38 mixture of **6a** and **7a** (166 mg, 69%).

*Reaction of 2-methyl-2-fluorenyl-1,3-dithiolane 4b with  $\text{Me}_3\text{SiCH}_2\text{MgCl}$ .* In a manner similar to that described in the general procedure, **4b** (249 mg, 0.87 mmol) and  $\text{NiCl}_2(\text{PPh}_3)_2$  (38 mg, 0.06 mmol) were allowed to react with  $\text{Me}_3\text{SiCH}_2\text{MgCl}$  (1.0 mol  $\text{dm}^{-3}$ ; 4.0  $\text{cm}^3$ , 4.0 mmol) in benzene to give a 90:10 mixture of **6b** and **7b** (177 mg, 72%).

*Reaction of 2-(4-methoxyphenyl)-2-methyl-1,3-dithiolane 4c with  $\text{Me}_3\text{SiCH}_2\text{MgCl}$ .* In a manner similar to that described in the general procedure, **4c** (226 mg, 1.0 mmol) and  $\text{NiCl}_2(\text{PPh}_3)_2$  (65.4 mg, 0.1 mmol) were treated with  $\text{Me}_3\text{SiCH}_2\text{MgCl}$  (1.5 mol  $\text{dm}^{-3}$ ; 3.5  $\text{cm}^3$ , 5.1 mmol) in benzene to give a 73:27 mixture of **6c** and **7c** (187 mg, 85%).

*Reaction of 2-methyl-2-(4-methylphenyl)-1,3-dithiolane 4d with  $\text{Me}_3\text{SiCH}_2\text{MgCl}$ .* In a manner similar to that described in the general procedure, **4d** (210 mg, 1.0 mmol) and  $\text{NiCl}_2(\text{PPh}_3)_2$  (65.4 mg, 0.1 mmol) were treated with  $\text{Me}_3\text{SiCH}_2\text{MgCl}$  (1.0 mol  $\text{dm}^{-3}$ ; 5.0  $\text{cm}^3$ , 5.0 mmol) in benzene to give a 86:14 mixture of **6d** and **7d** (158 mg, 77%).

*Reaction of 2-biphenyl-4-yl-2-methyl-1,3-dithiolane 4e with  $\text{Me}_3\text{SiCH}_2\text{MgCl}$ .* In a manner similar to that described in the general procedure, **4e** (281 mg, 1.03 mmol) and  $\text{NiCl}_2(\text{PPh}_3)_2$  (35 mg, 0.053 mmol) were allowed to react with  $\text{Me}_3\text{SiCH}_2\text{MgCl}$  (1.0 mol  $\text{dm}^{-3}$ ; 4.0  $\text{cm}^3$ , 4.0 mmol) in benzene to give a 89:11 mixture of **6e** and **7e** (216 mg, 81%).

*Reaction of 2-methyl-2-phenyl-1,3-dithiolane 4f with  $\text{Me}_3\text{SiCH}_2\text{MgCl}$ .* In a manner similar to that described in the general procedure, **4f** (196 mg, 0.96 mmol) and  $\text{NiCl}_2(\text{PPh}_3)_2$  (45 mg, 0.06 mmol) were reacted with  $\text{Me}_3\text{SiCH}_2\text{MgCl}$  (1.0 mol  $\text{dm}^{-3}$ ; 3.0  $\text{cm}^3$ , 3.0 mmol) in benzene to give a 85:15 mixture of **6f** and **7f** (150 mg, 82%).

*Reaction of 2-(3-methoxyphenyl)-2-methyl-1,3-dithiolane 4g with  $\text{Me}_3\text{SiCH}_2\text{MgCl}$ .* In a manner similar to that described in the general procedure, **4g** (226 mg, 1.0 mmol) and  $\text{NiCl}_2(\text{PPh}_3)_2$  (65.4 mg, 0.1 mmol) were treated with  $\text{Me}_3\text{SiCH}_2\text{MgCl}$  (1.5 mol  $\text{dm}^{-3}$ ; 3.5  $\text{cm}^3$ , 5.1 mmol) in benzene to give a 86:14 mixture of **6g** and **7g** (141 mg, 64%).

*Reaction of 2-(4-fluorophenyl)-2-methyl-1,3-dithiolane 4h with  $\text{Me}_3\text{SiCH}_2\text{MgCl}$ .* In a manner similar to that described in the general procedure, **4h** (204 mg, 1.0 mmol) and  $\text{NiCl}_2(\text{PPh}_3)_2$  (65.4 mg, 0.1 mmol) were treated with  $\text{Me}_3\text{SiCH}_2\text{MgCl}$  (1.5 mol  $\text{dm}^{-3}$ ; 3.5  $\text{cm}^3$ , 5.1 mmol) in benzene to give a 80:20 mixture of **6h** and **7h** (177 mg, 85%).

*Reaction of 2-methyl-2-(3-trifluoromethylphenyl)-1,3-dithiolane 4i with  $\text{Me}_3\text{SiCH}_2\text{MgCl}$ .* In a manner similar to that described in the general procedure, **4i** (264 mg, 1.0 mmol) and  $\text{NiCl}_2(\text{PPh}_3)_2$  (65.4 mg, 0.1 mmol) were treated with  $\text{Me}_3\text{SiCH}_2\text{MgCl}$  (1.5 mol  $\text{dm}^{-3}$ ; 3.5  $\text{cm}^3$ , 5.1 mmol) in benzene to give a 87:13 mixture of **6i** and **7i** (194 mg, 75%).

*Reaction of 2-ethyl-2-phenyl-1,3-dithiolane 8 with  $\text{Me}_3\text{SiCH}_2\text{MgCl}$ .* In a manner similar to that described in the general procedure, **8** (209 mg, 1.0 mmol) and  $\text{NiCl}_2(\text{PPh}_3)_2$  (65.4 mg, 0.1 mmol) were treated with  $\text{Me}_3\text{SiCH}_2\text{MgCl}$  (1.5 mol  $\text{dm}^{-3}$ ; 3.5  $\text{cm}^3$ , 5.1 mmol) in benzene to give a 62:38 mixture of **10** (*E:Z* = 1:3) and **11** (*E:Z* = 3:1) (164 mg, 80%). A mixture of (*Z*)-**10** and (*E*)-**11** were separated from the mixture (*E*)-**10** and (*Z*)-**11**. Attempts to further separate (*Z*)-**10** from (*E*)-**11** or (*E*)-**10** from (*Z*)-**11** were unsuccessful. For nonaromatic region for (*Z*)-**10**:  $\delta_{\text{H}}$  –0.16 (s, 9 H), 1.71 (d, *J* 6.7, 3 H, 3.1% enhancement upon irradiation at  $\delta$  1.98), 1.98 (s, 2 H) and 5.59 (q, *J* 6.7). For nonaromatic region for (*E*)-**11**:  $\delta_{\text{H}}$  0.17 (s, 9 H, 8% enhancement upon irradiation on  $\delta$  2.62), 0.96 (t, *J* 7.4, 3 H, 13% enhancement upon irradiation on  $\delta$  2.62), 2.62 (q, *J* 7.4, 2 H) and 5.72 (s, 1 H). The absorptions for the aromatic protons for the mixture of (*Z*)-**10** and (*E*)-**11** appeared at  $\delta$  7.16–7.41 (m); [Found:  $\text{M}^+$ , 204.1337. Calc. for  $\text{C}_{13}\text{H}_{20}\text{Si}$

(mixture of *Z*-**10** and *E*-**11**): <sup>7</sup> M, 204.1334]. For nonaromatic region for (*E*)-**10**: δ<sub>H</sub> -0.20 (s, 9 H), 1.57 (d, *J* 6.7, 3 H), 1.83 (s, 2 H) and 5.35 (q, *J* 6.7, 1 H). For nonaromatic region for (*Z*)-**11**: δ<sub>H</sub> -0.22 (s, 9 H), 0.99 (t, *J* 7.4, 3 H), 2.42 (q, *J* 7.4, 2 H) and 5.52 (t, *J* 1.4, 1 H). The absorptions for the aromatic protons for the mixture of (*E*)-**10** and (*Z*)-**11** resonated at δ 7.07–7.40 (m); [Found: M<sup>+</sup>, 204.1338. Calc. for C<sub>13</sub>H<sub>20</sub>Si (mixture of *E*-**10** and *Z*-**11**): M, 204.1334].

*Reaction of 2-ethyl-2-phenyl-1,3-dithiane 9 with Me<sub>3</sub>SiCH<sub>2</sub>-MgCl.* In a manner similar to that described in the general procedure, **9** (224 mg, 1.0 mmol) and NiCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (65.4 mg, 0.1 mmol) was treated with Me<sub>3</sub>SiCH<sub>2</sub>MgCl (1.0 mol dm<sup>-3</sup>; 5.0 cm<sup>3</sup>, 5.0 mmol) in benzene to give a 37:63 mixture of **10** (*E*:*Z* = 1:2) and **11** (*E*:*Z* > 99:1) (156 mg, 76%).

*Reaction of 2-phenyl-2-(trimethylsilylmethyl)-1,3-dithiane 12a with MeMgI.* In a manner similar to that described in the general procedure, 2-phenyl-2-(trimethylsilylmethyl)-1,3-dithiane (282 mg, 1.0 mmol) and NiCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (65.4 mg, 0.1 mmol) were treated with MeMgI (5.0 mol dm<sup>-3</sup>; 5.0 cm<sup>3</sup>, 5.0 mmol) in benzene to give a 12:88 mixture of **6f** and **7f** (167 mg, 85%).

*Reaction of 2-naphthyl-2-(trimethylsilylmethyl)-1,3-dithiane 12b with MeMgI.* In a manner similar to that described in the general procedure, 2-naphthyl-2-(trimethylsilylmethyl)-1,3-dithiane (332 mg, 1.0 mmol) and NiCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (65.4 mg, 0.1 mmol) were treated with MeMgI (1.0 mol dm<sup>-3</sup>; 5.0 cm<sup>3</sup>, 5.0 mmol) in benzene to give a 30:70 mixture of **6a** and **7a** (*E*:*Z* = 7:1) (215 mg, 90%).

*Reaction of 4b with Me<sub>3</sub>SiCH<sub>2</sub>MgCl in the presence of NiCl<sub>2</sub>(dppe).* According to the general procedure described above, a mixture of **4b** (284 mg, 1.0 mmol), NiCl<sub>2</sub>(dppe) (52.6 mg, 0.1 mmol) and Me<sub>3</sub>SiCH<sub>2</sub>MgCl (2.0 mol dm<sup>-3</sup>; 2.5 cm<sup>3</sup>, 5.0 mmol) in benzene (10 cm<sup>3</sup>) was refluxed for 20 h to afford a 51:49 mixture of **6b** and **7b** (174 mg, 63%).

*Reaction of 7b with Me<sub>3</sub>SiCH<sub>2</sub>MgCl in the presence of NiCl<sub>2</sub>(dppe).* In a similar manner as that described in the general procedure, a mixture of **7b** (298 mg, 1.0 mmol), NiCl<sub>2</sub>(dppe) (52.6 mg, 0.1 mmol) and Me<sub>3</sub>SiCH<sub>2</sub>MgCl (2.0 mol

dm<sup>-3</sup>; 2.5 cm<sup>3</sup>, 5.0 mmol) in benzene (10 cm<sup>3</sup>) was refluxed for 4 d to afford a 44:56 mixture of **6b** and **7b** (172 mg, 62%).

*Reaction of 4h with Me<sub>3</sub>SiCH<sub>2</sub>MgCl in the presence of NiCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> and excess of Ph<sub>3</sub>P.* In a manner similar to that described in the general procedure, **4h** (214 mg, 1.05 mmol) Ph<sub>3</sub>P (1.31 g, 5.0 mmol) and NiCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (65.4 mg, 0.1 mmol) were treated with Me<sub>3</sub>SiCH<sub>2</sub>MgCl (1.5 mol dm<sup>-3</sup>; 3.3 cm<sup>3</sup>, 5.0 mmol) in benzene to give a 77:23 mixture of **6h** and **7h** (161 mg, 74%).

*Reaction of 5h with Me<sub>3</sub>SiCH<sub>2</sub>MgCl in the presence of 6b and 7b.* A mixture of **6b** and **7b** (86:14) (234 mg), **5h** (228 mg, 1.0 mmol) and Me<sub>3</sub>SiCH<sub>2</sub>MgCl (1.5 mol dm<sup>-3</sup>; 4.0 cm<sup>3</sup>, 6.0 mmol) and NiCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (65.4 mg, 0.1 mmol) was refluxed in benzene for 18 h to afford a mixture (410 mg) of **6b** and **7b** (85:15), **6h** and **7h** (33:67) based on <sup>1</sup>H NMR spectroscopic analysis.

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