Tetrahedron 64 (2008) 9895–9900

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Selective synthesis of multiply substituted 7-norbornenone derivatives or Diels–Alder cycloadducts from 1,2,3,4-tetrasubstituted 1,3-butadienes and maleic anhydride with or without Lewis acids

Dongzhen Li [a], An Shi [a], Wen-Xiong Zhang [a], Guangzhen Liu [a], Zhenfeng Xi [a,b,*]

[a] Beijing National Laboratory for Molecular Sciences (BNLMS), Key Laboratory of Bioorganic Chemistry and Molecular Engineering of Ministry of Education, College of Chemistry, Peking University, Beijing 100871, China
[b] State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, China

ARTICLE INFO

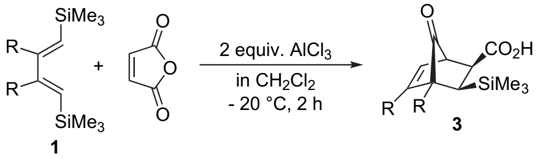
Article history:
Received 12 June 2008
Received in revised form 31 July 2008
Accepted 5 August 2008
Available online 9 August 2008

ABSTRACT

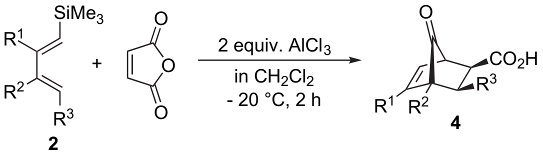
Reactions of 1,2,3,4-tetrasubstituted 1,3-butadienes with maleic anhydride and other dienophiles were investigated with or without addition of Lewis acid. When the silylated 1,3-butadienes, such as 1,4-bis(trimethylsilyl)-1,3-butadienes or 1-trimethylsilyl-1,3-butadienes, were treated with maleic anhydride in the presence of 2 equiv of $AlCl_3$, multi-substituted 7-norbornenones of well-defined *exo*,*exo*-disubstituted patterns were produced by an unprecedented and synthetically useful tandem process. Although some tetrasubstituted 1,3-butadienes could react directly with maleic anhydride under relative harsh conditions to afford Diels–Alder cycloadducts, the reactions, in the presence of 1 equiv of $AlCl_3$, afforded the corresponding cycloadducts in higher yields under mild conditions. These results showed that the size and substitution pattern of substituents on the butadienyl skeleton played a very important role in the reactivity of butadienes as a partner for the Diels–Alder reaction and Lewis acid could promote and/or realize the process of a Diels–Alder reaction.

1. Introduction

We have recently reported an interesting reaction leading to the formation of useful 7-norbornenones **3** and **4** of *exo*,*exo*-disubstituted patterns from 1,4-bis(trimethylsilyl)-1,3-butadienes **1** or 1-trimethylsilyl-1,3-butadienes **2** with maleic anhydride in the presence of newly sublimed $AlCl_3$ (Eqs. 1 and 2).[1] 7-Norbornenones have been widely used in various organic reactions and polymer chemistry.[2,3] In addition, 7-norbornenones have been well known to have the normal conformation of *endo*,*endo*-disubstitution.[4–6] Thus, our synthesis of 7-norbornenones **3** and **4** of *exo*,*exo*-disubstituted patterns with multiple substituents is of significant synthetic value and theoretic interest.



(1)



(2)

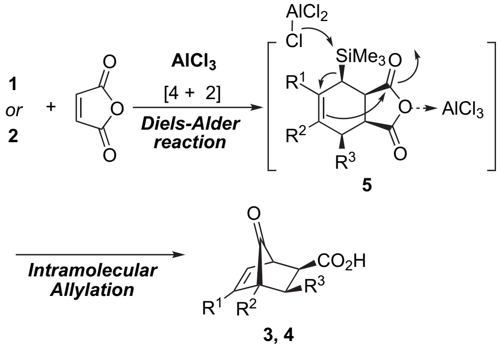
For the formation of 7-norbornenone derivatives **3** and **4** from 1,4-bis(trimethylsilyl)-1,3-butadienes **1** or 1-trimethylsilyl-1,3-butadienes **2** and maleic anhydride in the presence of $AlCl_3$, we have proposed that a key intermediate **5** might be firstly formed via the Lewis acid-mediated intermolecular Diels–Alder reaction. Again mediated by $AlCl_3$, the key intermediate **5** might undergo intramolecular allylation reaction of the carbonyl group by the in situ generated allylsilane moiety affording multi-substituted 7-norbornenones (Scheme 1). 1,4-Bis(trimethylsilyl)-1,3-butadienes **1** and 1-trimethylsilyl-1,3-butadienes **2**, which are synthetically useful silyl-substituted conjugated dienes,[7,8] have become readily available.[9] This cooperative application of these silyl-substituted conjugated dienes with the in situ generated allylsilane moiety is unprecedented.[7,8,10–14]

In this full paper, we have investigated systematically both Diels–Alder/intramolecular allylation reaction and Diels–Alder reaction with or without Lewis acids between a variety of multiply substituted 1,3-butadienes and dienophiles. Shown in Figure 1 are dienes and dienophiles applied in this study.

---

* Corresponding author. Tel./fax: +86 10 6275 9728.
E-mail address: zfxi@pku.edu.cn (Z. Xi).

0040-4020/$ – see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2008.08.006



Scheme 1. Formation of 7-norbornenones **3**,**4** via the Lewis acid-mediated intermolecular Diels–Alder/intramolecular allylation reaction of the carbonyl group by the in situ generated allylsilane.

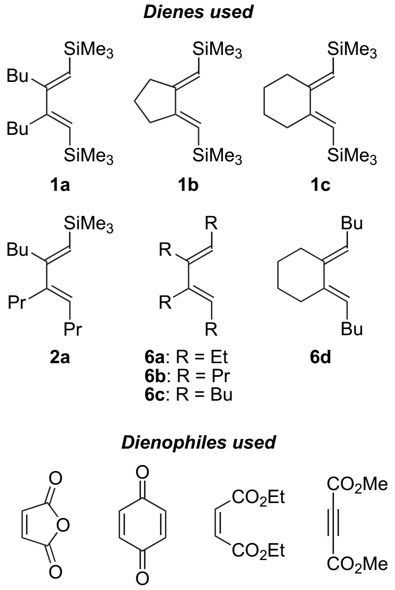


Figure 1. Representative dienes and dienophiles applied in this study.

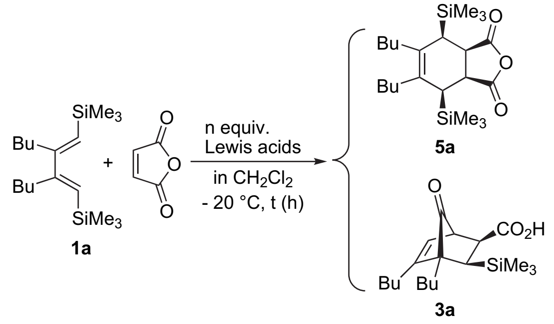
2. Results and discussion

2.1. Formation of either Diels–Alder cycloadducts 5 or 7-norbornenone derivatives 3 and 4 from bis-silylated or mono-silylated 1,3-butadienes and maleic anhydride with or without Lewis acids

Diels–Alder reaction has been one of the most useful methods to construct cyclic compounds, both intermolecularly from two components and intramolecularly from one molecule containing the dienyl moiety and the dienophile moiety.[7,8] It has been well known that the substituents on the diene skeleton have a remarkable effect on the reactivity. More attention has been paid to the electronic effect of these substituents, but less to the steric effect.[7,8,15]

Table 1

Formation of either Diels–Alder cycloadduct **5a** or 7-norbornenone derivative **3a** from **1a** and maleic anhydride in the presence of $AlCl_3$ or $EtAlCl_2$



Entry	n (equiv)	Time (h)	Yield of products[a] (%)	
			5a	**3a**
1	0.1[b]	1	0	0
		3	4	0
2	0.5[b]	1	20	0
		3	32	0
3	1.0[b]	1	54	0
		3	76	Trace
4	2.0[b]	1	0	59
		3	0	68
5	2.0[c]	3	0	63

[a] Isolated yields.

[b] Newly sublimed $AlCl_3$.

[c] $EtAlCl_2$.

Either the Diels–Alder cycloadducts **5** or 7-norbornenone derivatives **3** and **4** from 1,2,3,4-tetrasubstituted 1,3-butadienes and maleic anhydride with or without $AlCl_3$ have been obtained. As demonstrated by the reaction of **1a** shown in Table 1, no reaction was observed when Lewis acids such as $MgBr_2$, CuCl, $Ti(O^iPr)_4$, $AlMe_3$, BEt_3, $BF_3\cdot Et_2O$, $TiCl_4$, VCl_3, and $FeCl_3$ were used.[16] In some cases, desilylation of **1a** took place. $AlCl_3$ was found to be the most effective Lewis acid for this reaction. $EtAlCl_2$ could also be used but resulting in a slightly lower yield (entry 5). As shown in Table 1, the amount of $AlCl_3$ determines the type of products. Either the Diels–Alder cycloadduct **5a** or the 7-norbornenone derivative **3a** has been obtained. When 0.1 equiv, 0.5 equiv or 1.0 equiv of $AlCl_3$ was used (entries 1–3), no formation of 7-norbornenone derivative **3a** was observed. On the contrary, the Diels–Alder cycloadduct **5a** was formed in increasing yields with the increase of the amount of $AlCl_3$. A high isolation yield of **5a** (76%) was achieved when 1.0 equiv of $AlCl_3$ was used (entry 3). It should be noted that newly sublimed $AlCl_3$ should be used to realize a clean and high-yielding reaction. When 2.0 equiv of a Lewis acid such as $AlCl_3$ and $EtAlCl_2$ were used (entries 4 and 5), totally no cycloadduct **5a** was obtained. The 7-norbornenone derivative **3a** was isolated in good yields in both cases. The structure of **3a** has been previously determined.[1] These results showed that Lewis acids played a very important role in this reaction. More importantly, these results indicated that the 7-norbornenone derivative **3a** might be formed from an unprecedented Lewis acid-mediated intramolecular skeletal rearrangement of the Diels–Alder cycloadduct **5a**.

As shown in Figure 2, in addition to **1a**, other type of bis-silylated 1,3-butadienes **1b**,**c**, and even the mono-silylated 1,3-butadiene **2a** could also undergo similar reactions to afford the corresponding 7-norbornenones **3b**,**c** and **4a** in high isolated yields when 2 equiv of $AlCl_3$ was used in these reactions. The structure of **3c** has been reported previously.[1]

In addition to maleic anhydride as the dienophile, we have also tried other dienophiles shown in Figure 1. In most cases a messy mixture was obtained without formation of major isolable products.

Several experiments were attempted to make sure that Lewis acid was really necessary to promote the above-mentioned reactions. As demonstrated in Scheme 2, no reaction took place when **1a** was treated with maleic anhydride in reflux toluene at 110 °C for 3 h. This result, by comparison with the data (76% isolated yield) obtained by using 1 equiv of $AlCl_3$, demonstrated that $AlCl_3$ is indeed required for this case. However, under similar reaction condition, the butadiene derivative **1c** did react with maleic anhydride

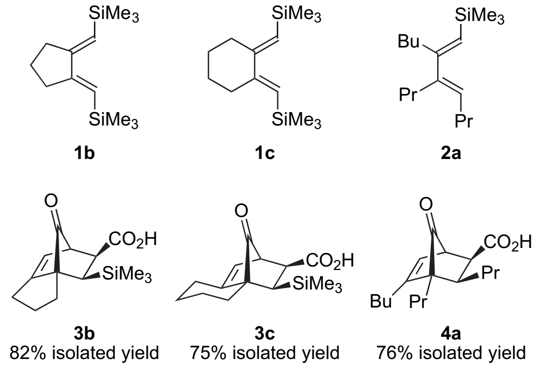
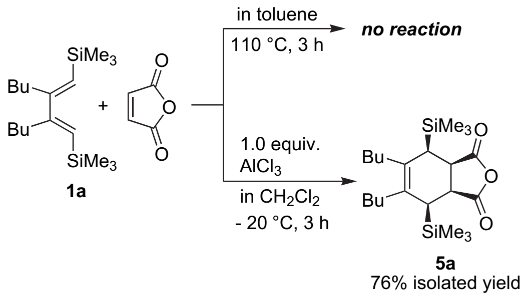
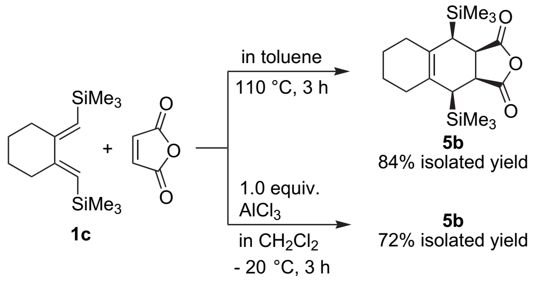


Figure 2. Formation of 7-norbornenone derivatives **3b**,**c** and **4a**.

to afford its corresponding Diels–Alder cycloadduct **5b** in 84% isolated yield without addition of $AlCl_3$ (Scheme 3). The same product **5b** could also be obtained in a good yield when 1.0 equiv of $AlCl_3$ was used. The structure of **5b** has been characterized by single-crystal X-ray structural analysis (Fig. 3). These results indicate that (1) steric effect of substituents of the butadienyl skeleton plays an important role in this Diels–Alder reaction, (2) **1c** has higher reactivity than **1a** for the Diels–Alder reaction, and (3) $AlCl_3$ can remarkably promote the Diels–Alder reaction.



Scheme 2. Reaction of **1a** with maleic anhydride with or without addition of $AlCl_3$.



Scheme 3. Reaction of **1c** with maleic anhydride with or without addition of $AlCl_3$.

We found that the reaction of mono-silylated 1,3-butadiene **2a** with maleic anhydride took place without addition of $AlCl_3$ to afford its corresponding Diels–Alder cycloadduct **5c** along with its desilylated derivative **5c**′ with the combined 49% yield (Scheme 4). However, **2a** reacted with maleic anhydride in the presence of 1.0 equiv of $AlCl_3$ to afford a mixture of products **5c** and **5c**′ with good combined yield of 88% (Scheme 5). As mentioned in Figure 2, in the case of **2a**, 7-norbornenone **4a** was obtained in 76% yield when 2 equiv of $AlCl_3$ was used (Fig. 2). These results show once more that the Lewis acid can promote this process of Diels–Alder reaction and the amount of the Lewis acid can also change effectively the reaction direction.

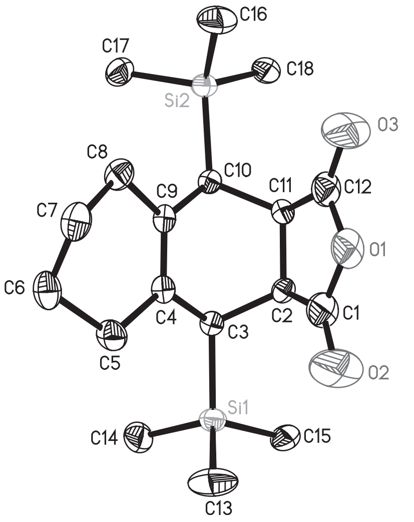
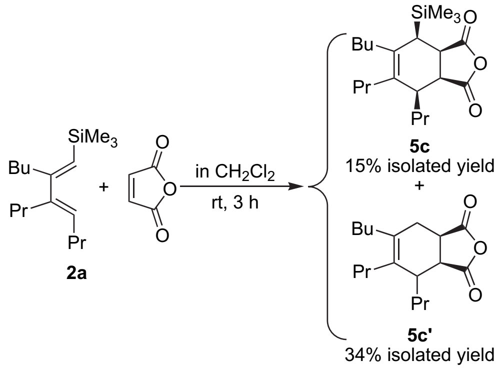
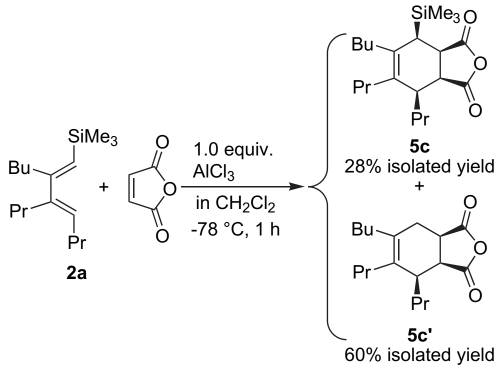


Figure 3. X-ray structure of **5b**.

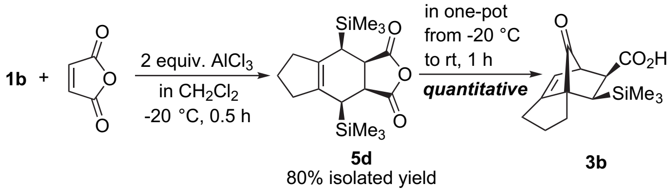


Scheme 4. Reaction of mono-silylated **2a** with maleic anhydride without addition of $AlCl_3$.



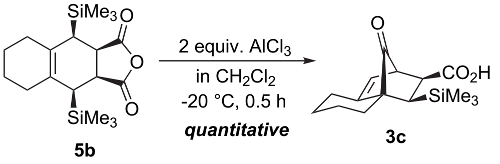
Scheme 5. Reaction of mono-silylated butadiene **2a** with maleic anhydride mediated by 1.0 equiv of $AlCl_3$.

For the reaction mechanism from the silylated 1,3-butadienes and maleic anhydride to form 7-norbornenones in the presence of $AlCl_3$, a key intermediate **5** might be involved, followed by Lewis acid-mediated intramolecular allylation reaction of the carbonyl group by the in situ generated allylsilane moiety (Scheme 1).[1] This proposal has been demonstrated by the following three experiments. As given in Scheme 6, the Diels–Alder cycloaddition adduct **5d** was obtained in 80% isolated yield when the reaction was carried out at −20 °C for 30 min. No 7-norbornenone **3b** was obtained under this reaction condition. Interestingly, when the reaction temperature increased to room temperature, **5d** disappeared completely after 1 h, affording the multi-substituted 7-norbornenone

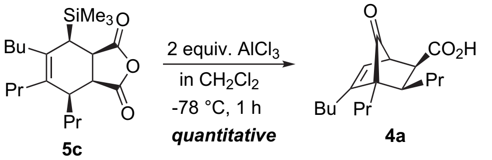


Scheme 6. One-pot formation of 7-norbornenone derivative **3b** via formation of the Diels–Alder cycloadduct **5d** in the presence of $AlCl_3$.

3b in quantitative conversion. When pure isolated Diels–Alder cycloadduct **5b** (Eq. 3) or **5c** (Eq. 4) was treated with $AlCl_3$ in CH_2Cl_2, both **5b** and **5c** could be completely transformed to their corresponding 7-norbornenone derivatives **3c** or **4a**, respectively. All these results strongly support the proposed pathway shown in Scheme 1.



(3)

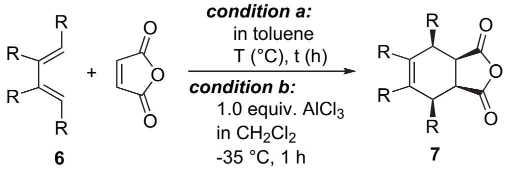


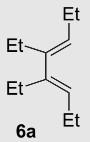
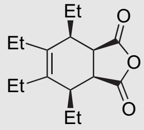
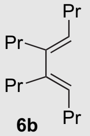
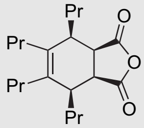
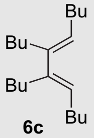
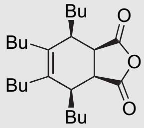
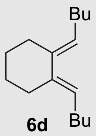
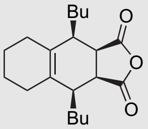
(4)

2.2. Formation of Diels–Alder cycloadducts 7 from non-silylated 1,3-butadienes and maleic anhydride with or without Lewis acids

The above-mentioned reactions show that the substituents on the butadienyl skeleton play a very important role in the reactivity of Diels–Alder reaction. Therefore, we applied other type of butadienes without $SiMe_3$ groups for the Diels–Alder reaction. Listed in Table 2 are representative results. The size and patterns of substituents on the butadienyl skeletons influenced remarkably the reactivity of the butadiene as a partner for the Diels–Alder reaction. 1,2,3,4-Tetraethyl substituted **6a** showed higher reactivity (yield of product **7a**: 94%) than that of 1,2,3,4-tetrapropyl substituted **6b** (yield of product **7b**: 80%). 1,2,3,4-Tetrabutyl substituted butadiene **6c** showed the lowest reactivity (yield of product **7c**: 75%). The butadiene **6d** showed the highest reactivity among these dienes, affording its corresponding product **7d** in 91% isolated yield even at 0 °C within 1 h. Moreover, addition of $AlCl_3$ promoted the reaction and made the reaction faster.

Table 2
Formation of Diels–Alder cycloadducts from non-silylated 1,3-butadienes **6a–d** and maleic anhydride with or without Lewis acids



Entry	1,3-Butadiene **6**	Product **7** and yield[a]
1	 **6a**	 **7a** *Condition a*: rt, 4 h, 78% *Condition a*: reflux, 1 h, 94% *Condition b*: 90%
2	 **6b**	 **7b** *Condition a*: reflux, 3 h, 80% *Condition b*: 86%
3	 **6c**	 **7c** *Condition a*: reflux, 3 h, 75% *Condition b*: 51%
4	 **6d**	 **7d** *Condition a*: 0 °C, 1 h, 91% *Condition b*: 93%

[a] Isolated yields.

3. Conclusion

Reactions between 1,2,3,4-tetrasubstituted 1,3-butadienes and dienophiles, such as maleic anhydride, were investigated to yield 7-norbornenones or Diels–Alder cycloadducts with or without addition of Lewis acid. When 1,4-bis(trimethylsilyl)-1,3-butadienes or 1-trimethylsilyl-1,3-butadienes were used, an unprecedented and synthetically useful tandem process was developed for the preparation of multi-substituted 7-norbornenones of well-defined *exo,exo*-disubstituted patterns, in which a new synthetic strategy was achieved through combining Lewis acid-mediated intermolecular Diels–Alder reaction with Lewis acid-mediated intramolecular allylation of the carbonyl group by the in situ generated allylsilane moiety. The size and pattern of substituents on the butadienyl skeleton were found to play a very important role on the reactivity of butadienes as a partner for the Diels–Alder reaction. Lewis acid was required in some cases to realize a successful Diels–Alder reaction, greatly depending on also the size and pattern of substituents.

4. Experimental section

4.1. General

Unless otherwise noted, all starting materials were commercially available and were used without further purification. All reactions involving organometallic compounds were run under a slightly positive pressure of dry N_2 with use of standard Schlenk techniques. Toluene was refluxed and distilled over sodium benzophenone ketyl under a nitrogen atmosphere. ^1H and ^{13}C NMR spectra were recorded on a JEOL-300 MHz spectrometer. GC analysis was performed on a gas chromatograph (Shimadzu 14B) equipped with a flame ionization detector and a capillary column (CBP1-M25-25).

4.2. A typical procedure for synthesis of 7-norbornenones 3 via reactions of 1,3-butadienes and maleic anhydride

1,3-Butadiene (1.0 mmol) was added to a CH_2Cl_2 solution of maleic anhydride (1.0 mmol) at room temperature. After the reaction mixture was cooled to −20 °C, newly sublimed $AlCl_3$ (2.0 mmol) was added and the reaction mixture was then stirred at −20 °C for 2 h. The above reaction mixture was quenched with water and extracted with $\mathrm{Et_2O}$. The extract was washed with brine and dried over $\mathrm{MgSO_4}$. The solvent was evaporated in vacuo and the residue purified by column chromatography ($\mathrm{Et_2O}$/hexane/acetic acid=10:100:1) to afford the products **3**.

4.2.1. *Compound* ***3a***

Colorless solid, 68% yield (228 mg); mp 106.3–106.8 °C; ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$, $\mathrm{Me_4Si}$, 25 °C): δ 0.12 (s, 9H, $\mathrm{CH_3}$), 0.89–0.96 (m, 7H, 2$\mathrm{CH_3}$ and 1CH), 1.32–2.18 (m, 12H, $\mathrm{CH_2}$), 2.48 (d, J=11.4 Hz, 1H, CH), 2.95 (d, J=3.6 Hz, 1H, CH), 6.09–6.10 (m, 1H, CH), 11.11 (br, 1H, COOH). ^{13}C NMR (75 MHz, $\mathrm{CDCl_3}$, $\mathrm{Me_4Si}$, 25 °C): δ 0.68 (3$\mathrm{CH_3}$), 13.90 (1$\mathrm{CH_3}$), 13.98 (1$\mathrm{CH_3}$), 22.62 (1$\mathrm{CH_2}$), 23.89 (1$\mathrm{CH_2}$), 26.84 (1$\mathrm{CH_2}$), 27.28 (1$\mathrm{CH_2}$), 27.92 (1$\mathrm{CH_2}$), 28.95 (1$\mathrm{CH_2}$), 34.29 (1CH), 45.96 (1CH), 51.02 (1CH), 55.94 (1 quart C), 122.83 (1CH), 153.03 (1 quart C), 181.94 (1 quart C), 203.17 (1 quart C). IR (neat): ν (C=O) 1782, 1704 cm^{-1}; HRMS-EI calcd for $\mathrm{C_{19}H_{32}O_3Si}$: 336.2121, found: 336.2122. Anal. Calcd for $\mathrm{C_{19}H_{32}O_3Si}$: C, 67.81; H, 9.58. Found: C, 67.62; H, 9.31.

4.2.2. *Compound* ***3b***

Colorless solid, 82% yield (216 mg); mp 134.0–136.0 °C; ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$, $\mathrm{Me_4Si}$, 25 °C): δ 0.11 (s, 9H, $\mathrm{CH_3}$), 1.16 (d, J=11.4 Hz, 1H, CH), 1.74–2.44 (m, 6H, $\mathrm{CH_2}$), 2.68 (d, J=11.7 Hz, 1H, CH), 3.16 (d, J=4.2 Hz, 1H, CH), 6.08–6.09 (m, 1H, CH), 10.70 (br, 1H, COOH). ^{13}C NMR (75 MHz, $\mathrm{CDCl_3}$, $\mathrm{Me_4Si}$, 25 °C): δ 0.25 (3$\mathrm{CH_3}$), 22.67 (1$\mathrm{CH_2}$), 26.82 (1$\mathrm{CH_2}$), 28.01 (1$\mathrm{CH_2}$), 31.34 (1CH), 45.96 (1CH), 54.84 (1CH), 61.69 (1 quart C), 119.41 (1CH), 160.73 (1 quart C), 182.53 (1 quart C), 196.58 (1 quart C). IR (neat): ν (C=O) 1774, 1703 cm^{-1}. Anal. Calcd for $\mathrm{C_{14}H_{20}O_3Si}$: C, 63.60; H, 7.62. Found: C, 63.81; H, 7.59.

4.2.3. *Compound* ***3c***

Colorless solid, 75% yield (209 mg); mp 185.6–186.7 °C; ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$, $\mathrm{Me_4Si}$): δ 0.12 (s, 9H, $\mathrm{CH_3}$), 0.16 (d, J=11.7 Hz, 1H, CH), 1.26–2.43 (m, 8H, $\mathrm{CH_2}$), 2.54 (d, J=11.4 Hz, 1H, CH), 2.97 (d, J=3.9 Hz, 1H, CH), 6.01–6.03 (m, 1H, CH), 10.22 (br, 1H, COOH). ^{13}C NMR (75 MHz, $\mathrm{CDCl_3}$, $\mathrm{Me_4Si}$, 25 °C): δ 0.31 (3$\mathrm{CH_3}$), 22.25 (1$\mathrm{CH_2}$), 22.85 (1$\mathrm{CH_2}$), 23.94 (1$\mathrm{CH_2}$), 26.81 (1$\mathrm{CH_2}$), 31.92 (1CH), 46.01 (1CH), 50.48 (1CH), 51.54 (1 quart C), 121.65 (1CH), 150.67 (1 quart C), 182.07 (1 quart C), 202.70 (1 quart C). IR (neat): ν (C=O) 1758, 1720 cm^{-1}. HRMS-SIMS calcd for $(\mathrm{C_{15}H_{21}O_3Si})^{-1}$: 277.1260, found: 277.1263. Anal. Calcd for $\mathrm{C_{15}H_{22}O_3Si}$: C, 64.71; H, 7.96. Found: C, 64.82; H, 8.19.

4.2.4. *Compound* ***4a***

Colorless oil, 76% yield (222 mg); ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$, $\mathrm{Me_4Si}$): δ 0.84–0.99 (m, 9H, 3$\mathrm{CH_3}$), 1.23–2.22 (m, 15H, 7$\mathrm{CH_2}$ and 1CH), 2.56 (d, J=10.8 Hz, 1H, CH), 2.94 (d, J=13.6 Hz, 1H, CH), 6.11–6.12 (m, 1H, CH), 11.18 (br, 1H, COOH). ^{13}C NMR (75 MHz, $\mathrm{CDCl_3}$, $\mathrm{Me_4Si}$, 25 °C): δ 13.96 (1$\mathrm{CH_3}$), 14.25 (1$\mathrm{CH_3}$), 15.33 (1$\mathrm{CH_3}$), 18.16 (1$\mathrm{CH_2}$), 22.01 (1$\mathrm{CH_2}$), 22.56 (1$\mathrm{CH_2}$), 26.58 (1$\mathrm{CH_2}$), 28.48 (1$\mathrm{CH_2}$), 28.79 (1$\mathrm{CH_2}$), 29.28 (1$\mathrm{CH_3}$), 42.44 (1CH), 45.96 (1CH), 49.41 (1CH), 56.81 (1 quart C), 124.09 (1CH), 152.12 (1 quart C), 180.20 (1 quart C), 203.79 (1 quart C). IR (neat): ν (C=O) 1778, 1705 cm^{-1}; HRMS-EI calcd for $\mathrm{C_{18}H_{28}O_3}$: 292.2038, found: 292.2038.

4.3. A typical procedure for synthesis of 5

1,3-Butadiene (1.0 mmol) was added to a $\mathrm{CH_2Cl_2}$ solution of maleic anhydride (1.0 mmol) at room temperature. After the reaction mixture was cooled to −20 °C, newly sublimed $\mathrm{AlCl_3}$ (1.0 mmol) was added and the reaction mixture was then stirred at −20 °C for 1 h. The above reaction mixture was quenched with water and extracted with $\mathrm{Et_2O}$. The extract was washed with brine and dried over $\mathrm{MgSO_4}$. The solvent was evaporated in vacuo and the residue purified by column chromatography ($\mathrm{Et_2O}$/hexane=1:12) to afford the products **5**.

4.3.1. *Compound* ***5a***

Colorless oil, 76% yield (310 mg); ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$, $\mathrm{Me_4Si}$, 25 °C): δ 0.26 (s, 18H, $\mathrm{CH_3}$), 0.90 (t, J=7.2 Hz, 6H, $\mathrm{CH_3}$), 1.12–1.36 (m, 8H, $\mathrm{CH_2}$), 1.55–1.57 (m, 2H, CH), 1.89–2.30 (m, 4H, $\mathrm{CH_2}$), 3.39–3.40 (m, 2H, CH). ^{13}C NMR (75 MHz, $\mathrm{CDCl_3}$, $\mathrm{Me_4Si}$, 25 °C): δ 13.78 (1$\mathrm{CH_3}$), 23.12 (1$\mathrm{CH_2}$), 31.83 (1CH), 32.01 (1$\mathrm{CH_2}$), 32.70 (1$\mathrm{CH_2}$), 45.70 (1CH), 138.85 (1 quart C), 174.54 (1 quart C). IR (neat): ν (C=O) 1777 cm^{-1}; HRMS-EI calcd for $\mathrm{C_{22}H_{40}O_3Si_2}$: 408.2516, found: 408.2503.

4.3.2. *Compound* ***5b***

Colorless single crystals suitable for X-ray analysis[17] were grown in ether/hexane mixed solvent at room temperature in 84% yield (299 mg); mp 132.0–133.0 °C; ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$, $\mathrm{Me_4Si}$, 25 °C): δ 0.25 (s, 18H, $\mathrm{CH_3}$), 1.52–1.58 (m, 6H, $\mathrm{CH_2}$ and CH), 2.14 (br, 4H, $\mathrm{CH_2}$), 3.41–3.42 (m, 2H, CH). ^{13}C NMR (75 MHz, $\mathrm{CDCl_3}$, $\mathrm{Me_4Si}$, 25 °C): δ 0.43 (3$\mathrm{CH_3}$), 22.93 (1$\mathrm{CH_2}$), 30.48 (1$\mathrm{CH_2}$), 31.66 (1CH), 45.43 (1CH), 135.53 (1 quart C), 174.18 (1 quart C). IR (neat): ν (C=O) 1780 cm^{-1}; HRMS-EI calcd for $\mathrm{C_{18}H_{30}O_3Si_2}$: 350.1733, found: 350.1728. Anal. Calcd for $\mathrm{C_{18}H_{30}O_3Si_2}$: C, 61.66; H, 8.62. Found: C, 61.40; H, 8.61.

4.3.3. *Compound* ***5c***

Colorless oil, 28% yield (82 mg); ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$, $\mathrm{Me_4Si}$, 25 °C): δ 0.24 (s, 9H, $\mathrm{CH_3}$), 0.88–1.04 (m, 10H, 3$\mathrm{CH_3}$ and CH), 1.26–2.28 (m, 15H, 7$\mathrm{CH_2}$ and CH), 3.34–3.43 (m, 2H, CH). ^{13}C NMR (75 MHz, $\mathrm{CDCl_3}$, $\mathrm{Me_4Si}$, 25 °C): δ −0.25 (3$\mathrm{CH_3}$), 13.54 (1$\mathrm{CH_3}$), 14.05 (1$\mathrm{CH_3}$), 14.33 (1$\mathrm{CH_3}$), 20.97 (1$\mathrm{CH_2}$), 22.84 (1$\mathrm{CH_2}$), 23.56 (1$\mathrm{CH_2}$), 29.28 (1$\mathrm{CH_2}$), 30.42 (1$\mathrm{CH_2}$), 31.57 (1$\mathrm{CH_2}$), 31.73 (1CH), 32.15 (1$\mathrm{CH_2}$), 39.32 (1CH), 43.71 (1CH), 44.23 (1CH), 135.81 (1 quart C), 138.98 (1 quart C), 172.35 (1 quart C), 174.18 (1 quart C); HRMS-EI calcd for $\mathrm{C_{21}H_{36}O_3Si}$: 364.2434, found: 364.2424.

4.3.4. *Compound* ***5c′***

Colorless oil, 60% yield (175 mg); ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$, $\mathrm{Me_4Si}$, 25 °C): δ 0.87–0.97 (m, 9H, $\mathrm{CH_3}$), 1.28–2.59 (m, 17H, 8$\mathrm{CH_2}$ and CH), 3.22–3.33 (m, 2H, CH). ^{13}C NMR (75 MHz, $\mathrm{CDCl_3}$, $\mathrm{Me_4Si}$, 25 °C): δ 13.92 (1$\mathrm{CH_3}$), 14.21 (2$\mathrm{CH_3}$), 21.27 (1$\mathrm{CH_2}$), 22.57 (1$\mathrm{CH_2}$), 22.81 (1$\mathrm{CH_2}$), 27.40 (1$\mathrm{CH_2}$), 30.39 (1$\mathrm{CH_2}$), 30.45 (1$\mathrm{CH_2}$), 32.58 (1$\mathrm{CH_2}$), 32.86 (1$\mathrm{CH_2}$), 39.44 (1CH), 40.33 (1CH), 44.29 (1CH), 132.42 (1 quart C), 135.90 (1 quart C), 172.52 (1 quart C), 174.70 (1 quart C). HRMS-EI calcd for $\mathrm{C_{18}H_{28}O_3}$: 292.2038, found: 292.2043.

4.3.5. *Compound* ***5d***

Colorless solid, 80% yield (261 mg); mp 121.0–122.1 °C; ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$, $\mathrm{Me_4Si}$, 25 °C): δ 0.23 (s, 18H, $\mathrm{CH_3}$), 1.58 (d, J=1.5 Hz, 2H, CH), 1.79–1.89 (m, 2H, $\mathrm{CH_2}$), 2.37–2.42 (m, 4H, $\mathrm{CH_2}$), 3.45–3.48 (m, 2H, CH). ^{13}C NMR (75 MHz, $\mathrm{CDCl_3}$, $\mathrm{Me_4Si}$, 25 °C): δ 0.21 (3$\mathrm{CH_3}$), 22.70 (1$\mathrm{CH_2}$), 27.41 (1CH), 34.65 (1$\mathrm{CH_2}$), 45.10 (1CH), 140.67 (1 quart C), 174.25 (1 quart C). IR (neat): ν (C=O) 1784 cm^{-1}; HRMS-EI calcd for $\mathrm{C_{17}H_{28}O_3Si_2}$: 336.1577, found: 336.1586. Anal. Calcd for $\mathrm{C_{17}H_{28}O_3Si_2}$: C, 60.66; H, 8.39. Found: C, 60.48; H, 8.31.

4.4. A typical procedure for synthesis of Diels–Alder cycloadduct 7 from non-silyated 1,3-butadienes and maleic anhydride in the presence $\mathrm{AlCl_3}$

1,3-Butadiene (1.0 mmol) was added to a $\mathrm{CH_2Cl_2}$ solution of maleic anhydride (1.0 mmol) at room temperature. After the reaction mixture was cooled to −35 °C, newly sublimed $\mathrm{AlCl_3}$ (1.0 mmol) was added and the reaction mixture was then stirred at −35 °C for 1 h. The above reaction mixture was quenched with water and extracted with $\mathrm{Et_2O}$. The extract was washed with brine and dried over $\mathrm{MgSO_4}$. The solvent was evaporated in vacuo and the residue was purified by column chromatography ($\mathrm{Et_2O}$/hexane=1:2) to afford the products **7**.

4.5. A typical procedure for synthesis of Diels–Alder cycloadduct 7 from non-silyated 1,3-butadienes and maleic anhydride without $AlCl_3$

1,3-Butadiene (1.0 mmol) was added to a toluene solution of maleic anhydride (1.0 mmol) at room temperature. The reaction mixture was then stirred at refluxing temperature for 1 h. The solvent was evaporated in vacuo and the residue was purified by column chromatography (Et_2O/hexane=1:2) to afford the products **7**.

4.5.1. *Compound **7a***

Colorless oil, 94% yield (248 mg).

4.5.2. *Compound **7b***

Colorless oil, 86% yield (275 mg).

4.5.3. *Compound **7c***

Colorless oil, 72% yield (270 mg).

The ^1H and ^{13}C NMR data of **7a**–**c** are consistent with the published data.[15]

4.5.4. *Compound **7d***

Colorless oil, 93% yield (295 mg); ^1H NMR (300 MHz, $CDCl_3$, Me_4Si, 25 °C): δ 0.95 (t, J=7.2 Hz, 6H, CH_3), 1.26–2.06 (m, 22H, 10CH_2 and 2CH), 3.34–3.36 (m, 2H, CH). ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si, 25 °C): δ 14.07 (1CH_3), 22.64 (1CH_2), 22.84 (1CH_2), 25.52 (1CH_2), 26.67 (1CH_2), 30.48 (1CH_2), 39.21 (1CH), 44.05 (1CH), 134.32 (1 quart C), 172.04 (1 quart C). HRMS-ESI calcd for $C_{20}H_{30}O_3H$ ($[M+H]^+$): 318.2273, found: 319.2280.

Acknowledgements

This work was supported by the Natural Science Foundation of China (20632010, 20521202, 20702003) and the Major State Basic Research Development Program (2006CB806105). Cheung Kong Scholars Programme, Qiu Shi Science & Technologies Foundation, BASF, Dow Corning Corporation, and Eli Lilly China are gratefully acknowledged.

References and notes

1. Li, D.; Liu, G.; Hu, Q.; Wang, C.; Xi, Z. *Org. Lett.* **2007**, *9*, 5433–5436.
2. (a) Mehta, G.; Khan, F. A. *Tetrahedron Lett.* **1992**, *33*, 3065–3068; (b) Kumar, V. A.; Venkatesan, K.; Ganguly, B.; Chandrasekhar, J.; Khan, F. A.; Mehta, G. *Tetrahedron Lett.* **1992**, *33*, 3069–3072; (c) Mehta, G.; Gagliardini, V.; Priyakumar, U. D.; Sastry, G. N. *Tetrahedron Lett.* **2002**, *43*, 2487–2490; (d) Priyakumar, U. D.; Sastry, G. N.; Mehta, G. *Tetrahedron* **2004**, *60*, 3465–3472.
3. (a) Chou, T.-C.; Hwa, C.-L.; Lin, J.-J.; Liao, K.-C.; Tseng, J.-C. *J. Org. Chem.* **2005**, *70*, 9717–9726; (b) Bio, M. M.; Leighton, J. L. *J. Am. Chem. Soc.* **1999**, *121*, 890–891.
4. (a) Lledo, A.; Benet-Buchholz, J.; Sole, A.; Olivella, S.; Verdaguer, X.; Riera, A. *Angew. Chem., Int. Ed.* **2007**, *46*, 5943–5946; See also: (b) Nishihara, Y.; Inoue, Y.; Itazaki, M.; Takagi, K. *Org. Lett.* **2005**, *7*, 2639–2641; (c) Nishihara, Y.; Miyasaka, M.; Inoue, Y.; Yamaguchi, T.; Kojima, M.; Takagi, K. *Organometallics* **2007**, *26*, 4054–4060.
5. (a) Mehta, G.; Ramesh, S. S. *Can. J. Chem.* **2005**, *83*, 581–594; (b) Mehta, G.; Kumaran, R. S. *Tetrahedron Lett.* **2001**, *42*, 8097–8100; (c) Mehta, G.; Reddy, D. S. *J. Chem. Soc., Perkin Trans. 1* **2001**, 1153–1161; (d) Schuda, P. F.; Heimann, M. R. *Tetrahedron* **1984**, *40*, 2365–2380; (e) Paquette, L. A.; Daivs, R. F.; James, D. R. *Tetrahedron Lett.* **1974**, *15*, 1615–1618; (f) Vogel, E.; Wyes, E. G. *Chem. Ber.* **1965**, *98*, 3680–3691; (g) Cookson, R. C.; Isaacs, N. S.; Szelke, M. *Tetrahedron* **1964**, *20*, 717–722.
6. (a) Quadrelli, P.; Romano, S.; Toma, L.; Caramella, P. *J. Org. Chem.* **2003**, *68*, 6035–6038; (b) Mehta, G.; Reddy, S. H. K. *Synlett* **1993**, 75–77; (c) Mehta, G.; Reddy, S. H. K. *Tetrahedron Lett.* **1991**, *32*, 6403–6406; (d) Eaton, P. E.; Cerefice, S. A. *J. Chem. Soc., Chem. Commun.* **1970**, 1494–1495.
7. For a review on tandem Diels–Alder cycloadditions in organic synthesis, see: Winkler, J. D. *Chem. Rev.* **1996**, *96*, 167–176.
8. (a) Bock, H.; Seidl, H. *J. Am. Chem. Soc.* **1968**, *90*, 5694–5700; (b) Fleming, I.; Percival, A. *J. Chem. Soc., Chem. Commun.* **1976**, 681; (c) Carter, M. J.; Fleming, I.; Percival, A. *J. Chem. Soc., Perkin Trans. 1* **1981**, 2415–2434; (d) Knolker, H.-J.; Baum, E.; Heber, J. *Tetrahedron Lett.* **1995**, *36*, 7647–7650; (e) Urabe, H.; Nakajima, R.; Sato, F. *Org. Lett.* **2000**, *2*, 3481–3484; (f) Delas, C.; Urabe, H.; Sato, F. *Chem. Commun.* **2002**, 820–821; (g) Morita, R.; Shirakawa, E.; Tsuchimoto, T.; Kawakami, Y. *Org. Biomol. Chem.* **2005**, *3*, 1263–1268.
9. (a) Xi, Z.; Song, Z.; Liu, G.; Liu, X.; Takahashi, T. *J. Org. Chem.* **2006**, *71*, 3154–3158; See also: (b) Negishi, E.; Cederbaum, F. E.; Takahashi, T. *Tetrahedron Lett.* **1986**, *27*, 2829–2832; (c) Negishi, E.; Holmes, S. J.; Tour, J. M.; Miller, J. A.; Cederbaum, F. K.; Swanson, D. R.; Takahashi, T. *J. Am. Chem. Soc.* **1989**, *111*, 3336–3346; (d) Xi, C.; Huo, S.; Afifi, T. H.; Hara, R.; Takahashi, T. *Tetrahedron Lett.* **1997**, *38*, 4099–4102; (e) Yamaguchi, S.; Jin, R.; Tamao, K.; Sato, F. *J. Org. Chem.* **1998**, *63*, 10060–10062; (f) Takahashi, T.; Kageyama, M.; Denisov, V.; Hara, R.; Negishi, E. *Tetrahedron Lett.* **1993**, *34*, 687–690; (g) Xi, Z.; Hara, R.; Takahashi, T. *J. Org. Chem.* **1995**, *60*, 4444–4448; (h) Hara, R.; Xi, Z.; Kotora, M.; Xi, C.; Takahashi, T. *Chem. Lett.* **1996**, 1003–1004; (i) Takahashi, T.; Xi, C.; Xi, Z.; Kageyama, M.; Fischer, R.; Nakajima, K.; Negishi, E. *J. Org. Chem.* **1998**, *63*, 6802–6806; (j) Buchwald, S. L.; Nielsen, R. B. *J. Am. Chem. Soc.* **1989**, *111*, 2870–2874.
10. Luh, T.-Y.; Wong, K.-T. *Synthesis* **1993**, 349–370.
11. For reviews on allylation reaction using allysilanes, see: (a) Chabaud, L.; James, P.; Landais, Y. *Eur. J. Org. Chem.* **2004**, 3173–3199; (b) Fleming, I.; Barbero, A.; Walter, D. *Chem. Rev.* **1997**, *97*, 2063–2192; (c) Masse, C. E.; Panek, J. S. *Chem. Rev.* **1995**, *95*, 1293–1316; (d) Yamamoto, Y.; Asao, N. *Chem. Rev.* **1993**, *93*, 2207–2293; (e) Schinzer, D. *Synthesis* **1988**, 263–273.
12. (a) Yamamoto, H.; Wadamoto, M. *J. Am. Chem. Soc.* **2005**, *127*, 14556–14557; (b) Hosomo, A.; Sakurai, H. *Tetrahedron Lett.* **1976**, 1295–1298.
13. (a) Peng, F.; Hall, D. G. *J. Am. Chem. Soc.* **2007**, *129*, 3070–3071; (b) Jervis, P. J.; Kariuki, B. M.; Cox, L. R. *Org. Lett.* **2006**, *8*, 4649–4652; (c) Barbero, A.; Castreno, P.; Garcia, C.; Pulido, F. J. *J. Org. Chem.* **2001**, *66*, 7723–7728; (d) Fujita, K.; Inoue, A.; Shinokubo, H.; Oshima, K. *Org. Lett.* **1999**, *1*, 917–919.
14. (a) Pidaparthi, R. R.; Welker, M. E.; Day, C. S.; Wright, M. W. *Org. Lett.* **2007**, *9*, 1623–1626; (b) Chung, S.-I.; Seo, J.; Cho, C.-G. *J. Org. Chem.* **2006**, *71*, 6701–6704; (c) De, S.; Welker, M. E. *Org. Lett.* **2005**, *7*, 2481–2484; (d) Kraus, G. A.; Kim, J. *Org. Lett.* **2004**, *6*, 3115–3117; (e) Davies, H. M. I.; Dai, X. *J. Am. Chem. Soc.* **2004**, *126*, 2692–2693; (f) Gao, X.; Hall, D. G. *Tetrahedron Lett.* **2003**, *44*, 2231–2235; (g) Organ, M. G.; Winkle, D. D.; Huffmann, J. *J. Org. Chem.* **1997**, *62*, 5254–5266.
15. Zhou, L.; Xi, C.; Wang, H.; Kong, F.; Takahashi, T. *Bull. Chem. Soc. Jpn.* **2006**, *79*, 950–952.
16. For a review on Lewis acid mediated reactions: Wang, C.; Xi, Z. *Chem. Soc. Rev.* **2007**, *36*, 1395–1406.
17. Crystallographic data for the structural analyses of **5b** have been deposited with the Cambridge Crystallographic Data Center. Copies of this information may be obtained free of charge from Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif, CCDC 686013.