The Cyclopropylmethylsilane Terminated Prins Reaction: Stereoelectronic Controlled Formation of (*E*)-Skipped Dienes

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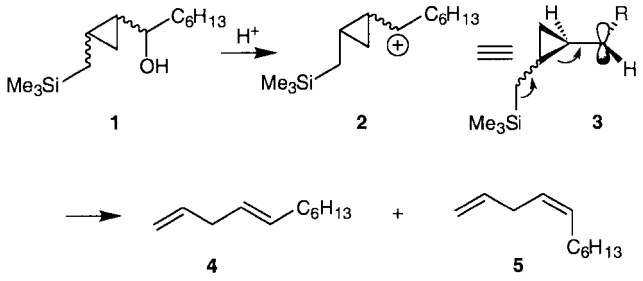
Abstract: The reaction of 1-phenyldimethylsilylmethyl-2-vinyl cyclopropane with acetals under the influence of TMSOTf proceeds smoothly to provide skipped dienes with exclusive *E*-olefin geometry regardless of the initial *cis/trans* configuration of the starting cyclopropane. The reaction is under stereoelectronic control where the intermediate Prins cation formed is stabilised by the adjacent cyclopropane grouping in a bisected conformation before undergoing silyl-directed collapse.

Key words: Prins, skipped dienes, stereoelectronic, cyclopropylmethyl cation, silanes

The Prins reaction is a fundamentally important carbon-carbon bond forming reaction consisting as it does of the attack of an olefin on an activated carbonyl compound.[1] In its classical guise (olefin, carbonyl compound and hydrochloric acid) the Prins reaction is often complicated by the various possible fates of the intermediate cation. However, when the fate of the carbocation can be controlled („terminated“) by an adjacent group, powerful synthetic methodologies arise.[2] For instance, Lewis acid catalysed processes including the Sakurai reaction,[3] the carbonyl ene reaction[4] and even the hetero Diels-Alder reaction of dienes with aldehydes[5] could formally be considered as terminated Prins reactions albeit with varying degrees of positive charge build-up. In this work we describe the use of the silylmethylcyclopropane functionality to terminate a Prins reaction.

Wilson et al. have shown that solvolysis of a mixture of all possible diastereomers of silylmethylcyclopropyl carbinol (**1**) resulted in the formation of *E*-skipped diene **4** with only traces of the corresponding *Z* isomer **5** (Scheme 1).[6] This was attributed to the participation of cation **2** which was stabilised by the cyclopropyl ring in the favoured bisected conformation[7] and where the long alkyl chain orientates itself *anti* to the cyclopropane unit (**3**; R = Hex). Silicon directed collapse automatically leads to the *E*-diene regardless of the original cyclopropane configuration. We therefore expected that if cations of the general type **3** could be alternatively generated via Prins reactivity of a suitable olefin then *E*-skipped dienes would result. In this letter we report on the reaction of 1-phenyldimethylsilylmethyl-2-vinyl cyclopropane (**6**) with aryl or alkyl acetals under the influence of trimethylsilyltrifluoromethanesulfonate (TMSOTf) to give skipped dienes of the type **7** (Figure) with exclusive 3,4-*E*-olefin geometry regardless of the initial *cis/trans* configuration of the starting cyclopropane.



Scheme 1

6 **7**

Figure

Vinyl cyclopropane **6** was prepared according to the general method of Lin and Turos[8] whereby allylsilanes are cyclopropanated with ethyldiazoacetate (EDA) under rhodium catalysis followed by LAH reduction of the ester, re-oxidation of the alcohol to the aldehyde followed by Wittig methenylation. Phenyldimethylallylsilane[9] (**8**) was selected as the allylsilane.[10] It was found that allylsilane **8** could be conveniently cyclopropanated with EDA **9** under copper(I) catalysis using readily available and inexpensive $Cu(CH_3CN)_4BF_4$[11] rather than rhodium acetate (Scheme 2). A 1:1 mixture of *cis*-**10a** and *trans*-**10b** cyclopropanes were produced which could be separated by somewhat tedious chromatography.

Once separated the two diastereomerically pure esters **10a** and **10b** were subjected to the same synthetic sequence. Reduction with LAH gave *cis* alcohol **11a** and *trans* alcohol **11b**. PCC reoxidation gave aldehydes **12b** and **12c** followed by Wittig methenylation to provide *cis*- and *trans* vinylcyclopropanes **6a** and **6b**.[12]

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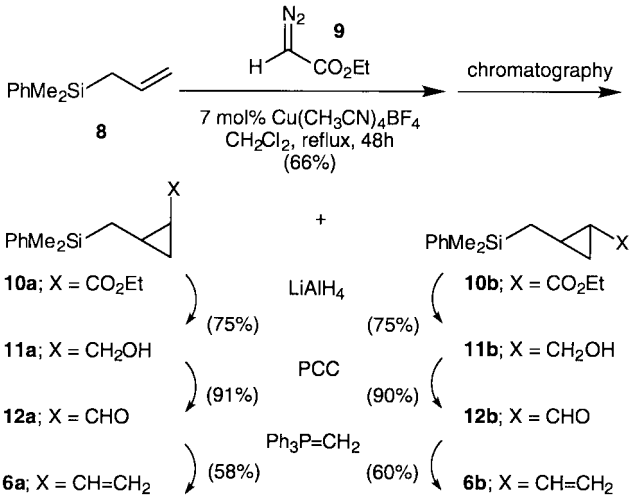
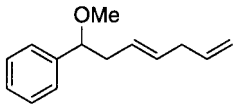
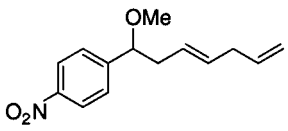
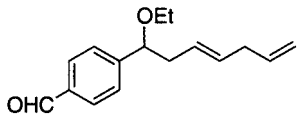
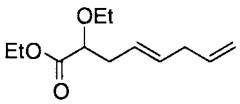
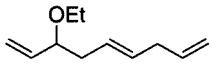
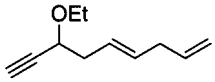
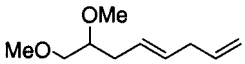
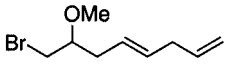
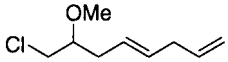


Scheme 2

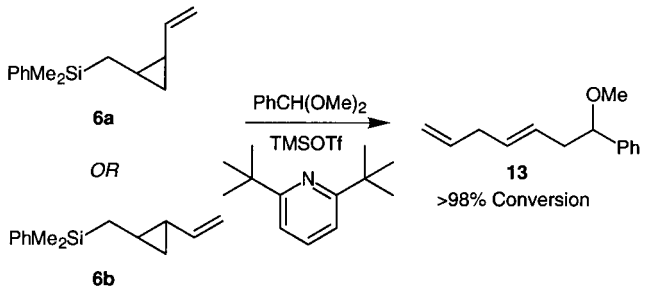
The relative configurations of the cyclopropanes **10a–12a** and **10b–12b** and thence **6a** and **6b** was assigned on the basis of previous work,[8] and was confirmed by inspection of the coupling constants in the ^{1}H NMR spectra of the various cyclopropanes.[13]

cis-Vinylcyclopropane **6a** was treated with benzaldehyde dimethylacetal, TMSOTf (1 equiv.) and 2,6-di-*tert*-butylpyridine (1.1 equiv.) in CH_2Cl_2 solution at -78 °C for 1 h in an attempt to trigger the cyclopropylmethylsilane terminated Prins reaction (Scheme 3). After a suitable work-up, ^{1}H NMR analysis revealed a single skipped diene compound (>98% conversion based on initial silane). This was assigned as the *E* isomer **13** on the basis of Wilsons' work,[6] and this was confirmed by inspection of the coupling constants for the olefinic resonances in the ^{1}H NMR spectrum in toluene-d_8 solution. The value of 15.3 Hz unambiguously defines the central olefin component

Table The Cyclopropylmethylsilane Terminated Prins Reaction of Cyclopropylvinylsilane **6a**/**6b** Mix with Acetals to give Skipped Dienes

Entry[a]	RCH(OR')$_2$	T/°C	t/h	Product		%Conversion[b,c]
1	R = Ph; R' = Me	–78	1		**13a**	>98 (88)
2	R = *p*-NO_2Ph; R' = Me	–78 to 10	4		**13b**	>98 (61)
3	R = *p*-OHCPh; R' = Et	–78 to 10	4.5		**13c**	>98(59)
4	R = CO_2Et; R' = Et	–78 to r.t.	24		**13d**	40[d]
5	R = CH=CH_2; R' = Et	–78 to r.t.	4		**13e**	-[e]
6	R = C≡CH; R' = Et	–78 to r.t	4		**13f**	>98(43)[f]
7	R = $MeOCH_2$; R' = Me	–78 to r.t	3		**13g**	>98(60)
8	R = $BrCH_2$; R' = Me	–78 to r.t	24		**13h**	>98(79)[f]
9	R = $ClCH_2$; R' = Me	–78 to r.t	24		**13i**	68[d]

[a] All reactions were performed using a 1:1 mixture of vinylcyclopropane **6a** and **6b** (200 mg, 0.92 mmol), TMSOTf (205 mg, 1 equiv.), 2,6-di-*tert*-butylpyridine (250 μL, 1.1 equiv.) and the corresponding acetal (1 equiv.) in dichloromethane (4.0 mL) under nitrogen for the given time and temperature.
[b] As determined by integration of the ^{1}H NMR spectrum of the crude reaction product.
[c] Isolated yield after chromatography in parentheses.
[d] Product not isolated.
[e] Decomposition only.
[f] Product slightly contaminated with $(PhMe_2Si)_2O$ which co-elutes (**13f**: 8%; **13h**: 14%).



Scheme 3

as having *E*-geometry. *trans*-Cyclopropane **6b** was also exposed to these conditions. Much to our delight, rapid reaction occurred at -78 °C (>98% conversion), also to give only the *E*-skipped diene **13**. Evidently, the bisected cyclopropane cation model postulated above is operating in both cases.

Unfortunately, attempts to render the process catalytic in TMSOTf were not successful. When 20 mol% TMSOTf was employed the reaction proceeded to a corresponding approximate 20% conversion. This can be rationalised by noting that the phenyldimethylsilylium cation necessarily released (as $PhMe_2SiOTf$) in the terminated Prins reaction is not as powerful as TMSOTf for activating acetals.

Having demonstrated that either *cis*-**6a** or *trans*-**6b** cyclopropane gives rise only to *E*-skipped diene **13**, gram quantity mixtures (ca. 5–10 g per batch) of the diastereomers (**6a**:**6b** 1:1) were prepared by the previous route (Scheme 2), omitting the tedious chromatographic separation of the esters **10a** and **10b**. This painstaking chromatographic separation represented a considerable bottleneck to synthesis of vinyl compounds **6a** and **6b**. With this constraint now removed by virtue of their common reactivity, gram-scale preparation of mixtures of **6a** and **6b** becomes extremely facile. 1:1 Diastereomeric mixture **6a**:**6b** was treated with benzaldehyde dimethylacetal, TMSOTf and 2,6-di-*tert*-butylpyridine as before (Table).[14] As expected, the *E*-skipped diene **13a** was the exclusive product (>98% conversion) and was isolated after column chromatography in 88% yield.

Other acetals were exposed to vinylcyclopropane **6a**:**6b** mix and TMSOTf (Table).[15] Inspection of the table shows that the cyclopropylmethylsilane terminated Prins reaction appears to be general for both aryl (entries 1–3) and alkyl (entries 4–9) acetals, although the use of vinyl acetal (entry 5) resulted in a complex product mixture. In all other cases only the *E*-skipped diene was produced. In the aryl series, *p*-nitro and *p*-formylbenzaldehyde acetals both gave essentially quantitative conversions to the skipped dienes **13b** and **13c**, albeit over slightly longer reaction times and required warming to 10 °C. It is noteworthy that the aldehyde group remains unscathed by the reaction conditions. In the aliphatic series the cyclopropylmethylsilane terminated Prins reaction could be performed on alkyne, ether and halide containing substrates (entries 6–8) under similar conditions to give skipped dienes **13f–i** in excellent yields. The caveat here is that strongly electron withdrawing groups attenuate the yield (entries 4 and 9) presumably since formation of the reactive oxonium species is retarded.

In conclusion we have demonstrated that *E*-configured skipped dienes can be conveniently prepared from silylmethylvinylcyclopropanes in good-to-excellent yields. The cyclopropane can be employed as a *cis/trans* diastereomeric mixture which is readily prepared in gram quantities. Modifications of this system to provide *Z*-configured skipped dienes and full experimental details of the present methodology will be reported in due course.

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(10) Both *cis* and *trans* 1-trimethylsilylmethyl-2-vinylcyclopropanes were also prepared (starting from allyltrimethylsilane) but proved to be too volatile to be readily handled.
(11) This reagent is easily prepared from copper(I) oxide and HBF_4 in refluxing acetonitrile.
(12) Data for compounds **10a–12a, 10b–12b, 6a** and **6b**. Ester **10a**: Colourless oil; R_f = 0.35 (1:1 CH_2Cl_2–petroleum ether, 40–60 °C); IR: 3069, 3050, 1724 cm^{-1}; ^1H NMR (270 MHz; $CDCl_3$) δ 7.55 (m, 2 H), 7.19 (m, 3 H), 4.10 (m, 2 H), 1.62 (m, 1 H), 1.26 (m, 4 H), 1.00 (m, 3 H), 0.85 (m, 1 H), 0.31 (s, 6 H); ^{13}C NMR (68 MHz; $CDCl_3$) δ 173.1, 139.0, 133.7, 129.0, 127.8, 60.3, 19.1, 17.8, 15.0, 14.5, 13.2, –2.9, –3.0; MS (CI^+, NH_3) *m/z* 280 $(M + NH_4)^+$, 185 $(M - Ph)^+$; HRMS (CI) calcd for $C_{15}H_{26}NO_2Si$: $(M + NH_4)^+$ 280.1733; found: $(M + NH_4)^+$, 280.1729. Ester **10b**: Colourless oil; R_f = 0.30 (1:1 CH_2Cl_2– petroleum ether, 40–60 °C); IR: 3069, 3050, 1724 cm^{-1}; ^1H NMR (270 MHz; $CDCl_3$) δ 7.49 (m, 2 H), 7.36 (m, 3 H), 4.08 (q, 2 H, *J* = 7.1 Hz), 1.28 (m, 3 H), 1.23 (t, 3 H, *J* = 7.1 Hz), 0.97 (dd, 1 H, *J* = 14.6, 7.7 Hz), 0.59 (m, 2 H), 0.32 (s, 3 H), 0.31 (s, 3 H); ^{13}C NMR (68 MHz; $CDCl_3$) δ 174.5, 138.7, 133.6, 129.1, 127.9, 60.31, 20.3, 19.0, 17.4, 15.7, 14.4, –2.8, –2.9; MS (CI^+, NH_3) *m/z* 280 $(M + NH_4)^+$, 263 $(M + 1)^+$, 185 $(M - Ph)^+$; HRMS (CI) calcd for

$C_{15}H_{26}NO_2Si$: $(M + NH_4)^+$ 280.1733; found: $(M + NH_4)^+$, 280.1730. Alcohol **11a:** Colourless oil; R_f = 0.15 (CH_2Cl_2); IR: 3329(br) cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 7.52 (m, 2 H), 7.35 (m, 3 H), 3.65 (dd, 1 H, *J* = 11.3, 6.5 Hz), 3.49 (dd, 1 H, *J* = 11.3, 8.3 Hz), 1.03 (m, 2 H), 0.90 (m, 1 H), 0.70 (dt, 1 H, *J* = 8.3, 4.6 Hz), 0.57 (dd, 1 H, *J* = 14.3, 9.9 Hz), 0.34 (s, 3 H), 0.31 (s, 3 H), –0.13 (q, 1 H, *J* = 5.1 Hz); ^{13}C NMR (68 MHz; $CDCl_3$) δ 139.2, 133.7, 129.0, 127.9, 63.2, 18.3, 14.2, 11.2, 11.1, –2.7, –3.1; MS (CI^+, NH_3) *m/z* 238 $(M + NH_4)^+$, 203 $(M + 1 – H_2O)^+$; HRMS (CI) calcd for $C_{13}H_{24}NOSi$: $(M + NH_4)^+$ 238.1627; found: $(M + NH_4)^+$, 238.1625. Alcohol **11b:** Colourless oil; R_f = 0.11 (CH_2Cl_2); IR: 3367(br) cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 7.52 (m, 2 H), 7.34 (m, 3 H), 3.33 (m, 2 H), 0.76 (m, 3 H), 0.55 (m, 1 H), 0.33 (dt, 1 H, *J* = 8.2, 4.7 Hz), 0.31 (s, 3 H), 0.29 (s, 3 H), 0.22 (dt, 1 H, *J* = 7.9, 4.8 Hz); ^{13}C NMR (68 MHz; $CDCl_3$) δ 139.3, 133.6, 129.0, 127.9, 67.2, 23.1, 20.5, 12.5, 12.0, –2.60, –2.80; MS (CI^+, NH_3) *m/z* 238 $(M + NH_4)^+$; HRMS (CI) calcd for $C_{13}H_{24}NOSi$: $(M + NH_4)^+$ 238.1627; found: $(M + NH_4)^+$, 238.1627. Aldehyde **12a**: Yellow oil; R_f = 0.36 (1:1 CH_2Cl_2–petroleum ether, 40–60 °C); IR: 1703 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 9.39 (d, 1 H, *J* = 4.6 Hz), 7.50 (m, 2 H), 7.35 (m, 3 H), 1.84 (m, 1 H), 1.46 (m, 1 H), 1.08 (m, 4 H), 0.32 (s, 3 H), 0.30 (s, 3 H); ^{13}C NMR (68 MHz; $CDCl_3$) δ 202.0, 138.3, 133.6, 129.2, 127.9, 28.2, 21.0, 16.3, 14.7, –2.9, –3.1; MS (CI^+, NH_3) *m/z* 236 $(M + NH_4)^+$, 219 $(M + 1)^+$; HRMS (CI) calcd for $C_{13}H_{19}OSi$: $(M + H)^+$ 219.1205; found: $(M + H)^+$, 219.1207. Aldehyde **12b**: Yellow oil; R_f = 0.27 (1:1 CH_2Cl_2– etroleum ether, 40–60 °C); IR: 1706 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 8.96 (d, 1 H, *J* = 5.3 Hz), 7.49 (m, 2 H), 7.35 (m, 3 H), 1.55 (m, 1 H), 1.41 (m, 1 H), 1.34 (m, 1 H), 1.00 (dd, 1 H, *J* = 6.0, 14.5 Hz), 0.85 (m, 1 H), 0.72 (dd, 1 H, *J* = 14.5, 8.1 Hz), 0.31 (s, 3 H), 0.30 (s, 3 H); ^{13}C NMR (68 MHz; $CDCl_3$) δ 200.9, 138.3, 133.5, 129.2, 128.0, 32.6, 20.0, 19.3, 17.0, –2.9, –3.0,; MS (CI^+, NH_3) *m/z* 236 $(M + NH_4)^+$, 219 $(M + 1)^+$. HRMS (CI) calcd for $C_{13}H_{19}OSi$: $(M + H)^+$ 219.1205; found: $(M + H)^+$, 219.1205. Vinylcyclopropane **6a**: Colourless oil; R_f = 0.86 (1:1 CH_2Cl_2–petroleum ether, 40–60 °C); IR: 1632 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 7.52 (m, 2 H), 7.35 (m, 3 H), 5.57 (ddd, 1 H, *J* = 17.0, 10.3, 8.8 Hz), 5.07 (dd, 1 H, *J* = 17.0, 1.4 Hz), 4.98 (dd, 1 H, *J* = 10.3, 1.4 Hz), 1.44 (m, 1 H), 0.92 (m, 3 H), 0.61 (dd, 1 H, *J* = 15.9, 10.2 Hz), 0.32 (s, 6 H), 0.15 (q, 1 H, *J* = 5.2 Hz); ^{13}C NMR (68 MHz; $CDCl_3$) δ 139.5, 138.7, 133.7, 128.9, 127.7, 114.0, 20.3, 15.1, 14.4, 14.2, –2.7, –2.8; MS (CI^+, NH_3) *m/z* 234 $(M + NH_4)^+$, 217 $(M + 1)^+$; HRMS (CI) calcd for $C_{14}H_{24}NSi$: $(M + NH_4)^+$ 234.1678; found: $(M + NH_4)^+$, 234.1680. Vinylcyclopropane **6b**: Colourless oil; R_f = 0.83 (1:1 CH_2Cl_2–petroleum ether 40–60 °C); IR: 1634 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 7.53 (m, 2 H), 7.36 (m, 3 H), 5.31 (ddd, 1 H, *J* = 17.1, 10.2, 8.7 Hz), 4.98 (dd, 1 H, *J* = 17.1, 1.8 Hz), 4.82 (dd, 1 H, *J* = 10.2, 1.8 Hz), 1.07, (m, 1 H), 0.79 (m, 3 H), 0.60 (m, 1 H), 0.47 (m, 1 H), 0.33 (s, 6 H); ^{13}C NMR (68 MHz; $CDCl_3$) δ 142.1, 139.4, 133.7, 128.9, 127.7, 111.1, 24.5, 20.7, 16.6, 16.1, –2.7; MS (CI^+, NH_3) *m/z* 234 $(M + NH_4)^+$, 217 $(M + 1)^+$; HRMS (CI) calcd for $C_{14}H_{24}NSi$: $(M + NH_4)^+$ 234.1678; found: $(M + NH_4)^+$, 234.1675.

(13) E.g., alcohol **11a** displays an apparent quartet at δ_H = –0.13 ppm, (*J* = 5.1 Hz). This corresponds to one of the methylene protons of the cyclopropane ring with a geminal coupling, and two *trans* vicinal couplings (for *cis* relationships *J* > 7 Hz): *syn* isomer. See: Williams, D. H.; Fleming, I. *Spectroscopic Methods in Organic Chemistry*; McGraw-Hill: New York, **1995**, 5th Ed.

(14) **General Procedure:** TMSOTf (205 mg, 167 μL, 0.92 mmol) was added dropwise to a stirring solution of benzaldehyde dimethylacetal (140 mg, 0.92 mmol), and vinylcyclopropane mix **6a** and **6b** (200 mg, 0.924 mmol), and 2,6-di-*tert*-butylpyridine (250 μL, 1.1 mmol) in CH_2Cl_2 (4.0 mL) at –78 °C. After the appropriate time (Table) the reaction was quenched by addition of water (20 mL), and the mixture was allowed to warm to room temperature. The layers were separated and the aqueous layer was extracted with CH_2Cl_2 and washed with water. The combined organic layers were dried ($MgSO_4$), and concentrated under vacuum to give a colourless oil (600 mg). Column chromatography (3:7 CH_2Cl_2–petroleum ether 40–60 °C) yielded the skipped diene **13a** (163 mg, 88%) as a colourless oil: IR: 1637 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 7.28 (m, 5 H), 5.75 (m, 1 H), 5.43 (m, 2 H), 4.92 (m, 2 H), 4.12 (t, 1 H, *J* = 6.6 Hz), 3.21 (s, 3 H), 2.70 (br t, 2 H, *J* = 5.7 Hz), 2.50 (m, 1 H), 2.38 (m, 1 H); ^1H NMR (270 MHz, toluene-d_8) δ 6.98 (m, 5 H), 5.72 (m, 1 H), 5.47 (dtt, 1 H, *J* = 15.3, 6.7, 1.2 Hz), 5.36 (ddt, 1 H, *J* = 15.3, 6.1, 1.2 Hz), 4.93 (m, 2 H), 3.98 (t, 1 H, *J* = 6.5 Hz), 3.05 (s, 3 H), 2.60 (br t, 2 H, *J* = 6.4 Hz), 2.53 (m, 1 H), 2.32 (m, 1 H); ^{13}C NMR (68 MHz; $CDCl_3$) δ 142.0, 137.1, 130.4, 128.4, 127.6, 127.4, 126.8, 115.0, 84.1, 56.7, 41.4, 36.8; MS (CI^+, NH_3) *m/z* 203 $(M + 1)^+$.

(15) ^1H NMR data for skipped diene products **13b**–**c, 13f**–**h**. Diene **13b**: ^1H NMR (270 MHz, $CDCl_3$) δ 8.18 (d, 2 H, *J* = 8.8 Hz), 7.41 (d, 2 H, *J* = 8.8 Hz), 5.72 (m, 1 H), 5.37 (m, 2 H), 4.95 (m, 2 H), 4.24 (t, 2 H, *J* = 6.4 Hz), 3.23 (s, 3 H), 2.69 (br t, 2 H, *J* = 5.3 Hz), 2.47 (1 H, m), 2.38 (1 H, m); Diene **13c**: ^1H NMR (270 MHz, $CDCl_3$) δ 9.97 (s, 1 H), 7.82 (d, 2 H, *J* = 8.3 Hz), 7.42 (d, 2 H, *J* = 8.3 Hz), 5.73 (ddt, 1 H, *J* = 16.0, 9.7, 6.5 Hz), 5.37 (m, 2 H), 4.95 (m, 2 H), 4.29 (t, 1 H, *J* = 6.7 Hz), 3.34 (q, 2 H, *J* = 6.9 Hz), 2.67 (br t, 2 H, *J* = 6.5 Hz), 2.47 (m, 1 H), 2.36 (m, 1 H), 1.16 (t, 3 H, *J* = 6.9 Hz); Diene **13f**: ^1H NMR (270 MHz, $CDCl_3$) δ 5.81 (ddt, 1 H, *J* = 16.4, 10.2, 6.2 Hz), 5.54 (m, 2 H), 5.03 (m, 2 H), 4.01 (dt, 1 H, *J* = 7.0, 1.8 Hz), 3.77 (m, 1 H), 3.43 (m, 1 H), 2.76 (br t, 2 H, *J* = 5.6 Hz), 2.41 (m, 3 H), 1.20 (t, 3 H, *J* = 7.2 Hz); Diene **13g**: ^1H NMR (270 MHz, $CDCl_3$) δ 5.80 (ddt, 1 H, *J* = 16.6, 10.2, 6.5 Hz), 5.47 (m, 2 H), 5.0 (m, 2 H), 3.39 (s, 3 H), 3.36 (m, 3 H), 3.34 (s, 3 H), 2.74 (br t, 2 H, *J* = 5.7 Hz), 2.24 (br t, 2 H, *J* = 5.7 Hz); Diene **13h**: ^1H NMR (270 MHz, $CDCl_3$) δ 5.80 (ddt, 1 H, *J* = 16.6, 10.2, 6.5 Hz), 5.53 (m, 1 H), 5.43 (m, 1 H), 5.00 (m, 2 H), 3.63–3.33 (m, 5 H), 2.75 (br t, 2 H, *J* = 6.2 Hz), 2.33 (m, 2 H), 1.20 (t, 1 H, *J* = 6.9 Hz).