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Iron-Catalyzed Diastereoselective Synthesis of α-(Methoxycarbonyl)allylsilanes

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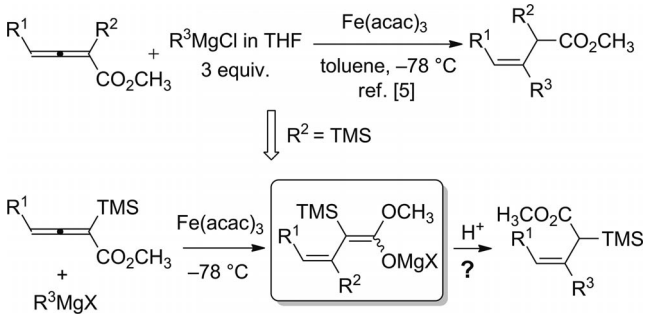
Stereodefined polysubstituted α-(methoxycarbonyl)allylsilanes were synthesized through iron-catalyzed conjugate additions between 1-(trimethylsilyl)allene-1-carboxylates and Grignard reagents in good to excellent yields. The use of Et_2O as solvent for Grignard reagents was found to be very important for the diastereoselectivity of the reaction. Applications of the prepared allylic silanes for the stereocontrolled synthesis of α,β-alkenoates, a β,γ-alkenoate, and an allylic fluoride have been demonstrated.

Introduction

Allylsilanes are important building blocks in organic synthesis[1] and are widely used for carbon–carbon and carbon–heteroatom bond formation, due to their ease of handling and high regiocontrollability.[2] Many synthetic methods for the preparation of these compounds have been developed during the past decades,[3,4] but allylsilanes with stereodefined C=C bonds and diversified functionalities remain difficult to prepare, so further development is still of considerable interest. Here we present our recent results on iron-catalyzed conjugate additions between 1-(trimethylsilyl)allene-1-carboxylates and Grignard reagents to afford α-(methoxycarbonyl)allylsilanes with stereodefined C=C bonds. In addition, further elaboration of the allylic silyl groups in the products highly selectively afforded α,β-alkenoates, a β,γ-alkenoate, and an allylic fluoride in stereodefined manner under different conditions.

Results and Discussion

In our previous work we developed efficient iron-catalyzed conjugate additions between allenecarboxylates and Grignard reagents, affording β,γ-unsaturated alkenoates with high regio- and diastereoselectivities.[5] On this basis, we reasoned that introduction of a silyl group into the reaction could be a convenient way to synthesize polysubstituted allylsilanes, each containing a stereodefined C=C bond and an ester functionality (Scheme 1).



Scheme 1. Concept for the synthesis of α-(methoxycarbonyl)allylsilanes.

Preliminary study showed that the under standard conditions developed in our previous reports,[5] the reaction between 2-trimethylsilylocta-2,3-dienoate **1a**[5d] (Scheme 2) and 3 equiv. of methylmagnesium chloride (3 M solution in THF) afforded the desired allylsilane product **2a** in 90% yield (Scheme 2, top). Unfortunately, though, the introduction of the trimethylsilyl group had a serious impact on the diastereoselectivity of the reaction: *the Z/E ratio was only 3:1*! Efforts were then devoted to improving the diastereoselectivity. Interestingly, after screening of the solvent effect of the Grignard reagent used, we were pleased to find that when Et_2O – a less coordinating solvent – was used as the solvent for the Grignard reagent, the reaction between 2-trimethylsilylocta-2,3-dienoate **1a** and 3 equiv. of CH_3MgBr (3 M solution in Et_2O) in toluene afforded the desired allylsilane product (*Z*)-**2a** (Scheme 2, bottom) in 91% yield with a high diastereoselectivity (*Z*/*E* 98:2).

The different diastereoselectivities observed here could be explained as follows (Scheme 3): when the more coordinating solvent THF is used, as a result of the immense steric effect arising from the presence of the bulky trimethylsilyl group at the 1-position, the magnesium 1,3(*Z*)-dienolate intermediate (*Z*)-**A**, formed from the addition of CH_3MgCl to **1a**, is prone to isomerize to the thermodynamically more stable magnesium 1,3(*E*)-dienolate intermediate (*E*)-**A**

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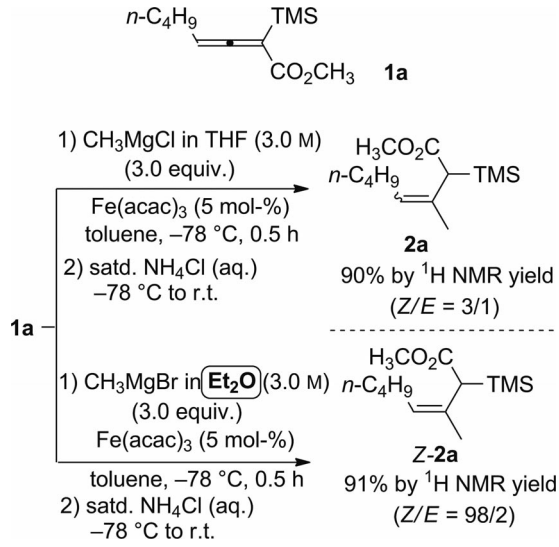
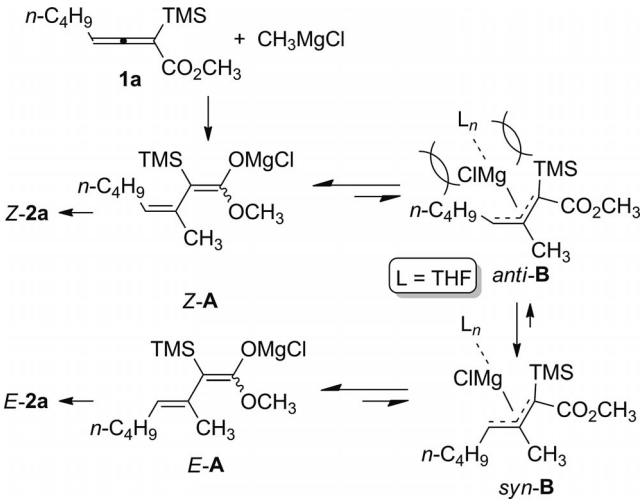


Scheme 2. Reactions between **1a** and methyl Grignard reagents.

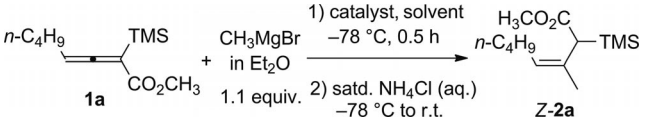
through the intermediacy of *anti*-**B** and *syn*-**B**.[5b,6c,6] Such isomerization should be much slower in Et_2O. Further protonation would afford a mixture of (*Z*)-**2a** and (*E*)-**2a**.



Scheme 3. Explanation of the different diastereoselectivities observed.

The reaction was next found to proceed to completion within 0.5 h without loss of selectivity even when 1.1 equiv. of CH_3MgBr in Et_2O (3 M) were used (Entry 1, Table 1). Further screening of reaction solvents revealed that Et_2O was also the best under these conditions, whereas use of THF decreased both the reactivity and diastereoselectivity (Entries 2 and 3, Table 1). The loading of catalyst Fe(acac)$_3$ could be further reduced to 2 mol-% without deterioration in yield or selectivity, but use of 1 mol-% of Fe(acac)$_3$ led to a slightly lower diastereoselectivity and absence of catalyst led to incomplete conversion (Entries 4–6, Table 1). Of the catalysts screened, Fe(acac)$_3$ showed the best activity and selectivity (compare Entry 5 and Entries 7–10, Table 1). We therefore defined the reactions between 1-(trimethylsilyl)allene-1-carboxylates and 1.1 equiv. of Grignard reagents (solution in Et_2O) in Et_2O at –78 °C as the standard reaction conditions (Entry 4, Table 1) for further study.

Table 1. Optimization of the reaction conditions for the synthesis of allylsilane (*Z*)-**2a**.

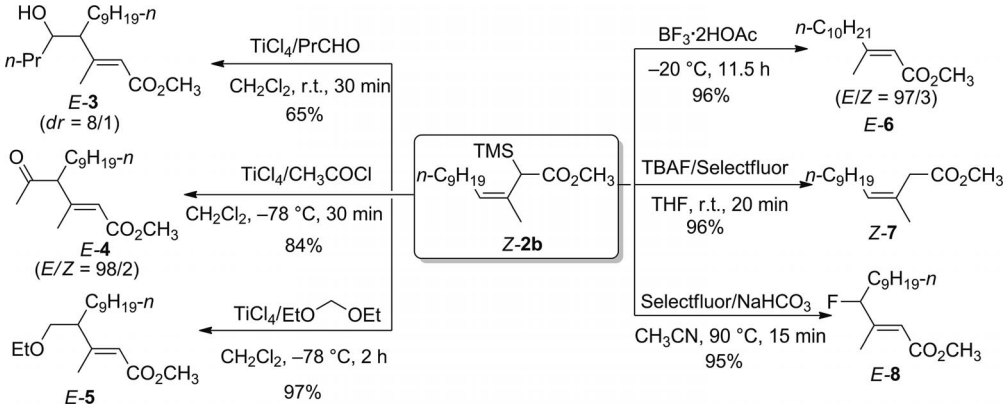


Entry	Catalyst [mol-%]	Solvent	Yield[a] of **2a** [%] (*Z*/*E*)[a]	Recovery of **1a** [%][a]
1	Fe(acac)$_3$ (5)	toluene	90 (98:2)	0
2	Fe(acac)$_3$ (5)	Et_2O	88 (>99:1)	0
3	Fe(acac)$_3$ (5)	THF	23 (93:7)	69
4	Fe(acac)$_3$ (2)	Et_2O	93 (>99:1)	0
5	Fe(acac)$_3$ (1)	Et_2O	88 (98:2)	0
6	–	Et_2O	43 (85:15)	51
7	$FeCl_3$ (2)	Et_2O	74 (97:3)	25
8	$FeCl_3 \cdot 6H_2O$ (2)	Et_2O	64 (98:2)	29
9	CuCl (2)	Et_2O	50 (84:16)	50
10	$CuCl_2$ (2)	Et_2O	52 (85:15)	40

[a] Determined by NMR analysis with dibromomethane as the internal standard.

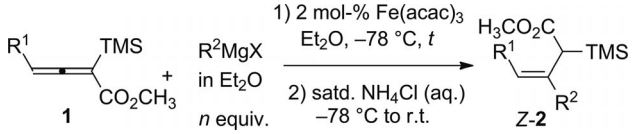
The scope of these reactions under the standard conditions was then investigated (Table 2): the reactions are quite general and proceeded well with a variety of 1-(trimethylsilyl)allene-1-carboxylates: R^1 could be a primary (**1a**, **1b**, **1d**, and **1e**), secondary (**1c**), or tertiary (**1f**) alkyl group. Similarly, primary (Entries 1–7, Table 2), secondary (Entries 8–12, Table 2), and tertiary (Entry 13, Table 2) alkyl groups could be introduced from Grignard reagents stereoselectively into the 3-position of a 1-(trimethylsilyl)allene-1-carboxylate in good to excellent yields. When primary alkyl Grignard reagents other than CH_3MgBr (i.e., EtMgBr and *n*-$C_5H_{11}MgBr$) were used, slightly lower diastereoselectivities and yields were observed (Entries 6 and 7, Table 2). In some cases, larger quantities of Grignard reagents were needed to allow the reactions to go to completion (Entries 7, 12, 13, and 18, Table 2). In addition to alkyl Grignard reagents, phenyl Grignard reagent could also be used to afford the corresponding allylic silanes (*Z*)-**2n** to (*Z*)-**2q** in good to excellent yields (Entries 14–17, Table 2). It should be noted that when vinylmagnesium bromide in THF (1 M) was used, the reaction could also afford product (*Z*)-**2r** stereospecifically (Entry 18, Table 2). Finally, the reaction could be easily conducted at a scale of 3.6 mmol of the substrate **1b** in a similar yield (Entry 19, Table 2).

The potential of the obtained stereodefined α-(methoxycarbonyl)allylsilanes was also examined (Scheme 4). 1) Product (*Z*)-**2b** could serve as an allylating reagent to react with various electrophiles such as *n*-butanal, acetyl chloride, and diethoxymethane in the presence of $TiCl_4$, affording stereodefined α,β-alkenoates (*E*)-**3** to (*E*)-**5** in moderate to high yields.[2,7] 2) α,β-Alkenoate (*E*)-**6** and β,γ-alkenoate (*Z*)-**7** could be synthesized under different desilylation conditions.[7] 3) Allylic fluoride (*E*)-**8** could also be obtained by electrophilic fluorination of (*Z*)-**2b** with Se-



Scheme 4. Regio- and diastereoselective transformations of α-(methoxycarbonyl)allylsilane (*Z*)-**2b**.

Table 2. Scope of the reaction.[a]



Entry	*n*/*t* [h]	R^1/R^2	(*Z*)-**2**[b] [%]
1	1.1/0.5	*n*-C_4H_9 (**1a**)/CH_3	93 [(*Z*)-**2a**]
2	1.1/1	*n*-C_9H_{19} (**1b**)/CH_3	92 [(*Z*)-**2b**]
3	1.1/1	*c*-C_6H_{11} (**1c**)/CH_3	83 [(*Z*)-**2c**][c]
4	1.1/1	CH_2=CH$(CH_2)_8$ (**1d**)/CH_3	93 [(*Z*)-**2d**]
5	1.1/1	Ph$(CH_2)_2$ (**1e**)/CH_3	91 [(*Z*)-**2e**]
6	1.1/1.5	*n*-C_4H_9 (**1a**)/Et	74 [(*Z*)-**2f**][d]
7	2/1.5	*n*-C_4H_9 (**1a**)/*n*-C_5H_{11}	78 [(*Z*)-**2g**][d]
8	1.1/1	*n*-C_4H_9 (**1a**)/*c*-C_6H_{11}	93 [(*Z*)-**2h**]
9	1.1/1	*n*-C_9H_{19} (**1b**)/*c*-C_6H_{11}	95 [(*Z*)-**2i**]
10	1.1/1	*c*-C_6H_{11} (**1c**)/*c*-C_6H_{11}	82 [(*Z*)-**2j**][c]
11	1.1/1	CH_2=CH$(CH_2)_8$ (**1d**)/*c*-C_6H_{11}	93 [(*Z*)-**2k**]
12	1.2/2	*t*-C_4H_9 (**1f**)/*c*-C_6H_{11}	79 [(*Z*)-**2l**]
13	3/2	*n*-C_4H_9 (**1a**)/*t*-C_4H_9	90 [(*Z*)-**2m**]
14	1.1/1	*n*-C_4H_9 (**1a**)/Ph	87 [(*Z*)-**2n**]
15	1.1/1	*n*-C_9H_{19} (**1b**)/Ph	91 [(*Z*)-**2o**]
16	1.1/1	*c*-C_6H_{11} (**1c**)/Ph	85 [(*Z*)-**2p**]
17	1.1/1.5	CH_2=CH$(CH_2)_8$ (**1d**)/Ph	86 [(*Z*)-**2q**]
18	1.3/1	*n*-C_9H_{19} (**1b**)/vinyl	98 [(*Z*)-**2r**]
19[e]	1.1/1	*n*-C_9H_{19} (**1b**)/CH_3	92 [(*Z*)-**2b**]

[a] The reactions were conducted with 0.6 mmol of allenecarboxylates, 5 mL of Et_2O, and *n* equiv. either of RMgX in Et_2O (3.0 M solution for CH_3MgBr, 3.0 M solution for PhMgBr, 2.0 M solution for *c*-$C_6H_{11}MgCl$, and 1.7 M solution for *t*BuMgCl) or of vinylmagnesium bromide (1.0 M solution in THF). [b] Isolated yields. *Z*/*E* ratios were determined by ^1H NMR analysis of the crude products and were >99:1 unless otherwise noted. [c] *Z*/*E* 98:2. [d] *Z*/*E* 97:3. [e] The reaction was conducted with **1b** on a 3.6 mmol scale (1.0652 g).

lectfluor.[8] It should be noted that both the regio- and diastereoselectivities observed here are very high, indicating the potential for broad applications of the polysubstituted allylsilane products.

Conclusions

In conclusion, we have developed iron-catalyzed conjugate additions between 1-(trimethylsilyl)allene-1-carboxylates and Grignard reagents for the synthesis of stereodefined polysubstituted α-methoxycarbonyl allylic silanes. The use of Et_2O rather than THF as solvent for the Grignard reagents perfectly solves the problems of diastereoselectivity arising from the introduction of the trimethylsilyl group. The obtained products could be used for highly diastereoselective syntheses of α,β-alkenoates, a β,γ-alkenoate, and an allylic fluoride, which are not easy to prepare. In view of the easy availability of the starting 1-(trimethylsilyl)allene-1-carboxylates[5a–5d] and Grignard reagents, as well as the broad potential for application of the products, these protocols should be of great interest in organic chemistry and related disciplines.

Experimental Section

General: THF, Et_2O, and toluene were distilled from Na/benzophenone before use. CH_3MgBr (3.0 M solution in Et_2O) used in this study was purchased from Arcos. CH_3MgCl (3.0 M solution in THF), EtMgBr (3.0 M solution in Et_2O), PhMgBr (3.0 M solution in Et_2O), *c*-$C_6H_{11}MgCl$ (2.0 M solution in Et_2O), *t*BuMgCl (1.7 M solution in Et_2O), and vinylmagnesium bromide (1.0 M solution in THF) were purchased from Sigma–Aldrich. *n*-$C_5H_{11}MgBr$ (2.0 M solution in Et_2O) was purchased from J&K Chemical. TBAF (1.0 M solution in THF) was purchased from Alfa Aesar. *n*-Butanal, acetyl chloride, and diethoxymethane were distilled before use. Other commercially available chemicals were purchased and used without additional purification unless noted otherwise. All ^1H NMR experiments were measured with use of the signals of residual chloroform (δ =7.26 ppm) in $CDCl_3$ or residual benzene (δ =7.16 ppm) in C_6D_6 as the internal references; ^{13}C NMR experiments were measured relative to the signals of $CDCl_3$ (δ = 77.0 ppm) or C_6D_6 (δ = 128.06 ppm).

Reactions between Allenecarboxylates 1 and Grignard Reagents to Afford α-(Methoxycarbonyl)allylsilanes 2

1. Methyl (3*Z*)-3-Methyl-2-(trimethylsilyl)oct-3-enoate [(*Z*)-2a]. Typical Procedure: $Fe(acac)_3$ (4.2 mg, 0.012 mmol, 2 mol-%), methyl 2-(trimethylsilyl)octa-2,3-dienoate (**1a**, 136.1 mg, 0.6 mmol), and Et_2O (5 mL) were placed sequentially, at room temperature under nitrogen, in a dried Schlenk tube containing a Teflon®-coated magnetic stirring bar. A solution of CH_3MgBr in Et_2O (0.22 mL, 3 M, 0.66 mmol, 1.1 equiv.) was added to the reaction mixture dropwise by syringe at –78 °C. After 0.5 h, the reaction

was complete as monitored by TLC, and the resulting mixture was quenched by dropwise addition of a saturated aqueous solution of NH_4Cl (0.5 mL) at –78 °C, followed by addition of water (5 mL) and warming up to room temperature. After extraction with Et_2O (3 × 20 mL), the organic layer was washed sequentially with a diluted aqueous solution of HCl (5%), a saturated aqueous solution of $NaHCO_3$, and brine, and dried with anhydrous Na_2SO_4. Filtration, concentration, and flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate 100:1) afforded (*Z*)-**2a** (135.7 mg, 93%) as a liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.17 (t, J = 7.1 Hz, 1 H, HC=C), 3.62 (s, 3 H, OCH_3), 3.34 (s, 1 H, CH), 2.01–1.80 (m, 5 H, CH_2 + CH_3), 1.36–1.20 (m, 4 H, 2 × CH_2), 0.87 (t, J = 7.1 Hz, 3 H, CH_3), 0.10 [s, 9 H, $Si(CH_3)_3$] ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 173.4, 130.3, 126.7, 51.0, 41.0, 31.9, 27.7, 23.2, 22.3, 13.9, –1.4 ppm. IR (neat): $\tilde{\nu}$ = 2956, 2859, 1731, 1433, 1378, 1357, 1305, 1251, 1194, 1155, 1113 cm^{-1}. MS (EI): *m*/*z* (%) = 242 (6.15) $[M]^+$, 95 (100). HRMS: calcd. for $C_{13}H_{26}O_2Si$ $[M]^+$ 242.1702; found 242.1695.

The following compounds were prepared by this procedure.

2. Methyl (3*Z*)-3-Methyl-2-(trimethylsilyl)tridec-3-enoate [(*Z*)-2b]: Use of the Typical Procedure with $Fe(acac)_3$ (4.3 mg, 0.012 mmol, 2 mol-%), **1b** (177.4 mg, 0.6 mmol), and CH_3MgBr (0.22 mL, 3 M solution in Et_2O, 0.66 mmol, 1.1 equiv.) in Et_2O (5 mL) afforded (*Z*)-**2b** (172.3 mg, 92%) as a liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.18 (tq, J_1 = 7.1, J_2 = 1.3 Hz, 1 H, HC=C), 3.63 (s, 3 H, OCH_3), 3.34 (s, 1 H, CH), 1.99–1.80 (m, 5 H, CH_2 + CH_3), 1.36–1.20 (m, 14 H, 7 × CH_2), 0.88 (t, J = 6.6 Hz, 3 H, CH_3), 0.11 [s, 9 H, $Si(CH_3)_3$] ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 173.4, 130.3, 126.8, 51.0, 41.0, 31.9, 29.8, 29.57, 29.53, 29.34, 29.31, 28.0, 23.2, 22.7, 14.1, –1.4 ppm. IR (neat): $\tilde{\nu}$ = 2954, 2925, 2854, 1728, 1456, 1432, 1378, 1358, 1305, 1251, 1189, 1152, 1117, 1073 cm^{-1}. MS (EI): *m*/*z* (%) = 312 (7.51) $[M]^+$, 95 (100). HRMS: calcd. for $C_{18}H_{36}O_2Si$ $[M]^+$ 312.2485; found 312.2487.

The 3.6-mmol-Scale Reaction between 1b and CH_3MgBr: Use of the Typical Procedure with $Fe(acac)_3$ (25.2 mg, 0.072 mmol, 2 mol-%), **1b** (1.0652 g, 3.6 mmol), and CH_3MgBr (1.32 mL, 3 M solution in Et_2O, 3.96 mmol, 1.1 equiv.) in Et_2O (30 mL) afforded (*Z*)-**2b** (1.0254 g, 92%): Liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.18 (tq, J_1 = 7.1, J_2 = 1.4 Hz, 1 H, HC=C), 3.64 (s, 3 H, OCH_3), 3.35 (s, 1 H, CH), 1.98–1.80 (m, 5 H, CH_2 + CH_3), 1.36–1.18 (m, 14 H, 7 × CH_2), 0.88 (t, J = 6.6 Hz, 3 H, CH_3), 0.12 [s, 9 H, $Si(CH_3)_3$] ppm.

3. Methyl (3*Z*)-4-Cyclohexyl-3-methyl-2-(trimethylsilyl)but-3-enoate [(*Z*)-2c]: Use of the Typical Procedure with $Fe(acac)_3$ (4.3 mg, 0.012 mmol, 2 mol-%), **1c** (151.6 mg, 0.6 mmol), and CH_3MgBr (0.22 mL, 3 M solution in Et_2O, 0.66 mmol, 1.1 equiv.) in Et_2O (5 mL) afforded (*Z*)-**2c** (133.6 mg, 83%, *Z*/*E* 98:2) as a liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.02 (dq, J_1 = 9.2, J_2 = 1.4 Hz, 1 H, HC=C), 3.64 (s, 3 H, OCH_3), 3.33 (s, 1 H, CH), 2.09–1.94 (m, 1 H, one proton in cyclohexyl group), 1.84 (d, J = 1.5 Hz, 3 H, CH_3), 1.73–1.48 (m, 5 H, five protons in cyclohexyl group), 1.34–0.92 (m, 5 H, five protons in cyclohexyl group), 0.12 [s, 9 H, $Si(CH_3)_3$] ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 173.5, 133.1, 128.4, 51.0, 41.1, 36.8, 33.3, 26.00, 25.95, 25.93, 23.3, –1.3 ppm. IR (neat): $\tilde{\nu}$ = 2924, 2850, 1728, 1448, 1432, 1251, 1198, 1157, 1116 cm^{-1}. MS (EI): *m*/*z* (%) = 268 (23.24) $[M]^+$, 121 (100). HRMS: calcd. for $C_{15}H_{28}O_2Si$ $[M]^+$ 268.1859; found 268.1864.

4. Methyl (3*Z*)-3-Methyl-2-(trimethylsilyl)tetradeca-3,13-dienoate [(*Z*)-2d]: Use of the Typical Procedure with $Fe(acac)_3$ (4.2 mg, 0.012 mmol, 2 mol-%), **1d** (184.0 mg, 0.6 mmol), and CH_3MgBr (0.22 mL, 3 M solution in Et_2O, 0.66 mmol, 1.1 equiv.) in Et_2O (5 mL) afforded (*Z*)-**2d** (180.6 mg, 93%): Liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.88–5.72 (m, 1 H, HC=C), 5.18 (t, J = 6.6 Hz, 1 H, HC=C), 5.03–4.88 (m, 2 H, H_2C=C), 3.64 (s, 3 H, OCH_3), 3.34 (s, 1 H, CH), 2.03 (q, J = 7.0 Hz, 2 H, CH_2), 1.97–1.80 (m, 5 H, CH_2 + CH_3), 1.42–1.20 (m, 12 H, 6 × CH_2), 0.12 [s, 9 H, $Si(CH_3)_3$] ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 173.4, 139.2, 130.3, 126.8, 114.1, 51.0, 41.0, 33.8, 29.8, 29.5, 29.4, 29.3, 29.1, 28.9, 28.0, 23.2, –1.3 ppm. IR (neat): $\tilde{\nu}$ = 3077, 2926, 2954, 1728, 1641, 1432, 1357, 1305, 1251, 1189, 1154, 1116 cm^{-1}. MS (EI): *m*/*z* (%) = 324 (9.99) $[M]^+$, 95 (100). HRMS: calcd. for $C_{19}H_{36}O_2Si$ $[M]^+$ 324.2485; found 324.2490.

5. Methyl (3*Z*)-3-Methyl-6-phenyl-2-(trimethylsilyl)hex-3-enoate [(*Z*)-2e]: Use of the Typical Procedure with $Fe(acac)_3$ (4.2 mg, 0.012 mmol, 2 mol-%), **1e** (164.8 mg, 0.6 mmol), and CH_3MgBr (0.22 mL, 3 M solution in Et_2O, 0.66 mmol, 1.1 equiv.) in Et_2O (5 mL) afforded (*Z*)-**2e** (158.9 mg, 91%) as a liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.34–7.25 (m, 2 H, Ar-H), 7.24–7.16 (m, 3 H, Ar-H), 5.27 (t, J = 7.1 Hz, 1 H, HC=C), 3.65 (s, 3 H, OCH_3), 3.37 (s, 1 H, CH), 2.66 (t, J = 8.0 Hz, 2 H, $PhCH_2$), 2.40–2.16 (m, 2 H, CH_2), 1.91 (s, 3 H, CH_3), 0.13 [s, 9 H, $Si(CH_3)_3$] ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 173.2, 142.0, 131.2, 128.35, 128.29, 125.8, 125.6, 51.0, 41.1, 36.0, 30.1, 23.2, –1.4 ppm. IR (neat): $\tilde{\nu}$ = 3027, 2951, 2857, 1726, 1496, 1454, 1432, 1308, 1251, 1189, 1165, 1110 cm^{-1}. MS (EI): *m*/*z* (%) = 290 (1.77) $[M]^+$, 95 (100). HRMS: calcd. for $C_{17}H_{26}O_2Si$ $[M]^+$ 290.1702; found 290.1704.

6. Methyl (3*Z*)-3-Ethyl-2-(trimethylsilyl)oct-3-enoate [(*Z*)-2f]: Use of the Typical Procedure with $Fe(acac)_3$ (4.3 mg, 0.012 mmol, 2 mol-%), **1a** (136.0 mg, 0.6 mmol), and EtMgBr (0.22 mL, 3 M solution in Et_2O, 0.66 mmol, 1.1 equiv.) in Et_2O (5 mL) afforded (*Z*)-**2f** (113.6 mg, 74%, *Z*/*E* 97:3, eluent: petroleum ether/Et_2O 100:1) as a liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.18 (t, J = 7.1 Hz, 1 H, HC=C), 3.63 (s, 3 H, OCH_3), 3.35 (s, 1 H, CH), 2.47–2.30 (m, 1 H, one proton in CH_2), 2.06–1.84 (m, 3 H, CH_2 + one proton in CH_2), 1.38–1.22 (m, 4 H, 2 × CH_2), 1.02 (t, J = 7.4 Hz, 3 H, CH_3), 0.89 (t, J = 6.8 Hz, 3 H, CH_3), 0.10 [s, 9 H, $Si(CH_3)_3$] ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 173.6, 135.8, 124.0, 51.1, 41.3, 32.1, 27.9, 27.6, 22.4, 14.0, 12.6, –1.2 ppm. IR (neat): $\tilde{\nu}$ = 2959, 2930, 2874, 1728, 1462, 1433, 1367, 1331, 1302, 1251, 1190, 1153, 1116 cm^{-1}. MS (EI): *m*/*z* (%) = 256 (8.76) $[M]^+$, 109 (100). HRMS: calcd. for $C_{14}H_{28}O_2Si$ $[M]^+$ 256.1859; found 256.1864.

7. Methyl (3*Z*)-3-Pentyl-2-(trimethylsilyl)oct-3-enoate [(*Z*)-2g]: Use of the Typical Procedure with $Fe(acac)_3$ (4.3 mg, 0.012 mmol, 2 mol-%), **1a** (135.2 mg, 0.6 mmol), and *n*-$C_5H_{11}MgBr$ (0.6 mL, 2 M solution in Et_2O, 1.2 mmol, 2 equiv.) in Et_2O (5 mL) afforded (*Z*)-**2g** (139.4 mg, 78%, *Z*/*E* 97:3, eluent: petroleum ether/Et_2O 100:1) as a liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.17 (t, J = 6.9 Hz, 1 H, HC=C), 3.62 (s, 3 H, OCH_3), 3.31 (s, 1 H, CH), 2.37–2.20 (m, 1 H, one proton in CH_2), 2.02–1.84 (m, 3 H, CH_2 + one proton in CH_2), 1.56–1.20 (m, 10 H, 5 × CH_2), 0.88 (t, J = 6.8 Hz, 6 H, 2 × CH_3), 0.10 [s, 9 H, $Si(CH_3)_3$] ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 173.6, 134.5, 124.8, 51.1, 41.4, 35.1, 32.1, 32.0, 28.3, 28.0, 22.7, 22.4, 14.1, 14.0, –1.2 ppm. IR (neat): $\tilde{\nu}$ = 2956, 2929, 2859, 1725, 1653, 1465, 1433, 1379, 1305, 1250, 1190, 1152, 1118, 1019 cm^{-1}. MS (EI): *m*/*z* (%) = 298 (13.18) $[M]^+$, 73 (100). HRMS: calcd. for $C_{17}H_{34}O_2Si$ $[M]^+$ 298.2328; found 298.2327.

8. Methyl (3*Z*)-3-Cyclohexyl-2-(trimethylsilyl)oct-3-enoate [(*Z*)-2h]: Use of the Typical Procedure with $Fe(acac)_3$ (4.1 mg, 0.012 mmol, 2 mol-%), **1a** (135.1 mg, 0.6 mmol), and *c*-$C_6H_{11}MgCl$ (0.33 mL, 2 M solution in Et_2O, 0.66 mmol, 1.1 equiv.) in Et_2O (5 mL) afforded (*Z*)-**2h** (171.8 mg, 93%) as a liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.19 (t, J = 7.1 Hz, 1 H, HC=C), 3.60 (s, 3 H, OCH_3), 3.16 (s, 1 H, CH), 2.08–1.86 (m, 3 H, CH + CH_2), 1.77–1.58 (m, 5 H, five protons in cyclohexyl group), 1.38–0.98 (m, 9 H, 2 × CH_2

+ five protons in cyclohexyl group), 0.87 (t, J = 7.1 Hz, 3 H, CH_3), 0.09 [s, 9 H, $Si(CH_3)_3$] ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 173.4, 139.6, 124.9, 51.0, 43.6, 41.4, 34.6, 33.6, 32.1, 28.4, 27.10, 27.06, 26.3, 22.4, 14.0, –1.2 ppm. IR (neat): $\tilde{\nu}$ = 2926, 2852, 1724, 1645, 1449, 1432, 1321, 1250, 1190, 1152, 1131, 1113 cm^{-1}. MS (EI): m/z (%) = 310 (24.15) $[M]^+$, 73 (100). HRMS: calcd. for $C_{18}H_{34}O_2Si$ $[M]^+$ 310.2328; found 310.2329.

9. Methyl (3*Z*)-3-Cyclohexyl-2-(trimethylsilyl)tridec-3-enoate [(*Z*)-2i]: Use of the Typical Procedure with $Fe(acac)_3$ (4.3 mg, 0.012 mmol, 2 mol-%), **1b** (177.2 mg, 0.6 mmol), and *c*-$C_6H_{11}MgCl$ (0.33 mL, 2 M solution in Et_2O, 0.66 mmol, 1.1 equiv.) in Et_2O (5 mL) afforded (*Z*)-**2i** (215.7 mg, 95%) as a liquid. ^1H NMR (300 MHz, $CDCl_3$): δ = 5.20 (t, J = 6.8 Hz, 1 H, HC=C), 3.62 (s, 3 H, OCH_3), 3.17 (s, 1 H, CH), 2.09–1.97 (m, 1 H, CH), 1.92 (q, J = 7.0 Hz, 2 H, CH_2), 1.78–1.60 (m, 5 H, five protons in cyclohexyl group), 1.38–0.96 (m, 19 H, 7× CH_2 + five protons in cyclohexyl group), 0.87 (t, J = 6.5 Hz, 3 H, CH_3), 0.10 [s, 9 H, $Si(CH_3)_3$] ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 173.4, 139.6, 125.0, 51.1, 43.6, 41.5, 34.7, 33.7, 31.9, 29.9, 29.6, 29.4, 29.3, 28.7, 27.12, 27.09, 26.4, 22.7, 14.1, –1.1 ppm. IR (neat): $\tilde{\nu}$ = 2925, 2853, 1725, 1645, 1449, 1432, 1320, 1249, 1192, 1149, 1131 cm^{-1}. MS (EI): m/z (%) = 380 (18.29) $[M]^+$, 73 (100). HRMS: calcd. for $C_{23}H_{44}O_2Si$ $[M]^+$ 380.3111; found 380.3114.

10. Methyl (3*Z*)-3,4-Dicyclohexyl-2-(trimethylsilyl)but-3-enoate [(*Z*)-2j]: Use of the Typical Procedure with $Fe(acac)_3$ (4.1 mg, 0.012 mmol, 2 mol-%), **1c** (152.8 mg, 0.6 mmol), and *c*-$C_6H_{11}MgCl$ (0.33 mL, 2 M solution in Et_2O, 0.66 mmol, 1.1 equiv.) in Et_2O (5 mL) afforded (*Z*)-**2j** (167.8 mg, 82%, *Z*/*E* 98:2) as a liquid. ^1H NMR (300 MHz, $CDCl_3$): δ = 5.01 (d, J = 9.6 Hz, 1 H, HC=C), 3.61 (s, 3 H, OCH_3), 3.16 (s, 1 H, CH), 2.06–1.92 (m, 2 H, 2× CH), 1.78–1.50 (m, 10 H, 10 protons in cyclohexyl groups), 1.34–0.90 (m, 10 H, 10 protons in cyclohexyl groups), 0.10 [s, 9 H, $Si(CH_3)_3$] ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 173.6, 137.9, 130.9, 51.1, 43.0, 41.8, 37.0, 35.0, 33.9, 33.4, 33.3, 27.2, 27.1, 26.4, 26.1, 26.04, 25.95 ppm. IR (neat): $\tilde{\nu}$ = 2925, 2851, 1725, 1449, 1432, 1249, 1192, 1155, 1119 cm^{-1}. MS (EI): m/z (%) = 336 (19.99) $[M]^+$, 73 (100). HRMS: calcd. for $C_{20}H_{36}O_2Si$ $[M]^+$ 336.2485; found 336.2491.

11. Methyl (3*Z*)-3-Cyclohexyl-2-(trimethylsilyl)tetradeca-3,13-dienoate [(*Z*)-2k]: Use of the Typical Procedure with $Fe(acac)_3$ (4.2 mg, 0.012 mmol, 2 mol-%), **1d** (184.0 mg, 0.6 mmol), and *c*-$C_6H_{11}MgCl$ (0.33 mL, 2 M solution in Et_2O, 0.66 mmol, 1.1 equiv.) in Et_2O (5 mL) afforded (*Z*)-**2k** (218.6 mg, 93%) as a liquid. ^1H NMR (300 MHz, $CDCl_3$): δ = 5.87–5.71 (m, 1 H, HC=C), 5.20 (t, J = 7.1 Hz, 1 H, HC=C), 5.03–4.87 (m, 2 H, H_2C=C), 3.61 (s, 3 H, OCH_3), 3.17 (s, 1 H, CH), 2.02 (q, J = 7.0 Hz, 3 H, CH_2 + CH), 1.92 (q, J = 6.9 Hz, 2 H, CH_2), 1.80–1.58 (m, 5 H, five protons in cyclohexyl group), 1.43–0.94 (m, 17 H, 6× CH_2 + five protons in cyclohexyl group), 0.10 [s, 9 H, $Si(CH_3)_3$] ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 173.4, 139.6, 139.1, 124.9, 114.1, 51.0, 43.6, 41.5, 34.7, 33.8, 33.6, 29.8, 29.5, 29.41, 29.36, 29.1, 28.9, 28.7, 27.10, 27.08, 26.3, –1.1 ppm. IR (neat): $\tilde{\nu}$ = 2925, 2852, 1724, 1641, 1448, 1432, 1320, 1249, 1192, 1151, 1129 cm^{-1}. MS (EI): m/z (%) = 392 (3.13) $[M]^+$, 163 (100). HRMS: calcd. for $C_{24}H_{44}O_2Si$ $[M]^+$ 392.3111; found 392.3117.

12. Methyl (3*Z*)-3-Cyclohexyl-5,5-dimethyl-2-(trimethylsilyl)hex-3-enoate [(*Z*)-2l]: Use of the Typical Procedure with $Fe(acac)_3$ (4.1 mg, 0.012 mmol, 2 mol-%), **1f** (135.4 mg, 0.6 mmol), and *c*-$C_6H_{11}MgCl$ (0.36 mL, 2 M solution in Et_2O, 0.72 mmol, 1.2 equiv.) in Et_2O (5 mL) afforded (*Z*)-**2l** (146.4 mg, 79%, eluent: petroleum ether/CH_2Cl_2 7:1) as a liquid. ^1H NMR (300 MHz, $CDCl_3$): δ = 5.22 (s, 1 H, HC=C), 3.63 (s, 3 H, OCH_3), 3.60 (s, 1 H, CH), 2.03 (t, J = 11.6 Hz, 1 H, one proton in *c*-hexyl group), 1.89 (d, J = 12.6 Hz, 1 H, one proton in *c*-hexyl group), 1.78–1.60 (m, 4 H, 4 protons in *c*-hexyl group), 1.36–0.93 [m, 14 H, $C(CH_3)_3$ + five protons in *c*-hexyl group], 0.14 [s, 9 H, $Si(CH_3)_3$] ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 173.4, 140.0, 135.4, 51.0, 42.8, 42.5, 36.1, 34.8, 31.84, 31.76, 27.4, 27.3, 26.4, –0.9 ppm. IR (neat): $\tilde{\nu}$ = 2927, 2851, 1727, 1635, 1448, 1432, 1364, 1301, 1251, 1214, 1164, 1144, 1125 cm^{-1}. MS (EI): m/z (%) = 310 (50.80) $[M]^+$, 191 (100). HRMS: calcd. for $C_{18}H_{34}O_2Si$ $[M]^+$ 310.2328; found 310.2322.

13. Methyl (3*Z*)-3-*tert*-Butyl-2-(trimethylsilyl)oct-3-enoate [(*Z*)-2m]: Use of the Typical Procedure with $Fe(acac)_3$ (4.3 mg, 0.012 mmol, 2 mol-%), **1a** (136.0 mg, 0.6 mmol), and *t*BuMgCl (1.1 mL, 1.7 M solution in Et_2O, 1.87 mmol, 3 equiv.) in Et_2O (5 mL) afforded (*Z*)-**2m** (153.2 mg, 90%) as a liquid. ^1H NMR (300 MHz, $CDCl_3$): δ = 5.40 (t, J = 6.9 Hz, 1 H, HC=C), 3.63 (s, 3 H, OCH_3), 3.13 (s, 1 H, CH), 2.15–1.99 (m, 1 H, one proton in CH_2), 1.84–1.69 (m, 1 H, one proton in CH_2), 1.52–1.26 (m, 4 H, 2× CH_2), 0.98 [s, 9 H, $C(CH_3)_3$], 0.90 (t, J = 7.1 Hz, 3 H, CH_3), 0.14 [s, 9 H, $Si(CH_3)_3$] ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 173.3, 140.3, 125.5, 51.1, 38.4, 37.2, 32.1, 30.8, 28.9, 22.8, 14.2, 0.2 ppm. IR (neat): $\tilde{\nu}$ = 2955, 2872, 1739, 1704, 1479, 1465, 1432, 1353, 1328, 1251, 1158, 1142 cm^{-1}. MS (EI): m/z (%) = 284 (15.07) $[M]^+$, 137 (100). HRMS: calcd. for $C_{16}H_{32}O_2Si$ $[M]^+$ 284.2172; found 284.2165.

14. Methyl (3*Z*)-3-Phenyl-2-(trimethylsilyl)oct-3-enoate [(*Z*)-2n]: Use of the Typical Procedure with $Fe(acac)_3$ (4.1 mg, 0.012 mmol, 2 mol-%), **1a** (135.6 mg, 0.6 mmol), and PhMgBr (0.22 mL, 3 M solution in Et_2O, 0.66 mmol, 1.1 equiv.) in Et_2O (5 mL) afforded (*Z*)-**2n** (159.1 mg, 87%) as a liquid. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.53–7.34 (m, 5 H, Ar-H), 5.88 (t, J = 7.2 Hz, 1 H, HC=C), 3.89 (s, 3 H, OCH_3), 3.70 (s, 1 H, CH), 2.44–2.20 (m, 2 H, CH_2), 1.70–1.50 (m, 4 H, 2× CH_2), 1.11 (t, J = 7.1 Hz, 3 H, CH_3), 0.23 [s, 9 H, $Si(CH_3)_3$] ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 173.6, 145.0, 135.5, 132.8, 127.8, 127.4, 126.5, 51.4, 41.3, 31.7, 29.6, 22.5, 14.0, –0.6 ppm. IR (neat): $\tilde{\nu}$ = 3056, 3020, 2955, 2929, 2872, 1728, 1493, 1443, 1433, 1250, 1190, 1154 cm^{-1}. MS (EI): m/z (%) = 304 (15.20) $[M]^+$, 157 (100). HRMS: calcd. for $C_{18}H_{28}O_2Si$ $[M]^+$ 304.1859; found 304.1850.

15. Methyl (3*Z*)-3-Phenyl-2-(trimethylsilyl)tridec-3-enoate [(*Z*)-2o]: Use of the Typical Procedure with $Fe(acac)_3$ (4.2 mg, 0.012 mmol, 2 mol-%), **1b** (177.0 mg, 0.6 mmol), and PhMgBr (0.22 mL, 3 M solution in Et_2O, 0.66 mmol, 1.1 equiv.) in Et_2O (5 mL) afforded (*Z*)-**2o** (204.1 mg, 91%) as a liquid. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.54–7.30 (m, 5 H, Ar-H), 5.88 (t, J = 7.4 Hz, 1 H, HC=C), 3.89 (s, 3 H, OCH_3), 3.69 (s, 1 H, CH), 2.43–2.20 (m, 2 H, CH_2), 1.70–1.35 (m, 14 H, 7× CH_2), 1.07 (t, J = 6.5 Hz, 3 H, CH_3), 0.23 [s, 9 H, $Si(CH_3)_3$] ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 173.6, 145.0, 135.5, 132.9, 127.8, 127.4, 126.5, 51.4, 41.3, 31.9, 29.9, 29.56, 29.52, 29.50, 29.3, 22.7, 14.1, –0.6 ppm. IR (neat): $\tilde{\nu}$ = 2925, 2854, 1728, 1492, 1464, 1432, 1250, 1153 cm^{-1}. MS (EI): m/z (%) = 374 (39.96) $[M]^+$, 157 (100). HRMS: calcd. for $C_{23}H_{38}O_2Si$ $[M]^+$ 374.2641; found 374.2646.

16. Methyl (3*Z*)-4-Cyclohexyl-3-phenyl-2-(trimethylsilyl)but-3-enoate [(*Z*)-2p]: Use of the Typical Procedure with $Fe(acac)_3$ (4.2 mg, 0.012 mmol, 2 mol-%), **1c** (151.0 mg, 0.6 mmol), and PhMgBr (0.22 mL, 3 M solution in Et_2O, 0.66 mmol, 1.1 equiv.) in Et_2O (5 mL) afforded (*Z*)-**2p** (167.3 mg, 85%) as a liquid. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.54–7.48 (m, 2 H, Ar-H), 7.47–7.34 (m, 3 H, Ar-H), 5.70 (d, J = 9.6 Hz, 1 H, HC=C), 3.90 (s, 3 H, OCH_3), 3.69 (s, 1 H, CH), 2.47–2.31 (m, 1 H, CH), 2.00–1.80 (m, 5 H, five protons in cyclohexyl group), 1.60–1.22 (m, 5 H, five protons in cyclohexyl group), 0.22 [s, 9 H, $Si(CH_3)_3$] ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 173.8, 144.9, 138.3, 133.7, 127.8, 127.6, 126.5, 51.5,

41.2, 38.3, 33.0, 32.8, 26.0, 25.9, 25.7, –0.7 ppm. IR (neat): $\tilde{\nu}$ = 2924, 2850, 1727, 1599, 1492, 1448, 1432, 1250, 1220, 1156 cm^{-1}. MS (EI): *m*/*z* (%) = 330 (51.58) $[M]^+$, 73 (100). HRMS: calcd. for $C_{20}H_{30}O_2Si$ $[M]^+$ 330.2015; found 330.2019.

17. Methyl (3*Z*)-3-Phenyl-2-(trimethylsilyl)tetradeca-3,13-dienoate [(*Z*)-2q]: Use of the Typical Procedure with $Fe(acac)_3$ (4.1 mg, 0.012 mmol, 2 mol-%), **1d** (184.2 mg, 0.6 mmol), and PhMgBr (0.22 mL, 3 M solution in Et_2O, 0.66 mmol, 1.1 equiv.) in Et_2O (5 mL) afforded (*Z*)-**2q** (199.0 mg, 86%) as a liquid. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.54–7.34 (m, 5 H, Ar-H), 6.08–5.92 (m, 1 H, HC=C), 5.88 (t, *J* = 7.2 Hz, 1 H, HC=C), 5.23–5.07 (m, 2 H, H_2C=C), 3.89 (s, 3 H, OCH_3), 3.69 (s, 1 H, CH), 2.43–2.16 (m, 4 H, 2× CH_2), 1.70–1.40 (m, 12 H, 6× CH_2), 0.23 [s, 9 H, $Si(CH_3)_3$] ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 173.6, 145.0, 139.2, 135.5, 132.8, 127.9, 127.4, 126.5, 114.1, 51.4, 41.3, 33.8, 29.9, 29.50, 29.47, 29.41, 29.1, 28.9, –0.6 ppm. IR (neat): $\tilde{\nu}$ = 2926, 2854, 1728, 1640, 1492, 1432, 1250, 1153 cm^{-1}. MS (EI): *m*/*z* (%) = 386 (5.93) $[M]^+$, 157 (100). HRMS: calcd. for $C_{24}H_{38}O_2Si$ $[M]^+$ 386.2641; found 386.2639.

18. Methyl (3*Z*)-2-(Trimethylsilyl)-3-vinyltridec-3-enoate [(*Z*)-2r]: Use of the Typical Procedure with $Fe(acac)_3$ (4.3 mg, 0.012 mmol, 2 mol-%), **1b** (176.8 mg, 0.6 mmol), and vinylmagnesium bromide (0.78 mL, 1 M solution in THF, 0.78 mmol, 1.3 equiv.) in Et_2O (5 mL) afforded (*Z*)-**2r** (188.7 mg, 98%) as a liquid. ^1H NMR (300 MHz, $CDCl_3$): δ = 6.43 (dd, J_1 = 17.4, J_2 = 10.8 Hz, 1 H, HC=C), 5.64 (t, *J* = 7.4 Hz, 1 H, HC=C), 5.12 (d, *J* = 17.4 Hz, 1 H, one proton in H_2C=C), 4.91 (d, *J* = 10.8 Hz, 1 H, one proton in H_2C=C), 3.64 (s, 3 H, OCH_3), 3.37 (s, 1 H, CH), 2.01 (q, *J* = 7.2 Hz, 2 H, CH_2), 1.44–1.18 (m, 14 H, 7× CH_2), 0.87 (t, *J* = 6.6 Hz, 3 H, CH_3), 0.11 [s, 9 H, $Si(CH_3)_3$] ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 173.2, 140.0, 133.7, 130.7, 111.6, 51.2, 38.2, 31.9, 29.52, 29.49, 29.44, 29.40, 29.3, 28.8, 22.6, 14.0, –1.0 ppm. IR (neat): $\tilde{\nu}$ = 2956, 2925, 2855, 1728, 1632, 1606, 1463, 1433, 1250, 1202, 1148, 1122 cm^{-1}. MS (EI): *m*/*z* (%) = 324 (9.29) $[M]^+$, 107 (100). HRMS: calcd. for $C_{19}H_{36}O_2Si$ $[M]^+$ 324.2485; found 324.2488.

Allylation Reactions between Electrophiles and (*Z*)-2b in the Presence of $TiCl_4$

1. Methyl (2*E*)-4-(1-Hydroxybutyl)-3-methyltridec-2-enoate [(*E*)-3]: Compound (*Z*)-**2b** (122.8 mg, 0.4 mmol), CH_2Cl_2 (2 mL), and *n*-butanal (54 μL, *d* = 0.8017 gmL^{-1}, 99%, 43.6 mg, 0.6 mmol, 1.5 equiv.) were placed sequentially in a dried Schlenk tube containing a Teflon®-coated magnetic stirring bar under nitrogen at room temperature. A solution of $TiCl_4$ in CH_2Cl_2 (1 mL, 1 M, 1 mmol, 2.5 equiv.) was added to the reaction mixture dropwise by syringe. After 0.5 h, the reaction was complete as monitored by TLC and the mixture was quenched by dropwise addition of a saturated aqueous solution of $NaHCO_3$ (1 mL) at 0 °C and then allowed to warm to room temperature. Extraction with Et_2O (3× 20 mL), drying with anhydrous Na_2SO_4, filtration, concentration, and flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate 20:1 to 10:1 to 5:1) afforded (*E*)-**3** (major isomer: 71.4 mg, 58%, minor isomer: 8.7 mg, 7%, *dr* = 8:1).

Major Isomer (Less Polar): Liquid. ^1H NMR (300 MHz, C_6D_6): δ = 5.88–5.85 (m, 1 H, HC=C), 3.41 (s, 3 H, OCH_3), 3.35–3.24 (m, 1 H, CH), 2.18 (d, *J* = 1.2 Hz, 3 H, CH_3), 1.98–1.86 (m, 1 H, CH), 1.83–1.69 (m, 1 H, one proton in CH_2), 1.53–1.02 (m, 20 H, one proton in CH_2 + 9× CH_2 + OH), 0.91 (t, *J* = 6.6 Hz, 3 H, CH_3), 0.83 (t, *J* = 7.1 Hz, 3 H, CH_3) ppm. ^{13}C NMR (C_6D_6, 75 MHz): δ = 166.7, 160.9, 118.0, 72.9, 57.5, 50.5, 38.2, 32.3, 30.3, 30.1, 30.0, 29.8, 29.0, 28.0, 23.1, 19.3, 16.3, 14.4, 14.2 ppm. IR (neat): $\tilde{\nu}$ = 3478, 2926, 2855, 1722, 1644, 1464, 1435, 1222, 1154 cm^{-1}. MS (EI): *m*/*z* (%) = 313 (1.71) $[M + 1]^+$, 127 (100). $C_{19}H_{36}O_3$ (312.49): calcd. C 73.63, H 11.61; found C 73.34, H 11.63.

Minor Isomer (More Polar): Liquid. ^1H NMR (300 MHz, $CDCl_3$): δ = 5.74–5.71 (m, 1 H, HC=C), 3.69 (s, 3 H, OCH_3), 3.60 (t, *J* = 6.9 Hz, 1 H, CH), 2.15 (d, *J* = 1.2 Hz, 3 H, CH_3), 2.08 (q, *J* = 7.4 Hz, 1 H, CH), 1.56–1.00 (m, 21 H, 10× CH_2 + OH), 0.93 (t, *J* = 6.8 Hz, 3 H, CH_3), 0.87 (t, *J* = 6.8 Hz, 3 H, CH_3) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 166.7, 160.6, 118.3, 72.6, 56.5, 50.9, 37.1, 31.9, 29.7, 29.6, 29.5, 29.3, 27.4, 22.7, 18.8, 16.2, 14.1 ppm. IR (neat): $\tilde{\nu}$ = 3508, 2926, 2855, 1721, 1644, 1465, 1435, 1221, 1154, 2926, 2854, 1728, 1640, 1492, 1432, 1250, 1153 cm^{-1}. MS (EI): *m*/*z* (%) = 281 (5.12) $[M – OMe]^+$, 127 (100). HRMS: calcd. for $C_{19}H_{34}O_2$ $[M – H_2O]^+$ 294.2559; found 294.2562.

2. Methyl (2*E*)-4-Acetyl-3-methyltridec-2-enoate [(*E*)-4]. Typical Procedure: Compound (*Z*)-**2b** (61.2 mg, 0.2 mmol), CH_2Cl_2 (0.5 mL), and CH_3COCl (29 μL, *d* = 1.105 gmL^{-1}, 32.0 mg, 0.4 mmol, 2 equiv.) were placed sequentially, under nitrogen at room temperature, in a dried Schlenk tube containing a Teflon®-coated magnetic stirring bar. A solution of $TiCl_4$ in CH_2Cl_2 (0.5 mL, 1.0 M solution in CH_2Cl_2, 0.5 mmol, 2.5 equiv.) was added to the reaction mixture dropwise by syringe at –78 °C. After 0.5 h, the reaction was complete as monitored by TLC and the mixture was quenched by dropwise addition of a saturated aqueous solution of $NaHCO_3$ (1 mL) at –78 °C and then allowed to warm to room temperature. Extraction with Et_2O (3× 20 mL), drying with anhydrous Na_2SO_4, filtration, concentration, and flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate 20:1 to 10:1) afforded (*E*)-**4** (46.7 mg, 84%, *E*/*Z* 98:2) as a liquid. ^1H NMR (300 MHz, $CDCl_3$): δ = 5.77 (d, *J* = 0.6 Hz, 1 H, HC=C), 3.64 (s, 3 H, OCH_3), 3.08 (t, *J* = 7.2 Hz, 1 H, CH), 2.06 (s, 3 H, CH_3), 2.01 (d, *J* = 1.5 Hz, 3 H, CH_3), 1.81–1.65 (m, 1 H, one proton in CH_2), 1.54–1.40 (m, 1 H, one proton in CH_2), 1.26–1.04 (m, 14 H, 7× CH_2), 0.80 (t, *J* = 6.8 Hz, 3 H, CH_3) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 206.8, 166.4, 156.0, 119.0, 63.7, 51.0, 31.8, 29.44, 29.42, 29.3, 29.2, 28.8, 28.6, 27.2, 22.6, 16.2, 14.0 ppm. IR (neat): $\tilde{\nu}$ = 2926, 2855, 1722, 1715, 1645, 1435, 1359, 1217, 1149 cm^{-1}. MS (EI): *m*/*z* (%) = 282 (2.58) $[M]^+$, 43 (100). HRMS: calcd. for $C_{17}H_{30}O_3$ $[M]^+$ 282.2195; found 282.2196.

The following compound was also prepared by this procedure.

3. Methyl (2*E*)-4-(Ethoxymethyl)-3-methyltridec-2-enoate [(*E*)-5]: Use of the above procedure with (*Z*)-**2b** (63.1 mg, 0.2 mmol), diethoxymethane (31.2 mg, 0.3 mmol, 1.5 equiv.), and $TiCl_4$ (0.5 mL, 1.0 M solution in CH_2Cl_2, 0.5 mmol, 2.5 equiv.) in CH_2Cl_2 (0.5 mL) at –78 °C afforded (*E*)-**5** (58.6 mg, 97%, eluent: petroleum ether/ethyl acetate 20:1) as a liquid. ^1H NMR (300 MHz, $CDCl_3$): δ = 5.69 (s, 1 H, HC=C), 3.66 (s, 3 H, OCH_3), 3.51–3.30 (m, 4 H, H_2COCH_2), 2.44–2.32 (m, 1 H, CH), 2.09 (d, *J* = 1.5 Hz, 3 H, CH_3), 1.51–1.10 (m, 19 H, 8× CH_2 + CH_3), 0.86 (t, *J* = 6.8 Hz, 3 H, CH_3) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 167.0, 161.0, 116.7, 72.6, 66.3, 50.7, 49.9, 31.8, 29.8, 29.6, 29.5, 29.4, 29.2, 27.2, 22.6, 15.5, 15.0, 14.0 ppm. IR (neat): $\tilde{\nu}$ = 2926, 2856, 1722, 1650, 1463, 1435, 1377, 1221, 1155, 1116, 1032 cm^{-1}. MS (EI): *m*/*z* (%) = 298 (1.21) $[M]^+$, 59 (100). HRMS: calcd. for $C_{18}H_{34}O_3$ $[M]^+$ 298.2508; found 298.2503.

Regioselective Desilylations of (*Z*)-2b

1. Methyl (2*E*)-3-Methyltridec-2-enoate [(*E*)-6]: Compound (*Z*)-**2b** (31.4 mg, 0.1 mmol) and CH_2Cl_2 (0.5 mL) were placed in a dried Schlenk tube containing a Teflon®-coated magnetic stirring bar under nitrogen at room temperature. A solution of BF_3·2HOAc in CH_2Cl_2 (0.12 mL, 1 M, 0.12 mmol, 1.2 equiv.) was added to the reaction mixture dropwise by syringe at –20 °C. After 11.5 h, the re-

action was complete as monitored by TLC and the mixture was quenched by dropwise addition of a saturated aqueous solution of $NaHCO_3$ (1 mL) at –20 °C, followed by addition of water (3 mL) and warming up to room temperature. Extraction with Et_2O (3 × 20 mL), drying with anhydrous Na_2SO_4, filtration, concentration, and flash column chromatography on silica gel (eluent: petroleum ether/Et_2O 100:1) afforded (*E*)-**6** (23.2 mg, 96%, *E*/*Z* 97:3) as a liquid. ^{1}H NMR (300 MHz, C_6D_6): δ = 5.82 (q, *J* = 1.2 Hz, 1 H, HC=C), 3.45 (s, 3 H, OCH_3), 2.20 (d, *J* = 1.2 Hz, 3 H, CH_3), 1.83 (t, *J* = 7.4 Hz, 2 H, CH_2), 1.38–1.06 (m, 16 H, 8 × CH_2), 0.93 (t, *J* = 6.8 Hz, 3 H, CH_3) ppm. ^{13}C NMR (C_6D_6, 75 MHz): δ = 166.9, 160.2, 115.7, 50.5, 41.0, 32.4, 30.1, 30.0, 29.85, 29.80, 29.5, 27.7, 23.2, 18.8, 14.4 ppm. IR (neat): $\tilde{\nu}$ = 2926, 2855, 1723, 1651, 1464, 1435, 1385, 1358, 1223, 1149, 1117 cm^{-1}. MS (EI): *m*/*z* (%) = 240 (5.29) $[M]^+$, 114 (100). HRMS: calcd. for $C_{15}H_{28}O_2$ $[M]^+$ 240.2089; found 240.2086.

2. Methyl (3*Z*)-3-Methyltridec-3-enoate [(*Z*)-7]: Selectfluor (54.0 mg, 0.15 mmol, 1.5 equiv.), (*Z*)-**2b** (29.7 mg, 0.1 mmol), and THF (1 mL) were placed in a dried Schlenk tube containing a Teflon®-coated magnetic stirring bar under nitrogen at room temperature. A solution of TBAF in THF (0.11 mL, 1 M, 0.11 mmol, 1.1 equiv.) was then added to the reaction mixture dropwise by syringe. After 20 min, the reaction was complete as monitored by TLC. The reaction mixture was then diluted with Et_2O and filtered through a short column of silica gel (eluent: Et_2O). Concentration and flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate 100:1) afforded (*Z*)-**7** (21.9 mg, 96%) as a liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.35 (t, *J* = 6.8 Hz, 1 H, HC=C), 3.68 (s, 3 H, OCH_3), 3.05 (s, 2 H, CH_2), 2.00 (q, *J* = 6.7 Hz, 2 H, CH_2), 1.77 (d, *J* = 1.5 Hz, 3 H, CH_3), 1.39–1.20 (m, 14 H, 7 × CH_2), 0.88 (t, *J* = 6.8 Hz, 3 H, CH_3) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 172.1, 129.4, 127.6, 51.7, 37.3, 31.9, 29.60, 29.57, 29.53, 29.3, 28.2, 23.9, 22.7, 14.1 ppm. IR (neat): $\tilde{\nu}$ = 2954, 2925, 2855, 1743, 1435, 1258, 1160 cm^{-1}. MS (EI): *m*/*z* (%) = 240 (6.71) $[M]^+$, 68 (100). HRMS: calcd. for $C_{15}H_{28}O_2$ $[M]^+$ 240.2089; found 240.2091.

Electrophilic Fluorination of (*Z*)-2b with Selectfluor

Methyl 4-Fluoro-3-methyltridec-2-enoate [(*E*)-8]: Compound (*Z*)-**2b** (31.3 mg, 0.1 mmol), CH_3CN (1 mL), $NaHCO_3$ (8.2 mg, 0.1 mmol, 1 equiv.), and Selectfluor (56.4 mg, 0.15 mmol, 1.5 equiv.) were placed sequentially at room temperature in a dried pressure vessel containing a Teflon®-coated magnetic stirring bar and the vessel was then sealed and submerged in an oil bath preheated to 90 °C. After 15 min, the reaction was complete as monitored by TLC. The reaction mixture was then allowed to cool to room temperature, diluted with Et_2O, and filtered through a short column of silica gel (eluent: Et_2O). Concentration and flash column chromatography on silica gel (eluent: petroleum ether/Et_2O 100:1) afforded (*E*)-**8** (24.5 mg, 95%) as a liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.89 (s, 1 H, HC=C), 4.81 (dt, J_1 = 48.6, J_2 = 5.9 Hz, 1 H, CH), 3.71 (s, 3 H, OCH_3), 2.10 (s, 3 H, CH_3), 1.80–1.63 (m, 2 H, CH_2), 1.40–1.18 (m, 14 H, 7 × CH_2), 0.87 (t, *J* = 6.3 Hz, 3 H, CH_3) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 166.8, 155.6 (d, *J* = 15.5 Hz), 115.1 (d, *J* = 11.7 Hz), 95.4 (d, *J* = 176.2 Hz), 51.1, 33.4 (d, *J* = 21.8 Hz), 31.9, 29.5, 29.4, 29.28, 29.26, 24.7 (d, *J* = 3.2 Hz), 22.7, 14.3 (d, *J* = 4.1 Hz), 14.1 ppm. ^{19}F NMR ($CDCl_3$, 282 MHz): δ = –181.1 ppm. IR (neat): $\tilde{\nu}$ = 2926, 2855, 1724, 1661, 1459, 1436, 1365, 1329, 1228, 1159 cm^{-1}. MS (EI): *m*/*z* (%) = 259 (1.46) $[M + 1]^+$, 258 (1.03) $[M]^+$, 125 (100). HRMS: calcd. for $C_{15}H_{27}FO_2$ $[M]^+$ 258.1995; found 258.1998.

Supporting Information (see footnote on the first page of this article): ^{1}H and ^{13}C NMR spectra of all the products.

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[1] For recent reviews, see: a) M. J. Curtis-Long, Y. Aye, *Chem. Eur. J.* **2009**, *15*, 5402; b) J. Gawronski, N. Wascinska, J. Gajewy, *Chem. Rev.* **2008**, *108*, 5227; c) L. Chabaud, P. James, Y. Landais, *Eur. J. Org. Chem.* **2004**, 3173; d) S. E. Denmark, J. Fu, *Chem. Rev.* **2003**, *103*, 2763; e) J. W. J. Kennedy, D. G. Hall, *Angew. Chem.* **2003**, *115*, 4880; *Angew. Chem. Int. Ed.* **2003**, *42*, 4732. For recent applications to synthesis of natural products, see: f) J. T. Lowe, J. S. Panek, *Org. Lett.* **2008**, *10*, 3813; g) W. Youngsaye, J. T. Lowe, F. Pohlki, P. Ralifo, J. S. Panek, *Angew. Chem.* **2007**, *119*, 9371; *Angew. Chem. Int. Ed.* **2007**, *46*, 9211.

[2] a) A. Hosomi, K. Miura, *Bull. Chem. Soc. Jpn.* **2004**, *77*, 835; b) A. Hosomi, *Acc. Chem. Res.* **1988**, *21*, 200.

[3] For reviews, see: a) A. Barbero, F. J. Pulido, *Acc. Chem. Res.* **2004**, *37*, 817; b) T. K. Sarkar, *Science of Synthesis* vol. 4, Thieme, Stuttgart, Germany, **2002**, pp. 837–925; c) T. K. Sarkar, *Synthesis* **1990**, 969; d) T. K. Sarkar, *Synthesis* **1990**, 1101.

[4] For some recent examples, see: a) F. J. Pulido, A. Barbero, Y. Blanco, *Org. Biomol. Chem.* **2011**, *9*, 1454; b) N. Selander, J. R. Paasch, K. J. Szabó, *J. Am. Chem. Soc.* **2011**, *133*, 409; c) J. M. Larsson, T. S. N. Zhao, K. J. Szabó, *Org. Lett.* **2011**, *13*, 1888; d) R. Moser, T. Nishikata, B. H. Lipshutz, *Org. Lett.* **2010**, *12*, 28; e) F. J. Pulido, A. Barbero, C. García, *Tetrahedron* **2009**, *65*, 5535; f) M.-O. Simon, R. Martinez, J.-P. Genêt, S. Darses, *Adv. Synth. Catal.* **2009**, *351*, 153; g) M. Tobisu, Y. Kita, Y. Ano, N. Chatani, *J. Am. Chem. Soc.* **2008**, *130*, 15982; h) Z. Li, C. Yang, H. Zheng, H. Qiu, G. Lai, *J. Organomet. Chem.* **2008**, *693*, 3771; i) S. Hayashi, K. Hirano, H. Yorimitsu, K. Oshima, *J. Am. Chem. Soc.* **2007**, *129*, 12650; j) R. Shintani, Y. Ichikawa, T. Hayashi, J. Chen, Y. Nakao, T. Hiyama, *Org. Lett.* **2007**, *9*, 4643.

[5] a) Z. Lu, G. Chai, S. Ma, *J. Am. Chem. Soc.* **2007**, *129*, 14546; b) Z. Lu, G. Chai, X. Zhang, S. Ma, *Org. Lett.* **2008**, *10*, 3517; c) G. Chai, Z. Lu, C. Fu, S. Ma, *Adv. Synth. Catal.* **2009**, *351*, 1946; d) G. Chai, C. Fu, S. Ma, *Org. Lett.* **2012**, *14*, 4058. For a related reference concerning on Michael additions of cyclopentyl enamine to allenecarboxylates, see: e) M. A. Silvestri, D. C. Bromfield, S. D. Lepore, *J. Org. Chem.* **2005**, *70*, 8239.

[6] It has been reported that the *syn*-allylic metallic species is thermodynamically more stable than the *anti*-allylic metallic species due to the steric interaction of the metal and the substituent(s) at the 1- and/or 3-positions. For a review, see: a) C. G. Frost, J. Howarth, J. M. J. Williams, *Tetrahedron: Asymmetry* **1992**, *3*, 1089. For some typical reports, see: b) B. Akermark, S. Hansson, A. J. Vitagliano, *J. Am. Chem. Soc.* **1990**, *112*, 4587; c) T. Hayashi, A. Yamamoto, T. Hagihara, *J. Org. Chem.* **1986**, *51*, 723.

[7] I. Fleming, *Org. React.* **1989**, *35*, 501.

[8] a) M. Tredwell, K. Tenza, M. Pacheco, V. Gouverneur, *Org. Lett.* **2003**, *5*, 4891; b) M. Sawicki, A. Kwok, M. Tredwell, V. Gouverneur, *Beilstein J. Org. Chem.* **2007**, *3*, no. 34, DOI: 10.1186/1860-5397-3-34.

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