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Doubly Diastereoconvergent Preparation and Microsolvation-Controlled Properties of (Z)- and (E)-1′-Lithio-1′-(2,6-dimethylphenyl)propenes

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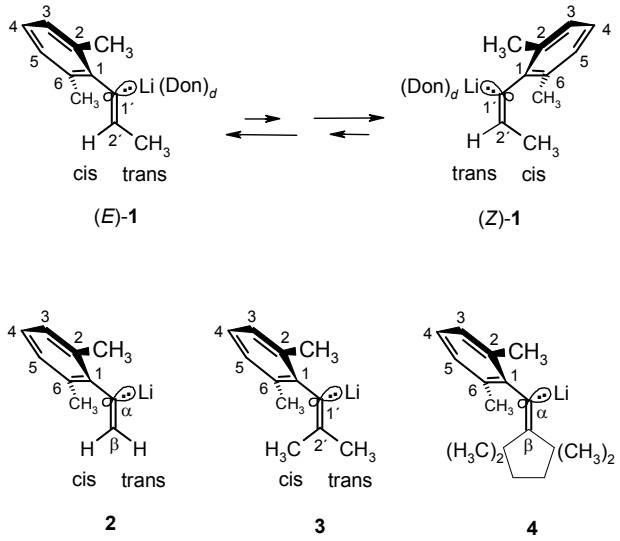
KEYWORDS Aggregation; *Z*,*E* configurational lability; ketone addition; broken kinetic order; microsolvation-controlled stereospecificity.

ABSTRACT: A doubly diastereoconvergent reaction can ad libitum generate either one or the other of two diastereomeric products with complete consumption of the diastereomeric precorsors or their mixtures. Thus, the preparation of configurationally pure (*Z*)-1′-lithio-1′-(2,6-dimethylphenyl)propene [(*Z*)-**1**] from any *Z*,*E* mixture of the corresponding bromoalkenes with *n*-butyllithium succeeded by means of a user-friendly (*E*)-**1** → (*Z*)-**1** configurational interconversion. The subsequent treatment of (*Z*)-**1** with a minimum amount of THF afforded exclusively (*E*)-**1** as the other diastereomeric product and was mediated by a beneficial (*Z*)-**1** → (*E*)-**1** interconversion. This behavior provided microsolvation-controlled choices of highly diastereoselective derivatizations of **1**. Low-temperature ^{13}C NMR spectra established that (*Z*)-**1** was dissolved as a trisolvated monomer in THF but as a disolvated dimer in monodentate, ethereal, non-THF solvents, whereas (*E*)-**1** was always monomeric. Backed by such knowledge, kinetic experiments indicated that the electrophiles 1-bromobutane or $ClSiMe_3$ in Et_2O reacted at 32 °C with the tiny (NMR-invisible) population of monomeric (*Z*)-**1** that was formed in a mobile equilibrium from the inactive, predominantly dimeric (*Z*)-**1**. The equilibration of monomeric (*Z*)-**1** and (*E*)-**1** in THF as the solvent was fast (seconds on the ^{1}H NMR time scale), whereas the corresponding stereoinversion of both solvated and unsolvated (*E*)-**1** → (*Z*)-**1** in non-THF solvents occurred on the laboratory time scale (minutes at ambient temperatures). Dicyclopropyl ketone added rapidly to the monomers (*Z*)-**1**&3THF and (*E*)-**1**&3THF with a rate ratio of at least 14:1 in THF at −78 °C. Di-*tert*-butyl ketone added less rapidly to the less shielded (*Z*)-**1** [but never to (*E*)-**1**]; this singly diastereoconvergent process was much more slowly reversible in THF.

1. INTRODUCTION

Stereoconvergent processes are attractive if they afford the same stereoisomer as the main product from different stereoisomeric sources or their mixtures. This will happen when one of the stereoisomers of the products or its precursors is sufficiently favored in a mobile equilibrium. With organolithium reagents,[1,2] for instance, the preparative stereoselectivity may depend on the configuration[3] of the lithium-bearing carbon atom (C-α). If so, configurational lability of C-α (mobile equilibrium) at sufficiently high temperatures may either deteriorate or improve the stereoselectivity according to the equilibrium constant. A recently[4] published example involved 3-siloxy-substituted *sec*-alkyl iodides whose syn or anti diastereomers or their mixtures were subjected to I/Li interchange reactions: The emerging 3-siloxy-substituted *sec*-alkyllithium compounds equilibrated very rapidly at –100 °C in Et_2O/hexane with formation of always the same (ca. 9:1) syn/anti mixture;[5] extensive derivatization experiments[4] afforded syn/anti product mixtures with diastereomeric ratios between 90:10 and 99:1. Obviously, such a single diastereoconvergence would not provide the alternative (anti) diastereomers as the predominant products. It was also shown[5] that replacement of the 3-siloxy substituent led to slower conversion at –90 °C with formation of ca. 55:45 syn/anti product mixtures. This suggests that suitable manipulations of a mobile equilibrium might provide the possibility of designing a doubly diastereoconvergent system: This should be able to furnish either the one or the other diastereomer as a preponderant product with *complete* consumption of the different diastereomeric precursors or their mixtures. We will report here on the suitably mobile equilibrium between the title compounds (*Z*)-**1** and (*E*)-**1** (Scheme 1) and its manipulation by judicious choices of the solvents and temperatures.

Scheme 1. (*E*)-**1**, (*Z*)-**1** and comparable, published 1′-alkenyllithiums with no (**2**) or with two substituents at C-2′ (= C-β) of **3** and **4**; Don = solvating, electron-pair donating ligand coordinated at Li; *d* = microsolvation number.



Although the bare preparation protocols will be explained in Section 2.1 for (*Z*)-**1** and in Section 2.3 for (*E*)-**1** and in more detail in the Experimental Section, we deemed it appropriate to offer also thorough analytic characterizations (Section 2.2) and detailed dynamic knowledge (Sections 2.4 – 2.6) of the protagonists (*Z*,*E*)-**1**, so that the structural assignments and kinetic relations become transparent. Comparisons of (*Z*,*E*)-**1** with the related 1′-arylalkenyllithiums **2**,[6] **3**,[7] and **4**[8] will be used to confirm the similarities of the ground states with respect to comparable structural traits, (non)aggregation states, charge delocalization, and microsolvation[9] by electron-pair donor ligands ("Don" in Scheme 1) that coordinate to lithium. The (non)influence of alkyl substituents at C-2′ (or C-β) will become evident in the series of **1** – **3** especially with respect to the important quantification of configurational lability which is essential for stereoconvergence: As a model for the expected thermal interconversion of (*Z*)-**1** and (*E*)-**1**, the cis/trans stereoinversion of monomeric **2** is known[6] to occur rapidly in tetrahydrofuran (THF) as the solvent at room temperature (rt) through a THF-catalyzed, ionic mechanism.[10] The corresponding stereoinversion of aggregated **2** happened less rapidly[6] through unconsolidated mechanisms in Et_2O or *tert*-butyl methyl ether (*t*-BuOMe) as the solvent and even in the absence of such solvating ligands. With this background, it will become comprehensible why (*Z*,*E*)-**1** could provide a suitable paradigm of a double diastereoconvergence.

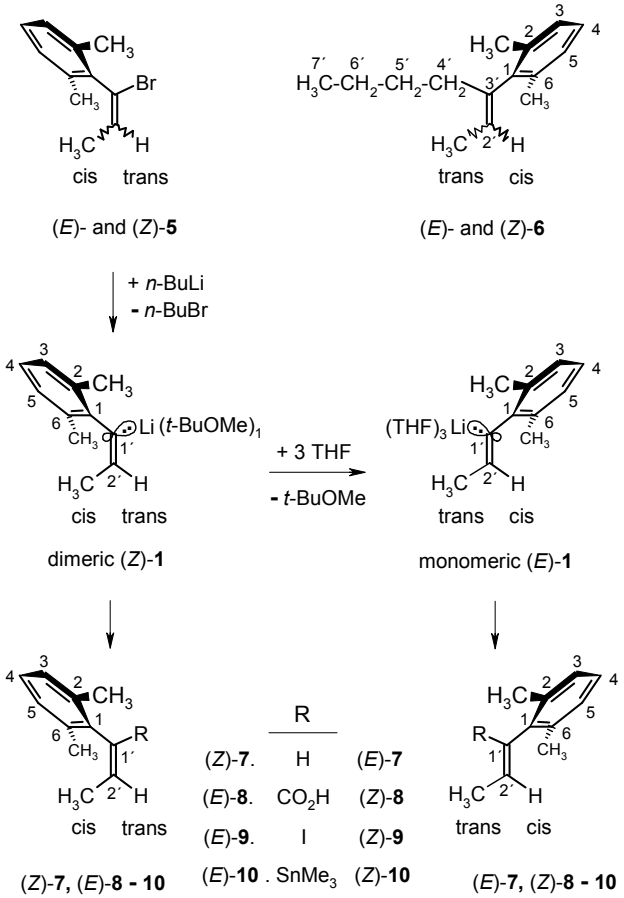
2. RESULTS AND DISCUSSION

2.1. Diastereoconvergent Preparation of (*Z*)-1&*t*-BuOMe and its Derivatives

The Br/Li interchange reaction (Scheme 2) of *n*-butyllithium (*n*-BuLi) with the 1-aryl-1-bromopropenes[11] (*Z*,*E*)-**5** to give the 1′-aryl-1′-lithiopropenes **1** should be expected to occur with configurational retention, so that (*Z*)-**5** (with the olefinic Me trans to aryl) should generate (*E*)-**1**. In *t*-BuOMe as the solvent, however, almost only (*Z*)-**1** could be detected by ^{1}H NMR

spectroscopy in situ after the complete, fast consumption of any (*Z*,*E*)-**5** mixture: Derivatization by solid CO_2 furnished the carboxylic acid (*E*)-**8** as the only detectable diastereomer whose configuration followed from the typically smaller cis $^{1}H,^{13}C$ NMR coupling constant ^{3}J(2′-H,CO_2H) = 6.9 Hz. Consistently, the alkene (*Z*)-**7** was obtained through protolysis of another such (*Z*)-**1** solution and exhibited the characteristic cis interproton NMR coupling constant ^{3}J(1′-H,2′-H) = 11.3 Hz. This diastereoconvergent preparation of (*Z*)-**1** provided a first (not unprecedented) indication of configurational lability of **1**: The primary product (*E*)-**1**, as generated from (*Z*)-**5**, appeared to have been converted rapidly and (almost) completely into (*Z*)-**1**. To be sure, we demonstrated that the bromopropene (*Z*)-**5** reacted hardly slower than the accompanying (*E*)-**5** with a deficient amount (0.5 equiv) of *n*-BuLi.

Scheme 2. Preparation and derivatization of the 1′-aryl-1′-lithiopropenes (*Z*)-**1** and (*E*)-**1**.



The *t*-BuOMe solutions of (*Z*)-**1** were unsuitable for long-term measurements, because (*Z*)-**1** was slowly butylated by its co-product 1-bromobutane (*n*-BuBr in Scheme 2) at rt with formation of LiBr and the hydrocarbons **6** (*Z*/*E* = 49:1), accompanied by ca. 10% of the alkenes **7** (*Z*/*E* = 9:1). A two-dimensional interproton NOESY experiment established that the olefinic 2′-H and the CH_2-4′ group of (*Z*)-**6** were on the same side of the C=C double bond and that 2′-H of (*E*)-**6**

was instead close to the 2,6-dimethyl groups. This butylation proceeded with comparable velocity (typical first half-reaction time $t_{1/2}$ = ca. 70 min at 32 °C in Section 2.5) in Et_2O as the solvent but afforded a significantly increased portion of the minor product (*E*)-**6** (*Z*/*E* = 86:14). In the absence of such electron-pair donor solvents, the butylation occurred more slowly in pentane, benzene, or toluene. In THF, however, it was regrettably fast even at –70 °C, yielding (*Z*)-**6** and (*E*)-**6** in a 62:38 ratio from the (*Z*)-**1**/(*E*)-**1** = 36:64 mixture to be reported further below; thus, the obviously faster butylation of (*Z*)-**1** afforded the main product (*Z*)-**6**. Hence, it appeared desirable to get rid of the interfering *n*-BuBr, at least for projected investigations in ethereal solvents. Gratifyingly, the generally applicable method of distillative removal of *n*-BuBr became unnecessary through the precipitation of (*Z*)-**1** from cold *t*-BuOMe solutions: Suitable manipulations (described in the Experimental Section) of the precipitate enabled us to grow colorless platelets that were sufficiently heavy to settle quickly down from the solution. The supernatant containing all contaminations (*n*-BuBr, LiBr, etc.) could then be withdrawn under inert gas cover, and the remnant platelets were washed with dry pentane. After dissolution in dry Et_2O or THF, the purified platelets appeared to have carried one *t*-BuOMe ligand per carbanion unit (found 1.1 ± 0.1 equiv, now at δ_H = 3.10 ppm since released from coordination to Li). This substance, (*Z*)-**1**&*t*-BuOMe, decomposed through proton transfer from the following two solvents at rt with rather long $t_{1/2}$ values in the absence of *n*-BuBr, moisture, and oxygen: In *t*-BuOMe, the formation of the alkenes **7** (*Z*/*E* = 81:19) and isobutene (from *t*-BuOMe) with $t_{1/2} \approx 8$ days pointed to an NMR-invisible amount of (*E*)-**1** that gave (*E*)-**7** and was more reactive than the preponderant diastereomer (*Z*)-**1** that furnished (*Z*)-**7.** In THF, the alkenes **7** (*Z*/*E* = ca. 1:1, along with ethylene from THF) emerged with $t_{1/2}$ = ca. 3 days and catalyzed[7] a slow vinyl-to-allyl anion isomerization of **1**. The LiBr-free crystals of (*Z*)-**1**&*t*-BuOMe were used in most of the following investigations, which implied that optimized purity may have been preferred to optimized yields (with respect to the initial bromopropenes **5**) of the crude products. For instance, purified (*Z*)-**1** in *t*-BuOMe and elemental iodine afforded only 43% of the iodoalkenes **9** in an *E*/*Z* = 94:6 ratio, which pointed again to an enhanced reactivity of an invisible trace of (*E*)-**1** that formed (*Z*)-**9** (6%).

Up to this point, we achieved a singly diastereoconvergent preparation of (*Z*)-**1** as the highly preponderant equilibrium component. This means that a planned diastereoconvergent formation of (*E*)-**1** rather than (*Z*)-**1** from the same precursors must employ a method that disturbs the *Z*,*E* equilibrium in the opposite direction, as will be shown in the later Section 2.3.

2.2. NMR Analyses and Properties of (*Z*)-1 and (*E*)-1 in Solution

The aggregational states of isotope-labeled [^{6}Li]**1** became evident through ^{13}C NMR spectroscopy at low temperatures, where intermolecular scrambling of the Li cations was so slow that nuclear magnetic coupling of a carbanionic center ^{13}C-1′ (= C-α) with n ^{6}Li nuclei became resolved. For the ^{6}Li isotope with its small nuclear quadrupole moment and its spin quantum number $I = 1$, this coupling can split the ^{13}C-1′ resonance line into $2nI + 1$ components, producing simpler multiplicities and often better resolution than the ^{7}Li ($I = 3/2$) isotope does. Thus, the CLi_2 moiety of a dimeric aggregate ($n = 2$) should be recognized through a quintet splitting of ^{13}C-1′ with a 1:2:3:2:1 intensity ratio. We discovered these quintets (Figure 1a–c) of crystalline (*Z*)-**1**&*t*-BuOMe in Et_2O, *t*-BuOMe, and [D_8]toluene as the solvents: The scalar, one-bond NMR coupling constants $^1J(^{13}C,^6Li) = 7.6$ or 7.5 Hz remained visible up to (at least) –40, –25, and –10 °C, respectively, at practically identical resonance positions of δ(C-1′) = 189.9(2) ppm; therefore, (*Z*)-**1**&*t*-BuOMe is a dimer rather than a cyclooligomer[12] (also with $n = 2$), just as had been observed with the corresponding α-arylvinyllithiums[13] **2**&*t*-BuOMe and **2**&Et_2O. [The full ^{13}C NMR spectra of clean dimeric (*Z*)-**1**&*t*-BuOMe as the only species of **1** in either *t*-BuOMe or toluene at both 25 and –70 °C are shown in Figure S4.][14] A similar quintet with $^1J_{CLi}$ = ca. 7 Hz was detected for the THF-solvated dimer of **1** in toluene solution; but its resonance position at δ(C-1′) = 192.8(2) ppm in Table S8a[14] seemed hardly compatible with δ(C-1′) of the dimers in Figure 1a–c, although all of its other δ_C values resembled those of dimeric (*Z*)-**1** with the non-THF donor ligands (Tables S5a–S7a).[14] Despite such doubt, the *Z* configuration of this THF-solvated dimer was confirmed by the characteristic magnitude of its three-bond NMR trans coupling constant ^3J(2′-H,C-1) = 13.5 Hz. Furthermore, the correlation peaks in a two-dimensional HOESY (^{6}Li,^{1}H) NMR experiment revealed that ^{6}Li was cis to either 2′-H in this dimer of (*Z*)-**1**&THF or to 2′-CH_3 in the accompanying monomeric (*E*)-**1**&3THF. (Of course, ^{6}Li correlated also with THF and the 2-/6-CH_3 protons.) We ascribed the increased δ(C-1′) value to a superior donor quality of coordinating THF as compared with the weaker non-THF donors.

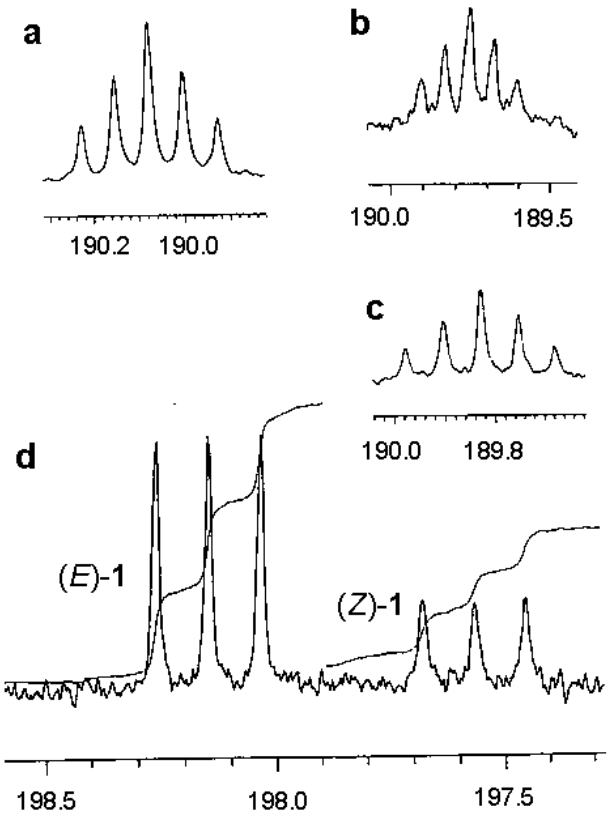


Figure 1. ^{13}C NMR splitting ($^{1}J_{CLi}$) of C-1′ (= C-α) by ^{6}Li: (a) Dimeric (*Z*)-**1** in Et_2O at –90 °C with $^{1}J_{CLi}$ = 7.6 Hz. (b) Dimeric (*Z*)-**1** in *t*-BuOMe at –70 °C with $^{1}J_{CLi}$ = 7.6 Hz. (c) Dimeric (*Z*)-**1**&*t*-BuOMe in [D_8]toluene at –70 °C with $^{1}J_{CLi}$ = 7.5 Hz. (d) Monomeric (*E*)-**1** and (*Z*)-**1** in THF at –88 °C, both with $^{1}J_{CLi}$ = 11.4 Hz. Scales are in ppm at 100.6 MHz.

Microsolvation numbers d of electron-pair donating ligands, coordinated at the ^{6}Li cation, may be read from the magnitudes of $^{1}J_{CLi}$ by means of the empirical equation 1,[9] where a is the number of carbanionic centers (C-1′ or C-α) that are in contact with a certain Li nucleus under consideration. Using the sensitivity factor L = 46 (±1) Hz, as published[6] for **2**, we calculated d = 1 per Li from the practically equal $^{1}J_{CLi}$ values (entries 1–5 in Table 1) of the dimers ($n = a = 2$). Hence, (*Z*)-**1** formed disolvated dimers in analogy with those encountered[13] in the X-ray structures of **2**; this applied also to the above-mentioned THF-solvated dimer (d = 1) of (*Z*)-**1**, as indicated in footnote a of Table S8a.[14] These results from the primary NMR criterion of $^{1}J_{CLi}$ (eq 1) enabled us to recognize disolvated dimers (*Z*)-**1** also by the secondary NMR criteria of lithiation shifts $\Delta\delta = \delta(\text{RLi}) - \delta(\text{RH})$, which serve to purge the chemical shift values δ(RLi) from special effects that are present also in the "parent" olefin RH, so that the effects of lithiation may be seen more clearly. Thus, most of the $\Delta\delta$ values of (*Z*)-**1** are closely similar in the three different solvents of entries 1–3 of Table 1, whereas the substantially greater $\Delta\delta$

magnitudes in entries 6 and 7 exclude a disolvated, dimeric structure for both (*Z*)-**1** and (*E*)-**1** in THF as the solvent. Actually, the ^{13}C-1′ resonances of both (*Z*)-**1** and (*E*)-**1** in THF were split by the ^{6}Li ($I = 1$) nucleus into $2nI + 1 = 3$ equally strong components (Figure 1d), which requires that $n = 1$ ^{6}Li nucleus only is in contact with the ^{13}C-1′ center. The temperature-dependent line-shapes of these triplets are shown[14] in Figure S5: triplet coalescences (loss of the ^{13}C,^{6}Li spin coherence) through intermolecular ^{6}Li scrambling is seen to be faster for the sterically less shielded (*Z*)-**1** than for (*E*)-**1**. Since both of these C–Li_1 species have neither bidentate ligands nor side-chain donors available for coordination to a second Li-bearing particle, both (*Z*)-**1** and (*E*)-**1** must be monomeric in THF, so that $a = 1$ in eq 1. With $L = 46$ Hz as above, the frequency intervals of $^{1}J_{CLi} = 11.4$ Hz of the ^{13}C-1′ triplet resonances were translated into the microsolvation number $d = 3$. Hence, trisolvation by THF applied not only to monomeric α-arylvinyllithium **2** (entry 9)[6] and monomeric **4** with two β-*tert*-alkyl groups[8] (entry 10), but also to the (*Z*)-**1** and (*E*)-**1** monomers and to monomeric 1′-lithio-2′-methylpropene[7] **3** (entry 8, and Table S13[14]). In contrast, most of the $\Delta\delta$ values in entries 6–9 depend significantly on the changing β- or 2′-substituents, with two exceptions: The *para*-positioned nuclei C-4 and 4-H are sufficiently remote from both C-1′ and C-2′ to be rather insensitive to proximity effects of both Li and the 2′-substituents. Instead, $\Delta\delta$(C-4) and $\Delta\delta$(4-H) in Table 1 were thought[6,9,15,16] to be partially due to the delocalization of negative electric charge from the Li–C(1′) bond into the π-electron system on the 1′-aryl plane that is held perpendicular to the C=C double-bond plane by means of a substantial energetic barrier against rotation about the C(1′)–C(1) single bond.[15] Compared with entries 6–10, this lihiation-caused π-charge accumulation at C-4 is weaker for the dimeric species (entries 1–5), because the second Li cation at C-1′ counteracts the π-electron delocalization from C-1′. Although interpretations of the other $\Delta\delta$ data are less obvious, their values characterize the various families of monomers and aggregates and their appertaining microsolvation numbers d within the validity limits imposed by ^{13}C-1′ NMR splitting. Complete $\Delta\delta$ sets of the various species may be inspected in Figure S1.[14]

$$d = L \times (n \times {}^{1}J_{CLi})^{-1} - a \qquad (1)$$

The results of this section established that the ground states of (*Z*,*E*)-**1** and **2** satisfy the same NMR-spectroscopic criteria and that all three of them are exclusively monomeric in THF. Like **2**, (*Z*)-**1**&*t*-BuOMe generated disolvated dimers in Et_2O, *t*-BuOMe, and toluene. On the other hand, (*E*)-**1** did not form a persistent dimer and not even a *Z*,*E*-mixed dimer, presumably due to its trans-2′-CH_3 substituent that shields the Li–C bond.

Table 1. Microsolvation Numbers *d* and NMR Data of 1′-Lithio-1′-(2,6-dimethylphenyl)propenes (**1**) compared with the Related α-Arylalkenyllithiums **2**, **3**, and **4**. [a]

entry	cpd. no.	solvent	donor (equiv)	agg [b]	$^1J(^{13}C,^6Li)$ [Hz]	d	lithiation NMR shifts $\Delta\delta$ [ppm] [c] C-1′	C-2′	C-1	C-4	4-H	°C [d]	. ref
1	(*Z*)-**1**	*t*-BuOMe	*t*-BuOMe	D	qi, 7.6	1	+62.2	–7.9	+17.5	–7.4	–0.45	–86	e
2	(*Z*)-**1**	Et_2O	Et_2O	D	qi, 7.6	1	+62.6	–7.4	+17.2	–7.3	–0.45	–90	e
3	(*Z*)-**1**	toluene	*t*-BuOMe (1.9)	D	qi, 7.5	1	+62.3	–7.4	+17.5	–7.0	–0.07 [f]	–70	e
4	**2**	toluene	*t*-BuOMe (1.3)	D	qi, 7.5	1	+68.2	–3.6	+19.6	–6.5	–0.02 [f]	–84	6
5	**3**	Et_2O	Et_2O	D	qi, 7.5	1	+57.5	–1.1	+19.6	–7.0	–0.48	–71	e
6	(*Z*)-**1**	THF	THF	M	t, 11.4	3	+69.7	–14.7	+21.6	–11.8	–0.80	–88	e
7	(*E*)-**1**	THF	THF	M	t, 11.4	3	+68.5	–15.8	+23.5	–10.7	–0.77	–88	e
8	**3**	THF	THF	M	t, 11.5(1)	3	+69.6	–13.6	+25.5	–10.9	–0.79	–117	e
9	**2**	THF	THF	M	t, 11.6	3	+76.4	–10.9	+24.2	–11.0	–0.76	–89	6
10	**4**	THF	THF	M	t, 10.7	3	+64.0	–17.4	+20.8	–12.6	–0.84	Z –85	8
11	(*Z*)-**1**	C_5H_{10}	none	> D	none	0	+52.0	+2.1	+13.8	–3.9	–0.21	–57	e
12	**2**	C_5H_{10}	none	> D	none	0	+57.4	+6.3	+15.5	–3.5	–0.19	–35	6

[a] 1′ = α, 2′ = β, qi = quintet (1:2:3:2:1), t = triplet (1:1:1), C_5H_{10} = cyclopentane. [b] "D" = dimer, "M" = monomer. [c] $\Delta\delta = \delta(RLi) - \delta(RH)$. [d] Temperature of $\Delta\delta$ determination. [e] This work. [f] Effect of the aromatic solvent.

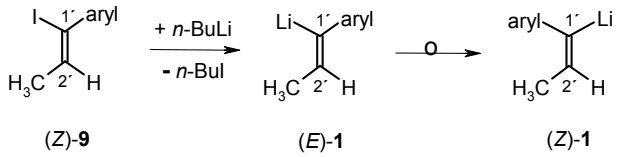
2.3. *Z*,*E* Equilibrations leading to (*E*)-1&3THF or Unsolvated (*Z*)-1 and their Derivatives

The disolvated dimer of (*Z*)-**1** remained unchanged in the solvents *t*-BuOMe, Et_2O, and toluene, as shown by the insignificant temperature-dependencies of almost all of their chemical shifts δ_H and δ_C between –90 and +25 °C (Figure S4 and Tables S5–S7).[14] In contrast, the purified crystals of (*Z*)-**1**&*t*-BuOMe changed in THF solution immdiately to the equilibrium mixture of monomeric (*Z*)-**1**&3THF and (*E*)-**1**&3THF in concentration-independent ratios that varied from 52:48 (at +25 °C) to 32:68 (at –88 °C) as shown[14] in Figures 1d and S5 and Table S10. This trend established that the fast $Z \rightarrow E$ transformation of the monomers is exothermic in THF. In fact, the quantitative analysis (Table S2)[14] furnished a stereoinversion enthalpy of $\Delta H^0(Z \rightarrow E) = -0.84$ (±0.05) kcal mol^{-1} and an entropic penalty of only $\Delta S^0 = -3.0$ (±0.3) cal mol^{-1} K^{-1}, the latter as expected[17] since unchanged microsolvation numbers (as encountered here) do not contribute to ΔS^0. Complete formation of monomeric (*E*)-**1** was achieved through perturbation of that equilibrium by crystallization in the following manner. Purified (*Z*)-**1**&*t*-BuOMe was completely dissolved in the minimum amount of anhydrous THF (ca. 4 equiv) and then cooled to –70 °C. The finely felted needles of (*E*)-**1**&3THF precipitated after 15 min and were kept undisturbed for a short while, whereupon (still and always at –70 °C) they were washed with dry pentane and dissolved for the immediate trapping with an electrophile, so to avoid the $E \rightarrow Z$ conversion that will be quantified in Section 2.4. For example, carboxylation of such a solution of (*E*)-**1**&3THF in dry toluene furnished the expected carboxylic acid (*Z*)-**8** (Scheme 2) exclusively, whose configuration followed from the NMR trans coupling constant $^3J(2'\text{-H},C\text{O}_2\text{H}) = 13.8$ Hz. Similarly, titration at –70 °C with a toluene solution of elemental iodine afforded the iodoalkene (*Z*)-**9** with not more than a trace of (*E*)-**9**; the *Z* configuration of this liquid diastereomer (*Z*)-**9** was established through the NOESY correlation peak of 2′-H with the 2,6-CH_3 protons. Trapping of (*E*)-**1**&3THF in dry toluene at –70 °C with $ClSnMe_3$ appeared to proceed less rapidly, since formation of the diastereomeric stannanes (*Z*)-**10** and (*E*)-**10** in a 92:8 ratio may have occurred in parallel with some (*E*)-**1** to (*Z*)-**1** transformation. The stannane configurations were recognized through the trans and cis NMR coupling constants $^3J(2'\text{-H},^{119}\text{Sn}) = 141.8$ Hz for (*Z*)-**10** and 76 Hz for (*E*)-**10**, respectively. Stannane (*Z*)-**10** was hoped to be a suitable precursor of unsolvated (*E*)-**1**. However, the Sn/Li interchange reaction of (*Z*)-**10** in pentane as the solvent with either *n*-BuLi or *tert*-butyllithium (*t*-BuLi) turned out to be limited to the extremely slow formation of methyllithium (MeLi) through Sn–Me bond cleavage. Admixtures of *t*-BuOMe (up to 20 equiv) induced the slow production of (*Z*)-**1** in parallel with the appearance of MeLi and isobutene (from *t*-BuOMe with *t*-BuLi); but significant

improvements were not achieved even in *t*-BuOMe as the solvent. On the other hand, the desired Sn–C(1′) bond cleavage of (*Z*)-**10** in pentane became the main route with *t*-BuLi (4 equiv) in presence of 1,2-bis(dimethylamino)ethane (TMEDA, at least 2 equiv) and was almost complete (87%) already within 15 min at rt. The *Z*/*E* = 3:1 ratio of the emerging **1** was confirmed through carboxylation; it revealed that the expected primary product (*E*)-**1** [from (*Z*)-**10**] had partially isomerized into (*Z*)-**1** at or below rt in TMEDA/pentane.

Donor-free (*Z*)-**1** was finally obtained through the instantaneous I/Li interchange reaction (Scheme 3) of *n*-BuLi (1.1 equiv) with the liquid iodoalkene (*Z*)-**9** in cyclopentane at rt. The co-product 1-iodobutane (*n*-BuI) did not react with (*Z*)-**1** in the donor-free solvent during many days at rt, whereafter carboxylation furnished the acid (*E*)-**8** exclusively. Again, the primary product (*E*)-**1**, expected from (*Z*)-**9**, was NMR-invisible because it had readily (< 5 min at ≤ rt) and entirely been converted into unsolvated (*Z*)-**1**. (The mechanism of this donor-free stereoinversion is unknown.[18]) The ^{1}H and ^{13}C NMR signals of donor-free (*Z*)-**1** were strangely broad at rt but became resolved on cooling (Table S11).[14] The resultant $\Delta\delta$ data (entry 11 of Table 1) deviated substantially from those of the solvated dimers and monomers (entries 1–10) in the direction of donor-free **2** (entry 12). For instance, the diminished magnitudes of $\Delta\delta$(C-4) and $\Delta\delta$(4-H) indicated that π-charge delocalization from the Li–C(1′) bond was much less efficient than in entries 1–10, possibly due to $n > 2$ donor-free Li cations bound to C(1′). Regrettably, unsolvated (*Z*)-**1** and **2** did not show resolved ^{6}Li,^{13}C(1′) splitting that would have established the CLi_n connectivities; but the diminution of $\Delta\delta$(C-1′) = +62 ppm for the disolvated dimers in entries 1–3 to +52 ppm (entry 11) resembled the decrease by 11 ppm from disolvated, dimeric **2** (entry 4 of Table 1) to +57 ppm for unsolvated **2** (entry 12). Only 4 ppm of these diminutions should be ascribed to the loss of the last donor ligand per Li, as suggested by a published series with the same connectivities $n = a = 2$ and $d = 1$ versus $d = 0$.[19] The remainder of roughly 6 ppm may be due to a higher than dimeric aggregation ($n = a > 2$) of unsolvated (*Z*)-**1** and **2**.

Scheme 3. Generation of donor-free (*E*)-**1** which rearranged readily to unsolvated (*Z*)-**1** (aryl = 2,6-dimethylphenyl).



(*Z*)-**9** (in cyclopentane) (*E*)-**1** (NMR-invisible) (*Z*)-**1** (> dimeric)

The preparative results of this section commend that derivatizations of the sterically less impeded (*Z*)-**1**&*t*-BuOMe should be performed in Et_2O, *t*-BuOMe, or hydrocarbons as the

solvents at or below rt, whereas (*E*)-**1**&3THF should be derivatized in toluene solution at or below –78 °C very soon after its preparation. The following two sections provide more instructive details of *Z*,*E* interconversion, dimerization of (*Z*)-**1**, a broken-order reaction mechanism of (*Z*)-**1** derivations, and the significantly different reactivities of (*Z*)-**1** and (*E*)-**1**.

2.4. Dynamics of the *Z*,*E* Stereoinversion of 1

The temperature-dependent time scales of *Z*,*E* stereoinversion collected in this Section are intended to provide approximate rate standards for use in the later Sections 2.5 and 2.6. Thus, the preceding Sections 2.1 and 2.3 presented already some qualitative evidence about the configurational lability of the diastereomeric alkenyllithiums (*Z*,*E*)-**1**: Unsolvated (donor-free) (*E*)-**1**, obtained from (*Z*)-**9** in Scheme 3, was NMR-invisible because it isomerized into donor-free (*Z*)-**1** within less than a few minutes (laboratory time scale). A similar behavior of **1** in *t*-BuOMe had led to the diastereoconvergent preparation of (*Z*)-**1**&*t*-BuOMe in Section 2.1. Other than in THF (to be described further below), the *Z*,*E* interconversion rates in these non-THF solvents remained far below the rate regime of possible NMR coalescences, as shown by the well-resolved NMR signals of the equilibrium component (*E*)-**1** at rt in Et_2O (Table S6b)[14] or toluene (with 4 or 15 equiv of THF in Tables S8 and S9). The crystalline, trisolvated monomer (*E*)-**1**&3THF (Section 2.3) maintained its configuration for some time if held at –78 °C in toluene as the solvent. We report now that such a toluene solution admitted stereoinversion with the first-order rate constant $k(E \rightarrow Z) = 0.00040\ s^{-1}$ at –25 °C, as recognized through its concentration-independent half-reaction time of 29 min that corresponds to a barrier of $\Delta G^{\ddagger}$(–25 °C) = 18.3 kcal mol^{-1}. This run (Figure S2, Table S1)[14] terminated with the *Z*/*E* = 83:17 equilibrium ratio. Due to the shortage of THF ligands (total only 3.4 equiv, as expected), this equilibrated mixture contained mainly disolvated dimeric (*Z*)-**1** along with trisolvated monomeric (*E*)-**1**. We notice that monomeric (*Z*)-**1** was NMR-visible only in cases of solvation by THF (Section 2.1 and Tables S8–S10).

In THF as the solvent, however, the (*E*)-**1**&3THF → (*Z*)-**1**&3THF stereoinversion was ≥185-fold faster than above in toluene at –25 °C, as estimated in the following manner. The two olefinic ^{1}H NMR quartets (2′-H) of monomeric (*Z*)-**1** and (*E*)-**1** in THF at 32 °C were unresolved because already in coalescence at 80 MHz, which means that their interconversion was a little faster than the corresponding diastereotopomerization[20] of LiBr-free **2**&3THF in THF. Regrettably, proper rate measurements by total line-shape analyses appeared not feasible with **1** in view of the menacing vinyl-to-allyl anion isomerization[7] mentioned in Section 2.1. It appeared reasonable, however, to anticipate that a single 2′-CH_3 substituent in **1** had little

influence on the *Z*,*E* (or cis,trans) interconversion rate of the monomers [as also on the dimerization equilibrium of (*Z*)-**1** to be detailed in Section 2.5], so that the known[6] stereoinversion rates of **2** might serve as lower limits for the rates of **1** also at other temperatures. Therefore, we used the extrapolated value $\Delta G^{\ddagger}$(–25 °C) = 15.7 kcal mol^{-1} of **2** in THF[6] for calculating k_{ψ}(–25 °C) = ca. 0.074 s^{-1} as a lower limit for **1**, which led to the above factor of k_{ψ}(–25 °C)/k($E\rightarrow Z$) ≥ 0.074/0.00040 = ca. 185. This acceleration is partially due to THF catalysis in the ionic stereoinversion mechanism.[10] For a further kinetic orientation, we list here the extrapolated half-reaction times [$t_{1/2}$ = (ln2)/k_{ψ}] of **2** as upper limits for (*Z*)-**1** in THF: 0.007 s at 95 °C, 0.16 s at 32 °C, 0.24 s at 25 °C, 9.4 s at –25 °C, 37 s at –40 °C, and 54 min at –78 °C. On the other hand, the second 2′-CH_3 group in **3** (Scheme 1) was shown as follows to decelerate the *E*,*Z* stereoinversion process considerably. In view of the known[7] vinyl-to-allyl anion isomerization at about rt, a THF solution of **3** was heated quickly up to 95 °C, where the two ^{1}H NMR (60 MHz) 2′-CH_3 singlets began to exhibit weak line broadening. The usual total line-shape analysis led to an estimated maximum of the first-order rate constant of k_{ψ}(+95 °C) ≤ 10 (±3) s^{-1} and a corresponding barrier of $\Delta G^{\ddagger}$(+95 °C) ≥ 20.0(3) kcal mol^{-1} for the cis/trans 2′-methyl interconversion (methyl diastereotopomerization) of **3**, to be compared with an extrapolated[20] value of $\Delta G^{\ddagger}$(+95 °C) = 18.4 kcal mol^{-1} for monomeric **2** in THF which pointed to a substantial (ca. 10-fold) retardation of monomeric **3** as compared with monmeric **2**.

The data collected in this section established the conditions which provide for a sufficiently high mobility of the *Z*,*E* equilibration of **1**.

2.5. Dimerization and the 1.5th-Order Rate Equations of (*Z*)-1 with RHal

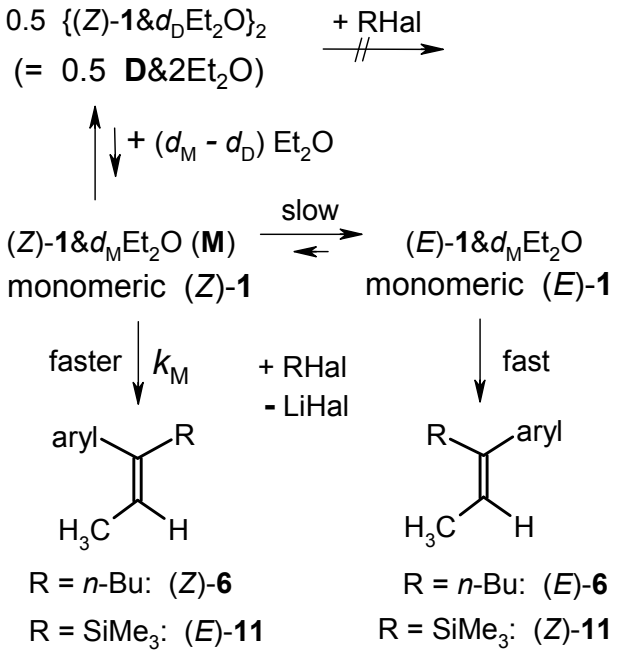
The much faster monomer/dimer (M/D) interconversion of **1** could not be measured in THF (because of no dimers) and in *t*-BuOMe (no monomers) or in Et_2O [no monomeric (*Z*)-**1**], but it was detected in toluene as the solvent with some THF (4 or 15 equiv, Tables S8 and S9)[14] to occur on the ^{1}H and ^{13}C NMR time scales (that is, very fast), as observed through line broadening and decoalescences between –32 and –68 °C. Recalling from above (Section 2.2 and footnote a in Table 8a) the determinations of d_D = 1 for disolvated, dimeric (*Z*)-**1**&THF ("D") and d_M = 3 for trisolvated, monomeric (*Z*)-**1**&3THF ("M") in toluene, we were able to measure a few of the temperature-dependent equilibrium constants K_{MD} (not reported here), as defined further below (eq 2). The small number of these measured K_{MD} values did not suffice for a reliable thermodynamic analysis; but they were found to be numerically similar to the K_{MD} values of the endothermic dimerization[21] of **2** under similar conditions. This agreement between (*Z*)-**1** and **2**

established that the single 2′-CH_3 cis-substituent in (*Z*)-**1** had little effect on the dimerization equilibrium.

In Et_2O as the solvent, the small amount (≤ 6%) of (*E*)-**1** in Et_2O did not provide ^{13}C NMR information, so that its aggregational state and microsolvation number remained undetermined. Dimeric, disolvated (*Z*)-**1** (namely, $d_D = 1$ in D&2Et_2O) was the main component (Table S6),[14] whereas monomeric (*Z*)-**1** (M&$d_M$$Et_2O$) remained NMR-invisible down to –90 °C, so that its equilibria with dimeric (*Z*)-**1** and with the minor component (*E*)-**1** (known to be mobile on the laboratory time scale) could not be measured. In spite of such a tiny population of monomeric (*Z*)-**1**, the following two kinetic experiments suggested that (*Z*)-**1** was the most reactive species in Et_2O solution. The reaction of **1** with $ClSiMe_3$ produced both diastereomers of **11** (Scheme 4), whose configurations were recognized through their interproton NOESY correlations: (*E*)-**11** had 2′-H near to $SiMe_3$ but 2′-CH_3 near to 2,6-CH_3, whereas (*Z*)-**11** showed 2′-CH_3 to be near to $SiMe_3$ but 2′-H near to 2,6-CH_3. If (*E*)-**11** and also the butyl derivative (*Z*)-**6** would be formed through a direct electrophilic attack of RHal ($ClSiMe_3$ or *n*-BuBr in the upper line of Scheme 4) on the dimeric portion D of (*Z*)-**1**, the reaction rate would be proportional to the concentrations of both RHal and D, that is, the rate would be of second order kinetically. We applied the simplifying condition of a sufficient excess (≥ 8 equiv) of RHal, so that its concentration [RHal] was practically constant; the rate would then be of pseudo-first order with respect to the concentration [D(*t*)], and the corresponding half-reaction time $t_{1/2}$ should be independent of the decreasing [D(*t*)]. Experimentally, however, $t_{1/2}$ was found to decrease, which excluded D from being the reactive species and left the NMR-invisible monomer M of (*Z*)-**1** for playing that role (Scheme 4). The rate should then be of first order in [M(*t*)] in eq 3, where it is seen to be defined as the time dependence of the increasing product concentration, which is twice as high as the time dependence of the decreasing [D(*t*)]. Together with eq 4 (from eq 2), this leads to the 0.5th-order (namely, square root) dependence on [D(*t*)] in eq 5, which defines also the 1.5th-order rate constant $k_{3/2} = k_\psi/[\text{RHal}]$. Both $k_{3/2}$ (in $L^{0.5}$ $mol^{-0.5}$ s^{-1}) and the concentration-dependent rate constant k_ψ (in $mol^{0.5}$ $L^{-0.5}$ s^{-1}) contain the numerically unknown equilibrium constant K_{MD} (eq 2) and the concentration [free Et_2O] with the difference ($d_M - d_D$) of the microsolvation numbers (eq 4). Integration of eq 5 afforded eq 6 in the convenient form of counting the dimer in terms of its two carbanionic units (as also measured through NMR integration). As derived before,[22] eq 6 implies a concentration-dependent pseudo-half-reaction time $^{\psi}t_{1/2}$ in eq 7. With the effective [RHal] as the average of the excessive initial and final values,, the experimental data of both electrophiles RHal (Tables S3 and S4)[14] obeyed the linear time dependence of the square roots $(2[D(t)])^{0.5}$ in eq 6 (Figures 2 and S3); the final product ratios were (*E*)-**11**/(*Z*)-**11** = 85:15 with

$ClSiMe_3$ and (*Z*)-**6**/(*E*)-**6** = 78:13 with *n*-BuBr. The $k_{3/2}$ values (Table 2) for either electrophile were numerically very similar (by factors of 1.5 and 0.6, respectively)[22] to those of **2**, suggesting that the 2′-CH_3 cis-substituent in (*Z*)-**1** had again little influence also on these rates. All four of these reactions of **1** and **2** ran on a convenient time scale at 32 °C because the predominating dimers of **2** or (*Z*)-**1** are inactive and must rapidly (albeit reversibly) deaggregate before reacting with RHal (Scheme 4). For comparison with *n*-BuBr, the methylation of a monomeric alkyllithium compound with CH_3I was very fast in THF/Me_2O at –132 °C and was shown[23] to proceed via a solvent-separated ion pair as the most reactive equilibrium component. Trimethylsilylation of (*Z*)-**1** occurred faster than butylation by a factor of 17 ($k_{3/2}$ values in Table 2); this factor mirrored the relative k_M values of the product-forming steps in Scheme 4, since all other parameters (eqs 3–5) and the temperatures were equal in the two runs; but the absolute values of these k_M of the two monomers remained unknown, of course. Since the interconversion of monomeric (*Z*)-**1** and (*E*)-**1** ("slow" in Scheme 4) was mobile on the laboratory time scale (Section 2.4), comparison of the equilibrium portion (6% in Table S6b)[14] of (*E*)-**1** in Et_2O with the increased (15 or 13%, respectively) minor products (*Z*)-**11** or (*E*)-**6** pointed to a certain partitioning of monomeric (*Z*)-**1** between the "faster" derivatization and the "slow" replenishment of (*E*)-**1**.

Scheme 4. Solvated, dimeric (*Z*)-**1**&$d_D$$Et_2O$ (= **D**&2Et_2O) reacts with electrophiles RHal (*n*-BuBr or $ClSiMe_3$) in Et_2O at 32 °C via monomeric (*Z*)-**1**&$d_M$$Et_2O$ ("**M**"); "slow" = mobile on the laboratory time scale; aryl = 2,6-dimethylphenyl.



$$K_{MD} = [M]^{-2}\,[D]\,[\text{free } Et_2O]^{2d_M - 2d_D} \quad (2)$$

$$\text{rate} = d[\text{product}]/dt = -2d[D(t)]/dt = k_M\,[RHal]\,[M(t)] \quad (3)$$

$$[M(t)] = (2K_{MD})^{-0.5}\,(2[D(t)])^{0.5}\,[\text{free } Et_2O]^{d_M - d_D} \quad (4)$$

$$\text{rate} = -d(2[D(t)])/dt = k_{3/2}\,[RHal]\,(2[D(t)])^{0.5} = k_\psi\,(2[D(t)])^{0.5} \quad (5)$$

$$\text{Integrated: } (2[D(t)])^{0.5} = -0.5\,k_\psi\,t + (2[D(t=0)])^{0.5} \quad (6)$$

$$^{\psi}t_{1/2} = 2(1 - 2^{-0.5})\,k_\psi^{-1}\,(2[D(t=0)])^{0.5} = 0.586\,k_\psi^{-1}\,(2[D(t=0)])^{0.5} \quad (7)$$

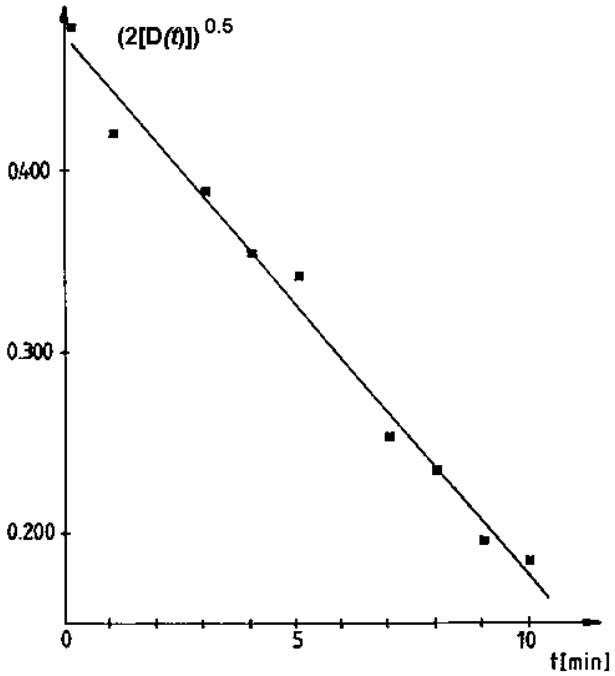


Figure 2. Time dependence of the square root (pseudo-0.5th order) of the doubled concentration 2[D(*t*)] of dimeric (*Z*)-**1** reacting with an excess of $ClSiMe_3$ in Et_2O at 32 °C.

Table 2. Rate measurements of dimeric (*Z*)-**1** ["D(*t*)"] with the electrophiles RHal in Et_2O at +32 (±1) °C: Pseudo-0.5th-order rate constants k_ψ (in $mol^{0.5}\ L^{-0.5}\ s^{-1}$), first pseudo-half-reaction times ${}^{\psi}t_{1/2}$, and 1.5th-order rate constants $k_{3/2}$ (in $L^{0.5}\ mol^{-0.5}\ s^{-1}$); M = mol/L.

R–Hal:	*n*-BuBr	$ClSiMe_3$
average [R–Hal]:	2.46 M	1.60 M
[D(*t*=0)]:	0.150 M	0.107 M
$(2[D(t=0)])^{0.5}$:	$0.548\ M^{0.5}$	$0.463\ M^{0.5}$
product fraction:	78% (*Z*)-**6** [a]	85% (*E*)-**11** [b]
$10^5 k_\psi$:	7.8	86
${}^{\psi}t_{1/2}$:	70 min	5.2 min
$10^5 k_{3/2}$:	3.2	54

[a] Accompaied by (*E*)-**6** (13%) and the alkenes **7** (9%). [b] With (*Z*)-**11** (15%).

The data in this section confirmed that the resemblance of (*Z*)-**1** and **2** extended to the dimerization equilibria which are highly mobile on the NMR time scale already at about –50 °C. It extended also to the reactivities against $ClSiMe_3$ or *n*-BuBr in Et_2O at 32 °C with their conveniently long first pseudo-half-reaction times of 70 or 5.2 min, respectively, which are due to the inactivity of dimeric (*Z*)-**1** that must deaggregate reversibly to maintain a tiny concentration of the reactive, monomeric (*Z*)-**1**.

2.6. Selectivities of (*Z*)-1 and (*E*)-1 toward fast and slow Ketones

Recent studies[24] revealed that addition reactions of monomeric aryllithium species to aryl ketones in THF/Me_2O can be extremely fast even at –140 °C, while the remnant aggregated species were observed to react independently but much more slowly. This suggested that monomeric (*Z*)-**1** and (*E*)-**1** should react with most ketones in THF not only rapidly but also independently of each other ("non-Curtin-Hammett condition")[22] under the important proviso that their *Z*,*E* equilibration (Section 2.4) would be significantly slower. If so, the adducts (*E*,*Z*)-**12** (Scheme 5) would be generated in proportion (eq 8) to the relative reactivities k_Z/k_E and populations of (*Z*,*E*)-**1**. However, this benefit of a high velocity of ketone addition may become a disadvantage if one or both competitors react extensively already within the boundary zone of incomplete microscopic mixing,[22,25,26] which would lead to the feared depressions of observed competition constants κ_{obs} ($1 \le \kappa_{obs} \le k_Z/k_E$ or k_E/k_Z) if calculated by eq 8. Convinced that we would anyhow be able to obtain only minimum (depressed) selectivities $\kappa_{obs} > 1$, we did not try to find out[22] how close our data came to the "true" quotients k_Z/k_E. Instead, we looked in the

following manner for qualitative information. Even without mixing problems (that is, at sufficiently low temperatures), eq 8 can be valid only as long as the known initial $[(E)\text{-}\mathbf{1}][(Z)\text{-}\mathbf{1}]^{-1}$ ratio does not change substantially, namely, either with a large excess of **1** or during the initial reaction phase only. Combining the latter choice with analyses of interrupted runs, we added deficient amounts of a ketone to solutions of (*Z,E*)-**1** and trapped remnant (*Z,E*)-**1** with solid CO_2. The carboxylic acids, (*E*)-**8** from (*Z*)-**1** and (*Z*)-**8** from (*E*)-**1** (Scheme 5 and Table 3), reported the final (*Z*)-**1**/(*E*)-**1** ratios and the rate of ketone addition to **1** (total yields of the adducts **12**). As an important confirmation of slow *Z,E* equilibration, the *E*/*Z* ratio of **8** may reveal a certain depletion of the faster diastereomer of **1** that furnished the higher portion of the two products **12**. Thus, a deficiency of the weakly (yet quickly) soluble dicyclopropyl ketone in a THF solution of monomeric (*Z,E*)-**1** at −78 °C (entry 1 of Table 3) afforded the adducts (*E,Z*)-**12a** within 30 s in a selectivity of $\kappa_{obs} \geq 14$. As expected for a continuing conversion (increasing yield), the corresponding depletion of (*Z*)-**1** was stronger after 65 s (entry 2), as reported by the progressively lowered ratios of the acids **8** with respect to the initial *Z*/*E* ratio of **1**. (For comparison, the *Z,E* equilibration in THF at −78 °C had been estimated in Section 2.4 to occur with $t_{1/2} \leq$ ca. 54 min). The actual rates of ketone addition cannot be read from entries 1 and 2 because of the slow introduction of dicyclopropyl ketone; however, an excess of this ketone was found to consume monomeric (*E*)-**1**&3THF completely within less than 4 min at −78 °C in THF, Et_2O, or toluene as the solvents. These rapid addition reactions (always faster than the *Z,E* interconversion) in any of these three solvents indicated that direct rate measurements with dicyclopropyl ketone would require either more advanced equipment or much lower temperatures.

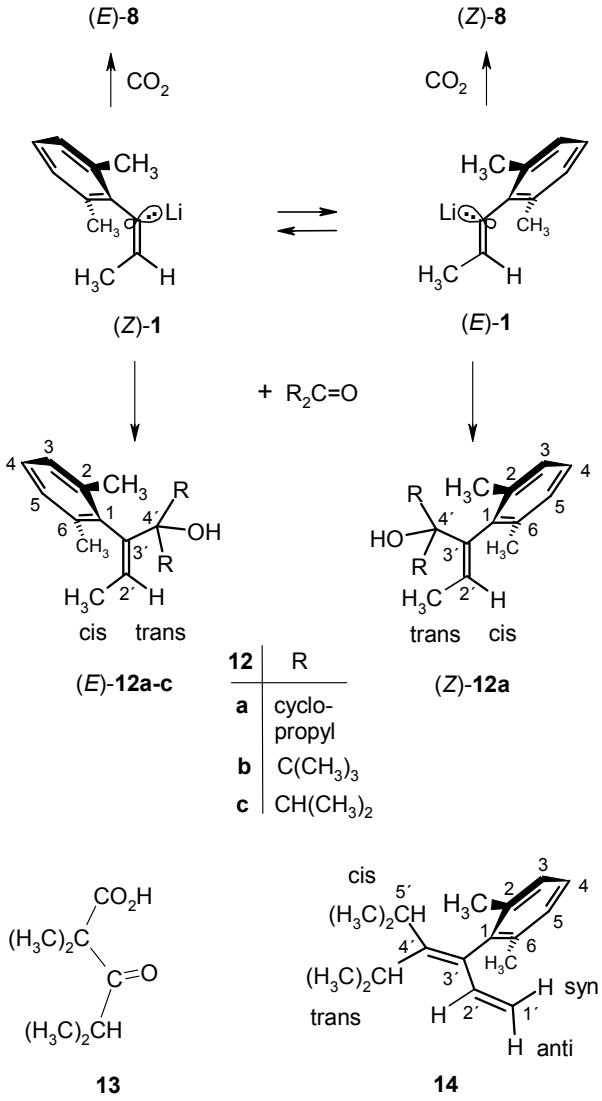
$$[(E)\text{-}\mathbf{12}][(Z)\text{-}\mathbf{12}]^{-1}[(E)\text{-}\mathbf{1}][(Z)\text{-}\mathbf{1}]^{-1} = k_Z/k_E = \kappa_{Z/E} \qquad (8)$$

Table 3. Relative reactivities κ_{obs} of (*Z,E*)-**1** in addition reactions to ketones: Adducts (*E,Z*)-**12**, olefins (*Z,E*)-**7**, and acids (*E,Z*)-**8**, the latter from remnant (*Z,E*)-**1**.

en-try	ketone (equiv)	sol-vent	temp. °C	time	**1** Z/E	acids **8** *E*/*Z*	adducts **12** *E*/*Z*	olefins **7** *Z*/*E*	yield [a] of **12**	κ_{obs} (eq 8)
1	$cpr_2C{=}O$ [b] (< 1.0)	THF	−78	30 s	34:66	24:76	88:12	–	53%	14 [c]
2	$cpr_2C{=}O$ [b] (< 1.0)	THF	−78	65 s	34:66	15:85	85:15	–	68%	11 [c]
3	*t*-$Bu_2C{=}O$ (≥ 1.0)	THF	rt	20 s	52:48	55:45	*E* only	trace	31%	∞ [d]
4	*t*-$Bu_2C{=}O$ (≥ 1.0)	THF	rt	27 min	52:48	none	*E* only	trace	100%	∞ [d]
5	*t*-$Bu_2C{=}O$ (< 1.0)	Et_2O	–40	33 min	96:4	85:15	*E* only	88:12	< 40%	∞ [d]
6	*t*-$Bu_2C{=}O$ (< 1.0)	Et_2O	–40	120 min	96:4	91:9	*E* only	none	53%	∞ [d]

[a] Fraction of **12** in the sum of **7**, **8**, and **12**. [b] Dicyclopropyl ketone. [c] Apparent (minimum) selectivity. [d] Stereospecific.

Scheme 5. (*Z*)-**1** and (*E*)-**1** compete for a ketone $R_2C{=}O$, whereupon carboxylation checks for the depletion of remnant (*Z*)-**1** or (*E*)-**1**.



As a counterexample, the more soluble di-*tert*-butyl ketone (t-$Bu_2C{=}O$)[27] in excess reacted with monomeric **1** in THF at rt more slowly than the *Z*,*E* stereoinversion of **1**. This became evident through the analysis (entry 3 of Table 3) of a portion (about one third of the run) that was quenched with solid CO_2 after 20 s: Although only 31% of (*E*)-**12b** [but no (*Z*)-**12b**] had been produced from **1**, the (*E*)-**8**/(*Z*)-**8** = 55:45 ratio indicated that the initial ratio of (*Z*)-**1**/(*E*)-**1** = 52:48 was maintained by means of a fast $E \rightarrow Z$ conversion in THFat rt ($t_{1/2}$ ≤ ca. 0.24 s in Section 2.4). With the remaining two thirds of this run, a rough estimate of the first half-reaction

time $^{1}t_{1/2}$ = ca. 50 s for (*E*)-**12b** formation was possible since the amount of (*Z*,*E*)-**1** had not yet been exhausted, as shown by the increasing yields of **12** in entries 3 and 4. In Et_2O (wherein **1** is mainly dimeric) at –40 °C, this reaction appeared to be significantly slower: Comparison of the first and the final yields of (*E*)-**12b** in entries 5 and 6, respectively, suggested a first $^{1}t_{1/2}$ = ca. 15 min, while a comparably slow *Z*,*E* interconversion had apparently replenished only part of the consumed (*Z*)-**1** after 33 min (acids **8** in entry 5) and approached the initial (*Z*)-**1**/(*E*)-**1** = 96:4 ratio rather slowly (increased ratio of **8** in entry 6). In consideration of the different temperatures, 15 min at –40 °C appeared again to be compatible with the time scale of 0.1 min at 22 °C as estimated previously[22] for *t*-Bu_2C=O with **2** in Et_2O. In accord with this time scale, only a trace of (*E*)-**12b** but a lot of the almost pure acid (*E*)-**8** were formed from (*Z*)-**1** at –78 °C in Et_2O in another run that was terminated through carboxylation after 145 min. In toluene as the solvent, monomeric (*E*)-**1**&3THF was completely consumed by *t*-Bu_2C=O within 35 min at rt, but produced again only (*E*)-**12b** (the inverted product) and some olefin (*E*)-**7**; clearly, once more only (*Z*)-**1** had reacted after its formation from the inactive (*E*)-**1**. This "slow" (*E*)-**1** → (*Z*)-**1** conversion was so easily recognized because *t*-Bu_2C=O consumed only (*Z*)-**1** but did not react directly with the source (*E*)-**1**. The lithium alkoxide of (*E*)-**12b** precipitated occasionally as a colorless powder from runs in Et_2O or THF after at least 30 min. Through simple washing with dry pentane and subsequent acidification, this powder afforded pure (*E*)-**12b**, whose configuration was established by a NOESY analysis. In analogy with the previously[22] reported retro-addition reaction that regenerated *t*-Bu_2C=O and **2**, the reversibility of (*E*)-**12b** formation was demonstrated as follows. In the presence of dicyclopropyl ketone (4 equiv) and the free alcohol (*E*)-**12b** (1 equiv) as a proton source, the lithium alkoxide of (*E*)-**12b** regenerated *t*-Bu_2C=O and (*Z*)-**1** in THF very slowly: After 22 hours at rt, the product mixture contained still some (*E*)-**12b** (12%), the adduct (*E*)-**12a** (12%) of dicyclopropyl ketone (the trap for **1**), and the olefins (*Z*)-**7** (71%) and (*E*)-**7** (5%) which arose through proton transfer from (*E*)-**12b** to **1**. The ratio of (*Z*)-**7**/(*E*)-**12a** = 71:12 indicated that the rate constant of that proton transfer to (*Z*)-**1** had been 24-times (namely, 4 × 71:12) higher than the rate constant of (*Z*)-**1** addition to dicyclopropyl ketone. The corresponding potassium alkoxide of (*E*)-**12b** was generated in THF by the slow, heterogeneous deprotonation reaction with an excess of KH in the presence of dicyclopropyl ketone (8 equiv) and decayed within 20 hours at rt to give (*E*)-**12a** and a trace of (*Z*)-**12a**.

Diisopropyl ketone reacted with monomeric (*Z*)-**1** in THF to give (*E*)-**12c** but did not (or not irreversibly) add to monomeric (*E*)-**1**. The NOESY cross-peaks of 2′-H with 5′-H and of 2′-C*H*$_3$ with the 2,6-dimethyl protons established the *E* configuration. The olefinic side-products (*Z*)-**7** and (*E*)-**7** (17:14 at rt) arose partially through proton transfer to (*Z*)-**1** and (*E*)-**1**, respectively,

from diisopropyl ketone whose enolate was recognized through final trapping with solid CO_2: The pure 2,2,4-trimethyl-3-oxopentanoic acid[28] (**13**) was isolated in an amount that could be expected from the olefinic product portion. In toluene as the solvent, dimeric (*Z*)-**1**&*t*-BuOMe was consumed completely by diisopropyl ketone within 150 s at +2 °C, affording again only (*E*)-**12c** (84%) and the olefin (*Z*)-**7** (16%). In most of these runs, (*E*)-**12c** was generated so selectively that an analytically almost pure sample could be obtained through simple evaporation of the accompanying volatiles in vacuo at rt. This was fortunate because modest heating (attempted distillation) of (*E*)-**12c** led to spontaneous H_2O elimination, which furnished the 1,3-diene **14**. A similar decomposition problem prevented us from purifying and presenting the adducts of acetone to **1**.

This section demonstrated that monomeric (*Z*)-**1** was at least 14-times more reactive than monomeric (*E*)-**1** in THF against dicyclopropyl ketone; this addition reaction was faster than the *Z*,*E* equilibration of **1**. Compared with that *Z*,*E* equilibration, however, the sterically hindered *t*-Bu_2C=O reacted more slowly with (*Z*)-**1** in THF but more rapidly in Et_2O, in accord with the selectivity reversal observed[22] for **2** with *t*-Bu_2C=O in THF versus Et_2O. Presumably due to steric shielding by its 2′-CH_3 substituent, (*E*)-**1** did not add to either *t*-Bu_2C=O or diisopropyl ketone, so that these two ketones consumed both (*Z*)-**1** and (*E*)-**1** with exclusive formation of the product from (*Z*)-**1** (an unexpected single diastereoconvergence).

3. CONCLUSION

(i) Both (*Z*)-**1** and (*E*)-**1** are trisolvated monomers in THF as the solvent wherein (*E*)-**1** is thermodynamically more stable than (*Z*)-**1** by only 0.84 kcal mol^{-1}. In contrast, (*Z*)-**1** is (almost) exclusively either a disolvated dimer in monodentate, non-THF ethereal solvents or an unsolvated higher aggregate in donor-free hydrocarbon solutions. The most reactive monomeric (*Z*)-**1** was NMR-visible only with microsolvation by THF. Armed with such knowledge, we became able to determine the following dynamic properties of **1**.

(ii) The endothermic dimerization of (*Z*)-**1**&3THF led to a THF-dependent equilibrium in toluene that was highly mobile on the ^1H and ^{13}C NMR time scales at about –50 °C already. Steric shielding of the Li–C(1′) bond of (*E*)-**1** by the neighboring 2′-CH_3 substituent may explain why (*E*)-**1** did not form a persistent dimer and did not furnish the expected adducts with *t*-Bu_2C=O or diisoproyl ketone. Even a mixed dimer of **1**, bearing one cis and one trans 2′-CH_3 group, was never observed because *E*,*Z* interconversion would provide for its removal. This mode of accomodation is not possible for **3** with its two 2′-methyl groups, so that **3** was found to be dimeric in Et_2O (Figure S6 and Table S12) and monomeric in THF (Table S13).

(iii) The formation of (*Z*)-**1** from monomeric (*E*)-**1**&3THF in toluene occurred with a conversion-independent half-reaction time of 29 min at –25 °C. A similar time scale (in min at rt) was estimated in Et_2O and in donor-free hydrocarbon solvents, confirming earlier observations with similar α-arylalkenyllithiums by, for examples, Curtin[29] et al. (in benzene), Panek[30] et al. (in hexane with donor additives), van Koten[31] et al. (in hexane), or Knorr[32] et al. (donor-free [β-D_1]**2** in hexane).

(iv) Disolvated, dimeric (*Z*)-**1** is unreactive and must deaggregate in order to consume *n*-BuBr or $ClSiMe_3$ in Et_2O. This followed from its 1.5th-order kinetics with these two electrophiles and can be ascribed to the intermediacy of the monomeric (NMR-invisible) species of (*Z*)-**1** as the more reactive equilibrium component.

(v) The close similarity of (*Z*)-**1** and the 2′-unsubstituted α-(2,6-dimethylphenyl)vinyllithium (**2**) included the above kinetics, the stereoinversion rates, the dimerization equilibrium and its mobility, the reaction rate with *t*-Bu_2C=O, the NMR coupling constants $^1J(^{13}C,^6Li)$ with derived microsolvation numbers at Li, and the degree of π-electron delocalization. Thus, a single 2′-CH_3 substituent in **1** has little influence if cis to the 1′-aryl group. Therefore, it appeared justified to use the published[6] cis/trans stereoinversion parameters of **2** as a model for **1**: The *E*/*Z* interconversion of THF-solvated **1** was estimated to be faster in THF at –25 °C ($t_{1/2} \leq$ ca. 9.4 s) than in toluene as the solvent by a factor of at least ca. 185 that appears compatible with catalysis by THF as expected for the ionic mechanism[6] via a THF-separated ion-pair intermediate.

(vi) These observations explain why we encountered the higly selective, doubly diastereoconvergent formation of either dimeric (*Z*)-**1**&*t*-BuOMe or monomeric (*E*)-**1**&3THF by Br/Li interchange reactions from any mixture of the (*Z*,*E*)-bromopropenes **5**. Of course, the commended preparative protocols apply verbatim only to the present paradigm example: (*Z*)-**1**&*t*-BuOMe may be used in Et_2O, *t*-BuOMe, or hydrocarbons as the solvents at or below rt, whereas (*E*)-**1**&3THF should be employed in toluene solution at or below –78 °C very soon after its preparation. THF was rarely suitable as a solvent for diastereospecific derivatizations of **1**.

(vii) In the rapid addition reactions of dicyclopropyl ketone (always faster than *Z*,*E* interconversion), monomeric (*Z*)-**1** was more successful than monomeric (*E*)-**1** by a factor of at least 14 in THF. The "slow" di-*tert*-butyl ketone reacted with (*Z*)-**1** only; the estimated time scales of this addition were ca. 50 s in THF at rt and ca. 15 min in Et_2O at –40 °C.

4. EXPERIMENTAL

General Remarks. For compatibility with our previously published alkenyllithiums such as **2** and **4**, we designate here the positions within the 2′-aryl groups by the numbers 1 through 6,

whereas C-1′ and C-2′ of the C=C double bond were alternatively also called C-α and C-β, respectively. Previously[9] desribed techniques and spectrometers were used. All ^{1}H and ^{13}C NMR shifts were referenced against internal TMS, and some of the spectra in THF could be measured down to –117 °C owing to the presence of saturated hydrocarbons as cosolvents. NMR abbreviations were d = doublet, m = multiplet, q = quartet, qi = quintet, quat = quaternary, sept = septet, t = triplet. Concentrations were determined through NMR integrations and comparison either with one of the ^{1}H NMR ^{13}C satellites of a nondeuteriated solvent or with a calibrated capillary in situ. Concentrations (M = molar) and molar ratios were counted in terms of the monomer formulas (such as the carbanionic units in **1**) as read from NMR integrals. With this choice, the numerical sum of reactants and products can remain constant during a transformation, so that the amounts of all participants can be compared on the same footing. In contrast, interpretations in terms of dimeric and monomeric particles would imply that the summed molecular concentrations of reactants and products are not necessarily constant.

(*Z*)-1′-Lithio-1′-(2,6-dimethylphenyl)propene [Dimeric and Monomeric (*Z*)-1]. A dry NMR tube (5 mm) was charged with a *Z*,*E* mixture of 1′-bromo-1′-(2,6-dimethylphenyl)propene[11] (**5**, 120 mg, 0.53 mmol) and anhydrous *t*-BuOMe (0.4 mL). After addition of *n*-BuLi (0.64 mmol) in hexane (0.27 mL) or cyclopentane at –30 °C under dry argon gas cover, the tube was tightly stoppered, cautiously moved for a partial mixing, and recooled quickly to –30 °C for mitigating the exothermic Br/Li interchange reaction that was complete within a few minutes. Dimeric (*Z*)-**1**&*t*-BuOMe began to crystallize in colorless platelets either soon at rt or with cooling to –20 °C. Too small crystals (< 1 mm) were dissolved through warming at 50 °C, then reprecipitated through slow cooling and keeping at –20 °C for (sometimes) up to two days. The crystals were purified at –70 °C under a stream of dry argon gas by means of a syringe with a long cannula as follows. The supernatant was withdrawn and replaced by dry pentane (ca. 0.3 mL). Short sucking and re-ejecting of a little pentane served to whirl up the solid components. The heavier crystals were allowed to settle down, whereas the powdery side-product LiBr was removed together with the pentane. This washing procedure was repeated up to four times and terminated by volatilization of remnant pentane in a short (3 s) stream of dry argon gas as introduced through a long pipette. The purified crystals of (*Z*)-**1**&*t*-BuOMe (yield up to 85%) were dissolved in the desired anhydrous solvent with cooling under argon gas cover. ^{1}H NMR of *dimeric* (*Z*)-**1** (*t*-BuOMe, 25 °C, 400 MHz) δ 1.37 (d, ^{3}J = 5.6 Hz, 3H, 2′-CH_3 cis to aryl), 1.99 (s, 6H, 2-/6-CH_3), 5.85 (q, ^{3}J = 5.5 Hz, 1H, 2′-H), 6.52 (t, ^{3}J = 7.3 Hz, 1H, 4-H), 6.75 (d, ^{3}J = 7.3 Hz, 2H, 3-/5-H) ppm, no (*E*)-**1**, assigned through comparison with (*Z*)-**1** in Et_2O; ^{1}H NMR of *dimeric* (*Z*)-**1** in a *Z*/*E* = 94:6 mixture (Et_2O, 0.35 M, 25 °C, 400

MHz) δ 1.37 (d, ^3J = 5.5 Hz, 3H, 2′-CH_3 cis to aryl), 2.00 (s, 6H, 2-/6-CH_3), 5.86 (q, ^3J = 5.5 Hz, 1H, 2′-H), 6.52 (t, ^3J = 7.3 Hz, 1H, 4-H), 6.75 (d, ^3J = 7.3 Hz, 2H, 3-/5-H) ppm; ^{1}H NMR of *dimeric* (*Z*)-**1**&*t*-BuOMe ([D_8]toluene, 0.34 M, –70 °C, 400 MHz) δ 1.68 (d, ^3J = 5.4 Hz, 3H, 2′-CH_3 cis to aryl), 2.15 (s, 6H, 2-/6-CH_3), 6.12 (q, ^3J = 5.4 Hz, 1H, 2′-H), 6.94 (t, ^3J = 7.4 Hz, 1H, 4-H), 7.12 (d, ^3J = 7.4 Hz, 2H, 3-/5-H), 0.89 and 2.73 (2 × s, coordinated *t*-BuOMe) ppm, no (*E*)-**1**; ^{1}H NMR of THF-solvated (4 equiv), *dimeric* (*Z*)-**1** ([D_8]toluene, –85 °C, 400 MHz) δ 1.74 (d, ^3J = 5.5 Hz, 3H, 2′-CH_3 cis to aryl), 2.20 (s, 6H, 2-/6-CH_3), 5.98 (q, ^3J = 5.5 Hz, 1H, 2′-H), 6.90 (t, ^3J = 7.4 Hz, 1H, 4-H), 7.10 (d, ^3J = 7.4 Hz, 2H, 3-/5-H) ppm, assigned through comparison with (*Z*)-**1** in Et_2O; ^{1}H NMR of THF-solvated (4 equiv), *monomeric* (*Z*)-**1** ([D_8]toluene, –85 °C, 400 MHz) δ 1.93 (d, ^3J = 5.5 Hz, 3H, 2′-CH_3 cis to aryl), 2.38 (s, 6H, 2-/6-CH_3), 5.93 (q, ^3J = 5.5 Hz, 1H, 2′-H), 6.85 (t, ^3J = 7.4 Hz, 1H, 4-H), 7.18 (d, ^3J = 7.4 Hz, 2H, 3-/5-H) ppm; ^{1}H NMR of *monomeric* (*Z*)-**1** in a *Z*/*E* = 47:53 mixture (THF, 0.68 M, –10 °C, 400 MHz) δ 1.92 (s, 6H, 2-/6-CH_3), (2′-CH_3 obscured), 5.46 (q, ^3J = 5.5 Hz, 1H, 2′-H), 6.21 (t, ^3J = 7.4 Hz, 1H, 4-H), 6.57 (d, ^3J = 7.4 Hz, 2H, 3-/5-H) ppm, see below for (*E*)-**1**; ^{13}C NMR of *dimeric* (*Z*)-**1** (*t*-BuOMe, 25 °C, 100.6 MHz) δ 17.0 (qd, ^1J = 124 Hz, ^2J = 8.5 Hz, 2′-CH_3 cis to aryl), 21.7 (qd, ^1J = 125 Hz, ^3J = ca. 5 Hz, 2-/6-CH_3), 120.0 (sharp d, ^1J = 156 Hz, C-4), 122.0 (dq, ^1J = 147 Hz, C-2′), 127.2 (dm, ^1J = 153 Hz, C-3/-5), 127.6 (m, apparent *J* = ca. 6 Hz, C-2/-6), 154.2 (unresolved m, C-1), 190.5 (dm. ^2J = 16 Hz, C-1′); assigned through the γ-aryl[33] effect and comparison with (*Z*)-**1** in Et_2O; ^{13}C NMR of *dimeric* (*Z*)-**1** in a *Z*/*E* = 94:6 mixture (Et_2O, 0.35 M, 25 °C, 100.6 MHz) δ 17.2 (qd, ^1J = 124 Hz, ^2J = 8.5 Hz, 2′-CH_3 cis to aryl), 21.5 (qd, ^1J = 125 Hz, ^3J = 4.9 Hz, 2-/6-CH_3), 120.2 (sharp d, ^1J = 155 Hz, C-4), 122.7 (dq, ^1J = 144 Hz, ^3J = ca. 5 Hu, C-2′), 127.4 (dm, ^1J = 155 Hz, C-3/-5), 127.9 (m, apparent *J* = ca. 6 Hz, C-2/-6), 154.1 (unresolved m, C-1), 191.0 (dm. ^2J = 16 Hz, C-1′), the quintet (1:2:3:2:1) splitting of C-1′ by $^1J(^{13}C,^6Li)$ was detected at –50 (7.6 Hz), –85 (7.6 Hz), and –90 °C (7.5 Hz); ^{13}C NMR of *dimeric* (*Z*)-**1**&*t*-BuOMe ([D_8]toluene, 0.34 M, –70 °C, 100.6 MHz) δ 17.4 (2′-CH_3 cis to aryl), 22.2 (2-/6-CH_3), 119.9 (C-4), 121.2 (C-2′), 127.2 (C-3/-5), 127.4 (C-2/-6), 154.1 (C-1), 189.8 (quintet 1:2:3:2:1, $^1J_{CLi}$ = 7.5 Hz, C-1′), 26.2, 49.0, and 74.2 (coordinated *t*-BuOMe) ppm, assigned through comparison with (*Z*)-**1** in Et_2O, the C-1′ quintet (7.5 Hz) was also detected at –45 and –18 °C; ^{13}C NMR of THF-solvated (4 equiv), *dimeric* (*Z*)-**1** ([D_8]toluene, –85 °C, 100.6 MHz) δ 18.2 (2′-CH_3 cis to aryl), 21.7 (2-/6-CH_3), 119.0 (C-4), 122.0 (C-2′), 127.0 (C-3/-5), 127.2 (C-2/-6), 154.8 (C-1), 192.6 (quintet 1:2:3:2:1, $^1J_{CLi}$ = ca. 6.5 Hz, C-1′) ppm, assigned through comparison with (*Z*)-**1** in Et_2O and confirmed at 25 °C through gated decoupling and selective {^{1}H} decoupling as follows: {2′-CH_3} → C-1′ as a d with ^2J = 16 Hz, 2′-*C*H_3 as a d

with ^2J = 8.5 Hz; {2-/6-CH_3} → C-1 as a dt with ^3J = 13.5 Hz and 5.5 Hz, C-1′as a d, C-2/-6 as a d with ^3J = 6.8 Hz, and 2-/6-CH$_3$ as two narrow d with ^2J = 4.9 Hz for (*Z*)-**1** and (*E*)-**1**; {2′-H} → 2′-CH$_3$ as a sharp q. ^{13}C NMR of THF-solvated (4 equiv), *monomeric* (*Z*)-**1** ([D$_8$]toluene, –85 °C, 100.6 MHz) δ 18.5 (2′-CH$_3$ cis to aryl), 22.3 (2-/6-CH$_3$), 114.9 (C-4), 116.0 (C-2′), (C-2/-6 obscured), 126.5 (C-3/-5), 158.5 (C-1), 197.4 (C-1′) ppm, assigned through comparison with monomeric (*Z*)-**1** in THF; ^{13}C NMR of *monomeric* (*Z*)-**1** in a *Z*/*E* = 32:68 mixture (THF, 0.24 M, –88 °C, 100.6 MHz) δ 18.0 (2′-CH$_3$ cis to aryl), 22.0 (2-/6-CH$_3$), 114.2 (C-2′), 114.9 (C-4), 125.0 (C-2/-6), 126.0 (C-3/-5), 158.4 (C-1), 197.6 (triplet 1:1:1, $^1J_{CLi}$ = 11.4 Hz, C-1′) ppm, assigned through the γ-aryl effect,[33] temperature dependent *Z*/*E* ratios and comparison with (*Z*)-**1** in Et$_2$O and *t*-BuOMe.

(*E*)-1′-Lithio-1′-(2,6-dimethylphenyl)propene [Monomeric (*E*)-1&3THF]. 1′-Bromo-1′-(2,6-dimethylphenyl)propene[11] [(*Z*,*E*)-**5**, 500 mg, 2.22 mmol)] was transformed as above into purified, dimeric (*Z*)-**1**&*t*-BuOMe. This product in the NMR tube (5 mm) was treated at rt with successive small amounts of anhydrous THF (total 0.85 mL) until the last few grains of (*Z*)-**1**&*t*-BuOMe were dissolved. (More THF will prevent the subsequent crystallization.) Fine white needles of (*E*)-**1**&3THF precipitated on cooling at –78 °C and were after 30 min purified through washing [see (*Z*)-**1**] with dry pentane (3× 0.5 mL, no cyclopentane!) under argon gas cover. Without warming, the needles were dissolved for NMR spectroscopy or derivatization. ^{1}H NMR of monomeric (*E*)-**1** in a *Z*/*E* = 94:6 mixture (Et$_2$O, 0.35 M, 25 °C, 400 MHz) δ 1.91 (d, ^3J = 6.0 Hz, 3H, 2′-CH$_3$ trans to aryl), 2.07 (s, 6H, 2-/6-CH$_3$), 6.14 (q, ^3J = 6.0 Hz, 1H, 2′-H), 6.46 (t, ^3J = 7.3 Hz, 1H, 4-H), 6.72 (d, ^3J = 7.3 Hz, 2H, 3-/5-H) ppm; ^{1}H NMR of THF-solvated (4 equiv), monomeric (*E*)-**1** ([D$_8$]toluene, –85 °C, 400 MHz) δ 2.38 (s, 6H, 2-/6-CH$_3$), (2′-CH$_3$ obscured), 6.44 (q, ^3J = 6 Hz, 1H, 2′-H), 6.83 (t, ^3J = 7.4 Hz, 1H, 4-H), 7.14 (d, ^3J = 7.4 Hz, 2H, 3-/5-H) ppm, assigned through comparison with (*E*)-**1** in THF; ^{1}H NMR of monomeric (*E*)-**1** in a *Z*/*E* = 47:53 mixture (THF, 0.68 M, –10 °C, 400 MHz) δ 1.94 (s, 6H, 2-/6-CH$_3$), (2′-CH$_3$ obscured), 5.72 (q, ^3J = 5.8 Hz, 1H, 2′-H), 6.20 (t, ^3J = 7.4 Hz, 1H, 4-H), 6.57 (d, ^3J = 7.4 Hz, 2H, 3-/5-H) ppm; ^{13}C NMR of THF-solvated (4 equiv), monomeric (*E*)-**1** ([D$_8$]toluene, –85 °C, 100.6 MHz) δ 23.0 (2-/6-CH$_3$), 25.2 (2′-CH$_3$ trans to aryl), 115.6 (C-4), 116.6 (C-2′), (C-2/-6 obscured), 127.2 (C-3/-5), 161.2 (C-1), 197.8 (C-1′) ppm, assigned through comparison with (*E*)-**1** in THF; ^{13}C NMR of monomeric (*E*)-**1** in a *Z*/*E* = 32:68 mixture (THF, 0.24 M, –88 °C, 100.6 MHz) δ 22.7 (2-/6-CH$_3$), 24.8 (2′-CH$_3$ trans to aryl), 115.4 (C-2′), 116.0 (C-4), 126.1 (C-3/-5), 126.6 (C-2/-6), 161.2 (C-1), 198.1 (triplet 1:1:1, $^1J_{CLi}$ = 11.4 Hz, C-1′) ppm, assigned through the γ-aryl effect,[33] the temperature dependent *Z*/*E* ratios, and comparison with (*Z*)-**1** in Et$_2$O and *t*-BuOMe.

Donor-free (*Z*)-1. A dry NMR tube (5 mm) was loaded with 1′-iodo-1′-(2,6-dimethylphenyl)propene [(*Z*)-**9**, 40 mg, 0.15 mmol], dry cyclopentane (0.4 mL), [D_{12}]cyclohexane (0.07 mL), and a trace of TMS, then cooled at –30 °C under argon gas cover. *n*-Bu^{6}Li (0.16 mmol) in cyclopentane (0.11 mL) was added to the tube, which was warmed up to rt after 15 min and showed that the I/Li interchange reaction was complete. ^{1}H NMR (saturated hydrocarbon solvents, –45 °C, 400 MHz) δ 1.73 (s, 6H, 2-/6-CH_3), (2′-CH_3 obscured), 5.74 (q, ^3J = 5.6 Hz, 2′-H), 6.71 (t, ^3J = 7.3 Hz, 1H, 4-H), 6.78 (d, ^3J = 7.3 Hz, 2H, 3-/5-H) ppm; ^{13}C NMR (saturated hydrocarbon solvents, –45 °C, 100.6 MHz) δ 17.3 (2′-CH_3 cis to aryl), 21.1 (qd, 2-/6-CH_3), 123.0 (d, C-4), 128.8 (narrow d, C-2/-6), 129.0 (dd, C-3/-5), 131.4 (d, C-2′), 150.3 (narrow m, C-1), 179.5 (unresolved narrowed m, C-1′) ppm, assigned through the γ-aryl effect[33] and selective {^{1}H} decouplimg. After the long-term measurements, the clear solution was poured onto dry CO_2, and the warmed-up material was dissolved in aqueous NaOH (3 M) and Et_2O. Acidification of the alkaline aqueous layer afforded the diastereomerically pure carboxylic acid (*E*)-**8** (12 mg, 42%).

1′-Lithio-2′-methyl-1′-phenylpropene (3).[7] Unsolvated **3** precipitated slowly from a solution of 1-bromo-2-methyl-1-phenylpropene[7] (2.10 g, 9.95 mmol) and *n*-Bu^{6}Li (11 mmol) in pentane (2.0 mL). After 4 hours at rt, the precipitate was washed with dry pentane under argon gas cover and dried in vacuo (ca. 30 min), then vented by slow admission of dry argon and weighed (yield 950 mg, 69%). ^{1}H NMR (hexane, 60 MHz) δ 6.69 (d, ^3J = ca. 7 Hz, 2H, 2-/6-H), 6.73 (t, ^3J = ca. 6 Hz, 1H, 4-H), 7.05 (overlaid t, 3-/5-H) ppm; ^{1}H NMR (Et_2O, 32 °C, 80 MHz) δ 1.60 (s, 3H, 2′-CH_3 cis to aryl), 1.85 (s, 3H, 2′-CH_3 trans), 6.56 (d, ^3J = 8.0 Hz, 2H, 2-/6-H), 6.60 (t, ^3J = 7.0 Hz, 1H, 4-H), 7.03 (t, ^3J = 7.2 Hz, 2H, 3-/5-H) ppm; ^{1}H NMR (THF, –37 °C): as in ref 7; ^{13}C NMR (Et_2O, –51 °C, 25.1 MHz) δ 20.2 (qq, ^1J = 122 Hz, 2′-CH_3 cis to aryl), 29.9 (qq, ^1J = 122.5 Hz, ^3J = ca. 4 Hz, 2′-CH_3 trans), 119.6 (dt, ^1J = 159 Hz, ^3J = 7.5 Hz, C-4), 124.6 (dt, ^1J = 154 Hz, ^3J = 6.5 Hz, C-2/-6), 128.2 (dd, ^1J = 156 Hz, ^3J = 7.5 Hz, C-3/-5), 134.4 (quasi-septet, apparent J = ca. 5 Hz, C-2′), 158.0 (t, ^3J = 6.5 Hz, C-1), 183.0 (qi 1:2:3:2:1, $^1J(^{13}C,^6Li)$ = 7.5 Hz, C-1′) ppm (Table S12),[14] assigned through the γ-aryl effect[33] and comparison with **1** in Et_2O, the qi $^1J(^{13}C,^6Li)$ = 7.5 Hz of C-1′ was observed also at –71 (Figure S6),[14] –79, –91 (prepared through Hg/Li interchange), –95 (with ^{6}LiBr), and –106 °C; ^{13}C NMR (THF, –81 °C, 25.1 MHz) δ 20.3 (q, 2′-CH_3 cis), 30.6 (q, 2′-CH_3 trans), 115.0 (d, C-4), 121.0 (quat, C-2′), 122.2 (d, C-2/-6), 127.2 (d, C-3/-5), 164.0 (quat, C-1), 194.0 (unresolved, C-1′) ppm, assigned through {^{1}H} off-resonance decoupling, the γ-aryl effect,[33] and comparison with **1** in THF; the

triplet (1:1:1) with $^1J(^{13}C,^6Li)$ = 11.5(1) Hz of C-1′ was observed at –106, –117, –124, and –126 °C (Table S13).[14]

3′-(2,6-Dimethylphenyl)hept-2′-ene [(*Z*)- and (*E*)-6]. A solution of unpurified, dimeric (*Z*)-**1** in *t*-BuOMe was prepared as above from the bromoalkenes[11] (*Z*,*E*)-**5** (116 mg, 0.51 mmol) and kept at rt for 19 hours. The crude, yellowish oil (60 mg), isolated after aqueous workup, contained (*Z*)-**6**, (*E*)-**6**, and the olefin (*Z*)-**7** in the molar ratio 90:2:8. The crude material (132 mg) from several runs was purified through chromatography on silica gel (3.5 g): Elution with low-boilimg petroleum ether (7 mL) furnished a clean sample of (*Z*,*E*)-**6**. ^{1}H NMR of (*Z*)-**6** ($CDCl_3$, 400 MHz) δ 0.89 (t, ^3J = 7.2 Hz, 3H, CH_3-7′), 1.30 and 1.42 (2 m, CH_2-5′/-6′), 1.31 (dt, ^3J = 6.7 Hz, ^5J = 1.5 Hz, 3H, CH_3-1′ cis to aryl), 2.14 (tm, ^3J = 8 Hz, CH_2-4′), 2.16 (s, 6H, 2-/6-CH_3), 5.57 (qt, ^3J = 6.7 Hz, ^4J = 1.5 Hz, 1H, 2′-H), 7.02 and 7.04 (A_2B system, ^3J = ca. 7 Hz, 2+1H, 3-/5-H and 4-H) ppm, assigned through the NOESY correlation 2′-H ↔ CH_2-4′; ^{1}H NMR of (*E*)-**6** ($CDCl_3$, 400 MHz) δ 0.86 (t, ^3J = 7.2 Hz, 3H, CH_3-7′), 1.77 (d, ^3J = 7.0 Hz, 3H, CH_3-1′ trans to aryl), 2.21 (s, 6H, 2-/6-CH_3), 5.24 (qt, ^3J = 6.9 Hz, 1H, 2′-H) ppm, others not identified, assigned through the NOESY correlation 2′-H ↔ 2-/6-CH_3; ^{13}C NMR of (*Z*)-**6** ($CDCl_3$, 100.6 MHz) δ 14.06 [qqi, ^1J = 124 Hz, (^2J + ^3J)/2 = 3.9 Hz, CH_3-7′], 14.11 (qd, ^1J = 125.2 Hz, ^2J = 4.5 Hz, CH_3-1′ cis to aryl), 19.61 (qm, ^1J = 126 Hz, 2-/6-CH_3), 22.90 (tm, ^1J = 126 Hz, CH_2-6′), 29.85 (tm, ^1J = 126 Hz, CH_2-5′), 37.25 (tm, ^1J = 124.5 Hz, CH_2-4′), 120.17 (dm, ^1J = 151.5 Hz, apparent ^3J and ^2J = 6 Hz, C-2′), 126.11 (sharp d, ^1J = 158.0 Hz, C-4), 127.19 (dm, ^1J = 156 Hz, C-3/-5), 135.33 (quasi-qi, apparent J = 5.3 Hz, 2-/6-C), 140.20 (unresolved, C-1), 140.86 (unresolved, C-3′) ppm, assigned through the γ-aryl[33] effect; ^{3}C NMR of (*E*)-**6** ($CDCl_3$, 100.6 MHz) δ 13.47 (q, CH_3-7′), 15.28 (q, CH_3-1′ trans to aryl), 20.3 (q, 2-/6-CH_3), 23.35 (t, CH_2-6′), 30.30 (t, CH_2-5′), 31.87 (t, CH_2-4′), 123.36 (d, C-2′), 125.93 (d, C-4), 127.24 (d, C-3/-5), 135.78 (C-2/-6), 139.78 (C-1), 144.82 (unresolved, C-3′) ppm, assigned as above. Anal. calcd for $C_{15}H_{22}$ (202.3): C, 89.04; H, 10.96. Found: C, 88.65; H, 10.88.

1′-(2,6-Dimethylphenyl)propene [(*Z*)- and (*E*)-7]. *Z*,*E* mixtures of this "parent" olefin **7** were obtained through protolysis and aqueous workup of **1**. A sample (183 mg) distilled at 70–88 °C (bath temp.)/13 Torr (ref 34: 75 °C/4 Torr) to give a colorless mixture (103 mg) of (*Z*)-**7** and (*E*)-**7** (63:37). ^{1}H NMR of (*Z*)-**7** ($CDCl_3$, 400 MHz) δ 1.45 (dd, ^3J = 6.8 Hz, ^4J = 1.7 Hz, 3H, 2′-CH_3 cis to aryl), 2.19 (s, 6H, 2-/6-CH_3), 5.83 (dq, ^3J = 11.3 Hz, ^3J = 6.8 Hz, 1H, 2′-H), 6.30 (dm, ^3J = 11.3 Hz, 1H, 1′-H), 7.02 and 7.06 (A_2B system, ^3J = 7.4 Hz, 2+1H, 3-/5-H and 4-H) ppm (the literature[35] values are too large by ca. 0.18 ppm); ^{1}H NMR of (*E*)-**7** ($CDCl_3$, 400 MHz)

δ 1.90 (dd, ^3J = 6.5 Hz, ^4J = 1.8 Hz, 3H, 2′-CH_3 trans to aryl), 2.28 (s, 6H, 2-/6-CH_3), 5.68 (dq, ^3J = 16.1 Hz, ^3J = 6.5 Hz, 1H, 2′-H), 6.33 (overlaid dm, ^3J = ca. 16 Hz, 1′-H) ppm (3-/4-/5-H obscured); ^{13}C NMR of (*Z*)-**7** ($CDCl_3$, 100.6 MHz) δ 14.2 (2′-CH_3 cis to aryl), 20.2 (2-/6-CH_3), 126.4 (C-4), 127.0 (C-3/-5), 127.3 (C-1′), 128.4 (C-2′), 136.1 (C-2/-6), 136.6 (C-1) ppm, assigned through the *Z*/*E* ratios and the γ-aryl[33] effect; ^{13}C NMR of (*E*)-**7** ($CDCl_3$, 100.6 MHz) δ 18.8 (2′-CH_3 trans to aryl), 20.9 (2-/6-CH_3), 126.1 (C-4), 127.6 (C-3/-5), 128.5 (C-1′), 130.3 (C-2′), 136.0 (C-2/-6), 137.7 (C-1) ppm, assigned as above (the published[35] ^{1}H and ^{13}C NMR spectra were not assigned and hence unsuitable for calculating $\Delta\delta$ values); IR (film, *Z*/*E* = 63:37) ν 3065, 3009, 2917, 2855, 1465, 768 cm^{-1}. Anal. calcd for $C_{11}H_{14}$ (146.23, *Z*/*E* = 63:37): C, 90.35; H, 9.65. Found: C, 89.57; H, 9.71.

(*E*)-2′-(2,6-Dimethylphenyl)but-2-enoic Acid [(*E*)-8]. Purified dimeric (*Z*)-**1**&*t*-BuOMe was prepared from the bromoalkenes[11] (*Z*,*E*)-**5** (200 mg, 0.89 mmol), then dissolved in anhydrous *t*-BuOMe (2.0 mL) and immediately poured onto solid CO_2, warmed up, and diluted with Et_2O (15 mL). The mixture was extracted with aqueous NaOH (2 M. 4 × 5 mL), and the Et_2O layer was discarded. The combined aqueous layers were acidified with conc. HCl, then shaken with Et_2O (3 × 15 mL), and thereafter discarded. The combined Et_2O phases were washed with distilled water until neutral, dried over $MgSO_4$, filtered, and concentrated. The dried product (*E*)-**8** (mp 134–139 °C, 73 mg, 43%) contained no (*Z*)-**8** and was recrystallized from cyclohexane (2×), yielding pure (*E*)-**8** with mp 144–146.5 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.58 (d, ^3J = 7.1 Hz, 3H, 3′-CH_3 cis to aryl), 2.12 (s, 6H, 2-/6-CH_3), 7.06 and 7.13 (A_2B system, ^3J = 7.4 Hz, 2+1H, 3-/5-H and 4-H), 7.33 (q, ^3J = 7.1 Hz, 1H, 3′-H) ppm; ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 15.1 (qd, ^1J = 127 Hz, ^2J = 3.8 Hz, 3′-CH_3 cis to aryl), 19.9 (qd, ^1J = 126.7 Hz, ^3J = 5.0 Hz, 2-/6-CH_3), 127.3 (ddq, ^1J = 158 Hz, ^3J = 7.3 Hz, ^3J = 5.0 Hz, C-3/-5), 127.7 (sharp d, ^1J = 159 Hz, C-4), 132.7 (q, ^3J = 6.1 Hz, ^2J = 0 Hz, C-2′), 133.7 (unresolved m, C-1), 136.5 (dq, ^3J = 7.5 Hz, ^2J = 6 Hz, C-2/-6), 143.1 (dq, ^1J = 157.7 Hz, ^2J = 7.0 Hz, C-3′), 172.0 (d, ^3J = 6.9 Hz, CO_2H) ppm, assigned through selective {2,6-CH_3} decoupling → C-1 as a pseudo-q ^3J = 7.3 Hz (to 3-/5-H and 3′-H), C-2/-6 as a distorted d ^3J = 7.5 Hz, and C-3/-5 as a sharp dd; IR (KBr) ν 3600–2300 (O–H), 2658, 2532, 1687, 1633, 1417, 1286, 936, 767, 714 cm^{-1}. Anal. calcd for $C_{12}H_{14}O_2$ (190.24): C, 75.76; H, 7.42. Found: C, 75.91; H, 7.63.

(*Z*)-2′-(2,6-Dimethylphenyl)but-2-enoic Acid [(*Z*)-8]. The purified dimeric (*Z*)-**1**&*t*-BuOMe was obtained from the bromoalkenes[11] (*Z*,*E*)-**5** (250 mg, 1.11 mmol), then converted into crystalline (*E*)-**1**&3THF that was dissolved at –70 °C in dry toluene (1.0 mL) and immediately

poured onto solid CO_2. After warm-up and dilution with Et_2O (15 mL), the mixture was extracted with aqueous NaOH (2 M. 4 × 5 mL) and the Et_2O layer discarded. The combined aqueous phases were acidified, shaken with Et_2O (3 × 15 mL), and thereafter discarded. The combined Et_2O extracts were washed with distilled water until neutral, dried over $MgSO_4$, filtered, and concentrated to yield the crude acid (*Z*)-**8** (mp 111–118 °C, 31 mg, 15%) without any trace of (*E*)-**8**. Pure (*Z*)-**8** had mp 120–122 °C (cyclohexane). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.20 (s, 6H, 2-/6-CH_3), 2.25 (d, ^3J = 7.3 Hz, 3H, 3′-CH_3 trans to aryl), 6.22 (q, ^3J = 7.3 Hz, 1H, 3′-H), 7.04 and 7.11 (A_2B system, ^3J = 7.5 Hz, 2+1H, 3-/5-H and 4-H) ppm; ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 16.2 (qd, ^1J = 128 Hz, ^2J = 3 Hz, 3′-CH_3 trans to aryl), 20.4 (qd, ^1J = 126 Hz, ^3J = 4.2 Hz, 2-/6-CH_3), 127.3 (dm, ^1J = 157 Hz, C-3/-5), 127.5 (sharp d, ^1J = 159.4 Hz, C-4), 131.4 (m, C-2′), 136.7 (dq, ^3J = 7 Hz, ^2J = 6 Hz, C-2/-6), 138.3 (unresolved, C-1), 145.2 (dq, ^1J = 153 Hz, ^2J = 7 Hz, C-3′), 171.1 (d, ^3J = 13.8 Hz, CO_2H) ppm, assigned through selective {3′-C*H*$_3$ and 2,6-C*H*$_3$} decoupling → 2-/6-*C*H$_3$ as a d ^3J = 4.2 Hz, C-2/-6 as a d ^3J = 7.0 Hz, C-2′as a s (^2J = 0), C-3′ as a sharp d ^1J = 152 Hz, C-3/-5 as a d ^3J = 7.5 Hz; IR (KBr) ν 3600–2400 (O–H), 1689, 1622, 1260, 1244, 1229, 776 cm^{-1}. Anal. calcd for $C_{12}H_{14}O_2$ (190.24): C, 75.76; H, 7.42. Found: C, 75.90; H, 7.49.

(*E*)-1′-Iodo-1′-(2,6-dimethylphenyl)propene [(*E*)-9]. The bromoalkenes[11] (*Z*,*E*)-**5** (200 mg, 0.89 mmol) were converted into the purified dimer (*Z*)-**1**&*t*-BuOMe, then dissolved in anhydrous *t*-BuOMe (1.0 mL) and stirred at 2 °C under argon gas cover during titration with a solution of elemental iodine (225 mg, 0.89 mmol) in *t*-BuOMe (1.5 mL) for a persisting coloring. After addition of two further droplets of the iodine solution, the mixture was kept at rt for 15 min and then diluted with water (12 mL) and Et_2O. The aqueous layer was shaken with Et_2O (3 × 4 mL); the four Et_2O phases were combined, shaken with aqueous $NaHSO_3$ (37%, 2 × 4 mL), washed with distilled water until neutral, dried over $MgSO_4$, filtered, and concentrated. The crude material (mp 57–62 °C, 104 mg, 43%) contained (*E*)-**9** and (*Z*)-**9** (94:6) and was recrystallized from methanol (ca. 1 mL) to give analytically pure, colorless (*E*)-**9** (53 mg, mp 63–65 °C). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.36 (d, ^3J = 7.0 Hz, 3H, 2′-CH_3 cis to aryl), 2.23 (s, 6H, 2-/6-CH_3), 6.56 (q, ^3J = 7.0 Hz, 1H, 2′-H), 7.01 and 7.09 (A_2B system, ^3J = 7.4 Hz, 2+1H, 3-/5-H and 4-H) ppm, assigned through comparison with (*Z*)-**9** and (*E*)-**5**; ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 17.0 (qd, ^1J = 127.6 Hz, ^2J = 3.4 Hz, 2′-CH_3 cis to aryl), 19.5 (qd, ^1J = 127 Hz, ^3J = ca. 5 Hz, 2-/6-CH_3), 94.7 (dq, ^2J = 6.0 Hz, ^3J = 8.0 Hz, C-1′), 127.6 (ddq, ^1J = 158.3 Hz, ^3J = 7.3 Hz, ^3J = 5.0 Hz, C-3/-5), 128.0 (sharp d, ^1J = 159.1 Hz, C-4), 135.4 (dq, ^3J = 7.5 Hz, ^2J = 6 Hz, C-2/-6), 137.9 (dq, ^3J = 16.0 Hz, ^2J = 6.7 Hz, C-2′), 139.5 (unresolved m, C-1) ppm, assigned through

comparison with (*Z*)-**9**, (*E*)-**5**, and α-iodo-2,6-dimethylstyrene,[6] combined with selective {2-/6-CH_3} decoupling that showed C-1 simplified and C-2/-6 as a d with ^3J = 7.5 Hz; IR (KBr) ν 3060, 3035, 3015, 2965, 2935, 2908, 2847, 1464 (s), 833, 772 (s), 704 (s) cm^{-1}. Anal. calcd for $C_{11}H_{13}I$ (272.13): C, 48.55; H, 4.81. Found: C, 48.86; H, 4.74.

(*Z*)-1′-Iodo-1′-(2,6-dimethylphenyl)propene [(*Z*)-9]. Purified dimeric (*Z*)-**1**&*t*-BuOMe, prepared from the bromoalkenes[11] (*Z*,*E*)-**5** (250 mg, 1.11 mmol), was transformed into crystalline (*E*)-**1**&3THF and dissolved at –70 °C in dry toluene (1.0 mL), then titrated with stirring at –70 °C under argon gas cover with a solution of elemental iodine (280g, 1.11 mmol) in dry toluene (1.5 mL) for a persisting coloring. After addition of two further droplets of the iodine solution, the mixture was kept at –70 °C for 15 min, then wamed up and diluted with water (12 mL) and Et_2O. The aqueous layer was shaken with Et_2O (3 × 4 mL); the four Et_2O phases were combined, shaken with aqueous $NaHSO_3$ (37%, 2 × 4 mL), washed with distilled water until neutral, dried over $MgSO_4$, filtered, and concentrated. The crude, slightly light-sensitive material (80 mg, 26%) contained (*Z*)-**9** and not more than a trace of (*E*)-**9**; it was kept and distilled with protection from light to give liquid (*Z*)-**9** with bp 104–127 °C (bath temp.)/13 Torr. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.91 (d, ^3J = 6.3 Hz, 3H, 2′-CH_3 trans to aryl), 2.23 (s, 6H, 2-/6-CH_3), 5.53 (q, ^3J = 6.3 Hz, 1H, 2′-H), 7.01 and 7.07 (A_2B system, ^3J = 7.5 Hz, 2+1H, 3-/5-H and 4-H) ppm, assigned through the NOESY correlations 2′-H ↔ 2-/6-CH_3 ↔ 3-/5-CH_3; ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 20.0 (qd, ^1J = 127 Hz, ^3J = ca. 4.5 Hz, 2-/6-CH_3), 22.6 (qd, ^1J = 127 Hz, ^2J = 3.4 Hz, 2′-CH_3 trans to aryl), 103.3 (dq, $^2J \approx {}^3J$ = 8.4 Hz, C-1′), 127.5 (ddq, ^1J = 158 Hz, ^3J = 7.5 Hz, ^3J = 5.0 Hz, C-3/-5), 127.9 (sharp d, ^1J = 159 Hz, C-4), 133.7 (dq, ^3J = 153.5 Hz, ^2J = 7.0 Hz, C-2′), 135.9 (dq, ^3J = 7.6 Hz, ^2J = 6.3 Hz, C-2/-6), 142.9 (unresolved m, C-1) ppm, assigned through the γ- aryl[33] effect, comparison with(*E*)-**9** and the bromoalkene[11] (*Z*)-**5**, and selective {2,6-CH_3} decoupling → 2-/6-*C*H_3 as a d, C-2/-6 as a d ^3J = 7.6 Hz, and C-3/-5 as a dd; IR (film) ν 3064, 3018, 2947, 2916, 2852, 1465, 769, 708 cm^{-1}. Anal. calcd for $C_{11}H_{13}I$ (272.13): C, 48.55; H, 4.81. Found: C, 49.87; H, 4.89.

1′-(2,6-Dimethylphenyl)-1′-(trimethylstannyl)propene [(*Z*)- and (*E*)-10]. Purified dimeric (*Z*)-**1**&*t*-BuOMe, obtained from the bromoalkenes[11] (*Z*,*E*)-**5** (500 mg, 2.22 mmol), was converted into crystalline (*E*)-**1**&3THF and dissolved at –70 °C in dry toluene (2.0 mL). Trimethylstannyl chloride (440 mg, 2.21 mmol) in dry toluene (3.0 mL) was added dropwis at –70 °C under argon gas cover to the stirred solution and produced a copious, colorless precipitate. After 20 min, the mixture was wamed up to rt and diluted with distilled water (50 mL). The

aqueous phase was shaken with Et_2O (3 × 15 mL), and the four Et_2O phases were combined, washed with distilled water until neutral, dried over $MgSO_4$, filtered, and concentrated. The crude oil (362 mg, 53%) distilled at 60–75 °C (bath temp.)/0.007 mbar to yield a pure mixture of (*Z*)-**10** and (*E*)-**10** (92:8). ^{1}H NMR of (*Z*)-**10** ($CDCl_3$, 400 MHz) δ 0.09 (s, ^{119}Sn satellites ^2J = 53.7 Hz, 9H, $SnMe_3$), 1.92 (d, ^3J = 6.5 Hz, ^{119}Sn satellites ^4J = 12 Hz, 3H, 2′-CH_3 trans to aryl), 2.09 (s, 6H, 2-/6-CH_3), 6.01 (q, ^3J = 6.5 Hz, ^{119}Sn satellites ^3J = 141.8 Hz, 1H, 2′-H), 6.93 and 6.97 (A_2B system, ^3J = 7.2 Hz, 2+1H, 3-/5-H and 4-H) ppm, assigned through comparison with $^3J(^{119}Sn,2'\text{-H})$ = 156.6 z (trans) and 73.9 Hz (cis) as published[36] for [α-(2,6-di-*tert*-butylphenyl)vinyl]trimethylstannane; ^{1}H NMR of (*E*)-**10** ($CDCl_3$, 400 MHz) δ 0.07 (s, $SnMe_3$), 1.45 (d, ^3J = 6.4 Hz, ^{119}Sn satellites ^4J = 11 Hz, 2′-CH_3 cis to aryl), 2.07 (s, 6H, 2-/6-CH_3), 5.96 (q, ^3J = 6.4 Hz, ^{119}Sn satellites ^3J = 76 Hz, 2′-H) ppm, others not identified, assigned as above; ^{13}C NMR of (*Z*)-**10** ($CDCl_3$, 100.6 MHz) δ –8.4 (s, ^{119}Sn satellites ^1J = 336.5 Hz, $SnMe_3$), 20.2 (^{119}Sn satellites ^3J = 45.5 Hz, 2′-CH_3 trans to aryl), 21.0 (2-/6-CH_3), 124.8 (C-4), 127.0 (C-3/-5), 133.9 (^{119}Sn satellites ^3J = 15 Hz, C-2/-6), 136.0 (^{119}Sn satellites ^2J = 22.5 Hz, C-2′), 145.5 (^{119}Sn satellites ^2J = 25 Hz, C-1), 146.2 ($^1J_{SnC}$ not detected, C-1′) ppm, assigned through comparison with the published[36] ^{119}Sn,^{13}C coupling constants of [α-(2,6-di-*tert*-butylphenyl)vinyl]trimethylstannane; ^{13}C NMR of (*E*)-**10** ($CDCl_3$, 100.6 MHz) δ –8.9 (s, $SnMe_3$), 133.3 (C-2/-6), 135.4 (C-2′) ppm, others not identified; IR (film) ν 3064, 3014, 2967 (s), 2913 (s), 1621, 1465, 765 (s), 527 cm^{-1}. Anal. calcd for $C_{14}H_{22}Sn$ (309.0): C, 54.41; H, 7.17. Found: C, 54.75; H, 7.22.

1′-(2,6-Dimethylphenyl)-1′-(trimethylsilyl)propene [(*Z*)- and (*E*)-11]. Purified (*Z*)-**1**&*t*-BuOMe, obtained from the bromoalkenes [11] (*Z*,*E*)-**5** (162 mg, 0.72 mmol), was dissolved in anhydrous THF (0.70 mL) under argon gas cover and cooled to –78 °C, then treated with chlorotrimethylsilane (0.183 mL, 1.44 mmol) and swirled shortly for mixing, warmed up, and diluted with Et_2O (5 mL) and distilled water (5 mL). The aqueous layer was shaken with Et_2O (2 × 5 mL) and discarded. The combined Et_2O phases were washed with water until neutral, dried over $MgSO_4$, filtered, and concentrated to yield an *E*/*Z* = 52:48 mixture of **11** as the only products (57 mg, 36%). A larger sample (*E*/*Z* = 6:4) from different runs was used for distillative purification and analytical characterizations: Bp 120–125 °C (bath temp.)/13 Torr with (*Z*)-**11** enriched in the higher-boiling fraction. ^{1}H NMR of (*E*)-**11** ($CDCl_3$, 400 MHz) δ 0.04 (s, 9H, $SiMe_3$), 1.42 (d, ^3J = 6.4 Hz, 3H, 2′-CH_3 cis to aryl), 2.08 (s, 6H, 2-/6-CH_3), 6.17 (q, ^3J = 6.4 Hz, 1H, 2′-H), 6.99 (quasi-s, 3H, 3-/4-/5-H) ppm, assigned through the NOESY correlations 3-/5-H ↔ 2-/6-CH_3 ↔ 2′-CH_3 ↔ 2′-H ↔ $SiMe_3$; ^{1}H NMR of (*Z*)-**11** ($CDCl_3$, 400 MHz) δ 0.09 (s, 9H,

SiMe$_3$), 1.95 (d, ^3J = 7.0 Hz, 3H, 2′-CH$_3$ trans to aryl), 2.12 (s, 6H, 2-/6-CH$_3$), 5.99 (q, ^3J = 7.0 Hz, 1H, 2′-H), 6.96 (quasi-s, 3H, 3-/4-/5-H) ppm, assigned through the NOESY correlations 3-/5-H ↔ 2-/6-CH$_3$ ↔ 2′-H ↔ 2′-CH$_3$ ↔ SiMe$_3$; ^{13}C NMR of (*E*)-**11** (CDCl$_3$, 100.6 MHz) δ –0.46 (q, SiMe$_3$), 15.90 (q, 2′-CH$_3$ cis to aryl), 20.39 (q, 2-/6-CH$_3$), 125.10 (d, C-4), 127.05 (d, C-3/-5), 134.31 (quat, C-2/-6), 136.24 (d, C-2′), 140.99 (quat, C-1), 144.17 (quat, C-1′) ppm, assigned through the following ^3J and ^2J COLOCS (7 Hz) cross-peaks. ^3J: 2′-C*H*$_3$ ↔ C-1′ ↔ Si(C*H*$_3$)$_3$ ↔ Si(*C*H$_3$)$_3$, 2-/6-C*H*$_3$ ↔ C-1, 3-/5-H ↔ 2-/6-*C*H$_3$, 4-H ↔ C-2/-6; ^2J: 2′-C*H*$_3$ ↔ C-2′, 2′-*C*H$_3$ ↔ 2′-H, 2-/6-C*H*$_3$ ↔ C-2/-6, 3-/5-H ↔ C-4, 4-H ↔ C-3/-5; ^{13}C NMR of (*Z*)-**11** (CDCl$_3$, 100.6 MHz) δ +0.20 (q, SiMe$_3$), 18.15 (q, 2′-CH$_3$ trans to aryl), 21.09 (q, 2-/6-CH$_3$), 124.96 (d, C-4), 126.94 (d, C-3/-5), 134.58 (quat, C-2/-6), 139.03 (d, C-2′), 142.89 (quat, C-1′), 145.87 (quat, C-1) ppm, assigned as above; IR (film) ν 2956, 1606 (w), 1463, 1249 (s), 893, 838 (s), 766 cm^{-1}. Anal. calcd for C$_{14}$H$_{22}$Si (218.41): C, 75.99; H, 10.15. Found: C, 77.59; H, 10.31.

1′,1′-Dicyclopropyl-2′-(2,6-dimethylphenyl)but-2′-en-1′-ol [(*Z*)- and (*E*)-12a]. Purified (*Z*)-**1**&*t*-BuOMe, prepared from the bromoalkenes[11] (*Z*,*E*)-**5** (152 mg, 0.67 mmol), was dissolved in anhydrous THF (0.50 mL) under argon gas cover and cooled to –78 °C. Dicyclopropyl ketone (0.10 mL, 0.89 mmol) was added; it precipitated but reacted during warm-up to rt. The mixture was dissolved in Et$_2$O (3 mL) and distilled water (5 mL), and the aqueous layer was extracted with Et$_2$O (2 × 5 mL). The combined Et$_2$O phases were washed with distilled water until neutral, dried over Na$_2$SO$_4$, filtered, and concentrated to give a yellow oil (96 mg, 55%) with (*E*)- and (*Z*)-**12a** (53:47). The NMR analyses were carried out with a sample that contained more (*Z*)-**12a** [prepared from (*E*)-**1**] and another sample of pure (*E*)-**12a** that distilled at 80–100 °C (bath temp.)/0.02 mbar as a colorless liquid. ^{1}H NMR of (*E*)-**12a** (CDCl$_3$, 400 MHz) δ 0.27 (a), 0.38 (b), 0.41 (c), 0.50 (d), and 1.01 (e) (5 × m, 5 × 2H, 2 × cycloporpyl), 0.97 (s, 1H, OH), 1.35 (d, ^3J = 6.7 Hz, 3H, 3′-CH$_3$ cis to aryl), 2.26 (s, 6H, 2-/6-CH$_3$), 6.22 (q, ^3J = 6.7 Hz, 1H, 3′-H), 7.03 and 7.07 (A$_2$B system, ^3J = 7.2 Hz, 2+1H, 3-/5-H and 4-H) ppm, assigned through COLOCS cross-peaks (see below) and the NOESY correlation 3′-H ↔ cyclopropyl-C*H*; ^{1}H NMR of (*Z*)-**12a** (CDCl$_3$, 400 MHz) δ 0.28 (a), 0.41 (b), 0.45 (c), 0.62 (d), and 1.22 (e) (5 × m, 5 × 2H, 2 × cycloporpyl), 1.05 (s, 1H, OH), 2.08 (d, ^3J = 7.5 Hz, 3H, 3′-CH$_3$ trans to aryl), 5.37 (q, ^3J = 7.5 Hz, 1H, 3′-H), 7.00 and 7.02 (A$_2$B system, ^3J = ca. 8 Hz, 2+1H, 3-/5-H and 4-H) ppm, assigned through comparison with (*E*)-**12a**; ^{13}C NMR of (*E*)-**12a** (CDCl$_3$, 100.6 MHz) δ 0.41 (a) and 1.89 (b) (2 × t, ^1J = 160 Hz, 2 × 2 cyclopropyl-CH$_2$), 14.38 (qd, ^1J = 126 Hz, ^3J = 3.9 Hz, 3′-CH$_3$ cis to aryl), 19.89 (d, ^1J = 156 Hz, 2 × cyclopropyl-CH), 20.90 (qd, ^1J = 126 Hz, 2-/6-CH$_3$), 73.44

(broadened s, C–OH), 122.37 (dq, ^1J = 152 Hz, ^2J = 6.7 Hz, C-3′), 126.54 (sharp d, ^1J = 158.4 Hz, C-4), 127.27 (dm, ^1J = 156 Hz, C-3/-5), 137.28 (m, C-1), 137.38 (m, C-2/-6), 147.02 (q, ^3J = 6.2 Hz, C-2′) ppm, assigned through HETCOR [showing protons (a) and (c) at ^{13}C(a) but protons (b) and (d) at ^{13}C(b)] and the following COLOCS (7 Hz) ^3J and ^2J cross peaks. ^3J: C-1 ↔ 3′-H ↔ C–OH ↔ CH_2(b, c, and d), cyclopropyl-C*H* ↔ cyclopropyl-*C*H (second ring), 3′-CH_3 ↔ C-2′, 4-H ↔ C-2/-6, C-3/-5 ↔ 5-/3-H ↔ C-1 ↔ 2-/6-CH_3; ^2J: 3′-CH_3 ↔ C-3′, 2-/6-CH_3 ↔ C-2/-6; ^2J and/or ^3J: CH_2(a) ↔ *C*H$_2$(b), CH_2(d) ↔ *C*H$_2$(a) ↔ CH_2(b) ↔ cyclopropyl-*C*H ↔ CH_2(c) ↔ *C*H$_2$(b); ^{13}C NMR of (*Z*)-**12a** ($CDCl_3$, 100.6 MHz) δ 0.91 and 2.78 (2 × t, 2 × 2 cyclopropyl-CH_2), 15.74 (q, 3′-CH_3 trans to aryl), 20.41 (d, 2 × cyclopropyl-CH), 21.64 (q, 2-/6-CH_3), 73.20 (quat, C–OH), 125.57 (d, C-3′), 126.36 (d, C-4), 127.18 (d, C-3/-5), 137.28 (quat, C-2/-6), 142.23 (quat, C-1), 147.38 (quat, C-2′) ppm, assigned through comparison with (*E*)-**12a**; IR of (*E*)-**12a** (film) ν 3572 (sharp O–H), 3011, 2957, 2926, 2857, 1461, 1376, 1023, 916, 769 cm^{-1}. Anal. calcd for $C_{18}H_{24}O$ (256.39): C, 84.32; H, 9.44. Found: C, 84.41; H, 9.52.

(*E*)-4′-*Tert*-butyl-5′,5′-dimethyl-3′-(2,6-dimethylphenyl)hex-2′-en-4′-ol [(*E*)-12b]. Purified (*Z*)-**1**&*t*-BuOMe, obtained from the bromoalkenes[11] (*Z*,*E*)-**5** (105 mg, 0.47 mmol), was suspended in anhydrous toluene (1.50 mL) at rt and treated with di-*tert*-butyl ketone[27] (0.080 mL, 0.47 mmol) under argon gas cover. The mixture was gently shaken until (*Z*)-**1** had completely gone into solution (13 min), whereafter the generated, voluminous alcoholate of (*E*)-**12b** began to precipitate. All of (*Z*)-**1** had been consumed, as shown after 55 min through termination with solid CO_2 and aqueous NaOH (2 M, 5 mL), which afforded no carboxylic acids. The non-acidic products were isolated from the washed Et_2O extracts (3 × 5 mL) as a 83:17 mixture of (*E*)-**12b** (57 mg, 35%) and the olefin (*Z*)-**7** only. A larger sample was distilled at 103–113 °C (bath temp.)/0.012 mbar. ^{1}H NMR of (*E*)-**12b** ($CDCl_3$, 400 MHz) δ 1.23 (s, 18H, 2 × *tert*-butyl), 1.43 (d, ^3J = 6.9 Hz, 3H, 2′-CH_3 cis to aryl), 1.73 (s, 1H, OH), 2.37 (s, 6H, 2-/6-CH_3), 6.02 (q, ^3J = 6.9 Hz, 1H, 2′-H), 7.00 and 7.04 (A_2B system, ^3J = 7.1 Hz, 2+1H, 3-/5-H and 4-H) ppm, assigned through the NOESY cross-peaks 2′-H ↔ C(CH_3)$_3$ ↔ 4′-OH ↔ 2-/6-CH_3 ↔ 2′-CH_3; ^{13}C NMR of (*E*)-**12b** ($CDCl_3$, 100.6 MHz) δ 15.66 (qd, ^1J = 126.1 Hz, ^3J = 3.8 Hz, 2′-CH_3 cis to aryl), 23.39 (qm, ^1J = 126.6 Hz, apparent J = 5.4 Hz, 2-/6-CH_3), 30.76 (broadened qm, ^1J = 125 Hz, 6 × *tert*-butyl-CH_3), 43.32 (dm, ^3J = 2.9 Hz, ^2J = ca. 3.5 Hz, 2 × C-5′), 86.09 (unresolved, C–OH), 126.74 (sharp d, ^1J = 159.0 Hz, C-4), 128.53 (ddqd, ^1J = 157 5 Hz, ^3J = 7.5 Hz, ^3J = 6 Hz, ^2J = 1.15 Hz, C-3/-5), 128.67 (dq, ^1J = 150 2 Hz, ^2J = 6.9 Hz, C-2′), 138.85 (unresolved, C-1), 139.48 (dq, ^3J = 7.2 Hz, ^2J = 6 Hz, C-2/-6), 142.78 (broadened q, ^3J = 6 Hz, ^2J

= ca. 0, C-3′) ppm, assigned through selective {^{1}H} decoupling as follows: {C(CH_3)$_3$} → C-5′ as a d ^3J = 2.9 Hz and C–OH as a very broad d ^3J = ca. 4 Hz, {2′-CH$_3$} → C-2′ as a sharp d 150.2 Hz and C-3′as a sharp s, {2-/6-CH_3} → C-3/-5 as a ddd with ^1J = 157 5 Hz, ^3J = 7.5 Hz, ^2J = 1.15 Hz, C-1 as dt with ^3J = 9 Hz, ^3J = ca. 6.3 Hz, and C-2/-6 as a sharp d ^3J = 7.2 Hz; IR of (*E*)-**12b** (film) ν 3588 (sharp O–H), 2962, 2928, 1468, 1456, 1392, 1371, 981, 770 cm^{-1}. Anal. calcd for $C_{20}H_{32}O$ (288.41): C, 83.27; H, 11.18. Found: C, 82.78; H, 10.98.

(*E*)-4′-Isopropyl-5′-methyl-3′-(2,6-dimethylphenyl)hex-2′-en-4′-ol [(*E*)-12c]. Purified (*Z*)-**1**&*t*-BuOMe, prepared from the bromoalkenes[11] (*Z*,*E*)-**5** (177 mg, 0.79 mmol), was covered with dry toluene (1.30 mL) and cooled under argon gas in an ice-bath. After a few minutes and subsequent addition of diisopropyl ketone (0.113 mL, 0.79 mmol), the mixture was gently shaken several times in the ice-bath during 120 s, whereupon almost all of the starting material had disappeared. After another 30 s, the mixture was poured onto solid CO_2, warmed up, and dissolved in Et_2O (5 mL) and aqueous NaOH (2 M, 5 mL). The aqueous layer was extracted with Et_2O (2 × 5 mL) and then acidified, but it delivered no acids which would have pointed to the enolate of diisopropyl ketone or to unconsumed (*Z*)-**1**&*t*-BuOMe. The three Et_2O layers were combined, washed with distilled water until neutral, dried over $MgSO_4$, filtered, and concentrated to yield (*E*)-**12c** and a trace of the olefin (*Z*)-**7** as the only products. (*E*)-**12c** decomposed on distillation (see **14**), but it was obtained as an almost pure liquid (30 mg, 15%) through sharp drying at rt. ^{1}H NMR of (*E*)-**12c** ($CDCl_3$, 400 MHz) δ 1.04 and 1.06 (2 × d, ^3J = 6.9 Hz, 6+6H, 2 × CH$_3$-6′a and 2 × CH$_3$-6′b, respectively), 1.35 (d, ^3J = 6.7 Hz, 3H, 2′-CH$_3$ cis to aryl), 2.10 (sept, ^3J = 6.9 Hz, 2H, 2 × 5′-H), (OH not detected), 2.21 (s, 6H, 2-/6-CH$_3$), 5.68 (q, ^3J = 6.7 Hz, 1H, 2′-H), 7.03 and 7.08 (A_2B system, ^3J = 7.2 Hz, 2+1H, 3-/5-H and 4-H) ppm, assigned through the NOESY correlations 5′-H ↔ 2′-H ↔ 2′-CH$_3$ ↔ 2-/6-CH$_3$ ↔ 3-/5-H; ^{13}C NMR of (*E*)-**12c** ($CDCl_3$, 100.6 MHz) δ 14.91 (qd, ^1J = 125.9 Hz, ^2J = 4.2 Hz, 2′-CH$_3$ cis to aryl), 18.13 and 18.71 (2 × qqi, ^1J = 125.5 Hz, apparent J = ca. 5 Hz, 2 × CH$_3$-6′a and 2 × CH$_3$-6′b, respectively), 21.20 (qd, ^1J = 126.7 Hz, apparent J = 5 Hz, 2-/6-CH$_3$), 33.04 (broadened d, ^1J = 124.7 Hz, 2 × C-5′), 81.43 (unresolved, C–OH), 123.12 (dq, ^1J = 151.1 Hz, ^2J = 6.9 Hz, C-2′), 126.77 (sharp d, ^1J = 159.1 Hz, C-4), 127.58 (dqd, ^1J = 157.6 Hz, C-3/-5), 136.28 (unresolved, C-1), 138.77 (dq, appparent J = 6.1 Hz, C-2/-6), 142.41 (unresolved, C-3′) ppm, assigned through HSQC (including a ↔ a and b ↔ b) and the following ^3J and ^2J HMBC cross-peaks. ^3J: *C*H$_3$-6′a ↔ C*H*$_3$-6′b ↔ C–OH ↔ C*H*$_3$-6′a ↔ *C*H$_3$-6′b, C-1 ↔ 2-/6-C*H*$_3$ ↔ C-3/-5 ↔ 5-/3-H ↔ 6-/2-*C*H$_3$, 3-/5-H ↔ C-1 ↔ 2′-H ↔ *C*–OH, 5′-H ↔ second C-5′, 2′-C*H*$_3$ ↔ C-3′, 4-H ↔ C-2/-

6; ^2J: CH_3-6′a ↔ C-5′ ↔ CH_3-6′b, CH_3-6′a and b ↔ 5′-H ↔ *C*-OH, 2-/6-CH_3 ↔ C-2/-6, 2′-H ↔ 2′-*C*H$_3$, C-2′ ↔ 2′-CH_3, no correlation to C-3′; IR of (*E*)-**12b** (film) ν 3580 (sharp O–H), ca. 3540 (broad O–H), 2969, 2925, 2878, 1469, 1459, 1387, 993, 770 cm^{-1}. Anal. calcd for $C_{18}H_{28}O$ (260.42): C, 83.02; H, 10.84. Found: C, 82.45; H, 10.69.

2,2,4-Trimethyl-3-oxopentanoic Acid[28] (13). This carboxylation product of the enolate of diisopropyl ketone was found in the aqueous alkaline phases of several runs in THF. ^{1}H NMR (CCl_4, 80 MHz) δ 1.07 (d, ^3J = 6.9 Hz, 6H, 2 × 4-CH$_3$), 1.37 (s, 6H, 2 × 2-CH$_3$), 2.91 (sept, ^3J = 6.9 Hz, 1H, 4-H) ppm.

4′-Isopropyl-5′-methyl-3′-(2,6-dimethylphenyl)hexa-1′,3′-diene (14). This product of H_2O elimination was formed during attempted distillations of (*E*)-**12c** at 140–152 °C (bath temp.)/13 Torr and even at 63–65 °C (bath temp.)/0.02 mbar as a colorless liquid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.88 (d, ^3J = 6.8 Hz, 6H, 2 × 5′-CH$_3$ cis to aryl), 1.38 (d, ^3J = 7.3 Hz, 6H, 2 × 5′-CH$_3$ trans), 2.11 (s, 6H, 2-/6-CH$_3$), 2.23 (sept, ^3J = 6.8 Hz, 1H, 5′-H cis), 2.66 (sept, ^3J = 7.3 Hz, 1H, 5′-H trans), 4.26 (dd, ^3J = 17.0 Hz, ^2J = 2.1 Hz, 1H, 1′-H syn to C-3′), 4.85 (dd, ^3J = 10.5 Hz, ^2J = 2.1 Hz, 1H, 1′-H anti), 7.02 and 7.07 (A_2B system, ^3J = 7.5 Hz, 2+1H, 3-/5-H and 4-H), 7.09 (dd, ^3J = 17.0 and 10.5 Hz, 1H, 2′-H) ppm, assigned through HSQC and HMBC cross-peaks (see below); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 19.52 (q, 2-/6-CH$_3$), 20.06 (q, 2 × 5′-CH$_3$ cis to aryl), 23.15 (q, 2 × 5′-CH$_3$ trans), 27.15 (d, C-5′ trans), 33.69 (d, C-5′ cis), 113.3 (t, CH$_2$-1′), 126.04 (d, C-4) 127.02 (C-3/-5), 132.41 (quat, C-3′), 134.84 (d, C-2′), 136.48 (quat, C-2/-6), 139.47 (quat, C-1), 150.46 (quat, C-4′) ppm, assigned through HSQC (cis and trans 5′-CH$_3$) and the following ^3J and ^2J HMBC cross-peaks. ^3J: CH_3-6′ cis ↔ second CH_3-6′ cis ↔ C-4′ ↔ CH_3-6′ trans ↔ second CH_3-6′ trans, C-1 ↔ 2-/6-CH_3 ↔ C-3/-5; ^2J: CH_3-6′ cis ↔ C-5′ cis, CH_3-6′ trans ↔ C-5′ trans, 2-/6-CH_3 ↔ C-2/-6; IR (film) ν 2961, 2928, 2872, 1615 (w), 1462, 768 cm^{-1}. Anal. calcd for $C_{18}H_{26}$ (242.40): C, 89.19; H, 10.81. Found: C, 88.72; H, 11.06.

ASSOCIATED CONTENT

Lithiation shifts of **1** and **3** (Figure S1); rate and equilibria measurements (Figures S2 and S3, Tables S1–S4); ^{13}C NMR spectra of dimeric (*Z*)-**1** (Figure S4), monomeric (*Z*,*E*)-**1** (Figure S5), and dimeric **3** (Figure S6); primary NMR data (Tables S5–S13). This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

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