A Convenient Allylic Functionalization of Bis(prop-2-enyl)methanol by Direct Trimetalation

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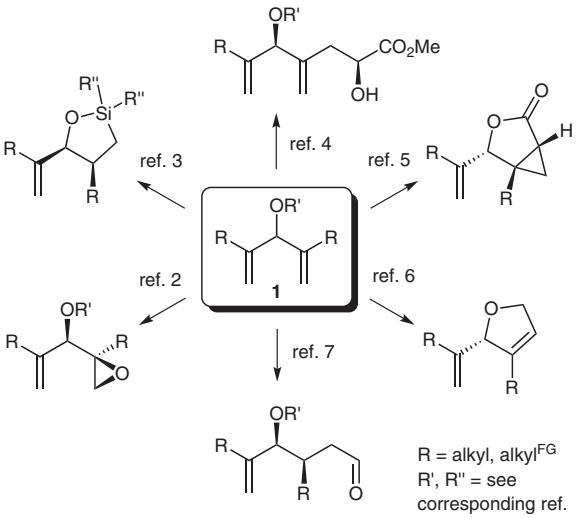
Abstract: A practical synthesis of functionalized symmetrical dialkenylcarbinols has been developed. Key feature is a direct trilithiation of readily available bis(prop-2-enyl)methanol followed by trapping of the trianion with various electrophiles. This simple protocol allows rapid derivatization and preparation of compounds inaccessible by currently existing methods.

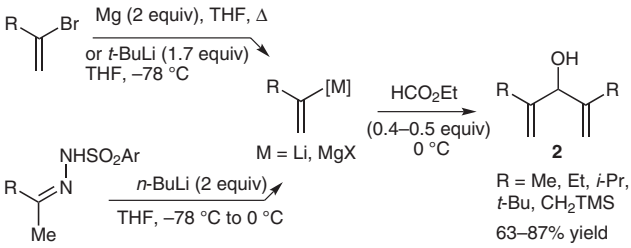
Key words: alkenes, alcohols, lithiation, metalations, organometallic reagent

Mirror symmetrical dialkenylcarbinol moieties of type **1** are important building blocks particularly appealing for desymmetrizing processes.[1] A growing number of useful enantioselective transformations have appeared in these past years such as asymmetric epoxidation,[2] hydrosilylation,[3] carbonyl ene addition,[4] cyclopropanation,[5] ring-closing metathesis,[6] and hydroformylation[7] (Scheme 1).



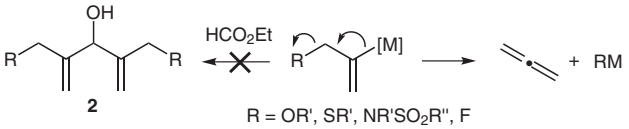
Scheme 1 Enantioselective desymmetrizing processes of dialkenylcarbinol ethers and esters **1**

Nevertheless the scope of these methodologies is limited by the scarcity of efficient synthetic procedures to access dialkenylcarbinols **2** bearing diversely functionalized substituents R (Scheme 2). In the course of our investigation towards a desymmetrizing hydroformylation reaction, we have developed an efficient access to this class of compounds through the addition of 2 equivalents of an alkenylmetal species to ethyl formate.[7b] The alkenylmetal intermediate is generated through Grignard synthesis, halogen/lithium exchange with *t*-BuLi or, alternatively, through a Shapiro reaction of the trisylhydrazone (trisyl = 2,4,6-triisopropylphenyl).



Scheme 2 Synthetic route to dialkenylcarbinols bearing alkyl substituents

Unfortunately, this approach failed as we tried to prepare dialkenylcarbinols having electron-withdrawing groups at the allylic position. This is mainly due to the propensity of the alkenylmetal to undergo 1,2-elimination, even at low temperatures, to furnish the allene (Scheme 3).[8]



Scheme 3 Competitive 1,2-elimination of the alkenylmetal species

To circumvent this problem we wondered whether such functionalized dialkenylcarbinol derivatives could be accessed through a direct functionalization of bis(prop-2-enyl)methanol (**3**) by deprotonation of both allylic positions and subsequent trapping of the trianion with an appropriate electrophile. This would additionally offer the opportunity for rapid derivatization from a common and readily available precursor.[9]

The deprotonation of methallylic alcohols is known.[10] Trost et al. have optimized and extensively used a lithiation protocol using an excess of *n*-BuLi/TMEDA complex in a Et_2O–THF mixture for silylation and stannylation of the formed dianions.[11] However, this method suffers from moderate yields mainly due to the formation of side prod-

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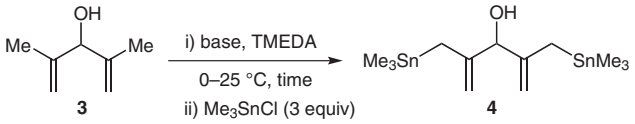
ucts resulting from undesired vinylic deprotonation. We report herein a general and efficient extension of this method allowing for the direct functionalization of bis(prop-2-enyl)methanol (**3**) through trimetalation.

We started our investigations by adapting the Trost protocol to our system,[11a] using Me_3SnCl as the electrophile as we were particularly interested in the rapid generation of carbinols bearing various trialkylstannane moieties (Table 1). Treatment of **3** with 5 equivalents of *n*-BuLi in a mixture of Et_2O–hexane–THF in the presence of TMEDA (6 equiv) at 0 °C, further stirring for 4 hours at 25 °C, and subsequent quenching with Me_3SnCl led to the detection of only traces of desired product **4** (entry 1). However, the reaction proved to proceed very cleanly with only unreacted starting material present, which left us optimistic for possible improvement. Indeed, switching to slightly more basic *s*-BuLi under otherwise identical conditions afforded smoothly the desired product in 44% isolated yield together with recovered **3** and only traces of monostannylated product (entry 2). While an increased reaction time led mostly to degradation (entry 3), the modification of the solvent polarity (without THF)[12] furnished after standard workup the desired product in 64% yield (entry 4). Finally, treatment of **3** with 2 additional equivalents of *s*-BuLi and TMEDA allowed the complete conversion to the trianion. Trapping with the tin electrophile gave **4** in 80% isolated yield (entry 5).

Table 1 Optimization of the Trimetalation Protocol of **3**

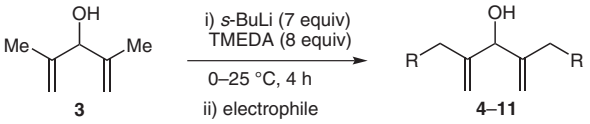


Entry	Base (equiv)	TMEDA (equiv)	Solvent (ratio)[a]	Time (h)	Yield (%)[b]
1	*n*-BuLi (5)	6	Et_2O–hexane–THF (2:1:1)	4	n.d.[c]
2	*s*-BuLi (5)	6	Et_2O–Cy–THF (2:1:1)	4	44
3	*s*-BuLi (5)	6	Et_2O–Cy–THF (2:1:1)	20	n.d.[d]
4	*s*-BuLi (5)	6	Et_2O–Cy (3:1)	4	64
5	*s*-BuLi (7)	8	Et_2O–Cy (3:2)	4	80

[a] Cy = cyclohexane.
[b] Isolated yields of pure **4**.
[c] Trace of product is detected according to TLC.
[d] Complex mixture.

With these optimized conditions in hand, we next turned our attention to investigate the reaction scope (Table 2). The method proved to tolerate even bulky electrophiles allowing a clean introduction of a Bu_3Sn substituent in good yields (entry 2). Trapping the trianion with an oxygen electrophile (Davis oxaziridine, entry 3) or with sulfur electrophiles (entries 4, 5) led to the desired products in fair to good yields, demonstrating the utility of this method since the corresponding products could not be obtained by our previous route. A range of allylsilane carbinols could be prepared (entries 6–8) as well. In this case, in situ deprotection of the silylated hydoxyl function occurred upon acidic workup.[13]

Table 2 Scope of the Transformation of **3**

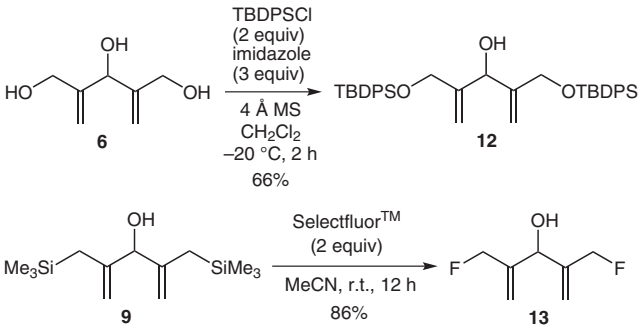


Entry	Electrophile (equiv)	Product (R)	Yield (%)
1	Me_3SnCl (3)	**4** (Me_3Sn)	80
2	Bu_3SnCl (3)	**5** (Bu_3Sn)	73
3	Davis oxaziridine (5)	**6** (OH)	31
4	PhSSPh (3)	**7** (PhS)	38
5	MeSSMe (5)	**8** (MeS)	60
6	Me_3SiCl (5)	**9** (Me_3Si)	75[a]
7	$Me_2PhSiCl$ (5)	**10** (Me_2PhSi)	72[a]
8	Et_3SiCl (5)	**11** (Et_3Si)	79[a]

[a] Overall yields after desilylation of the hydroxy group (see experimental section).

For further synthetic use, we could selectively protect the primary hydroxy functions of triol **6** to provide carbinol **12** in good yield (Scheme 4), which is a particularly interesting building block for polypropionate synthesis. While our attempts of trapping the trianion with various fluorine electrophiles were unsuccessful, we envisoned to get access to this interesting compound by functionalization of the diallylsilane **9** via an electrophilic fluorodesilylation reaction. Indeed, treatment of diallylsilane **9** with Selectfluor™ in acetonitrile overnight at room temperature furnished smoothly the difluoride **13** in high yield.[14]

In summary, we have developed a practical and efficient complementary access to functionalized symmetrical dialkenylcarbinols involving a direct trimetalation of readily available bis(prop-2-enyl)methanol (**3**). This method



Scheme 4 Further functionalization of the products

allows rapid derivatization and preparation of compounds otherwise inaccessible by previously developed strategies.

Reactions were performed in flame-dried glassware under argon (purity >99.998%). The solvents were dried by standard procedures, distilled, and stored under argon. Petroleum ether (PE) refers to the fraction with bp 40–60 °C. All temperatures quoted are uncorrected. ^{1}H, ^{13}C NMR spectra: Varian Mercury 300 HFCP, Bruker AM 400 with $CHCl_3$ as internal standard. ^{19}F NMR spectra: Bruker AM 400 with CCl_3F as external standard. Melting points: apparatus by Dr. Tottoli (Büchi). Elemental analyses: VarioEL (Elementaranalysen GmbH). Mass spectrometry: Thermo Finnigan MAT 8200 and TSQ 7000. Flash chromatography: Silica gel 40–63 mm (230–400 mesh, Macherey-Nagel). Organolithium reagents were titrated with 2-(phenylhydrazonomethyl)phenol.[15] The following compounds were prepared according to literature procedure: 2,4-dimethylpenta-1,4-dien-3-ol (**3**)[9] and 3-phenyl-2-(phenylsulfonyl)-1,2-oxaziridine (Davis oxaziridine).[16]

Functionalized Carbinols from 2,4-Dimethylpenta-1,4-dien-3-ol (3); General Procedure

To a stirred solution of **3** and freshly distilled TMEDA (8 equiv) in anhyd Et_2O (concd of **3** = 0.1 M) was added dropwise *s*-BuLi (7 equiv, 1.15–1.36 M in cyclohexane) at 0 °C, then the ice bath was removed and the resulting yellow mixture was stirred for 4 h at 25 °C. After cooling to 0 °C, the electrophile (3–5 equiv) was added (pure or dissolved in anhyd Et_2O or THF) in one portion and the mixture was allowed to warm to 25 °C and further stirred for 30 min. The mixture was diluted with Et_2O (5 mL/mmol of **3**), washed with an aq sat. $CuSO_4$ (10 mL/mmol of **3**), back extracted once with Et_2O (10 mL/mmol of **3**) and the combined organic layers were washed with H_2O (10 mL/mmol of **3**) and brine (10 mL/mmol of **3**), dried (K_2CO_3), and the solvents were removed in vacuo. Flash chromatography on silica gel furnished the corresponding carbinol (Table 2).

2,4-Bis[(trimethylstannyl)methyl]penta-1,4-dien-3-ol (4)

According to the general procedure, deprotonation of **3** (500 mg, 4.4 mmol) with *s*-BuLi (27.1 mL, 31.2 mmol, 7 equiv, 1.15 M) in the presence of TMEDA (5.3 mL, 35.6 mmol, 8 equiv) in Et_2O (44.5 mL) and subsequent quenching with Me_3SnCl (13.3 mL, 13.3 mmol, 3 equiv, 1 M in Et_2O) furnished after workup and chromatography [PE–Et_2O, 25:1 with 1% Et_3N, R_f = 0.50 (PE–EtOAc, 9:1)] the title compound **4** (1.55 g, 3.5 mmol, 80%) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.09 (t, *J* = 26 Hz, 18 H), 1.54 (d, *J* = 3.8 Hz, 1 H), 1.63 (dd, *J* = 11.7, 0.9 Hz, 2 H), 1.77 (dd, *J* = 11.7, 0.9 Hz, 2 H), 4.31 (pq, *J* = 3.9, 3.4 Hz, 1 H), 4.68 (pt, *J* = 10.6 Hz, 2 H), 4.82 (ptt, *J* = 10.5 Hz, 1.35 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = –8.9 (6 C), 16.4 (2 C), 80.1, 106.6 (2 C), 149.6 (2 C).

Anal. Calcd for $C_{13}H_{28}OSn_2$ (437.78): C, 35.67; H, 6.45. Found: C, 35.86; H, 6.37.

2,4-Bis[(tributylstannyl)methyl]penta-1,4-dien-3-ol (5)

According to the general procedure, deprotonation of **3** (400 mg, 3.5 mmol) with *s*-BuLi (19.2 mL, 24.9 mmol, 7 equiv, 1.30 M) in the presence of TMEDA (4.2 mL, 28.4 mmol, 8 equiv) in Et_2O (35.6 mL) and subsequent quenching with pure Bu_3SnCl (2.8 mL, 10.6 mmol, 3 equiv) furnished after workup and chromatography (PE–Et_2O, 25:1 with 1% Et_3N, R_f = 0.74 (PE–EtOAc, 9:1)] the title compound **5** (1.7 g, 2.5 mmol, 73%) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.83–0.93 (m, 30 H), 1.25–1.35 (m, 12 H), 1.43–1.53 (m, 12 H), 1.61 (dd, *J* = 11.8, 0.9 Hz, 2 H), 1.77 (dd, *J* = 11.7, 0.9 Hz, 2 H), 4.31 (pq, *J* = 3.4, 3.3 Hz, 1 H), 4.68 (td, *J* = 9.3, 1.0 Hz, 2 H), 4.83 (tt, *J* = 9.9 Hz, 1.2 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 9.9 (6 C), 13.8 (6 C), 14.1 (2 C), 27.4 (6 C), 29.2 (6 C,), 80.3, 106.5 (2 C), 150.2 (2 C).

HRMS: *m*/*z* calcd for $C_{27}H_{55}OSn_2$ [M – Bu]$^+$: 633.2290; found: 633.2299.

2,4-Bis[(*tert*-butyldiphenylsilyloxy)methyl]penta-1,4-dien-3-ol (12)

According to the general procedure (except for the workup), deprotonation of **3** (500 mg, 4.4 mmol) with *s*-BuLi (23.0 mL, 31.2 mmol, 7 equiv, 1.36 M) in the presence of TMEDA (5.3 mL, 35.6 mmol, 8 equiv) in Et_2O (44.5 mL) and subsequent quenching with Davis oxaziridine (5.82 g, 22.2 mmol, 5 equiv) dissolved in THF (18 mL) afforded, after workup (few drops of aq sat. NH_4Cl were added at 25 °C, 2 g of silica gel was poured into the mixture, and all volatile materials were removed in vacuo) and chromatography [EtOAc–MeOH, 95:5, R_f = 0.21 (EtOAc–MeOH, 95:5)] the triol **6** (199 mg, 1.3 mmol, 31%) as a light yellow oil, which was directly converted into **12**, as follows. Triol **6** (199 mg, 1.3 mmol) was suspended in CH_2Cl_2 (13 mL) in the presence of 4 Å MS and the mixture was stirred 1 h at 25 °C and then cooled to –20 °C. TBDPSCl (0.7 mL, 2.7 mmol, 2 equiv) was added to the mixture and a solution of imidazole (282 mg, 4.1 mmol, 3 equiv) in CH_2Cl_2 (5 mL) was slowly dropped into the mixture and the whole stirred for 2 h at this temperature. After warming to 25 °C, H_2O (5 mL) was added, the aqueous phase extracted with CH_2Cl_2 (3 × 8 mL), the combined organic phases were dried ($MgSO_4$) and the solvents removed in vacuo. Chromatography on silica gel (PE–CH_2Cl_2–EtOAc, 10:10:1, R_f = 0.24 (PE–EtOAc, 9:1)] furnished the title compound **12** (565 mg, 0.9 mmol, 66%) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.04 (s, 18 H), 3.08 (d, *J* = 5.8 Hz, 1 H), 4.06 (dt, *J* = 13.3, 1.0 Hz, 2 H), 4.15 (d, *J* = 13.4 Hz, 2 H), 4.76 (d, *J* = 5.6 Hz, 1 H), 5.21 (m, 2 H), 5.24 (m, 2 H), 7.31–7.43 (m, 12 H), 7.62–7.67 (m, 8 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.5 (2 C), 26.8 (6 C), 64.9 (2 C), 75.1, 112.5 (2 C), 127.7 (4 C), 129.8 (4 C), 133.2 (2 C), 135.6 (2 C), 147.1 (2 C, 2).

MS (CI, NH_3): *m*/*z* (%) = 621 ([M + H]$^+$, 16), 620 (36), 619 (72), 381 (29), 364 (27), 255 (100).

HRMS: *m*/*z* calcd for $C_{35}H_{39}O_3Si_2$ [M – *t*-Bu]$^+$: 563.2437; found: 563.2429.

2,4-Bis[(phenylsulfanyl)methyl]penta-1,4-dien-3-ol (7)

According to the general procedure, deprotonation of **3** (100 mg, 0.8 mmol) with *s*-BuLi (5.4 mL, 6.2 mmol, 7 equiv, 1.15 M) in the presence of TMEDA (1.0 mL, 7.1 mmol, 8 equiv) in Et_2O (8.9 mL) and subsequent quenching with PhSSPh (584 mg, 2.6 mmol, 3 equiv) dissolved in THF (3 mL) furnished after workup and chromatography [PE–EtOAc, 95:5, R_f = 0.14 (PE–EtOAc, 9:1)] the title compound **7** (99 mg, 0.3 mmol, 38%) as a light yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.21 (br s, 1 H), 3.42 (dd, *J* = 14.2, 1.2 Hz, 2 H), 3.59 (dd, *J* = 14.1, 1.1 Hz, 2 H), 5.03 (br s, 1 H), 5.13 (m, 2 H), 5.25 (pt, *J* = 1.1 Hz, 2 H), 7.17–7.21 (m, 2 H), 7.24–7.29 (m, 4 H), 7.31–7.35 (m, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 36.4 (2 C), 75.6, 115.7 (2 C), 126.6 (2 C), 128.9 (4 C), 130.3 (4 C), 135.9 (2 C), 143.8 (2 C).

MS (CI, NH_3): *m*/*z* (%) = 329 ([M + H]$^+$, 8), 311 (100), 219 (51), 201 (14).

Anal. Calcd for $C_{19}H_{20}OS_2$ (328.49): C, 69.47; H, 6.14; S, 19.52. Found: C, 69.29; H, 5.97; S, 19.60.

2,4-Bis[(methylsulfanyl)methyl]penta-1,4-dien-3-ol (8)
According to the general procedure, deprotonation of **3** (500 mg, 4.4 mmol) with *s*-BuLi (24.0 mL, 31.2 mmol, 7 equiv, 1.30 M) in the presence of TMEDA (5.3 mL, 35.6 mmol, 8 equiv) in Et_2O (44.5 mL) and subsequent quenching with pure MeSSMe (1.9 mL, 22.2 mmol, 5 equiv) afforded after workup and chromatography (PE–EtOAc, 95:5, R_f = 0.14 (PE–EtOAc, 9:1)] the title compound **8** (552 mg, 2.7 mmol, 60%) as a light yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.03 (s, 6 H), 2.92 (d, *J* = 5.7 Hz, 1 H), 3.02 (dd, *J* = 13.9, 1.1 Hz, 2 H), 3.18 (dd, *J* = 13.9, 1.0 Hz, 2 H), 4.98 (d, *J* = 5.1 Hz, 1 H), 5.11 (m, 2 H), 5.33 (t, *J* = 1.3 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.9 (2 C), 36.2 (2 C), 75.8, 115.3 (2 C), 143.5 (2 C).

MS (CI, NH_3): *m*/*z* (%) = 205 ([M + H]$^+$, 4), 186 (100), 157 (20), 139 (32), 109 (11).

Anal. Calcd for $C_9H_{16}OS_2$ (204.35): C, 52.90; H, 7.89; S, 31.38. Found: C, 52.86; H, 7.77; S, 31.23.

2,4-Bis[(trimethylsilyl)methyl]penta-1,4-dien-3-ol (9)
According to the general procedure, deprotonation of **3** (1.0 g, 8.9 mmol) with *s*-BuLi (45.8 mL, 62.4 mmol, 7 equiv, 1.36 M) in the presence of TMEDA (10.6 mL, 71.3 mmol, 8 equiv) in Et_2O (90 mL) and subsequent quenching with pure Me_3SiCl (5.7 mL, 44.5 mmol, 5 equiv) furnished after workup the crude trisilylated compound, which was hydrolyzed as follows. The crude mixture was dissolved in THF (72 mL), H_2SO_4 (18 mL, 1 M) was slowly added, and the mixture was stirred 30 min at 25 °C. Subsequently, Et_2O (70 mL) was added, the phases were separated, and the aqueous phase was extracted with additional Et_2O (3 × 40 mL). The combined organic phases were washed with aq sat. Na_2CO_3 (150 mL), dried (K_2CO_3), and the solvents were removed in vacuo. Flash chromatography [PE–Et_2O, 9:1, R_f = 0.32 (PE–Et_2O, 9:1)] and final bulb-to-bulb distillation (120–130 °C/0.1 mbar) afforded the title compound **9** (1.71 g, 6.6 mmol, 75%) as a colorless oil.

Analytical data are identical with the literature values.[7b]

2,4-Bis[(dimethylphenylsilyl)methyl]penta-1,4-dien-3-ol (10)
According to the general procedure, deprotonation of **3** (500 mg, 4.4 mmol) with *s*-BuLi (22.9 mL, 31.2 mmol, 7 equiv, 1.36 M) in the presence of TMEDA (5.3 mL, 35.6 mmol, 8 equiv) in Et_2O (45 mL) and subsequent quenching with pure $PhMe_2SiCl$ (3.7 mL, 22.2 mmol, 5 equiv) afforded after workup the crude trisilylated compound, which was hydrolyzed as follows. The crude was dissolved in THF (28 mL) and H_2SO_4 (10 mL, 1 M) was slowly added and the whole stirred for 1 h at 25 °C. Subsequent workup as for **9** and flash chromatography (PE–Et_2O, 9:1, R_f = 0.28 (PE–Et_2O 95:5)] furnished the title compound **10** (1.22 g, 3.1 mmol, 72%) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.291 (s, 6 H), 0.296 (s, 6 H), 1.55 (dd, *J* = 14.2, 1.0 Hz, 2 H), 1.73 (dd, *J* = 14.2, 1.0 Hz, 2 H), 4.02 (d, *J* = 3.0 Hz, 1 H), 4.70 (d, *J* = 0.8 Hz, 2 H), 4.86 (pt, *J* = 1.26 Hz, 2 H), 7.33–7.35 (m, 6 H), 7.48–7.50 (m, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = –2.7 (s, 4 C), 21.0 (2 C), 79.7, 110.3 (2 C), 127.8 (4 C), 129.1 (2 C), 133.7 (4 C), 139.0 (2 C), 146.4 (2 C).

MS (EI): *m*/*z* (%) = 380 (M$^+$, 0.5), 228 (5), 209 (17), 135 (100), 107 (5).

Anal. Calcd for $C_{23}H_{32}OSi_2$ (380.67): C, 72.57; H, 8.47. Found: C, 72.29; H, 8.40.

2,4-Bis[(triethylsilyl)methyl]penta-1,4-dien-3-ol (11)
According to the general procedure, deprotonation of **3** (500 mg, 4.4 mmol) with *s*-BuLi (22.9 mL, 31.2 mmol, 7 equiv, 1.36 M) in the presence of TMEDA (5.3 mL, 35.6 mmol, 8 equiv) in Et_2O (45 mL) and subsequent quenching with Et_3SiCl (3.8 mL, 22.2 mmol, 5 equiv) furnished after workup the crude trisilylated compound, which was hydrolyzed as follows. The crude mixture was dissolved in THF (23 mL), H_2SO_4 (12 mL, 3 M) was slowly added, and the mixture was stirred overnight at 25 °C. Subsequent workup as described for **9**, flash chromatography (PE–Et_2O, 95:5, R_f = 0.50 (PE–Et_2O, 9:1)] and final bulb-to-bulb distillation (200–210 °C/0.1 mbar) afforded the title compound **11** (1.19 g, 3.5 mmol, 79%) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.57 (q, *J* = 8.1 Hz, 12 H), 0.94 (t, *J* = 8.0 Hz, 18 H), 1.37 (dd, *J* = 14.3, 1.0 Hz, 2 H), 1.52 (d, *J* = 4.0 Hz, 1 H), 1.58 (dd, *J* = 14.3, 1.0 Hz, 2 H), 4.31 (d, *J* = 3.2 Hz, 1 H), 4.79 (m, 2 H), 4.99 (t, *J* = 1.3 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 3.6 (6 C), 7.4 (6 C), 16.4 (2 C), 80.2, 109.6 (2 C), 147.4 (2 C).

MS (CI, NH_3): *m*/*z* (%) = 341 ([M + H]$^+$, 21), 323 (47), 311 (55), 209 (100), 131 (97), 115 (36), 103 (33).

Anal. Calcd for $C_{19}H_{40}OSi_2$ (340.69): C, 66.98; H, 11.83. Found: C, 67.29; H, 11.82.

2,4-Bis(fluoromethyl)penta-1,4-dien-3-ol (13)
To a solution of **9** (1.0 g, 3.9 mmol) in MeCN (30 mL) was added Selectfluor™ (2.7 g, 7.7 mmol, 2 equiv) under argon and the mixture was stirred overnight. Then silica gel (2 g) was added, and the mixture was evaporated to dryness. Flash chromatography of the residue (PE–Et_2O, 8:2, R_f = 0.11 (PE–EtOAc, 9:1)] furnished the title compound **13** (513 mg, 3.4 mmol, 86%) as a light yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.96 (d, *J* = 4.5 Hz, 1 H), 4.82 (dd, *J* = 19.2, 11.6 Hz, 2 H), 4.90 (br s, 1 H), 4.94 (dd, *J* = 19.5, 11.6 Hz, 2 H), 5.39 (dq, *J* = 2.1, 1.1 Hz, 1 H), 5.42 (br s, 2 H).

^{13}C NMR (100.620 MHz, $CDCl_3$): δ = 73.2, 82.8 (2 C, $J_{C,F}$ = 163.0 Hz), 116.1 (2 C, $J_{C,F}$ = 10.2 Hz), 143.8 (2 C, $J_{C,F}$ = 13.6 Hz).

^{19}F NMR (235 MHz, $CDCl_3$): δ = –217.3 (td, $J_{H,F}$ = 47.2, 4.0 Hz, 2 F).

MS (CI, NH_3): *m*/*z* (%) = 166 ([M + NH_4]$^+$, 100), 86 (8).

HRMS: *m*/*z* calcd for C_6H_8FO [M – CH_2F]$^+$: 115.0559; found: 115.0559.

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