Synthesis Y. Watabe et al. Special Topic

# Nickel-Catalyzed Hydroalkenylation of Alkynes through C–F Bond Activation: Synthesis of 2-Fluoro-1,3-dienes

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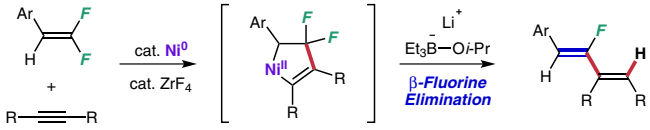


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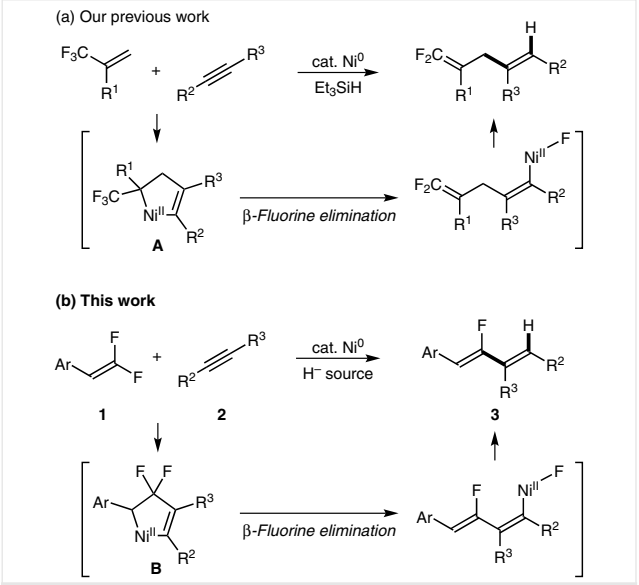
**Abstract** 2-Fluoro-1,3-dienes were synthesized through nickel-catalyzed coupling reactions between β,β-difluorostyrenes and alkynes in the presence of $ZrF_4$ as co-catalyst and a hydride source derived from triethylborane and lithium isopropoxide. Mechanistic studies revealed that the carbon–fluorine bond was cleaved by β-fluorine elimination from intermediary nickelacyclopentenes generated through oxidative cyclization of the two substrates.

**Key words** C–F bond activation, nickel, hydroalkenylation, β-fluorine elimination, oxidative cyclization, 1,3-dienes, fluorine, alkynes

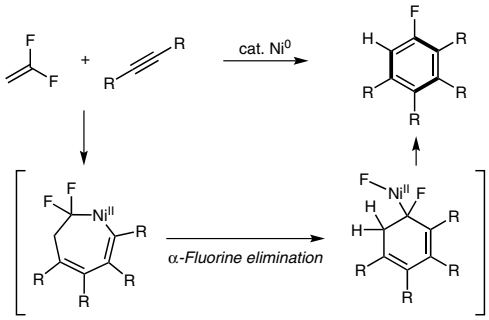
Conjugated dienes, often found in naturally occurring compounds,[1] are used as key substrates in various organic transformations such as cycloaddition[2] and polymerization.[3] Thus, methods for their synthesis have been extensively studied for decades.[4] Among them, transition-metal-catalyzed hydroalkenylation[5] of alkynes is a straightforward method for regio- and stereoselective synthesis of unsymmetrical 1,3-dienes. Conventional methods for formation of 1,3-dienes through hydroalkenylation are classified into three major categories according to the reaction mechanism: (a) through insertion of alkynes into alkenyl transition-metal species,[6] (b) though insertion of alkynes into transition-metal hydrides,[7] or (c) through oxidative cyclization of alkynes and alkenes followed by β-hydrogen elimination from metalacycropentenes.[8] Although the method (c) is considered to use highly atom-economical protocols, the alkenes employed in oxidative cyclization are limited to α,β-unsaturated carbonyl compounds in most cases.

Recently, we reported nickel-catalyzed hydroallylation of alkynes with 2-trifluoromethyl-1-alkenes through oxidative cyclization and exocyclic β-fluorine elimination (Scheme 1a).[9] In this reaction, β-fluorine elimination[10] proceeds from intermediary nickelacyclopentenes **A** to generate vinylnickels, providing 1,1-difluoro-1,4-dienes through transmetalation with triethylsilane. As the next challenge, we explored the synthesis of fluorinated 1,3-dienes through nickel-catalyzed hydroalkenylation of alkynes with 1,1-difluoro-1-alkenes. However, in the case of the nickel-catalyzed reaction of 1,1-difluoroethylene with alkynes, α,α-difluorinated nickelacycloheptadienes were generated from one 1,1-difluoroethylene with two alkynes through oxidative cyclization and insertion (Scheme 2).[11] Subsequent α-fluorine elimination afforded fluoroarenes. In contrast, we hypothesized that the reaction of β,β-difluorostyrenes **1** might be controlled by coordination of the arene




**Scheme 1** Nickel-catalyzed (a) hydroallylation or (b) hydroalkenylation of alkynes through oxidative cyclization and β-fluorine elimination

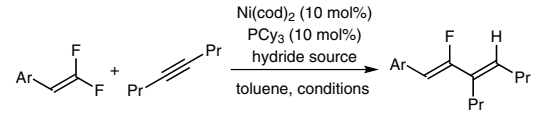
moieties to the nickel center, generating β,β-difluorinated nickelacyclopentenes **B** through oxidative cyclization of one molecule each of **1** and alkyne **2** with Ni(0) (Scheme 1b).[12] Subsequent endocyclic β-fluorine elimination from **B** would produce 2-fluoro-1,3-dienes **3**.




**Scheme 2** Nickel-catalyzed [2+2+2] cyclization through oxidative cyclization of 1,1-difluoroethylene with alkynes and α-fluorine elimination

We sought suitable conditions for the synthesis of 2-fluorohepta-1,3-diene **3aa** by using β,β-difluorostyrene **1a** and 4-octyne (**2a**) as model substrates (Table 1). Initially, we adopted the $Ni(cod)_2/PCy_3$ catalyst system, which was effective in defluorinative coupling between fluoroalkenes and alkynes.[9,11,13] No product was obtained without a hydride source (entry 1). Whereas $ZnEt_2$, $Et_3SiH$, and $Et_3B$ were not effective hydride sources (entries 2–4), the combination of $Et_3B$ and *i*-PrOLi afforded **3aa** in 46% yield as the sole product, without formation of fluoroarenes (entry 5). As the result of screening extra additives, a catalytic amount of $ZrF_4$[14] was found to improve the yield to 59% (entry 6). Additionally, the yield of **3aa** was drastically increased to 89% by lowering the reaction temperature to room temperature (entry 7).

**Table 1** Optimization of Reaction Conditions for Ni-Catalyzed Hydroalkenylation[a]



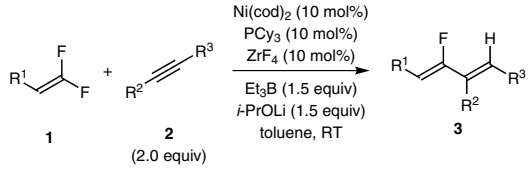

**1a** Ar = $C_6H_4$(*p*-Ph) **2a** (2.0 equiv) **3aa**

| Entry | Hydride source (equiv) | Temp. (°C) | Time (h) | Yield (%)[b] |
|---|---|---|---|---|
| 1 | – | 40 | 12 | N.D.[c] |
| 2 | $Et_2Zn$ (1.0) | 40 | 12 | N.D. |
| 3 | $Et_3SiH$ (1.0) | 40 | 16 | N.D. |
| 4 | $Et_3B$ (1.5) | 40 | 10 | N.D. |
| 5 | $Et_3B$ + *i*-PrOLi[d] (1.5) | 40 | 12 | 46 |
| 6 | $Et_3B$ + *i*-PrOLi (1.5) + $ZrF_4$ (0.1) | 40 | 3.5 | 59 |
| 7 | $Et_3B$ + *i*-PrOLi (1.5) + $ZrF_4$ (0.1) | r.t. | 24 | 89 (89) |

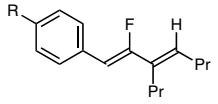
[a] Reaction conditions: $Ni(cod)_2$ (0.025 mmol), $PCy_3$ (0.025 mmol), **1a** (0.25 mmol), **2a** (0.50 mmol), toluene (2.0 mL).
[b] Yield was determined by $^{19}F$ NMR spectroscopy using $PhCF_3$ as internal standard. Yield of isolated product given in parentheses.
[c] N.D. = Not detected.
[d] *i*-PrOLi was generated in situ from *i*-PrOH and *n*-BuLi.

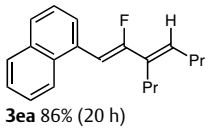
With the optimal conditions established, the scope of the reaction with respect to β,β-difluorostyrenes **1** and alkynes **2** was investigated (Table 2). When simple β,β-difluorostyrene (**1b**) was employed, the corresponding 2-fluoro-1,3-diene **3ba** was obtained in 77% yield. β,β-Difluorostyrene **1c**, bearing an electron-donating substituent (*i*-Pr), successfully underwent hydroalkenylation to afford the corresponding 2-fluoro-1,3-diene **3ca** in 62% yield. The reaction of chlorine-bearing β,β-difluorostyrene **1d** also provided **3da** in 84% yield without C–Cl bond cleavage. The hydroalkenylation of **2a** with 1-(2,2-difluoro-ethenyl)naphthalene (**1e**) proceeded smoothly to afford **3ea** in 86% yield. Heterocycle-containing 1,3-dienes **3fa** and **3ga** were obtained by reaction with 2-(2,2-difluoroethenyl)benzofuran (**1f**) and -benzothiophene (**1g**), respectively. In addition to symmetrical alkynes such as **2a** and **2b**, unsymmetrical alkynes **2c** and **2d** participated in the hydroalkenylation to afford the corresponding 2-fluoro-1,3-dienes **3ac** and **3ad** with strict regioselectivities.[12] Furthermore, hydrodienyla-

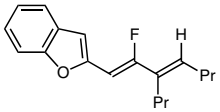
**Table 2** Ni-Catalyzed Synthesis of 2-Fluoro-1,3-dienes **3**[a]

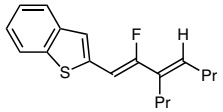


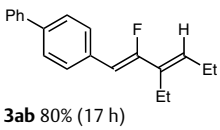

**1** **2** (2.0 equiv) **3**

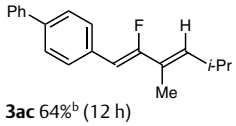

**3aa** (R = Ph), 89% (24 h)
**3ba** (R = H), 77% (11 h)
**3ca** (R = *i*-Pr), 62% (18 h)
**3da** (R = Cl), 84% (20 h)

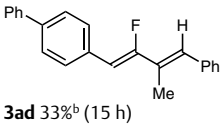

**3ea** 86% (20 h)


**3fa** 77% (10 h)


**3ga** 85% (12 h)

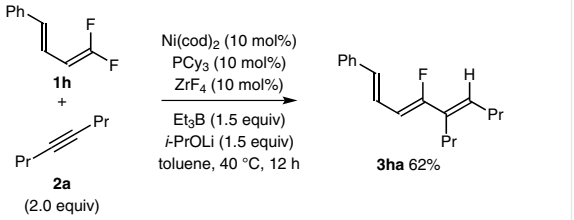

**3ab** 80% (17 h)


**3ac** 64%[b] (12 h)


**3ad** 33%[b] (15 h)

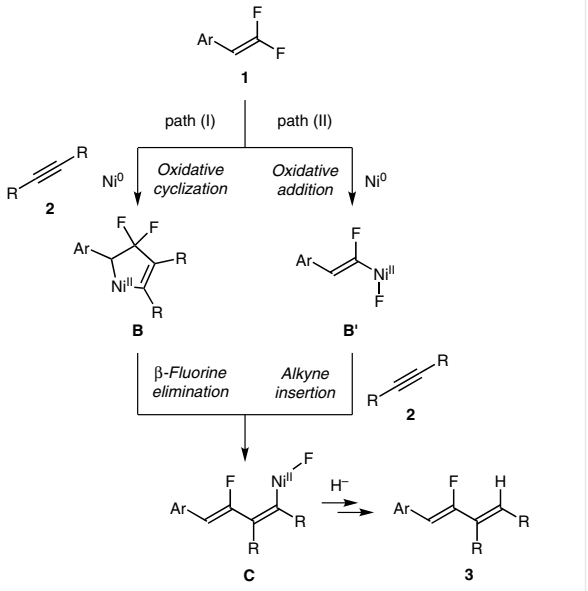
[a] Reaction conditions: $Ni(cod)_2$ (0.025 mmol), $PCy_3$ (0.025 mmol), $ZrF_4$ (0.025 mmol), **1** (0.25 mmol), **2** (0.50 mmol), $Et_3B$ (0.38 mmol), *i*-PrOLi (0.38 mmol), toluene (2.0 mL).
[b] Single regioisomer.

tion of **2a** with 1,1-difluorobuta-1,3-diene **1h** also proceeded to give 3-fluorinated 1,3,5-triene **3ha** in 62% yield (Scheme 3).




**Scheme 3** Hydrodienylation of alkyne **2a** with difluorodiene **1h**

For hydroalkenylation of alkynes **2** with difluorostyrenes **1**, there are two possible reaction pathways initiated by different elementary steps that involve **1** (Scheme 4). Path (I) starts with oxidative cyclization of **1** and **2** with the Ni catalyst, inducing regioselective formation of β,β-difluorinated nickelacyclopentenes **B** with the help of coordination of the aryl groups to the Ni center (Scheme 4). Subsequent β-fluorine elimination from **B** generates vinylnickels **C**. Thus, 2-fluoro-1,3-dienes **3** are obtained through transmetalation of **C** with borate generated from $Et_3B$ and *i*-PrOLi. In path (II), vinylnickel intermediates **B′** are initially formed by oxidative addition of a vinylic C–F bond of **1** to $Ni^0$ (Scheme 4). Subsequent insertion of **2** to **B′** affords the common intermediates **C**.




**Scheme 4** Possible reaction pathways (I) and (II)

To determine the initial steps of the reaction pathway, we examined the dependency in the initial formation rate of 2-fluoro-1,3-diene **3ea** $[(\Delta[\mathbf{3ea}]/\Delta t)_{t=0}]$ based on changing the initial concentrations of difluorostyrene **1e** ($[\mathbf{1e}]_0$), alkyne **2a** ($[\mathbf{2a}]_0$), and Ni catalyst ($[\mathbf{Ni}]_0$) (Figure 1). On the basis of these experiments, linear correlations of $(\Delta[\mathbf{3ea}]/\Delta t)_{t=0}$ with $[\mathbf{1e}]_0$ and $[\mathbf{2a}]_0$ were obtained (Figure 1a and 1c). In addition, linear fitting of the corresponding log–log plots with slopes of 1.01 and 1.08 exhibited first-order dependence of $(\Delta[\mathbf{3ea}]/\Delta t)_{t=0}$ on $[\mathbf{1e}]_0$ and $[\mathbf{2a}]_0$, respectively (Figure 1b and 1d). Thus, both **1e** and **2a** were shown to be involved in the rate-limiting initial step. Furthermore, when a similar analysis was performed on the dependency of $(\Delta[\mathbf{3ea}]/\Delta t)_{t=0}$ on $[\mathbf{Ni}]_0$, first-order dependence (slope of 0.910) was confirmed (Figure 1e and 1f). These results indicate that oxidative cyclization of **1e** and **2a** with $Ni^0$ is involved in the rate-limiting initial step as path (I).

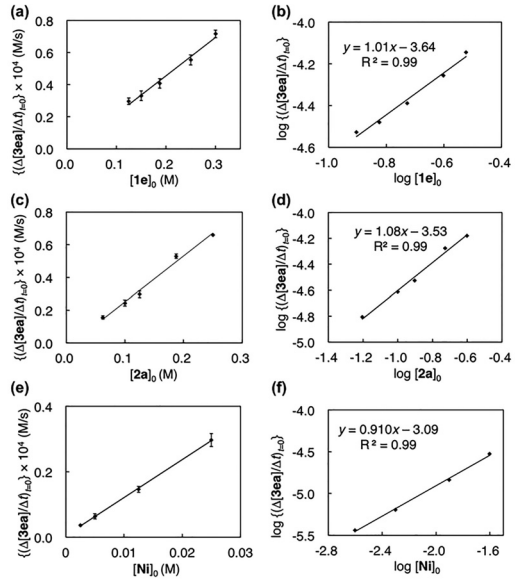
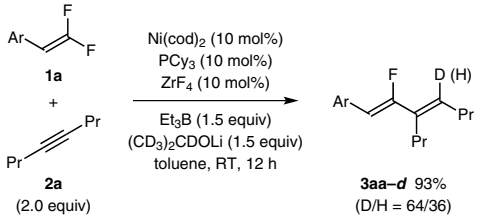


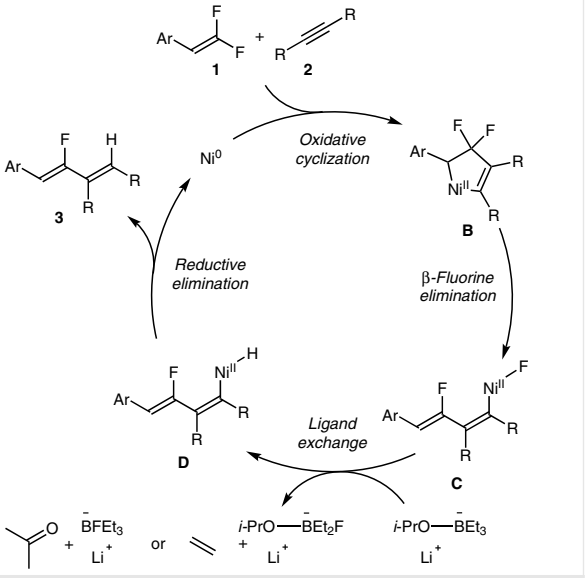

**Figure 1** (a) Initial reaction rate versus $[\mathbf{1e}]_0$ and (b) the corresponding log–log plot. Reaction conditions: $Ni(cod)_2$ (0.025 mmol), $PCy_3$ (0.025 mmol), $ZrF_4$ (0.025 mmol), **1e** (0.25–0.60 mmol), **2a** (0.50 mmol), $Et_3B$ (0.38 mmol), *i*-PrOLi (0.38 mmol), toluene (2.0 mL), RT, 10 min. (c) Initial reaction rate versus $[\mathbf{2a}]_0$ and (d) the corresponding log–log plot. Reaction conditions: $Ni(cod)_2$ (0.025 mmol), $PCy_3$ (0.025 mmol), $ZrF_4$ (0.025 mmol), **1e** (0.25 mmol), **2a** (0.12–0.50 mmol), $Et_3B$ (0.38 mmol), *i*-PrOLi (0.38 mmol), toluene (2.0 mL), RT, 10 min. (e) Initial reaction rate versus $[Ni]_0$ and (f) the corresponding log–log plot. Reaction conditions: $Ni(cod)_2$ (0.0050–0.05 mmol), $PCy_3$ (0.0050–0.050 mmol), **1e** (0.50 mmol), **2a** (1.0 mmol), $Et_3B$ (0.75 mmol), *i*-PrOLi (0.75 mmol), toluene (2.0 mL), RT, 10 min.

To clarify which hydrogen of the borate formed from triethylborane and lithium isopropoxide was installed as a hydride source in the 2-fluoro-1,3-dienes **3**, a deuterium-labeling experiment was conducted using *i*-PrOLi-$d_7$ (Scheme 5). Nickel-catalyzed hydroalkenylation of **2a** with **1a** in the presence of the borate generated from $Et_3B$ and *i*-PrOLi-$d_7$ gave a 64:36 mixture of deuterated 2-fluoro-1,3-diene ***3aa-d*** and non-deuterated diene **3aa**. This result indicates that both an ethyl group on boron and an isopropyl group on oxygen serve as the hydride source.




**Scheme 5** Deuterium-labeling experiments

On the basis of the aforementioned experiments, we propose the following reaction mechanism (Scheme 6). This reaction is initiated by regioselective oxidative cyclization of difluoroalkene **1** and alkyne **2** with $Ni^0$ to generate the intermediary β,β-difluorinated nickelacyclopentenes **B**. β-Fluorine elimination proceeds from **B** to generate vinylnickel fluorides **C**. Replacement of the fluorine on the nickel in **C** with an isopropoxy group or an ethyl group is accomplished through transmetalation with the borate, derived from $Et_3B$ and *i*-PrOLi. Subsequent β-hydrogen elimination induces the formation of vinylnickel hydrides **D** along with acetone or ethylene. Finally, reductive elimination from **D** affords 1,3-dienes **3** to regenerate nickel(0).




**Scheme 6** Proposed catalytic cycle

In summary, we have developed a method for the synthesis of 2-fluoro-1,3-dienes through nickel-catalyzed hydroalkenylation of alkynes **2** with β,β-difluorostyrenes **1** and a borate. The vinylic C–F bonds of **1** are readily cleaved through β-fluorine elimination under mild conditions. The monofluorinated 1,3-dienes[15] obtained above are expected to serve as components of bioactive compounds in pharmaceuticals and monomers for functional polymers.

$^1H$, $^{13}C$, and $^{19}F$ NMR spectra were recorded with a Bruker Avance 500 or a JEOL ECS-400 spectrometer. Chemical shift values are given in ppm relative to internal $Me_4Si$ (for $^1H$ NMR: δ = 0.00 ppm), $CDCl_3$ (for $^{13}C$ NMR: δ = 77.0 ppm), and $C_6F_6$ (for $^{19}F$ NMR: δ = 0.00 ppm). IR spectra were recorded with a Horiba FT-300S spectrometer by the attenuated total reflectance (ATR) method. Mass spectra were measured with a JEOL JMS-T100GCV or a JMS-T100CS spectrometer. Elemental analyses were carried out at the Elemental Analysis Laboratory, Division of Chemistry, Faculty of Pure and Applied Sciences, University of Tsukuba. Melting points were measured with a Yanaco micro melting point apparatus, and are uncorrected. Column chromatography was performed on silica gel (Silica Gel 60N, Kanto Chemical Co., Inc., 63–210 µm). All the reactions were conducted under argon or nitrogen. Diethyl ether ($Et_2O$), tetrahydrofuran (THF), and toluene were purified with a solvent-purification system (GlassContour) equipped with columns of activated alumina and supported-copper catalyst (Q-5) before use. Benzene was dried over $CaCl_2$ for one day, then distilled from $CaCl_2$, and stored over activated 4 Å molecular sieves. *i*-PrOH was distilled from $CaH_2$ prior to use. Difluorostyrenes **1a**, **1b** and **1d–h**[16] and 1-phenyl-1-propyne[17] (**2d**) were prepared according to reported procedures. Unless otherwise noted, materials were obtained from commercial sources and used directly without further purification.

### 1-(2,2-Difluoroethenyl)-4-isopropylbenzene (1c)

To an *N*-methylpyrrolidone (20 mL) solution of (triphenylphosphonio)difluoroacetate (7.06 g, 19.8 mmol) was added 4-isopropylbenzaldehyde (1.48 g, 10.0 mmol). After stirring at 80 °C for 11 h, the reaction was quenched with brine. Organic materials were extracted with ether three times. The combined extracts were washed with brine and dried over anhydrous $Na_2SO_4$. After the solvent was removed under reduced pressure, the residue was purified by silica gel column chromatography (hexane) to give difluorostyrene **1c**.

Yield: 1.29 g (71%); colorless oil.

IR (neat): 2962, 1730, 1516, 1466, 1421, 1348, 1248, 1165, 1055, 937, 841, 544 $cm^{-1}$.

$^1H$ NMR ($CDCl_3$, 500 MHz): δ = 1.24 (d, *J* = 6.9 Hz, 6 H), 2.88 (sept, *J* = 6.9 Hz, 1 H), 5.22 (dd, $J_{H-F}$ = 26.5, 3.8 Hz, 1 H), 7.19 (d, *J* = 8.2 Hz, 2 H), 7.25 (d, *J* = 8.2 Hz, 2 H).

$^{13}C$ NMR ($CDCl_3$, 126 MHz): δ = 23.9, 33.8, 81.9 (dd, $J_{C-F}$ = 29, 14 Hz), 126.7, 127.6 (dd, $J_{C-F}$ = 6, 4 Hz), 127.8 (dd, $J_{C-F}$ = 6, 6 Hz), 147.8, 156.2 (dd, $J_{C-F}$ = 298, 288 Hz).

$^{19}F$ NMR ($CDCl_3$, 471 MHz): δ = 77.6 (dd, $J_{F-F}$ = 34 Hz, $J_{F-H}$ = 4 Hz, 1 F), 79.7 (dd, $J_{F-F}$ = 34 Hz, $J_{F-H}$ = 26 Hz, 1 F).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{11}H_{12}F_2$: 182.0907; found: 182.0904.

Anal. Calcd for $C_{11}H_{12}F_2$: C, 72.51; H, 6.64. Found: C, 72.37; H, 6.88.

### 4-[(1*Z*,3*E*)-2-Fluoro-3-propylhepta-1,3-dien-1-yl]-1,1′-biphenyl (3aa); Typical Procedure

Typical procedure for the synthesis of fluoro-1,3-dienes **3** in a nickel-catalyzed reaction. In an argon-purged 50 mL test tube equipped with a PTFE cap (EYELA, PPS25-TC) were placed *i*-PrOH (29 µL, 0.38 mmol) and toluene (1.0 mL). To the mixture was slowly added *n*-BuLi (1.57 M in hexane, 0.24 mL, 0.38 mmol) at 0 °C. After stirring at 0 °C for 10 min, $Et_3B$ (1.0 M in hexane, 0.38 mL, 0.38 mmol) was added to the reaction mixture at the same temperature. The reaction mixture was warmed to r.t., and was stirred for another 30 min. To the reaction mixture were added β,β-difluorostyrene (**1a**; 54 mg, 0.25 mmol), 4-octyne (**2a**; 55 mg, 0.50 mmol), $Ni(cod)_2$ (6.9 mg, 0.025 mmol), $PCy_3$ (7.0 mg, 0.025 mmol), $ZrF_4$ (4.1 mg, 0.025 mmol), and toluene (1.0

mL). After stirring at r.t. for 24 h, the reaction mixture was filtered through a pad of silica gel (EtOAc). The filtrate was concentrated under reduced pressure and the residue was purified by silica gel column chromatography (hexane/EtOAc, 20:1) to give 2-fluoro-1,3-diene **3aa**.

Yield: 69 mg (89%); white solid; mp 90.6–92.2 °C.

IR (neat): 2958, 2929, 2871, 1639, 1487, 856, 839, 760, 723, 694 $cm^{-1}$.

$^1H$ NMR ($CDCl_3$, 500 MHz): δ = 0.97 (t, *J* = 7.4 Hz, 3 H), 0.99 (t, *J* = 7.4 Hz, 3 H), 1.45–1.57 (m, 4 H), 2.18 (td, *J* = 7.4, 7.4 Hz, 2 H), 2.28 (t, *J* = 7.4 Hz, 2 H), 5.78 (d, $J_{H-F}$ = 40.4 Hz, 1 H), 6.09 (t, *J* = 7.4 Hz, 1 H), 7.33 (tt, *J* = 7.4, 1.4 Hz, 1 H), 7.43 (dd, *J* = 7.4, 7.4 Hz, 2 H), 7.57 (d, *J* = 8.6 Hz, 2 H), 7.60–7.63 (m, 4 H).

$^{13}C$ NMR ($CDCl_3$, 126 MHz): δ = 14.0, 14.2, 22.4, 22.7, 29.0 (d, $J_{C-F}$ = 3 Hz), 30.3, 104.4 (d, $J_{C-F}$ = 11 Hz), 126.9, 127.1, 127.2, 128.8, 129.2 (d, $J_{C-F}$ = 8 Hz), 130.2 (d, $J_{C-F}$ = 9 Hz), 131.8 (d, $J_{C-F}$ = 19 Hz), 133.5 (d, $J_{C-F}$ = 2 Hz), 139.3 (d, $J_{C-F}$ = 2 Hz), 140.7, 158.8 (d, $J_{C-F}$ = 260 Hz).

$^{19}F$ NMR ($CDCl_3$, 471 MHz): δ = 48.6 (d, $J_{F-H}$ = 40 Hz).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{22}H_{25}F$: 308.1940; found: 308.1943.

### [(1*Z*,3*E*)-2-Fluoro-3-propylhepta-1,3-dien-1-yl]benzene (3ba)

Compound **3ba** was synthesized according to the procedure described for **3aa** using *i*-PrOH (29 µL, 0.38 mmol), *n*-BuLi (0.24 mL, 0.38 mmol), $Et_3B$ (0.38 mL, 0.38 mmol), **1b** (35 mg, 0.25 mmol), **2a** (56 mg, 0.51 mmol), $Ni(cod)_2$ (7.0 mg, 0.025 mmol), $PCy_3$ (7.0 mg, 0.025 mmol), $ZrF_4$ (4.1 mg, 0.025 mmol), and toluene (2.0 mL). The reaction was conducted at r.t. for 11 h. Purification by silica gel column chromatography (hexane) gave **3ba**.

Yield: 45 mg (77%); colorless oil.

IR (neat): 2958, 2871, 1639, 1456, 1377, 831, 748, 690 $cm^{-1}$.

$^1H$ NMR ($CDCl_3$, 500 MHz): δ = 0.94 (t, *J* = 7.4 Hz, 3 H), 0.96 (t, *J* = 7.4 Hz, 3 H), 1.46 (qt, *J* = 7.4, 7.4 Hz, 2 H), 1.51 (qt, *J* = 7.4, 7.4 Hz, 2 H), 2.15 (td, *J* = 7.4, 7.4 Hz, 2 H), 2.25 (t, *J* = 7.4 Hz, 2 H), 5.73 (d, $J_{H-F}$ = 40.4 Hz, 1 H), 6.07 (t, *J* = 7.4 Hz, 1 H), 7.17 (t, *J* = 7.5 Hz, 1 H), 7.30 (dd, *J* = 7.5, 7.5 Hz, 2 H), 7.53 (d, *J* = 7.5 Hz, 2 H).

$^{13}C$ NMR ($CDCl_3$, 126 MHz): δ = 13.9, 14.1, 22.4, 22.7, 29.0 (d, $J_{C-F}$ = 3 Hz), 30.3, 104.8 (d, $J_{C-F}$ = 12 Hz), 126.7 (d, $J_{C-F}$ = 2 Hz), 128.4, 128.8 (d, $J_{C-F}$ = 8 Hz), 130.0 (d, $J_{C-F}$ = 9 Hz), 131.7 (d, $J_{C-F}$ = 19 Hz), 134.3 (d, $J_{C-F}$ = 2 Hz), 158.5 (d, $J_{C-F}$ = 260 Hz).

$^{19}F$ NMR ($CDCl_3$, 471 MHz): δ = 48.3 (d, $J_{F-H}$ = 40 Hz).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{16}H_{21}F$: 232.1627; found: 232.1628.

Anal. Calcd for $C_{16}H_{21}F$: C, 82.71; H, 9.11. Found: C, 82.33; H, 9.14.

### 1-[(1*Z*,3*E*)-2-Fluoro-3-propylhepta-1,3-dien-1-yl]-4-isopropylbenzene (3ca)

Compound **3ca** was synthesized according to the procedure described for **3aa** using *i*-PrOH (29 µL, 0.38 mmol), *n*-BuLi (0.24 mL, 0.38 mmol), $Et_3B$ (0.38 mL, 0.38 mmol), **1c** (46 mg, 0.25 mmol), **2a** (55 mg, 0.50 mmol), $Ni(cod)_2$ (6.9 mg, 0.025 mmol), $PCy_3$ (7.0 mg, 0.025 mmol), $ZrF_4$ (4.2 mg, 0.025 mmol), and toluene (2.0 mL). The reaction was conducted at r.t. for 18 h. Purification by silica gel column chromatography (hexane) gave **3ca**.

Yield: 42 mg (62%); colorless oil.

IR (neat): 2958, 2871, 1643, 1510, 1458, 1419, 1379, 1055, 1018, 964, 895, 854, 561 $cm^{-1}$.

$^1H$ NMR ($CDCl_3$, 500 MHz): δ = 0.95 (t, *J* = 7.4 Hz, 3 H), 0.96 (t, *J* = 7.4 Hz, 3 H), 1.24 (d, *J* = 6.9 Hz, 6 H), 1.43–1.55 (m, 4 H), 2.16 (td, *J* = 7.4, 7.4 Hz, 2 H), 2.25 (t, *J* = 7.4 Hz, 2 H), 2.88 (sept, *J* = 6.9 Hz, 1 H), 5.71 (d, $J_{H-F}$ = 40.7 Hz, 1 H), 6.04 (t, *J* = 7.4 Hz, 1 H), 7.18 (d, *J* = 8.2 Hz, 2 H), 7.47 (d, *J* = 8.2 Hz, 2 H).

$^{13}C$ NMR ($CDCl_3$, 126 MHz): δ = 14.0, 14.1, 22.4, 22.8, 23.9, 29.0 (d, $J_{C-F}$ = 3 Hz), 30.3, 33.9, 104.7 (d, $J_{C-F}$ = 12 Hz), 126.5, 128.8 (d, $J_{C-F}$ = 8 Hz), 129.5 (d, $J_{C-F}$ = 9 Hz), 131.8 (d, $J_{C-F}$ = 19 Hz), 131.9, 147.5 (d, $J_{C-F}$ = 2 Hz), 158.1 (d, $J_{C-F}$ = 259 Hz).

$^{19}F$ NMR ($CDCl_3$, 471 MHz): δ = 47.1 (d, $J_{F-H}$ = 41 Hz).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{19}H_{27}F$: 274.2097; found: 274.2096.

### 1-Chloro-4-[(1*Z*,3*E*)-2-fluoro-3-propylhepta-1,3-dien-1-yl]-benzene (3da)

Compound **3da** was synthesized according to the procedure described for **3aa** using *i*-PrOH (29 µL, 0.38 mmol), *n*-BuLi (0.24 mL, 0.38 mmol), $Et_3B$ (0.38 mL, 0.38 mmol), **1d** (44 mg, 0.25 mmol), **2a** (55 mg, 0.50 mmol), $Ni(cod)_2$ (6.9 mg, 0.025 mmol), $PCy_3$ (7.0 mg, 0.025 mmol), $ZrF_4$ (4.1 mg, 0.025 mmol), and toluene (2.0 mL). The reaction was conducted at r.t. for 20 h. Purification by silica gel column chromatography (hexane/EtOAc, 20:1) gave **3da**.

Yield: 56 mg (84%); colorless oil.

IR (neat): 2958, 2871, 1641, 1491, 1456, 1092, 1012, 849, 748, 548, 511 $cm^{-1}$.

$^1H$ NMR ($CDCl_3$, 500 MHz): δ = 0.96 (t, *J* = 7.5 Hz, 3 H), 0.97 (t, *J* = 7.5 Hz, 3 H), 1.43–1.54 (m, 4 H), 2.17 (td, *J* = 7.5, 7.5 Hz, 2 H), 2.25 (t, *J* = 7.5 Hz, 2 H), 5.69 (d, $J_{H-F}$ = 39.9 Hz, 1 H), 6.08 (t, *J* = 7.5 Hz, 1 H), 7.28 (d, *J* = 8.6 Hz, 2 H), 7.46 (d, *J* = 8.6 Hz, 2 H).

$^{13}C$ NMR ($CDCl_3$, 126 MHz): δ = 13.9, 14.1, 22.4, 22.7, 28.9 (d, $J_{C-F}$ = 3 Hz), 30.3, 103.7 (d, $J_{C-F}$ = 12 Hz), 128.6, 130.0 (d, $J_{C-F}$ = 8 Hz), 130.7 (d, $J_{C-F}$ = 9 Hz), 131.6 (d, $J_{C-F}$ = 18 Hz), 132.2 (d, $J_{C-F}$ = 3 Hz), 132.9 (d, $J_{C-F}$ = 2 Hz), 158.9 (d, $J_{C-F}$ = 261 Hz).

$^{19}F$ NMR ($CDCl_3$, 471 MHz): δ = 48.7 (d, $J_{F-H}$ = 40 Hz).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{16}H_{20}ClF$: 266.1238; found: 266.1238.

### 1-[(1*Z*,3*E*)-2-Fluoro-3-propylhepta-1,3-dien-1-yl]naphthalene (3ea)

Compound **3ea** was synthesized according to the procedure described for **3aa** using *i*-PrOH (29 µL, 0.38 mmol), *n*-BuLi (0.24 mL, 0.38 mmol), $Et_3B$ (0.38 mL, 0.38 mmol), **1e** (47 mg, 0.25 mmol), **2a** (55 mg, 0.50 mmol), $Ni(cod)_2$ (6.8 mg, 0.025 mmol), $PCy_3$ (6.9 mg, 0.025 mmol), $ZrF_4$ (4.1 mg, 0.025 mmol), and toluene (2.0 mL). The reaction was conducted at r.t. for 20 h. Purification by silica gel column chromatography (hexane/EtOAc, 50:1) gave **3ea**.

Yield: 60 mg (86%); colorless oil.

IR (neat): 2958, 2871, 1637, 1508, 1458, 1394, 1381, 1103, 899, 795, 773, 731 $cm^{-1}$.

$^1H$ NMR ($CDCl_3$, 500 MHz): δ = 0.98 (t, *J* = 7.4 Hz, 3 H), 1.04 (t, *J* = 7.4 Hz, 3 H), 1.49 (qt, *J* = 7.4, 7.4 Hz, 2 H), 1.64 (qt, *J* = 7.4, 7.4 Hz, 2 H), 2.20 (td, *J* = 7.4, 7.4 Hz, 2 H), 2.39 (t, *J* = 7.4 Hz, 2 H), 6.13 (t, *J* = 7.4 Hz, 1 H), 6.40 (d, $J_{H-F}$ = 37.8 Hz, 1 H), 7.45–7.52 (m, 3 H), 7.74 (d, *J* = 7.9 Hz, 1 H), 7.81 (d, *J* = 7.9 Hz, 1 H), 7.83 (d, *J* = 7.9 Hz, 1 H), 8.00 (d, *J* = 7.9 Hz, 1 H).

$^{13}C$ NMR ($CDCl_3$, 126 MHz): δ = 14.0, 14.2, 22.6, 22.7, 29.2 (d, $J_{C-F}$ = 3 Hz), 30.3, 101.3 (d, $J_{C-F}$ = 14 Hz), 124.0, 125.52, 125.53, 125.9, 127.31 (d, $J_{C-F}$ = 6 Hz), 127.34, 128.6, 130.3 (d, $J_{C-F}$ = 6 Hz), 130.4 (d, $J_{C-F}$ = 9 Hz), 131.5, 131.7 (d, $J_{C-F}$ = 19 Hz), 133.7, 158.9 (d, $J_{C-F}$ = 259 Hz).

$^{19}F$ NMR ($CDCl_3$, 471 MHz): δ = 46.7 (d, $J_{F-H}$ = 38 Hz).

HRMS (EI): *m*/*z* [M]$^+$ calcd for $C_{20}H_{23}F$: 282.1784; found: 282.1784.

**2-[(1*Z*,3*E*)-2-Fluoro-3-propylhepta-1,3-dien-1-yl]benzofuran (3fa)**

Compound **3fa** was synthesized according to the procedure described for **3aa** using *i*-PrOH (29 μL, 0.38 mmol), *n*-BuLi (0.24 mL, 0.38 mmol), $Et_3B$ (0.38 mL, 0.38 mmol), **1f** (45 mg, 0.25 mmol), **2a** (54 mg, 0.49 mmol), $Ni(cod)_2$ (6.9 mg, 0.025 mmol), $PCy_3$ (6.9 mg, 0.025 mmol), $ZrF_4$ (4.1 mg, 0.025 mmol), and toluene (2.0 mL). The reaction was conducted at r.t. for 10 h. Purification by silica gel column chromatography (hexane/EtOAc, 20:1) gave **3fa**.

Yield: 53 mg (77%); colorless oil.

IR (neat): 2960, 2931, 2873, 1641, 1558, 1450, 1259, 1169, 1099, 1011, 978, 812, 739 cm$^{-1}$.

$^1$H NMR ($CDCl_3$, 500 MHz): δ = 0.93 (t, *J* = 7.5 Hz, 3 H), 0.95 (t, *J* = 7.5 Hz, 3 H), 1.42–1.53 (m, 4 H), 2.16 (td, *J* = 7.5, 7.5 Hz, 2 H), 2.23 (t, *J* = 7.5 Hz, 2 H), 5.91 (d, $J_{H-F}$ = 38.7 Hz, 1 H), 6.13 (t, *J* = 7.5 Hz, 1 H), 6.91 (s, 1 H), 7.15–7.22 (m, 2 H), 7.39 (d, *J* = 7.6 Hz, 1 H), 7.51 (d, *J* = 7.6 Hz, 1 H).

$^{13}$C NMR ($CDCl_3$, 126 MHz): δ = 13.9, 14.1, 22.4, 22.6, 28.8 (d, $J_{C-F}$ = 4 Hz), 30.4, 95.4 (d, $J_{C-F}$ = 14 Hz), 105.7 (d, $J_{C-F}$ = 13 Hz), 110.7, 120.7, 122.8, 124.0, 129.4, 130.9 (d, $J_{C-F}$ = 17 Hz), 131.8 (d, $J_{C-F}$ = 8 Hz), 151.6, 153.9, 159.8 (d, $J_{C-F}$ = 263 Hz).

$^{19}$F NMR ($CDCl_3$, 471 MHz): δ = 55.4 (d, $J_{F-H}$ = 39 Hz).

HRMS (EI): *m*/*z* [M]$^+$ calcd for $C_{18}H_{21}FO$: 272.1576; found: 272.1576.

**2-[(1*Z*,3*E*)-2-Fluoro-3-propylhepta-1,3-dien-1-yl]benzo[*b*]thiophene (3ga)**

Compound **3ga** was synthesized according to the procedure described for **3aa** using *i*-PrOH (29 μL, 0.38 mmol), *n*-BuLi (0.24 mL, 0.38 mmol), $Et_3B$ (0.38 mL, 0.38 mmol), **1g** (48 mg, 0.25 mmol), **2a** (55 mg, 0.50 mmol), $Ni(cod)_2$ (7.0 mg, 0.025 mmol), $PCy_3$ (7.0 mg, 0.025 mmol), $ZrF_4$ (4.1 mg, 0.025 mmol), and toluene (2.0 mL). The reaction was conducted at r.t. for 12 h. Purification by silica gel column chromatography (hexane/EtOAc, 20:1) gave **3ga**.

Yield: 60 mg (85%); colorless solid; mp 50.6–51.2 °C.

IR (neat): 3049, 2956, 2870, 1633, 1456, 1311, 1230, 845, 742, 577 cm$^{-1}$.

$^1$H NMR ($CDCl_3$, 500 MHz): δ = 0.96 (t, *J* = 7.5 Hz, 3 H), 0.98 (t, *J* = 7.5 Hz, 3 H), 1.44–1.56 (m, 4 H), 2.18 (td, *J* = 7.5, 7.5 Hz, 2 H), 2.26 (t, *J* = 7.5 Hz, 2 H), 6.12 (d, $J_{H-F}$ = 38.9 Hz, 1 H), 6.14 (t, *J* = 7.5 Hz, 1 H), 7.23–7.32 (m, 3 H), 7.69 (d, *J* = 7.6 Hz, 1 H), 7.78 (d, *J* = 7.6 Hz, 1 H).

$^{13}$C NMR ($CDCl_3$, 126 MHz): δ = 13.9, 14.1, 22.4, 22.7, 28.8 (d, $J_{C-F}$ = 3 Hz), 30.4, 99.9 (d, $J_{C-F}$ = 15 Hz), 121.9, 122.9 (d, $J_{C-F}$ = 4 Hz), 123.0 (d, $J_{C-F}$ = 1 Hz), 124.1, 124.2, 130.8 (d, $J_{C-F}$ = 17 Hz), 131.3 (d, $J_{C-F}$ = 8 Hz), 137.2 (d, $J_{C-F}$ = 4 Hz), 139.4, 140.3 (d, $J_{C-F}$ = 9 Hz), 158.6 (d, $J_{C-F}$ = 261 Hz).

$^{19}$F NMR ($CDCl_3$, 471 MHz): δ = 51.3 (d, $J_{F-H}$ = 39 Hz).

Anal. Calcd for $C_{18}H_{21}FS$: C, 74.96; H, 7.34. Found: C, 74.64; H, 7.25.

**4-[(1*Z*,3*E*)-3-Ethyl-2-fluorohexa-1,3-dien-1-yl]-1,1′-biphenyl (3ab)**

Compound **3ab** was synthesized according to the procedure described for **3aa** using *i*-PrOH (29 μL, 0.38 mmol), *n*-BuLi (0.24 mL, 0.38 mmol), $Et_3B$ (0.38 mL, 0.38 mmol), **1a** (54 mg, 0.25 mmol), 3-hexyne (**2b**; 41 mg, 0.50 mmol), $Ni(cod)_2$ (7.0 mg, 0.025 mmol), $PCy_3$ (6.9 mg, 0.025 mmol), $ZrF_4$ (4.1 mg, 0.025 mmol), and toluene (2.0 mL). The reaction was conducted at r.t. for 17 h. Purification by silica gel column chromatography (hexane/EtOAc, 20:1) gave **3ab**.

Yield: 56 mg (80%); colorless solid; mp 64.3–65.9 °C.

IR (neat): 2972, 2937, 1722, 1689, 1489, 1458, 1279, 1115, 1076, 1009, 764, 698, 667 cm$^{-1}$.

$^1$H NMR ($CDCl_3$, 500 MHz): δ = 1.07 (t, *J* = 7.5 Hz, 3 H), 1.11 (t, *J* = 7.5 Hz, 3 H), 2.21 (qd, *J* = 7.5, 7.5 Hz, 2 H), 2.31 (q, *J* = 7.5 Hz, 2 H), 5.79 (d, $J_{H-F}$ = 40.4 Hz, 1 H), 6.04 (t, *J* = 7.5 Hz, 1 H), 7.33 (t, *J* = 7.6 Hz, 1 H), 7.43 (dd, *J* = 7.6, 7.6 Hz, 2 H), 7.54–7.63 (m, 6 H).

$^{13}$C NMR ($CDCl_3$, 126 MHz): δ = 13.9, 14.1, 20.1 (d, $J_{C-F}$ = 4 Hz), 21.3, 104.4 (d, $J_{C-F}$ = 12 Hz), 126.9, 127.1, 127.2, 128.8, 129.2 (d, $J_{C-F}$ = 8 Hz), 131.1 (d, $J_{C-F}$ = 9 Hz), 132.9 (d, $J_{C-F}$ = 19 Hz), 133.5 (d, $J_{C-F}$ = 2 Hz), 139.3 (d, $J_{C-F}$ = 2 Hz), 140.7, 158.4 (d, $J_{C-F}$ = 260 Hz).

$^{19}$F NMR ($CDCl_3$, 471 MHz): δ = 48.0 (d, $J_{F-H}$ = 40 Hz).

HRMS (EI): *m*/*z* [M]$^+$ calcd for $C_{20}H_{21}F$: 280.1627; found: 280.1628.

**4-[(1*Z*,3*E*)-2-Fluoro-3,5-dimethylhexa-1,3-dien-1-yl]-1,1′-biphenyl (3ac)**

Compound **3ac** was synthesized according to the procedure described for **3aa** using *i*-PrOH (29 μL, 0.38 mmol), *n*-BuLi (0.24 mL, 0.38 mmol), $Et_3B$ (0.38 mL, 0.38 mmol), **1a** (55 mg, 0.25 mmol), 4-methyl-2-pentyne (**2c**, 41 mg, 0.50 mmol), $Ni(cod)_2$ (6.9 mg, 0.025 mmol), $PCy_3$ (6.9 mg, 0.025 mmol), $ZrF_4$ (4.1 mg, 0.025 mmol), and toluene (2.0 mL). The reaction was conducted at r.t. for 12 h. Purification by silica gel column chromatography (hexane/EtOAc, 20:1) gave **3ac**.

Yield: 45 mg (64%); colorless solid; mp 112.9–114.3 °C.

IR (neat): 2960, 2866, 1641, 1489, 1410, 1362, 1323, 1138, 1059, 995, 860, 760, 719, 688 cm$^{-1}$.

$^1$H NMR ($CDCl_3$, 500 MHz): δ = 1.04 (d, *J* = 6.6 Hz, 6 H), 1.88 (s, 3 H), 2.69 (d sept, *J* = 9.5, 6.6 Hz, 1 H), 5.75 (d, $J_{H-F}$ = 40.1 Hz, 1 H), 5.94 (d, *J* = 9.5 Hz, 1 H), 7.33 (t, *J* = 7.4 Hz, 1 H), 7.43 (dd, *J* = 7.8, 7.8 Hz, 2 H), 7.56–7.58 (m, 2 H), 7.60–7.62 (m, 4 H).

$^{13}$C NMR ($CDCl_3$, 126 MHz): δ = 12.6 (d, $J_{C-F}$ = 4 Hz), 22.8, 27.6, 104.7 (d, $J_{C-F}$ = 11 Hz), 124.7 (d, $J_{C-F}$ = 20 Hz), 126.9, 127.1, 127.2, 128.8, 129.2 (d, $J_{C-F}$ = 8 Hz), 133.4 (d, $J_{C-F}$ = 2 Hz), 136.9 (d, $J_{C-F}$ = 8 Hz), 139.3 (d, $J_{C-F}$ = 2 Hz), 140.7, 159.2 (d, $J_{C-F}$ = 260 Hz).

$^{19}$F NMR ($CDCl_3$, 471 MHz): δ = 47.1 (d, $J_{F-H}$ = 40 Hz).

HRMS (EI): *m*/*z* [M]$^+$ calcd for $C_{20}H_{21}F$: 280.1627; found: 280.1628.

**4-[(1*Z*,3*E*)-2-Fluoro-3-methyl-4-phenylbuta-1,3-dien-1-yl]-1,1′-biphenyl (3ad)**

Compound **3ad** was synthesized according to the procedure described for **3aa** using *i*-PrOH (29 μL, 0.38 mmol), *n*-BuLi (0.24 mL, 0.38 mmol), $Et_3B$ (0.38 mL, 0.38 mmol), **1a** (55 mg, 0.25 mmol), 1-phenyl-1-propyne (**2d**, 58 mg, 0.50 mmol), $Ni(cod)_2$ (6.9 mg, 0.025 mmol), $PCy_3$ (6.9 mg, 0.025 mmol), $ZrF_4$ (4.2 mg, 0.025 mmol), and toluene (2.0 mL). The reaction was conducted at r.t. for 15 h. Purification by silica gel column chromatography (hexane/EtOAc, 20:1) gave **3ad**.

Yield: 26 mg (33%); colorless solid; mp 149.9–150.2 °C.

IR (neat): 3028, 2970, 1489, 1441, 1219, 1068, 856, 771, 698 cm$^{-1}$.

$^1$H NMR ($CDCl_3$, 500 MHz): δ = 2.12 (s, 3 H), 5.98 (d, $J_{H-F}$ = 39.8 Hz, 1 H), 7.13 (s, 1 H), 7.25–7.29 (m, 1 H), 7.36–7.39 (m, 5 H), 7.45 (dd, *J* = 7.4, 7.4 Hz, 2 H), 7.62 (dd, *J* = 9.4, 9.4 Hz, 4 H), 7.68 (d, *J* = 8.0 Hz, 2 H).

$^{13}$C NMR ($CDCl_3$, 126 MHz): δ = 14.1 (d, $J_{C-F}$ = 3 Hz), 106.8 (d, $J_{C-F}$ = 11 Hz), 126.9, 127.1, 127.2, 127.3, 127.7 (d, $J_{C-F}$ = 10 Hz), 128.2, 128.4 (d, $J_{C-F}$ = 19 Hz), 128.8, 129.44 (d, $J_{C-F}$ = 8 Hz), 129.45, 133.1, 137.1, 139.8, 140.6, 159.2 (d, $J_{C-F}$ = 260 Hz).

$^{19}$F NMR ($CDCl_3$, 471 MHz): δ = 48.1 (d, $J_{F-H}$ = 40 Hz).

HRMS (EI): *m*/*z* [M]$^+$ calcd for $C_{23}H_{19}F$: 314.1471; found: 314.1474.

**[(1*E*,3*Z*,5*E*)-4-Fluoro-5-propylnona-1,3,5-trien-1-yl]benzene (3ha)**

Compound **3ha** was synthesized according to the procedure described for **3aa** using *i*-PrOH (29 µL, 0.38 mmol), *n*-BuLi (0.24 mL, 0.38 mmol), $Et_3B$ (0.38 mL, 0.38 mmol), **1h** (42 mg, 0.25 mmol), **2a** (55 mg, 0.50 mmol), $Ni(cod)_2$ (6.9 mg, 0.025 mmol), $PCy_3$ (7.0 mg, 0.025 mmol), $ZrF_4$ (4.2 mg, 0.025 mmol), and toluene (2.0 mL). The reaction was conducted at 40 °C for 12 h. Purification by silica gel column chromatography (hexane/EtOAc, 50:1) gave **3ha**.

Yield: 40 mg (62%); colorless oil.

IR (neat): 2958, 2871, 1624, 1595, 1495, 1454, 1377, 1309, 1113, 1072, 964, 860, 746, 690 $cm^{-1}$.

$^1H$ NMR ($CDCl_3$, 500 MHz): δ = 0.95 (t, *J* = 7.8 Hz, 3 H), 0.96 (t, *J* = 7.8 Hz, 3 H), 1.42–1.52 (m, 4 H), 2.15 (td, *J* = 7.6, 7.6 Hz, 2 H), 2.20 (t, *J* = 7.9 Hz, 2 H), 5.71 (dd, $J_{H-F}$ = 35.3, 10.9 Hz, 1 H), 6.02 (t, *J* = 7.6 Hz, 1 H), 6.55 (d, *J* = 15.8 Hz, 1 H), 7.15 (dd, *J* = 15.8, 10.9 Hz, 1 H), 7.21 (t, *J* = 7.5 Hz, 1 H), 7.31 (dd, *J* = 7.5, 7.5 Hz, 2 H), 7.43 (d, *J* = 7.5 Hz, 2 H).

$^{13}C$ NMR ($CDCl_3$, 126 MHz): δ = 14.0, 14.2, 22.5, 22.7, 28.8 (d, $J_{C-F}$ = 4 Hz), 30.3, 106.1 (d, $J_{C-F}$ = 15 Hz), 121.7 (d, $J_{C-F}$ = 7 Hz), 126.3, 127.3, 128.6, 130.1 (d, $J_{C-F}$ = 8 Hz), 130.9 (d, $J_{C-F}$ = 3 Hz), 131.1, 137.6, 158.5 (d, $J_{C-F}$ = 258 Hz).

$^{19}F$ NMR ($CDCl_3$, 471 MHz): δ = 45.1 (d, $J_{F-H}$ = 35 Hz).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{18}H_{23}F$: 258.1784; found: 258.1784.

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## Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/s-0036-1588842.

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